

3-hydroxy-3-((3-methyl-4-nitroisoxazol-5-yl)methyl)indolin-2-one as versatile intermediate for retro-Henry and Friedel-Crafts alkylation reactions in aqueous medium

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General procedure for one-pot synthesis 3-hydroxy-indolyl-2-oxindole (15a-15z): To a solution of Henry adduct (1 mmol) in water (2 mL) was added indole (1 mmol) and stirred at 80 °C for 2 h. After completion of the reaction (monitored by TLC), the contents were cooled to room temperature and filtered [by washing with water (3X10 mL) followed by EtOAc:Hexane (1:9; 2X5 mL) to remove unreacted isatin derivative and 3,5-dimethyl-4-nitroisoxazole] to give the desired product as solid in pure form.

General procedure for one-pot synthesis of bis-3,3-(indol-3-yl)indolin-2-ones derivatives (16a-16n, 19a-19n and 21a-21e): To a solution of Henry adduct (1 mmol) in water (2 mL) was added indole (1 mmol) and stirred at 80 °C for 2 h. After completion of the reaction (monitored by TLC), different/same indole/electron rich arene (1 mmol) and 10 mol% of *p*TsOH were added and refluxing continued for another 30 min. After completion of reaction, the contents were cooled to room temperature and filtered [by washing with water (3X10 mL) followed by EtOAc:Hexane (1:9; 2X5 mL) to remove unreacted isatin derivative and 3,5-dimethyl-4-nitroisoxazole] to give the desired product as solid in pure form.

Procedure for synthesis of 2-(3-Hydroxy-2-oxoindolin-3-yl)acetic acids (24a-24h): To a solution of Henry adduct (1 mmol) in THF (2 mL) was added KMnO₄ [12 mmol; in acetone and water (3:3 mL)] and stirred at room temperature for 2 h. After completion of the reaction (monitored by TLC), the reaction mixture was extracted with EtOAc (3X10 mL). The combined organic layers were dried using sodium sulfate. Evaporation of the solvent under reduced pressure gave crude product which was purified by silica gel column chromatography. Elution of the column with EtOAc:Hexane (1:1) gave desired products as solids.

**Comparison of the melting point of the reported compounds
3-hydroxy-3-indolyl-oxindole derivatives (15a-15k, 15r)**

S. No.	Compound. No.	Found MP °C	Reported MP °C
1	15a	293-295	294-296 ^{1a}
2	15b	192-193	196-198 ^{1a}
3	15c	206-208	206-208 ^{1c}
4	15d	234-236	236-238 ^{1b}
5	15e	>300	>300 ^{1c}
6	15f	154-156	155-157 ^{1c}
7	15g	177-178	178-180 ^{1a}
8	15h	214-216	212-214 ^{1a}
9	15i	189-191	191-193 ^{1c}
10	15j	135-137	138-139 ^{1d}
11	15k	118-120	115-118 ^{1b}
12	15r	146-147	148-150 ^{1d}

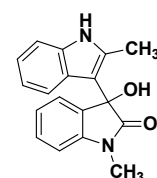
Symmetrical/unsymmetrical bis-3,3-(indol-3-yl)indolin-2-ones (16a-16e, 16g-16j, 16l, 16m and 19a)

S. No.	Compound. No.	Found MP (°C)	Reported MP (°C)
1	16a	>300	>300 ^{2a}
2	16b	174-176	-
3	16c	288-290	290-291 ^{2a}
4	16d	288-289	284-286 ^{2e}
5	16e	180-182	-
6	16g	>300	298-300 ^{2b}
7	16h	136-137	136-138 ^{2b}
8	16i	>300	302-303 ^{2b, 2c}
9	16j	>300	>300 ^{2b}
10	16l	286-288	284-286 ^{2d}
11	16m	290-292	294-296 ^{2a}
13	19a	295-297	297-291 ^{2c}

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- G. Brahmachari, B. Banerjee, *ACS Sustainable Chem. Eng.* 2014, **2**, 2802; b) P. Paira *et al.*, *Bioorg. Med. Chem. Lett.*, 2009, **19**, 4786. c) M. Nikpassand, M. Mamaghani, K. Tabatabaeian, H. Alah Samimi, *Syn. Comm.*, 2010, **40**, 3552; d) K. Rad-Moghadam, M. Sharifi-Kiasaraie, H. Taheri-Amlashi, *Tetrahedron*, 2010, **66**, 2316. e) K. Nikoofar, *Arabian Journal of Chemistry*, 2017, **10**, 283.

3-hydroxy-1-methyl-3-(2-methyl-1H-indol-3-yl)indolin-2-one (15i):

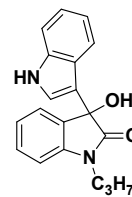
Yellow solid, (90% yield), M.P: 189 - 191 °C; ¹H NMR (300 MHz, CDCl₃+DMSO): δ 10.35 (s, 1H), 7.31 (dd, *J* = 12.0, 7.4 Hz, 2H), 7.16 (dd, *J* =



19.0, 7.9 Hz, 2H), 7.02 – 6.89 (m, 3H), 6.80 (t, $J = 7.4$ Hz, 1H), 6.13 (s, 1H), 3.24 (s, 3H), 2.41 (s, 3H)

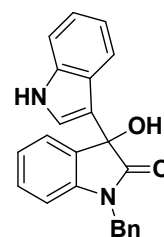
3-hydroxy-3-(1H-indol-3-yl)-1-propylindolin-2-one (15l):

Yellow solid, (88% yield), M.P: 132 - 134 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.22 (s, 1H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.47 (d, $J = 7.1$ Hz, 1H), 7.34 (ddd, $J = 8.1, 7.1, 3.1$ Hz, 2H), 7.16 (t, $J = 7.3$ Hz, 1H), 7.06 (dd, $J = 13.4, 6.1$ Hz, 2H), 6.95 (d, $J = 7.8$ Hz, 1H), 4.00 – 3.59 (m, 2H), 3.53 – 3.29 (m, 1H), 1.74 – 1.54 (m, 2H), 1.32 (t, $J = 7.2$ Hz, 3H).



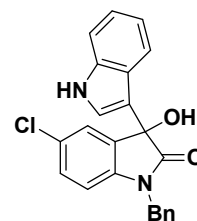
1-benzyl-3-hydroxy-3-(1H-indol-3-yl)indolin-2-one (15m):

White solid, (88% yield), M.P: 134 - 136 °C; ^1H NMR (400 MHz, DMSO): δ (ppm) 11.05 (s, 1H), 7.36 – 7.32 (m, 4H), 7.30 (d, $J = 7.2$ Hz, 2H), 7.28 – 7.24 (m, 2H), 7.11 (s, 1H), 7.00 (dt, $J = 12.3, 8.9$ Hz, 3H), 6.82 (dd, $J = 11.6, 7.1$ Hz, 1H), 6.62 (d, $J = 4.3$ Hz, 1H), 4.91 (s, 2H). ^{13}C NMR (101 MHz, DMSO): δ (ppm) 177.31, 142.59, 137.31, 136.82, 133.23, 129.58, 129.04, 127.89, 125.32, 125.06, 124.15, 123.01, 121.66, 120.87, 118.99, 115.62, 112.05, 109.68, 75.22, 43.17. Mass (ESI-MS): m/z Calculated: $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_2$: 354; Observed: 353 (M-1).



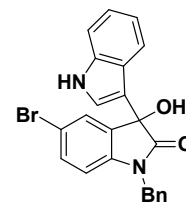
1-benzyl-5-chloro-3-hydroxy-3-(1H-indol-3-yl)indolin-2-one (15n):

White solid, (92% yield), M.P: 134 - 136 °C; ^1H NMR (400 MHz, DMSO): δ (ppm) 11.11 (s, 1H), 7.36 – 7.32 (m, 9H), 7.04 (d, $J = 7.2$ Hz, 2H), 6.85 – 6.77 (m, 2H), 4.93 (s, 2H). ^{13}C NMR (101 MHz, DMSO): δ (ppm) 176.89, 141.43, 137.31, 136.48, 135.23, 129.38, 129.08, 127.89, 125.11, 125.06, 124.99, 123.01, 121.76, 120.63, 119.99, 114.86, 112.16, 111.32, 93.99, 75.20, 43.23. Mass (ESI-MS): m/z Calculated: $\text{C}_{23}\text{H}_{17}\text{ClN}_2\text{O}_2$: 388; Observed: 387 (M-1).



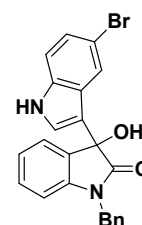
1-benzyl-5-bromo-3-hydroxy-3-(1H-indol-3-yl)indolin-2-one (15o):

White solid, (88% yield), M.P: 197 - 199 °C; ^1H NMR (400 MHz, DMSO): δ (ppm) 11.32 (s, 1H), 7.75 (s, 1H), 7.49 (d, $J = 11.6$ Hz, 2H), 7.26 (d, $J = 36.4$ Hz, 7H), 7.01 (d, $J = 32.6$ Hz, 2H), 6.83 (s, 1H), 4.90 (s, 2H). ^{13}C NMR (101 MHz, DMSO): δ (ppm) 176.52, 141.88, 136.32, 136.08, 134.91, 132.53, 129.17, 128.01, 127.78, 127.62, 127.32, 127.17, 125.85, 124.43, 123.48, 114.99, 114.56, 114.26, 111.94, 74.90, 43.21. Mass (ESI-MS): m/z Calculated: $\text{C}_{23}\text{H}_{17}\text{BrN}_2\text{O}_2$: 432.05; Observed: 455.0380 (M+Na).



1-benzyl-3-(5-bromo-1H-indol-3-yl)-3-hydroxyindolin-2-one (15p):

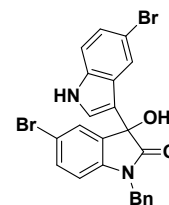
White solid (92% yield), M.P: 183 - 185 °C; ^1H NMR (400 MHz, DMSO): δ (ppm) 11.27 (s, 1H), 7.70 (d, $J = 6.8$ Hz, 1H), 7.38 – 7.28 (m, 7H), 7.18 (d, $J =$



8.6 Hz, 1H), 7.07 (t, $J = 7.5$ Hz, 1H), 7.03 – 6.94 (m, 2H), 6.68 (s, 1H), 4.95 – 4.83 (m, 2H). ^{13}C NMR (101 MHz, DMSO): δ (ppm) 177.05, 142.64, 136.79, 136.04, 132.30, 129.76, 129.10, 127.68, 125.64, 125.01, 124.19, 123.77, 122.99, 117.48, 115.37, 114.08, 111.75, 109.70, 74.93, 43.14. Mass (ESI-MS): m/z Calculated: $\text{C}_{23}\text{H}_{17}\text{BrN}_2\text{O}_2$: 432.05; Observed: 455.0380 (M+Na).

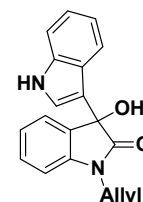
1-benzyl-5-bromo-3-(5-bromo-1H-indol-3-yl)-3-hydroxyindolin-2-one (15q):

White solid, (88% yield), M.P: 209 - 211 °C; ^1H NMR (400 MHz, DMSO): δ 11.32 (s, 1H), 7.75 (s, 1H), 7.49 (d, $J = 11.6$ Hz, 1H), 7.26 (d, $J = 36.4$ Hz, 7H), 7.01 (d, $J = 32.6$ Hz, 2H), 6.83 (s, 1H), 4.90 (s, 2H). ^{13}C NMR (101 MHz, DMSO): δ 176.52, 141.88, 136.32, 136.08, 134.91, 132.53, 129.17, 128.01, 128.01, 127.78, 127.62, 127.17, 125.85, 124.43, 123.48, 114.99, 114.56, 114.26, 111.94, 74.90, 43.21. Mass (ESI-MS): m/z Calculated: $\text{C}_{23}\text{H}_{16}\text{Br}_2\text{N}_2\text{O}_2$: 509.96; Observed: 532.9479 (M+Na).



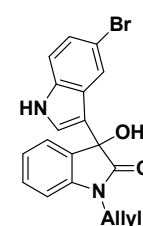
1-allyl-3-hydroxy-3-(1H-indol-3-yl)indolin-2-one (15r):

White solid, (89% yield), M.P: 146 - 147 °C; ^1H NMR (400 MHz, DMSO): δ (ppm) 11.04 (s, 1H), 7.33 (t, $J = 7.3$ Hz, 4H), 7.09 – 6.98 (m, 4H), 6.87 (t, $J = 7.4$ Hz, 1H), 6.52 (s, 1H), 5.92 – 5.76 (m, 1H), 5.28 – 5.10 (m, 2H), 4.42 – 4.21 (m, 2H). ^{13}C NMR (101 MHz, DMSO): δ (ppm) 176.89, 142.65, 137.30, 133.18, 132.43, 129.55, 125.40, 124.99, 124.11, 122.86, 121.61, 120.91, 119.02, 117.45, 115.65, 112.04, 109.60, 75.13, 41.92. Mass (ESI-MS): m/z Calculated: $\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_2$: 304; Observed: 303 (M-1).



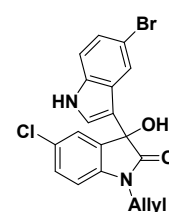
1-allyl-3-(5-bromo-1H-indol-3-yl)-3-hydroxyindolin-2-one (15t):

White solid, (92% yield), M.P: 185 - 187 °C; ^1H NMR (400 MHz, DMSO): δ (ppm) 11.30 (s, 1H), 7.81 (d, $J = 5.4$ Hz, 1H), 7.44 (dd, $J = 8.3, 1.9$ Hz, 1H), 7.40 – 7.31 (m, 2H), 7.20 (d, $J = 8.6$ Hz, 1H), 7.07 (d, $J = 8.4$ Hz, 1H), 7.02 (s, 1H), 6.75 (d, $J = 4.2$ Hz, 1H), 5.83 (ddd, $J = 15.7, 9.9, 4.8$ Hz, 1H), 5.26 – 5.10 (m, 2H), 4.31 (qd, $J = 16.6, 4.3$ Hz, 2H). ^{13}C NMR (101 MHz, DMSO): δ (ppm) 176.24, 141.50, 136.08, 134.59, 131.99, 129.58, 127.28, 127.09, 125.74, 125.02, 124.34, 123.70, 117.65, 114.71, 114.19, 111.88, 111.36, 74.89, 41.96. Mass (ESI-MS): m/z Calculated: $\text{C}_{19}\text{H}_{15}\text{BrN}_2\text{O}_2$: 383; Observed: 381 (M-2).



1-allyl-3-(5-bromo-1H-indol-3-yl)-5-chloro-3-hydroxyindolin-2-one (15u):

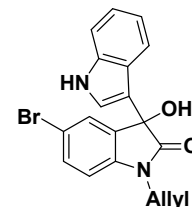
White solid, (90% yield), M.P: 169 - 172 °C; ^1H NMR (400 MHz, DMSO) δ 11.29 (s, 1H), 7.80 (s, 1H), 7.44 (d, $J = 7.9$ Hz, 1H), 7.36 (s, 1H), 7.20 (d, $J = 8.4$ Hz, 1H),



7.07 (d, $J = 8.3$ Hz, 1H), 7.01 (s, 1H), 6.74 (s, 1H), 5.88 – 5.76 (m, 1H), 5.23 – 5.12 (m, 2H), 4.30 (dd, $J = 33.0, 14.6$ Hz, 2H). ^{13}C NMR (101 MHz, DMSO): δ 176.23, 141.49, 136.08, 134.58, 131.99, 129.58, 127.29, 127.09d, 125.74, 125.02, 124.33, 123.70, 117.65, 114.70, 114.19, 111.87, 111.36, 74.89, 41.96.

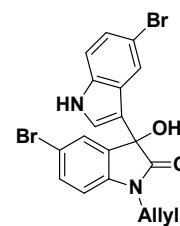
1-allyl-5-bromo-3-hydroxy-3-(1H-indol-3-yl)indolin-2-one (15v):

White solid, (92% yield), M.P: 139 - 141 °C; ^1H NMR (400 MHz, DMSO): δ (ppm) 11.29 (s, 1H), 7.79 (s, 1H), 7.57 (d, $J = 8.3$ Hz, 1H), 7.47 (s, 1H), 7.35 (d, $J = 8.6$ Hz, 1H), 7.20 (d, $J = 7.6$ Hz, 1H), 7.03 (d, $J = 8.6$ Hz, 2H), 6.74 (s, 1H), 5.82 (m, 1H), 5.18 (t, 2H), 4.30 (qd, $J = 16.5, 4.5$ Hz, 2H). ^{13}C NMR (101 MHz, DMSO): δ (ppm) 176.11, 141.91, 136.07, 134.94, 132.44, 131.96, 127.70, 127.25, 125.73, 124.34, 123.66, 117.65, 114.80, 114.69, 114.20, 111.90, 74.84, 41.93. Mass (ESI-MS): m/z Calculated: $\text{C}_{19}\text{H}_{15}\text{BrN}_2\text{O}_2$: 383; Observed: 383 (M).



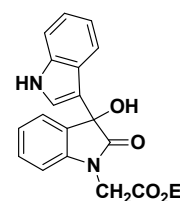
1-allyl-5-bromo-3-(5-bromo-1H-indol-3-yl)-3-hydroxyindolin-2-one (15w):

White solid, (92% yield), M.P: 198 - 200 °C; ^1H NMR (400 MHz, DMSO): δ 11.29 (s, 1H), 7.79 (s, 1H), 7.57 (d, $J = 8.3$ Hz, 1H), 7.47 (s, 1H), 7.35 (d, $J = 8.6$ Hz, 1H), 7.20 (d, $J = 7.6$ Hz, 1H), 7.01 (s, 1H), 6.74 (s, 1H), 5.82 (ddd, $J = 15.4, 9.9, 4.9$ Hz, 1H), 5.24 – 5.12 (m, 2H), 4.30 (qd, $J = 16.5, 4.5$ Hz, 2H). ^{13}C NMR (101 MHz, DMSO): δ 176.11, 141.91, 136.07, 134.94, 132.44, 131.96, 127.70, 127.25, 125.73, 124.34, 123.66, 117.65, 114.80, 114.69, 114.20, 111.90, 74.84, 41.93.



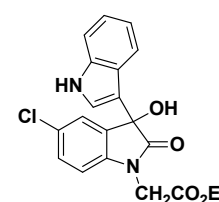
Ethyl 2-(3-hydroxy-3-(1H-indol-3-yl)-2-oxoindolin-1-yl)acetate (15x):

White solid, (92% yield), M.P: 124 - 126 °C; ^1H NMR (400 MHz, DMSO): δ (ppm) 11.04 (s, 1H), 7.47 (d, $J = 7.7$ Hz, 1H), 7.32 (t, $J = 9.2$ Hz, 3H), 7.14 – 6.98 (m, 4H), 6.87 (t, $J = 7.2$ Hz, 1H), 6.59 (s, 1H), 4.57 (dd, $J = 42.1, 17.7$ Hz, 2H), 4.15 (dd, $J = 13.5, 6.5$ Hz, 2H), 1.19 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO): δ (ppm) 177.15, 168.42, 142.42, 137.21, 132.92, 129.53, 125.32, 124.91, 124.14, 123.10, 121.62, 121.01, 119.01, 115.53, 111.92, 109.37, 75.02, 61.60, 14.47. Mass (ESI-MS): m/z Calculated: $\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_4$: 350; Observed: 349 (M-1).



ethyl 2-(5-chloro-3-hydroxy-3-(1H-indol-3-yl)-2-oxoindolin-1-yl)acetate (15y):

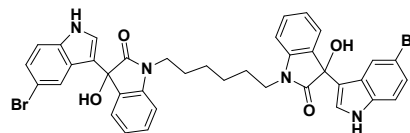
White solid, (90% yield), M.P: 162 - 164 °C; ^1H NMR (400 MHz, DMSO): δ (ppm) 11.09 (s, 1H), 7.49 (d, $J = 7.9$ Hz, 1H), 7.38 (dd, $J = 20.0, 8.1$ Hz, 2H), 7.29 (s, 1H),



7.13 (d, $J = 8.1$ Hz, 2H), 7.05 (t, $J = 7.4$ Hz, 1H), 6.90 (t, $J = 7.4$ Hz, 1H), 6.74 (s, 1H), 4.60 (q, $J = 17.7$ Hz, 2H), 4.15 (q, $J = 6.9$ Hz, 2H), 1.19 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO): δ (ppm) 176.69, 168.25, 141.35, 137.23, 134.93, 129.32, 127.11, 125.14, 124.81, 124.25, 121.75, 120.81, 119.19, 114.80, 112.05, 111.20, 75.01, 61.64, 41.61, 14.47. Mass (ESI-MS): m/z Calculated: $\text{C}_{20}\text{H}_{17}\text{ClN}_2\text{O}_4$: 384; Observed: 383 (M-1).

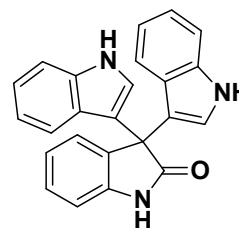
1,1'-(hexane-1,6-diyl)bis(3-(5-bromo-1H-indol-3-yl)-3-hydroxyindolin-2-one) (15z):

White solid, (87% yield), M.P: 218 - 220 °C; ^1H NMR (400 MHz, DMSO): δ (ppm) 11.21 (s, 4H), 7.58 (s, 4H), 7.35-7.29 (m, 5H), 7.14 (d, $J = 8.1$ Hz, 2H), 7.07 – 7.01 (m, 5H), 6.50 (s, 2H), 3.59 (d, $J = 36.6$ Hz, 4H), 1.53 (s, 4H), 1.29 (s, 4H). ^{13}C NMR (101 MHz, DMSO): δ (ppm) 176.75, 142.88, 135.97, 132.74, 129.85, 127.22, 125.61, 125.01, 124.09, 123.35, 122.81, 115.50, 114.04, 111.68, 109.21, 74.78, 27.33, 26.49. Mass (ESI-MS): m/z Calculated: 766.08; Observed: 789.0735(M+ Na).



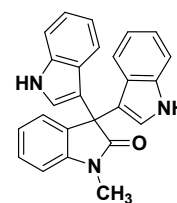
[3,3':3',3''-terindolin]-2'-one (16b)

Yield = (93 %) m.p: 174-176 °C; ^1H NMR (400 MHz, CDCl_3 +DMSO) δ 10.43 (s, 2H), 10.24 (s, 1H), 7.33 (dd, $J = 6.0, 3.5$ Hz, 4H), 7.24 – 7.14 (m, 2H), 7.01 (dd, $J = 13.7, 7.2$ Hz, 3H), 6.95 – 6.88 (m, 3H), 6.81 (t, $J = 7.4$ Hz, 2H).



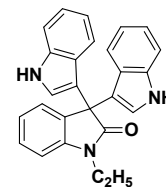
1'-methyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (16c):

White solid (95% yield), m.p: 288 - 290 °C; ^1H NMR (400 MHz, DMSO): δ (ppm) 10.63 (s, 1H), 7.37 (d, $J = 8.2$ Hz, 2H), 7.22 (t, $J = 7.7$ Hz, 4H), 7.08 (t, $J = 7.5$ Hz, 2H), 6.98 (d, $J = 7.6$ Hz, 1H), 6.92 (t, $J = 7.6$ Hz, 1H), 6.88 (s, 2H), 6.83 (t, $J = 7.5$ Hz, 2H), 2.49 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ (ppm) 179.04, 141.73, 137.80, 134.98, 128.93, 128.38, 126.50, 125.36, 122.05, 121.56, 121.41, 118.88, 113.92, 110.23, 52.87, 32.80.



1'-ethyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (16d):

White solid, (90% yield), M.P: 288 - 289 °C; ^1H NMR (400 MHz, DMSO): δ (ppm) 10.97 (s, 2H), 7.35 (d, $J = 8.3$ Hz, 2H), 7.32 – 7.29 (m, 2H), 7.19 (t, $J = 7.4$ Hz, 3H), 7.00 (q, $J = 7.1$ Hz, 3H), 6.85 (d, $J = 2.0$ Hz, 2H), 6.79 (t, $J = 7.5$ Hz, 2H), 3.82 (q, $J = 6.8$ Hz, 2H), 1.24 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO): δ (ppm) 176.99, 142.13, 137.42, 134.42, 128.46, 126.12, 125.30, 124.79, 122.48, 121.46, 121.17, 118.76, 114.56, 112.14, 109.16, 52.69, 34.80, 13.00.

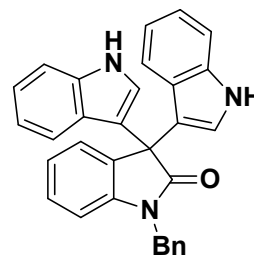


1'-benzyl-[3,3':3',3''-terindolin]-2'-one(16e)

Yield = (95 %) m.p: 180-182 °C; ¹H NMR (400 MHz, CDCl₃+DMSO)

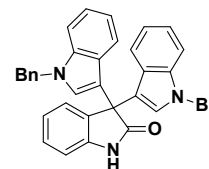
δ 10.43 (s, 2H), 7.34 (d, *J* = 7.2 Hz, 5H), 7.28 (d, *J* = 7.0 Hz, 3H), 7.21 (dd, *J* = 13.8, 7.8 Hz, 3H), 7.03 (t, *J* = 7.4 Hz, 2H), 6.94 (q, *J* = 7.6 Hz, 4H), 6.78 (t, *J* = 7.4 Hz, 1H), 5.00 (s, 2H). ¹³C NMR (101 MHz, CDCl₃+DMSO) δ 177.87, 141.99, 137.32, 136.24, 134.21, 128.71,

127.86, 127.62, 125.96, 125.21, 124.66, 122.49, 121.30, 121.19, 118.64, 114.46, 111.65, 109.14, 52.81, 43.85. Mass (ESI-MS): *m/z* Calculated: 453; Observed: 454(M+1) and 476 (M+Na).



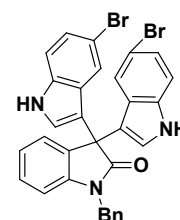
1,1''-dibenzyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (16f):

White solid, (90% yield), M.P: 164 - 166 °C; ¹H NMR (400 MHz, DMSO): δ (ppm) 10.68 (s, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.30 (dd, *J* = 13.6, 6.1 Hz, 7H), 7.23 (t, *J* = 7.0 Hz, 4H), 7.13 (d, *J* = 7.3 Hz, 4H), 7.09 (s, 2H), 7.04-6.97 (m, 3H), 6.83 (t, *J* = 7.5 Hz, 2H), 5.37 (s, 4H). ¹³C NMR (101 MHz, DMSO): δ (ppm) 178.91, 143.11, 141.76, 138.73, 137.26, 134.66, 130.49, 128.97, 128.51, 127.74, 127.28, 126.82, 125.37, 121.75, 119.03, 114.67, 110.81, 110.22, 52.89, 49.31.



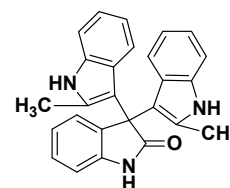
1'-benzyl-5,5''-dibromo-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (16h):

White solid, (90% yield), M.P: 279 - 281 °C; ¹H NMR (400 MHz, DMSO): δ (ppm) 11.28 (s, 2H), 7.38 – 7.25 (m, 11H), 7.15 (dd, *J* = 13.2, 8.3 Hz, 3H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.94 (s, 2H), 5.01 (s, 2H). ¹³C NMR (101 MHz, DMSO): δ (ppm) 177.18, 142.15, 136.95, 136.18, 133.20, 129.27, 128.80, 127.97, 127.79, 127.66, 126.56, 125.17, 124.25, 123.09, 114.39, 113.96, 111.66, 110.09, 52.35, 43.60.



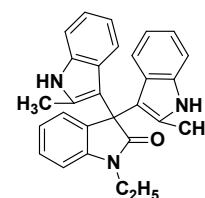
2,2''-dimethyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (16i):

White solid, (90% yield), M.P: >300; ¹H NMR (400 MHz, DMSO): δ (ppm) 10.87 (s, 1H), 10.33 (s, 2H), 7.23 (t, 4H), 6.91 (d, *J* = 12.6 Hz, 5H), 6.73 (d, *J* = 6.2 Hz, 2H), 6.27 (s, 1H), 2.50 (s, 3H), 2.40 (s, 3H).



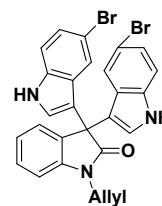
1'-ethyl-2,2''-dimethyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (16j):

White solid, (88% yield), M.P: >300 °C; ¹H NMR (400 MHz, DMSO): δ (ppm) 10.90 (s, 1H), 10.86 (s, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.9 Hz, 3H), 7.16 (d, *J* = 7.8 Hz, 1H), 6.95-6.86 (m, 3H), 6.68 – 6.57 (m, 3H), 6.34 (d, *J* = 8.1 Hz, 1H), 3.83 – 3.74 (m, 2H), 2.02 (s, 3H), 1.92 (s, 3H), 1.20 (t, *J* = 7.0 Hz, 3H).



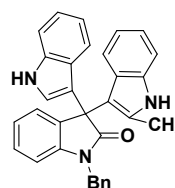
1'-allyl-5,5''-dibromo-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (16k):

White solid, (90% yield), M.P: 284 - 286 °C; ¹H NMR (400 MHz, DMSO): δ (ppm) 11.26 (d, *J* = 1.7 Hz, 2H), 7.37 – 7.32 (m, 5H), 7.26 (d, *J* = 7.3 Hz, 1H), 7.18 – 7.14 (m, 3H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 2.5 Hz, 2H), 5.98-5.89 (m, 1H), 5.27-5.22 (m, 2H), 4.43 (d, *J* = 5.1 Hz, 2H). ¹³C NMR (101 MHz, DMSO): δ (ppm) 176.75, 142.07, 136.16, 133.16, 132.15, 128.78, 127.65, 126.44, 125.17, 124.18, 123.12, 123.03, 118.19, 114.36, 114.03, 111.61, 110.01, 52.24, 42.24.



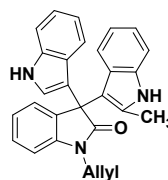
1'-benzyl-2-methyl-1H, 1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (19c):

White solid, (87% yield), M.P: 248 - 250 °C; ¹H NMR (400 MHz, DMSO): δ (ppm) 11.00 – 10.84 (m, 2H), 7.29 (s, 10H), 7.07 (d, *J* = 32.8 Hz, 3H), 6.80 (dd, *J* = 45.4, 16.7 Hz, 4H), 6.58 (s, 1H), 4.98 (t, *J* = 19.3 Hz, 2H), 1.81 (d, *J* = 65.9 Hz, 3H). ¹³C NMR (101 MHz, DMSO): δ (ppm) 177.62, 142.21, 141.93, 137.49, 136.94, 135.36, 134.99, 134.69, 134.01, 128.99, 128.13, 127.89, 127.74, 126.75, 125.22, 123.81, 123.05, 122.74, 122.10, 121.62, 120.13, 119.52, 118.77, 118.43, 115.48, 112.07, 110.83, 109.76, 109.04, 52.68, 43.38, 13.10. Mass (ESI-MS): *m/z* Calculated: C₃₂H₂₅N₃O: 467.20; Observed: 467.1587 (M).



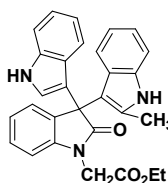
1'-allyl-2-methyl-1H, 1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (19d):

White solid, (92% yield), M.P: 272 - 274 °C; ¹H NMR (400 MHz, DMSO): δ (ppm) 10.98 (s, 1H), 10.88 (d, *J* = 27.9 Hz, 1H), 7.36 – 7.19 (m, 5H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.00 (s, 2H), 6.90 – 6.70 (m, 4H), 6.53 (s, 1H), 5.89 (s, 1H), 5.15 (s, 2H), 4.41 (s, 2H), 1.84 (d, *J* = 76.1 Hz, 3H). ¹³C NMR (101 MHz, DMSO): δ (ppm) 177.16, 142.18, 137.44, 135.37, 134.89, 133.86, 132.44, 128.21, 126.77, 125.13, 123.79, 122.98, 122.63, 121.59, 120.31, 120.09, 119.45, 118.73, 118.49, 117.25, 116.12, 112.04, 110.85, 109.66, 108.64, 52.58, 42.05, 13.27.



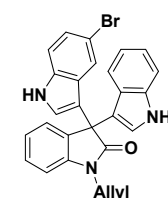
Ethyl 2-(2-methyl-2'-oxo-1H, 1''H-[3,3':3',3''-terbenzo[b]pyrrol]-1'(2'H)-yl)acetate (19e):

White solid (81% yield), M.P: 238 - 240 °C; ¹H NMR (400 MHz, DMSO): δ (ppm) 11.25 (s, 1H), 11.02 (s, 1H), 7.51 (s, 1H), 7.37 – 7.22 (m, 5H), 7.16 – 7.13 (m, 2H), 7.03 (dd, *J* = 17.9, 7.7 Hz, 2H), 6.87 (d, *J* = 2.5 Hz, 2H), 6.79 (t, *J* = 7.4 Hz, 1H), 4.66 (s, 2H), 4.18 (q, *J* = 7.0 Hz, 2H), 2.50 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, DMSO): δ (ppm) 177.40, 168.49, 142.04, 137.32, 136.18, 133.49, 128.51, 127.90, 126.41, 125.91, 125.06, 124.95, 124.10, 123.89, 122.99, 121.58, 120.81, 118.95, 114.23, 114.14, 114.05, 112.14, 111.49, 109.63, 61.63, 52.32, 41.77, 40.59, 14.49.



1'-allyl-5-bromo-[3,3':3',3''-terindolin]-2'-one (19f):

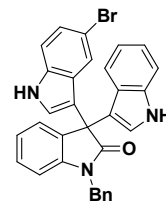
White solid, (85% yield), M.P: 280 - 283 °C; ¹H NMR (400 MHz, DMSO): δ (ppm) 11.25 (s, 1H), 11.04 (s, 1H), 7.42 - 7.31 (m, 5H), 7.08 (d, *J* = 38.0 Hz,



5H), 6.90 (d, $J = 8.0$ Hz, 2H), 6.81 (s, 1H), 5.91 (s, 1H), 5.19 (d, $J = 12.1$ Hz, 2H), 4.43 (s, 2H). ^{13}C NMR (101 MHz, DMSO): δ (ppm) 176.98, 142.12, 137.37, 136.18, 133.66, 132.35, 128.58, 127.88, 126.27, 125.90, 125.16, 124.77, 124.09, 123.66, 123.12, 122.86, 121.63, 120.63, 118.99, 117.72, 114.36, 114.29, 111.27, 111.47, 109.87, 52.46, 42.16. Mass (ESI-MS): m/z Calculated: $\text{C}_{27}\text{H}_{20}\text{BrN}_3\text{O}$: 481.08; Observed: 504.0699 (M+2).

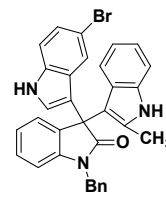
1'-benzyl-5-bromo-[3,3':3',3''-terindolin]-2'-one (19g):

White solid, (90% yield), M.P: 260 - 262 °C; ^1H NMR (400 MHz, DMSO): δ (ppm) 11.29 (s, 2H), 7.70 (d, $J = 24.0$ Hz, 1H), 7.33 (d, $J = 22.2$ Hz, 11H), 7.17 – 7.12 (m, 3H), 7.06 (s, 1H), 6.94 (s, 2H), 5.01 (s, 2H). ^{13}C NMR (101 MHz, DMSO): δ (ppm) 177.20, 142.12, 136.90, 136.16, 133.18, 132.13, 131.99, 129.27, 129.12, 128.82, 128.37, 128.00, 127.77, 127.64, 126.72, 126.52, 126.19, 125.33, 125.15, 124.56, 124.28, 123.17, 123.06, 114.40, 113.96, 111.66, 110.09, 61.84, 52.35. Mass (ESI-MS): m/z Calculated: $\text{C}_{31}\text{H}_{22}\text{BrN}_3\text{O}$: 532.42; Observed: 534.48 (M+2).



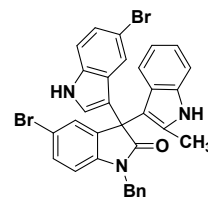
1'-benzyl-5''-bromo-2-methyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (19h):

white solid, (90% yield), M.P: 216 - 218 °C; ^1H NMR (400 MHz, DMSO): δ (ppm) 11.25 (s, 1H), 10.93 (d, $J = 40.7$ Hz, 1H), 7.56 (d, $J = 55.9$ Hz, 1H), 7.34 - 7.11 (m, 11H), 7.01 – 6.87 (m, 3H), 6.74 – 6.55 (m, 2H), 5.10 – 4.95 (m, 2H), 1.83 (d, $J = 92.9$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO): δ (ppm) 177.28, 142.19, 136.83 (s), 136.28, 135.35, 134.14, 129.02, 128.45, 128.23, 127.83, 127.07, 125.56, 125.26, 124.95, 124.26, 123.89, 122.94, 120.33, 119.21, 118.61, 115.16, 114.21, 111.51, 110.91, 109.85, 108.80, 99.48, 52.52, 43.48, 12.91. Mass (ESI-MS): m/z Calculated: $\text{C}_{32}\text{H}_{24}\text{BrN}_3\text{O}$: 545.11; Observed: 568.0978 (M+Na).



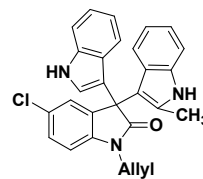
1'-benzyl-5',5''-dibromo-2-methyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (19i):

White solid, (82% yield), M.P: 257 - 259 °C; ^1H NMR (400 MHz, DMSO): δ (ppm) 11.31 (s, 1H), 11.00 (d, $J = 46.5$ Hz, 1H), 7.57 (d, $J = 69.8$ Hz, 2H), 7.32 - 7.27 (m, 10H), 6.87 (d, $J = 44.9$ Hz, 2H), 6.47 (d, $J = 104.2$ Hz, 2H), 5.00 (d, $J = 42.1$ Hz, 2H), 1.83 (d, $J = 104.6$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO): δ (ppm) 176.82, 141.41, 136.26, 135.26, 131.41, 131.36, 131.25, 129.09, 128.22, 127.85, 127.74, 125.51, 124.92, 124.52, 120.88, 120.76, 120.59, 119.04, 118.95, 118.85, 118.78, 114.78, 114.36, 114.22, 112.10, 111.29, 107.92, 52.63, 43.54, 12.74. Mass (ESI-MS): m/z Calculated: $\text{C}_{32}\text{H}_{23}\text{Br}_2\text{N}_3\text{O}$: 623.02; Observed: 646.0022 (M+Na).



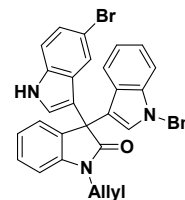
1'-allyl-5'-chloro-2-methyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one(19j):

White solid (82% yield), M.P: 279 - 281 °C; ¹H NMR (400 MHz, DMSO): δ 11.06 (s, 2H), 7.37 (s, 3H), 7.24 (s, 2H), 7.08 (d, *J* = 38.8 Hz, 2H), 6.83 (d, *J* = 29.5 Hz, 4H), 6.58 (s, 1H), 5.88 (s, 1H), 5.16 (s, 2H), 4.42 (s, 2H), 1.86 (d, *J* = 81.7 Hz, 3H). ¹³C NMR (101 MHz, DMSO): δ 176.58, 141.09, 137.39, 136.24, 135.62, 135.39, 132.08, 128.54, 127.71, 126.91, 125.70, 124.19, 123.54, 121.73, 120.32, 119.18, 117.98, 114.35, 113.59, 112.41, 111.56, 111.48, 61.71, 52.64, 14.48. Mass (ESI-MS): *m/z* Calculated: C₂₈H₂₂ClN₃O: 451.15; Observed: 474.1360 (M+Na).



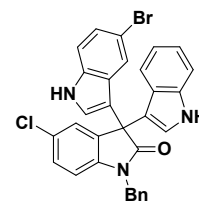
1'-allyl-1-benzyl-5''-bromo-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (19k):

White solid, (84% yield), M.P: 200 - 202 °C; ¹H NMR (400 MHz, DMSO): δ (ppm) 11.26 (s, 1H), 7.58 (s, 1H), 7.36 – 7.34 (m, 6H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 8.1 Hz, 5H), 7.07–6.99 (m, 3H), 6.91 (s, 1H), 6.81 (t, *J* = 7.5 Hz, 1H), 5.94 - 5.86 (m, 1H), 5.38 (s, 2H), 5.19 – 5.14 (m, 2H), 4.43 (d, *J* = 3.7 Hz, 2H). ¹³C NMR (101 MHz, DMSO): δ (ppm) 176.80, 142.12, 138.65, 137.03, 136.29, 133.43, 132.34, 129.09, 128.86, 128.65, 127.95, 127.71, 127.05, 126.55, 125.89, 125.10, 124.16, 124.08, 122.95, 121.85, 120.66, 119.35, 117.64, 114.30, 114.25, 114.04, 111.51, 110.93, 109.95, 52.35, 49.34, 42.13. Mass (ESI-MS): *m/z* Calculated: C₃₄H₂₆BrN₃O: 571.49; Observed: 594.13 (M+Na).



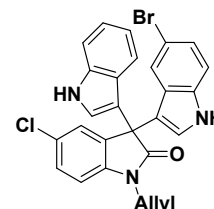
1'-benzyl-5-bromo-5'-chloro-[3,3':3',3''-terindolin]-2'-one (19l):

White solid, (90% yield), m.p: 245 - 247 °C; ¹H NMR (400 MHz, DMSO): δ 11.35 (s, 2H), 7.64 – 6.85 (m, 17H), 5.02 (s, 2H). ¹³C NMR (101 MHz, DMSO): δ 176.84, 141.11, 136.60, 136.21, 135.12, 129.33, 128.82, 128.10, 127.83, 127.45, 127.21, 126.81, 125.10, 124.38, 122.88, 114.52, 113.17, 111.78, 52.53, 43.71.



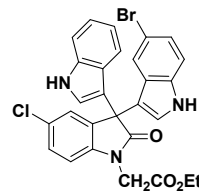
1'-allyl-5-bromo-5'-chloro-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one(19m):

White solid, (85% yield), M.P: 285 - 287 °C; ¹H NMR (400 MHz, DMSO): δ 11.32 (s, 1H), 11.11 (s, 1H), 7.45 – 7.34 (m, 4H), 7.27 (s, 1H), 7.18 (t, *J* = 8.1 Hz, 2H), 7.06 (dd, *J* = 17.5, 10.0 Hz, 2H), 6.97 (s, 1H), 6.93 (s, 1H), 6.83 (t, *J* = 7.3 Hz, 1H), 5.91 (ddd, *J* = 15.9, 10.3, 5.1 Hz, 1H), 5.26 – 5.12 (m, 2H), 4.44 (s, 2H). ¹³C NMR (101 MHz, DMSO): δ 177.16, 142.18, 137.44, 135.37, 134.89, 133.86, 132.44, 128.21, 126.77, 125.13, 123.79, 122.98, 122.63, 121.59, 120.09, 119.45, 118.73, 118.49, 117.25, 116.12, 112.04, 110.85, 109.66, 108.64, 52.58, 42.05. Mass (ESI-MS): *m/z* Calculated: C₂₇H₁₉BrClN₃O: 515.04; Observed: 538.0309 (M+Na).



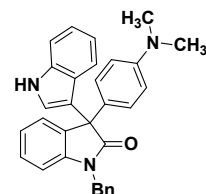
Ethyl-2-(5-bromo-5'-chloro-2'-oxo-1*H*,1''*H*-[3,3':3',3''-terbenzo[*b*]pyrrol]-1'(2'*H*)-

yl)acetate (19n): White solid, (88% yield), M.P: 280 - 283 °C; ¹H NMR (400 MHz, DMSO): δ (ppm) 11.31 (s, 1H), 11.10 (s, 1H), 7.52 (s, 1H), 7.43 – 7.36 (m, 3H), 7.23 (d, *J* = 7.3 Hz, 3H), 7.16 (d, *J* = 8.6 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 11.3 Hz, 2H), 6.82 (t, *J* = 7.5 Hz, 1H), 4.69 (s, 2H), 4.19 (q, *J* = 7.0 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, DMSO): δ (ppm) 177.02, 168.33, 141.03, 137.32, 136.22, 135.37, 128.51, 127.71, 127.03, 126.54, 125.69, 125.16, 124.89, 124.25, 123.74, 121.75, 120.52, 119.18, 114.27, 113.47, 113.23, 112.29, 111.61, 111.38, 61.73, 52.51, 41.88, 14.46. Mass (ESI-MS): *m/z* Calculated: C₂₈H₂₁BrClN₃O₃: 562.84; Observed: 580.56 (M+18).



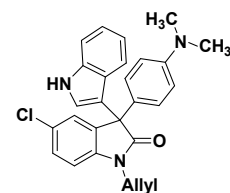
1-benzyl-3-(4-(dimethylamino)phenyl)-3-(1*H*-indol-3-yl)indolin-2-one (21b):

White solid, (95% yield), ¹H NMR (400 MHz, CDCl₃+DMSO): δ 10.91 (s, 1H), 7.36 – 7.23 (m, 7H), 7.18 (dd, *J* = 21.2, 8.0 Hz, 3H), 7.06 – 6.93 (m, 4H), 6.83 – 6.68 (m, 4H), 4.98 (q, *J* = 15.7 Hz, 2H), 2.92 (s, 6H). ¹³C NMR (101 MHz, CDCl₃+DMSO) δ 177.81, 142.04, 137.50, 136.71, 134.27, 128.92, 128.63, 128.08, 127.74, 127.53, 125.89, 125.41, 124.79, 122.67, 121.38, 118.74, 115.71, 113.13, 111.96, 109.61, 56.65, 43.49.



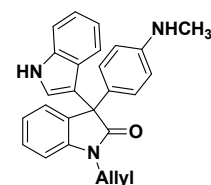
1-allyl-5-chloro-3-(4-(dimethylamino)phenyl)-3-(1*H*-indol-3-yl)indolin-2-one (21c):

White solid, (93% yield), ¹H NMR (400 MHz, CDCl₃+DMSO): δ 10.88 (s, 1H), 7.68 (d, *J* = 7.4 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.15 (d, *J* = 7.3 Hz, 2H), 7.07 (d, *J* = 5.6 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.87 (d, *J* = 11.4 Hz, 2H), 5.96 – 5.79 (m, 1H), 5.19 (t, *J* = 15.5 Hz, 2H), 4.41 (s, 2H), 3.18 (s, 6H). ¹³C NMR (101 MHz, CDCl₃+DMSO): δ 176.23, 143.50, 143.24, 140.69, 139.40, 137.56, 134.73, 131.17, 129.53, 128.66, 128.47, 127.70, 125.92, 125.36, 125.23, 124.85, 121.76, 120.91, 119.81, 119.19, 117.60, 113.81, 112.15, 110.94, 57.27, 45.62, 42.42, 21.30.



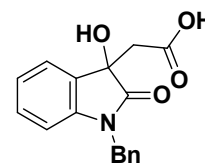
1-allyl-3-(1*H*-indol-3-yl)-3-(4-(methylamino)phenyl)indolin-2-one (21d):

White solid, (90% yield), ¹H NMR (400 MHz, CDCl₃+DMSO): δ 10.71 (s, 1H), 7.36 – 7.22 (m, 3H), 7.10 (d, *J* = 6.6 Hz, 3H), 7.02 (t, *J* = 7.2 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.81 (s, 2H), 6.61 (d, *J* = 7.7 Hz, 2H), 5.97 – 5.81 (m, 1H), 5.23 – 5.10 (m, 2H), 4.40 (s, 2H), 2.75 (s, 3H). ¹³C NMR (101 MHz, CDCl₃+DMSO) δ 177.54, 147.09, 141.93, 137.44, 134.21, 131.78, 130.15, 128.63, 127.93, 125.95, 125.85, 125.26, 124.58, 122.49, 121.38, 118.70, 117.13, 115.72, 113.42, 111.81, 109.33, 56.75, 42.14, 31.33.

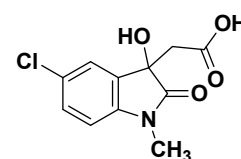


2-(1-benzyl-3-hydroxy-2-oxoindolin-3-yl)acetic acid (24a):

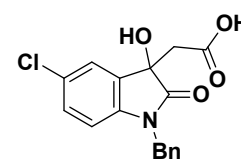
White solid, (90% yield), ¹H NMR (400 MHz, CDCl₃+DMSO): (90% yield), δ 7.40 – 7.27 (m, 3H), 7.20 (dt, *J* = 22.5, 7.2 Hz, 3H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 4.83 (dd, *J* = 72.2, 15.8 Hz, 2H), 3.01 (dd, *J* = 41.1, 15.7 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃+DMSO): δ 176.99, 171.60, 143.10, 135.75, 130.25, 129.51, 128.66, 127.38 (d, *J* = 14.2 Hz), 123.86, 122.74, 109.30, 73.15, 43.75, 41.71. Mass (ESI-MS): *m/z* Calculated: C₁₇H₁₅NO₄: 297.31; Observed: 298.10 (M+1).

**2-(5-chloro-3-hydroxy-1-methyl-2-oxoindolin-3-yl)acetic acid (24b):**

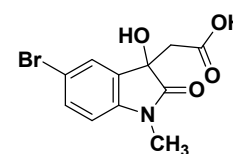
White solid, (92% yield), ¹H NMR (400 MHz, CDCl₃+DMSO): δ 7.39 (s, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 3.16 (s, 3H), 3.06 – 2.94 (m, 2H), 2.56 (d, *J* = 9.6 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃+DMSO) δ 176.50, 174.49, 142.63, 131.99, 129.44, 127.76, 124.30, 109.49, 73.09, 41.57, 26.36. Mass (ESI-MS): *m/z* Calculated: C₁₁H₁₀ClNO₄: 255.65; Observed: 276.33 (M+23).

**2-(1-benzyl-5-chloro-3-hydroxy-2-oxoindolin-3-yl)acetic acid (24c):**

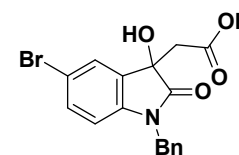
White solid, (92% yield), ¹H NMR (400 MHz, CDCl₃+DMSO): (90% yield), δ 7.34 (d, *J* = 6.9 Hz, 1H), 7.23 (ddd, *J* = 20.5, 13.5, 7.0 Hz, 4H), 7.05 (d, *J* = 8.3 Hz, 1H), 6.48 (d, *J* = 8.3 Hz, 1H), 4.94 – 4.71 (m, 2H), 3.11 – 2.91 (m, 2H). ¹³C NMR (101 MHz, CDCl₃+DMSO): δ 176.61, 171.59, 141.71, 135.28, 132.17, 129.21, 128.71, 127.90, 127.55, 127.19, 124.39, 110.35, 73.16, 43.82, 41.58. Mass (ESI-MS): *m/z* Calculated: C₁₇H₁₄ClNO₄: 331.75; Observed: 354 (M+23).

**2-(5-bromo-3-hydroxy-1-methyl-2-oxoindolin-3-yl)acetic acid (24d):**

White solid, (88% yield), ¹H NMR (400 MHz, CDCl₃+DMSO): (88% yield), δ 7.50 (s, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 3.16 (s, 3H), 3.02 (q, *J* = 16.0 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃+DMSO): δ 176.39, 174.20, 143.44, 132.74, 132.16, 126.93, 114.79, 109.89, 72.87, 41.94, 29.13. Mass (ESI-MS): *m/z* Calculated: C₁₁H₁₀BrNO₄: 300.10; Observed: 323.96 (M+Na).

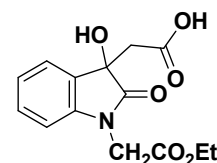
**2-(1-benzyl-5-bromo-3-hydroxy-2-oxoindolin-3-yl)acetic acid (24e):**

White solid, (85% yield), ¹H NMR (400 MHz, CDCl₃+DMSO) (85% yield), δ 7.48 (s, 1H), 7.24 (tt, *J* = 19.4, 9.7 Hz, 6H), 6.46 (d, *J* = 8.3 Hz, 1H), 4.82 (dd, *J* = 70.0, 15.9 Hz, 2H), 3.04 (dd, *J* = 38.8, 16.1 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃+DMSO): δ 176.48, 171.42, 142.27, 135.25, 132.49, 132.17, 128.73, 127.58, 127.21, 127.10, 115.25, 110.93, 73.08, 43.82, 41.54. Mass (ESI-MS): *m/z* Calculated: C₁₇H₁₄BrNO₄: 376.20; Observed: 376.01 (M)



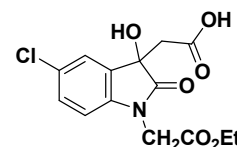
2-(1-(2-ethoxy-2-oxoethyl)-3-hydroxy-2-oxoindolin-3-yl)acetic acid (24f):

white solid, (92% yield), ¹H NMR (400 MHz, CDCl₃): (92% yield), δ 7.44 (d, *J* = 6.9 Hz, 1H), 7.35 – 7.26 (m, 1H), 7.10 (t, *J* = 7.1 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 4.42 (s, 2H), 4.20 (dd, *J* = 13.3, 6.4 Hz, 2H), 2.97 (s, 2H), 1.25 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 176.86, 173.20, 167.71, 141.84, 130.18, 129.05, 124.29, 123.87, 108.78, 73.41, 62.15, 41.43, 41.01, 14.05. Mass (ESI-MS): *m/z* Calculated: C₁₄H₁₅NO₆: 293.27; Observed: 292.04 (M-1).



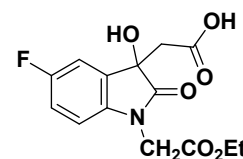
2-(5-chloro-1-(2-ethoxy-2-oxoethyl)-3-hydroxy-2-oxoindolin-3-yl)acetic acid (24g):

white solid, (90% yield), ¹H NMR (400 MHz, CDCl₃): (90% yield), δ 7.34 (s, 1H), 7.17 (d, *J* = 8.3 Hz, 1H), 6.57 (d, *J* = 8.3 Hz, 1H), 4.33 (d, *J* = 4.6 Hz, 2H), 4.11 (q, *J* = 7.0 Hz, 2H), 2.89 (s, 2H), 1.17 (t, *J* = 7.0 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ 176.50, 172.70, 167.64, 140.56, 130.84, 129.97, 129.06, 124.90, 109.89, 73.37, 62.29, 41.48, 40.86, 14.02. Mass (ESI-MS): *m/z* Calculated: C₁₄H₁₄ClNO₆: 327.72; Observed: 350.04 (M+23).



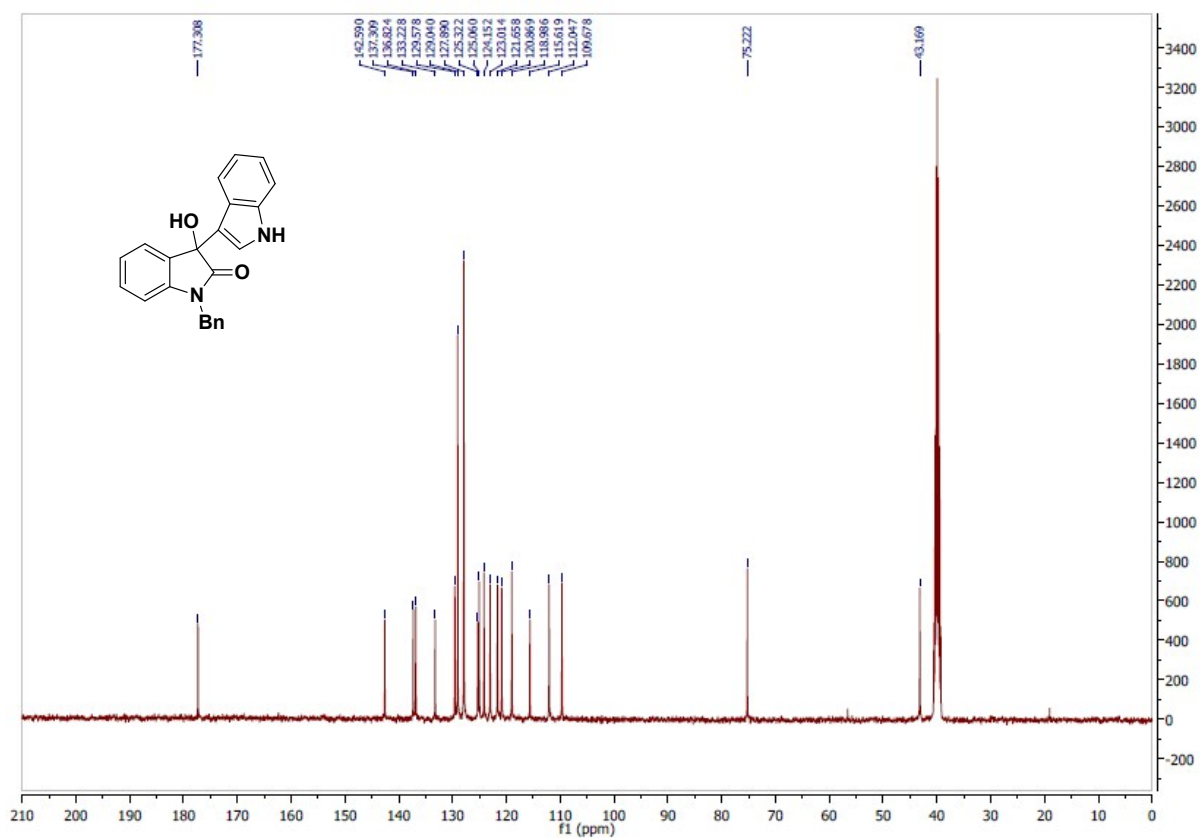
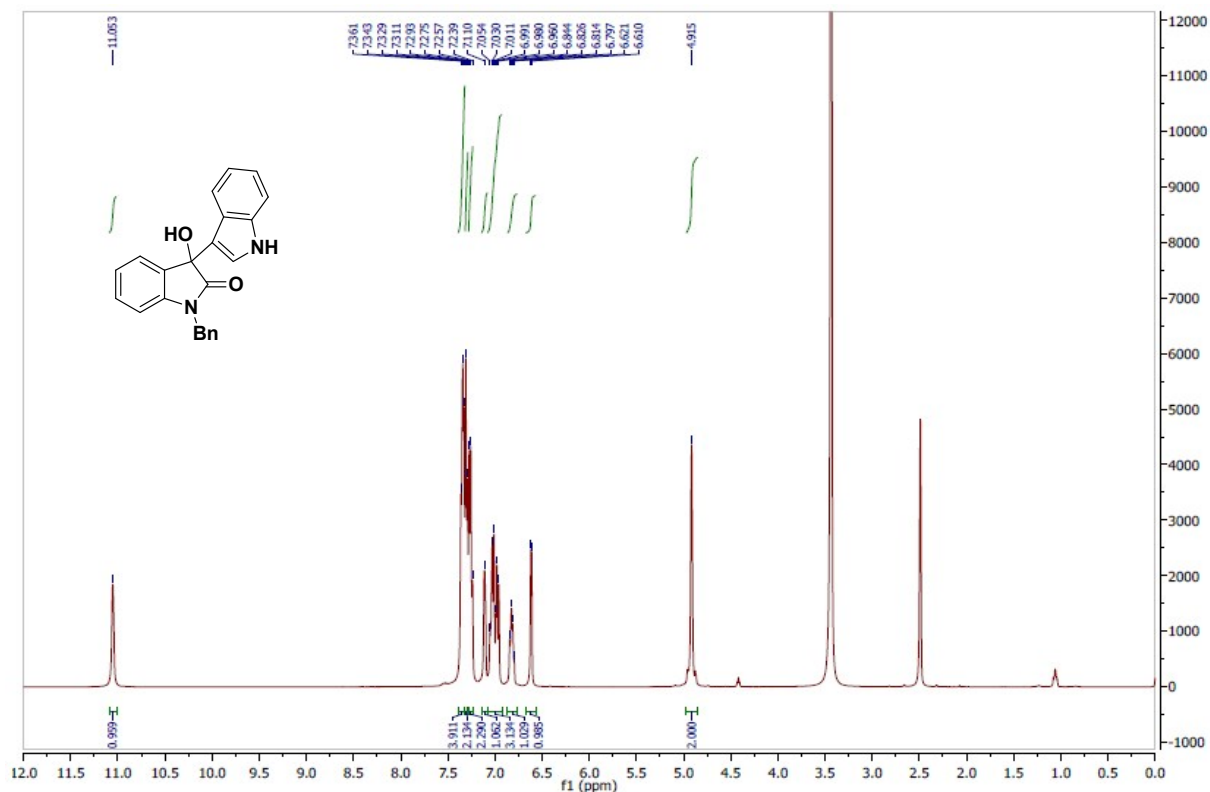
2-(1-(2-ethoxy-2-oxoethyl)-5-fluoro-3-hydroxy-2-oxoindolin-3-yl)acetic acid (24h):

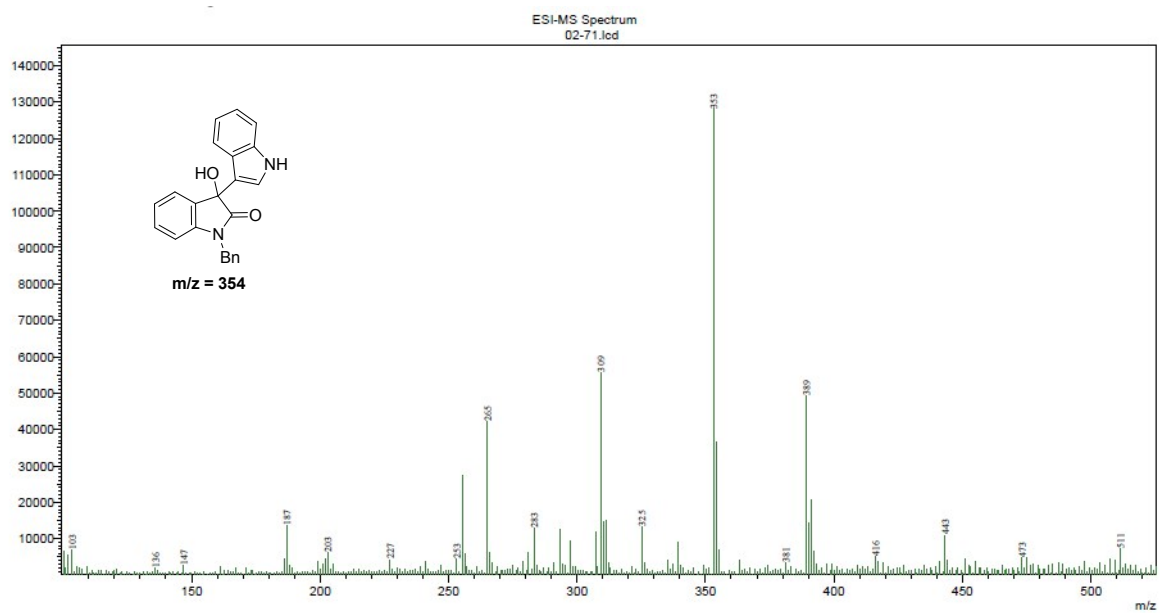
white solid, (85% yield), ¹H NMR (400 MHz, CDCl₃+DMSO): (85% yield), δ 7.17 (d, *J* = 7.5 Hz, 1H), 6.91 (t, *J* = 8.8 Hz, 1H), 6.61 (dd, *J* = 8.4, 3.7 Hz, 1H), 4.34 (dt, *J* = 27.3, 13.4 Hz, 2H), 4.14 (q, *J* = 7.0 Hz, 2H), 2.95 – 2.85 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃+DMSO): δ 176.52, 171.56, 167.47, 158.09, 138.38, 131.63 (d, *J* = 7.7 Hz), 115.86, 115.63, 112.55, 112.30, 109.23 (d, *J* = 7.9 Hz), 73.33, 68.61, 61.75, 41.46, 14.09. Mass (ESI-MS): *m/z* Calculated: C₁₄H₁₄FNO₆: 311.26; Observed: 334.07 (M+Na).



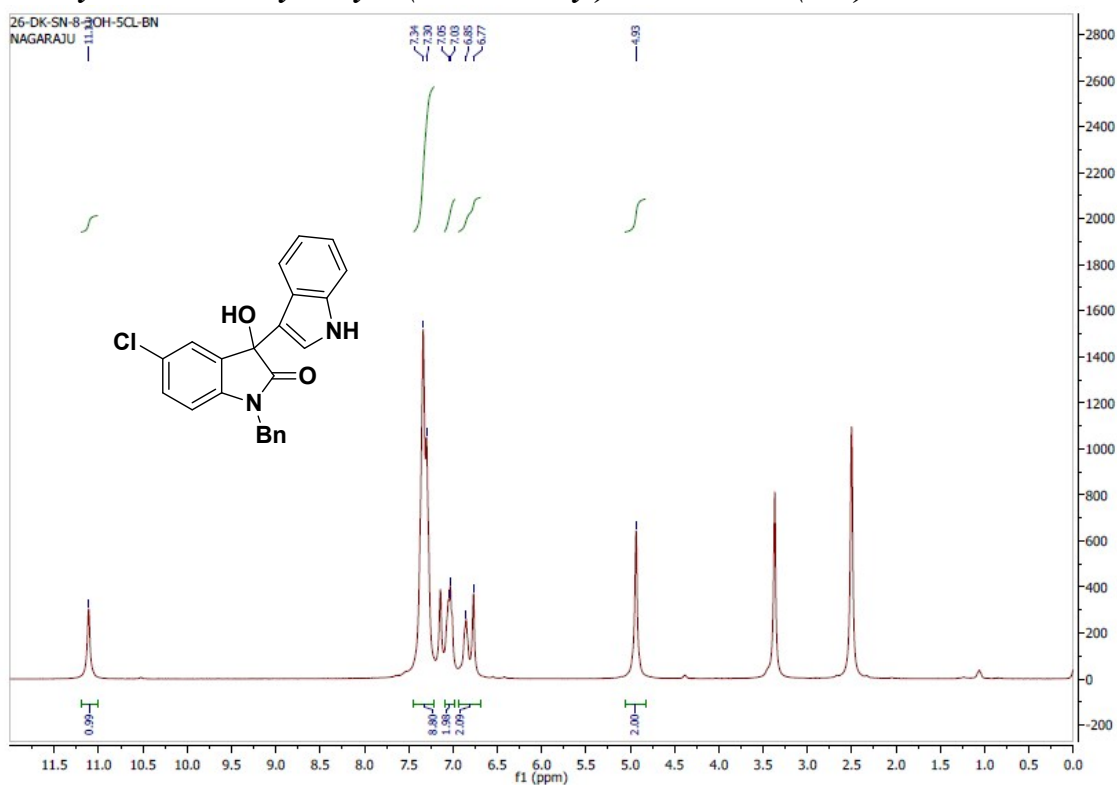
3-hydroxy-1-methyl-3-(2-methyl-1H-indol-3-yl)indolin-2-one (15i):

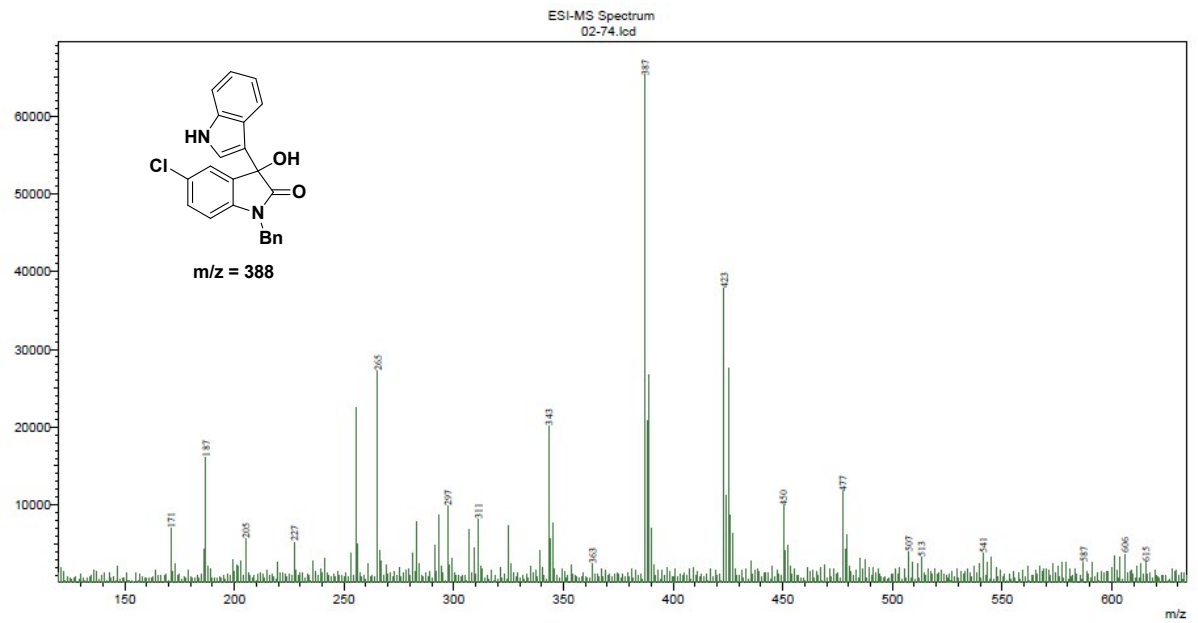
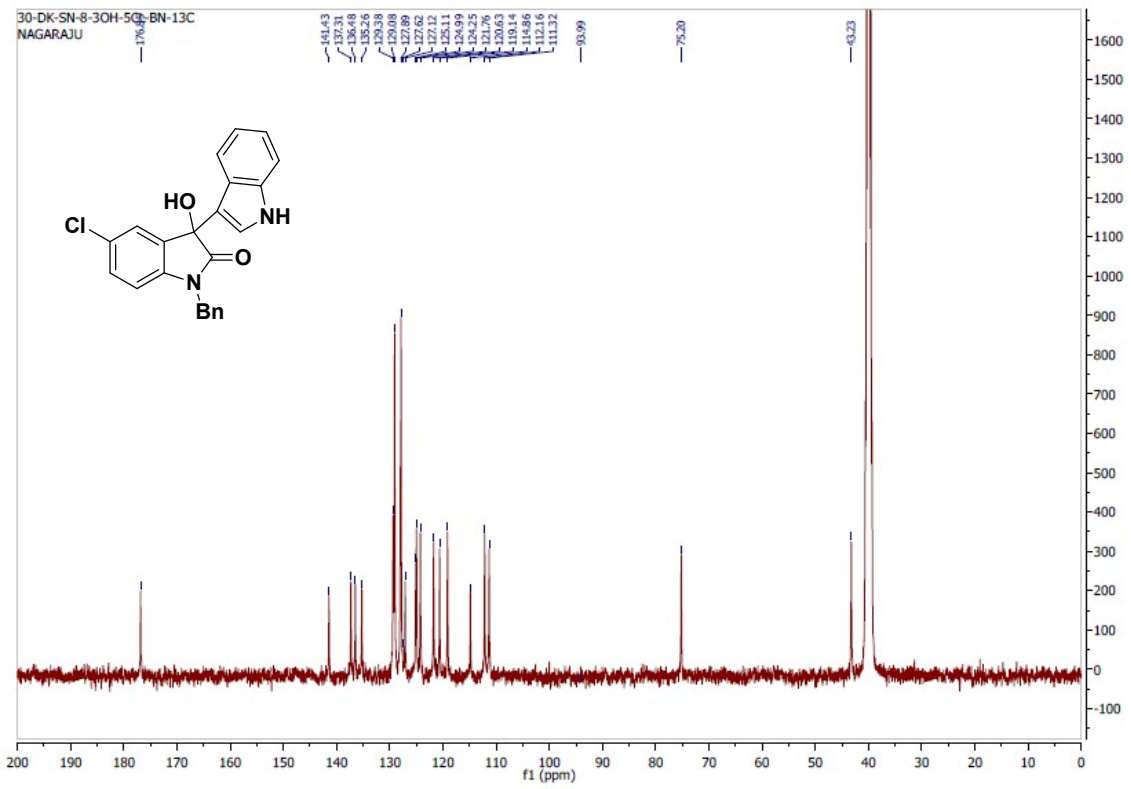
1-benzyl-3-hydroxy-3-(1H-indol-3-yl)indolin-2-one (15m):



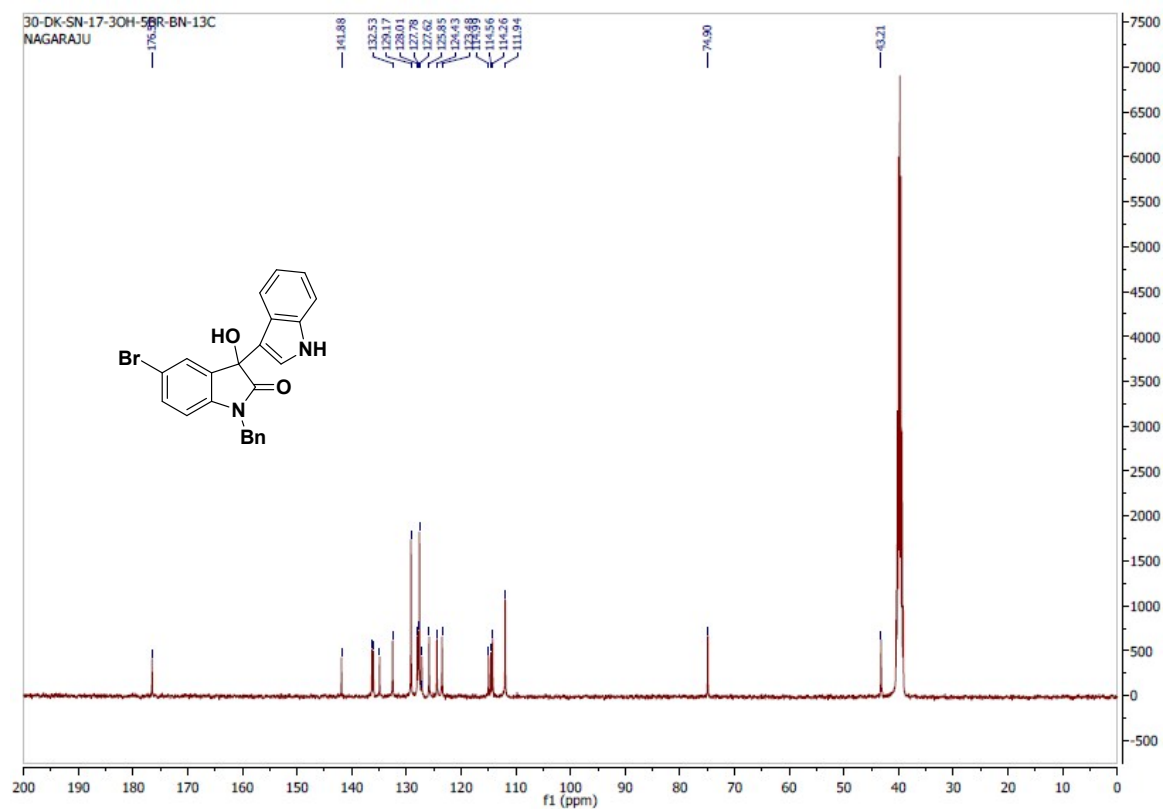
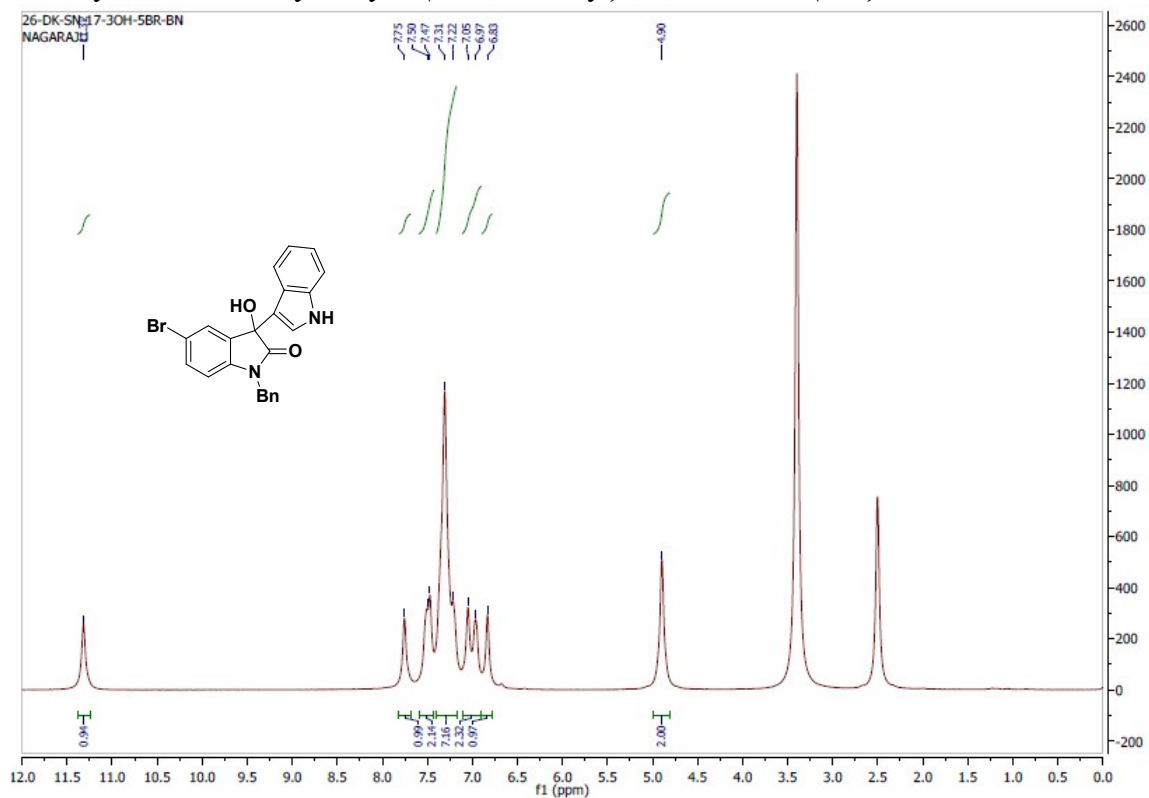


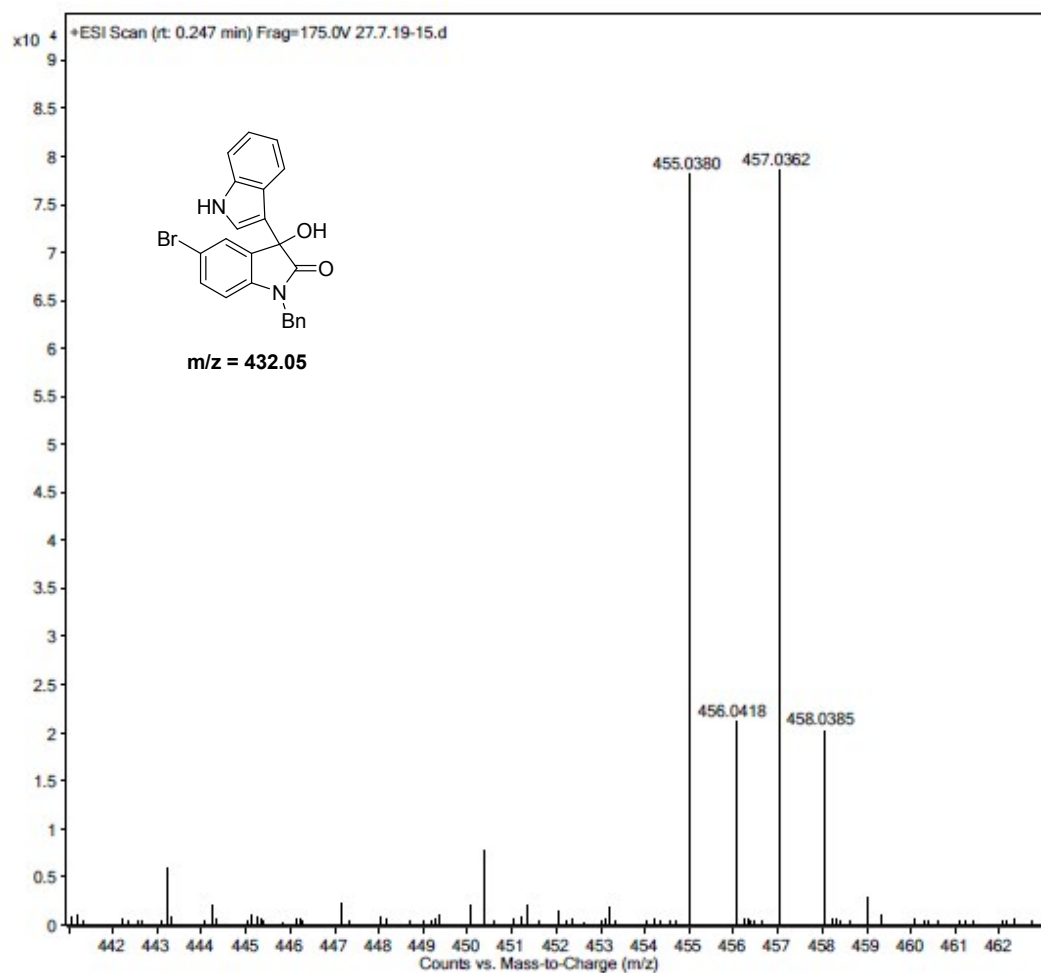
1-benzyl-5-chloro-3-hydroxy-3-(1H-indol-3-yl)indolin-2-one (15n):



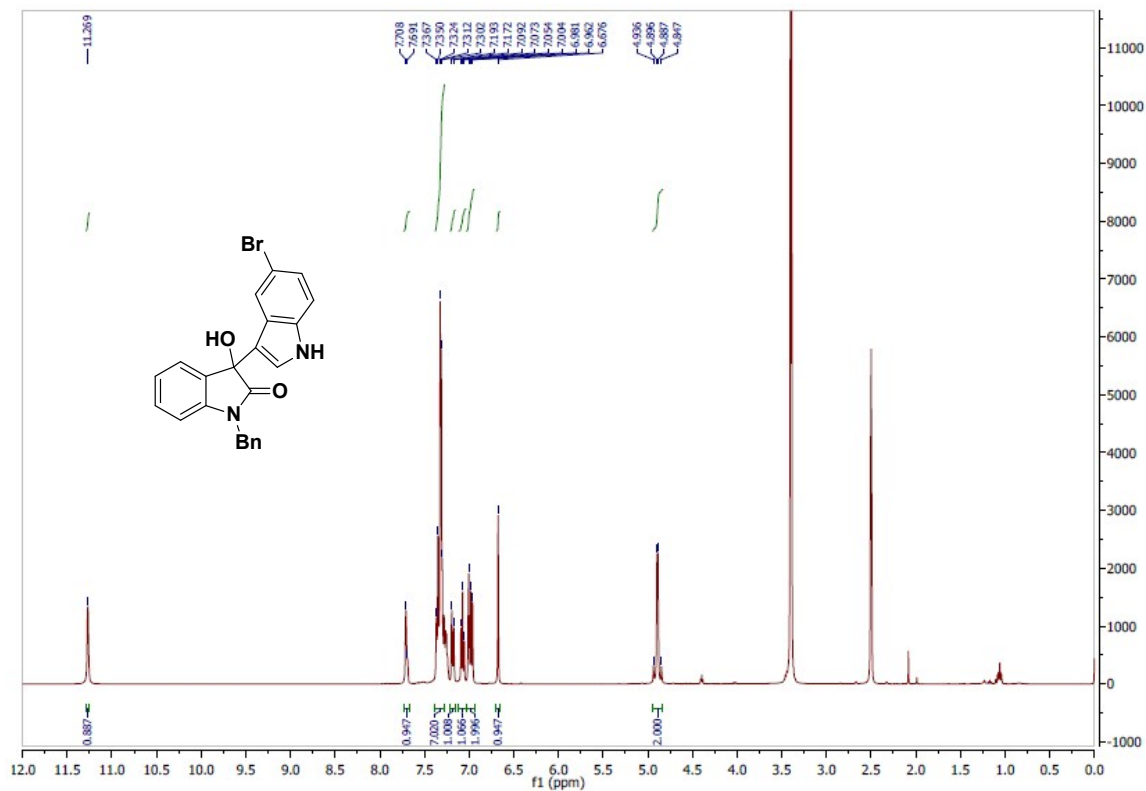


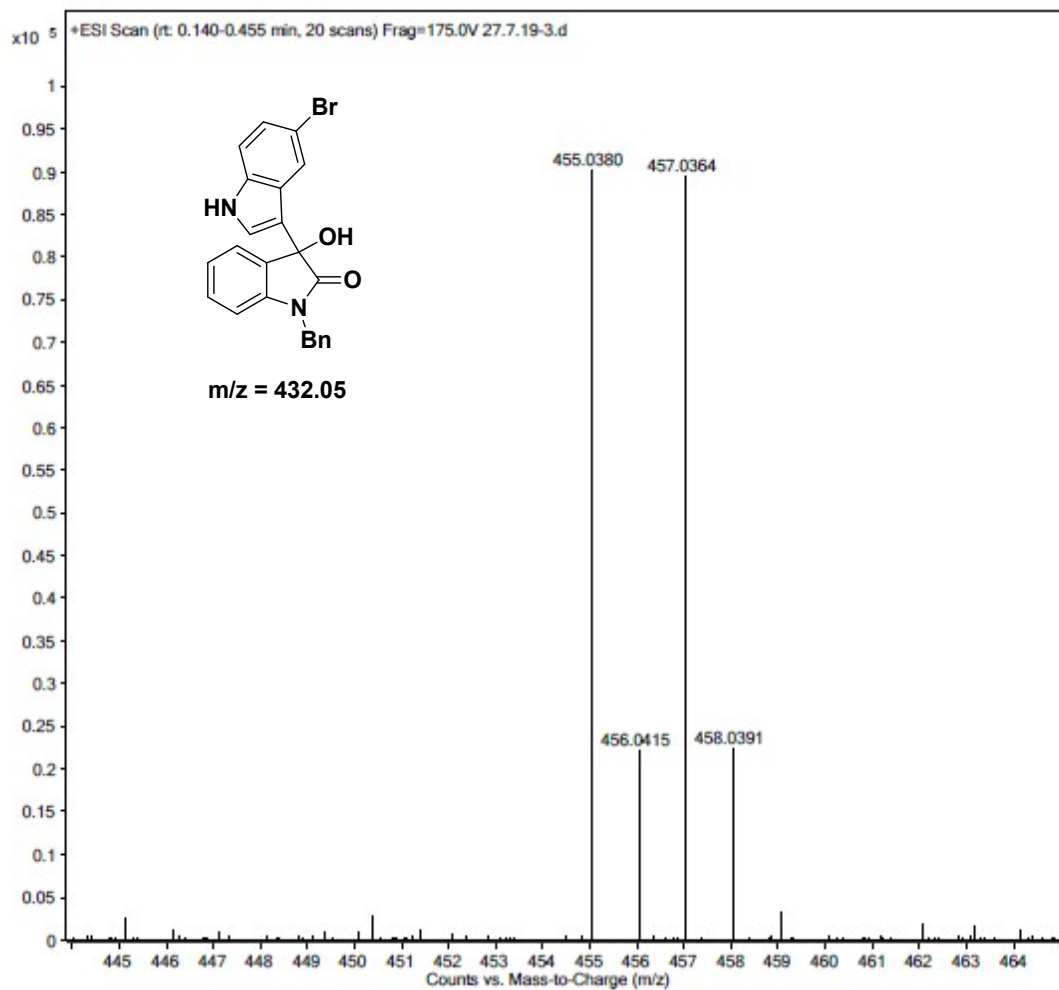
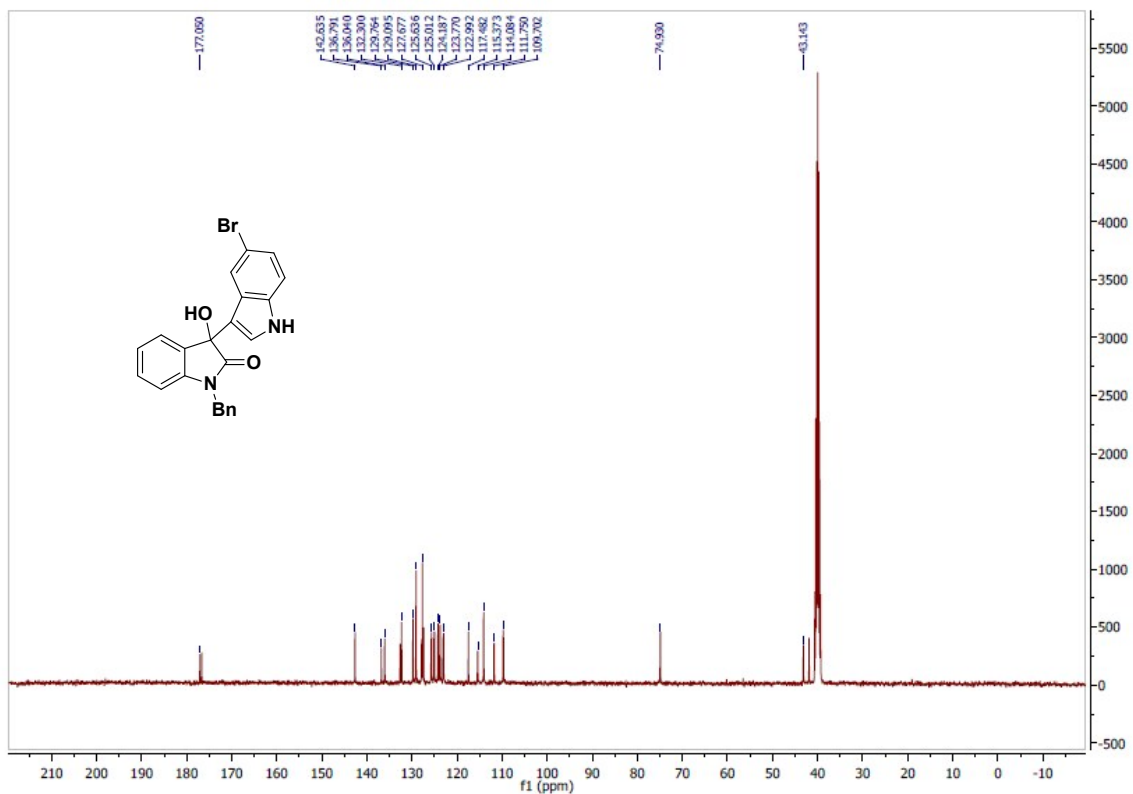
1-benzyl-5-bromo-3-hydroxy-3-(1H-indol-3-yl)indolin-2-one (15o):



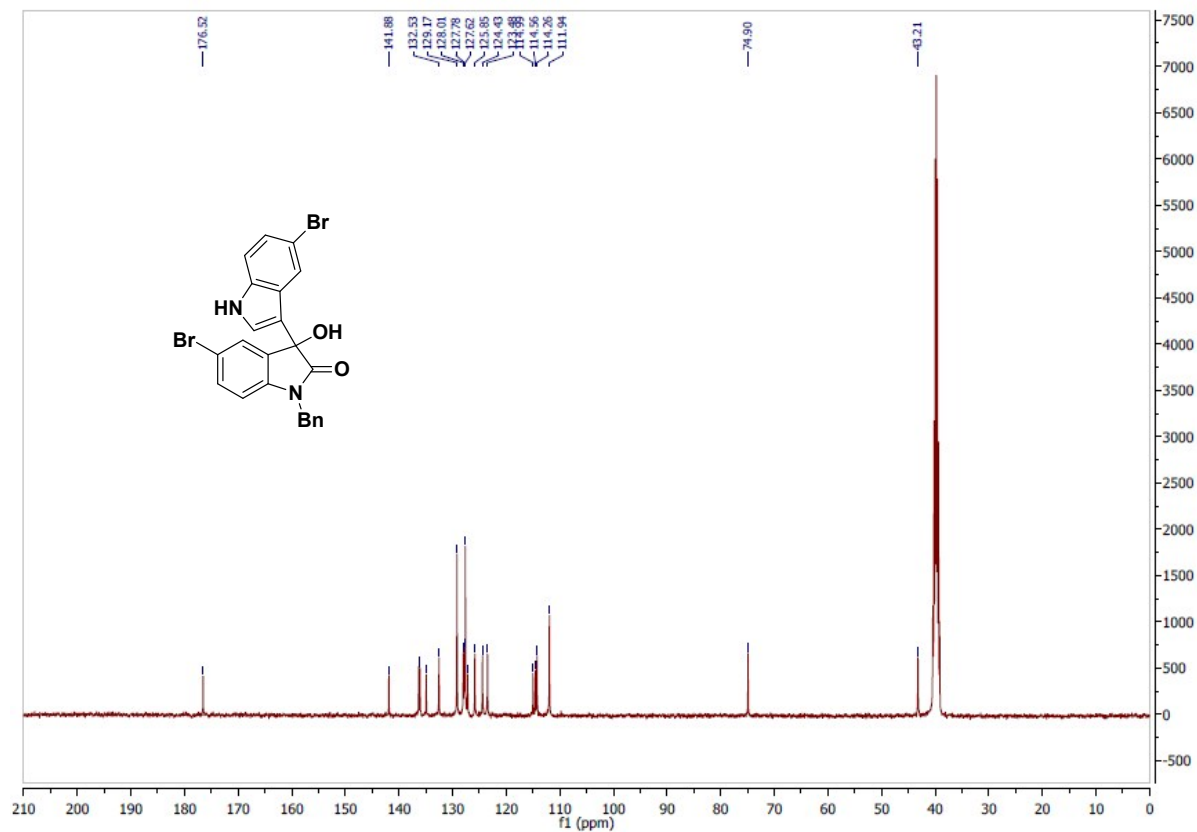
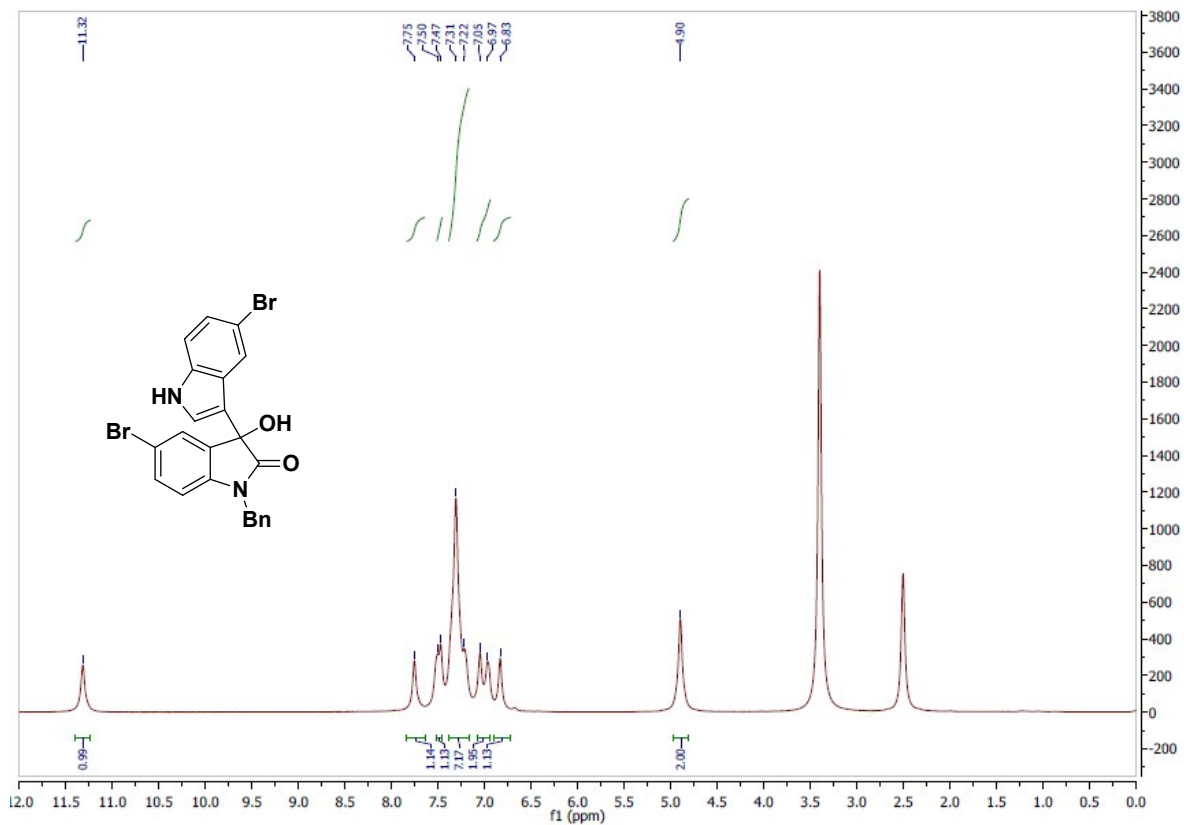


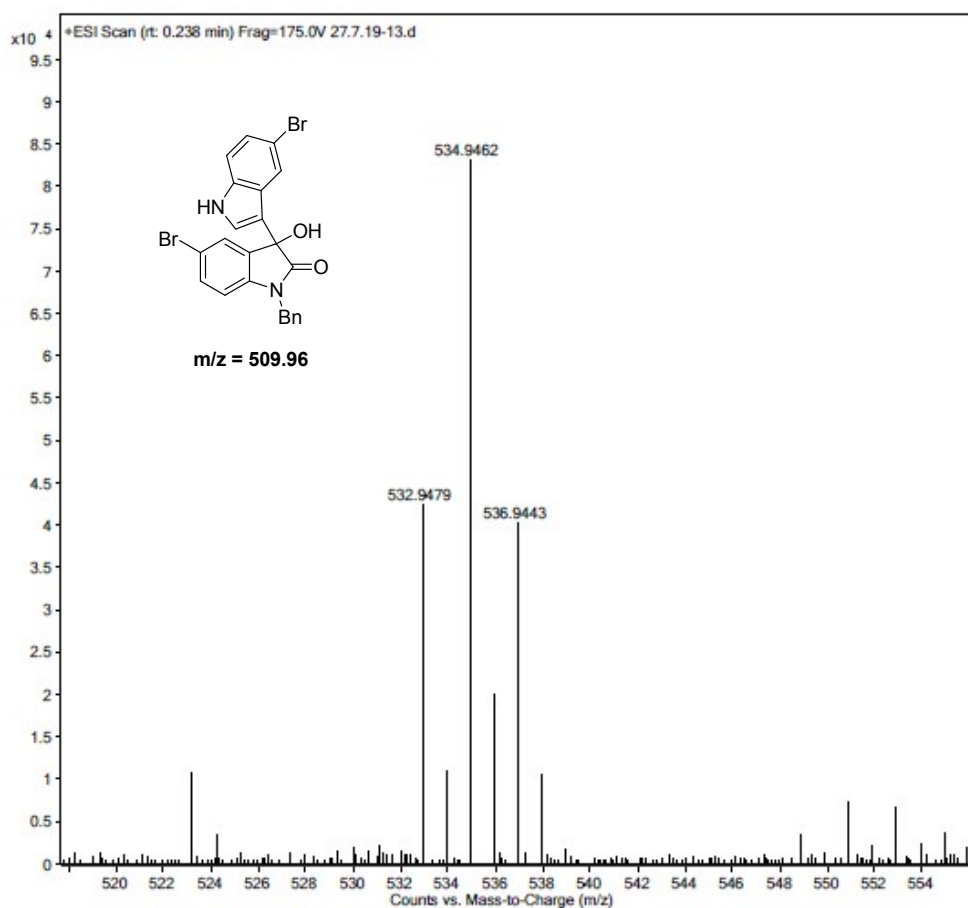
1-benzyl-3-(5-bromo-1H-indol-3-yl)-3-hydroxyindolin-2-one (15p):



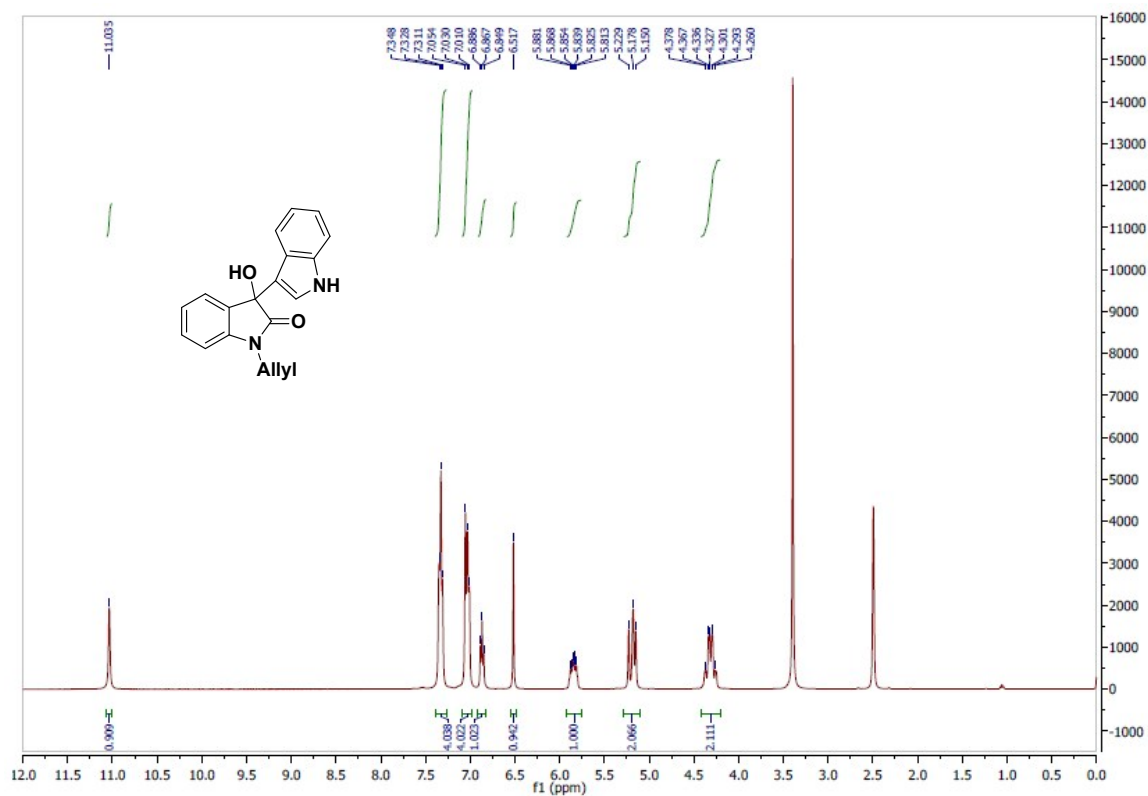


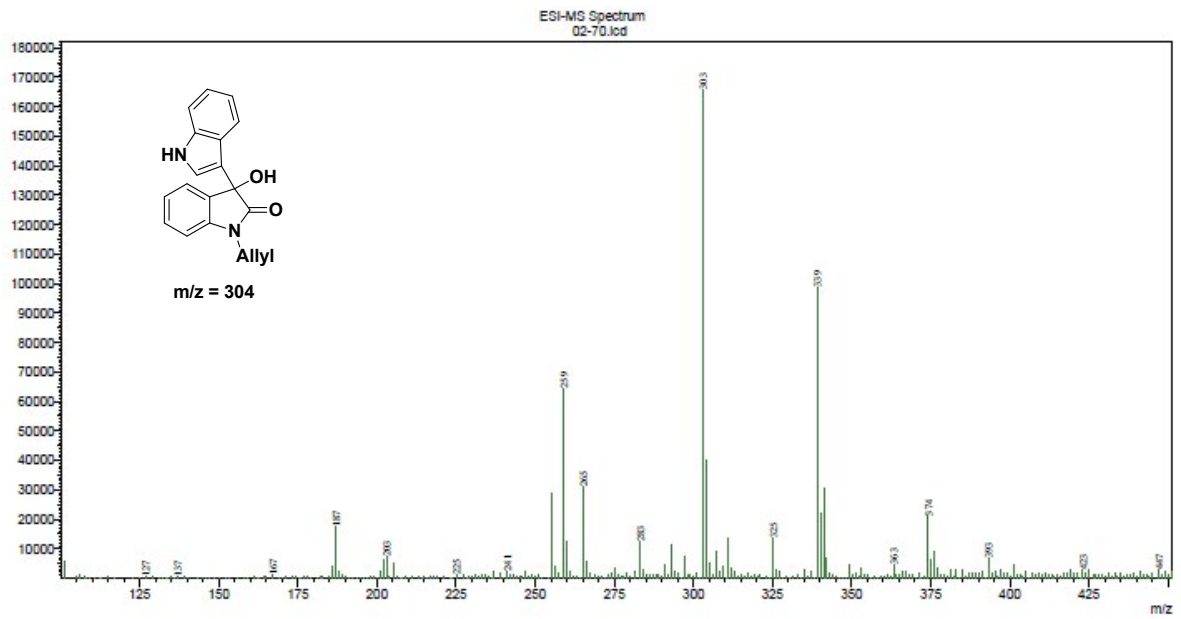
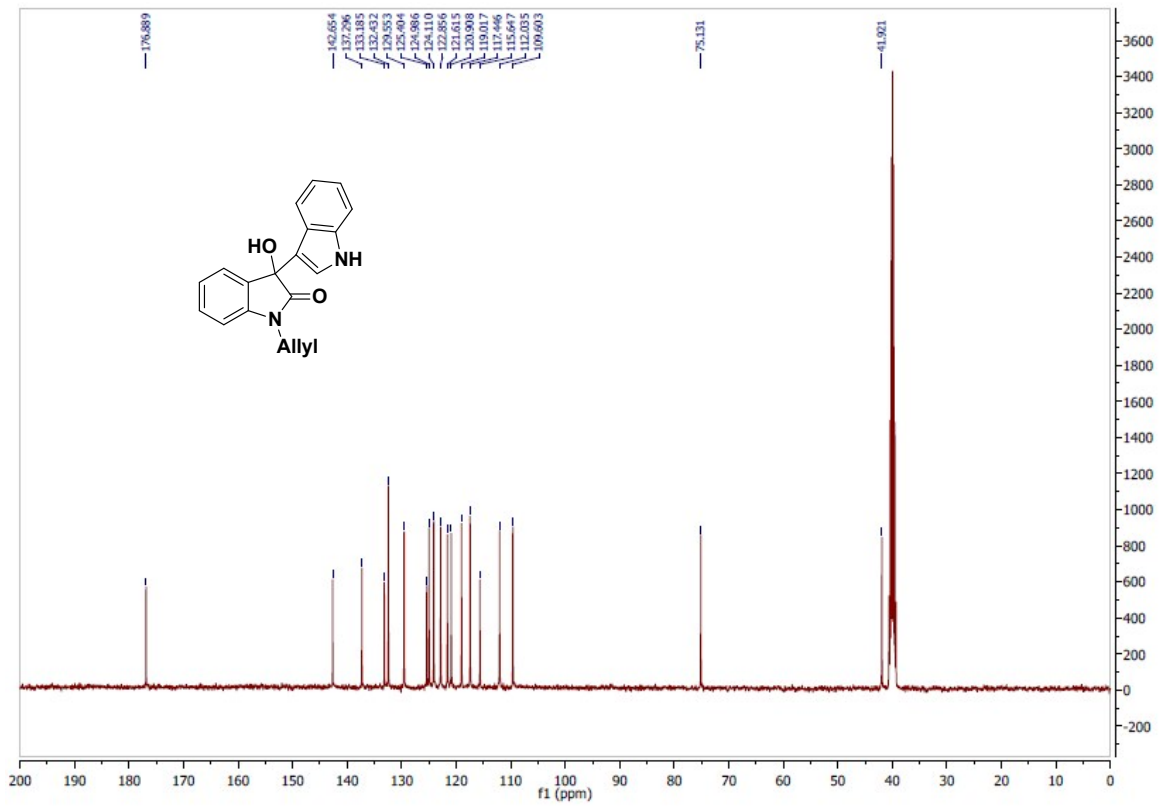
1-benzyl-5-bromo-3-hydroxy-3-(1H-indol-3-yl)indolin-2-one (15q):



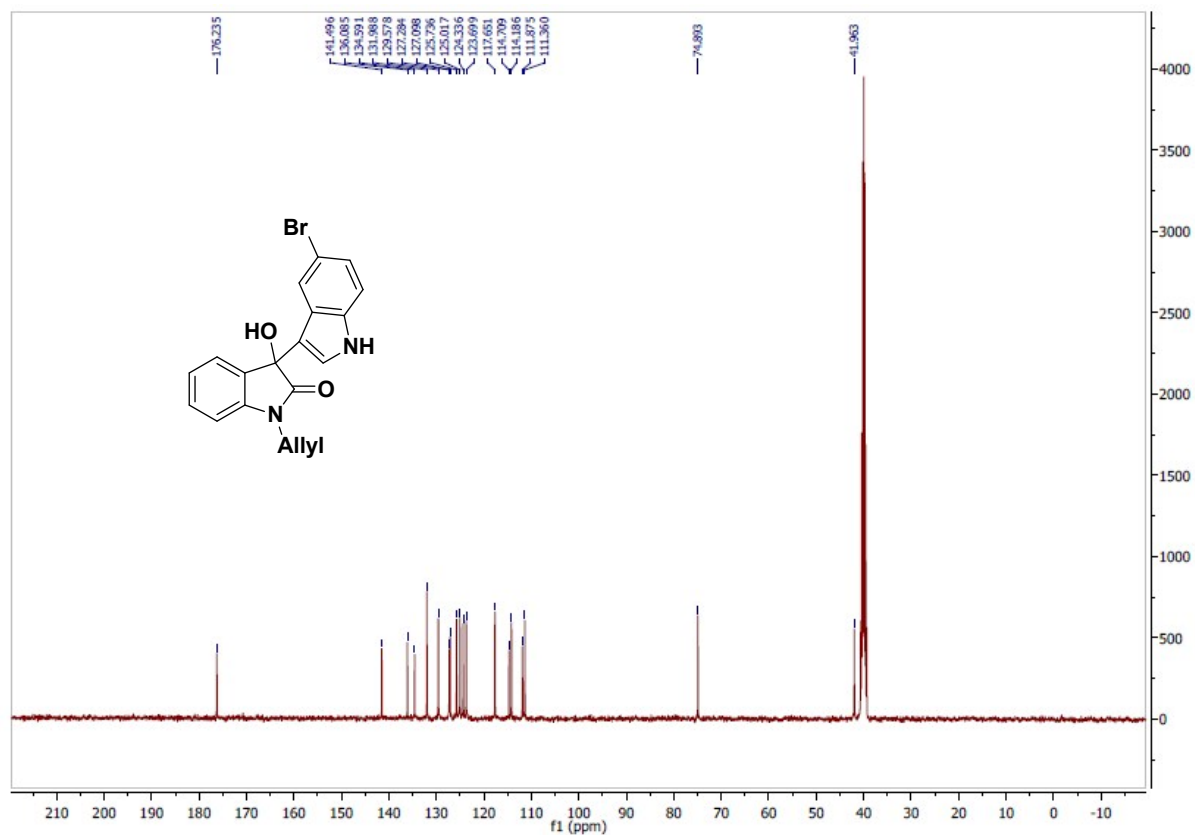
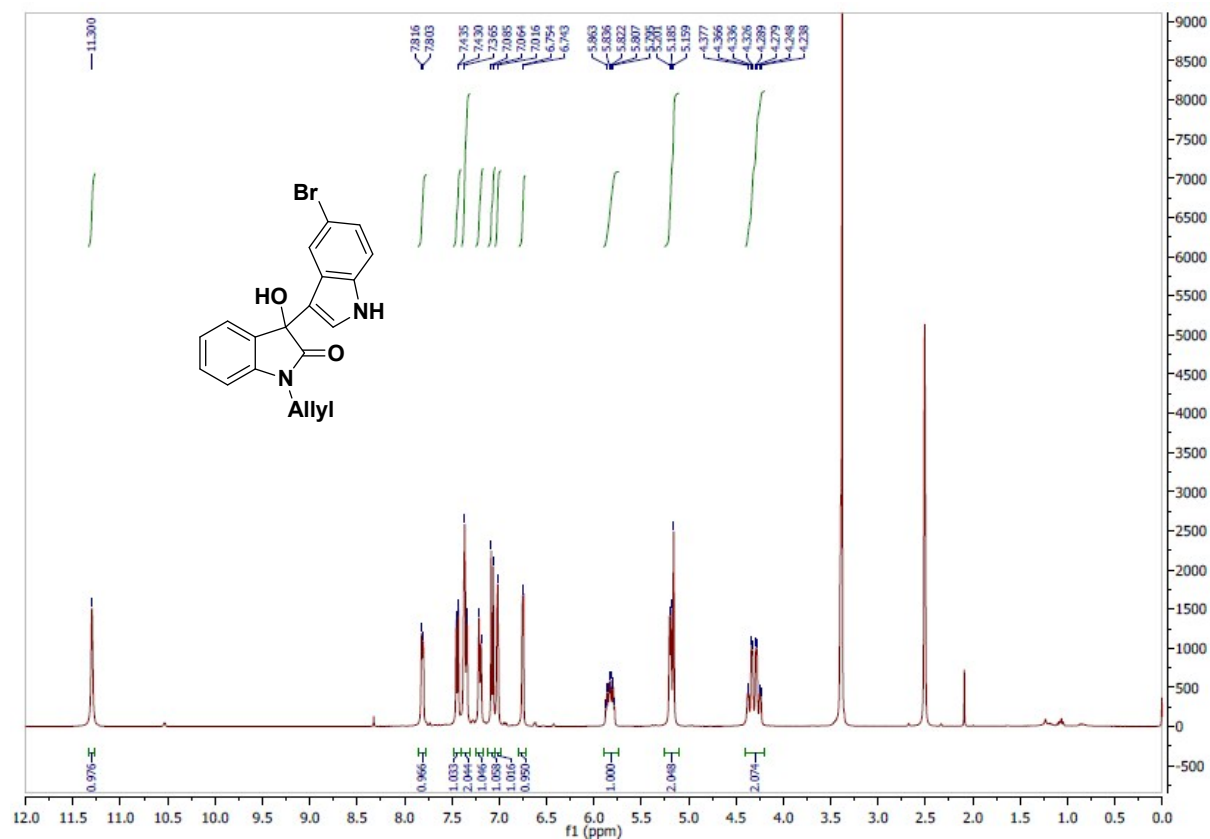


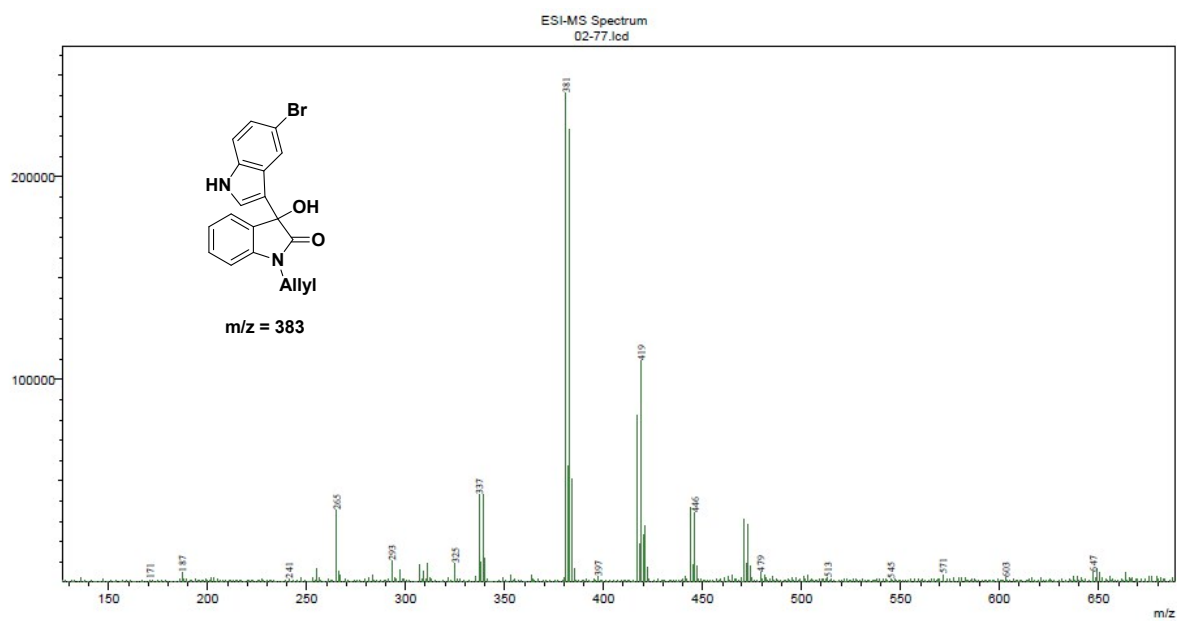
1-allyl-3-hydroxy-3-(1H-indol-3-yl)indolin-2-one (15r):



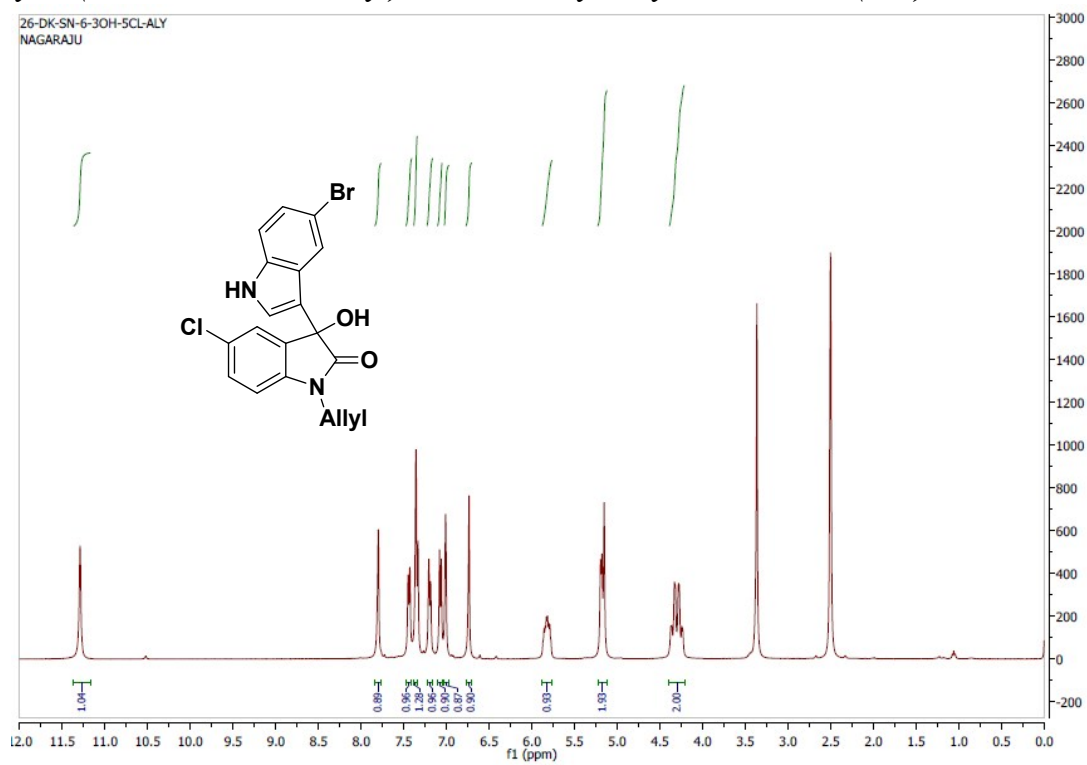


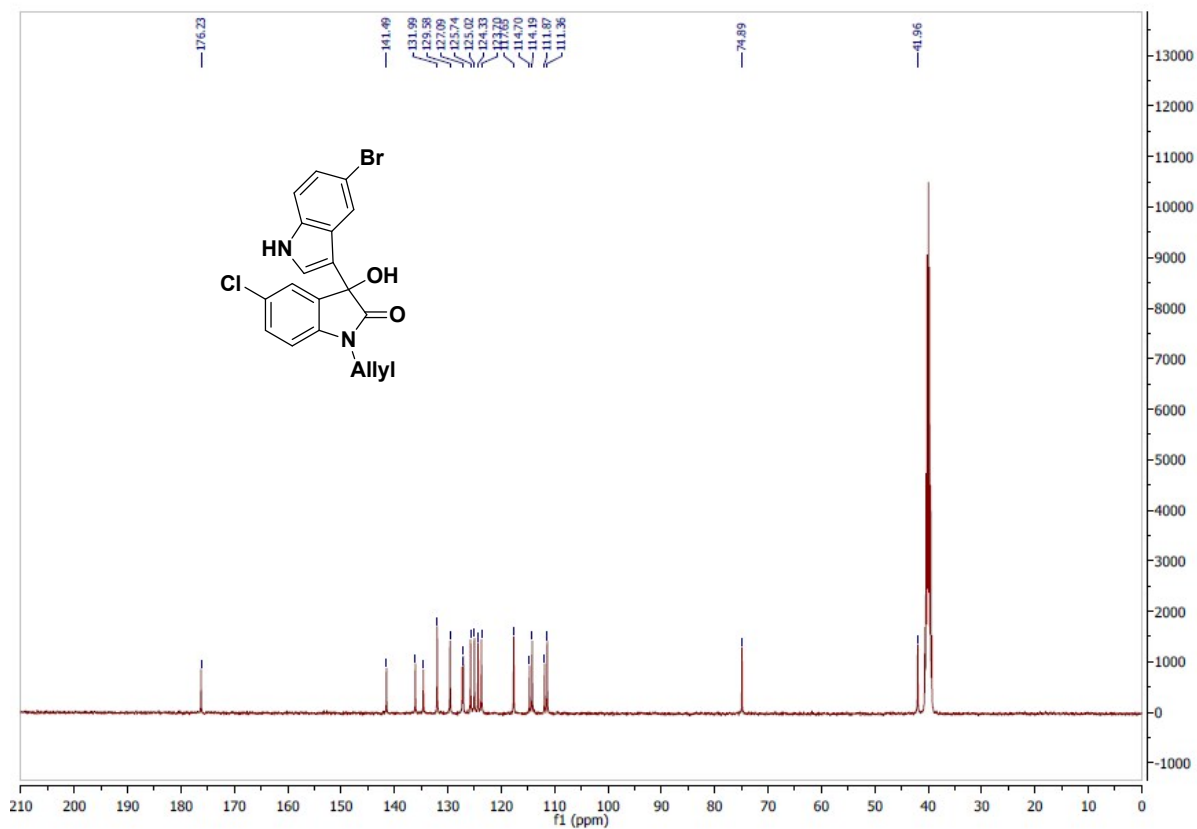
1-allyl-3-(5-bromo-1H-indol-3-yl)-3-hydroxyindolin-2-one (15t):



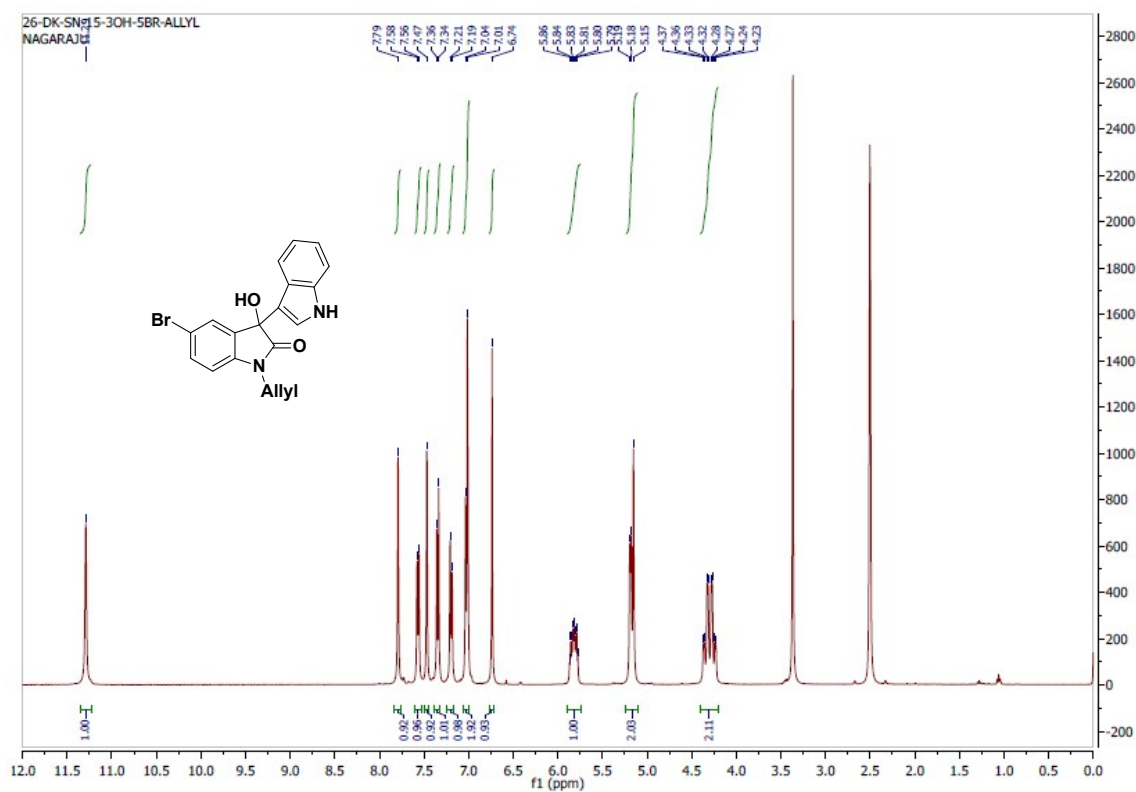


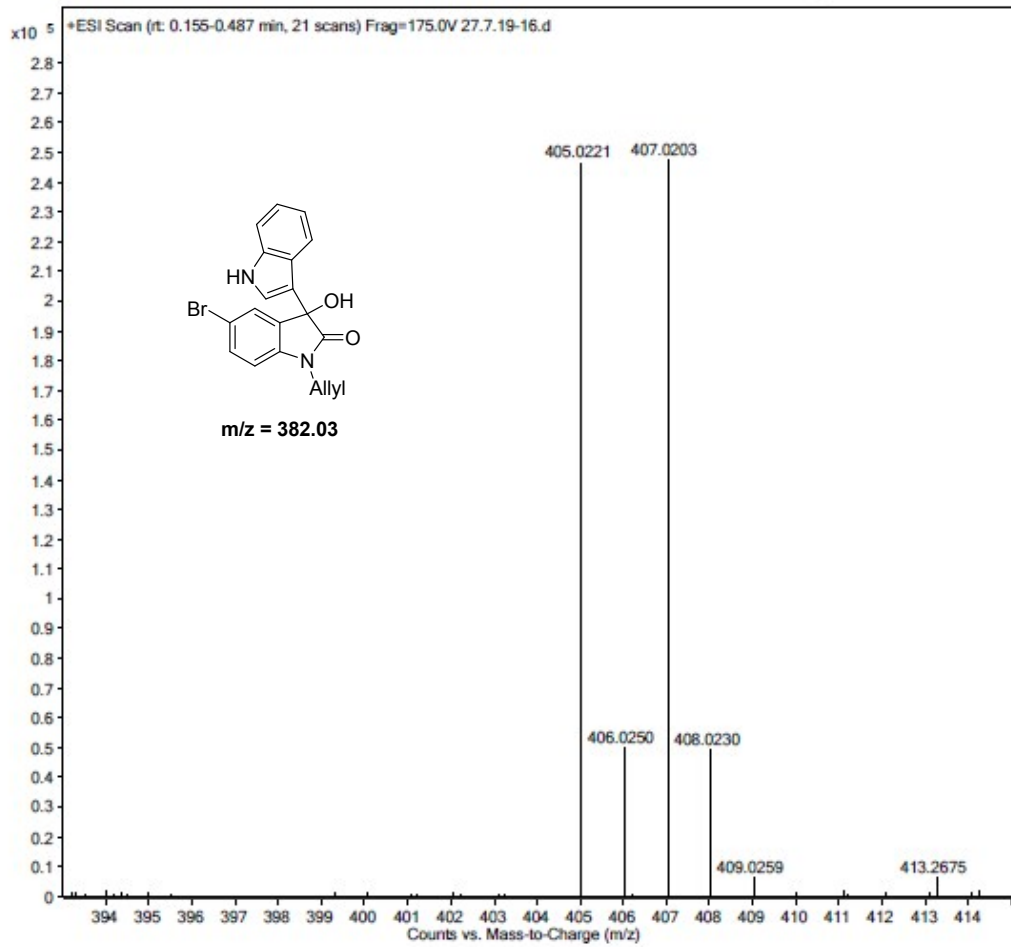
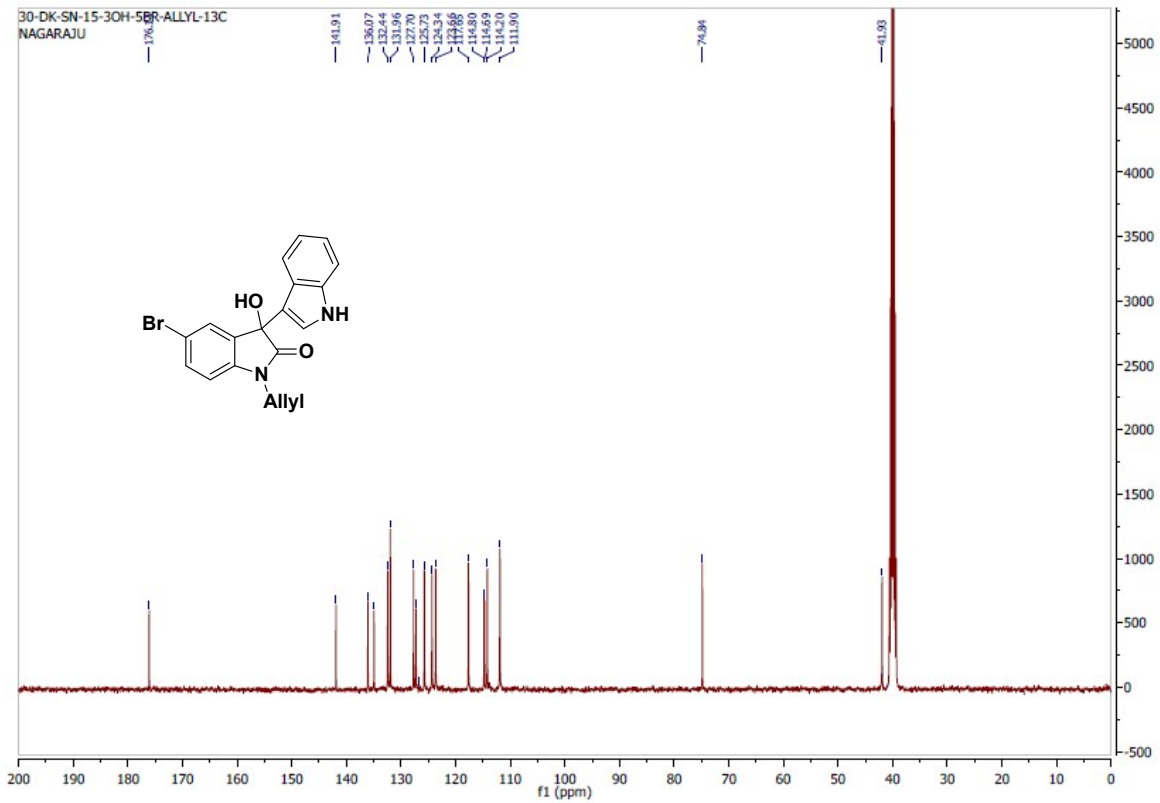
1-allyl-3-(5-bromo-1H-indol-3-yl)-5-chloro-3-hydroxyindolin-2-one (15u):



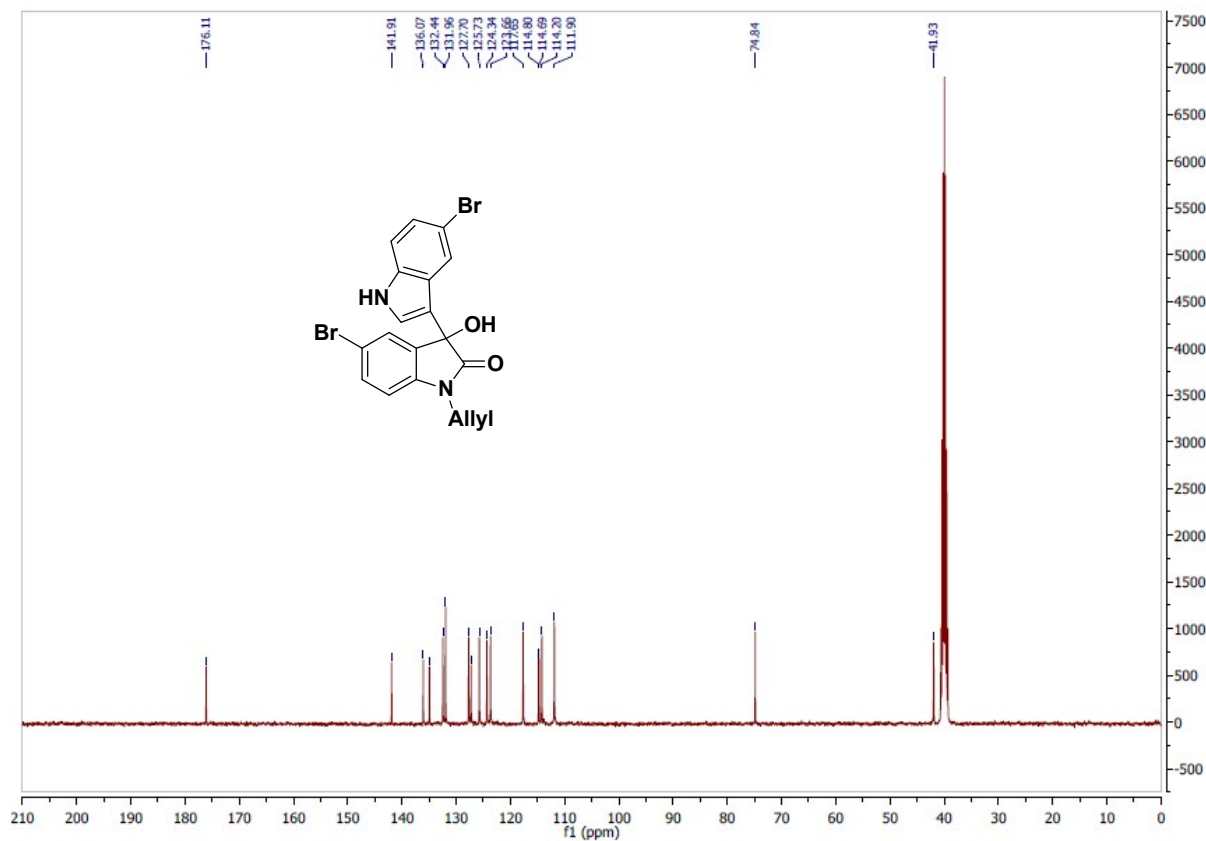
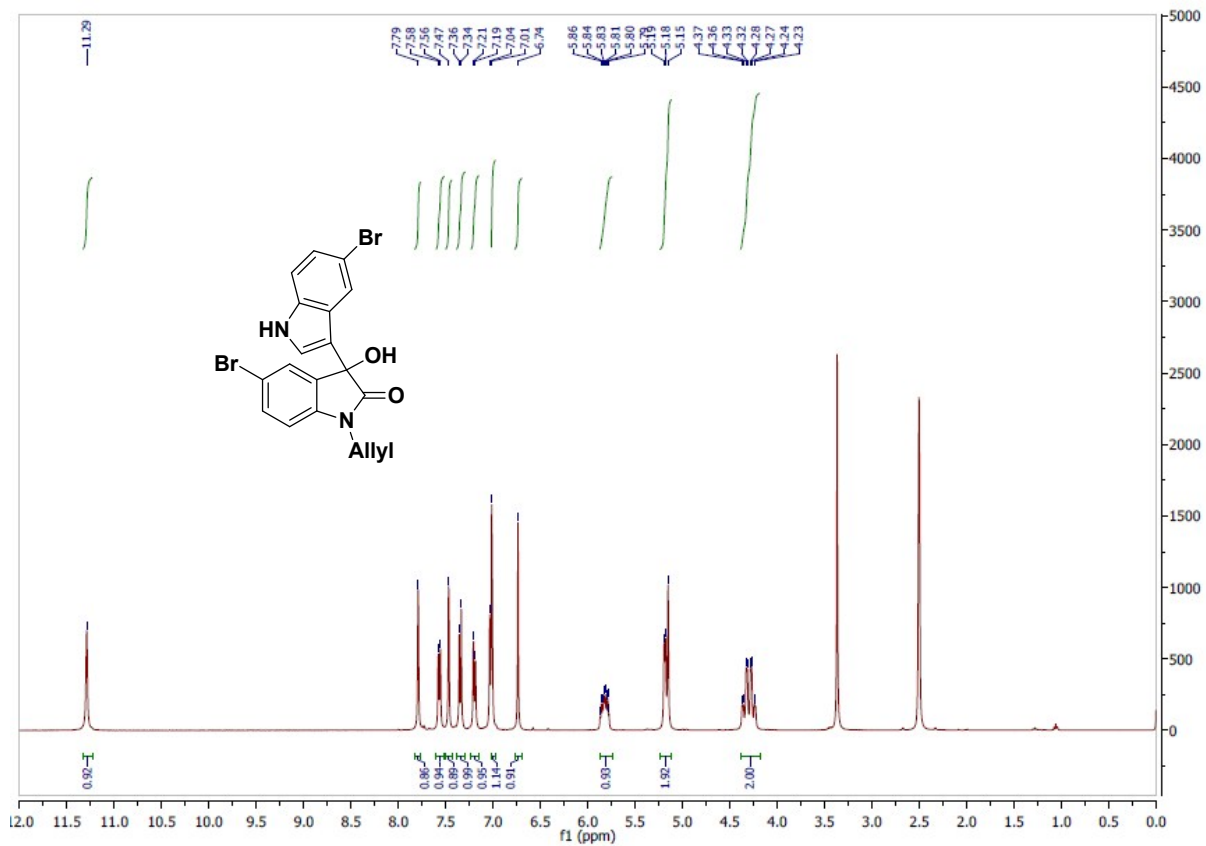


1-allyl-5-bromo-3-hydroxy-3-(1H-indol-3-yl)indolin-2-one (15v):

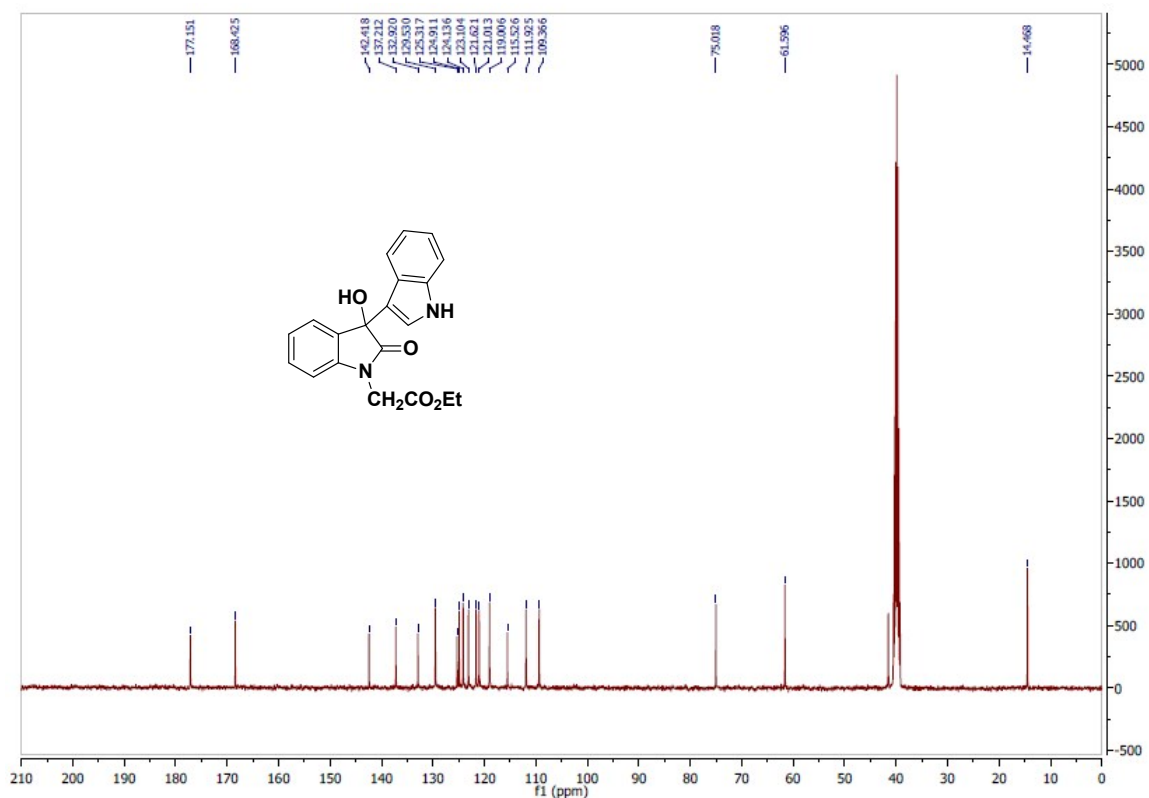
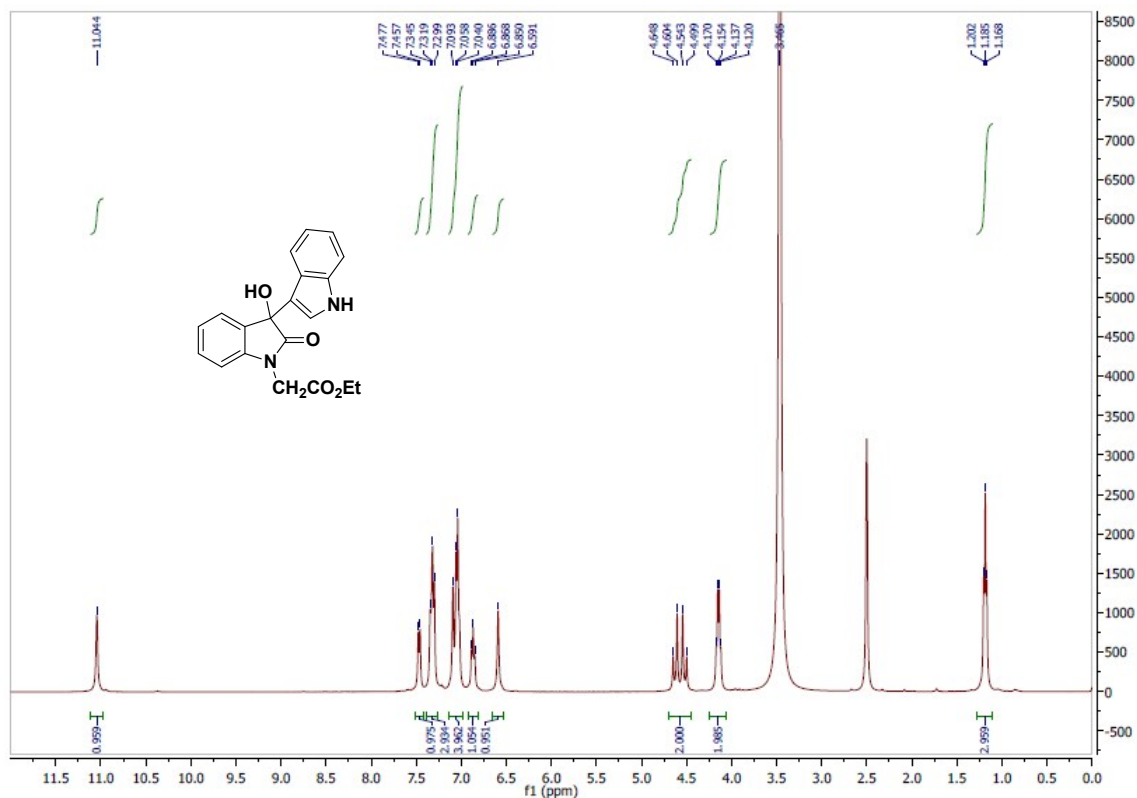


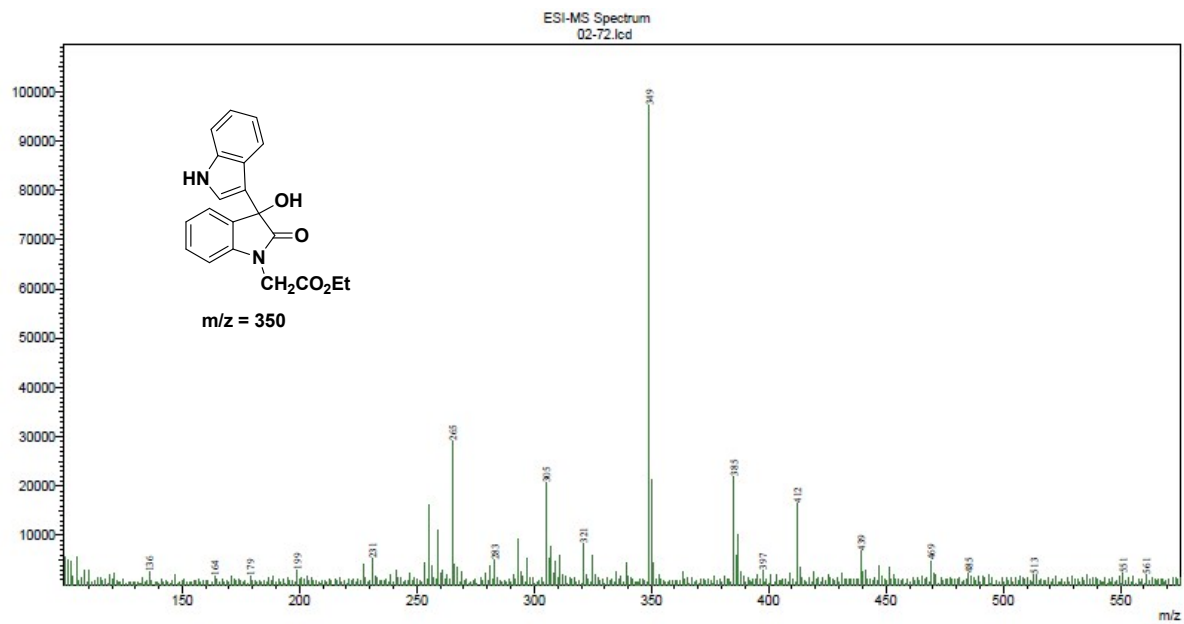


1-allyl-5-bromo-3-(5-bromo-1H-indol-3-yl)-3-hydroxyindolin-2-one (15w):

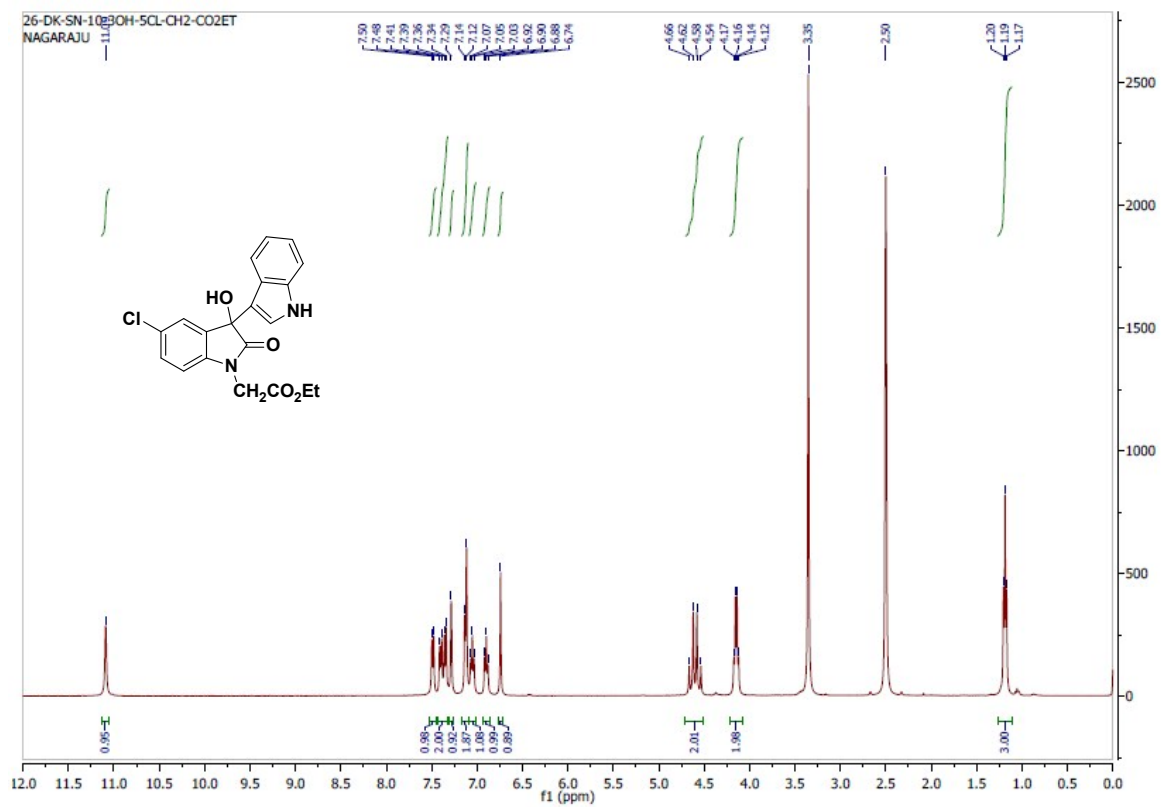


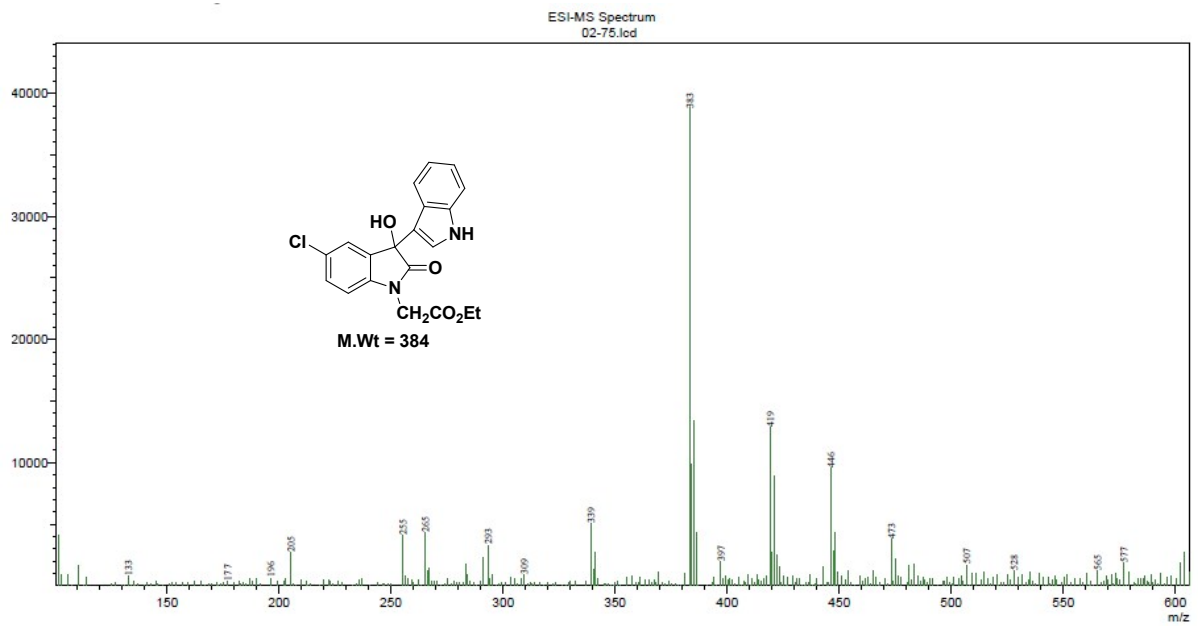
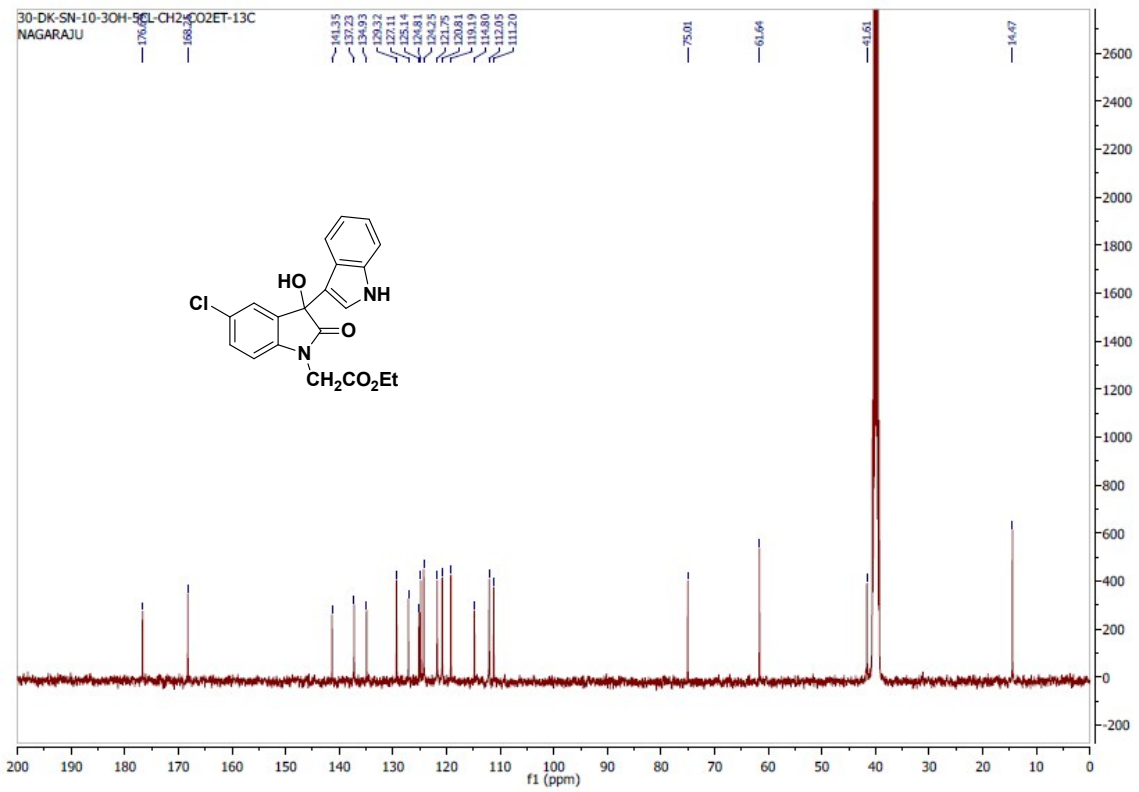
Ethyl 2-(3-hydroxy-3-(1H-indol-3-yl)-2-oxindolin-1-yl)acetate (15x):



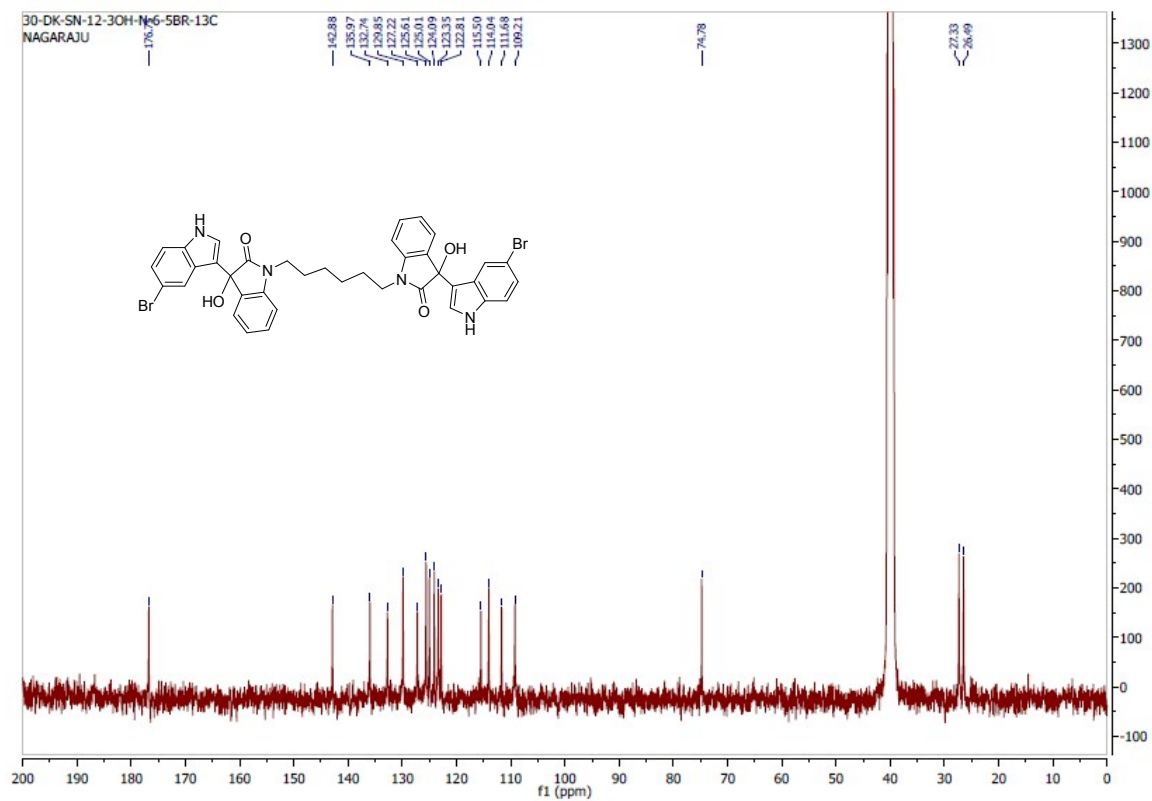
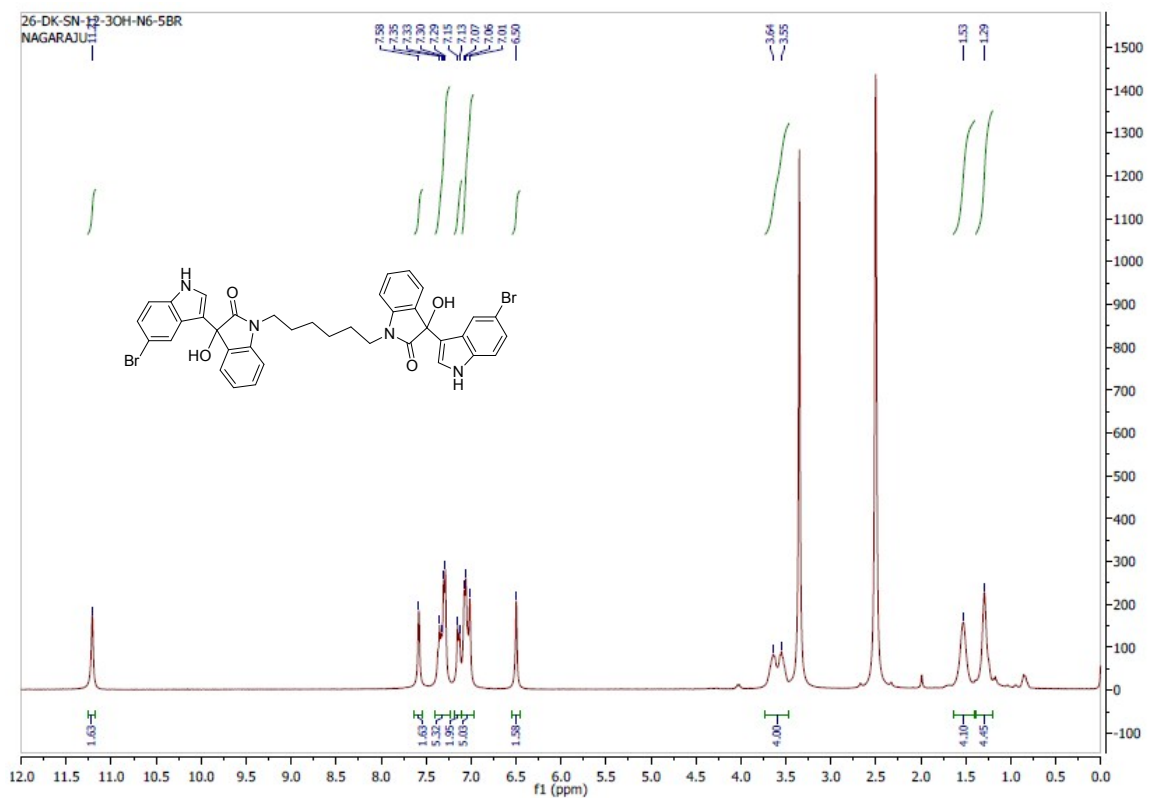


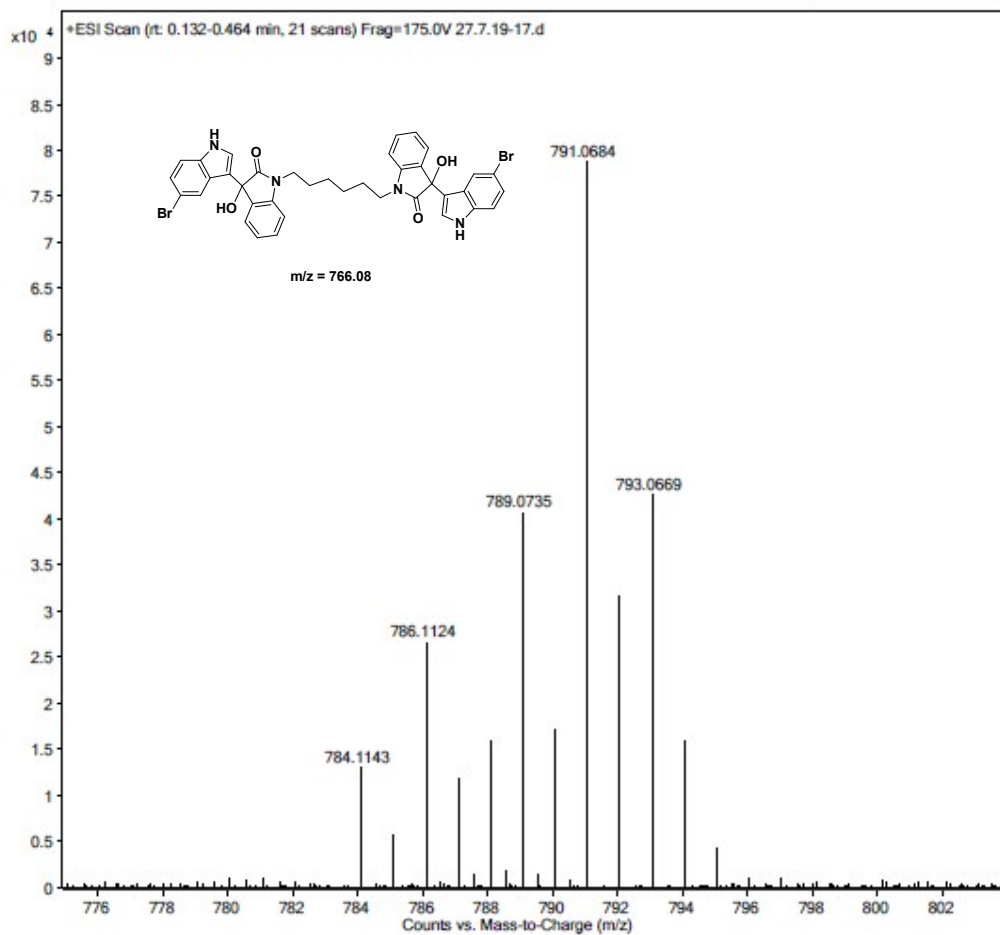
Ethyl 2-(5-chloro-3-hydroxy-3-(1H-indol-3-yl)-2-oxindolin-1-yl)acetate (15y):



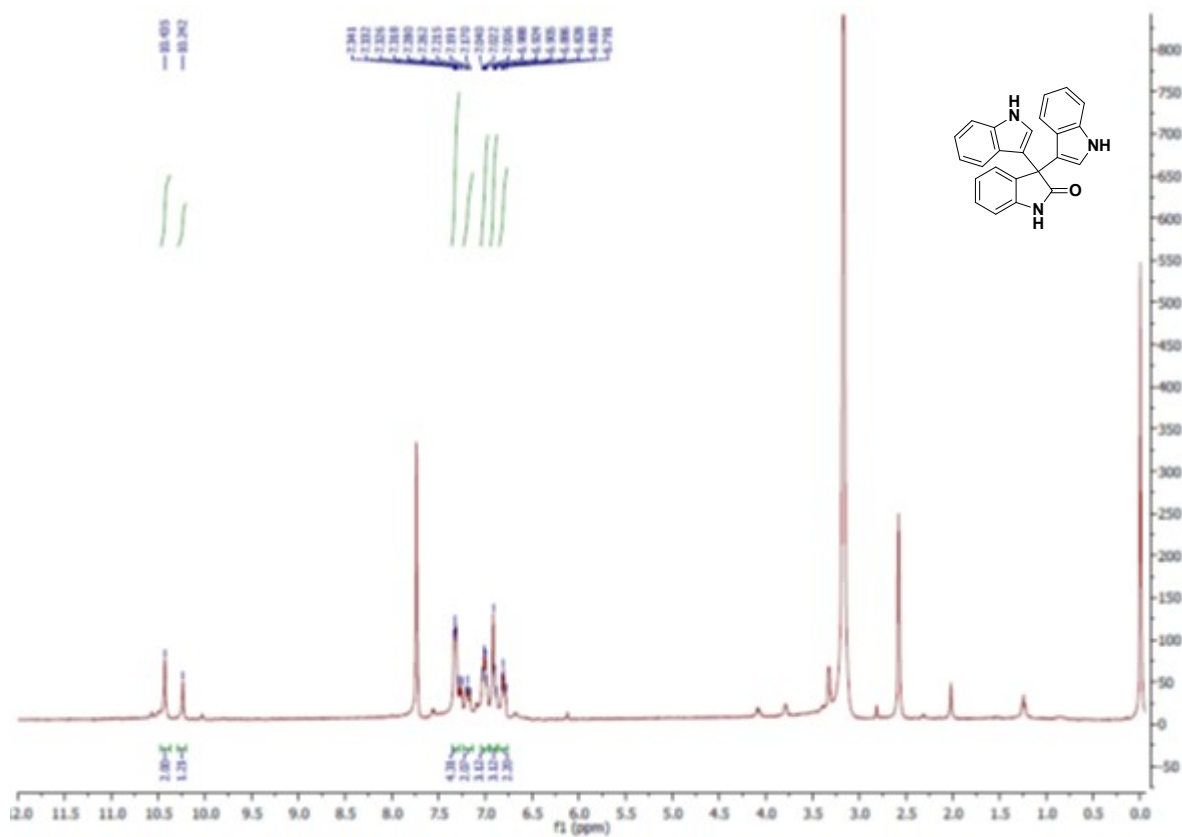


1,1'-(hexane-1,6-diyl)bis(3-(5-bromo-1H-indol-3-yl)-3-hydroxyindolin-2-one) (15z):

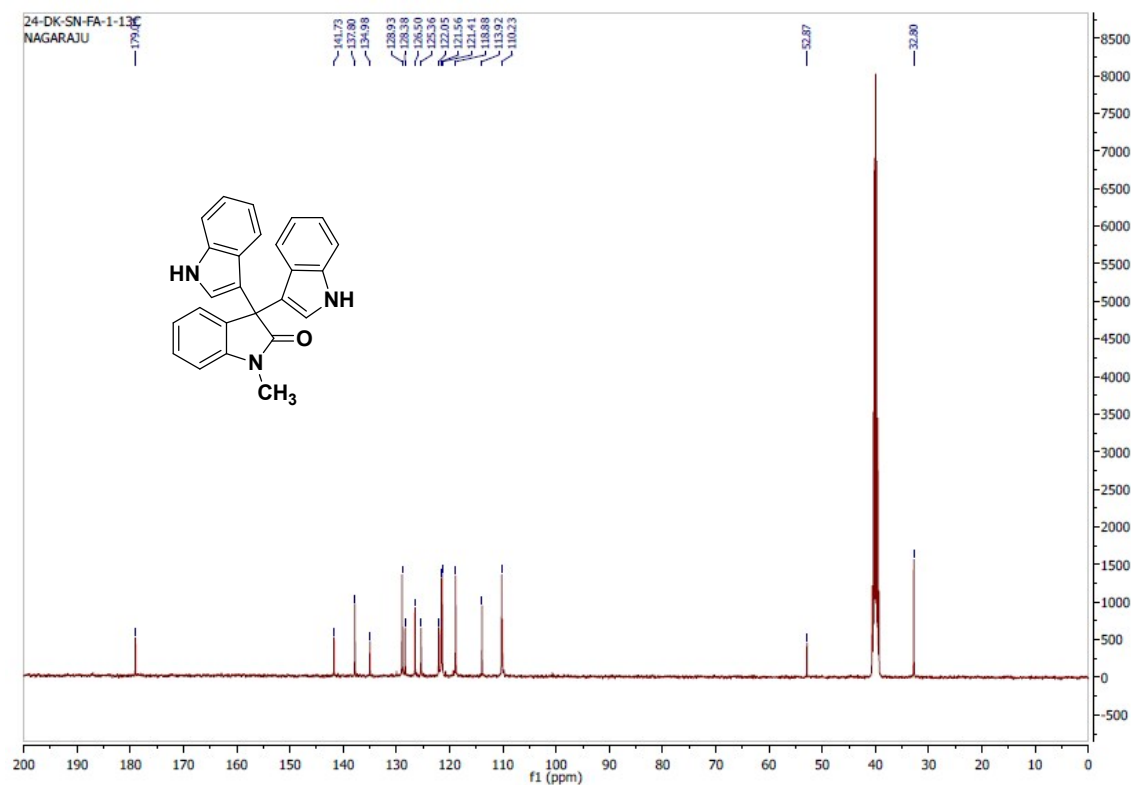
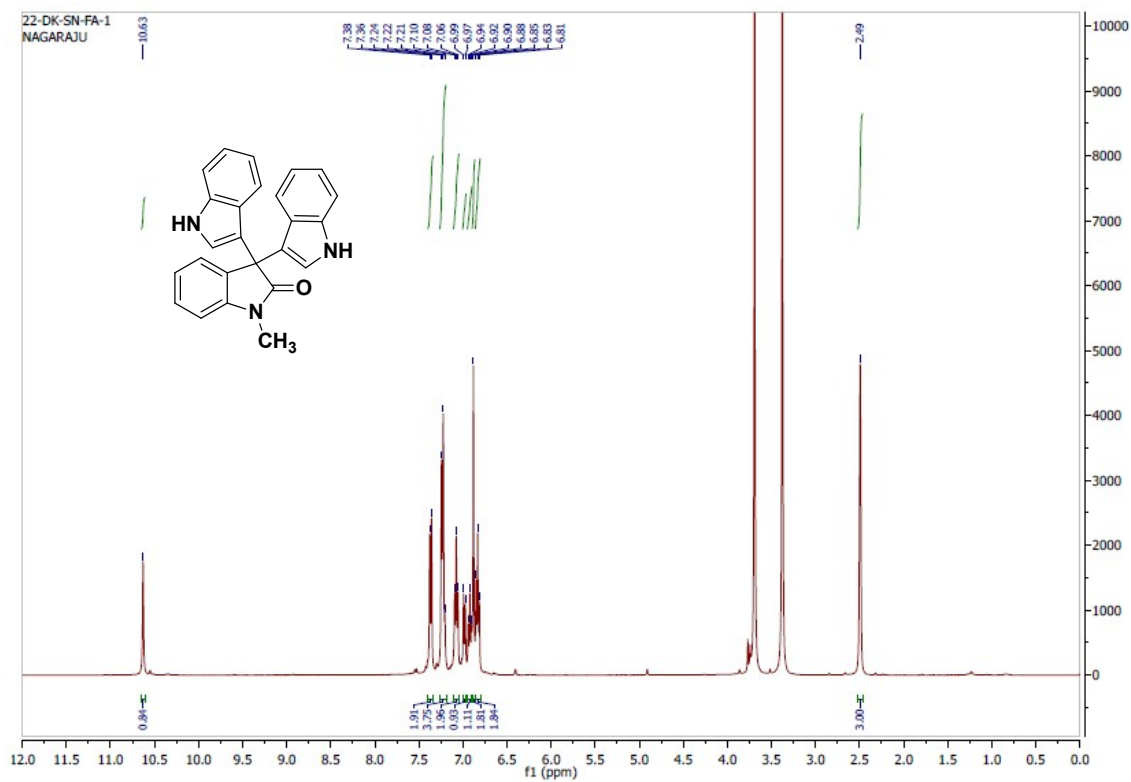




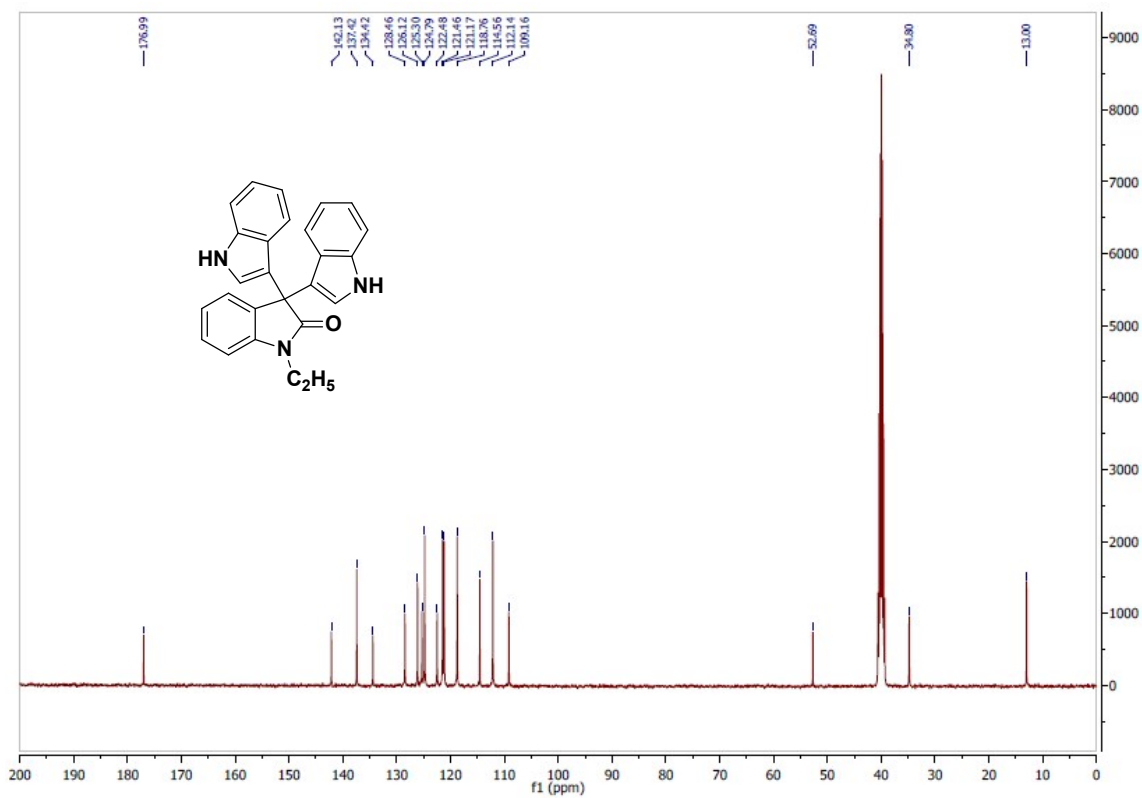
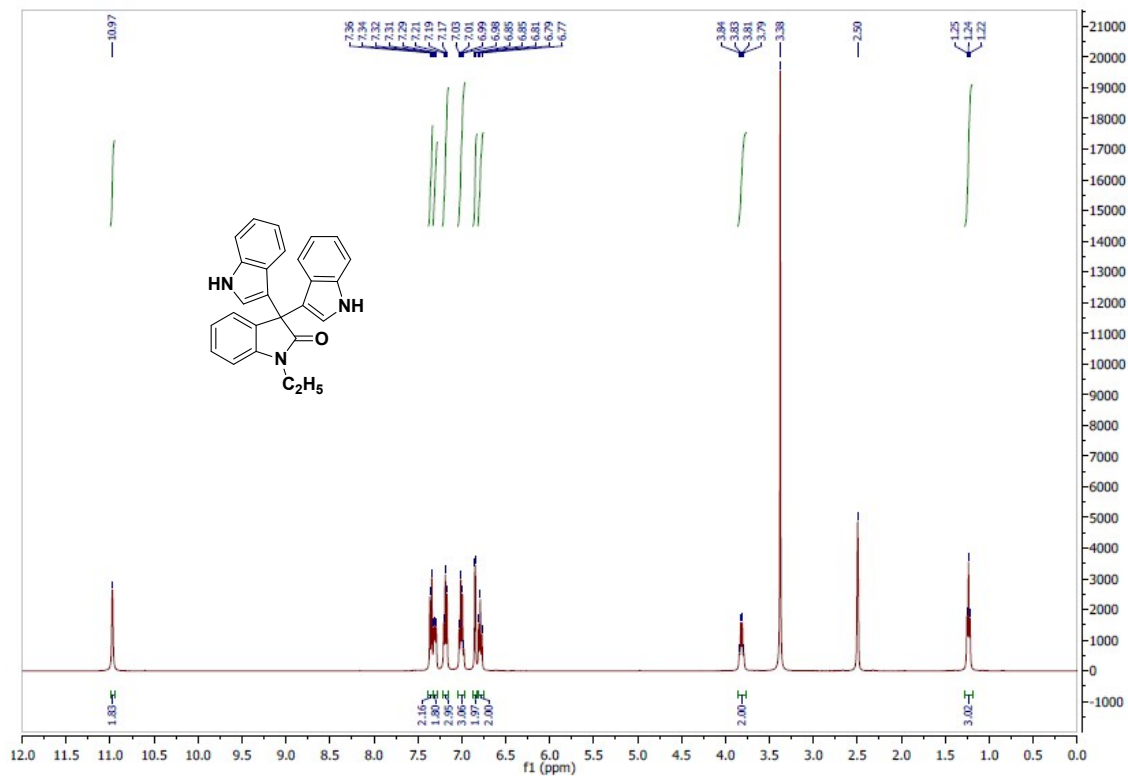
[3,3':3',3''-terindolin]-2'-one (16b)



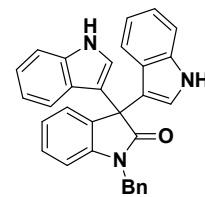
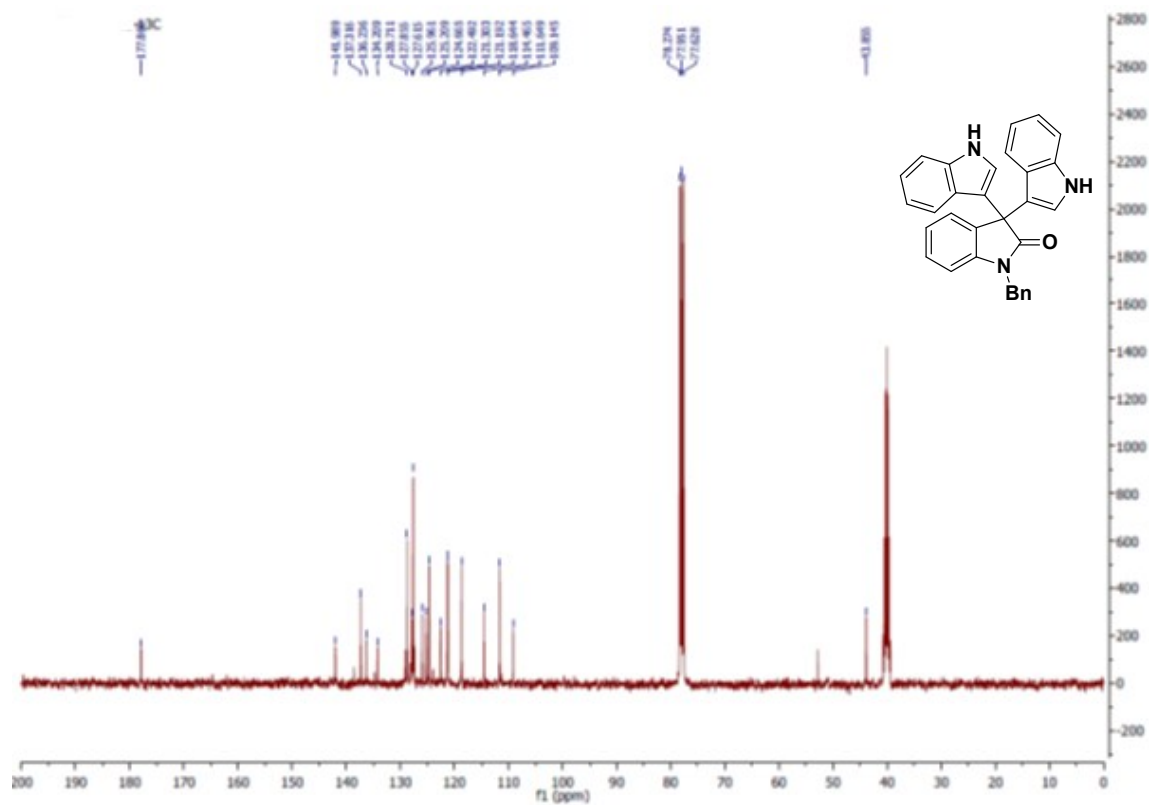
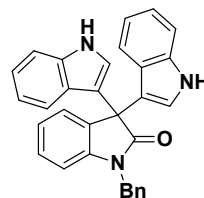
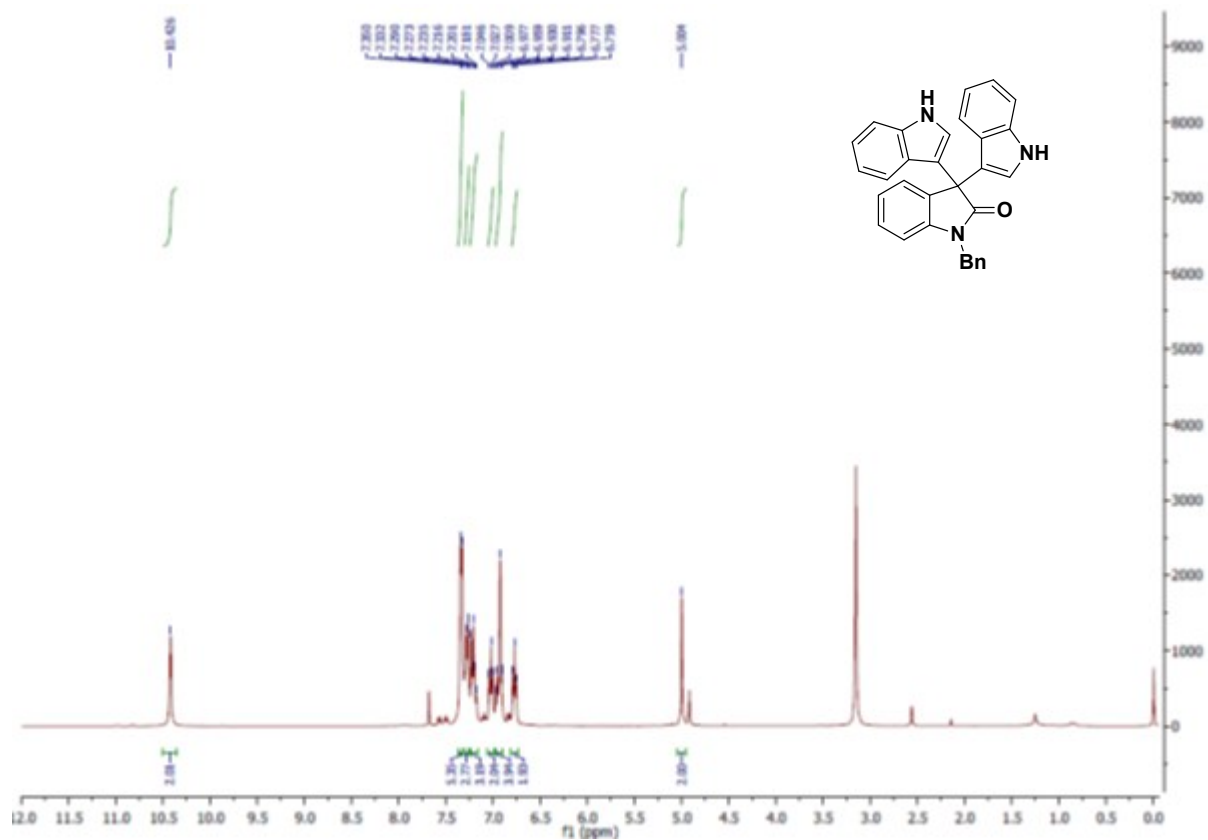
1'-methyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (16c):



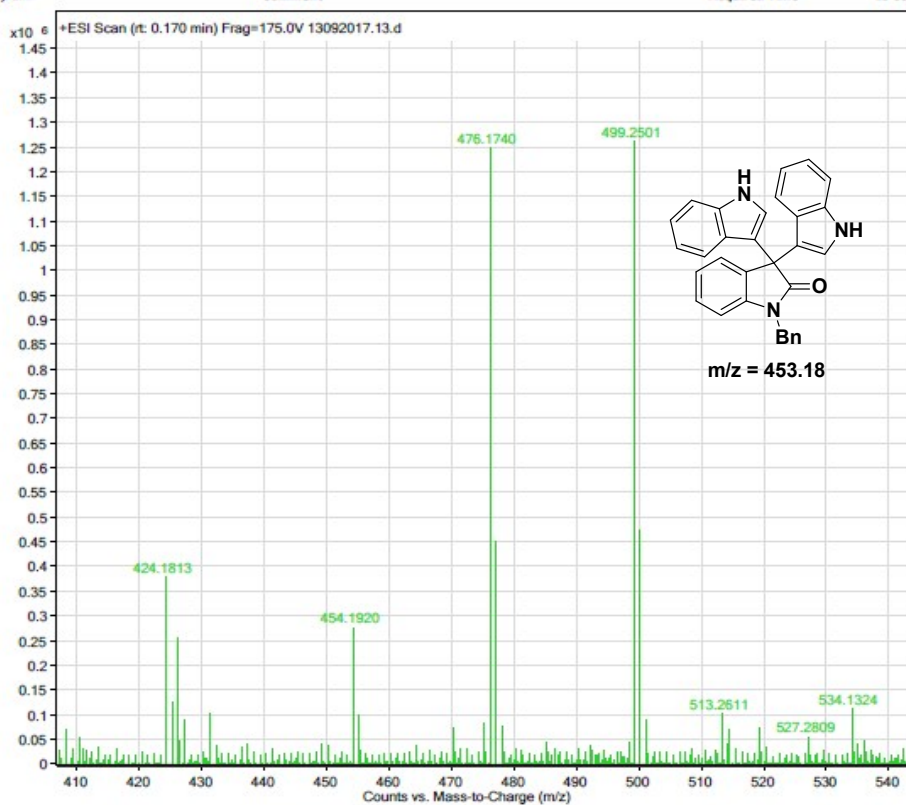
1'-ethyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (16d):



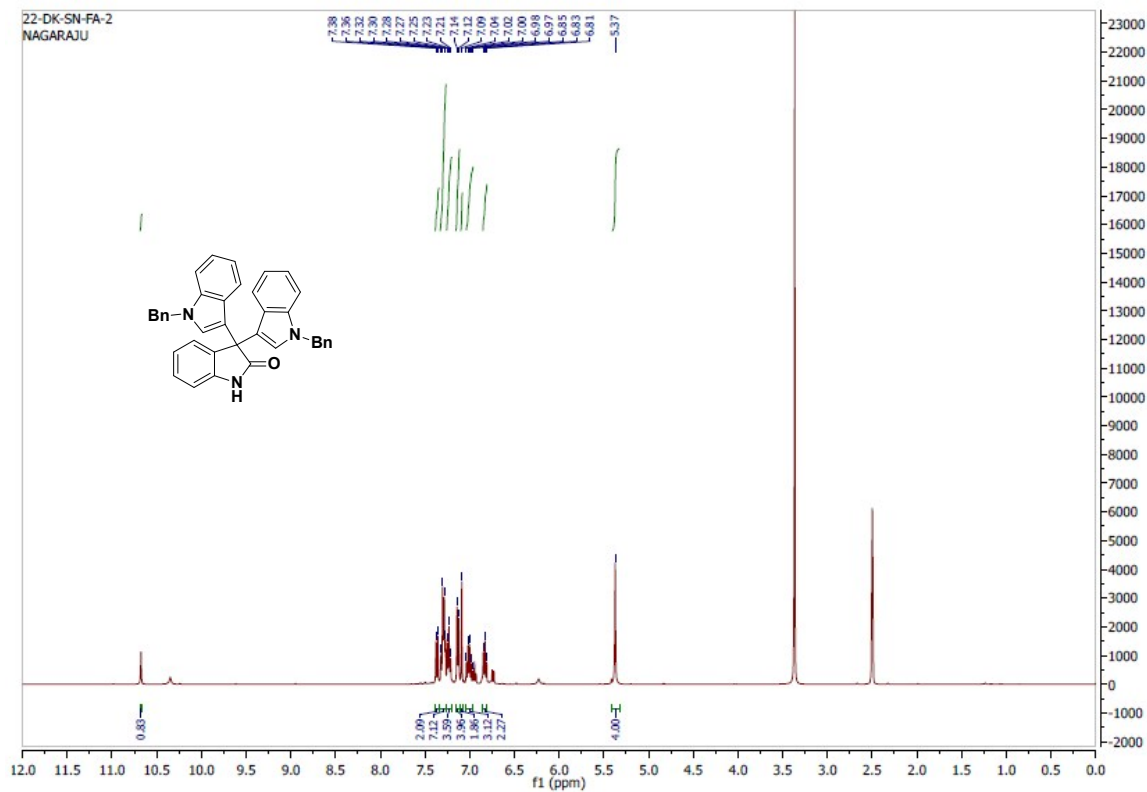
1'-benzyl-[3,3':3',3''-terindolin]-2'-one(16e)

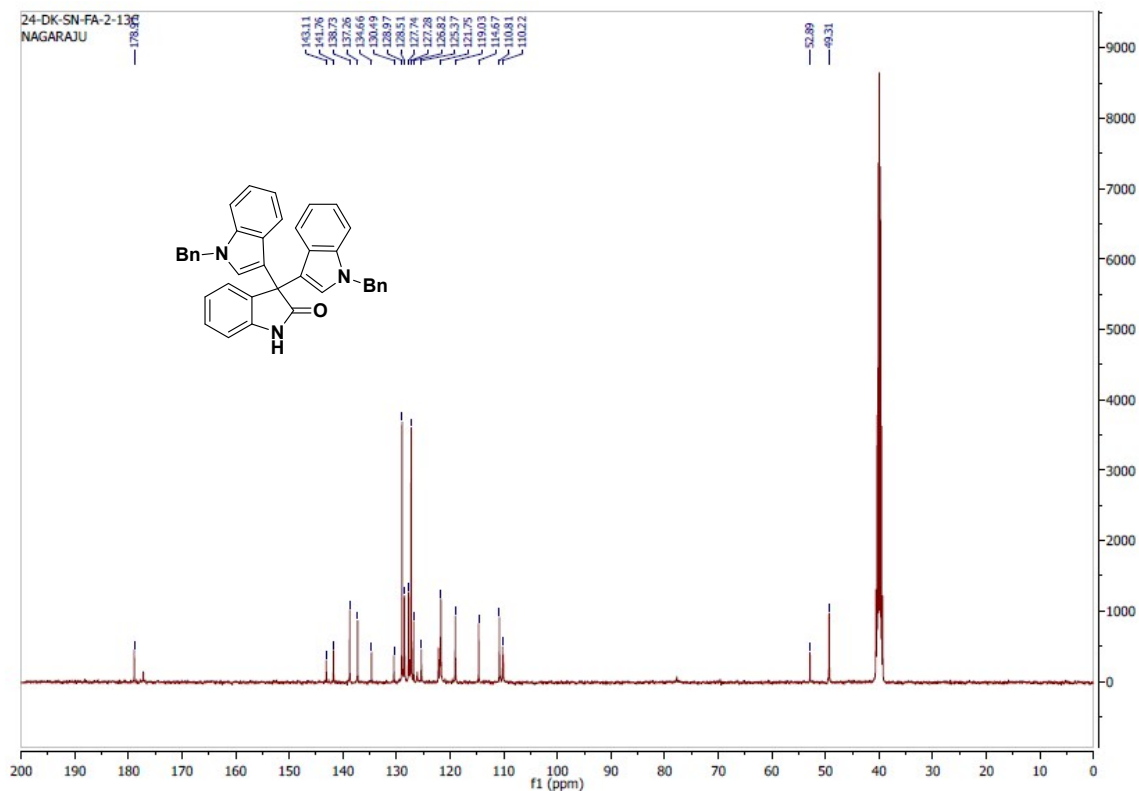


Sample Name	548	Position	P1-A9	Instrument Name	Instrument 1
User Name		Inj Vol	1	InjPosition	
Sample Type	Sample	IRM Calibration Status	Success	Data Filename	13092017.13.d
ACQ Method	babji 2.m	Comment		Acquired Time	13-Sep-17 5:30:30 PM

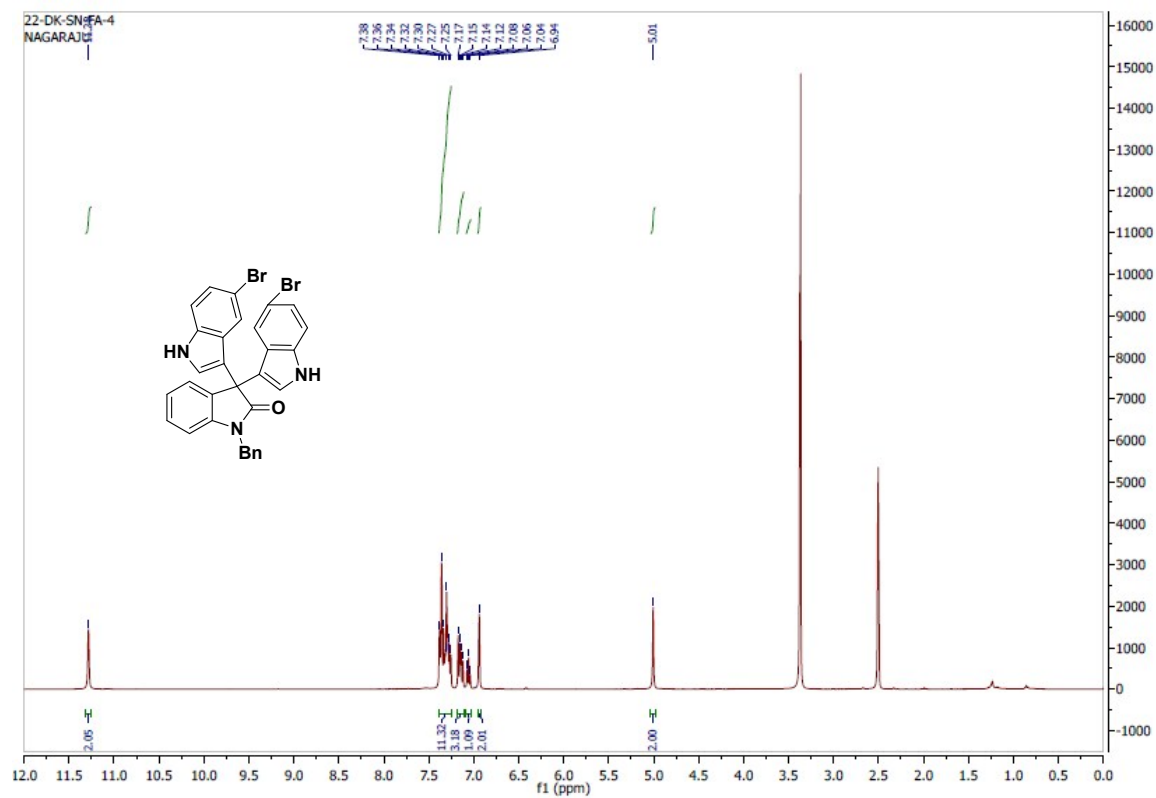


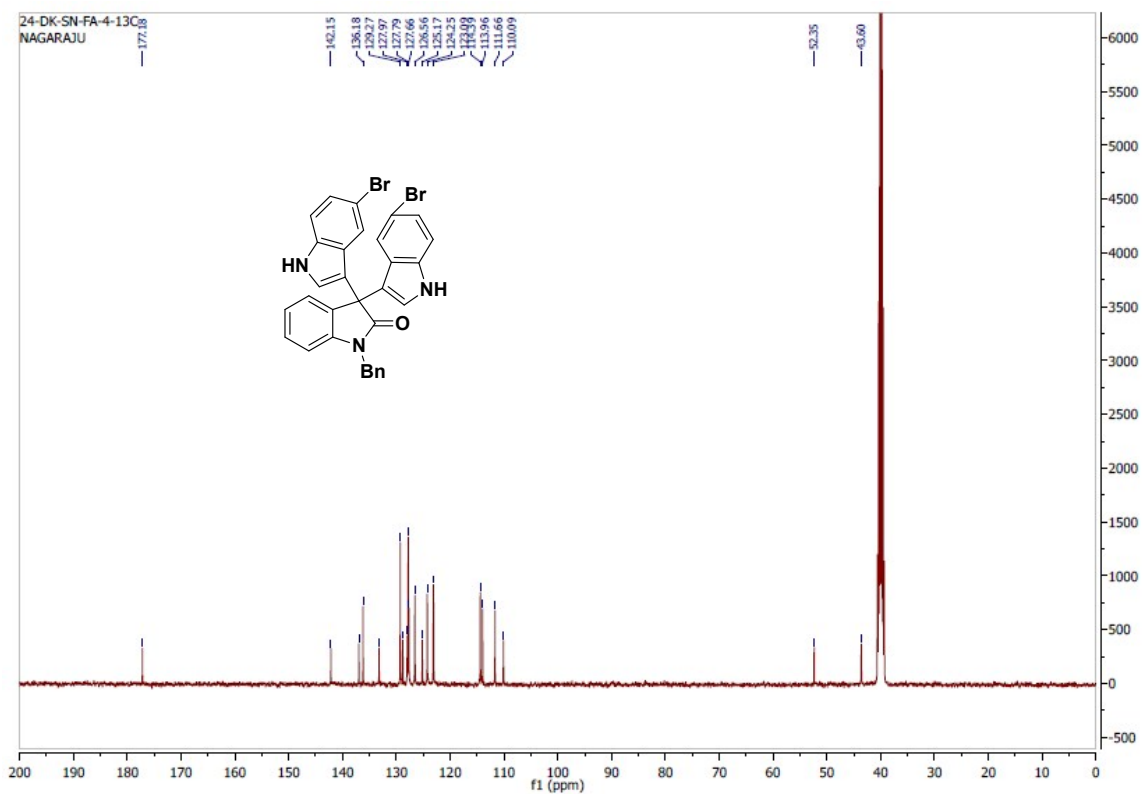
1,1''-dibenzyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (16f):



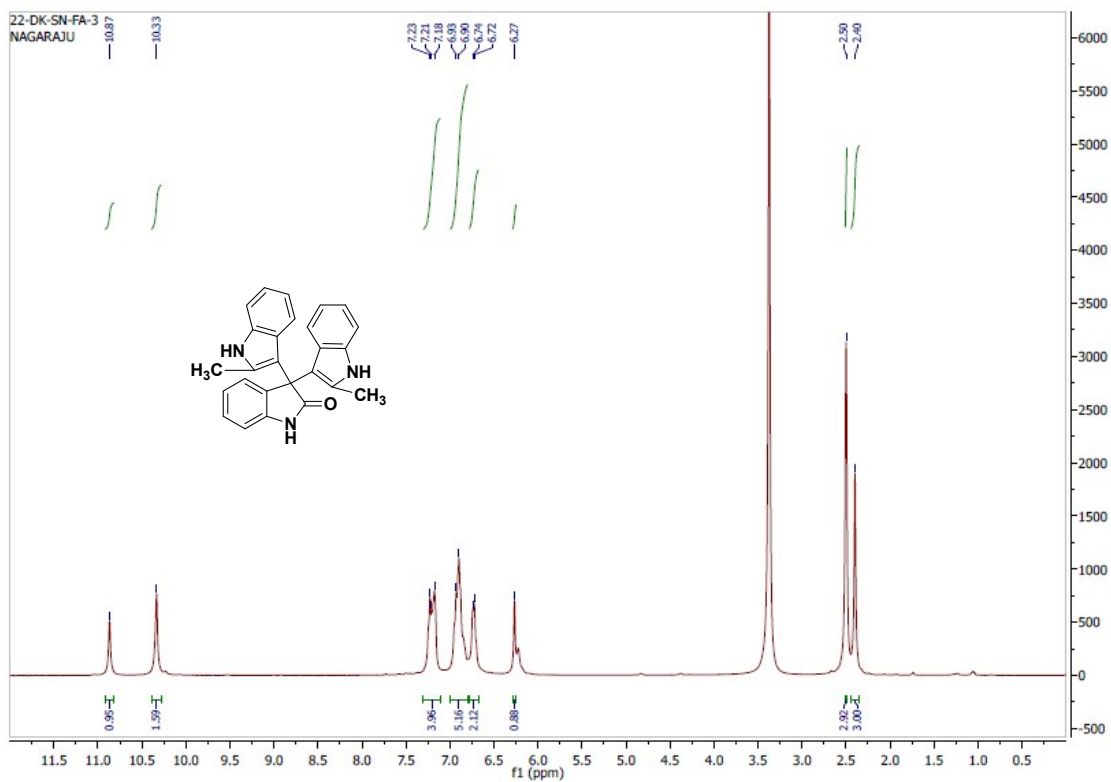


1'-benzyl-5,5''-dibromo-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (16h):

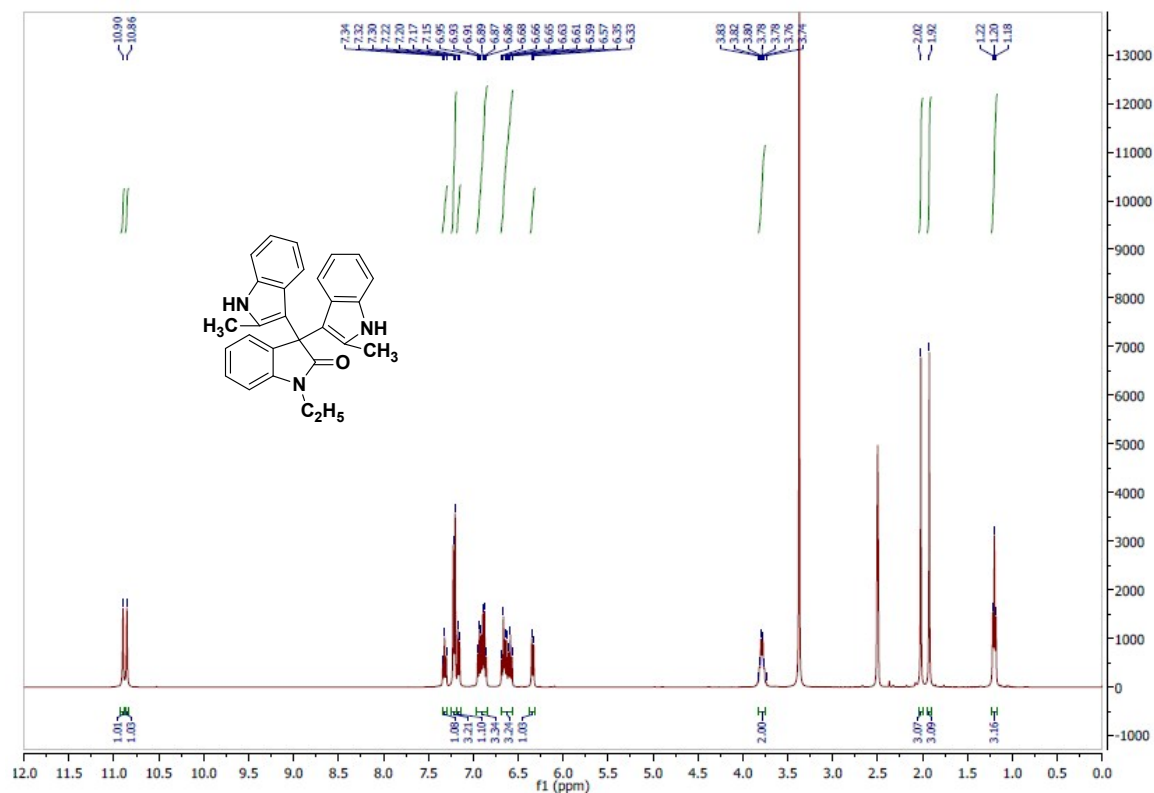




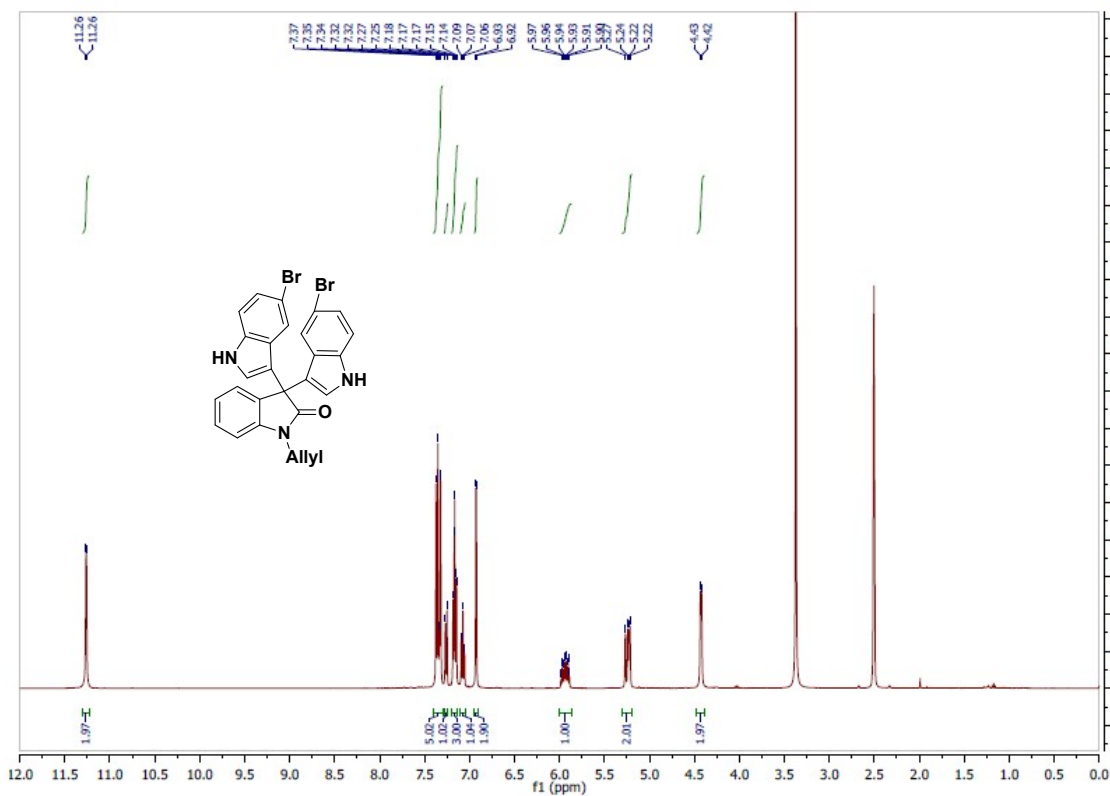
2,2''-dimethyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (16i):

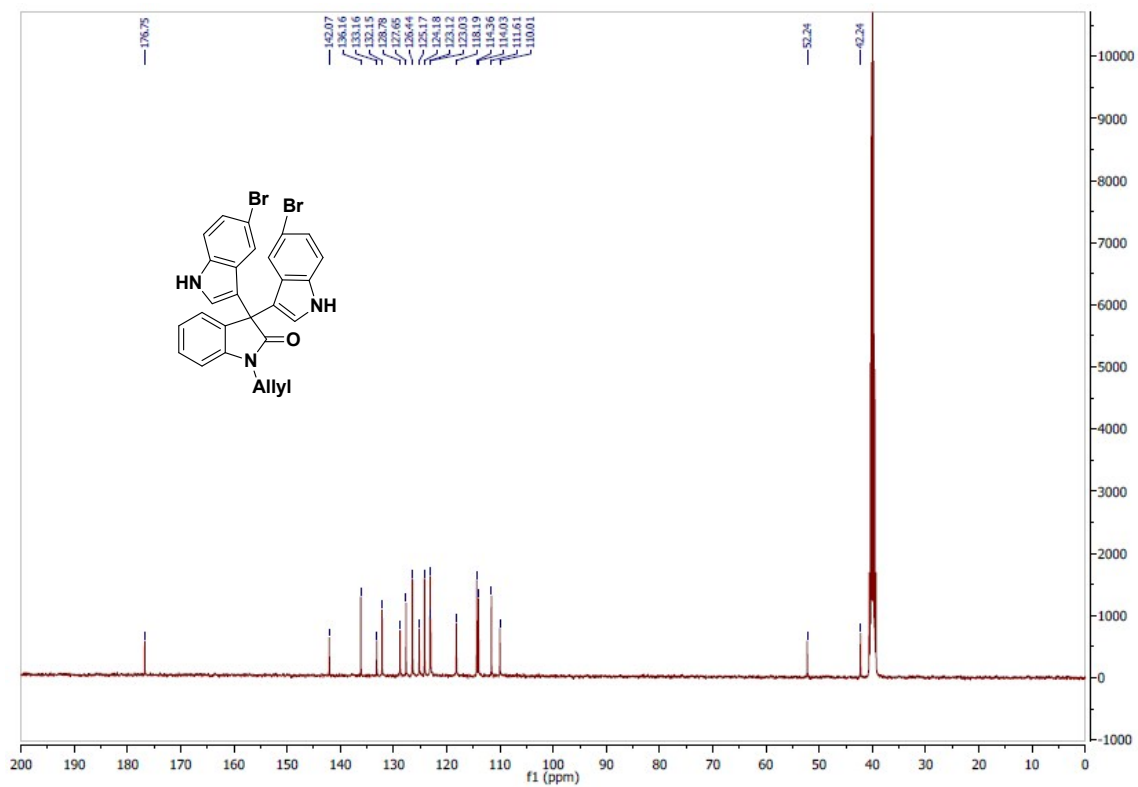


1'-ethyl-2,2''-dimethyl-1H,1''H-[3,3':3,3''-terbenzo[b]pyrrol]-2'(1'H)-one (16j):

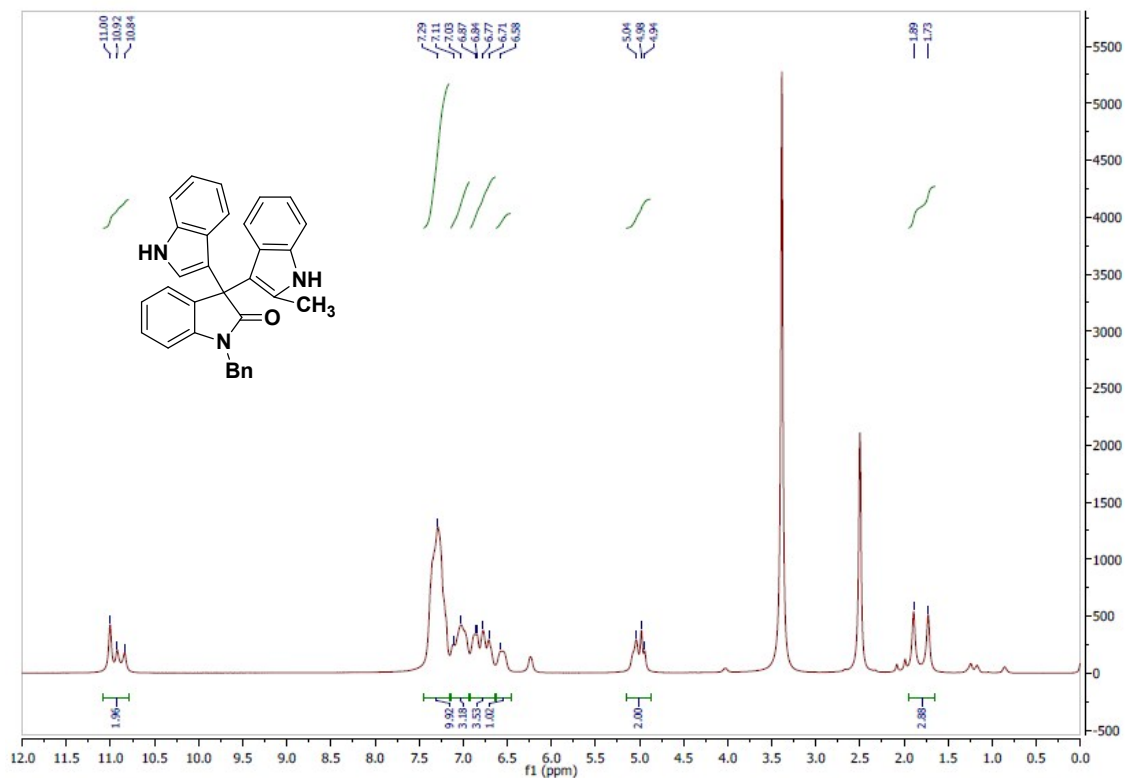


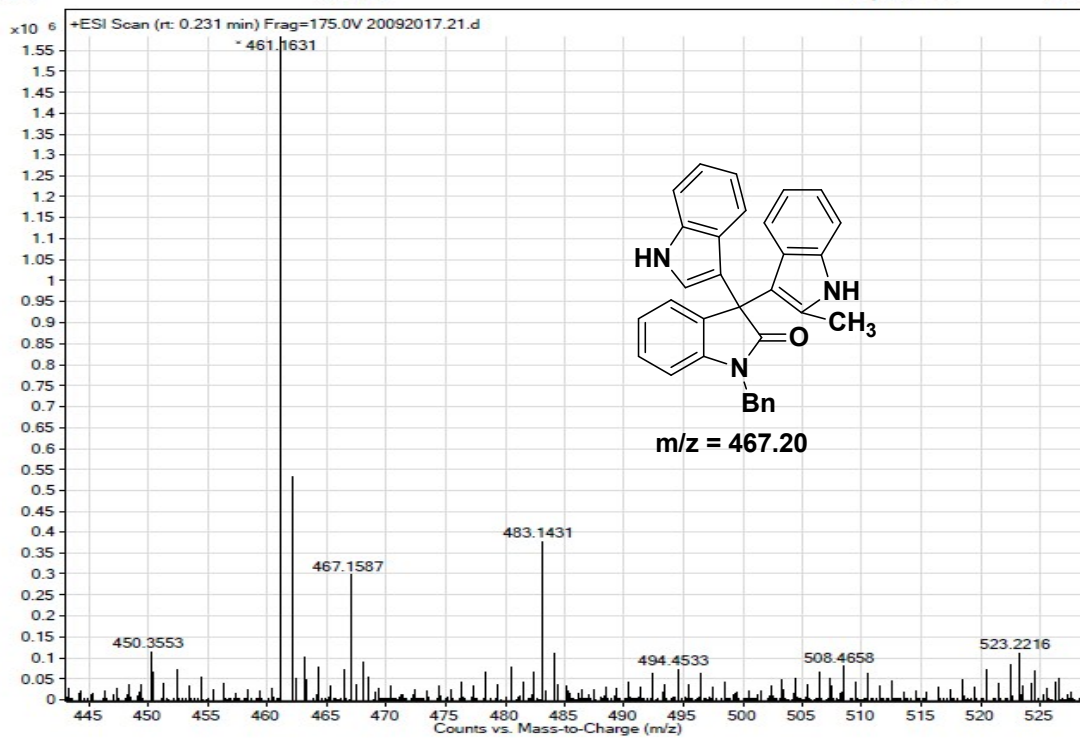
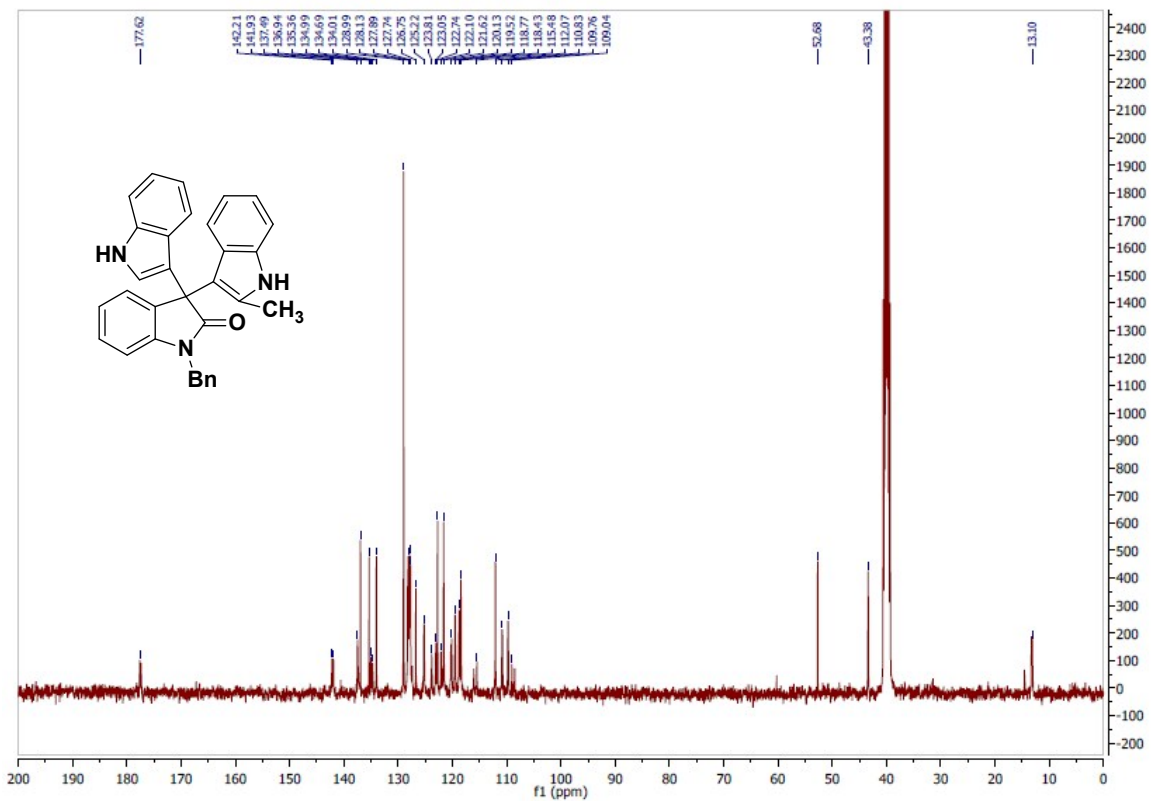
1'-allyl-5,5''-dibromo-1H,1''H-[3,3':3,3''-terbenzo[b]pyrrol]-2'(1'H)-one (16k):



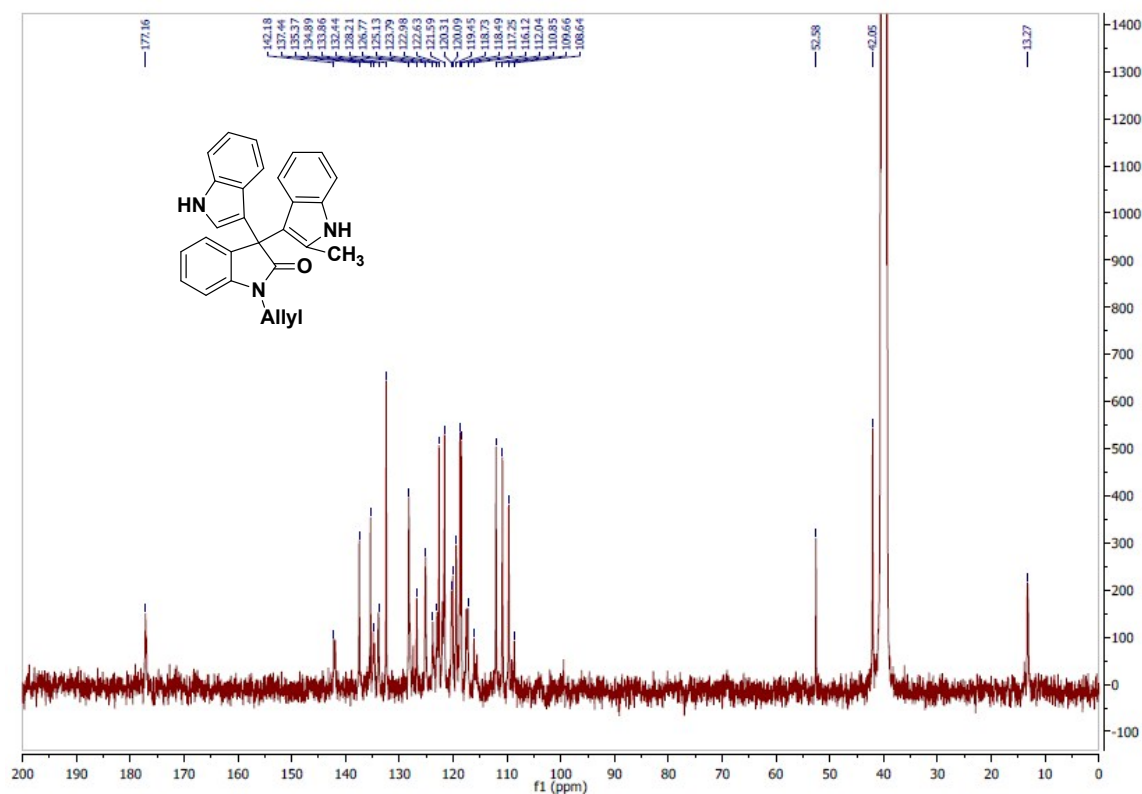
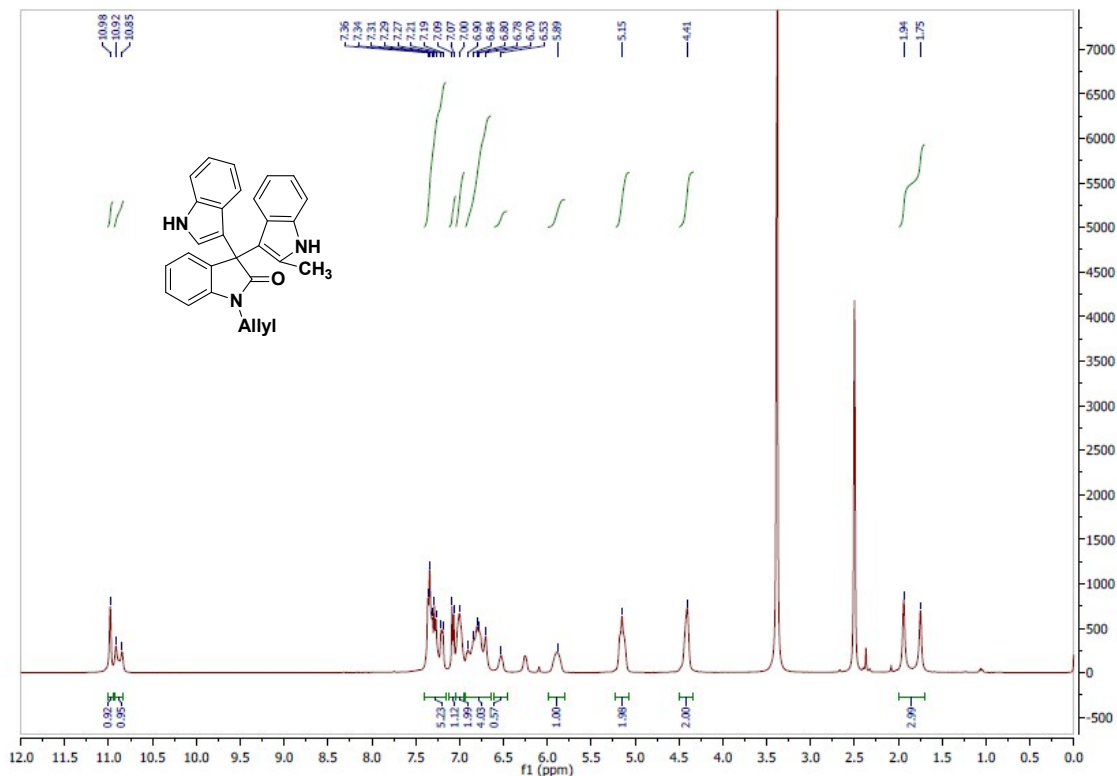


1'-benzyl-2-methyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (19c):

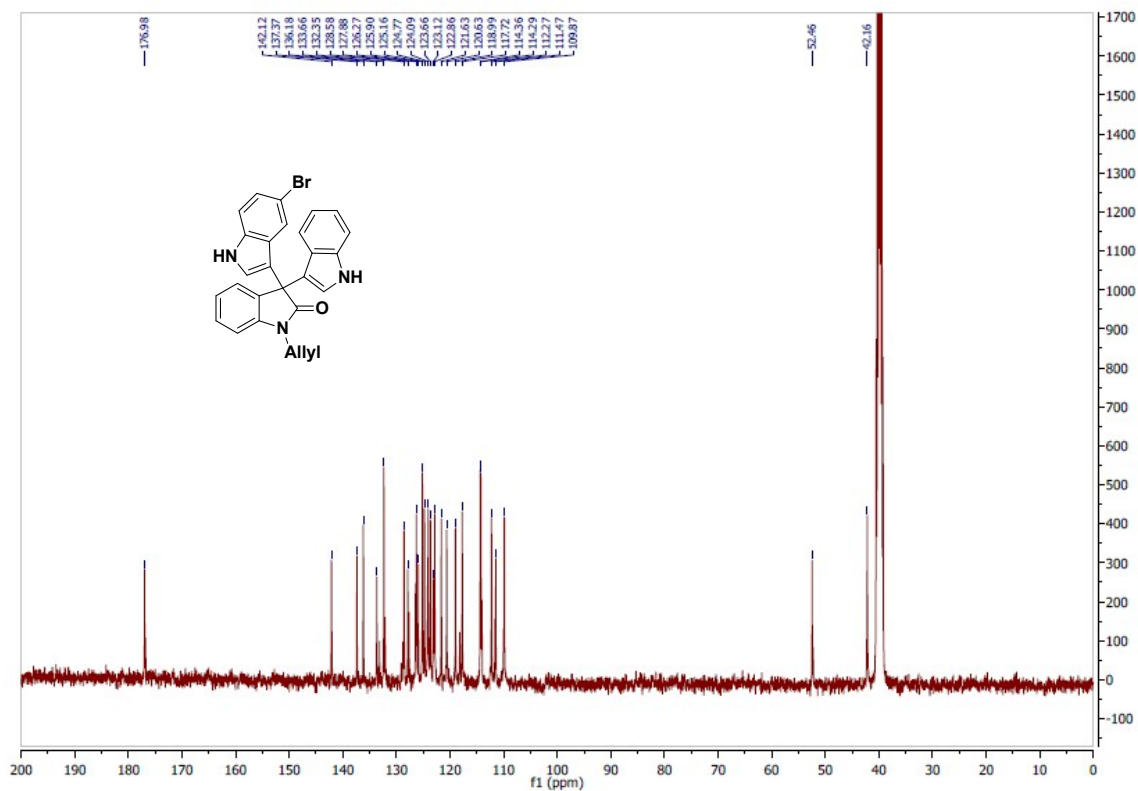
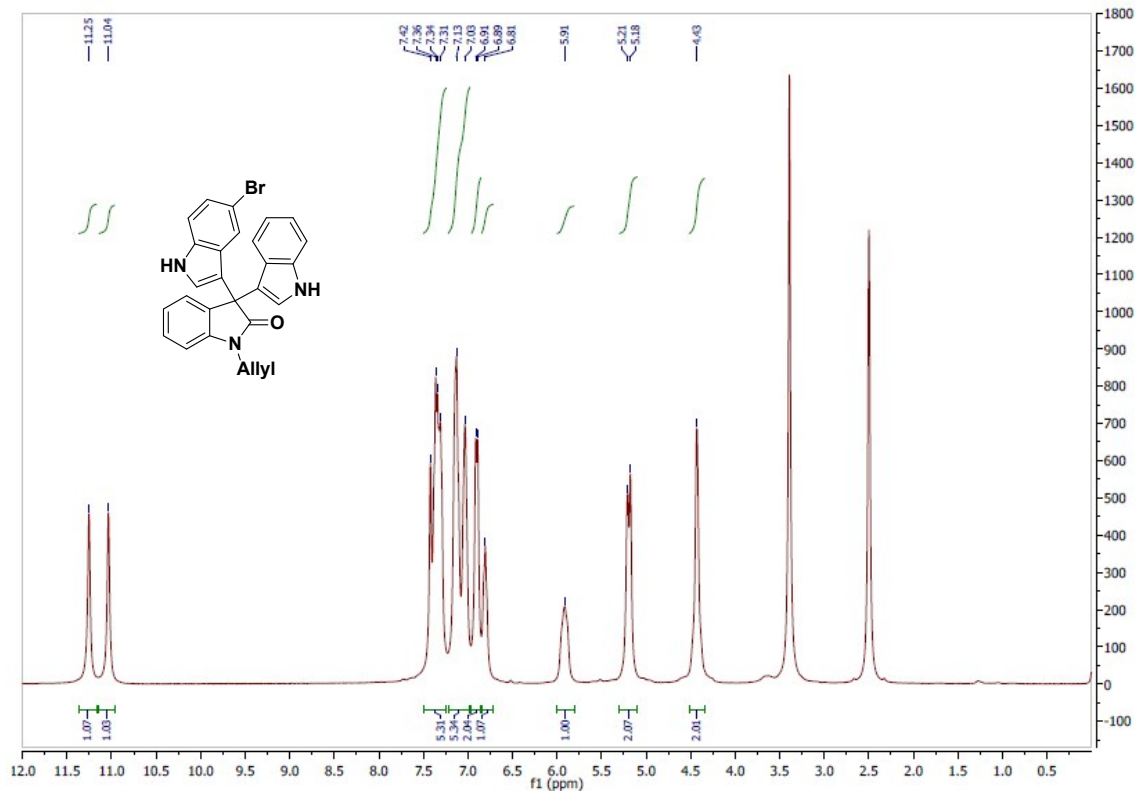


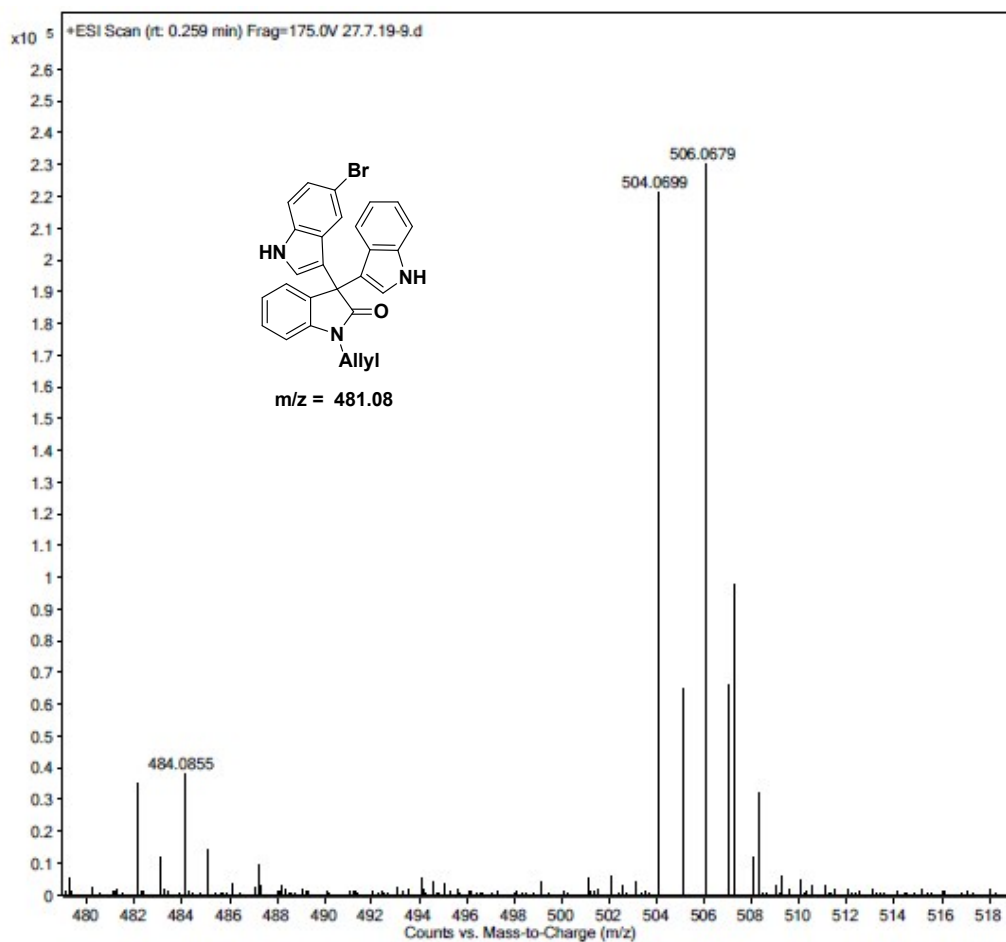


1'-allyl-2-methyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (19d):

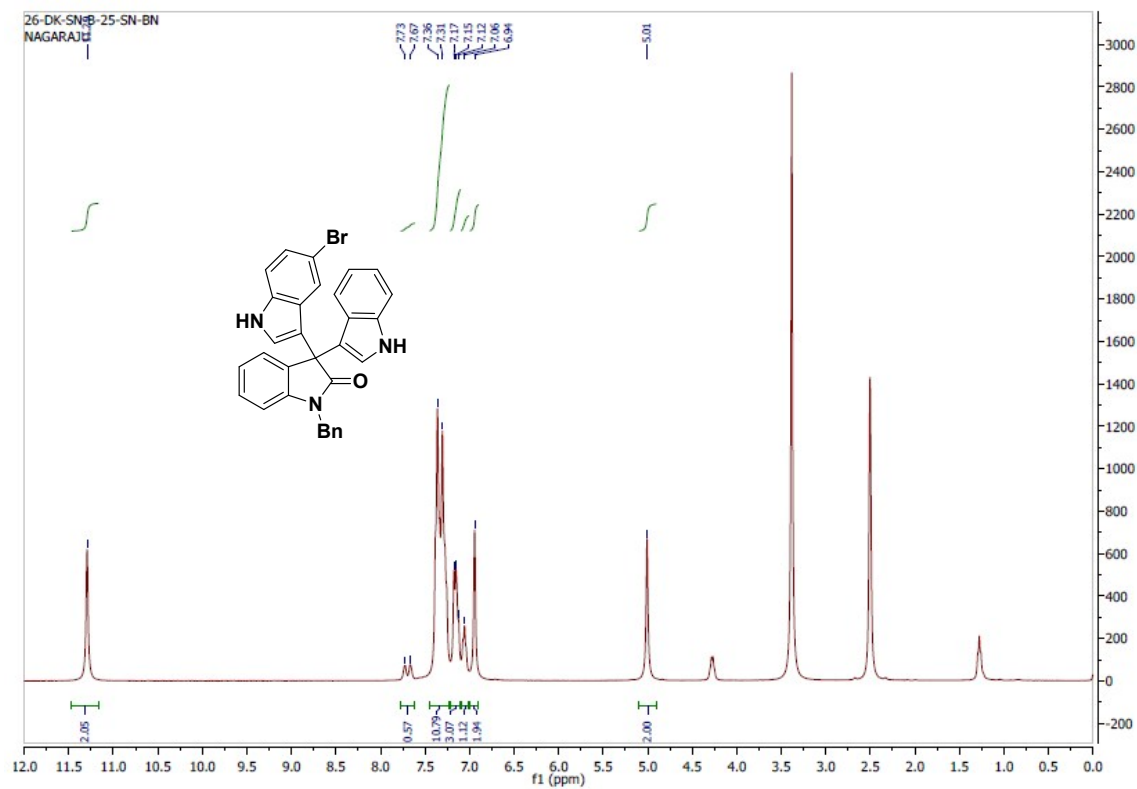


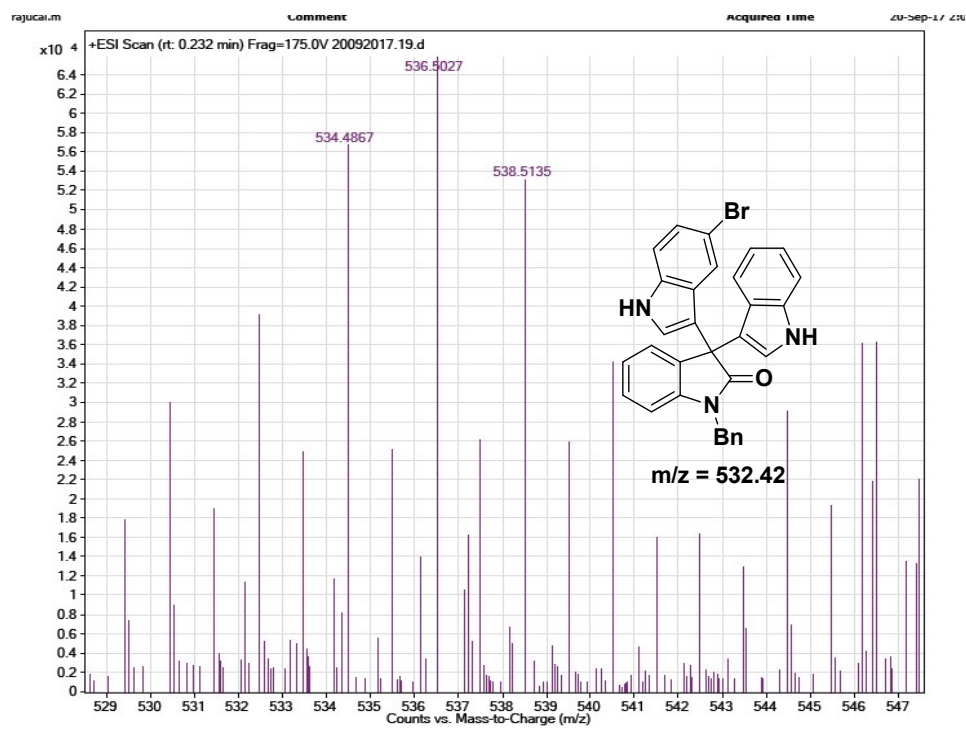
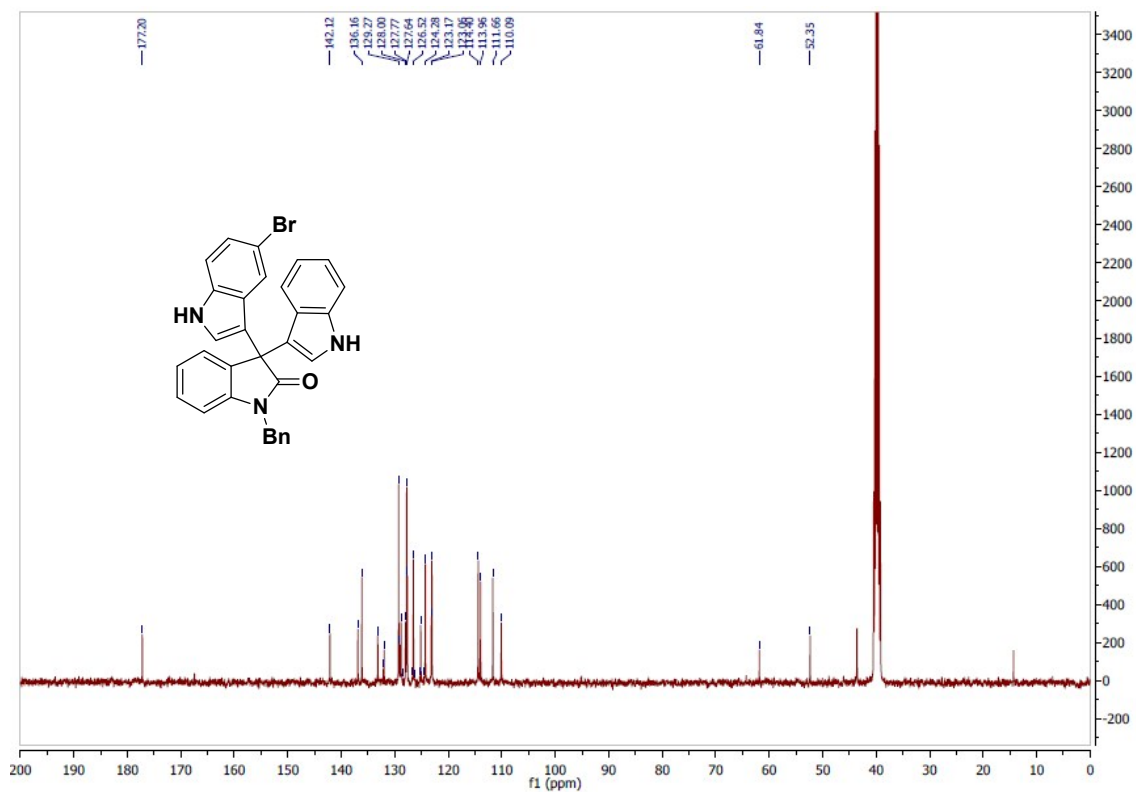
1'-allyl-5-bromo-[3,3':3',3''-terindolin]-2'-one (19f):



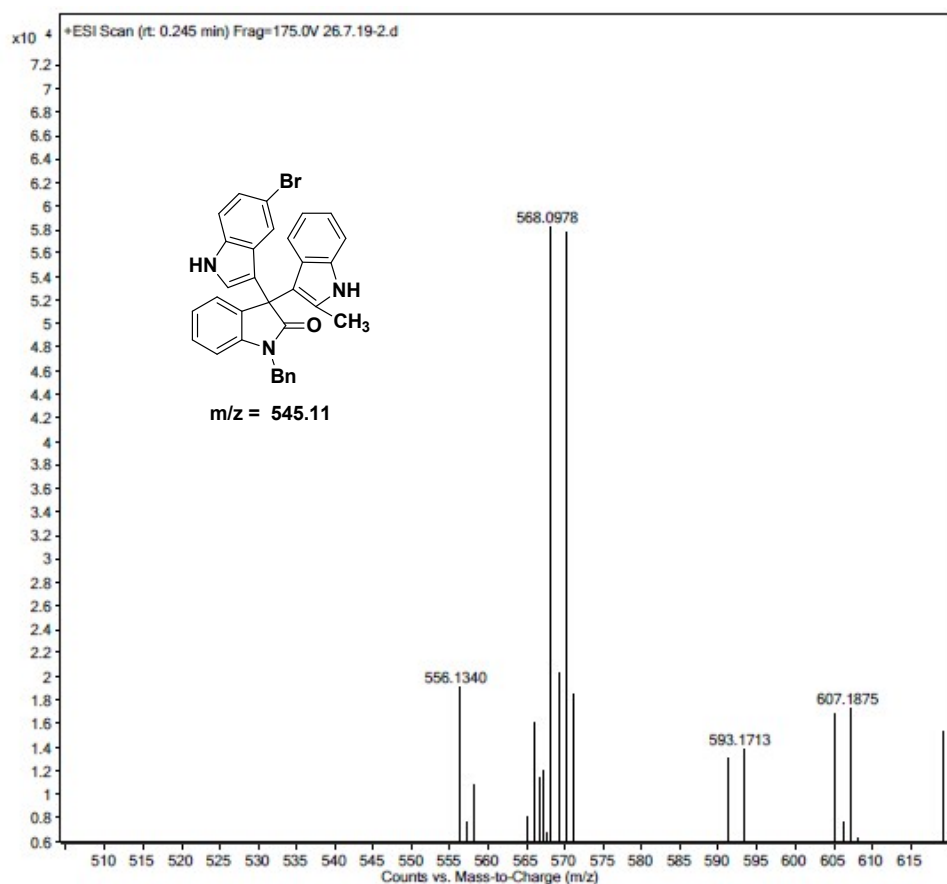


1'-benzyl-5-bromo-[3,3':3',3''-terindolin]-2'-one (19g):

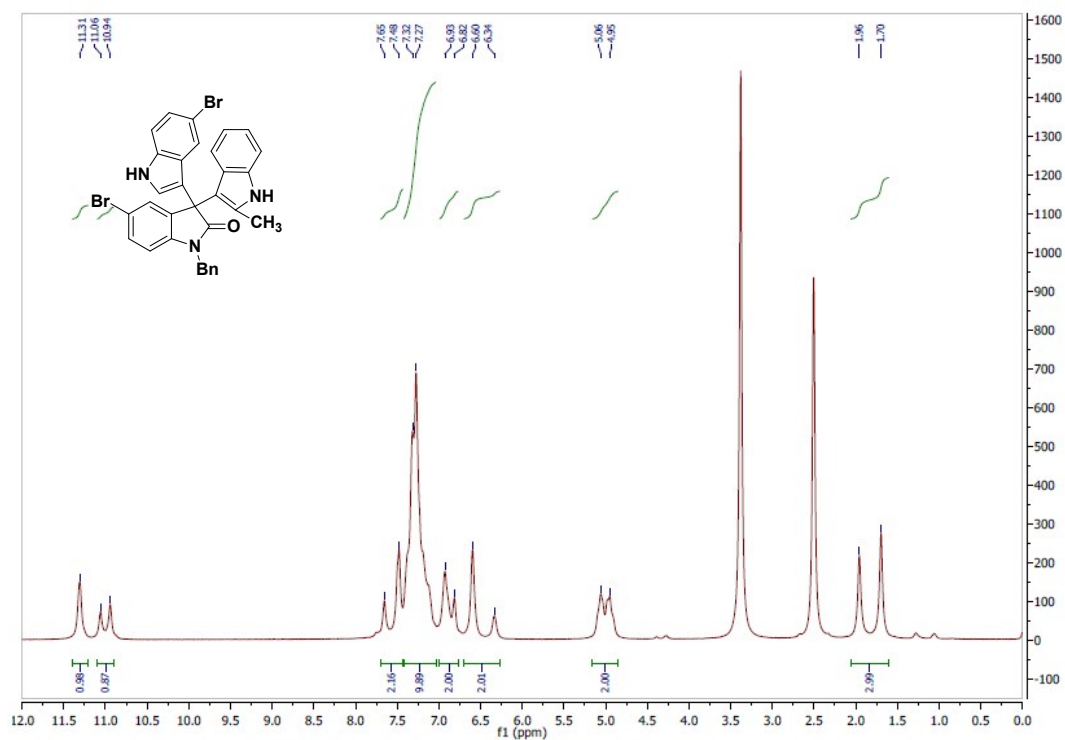


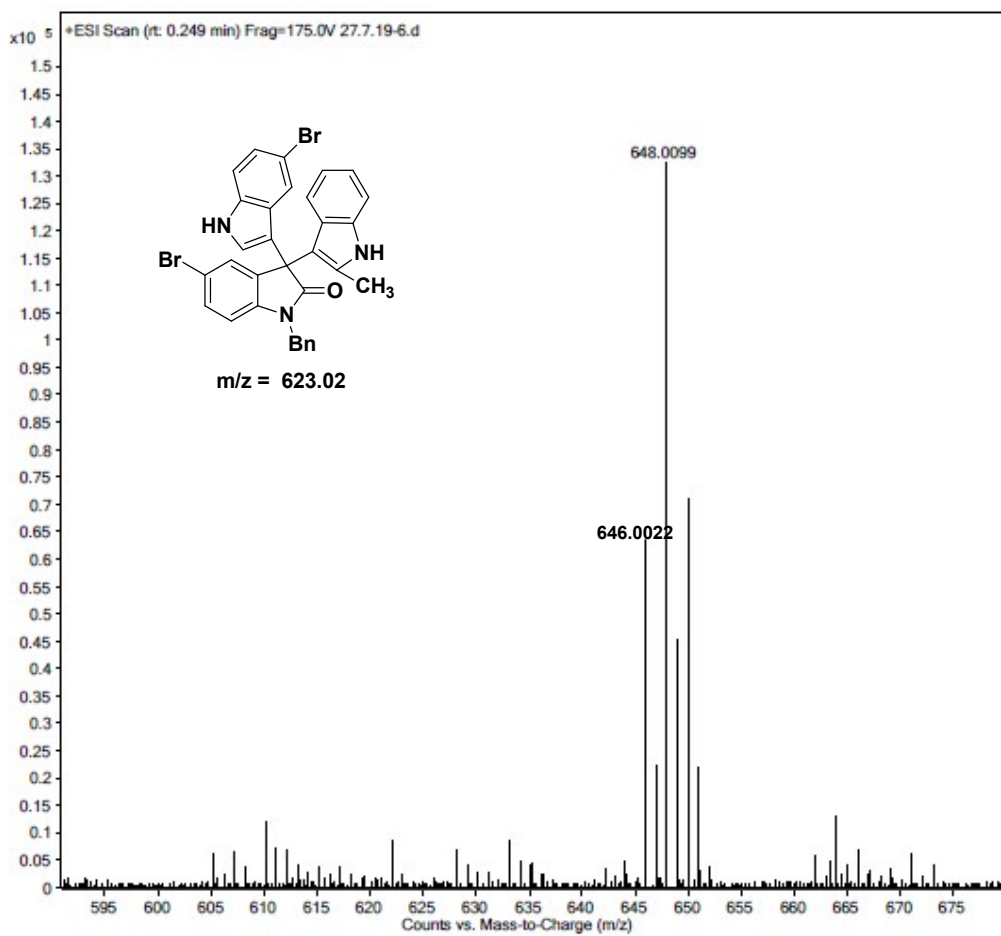
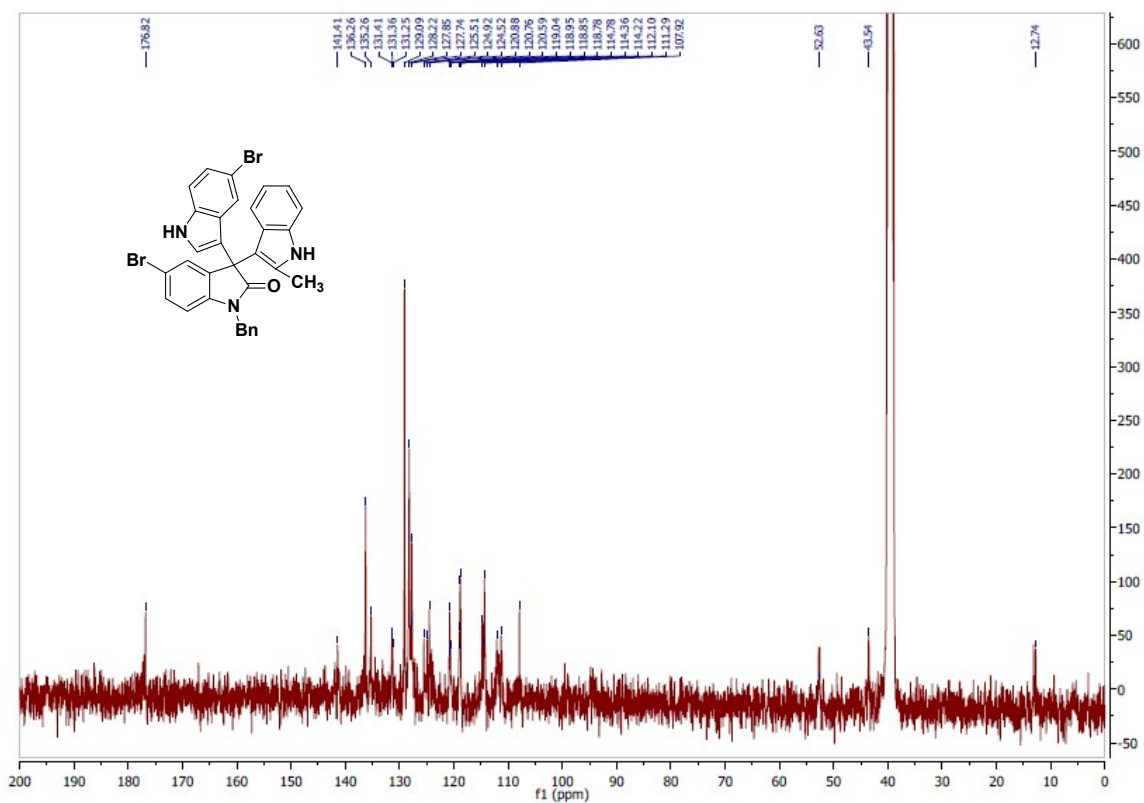


1'-benzyl-5''-bromo-2-methyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (19h):

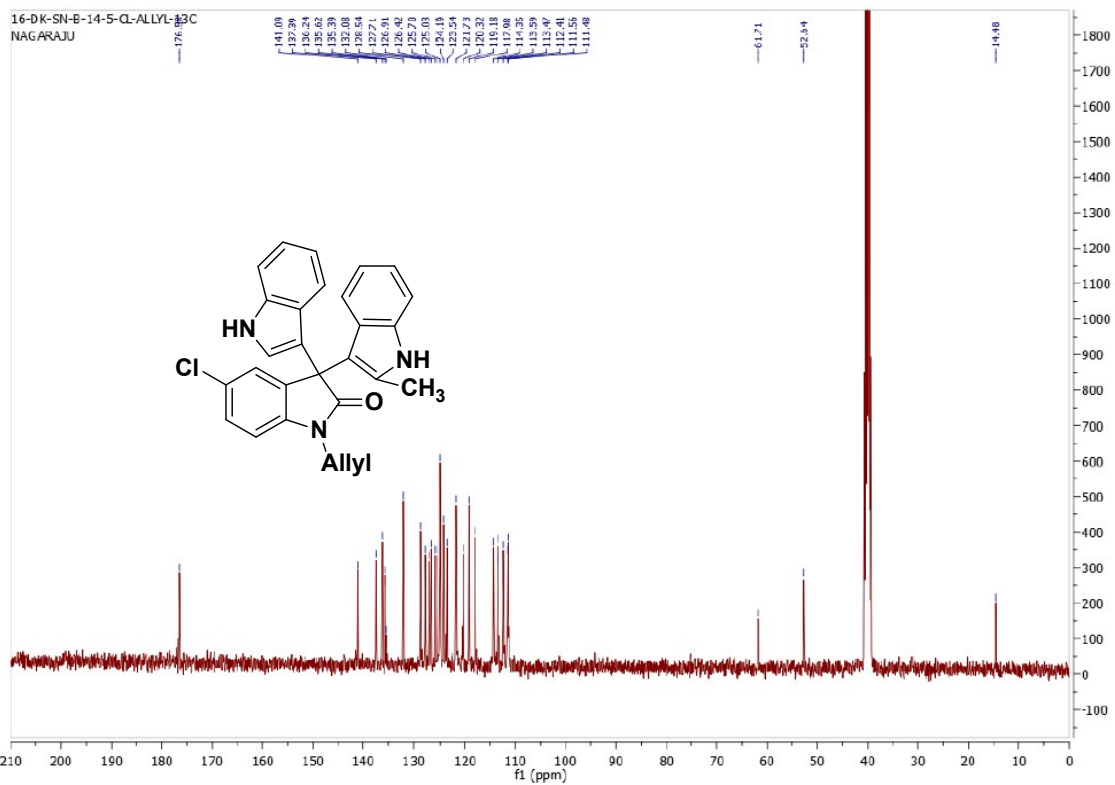
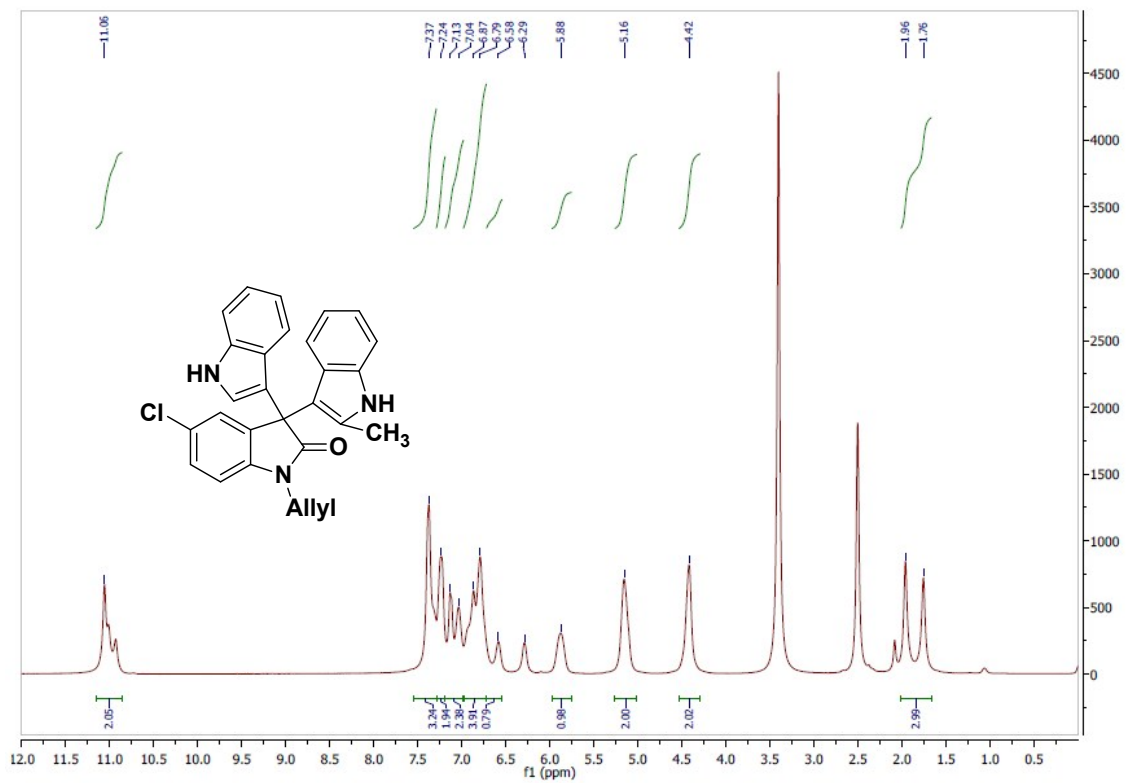


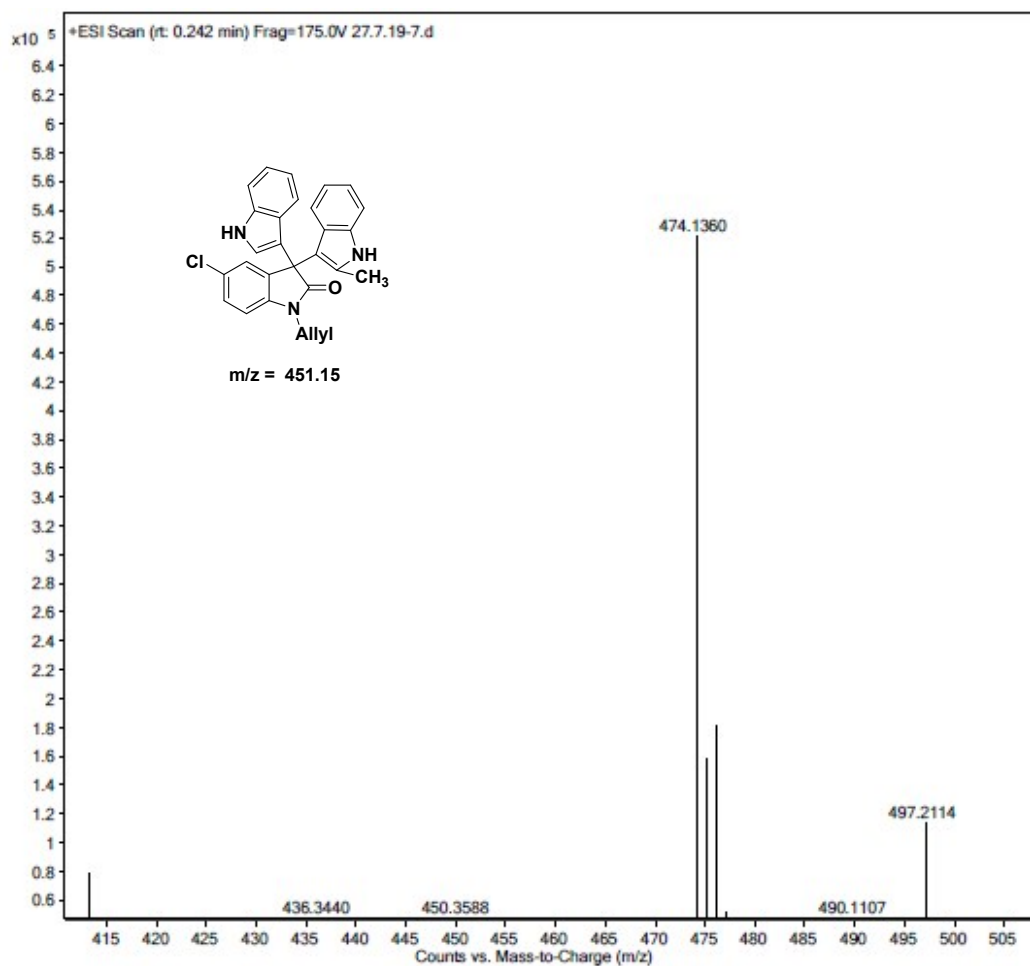
1'-benzyl-5',5''-dibromo-2-methyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (19i):



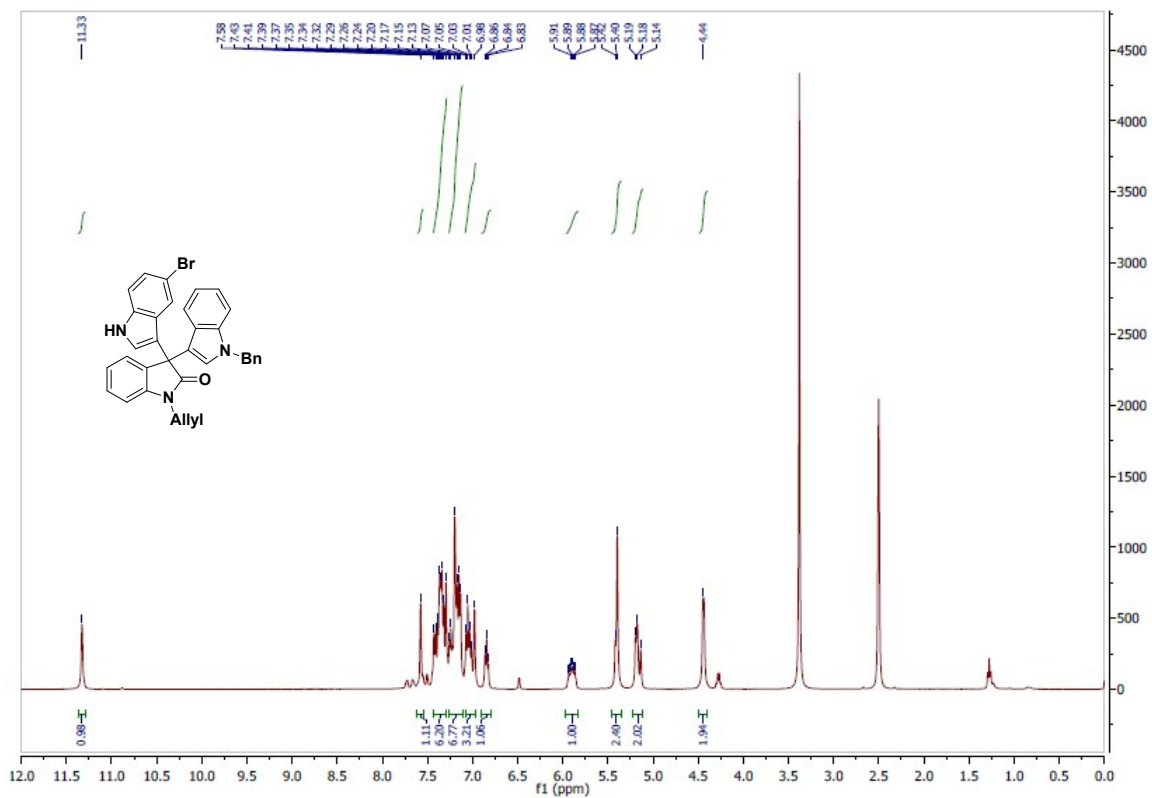


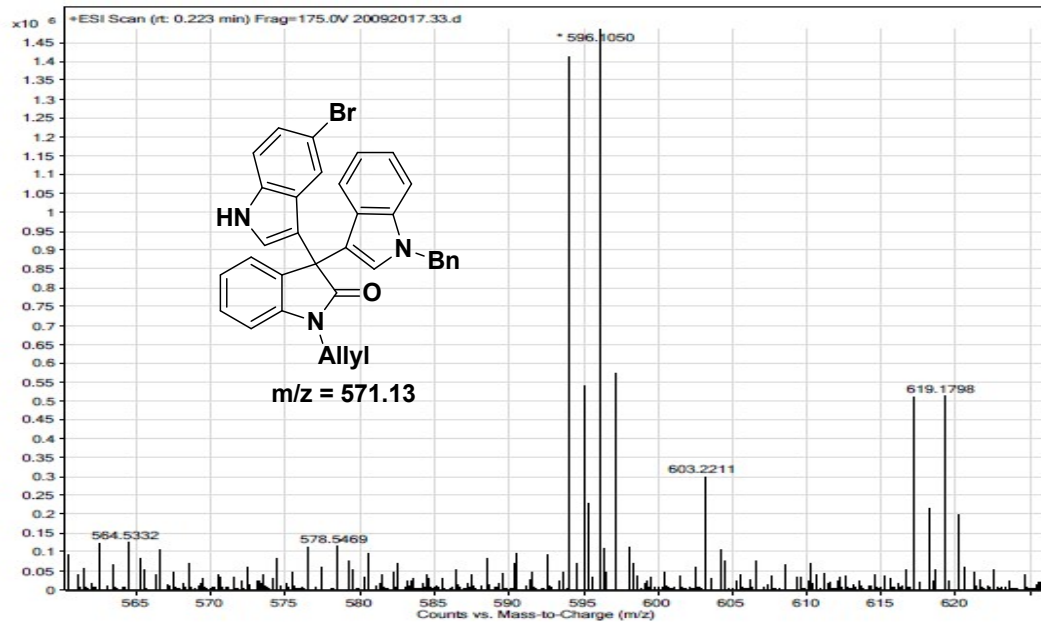
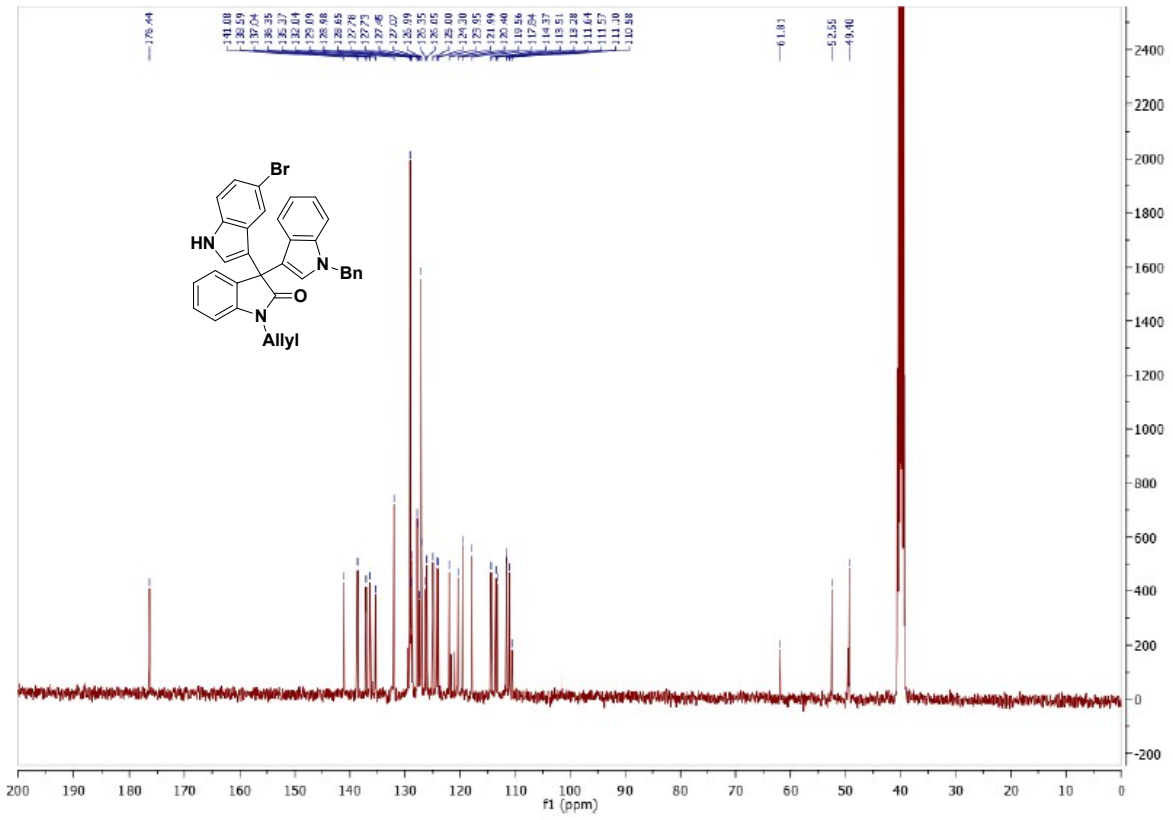
1'-allyl-5'-chloro-2-methyl-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (19j):



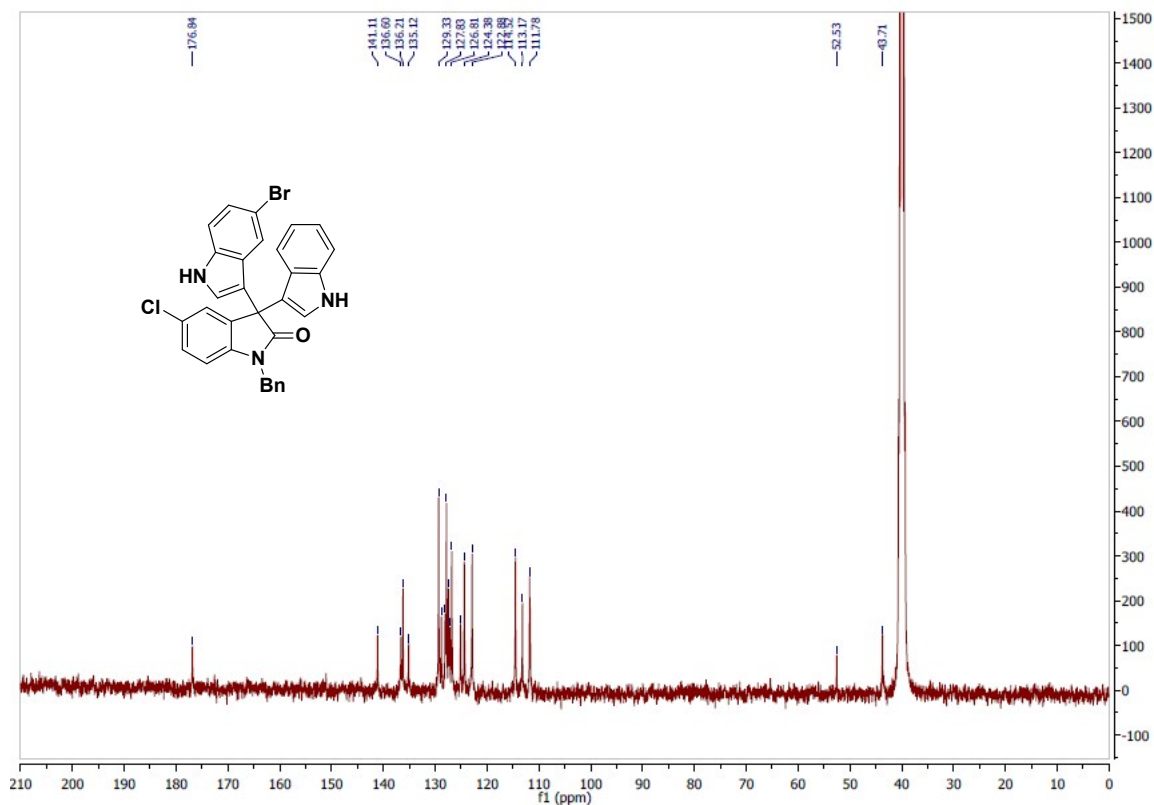
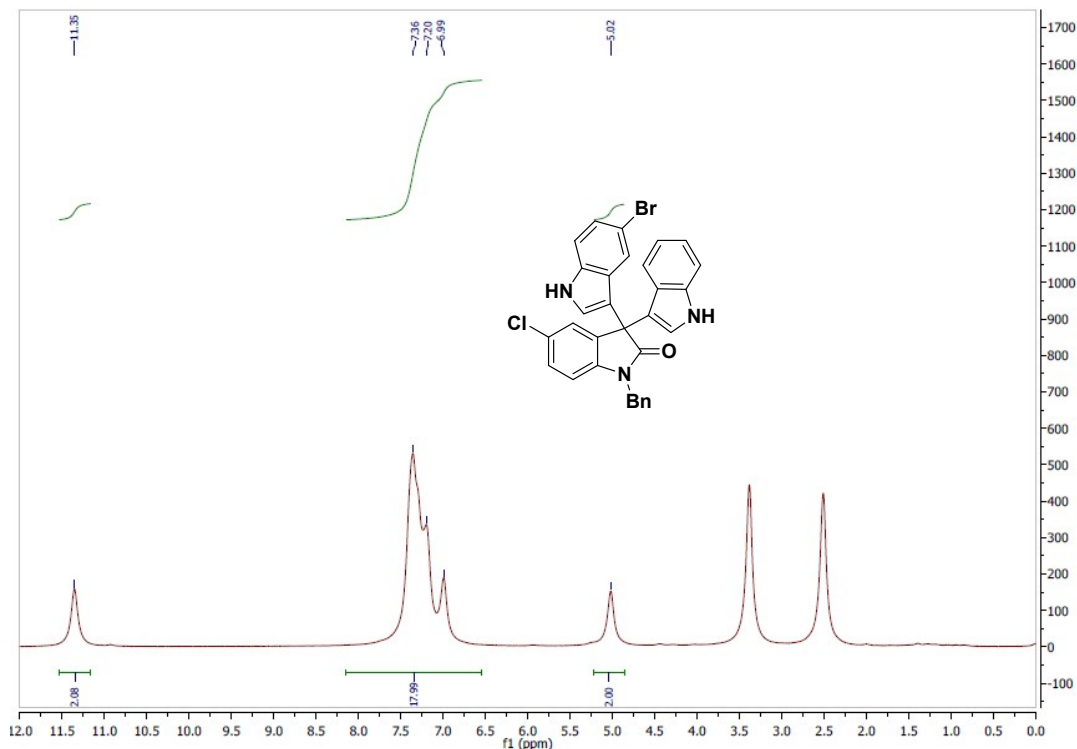


1'-allyl-1-benzyl-5''-bromo-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (19k):

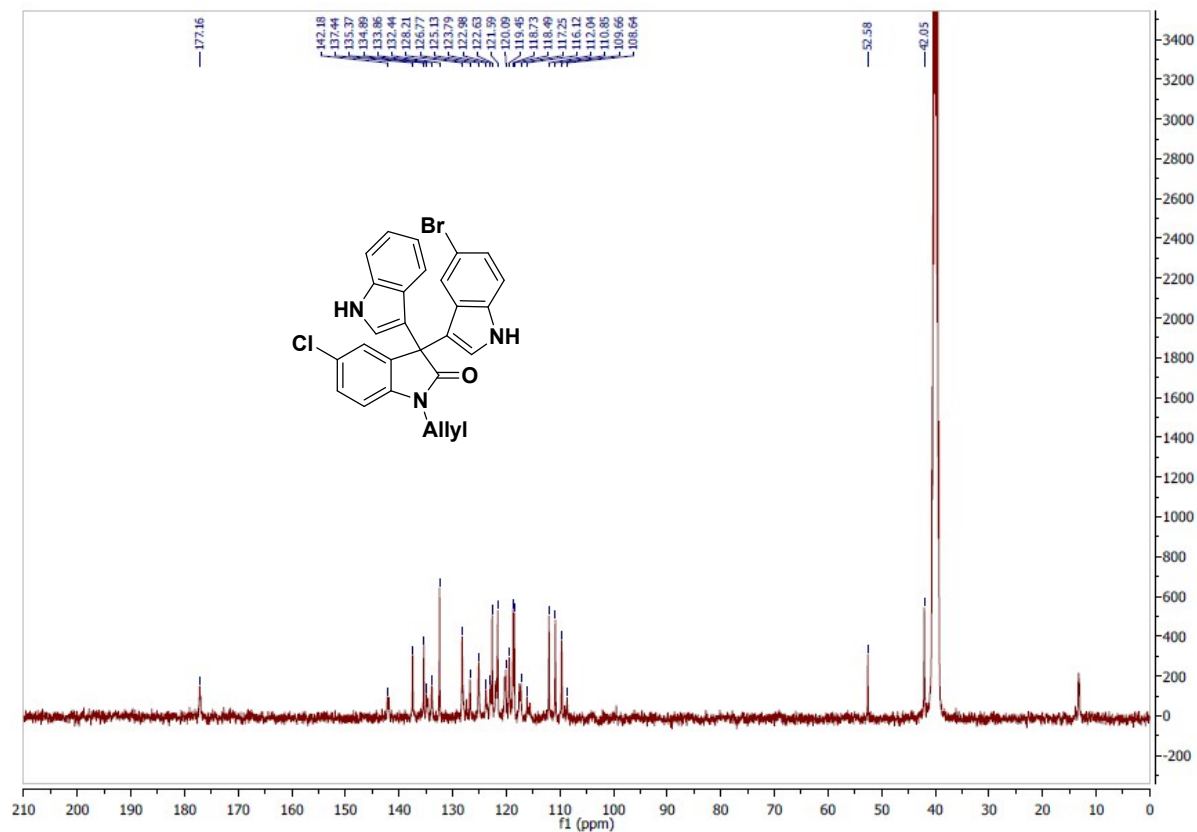
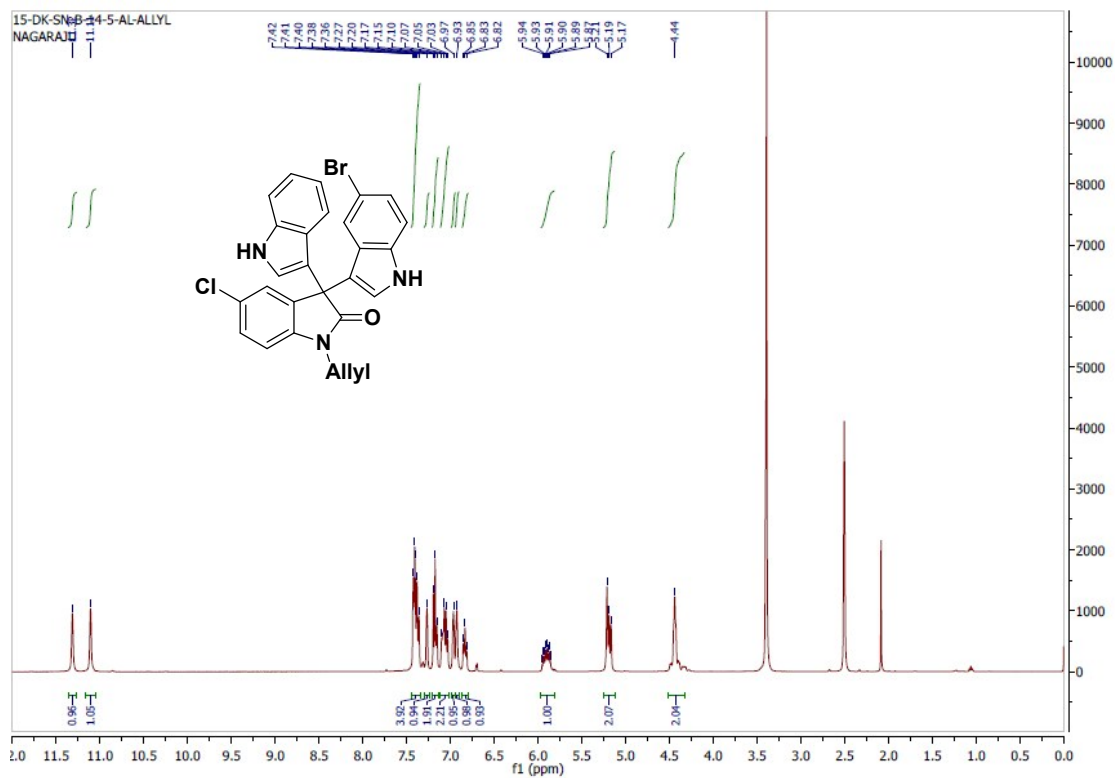


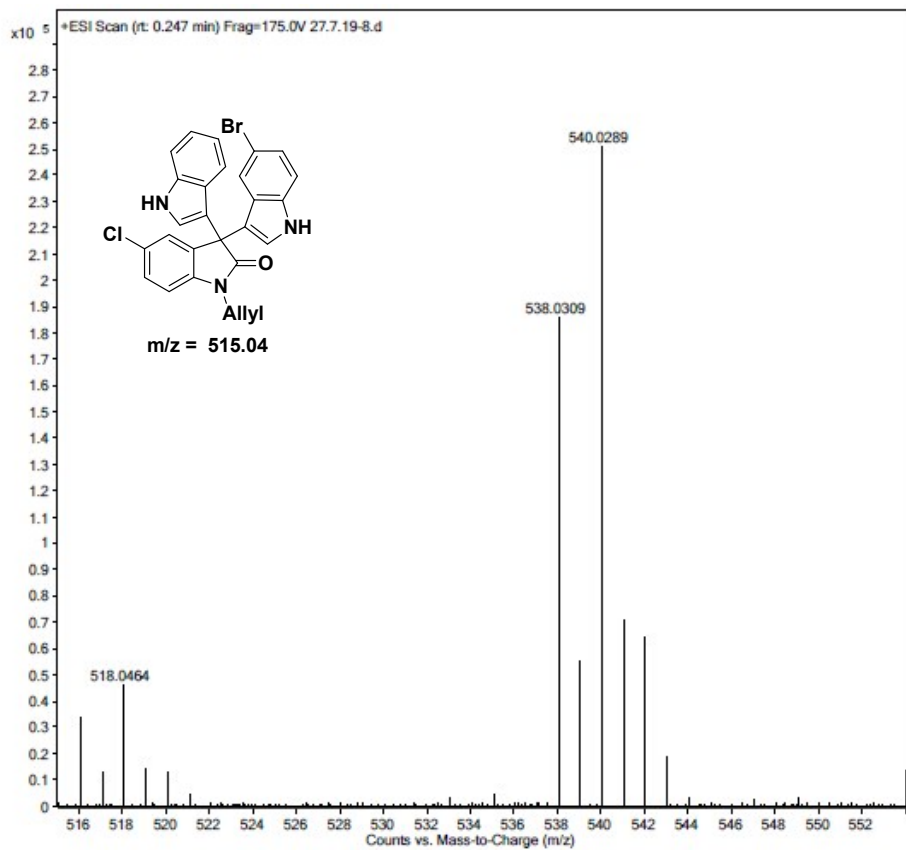


1'-benzyl-5-bromo-5'-chloro-[3,3':3',3''-terindolin]-2'-one (19l):

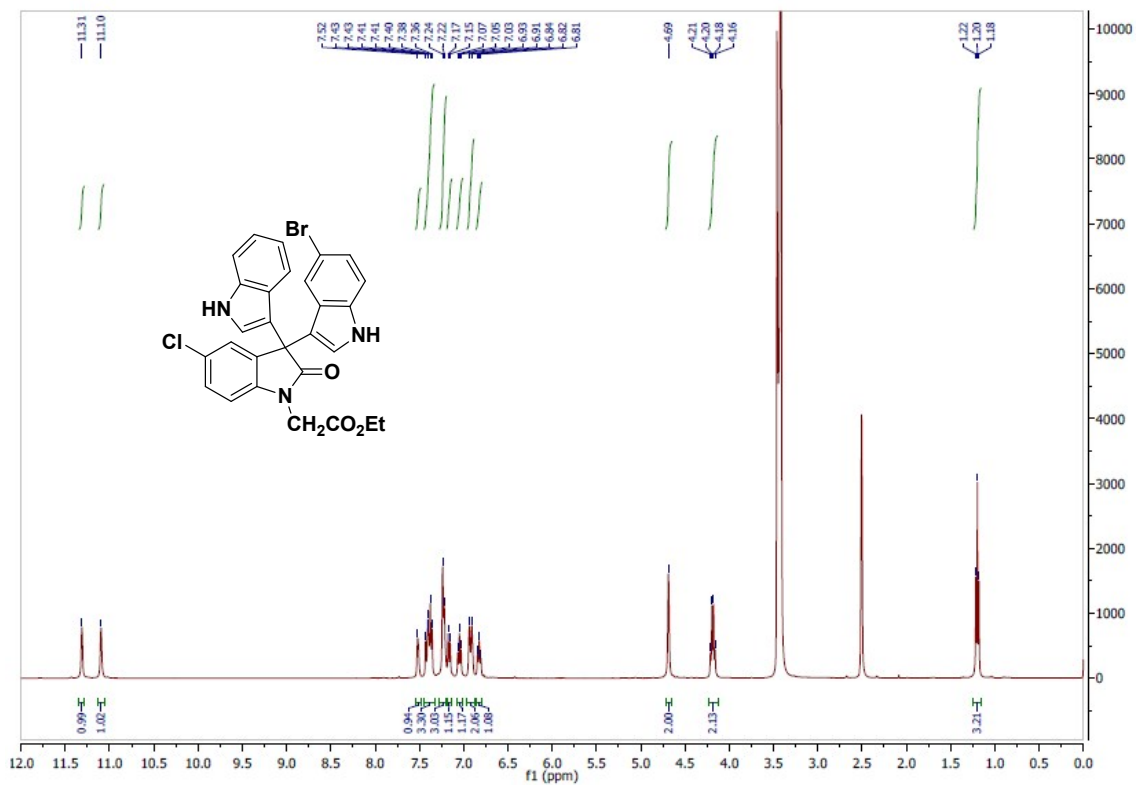


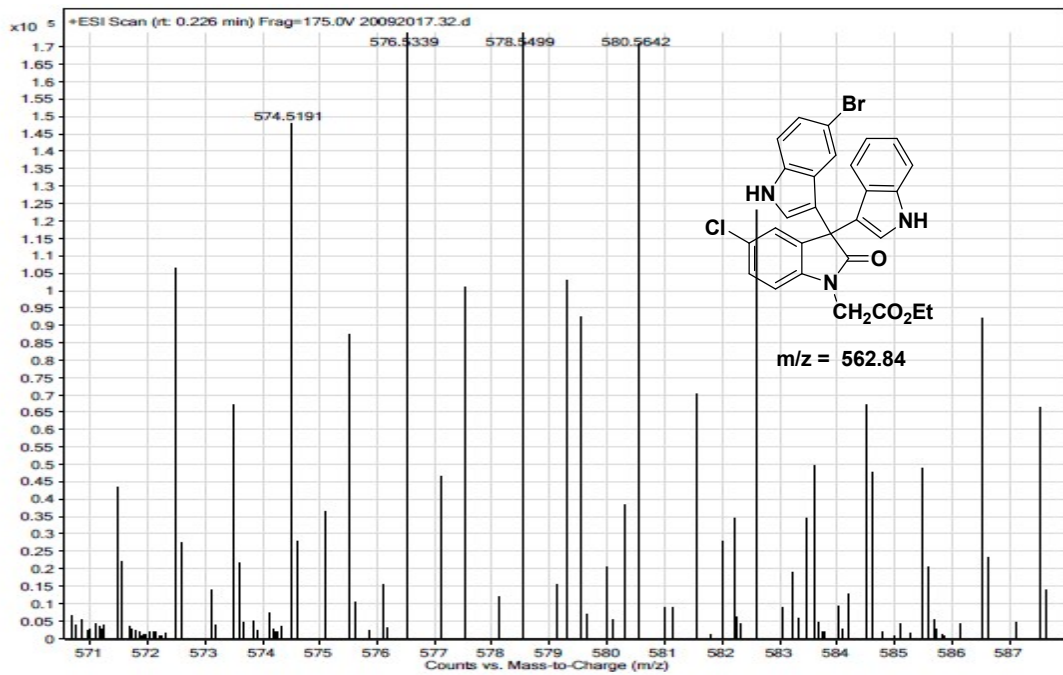
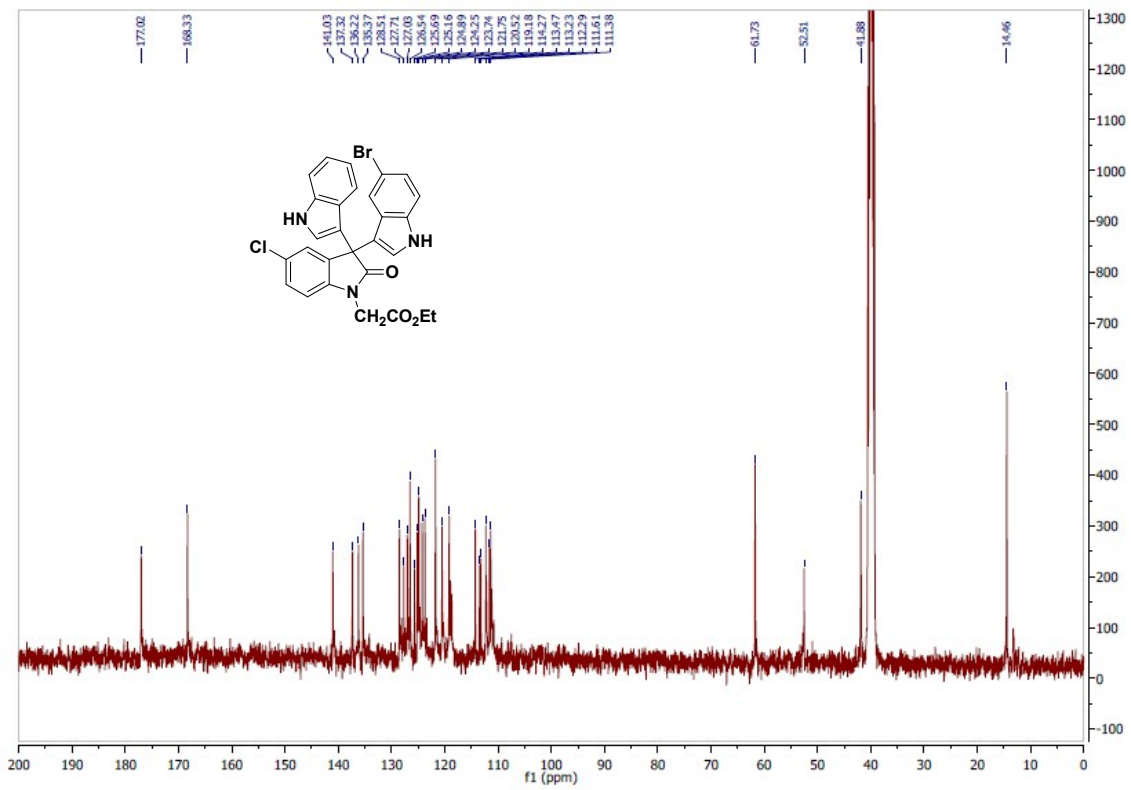
1'-allyl-5-bromo-5'-chloro-1H,1''H-[3,3':3',3''-terbenzo[b]pyrrol]-2'(1'H)-one (19m):



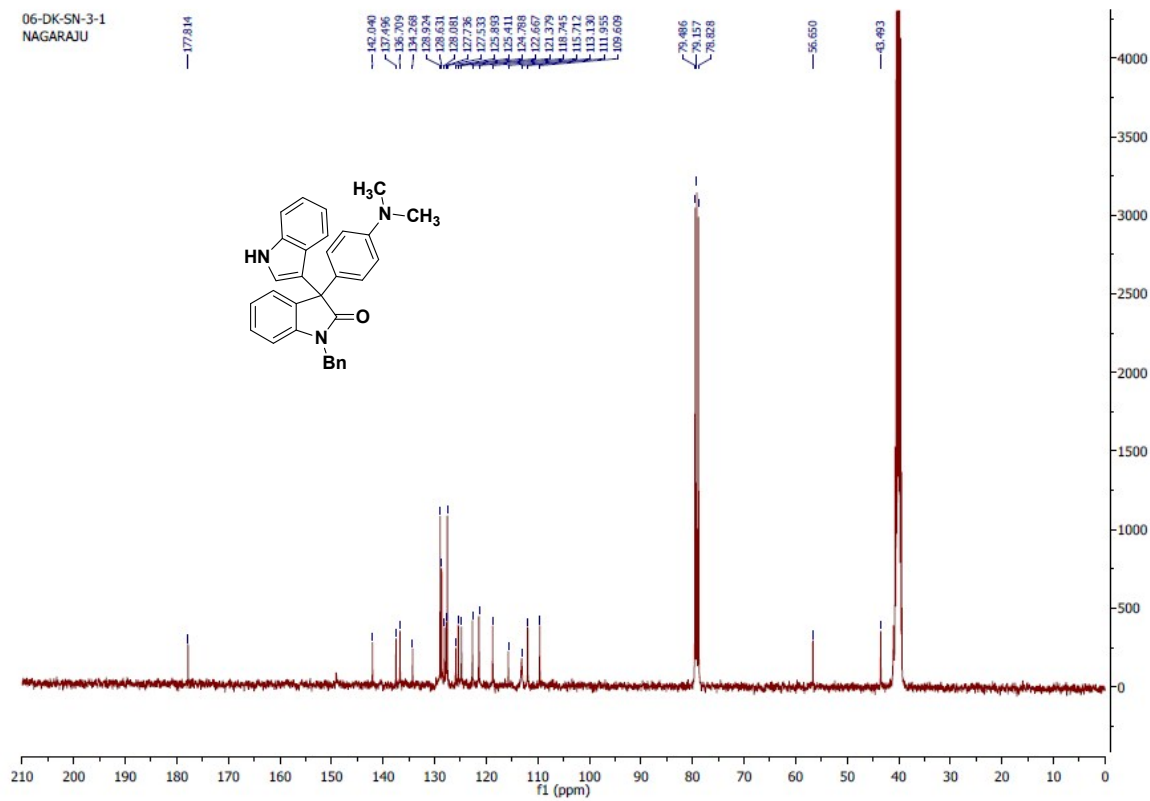
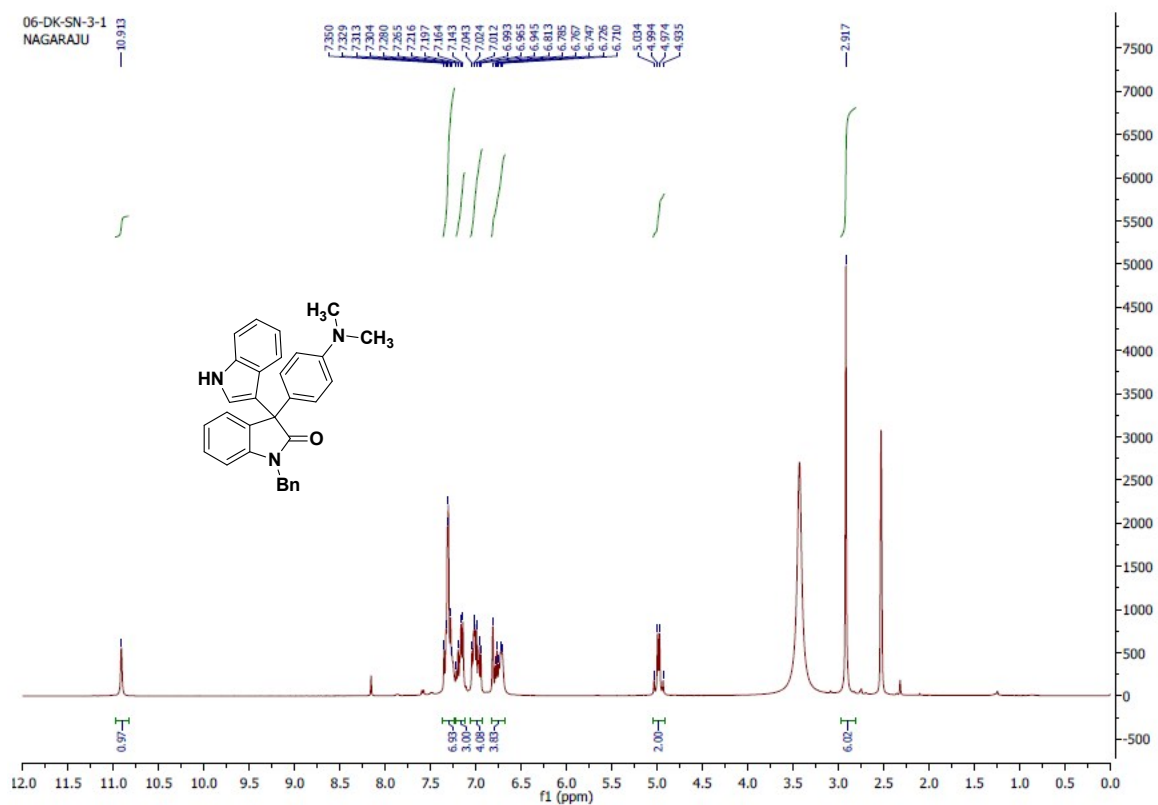


Ethyl 2-(5-bromo-5'-chloro-2'-oxo-1H,1''H-[3,3':3'',3''-terbenzo[b]pyrrol]-1'(2'H)-yl)acetate (19n):

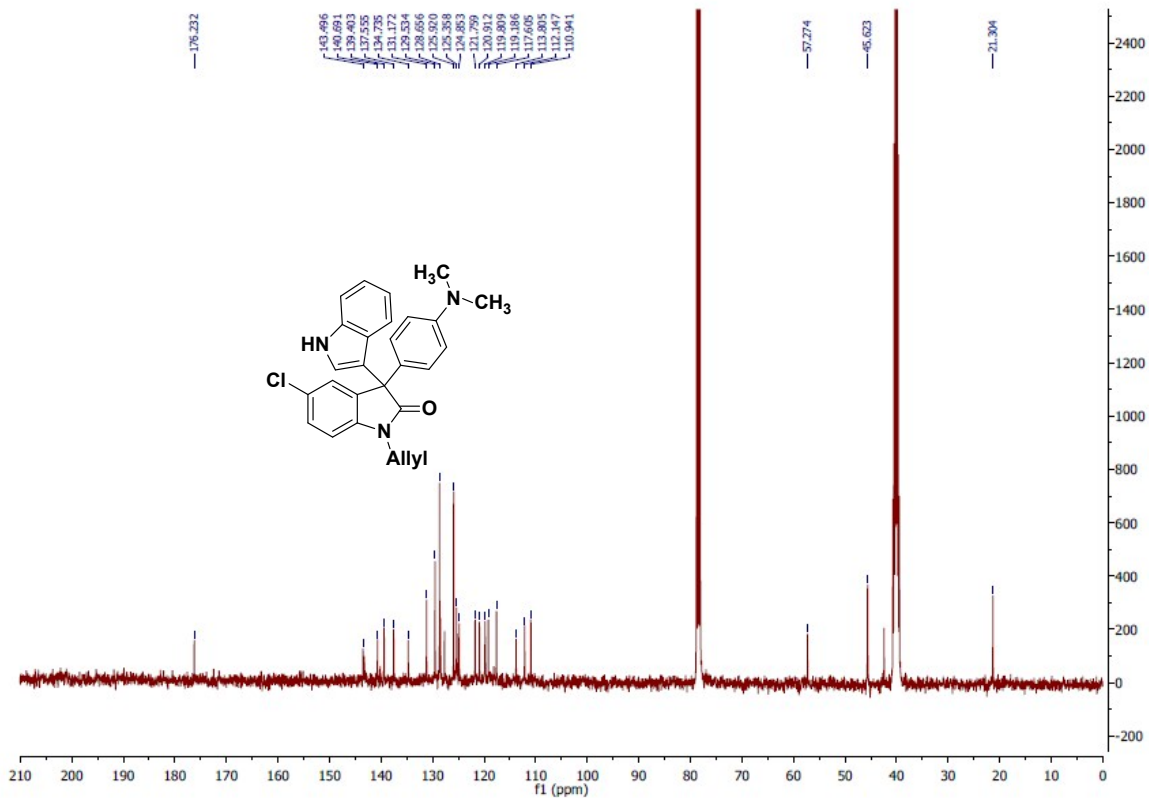
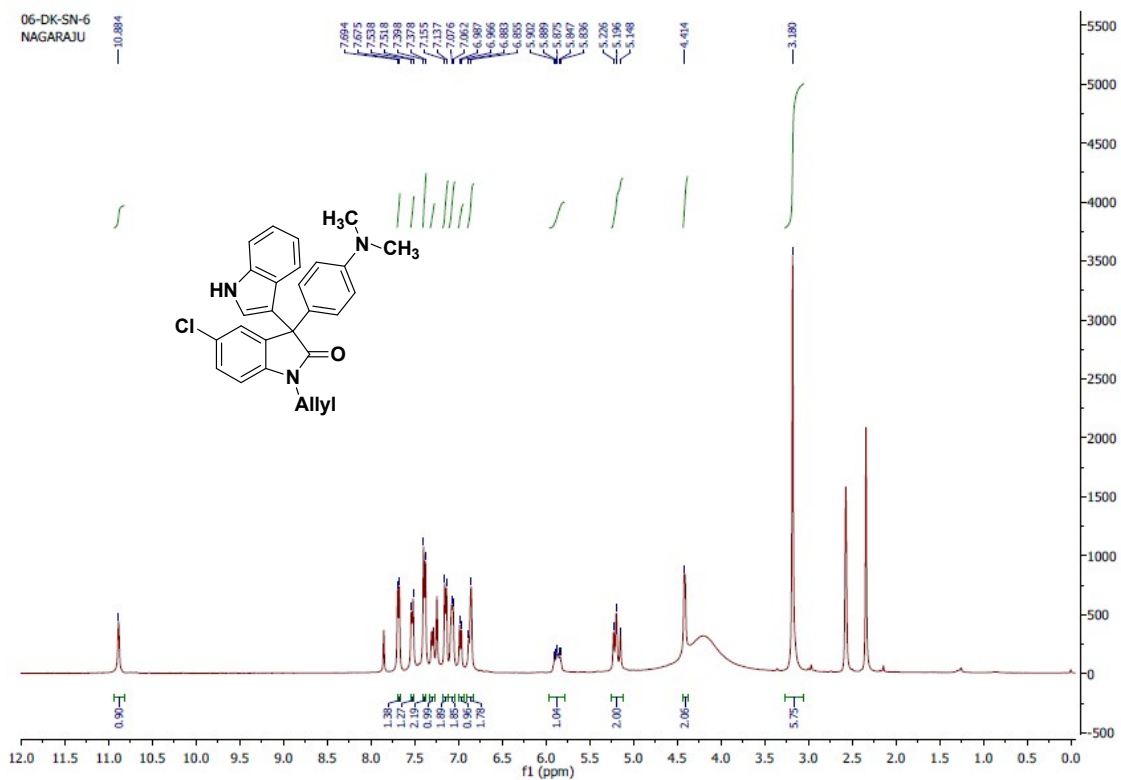




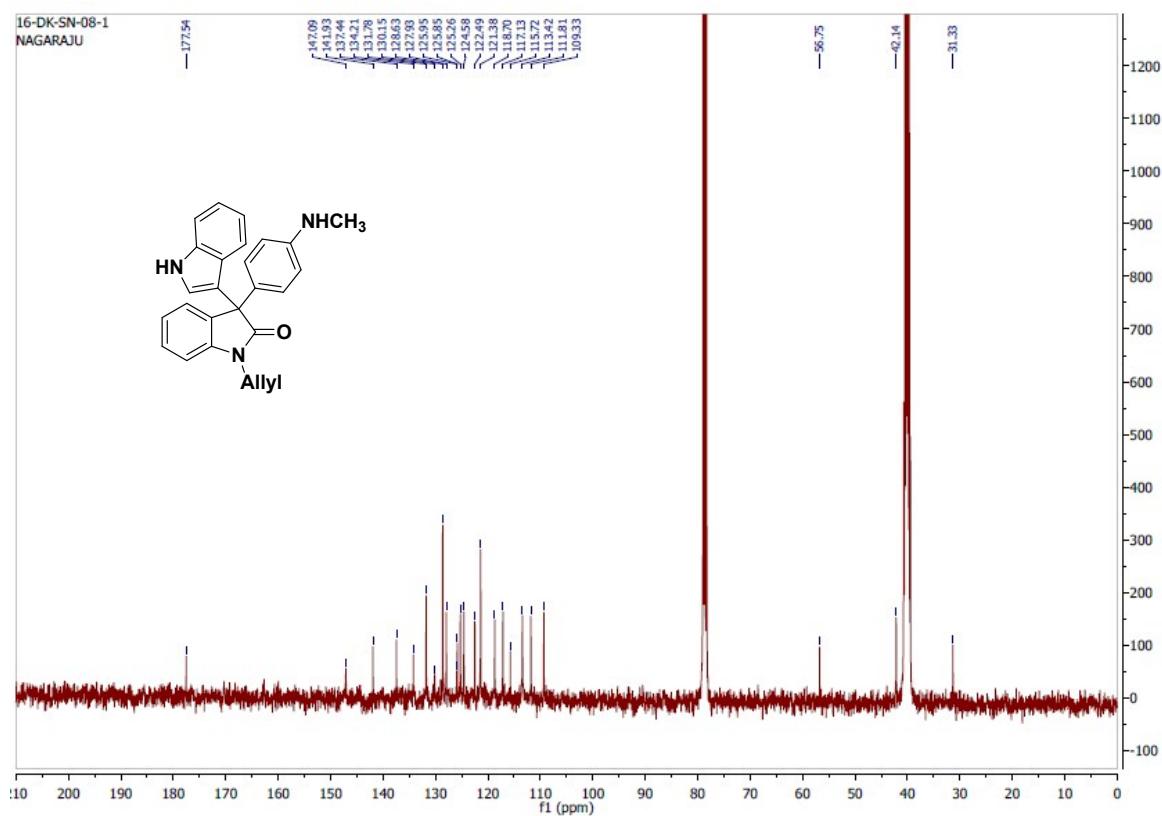
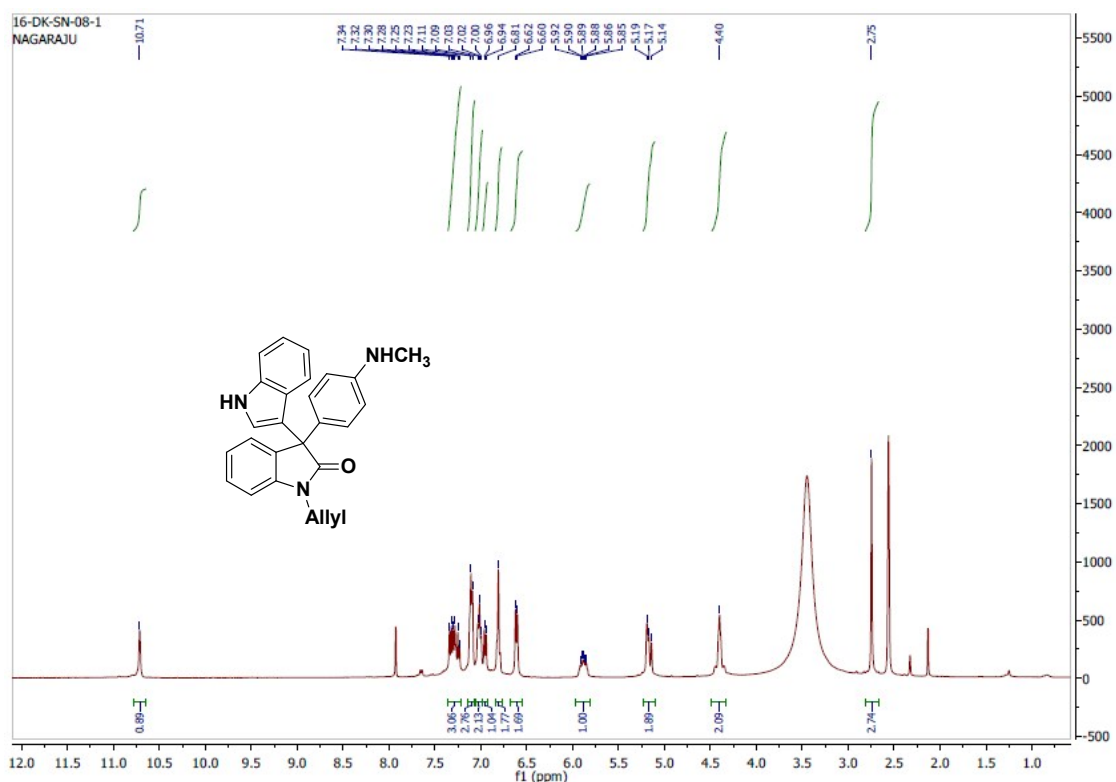
1-benzyl-3-(4-(dimethylamino)phenyl)-3-(1H-indol-3-yl)indolin-2-one (21b):



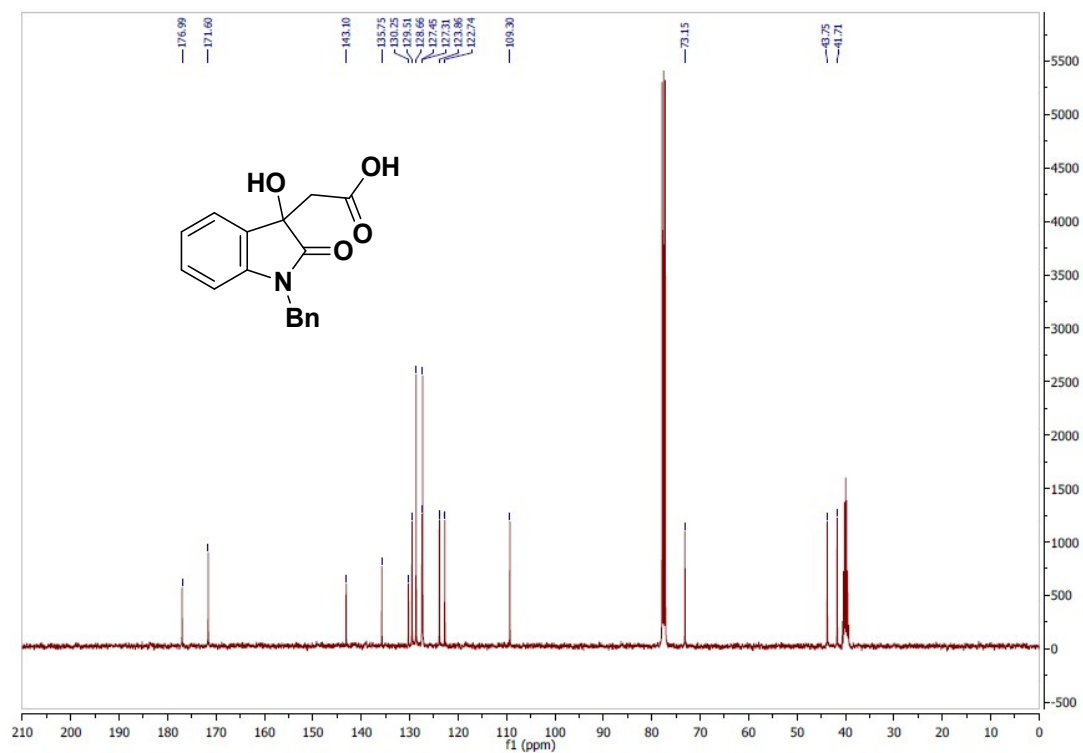
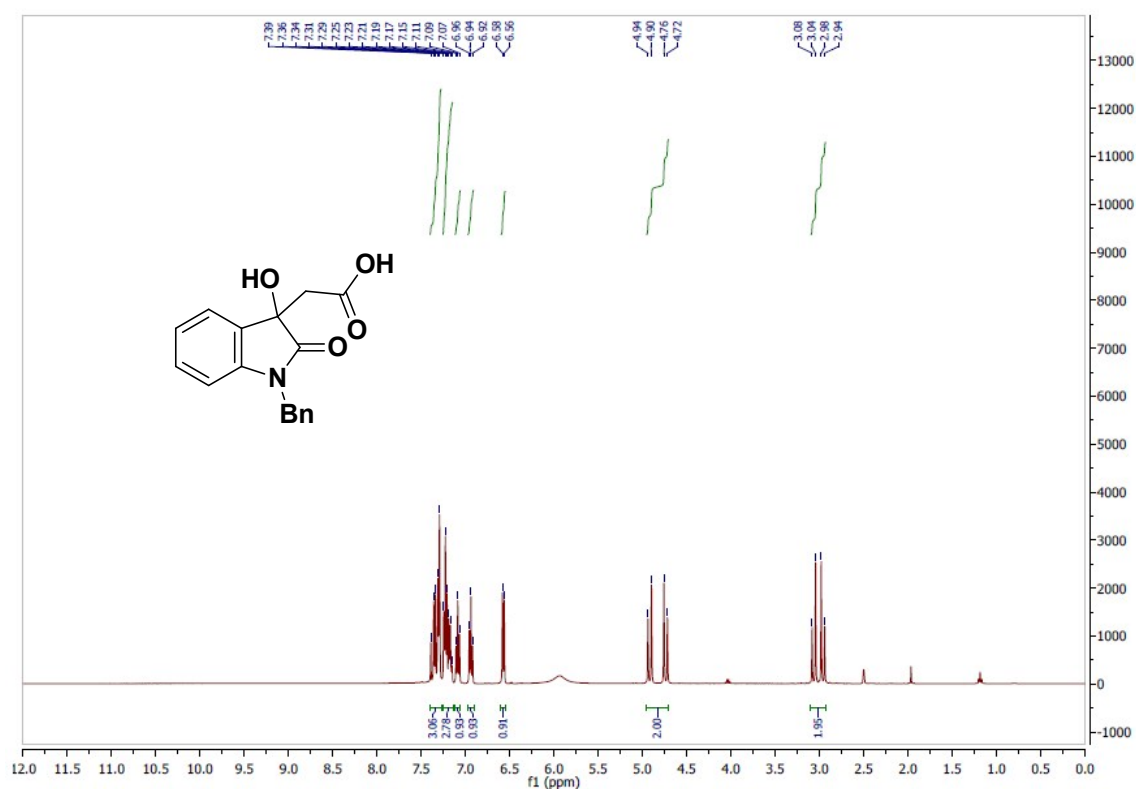
1-allyl-5-chloro-3-(4-(dimethylamino)phenyl)-3-(1H-indol-3-yl)indolin-2-one (21c):

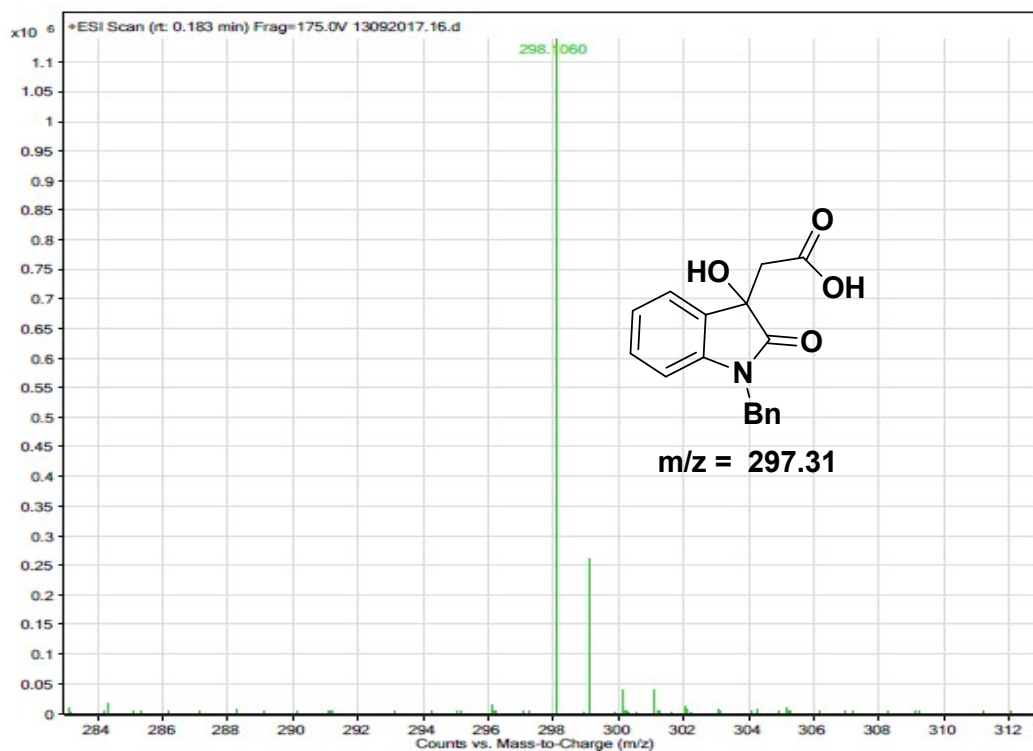


1-allyl-3-(1H-indol-3-yl)-3-(4-(methylamino)phenyl)indolin-2-one (21d):

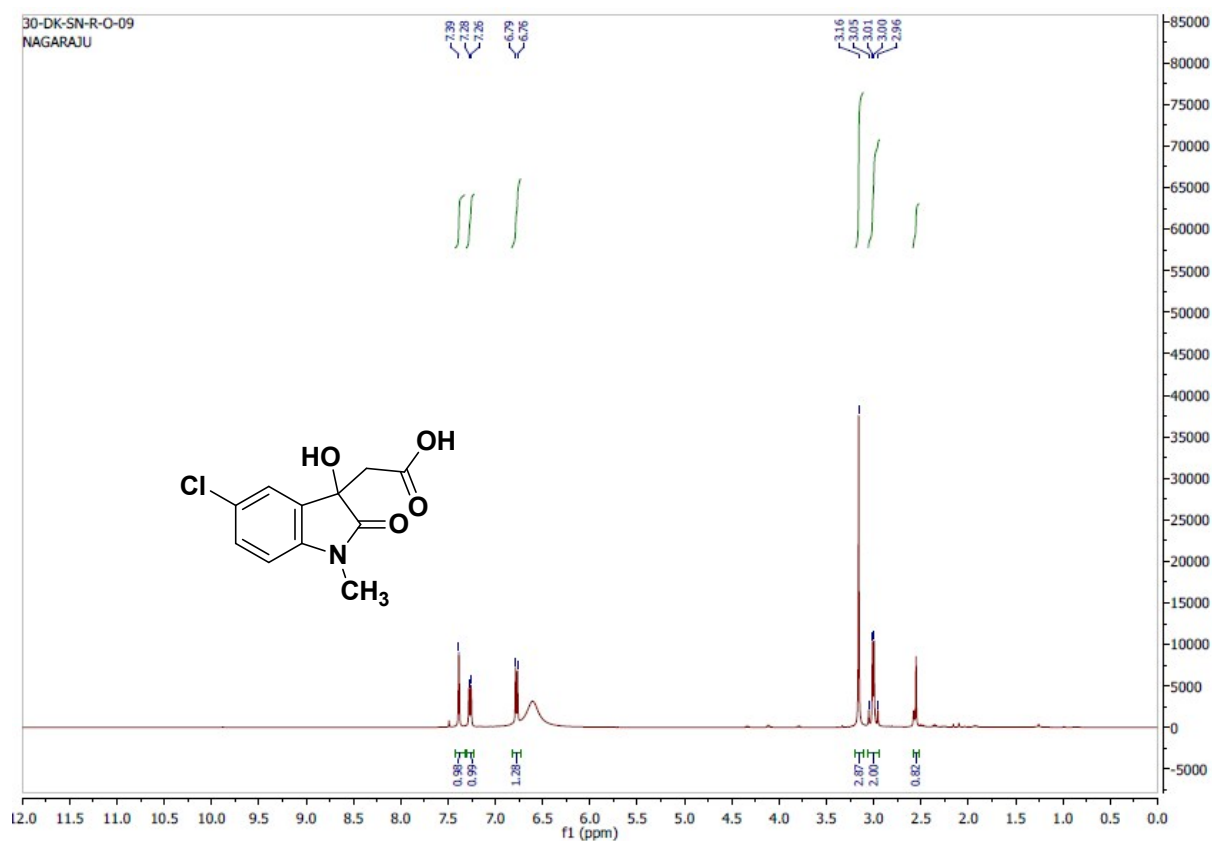


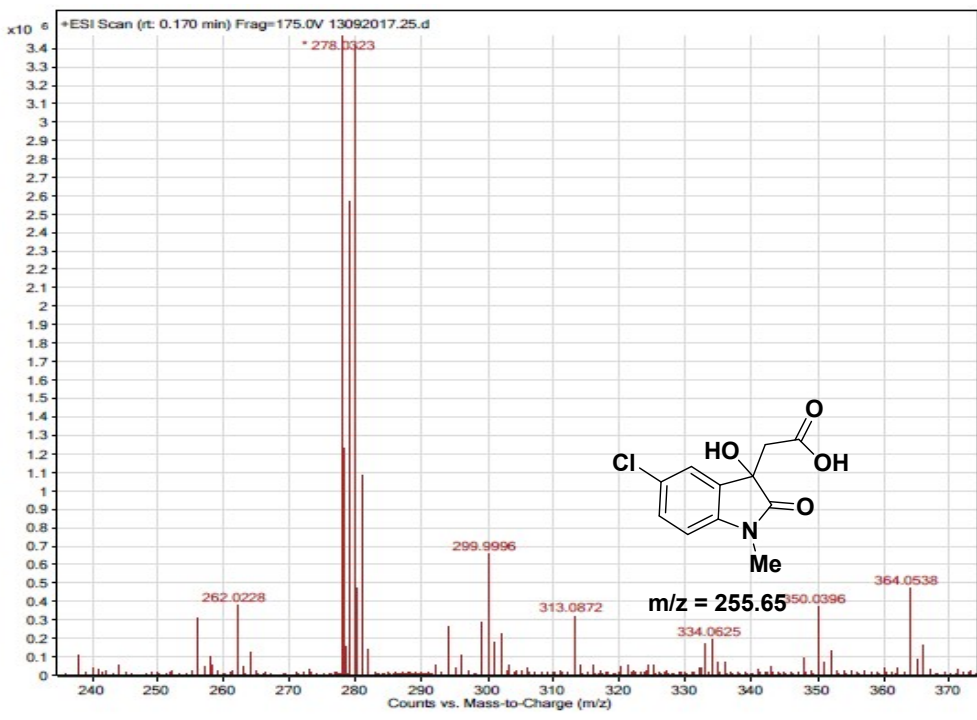
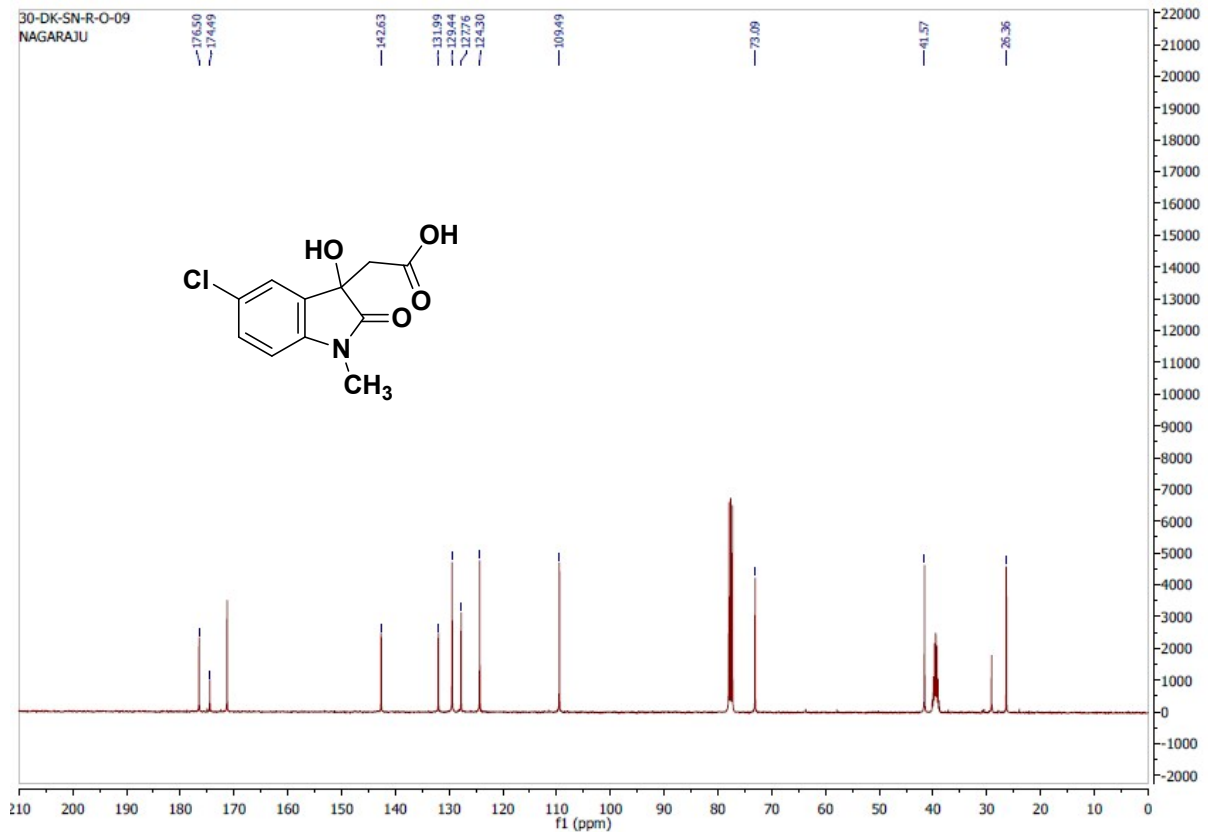
2-(1-benzyl-3-hydroxy-2-oxindolin-3-yl)acetic acid (24a):



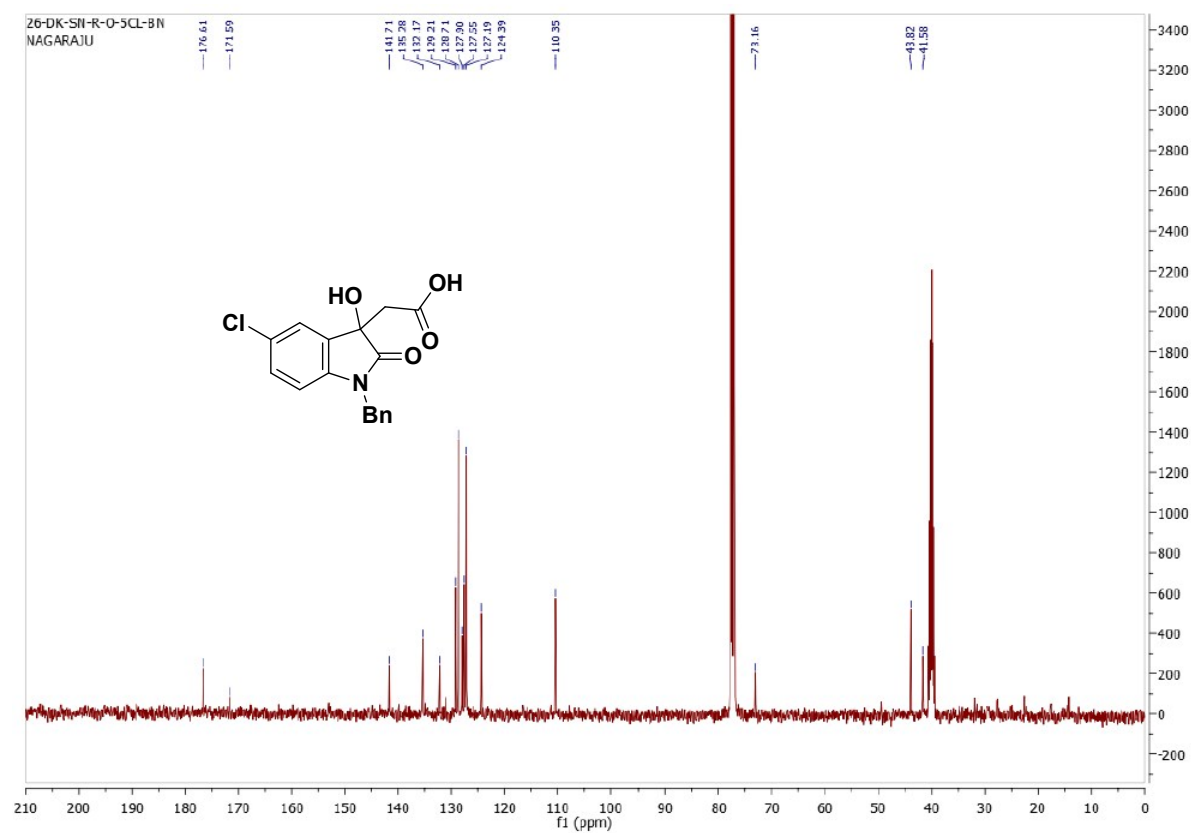
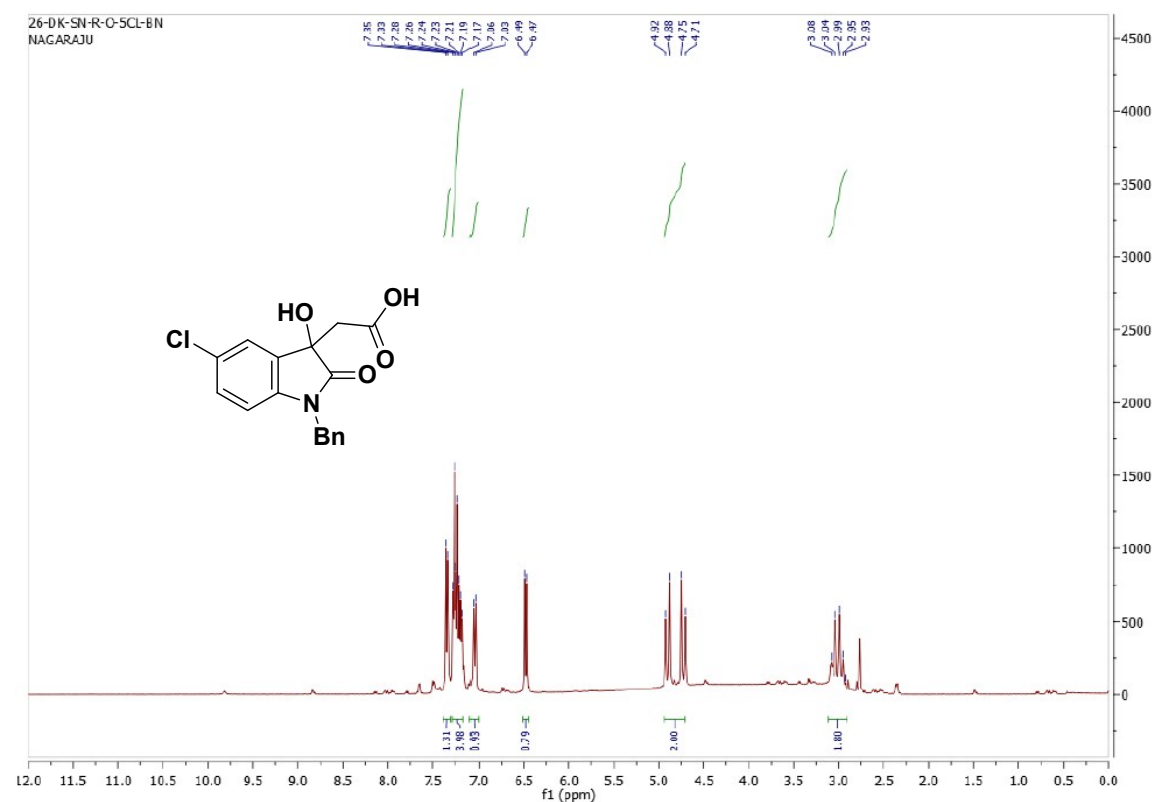


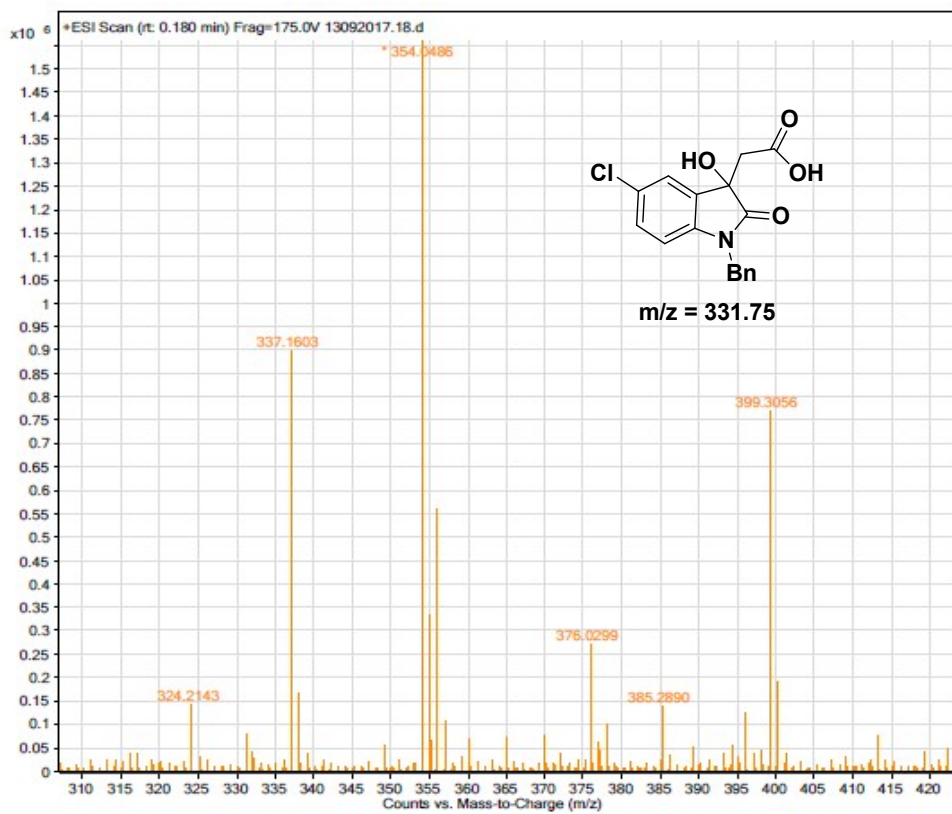
2-(5-chloro-3-hydroxy-1-methyl-2-oxindolin-3-yl)acetic acid (24b):



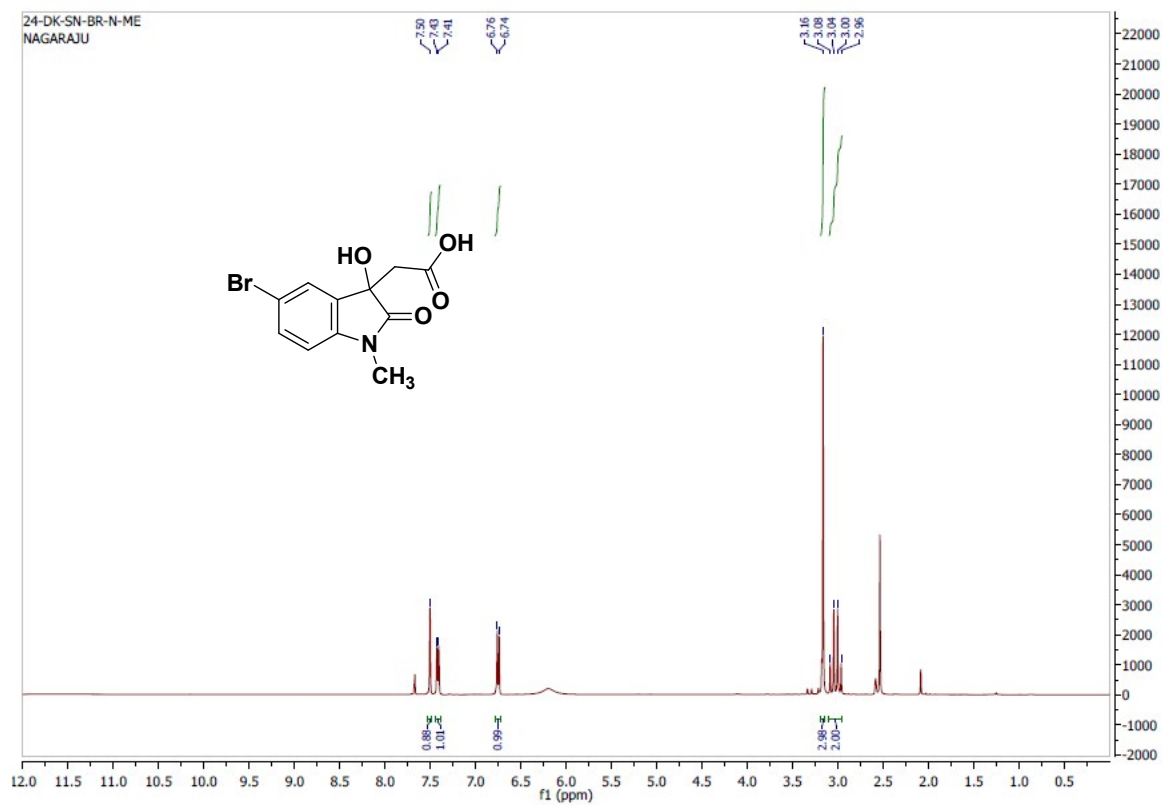


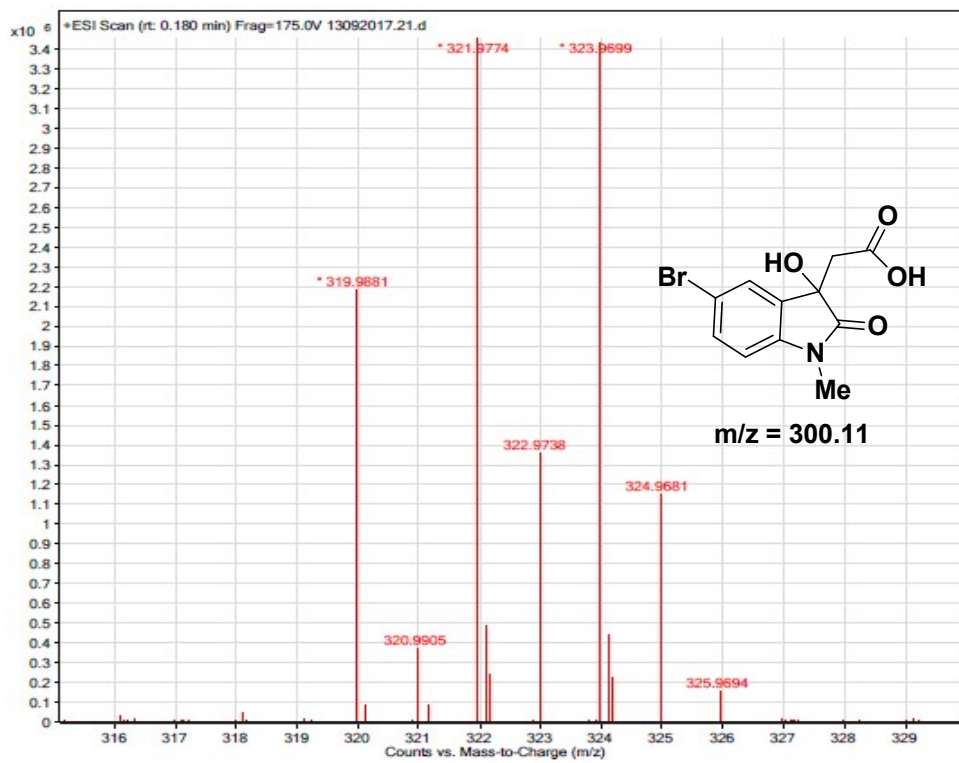
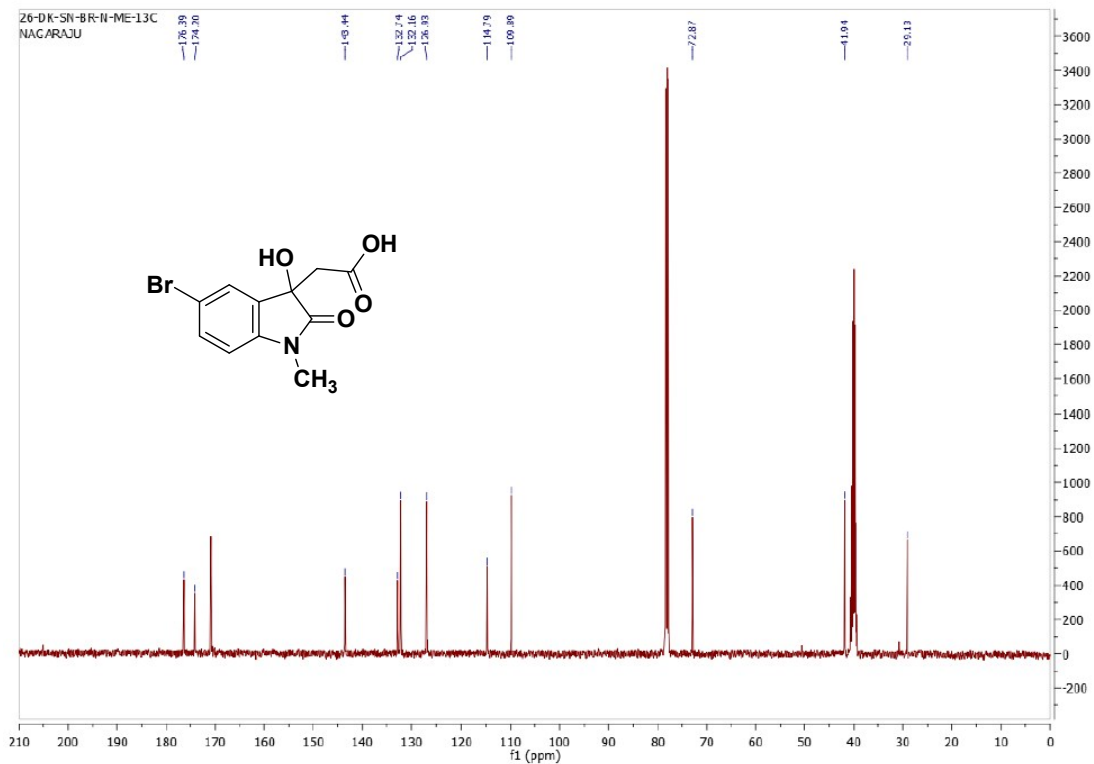
2-(1-benzyl-5-chloro-3-hydroxy-2-oxindolin-3-yl)acetic acid (24c):



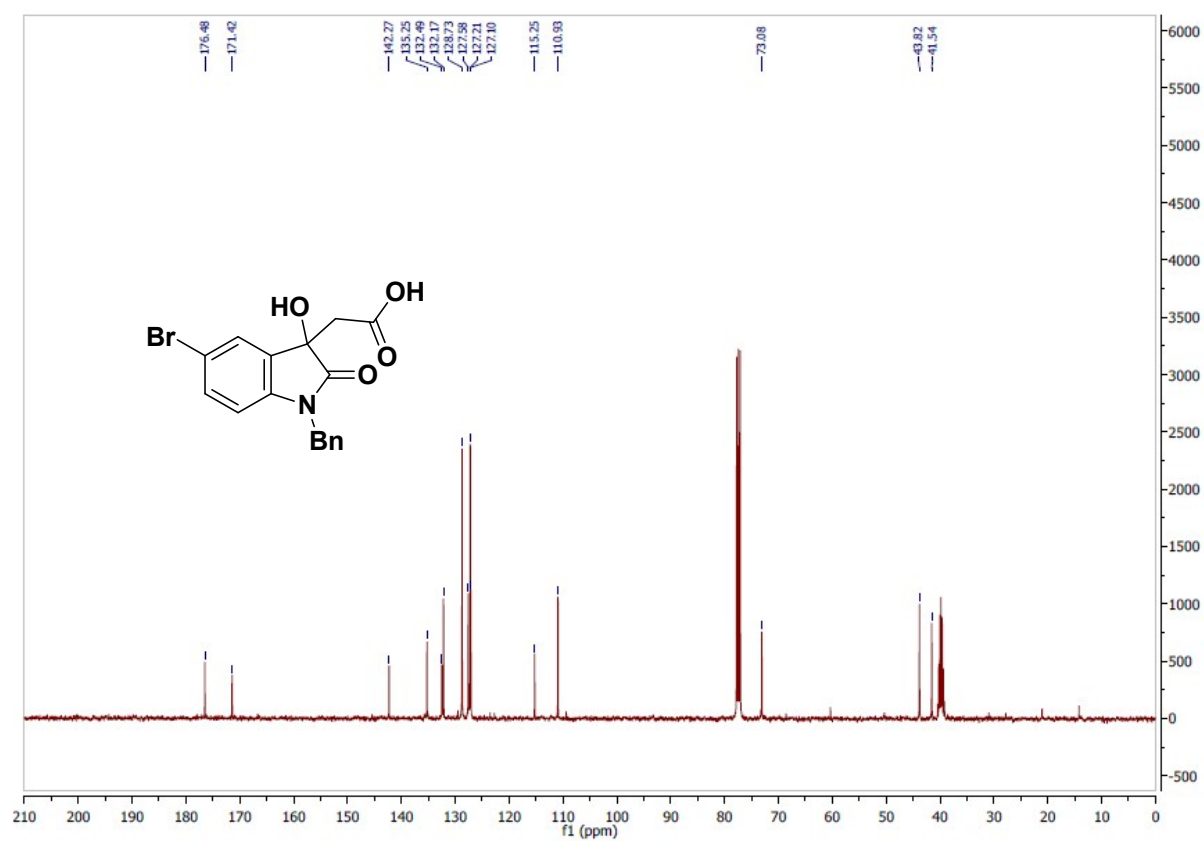
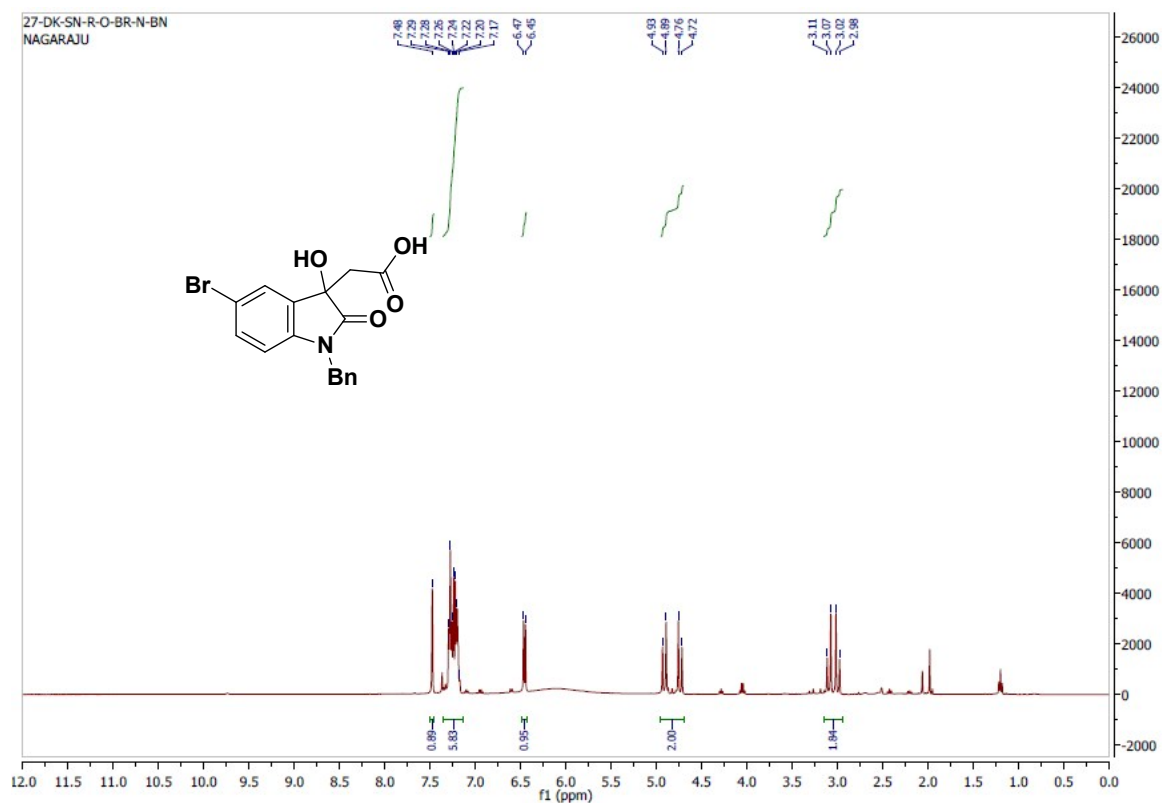


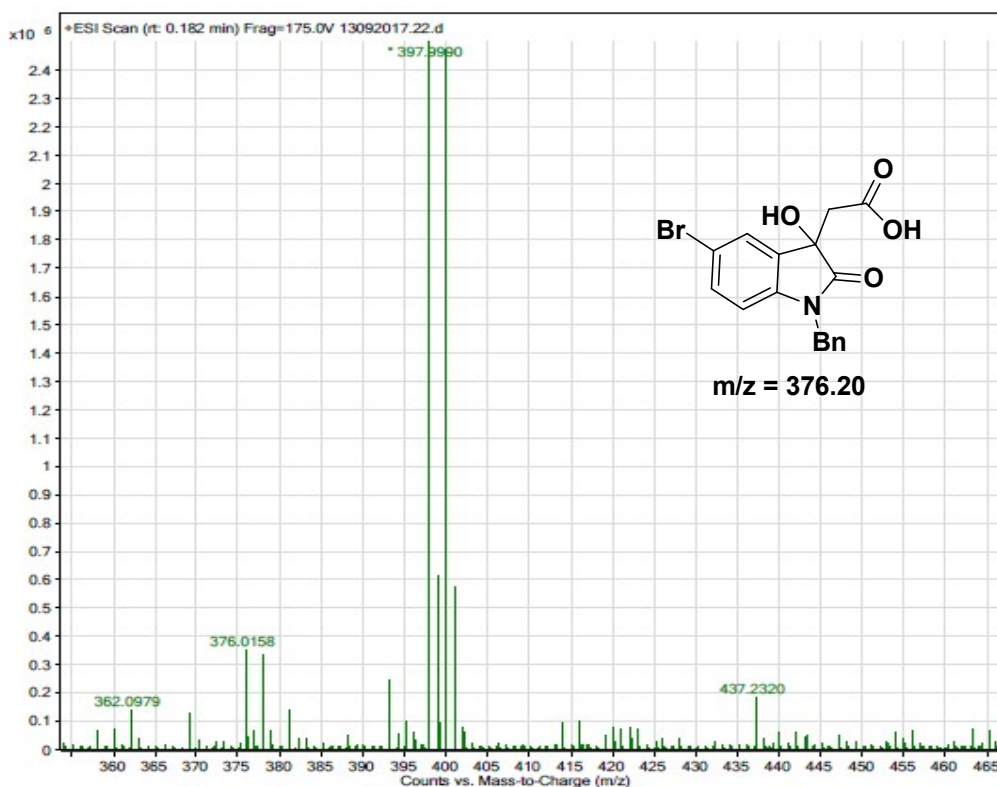
2-(5-bromo-3-hydroxy-1-methyl-2-oxindolin-3-yl)acetic acid (24d):



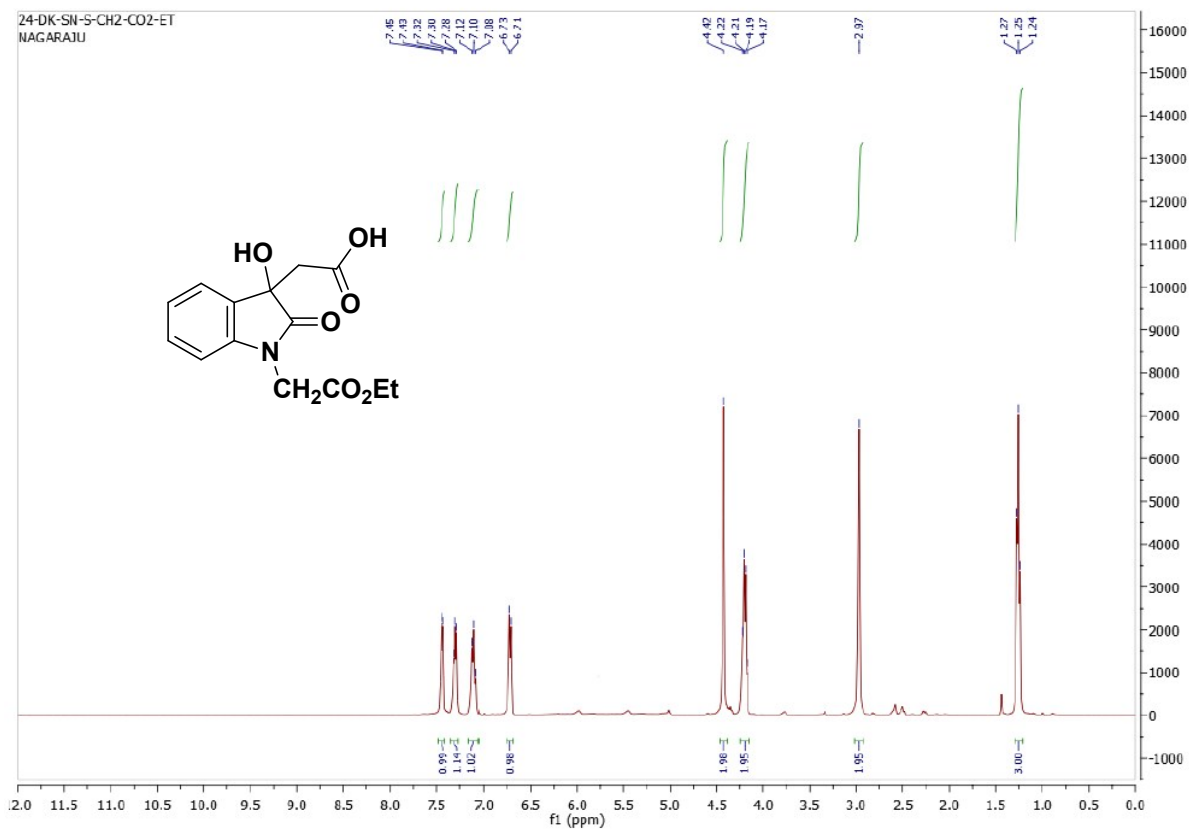


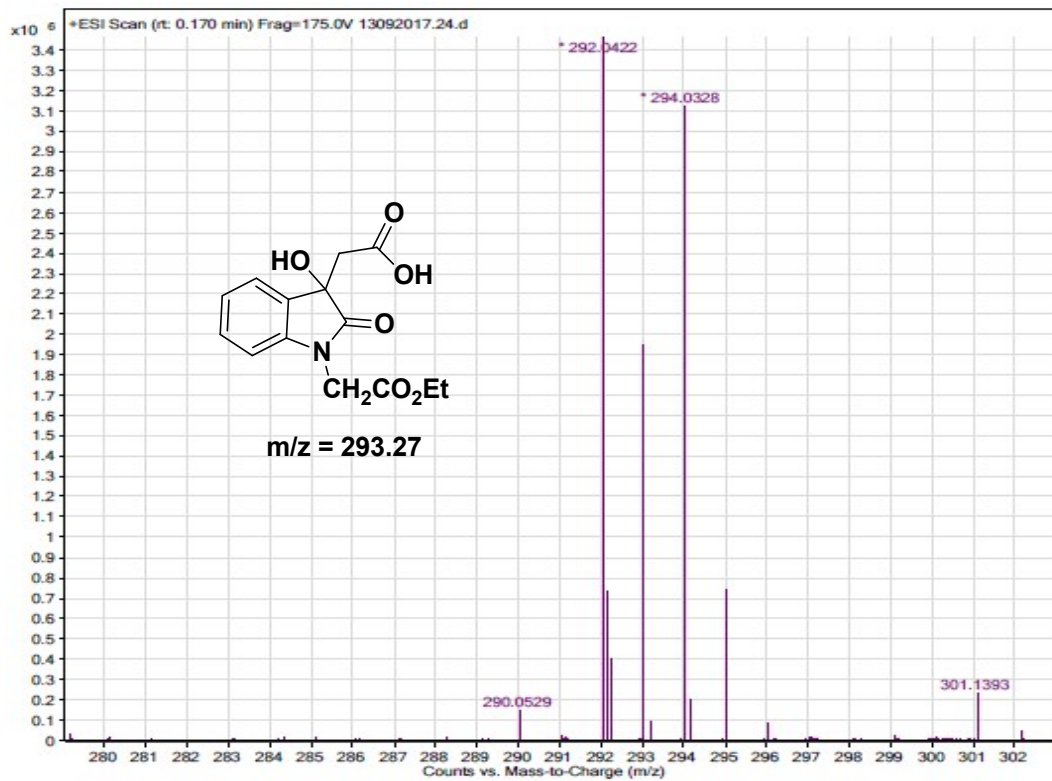
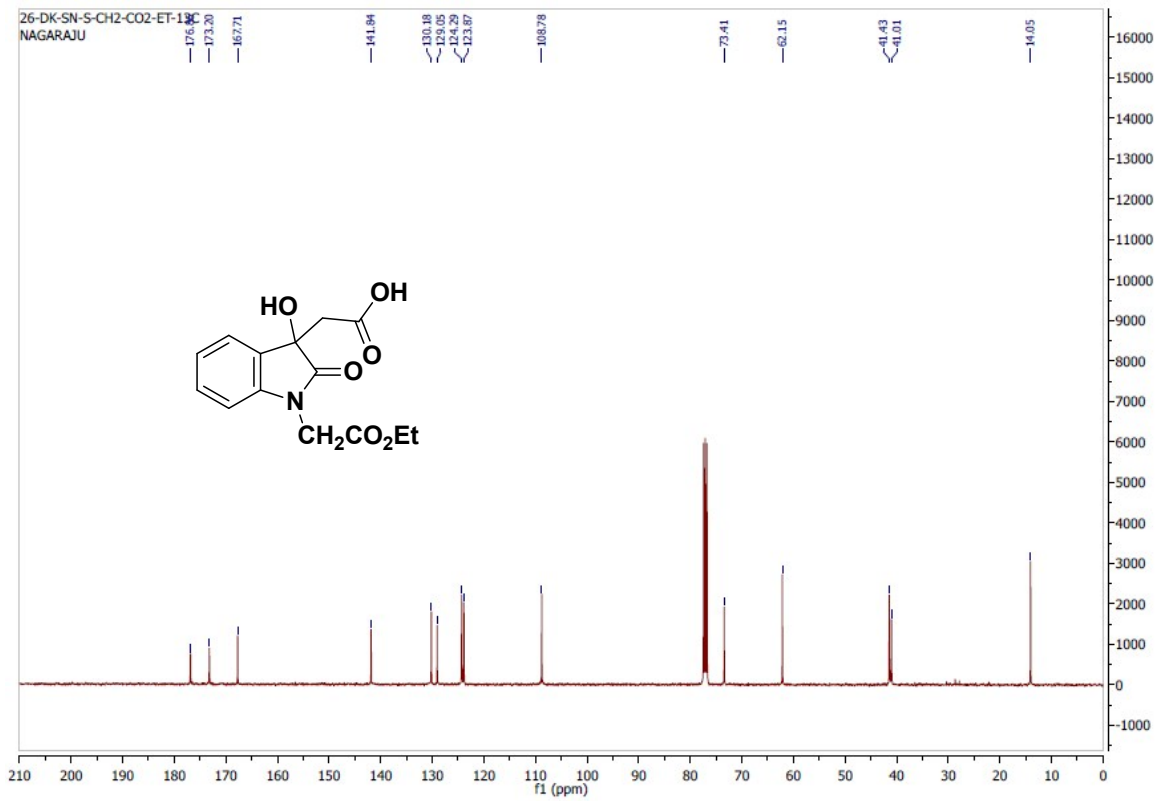
2-(1-benzyl-5-bromo-3-hydroxy-2-oxindolin-3-yl)acetic acid (24e):



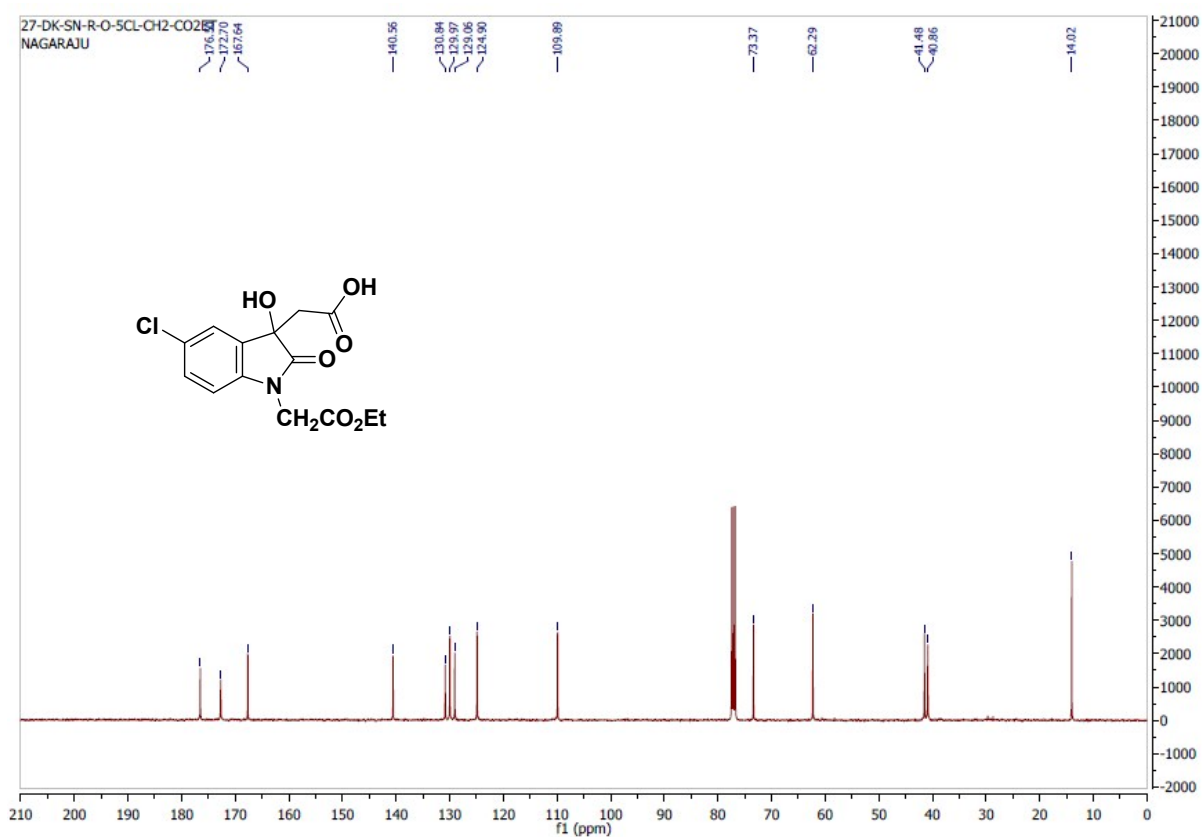
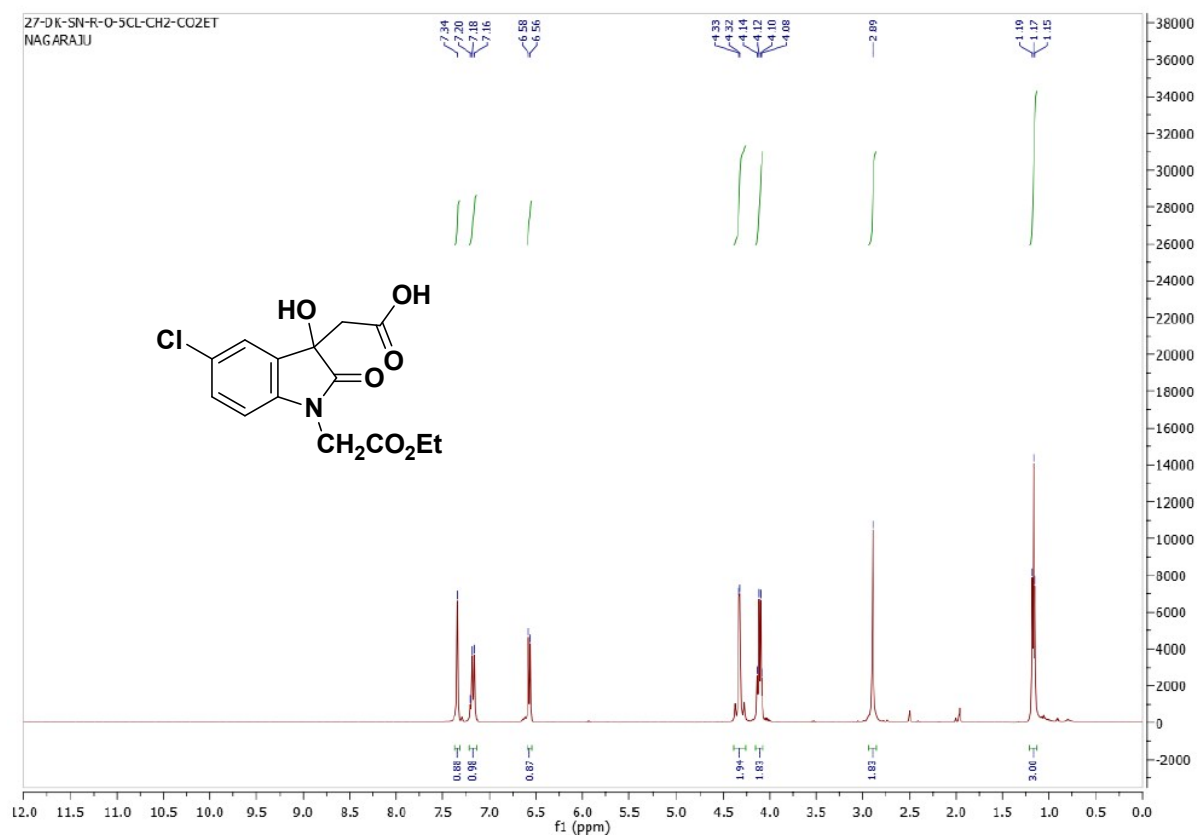


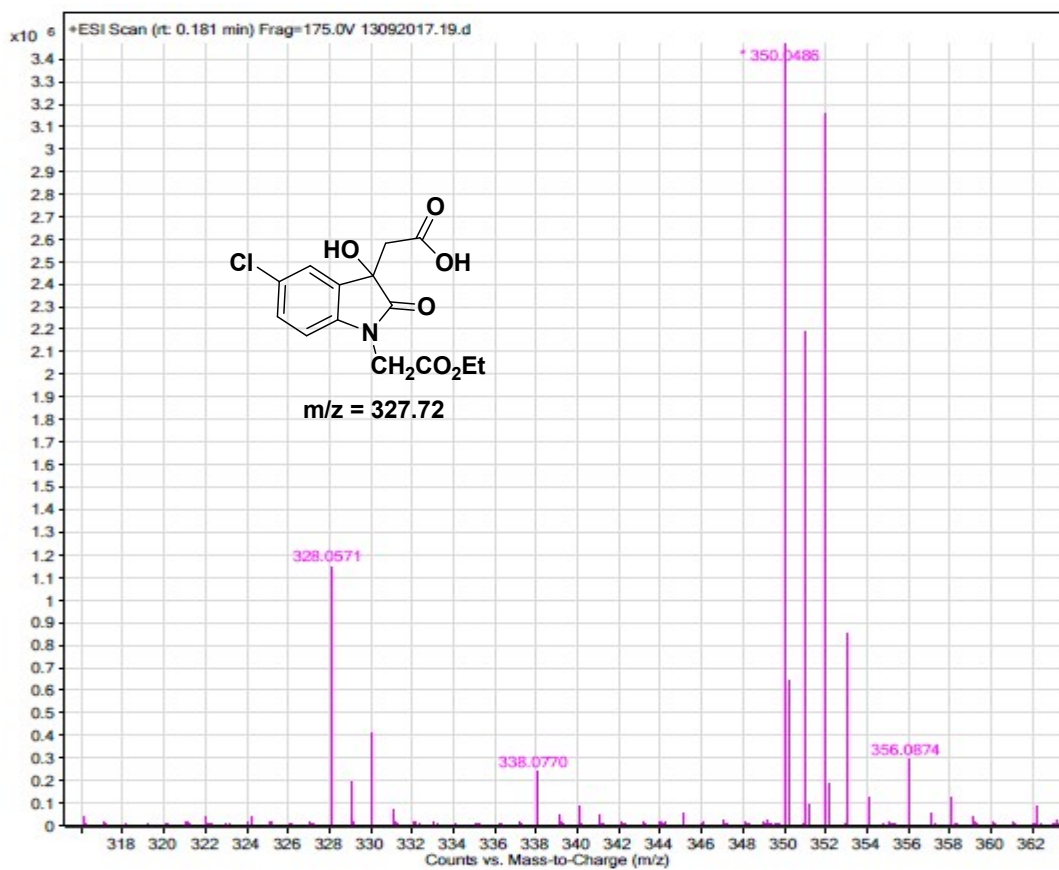
2-(1-(2-ethoxy-2-oxoethyl)-3-hydroxy-2-oxoindolin-3-yl)acetic acid (24f):





2-(5-chloro-1-(2-ethoxy-2-oxoethyl)-3-hydroxy-2-oxindolin-3-yl)acetic acid (24g):





2-(1-(2-ethoxy-2-oxoethyl)-5-fluoro-3-hydroxy-2-oxoindolin-3-yl)acetic acid (24h):

