An Improved Catalyst Architecture for Rhodium (III) Catalyzed C–H Activation in Pyridone Syntheses

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Supporting Information

General Methods. All reactions were carried out in 1.5 dram sealed vials under an atmosphere of air with magnetic stirring in an aluminum-heating block without drying or degassing of the vial. ACS grade 1,2 dichloroethane was purchased from Fischer Scientific and used without further purification. 1-phenyl-1-buyne, methylphenyl propiolate, 4-methyl-2-pentyne, di-phenyl acetylene, and 1-phenyl-1-hexyne, 2-methylpent-1-en-3-yne, benzaldehyde-α-d_1, 2-Acetyl-*N*-methyl pyrrole, and hept-2-yne were purchased Sigma-Aldrich Chemical Company and used without further purification. Angelic Acid was purchased from TCI Chemical Company and used without further purification. Triethylsilyl phenylacetylene,[1] 1-methoxy-4-((4-(trifluoromethyl)phenyl)ethynyl)benzene,[2] (cyclopropylethynyl)-benzene,[3] and tert-butyl (3-phenylprop-2-yn-1-yl)carbamate,[4] was prepared via literature procedure. Tert-butyldimethyl((3-phenylprop-2-yn-1-yl)oxy)silane was prepared using a standard silyl protecting group procedure. $[RhCp^*Cl_2]_2$ was prepared via a literature procedure or purchased from Strem Chemical Company.[5] Di(*tert*-butyl)cyclopentadiene,[6] $[RhCp^tCl_2]_2$,[7] $RhCp^*(MeCN)_3(SbF_6)_2$, and $RhCp^t(MeCN)_3(SbF_6)_2$ [8]were prepared via literature procedure from or purchased from Strem Chemical Company. Column chromatography was performed on SiliCycle® Silica Flash® 40-63µm 60A. Thin Layer chromatography was performed on SiliCycle® 250 µm 60A plates. Visualization was accomplished with UV light (254 nm), $KMnO_4$, and CAM.

^1H NMR and ^{13}C NMR spectra were recorded on a Varian 300 and 400 MHz spectrometers at ambient temperature. ^1H NMR data are reported as the following: chemical shift in parts per million (δ, ppm) from chloroform ($CHCl_3$) taken as 7.26 ppm, integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, dd=doublet of doublets) and coupling constant (Hz). ^{13}C NMR are reported as the following: chemical shifts are reported in ppm from $CDCl_3$ taken as 77.0 ppm. Mass spectra were obtained on a Fisons VG Autospec. Infrared spectra (IR) were obtained on Bruker Tensor 27 FT-IR spectrometer. Regioselectivity was determined from nOe spectroscopy. Regioselectivities were assigned based on the shift of the N-methyl peak and correlation with known compounds.

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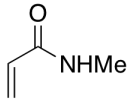
[1] Batail, N.; Bendjeriou, A.; Lomberget, T.; Barret, R.; Dufaud, V.; Djakovitch, L. *Adv. Synth. Catal.* **2009**, *351*, 2055.
[2] Shirajawa, E.; Kitabata, T.; Otsuka, H.; Tsuchimoto, T. *Tetrahedron* **2005**, *61*, 9878.
[3] Ma, S.; He, Q. *Tetrahedron* **2006**, *62*, 2769.
[4] Chen, M.; Weng, Y.; Gua, M.; Zhang, H.; Lei, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 2279.
[5] Fujita, K.; Takahashi, Y.; Owaki, M.; Yamamoto, K.; Yamaguchi, R. *Org. Lett.* **2004**, *6*, 2785.
[6] Venier, C. G.; Casserly, E. W. *J. Am. Chem. Soc.* **1990**, *112*, 2808.
[7] Qing-an, K.; Guo-xin, J. *Yingyong Huaxue* **2001**, *18*, 322.
[8] White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654.

General procedure for synthesis of Amides:

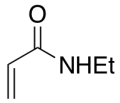
Amides **1a**, **1f**, **1h**, and **1i** were prepared from the corresponding acid chloride via a literature procedure.[9] Amide **1c** was purchased from TCI America and was distilled prior to use. All other amides were prepared from the corresponding carboxylic acid using the general procedure:

To a flame dried round bottom flask charged with a magnetic stir bar under argon was added the carboxylic acid (1 equiv), amine (1.05 equiv), HOBt (0.3 equiv), EDC (1.2 equiv) and acetonitrile (2 M). To the reaction mixture was added triethylamine (1.05 equiv) over 5 minutes at room temperature. The reaction was allowed to stir under the reaction was complete as indicated by TLC. The reaction was concentrated *in vacuo* before dissolving in dichloromethane and washed with water (2 x 20 ml), brine (1 x 20 ml) dried over $MgSO_4$, and concentrated *in vacuo* and purified via column chromatography.

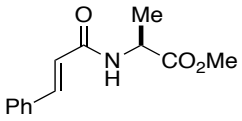
Acrylamide Characterization



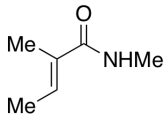
N-methylacrylamide (1a): ^{1}H (400 MHz, $CDCl_3$) δ 6.22 (dd, 1H, *J*=16.8 Hz, *J*=1.6 Hz), 6.08 (dd, 1H, *J*=16 Hz, *J*=10.4 Hz), 5.95 (s, br, 1H) 5.58 (dd, 1H, *J*=10 Hz, *J*=1.6 Hz), 2.85 (s, 1.5H), 2.84 (s, 1.5H);^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 130.7, 126.0, 26.2.



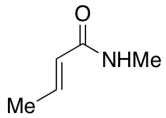
N-ethylacrylamide (1b): ^{1}H (400 MHz, $CDCl_3$) δ 6.6 (s, br, 1H) 6.13 (m, 2H), 6.08 (dd, 1H, *J*=16 Hz, *J*=10.4 Hz), 5.52 (dd, 1H, *J*=9.6 Hz, *J*=2 Hz), 3.27 (m, 2H), 1.09 (t, 3H, *J*=4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 131.1, 125.6, 34.3, 14.5.



(*S*)-methyl 2-cinnamamidopropanoate (1c): ^{1}H (400 MHz, $CDCl_3$) δ 7.59 (dd, 1H, *J*=15.6 Hz, *J*=1.2 Hz), 7.47-7.43 (m, 2H), 7.36-7.29 (m, 3H), 6.49-6.41 (m, 1H), 4.74 (q, 1H, *J*=7.6 Hz), 3.73 (d, 3H, rotamer), 1.45 (dd, 3H, rotamer, *J*=4.4 Hz, *J*=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 141.6, 134.6, 130.4, 129.7, 129.0, 128.8, 128.2, 127.8, 120.1, 52.5, 48.1, 18.5.

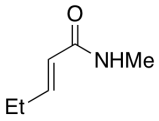


(*E*)-*N*,2-dimethylbut-2-enamide (1e): ^{1}H (400 MHz, $CDCl_3$) δ 6.40 (dq, 1H, *J*=6.8 Hz), 5.7 (s, br, 1H), 2.85 (s, 1.5H), 2.84 (s, 1.5H), 1.82 (s, 3H), 1.72 (d, 3H, *J*=6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 131.6, 130.4, 26.4, 13.8, 12.3.

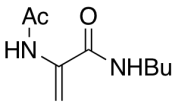


(*E*)-*N*-methylbut-2-enamide (1f): ^{1}H (400 MHz, $CDCl_3$) δ 6.77 (dt, 1H, *J*=14 Hz, *J*=6.8 Hz), 5.71 (dd, 1H, *J*=13.6 Hz, *J*=1.6 Hz), 5.41 (s,br, 1H), 2.80 (s, 1.5H), 2.79 (s, 1.5H), 1.77 (dd, 3H, *J*=6.8 Hz, *J*=1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 139.6, 124.8, 26.2, 17.6.

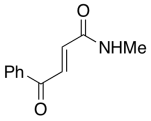
[9] Hyster, T. K.; Rovis, T. *J. Am. Chem. Soc.* **2010**, *132*, 10565.



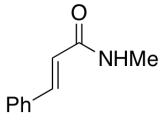
(*E*)-*N*-methylpent-2-enamide (1g): ^{1}H (400 MHz, $CDCl_3$) δ 6.81 (dt, 1H, *J*=6.4 Hz, *J*=15.6 Hz), 5.67 (dt, 1H, *J*=15.6 Hz, *J*=1.6 Hz), 5.45 (s, br, 1H), 2.81 (s, 1.5H), 2.80 (s, 1.5H), 2.13 (dq, 2H, *J*=7.2 Hz, *J*=1.2 Hz), 0.98 (t, 3H, *J*=7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 145.9, 122.3, 26.2, 25.0, 12.4.



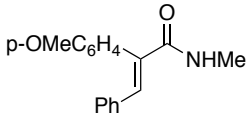
2-acetamido-*N*-butylacrylamide (1h): ^{1}H (400 MHz, $CDCl_3$) δ 8.08 (s, br, 1H), 6.39 (s, 1H), 6.18 (s, br, 1H), 5.13 (s, 1H), 3.32 (m, 2H), 2.09 (s, 1.5H), 2.08 (s, 1.5H), 1.52 (m, 2H), 1.33 (m, 2H), 0.91 (dt, 3H, *J*=7.2 Hz, *J*=1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 163.8, 134.4, 100.1, 39.8, 31.4, 24.7, 19.9, 13.6.



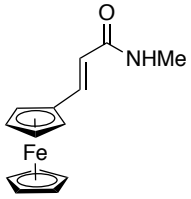
(E)-N-methyl-4-oxo-4-phenylbut-2-enamide (1i): ^{1}H (400 MHz, $CDCl_3$) δ 7.95 (m, 3H), 7.54 (m, 1H), 7.43 (m, 2H), 6.90 (d, 1H, *J*=14.8 Hz), 2.92 (s, 1.5H), 2.90 (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 164.6, 136.8, 134.9, 133.7, 133.0, 128.8, 26.7.



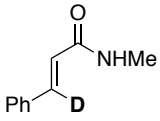
***N*-methylcinnamamide (1j)**: ^{1}H (400 MHz, $CDCl_3$) δ 7.55 (d, 1H, 15.6 Hz), 7.40 (m. 2H), 7.26 (m, 3H), 6.35 (dd, 1H, *J*=16 Hz, *J*= 4 Hz), 5.9 (s, br, 1H), 2.88 (s, 1.5H), 2.87 (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 140.7, 134.8, 129.5, 128.7, 127.7, 120.5, 26.5.



(*E*)-2-(4-methoxyphenyl)-*N*-methyl-3-phenylacrylamide (1k): ^{1}H (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.14-7.11 (m, 5H), 7.00-6.93 (m, 4H), 5.6 (s, br, 1H), 3.83 (s, 3H), 2.83 (s, 1.5H), 2.82 (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 159.6, 136.7, 135.1, 133.9, 131.1, 130.8, 128.3, 128.1, 55.2, 26.9.



(*E*)-3-(ferrocene)-*N*-methylacrylamide (1l): ^{1}H (400 MHz, $CDCl_3$) δ 7.44 (d, 1H, *J*=15.2), 5.99 (dd, 1H, *J*=15.6 Hz, *J*=3.2 Hz), 4.42 (s, 2H), 4.32 (s, 2H), 4.11 (s, 5H), 2.89 (s, 1.5H), 2.88 (s, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 140.9, 128.3, 117.5, 79.4, 780.24, 69.6, 69.4, 68.2, 36.3.



***N*-methylcinnamamide (1j'):** A 50 ml flask was charged with a stir-bar and flame dried under vacuum and cooled under argon. The flask was charged with benzaldehyde-α-d_1 (1 equiv, 5 mmol) and ethyl 2-(triphenylphosphoranylidene)acetate (1.1 equiv, 5.5 mmol). The mixture was dissolved in dichloromethane (.33 M, 15 ml) and allowed to stir at 21 °C. After the reaction was determined to be complete by TLC the mixture was concentrated *in vacuo*. The resulting residue was purified via column chromatography (9:1 Hex/EtOAc) to yield the desired α,β unsaturated ethyl ester (75% yield).

A 25 ml flask was charged with a stir-bar and flame dried under vacuum and cooled under argon. The flask was charged with methylamine hydrochloride (2 equiv, 7 mmol) and dissolved in dichloromethane. The flask was cooled to 0 °C and Me_3Al (2M in Toluene, 2 equiv, 7 mmol) was added dropwise over 30 min. The flask was allowed to stir for an additional 2h at 0 °C before the α,β unsaturated ethyl ester (1 equiv, 3.5 mmol) was added dropwise over 15 min. The resulting solution was allowed to warm to 21 °C

and stir overnight. The solution was cooled 0 °C and H_2O was added dropwise until methane loss ceased. A saturated solution of sodium potassium tartrate was added to the mixture and allowed to stir for 1h. The solution was extracted with dichloromethane (3 x 20 ml), washed with brine (1 x 20 ml), dried over $MgSO_4$, and concentrated *in vacuo*. The resulting residue was purified via column chromatography (EtOAc) to yield the desired amide as a white solid (50% yield).

General procedure for rhodium catalyzed pyridone synthesis: A 1.5 dram vial with a stir bar was charged with freshly purified amide (0.22 mmol, 1 equiv), $Cu(OAc)_2•H_2O$ (0.46 mmol, 210 mol %), and $RhCp^*(MeCN)_3(SbF_6)_2$ or $RhCp^t(MeCN)_3(SbF_6)_2$ (0.011 mmol, 5 mol %).[10] If the alkyne is a solid, it was added (0.24 mmol, 1.1 equiv) followed by 0.75 ml of dichloroethane. If the alkyne is a liquid, 0.75 ml of dichloroethane was added followed by the alkyne (0.24 mmol, 1.1 equiv). The vial was sealed and placed into a 80 °C heating block for 8-16 h. The reaction was allowed to cool and poured into a separatory funnel with excess ethyl acetate and extracted twice with 10% NH_4OH. The organic portion was extracted once with brine, dried over magnesium sulfate, and concentrated. Regioselectivities were determined from diagnostic N-Me shifts, and by GC/MS of the crude reaction mixture. The residue was dissolved in 1 ml of dichloromethane and loaded onto a column of silica gel and eluted with a suitable solution of ethyl acetate and hexanes (typically 1:1 EtOAc/Hexanes). Evaporation of solvent afforded the product.

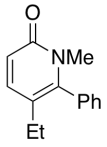
General procedure for rhodium catalyzed pyridone synthesis with catalytic $Cu(OAc)_2•H_2O$: A 16 ml test-tube with a stir bar was charged with freshly purified amide (0.22 mmol, 1 equiv), $Cu(OAc)_2•H_2O$ (0.022 mmol, 20 mol %), $RhCp^*(MeCN)_3(SbF_6)_2$ (0.011 mmol, 5 mol %), 0.75 ml of dichloroethane, and 1-phenyl-1-butyne (.24 mmol, 1.1 equiv) sequentially. The vial was capped with a septum penetrated by a needle and placed into a 80 °C heating block for 16 h. The reaction was allowed to cool and poured into a separatory funnel with excess ethyl acetate and extracted twice with 10% NH_4OH. The organic portion was extracted once with brine, dried over magnesium sulfate, and concentrated. The residue was dissolved in 1 ml of dichloromethane and loaded onto a column of silica gel and eluted with a suitable solution of ethyl acetate and hexanes (typically 1:1 EtOAc/Hexanes). Evaporation of solvent afforded the product.

General Procedure of 6.22 mmol scale reaction: To a 50 ml round bottom equipped with a stir bar was added amide (6.22 mmol), $Cu(OAc)_2•H_2O$ (1.244 mmol), and $RhCp^*(MeCN)_3(SbF_6)_2$ (2.0 mol %) followed by 10.5 ml of dichloroethane. The flask was heated to 80 °C (sand bath temperature) and allowed to stir at this temperature. 1-phenyl-1-butyne (6.22 mmol) was added portionwise at 0,1,3,5,and 8 hours (5 portions for 6.22 mmol total). After the final addition of alkyne, the reaction mixture was allowed to reflux for 14 hours. The reaction was allowed to cool and then poured into a separatory funnel with excess ethyl acetate and extracted twice with 10% NH_4OH in saturated NH_4Cl. The organic portion was extracted once with brine, dried over magnesium sulfate, and concentrated. The residue was purified via flash chromatography (EtOAc) to yield

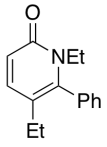
[10] **1a** and **1b** were stored as 0.88 M solutions in DCE. When these substrates were used the solids were added followed by 0.25 mL of the amide solution. The total volume remained 0.75 ml.

the product with unreacted starting material. The yield of the desired product was determined use ^{1}H NMR integration of the diagnostic methyl peaks to determine the ratio. This ratio consequently was applied to the semi-pure yield (69% yield).

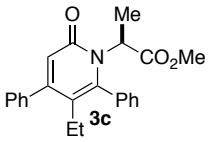
Characterization of pyridone products:



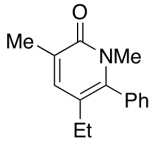
5-ethyl-1-methyl-6-phenylpyridin-2(1H)-one (3a): According to the general procedure, the desired pyridone was isolated as a yellow oil (90%, Cp* 6.8:1 rs, Cp^t 14:1): R_f = .24 (2:1 Hexanes/EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.48-7.31 (m, 3H), 7.29 (d, 1H, *J* = 8.8 Hz, major), 7.23 (d, 1H, *J* = 0.8 Hz, minor), 7.18-7.16 (m, 2H), 6.62 (d, 1H, *J* = 8.8 Hz, major), 6.50 (d, 1H, *J*=9.2 Hz, minor), 3.62 (s, 3H), 3.17 (s, 3H), 2.59 (q, 2H, *J* = 7.6 Hz, minor), 2.03 (q, 2H, *J* = 7.6 Hz, major), 1.10 (td, 3H, *J* = 7.6 Hz, *J* = 0.8 Hz minor), 0.92 (td, 3H, *J* = 7.6 Hz, *J* = 0.8 Hz major); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 163.1, 148.5, 145.9, 141.4, 139.2, 134.4, 130.8, 129.3, 128.86, 128.81, 128.7, 128.4, 127.3, 120.3, 120.3, 116.7, 40.2, 39.3, 34.2, 31.5, 29.6, 26.2, 24.4, 23.9; IR (thin film) 2966, 1653, 1162, 735, 705 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 214.1226; found 214.1231.



1,5-diethyl-6-phenylpyridin-2(1H)-one (3b): According to the general procedure, the desired pyridone was isolated as a yellow oil (85%, Cp* 5:1 rs, Cp^t 15:1): R_f = .24 (2:1 Hexanes/EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.43 (m, 3H), 7.25-7.20 (m, 3H), 6.56 (d, 1H, *J*=9.2 Hz, major), 6.43 (d, 1H, *J*=9.6, minor), 4.14 (q, 2H, *J*=6.8 Hz, minor), 3.72 (q, 2H, *J*=6.8 Hz, major), 2.55 (q, 2H, *J*=7.2 Hz, minor), 1.95 (q, 2H, *J*=10 Hz, major), 1.32 (t, 3H, *J*=6.4 Hz, minor), 1.04 (t, 3H, *J*=6.8, major), 0.89 (t, 3H, *J*=7.2 Hz, major); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 162.0, 147.9, 145.6, 141.4, 140.4, 139.4, 134.4, 134.1, 129.4, 129.17. 129.12, 129.0, 128.79, 128.74, 128.4, 127.2, 120.3, 120.1, 117.3, 41.3, 39.3, 24.5, 23.2, 15.3, 14.3, 14.2, 14.0; IR (thin film) 2969, 1655, 1584, 1541, 733 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 228.1383; found 228.1387.

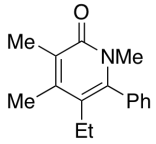


(*S*)-methyl 2-(5-ethyl-2-oxo-4,6-diphenylpyridin-1(2*H*)-yl)propanoate (3c):According to the general procedure, the desired pyridone was isolated as a off-white solid (85%, Cp^t 15:1): R_f = .56 (EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.43 (m, 3H), 7.32 (m, 4H), 7.26 (m, 3H), 6.39 (s, 1H), 4.15 (q, 1H, *J*=6.8 Hz), 3.66 (s, 3H), 1.97 (q, 2H, *J*=7.6 Hz), 1.46 (d, 3H, *J*=6.8 Hz), 0.5 (t, 3H, *J*=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 160.8, 154.8, 145.9, 139.0, 134.5, 129.2, 129.2, 128.5, 128.1, 127.9, 127.8, 120.5, 119.5, 56.6, 52.3, 22.3, 14.8.; IR (thin film) 1749, 1658, 1221, 1084, 703 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 362.1751; found 362.176.

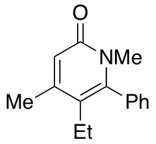


5-ethyl-1,3-dimethyl-6-phenylpyridin-2(1H)-one (3d): According to the general procedure, the desired pyridone was isolated as a off-white solid (98%, Cp* 5:1 rs, Cp^t 8.3:1): R_f = .43/.20 (2:1 Hexanes/EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.46 (m, 3H), 7.12 (m, 3H), 3.58 (s, 3H, minor), 3.13 (s, 3H, major), 2.52 (q, 2H, *J*=7.6 Hz, minor), 2.14 (s, 3H, major), 2.08 (s, 3H, minor), 1.97 (q, 2H, *J*= 7.6 Hz, major), 1.05 (t, 3H, *J*=7.6 Hz, minor), 0.88 (t, 3H, *J*=7.6 Hz, major); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 162.8, 145.4, 143.1, 139.6, 139.1, 138.2, 134.7, 129.4, 128.9, 128.8, 128.7, 128.3, 128.0, 127.1, 125.4, 119.6, 119.5, 46.6,

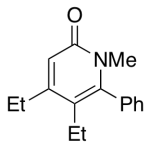
43.9, 34.3, 31.6, 24.5, 23.7, 20.9, 17.3, 15.9, 15.4, 13.3; IR (thin film) 2926, 1651, 1602, 1557, 764 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 228.1383; found 228.1384.



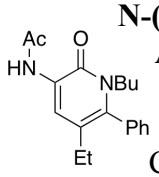
5-ethyl-1,3,4-trimethyl-6-phenylpyridin-2(1H)-one (3e): According to the general procedure, the desired pyridone was isolated as a yellow oil (85%, Cp* 3.3:1 rs, Cp^t 4.8:1): R_f = .44 (2:1 Hexanes/EtOAc); ^1H (400 MHz, $CDCl_3$) δ 7.43 (m, 3H), 7.19 (dd, 2H, *J*=7.6 Hz, *J*=1.6 Hz, major), 7.12 (dd, 2H, *J*=8.0 Hz, *J*=1.6 Hz, minor), 3.63 (s, 3H, minor), 3.16 (s, 3H), 2.39 (q, 2H, *J*=7.6 Hz, minor), 2.20 (s, 6H, major), 2.15 (s, 3H, minor), 2.12 (q, 2H, *J*=7.2 Hz, major), 1.77 (s, 3H, minor), 1.01 (t, 3H, *J*=7.6 Hz, minor), 0.88 (t, 3H, *J*=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.3, 145.3, 145.1, 144.2, 142.4, 138.9, 135.4, 130.2, 128.88, 128.83, 128.63, 128.5, 127.1, 125.3, 122.7, 121.2, 119.9, 34.5, 31.7, 29.6, 24.1, 22.5, 18.1, 16.1, 14.9, 13.3, 13.2, 13.0; IR (thin film) 2929, 1636, 1585, 1491, 764 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 242.1539; found 242.1542.



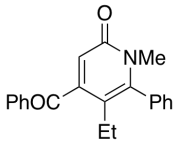
5-ethyl-1,4-dimethyl-6-phenylpyridin-2(1H)-one (3f): According to the general procedure, the desired pyridone was isolated as a off-white solid (75%, Cp* 3.6:1 rs, Cp^t 4.6:1): R_f = .16 (2:1 Hexanes/EtOAc); ^1H (400 MHz, $CDCl_3$) δ 7.46 (m, 3H, major), 7.38 (m, 3H, minor), 7.20 (dd, 2H, *J*=8.4 Hz, *J*=1.6 Hz, major), 7.12 (dd, 2H, *J*=8.4 Hz, *J*=1.6 Hz, minor), 6.48 (s, 1H, major), 6.39 (s, 1H, minor), 3.60 (s, 3H, minor), 3.12 (s, 3H, major), 2.42 (q, 2H, *J*=7.2 Hz, minor), 2.22 (s, 3H, major), 2.08 (q, 2H, *J*=7.2 Hz, major), 1.77 (s, 3H, minor), 1.03 (t, 3H, *J*=7.6 Hz, minor), 0.86 (t, 3H, *J*=7.2 Hz, major); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 162.4, 150.3, 147.8, 145.7, 142.06, 142.02, 137.9, 134.9, 130.0, 128.9, 128.8, 128.6, 127.4, 120.4, 118.9, 116.3, 107.1, 34.0, 31.2, 24.2, 21.9, 21.3, 19.6, 14.7, 12.8; IR (thin film) 2967, 1655, 1583, 1348, 707 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 228.1383; found 228.1383.



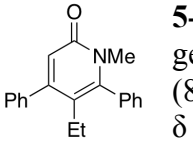
4,5-diethyl-1-methyl-6-phenylpyridin-2(1H)-one (3g): According to the general procedure, the desired pyridone was isolated as a yellow oil (82%, Cp* 3.8:1 rs, Cp^t 4.6:1): R_f = .16 (2:1 Hexanes/EtOAc); ^1H (400 MHz, $CDCl_3$) δ 7.49 (m, 3H, major), 7.22 (dd, 2H, *J*=7.6 Hz, *J*=2.0 Hz, major), 6.55 (s, 1H, major), 3.63 (s, 3H, minor), 3.15 (s, 3H, major), 2.56 (q, 2H, *J*=7.2 Hz), 2.13 (q, 2H, *J*=7.2 Hz), 1.25 (t, 3H, *J*=7.6 Hz), 0.87 (t, 3H, *J*=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 155.7, 145.8, 135.0, 128.9, 128.8, 128.6, 120.2, 116.8, 34.0, 29.6, 25.0, 21.3, 15.1, 13.3; IR (thin film) 2966, 1653, 1532, 1488, 766, 706 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 242.1539; found 242.1541.



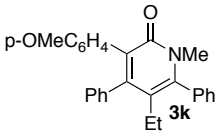
N-(1-butyl-5-ethyl-2-oxo-6-phenyl-1,2-dihydropyridin-3-yl)acetamide (3h): According to the general procedure, the desired pyridone was isolated as a yellow oil (85%, Cp* >19:1, rotamers): R_f = .73 (2:1 Hexanes/EtOAc); ^1H (400 MHz, $CDCl_3$) Mixture of rotamers see spectra; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 165.8, 161.0, 136.0, 132.5, 131.5, 128.8, 128.6, 128.1, 127.1, 127.0, 126.2, 125.1, 124.5, 118.0, 109.4, 46.6, 39.1, 31.9, 31.0, 25.2, 20.2, 20.0, 19.5 19.4, 15.2, 15.0, 13.74, 13.7; IR (thin film) 2961, 1645, 1630, 1287, 696 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 313.1911; found 313.1912.



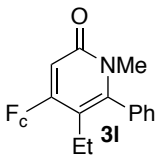
4-benzoyl-5-ethyl-1-methyl-6-phenylpyridin-2(1H)-one (3i): According to the general procedure, the desired pyridone was isolated as a red solid (75%, Cp* 6.8:1 rs, Cp^t >19:1): R_f = .16 (2:1 Hexanes/EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.88 (dd, 2H, *J*=8.4 Hz, *J*=1.2 Hz), 7.56 (tt, 1H, *J*=7.2 Hz, *J*=1.2 Hz), 7.43 (m, 5H), 7.20 (m, 2H), 6.47 (s, 1H), 6.43 (s, 1H), 3.63 (s, 3H, minor), 3.16 (s, 3H, major), 2.02 (q, 2H, *J*=7.6 Hz), 0.66 (t, 3H, *J*=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 161.6, 150.5, 148.1, 135.5, 134.2, 134.1, 130.1, 129.3, 129.1, 128.7, 128.5, 117.8, 117.7, 34.5, 21.7, 15.6; IR (thin film) 2969, 1652, 1568, 1262, 727 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 318.1489; found 318.149.



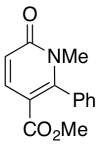
5-ethyl-1-methyl-4,6-diphenylpyridin-2(1H)-one (3j): According to the general procedure, the desired pyridone was isolated as a yellow solid (85%, Cp* 17.6:1 rs): R_f = .16 (2:1 Hexanes/EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.41 (m, 3H), 7.22 (m , 3H), 7.05 (m, 4H), 6.45 (s, 1H), 3.62 (s, 3H, minor), 3.14 (s, 3H, major), 2.51 (q, 2H, *J*=7.2 Hz, minor), 1.99 (q, 2H, *J*=7.6 Hz, major), 1.04 (t, 3H, *J*=7.2 Hz, minor), 0.49 (t, 3H, *J*=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 154.5, 153.3, 149.0, 146.6, 139.1, 134.9, 131.0, 129.0, 128.9, 128.7, 128.1, 127.9, 127.8, 119.6, 119.5, 117.0, 34.2, 31.5, 24.3, 22.0, 14.9, 13.0; IR (thin film) 2968, 1655, 1523, 1074, 750 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 290.1539; found 290.1543.



5-ethyl-3-(4-methoxyphenyl)-1-methyl-4,6-diphenylpyridin-2(1*H*)-one (3k): According to the general procedure, the desired pyridone was isolated as a off-white solid (This reaction did not react complication, as a consequence the starting material could not be completely removed from the product) (85%, Cp^* >19:1): R_f = .53 (EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.44 (m, 3H), 7.27 (dd, 2H, *J*=8.4 Hz, *J*=2.0 Hz), 7.10 (m, 3H), 6.97 (m, 4H), 6.59 (d, 2H, *J*=8.8 Hz), 3.64 (s, 3H), 3.19 (s, 3H), 1.92 (q, 2H, *J*=7.2 Hz), 0.49 (t, 3H, *J*=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 157.8, 151.2, 145.0, 138.1, 136.7, 135.3, 138.1, 136.7, 135.2, 132.6, 131.7, 131.0, 130.2, 129.2, 129.1, 128.9, 128.8, 128.7, 128.3, 128.1, 127.6, 126.7, 119.3, 114.9, 112.8, 55.0, 34.8, 22.8, 15.0; IR (thin film) 1632, 1442, 1245, 912, 703 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 396,1958 ; found 396.1966 .

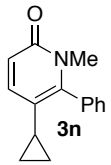


5-ethyl-1-methyl-4-ferrocene-6-diphenylpyridin-2(1*H*)-one (3l): According to the general procedure, the desired pyridone was isolated as a red solid (85%, Cp^* >19:1): R_f = .28 (EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.42 (m, 3H), 7.17 (m, 2H), 7.06 (s, 1H), 4.42 (t, 2H, *J*=1.6 Hz), 4.26 (t, 2H, *J*=1.6 Hz), 4.15 (s, 5H), 3.09 (s, 3H), 2.15 (q, 2H, *J*=7.6 Hz), 0.59 (t, 3H, *J*=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 151.7, 145.8, 135.1, 129.0, 128.8, 128.7, 119.9, 70.3, 69.8, 69.4, 68.6, 34.1, 22.0, 15.2; IR (thin film) 1648, 1562, 1229, 821, 705 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 398.1212; found 398.1209.

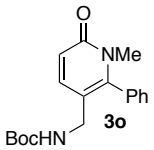


1-methyl-6-oxo-2-phenyl-1,6-dihydropyridine-3-carboxylate (3m): According to the general procedure, the desired pyridone was isolated as a yellow oil (62%, Cp* 4.7:1 rs, Cp^t >19:1): R_f = .24 (EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.88 (d, 1H, *J*=10 Hz), 7.44 (m, 3H), 7.14 (m, 2H), 6.63 (d, 1H, *J*=9.6 Hz), 6.54 (d, 1H, *J*=9.6 Hz), 3.58 (s, 3H, minor), 3.47 (s, 3H, major+minor),

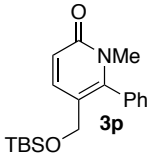
3.15 (s, 3H, major); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 163.0, 154.3, 134.6, 129.2, 128.7, 128.6, 127.4, 118.1, 51.7, 34.2; IR (thin film) 2924, 1728, 1662, 1117, 704 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 244.0968; found 244.0971.



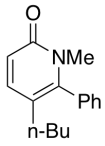
5-cyclopropyl-1-methyl-6-phenylpyridin-2(1*H*)-one (3n):According to the general procedure, the desired pyridone was isolated as a yellow oil (78%, Cp* 11:1): R_f = .30 (EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.45-7.39 (m, 3H), 7.31-7.29 (m, 1H), 7.24-7.19 (m, 3H), 6.92 (d, 1H, *J*=5.6 Hz), 6.51 (d, 1H, *J*=5.6 Hz), 3.73 (s, 3H, minor), 3.16 (s, 3H, major), 1.24-1.19 (m, 1H), 0.85-0.78 (m, 1H), 0.55-0.51 (m, 2H), 0.39-0.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 147.1, 146.4, 141.8, 139.0, 137.1, 134.5, 129.2, 139.0, 128.8, 126.7, 121.6, 119.0, 119.0, 118.2, 34.3, 32.3, 13.5, 11.7, 10.5, 7.26; IR (thin film) 1659, 1585, 1534, 829, 721 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 226.1226; found 226.1230.



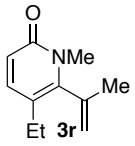
***tert*-butyl ((1-methyl-6-oxo-2-phenyl-1,6-dihydropyridin-3-yl)methyl)carbamate (3o):** According to the general procedure, the desired pyridone was isolated as a yellow oil (65%, Cp* 2.5:1; 58%, Cp^t 4.8:1): R_f = .28 (EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.45-7.42 (m, 4H), 7.17-7.13 (m, 2H), 6.56 (d, 1H, *J*=8.8 Hz, major), 6.43 (d, 1H, *J*=8.8 Hz, minor), 4.76 (s, br, 1H, minor), 4.49 (s, br, 1H, major), 4.20 (d, 2H, *J*=5.6 Hz, minor), 3.67 (d, 2H, *J*=5.6 Hz, major), 3.57 (s, 3H, minor), 3.12 (s, 3H, major), 1.36 (s, 9H, minor), 1.34 (s, 9H, major); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 155.5, 147.3, 141.0, 140.3, 133.3, 129.4, 129.3, 129.2, 128.7, 128.4, 127.7, 119.4, 115.7, 40.7, 34.1, 28.3; IR (thin film) 1709, 1656, 1583, 1168, 731, 704 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 315.1703; found 315.1711.



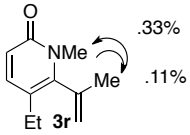
5-(((*tert*-butyldimethylsilyl)oxy)methyl)-1-methyl-6-phenylpyridin-2(1*H*)-one (3p): According to the general procedure, the desired pyridone was isolated as a yellow oil (69%, Cp* 2.1:1; 58%, Cp^t 7.2:1): R_f = .33 (EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.61-7.59 (m, 2H), 7.50-7.42 (m, 1H), 7.41-7.35 (m, 1H), 7.36-7.29 (m, 2H), 6.73 (d, 1H, *J*=9.2 Hz, major), 6.71 (d, 1H, *J*=9.2 Hz, minor), 4.58 (s, 2H, minor), 4.14 (s, 2H, major), 3.82 (s, 3H, minor), 3.30 (s, 3H, major), 0.96 (s, 9H, minor), 0.91 (s, 9H, major), 0.06 (s, 6H, minor), 0.00 (s, 6H, major); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 152.2, 148.9, 146.9, 145.7, 143.8, 139.0, 135.1, 135.0, 134.9, 134.7, 134.6, 134.5, 134.3, 134.2, 134.0, 133.1, 127.2, 125.3, 124.8, 123.3, 67.1, 65.4, 39.7, 37.0, 31.4, 31.2, 23.8; IR (thin film) 1741, 1589, 1461, 1070, 836 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 330.1884; found 330.1890.

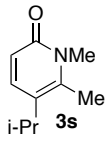


5-butyl-1-methyl-6-phenylpyridin-2(1H)-one (3q): According to the general procedure, the desired pyridone was isolated as a yellow oil (81%, Cp* 5:1 rs, Cp^t 12.3:1): R_f = .20 (2:1 Hexanes/EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.41 (m, 3H), 7.21 (m, 1H), 7.12 (m, 2H), 6.54 (d, 1H, *J*=9.2 Hz, major), 6.43 (d, 1H, *J*=9.2 Hz, minor), 3.56 (s, 3H, minor), 3.13 (s, 3.13, major), 1.97 (t, 2H, *J*=8.0 Hz); 1.24 (m, 2H, major + minor), 1.07 (sextet, 2H, *J*=7.6 Hz, major), 0.7 (t, 3H, *J*=7.6 Hz, major + minor); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 162.7, 147.5, 136.1, 141.4, 141.1, 139.3, 134.4, 129.5, 128.9, 128.7, 127.2, 120.4, 119.1, 119.0, 118.7, 116.7, 34.2, 32.9, 31.7, 30.8, 30.6, 30.3, 22.3, 22.1, 13.6, 13.4; IR (thin film) 2956, 1656, 1543, 830, 766 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 242.1539; found 242.1544.

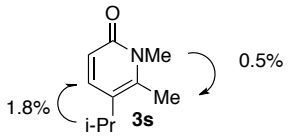


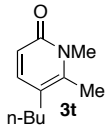
5-ethyl-1-methyl-6-(prop-1-en-2-yl)pyridin-2(1H)-one (3r): According to the general procedure, the desired pyridone was isolated as a yellow oil (60%, Cp* 4.8:1; 79%, Cp^t 16:1): R_f = .25 (EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.16 (d, 1H, *J*=5.6 Hz), 6.44 (d, 1H, *J*=5.2 Hz), 5.37 (t, 1H, *J*=1.6 Hz), 4.97 (t, 1H, *J*=1.6 Hz), 3.52 (s, 3H, minor), 3.40 (s, 3H, major), 2.26 (m, 2H), 1.91 (t, 3H, *J*=1.6 Hz), 1.01 (t, 3H, *J*=7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 147.1, 140.8, 138.4, 119.3, 118.5, 117.9, 116.5, 32.7, 24.2, 22.9, 15.9; IR (thin film) 1661, 1585, 1540, 1084, 830 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 178.1226; found 178.1229.



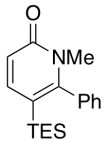


5-isopropyl-1,6-dimethylpyridin-2(1*H*)-one (3s): According to the general procedure, the desired pyridone was isolated as a yellow oil (74%, Cp* 11:1): R_f = .16 (EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.34 (d, 1H, *J*=9.6 Hz), 6.65 (d, 1H, *J*=9.2 Hz), 3.65 (s, 3H, minor), 3.6 (s, 3H, major), 2.96 (septet, 1H, *J*=9.2 Hz), 2.36 (s, 3H), 1.16 (d, 6H, *J*=6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 147.1, 141.9, 137.6, 117.0, 98.5, 32.0, 28.5, 22.9, 19.5, 15.8; IR (thin film) 1659, 1461, 1414, 1159, 829 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 166,1226; found 166.1229.

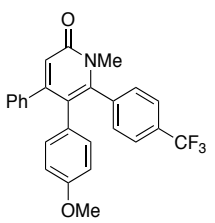


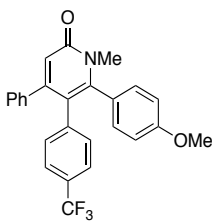


5-butyl-1,6-dimethylpyridin-2(1*H*)-one (3t): According to the general procedure, the desired pyridone was isolated as a yellow oil (74%, Cp* 11:1): R_f = .25 (EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.06 (d, 1H, *J*=9.2 Hz, major), 7.04 (d, 1H, *J*=9.2 Hz, minor), 6.35 (m, 1H), 3.51 (s, 3H), 3.48 (s, 3H), 2.32 (t, 2H, *J*=8.0 Hz), 2.32 (s, 3H, major), 2.01 (s, 3H, minor), 1.53-1.07 (m, 4H, major and minor), 0.95-8.82 (m, 3H, major and minor); ^{13}C NMR (100 MHz, $CDCl_3$) δ ; IR (thin film) 1766, 1661, 1460, 1198, 826 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 180.1383; found 180.1381.



1-methyl-6-phenyl-5-(triethylsilyl)pyridin-2(1H)-one (3u): According to the general procedure, the desired pyridone was isolated as a yellow oil (61%, Cp* 3.8:1 rs, Cp^t 3:1): R_f = .30 (EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.45 (m, 4H), 7.22 (m, 2H), 6.66 (d, 1H, *J*=8.8 Hz), 3.70 (s, 3H, minor), 3.20 (s, 3H, major), 0.78 (t, 6H, *J*=7.6 Hz), 0.27 (q, 9H, *J*=8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 151.6, 141.2, 132.7, 126.5, 125.9, 125.4, 125.1, 124.6, 114.6, 30.6, 4.3, 3.8, 1.7, .00; IR (thin film) 2924, 1656, 1512, 1171, 826 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 300.1778; found 242.1542.

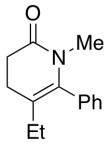




6-(4-methoxyphenyl)-1-methyl-4-phenyl-5-(4-(trifluoromethyl)phenyl)pyridin-2(1H)-one (3u) and 5-(4-methoxyphenyl)-1-methyl-4-phenyl-6-(4-

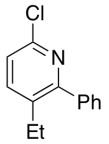
(trifluoromethyl)phenyl)pyridin-2(1H)-one (3u'): According to the general procedure, the desired pyridone was isolated as a yellow oil (82%, Cp* 1.6:1/ 82% Cp^t 2:1): R_f = .44 (2:1 Hexanes/EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ Mixture of Isomers, see ^{1}H NMR; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 162.1, 159.6, 157.5, 152.8, 147.9, 146.0, 138.55, 138.5, 138.3, 132.4, 131.8, 130.7, 130.6, 130.3, 130.0, 128.7, 128.6, 128.2, 127.9, 127.8, 127.9, 127.8, 127.7, 126.4, 125.4, 125.4, 124.19, 124.12, 130.3, 119.48, 119.4, 119.0, 113.9, 112.9, 55.1, 54.9, 34.6, 34.5; HRMS (ESI) *m/e* calcd (M+H) 436.1519; found 436.1521.

Product Elaboration



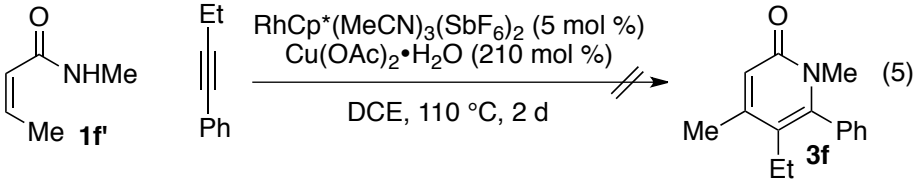
5-ethyl-1-methyl-6-phenyl-3,4-dihydropyridin-2(1*H*)-one (3j''): A flame-dried 50 ml flask with a stir bar under argon was charged with pyridine **2a** (.5 mmol, 1 equiv) and dry THF (15 ml). The reaction was cooled to -35 °C and 1M L-Selectride in THF was added dropwise over 15 minutes. The reaction was allowed to stir for 2 hrs at -35 °C before warming to 0 °C and stiring for 1 hr. At 0 °C brine (2 ml) was added. After 20 min 30% H_2O_2 (5 ml) and then NaOH (2 ml of 3M). The reaction was extracted with ether (3 x 10 ml), washed with brine (10 ml), dried over $MgSO_4$, and concentrated *in vacuo*. The crude mixture was purified via column chromatography (1:1 Hexanes/EtOAc) to yield the desire product as a yellow oil (80%) R_f = .20 (2:1 Hexanes/EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.32-7.27 (m, 3H), 7.09 (m, 2H), 3.15 (s, 3H), 2.64 (s, 3H), 2.50 (m, 2H), 2.25 (m, 2H), 1.85 (q, 2H, *J*=7.6 Hz), 0.934 (t, 3H, *J*=7.6 Hz minor), 0.86 (t, 3H, *J*=7.6 Hz, major); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 135.4, 134.9, 129.5, 128.5, 128.4, 128.3, 127.9, 121.1, 71.9, 47.8, 35.0, 31.7, 31.4, 27.5, 25.9, 24.2, 23.7, 18.5, 12.9; HRMS (ESI) *m/e* calcd (M+H) 216.1383; found 216.1388.

Chloropyridine Formation



6-chloro-3-ethyl-2-phenylpyridine (3j'): A 25 ml vial with a stir bar was charged pyridone **2a** (.15 mmol, 1 equiv), PCl_5 (.15 mmol, 1 equiv), and 1.25 ml. The vial was sealed and warmed to reflux. After 24 h reaction was cooled to room temperature and concentrated *in vacuo*. The crude mixture was purified via column chromatography in neutral silica (9:1 Hexanes/EtOAc).to yield the product as a yellow oil (90%). R_f = .31 (9:1 Hexanes/EtOAc/EtOAc); ^{1}H (400 MHz, $CDCl_3$) δ 7.57 (m, 1H), 7.41 (m, 5H), 7.23 (m, 1H), 2.62 (q, 2H, *J*=7.2 Hz), 1.11 (t, 3H, *J*=7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 158.8, 147.8, 140.1, 139.6, 139.1, 135.7, 128.9, 128.8, 128.4, 128.3, 129.2, 128.1, 122.7, 121.1, 28.4, 24.8, 15.1, 13.9; IR (thin film) 2863, 1656, 1639, 1511, 700 cm^{-1}; HRMS (ESI) *m/e* calcd (M+H) 218.0731; found 218.073.

Angelic *N*-methyl Amide Experiment



Kinetic Isotope Effect Studies in Pyridone Formation

DKIE Experiment

A 1.5 dram vial was charged with a stir-bar, *N*-methyl cinnamamide or D-*N*-methyl cinnamamide (.22 mmol), $Cu(OAc)_2 \bullet H_2O$ (.46 mmol), and 1,3,5 trimethoxy-benzene (.22 mmol). The vial was fitted with a septa and charged with dichloroethane (.50 ml). 1-phenyl-1-butyne (.22 mmol) was added to the reaction solution and the vial was placed into an 80 °C heating block and stirred for 5 min. A separate vial was charged with $[RhCp^*(MeCN)_3](SbF_6)_2$ (5 mol %), .25 ml of dichloroethane, and .15 ml of acetone to yield a bright yellow solution. This solution was added to the reaction vessel in the heating block. 0.1 ml aliquots were taken every minute for 4 minutes (after 1,2,3,and 4 minutes), diluted with ethyl acetate and extracted with 10 % NH_4OH in H_2O. The aliquots were interpreted using GC/MS.

Charts S1-S3 indicate the kinetic isotope effects for the variously substituted cinnamides.

Chart S1. Plot of Initial Rates for Pyridone Formation with *N*-Methyl cinnamide

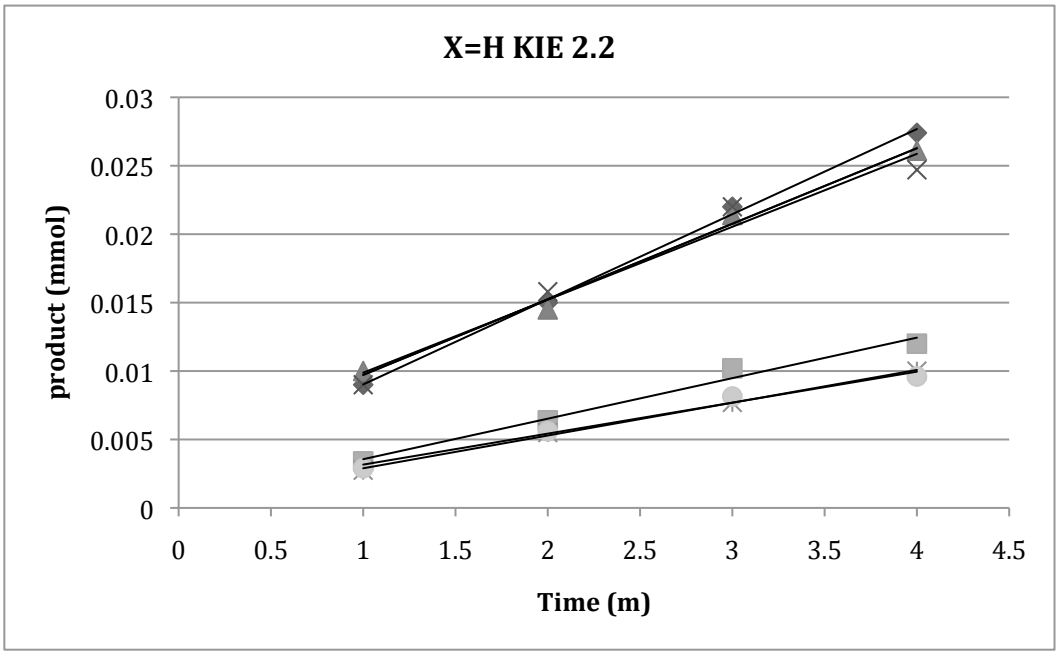


Chart S2. Plot of Initial Rates for Pyridone Formation with *N*-Methyl-*p*-Methyl cinnamide

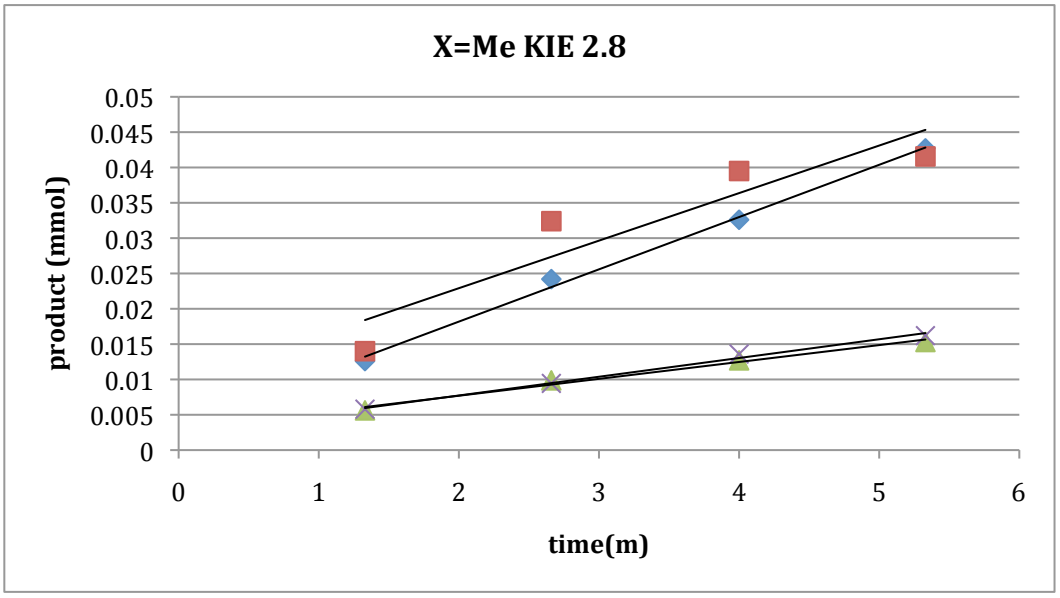


Chart S3. Plot of Initial Rates for Pyridone Formation with *N*-Methyl-*p*-triflouromethyl cinnamide

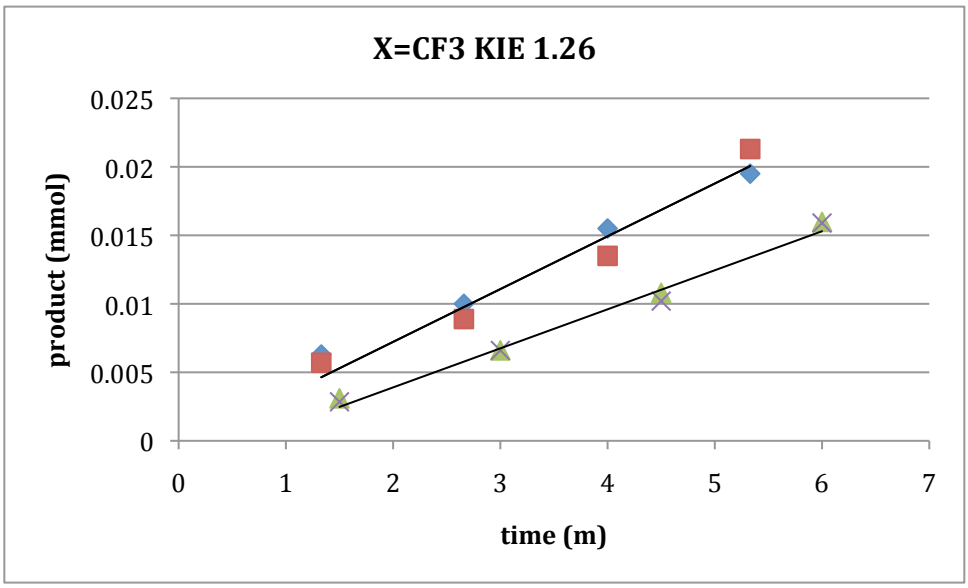


Chart S4 is a comparison of the rates of reaction of variously substituted cinnamides as compared to the parent cinnamide (X=Y=H). The break in the plot is indicative of a change in mechanism. Plots of raw data are included after the main plot.

Chart S4. Hammett Plot based on Initial Rates

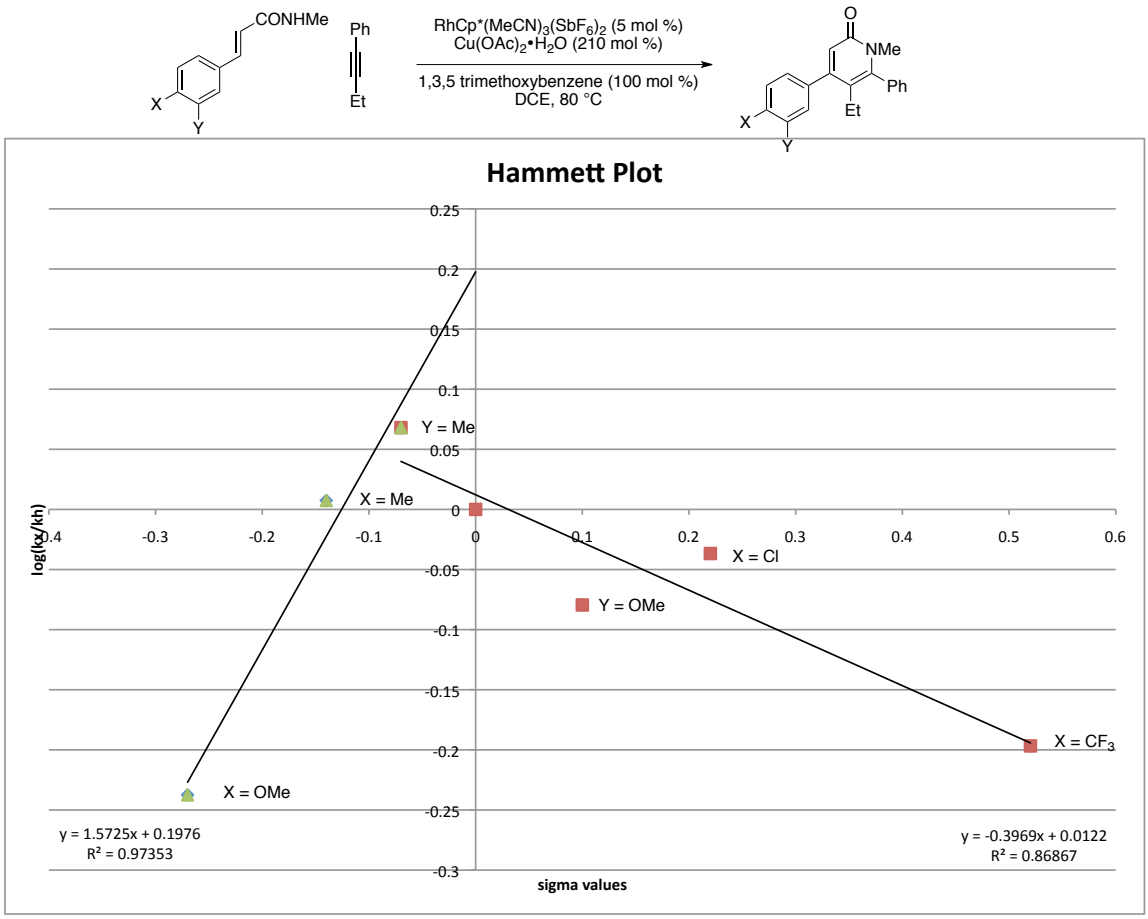


Chart S5. Initial Rates X=H

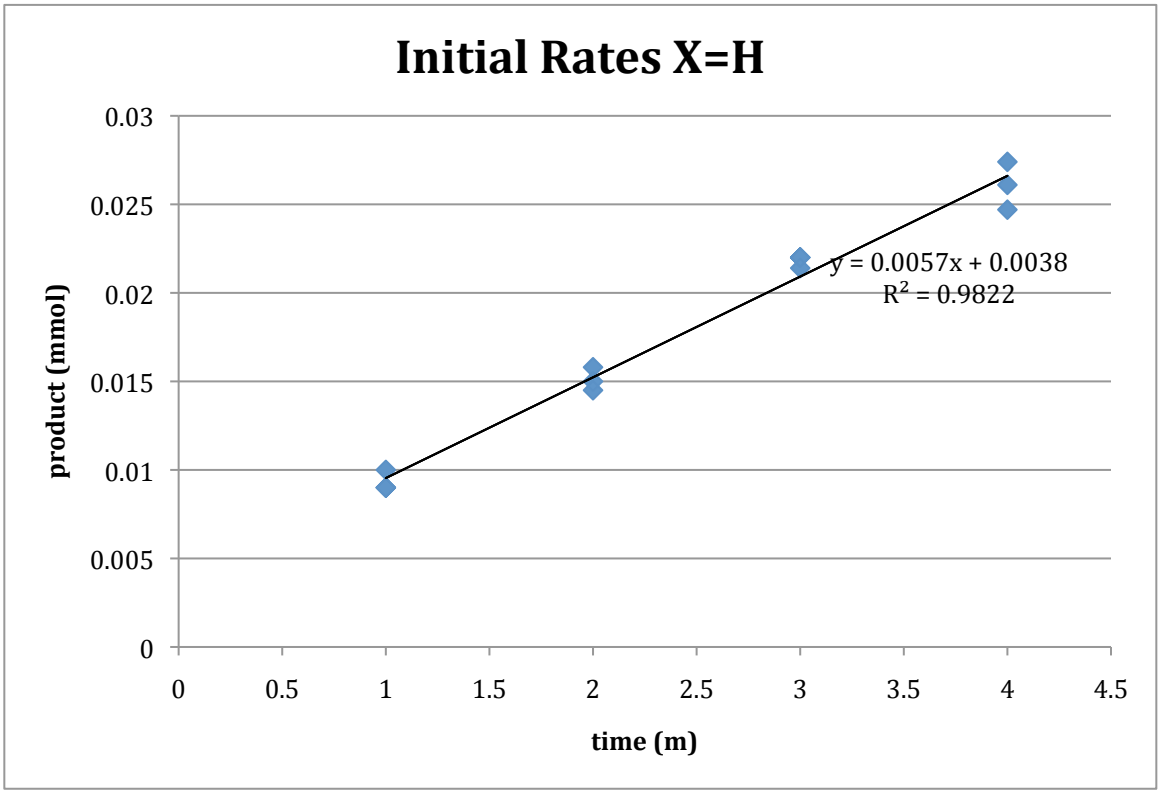


Chart S6. Initial Rates X=CF_3

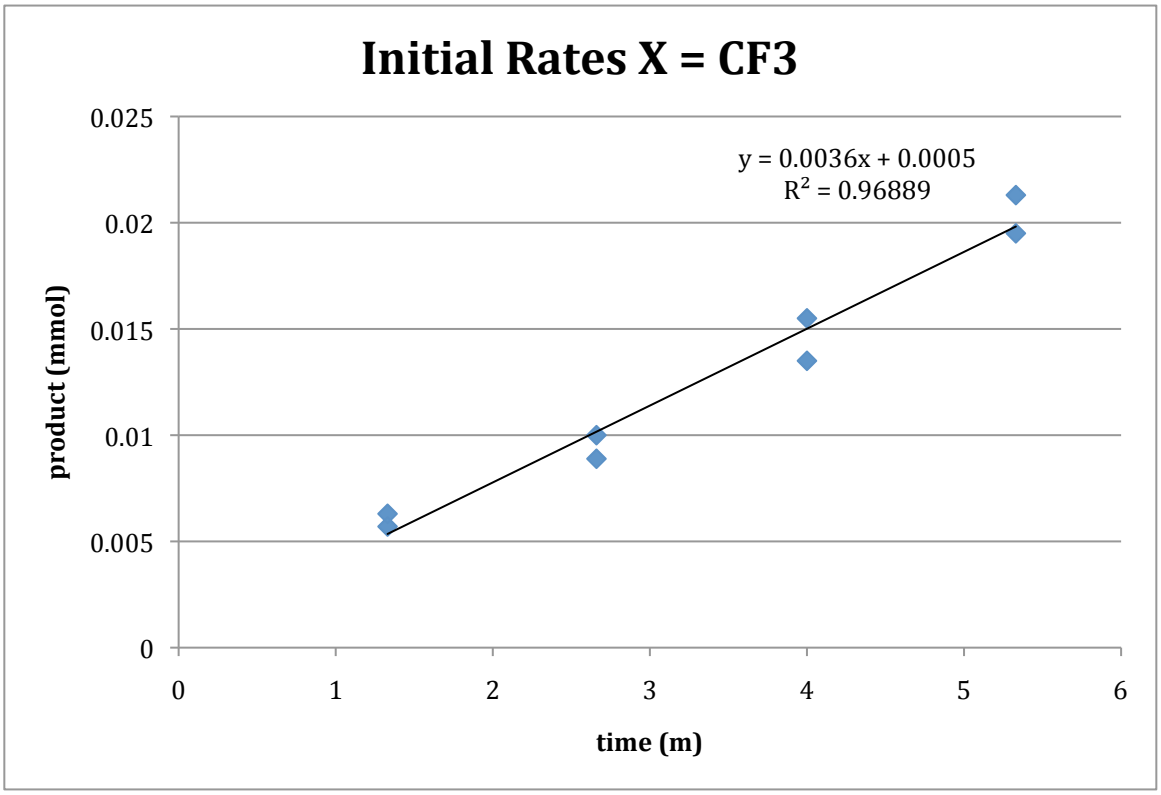


Chart S7. Initial Rates Y=OMe

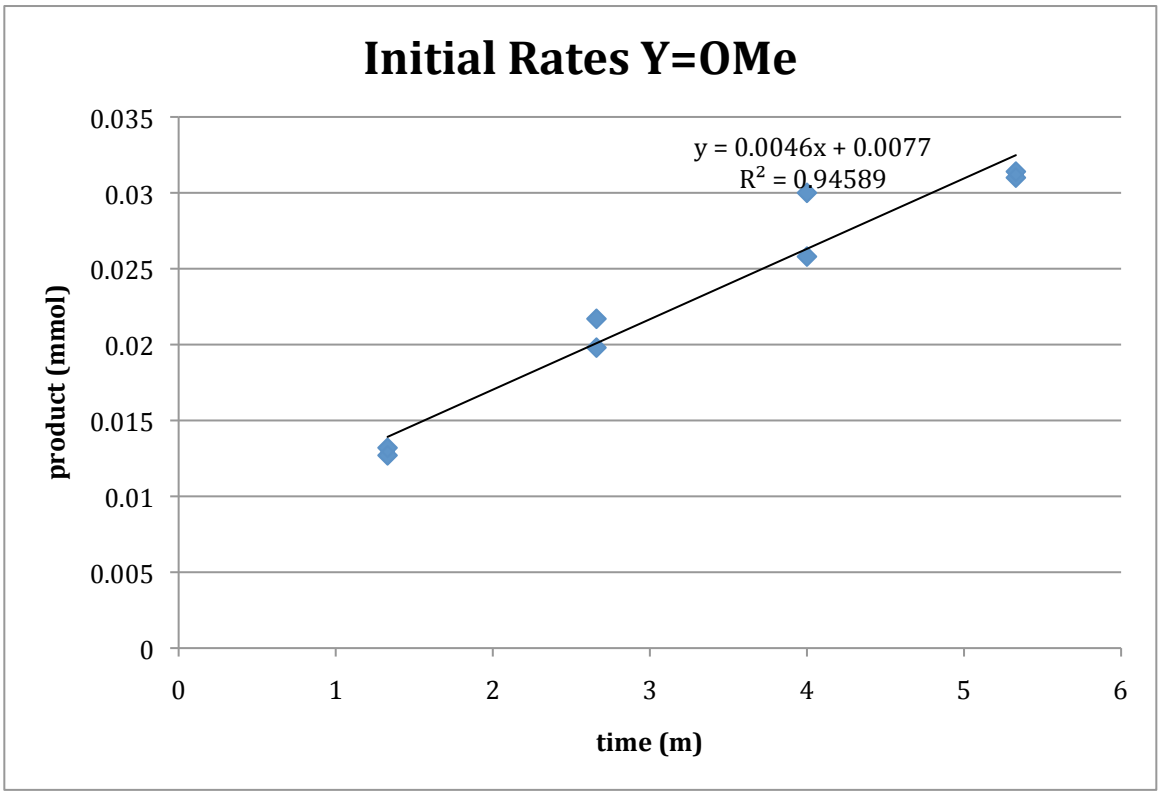


Chart S8. Initial Rates X=Me

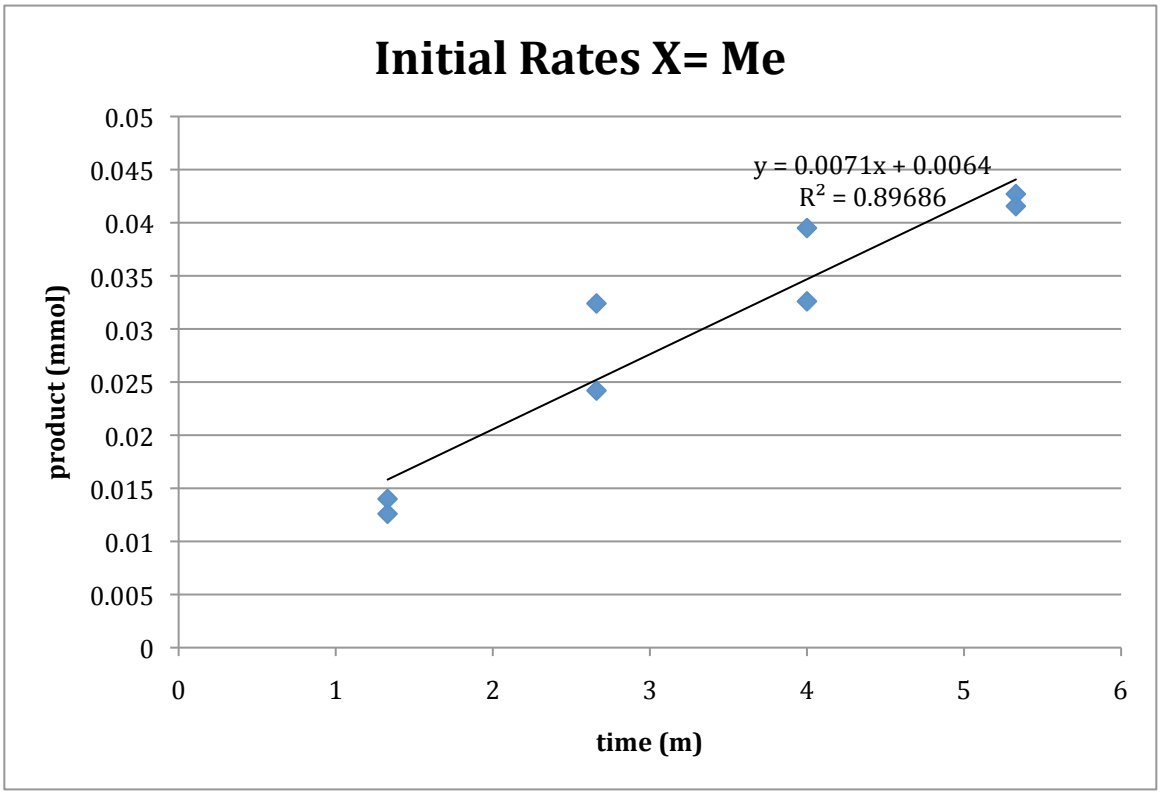


Chart S9. Initial Rates X=Cl

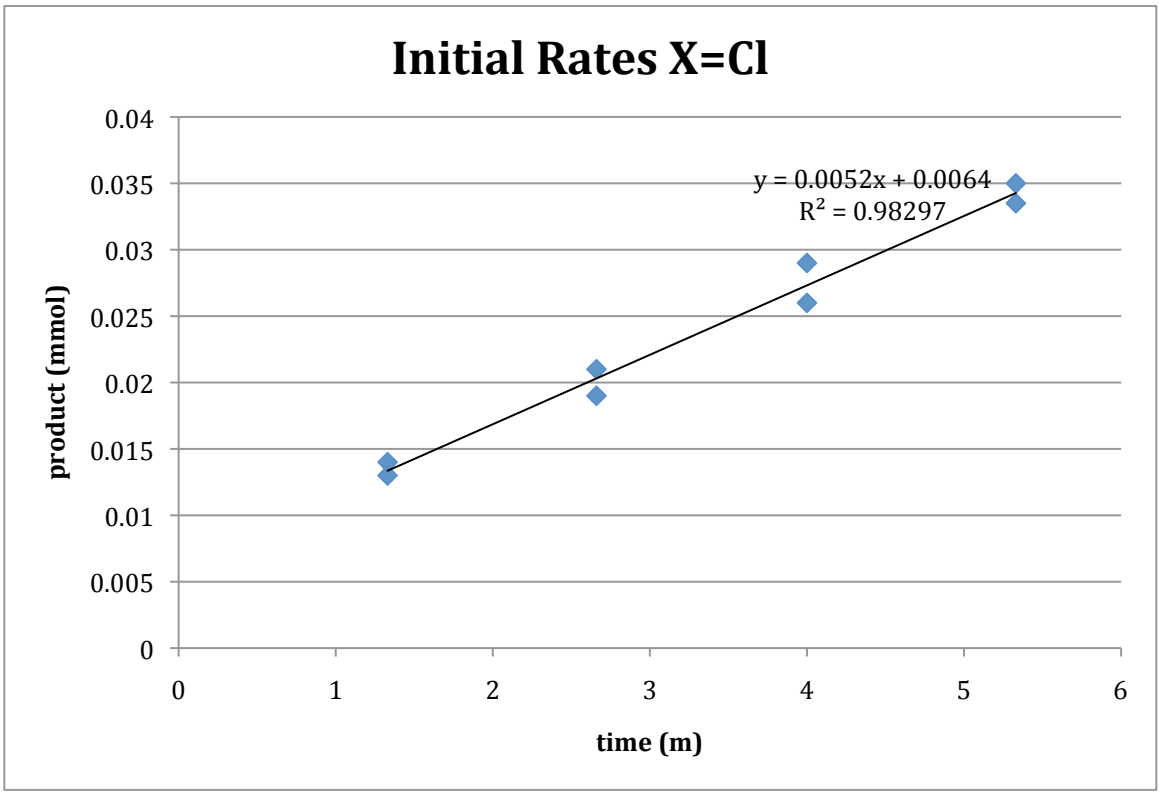


Chart S10. Initial Rates Y=Me

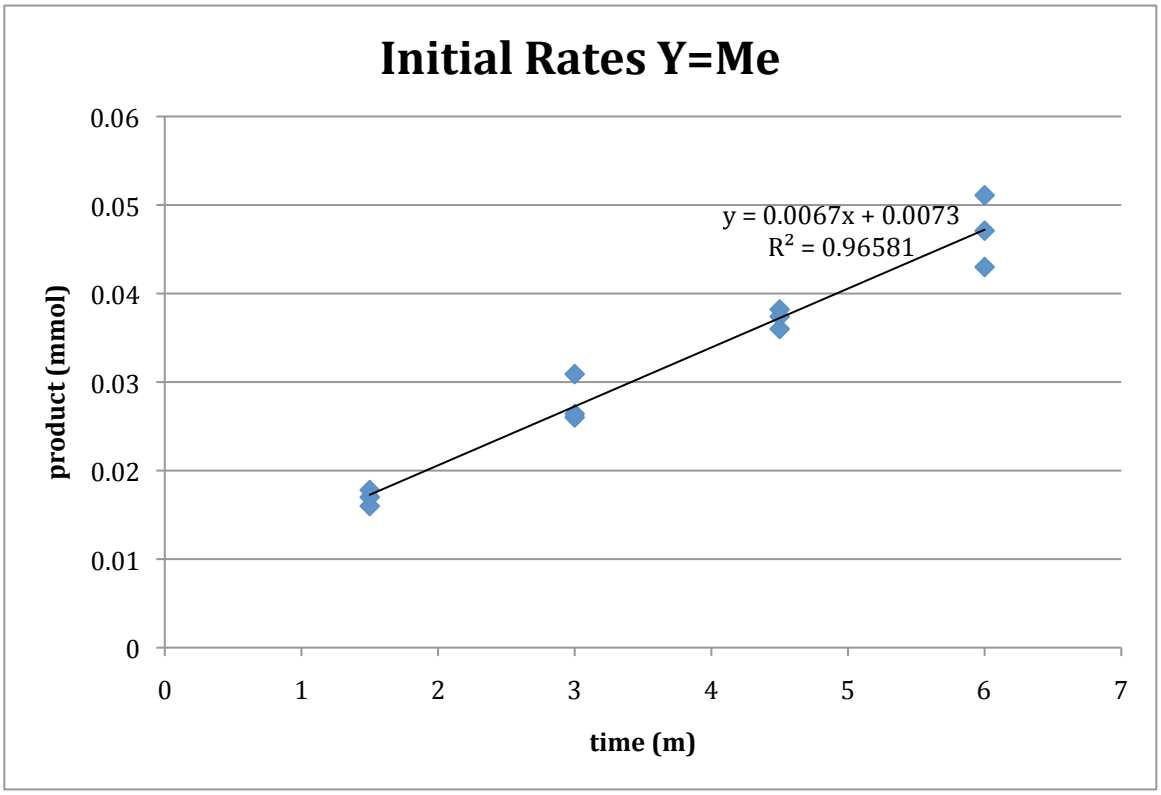
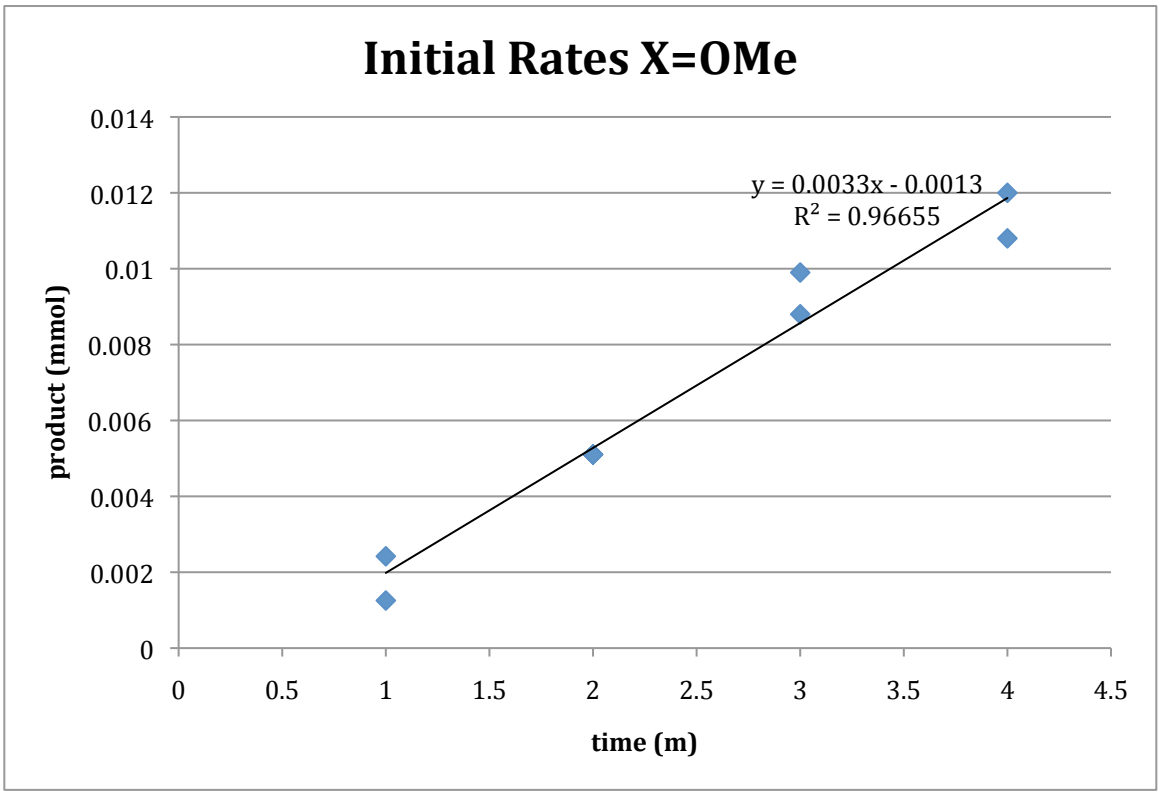
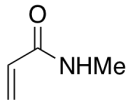
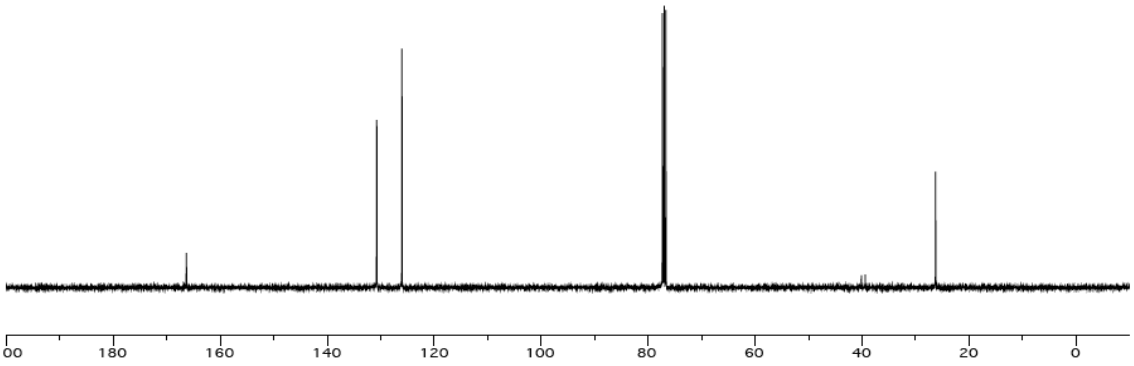


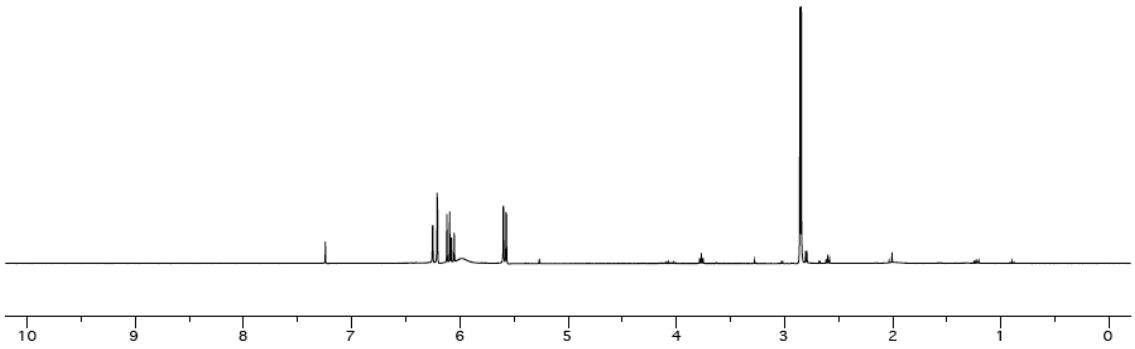
Chart S11. Initial Rates X=OMe



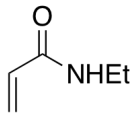
Starting Material 1a

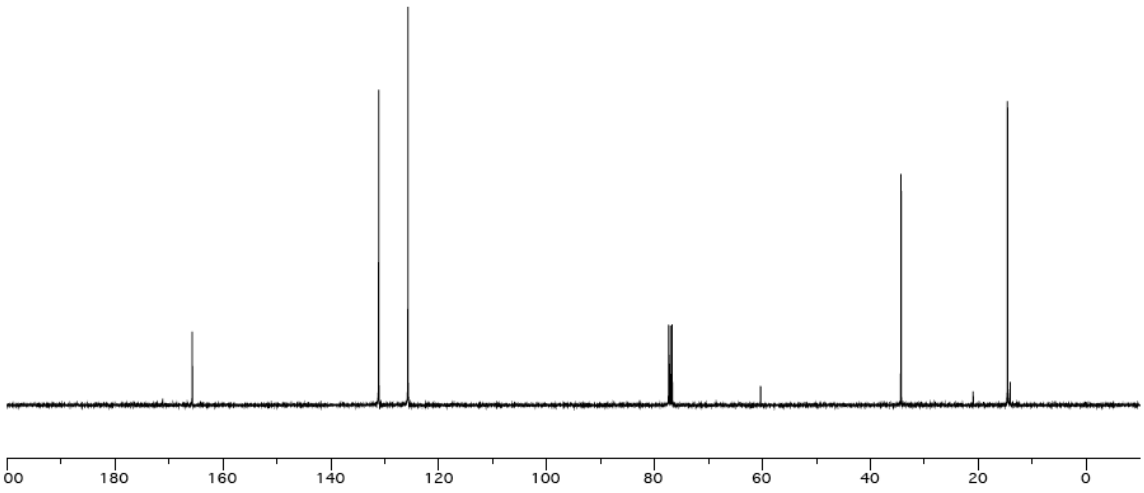


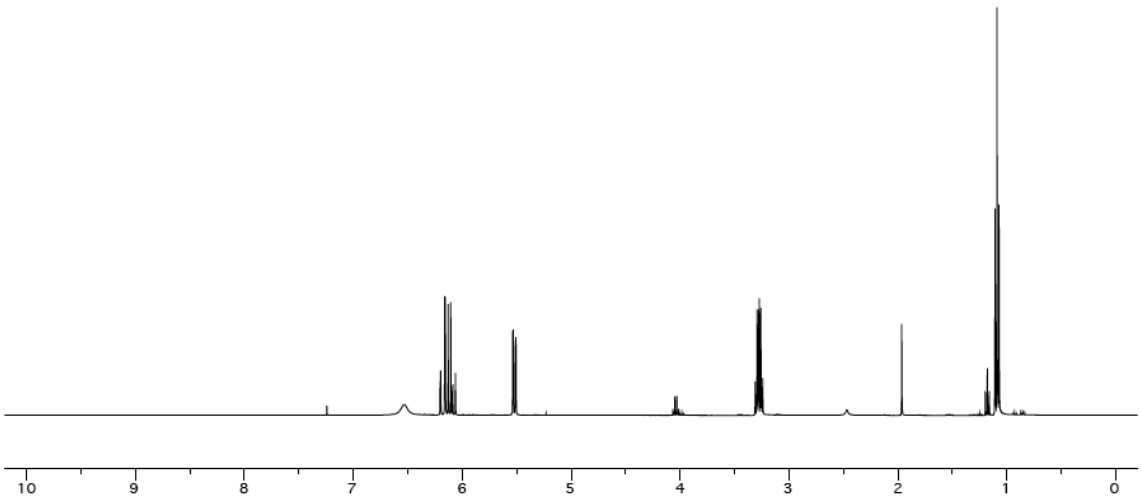




Starting Material 1b







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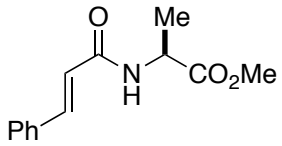

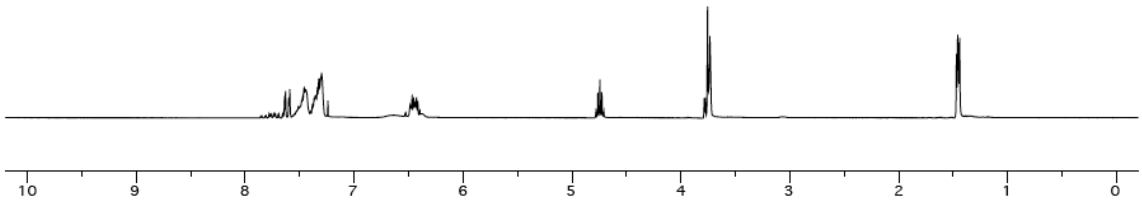

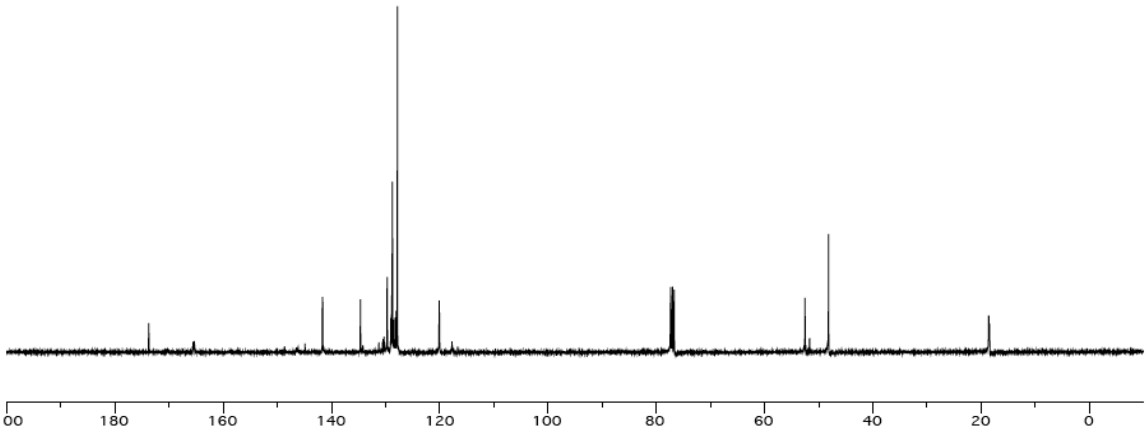

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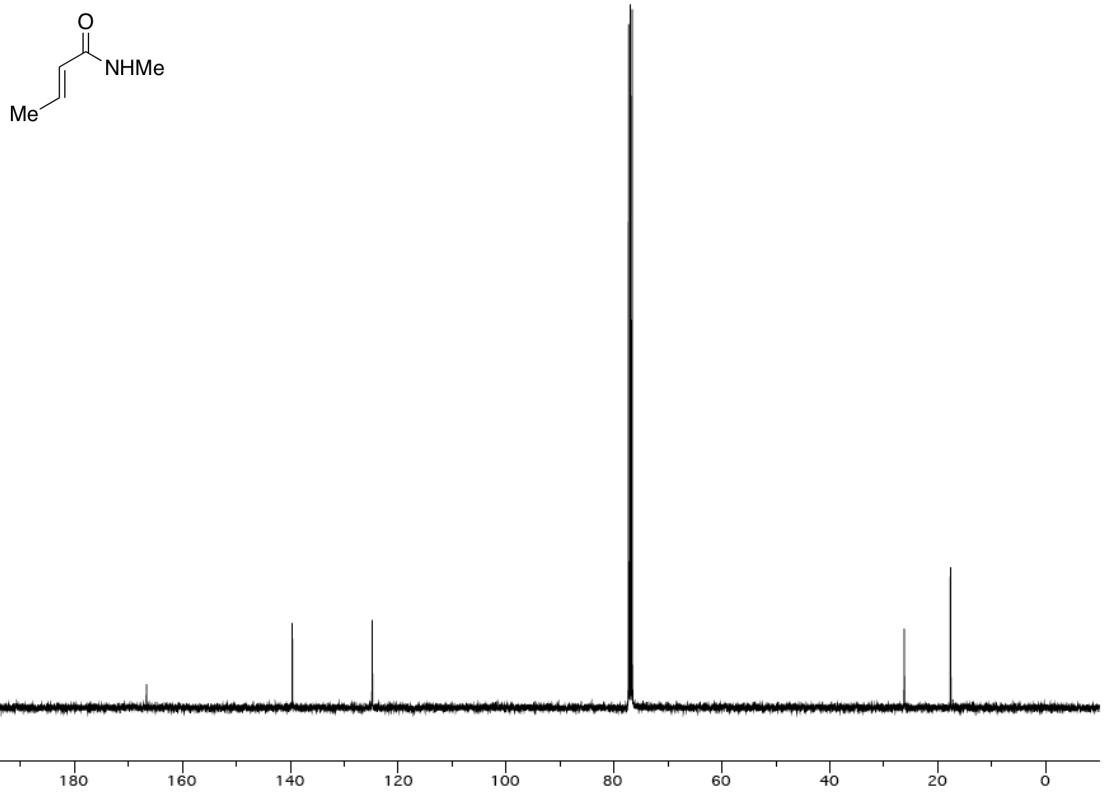
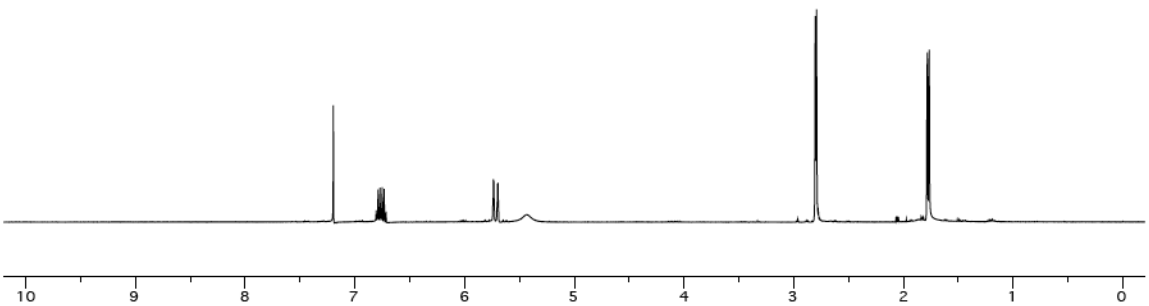
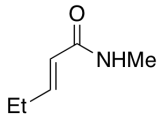
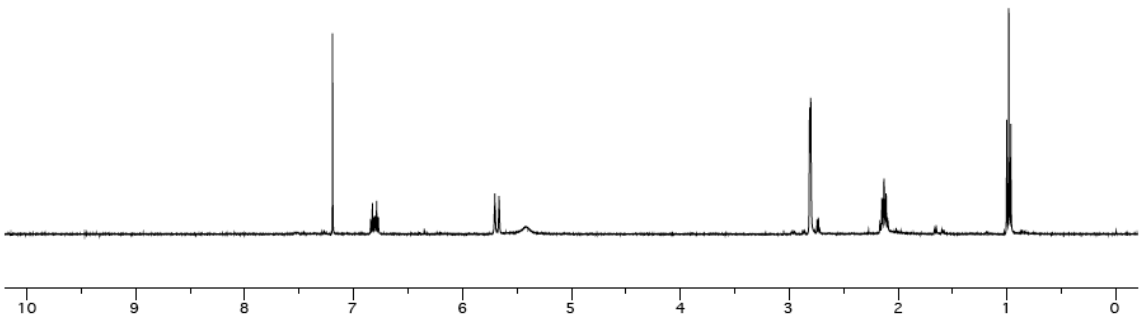


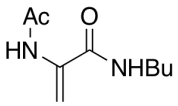


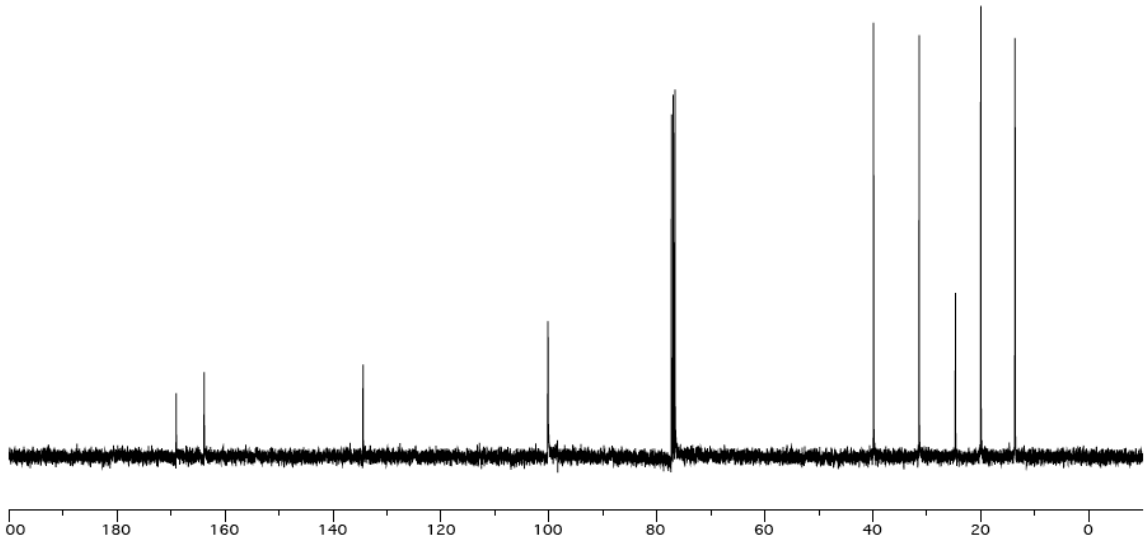
Starting Material 1g

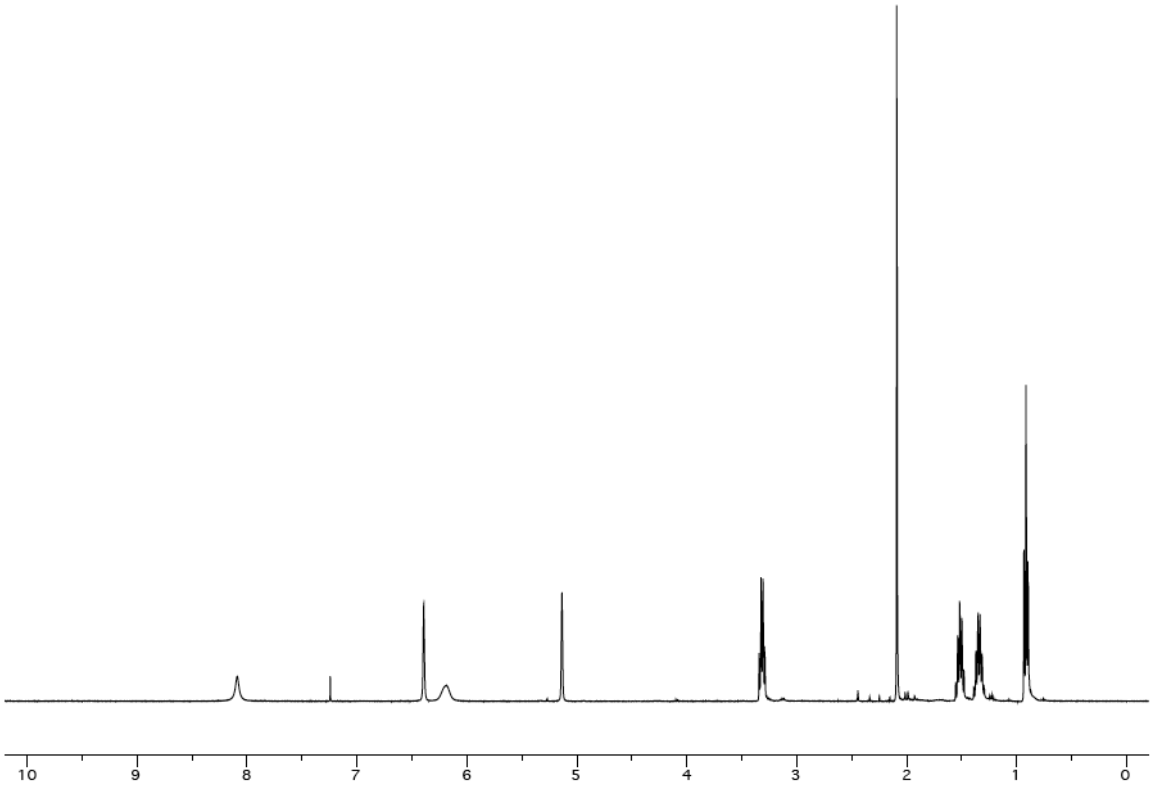




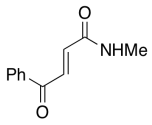
Starting Material 1h

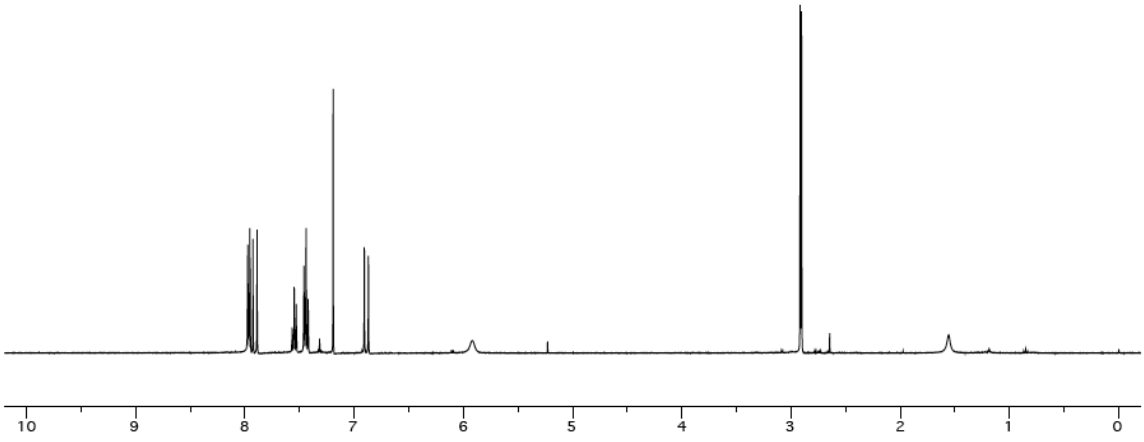




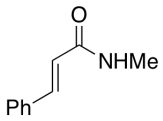


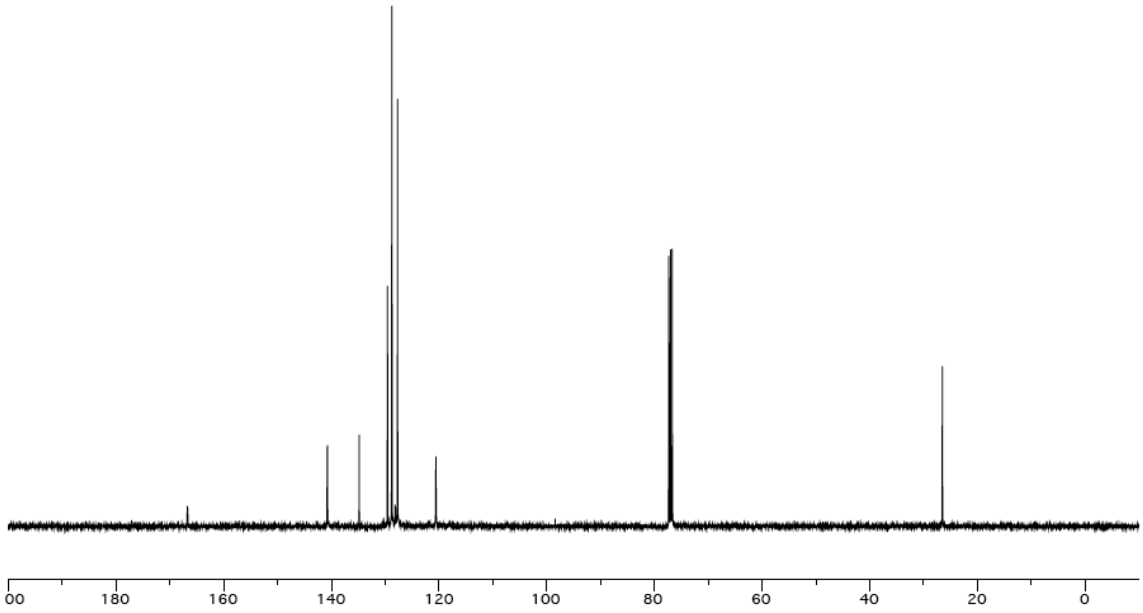
Starting Material 1i

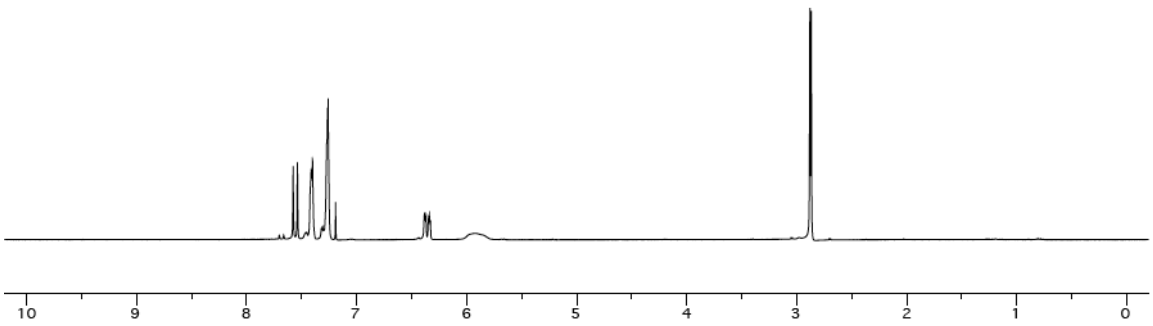




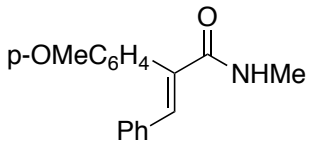
Starting Material 1j

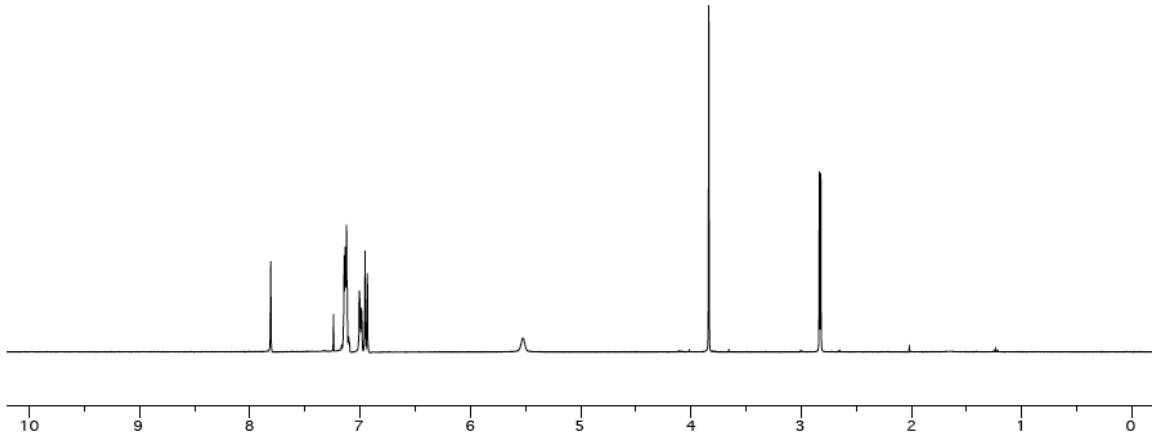


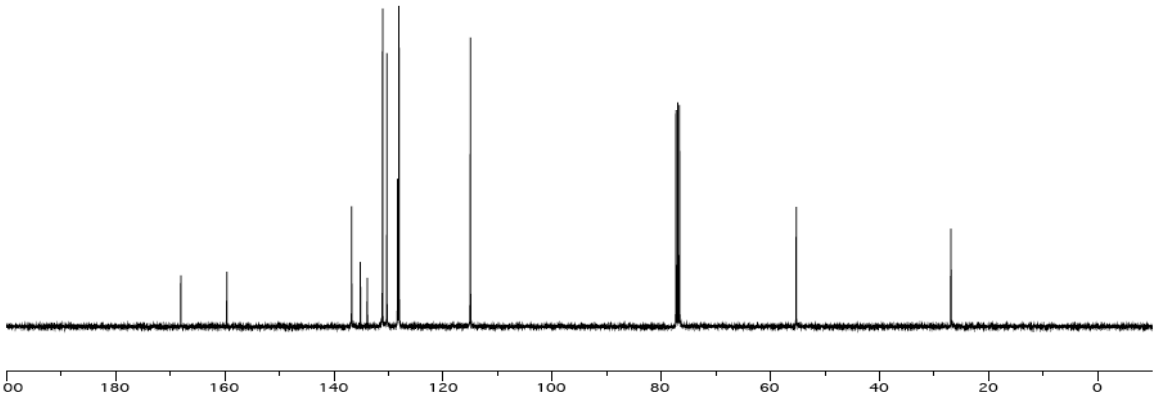




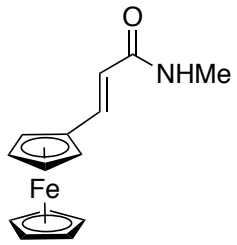
Starting Material 1k

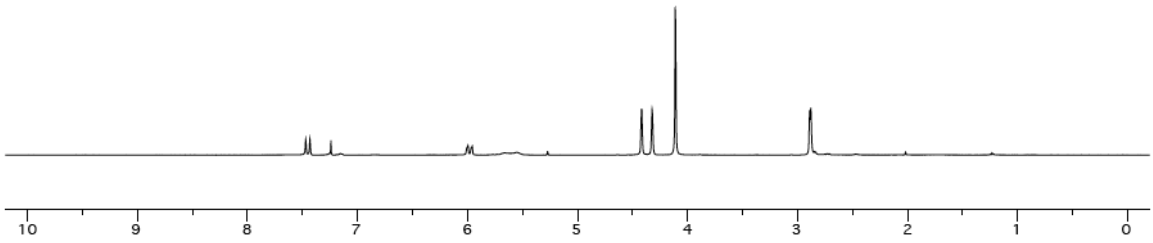


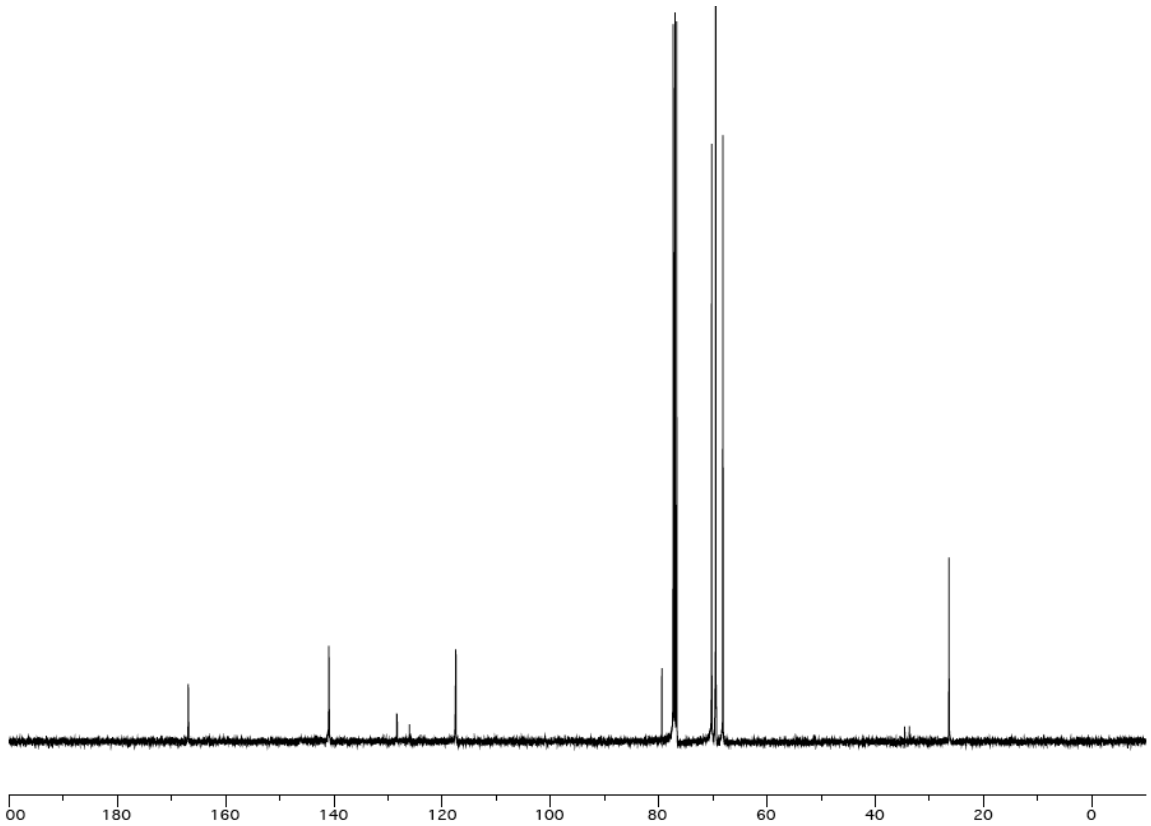




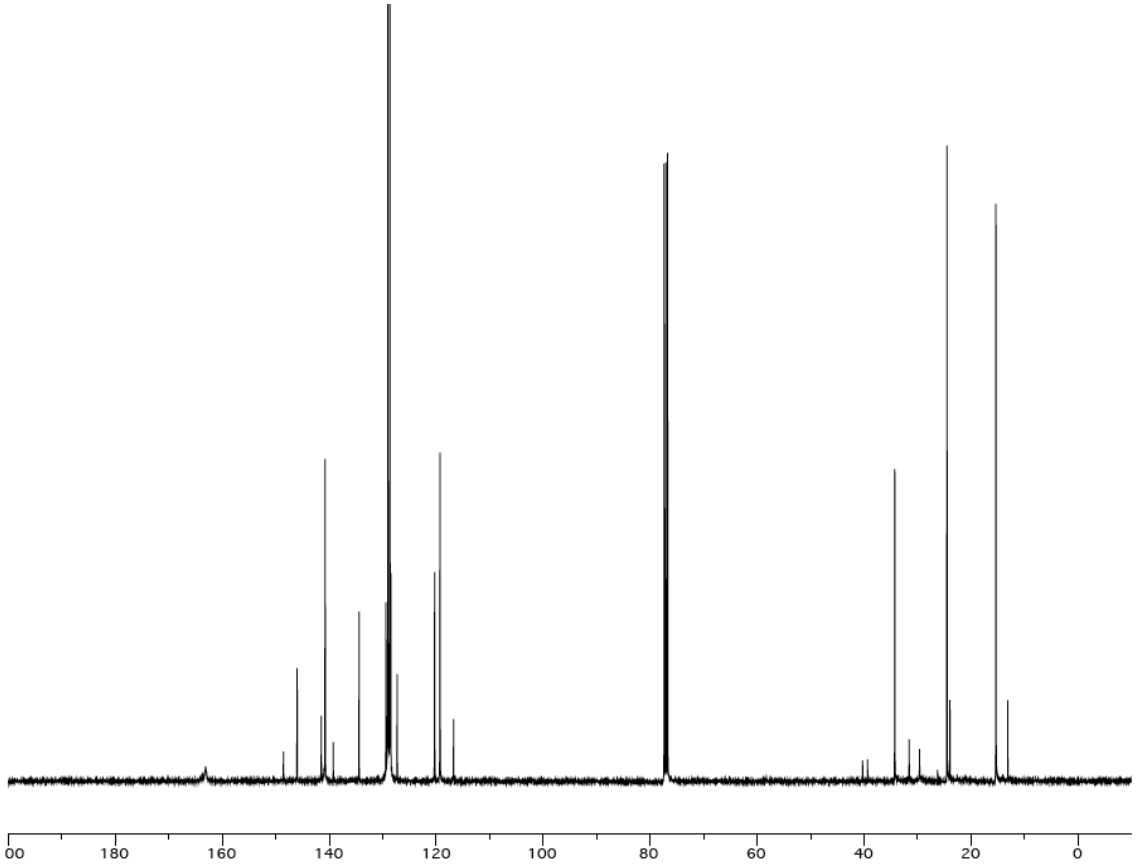
Starting Material 1l

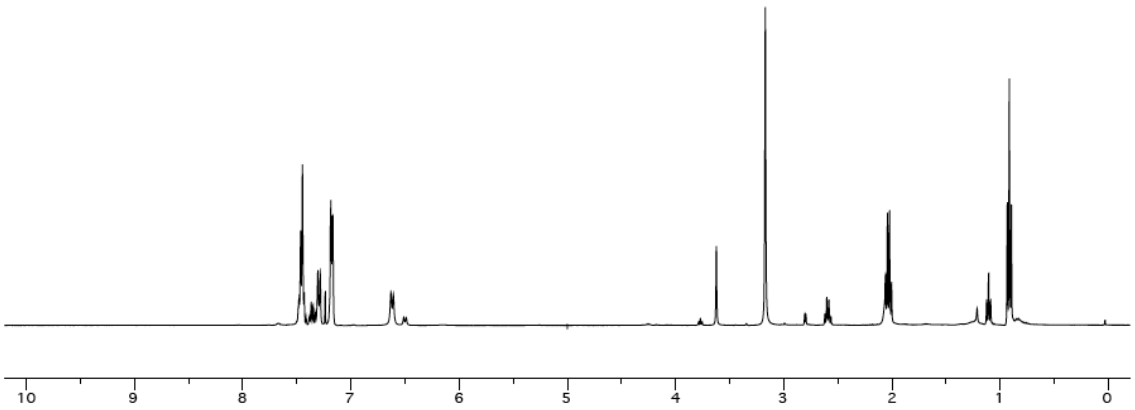




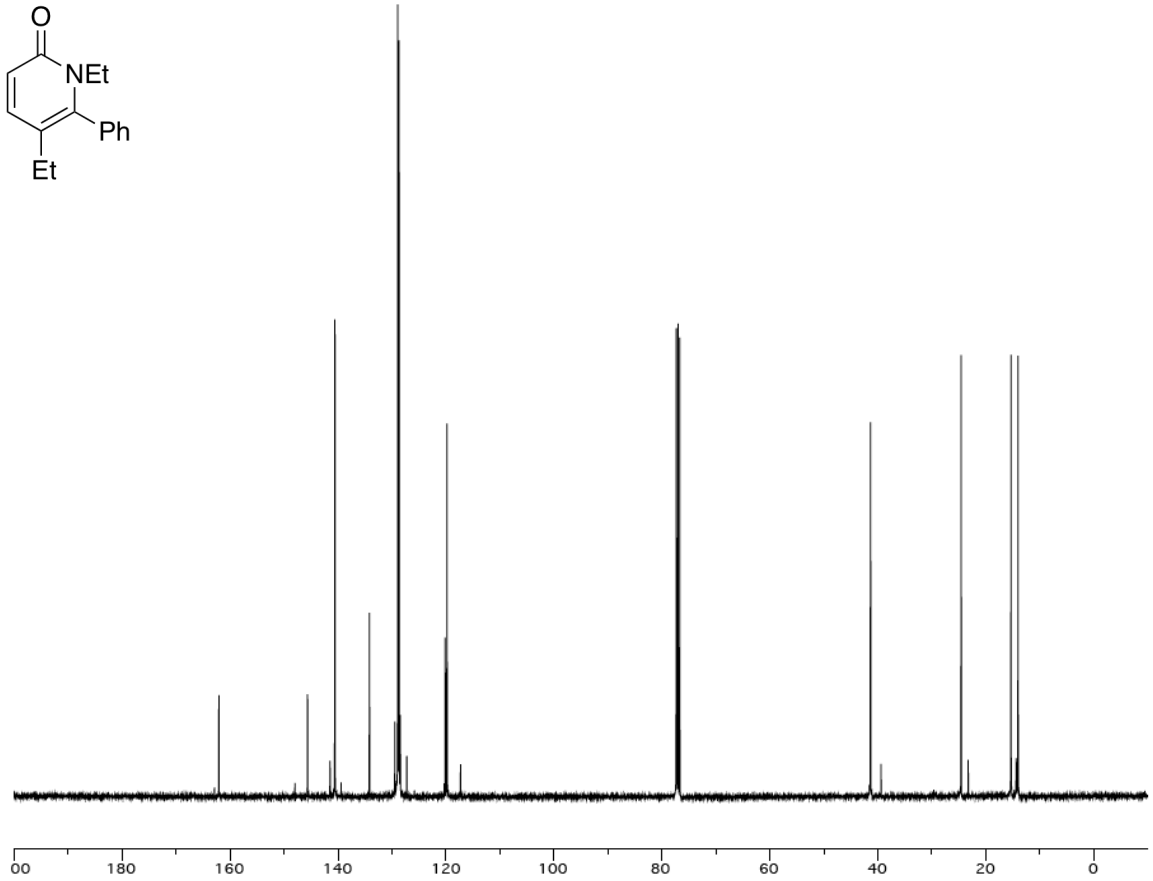


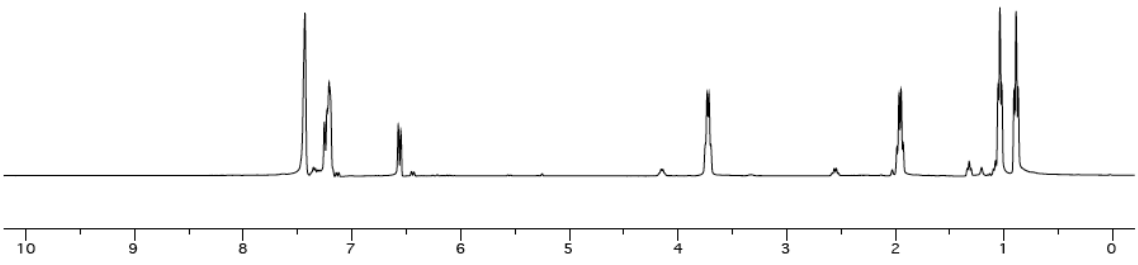
Pyridone 3a



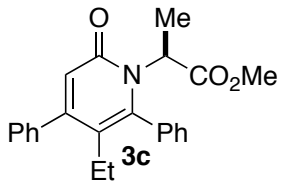


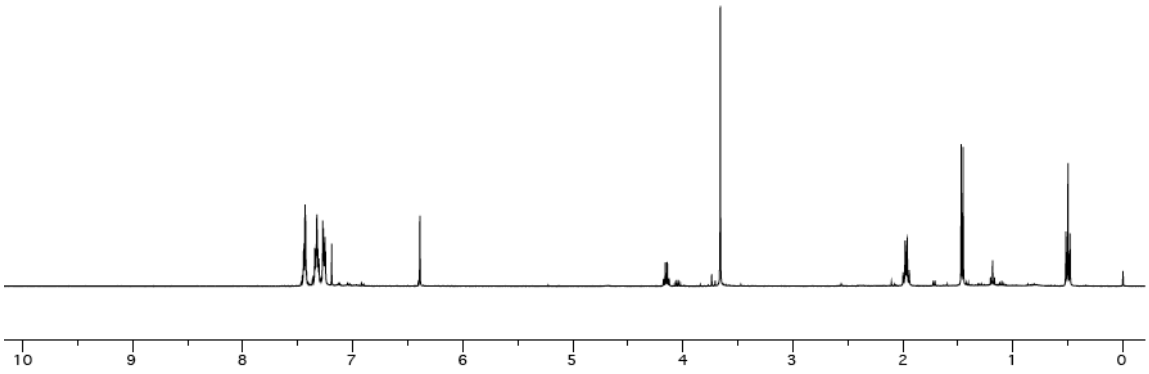
Pyridone 3b

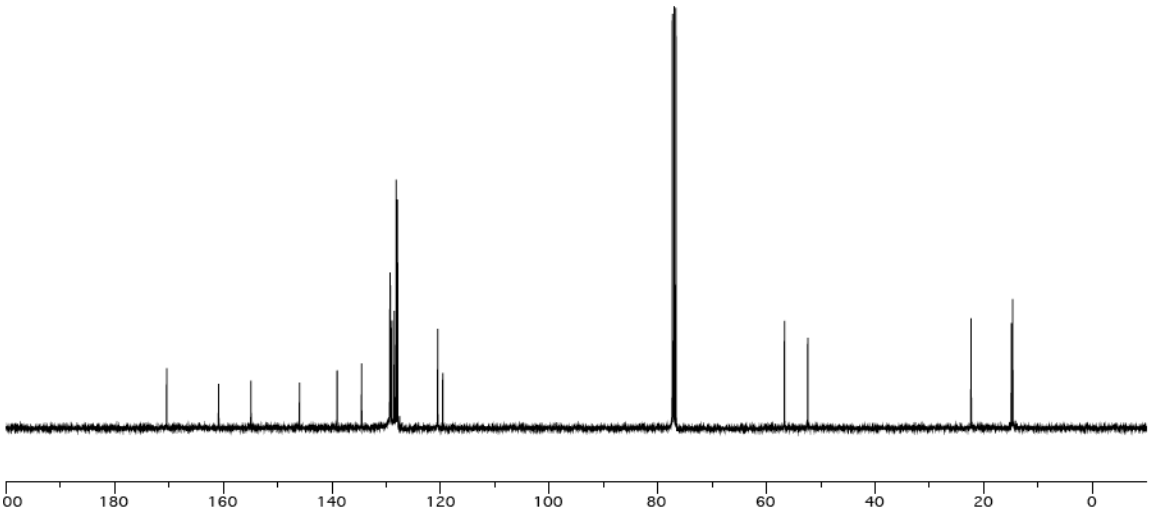




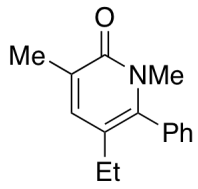
Pyridone 3c

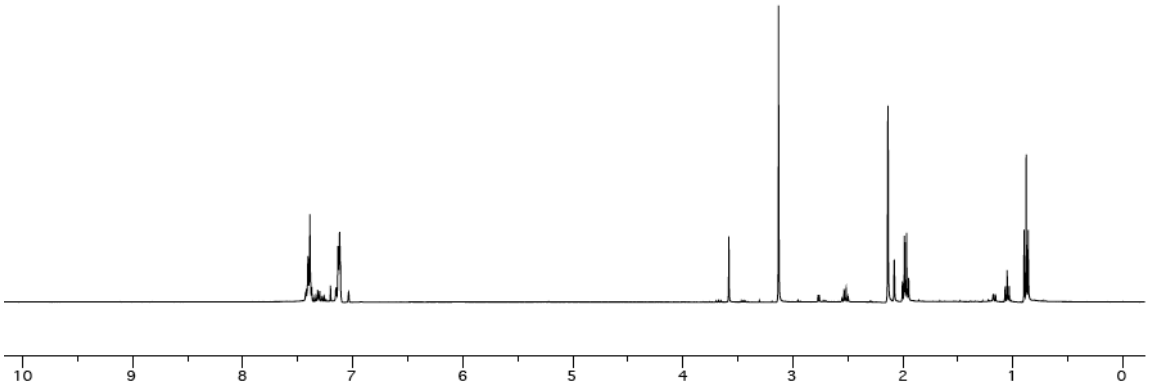


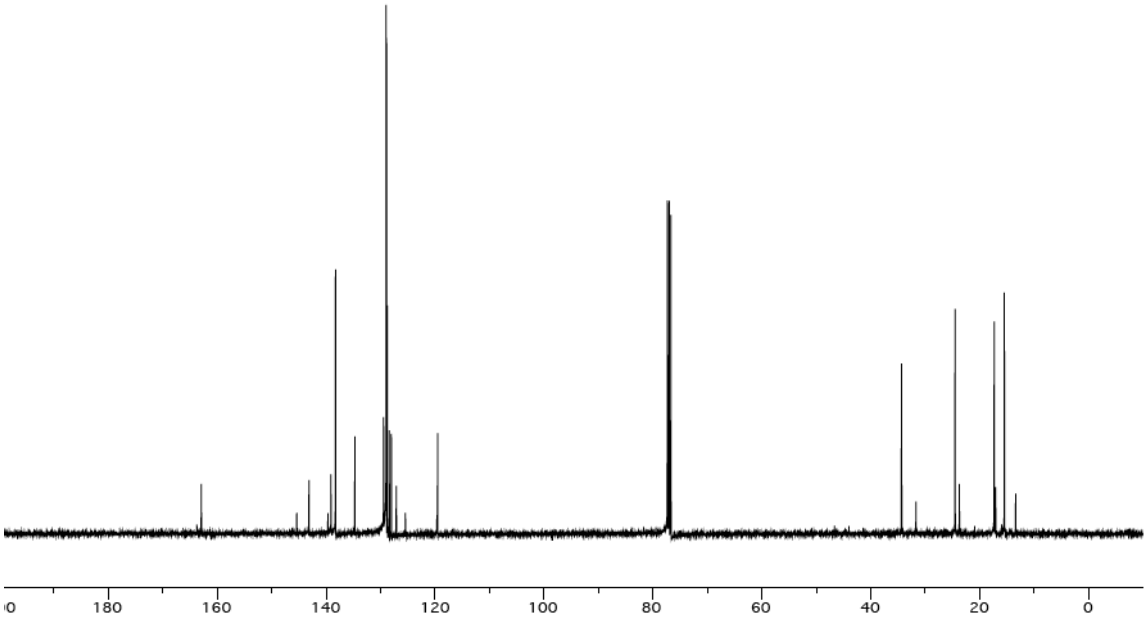




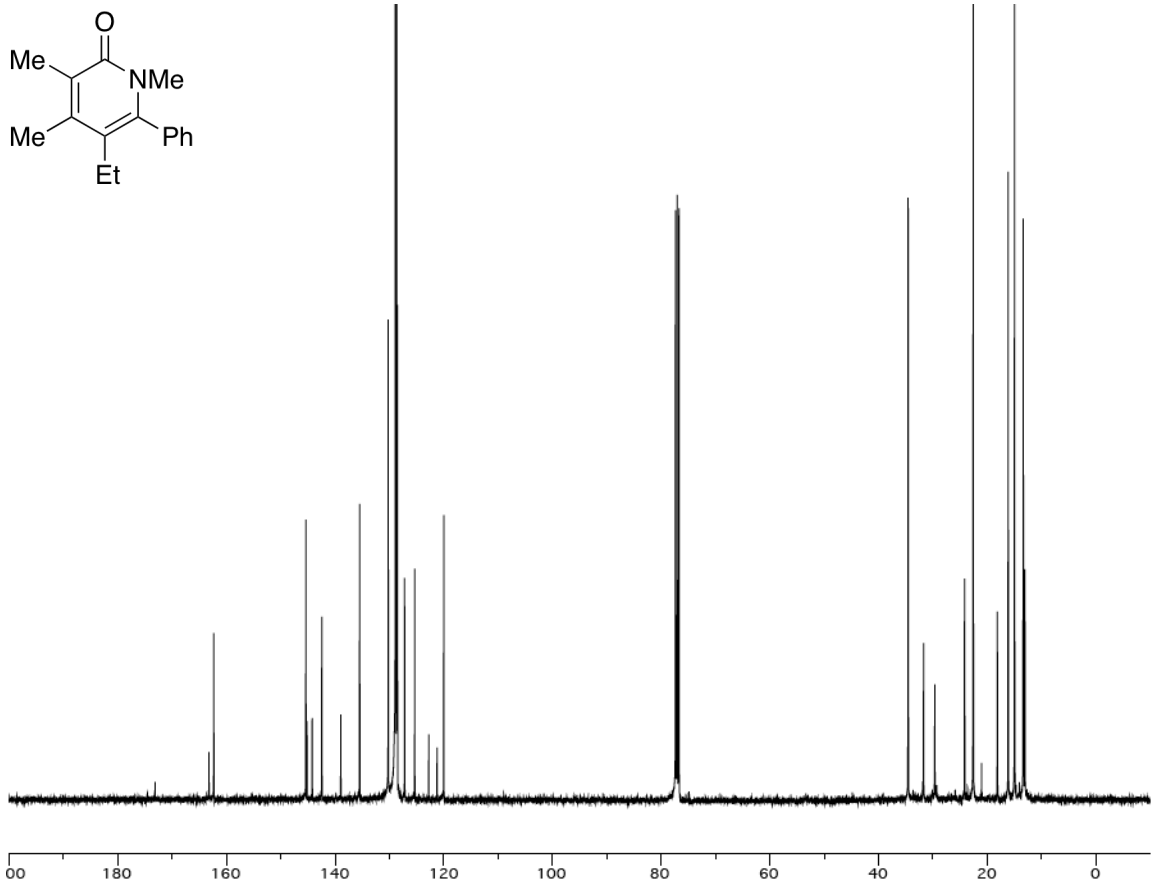
Pyridone 3d

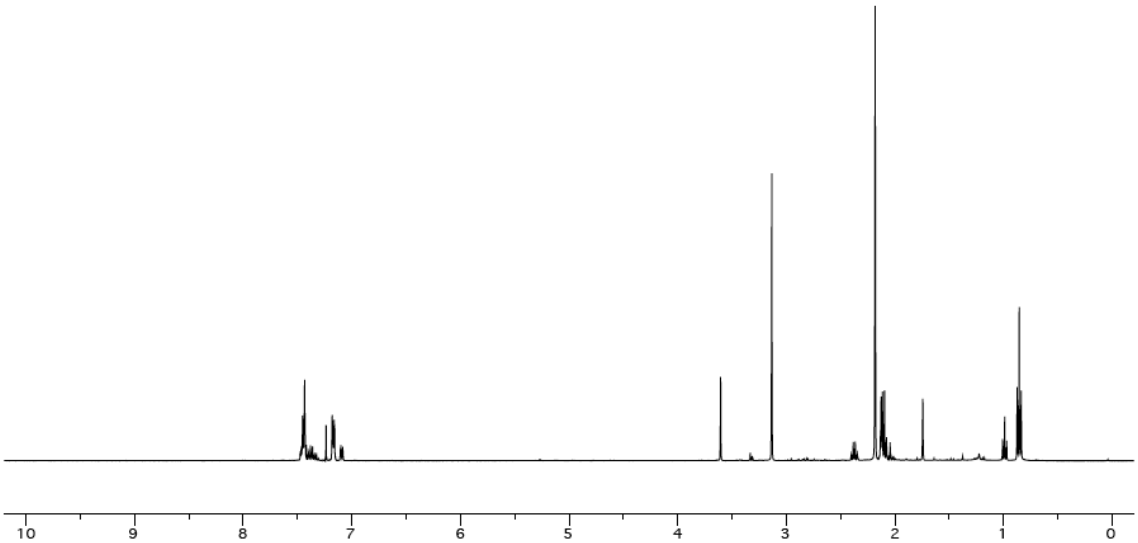




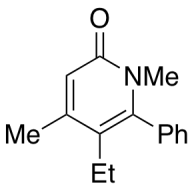


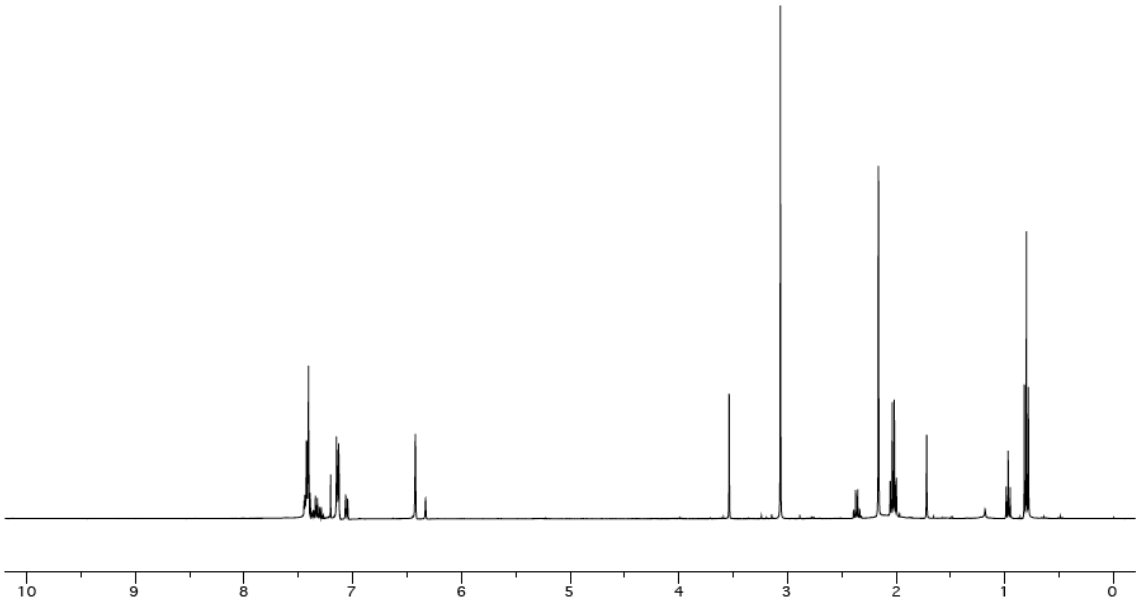
Pyridone 3e



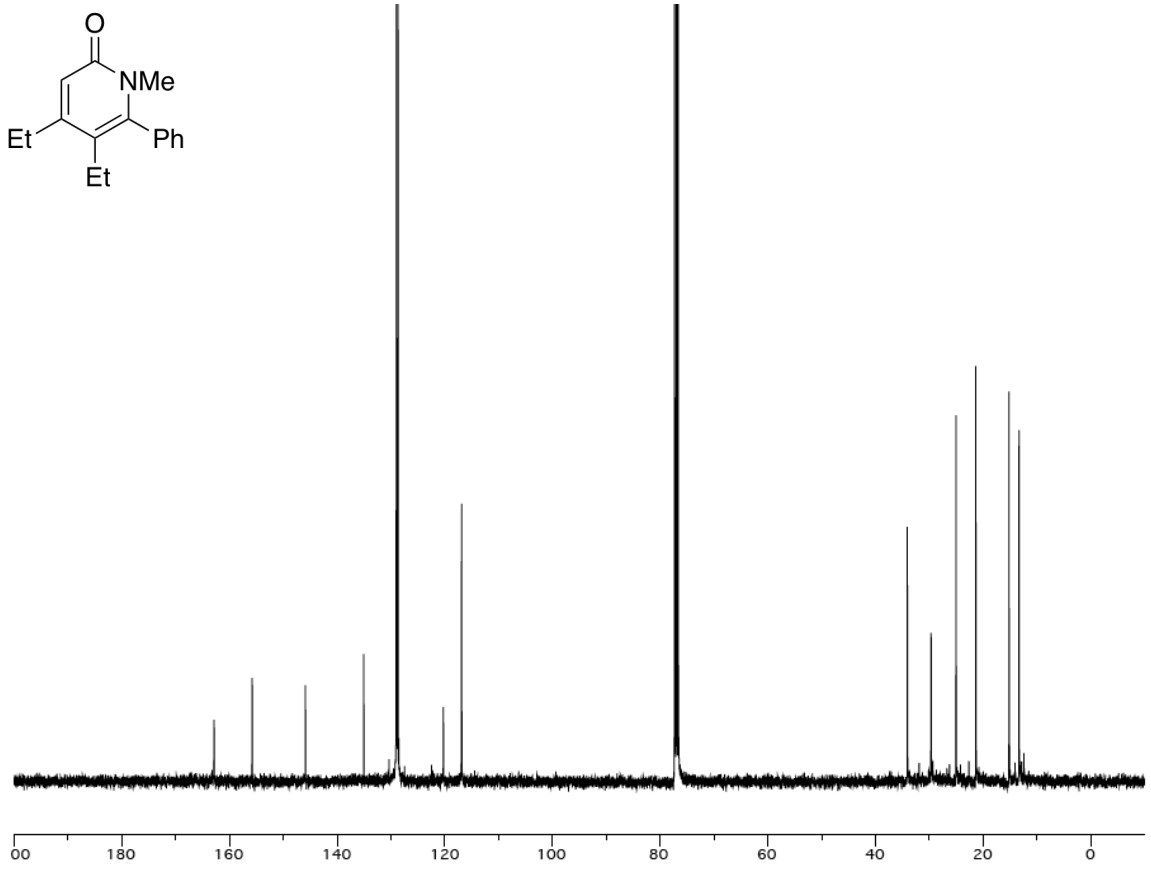


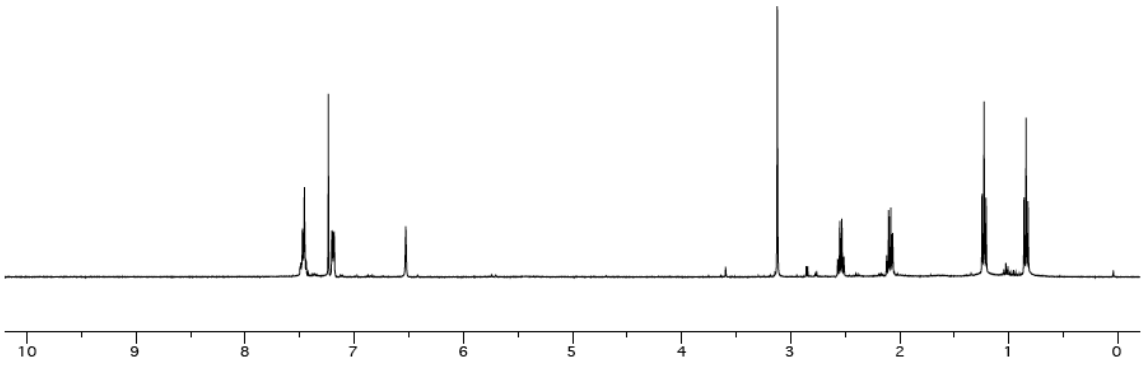
Pyridone 3f



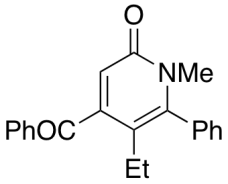


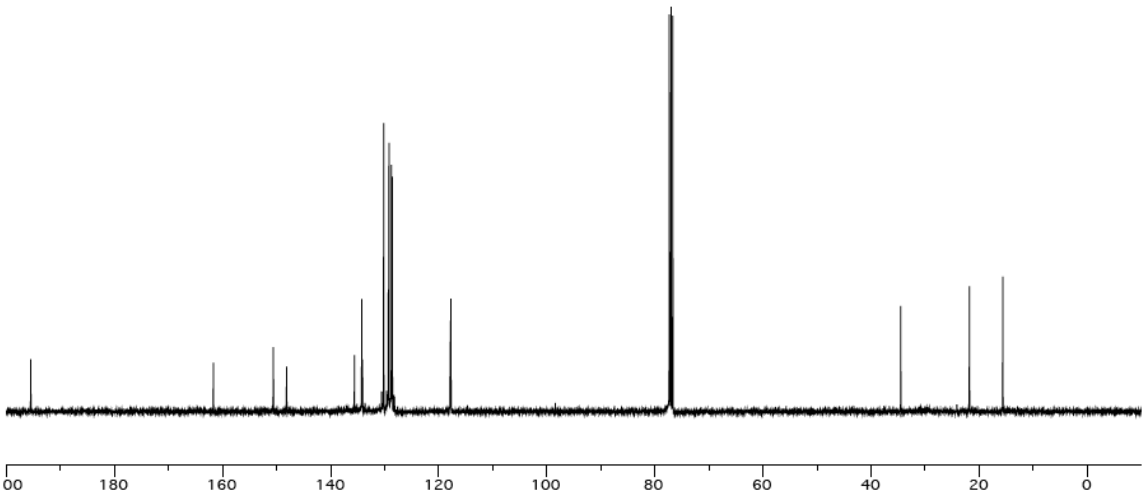
Pyridone 3g

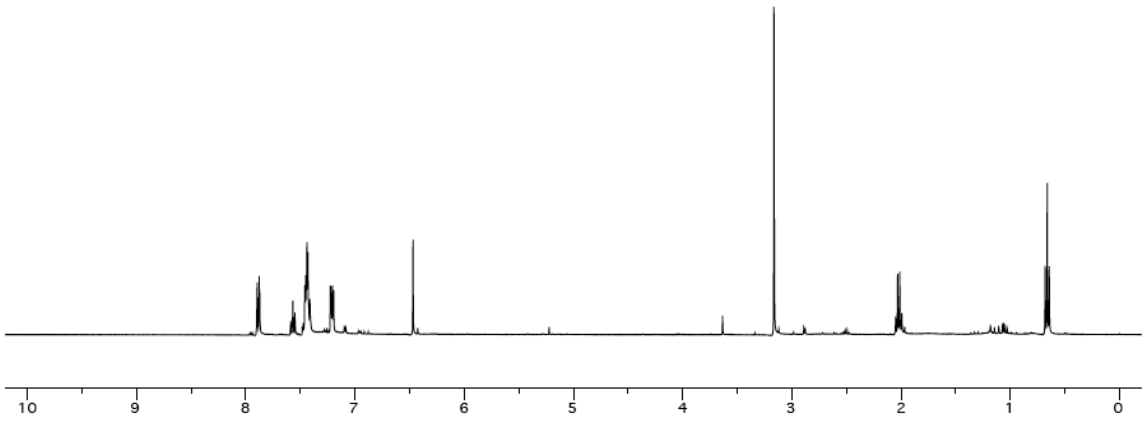




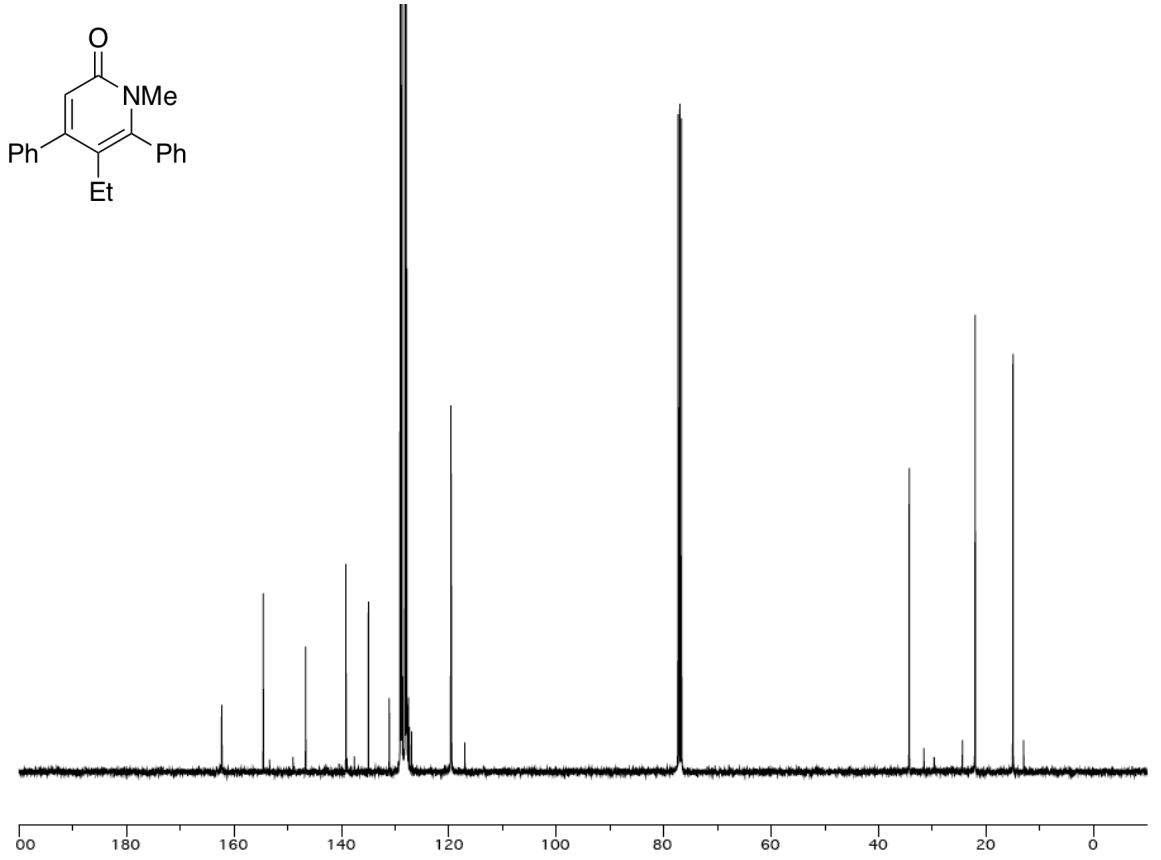
Pyridone 2l

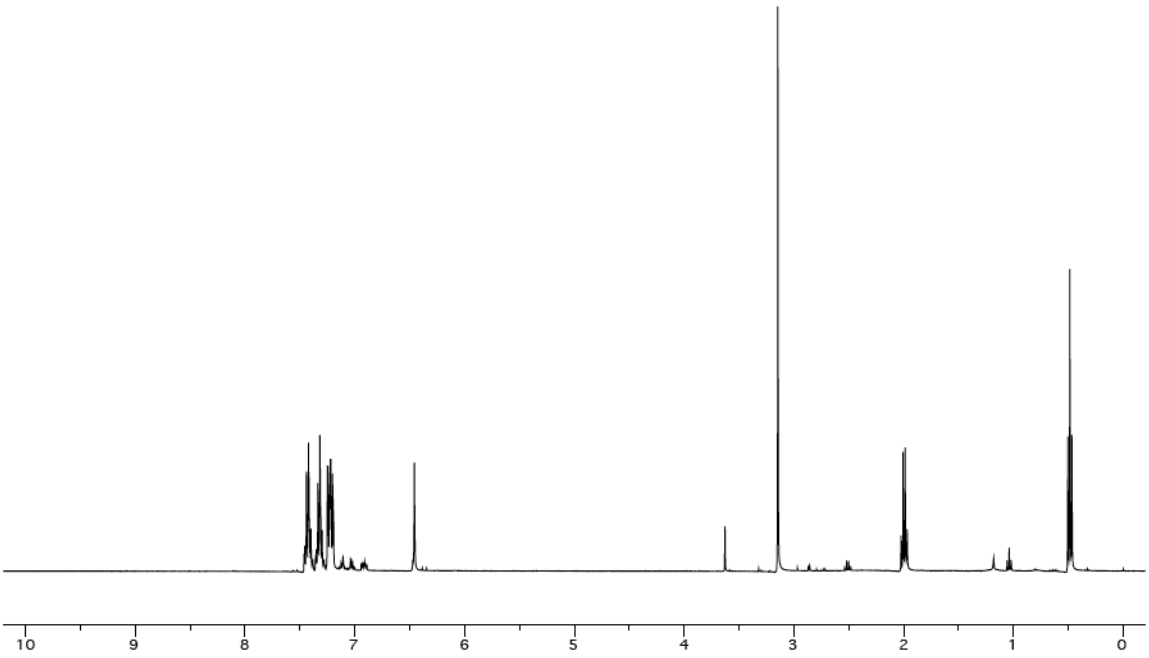




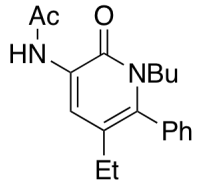


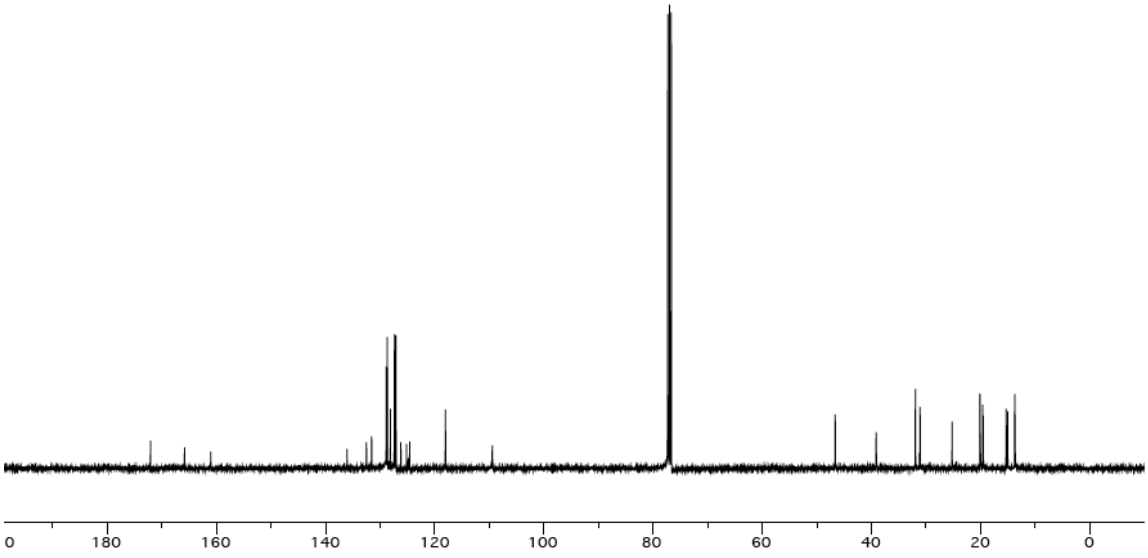
Pyridone 3j

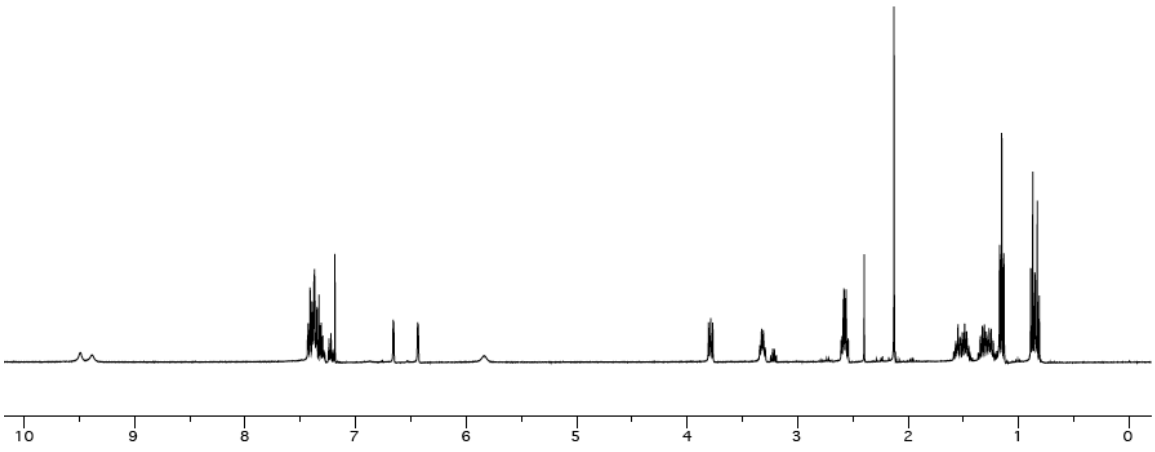




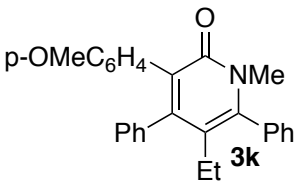
Pyridone 3h

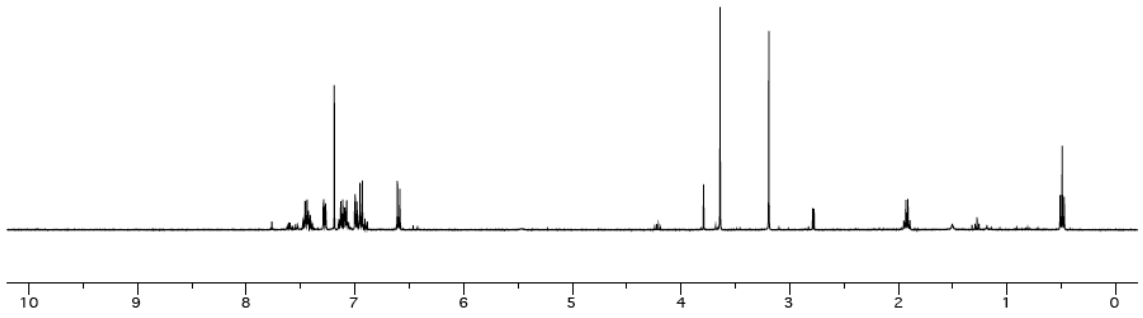


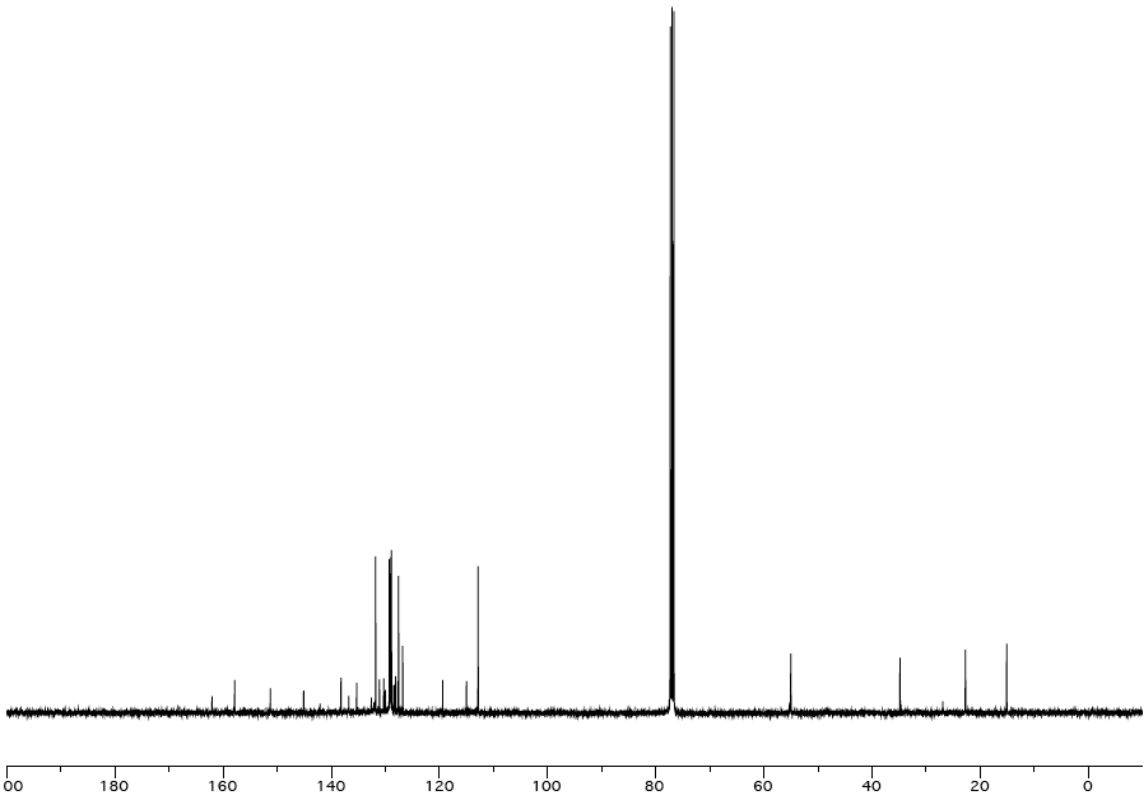




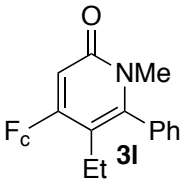
Pyridone 3k – Inseparable from unreacted starting material

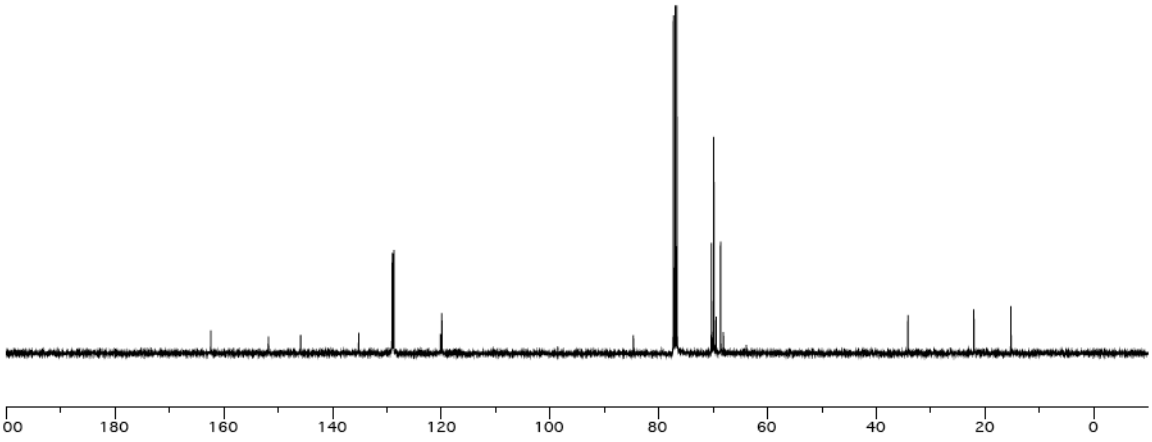


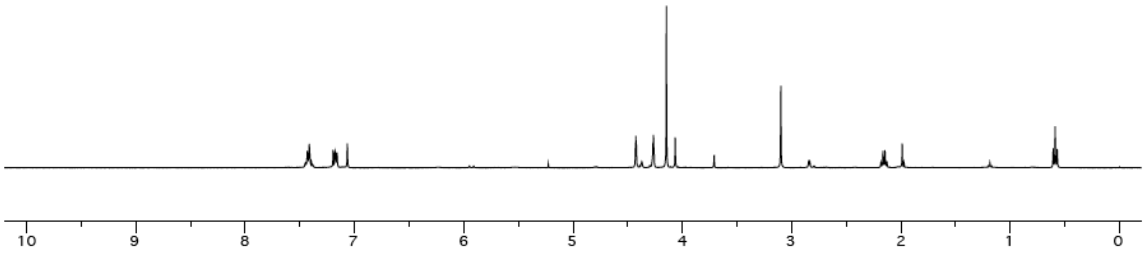




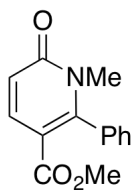
Pyridone 3l

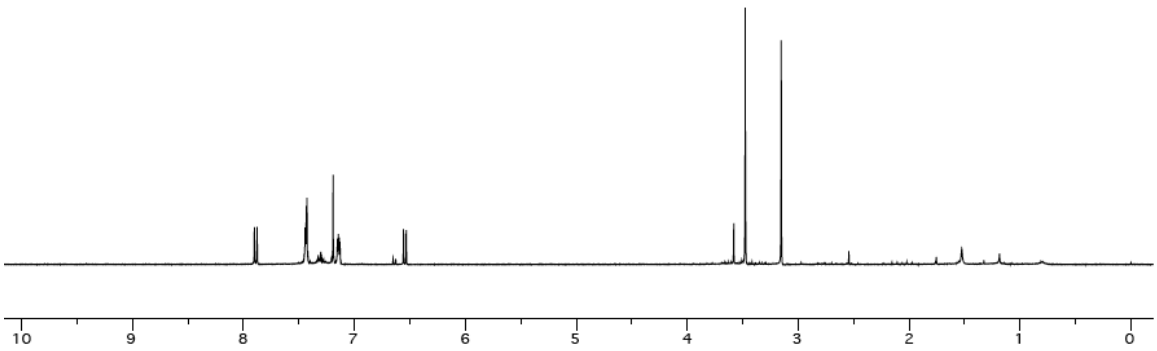




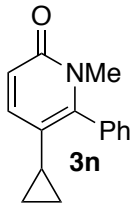


Pyridone 3m

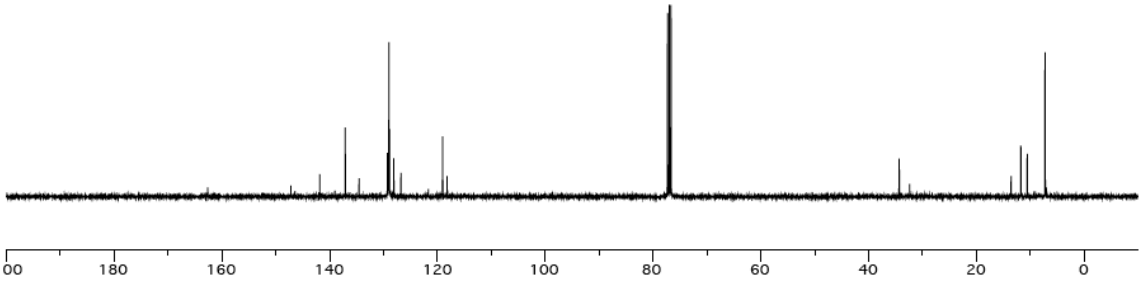


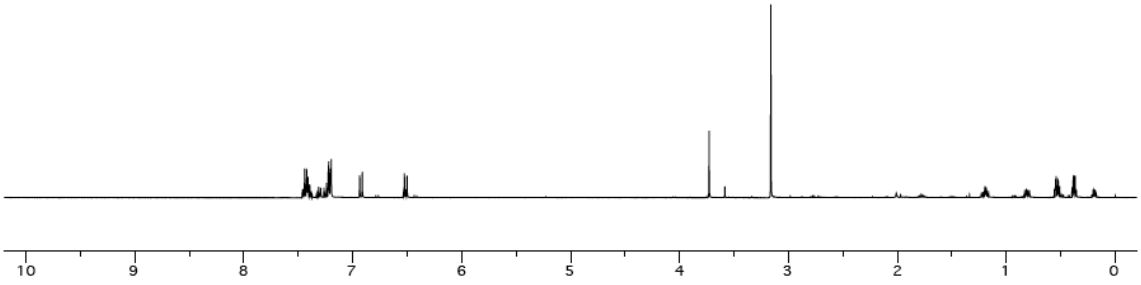


Pyridone 3n

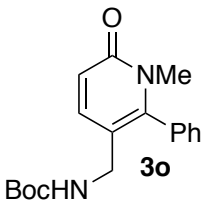


3n

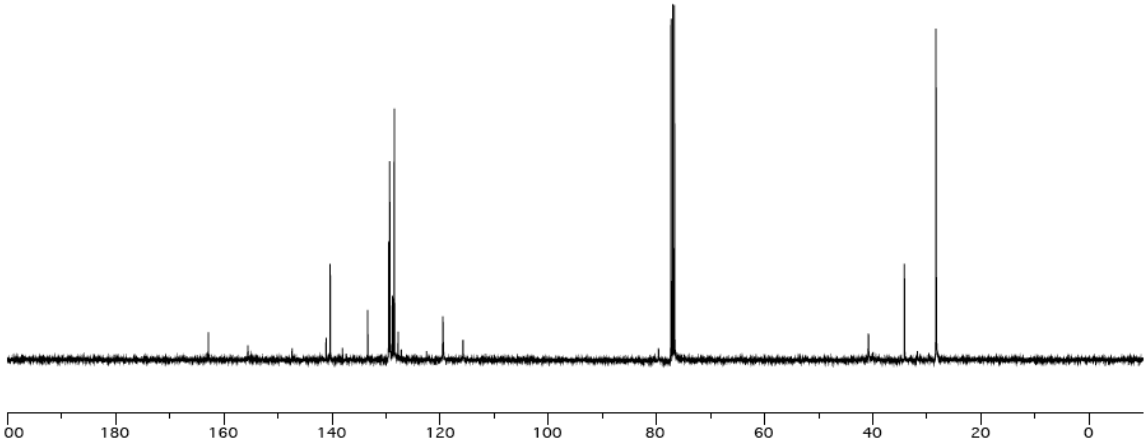


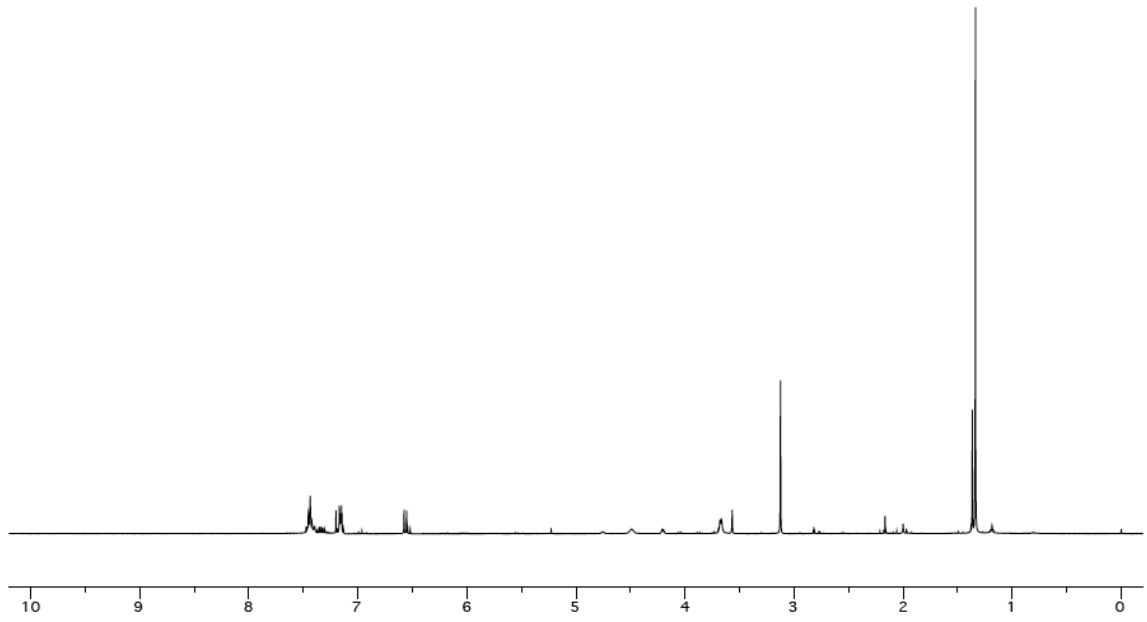


Pyridone 3o

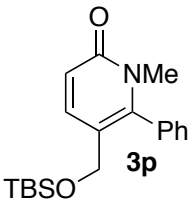


3o





Pyridone 3p



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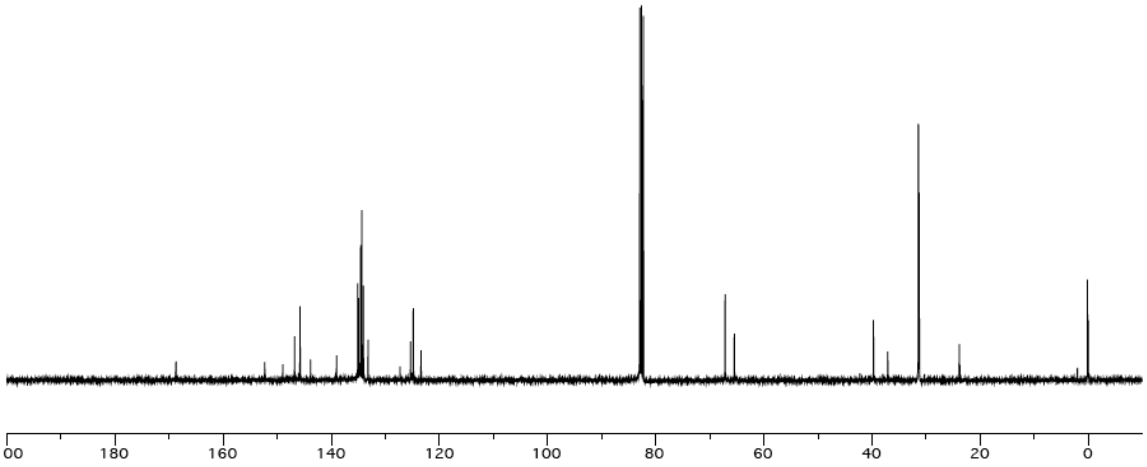
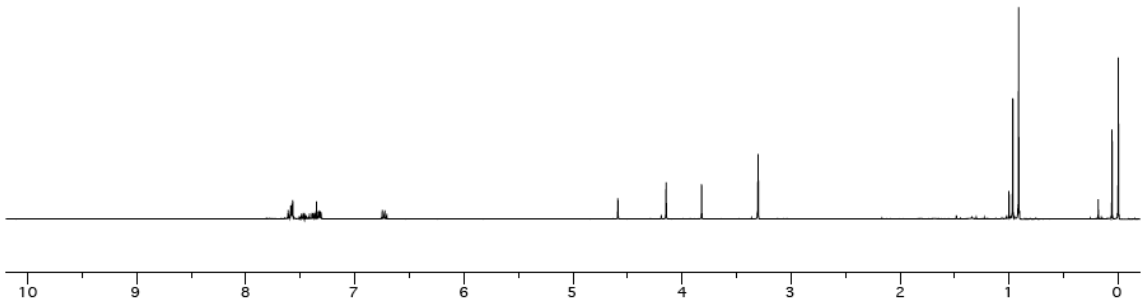
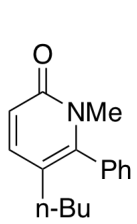
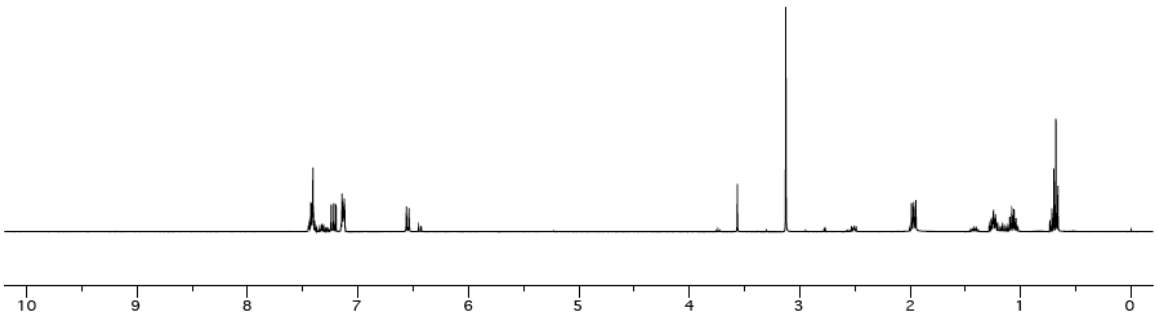


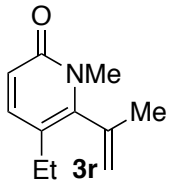


Pyridone 3q





Pyridone 3r



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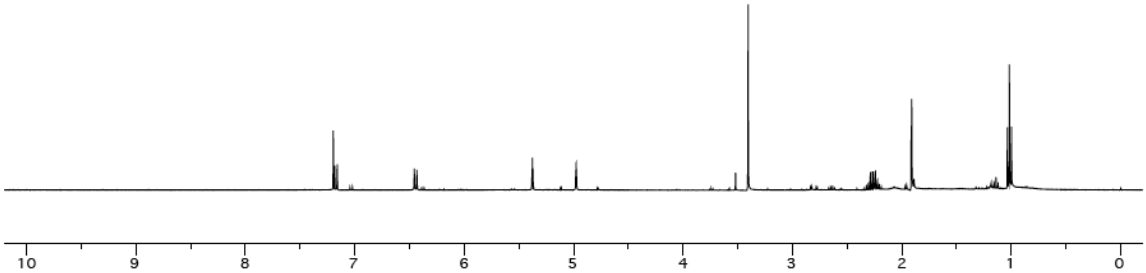
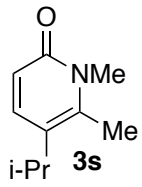


Pyridone 3s



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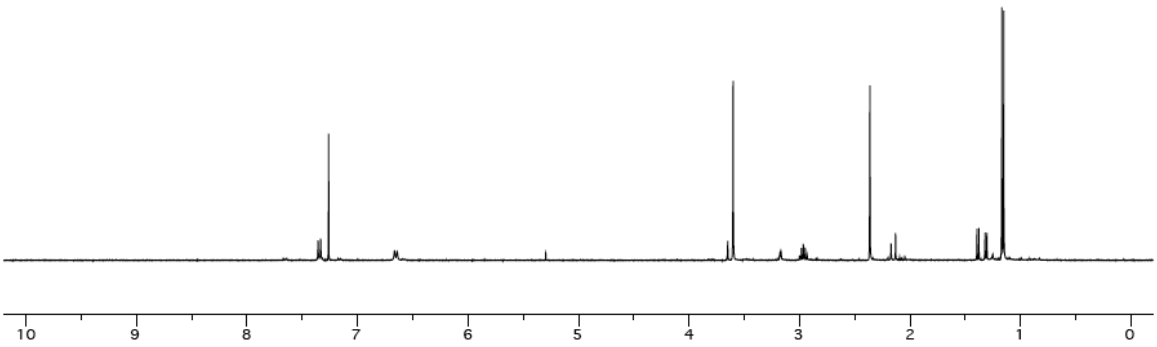

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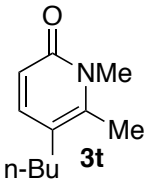

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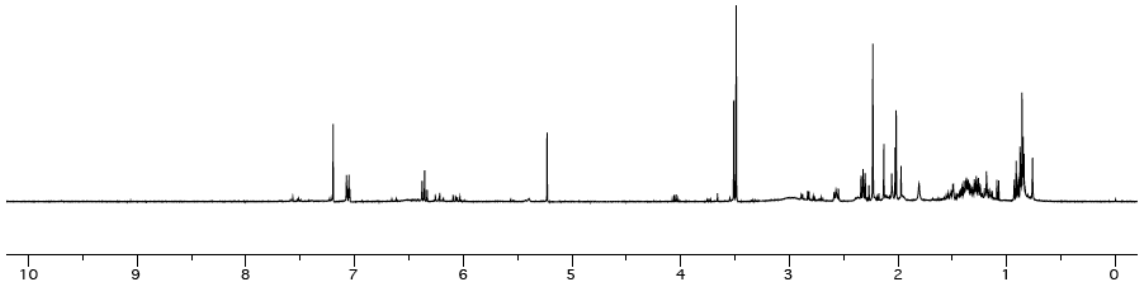
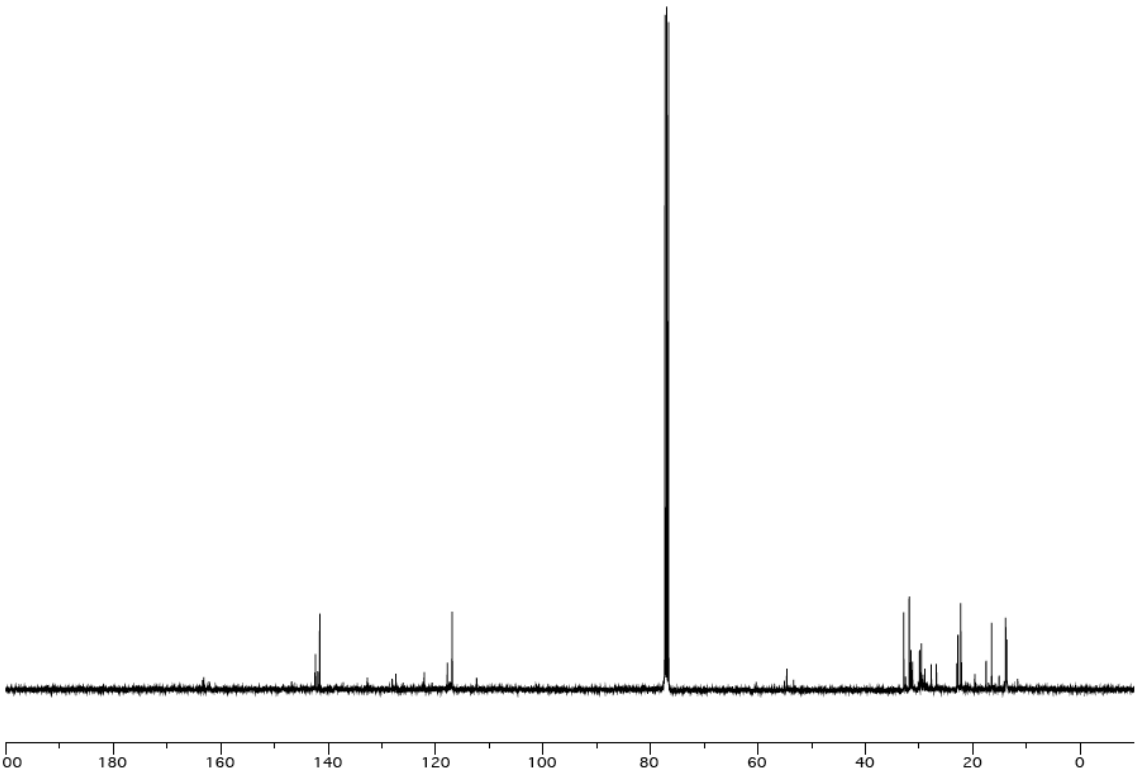
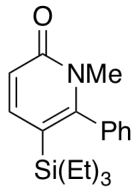
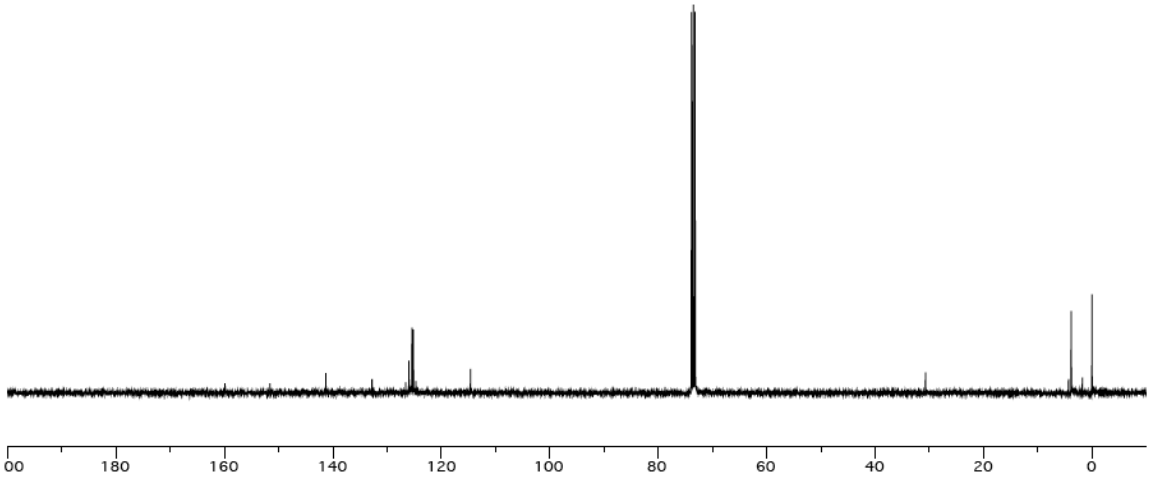
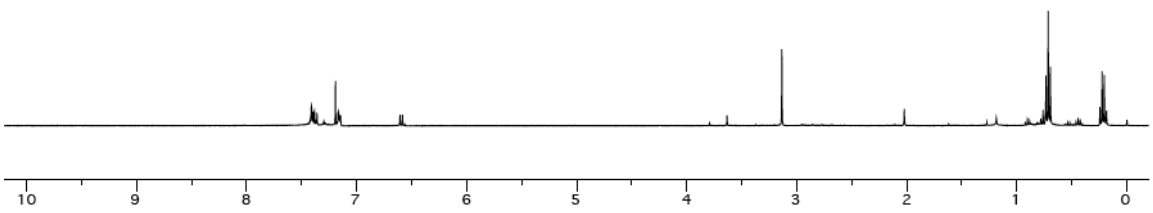




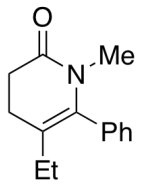
Pyridone 3u

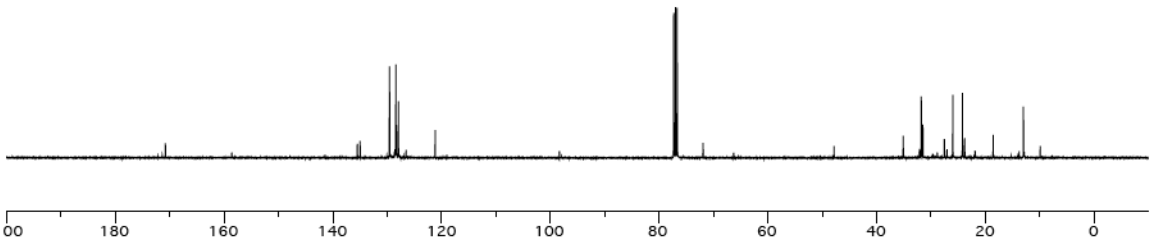


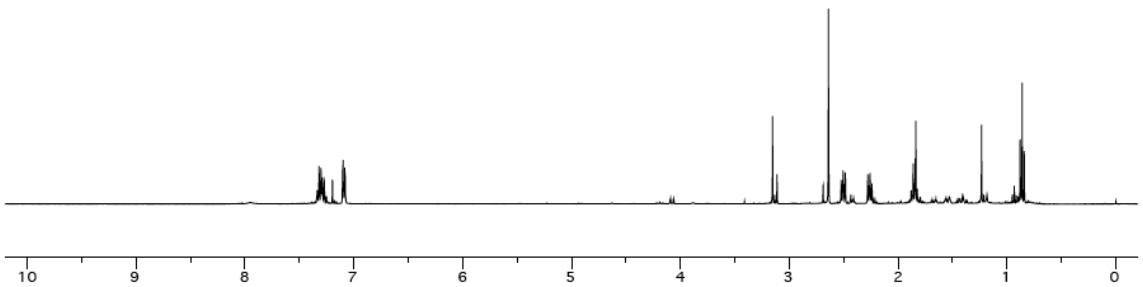




Dihydropyridone 3j'







Pyridine 3j''