

Supporting Information

## **Copper Catalyzed Direct C–H Double Methylation of Aromatic Aldehydes Employing Methanol as an Alkylating Agent**

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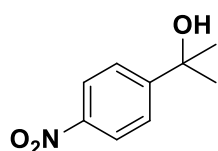
## 1. General Information

UV-Visible spectra were recorded on a Shimadzu UV2600 instrument. FT-IR spectra of the compounds were recorded as their KBr pellets (thin film) using a ThermoScientific Nicolet iS5 spectrometer.  $^1\text{H}$  NMR (TMS as the internal standard) and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 500 MHz spectrometer. Chemical shifts ( $\delta$ ) are reported in ppm and coupling constants ( $J$ ) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, m = multiplet. Mass spectra were recorded on the Agilent Q-TOF HRMS instrument. Unless otherwise noted, all the reagents were obtained commercially and used without further purification. Hexane for silica gel column chromatography was distilled prior to use. Methanol was dried based on the standard procedure. XploSens PS<sup>TM</sup> peroxides detection strip has been purchased from Sigma.

## 2. General Procedure A

A 10 ml round bottom flask was charged with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.025 mmol, 5 mol %) in 1 ml methanol. The mixture was stirred for 30 min, then aldehyde (0.5 mmol) was added. Then the reaction mixture was stirred at room temperature for 24 h. Then the solvent was removed under reduced pressure and the crude reaction mixture was purified by silica gel column chromatography (Hexane/EtOAc = 995/5 to 85/15) to obtain the title compounds. Silica gel was neutralized with triethylamine before isolating **3ai**.

### 2-(4-nitrophenyl)propan-2-ol (**3aa**)

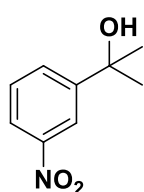


Colourless oil (82 mg, 90 %);  $R_f$  = 0.4 (10 % EtOAc in hexane)

UV-Vis (MeOH):  $\lambda_{\text{max}}$  (nm): 264, 203.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  8.24 - 8.21 (m, 2H), 7.65 - 7.63 (m, 2H), 5.47 (s, 1H), 3.34 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  148.2, 145.2, 128, 123.6, 101.7, 52.9. FT-

IR (Thin film):  $\nu$  3426, 1525, 1346  $\text{cm}^{-1}$ . HR-MS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_9\text{H}_{11}\text{NO}_3]$  166.0504 ( $[\text{M}-\text{CH}_3]^+$ ); Found 166.0504.

### 2-(3-nitrophenyl)propan-2-ol (**3ab**)



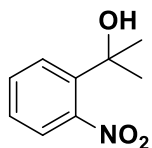
Pale yellow oil (85 mg, 94 %);  $R_f$  = 0.4 (10 % EtOAc in hexane)

UV-Vis (MeOH),  $\lambda_{\text{max}}$  (nm): 260, 204.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  8.32 - 8.31 (m, 1H), 8.18 - 8.16 (m, 1H), 7.78 - 7.76 (m, 1H), 7.54 (t,  $J$  = 7.95 Hz, 1H), 5.46 (s, 1H), 3.33 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  148.3, 140.4, 132.9, 129.3, 123.4, 122.0, 101.5, 52.7. FT-IR (Thin film):  $\nu$  3444, 1531, 1349

$\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_9\text{H}_{11}\text{NO}_3]$  166.0504 ( $[\text{M}-\text{CH}_3]^+$ ); Found: 166.0504.

### 2-(2-nitrophenyl)propan-2-ol (3ac)

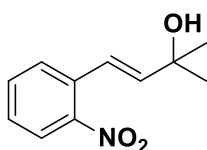
Colourless oil (75 mg, 83 %);  $R_f = 0.4$  (10 % EtOAc in Hexane)



UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 253, 205.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.81 - 7.77 (m, 2H), 7.59 (td,  $J = 7.5$ ,  $J = 1$  Hz, 1H), 7.46 (td,  $J = 7.8$ ,  $J = 1.4$  Hz, 1H), 5.91 (s, 1H), 3.39 (s, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  149.3, 133.0, 132.8, 129.7, 128.4, 124.5, 100.2, 54.9. FT-IR (Thin film):  $\nu$  3446, 1532, 1362  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_9\text{H}_{11}\text{NO}_3]$  166.0504 ( $[\text{M}-\text{CH}_3]^+$ ); Found: 166.0505.

### (E)-2-methyl-4-(2-nitrophenyl)but-3-en-2-ol (3ad)

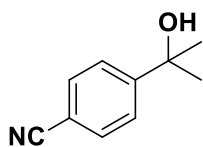
Colourless oil (75 mg, 72 %);  $R_f = 0.3$  (10 % EtOAc in hexane).



UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 311, 234, 203.  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  7.97 (dd,  $J = 8.2$ ,  $J = 1.2$  Hz, 1H), 7.82 (dd,  $J = 7.9$ ,  $J = 1.3$  Hz, 1H), 7.57 - 7.54 (m, 1H), 6.98 (d,  $J = 15.8$  Hz, 1H), 6.28 (dd,  $J = 16$ ,  $J = 4.8$  Hz, 1H), 4.99 (dd,  $J = 4.8$ ,  $J = 1.2$  Hz, 1H) 2.5 (s, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  148.1, 133.7, 131.4, 130.8, 129.4, 128.8, 127.7, 124.5, 101.9, 52.6. FT-IR (Thin film):  $\nu$  3449, 1525, 1347  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{11}\text{H}_{13}\text{NO}_3]$  192.0661 ( $[\text{M}-\text{CH}_3]^+$ ); Found: 192.0661.

### 4-(2-hydroxypropan-2-yl)benzotrile (3ae)

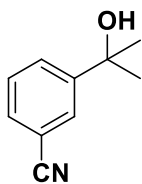
Colourless oil (62 mg, 76 %);  $R_f = 0.4$  (10 % EtOAc in Hexane)



UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 269, 229, 202.  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  7.84 - 7.82 (m, 2H), 7.57 - 7.55 (m, 2H), 5.45 (s, 1H), 3.25 (s, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  143.8, 132.6, 128, 119.1, 111.7, 102.1, 53.2. FT-IR (Thin film):  $\nu$  3421, 2229  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{10}\text{H}_{11}\text{NO}]$  146.0606 ( $[\text{M}-\text{CH}_3]^+$ ); Found: 146.0607.

### 3-(2-hydroxypropan-2-yl)benzotrile (3af)

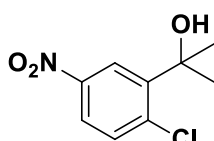
Colourless oil (65 mg, 80 %);  $R_f = 0.4$  (10 % EtOAc in Hexane)



UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 272, 225.  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  7.84 - 7.82 (m, 1H), 7.78 (s, 1H), 7.72 (d,  $J = 7.85$ , 1H), 7.61 (t,  $J = 7.75$ , 1H), 5.45 (s, 1H), 3.27 (s, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  140.2, 132.8, 131.9, 130.5, 130.0, 119.0, 111.7, 101.9, 53.2. FT-IR (Thin film):  $\nu$  3380, 2230  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{10}\text{H}_{11}\text{NO}]$  146.0606 ( $[\text{M}-\text{CH}_3]^+$ ); Found: 146.0603.

### 2-(2-chloro-5-nitrophenyl)propan-2-ol (3ag)

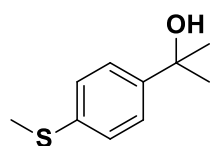
Yellow oil (74 mg, 68 %);  $R_f = 0.5$  (10 % EtOAc in Hexane)



UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 270, 203.  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  8.26 (d,  $J = 2.85$ , 1H), 8.21 (dd,  $J = 8.75$ ,  $J = 2.85$  Hz, 1H), 7.77 (d,  $J = 8.75$  Hz, 1H), 5.61 (s, 1H), 3.34 (s, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  146.7,

139.4, 137.5, 131.7, 125.4, 123.1, 99.9, 54.2. FT-IR (Thin film):  $\nu$  3449, 1526, 1348  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_9\text{H}_{10}\text{ClNO}_3]$  200.0114 ( $[\text{M}-\text{CH}_3]^+$ ); Found: 200.0111

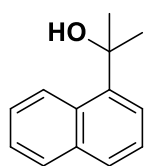
### 2-(4-(methylthio)phenyl)propan-2-ol (3ai)



Colourless oil (71 mg, 78 %);  $R_f$  = 0.5 (10 % EtOAc in Hexane)

UV-Vis (MeOH),  $\lambda_{\text{max}}$  (nm): 258, 210.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  7.33 - 7.31 (m, 2H), 7.27 - 7.25 (m, 2H), 5.35 (s, 1H), 3.23 (s, 6H), 2.47 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  138.8, 135.2, 127.5, 125.8, 102.7, 52.8, 14.9. FT-IR (Thin film):  $\nu$  3446  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{10}\text{H}_{14}\text{OS}]$  167.0531 ( $[\text{M}-\text{CH}_3]^+$ ); Found: 167.0535.

### 2-(naphthalen-1-yl)propan-2-ol (3ak)

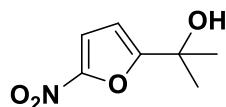


Pale yellow oil (56 mg, 60 %);  $R_f$  = 0.7 (10 % EtOAc in Hexane)

UV-Vis (MeOH),  $\lambda_{\text{max}}$  (nm): 280, 217.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  8.26 - 8.24 (m, 1H), 7.96 - 7.92 (m, 2H), 7.67 - 7.66 (m, 1H), 7.57 - 7.50 (m, 3H), 5.92 (s, 1H), 3.31 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  133.8, 133.7, 130.7, 129.4, 128.8, 126.5, 126.1, 125.3, 125.1, 124.8, 102.7, 53.6. FT-IR (Thin film):  $\nu$  3444,  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{13}\text{H}_{14}\text{O}]$  171.0810 ( $[\text{M}-\text{CH}_3]^+$ ); Found: 171.0813.

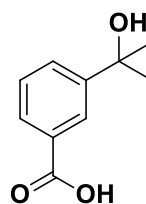
### 2-(5-nitrofuran-2-yl)propan-2-ol (3al)

Yellow oil (46 mg, 54 %);  $R_f$  = 0.3 (10 % EtOAc in Hexane)



UV-Vis (MeOH),  $\lambda_{\text{max}}$  (nm): 305, 227, 200.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  7.68 (d,  $J$  = 3.75, 1H), 6.86 - 6.85 (m, 1H), 5.59 (s, 1H), 3.33 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  154.3, 151.6, 113.4, 112.5, 96.7, 53.3. FT-IR (Thin film):  $\nu$  3448, 1535, 1355  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_7\text{H}_9\text{NO}_4]$  156.0297 ( $[\text{M}-\text{CH}_3]^+$ ); Found: 156.0296.

### 3-(2-hydroxypropan-2-yl)benzoic acid (3an)



White solid (59 mg, 65 %);  $R_f$  = 0.4 (25 % EtOAc in Hexane)

UV-Vis (MeOH),  $\lambda_{\text{max}}$  (nm): 255, 217.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  13.03 (bs, 1H), 7.99 (s, 1H), 7.94 - 7.93 (m, 1H), 7.62 (d,  $J$  = 7.65, 1H), 7.52 (t,  $J$  = 7.65, 1H), 5.46 (s, 1H), 3.26 (s, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO}-d_6$ , ppm):  $\delta$  167.6, 139.1, 131.4, 131.1, 129.7, 127.8, 102.5, 53.0. FT-IR (Thin film):  $\nu$  3433, 1693  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{10}\text{H}_{12}\text{O}_3]$  165.0552 ( $[\text{M}-\text{CH}_3]^+$ ); Found: 165.0556.

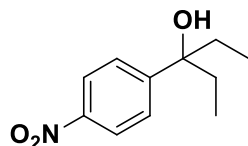
## 3. General Procedure B

A 10 ml round bottom flask was charged with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.025 mmol, 5 mol %) in 1 ml ethanol. The mixture was stirred for 30 min, then aldehyde (0.5 mmol) was added. Then the reaction mixture was stirred at room temperature for 24 h. Then the solvent was removed under

reduced pressure and the crude reaction mixture was purified by silica gel column chromatography (Hexane/EtOAc = 995/5 to 99/1) to obtain the title compounds. Silica gel was neutralized with triethylamine before isolating **4af**.

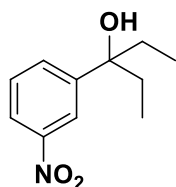
### 3-(4-nitrophenyl)pentan-3-ol (**4aa**)

Colourless oil (93 mg, 89 %);  $R_f = 0.5$  (10 % EtOAc in Hexane)



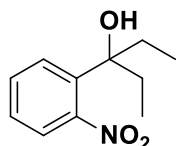
UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 265, 203.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , ppm):  $\delta$  8.26 - 8.23 (m, 2H), 7.69 - 7.66 (m, 2H), 5.63 (s, 1H), 3.60 - 3.50 (m, 4H), 1.16 (t,  $J = 7.1$  Hz, 6H).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ , ppm):  $\delta$  147.9, 146.9, 128.4, 123.9, 100.3, 61.8, 15.7. FT-IR (Thin film):  $\nu$  3427, 1524, 1346  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{11}\text{H}_{15}\text{NO}_3]$  180.0661 ( $[\text{M}-\text{CH}_2\text{CH}_3]^+$ ); Found: 180.0658.

### 3-(3-nitrophenyl)pentan-3-ol (**4ab**)



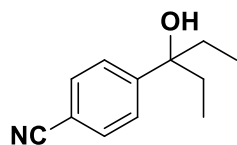
Colourless oil (95 mg, 90 %);  $R_f = 0.5$  (10 % EtOAc in Hexane)  
UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 261, 203.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , ppm):  $\delta$  8.22 - 8.20 (m, 2H), 7.86 - 7.84 (m, 1H), 7.71 - 7.68 (m, 1H), 5.65 (s, 1H), 3.61 - 3.50 (m, 4H), 1.16 (t,  $J = 7.05$  Hz, 6H).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ , ppm):  $\delta$  147.7, 141.5, 133.1, 129.8, 123.2, 121.0, 99.6, 61.2, 15.1. FT-IR (Thin film):  $\nu$  3447, 1531, 1349  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{11}\text{H}_{15}\text{NO}_3]$  180.0661 ( $[\text{M}-\text{CH}_2\text{CH}_3]^+$ ); Found: 180.0661.

### 3-(2-nitrophenyl)pentan-3-ol (**4ac**)



Pale yellow oil (45 mg, 43 %);  $R_f = 0.55$  (10 % EtOAc in Hexane)  
UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 252, 203.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , ppm):  $\delta$  7.88 - 7.86 (m, 1H), 7.74 - 7.70 (m, 2H), 7.62 - 7.59 (m, 1H), 5.89 (s, 1H), 3.65 - 3.50 (m, 4H), 1.13 (t,  $J = 7.05$  Hz, 6H).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ , ppm):  $\delta$  149.2, 133.1, 130.2, 128.1, 124.4, 98.2, 63.2, 15.4. FT-IR (Thin film):  $\nu$  3448, 1532, 1361  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{11}\text{H}_{15}\text{NO}_3]$  180.0661 ( $[\text{M}-\text{CH}_2\text{CH}_3]^+$ ); Found: 180.0660.

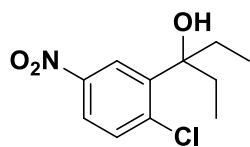
### 4-(3-hydroxypentan-3-yl)benzotrile (**4ad**)



Colourless oil (57 mg, 60 %);  $R_f = 0.5$  (10 % EtOAc in Hexane)  
UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 271, 230, 201.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , ppm):  $\delta$  7.84 - 7.83 (m, 2H), 7.59 - 7.57 (m, 2H), 5.56 (s, 1H), 3.57 - 3.46 (m, 4H), 1.14 (t,  $J = 7.05$  Hz, 6H).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ , ppm):  $\delta$  144.8, 132.5, 127.8, 119.0, 111.4, 100.3, 61.5, 15.4. FT-IR (Thin film):  $\nu$  3420, 2229  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{11}\text{H}_{15}\text{NO}]$  160.0762 ( $[\text{M}-\text{CH}_2\text{CH}_3]^+$ ); Found: 160.0763.

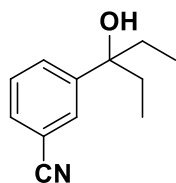
### 3-(2-chloro-5-nitrophenyl)pentan-3-ol (**4ae**)

Pale yellow oil (49 mg, 40 %);  $R_f = 0.6$  (10 % EtOAc in Hexane)



UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 269, 204.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , ppm):  $\delta$  8.30 - 8.29 (m, 1H), 8.23 - 8.21 (m, 1H), 7.78 - 7.77 (m, 1H), 5.72 (s, 1H), 3.70 - 3.56 (m, 4H), 1.16 (t,  $J = 7.05$  Hz, 6H).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ , ppm):  $\delta$  146.8, 139.4, 138.6, 131.7, 125.3, 122.9, 98.2, 62.7, 15.5. FT-IR (Thin film):  $\nu$  3446, 1528, 1347  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{11}\text{H}_{14}\text{ClNO}_3]$  214.0271 ( $[\text{M}-\text{CH}_2\text{CH}_3]^+$ ); Found: 214.0270.

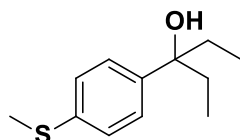
### 3-(3-hydroxy-3-ethylphenyl)benzonitrile (4af)



Colourless oil (59 mg, 62 %);  $R_f = 0.4$  (10 % EtOAc in Hexane)

UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 272, 225.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , ppm):  $\delta$  7.82 - 7.79 (m, 2H), 7.74 - 7.73 (m, 1H), 7.60 (t,  $J = 7.75$  Hz, 1H), 5.55 (s, 1H), 3.58 - 3.47 (m, 4H), 1.16 (t,  $J = 7.05$  Hz, 6H).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ , ppm):  $\delta$  141.3, 132.5, 131.7, 130.4, 129.9, 119.1, 111.7, 100.2, 61.7, 15.5. FT-IR (Thin film):  $\nu$  3380, 2230  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{11}\text{H}_{15}\text{NO}]$  160.0762 ( $[\text{M}-\text{CH}_2\text{CH}_3]^+$ ); Found: 160.0757.

### 3-(4-(methylthio)phenyl)pentan-3-ol (4ag)



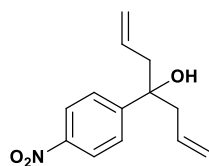
Colourless oil (51 mg, 48 %);  $R_f = 0.6$  (10 % EtOAc in Hexane)

UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 258, 210.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , ppm):  $\delta$  7.34 - 7.32 (m, 2H), 7.26 - 7.24 (m, 2H), 5.45 (s, 1H), 3.56 - 3.43 (m, 4H), 2.47 (s, 3H), 1.14 (t,  $J = 7.05$  Hz, 6H).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ , ppm):  $\delta$  138.5, 136.3, 127.4, 125.9, 101.0, 61.0, 15.5, 15.0. FT-IR (Thin film):  $\nu$  3434  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{12}\text{H}_{18}\text{OS}]$  181.0687 ( $[\text{M}-\text{CH}_2\text{CH}_3]^+$ ); Found: 181.0688.

## 4. General Procedure C

A 10 ml round bottom flask was charged with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.025 mmol, 5 mol %) in 1 ml allyl alcohol. The mixture was stirred for 30 min, then aldehyde (0.5 mmol) was added. Then the reaction mixture was stirred at room temperature for 24 h. Then the solvent was removed under reduced pressure and the crude reaction mixture was purified by silica gel column chromatography (Hexane/EtOAc = 995/5 to 99/1) to obtain the title compounds. Silica gel was neutralized with triethylamine before isolating **4aa-4ag**.

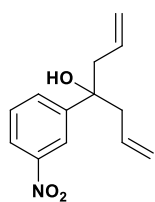
### 4-(4-nitrophenyl)hepta-1,6-dien-4-ol (5aa)



Yellow oil (108 mg, 92 %);  $R_f = 0.5$  (10 % EtOAc in Hexane)

UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 265, 211.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , ppm):  $\delta$  8.26 - 8.25 (m, 2H), 7.72 - 7.70 (m, 2H), 5.97 - 5.90 (m, 1H), 5.74 (s, 1H), 5.33 - 5.28 (m, 2H), 5.18 - 5.16 (m, 2H), 4.08 - 4.07 (m, 4H).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ , ppm):  $\delta$  147.9, 146.1, 134.9, 128.3, 123.9, 117.1, 99.8, 67.0. FT-IR (Thin film):  $\nu$  3428, 1524, 1347  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{13}\text{H}_{15}\text{NO}_3]$  192.0661 ( $[\text{M}-\text{CH}_2\text{CH}=\text{CH}_2]^+$ ); Found: 192.0656.

#### 4-(3-nitrophenyl)hepta-1,6-dien-4-ol (5ab)

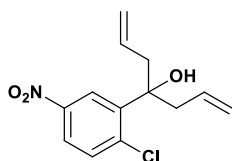


Pale yellow oil (100 mg, 85 %);  $R_f$  = 0.5 (10 % EtOAc in Hexane)

UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 261, 210.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , ppm):  $\delta$  8.24 - 8.22 (m, 2H), 7.89 - 7.88 (m, 1H), 7.73 - 7.70 (m, 1H), 5.98 - 5.91 (m, 1H), 5.77 (s, 1H), 5.33 - 5.29 (m, 2H), 5.18 - 5.16 (m, 2H), 4.09 - 4.08 (m, 4H).

$^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ , ppm):  $\delta$  148.2, 141.3, 135.0, 133.6, 130.4, 123.8, 121.5, 117.1, 99.6, 67.0. FT-IR (Thin film):  $\nu$  3445, 1531, 1349  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{13}\text{H}_{15}\text{NO}_3]$  192.0661 ( $[\text{M}-\text{CH}_2\text{CH}=\text{CH}_2]^+$ ); Found: 192.0655.

#### 4-(2-chloro-5-nitrophenyl)hepta-1,6-dien-4-ol (5ac)

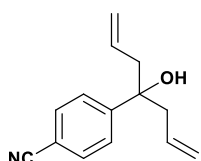


Colourless oil (54 mg, 40 %);  $R_f$  = 0.6 (10 % EtOAc in Hexane)

UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 270, 210.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , ppm):  $\delta$  8.35 (d,  $J$  = 2.85 Hz, 1H), 8.24 (dd,  $J$  = 2.9 Hz,  $J$  = 8.75 Hz, 1H), 7.79 (d,  $J$  = 8.8 Hz, 1H), 5.97 - 5.89 (m, 1H), 5.84 (s, 1H), 5.32 - 5.28 (m,

2H), 5.19 - 5.16 (m, 2H), 4.15 - 4.14 (m, 4H).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ , ppm):  $\delta$  146.7, 139.4, 138.1, 134.7, 131.7, 125.4, 123.1, 117.5, 97.5, 67.9. FT-IR (Thin film):  $\nu$  3442, 1528, 1347  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{13}\text{H}_{14}\text{ClNO}_3]$  226.0271 ( $[\text{M}-\text{CH}_2\text{CH}=\text{CH}_2]^+$ ); Found: 226.0272.

#### 4-(4-hydroxyhepta-1,6-dien-4-yl)benzotrile (5ad)

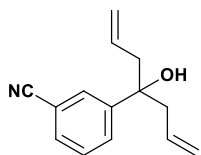


Colourless oil (64 mg, 60 %);  $R_f$  = 0.5 (10 % EtOAc in Hexane)

UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 271, 229.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , ppm):  $\delta$  7.88 - 7.86 (m, 2H), 7.63 - 7.62 (m, 2H), 5.97 - 5.89 (m, 1H), 5.69 (s, 1H), 5.32 - 5.27 (m, 2H), 5.18 - 5.15 (m, 2H), 4.07 - 4.05 (m, 4H).  $^{13}\text{C}$  NMR (126

MHz, DMSO- $d_6$ , ppm):  $\delta$  144.2, 135.0, 132.7, 127.9, 119.1, 117.0, 111.7, 100.0, 66.9. FT-IR (Thin film):  $\nu$  3421, 2229  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{14}\text{H}_{15}\text{NO}]$  172.0762 ( $[\text{M}-\text{CH}_2\text{CH}=\text{CH}_2]^+$ ); Found: 172.0760.

#### 3-(4-hydroxyhepta-1,6-dien-4-yl)benzotrile (5ae)



Colourless oil (48 mg, 45 %);  $R_f$  = 0.4 (10 % EtOAc in Hexane)

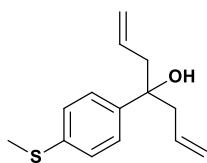
UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 272, 224.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , ppm):  $\delta$  7.85 - 7.83 (m, 2H), 7.78 - 7.76 (m, 1H), 7.64 - 7.61 (m, 1H), 5.97 - 5.90 (m, 1H), 5.67 (s, 1H), 5.32 - 5.28 (m, 2H), 5.18 - 5.15 (m, 2H), 4.07 - 4.05

(m, 4H).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ , ppm):  $\delta$  140.7, 135.0, 132.8, 131.8, 130.5, 130.9, 119.0, 117.0, 111.8, 99.8, 66.9. FT-IR (Thin film):  $\nu$  3458, 2230  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{14}\text{H}_{15}\text{NO}]$  172.0762 ( $[\text{M}-\text{CH}_2\text{CH}=\text{CH}_2]^+$ ); Found: 172.0756.

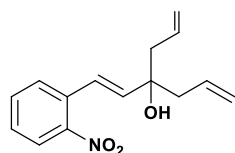
#### 4-(4-(methylthio)phenyl)hepta-1,6-dien-4-ol (5af)

Colourless oil (82 mg, 70 %);  $R_f$  = 0.8 (10 % EtOAc in Hexane)

UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 259, 210.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , ppm):  $\delta$  7.38 - 7.36 (m, 2H), 7.28 - 7.27 (m, 2H), 5.96 - 5.89 (m, 1H), 5.58 (s, 1H), 5.31 - 5.27 (m, 2H), 5.16 - 5.13 (m, 2H), 4.03 - 4.02 (m, 4H), 2.48 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ , ppm):  $\delta$  138.9, 135.6, 135.3, 127.5, 125.9, 116.7, 100.5, 66.47, 15.0. FT-IR (Thin film):  $\nu$  3425  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{14}\text{H}_{18}\text{OS}]$  193.0687 ( $[\text{M}-\text{CH}_2\text{CH}=\text{CH}_2]^+$ ); Found: 193.0683.



#### (E)-4-(2-nitrostyryl)hepta-1,6-dien-4-ol (5af)



Pale yellow oil (78 mg, 60 %);  $R_f$  = 0.4 (10 % EtOAc in Hexane)

UV-Vis (MeOH),  $\lambda_{\max}$  (nm): 314, 235, 210.  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ , ppm):  $\delta$  7.99 - 7.97 (m, 1H), 7.84 - 7.82 (m, 1H), 7.73 - 7.70 (m, 1H), 7.58 - 7.54 (m, 1H), 7.05 - 7.02 (m, 1H), 6.37 - 6.32 (m, 1H), 5.99 - 5.91 (m, 4H), 5.33 - 5.29 (m, 2H), 5.23 - 5.22 (dd,  $J$  = 1.1 Hz,  $J$  = 4.85 Hz, 1H) 5.58 (s, 1H), 5.18 - 5.15 (m, 2H), 5.16 - 5.13 (m, 2H), 4.17 - 4.12 (m, 2H), 4.08 - 4.04 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz, DMSO- $d_6$ , ppm):  $\delta$  148.4, 135.4, 133.9, 131.9, 131.0, 129.6, 129.0, 127.7, 124.7, 116.8, 100.0, 66.4. FT-IR (Thin film):  $\nu$  3447, 1523, 1345  $\text{cm}^{-1}$ . HRMS (ESI-TOF):  $m/z$  Calcd. for  $[\text{C}_{15}\text{H}_{17}\text{NO}_3]$  218.0817 ( $[\text{M}-\text{CH}_2\text{CH}=\text{CH}_2]^+$ ); Found: 218.0811.

### 5. Mechanistic Studies

#### a) Radical trapping experiment with TEMPO

A 10 ml round bottom flask was charged with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.025 mmol, 5 mol %) in 1 ml methanol. The mixture was stirred for 30 min, then aldehyde (0.05 mmol) and TEMPO (0.75 mmol) were added. Then the reaction mixture was stirred at room temperature for 24 h. A portion of the reaction mixture was collected and analysed by HR-MS. The TEMPO adduct **5** was not detected.

#### b) Radical trapping experiment with BHT

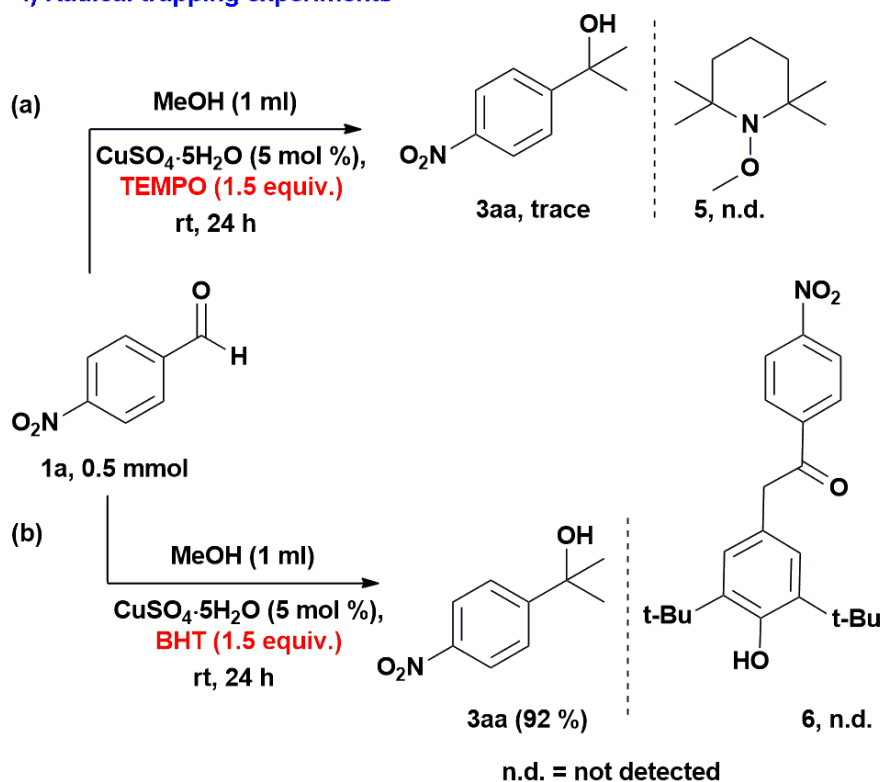
A 10 ml round bottom flask was charged with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.025 mmol, 5 mol %) in 1 ml methanol. The mixture was stirred for 30 min, then aldehyde (0.05 mmol) and BHT (0.75 mmol) were added. Then the reaction mixture was stirred at room temperature for 24 h. A portion of the reaction mixture was collected and analysed by HR-MS. Unfortunately, we could not able to detect the adduct **6** in the HR-MS.

#### c) Deuterium labelling experiment

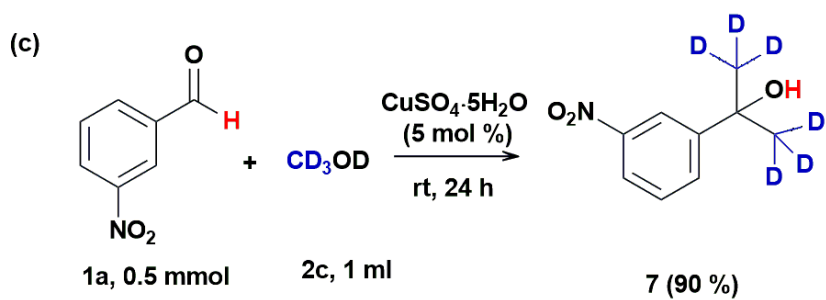
A 10 ml round bottom flask was charged with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.025 mmol, 5 mol %) in 1 ml  $\text{CD}_3\text{OD}$ . The mixture was stirred for 30 min, then aldehyde (0.05 mmol) was added. Then the reaction mixture was stirred at room temperature for 24 h. Then the solvent was removed under reduced pressure and the crude reaction mixture was purified by silica gel column chromatography (Hexane/EtOAc = 99/1) to obtain the corresponding deuterated product which was analysed by NMR spectroscopy (**Figure S27 & 28**). Since there was an interference of  $\text{CH}_3$  proton peak and water peak at 3.33 ppm in  $\text{dmsO}-d_6$ , we have analysed product **7** in  $\text{CDCl}_3$  also to avoid the misinterpretation of the data.



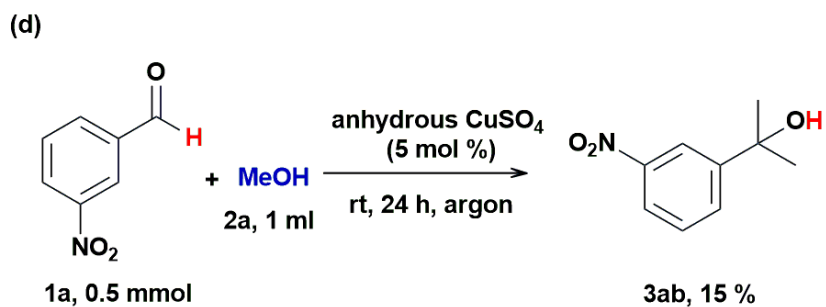
### I) Radical trapping experiments



### II) Deuterium labelling experiment



### III) Inert reaction

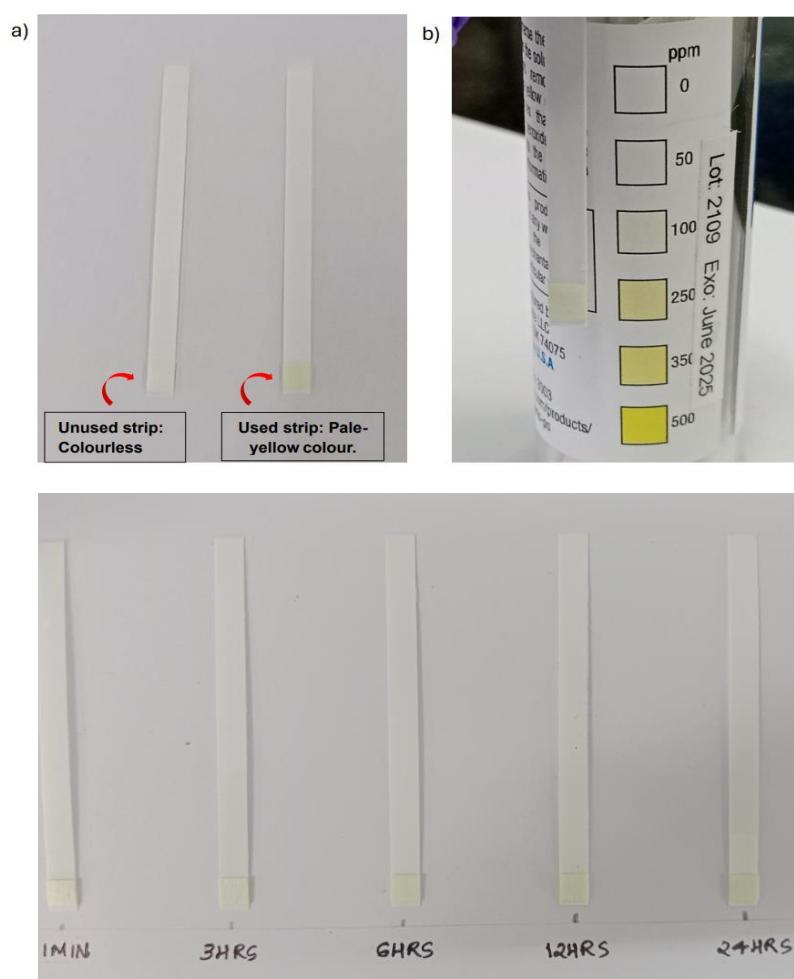


#### d) Inert reaction

A 10 ml round bottom flask was charged with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.025 mmol, 5 mol %) under an argon atmosphere. Then, 1 ml of dry MeOH was added using syringe. The mixture was stirred for 30 min, then aldehyde (0.05 mmol) was added under argon atmosphere. The reaction mixture was stirred at room temperature for 24 h under argon atmosphere. Then the solvent was removed under reduced pressure and the crude reaction mixture was purified by silica gel column chromatography (Hexane/EtOAc = 99/1) to obtain the corresponding product **3ab**.

#### e) Hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) detection using XploSens PS™ peroxides detection strip

A 10 ml round bottom flask was charged with  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.025 mmol, 5 mol %) in 1 ml  $\text{CD}_3\text{OD}$ . The mixture was stirred for 30 min, then aldehyde (0.05 mmol) was added. Then, the XploSens PS™ peroxides detection strip was immersed in the reaction mixture for 5 seconds and the resulting color change was noted. This procedure was repeated at 3, 6, 12, and 24 h to monitor peroxide levels over time. The appearance of pale-yellow colour was observed indicating the presence of peroxide in the solution ( $\approx 100$ -250 ppm).



**Figure S1:** a) XploSens PS™ peroxides detection strip before and after immersion. b) Immersed strip and quantification scale c) At different time intervals; 1min – just after the addition of substrate

## 6. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra of Methylated Products

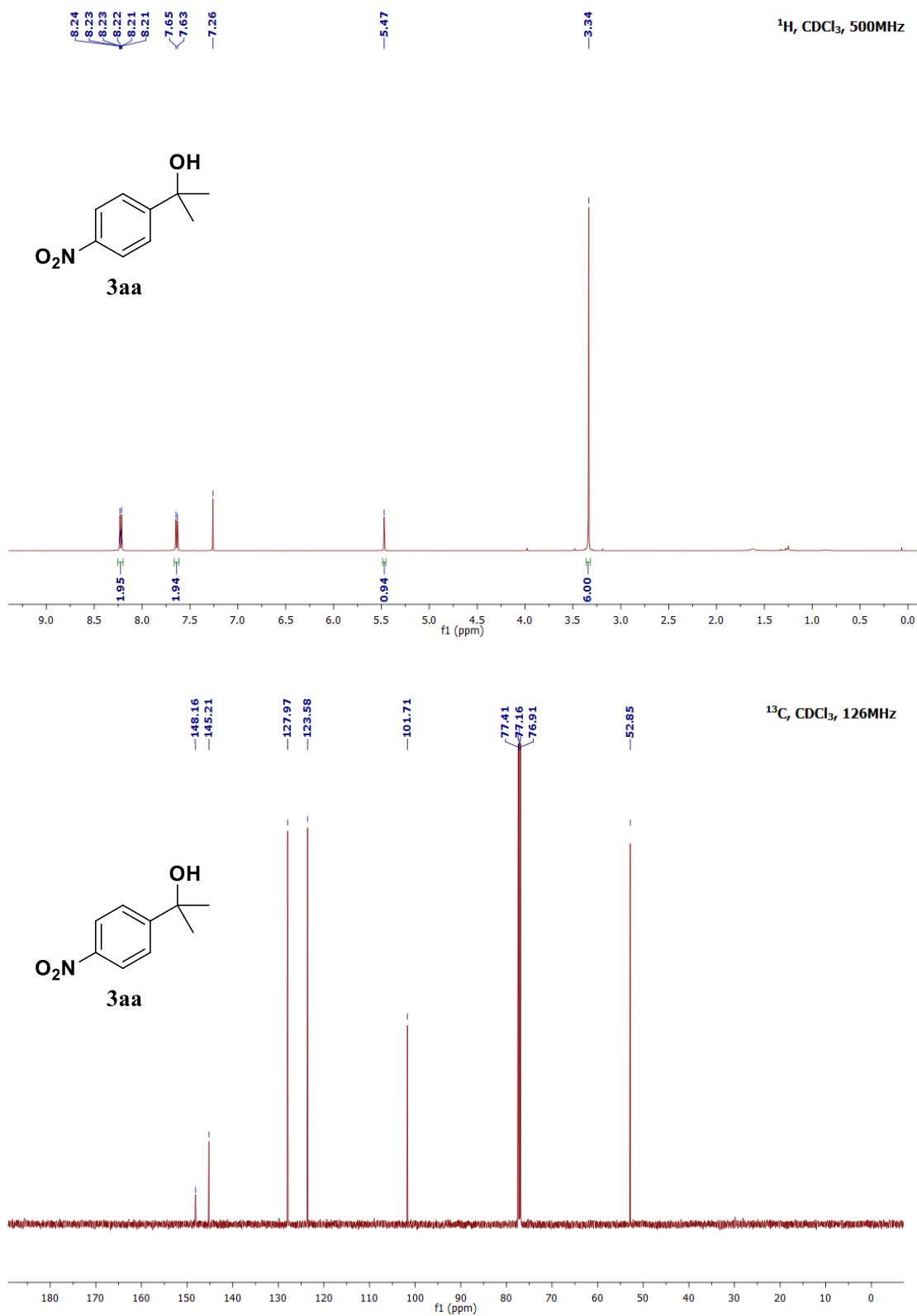


Figure S2:  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR Spectra of 2-(4-nitrophenyl)propan-2-ol (3aa)

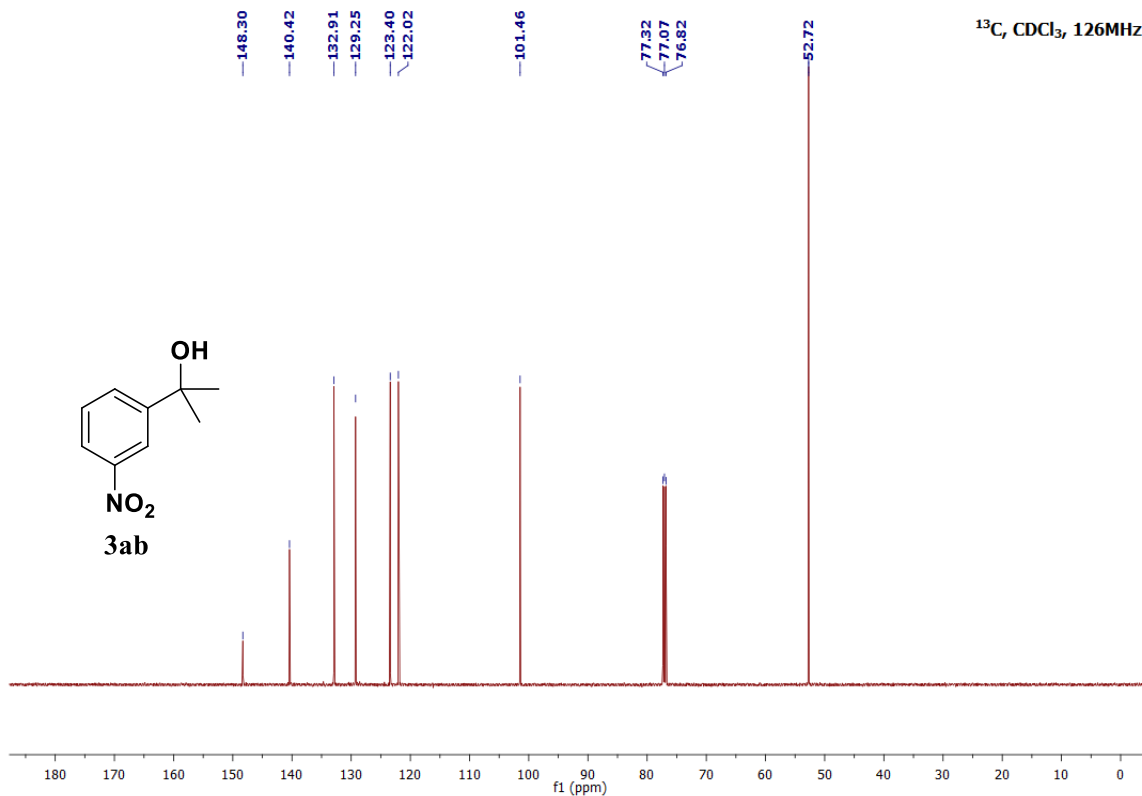
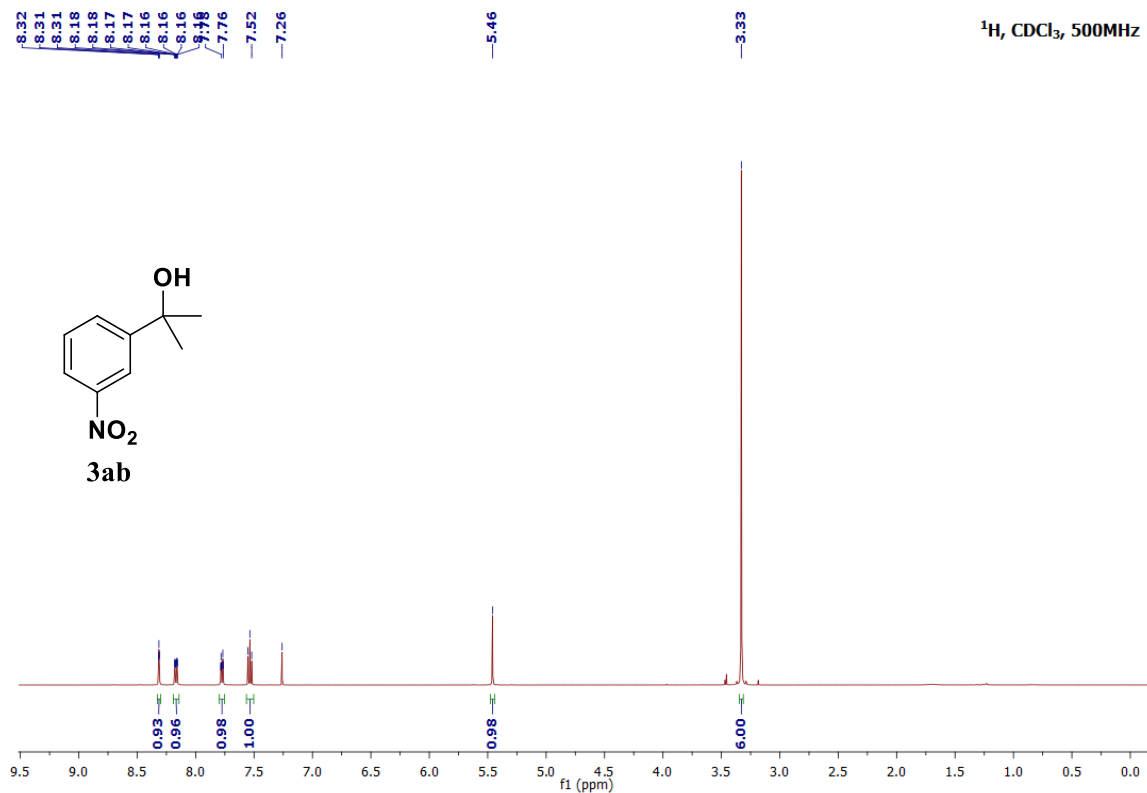
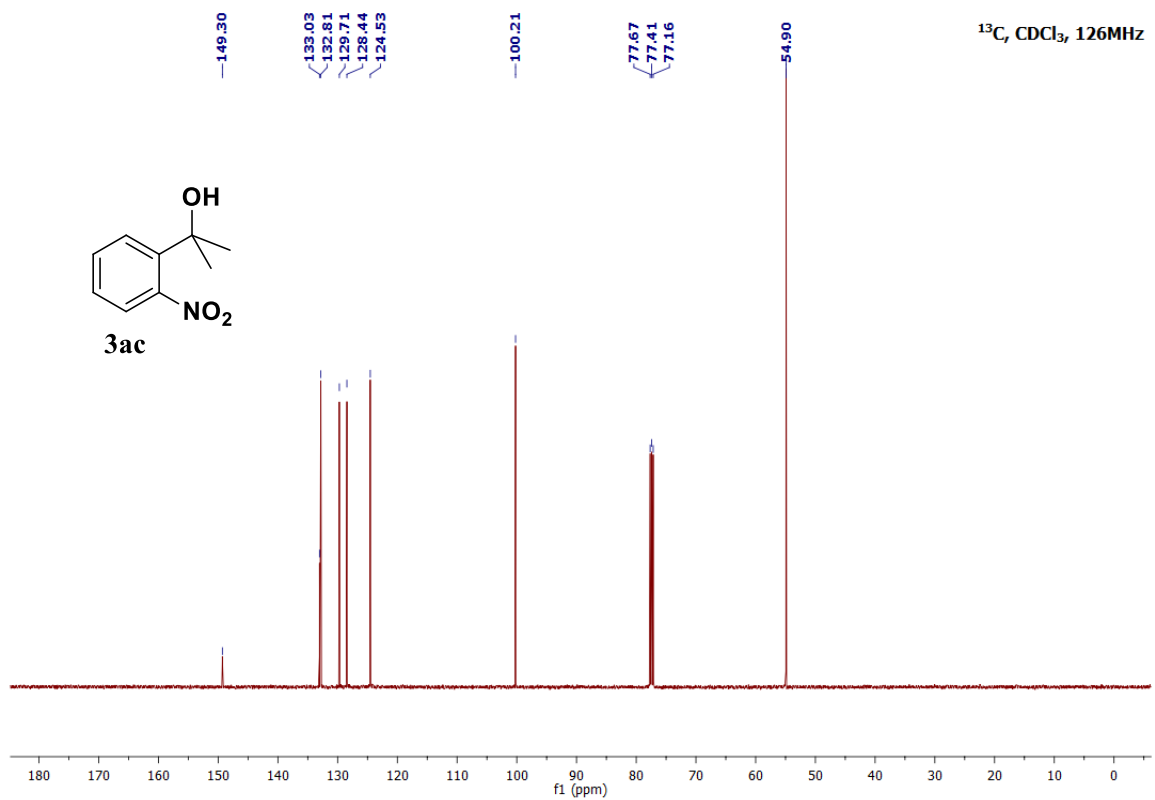
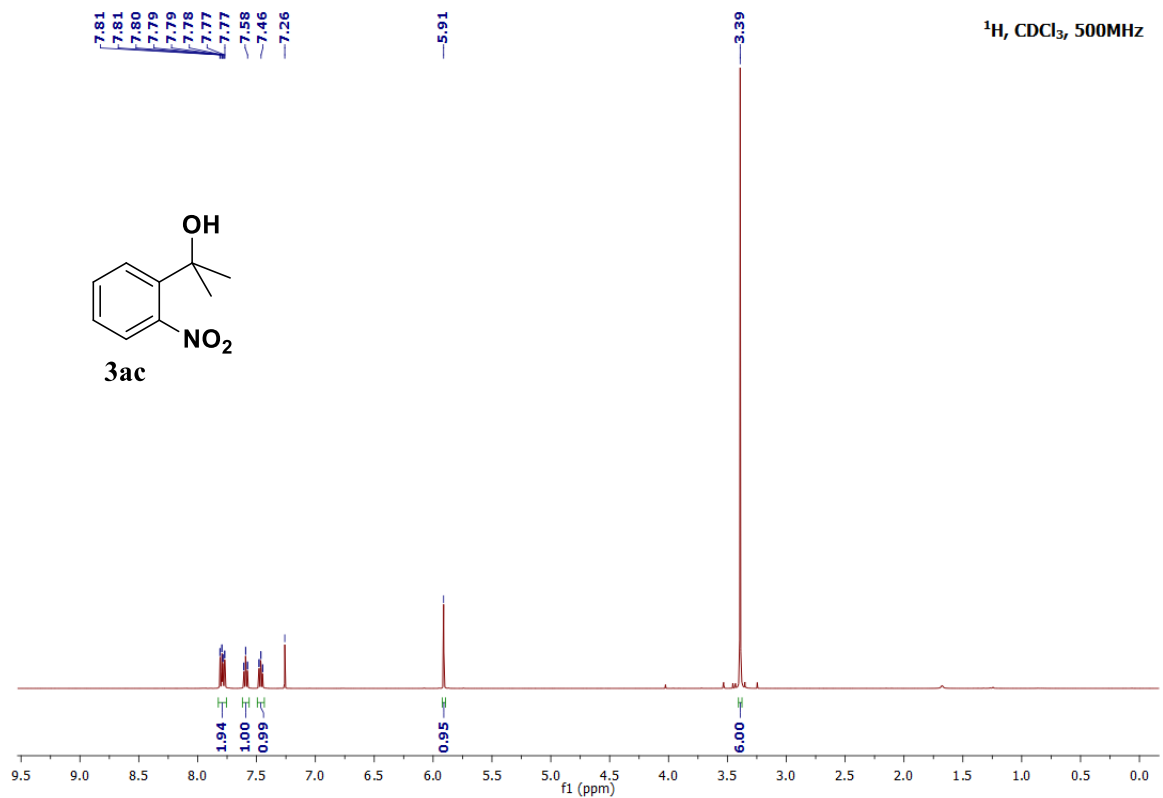


Figure S3: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 2-(3-nitrophenyl)propan-2-ol (3ab)



**Figure S4: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 2-(2-nitrophenyl)propan-2-ol (3ac)**

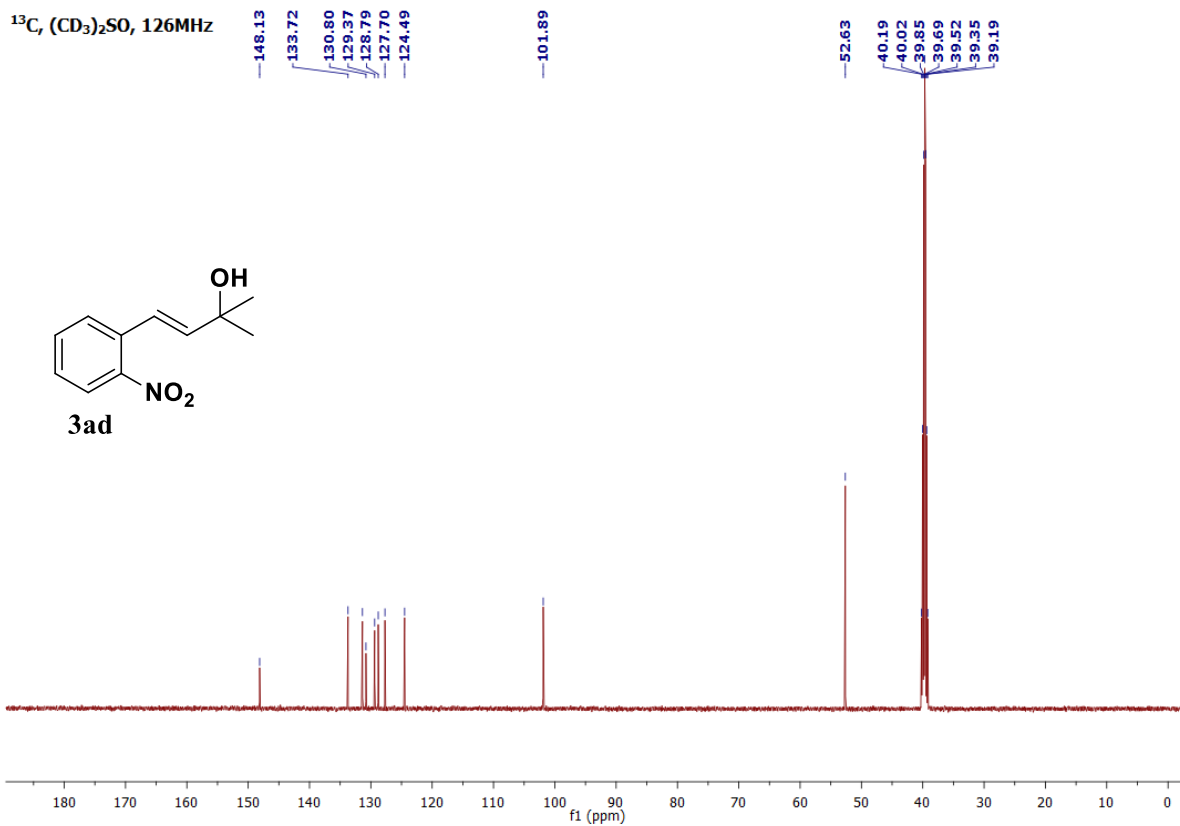
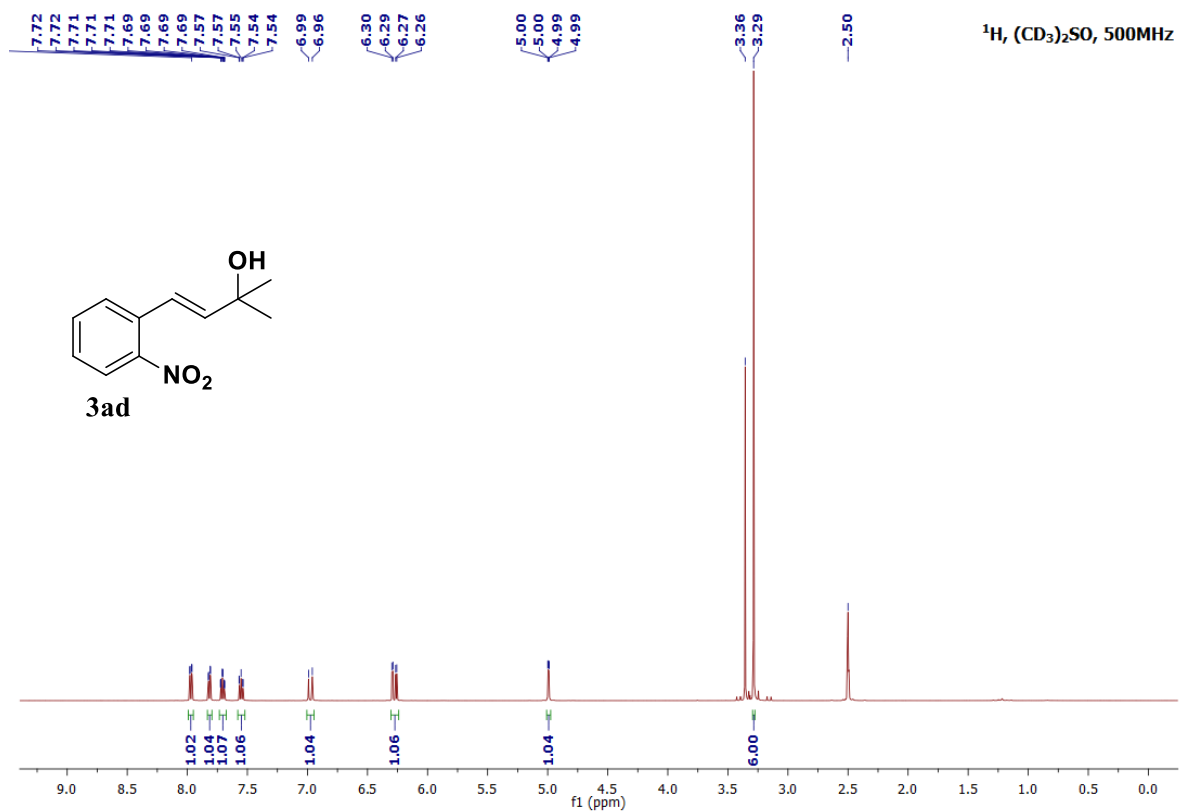
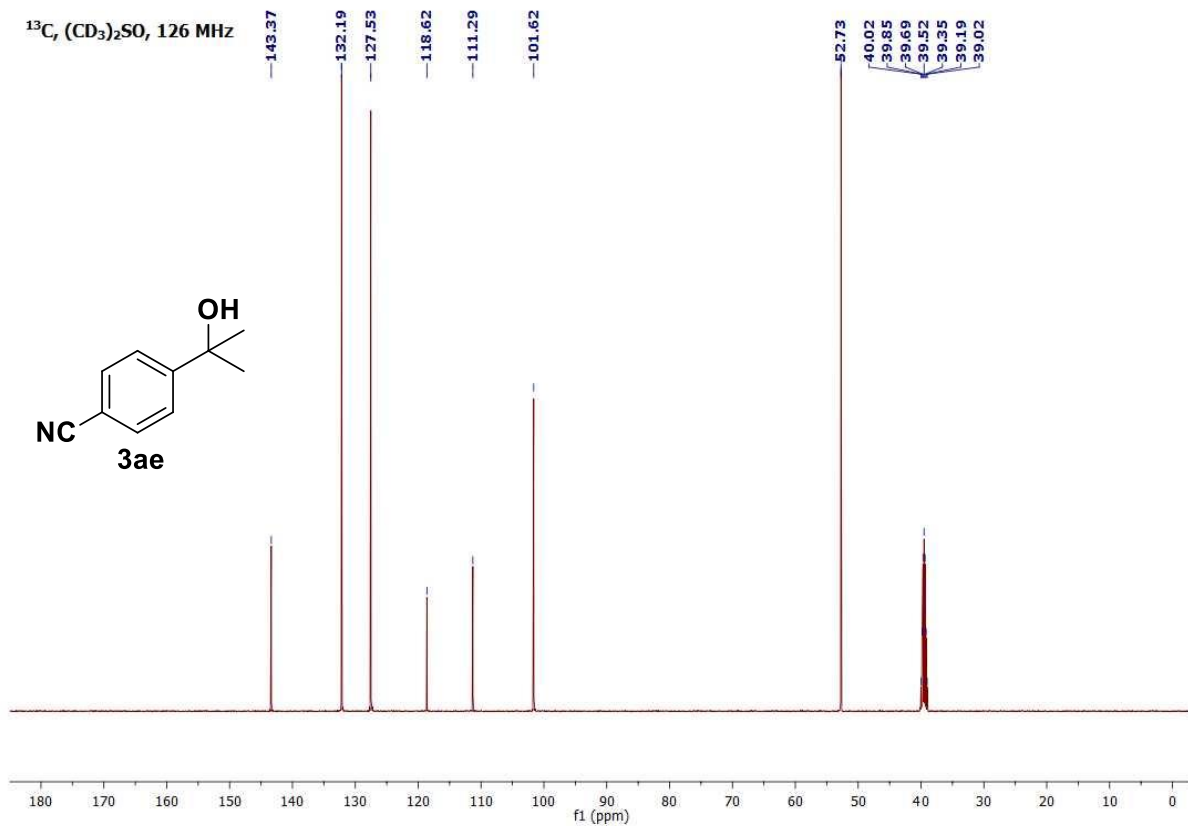
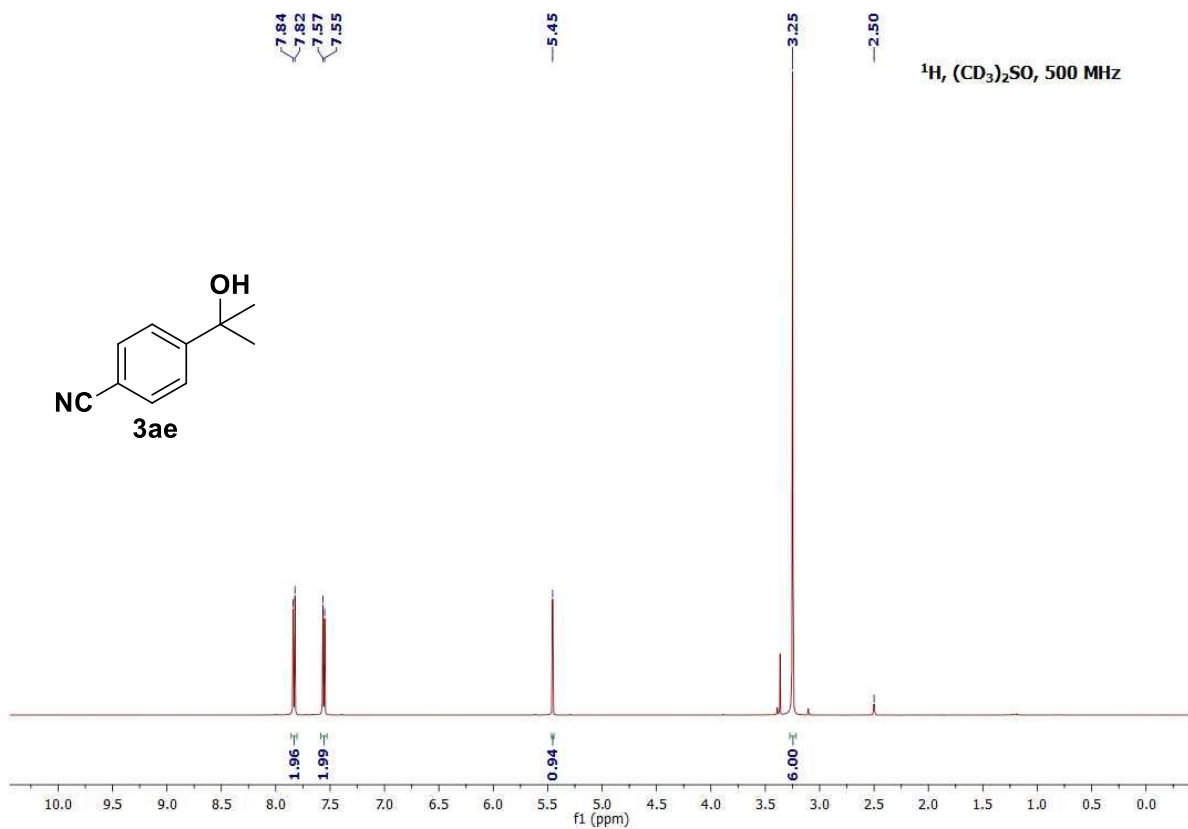
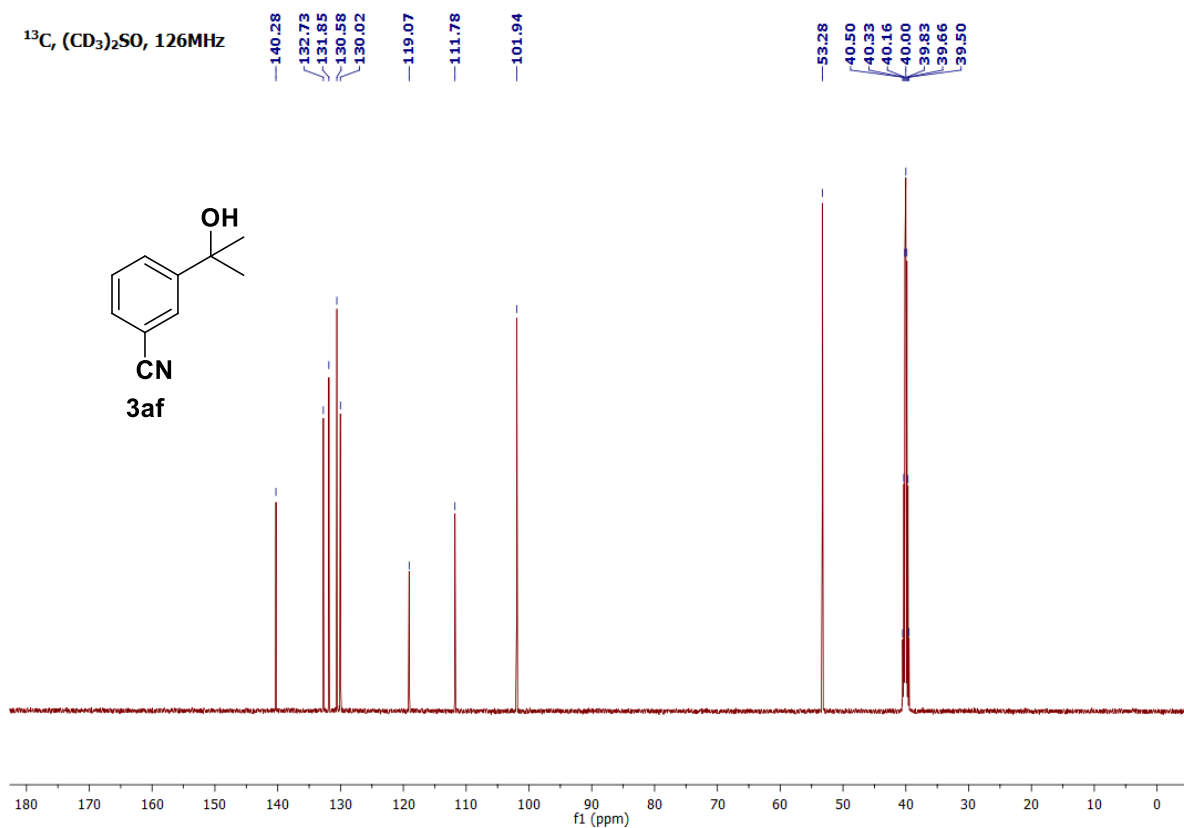
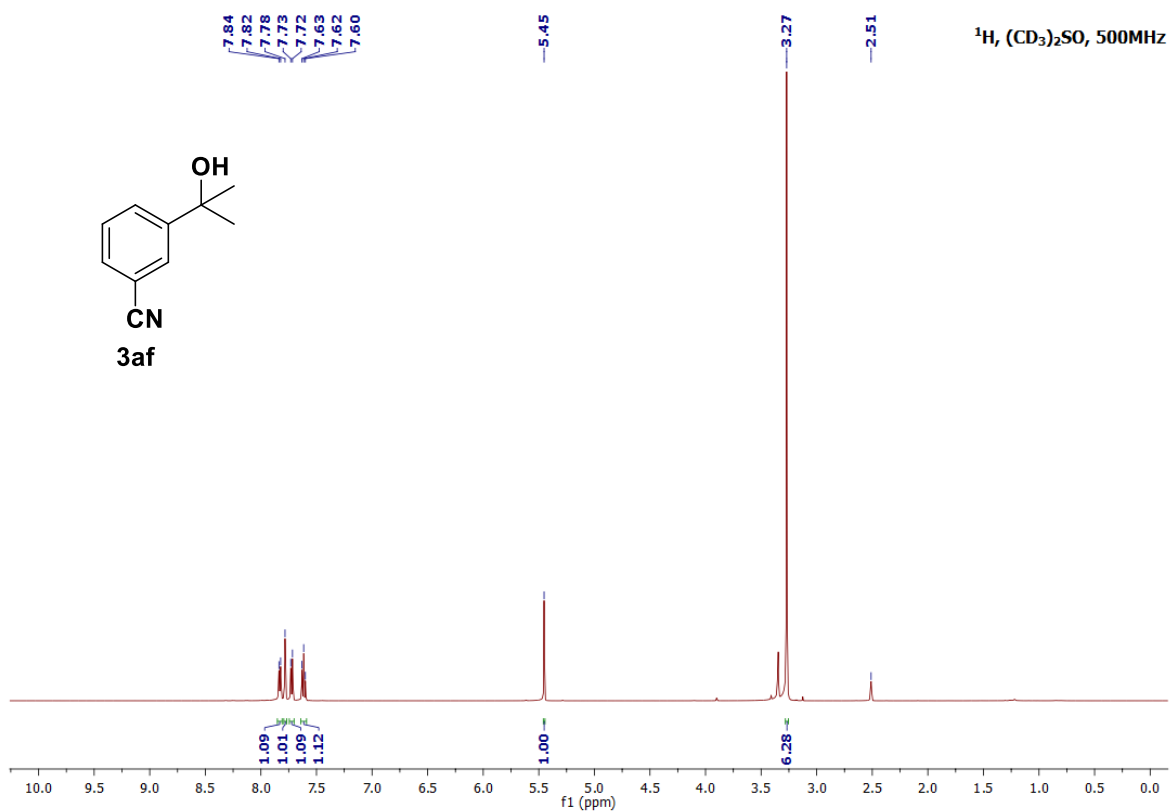


Figure S5: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of (*E*)-2-methyl-4-(2-nitrophenyl)but-3-en-2-ol (**3ad**)

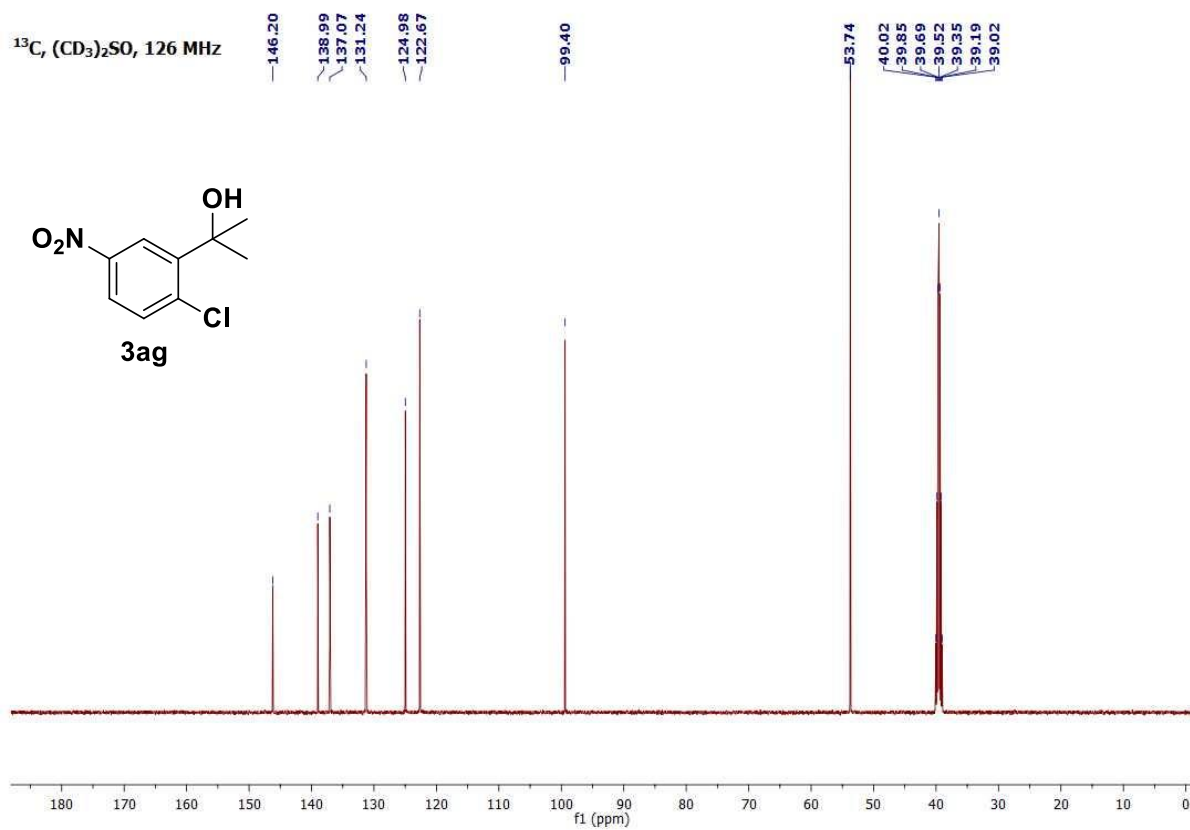
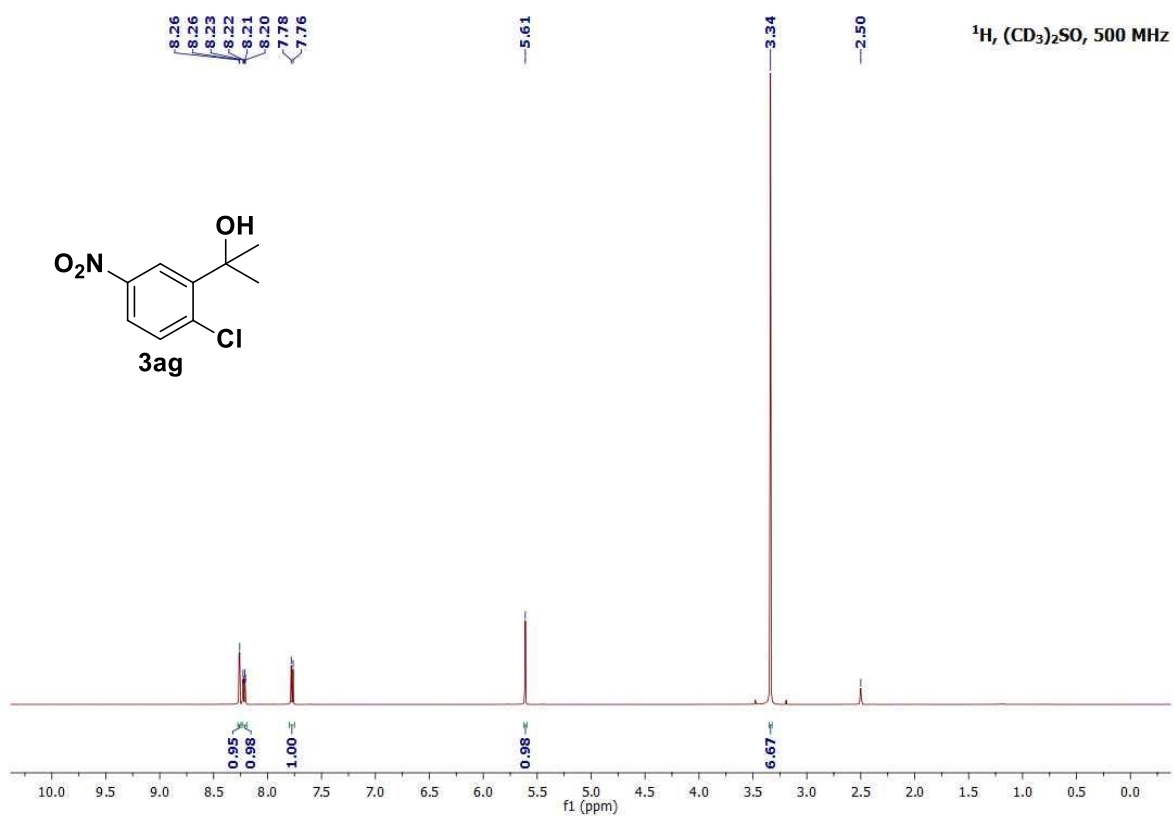


**Figure S6: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 4-(2-hydroxypropan-2-yl)benzonitrile (3ae)**



**Figure S7: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 3-(2-hydroxypropan-2-yl)benzonitrile (3ae)**





**Figure S8: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 2-(2-chloro-5-nitrophenyl)propan-2-ol (3ag)**

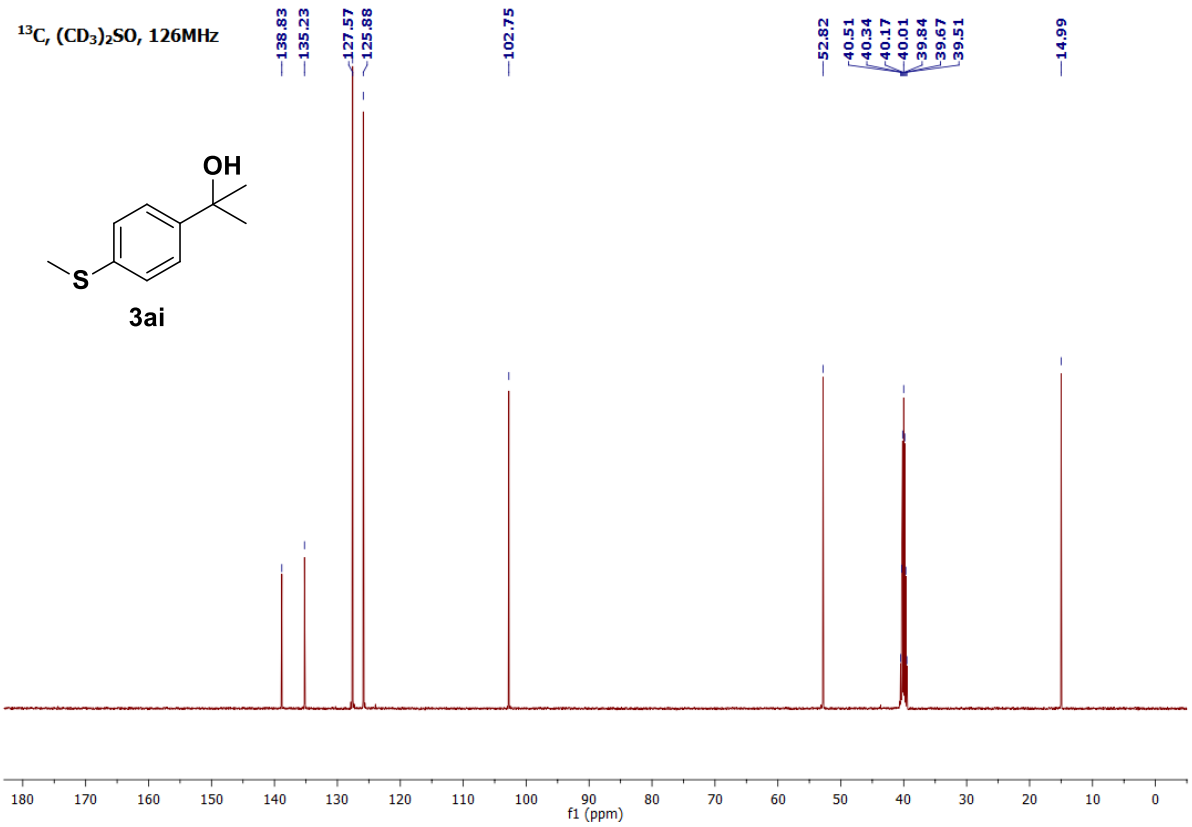
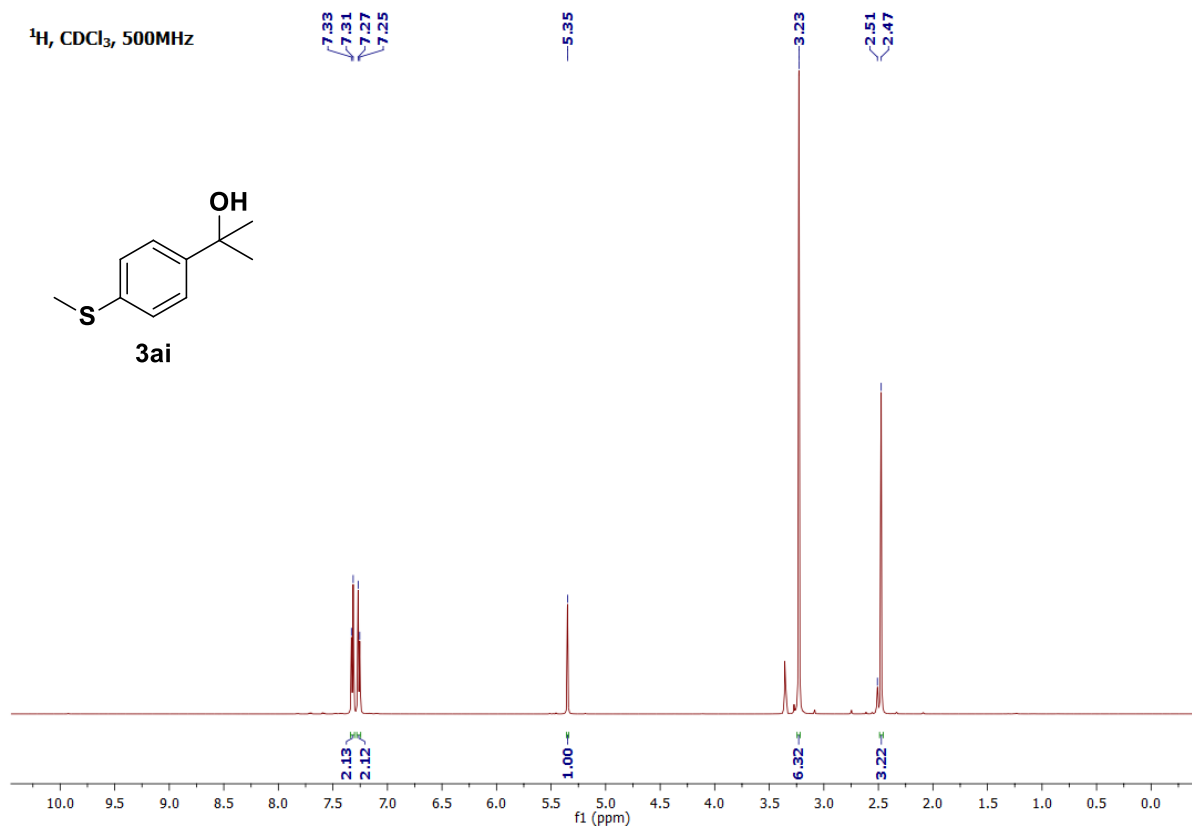
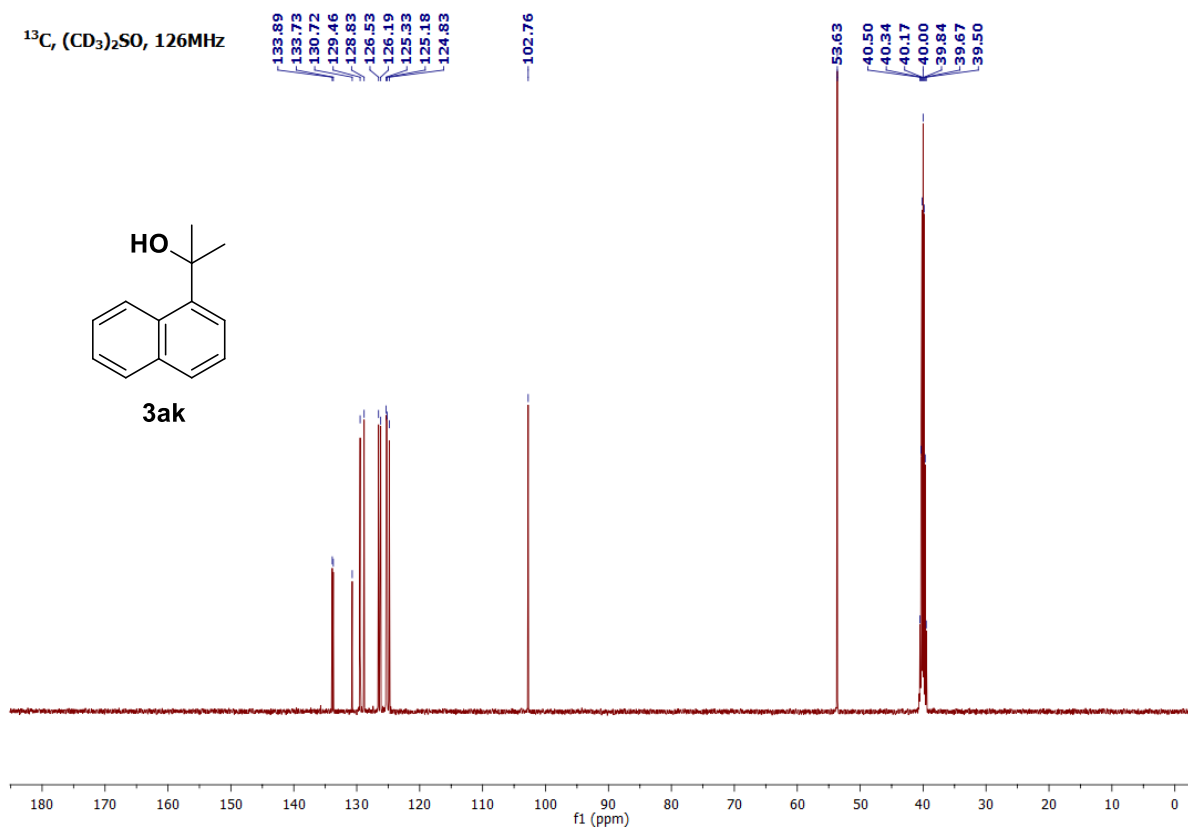
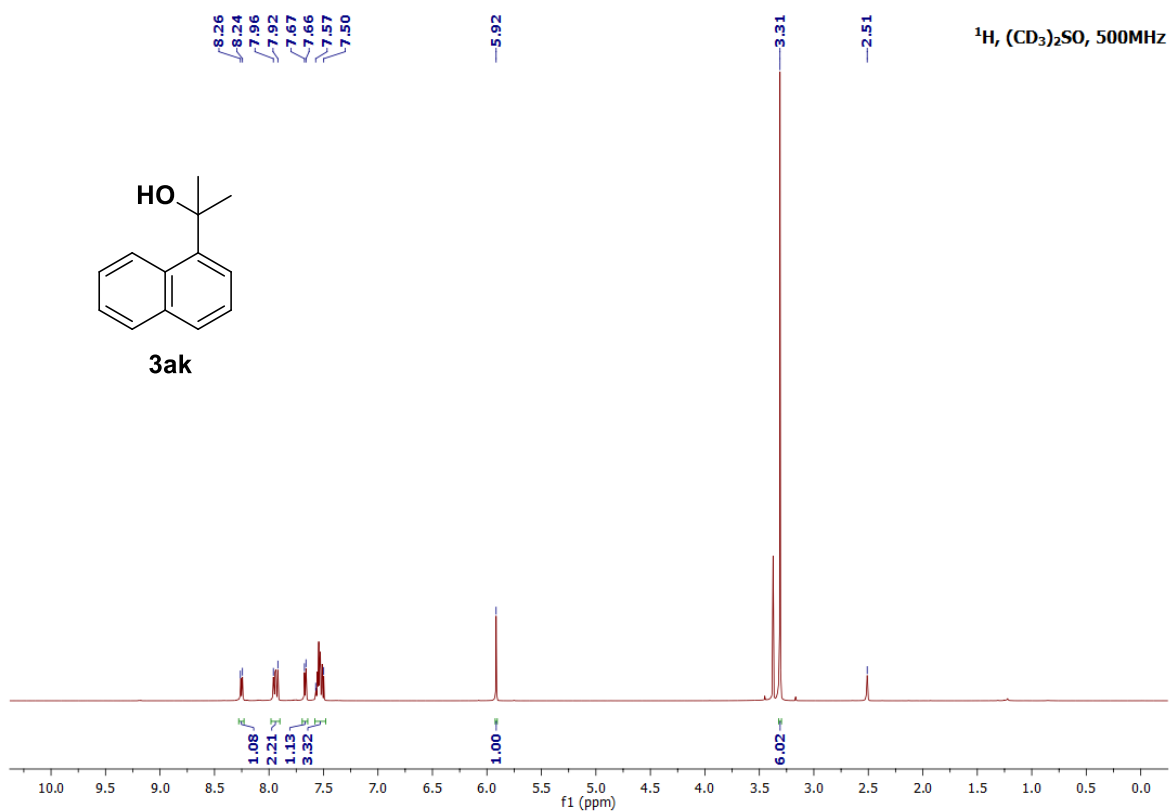


Figure S9: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 2-(4-(methylthio)phenyl)propan-2-ol (3ai)



**Figure S10: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 2-(naphthalen-1-yl)propan-2-ol (3ak)**

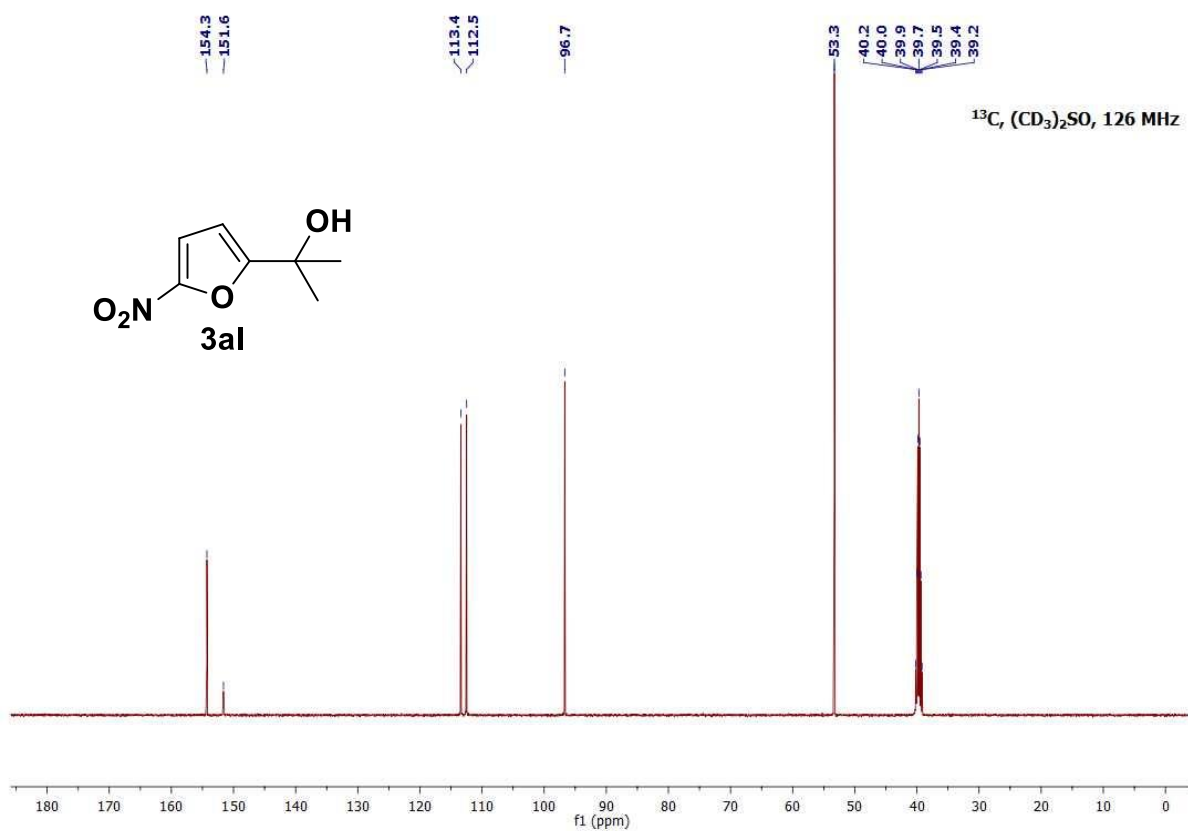
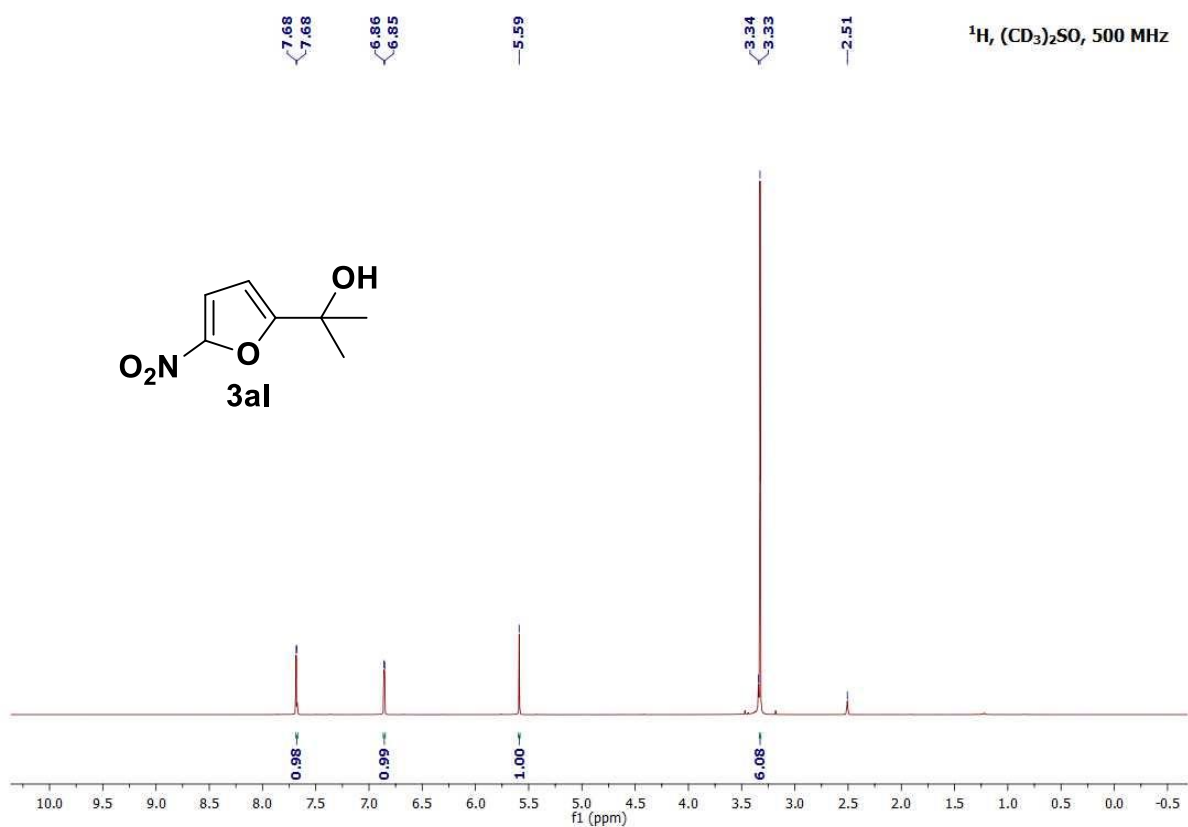
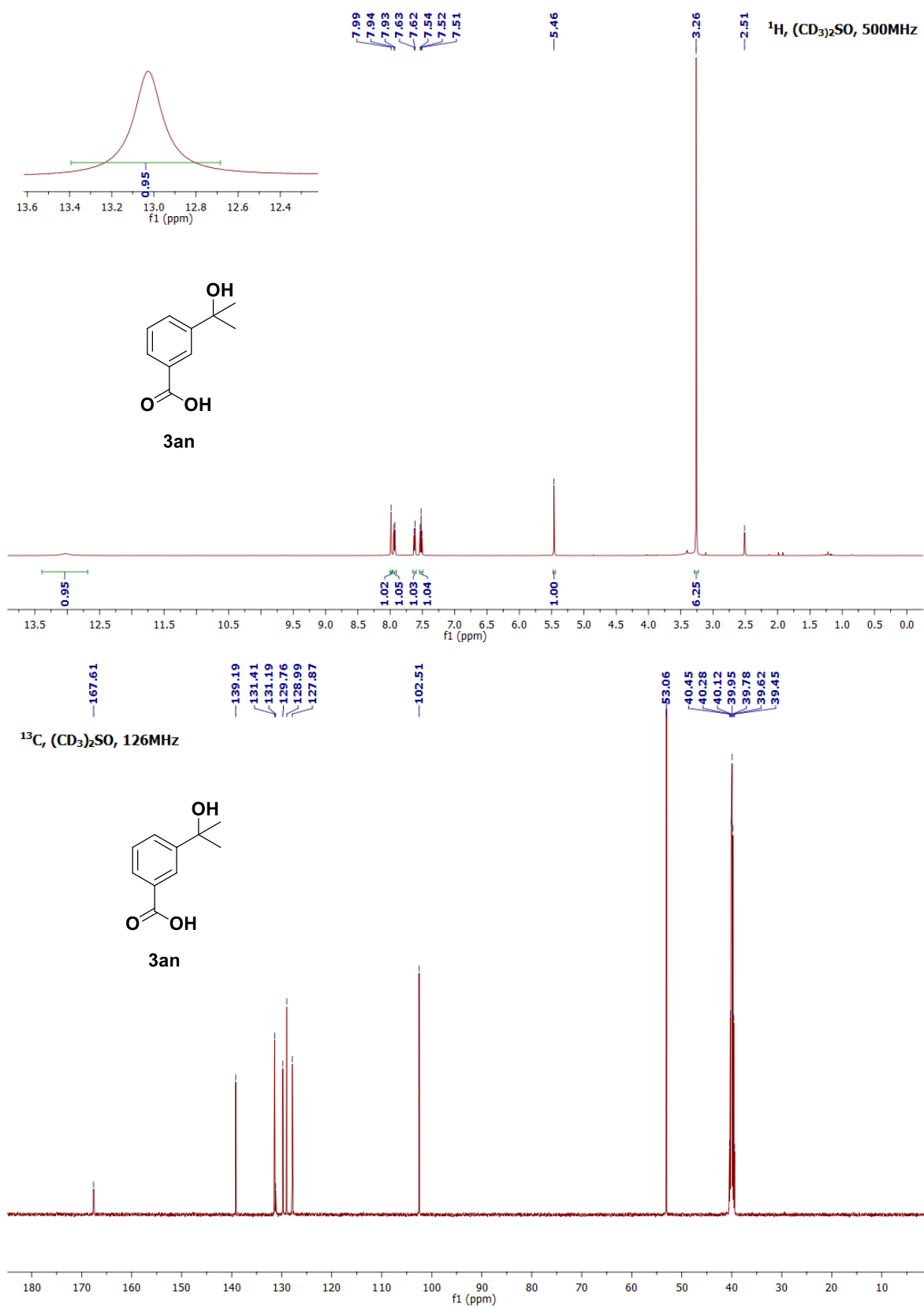


Figure S11: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 2-(5-nitrofuran-2-yl)propan-2-ol (3al)



**Figure S12: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 3-(2-hydroxypropan-2-yl)benzoic acid (3an)**

## 7. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra of Ethylated Products

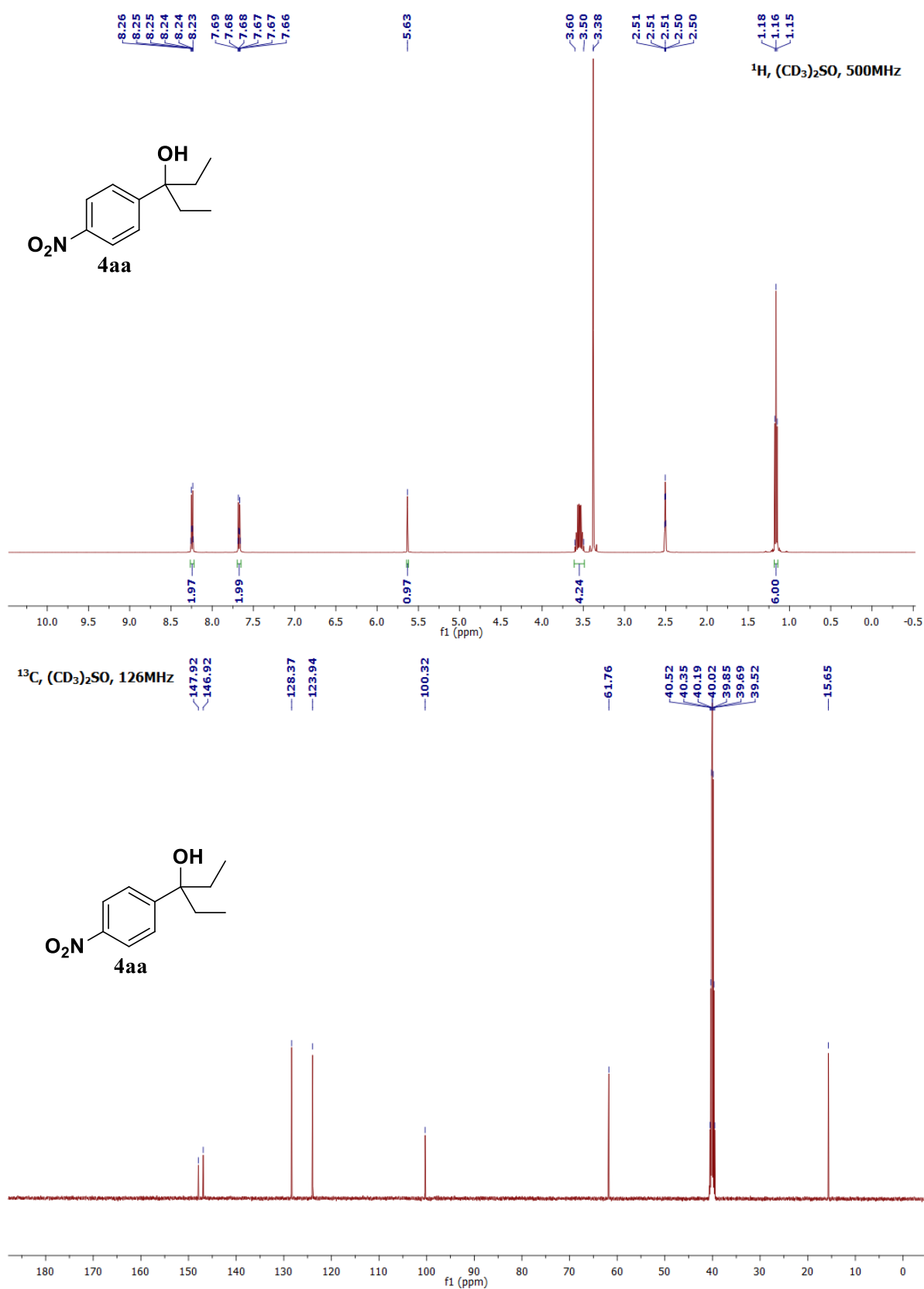


Figure S13:  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR Spectra of 3-(4-nitrophenyl)pentan-3-ol (4aa)

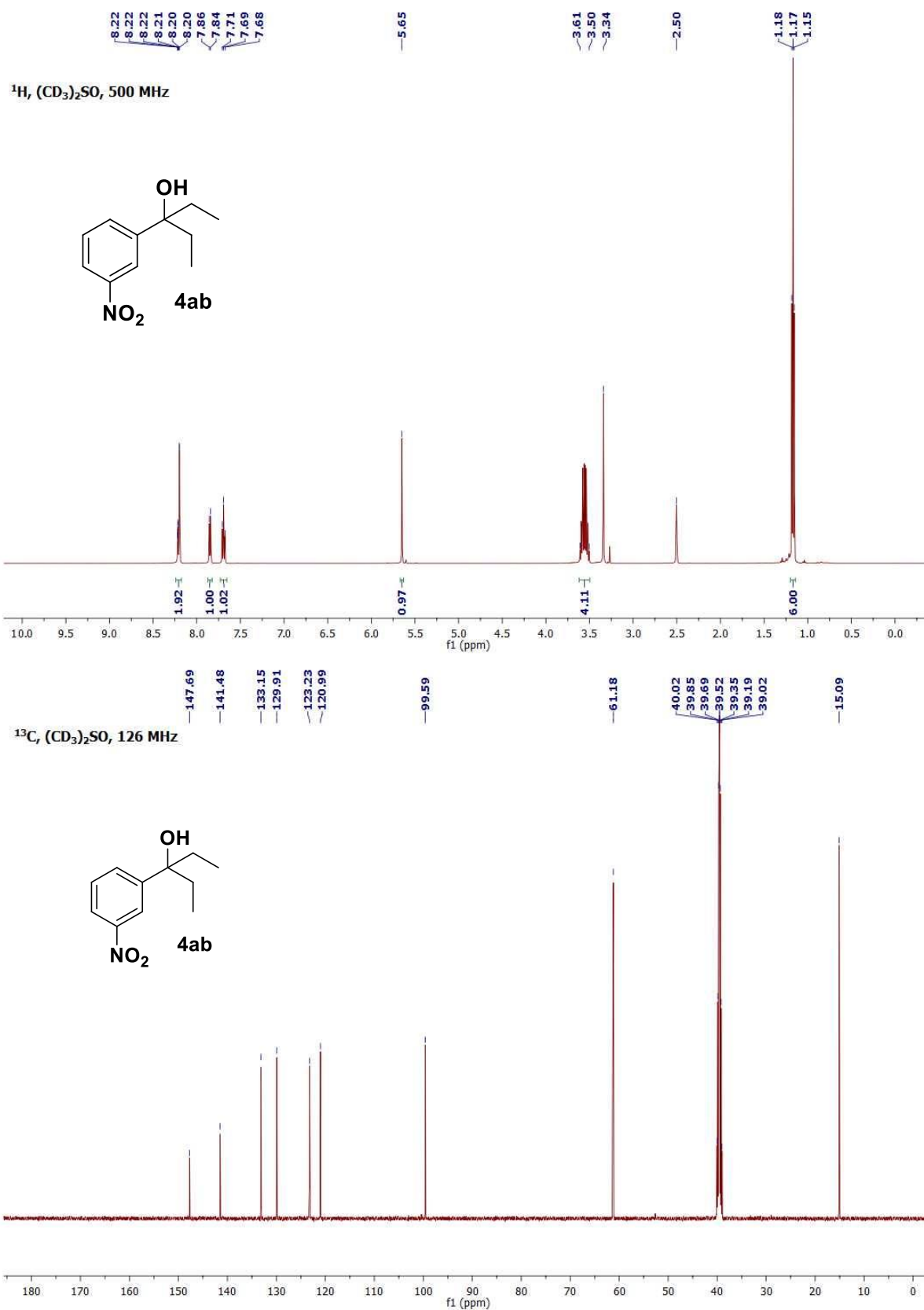


Figure S14: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 3-(3-nitrophenyl)pentan-3-ol (4ab)

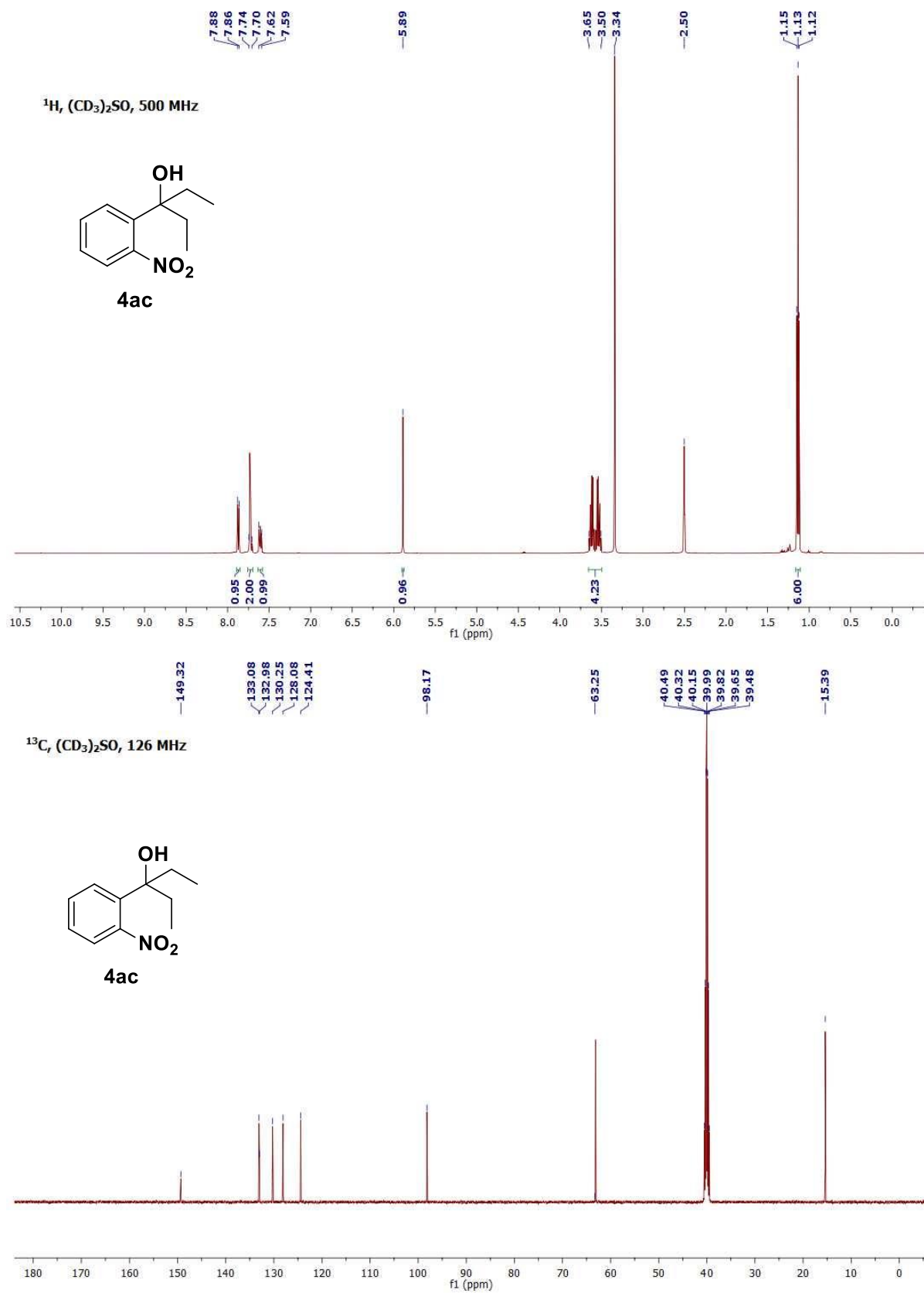


Figure S15: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 3-(2-nitrophenyl)pentan-3-ol (4ac)



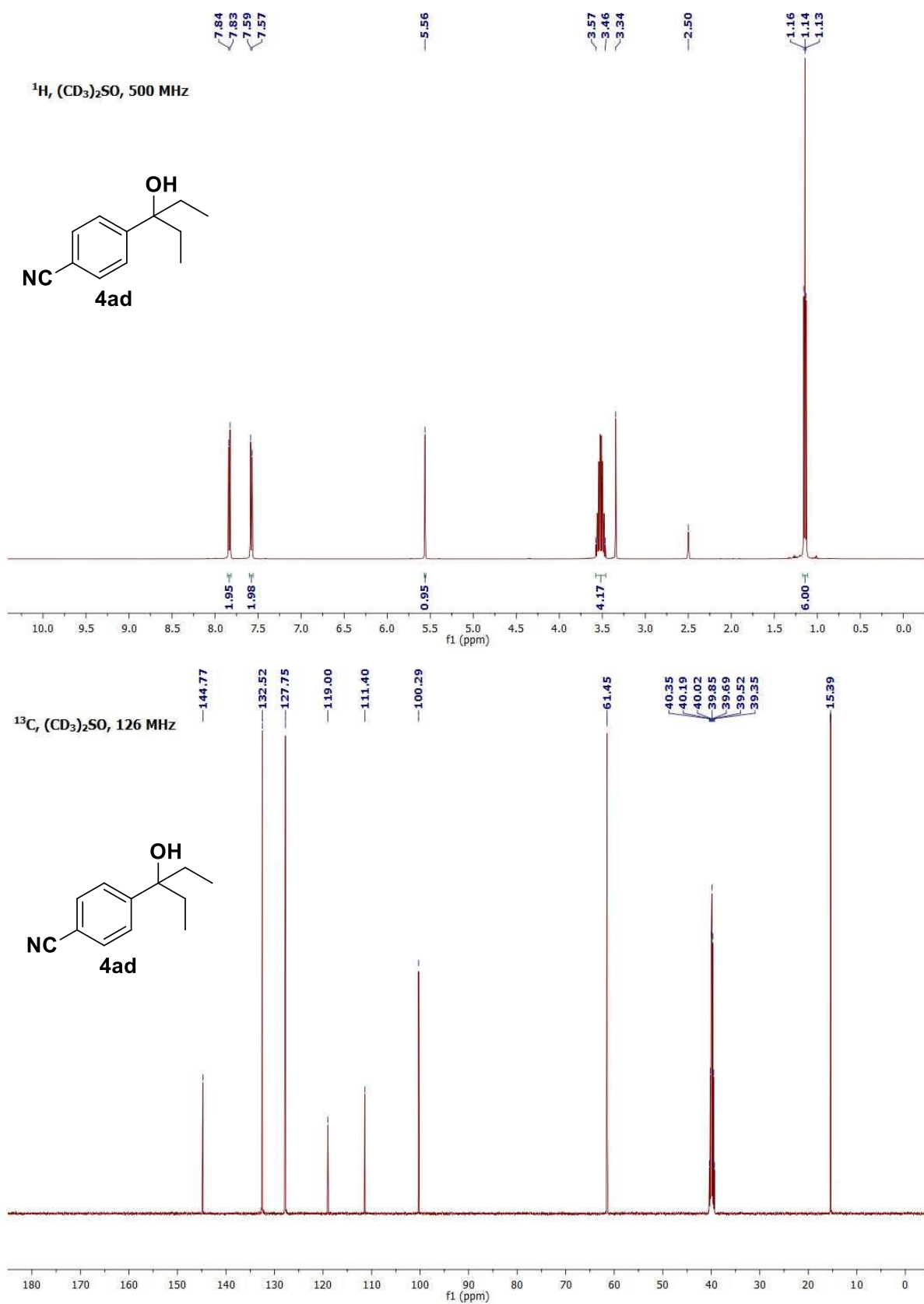


Figure S16: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 4-(3-hydroxypentan-3-yl)benzonitrile (4ad)

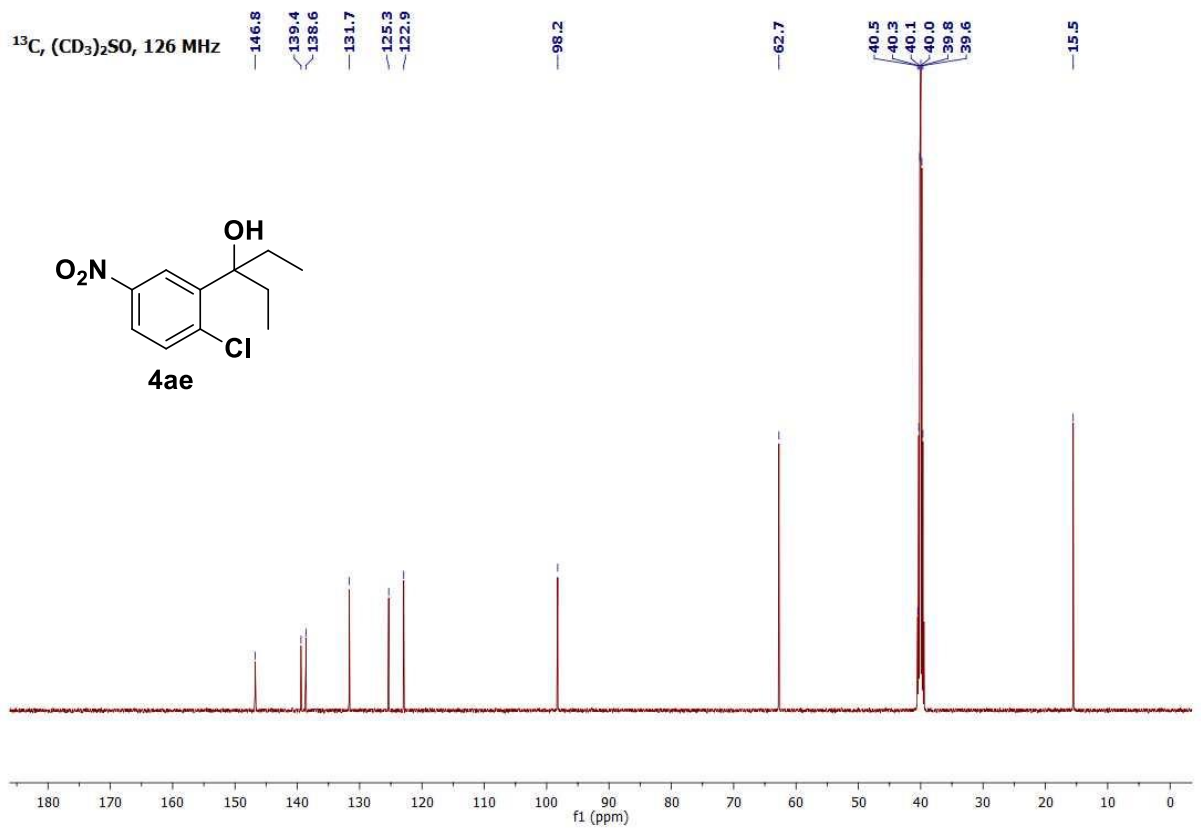
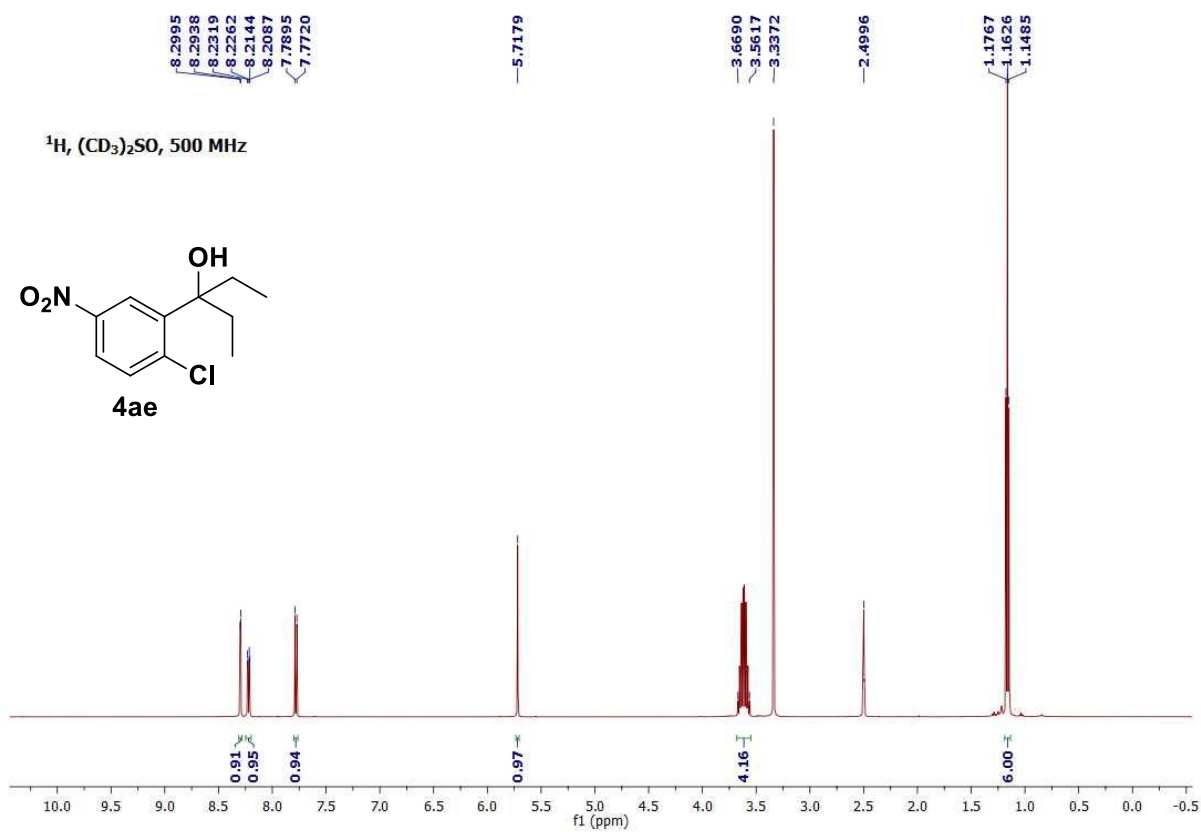


Figure S17: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 3-(2-chloro-5-nitrophenyl)pentan-3-ol (4ae)

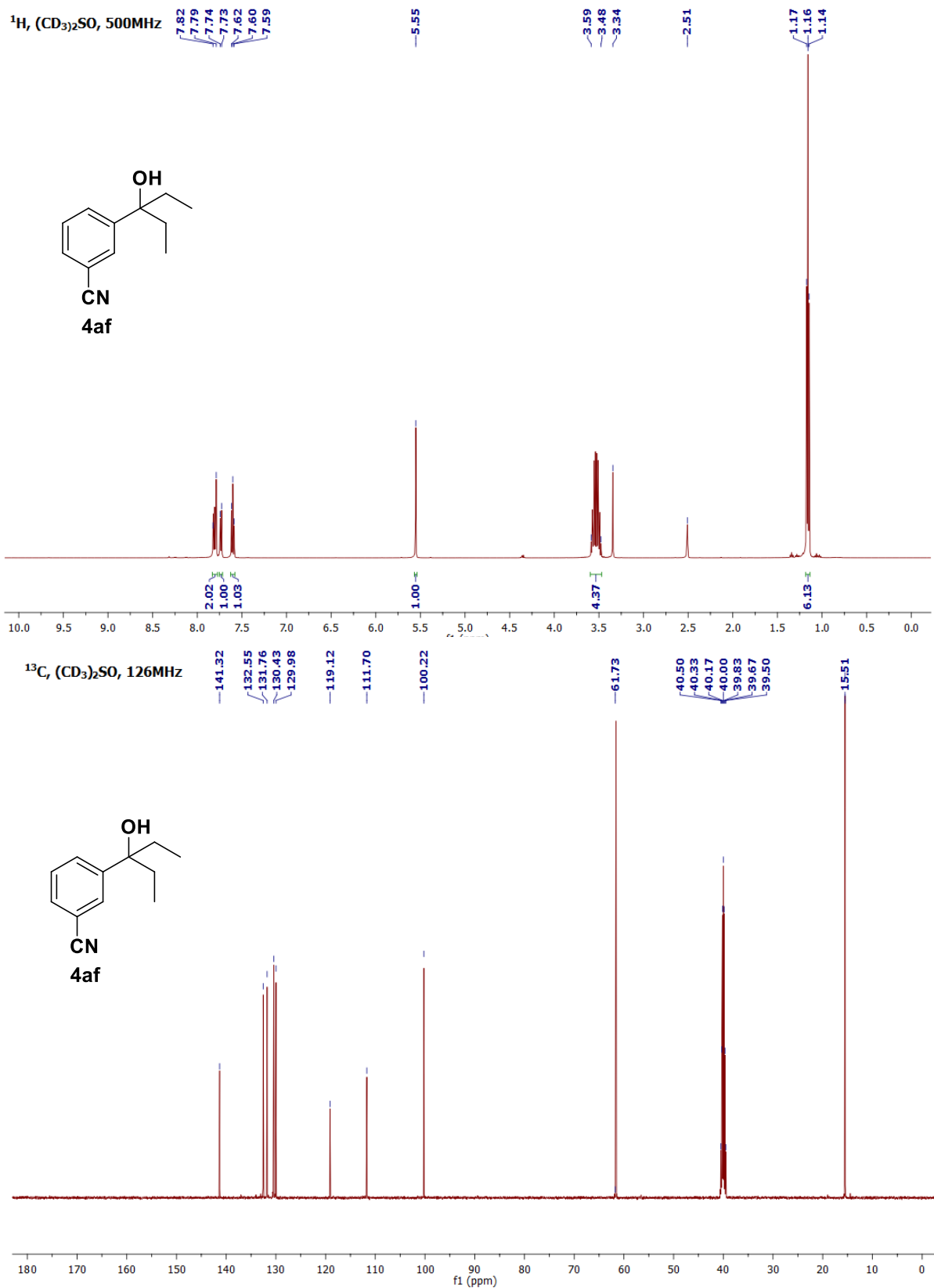


Figure S18: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 3-(3-hydroxypentan-3-yl)benzonitrile (4af)

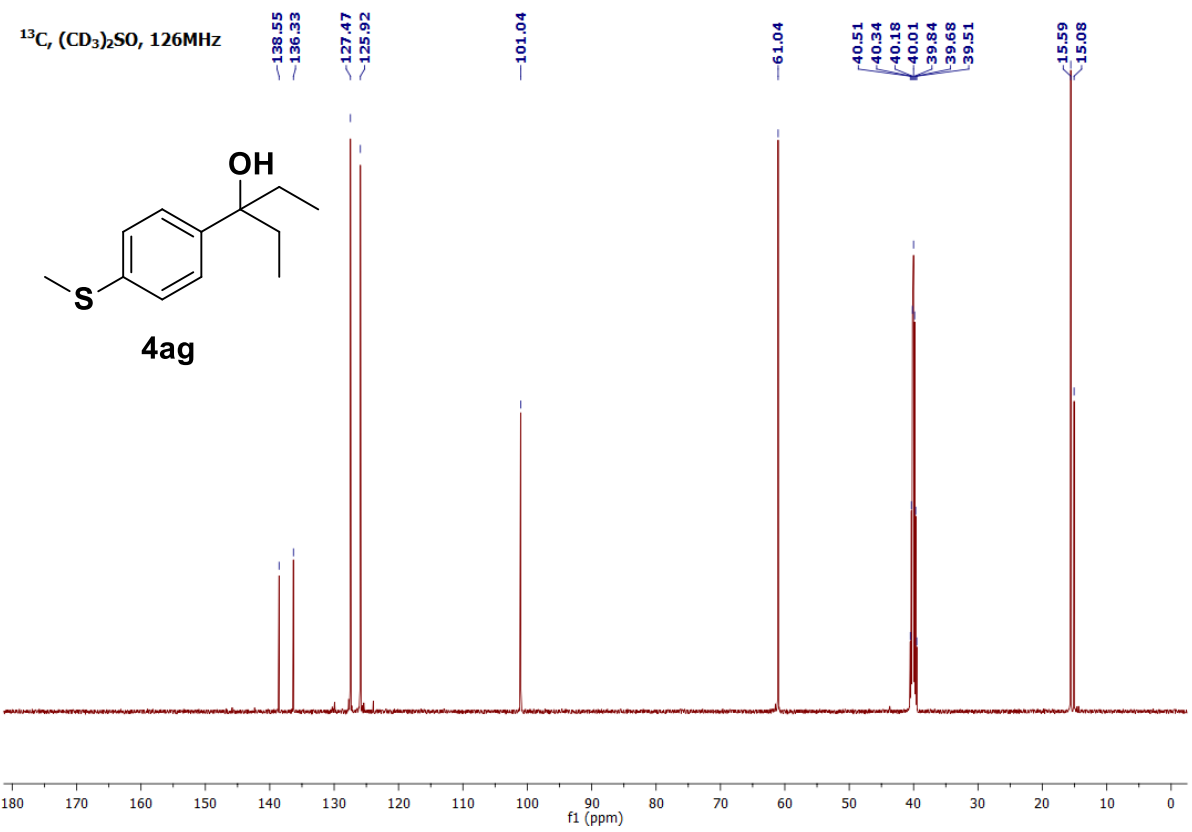
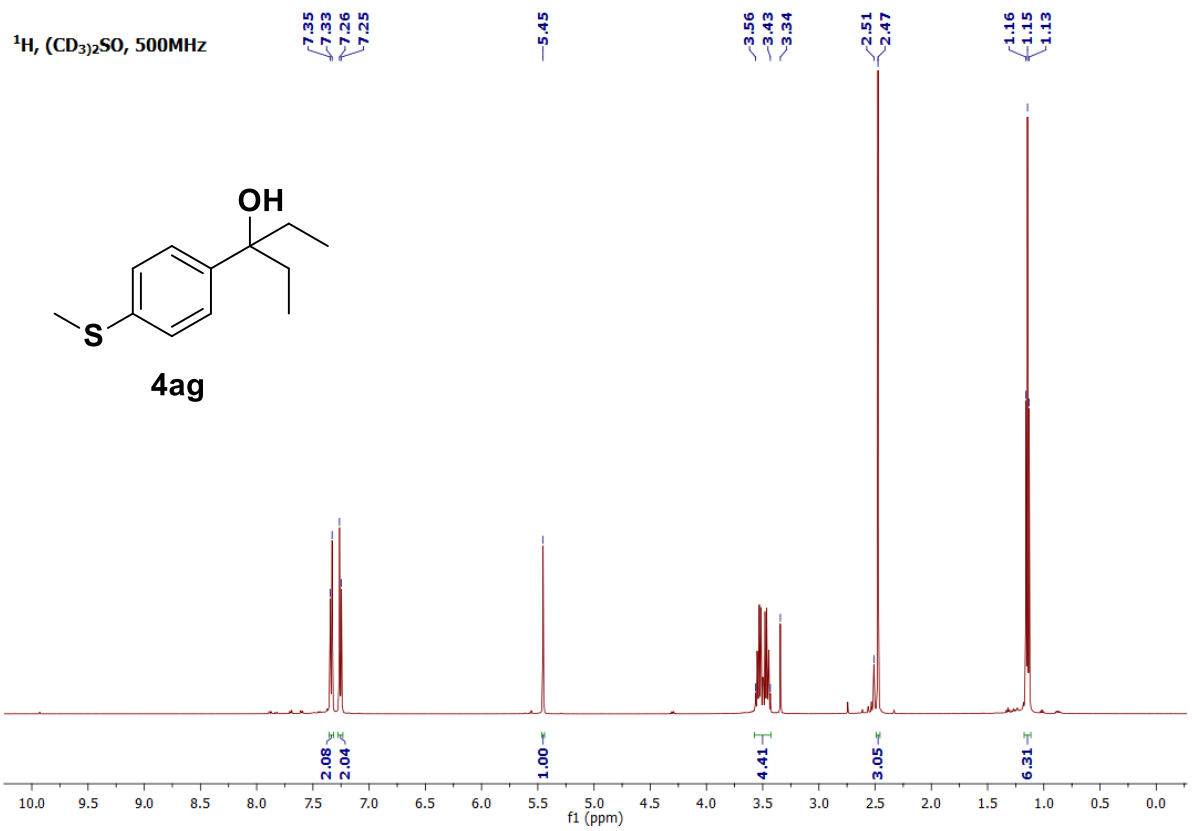


Figure S19: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 3-(4-(methylthio)phenyl)pentan-3-ol (4ag)

## 8. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR Spectra of Allylated Products

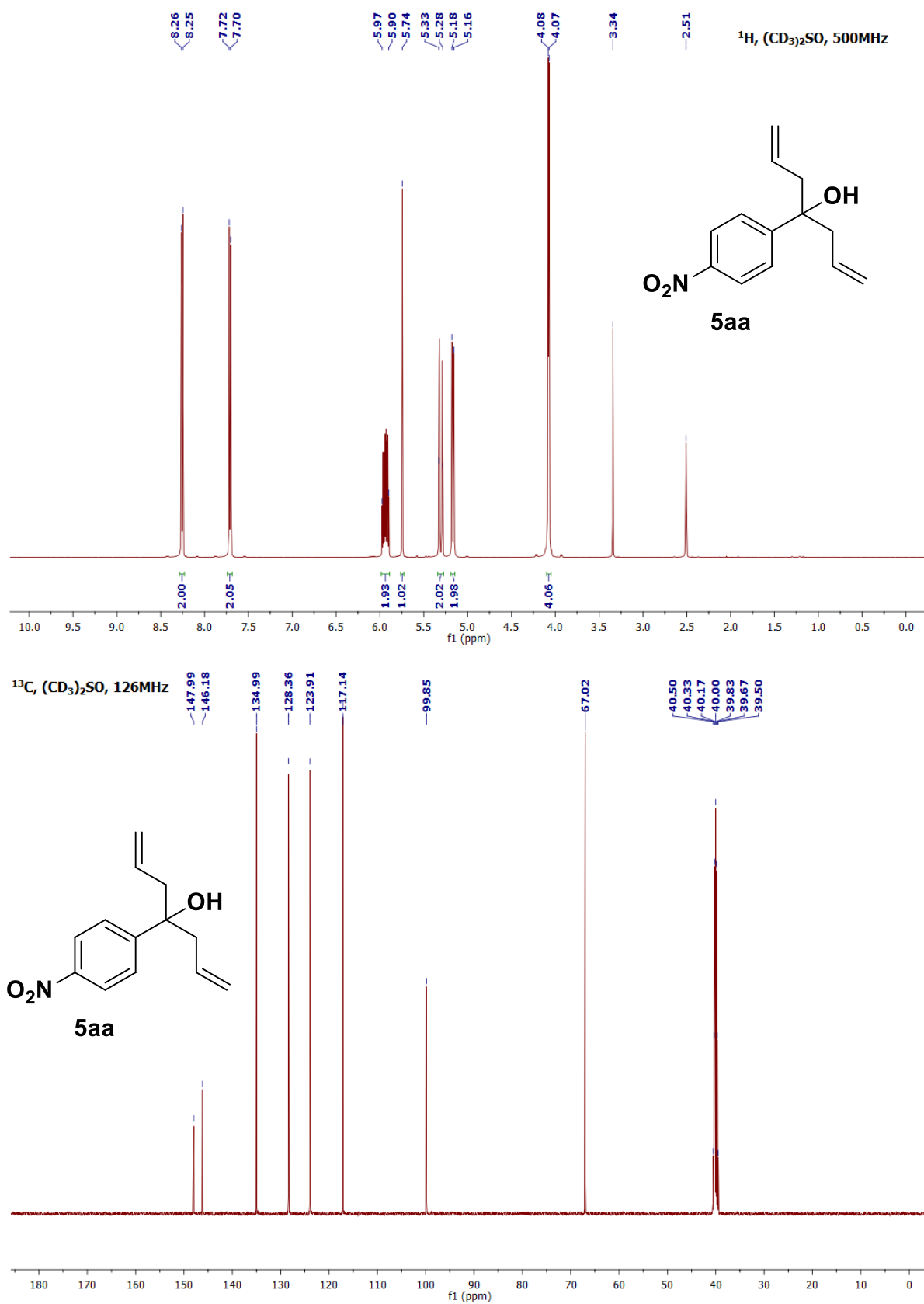


Figure S20:  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR Spectra of 4-(4-nitrophenyl)hepta-1,6-dien-4-ol (5aa)

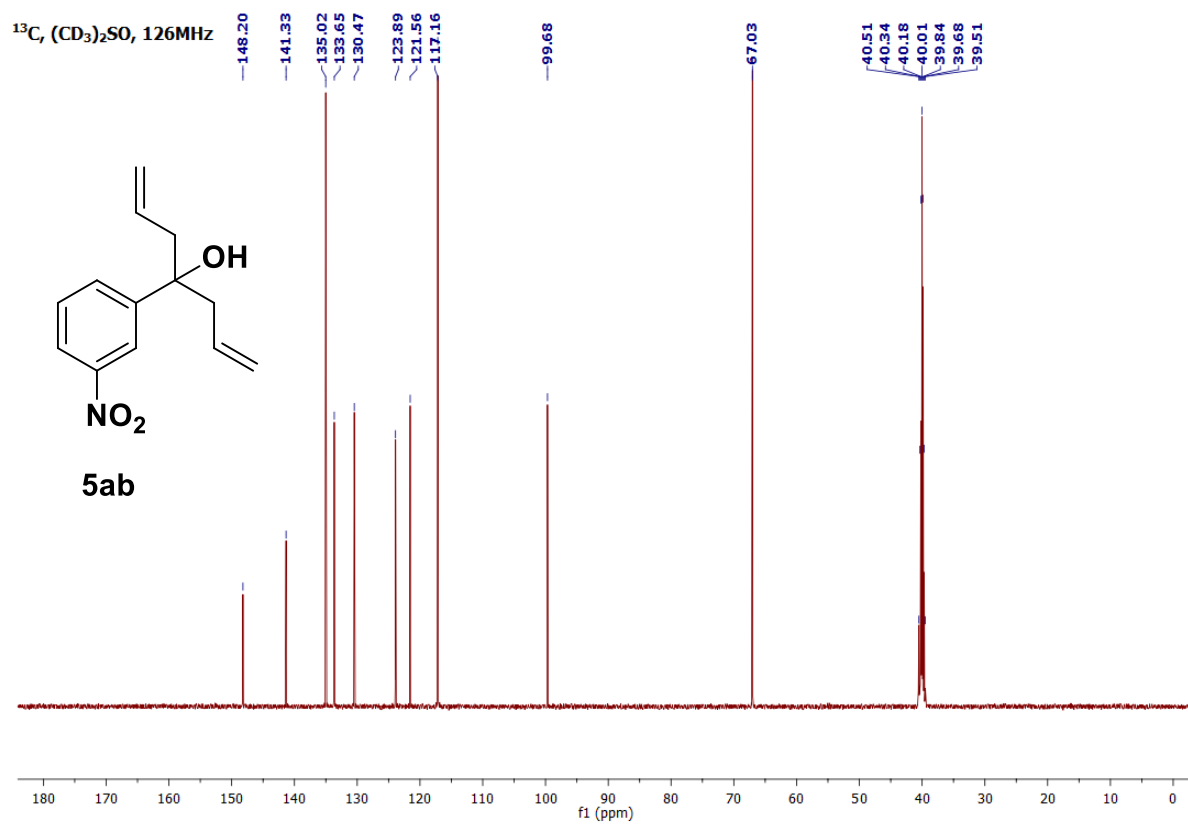
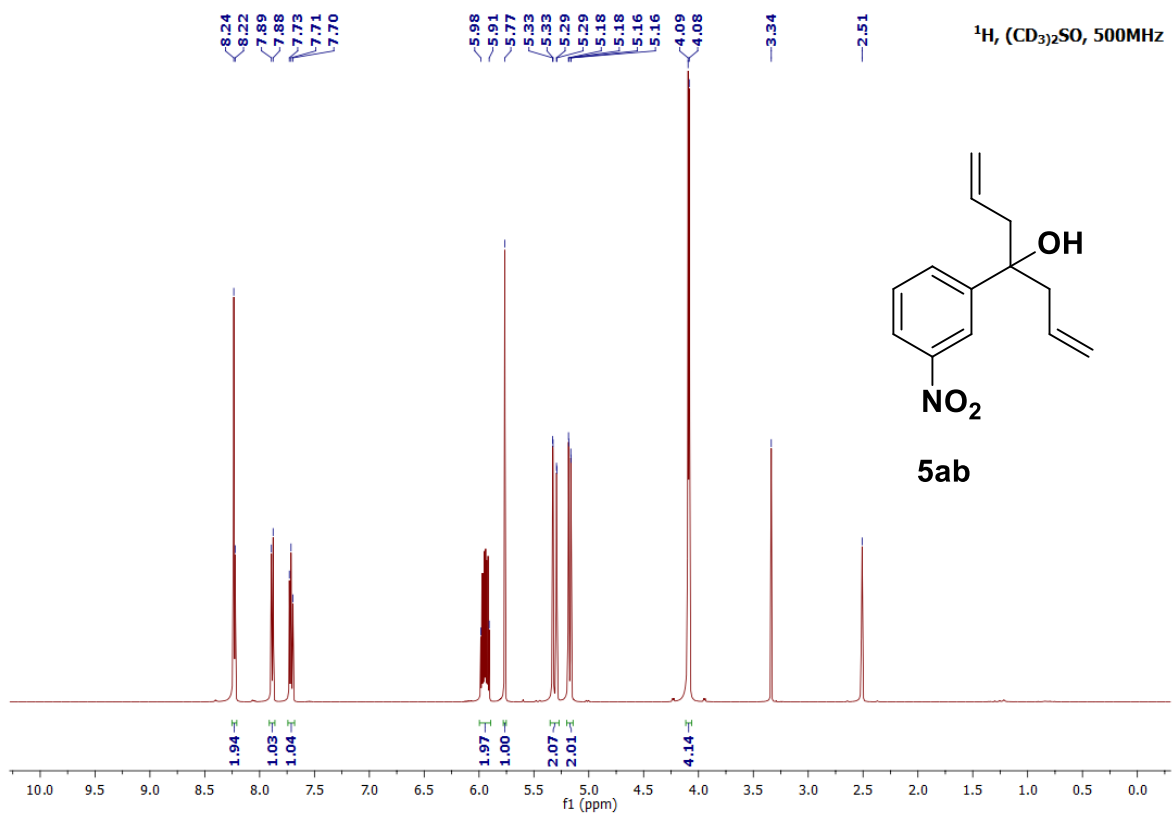
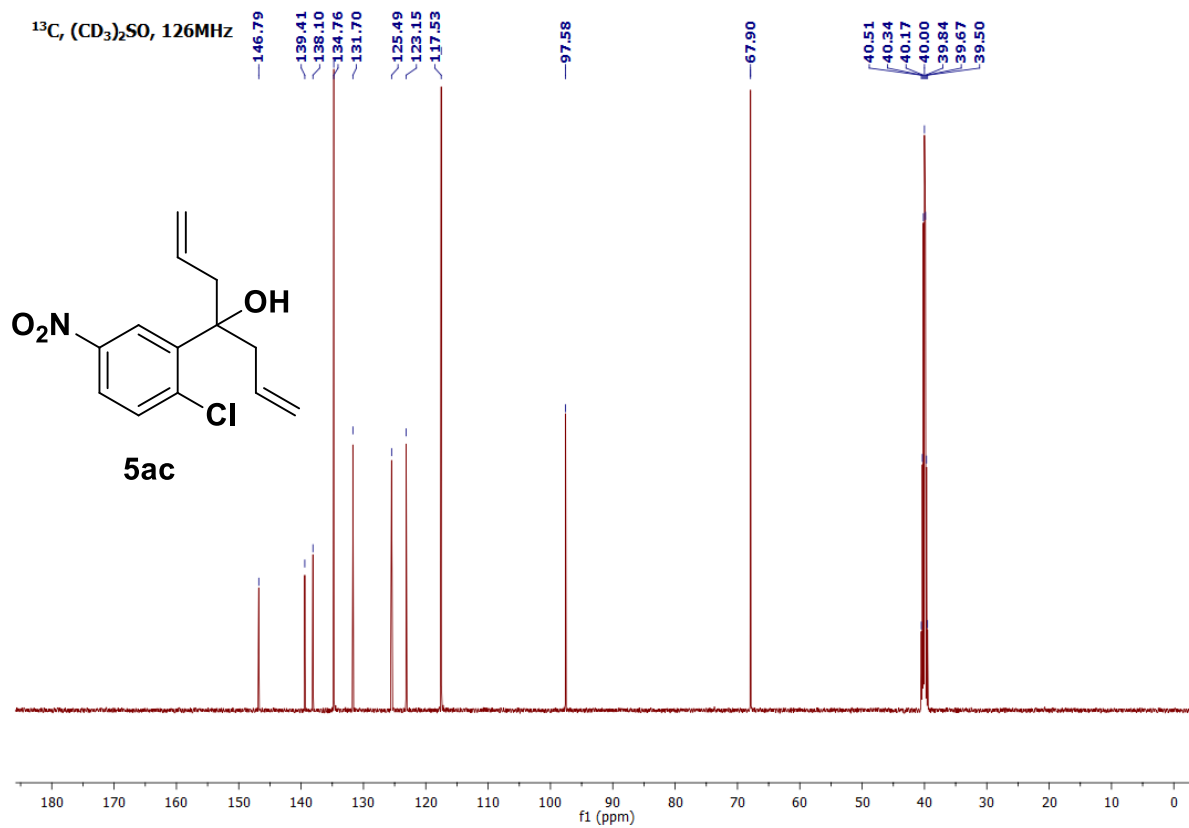
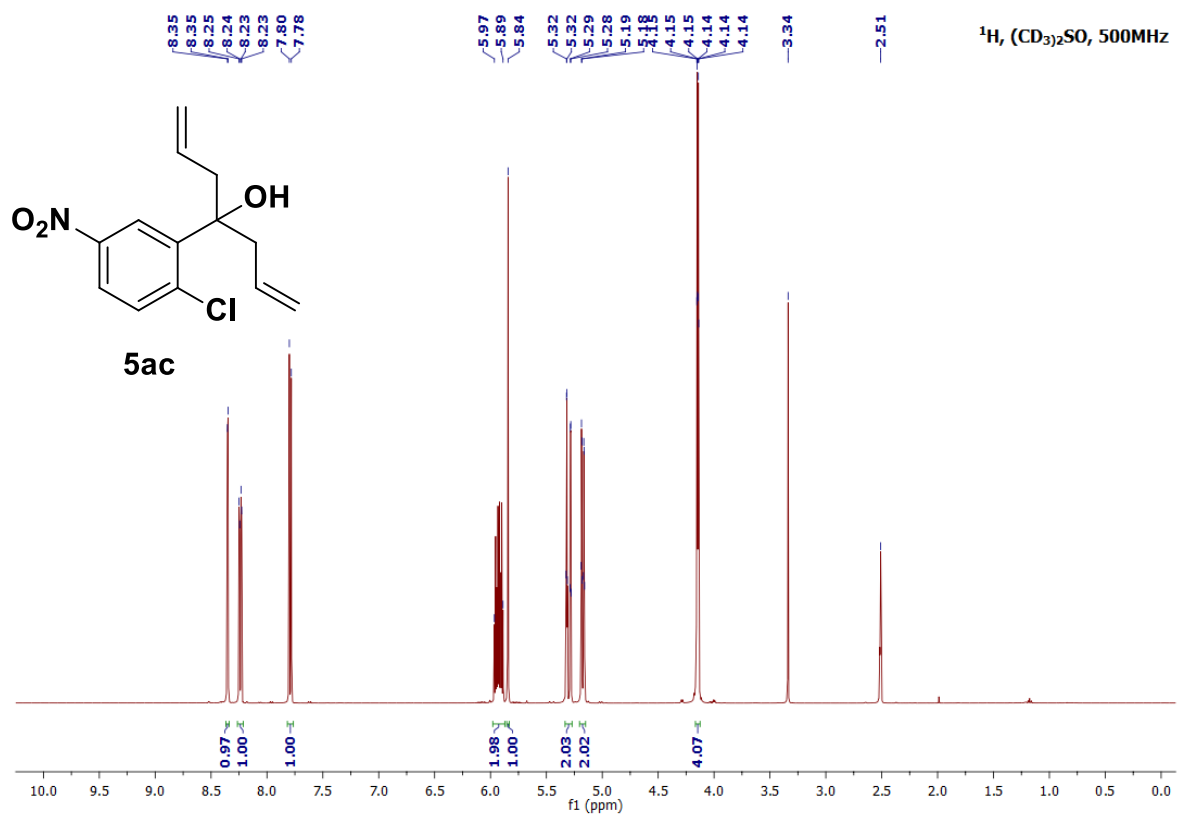


Figure S21: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 4-(3-nitrophenyl)hepta-1,6-dien-4-ol (5ab)



**Figure S22: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 4-(2-chloro-5-nitrophenyl)hepta-1,6-dien-4-ol (5ac)**

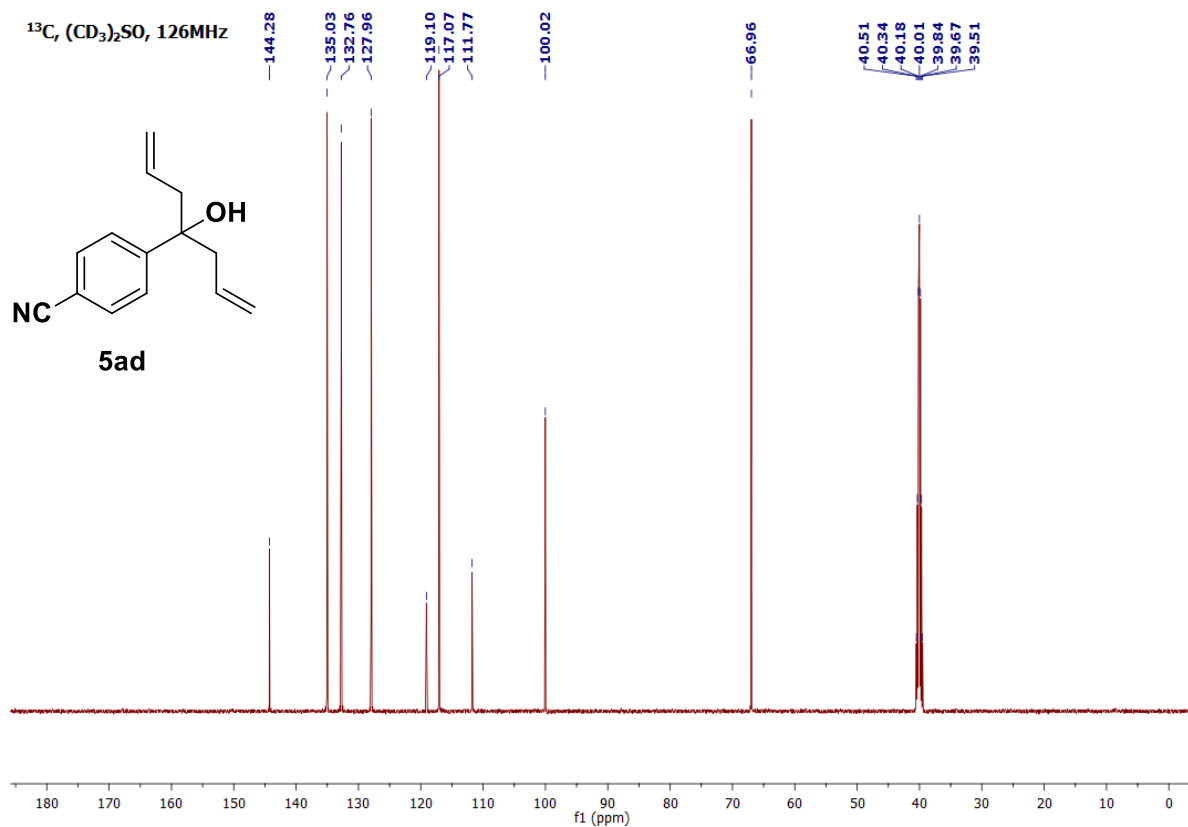
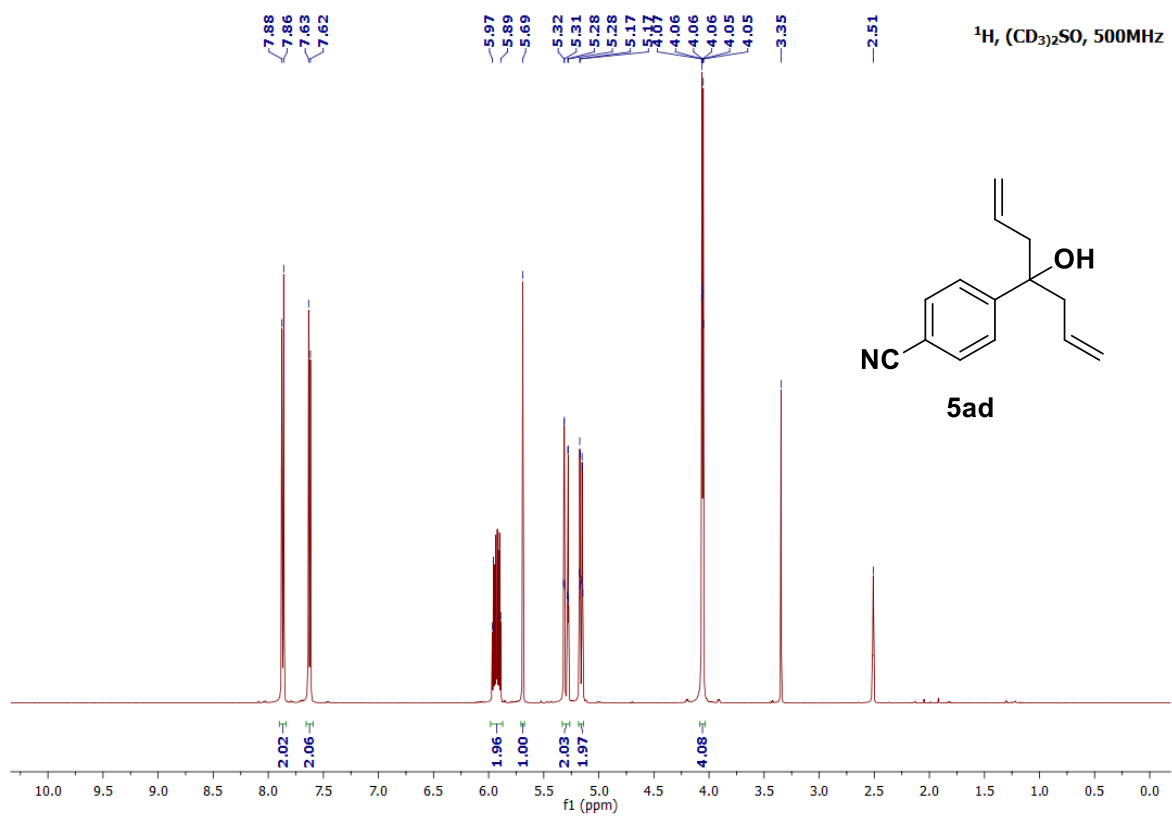
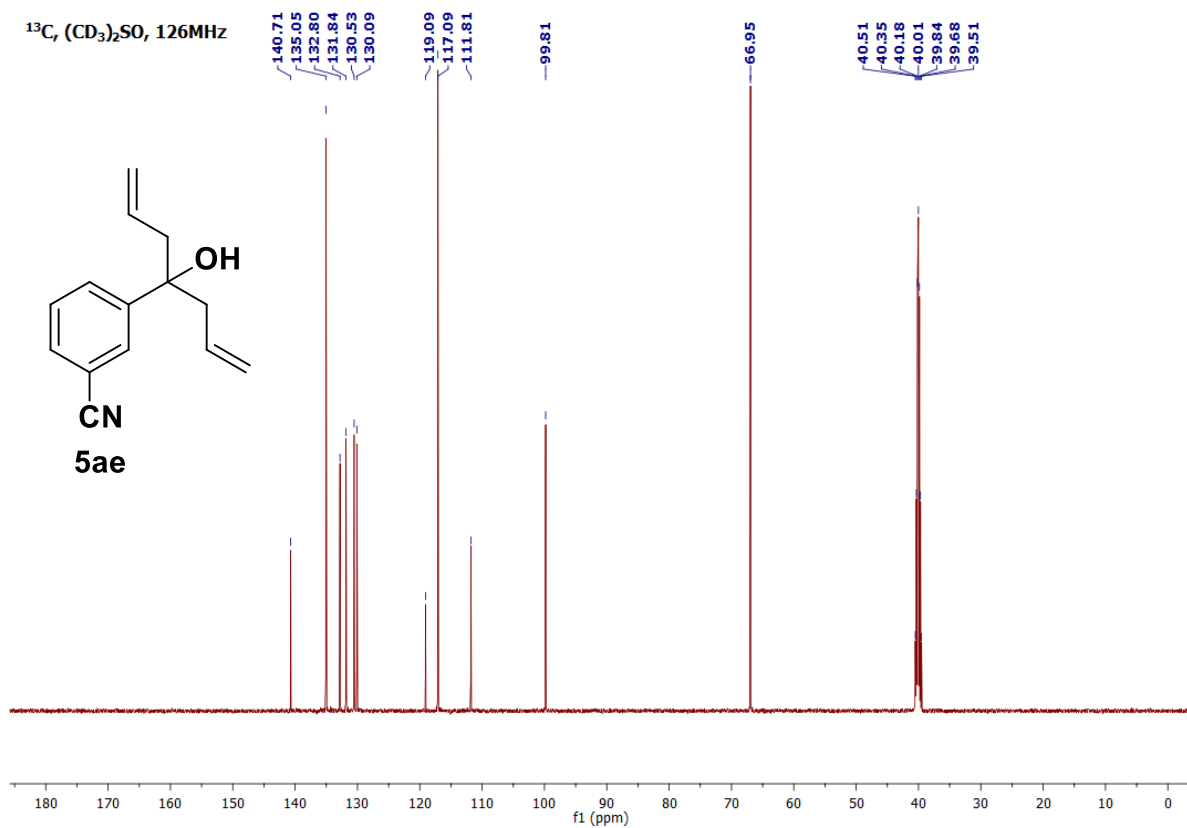
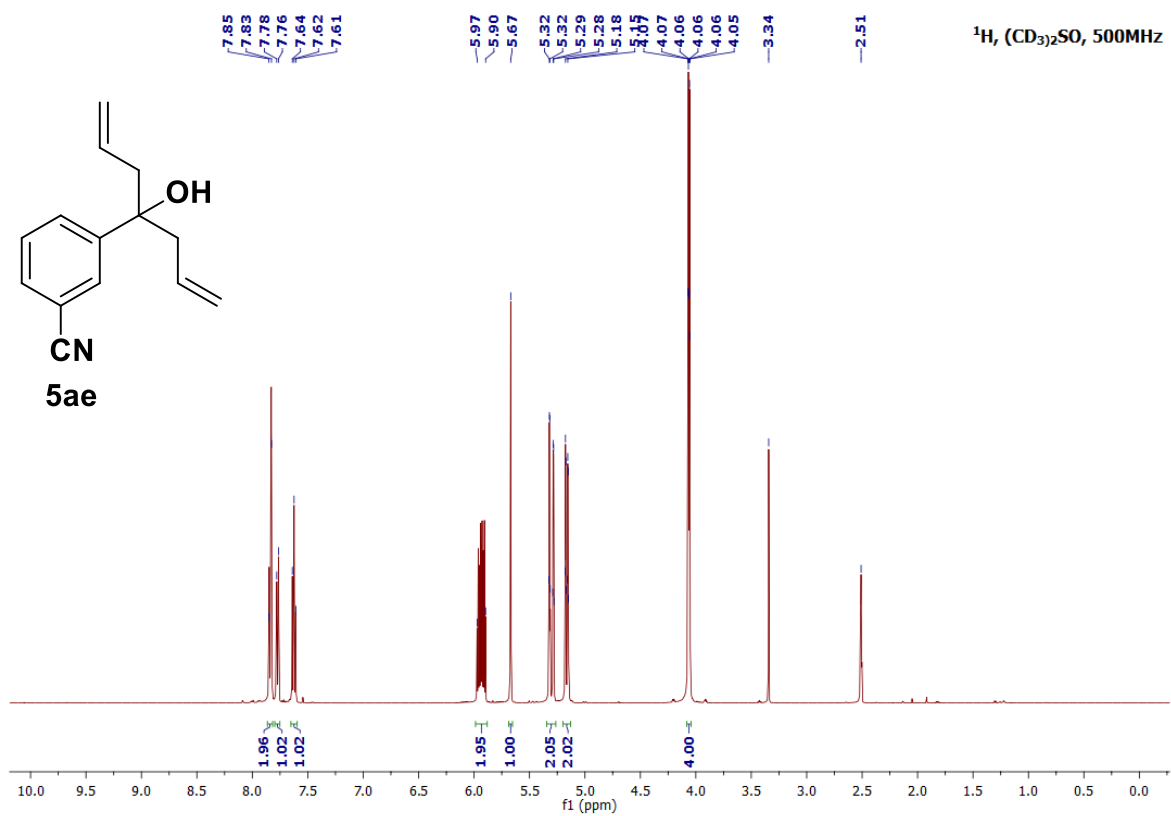
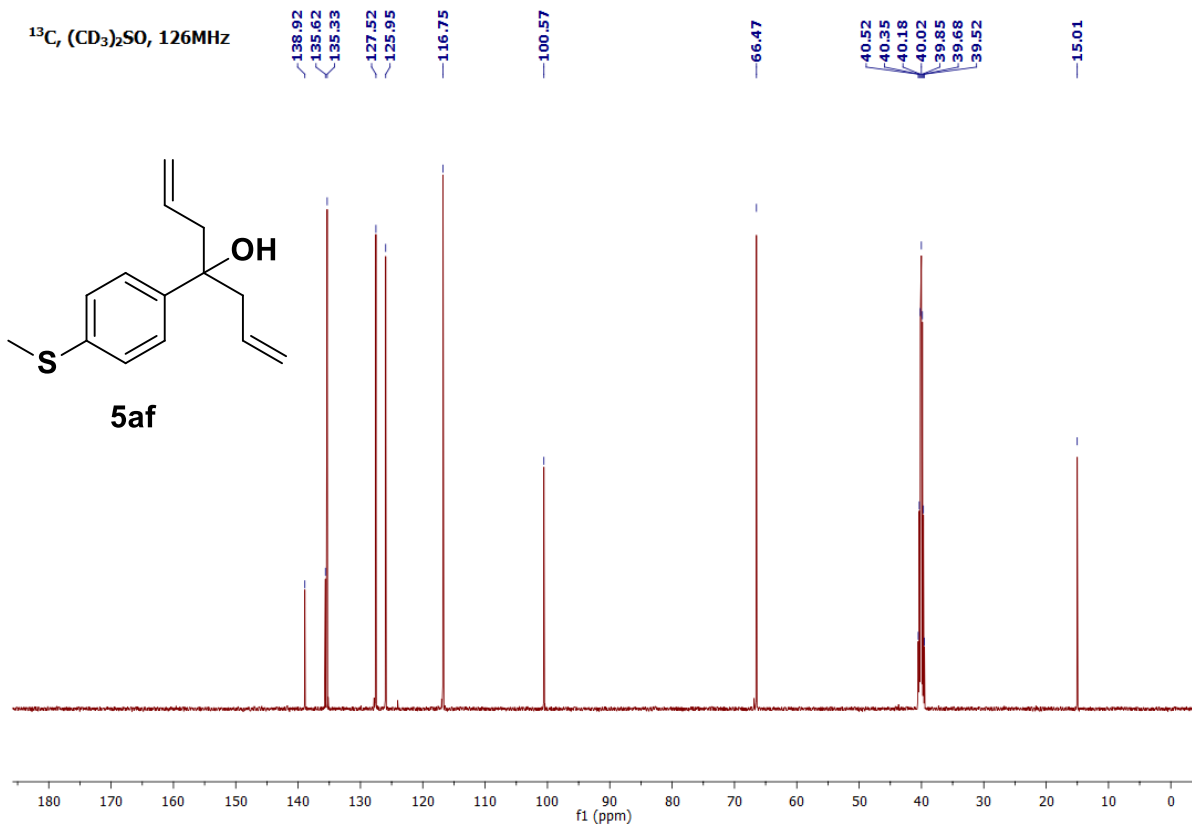
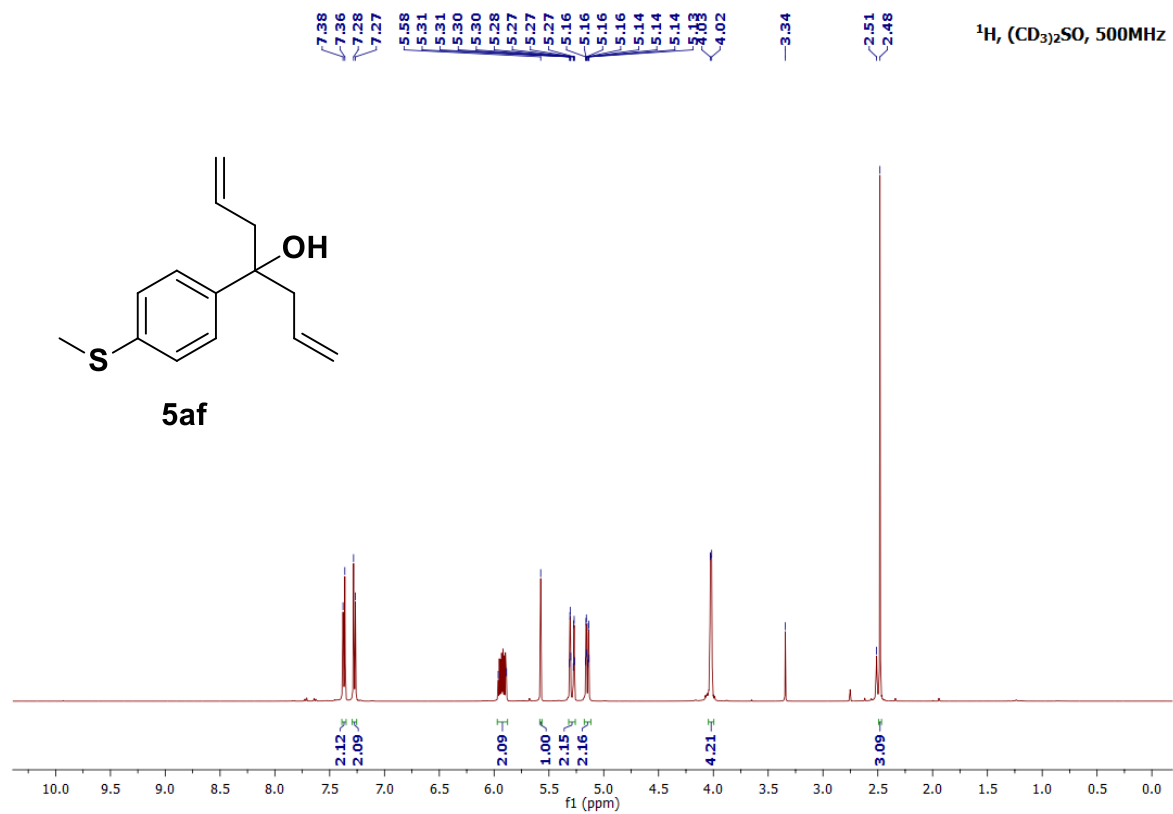


Figure S23: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 4-(4-hydroxyhepta-1,6-dien-4-yl) benzonitrile (5ad)

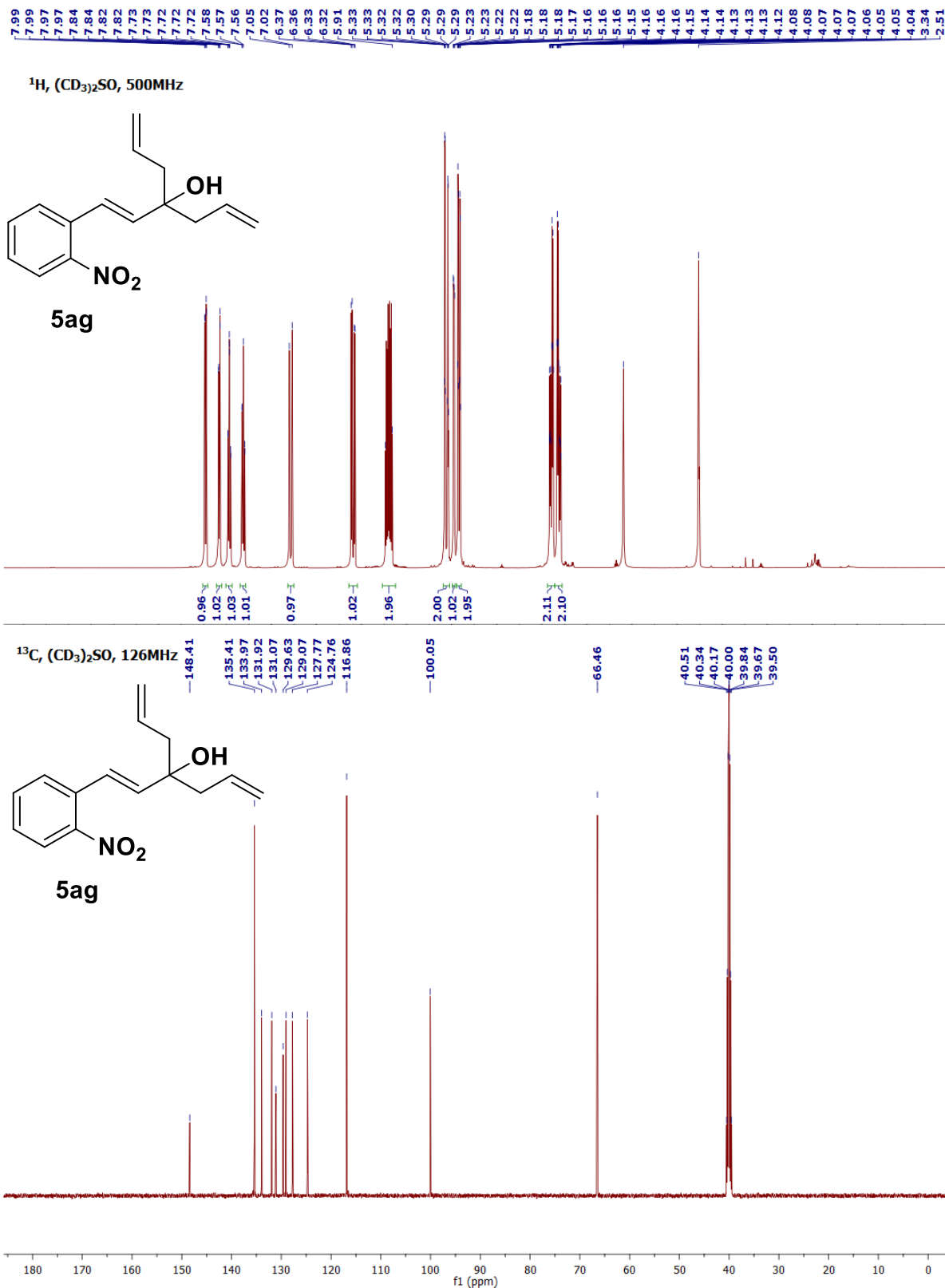




**Figure S24: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 3-(4-hydroxyhepta-1,6-dien-4-yl) benzonitrile (5ae)**



**Figure S25: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of 4-(4-(methylthio)phenyl)hepta-1,6-dien-4-ol (5af)**



**Figure S26: <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra of (*E*)-4-(2-nitrostyryl)hepta-1,6-dien-4-ol (5ag)**

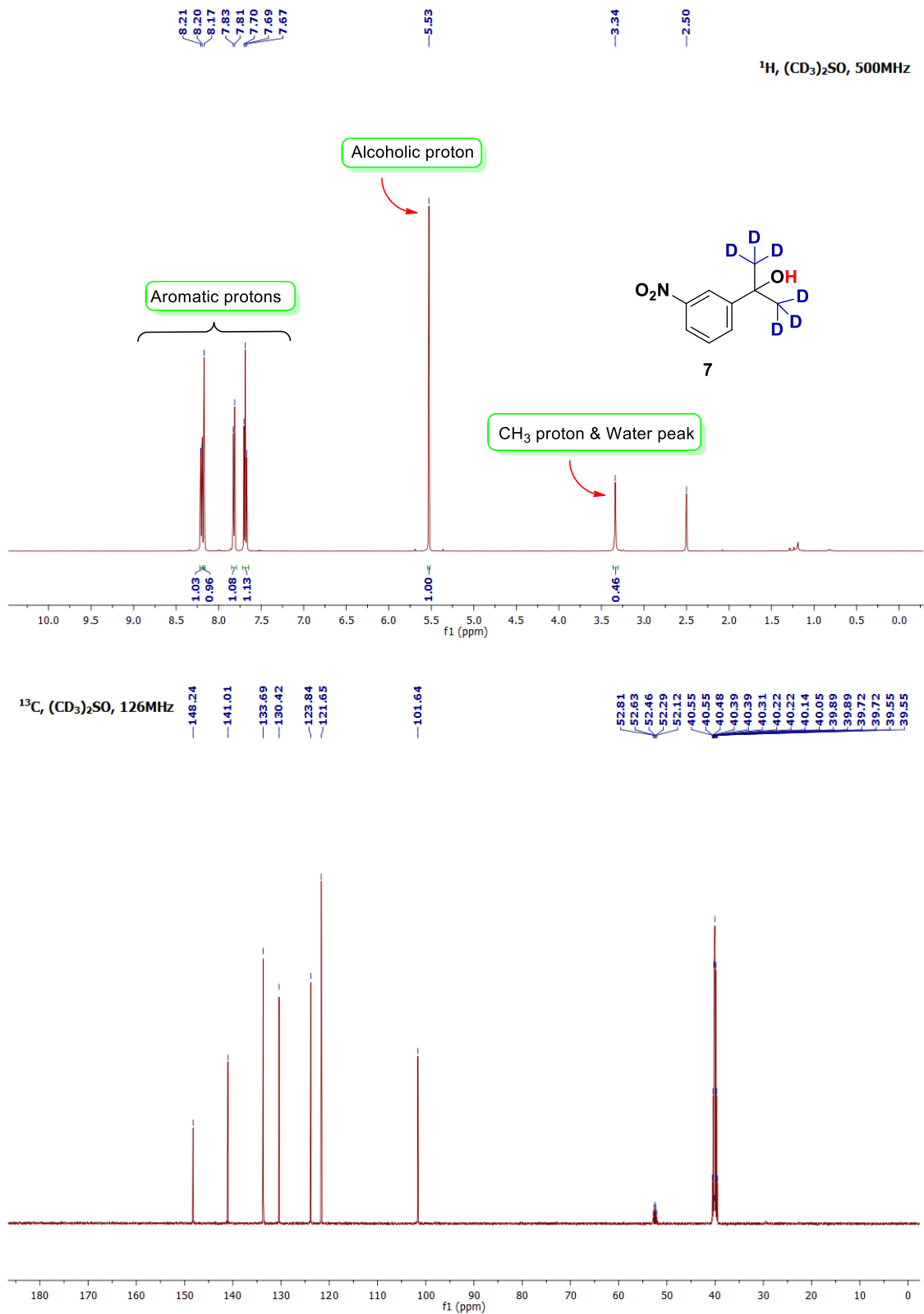


Figure S27:  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR Spectra of 3ab (recorded in  $\text{DMSO}-d^6$ )

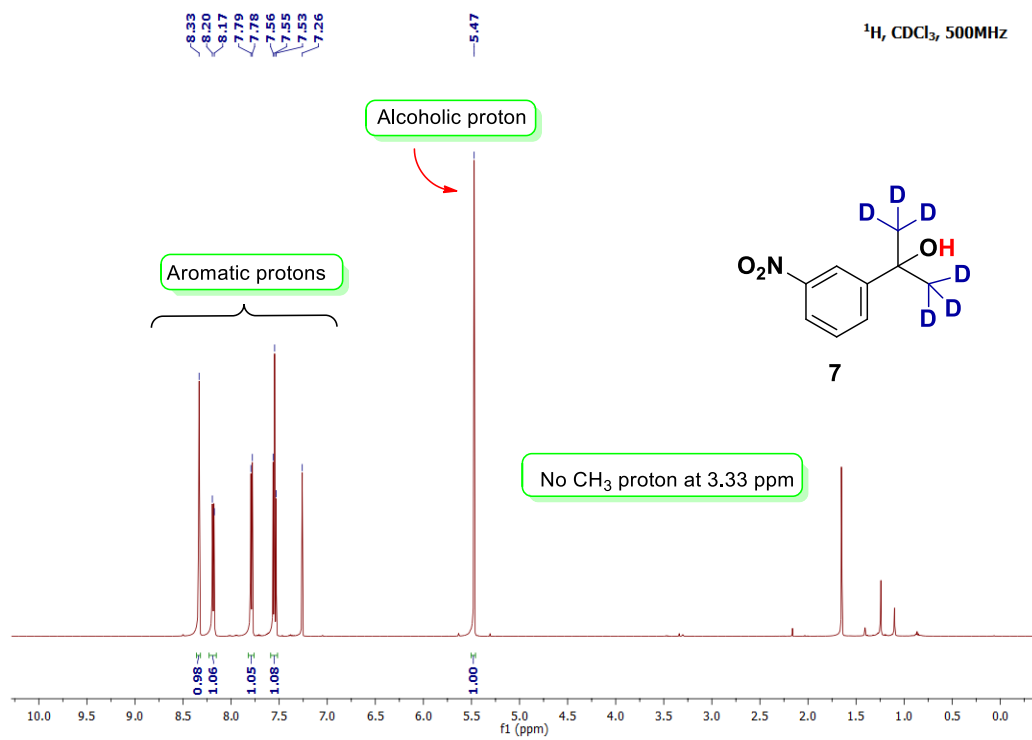
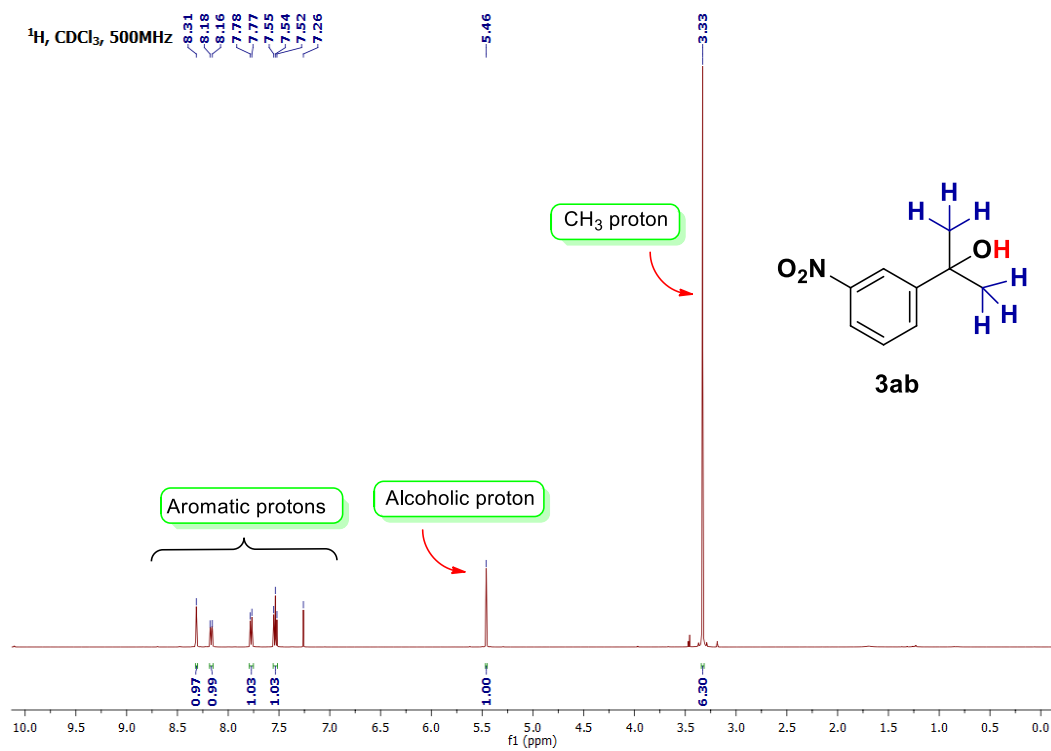


Figure S28:  $^1\text{H}$  NMR Spectra of **3ab** and **7** (recorded in  $\text{CDCl}_3$ )

## HR-MS Spectra of the Products

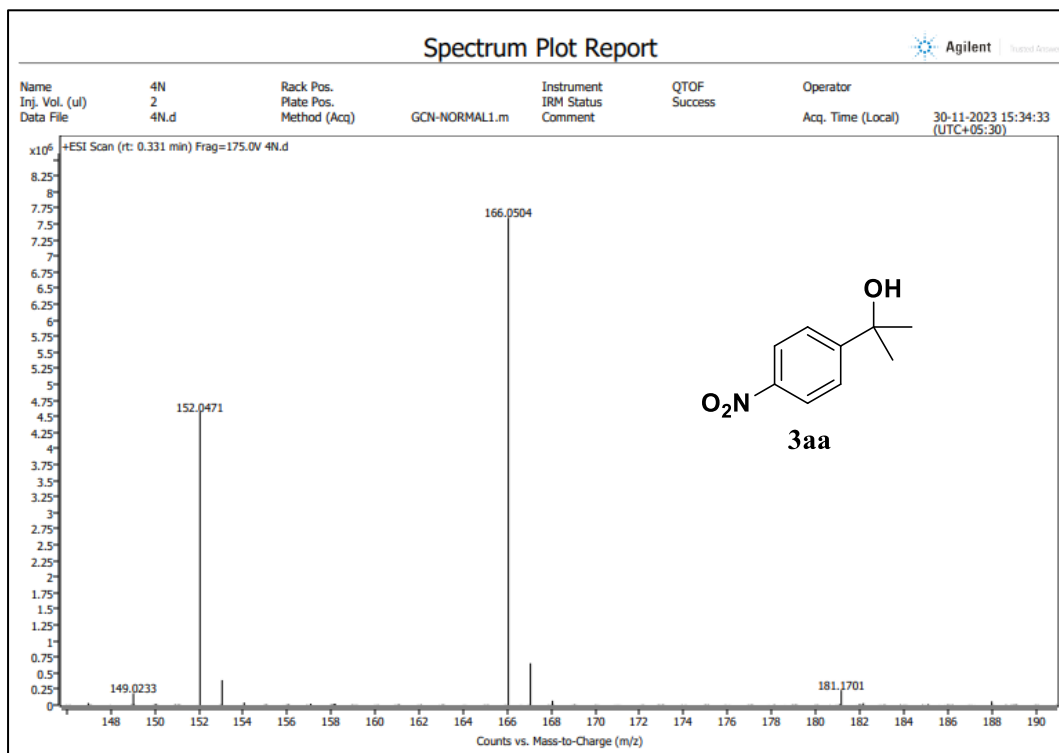


Figure S29: HR-MS Spectrum of 3aa

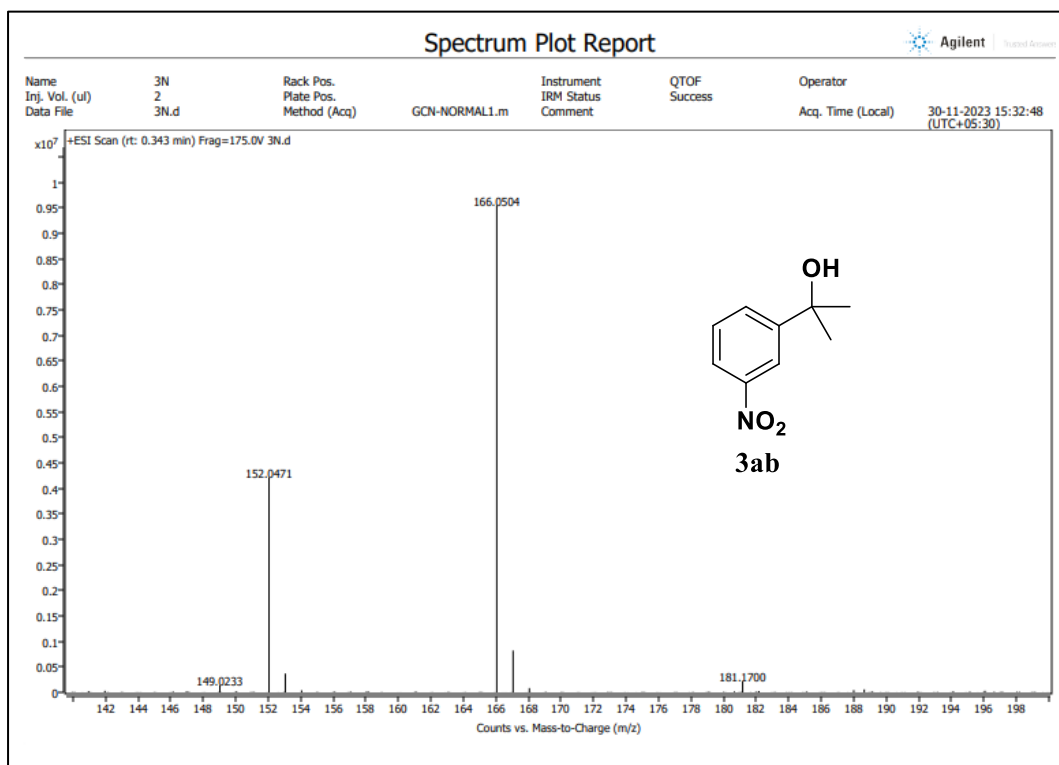
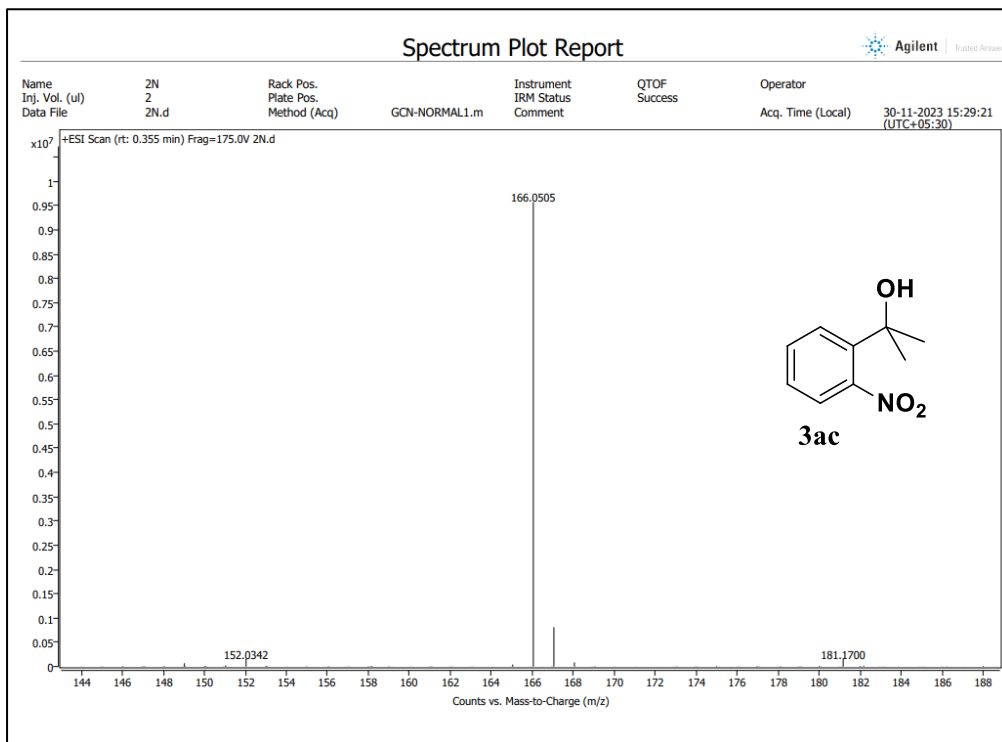
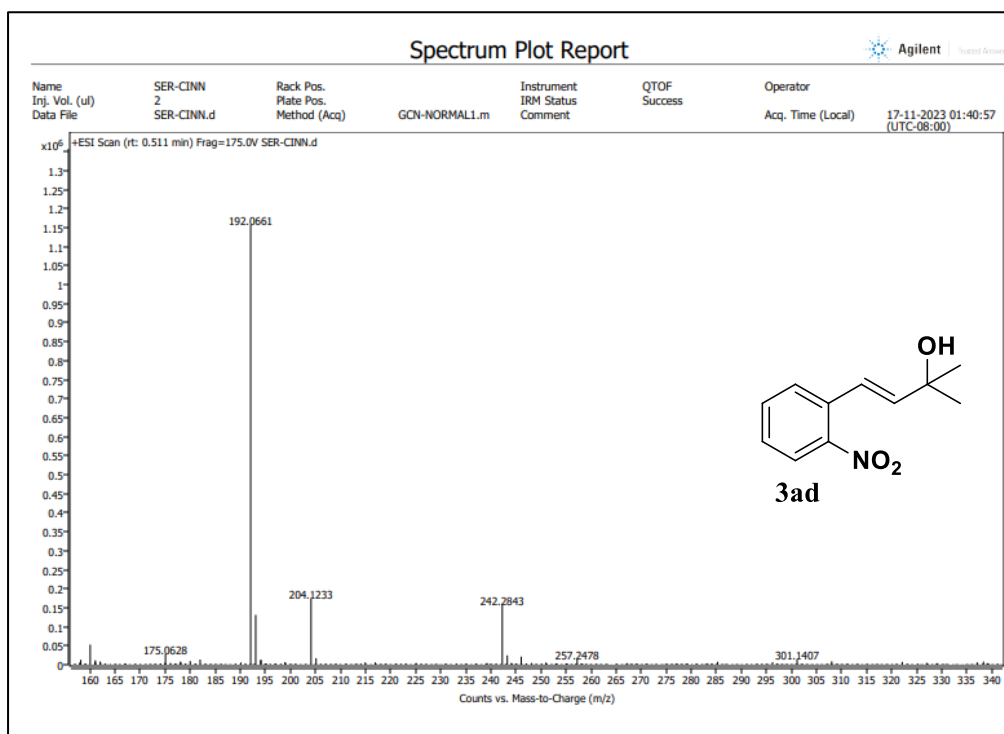


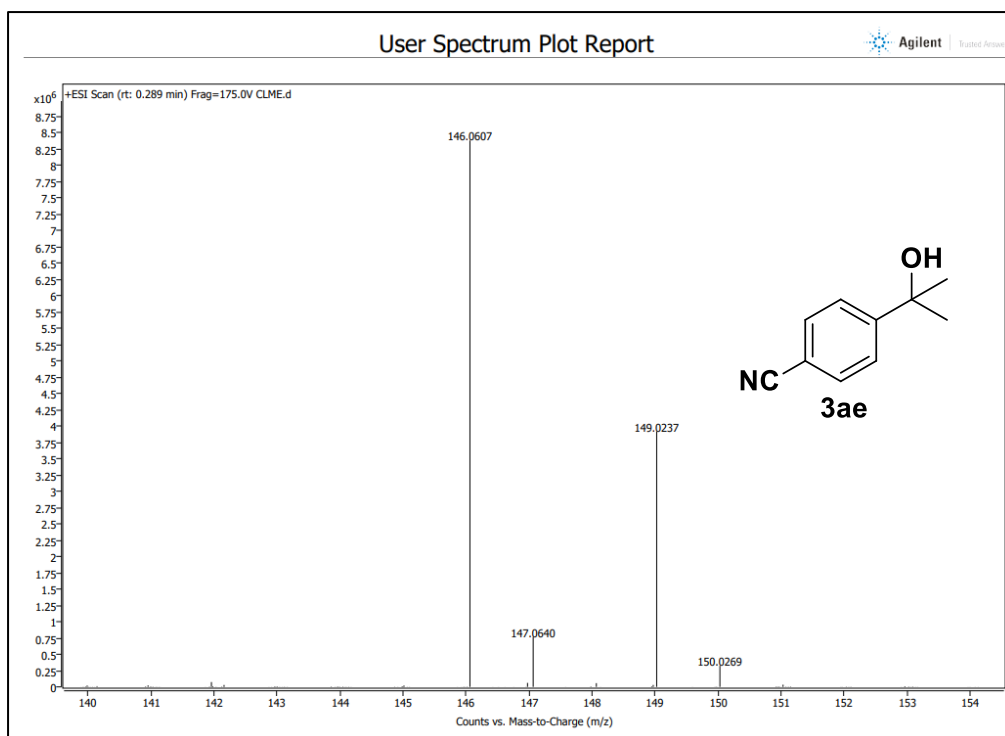
Figure S30: HR-MS Spectrum of 3ab



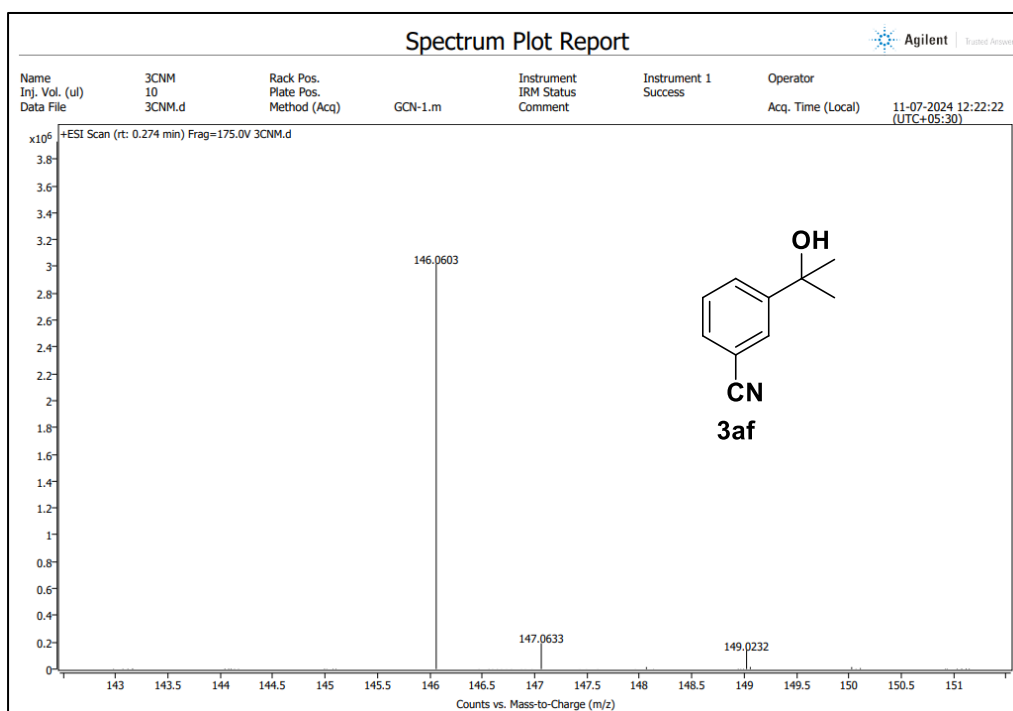
**Figure S31: HR-MS Spectrum of 3ac.**



**Figure S32: HR-MS Spectrum of 3ad.**

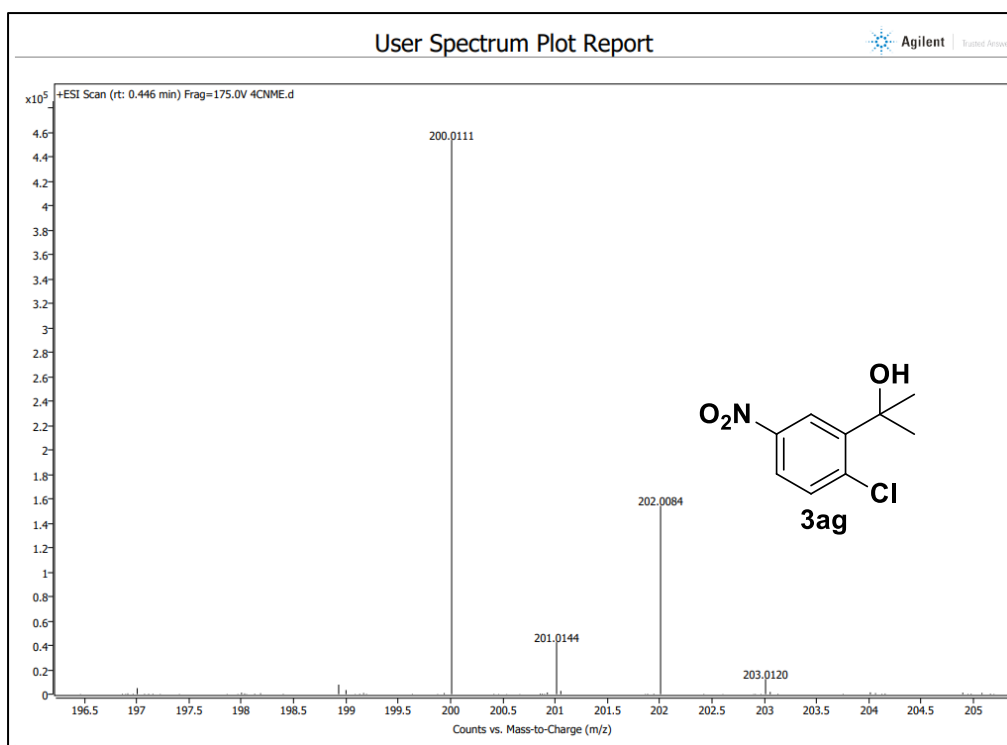


**Figure S33: HR-MS Spectrum of 3ae.**

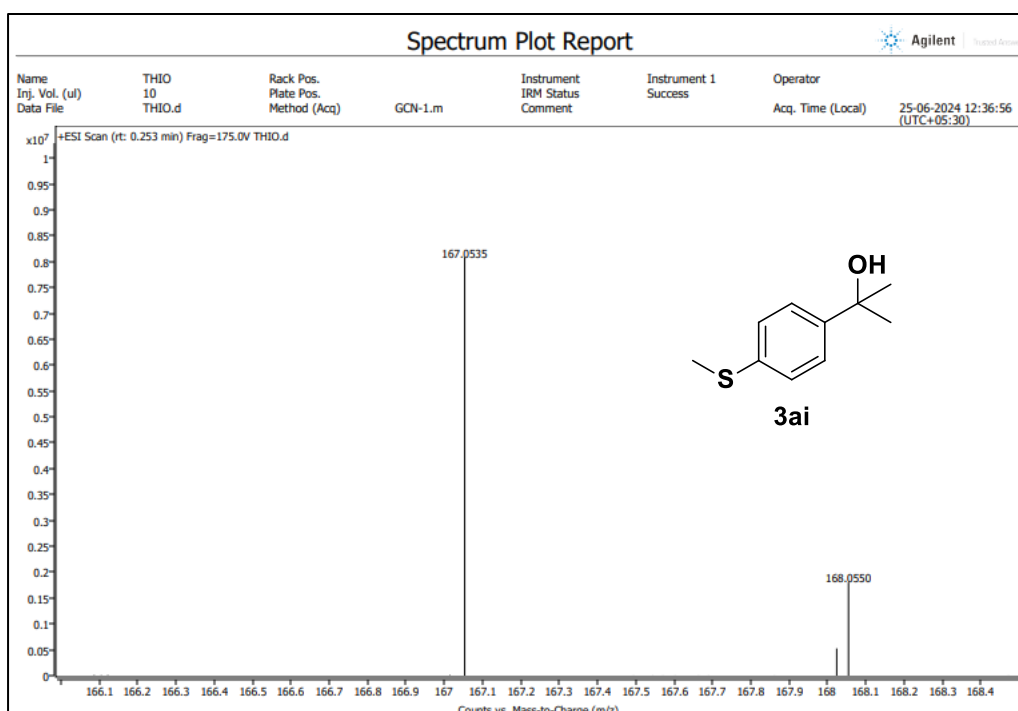


**Figure S34: HR-MS Spectrum of 3af**

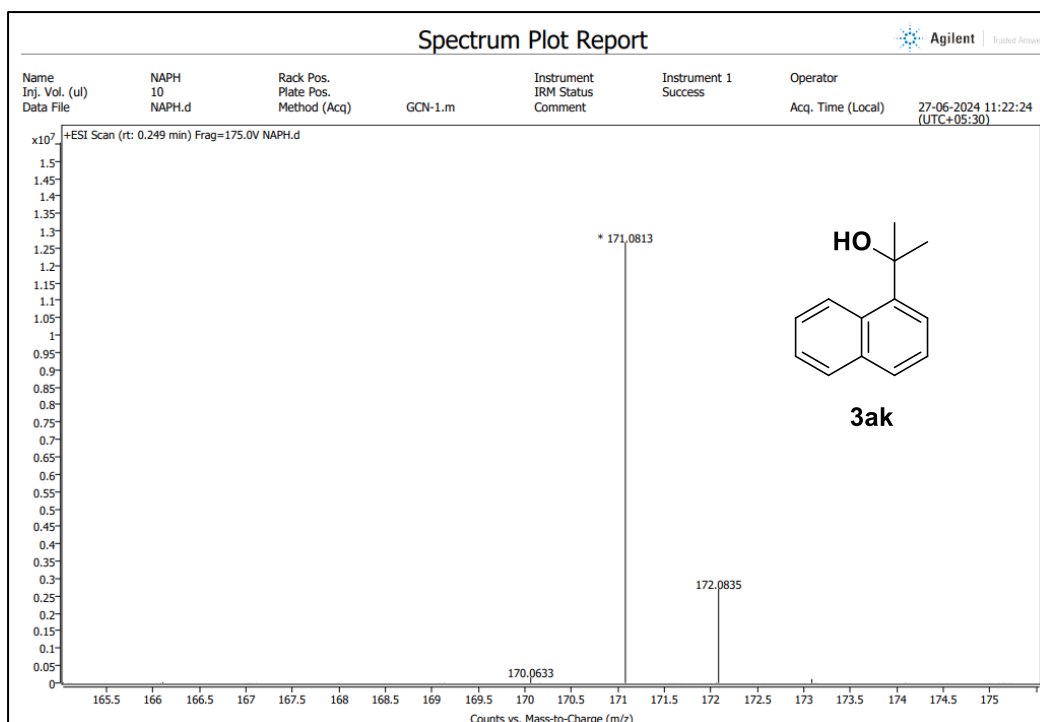




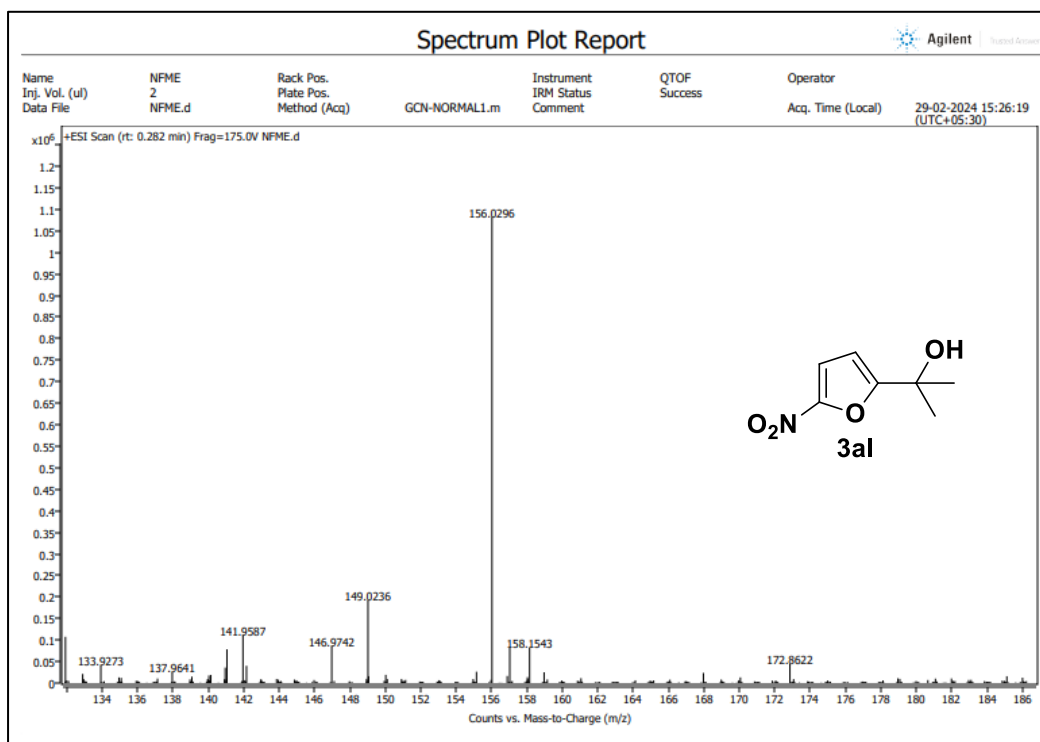
**Figure S35: HR-MS Spectrum of 3ag.**



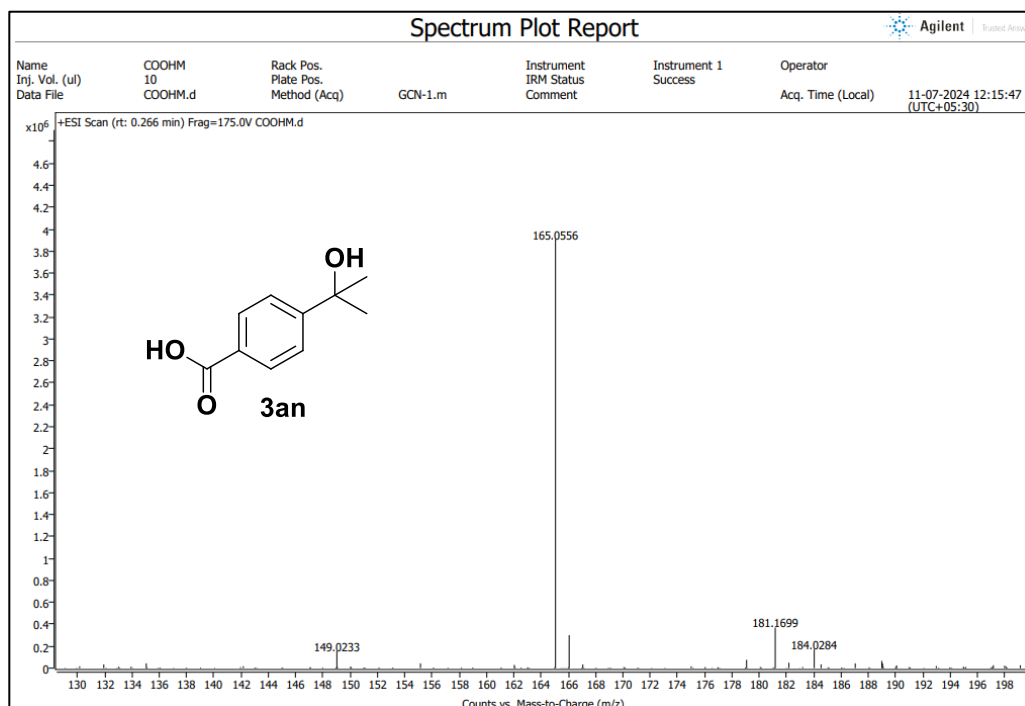
**Figure S36: HR-MS Spectrum of 3ai.**



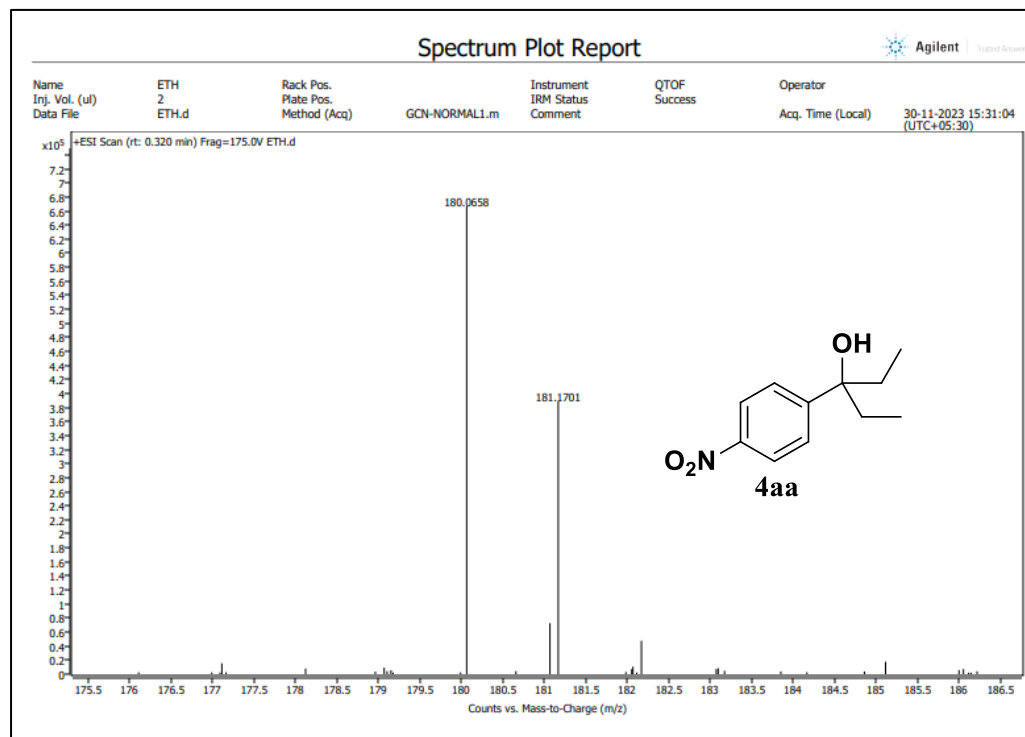
**Figure S37: HR-MS Spectrum of 3ak**



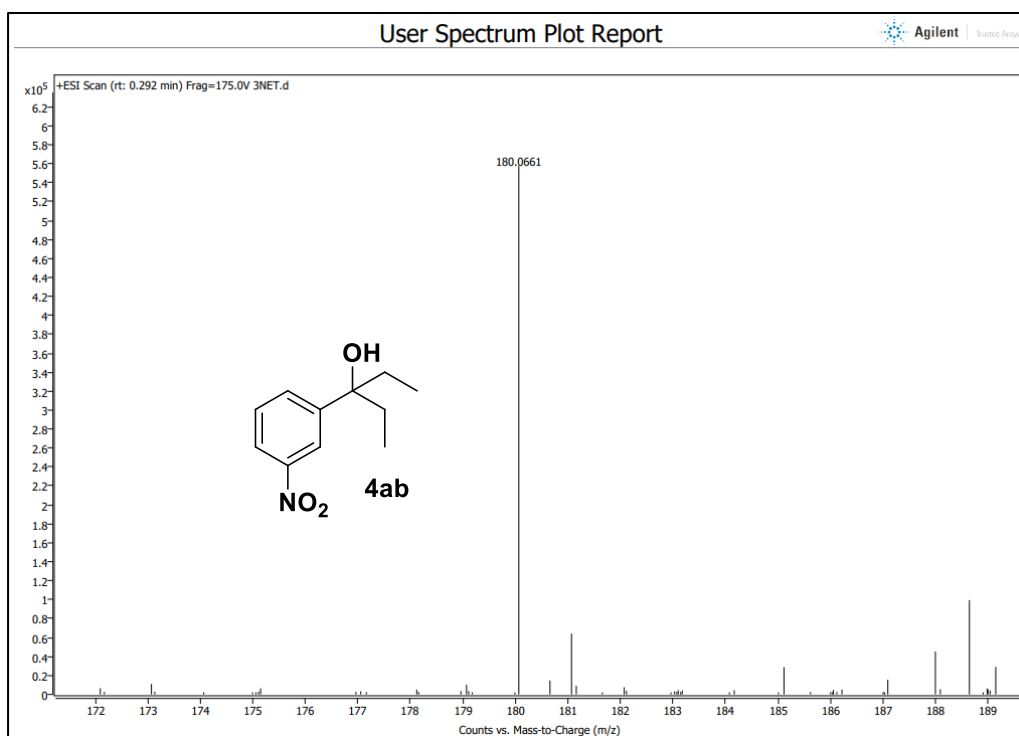
**Figure S38: HR-MS Spectrum of 3al.**



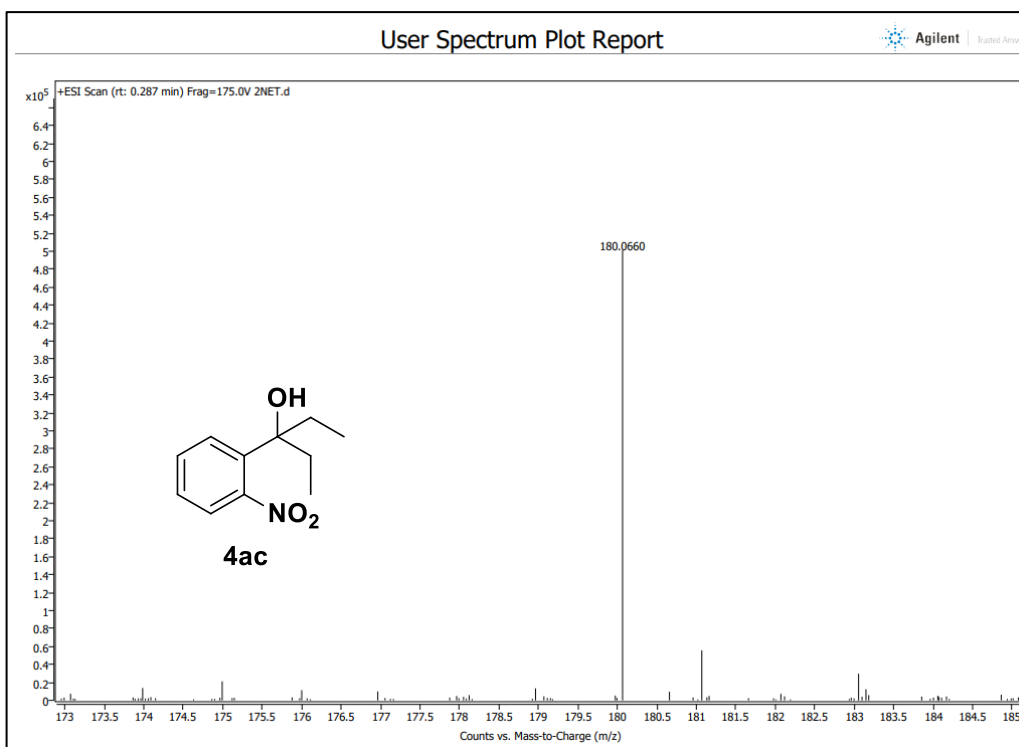
**Figure S39: HR-MS Spectrum of 3an.**



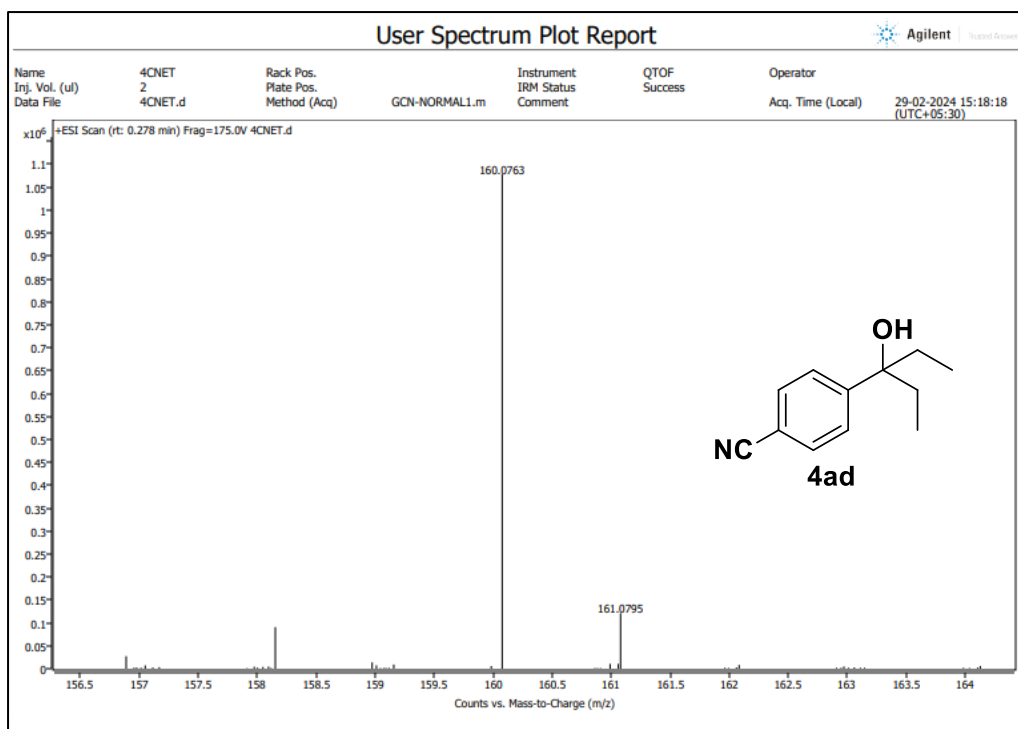
**Figure S40: HR-MS Spectrum of 4aa.**



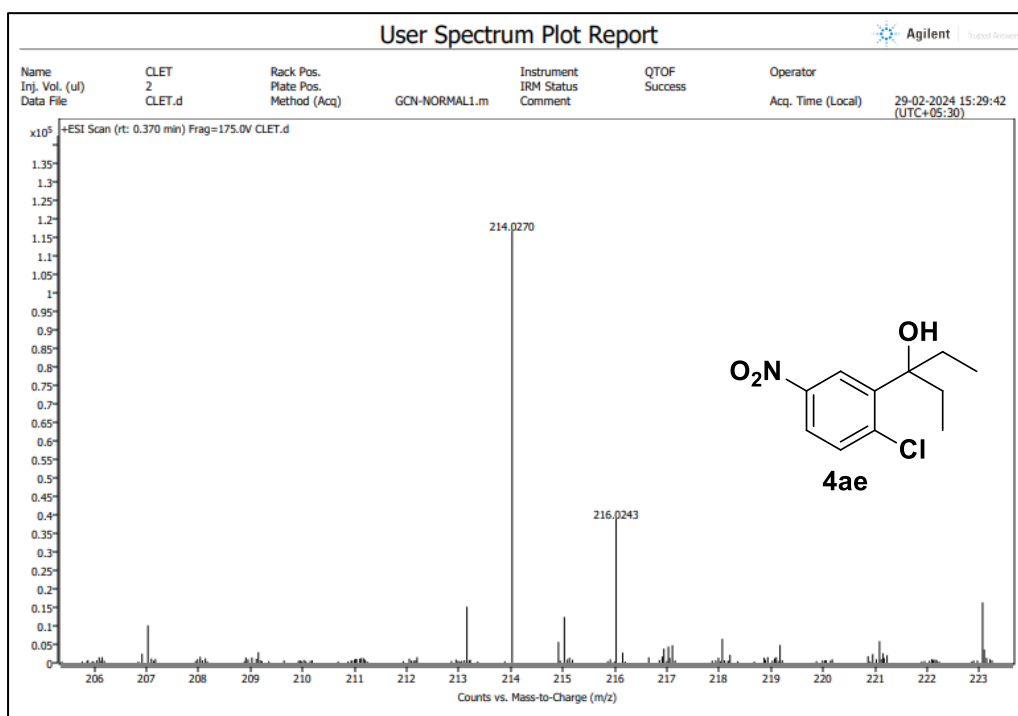
**Figure S41: HR-MS Spectrum of 4ab.**



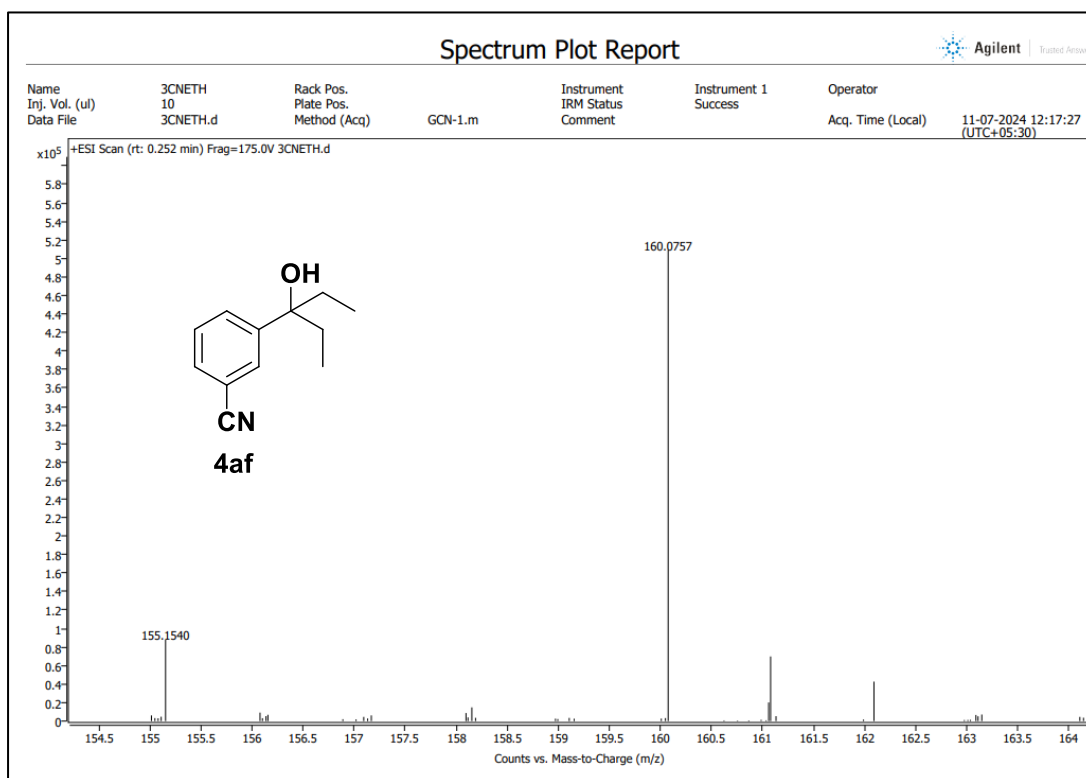
**Figure S42: HR-MS Spectrum of 4ac.**



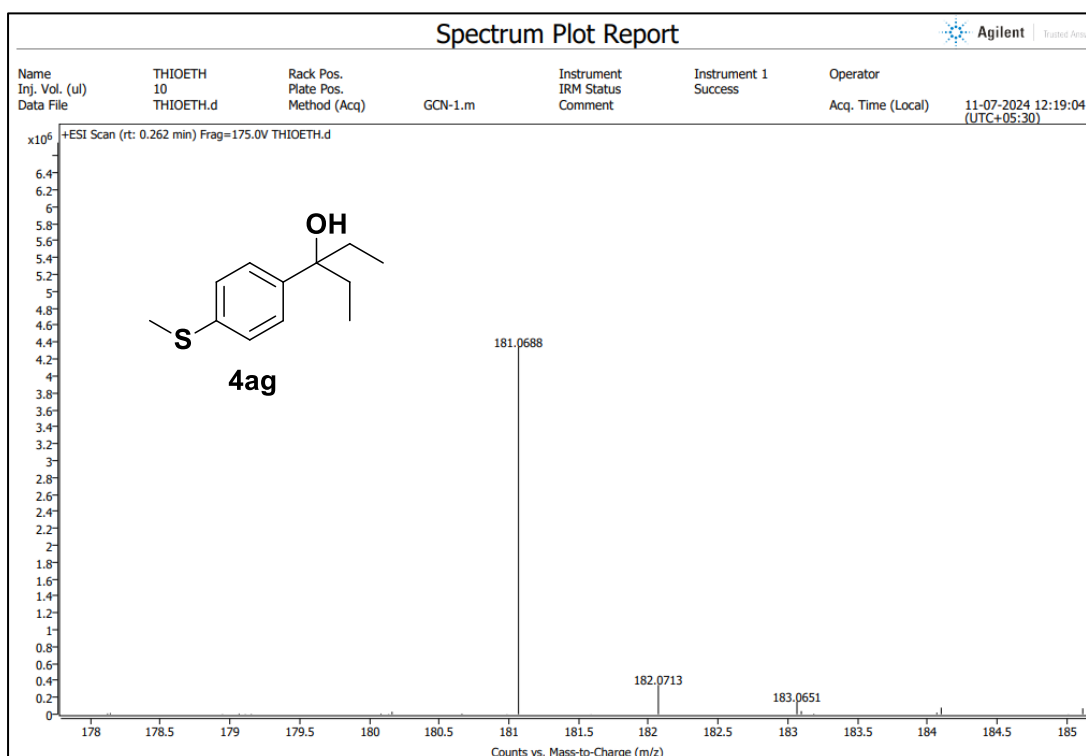
**Figure S43: HR-MS Spectrum of 4ad.**



**Figure S44: HR-MS Spectrum of 4ae.**



**Figure S45: HR-MS Spectrum of 4af.**



**Figure S46: HR-MS Spectrum of 4ag.**

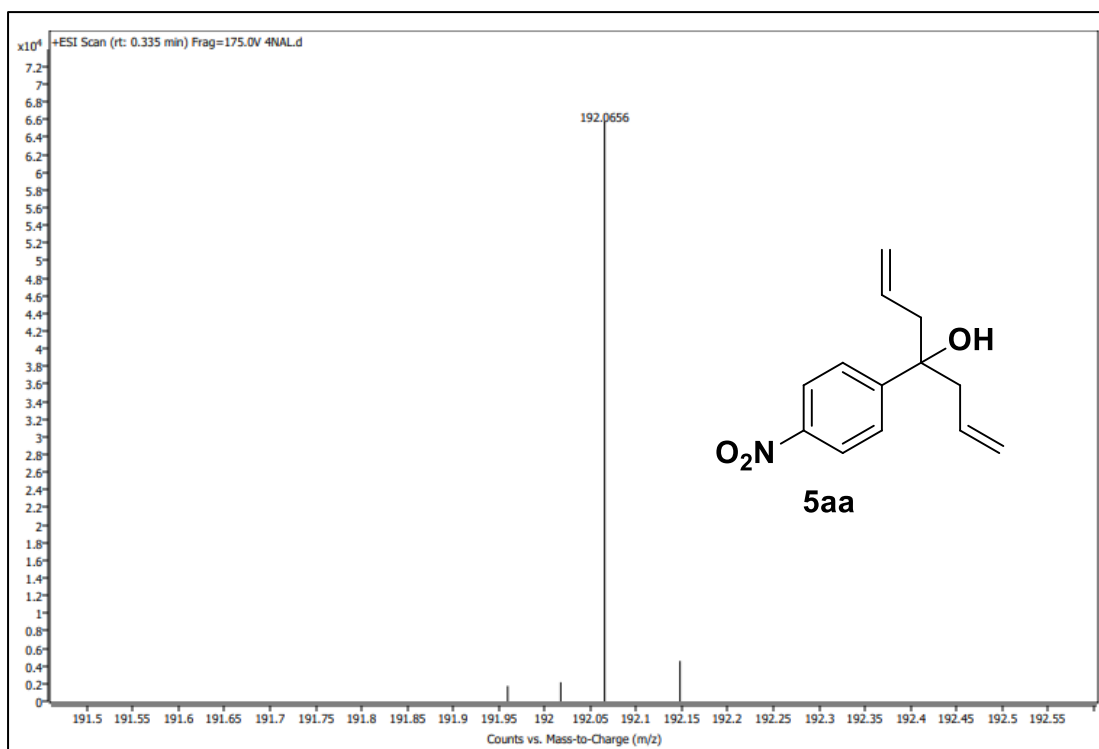


Figure S47: HR-MS Spectrum of 5aa.

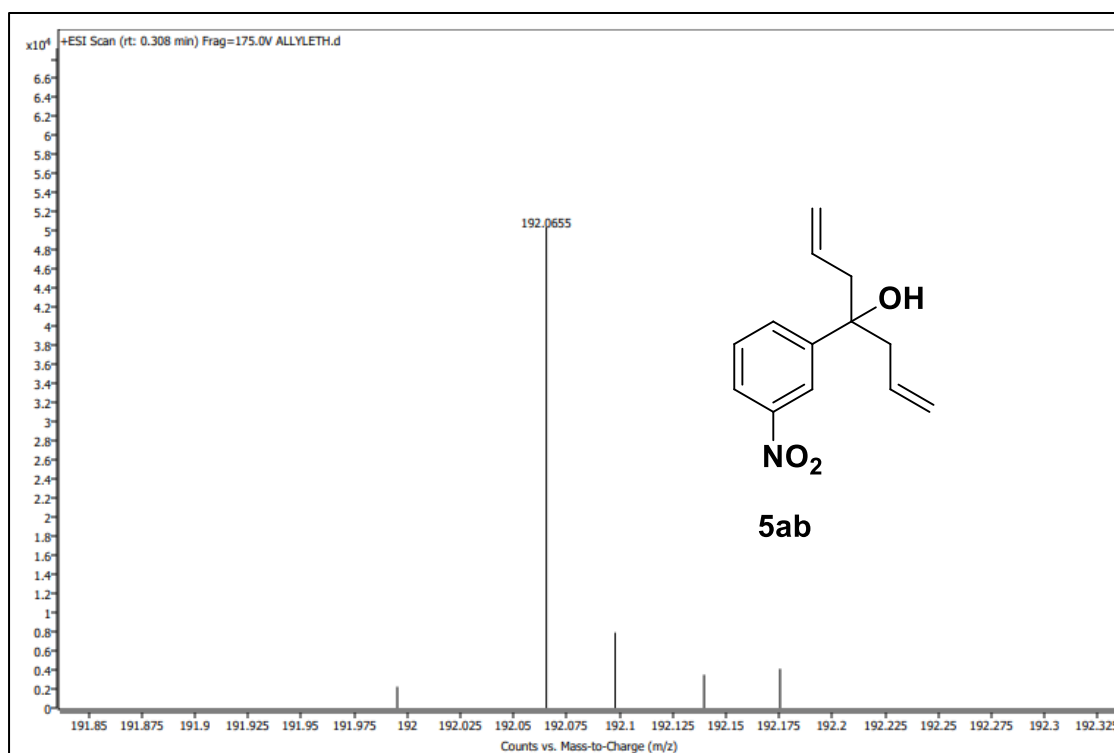
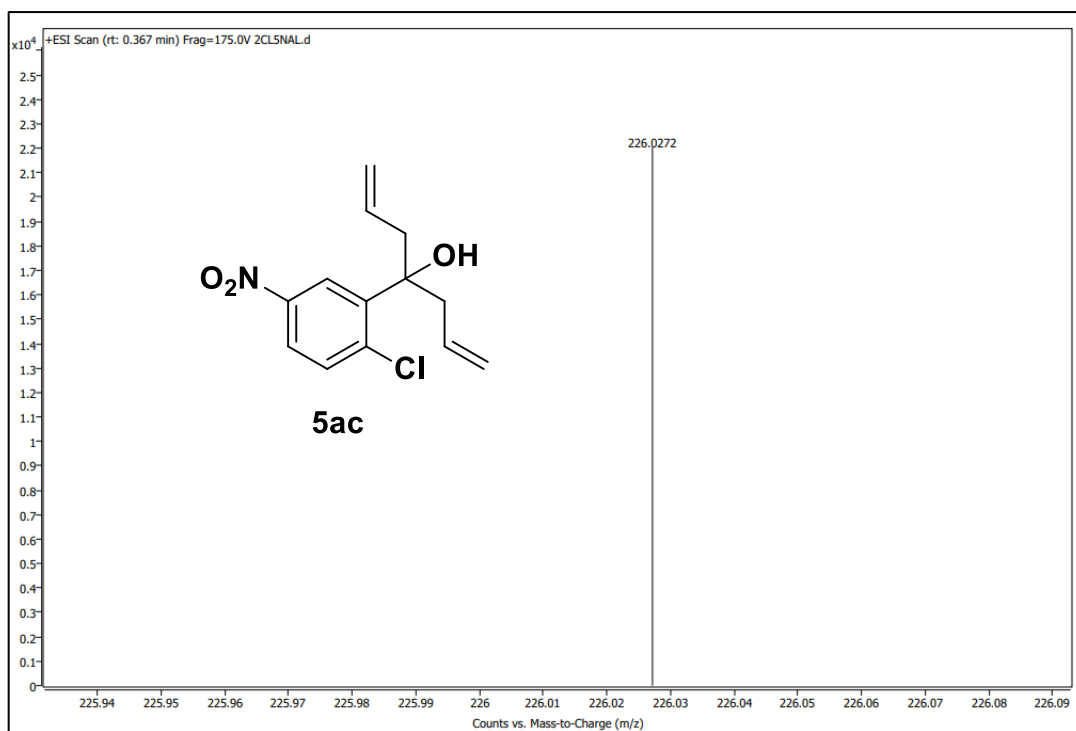
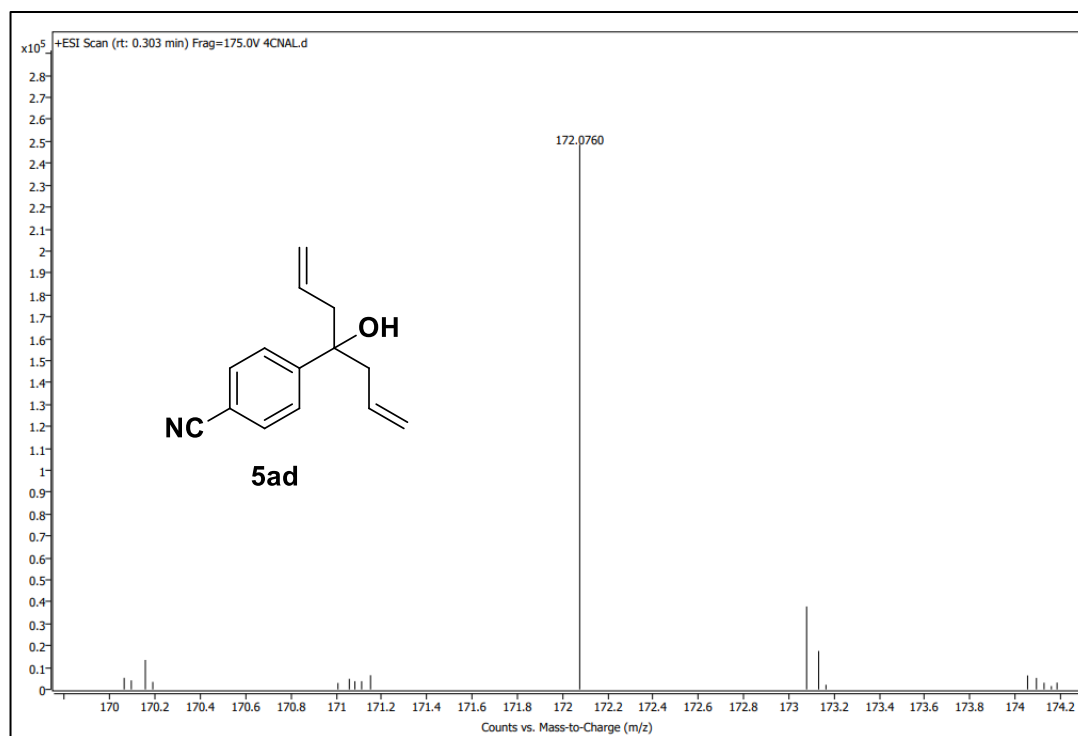


Figure S48: HR-MS Spectrum of 5ab.



**Figure S49: HR-MS Spectrum of 5ac**

.



**Figure S50: HR-MS Spectrum of 5ad**



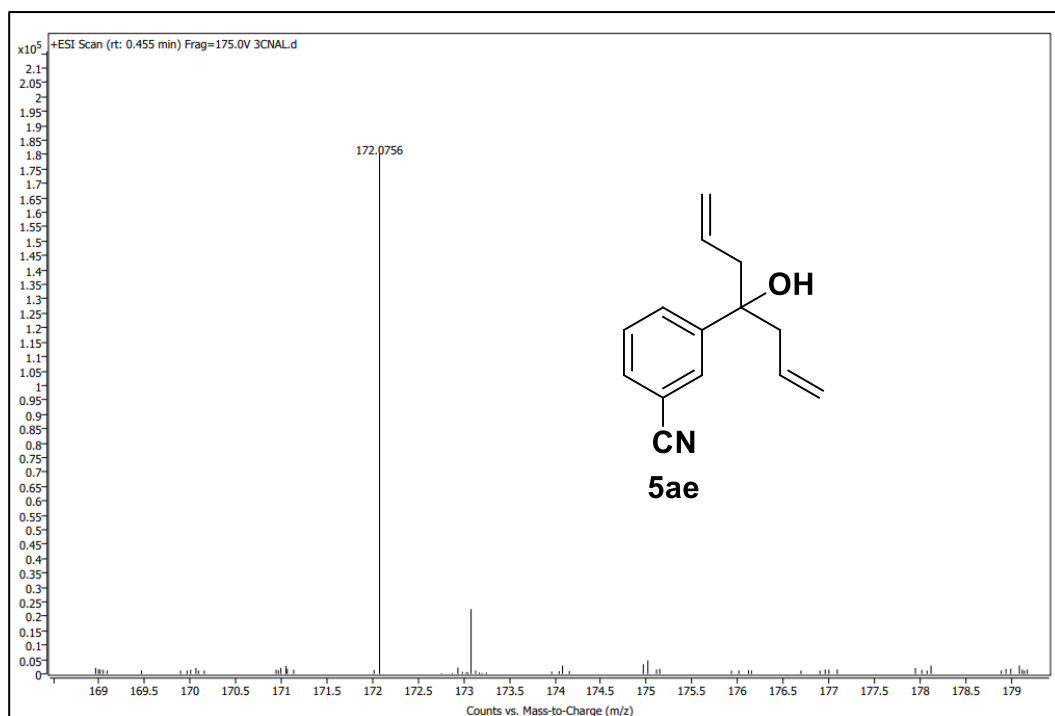


Figure S51: HR-MS Spectrum of 5ae.

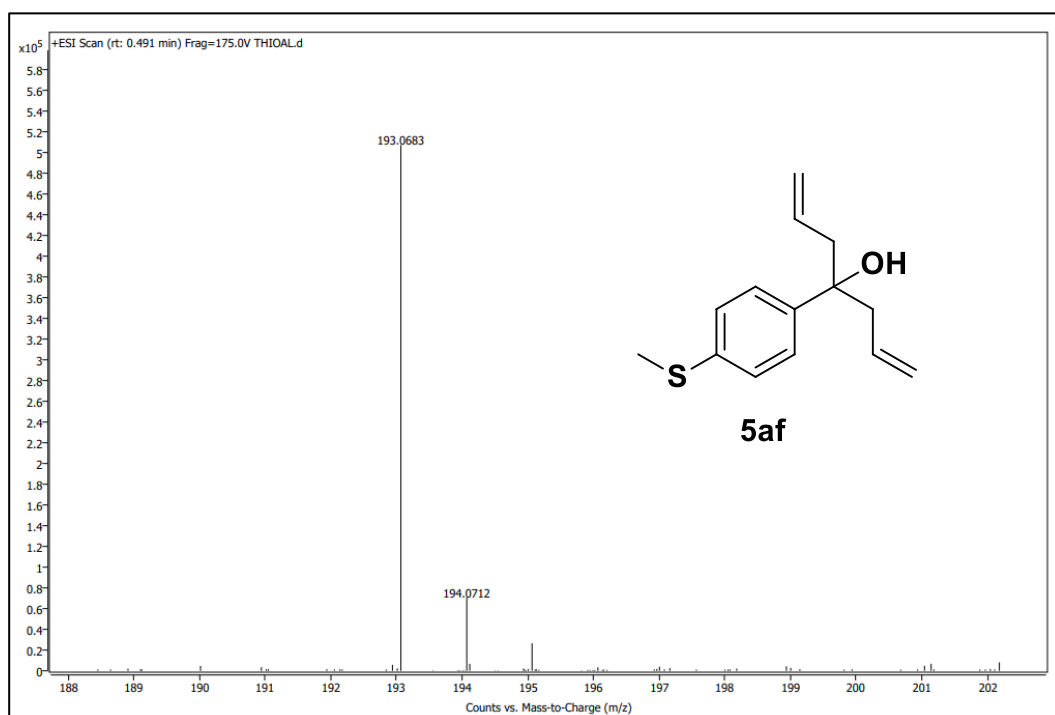


Figure S52: HR-MS Spectrum of 5af

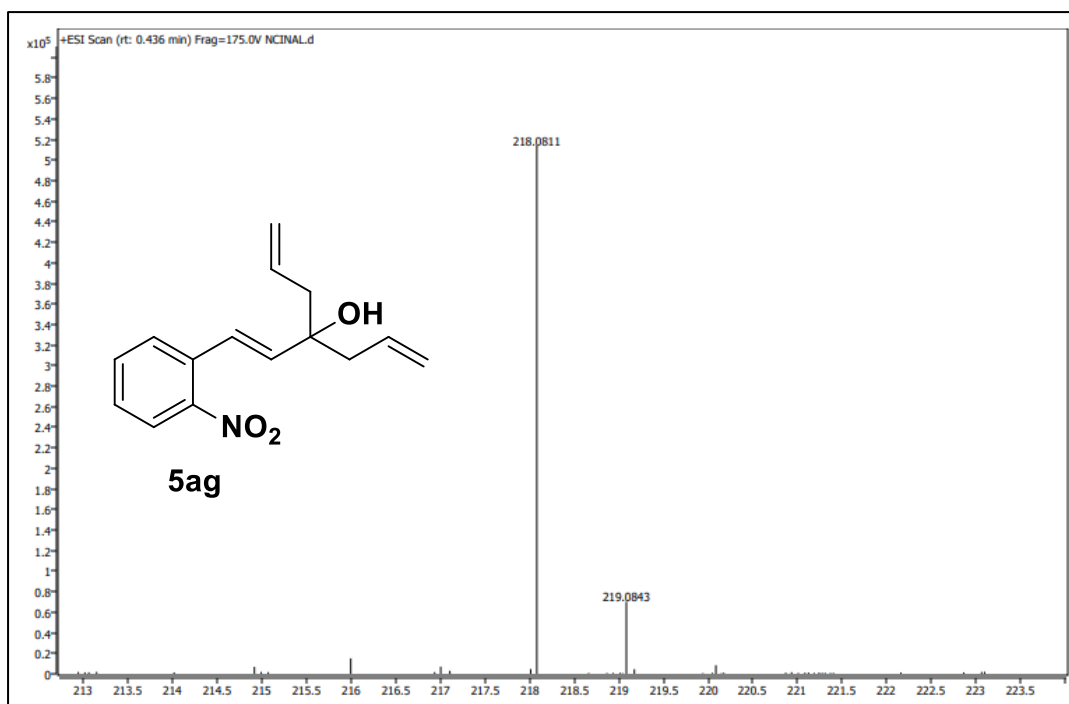


Figure S53: HR-MS Spectrum of 5ag.

## 11. Green Chemistry Metrics Calculation

### a) Atom Economy Calculation

Atom Economy = (Molecular weight of Desired Product/ $\Sigma$  Molecular weight of all the reagents) \*100

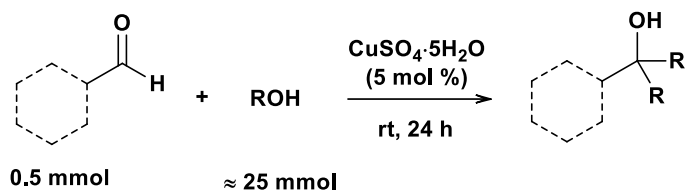
<b>Considering Methanol as a Reagent</b> (Only stoichiometric amount of alcohol was considered for calculation)				
Compound	Molecular weight of aldehyde	Molecular weight of alcohol * 2	Molecular weight of product	Atom economy
<b>3aa</b>	151.12	64.08	181.1885	84
<b>3ab</b>	151.12	64.08	181.1885	84
<b>3ac</b>	151.12	64.08	181.1885	84
<b>3ad</b>	177.16	64.08	207.2258	86
<b>3ae</b>	131.13	64.08	161.2004	83
<b>3af</b>	131.13	64.08	161.2004	83
<b>3ag</b>	185.56	64.08	215.6336	86
<b>3ai</b>	152.21	64.08	182.2826	84
<b>3ak</b>	156.18	64.08	186.2497	85
<b>3al</b>	141.082	64.08	171.1507	83
<b>3an</b>	150.133	64.08	180.2005	84
<b>4aa</b>	151.12	92.136	209.2417	86
<b>4ab</b>	151.12	92.136	209.2417	86
<b>4ac</b>	151.12	92.136	209.2417	86
<b>4ad</b>	131.13	92.136	189.2536	85
<b>4ae</b>	185.56	92.136	243.6868	88
<b>4af</b>	131.13	92.136	189.2536	85
<b>4ag</b>	152.21	92.136	210.3357	86
<b>5aa</b>	151.12	116.16	233.2631	87
<b>5ab</b>	151.12	116.16	233.2631	87
<b>5ac</b>	185.56	116.16	267.7082	89
<b>5ad</b>	131.13	116.16	213.2750	86
<b>5ae</b>	131.13	116.16	213.2750	86
<b>5af</b>	152.21	116.16	234.3571	87
<b>5ag</b>	177.16	116.16	259.3004	88

**Table S1: Atom economy calculation of products**

### b) Process Mass Intensity Calculation (PMI)

PMI = Total mass used in the synthesis (Kg) / Mass of product (Kg)

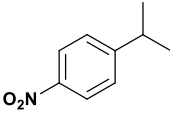
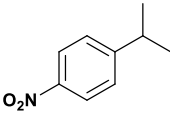
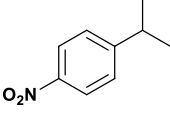
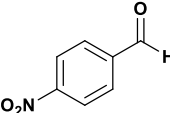
Solvents used for the separation are excluded from calculations due to their recyclability.



Mass of alcohol = Density \* Volume (1 ml)

Compound	Mass of aldehyde (0.5 mmol)	Mass of alcohol (25 mmol)	Mass of catalyst (0.025 mmol)	Mass of silica (≈20 g)	Mass of product	PMI
3aa	7.556E-05	0.00079	6.225E-06	0.02	0.000082	255
3ab	7.556E-05	0.00079	6.225E-06	0.02	0.000085	246
3ac	7.556E-05	0.00079	6.225E-06	0.02	0.000075	278
3ad	8.858E-05	0.00079	6.225E-06	0.02	0.000075	278
3ae	6.557E-05	0.00079	6.225E-06	0.02	0.000062	337
3af	6.557E-05	0.00079	6.225E-06	0.02	0.000065	321
3ag	9.278E-05	0.00079	6.225E-06	0.02	0.000074	282
3ai	7.611E-05	0.00079	6.225E-06	0.02	0.000071	294
3ak	7.809E-05	0.00079	6.225E-06	0.02	0.000056	373
3al	7.054E-05	0.00079	6.225E-06	0.02	0.000046	454
3an	7.507E-05	0.00079	6.225E-06	0.02	0.000059	354
4aa	7.556E-05	0.00079	6.225E-06	0.02	0.000093	224
4ab	7.556E-05	0.00079	6.225E-06	0.02	0.000095	220
4ac	7.556E-05	0.00079	6.225E-06	0.02	0.000045	464
4ad	6.557E-05	0.00079	6.225E-06	0.02	0.000057	366
4ae	9.278E-05	0.00079	6.225E-06	0.02	0.000049	426
4af	6.557E-05	0.00079	6.225E-06	0.02	0.000059	354
4ag	7.611E-05	0.00079	6.225E-06	0.02	0.000051	409
5aa	7.556E-05	0.00085	6.225E-06	0.02	0.000108	194
5ab	7.556E-05	0.00085	6.225E-06	0.02	0.0001	209
5ac	9.278E-05	0.00085	6.225E-06	0.02	0.000054	388
5ad	6.557E-05	0.00085	6.225E-06	0.02	0.000064	327
5ae	6.557E-05	0.00085	6.225E-06	0.02	0.000048	436
5af	7.611E-05	0.00085	6.225E-06	0.02	0.000082	255
5ag	8.858E-05	0.00085	6.225E-06	0.02	0.000078	269

**Table S2: Process Mass Intensity calculation of products**

Entry	Substrate	Catalytic condition	Temperature	Yield (%)	Atom economy	References
1		Blue light, $\text{UO}_2^{2+}$ , MeOH (1 ml), $\text{O}_2$ (1 atm), 30 h	rt	60	92	24b
2		$\text{O}_2$ (1.8 MPa), NaOH (4.5 M), EtOH/ $\text{H}_2\text{O}$ , 24 h	60 °C	76	92	24c
3		<i>cis</i> -[Ru(dtbpv) $_2$ Cl $_2$ ] (5 mol %), $\text{H}_5\text{IO}_6$ , CF $_3$ SO $_3$ H, AcOH/ $\text{H}_2\text{O}$ (1:1), 4 h	rt	92	46	24a
4		CuSO $_4$ . $\text{H}_2\text{O}$ (5 mol %), MeOH, 24 h	rt	90	84	this work

**Table S3: Literature comparison of AE of 3aa with present work.**