*(Supporting Information)*

# *GaN Nanowire as a Reusable Photoredox Catalyst for Radical Coupling of Carbonyl under Blacklight-Irradiation*

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## Materials and Methods

### 1. Growth of GaN Nanowires.

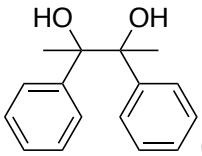
The nanowires are grown on a Si (111) wafer using radio frequency plasma-assisted molecular beam epitaxy (MBE) in nitrogen rich conditions. The Si substrates were cleaned in clean room in sequence by absolute methanol, acetone, and hydrofluoric acid prior of loading into the MBE system. Growth conditions: temperature ~750 ºC, nitrogen flow rate 1 sccm, forward plasma power ~400 W. The typical growth time for each catalyst is three hours, giving the equivalence of 2 mg GaN NW on a 2-inches wafer. The as-synthesized nanowires can be doped with tetravalent ($Si^{4+}$) or divalent ($Mg^{2+}$) ions for making n- and p- type semiconductors, respectively. The doping density is controlled by tuning the effusion cell temperatures of Si and Mg. For n-type doping, the Si effusion cell temperature is 1100 °C. For p-type doping, the Mg effusion cell temperature is 265 °C. The electron and hole concentrations for the Si-doped n-type and Mg-doped p-type GaN NWs were estimated to be on the order of $n = 5 \times 10^{18}$ $cm^{-3}$ and $p = 1 \times 10^{18}$ $cm^{-3}$, respectively. Other growth parameters were kept constant.

### 2. Photo-driven pinacol coupling reaction.

A slice (3.5 $cm^2$) of GaN NW (equivalent to 0.35 mg GaN) grown on Si(111) wafer was placed at the bottom of a glass flange equipped with a venting hose and a quartz window. The flange was then evacuated by oil pump for 30 min before the injection of ketone reactant (0.2 mmol) dissolved in 2 mL methanol. The flange was kept under a UV box equipped with HITACHI FL8BL-B black light bulb under room temperature for 12 h. After reaction, the crude reaction mixture can be characterized either by taking a drop of the methanol solution into NMR solvent for NMR study (solvent suppression mode can be applied to eliminate the huge methanol signal) or directly

stripped of methanol to give the desired product, which can be further purified by flash chromatography to obtain a higher purity grade.

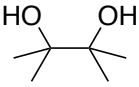
**3. Identification of product.**




**2a**[8] (iso. yield > 99%, calc. based on ketone; rac- : meso- = 1:1)

$^{1}$H-NMR ($CDCl_3$, ppm): rac-, 7.27 (m, 6H), 7.24 (m, 4H), 1.54 (s, 6H); meso-, 7.27 (m, 6H), 7.24 (m, 4H), 1.62 (s, 6H)

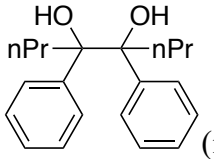
$^{13}$C-NMR ($CDCl_3$, ppm): rac-, 143.4, 127.4, 127.3, 126.9, 78.6, 25.0; meso-, 143.8, 127.4, 127.3, 126.9, 78.9, 25.1




**2b**[31] (iso. yield > 99%, calc. based on ketone)

$^{1}$H-NMR ($CDCl_3$, ppm): 2.17 (br, 2H), 1.24 (s, 12H)

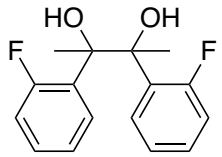
$^{13}$C-NMR ($CDCl_3$, ppm): 75.1, 24.9




**2c**[32] (iso. yield 97%, calc. based on ketone; rac- : meso- = 1:1.1)

$^{1}$H-NMR ($CDCl_3$, ppm): rac-, 7.25 (m, 6H), 7.15 (m, 4H), 2.06 (m, 4H),1.58 (m, 4H), 0.59 (m, 6H); meso-, 7.25 (m, 6H), 7.15 (m, 4H), 2.34 (m, 4H), 1.71 (m, 4H), 0.59 (m, 6H)

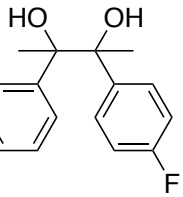
$^{13}$C-NMR ($CDCl_3$, ppm): rac-, 140.3, 128.3, 127.1, 126.6, 81.9, 27.7, 7.5, 7.5; meso-, 141.3, 128.3, 127.1, 126.8, 81.9, 28.1, 7.5, 7.5




**2d**[33] (iso. yield 95%, calc. based on ketone; rac- : meso- = 1.1:1)

$^{1}$H-NMR ($CDCl_3$, ppm): rac-, 7.45 (m, 2H), 7.26-7.10 (m, 4H), 6.95 (m, 2H), 3.09 (br, 2H), 1.64(s, 6H); meso-, 7.45 (m, 2H), 7.26-7.10 (m, 4H), 6.95 (m, 2H), 3.18 (br, 2H), 1.76 (s, 6H)

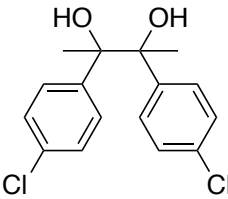
$^{13}$C-NMR ($CDCl_3$, ppm): rac-, 160.9 ($^{1}J_{C-F}$ = 201 Hz), 130.2, 129.3, 123.6, 123.2, 116.0 ($^{2}J_{C-F}$ = 45 Hz), 79.6, 24.0; meso-, 160.9 ($^{1}J_{C-F}$ = 201 Hz), 130.2, 129.3, 123.6, 123.2, 116.0 ($^{2}J_{C-F}$ = 45 Hz), 79.7, 24.5




**2e**[34] (iso. yield 98%, calc. based on ketone; rac- : meso- = 1:1)

$^{1}$H-NMR ($CDCl_3$, ppm): rac-, 7.20 (m, 2H), 7.14 (m, 2H), 6.94 (m, 4H), 1.52 (s, 6H); meso-, 7.20 (m, 2H), 7.14 (m, 2H), 6.94 (m, 4H), 1.60 (s, 6H)

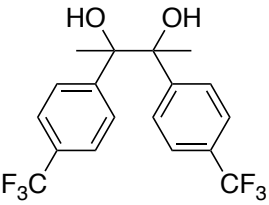
$^{13}$C-NMR ($CDCl_3$, ppm): rac-, 162.0 ($^{1}J_{C-F}$ = 245 Hz), 139.1, 128.8 ($^{2}J_{C-F}$ = 38 Hz), 114.0, 78.3, 24.9; meso-, 162.0 ($^{1}J_{C-F}$ = 245 Hz), 139.5, 128.8 ($^{2}J_{C-F}$ = 38 Hz), 114.0, 78.6, 25.2




**2f**[35] (iso. yield 93%, calc. based on ketone; rac- : meso- = 1:1.1)

$^{1}$H-NMR ($CDCl_3$, ppm): rac-, 7.23-7.08 (m, 8H), 1.47 (s, 6H); meso-, 7.23-7.08 (m, 8H), 1.55 (s, 6H)

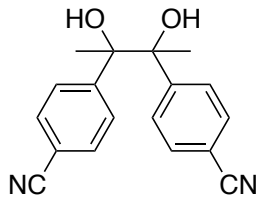
$^{13}$C-NMR ($CDCl_3$, ppm): rac-, 141.7, 133.0, 128.8, 127.3, 78.2, 24.8; meso-, 141.7, 133.0, 128.8, 127.3, 78.2, 25.1




**2g**[8] (iso. yield 99%, calc. based on ketone; rac- : meso- = 1.2:1)

$^{1}$H-NMR ($CDCl_3$, ppm): rac-, 7.50 (m, 6H), 7.29 (m, 2H), 1.53 (s, 6H); meso-, 7.50 (m, 6H), 7.29 (m, 2H), 1.57 (s, 6H)

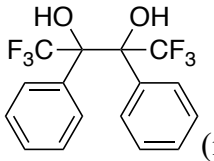
$^{13}$C-NMR ($CDCl_3$, ppm): rac-, 147.7, 147.1, 127.5, 127.4, 125.8 ($^{1}J_{C-F}$ = 240 Hz), 78.2, 24.8; meso-, 147.7, 147.1, 127.5, 127.4, 125.8 ($^{1}J_{C-F}$ = 240 Hz), 78.6, 25.2

**2h**[36] 

(iso. yield 94%, calc. based on ketone; rac- : meso- = 1:1.3)

$^{1}$H-NMR (acetone-d6, ppm): rac-, 7.68 (m, 4H), 7.41 (m, 4H), 4.59 (br, 2H), 1.48 (s, 6H); meso-, 7.75 (m, 4H), 7.49 (m, 4H), 4.77 (br, 2H), 1.75 (s, 6H)

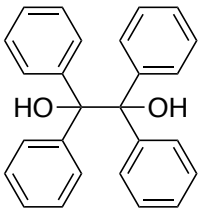
$^{13}$C-NMR (DMSO-d6, ppm): rac-, 152.5, 131.0, 128.4, 119.6, 108.9, 77.4, 24.7; meso-, 152.5, 130.9, 129.1, 119.6, 109.3, 77.4, 24.7

**2i**[37] 

(iso. yield 97%, calc. based on ketone; rac- : meso- = 1:1.2)

$^{1}$H-NMR ($CDCl_3$, ppm): rac-, 7.48 (m, 2H), 7.33 (m, 8H), 3.51 (br, 2H), meso-, 7.48 (m, 2H), 7.33 (m, 8H), 3.58 (br, 2H)

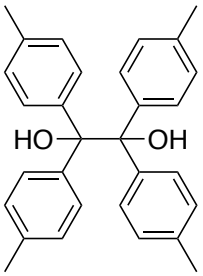
$^{13}$C-NMR ($CDCl_3$, ppm): rac-, 133.5, 129.0, 127.8, 127.1 ($^{1}J_{C-F}$ = 201 Hz), 126.9, 80.2; meso-, 133.6, 129.0, 127.8, 127.1 ($^{1}J_{C-F}$ = 201 Hz), 126.9, 80.4

**2j**[8] 

(iso. yield > 99%, calc. based on ketone)

$^{1}$H-NMR ($CDCl_3$, ppm): 7.28 (m, 8H), 7.18 (m, 12H), 3.02 (br, 2H)

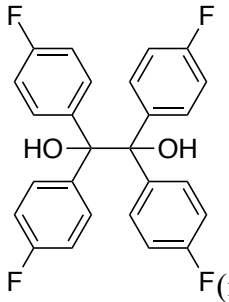
$^{13}$C-NMR ($CDCl_3$, ppm): 144.1, 128.6, 127.3, 126.9, 83.0




**2k**[38] (iso. yield 98%, calc. based on ketone)

$^{1}$H-NMR ($CDCl_3$, ppm): 7.15 (m, 8H), 6.97 (m, 8H), 2.28 (s, 12H)

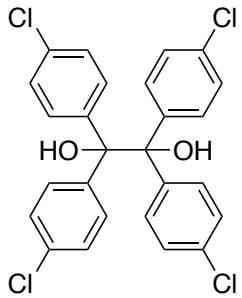
$^{13}$C-NMR ($CDCl_3$, ppm): 141.5, 136.3, 128.5, 127.9, 82.8, 21.0




**2l**[8] (iso. yield 96%, calc. based on ketone)

$^{1}$H-NMR ($CDCl_3$, ppm): 7.25 (m, 8H), 6.90 (m, 8H), 2.88 (br, 2H)

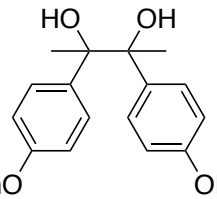
$^{13}$C-NMR ($CDCl_3$, ppm): 161.8 ($^{1}J_{C\text{-}F}$ = 250 Hz), 139.7, 130.3, 114.3 ($^{2}J_{C\text{-}F}$ = 21 Hz), 82.6




**2m**[8] (iso. yield 97%, calc. based on ketone)

$^{1}$H-NMR ($CDCl_3$, ppm): 7.19 (m, 16H), 2.84 (br, 2H)

$^{13}$C-NMR ($CDCl_3$, ppm): 142.0, 133.5, 129.8, 127.7, 82.5

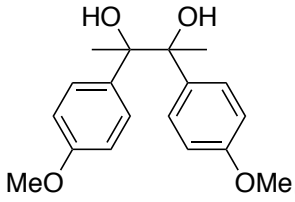



**2n** (iso. yield > 99%, calc. based on ketone; rac- : meso- = 1.1:1)

$^{1}$H-NMR ($CDCl_3$, ppm): rac-, 7.36-6.92 (m, 18H), 1.55 (s, 6H); meso-, 7.36-6.92 (m, 18H), 1.64 (s, 6H)

$^{13}$C-NMR ($CDCl_3$, ppm): rac-, 157.1, 156.3, 138.3, 129.7, 128.4, 123.3, 118.9, 117.4, 78.7, 25.0; meso-, 157.1, 156.3, 138.3, 129.7, 128.8, 123.3, 118.9, 117.4, 78.7, 25.0

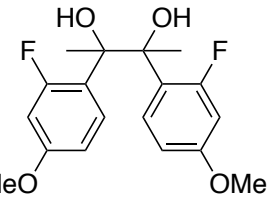
HR-MS: ESI $[C_{28}H_{25}O_4Na]^+$ calc.: 448.1651, found: 448.1610




**2o**[33] (iso. yield > 99%, calc. based on ketone; rac- : meso- = 1.3:1)

$^{1}$H-NMR ($CDCl_3$, ppm): rac-, 7.09 (m, 4H), 6.79 (m, 4H), 3.79 (s, 6H), 1.46 (s, 6H); meso-, 7.09 (m, 4H), 6.79 (m, 4H), 3.81 (s, 6H), 1.55 (s, 6H)

$^{13}$C-NMR ($CDCl_3$, ppm): rac-, 158.5, 135.6, 128.5, 112.4, 78.7, 55.1, 25.0; meso-, 158.5, 135.6, 128.5, 112.4, 78.7, 55.1, 25.0

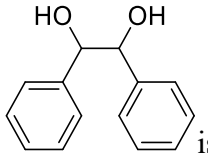



**2p** (iso. yield > 99%, calc. based on ketone; rac- : meso- = 1:1)

$^{1}$H-NMR ($CDCl_3$, ppm): rac-, 7.35 (t, 1H), 7.04 (t, 1H), 6.67 (m, 1H), 6.56 (m, 2H), 6.44 (m, 1H), 3.79 (s, 6H), 2.99 (br, 2H), 1.62 (s, 6H); meso-, 7.35 (t, 1H), 7.04 (t, 1H), 6.67 (m, 1H), 6.56 (m, 2H), 6.44 (m, 1H), 3.82 (s, 6H), 3.09 (br, 2H), 1.74 (s, 6H)

$^{13}$C-NMR ($CDCl_3$, ppm): rac-, 161.0 ($^{1}J_{C\text{-}F}$ = 245 Hz), 160.0, 130.5, 122.0, 109.2, 101.8 ($^{2}J_{C\text{-}F}$ = 57 Hz), 79.4, 55.5, 24.1; meso-, 161.1 ($^{1}J_{C\text{-}F}$ = 245 Hz), 160.1, 130.6, 122.2, 109.3, 101.8 ($^{2}J_{C\text{-}F}$ = 57 Hz), 79.4, 55.5, 24.5

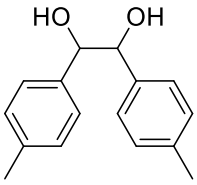
HR-MS: ESI $[C_{18}H_{19}O_4F_2Na]^+$ calc.: 360.1149, found: 360.1111



**2q**[39] iso. yield 75%, calc. based on aldehyde; rac- : meso- = 1:1)

$^{1}$H-NMR ($CDCl_3$, ppm, rac- and meso-): 7.33-7.28 (m, 10H), 4.86 (s, 2H), 2.22 (br, 2H)

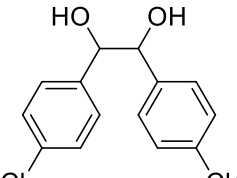
$^{13}$C-NMR ($CDCl_3$, ppm, rac- and meso-): 139.8, 128.3, 128.1, 127.1, 78.1



**2r**[39] (iso. yield 75%, calc. based on aldehyde; rac- : meso- = 1:1.3)

$^{1}$H-NMR ($CDCl_3$, ppm): rac-, 7.17-7.03 (m, 8H), 4.66 (s, 2H) 2.29 (s, 6H); meso-, 7.17-7.03 (m, 8H), 4.73 (s, 2H), 2.33 (s, 6H)

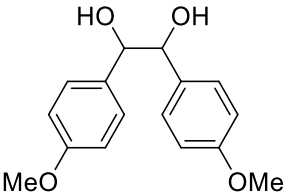
$^{13}$C-NMR ($CDCl_3$, ppm): rac-, 137.8, 136.9, 128.9, 127.0, 78.0, 21.1; meso-, 137.8, 136.9, 128.9, 127.0, 78.7, 21.1



**2s**[39] (iso. yield 69%, calc. based on aldehyde; rac- : meso- = 1.2:1)

$^{1}$H-NMR ($CDCl_3$, ppm): rac-, 7.25-7.01 (m, 8H), 4.59 (s, 2H) 2.61 (br, 2H); meso-, 7.25-7.01 (m, 8H), 4.81 (s, 2H) 2.61 (br, 2H)

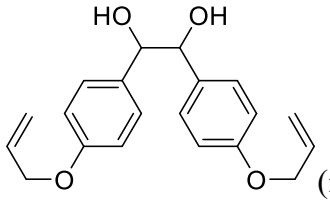
$^{13}$C-NMR ($CDCl_3$, ppm, rac- and meso-): 137.9, 133.8, 128.4, 128.3, 78.5



**2t**[39] (iso. yield 61%, calc. based on aldehyde; rac- : meso- = 1:1)

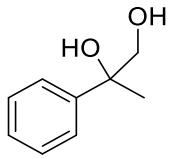
$^{1}$H-NMR ($CDCl_3$, ppm, rac- and meso-): 7.20 (d, 4H), 6.84 (d, 4H), 4.72 (s, 2H), 3.79 (s, 6H), 2.14 (br, 2H)

$^{13}$C-NMR (DMSO-d6, ppm, rac- and meso-): 158.4, 134.8, 128.8, 113.4, 76.8, 55.3

**2u**[39]  (iso. yield 54%, calc. based on aldehyde; rac- : meso- = 1:1.7)

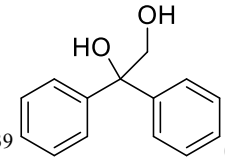
$^{1}$H-NMR (DMSO-d6, ppm): rac-, 6.99 (d, 4H), 6.75 (d, 4H), 6.00 (m, 2H), 5.41 (m, 4H), 5.03 (br, 2H), 4.52 (m, 4H); meso-, 7.11 (d, 4H), 6.83 (d, 4H), 6.00 (m, 2H), 5.26 (m, 4H), 5.03 (br, 2H), 4.51 (m, 4H)

$^{13}$C-NMR ($CDCl_3$, ppm): rac-, 158.2, 133.2, 133.1, 128.1, 117.7, 114.3, 78.8, 68.8; meso-, 158.2, 133.2, 133.1, 128.1, 117.7, 114.5, 77.8, 68.8

**5a**[39]  (iso. yield 91%)

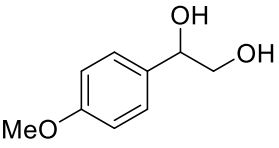
$^{1}$H-NMR ($CDCl_3$, ppm): 7.38-7.23 (m, 5H), 3.65-3.53 (m, 2H), 3.35 (br, 1H), 2.91 (br, 1H), 1.45 (s, 3H)

$^{13}$C-NMR ($CDCl_3$, ppm): 145.1, 128.3, 127.5, 125.1, 74.9, 70.8, 25.9

**5b**[39]  (iso. yield 93%)

$^{1}$H-NMR ($CDCl_3$, ppm): 7.42-7.24 (m, 10H), 4.16 (d, 2H), 3.22 (br, 1H), 1.94 (br, 1H)

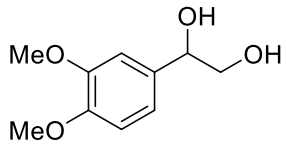
$^{13}$C-NMR ($CDCl_3$, ppm): 143.8, 128.4, 127.4, 126.4, 78.5, 69.4




**5c**[39] (iso. yield 83%)

$^1$H-NMR ($CDCl_3$, ppm): 7.26 (d, 2H), 6.87 (d, 2H), 4.75 (m, 1H), 3.78 (s, 3H), 3.62 (m, 2H), 2.80 (br, 1H), 2.42 (br, 1H)

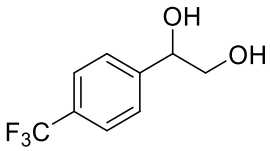
$^{13}$C-NMR ($CDCl_3$, ppm): 159.4, 132.6, 127.3, 113.9, 74.3, 68.0, 55.3




**5d**[39] (iso. yield 81%)

$^1$H-NMR ($CDCl_3$, ppm): 6.90-6.83 (m, 3H), 4.75 (m, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.67 (m, 2H), 2.64 (br, 1H), 2.20 (br, 1H)

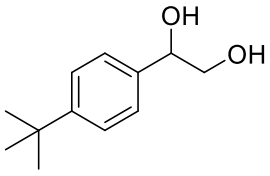
$^{13}$C-NMR ($CDCl_3$, ppm): 148.8, 148.7, 133.11, 118.3, 111.1, 109.1, 74.4, 68.1, 55.9




**5e**[39] (iso. yield 82%)

$^1$H-NMR ($CDCl_3$, ppm): 7.60 (d, 2H), 7.50 (d, 2H), 4.86 (m, 1H), 3.79-3.63 (m, 2H), 2.81 (br, 1H), 2.20 (br, 1H)

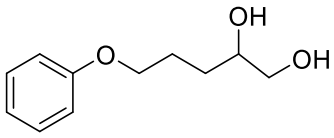
$^{13}$C-NMR ($CDCl_3$, ppm): 144.4, 129.9 ($^2J_{C\text{-}F}$ = 130 Hz), 126.4, 125.4, 124.1 ($^1J_{C\text{-}F}$ = 272 Hz) 74.0, 67.9




**5f**[39] (iso. yield 91%)

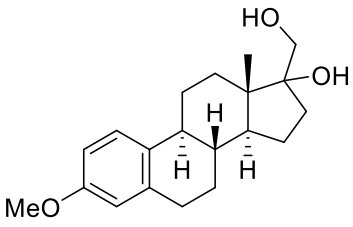
$^1$H-NMR ($CDCl_3$, ppm): 7.38 (d, 2H), 7.28 (d, 2H), 4.80 (m, 1H), 3.69 (m, 2H), 2.58 (br, 1H), 2.21 (br, 1H), 1.30 (s, 9H)

$^{13}$C-NMR ($CDCl_3$, ppm): 151.0, 137.5, 125.8, 125.5, 74.5, 68.0, 34.5, 31.3

**5g**[39]  (iso. yield 89%)

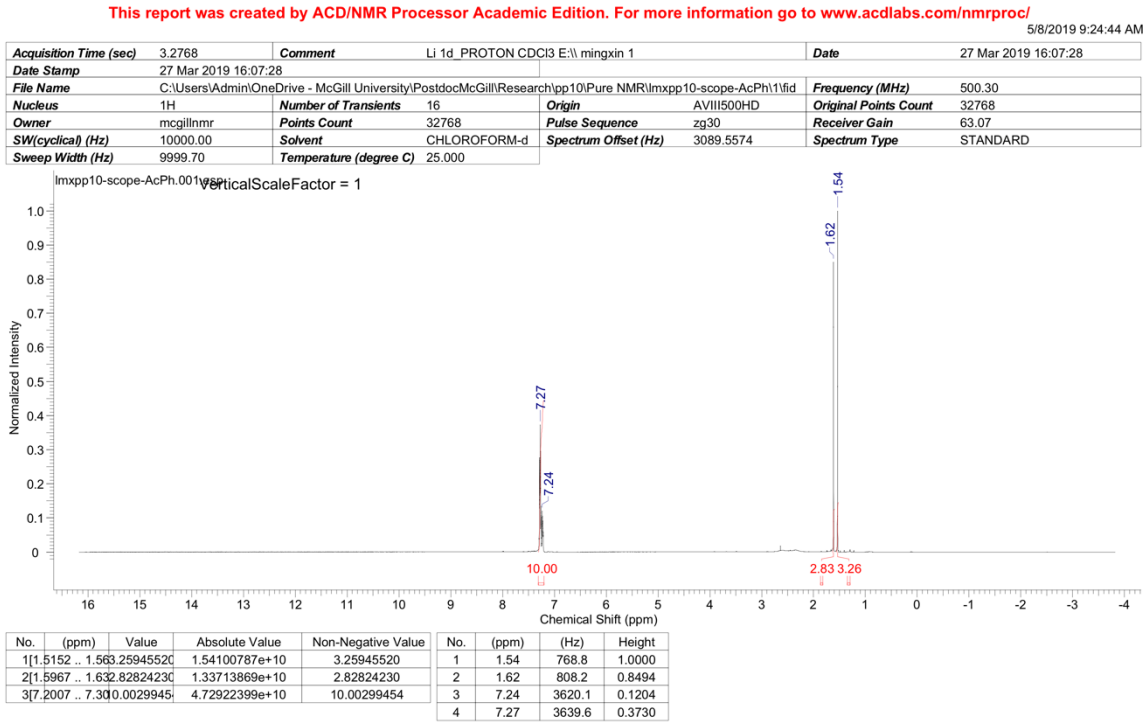
$^{1}$H-NMR ($CDCl_3$, ppm): 7.30 (m, 2H), 6.92 (m, 3H), 4.01 (m, 2H), 3.80 (m, 1H), 3.68-3.50 (m, 2H), 3.05 (br, 1H), 2.76 (br, 1H), 1.99-1.88 (m, 2H), 1.62 (m, 2H)

$^{13}$C-NMR ($CDCl_3$, ppm): 158.8, 129.5, 120.8, 114.5, 72.0, 67.7, 66.8, 29.9, 25.5

**5h**[39]  (iso. yield 62%)

$^{1}$H-NMR ($CDCl_3$, ppm): 7.18 (d, 1H), 6.71 (dd, J = 8.5, 2.1 Hz, 1H), 6.62 (s, 1H), 3.79 (d, 1H), 3.76 (s, 3H), 3.61 (d, 1H), 2.84 (dd, J = 22.0, 11.3 Hz, 2H), 2.35-2.20 (m, 2H), 2.20 (s, 1H), 2.01-1.76 (m, 6H), 1.75-1.63 (m, 2H), 1.57-1.39 (m, 3H), 1.31 (dt, J = 17.5, 8.2 Hz, 1H), 0.78 (s, 3H)

$^{13}$C-NMR ($CDCl_3$, ppm): 157.4, 138.0, 132.7, 126.3, 113.8, 111.5, 83.9, 66.9, 55.2, 49.6, 46.6, 43.6, 38.8, 34.6, 31.7, 29.9, 27.8, 26.2, 23.6, 15.1




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
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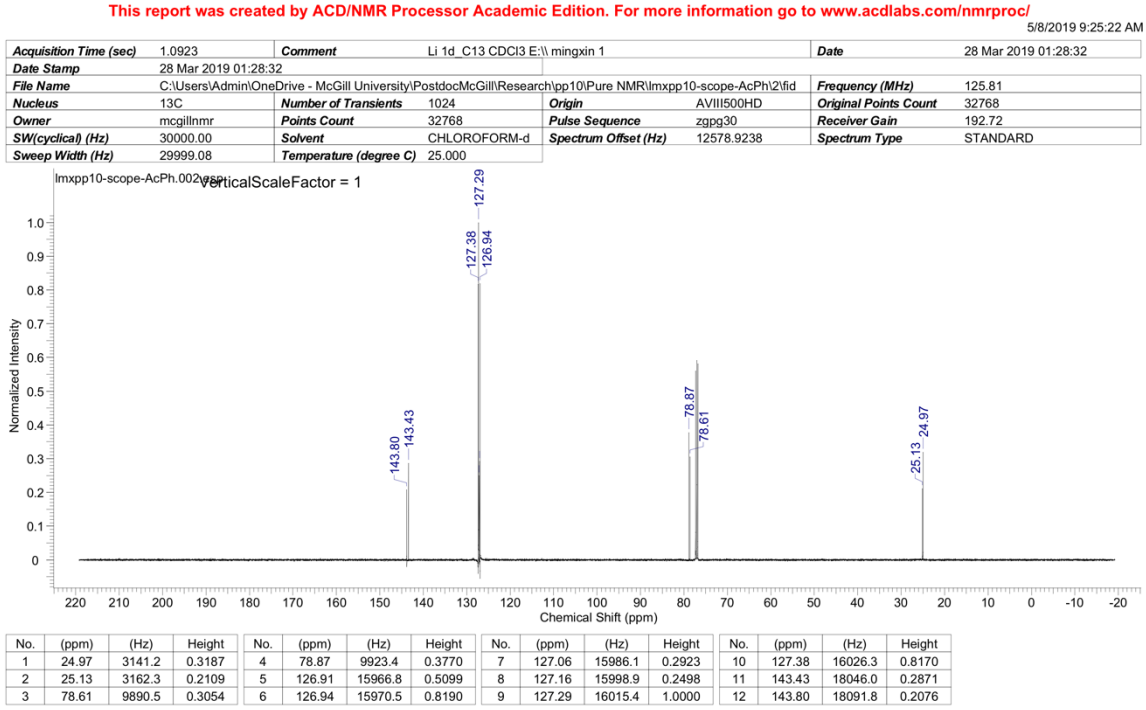
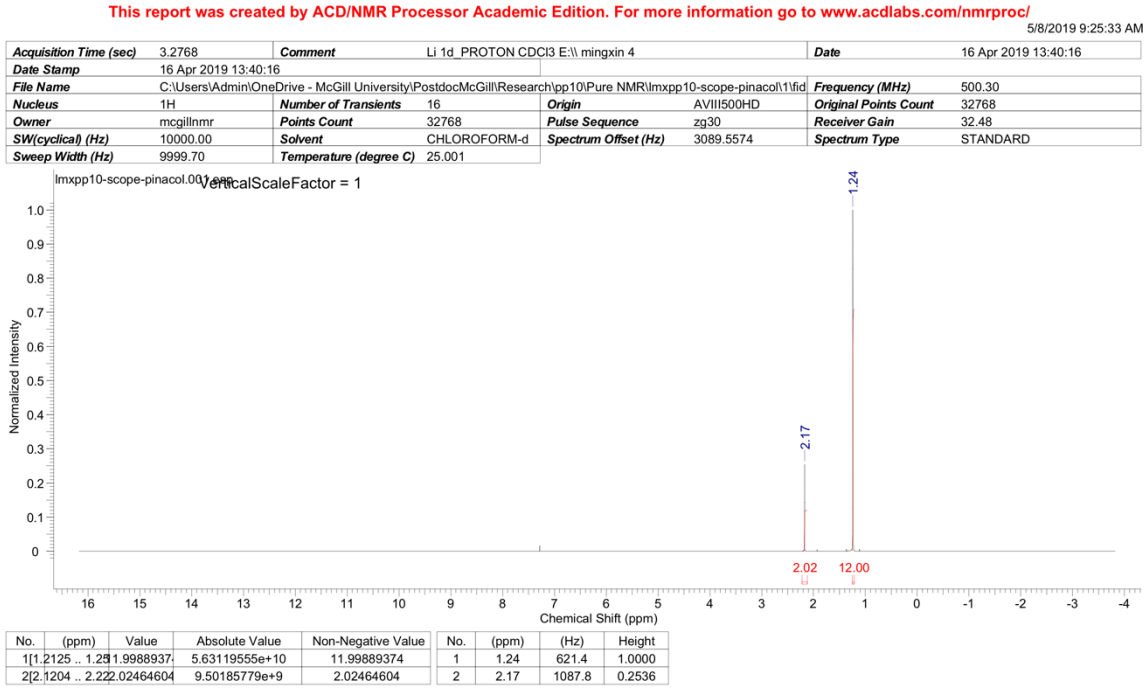
| 1 | [1.5152 .. 1.563 | 3.25945520 | 1.54100787e+10 | 3.25945520 |
| 2 | [1.5967 .. 1.632 | 2.82824230 | 1.33713869e+10 | 2.82824230 |
| 3 | [7.2007 .. 7.301 | 0.0029945 | 4.72922399e+10 | 10.00299454 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 1.54 | 768.8 | 1.0000 |
| 2 | 1.62 | 808.2 | 0.8494 |
| 3 | 7.24 | 3620.1 | 0.1204 |
| 4 | 7.27 | 3639.6 | 0.3730 |




| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 24.97 | 3141.2 | 0.3187 |
| 2 | 25.13 | 3162.3 | 0.2109 |
| 3 | 78.61 | 9890.5 | 0.3054 |
| 4 | 78.87 | 9923.4 | 0.3770 |
| 5 | 126.91 | 15966.8 | 0.5099 |
| 6 | 126.94 | 15970.5 | 0.8190 |
| 7 | 127.06 | 15986.1 | 0.2923 |
| 8 | 127.16 | 15998.9 | 0.2498 |
| 9 | 127.29 | 16015.4 | 1.0000 |
| 10 | 127.38 | 16026.3 | 0.8170 |
| 11 | 143.43 | 18046.0 | 0.2871 |
| 12 | 143.80 | 18091.8 | 0.2076 |

Figure S1. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2a**



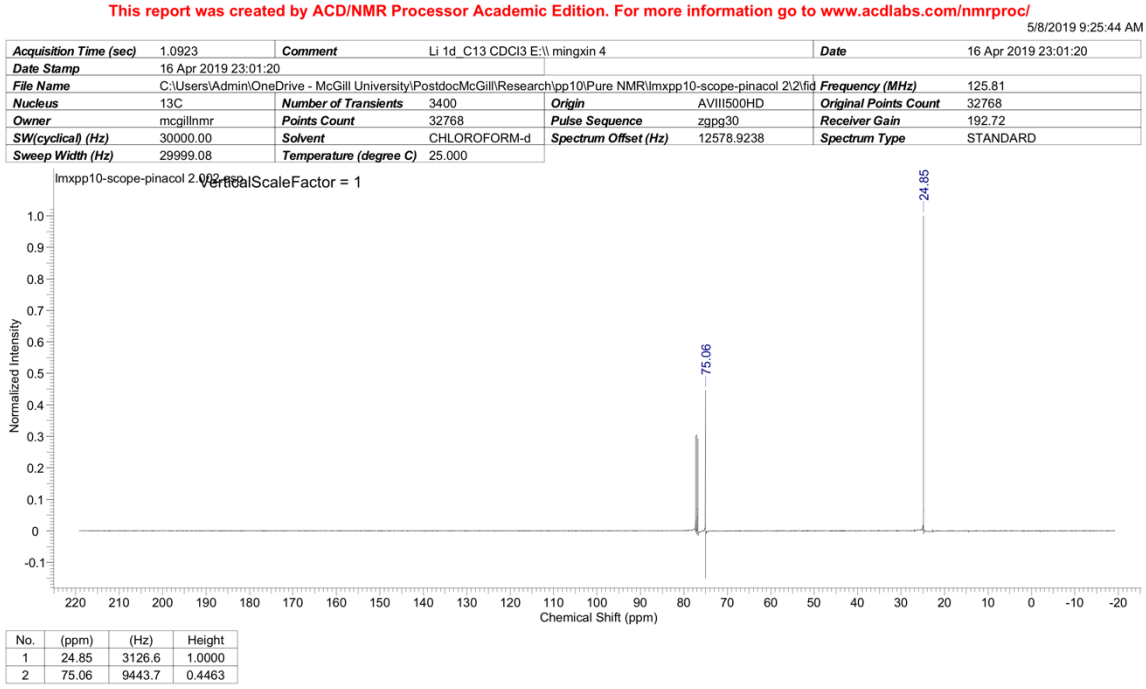




Figure S2. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2b**

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| | | | | | | | |
|---|---|---|---|---|---|---|---|
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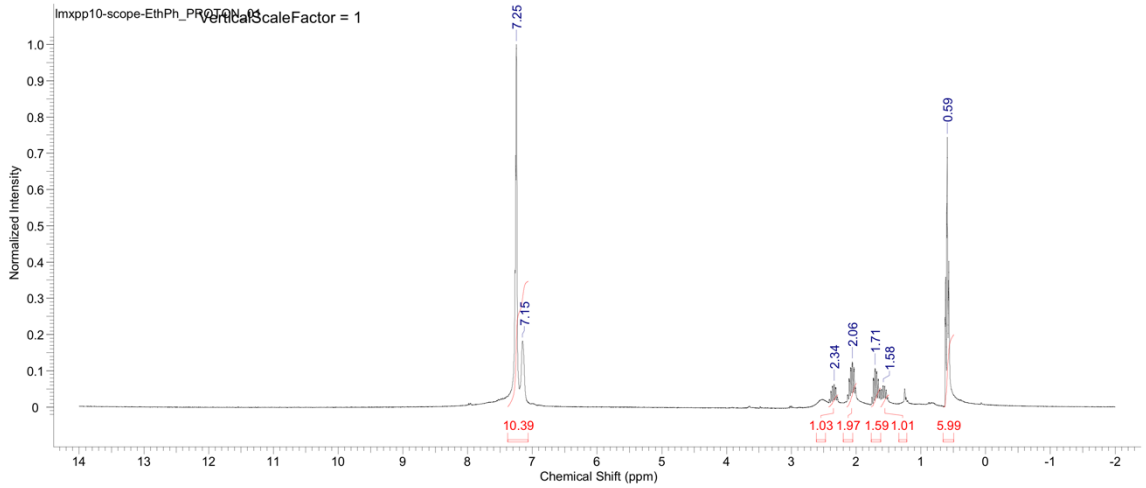
| ***Frequency (MHz)*** | 299.63 | ***Nucleus*** | 1H | ***Number of Transients*** | 16 | ***Original Points Count*** | 11985 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 30.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 1797.7679 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 4793.86 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
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| 1 | [0.4911 .. 0.65 | 5.99060392 | 7.41002432e+8 | 5.99060392 |
| 2 | [1.4949 .. 1.61 | 1.01372254 | 1.25391512e+8 | 1.01372254 |
| 3 | [1.6195 .. 1.76 | 1.59224856 | 1.96951760e+8 | 1.59224856 |
| 4 | [1.9960 .. 2.14 | 1.96768641 | 2.43391216e+8 | 1.96768641 |
| 5 | [2.2809 .. 2.42 | 1.02946806 | 1.27339136e+8 | 1.02946806 |
| 6 | [7.0654 .. 7.37 | 10.3895235 | 1.28512282e+9 | 10.38952351 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 0.59 | 177.7 | 0.7442 |
| 2 | 1.58 | 474.1 | 0.0594 |
| 3 | 1.71 | 512.5 | 0.1070 |
| 4 | 2.06 | 617.5 | 0.1245 |
| 5 | 2.34 | 700.6 | 0.0636 |
| 6 | 7.15 | 2142.9 | 0.1827 |
| 7 | 7.25 | 2171.9 | 1.0000 |



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| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 30.00 | ***Solvent*** | CHLOROFORM-d |
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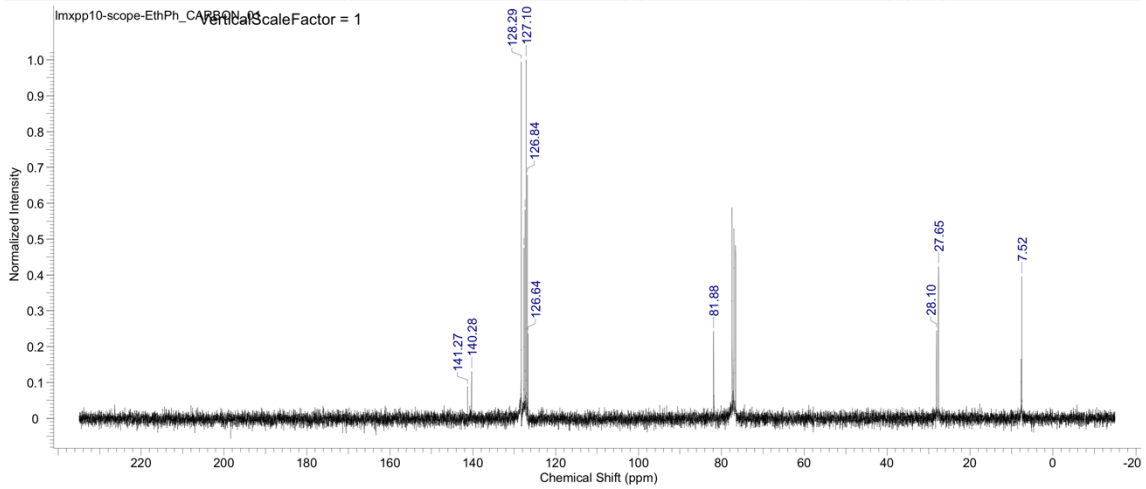


| No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height | No. | (ppm) | (Hz) | Height |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 7.52 | 566.9 | 0.3952 | 4 | 81.88 | 6169.6 | 0.2426 | 7 | 127.10 | 9576.7 | 1.0000 | 10 | 128.29 | 9666.4 | 0.9933 |
| 2 | 27.65 | 2083.1 | 0.4228 | 5 | 126.64 | 9542.2 | 0.2363 | 8 | 127.36 | 9596.3 | 0.5810 | 11 | 140.28 | 10569.9 | 0.1310 |
| 3 | 28.10 | 2117.6 | 0.2444 | 6 | 126.84 | 9557.2 | 0.6779 | 9 | 127.63 | 9617.0 | 0.4743 | 12 | 141.27 | 10644.6 | 0.0888 |

Figure S3. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2c**

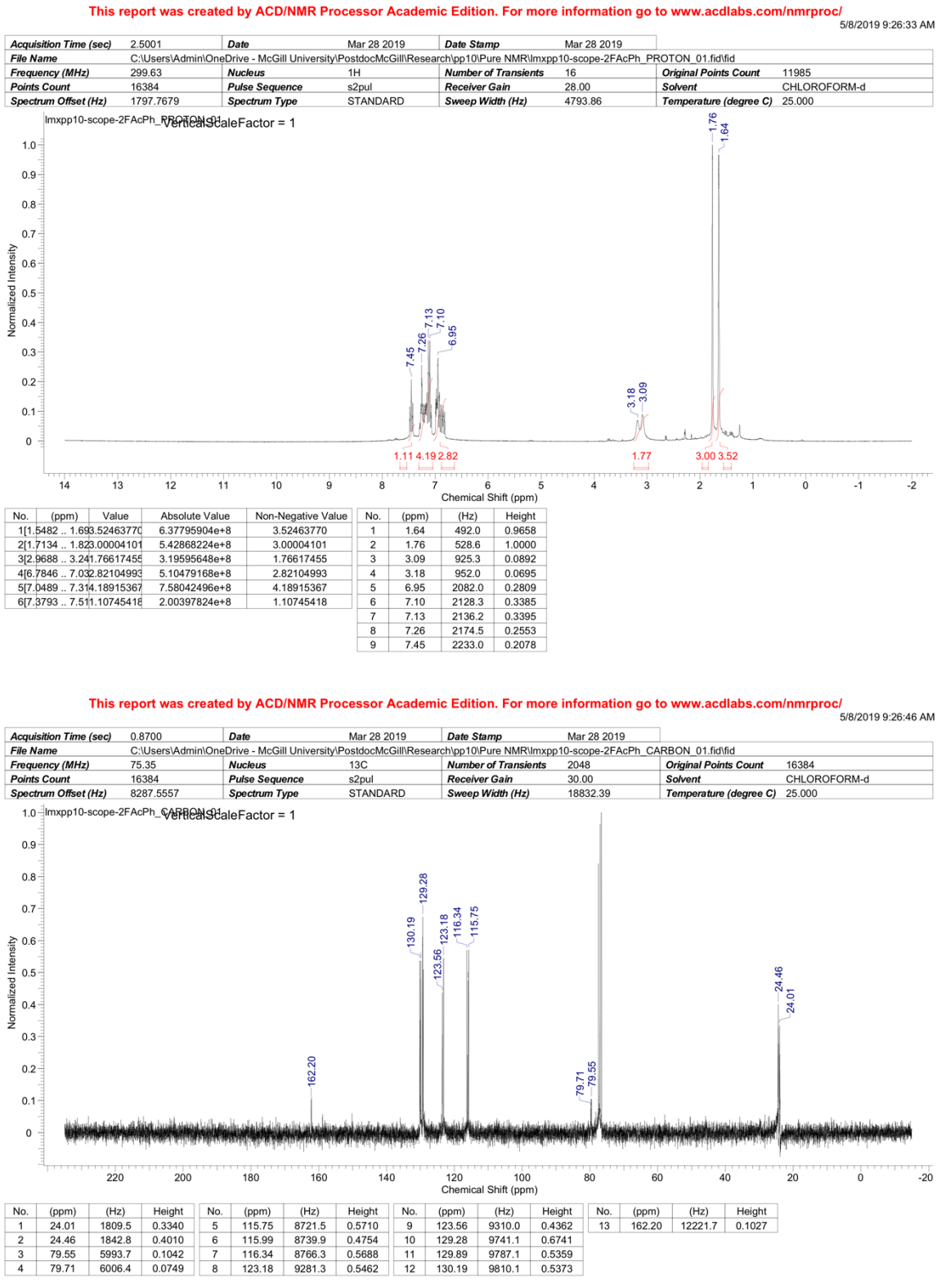


Figure S4. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2d**

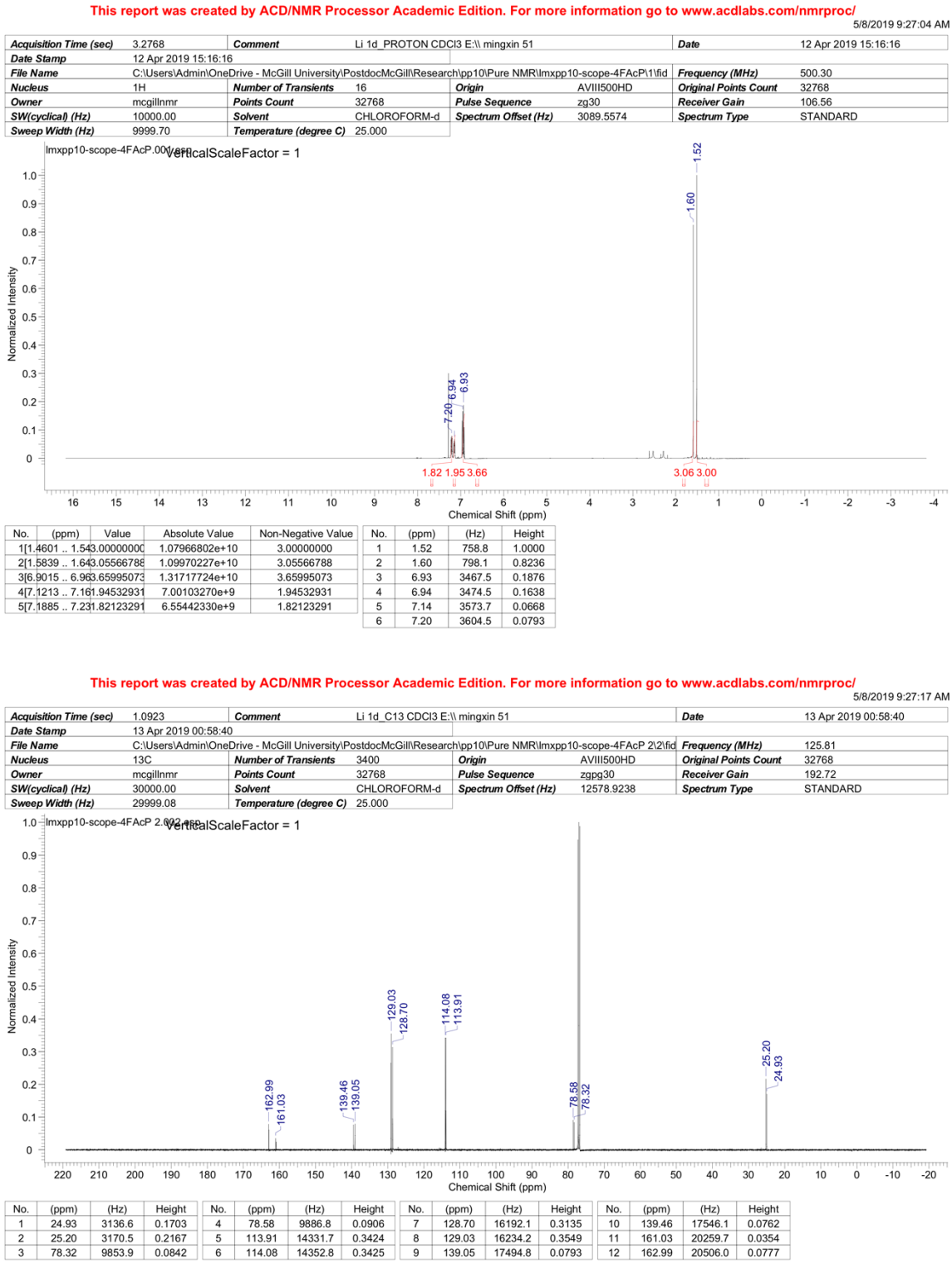


Figure S5. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2e**

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| ***Frequency (MHz)*** | 299.63 | ***Nucleus*** | 1H | ***Number of Transients*** | 16 | ***Original Points Count*** | 11985 |
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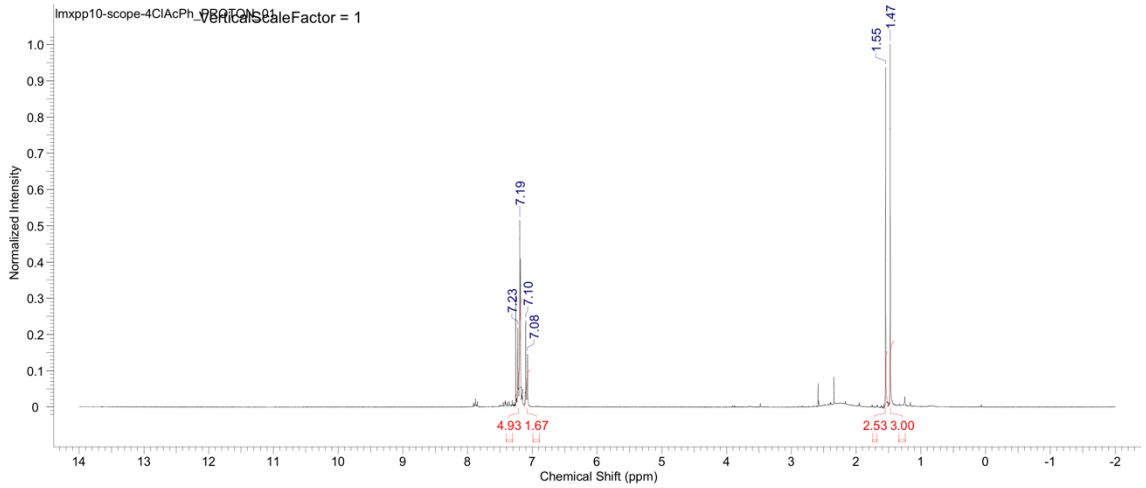
| ***Spectrum Offset (Hz)*** | 1797.7679 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 4793.86 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
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| 1 | [1.4161 .. 1.513 | 3.00000000 | 4.88138016e+8 | 3.00000000 |
| 2 | [1.5152 .. 1.582 | 2.53366017 | 4.12258624e+8 | 2.53366017 |
| 3 | [7.0324 .. 7.131 | 1.66799212 | 2.71403456e+8 | 1.66799212 |
| 4 | [7.1645 .. 7.264 | 4.93404675 | 8.02831936e+8 | 4.93404675 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 1.47 | 441.7 | 1.0000 |
| 2 | 1.55 | 463.0 | 0.9368 |
| 3 | 7.08 | 2120.1 | 0.1453 |
| 4 | 7.10 | 2128.6 | 0.2373 |
| 5 | 7.19 | 2155.5 | 0.5146 |
| 6 | 7.23 | 2165.1 | 0.2181 |

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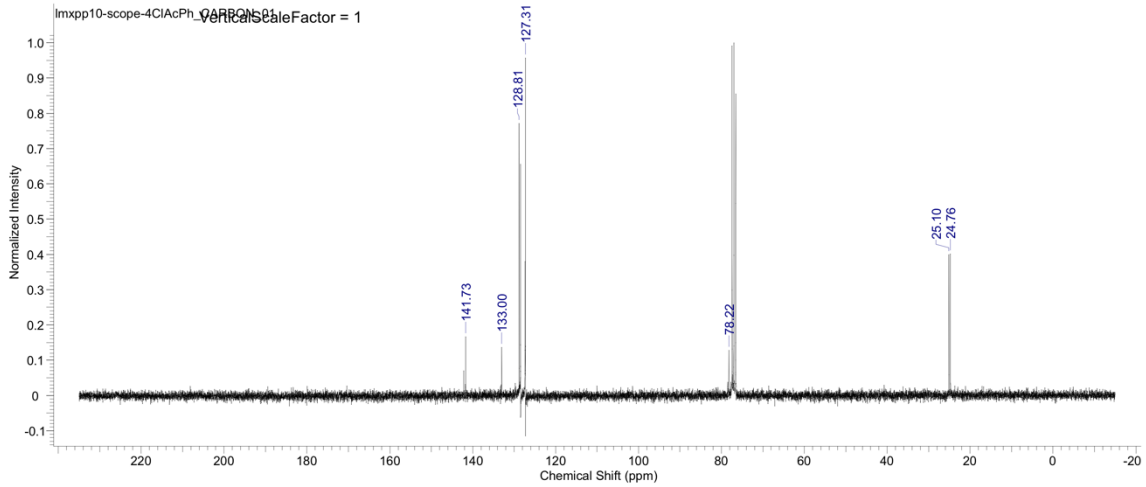


| No. | (ppm) | (Hz) | Height |
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| 1 | 24.76 | 1865.8 | 0.4019 |
| 2 | 25.10 | 1891.1 | 0.4000 |
| 3 | 78.22 | 5893.7 | 0.1286 |
| 4 | 127.31 | 9592.8 | 0.9571 |
| 5 | 128.81 | 9705.5 | 0.7721 |
| 6 | 133.00 | 10021.6 | 0.1368 |
| 7 | 141.73 | 10679.1 | 0.1667 |

Figure S6. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2f**

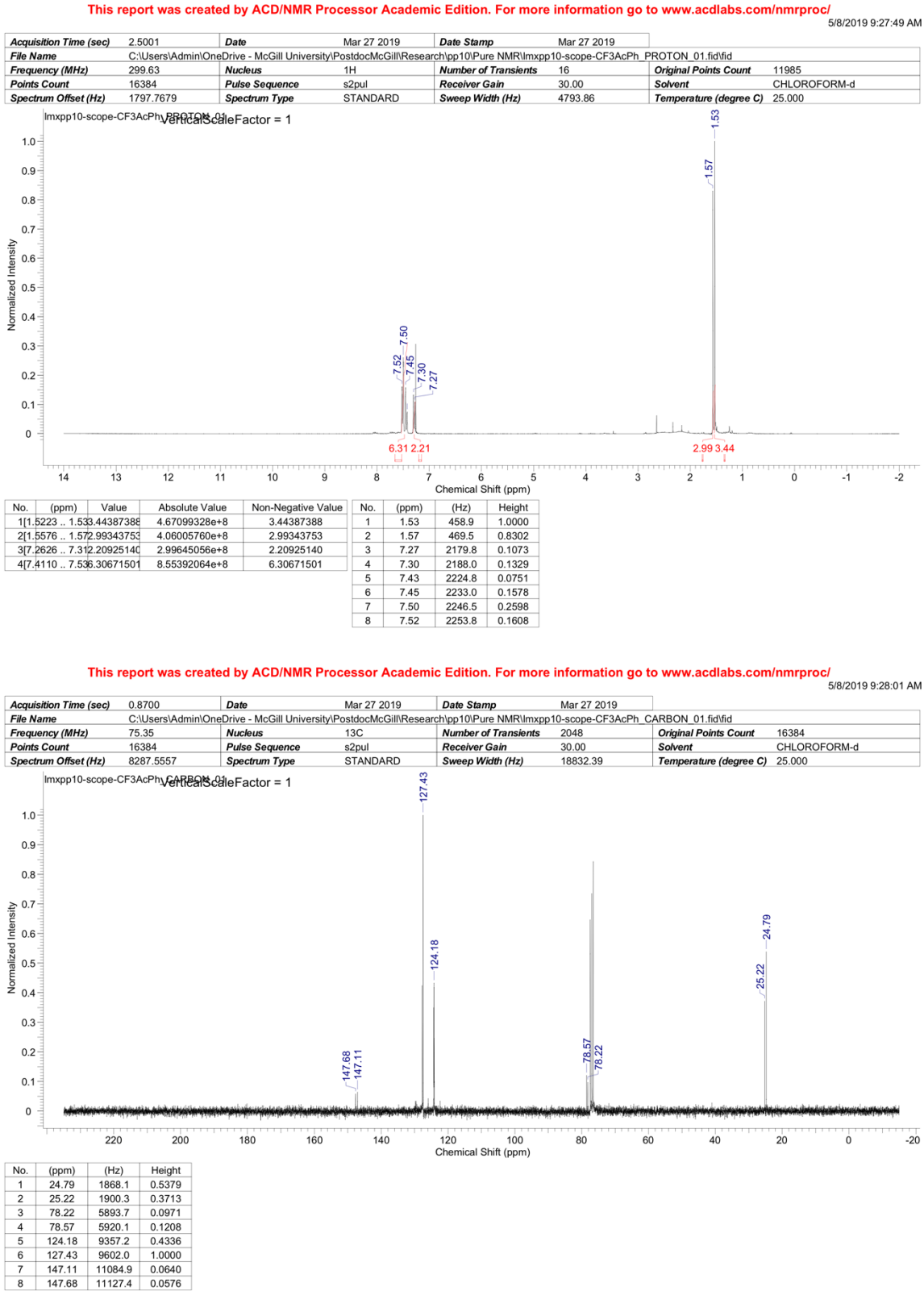
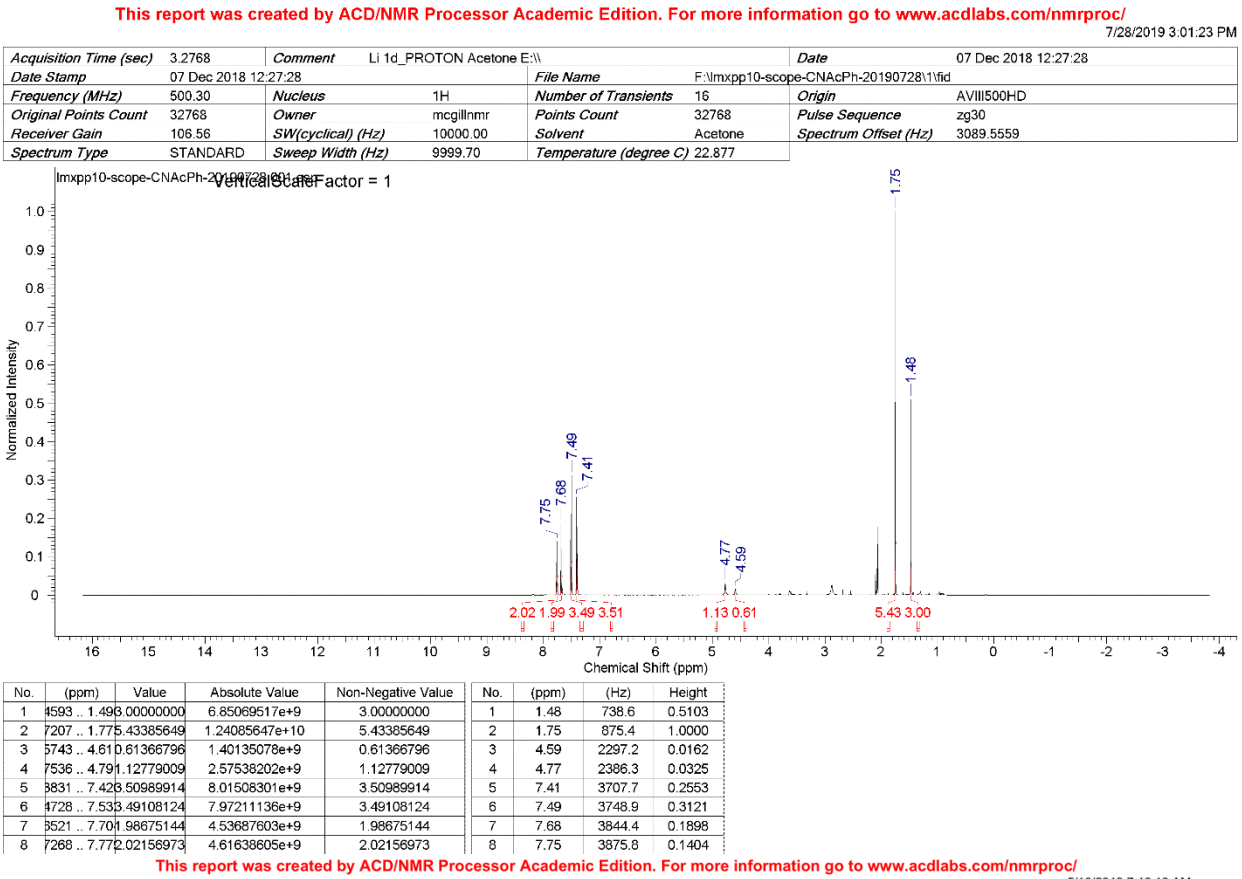
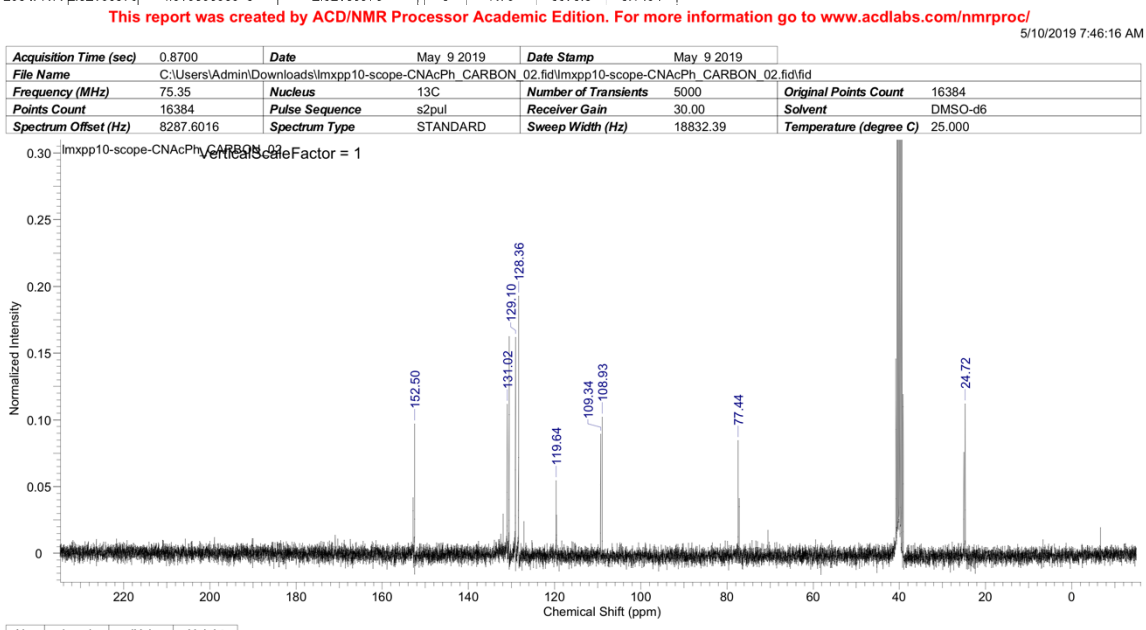



Figure S7. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2g**




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | 4593 .. 1.493 | 3.00000000 | 6.85069517e+9 | 3.00000000 |
| 2 | 7207 .. 1.775 | 5.43385649 | 1.24085647e+10 | 5.43385649 |
| 3 | 5743 .. 4.611 | 0.61366796 | 1.40135078e+9 | 0.61366796 |
| 4 | 7536 .. 4.791 | 1.12779009 | 2.57538202e+9 | 1.12779009 |
| 5 | 3831 .. 7.428 | 3.50989914 | 8.01508301e+9 | 3.50989914 |
| 6 | 4728 .. 7.533 | 3.49108124 | 7.97211136e+9 | 3.49108124 |
| 7 | 3521 .. 7.701 | 1.98675144 | 4.53687603e+9 | 1.98675144 |
| 8 | 7268 .. 7.772 | 2.02156973 | 4.61638605e+9 | 2.02156973 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 1.48 | 738.6 | 0.5103 |
| 2 | 1.75 | 875.4 | 1.0000 |
| 3 | 4.59 | 2297.2 | 0.0162 |
| 4 | 4.77 | 2386.3 | 0.0325 |
| 5 | 7.41 | 3707.7 | 0.2553 |
| 6 | 7.49 | 3748.9 | 0.3121 |
| 7 | 7.68 | 3844.4 | 0.1898 |
| 8 | 7.75 | 3875.8 | 0.1404 |




| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 24.72 | 1862.4 | 0.1120 |
| 2 | 77.44 | 5835.1 | 0.0846 |
| 3 | 108.93 | 8207.7 | 0.1021 |
| 4 | 109.34 | 8238.7 | 0.0893 |
| 5 | 119.64 | 9014.7 | 0.0546 |
| 6 | 128.36 | 9672.2 | 0.1928 |
| 7 | 129.10 | 9727.4 | 0.1620 |
| 8 | 131.02 | 9872.2 | 0.1118 |
| 9 | 152.50 | 11490.7 | 0.0970 |

Figure S8. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2h**

5/8/2019 9:28:54 AM

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| *Acquisition Time (sec)* | 3.2768 | *Comment* | Li 1d_PROTON CDCl3 E:\\ mingxin 10 | | | *Date* | 27 Mar 2019 16:20:16 |
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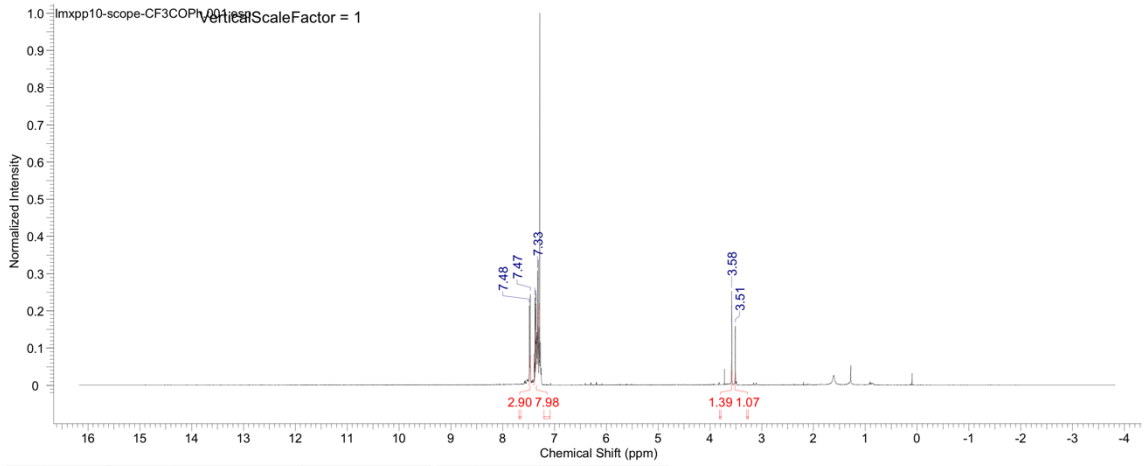
| *Receiver Gain* | 169.11 | *SW(cyclical) (Hz)* | 10000.00 | *Solvent* | CHLOROFORM-d | *Spectrum Offset (Hz)* | 3089.5574 |
| *Spectrum Type* | STANDARD | *Sweep Width (Hz)* | 9999.70 | *Temperature (degree C)* | 24.999 | | |




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [3.4975 .. 3.521 | 1.07190824 | 2.23802752e+9 | 1.07190824 |
| 2 | [3.5634 .. 3.591 | 1.39281428 | 2.90804429e+9 | 1.39281428 |
| 3 | [7.2897 .. 7.407 | 7.98062992 | 1.66626847e+10 | 7.98062992 |
| 4 | [7.4544 .. 7.492 | 2.90106130 | 6.05709926e+9 | 2.90106130 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 3.51 | 1756.4 | 0.1597 |
| 2 | 3.58 | 1790.6 | 0.2527 |
| 3 | 7.33 | 3665.3 | 0.3070 |
| 4 | 7.36 | 3680.5 | 0.2192 |
| 5 | 7.37 | 3689.4 | 0.2351 |
| 6 | 7.47 | 3735.5 | 0.2445 |
| 7 | 7.48 | 3743.4 | 0.2129 |



7/29/2019 10:01:14 AM

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|---|---|---|---|---|---|
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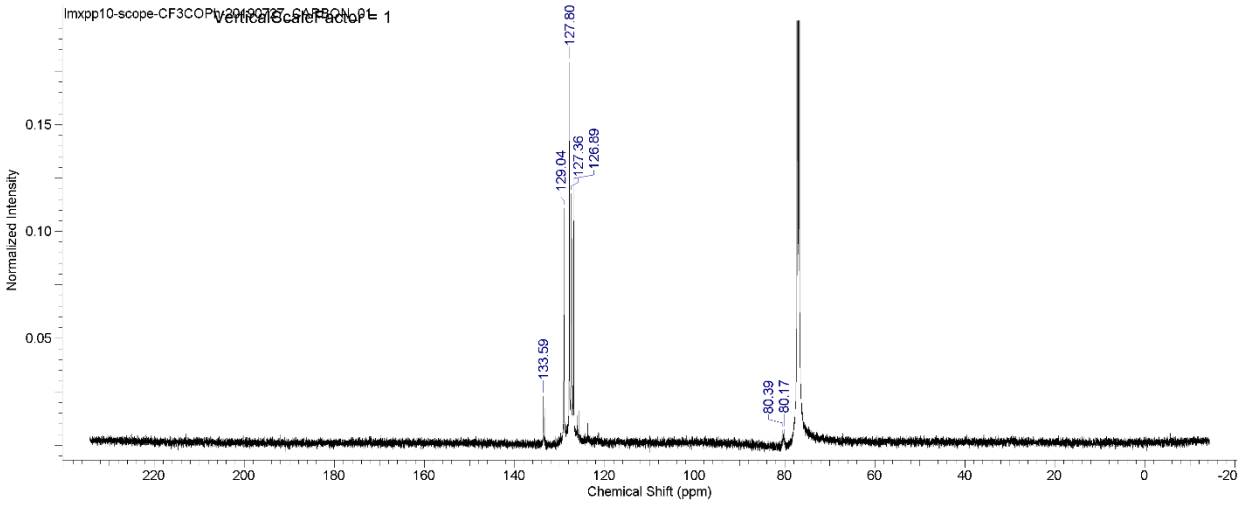
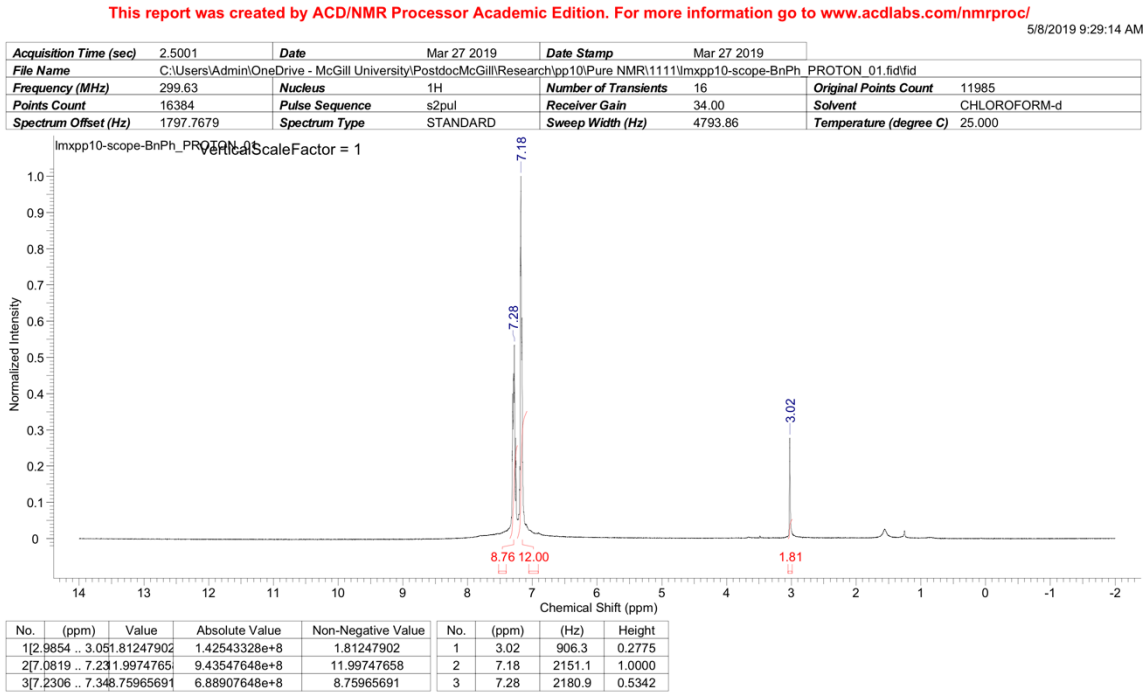
| *Receiver Gain* | 30.00 | *Solvent* | CHLOROFORM-d | *Spectrum Offset (Hz)* | 13826.9287 |
| *Spectrum Type* | STANDARD | *Sweep Width (Hz)* | 31250.00 | *Temperature (degree C)* | 25.000 |



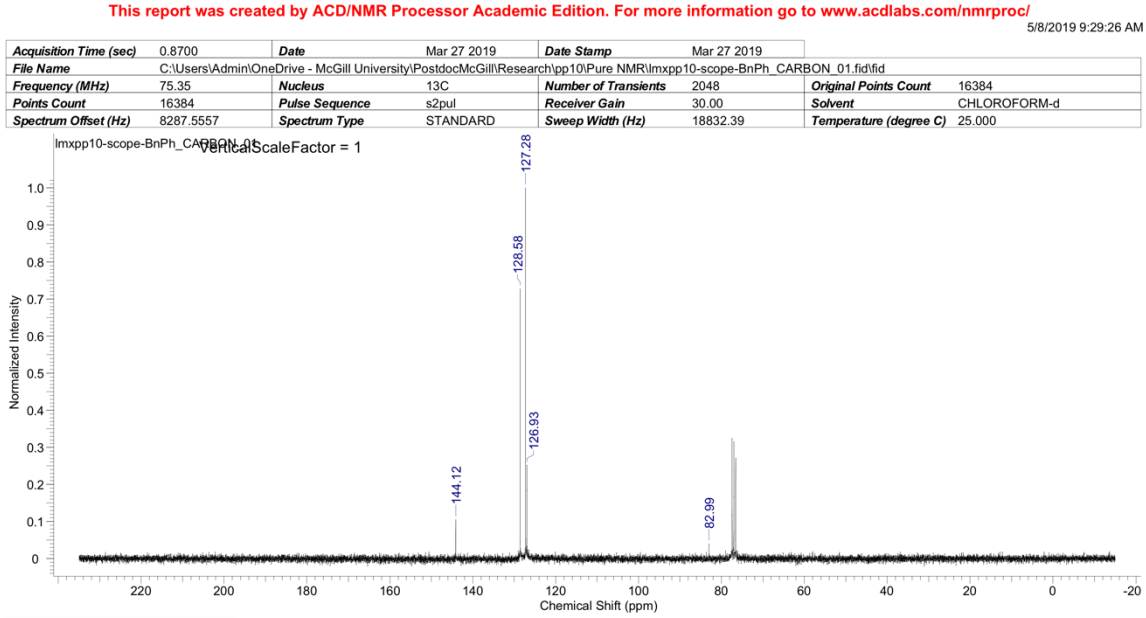

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 80.17 | 10078.4 | 0.0072 |
| 2 | 80.39 | 10106.1 | 0.0069 |
| 3 | 126.89 | 15952.3 | 0.1212 |
| 4 | 127.36 | 16010.4 | 0.1179 |
| 5 | 127.80 | 16065.7 | 0.1790 |
| 6 | 129.04 | 16222.2 | 0.1109 |
| 7 | 133.59 | 16793.4 | 0.0229 |

Figure S9. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2i**



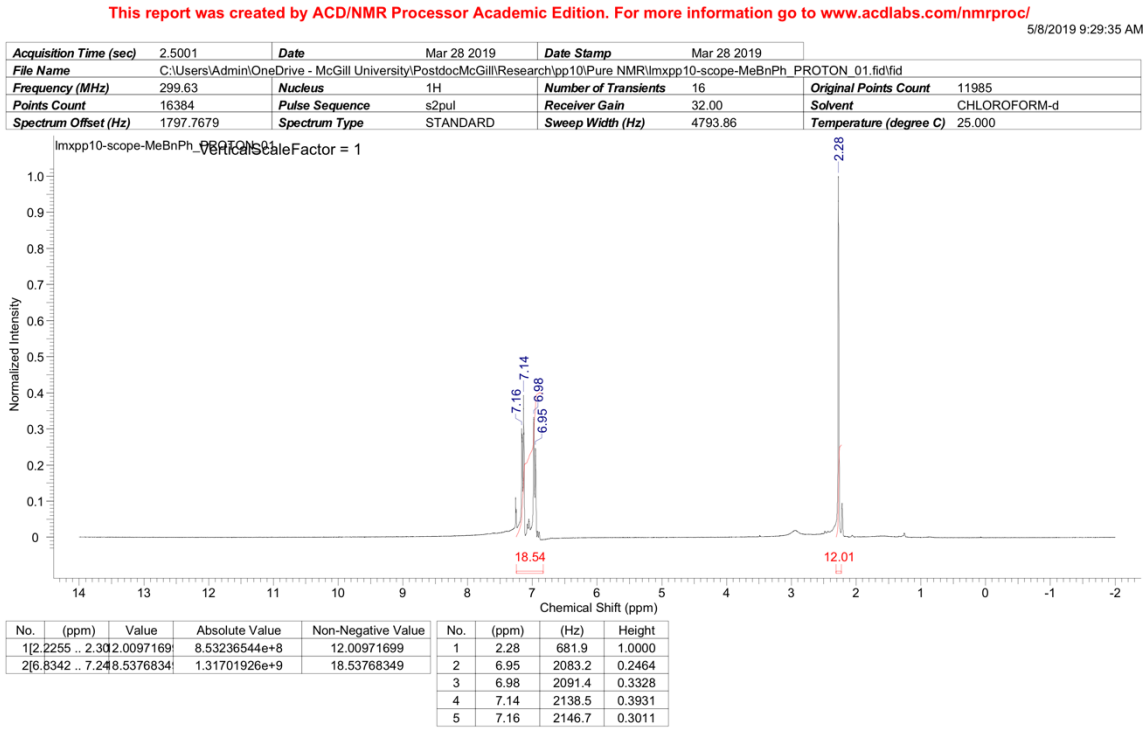

| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [2.9854 .. 3.051 | 1.81247902 | 1.42543328e+8 | 1.81247902 |
| 2 | [7.0819 .. 7.231 | 1.99747651 | 9.43547648e+8 | 11.99747658 |
| 3 | [7.2306 .. 7.348 | 8.75965691 | 6.88907648e+8 | 8.75965691 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 3.02 | 906.3 | 0.2775 |
| 2 | 7.18 | 2151.1 | 1.0000 |
| 3 | 7.28 | 2180.9 | 0.5342 |



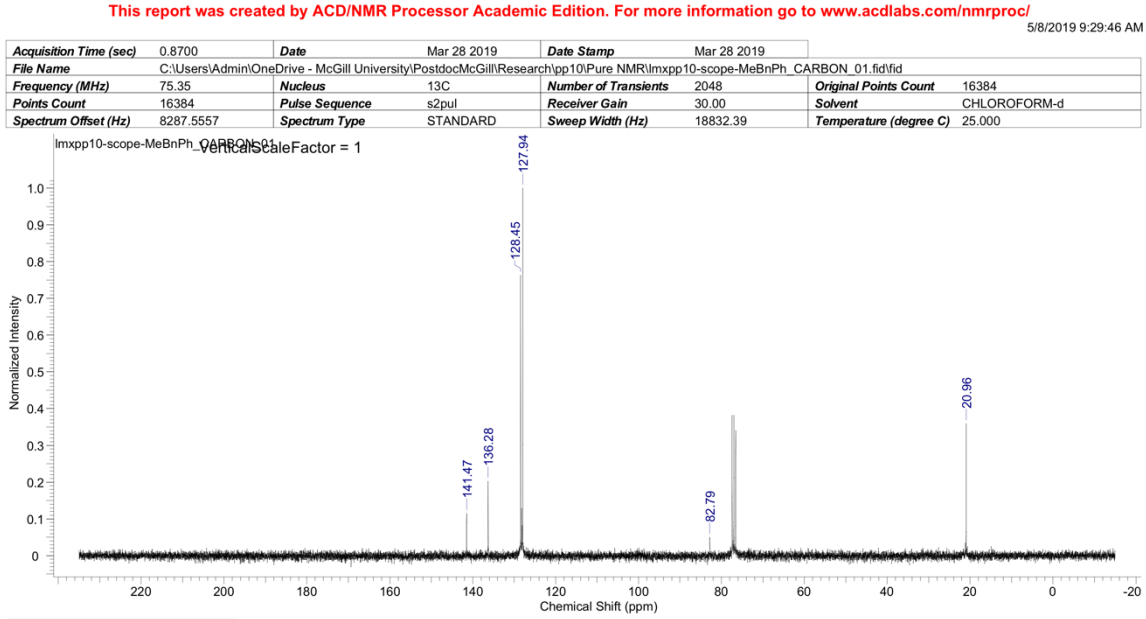

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 82.99 | 6253.5 | 0.0397 |
| 2 | 126.93 | 9564.1 | 0.2522 |
| 3 | 127.28 | 9590.5 | 1.0000 |
| 4 | 128.58 | 9688.2 | 0.7278 |
| 5 | 144.12 | 10859.6 | 0.1051 |

Figure S10. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2j**




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [2.2255 .. 2.30 | 12.0097169 | 8.53236544e+8 | 12.00971699 |
| 2 | [6.8342 .. 7.24 | 18.5376834 | 1.31701926e+9 | 18.53768349 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 2.28 | 681.9 | 1.0000 |
| 2 | 6.95 | 2083.2 | 0.2464 |
| 3 | 6.98 | 2091.4 | 0.3328 |
| 4 | 7.14 | 2138.5 | 0.3931 |
| 5 | 7.16 | 2146.7 | 0.3011 |




| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 20.96 | 1579.6 | 0.3592 |
| 2 | 82.79 | 6238.6 | 0.0500 |
| 3 | 127.94 | 9640.0 | 1.0000 |
| 4 | 128.45 | 9679.0 | 0.7636 |
| 5 | 136.28 | 10268.7 | 0.2024 |
| 6 | 141.47 | 10659.6 | 0.1147 |

Figure S11. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2k**

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|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 3.2768 | ***Comment*** | Li 1d_PROTON CDCl3 E:\\ mingxin 9 | | | ***Date*** | 27 Mar 2019 16:16:00 |
| ***Date Stamp*** | 27 Mar 2019 16:16:00 | | | | | | |
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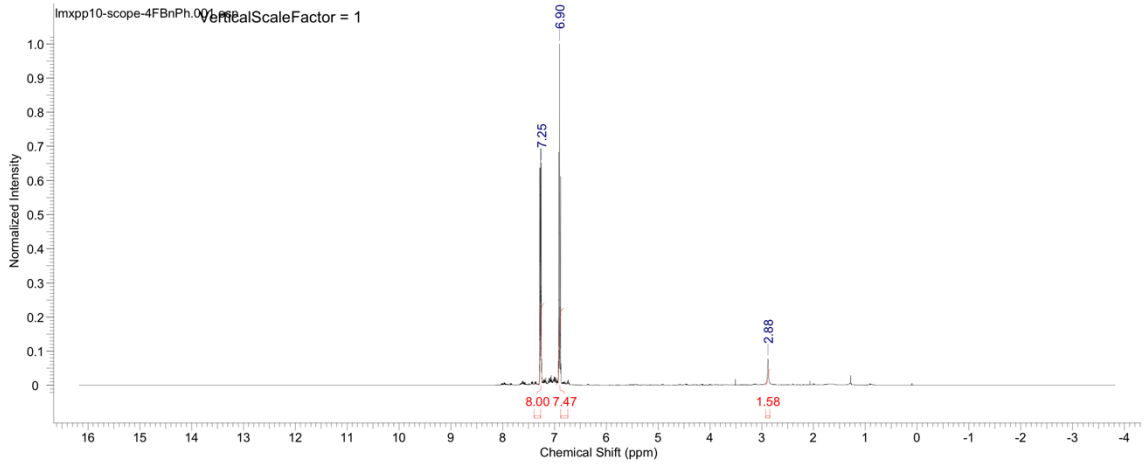
| ***Owner*** | mcgillnmr | ***Points Count*** | 32768 | ***Pulse Sequence*** | zg30 | ***Receiver Gain*** | 106.56 |
| ***SW(cyclical) (Hz)*** | 10000.00 | ***Solvent*** | CHLOROFORM-d | ***Spectrum Offset (Hz)*** | 3089.5559 | ***Spectrum Type*** | STANDARD |
| ***Sweep Width (Hz)*** | 9999.70 | ***Temperature (degree C)*** | 24.999 | | | | |




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [2.8427 .. 2.92 | 1.57560956 | 3.38710861e+9 | 1.57560956 |
| 2 | [6.8254 .. 6.96 | 7.47271776 | 1.60641997e+10 | 7.47271776 |
| 3 | [7.1969 .. 7.32 | 7.99865055 | 1.71948052e+10 | 7.99865055 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 2.88 | 1440.5 | 0.0779 |
| 2 | 6.90 | 3452.0 | 1.0000 |
| 3 | 7.25 | 3629.3 | 0.6510 |

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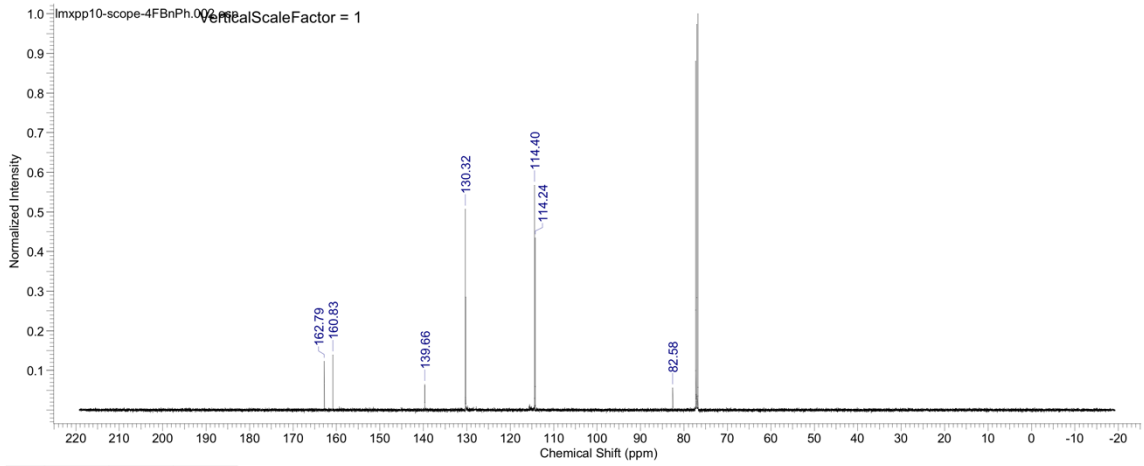
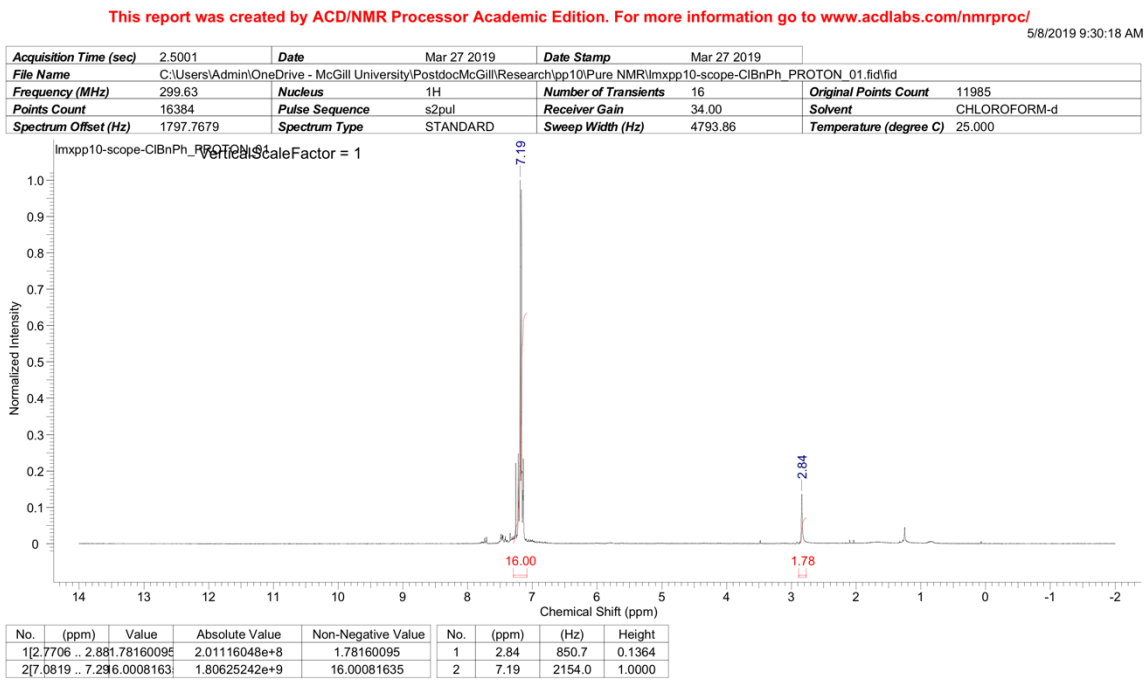
| ***Acquisition Time (sec)*** | 1.0923 | ***Comment*** | Li 1d_C13 CDCl3 E:\\ mingxin 9 | | | ***Date*** | 28 Mar 2019 04:23:28 |
| ***Date Stamp*** | 28 Mar 2019 04:23:28 | | | | | | |
| ***File Name*** | C:\Users\Admin\OneDrive - McGill University\PostdocMcGill\Research\pp10\Pure NMR\lmxpp10-scope-4FBnPh\2\fid | | | | | ***Frequency (MHz)*** | 125.80 |
| ***Nucleus*** | 13C | ***Number of Transients*** | 1024 | ***Origin*** | AVIII500HD | ***Original Points Count*** | 32768 |
| ***Owner*** | mcgillnmr | ***Points Count*** | 32768 | ***Pulse Sequence*** | zgpg30 | ***Receiver Gain*** | 192.72 |
| ***SW(cyclical) (Hz)*** | 30000.00 | ***Solvent*** | CHLOROFORM-d | ***Spectrum Offset (Hz)*** | 12578.9248 | ***Spectrum Type*** | STANDARD |
| ***Sweep Width (Hz)*** | 29999.08 | ***Temperature (degree C)*** | 25.000 | | | | |



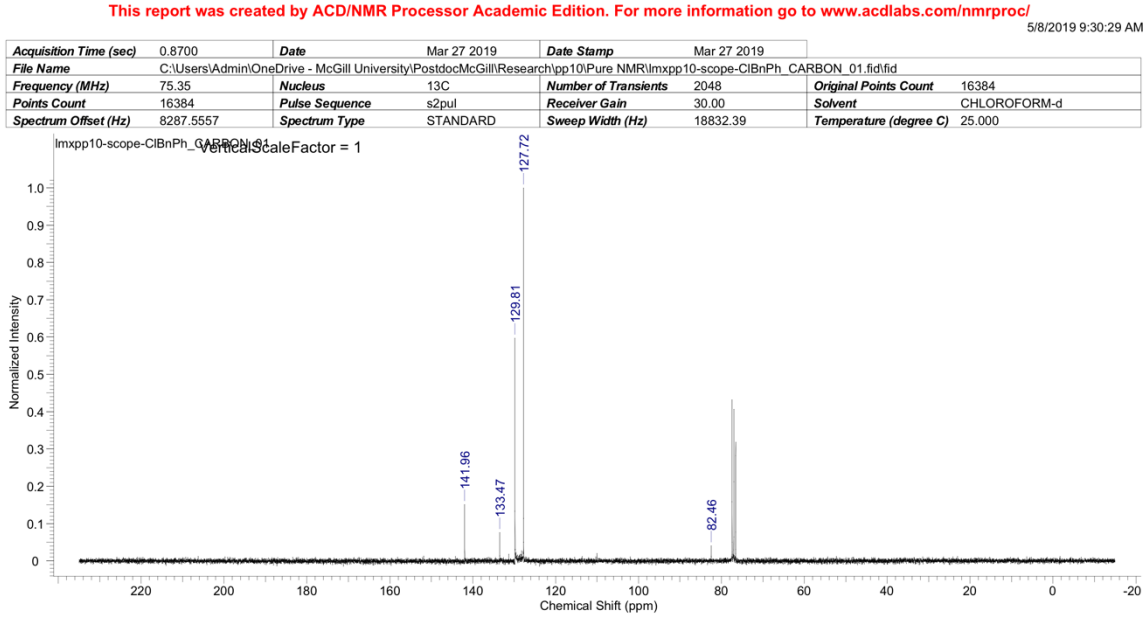

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 82.58 | 10388.5 | 0.0561 |
| 2 | 114.24 | 14371.1 | 0.4347 |
| 3 | 114.40 | 14392.1 | 0.5676 |
| 4 | 130.32 | 16394.4 | 0.5076 |
| 5 | 139.66 | 17569.0 | 0.0651 |
| 6 | 160.83 | 20232.3 | 0.1396 |
| 7 | 162.79 | 20479.5 | 0.1236 |

Figure S12. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2l**




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [2.7706 .. 2.881 | 1.78160095 | 2.01116048e+8 | 1.78160095 |
| 2 | [7.0819 .. 7.291 | 6.0008163 | 1.80625242e+9 | 16.00081635 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 2.84 | 850.7 | 0.1364 |
| 2 | 7.19 | 2154.0 | 1.0000 |




| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 82.46 | 6213.3 | 0.0412 |
| 2 | 127.72 | 9623.9 | 1.0000 |
| 3 | 129.81 | 9781.3 | 0.5973 |
| 4 | 133.47 | 10057.2 | 0.0761 |
| 5 | 141.96 | 10696.3 | 0.1518 |

Figure S13. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2m**

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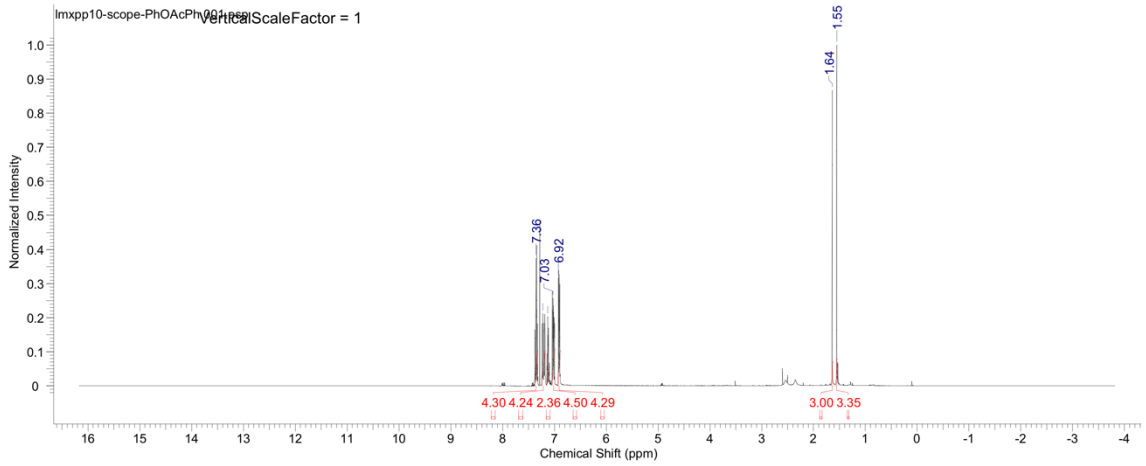
| ***Frequency (MHz)*** | 500.30 | ***Nucleus*** | 1H | ***Number of Transients*** | 16 | ***Origin*** | AVIII500HD |
| ***Original Points Count*** | 32768 | ***Owner*** | mcgillnmr | ***Points Count*** | 32768 | ***Pulse Sequence*** | zg30 |
| ***Receiver Gain*** | 106.56 | ***SW(cyclical) (Hz)*** | 10000.00 | ***Solvent*** | CHLOROFORM-d | ***Spectrum Offset (Hz)*** | 3089.5574 |
| ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 9999.70 | ***Temperature (degree C)*** | 24.999 | | |




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [1.5402 .. 1.573 | 3.35363960 | 6.95872717e+9 | 3.35363960 |
| 2 | [1.6190 .. 1.662 | 2.99999094 | 6.22491392e+9 | 2.99999094 |
| 3 | [6.8730 .. 6.934 | 4.28895044 | 8.89947648e+9 | 4.28895044 |
| 4 | [6.9822 .. 7.044 | 4.49557543 | 9.32821811e+9 | 4.49557543 |
| 5 | [7.0853 .. 7.152 | 2.36461210 | 4.90651750e+9 | 2.36461210 |
| 6 | [7.1703 .. 7.254 | 4.23869038 | 8.79518822e+9 | 4.23869038 |
| 7 | [7.3159 .. 7.384 | 4.30447006 | 8.93167923e+9 | 4.30447006 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 1.55 | 777.7 | 1.0000 |
| 2 | 1.64 | 820.4 | 0.8665 |
| 3 | 6.92 | 3464.2 | 0.3163 |
| 4 | 7.03 | 3514.8 | 0.2579 |
| 5 | 7.13 | 3566.7 | 0.2037 |
| 6 | 7.22 | 3612.5 | 0.2121 |
| 7 | 7.36 | 3680.8 | 0.3742 |



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|---|---|---|---|---|---|---|---|
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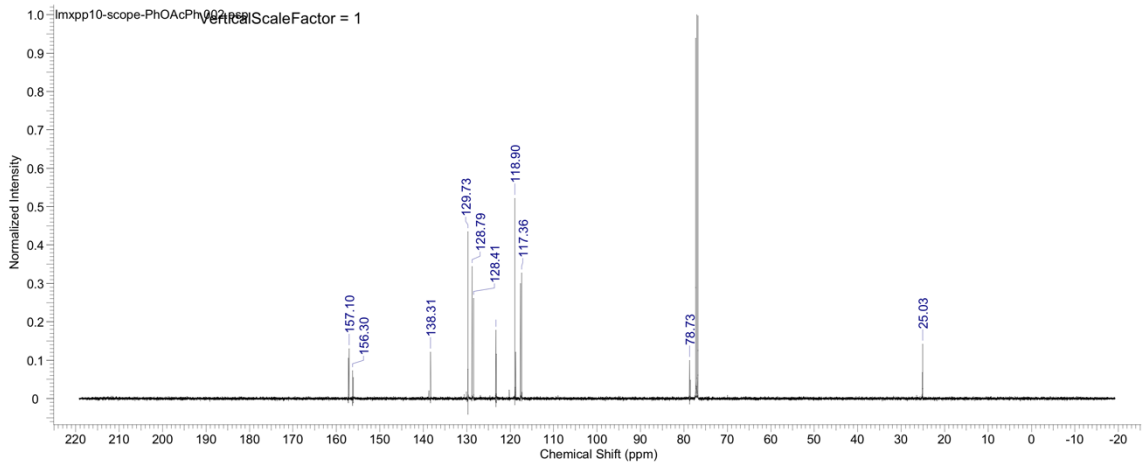
| ***Frequency (MHz)*** | 125.81 | ***Nucleus*** | 13C | ***Number of Transients*** | 1024 | ***Origin*** | AVIII500HD |
| ***Original Points Count*** | 32768 | ***Owner*** | mcgillnmr | ***Points Count*** | 32768 | ***Pulse Sequence*** | zgpg30 |
| ***Receiver Gain*** | 192.72 | ***SW(cyclical) (Hz)*** | 30000.00 | ***Solvent*** | CHLOROFORM-d | ***Spectrum Offset (Hz)*** | 12578.9238 |
| ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 29999.08 | ***Temperature (degree C)*** | 24.999 | | |




| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 25.03 | 3149.5 | 0.1419 |
| 2 | 78.73 | 9905.1 | 0.0991 |
| 3 | 117.36 | 14765.7 | 0.3276 |
| 4 | 118.90 | 14958.8 | 0.5219 |
| 5 | 123.30 | 15512.7 | 0.1788 |
| 6 | 128.41 | 16155.4 | 0.2611 |
| 7 | 128.79 | 16204.0 | 0.3442 |
| 8 | 129.73 | 16321.1 | 0.4353 |
| 9 | 138.31 | 17401.5 | 0.1210 |
| 10 | 156.30 | 19664.6 | 0.0727 |
| 11 | 157.10 | 19765.4 | 0.1297 |

Figure S14. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2n**

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| | | | | | | | |
|---|---|---|---|---|---|---|---|
| *Acquisition Time (sec)* | 2.5001 | *Date* | Mar 27 2019 | *Date Stamp* | Mar 27 2019 | | |
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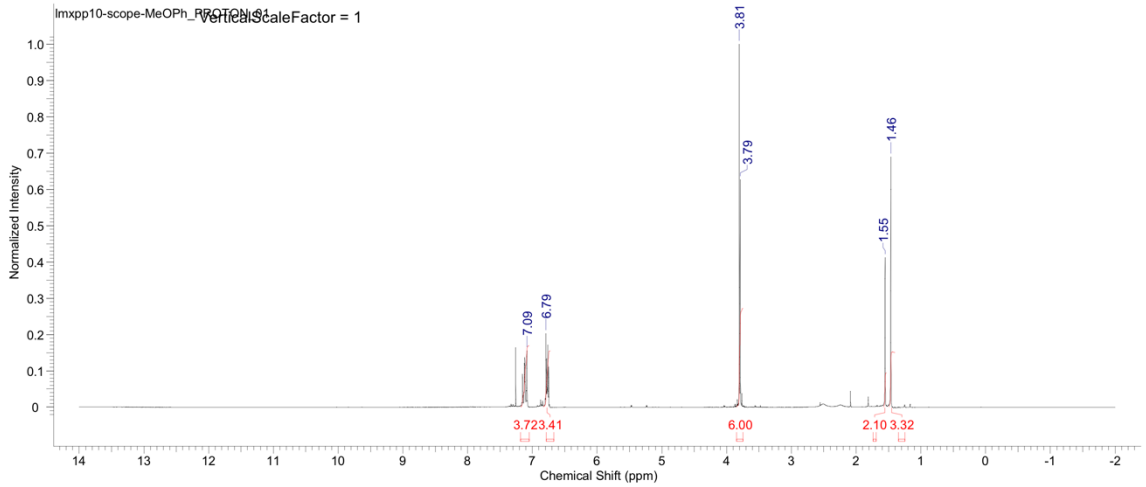
| *Frequency (MHz)* | 299.63 | *Nucleus* | 1H | *Number of Transients* | 16 | *Original Points Count* | 11985 |
| *Points Count* | 16384 | *Pulse Sequence* | s2pul | *Receiver Gain* | 30.00 | *Solvent* | CHLOROFORM-d |
| *Spectrum Offset (Hz)* | 1797.7679 | *Spectrum Type* | STANDARD | *Sweep Width (Hz)* | 4793.86 | *Temperature (degree C)* | 25.000 |




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [1.3996 .. 1.49 | 3.31649065 | 6.08679744e+8 | 3.31649065 |
| 2 | [1.5317 .. 1.58 | 2.10125971 | 3.85646880e+8 | 2.10125971 |
| 3 | [3.7452 .. 3.84 | 5.99967670 | 1.10112832e+9 | 5.99967670 |
| 4 | [6.7185 .. 6.83 | 3.40655589 | 6.25209536e+8 | 3.40655589 |
| 5 | [7.0489 .. 7.18 | 3.71876693 | 6.82510016e+8 | 3.71876693 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 1.46 | 438.7 | 0.6890 |
| 2 | 1.55 | 465.4 | 0.4124 |
| 3 | 3.79 | 1135.7 | 0.6268 |
| 4 | 3.81 | 1140.1 | 1.0000 |
| 5 | 6.79 | 2034.9 | 0.2029 |
| 6 | 7.09 | 2123.3 | 0.1555 |



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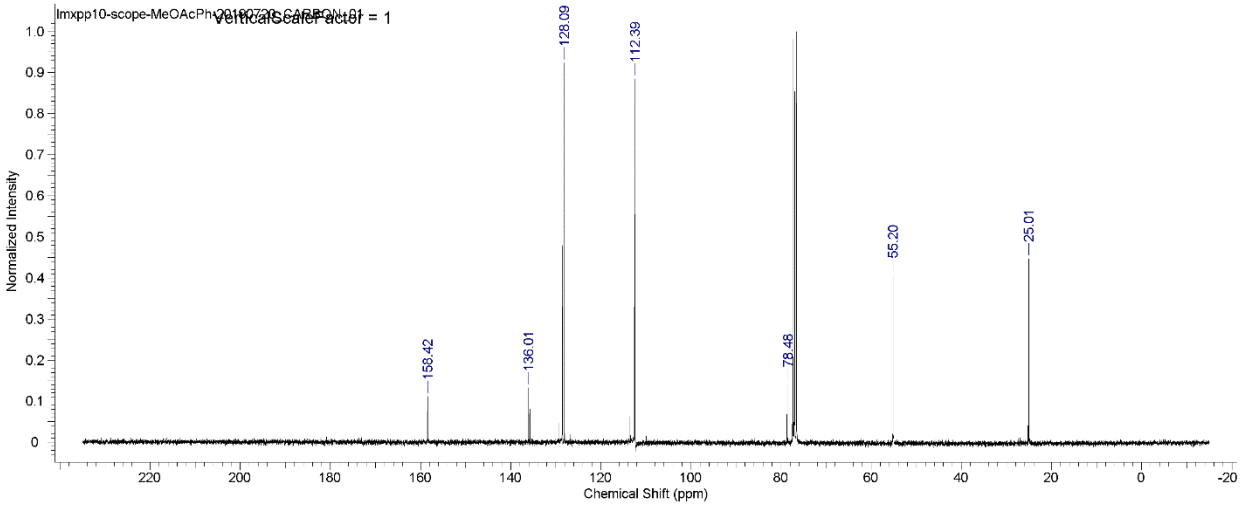
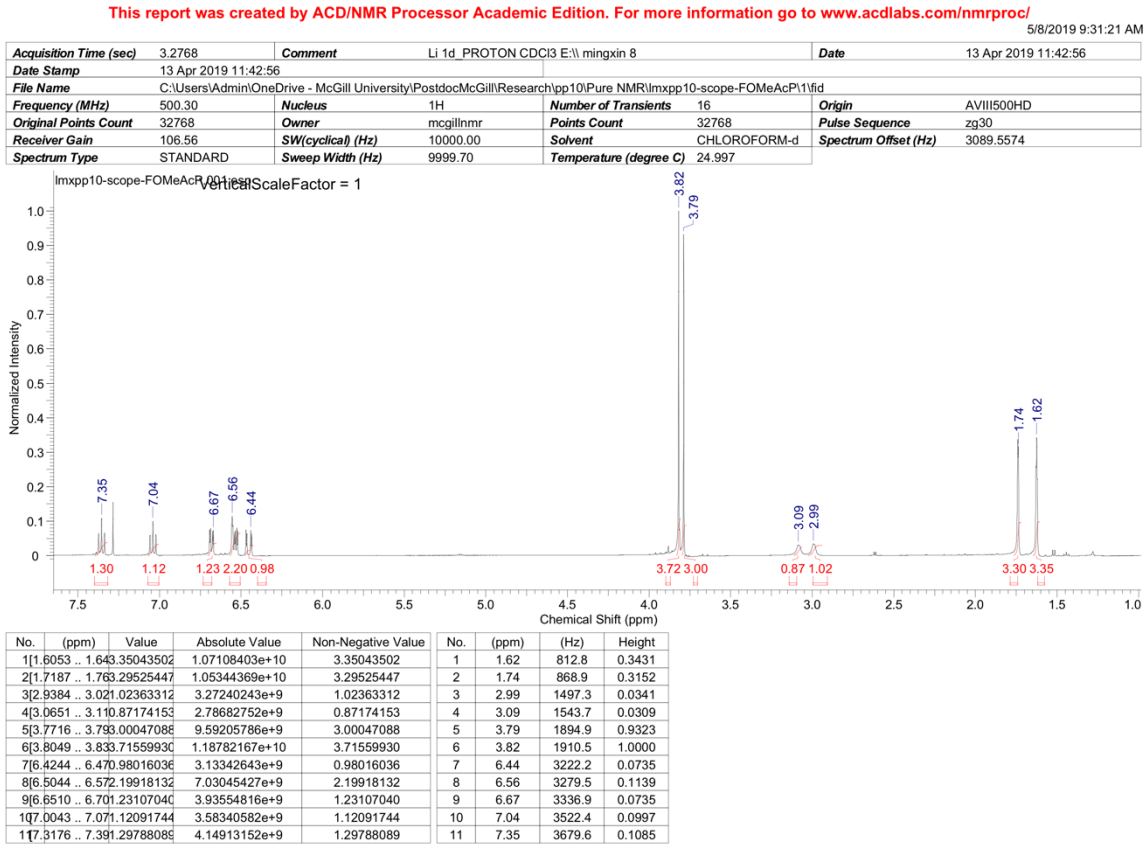
| *Frequency (MHz)* | 75.35 | *Nucleus* | 13C | *Number of Transients* | 20000 |
| *Original Points Count* | 16384 | *Points Count* | 16384 | *Pulse Sequence* | s2pul |
| *Receiver Gain* | 30.00 | *Solvent* | CHLOROFORM-d | *Spectrum Offset (Hz)* | 8287.5654 |
| *Spectrum Type* | STANDARD | *Sweep Width (Hz)* | 18832.39 | *Temperature (degree C)* | 25.000 |



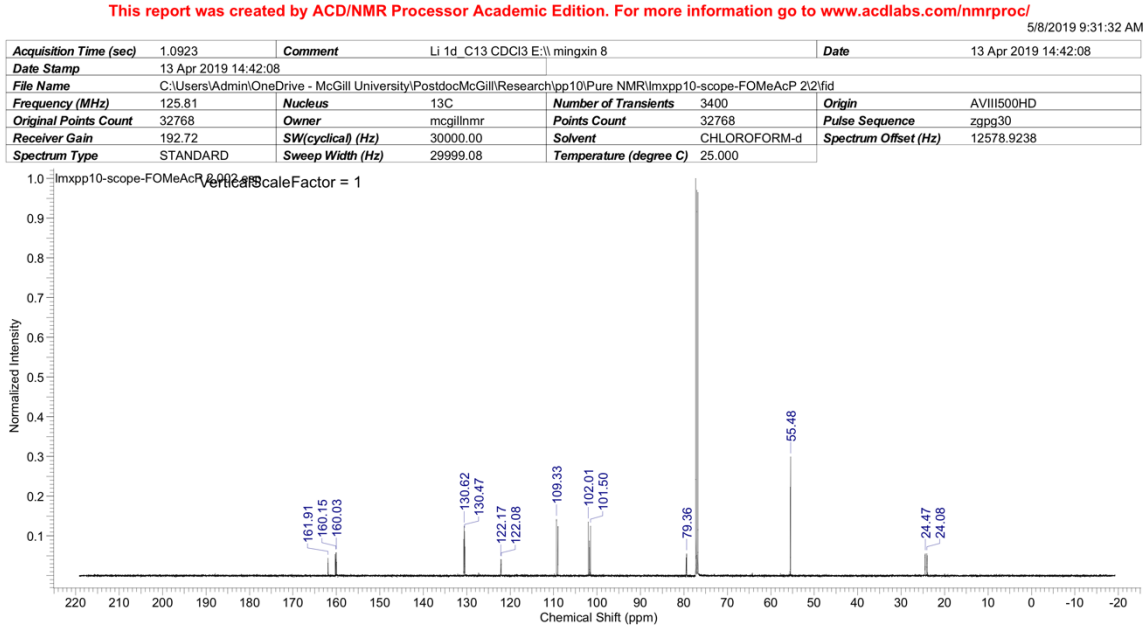

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 25.01 | 1884.2 | 0.4468 |
| 2 | 55.20 | 4159.1 | 0.4074 |
| 3 | 78.48 | 5913.3 | 0.1424 |
| 4 | 112.39 | 8468.6 | 0.8844 |
| 5 | 128.09 | 9651.5 | 0.9238 |
| 6 | 136.01 | 10248.1 | 0.1325 |
| 7 | 158.42 | 11936.7 | 0.1113 |

Figure S15. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2o**




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [1.6053 .. 1.643 | 3.35043502 | 1.07108403e+10 | 3.35043502 |
| 2 | [1.7187 .. 1.763 | 3.29525447 | 1.05344369e+10 | 3.29525447 |
| 3 | [2.9384 .. 3.021 | 1.02363312 | 3.27240243e+9 | 1.02363312 |
| 4 | [3.0651 .. 3.110 | 0.87174153 | 2.78682752e+9 | 0.87174153 |
| 5 | [3.7716 .. 3.793 | 3.00047088 | 9.59205786e+9 | 3.00047088 |
| 6 | [3.8049 .. 3.833 | 3.71559930 | 1.18782167e+10 | 3.71559930 |
| 7 | [6.4244 .. 6.470 | 0.98016036 | 3.13342643e+9 | 0.98016036 |
| 8 | [6.5044 .. 6.572 | 2.19918132 | 7.03045427e+9 | 2.19918132 |
| 9 | [6.6510 .. 6.701 | 2.31070400 | 3.93554816e+9 | 1.23107040 |
| 10 | [7.0043 .. 7.071 | 1.12091744 | 3.58340582e+9 | 1.12091744 |
| 11 | [7.3176 .. 7.391 | 2.97880895 | 4.14913152e+9 | 1.29788089 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 1.62 | 812.8 | 0.3431 |
| 2 | 1.74 | 868.9 | 0.3152 |
| 3 | 2.99 | 1497.3 | 0.0341 |
| 4 | 3.09 | 1543.7 | 0.0309 |
| 5 | 3.79 | 1894.9 | 0.9323 |
| 6 | 3.82 | 1910.5 | 1.0000 |
| 7 | 6.44 | 3222.2 | 0.0735 |
| 8 | 6.56 | 3279.5 | 0.1139 |
| 9 | 6.67 | 3336.9 | 0.0735 |
| 10 | 7.04 | 3522.4 | 0.0997 |
| 11 | 7.35 | 3679.6 | 0.1085 |




| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 24.08 | 3029.5 | 0.0557 |
| 2 | 24.47 | 3079.0 | 0.0558 |
| 3 | 55.48 | 6980.0 | 0.2998 |
| 4 | 79.36 | 9984.8 | 0.0552 |
| 5 | 101.50 | 12769.8 | 0.1255 |
| 6 | 102.01 | 12834.8 | 0.1352 |
| 7 | 109.33 | 13754.9 | 0.1424 |
| 8 | 122.08 | 15359.8 | 0.0406 |
| 9 | 122.17 | 15370.8 | 0.0410 |
| 10 | 130.47 | 16414.5 | 0.1121 |
| 11 | 130.62 | 16433.8 | 0.1251 |
| 12 | 160.03 | 20133.4 | 0.0582 |
| 13 | 160.15 | 20149.0 | 0.0571 |
| 14 | 161.91 | 20370.5 | 0.0447 |

Figure S16. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2p**

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| ***Acquisition Time (sec)*** | 3.2768 | ***Comment*** | Li 1d PROTON CDCl3 E:\\ mingxin 1 | | | ***Date*** | 15 Apr 2019 15:05:36 |
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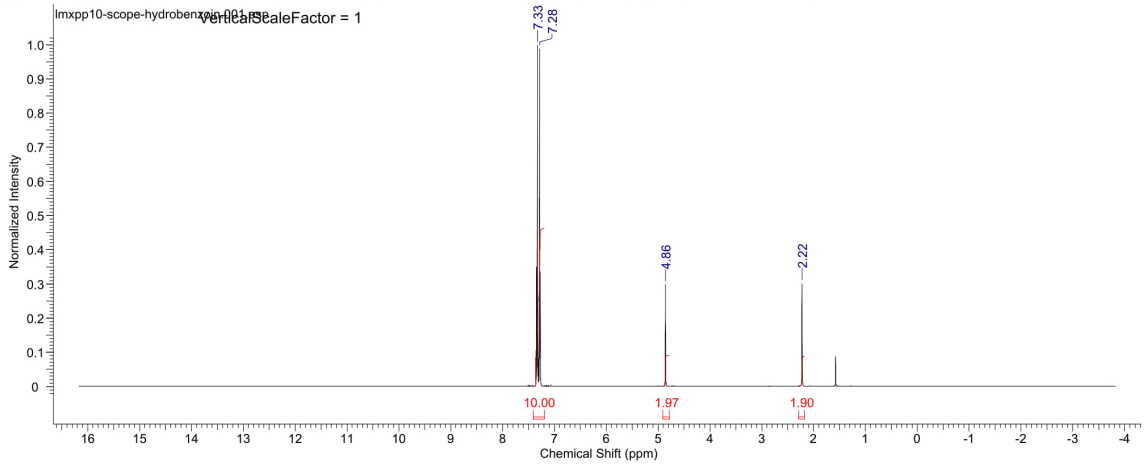
| ***Frequency (MHz)*** | 500.30 | ***Nucleus*** | 1H | ***Number of Transients*** | 16 | ***Origin*** | AVIII500HD |
| ***Original Points Count*** | 32768 | ***Owner*** | mcgillnmr | ***Points Count*** | 32768 | ***Pulse Sequence*** | zg30 |
| ***Receiver Gain*** | 106.56 | ***SW(cyclical) (Hz)*** | 10000.00 | ***Solvent*** | CHLOROFORM-d | ***Spectrum Offset (Hz)*** | 3089.5574 |
| ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 9999.70 | ***Temperature (degree C)*** | 24.997 | | |




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [2.1823 .. 2.281 | 1.89957368 | 5.26521805e+9 | 1.89957368 |
| 2 | [4.7825 .. 4.901 | 1.96805561 | 5.45503539e+9 | 1.96805561 |
| 3 | [7.1968 .. 7.401 | 10.0002813 | 2.77186724e+10 | 10.00028133 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 2.22 | 1113.1 | 0.3022 |
| 2 | 4.86 | 2429.9 | 0.2981 |
| 3 | 7.28 | 3644.5 | 0.9880 |
| 4 | 7.33 | 3666.2 | 1.0000 |

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2019/10/9 20:03:02

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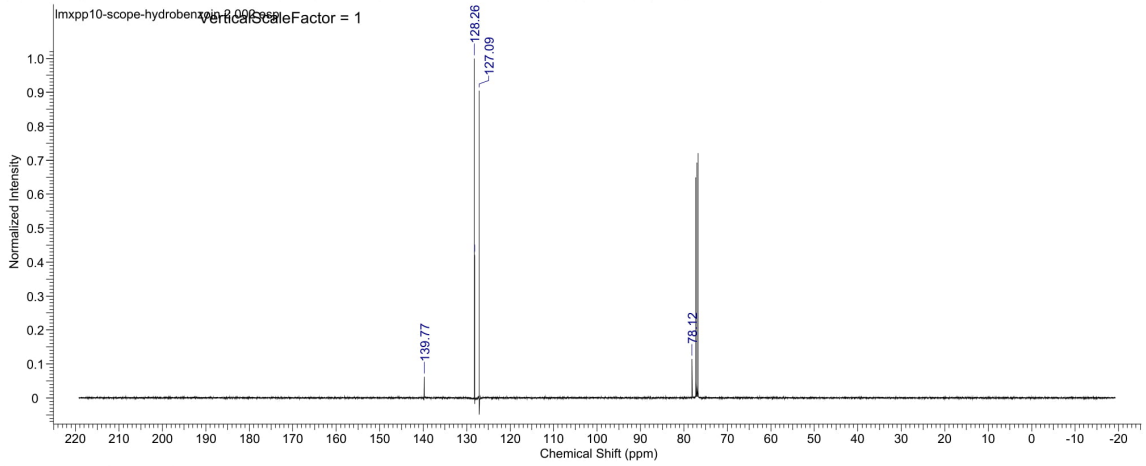
|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 1.0923 | ***Comment*** | Li 1d C13 CDCl3 E:\\ mingxin 1 | | | ***Date*** | 15 Apr 2019 23:52:32 |
| ***Date Stamp*** | 15 Apr 2019 23:52:32 | | | | | | |
| ***File Name*** | C:\Users\Admin\OneDrive - McGill University\PostdocMcGill\Research\pp10\Pure NMR\lmxpp10-scope-hydrobenzoin 2\2\fid | | | | | | |
| ***Frequency (MHz)*** | 125.81 | ***Nucleus*** | 13C | ***Number of Transients*** | 3400 | ***Origin*** | AVIII500HD |
| ***Original Points Count*** | 32768 | ***Owner*** | mcgillnmr | ***Points Count*** | 32768 | ***Pulse Sequence*** | zgpg30 |
| ***Receiver Gain*** | 192.72 | ***SW(cyclical) (Hz)*** | 30000.00 | ***Solvent*** | CHLOROFORM-d | ***Spectrum Offset (Hz)*** | 12578.9238 |
| ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 29999.08 | ***Temperature (degree C)*** | 24.998 | | |




| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 78.12 | 9829.1 | 0.1146 |
| 2 | 127.09 | 15989.7 | 0.9048 |
| 3 | 128.13 | 16120.6 | 0.4205 |
| 4 | 128.26 | 16136.2 | 1.0000 |
| 5 | 139.77 | 17584.6 | 0.0625 |

Figure S17. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2q**

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2019/10/8 17:06:39

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|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 2.5001 | ***Date*** | Oct 7 2019 | ***Date Stamp*** | Oct 7 2019 | | |
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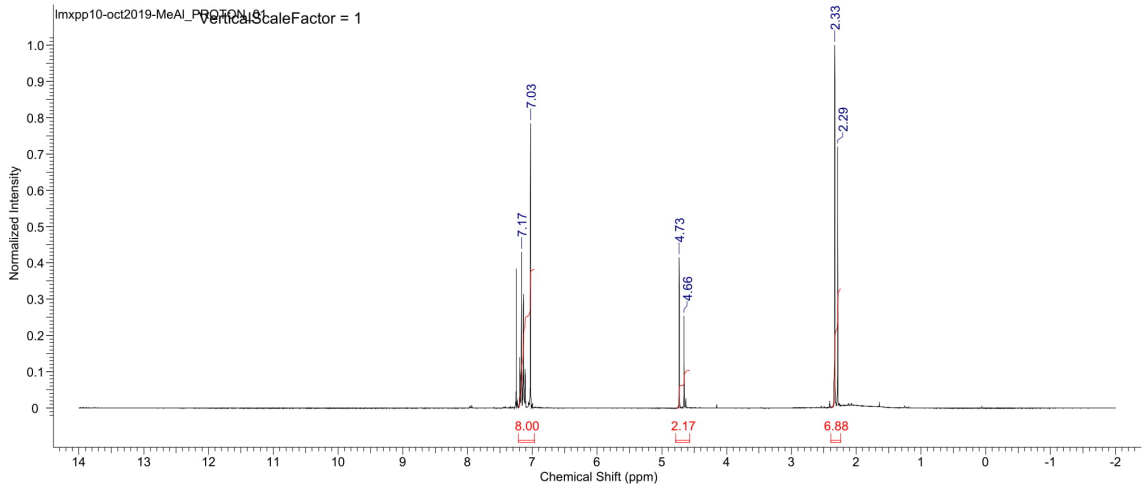
| ***Frequency (MHz)*** | 299.63 | ***Nucleus*** | 1H | ***Number of Transients*** | 16 | ***Original Points Count*** | 11985 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 32.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 1797.7679 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 4793.86 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [2.2420 .. 2.39 | 6.87540817 | 7.60036352e+8 | 6.87540817 |
| 2 | [4.5711 .. 4.782 | 2.17211890 | 2.40115120e+8 | 2.17211890 |
| 3 | [6.9663 .. 7.217 | 7.99976063 | 8.84326976e+8 | 7.99976063 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 2.29 | 684.8 | 0.7196 |
| 2 | 2.33 | 698.3 | 1.0000 |
| 3 | 4.66 | 1395.9 | 0.2534 |
| 4 | 4.73 | 1418.1 | 0.4149 |
| 5 | 7.03 | 2105.7 | 0.7842 |
| 6 | 7.17 | 2147.3 | 0.4293 |

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2019/10/8 17:08:03

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|---|---|---|---|---|---|---|---|
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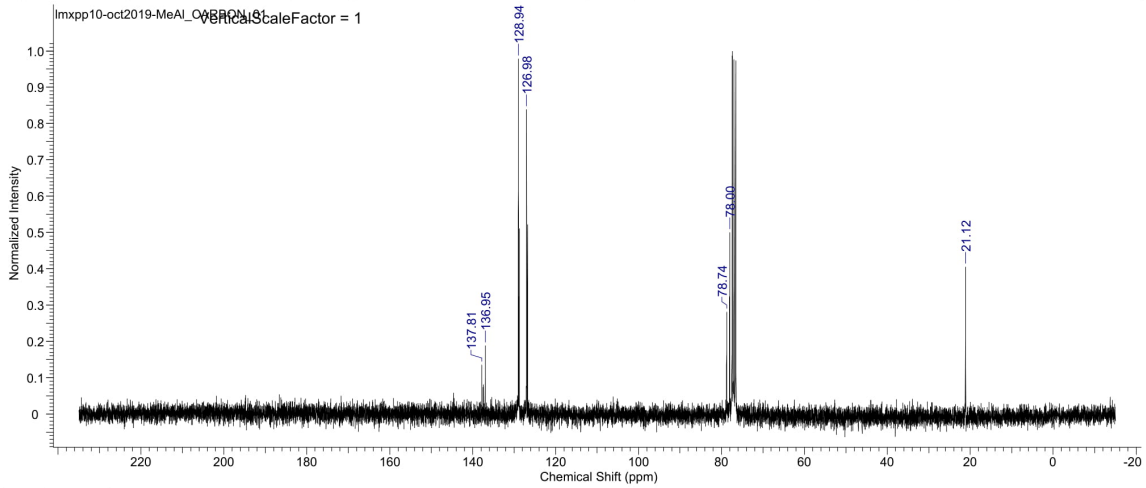
| ***Frequency (MHz)*** | 75.35 | ***Nucleus*** | 13C | ***Number of Transients*** | 5650 | ***Original Points Count*** | 16384 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 30.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 8287.5654 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 18832.39 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 21.12 | 1591.1 | 0.4057 |
| 2 | 78.00 | 5877.6 | 0.5000 |
| 3 | 78.74 | 5932.8 | 0.2812 |
| 4 | 126.98 | 9567.5 | 0.8388 |
| 5 | 128.94 | 9715.8 | 0.9787 |
| 6 | 136.95 | 10319.3 | 0.1881 |
| 7 | 137.81 | 10383.7 | 0.1358 |

Figure S18. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2r**

2019/10/8 17:09:36

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|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 2.5001 | ***Date*** | Oct 7 2019 | ***Date Stamp*** | Oct 7 2019 | | |
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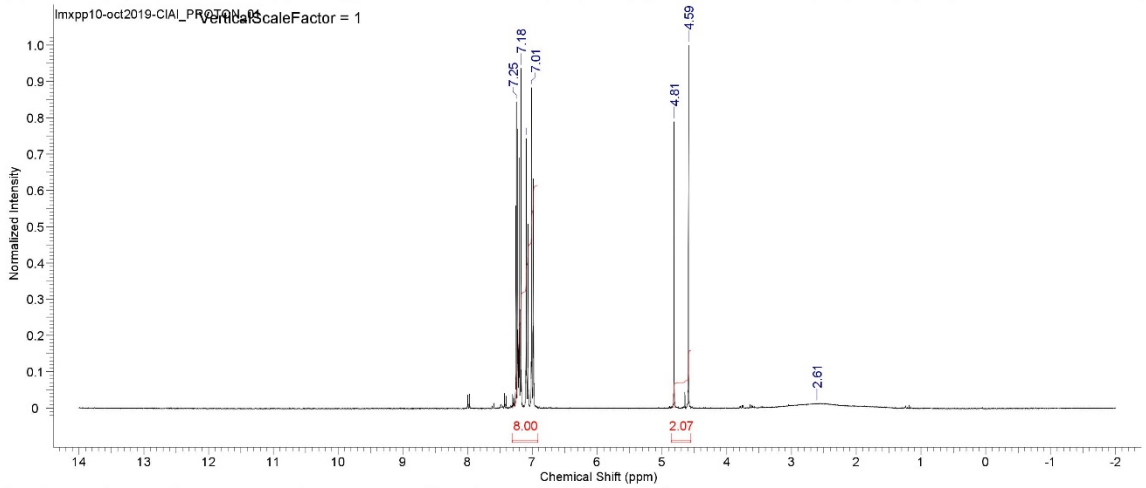
| ***Frequency (MHz)*** | 299.63 | ***Nucleus*** | 1H | ***Number of Transients*** | 16 | ***Original Points Count*** | 11985 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 36.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 1797.7679 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 4793.86 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [4.5546 .. 4.85 | 2.07204819 | 5.36881664e+8 | 2.07204819 |
| 2 | [6.9167 .. 7.31 | 8.00031185 | 2.07293491e+9 | 8.00031185 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 2.61 | 780.8 | 0.0129 |
| 2 | 4.59 | 1375.4 | 1.0000 |
| 3 | 4.81 | 1441.8 | 0.7895 |
| 4 | 7.01 | 2101.1 | 0.8831 |
| 5 | 7.10 | 2125.9 | 0.7436 |
| 6 | 7.18 | 2150.8 | 0.9367 |
| 7 | 7.25 | 2171.0 | 0.8436 |



2019/10/8 17:10:51

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|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 0.8700 | ***Date*** | Oct 7 2019 | ***Date Stamp*** | Oct 7 2019 | | |
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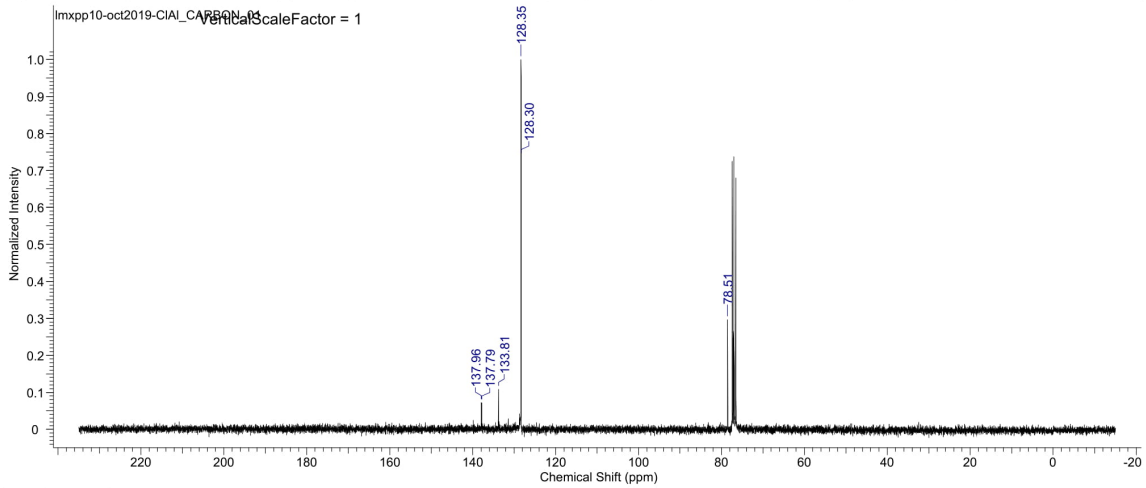
| ***Frequency (MHz)*** | 75.35 | ***Nucleus*** | 13C | ***Number of Transients*** | 5650 | ***Original Points Count*** | 16384 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 30.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 8287.5654 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 18832.39 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 78.51 | 5915.6 | 0.2973 |
| 2 | 128.27 | 9665.3 | 0.5105 |
| 3 | 128.30 | 9667.5 | 0.7381 |
| 4 | 128.35 | 9671.0 | 1.0000 |
| 5 | 133.81 | 10082.5 | 0.1091 |
| 6 | 137.79 | 10382.5 | 0.0716 |
| 7 | 137.96 | 10395.2 | 0.0730 |

Figure S19. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2s**

2019/10/8 17:14:09

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|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 2.5001 | ***Date*** | Oct 7 2019 | ***Date Stamp*** | Oct 7 2019 | | |
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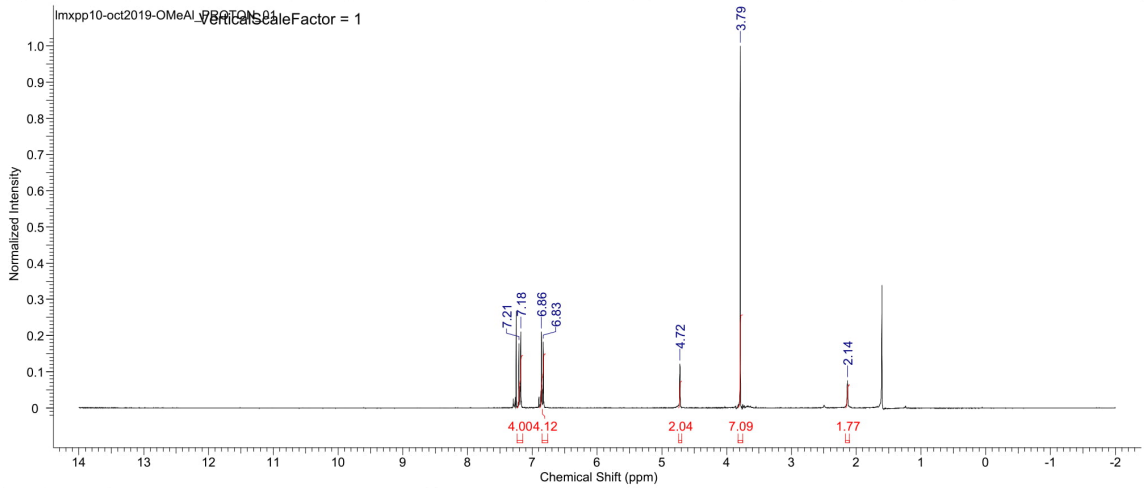
| ***Frequency (MHz)*** | 299.63 | ***Nucleus*** | 1H | ***Number of Transients*** | 16 | ***Original Points Count*** | 11985 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 38.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 1797.7679 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 4793.86 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [2.1026 .. 2.161 | 1.77449143 | 2.03573520e+8 | 1.77449143 |
| 2 | [3.7522 .. 3.827 | 7.08814287 | 8.13167168e+8 | 7.08814287 |
| 3 | [4.6940 .. 4.742 | 2.03940320 | 2.33964768e+8 | 2.03940320 |
| 4 | [6.7999 .. 6.884 | 4.11550617 | 4.72139808e+8 | 4.11550617 |
| 5 | [7.1508 .. 7.233 | 3.99922132 | 4.58799360e+8 | 3.99922132 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 2.14 | 639.8 | 0.0760 |
| 2 | 3.79 | 1135.7 | 1.0000 |
| 3 | 4.72 | 1414.9 | 0.1223 |
| 4 | 6.83 | 2046.9 | 0.1821 |
| 5 | 6.86 | 2055.4 | 0.2111 |
| 6 | 7.18 | 2151.4 | 0.2104 |
| 7 | 7.21 | 2159.9 | 0.1786 |



2019/10/9 19:48:22

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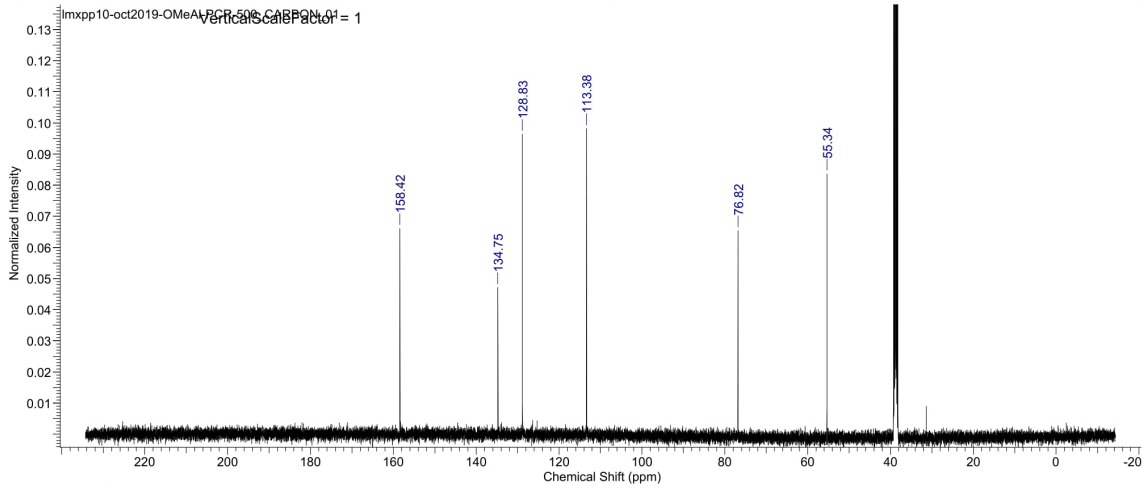
|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 1.0486 | ***Comment*** | lmxpp10-oct2019-OMeAl-PCR-500 | | | ***Date*** | Oct 9 2019 |
| ***Date Stamp*** | Oct 9 2019 | ***File Name*** | C:\Users\Admin\Desktop\lmxpp10-oct2019-OMeAl-PCR-500_CARBON_01.fid\fid | | | | |
| ***Frequency (MHz)*** | 125.71 | ***Nucleus*** | 13C | ***Number of Transients*** | 3500 | ***Original Points Count*** | 32768 |
| ***Points Count*** | 32768 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 30.00 | ***Solvent*** | DMSO-d6 |
| ***Spectrum Offset (Hz)*** | 13826.9600 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 31250.00 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 55.34 | 6957.0 | 0.0836 |
| 2 | 76.82 | 9656.9 | 0.0654 |
| 3 | 113.38 | 14253.7 | 0.0982 |
| 4 | 128.83 | 16195.5 | 0.0964 |
| 5 | 134.75 | 16940.3 | 0.0473 |
| 6 | 158.42 | 19914.9 | 0.0662 |

Figure S20. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2t**

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2019/10/9 19:55:37

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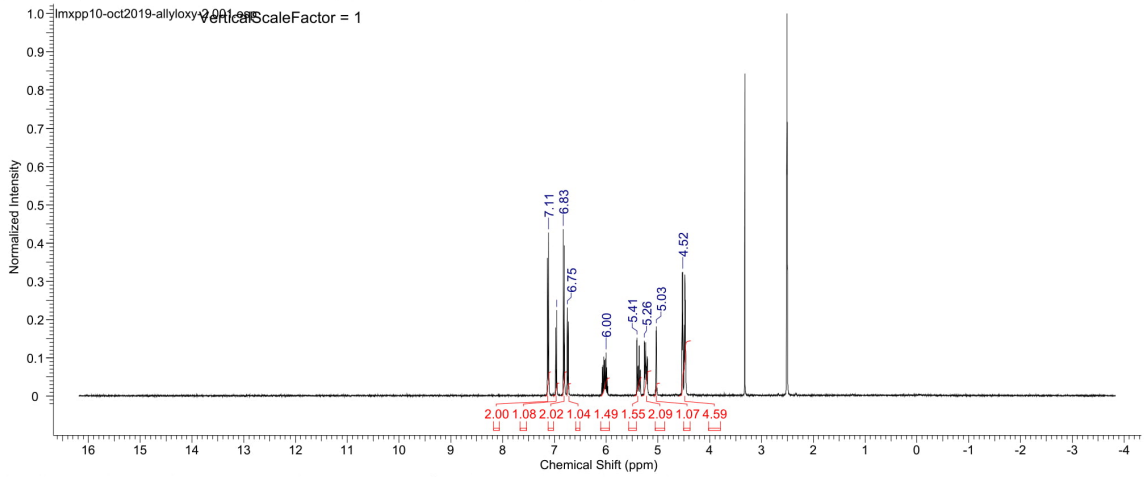
| ***Acquisition Time (sec)*** | 4.0894 | ***Comment*** | Li 1d PROTON DMSO C:\\ mingxin 101 | | | ***Date*** | 09 Oct 2019 09:20:00 |
| ***Date Stamp*** | 09 Oct 2019 09:20:00 | | | ***File Name*** | C:\Users\Admin\Desktop\lmxpp10-oct2019-allyloxy-2\1\fid | | |
| ***Frequency (MHz)*** | 400.35 | ***Nucleus*** | 1H | ***Number of Transients*** | 8 | ***Origin*** | B400 |
| ***Original Points Count*** | 32768 | ***Owner*** | mcgillnmr | ***Points Count*** | 32768 | ***Pulse Sequence*** | zg30 |
| ***Receiver Gain*** | 202.76 | ***SW(cyclical) (Hz)*** | 8012.82 | ***Solvent*** | DMSO-d6 | ***Spectrum Offset (Hz)*** | 2472.3252 |
| ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 8012.58 | ***Temperature (degree C)*** | 25.131 | | |




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [4.3673 .. 4.594 | 4.58976555 | 4.34390938e+9 | 4.58976555 |
| 2 | [4.9666 .. 5.091 | 1.07480085 | 1.01722797e+9 | 1.07480085 |
| 3 | [5.1319 .. 5.312 | 2.09083700 | 1.97883891e+9 | 2.09083700 |
| 4 | [5.3178 .. 5.461 | 1.54613805 | 1.46331738e+9 | 1.54613805 |
| 5 | [5.9377 .. 6.101 | 1.49473548 | 1.41466829e+9 | 1.49473548 |
| 6 | [6.6816 .. 6.761 | 1.04085875 | 9.85104000e+8 | 1.04085875 |
| 7 | [6.7643 .. 6.862 | 2.02112317 | 1.91285952e+9 | 2.02112317 |
| 8 | [6.9089 .. 7.031 | 1.08312392 | 1.02510522e+9 | 1.08312392 |
| 9 | [7.0742 .. 7.172 | 2.00056648 | 1.89340378e+9 | 2.00056648 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 4.52 | 1810.0 | 0.3245 |
| 2 | 5.03 | 2013.2 | 0.1824 |
| 3 | 5.26 | 2107.6 | 0.1443 |
| 4 | 5.41 | 2164.1 | 0.1520 |
| 5 | 6.00 | 2403.7 | 0.1140 |
| 6 | 6.75 | 2703.3 | 0.2319 |
| 7 | 6.83 | 2733.4 | 0.4362 |
| 8 | 6.96 | 2784.5 | 0.2250 |
| 9 | 7.11 | 2847.6 | 0.4276 |

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2019/10/8 17:24:08

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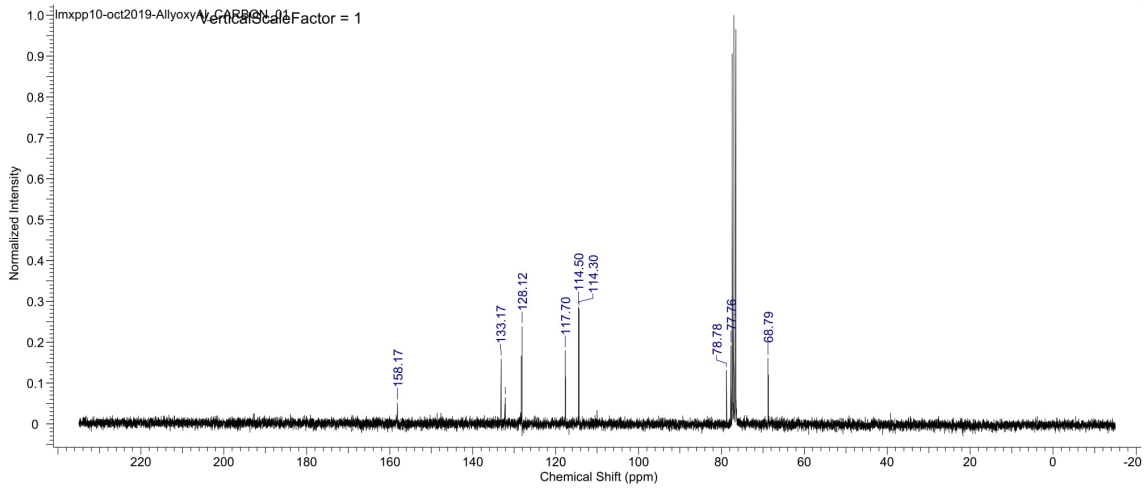
| ***Frequency (MHz)*** | 75.35 | ***Nucleus*** | 13C | ***Number of Transients*** | 5650 | ***Original Points Count*** | 16384 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 30.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 8287.5654 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 18832.39 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 68.79 | 5183.3 | 0.1609 |
| 2 | 77.76 | 5859.2 | 0.1918 |
| 3 | 78.78 | 5936.2 | 0.1313 |
| 4 | 114.30 | 8612.3 | 0.2822 |
| 5 | 114.50 | 8627.2 | 0.2872 |
| 6 | 117.70 | 8868.6 | 0.1791 |
| 7 | 128.12 | 9653.8 | 0.2385 |
| 8 | 132.16 | 9958.4 | 0.0646 |
| 9 | 133.17 | 10034.2 | 0.1591 |
| 10 | 158.17 | 11918.3 | 0.0516 |

Figure S21. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **2u**

2019/10/4 11:04:41

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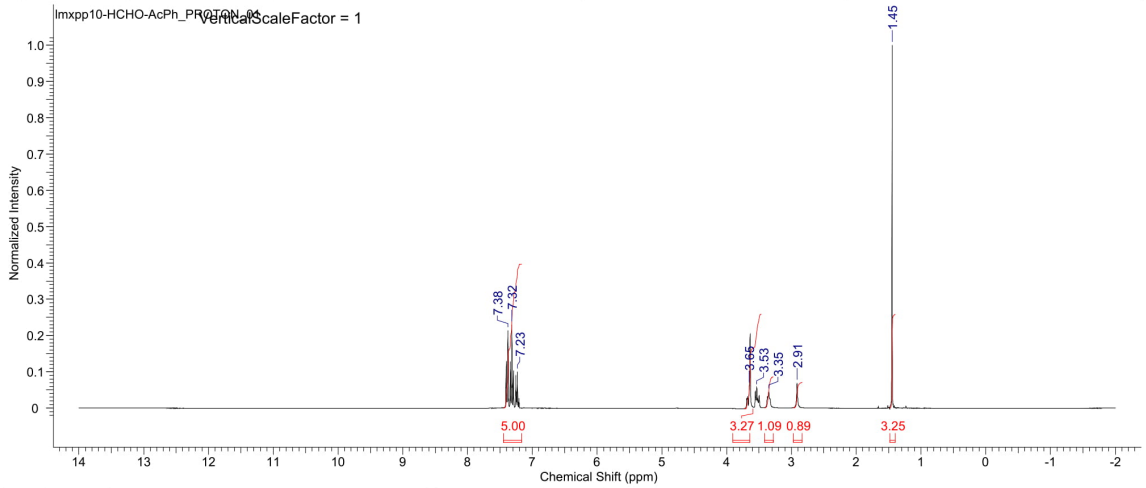
|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 2.5001 | ***Date*** | Oct 2 2019 | ***Date Stamp*** | Oct 2 2019 | | |
| ***File Name*** | C:\Users\Admin\OneDrive - McGill University\PostdocMcGill\Research\pp10\Angew\Oct2019\NMRs\lmxpp10-HCHO-AcPh_PROTON_01.fid\fid | | | | | | |
| ***Frequency (MHz)*** | 299.63 | ***Nucleus*** | 1H | ***Number of Transients*** | 16 | ***Original Points Count*** | 11985 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 14.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 1797.7679 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 4793.86 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [1.3996 .. 1.48 | 3.25487995 | 8.66399488e+8 | 3.25487995 |
| 2 | [2.8367 .. 2.96 | 0.89244324 | 2.37554800e+8 | 0.89244324 |
| 3 | [3.2827 .. 3.41 | 1.08941019 | 2.89984416e+8 | 1.08941019 |
| 4 | [3.4644 .. 3.72 | 3.26746225 | 8.69748672e+8 | 3.26746225 |
| 5 | [7.1645 .. 7.44 | 4.99931717 | 1.33074214e+9 | 4.99931717 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 1.45 | 433.5 | 1.0000 |
| 2 | 2.91 | 873.0 | 0.0689 |
| 3 | 3.35 | 1004.1 | 0.0449 |
| 4 | 3.53 | 1059.1 | 0.0560 |
| 5 | 3.65 | 1094.2 | 0.0620 |
| 6 | 7.23 | 2166.3 | 0.1002 |
| 7 | 7.32 | 2192.1 | 0.2296 |
| 8 | 7.38 | 2210.5 | 0.2137 |



2019/10/4 11:06:45

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|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 0.8700 | ***Date*** | Oct 2 2019 | ***Date Stamp*** | Oct 2 2019 | | |
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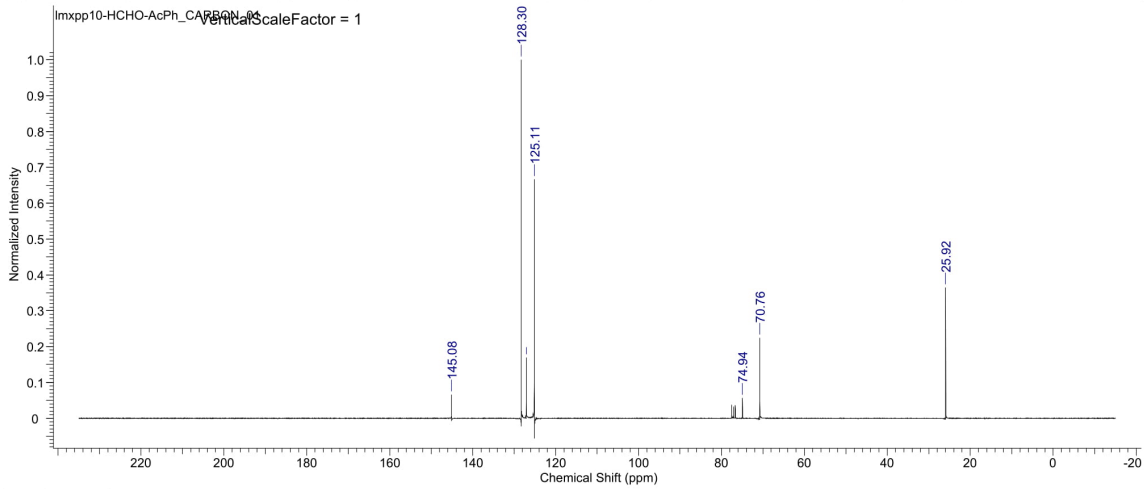
| ***Frequency (MHz)*** | 75.35 | ***Nucleus*** | 13C | ***Number of Transients*** | 5650 | ***Original Points Count*** | 16384 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 30.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 8287.5654 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 18832.39 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 25.92 | 1953.2 | 0.3645 |
| 2 | 70.76 | 5331.6 | 0.2245 |
| 3 | 74.94 | 5646.6 | 0.0565 |
| 4 | 125.11 | 9427.3 | 0.6664 |
| 5 | 127.04 | 9572.1 | 0.1692 |
| 6 | 128.30 | 9667.5 | 1.0000 |
| 7 | 145.08 | 10932.0 | 0.0661 |

Figure S22. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **5a**

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2019/10/4 11:10:19

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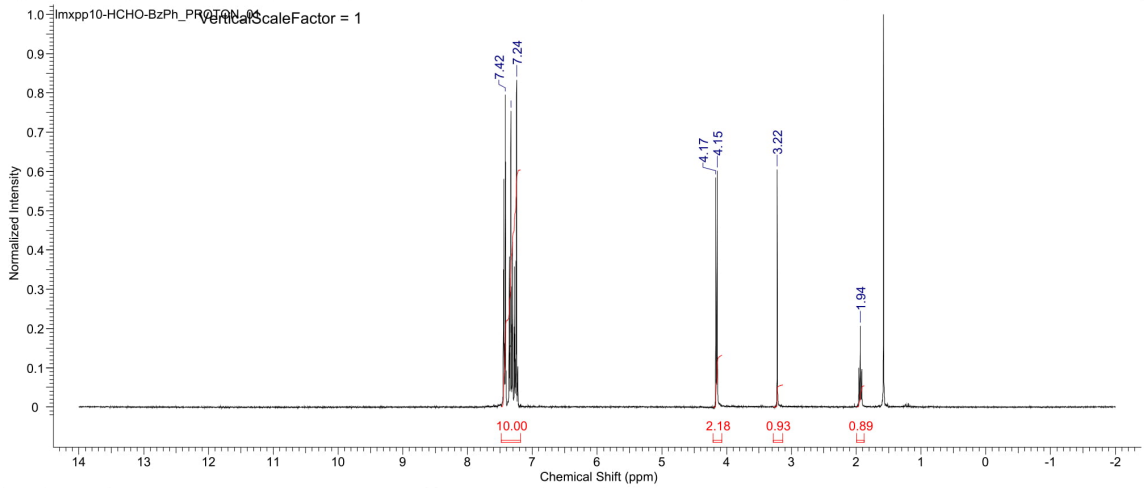
| ***Acquisition Time (sec)*** | 2.5001 | ***Date*** | Oct 2 2019 | ***Date Stamp*** | Oct 2 2019 | | |
| ***File Name*** | C:\Users\Admin\OneDrive - McGill University\PostdocMcGill\Research\pp10\Angew\Oct2019\NMRs\lmxpp10-HCHO-BzPh_PROTON_01.fid\fid | | | | | | |
| ***Frequency (MHz)*** | 299.63 | ***Nucleus*** | 1H | ***Number of Transients*** | 16 | ***Original Points Count*** | 11985 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 38.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 1797.7679 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 4793.86 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [1.8786 .. 1.99 | 0.89197105 | 1.57003296e+8 | 0.89197105 |
| 2 | [3.1340 .. 3.28 | 0.92570722 | 1.62941488e+8 | 0.92570722 |
| 3 | [4.0756 .. 4.20 | 2.17664003 | 3.83128640e+8 | 2.17664003 |
| 4 | [7.1810 .. 7.47 | 10.0006494 | 1.76029811e+9 | 10.00064945 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 1.94 | 580.4 | 0.2070 |
| 2 | 3.22 | 964.8 | 0.6048 |
| 3 | 4.15 | 1242.2 | 0.6019 |
| 4 | 4.17 | 1248.7 | 0.5846 |
| 5 | 7.24 | 2170.4 | 0.8333 |
| 6 | 7.33 | 2196.7 | 0.7543 |
| 7 | 7.42 | 2222.5 | 0.7960 |

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2019/10/4 11:12:38

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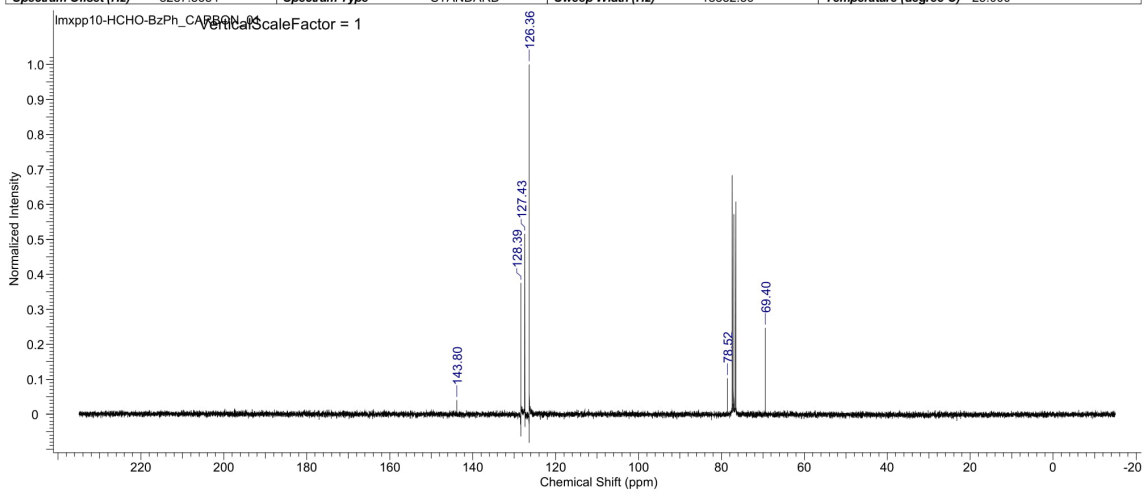
| ***Acquisition Time (sec)*** | 0.8700 | ***Date*** | Oct 2 2019 | ***Date Stamp*** | Oct 2 2019 | | |
| ***File Name*** | C:\Users\Admin\OneDrive - McGill University\PostdocMcGill\Research\pp10\Angew\Oct2019\NMRs\lmxpp10-HCHO-BzPh_CARBON_01.fid\fid | | | | | | |
| ***Frequency (MHz)*** | 75.35 | ***Nucleus*** | 13C | ***Number of Transients*** | 5650 | ***Original Points Count*** | 16384 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 30.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 8287.5654 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 18832.39 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 69.40 | 5229.3 | 0.2467 |
| 2 | 78.52 | 5916.7 | 0.1027 |
| 3 | 126.36 | 9521.6 | 1.0000 |
| 4 | 127.43 | 9602.0 | 0.5161 |
| 5 | 128.39 | 9674.4 | 0.3751 |
| 6 | 143.80 | 10835.5 | 0.0400 |

Figure S23. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **5b**

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2019/10/4 11:36:41

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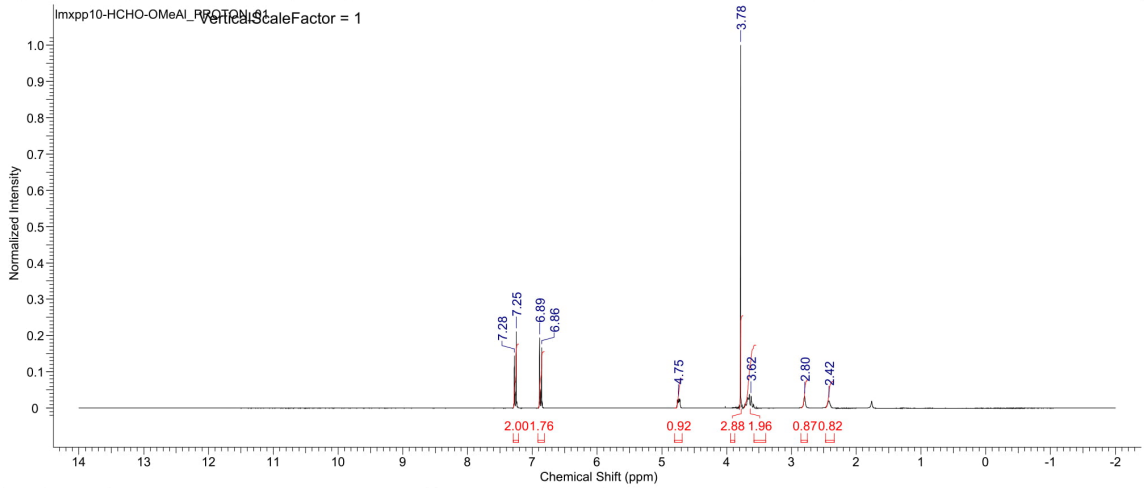
|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 2.5001 | ***Date*** | Oct 3 2019 | ***Date Stamp*** | Oct 3 2019 | | |
| ***File Name*** | C:\Users\Admin\OneDrive - McGill University\PostdocMcGill\Research\pp10\Angew\Oct2019\NMRs\lmxpp10-HCHO-OMeAl_PROTON_01.fid\fid | | | | | | |
| ***Frequency (MHz)*** | 299.63 | ***Nucleus*** | 1H | ***Number of Transients*** | 16 | ***Original Points Count*** | 11985 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 30.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 1797.7679 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 4793.86 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [2.3411 .. 2.47 | 0.82301807 | 2.30894752e+8 | 0.82301807 |
| 2 | [2.7541 .. 2.85 | 0.86641610 | 2.43069920e+8 | 0.86641610 |
| 3 | [3.5470 .. 3.72 | 1.95533931 | 5.48563392e+8 | 1.95533931 |
| 4 | [3.7452 .. 3.81 | 2.88269401 | 8.08729408e+8 | 2.88269401 |
| 5 | [4.6868 .. 4.80 | 0.91506767 | 2.56718944e+8 | 0.91506767 |
| 6 | [6.8176 .. 6.91 | 1.75994647 | 4.93746624e+8 | 1.75994647 |
| 7 | [7.2141 .. 7.29 | 2.00040817 | 5.61207296e+8 | 2.00040817 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 2.42 | 725.8 | 0.0198 |
| 2 | 2.80 | 838.1 | 0.0317 |
| 3 | 3.62 | 1085.4 | 0.0326 |
| 4 | 3.78 | 1134.0 | 1.0000 |
| 5 | 4.75 | 1423.1 | 0.0240 |
| 6 | 6.86 | 2054.8 | 0.1674 |
| 7 | 6.89 | 2063.6 | 0.1944 |
| 8 | 7.25 | 2171.6 | 0.2111 |
| 9 | 7.28 | 2180.7 | 0.1436 |

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2019/10/4 11:39:10

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| ***Acquisition Time (sec)*** | 0.8700 | ***Date*** | Oct 3 2019 | ***Date Stamp*** | Oct 3 2019 | | |
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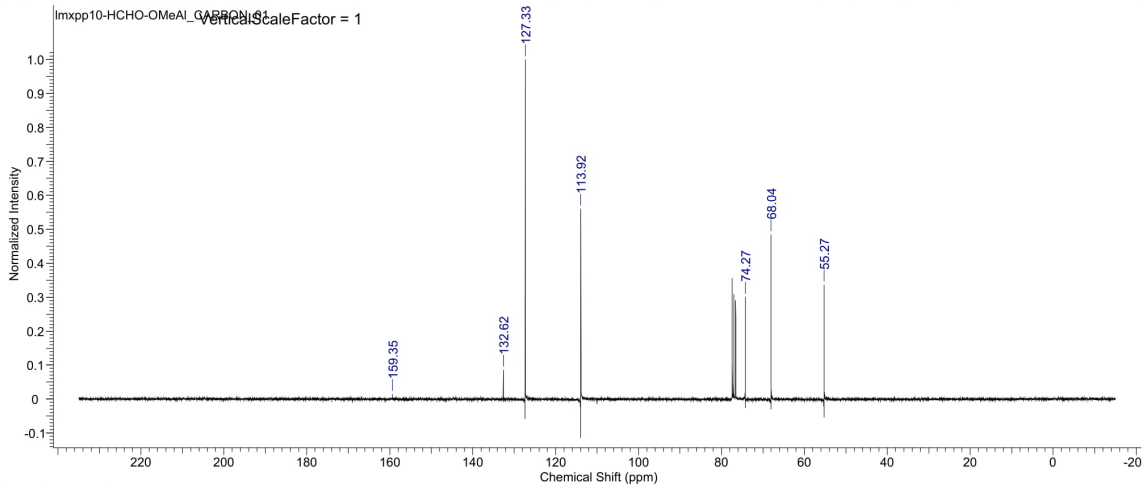
| ***Frequency (MHz)*** | 75.35 | ***Nucleus*** | 13C | ***Number of Transients*** | 5650 | ***Original Points Count*** | 16384 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 30.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 8287.5654 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 18832.39 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 55.27 | 4164.9 | 0.3360 |
| 2 | 68.04 | 5127.0 | 0.4848 |
| 3 | 74.27 | 5596.0 | 0.3006 |
| 4 | 113.92 | 8583.6 | 0.5598 |
| 5 | 127.33 | 9594.0 | 1.0000 |
| 6 | 132.62 | 9992.9 | 0.0861 |
| 7 | 159.35 | 12006.8 | 0.0151 |

Figure S24. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **5c**

2019/10/4 10:45:09

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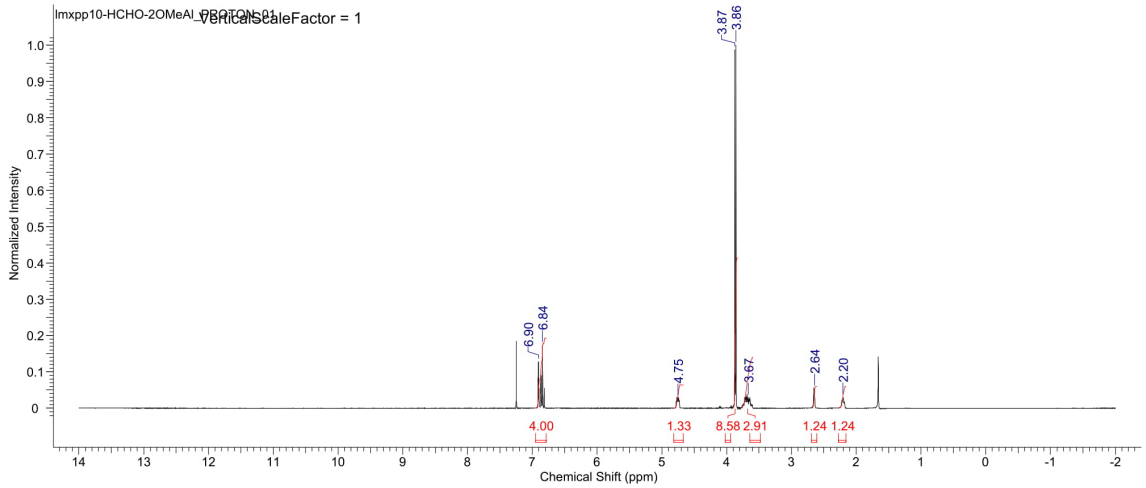
|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 2.5001 | ***Date*** | Oct 3 2019 | ***Date Stamp*** | Oct 3 2019 | | |
| ***File Name*** | C:\Users\Admin\OneDrive - McGill University\PostdocMcGill\Research\pp10\Angew\Oct2019\NMRs\lmxpp10-HCHO-2OMeAl_PROTON_01.fid\fid | | | | | | |
| ***Frequency (MHz)*** | 299.63 | ***Nucleus*** | 1H | ***Number of Transients*** | 16 | ***Original Points Count*** | 11985 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 32.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 1797.7679 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 4793.86 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [2.1594 .. 2.27 | 1.23607671 | 1.40372000e+8 | 1.23607671 |
| 2 | [2.6054 .. 2.68 | 1.24363351 | 1.41230176e+8 | 1.24363351 |
| 3 | [3.5965 .. 3.76 | 2.91378832 | 3.30897184e+8 | 2.91378832 |
| 4 | [3.8278 .. 3.91 | 8.58301640 | 9.74709056e+8 | 8.58301640 |
| 5 | [4.6702 .. 4.81 | 1.32541454 | 1.50517440e+8 | 1.32541454 |
| 6 | [6.7846 .. 6.94 | 3.99910522 | 4.54148512e+8 | 3.99910522 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 2.20 | 660.2 | 0.0294 |
| 2 | 2.64 | 792.5 | 0.0537 |
| 3 | 3.67 | 1099.2 | 0.0288 |
| 4 | 3.86 | 1155.6 | 1.0000 |
| 5 | 3.87 | 1160.9 | 0.9878 |
| 6 | 4.75 | 1424.5 | 0.0262 |
| 7 | 6.84 | 2050.7 | 0.1738 |
| 8 | 6.90 | 2068.9 | 0.1279 |



2019/10/4 10:53:15

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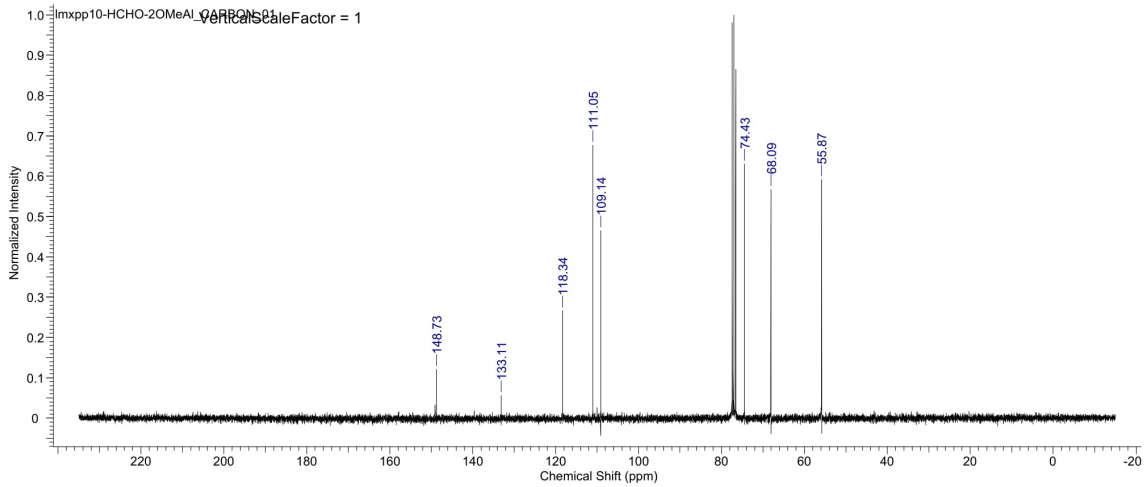
|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 0.8700 | ***Date*** | Oct 3 2019 | ***Date Stamp*** | Oct 3 2019 | | |
| ***File Name*** | C:\Users\Admin\OneDrive - McGill University\PostdocMcGill\Research\pp10\Angew\Oct2019\NMRs\lmxpp10-HCHO-2OMeAl_CARBON_01.fid\fid | | | | | | |
| ***Frequency (MHz)*** | 75.35 | ***Nucleus*** | 13C | ***Number of Transients*** | 5650 | ***Original Points Count*** | 16384 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 30.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 8287.5654 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 18832.39 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 55.87 | 4209.7 | 0.5920 |
| 2 | 68.09 | 5130.4 | 0.5678 |
| 3 | 74.43 | 5608.6 | 0.6307 |
| 4 | 109.14 | 8223.8 | 0.4658 |
| 5 | 111.05 | 8367.5 | 0.6777 |
| 6 | 118.34 | 8916.9 | 0.2663 |
| 7 | 133.11 | 10029.6 | 0.0570 |
| 8 | 148.73 | 11206.7 | 0.1210 |

Figure S25. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **5d**

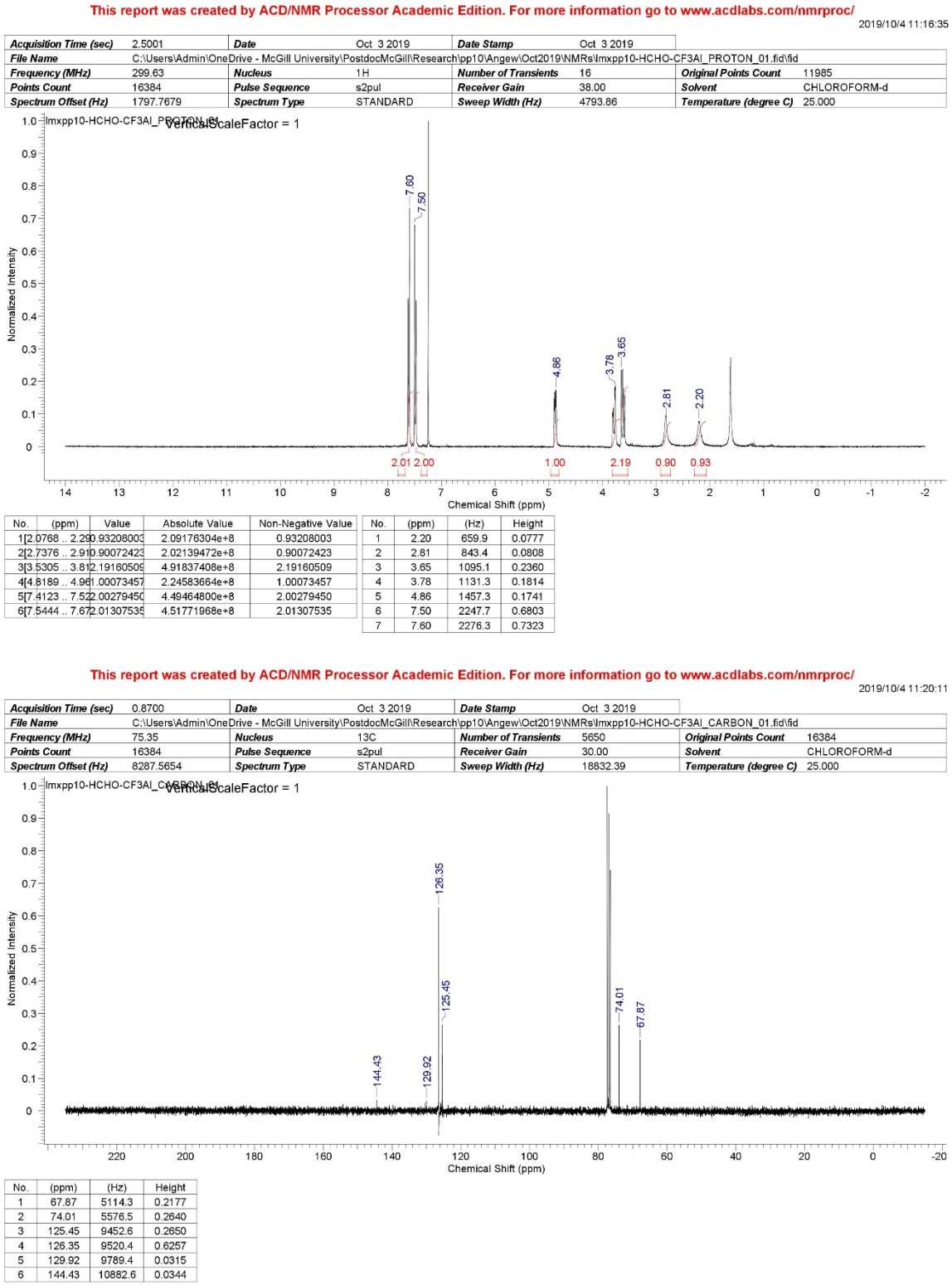



Figure S26. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **5e**

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2019/10/4 11:43:27

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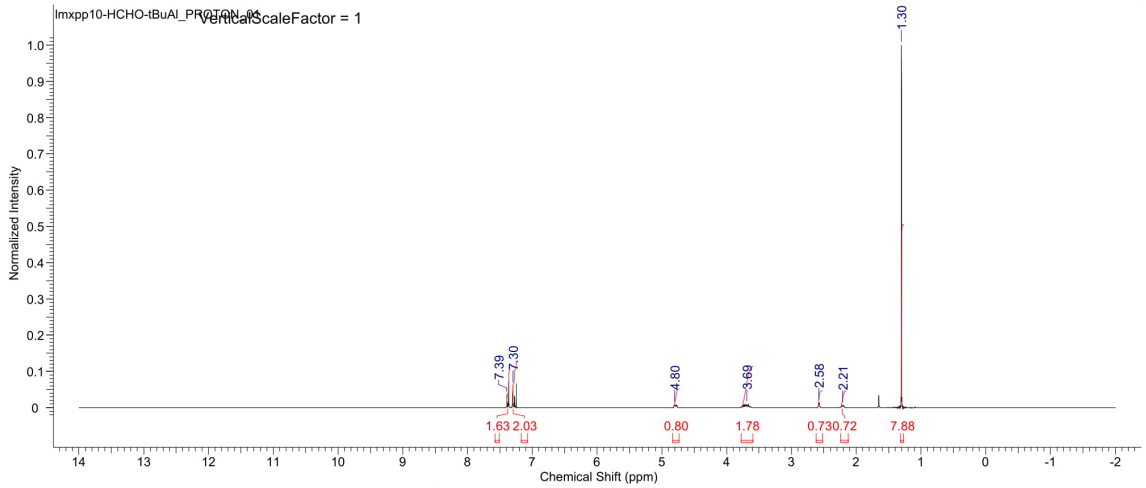
| ***Acquisition Time (sec)*** | 2.5001 | ***Date*** | Oct 3 2019 | ***Date Stamp*** | Oct 3 2019 | | |
| ***File Name*** | C:\Users\Admin\OneDrive - McGill University\PostdocMcGill\Research\pp10\Angew\Oct2019\NMRs\lmxpp10-HCHO-tBuAl_PROTON_01.fid\fid | | | | | | |
| ***Frequency (MHz)*** | 299.63 | ***Nucleus*** | 1H | ***Number of Transients*** | 16 | ***Original Points Count*** | 11985 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 32.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 1797.7679 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 4793.86 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [1.2674 .. 1.31 | 7.87904215 | 1.46455104e+9 | 7.87904215 |
| 2 | [2.1594 .. 2.27 | 0.72184086 | 1.34175296e+8 | 0.72184086 |
| 3 | [2.5228 .. 2.62 | 0.72592765 | 1.34934944e+8 | 0.72592765 |
| 4 | [3.5965 .. 3.77 | 1.77667797 | 3.30247712e+8 | 1.77667797 |
| 5 | [4.7363 .. 4.83 | 0.79797387 | 1.48326848e+8 | 0.79797387 |
| 6 | [7.2471 .. 7.34 | 2.03198552 | 3.77704096e+8 | 2.03198552 |
| 7 | [7.3462 .. 7.41 | 1.62907398 | 3.02811168e+8 | 1.62907398 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 1.30 | 390.2 | 1.0000 |
| 2 | 2.21 | 663.2 | 0.0066 |
| 3 | 2.58 | 773.5 | 0.0122 |
| 4 | 3.69 | 1105.6 | 0.0080 |
| 5 | 4.80 | 1439.2 | 0.0069 |
| 6 | 7.30 | 2187.7 | 0.0612 |
| 7 | 7.39 | 2215.5 | 0.0358 |

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2019/10/4 11:44:16

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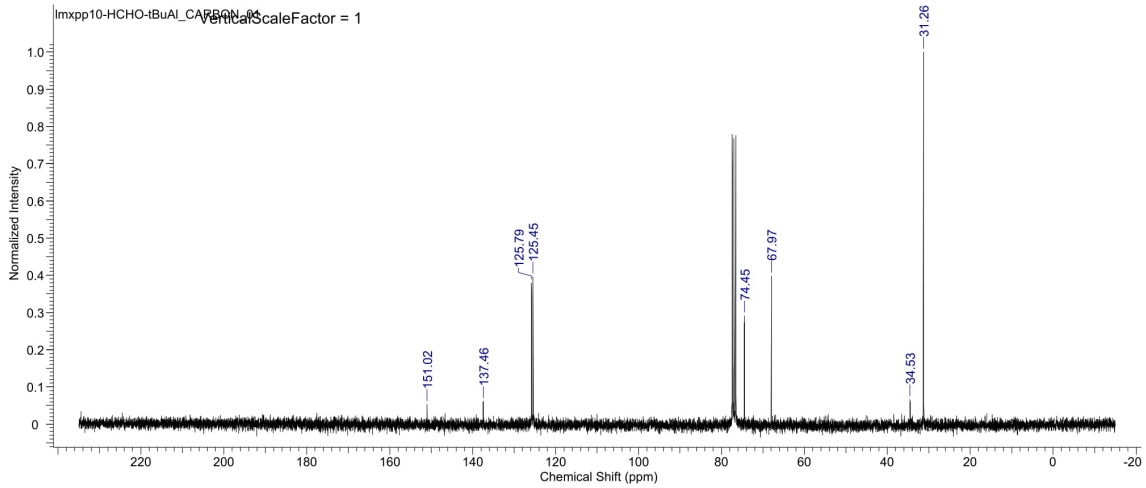
| ***Acquisition Time (sec)*** | 0.8700 | ***Date*** | Oct 3 2019 | ***Date Stamp*** | Oct 3 2019 | | |
| ***File Name*** | C:\Users\Admin\OneDrive - McGill University\PostdocMcGill\Research\pp10\Angew\Oct2019\NMRs\lmxpp10-HCHO-tBuAl_CARBON_01.fid\fid | | | | | | |
| ***Frequency (MHz)*** | 75.35 | ***Nucleus*** | 13C | ***Number of Transients*** | 5650 | ***Original Points Count*** | 16384 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 30.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 8287.5654 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 18832.39 | ***Temperature (degree C)*** | 25.000 |

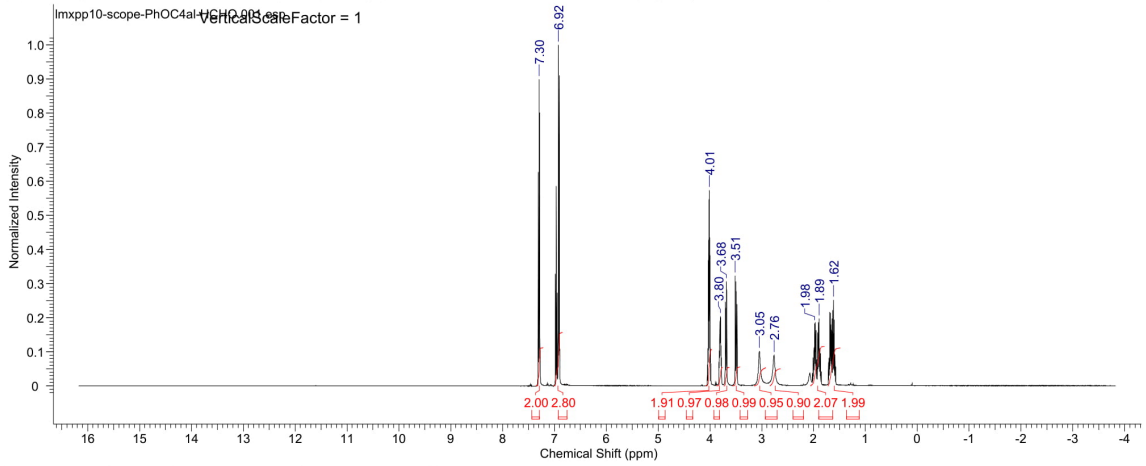



| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 31.26 | 2355.5 | 1.0000 |
| 2 | 34.53 | 2601.5 | 0.0666 |
| 3 | 67.97 | 5121.2 | 0.3987 |
| 4 | 74.45 | 5609.8 | 0.2918 |
| 5 | 125.45 | 9452.6 | 0.3966 |
| 6 | 125.79 | 9477.9 | 0.3795 |
| 7 | 137.46 | 10357.3 | 0.0614 |
| 8 | 151.02 | 11379.2 | 0.0530 |

Figure S27. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **5f**

2019/10/4 11:56:57

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 3.2768 | ***Comment*** | Li 1d_PROTON CDCl3 E:\\ mingxin 4 | | | ***Date*** | 01 Oct 2019 17:28:32 |
| ***Date Stamp*** | 01 Oct 2019 17:28:32 | | | | | | |
| ***File Name*** | C:\Users\Admin\OneDrive - McGill University\PostdocMcGill\Research\pp10\Angew\Oct2019\NMRs\lmxpp10-scope-PhOC4al-HCHO\1\fid | | | | | | |
| ***Frequency (MHz)*** | 500.30 | ***Nucleus*** | 1H | ***Number of Transients*** | 16 | ***Origin*** | AVIII500HD |
| ***Original Points Count*** | 32768 | ***Owner*** | mcgillnmr | ***Points Count*** | 32768 | ***Pulse Sequence*** | zg30 |
| ***Receiver Gain*** | 71.03 | ***SW(cyclical) (Hz)*** | 10000.00 | ***Solvent*** | CHLOROFORM-d | ***Spectrum Offset (Hz)*** | 3089.5574 |
| ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 9999.70 | ***Temperature (degree C)*** | 25.001 | | |



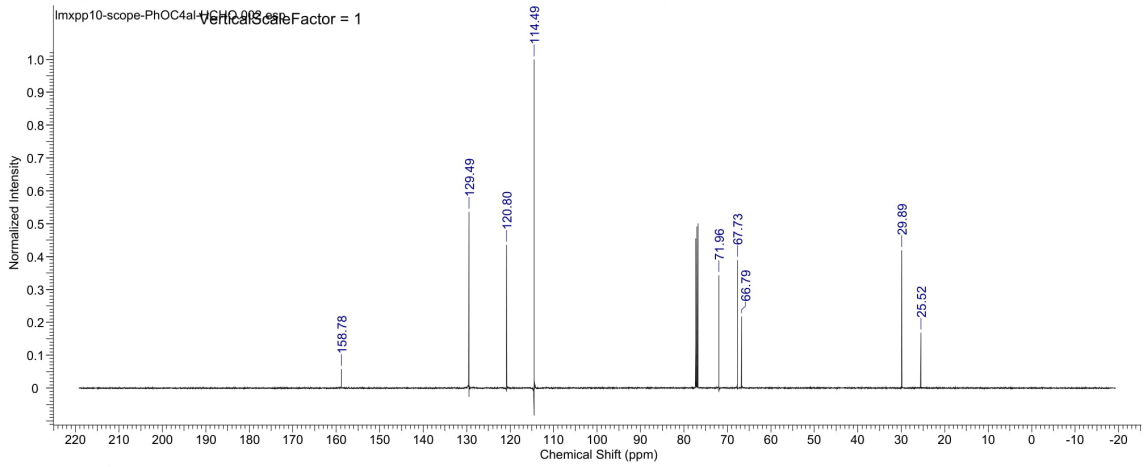

| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [1.4807 .. 1.72 | 1.99237180 | 1.26128507e+10 | 1.99237180 |
| 2 | [1.7903 .. 2.05 | 2.07298493 | 1.31231775e+10 | 2.07298493 |
| 3 | [2.6363 .. 2.84 | 0.90484548 | 5.72818842e+9 | 0.90484548 |
| 4 | [2.9252 .. 3.15 | 0.95175987 | 6.02518323e+9 | 0.95175987 |
| 5 | [3.4205 .. 3.56 | 0.99218309 | 6.28108544e+9 | 0.99218309 |
| 6 | [3.6268 .. 3.73 | 0.98026651 | 6.20564634e+9 | 0.98026651 |
| 7 | [3.7507 .. 3.87 | 0.97099584 | 6.14695782e+9 | 0.97099584 |
| 8 | [3.9570 .. 4.08 | 1.91321063 | 1.21117153e+10 | 1.91321063 |
| 9 | [6.8460 .. 7.01 | 2.80365300 | 1.77487237e+10 | 2.80365300 |
| 10 | [7.2175 .. 7.36 | 2.00014353 | 1.26620498e+10 | 2.00014353 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 1.62 | 810.4 | 0.2523 |
| 2 | 1.89 | 947.1 | 0.1981 |
| 3 | 1.98 | 991.9 | 0.1828 |
| 4 | 2.76 | 1382.9 | 0.0898 |
| 5 | 3.05 | 1524.5 | 0.1021 |
| 6 | 3.51 | 1757.6 | 0.3227 |
| 7 | 3.68 | 1841.5 | 0.3068 |
| 8 | 3.80 | 1902.3 | 0.2048 |
| 9 | 4.01 | 2007.3 | 0.5740 |
| 10 | 6.92 | 3462.3 | 1.0000 |
| 11 | 7.30 | 3650.0 | 0.8981 |



2019/10/4 11:59:20

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 1.0923 | ***Comment*** | Li 1d_C13 CDCl3 E:\\ mingxin 4 | | | ***Date*** | 02 Oct 2019 00:18:08 |
| ***Date Stamp*** | 02 Oct 2019 00:18:08 | | | | | | |
| ***File Name*** | C:\Users\Admin\OneDrive - McGill University\PostdocMcGill\Research\pp10\Angew\Oct2019\NMRs\lmxpp10-scope-PhOC4al-HCHO\2\fid | | | | | | |
| ***Frequency (MHz)*** | 125.81 | ***Nucleus*** | 13C | ***Number of Transients*** | 3400 | ***Origin*** | AVIII500HD |
| ***Original Points Count*** | 32768 | ***Owner*** | mcgillnmr | ***Points Count*** | 32768 | ***Pulse Sequence*** | zgpg30 |
| ***Receiver Gain*** | 192.72 | ***SW(cyclical) (Hz)*** | 30000.00 | ***Solvent*** | CHLOROFORM-d | ***Spectrum Offset (Hz)*** | 12578.9238 |
| ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 29999.08 | ***Temperature (degree C)*** | 25.000 | | |

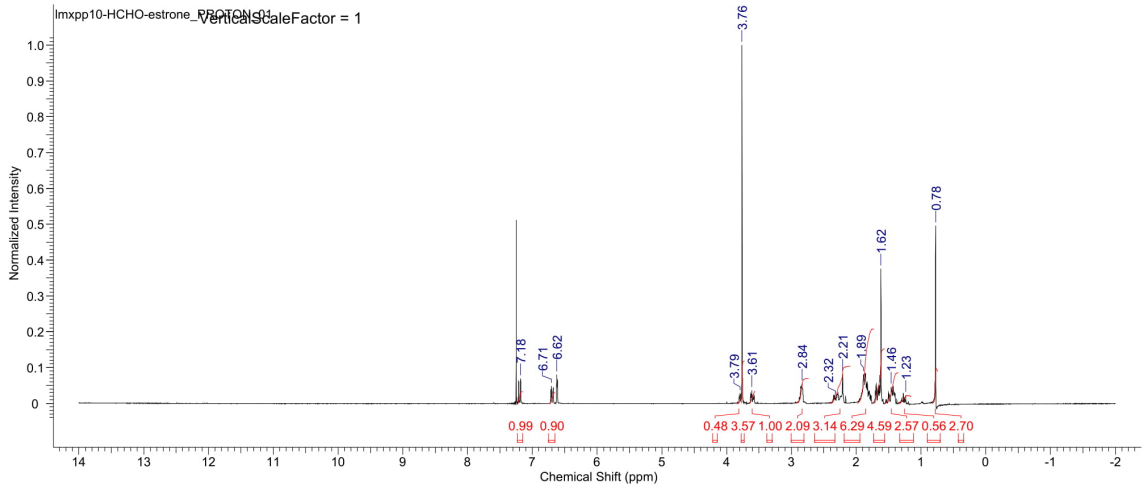



| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 25.52 | 3210.8 | 0.1684 |
| 2 | 29.89 | 3761.0 | 0.4193 |
| 3 | 66.79 | 8403.7 | 0.2177 |
| 4 | 67.73 | 8520.8 | 0.3890 |
| 5 | 71.96 | 9053.7 | 0.3430 |
| 6 | 114.49 | 14404.9 | 1.0000 |
| 7 | 120.80 | 15197.8 | 0.4356 |
| 8 | 129.49 | 16291.8 | 0.5354 |
| 9 | 158.78 | 19976.8 | 0.0581 |

Figure S28. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **5g**

2019/10/4 11:31:26

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 2.5001 | ***Date*** | Oct 3 2019 | ***Date Stamp*** | Oct 3 2019 | | |
| ***File Name*** | C:\Users\Admin\OneDrive - McGill University\PostdocMcGill\Research\pp10\Angew\Oct2019\NMRs\lmxpp10-HCHO-estrone_PROTON_01.fid\fid | | | | | | |
| ***Frequency (MHz)*** | 299.63 | ***Nucleus*** | 1H | ***Number of Transients*** | 16 | ***Original Points Count*** | 11985 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 36.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 1797.7679 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 4793.86 | ***Temperature (degree C)*** | 25.000 |




| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 1 | [0.7388 .. 0.82 | 2.69916272 | 3.51316640e+8 | 2.69916272 |
| 2 | [1.1518 .. 1.35 | 0.56387389 | 7.33924960e+7 | 0.56387389 |
| 3 | [1.3500 .. 1.56 | 2.57165599 | 3.34720672e+8 | 2.57165599 |
| 4 | [1.5648 .. 1.72 | 4.59162569 | 5.97635136e+8 | 4.59162569 |
| 5 | [1.7299 .. 1.97 | 6.29179573 | 8.18925248e+8 | 6.29179573 |
| 6 | [2.0934 .. 2.40 | 3.13862419 | 4.08515904e+8 | 3.13862419 |

| No. | (ppm) | Value | Absolute Value | Non-Negative Value |
|---|---|---|---|---|
| 7 | [2.7376 .. 2.93 | 2.09004426 | 2.72035232e+8 | 2.09004426 |
| 8 | [3.5635 .. 3.64 | 0.99923056 | 1.30057488e+8 | 0.99923056 |
| 9 | [3.7287 .. 3.77 | 3.56983948 | 4.64641888e+8 | 3.56983948 |
| 10 | [3.7782 .. 3.84 | 0.47600257 | 6.19553720e+7 | 0.47600257 |
| 11 | [6.6524 .. 6.75 | 0.89890718 | 1.16999640e+8 | 0.89890718 |
| 12 | [7.1480 .. 7.23 | 0.99454361 | 1.29447448e+8 | 0.99454361 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 0.78 | 232.4 | 0.4966 |
| 2 | 1.23 | 370.0 | 0.0226 |
| 3 | 1.46 | 438.1 | 0.0461 |
| 4 | 1.62 | 485.0 | 0.3756 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 5 | 1.64 | 491.4 | 0.0506 |
| 6 | 1.89 | 566.0 | 0.0808 |
| 7 | 2.21 | 662.3 | 0.0824 |
| 8 | 2.32 | 695.9 | 0.0156 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 9 | 2.84 | 850.1 | 0.0542 |
| 10 | 3.61 | 1082.8 | 0.0366 |
| 11 | 3.76 | 1127.2 | 1.0000 |
| 12 | 3.79 | 1136.0 | 0.0270 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 13 | 6.62 | 1984.3 | 0.0802 |
| 14 | 6.71 | 2009.2 | 0.0478 |
| 15 | 7.18 | 2152.0 | 0.0695 |



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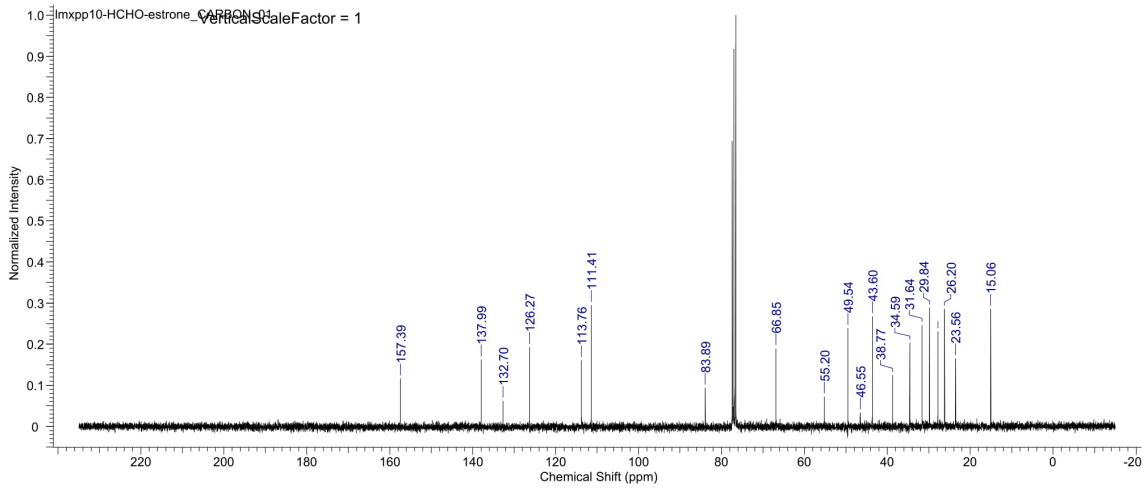
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| ***Acquisition Time (sec)*** | 0.8700 | ***Date*** | Oct 3 2019 | ***Date Stamp*** | Oct 3 2019 | | |
| ***File Name*** | C:\Users\Admin\OneDrive - McGill University\PostdocMcGill\Research\pp10\Angew\Oct2019\NMRs\lmxpp10-HCHO-estrone_CARBON_01.fid\fid | | | | | | |
| ***Frequency (MHz)*** | 75.35 | ***Nucleus*** | 13C | ***Number of Transients*** | 5650 | ***Original Points Count*** | 16384 |
| ***Points Count*** | 16384 | ***Pulse Sequence*** | s2pul | ***Receiver Gain*** | 30.00 | ***Solvent*** | CHLOROFORM-d |
| ***Spectrum Offset (Hz)*** | 8287.5654 | ***Spectrum Type*** | STANDARD | ***Sweep Width (Hz)*** | 18832.39 | ***Temperature (degree C)*** | 25.000 |



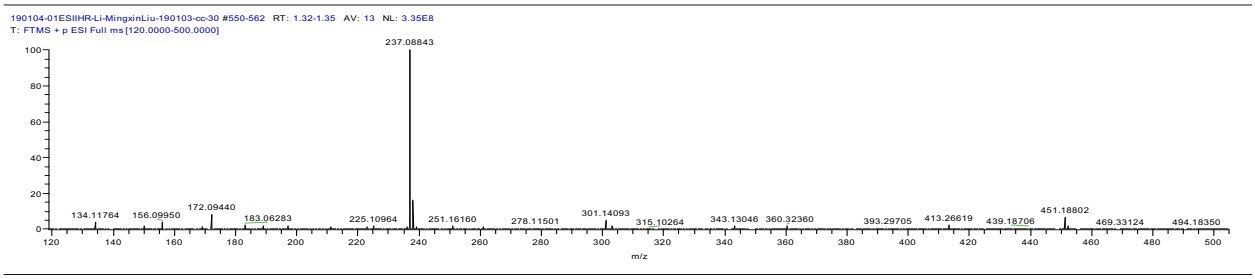

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 1 | 15.06 | 1134.8 | 0.2856 |
| 2 | 23.56 | 1775.0 | 0.1654 |
| 3 | 26.20 | 1973.9 | 0.2856 |
| 4 | 27.81 | 2095.7 | 0.2310 |
| 5 | 29.84 | 2248.6 | 0.2884 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 6 | 31.64 | 2384.3 | 0.2461 |
| 7 | 34.59 | 2606.1 | 0.2028 |
| 8 | 38.77 | 2921.1 | 0.1244 |
| 9 | 43.60 | 3285.5 | 0.2673 |
| 10 | 46.55 | 3507.3 | 0.0335 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 11 | 49.54 | 3732.6 | 0.2384 |
| 12 | 55.20 | 4159.1 | 0.0726 |
| 13 | 66.85 | 5037.3 | 0.1896 |
| 14 | 83.89 | 6321.3 | 0.0936 |
| 15 | 111.41 | 8395.0 | 0.2950 |

| No. | (ppm) | (Hz) | Height |
|---|---|---|---|
| 16 | 113.76 | 8572.1 | 0.1609 |
| 17 | 126.27 | 9514.7 | 0.1926 |
| 18 | 132.70 | 9998.6 | 0.0619 |
| 19 | 137.99 | 10397.5 | 0.1627 |
| 20 | 157.39 | 11859.7 | 0.1162 |

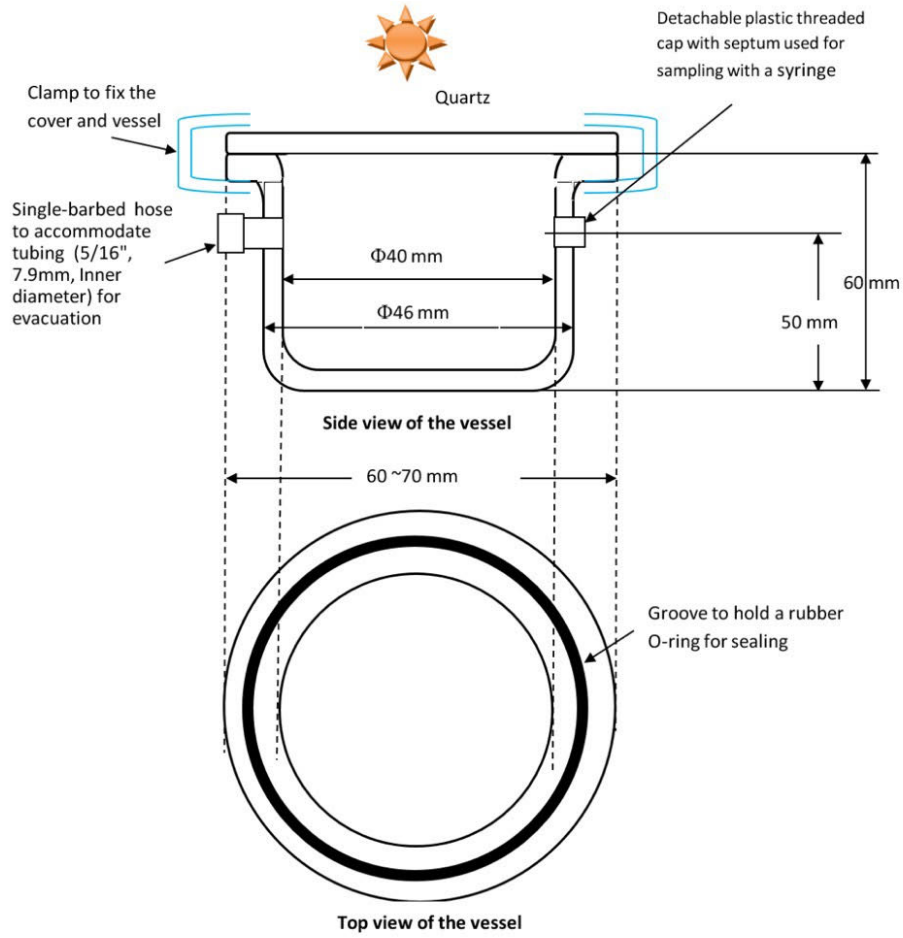
Figure S29. $^{1}$H-(upper), and $^{13}$C-(lower)-NMR of compound **5h**




190104-01ESIIHR-Li-MingxinLiu-190103-cc-30#550-562 RT: 1.32-1.35 AV: 13
T: FTMS + p ESI Full ms [120.0000-500.0000]
m/z= 237.08032-237.09775

| m/z | Intensity | Relative | Resolution | Charge | Theo. Mass | Delta (ppm) | RDB equiv. | Composition |
|---|---|---|---|---|---|---|---|---|
| 237.08843 | 342815456.0 | 100.00 | 34913.27 | 1.00 | 237.08860 | -0.71 | 7.5 | $C_{14}H_{14}O_2Na$ |
| | | | | | 237.08726 | 4.95 | 8.0 | $C_{12}H_{12}ON_3Na$ |

Figure S30. HR-ESI spectrum of the reaction mixture of Table 4, entry 3.



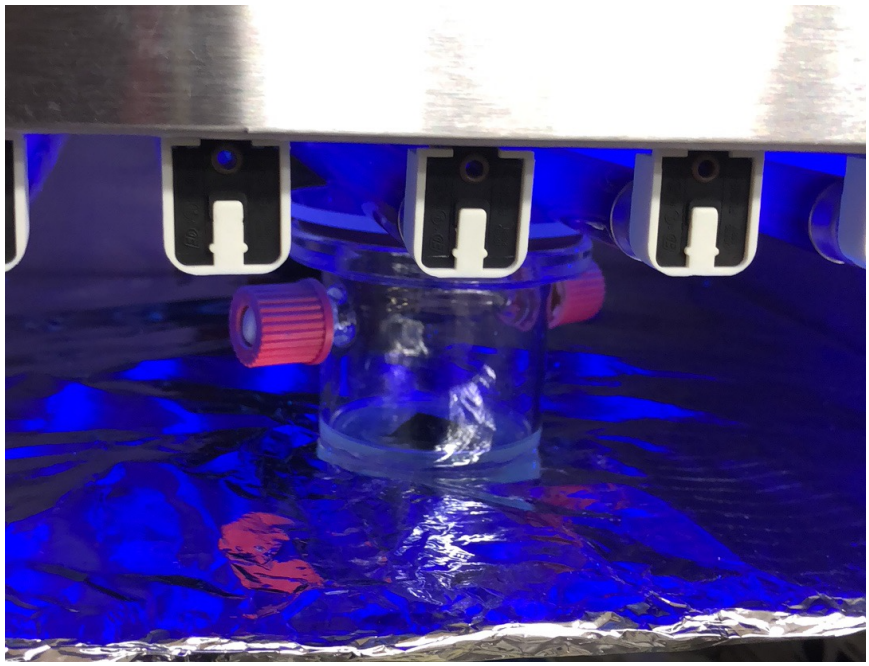



Figure S31. Photo-induced reaction setup.

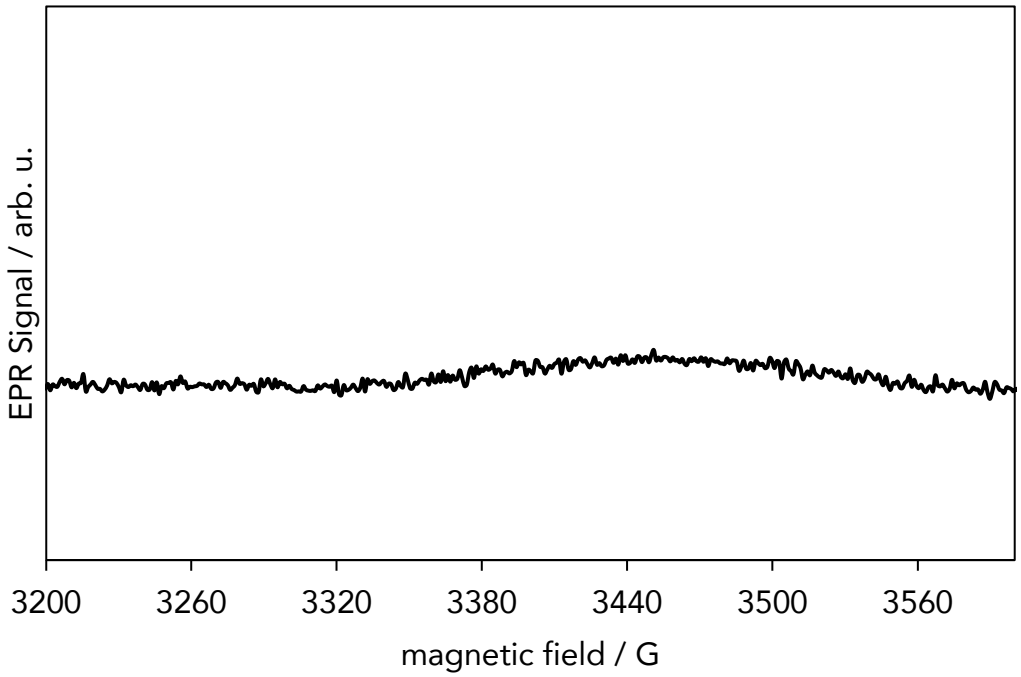



Figure S32. EPR signal of p-GaN in dark.

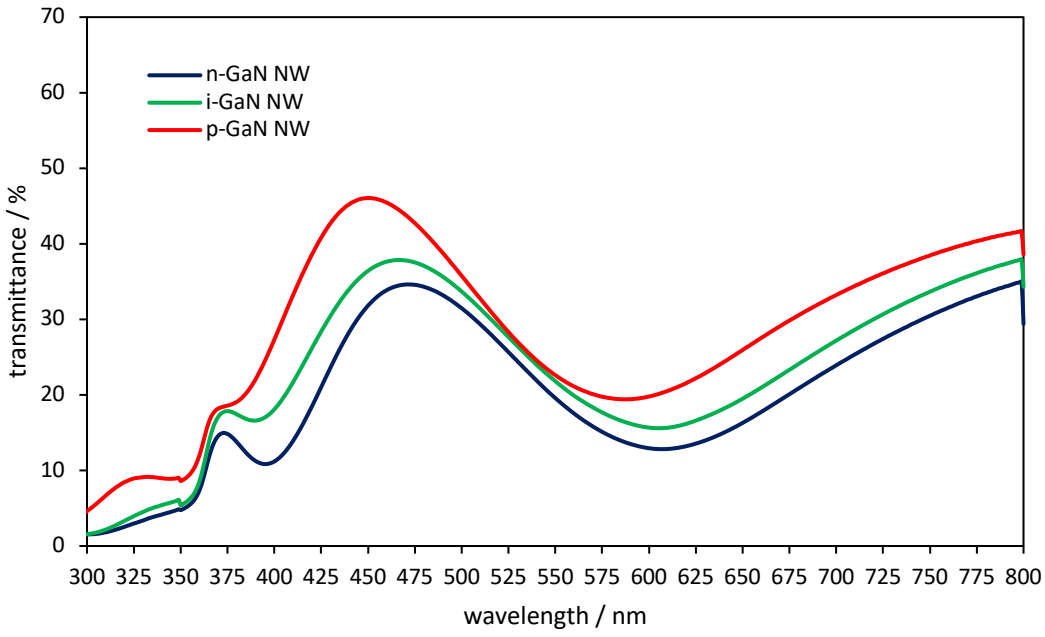
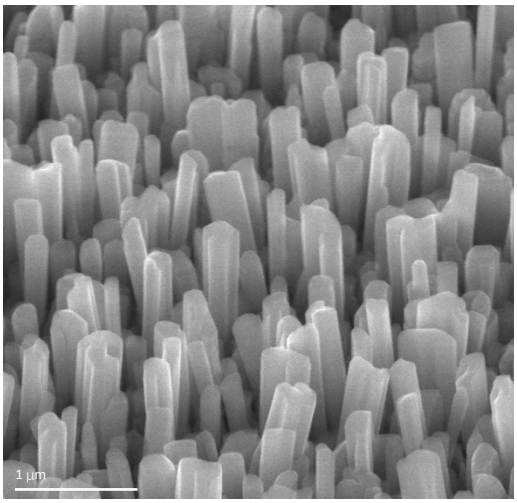



Figure S33. UV-Vis absorption spectrum for GaN NW catalysts. The glitches at 350 nm on the spectra were system error caused by the spectrometer's lamp switching.



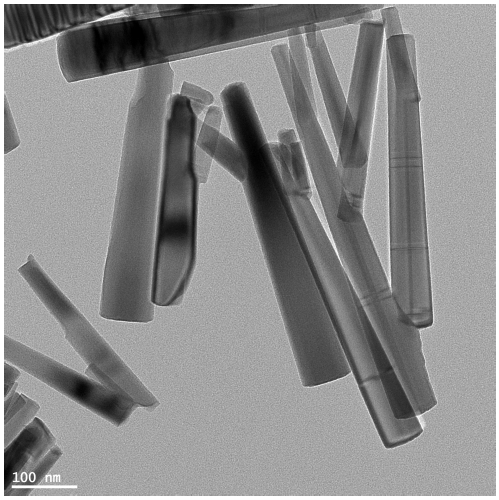



Figure S34. SEM (left) and TEM (right) of the GaN NW after 13 consecutive catalyses.

Table S1. Band edge energy of various photosensitizing semiconductors and their PCR reactivity

| semiconductor[a] | band gap / eV | reference | PCR yield of **2a** (same conditions as Table 1) / % |
|---|---|---|---|
| GaN (commercial powder) | 3.4 | (*13*) | 21 |
| $TiO_2$ | 3.05 | (40) | 44 |
| CdS | 2.42 | (41) | 89 |
| $C_3N_4$ | 2.7 | (*42*) | 62 |
| ZnO | 3.3 | (*43*) | not detected |

[a]All reagents used were commercially available. Catalysts were introduced as 1 mg powder into 0.5 mmol MeOH.

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