

## Supporting Information

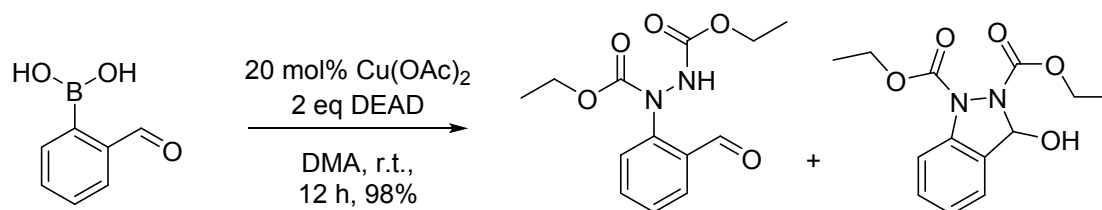
### Synthesis of indazoles from 2-formylphenylboronic acids

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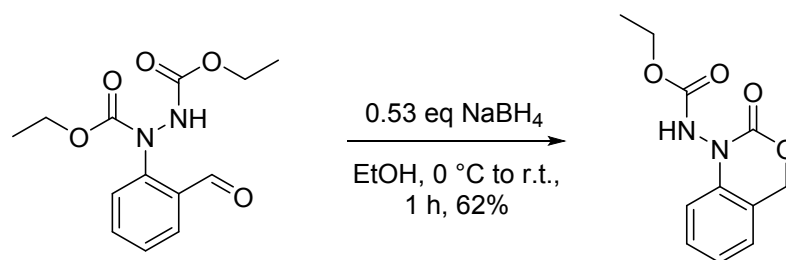
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#### Procedure of synthesis of diethyl 1-(2-formylphenyl)hydrazine-1,2-dicarboxylate (**3a**) from (2-formylphenyl)boronic acid (**1a**)



To a stirred solution of (2-formylphenyl)boronic acid (150 mg, 1 mmol), N,N-Dimethylacetamide (5 mL) and DEAD (315  $\mu$ L, 2 eq), catalytic Cu(OAc)<sub>2</sub> was added (20 mol%, 37 mg). Reaction sealed under air, and stirred overnight at room temperature. Then r.m. partitioned between EtOAc (20 mL) and brine (20 mL) washed with brine (3x15 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo* to obtain crude material. Compound was purified on silica gel, using EtOAc in PE gradient to obtain product **3a** (as a mixture with the cyclic tautomer) as colourless oil (283 mg, 98%).

Compound **3a** was difficult to characterize due to the mixture of tautomers. Therefore it was transformed to product **S1**, using reduction with NaBH<sub>4</sub>.

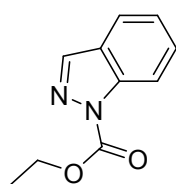


To a stirred solution of **3a** (120 mg, 0.43 mmol) in 2 ml EtOH, cooled to 0 °C, NaBH<sub>4</sub> (8.6 mg, 0.53 eq) added in one portion. After warming up to room temperature, reaction stirred for 1 h and quenched with 1 M aqueous HCl (5 mL) and stirred for additional 15 min. Reaction mixture partitioned between EtOAc (20 mL) and brine (10 mL), washed with saturated NaHCO<sub>3</sub> solution (10 mL) and brine (10 ml), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo* to obtain crude material. Compound purified using reverse phase chromatography to obtain product **S1** as viscous oil (63 mg, 62%). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  7.34 (ddd, *J* = 8.3, 6.6, 2.3 Hz, 1H), 7.19 – 7.08 (m, 3H), 7.03 (s, 1H), 5.40 – 5.20 (m, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 18.5 Hz, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  155.9, 152.4, 138.4, 129.5, 124.3, 124.0, 119.1, 112.7, 68.1, 63.0, 14.5. HRMS C<sub>11</sub>H<sub>13</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup>, calculated 237.0875, found 237.0886.

### General Procedure A for the synthesis of alkoxy carbonyl-protected indazoles.

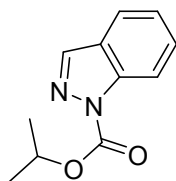
To a stirred solution of (2-formylphenyl)boronic acid (150 mg, 1 mmol), MeCN (5 mL) and DIAD (296  $\mu$ L, 1.5 eq), catalytic Cu(OAc)<sub>2</sub> was added (20 mol%, 37 mg). Reaction sealed under air, and stirred overnight at room temperature. Then TFA (384  $\mu$ L, 5 eq) added at room temperature, and reaction stirred for 2 h before evaporated to dryness. Resulting residue partitioned between EtOAc (20 mL) and saturated NaHCO<sub>3</sub> solution (30 mL), washed with brine (2x15 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo* to obtain crude material. Compound purified on silica, using EtOAc in PE gradient to obtain product **4b** as yellowish oil (176 mg, 86%).

Ethyl 1H-indazole-1-carboxylate (**4a**) (Reported in literature<sup>1</sup>)



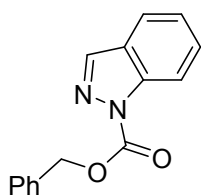
Prepared according to the General Procedure A, replacing DIAD with DEAD. Purified by silica gel column chromatography (gradient 5% to 20% EtOAc in PE), R<sub>f</sub> 0.76 (EtOAc:PE 1:1), white yellow oil; 78% (150 mg). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.24 (d, *J* = 8.5 Hz, 1H), 8.18 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 4.59 (q, *J* = 7.1 Hz, 2H), 1.52 (t, *J* = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  150.8, 140.2, 139.9, 129.3, 125.9, 124.1, 121.2, 114.6, 64.1, 14.5. HRMS: C<sub>10</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup>; calculated 191.0821, found 191.0826.

Isopropyl 1H-indazole-1-carboxylate (**4b**) (Reported in literature<sup>1</sup>)



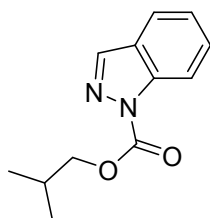
Prepared according to the General Procedure A. Purified by silica gel column chromatography (gradient 5 to 15% EtOAc in PE), R<sub>f</sub> 0.48 (EtOAc:PE 1:4), yellowish oil; 86% (176 mg). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.24 (d, *J* = 8.5 Hz, 1H), 8.19 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 5.38 (hept, *J* = 6.3 Hz, 1H), 1.52 (d, *J* = 6.3 Hz, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  150.4, 140.1, 140.0, 129.2, 126.0, 124.0, 121.3, 114.7, 72.5, 22.1. HRMS: C<sub>11</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup>; calculated 227.0796, found 227.0803.

Benzyl 1H-indazole-1-carboxylate (**4c**) (Reported in literature<sup>2</sup>)



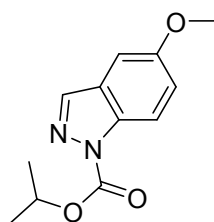
Prepared according to the General Procedure A, replacing DIAD with di-benzyl azodicarboxylate. Purified by silica gel column chromatography (gradient 5% to 20% EtOAc in PE), Rf 0.55 (EtOAc:PE 1:3), white solid; m.p. 78-80 °C, 60% (76 mg). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 8.5 Hz, 1H), 8.20 (s, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.44 – 7.30 (m, 4H), 5.55 (s, 2H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 150.8, 140.5, 140.0, 135.0, 129.4, 128.9, 128.9, 128.9, 126.0, 124.2, 121.3, 114.7, 69.5.

Isobutyl 1H-indazole-1-carboxylate (**4d**)



Prepared according to the General Procedure A, replacing DIAD with di-isobutyl azodicarboxylate. Purified by silica gel column chromatography (gradient 5% to 10% EtOAc in PE), Rf 0.23 (EtOAc:PE 1:10), yellow oil; 45% (99 mg). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 9.0 Hz, 1H), 8.18 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.3 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 4.30 (d, *J* = 6.9 Hz, 2H), 2.21 (dh, *J* = 13.5, 6.8 Hz, 1H), 1.06 (d, *J* = 6.7 Hz, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 150.9, 140.2, 139.8, 129.2, 126.0, 124.0, 121.2, 114.5, 73.9, 28.0, 19.2. HRMS: C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup>; calculated 241.0953, found 241.0962.

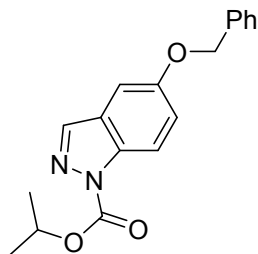
Isopropyl 5-methoxy-1H-indazole-1-carboxylate (**4e**)



Prepared according to the General Procedure A. Purified by silica gel column chromatography (gradient 5% to 35% EtOAc in PE), Rf 0.38 (EtOAc:PE 1:3), white oil, solidifies on standing; m.p. 73-75 °C, 76% (99 mg). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 9.5 Hz, 2H), 7.18 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.09 (d, *J* = 2.4 Hz, 1H), 5.35 (hept, *J* = 6.3 Hz, 1H), 3.86 (s, 3H), 1.51 (d, *J* = 6.3 Hz, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ

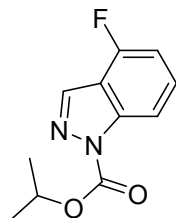
156.7, 150.4, 139.7, 135.3, 126.7, 120.0, 115.5, 101.4, 72.5, 55.8, 22.1. HRMS:  $C_{12}H_{14}N_2O_3Na$   $[M+Na]^+$ ; calculated 257.0902, found 257.0911.

Isopropyl 5-(benzyloxy)-1H-indazole-1-carboxylate (**4f**)



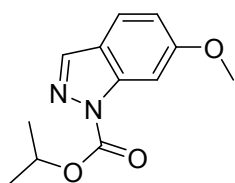
Prepared according to the General Procedure A. Purified by silica gel column chromatography (gradient 5% to 20% EtOAc in PE), Rf 0.45 (EtOAc:PE 1:3), white solid; m.p. 110-111 °C, 74% (89.5 mg).  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.13 (d,  $J = 9.1$  Hz, 1H), 8.09 (s, 1H), 7.50 – 7.43 (m, 2H), 7.43 – 7.37 (m, 2H), 7.37 – 7.31 (m, 1H), 7.27 (dd,  $J = 9.1, 2.4$  Hz, 1H), 7.17 (d,  $J = 2.1$  Hz, 1H), 5.36 (hept,  $J = 6.3$  Hz, 1H), 5.12 (s, 2H), 1.51 (d,  $J = 6.3$  Hz, 6H);  $^{13}C$  NMR (101 MHz, Chloroform-*d*)  $\delta$  155.8, 150.3, 139.7, 136.8, 135.4, 128.8, 128.3, 127.6, 126.7, 120.5, 115.6, 103.0, 72.5, 70.7, 22.1. HRMS:  $C_{18}H_{19}N_2O_3$   $[M+H]^+$ ; calculated 311.1396, found 311.1400.

Isopropyl 4-fluoro-1H-indazole-1-carboxylate (**4g**)



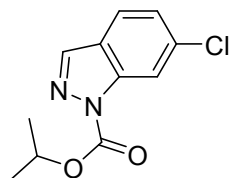
Prepared according to the General Procedure A. Purified by silica gel column chromatography (gradient 5% to 15% EtOAc in PE), Rf 0.85 (EtOAc:PE 1:3), white yellow solid; m.p. 80-82 °C, 33% (44 mg).  $^1H$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.24 (s, 1H), 7.99 (d,  $J = 8.4$  Hz, 1H), 7.46 (td,  $J = 8.2, 5.2$  Hz, 1H), 6.95 (ddd,  $J = 9.4, 7.9, 0.5$  Hz, 1H), 5.35 (hept,  $J = 6.3$  Hz, 1H), 1.50 (d,  $J = 6.3$  Hz, 6H);  $^{13}C$  NMR (101 MHz, Chloroform-*d*)  $\delta$  155.4 (d,  $J = 253.5$  Hz), 150.2, 142.1 (d,  $J = 7.6$  Hz), 135.9 (d,  $J = 1.6$  Hz), 130.4 (d,  $J = 7.5$  Hz), 115.9 (d,  $J = 22.7$  Hz), 110.7 (d,  $J = 4.4$  Hz), 108.8 (d,  $J = 18.0$  Hz), 72.9, 22.0.  $^{19}F$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -117.70. HRMS:  $C_{11}H_{11}N_2O_2NaF$   $[M+Na]^+$ ; calculated 245.0702, found 245.0707.

Isopropyl 6-methoxy-1H-indazole-1-carboxylate (**4h**)



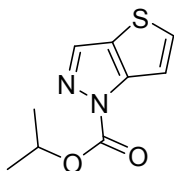
Prepared according to the General Procedure A. Purified by silica gel column chromatography (gradient 5% to 35% EtOAc in PE), Rf 0.36 (EtOAc:PE 1:4), white crystalline solid; m.p. 69-70 °C, 55% (72 mg). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.69 (d, *J* = 1.9 Hz, 1H), 7.55 (dd, *J* = 8.7, 0.4 Hz, 1H), 6.92 (dd, *J* = 8.7, 2.2 Hz, 1H), 5.33 (hept, *J* = 6.3 Hz, 1H), 3.89 (s, 3H), 1.49 (d, *J* = 6.3 Hz, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 161.4, 150.6, 141.7, 139.9, 121.7, 120.0, 115.2, 96.7, 72.4, 55.7, 22.0. HRMS: C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup>; calculated 257.0902, found 257.0909.

Isopropyl 6-chloro-1H-indazole-1-carboxylate (**4i**)



Prepared according to the General Procedure A. Purified by silica gel column chromatography (gradient 5% to 15% EtOAc in PE), Rf 0.55 (EtOAc:PE 1:4), white yellow solid; m.p. 76-78 °C, 28% (36 mg). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.25 (s, 1H), 8.13 (s, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.29 (dd, *J* = 8.5, 1.8 Hz, 1H), 5.36 (hept, *J* = 6.3 Hz, 1H), 1.51 (d, *J* = 6.3 Hz, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 150.1, 140.4, 139.7, 135.7, 125.0, 124.5, 122.0, 114.8, 73.0, 22.0. HRMS: C<sub>11</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>NaCl [M+Na]<sup>+</sup>; calculated 261.0407, found 261.0410.

Isopropyl 1H-thieno[3,2-*c*]pyrazole-1-carboxylate (**9**)

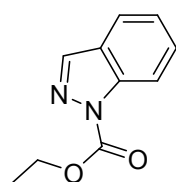


Prepared according to the General Procedure A. Purified by silica gel column chromatography (gradient 5% to 20% EtOAc in PE), Rf 0.29 (EtOAc:PE 1:10), yellow oil; 69% (112 mg). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.55 (d, *J* = 5.2 Hz, 1H), 7.37 (d, *J* = 5.2 Hz, 1H), 5.33 (hept, *J* = 6.3 Hz, 1H), 1.49 (d, *J* = 6.3 Hz, 6H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 149.1, 148.7, 135.9, 134.2, 125.3, 113.4, 73.0, 22.0. HRMS: C<sub>9</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>SNa [M+Na]<sup>+</sup>; calculated 233.0361, found 233.0368.

### General Procedure B for the synthesis of alkoxy-carbonyl-protected indazoles from dialkyl hydrazine-1,2-dicarboxylates.

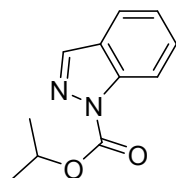
To a stirred solution of (2-formylphenyl)boronic acid (100 mg, 0.67 mmol), MeCN (5 mL), diethyl hydrazine-1,2-dicarboxylate (235 mg, 2 eq) and  $\text{Cu}(\text{OAc})_2$  (121 mg, 1 eq), TMEDA was added (200  $\mu\text{L}$ , 2 eq). Reaction sealed under air, and stirred overnight at room temperature. Then TFA (768  $\mu\text{L}$ , 15 eq) added dropwise at room temperature, and reaction stirred for 4 h before evaporated to dryness. Resulting residue partitioned between EtOAc (20 mL) and saturated  $\text{NaHCO}_3$  solution (20 mL), washed with brine (2x15 mL), dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated *in vacuo* to obtain crude material. Compound purified on silica, using EtOAc in PE gradient to obtain product **4a** as a light yellow oil (80.2 mg, 63%).

#### Ethyl 1H-indazole-1-carboxylate (**4a**)



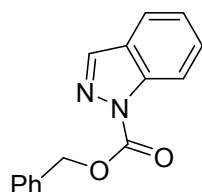
Prepared according to the General Procedure B. Purified by silica gel column chromatography (gradient 5% to 25% EtOAc in PE); 63% (80.2 mg). Analytical data corresponds to the previously described compound **4a**.

#### Isopropyl 1H-indazole-1-carboxylate (**4b**)



Prepared according to the General Procedure B, using diisopropyl hydrazine-1,2-dicarboxylate instead of diethyl hydrazine-1,2-dicarboxylate. Purified by silica gel column chromatography (gradient 5% to 15% EtOAc in PE); 46% (76 mg). Analytical data corresponds to the previously described compound **4b**.

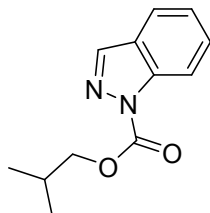
#### Benzyl 1H-indazole-1-carboxylate (**4c**)



Prepared according to the General Procedure B, using dibenzyl hydrazine-1,2-dicarboxylate instead of diethyl hydrazine-1,2-dicarboxylate. Purified by silica gel column chromatography

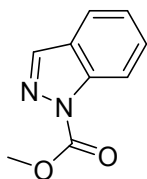
(gradient 5% to 20% EtOAc in PE); 46% (54 mg). Analytical data corresponds to the previously described compound **4c**.

#### Isobutyl 1H-indazole-1-carboxylate (**4d**)



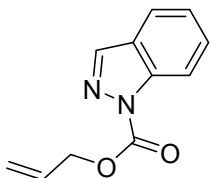
Prepared according to the General Procedure B, using diisobutyl hydrazine-1,2-dicarboxylate instead of diethyl hydrazine-1,2-dicarboxylate. Purified by silica gel column chromatography (gradient 5% to 10% EtOAc in PE); 61% (107 mg). Analytical data corresponds to the previously described compound **4d**.

#### Methyl 1H-indazole-1-carboxylate (**4j**) (Reported in literature<sup>3</sup>)



Prepared according to the General Procedure B, using dimethyl hydrazine-1,2-dicarboxylate instead of diethyl hydrazine-1,2-dicarboxylate. Purified by silica gel column chromatography (gradient 5% to 25% EtOAc in PE), R<sub>f</sub> 0.3 (EtOAc:PE 1:4), white crystalline solid; m.p. 56-57 °C, 64% (75 mg). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.24 (d, *J* = 8.5 Hz, 1H), 8.19 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 8.3 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 1H), 4.14 (s, 3H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 151.0, 140.1, 139.7, 129.1, 125.7, 123.9, 121.0, 114.3, 54.3. HRMS: C<sub>9</sub>H<sub>9</sub>N<sub>2</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup>; calculated 177.0664, found 177.0688.

#### Allyl 1H-indazole-1-carboxylate (**4k**)



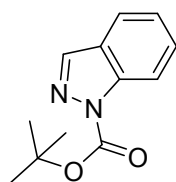
Prepared according to the General Procedure B, using diallyl hydrazine-1,2-dicarboxylate instead of diethyl hydrazine-1,2-dicarboxylate. Purified by silica gel column chromatography (gradient 5% to 20% EtOAc in PE), R<sub>f</sub> 0.42 (EtOAc:PE 1:4), yellow oil; 40% (64 mg). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 8.5 Hz, 1H), 8.16 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.52 (t, *J* = 8.4 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 6.20 – 6.02 (m, 1H), 5.49 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.35 (dq, *J* = 10.4, 1.1 Hz, 1H), 4.99 (dt, *J* = 6.0, 1.3 Hz, 2H); <sup>13</sup>C NMR (101

MHz, Chloroform-*d*)  $\delta$  150.5, 140.3, 139.9, 131.2, 129.3, 125.9, 124.1, 121.2, 120.2, 114.5, 68.4. HRMS: C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup>; calculated 225.0640, found 225.0647

### General Procedure C for the synthesis of 1*N*-Boc-protected indazoles from di-*tert*-butyl hydrazine-1,2-dicarboxylate.

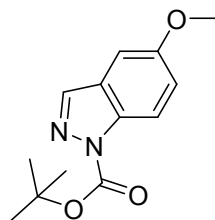
To a stirred solution of (2-formylphenyl)boronic acid (120 mg, 0.8 mmol), MeCN (7 mL), di-*tert*-butyl hydrazine-1,2-dicarboxylate (372 mg, 2 eq) and Cu(OAc)<sub>2</sub> (145 mg, 1 eq), TMEDA was added (240  $\mu$ L, 2 eq). Reaction sealed under air, and stirred overnight at room temperature. Then AcOH (916  $\mu$ L, 20 eq) added dropwise at room temperature, and reaction heated at 50 °C for 2 h before evaporated to dryness. Resulting residue partitioned between EtOAc (20 mL) and saturated NaHCO<sub>3</sub> solution (30 mL), washed with brine (2x20 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated *in vacuo* to obtain crude material. Compound purified on silica, using EtOAc in PE gradient to obtain product **4l** as a yellow oil (128 mg, 73%). Major isolated by-product identified as 1-(1*H*-indazol-1-yl)ethan-1-one **10a**, which <sup>1</sup>H and <sup>13</sup>C NMR data are consistent with those previously reported in literature<sup>4</sup>.

Tert-butyl 1*H*-indazole-1-carboxylate (**4l**) (Reported in literature<sup>5</sup>)



Prepared according to the General Procedure C. Purified by silica gel column chromatography (gradient 5% to 12% EtOAc in PE), R<sub>f</sub> 0.47 (EtOAc:PE 1:4), yellow oil; 73% (128 mg). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.19 (d, *J* = 9.1 Hz, 1H), 8.17 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.3 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 1.73 (s, 9H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  149.4, 139.8, 139.7, 129.0, 126.0, 123.8, 121.2, 114.7, 85.0, 28.3. HRMS: C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup>; calculated 241.0953, found 241.0953.

Tert-butyl 5-methoxy-1*H*-indazole-1-carboxylate (**4m**)

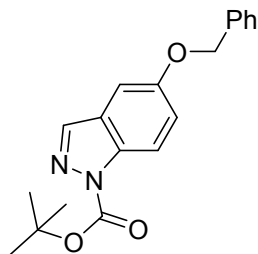


Prepared according to the General Procedure C. Purified by silica gel column chromatography (gradient 5% to 15% EtOAc in PE), R<sub>f</sub> 0.28 (EtOAc:PE 1:4), white oil; 50% (69 mg). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.10 – 8.02 (m, 2H), 7.15 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.08 (d, *J* = 2.3 Hz, 1H), 3.85 (s, 3H), 1.71 (s, 9H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)



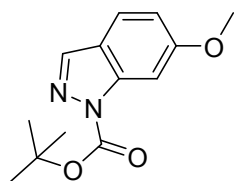
$\delta$  156.5, 149.3, 139.2, 135.2, 126.6, 119.8, 115.6, 101.2, 84.8, 55.8, 28.3. HRMS:  $C_{13}H_{16}N_2O_3Na$   $[M+Na]^+$ ; calculated 271.1059, found 271.1070.

Tert-butyl 5-(benzyloxy)-1H-indazole-1-carboxylate (**4n**)



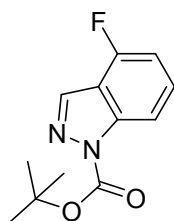
Prepared according to the General Procedure C. Purified by silica gel column chromatography (gradient 5% to 20% EtOAc in PE), R<sub>f</sub> 0.31 (EtOAc:PE 1:4), white solid; m.p. 92-94 °C, 58% (74 mg). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.09 (s, 1H), 8.07 (s, 1H), 7.49 – 7.44 (m, 2H), 7.44 – 7.37 (m, 2H), 7.37 – 7.31 (m, 1H), 7.25 (d, *J* = 9.1 Hz, 1H), 7.16 (d, *J* = 2.2 Hz, 1H), 5.12 (s, 2H), 1.72 (s, 9H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  155.6, 149.3, 139.2, 136.8, 135.3, 128.8, 128.2, 127.6, 126.6, 120.4, 115.6, 102.9, 84.9, 70.7, 28.3. HRMS:  $C_{19}H_{20}N_2O_3Na$   $[M+Na]^+$ ; calculated 347.1372, found 347.1373.

Tert-butyl 6-methoxy-1H-indazole-1-carboxylate (**4o**)



Prepared according to the General Procedure C. Purified by reverse phase chromatography (gradient 5% to 60% MeCN in H<sub>2</sub>O), slightly yellow viscous oil; 71% (98 mg). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*)  $\delta$  8.06 (s, 1H), 7.68 (s, 1H), 7.57 (d, *J* = 8.7 Hz, 1H), 6.94 (dd, *J* = 8.7, 2.2 Hz, 1H), 3.91 (s, 3H), 1.72 (s, 9H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*)  $\delta$  161.3, 149.7, 141.6, 139.6, 121.8, 120.1, 115.2, 96.8, 84.9, 55.8, 28.3. HRMS:  $C_{13}H_{16}N_2O_3Na$   $[M+Na]^+$ ; calculated 271.1059, found 271.1062.

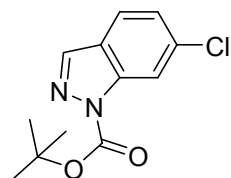
Tert-butyl 4-fluoro-1H-indazole-1-carboxylate (**4p**)



Prepared according to the General Procedure C. Purified by silica gel column chromatography (gradient 5% to 15% EtOAc in PE), R<sub>f</sub> 0.69 (EtOAc:PE 1:4), yellow oil;

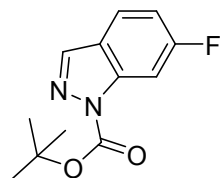
35% (49 mg).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.23 (s, 1H), 7.96 (d,  $J = 8.4$  Hz, 1H), 7.49 – 7.41 (m, 1H), 6.95 (t,  $J = 9.1$  Hz, 1H), 1.72 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  155.4 (d,  $J = 253.3$  Hz), 149.1, 142.0 (d,  $J = 7.6$  Hz), 135.5, 130.2 (d,  $J = 7.5$  Hz), 115.9 (d,  $J = 22.7$  Hz), 110.8 (d,  $J = 4.3$  Hz), 108.5 (d,  $J = 18.0$  Hz), 85.5, 28.2;  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -117.89. HRMS:  $\text{C}_{12}\text{H}_{13}\text{N}_2\text{O}_2\text{FNa}$   $[\text{M}+\text{Na}]^+$ ; calculated 259.0859, found 259.0858.

#### Tert-butyl 6-chloro-1H-indazole-1-carboxylate (**4q**)



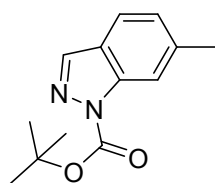
Prepared according to the General Procedure C. Purified by silica gel column chromatography (gradient 5% to 30% EtOAc in PE), Rf 0.38 (EtOAc:PE 1:4), white yellow oil; 56% (77 mg).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.24 (s, 1H), 8.13 (s, 1H), 7.64 (dd,  $J = 8.5, 0.6$  Hz, 1H), 7.29 (dd,  $J = 8.5, 1.8$  Hz, 1H), 1.72 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  149.1, 140.3, 139.3, 135.6, 124.8, 124.4, 121.9, 114.9, 85.6, 28.3. HRMS:  $\text{C}_{12}\text{H}_{13}\text{N}_2\text{O}_2\text{NaCl}$   $[\text{M}+\text{Na}]^+$ ; calculated 275.0563, found 275.0567.

#### Tert-butyl 6-fluoro-1H-indazole-1-carboxylate (**4r**)



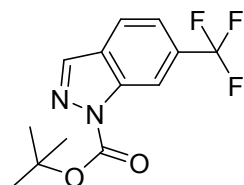
Prepared according to the General Procedure C. Purified by silica gel column chromatography (gradient 5% to 12% EtOAc in PE), Rf 0.34 (EtOAc:PE 1:4), white yellow oil; 43% (60 mg).  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.13 (s, 1H), 7.88 (d,  $J = 9.6$  Hz, 1H), 7.67 (dd,  $J = 8.7, 5.2$  Hz, 1H), 7.08 (td,  $J = 8.8, 2.3$  Hz, 1H), 1.72 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz, Chloroform-*d*)  $\delta$  163.6 (d,  $J = 247.5$  Hz), 149.1, 140.5 (d,  $J = 13.3$  Hz), 139.4, 122.5, 122.4 (d,  $J = 10.9$  Hz), 113.2 (d,  $J = 25.7$  Hz), 101.6 (d,  $J = 28.6$  Hz), 85.4, 28.3;  $^{19}\text{F}$  NMR (376 MHz, Chloroform-*d*)  $\delta$  -110.49. HRMS:  $\text{C}_{12}\text{H}_{13}\text{N}_2\text{O}_2\text{FNa}$   $[\text{M}+\text{Na}]^+$ ; calculated 259.0859, found 259.0859.

Tert-butyl 6-methyl-1H-indazole-1-carboxylate (**4s**) (Reported in literature<sup>6</sup>)



Prepared according to the General Procedure C. Purified by silica gel column chromatography (gradient 5% to 15% EtOAc in PE), Rf 0.53 (EtOAc:PE 1:4), yellow oil; 46% (66 mg). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 8.03 (s, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.14 (d, *J* = 8.1 Hz, 1H), 2.52 (s, 3H), 1.72 (s, 9H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 149.6, 140.5, 139.7, 139.6, 125.7, 124.0, 120.7, 114.6, 84.8, 28.3, 22.3. HRMS: C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>Na [M+Na]<sup>+</sup>; calculated 255.1109, found 255.1115.

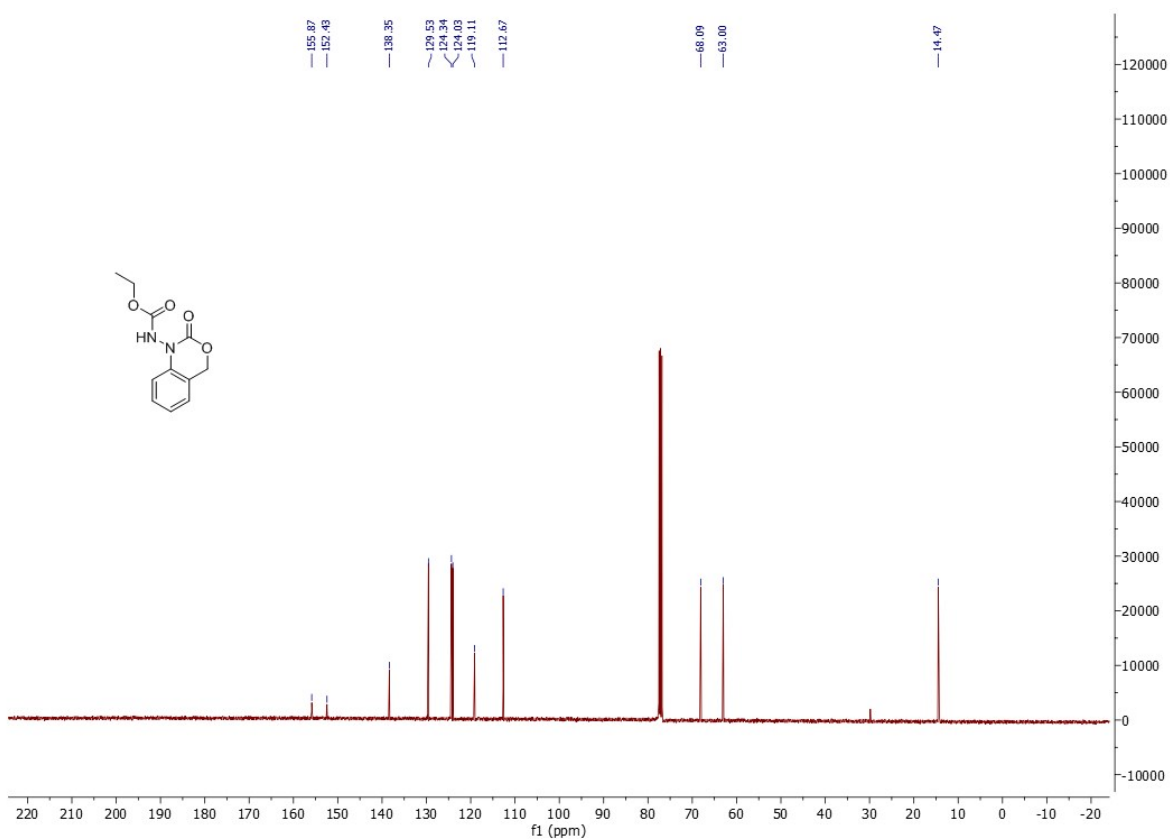
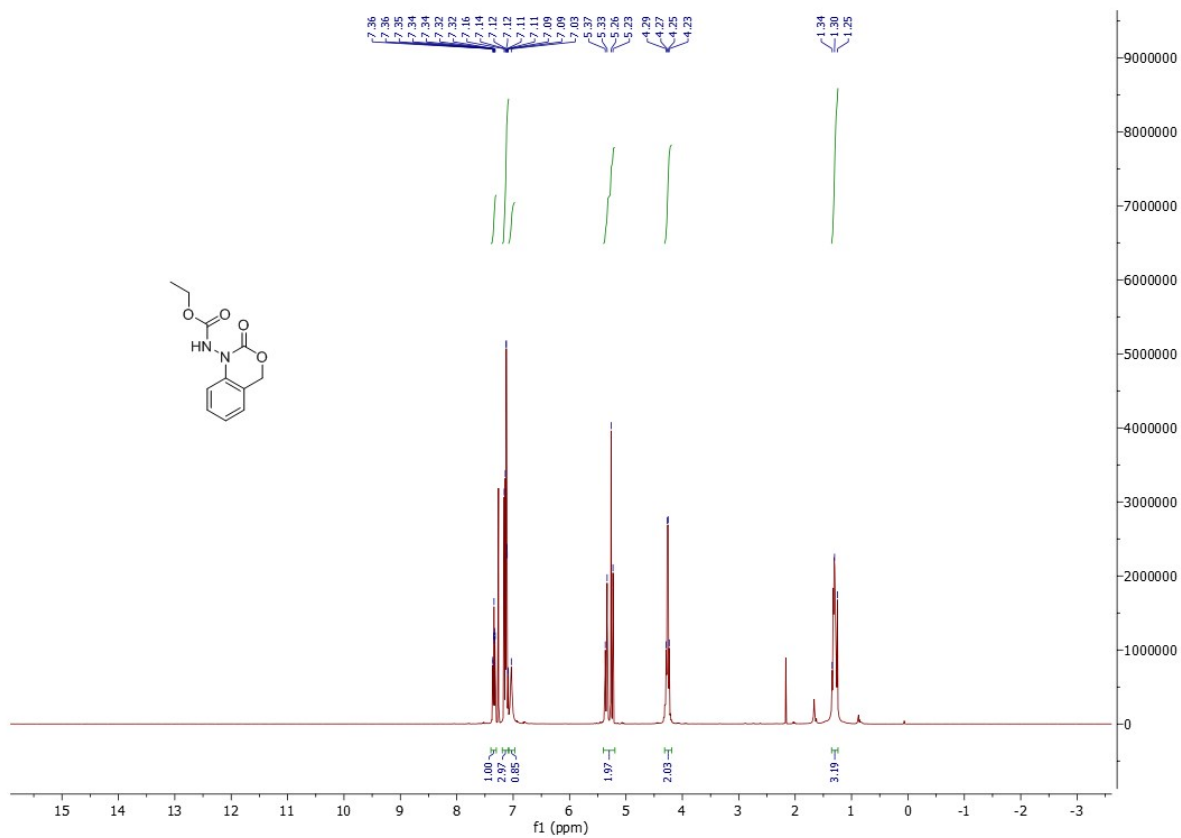
Tert-butyl 6-(trifluoromethyl)-1H-indazole-1-carboxylate (**4t**) (Reported in literature<sup>7</sup>)



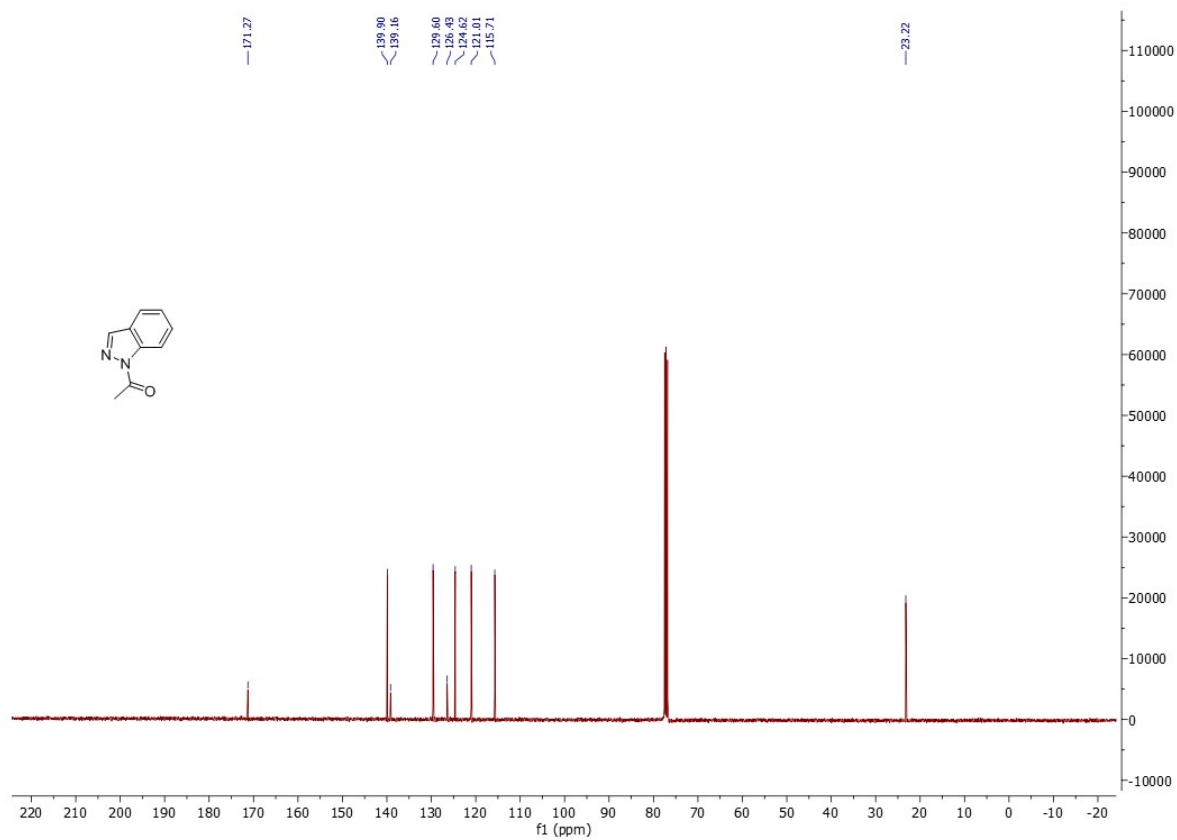
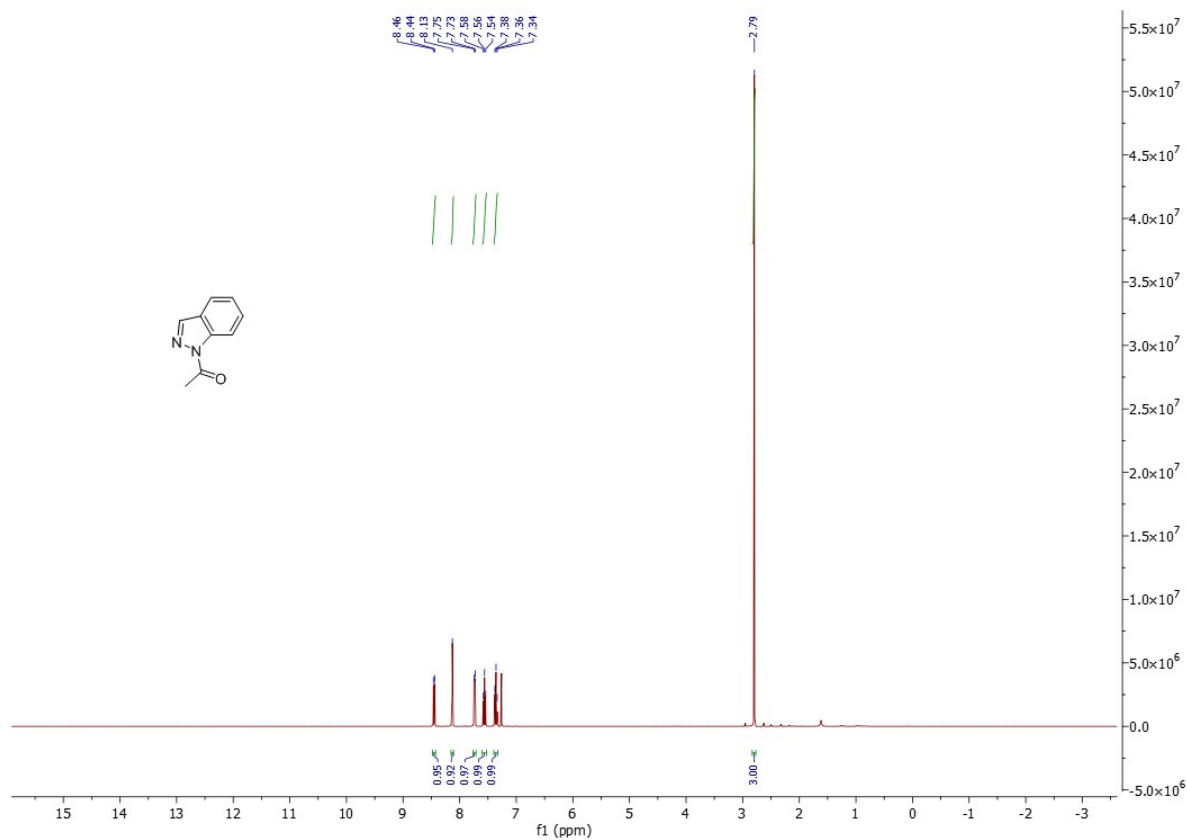
Prepared according to the General Procedure C. Purified by silica gel column chromatography (gradient 5% to 20% EtOAc in PE), Rf 0.46 (EtOAc:PE 1:4), white solid; m.p. 63-65 °C, 25% (32 mg). <sup>1</sup>H NMR (400 MHz, Chloroform-*d*) δ 8.54 (s, 1H), 8.24 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 1.74 (s, 9H); <sup>13</sup>C NMR (101 MHz, Chloroform-*d*) δ 148.9, 139.2, 139.1, 131.0 (q, *J* = 32.3 Hz), 127.8, 124.3 (q, *J* = 272.7 Hz), 122.0, 120.5 (q, *J* = 3.3 Hz), 112.6 (q, *J* = 4.7 Hz), 85.9, 28.2; <sup>19</sup>F NMR (376 MHz, Chloroform-*d*) δ -61.82. LCMS: C<sub>9</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub>F<sub>3</sub> [M-(t-Bu)+H]<sup>+</sup> 231.27.

# Copies of NMR spectra

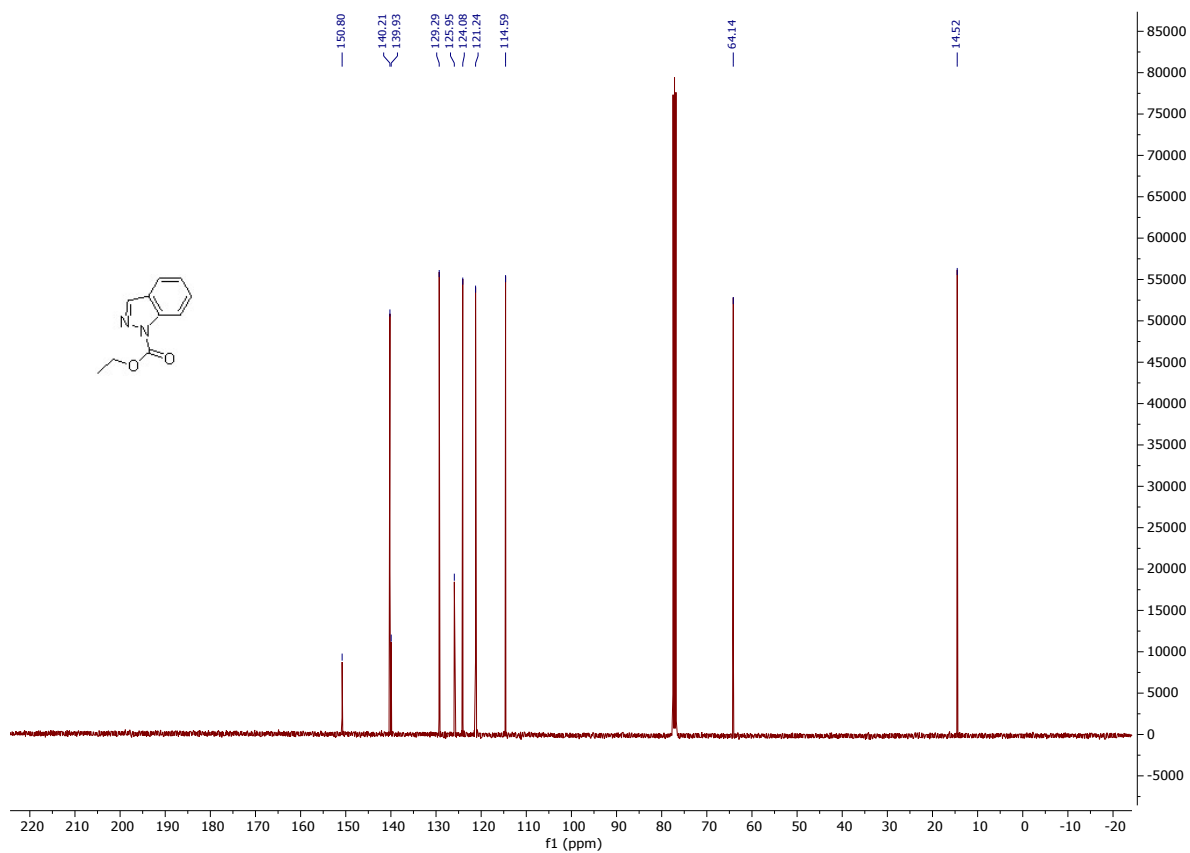
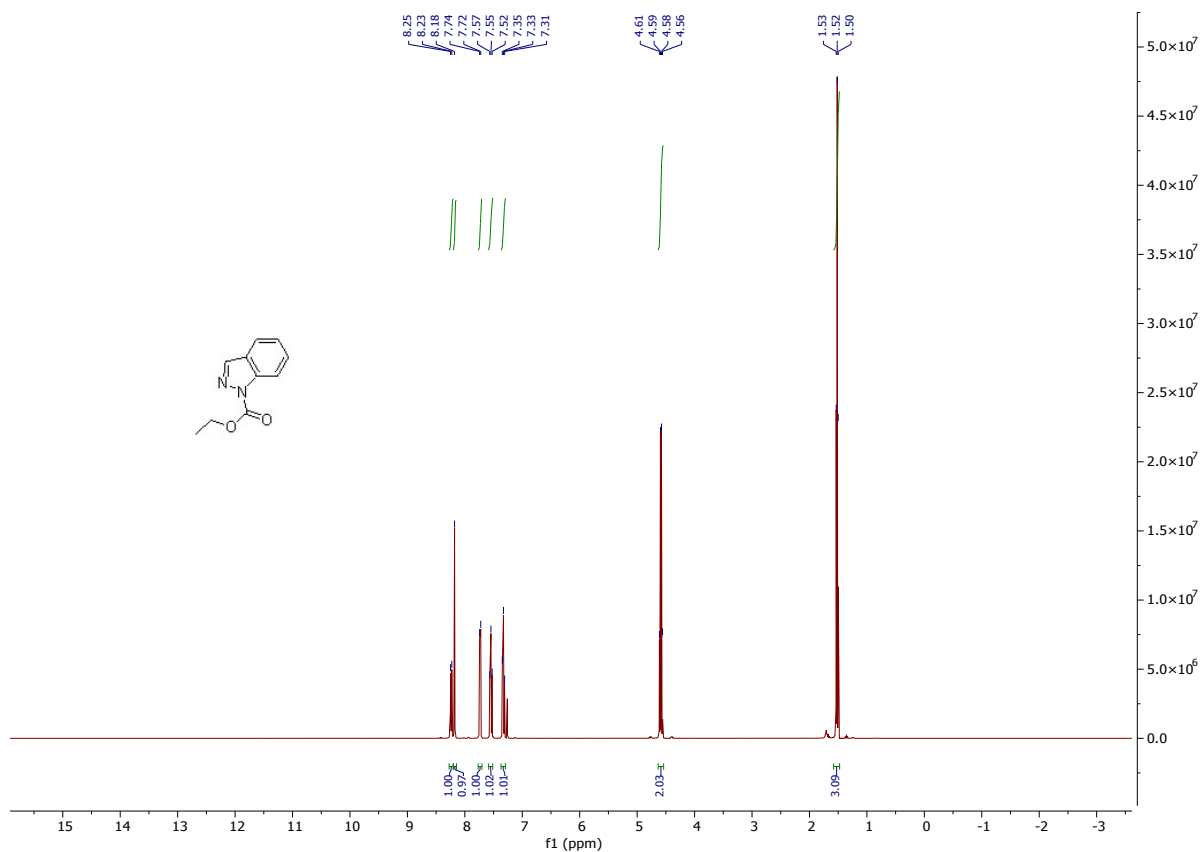
## (2-Oxo-2H-benzo[d][1,3]oxazin-1(4H)-yl)carbamate (S1)



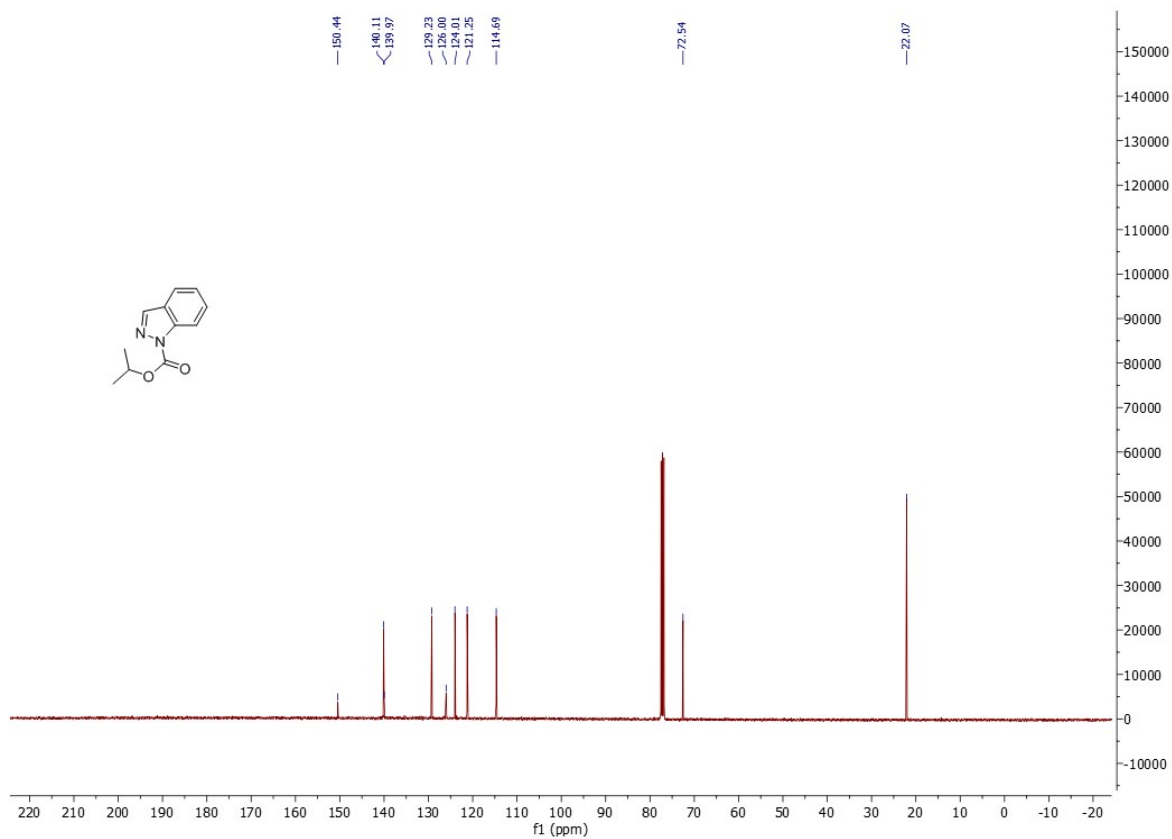
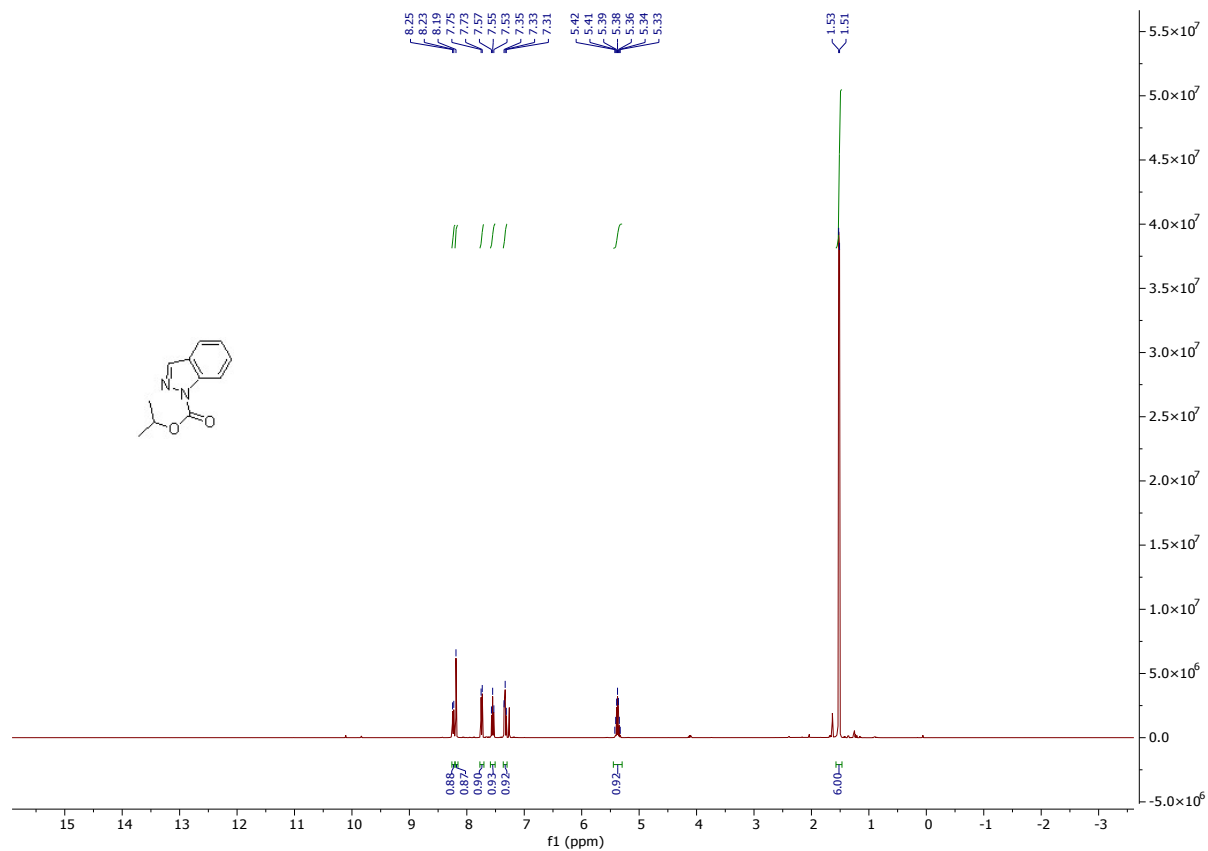
# 1-(1H-indazol-1-yl)ethan-1-one (10a)



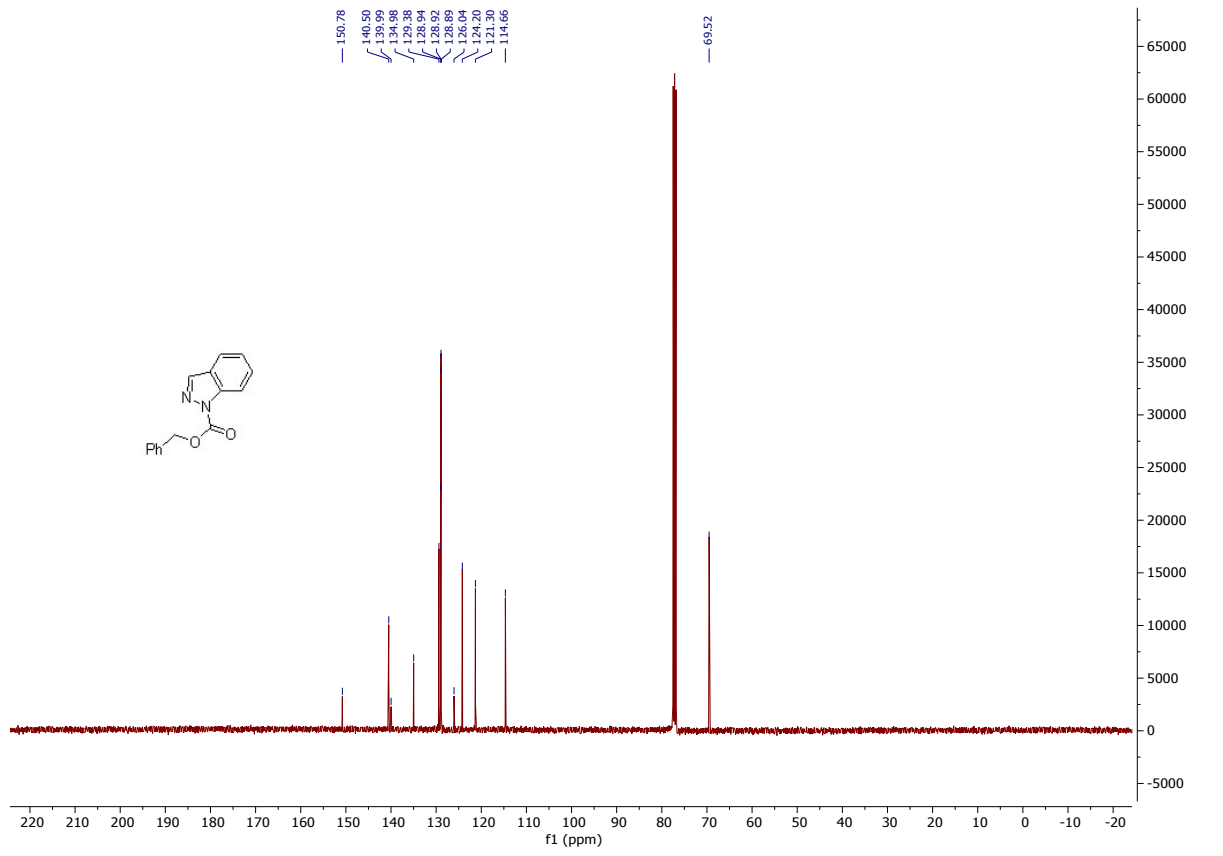
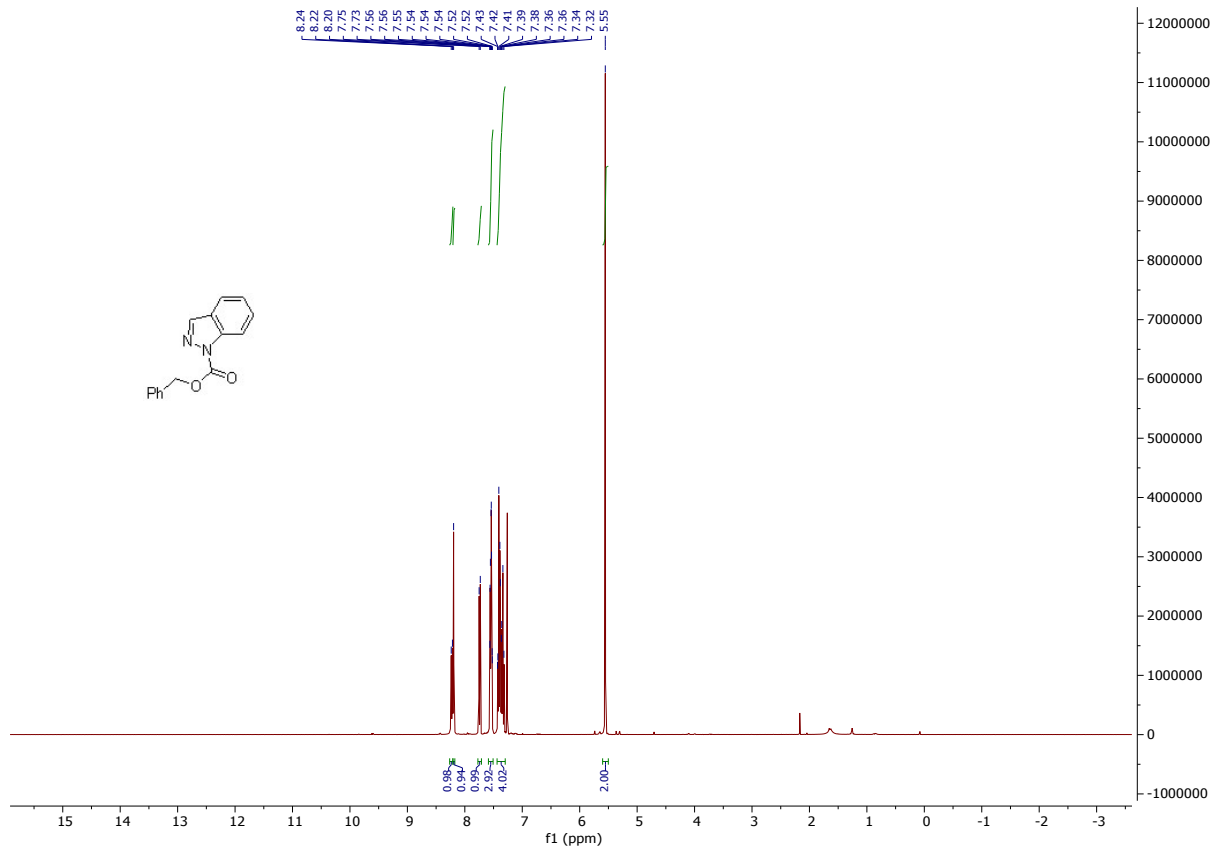
# Ethyl 1H-indazole-1-carboxylate (**4a**)



# Isopropyl 1H-indazole-1-carboxylate (**4b**)

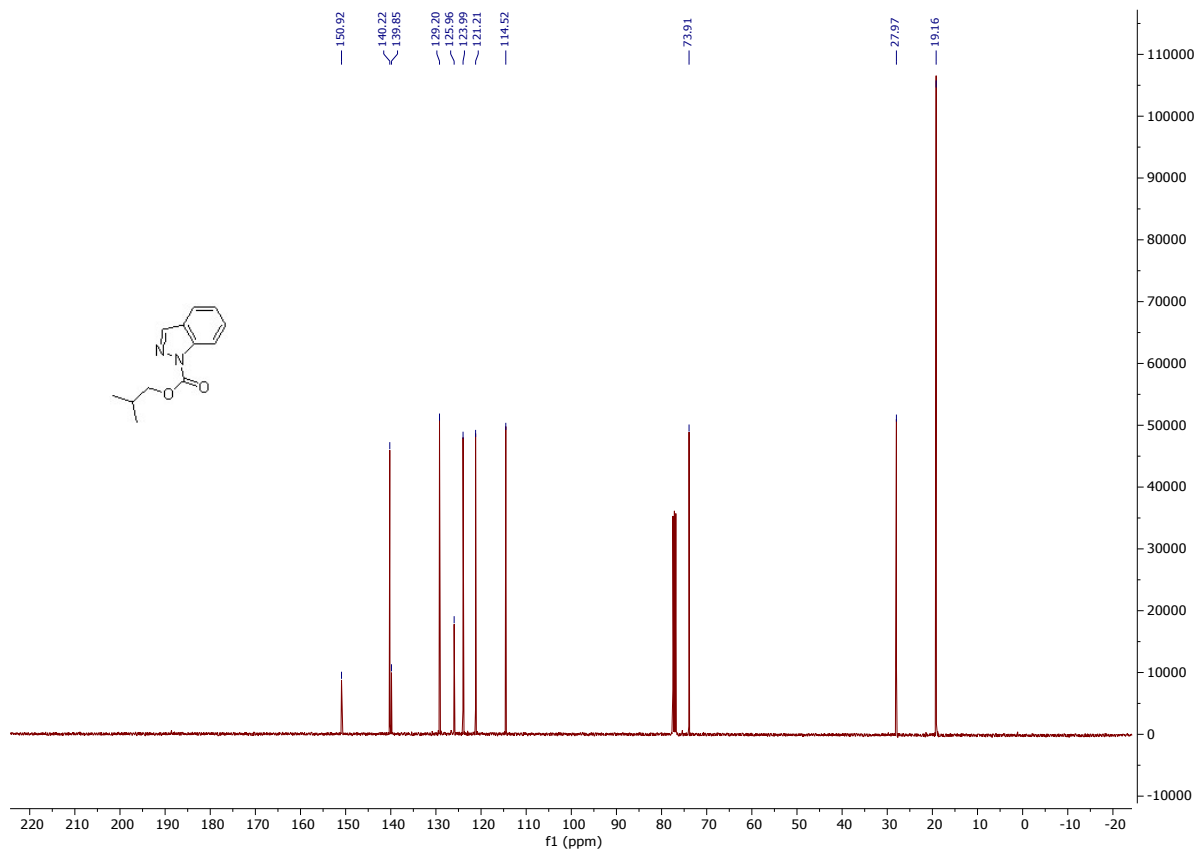
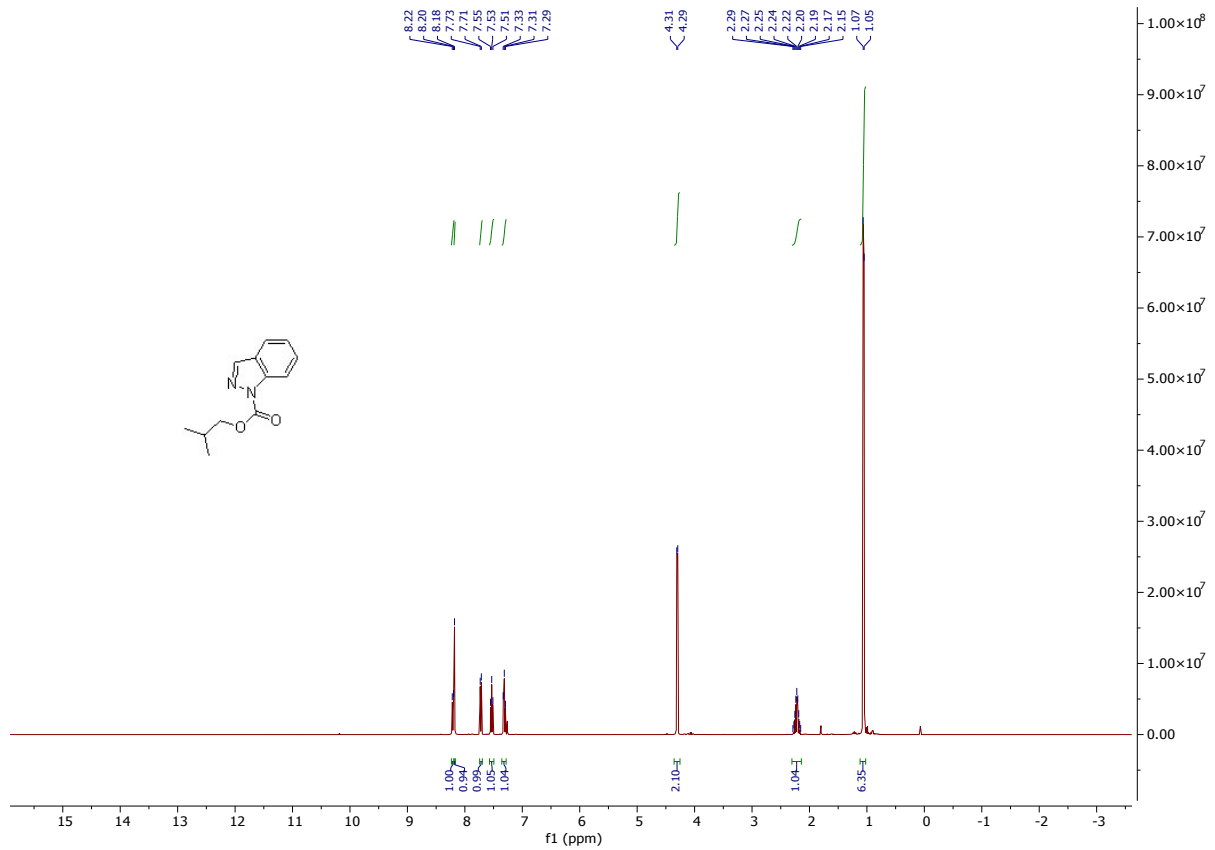


# Benzyl 1H-indazole-1-carboxylate (4c)

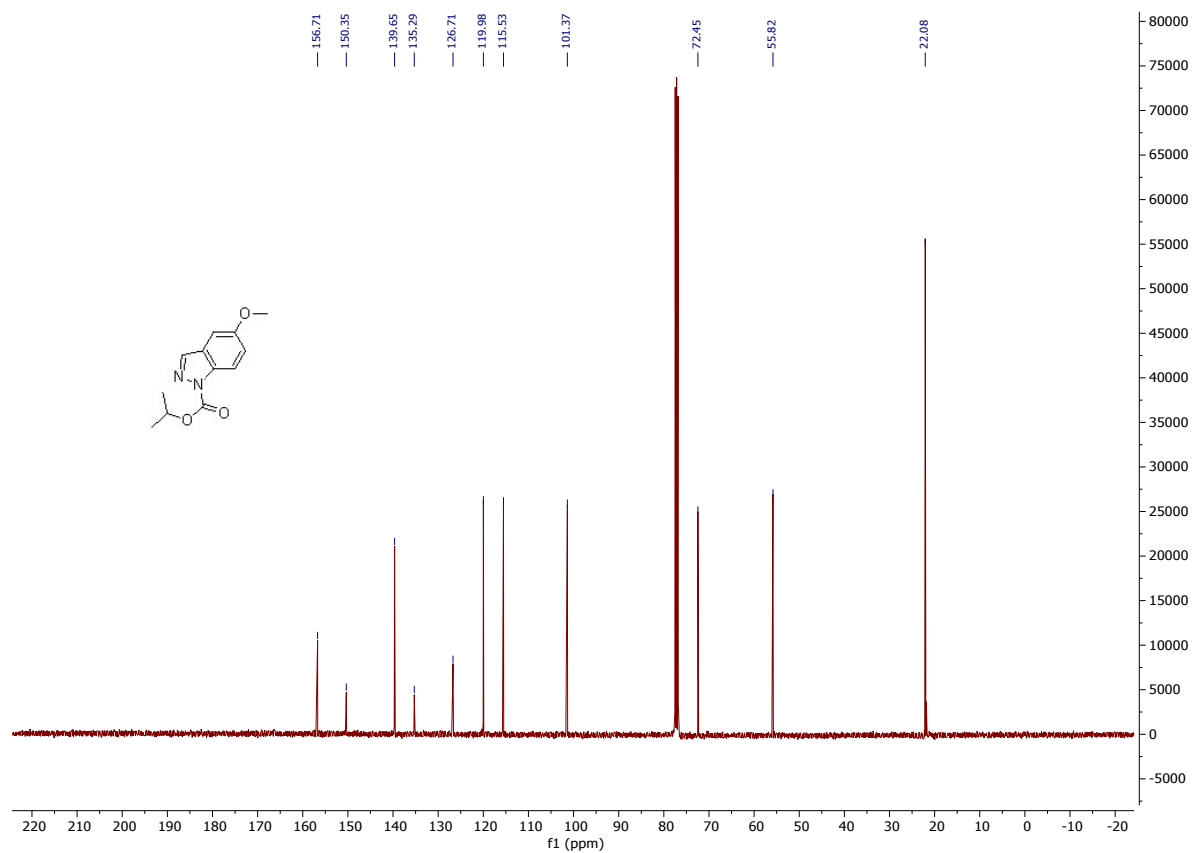
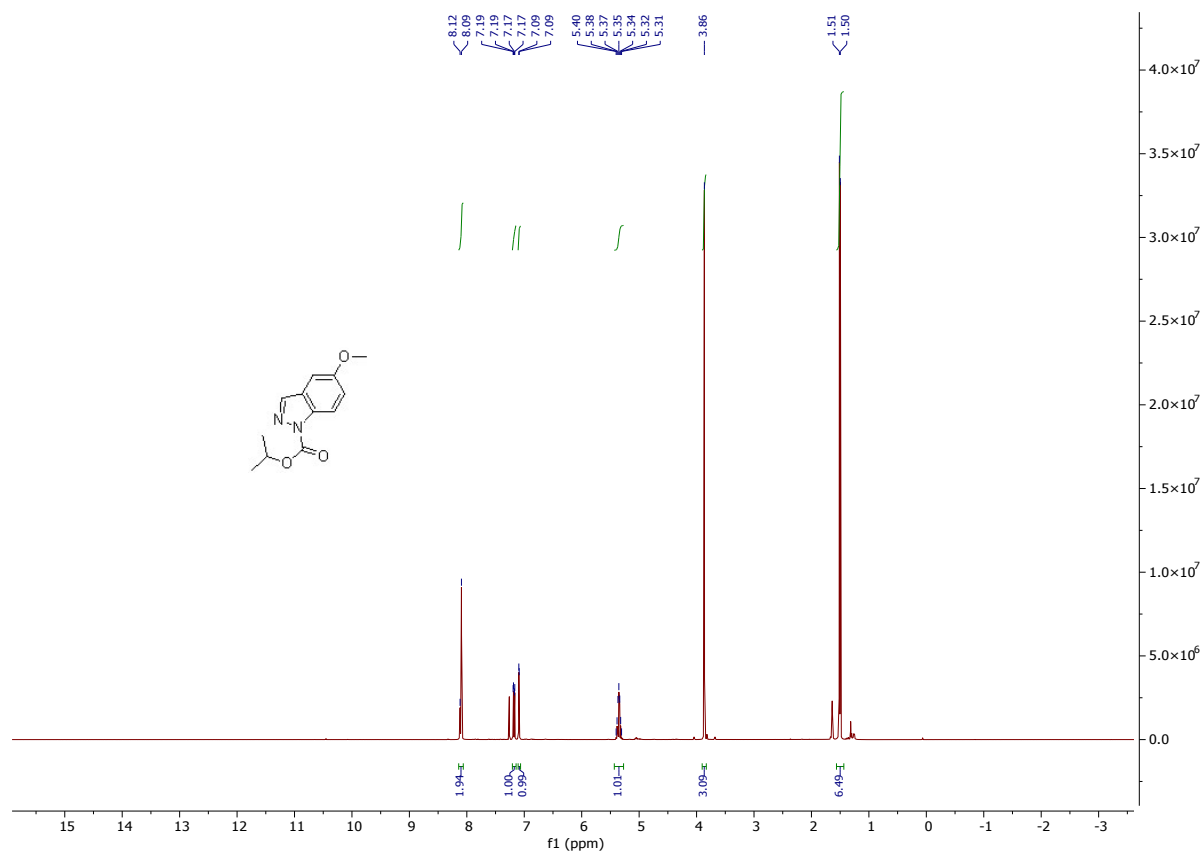




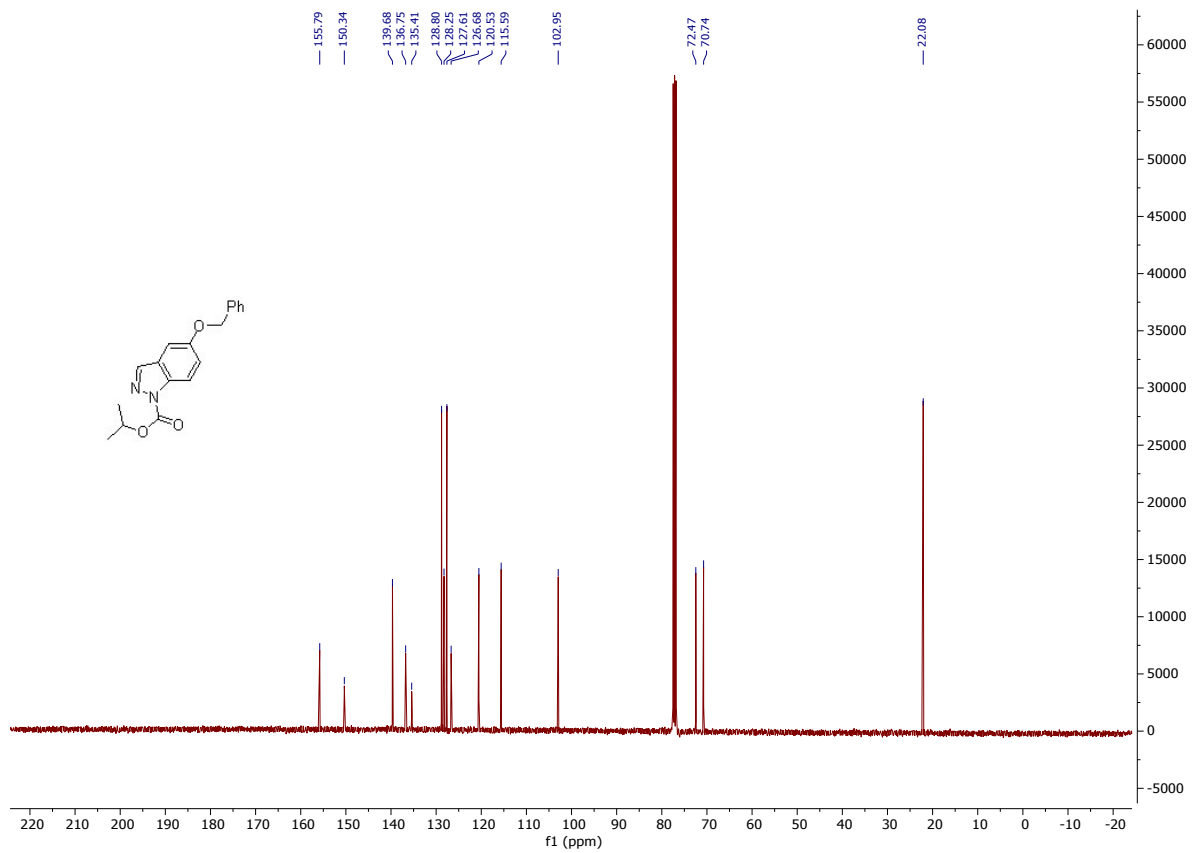
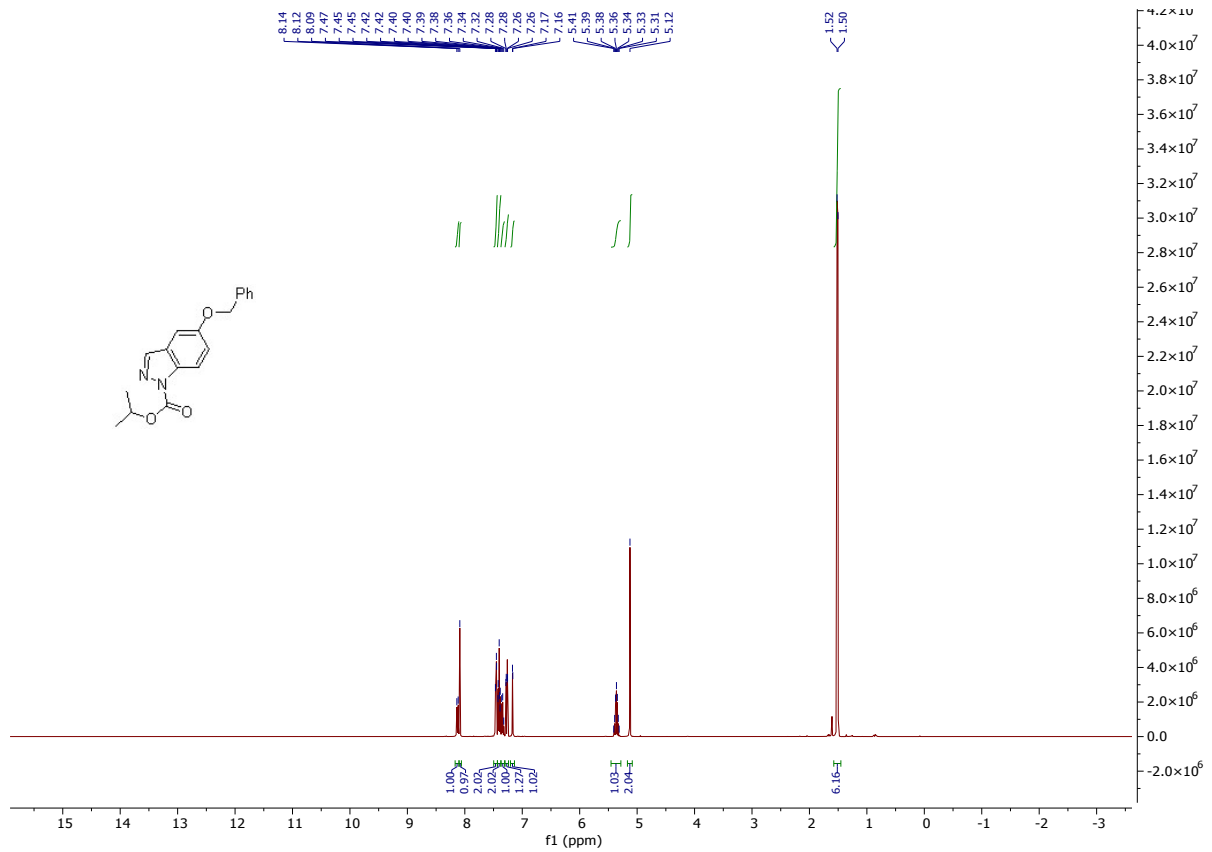
# Isobutyl 1H-indazole-1-carboxylate (4d)



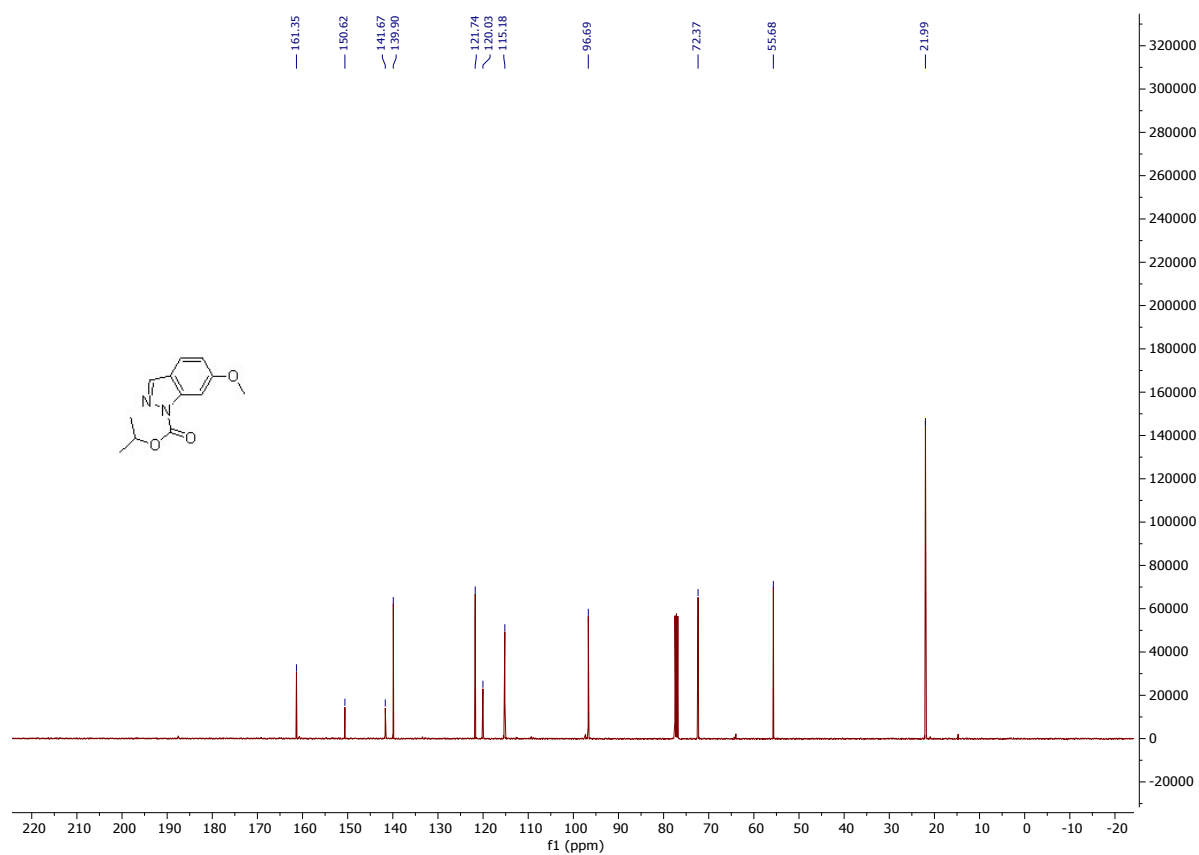
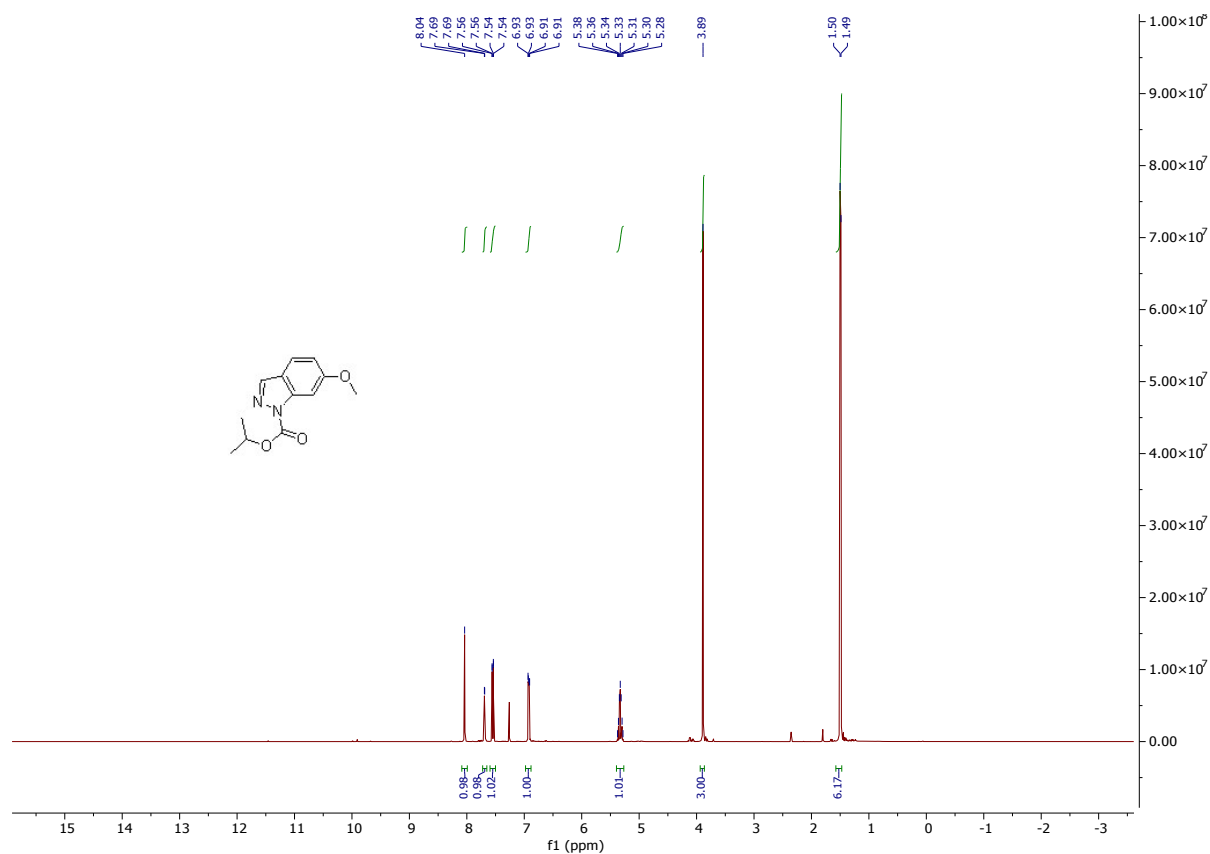
# Isopropyl 5-methoxy-1H-indazole-1-carboxylate (4e)



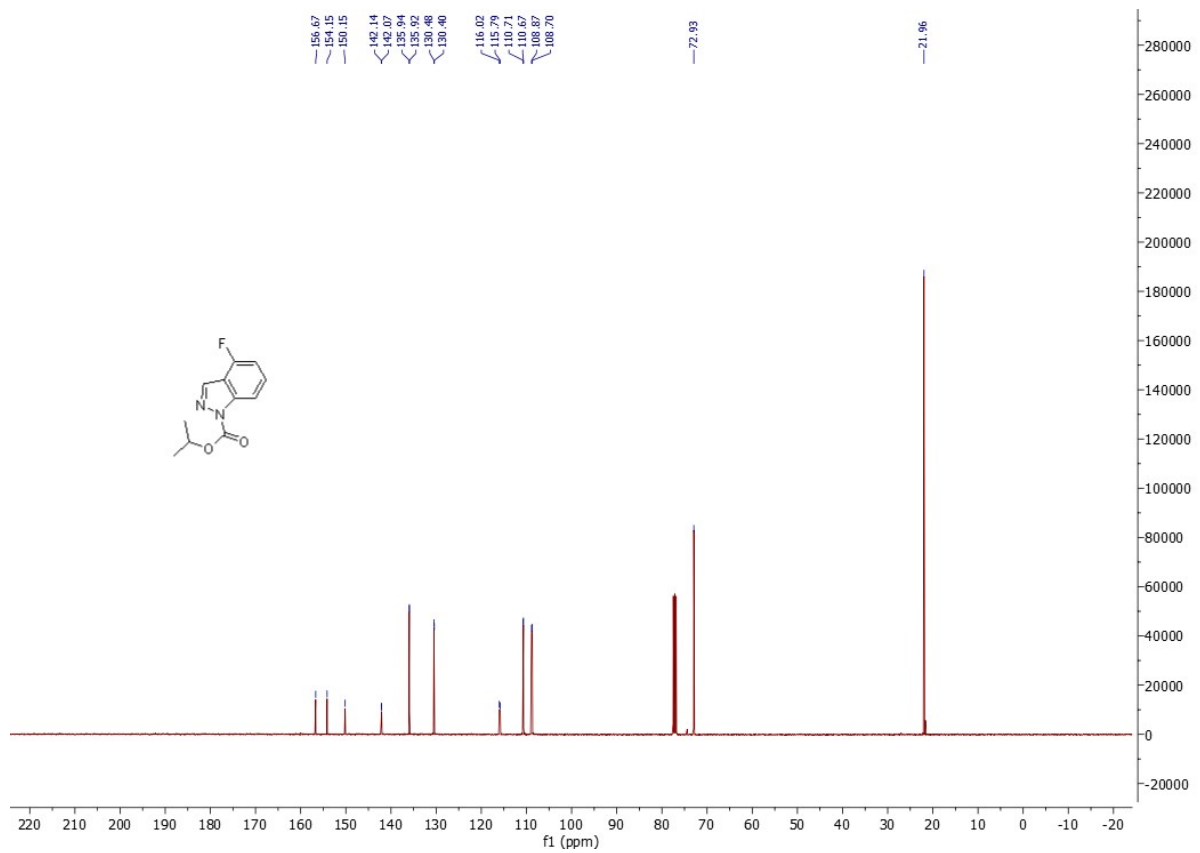
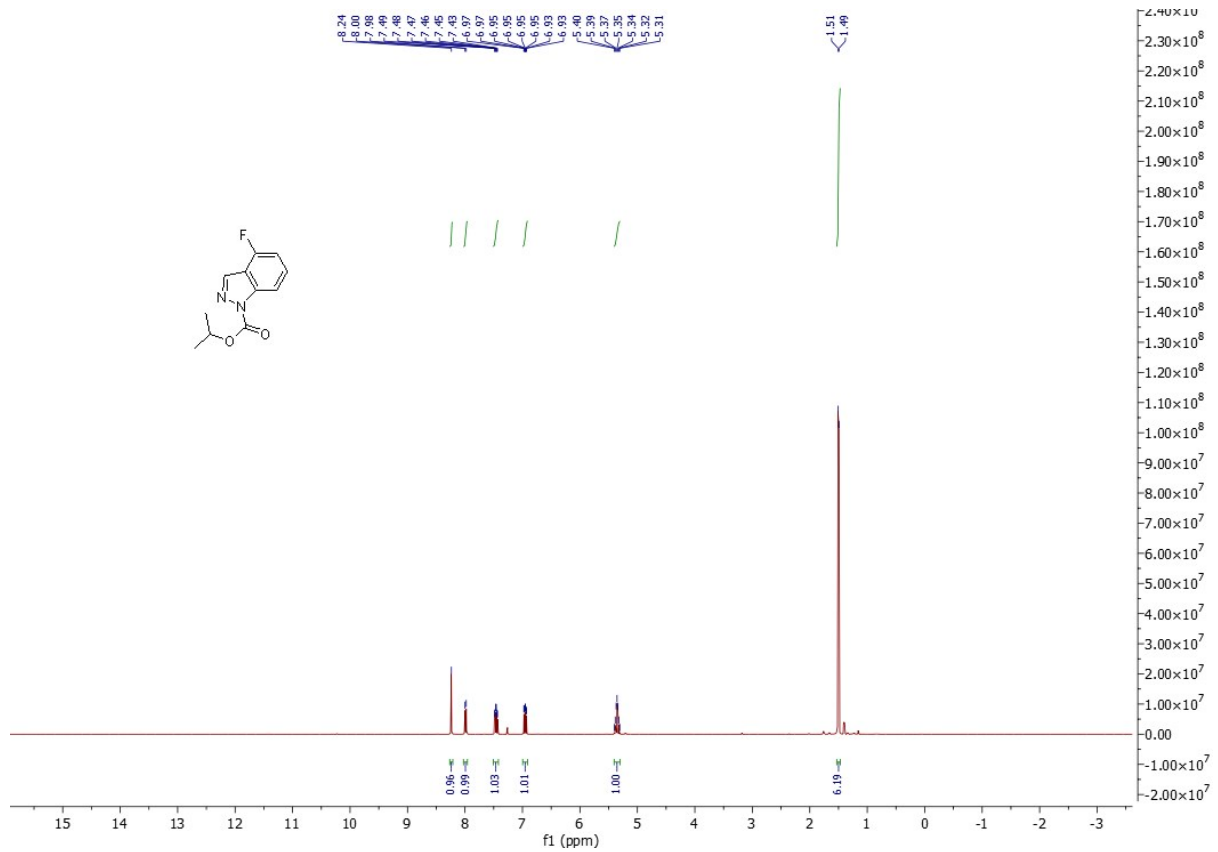
# Isopropyl 5-(benzyloxy)-1H-indazole-1-carboxylate (4f)

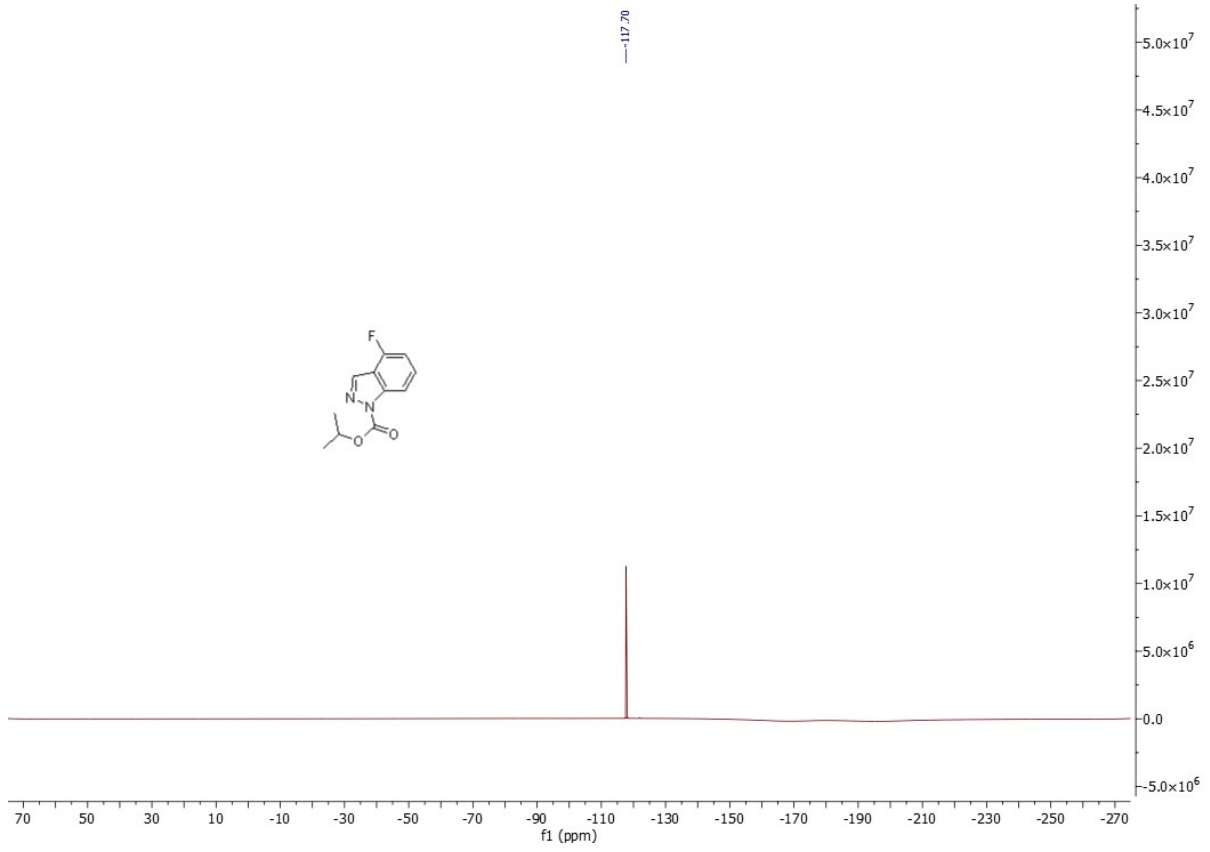
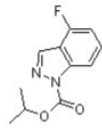


# Isopropyl 6-methoxy-1H-indazole-1-carboxylate (4g)

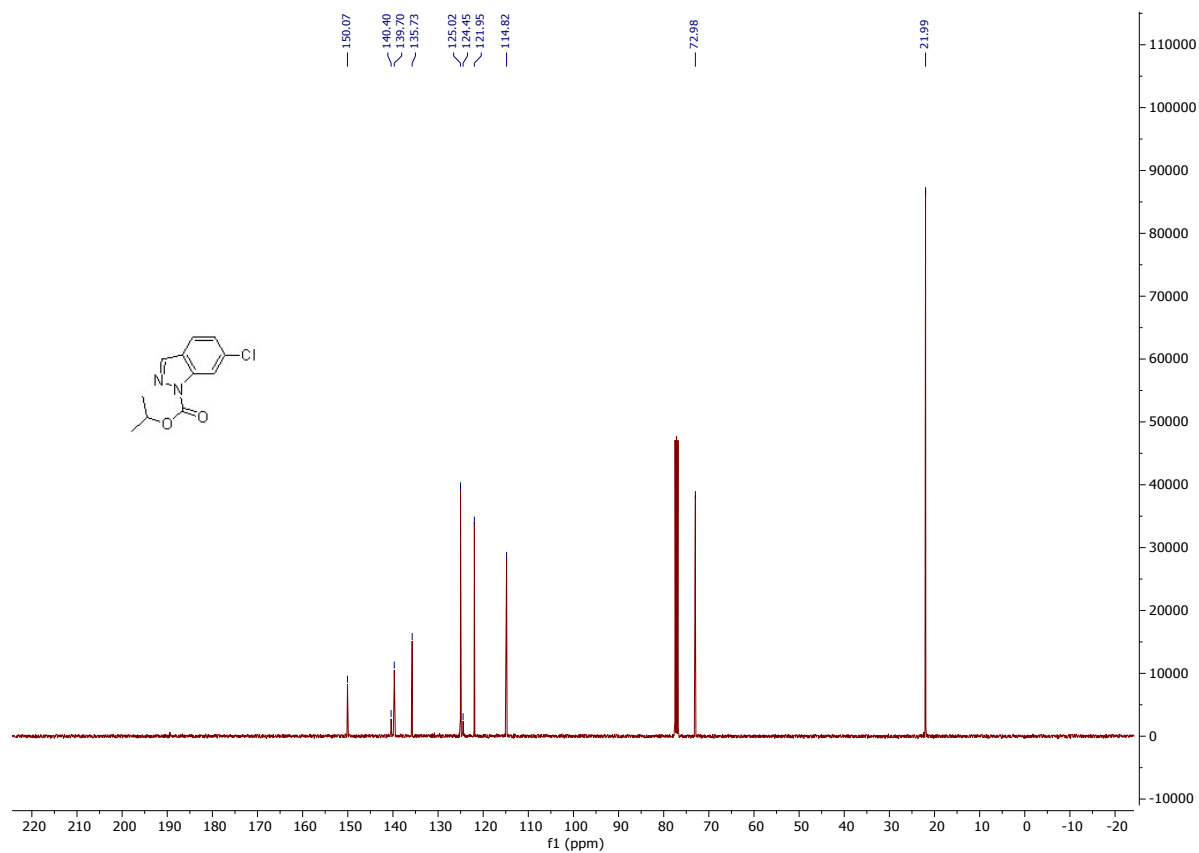
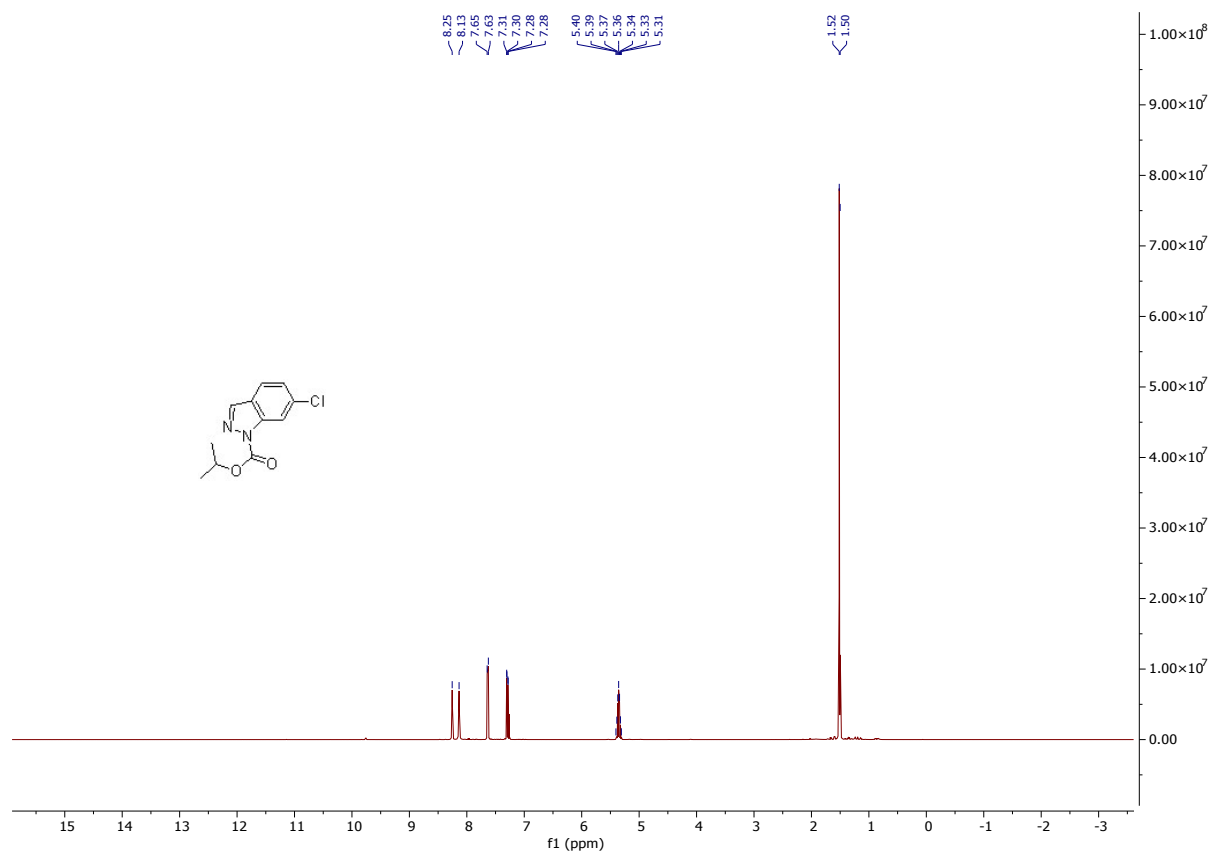


Isopropyl 4-fluoro-1H-indazole-1-carboxylate (**4h**)

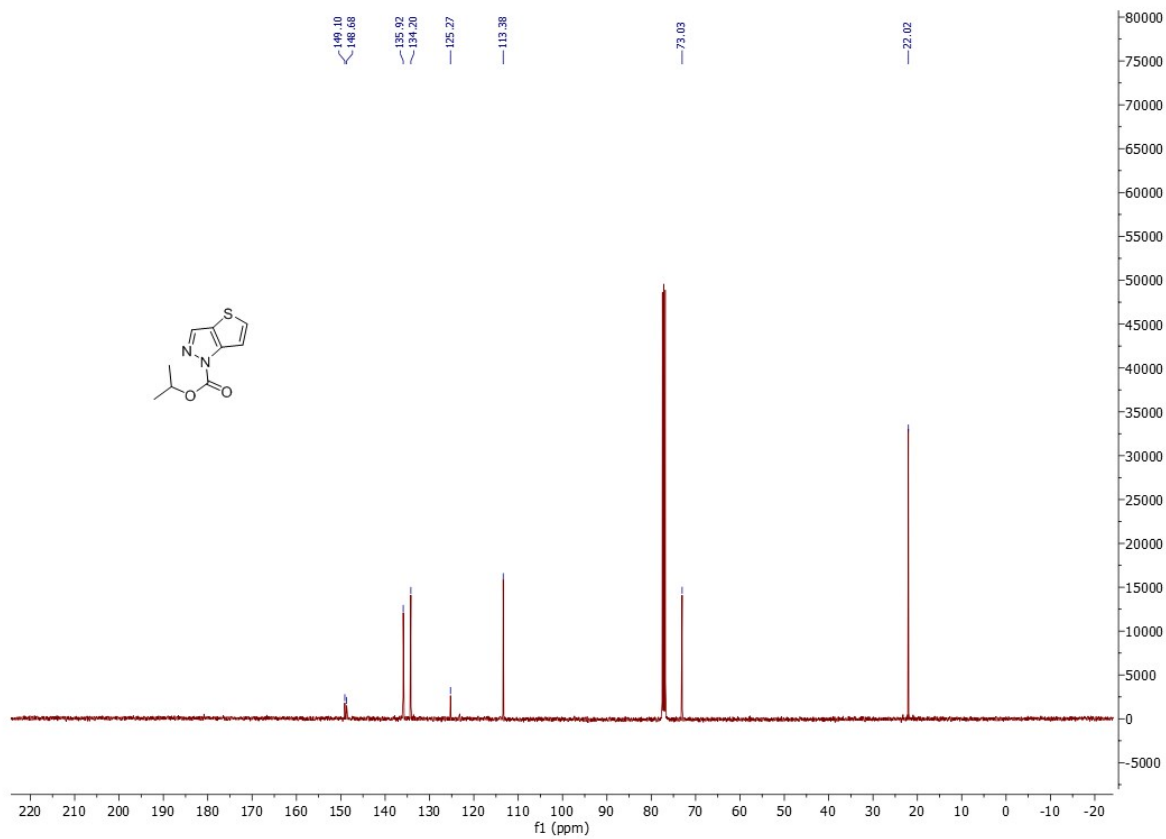
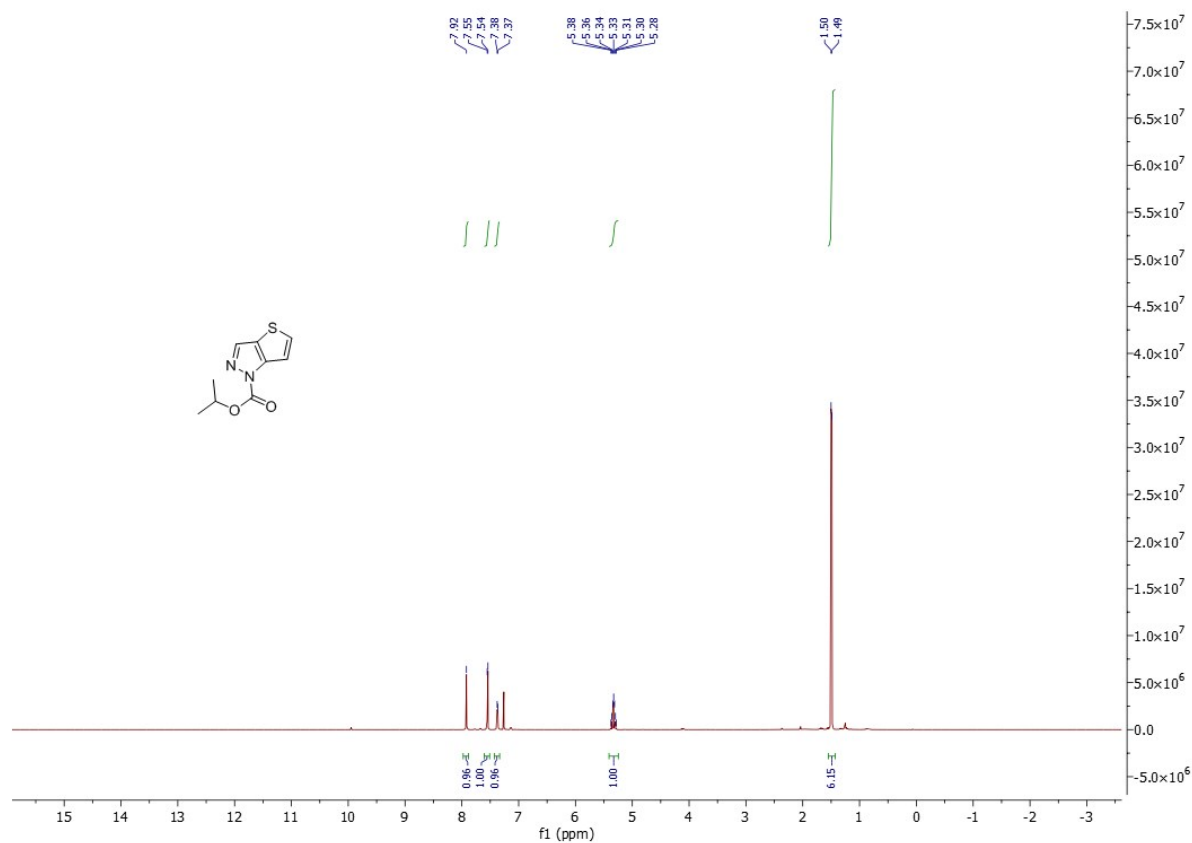




# Isopropyl 6-chloro-1H-indazole-1-carboxylate (4i)

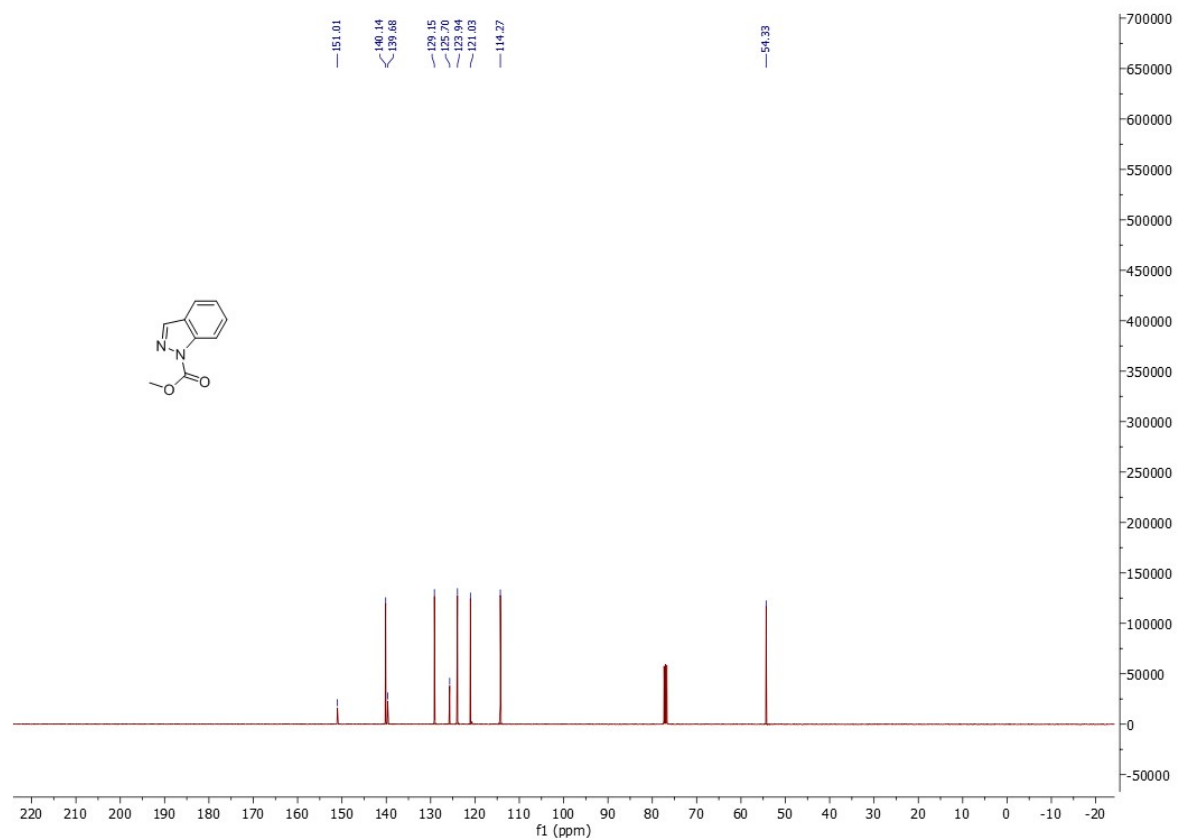
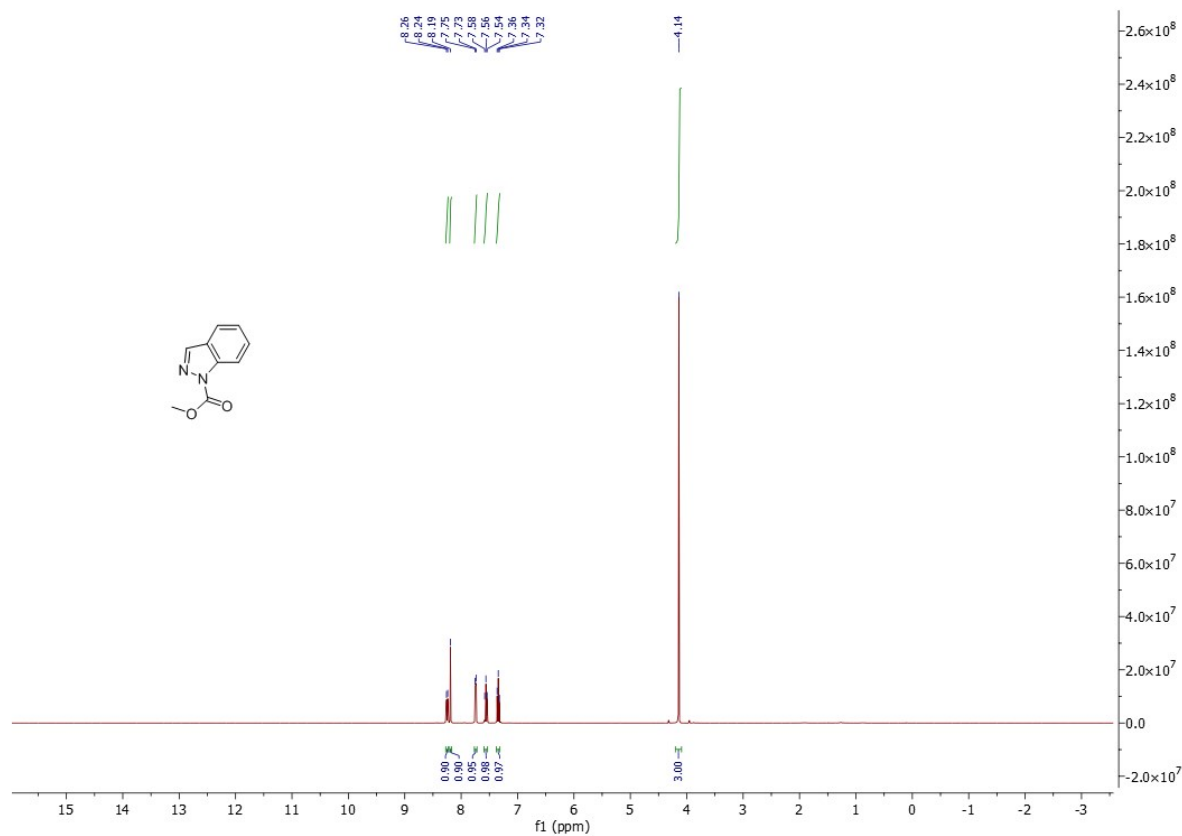


# Isopropyl 1H-thieno[3,2-c]pyrazole-1-carboxylate (9)

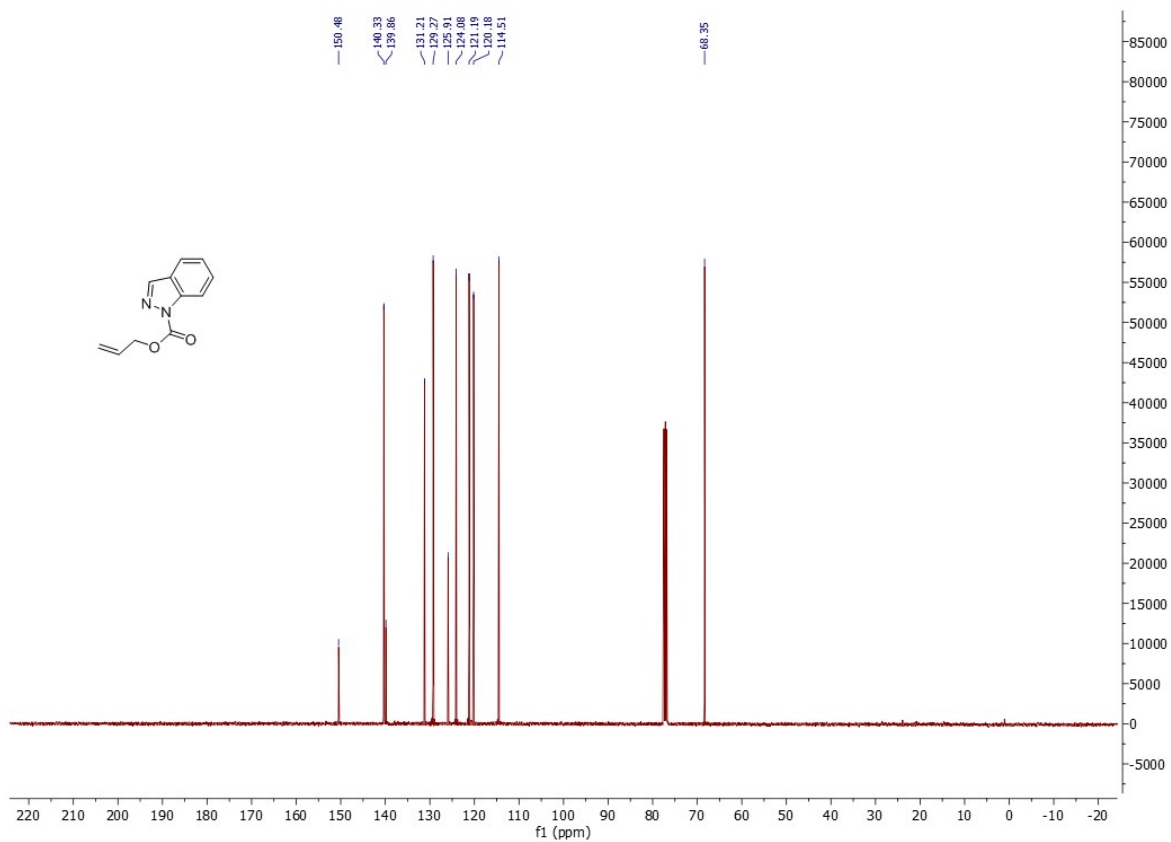
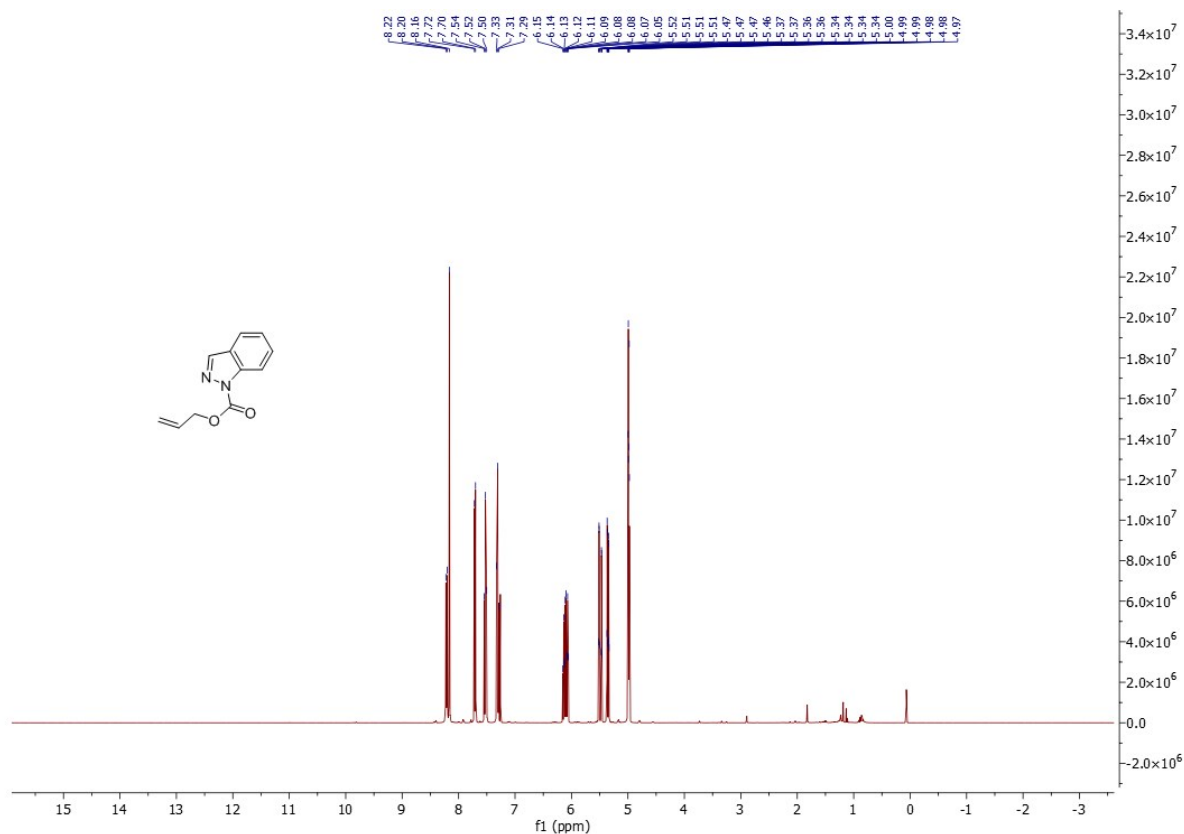




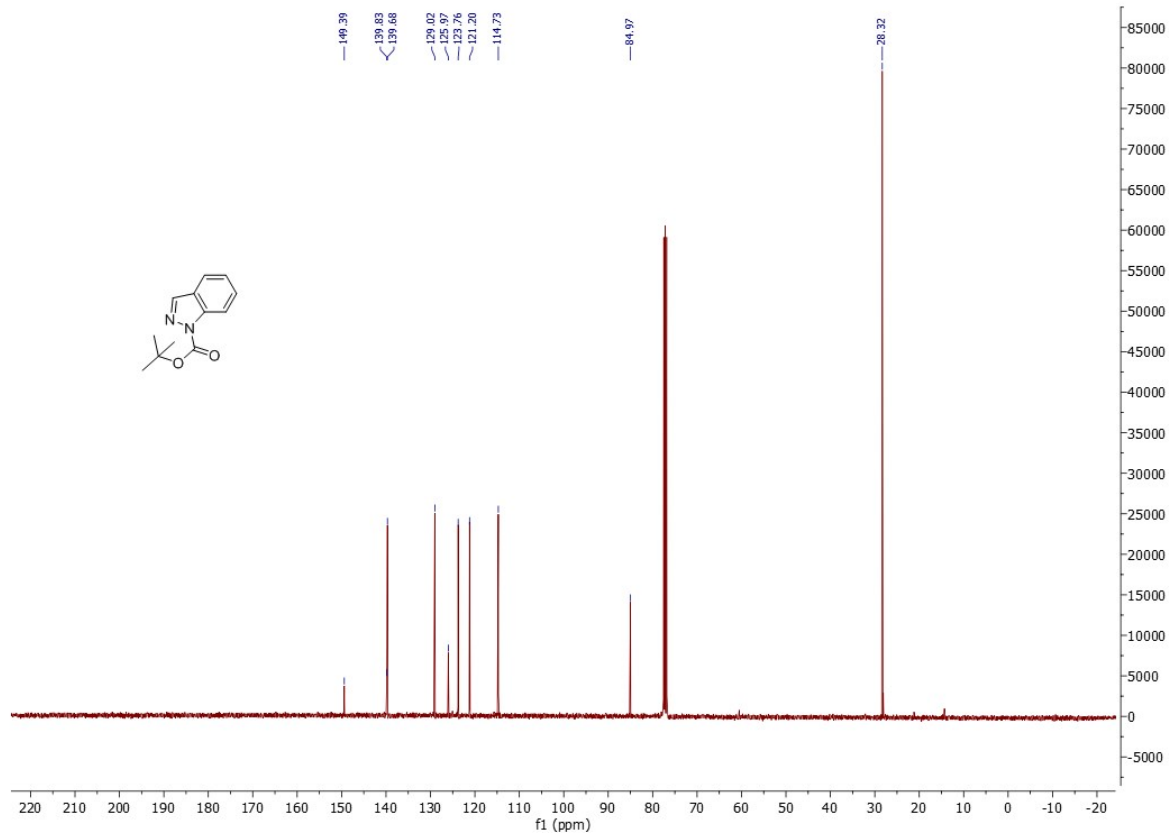
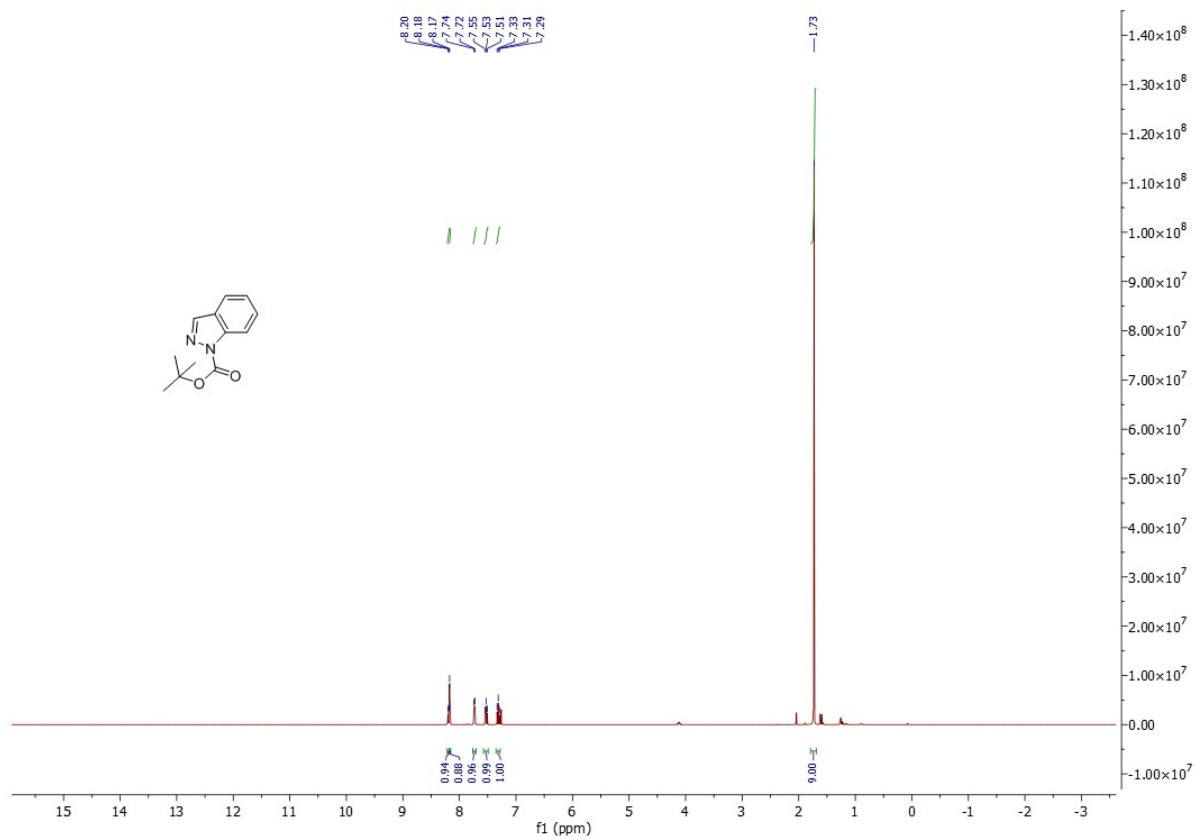
# Methyl 1H-indazole-1-carboxylate (4j)



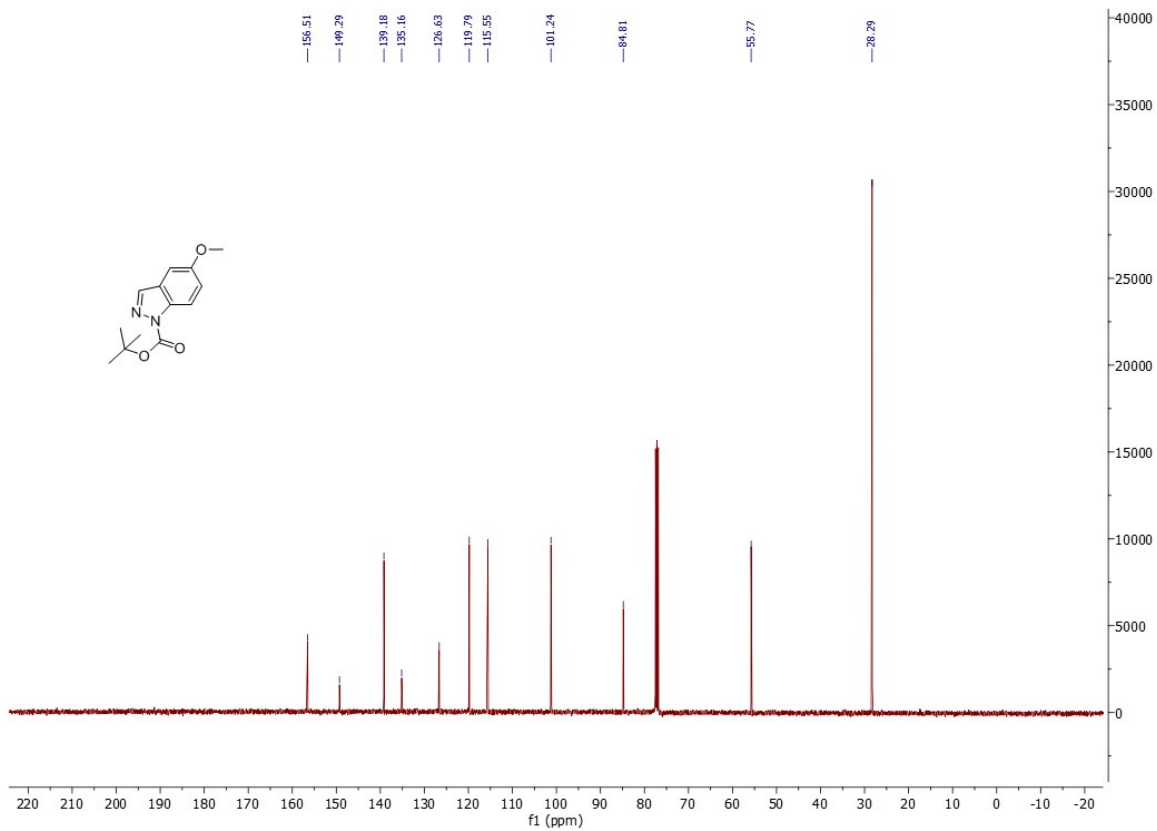
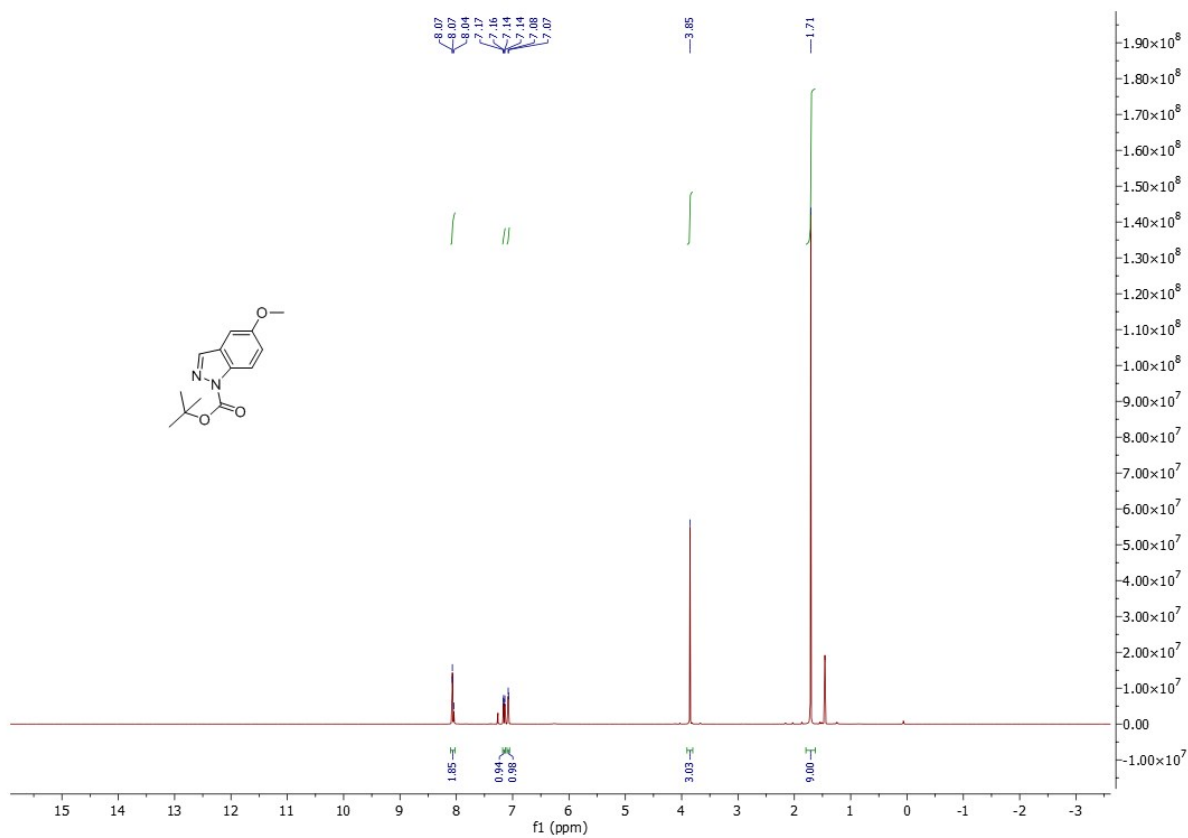
# Allyl 1H-indazole-1-carboxylate (**4k**)



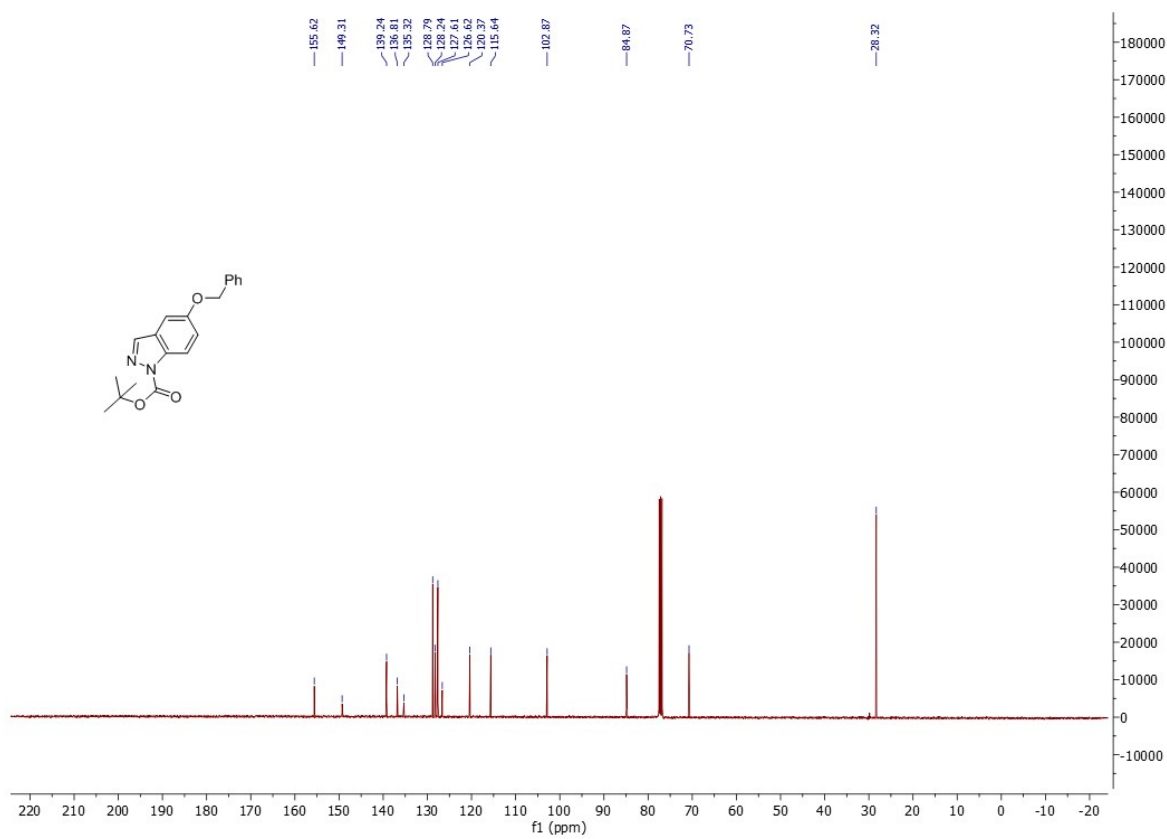
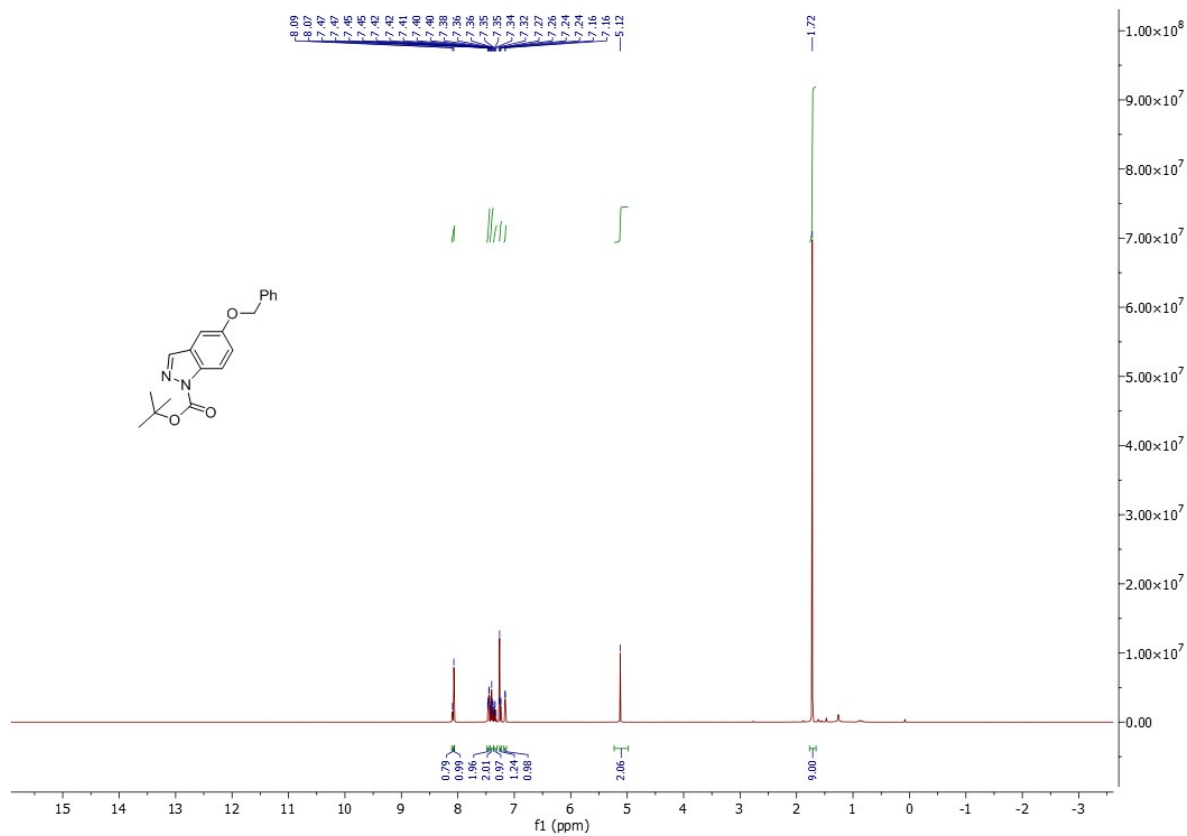
# Tert-butyl 1H-indazole-1-carboxylate (**41**)



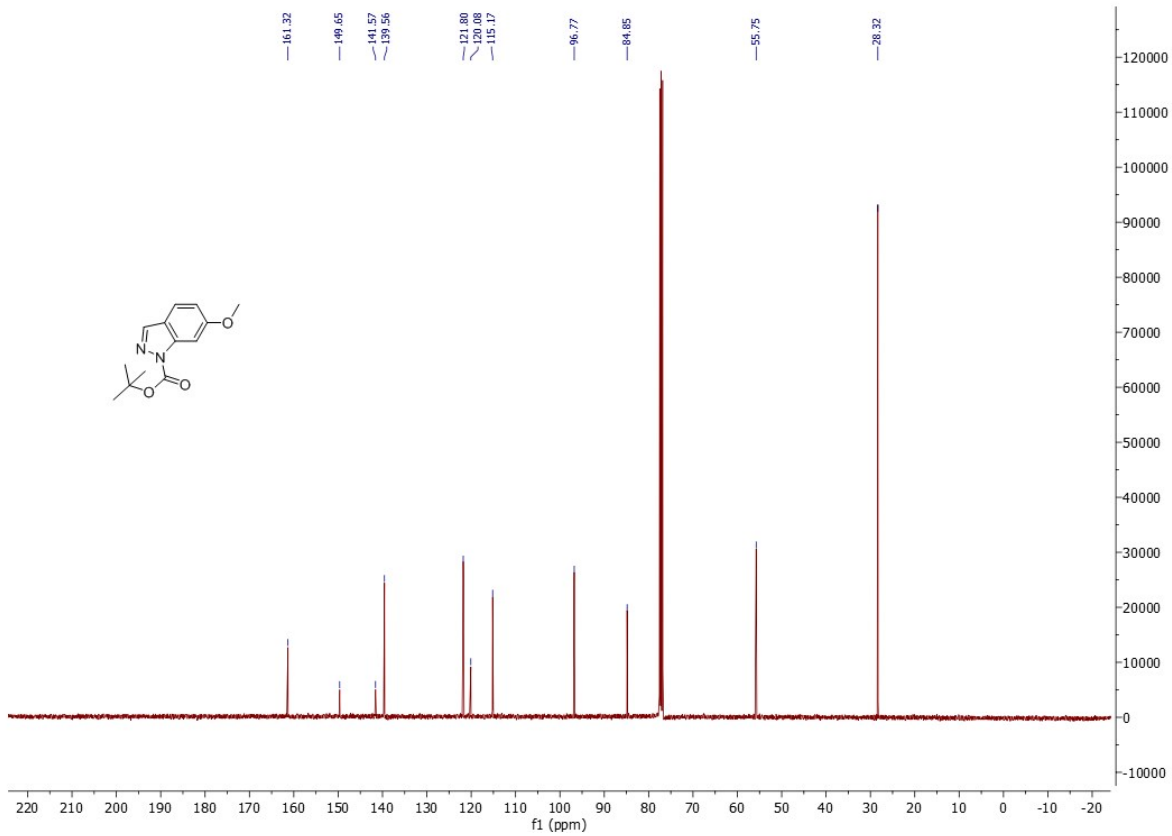
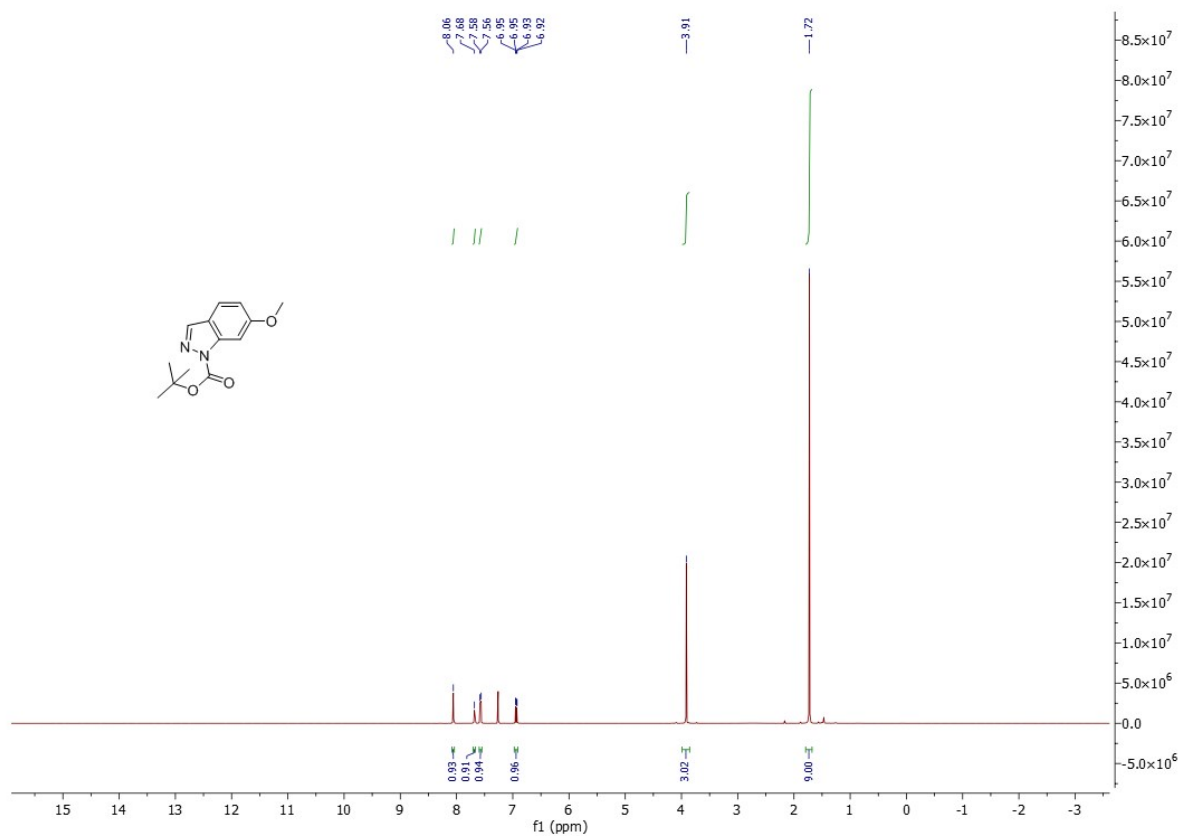
# Tert-butyl 5-methoxy-1H-indazole-1-carboxylate (**4m**)



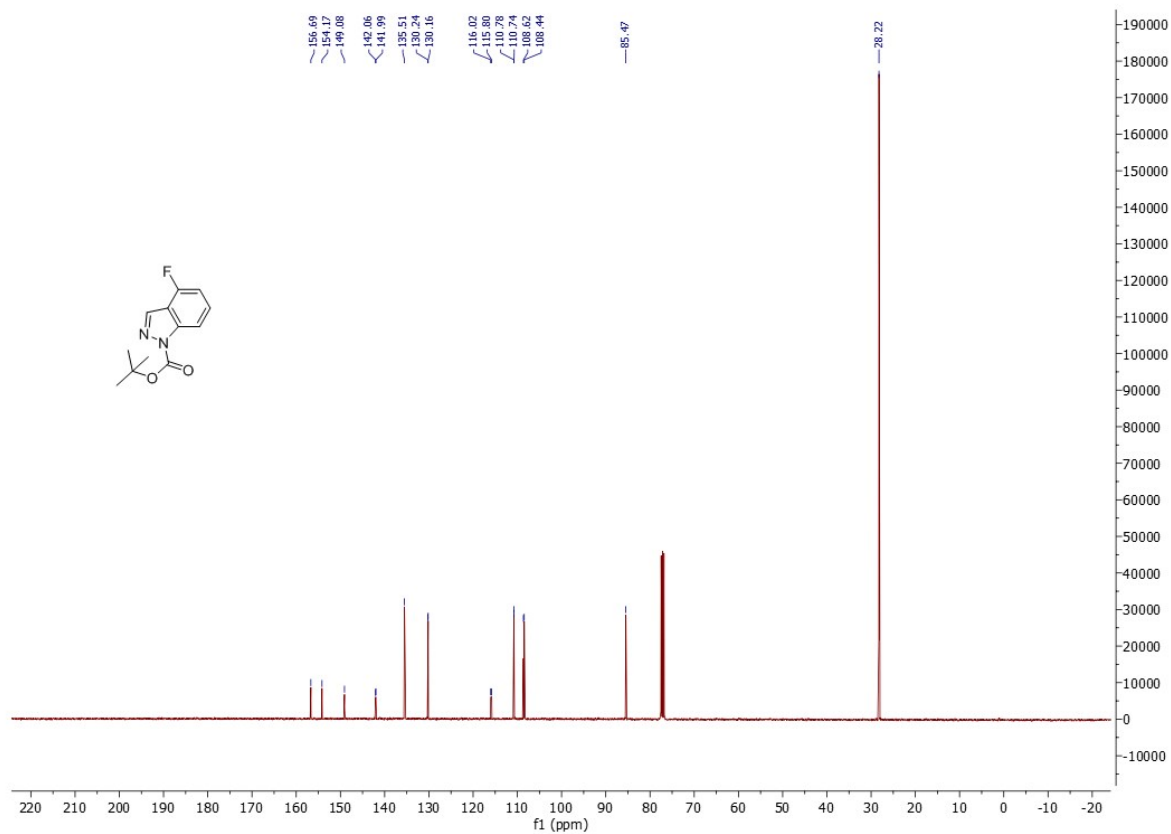
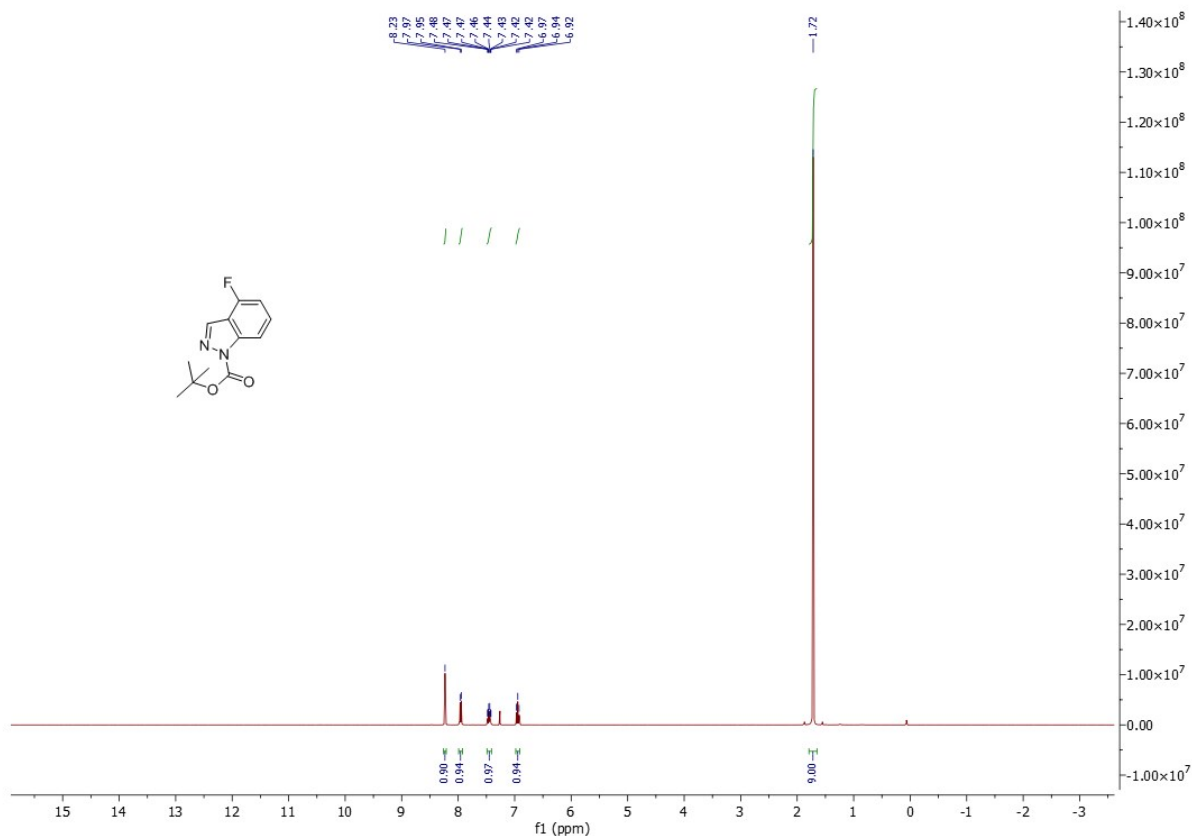
# Tert-butyl 5-(benzyloxy)-1H-indazole-1-carboxylate (**4n**)

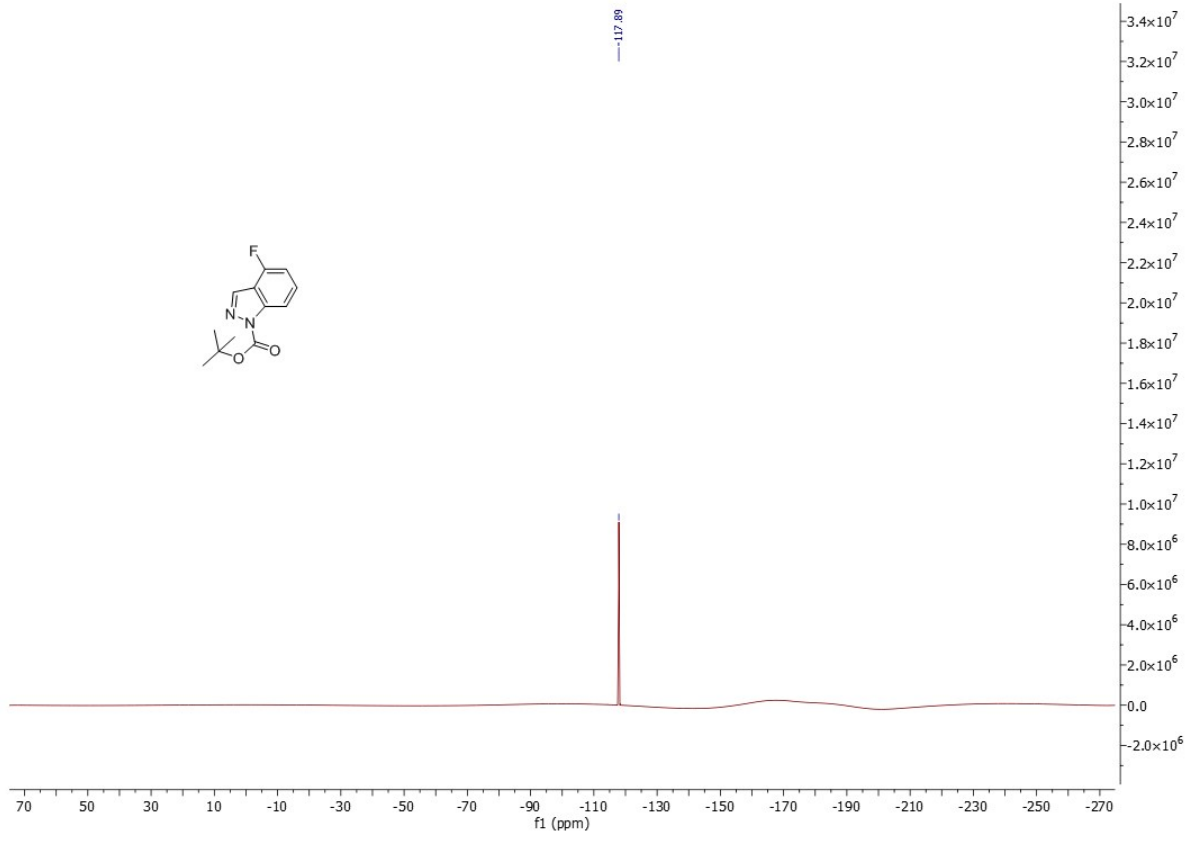
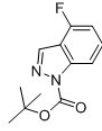


# Tert-butyl 6-methoxy-1H-indazole-1-carboxylate (**4o**)



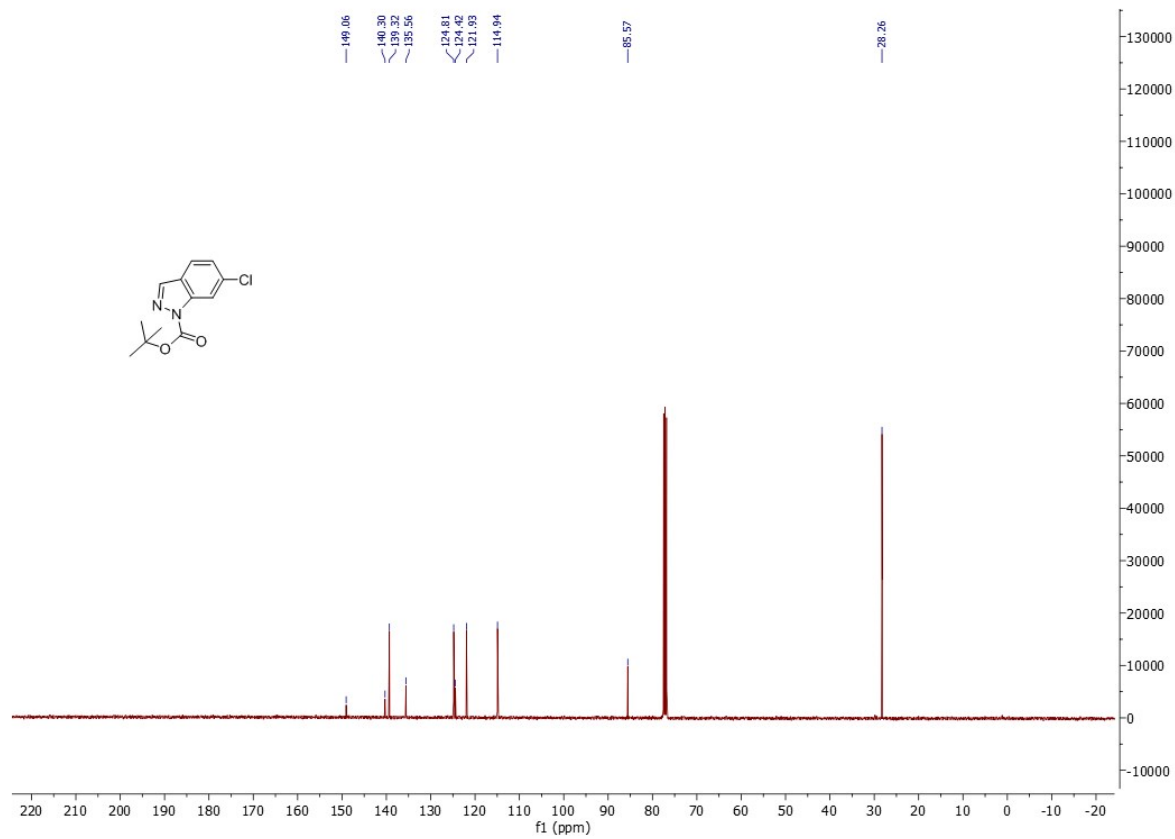
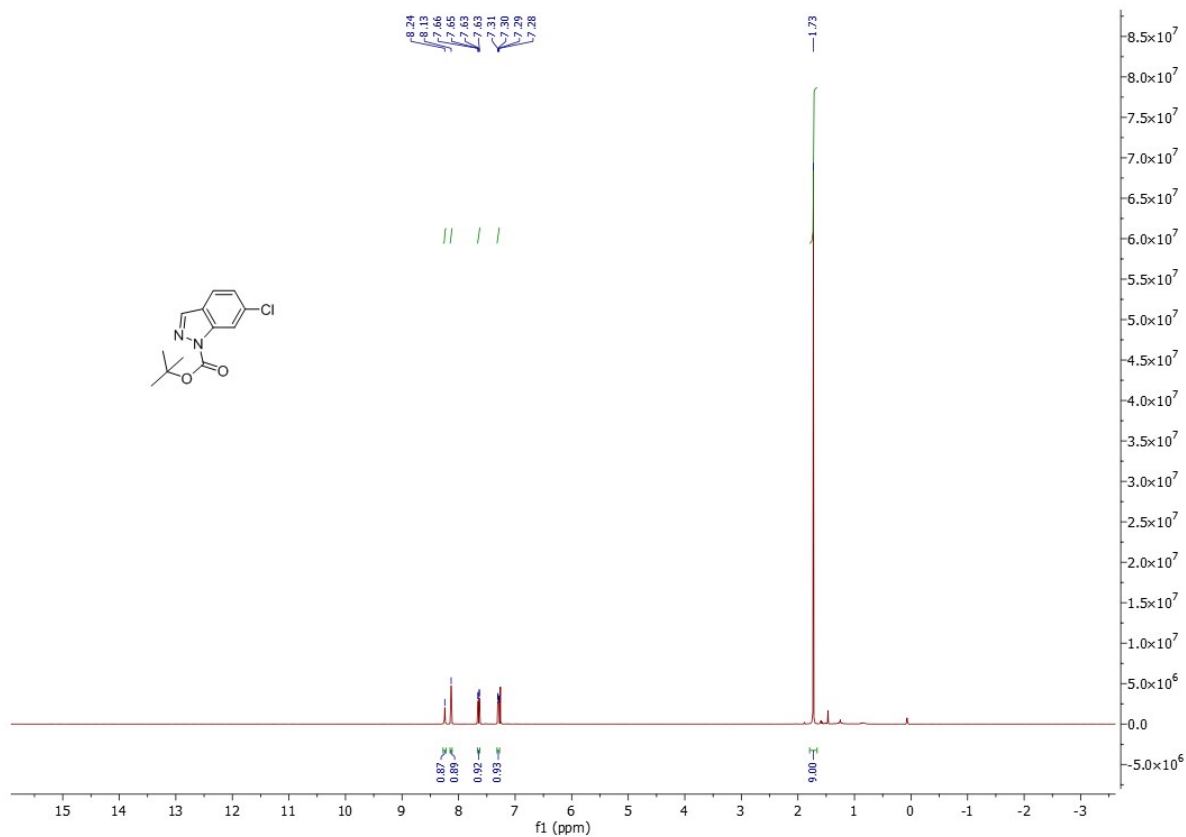
# Tert-butyl 4-fluoro-1H-indazole-1-carboxylate (**4p**)



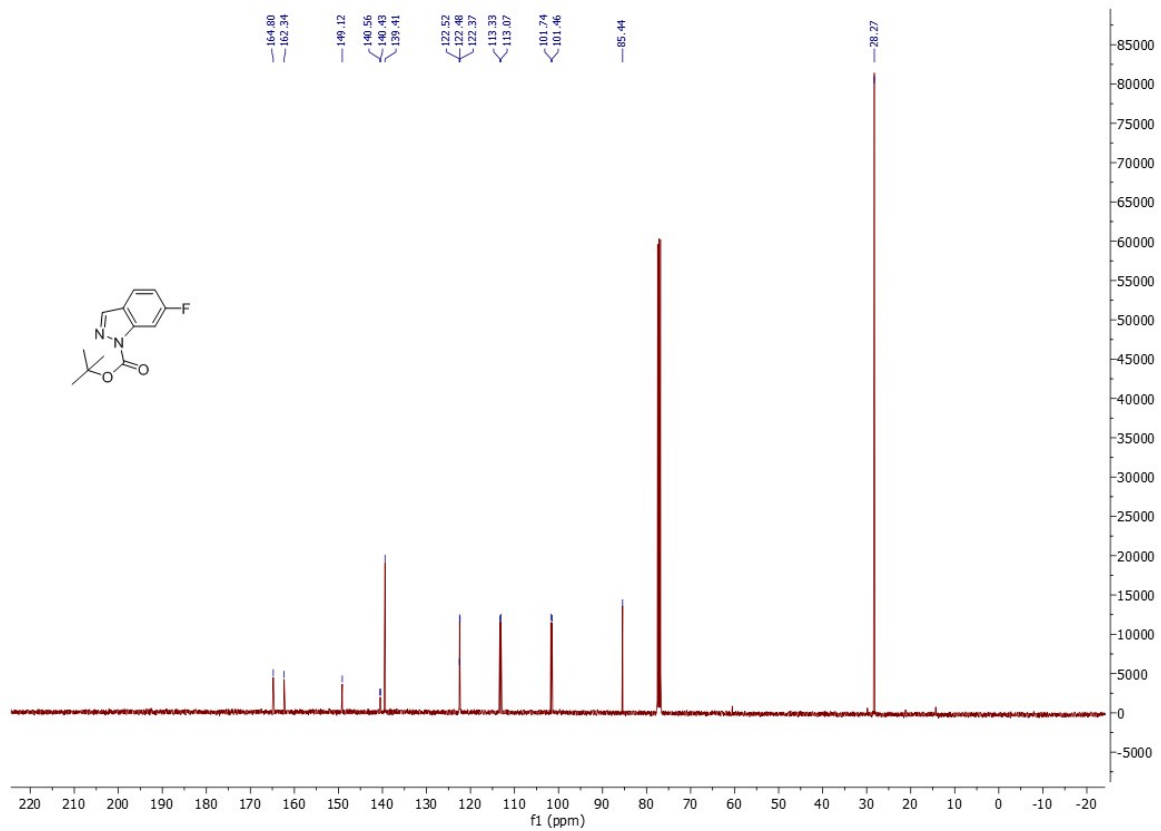
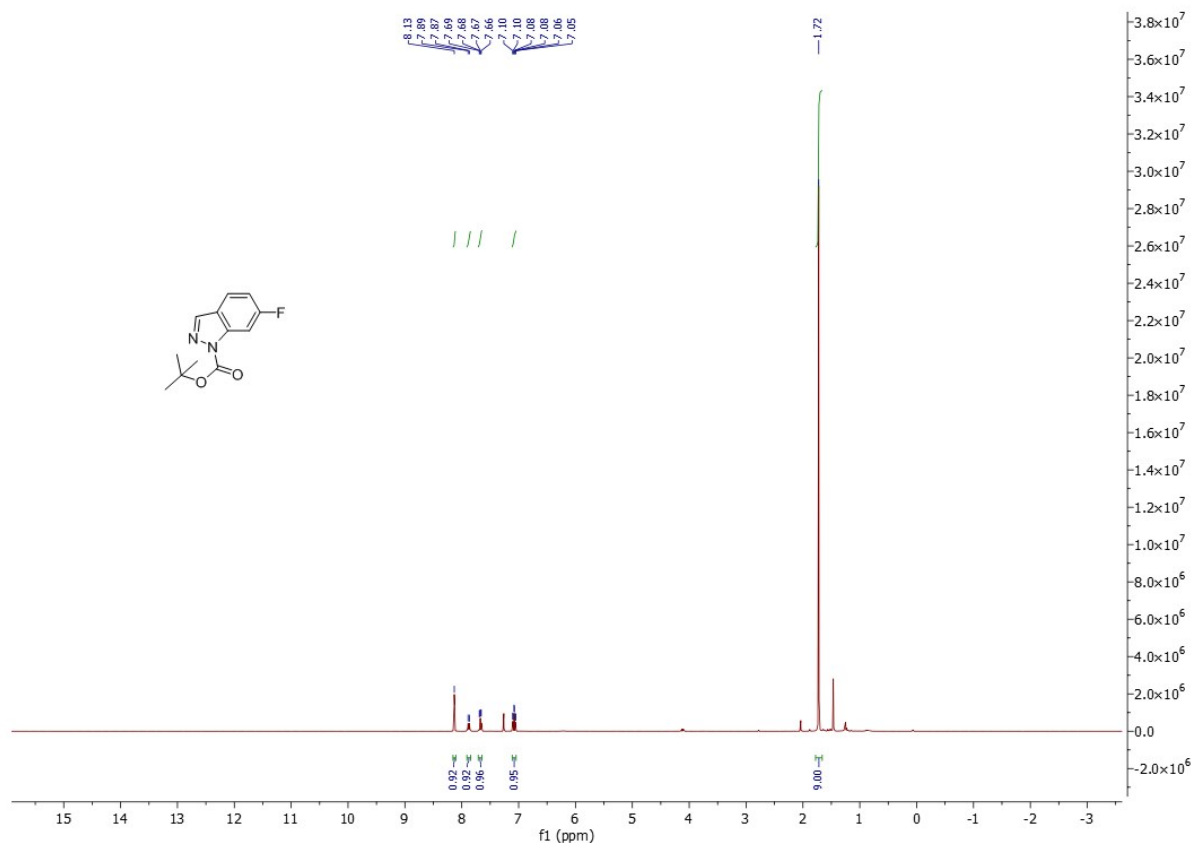


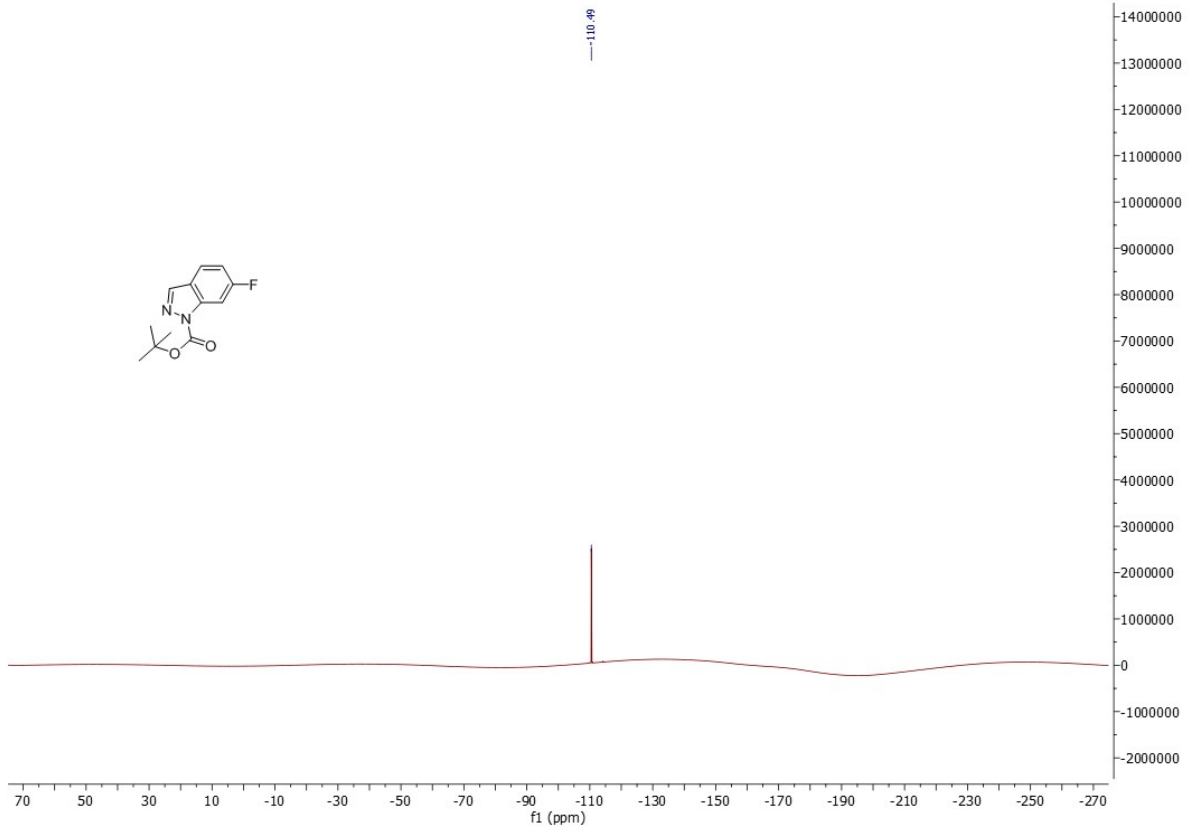
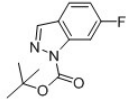


# Tert-butyl 6-chloro-1H-indazole-1-carboxylate (4q)

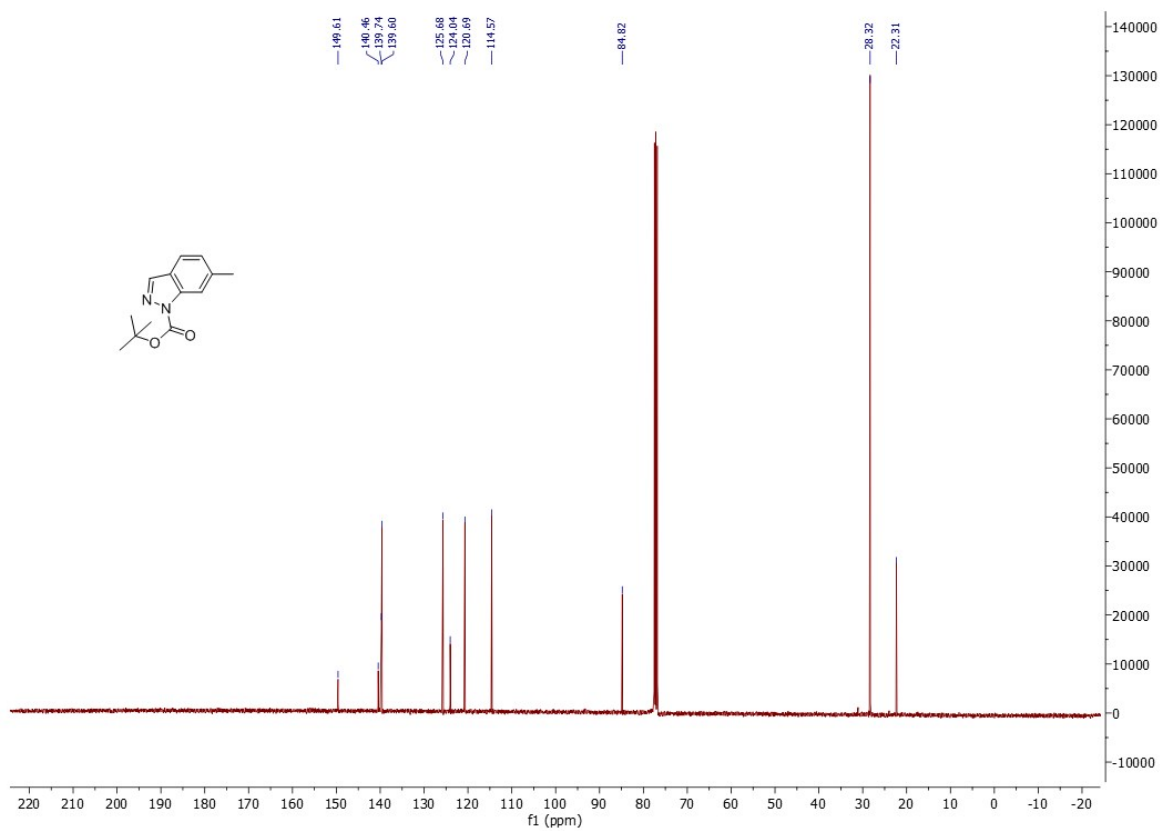
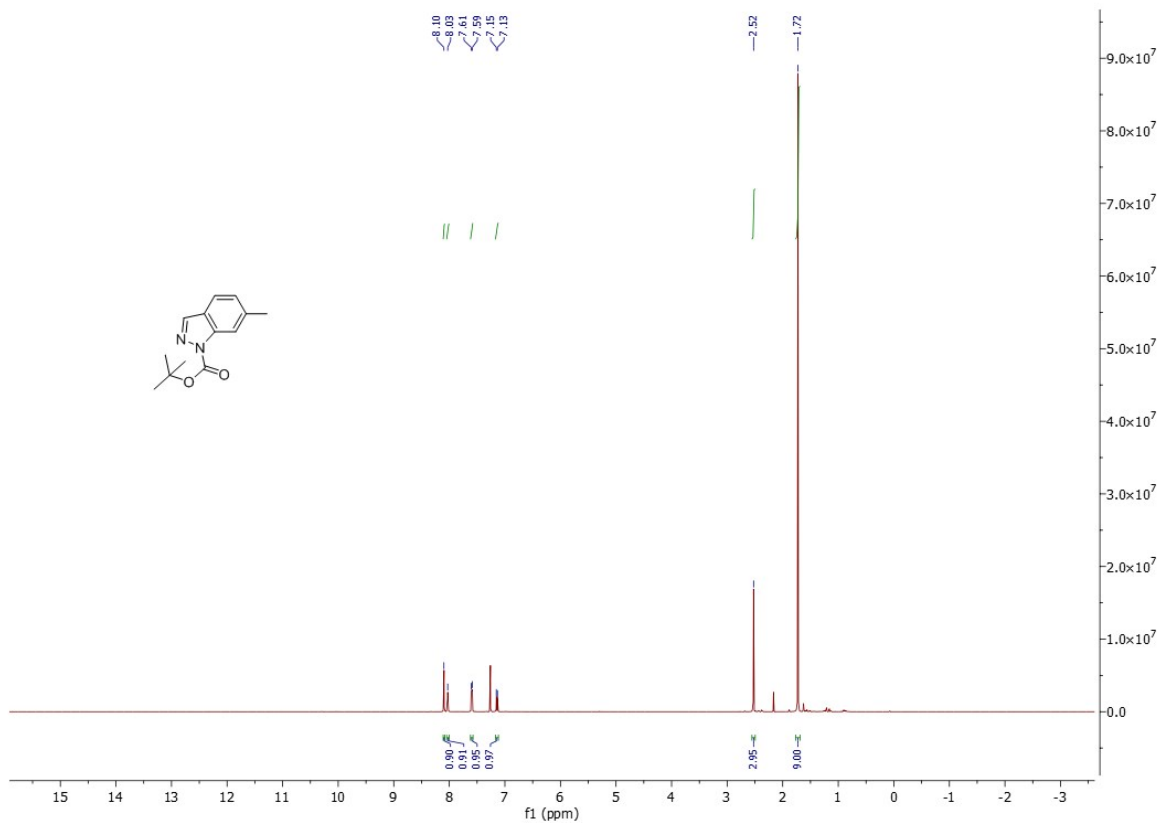


# Tert-butyl 6-fluoro-1H-indazole-1-carboxylate (**4r**)

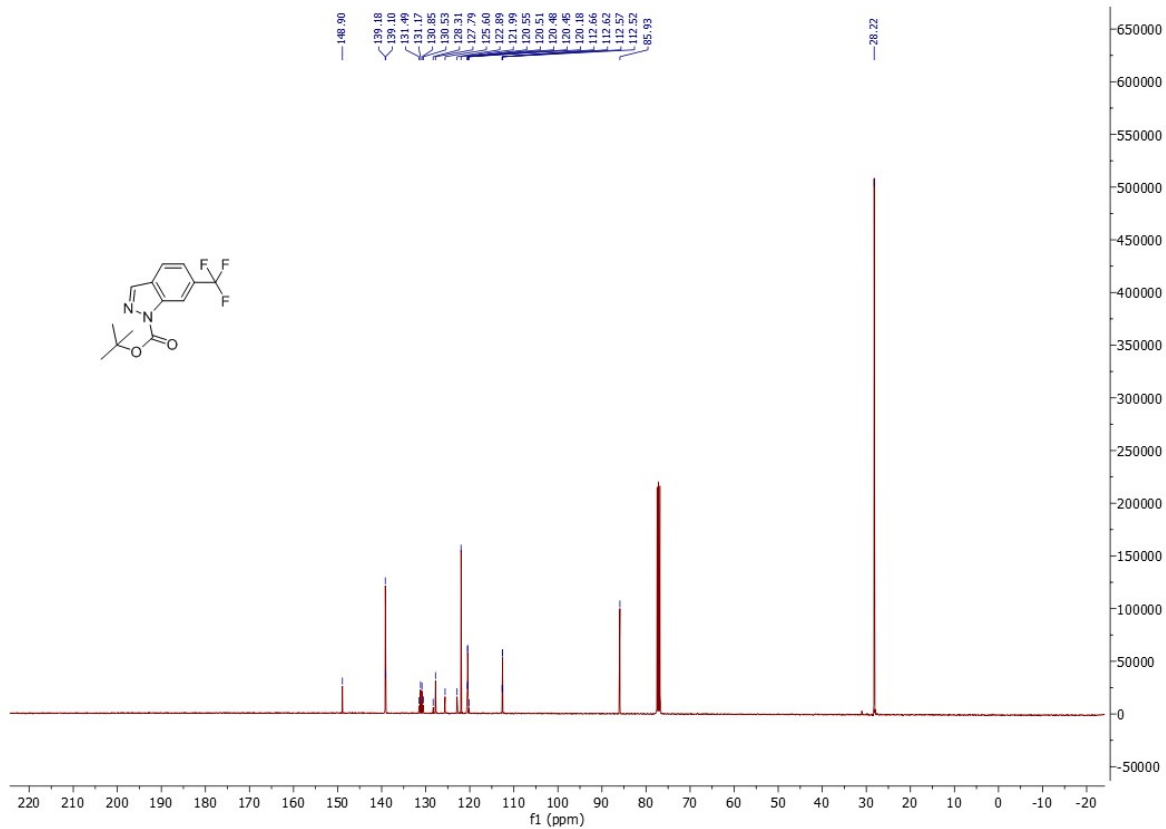
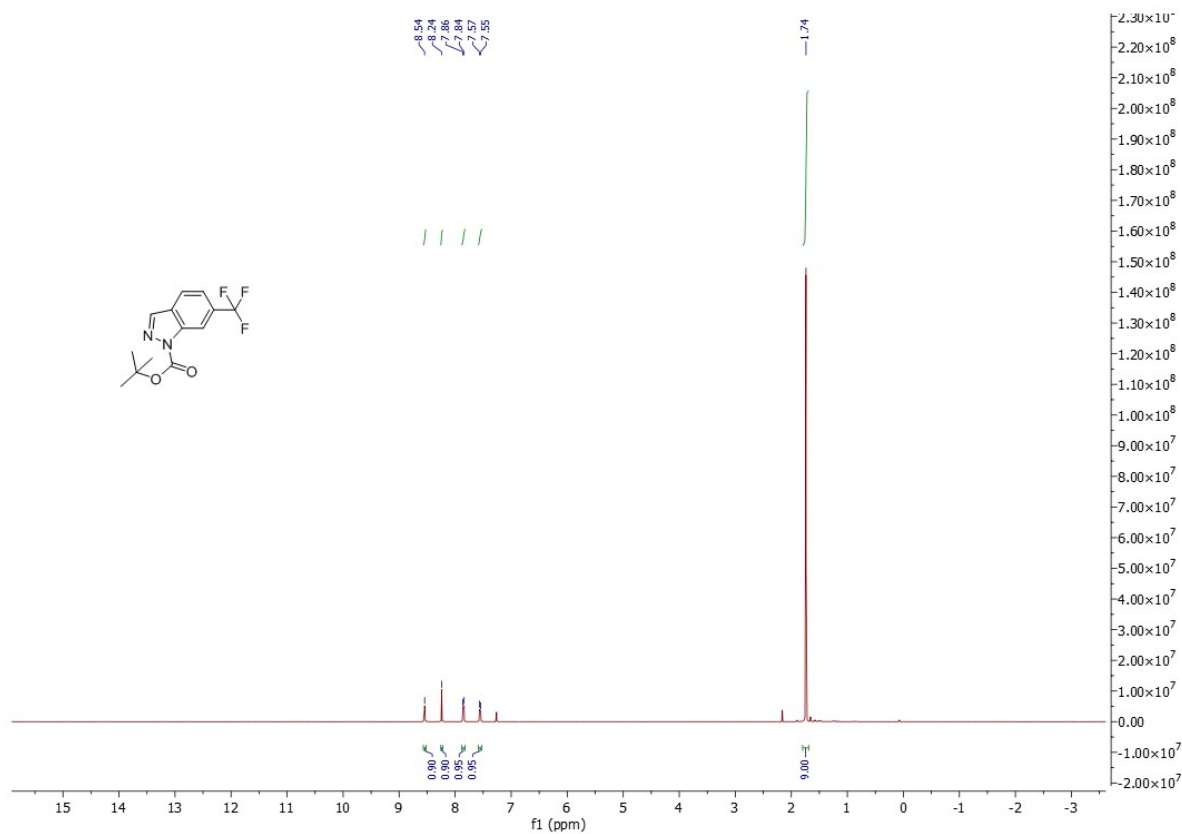


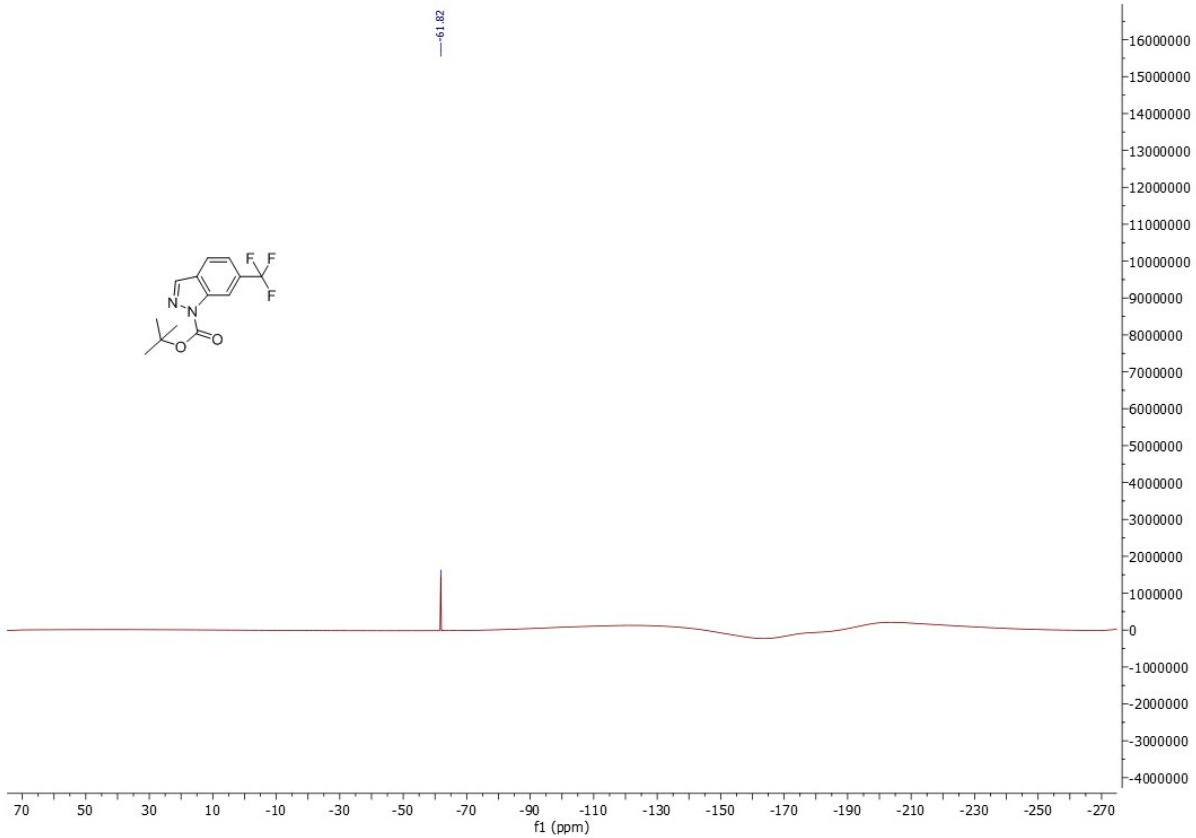
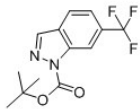


# Tert-butyl 6-methyl-1H-indazole-1-carboxylate (**4s**)



# Tert-butyl 6-(trifluoromethyl)-1H-indazole-1-carboxylate (**4t**)





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