Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Rapid and halide compatible synthesis of 2-N-substituted indazolone derivatives via photochemical cyclization in aqueous media

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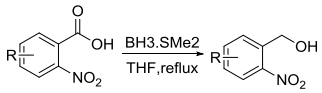
1. General information

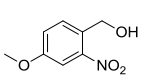
Unless otherwise stated, all starting materials, catalysts, and solvents were commercially available and were used as purchased without any pretreatment. Analytical TLC was performed using pre-coated plates (HSGF254) and visualized with UV light or an I_2 chamber. Flash column chromatography was performed using the indicated solvent system on Sinopharm Chemical Reagent silica gel (200−300 mesh). ^{1}H NMR spectra and proton decoupled ^{13}C NMR spectra were obtained on a 400 MHz Bruker, 500 MHz Bruker NMR spectrometer. ^{1}H and ^{13}C chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent peaks. Multiplicities are given as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Coupling constants (*J*) are given in Hz. For HRMS analysis, samples were analyzed by flow-injection analysis into a Agilent G6520 Q-TOF. LCMS analysis was carried out using a Waters UPLC-MS（ESI）, UPLC: Waters HPLC H-CLASS, MS: Waters SQ Detector 2. Photochemical reactions were carried out in Shanghai Heqi glassware B-002601 40×25mm flat bottom flask. Light sources used were a ZF-7A 16W 365nm UV source. Melting points were determined on a SGWX-4 melting point apparatus.

2. Experimental procedures and compound characterization data

General Procedure (Ⅰ) for the preparation of Substituted (2-Nitrophenyl)methanols.[1]

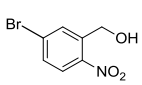


To a solution of the substituted 2-nitrobenzoic acid in dried THF was added drop wise a 2M solution of borane dimethylsulfide complex (1.3 equiv - 5equiv). The resulting solution was then reflux over for 3 h. After allowed to room temperature, 3M aqueous solution of hydrochloric acid was added drop wise into this reaction system until effervescence was no longer observed. The resulting mixture was then extracted with (3 × 30 mL) of ethyl acetate. The combined organic phases were washed with a saturated aqueous solution of Na_2CO_3 followed by brine. The resulting organic phase was dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by chromatograph on silica gel with petroleum ether/ethyl acetate as the eluent to afford the desired products.



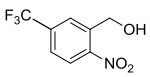
14a

(4-methoxy-2-nitrophenyl)methanol (14a)[1]: The general procedure (I) was followed using 2 g of 4-methoxy-2-nitrobenzoic acid (10.14 mmol) in 40 mL THF and 6.6 mL of BH_3-Me_2S (13.19 mmol, 1.3 equiv). Intermediate **14a** was obtained as yellow solid (1.75 g ， 94%). ^{1}H NMR (400 MHz, DMSO) δ 7.70 (d, *J* = 8.7 Hz, 1H), 7.54 (d, *J* = 2.6 Hz, 1H), 7.34 (dd, *J* = 8.6, 2.6 Hz, 1H), 5.45 (t, *J* = 5.5 Hz, 1H), 4.72 (d, *J* = 5.5 Hz, 2H), 3.84 (s, 3H).The ^{1}H NMR data are good in agreement with the literature date. [1]



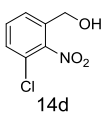
14b

(5-bromo-2-nitrophenyl)methanol (14b)[2]: The general procedure (I) was followed using 2 g of 5-bromo-2-nitrobenzoic acid (8.13 mmol) in 40 mL THF and 5.3 mL of BH_3-Me_2S (10.57 mmol, 1.3 equiv), intermediate **14b** as obtained as yellow solid(1.21 g , 64%).^{1}H NMR (400 MHz, DMSO) δ 8.06 – 7.96 (m, 2H), 7.75 (dd, *J* = 8.7, 2.2 Hz, 1H), 5.70 (t, *J* = 5.6 Hz, 1H), 4.83 (d, *J* = 5.6Hz, 2H).



14c

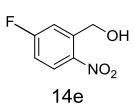
(2-nitro-5-(trifluoromethyl)phenyl)methanol (14c)[3]: The general procedure (I) was followed using 2 g of 2-nitro-5-(trifluoromethyl) benzoic acid (8.51 mmol) in 40 mL THF and 5.5 mL of BH_3-Me_2S (10.06 mmol, 1.3 equiv) . Intermediate **14c** as obtained as yellow solid (1.73 g , 92%). ^{1}H NMR (400 MHz, DMSO) δ 8.36 (s, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 5.77 (t, *J* = 5.5 Hz, 1H), 4.90 (d, *J* = 5.5 Hz, 2H).



14d

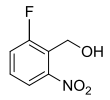
(3-chloro-2-nitrophenyl)methanol (14d)[4]: The general procedure (I) was followed using 4g of 3-chloro-2-nitrobenzoic acid (19.85 mmol) in 60 mL THF and 12.9 mL of BH_3-Me_2S (25.80 mmol, 1.3 equiv). Intermediate **14d** as obtained as yellow solid (3.36 g , 90%). ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (dt, *J* = 8.3, 4.2 Hz,

1H), 7.49 – 7.45 (m, 2H), 4.70 (d, *J* = 6.2 Hz, 2H), 2.10 (t, *J* = 6.2 Hz, 1H).



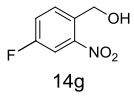
14e

(5-fluoro-2-nitrophenyl)methanol (14e)[5]: The general procedure (I) was followed using 2 g of 5-fluoro-2-nitrobenzoic acid (10.80 mmol) in 40 mL THF and 7.02 mL of BH_3-Me_2S (14.04mmol, 1.3 equiv), intermediate **14e** as obtained as yellow solid(1.73g , 92%) as obtained as yellow solid (1.7 g , 92%). ^{1}H NMR (400 MHz, DMSO) δ 8.20 (dd, *J* = 9.0, 5.2 Hz, 1H), 7.59 (d, *J* = 10.1 Hz, 1H), 7.36 (dd, *J* = 11.0, 5.5 Hz, 1H), 5.71 (t, *J* = 5.5 Hz, 1H), 4.84 (d, *J* = 5.5 Hz, 2H).



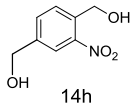
14f

(2-fluoro-6-nitrophenyl)methanol (14f)[3]: The general procedure (I) was followed using 2 g of 2-fluoro-6-nitrobenzoic acid (10.80 mmol) in 40 mL THF and 7.02 mL of BH_3-Me_2S (14.04mmol, 1.3 equiv), intermediate **14f** as obtained as yellow solid (1.38 g , 75%) ^{1}H NMR (400 MHz, DMSO) δ 7.78 – 7.70 (m, 1H), 7.63 – 7.53 (m, 2H), 5.41 (t, *J* = 5.6 Hz, 1H), 4.70 (d, *J* = 5.6 Hz, 2H).



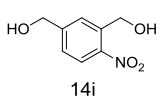
14g

(4-fluoro-2-nitrophenyl)methanol (14g)[6]: The general procedure (I) was followed using 2 g of 4-fluoro-2-nitrobenzoic acid (10.80 mmol) in 40 mL THF and 7.02 mL of BH_3-Me_2S (14.04mmol, 1.3 equiv), intermediate **14g** as obtained as yellow solid (1.79 g , 97%). ^{1}H NMR (400 MHz, DMSO) δ 7.97-7.88 (m, 1H), 7.85 (dd, *J* = 8.6, 6.0 Hz, 1H), 7.70 – 7.60 (m, 1H), 5.59 (t, *J* = 5.5 Hz, 1H), 4.78 (d, *J* = 5.5 Hz, 2H).



14h

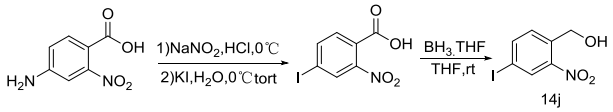
(2-nitro-1, 4-phenylene)dimethanol (14h)[7]: The general procedure (I) was followed using 4g of 2-nitroterephthalic acid (18.95 mmol) in 47mL of BH_3-Me_2S (94.75 mmol , 5equiv), intermediate **14h** was obtained as white solid (3.5 g , 100%) . ^{1}H NMR (400 MHz, DMSO) δ 7.97 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 5.50 (t, *J* = 5.5 Hz, 1H), 5.46 (t, *J* = 5.7 Hz, 1H), 4.80 (d, *J* = 5.3 Hz, 2H), 4.59 (d, *J* = 5.4 Hz, 2H).



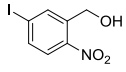
14i

(4-nitro-1,3-phenylene)dimethanol (14i)[8]: The general procedure (I) was followed using 1g of 4-nitroisophthalic acid (4.74mol) in 11.85mL of BH_3-Me_2S (23.70 mmol , 5equiv), intermediate **14i** was obtained as white solid (0.88 g , 88%) ^{1}H NMR (400 MHz, DMSO) δ 7.99 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.69 (d, *J* = 7.3 Hz, 1H), 5.55 – 5.46 (m, 2H), 4.81 (d, *J* = 3.8 Hz, 2H), 4.60 (d, *J* = 2.6 Hz, 2H).

General Procedure(Ⅱ) for 14j and 14k

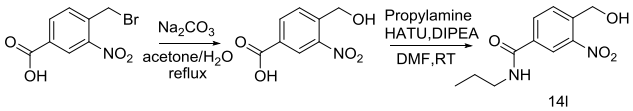


(4-iodo-2-nitrophenyl)methanol (14j): To a suspension of 4-amino-2-nitrozoic (960 mg, 5.27 mmol) in water (40ml) was added Concentrated hydrochloric acid (1.3mL) and cooled to 0℃. A solution of $NaNO_2$ (437 mg, 6.65 mmol) in water (2mL) was added. After stirring for 10min.A solution of KI (1.05 g, 12.65 mmol) in water (2mL) was added. The reaction mixture was stirred at room temperature for 3hr.And excess iodine was destroyed with saturated $NaHSO_3$ solution. The mixture was extracted with ethyl acetate and the organic phase was washed with saturated sodium chloride solution and dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure to give crude product [9];The crude product was dissolved in 20mL dried THF followed by dropping 1M borane tetrahydrofuran complex (15.9 mL, 15.9 mmol), the reaction mixture was stirred at room temperature over night.an 3M aqueous solution of hydrochloric acid was added drop wise into this reaction system until effervescence was no longer observed. The resulting mixture was then extracted with (3 × 30 mL） of ethyl acetate. The combined organic phases were washed with a saturated aqueous solution of Na_2CO_3 followed by brine. The resulting organic phase was dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure .The residue was purified by chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford **14j** as a yellow solid (305 mg , two steps 21%). ^{1}H NMR (500 MHz, DMSO) δ 8.32 (d, *J* = 1.7 Hz, 1H), 8.12 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 5.61 (t, *J* = 5.5 Hz, 1H), 4.74 (d, *J* = 5.6 Hz, 2H).


14k

(5-iodo-2-nitrophenyl)methanol (14k)[10]: Prepared according to the procedure for the preparation of **14j**. Intermediate**14k** was obtained as yellow solid (576mg , two steps 39%). ^{1}H NMR (400 MHz, DMSO) δ 8.18 (d, *J* = 0.8 Hz, 1H), 7.92 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 5.66 (t, *J* = 5.1 Hz, 1H), 4.80 (d, *J* = 4.0 Hz, 2H).

Procedure for synthesis of 14l



A solution of 4-(bromomethyl)-3-nitrobenzoic acid (2 g, 7.69 mmol) and Na_2CO_3 (4.07 g, 38.43 mmol) in water/acetone (1:1 v/v, 60 mL) was heated at reflux temperature. After 5 h, the acetone was evaporated. The resulting aqueous solution was washed with ether (40 mL), acidified with 6M HCl and extracted with EtOAc (3×40mL). The combined organic layers were washed with water (40 mL), dried over Na_2SO4 and concentrated in vacuo to yield 1.51 g (100%) of 4-(hydroxymethyl)-3-nitrobenzoic acid as a yellow solid[11]. ^{1}H NMR (400 MHz, DMSO) δ 13.58

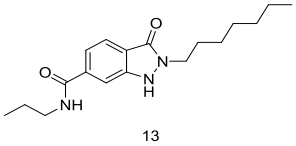
(s, 1H), 8.48 (d, *J* = 1.6 Hz, 1H), 8.28 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 5.73 (s, 1H), 4.89 (s, 2H).

To a solution of 4-(hydroxymethyl)-3-nitrobenzoic acid (1.51g, 7.69mmol), Propylamine (948 ul, 11.53 mmol) and HATU (3.22 g, 8.46 mmol) in dry DMF (25mL) was added N, N-diisopropyl -ethylamine (3.81 mL, 23.07 mmol).The reaction mixture was stirred at room temperature overnight. The reaction system was quenched with water (40 mL) and extracted with EtOAc (2×60mL).he combined organic layers were washed with brine (3×40mL).The resulting organic phase was dried over Na_2SO_4 and filtered. The filtrate was concentrated under reduced pressure .The residue was purified by chromatography on silica gel with dichloromethane/methanol as the eluent to afford **14l** as a yellow solid (1.26 g , 69%). ^{1}H NMR (400 MHz, DMSO) δ 8.76 (t, *J* = 5.4 Hz, 1H), 8.50 (d, *J* = 1.7 Hz, 1H), 8.22 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.92 (d, *J* = 8.1 Hz, 1H), 5.65 (t, *J* = 5.5 Hz, 1H), 4.87 (d, *J* = 5.5 Hz, 2H), 3.25 (dd, *J* = 12.9, 6.9 Hz, 2H), 1.61 – 1.49 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H)

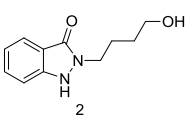
General Procedure(Ⅲ) for indazolone synthesis:

A 40×25mm flat bottom flask was charge with a stir bar, o-nitrobenzyl alcohol (0.75 mmol), amine (0.3 mmol), 1-Butanol (4.5 mL), water (1.5 mL). The reaction mixture was placed under a UV lamp for 3h.The solution was concentrated by rotary evaporation and purified by chromatography on silica gel with dichloromethane/methanol as the eluent to afford the desired products.

2-heptyl-3-oxo-N-propyl-2, 3-dihydro-1H-indazole-6-carboxamide (13). Following general procedure (Ⅲ) : the substrate **13** was obtained as a yellow solid (78 mg , 82%). Mp: 145-147℃ ^{1}H NMR (400 MHz, DMSO) δ 10.44 (s, 1H), 8.59 (t, *J* =5.5Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 3.80 (t, *J* = 6.7 Hz, 2H), 3.23 (dd, *J* = 12.5, 6.5 Hz, 2H), 1.75 – 1.62 (m, 2H), 1.54 (dd, *J* = 14.2, 7.1 Hz, 2H), 1.34-1.14 (m, 8H), 0.86 (dd, *J* = 21.2, 14.9 Hz, 6H). ^{13}C NMR (101 MHz, DMSO) δ 165.99, 159.96, 145.35, 137.69, 122.99, 119.69, 119.09, 111.24, 43.29, 41.28, 31.30, 28.34, 27.91, 26.16, 22.49, 22.17, 14.06, 11.61. HRMS (ESI-ion trap): m/z [M-H]$^-$ Calcd for $C_{18}H_{26}N_3O_2$: 316.2031; found: 316.2034.



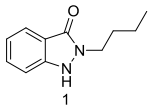
13



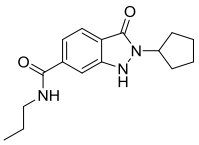
2

2-(4-hydroxybutyl)-1, 2-dihydro-3H-indazol-3-one (2)[12]**.** Following general procedure (Ⅲ) : the substrate **2** was obtained as a yellow oil (42mg，68%). ^{1}H NMR (500 MHz, DMSO) δ 10.18 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 3.79 (t, *J* = 7.0 Hz, 2H), 3.40 (t, *J* = 6.5 Hz, 2H), 1.71 (dt, *J* = 14.9, 7.3 Hz, 2H), 1.43-1.36 (m, 2H).^{13}C NMR (101 MHz, DMSO) δ 160.73, 146.04, 131.36, 123.10, 120.97, 117.57, 112.26, 60.41, 43.18, 29.75, 24.80. HRMS (ESI-ion trap): m/z [M-H]$^-$ Calcd for $C_{11}H_{13}N_2O_2$: 205.0983; found : 205.098.

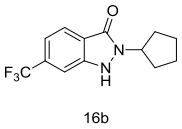
2-butyl-1,2-dihydro-3H-indazol-3-one (1)[13]. Following general procedure (Ⅲ) : the substrate **1**


1

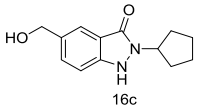
was obtained as a yellow oil (54 mg ， 95%). ^{1}H NMR (400 MHz , DMSO) δ 10.28 (s, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 3.79 (t, *J* = 7.0 Hz, 2H), 1.73 – 1.60 (m, 2H), 1.25 (dq, *J* = 14.7, 7.4 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 160.70, 146.06, 131.29, 123.06, 120.91, 117.57, 112.24, 42.87, 30.01, 19.47, 13.62. HRMS (ESI-ion trap): m/z [M-H]$^{-}$ Calcd for $C_{11}H_{13}N_2O$:189.1033 ; found : 189.1037.


16a

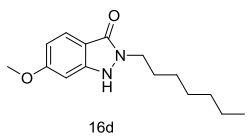
2-cyclopentyl-3-oxo-N-propyl-2, 3-dihydro-1H-indazole-6-carboxamide (16a). Following general procedure (Ⅲ) : the substrate **16a** was obtained as a yellow solid (66 mg , 77%). Mp: 90-92℃. ^{1}H NMR (400 MHz, DMSO) δ 10.14 (s, 1H), 8.58 (t, *J* = 5.5 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.53 (d, *J* = 9.0 Hz, 1H), 4.85 – 4.76 (m, 1H), 3.23 (dd, *J* = 13.1, 6.7 Hz, 2H), 2.01 – 1.89 (m, 2H), 1.85-1.72 (m, 4H), 1.66-1.49 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 165.98, 160.49, 146.03, 137.78, 122.94, 119.86, 119.51, 111.62, 54.41, 41.29, 29.99, 24.37, 22.48, 11.61. HRMS (ESI-ion trap): m/z [M-H]$^{-}$ Calcd for $C_{16}H_{20}N_3O_2$: 286.1561; found: 286.1564


16b

3-**cyclopentyl-6-(trifluoromethyl)-1, 2-dihydro-3H-indazol-3-one (16b).** Following general procedure (Ⅲ) : the substrate **16b** was obtained as a brown solid (51 mg , 63%). Mp: 156-158℃. ^{1}H NMR (400 MHz, DMSO) δ 10.53 (s, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.59 (s, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 4.88 – 4.78 (m, 1H), 2.04 – 1.90 (m, 2H), 1.88-1.72 (m, 4H), 1.71-1.55 (m, 2H). ^{13}C NMR (126 MHz, DMSO) δ 159.65, 145.21, 131.53 (q, *J* = 31.6 Hz), 124.63, 124.26 (q, *J* = 272.7 Hz),120.34, 117.08(d, *J* = 2.9Hz), 109.78 (d, *J* = 4.2 Hz), 54.49, 30.05, 24.39. HRMS (ESI-ion trap): m/z [M-H]$^{-}$ Calcd for $C_{13}H_{12}F_3N_2O$: 269.0907 ; found: 269.0908.

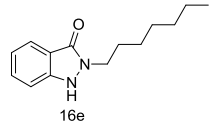

16c

2-cyclopentyl-5-(hydroxymethyl)-1, 2-dihydro-3H-indazol-3-one (16c). Following general procedure (Ⅲ) : the substrate **16c** was obtained as a yellow solid (50 mg , 71%). Mp: 134-136℃. ^{1}H NMR (400 MHz, DMSO) δ 9.81 (s, 1H), 7.55 (s, 1H), 7.46 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 5.19 (t, *J* = 5.7 Hz, 1H), 4.84 – 4.73 (m, 1H), 4.52 (d, *J* = 5.5 Hz, 2H), 1.98 – 1.85 (m, 2H), 1.83 – 1.71 (m, 4H), 1.67 – 1.52 (m, 2H).^{13}C NMR (101 MHz, DMSO) δ 161.44, 146.01, 135.75, 130.72, 120.58, 117.87, 112.37, 62.93, 54.28, 29.94, 24.44. HRMS (ESI-ion trap): m/z [M-H]$^{-}$ Calcd for $C_{13}H_{15}N_2O_2$: 231.1139; found: 231.1142.

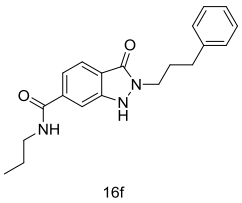

16d

2-**heptyl-6-methoxy-1, 2-dihydro-3H-indazol-3-one (16d).** Following general procedure (Ⅲ) : the substrate **16d** was obtained as a yellow solid (44 mg , 56%). Mp: 61-63℃. ^{1}H NMR (400 MHz, DMSO) δ 10.08 (s, 1H),

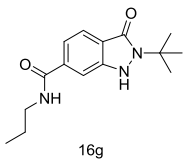
7.49 (d, *J* = 8.5 Hz, 1H), 6.72 – 6.60 (m, 2H), 3.80 (s, 3H), 3.70 (t, *J* = 7.0 Hz, 2H), 1.68 – 1.58 (m, 2H), 1.31 – 1.17 (m, 8H), 0.83 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 162.64, 160.98, 148.01, 124.17, 110.99, 110.91, 94.58, 55.68, 43.30, 31.37, 28.44, 27.95, 26.24, 22.23, 14.12. HRMS (ESI-ion trap): m/z [M-H]$^-$ Calcd for $C_{15}H_{21}N_2O_2$: 261.1609; found: 261.1611.


16e

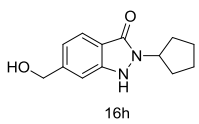
2-heptyl-1,2-dihydro-3H-indazol-3-one(16e)[13]. Following general procedure (Ⅲ) : the substrate **16e** was obtained as a yellow solid (56 mg ,80%).^{1}H NMR (400 MHz, DMSO) δ 10.34 (s, 1H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.52 – 7.41 (m, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 3.77 (t, *J* = 7.0 Hz, 2H), 1.74 – 1.59 (m, 2H), 1.28-1.17 (m, 8H), 0.82 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 160.63, 146.03, 131.26, 123.06, 120.87, 117.55, 112.25, 43.19, 31.36, 28.43, 27.98, 26.24, 22.23, 14.09. LCMS: [M+H]$^+$ 233.21.


16f

3-oxo-2-(3-phenylpropyl)-N-propyl-2, 3-dihydro-1H-indazole-6-carboxamide (16f). Following general procedure (Ⅲ) : the substrate **16f** was obtained as a yellow solid (77 mg , 76%). Mp: 153-155℃. ^{1}H NMR (400 MHz, DMSO) δ 10.47 (s, 1H), 8.60 (t, *J* = 5.5 Hz, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 9.1 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 7.0 Hz, 2H), 7.18 (t, *J* = 7.1 Hz, 1H), 3.84 (t, *J* = 7.0 Hz, 2H), 3.23 (dd, *J* = 13.1, 6.6 Hz, 2H), 2.59 (t, *J* = 7.7 Hz, 2H), 2.05 – 1.93 (m, 2H), 1.60 – 1.49 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 166.01, 160.20, 145.58, 141.40, 137.79, 128.54, 126.08, 123.09, 119.83, 119.17, 111.35, 43.13, 41.32, 32.38, 29.79, 22.53, 11.66. HRMS (ESI-ion trap): m/z [M-H]$^-$ Calcd for $C_{20}H_{22}N_3O_2$: 336.1718; found: 336.1725.

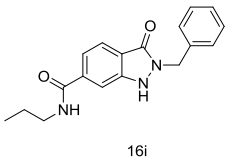

16g

3-(tert-butyl)-3-oxo-N-propyl-2, 3-dihydro-1H-indazole-6-carboxamide (16g). Following general procedure (Ⅲ) : the substrate **16g** was obtained as a yellow solid (45 mg , 55%). Mp: 179-181℃. ^{1}H NMR (400 MHz, DMSO) δ 9.85 (s, 1H), 8.57 (t, *J* = 5.5 Hz, 1H), 7.67 (s, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.52 (dd, *J* = 8.2, 1.1 Hz, 1H), 3.23 (dd, *J* = 13.1, 6.7 Hz, 2H), 1.60 – 1.49 (m, 11H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 166.02, 161.93, 146.05, 137.76, 122.76, 121.04, 119.79, 111.79, 57.86, 41.30, 27.37, 22.50, 11.64. HRMS (ESI-ion trap): m/z [M-H]$^-$ Calcd for $C_{15}H_{20}N_3O_2$: 274.1561; found: 274.1569


16h

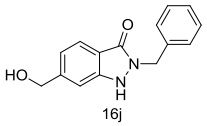
2-cyclopentyl-6-(hydroxymethyl)-1, 2-dihydro-3H-indazol-3-one (16h). Following general procedure (Ⅲ) : the substrate **16h** was obtained as a brown solid (49 mg , 70%). Mp: 165-167℃. ^{1}H NMR (400 MHz, DMSO) δ 9.82 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.18 (s, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 5.34 (t, *J* = 5.8 Hz, 1H), 4.82-4.72 (m, 1H), 4.58 (d, *J* = 5.7 Hz, 2H), 1.95-1.85 (m, 2H), 1.84 – 1.71 (m, 4H), 1.66-1.55 (m, 2H).^{13}C NMR (101 MHz, DMSO) δ 161.36, 147.07, 146.85, 122.61, 119.73, 116.61, 109.58, 62.96, 54.27, 29.87,

24.38. LCMS M+H 233.18. HRMS (ESI-ion trap): m/z [M-H]$^-$ Calcd for $C_{13}H_{15}N_2O_2$: 231.1139; found: 231.1138.



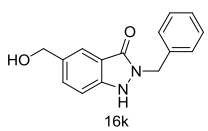
16i

2-benzyl-3-oxo-N-propyl-2, 3-dihydro-1H-indazole-6-carboxamide (16i). Following general procedure (Ⅲ) : the substrate **16i** was obtained as a white solid (54 mg , 58%) . Mp: 192-194℃. ^{1}H NMR (400 MHz, DMSO) δ 10.46 (s, 1H), 8.56 (t, *J* = 5.5 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.64 (s, 1H), 7.53 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.37-7.24 (m, 5H), 5.03 (s, 2H), 3.22 (dd, *J* = 13.2, 6.6 Hz, 2H), 1.59 – 1.48 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).^{13}C NMR (101 MHz, DMSO) δ 165.99, 160.33, 145.60, 138.04, 136.91, 128.76, 127.73, 123.22, 119.82, 118.75, 111.42, 47.05, 41.30, 22.50, 11.64. HRMS (ESI-ion trap): m/z [M-H]$^-$ Calcd for $C_{18}H_{18}N_3O_2$: 308.1405; found: 308.1411



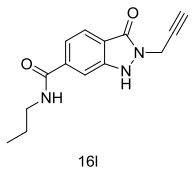
16j

2-benzyl-6-(hydroxymethyl)-1, 2-dihydro-3H-indazol-3-one (16j). Following general procedure (Ⅲ) : the substrate **16j** was obtained as a white solid (42 mg , 55%). Mp: 150-152℃. ^{1}H NMR (400 MHz, DMSO) δ 10.17 (s, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.28 (dd, *J* = 6.0, 3.9 Hz, 1H), 7.24 (t, *J* = 5.8 Hz, 2H), 7.15 (s, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 5.33 (t, *J* = 4.2 Hz, 1H), 4.98 (s, 2H), 4.57 (d, *J* = 4.2 Hz, 2H).^{13}C NMR (101 MHz, DMSO) δ 161.10, 147.10, 146.65, 137.16, 128.68, 127.67, 127.61, 122.85, 119.71, 115.88, 109.38, 62.95, 46.97. HRMS (ESI-ion trap): m/z [M-H]$^-$ Calcd for $C_{15}H_{13}N_2O_2$: 253.0983; found: 253.0985.



16k

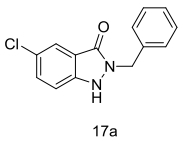
2-benzyl-5-(hydroxymethyl)-1, 2-dihydro-3H-indazol-3-one (16k). Following general procedure (Ⅲ) : the substrate **16k** was obtained as a brown oil (33 mg , 43%) . ^{1}H NMR (400 MHz, DMSO) δ 10.18 (s, 1H), 7.60 (s, 1H), 7.45 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.23 (d, *J* = 7.0 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 1H), 5.21 (s, 1H), 4.98 (s, 2H), 4.52 (s, 2H).^{13}C NMR (101 MHz, DMSO) δ 161.19, 145.61, 137.15, 135.70, 130.94, 128.70, 127.74, 127.64, 120.80, 117.15, 112.21, 62.91, 47.00. HRMS (ESI-ion trap): m/z [M-H]$^-$ Calcd for $C_{15}H_{13}N_2O_2$: 253.0983; found: 253.0984.



16l

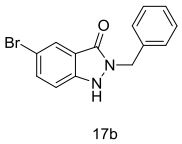
oxo-2-(prop-2-yn-1-yl)-N-propyl-2, 3-dihydro-1H-indazole-6-carboxamide (16l). Following general procedure (Ⅲ) : the substrate **16l** was obtained as a yellow solid (17 mg , 22%). Mp: 130-132℃. ^{1}H NMR (400 MHz, DMSO) δ 10.50 (s, 1H), 8.62 (t, *J* = 5.5 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.54 (dd, *J* = 8.2, 1.1 Hz, 1H), 4.63 (d, *J* = 2.4 Hz, 2H), 3.36 (t, *J* = 2.4 Hz, 1H), 3.23 (dd, *J* = 13.1, 6.7 Hz, 2H), 1.61 – 1.48 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 165.84, 160.74, 146.59, 138.40, 123.28, 119.89, 118.41, 111.70,

78.45, 75.40, 41.33, 33.52, 22.50, 11.65. HRMS (ESI-ion trap): m/z $[M-H]^-$ Calcd for $C_{14}H_{14}N_3O_2$: 256.1092; found: 256.1091.



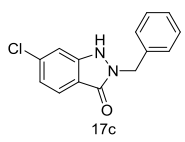
17a

2-benzyl-5-chloro-1, 2-dihydro-3H-indazol-3-one (17a). Following general procedure (Ⅲ) : the substrate **17a** was obtained as a yellow solid (64 mg , 82%). Mp: 219-221℃. ^{1}H NMR (400 MHz, DMSO) δ 10.57 (s, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.52 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.34 (t, *J* = 7.1 Hz, 2H), 7.31 – 7.23 (m, 4H), 5.00 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 159.64, 144.35, 136.78, 131.81, 128.79, 127.82, 125.28, 122.50, 118.20, 114.29, 47.04. LCMS: $[M+H]^+$ M+1 259.10.



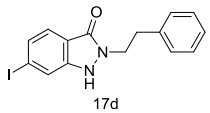
17b

2-benzyl-6-bromo-1, 2-dihydro-3H-indazol-3-one (17b). Following general procedure (Ⅲ) : the substrate **17b** was obtained as a white solid (71 mg , 78%). Mp: 190-192℃. ^{1}H NMR (400 MHz, DMSO) δ 10.60 (s, 1H), 7.82 (d, *J* = 1.8 Hz, 1H), 7.62 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.34 (t, *J* = 7.1 Hz, 2H), 7.26 (dt, *J* = 17.2, 8.0 Hz, 4H),5.01(s,2H).^{13}C NMR (101 MHz, DMSO) δ 159.42, 144.54, 136.78, 134.31, 128.78, 127.80, 125.53, 118.74, 114.62, 112.77, 47.04. HRMS (ESI-ion trap): m/z $[M-H]^-$ Calcd for $C_{14}H_{10}BrN_2O$: 300.9982; found: 300.9987.



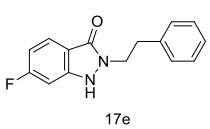
17c

2-benzyl-6-chloro-1, 2-dihydro-3H-indazol-3-one (17c). Following general procedure (Ⅲ) : the substrate **17c** was obtained as a brown solid (44 mg , 56%). Mp: 185-187℃. ^{1}H NMR (400 MHz, DMSO) δ 10.60 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.38 – 7.22 (m, 6H), 7.10 (dd, *J* = 8.3, 1.4 Hz, 1H), 4.99 (s, 2H). ^{13}C NMR (101 MHz, DMSO) δ 159.85, 146.15, 136.63, 136.33, 128.56, 127.59, 124.84, 121.20, 115.58, 111.77, 46.80. LCMS: $[M+H]^+$ 259.13.



17d

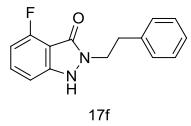
6-iodo-2-phenethyl-1, 2-dihydro-3H-indazol-3-one (17d). Following general procedure (Ⅲ) : the substrate **17d** was obtained as a brown solid (103 mg ，94%). Mp:176-178℃. ^{1}H NMR (500 MHz, DMSO) δ 10.55 (s, 1H), 7.70 (s, 1H), 7.38 (s, 2H), 7.29-7.24(m, 2H), 7.22-7.16(m, 3H), 4.00 (t, *J* = 7.4 Hz, 2H), 2.99 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 159.95, 146.64, 138.43, 129.62, 128.78, 128.58, 126.55, 124.90, 120.71, 116.72, 98.63, 44.55, 33.81. HRMS (ESI-ion trap): m/z $[M-H]^-$ Calcd for $C_{15}H_{12}IN_2O$: 363; found: 362.9997.



17e

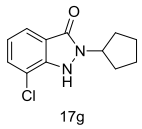
6-fluoro-2-phenethyl-1, 2-dihydro-3H-indazol-3-one (17e). Following general procedure (Ⅲ) : the substrate **17e** was obtained as a yllow solid (55 mg ， 71%). Mp: 179-181℃. ^{1}H NMR (500 MHz, DMSO) δ 10.62 (s, 1H), 7.65 (dd, *J* = 8.5, 5.6 Hz, 1H), 7.29-7.16 (m, 5H), 7.14-7.11 (m, 1H),6.94-6.88(m, 1H), 4.01 (t, *J* = 7.4 Hz, 2H), 2.99 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 164.80 (d, *J* = 245.6 Hz), 160.00, 146.71 (d, *J* = 13.8 Hz), 138.49, 128.80, 128.60, 126.55, 125.50 (d,

J = 11.4 Hz), 114.03, 109.61 (d, *J* = 25.0 Hz), 98.50 (d, *J* = 26.7 Hz), 44.74, 33.85. ^{19}F NMR (471 MHz, DMSO) δ -108.61. HRMS (ESI-ion trap): m/z [M-H]$^-$ Calcd for $C_{15}H_{12}FN_2O$: 255.0939; found: 255.0945.



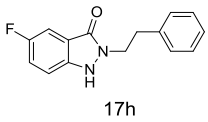
17f

4-fluoro-2-phenethyl-1, 2-dihydro-3H-indazol-3-one (17f) Following general procedure (Ⅲ) : the substrate **17f** was obtained as a yellow solid (52 mg , 68%). Mp: 169-171℃. ^{1}H NMR (500 MHz, DMSO) δ 10.77 (s, 1H), 7.51 – 7.43 (m, 1H), 7.30 – 7.25 (m, 2H), 7.24 – 7.17 (m, 3H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.76 (dd, *J* = 10.0, 8.0 Hz, 1H), 4.02 – 3.97 (m, 2H), 3.00 (t, *J* = 7.4 Hz, 2H).^{13}C NMR (126 MHz, DMSO) δ 159.05, 157.27 (d, *J* = 63.4 Hz), 147.62 (d, *J* = 7.1 Hz), 138.41,133.10 (d, *J* = 8.8 Hz),128.78, 128.60, 126.57, 112.29,108.27 (d, *J* = 4.1 Hz), 105.94 (d, *J* = 18.5 Hz), 44.44,33.75.^{19}F NMR (471 MHz, DMSO) δ -119.35. HRMS (ESI-ion trap): m/z [M-H]$^-$ Calcd for $C_{15}H_{12}FN_2O$: 255.0939; found: 255.0943.



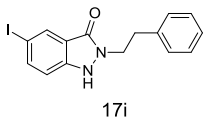
17g

7-chloro-2-cyclopentyl-1, 2-dihydro-3H-indazol-3-one (17g) Following general procedure (Ⅲ) : the substrate **17g** was obtained as a red solid (29 mg , 41%). Mp: 149-151℃. ^{1}H NMR (400 MHz, DMSO) δ 10.25 (s, 1H), 7.61 (d, *J* = 7.7 Hz, 2H), 7.12 (t, *J* = 7.7 Hz, 1H), 4.77 (p, *J* = 8.1 Hz, 1H), 1.95-1.86 (m, 4H), 1.85 – 1.74 (m, 2H), 1.65 – 1.54 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 160.79, 143.37, 131.18, 122.43, 122.01, 120.35, 117.28, 55.04, 29.66, 24.30. HRMS (ESI-ion trap): m/z [M-H]$^-$ Calcd for $C_{12}H_{12}ClN_2O$: 235.0644; found: 235.0648.



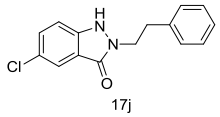
17h

5-fluoro-2-phenethyl-1,2-dihydro-3H-indazol-3-one (17h) Following general procedure (Ⅲ) : the substrate **17h** was obtained as a yellow solid (53 mg , 69%). Mp: 162-164℃. ^{1}H NMR (500 MHz, DMSO) δ 10.31 (s, 1H), 7.43-7.31 (m, 3H), 7.30 – 7.16 (m, 5H), 4.02 (t, *J* = 7.5 Hz, 2H), 3.00 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 160.16 (d, *J* = 3.7 Hz), 157.52 (d, *J* = 237.1 Hz), 142.77, 138.47,128.78, 128.59, 126.55,120.03 (d, *J* = 25.7 Hz), 118.11 (d, *J* = 9.0 Hz), 114.22 (d, *J* = 8.5 Hz), 108.11 (d, *J* = 23.6 Hz), 44.72, 33.84. ^{19}F NMR (471 MHz, DMSO) δ -122.38. HRMS (ESI-ion trap): m/z [M-H]$^-$ Calcd for $C_{15}H_{12}FN_2O$: 255.0939; found: 255.0941.

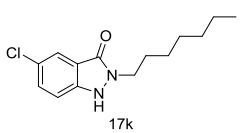


17i

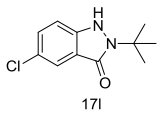
5-iodo-2-phenethyl-1, 2-dihydro-3H-indazol-3-one (17i). Following general procedure (Ⅲ) : the substrate **17i** was obtained as a yellow solid (75 mg，69%). Mp: 177-179℃. ^{1}H NMR (500 MHz, DMSO) δ 10.60 (s, 1H), 7.89 (d, *J* = 1.3 Hz, 1H), 7.75 (d, *J* = 8.5 Hz, 1H), 7.29 – 7.23 (m, 2H), 7.20 (dd, *J* = 8.1, 4.4 Hz, 3H), 7.16 (t, *J* = 5.5 Hz, 1H), 4.02 (t, *J* = 7.4 Hz, 2H), 2.99 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, DMSO) δ 158.80, 144.68, 139.42, 138.40, 131.42, 128.77, 128.59, 126.56, 119.76, 114.69, 83.67, 44.58, 33.81. HRMS (ESI-ion trap): m/z [M-H]$^-$ Calcd for $C_{15}H_{12}IN_2O$: 363; found: 363.0003.



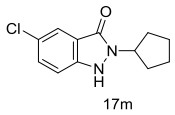
5-chloro-2-phenethyl-1, 2-dihydro-3H-indazol-3-one (17j). Following general procedure (Ⅲ) : the substrate **17j** was obtained as a brown solid (71 mg , 87%). Mp: 158-160℃. ^{1}H NMR (400 MHz, DMSO) δ 10.58 (s, 1H), 7.61 (d, *J* = 1.8 Hz, 1H), 7.51 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.33 (d, *J* = 8.7 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.23 – 7.16 (m, 3H), 4.03 (t, *J* = 7.4 Hz, 2H), 3.00 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 159.12, 143.99, 138.20, 131.39, 128.56, 128.38, 126.36, 124.99, 122.16, 118.34, 113.94, 44.45, 33.61. LCMS: $[M+H]^{+}$ 273.16



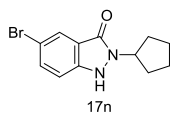
5-chloro-2-heptyl-1, 2-dihydro-3H-indazol-3-one (17k). Following general procedure (Ⅲ): the substrate **17k** was obtained as a yellow solid (79 mg , 99%). Mp: 102-105℃. ^{1}H NMR (400 MHz, DMSO) δ 10.48 (s, 1H), 7.63 (d, *J* = 1.9 Hz, 1H), 7.50 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.30 (d, *J* = 8.7 Hz, 1H), 3.78 (t, *J* = 7.0 Hz, 2H), 1.73 – 1.60 (m, 2H), 1.29 – 1.20 (m, 8H), 0.83 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, DMSO) δ 159.30, 144.09, 131.41, 125.10, 122.29, 118.52, 114.06, 43.28, 31.27, 28.32, 27.86, 26.13, 22.16, 14.05. HRMS (ESI-ion trap): m/z $[M-H]^{-}$ Calcd for $C_{14}H_{18}ClN_2O$: 265.1113; found: 265.112.



2-(tert-butyl)-5-chloro-1, 2-dihydro-3H-indazol-3-one (17l). Following general procedure (Ⅲ) : the substrate **17l** was obtained as a brown solid (43 mg , 64%). Mp: 178-180℃. ^{1}H NMR (400 MHz, DMSO) δ 9.89 (s, 1H), 7.57 (d, *J* = 1.9 Hz, 1H), 7.51 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 1H), 1.53 (s, 9H). ^{13}C NMR (101 MHz, DMSO) δ 161.12, 144.76, 131.55, 125.26, 122.02, 120.43, 114.55, 57.91, 27.34. HRMS (ESI-ion trap): m/z $[M-H]^{-}$ Calcd for $C_{11}H_{12}ClN_2O$: 223.0644; found: 223.0644.

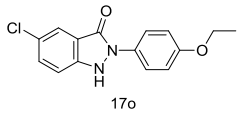


5-chloro-2-cyclopentyl-1, 2-dihydro-3H-indazol-3-one (17m). Following general procedure (Ⅲ) : the substrate **17m** was obtained as a gray solid (43 mg , 61%). Mp: 176-178℃. ^{1}H NMR (400 MHz, DMSO) δ 10.20 (s, 1H), 7.62 (d, *J* = 1.9 Hz, 1H), 7.51 (d, *J* = 8.6 Hz, 1H), 7.29 (d, *J* = 8.7 Hz, 1H), 4.84 – 4.73 (m, 1H), 2.00 – 1.88 (m, 2H), 1.85-1.71(m, 4H), 1.67-1.53 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ 159.75, 144.74, 131.52, 125.27, 122.21, 118.91, 114.41, 54.39, 29.99, 24.37. HRMS (ESI-ion trap): m/z $[M-H]^{-}$ Calcd for $C_{12}H_{12}ClN_2O$: 235.0644 ; found: 235.065



5-bromo-2-cyclopentyl-1, 2-dihydro-3H-indazol-3-one (17n). Following general procedure (Ⅲ) : the substrate **17n** was obtained as a brown solid(61 mg , 72%). Mp: 175-177℃. ^{1}H NMR (400 MHz, DMSO) δ 10.25 (s, 1H), 7.75 (d, *J* = 1.7 Hz, 1H), 7.62 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.24 (d, *J* = 8.7 Hz, 1H), 4.84 – 4.73 (m, 1H), 1.97 – 1.89 (m, 2H), 1.84-1.69 (m, 4H), 1.65-1.54(m, 2H) ^{13}C NMR (126 MHz, DMSO) δ 159.44, 144.85, 134.07,

125.27, 119.43, 114.79, 112.79, 54.41, 30.02, 24.39. HRMS (ESI-ion trap):m/z [M-H]$^-$ Calcd for $C_{12}H_{12}BrN_2O$: 279.0138; found: 279.0142



17o

5-chloro-2-(4-ethoxyphenyl)-1, 2-dihydro-3H-indazol-3-one (17o). Following general procedure (Ⅲ) : the substrate **17o** was obtained as a yellow solid (38 mg , 44%). Mp: 139-141℃. ^{1}H NMR (400 MHz, DMSO) δ 8.12 (s, 1H), 7.78 (s, 1H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 9.3 Hz, 1H), 7.23 (d, *J* = 9.1 Hz, 1H), 7.14 (d, *J* = 8.9 Hz, 2H), 4.13 (q, *J* = 7.0 Hz, 2H), 1.37 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, DMSO) δ 159.89, 128.54, 128.23, 127.63, 126.76, 126.68, 120.25, 115.96, 115.45, 115.20, 110.90, 64.20, 14.92. HRMS (ESI-ion trap): m/z [M-H]$^-$ Calcd for $C_{15}H_{12}ClN_2O_2$: 287.0593; found: 287.0594

The product yield of indazolones with different methods [13, 18]

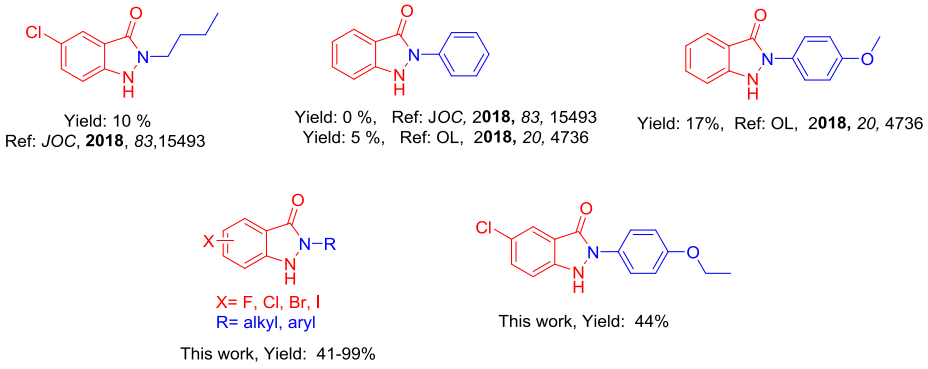


Figure S1. The product yield of indazolones with different methods

Proposed reaction mechanism

Previous research reported that o-nitrobenzyl alcohol derivatives generated corresponding aryl-nitroso compounds via photoisomerization, upon UV light-activation (for details, please see references, *J. Am. Chem. Soc.* **2004**, *126*, 4581; *Chem. Rev.*, 2013, **113**, 119; *Chem. Commun.*, 2011, **47**, 3822).[14-16]

The photogenerated intermediate is reactive and not very stable for subsequent isolation. We could detect the aryl-nitroso compound (exact mass 220.08) with UPLC-MS analysis as follows:

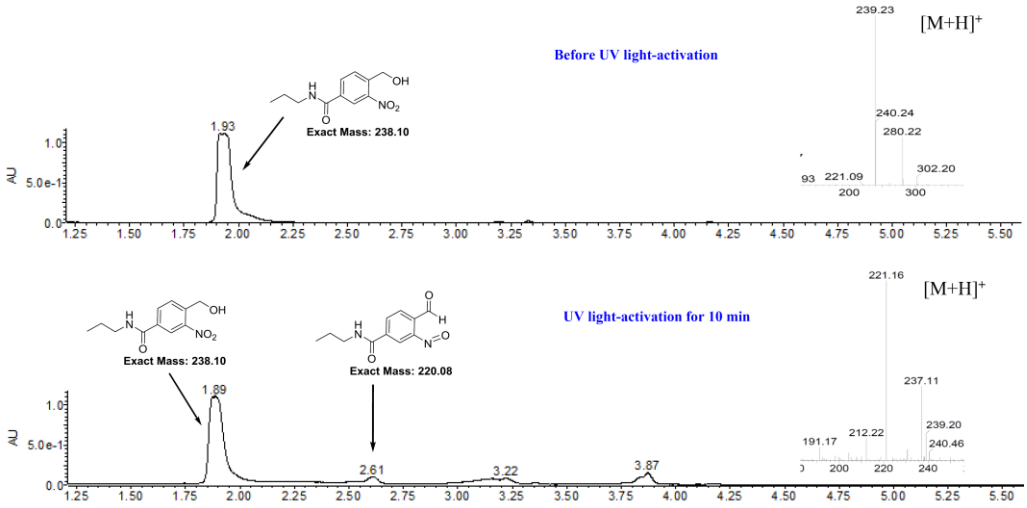


Figure S2. Photogenerated intermediate aryl-nitroso compound detected on UPLC-MS analysis

This date can support our proposed mechanism that the intermediate aryl-nitroso compound *in situ* generated from o-nitrobenzyl alcohol upon UV light-activation. In the presence of primary amines, the aryl-nitroso compound can rapidly form indazolones via cyclization in suitable reaction conditions, subsequent for dehydration and tautomerization (Ref, *J.Org. Chem.* **2005**, *70*, 1060-1062). We have proposed the reaction mechanism combining this date and previous references. [17-18]

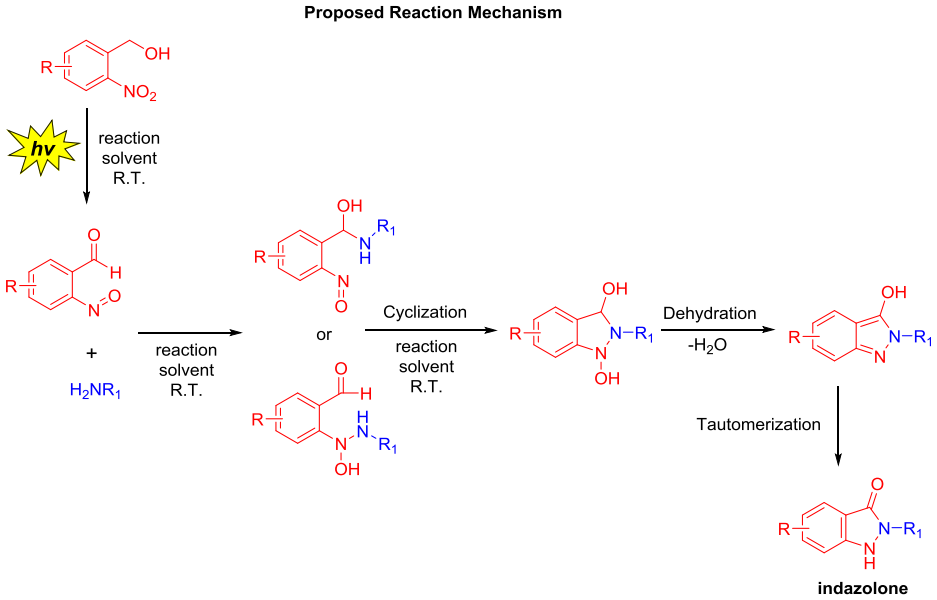


Figure S3. Proposed reaction mechanism

References

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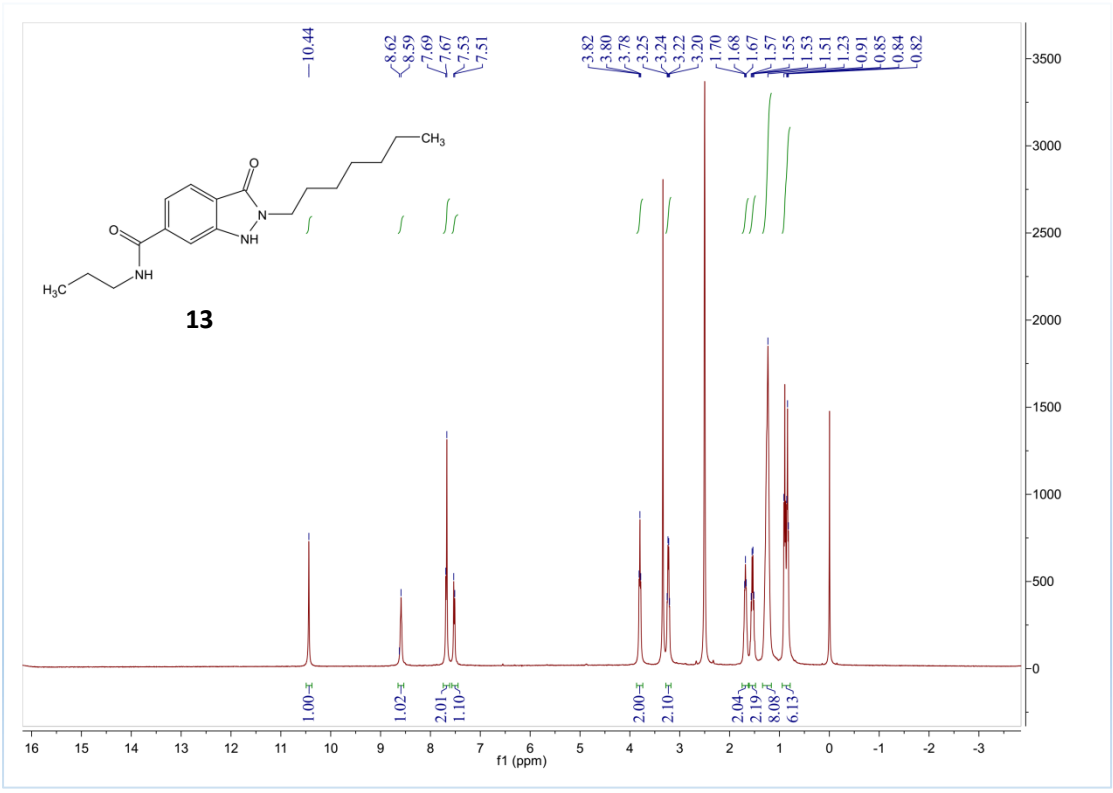
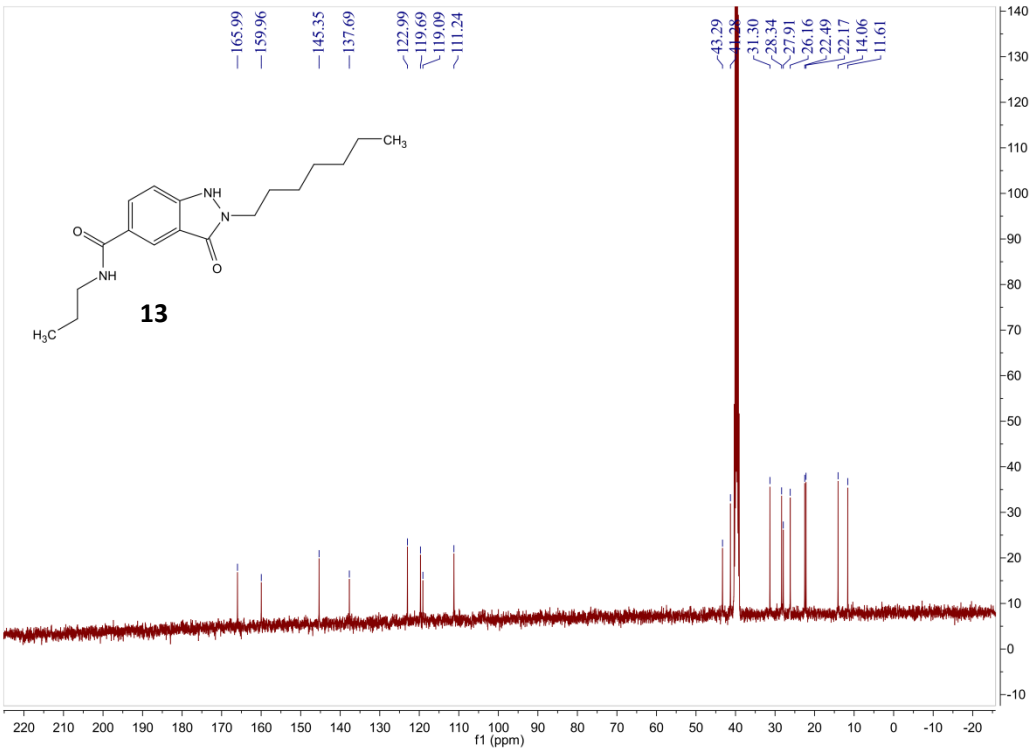
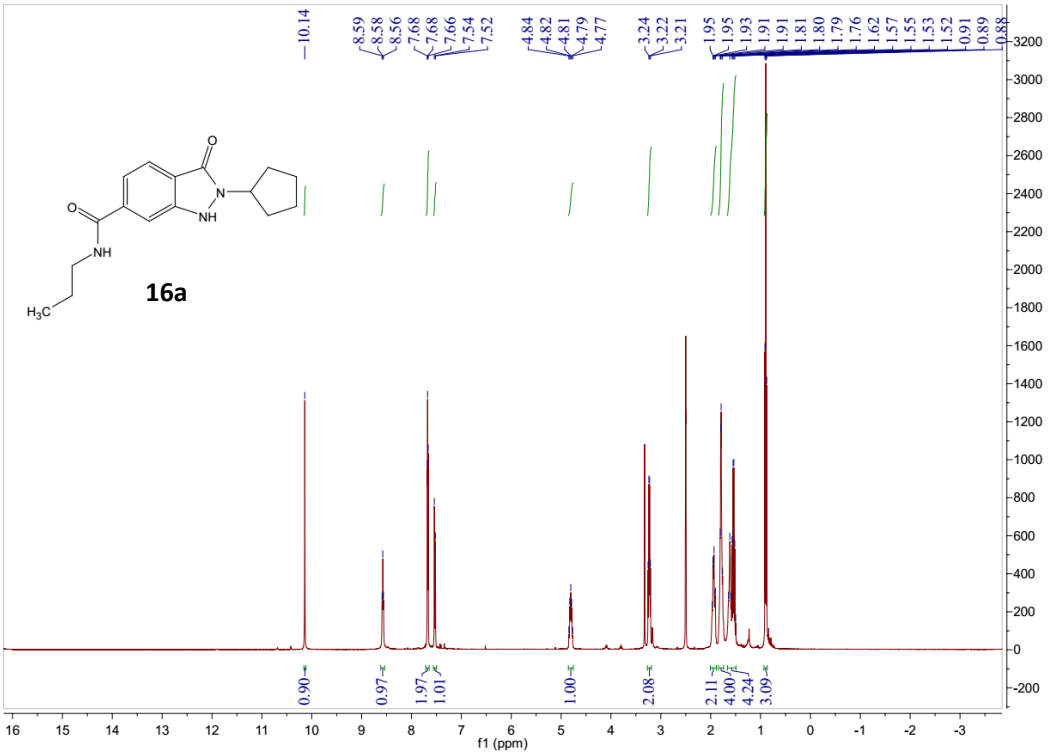
3. 1H , 13C NMR and 19F NMR spectra



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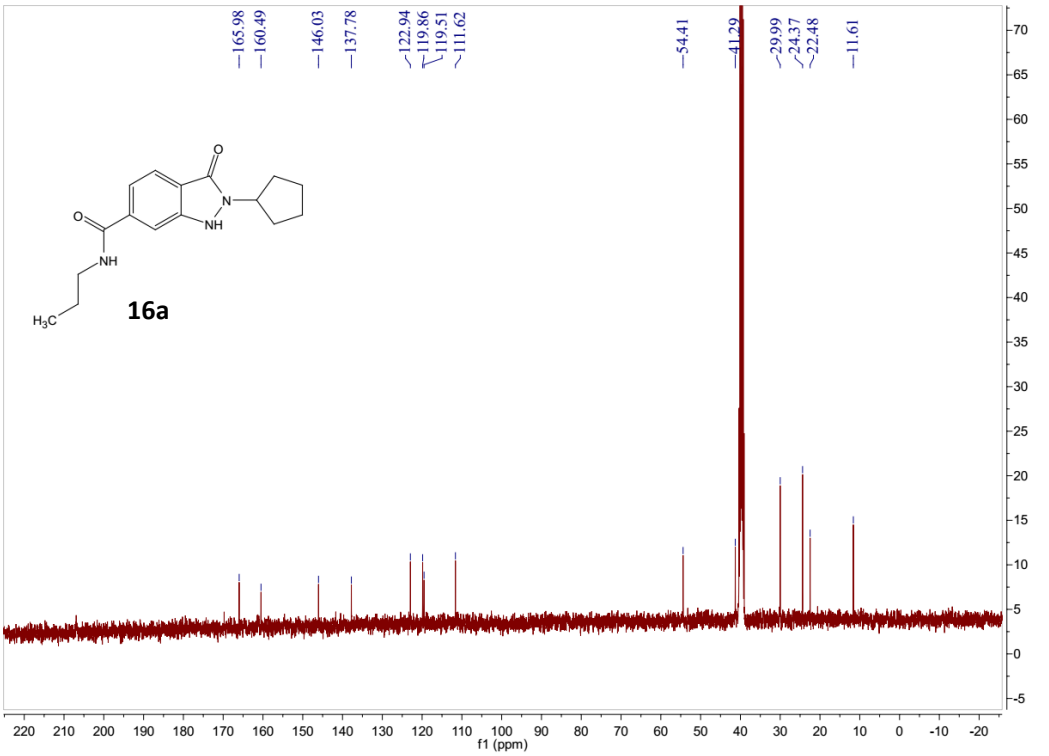
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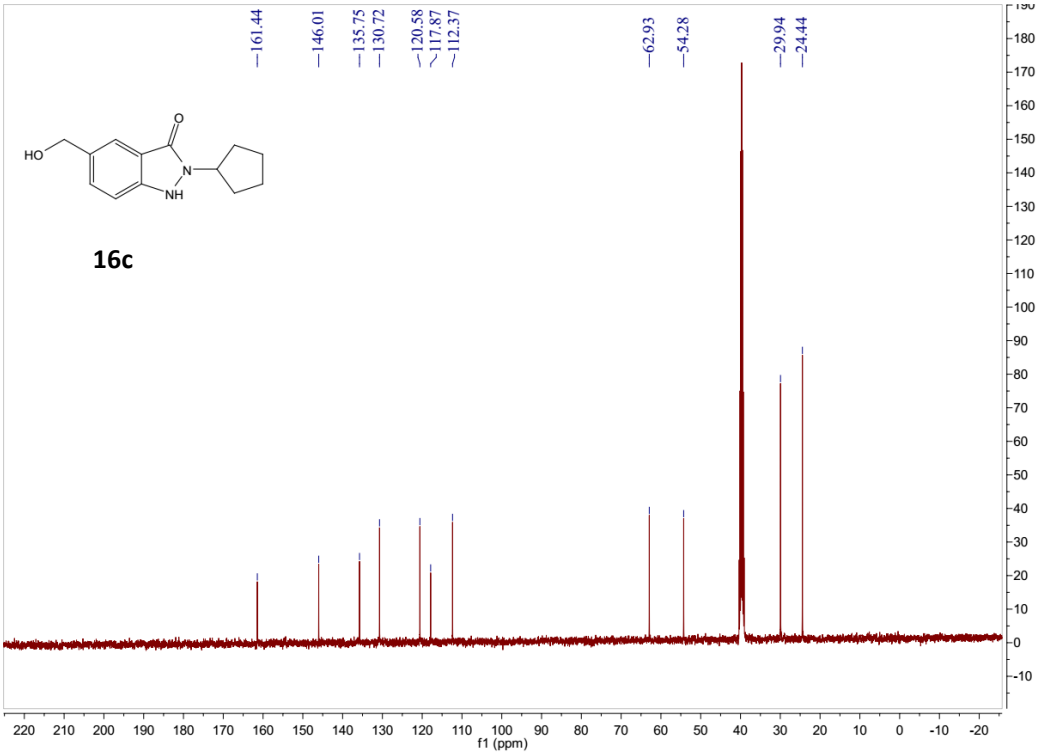
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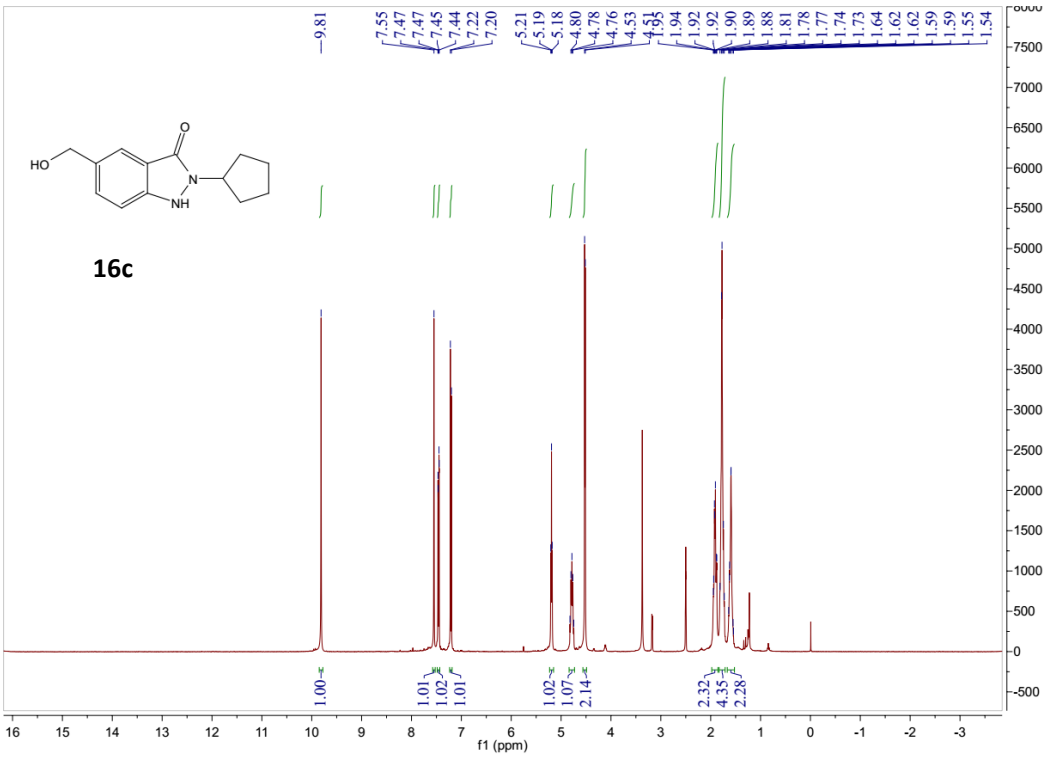
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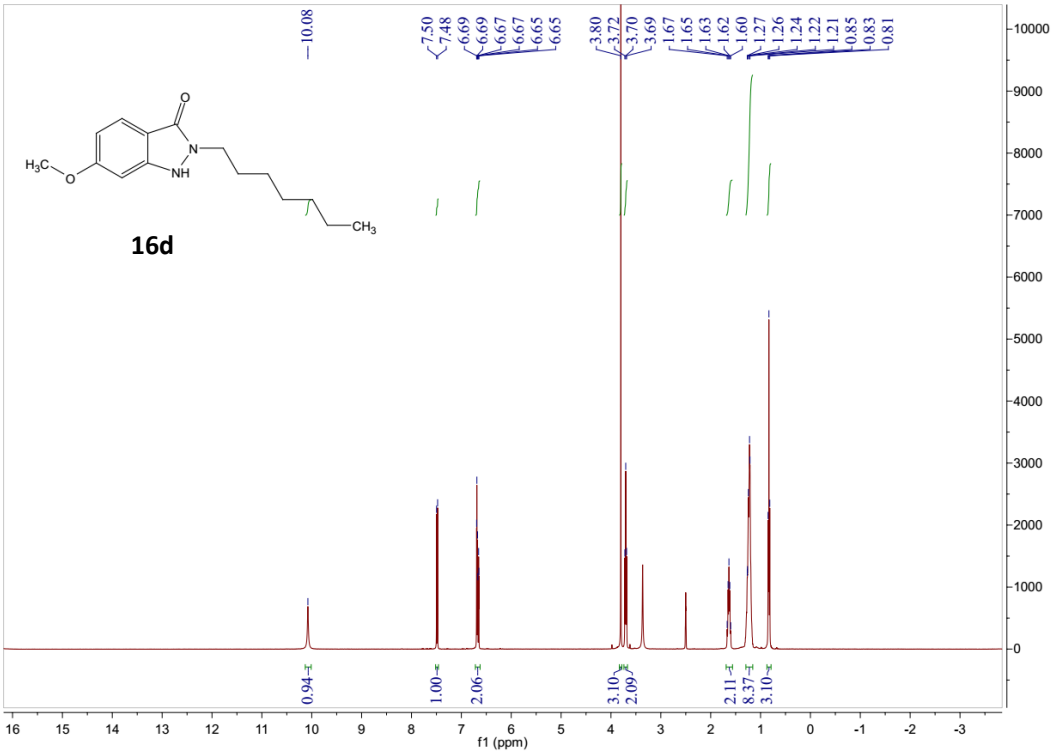
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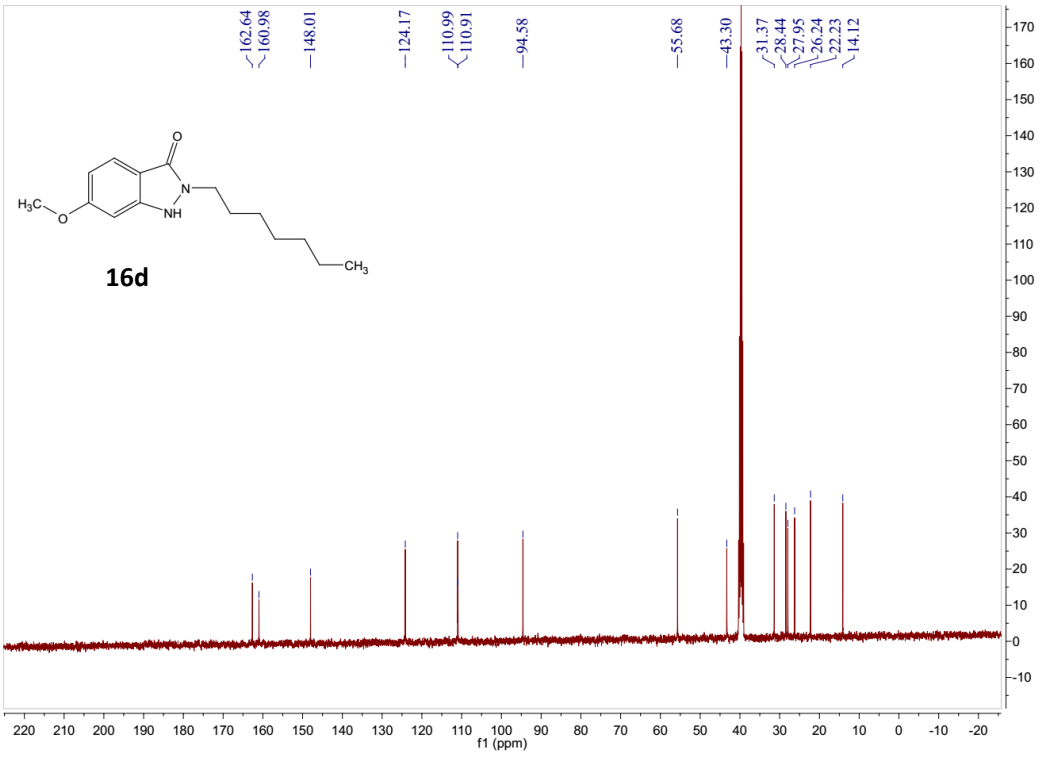
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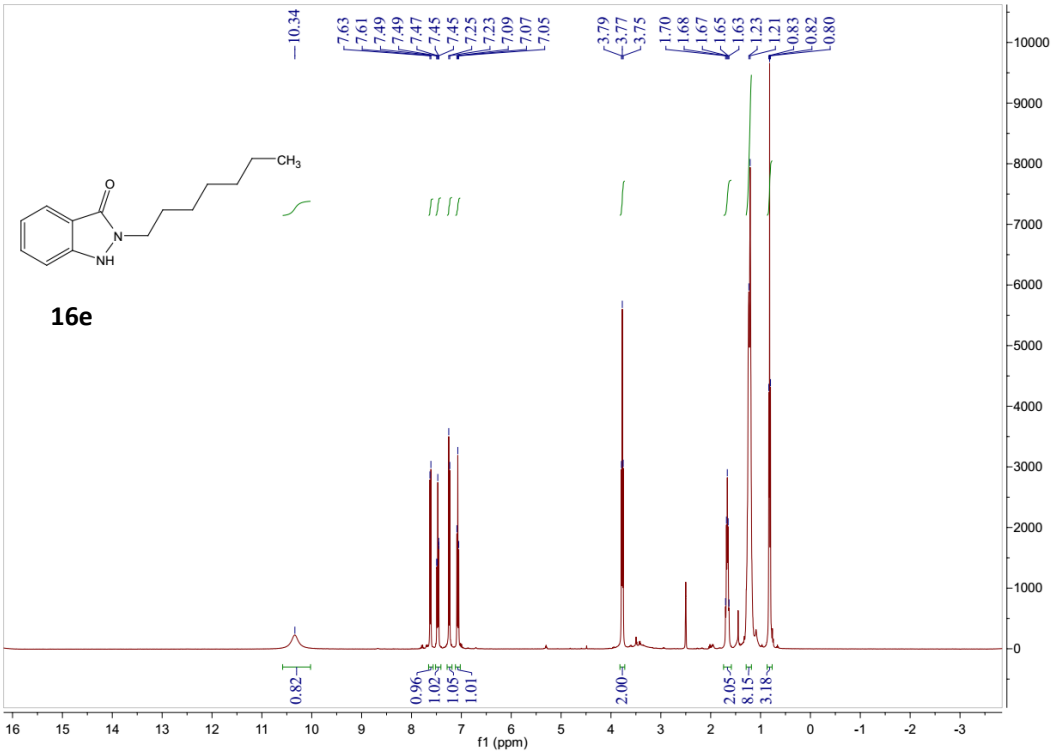
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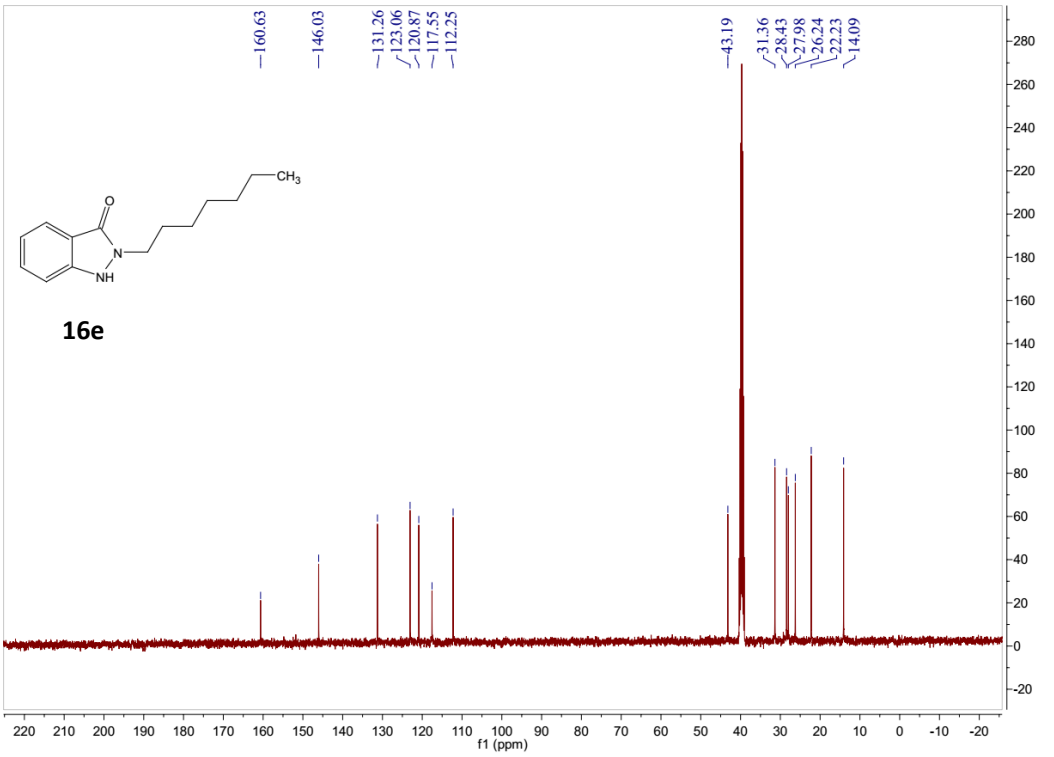
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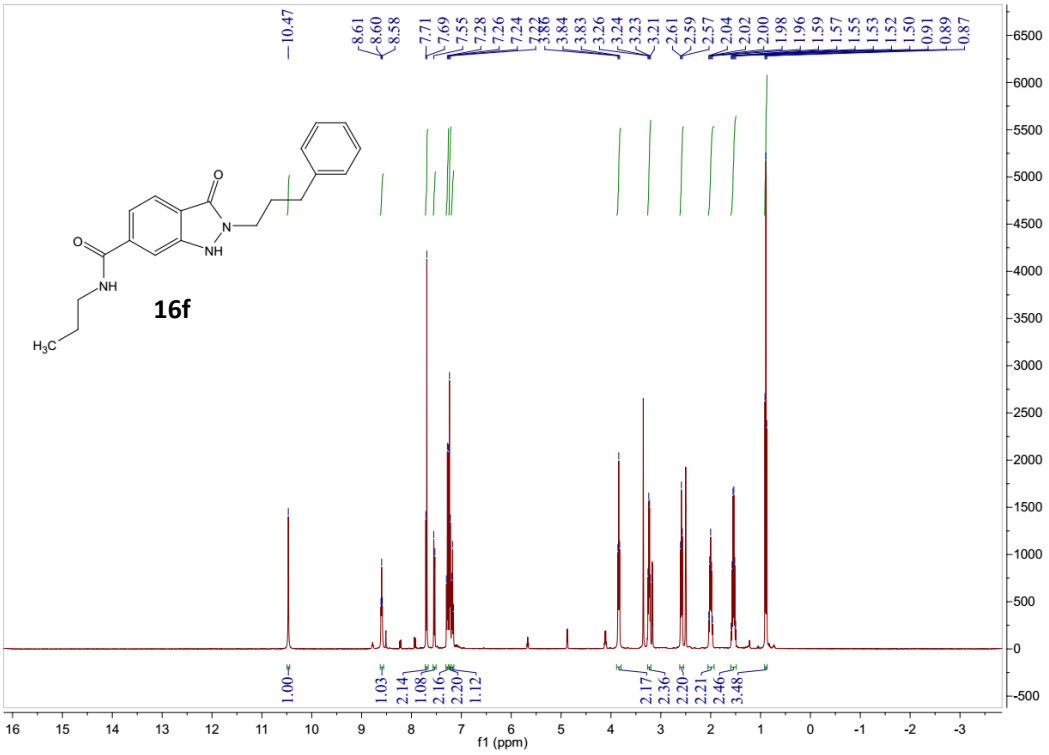
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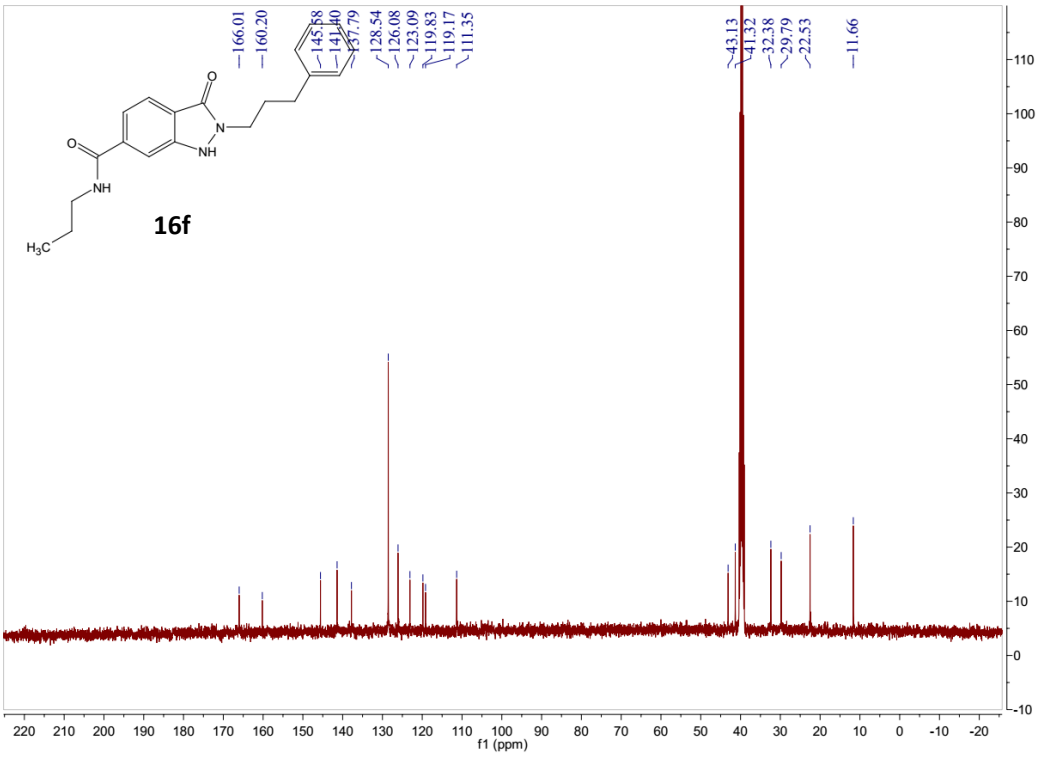
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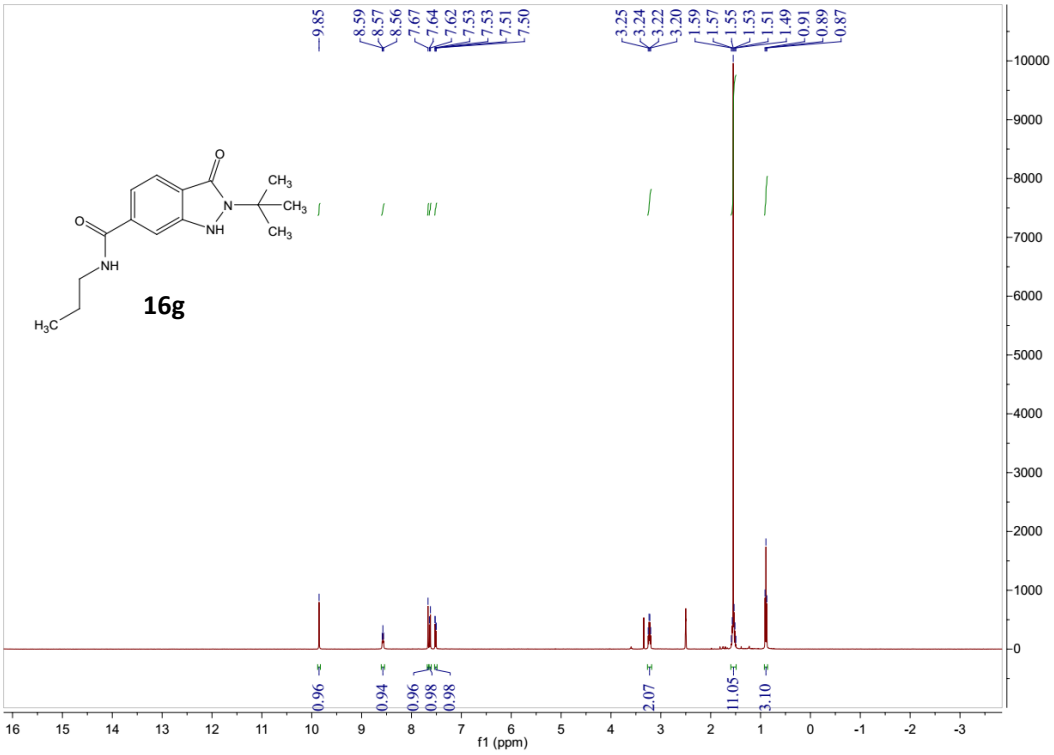
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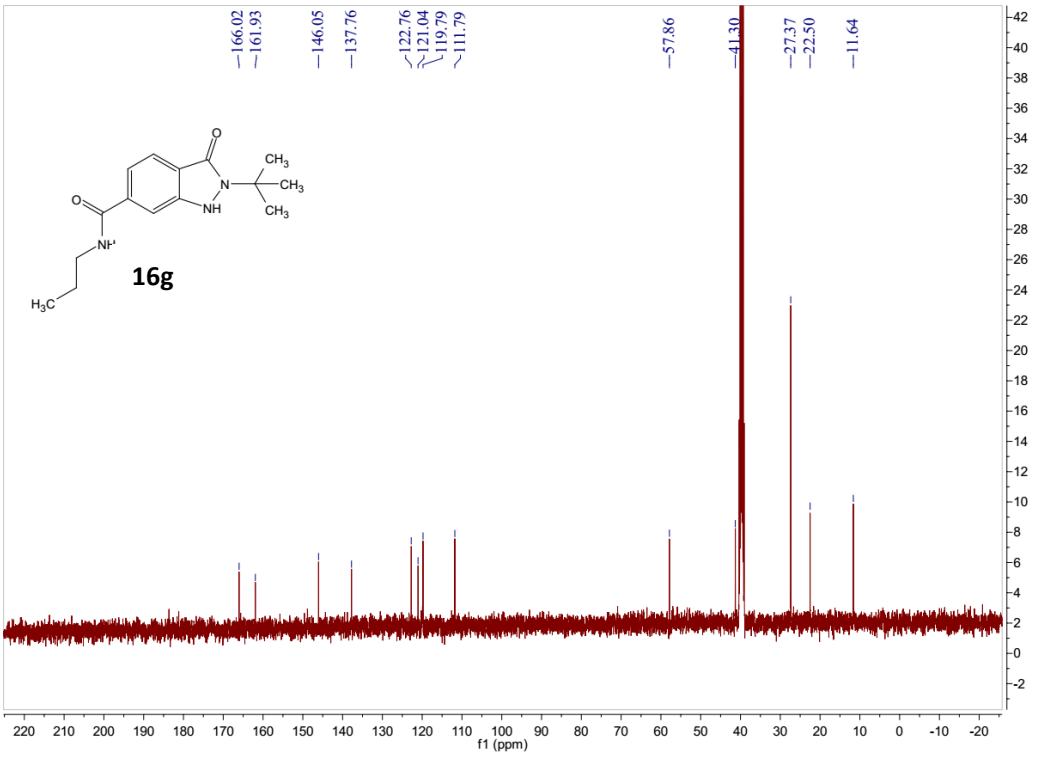
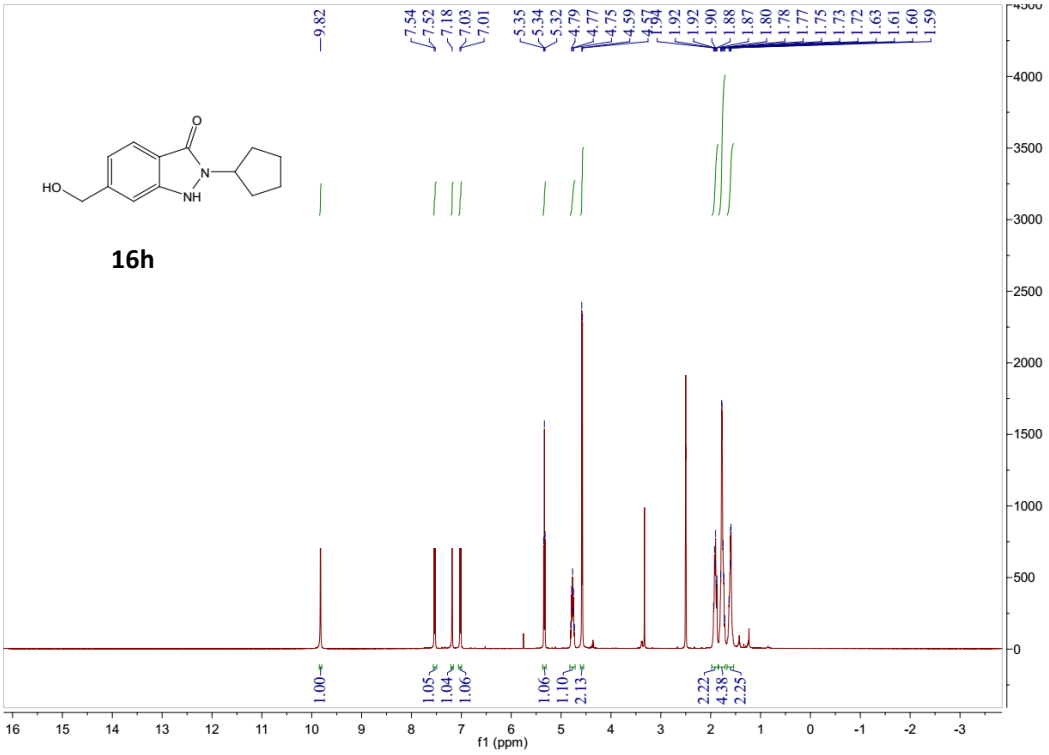
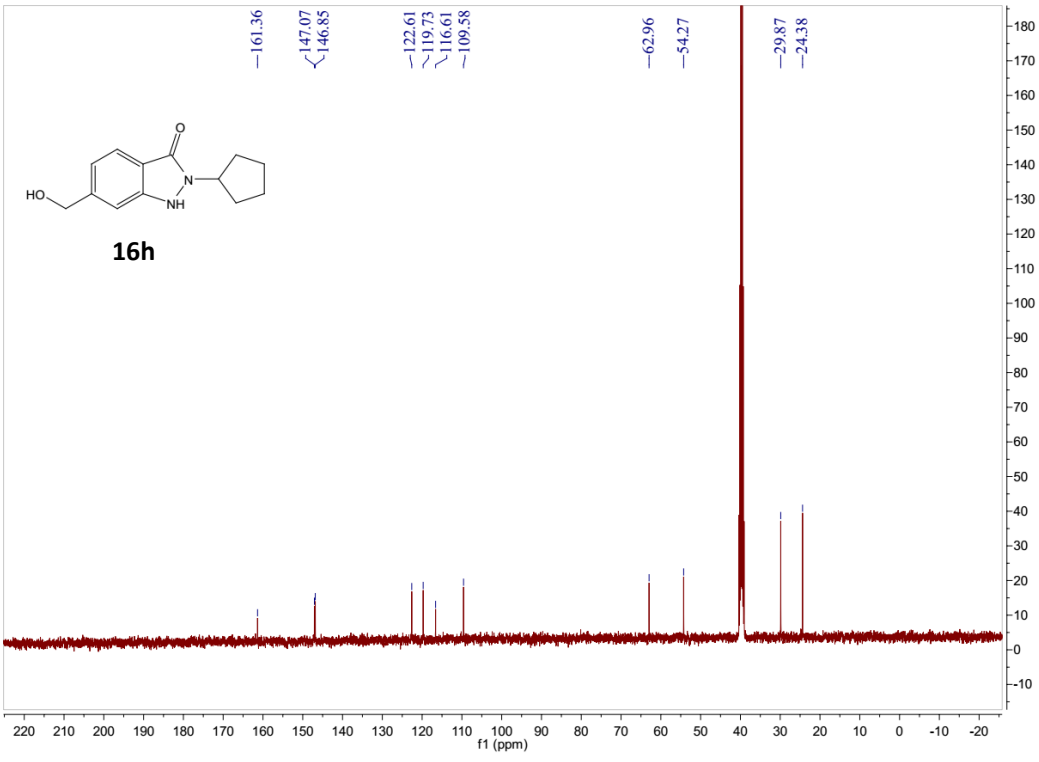
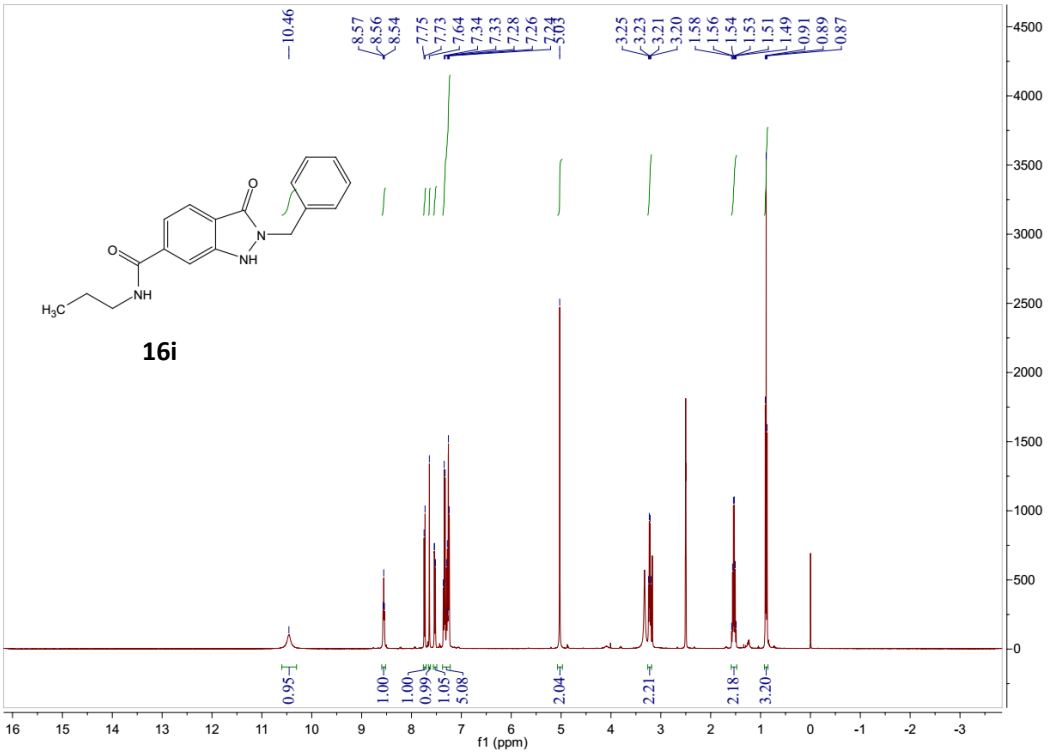
f1 (ppm)
16g

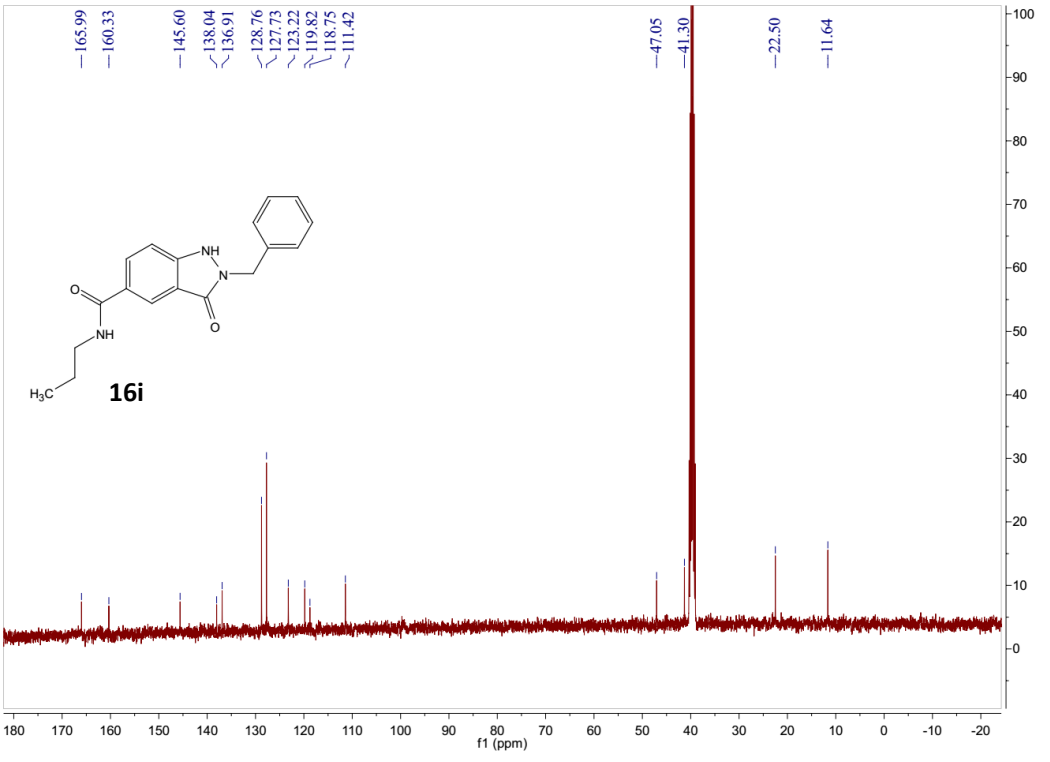

166.02
161.93
146.05
137.76
122.76
121.04
119.79
111.79
57.86
41.30
27.37
22.50
11.64
f1 (ppm)
16g


HO
O
N
NH
16h
9.82
7.54
7.52
7.18
7.03
7.01
5.35
5.34
5.32
4.79
4.77
4.75
4.59
4.57
1.94
1.92
1.92
1.90
1.88
1.87
1.80
1.78
1.77
1.75
1.73
1.72
1.63
1.61
1.60
1.59
1.00
1.05
1.04
1.06
1.06
1.10
2.13
2.22
4.38
2.25
f1 (ppm)

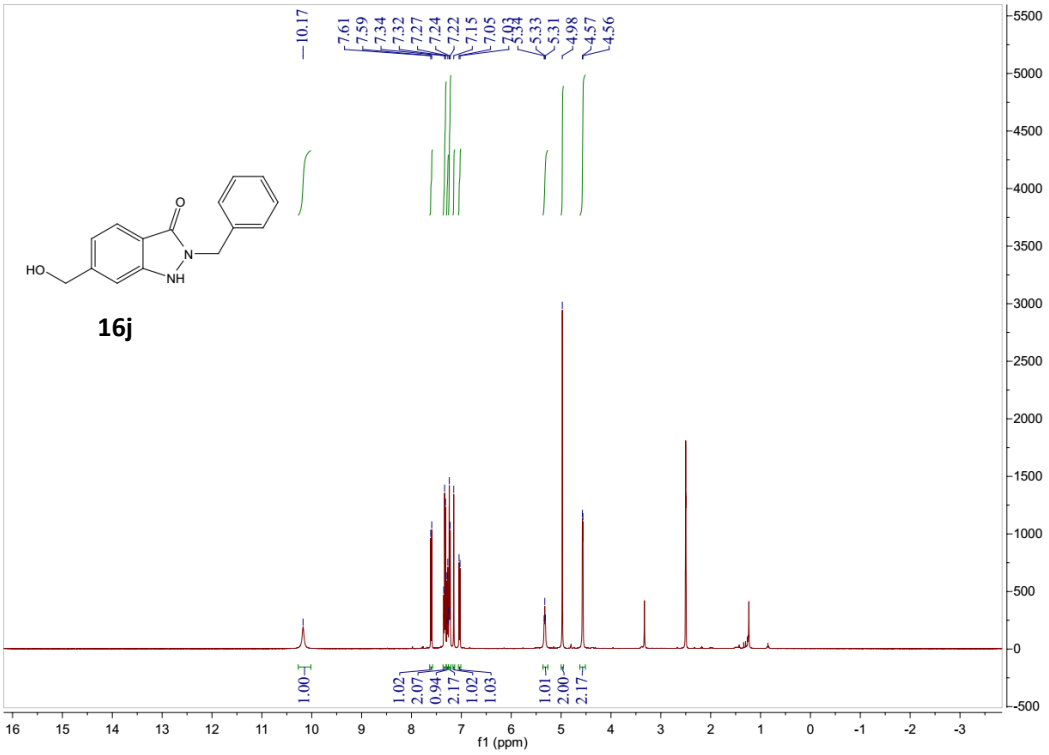

HO
O
N
NH
16h
161.36
147.07
146.85
122.61
119.73
116.61
109.58
62.96
54.27
29.87
24.38
f1 (ppm)


10.46
8.57
8.56
8.54
7.75
7.73
7.64
7.34
7.33
7.28
7.26
7.24
7.03
3.25
3.23
3.21
3.20
1.58
1.56
1.54
1.53
1.51
1.49
0.91
0.89
0.87
0.95
1.00
1.00
0.99
1.05
5.08
2.04
2.21
2.18
3.20
f1 (ppm)

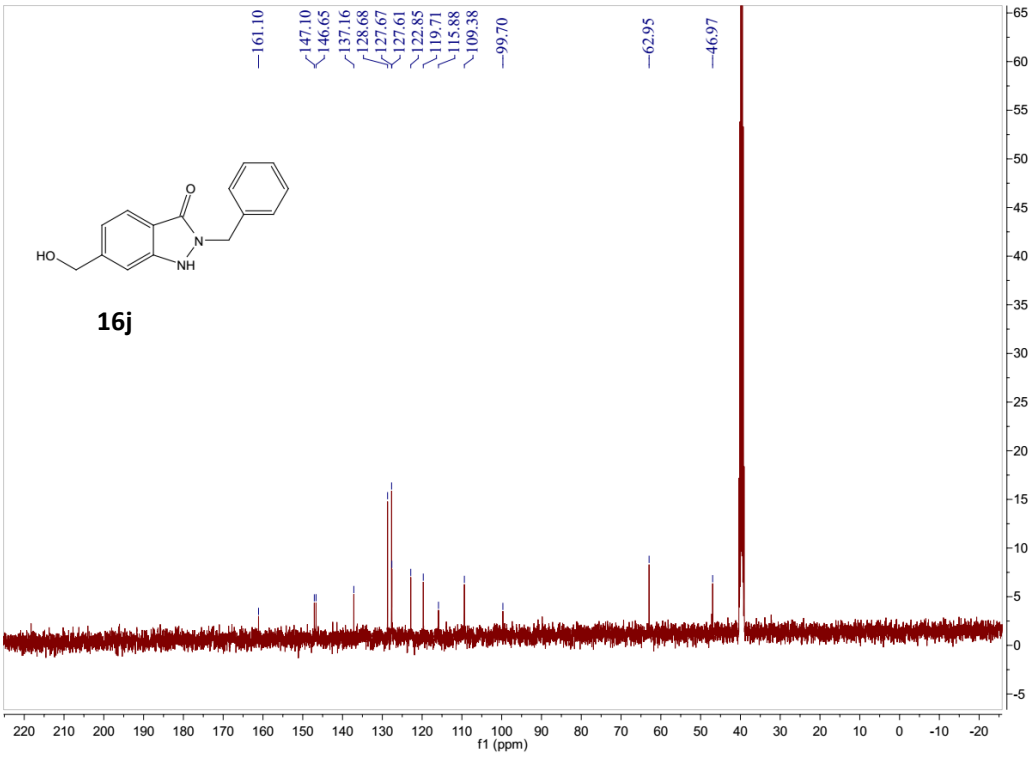
16i


165.99
160.33
145.60
138.04
136.91
128.76
127.73
123.22
119.82
118.75
111.42
47.05
41.30
22.50
11.64
f1 (ppm)

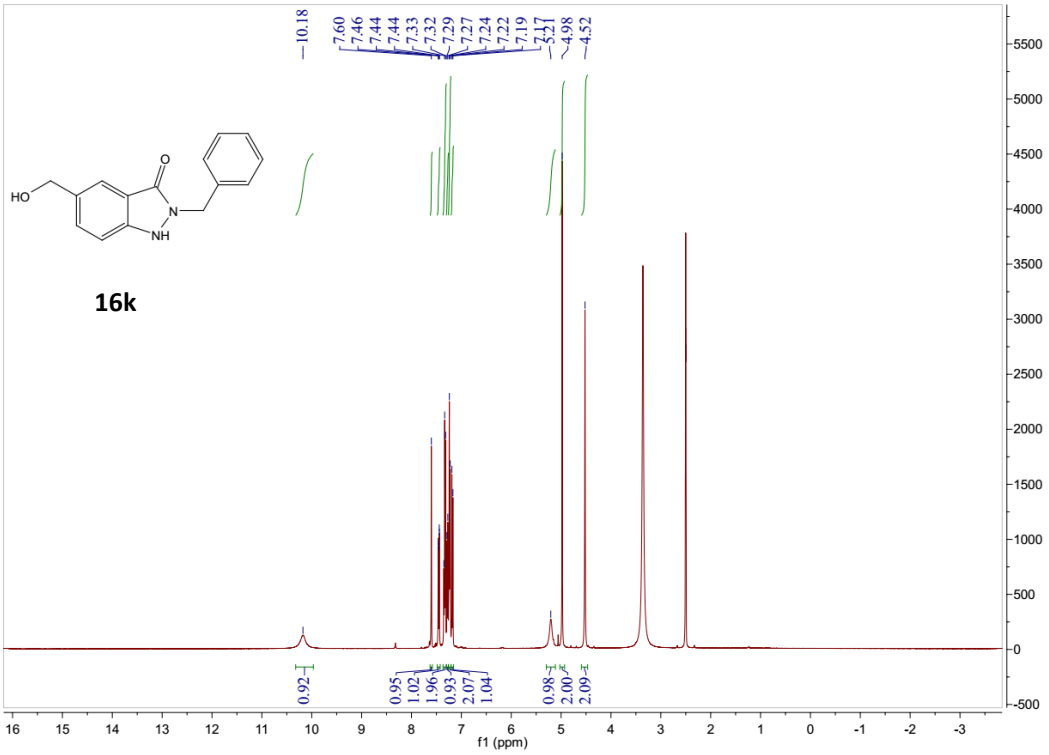
16i


10.17
7.61
7.59
7.34
7.32
7.27
7.24
7.22
7.15
7.05
7.03
5.34
5.33
5.31
4.98
4.57
4.56
HO
O
N
NH
1.00
1.02
2.07
0.94
2.17
1.02
1.03
1.01
2.00
2.17
f1 (ppm)

16j


161.10
147.10
146.65
137.16
128.68
127.67
127.61
122.85
119.71
115.88
109.38
99.70
62.95
46.97
HO
O
N
NH
f1 (ppm)

16j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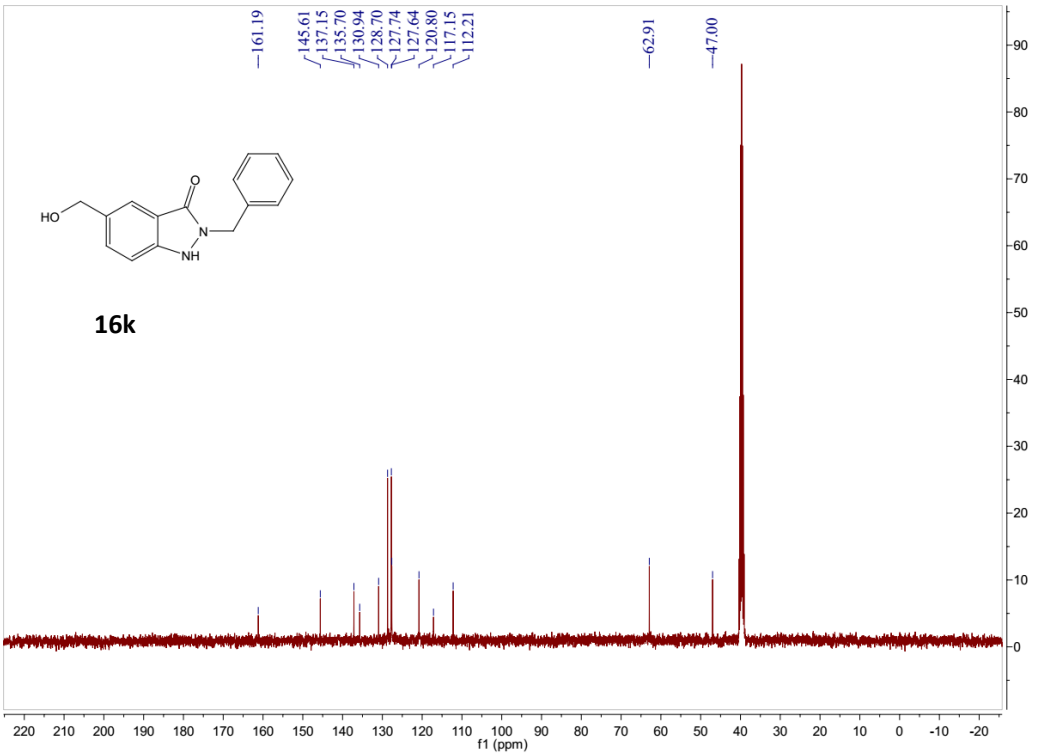
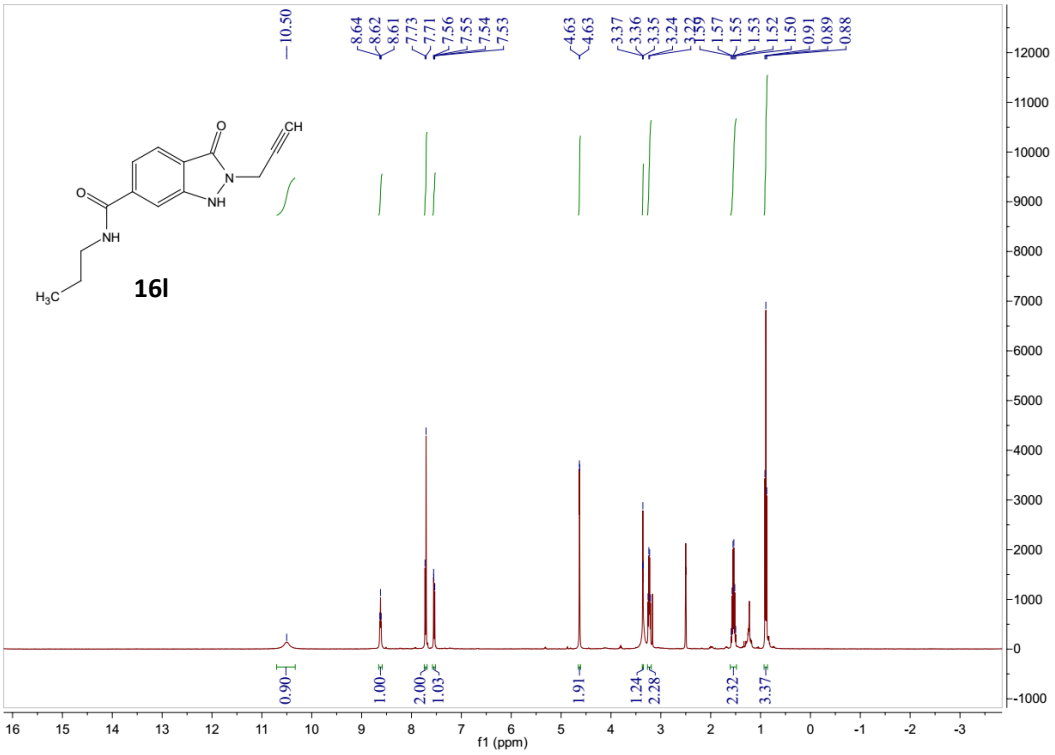
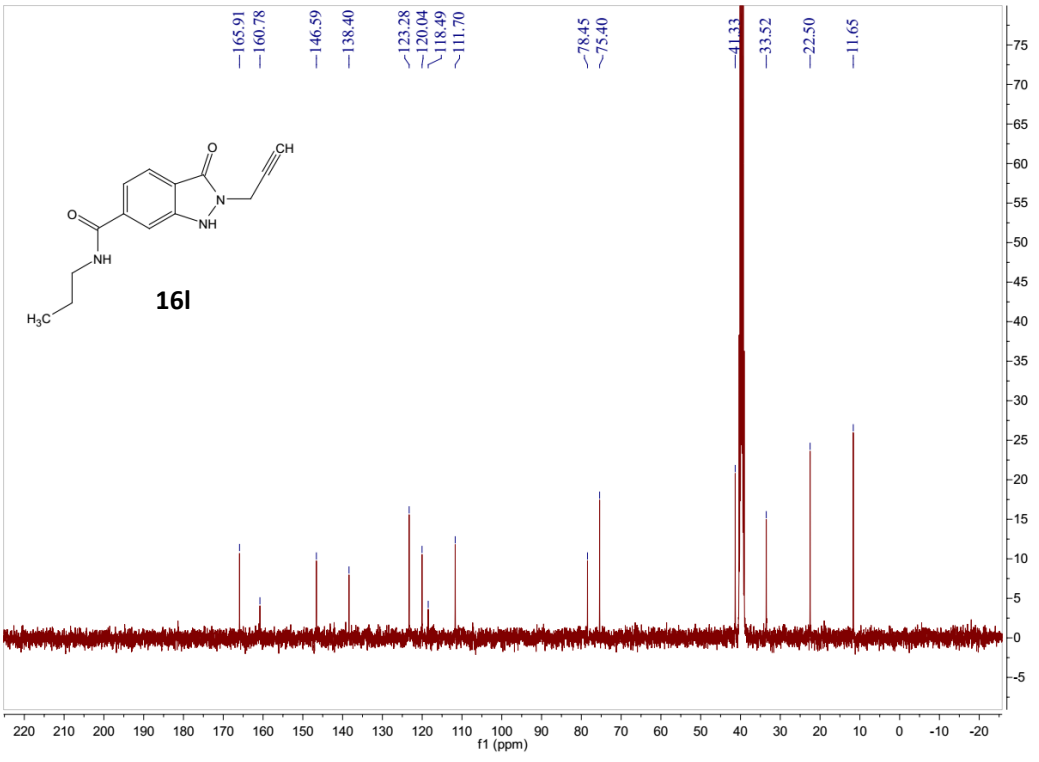
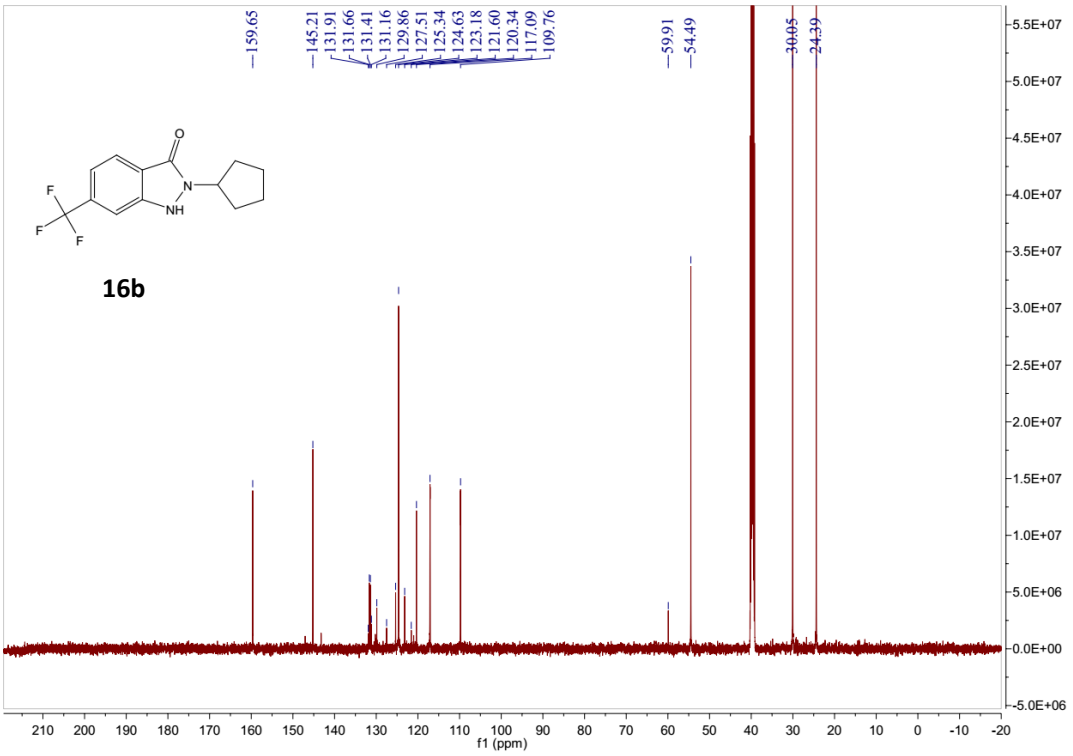
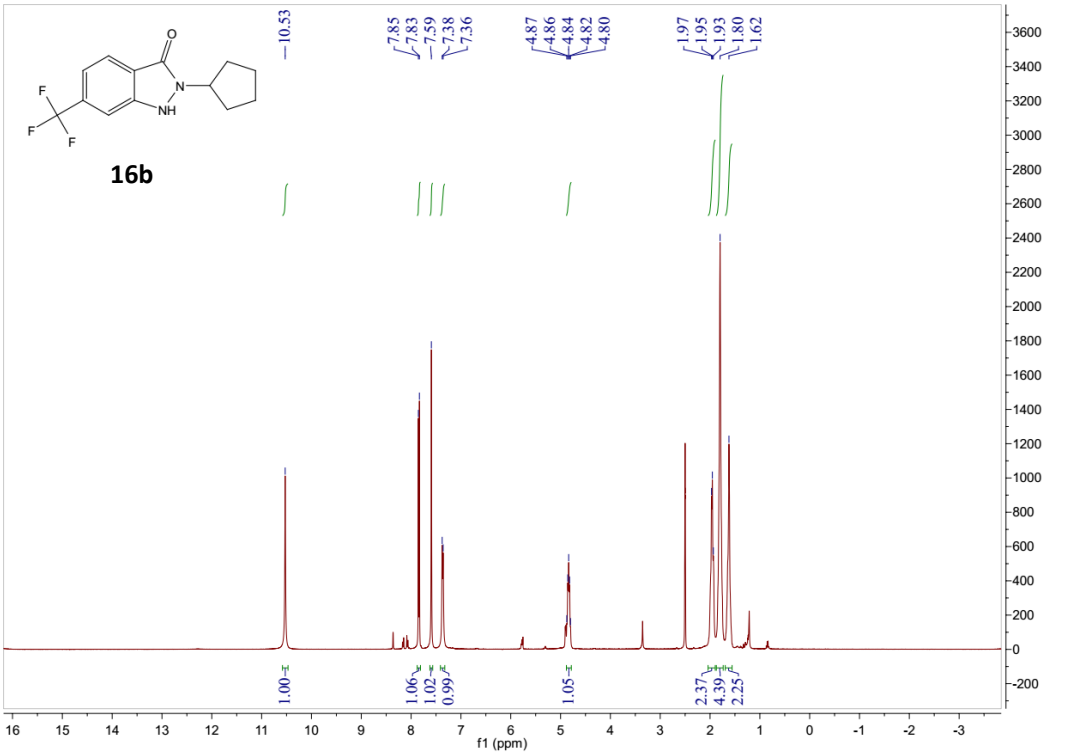
7.60
7.46
7.44
7.44
7.33
7.32
7.29
7.27
7.24
7.22
7.19
7.17
5.21
4.98
4.52
HO
O
N
NH
16k
0.92
0.95
1.02
1.96
0.93
2.07
1.04
0.98
2.00
2.09
f1 (ppm)

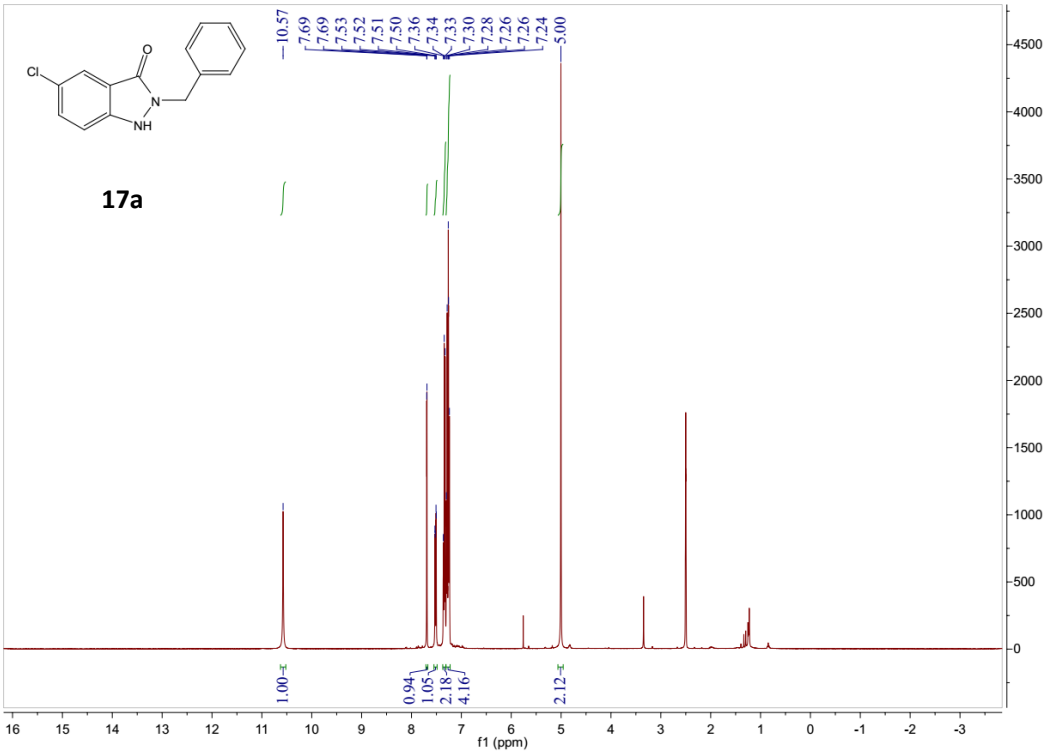

161.19
145.61
137.15
135.70
130.94
128.70
127.74
127.64
120.80
117.15
112.21
62.91
47.00
HO
O
N
NH
16k
f1 (ppm)

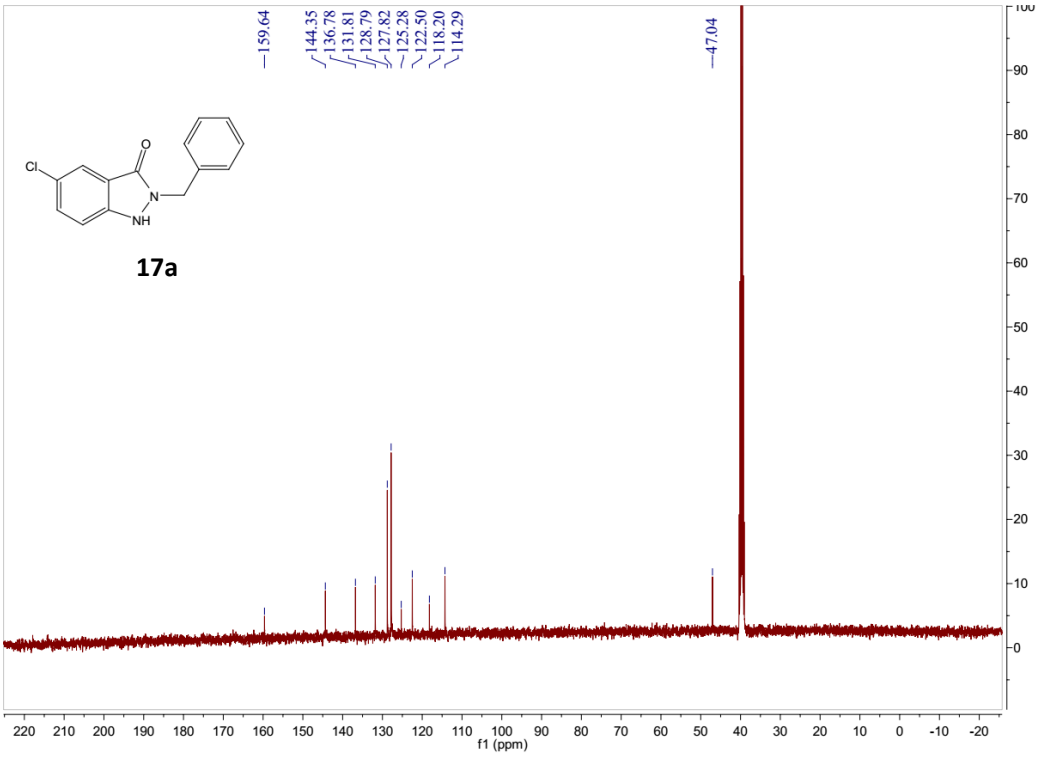

16l
10.50
8.64
8.62
8.61
7.73
7.71
7.56
7.55
7.54
7.53
4.63
4.63
3.37
3.36
3.35
3.24
3.22
1.59
1.57
1.55
1.53
1.52
1.50
0.91
0.89
0.88
0.90
1.00
2.00
1.03
1.91
1.24
2.28
2.32
3.37
f1 (ppm)

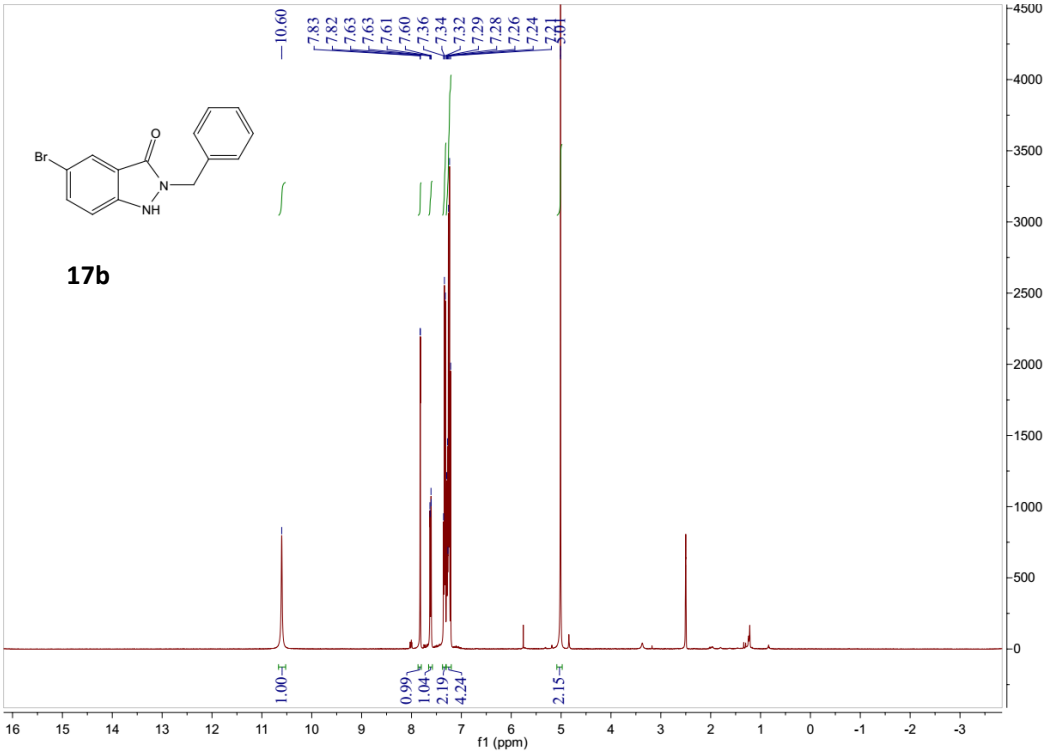

16l
165.91
160.78
146.59
138.40
123.28
120.04
118.49
111.70
78.45
75.40
41.33
33.52
22.50
11.65
f1 (ppm)

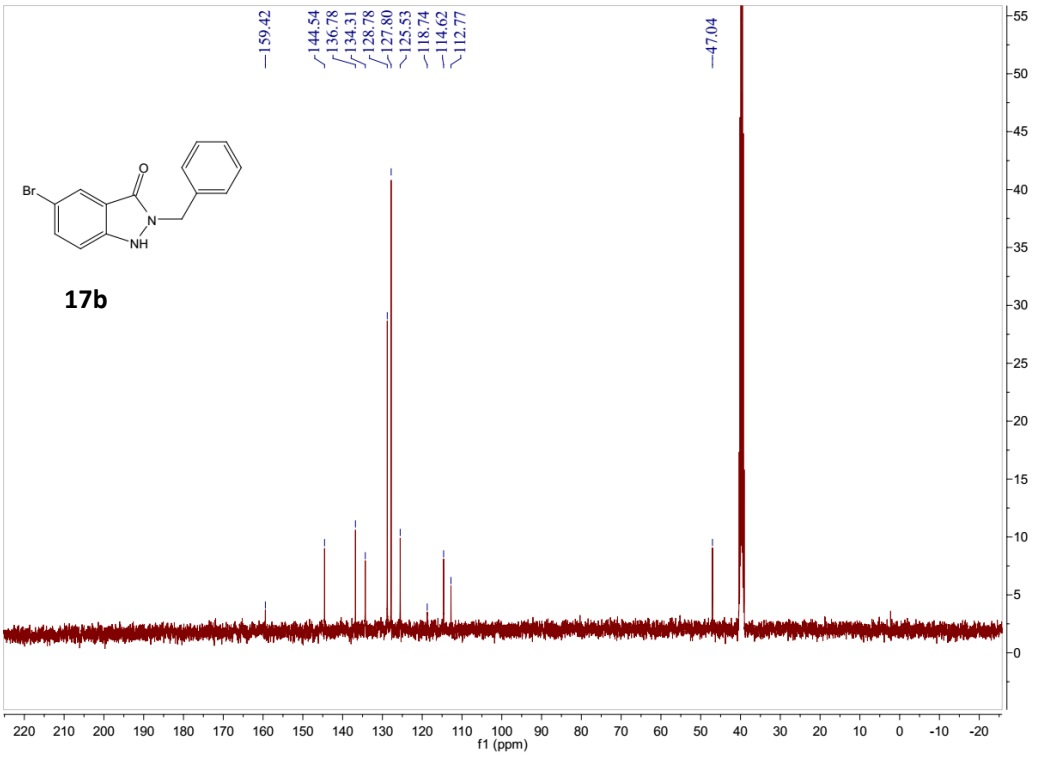

159.65
145.21
131.91
131.66
131.41
131.16
129.86
127.51
125.34
124.63
123.18
121.60
120.34
117.09
109.76
59.91
54.49
30.05
24.39
16b
f1 (ppm)

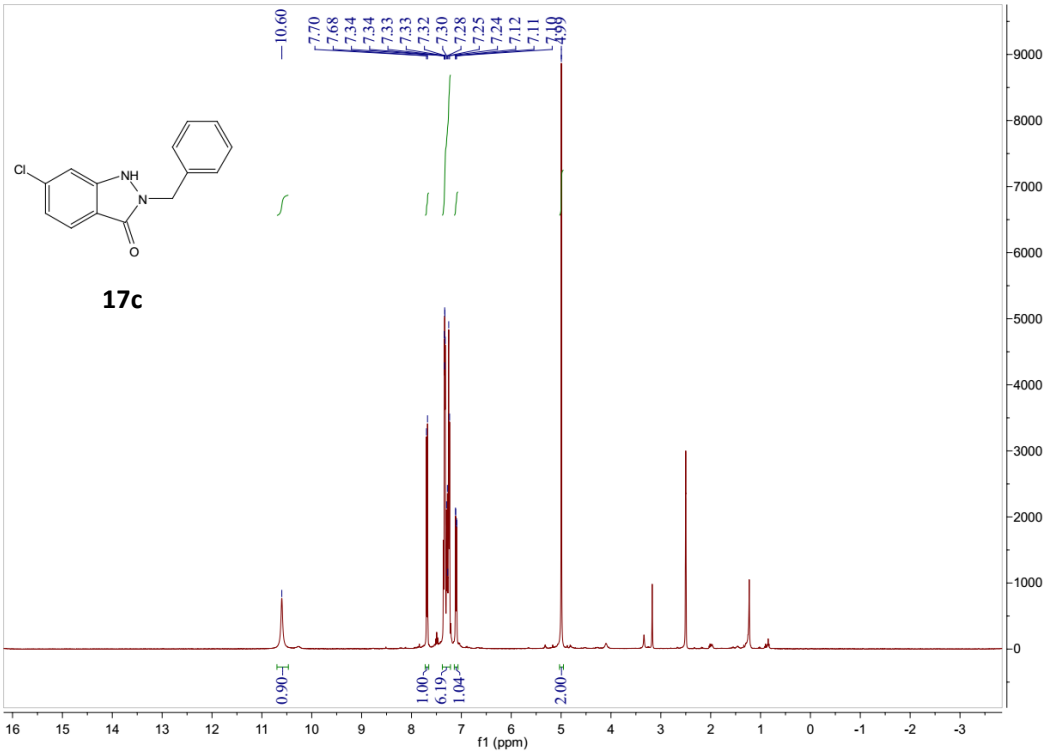

10.53
7.85
7.83
7.59
7.38
7.36
4.87
4.86
4.84
4.82
4.80
1.97
1.95
1.93
1.80
1.62
16b
1.00
1.06
1.02
0.99
1.05
2.37
4.39
2.25
f1 (ppm)

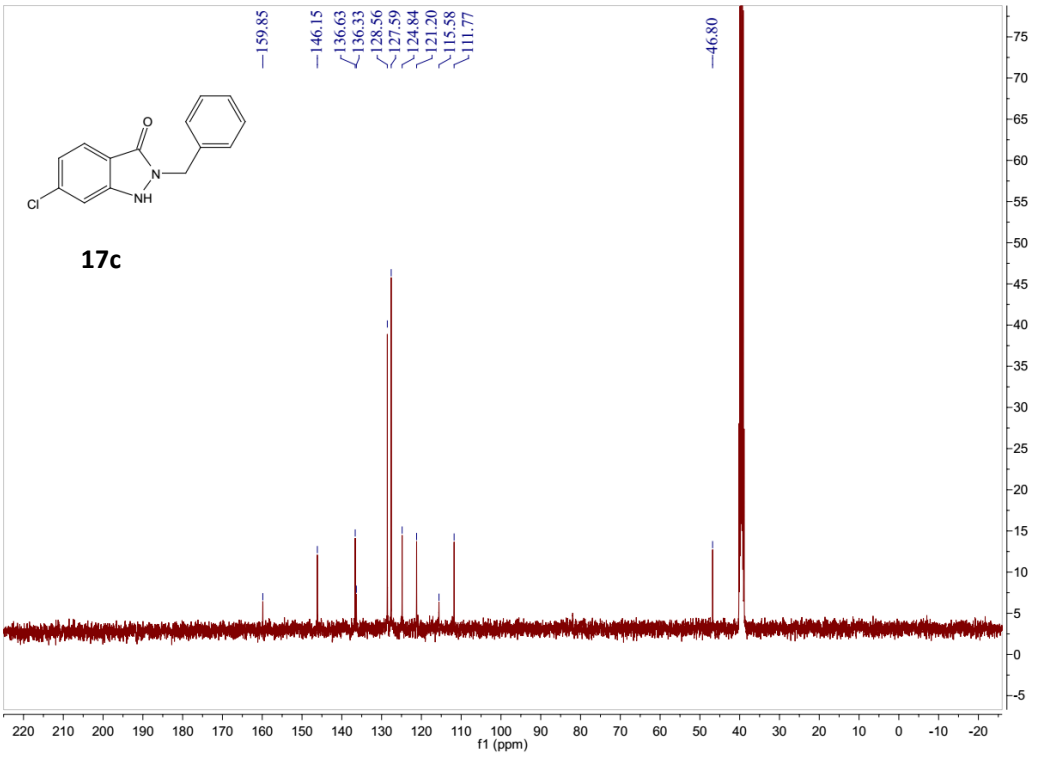

17a
10.57
7.69
7.69
7.53
7.52
7.51
7.50
7.36
7.34
7.33
7.30
7.28
7.26
7.26
7.24
5.00
1.00
0.94
1.05
2.18
4.16
2.12
f1 (ppm)

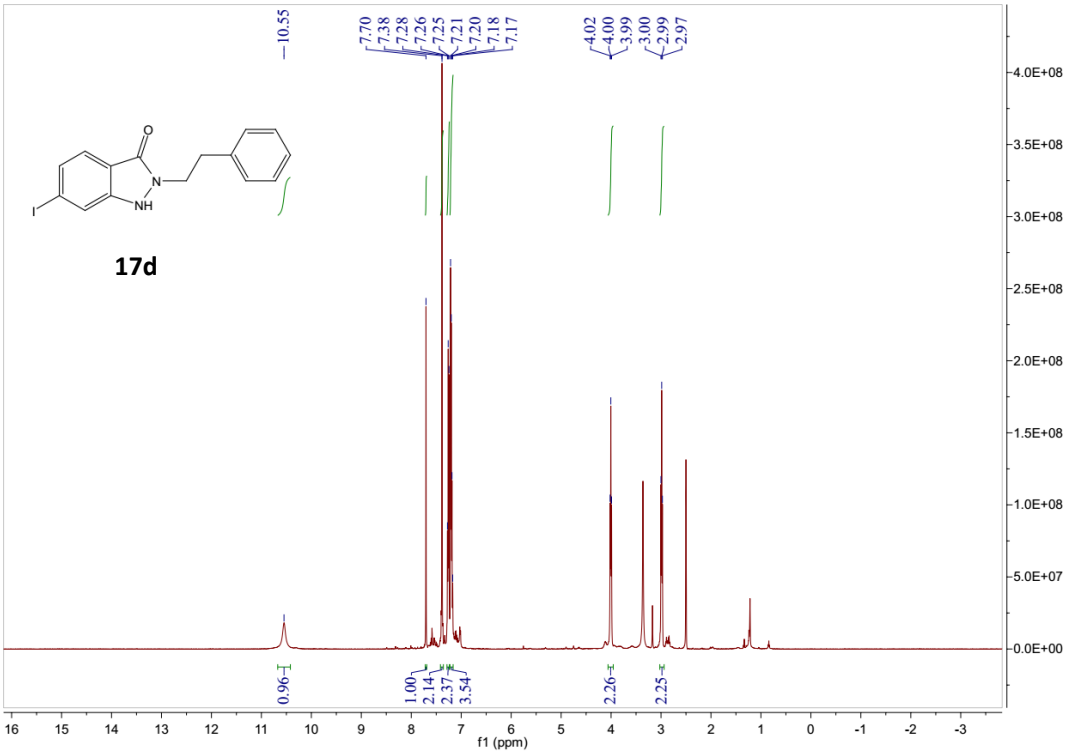

17a
159.64
144.35
136.78
131.81
128.79
127.82
125.28
122.50
118.20
114.29
47.04
f1 (ppm)

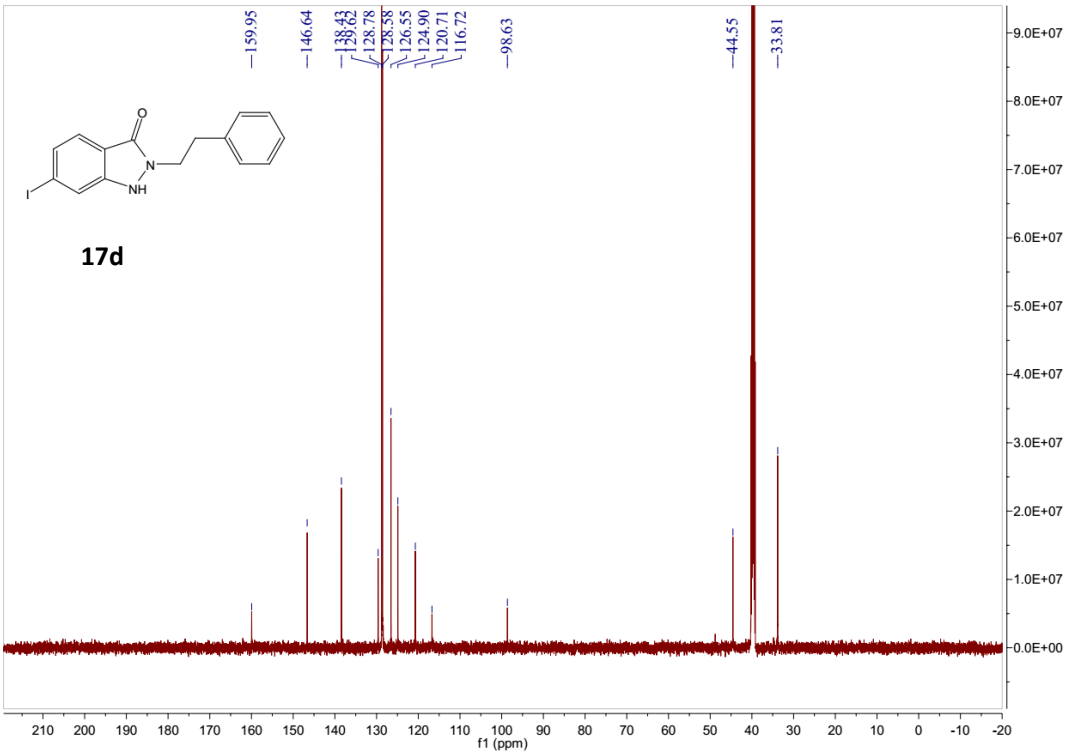

10.60
7.83
7.82
7.63
7.63
7.61
7.60
7.36
7.34
7.32
7.29
7.28
7.26
7.24
7.21
3.81
Br
O
N
NH
17b
1.00
0.99
1.04
2.19
4.24
2.15
f1 (ppm)


159.42
144.54
136.78
134.31
128.78
127.80
125.53
118.74
114.62
112.77
47.04
Br
O
N
NH
17b
f1 (ppm)


10.60
7.70
7.68
7.34
7.34
7.33
7.33
7.32
7.30
7.28
7.25
7.24
7.12
7.11
4.99
Cl
NH
N
O
17c
0.90
1.00
6.19
1.04
2.00
f1 (ppm)


159.85
146.15
136.63
136.33
128.56
127.59
124.84
121.20
115.58
111.77
46.80
O
N
NH
Cl
17c
f1 (ppm)


10.55
7.70
7.38
7.28
7.26
7.25
7.21
7.20
7.18
7.17
4.02
4.00
3.99
3.00
2.99
2.97
O
N
NH
I
17d
0.96
1.00
2.14
2.37
3.54
2.26
2.25
f1 (ppm)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128.78
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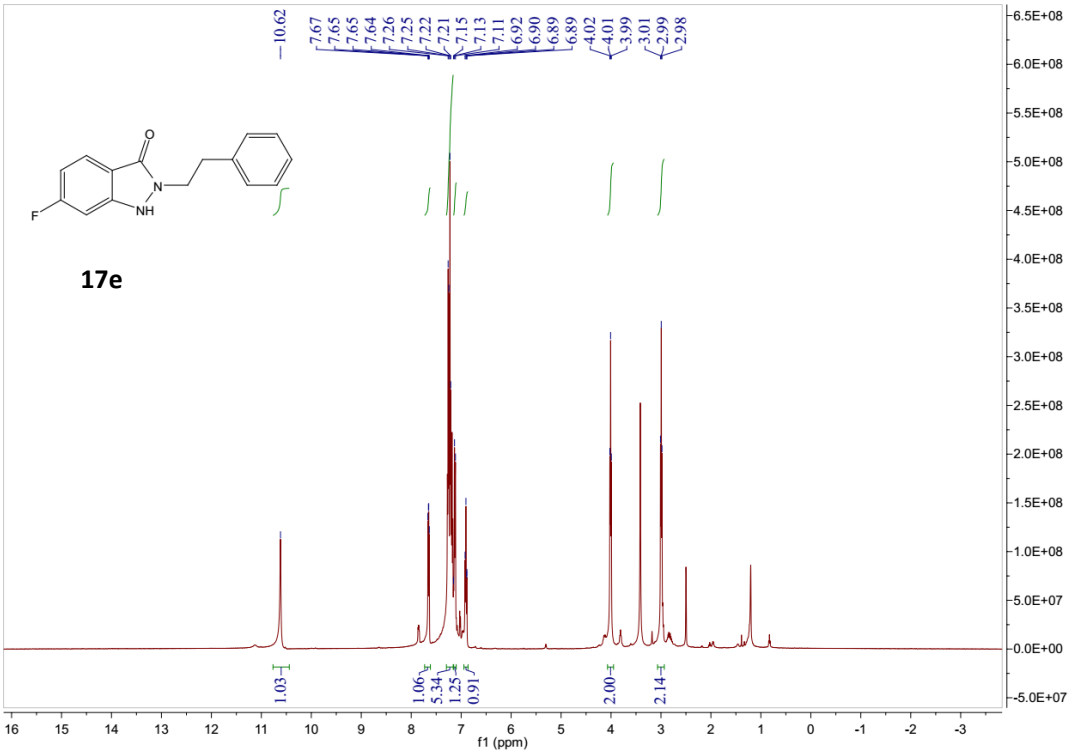
120.71
116.72
98.63
44.55
33.81
O
N
NH
I
17d
f1 (ppm)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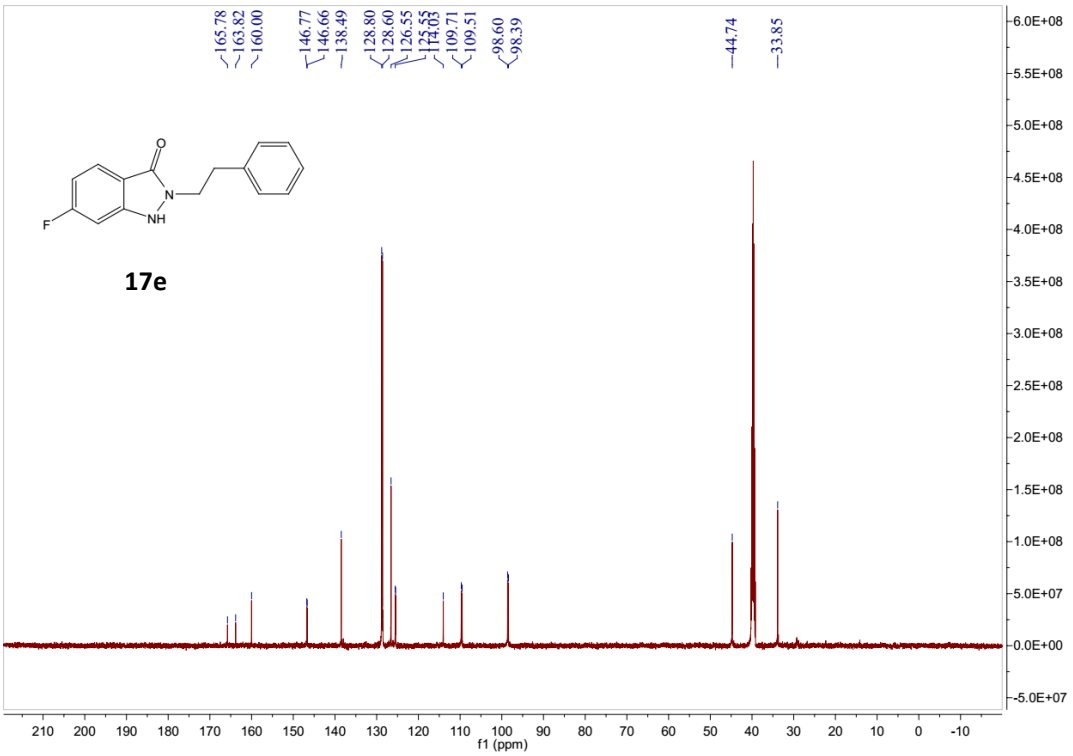
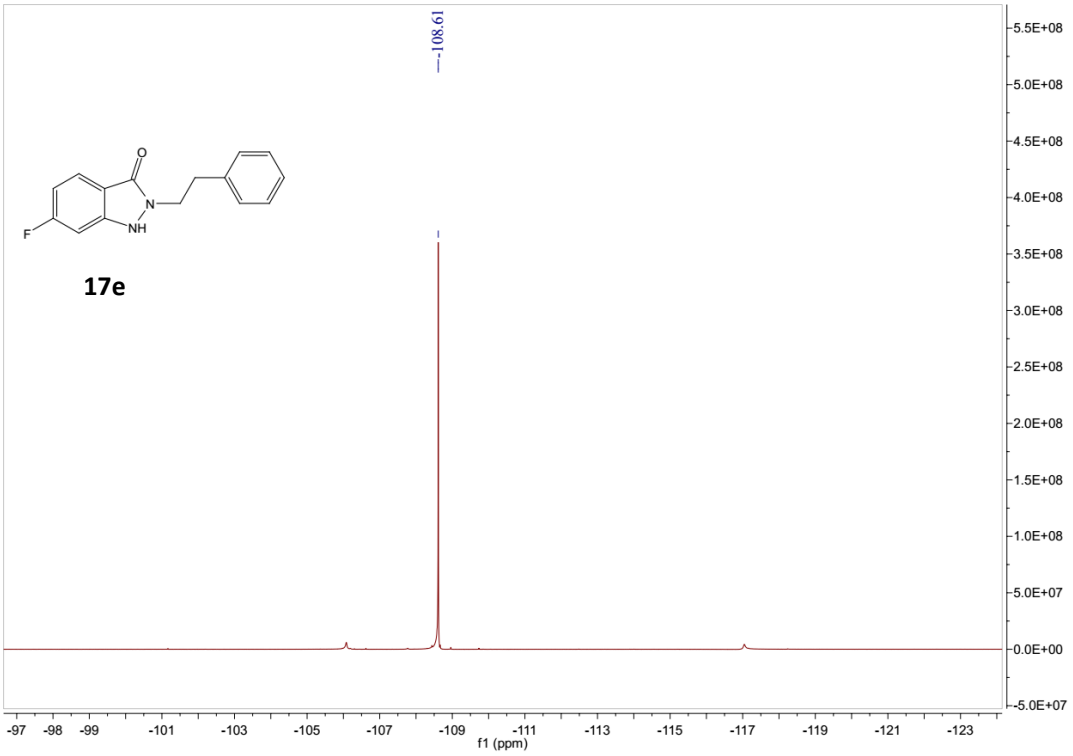
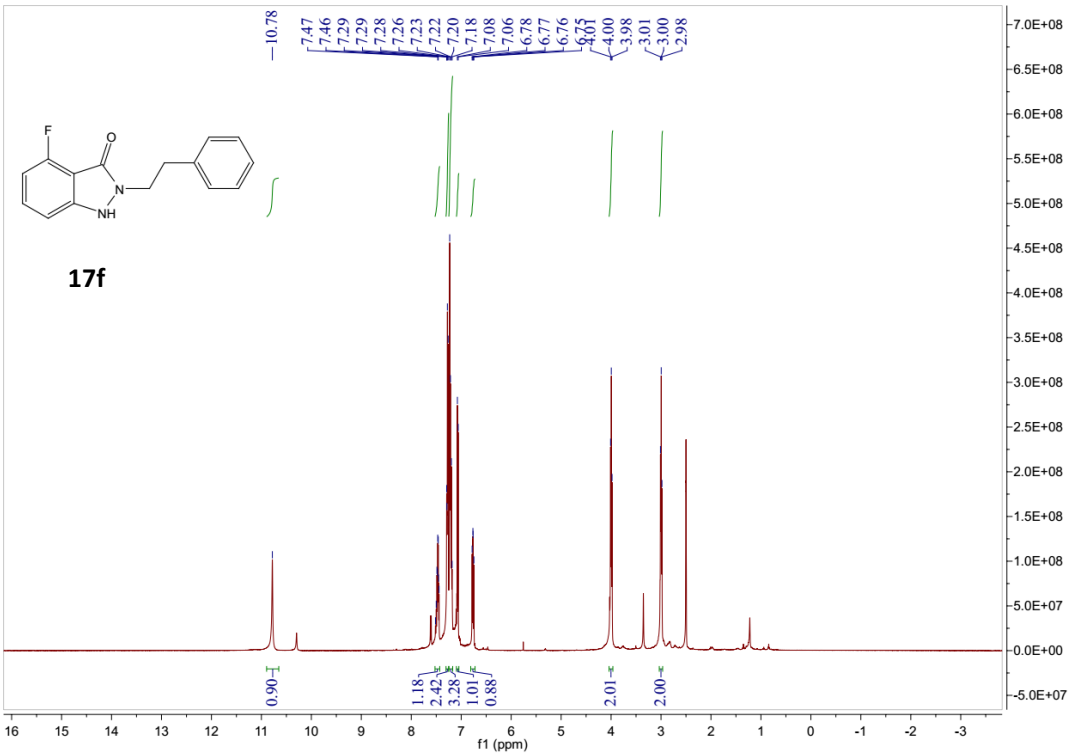
7.64
7.26
7.25
7.22
7.21
7.15
7.13
7.11
6.92
6.90
6.89
6.89
4.02
4.01
3.99
3.01
2.99
2.98
1.03
1.06
5.34
1.25
0.91
2.00
2.14
f1 (ppm)

17e


165.78
163.82
160.00
146.77
146.66
138.49
128.80
128.60
126.55
125.55
114.03
109.71
109.51
98.60
98.39
44.74
33.85
f1 (ppm)

17e


-108.61
O
N
NH
F
17e
-97 -98 -99 -101 -103 -105 -107 -109 -111 -113 -115 -117 -119 -121 -123
f1 (ppm)
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07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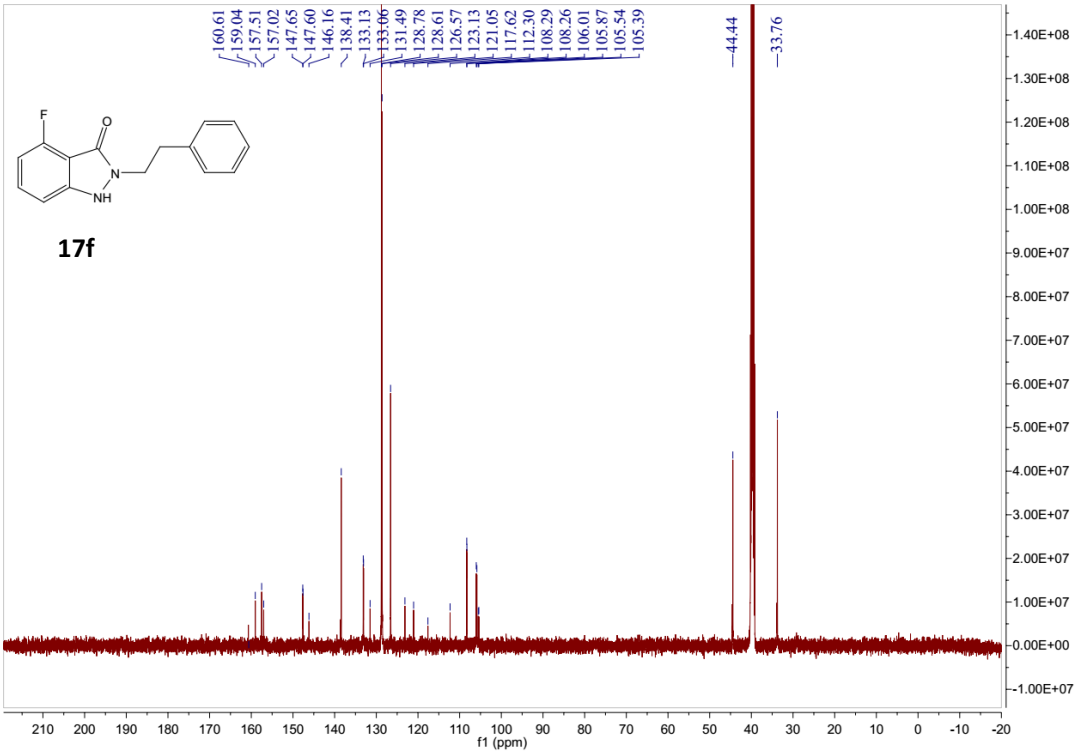
7.28
7.26
7.23
7.22
7.20
7.18
7.08
7.06
6.78
6.77
6.76
6.75
4.01
4.00
3.98
3.01
3.00
2.98
F
O
N
NH
17f
0.90
1.18
2.42
3.28
1.01
0.88
2.01
2.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)
7.0E+08
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07


160.61
159.04
157.51
157.02
147.65
147.60
146.16
138.41
133.13
133.06
131.49
128.78
128.61
126.57
123.13
121.05
117.62
112.30
108.29
108.26
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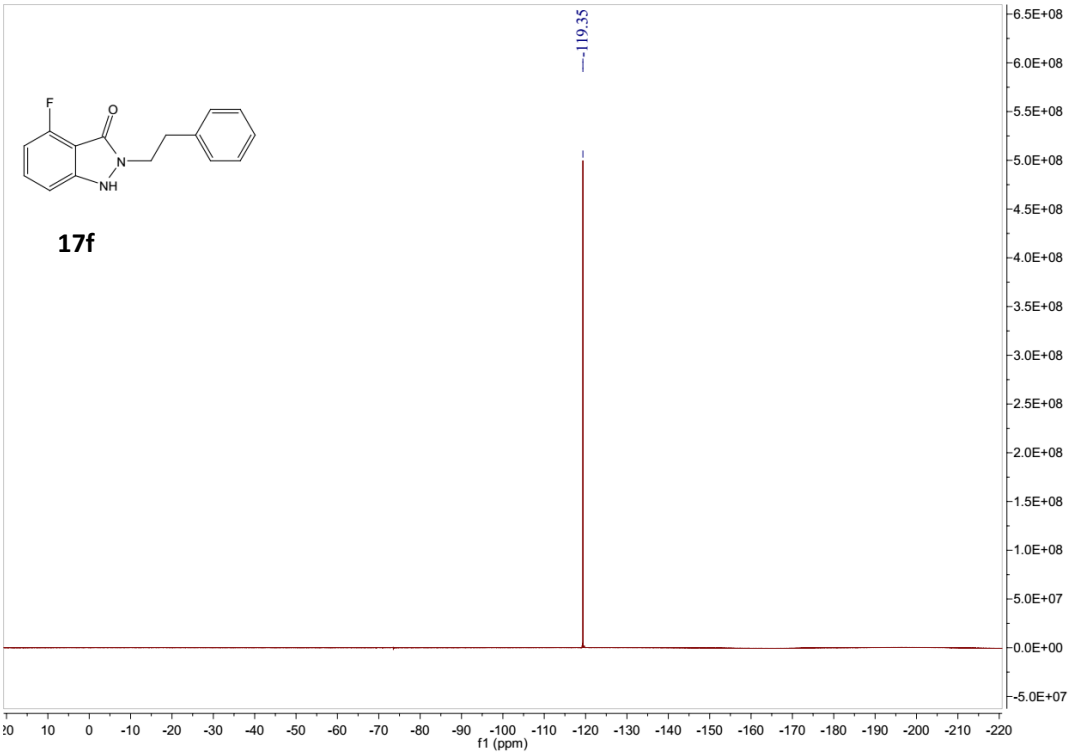
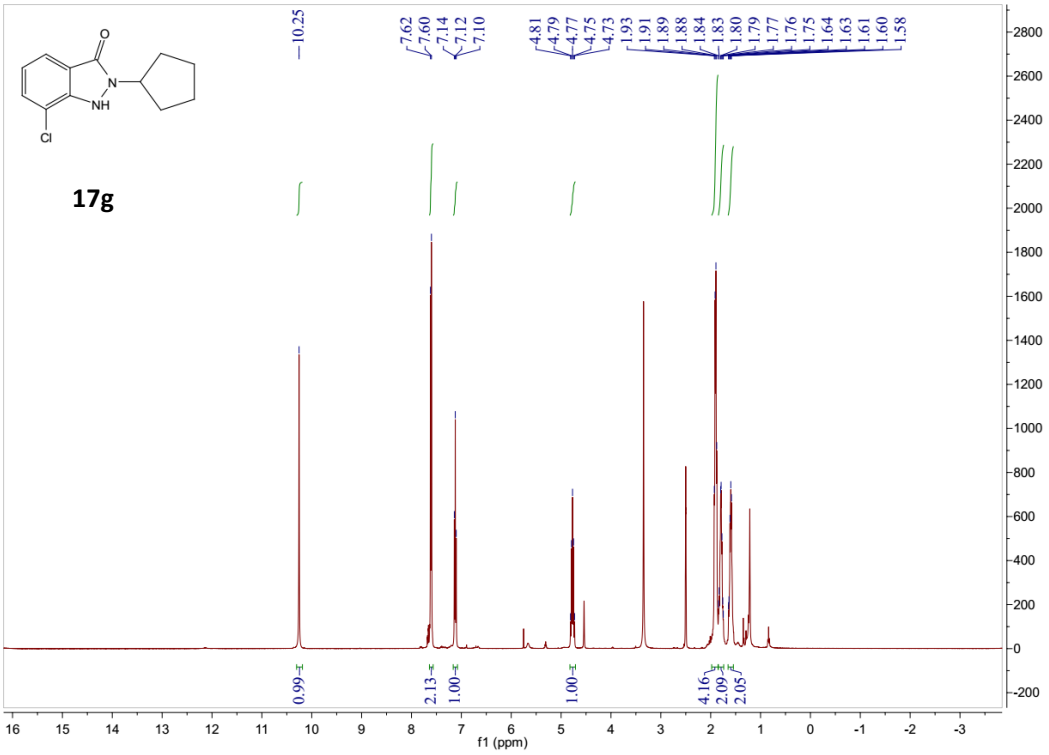
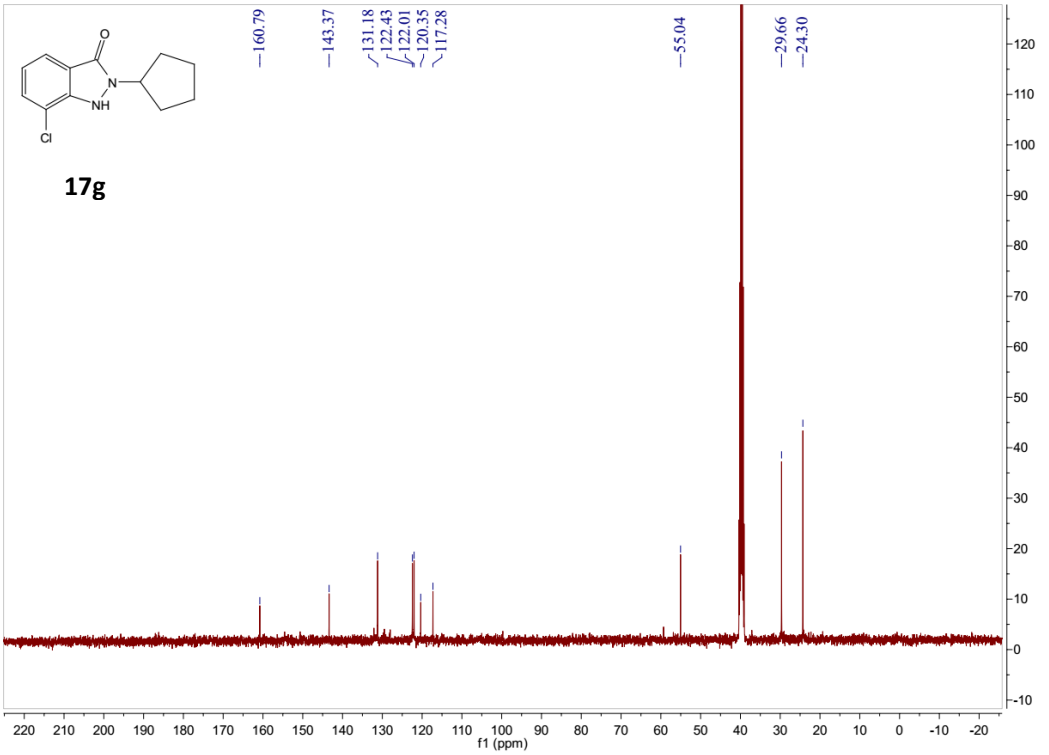
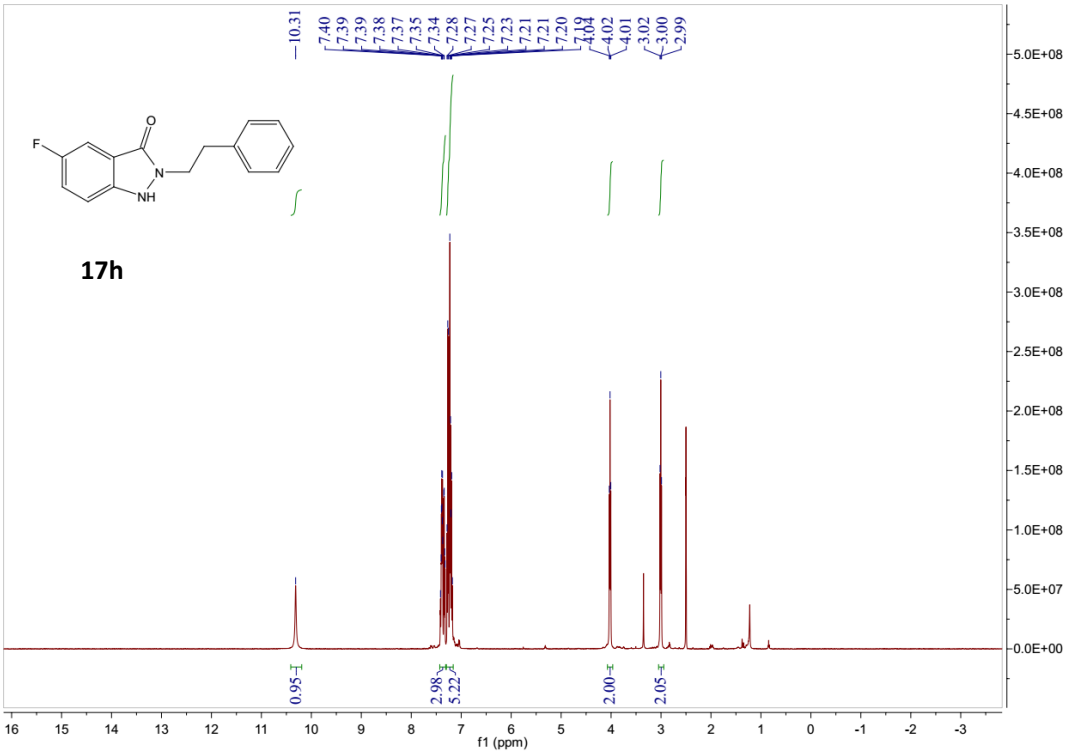
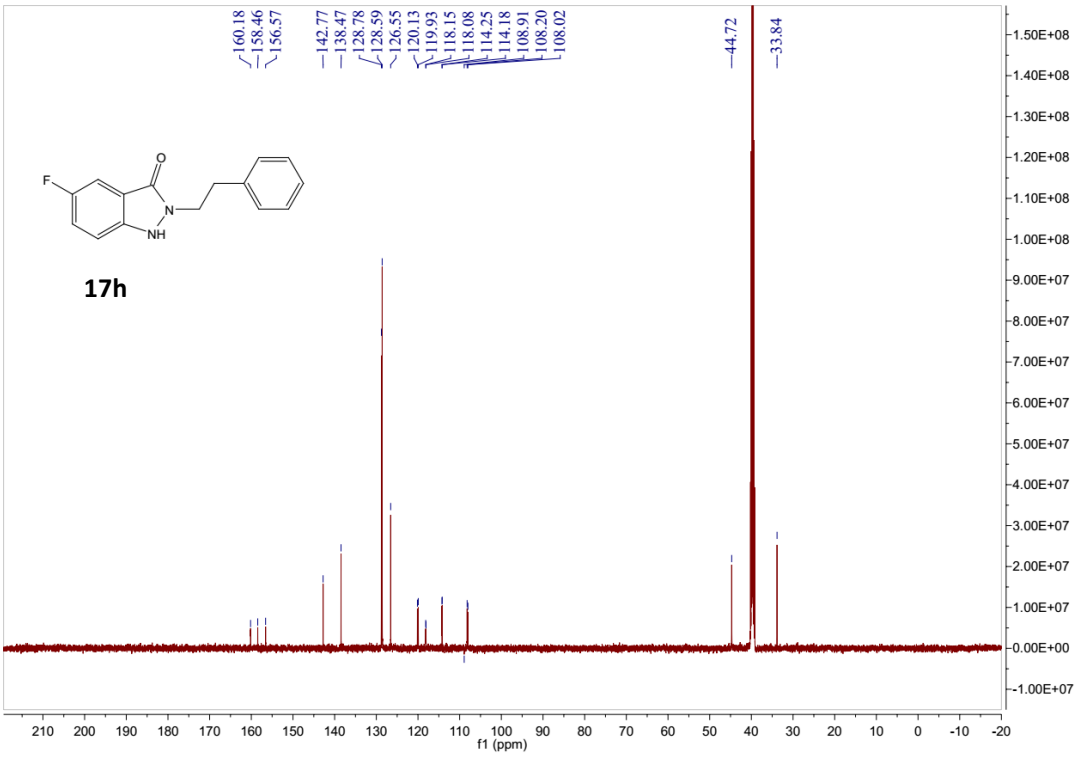
105.87
105.54
105.39
44.44
33.76
F
O
N
NH
17f
f1 (ppm)

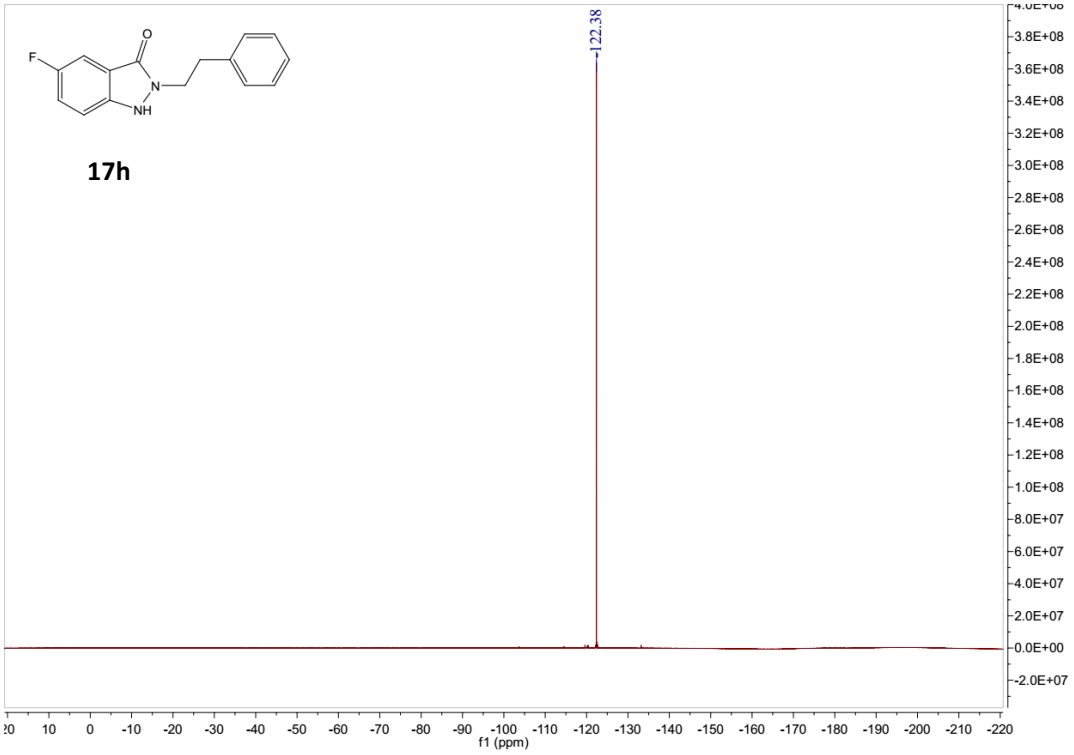

119.35
F
O
N
NH
17f
f1 (ppm)

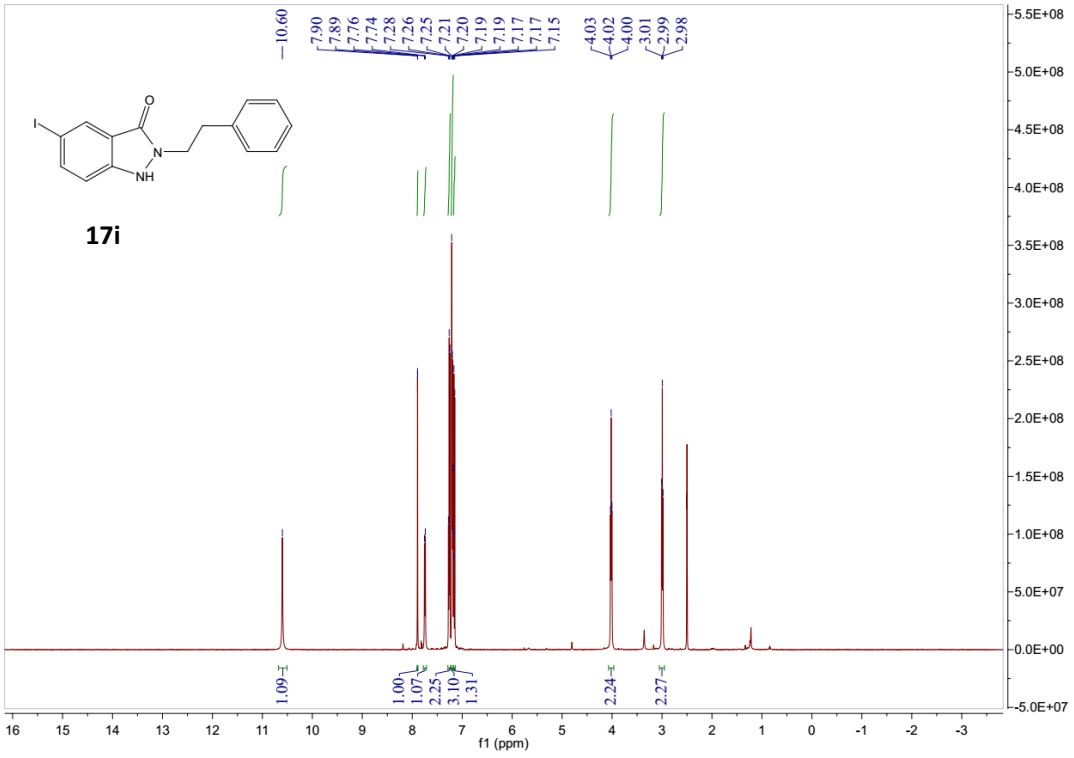

17g
10.25
7.62
7.60
7.14
7.12
7.10
4.81
4.79
4.77
4.75
4.73
1.93
1.91
1.89
1.88
1.84
1.83
1.80
1.79
1.77
1.76
1.75
1.64
1.63
1.61
1.60
1.58
0.99
2.13
1.00
1.00
4.16
2.09
2.05
f1 (ppm)

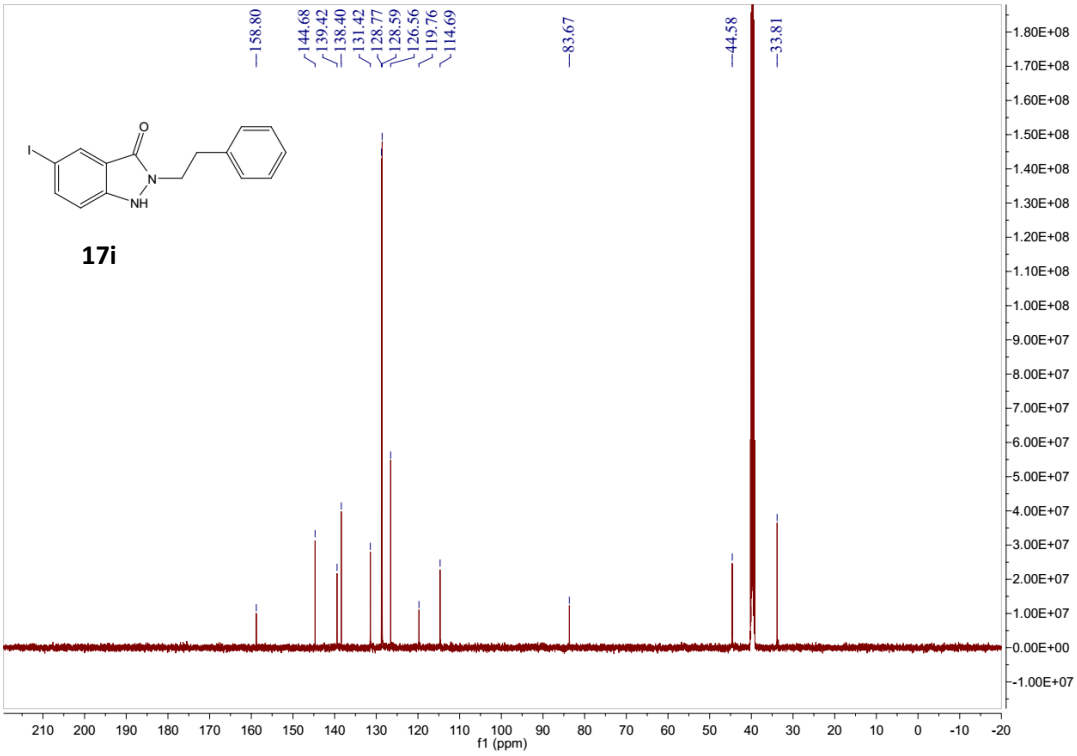

17g
160.79
143.37
131.18
122.43
122.01
120.35
117.28
55.04
29.66
24.30
f1 (ppm)


10.31
7.40
7.39
7.39
7.38
7.37
7.35
7.34
7.28
7.27
7.25
7.23
7.21
7.21
7.20
7.19
4.04
4.02
4.01
3.02
3.00
2.99
F
O
N
NH
17h
0.95
2.98
5.22
2.00
2.05
f1 (ppm)

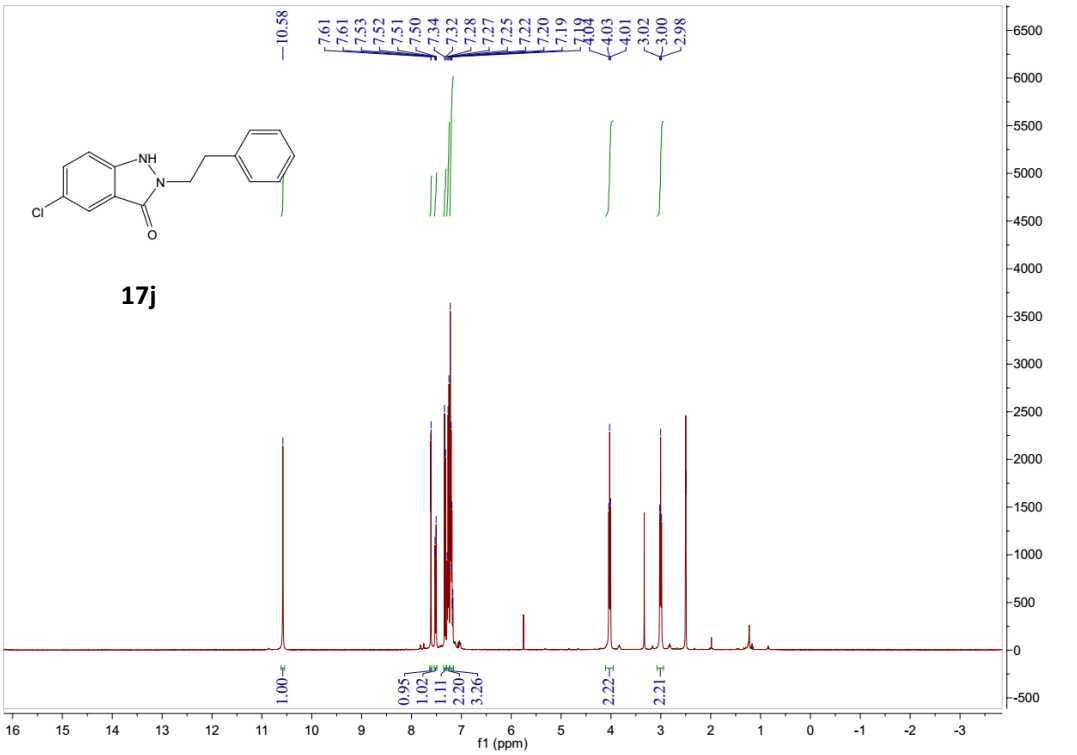

160.18
158.46
156.57
142.77
138.47
128.78
128.59
126.55
120.13
119.93
118.15
118.08
114.25
114.18
108.91
108.20
108.02
44.72
33.84
F
O
N
NH
17h
f1 (ppm)


F
O
N
NH
17h
122.38
f1 (ppm)

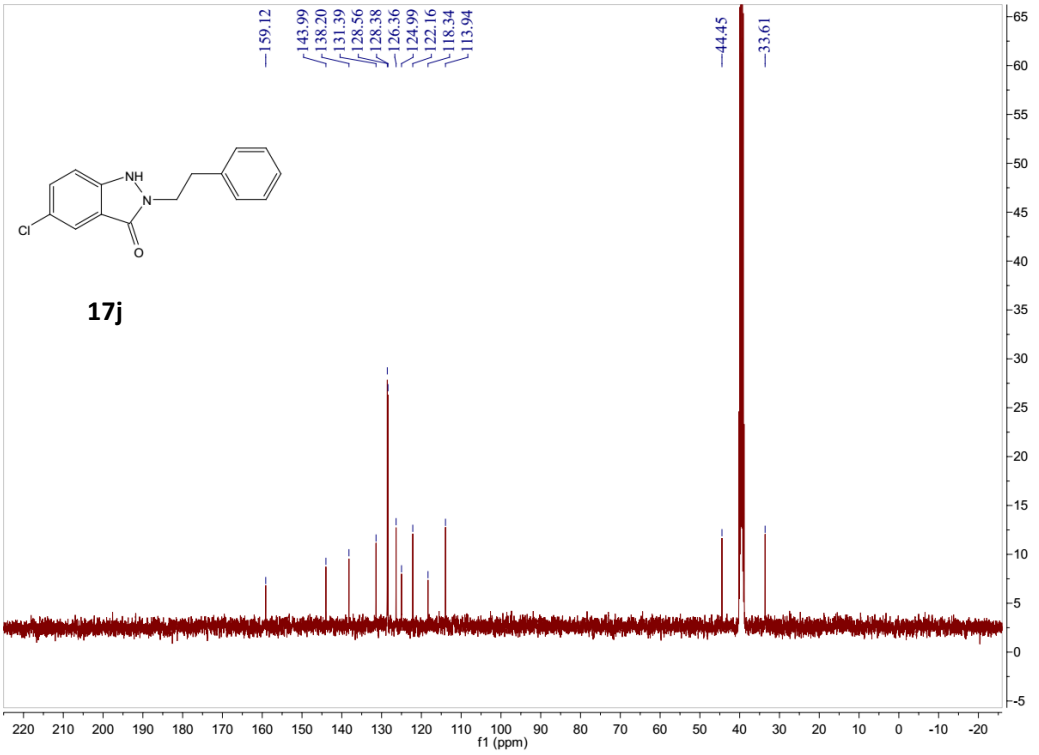

I
O
N
NH
17i
10.60
7.90
7.89
7.76
7.74
7.28
7.26
7.25
7.21
7.20
7.19
7.19
7.17
7.17
7.15
4.03
4.02
4.00
3.01
2.99
2.98
1.09
1.00
1.07
2.25
3.10
1.31
2.24
2.27
f1 (ppm)


158.80
144.68
139.42
138.40
131.42
128.77
128.59
126.56
119.76
114.69
83.67
44.58
33.81
O
I
N
NH
f1 (ppm)

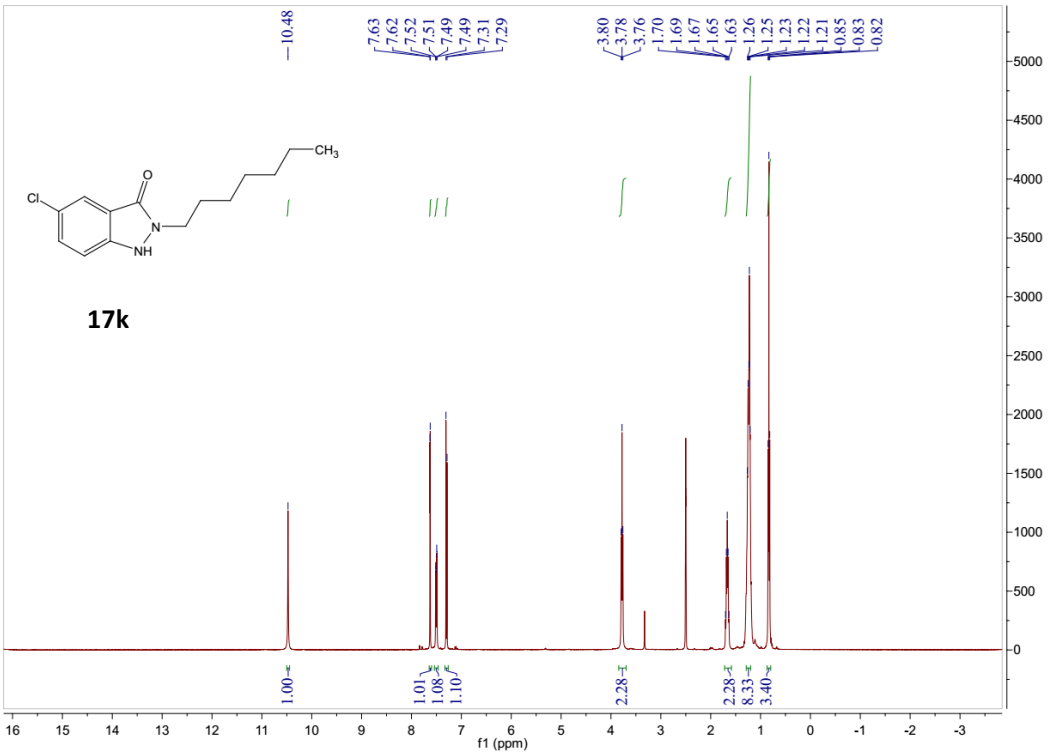
17i


10.58
7.61
7.61
7.53
7.52
7.51
7.50
7.34
7.32
7.28
7.27
7.25
7.22
7.20
7.19
4.04
4.03
4.01
3.02
3.00
2.98
NH
N
Cl
O
1.00
0.95
1.02
1.11
2.20
3.26
2.22
2.21
f1 (ppm)

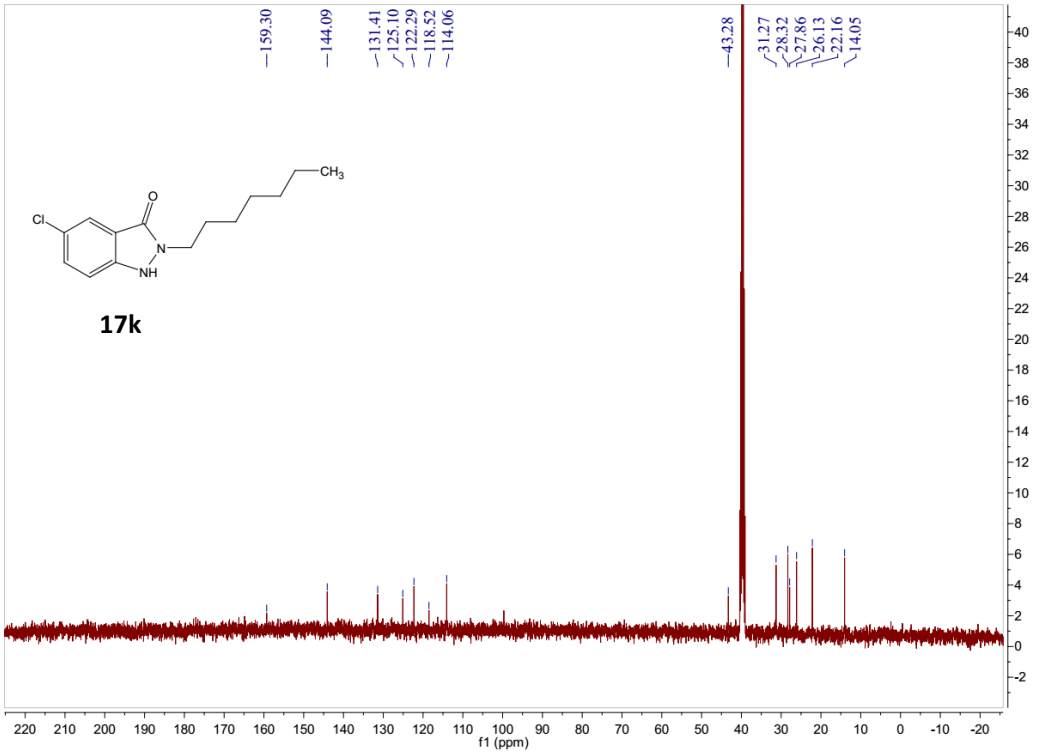
17j


159.12
143.99
138.20
131.39
128.56
128.38
126.36
124.99
122.16
118.34
113.94
44.45
33.61
NH
N
Cl
O
f1 (ppm)

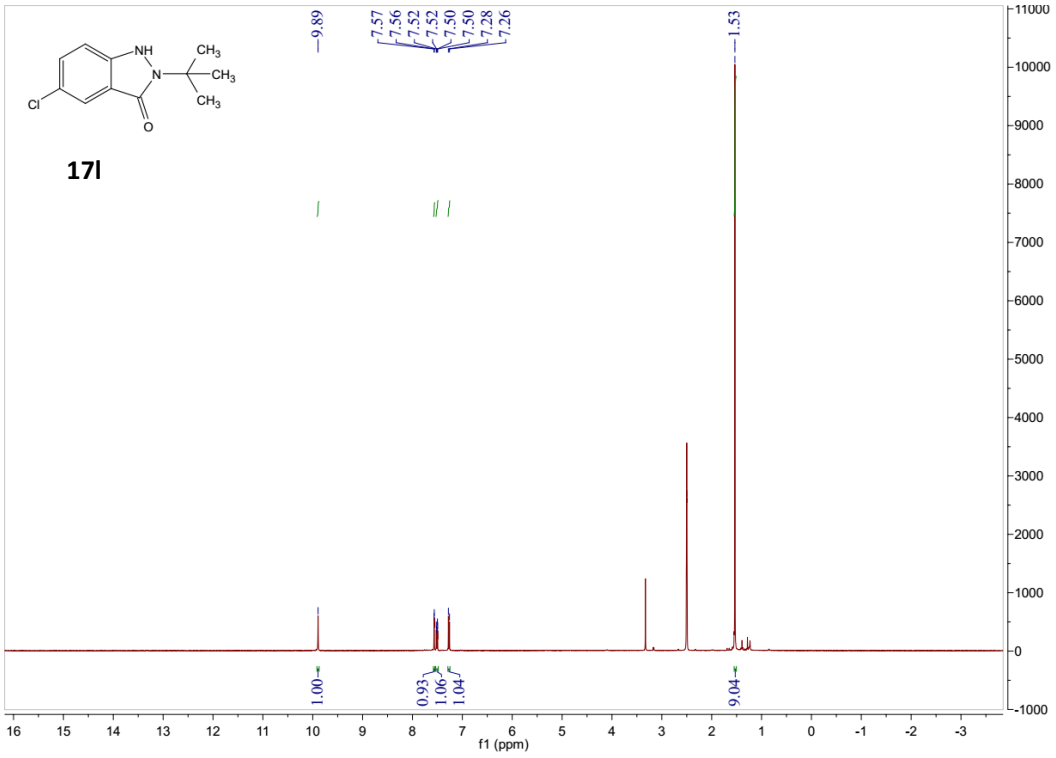
17j


10.48
7.63
7.62
7.52
7.51
7.49
7.49
7.31
7.29
3.80
3.78
3.76
1.70
1.69
1.67
1.65
1.63
1.26
1.25
1.23
1.22
1.21
0.85
0.83
0.82
CH3
O
Cl
N
NH
1.00
1.01
1.08
1.10
2.28
2.28
8.33
3.40
f1 (ppm)

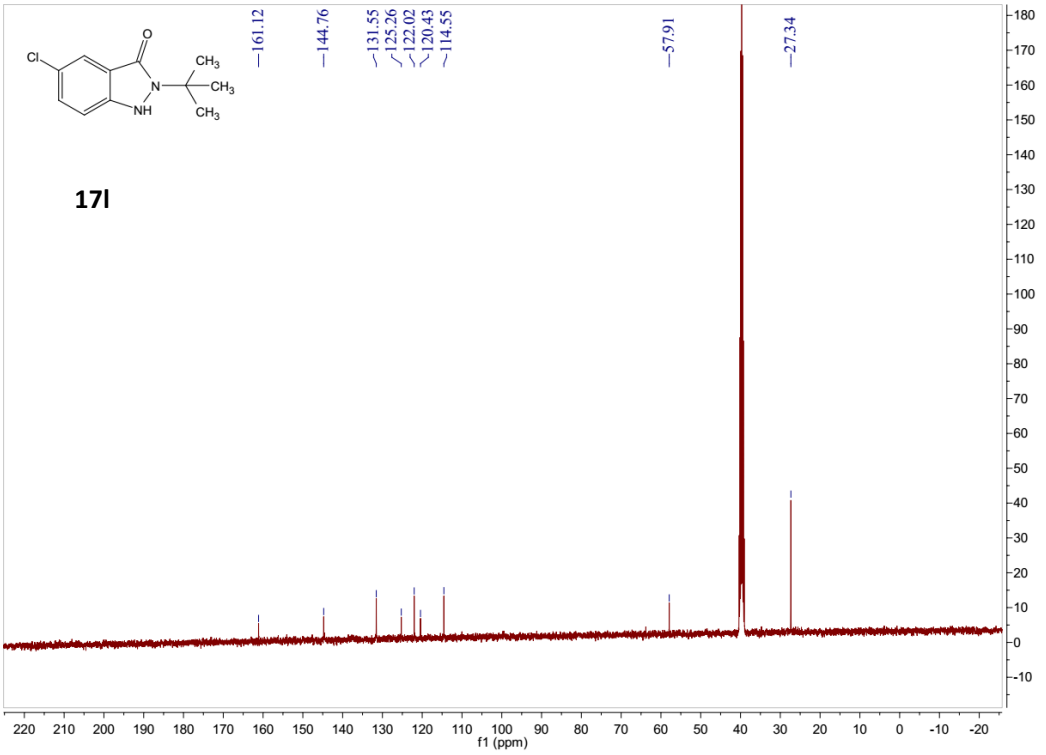
17k


159.30
144.09
131.41
125.10
122.29
118.52
114.06
43.28
31.27
28.32
27.86
26.13
22.16
14.05
Cl
O
N
NH
CH3
f1 (ppm)

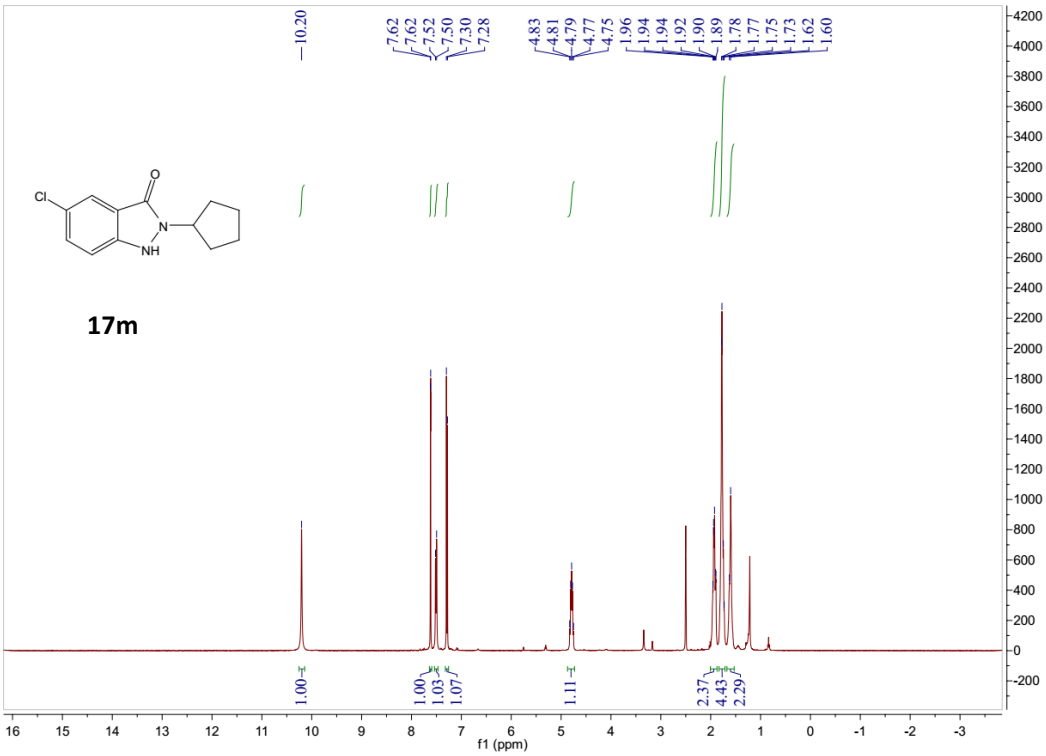
17k


9.89
7.57
7.56
7.52
7.52
7.50
7.50
7.28
7.26
1.53
NH
N
CH3
CH3
CH3
Cl
O
1.00
0.93
1.06
1.04
9.04
f1 (ppm)

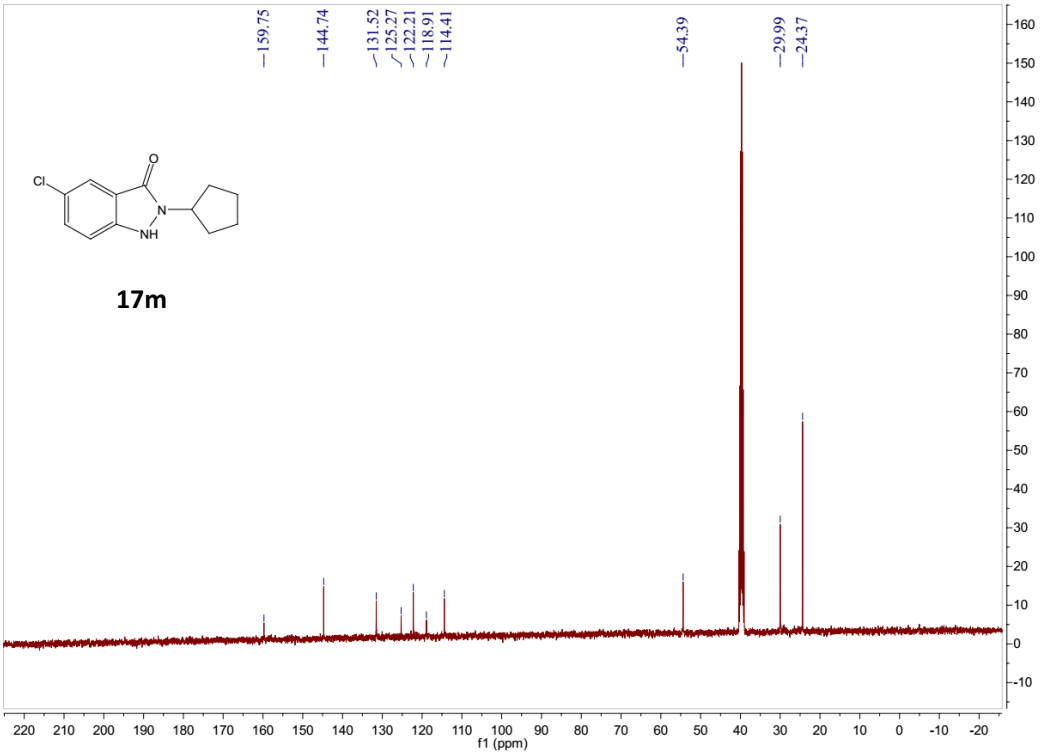
17l


161.12
144.76
131.55
125.26
122.02
120.43
114.55
57.91
27.34
Cl
O
N
NH
CH3
CH3
CH3
f1 (ppm)

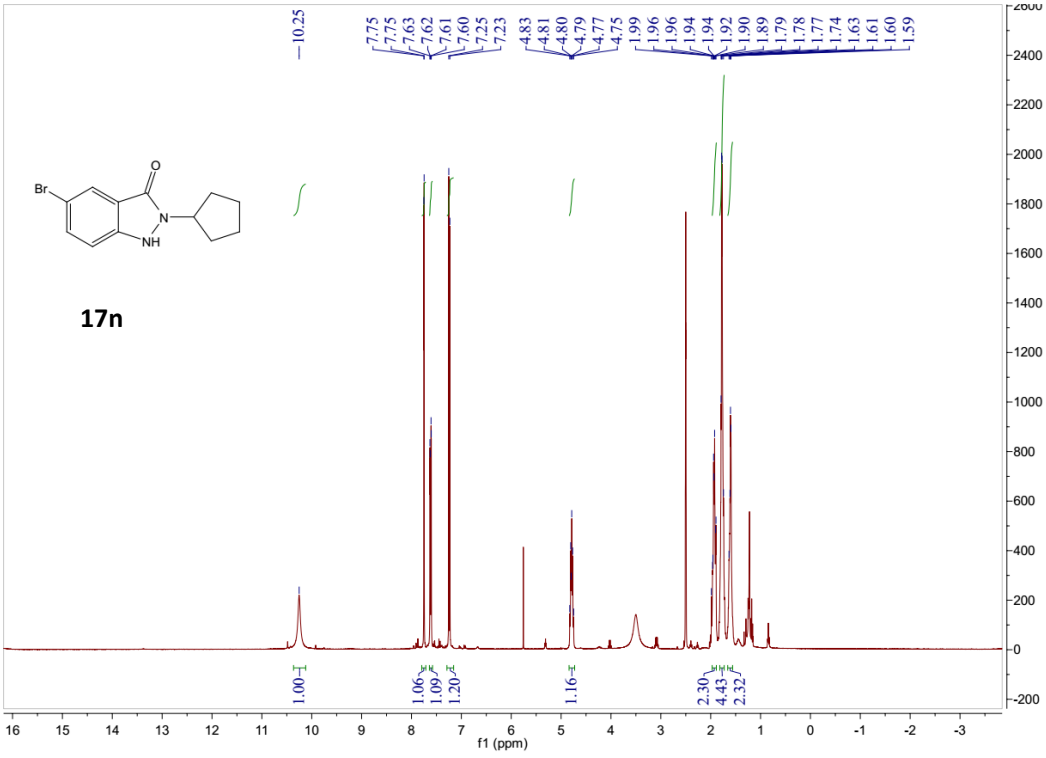
17l


10.20
7.62
7.62
7.52
7.50
7.30
7.28
4.83
4.81
4.79
4.77
4.75
1.96
1.94
1.94
1.92
1.90
1.89
1.78
1.77
1.75
1.73
1.62
1.60
1.00
1.00
1.03
1.07
1.11
2.37
4.43
2.29
Cl
O
N
NH
f1 (ppm)

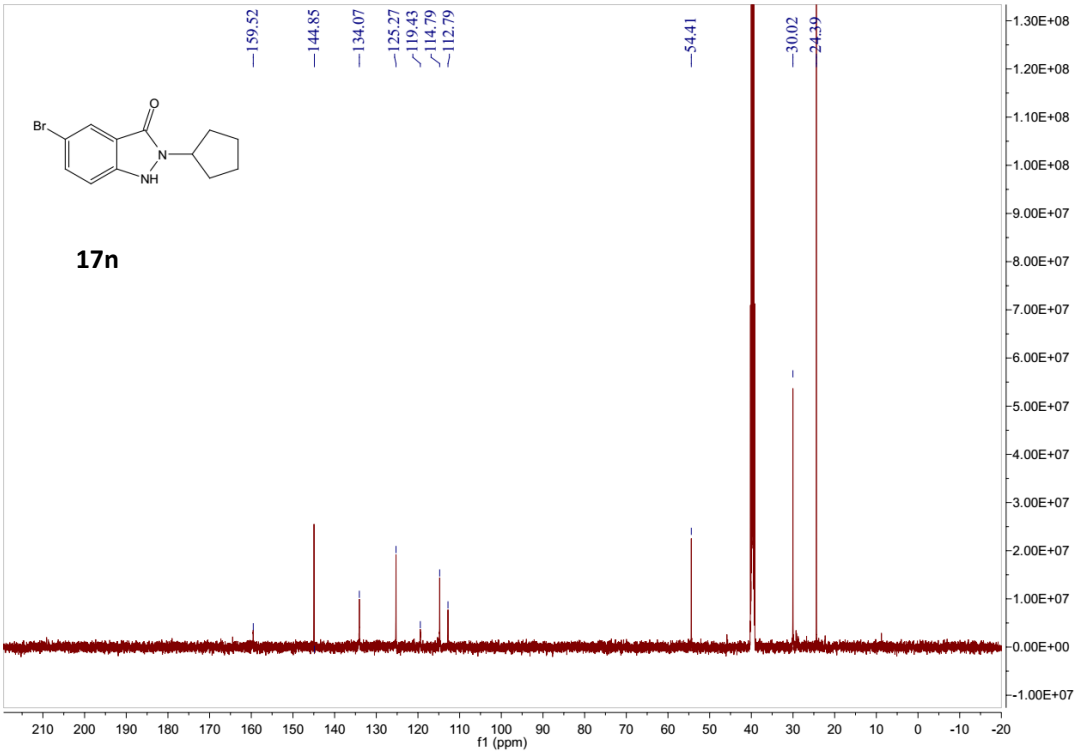
17m


159.75
144.74
131.52
125.27
122.21
118.91
114.41
54.39
29.99
24.37
Cl
O
N
NH
f1 (ppm)

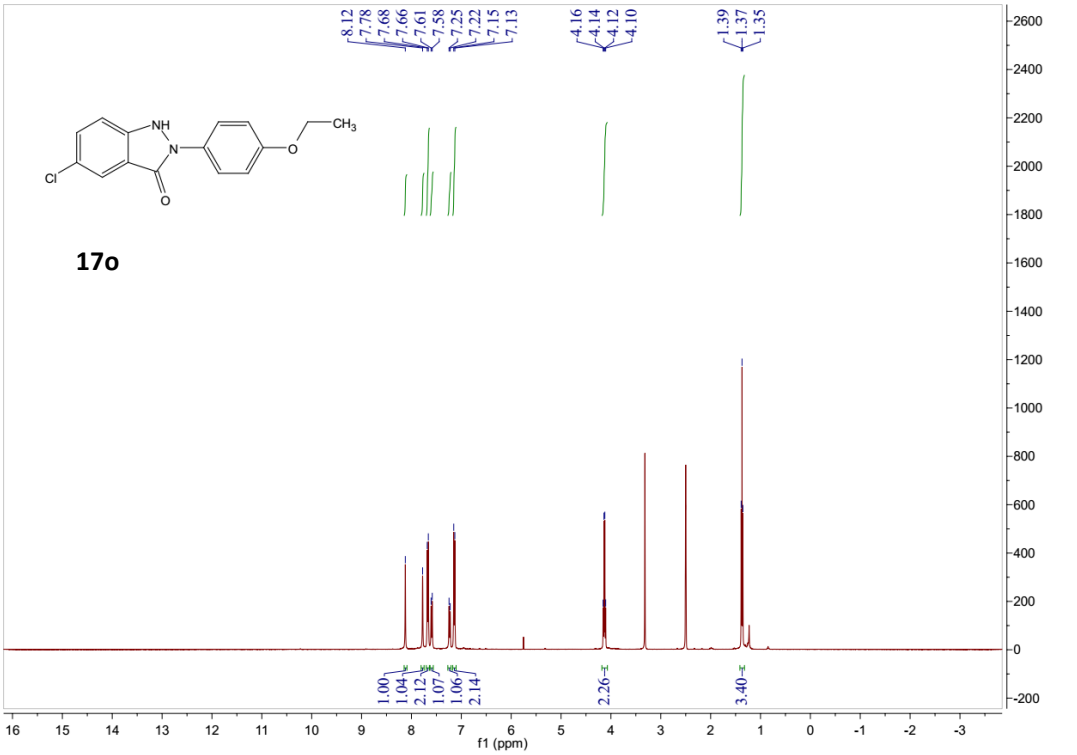
17m


10.25
7.75
7.75
7.63
7.62
7.61
7.60
7.25
7.23
4.83
4.81
4.80
4.79
4.77
4.75
1.99
1.96
1.96
1.94
1.94
1.92
1.90
1.89
1.79
1.78
1.77
1.74
1.63
1.61
1.60
1.59
1.00
1.06
1.09
1.20
1.16
2.30
4.43
2.32
Br
O
N
NH
f1 (ppm)

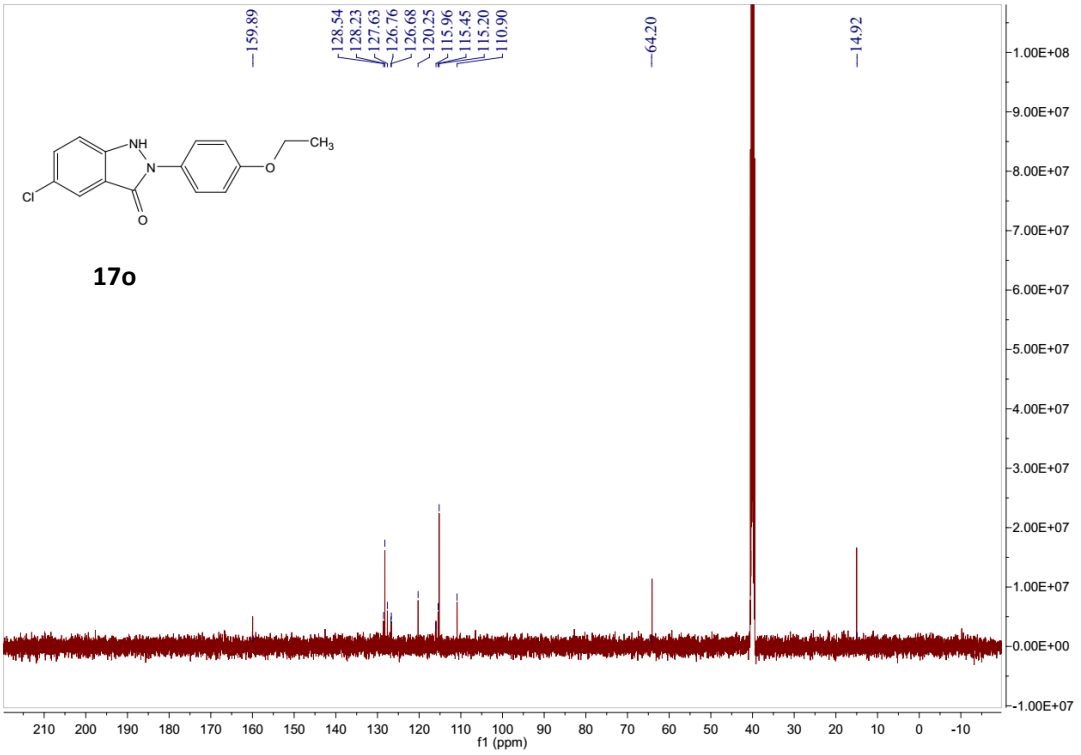
17n

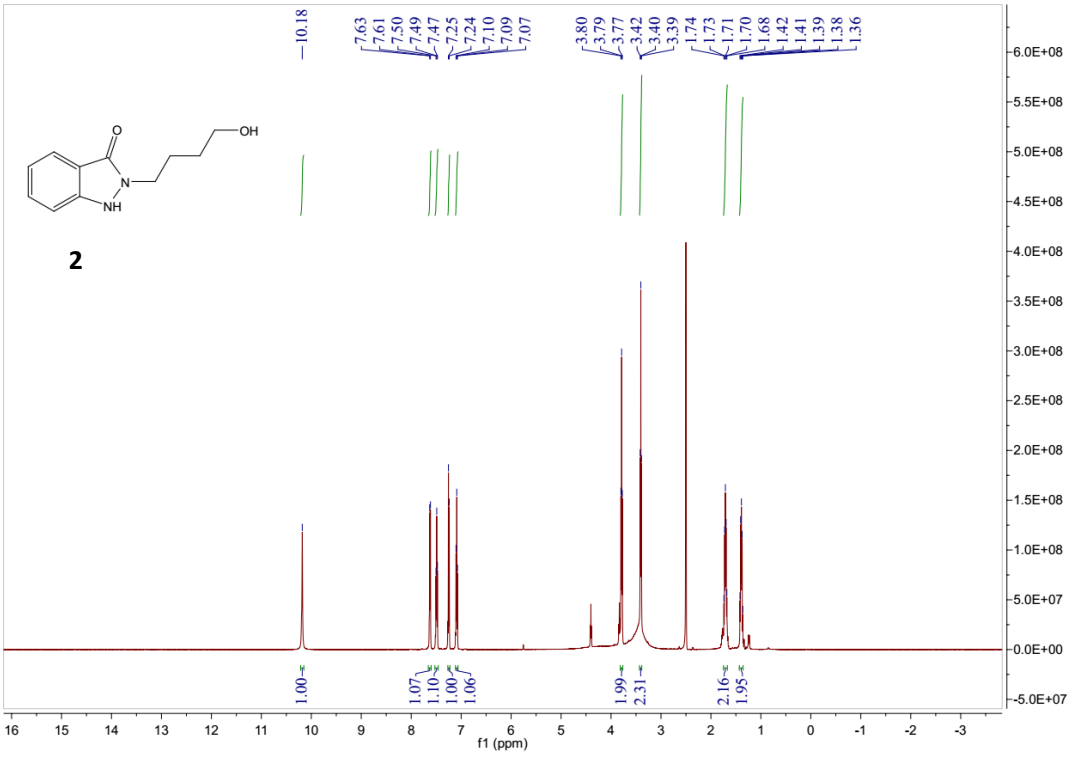

159.52
144.85
134.07
125.27
119.43
114.79
112.79
54.41
30.02
24.39
Br
O
N
NH
f1 (ppm)

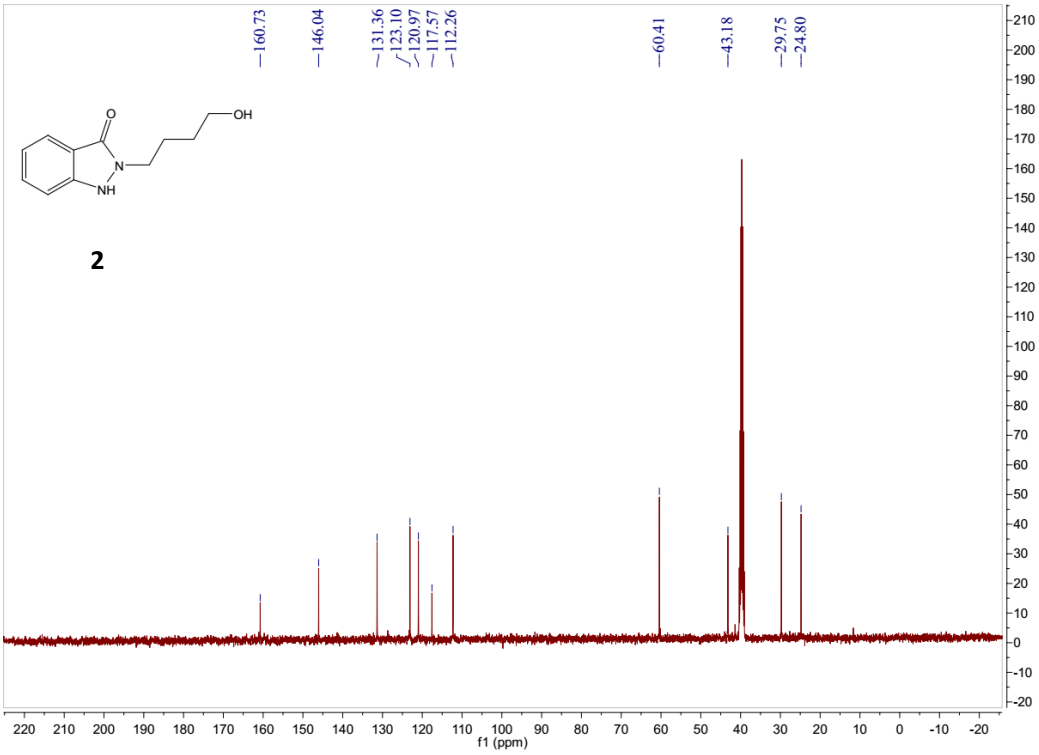
17n


8.12
7.78
7.68
7.66
7.61
7.58
7.25
7.22
7.15
7.13
4.16
4.14
4.12
4.10
1.39
1.37
1.35
NH
N
O
CH3
Cl
O
1.00
1.04
2.12
1.07
1.06
2.14
2.26
3.40
f1 (ppm)

17o


159.89
128.54
128.23
127.63
126.76
126.68
120.25
115.96
115.45
115.20
110.90
64.20
14.92
NH
N
O
Cl
O
CH3
17o
1.00E+08
9.00E+07
8.00E+07
7.00E+07
6.00E+07
5.00E+07
4.00E+07
3.00E+07
2.00E+07
1.00E+07
0.00E+00
-1.00E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


10.18
7.63
7.61
7.50
7.49
7.47
7.25
7.24
7.10
7.09
7.07
3.80
3.79
3.77
3.42
3.40
3.39
1.74
1.73
1.71
1.70
1.68
1.42
1.41
1.39
1.38
1.36
O
N
NH
OH
2
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
1.00
1.07
1.10
1.00
1.06
1.99
2.31
2.16
1.95
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


160.73
146.04
131.36
123.10
120.97
117.57
112.26
60.41
43.18
29.75
24.80
O
N
NH
OH
2
f1 (ppm)