Electronic Supplementary Material (ESI) for RSC Advances.


# Copper-Catalyzed Cross Coupling Reaction of Sulfonyl Hydrazides with 3-Aminoindazoles

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Supporting Information

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# 1. General information

All manipulations were carried out under air atmosphere. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The $^{1}H$ NMR (400 MHz), $^{13}C$ NMR (100 MHz) and $^{19}F$ NMR (376 MHz) data were recorded with $CDCl_3$ or DMSO-d6 as solvent at room temperature unless specified otherwise. The chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. $^{1}H$ NMR spectra was recorded with in deuterated solvents and calibrated to the residual solvent peak or tetramethylsilane (δ = 0 ppm).; HRMS were performed on Agilent ESI-quadrupole.

# 2. General procedures for reactions

### 2.1 General procedures of synthesis of 3 or 4

To an oven-dried 10 mL Schlenk tube equipped with a stir bar, were added substituted 1*H*-indazol-3-amine **1** (0.3 mmol, 1.5 equiv), sulfonyl hydrazides **2** (0.2 mmol), CuI (0.04 mmol, 20 mol%), $K_2CO_3$ (0.4 mmol, 2.0 equiv). Then DMSO (2.0 mL) and cumene hydroperoxide (0.8 mmol, 4.0 equiv) were added in sequence. The solution was then stirred at 40 °C for 18 h. After completion of the reaction, 5 mL of water was added and extracted by ethyl acetate (3 × 5 mL). The combined organic layer was washed with brine (5 mL) and then dried over anhydrous $Na_2SO_4$ and evaporated in vacuum. The desired products were obtained in the corresponding yields after purification by column chromatography on silica gel eluting with petroleum ether / ethyl acetate.

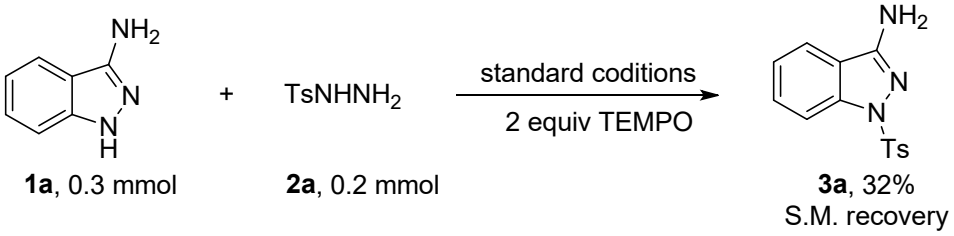
### 2.2 General procedures of synthesis of gram scale of 3a

To an oven-dried 20 mL Schlenk tube equipped with a stir bar, were added substituted 1*H*-indazol-3-amine **1a** (7.5 mmol, 0.997g), 4-methylbenzenesulfonohydrazide **2a** (5.0 mmol, 0.93g), CuI (1.0 mmol, 190 mg), $K_2CO_3$ (10.0 mmol, 1.38 g). Then DMSO (20 mL) and cumene hydroperoxide (20 mmol, 3.04 g) were added in sequence. The solution was then stirred at 40 °C for 18 h. After completion of the reaction, 30 mL of water was added and extracted by ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine (5 mL) and then dried over anhydrous $Na_2SO_4$ and evaporated in vacuum. The desired **3a** was obtained in 64% yield (0.92 g) after purification by column chromatography on silica gel eluting with petroleum ether / ethyl acetate (2:1).

# 3. Preliminary mechanism study

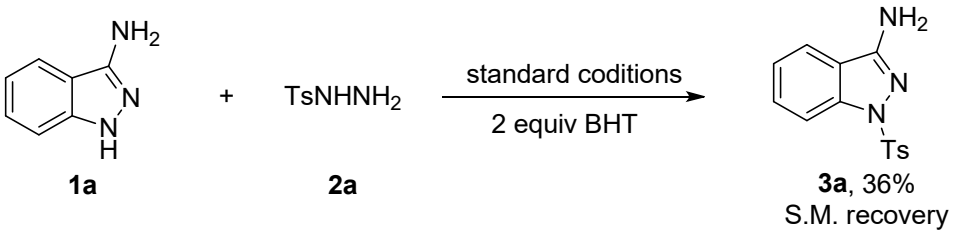
### 3.1 General procedures of synthesis of 3a in the presence of TEMPO

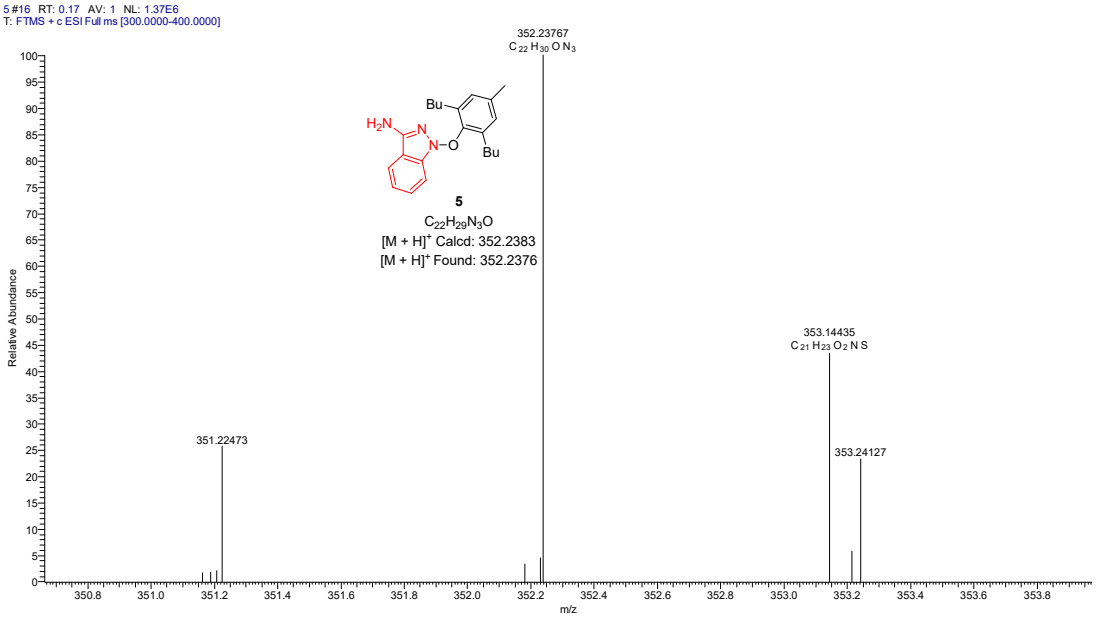
To an oven-dried 10 mL Schlenk tube equipped with a stir bar, were added 1*H*-indazol-3-amine **1a** (0.3 mmol, 40 mg), 4-methylbenzenesulfonhydrazide **2a** (0.2 mmol, 37.2 mg), CuI (20 mol%, 7.6 mg), $K_2CO_3$ (0.4 mmol, 55.2 mg) and TEMPO (0.4 mmol, 62.5 mg). Then DMSO (2.0 mL) and cumene hydroperoxide (0.8 mmol, 118 uL) were added in sequence. The solution was then stirred at 40 °C for 18 h. After completion of the reaction, apart from the target product and the starting material, no other separable substances were found by TLC detection. The desired product **3a** were obtained in 32% yield (18.4 mg) after purification by column chromatography.




### 3.2 General procedures of synthesis of 3a in the presence of BHT

To an oven-dried 10 mL Schlenk tube equipped with a stir bar, were added 1*H*-indazol-3-amine **1a** (0.3 mmol, 40 mg), 4-methylbenzenesulfonhydrazide **2a** (0.2 mmol, 37.2 mg), CuI (20 mol%, 7.6 mg), $K_2CO_3$ (0.4 mmol, 55.2 mg) and BHT (0.4 mmol, 88 mg). Then DMSO (2.0 mL) and cumene hydroperoxide (0.8 mmol, 118 uL) were added in sequence. The solution was then stirred at 40 °C for 18 h. After completion of the reaction, we observed unreacted starting materials, target product, and new compounds that could not be separated (trace amounts). Then the reaction solution was analyzed by LC-MS, compounds **5** and **6** were detected by LC-MS. And product **3a** were also obtained in 36% yield (20.6 mg) after purification by column chromatography.

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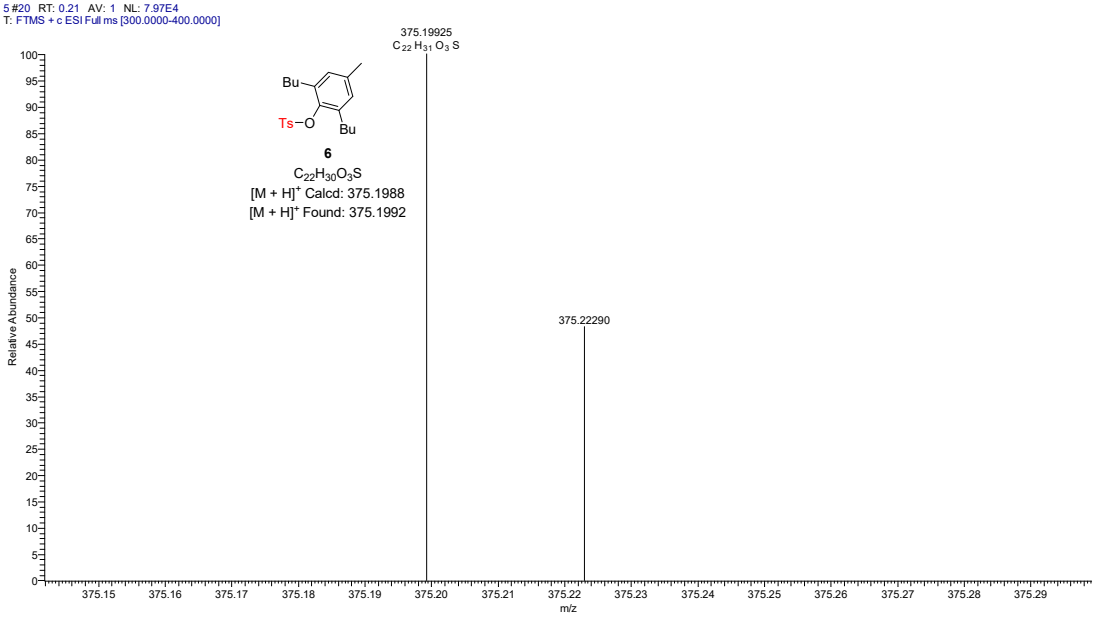
T: FTMS + c ESI Full ms [300.0000-400.0000]
352.23767
C 22 H 30 O N 3
Bu
H2N
N
N
O
Bu
5
C22H29N3O
[M + H]+ Calcd: 352.2383
[M + H]+ Found: 352.2376
353.14435
C 21 H 23 O 2 N S
351.22473
353.24127
Relative Abundance
m/z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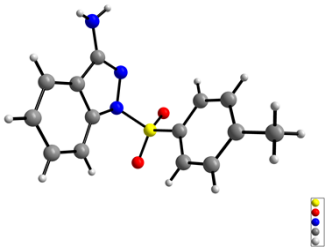
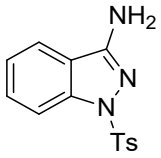
T: FTMS + c ESI Full ms [300.0000-400.0000]
375.19925
C 22 H 31 O 3 S
Bu
Ts
O
Bu
6
C22H30O3S
[M + H]+ Calcd: 375.1988
[M + H]+ Found: 375.1992
375.22290
Relative Abundance
m/z

# 4. X-ray crystal structure of 3a






**3a (CCDC 2203869 )**

***Table S1***. Crystal data and structure refinement for **3a**.

| | |
|---|---|
| Empirical formula | $C_{14}H_{13}N_3O_2S$ |
| Formula weight | 287.33 |
| Temperature | 296(2) K |
| Wavelength | 0.71073 A |
| Crystal system | Monoclinic |
| Space group | P 21/n |
| Unit cell dimensions | a = 8.3551(8) Å<br>α= 90° |
| | b = 11.7955(11) Å<br>β= 104.633(2)° |
| | c = 14.7480(13) Å<br>γ = 90° |
| Volume | 1406.3(2) $Å^3$ |
| Z | 4 |
| Density (calculated) | 1.357 $g/cm^3$ |
| Absorption coefficient | 0.235 $mm^{-1}$ |
| F(000) | 600 |
| Crystal size | 0.260 x 0.250 x 0.240 $mm^3$ |
| Theta range for data collection | 3.055 to 24.996°. |
| Index ranges | -9<=h<=9, -13<=k<=14, -17<=l<=8 |
| Reflections collected | 7002 |
| Independent reflections | 2466 [R(int) = 0.0203] |
| Completeness to theta = 24.996° | 99.8 % |
| Data / restraints / parameters | 2466 / 0 / 190 |
| Goodness-of-fit on $F^2$ | 0.989 |
| Final R indices [I>2sigma(I)] | R1 = 0.0405, wR2 = 0.1073 |

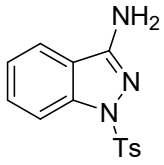
| | |
|---|---|
| R indices (all data) | R1 = 0.0498, wR2 = 0.1137 |
| Largest diff. peak and hole | 0.250 and -0.488 e.Å$^{-3}$ |

***Table S2.*** Bond lengths [pm] and angles [°] for **3a**.

| | | | | | |
|---|---|---|---|---|---|
| S(1)-O(1) | 1.4230(16) | C(7)-H(7) | 0.9300 | C(10)-C(9)-C(8) | 116.9(2) |
| S(1)-O(2) | 1.4237(17) | C(1)-H(1C) | 0.9600 | C(10)-C(9)-H(9) | 121.5 |
| S(1)-N(3) | 1.6605(16) | C(1)-H(1D) | 0.9600 | C(8)-C(9)-H(9) | 121.5 |
| S(1)-C(5) | 1.7464(18) | C(1)-H(1E) | 0.9600 | C(3)-C(4)-C(5) | 119.23(19) |
| N(3)-C(8) | 1.404(2) | O(1)-S(1)-O(2) | 120.27(11) | C(3)-C(4)-H(4) | 120.4 |
| N(3)-N(2) | 1.419(2) | O(1)-S(1)-N(3) | 106.37(9) | C(5)-C(4)-H(4) | 120.4 |
| N(2)-C(14) | 1.310(2) | O(2)-S(1)-N(3) | 104.39(9) | C(7)-C(2)-C(3) | 118.16(19) |
| C(13)-C(12) | 1.388(3) | O(1)-S(1)-C(5) | 109.95(9) | C(7)-C(2)-C(1) | 121.0(2) |
| C(13)-C(8) | 1.390(3) | O(2)-S(1)-C(5) | 108.47(10) | C(3)-C(2)-C(1) | 120.8(2) |
| C(13)-C(14) | 1.451(3) | N(3)-S(1)-C(5) | 106.45(8) | C(9)-C(10)-C(11) | 121.8(2) |
| N(1)-C(14) | 1.357(3) | C(8)-N(3)-N(2) | 110.09(15) | C(9)-C(10)-H(10) | 119.1 |
| N(1)-H(1A) | 0.75(3) | N(2)-N(3)-S(1) | 115.40(12) | C(11)-C(10)-H(10) | 119.1 |
| N(1)-H(1B) | 0.84(3) | C(14)-N(2)-N(3) | 105.51(15) | C(4)-C(3)-C(2) | 121.5(2) |
| C(8)-C(9) | 1.385(3) | C(12)-C(13)-C(8) | 120.69(18) | C(4)-C(3)-H(3) | 119.2 |
| C(5)-C(6) | 1.377(3) | C(12)-C(13)-C(14) | 133.97(18) | C(2)-C(3)-H(3) | 119.2 |
| C(5)-C(4) | 1.384(3) | C(8)-C(13)-C(14) | 105.25(16) | C(7)-C(6)-C(5) | 119.6(2) |
| C(12)-C(11) | 1.373(3) | C(14)-N(1)-H(1A) | 112(2) | C(7)-C(6)-H(6) | 120.2 |
| C(12)-H(12) | 0.9300 | C(14)-N(1)-H(1B) | 122(2) | C(5)-C(6)-H(6) | 120.2 |
| C(9)-C(10) | 1.378(3) | H(1A)-N(1)-H(1B) | 119(3) | C(12)-C(11)-C(10) | 121.0(2) |
| C(9)-H(9) | 0.9300 | C(9)-C(8)-C(13) | 121.71(18) | C(12)-C(11)-H(11) | 119.5 |
| C(4)-C(3) | 1.373(3) | C(9)-C(8)-N(3) | 131.79(19) | C(10)-C(11)-H(11) | 119.5 |
| C(4)-H(4) | 0.9300 | C(13)-C(8)-N(3) | 106.50(16) | C(6)-C(7)-C(2) | 121.3(2) |
| C(2)-C(7) | 1.378(3) | C(6)-C(5)-C(4) | 120.16(18) | C(6)-C(7)-H(7) | 119.3 |
| C(2)-C(3) | 1.382(3) | C(6)-C(5)-S(1) | 120.24(15) | C(2)-C(7)-H(7) | 119.3 |
| C(2)-C(1) | 1.511(3) | C(4)-C(5)-S(1) | 119.59(15) | C(2)-C(1)-H(1C) | 109.5 |

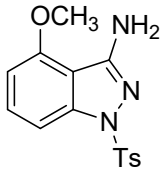
| | | | | | |
|---|---|---|---|---|---|
| C(10)-C(11) | 1.394(3) | N(2)-C(14)-N(1) | 121.1(2) | C(2)-C(1)-H(1D) | 109.5 |
| C(10)-H(10) | 0.9300 | N(2)-C(14)-C(13) | 112.13(17) | H(1C)-C(1)-H(1D) | 109.5 |
| C(3)-H(3) | 0.9300 | N(1)-C(14)-C(13) | 126.8(2) | C(2)-C(1)-H(1E) | 109.5 |
| C(6)-C(7) | 1.375(3) | C(11)-C(12)-C(13) | 117.9(2) | H(1C)-C(1)-H(1E) | 109.5 |
| C(6)-H(6) | 0.9300 | C(11)-C(12)-H(12) | 121.1 | H(1D)-C(1)-H(1E) | 109.5 |
| C(11)-H(11) | 0.9300 | C(13)-C(12)-H(12) | 121.1 | | |

# 5. Compound characterizations



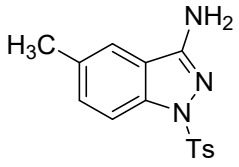
**3a**

**1-tosyl-1*H*-indazol-3-amine (3a)**. Brown solid (42 mg, 73% yield); mp 184-186 °C; $^1$H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.27 (dd, *J* = 9.2, 5.7 Hz, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 4.79 (s, 2H), 2.31 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 154.0, 144.6, 142.4, 133.9, 129.7, 129.5, 127.4, 123.8, 119.7, 119.4, 114.3, 21.5; HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{13}N_3O_2S$: 288.0801, Found: 288.0798 ($M+H^+$).



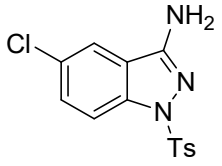
**3b**

**4-methoxy-1-tosyl-1*H*-indazol-3-amine (3b)**. White solid (41.8 mg, 66% yield); mp 212-213 °C; $^1$H NMR (400 MHz, DMSO) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.55 – 7.44 (m, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 7.7 Hz, 1H), 6.08 (s, 2H), 3.84 (s, 3H), 2.27 (s, 3H); $^{13}$C NMR (101 MHz, DMSO) δ 155.2, 154.9, 145.3, 144.6, 133.5, 132.1, 130.1, 127.4, 110.3, 106.6, 105.2, 56.1, 21.4; HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{15}N_3O_3S$: 318.0907, Found: 318.0907 ($M+H^+$).



**3c**

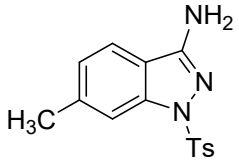
**5-methyl-1-tosyl-1*H*-indazol-3-amine (3c)**. Yellow solid (51.2 mg, 85% yield); mp 204-205 °C; $^1$H NMR (400 MHz, DMSO) δ 7.85 (d, *J* = 8.5 Hz, 1H), 7.56 (d, *J* = 7.4 Hz, 3H), 7.39 (d, *J* = 8.5 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.46 (s, 2H), 2.37 (s, 3H), 2.27 (s, 3H); $^{13}$C NMR (101 MHz, DMSO) δ 156.0, 145.1, 141.1, 133.9, 133.4, 131.5, 130.1, 127.4, 121.6, 121.0, 114.1, 21.4, 21.2; HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{15}N_3O_2S$: 302.0958, Found: 302.0954 ($M+H^+$).



**3d**

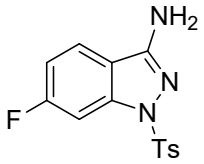
**5-chloro-1-tosyl-1*H*-indazol-3-amine (3d)**. Yellow solid (31.5 mg, 49% yield); mp 148-150 °C;

$^1$H NMR (400 MHz, DMSO) δ 7.97 (d, *J* = 8.9 Hz, 1H), 7.92 (s, 1H), 7.61 (t, *J* = 8.3 Hz, 3H), 7.32 (d, *J* = 7.9 Hz, 2H), 6.60 (s, 2H), 2.31 (s, 3H); $^{13}$C NMR (101 MHz, DMSO) δ 155.1, 145.5, 141.2, 133.2, 130.3, 130.2, 128.7, 127.5, 122.4, 121.2, 115.9, 21.5; HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{12}ClN_3O_2S$: 322.0412, Found: 322.0407 ($M+H^+$).



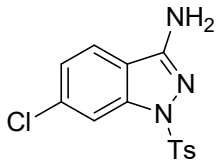

**3e**

**6-methyl-1-tosyl-1*H*-indazol-3-amine (3e)**. Brown solid (48.2 mg, 80% yield); mp 200-201 °C; $^1$H NMR (400 MHz, DMSO) δ 7.80 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 1H), 6.46 (s, 2H), 2.47 (s, 3H), 2.26 (s, 3H); $^{13}$C NMR (101 MHz, DMSO) δ 155.9, 145.1, 143.2, 140.3, 133.7, 130.1, 127.5, 126.0, 121.1, 119.2, 114.1, 22.1, 21.4; HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{15}N_3O_2S$ 302.0958, Found: 302.0954 ($M+H^+$).



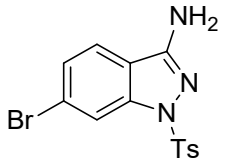

**3f**

**6-fluoro-1-tosyl-1*H*-indazol-3-amine (3f)**. Yellow solid (50 mg, 82% yield); mp 68-70 °C; $^1$H NMR (400 MHz, DMSO) δ 7.88 (dd, *J* = 8.4, 5.3 Hz, 1H), 7.66 (dd, *J* = 15.7, 8.8 Hz, 3H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 8.9 Hz, 1H), 6.61 (s, 2H), 2.30 (s, 3H); $^{13}$C NMR (101 MHz, DMSO) δ 164.8, 162.3, 155.6, 145.5, 143.4, 143.2, 133.3, 130.3, 127.6, 123.7, 123.6, 117.9, 113.2, 113.0, 101.2, 100.9, 21.5; HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{12}FN_3O_2S$ 306.0707, Found: 306.0703 ($M+H^+$).



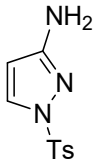

**3g**

**6-chloro-1-tosyl-1*H*-indazol-3-amine (3g)**. Yellowish brown solid (50.7 mg, 79% yield); mp 210-212 °C; $^1$H NMR (400 MHz, DMSO) δ 7.96 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 2H), 6.62 (s, 2H), 2.30 (s, 3H); $^{13}$C NMR (101 MHz, DMSO) δ 155.4, 145.6, 143.0, 135.2, 133.4, 130.3, 127.6, 124.9, 123.2, 119.9, 113.8, 21.5; HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{12}ClN_3O_2S$ 322.0412, Found: 322.0408 ($M+H^+$).



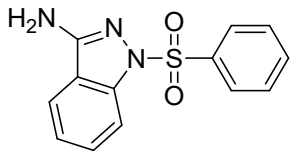
**3h**

**6-bromo-1-tosyl-1*H*-indazol-3-amine (3h)**. Brown solid (47.5 mg, 65% yield); mp 206-207 °C; $^1$H NMR (400 MHz, DMSO) δ 8.11 (s, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.63 (s, 2H), 2.30 (s, 3H); $^{13}$C NMR (101 MHz, DMSO) δ 155.5, 145.6, 143.2, 133.4, 130.3, 127.6, 127.5, 123.7, 123.4, 120.2, 116.7, 21.5; HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{12}BrN_3O_2S$ 365.9906, Found: 365.9901 ($M+H^+$).



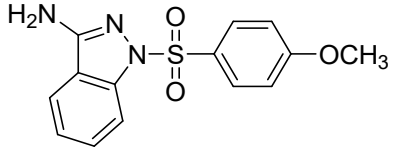
**3i**

**1-tosyl-1*H*-pyrazol-3-amine (3i)**. White solid (27.2 mg, 57%); mp 150-152 °C; $^1$H NMR (400 MHz, DMSO) δ 7.99 (d, *J* = 2.4 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 5.85 (d, *J* = 2.5 Hz, 1H), 5.59 (s, 2H), 2.38 (s, 3H); $^{13}$C NMR (101 MHz, DMSO) δ 161.1, 145.5, 134.9, 134.4, 130.4, 127.7, 102.2, 21.6; HRMS (ESI-TOF): Anal. Calcd. For $C_{10}H_{11}N_3O_2S$ 238.0645, Found: 238.0647 ($M+H^+$).



**4a**

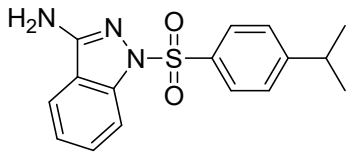
**1-(phenylsulfonyl)-1*H*-indazol-3-amine (4a)**. Yellow solid (45.3 mg, 83% yield); mp 187-190 °C; $^1$H NMR (400 MHz, DMSO) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.66 – 7.56 (m, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 6.56 (s, 2H); $^{13}$C NMR (101 MHz, DMSO) δ 156.2, 142.6, 136.3, 134.5, 130.2, 129.7, 127.4, 124.5, 121.6, 121.2, 114.3; HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{11}N_3O_2S$ 274.0645, Found: 274.0641 ($M+H^+$).



**4b**

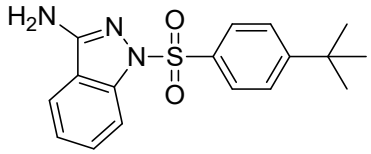
**1-((4-methoxyphenyl)sulfonyl)-1*H*-indazol-3-amine (4b)**. Yellow solid (42.4 mg, 70% yield); mp 110-112 °C; $^1$H NMR (400 MHz, DMSO) δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.52 (s, 2H), 3.76 (s, 3H).; $^{13}$C NMR (101 MHz, DMSO) δ 163.8, 156.0, 142.6, 130.1, 129.8, 127.9, 124.4,

121.5, 114.9, 114.3, 79.6, 56.2; HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{13}N_3O_3S$ 304.0750, Found: 304.0746 ($M+H^+$).



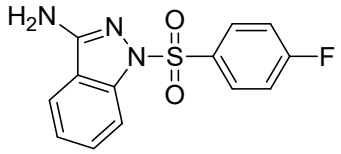
**4c**

**1-((4-isopropylphenyl)sulfonyl)-1*H*-indazol-3-amine (4c)**. Yellow solid (44.1 mg, 70% yield); mp 118-120 °C; $^1$H NMR (400 MHz, DMSO) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.40 – 7.29 (m, 3H), 6.54 (s, 2H), 2.93 – 2.82 (m, 1H), 1.12 (s, 3H), 1.11 (s, 3H); $^{13}$C NMR (101 MHz, DMSO) δ 155.9, 155.5, 142.4, 134.1, 130.2, 127.7, 127.6, 124.4, 121.6, 121.0, 114.1, 33.8, 23.7; HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{17}N_3O_2S$ 316.1114, Found: 316.1111 ($M+H^+$).



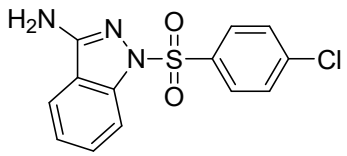
**4d**

**1-((4-(*tert*-butyl)phenyl)sulfonyl)-1*H*-indazol-3-amine (4d)**. Yellow solid (54 mg, 82% yield); mp 116-118 °C; $^1$H NMR (400 MHz, DMSO) δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.61 – 7.49 (m, 3H), 7.33 (t, *J* = 7.5 Hz, 1H), 6.54 (s, 2H), 1.21 (s, 9H); $^{13}$C NMR (101 MHz, DMSO) δ 157.7, 155.8, 142.4, 133.9, 130.2, 127.4, 126.7, 124.4, 121.6, 121.0, 114.1, 35.4, 31.1; HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{19}N_3O_2S$ 330.1271, Found: 330.1267 ($M+H^+$).



**4e**

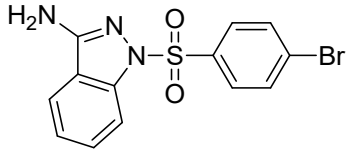
**1-((4-fluorophenyl)sulfonyl)-1*H*-indazol-3-amine (4e)**. Brown solid (44.8 mg, 77% yield); mp 182-184 °C; $^1$H NMR (400 MHz, DMSO) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.88 – 7.69 (m, 3H), 7.59 (t, *J* = 7.7 Hz, 1H), 7.35 (dd, *J* = 10.5, 6.9 Hz, 3H), 6.59 (s, 2H); $^{19}$F NMR (376 MHz, DMSO) δ -103.76; $^{13}$C NMR (101 MHz, DMSO) δ 165.5 (d, *J* = 255.5 Hz), 156.3, 142.6, 132.6 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 10.1 Hz), 130.3, 124.7, 121.6, 121.3, 117.1 (d, *J* = 22.2 Hz), 114.3; HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{10}FN_3O_2S$ 292.0551, Found: 292.0546 ($M+H^+$).



**4f**

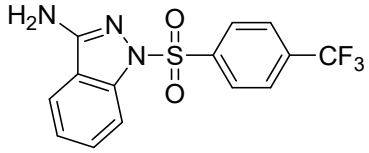
**1-((4-chlorophenyl)sulfonyl)-1*H*-indazol-3-amine (4f)**. Brown solid (47.9 mg, 78% yield); mp

169-170 °C; $^1$H NMR (400 MHz, DMSO) δ 7.97 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 3H), 7.35 (t, *J* = 7.5 Hz, 1H), 6.61 (s, 2H); $^{13}$C NMR (101 MHz, DMSO) δ 156.4, 142.5, 139.6, 135.0, 130.4, 129.9, 129.3, 124.8, 121.7, 121.3, 114.3; HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{10}ClN_3O_2S$ 308.0250, Found: 308.0250 ($M+H^+$).



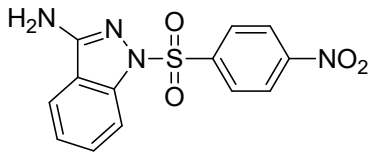
**4g**

**1-((4-bromophenyl)sulfonyl)-1*H*-indazol-3-amine (4g)**. Yellow solid (49.8 mg, 71% yield); mp 110-111 °C; $^1$H NMR (400 MHz, DMSO) δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.65 – 7.56 (m, 3H), 7.36 (t, *J* = 7.5 Hz, 1H), 6.61 (s, 2H); $^{13}$C NMR (101 MHz, DMSO) δ 156.4, 142.5, 135.4, 132.9, 130.4, 129.3, 128.7, 124.8, 121.7, 121.3, 114.3; HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{10}BrN_3O_2S$ 351.9750, Found: 351.9743 ($M+H^+$).



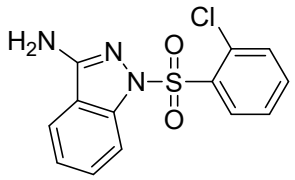
**4h**

**1-((4-(trifluoromethyl)phenyl)sulfonyl)-1*H*-indazol-3-amine (4h)**. Yellow solid (57.3 mg, 84% yield); mp 182-183 °C; $^1$H NMR (400 MHz, DMSO) δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.91 (q, *J* = 9.1 Hz, 4H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 6.64 (s, 2H); $^{19}$F NMR (376 MHz, DMSO) δ -61.92; $^{13}$C NMR (101 MHz, DMSO) δ 156.5, 142.4, 140.0, 133.0 (q, *J* = 32.3 Hz), 130.5, 128.5, 127.0 (d, *J* = 3.0 Hz), 124.9, 122.2, 121.8, 121.4, 114.2; HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{10}F_3N_3O_2S$ 342.0519, Found: 342.0514 ($M+H^+$).



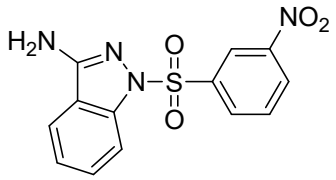
**4i**

**1-((4-nitrophenyl)sulfonyl)-1*H*-indazol-3-amine (4i)**. Brown solid (54.1 mg, 85% yield); mp 196-198 °C; $^1$H NMR (400 MHz, DMSO) δ 8.32 (d, *J* = 8.5 Hz, 2H), 7.98 (t, *J* = 9.9 Hz, 3H), 7.82 (d, *J* = 7.9 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 6.68 (s, 2H); $^{13}$C NMR (101 MHz, DMSO) δ 156.6, 151.0, 142.3, 141.2, 130.6, 129.1, 125.0, 121.8, 121.4, 114.3; HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{10}N_4O_4S$ 319.0496, Found: 319.0491 ($M+H^+$).



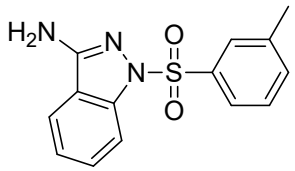
**4j**

**1-((2-chlorophenyl)sulfonyl)-1*H*-indazol-3-amine (4j)**. Brown solid (24.6 mg, 40% yield); mp 156-158 °C; $^{1}$H NMR (400 MHz, DMSO) δ 8.03 (d, *J* = 7.9 Hz, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.73 – 7.67 (m, 1H), 7.66 – 7.56 (m, 3H), 7.35 (t, *J* = 7.5 Hz, 1H), 6.53 (s, 2H); $^{13}$C NMR (101 MHz, DMSO) δ 155.1, 142.4, 136.0, 135.8, 132.6, 132.2, 132.1, 130.0, 128.4, 123.9, 121.7, 119.7, 114.1; HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{10}ClN_3O_2S$ 308.0255, Found: 308.0251 ($M+H^+$).



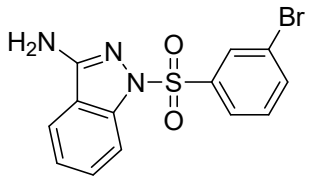
**4k**

**1-((3-nitrophenyl)sulfonyl)-1*H*-indazol-3-amine (4k)**. Yellow solid (26.7 mg, 42% yield); mp 74-76 °C; $^{1}$H NMR (400 MHz, DMSO) δ 8.45 (d, *J* = 8.2 Hz, 1H), 8.38 (s, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 8.07 – 7.89 (m, 2H), 7.82 (t, *J* = 7.6 Hz, 2H), 7.64 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 6.69 (s, 2H); $^{13}$C NMR (101 MHz, DMSO) δ 156.8, 148.1, 142.4, 137.4, 133.2, 131.9, 130.6, 129.2, 125.13, 122.1, 121.8, 121.5, 114.3; HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{10}N_4O_4S$ 319.0496, Found: 319.0493 ($M+H^+$).



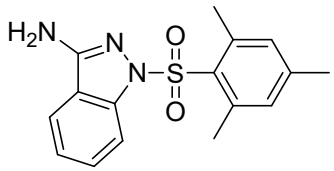
**4l**

**1-(m-tolylsulfonyl)-1*H*-indazol-3-amine (4l)**. Yellow solid (46 mg, 80% yield); mp 224-226 °C; $^{1}$H NMR (400 MHz, DMSO) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.39 – 7.29 (m, 3H), 7.24 (s, 1H), 6.53 (s, 2H); $^{13}$C NMR (101 MHz, DMSO) δ 155.9, 142.4, 139.3, 136.5, 136.0, 130.1, 124.8, 124.4, 121.6, 121.0, 114.2, 21.1; HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{13}N_3O_2S$ 288.3443, Found: 288.3441 ($M+H^+$).



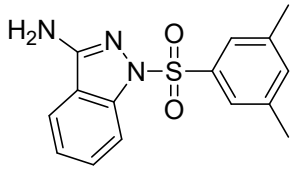
**4m**

**1-((3-bromophenyl)sulfonyl)-1*H*-indazol-3-amine (4m)**. Yellow solid (67.4 mg, 96% yield), mp 199-200 °C; $^1$H NMR (400 MHz, DMSO) δ 7.98 (d, *J* = 8.4 Hz, 1H), 7.83 (t, *J* = 6.6 Hz, 3H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 6.66 (s, 2H); $^{13}$C NMR (101 MHz, DMSO) δ 156.6, 142.5, 138.0, 137.4, 132.0, 130.4, 129.7, 126.4, 124.9, 122.4, 121.7, 121.4, 114.3; HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{10}BrN_3O_2S$ 351.9750, Found: 351.9744 ($M+H^+$).



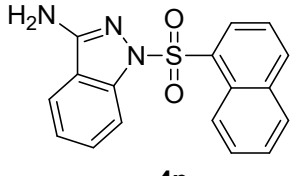
**4n**

**1-(mesitylsulfonyl)-1*H*-indazol-3-amine (4n)**. Yellow solid (50.4 mg, 80% yield), mp 106-108 °C; $^1$H NMR (400 MHz, DMSO) δ 7.94 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.07 (s, 2H), 6.40 (s, 2H), 2.52 (s, 6H), 2.27 (s, 3H); $^{13}$C NMR (101 MHz, DMSO) δ 154.5, 144.0, 141.8, 140.6, 132.9, 132.4, 129.8, 123.4, 121.7, 119.6, 113.7, 23.0, 20.9; HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{17}N_3O_2S$ 316.1114, Found: 316.1111 ($M+H^+$).



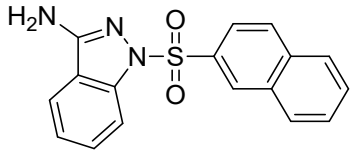
**4o**

**1-((3,5-dimethylphenyl)sulfonyl)-1*H*-indazol-3-amine (4o)**. Brown solid (45.8 mg, 76% yield); mp 214-216 °C; $^1$H NMR (400 MHz, DMSO) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 1H), 7.42 – 7.27 (m, 3H), 7.23 (s, 1H), 6.54 (s, 2H), 2.23 (s, 6H); $^{13}$C NMR (101 MHz, DMSO) δ 155.9, 142.4, 139.3, 136.6, 135.9, 130.1, 124.8, 124.3, 121.6, 121.0, 114.2, 21.1; HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{15}N_3O_2S$ 302.0958, Found: 302.0953 ($M+H^+$).



**4p**

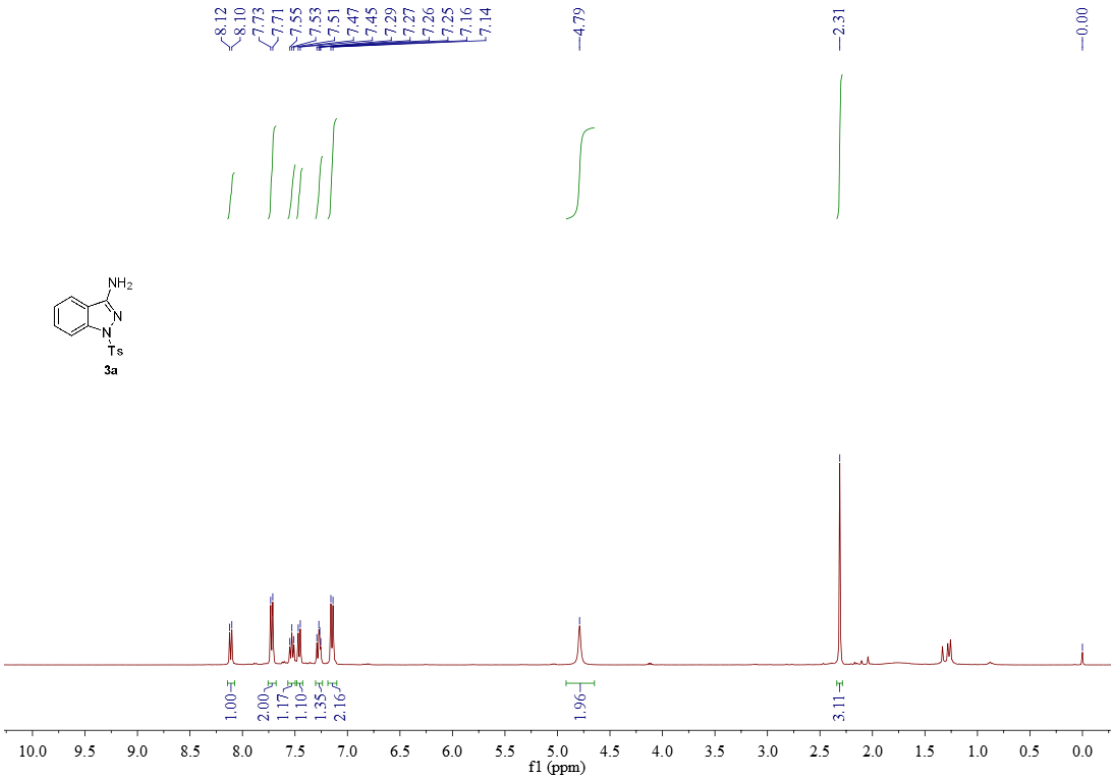
**1-(naphthalen-1-ylsulfonyl)-1*H*-indazol-3-amine (4p)**. Brown solid (53 mg, 82% yield); mp 90-92 °C; $^1$H NMR (400 MHz, DMSO) δ 8.81 (d, *J* = 8.3 Hz, 1H), 8.26 (dd, *J* = 13.8, 7.8 Hz, 2H), 8.04 (t, *J* = 9.3 Hz, 2H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.62 (dt, *J* = 15.2, 7.9 Hz, 4H), 7.32 (t, *J* = 7.5 Hz, 1H), 6.47 (s, 2H); $^{13}$C NMR (101 MHz, DMSO) δ 155.1, 141.8, 136.0, 134.2, 132.9, 130.8, 130.1, 129.4, 128.7, 128.3, 127.6, 125.0, 125.0, 124.2, 121.7, 120.6, 113.9;; HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{13}N_3O_2S$ 324.0801, Found: 324.0797 ($M+H^+$).

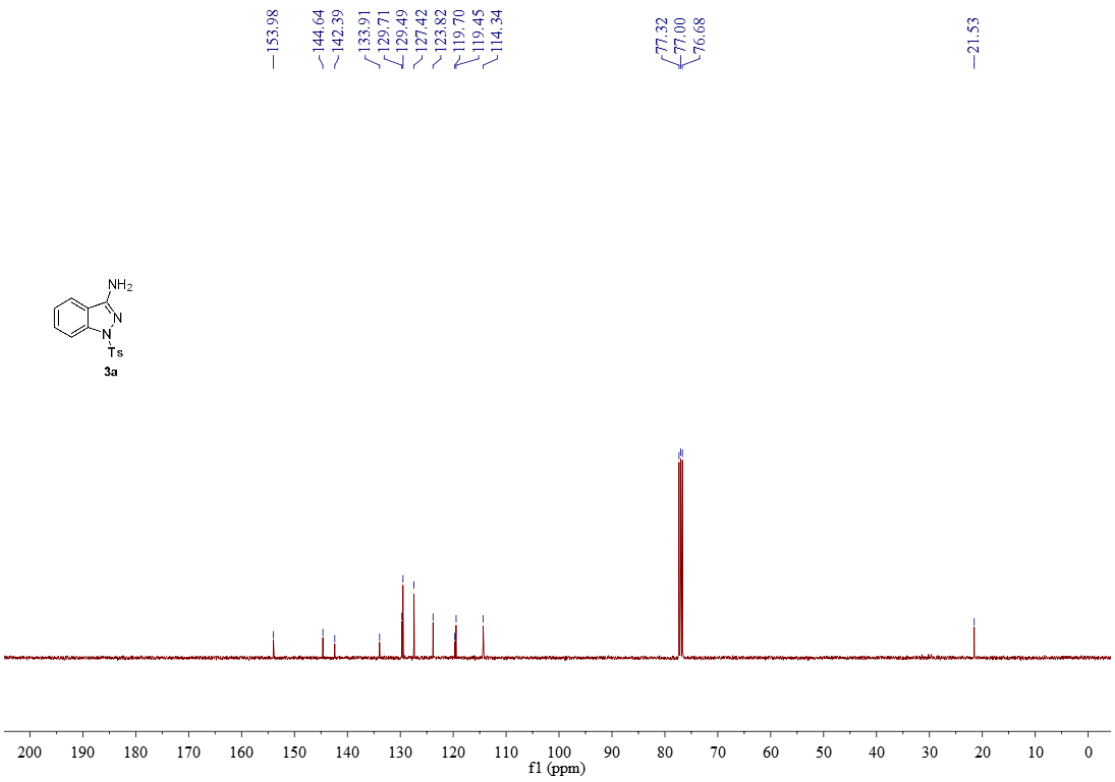


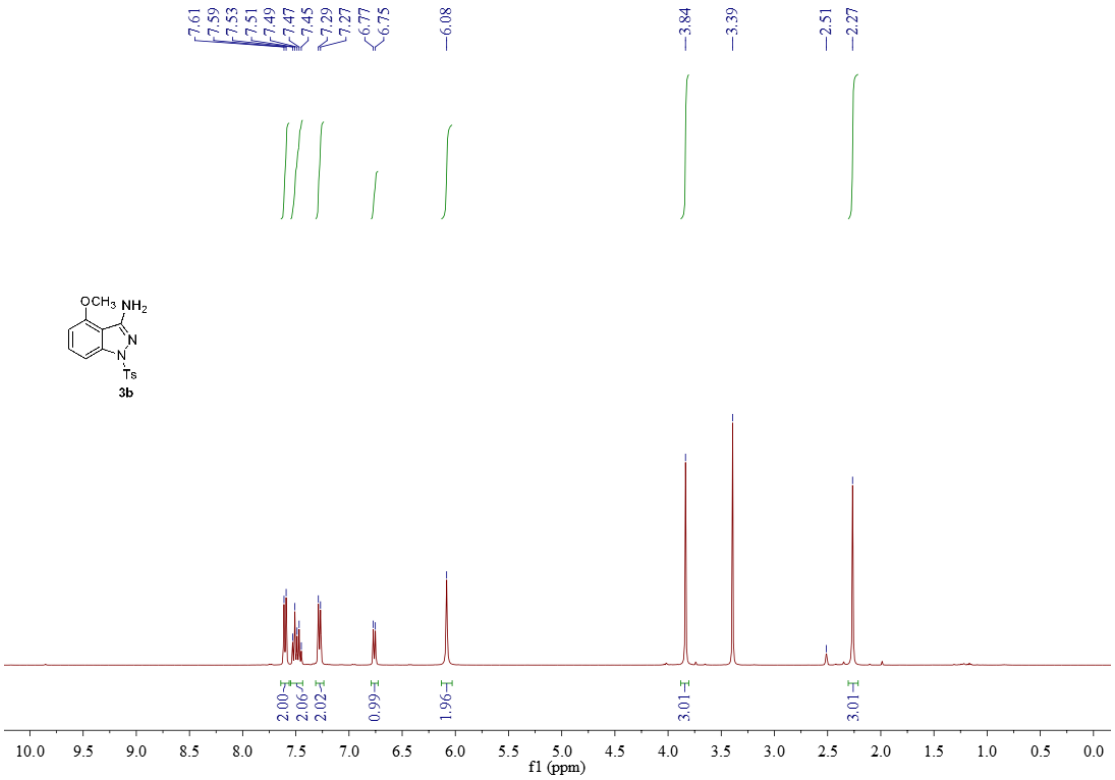
**4q**

**1-(naphthalen-2-ylsulfonyl)-1*H*-indazol-3-amine (4q)**. Brown solid (49.2 mg, 76% yield); mp 90-92 °C; $^{1}$H NMR (400 MHz, DMSO) δ 8.50 (s, 1H), 8.10 (dd, *J* = 17.1, 8.1 Hz, 2H), 7.96 (dd, *J* = 15.7, 8.3 Hz, 2H), 7.78 (d, *J* = 7.9 Hz, 1H), 7.70 – 7.56 (m, 4H), 7.32 (t, *J* = 7.5 Hz, 1H), 6.55 (s, 2H); $^{13}$C NMR (101 MHz, DMSO) δ 156.1, 142.6, 135.1, 133.5, 131.8, 130.2, 130.0, 129.8, 129.7, 129.2, 128.34, 128.31, 124.5, 122.3, 121.6, 121.2, 114.3; HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{13}N_3O_2S$ 324.0801, Found: 324.0796 ($M+H^+$).

# 6. Spectroscopic data for products

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7.45
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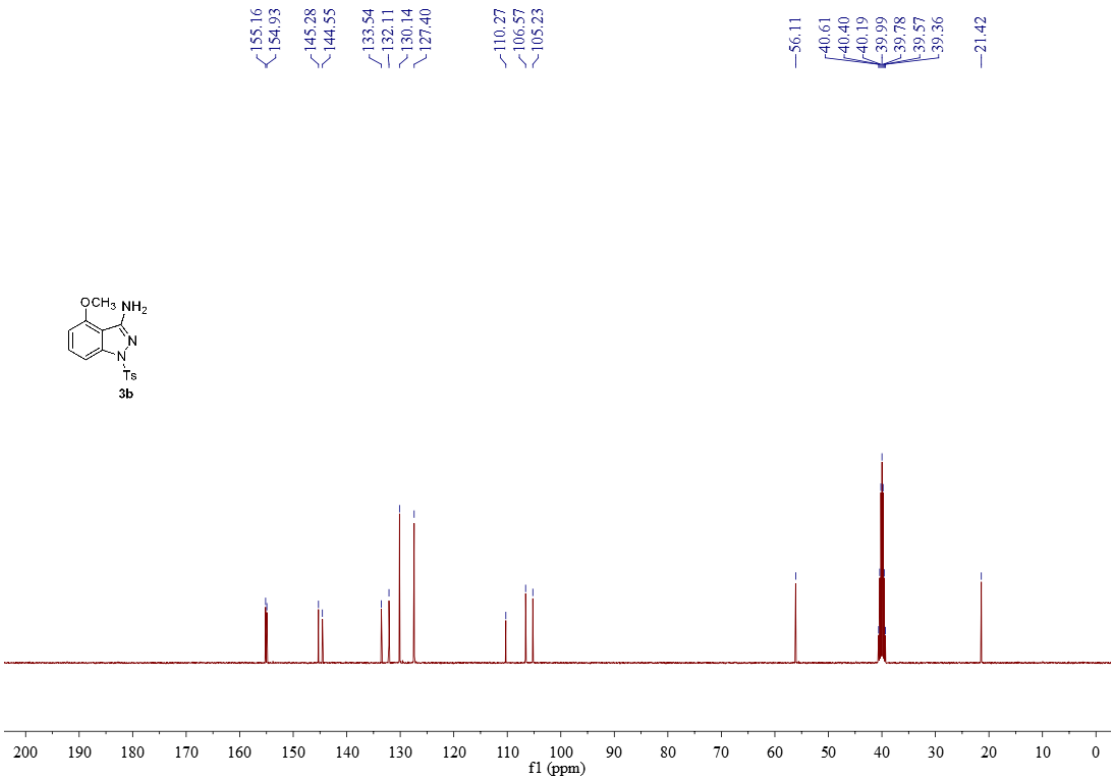
6.77
6.75
6.08
3.84
3.39
2.51
2.27
OCH3
NH2
N
N
Ts
3b
2.00
2.06
2.02
0.99
1.96
3.01
3.01
f1 (ppm)


155.16
154.93
145.28
144.55
133.54
132.11
130.14
127.40
110.27
106.57
105.23
56.11
40.61
40.40
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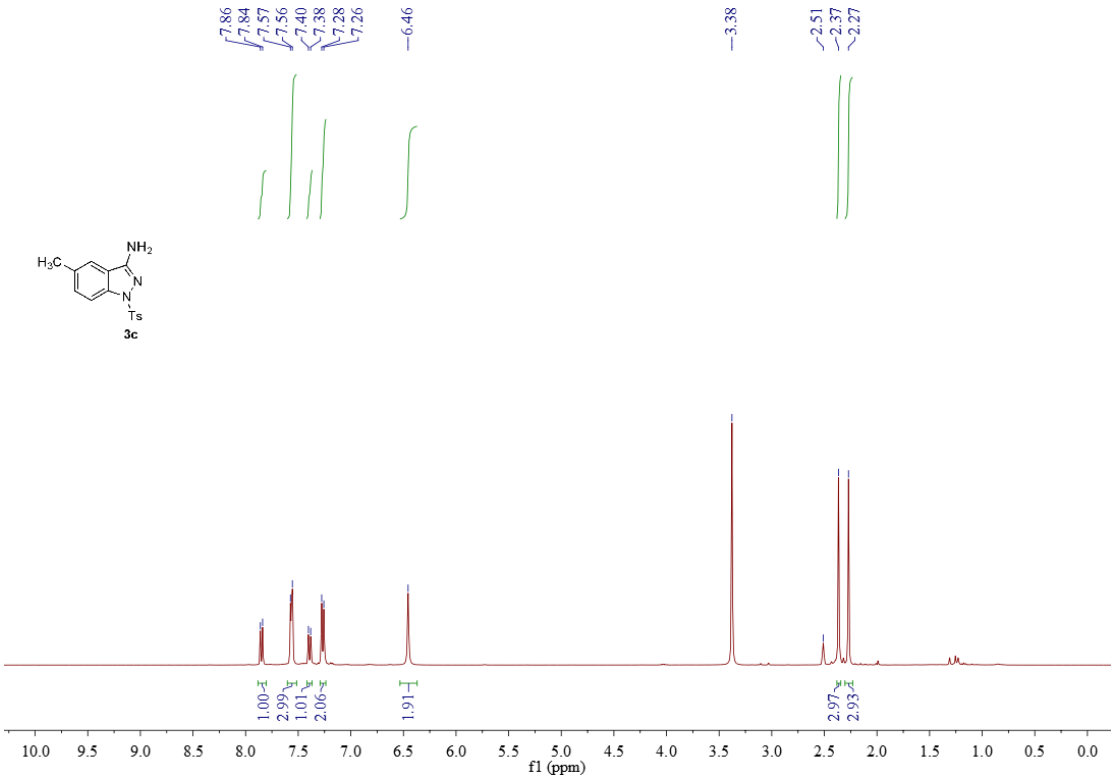
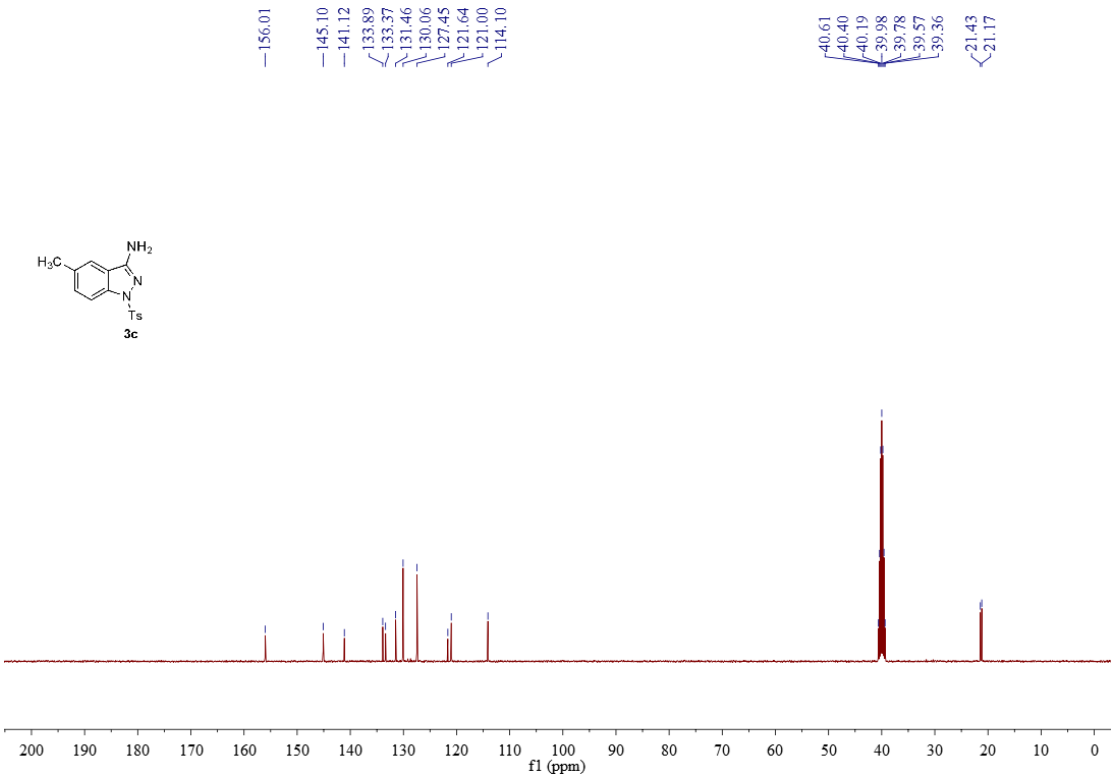
39.78
39.57
39.36
21.42
OCH3
NH2
N
N
Ts
3b
f1 (ppm)


7.86
7.84
7.57
7.56
7.40
7.38
7.28
7.26
6.46
3.38
2.51
2.37
2.27
NH2
H3C
N
N
Ts
3c
1.00
2.99
1.01
2.06
1.91
2.97
2.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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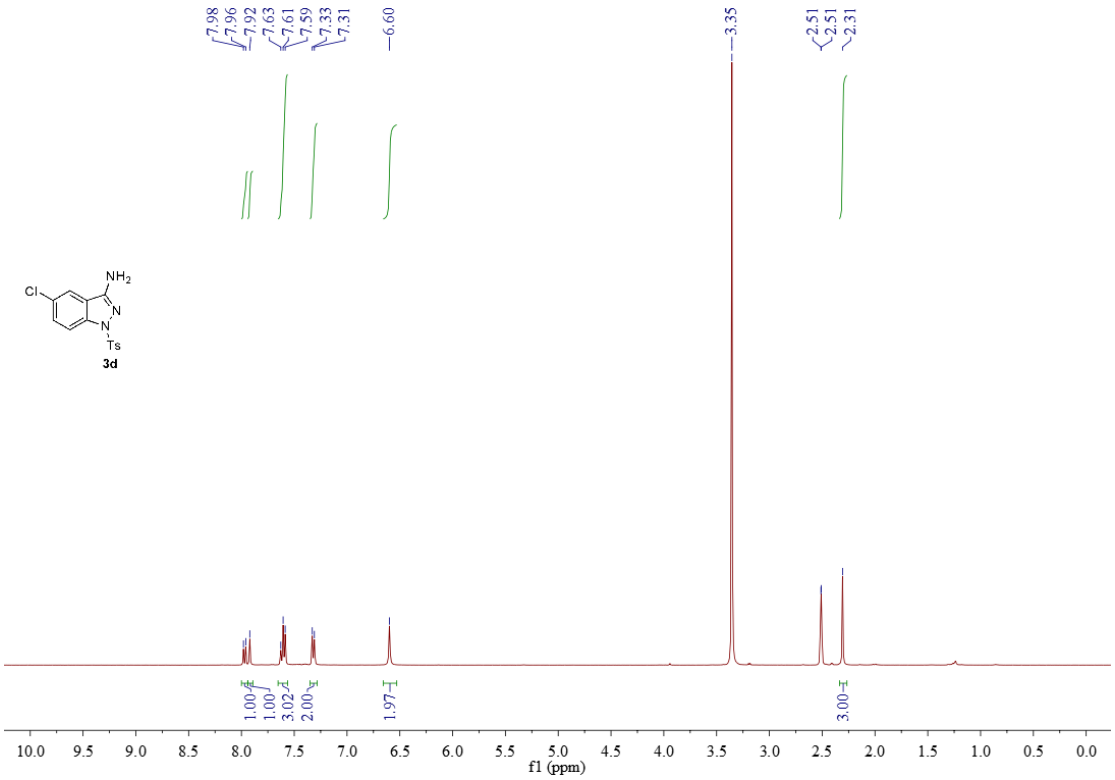
145.10
141.12
133.89
133.37
131.46
130.06
127.45
121.64
121.00
114.10
40.61
40.40
40.19
39.98
39.78
39.57
39.36
21.43
21.17
NH2
H3C
N
N
Ts
3c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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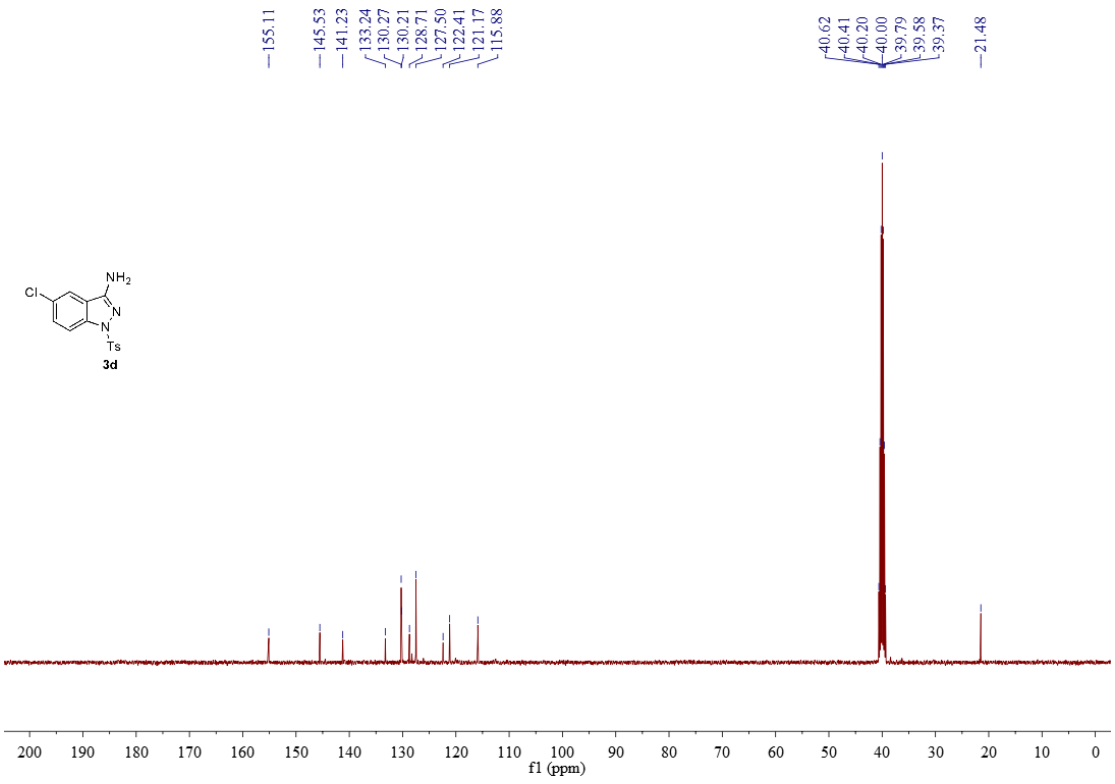
7.96
7.92
7.63
7.61
7.59
7.33
7.31
6.60
3.35
2.51
2.51
2.31
NH2
Cl
N
N
Ts
3d
1.00
1.00
3.02
2.00
1.97
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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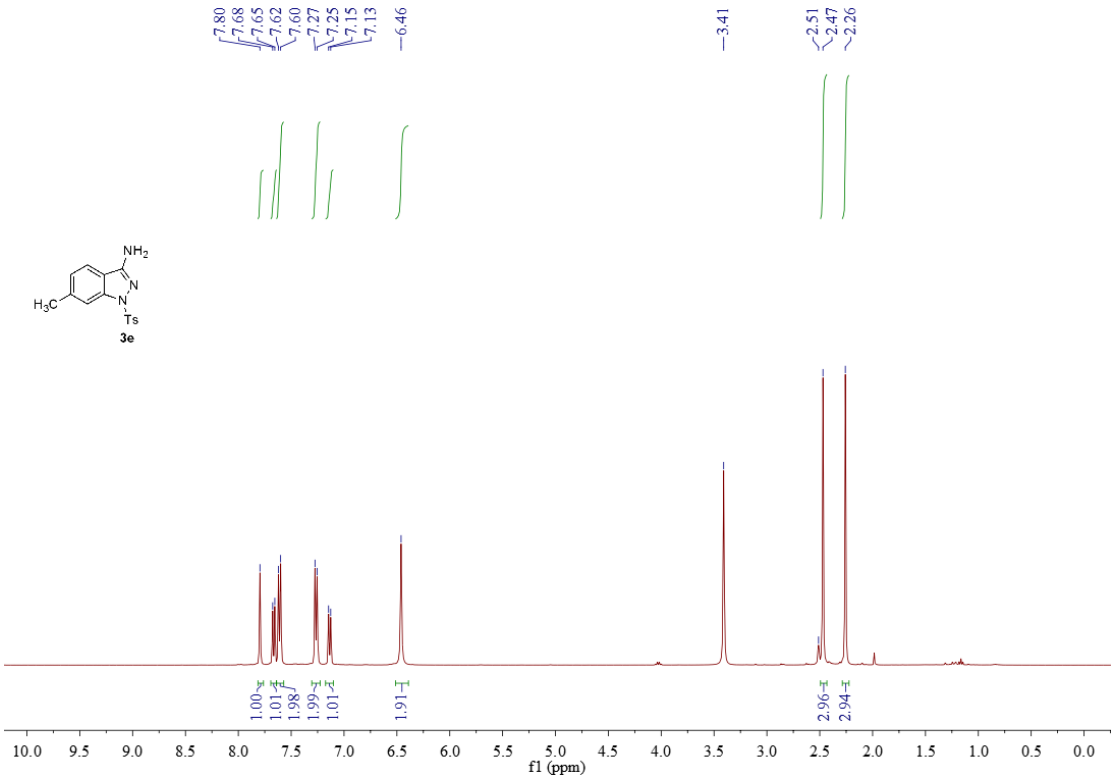
128.71
127.50
122.41
121.17
115.88
40.62
40.41
40.20
40.00
39.79
39.58
39.37
21.48
NH2
Cl
N
N
Ts
3d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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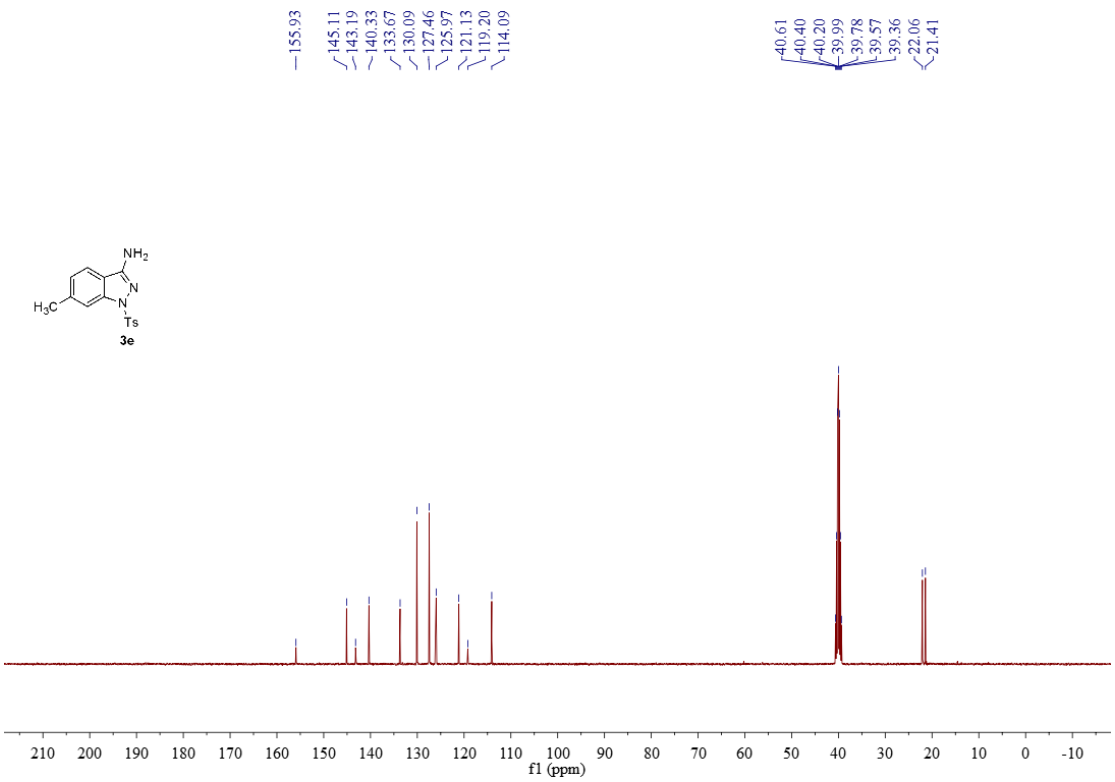
7.68
7.65
7.62
7.60
7.27
7.25
7.15
7.13
6.46
3.41
2.51
2.47
2.26
NH2
N
N
Ts
H3C
3e
1.00
1.01
1.98
1.99
1.01
1.91
2.96
2.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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140.33
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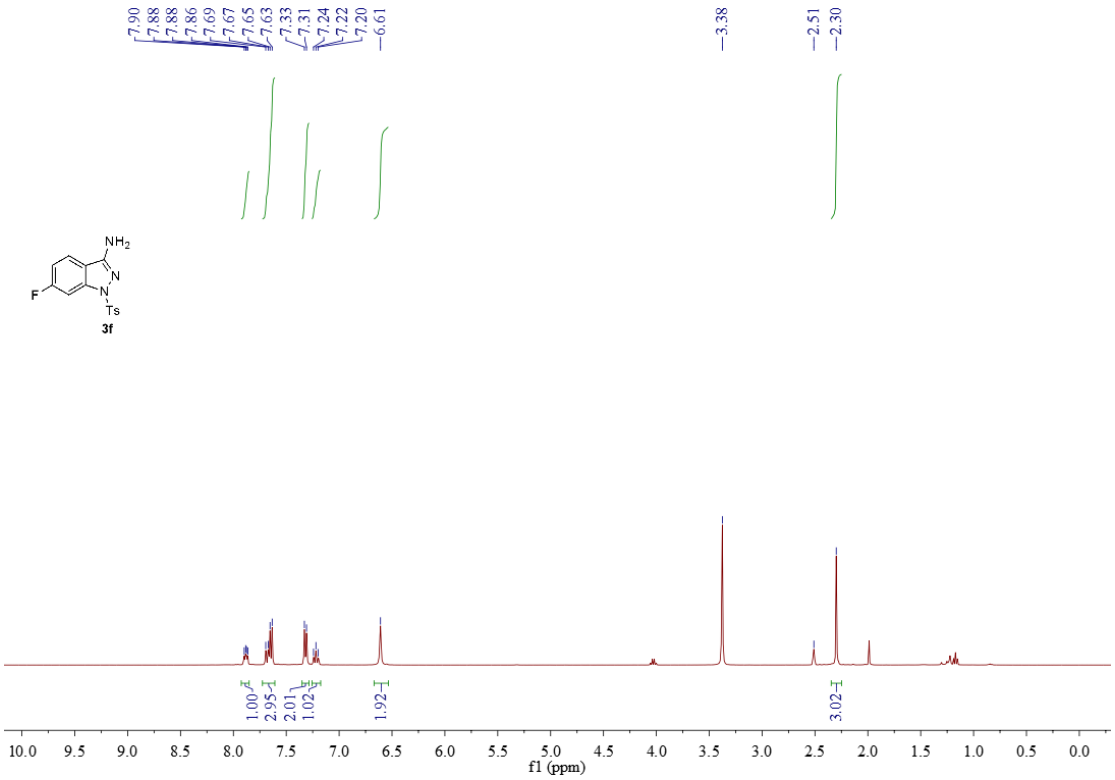
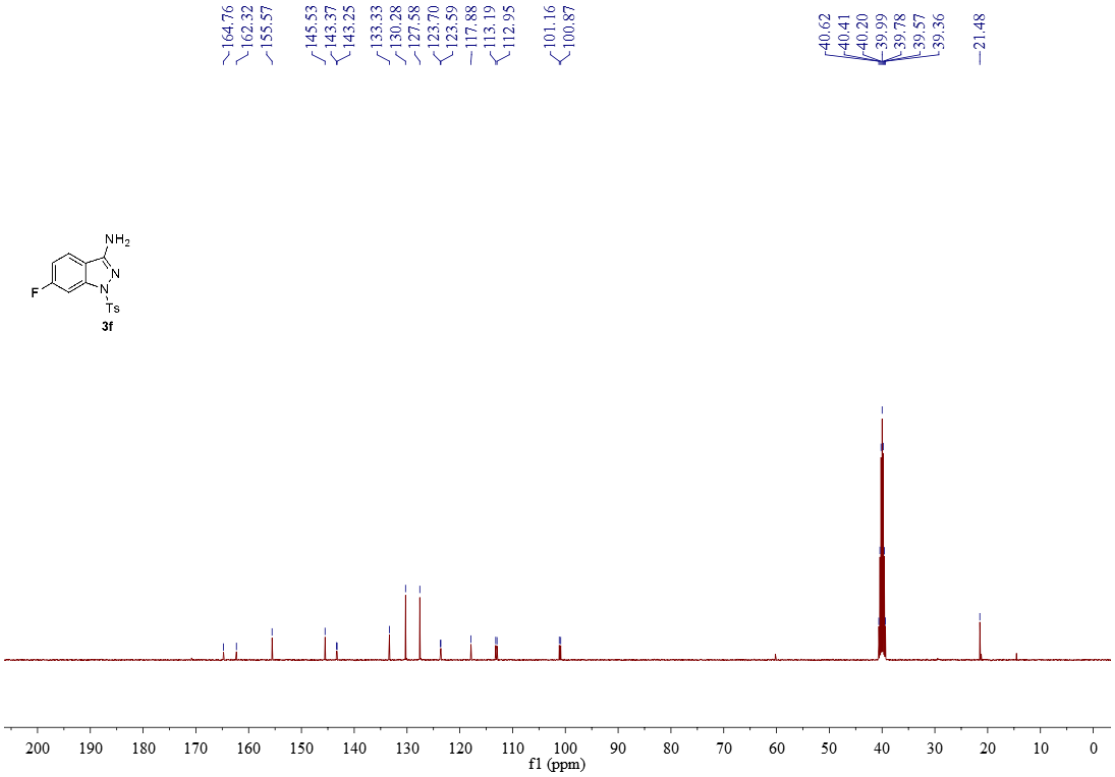
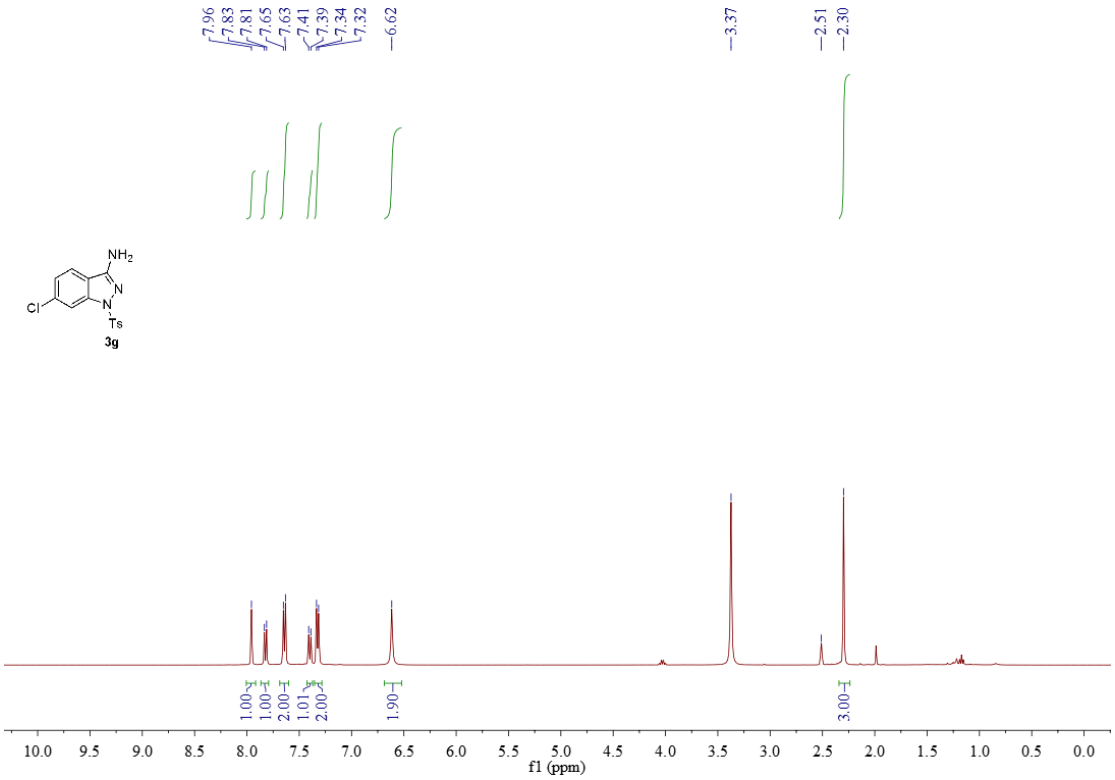
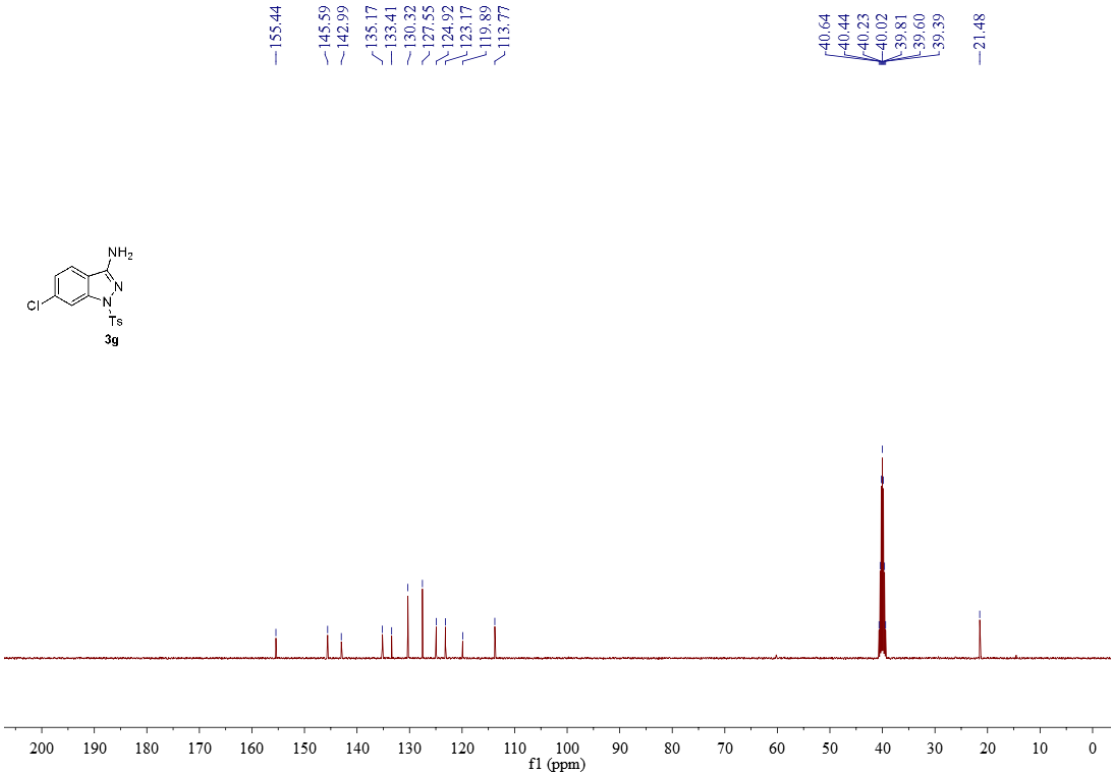
130.09
127.46
125.97
121.13
119.20
114.09
40.61
40.40
40.20
39.99
39.78
39.57
39.36
22.06
21.41
NH2
N
N
Ts
H3C
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.90
7.88
7.88
7.86
7.69
7.67
7.65
7.63
7.33
7.31
7.24
7.22
7.20
6.61
3.38
2.51
2.30
NH2
N
F
N
Ts
3f
1.00
2.95
2.01
1.02
1.92
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


164.76
162.32
155.57
145.53
143.37
143.25
133.33
130.28
127.58
123.70
123.59
117.88
113.19
112.95
101.16
100.87
40.62
40.41
40.20
39.99
39.78
39.57
39.36
21.48
NH2
N
F
N
Ts
3f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.96
7.83
7.81
7.65
7.63
7.41
7.39
7.34
7.32
6.62
3.37
2.51
2.30
NH2
Cl
N
N
Ts
3g
1.00
1.00
2.00
1.01
2.00
1.90
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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145.59
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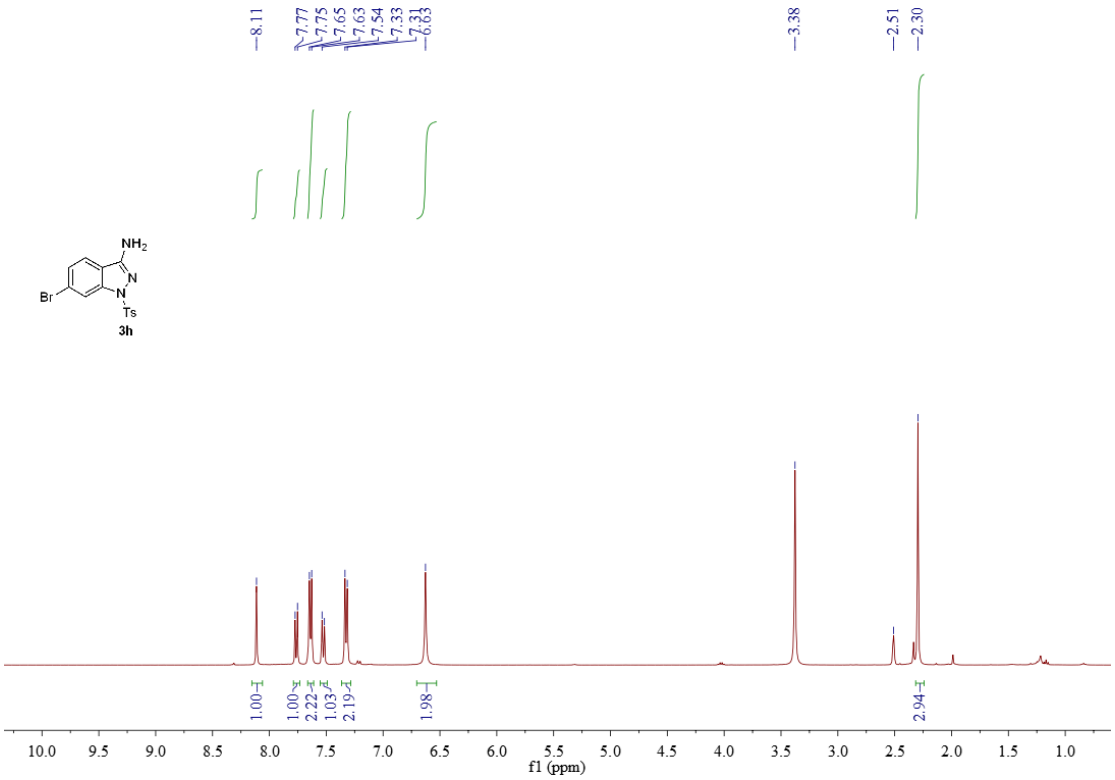
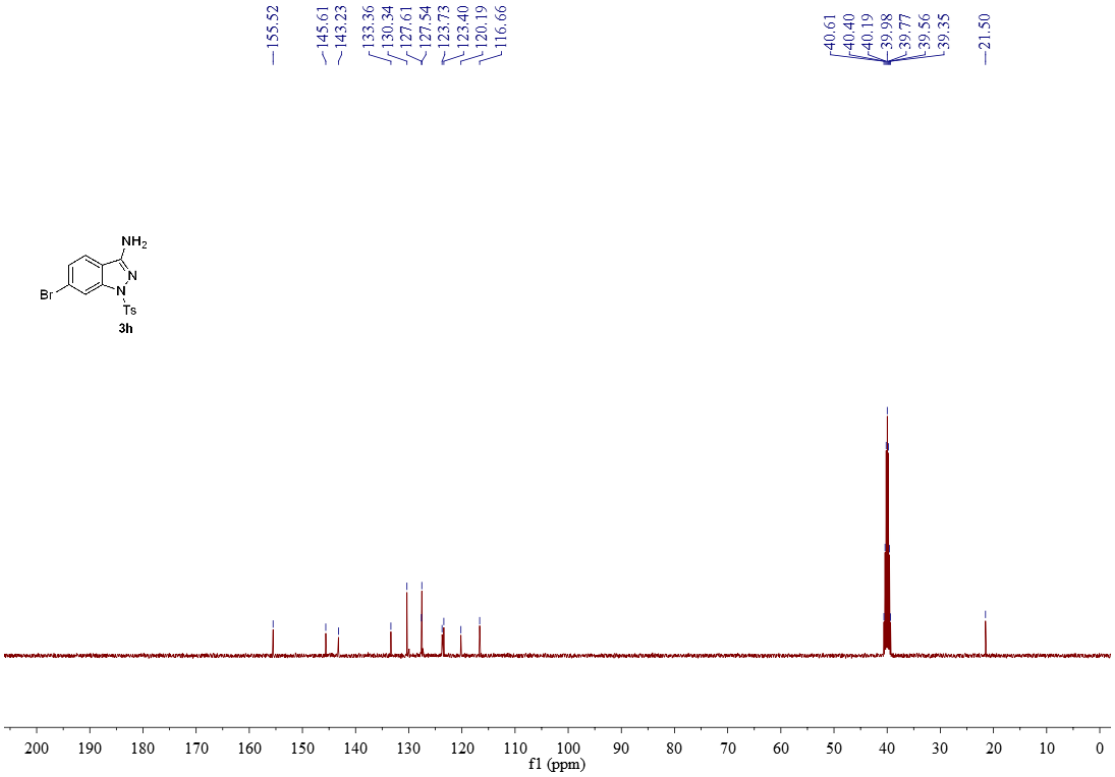
135.17
133.41
130.32
127.55
124.92
123.17
119.89
113.77
40.64
40.44
40.23
40.02
39.81
39.60
39.39
21.48
NH2
Cl
N
N
Ts
3g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.11
7.77
7.75
7.65
7.63
7.54
7.33
7.31
6.63
3.38
2.51
2.30
NH2
Br
N
N
Ts
3h
1.00
1.00
2.22
1.03
2.19
1.98
2.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)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145.61
143.23
133.36
130.34
127.61
127.54
123.73
123.40
120.19
116.66
40.61
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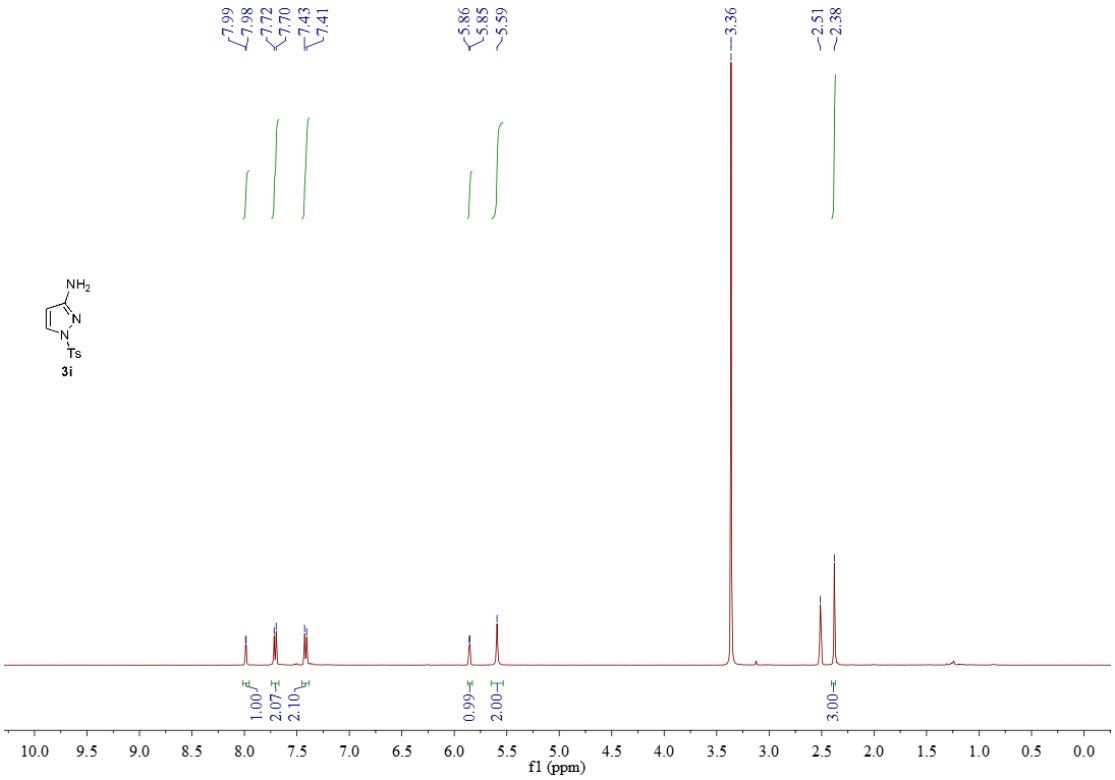
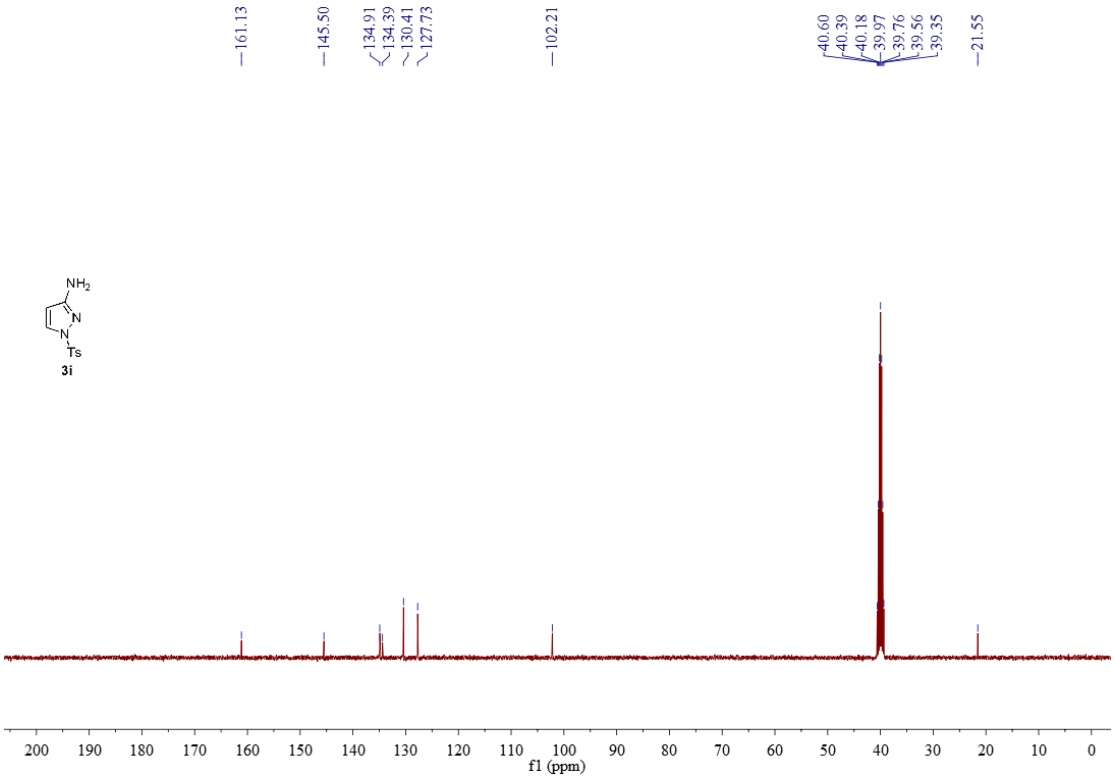
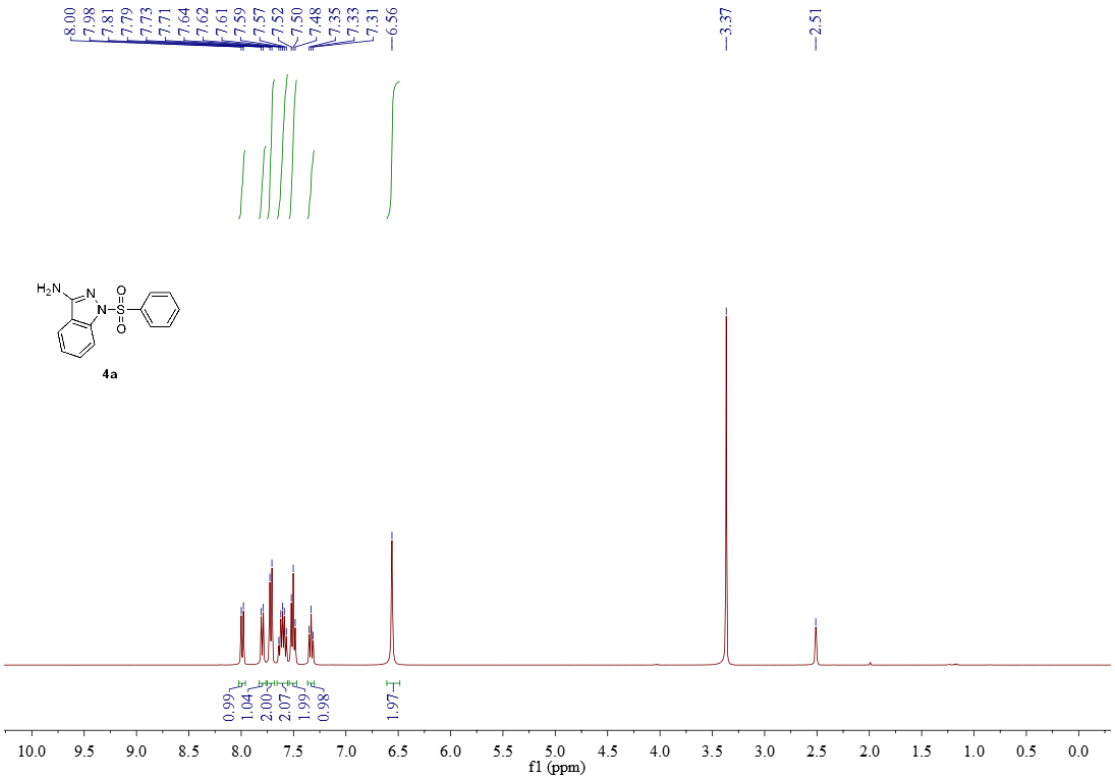
40.19
39.98
39.77
39.56
39.35
21.50
NH2
Br
N
N
Ts
3h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.99
7.98
7.72
7.70
7.43
7.41
5.86
5.85
5.59
3.36
2.51
2.38
NH2
N
N
Ts
3i
1.00
2.07
2.10
0.99
2.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


161.13
145.50
134.91
134.39
130.41
127.73
102.21
40.60
40.39
40.18
39.97
39.76
39.56
39.35
21.55
NH2
N
N
Ts
3i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.98
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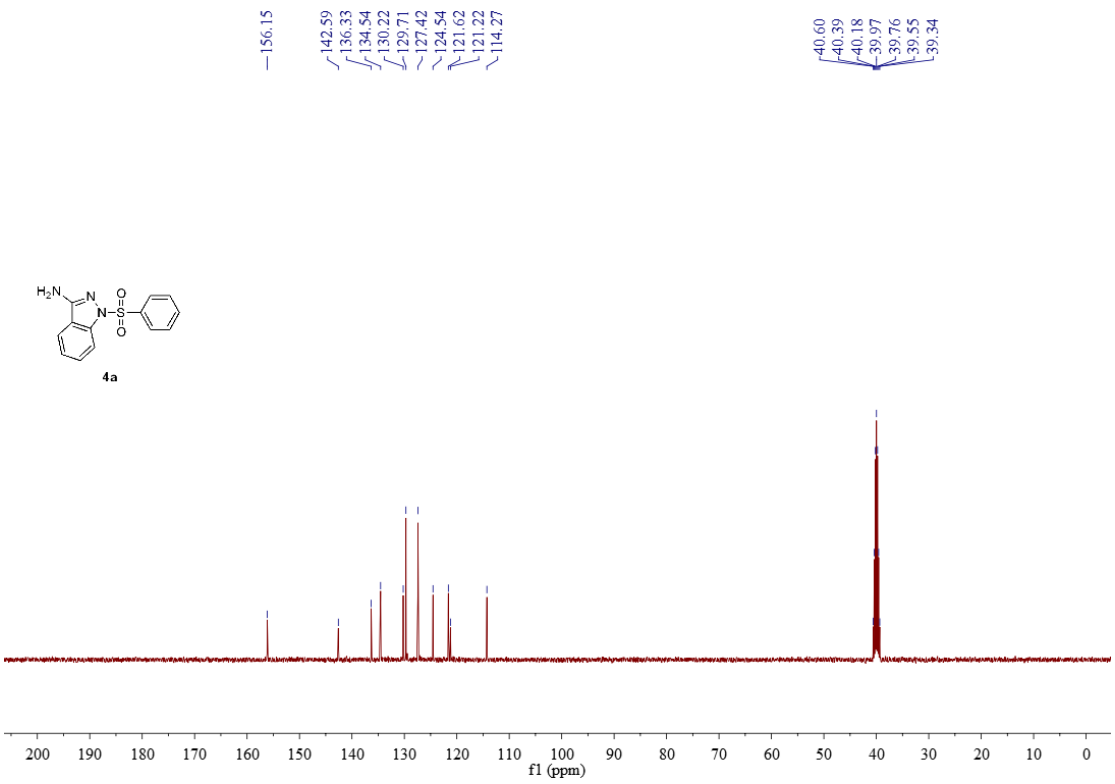
7.71
7.64
7.62
7.61
7.59
7.57
7.52
7.50
7.48
7.35
7.33
7.31
6.56
3.37
2.51
4a
0.99
1.04
2.00
2.07
1.99
0.98
1.97
f1 (ppm)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130.22
129.71
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124.54
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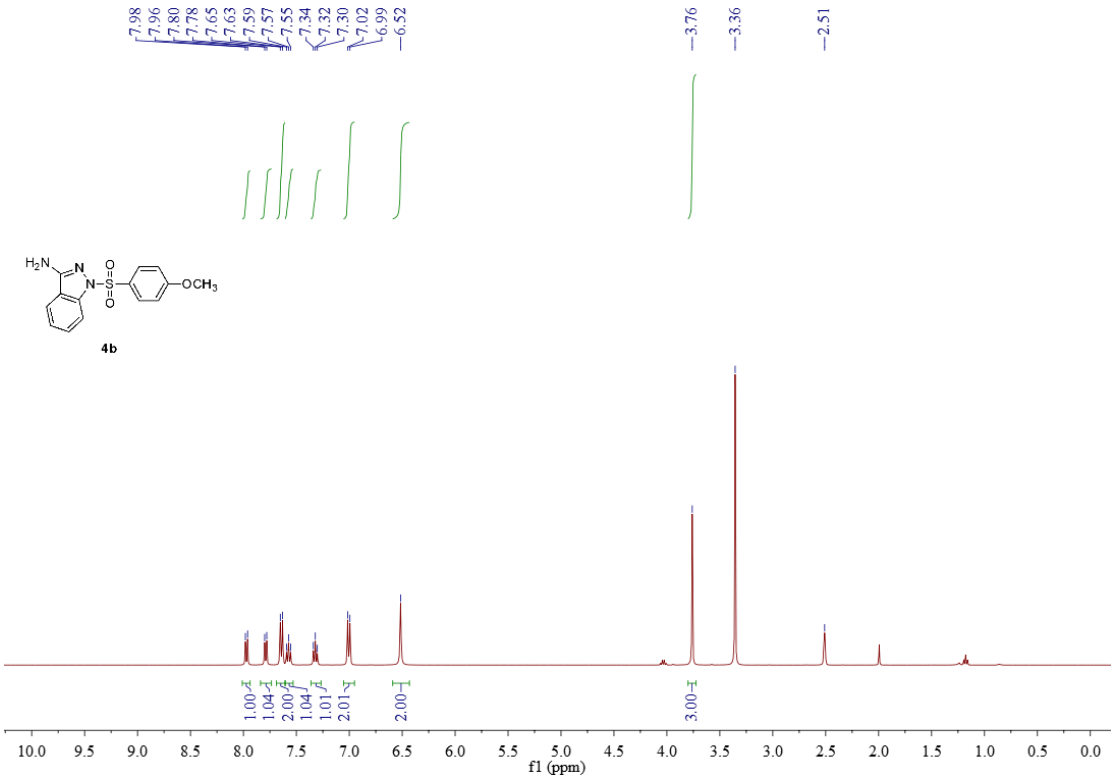
40.60
40.39
40.18
39.97
39.76
39.55
39.34
4a
f1 (ppm)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7.80
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7.65
7.63
7.59
7.57
7.55
7.34
7.32
7.30
7.02
6.99
6.52
3.76
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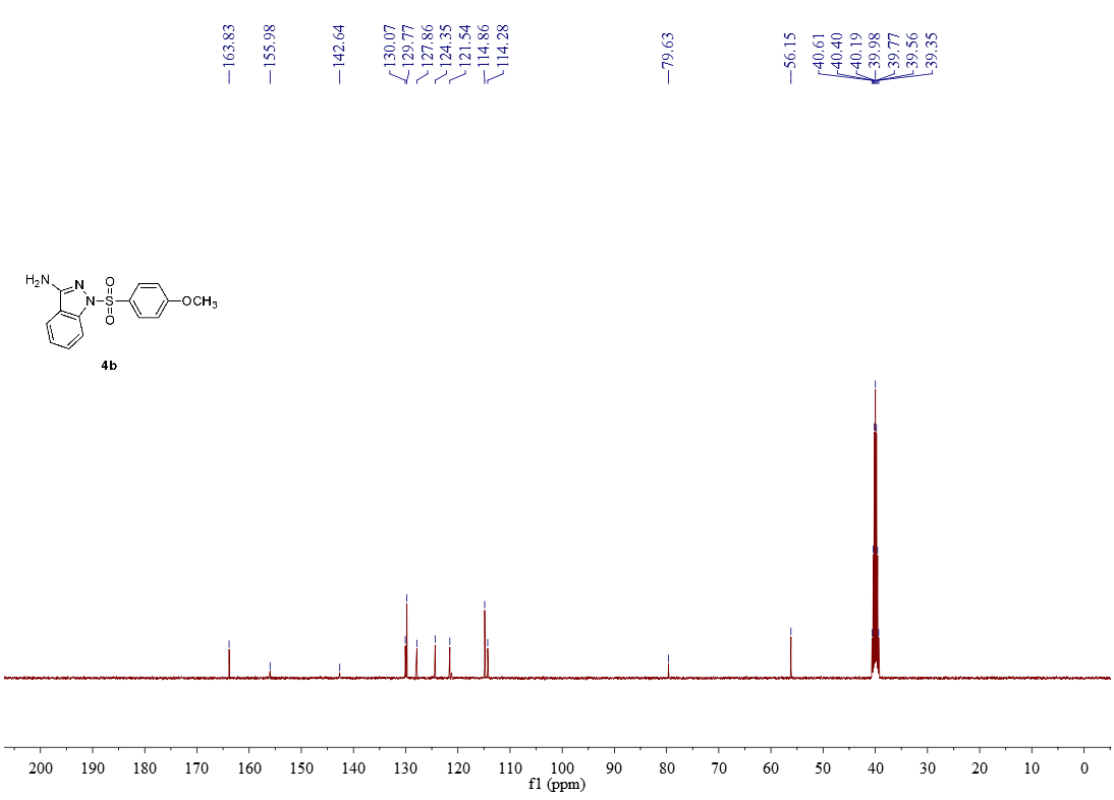
2.51
4b
1.00
1.04
2.00
1.04
1.01
2.01
2.00
3.00
f1 (ppm)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127.86
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121.54
114.86
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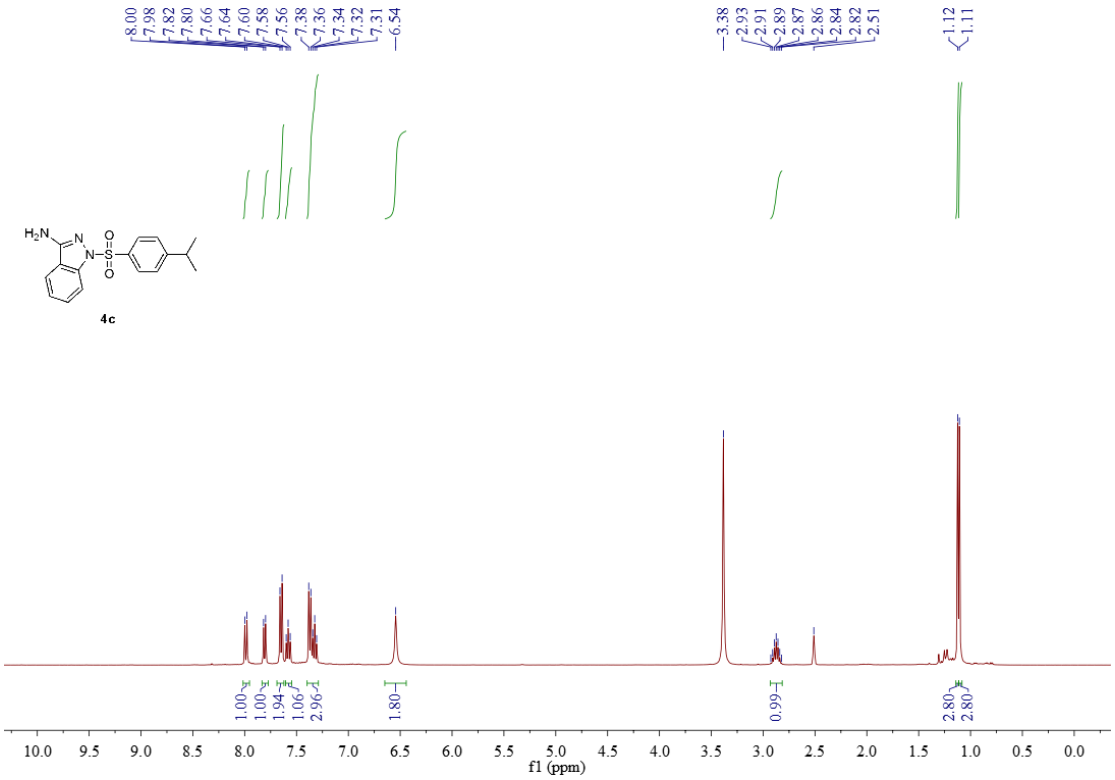
40.19
39.98
39.77
39.56
39.35
4b
f1 (ppm)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7.80
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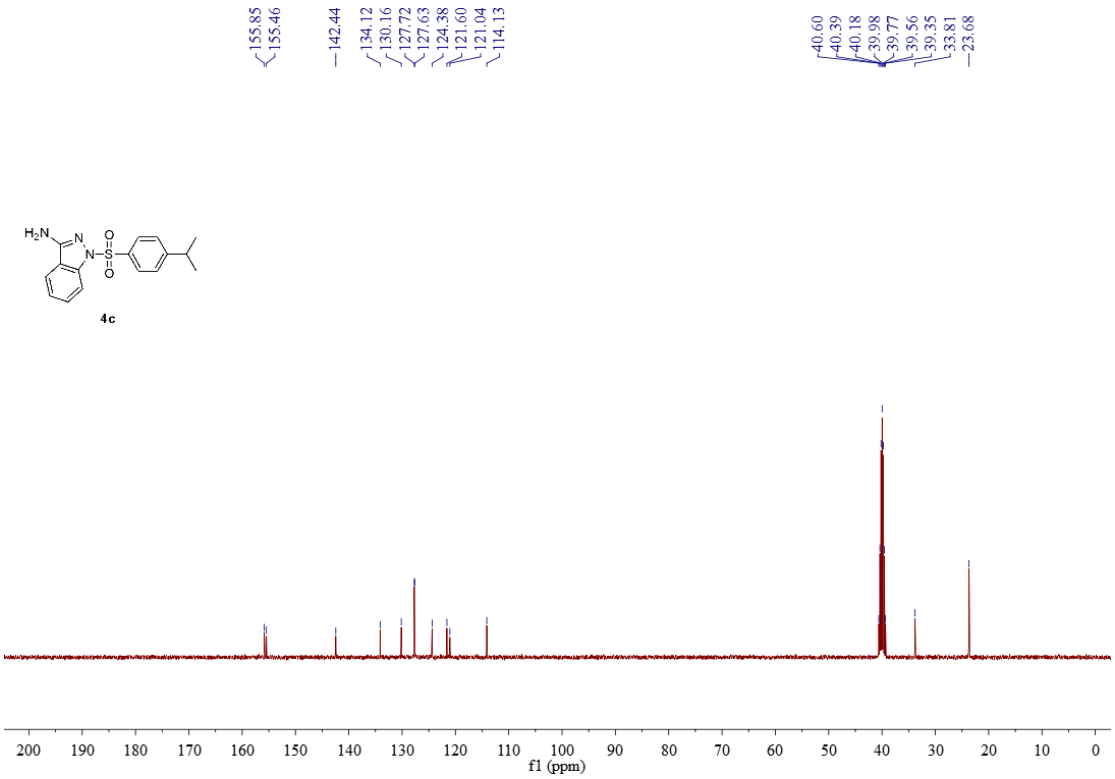
7.64
7.60
7.58
7.56
7.38
7.36
7.34
7.32
7.31
6.54
3.38
2.93
2.91
2.89
2.87
2.86
2.84
2.82
2.51
1.12
1.11
4c
1.00
1.00
1.94
1.06
2.96
1.80
0.99
2.80
2.80
f1 (ppm)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121.04
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40.18
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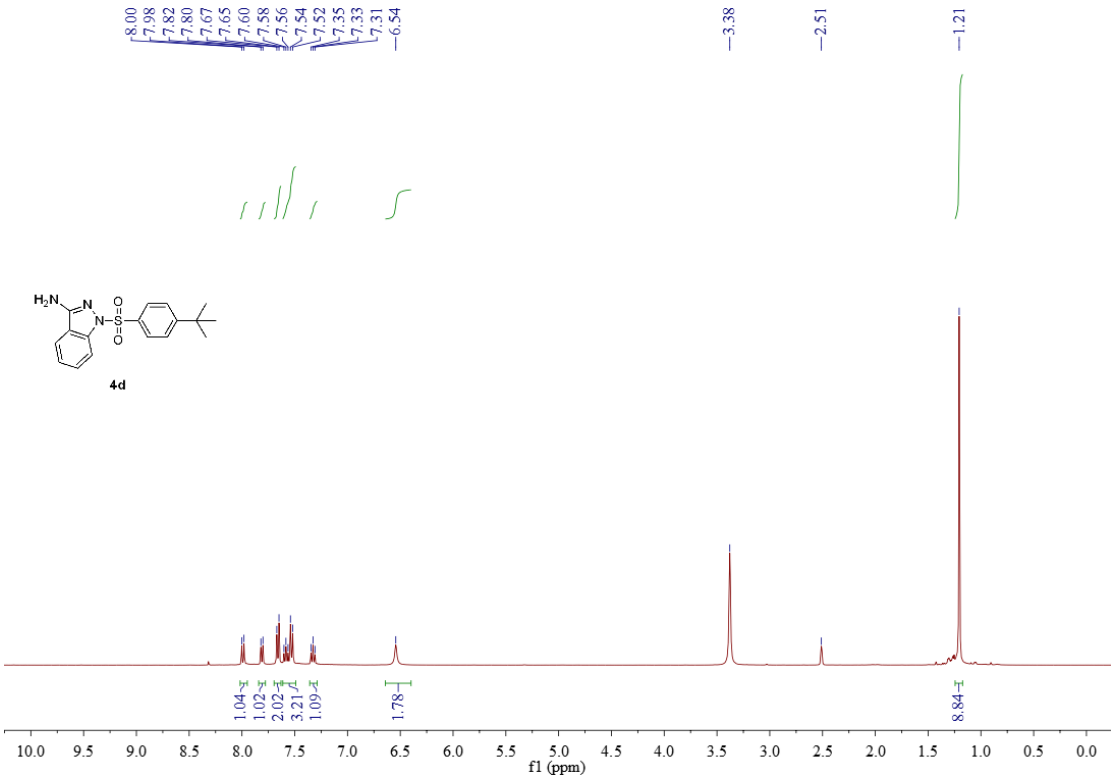
39.77
39.56
39.35
33.81
23.68
4c
f1 (ppm)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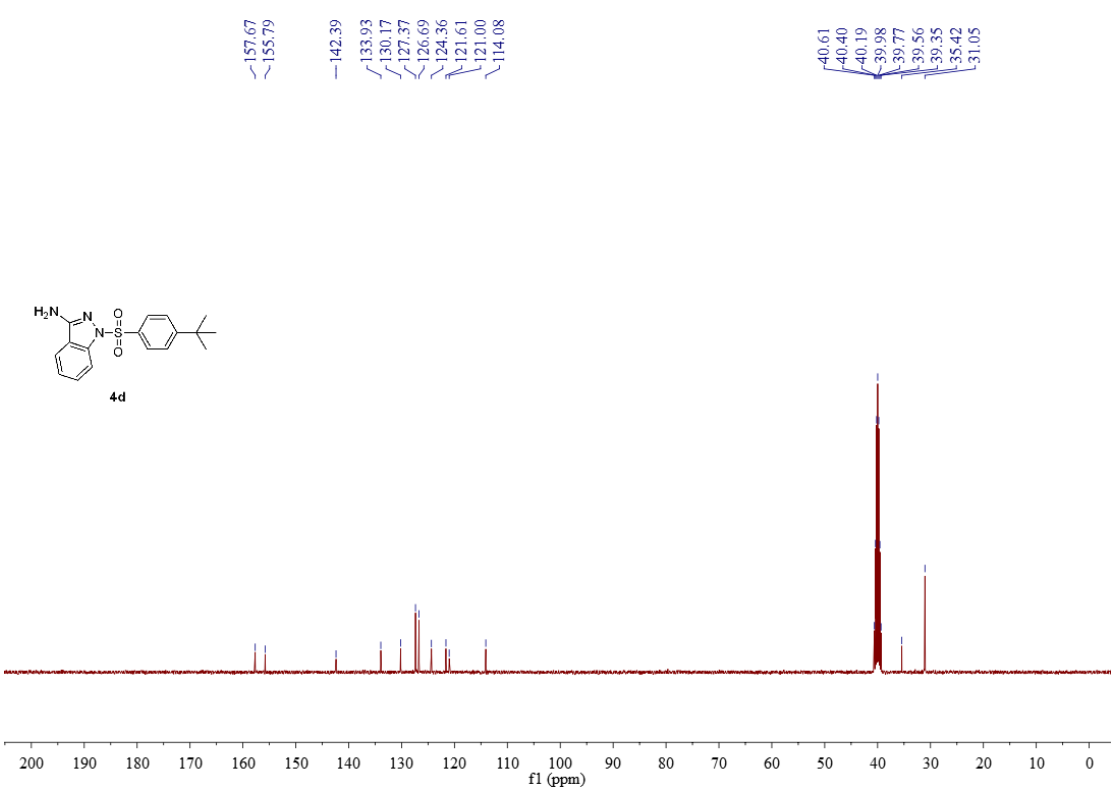
7.80
7.67
7.65
7.60
7.58
7.56
7.54
7.52
7.35
7.33
7.31
6.54
3.38
2.51
1.21
4d
1.04
1.02
2.02
3.21
1.09
1.78
8.84
f1 (ppm)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133.93
130.17
127.37
126.69
124.36
121.61
121.00
114.08
40.61
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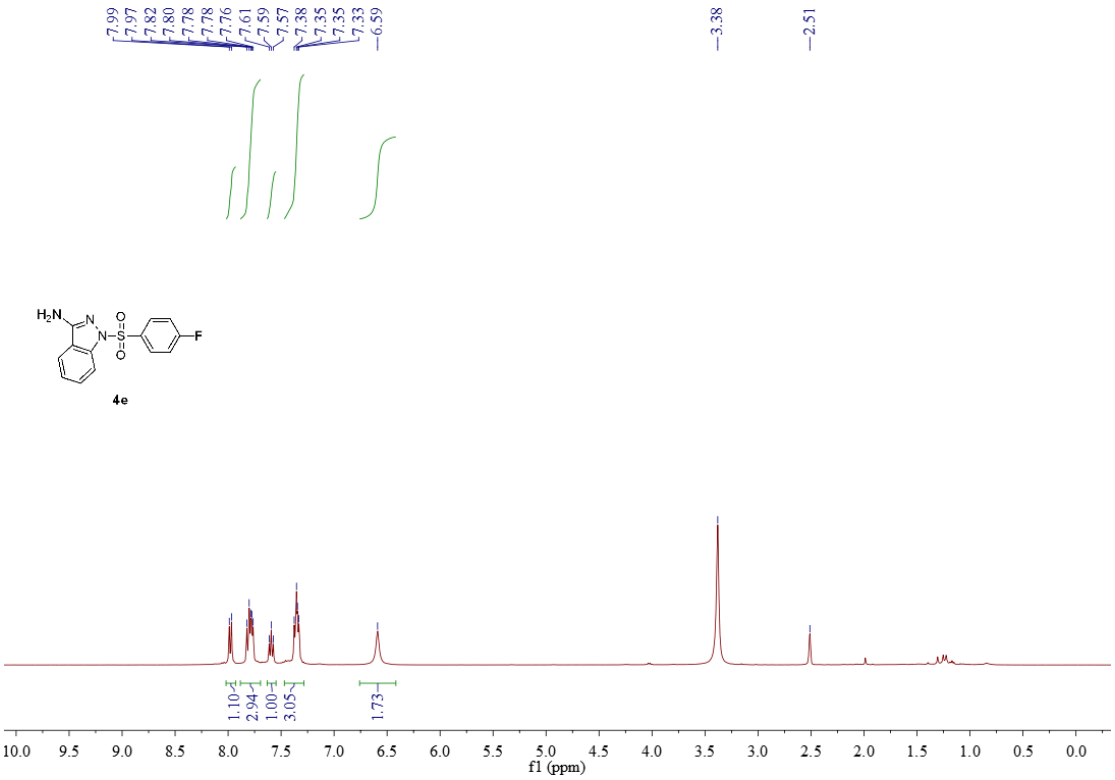
40.19
39.98
39.77
39.56
39.35
35.42
31.05
4d
f1 (ppm)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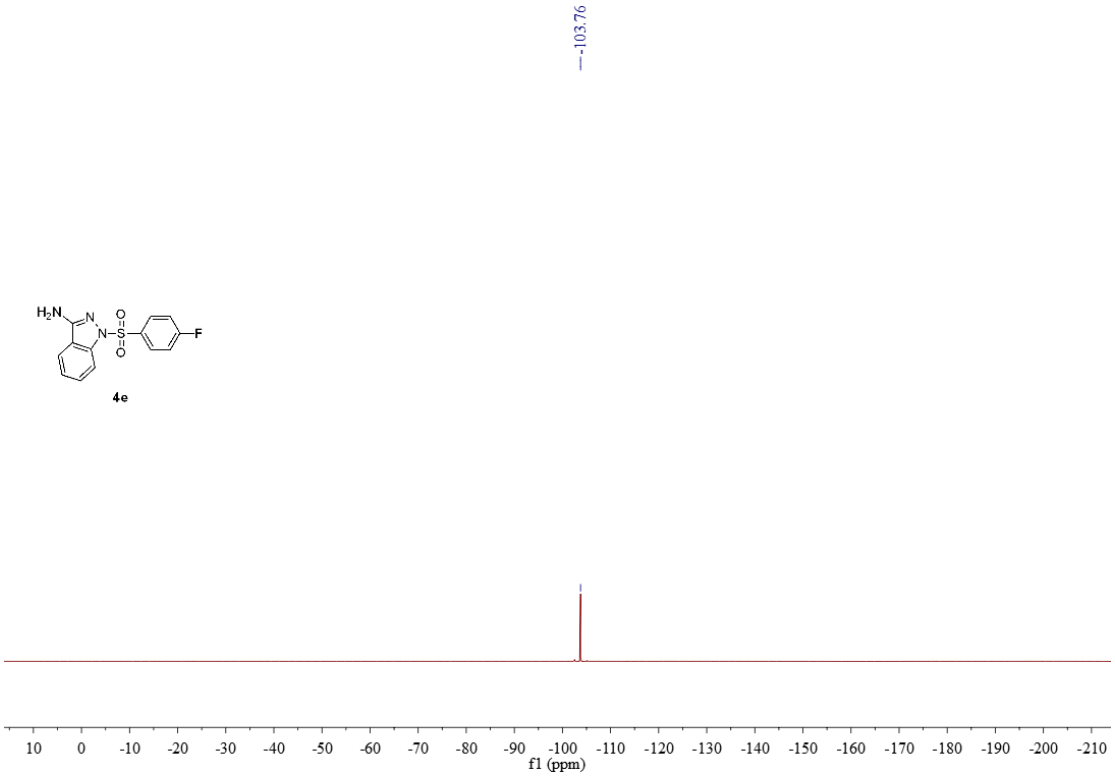
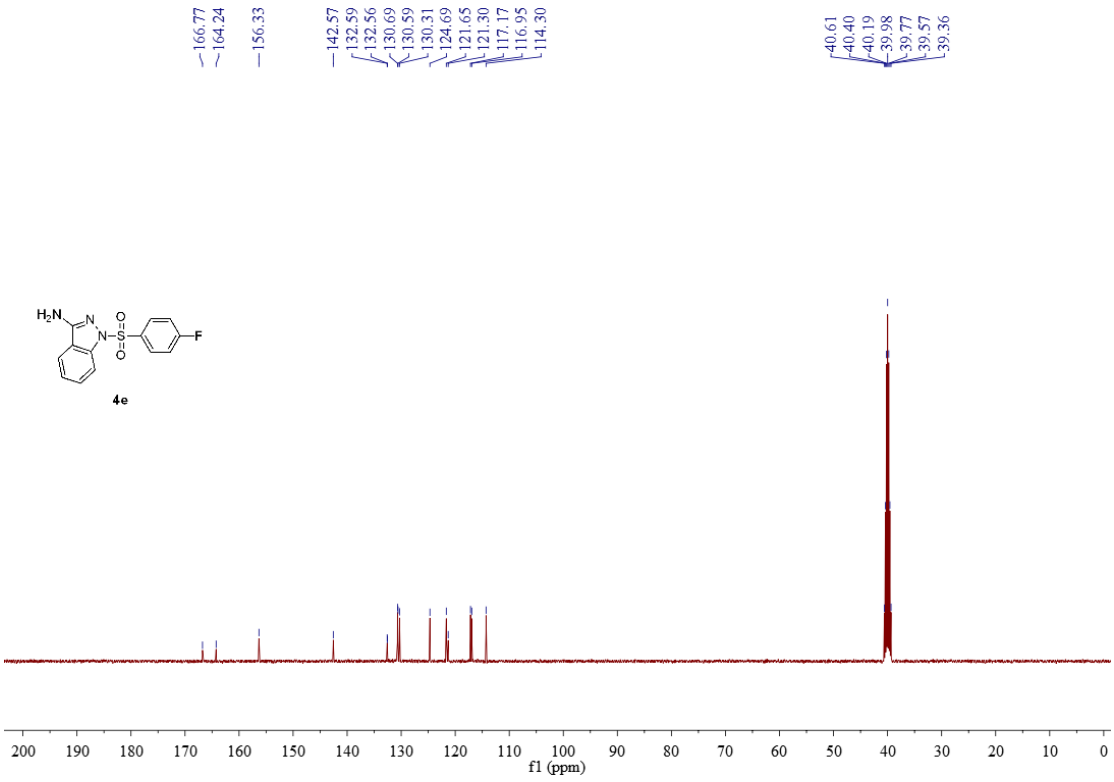
7.97
7.82
7.80
7.78
7.78
7.78
7.76
7.61
7.59
7.57
7.38
7.35
7.35
7.33
6.59
3.38
2.51
H2N
N
N
O
S
O
F
4e
1.10
2.94
1.00
3.05
1.73
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


-103.76
H2N
N
N
O
S
O
F
4e
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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164.24
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132.56
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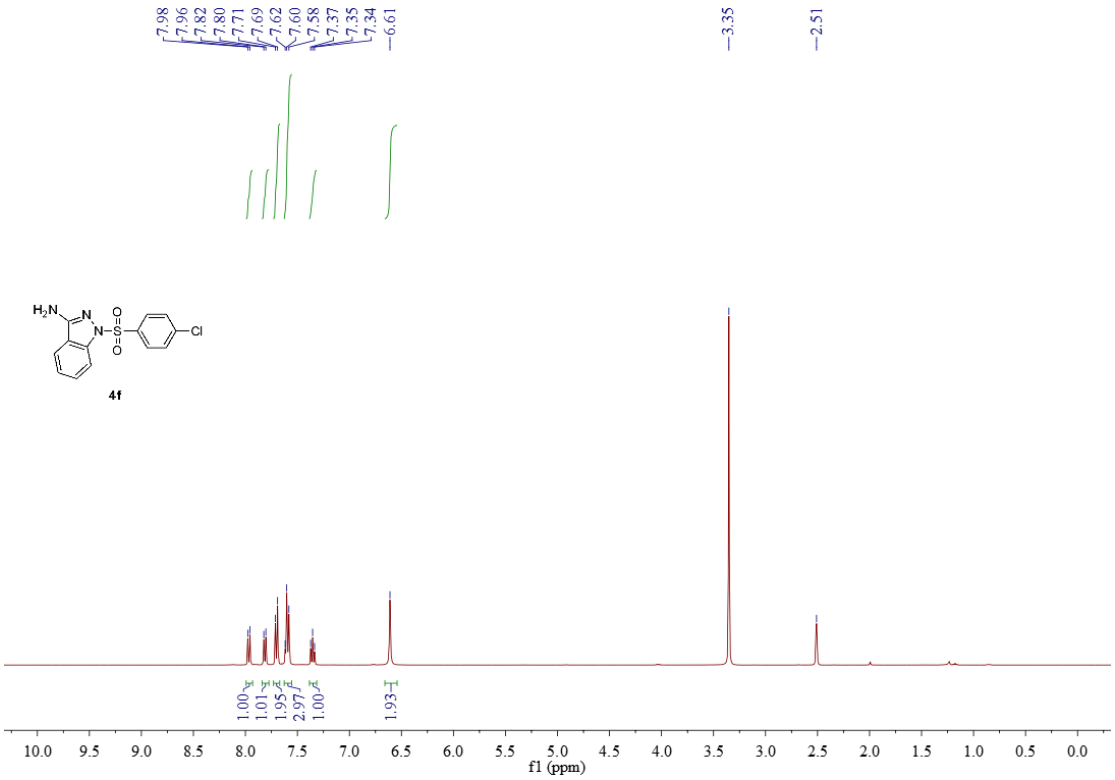
130.59
130.31
124.69
121.65
121.30
117.17
116.95
114.30
40.61
40.40
40.19
39.98
39.77
39.57
39.36
H2N
N
N
O
S
O
F
4e
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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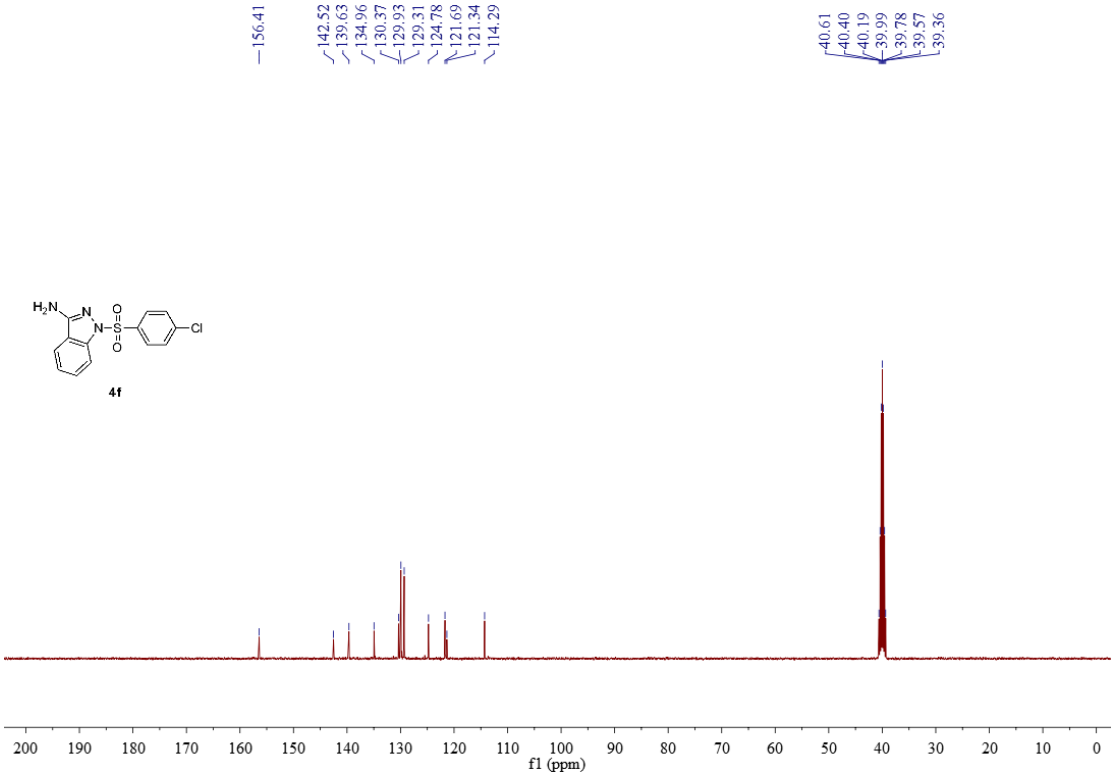
7.96
7.82
7.80
7.71
7.69
7.62
7.60
7.58
7.37
7.35
7.34
6.61
3.35
2.51
4f
1.00
1.01
1.95
2.97
1.00
1.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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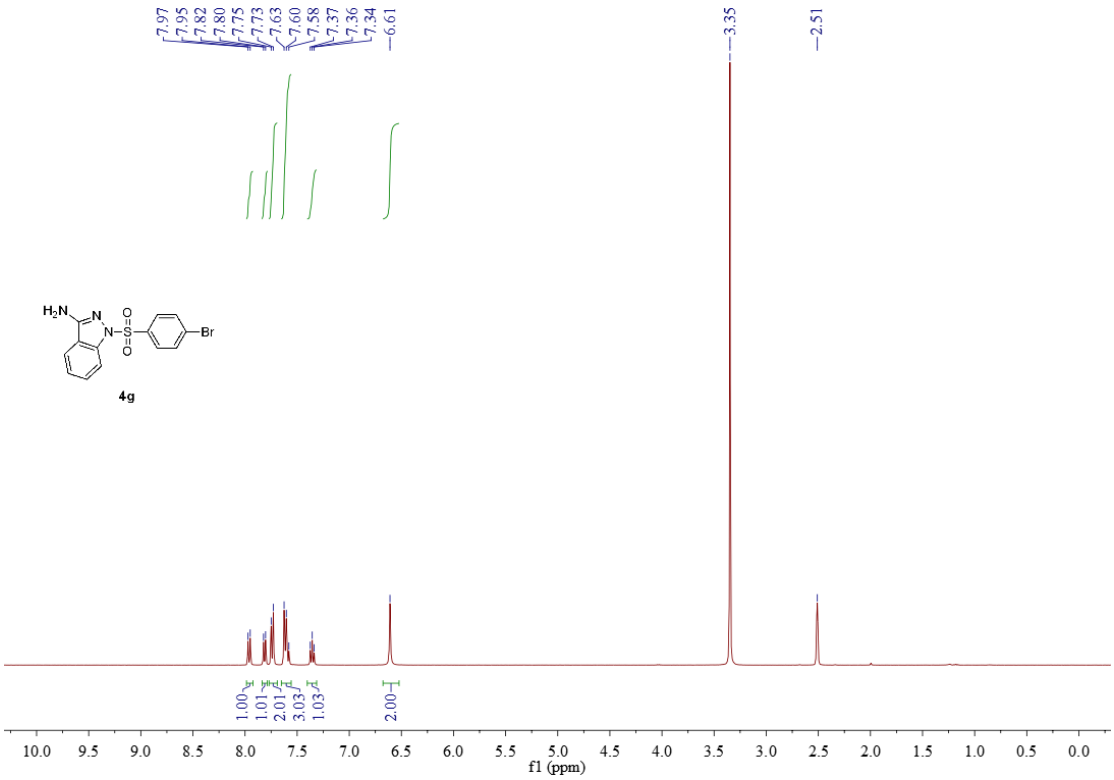
134.96
130.37
129.93
129.31
124.78
121.69
121.34
114.29
40.61
40.40
40.19
39.99
39.78
39.57
39.36
4f
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.80
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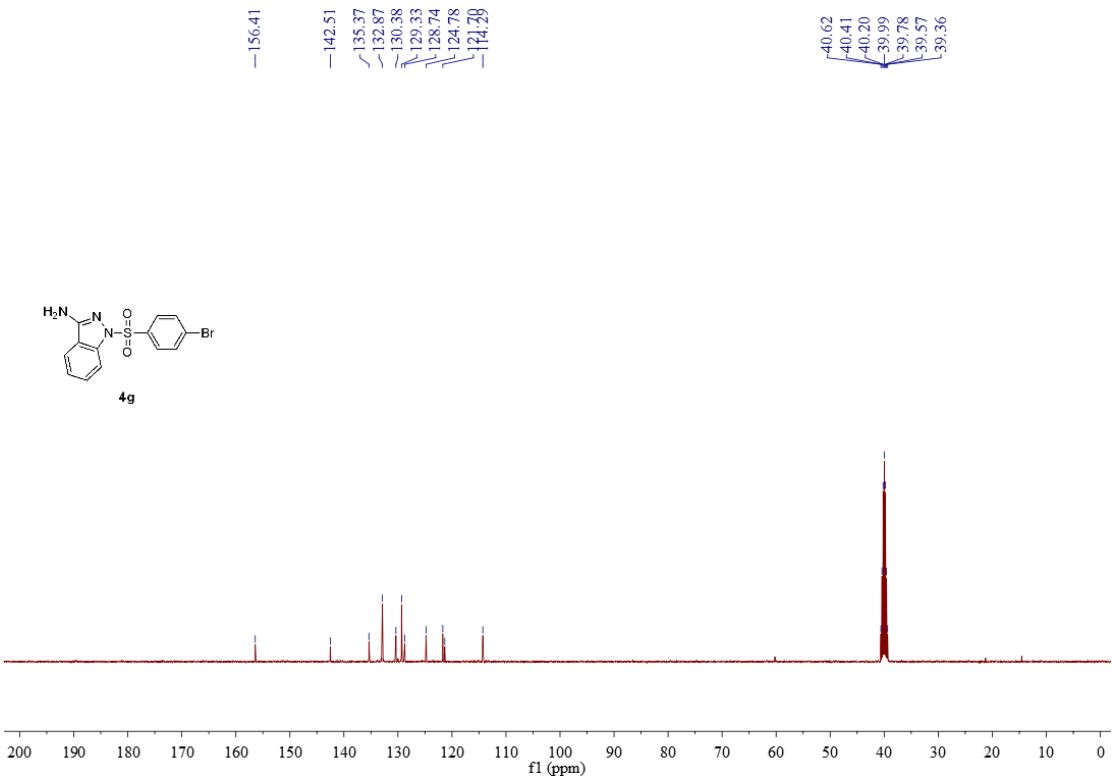
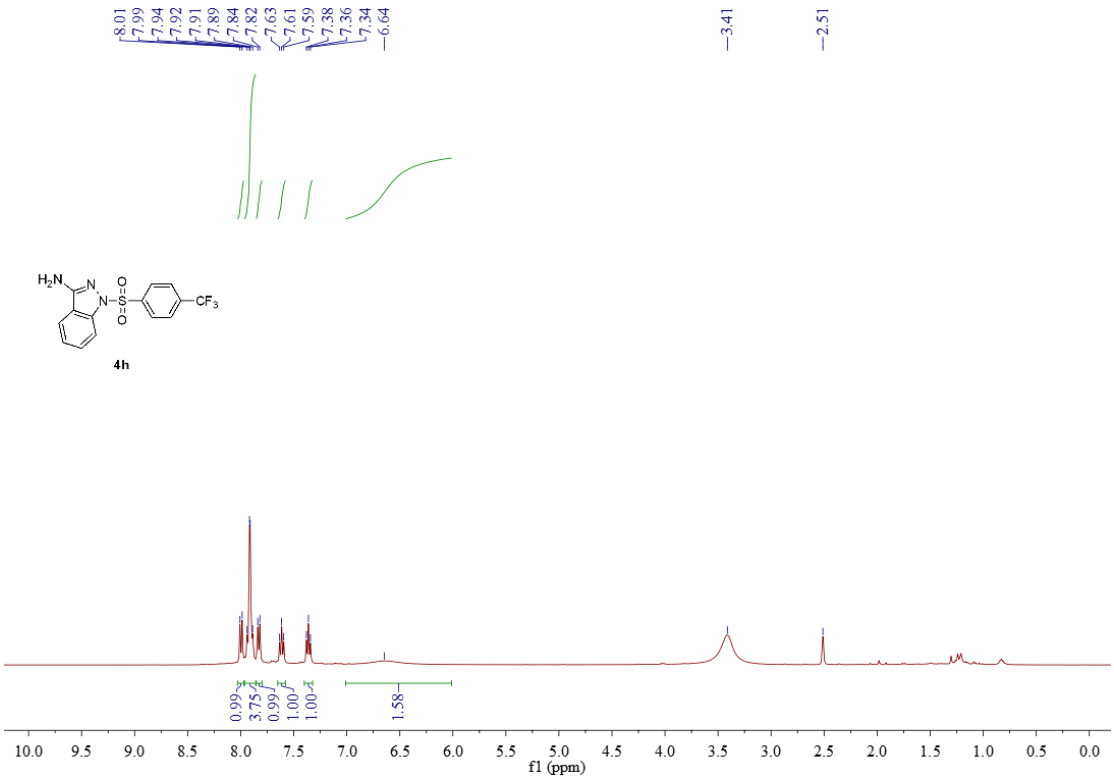
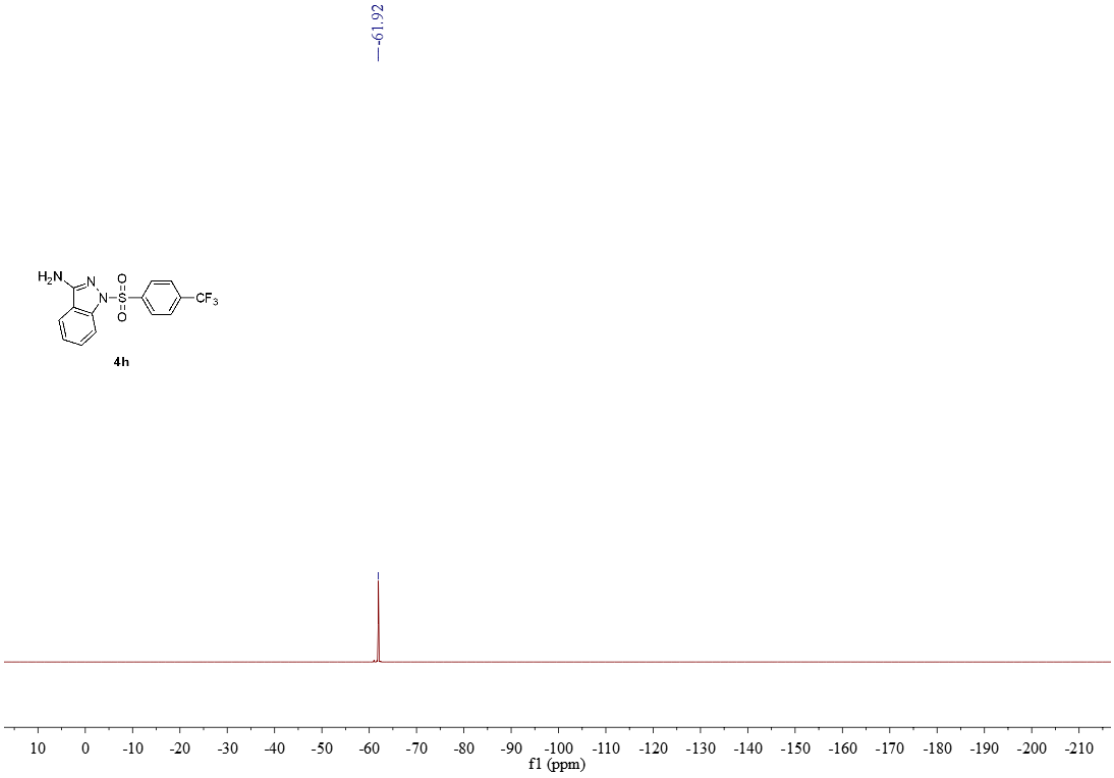
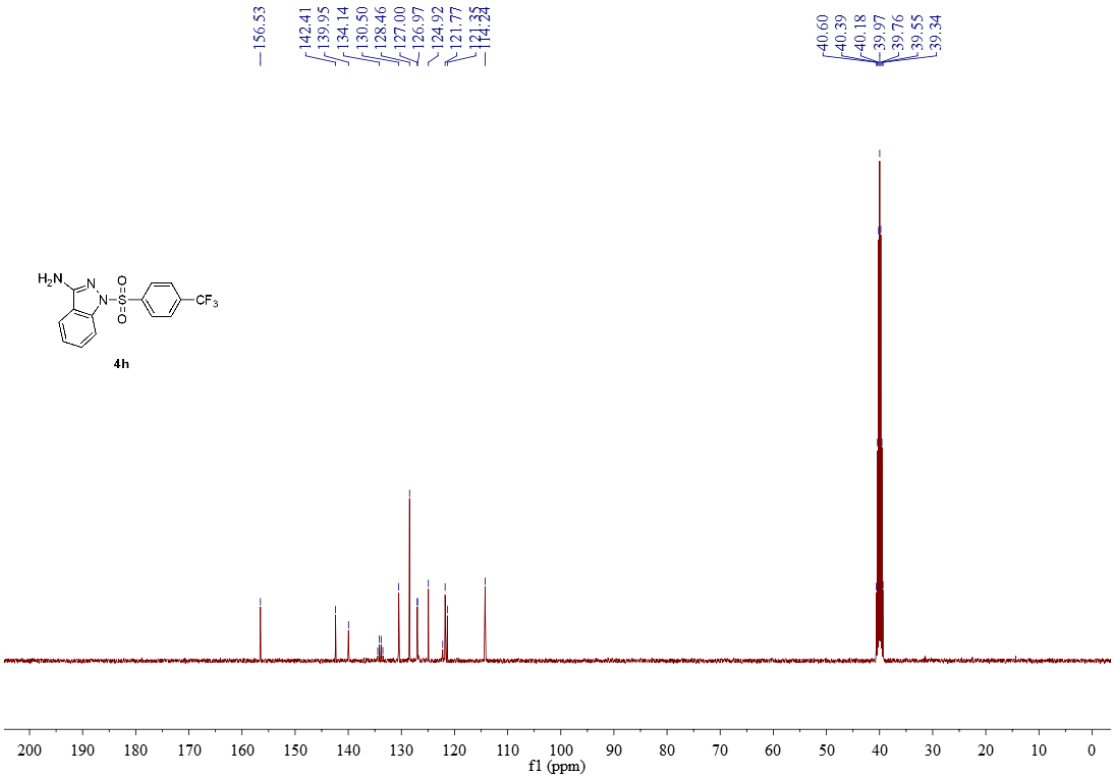
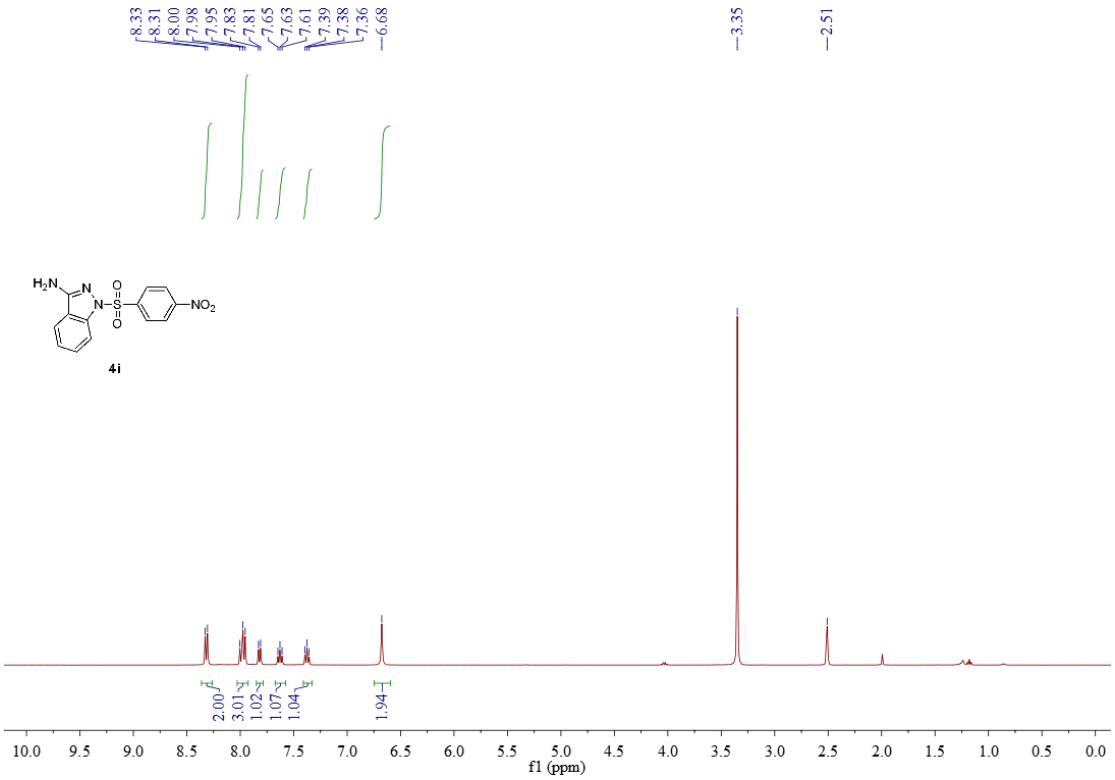
7.73
7.63
7.60
7.58
7.37
7.36
7.34
6.61
3.35
2.51
1.00
1.01
2.01
3.03
1.03
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
Br
4g


156.41
142.51
135.37
132.87
130.38
129.33
128.74
124.78
121.70
114.29
40.62
40.41
40.20
39.99
39.78
39.57
39.36
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
Br
4g


8.01
7.99
7.94
7.92
7.91
7.89
7.84
7.82
7.63
7.61
7.59
7.38
7.36
7.34
6.64
3.41
2.51
4h
0.99
3.75
0.99
1.00
1.00
1.58
f1 (ppm)

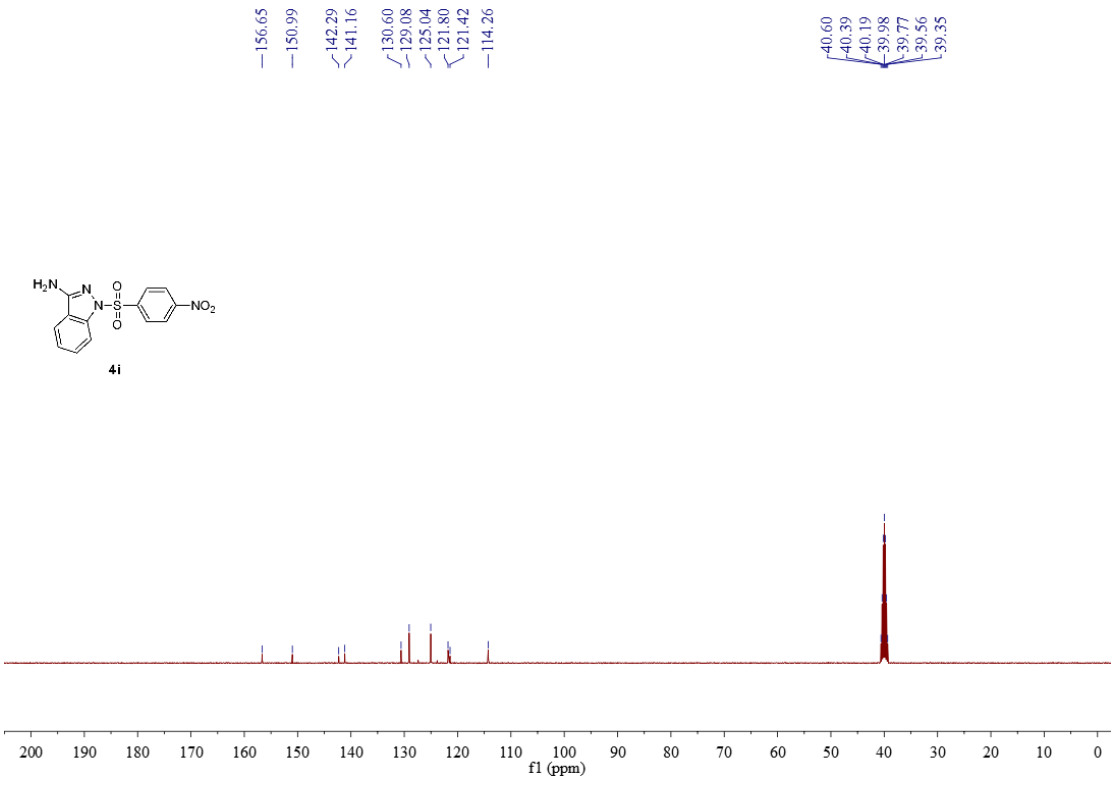

61.92
4h
f1 (ppm)


156.53
142.41
139.95
134.14
130.50
128.46
127.00
126.97
124.92
121.77
121.35
114.24
40.60
40.39
40.18
39.97
39.76
39.55
39.34
4h
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.33
8.31
8.00
7.98
7.95
7.83
7.81
7.65
7.63
7.61
7.39
7.38
7.36
6.68
3.35
2.51
2.00
3.01
1.02
1.07
1.04
1.94
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

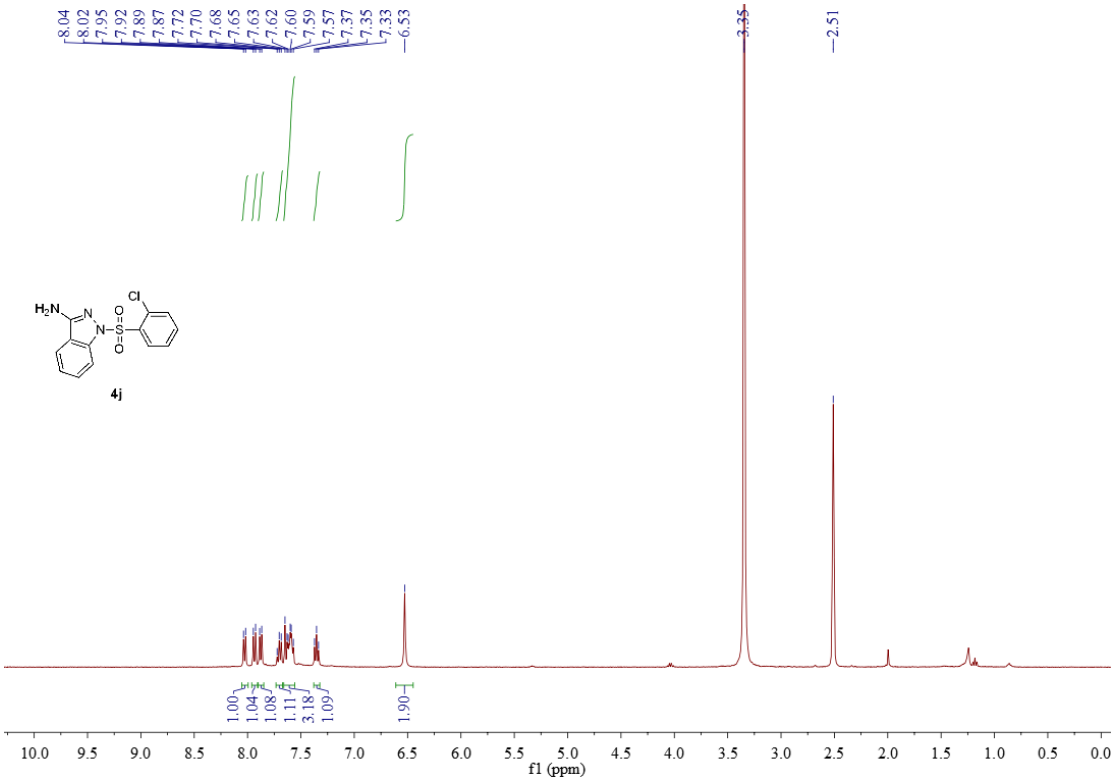

H2N
N
N
S
O
O
NO2

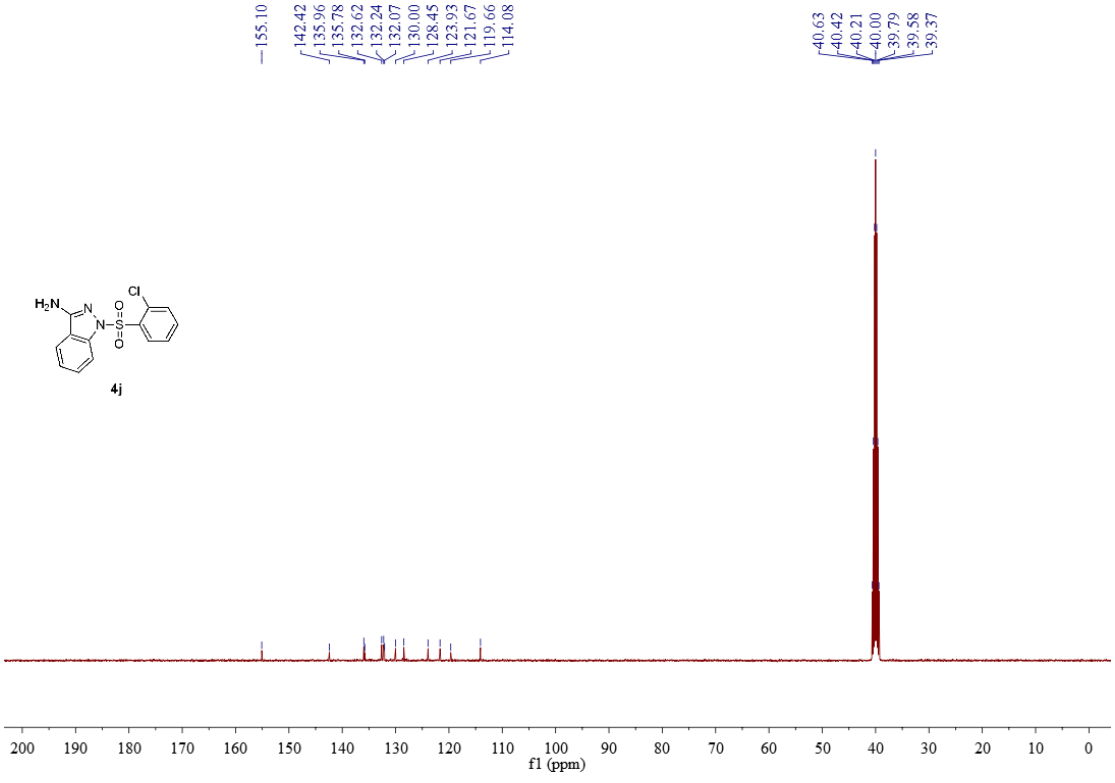
**4i**

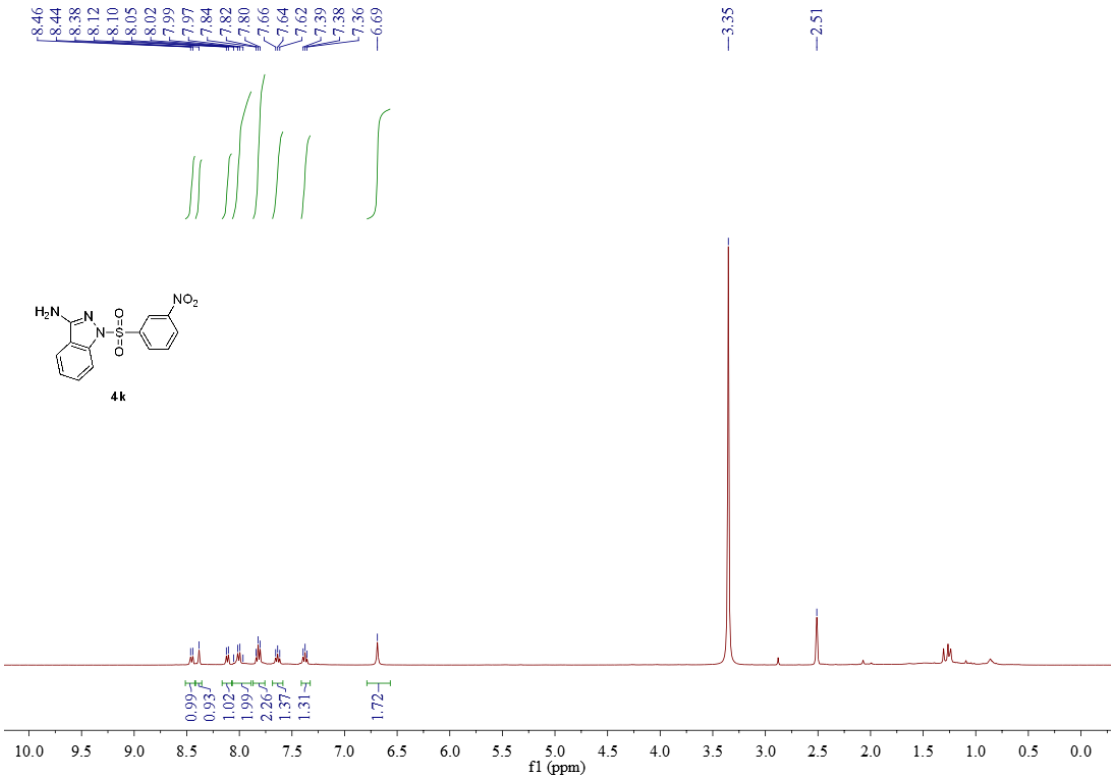

156.65
150.99
142.29
141.16
130.60
129.08
125.04
121.80
121.42
114.26
40.60
40.39
40.19
39.98
39.77
39.56
39.35
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

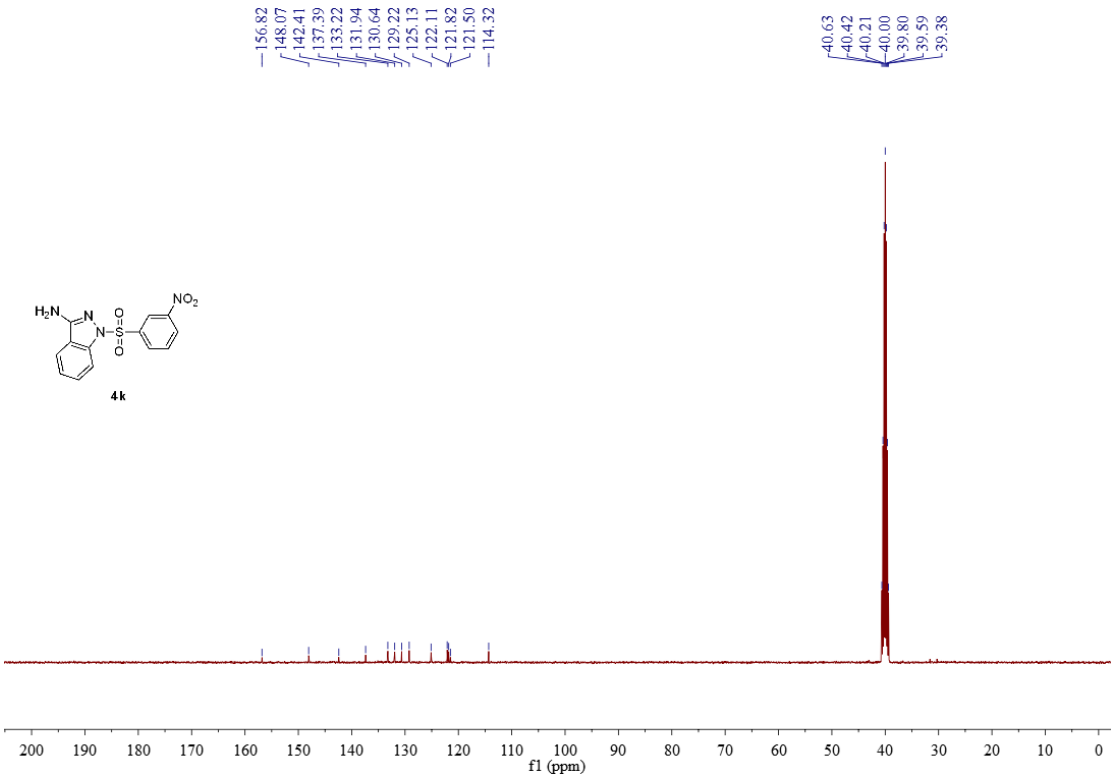

H2N
N
N
S
O
O
NO2

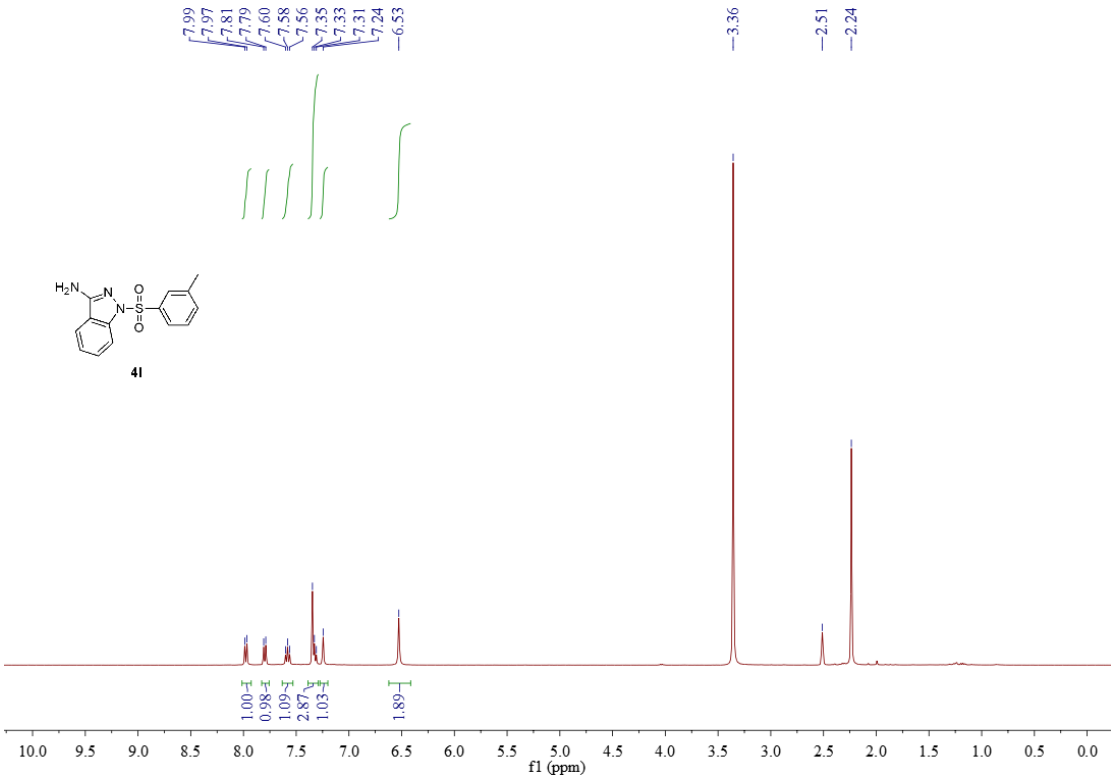
**4i**


8.04
8.02
7.95
7.92
7.89
7.87
7.72
7.70
7.68
7.65
7.63
7.62
7.60
7.59
7.57
7.37
7.35
7.33
6.53
3.35
2.51
Cl
$H_2N$
N
N
S
O
O
4j
1.00
1.04
1.08
1.11
3.18
1.09
1.90
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


155.10
142.42
135.96
135.78
132.62
132.24
132.07
130.00
128.45
123.93
121.67
119.66
114.08
40.63
40.42
40.21
40.00
39.79
39.58
39.37
Cl
$H_2N$
N
N
S
O
O
4j
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

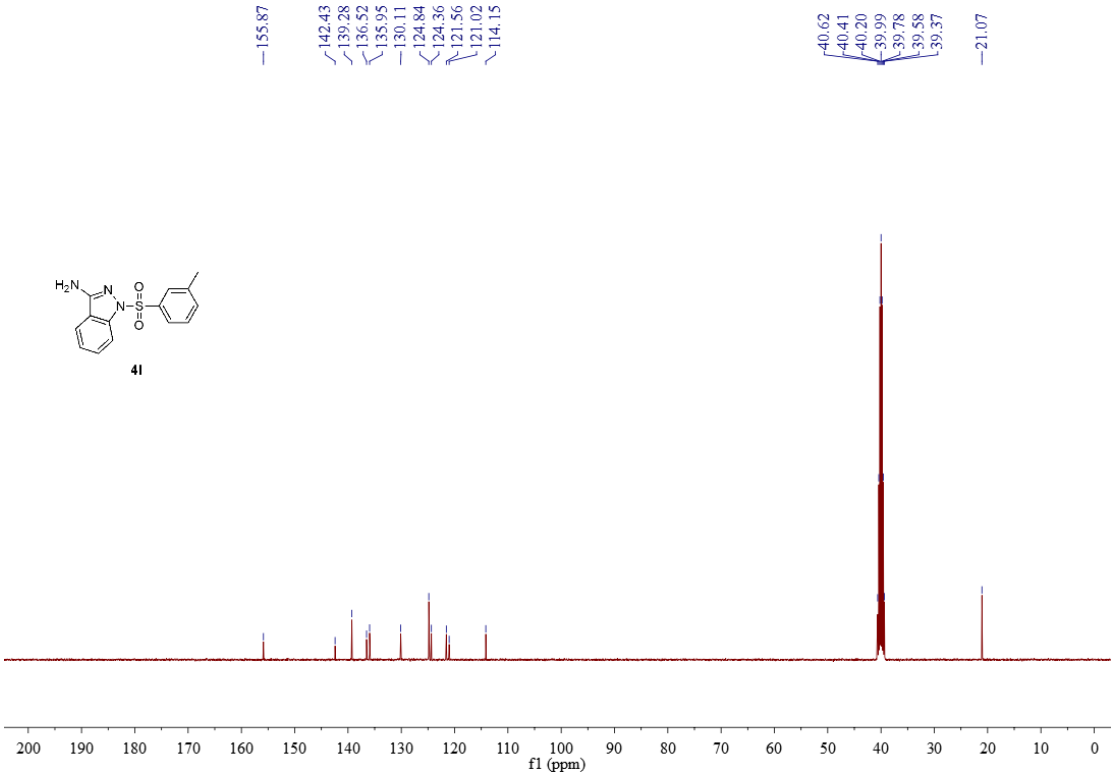

8.46
8.44
8.38
8.12
8.10
8.05
8.02
7.99
7.97
7.84
7.82
7.80
7.66
7.64
7.62
7.39
7.38
7.36
6.69
3.35
2.51
0.99
0.93
1.02
1.99
2.26
1.37
1.31
1.72
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
H2N
N
N
O=S=O
NO2
4k


156.82
148.07
142.41
137.39
133.22
131.94
130.64
129.22
125.13
122.11
121.82
121.50
114.32
40.63
40.42
40.21
40.00
39.80
39.59
39.38
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
H2N
N
N
O=S=O
NO2
4k


7.99
7.97
7.81
7.79
7.60
7.58
7.56
7.35
7.33
7.31
7.24
6.53
3.36
2.51
2.24
1.00
0.98
1.09
2.87
1.03
1.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

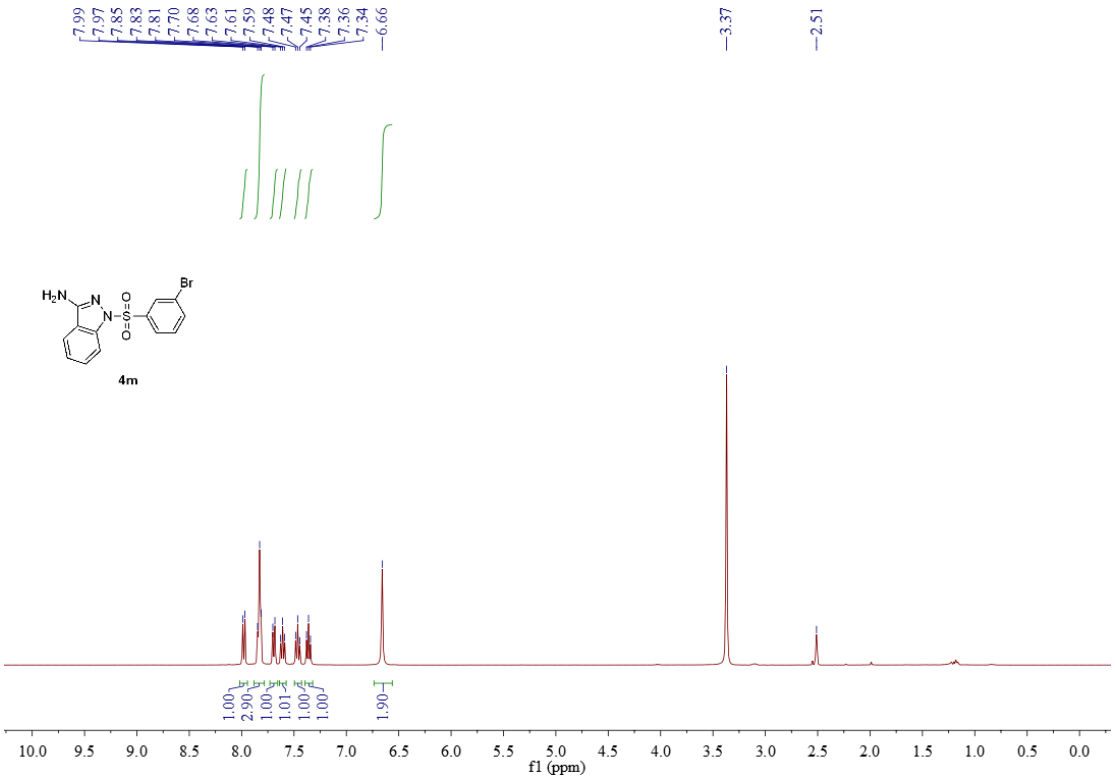


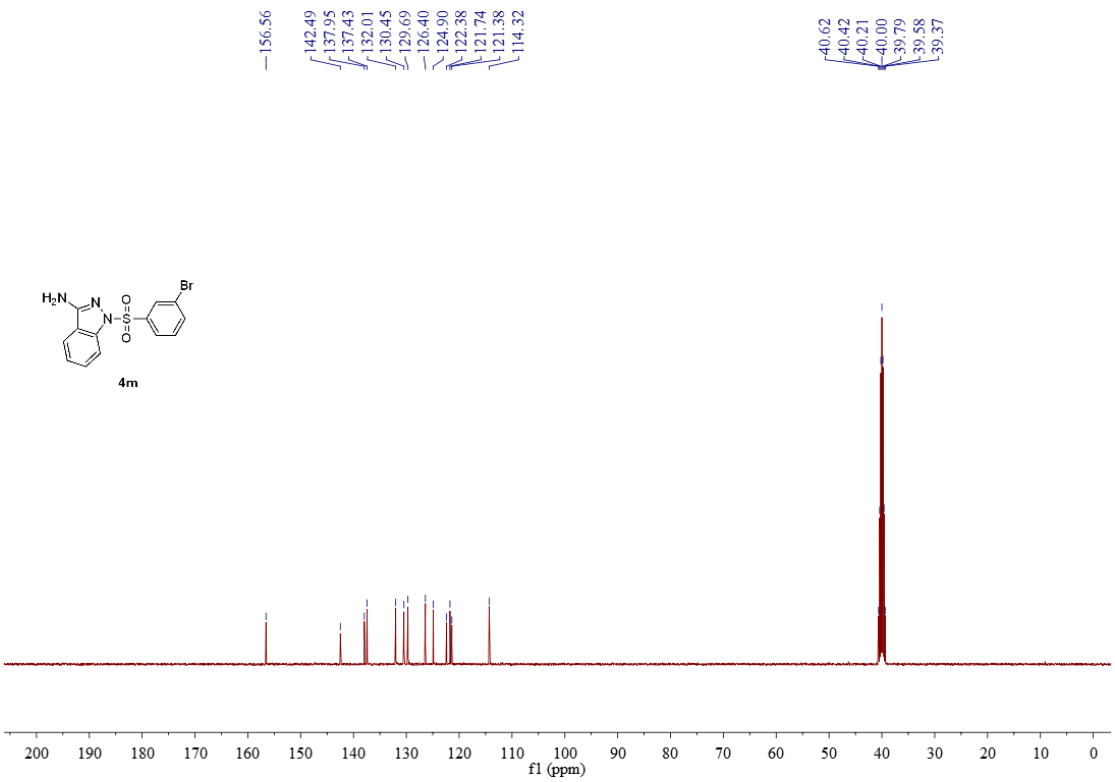
**4l**


155.87
142.43
139.28
136.52
135.95
130.11
124.84
124.36
121.56
121.02
114.15
40.62
40.41
40.20
39.99
39.78
39.58
39.37
21.07
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



**4l**


7.99
7.97
7.85
7.83
7.81
7.70
7.68
7.63
7.61
7.59
7.48
7.47
7.45
7.38
7.36
7.34
6.66
3.37
2.51
Br
4m
1.00
2.90
1.00
1.01
1.00
1.00
1.90
f1 (ppm)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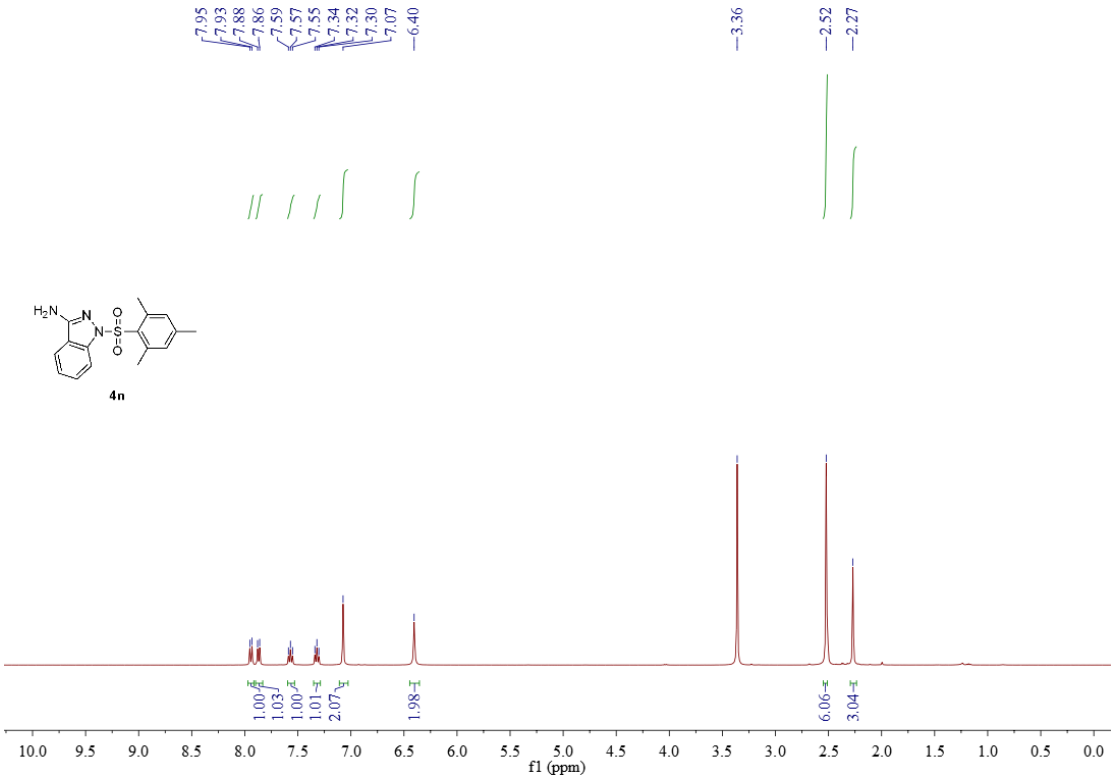
137.95
137.43
132.01
130.45
129.69
126.40
124.90
122.38
121.74
121.38
114.32
40.62
40.42
40.21
40.00
39.79
39.58
39.37
Br
4m
f1 (ppm)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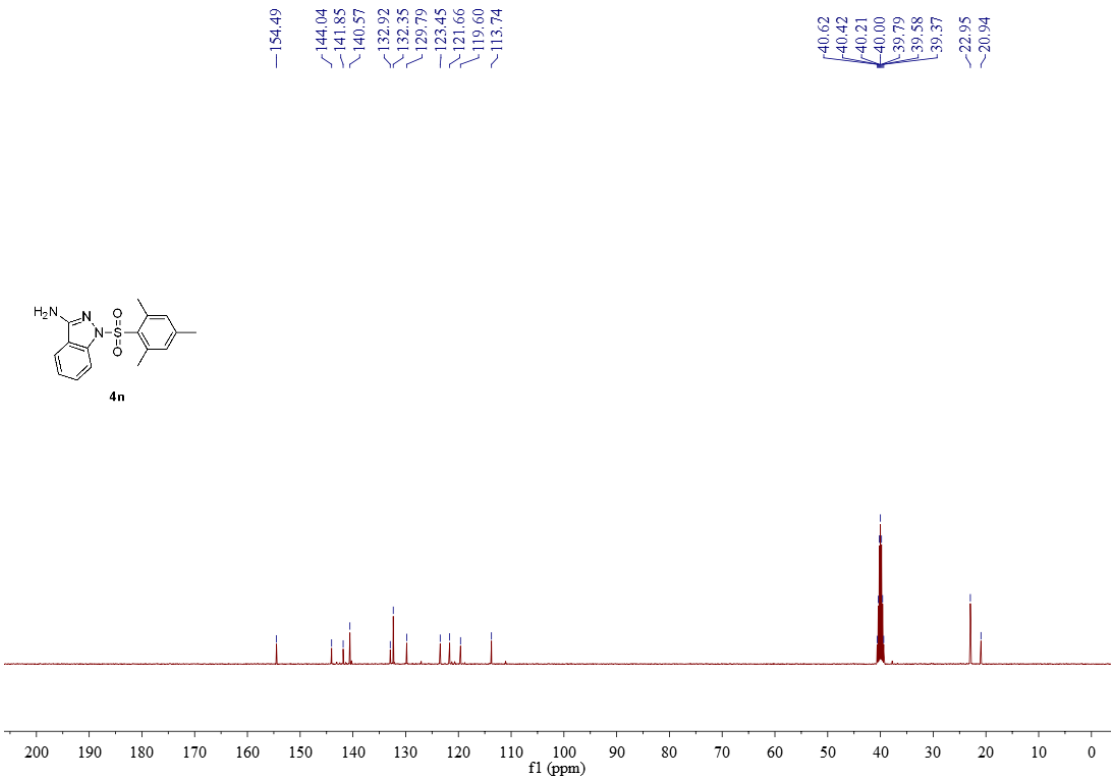
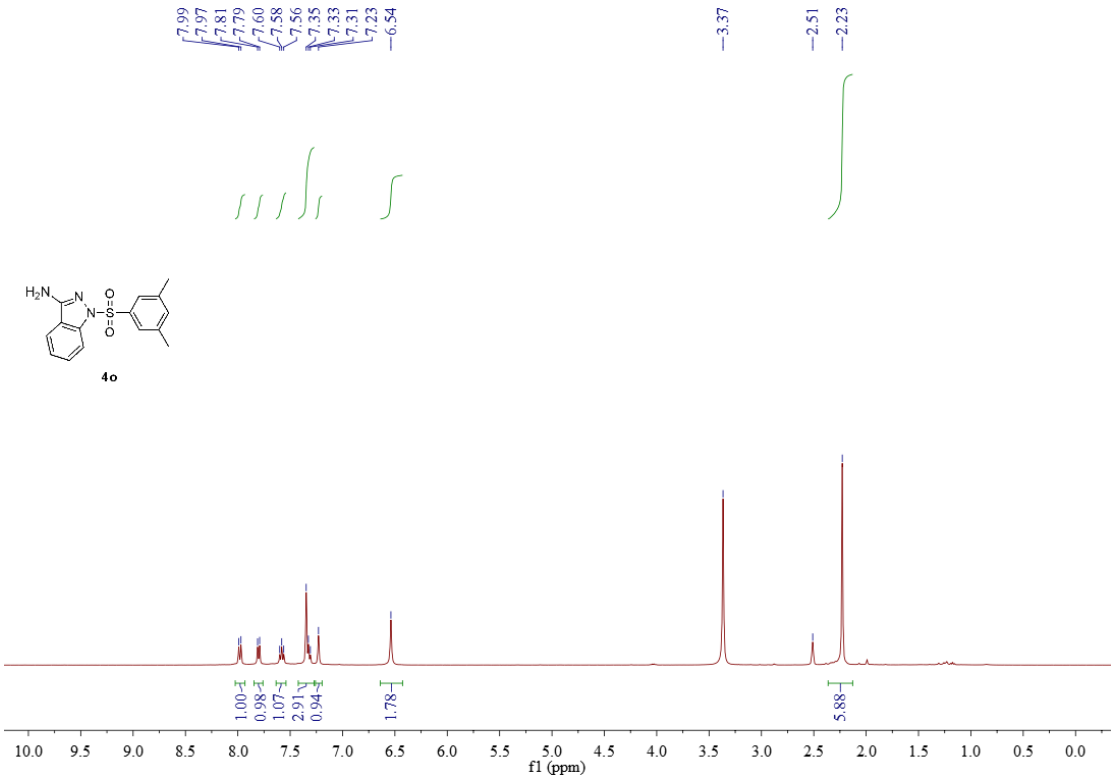
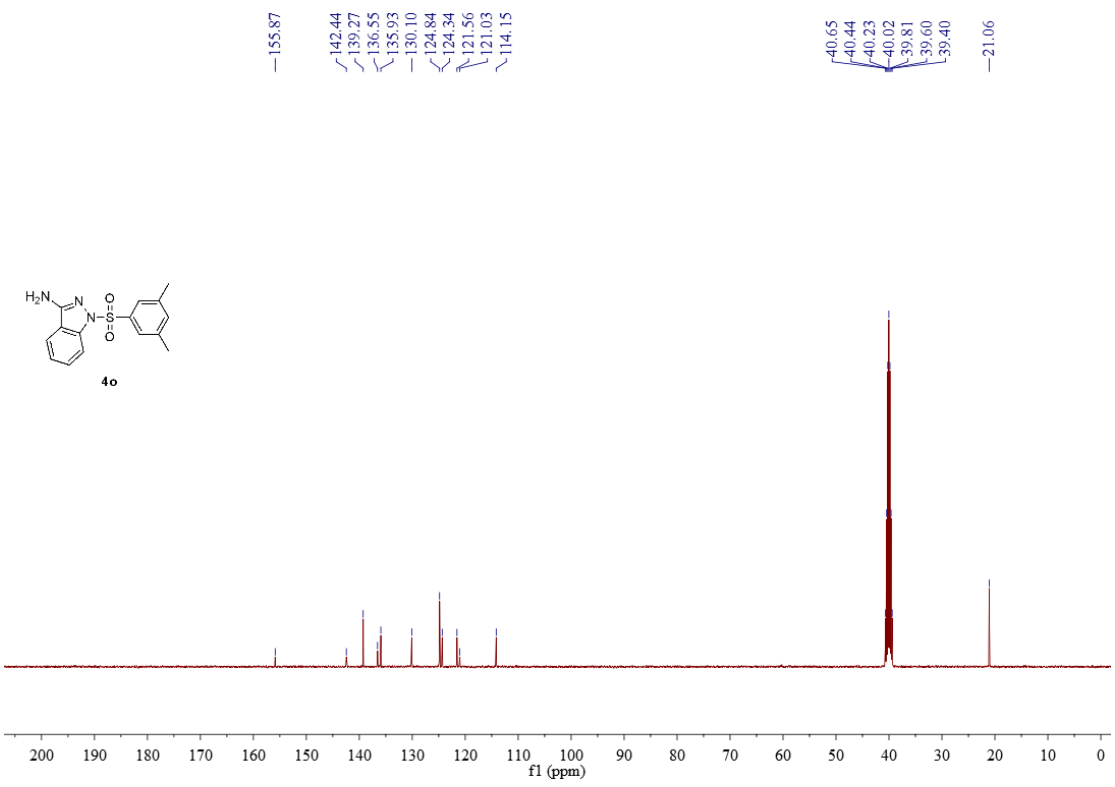
7.93
7.88
7.86
7.59
7.57
7.55
7.34
7.32
7.30
7.07
6.40
3.36
2.52
2.27
4n
1.00
1.03
1.00
1.01
2.07
1.98
6.06
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


154.49
144.04
141.85
140.57
132.92
132.35
129.79
123.45
121.66
119.60
113.74
40.62
40.42
40.21
40.00
39.79
39.58
39.37
22.95
20.94
4n
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.99
7.97
7.81
7.79
7.60
7.58
7.56
7.35
7.33
7.31
7.23
6.54
3.37
2.51
2.23
4o
1.00
0.98
1.07
2.91
0.94
1.78
5.88
f1 (ppm)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142.44
139.27
136.55
135.93
130.10
124.84
124.34
121.56
121.03
114.15
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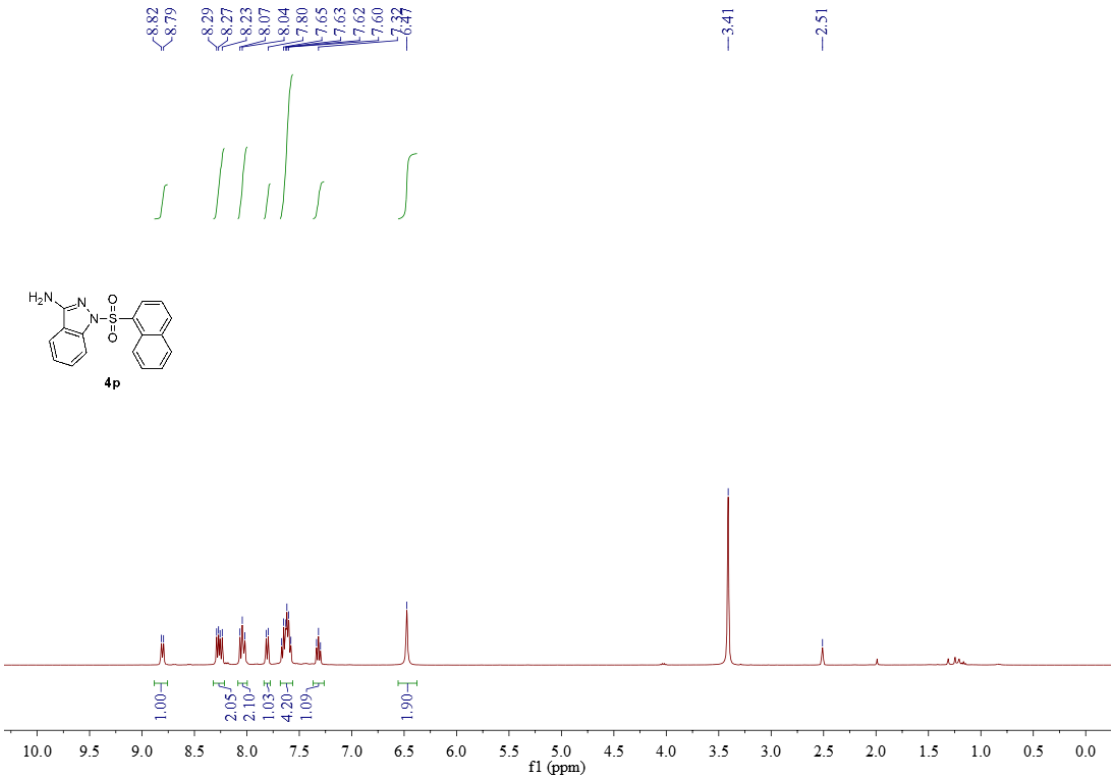
40.44
40.23
40.02
39.81
39.60
39.40
21.06
4o
f1 (ppm)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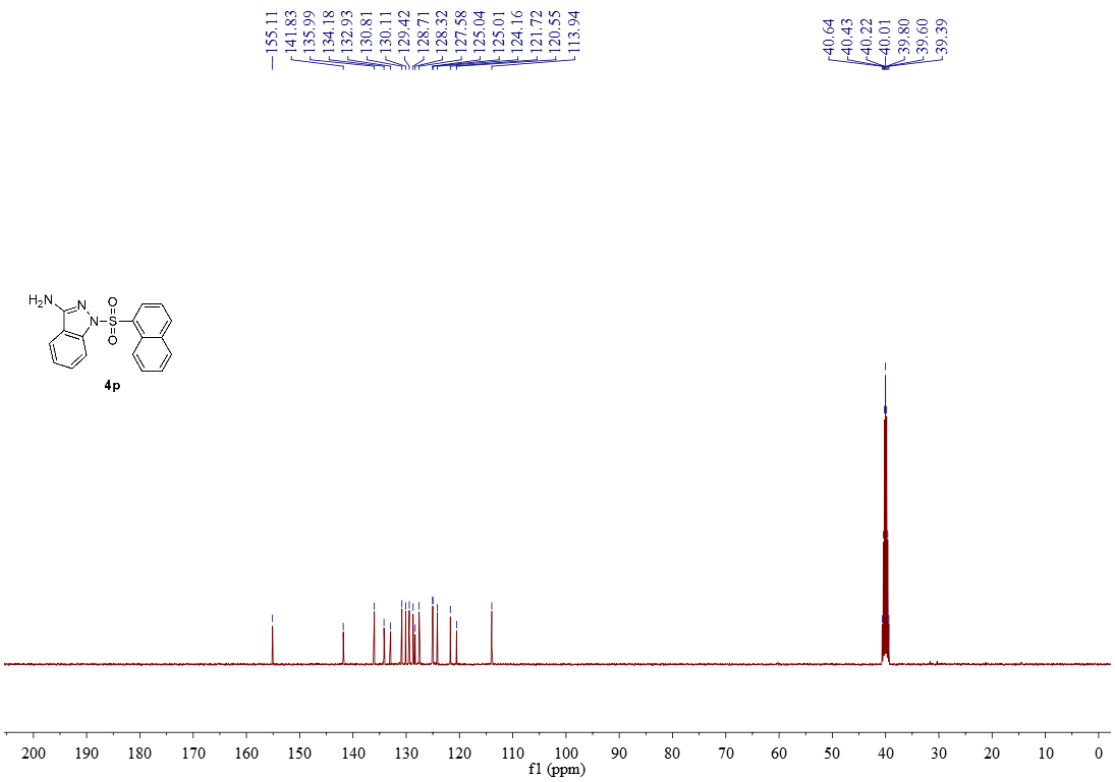
8.79
8.29
8.27
8.23
8.07
8.04
7.80
7.65
7.63
7.62
7.60
7.37
6.47
3.41
2.51
1.00
2.05
2.10
1.03
4.20
1.09
1.90
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



4p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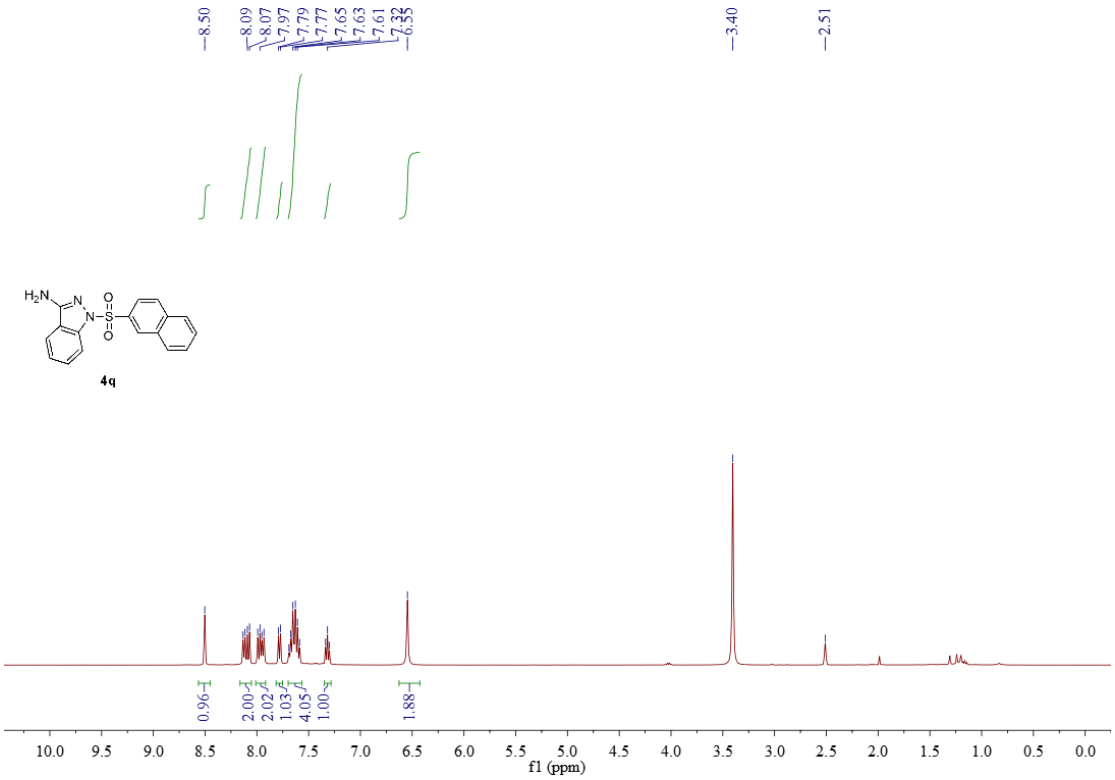
134.18
132.93
130.81
130.11
129.42
128.71
128.32
127.58
125.04
125.01
124.16
121.72
120.55
113.94
40.64
40.43
40.22
40.01
39.80
39.60
39.39
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



4p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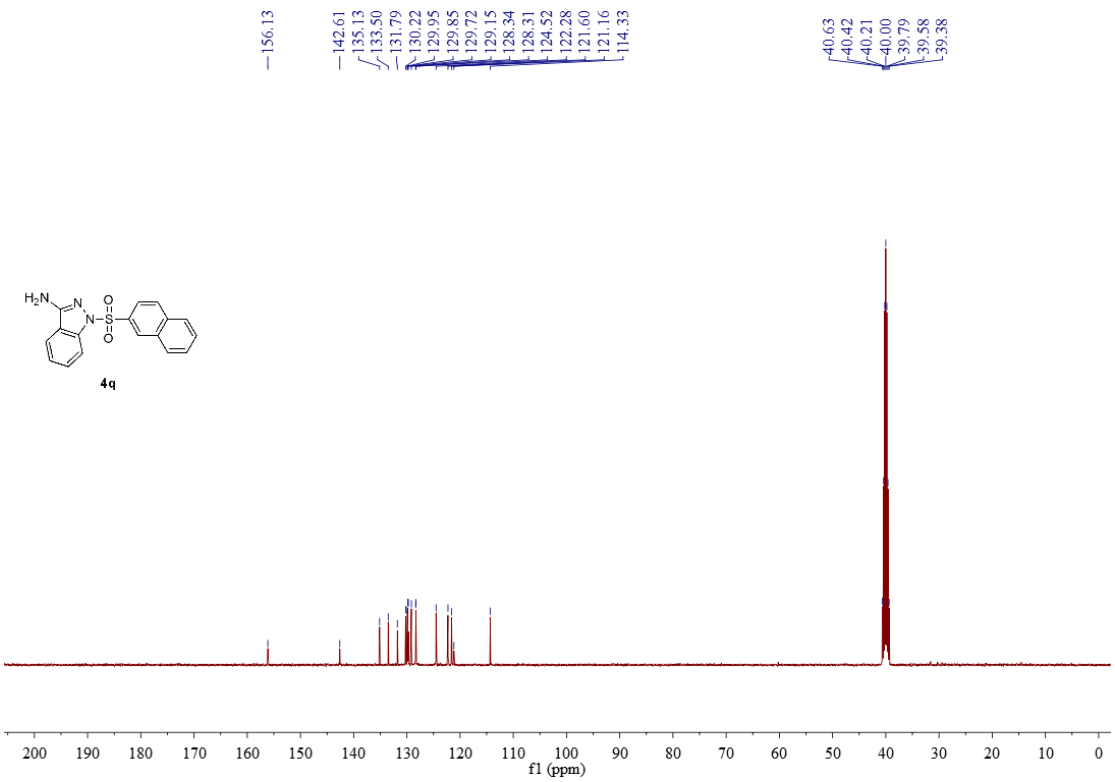
8.09
8.07
7.97
7.79
7.77
7.65
7.63
7.61
6.55
3.40
2.51
4q
0.96
2.00
2.02
1.03
4.05
1.00
1.88
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


156.13
142.61
135.13
133.50
131.79
130.22
129.95
129.85
129.72
129.15
128.34
128.31
124.52
122.28
121.60
121.16
114.33
40.63
40.42
40.21
40.00
39.79
39.58
39.38
4q
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)