



Supporting Information

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**Supporting information for**  
**Ru-Catalyzed Tandem Cross Metathesis/Intramolecular**  
**Hydroarylation Sequence**

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**Supporting Information**

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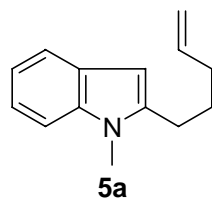
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## Experimental Section

**General Information:** Unless otherwise noted, material were purchased from commercial suppliers and used without further purification. Dichloromethane and 1, 2-dichloroethane were freshly distilled from calcium hydride. Hexane and ethyl acetate for flash column chromatography were distilled before use. Flash column chromatography was performed using 200-300 mesh silica gel. <sup>1</sup>H NMR spectra were recorded on Varian Mercury 400 (400 MHz) spectrophotometers. Chemical shifts are reported in ppm from the solvent resonance as the internal standard (CDCl<sub>3</sub>: 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. <sup>13</sup>C NMR spectra were recorded on Varian Mercury 400 (100 MHz) with complete proton decoupling spectrophotometers (CDCl<sub>3</sub>: 77.0 ppm). Chiral HPLC was performed on Agilent 1100 series with chiral columns (Chirapak AD column, (Daicel Chemical Ind., Ltd.)). Elementary analysis was taken on a Vario EL III elementary analysis instrument. Alkenyl indoles (**5a-5p**), **8a-c**, and 1-Boc-2-alkenyl indole (**10**) were synthesized employing the known procedures.<sup>1-6</sup> Metathesis catalysts were provided by Materia, Inc., CA.

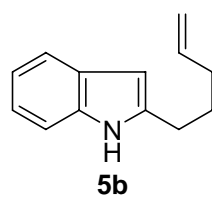
### 2-Alkenyl Indoles

#### Compound 5a: 1-Methyl-2-(4-pentenyl)-1 H-Indole



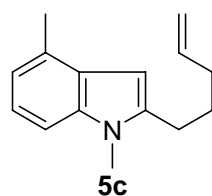
<sup>1</sup>H NMR  $\delta$  1.78-1.86 (m, 2H), 2.17-2.26 (m, 2H), 2.75 (t,  $J = 7.8$  Hz, 2H), 3.66 (s, 1H), 5.00-5.09 (m, 1H), 5.81-5.91 (m, 1H), 6.26 (s, 1H), 7.04-7.08 (m, 1H), 7.13-7.17 (m, 1H), 7.26 (d,  $J = 8.0$  Hz, 1H), 7.53 (d,  $J = 7.6$  Hz, 1H), <sup>13</sup>C NMR  $\delta$  26.0, 27.6, 29.4, 33.3, 98.8, 108.6, 115.1, 119.1, 119.6, 120.4, 127.8, 137.2, 138.1, 140.9; MS (EI)  $m/z$  200 (rel intensity) ( $M^+ + 1$ ); Analysis calculated for C<sub>14</sub>H<sub>17</sub>N: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.56; H, 8.70; N, 7.00.

#### Compound 5b: 2-(4-Pentenyl)-1 H-Indole



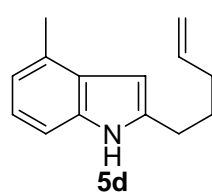
<sup>1</sup>H NMR  $\delta$  1.76-1.83 (m, 2H), 2.13 (q,  $J = 6.8, 14.0$  Hz, 1H), 2.73 (t,  $J = 7.4$  Hz, 2H), 4.99-5.06 (m, 1H), 5.77-5.87 (m, 1H), 6.23 (s, 1H), 7.04-7.12 (m, 2H), 7.26 (d,  $J = 7.6$  Hz, 1H), 7.52 (d,  $J = 7.6$  Hz, 2H), 7.78 (brs, 1H), <sup>13</sup>C NMR  $\delta$  27.4, 28.2, 33.1, 99.5, 110.2, 115.1, 119.5, 119.7, 120.9, 128.7, 135.7, 138.1, 139.4; MS (EI)  $m/z$  185 (rel intensity) ( $M^+$ ); Analysis calculated for C<sub>13</sub>H<sub>15</sub>N: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.40; H, 8.02; N, 7.50.

#### Compound 5c: 4-Methyl-1-methyl-2-(4-pentenyl)-1 H-Indole



<sup>1</sup>H NMR  $\delta$  1.76-1.83 (m, 1H), 2.17 (q,  $J = 7.2, 14.4$  Hz, 2H), 2.50 (s, 3H), 2.70 (t,  $J = 7.8$  Hz, 2H), 3.57 (s, 3H), 4.98-5.08 (m, 2H), 5.78-5.89 (m, 1H), 6.23 (s, 1H), 6.85 (d,  $J = 4.8$  Hz, 1H), 7.02-7.07 (m, 2H), <sup>13</sup>C NMR  $\delta$  18.6, 26.1, 27.7, 29.4, 33.3, 97.2, 106.3, 115.0, 119.4, 120.6, 127.5, 129.0, 136.9, 138.1, 140.2; MS (EI)  $m/z$  213 (rel intensity) ( $M^+$ ); Analysis calculated for C<sub>15</sub>H<sub>19</sub>N: C, 84.46; H, 8.98; N, 6.57. Found: C, 84.60; H, 8.90; N, 6.60.

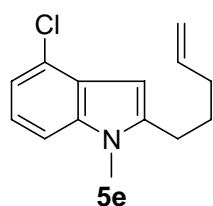
#### Compound 5d: 4-Methyl-2-(4-pentenyl)-1 H-Indole



<sup>1</sup>H NMR  $\delta$  1.78-1.86 (m, 2H), 2.15 (q,  $J = 7.2, 14.0$  Hz, 1H), 2.51 (s, 3H), 2.76 (t,  $J = 7.6$  Hz, 2H), 4.99-5.07 (m, 1H), 5.78-5.89 (m, 1H), 6.25 (s, 1H), 6.86 (d,  $J = 7.2$  Hz, 1H), 7.02 (t,  $J = 7.2$  Hz, 1H), 7.13 (d,  $J = 8.4$  Hz, 1H), 7.84 (brs, 1H), <sup>13</sup>C NMR  $\delta$  18.7, 27.5, 28.3,

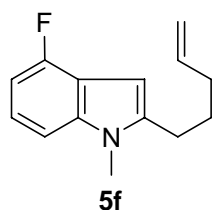
33.1, 98.0, 107.8, 115.0, 119.7, 121.0, 128.5, 129.1, 135.3, 138.1, 138.8; MS (EI)  $m/z$  200 (rel intensity) ( $M^+ + 1$ ); Analysis calculated for  $C_{14}H_{17}N$ : C, 84.37; H, 8.60; N, 7.03. Found: C, 84.30; H, 8.75; N, 7.21.

**Compound 5e: 4-Chloro-1-methyl-2-(4-pentenyl)-1 *H*-Indole**



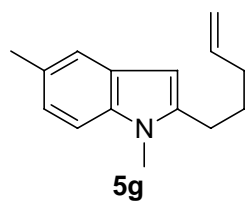
$^1H$  NMR  $\delta$  1.81-1.88 (m, 2H), 2.21 (q,  $J = 6.8, 14.0$  Hz, 2H), 2.74 (t,  $J = 7.6$  Hz, 2H), 3.65 (s, 3H), 5.01-5.10 (m, 2H), 5.82-5.89 (m, 1H), 6.35 (s, 1H), 7.04-7.07 (m, 2H), 7.14-7.16 (m, 1H), 7.25 (brs, 1H).  $^{13}C$  NMR  $\delta$  26.0, 27.5, 29.7, 33.2, 97.4, 107.3, 106.3, 115.2, 115.3, 118.9, 120.9, 124.9, 126.5, 138.0, 141.8; MS (EI)  $m/z$  233 (rel intensity) ( $M^+$ ); Analysis calculated for  $C_{14}H_{16}ClN$ : C, 71.94; H, 6.90; N, 5.99. Found: C, 72.03; H, 7.01; N, 5.85.

**Compound 5f: 4-Fluoro-1-methyl-2-(4-pentenyl)-1 *H*-Indole**



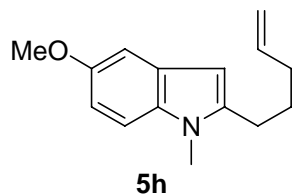
$^1H$  NMR  $\delta$  1.79-1.87 (m, 2H), 2.20 (q,  $J = 6.8, 14.0$  Hz, 2H), 2.73 (t,  $J = 7.6$  Hz, 2H), 3.65 (s, 3H), 5.01-5.09 (m, 2H), 5.80-5.88 (m, 1H), 6.32 (s, 1H), 6.71-6.76 (m, 1H), 7.03-7.06 (m, 2H).  $^{13}C$  NMR  $\delta$  26.0, 27.4, 29.8, 33.2, 94.6, 94.7, 103.9, 104.0, 104.1, 104.2, 104.8, 104.9, 115.2, 116.4, 116.6, 120.7, 120.80, 120.83, 120.9, 137.9, 139.9, 140.1, 140.9, 154.5, 156.9; MS (EI)  $m/z$  217 (rel intensity) ( $M^+$ ); Analysis calculated for  $C_{14}H_{16}FN$ : C, 77.39; H, 7.42; N, 6.45. Found: C, 77.45; H, 7.40; N, 6.50.

**Compound 5g: 5-Methyl-1-methyl-2-(4-pentenyl)-1 *H*-Indole**



$^1H$  NMR  $\delta$  1.80-1.87 (m, 2H), 2.19-2.26 (m, 1H), 2.46 (s, 3H), 2.74 (t,  $J = 7.6$  Hz, 2H), 3.64 (s, 3H), 5.02-5.11 (m, 2H), 5.83-5.93 (m, 1H), 6.19 (s, 1H), 6.99 (d,  $J = 8.0$  Hz, 1H), 7.12 (d,  $J = 8.4$  Hz, 2H), 7.34 (s, 1H).  $^{13}C$  NMR  $\delta$  21.3, 26.1, 27.7, 29.3, 33.8, 98.2, 108.3, 115.0, 119.4, 121.9, 128.0, 128.2, 135.7, 138.8, 140.9; MS (EI)  $m/z$  214 (rel intensity) ( $M^+ + 1$ ); Analysis calculated for  $C_{15}H_{19}N$ : C, 84.46; H, 8.98; N, 6.57. Found: C, 84.55; H, 8.92; N, 6.50.

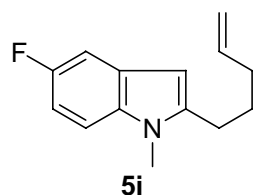
**Compound 5h: 5-Methoxy-1-methyl-2-(4-pentenyl)-1 *H*-Indole**



$^1H$  NMR  $\delta$  1.77-1.84 (m, 2H), 2.19 (q,  $J = 7.2, 14.0$  Hz, 2H), 2.71 (t,  $J = 8.0$  Hz, 2H), 3.62 (s, 3H), 3.83 (s, 3H), 4.99-5.08 (m, 2H), 5.80-5.90 (m, 1H), 6.17 (s, 1H), 6.80 (dd,  $J = 1.2, 8.0$  Hz, 1H), 7.01 (d,  $J = 2.4$  Hz, 1H), 7.14 (d,  $J = 8.8$  Hz, 1H).  $^{13}C$  NMR  $\delta$  26.1, 27.7, 29.3, 33.2, 55.9, 98.4, 101.9, 109.3, 110.3, 115.0, 128.0, 132.6, 138.1, 141.5, 153.9; MS (EI)  $m/z$  229 (rel intensity) ( $M^+$ ); Analysis

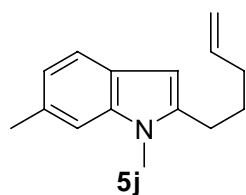
calculated for  $C_{15}H_{19}NO$ : C, 78.56; H, 8.35; N, 6.11. Found: C, 78.80; H, 8.40; N, 6.02.

**Compound 5i: 5-Fluoro-1-methyl-2-(4-pentenyl)-1 *H*-Indole**



$^1H$  NMR  $\delta$  1.78-1.85 (m, 2H), 2.19 (q,  $J = 6.8, 14.0$  Hz, 2H), 2.72 (t,  $J = 7.6$  Hz, 2H), 3.64 (s, 3H), 5.00-5.09 (m, 2H), 5.810-5.88 (m, 1H), 6.21 (s, 1H), 6.85-6.90 (m, 1H), 7.12-7.24 (m, 2H).  $^{13}C$  NMR  $\delta$  26.10, 27.5, 29.4, 33.2, 98.71, 98.73, 104.4, 104.6, 108.2, 108.5, 109.0, 115.2, 127.9, 128.0, 133.9, 138.0, 142.7, 156.6, 158.9; MS (EI)  $m/z$  217 (rel intensity) ( $M^+$ ); Analysis calculated for  $C_{14}H_{16}FN$ : C, 77.39; H, 7.42; N, 6.45. Found: C, 77.42; H, 7.50; N, 6.40.

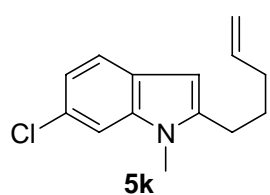
**Compound 5j: 6-Methyl-1-methyl-2-(4-pentenyl)-1 *H*-Indole**



$^1H$  NMR  $\delta$  1.83-1.91 (m, 2H), 2.25 (q,  $J = 7.2, 14.8$  Hz, 1H), 2.55 (s, 3H), 2.78 (t,  $J = 7.6$  Hz, 2H), 3.67 (s, 3H), 5.07-5.16 (m, 2H), 5.87-5.97 (m, 1H), 6.26 (s, 1H), 6.97 (d,  $J = 8.0$  Hz, 1H), 7.12 (s, 1H), 7.48 (d,  $J = 8.0$  Hz, 1H).  $^{13}C$  NMR  $\delta$  21.8, 26.0, 27.7, 29.2, 33.2, 98.4, 108.8, 115.0, 119.3, 120.8, 125.5, 130.1, 137.6, 138.2, 140.2; MS (EI)  $m/z$  213 (rel intensity) ( $M^+$ ); Analysis calculated for  $C_{15}H_{19}N$ : C, 84.46; H, 8.98; N,

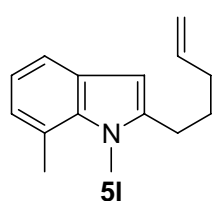
6.57. Found: C, 84.52; H, 8.93; N, 6.50.

**Compound 5k: 6-Chloro-1-methyl-2-(4-pentenyl)-1 H-Indole**



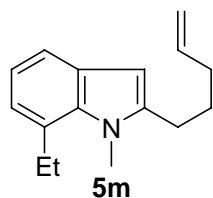
$^1\text{H NMR } \delta$  1.77-1.85 (m, 2H), 2.19 (q,  $J = 6.8$  Hz, 14.0 Hz, 2H), 2.71 (t,  $J = 7.6$  Hz, 2H), 3.61 (s, 3H), 5.00-5.09 (m, 2H), 5.79-5.89 (m, 1H), 6.22 (s, 1H), 7.02 (dd,  $J = 1.6, 8.0$  Hz, 1H), 7.24 (t,  $J = 2.4$  Hz, 1H), 7.41 (d,  $J = 8.4$  Hz, 1H),  $^{13}\text{C NMR } \delta$  26.0, 27.5, 29.5, 33.2, 98.8, 108.7, 115.2, 119.6, 119.7, 120.4, 126.3, 137.7, 138.0, 141.8; MS (EI)  $m/z$  235 (rel intensity) ( $\text{M}^+ + 2$ ); Analysis calculated for  $\text{C}_{14}\text{H}_{16}\text{ClN}$ : C, 71.94; H, 6.90; N, 5.99. Found: C, 71.98; H, 6.85; N, 5.93.

**Compound 5l: 7-Methyl-1-methyl-2-(4-pentenyl)-1 H-Indole**



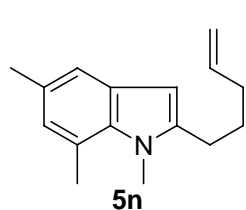
$^1\text{H NMR } \delta$  1.87-1.95 (m, 2H), 2.30 (q,  $J = 6.4, 13.6$  Hz, 1H), 2.79 (t,  $J = 8.0$  Hz, 3H), 2.86 (s, 3H), 3.98 (s, 3H), 5.12-5.21 (m, 2H), 5.92-6.00 (m, 1H), 6.33 (s, 1H), 6.94 (d,  $J = 6.8$  Hz, 1H), 7.03 (t,  $J = 7.6$  Hz, 1H), 7.47 (d,  $J = 7.6$  Hz, 1H),  $^{13}\text{C NMR } \delta$  20.3, 26.3, 27.6, 32.3, 33.3, 99.4, 115.0, 117.8, 119.2, 120.4, 123.7, 128.5, 136.1, 138.1, 141.1; MS (EI)  $m/z$  214 (rel intensity) ( $\text{M}^+ + 1$ ); Analysis calculated for  $\text{C}_{15}\text{H}_{19}\text{N}$ : C, 84.46; H, 8.98; N, 6.57. Found: C, 84.52; H, 8.90; N, 6.51.

**Compound 5m: 7-Ethyl-1-methyl-2-(4-pentenyl)-1 H-Indole**



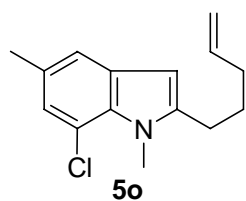
$^1\text{H NMR } \delta$  1.38 (t,  $J = 7.6$  Hz, 3H), 1.81-1.88 (m, 2H), 2.20-2.26 (m, 2H), 2.75 (q,  $J = 7.6, 15.2$  Hz, 2H), 3.14 (q,  $J = 7.6, 15.2$  Hz, 2H), 3.90 (s, 3H), 5.03-5.12 (m, 2H), 5.84-5.93 (m, 1H), 6.28 (s, 1H), 6.92-7.02 (m, 2H), 7.38-7.41 (m, 1H),  $^{13}\text{C NMR } \delta$  16.8, 25.9, 26.5, 27.6, 32.3, 33.3, 99.6, 115.0, 117.8, 119.3, 122.1, 127.0, 128.9, 135.3, 138.2, 141.2; MS (EI)  $m/z$  227 (rel intensity) ( $\text{M}^+$ ); Analysis calculated for  $\text{C}_{15}\text{H}_{19}\text{N}$ : C, 84.53; H, 9.31; N, 6.16. Found: C, 84.60; H, 9.41; N, 6.26.

**Compound 5n: 5, 7-Dimethyl-1-methyl-2-(4-pentenyl)-1 H-Indole**



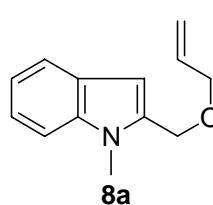
$^1\text{H NMR } \delta$  1.77-1.84 (m, 2H), 2.18-2.23 (m, 2H), 2.40 (s, 3H), 2.68 (t,  $J = 8.0$  Hz, 2H), 2.72 (s, 3H), 3.84 (s, 3H), 5.04-5.12 (m, 2H), 5.84-5.93 (m, 1H), 6.15 (s, 1H), 6.70 (s, 1H), 7.17 (s, 1H),  $^{13}\text{C NMR } \delta$  20.1, 20.9, 26.3, 27.6, 32.2, 33.2, 98.8, 114.9, 117.4, 120.0, 125.3, 128.1, 128.8, 134.4, 138.1, 141.1; MS (EI)  $m/z$  227 (rel intensity) ( $\text{M}^+$ ); Analysis calculated for  $\text{C}_{15}\text{H}_{19}\text{N}$ : C, 84.53; H, 9.31; N, 6.16. Found: C, 84.50; H, 9.35; N, 6.06.

**Compound 5o: 5-Methyl-7-chloro-1-methyl-2-(4-pentenyl)-1 H-Indole**

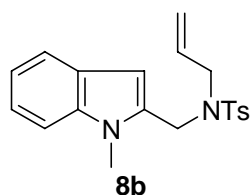


$^1\text{H NMR } \delta$  1.76-1.83 (m, 2H), 2.18 (q,  $J = 6.8, 13.6$  Hz, 2H), 2.35 (s, 3H), 2.68 (t,  $J = 7.6$  Hz, 2H), 3.98 (s, 3H), 5.00-5.08 (m, 2H), 5.79-5.89 (m, 1H), 6.15 (s, 1H), 6.90 (s, 1H), 7.24 (s, 1H),  $^{13}\text{C NMR } \delta$  20.8, 26.2, 27.5, 32.1, 33.2, 99.2, 115.1, 115.7, 118.3, 123.8, 129.3, 130.9, 131.0, 138.0, 142.7; MS (EI)  $m/z$  247 (rel intensity) ( $\text{M}^+$ ); Analysis calculated for  $\text{C}_{15}\text{H}_{19}\text{N}$ : C, 72.71; H, 7.32; N, 5.65. Found: C, 72.69; H, 7.36; N, 5.67.

**Compound 8a: 2-(Allyloxymethyl)-1-methyl-1 H-indole**

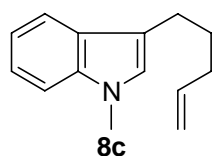


$^1\text{H NMR } \delta$  3.78 (s, 3H), 3.99 (d,  $J = 5.6$  Hz, 2H), 4.67 (s, 2H), 5.20 (d,  $J = 10.4$  Hz, 1H), 5.29 (d,  $J = 17.2$  Hz, 1H), 5.86-5.96 (m, 1H), 6.46 (s, 1H), 7.09 (t,  $J = 7.6$  Hz, 1H), 7.22 (t,  $J = 7.2$  Hz, 1H), 7.31 (d,  $J = 8.4$  Hz, 1H), 7.58 (d,  $J = 7.6$  Hz, 1H),  $^{13}\text{C NMR } \delta$  29.6, 63.9, 70.1, 102.8, 109.1, 117.3, 119.4, 120.6, 121.8, 127.1, 134.4, 135.6, 138.0; MS (EI)  $m/z$  201 (rel intensity) ( $\text{M}^+$ ); Analysis calculated for  $\text{C}_{13}\text{H}_{15}\text{NO}$ : C, 77.58; H, 7.51; N, 6.96. Found: C, 77.60; H, 7.54; N, 6.90.

**Compound 8b: N-Allyl-N-((1-methyl-1H-indol-2-yl) methyl)-4-methylbenzene Sulfonamide**

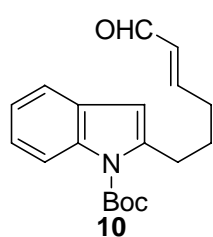
$^1\text{H NMR } \delta$  2.45 (s, 3H), 3.70 (d,  $J = 6.4$  Hz, 2H), 3.80 (s, 3H), 4.52 (s, 2H), 4.92-4.99 (m, 2H), 5.28-5.32 (m, 1H), 6.31 (s, 1H), 7.09 (t,  $J = 7.2$  Hz, 1H), 7.21-7.31 (m, 2H), 7.34 (d,  $J = 8.0$  Hz, 2H), 7.53 (d,  $J = 7.6$  Hz, 1H), 7.75 (d,  $J = 8.4$  Hz, 2H),  $^{13}\text{C NMR } \delta$  21.5, 30.0, 43.5, 48.9, 103.7, 103.9, 109.2, 119.5, 120.0, 121.8, 126.8, 127.2, 129.8, 131.5, 132.4, 136.3, 138.0, 143.5; MS (EI)  $m/z$  354 (rel intensity) ( $\text{M}^+$ ); Analysis

calculated for  $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2\text{S}$ : C, 67.77; H, 6.26; N, 7.90; S, 9.05, Found: C, 67.69; H, 6.29; N, 7.95; S, 9.01.

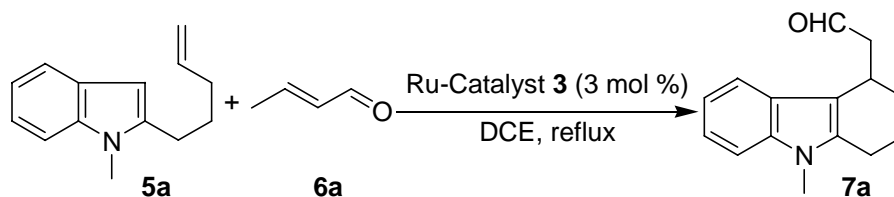
**Compound 8c: 1-Methyl-3-(pent-4-enyl)-1 H-indole**

$^1\text{H NMR } \delta$  ( $\text{CDCl}_3$ , 600 Mz) 1.77-1.82 (m, 2H), 2.15 (q,  $J = 7.2$ , 14.4 Hz, 2H), 2.75 (t,  $J = 7.2$  Hz, 2H), 3.74 (s, 3H), 4.52 (s, 2H), 4.96-5.05 (m, 2H), 5.83-5.90 (m, 1H), 6.82 (s, 1H), 7.09 (t,  $J = 7.2$  Hz, 1H), 7.21 (t,  $J = 7.2$  Hz, 1H), 7.28 (d,  $J = 8.4$  Hz, 1H), 7.59 (d,  $J = 8.4$  Hz, 1H),  $^{13}\text{C NMR } \delta$  ( $\text{CDCl}_3$ , 150 Mz) 24.4, 29.5, 32.5, 33.5, 109.0, 114.4, 115.0, 118.3,

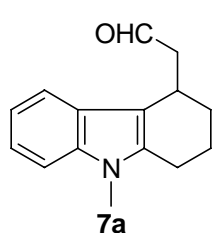
119.0, 121.3, 126.0, 127.8, 136.9, 138.8; MS (EI)  $m/z$  199 (rel intensity) ( $\text{M}^+$ ); Analysis calculated for  $\text{C}_{14}\text{H}_{17}\text{N}$ : C, 84.37; H, 8.60; N, 7.03, Found: C, 84.38; H, 8.63; N, 7.01.

**Compound 10: (E)-tert-Butyl 2-(6-oxohex-4-enyl)-1 H-indole-1-carboxylate**

$^1\text{H NMR } \delta$  1.67 (s, 9H), 1.90-1.97 (m, 2H), 2.46 (q,  $J = 7.2$ , 14.0 Hz, 2H), 3.07 (t,  $J = 7.6$  Hz, 2H), 6.16 (q,  $J = 8.0$ , 15.6 Hz, 1H), 6.35 (s, 1H), 6.84-6.90 (m, 1H), 7.17-7.25 (m, 2H), 7.45 (d,  $J = 7.2$  Hz, 1H), 8.06 (d,  $J = 8.4$  Hz, 1H), 9.51 (d,  $J = 8.0$  Hz, 1H),  $^{13}\text{C NMR } \delta$  26.9, 28.2, 29.4, 32.1, 83.8, 107.6, 115.6, 119.7, 122.6, 123.3, 129.0, 133.1, 136.4, 140.9, 150.3, 158.1, 193.9; MS (EI)  $m/z$  313 (rel intensity) ( $\text{M}^+$ ); Analysis calculated for  $\text{C}_{19}\text{H}_{23}\text{NO}_3$ : C, 72.82; H, 7.40; N, 4.47, Found: C, 72.90; H, 7.46; N, 4.42.

**General procedure for the Cross Metathesis/Intramolecular Hydroarylation Sequence of akenyl indoles 5 with 6**

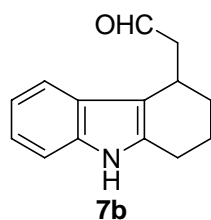
To a mixture of alkenyl indole **5a** (0.30 mmol), crotonaldehyde (**6a**) (1.5 mmol), and DCE (dichloroethane) (3 mL), Ru-Catalyst **3** (0.009 mmol, 3 mol % based on **5a**) was added. The reaction mixture was then stirred under boiling DCE. Upon the completion of reaction monitored by TLC, the reaction mixture was then cooled to room temperature and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane/ ethyl acetate (10:1)) to give pure cyclization product **7a**.

**Compound 7a: 2-(9-Methyl-2,3,4,9-tetrahydro-1 H-carbazol-4-yl)acetaldehyde**

$^1\text{H NMR } \delta$  1.66-1.72 (m, 1H), 1.88-1.98 (m, 3H), 2.60-2.72 (m, 3H), 2.97 (dd,  $J = 2.8$ , 16.8 Hz, 1H), 3.56 (s, 3H), 3.59-3.63 (m, 1H), 7.05 (t,  $J = 7.6$  Hz, 1H), 7.14 (t,  $J = 7.2$  Hz, 1H), 7.24 (d,  $J = 8.0$  Hz, 1H), 7.45 (d,  $J = 7.6$  Hz, 1H), 9.84 (s, 1H),  $^{13}\text{C NMR } \delta$  19.4, 21.8, 26.7, 28.6, 28.8, 49.2, 108.7, 110.5, 117.8, 118.7, 120.6, 125.9, 136.2, 136.7, 203.0; MS

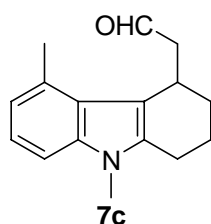
(EI)  $m/z$  227 (rel intensity) ( $M^+$ ); Analysis calculated for  $C_{15}H_{17}NO$ : C, 79.26; H, 7.54; N, 6.16. Found: C, 79.30; H, 7.50; N, 6.20.

**Compound 7b: 2-(2,3,4,9-tetrahydro-1H-carbazol-4-yl)acetaldehyde**



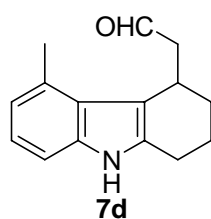
$^1H$  NMR  $\delta$  1.69-1.74 (m, 1H), 1.86-2.04 (m, 3H), 2.63-2.71 (m, 3H), 2.96-3.02 (m, 1H), 3.58-3.64 (m, 1H), 7.05-7.14 (m, 2H), 7.27 (d,  $J$  = 7.6 Hz, 1H), 7.45 (d,  $J$  = 7.6 Hz, 1H), 7.78 (brs, 1H), 9.86 (t,  $J$  = 1.6 Hz, 1H),  $^{13}C$  NMR  $\delta$  19.5, 22.9, 26.7, 28.9, 49.0, 110.6, 111.2, 117.8, 119.2, 121.0, 126.4, 134.7, 135.6, 203.2; MS (EI)  $m/z$  213 (rel intensity) ( $M^+$ ); Analysis calculated for  $C_{14}H_{15}NO$ : C, 78.84; H, 7.09; N, 6.57. Found: C, 78.88; H, 7.02; N, 6.50.

**Compound 7c: 2-(5,9-Dimethyl-2,3,4,9-tetrahydro-1H-carbazol-4-yl)acetaldehyde**



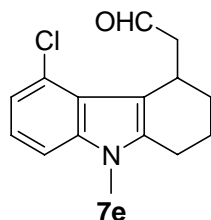
$^1H$  NMR  $\delta$  1.86-1.97 (m, 4H), 2.63 (s, 3H), 2.73-2.80 (m, 3H), 2.87 (dd,  $J$  = 2.4, 17.6 Hz, 1H), 3.57 (s, 3H), 3.93-3.96 (m, 1H), 6.81 (d,  $J$  = 7.2 Hz, 1H), 7.02-7.10 (m, 2H), 9.86 (t,  $J$  = 2.0 Hz, 1H),  $^{13}C$  NMR  $\delta$  17.2, 19.8, 21.7, 26.3, 27.2, 28.8, 29.6, 50.9, 106.3, 111.7, 120.6, 124.6, 129.0, 135.1, 136.9, 202.2; MS (EI)  $m/z$  241 (rel intensity) ( $M^+$ ); Analysis calculated for  $C_{16}H_{19}NO$ : C, 79.63; H, 7.94; N, 5.80. Found: C, 79.58; H, 7.90; N, 5.85.

**Compound 7d: 2-(5-Methyl-2,3,4,9-tetrahydro-1H-carbazol-4-yl)acetaldehyde**



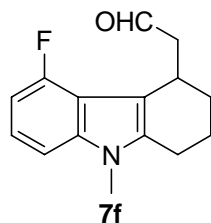
$^1H$  NMR  $\delta$  1.85-1.90 (m, 4H), 2.62 (s, 3H), 2.70-2.73 (m, 2H), 2.79 (dd,  $J$  = 2.8, 10.4 Hz, 1H), 2.86 (dd,  $J$  = 2.4, 17.6 Hz, 1H), 3.90-3.93 (m, 1H), 6.81 (d,  $J$  = 7.2 Hz, 1H), 6.99 (t,  $J$  = 7.2 Hz, 1H), 7.10 (d,  $J$  = 8.0 Hz, 1H), 7.75 (brs, 1H), 9.86 (t,  $J$  = 2.4 Hz, 1H),  $^{13}C$  NMR  $\delta$  17.3, 19.8, 22.8, 26.3, 27.5, 50.7, 108.3, 112.5, 121.0, 121.1, 125.3, 129.0, 133.7, 135.8, 202.4; MS (EI)  $m/z$  227 (rel intensity) ( $M^+$ ); Analysis calculated for  $C_{15}H_{17}NO$ : C, 79.26; H, 7.54; N, 6.16. Found: C, 79.30; H, 7.58; N, 6.10.

**Compound 7e: 2-(5-Chloro-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-4-yl)acetaldehyde**



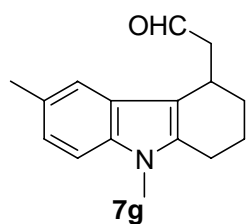
$^1H$  NMR  $\delta$  1.83-1.98 (m, 4H), 2.60-2.68 (m, 2H), 2.75 (dd,  $J$  = 4.0, 16.8 Hz, 1H), 3.10 (dd,  $J$  = 2.4, 17.2 Hz, 1H), 3.57 (s, 3H), 4.09 (dd,  $J$  = 2.0, 10.8 Hz, 1H), 7.00-7.15 (m, 2H), 7.12-7.14 (m, 1H), 9.85 (d,  $J$  = 3.2 Hz, 1H),  $^{13}C$  NMR  $\delta$  17.3, 21.8, 25.7, 26.9, 29.1, 50.7, 107.3, 111.3, 121.0, 121.1, 123.1, 124.8, 136.8, 138.1, 202.7; MS (EI)  $m/z$  263 (rel intensity) ( $M^+ + 2$ ); Analysis calculated for  $C_{15}H_{16}ClNO$ : C, 68.83; H, 6.16; N, 5.35. Found: C, 68.87; H, 6.20; N, 5.38.

**Compound 7f: 2-(5-Fluoro-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-4-yl)acetaldehyde**



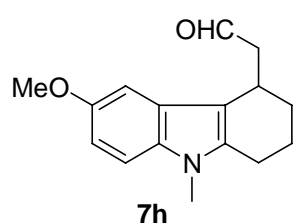
$^1H$  NMR  $\delta$  1.75-1.79 (m, 1H), 1.90-1.95 (m, 3H), 2.61-2.74 (m, 3H), 3.01 (dd,  $J$  = 3.2, 16.4 Hz, 1H), 3.60 (s, 3H), 3.76 (dd,  $J$  = 2.0, 6.8 Hz, 1H), 6.69-6.74 (m, 1H), 7.03-7.05 (m, 2H), 9.85 (d,  $J$  = 2.4 Hz, 1H),  $^{13}C$  NMR  $\delta$  18.4, 21.8, 26.8, 27.8, 29.1, 29.3, 50.1, 103.9, 104.1, 104.2, 104.7, 109.6, 114.5, 114.7, 121.0, 136.0, 139.5, 139.6, 154.9, 157.3, 202.9; MS (EI)  $m/z$  245 (rel intensity) ( $M^+$ ); Analysis calculated for  $C_{15}H_{16}FNO$ : C, 73.45; H, 6.57; N, 5.71. Found: C, 73.49; H, 6.61; N, 5.69.

**Compound 7g: 2-(6,9-Dimethyl-2,3,4,9-tetrahydro-1H-carbazol-4-yl)acetaldehyde**



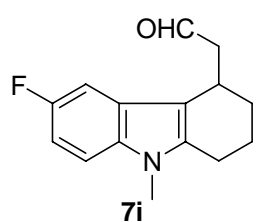
$^1H$  NMR  $\delta$  1.66-1.71 (m, 1H), 1.86-1.95 (m, 3H), 2.43 (s, 3H), 2.59-2.70 (m, 3H), 2.94-2.99 (m, 1H), 3.53 (s, 3H), 3.55-3.59 (m, 1H), 6.95-6.97 (m, 1H), 7.12 (d,  $J$  = 8.0 Hz, 1H), 7.23 (s, 1H), 9.84 (dd,  $J$  = 1.2, 2.8 Hz, 1H),  $^{13}C$  NMR  $\delta$  19.4, 21.4, 21.9, 26.7, 28.6, 28.8, 49.1, 108.4, 109.9, 117.6, 122.0, 126.1, 127.9, 135.2, 136.2, 203.2; MS (EI)  $m/z$  241 (rel intensity) ( $M^+$ ); Analysis calculated for  $C_{16}H_{19}NO$ : C, 79.63; H, 7.94; N, 5.80. Found: C, 79.69; H, 7.89; N, 5.89.

**Compound 7h: 2-(6-Methoxy-9-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)acetaldehyde**



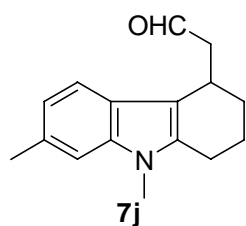
$^1\text{H NMR } \delta$  1.68-1.71 (m, 1H), 1.87-1.95 (m, 3H), 2.59-2.67 (m, 3H), 2.91-2.97 (m, 1H), 3.53 (s, 3H), 3.55-3.60 (m, 1H), 3.83 (s, 3H), 6.80 (dd,  $J = 2.4, 8.8$  Hz, 1H), 6.91 (d,  $J = 2.4$  Hz, 1H), 7.12 (d,  $J = 8.8$  Hz, 1H), 9.85 (t,  $J = 2.4$  Hz, 1H),  $^{13}\text{C NMR } \delta$  19.3, 22.0, 26.7, 28.7, 29.1, 49.0, 56.1, 100.7, 109.3, 110.1, 110.2, 126.2, 132.2, 136.9, 153.6, 203.1; MS (EI)  $m/z$  257 (rel intensity) ( $\text{M}^+$ ); Analysis calculated for  $\text{C}_{16}\text{H}_{19}\text{NO}_2$ : C, 74.68; H, 7.44; N, 5.44. Found: C, 74.64; H, 7.48; N, 5.40.

**Compound 7i: 2-(6-Fluoro-9-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)acetaldehyde**



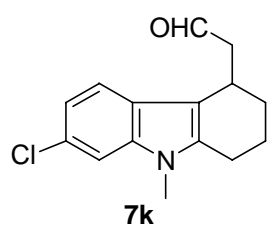
$^1\text{H NMR } \delta$  1.67-1.73 (m, 1H), 1.87-1.98 (m, 3H), 2.60-2.70 (m, 3H), 2.89-2.95 (m, 1H), 3.57 (s, 4H), overlapped, 6.85-6.90 (m, 1H), 7.08-7.15 (m, 2H), 9.84 (dd,  $J = 1.6, 2.8$  Hz, 1H),  $^{13}\text{C NMR } \delta$  19.3, 22.0, 26.6, 28.6, 29.1, 48.9, 102.9, 103.1, 108.4, 108.6, 109.1, 110.7, 126.0, 126.1, 133.4, 138.0, 156.3, 158.6, 202.7; MS (EI)  $m/z$  245 (rel intensity) ( $\text{M}^+$ ); Analysis calculated for  $\text{C}_{15}\text{H}_{16}\text{FNO}$ : C, 73.45; H, 6.57; N, 5.71. Found: C, 73.50; H, 6.50; N, 5.76.

**Compound 7j: 2-(7,9-Dimethyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)acetaldehyde**



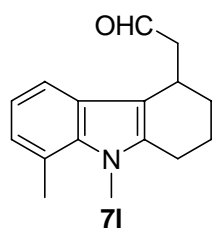
$^1\text{H NMR } \delta$  1.65-1.71 (m, 1H), 1.88-1.99 (m, 3H), 2.47 (s, 3H), 2.62-2.68 (m, 3H), 2.94-3.00 (m, 1H), 3.53 (s, 3H), 3.57-3.61 (m, 1H), 6.90 (d,  $J = 8.0$  Hz, 1H), 7.05 (s, 1H), 7.34 (d,  $J = 8.0$  Hz, 1H), 9.85 (dd,  $J = 1.6, 2.8$  Hz, 1H),  $^{13}\text{C NMR } \delta$  19.6, 21.7, 21.9, 26.9, 28.8, 29.6, 49.2, 108.8, 110.3, 117.5, 120.4, 123.8, 130.4, 135.5, 137.2, 203.2; MS (EI)  $m/z$  241 (rel intensity) ( $\text{M}^+$ ); Analysis calculated for  $\text{C}_{16}\text{H}_{19}\text{NO}$ : C, 79.63; H, 7.94; N, 5.80. Found: C, 79.68; H, 7.86; N, 5.88.

**Compound 7k: 2-(7-Chloro-9-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)acetaldehyde**



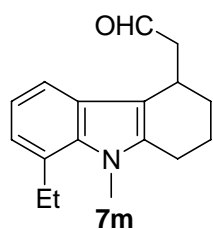
$^1\text{H NMR } \delta$  1.69-1.74 (m, 1H), 1.90-1.98 (m, 3H), 2.65-2.70 (m, 3H), 2.92-2.97 (m, 1H), 3.58 (s, 3H), 3.60-3.62 (m, 1H), 7.03 (dd,  $J = 1.6, 8.4$  Hz, 1H), 7.25 (t,  $J = 2.0$  Hz, 1H), 7.35 (d,  $J = 8.4$  Hz, 1H), 9.86 (dd,  $J = 1.6, 2.4$  Hz, 1H),  $^{13}\text{C NMR } \delta$  19.3, 21.8, 26.6, 28.5, 28.9, 49.1, 108.8, 110.8, 118.5, 119.1, 124.5, 126.5, 137.0, 137.2, 202.7; MS (EI)  $m/z$  263 (rel intensity) ( $\text{M}^+ + 2$ ); Analysis calculated for  $\text{C}_{15}\text{H}_{16}\text{ClNO}$ : C, 68.83; H, 6.16; N, 5.35. Found: C, 68.89; H, 6.10; N, 5.41.

**Compound 7l: 2-(8,9-Dimethyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)acetaldehyde**



$^1\text{H NMR } \delta$  1.71-1.78 (m, 1H), 1.90-1.96 (m, 3H), 2.63-2.71 (m, 3H), 2.77 (s, 1H), 2.95-3.00 (m, 1H), 3.61-3.65 (m, 1H), 3.88 (s, 3H), 6.87 (d,  $J = 7.2$  Hz, 1H), 6.95 (t,  $J = 7.6$  Hz, 1H), 7.31 (d,  $J = 7.6$  Hz, 1H), 9.88 (dd,  $J = 1.6, 2.8$  Hz, 1H),  $^{13}\text{C NMR } \delta$  19.3, 20.2, 22.2, 26.4, 28.4, 32.0, 49.1, 110.8, 115.8, 119.0, 120.8, 123.9, 126.7, 135.6, 136.6, 203.1; MS (EI)  $m/z$  241 (rel intensity) ( $\text{M}^+$ ); Analysis calculated for  $\text{C}_{16}\text{H}_{19}\text{NO}$ : C, 79.63; H, 7.94; N, 5.80. Found: C, 79.68; H, 7.98; N, 5.76.

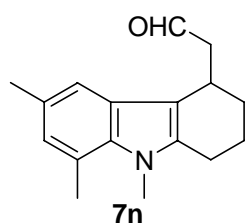
**Compound 7m: 2-(8-Ethyl-9-methyl-2,3,4,9-tetrahydro-1*H*-carbazol-4-yl)acetaldehyde**



$^1\text{H NMR } \delta$  1.40 (t,  $J = 7.2$  Hz, 3H), 1.77-1.81 (m, 1H), 1.94-1.99 (m, 3H), 2.66-2.78 (m, 3H), 2.99-3.04 (m, 1H), 3.14 (q,  $J = 7.6, 14.8$  Hz, 2H), 3.65-3.69 (m, 1H), 3.87 (s, 1H), 6.98 (d,  $J = 7.2$  Hz, 1H), 7.04 (t,  $J = 7.6$  Hz, 1H), 7.35 (d,  $J = 4.0$  Hz, 1H), 9.91 (dd,  $J = 1.2, 2.8$  Hz, 1H),  $^{13}\text{C NMR } \delta$  16.7, 19.2, 22.2, 25.8, 26.3, 28.3, 31.8, 49.0, 110.9, 115.6, 119.1, 122.3, 127.1, 127.3, 134.8, 136.6, 202.9; MS (EI)  $m/z$  255 (rel intensity) ( $\text{M}^+$ ); Analysis calculated for  $\text{C}_{17}\text{H}_{21}\text{NO}$ : C, 79.96; H, 8.29; N, 5.49. Found: C, 79.90; H, 8.32;

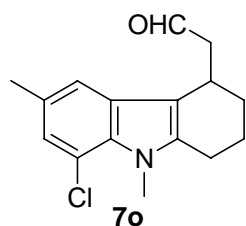
N, 5.46.

**Compound 7n: 2-(6,8,9-Trimethyl-2,3,4,9-tetrahydro-1H-carbazol-4-yl)acetaldehyde**



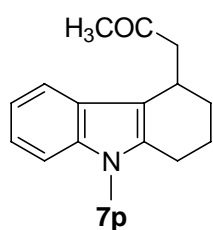
$^1\text{H NMR } \delta$  1.70-1.74 (m, 1H), 1.87-1.91 (m, 3H), 2.37 (s, 3H), 2.59-2.67 (m, 3H), 2.70 (s, 3H), 2.96 (dd,  $J = 3.2, 16.4$  Hz, 1H), 3.57-3.59 (m, 1H), 3.82 (s, 1H), 6.68 (s, 1H), 7.06 (s, 1H), 9.87 (t,  $J = 1.6$  Hz, 1H),  $^{13}\text{C NMR } \delta$  19.3, 20.0, 21.1, 22.2, 26.4, 28.3, 31.9, 49.0, 110.2, 115.4, 120.4, 125.5, 127.0, 128.1, 134.0, 136.6, 203.3; MS (EI)  $m/z$  255 (rel intensity) ( $\text{M}^+$ ); Analysis calculated for  $\text{C}_{17}\text{H}_{21}\text{NO}$ : C, 79.96; H, 8.29; N, 5.49. Found: C, 79.91; H, 8.35; N, 5.41.

**Compound 7o: 2-(8-Chloro-6,9-dimethyl-2,3,4,9-tetrahydro-1H-carbazol-4-yl)acetaldehyde**



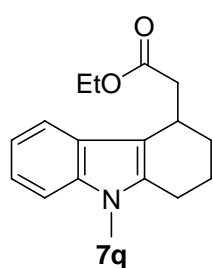
$^1\text{H NMR } \delta$  1.72-1.76 (m, 1H), 1.88-1.96 (m, 3H), 2.37 (s, 1H), 2.61-2.72 (m, 3H), 2.92 (dd,  $J = 3.2, 16.8$  Hz, 1H), 3.56-3.59 (m, 1H), 3.93 (s, 3H), 6.91 (s, 1H), 7.08 (s, 1H), 9.87 (dd,  $J = 1.2, 2.8$  Hz, 1H),  $^{13}\text{C NMR } \delta$  19.0, 20.8, 22.1, 26.2, 28.2, 31.6, 48.8, 110.7, 116.0, 116.1, 123.8, 129.0, 129.1, 130.4, 138.0, 202.6; MS (EI)  $m/z$  277 (rel intensity) ( $\text{M}^+ + 2$ ); Analysis calculated for  $\text{C}_{16}\text{H}_{18}\text{ClNO}$ : C, 69.68; H, 6.58; N, 5.08. Found: C, 69.60; H, 6.51; N, 5.18.

**Compound 7p: 1-(9-Methyl-2,3,4,9-tetrahydro-1H-carbazol-4-yl)propan-2-one**



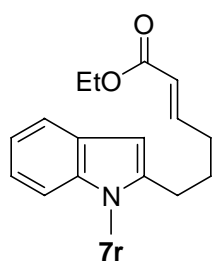
$^1\text{H NMR } \delta$  1.65-1.70 (m, 1H), 1.86-1.93 (m, 3H), 2.18 (s, 1H), 2.56-2.70 (m, 3H), 3.05 (dd,  $J = 3.6, 16.4$  Hz, 1H), 3.58 (s, 3H), 3.60-3.61 (m, 1H), 7.03-7.07 (m, 1H), 7.12-7.16 (m, 1H), 7.25 (d,  $J = 8.4$  Hz, 1H), 7.45 (d,  $J = 7.6$  Hz, 1H),  $^{13}\text{C NMR } \delta$  19.3, 21.9, 27.6, 28.2, 28.8, 30.5, 49.0, 108.6, 111.3, 117.7, 118.6, 120.4, 125.9, 136.0, 136.7, 208.8; MS (EI)  $m/z$  241 (rel intensity) ( $\text{M}^+$ ); Analysis calculated for  $\text{C}_{16}\text{H}_{19}\text{NO}$ : C, 79.63; H, 7.94; N, 5.80. Found: C, 79.68; H, 7.90; N, 5.83.

**Compound 7q: Ethyl 2-(9-methyl-2,3,4,9-tetrahydro-1H-carbazol-4-yl)acetate**



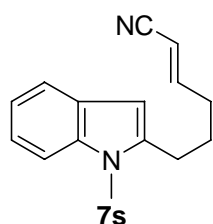
$^1\text{H NMR } \delta$  ( $\text{CDCl}_3$ , 600 Mz) 1.37 (t,  $J = 7.2$  Hz, 3H), 1.76-1.93 (m, 4H), 2.39 (q,  $J = 10.8, 15.0$  Hz, 1H), 2.61-2.73 (m, 2H), 2.61-2.73 (m, 2H), 2.97 (dd,  $J = 3.6, 15.0$  Hz, 1H), 3.55 (q,  $J = 4.2, 10.2$  Hz, 1H), 3.60 (s, 3H), 4.18 (q,  $J = 1.8, 7.2$  Hz, 2H), 7.06 (t,  $J = 7.8$  Hz, 1H), 7.15 (t,  $J = 7.2$  Hz, 1H), 7.25 (d,  $J = 8.4$  Hz, 1H), 7.53 (d,  $J = 4.8$  Hz, 1H),  $^{13}\text{C NMR } \delta$  ( $\text{CDCl}_3$ , 150 Mz) 14.2, 19.1, 21.9, 28.0, 28.7, 39.9, 60.1, 108.5, 111.0, 117.8, 118.5, 120.4, 126.0, 135.9, 136.6, 173.0; MS (EI)  $m/z$  271 (rel intensity) ( $\text{M}^+$ ); Analysis calculated for  $\text{C}_{17}\text{H}_{21}\text{NO}_2$ : C, 75.25; H, 7.80; N, 5.16. Found: C, 75.27; H, 7.82; N, 5.15.

**Compound 7r: (E)-Ethyl 6-(1-methyl-1H-indol-2-yl)hex-2-enoate**



$^1\text{H NMR } \delta$  1.29 (t,  $J = 6.8$  Hz, 3H), 1.84-1.96 (m, 2H), 2.31-2.37 (m, 2H), 2.76 (t,  $J = 7.6$  Hz, 2H), 3.65 (s, 3H), 4.19 (q,  $J = 7.2, 14.4$  Hz, 2H), 5.84-5.89 (m, 1H), 6.25 (s, 1H), 6.95-7.03 (m, 1H), 7.04-7.08 (m, 1H), 7.13-7.17 (m, 1H), 7.26 (d,  $J = 8.4$  Hz, 1H), 7.53 (d,  $J = 7.6$  Hz, 1H),  $^{13}\text{C NMR } \delta$  14.4, 26.0, 26.6, 29.3, 31.4, 60.1, 98.8, 108.6, 119.1, 119.6, 120.5, 121.8, 127.6, 137.2, 140.0, 148.1, 166.4; MS (EI)  $m/z$  271 (rel intensity) ( $\text{M}^+$ ); Analysis calculated for  $\text{C}_{17}\text{H}_{21}\text{NO}_2$ : C, 75.25; H, 7.80; N, 5.16. Found: C, 75.29; H, 7.84; N, 5.10.

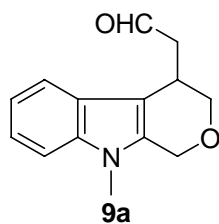
**Compound 7s: (E)-6-(1-methyl-1H-indol-2-yl)hex-2-enitrile**



$^1\text{H NMR } \delta$  1.86-1.94 (m, 2H), 2.53-2.59 (m, 2H), 2.78 (t,  $J = 7.6$  Hz, 2H), 3.65 (s, 3H), 5.33 (d,  $J = 11.2$  Hz, 2H), 6.25 (s, 1H), 6.45-6.52 (m, 1H), 7.04-7.08 (m, 1H), 7.13-7.17 (m, 1H), 7.26 (d,  $J = 8.4$  Hz, 1H), 7.53 (d,  $J = 7.6$  Hz, 1H),  $^{13}\text{C NMR } \delta$  26.1, 27.1, 29.4, 31.4, 99.0, 100.1, 108.7, 115.8, 119.3, 119.7, 120.7, 127.6, 137.3, 139.7, 154.1; MS (EI)

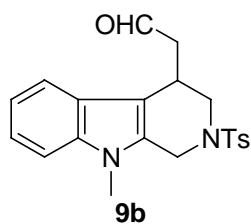
$m/z$  243 (rel intensity) ( $M^+$ ); Analysis calculated for  $C_{15}H_{16}N_2$ : C, 80.32; H, 7.19; N, 12.49. Found: C, 80.35; H, 7.15; N, 12.51.

**Compound 9a: 2-(9-Methyl-1,3,4,9-tetrahydropyrano[3,4-b]indol-4-yl)acetaldehyde**



$^1H$  NMR  $\delta$  2.93 (dd,  $J = 1.2, 6.8$  Hz, 2H), 3.50-3.56 (m, 2H), 3.58 (s, 3H), 3.88 (dd,  $J = 3.6, 11.2$  Hz, 1H), 4.00 (dd,  $J = 2.0, 11.2$  Hz, 1H), 7.11 (t,  $J = 8.0$  Hz, 1H), 7.21 (t,  $J = 8.0$  Hz, 1H), 7.30 (d,  $J = 8.0$  Hz, 1H), 7.48 (d,  $J = 7.6$  Hz, 1H), 9.87 (t,  $J = 1.6$  Hz, 1H),  $^{13}C$  NMR  $\delta$  27.7, 29.3, 47.4, 63.0, 69.5, 108.4, 108.9, 117.9, 119.2, 121.2, 125.5, 133.1, 136.9, 202.1; MS (EI)  $m/z$  229 (rel intensity) ( $M^+$ ); Analysis calculated for  $C_{14}H_{15}NO_2$ : C, 73.34; H, 6.59; N, 6.11. Found: C, 73.38; H, 6.50; N, 6.19.

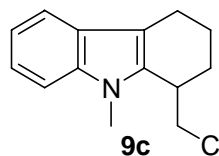
**Compound 9b: 2-(9-Methyl-2-tosyl-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indol-4-yl)acetaldehyde**



$^1H$  NMR  $\delta$  2.43 (s, 1H), 2.83-2.91 (m, 2H), 3.03 (q,  $J = 9.6, 18.8$  Hz, 1H), 3.59 (s, 3H), 3.65-3.67 (m, 1H), 3.82-3.88 (m, 2H), 4.75 (d,  $J = 14.0$  Hz, 1H), 7.01 (t,  $J = 7.4$  Hz, 1H), 7.19 (t,  $J = 7.0$  Hz, 1H), 7.26 (d,  $J = 8.0$  Hz, 1H), 7.35 (d,  $J = 8.0$  Hz, 2H), 7.41 (d,  $J = 7.6$  Hz, 1H), 7.74 (d,  $J = 8.0$  Hz, 2H), 9.85 (s, 1H),  $^{13}C$  NMR  $\delta$  21.4, 26.7, 29.3, 42.9, 47.3, 48.4, 109.0, 109.6, 117.9, 119.5, 121.6, 125.0, 127.4, 129.8, 130.3, 133.3, 137.1, 143.9, 201.5; MS (EI)  $m/z$  382 (rel intensity) ( $M^+$ ); Analysis calculated

for  $C_{21}H_{22}N_2O_3S$ : C, 65.95; H, 5.80; N, 7.32; S, 8.38. Found: C, 65.90; H, 5.85; N, 7.36; S, 8.40.

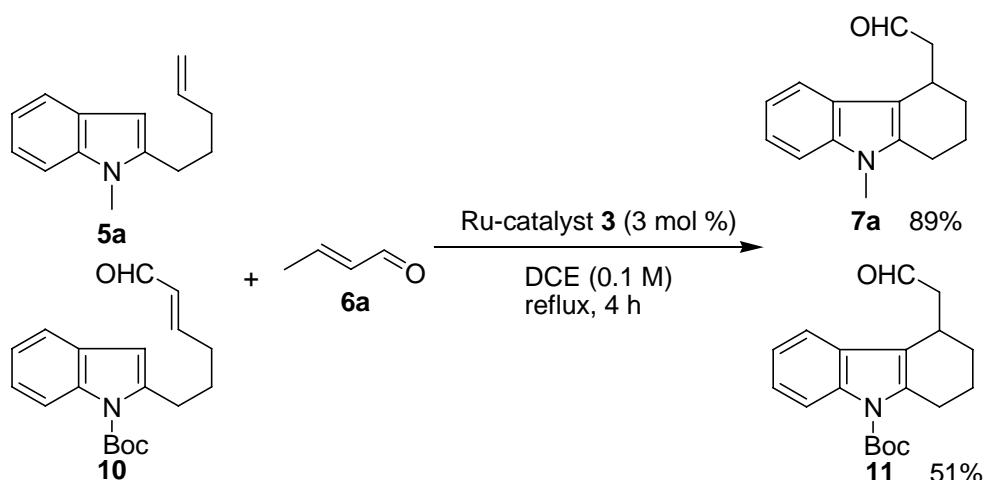
**Compound 9c: 2-(9-Methyl-2,3,4,9-tetrahydro-1H-carbazol-1-yl)acetaldehyde**



$^1H$  NMR  $\delta$  ( $CDCl_3$ , 600 Mz) 1.76-1.81 (m, 1H), 1.86-1.98 (m, 3H), 2.60-2.70 (m, 2H), 2.80-2.86 (m, 2H), 3.61 (s, 3H), 3.59-3.63 (m, 1H), 7.08 (t,  $J = 7.8$  Hz, 1H), 7.19 (t,  $J = 7.2$  Hz, 1H), 7.26 (d,  $J = 8.4$  Hz, 1H), 7.47 (d,  $J = 7.8$  Hz, 1H), 9.85 (s, 1H),  $^{13}C$  NMR  $\delta$  ( $CDCl_3$ , 150 Mz) 18.2, 20.6, 25.2, 28.0, 29.1, 47.9, 108.5, 109.8,

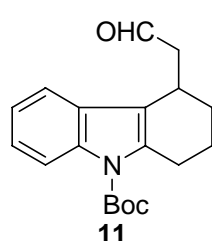
117.9, 118.7, 121.0, 126.6, 136.3, 136.9, 200.8; MS (EI)  $m/z$  227 (rel intensity) ( $M^+$ ); Analysis calculated for  $C_{15}H_{17}NO$ : C, 79.26; H, 7.54; N, 6.16. Found: C, 79.23; H, 7.56; N, 6.18.

### Initial experiment about mechanism investigation



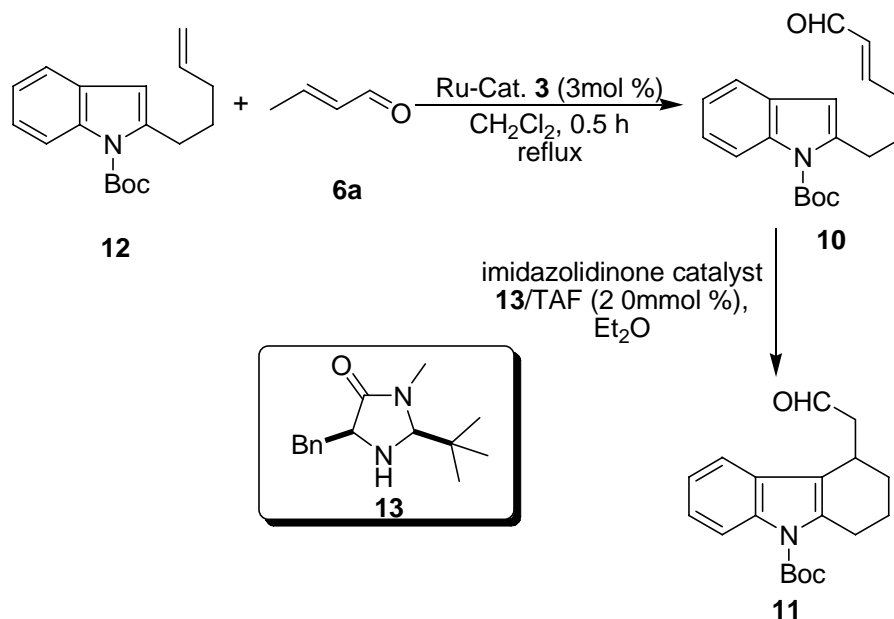
To a mixture of alkenyl indole **5a** (0.30 mmol), indolyl aldehyde **10** (0.30 mmol), crotonaldehyde **6a** (1.5 mmol), and DCE (dichloroethane) (3 mL), Ru-Catalyst **3** (0.009 mmol) was added. The reaction mixture was then stirred under boiling DCE. Upon the completion of reaction monitored by TLC, the solvent was removed in vacuo to give pure cyclization product **7a** and **11** respectively, through column chromatography on silica gel (hexane/ ethyl acetate (10:1-5:1)).

#### Compound **11**: *tert*-Butyl 4-(2-oxoethyl)-1,2,3,4-tetrahydrocarbazole-9-carboxylate



$^1\text{H}$  NMR  $\delta$  1.66 (s, 9H), 1.69-1.96 (m, 4H), 2.64-2.71 (m, 1H), 2.85-2.96 (m, 2H), 3.06-3.13 (m, 1H), 3.59 (d,  $J = 4.0$  Hz, 1H), 7.18-7.26 (m, 2H), 7.38 (d,  $J = 6.8$  Hz, 1H), 8.14 (d,  $J = 7.6$  Hz, 1H), 9.87 (d,  $J = 1.2$  Hz, 1H),  $^{13}\text{C}$  NMR  $\delta$  19.3, 25.9, 26.0, 27.3, 28.1, 48.2, 83.4, 115.5, 117.4, 117.8, 122.4, 123.4, 128.3, 135.9, 136.4, 150.4, 202.0; MS (EI)  $m/z$  313 (rel intensity) ( $\text{M}^+$ ); Analysis calculated for  $\text{C}_{19}\text{H}_{23}\text{NO}_3$ : C, 72.82; H, 7.40; N, 4.47. Found: C, 72.92; H, 7.48; N, 4.39.

## Initial study on asymmetric Tandem Cross Metathesis/Intramolecular Hydroarylation Sequence



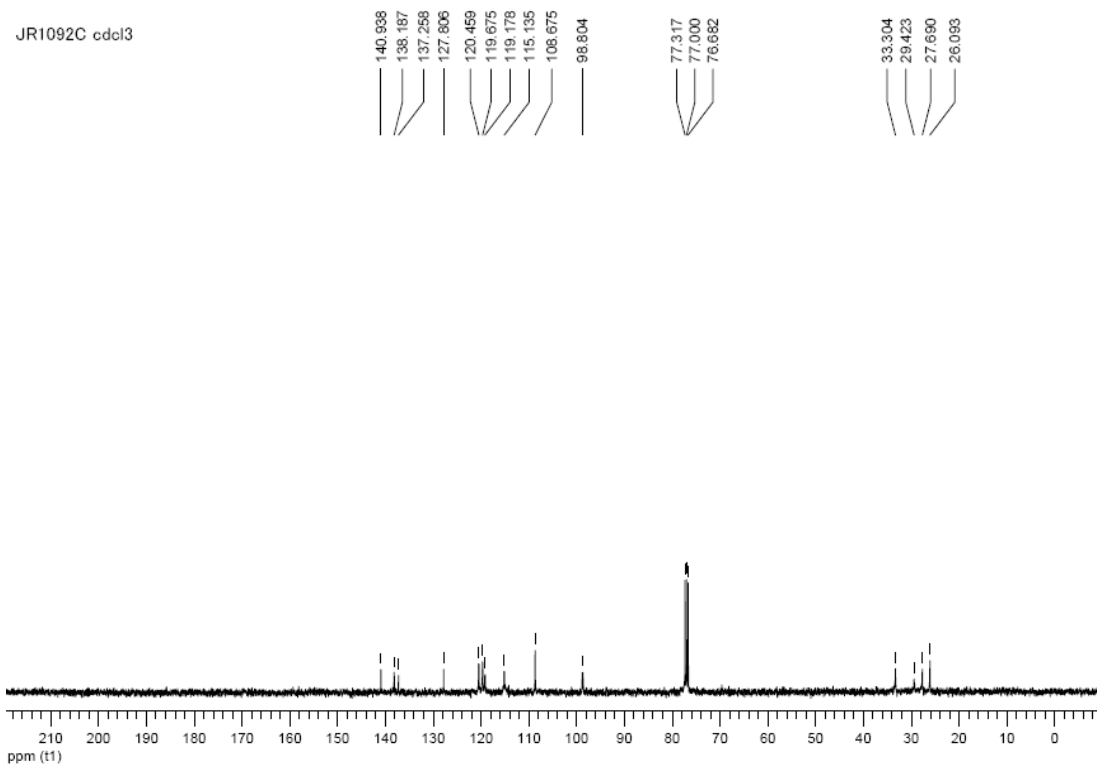
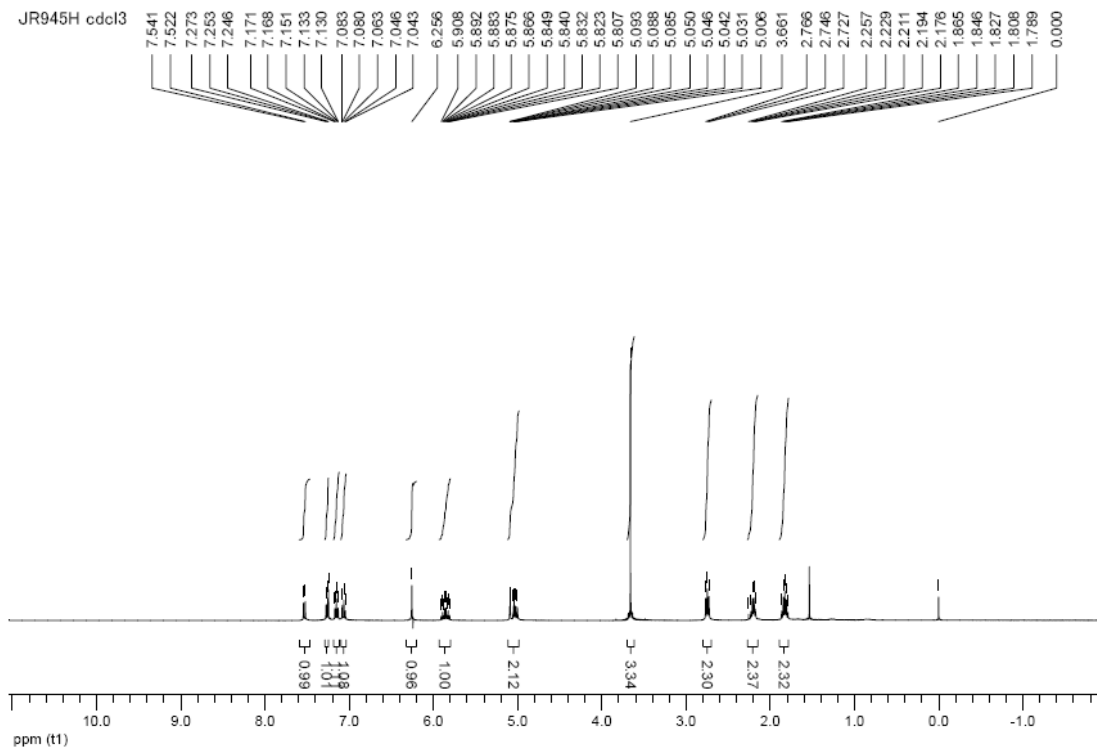
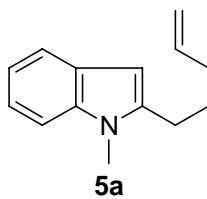
To a mixture of alkenyl indole **12** (0.30 mmol), crotonaldehyde **6a** (1.5 mmol), and DME (dichloromethane) (3 mL), Ru-Catalyst **3** (0.009 mmol) was added. The reaction mixture was then stirred under boiling DME for 0.5 h. Upon the completion of reaction monitored by TLC, the solvent was removed. Then, Et<sub>2</sub>O (3 mL) was added and the mixture was cooled to -40 °C. And 20 mol % of imidazolidinone catalyst and 20 mol % of TFA were added. Upon the completion of reaction, the cyclization product **11** was obtained through column chromatography on silica gel (hexane/ ethyl acetate (10:1-5:1)).

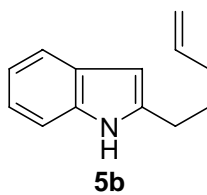
The enantioselectivity was determined by subjecting approximately 10 mg of the title compound to an excess of NaBH<sub>4</sub> and 1 mL of methanol. After 15 min, the solution was treated with saturated aqueous NaHCO<sub>3</sub>, and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was separated, filtered through a silica gel plug and subjected to chiral HPLC analysis. The enantiomeric ratio was determined by HPLC analysis of the alcohol, obtained by NaBH<sub>4</sub> reduction of the aldehyde; Chiralpak AD-H, isopropanol/hexanes = 10:90, 254 nm, 1 mL/min;  $t_{\text{minor}} = 7.8$  min,  $t_{\text{major}} = 9.8$  min. ee = 82%

## References

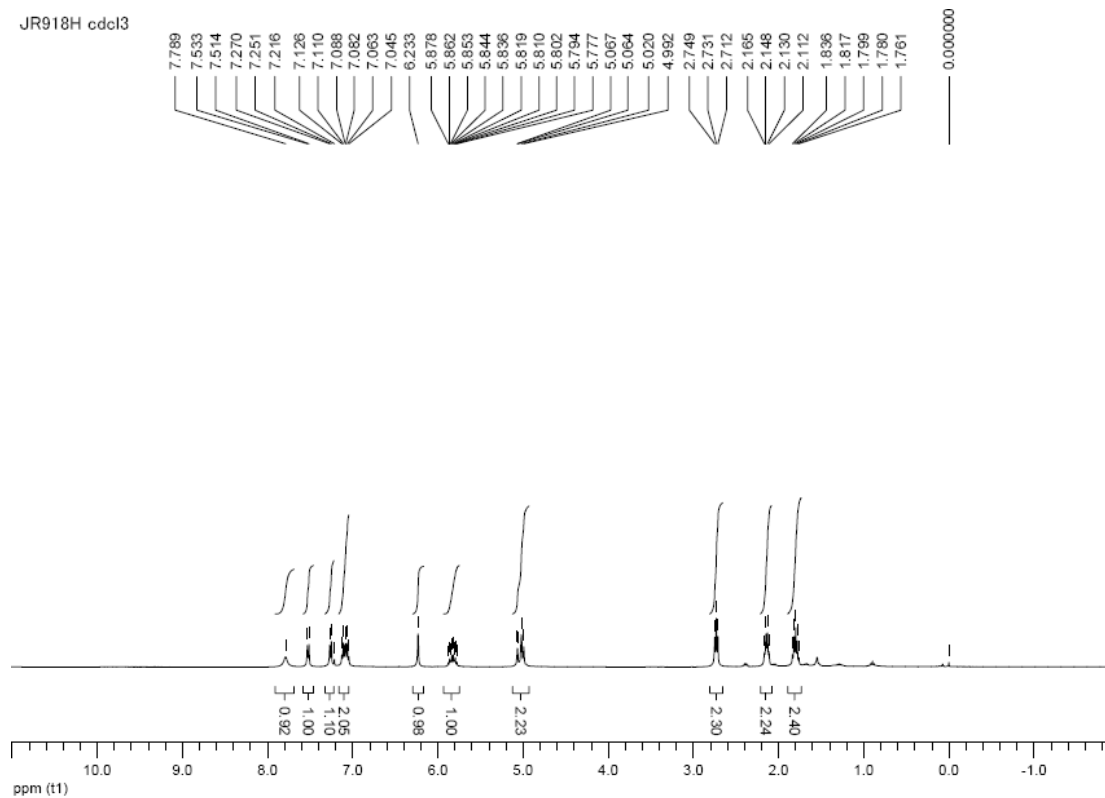
- 1) A. B. III Smith, M. Visnick, J. N. Haseltine, P. A. Sprengeler, *Tetrahedron* **1986**, *42*, 2957.
- 2) W. J. Houlihan, V. A. Parrino, Y. Uike, *J. Org. Chem.* **1981**, *46*, 4511.
- 3) Z. Zhang, C. Liu, R. E. Kinder, X. Han, H. Qian, R. A. Widenhofer, *J. Am. Chem. Soc.* **2006**, *128*, 9066.
- 4) C. Liu, X. Han, X. Wang, R. A. Widenhofer, *J. Am. Chem. Soc.* **2004**, *126*, 3700.
- 5) C.-F. Li, H. Liu, J. Liao, Y.-J. Cao, X.-P. Liu, W.-J. Xiao, *Org. Lett.* **2007**, *9*, 1847.
- 6) S. W. Youn, S. J. Pastine, D. Sames, *Org. Lett.* **2005**, *6*, 581.

# NMR Spectra

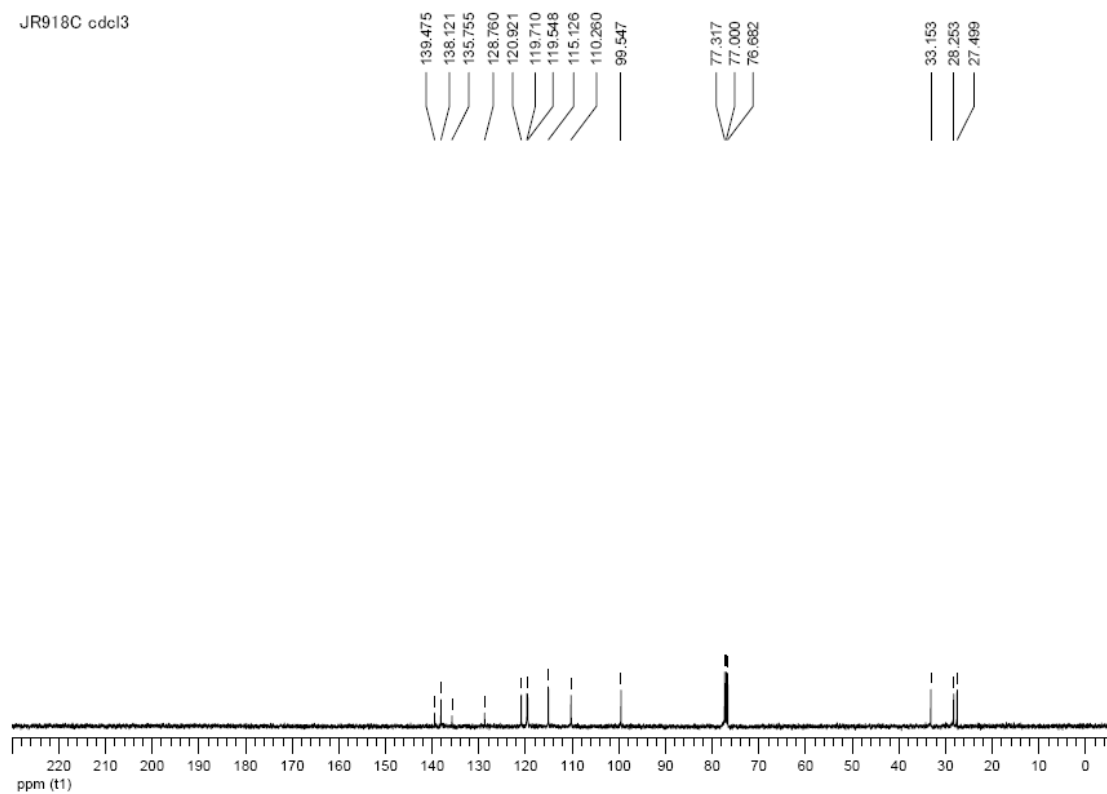


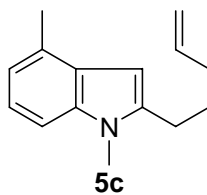


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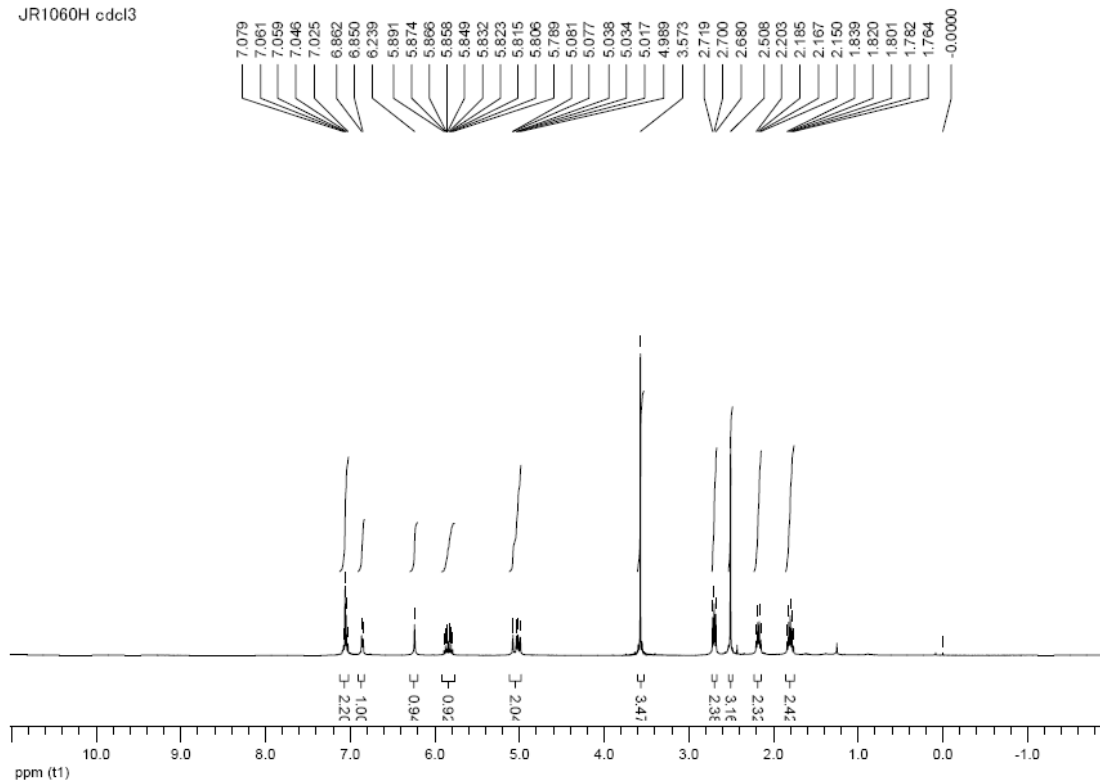


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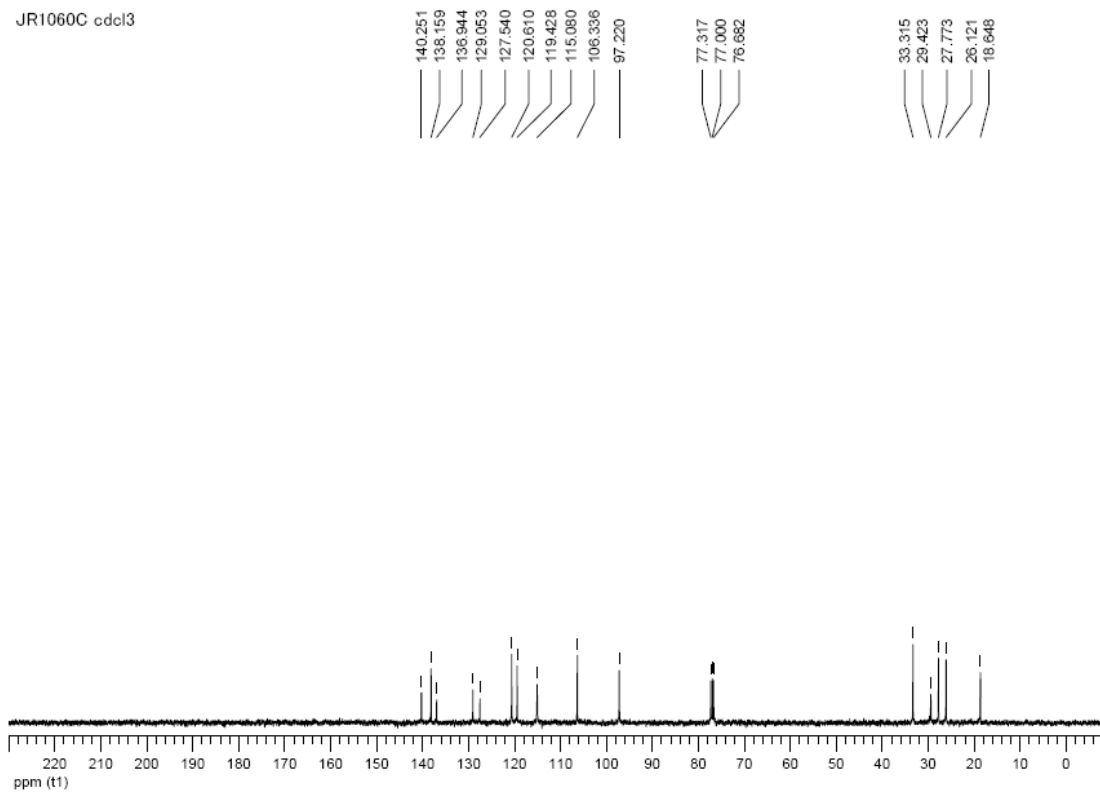


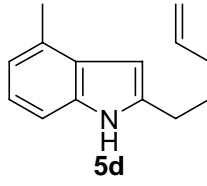


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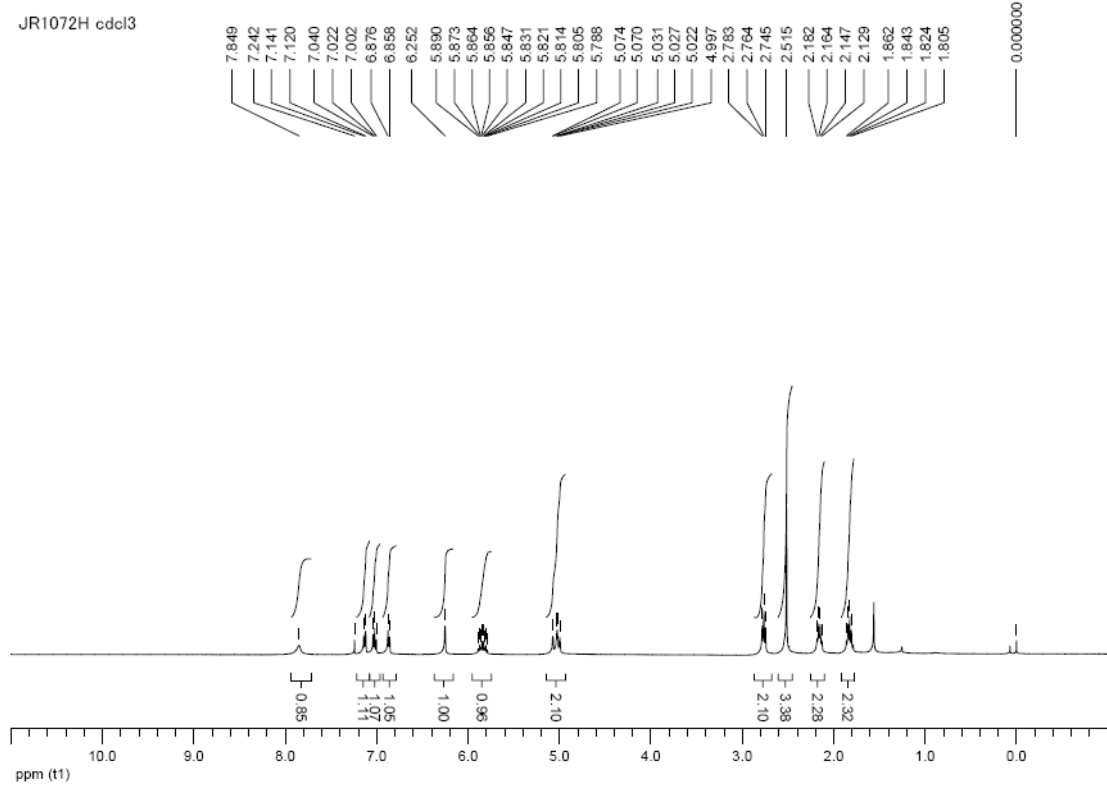


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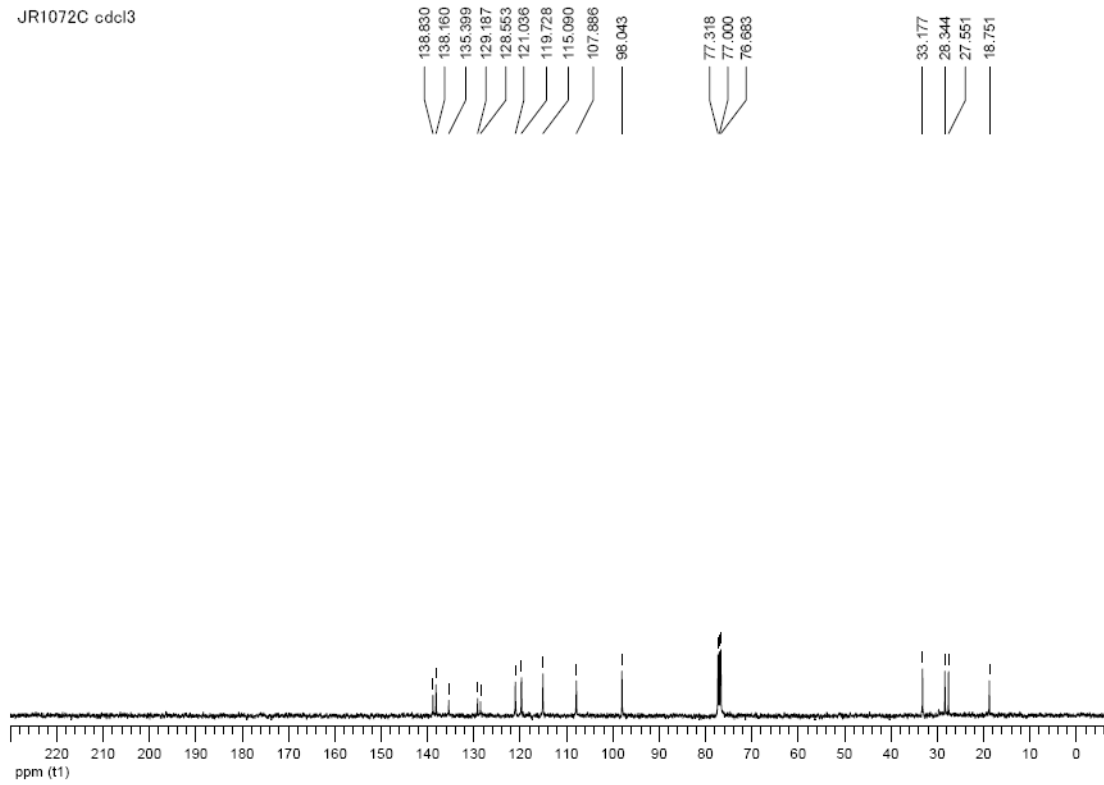




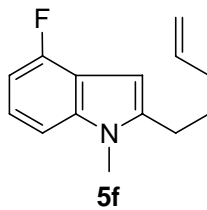
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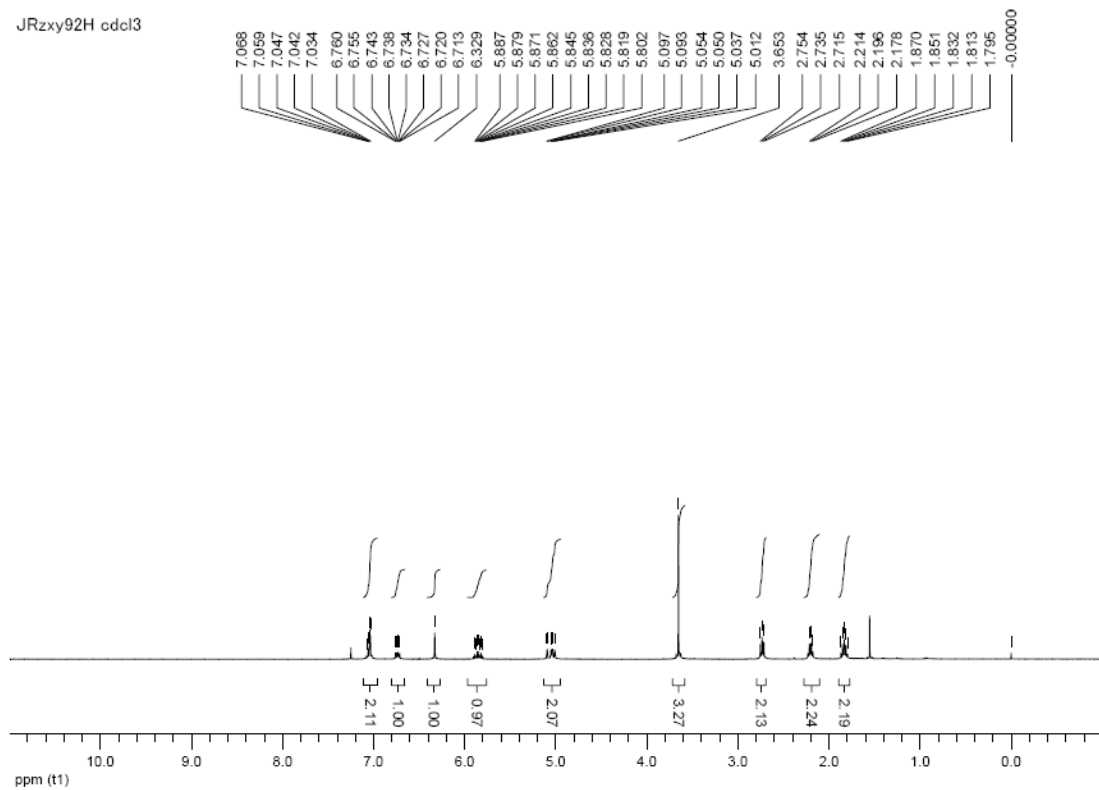
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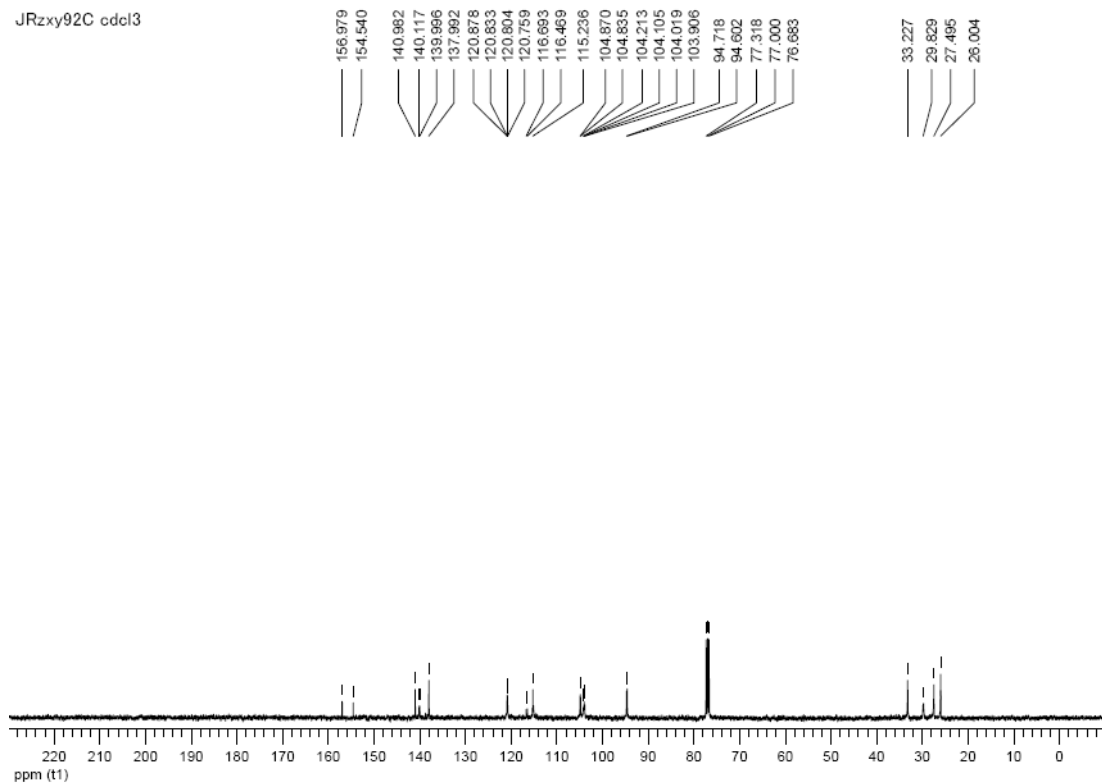


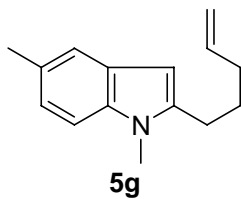


JRzxy92H cdcl3

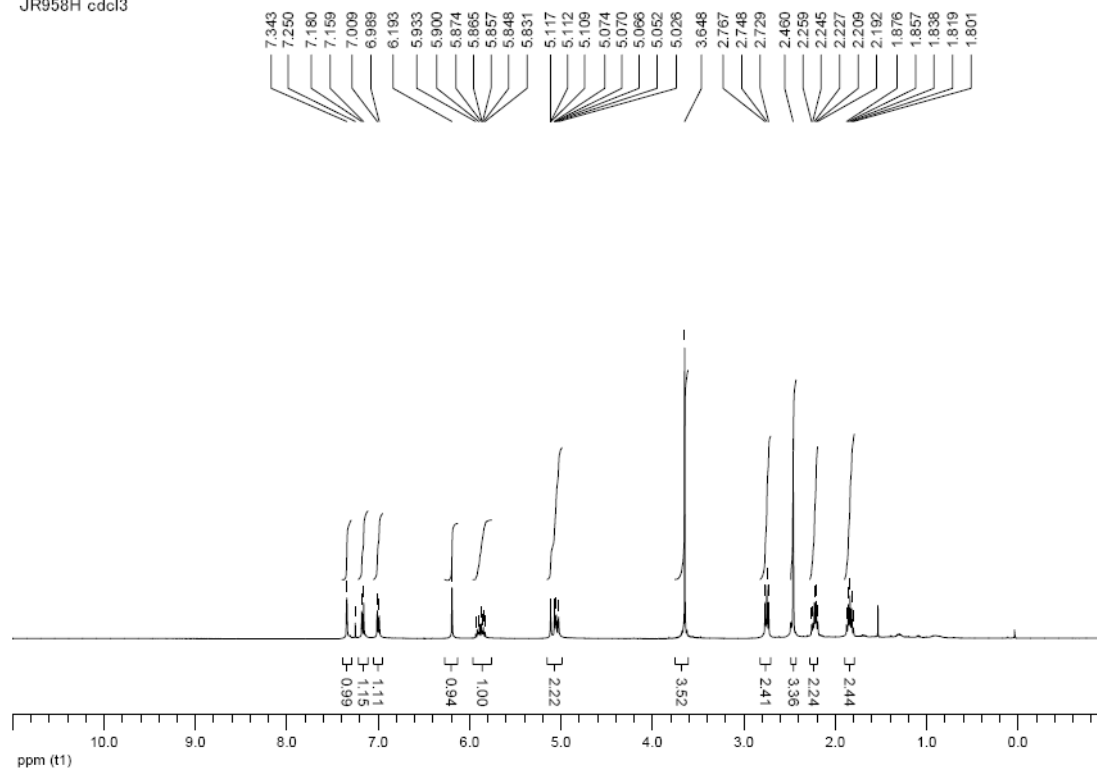


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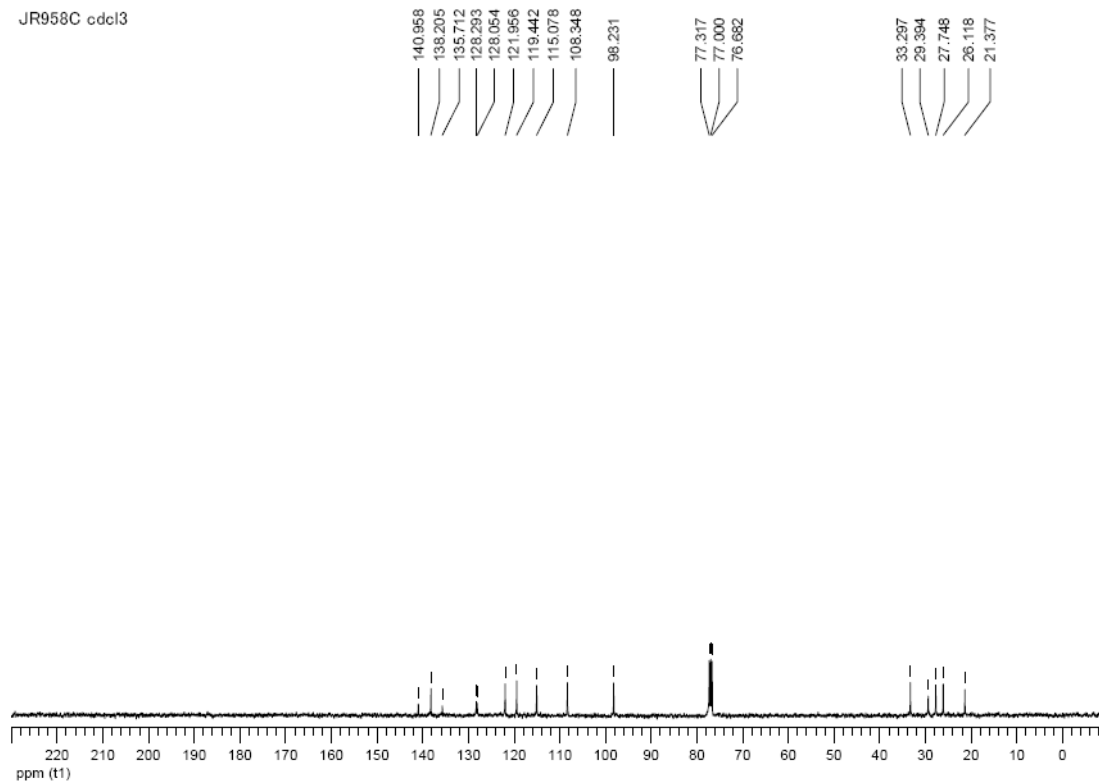


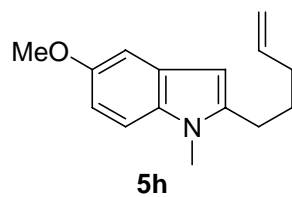


JR958H cdcl3

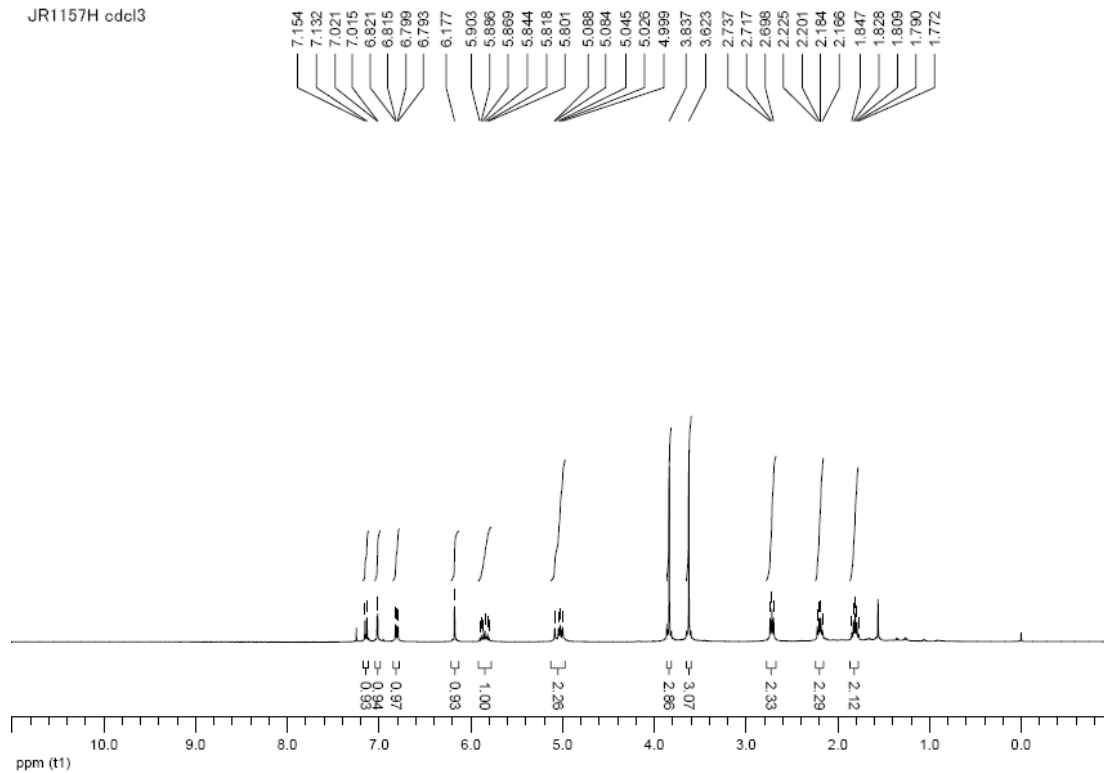


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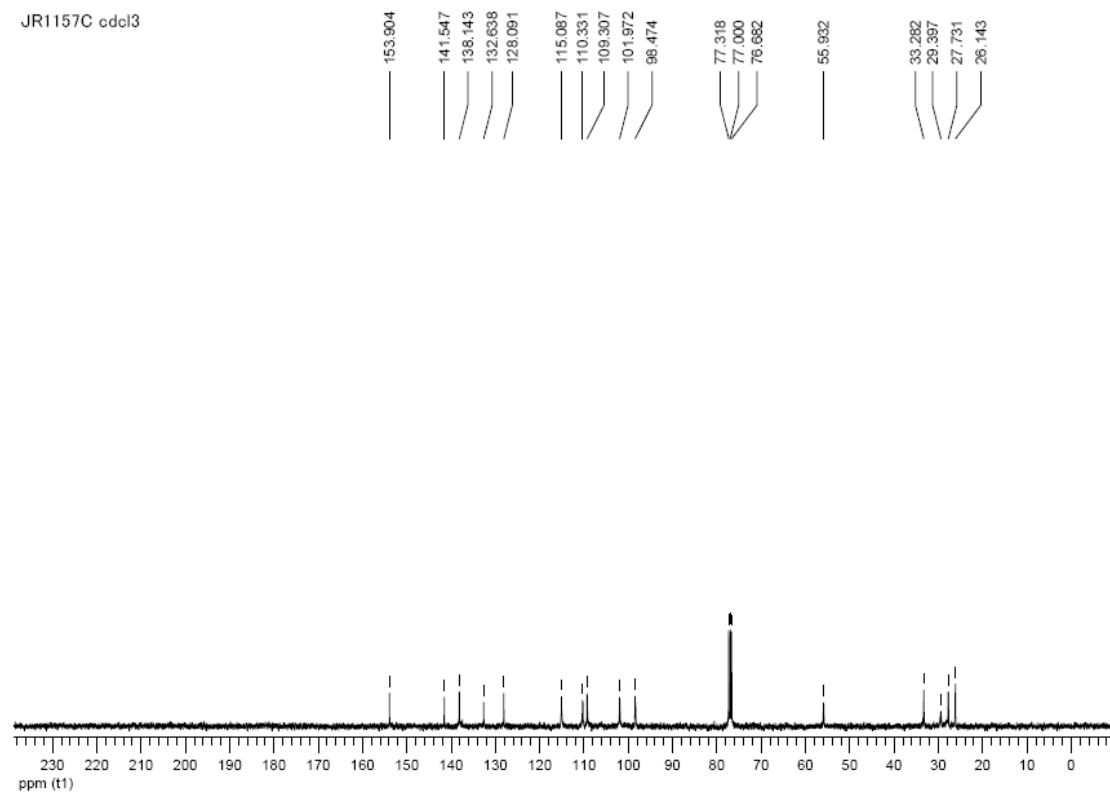


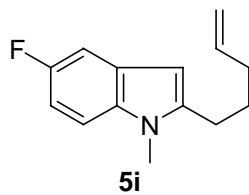


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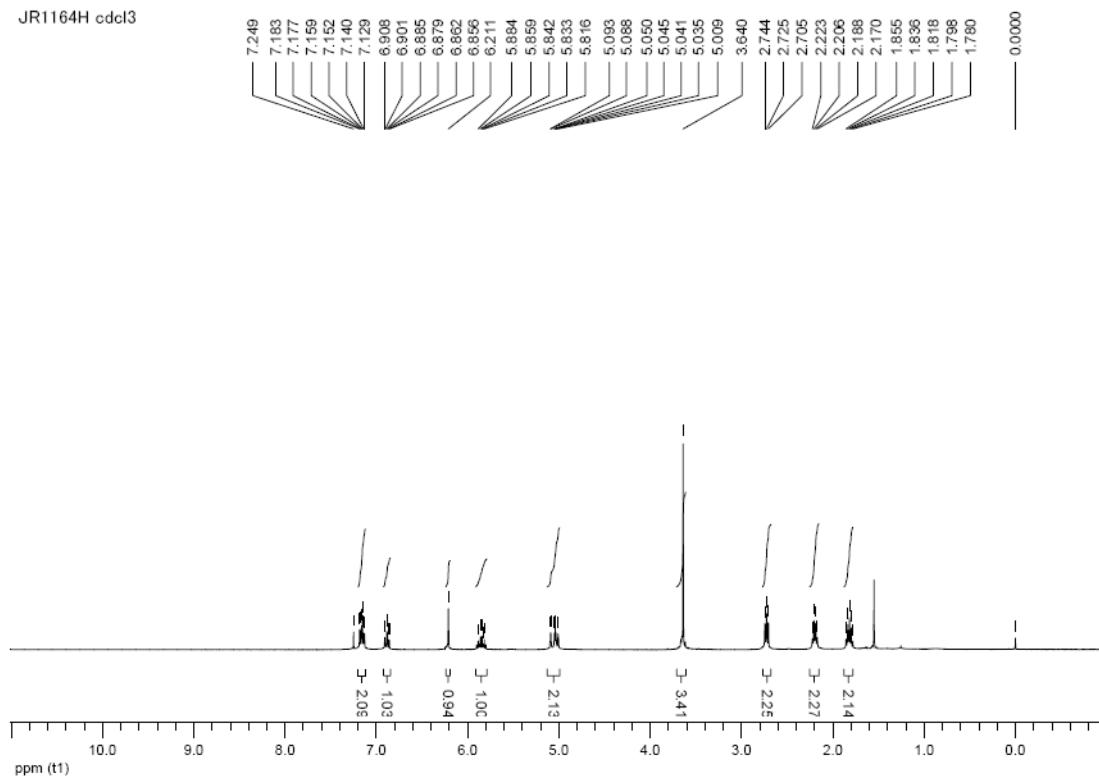


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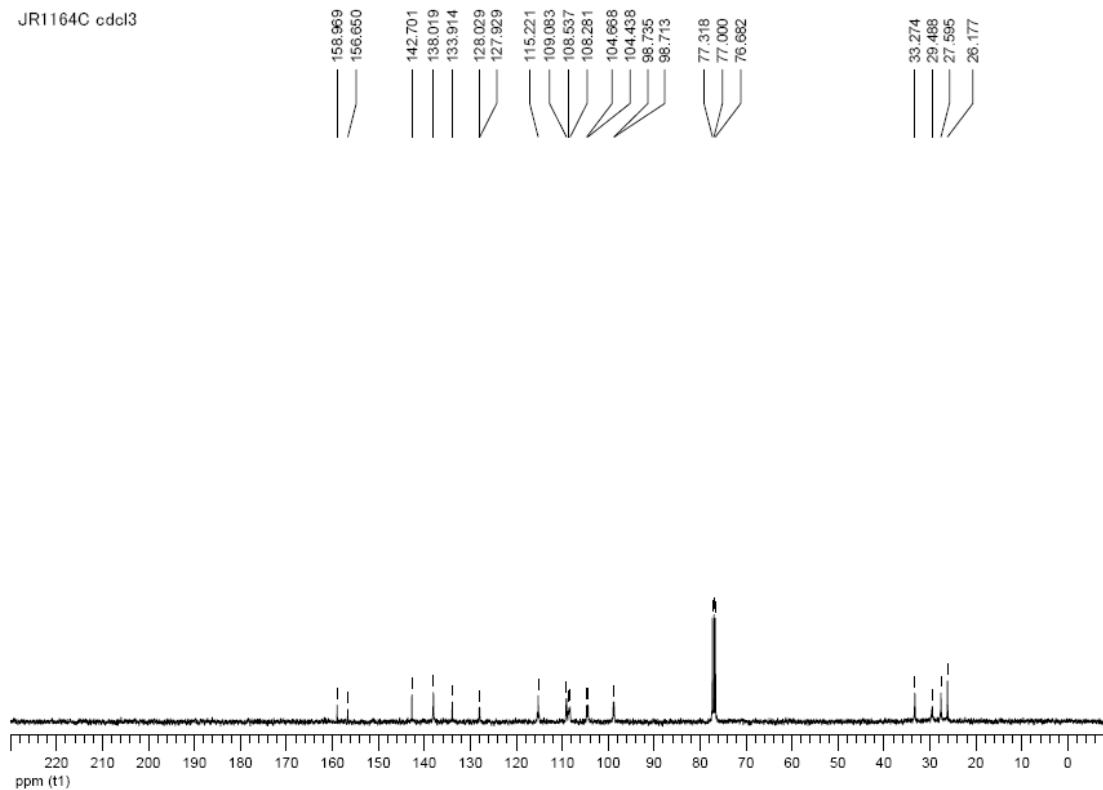


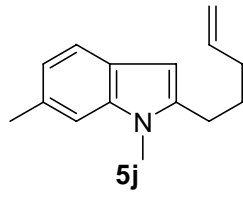


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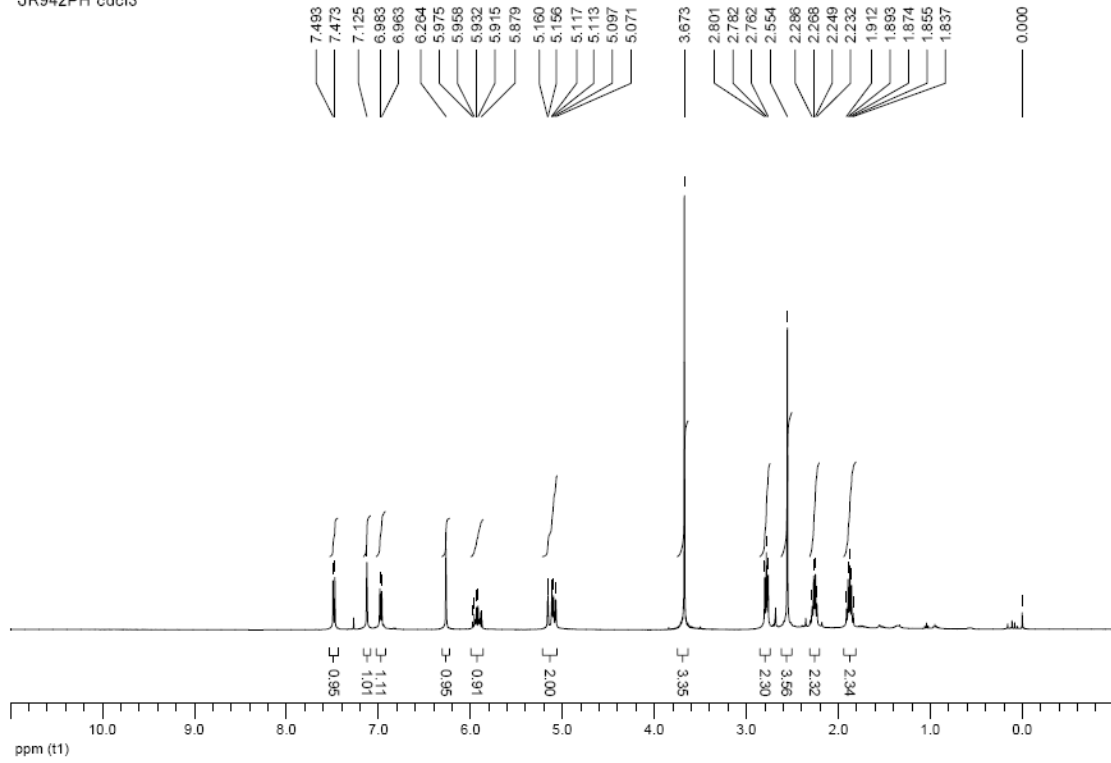


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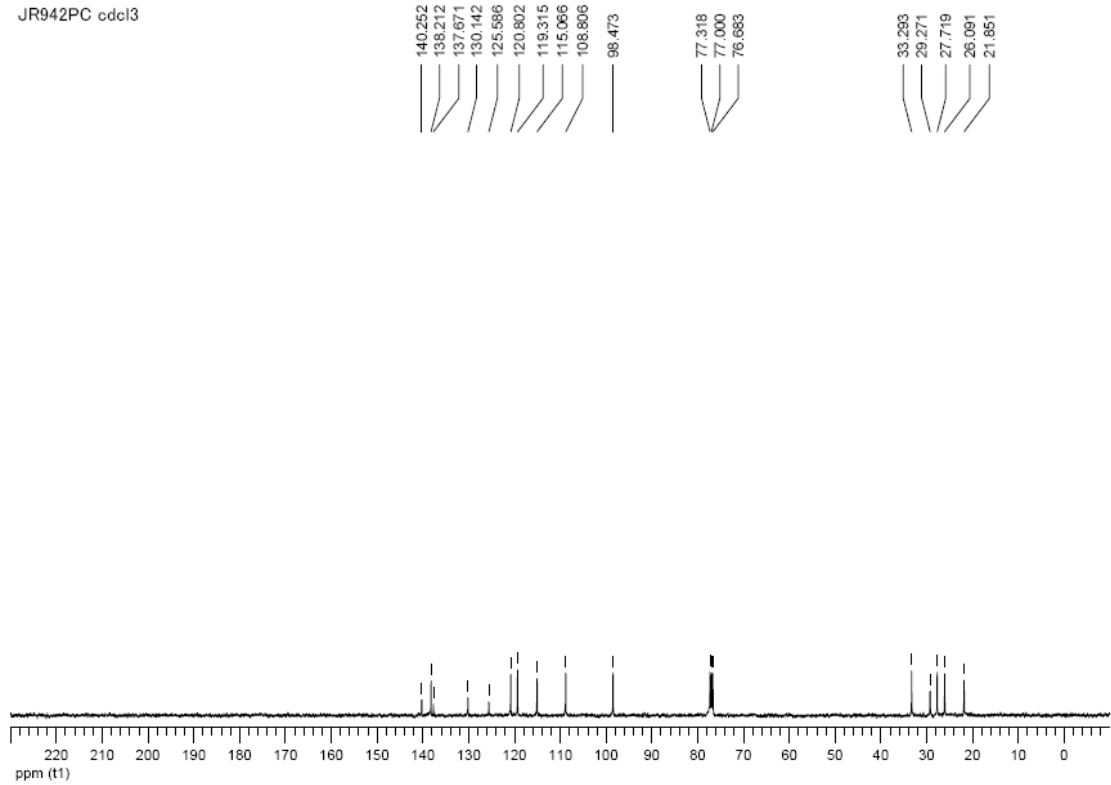


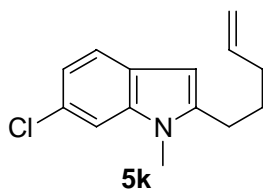


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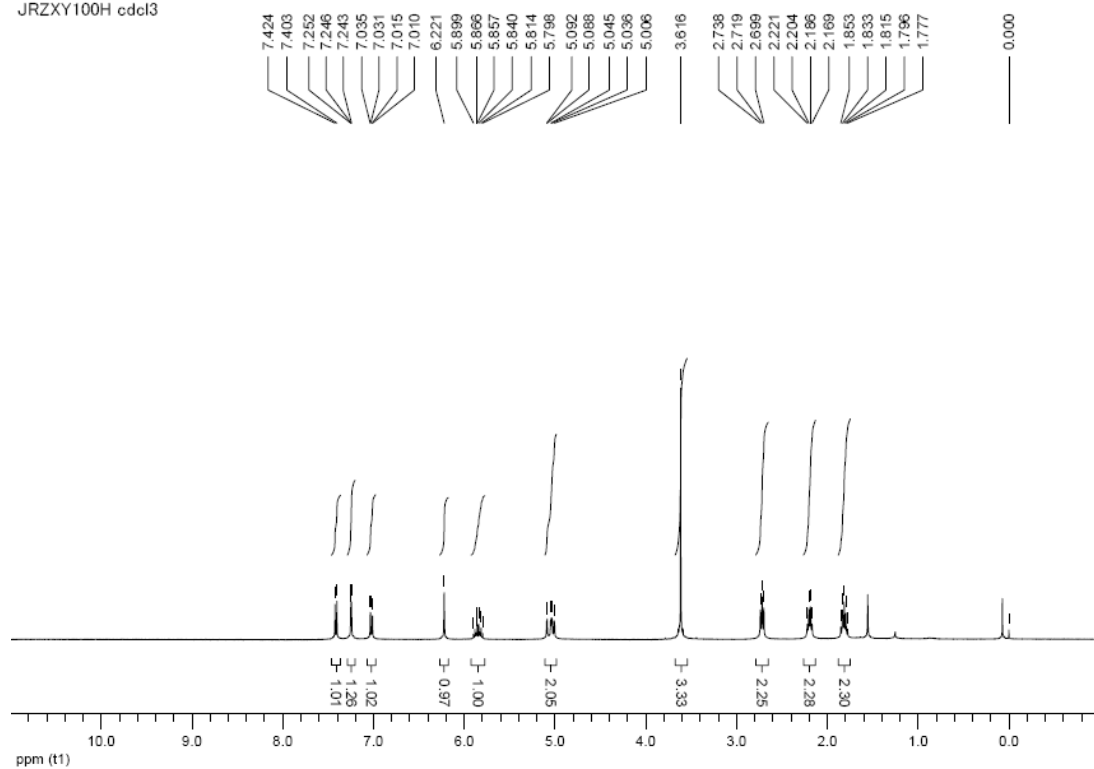


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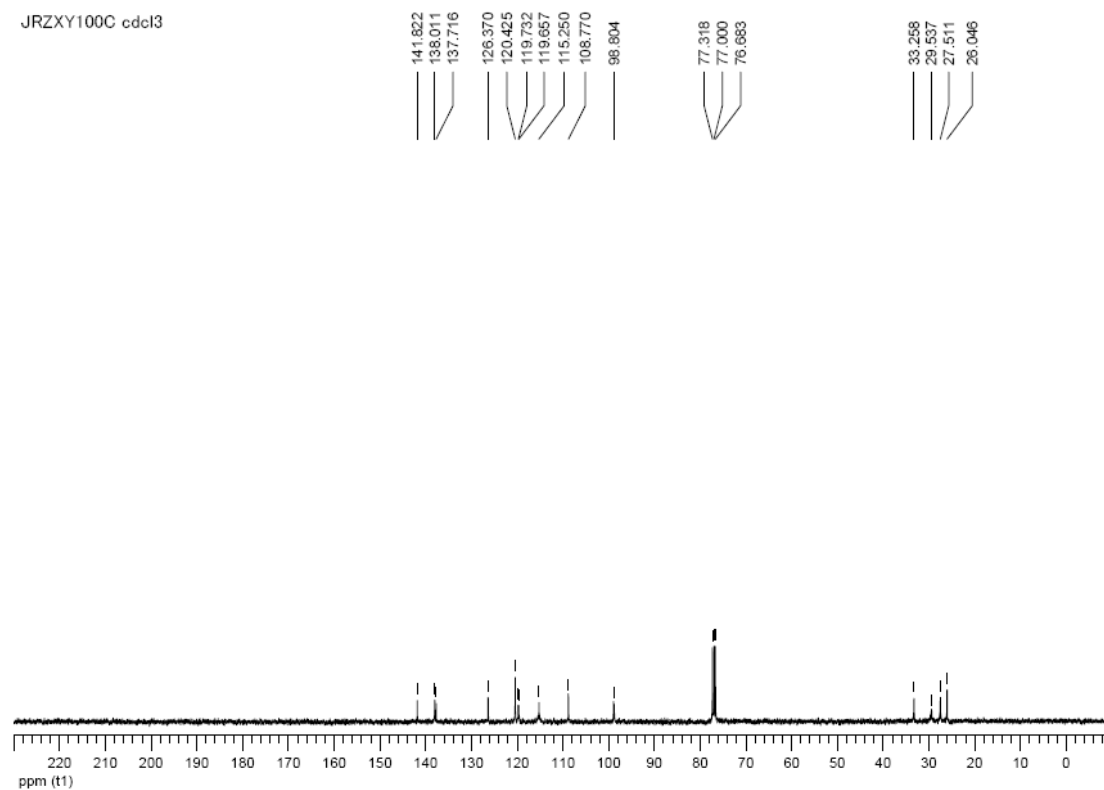


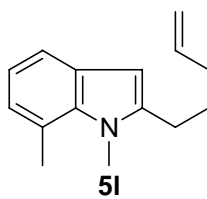


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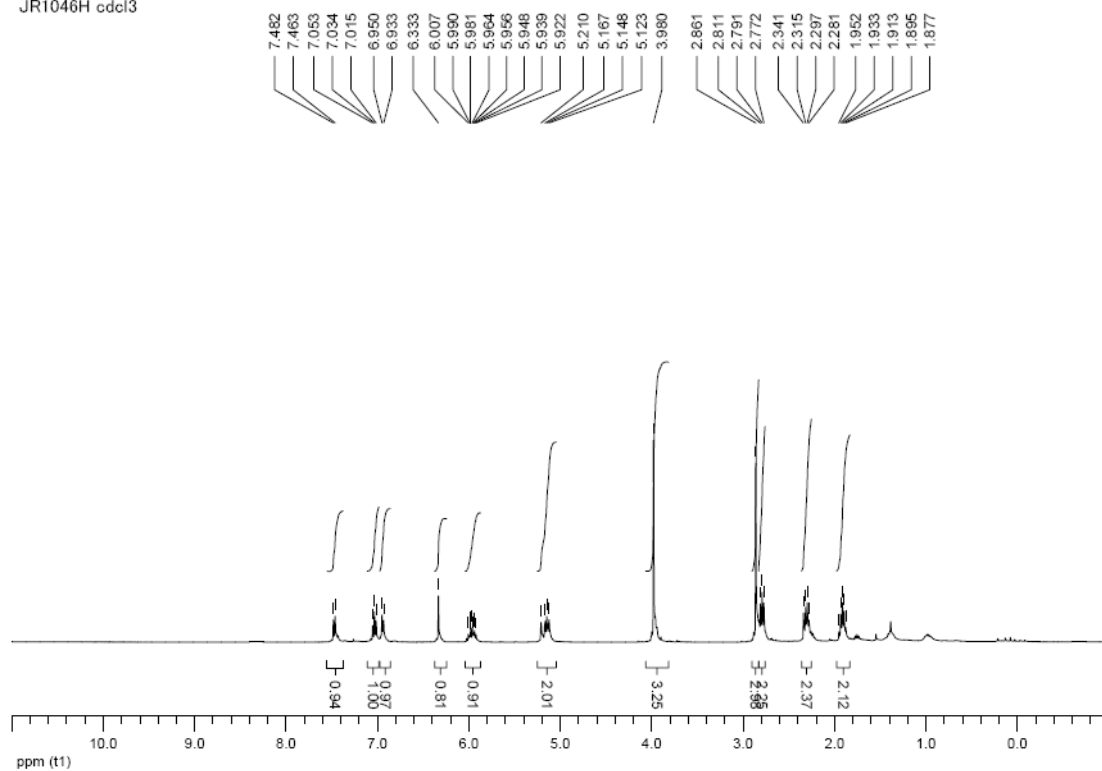


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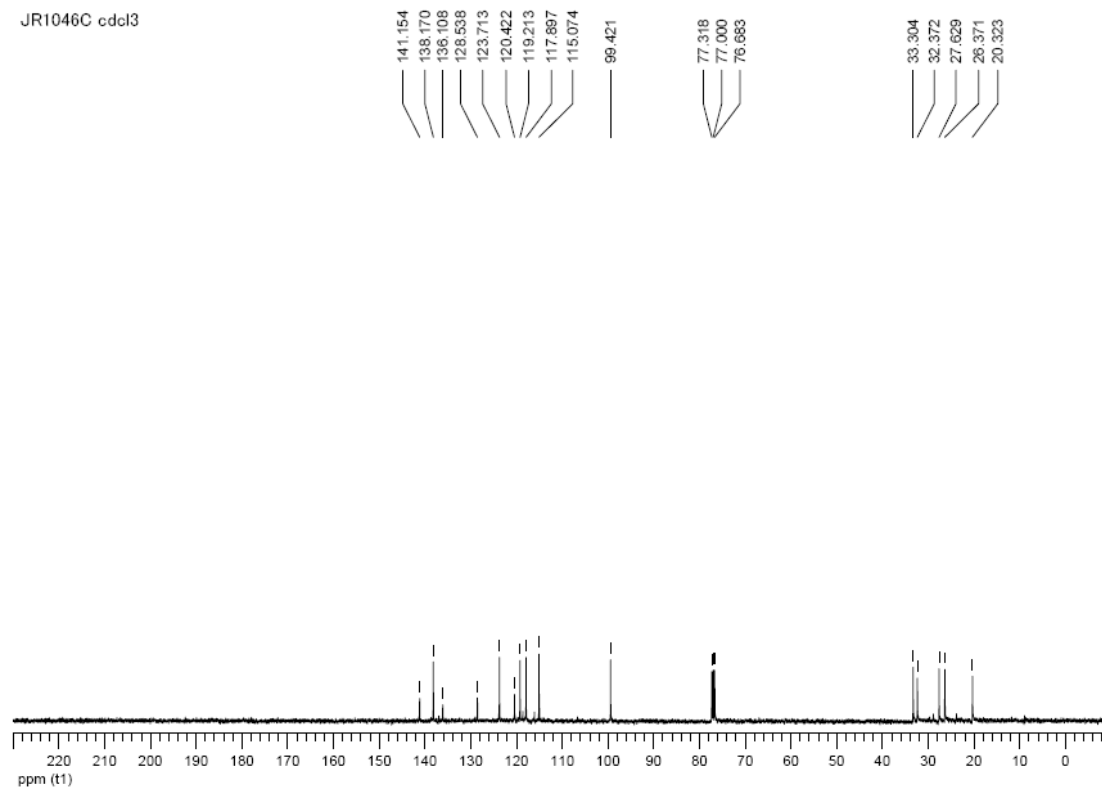


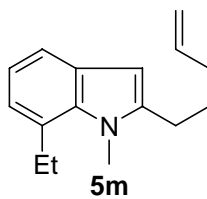


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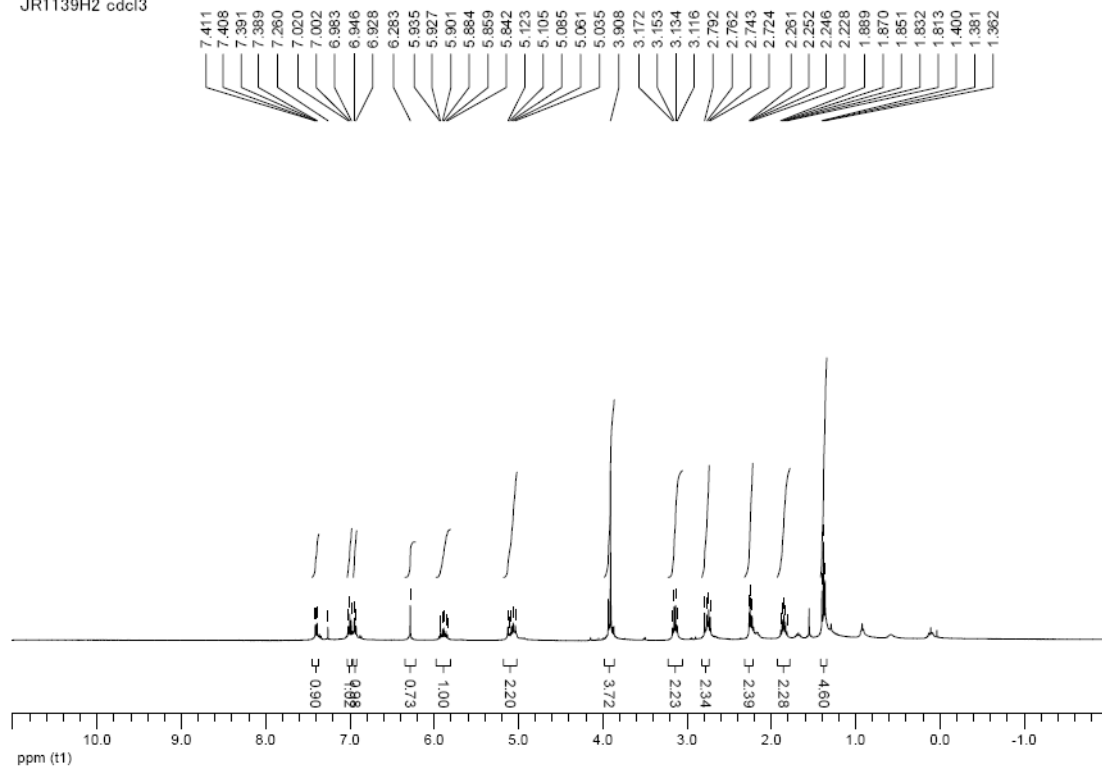


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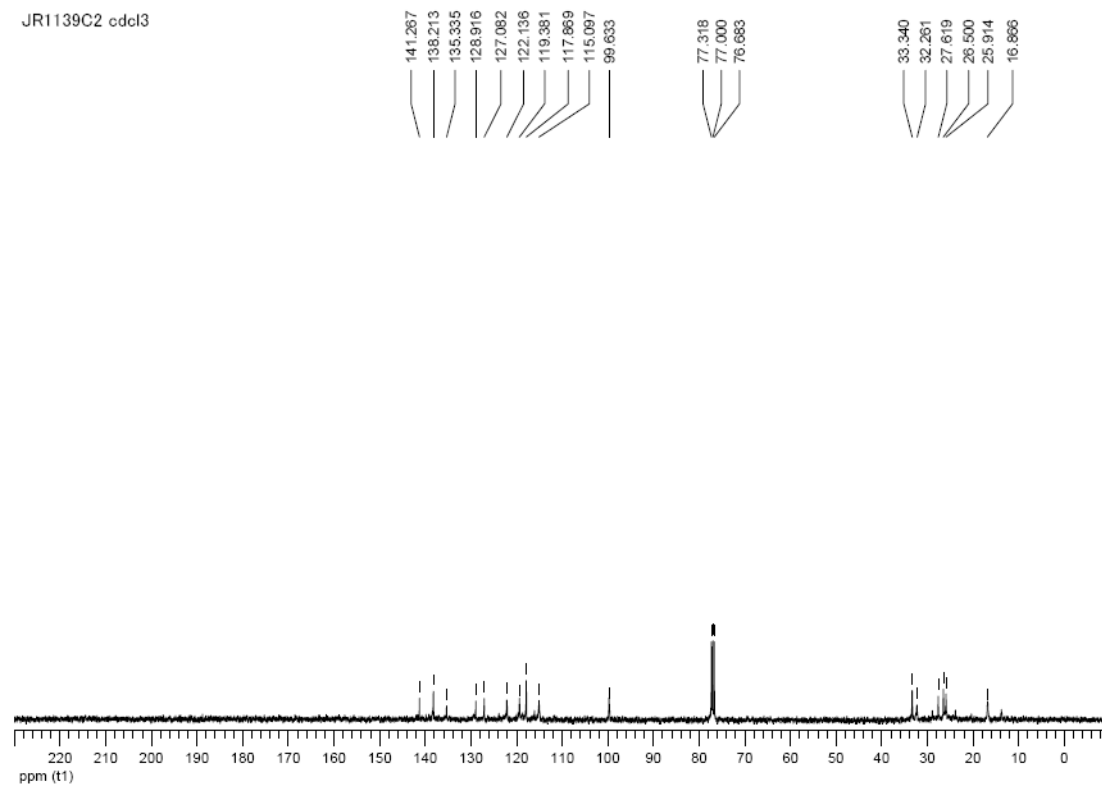


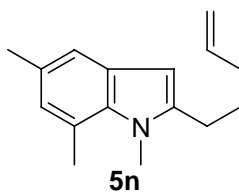


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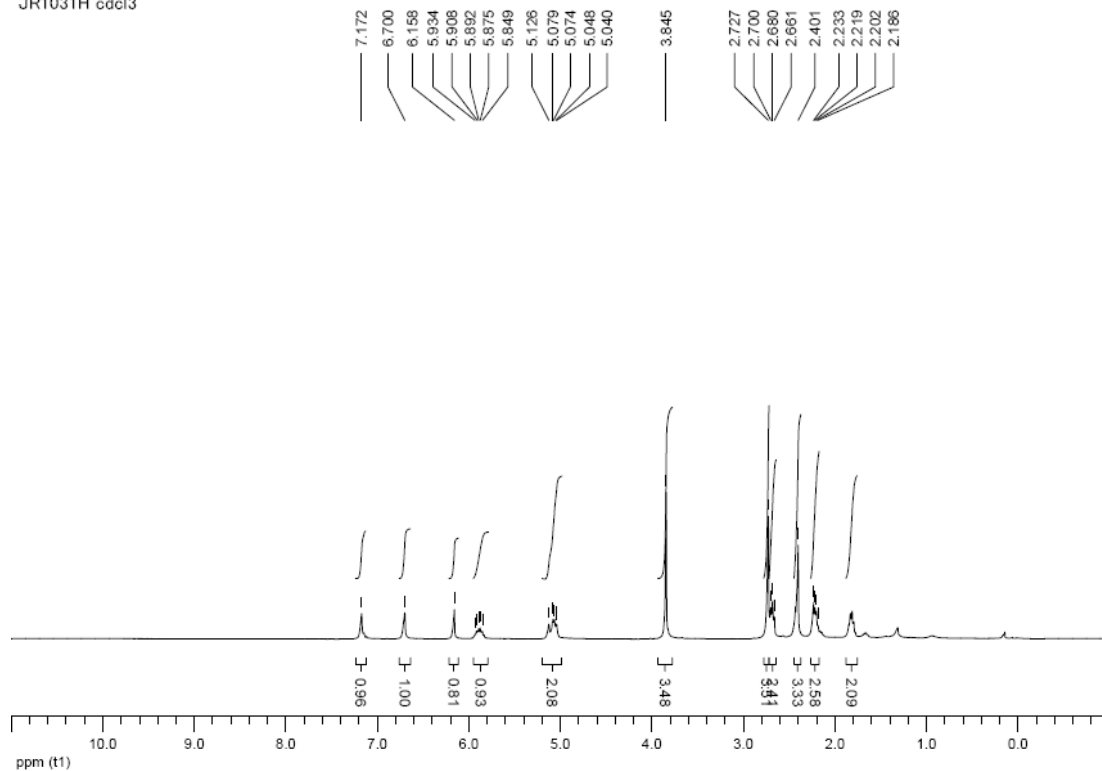


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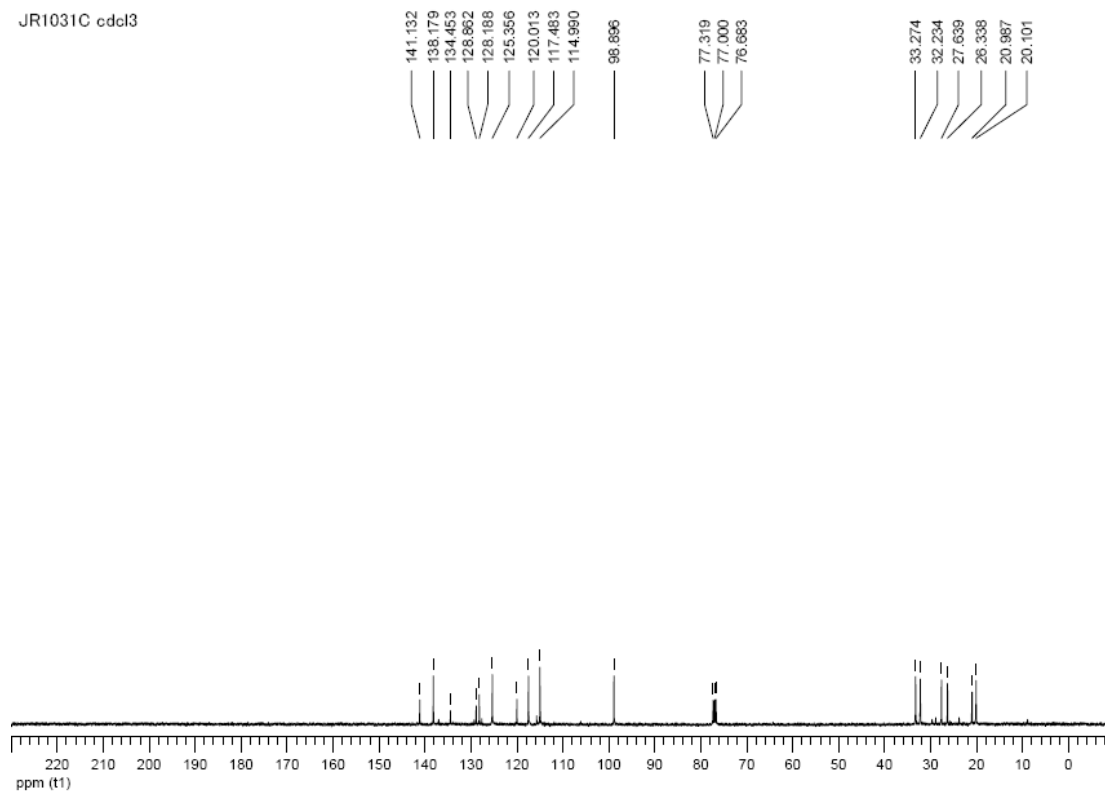


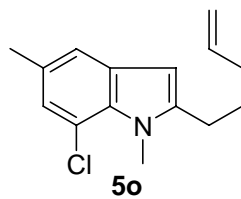


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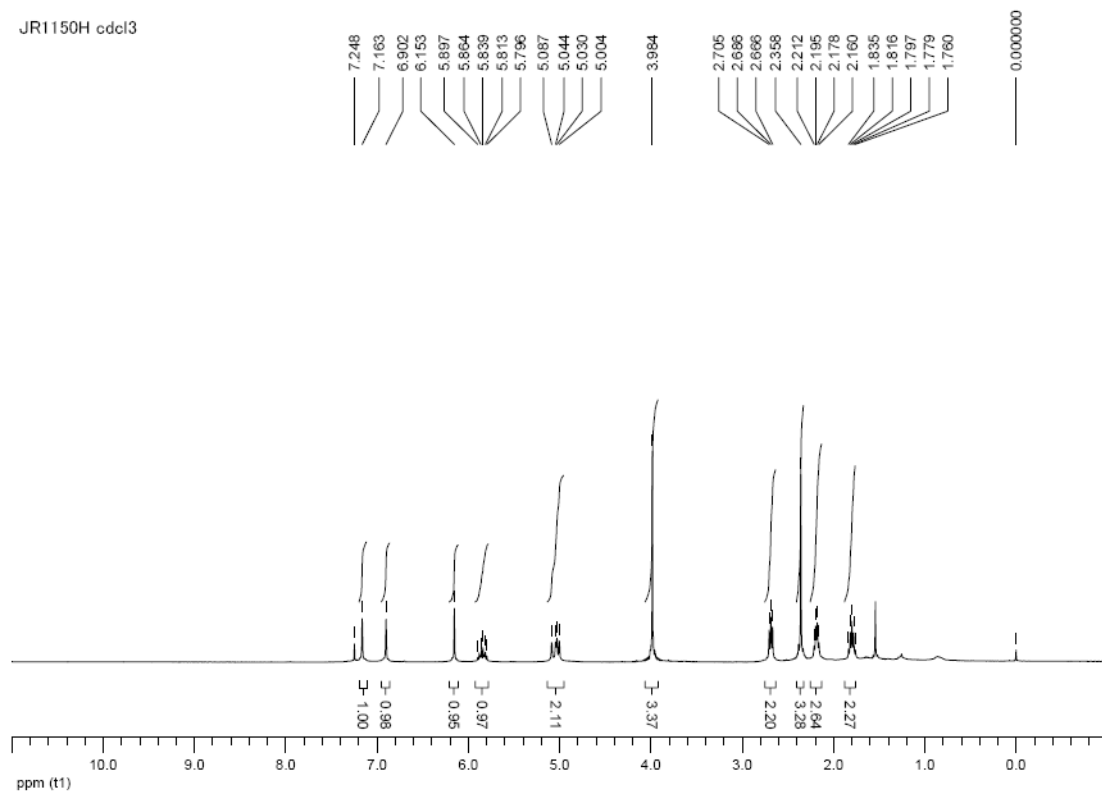


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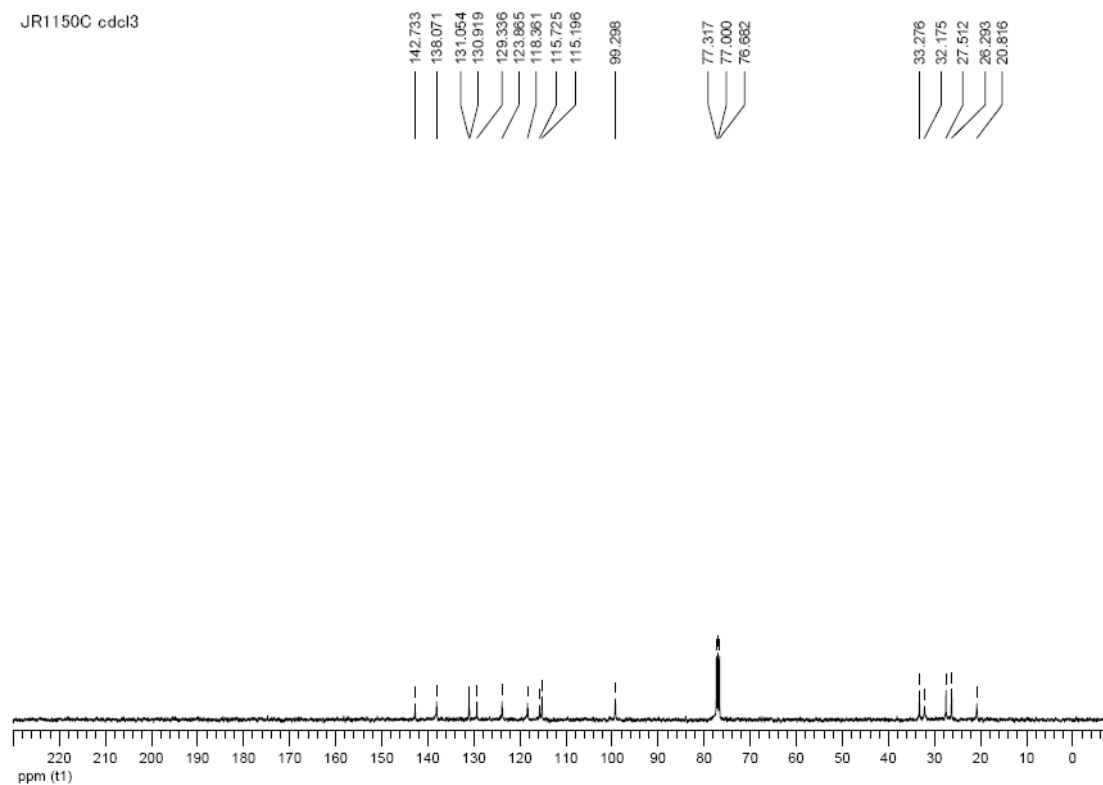


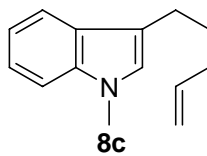


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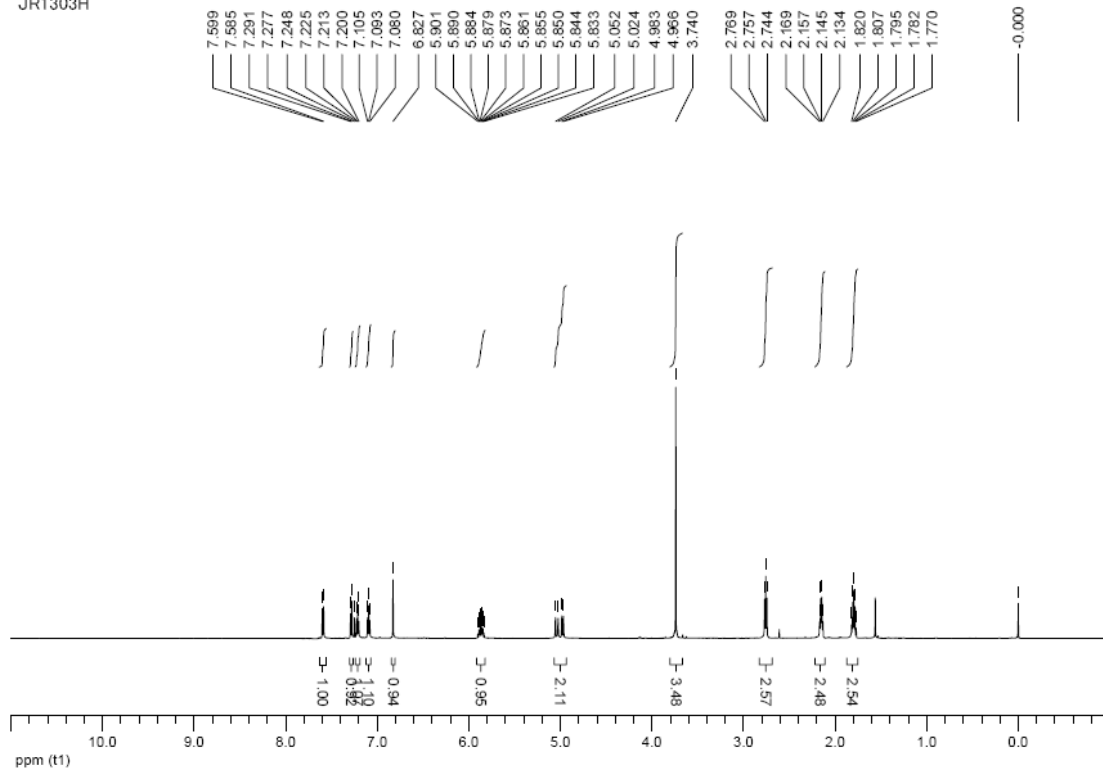


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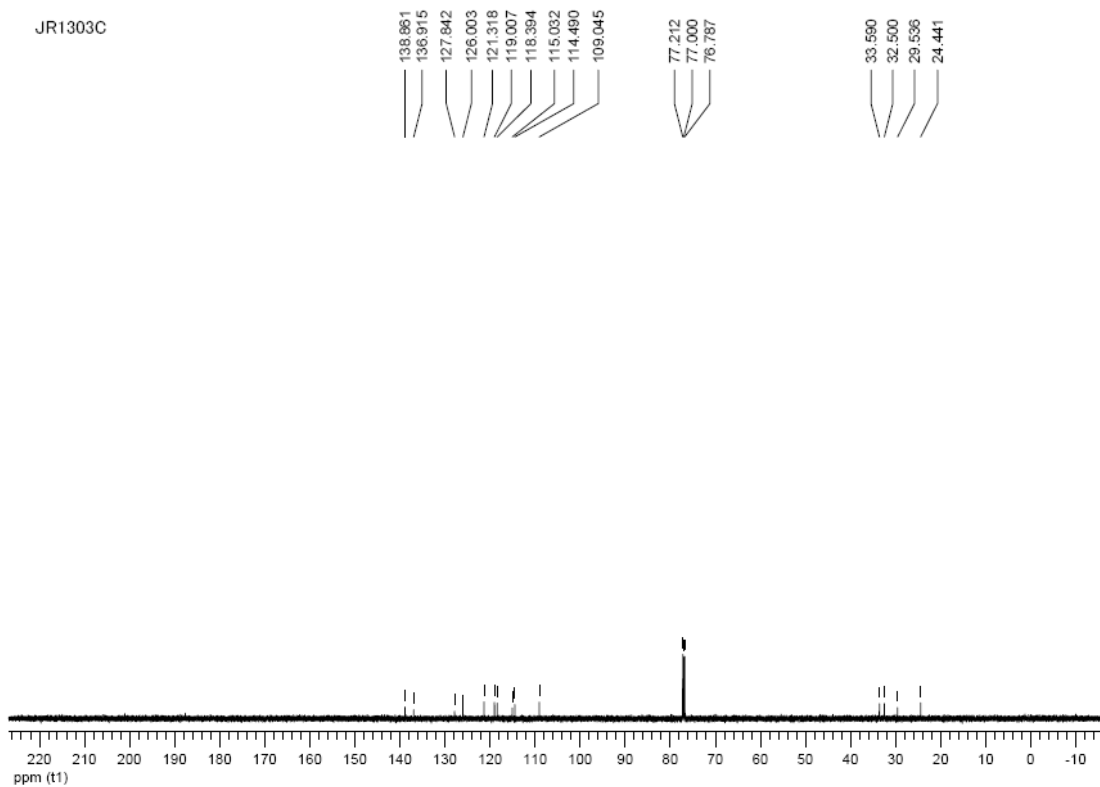


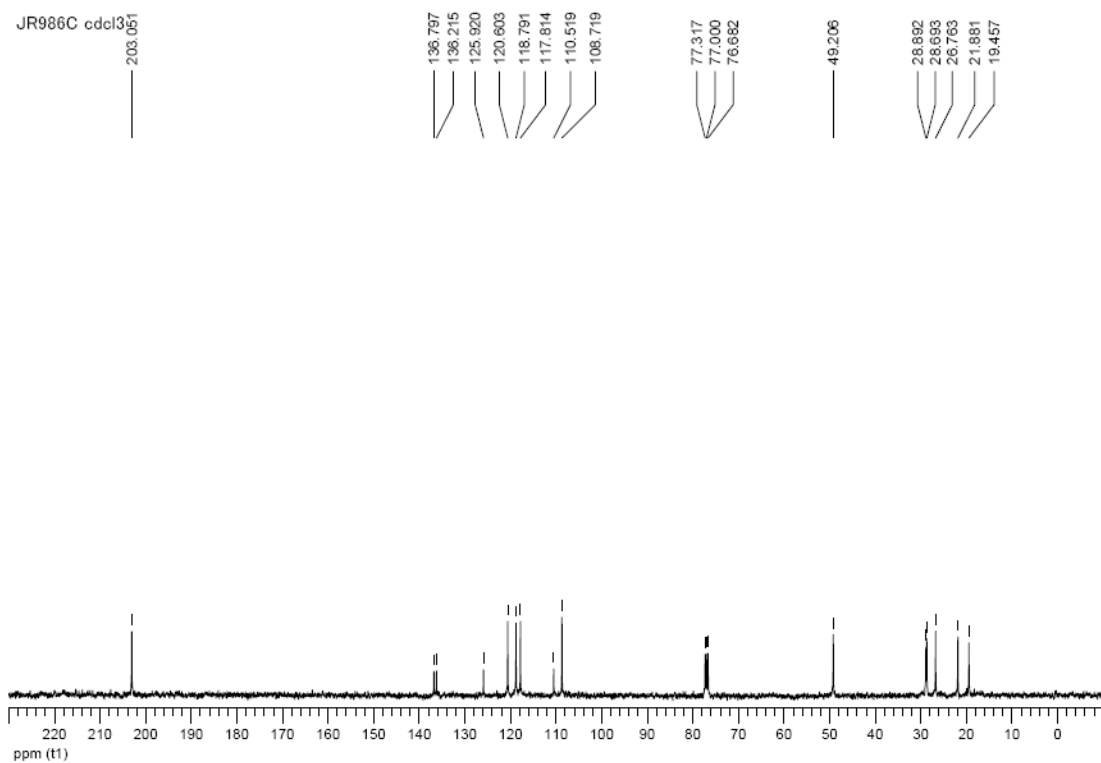
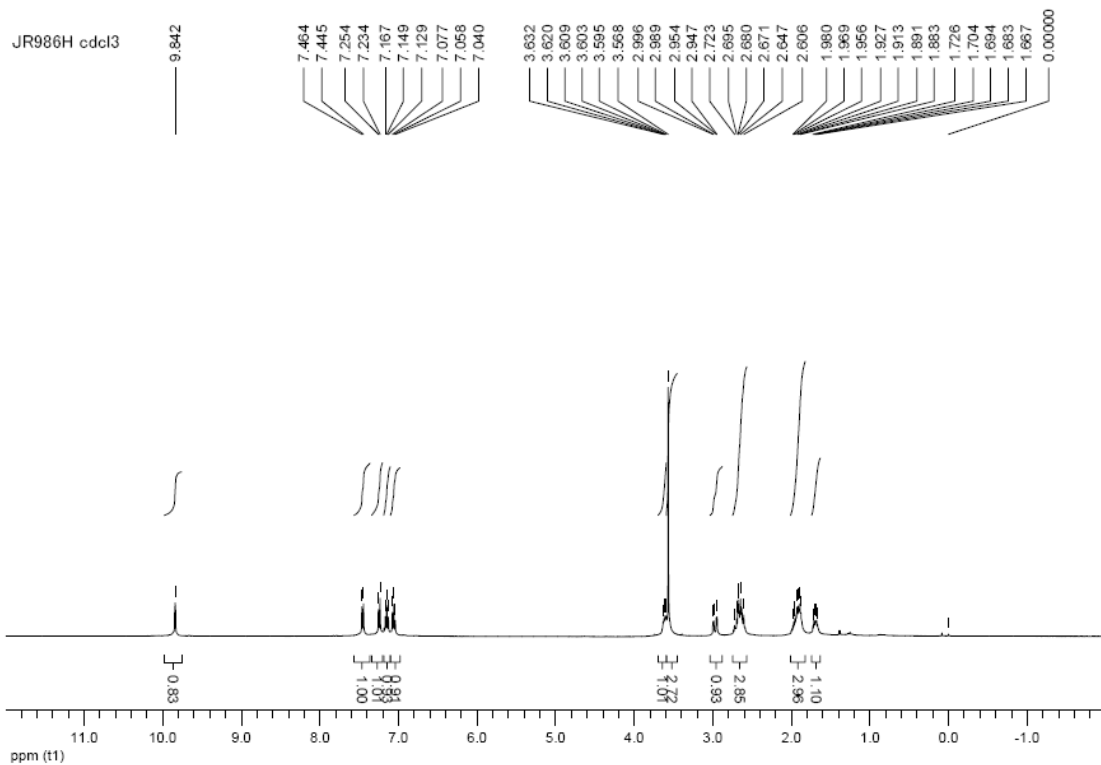
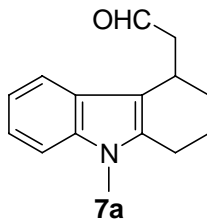


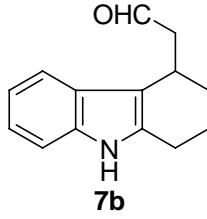
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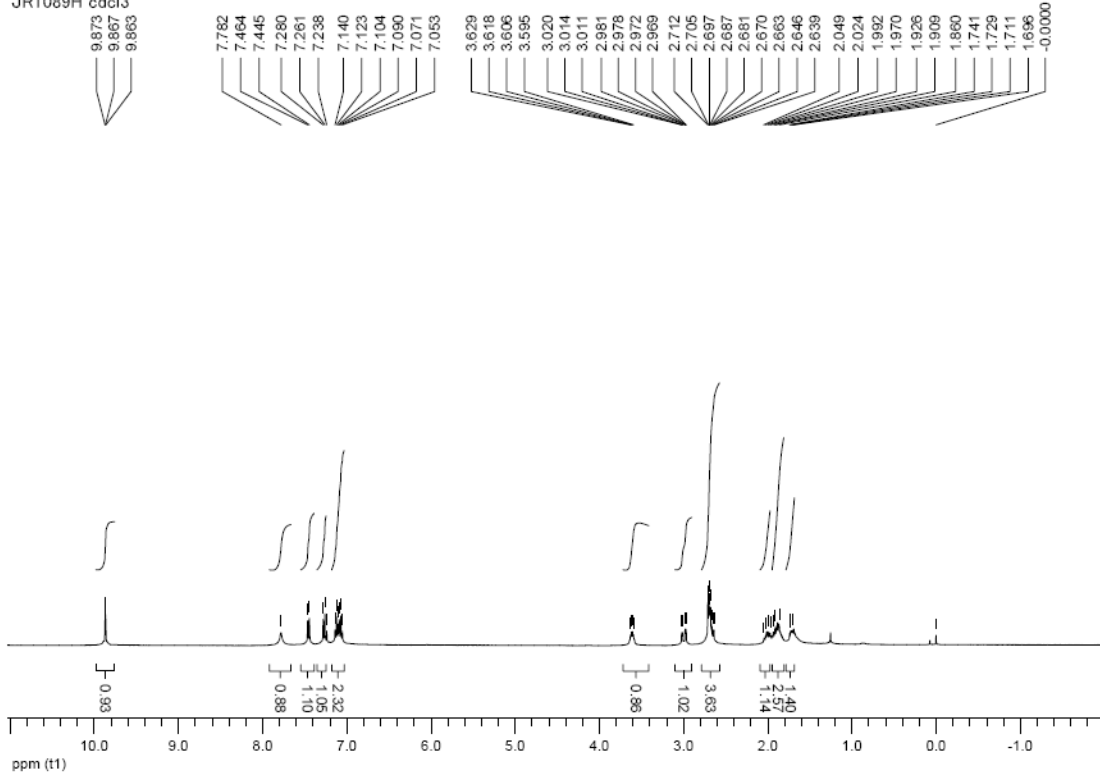
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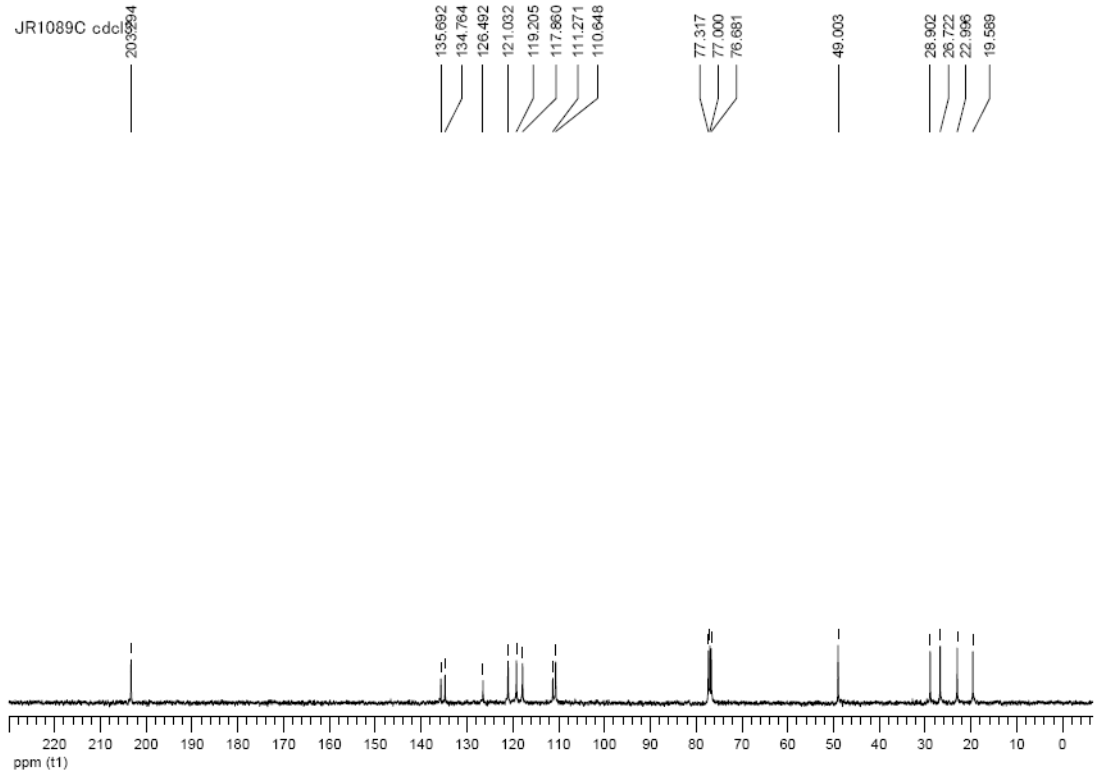


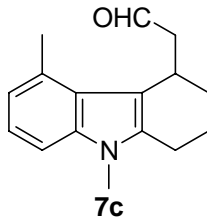


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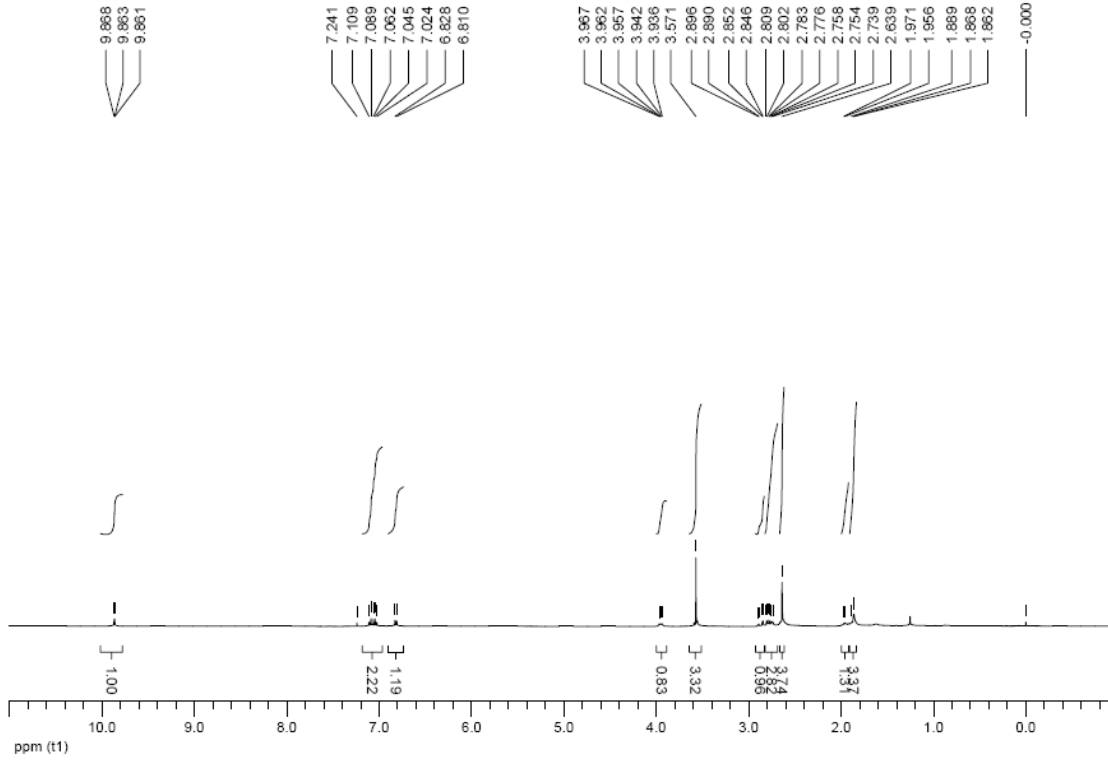


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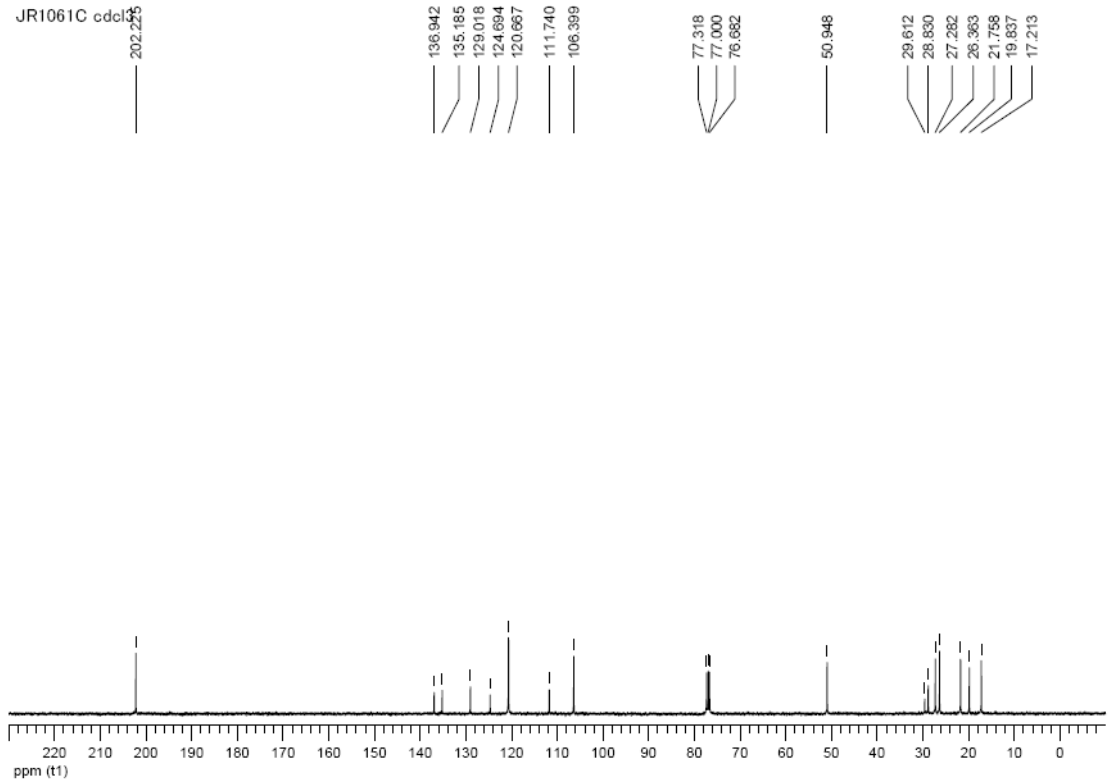


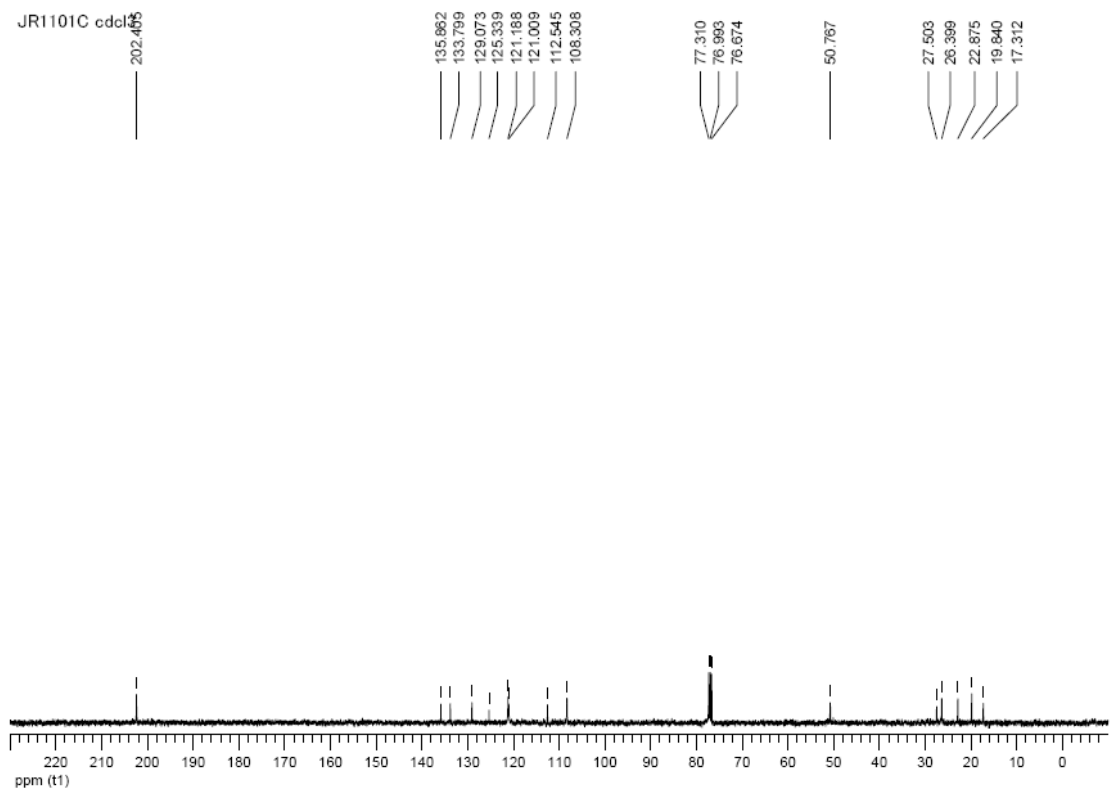
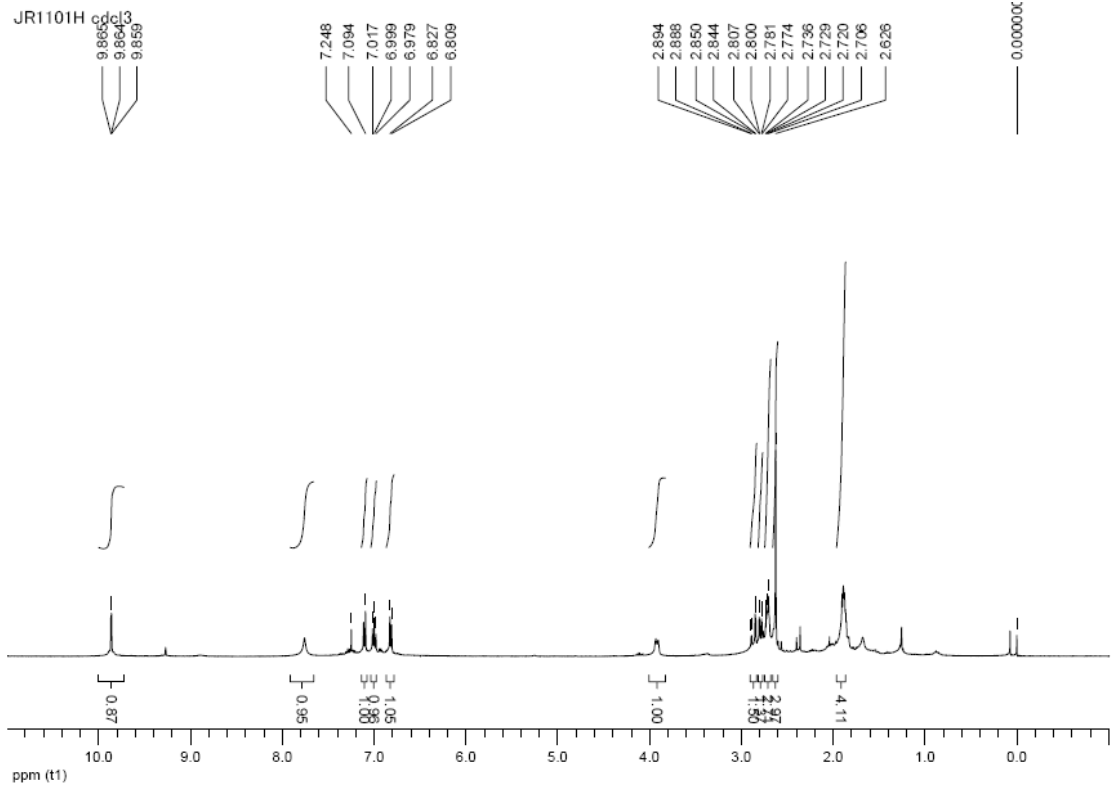
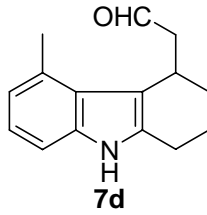


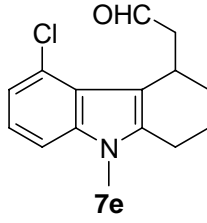
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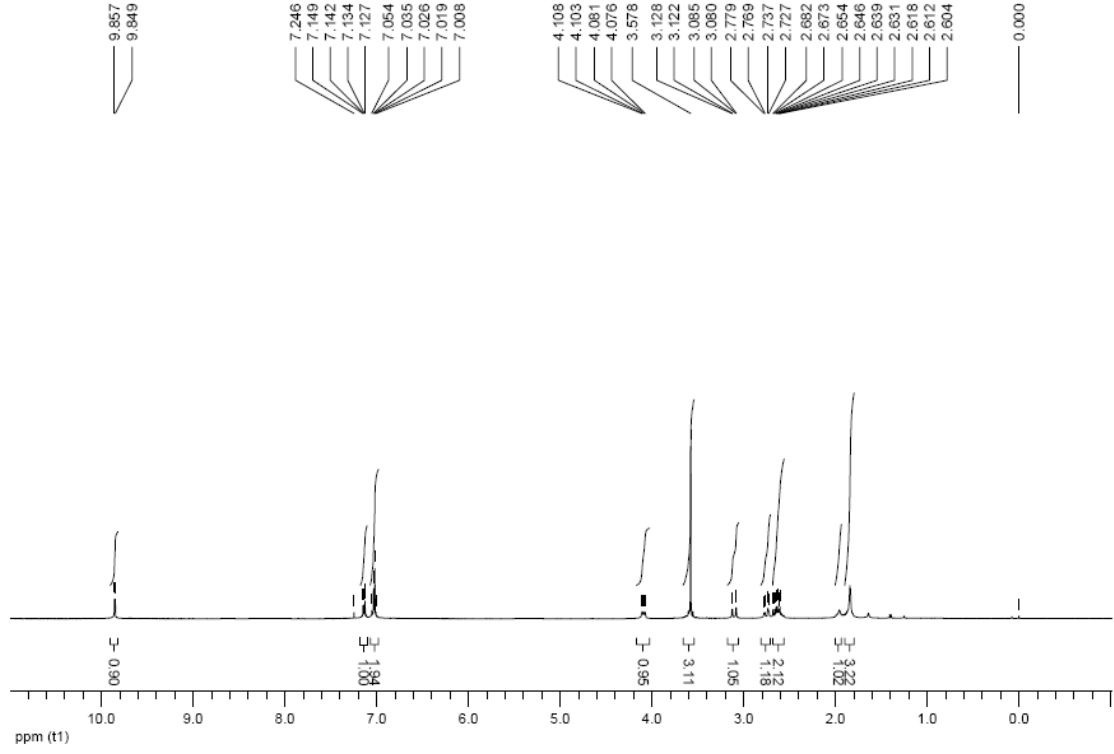
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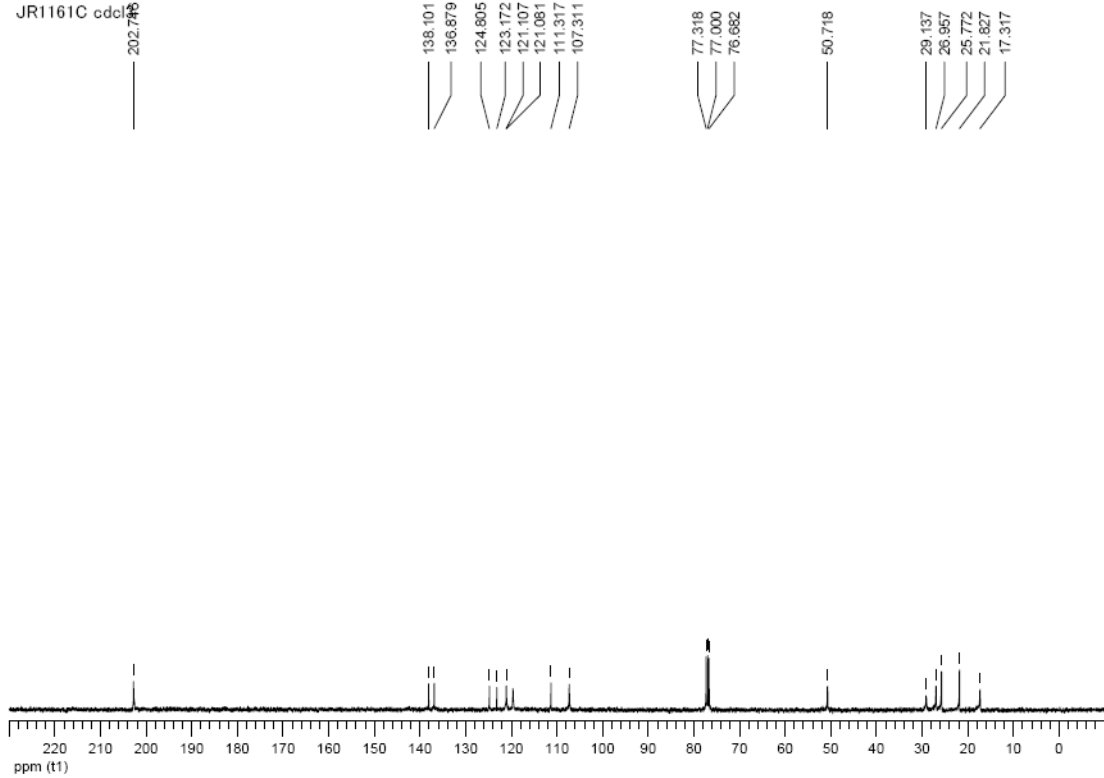


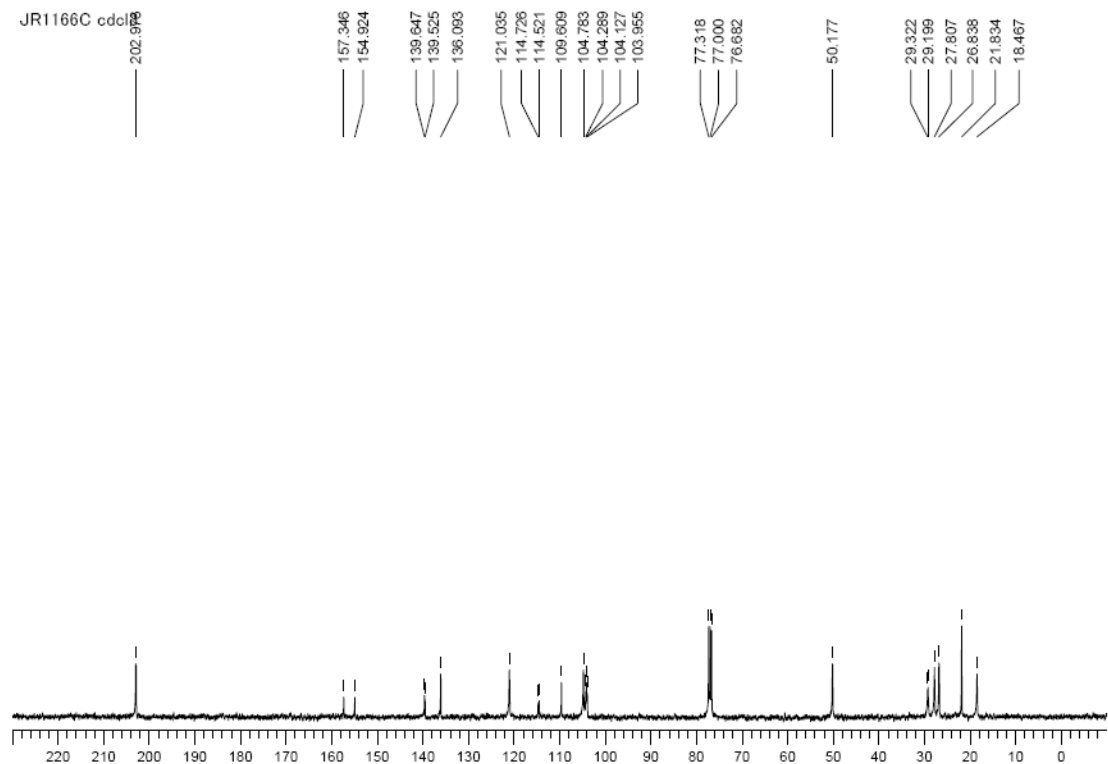
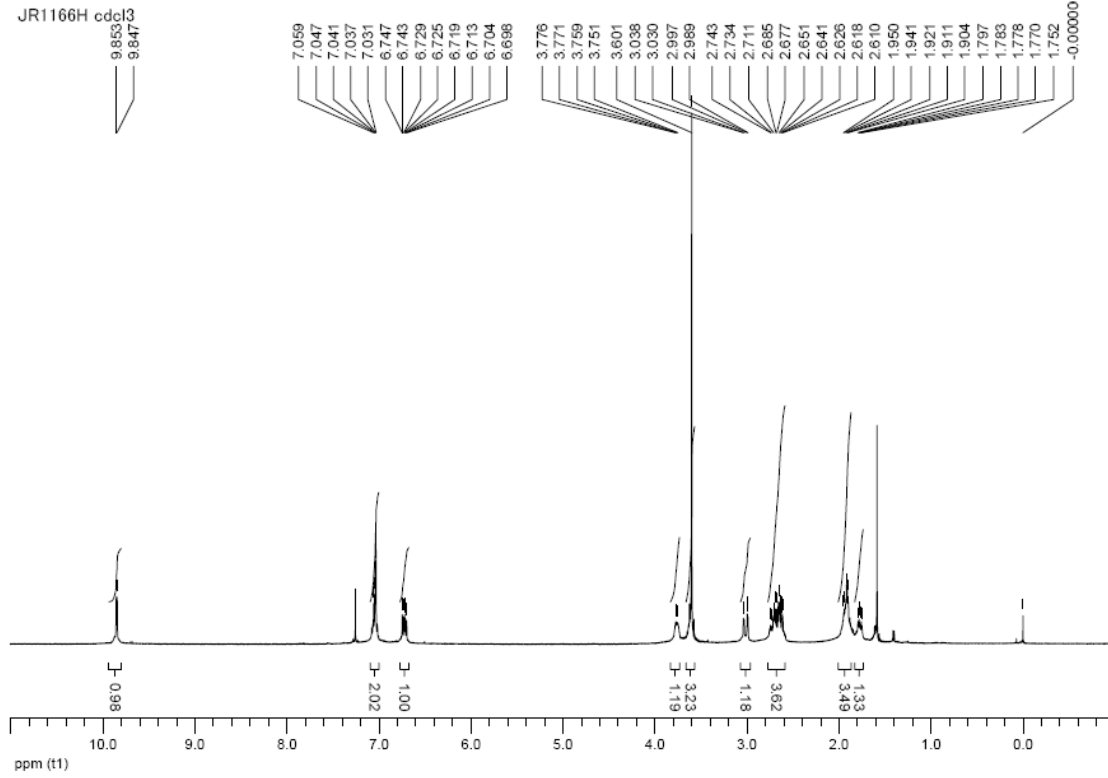
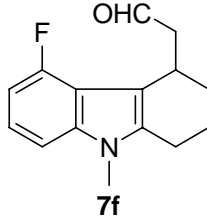


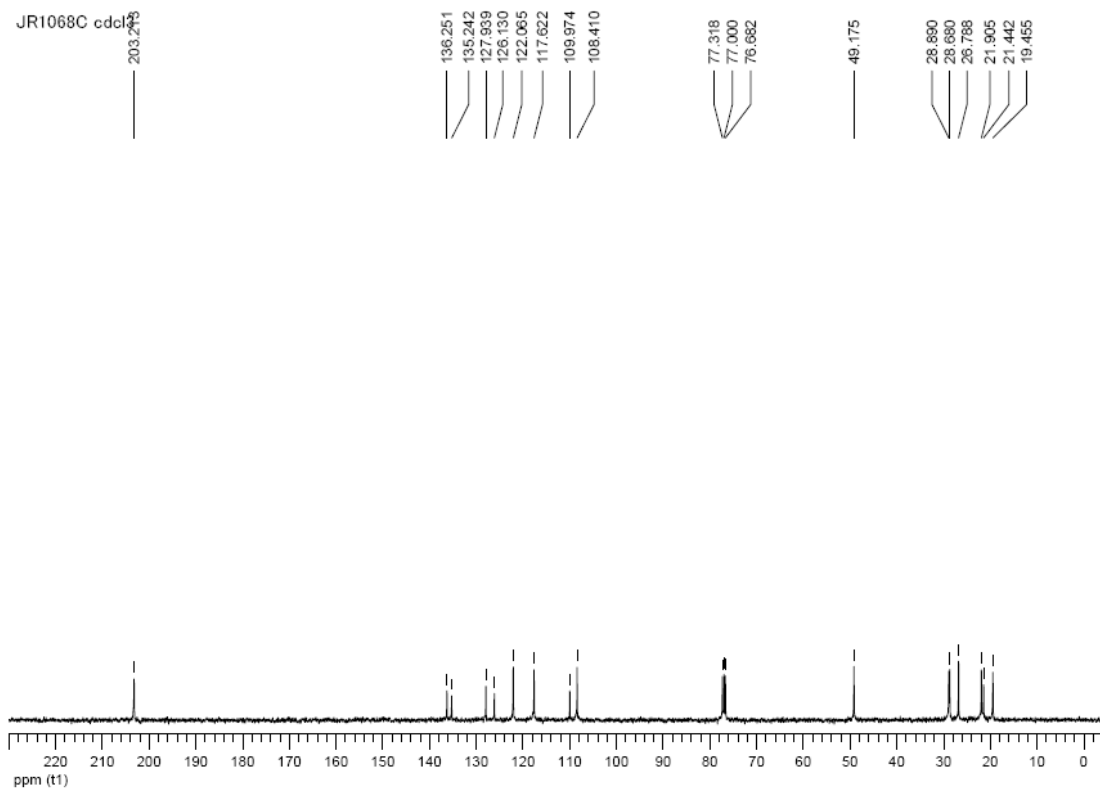
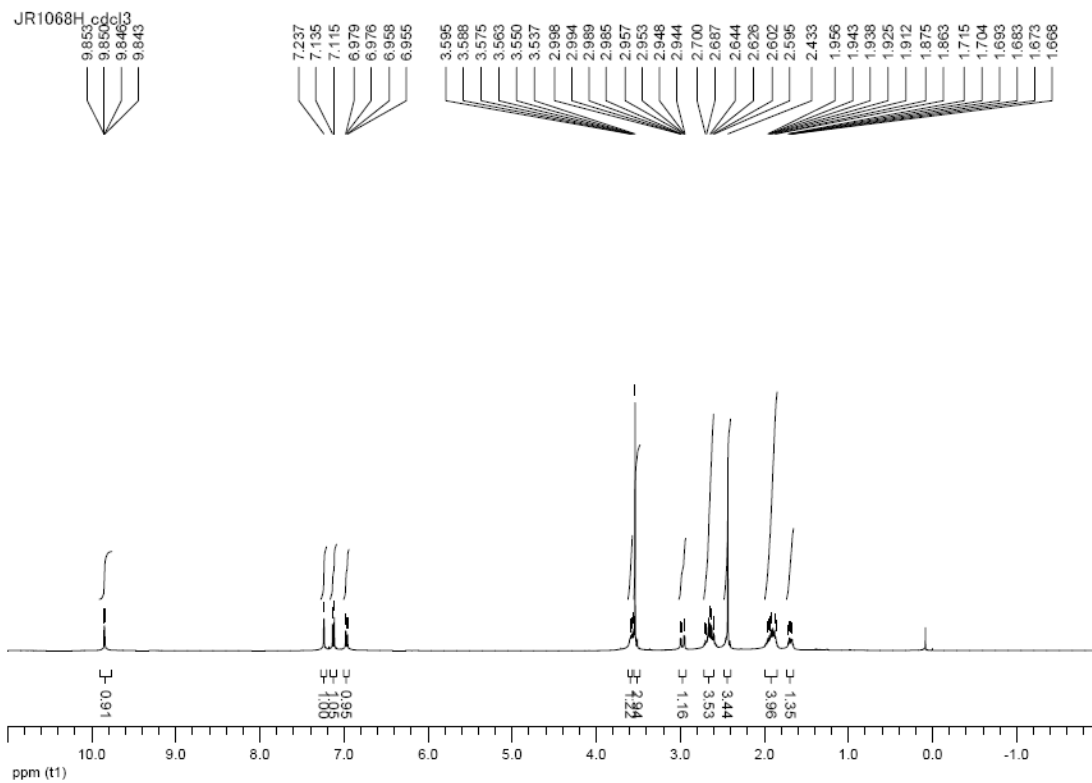
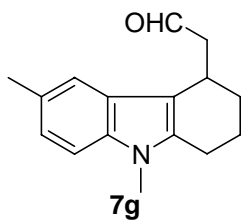
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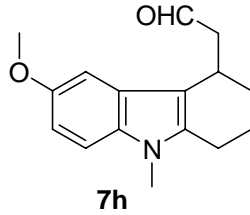


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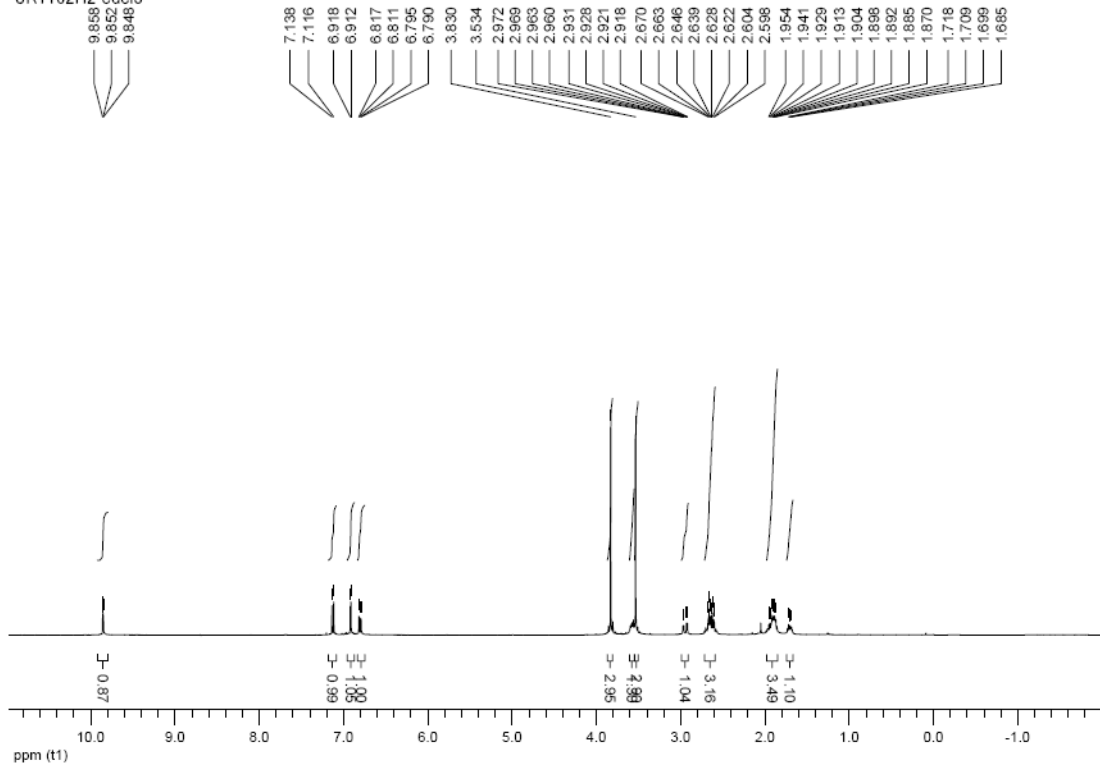




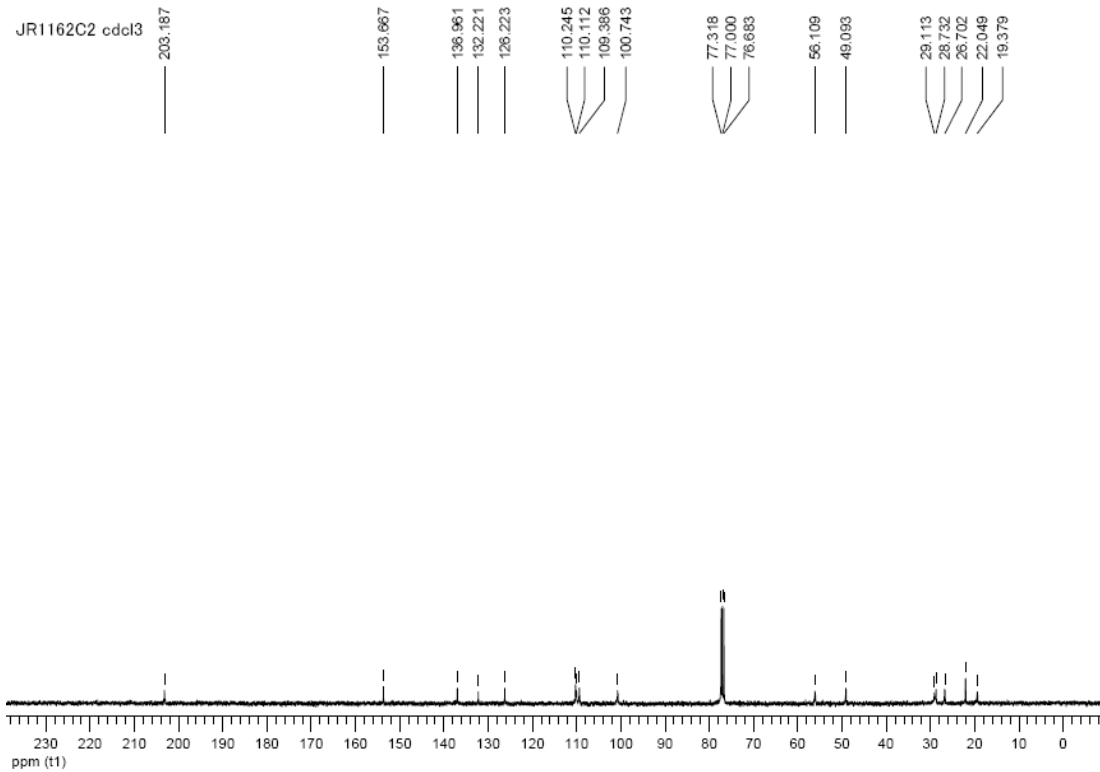


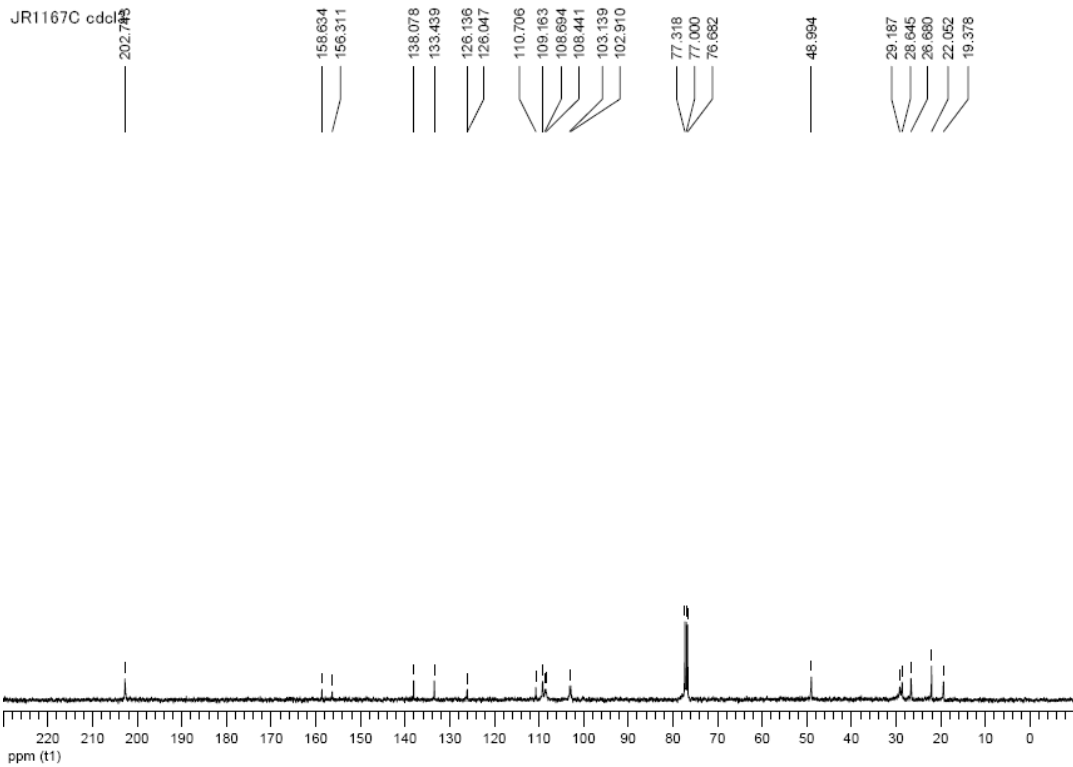
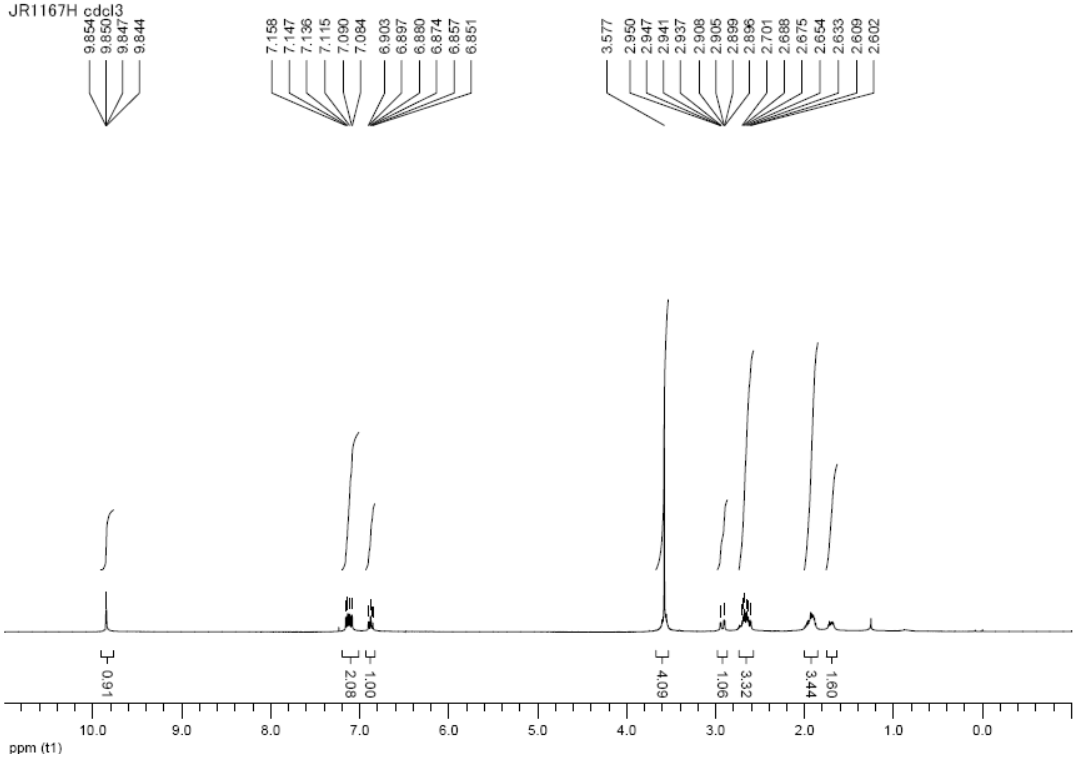
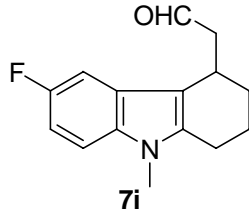


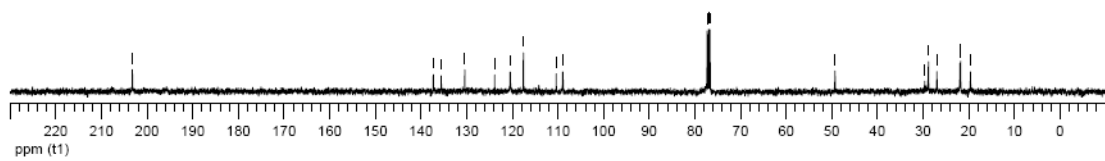
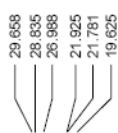
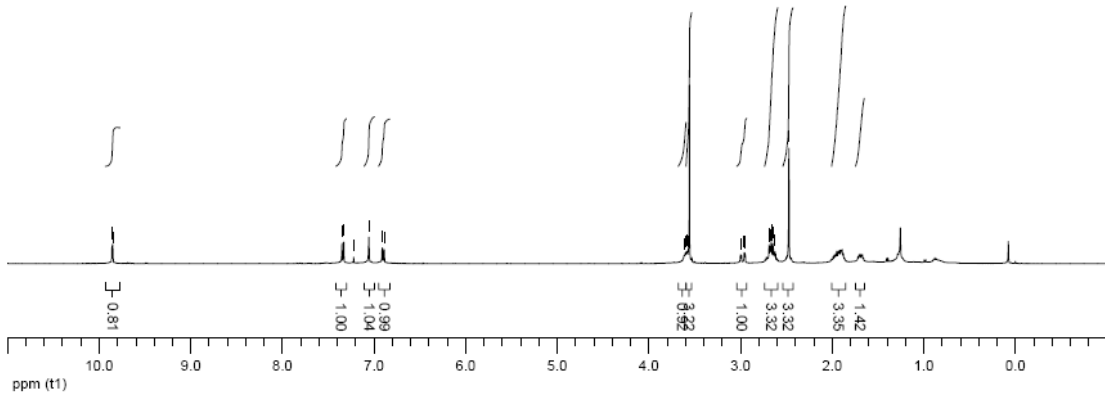
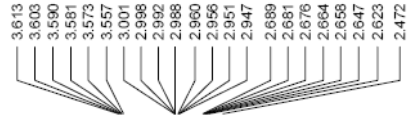
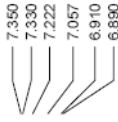
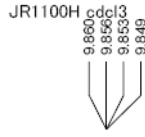
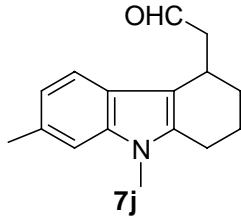
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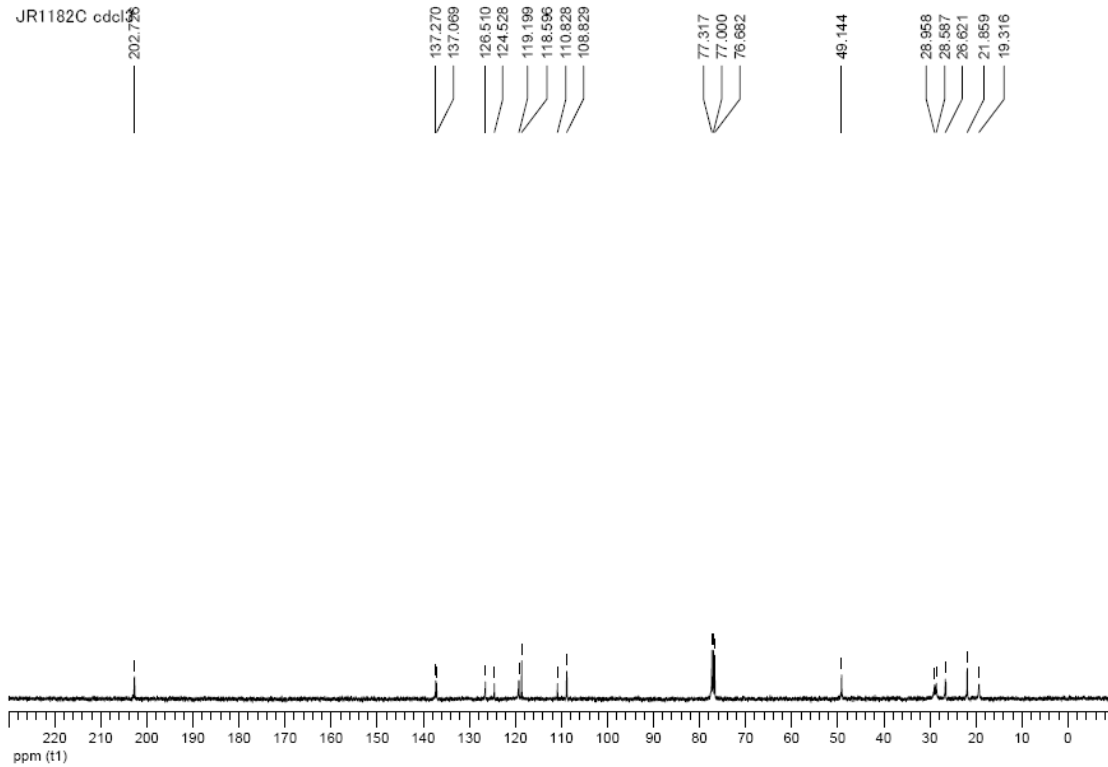
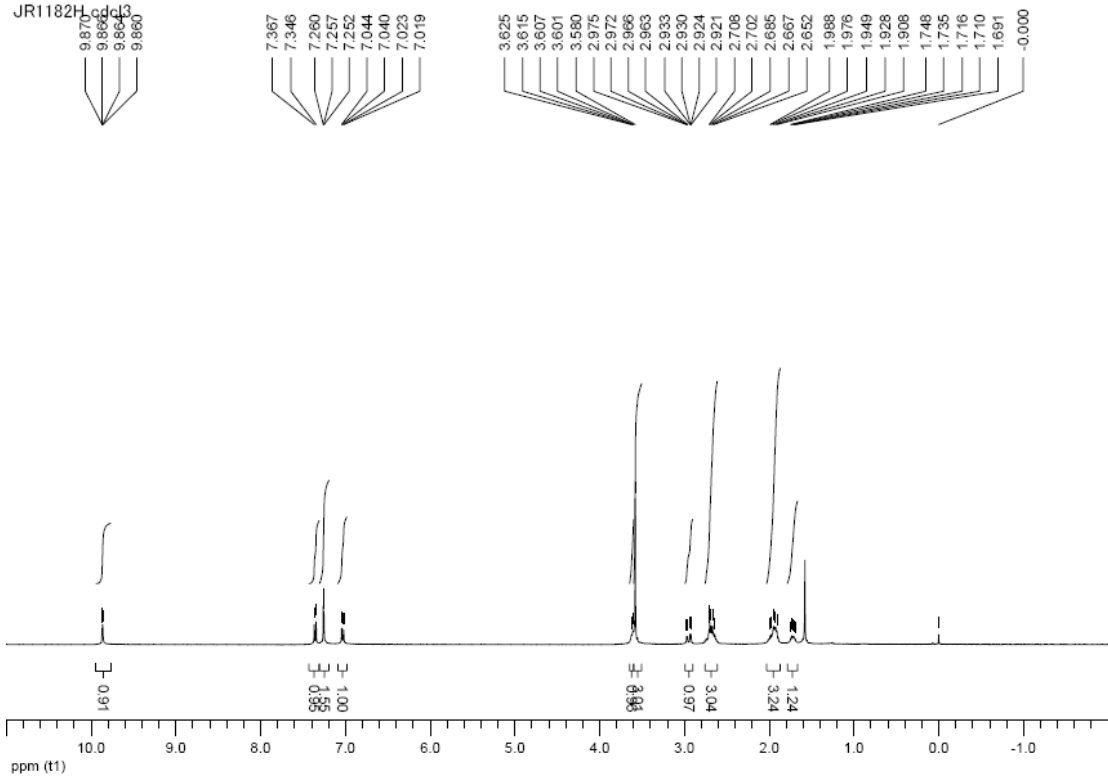
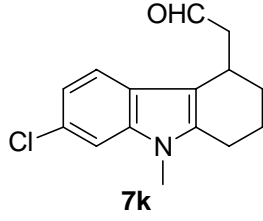


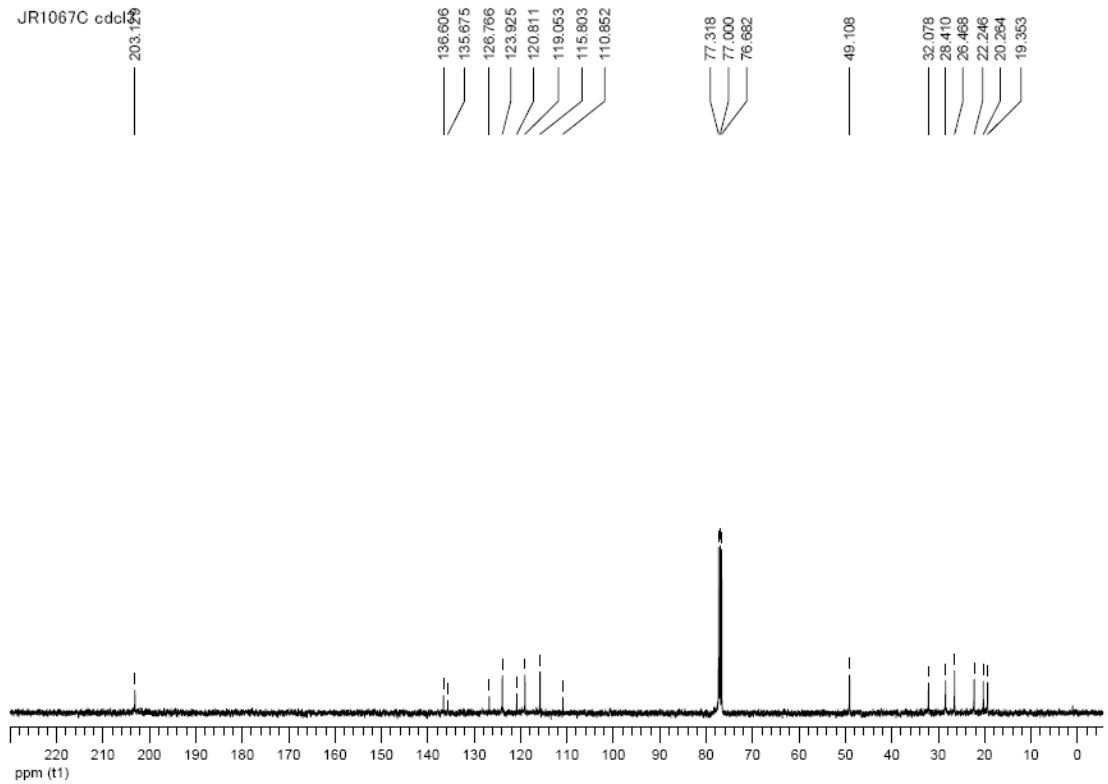
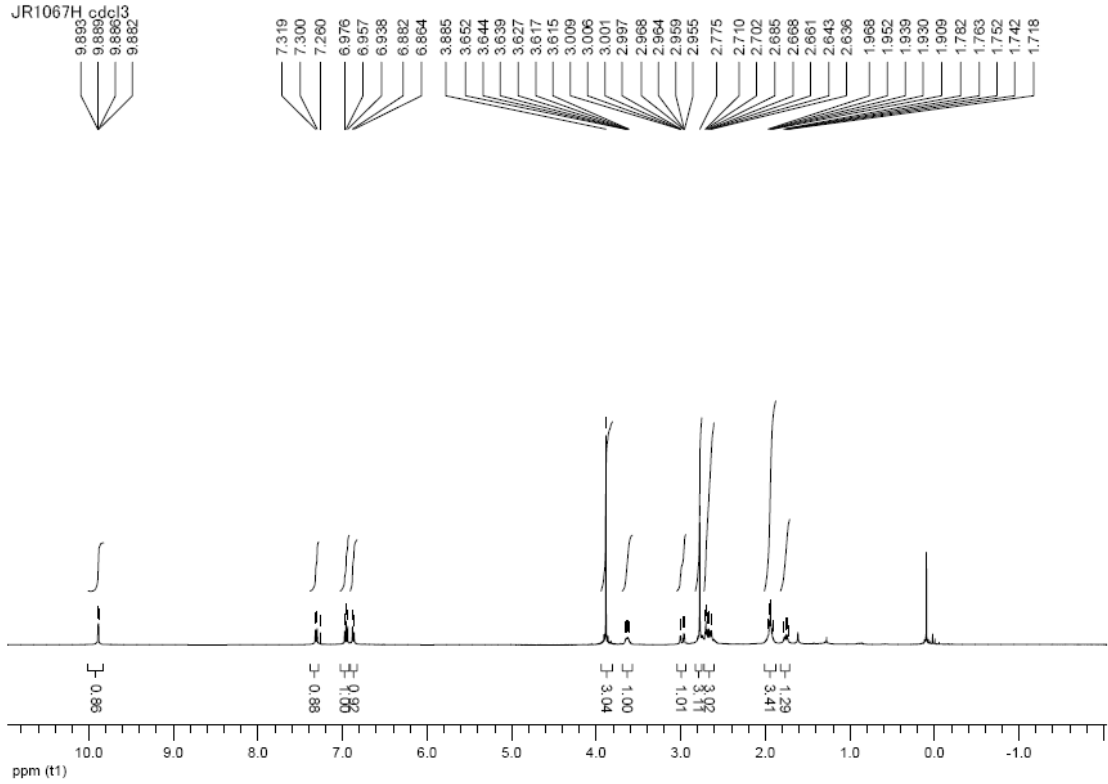
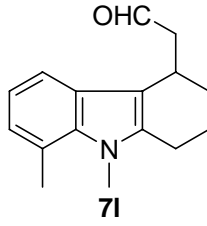
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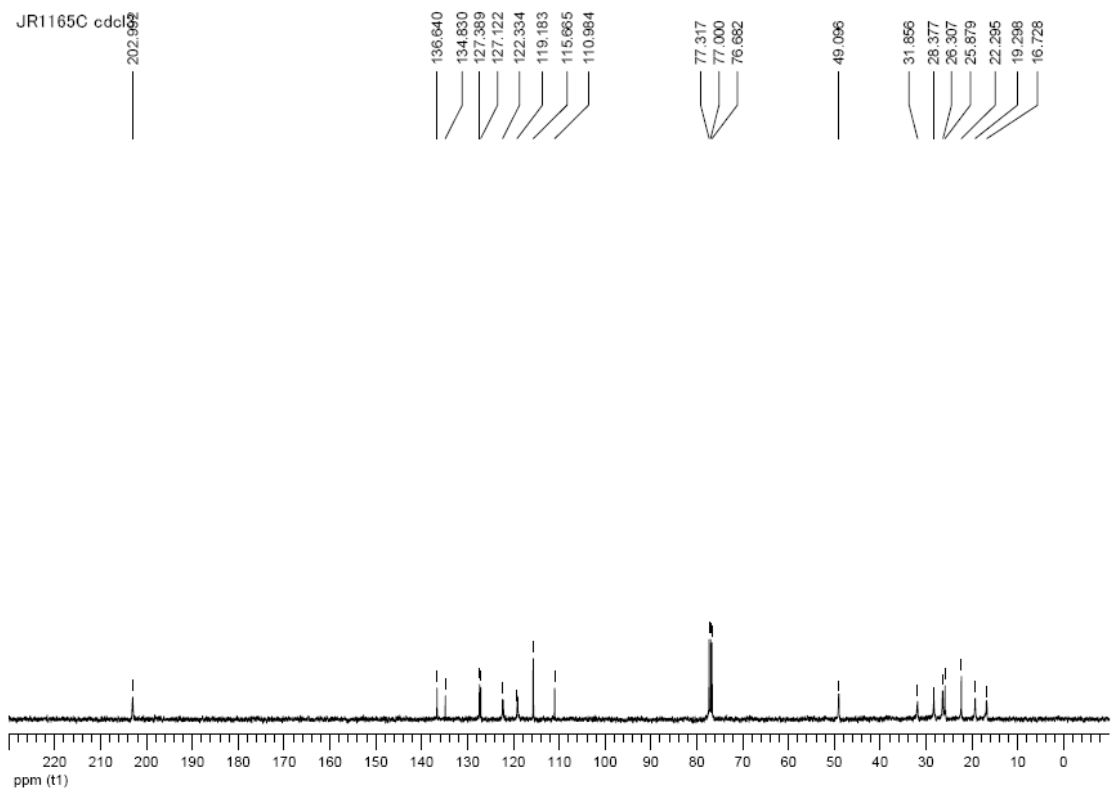
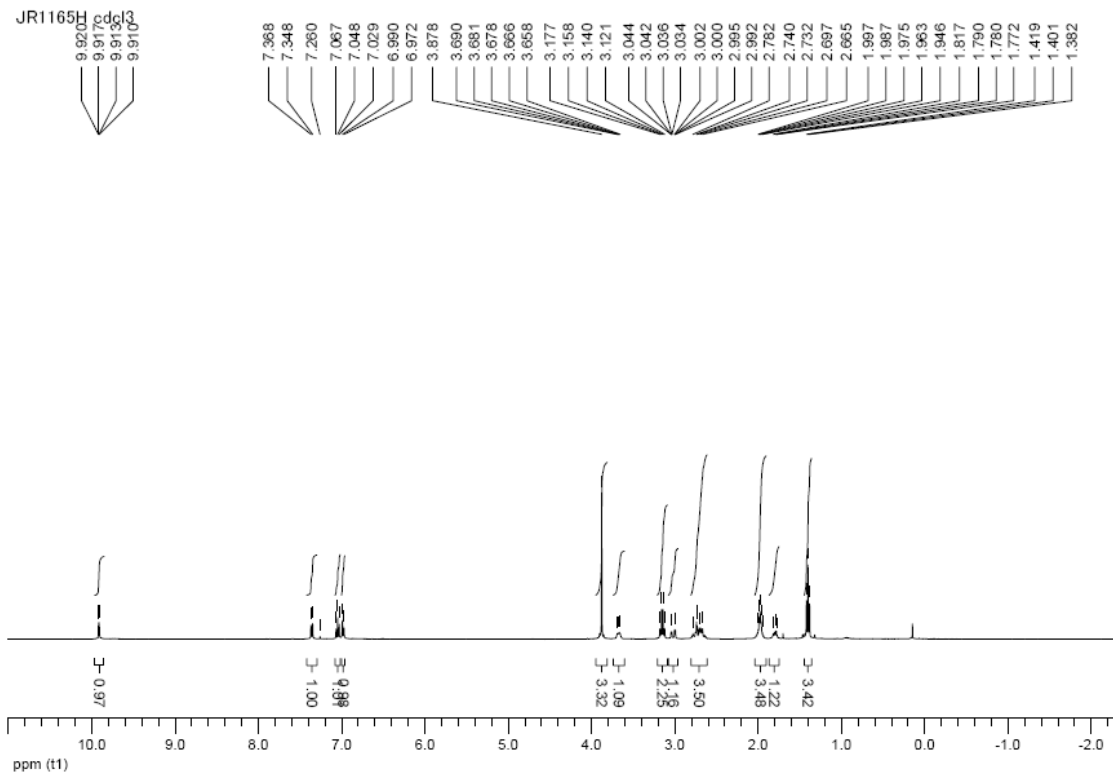
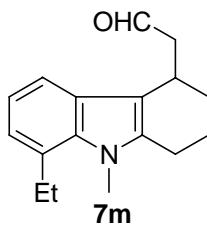


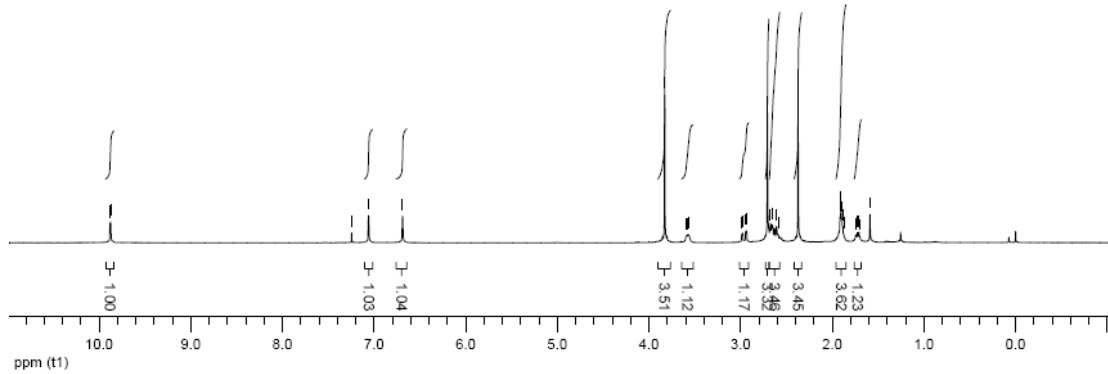
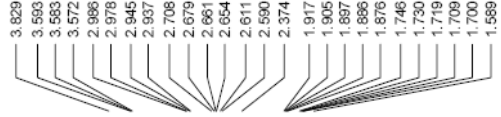
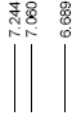
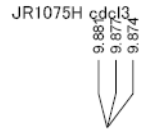
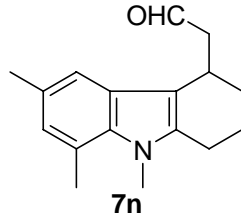




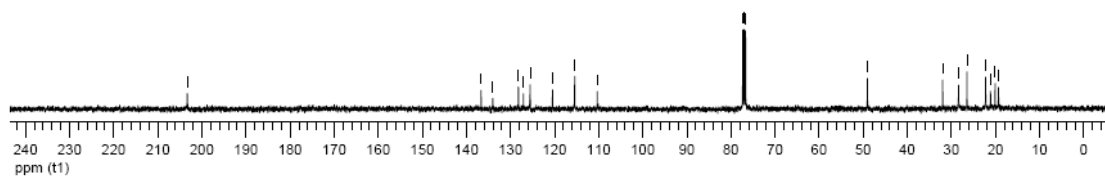
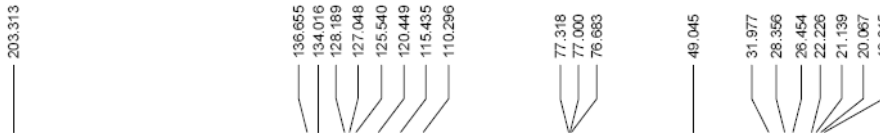


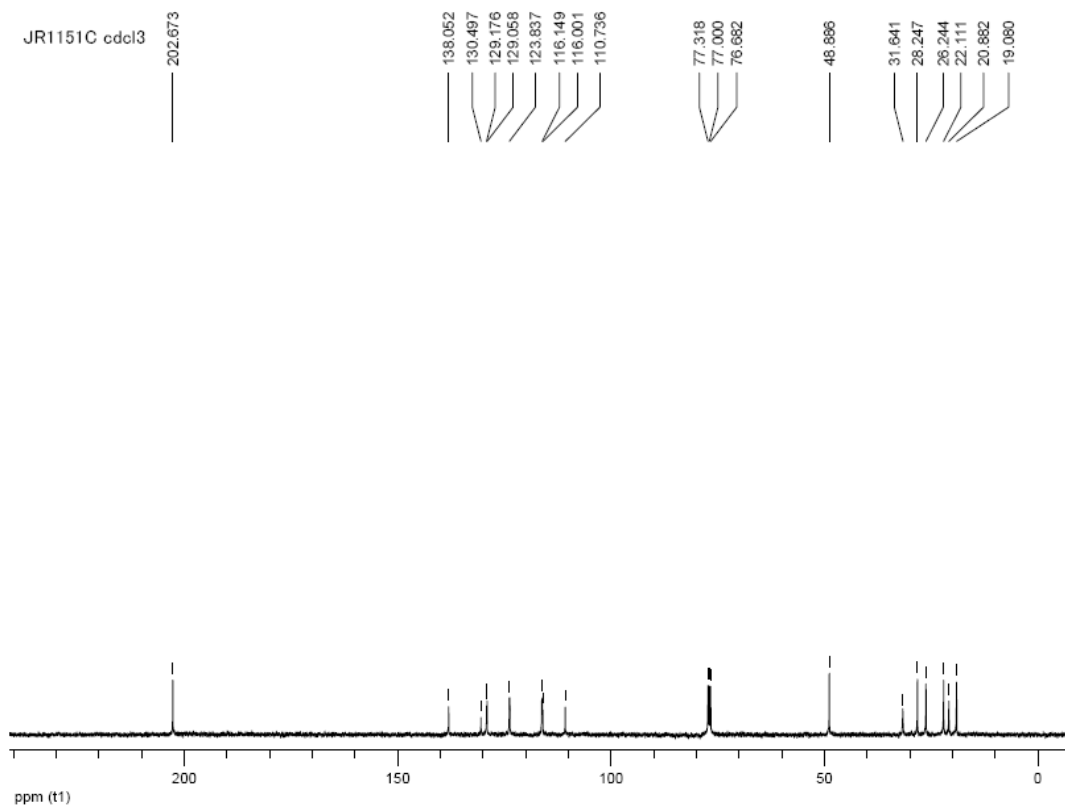
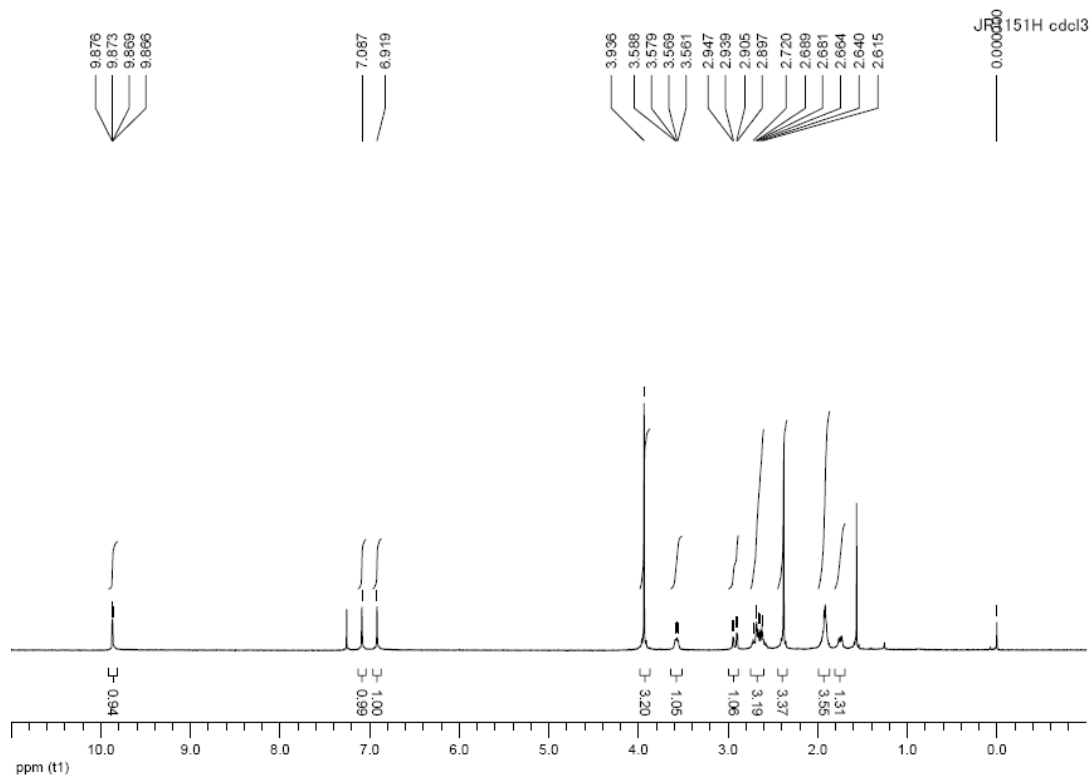
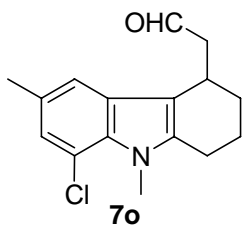


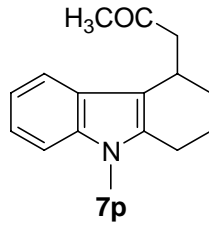




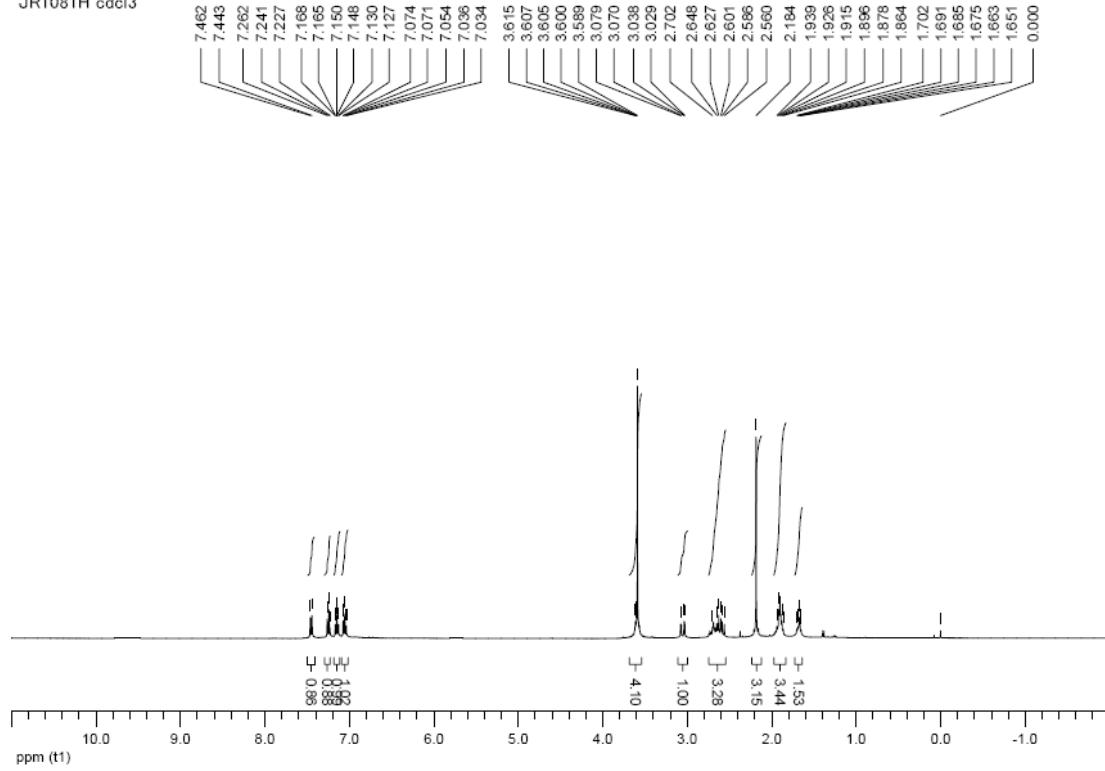
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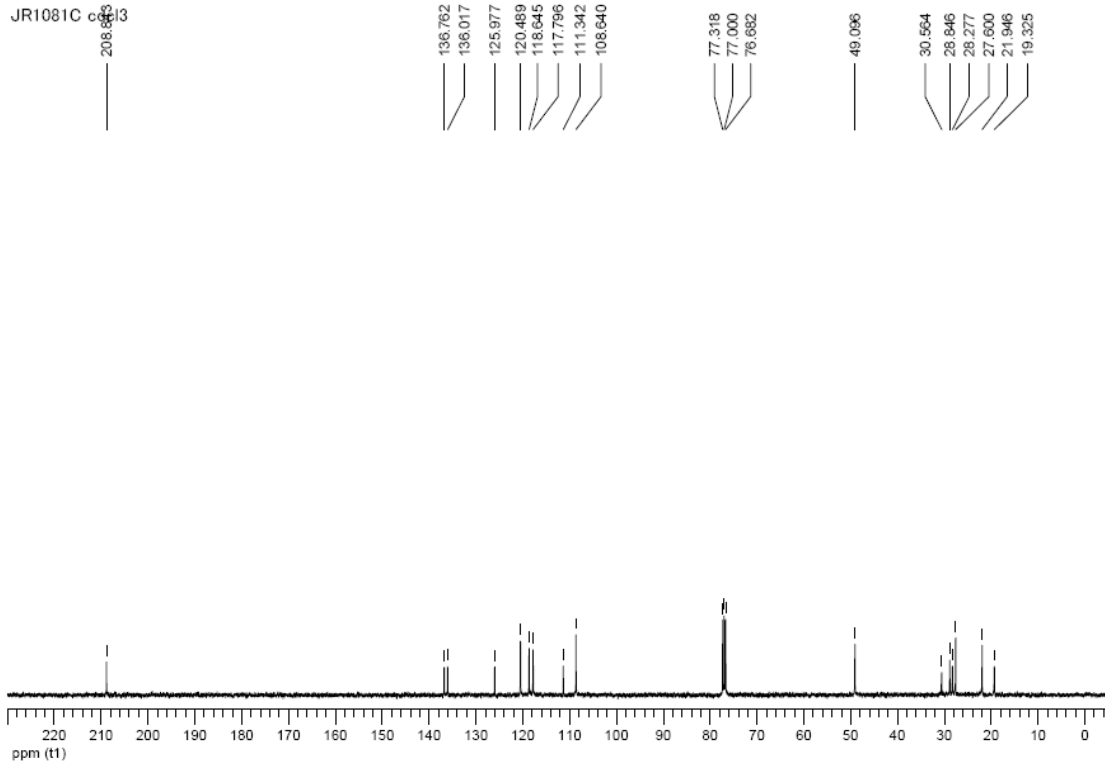


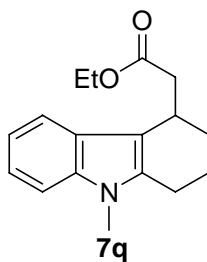


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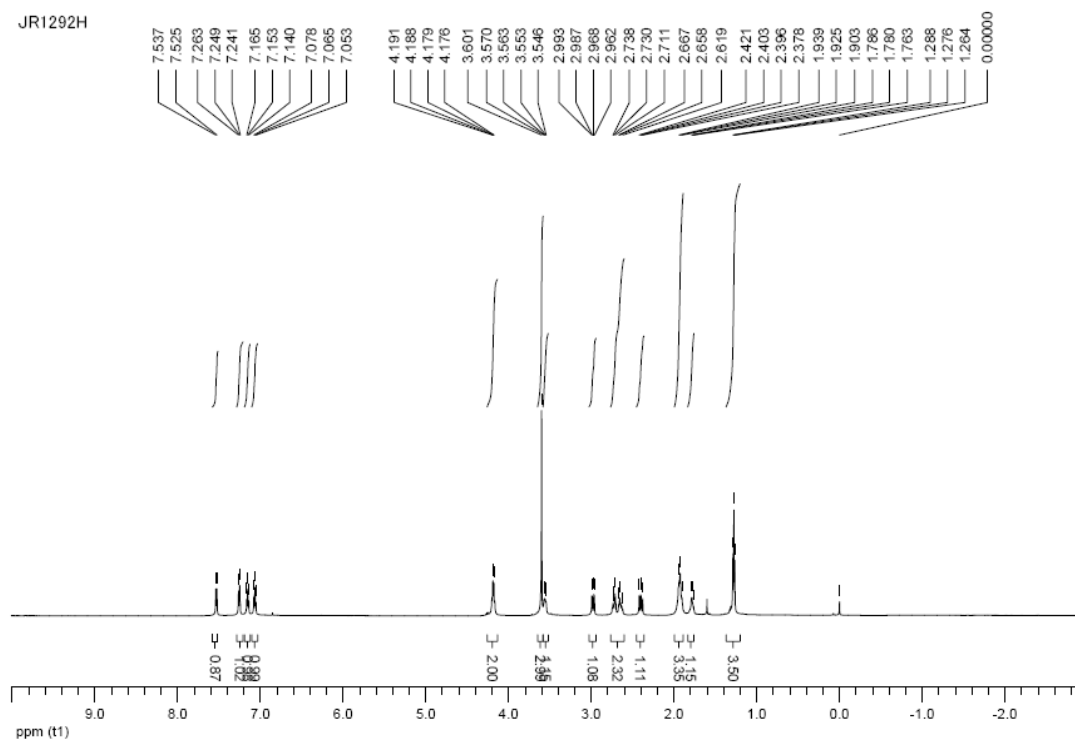


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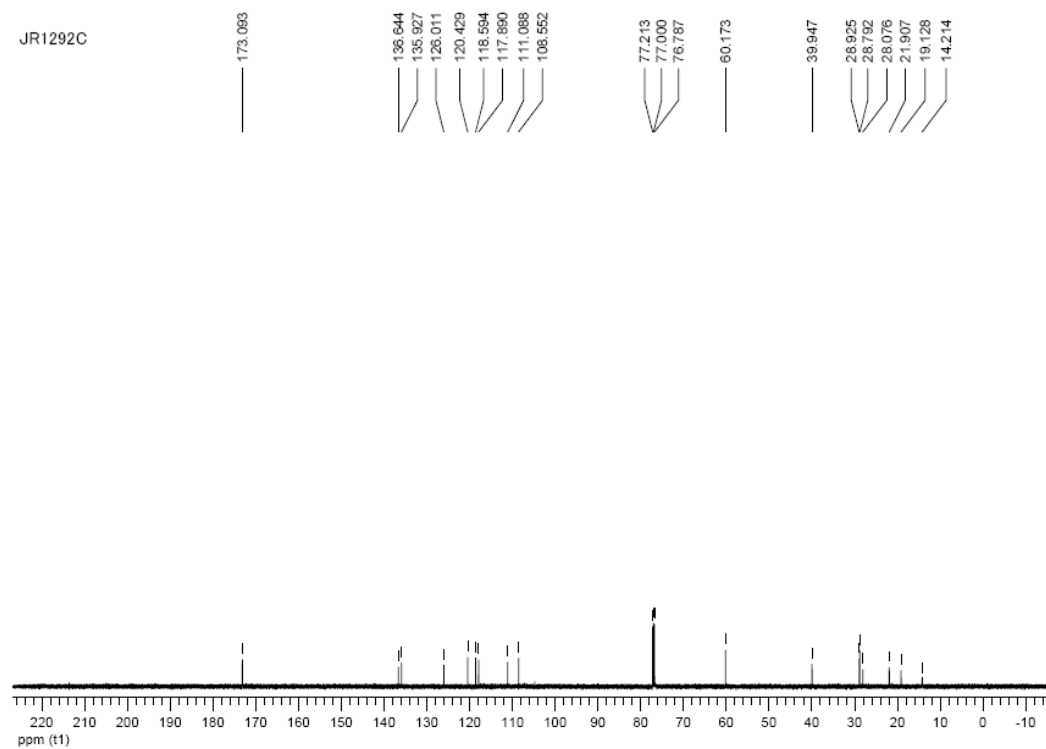


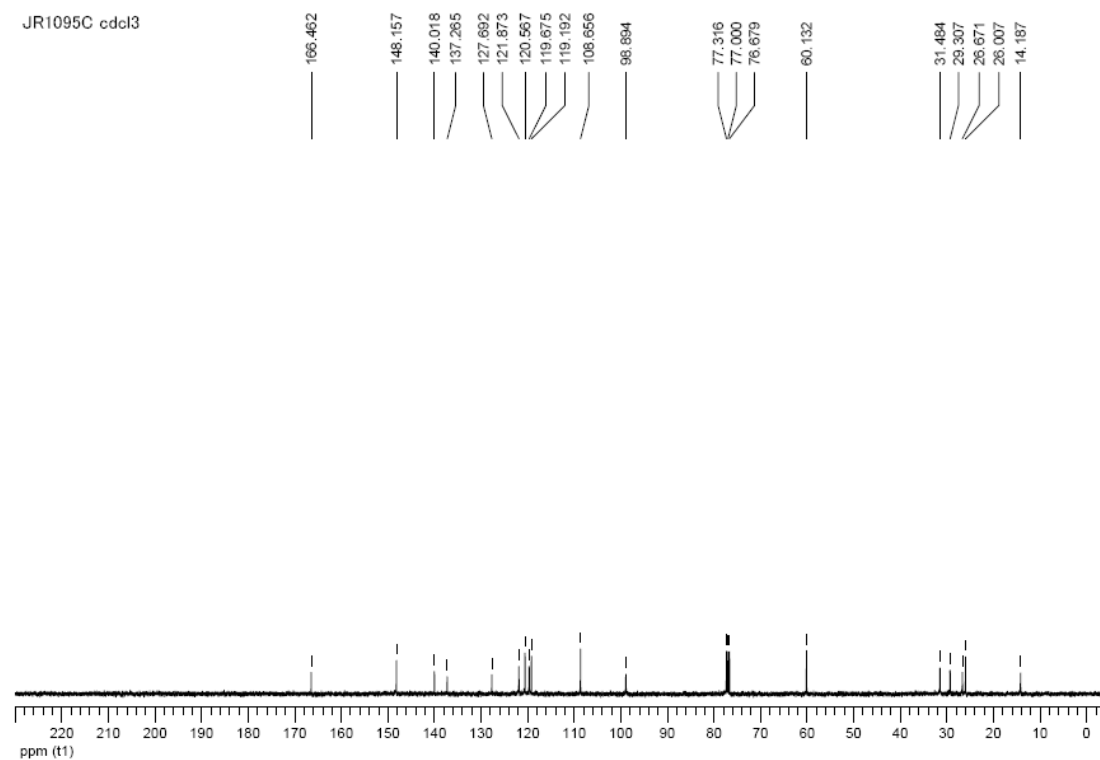
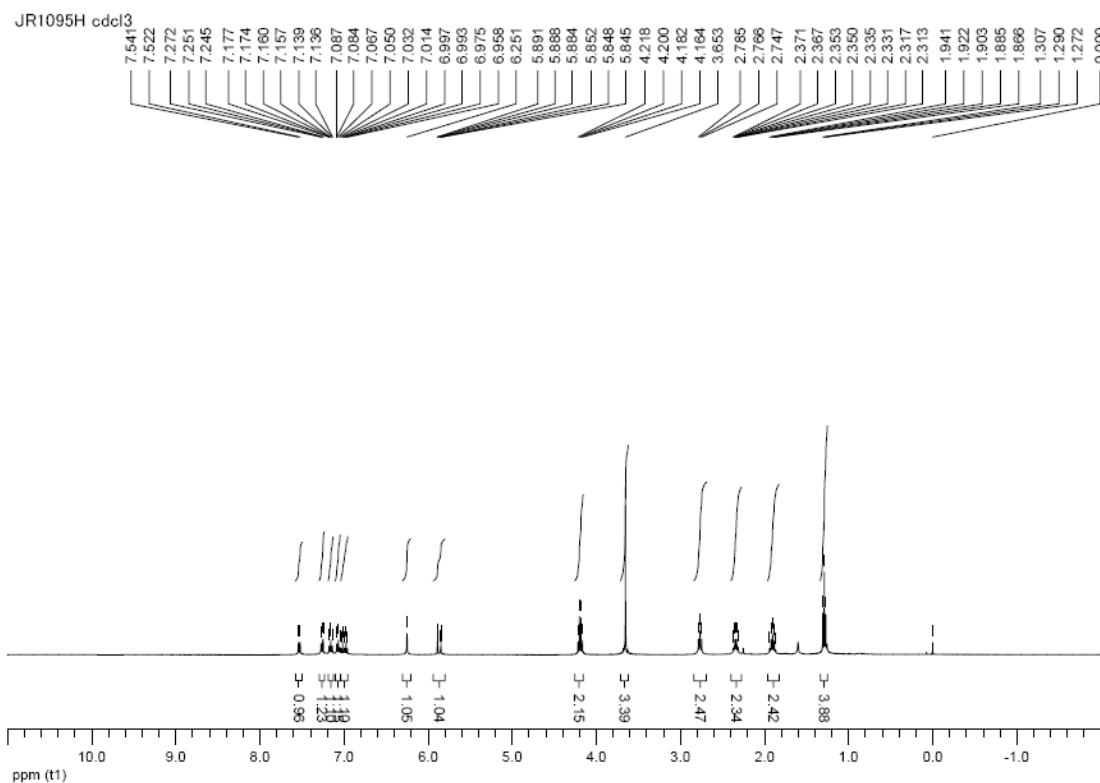
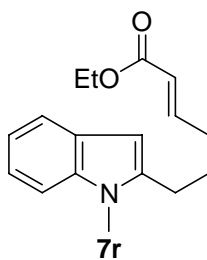


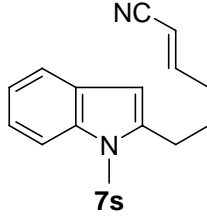
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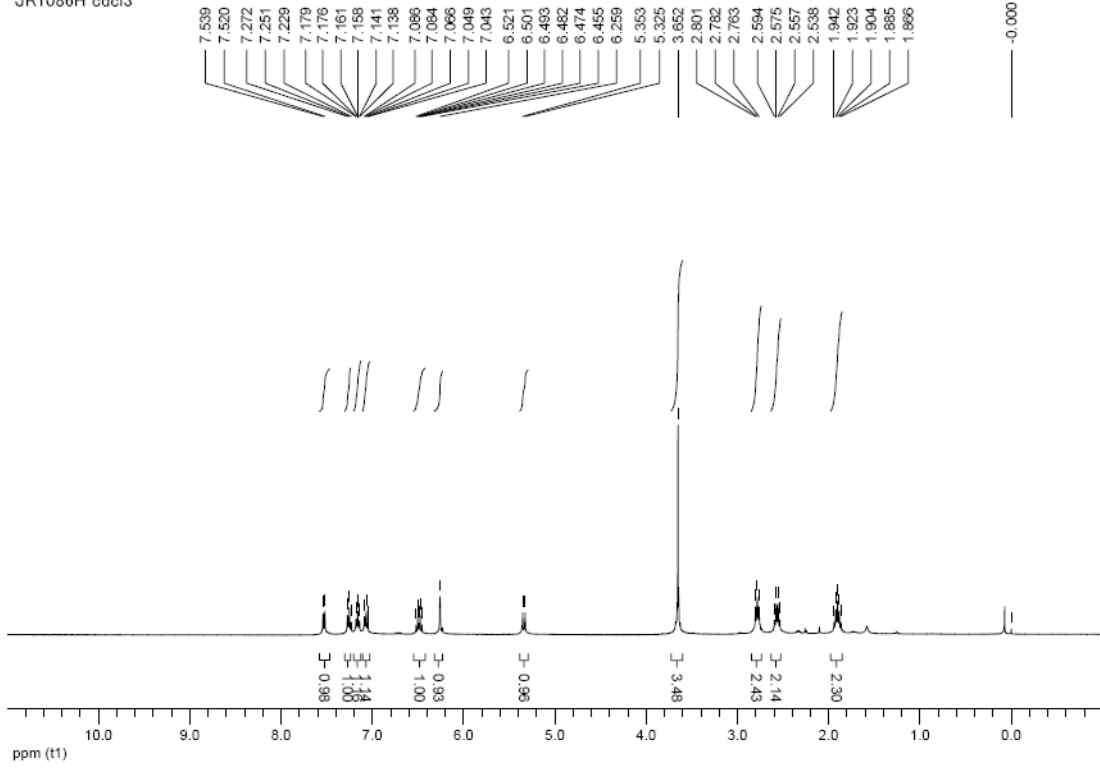
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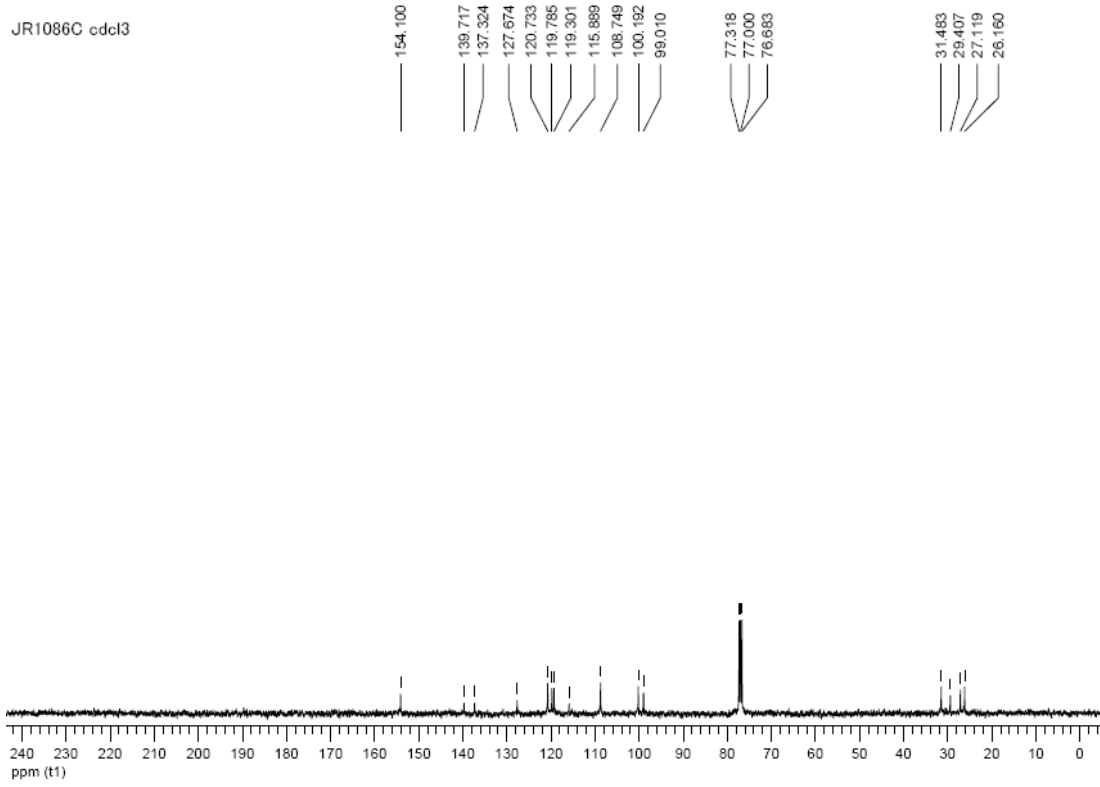


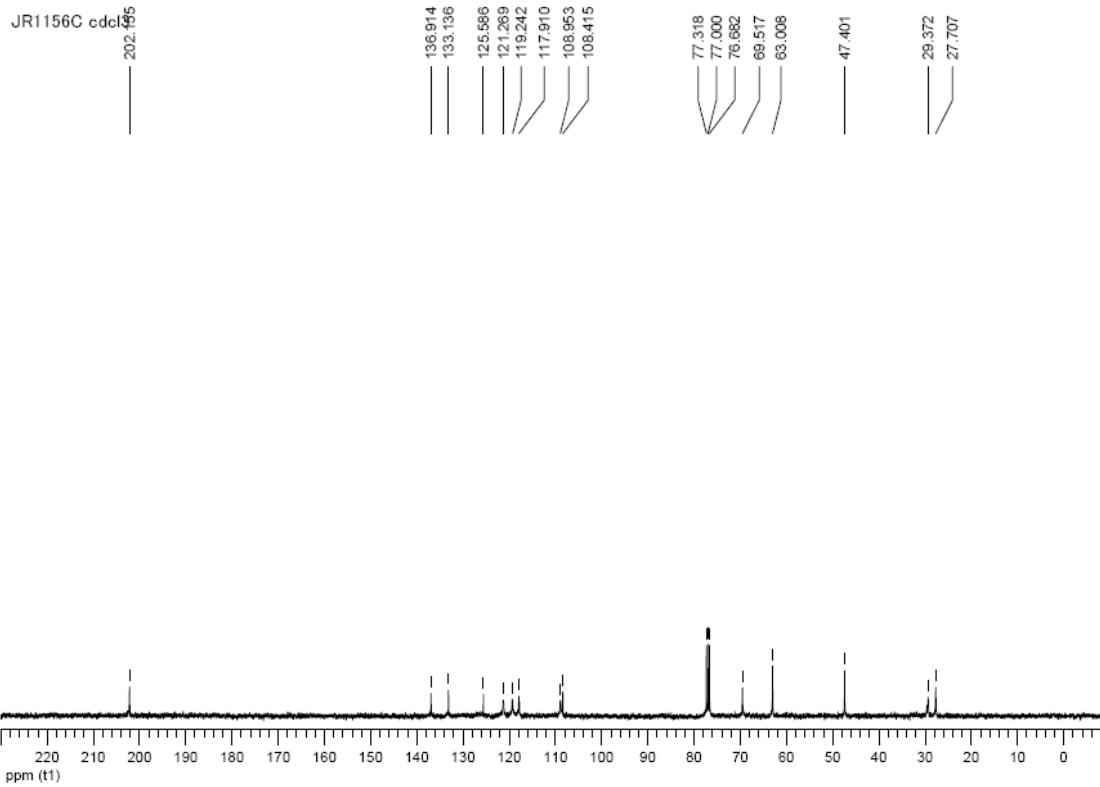
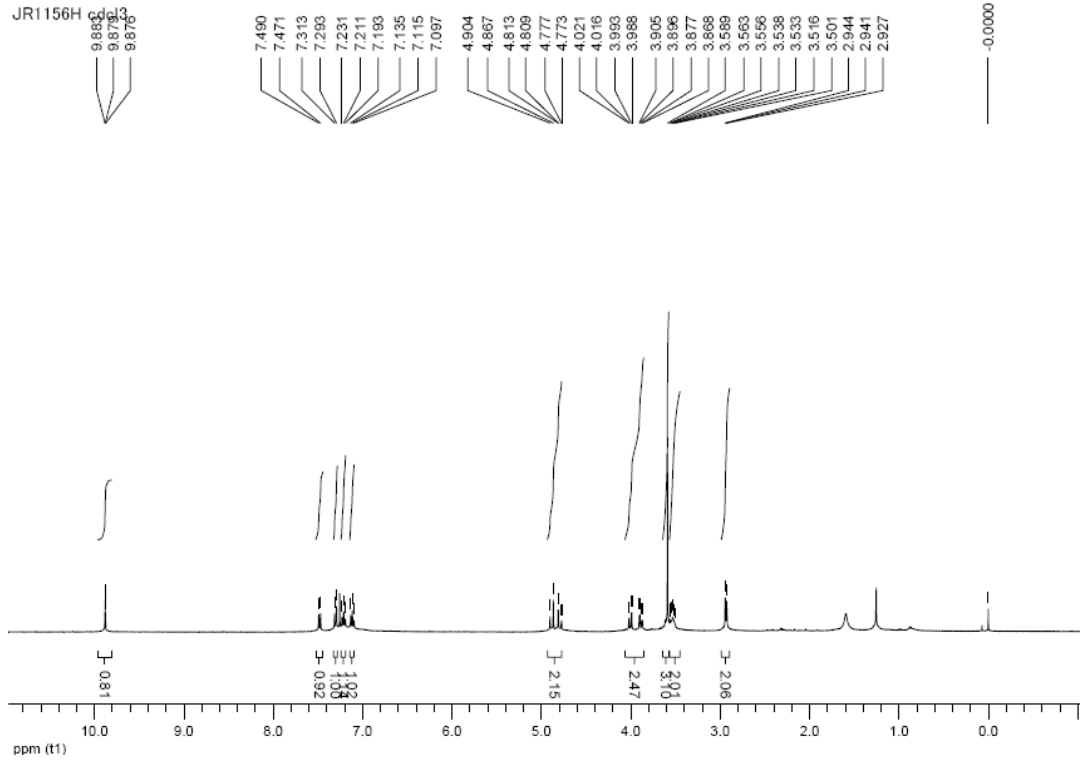
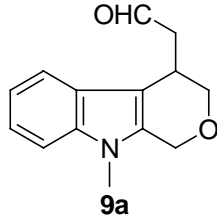


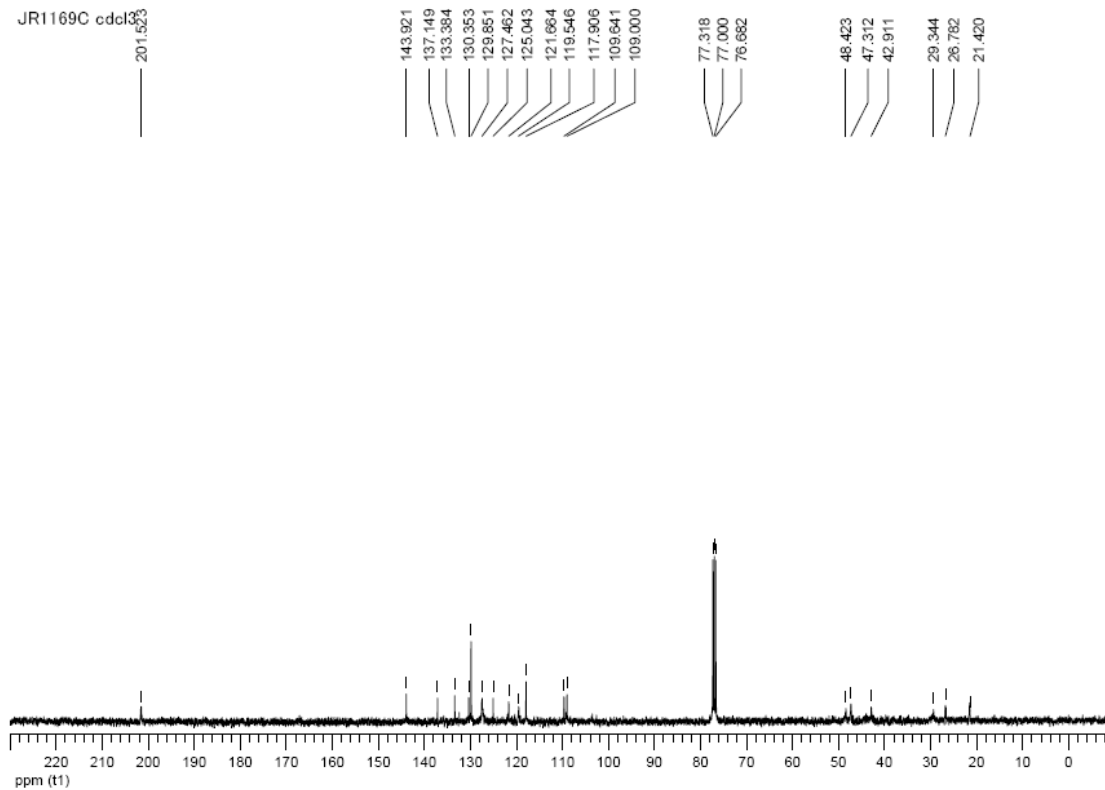
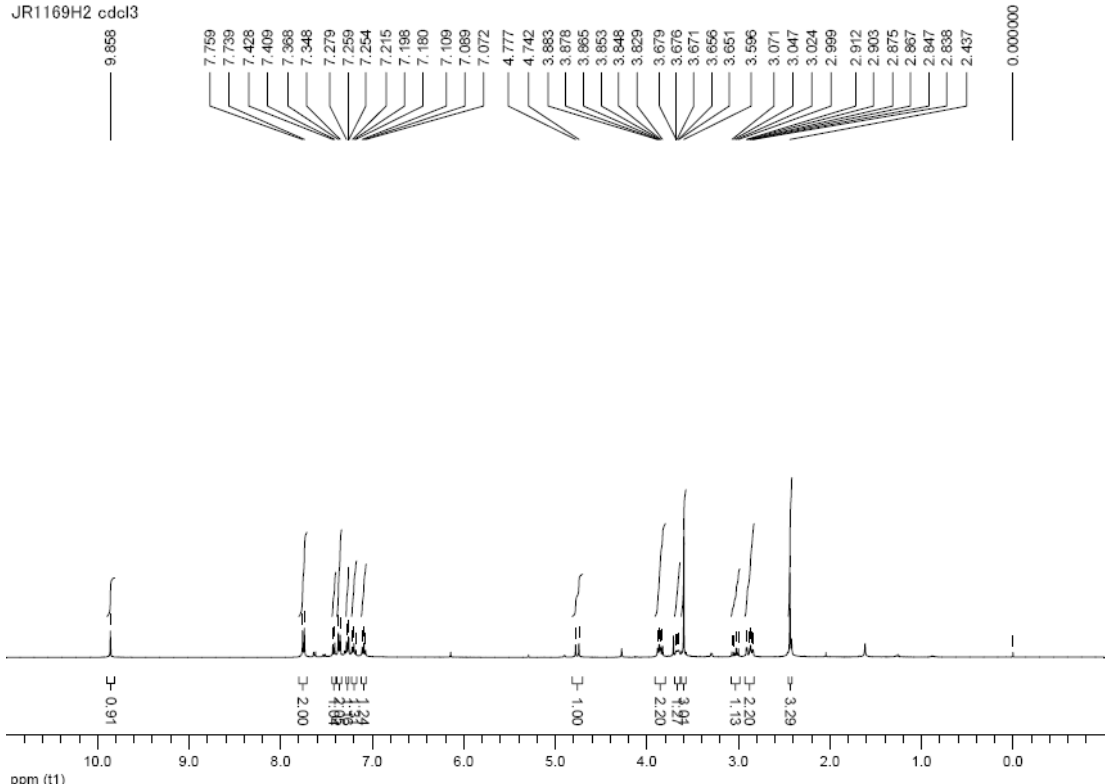
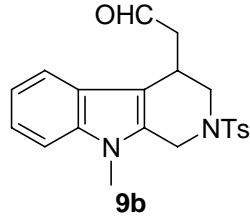
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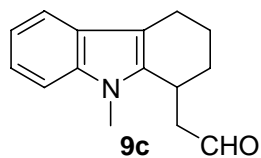


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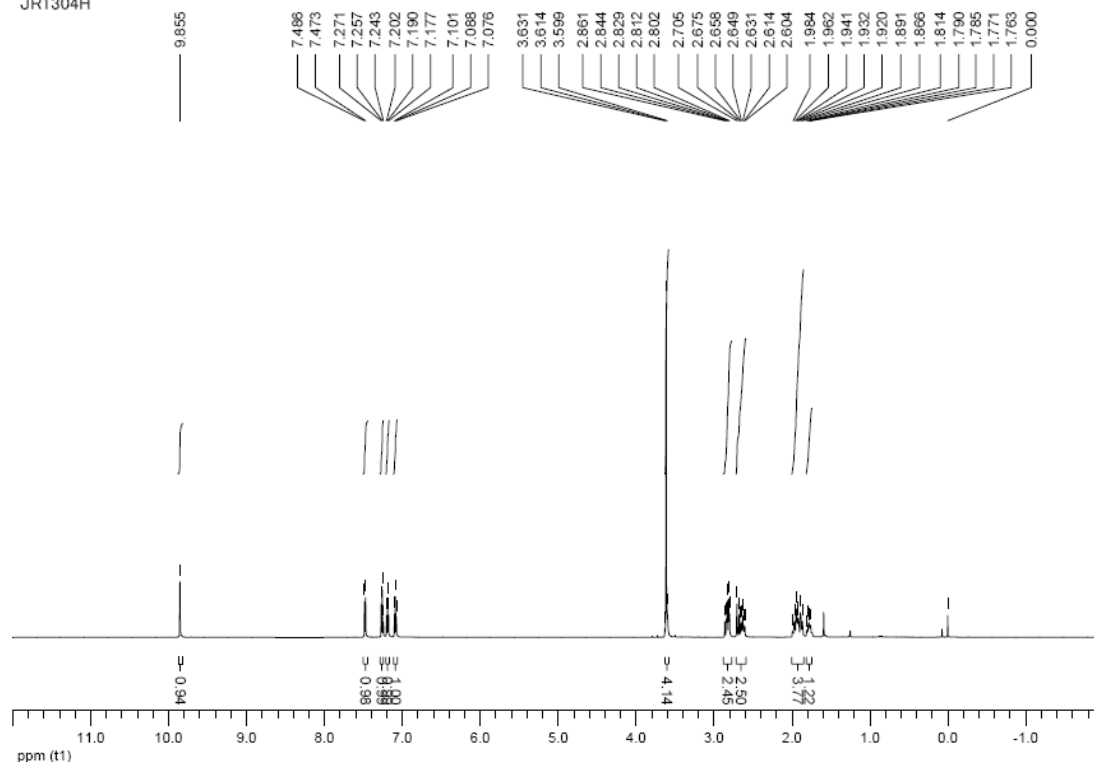




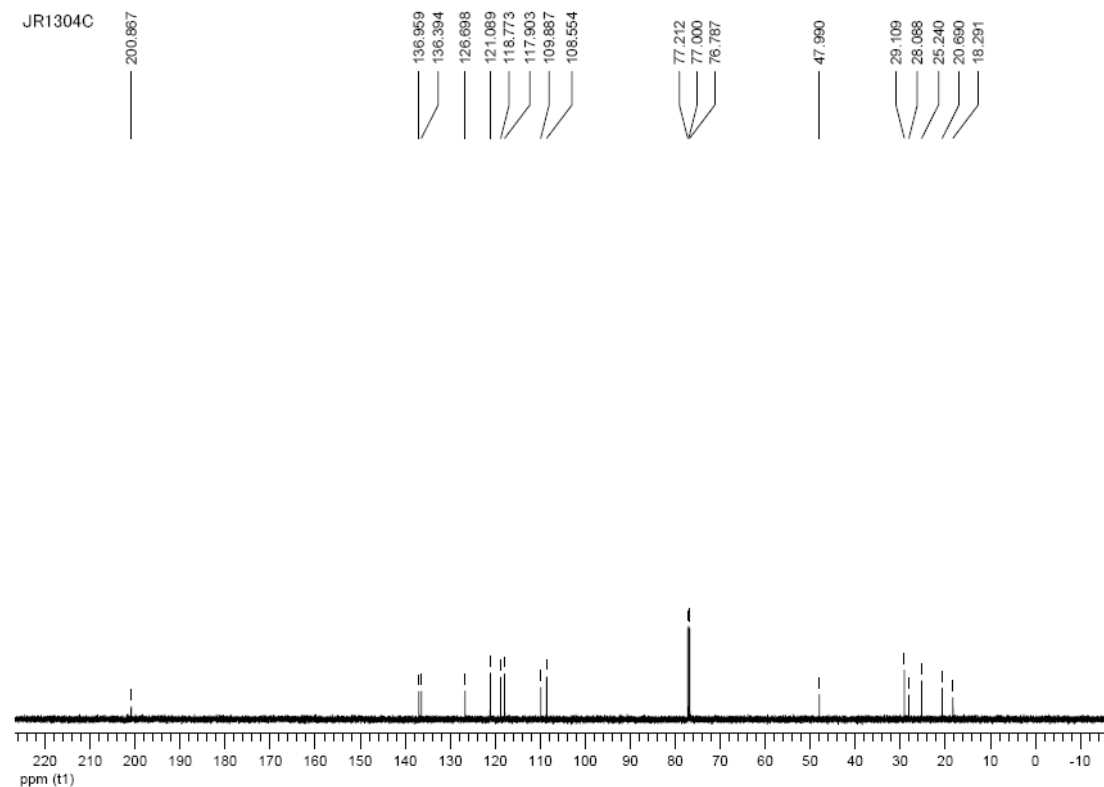


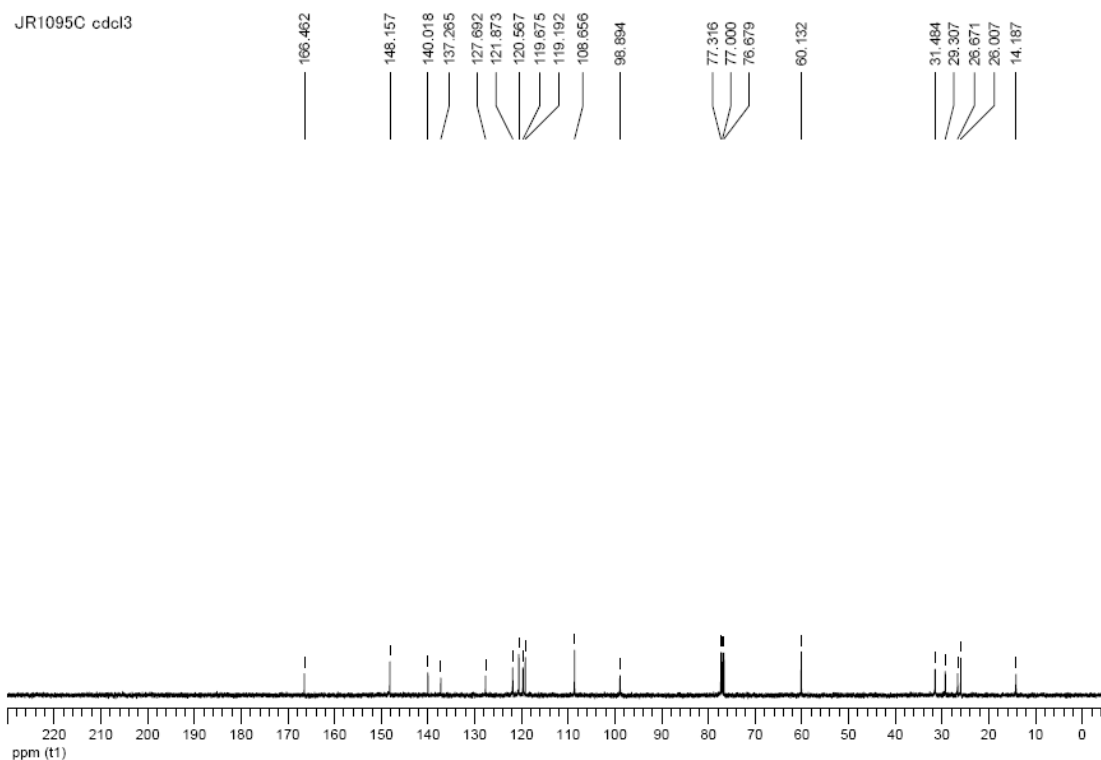
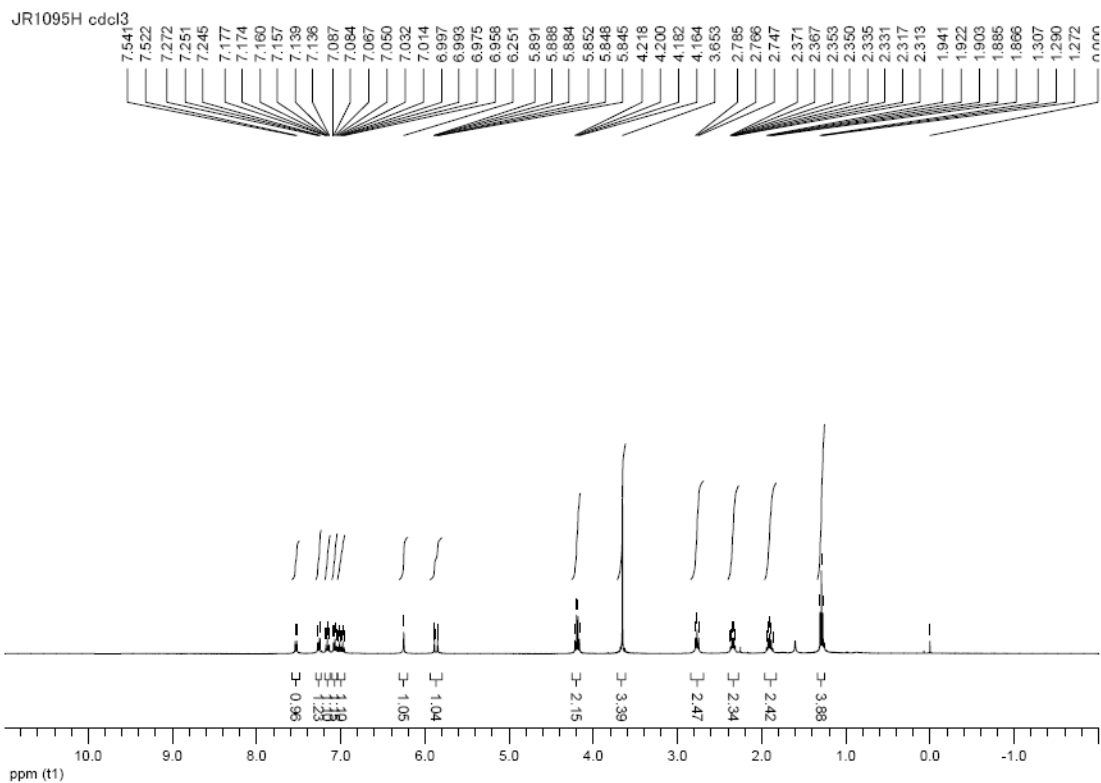
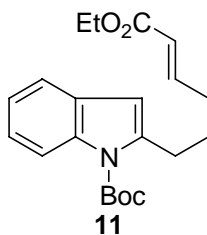


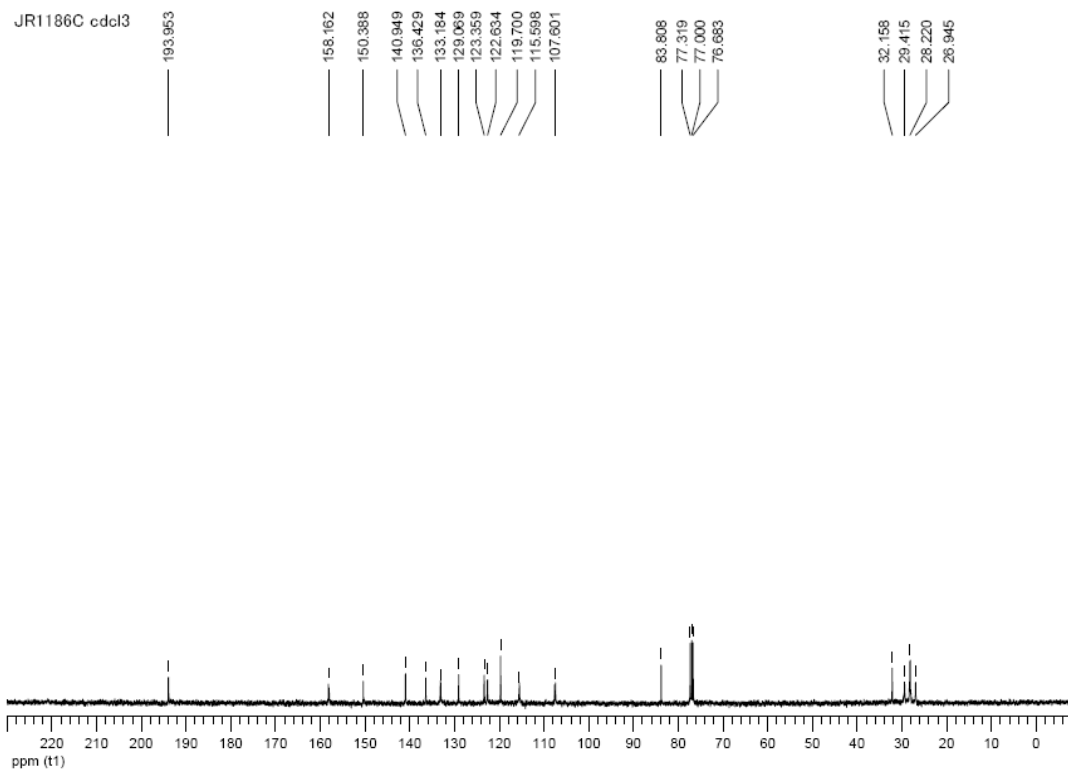
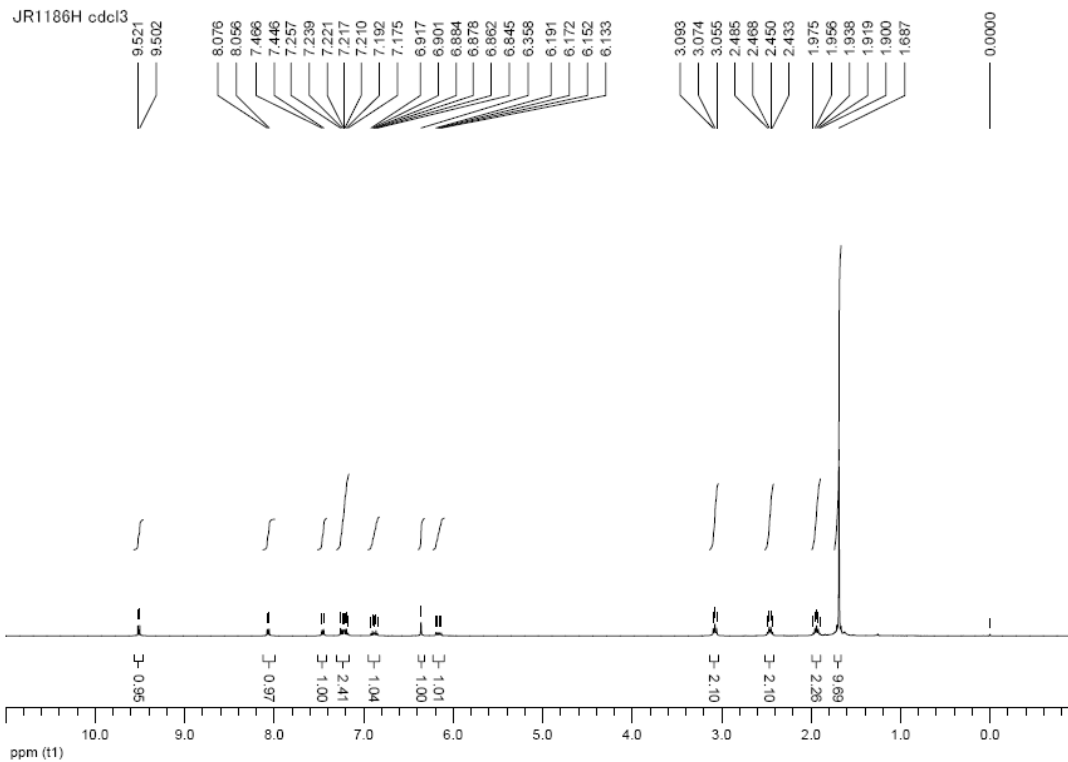
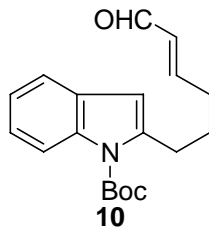
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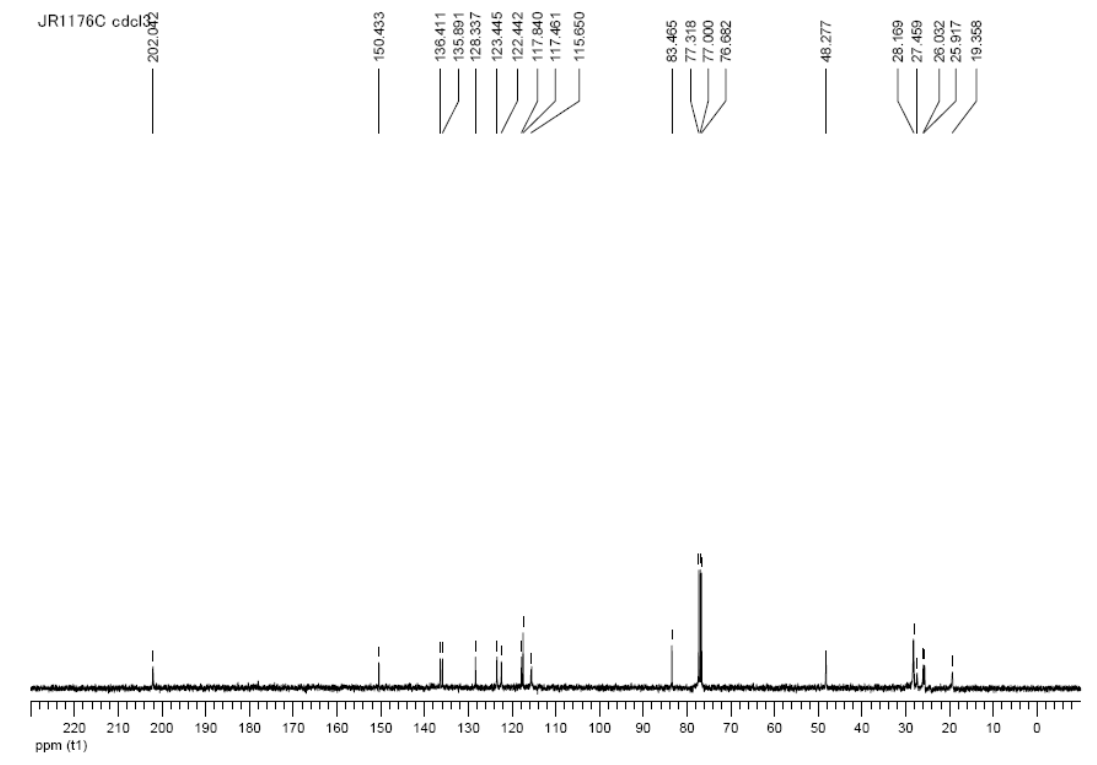
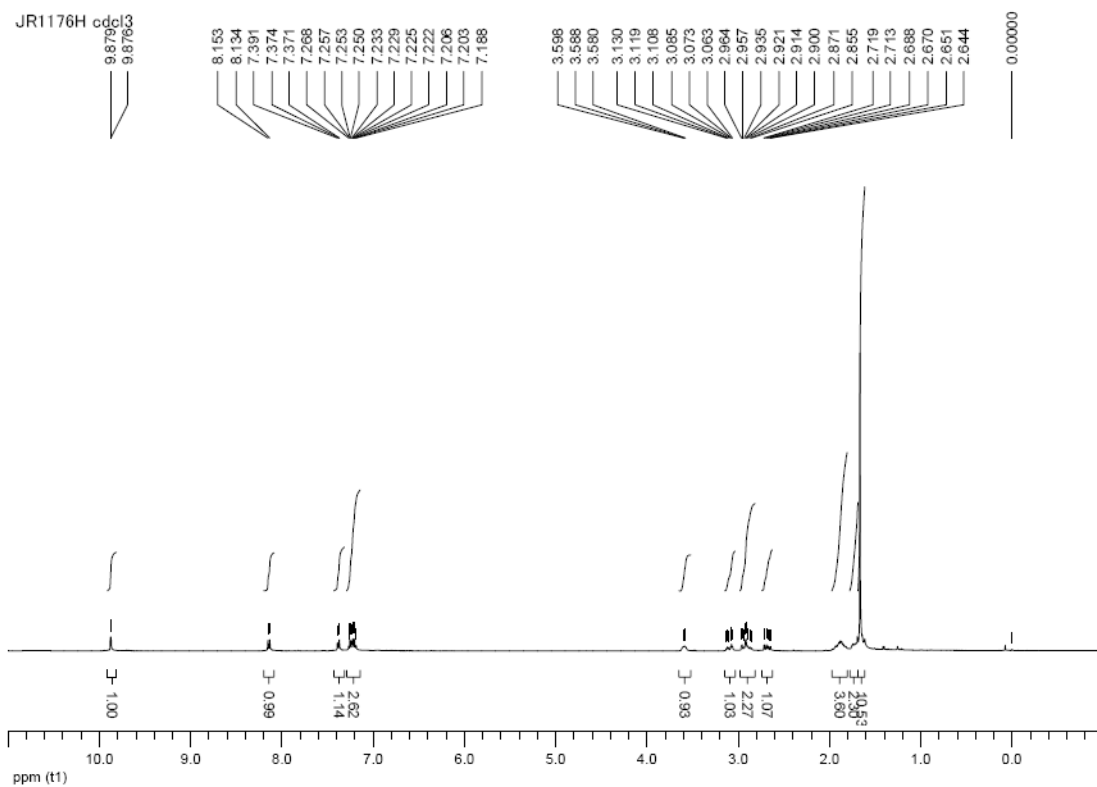
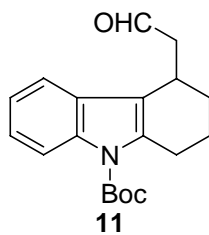


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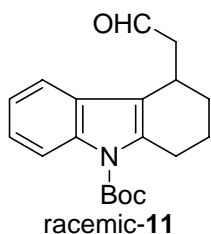
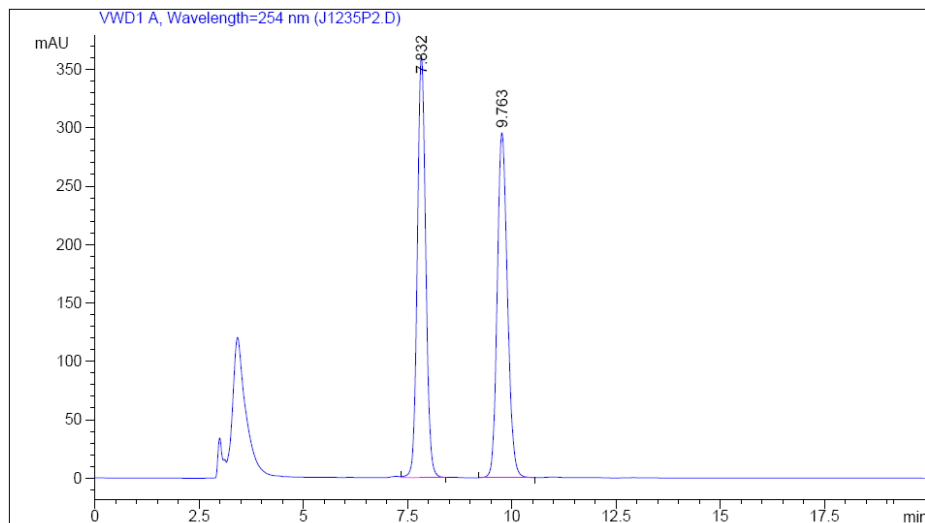




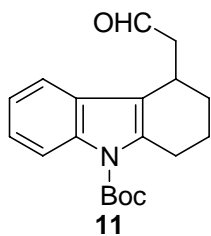
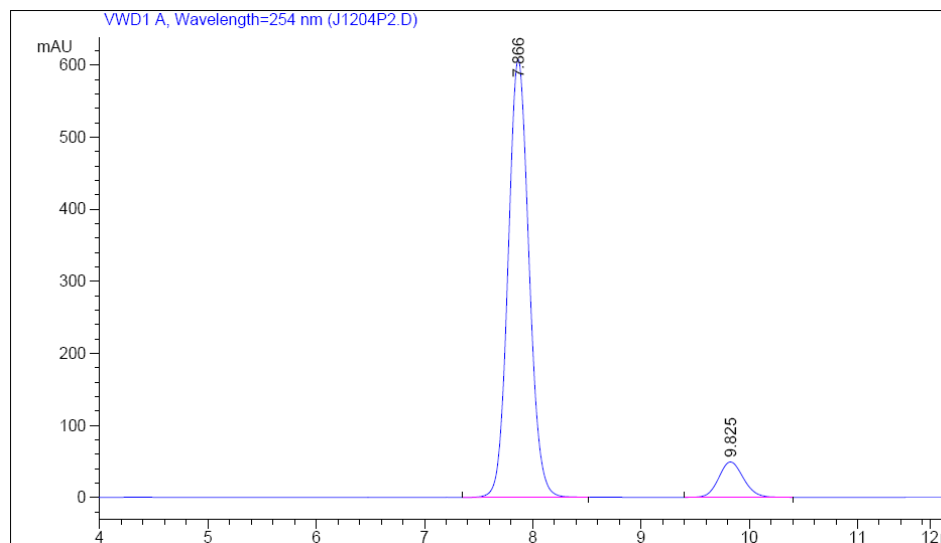




### HPLC spectra of 11



| Peak #   | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU] | Area %  |
|----------|---------------|------|-------------|-------------|--------------|---------|
| 1        | 7.832         | VB   | 0.2175      | 5060.74707  | 360.83337    | 50.1380 |
| 2        | 9.763         | BB   | 0.2643      | 5032.87939  | 295.37946    | 49.8620 |
| Totals : |               |      |             | 1.00936e4   | 656.21283    |         |



| Peak #   | RetTime [min] | Type | Width [min] | Area mAU *s | Height [mAU] | Area % |
|----------|---------------|------|-------------|-------------|--------------|--------|
| 1        | 7.866         | VB   | 0.2086      | 8133.73926  | 607.60486    | 91.182 |
| 2        | 9.825         | BB   | 0.2475      | 786.59705   | 49.23938     | 8.818  |
| Totals : |               |      |             | 8920.33630  | 656.84424    |        |