

# Versatile *O*- and *S*-Functionalized 1,2,3-Triazoliums: Ionic Liquids for the Baylis-Hillman Reaction and Ligand Precursors for Stable MIC-transition Metal Complexes

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## Supporting information

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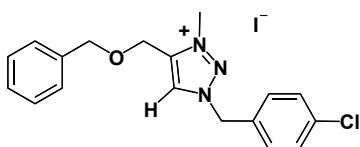
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## Experimental section

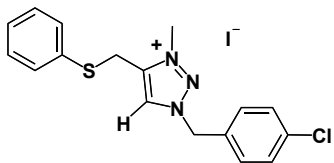
### General methods

Commercially available reagents and solvents were used as received. 1-(4-chlorobenzyl)-4-(benzyloxymethyl)-1*H*-1,2,3-triazole and 1-(4-chlorobenzyl)-4-(phenylthiomethyl)-1*H*-1,2,3-triazole, were synthesized as reported in the literature.<sup>1</sup> All manipulations related to the synthesis of triazolium salts **I** and **II** were performed under air. Synthesis of all metal complexes was performed under an atmosphere of dry nitrogen using standard Schlenk techniques. All Baylis-Hillman reactions were performed under air and room temperature. Solvents were dried by standard methods and distilled under nitrogen. Melting points were determined on a Fisher-Johns apparatus and are uncorrected. IR spectra were recorded on a Bruker Alpha FT-IR/ATR spectrometer. Flash column chromatography was performed on Kieselgel silica gel 60 (230-400 mesh). NMR spectra were obtained with a Bruker (400 MHz) spectrometer. High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-SX 102a and Agilent-MSD-TOF-1069A spectrometers 41. Elemental analyses were obtained with a Thermo Finnegan CHNSO-1112 apparatus.

### Synthesis of triazolium salts



**IL (I).** Methyl iodide (678 mg, 4.78 mmol) was added to a 10 mL acetonitrile solution of 1-(4-chlorobenzyl)-4-(benzyloxymethyl)-1*H*-1,2,3-triazole (500 mg, 1.59 mmol) and the resulting clear solution was refluxed for 24 h. After reaching room temperature, the solvent was reduced to 1/3 of the original volume and diethyl ether was added until an oily residue is formed. The residue was washed thoroughly with cold diethyl ether (3 x10 mL) and dried under vacuum. Pure product as orange oil is obtained in 94% yield (681 mg, 1.49 mmol) after column chromatographic purification using CH<sub>2</sub>Cl<sub>2</sub>/methanol (98:2) as eluent. Upon exposure to air for several days the product solidifies as a yellow wax. mp = 45-46 °C. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ = 4.23 (s, 3H, NCH<sub>3</sub>), 4.63 (s, 2H, ArCH<sub>2</sub>N), 4.84 (s, 2H, C-CH<sub>2</sub>O), 5.87 (s, 2H, ArCH<sub>2</sub>O), 7.29 (t, *J* = 7.7 Hz, 1H, CH<sub>ar</sub>), 7.34 (d, *J* = 7.8 Hz, 4H, CH<sub>ar</sub>), 7.49 (m, 4H, CH<sub>ar</sub>), 9.00 (s, 1H, CH<sub>triazolium</sub>). <sup>13</sup>C-NMR (DMSO-*d*<sub>6</sub>, 100 MHz): δ = 39.6 (NCH<sub>3</sub>), 56.5 (ArCH<sub>2</sub>N), 60.8 (C-CH<sub>2</sub>O), 73.6 (ArCH<sub>2</sub>O), 128.9 (CH<sub>ar</sub>), 129.0 (CH<sub>ar</sub>), 129.4 (CH<sub>ar</sub>), 130.0 (CH<sub>ar</sub>), 130.6 (CH<sub>triazolium</sub>), 132.0 (CH<sub>ar</sub>), 132.7 (C<sub>ar</sub>), 135.1 (C<sub>triazolium</sub>), 138.0 (C<sub>ar</sub>), 141.7 (C<sub>ar</sub>). FT-IR/ATR ν<sub>max</sub> cm<sup>-1</sup>: 3149, 3115, 3058, 3032, 2997, 2940, 2882, 2863, 2846, 1655, 1573, 1483, 1469, 1454. Found: C, 47.21; H, 4.15; N, 9.34; Calc for: C<sub>18</sub>H<sub>19</sub>N<sub>3</sub>OCl, 47.44; H, 4.20; N, 9.22.

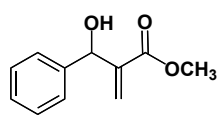


**IL (II).** Methyl iodide (674 mg, 4.75 mmol) was added to a 10 mL acetonitrile solution of 1-(4-chlorobenzyl)-4-(phenylthiomethyl)-1*H*-1,2,3-triazole (500 mg, 1.58 mmol) and the resulting clear solution was refluxed for 24 h. After reaching room temperature, the solvent was reduced to 1/3 of the original volume and diethyl ether was added until an oily residue is formed. The residue was washed thoroughly with cold diethyl ether (3 x10 mL) and dried under vacuum. Pure product as orange oil is obtained in 90% yield (651 mg, 1.42 mmol) after column chromatographic purification using CH<sub>2</sub>Cl<sub>2</sub>/ethanol (97:3) as eluent. Upon exposure to air for several days the product solidifies as a yellow wax. mp = 60-61 °C. <sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ = 4.38 (s, 3H, NCH<sub>3</sub>), 5.49 (s, 2H, ArCH<sub>2</sub>N), 5.91 (s, 2H, ArCH<sub>2</sub>S), 7.02

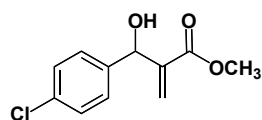
(t,  $J = 7.7$  Hz, 1H,  $CH_{ar}$ ), 7.09 (d,  $J = 7.8$  Hz, 2H,  $CH_{ar}$ ), 7.32-7.35 (m, 2H,  $CH_{ar}$ ), 7.44 (d,  $J = 7.8$  Hz, 2H,  $CH_{ar}$ ), 7.63 (d,  $J = 7.9$  Hz, 2H,  $CH_{ar}$ ), 9.02 (s, 1H,  $CH_{triazolium}$ ).  $^{13}C$ -NMR (DMSO- $d_6$ , 100 MHz):  $\delta = 39.9$  (NCH<sub>3</sub>), 56.7 (ArCH<sub>2</sub>N), 59.5 (ArCH<sub>2</sub>S), 115.9 ( $CH_{ar}$ ), 123.1 ( $CH_{ar}$ ), 123.8 ( $CH_{triazolium}$ ), 130.7 ( $CH_{ar}$ ), 130.9 ( $C_{ar}$ ), 132.2 ( $CH_{ar}$ ), 133.0 ( $CH_{ar}$ ), 133.1 ( $C_{triazolium}$ ), 140.9 ( $C_{ar}$ ), 157.9 ( $C_{ar}$ ). FT-IR/ATR  $\nu_{max}$   $cm^{-1}$ : 3040, 2930, 2914, 2871, 2826, 1596, 1490, 1459, 1407, 1329, 1225, 1171, 1063, 1012, 789. Found: C, 47.83; H, 4.01; N, 9.27; Calc for: C<sub>17</sub>H<sub>17</sub>N<sub>3</sub>SClI C, 47.60; H, 3.74; N, 9.18.

*General procedure for the Baylis-Hillman reaction of aldehydes with methyl acrylate in ionic liquid media (Table 1).*

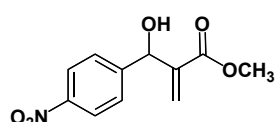
In an oven dried screw cap vial were added sequentially the aldehyde derivative (1 mmol), the ionic liquid (100 mg), DABCO (1.2 mmol), and the mixture was stirred for 10 min. Methyl acrylate (1.2 mmol) was then added and the reaction was stirred at room temperature until all starting aldehyde was consumed (See Table 1). The coupling product was purified by chromatographic column on silica gel using appropriate mixtures of petroleum ether and ethyl acetate as shown below:



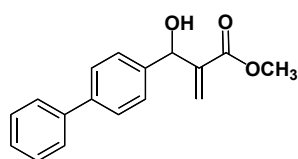
**Methyl 2-(hydroxy(phenyl)methyl)acrylate (1a).** Petroleum ether/Ethyl acetate (4:1). Colorless oil (167 mg, 87% yield). Spectral data were consistent to those previously reported.  $^1H$ -NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 2.98$  (bs, 1H), 3.55 (s, 3H), 5.39 (bs, 1H), 5.67 (s, 1H), 6.17 (s, 1H), 7.09-7.13 (m, 1H), 7.15-7.17 (m, 1H), 7.19-7.22 (m, 3H).  $^{13}C$ -NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 50.4$ , 71.9, 125.0, 125.6, 126.8, 127.4, 140.4, 141.2, 166.0



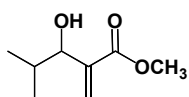
**Methyl 2-((4-chlorophenyl)(hydroxy)methyl)acrylate (1b).** Petroleum ether/Ethyl acetate (5:1). Colorless solid (222 mg, 98% yield). Spectral data were consistent to those previously reported.  $^1H$ -NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 3.05$  (d,  $J = 8.0$  Hz, 1H), 3.54 (3H), 5.35 (d,  $J = 8.0$  Hz, 1H), 5.66 (1H), 6.16 (1H), 7.13 (s, 4H).  $^{13}C$ -NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 50.5$ , 71.3, 125.3, 127.0, 127.6, 132.6, 138.9, 140.8, 166.8.



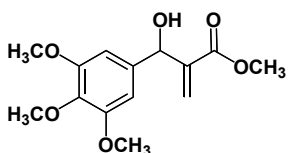
**Methyl 2-(hydroxy(4-nitrophenyl)methyl)acrylate (1c).** Petroleum ether/Ethyl acetate (6:1). Yellow solid (202 mg, 85% yield). Spectral data were consistent to those previously reported.  $^1H$ -NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 3.29$  (d,  $J = 8.0$  Hz, 1H), 3.55 (3H), 5.45 (d,  $J = 8.0$  Hz, 1H), 5.71 (1H), 6.20 (1H), 7.38 (d,  $J = 8.0$  Hz, 2H), 7.99 (d,  $J = 8.0$  Hz, 2H).  $^{13}C$ -NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 50.5$ , 71.3, 125.3, 127.0, 127.6, 132.6, 138.9, 140.8, 166.8.



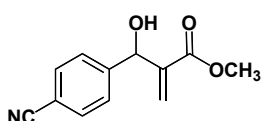
**Methyl 2-(hydroxy(4-biphenyl)methyl)acrylate (1d).** Petroleum ether/Ethyl acetate (4:1). White solid (217 mg, 81% yield). mp = 105-107 °C.  $^1H$ -NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta = 2.95$  (d,  $J = 8.0$  Hz, 1H), 3.58 (3H), 5.45 (d,  $J = 8.0$  Hz, 1H), 5.75 (1H), 6.21 (1H), 7.18 (t,  $J = 7.8$  Hz, 1H), 7.26-7.20 (m, 4H), 7.40-7.43 (m, 4H).  $^{13}C$ -NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta = 50.5$ , 71.8, 125.1, 126.0, 126.1, 126.2, 126.3, 127.8, 139.4, 139.8, 141.1, 166.0. HRMS (ESI-TOF):  $m/z$  calcd for C<sub>17</sub>H<sub>15</sub>O<sub>2</sub> [M-OH]<sup>+</sup>: 251.1067; found: 251.1066.



**Methyl 3-hydroxy-4-methyl-2-methylenepentanoate (1e).** Petroleum ether/Ethyl acetate (5:1). Colorless oil (122 mg, 77% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ = 0.66 (d, *J* = 5.8 Hz, 3H), 0.73 (d, *J* = 5.8 Hz, 3H), 1.70 (septet, 1H), 2.54 (d, *J* = 8.0 Hz, 1H), 3.55 (s, 3H), 3.88 (d, *J* = 8.0 Hz, 1H), 5.56 (1H), 6.04 (1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ = 15.7, 17.9, 31.0, 50.3, 76.0, 124.9, 140.6, 166.4. HRMS (ESI-TOF): *m/z* calcd for C<sub>18</sub>H<sub>15</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 159.1016; found: 159.1015.



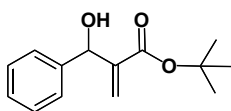
**Methyl 2-(hydroxy(3,4,5-trimethoxyphenyl)methyl)acrylate (1f).** Petroleum ether/Ethyl acetate (4:1). Colorless oil (234 mg, 83% yield). Spectral data were consistent to those previously reported. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ = 3.01 (bs, 1H), 3.56 (3H), 3.64 (3H), 3.65 (6H), 5.32 (1H), 5.65 (1H), 6.14 (1H), 6.41 (2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ = 50.5, 54.6, 59.3, 71.8, 102.5, 125.0, 136.0, 136.5, 141.0, 152.3, 166.1.



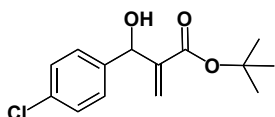
**Methyl 2-((4-cyanophenyl)(hydroxy)methyl)acrylate (1g).** Petroleum ether/Ethyl acetate (5:1). Colorless oil (206 mg, 95% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ = 1.98 (bs, 1H), 3.55 (3H), 5.41 (bs, 1H), 5.69 (1H), 6.20 (1H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.46 (d, *J* = 7.8 Hz, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ = 50.6, 71.4, 110.5, 117.6, 125.9, 126.2, 131.2, 140.3, 145.9, 165.6. HRMS (ESI-TOF): *m/z* calcd for C<sub>12</sub>H<sub>12</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 218.0815; found: 218.0811.

*General procedure for the Baylis-Hillman reaction of aldehydes with tert-butyl acrylate in ionic liquid media.*

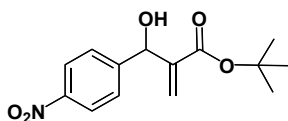
In an oven dried screw cap vial were added sequentially the aldehyde derivative (1 mmol), the ionic liquid (100 mg), DABCO (2.0 mmol), and the mixture was stirred for 10 min. *tert*-Butyl acrylate (2.0 mmol) was then added and the reaction was stirred at room temperature until all starting aldehyde was consumed (See Table 1). The coupling product was purified by chromatographic column on silica gel using appropriate mixtures of petroleum ether and ethyl acetate as shown below:



***tert*-Butyl-2-(hydroxy(phenyl)methyl)acrylate (2a).** Petroleum ether/Ethyl acetate (95:5). Colorless oil (194 mg, 83% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ = 1.19 (s, 9H), 3.30 (bs, 1H), 5.28 (bs, 1H), 5.58 (s, 1H), 6.05 (s, 1H), 7.06-7.16 (m, 5H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ = 26.3, 71.8, 80.1, 123.8, 125.7, 126.6, 127.2, 140.9, 142.8, 164.8. HRMS (ESI-TOF): *m/z* calcd for C<sub>14</sub>H<sub>18</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup>: 257.1150; found: 257.1148.

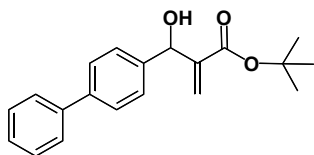


***tert*-Butyl-2-((4-chlorophenyl)(hydroxy)methyl)acrylate (2b).** Petroleum ether/Ethyl acetate (9:1). Colorless oil (250 mg, 93% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz): δ = 1.21 (s, 9H), 3.27 (bs, 1H), 5.25 (bs, 1H), 5.54 (s, 1H), 6.05 (s, 1H), 7.10 (s, 4H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz): δ = 26.3, 71.4, 80.5, 124.3, 127.0, 127.4, 132.4, 139.4, 142.3, 164.7. HRMS (ESI-TOF): *m/z* calcd for C<sub>14</sub>H<sub>17</sub>O<sub>3</sub>NaCl [M+Na]<sup>+</sup>: 291.0763; found: 291.0758.

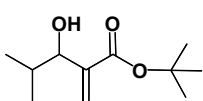


***tert*-Butyl-2-((4-nitrophenyl)(hydroxy)methyl)acrylate (2c).** Petroleum ether/Ethyl acetate (9:1). Yellow oil (240 mg, 86% yield). <sup>1</sup>H-NMR

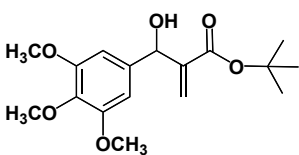
(CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 1.20 (s, 9H), 3.53 (bs, 1H), 5.36 (bs, 1H), 5.59 (s, 1H), 6.08 (s, 1H), 7.35 (d,  $J$  = 7.8 Hz, 2H), 7.96 (d,  $J$  = 7.8 Hz, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 26.3, 71.3, 80.9, 122.4, 125.2, 126.3, 141.6, 146.4, 148.3, 164.4. HRMS (ESI-TOF):  $m/z$  calcd for C<sub>14</sub>H<sub>18</sub>NO<sub>5</sub> [M+H]<sup>+</sup>: 280.1140; found: 280.1137.



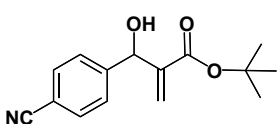
**tert-Butyl-2-((4-biphenyl)(hydroxy)methyl)acrylate (2d).** Petroleum ether/Ethyl acetate (9:1). White solid (267 mg, 86% yield). m.p. = 100-102°C. <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 1.27 (s, 9H), 3.10 (d,  $J$  = 8.0 Hz, 1H), 5.40 (d,  $J$  = 8.0 Hz, 1H), 5.64 (s, 1H), 6.13 (s, 1H), 7.19 (t,  $J$  = 7.8 Hz, 1H), 7.26-7.30 (m, 4H), 7.42-7.46 (m, 4H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 26.4, 72.0, 80.4, 124.2, 126.0, 126.1, 126.3, 127.8, 139.6, 139.9, 140.0, 142.6, 164.9. HRMS (ESI-TOF):  $m/z$  calcd for C<sub>20</sub>H<sub>21</sub>O<sub>2</sub> [M-OH]<sup>+</sup>: 293.1540; found: 293.1536.



**tert-Butyl-3-hydroxy-4-methyl-2-methylenepentanoate (2e).** Petroleum ether/Ethyl acetate (9:1). Colorless oil (144 mg, 72% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 0.87 (d,  $J$  = 6.8 Hz, 3H), 0.96 (d,  $J$  = 6.8 Hz, 3H), 1.50 (9H), 1.89 (sept,  $J$  = 6.8 Hz, 1H), 2.75 (d,  $J$  = 7.4 Hz, 1H), 4.03 (d,  $J$  = 7.4 Hz, 1H), 5.65 (1H), 6.14 (1H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 16.1, 17.8, 26.4, 31.4, 80.0, 123.9, 141.9, 165.4. HRMS (ESI-TOF):  $m/z$  calcd for C<sub>11</sub>H<sub>20</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup>: 233.1306; found: 223.1304.



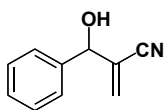
**tert-Butyl-2-(hydroxy(3,4,5-trimethoxyphenyl)methyl)acrylate (2f).** Petroleum ether/Ethyl acetate (4:1). Colorless oil (259 mg, 80% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 1.23 (s, 9H), 3.06 (bs, 1H), 3.62 (3H), 3.64 (6H), 5.25 (s, 1H), 5.53 (1H), 6.03 (1H), 6.40 (2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 26.3, 54.6, 58.9, 59.4, 71.9, 80.4, 102.4, 124.2, 136.4, 142.5, 152.3, 165.1. HRMS (ESI-TOF):  $m/z$  calcd for C<sub>17</sub>H<sub>23</sub>O<sub>5</sub> [M-OH]<sup>+</sup>: 307.1540; found: 307.1540.



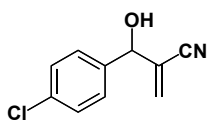
**tert-Butyl-2-((4-cyanophenyl)(hydroxy)methyl)acrylate (2g).** Petroleum ether/Ethyl acetate (9:1). Colorless oil (218 mg, 84% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 1.21 (s, 9H), 3.41 (d,  $J$  = 5.04 Hz, 1H), 5.32 (d,  $J$  = 5.04 Hz, 1H), 5.57 (s, 1H), 6.09 (s, 1H), 7.30 (d,  $J$  = 8.2 Hz, 2H), 7.43 (d,  $J$  = 8.2 Hz, 2H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 26.3, 71.5, 80.9, 110.2, 117.7, 125.2, 126.2, 131.4, 141.6, 146.3, 164.5. HRMS (ESI-TOF):  $m/z$  calcd for C<sub>15</sub>H<sub>18</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 260.1282; found: 260.1281.

*General procedure for the Baylis-Hillman reaction of aldehydes with acrylonitrile in ionic liquid media.*

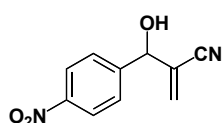
In an oven dried screw cap vial were added sequentially the aldehyde derivative (1.0 mmol), the ionic liquid (100 mg), DABCO (1.5 mmol), and the mixture was stirred for 10 min. Acrylonitrile (1.5 mmol) was then added and the reaction was stirred at room temperature until all starting aldehyde was consumed (See Table 1). The coupling product was purified by chromatographic column on silica gel using appropriate mixtures of petroleum ether and ethyl acetate as shown below:



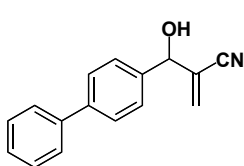
**2-(hydroxy(phenyl)methyl)acrylonitrile (3a).** Petroleum ether/Ethyl acetate (4:1). Colorless oil (153 mg, 96% yield). Spectral data were consistent to those previously reported.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 2.66$  (bs, 1H), 5.09 (d,  $J = 4.0$  Hz, 1H), 5.84 (d,  $J = 1.6$  Hz, 1H), 5.91 (d,  $J = 1.6$  Hz, 1H), 7.18-7.23 (m, 5H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 72.8, 115.9, 125.3, 125.5, 128.0, 128.9, 138.3$ .



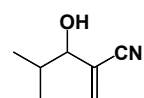
**2-(hydroxy(4-chlorophenyl)methyl)acrylonitrile (3b).** Petroleum ether/Ethyl acetate (4:1). Colorless oil (191 mg, 99% yield). Spectral data were consistent to those previously reported.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 2.77$  (bs, 1H), 5.09 (bs, 1H), 5.85 (d,  $J = 1.2$  Hz, 1H), 5.92 (d,  $J = 1.5$  Hz, 1H), 7.14 (d,  $J = 8.4$  Hz, 2H), 7.14 (d,  $J = 8.4$  Hz, 2H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 72.1, 115.7, 125.0, 126.9, 128.1, 129.1, 133.8, 136.8$ .



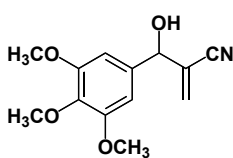
**2-(hydroxy(4-nitrophenyl)methyl)acrylonitrile (3c).** Petroleum ether/Ethyl acetate (5:1). Yellow oil (192 mg, 94% yield). Spectral data were consistent to those previously reported.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 2.71$  (d,  $J = 3.84$  Hz, 1H), 5.29 (d,  $J = 3.84$  Hz, 1H), 5.94 (d,  $J = 1.4$  Hz, 1H), 6.02 (s,  $J = 1.5$  Hz, 1H), 7.45 (d,  $J = 8.7$  Hz, 2H), 8.10 (d,  $J = 8.7$  Hz, 2H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 71.2, 122.6, 124.5, 124.6, 126.2, 128.9, 129.7, 144.8$ .



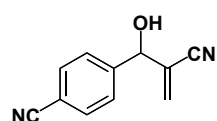
**2-(hydroxy(4-biphenyl)methyl)acrylonitrile (3d).** Petroleum ether/Ethyl acetate (4:1). Colorless solid (216 mg, 92% yield). m.p. = 110-112.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 2.37$  (d,  $J = 4.04$  Hz, 1H), 5.19 (d,  $J = 4.04$  Hz, 1H), 5.90 (d,  $J = 1.2$  Hz, 1H), 5.99 (d,  $J = 1.5$  Hz, 1H), 7.22 (t,  $J = 7.8$  Hz, 1H), 7.26-7.31 (m, 4H), 7.41-7.47 (m, 4H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 72.7, 115.9, 125.2, 126.0, 126.1, 126.6, 126.7, 127.8, 128.8, 131.2, 139.5, 141.1$ . HRMS (ESI-TOF):  $m/z$  calcd for  $\text{C}_{16}\text{H}_{12}\text{N}$   $[\text{M-OH}]^+$ : 218.0967; found: 218.0964.



**3-hydroxy-4-methyl-2-methylenepentanenitrile (3e).** Petroleum ether/Ethyl acetate (9:1). Colorless oil (117 mg, 93% yield).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 0.76$  (d,  $J = 6.76$  Hz, 6H), 1.76 (m, 1H), 2.70 (d,  $J = 5.92$  Hz, 1H), 3.76 (d,  $J = 5.92$  Hz, 1H), 5.78 (d,  $J = 1.4$  Hz, 1H), 5.82 (d,  $J = 1.5$  Hz, 1H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 16.9, 19.0, 32.6, 118.1, 126.8, 131.7$ . HRMS (ESI-TOF):  $m/z$  calcd for  $\text{C}_7\text{H}_{12}\text{NO}$   $[\text{M+H}]^+$ : 126.0913; found: 126.0913.



**2-(hydroxy(3,4,5-trimethoxyphenyl)methyl)acrylonitrile (3f).** Petroleum ether/Ethyl acetate (3:1). Colorless oil (202 mg, 81% yield). Spectral data were consistent to those previously reported.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 2.67$  (d,  $J = 4.04$  Hz, 1H), 3.79 (s, 3H), 3.87 (s, 6H), 5.18 (s, 1H), 5.98 (d,  $J = 1.6$  Hz, 1H), 6.06 (d,  $J = 1.6$  Hz, 1H), 6.56 (s, 2H).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 54.8, 59.4, 73.5, 102.5, 105.7, 125.5, 128.6, 131.1, 133.8, 152.8$ .



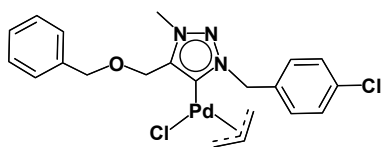
**2-(hydroxy(3,4,5-trimethoxyphenyl)methyl)acrylonitrile (3g).** Petroleum ether/Ethyl acetate (3:1). Colorless oil (181 mg, 98% yield).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 2.41$  (bs, 1H), 5.18 (bs, 1H), 5.80 (d,  $J = 1.2$  Hz, 1H), 5.92 (d,  $J$

= 1.5 Hz, 1H), 7.31 (d,  $J = 7.8$  Hz, 2H), 7.43 (d,  $J = 7.8$  Hz, 2H).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 55.9, 73.5, 110.9, 117.5, 125.1, 126.2, 129.6, 131.5, 144.3$ . HRMS (ESI-TOF):  $m/z$  calcd for  $\text{C}_{11}\text{H}_9\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$ : 185.0670; found: 185.0673.

#### Recyclability of IL (**I**) in the coupling of *p*-cyanobenzaldehyde with acrylonitrile

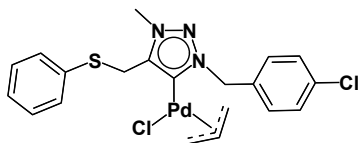
In an oven dried screw cap vial were added sequentially *p*-cyanobenzaldehyde (1.0 mmol), the ionic liquid **I** (100 mg), DABCO (1.5 mmol), and the mixture was stirred for 10 min. Acrylonitrile (1.5 mmol) was then added and the reaction was stirred at room temperature until all starting aldehyde was consumed (See Table 1). The coupling product was purified by chromatographic column on silica gel using a 4:1 petroleum ether/ethyl acetate mixture yield 99% (180 mg). After isolation of the product, the ionic liquid **I** (stocked at the top of the chromatographic column) was easily recovered in high purity by changing the column eluent mixture to DCM/ethanol (97:3). The recovered IL (**I**) can be reused in the coupling process for at least four more times with no significant loss in the product yield (96-98%).

#### General preparation of transition metal complexes of ionic liquid precursors illustrated by the synthesis of complex **4a**



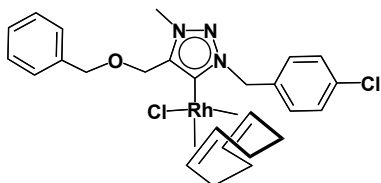
Complex **4a**. Allyl palladium chloride dimer (19 mg, 0.52 mmol), potassium hexamethyl disylazide (24 mg, 1.2 mmol) and ionic liquid **I** (46 mg, 1.0 mmol) were combined in a Schlenk Flask and dissolved in THF (10 mL) at 0 °C. The resulting mixture was stirred for 12 h. The final yellow suspension was

dried under vacuum and the residue was washed with petroleum ether and extracted with diethyl ether. After cannula filtration and removal of the solvent the crude product is obtained as yellow solid in 93% yield (48 mg, 0.93 mmol). mp = 84-86 °C.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 2.85$  (b, 2H,  $\text{CH}(\text{CH}_2)_2$ ), 3.88 (s, 3H,  $\text{NCH}_3$ ), 4.17 (b, 2H,  $\text{CH}(\text{CH}_2)_2$ ), 4.41 (s, 2H,  $\text{ArCH}_2\text{N}$ ), 4.46 (s, 2H,  $\text{ArOCH}_2$ ), 5.12 (b, 1H,  $\text{CH}(\text{CH}_2)_2$ ), 5.59 (m, 2H,  $\text{OCH}_2\text{-C}$ ), 7.09-7.12 (m, 2H,  $\text{CH}_{\text{ar}}$ ), 7.13-7.15 (m, 2H,  $\text{CH}_{\text{ar}}$ ), 7.16-7.18 (m, 5H,  $\text{CH}_{\text{ar}}$ ).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta = 35.1, 55.9, 60.5, 66.8, 71.4, 108.4, 112.5, 127.2, 127.3, 127.6, 127.7, 129.4, 132.3, 133.5, 136.1, 141.3, 165.2$  (Pd=C). FT-IR/ATR  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 3032, 2957, 2923, 2846, 1720, 1576, 1592, 1489, 1456, 1408, 1377, 1318, 1292, 1201, 1029, 991. Found: C, 49.44; H, 4.27; N, 8.42; Calc for:  $\text{C}_{21}\text{H}_{23}\text{N}_3\text{OCl}_2\text{Pd}$  C, 49.38; H, 4.54; N, 8.23.

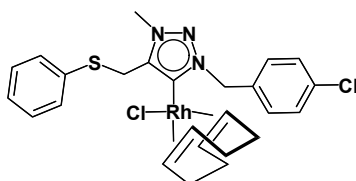


Complex **5a**. According to the general procedure but using allyl palladium chloride dimer (0.52 mmol), potassium hexamethyl disylazide (1.2 mmol) and ionic liquid **II** (46 mg, 1.0 mmol), the title product is obtained in 91% yield as a yellow solid (47 mg, 0.91 mmol). mp = 87-89 °C.  $^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta = 1.98$  (b, 1H,  $\text{CH}(\text{CH}_2)_2$ ), 2.75 (b, 1H,  $\text{CH}(\text{CH}_2)_2$ ), 3.30 (b, 1H,  $\text{CH}(\text{CH}_2)_2$ ), 3.96 (s, 3H,  $\text{NCH}_3$ ), 4.08 (b, 1H,  $\text{CH}(\text{CH}_2)_2$ ), 4.84 (b, 1H,  $\text{CH}(\text{CH}_2)_2$ ), 5.06 (s, 2H,  $\text{ArCH}_2\text{N}$ ), 5.55 (b, 2H,  $\text{ArSCH}_2$ ), 6.47-6.50 (m, 2H,  $\text{CH}_{\text{ar}}$ ), 7.02 (t,  $J = 7.8$  Hz, 1H,  $\text{CH}_{\text{ar}}$ ), 7.11-7.13 (m, 2H,  $\text{CH}_{\text{ar}}$ ), 7.17-7.19 (m, 4H,  $\text{CH}_{\text{ar}}$ ).  $^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta =$

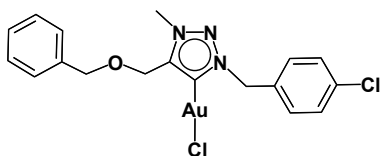
35.6, 56.2, 59.7, 66.5, 101.2, 107.3, 112.7, 127.3, 127.8, 129.7, 129.4, 132.1, 133.7, 140.3, 157.9, 166.1 (Pd=C). FT-IR/ATR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3028, 2921, 2943, 2741, 1676, 1562, 1449, 1478, 1422, 1408, 1376, 1309, 1251, 1029, 997. Found: C, 47.02; H, 4.35; N, 8.04; Calc for:  $\text{C}_{20}\text{H}_{21}\text{N}_3\text{SCl}_2\text{Pd}$  C, 46.84; H, 4.13; N, 8.19.



**Complex 4b.** According to the general procedure but using cyclooctadiene rhodium chloride dimer (25 mg, 0.51 mmol), potassium hexamethyl disylazide (24 mg, 1.2 mmol) and ionic liquid **I** (46 mg, 1.0 mmol) pure **4b** is obtained in 89% yield (52 mg, 0.89 mmol). mp = 95-97 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 1.41-1.63 (m, 4H,  $\text{CH}_2$ , COD), 1.73-1.81 (m, 2H,  $\text{CH}_2$ , COD), 1.98-2.14 (m, 2H,  $\text{CH}_2$ , COD), 2.69-2.72 (m, 1H,  $\text{CH}$ , COD), 3.18-3.22 (m, 1H,  $\text{CH}$ , COD), 3.81 (s, 3H,  $\text{NCH}_3$ ), 4.51 (d,  $J$  = 11.8 Hz, 1H,  $\text{ArCH}_2\text{N}$ ), 4.52 (d,  $J$  = Hz, 12.3 Hz, 1H,  $\text{ArOCH}_2$ ), 4.55 (d,  $J$  = 11.8 Hz, 1H,  $\text{ArCH}_2\text{N}$ ), 4.89 (d,  $J$  = 12.3 Hz, 1H,  $\text{ArOCH}_2$ ), 4.92-4.96 (m, 1H,  $\text{CH}$ , COD), 5.01-5.04 (m, 1H,  $\text{CH}$ , COD), 5.57 (d,  $J$  = 14.5 Hz, 1H,  $\text{OCH}_2\text{-C}$ ), 5.88 (d,  $J$  = 14.5 Hz, 1H,  $\text{OCH}_2\text{-C}$ ), 7.14-7.21 (m, 5H,  $\text{CH}_{\text{ar}}$ ), 7.23-7.26 (m, 2H,  $\text{CH}_{\text{ar}}$ ), 7.31-7.35 (m, 2H,  $\text{CH}_{\text{ar}}$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 27.4, 28.1, 28.5, 30.2, 31.2, 35.1, 56.5, 60.6, 69.5 (d,  $J$  = 14.1 Hz), 71.9, 72.5 (d,  $J$  = 14.1 Hz), 93.9 (d,  $J$  = 7.0 Hz), 94.4 (d,  $J$  = 7.0 Hz), 127.1, 127.3, 127.6, 127.8, 129.5, 132.4, 133.5, 136.2, 139.4, 171.5 (d,  $J$  = 44.9 Hz,  $\text{Rh}=\text{C}$ ). FT-IR/ATR  $\nu_{\max}$   $\text{cm}^{-1}$ : 3020, 2972, 2931, 2871, 2845, 1576, 1489, 1478, 1407, 1328, 1225, 1171, 1053, 1022. Found: C, 54.21; H, 5.00; N, 7.51; Calc for:  $\text{C}_{26}\text{H}_{30}\text{N}_3\text{OCl}_2\text{Rh}$  C, 54.37; H, 5.26; N, 7.32.



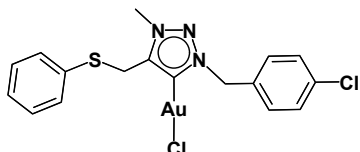
**Complex 5b.** According to the general procedure but using cyclooctadiene rhodium chloride dimer (0.51 mmol), potassium hexamethyl disylazide (1.2 mmol) and ionic liquid **II** (46 mg, 1.0 mmol), the title product is obtained in 84% yield (48 mg, 0.84 mmol). mp = 99-101 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 1.54-1.67 (m, 2H,  $\text{CH}_2$ , COD), 1.92-1.97 (m, 2H,  $\text{CH}_2$ , COD), 2.06-2.12 (m, 2H,  $\text{CH}_2$ , COD), 2.28-2.36 (m, 2H,  $\text{CH}_2$ , COD), 2.92-2.94 (m, 1H,  $\text{CH}$ , COD), 3.43-3.46 (m, 1H,  $\text{CH}$ , COD), 4.06 (s, 3H,  $\text{NCH}_3$ ), 5.10 (d,  $J$  = 11.8 Hz, 1H,  $\text{ArCH}_2\text{N}$ ), 5.13-5.15 (m, 1H,  $\text{CH}$ , COD), 5.18-5.21 (m, 1H,  $\text{CH}$ , COD), 5.74 (d,  $J$  = Hz, 11.8 Hz, 1H,  $\text{ArCH}_2\text{N}$ ), 5.79 (d,  $J$  = 14.5 Hz, 1H,  $\text{ArSCH}_2$ ), 6.04 (d,  $J$  = 14.5 Hz, 1H,  $\text{ArSCH}_2$ ), 7.03-7.09 (m, 3H,  $\text{CH}_{\text{ar}}$ ), 7.35-7.39 (m, 4H,  $\text{CH}_{\text{ar}}$ ), 7.55 (d,  $J$  = 8.4 Hz, 2H,  $\text{CH}_{\text{ar}}$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 29.1, 29.9, 30.3, 31.9, 33.1, 37.0, 58.2, 61.1, 71.4 (d,  $J$  = 14.1 Hz), 74.6 (d,  $J$  = 14.1 Hz), 96.0 (d,  $J$  = 6.9 Hz), 96.3 (d,  $J$  = 6.9 Hz), 115.3, 122.7, 129.6, 130.5, 131.3, 133.9, 135.3, 139.8, 158.5, 174.0 (d,  $J$  = 47.6 Hz,  $\text{Rh}=\text{C}$ ). FT-IR/ATR  $\nu_{\max}$   $\text{cm}^{-1}$ : 2959, 2916, 2872, 2826, 1593, 1489, 1446, 1407, 1329, 1258, 1173, 1145, 1085, 1064, 1013, 836. Found: C, 52.31; H, 4.67; N, 7.95; Calc for:  $\text{C}_{25}\text{H}_{28}\text{N}_3\text{SCl}_2\text{Rh}$  C, 52.09; H, 4.90; N, 7.29.



**Complex 6.** According to the general procedure but using chloro(dimethylsulfide)gold(I) (1.0 mmol), potassium hexamethyl

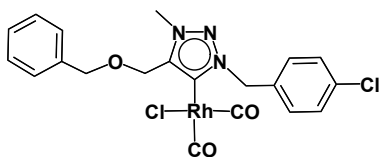


disylazide (1.2 mmol) and ionic liquid **II** (46 mg, 1.0 mmol), the title product is obtained in 89% yield as a white solid (50 mg, 0.89 mmol). mp = 96-98 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 4.11 (s, 3H,  $\text{NCH}_3$ ), 4.57 (s, 2H,  $\text{ArCH}_2\text{N}$ ), 4.69 (s, 2H,  $\text{ArOCH}_2$ ), 5.55 (s, 2H,  $\text{OCH}_2\text{-C}$ ), 7.29-7.32 (m, 2H,  $\text{CH}_{\text{ar}}$ ), 7.33-7.36 (m, 5H,  $\text{CH}_{\text{ar}}$ ), 7.50 (d,  $J$  = 7.8 Hz, 2H,  $\text{CH}_{\text{ar}}$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 37.6, 57.8, 61.1, 72.9, 128.3, 128.7, 129.1, 129.2, 129.9, 130.4, 135.3, 136.6, 143.1, 169.9 ( $\text{Au=C}$ ). FT-IR/ATR  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 3002, 2941, 2823, 2531, 1676, 1592, 1475, 1472, 1466, 1400, 1376, 1338, 1251, 1129, 955. Found: C, 38.45; H, 3.55; N, 7.37; Calc for:  $\text{C}_{18}\text{H}_{18}\text{N}_3\text{OCl}_2\text{Au}$  C, 38.59; H, 3.24; N, 7.50.

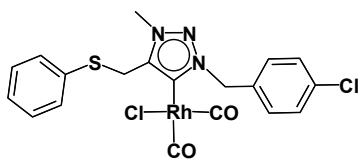


Complex **7**. According to the general procedure but using chloro(dimethylsulfide)gold(I) (1.0 mmol), potassium hexamethyl disylazide (1.2 mmol) and ionic liquid **II** (46 mg, 1.0 mmol), the title product is obtained in 92% yield as a white solid (52 mg, 0.92 mmol). mp = 92-94 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 4.39 (s, 3H,  $\text{NCH}_3$ ), 5.24 (s, 2H,  $\text{ArCH}_2\text{N}$ ), 5.58 (b, 2H,  $\text{ArSCH}_2$ ), 7.02-7.04 (m, 2H,  $\text{CH}_{\text{ar}}$ ), 7.22 (t,  $J$  = 7.8 Hz, 1H,  $\text{CH}_{\text{ar}}$ ), 7.31-7.34 (m, 4H,  $\text{CH}_{\text{ar}}$ ), 7.49 (d,  $J$  = 7.8 Hz, 2H,  $\text{CH}_{\text{ar}}$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 36.1, 57.9, 59.7, 114.8, 122.3, 129.1, 129.2, 129.8, 130.4, 135.2, 142.1, 157.0, 170.2 ( $\text{Au=C}$ ). FT-IR/ATR  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 3016, 2911, 2803, 2649, 1696, 1565, 1457, 1478, 1421, 1408, 1396, 1334, 1251, 1029, 995. Found: C, 36.07; H, 2.65; N, 7.76; Calc for:  $\text{C}_{17}\text{H}_{16}\text{N}_3\text{SCl}_2\text{Au}$  C, 36.31; H, 2.87; N, 7.47.

#### Cyclooctadiene displacement by carbon monoxide in Rhodium complexes



Complex **8**. Carbon monoxide was bubbled for 15 minutes to a solution of **4b** (58 mg, 1.0 mmol) in 10 mL of  $\text{CH}_2\text{Cl}_2$ . The light yellow solution turned slightly orange. The solvent was removed under vacuum and the residue was washed twice with 5 ml of hexanes. Complex **8** is obtained as a brownish solid in 97% yield (51 mg, 0.97 mmol). mp = 89-91 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 3.90 (s, 3H,  $\text{NCH}_3$ ), 4.44 (bs, 2H,  $\text{ArCH}_2\text{N}$ ), 5.42 (bs, 2H,  $\text{ArOCH}_2$ ), 5.60 (bs, 2H,  $\text{OCH}_2\text{-C}$ ), 7.12-7.16 (m, 2H,  $\text{CH}_{\text{ar}}$ ), 7.17-7.20 (m, 5H,  $\text{CH}_{\text{ar}}$ ), 7.26 (d,  $J$  = 8.0 Hz, 2H,  $\text{CH}_{\text{ar}}$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 35.5, 56.8, 60.6, 71.9, 127.1, 127.2, 127.6, 128.0, 129.6, 131.2, 134.1, 136.0, 141.7, 160.4 (d,  $J$  = 37.1 Hz,  $\text{Rh=C}$ ), 181.1 (d,  $J$  = 77.7 Hz,  $\text{Rh-C=O}$ ), 186.6 (d,  $J$  = 53.3 Hz,  $\text{Rh-C=O}$ ). FT-IR/ATR  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 2961, 2923, 2854, 2063, 1989, 1594, 1490, 1446, 1408, 1315, 1259, 1214, 1174, 795. Found: C, 45.82; H, 3.22; N, 8.07; Calc for:  $\text{C}_{20}\text{H}_{18}\text{N}_3\text{O}_3\text{Cl}_2\text{Rh}$  C, 46.00; H, 3.47; N, 8.05.



Complex **9**. Carbon monoxide was bubbled for 15 minutes to a solution of **5b** (58 mg, 1 mmol) in 10 mL of  $\text{CH}_2\text{Cl}_2$ . The light yellow solution turned slightly orange. The solvent was removed under vacuum and the residue was washed twice with 5 ml of hexanes. Complex **9** is obtained as a brownish solid in 95% yield (50 mg, 0.95 mmol). mp = 93-95 °C.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 3.98 (s, 3H,  $\text{NCH}_3$ ), 5.42 (bs, 2H,  $\text{ArCH}_2\text{N}$ ), 5.57 (bs, 2H,  $\text{ArSCH}_2$ ), 6.85-6.89 (m, 3H,  $\text{CH}_{\text{ar}}$ ), 7.14-7.21 (m, 4H,  $\text{CH}_{\text{ar}}$ ), 7.27 (d,  $J$  = 8.5 Hz, 2H,  $\text{CH}_{\text{ar}}$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 35.9, 56.9, 59.2, 113.9, 121.2, 127.7, 128.1, 128.8, 129.6, 131.0, 134.2, 140.8, 156.3, 161.1 (d,  $J$  = 37.9 Hz,  $\text{Rh=C}$ ), 180.6 (d,  $J$  = 77.2 Hz,  $\text{Rh-C=O}$ ), 186.5 (d,  $J$  = 53.3 Hz,  $\text{Rh-C=O}$ ). FT-IR/ATR  $\nu_{\text{max}}$   $\text{cm}^{-1}$ : 2956, 2922, 2852, 2064

(CO), 1992(CO), 1597, 1491, 1456, 1408, 1376, 1328, 1290, 1259, 1172, 1029, 789. Found: C, 43.72; H, 3.39; N, 7.89; Calc for: C<sub>19</sub>H<sub>16</sub>N<sub>3</sub>SO<sub>2</sub>Cl<sub>2</sub>Rh C, 43.53; H, 3.08; N, 8.02.

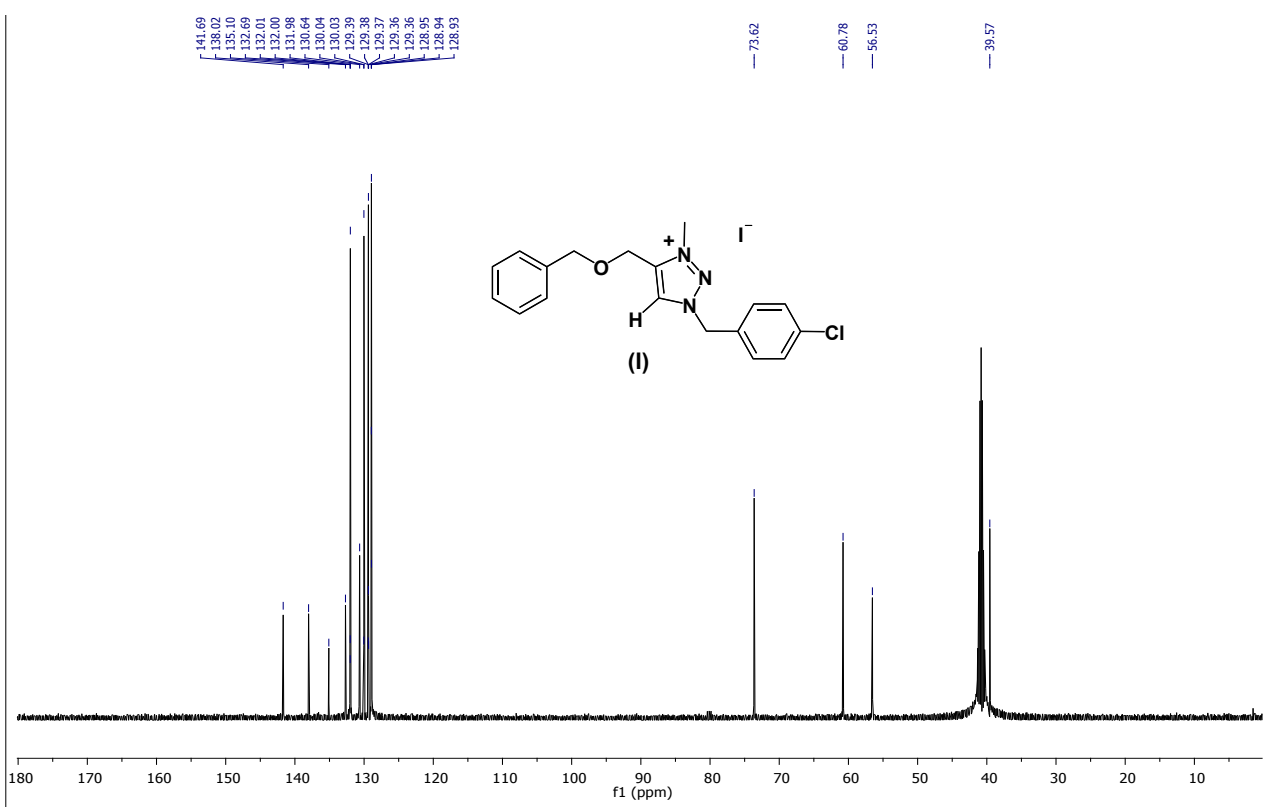
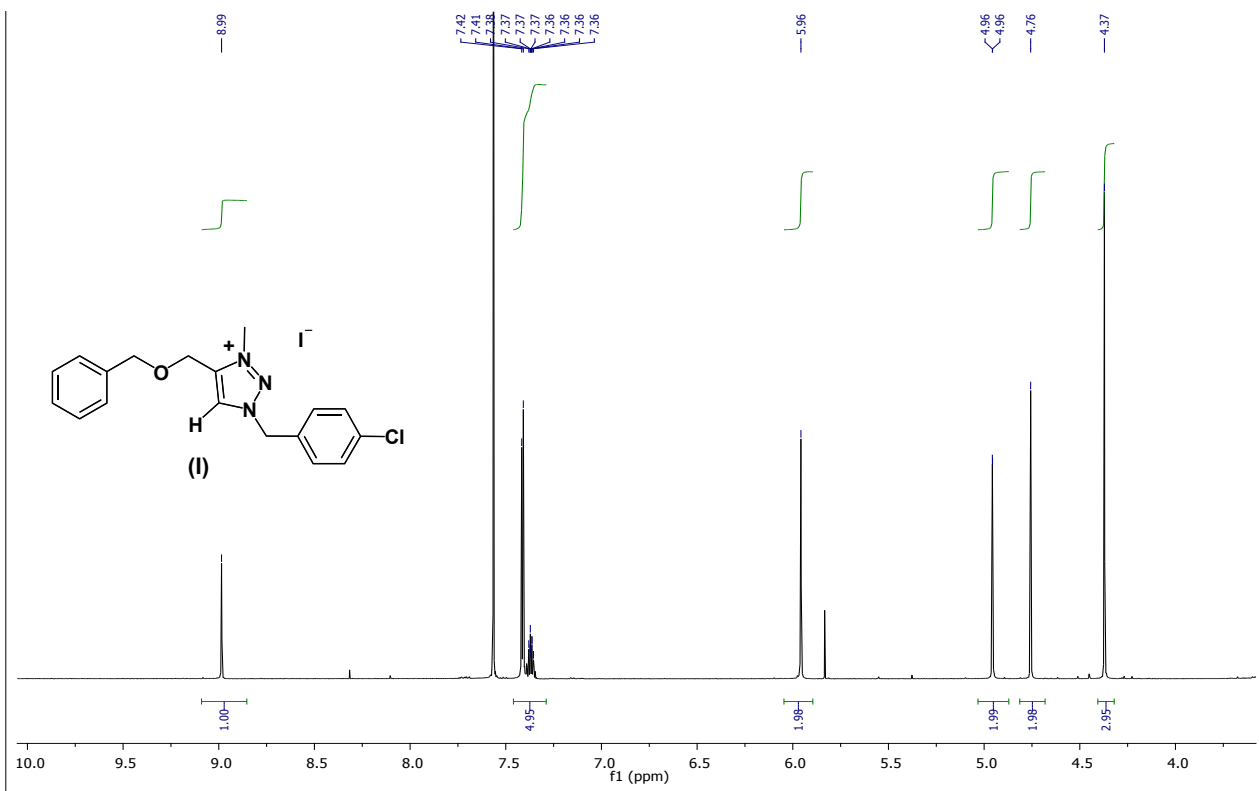
*General procedure for the alpha-arylation of propiophenone (Table 5).*

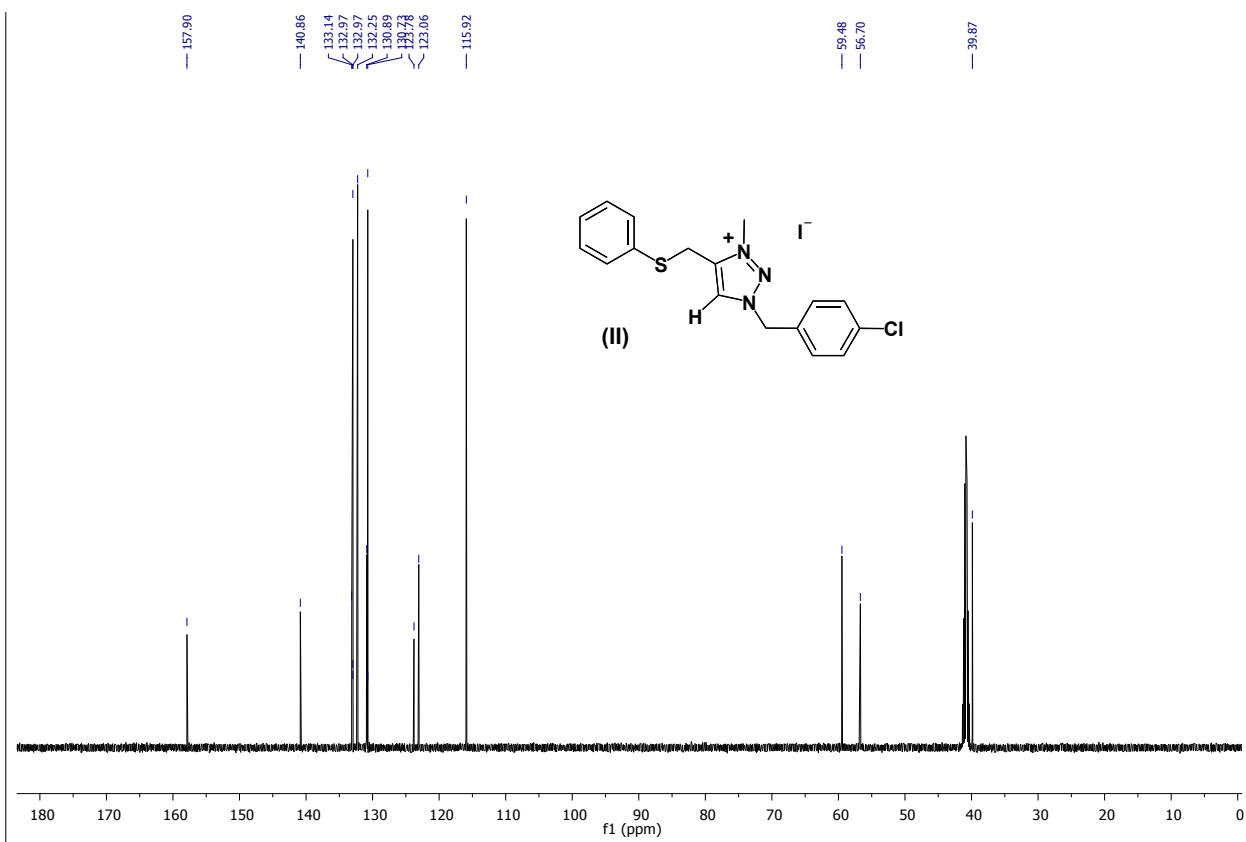
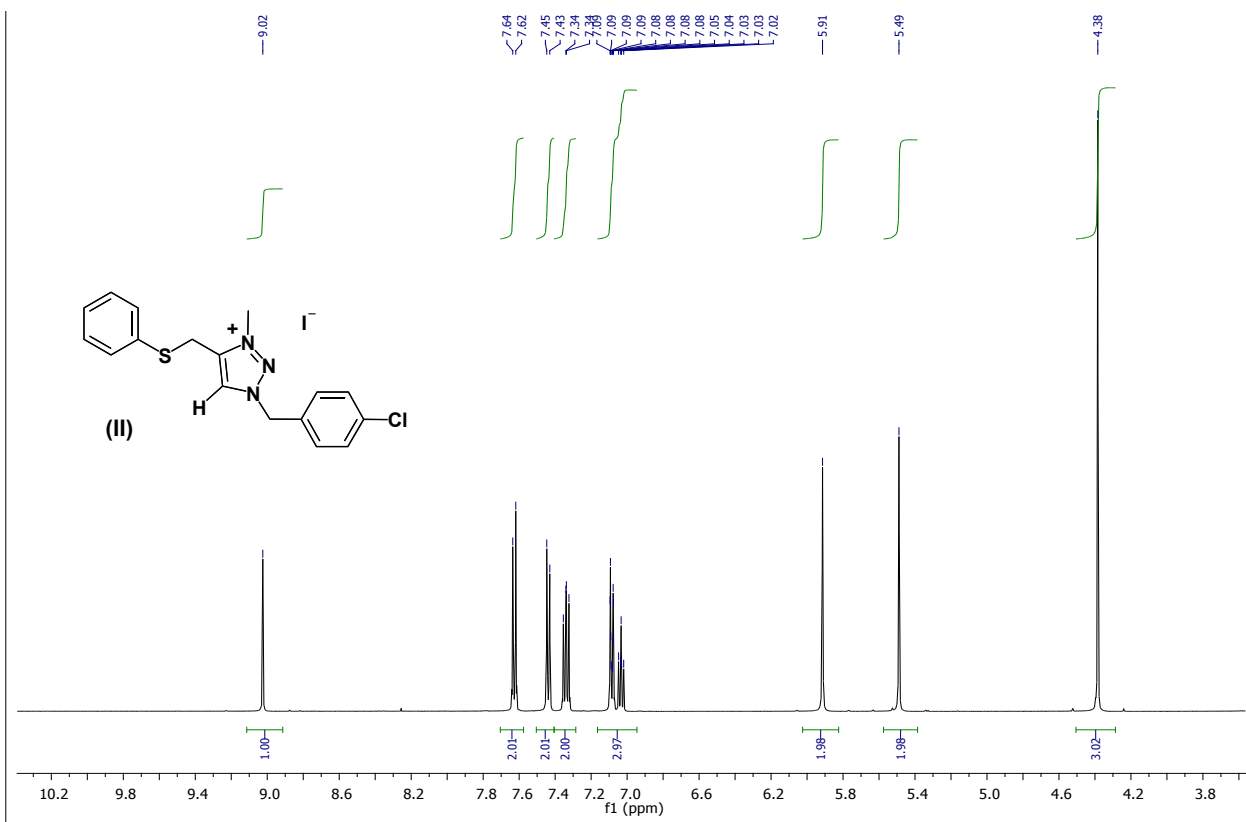
The catalyst (3 mol%), and NaO<sup>t</sup>Bu (1.5 mmol) were charged in a screw capped vial equipped with a magnetic bar. 5 mL of anhydrous THF were added and the mixture was stirred for 5 minutes followed by the addition of the aryl bromide (1.1 mmol) and propiophenone (1.5 mmol). The reaction mixture was heated at 80°C for 3h. Water was added to the reaction mixture, the organic layer was extracted with ethyl acetate, dried with magnesium sulfate, and the solvent was evaporated under vacuum. When necessary, the reaction mixture was purified by column chromatography on silica gel using 5-15% ethylacetate/hexane as eluent.

### **References:**

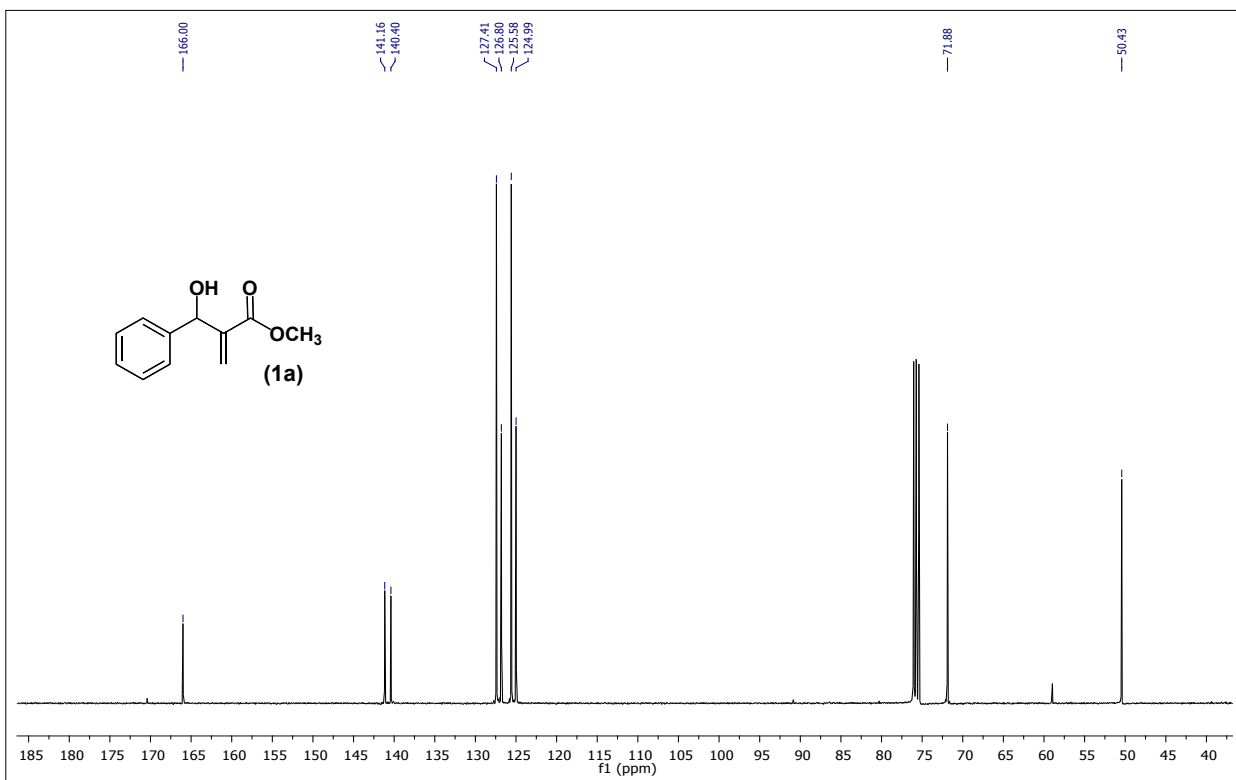
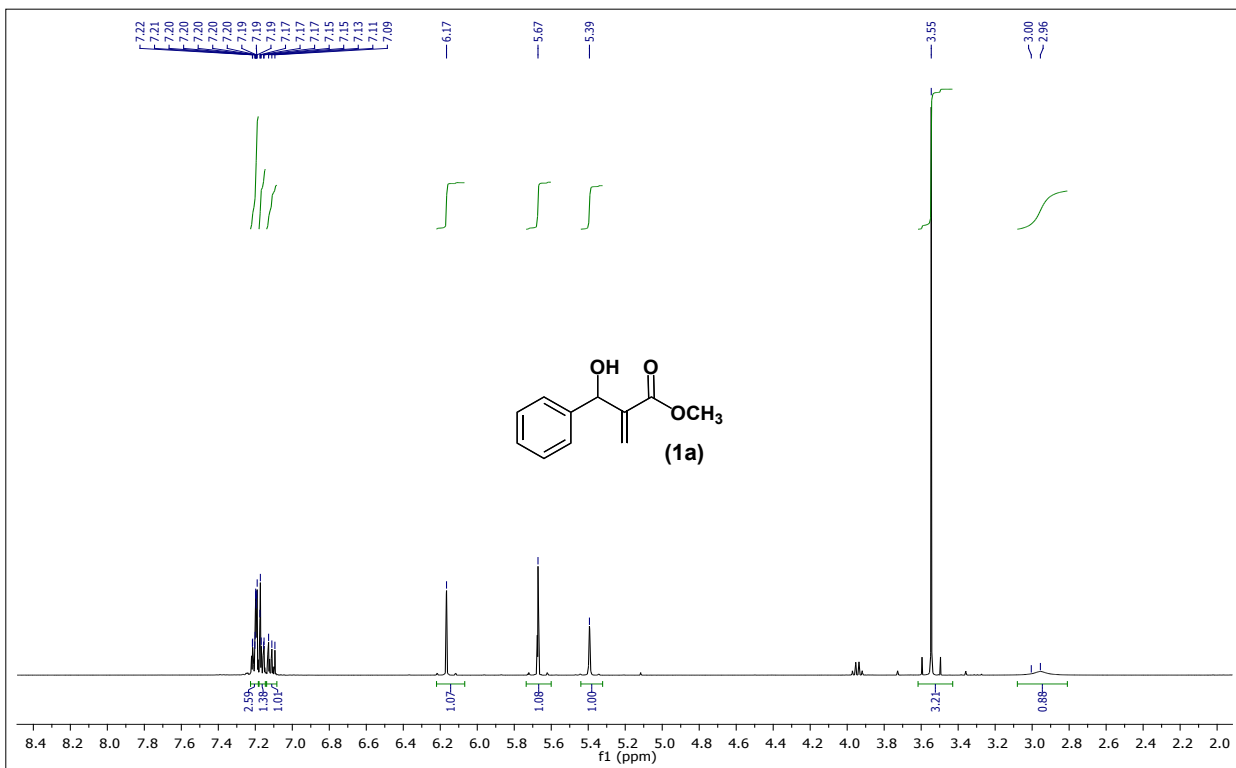
- 1) (a) Mendoza-Espinosa, D.; Negrón-Silva, G.; Lomas-Romero, L.; Gutiérrez-Carrillo, A.; Soto-Castro, D. *Synthesis*, **2013**, *45*, 2431-2437. (b) Mendoza-Espinosa, D.; Negrón-Silva, G.; Lomas-Romero, L.; Gutiérrez-Carrillo, A.; Santillán, R. *Synthetic Commun.* **2014**, *44*, 807-817.

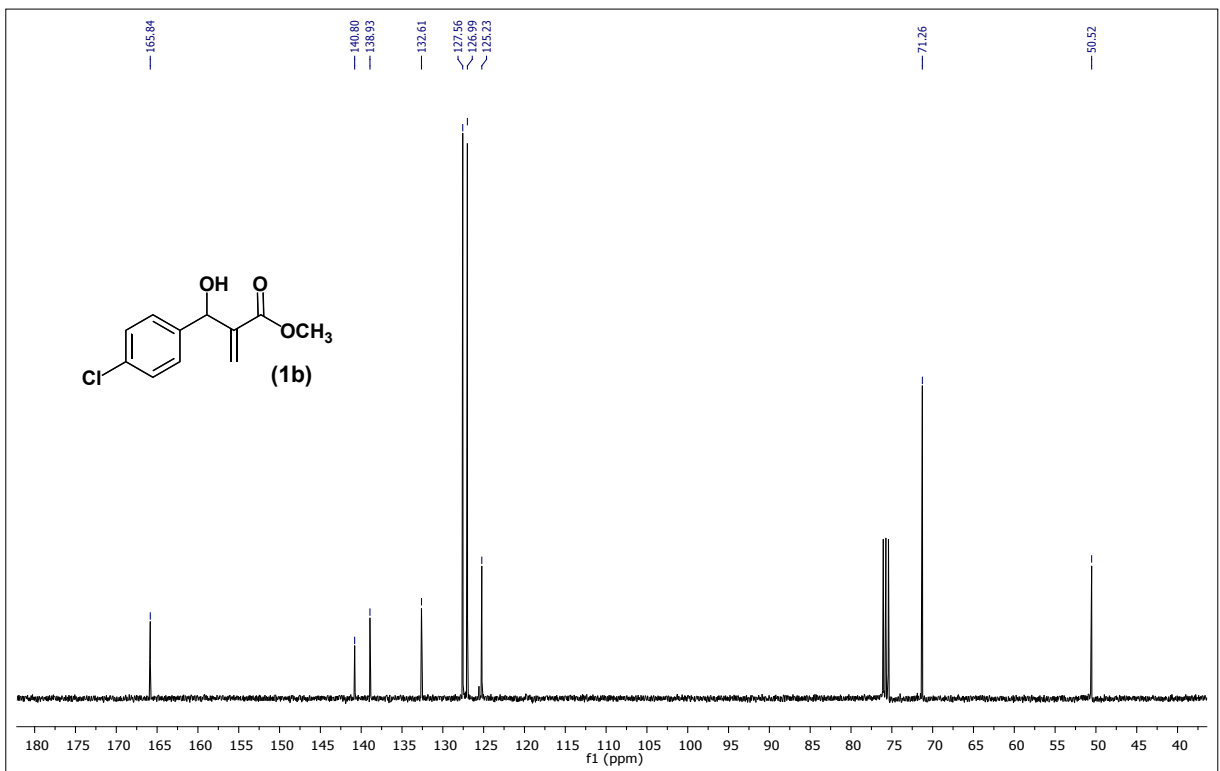
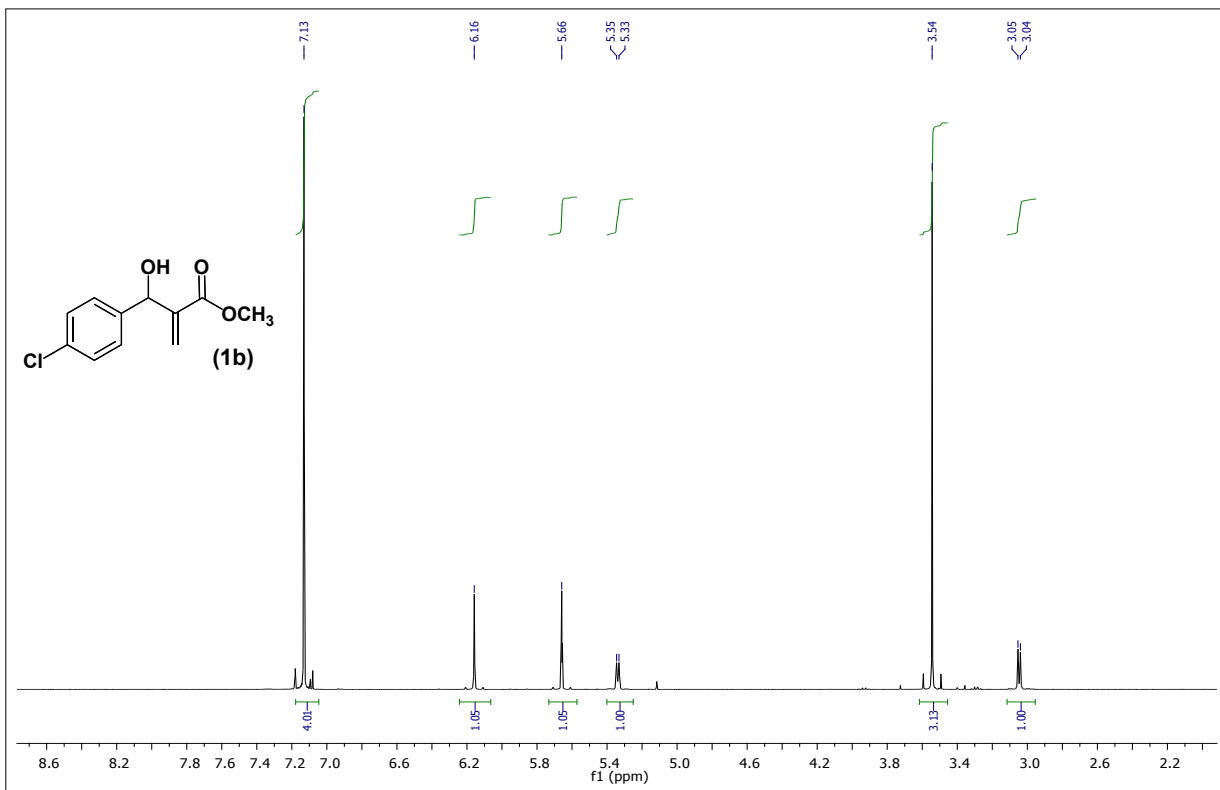
<sup>1</sup>H (400 MHz) and <sup>13</sup>C NMR (100 MHz) Spectra for triazolium salts (**I**) and (**II**) in DMSO-d<sub>6</sub>

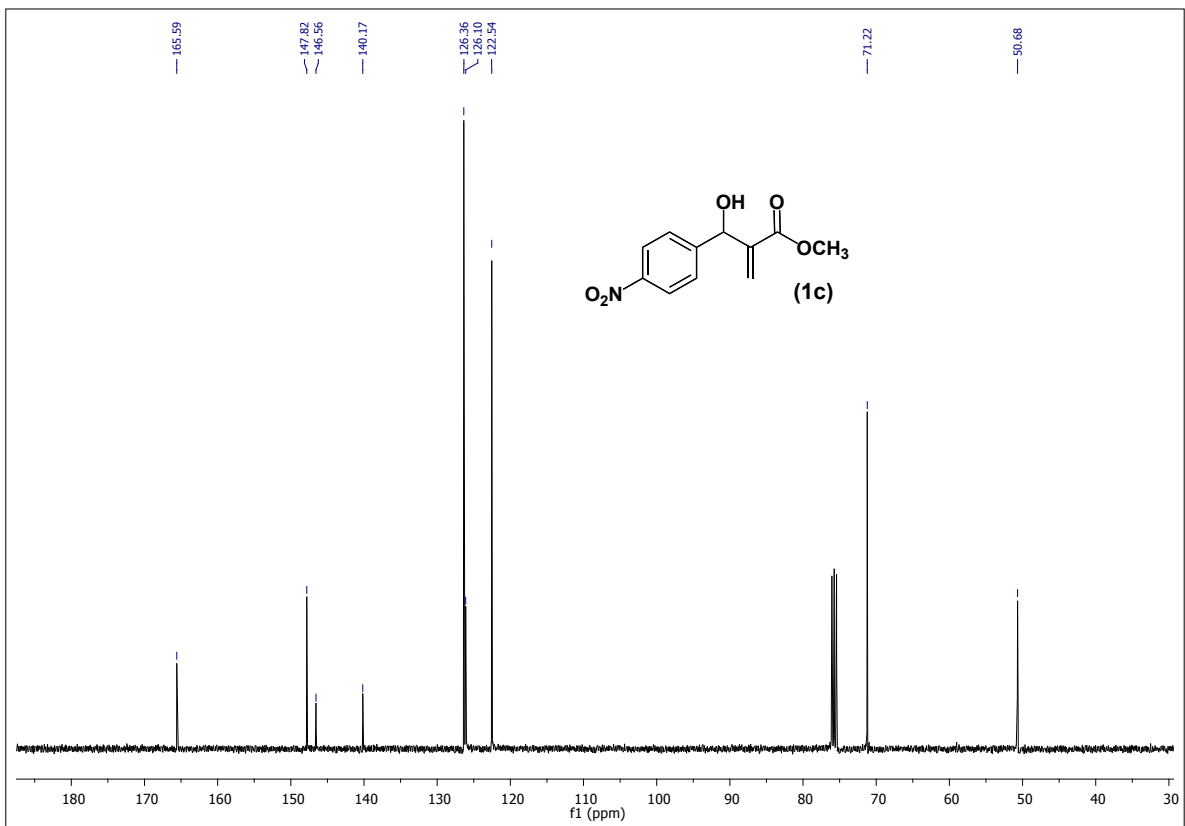
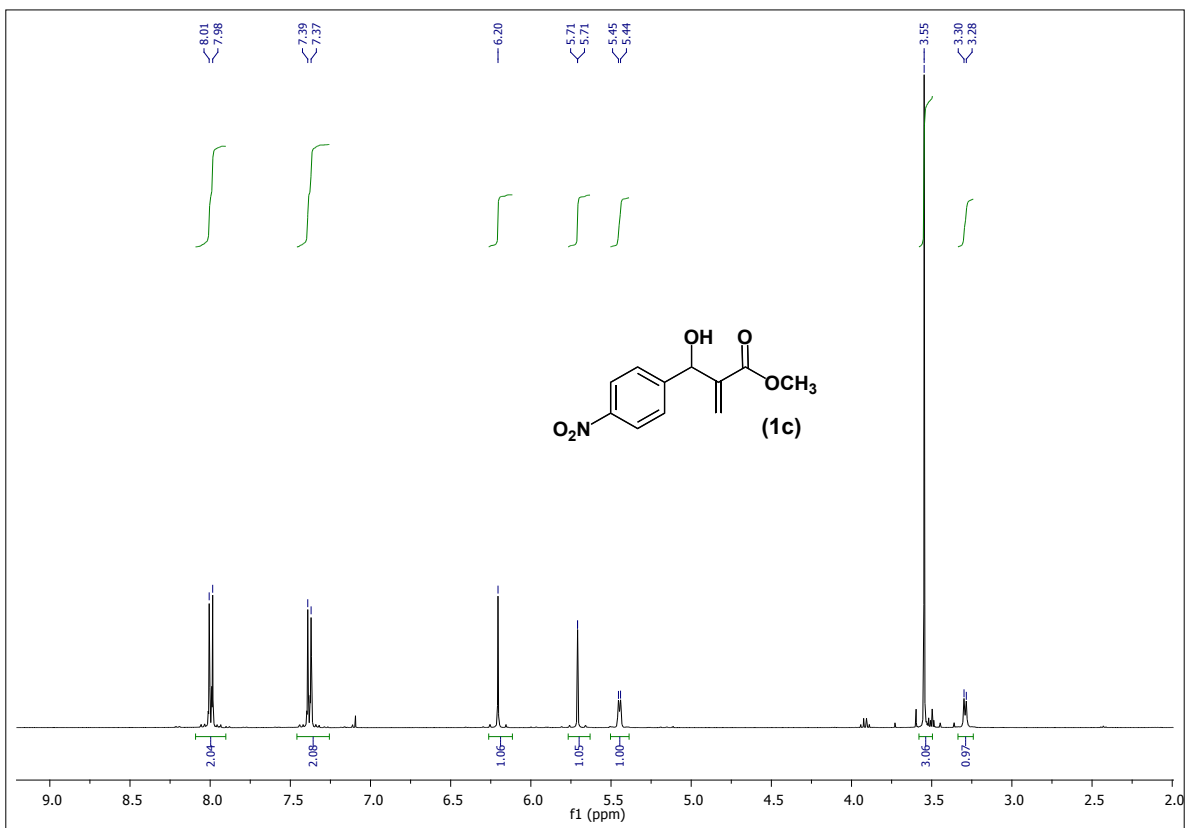


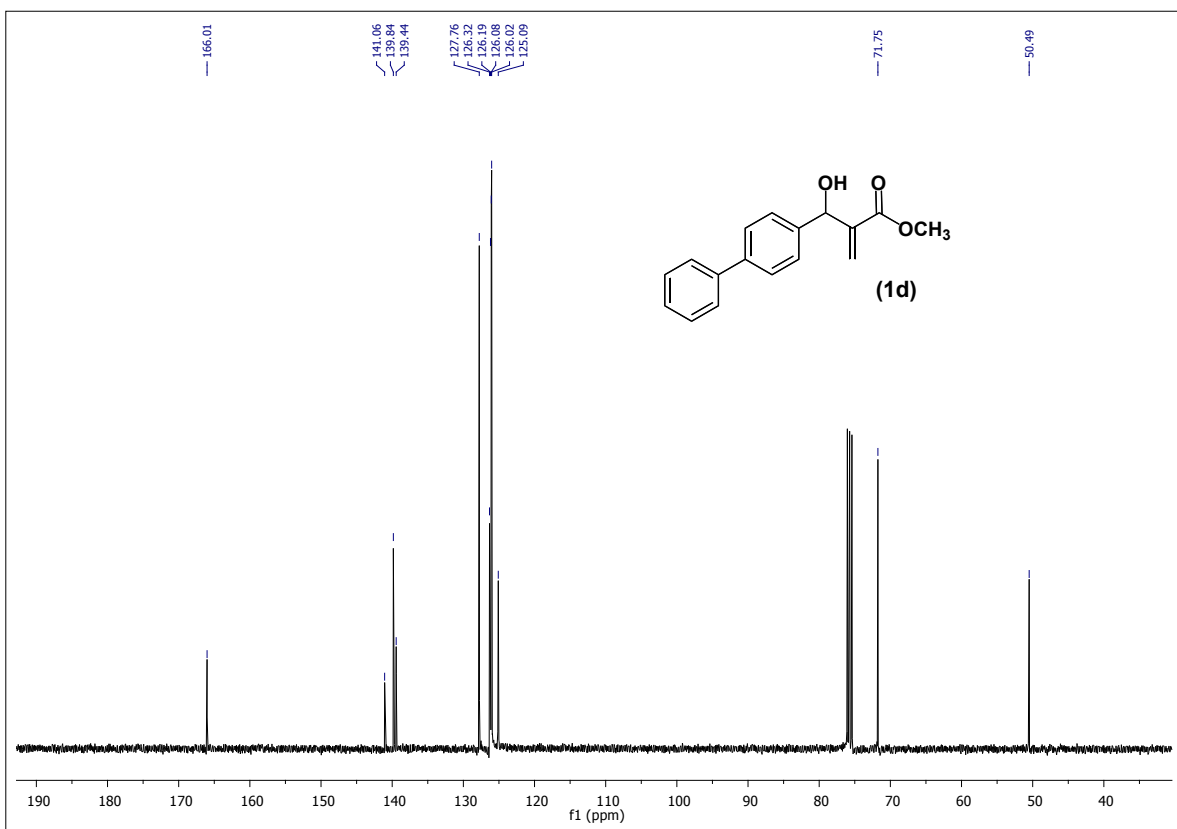
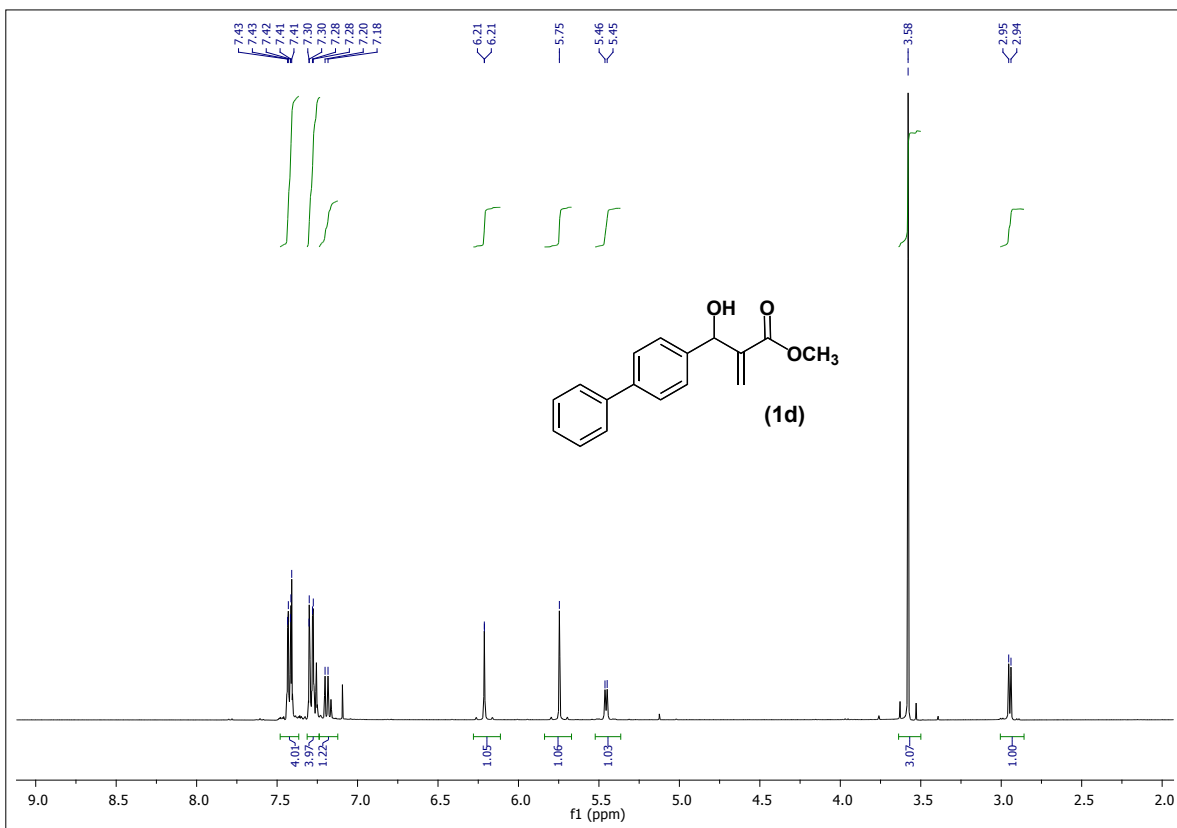


$^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) Spectra for Baylis-Hillman Products with Methyl Acrylate in  $\text{CDCl}_3$

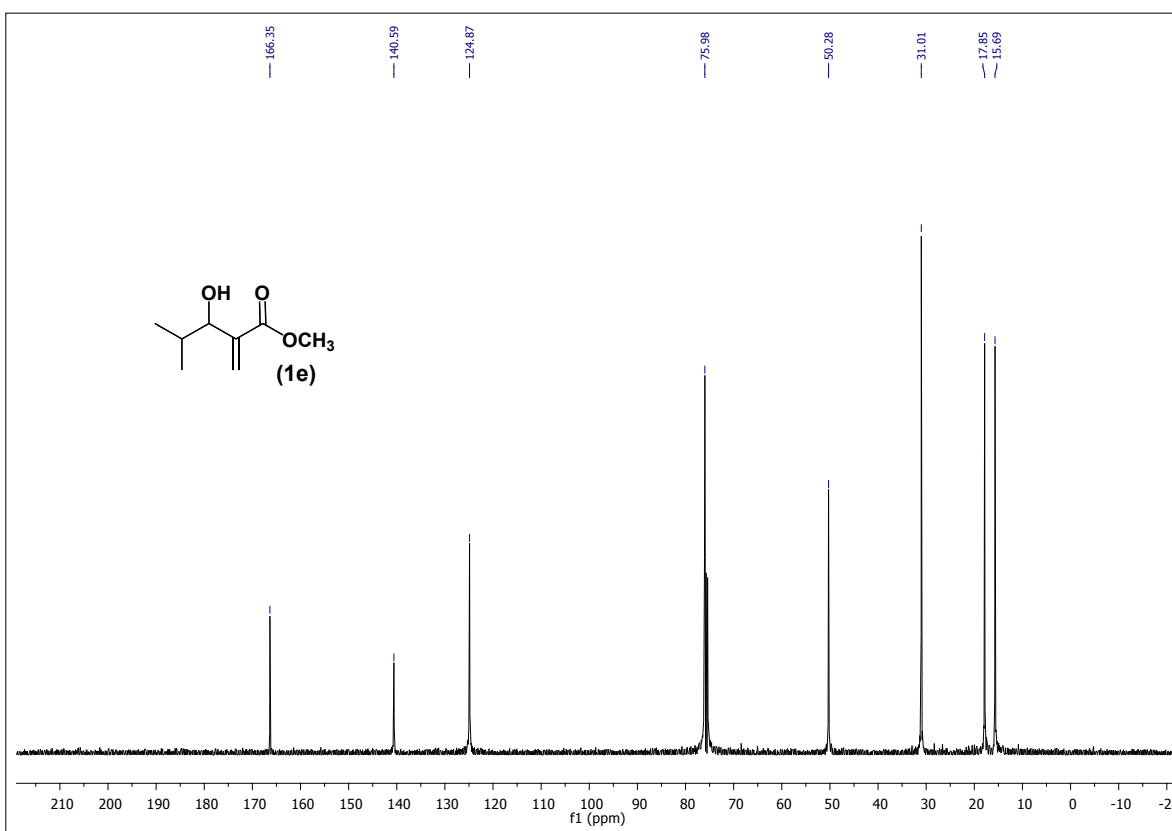
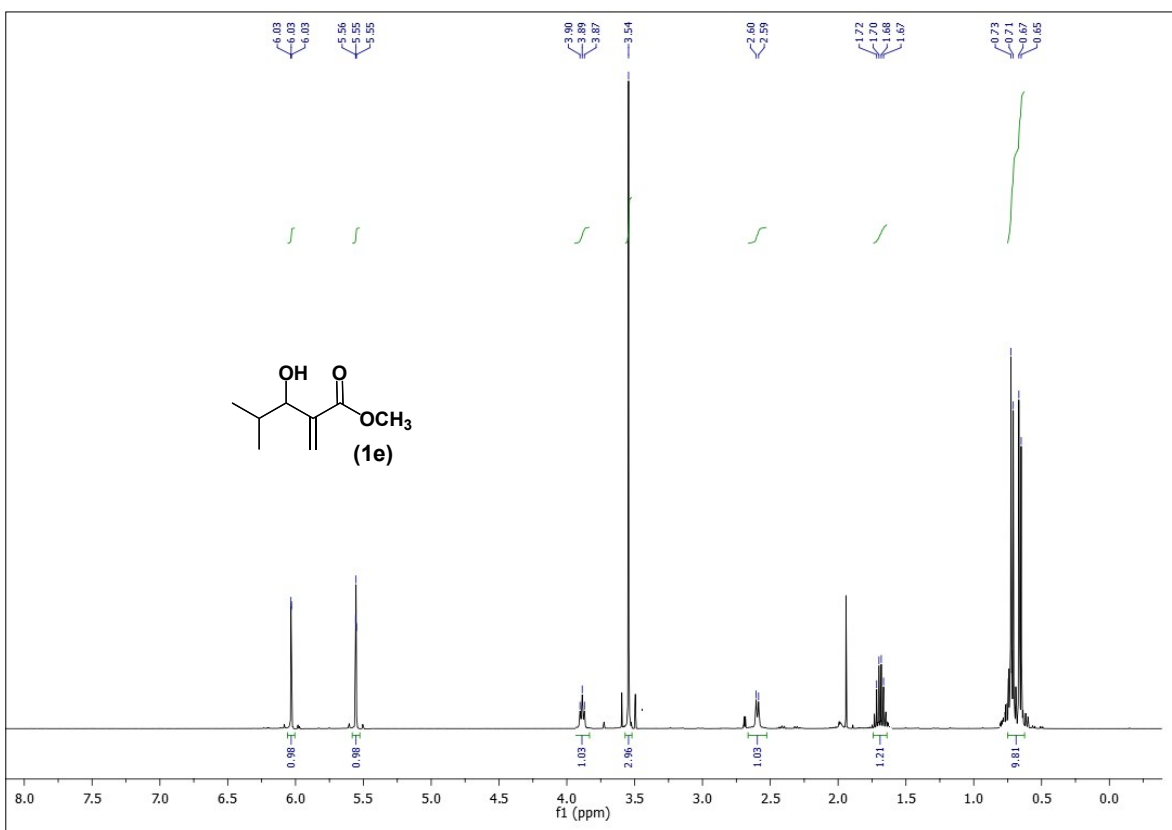


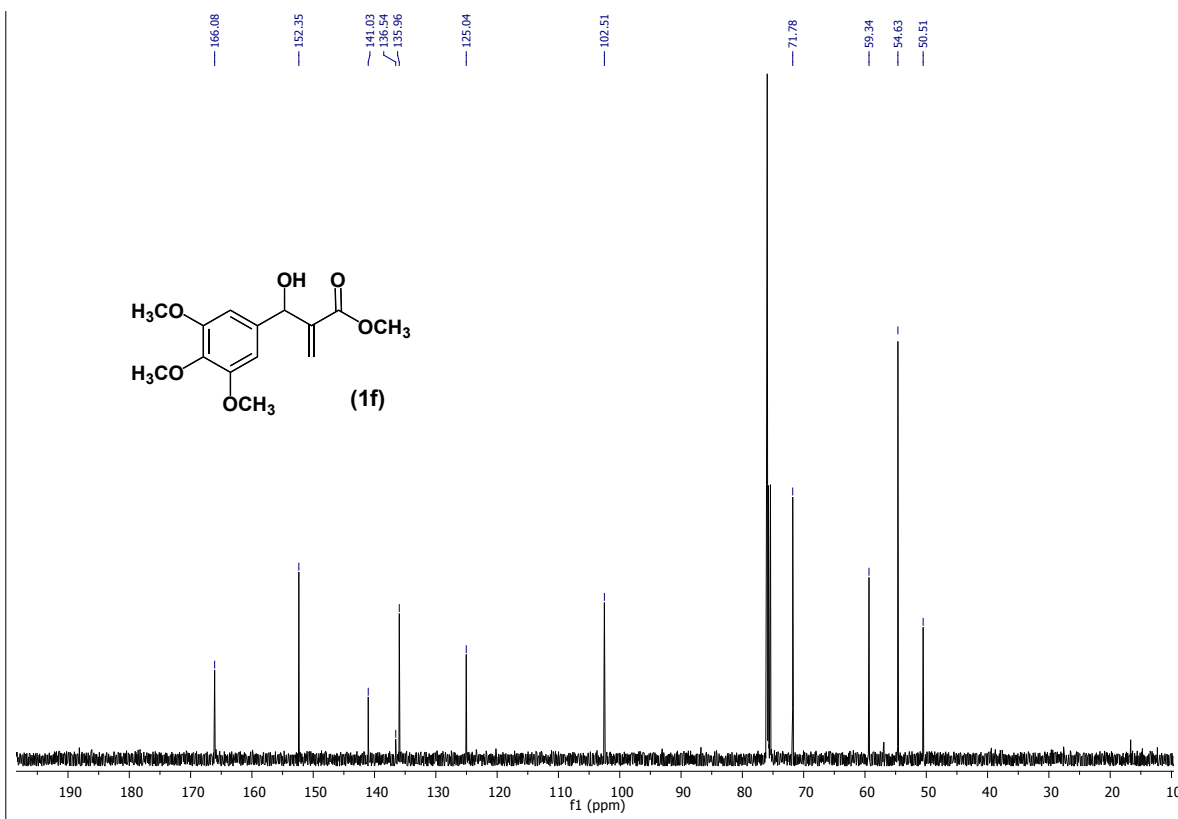
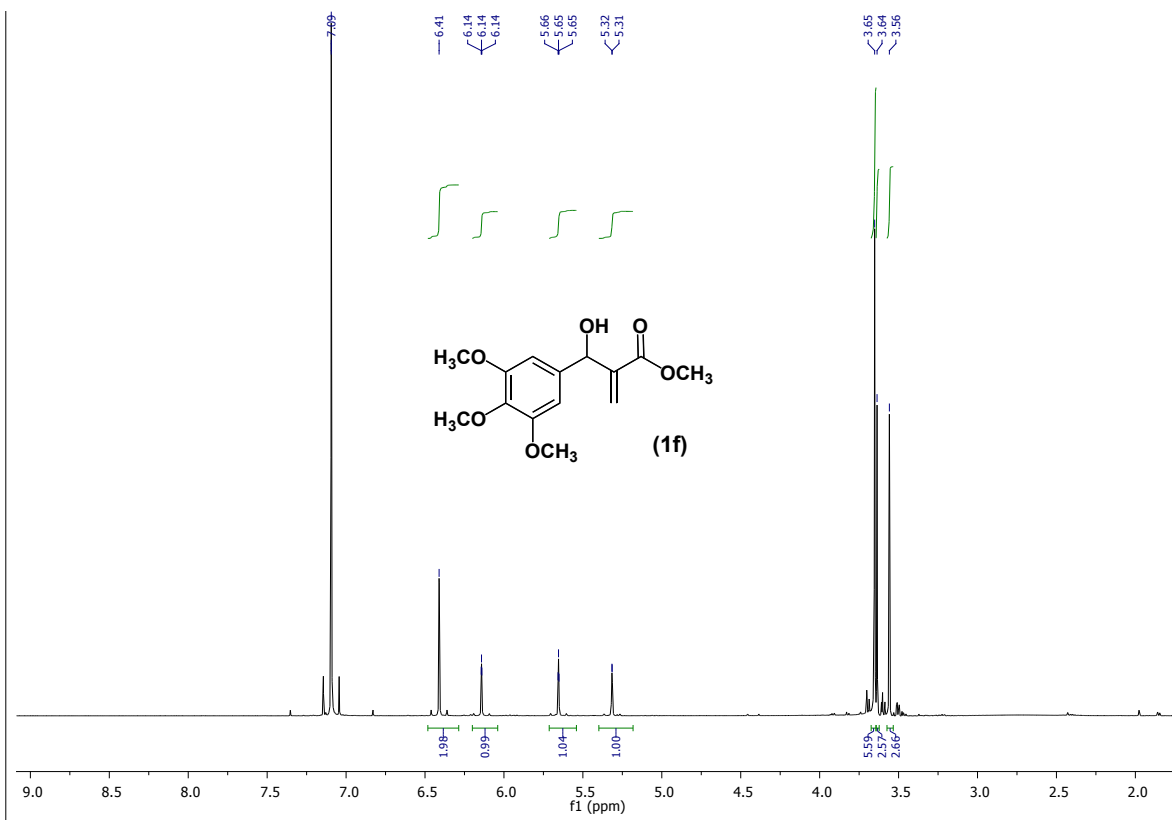


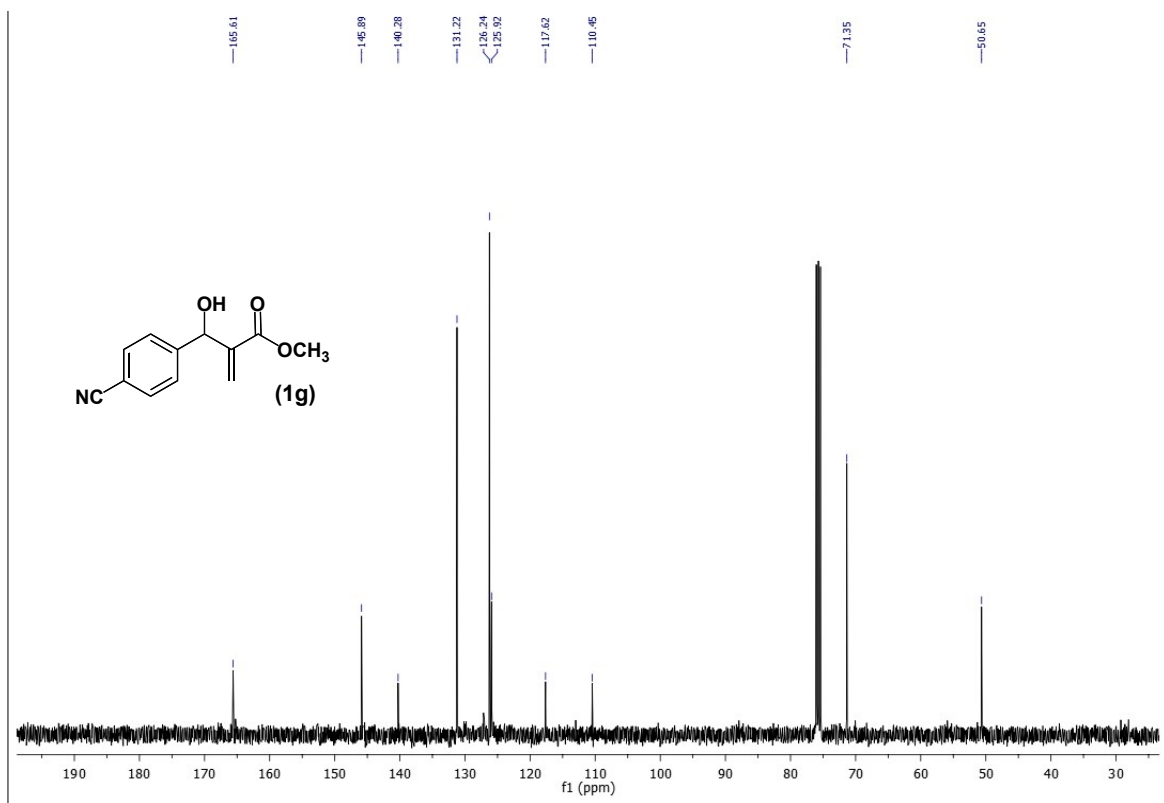
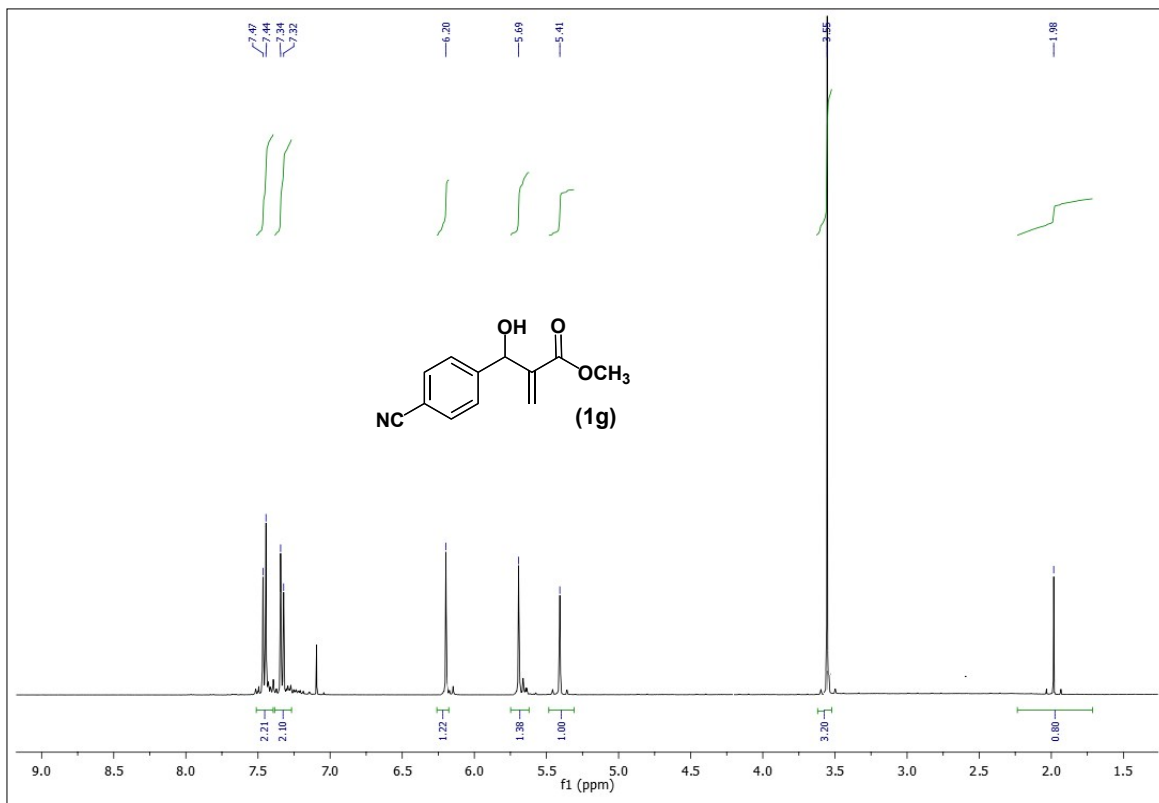




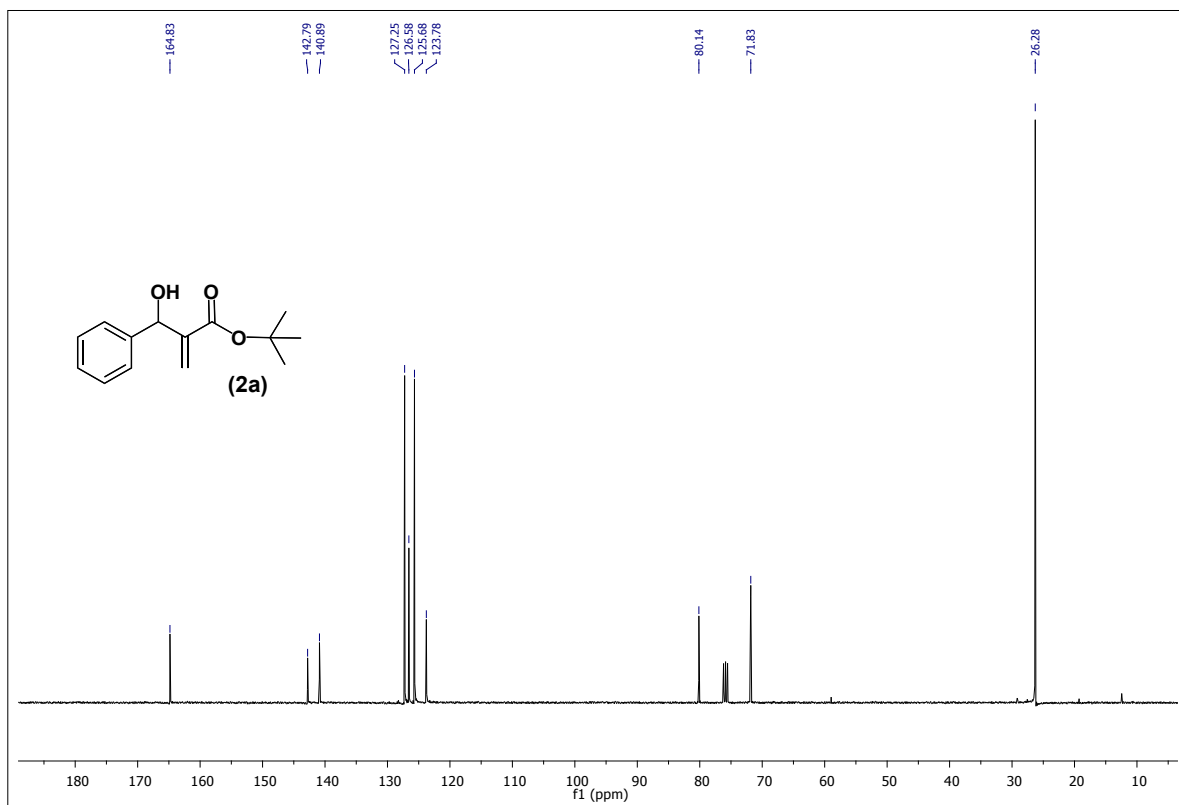
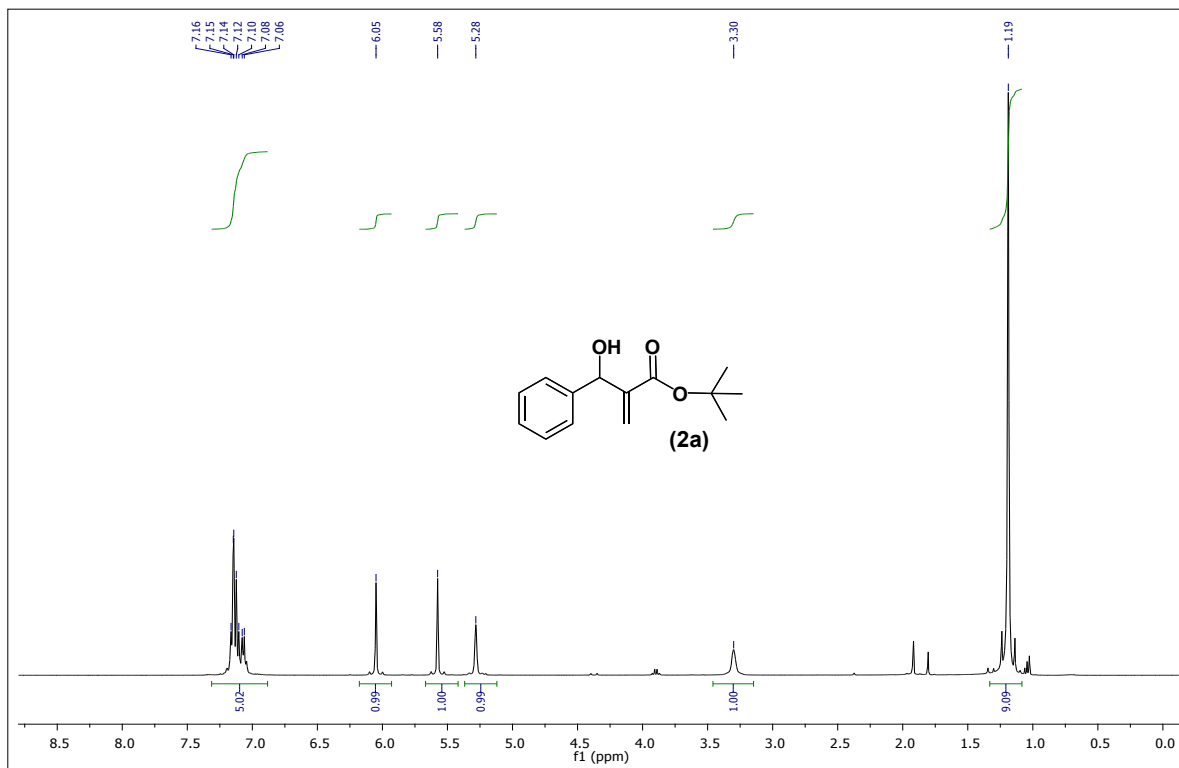


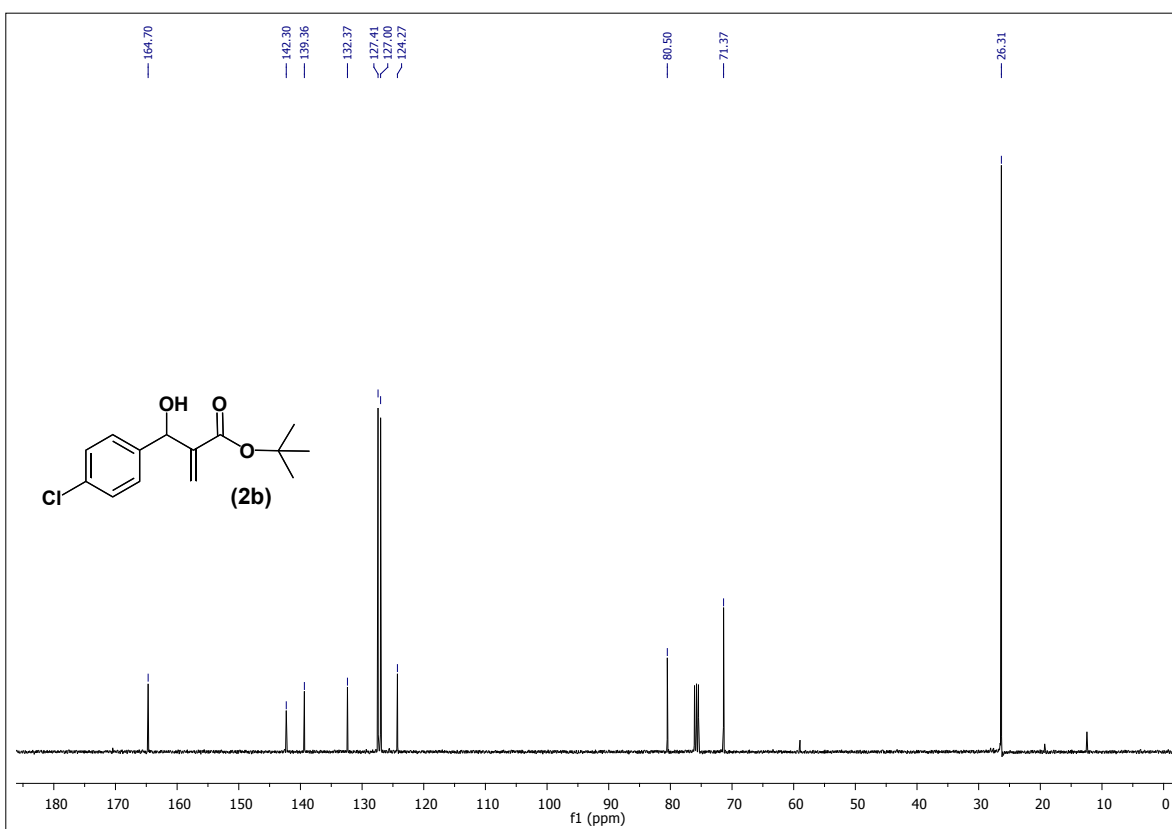
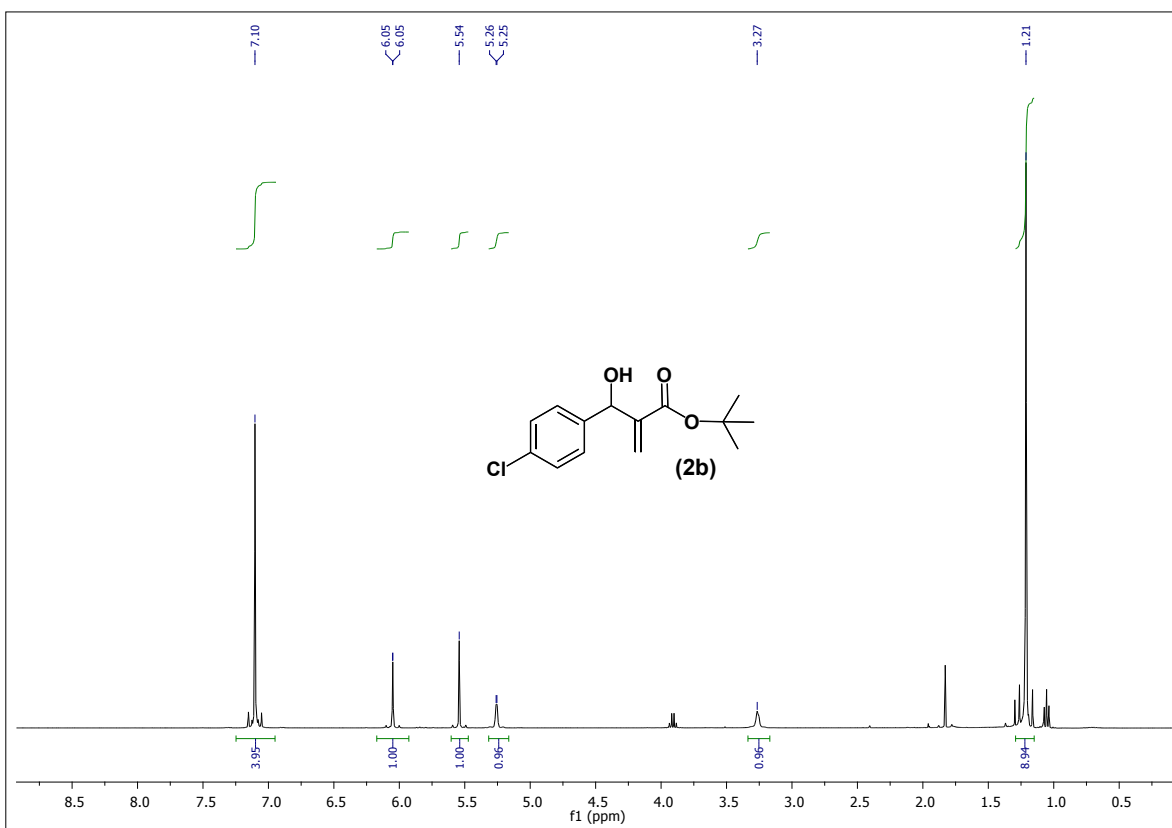


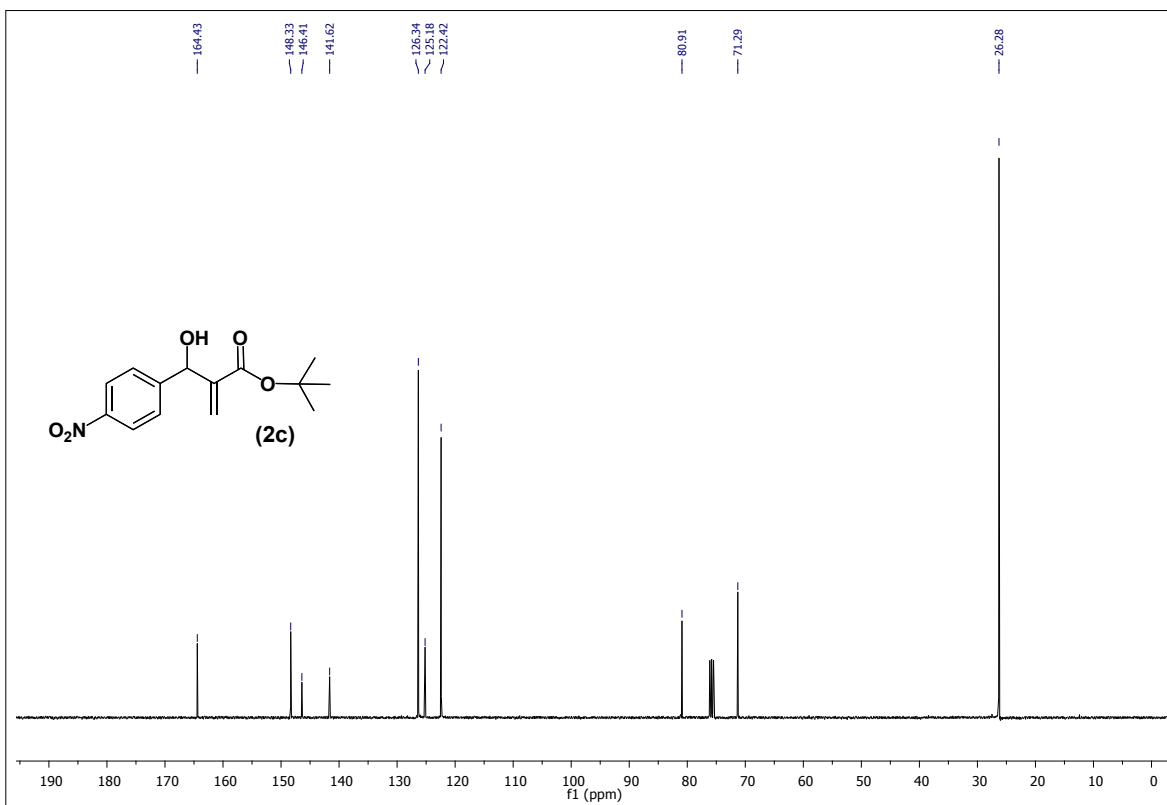
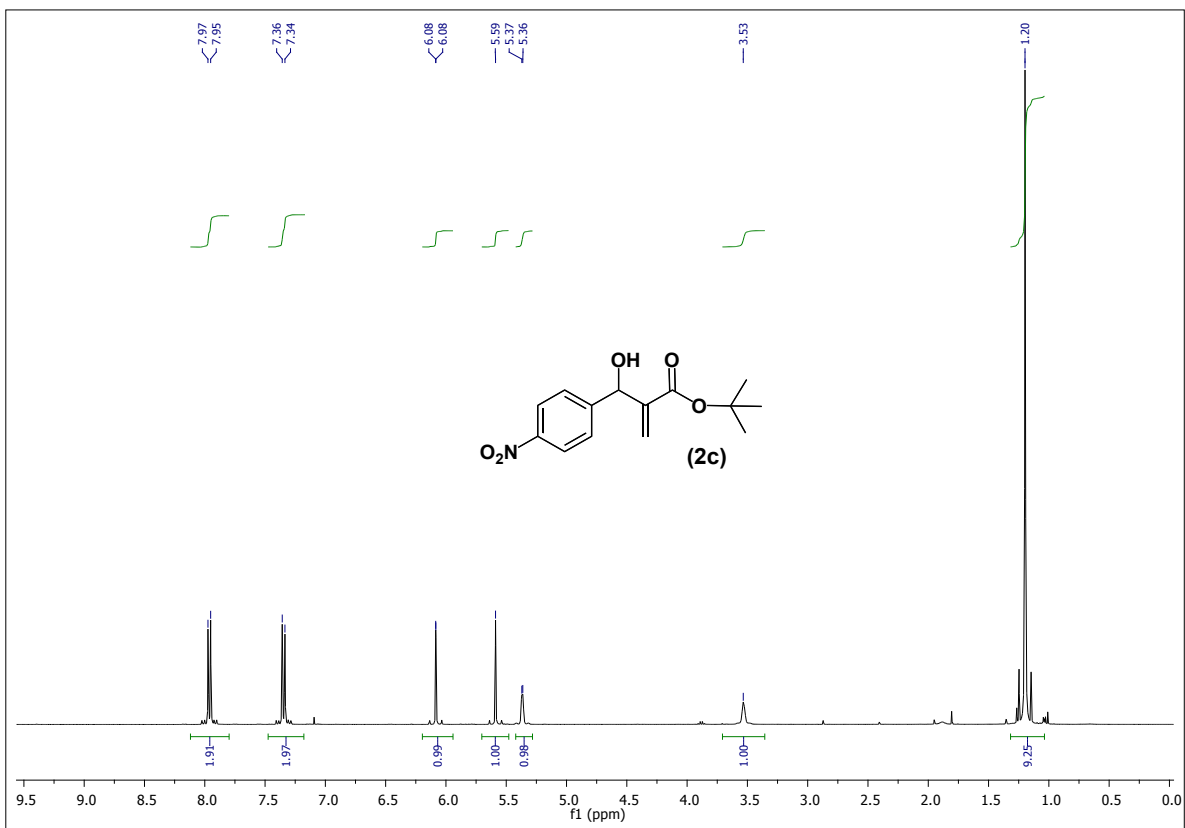


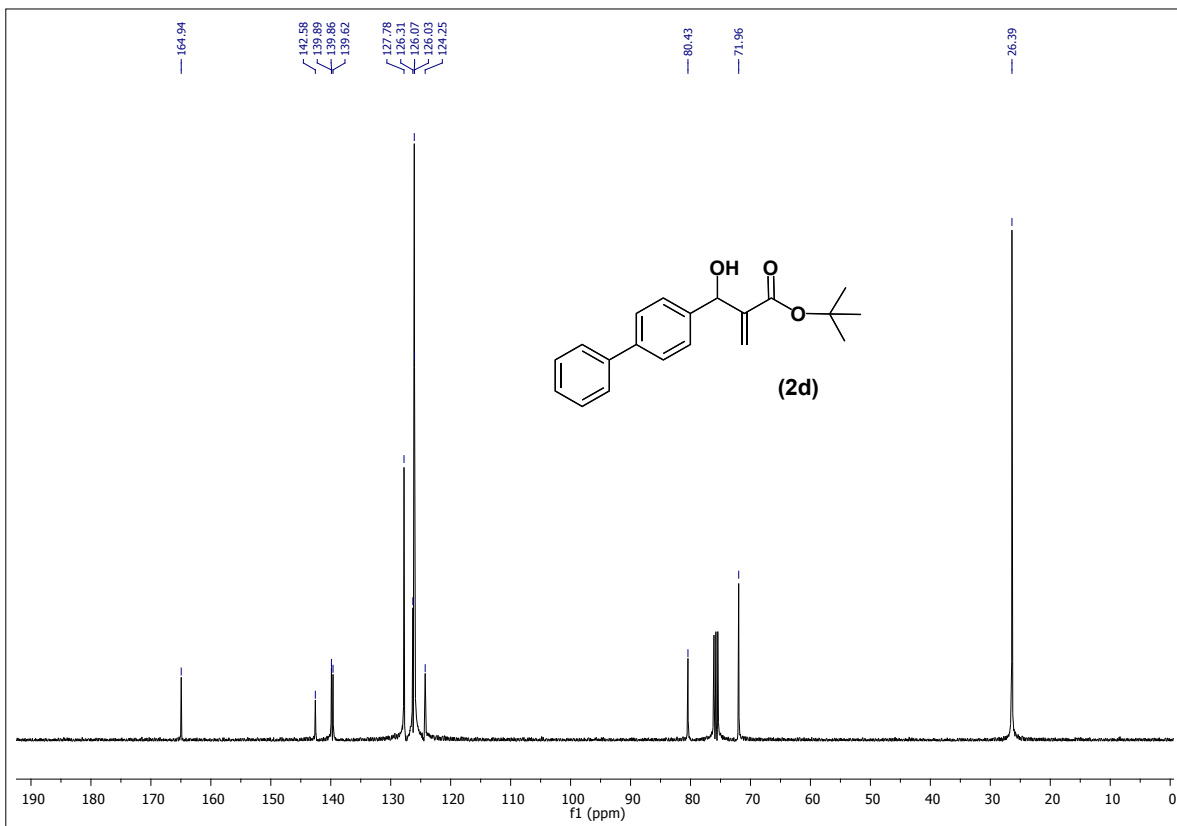
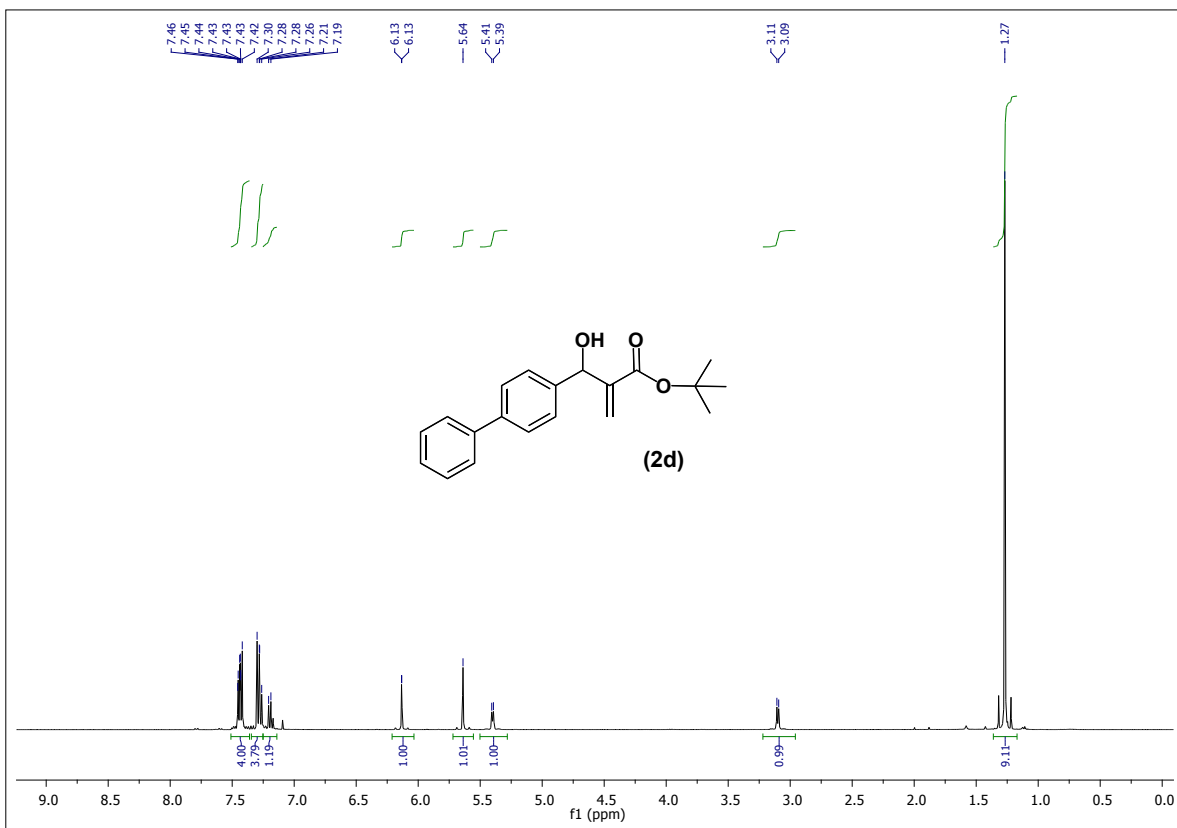


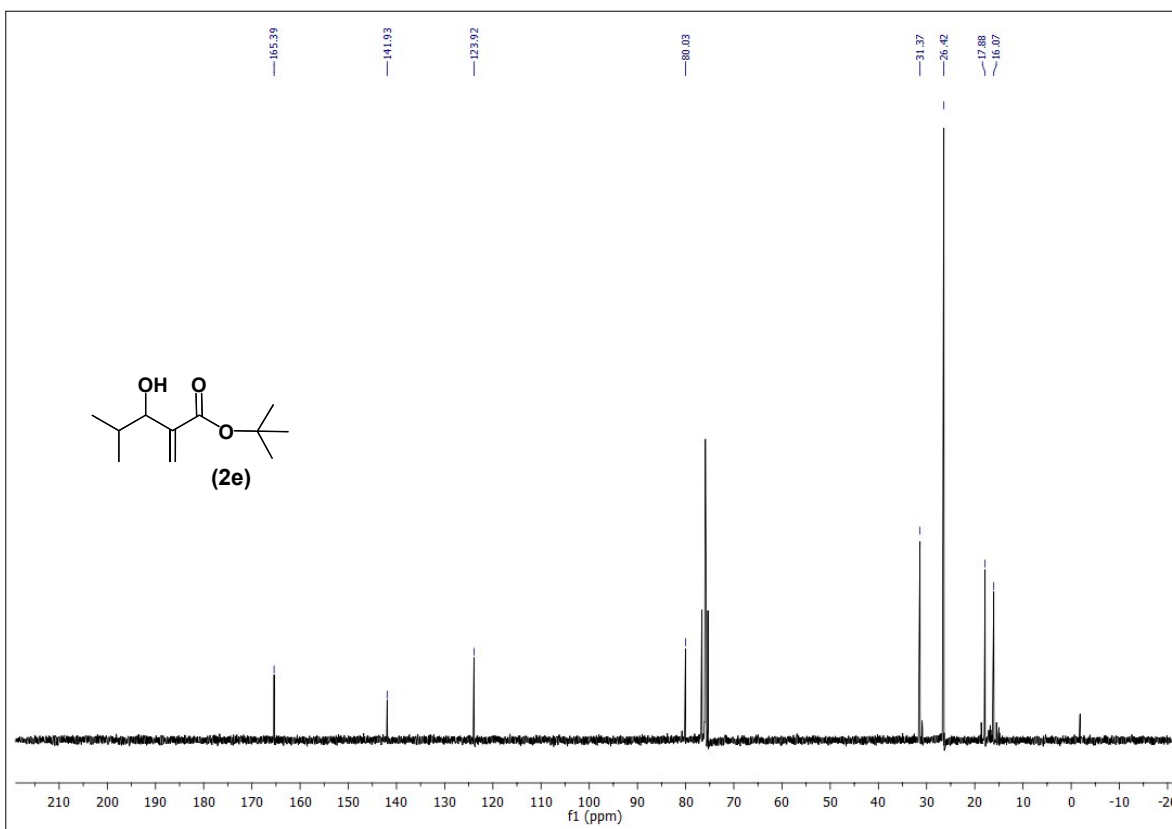
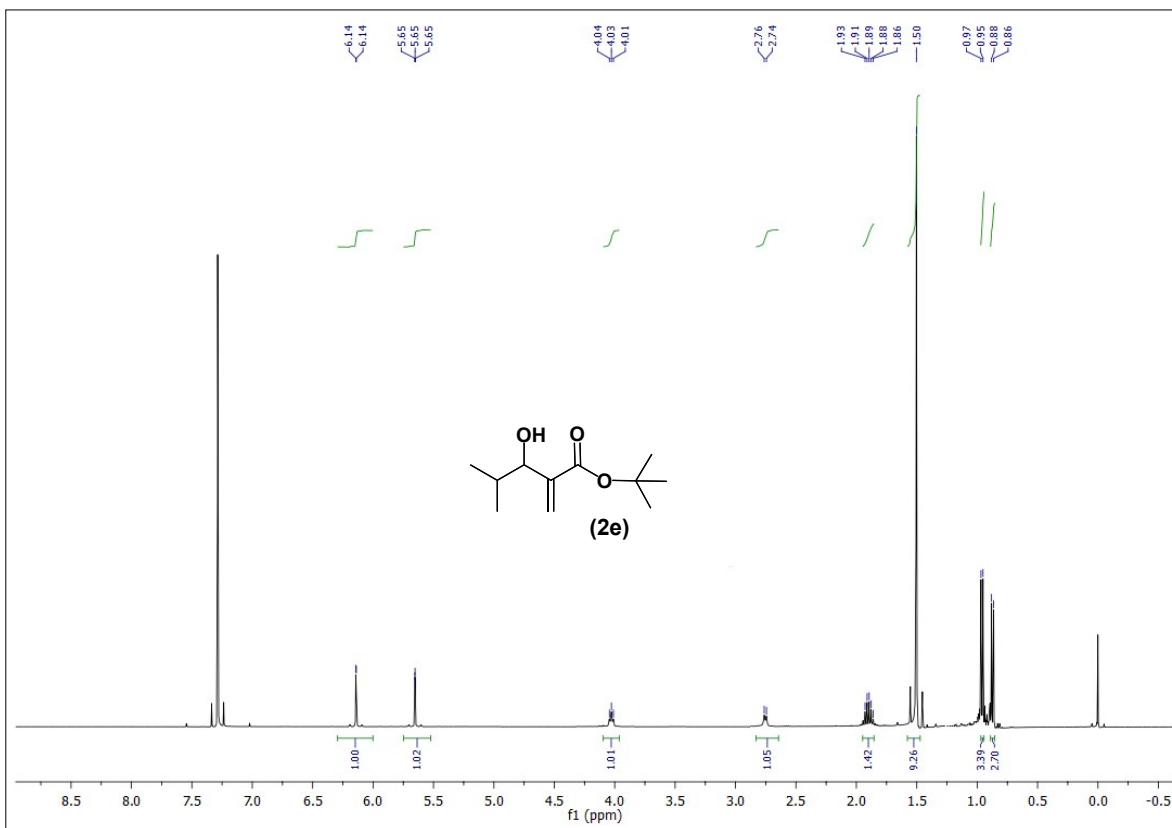
$^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) Spectra for Baylis-Hillman Products with *tert*-Butyl Acrylate in  $\text{CDCl}_3$



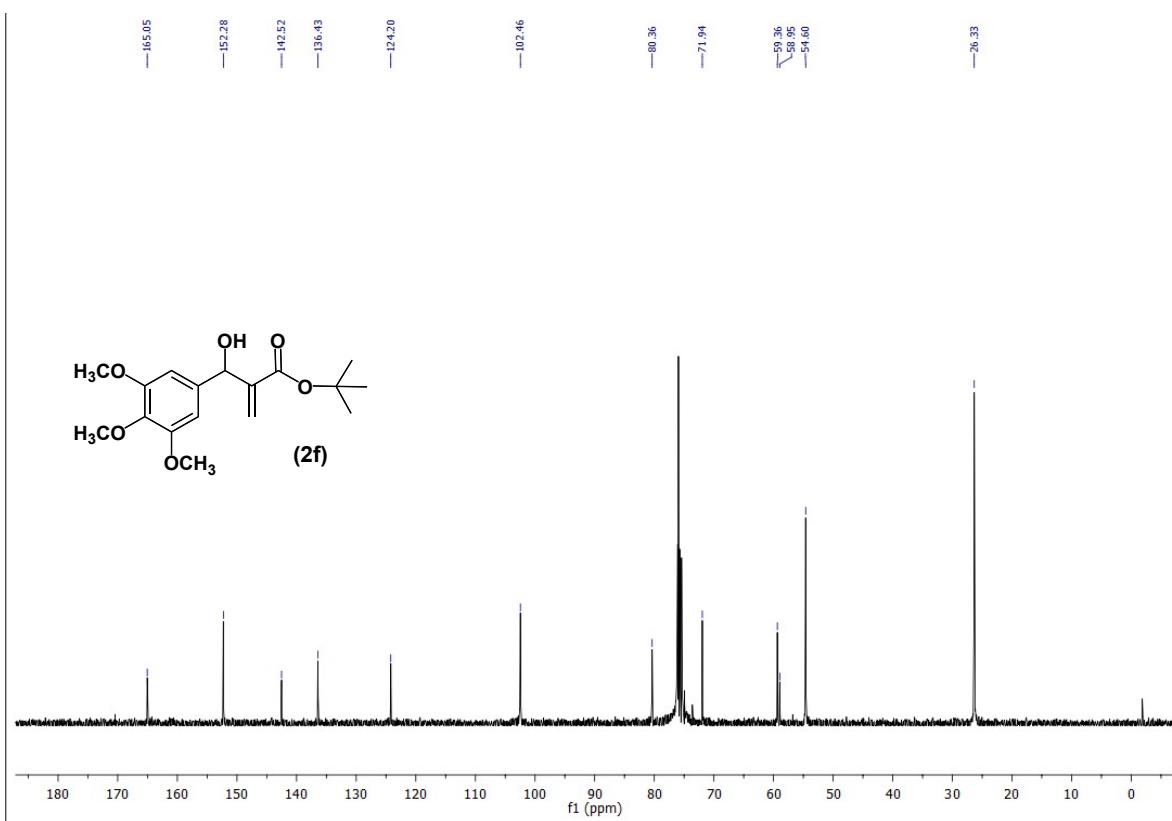
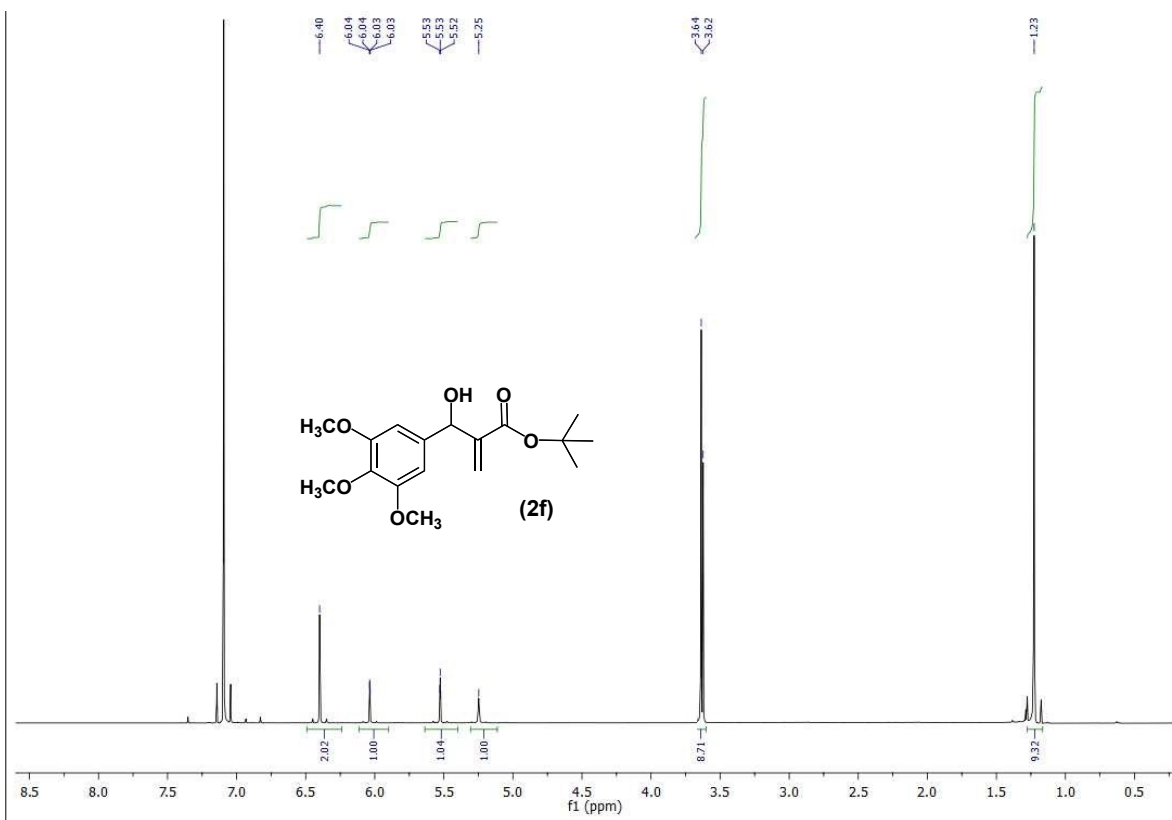


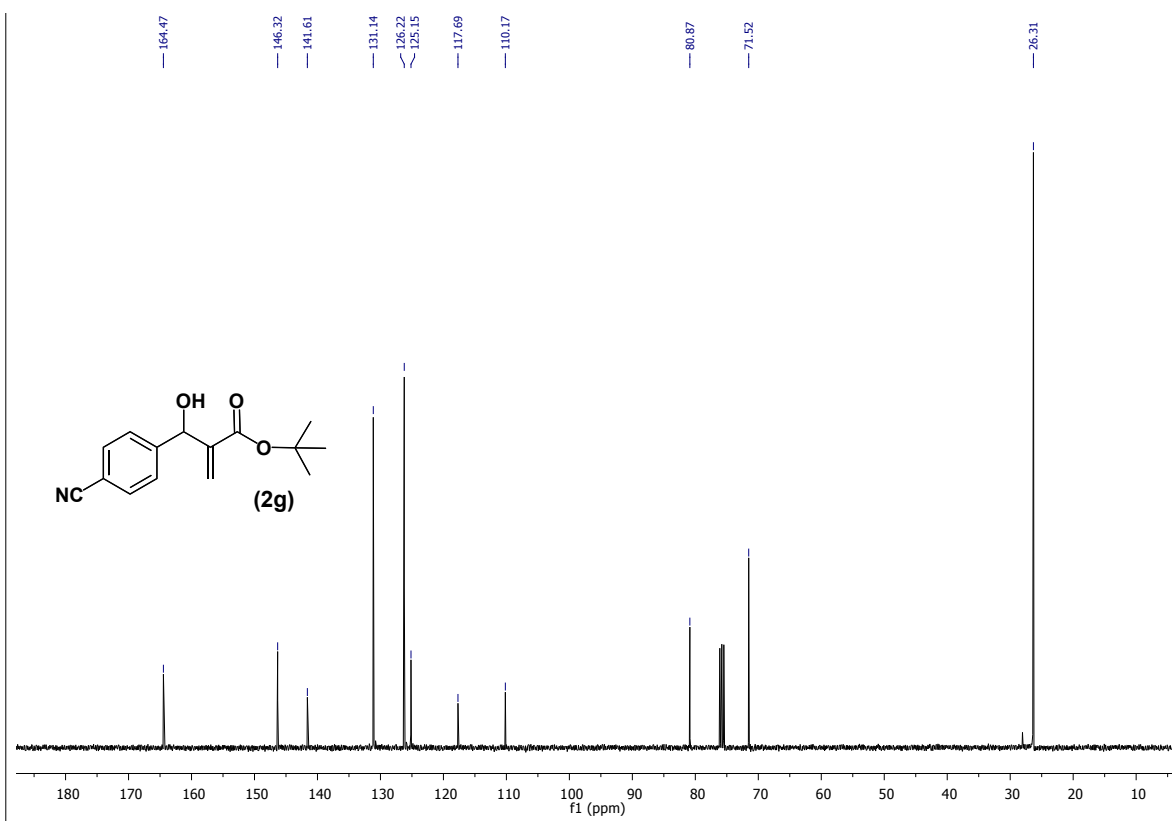
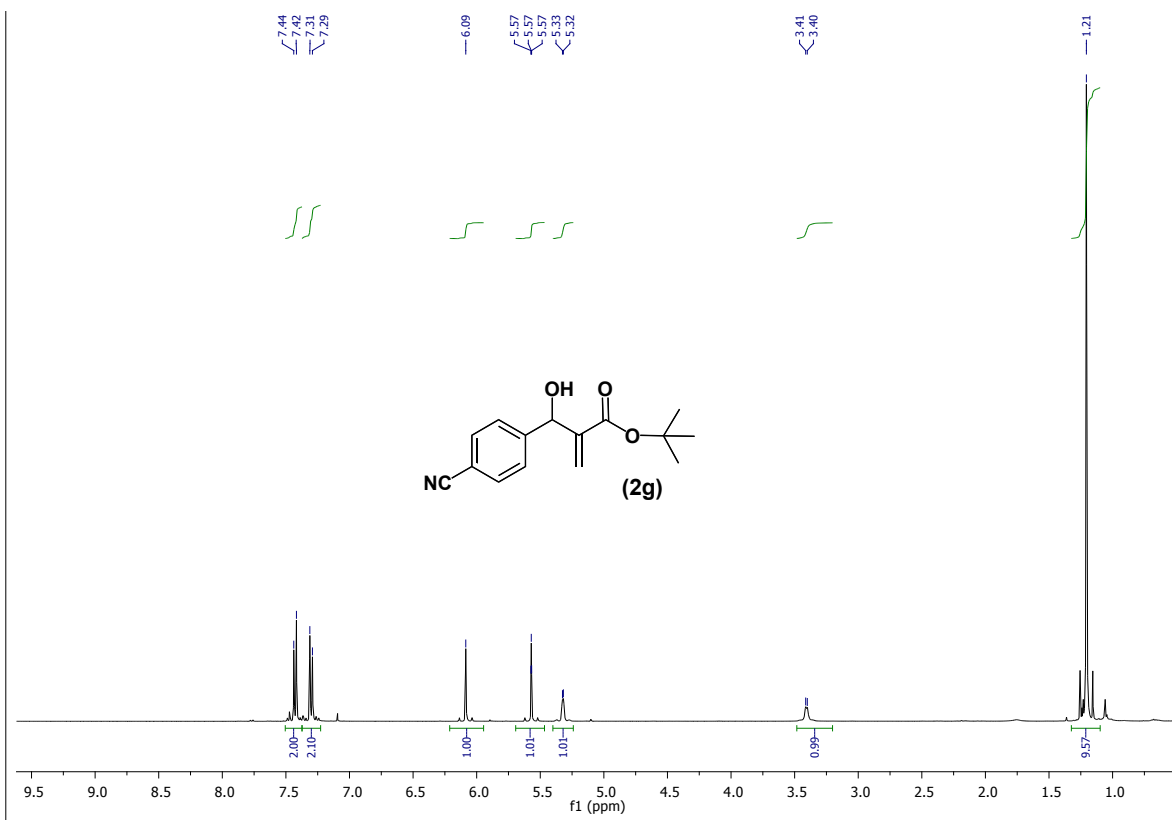




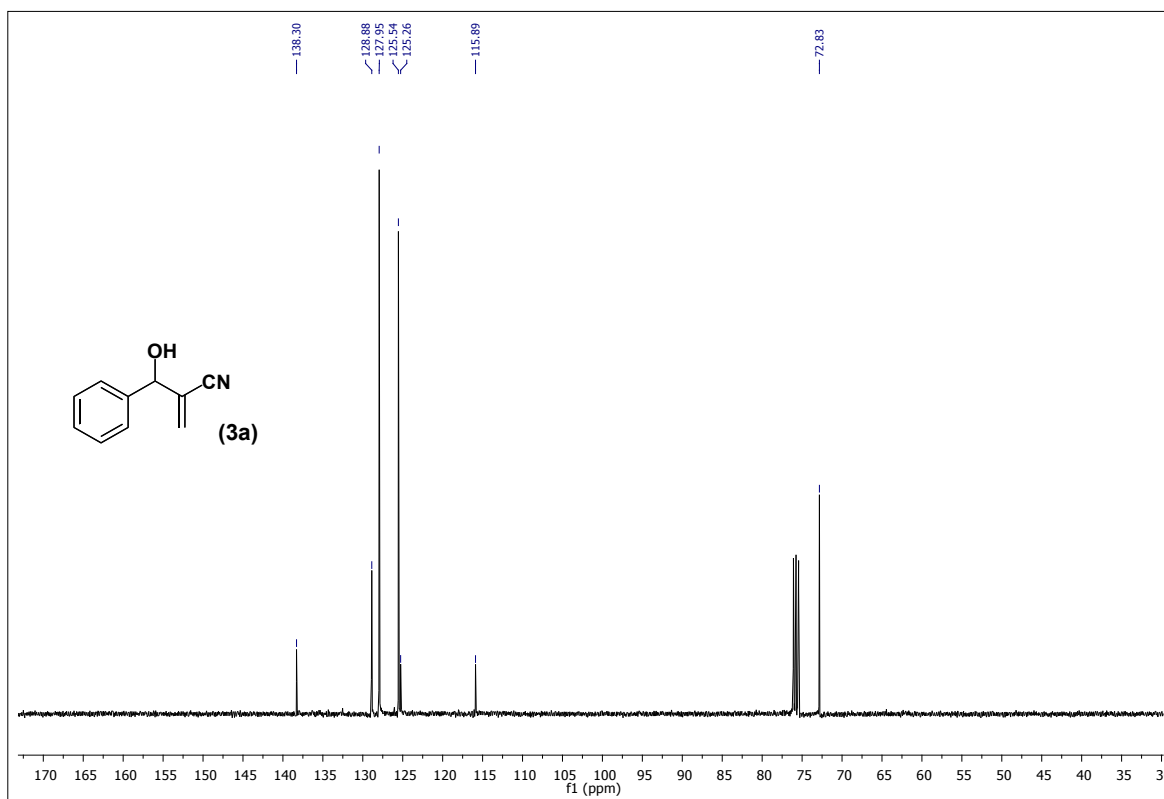
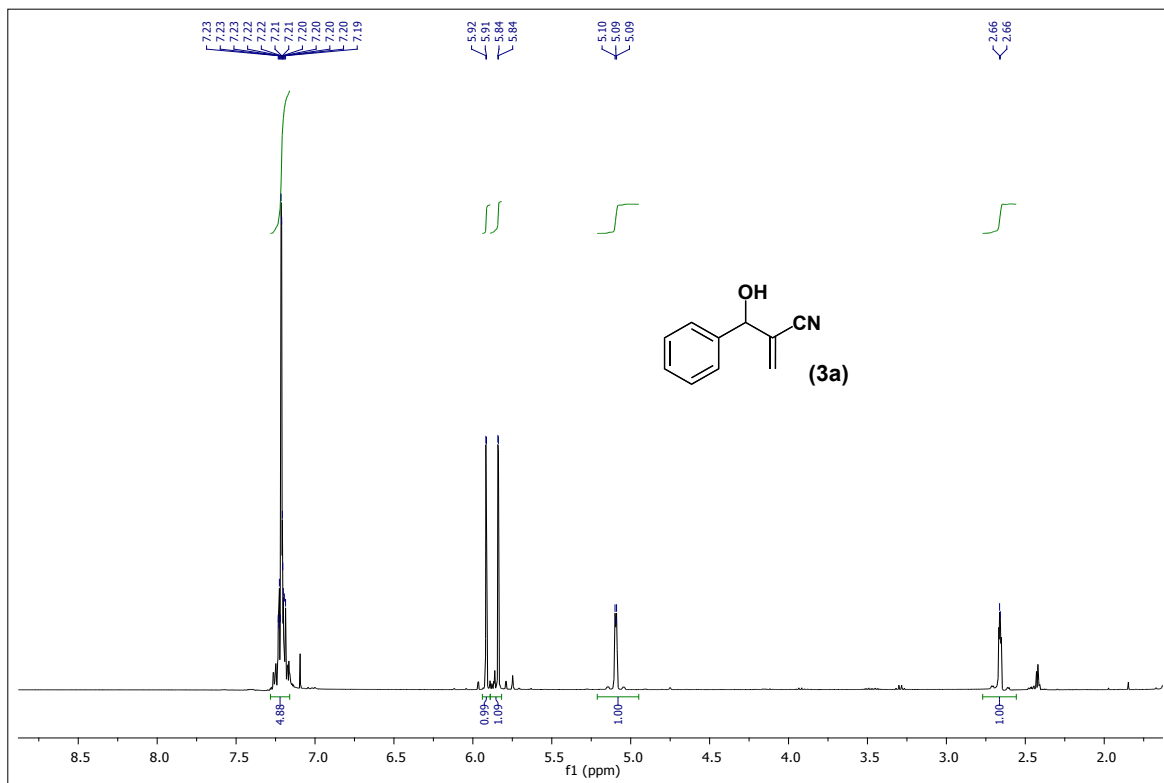


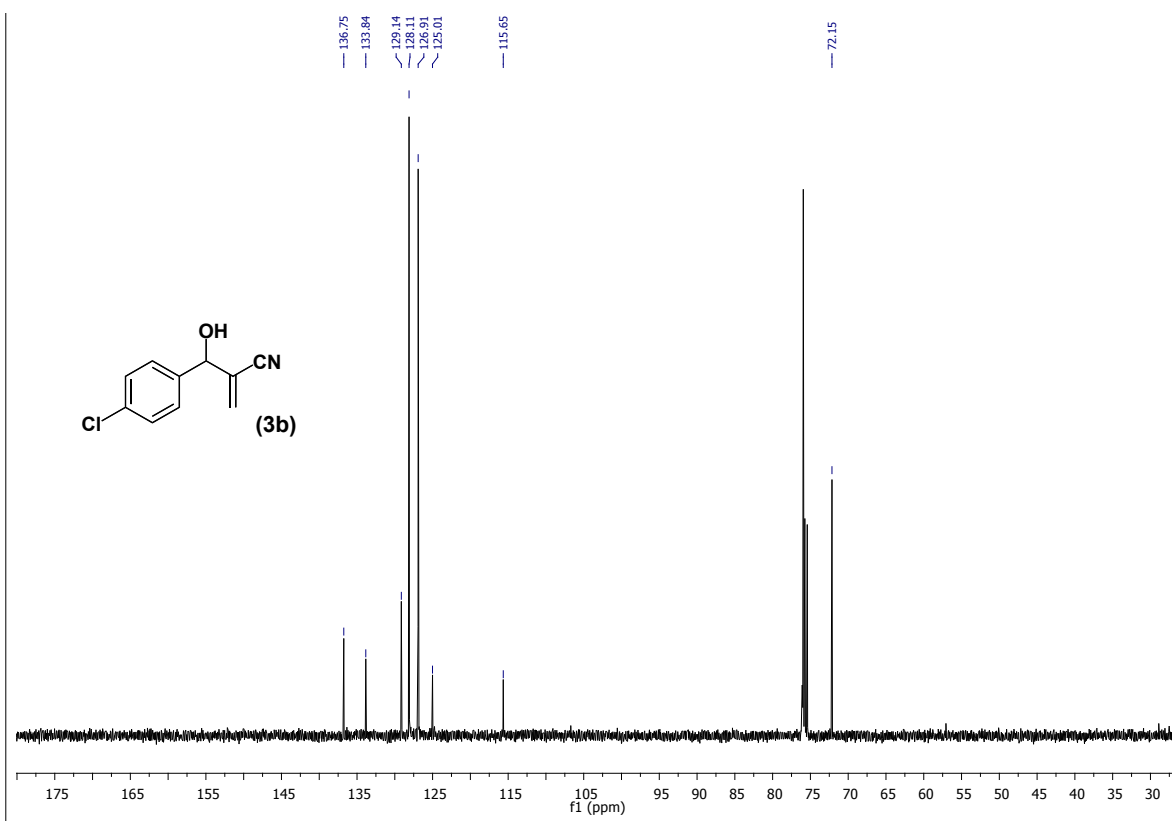
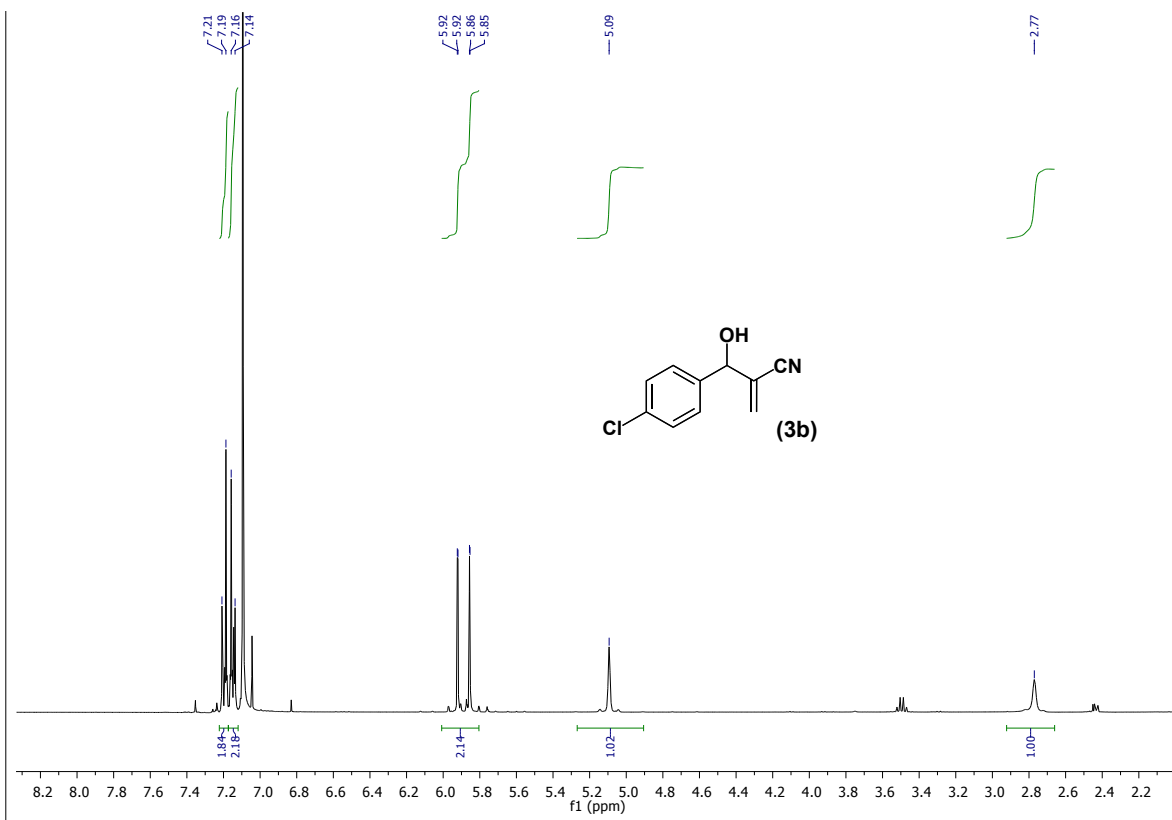


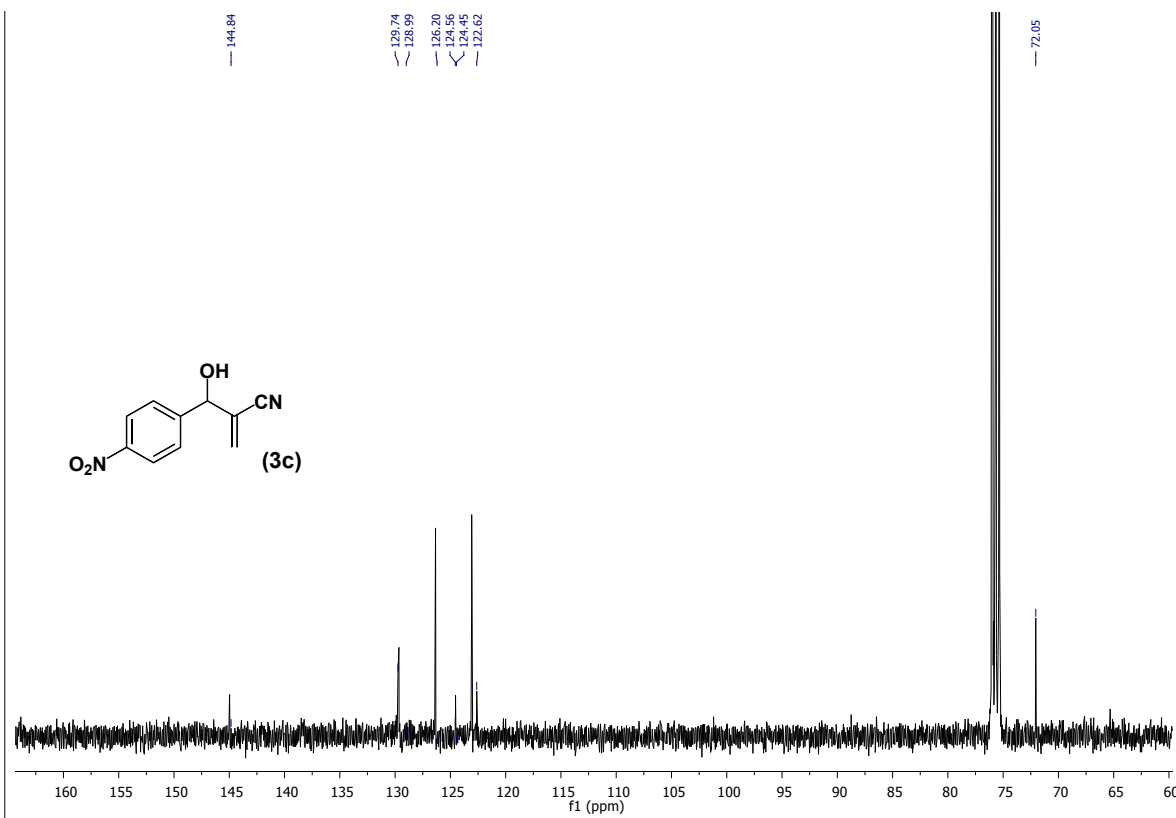
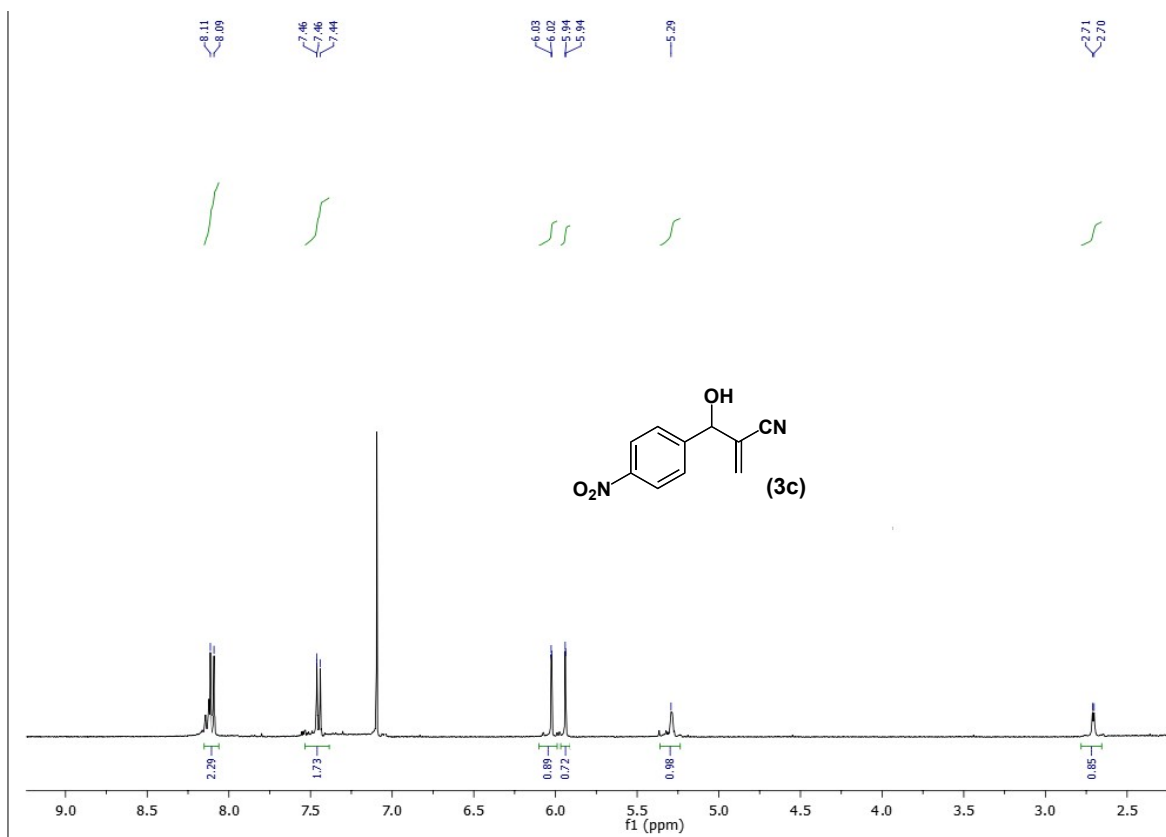


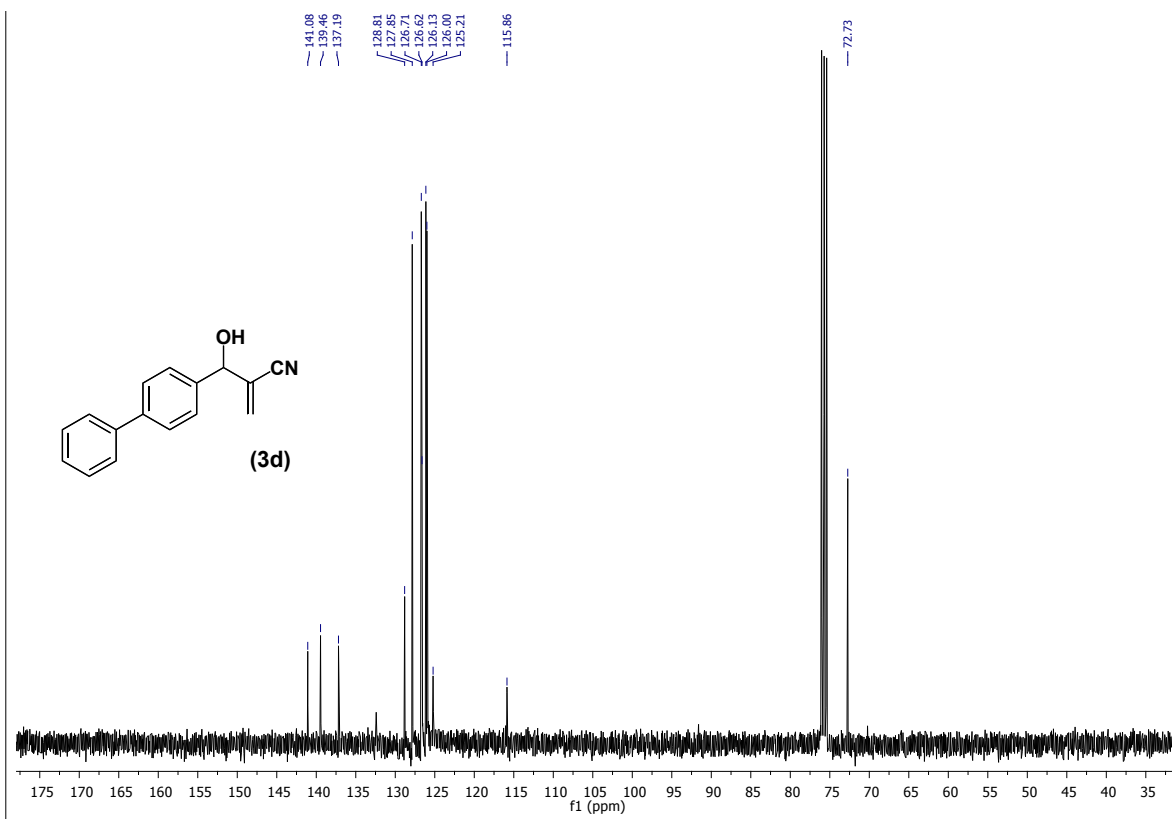
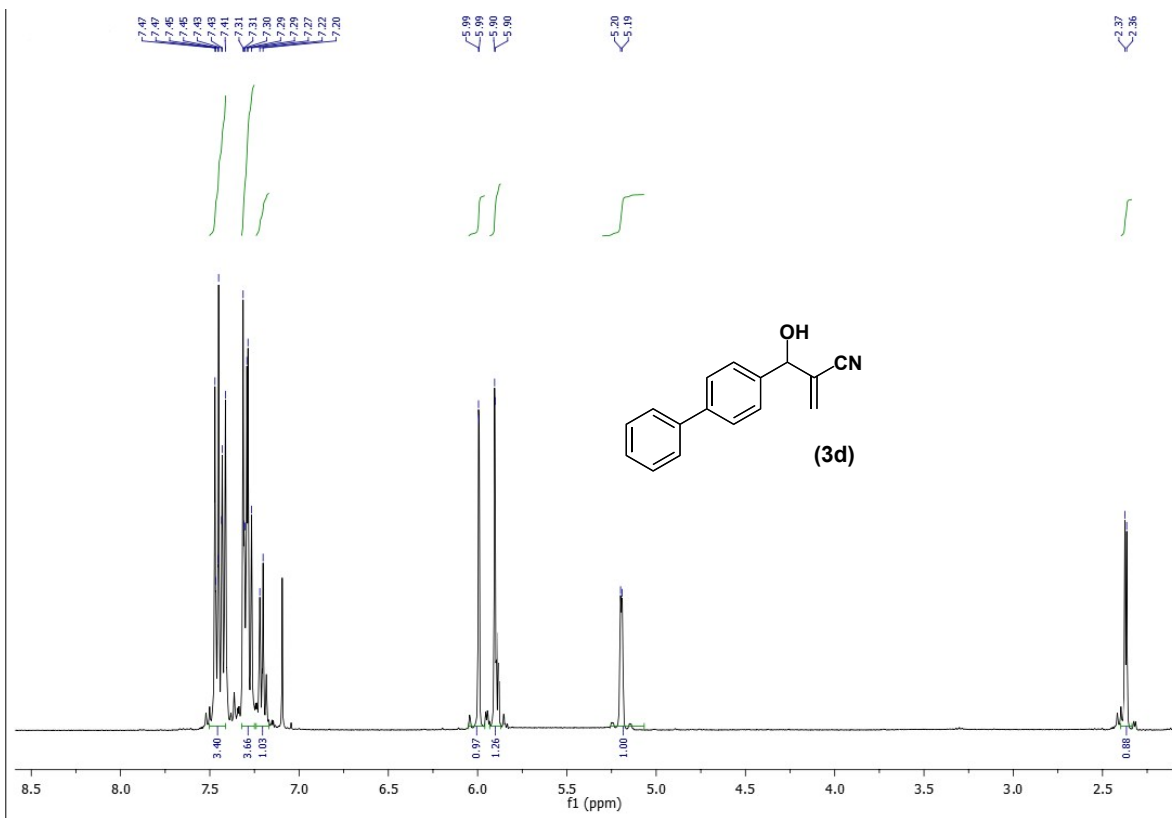


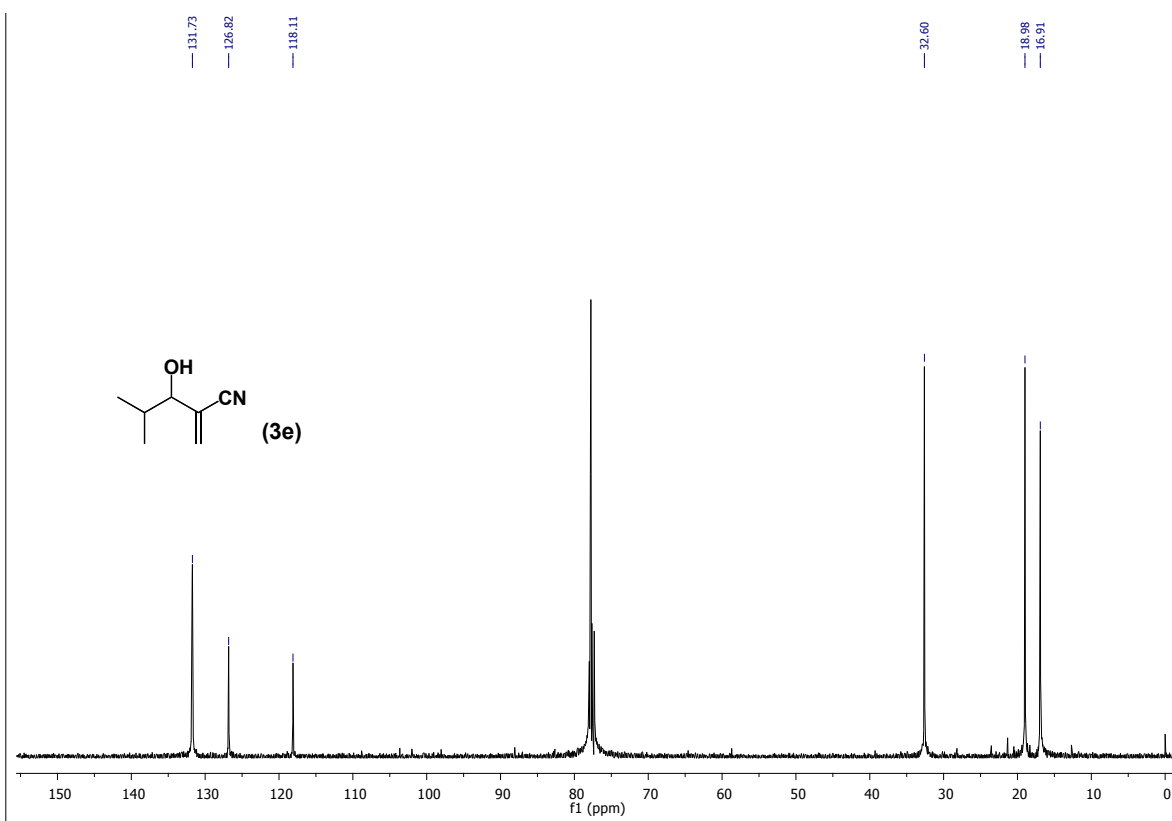
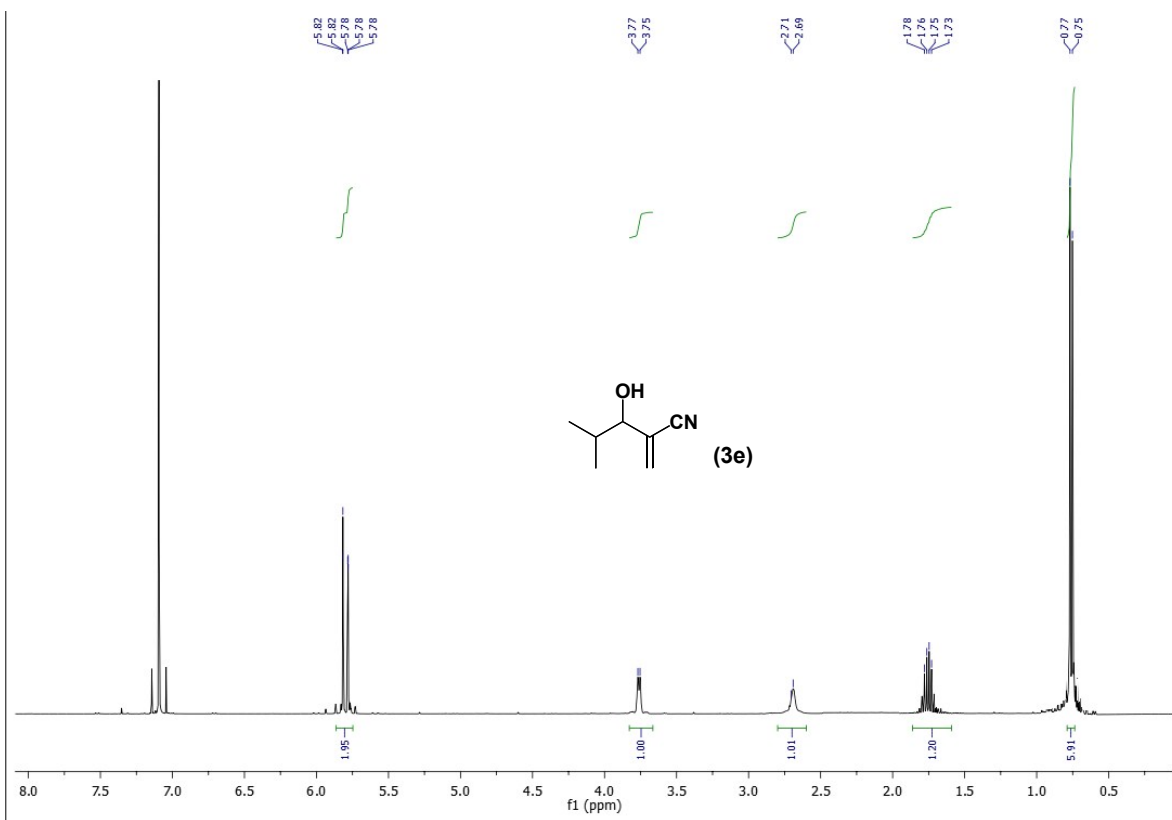
$^1\text{H}$  (400 MHz) and  $^{13}\text{C}$  NMR (100 MHz) Spectra for Baylis-Hillman Products with Acrylonitrile in  $\text{CDCl}_3$

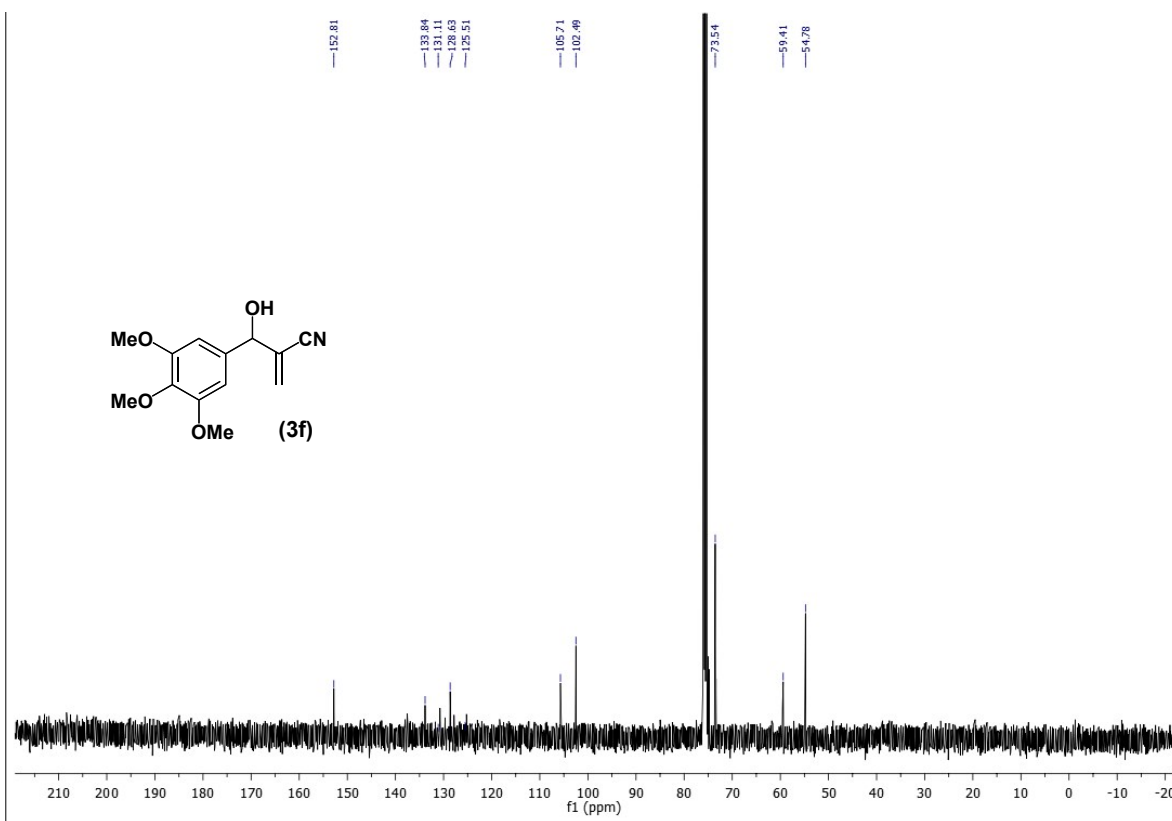
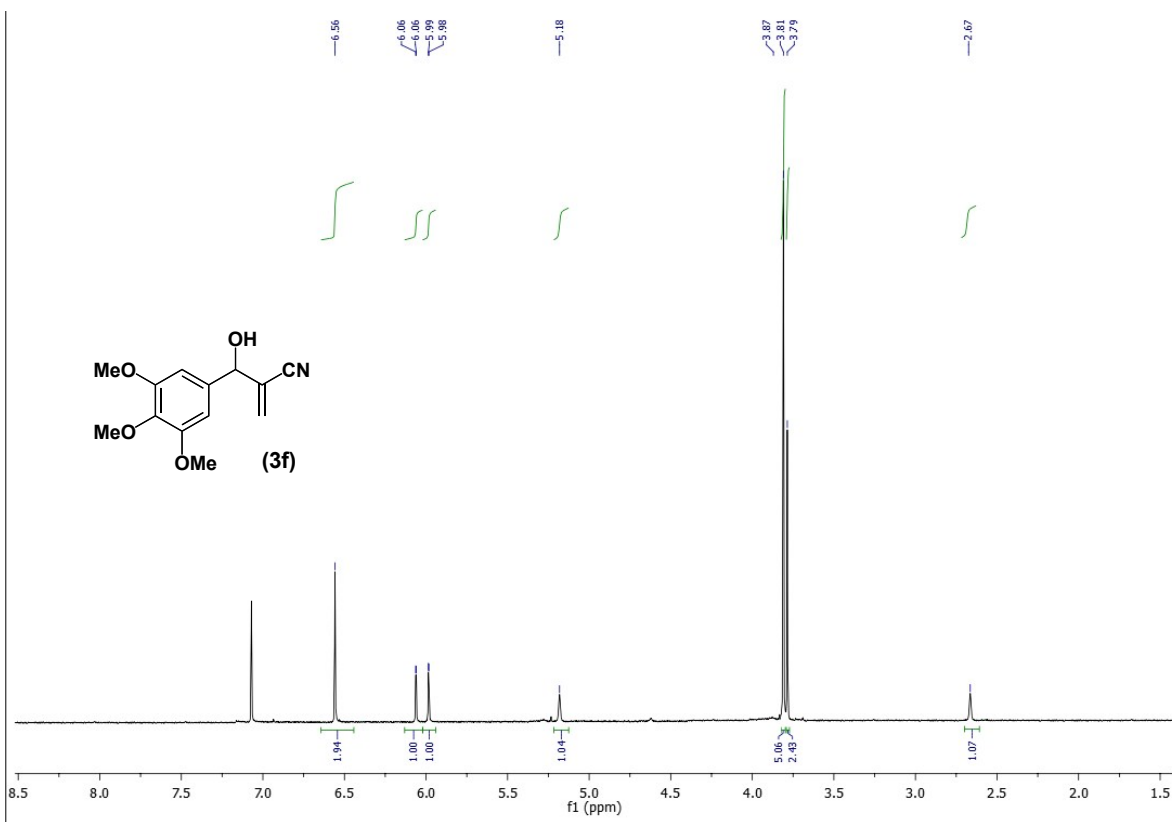




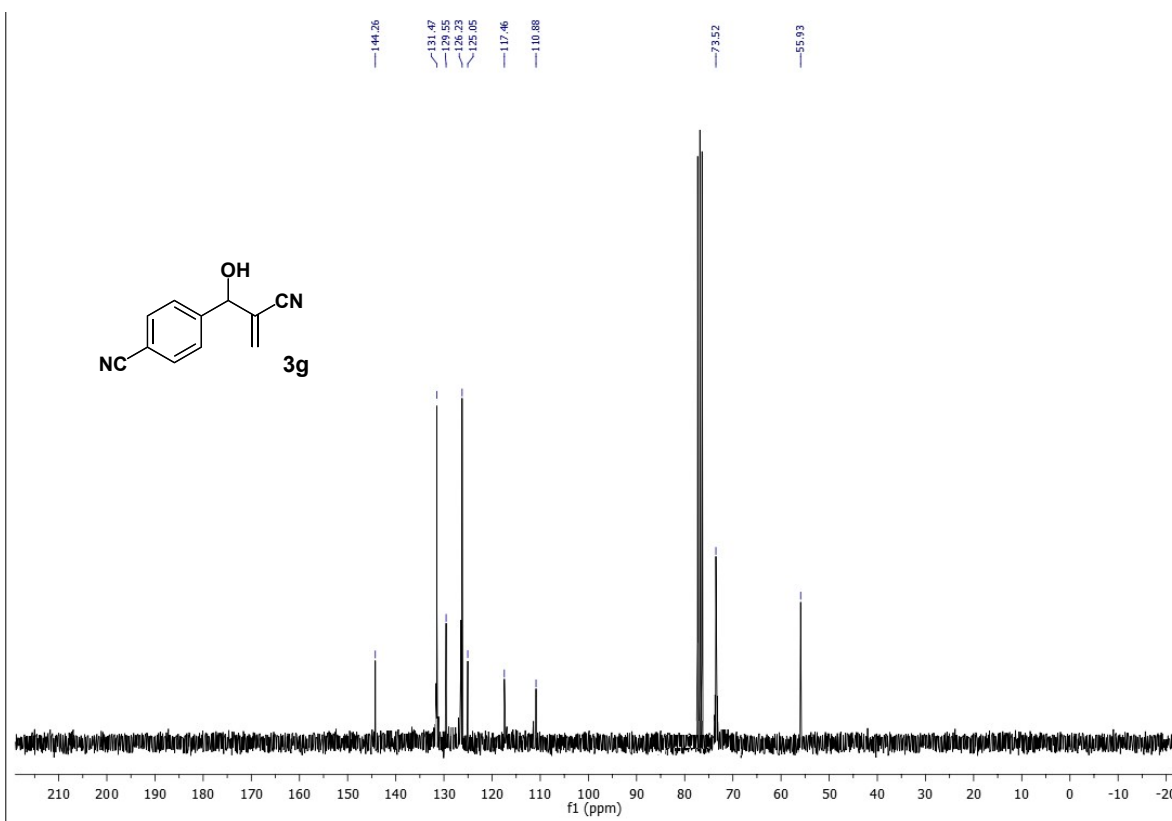
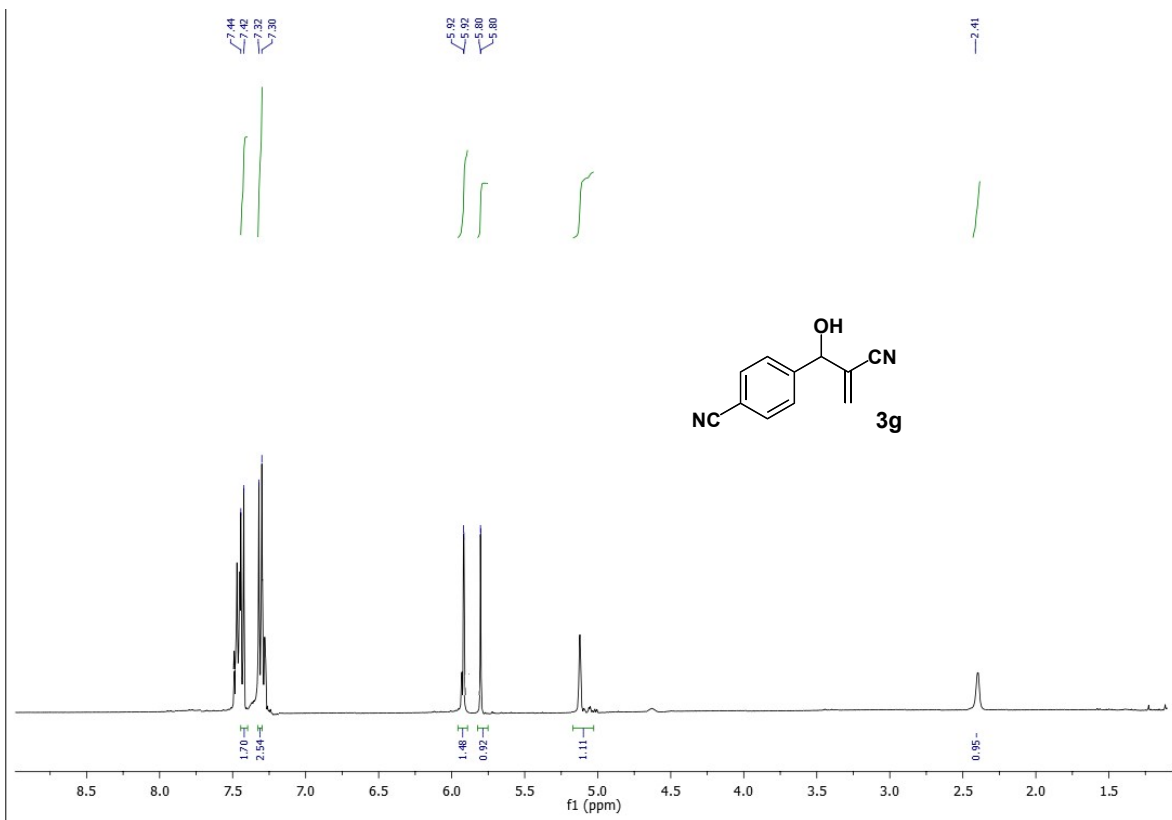




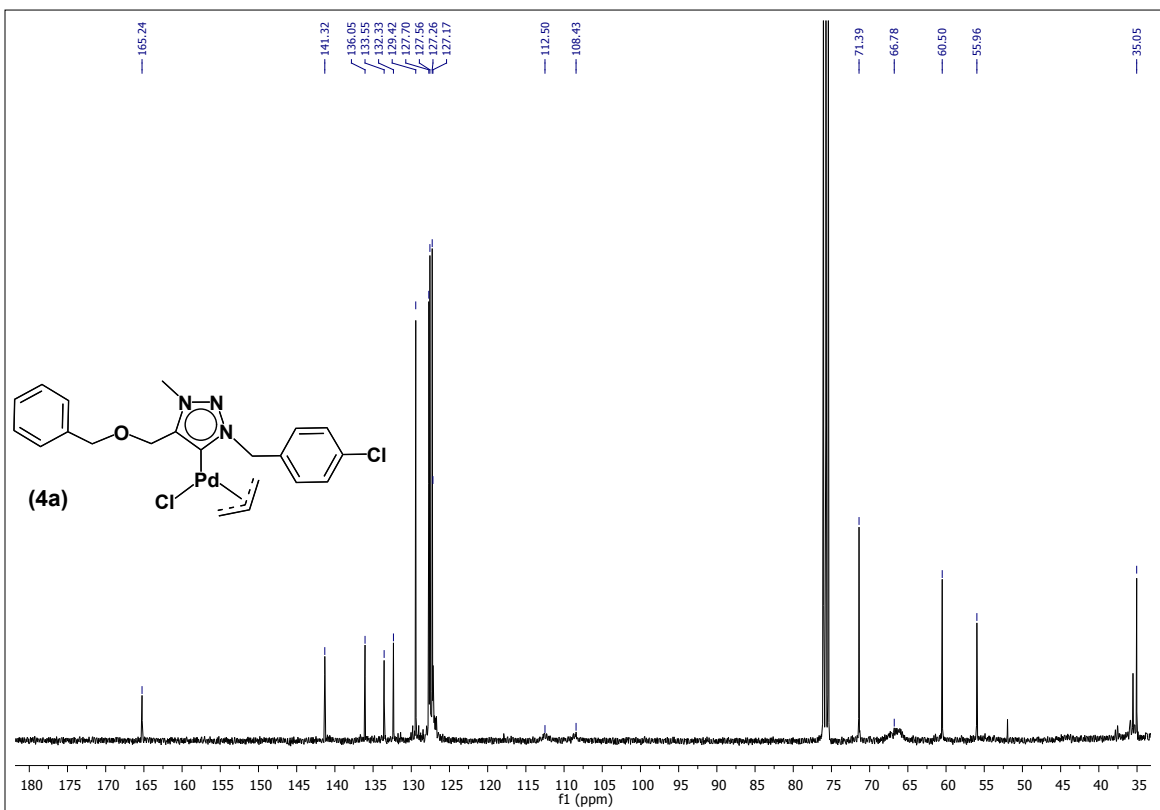
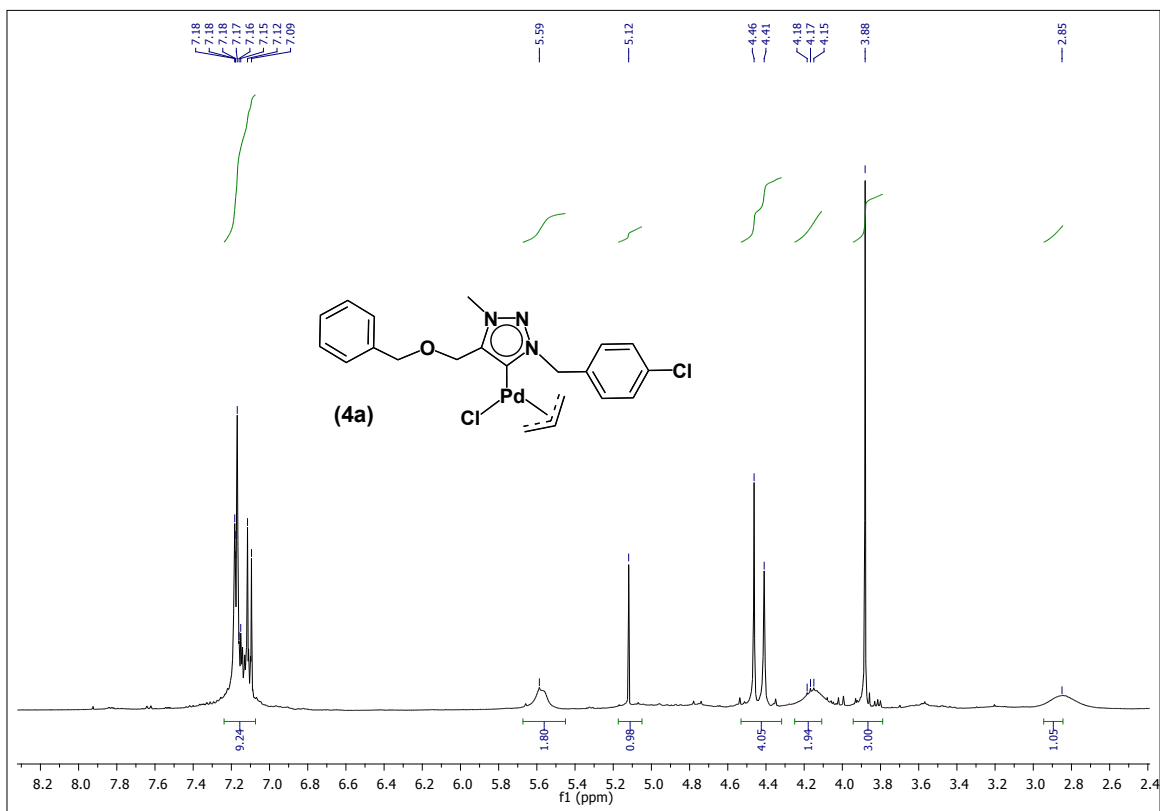


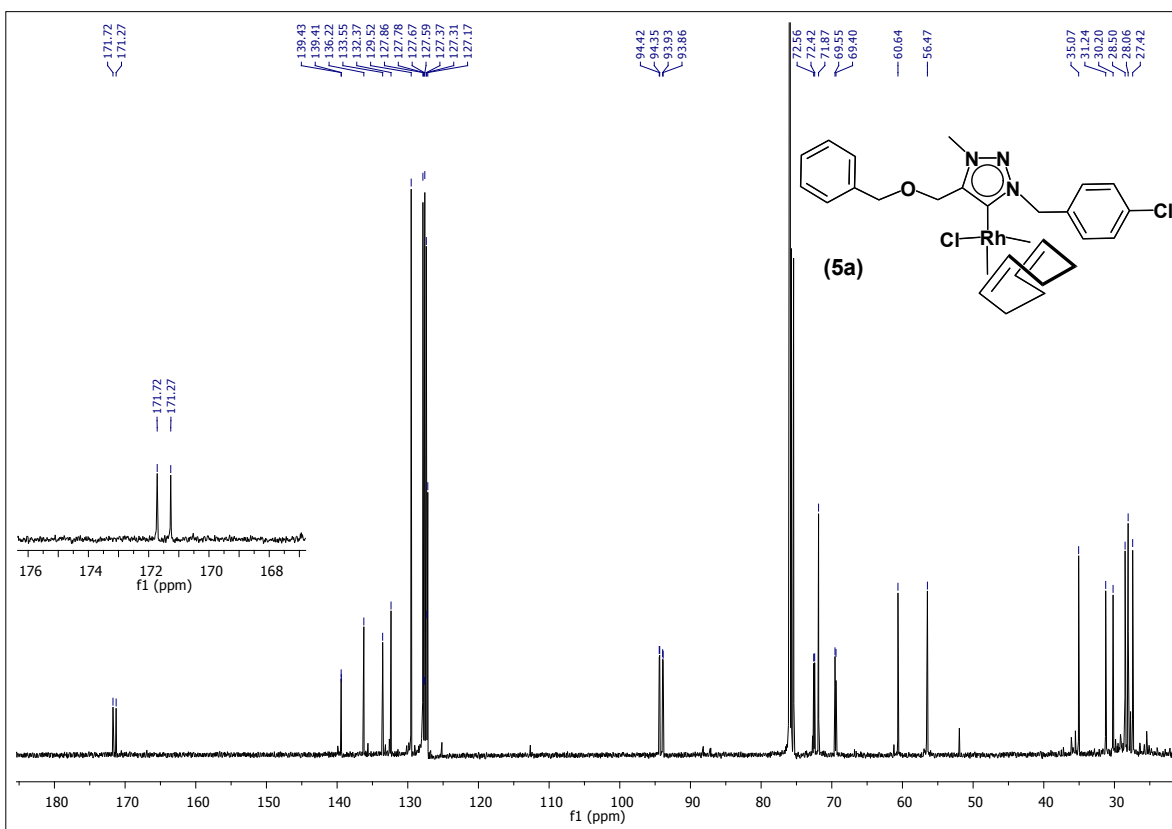
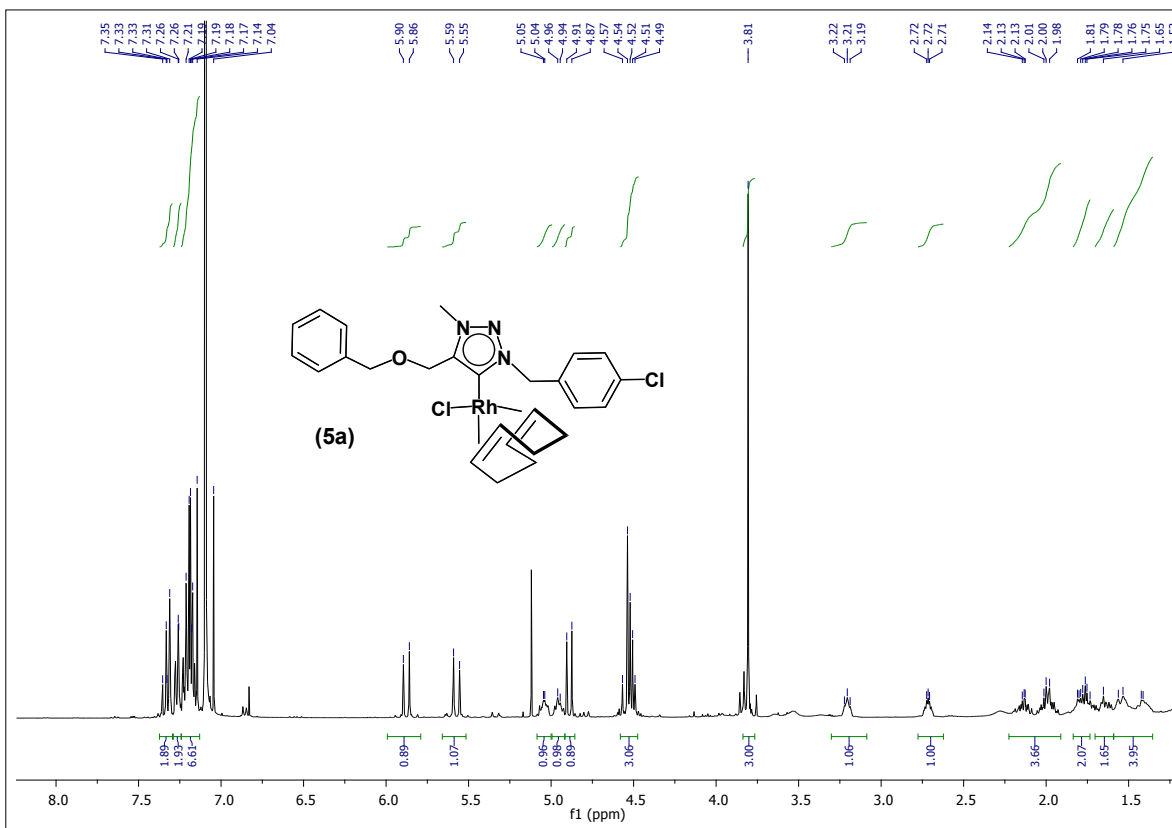


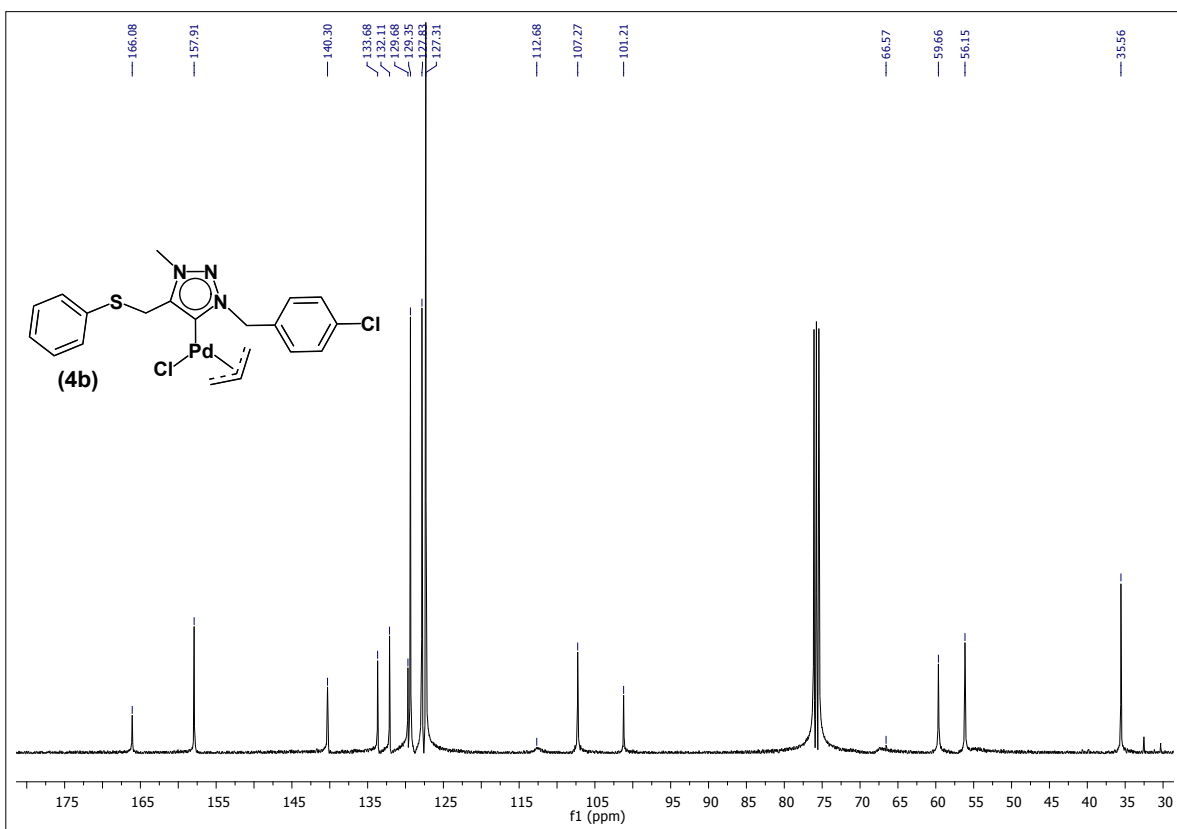
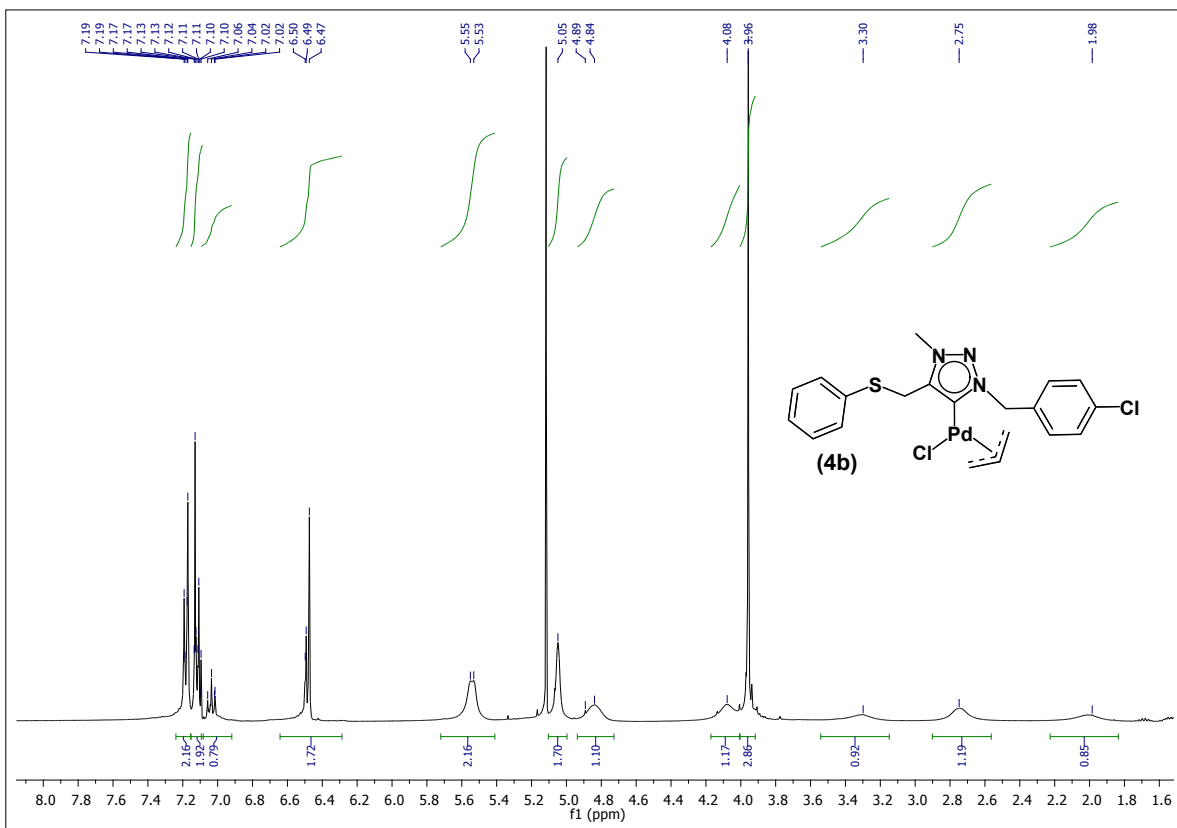


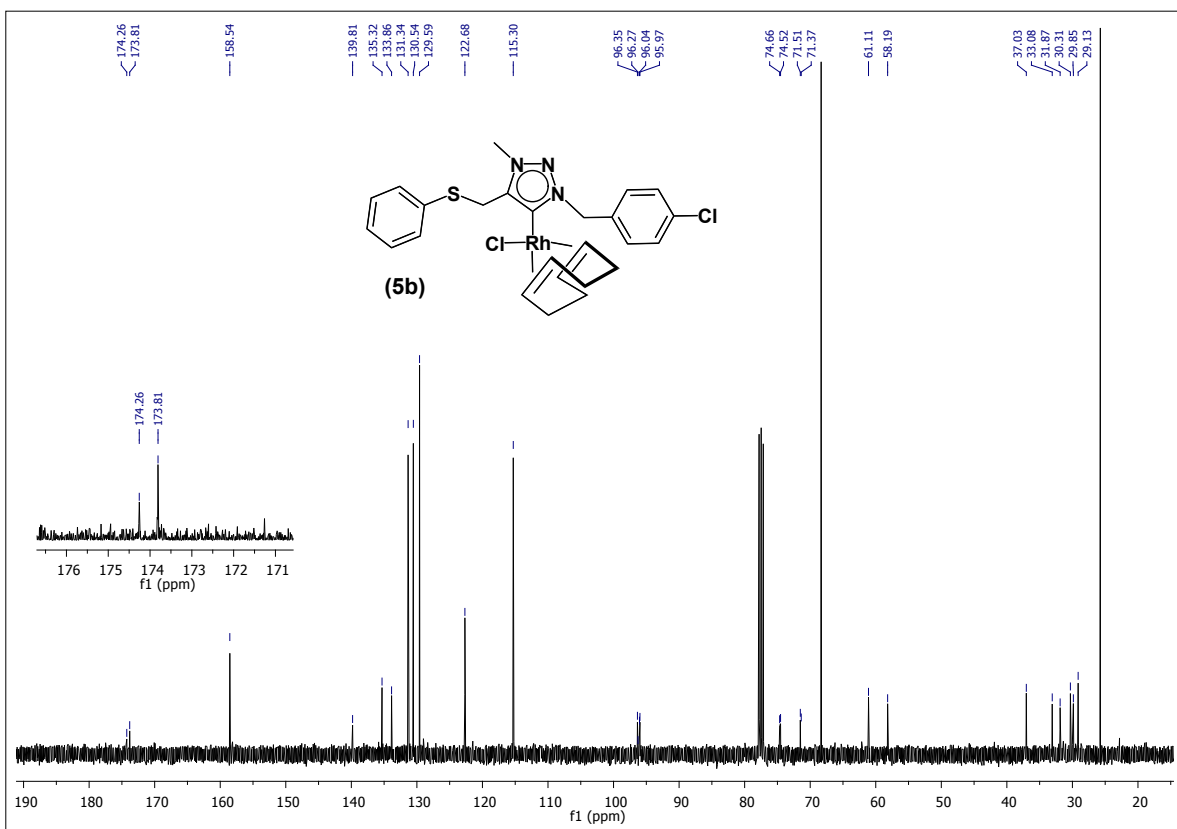
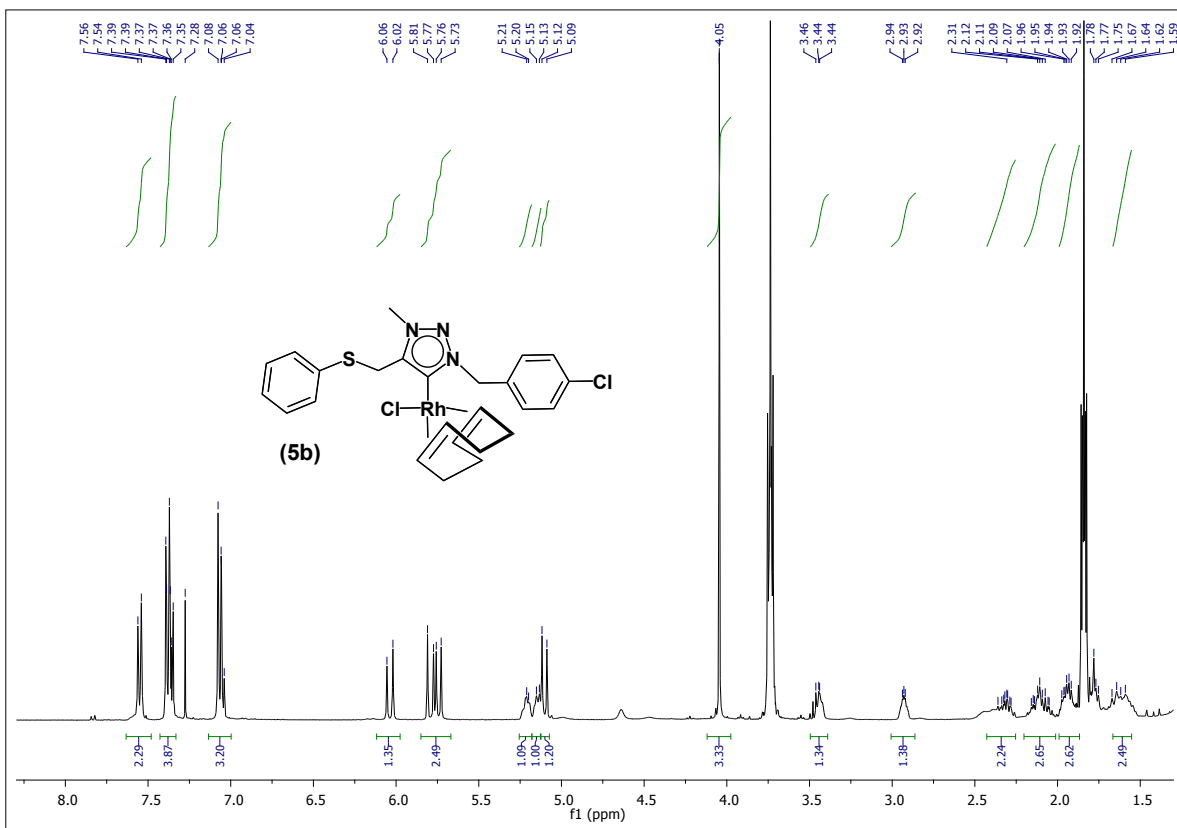


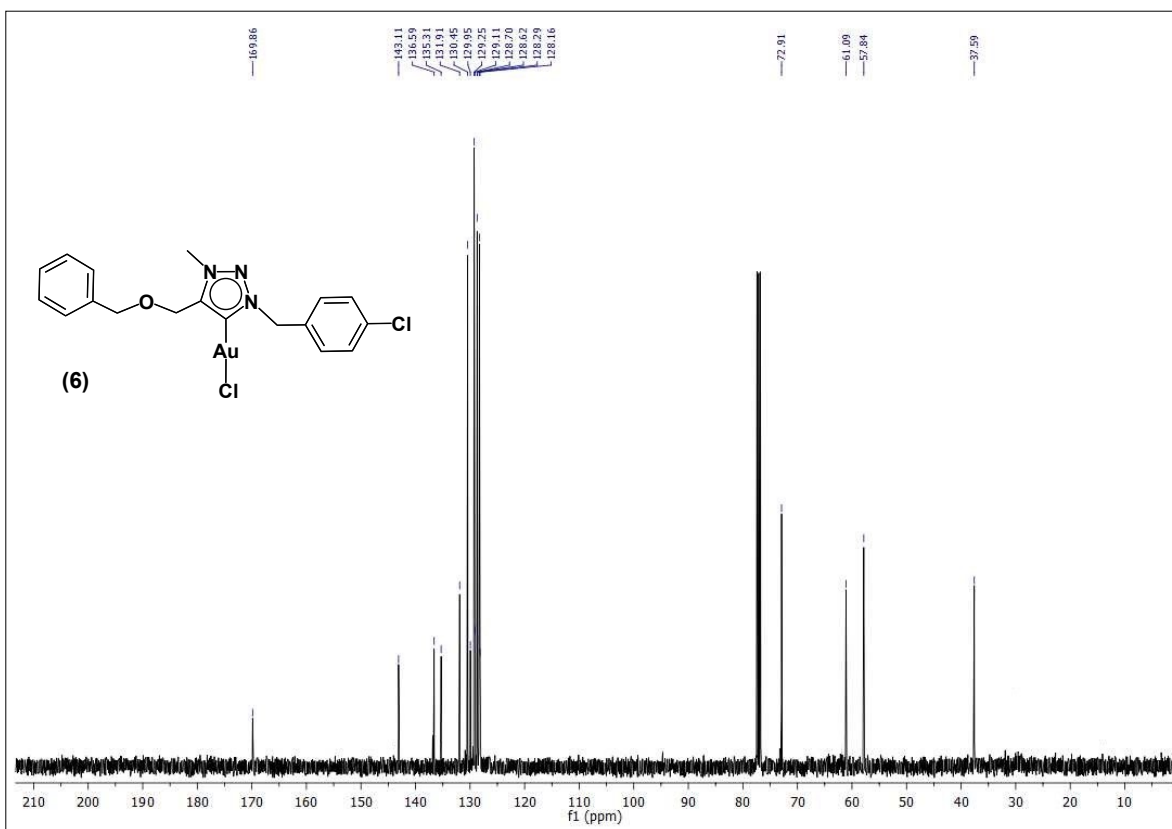
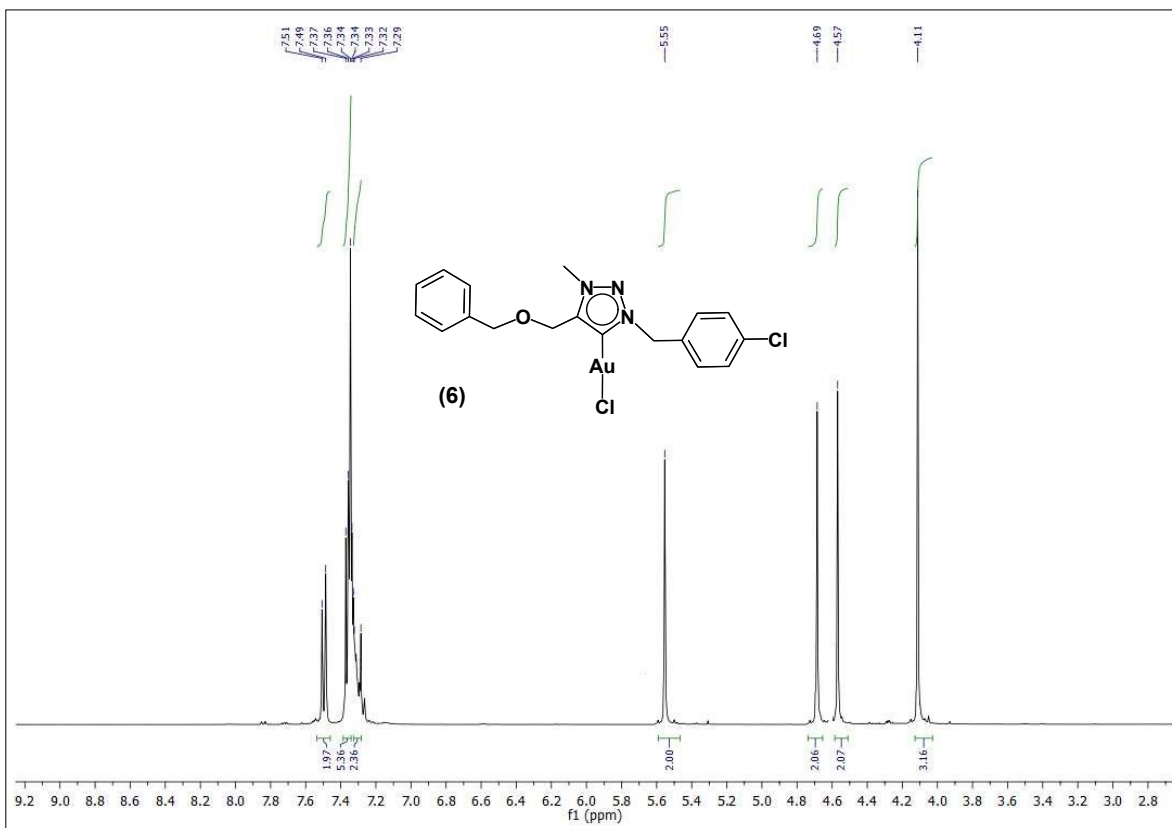
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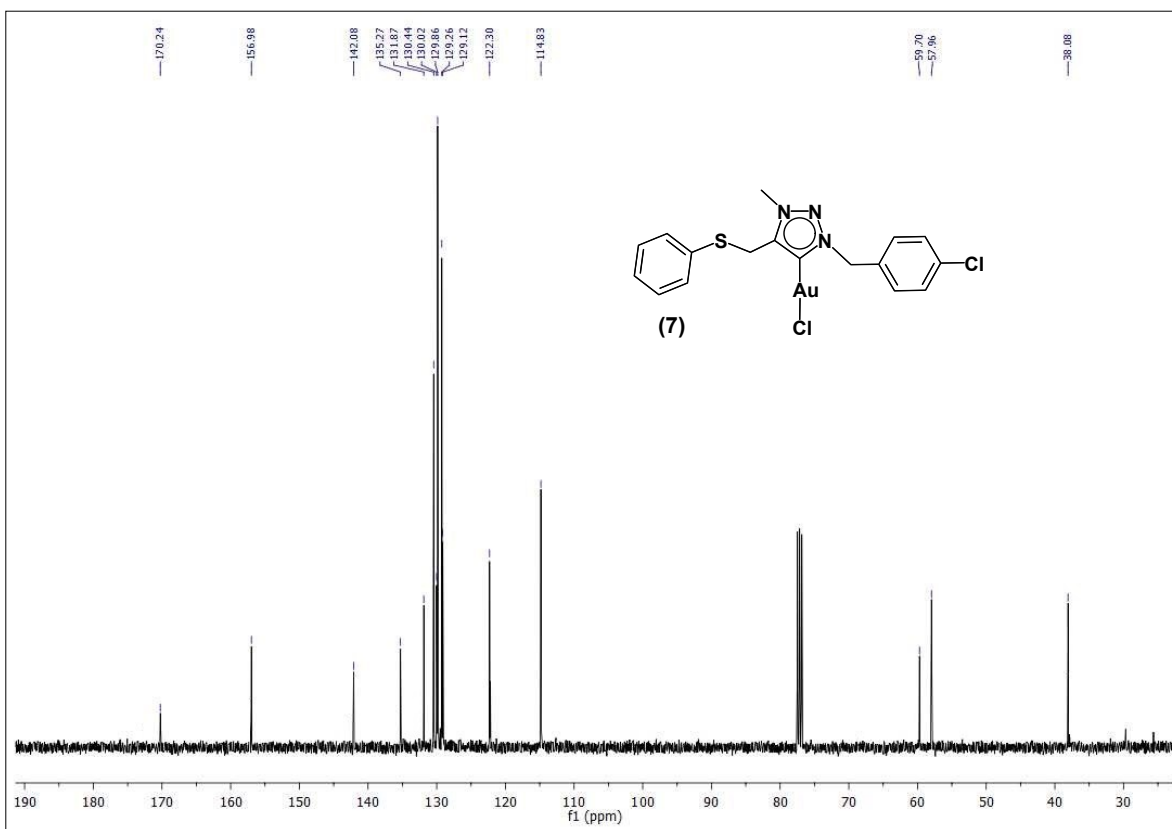
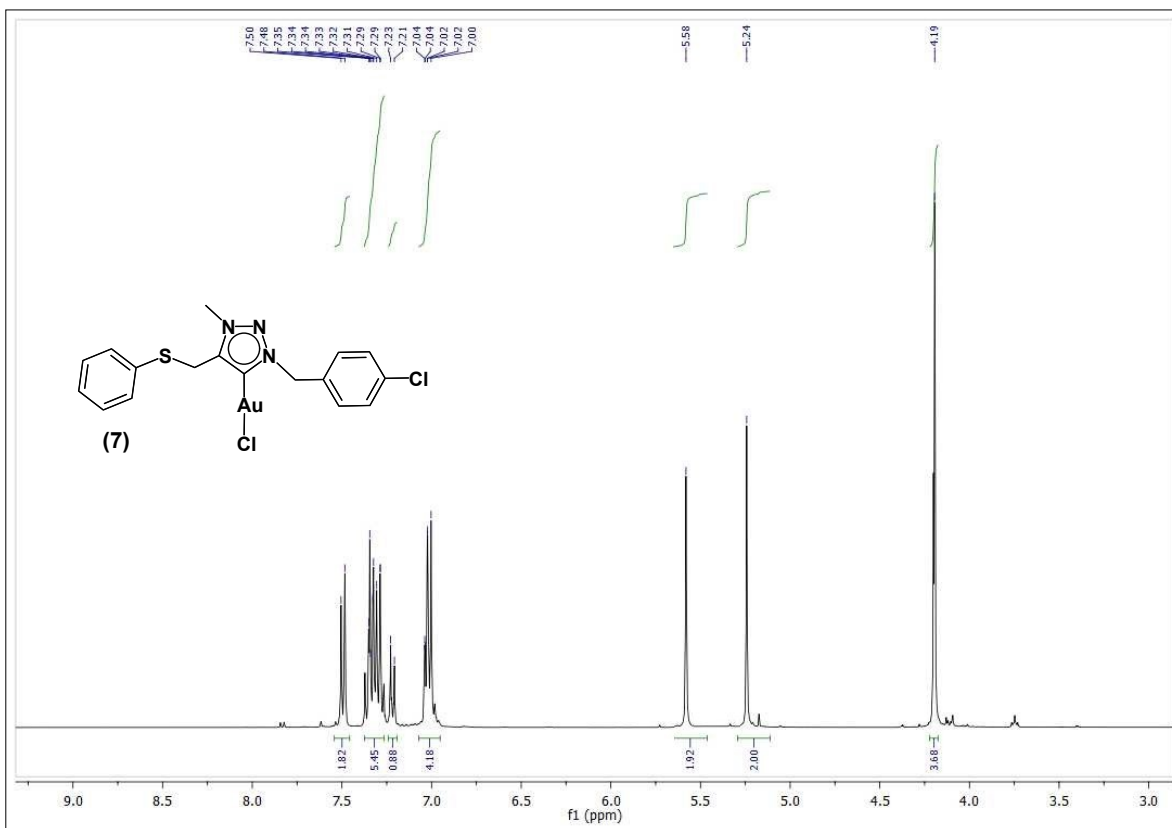


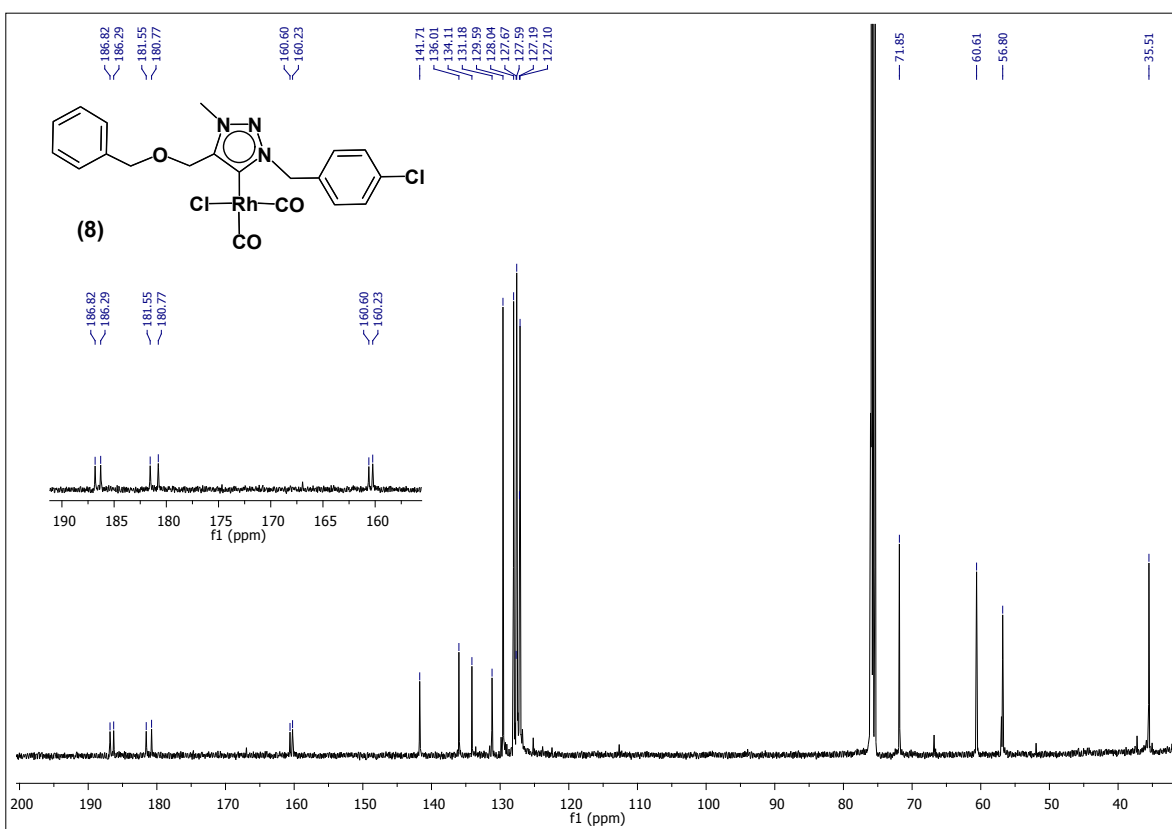
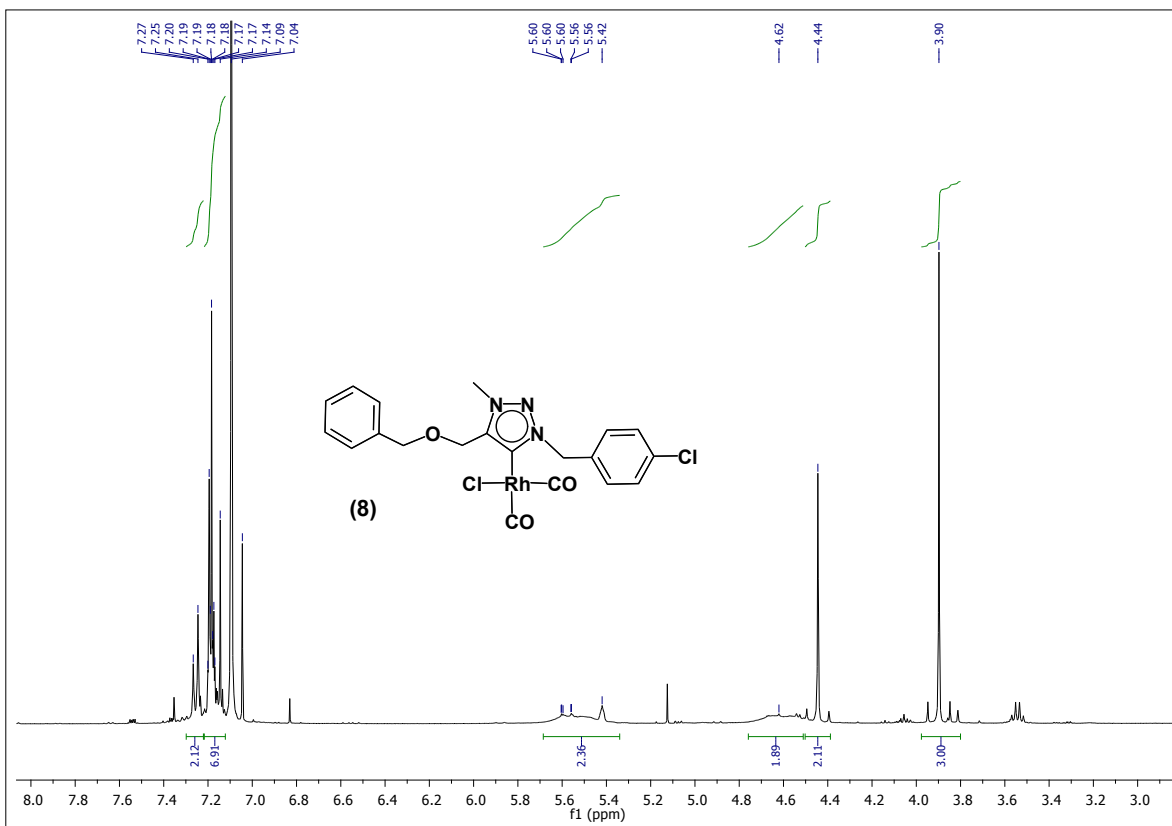




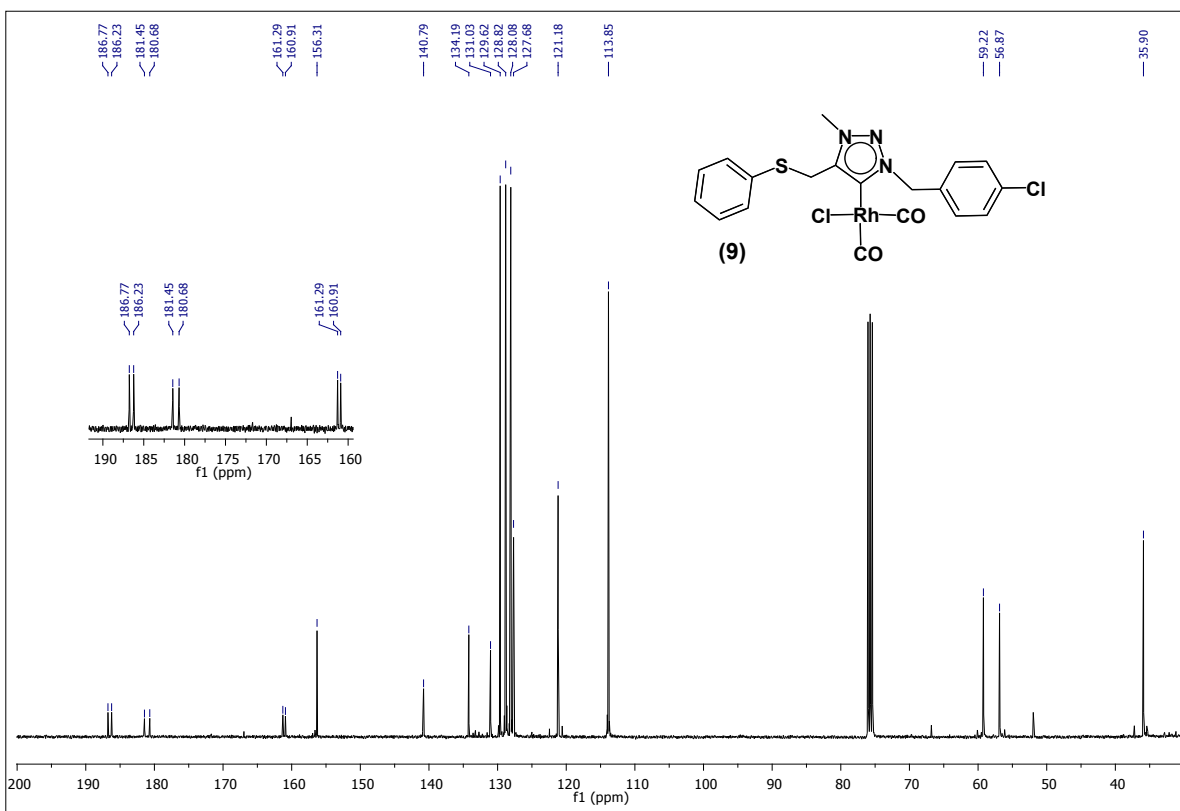
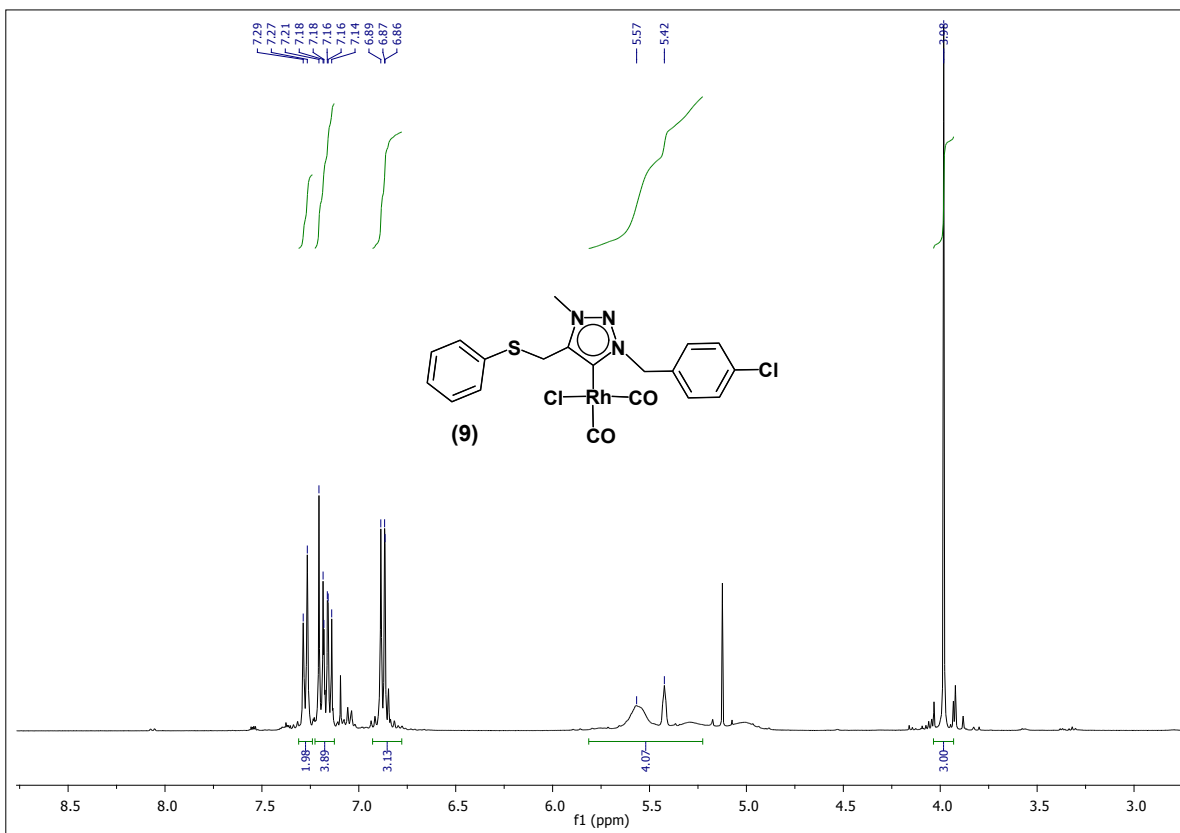












FT-IR Spectra of complexes **8** and **9** (neat)

