

SUPPORTING INFORMATION

Iron Catalyzed Reactions of 2-Pyridone Derivatives: 1,6-Addition and Formal Ring Opening/Cross Coupling

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SUPPORTING CRYSTALLOGRAPHIC INFORMATION

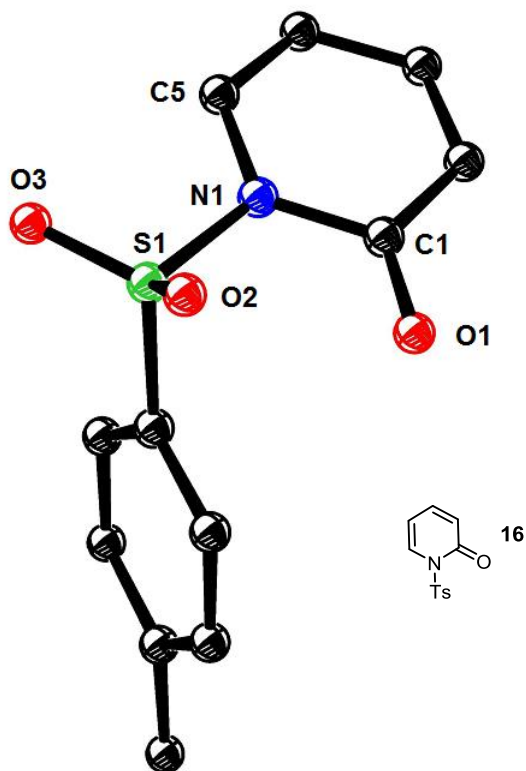


Figure S-1. Structure of pyridone **16** in the solid state; hydrogen atoms are omitted for clarity

X-ray Crystal Structure Analysis of Compound 16: C₁₂ H₁₁ N O₃ S, *Mr* = 249.28 g · mol⁻¹, colorless prism, crystal size 0.08 x 0.08 x 0.06 mm³, triclinic, space group *P1*, *a* = 6.6271(10) Å, *b* = 7.6892(18) Å, *c* = 11.836(4) Å, α = 87.57(2)°, β = 82.410(17)°, γ = 67.975(17)°, *V* = 554.2(3) Å³, *T* = 100(2) K, *Z* = 2, *D*_{calc} = 1.494 g · cm³, λ = 0.71073 Å, μ (*Mo-K*α) = 0.287 mm⁻¹, Gaussian absorption correction (*T*_{min} = 0.98, *T*_{max} = 0.99), Bruker-AXS Kappa Mach3 APEX-II diffractometer, 3.333 < Θ < 33.047°, 18368 measured reflections, 4182 independent reflections, 2916 reflections with *I* > 2σ(*I*), *R*_{int} = 0.0642.

The structure was solved by direct methods and refined by full-matrix least-squares against *F*² to *R*₁ = 0.053 [*I* > 2σ(*I*)], *wR*₂ = 0.117, 155 parameters. The H atoms were refined using a riding model, *S* = 1.037, residual electron density 0.6 (0.70 Å from C11)/ -0.4 (0.57 Å from S1) e · Å⁻³. **CCDC- 1917191.**

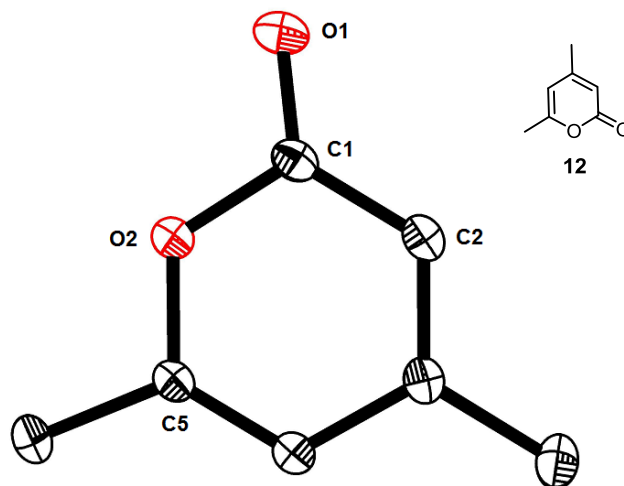


Figure S-2. Structure of pyrone **12** in the solid state; hydrogen atoms are omitted for clarity

X-ray Crystal Structure Analysis of Compound 12: $C_7H_8O_2$, $M_r = 124.13 \text{ g} \cdot \text{mol}^{-1}$, colorless block, crystal size $0.32 \times 0.14 \times 0.12 \text{ mm}^3$, monoclinic, space group $P2_1/c$, $a = 7.3014(7) \text{ \AA}$, $b = 11.8309(10) \text{ \AA}$, $c = 7.4752(5) \text{ \AA}$, $\beta = 91.565(7)^\circ$, $V = 645.48(9) \text{ \AA}^3$, $T = 160(2) \text{ K}$, $Z = 4$, $D_{calc} = 1.277 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 0.093 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{min} = 0.98$, $T_{max} = 0.99$), Bruker-AXS Kappa Mach3 APEX-II diffractometer, $3.280 < \Theta < 33.035^\circ$, 9708 measured reflections, 2417 independent reflections, 2037 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0319$.

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.046 [I > 2\sigma(I)]$, $wR_2 = 0.144$, 84 parameters, absolute structure parameter = $0.44(6)$.

The H atoms were refined using a riding model, $S = 1.128$, residual electron density 0.4 (0.72 \AA from C5)/ -0.3 (0.80 \AA from C3) $e \cdot \text{\AA}^{-3}$. **CCDC- 1917198.**

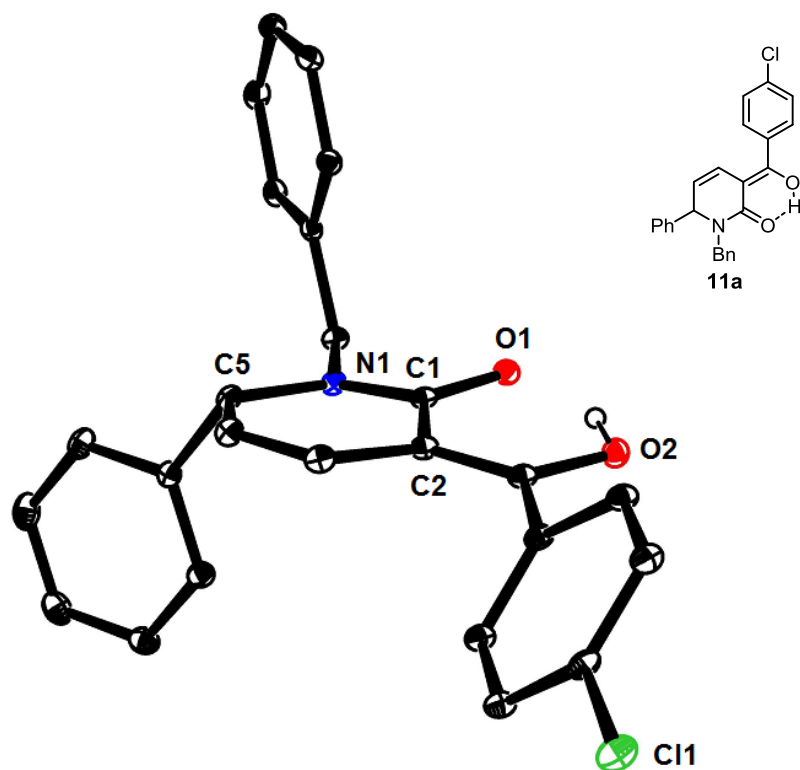


Figure S-3. Structure of compound **11a** in the solid state; all hydrogen atoms except the –OH involved in hydrogen bonding as well as CH₂Cl₂ contained in the unit cell are omitted for clarity

X-ray Crystal Structure Analysis of Compound 11a: C₂₆H₂₂Cl₃N O₂, *Mr* = 486.79 g · mol⁻¹, colorless needle, crystal size 0.158 x 0.032 x 0.031 mm³, monoclinic, space group *P*2₁/*c*, *a* = 6.8389(11) Å, *b* = 19.279(3) Å, *c* = 17.827(3) Å, *β* = 100.843(3)°, *V* = 2308.5(7) Å³, *T* = 100(2) K, *Z* = 4, *D*_{calc} = 1.401 g · cm³, *λ* = 0.71073 Å, *μ*(*Mo*-*Kα*) = 0.421 mm⁻¹, Gaussian absorption correction (*T*_{min} = 0.95, *T*_{max} = 0.99), Bruker-AXS Kappa Mach3 APEX-II diffractometer, 2.326 < *Θ* < 33.984°, 71776 measured reflections, 9283 independent reflections, 6581 reflections with *I* > 2σ(*I*), *R*_{int} = 0.0600.

The structure was solved by direct methods and refined by full-matrix least-squares against *F*² to *R*₁ = 0.047 [*I* > 2σ(*I*)], *wR*₂ = 0.129, 293 parameters, absolute structure parameter = 0.44(6).

The H atom at O2 was found and refined, all other H atoms were refined using a riding model, *S* = 1.035, residual electron density 0.7 (0.74 Å from Cl2)/ –0.9 (0.79 Å from Cl2) e · Å⁻³. **CCDC- 1917196.**

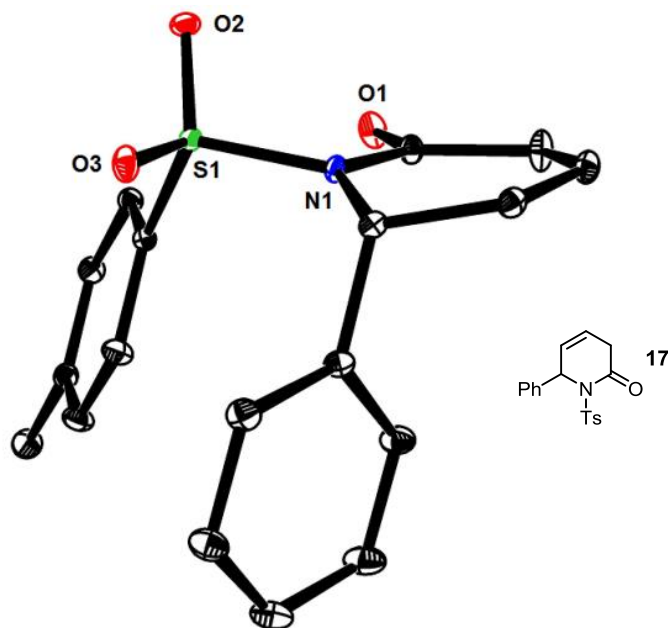


Figure S-4. Structure of compound **17** in the solid state; H-atoms are omitted for clarity

X-ray Crystal Structure Analysis of Compound 17: $C_{18}H_{17}NO_3S$, $M_r = 327.38 \text{ g} \cdot \text{mol}^{-1}$, colorless block, crystal size $0.35 \times 0.28 \times 0.15 \text{ mm}^3$, orthorhombic, space group $Pna2_1$, $a = 11.818(3) \text{ \AA}$, $b = 16.341(4) \text{ \AA}$, $c = 8.1630(10) \text{ \AA}$, $V = 1576.4(5) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $D_{calc} = 1.379 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 0.220 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{min} = 0.94$, $T_{max} = 0.97$), Bruker-AXS Kappa Mach3 APEX-II diffractometer, $2.789 < \Theta < 33.010^\circ$, 29492 measured reflections, 5883 independent reflections, 5698 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0283$.

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.026 [I > 2\sigma(I)]$, $wR_2 = 0.068$, 209 parameters, absolute structure parameter = $0.045(11)$.

The H atoms were refined using a riding model, $S = 1.077$, residual electron density $0.3 (0.76 \text{ \AA} \text{ from O2}) / -0.2 (0.57 \text{ \AA} \text{ from S1}) \text{ e} \cdot \text{\AA}^{-3}$. **CCDC- 1917193**.

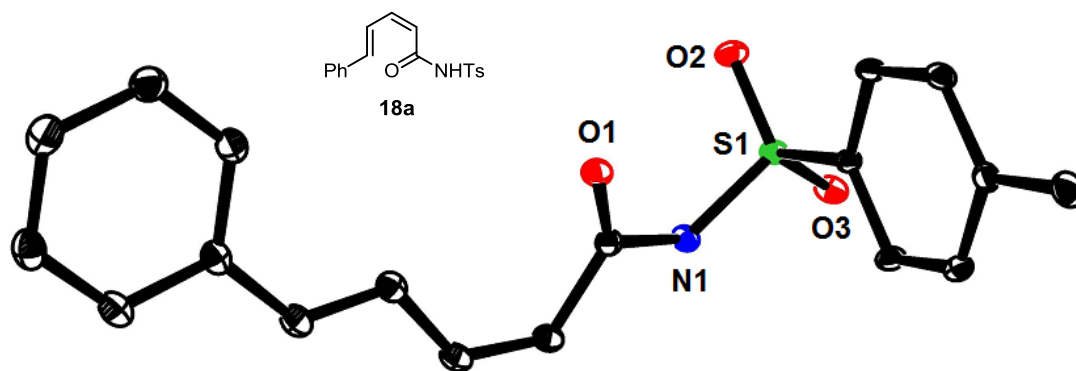


Figure S-5. Structure of compound **18a** in the solid state; H-atoms are omitted for clarity

X-ray Crystal Structure Analysis of Compound 18a: $C_{18}H_{17}NO_3S$, $M_r = 327.38 \text{ g} \cdot \text{mol}^{-1}$, colorless plate, crystal size $0.173 \times 0.171 \times 0.031 \text{ mm}^3$, monoclinic, space group $P2_1/n$, $a = 5.9691(7) \text{ \AA}$, $b = 9.9398(11) \text{ \AA}$, $c = 27.354(3) \text{ \AA}$, $\beta = 91.067(2)^\circ$, $V = 1622.7(3) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $D_{calc} = 1.340 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 0.214 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{min} = 0.98$, $T_{max} = 0.99$), Bruker-AXS Kappa Mach3 APEX-II diffractometer, $2.533 < \Theta < 31.064^\circ$, 47162 measured reflections, 5194 independent reflections, 7804 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0310$.

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.042$ [$I > 2\sigma(I)$], $wR_2 = 0.113$, 213 parameters. The H atom at N1 was found and refined, all other H atoms were refined using a riding model, $S = 1.077$, residual electron density 0.5 (0.67 \AA from C16)/ -0.3 (0.38 \AA from S1) $e \cdot \text{\AA}^{-3}$. **CCDC- 1917194**.

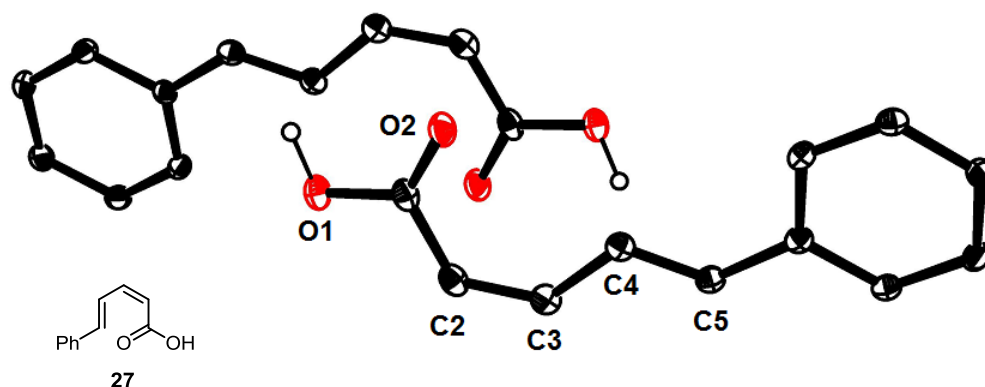


Figure S-6. Structure of dienoic acid **27** in the solid state showing two independent molecules in the unit cell; all but the acidic hydrogen atoms are omitted for clarity

X-ray Crystal Structure Analysis of Compound 27. $C_{11}H_{10}O_2$, $M_r = 174.19 \text{ g} \cdot \text{mol}^{-1}$, colorless needle, crystal size $0.35 \times 0.28 \times 0.15 \text{ mm}^3$, orthorhombic, space group $Pca2_1$, $a = 22.5169(14) \text{ \AA}$, $b = 5.5867(4) \text{ \AA}$, $c = 14.4515(9) \text{ \AA}$, $V = 1817.9(2) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 8$, $D_{calc} = 1.273 \text{ g} \cdot \text{cm}^3$, $\lambda = 1.54178 \text{ \AA}$, $\mu(Cu-K\alpha) = 0.706 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{min} = 0.90$, $T_{max} = 0.97$), Bruker-AXS Kappa Mach3 APEX-II diffractometer, $3.926 < \Theta < 63.626^\circ$, 26900 measured reflections, 2894 independent reflections, 2807 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0355$.

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.023$ [$I > 2\sigma(I)$], $wR_2 = 0.058$, 244 parameters, absolute structure parameter = $-0.10(6)$, extinction coefficient = $0.0008(2)$.

The H atoms at O1 and O11 were found and refined, all other H atoms were refined using a riding model, $S = 1.057$, residual electron density 0.1 (0.78 \AA from C7)/ -0.1 (0.71 \AA from H25) $e \cdot \text{\AA}^{-3}$. **CCDC- 1917195**.

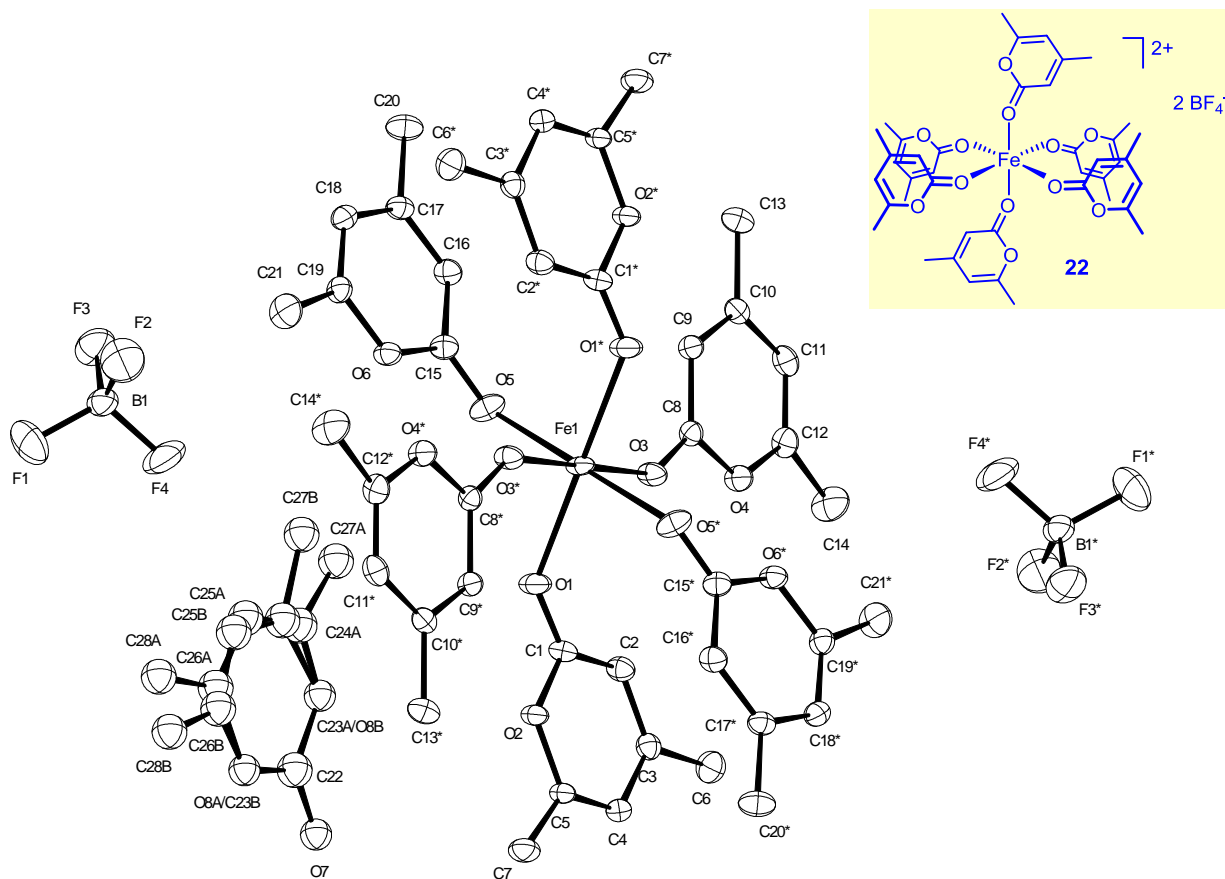


Figure S-7. Structure of the homoleptic iron complex **22** in the solid state; the additional molecule of pyrone **12** contained in the unit cell, which is not coordinated to the iron center, is disordered over two positions

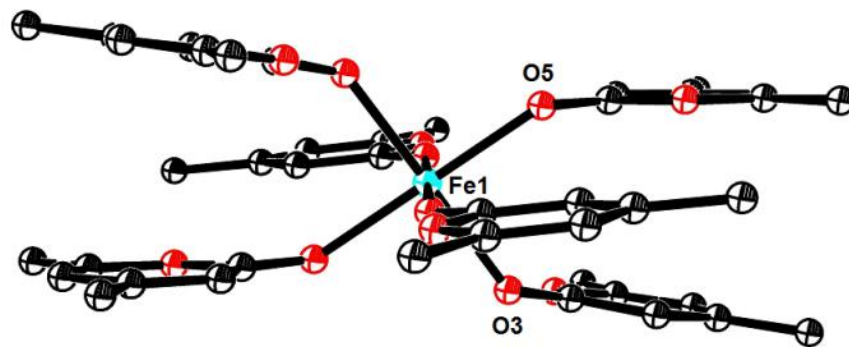


Figure S-8. Structure of the Lewis acid/Lewis base adduct **22** in an orientation that reveals the peculiar organization of the pyrone units; the BF_4^- counterions as well as an additional cocrystallized but unbound molecule of **12** are not shown for clarity

X-ray Crystal Structure Analysis of Complex 22: $C_{56}H_{64}B_2F_8FeO_{16}$, $Mr = 1222.54 \text{ g} \cdot \text{mol}^{-1}$, yellow prism, crystal size $0.165 \times 0.083 \times 0.050 \text{ mm}^3$, monoclinic, space group $P2_1/n$, $a = 7.1049(10) \text{ \AA}$, $b = 28.244(4) \text{ \AA}$, $c = 14.292(2) \text{ \AA}$, $\beta = 96.654(3)^\circ$, $V = 2848.6(7) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 2$, $D_{calc} = 1.425 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 0.359 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{min} = 0.88$, $T_{max} = 0.95$), Bruker-AXS Kappa Mach3 APEX-II diffractometer, $2.034 < \Theta < 33.142^\circ$, 82422 measured reflections, 10847 independent reflections, 7804 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0847$.

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.051 [I > 2\sigma(I)]$, $wR_2 = 0.152$, 431 parameters. The H atoms were refined using a riding model, $S = 0.959$, residual electron density $0.8 (0.89 \text{ \AA} \text{ from Fe1}) / -0.9 (0.55 \text{ \AA} \text{ from Fe1}) \text{ e} \cdot \text{\AA}^{-3}$. **CCDC- 1917197**.

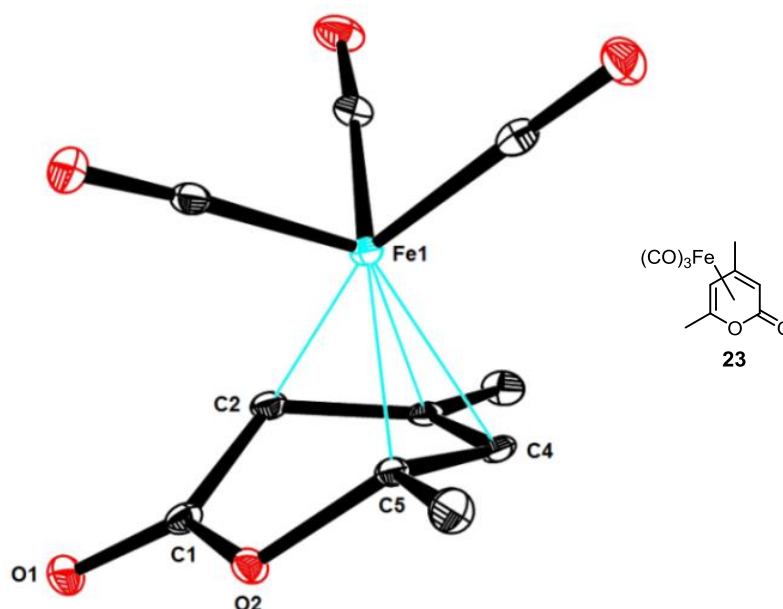


Figure S-9. Structure of the pyrone tricarbonyliron complex **23** in the solid state; hydrogen atoms are omitted for clarity

X-ray Crystal Structure Analysis of Complex 23: $C_{10}H_8FeO_5$, $M_r = 519.9(2) \text{ g} \cdot \text{mol}^{-1}$, yellow plate, crystal size $0.07 \times 0.05 \times 0.05 \text{ mm}^3$, monoclinic, space group $P2_1$, $a = 6.9641(14) \text{ \AA}$, $b = 10.957(2) \text{ \AA}$, $c = 7.5654(15) \text{ \AA}$, $\beta = 115.76(3)^\circ$, $V = 1622.7(3) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 2$, $D_{calc} = 1.686 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 1.451 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{min} = 0.98$, $T_{max} = 0.99$), Bruker-AXS Kappa Mach3 APEX-II diffractometer, $2.990 < \Theta < 30.079^\circ$, 1586 measured reflections, 1586 independent reflections, 1389 reflections with $I > 2\sigma(I)$, $R_{int} = 0$.

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.040 [I > 2\sigma(I)]$, $wR_2 = 0.068$, 148 parameters, absolute structure parameter = $0.44(6)$.

The H atoms were refined using a riding model, $S = 1.143$, residual electron density 0.4 (0.82 \AA from C9)/ -0.6 (0.78 \AA from Fe1) $e \cdot \text{\AA}^{-3}$. **CCDC- 1917190**.

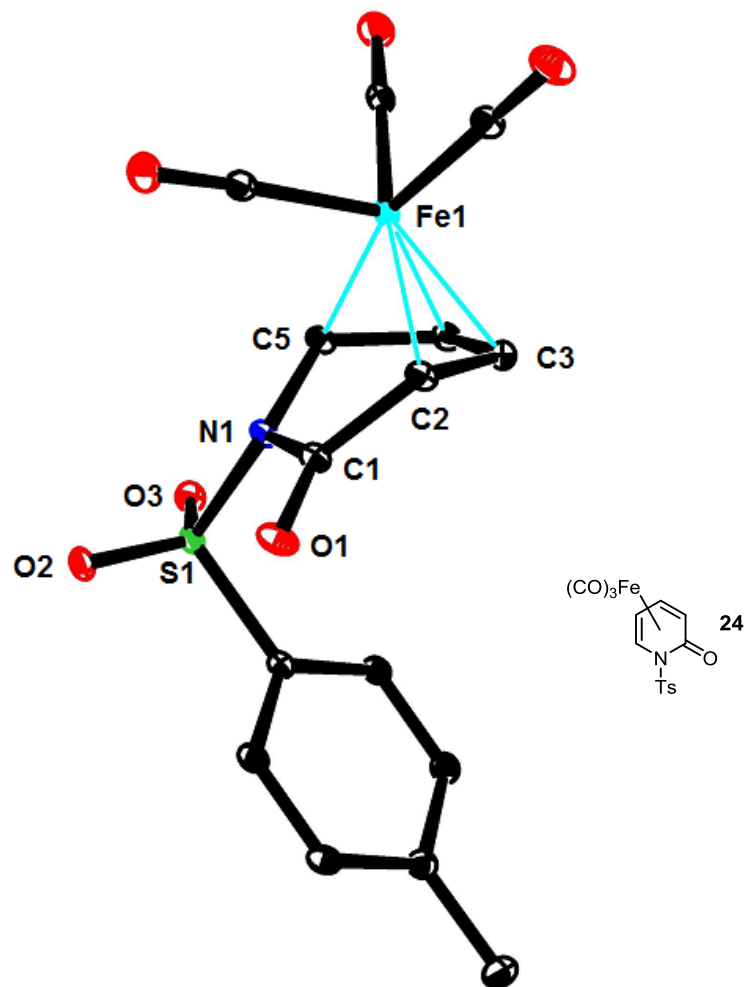


Figure S-10. Structure of the pyridone tricarbonyliron complex **24** in the solid state; hydrogen atoms are omitted for clarity

X-ray Crystal Structure Analysis of Complex 24: $C_{15}H_{11}FeNO_6S$, $M_r = 389.16 \text{ g} \cdot \text{mol}^{-1}$, yellow needle, crystal size $0.40 \times 0.36 \times 0.19 \text{ mm}^3$, triclinic, space group $P1$, $a = 6.3777(5) \text{ \AA}$, $b = 6.9416(3) \text{ \AA}$, $c = 18.0314(19) \text{ \AA}$, $\alpha = 96.474(7)^\circ$, $\beta = 93.427(8)^\circ$, $\gamma = 107.045(5)^\circ$, $V = 754.72(11) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 2$, $D_{calc} = 1.712 \text{ g} \cdot \text{cm}^3$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 1.170 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{min} = 0.86$, $T_{max} = 0.97$), Bruker-AXS Kappa Mach3 APEX-II diffractometer, $3.098 < \Theta < 33.036^\circ$, 14110 measured reflections, 5672 independent reflections, 4717 reflections with $I > 2\sigma(I)$, $R_{int} = 0.0387$.

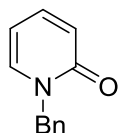
The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.040$ [$I > 2\sigma(I)$], $wR_2 = 0.099$, 218 parameters. The H atoms were refined using a riding model, $S = 1.058$, residual electron density 0.6 (0.80 \AA from Fe1)/ -1.0 (0.72 \AA from Fe1) $e \cdot \text{\AA}^{-3}$. **CCDC- 1917192.**

General. Unless stated otherwise, all reactions were carried out in flame-dried glassware using anhydrous solvents under argon. The solvents were purified by distillation over the following drying agents and were transferred under argon: THF, Et₂O, *n*-Bu₂O, DME (Mg/anthracene), CH₂Cl₂, toluene (Na/K); DMF, Et₃N and pyridine were dried by an adsorption solvent purification system based on molecular sieves. Thin layer chromatography (TLC): Macherey-Nagel precoated plates (POLYGRAM®SIL/UV254). Flash chromatography: Merck silica gel 60 (40–63 μm) or Macherey-Nagel fine silica gel 60 (15–40 μm) with predistilled or HPLC grade solvents; NMR: Spectra were recorded on Bruker DPX 300 or AV 400 spectrometers in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: δ_C = 77.16 ppm; residual CHCl₃ in CDCl₃: δ_H = 7.26 ppm). IR: Spectrum One (Perkin-Elmer) spectrometer, wavenumbers (ν̄) in cm⁻¹. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ3000 (Bruker), accurate mass determinations: Bruker APEX III FTMS (7 T magnet) or Mat 95 (Finnigan).

Unless stated otherwise, all commercially available compounds (ABCR, Acros, Alfa Aesar, Aldrich, TCI, Strem Chemicals) were used as received.

Substrates

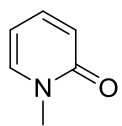
Representative Procedure for the Synthesis of 1-Substituted Pyridin-2(1*H*)-ones. 1-Benzylpyridin-



2(1*H*)-one (1). A mixture of 2-pyridin-2(1*H*)-one (2.00 g, 21 mmol), benzyl bromide (5.14 g, 30 mmol) and K₂CO₃ (5.80 g mg, 47 mmol) in DME (40 mL) was stirred for 16 h at 70 °C. After reaching ambient temperature, the reaction was quenched with water and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over MgSO₄, filtered and evaporated. The residue was purified by flash chromatography (pentane/EtOAc, 1/1 to 1/7) to afford the title compound as a white solid (3.14 g, 96%). m.p. = 74.0-74.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.20 (m, 7H), 6.61 (d, *J* = 9.2 Hz, 1H), 6.13 (td, *J* = 6.8, 1.4 Hz, 1H), 5.15 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 162.8, 139.5, 137.3, 136.5, 129.0, 128.3, 128.1, 121.4, 106.3, 52.0. IR (film, cm⁻¹): 3061, 3033, 2928, 1655, 1575, 1422, 1168, 1022, 949, 867, 727, 560. HRMS (EI): *m/z*: calcd for C₁₂H₁₁NO [*M*⁺]: 185.08351, found: 185.08364.

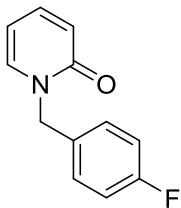
The following compounds were prepared analogously:

Compound S1. Using MeI instead of BnBr as the alkylating agent; colorless oil (1.27 g, 86%). ¹H NMR (400

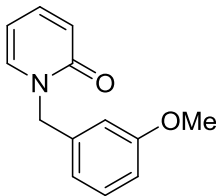


MHz, CDCl₃) δ 7.32 (ddd, *J* = 9.0, 6.6, 2.1 Hz, 1H), 7.29 – 7.26 (m, 1H), 6.57 (d, *J* = 9.0 Hz, 1H), 6.14 (td, *J* = 6.6, 1.4 Hz, 1H), 3.54 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 163.3, 139.6, 138.4, 120.9, 106.0, 37.8. IR (film, cm⁻¹): 3080, 3031, 2916, 1650, 1575, 1537, 1412, 1317, 1153, 1051, 875, 843, 761, 728, 528, 459. HRMS (EI): *m/z*: calcd for C₆H₇NO [*M*⁺]: 109.05221, found: 109.05228.

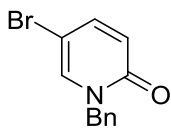
Compound S2. White solid (1.00 g, 98%); m.p. = 85.5-86.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.23 (m, 4H), 7.06 – 6.98 (m, 2H), 6.61 (d, *J* = 8.8 Hz, 1H), 6.15 (td, *J* = 6.7, 1.3 Hz, 1H), 5.10 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 162.9, 162.6 (d, *J* = 246.7 Hz), 139.6, 137.2, 132.4 (d, *J* = 3.4 Hz), 130.1 (d, *J* = 8.4 Hz), 121.6, 115.9 (d, *J* = 21.6 Hz), 106.5, 51.5. ¹⁹F NMR (282 MHz, CDCl₃) δ –114.1. IR (film, cm⁻¹): 3086, 3066, 3029, 2997, 2957, 1652, 1579, 1505, 1434, 1351, 1221, 1147, 1086, 940, 831, 757, 573, 472. HRMS (EI): *m/z*: calcd for C₁₂H₁₀NOF [*M*⁺]: 203.07409, found: 203.07448.



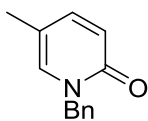
Compound S3. White solid (1.04 g, 97%); m.p. = 61.4-62.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.31 (ddd, *J* = 9.0, 6.6, 2.0 Hz, 1H), 7.28 – 7.23 (m, 2H), 6.92 – 6.80 (m, 3H), 6.61 (ddd, *J* = 9.0, 1.4, 0.8 Hz, 1H), 6.14 (td, *J* = 6.7, 1.4 Hz, 1H), 5.12 (s, 2H), 3.78 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 162.8, 160.1, 139.5, 138.0, 137.3, 130.1, 121.4, 120.5, 113.9, 113.6, 106.3, 55.4, 51.9. IR (film, cm⁻¹): 3070, 3054, 3029, 3001, 2970, 2929, 2843, 1652, 1584, 1538, 1490, 1439, 1422, 1341, 1287, 1261, 1136, 1048, 871, 845, 765, 691, 571, 522. HRMS (EI): *m/z*: calcd for C₁₃H₁₃NO₂ [*M*⁺]: 215.09408, found: 215.09427.



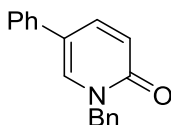
Compound S4. White solid (7.21 g, 95%); m.p. = 90.2-90.8 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.27 (m, 7H), 6.53 (dd, *J* = 9.7, 0.6 Hz, 1H), 5.10 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 161.2, 142.6, 137.1, 135.8, 129.2, 128.5, 128.4, 122.6, 98.2, 52.2. IR (film, cm⁻¹): 3064, 3043, 2995, 1654, 1579, 1525, 1492, 1433, 1349, 1241, 1150, 1067, 826, 742, 692, 642, 573, 514. HRMS (EI): *m/z*: calcd for C₁₂H₁₀NOBr [*M*⁺]: 262.99404, found: 262.99423.



1-Benzyl-5-methylpyridin-2(1H)-one (S5). Under Ar atmosphere, a mixture of 1-benzyl-5-bromopyridin-2(1H)-one **S4** (792 mg, 3.0 mmol), potassium methyltrifluoroborate (476 mg, 3.9 mmol), Pd(OAc)₂ (33.7 mg, 0.15 mmol), RuPhos (140 mg, 0.30 mmol, 10 mol%) and K₂CO₃ (1.24 g, 9 mmol) in toluene/H₂O (*v/v* = 4/1, 5 mL) was stirred for 5 h at 90 °C (bath temperature) until the reaction was completed. The mixture was cooled to ambient temperature before the reaction was quenched with water and the aqueous phase was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over MgSO₄, filtered and evaporated. The residue was purified by flash chromatography (pentane/EtOAc, 2/1 to 1/2) to afford the title compound as a white solid (420 mg, 70%). m.p. = 76.2-78.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.26 (m, 5H), 7.17 (dd, *J* = 9.3, 2.5 Hz, 1H), 7.02 (s, 1H), 6.56 (d, *J* = 9.3 Hz, 1H), 5.11 (s, 2H), 2.02 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 162.1, 142.2, 136.8, 134.7, 129.0, 128.2, 128.0, 121.0, 115.4, 51.8, 17.3. IR (film, cm⁻¹): 3035, 2952, 2925, 1664, 1584, 1537, 1495, 1430, 1265, 1144, 1073, 916, 828, 715, 697, 522, 481. HRMS (EI): *m/z*: calcd for C₁₃H₁₃NO [*M*⁺]: 199.09916, found: 199.09931.

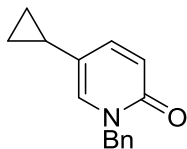


Compound S6. Prepared analogously using potassium phenyltrifluoroborate as the reagent; white solid (684 mg, 87%); m.p. = 73.6-75.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.51 (d, *J* = 2.3 Hz, 1H), 7.41 – 7.29 (m, 10H), 6.73 (d, *J* = 9.2 Hz,



1H), 5.23 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 162.4, 139.4, 136.5, 136.4, 134.7, 134.1, 129.2, 129.1, 128.3, 127.5, 125.9, 121.3, 120.7, 52.4. IR (film, cm⁻¹): 3054, 3029, 2947, 1656, 1584, 1532, 1495, 1423, 1365, 1299, 1151, 1076, 893, 833, 764, 694, 597, 490. HRMS (EI): *m/z*: calcd for C₁₈H₁₅NO [*M*⁺]: 261.11481, found: 261.11516.

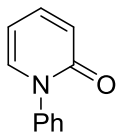
Compound S7. Prepared analogously using potassium cyclopropyltrifluoroborate as the reagent; pale



yellow oil (651 mg, 97%); ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.26 (m, 5H), 7.09 (dd, *J* = 9.3, 2.6 Hz, 1H), 7.05 (d, *J* = 2.6 Hz, 1H), 6.56 (d, *J* = 9.3 Hz, 1H), 5.12 (s, 2H), 1.61 (tt, *J* = 8.4, 5.1 Hz, 1H), 0.80 (ddd, *J* = 8.4, 6.2, 4.8 Hz, 2H), 0.47 (dt, *J* = 6.2, 4.8 Hz, 2H). ¹³C

NMR (101 MHz, CDCl₃) δ 162.2, 139.3, 136.7, 134.1, 129.0, 128.2, 128.0, 121.4, 121.1, 52.0, 12.0, 6.7. IR (film, cm⁻¹): 3080, 3065, 3031, 3004, 2930, 2851, 1662, 1592, 1535, 1454, 1368, 1260, 1155, 878, 830, 731, 699, 559. HRMS (EI): *m/z*: calcd for C₁₅H₁₅NO [*M*⁺]: 225.11481, found: 225.11500.

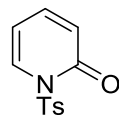
1-Phenyl-pyridin-2(1H)-one (S8).² A mixture of 2-pyridone (1.00 g, 10.5 mmol), CuI (0.2 g, 1.06 mmol, 10



mol%), iodobenzene (2.35 mL, 21 mmol) and K₂CO₃ (1.47 g, 10.5 mmol) in DMF (2 mL) was stirred for 12 h at 150 °C under Ar. The mixture was allowed to cool before the reaction was quenched with water and the aqueous phase extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over MgSO₄, filtered and evaporated,

and the residue was purified by flash chromatography to afford the title compound as a white solid (1.52 g, 85%). m.p. = 128.0-129.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.52 – 7.46 (m, 2H), 7.45 – 7.36 (m, 4H), 7.33 (ddd, *J* = 6.9, 2.1, 0.6 Hz, 1H), 6.66 (d, *J* = 9.3 Hz, 1H), 6.23 (td, *J* = 6.7, 1.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 162.5, 141.1, 139.9, 138.1, 129.5, 128.6, 126.7, 122.1, 106.0. IR (film, cm⁻¹): 3052, 3041, 3014, 2913, 1656, 1578, 1526, 1488, 1272, 1252, 1126, 983, 839, 756, 692, 582, 453. HRMS (EI): *m/z*: calcd for C₁₁H₉NO [*M*⁺]: 171.06786, found: 171.06795.

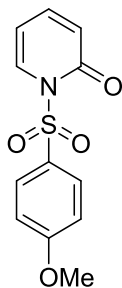
1-Tosyl-pyridin-2(1H)-one (16). A mixture of 2-pyridone (2.00 g, 21 mmol), tosyl chloride (4.41 g, 23



mmol) and Et₃N (4.26 g, 42 mmol) in THF (20 mL) was stirred at ambient temperature for 12 h. The reaction was quenched with water and the aqueous phase extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried over MgSO₄, filtered

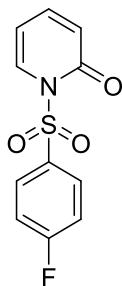
and evaporated. The residue was purified by flash chromatography (pentane/EtOAc, 4/1 to 1/1) to afford the title compound as a white solid (1.15 g, 21%). m.p. = 141.3-142.0 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.09 (ddd, *J* = 7.6, 2.0, 0.8 Hz, 1H), 8.02 – 7.96 (m, 2H), 7.38 – 7.27 (m, 3H), 6.41 (dt, *J* = 9.3, 1.2 Hz, 1H), 6.24 (ddd, *J* = 7.6, 6.4, 1.2 Hz, 1H), 2.43 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 160.3, 146.4, 141.3, 133.4, 131.8, 130.1, 129.6, 123.6, 106.4, 22.0. IR (film, cm⁻¹): 3354, 3260, 3121, 3106, 1673, 1601, 1530, 1359, 1245, 1163, 1123, 1086, 1020, 819, 770, 686, 646, 544, 512. HRMS (ESI): *m/z*: calcd for C₁₂H₁₁NO₃Na [*M*+Na⁺]: 272.03519, found: 272.03505.

Compound S9. Prepared analogously using potassium *p*-methoxyphenylsulfonyl chloride as the reagent;



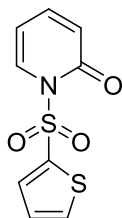
white solid (1.05 g, 19%); m.p. = 120.4-122.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.14 – 8.01 (m, 3H), 7.30 (ddd, *J* = 9.3, 6.4, 2.0 Hz, 1H), 7.00 (dt, *J* = 9.2, 2.0 Hz, 2H), 6.41 (dt, *J* = 9.4, 1.0 Hz, 1H), 6.23 (ddd, *J* = 7.6, 6.4, 1.3 Hz, 1H), 3.88 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 164.8, 160.3, 141.2, 132.6, 131.8, 127.4, 123.6, 114.2, 106.2, 55.9. IR (film, cm⁻¹): 3118, 3103, 3023, 2988, 2954, 2851, 1673, 1592, 1536, 1497, 1359, 1271, 1251, 1167, 1127, 1089, 1016, 829, 801, 765, 684, 569, 550. HRMS (ESI): *m/z*: calcd for C₁₂H₁₂NO₄S [*M*+*H*⁺]: 266.04816, found:266.04823.

Compound S10. Prepared analogously using potassium *p*-fluorophenylsulfonyl chloride as the reagent;



white solid (327 mg, 45%); m.p. = 172.0-173.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.22 – 8.11 (m, 2H), 8.07 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.32 (ddd, *J* = 9.4, 6.4, 2.0 Hz, 1H), 7.26 – 7.18 (m, 2H), 6.43 (dt, *J* = 9.4, 1.0 Hz, 1H), 6.26 (ddd, *J* = 7.6, 6.4, 1.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 166.5 (d, *J* = 258.6 Hz), 160.2, 141.5, 133.2 (d, *J* = 10.1 Hz), 132.3 (d, *J* = 3.1 Hz), 131.6, 123.6, 116.4 (d, *J* = 23.1 Hz), 106.6. ¹⁹F NMR (282 MHz, CDCl₃) δ -100.9. IR (film, cm⁻¹): 3116, 3097, 3065, 3042, 1675, 1583, 1534, 1488, 1362, 1233, 1181, 1127, 1084, 1009, 819, 759, 692, 543, 503. HRMS (ESI): *m/z*: calcd for C₁₁H₈FNO₃SNa [*M*+*Na*⁺]: 276.01011, found: 26.01000.

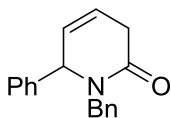
Compound S11. Prepared analogously using potassium thiophene-2-sulfonyl chloride as the reagent;



white solid (2.49 g, 62%); m.p. = 134.1-134.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.07 (dd, *J* = 3.9, 1.5 Hz, 1H), 8.02 (ddd, *J* = 7.6, 2.0, 0.8 Hz, 1H), 7.78 (dd, *J* = 5.0, 1.4 Hz, 1H), 7.32 (ddd, *J* = 9.4, 6.4, 1.9 Hz, 1H), 7.14 (dd, *J* = 5.0, 3.9 Hz, 1H), 6.48 (dt, *J* = 9.4, 1.0 Hz, 1H), 6.24 (ddd, *J* = 7.6, 6.4, 1.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 160.3, 141.3, 138.0, 136.5, 135.7, 131.5, 127.5, 123.5, 106.6. IR (film, cm⁻¹): 3110, 3097, 1679, 1600, 1530, 1376, 1340, 1246, 1227, 1170, 1128, 1011, 824, 747, 682, 562, 511. HRMS (ESI): *m/z*: calcd for C₉H₇NO₃SNa [*M*+*Na*⁺]: 263.97596, found: 263.97607.

Iron Catalyzed Reactions

Representative Procedure for the Iron Catalyzed Pyridone 1,6-Addition Reaction. 1-Benzyl-6-phenyl-



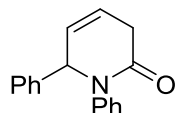
3,6-dihydropyridin-2(1H)-one (2a). A solution of PhMgBr (3 M in THF, 0.15 mL, 0.45 mmol) was added dropwise to a rapidly stirred solution of compound **1** (55.6 mg, 0.3 mmol) and Fe(acac)₃ (5.3 mg, 0.015 mmol) in THF (3 mL) at -45 °C. The mixture was stirred for 50 min at this temperature before the reaction was quenched with sat. aq.

NH₄Cl. The aqueous phase was extracted with EtOAc (3 x 10 mL), the combined organic layers were washed with brine, dried over MgSO₄, filtered and evaporated, and the residue was purified by flash chromatography (pentane/EtOAc = 10/1, 6/1, 4/1, 2/1) to afford the title compound as a pale yellow solid (76.1 mg, 96%). m.p. = 117.2-118.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.41 – 7.26 (m, 6H), 7.22 – 7.15 (m, 4H), 5.81 – 5.72 (m, 1H), 5.72 – 5.65 (m, 1H), 5.61 (d, *J* = 14.9 Hz, 1H), 4.81 (qd, *J* = 3.9, 1.2 Hz, 1H),

3.42 (d, $J = 14.9$ Hz, 1H), 3.33 – 3.14 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.7, 140.2, 136.9, 129.2, 128.8, 128.4, 128.3, 127.6, 127.2, 126.5, 120.6, 61.8, 46.4, 32.3. IR (film, cm^{-1}): 3086, 3057, 3022, 3006, 2925, 2891, 1638, 1449, 1402, 1316, 1262, 1147, 1027, 940, 841, 767, 700, 481. HRMS (EI): m/z : calcd for $\text{C}_{18}\text{H}_{17}\text{NO}$ [M^+]: 263.13046, found: 263.13065.

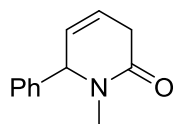
The following compounds were prepared analogously on 0.2 mmol scale:

Compound 2b. The reaction was performed using 3 equiv of ArMgBr ; pale yellow solid (36.8 mg, 72%).



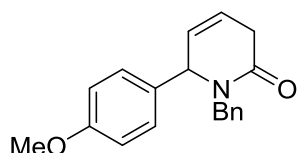
m.p. = 95.4-96.9 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.15 (m, 6H), 7.10 – 7.06 (m, 2H), 6.97 – 6.91 (m, 2H), 5.95 – 5.85 (m, 2H), 5.26 (q, $J = 3.3$ Hz, 1H), 3.42 – 3.32 (m, 1H), 3.30 – 3.21 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.4, 141.1, 140.0, 129.1, 128.8, 128.2, 128.1, 127.6, 127.4, 126.4, 121.2, 67.2, 32.8. IR (film, cm^{-1}): 3083, 3059, 3030, 3006, 2931, 2880, 1643, 1431, 1403, 1288, 1141, 1074, 759, 693, 559. HRMS (EI): m/z : calcd for $\text{C}_{17}\text{H}_{15}\text{NO}$ [M^+]: 249.11481, found: 249.11503.

Compound 2c. The reaction was performed using 3 equiv of ArMgBr at -20 °C; white solid (17.9 mg,



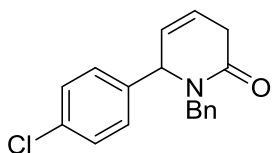
46%). m.p. = 63.3-64.6 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.27 (m, 3H), 7.23 – 7.16 (m, 2H), 5.80 – 5.67 (m, 2H), 4.87 (dd, $J = 3.3$ Hz, 1H), 3.21 – 3.03 (m, 2H), 2.82 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.7, 140.3, 129.2, 128.3, 126.9, 126.2, 120.9, 65.7, 32.8, 32.0. IR (film, cm^{-1}): 3082, 3055, 3026, 2907, 2797, 1630, 1487, 1448, 1398, 1311, 1242, 1060, 836, 759, 695, 437. HRMS (EI): m/z : calcd for $\text{C}_{12}\text{H}_{13}\text{NO}$ [M^+]: 187.09916, found: 187.09931.

Compound 3a. The reaction was performed using 3 equiv of ArMgBr at -20 °C; pale yellow oil (37.6 mg,



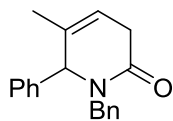
62%). ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.26 (m, 3H), 7.22 – 7.17 (m, 2H), 7.12 – 7.07 (m, 2H), 6.93 – 6.87 (m, 2H), 5.78 – 5.63 (m, 2H), 5.59 (d, $J = 15.0$ Hz, 1H), 4.75 (ddd, $J = 8.4, 2.8, 1.0$ Hz, 1H), 3.81 (s, 3H), 3.43 (d, $J = 15.0$ Hz, 1H), 3.31 – 3.13 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.6, 159.6, 136.9, 132.0, 128.7, 128.4, 128.3, 127.5, 126.7, 120.3, 114.5, 61.1, 55.4, 46.2, 32.2. IR (film, cm^{-1}): 3031, 3001, 2932, 2836, 1639, 1509, 1450, 1407, 1241, 1173, 1030, 909, 829, 725, 684, 496. HRMS (EI): m/z : calcd for $\text{C}_{19}\text{H}_{19}\text{NO}$ [M^+]: 293.14103, found: 293.14099.

Compound 3b. The reaction was performed using 3 equiv of ArMgBr at -20 °C; pale yellow oil (48.5 mg,

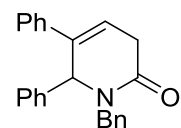


82%). ^1H NMR (400 MHz, CDCl_3) δ 7.36 – 7.27 (m, 5H), 7.19 – 7.15 (m, 2H), 7.14 – 7.09 (m, 2H), 5.81 – 5.57 (m, 3H), 4.79 (ddd, $J = 3.9, 1.4$ Hz, 1H), 3.39 (d, $J = 14.9$ Hz, 1H), 3.32 – 3.13 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.5, 138.7, 136.6, 134.1, 129.4, 128.8, 128.5, 128.3, 127.6, 126.0, 121.1, 61.1, 46.4, 32.2. IR (film, cm^{-1}): 3087, 3062, 3029, 2927, 2852, 1642, 1450, 1404, 1246, 1089, 1014, 821, 729, 698, 495. HRMS (EI): m/z : calcd for $\text{C}_{18}\text{H}_{16}\text{NOCl}$ [M^+]: 297.09149, found: 297.09163.

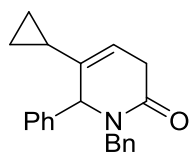
Compound 4a. The reaction was performed using 3 equiv of ArMgBr at $-45\text{ }^{\circ}\text{C}$ to RT; pale yellow oil (50.6 mg, 91%). ^1H NMR (400 MHz, CDCl_3) δ 7.32 – 7.17 (m, 6H), 7.15 – 7.08 (m, 4H), 5.47 (d, $J = 15.0$ Hz, 1H), 5.41 (ddp, $J = 4.0, 2.6, 1.3$ Hz, 1H), 4.40 (t, $J = 3.2$ Hz, 1H), 3.29 (d, $J = 15.0$ Hz, 1H), 3.26 – 3.04 (m, 2H), 1.43 – 1.36 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.7, 140.0, 136.9, 132.5, 129.0, 128.7, 128.4, 128.3, 127.7, 127.5, 117.0, 65.6, 46.4, 32.5, 20.1. IR (film, cm^{-1}): 3085, 3062, 3028, 2917, 2851, 1643, 1449, 1247, 1065, 846, 806, 698, 498. HRMS (EI): m/z : calcd for $\text{C}_{19}\text{H}_{19}\text{NO}$ [M^+]: 277.14611, found: 277.14637.



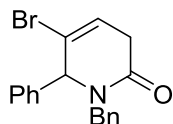
Compound 4b. The reaction was performed using 3 equiv of ArMgBr at $-20\text{ }^{\circ}\text{C}$; pale yellow oil (70.0 mg, 96%). ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.12 (m, 8H), 7.11 – 7.06 (m, 3H), 7.02 (dd, $J = 7.6, 1.8$ Hz, 2H), 6.94 (dd, $J = 6.6, 2.8$ Hz, 2H), 5.90 (dd, $J = 4.7, 2.8$ Hz, 1H), 5.57 (d, $J = 15.2$ Hz, 1H), 5.14 (t, $J = 2.6$ Hz, 1H), 3.48 (d, $J = 15.2$ Hz, 1H), 3.43 – 3.26 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.9, 139.3, 138.3, 138.2, 136.8, 128.92, 128.88, 128.5, 128.2, 128.0, 127.8, 127.6, 127.5, 126.7, 119.8, 63.5, 46.7, 33.1. IR (film, cm^{-1}): 3085, 3061, 3028, 2923, 1641, 1451, 1253, 1072, 908, 727, 695. HRMS (ESI): m/z : calcd for $\text{C}_{24}\text{H}_{21}\text{NONa}$ [$M+\text{Na}^+$]: 362.15153, found: 362.15143.



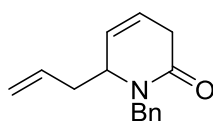
Compound 5. The reaction was performed using 3 equiv of ArMgBr; pale yellow oil (52.1 mg, 89%). ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.18 (m, 6H), 7.17 – 7.09 (m, 4H), 5.46 (d, $J = 15.1$ Hz, 1H), 5.32 (s, 1H), 4.60 (t, $J = 3.0$ Hz, 1H), 3.35 (d, $J = 15.1$ Hz, 1H), 3.27 – 3.02 (m, 2H), 0.91 – 0.77 (m, 1H), 0.42 – 0.34 (m, 1H), 0.34 – 0.26 (m, 1H), 0.16 (dtd, $J = 9.3, 5.5, 3.9$ Hz, 1H), 0.04 (dtd, $J = 9.5, 5.5, 4.1$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.8, 140.4, 138.1, 136.9, 128.9, 128.7, 128.3, 128.1, 127.8, 127.4, 114.2, 65.5, 46.4, 32.3, 13.9, 6.1, 5.1. IR (film, cm^{-1}): 3084, 3063, 3028, 3005, 2920, 2874, 1643, 1450, 1409, 1248, 1077, 1021, 848, 729, 699, 493. HRMS (EI): m/z : calcd for $\text{C}_{21}\text{H}_{21}\text{NO}$ [M^+]: 303.16176, found: 303.16186.



Compound 6. The reaction was performed using 3 equiv of ArMgBr at $-20\text{ }^{\circ}\text{C}$; pale yellow oil (60.6 mg, 91%). ^1H NMR (400 MHz, CDCl_3) δ 7.44 – 7.29 (m, 6H), 7.26 – 7.23 (m, 2H), 7.22 – 7.17 (m, 2H), 6.13 (dd, $J = 4.2, 3.0$ Hz, 1H), 5.53 (d, $J = 15.0$ Hz, 1H), 4.76 (t, $J = 3.4$ Hz, 1H), 3.42 – 3.21 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.8, 138.0, 136.2, 129.14, 129.10, 128.9, 128.4, 128.1, 127.9, 124.2, 118.7, 66.7, 46.8, 34.3. IR (film, cm^{-1}): 3085, 3062, 3029, 2920, 2850, 1645, 1449, 1405, 1243, 1072, 840, 729, 696, 496. HRMS (EI): m/z : calcd for $\text{C}_{18}\text{H}_{16}\text{NOBr}$ [M^+]: 341.04099, found: 341.04096.

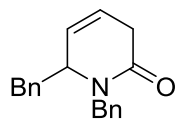


Compound 7. The reaction was performed using 3 equiv of allylmagnesium bromide at $-20\text{ }^{\circ}\text{C}$ to RT; pale yellow oil (27.7 mg, 62%). ^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.13 (m, 5H), 5.75 (dtd, $J = 10.0, 3.4, 0.9$ Hz, 1H), 5.68 – 5.55 (m, 2H), 5.45 (d, $J = 15.2$ Hz, 1H), 5.06 – 4.97 (m, 2H), 3.91 (d, $J = 15.2$ Hz, 1H), 3.86 – 3.80 (m, 1H), 2.98 – 2.91 (m, 2H), 2.42 – 2.33 (m, 1H), 2.25 (dddd, $J = 12.8, 6.5, 3.1, 1.5$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 168.6, 137.0, 132.1, 128.7, 128.0, 127.5, 125.8, 123.1, 119.4, 56.5, 46.5, 37.5, 32.7. IR (film, cm^{-1}): 3074, 3030,



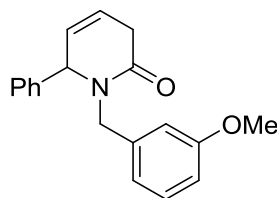
2978, 2925, 1637, 1451, 1408, 1322, 1253, 1149, 1071, 996, 917, 703, 497. HRMS (ESI): m/z : calcd for $C_{15}H_{17}NONa$ [$M+Na^+$]: 250.12023, found: 250.12026.

Compound 8. The reaction was performed using 3 equiv of benzylmagnesium bromide; white solid (50.1



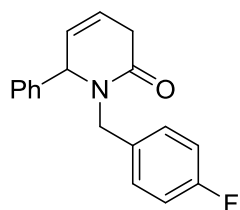
mg, 91%). m.p. = 99.2-100.9°C. 1H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.22 (m, 2H), 7.21 – 7.11 (m, 6H), 7.02 – 6.95 (m, 2H), 5.63 (ddd, J = 10.0, 4.8, 2.0 Hz, 1H), 5.60 – 5.52 (m, 2H), 4.02 – 3.95 (m, 1H), 3.92 (d, J = 15.1 Hz, 1H), 2.87 (dd, J = 13.4, 6.8 Hz, 1H), 2.80 – 2.65 (m, 2H), 2.17 – 2.06 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 137.1, 135.9, 130.1, 128.8, 128.3, 127.9, 127.5, 126.8, 125.5, 124.0, 57.7, 46.8, 39.3, 32.4. IR (film, cm^{-1}): 3051, 3028, 2955, 2925, 2895, 1626, 1454, 1405, 1261, 1163, 1081, 1029, 967, 724, 693, 494. HRMS (ESI): m/z : calcd for $C_{19}H_{19}NONa$ [$M+Na^+$]: 300.13588, found: 300.13582.

Compound 9. Yellow oil (54.8 mg, 96%). 1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 3H), 7.27 – 7.15 (m,



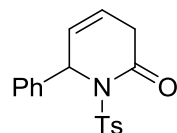
3H), 6.86 – 6.71 (m, 3H), 5.79 – 5.65 (m, 2H), 5.59 (d, J = 14.9 Hz, 1H), 4.83 (dd, J = 3.6 Hz, 1H), 3.78 (s, 3H), 3.39 (d, J = 14.9 Hz, 1H), 3.32 – 3.12 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 159.9, 140.1, 138.4, 129.7, 129.2, 128.3, 127.1, 126.5, 120.6, 120.6, 113.9, 112.9, 61.8, 55.3, 46.3, 32.2. IR (film, cm^{-1}): 3047, 3029, 3000, 2935, 2835, 1643, 1449, 1260, 1145, 1044, 838, 695, 485. HRMS (EI): m/z : calcd for $C_{19}H_{19}NO_2$ [M^+]: 293.14103, found: 293.14129.

Compound 12. The reaction was performed using 3 equiv of ArMgBr; pale yellow solid (48.8 mg, 88%).



m.p. = 130.6-131.1°C. 1H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 3H), 7.21 – 7.12 (m, 4H), 6.98 (t, J = 8.7 Hz, 2H), 5.78 – 5.64 (m, 2H), 5.50 (d, J = 14.9 Hz, 1H), 4.79 (dq, J = 3.9, 1.2 Hz, 1H), 3.44 (d, J = 14.9 Hz, 1H), 3.26 (ddt, J = 22.3, 4.5, 2.1 Hz, 1H), 3.17 (dtd, J = 22.3, 3.7, 1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 162.3 (d, J = 245.5 Hz), 140.0, 132.7 (d, J = 3.3 Hz), 130.1 (d, J = 8.0 Hz), 129.2, 128.4, 127.1, 126.4, 120.6, 115.5 (d, J = 21.4 Hz), 61.9, 45.8, 32.2. ^{19}F NMR (282 MHz, $CDCl_3$) δ –115.1. IR (film, cm^{-1}): 3070, 3053, 3029, 3004, 2931, 2891, 1638, 1508, 1450, 1402, 1264, 1215, 1156, 1027, 920, 842, 806, 768, 699, 461. HRMS (EI): m/z : calcd for $C_{18}H_{16}NOF$ [M^+]: 281.12104, found: 281.12128.

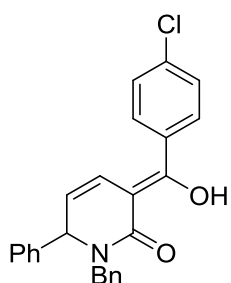
Compound 17. The reaction was performed in the presence of PPh_3 (10 mol%) to give the product as a



white solid (20.4 mg, 62%). m.p. = 192.4-193.2°C. 1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 5H), 7.25 – 7.21 (m, 2H), 7.07 (d, J = 8.6 Hz, 2H), 6.03 – 5.93 (m, 2H), 5.73 (dt, J = 9.5, 3.6 Hz, 1H), 3.20 (dt, J = 3.8, 2.2 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 144.6, 139.8, 135.6, 129.3, 128.9, 128.7, 128.3, 127.4, 127.1, 119.5, 62.0, 34.2, 21.6. IR (film, cm^{-1}): 3086, 3063, 3027, 2962, 2921, 1687, 1595, 1451, 1353, 1243, 1162, 1085, 811, 701, 684, 537. HRMS (ESI): m/z : calcd for $C_{18}H_{17}NO_3Na$ [$M+Na^+$]: 350.08214, found: 350.08245. Single crystals

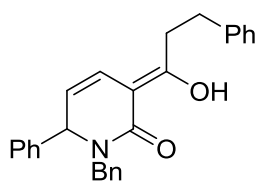
suitable for X-ray diffraction were grown by slow evaporation of a solution of this product in CH₂Cl₂/pentane.

Representative Procedure for the Iron Catalyzed Three Component Reaction. (Z)-1-Benzyl-3-((4-chlorophenyl)(hydroxy)methylene)-6-phenyl-3,6-dihydropyridin-2(1H)-one (11a).



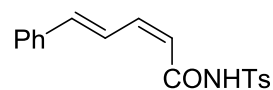
(1.18 M in THF, 0.51 mL, 0.60 mmol) was slowly added to a rapidly stirred solution of compound **1** (37.0 mg, 0.2 mmol), methyl 4-chlorobenzoate (68.2 mg, 0.4 mmol) and Fe(acac)₃ (3.5 mg, 0.01 mmol, 5 mol%) in THF (2 mL) at -45 °C. The mixture was stirred for 30 min at this temperature before the reaction was quenched with sat. aq. NH₄Cl. The aqueous phase was extracted with EtOAc (3 x 10 mL) and the combined organic layers were washed with brine, dried over MgSO₄, filtered and evaporated. The residue was purified by flash chromatography (hexane/EtOAc = 50/1, 20/1, 10/1, 6/1) to afford the title compound as a pale yellow solid (39.7 mg, 87%). m.p. = 91.7-92.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 15.18 (s, 1H), 7.56 – 7.50 (m, 2H), 7.43 – 7.23 (m, 12H), 6.29 (dd, *J* = 10.1, 1.3 Hz, 1H), 5.57 (d, *J* = 15.0 Hz, 1H), 5.30 (dd, *J* = 10.1, 4.5 Hz, 1H), 5.01 (dd, *J* = 4.5, 1.1 Hz, 1H), 3.54 (d, *J* = 15.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 169.6, 167.4, 140.5, 136.4, 136.1, 133.2, 130.4, 129.3, 128.9, 128.7, 128.5, 128.3, 127.8, 127.1, 121.0, 119.5, 98.8, 62.7, 46.4. IR (film, cm⁻¹): 3085, 3059, 3028, 2977, 2950, 2925, 1724, 1654, 1594, 1469, 1450, 1341, 1264, 1089, 1014, 906, 836, 728, 523. HRMS (ESI): *m/z*: calcd for C₂₅H₂₁ClNO₂ [*M+H*⁺]: 402.12553, found: 402.12548. Single crystals suitable for X-ray diffraction were grown by slow evaporation of a solution of this product in CH₂Cl₂/pentane.

Compound 11b. Prepared analogously using methyl 3-phenylpropanoate as the electrophilic coupling



partner; pale yellow oil (76.6 mg, 93%). ¹H NMR (400 MHz, CDCl₃) δ 14.94 (s, 1H), 7.31 – 7.07 (m, 15H), 6.09 (dd, *J* = 10.1, 1.3 Hz, 1H), 5.42 (d, *J* = 15.1 Hz, 1H), 5.10 (dd, *J* = 10.1, 4.3 Hz, 1H), 4.85 (d, *J* = 4.2 Hz, 1H), 3.37 (d, *J* = 15.1 Hz, 1H), 2.91 (t, *J* = 7.9 Hz, 2H), 2.70 – 2.52 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 171.7, 169.3, 141.0, 140.8, 136.6, 133.2, 129.2, 128.8, 128.6, 128.4, 128.2, 127.6, 127.2, 126.3, 119.8, 118.1, 98.1, 62.6, 46.1, 33.4, 33.1. IR (film, cm⁻¹): 3085, 3061, 3027, 2930, 2863, 1736, 1654, 1596, 1469, 1451, 1358, 1256, 1211, 1028, 912, 747, 723, 696, 510. HRMS (ESI): *m/z*: calcd for C₂₇H₂₆NO₂ [*M+H*⁺]: 396.19580, found: 396.19585.

Representative Procedure for the Iron Catalyzed Formal Ring-opening/Cross Coupling of 2-Pyridone

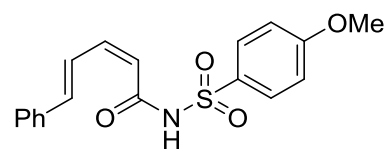


Derivatives. (Z,E)-5-Phenyl-N-tosylpenta-2,4-dienamide (18a). A solution of PhMgBr (1 M in THF, 0.6 mL, 0.6 mmol) was added dropwise to a rapidly stirred solution of compound **16** (49.9 mg, 0.2 mmol), Fe(acac)₃ (3.5 mg, 0.01 mmol, 5 mol%) and PPh₃ (5.2 mg, 0.02 mmol, 10 mol%) in Et₂O (2 mL) at -30 °C. The mixture was stirred for 30 min at this temperature before DMF (4 mL) was introduced and the temperature raised to -10 °C

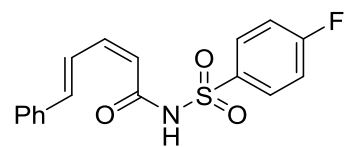
over the course of 2 h. The reaction was quenched with sat. aq. NH_4Cl and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine, dried over MgSO_4 , filtered and evaporated. The residue was purified by flash chromatography (pentane/ethyl acetate = 4/1, 2/1, 1/1) to afford the title compound as a pale yellow solid (38.3 mg, 60%, 2Z/2E = 15/1). m.p. = 139.1-141.2 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.71 (s, 1H), 8.10 (ddd, J = 15.7, 11.5, 0.8 Hz, 1H), 8.00 (d, J = 8.4 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.38 – 7.29 (m, 5H), 6.80 (d, J = 15.7 Hz, 1H), 6.71 (t, J = 11.5 Hz, 1H), 5.62 (d, J = 11.1 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.0, 147.5, 145.2, 143.8, 136.03, 136.00, 129.8, 129.6, 128.9, 128.5, 128.0, 124.8, 115.8, 21.9. IR (film, cm^{-1}): 3253, 3074, 3057, 3025, 2922, 2873, 1697, 1615, 1592, 1435, 1329, 1235, 1122, 1083, 984, 878, 657, 542. HRMS (ESI): m/z : calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_3\text{SNa}$ [$M+\text{Na}^+$]: 350.08214, found: 350.08242. Single crystals suitable for X-ray diffraction were grown by slow evaporation of a solution of this product in CH_2Cl_2 /pentane.

The following compounds were prepared analogously:

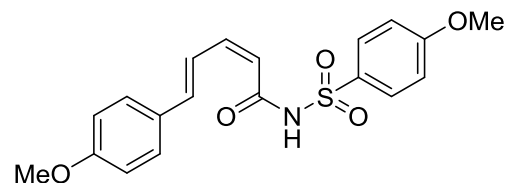
Compound 18b. Pale yellow oil (47.5 mg, 70%, 2Z/2E = 15/1). ^1H NMR (400 MHz, CDCl_3) δ 9.10 (s, 1H), 8.16 – 8.03 (m, 3H), 7.47 (dd, J = 7.8, 1.8 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.03 – 6.95 (m, 2H), 6.79 (d, J = 15.7 Hz, 1H), 6.70 (t, J = 11.2 Hz, 1H), 5.66 (d, J = 11.2 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.0, 163.4, 147.2, 143.5, 136.0, 130.7, 130.2, 129.5, 128.8, 127.9, 124.8, 116.2, 114.4, 55.8. IR (film, cm^{-1}): 3239, 3077, 3064, 2929, 2841, 1688, 1590, 1497, 1433, 1335, 1261, 1163, 1124, 1080, 1023, 864, 832, 803, 729, 665, 576, 553. HRMS (ESI): m/z : calcd for $\text{C}_{18}\text{H}_{17}\text{NO}_4\text{SNa}$ [$M+\text{Na}^+$]: 366.07705, found: 366.07737.



Compound 18c. Pale yellow solid (32.4 mg, 47%, 2Z/2E = 18/1). m.p. = 69.0-71.4 °C. ^1H NMR (400 MHz, CDCl_3) δ 9.01 (s, 1H), 8.20 – 8.13 (m, 2H), 8.09 (ddd, J = 15.7, 11.5, 1.0 Hz, 1H), 7.47 (dd, J = 7.6, 1.8 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.22 (t, J = 8.6 Hz, 2H), 6.81 (d, J = 15.7 Hz, 1H), 6.73 (t, J = 11.6 Hz, 1H), 5.65 (d, J = 11.1 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.0 (d, J = 256.8 Hz), 163.2, 147.8, 144.1, 135.9, 134.8, 131.5 (d, J = 9.7 Hz), 129.7, 128.9, 127.9, 124.7, 116.5 (d, J = 22.8 Hz), 115.7. ^{19}F NMR (282 MHz, CDCl_3) δ -102.9. IR (film, cm^{-1}): 3245, 3106, 3074, 2859, 1692, 1612, 1586, 1431, 1338, 1122, 1079, 868, 838, 754, 665, 576, 544. HRMS (ESI): m/z : calcd for $\text{C}_{17}\text{H}_{13}\text{FNO}_3\text{S}$ [M]: 330.06057, found: 330.06064.

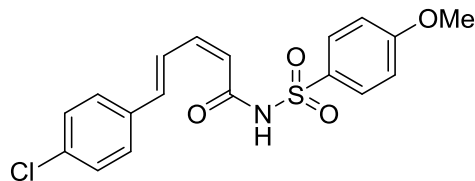


Compound 19a. Pale yellow solid (55.0 mg, 74%, 2Z/2E = 8/1). m.p. = 162.8-163.5 °C. ^1H NMR (400 MHz, CDCl_3) δ 8.57 (s, 1H), 8.09 – 7.94 (m, 3H), 7.44 (d, J = 8.8 Hz, 2H), 7.00 (d, J = 9.0 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 15.5 Hz, 1H), 6.69 (t, J = 11.2 Hz, 1H), 5.54 (d, J = 11.2 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.0, 163.3, 160.9, 147.8, 143.6, 130.8, 130.5, 129.5, 129.1,



128.9, 122.9, 114.7, 114.4, 55.8, 55.5. IR (film, cm^{-1}): 3270, 3064, 2984, 2933, 2910, 2872, 1687, 1589, 1500, 1417, 1252, 1162, 1114, 1080, 1018, 993, 834, 799, 668, 556. HRMS (ESI): m/z : calcd for $\text{C}_{19}\text{H}_{18}\text{NO}_5\text{S}$ [M]: 372.09112, found: 372.09120.

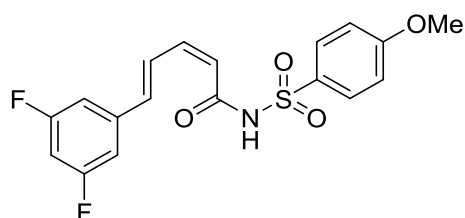
Compound 19b. Pale yellow solid (45.1 mg, 61%, 2Z/2E = 13/1). m.p. = 160.3-161.5 °C. ^1H NMR (400 MHz,



CDCl_3) δ 8.61 (s, 1H), 8.13 – 7.99 (m, 3H), 7.41 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 8.5 Hz, 2H), 7.02 (d, J = 9.0 Hz, 2H), 6.79 – 6.64 (m, 2H), 5.62 (d, J = 11.1 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.1, 163.0, 146.9, 142.0, 135.3, 134.6, 130.8, 130.2, 129.1, 129.0, 125.3, 116.5, 114.4, 55.9. IR (film, cm^{-1}):

3272, 3064, 3039, 2978, 2946, 2841, 1691, 1591, 1498, 1409, 1264, 1161, 1079, 994, 830, 797, 666, 556. HRMS (ESI): m/z : calcd for $\text{C}_{18}\text{H}_{15}\text{ClNO}_4\text{S}$ [$M-H$]: 376.04158, found: 376.04179.

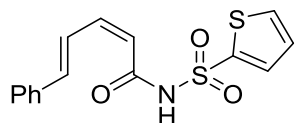
Compound 20. Pale yellow solid (52.4 mg, 69%, 2Z/2E = 23/1). m.p. = 215.4-217.2 °C. ^1H NMR (400 MHz,



CDCl_3) δ 9.14 (s, 1H), 8.14 – 8.00 (m, 3H), 7.06 – 6.93 (m, 4H), 6.76 – 6.61 (m, 3H), 5.72 (d, J = 11.2 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 164.1, 163.2 (dd, J = 248.6, 12.9 Hz), 163.1, 145.8, 140.4 (t, J = 3.1 Hz), 139.4 (t, J = 9.5 Hz), 130.8, 130.0, 127.1, 118.1, 114.4, 110.3 (dd, J = 25.7, 6.9 Hz), 104.5 (t, J = 25.6 Hz). ^{19}F NMR (282 MHz, CDCl_3) δ -109.7. IR (film, cm^{-1}):

3228, 3086, 2983, 2871, 2845, 1733, 1706, 1593, 1431, 1334, 1259, 1165, 1115, 1079, 980, 851, 830, 663, 553. HRMS (ESI): m/z : calcd for $\text{C}_{18}\text{H}_{14}\text{F}_2\text{NO}_4\text{S}$ [$M-H$]: 378.06171, found: 378.06186.

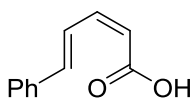
Compound 21. Pale yellow solid (34.1 mg, 55%, 2Z/2E = 18/1). m.p. = 134.1-134.9 °C. ^1H NMR (400 MHz,



CDCl_3) δ 8.08 (ddd, J = 15.7, 11.5, 0.9 Hz, 1H), 7.88 (dd, J = 3.8, 1.2 Hz, 1H), 7.62 (dd, J = 5.0, 1.2 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.31 – 7.23 (m, 3H), 7.06 (dd, J = 4.9, 3.9 Hz, 1H), 6.78 (d, J = 15.7 Hz, 1H), 6.70 (t, J = 11.5 Hz, 1H), 5.55 (dt, J

= 11.0, 0.9 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 163.0, 147.8, 144.1, 139.3, 136.0, 135.2, 134.0, 129.7, 128.9, 128.0, 127.6, 124.8, 115.7. IR (film, cm^{-1}): 3245, 3098, 3026, 2873, 1685, 1612, 1585, 1433, 1340, 1178, 1123, 1090, 1019, 876, 809, 726, 591, 567. HRMS (ESI): m/z : calcd for $\text{C}_{15}\text{H}_{13}\text{NO}_3\text{S}_2\text{Na}$ [$M+\text{Na}^+$]: 342.02291, found: 342.02329.

Compound 27. A solution of PhMgBr (3 M in Et_2O , 0.1 mL, 0.3 mmol) was slowly added to a rapidly



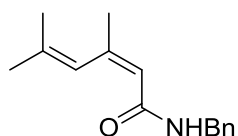
stirred solution of 2-pyrone (19.2 mg, 0.2 mmol) and $\text{Fe}(\text{acac})_3$ (3.5 mg, 0.01 mmol, 5 mol%) in Et_2O (2 mL) at -30 °C. After stirring for 20 min at this temperature, the reaction was quenched with sat. aq. NH_4Cl and the pH of the aqueous layer adjusted

to \approx 2-3 upon addition of HCl (1 M). The aqueous phase was extracted with EtOAc (5 x 20 mL), the combined organic layers were washed with brine, dried over MgSO_4 , filtered and evaporated. The residue was purified by flash chromatography (pentane/ EtOAc = 10/1, 4/1, 2/1) to afford the title

compound as a pale yellow solid material (15.5 mg, 44%). m.p. = 130.2-130.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 11.20 (s, 1H), 8.11 (ddd, *J* = 15.3, 11.6, 1.1 Hz, 1H), 7.55 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.42 – 7.29 (m, 3H), 6.93 – 6.82 (m, 2H), 5.77 (d, *J* = 11.0 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 171.4, 147.2, 142.6, 136.3, 129.4, 128.9, 127.8, 125.0, 116.5. IR (film, cm⁻¹): 3033, 2953, 2922, 2825, 2745, 2565, 1685, 1608, 1585, 1434, 1246, 1227, 958, 821, 744, 698. HRMS (ESI): *m/z*: calcd for C₁₁H₉NO₂ [*M-H*]: 173.06081, found: 173.06071. Single crystals suitable for X-ray diffraction were grown by slow evaporation of a solution of this product in CH₂Cl₂/pentane.

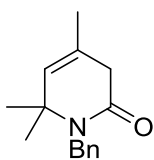
Control Experiments

Compound 14. Triethylamine (0.6 mL, 4.3 mmol, 1.5 equiv), HOBt (0.43 g, 3.15 mmol) and EDC·HCl (0.83 g, 4.3 mmol) were added to a solution of benzylamine (0.34 mL, 3.15 mmol) and acid **13** (0.4 g, 2.9 mmol)³ in DMF (1.5 mL) and CH₂Cl₂ (20 mL). The mixture was stirred for 4 h before the solvent was evaporated. The residue was suspended in water (30 mL) and extracted from the aqueous phase with EtOAc (3 x 20 mL). The



combined organic layers were washed with aq. citric acid solution (0.5 M), sat. aq. NaHCO₃ and brine, dried over MgSO₄, and evaporated. The residue was purified by flash chromatography (hexane/EtOAc = 6/1, 4/1, 2/1, 1/1) to give the title compound as a pale orange oil (0.61 g, 92%). ¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.30 (m, 2H), 7.29 – 7.24 (m, 3H), 6.27 (s, 1H), 5.96 (s, 1H), 5.73 (td, *J* = 1.4, 1.3 Hz, 1H), 4.45 (d, *J* = 5.5 Hz, 2H), 1.89 (dd, *J* = 1.4, 0.7 Hz, 3H), 1.68 (d, *J* = 1.4 Hz, 3H), 1.60 (d, *J* = 1.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.6, 146.1, 138.7, 138.6, 128.8, 128.0, 127.6, 123.7, 122.3, 43.8, 26.0, 25.5, 19.7. IR (film, cm⁻¹): 3306, 3064, 3031, 2975, 2929, 2874, 1724, 1646, 1525, 1454, 1376, 1265, 1075, 1029, 733, 697. HRMS (EI): *m/z*: calcd for C₁₅H₁₉NO [*M*⁺]: 229.14611, found: 229.14612.

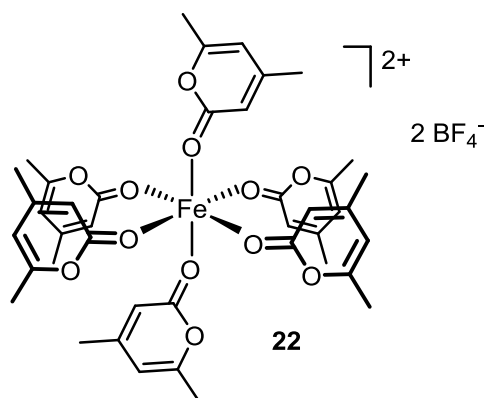
Compound 15. LiHMDS (40.7 mg, 0.24 mmol, 2.4 equiv) was added to a stirred solution of amide **14** (47.2 mg, 0.2 mmol, 1 equiv) in DMF (2 mL) and the resulting mixture was stirred at 100 °C for 3 h. After reaching ambient temperature, the reaction was quenched with sat. aq. NH₄Cl and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine, dried over MgSO₄, filtered and concentrated, and



the residue was purified by flash chromatography (pentane/EtOAc, 5:1 to 1/1) to afford the title compound as a white solid material (31.8 mg, 67%). m.p. = 77.7-78.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.31 – 7.15 (m, 5H), 5.86 (t, *J* = 1.5 Hz, 1H), 4.66 (s, 2H), 2.24 (t, *J* = 1.1 Hz, 2H), 1.89 (s, 3H), 1.20 (s, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 165.9, 148.4, 140.3, 128.4, 127.1, 126.6, 120.1, 56.6, 44.6, 44.1, 26.8, 23.0. IR (film, cm⁻¹): 3061, 3031, 2980, 2930, 1668, 1605, 1433, 1409, 1350, 1192, 1029, 885, 847, 718, 693. HRMS (ESI): *m/z*: calcd for C₁₅H₁₉NONa [*M+Na*⁺]: 252.13588, found: 252.13574.

Iron Complexes

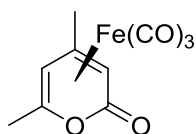
Preparation of Adduct [22·(4,6-dimethyl-2H-pyran-2-one)]. AgBF₄ (227 mg, 1.2 mmol) was added to a



solution of FeCl₂(THF)_{1.5} (143 mg, 0.61 mmol) in THF (3 mL), causing the formation of a white precipitate. The suspension was stirred for 2 h before the mixture was filtered through a pad of Celite under Ar, which was thoroughly washed with THF (8 mL). 4,6-Dimethyl-2-pyrone **12** (455 mg, 3.7 mmol) was added to the combined filtrates, resulting in the appearance of a yellow color. The mixture was stirred for 5 h before all volatile materials were evaporated. The remaining yellow solid was rinsed with

pentane and Et₂O and then dried in vacuo to give the title complex as a brown crystalline material (528 mg, 79%) which is an adduct of complex 22 with unbound 4,6-dimethyl-2H-pyran-2-one, see Figure S-7. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a solution of this complex in CH₂Cl₂.

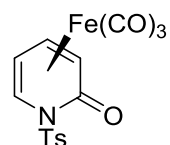
(Tricarbonyl)iron Pyrone Complex 23. A Schlenk flask was charged with Fe₂(CO)₉ (293 mg, 0.81 mmol)



and 2-pyrone **12** (200 mg, 1.61 mmol) under Ar. Degassed anhydrous *n*-Bu₂O/THF (*v/v* 5/1, 24 mL) was added and the solution was stirred at 65 °C for 0.5 h while argon was slowly bubbled through the mixture. Two further portions of Fe₂(CO)₉ (291 mg, 0.81 mmol each) were added at 0.5 h intervals. After stirring for another 2 h, the mixture

was allowed to reach ambient temperature before the solvent was evaporated. Purification of the residue by flash chromatography (hexane/EtOAc = 10/1 to 4/1) yielded the title compound as a yellow solid material (92.6 mg, 19%). m. p. (decomp.) = 100.4-101.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 5.43 (s, 1H), 2.99 (d, *J* = 1.6 Hz, 1H), 2.41 (s, 3H), 1.86 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 208.0, 170.7, 105.8, 100.9, 78.0, 53.1, 22.6, 20.4. IR (film, cm⁻¹): 3065, 2992, 2961, 2927, 2895, 2055, 1973, 1715, 1439, 1356, 1264, 1167, 1052, 1001, 860, 754, 606, 568. HRMS (ESI): *m/z*: calcd for C₁₀H₈FeO₅Na [*M*+Na⁺]: 286.96133, found: 286.96122. Single crystals suitable for X-ray diffraction were grown by slowly lowering the temperature of a saturated solution of this product in EtOAc/pentane from +20 °C to -30 °C.

(Tricarbonyl)iron Pyridone Complex 24. Prepared analogously as a yellow solid material (177 mg, 21%).

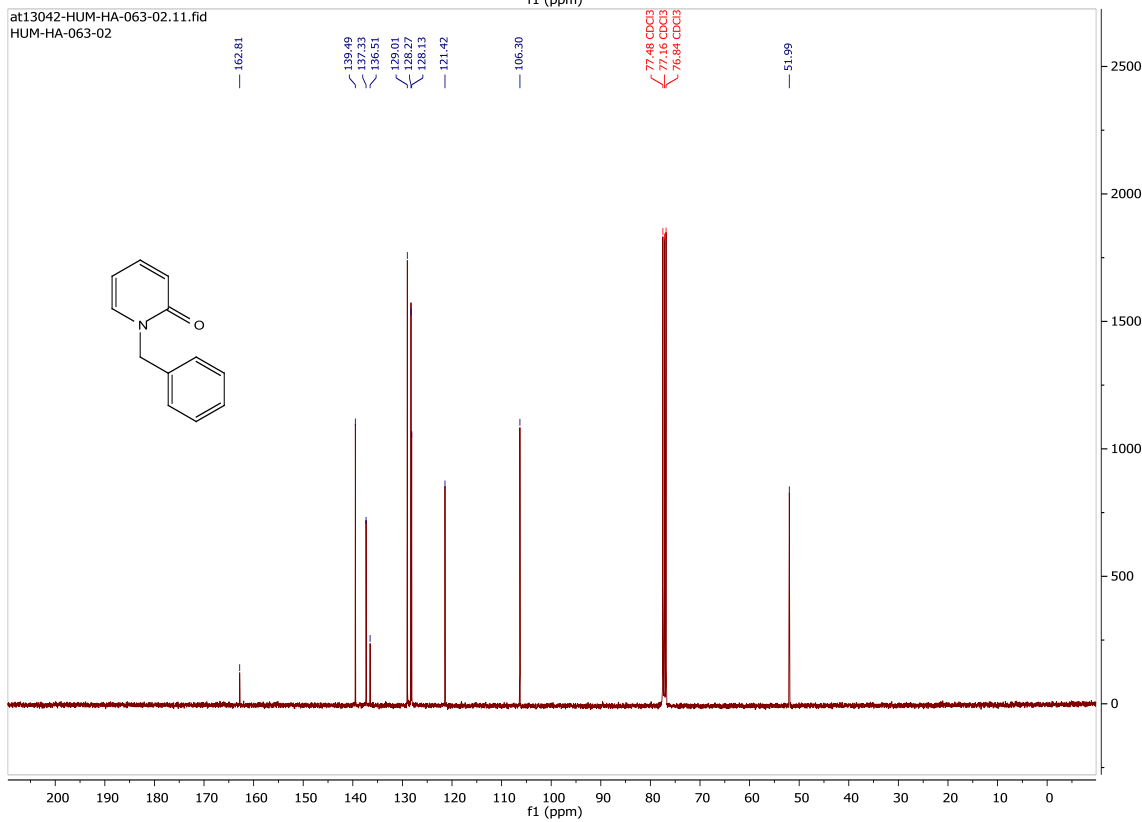
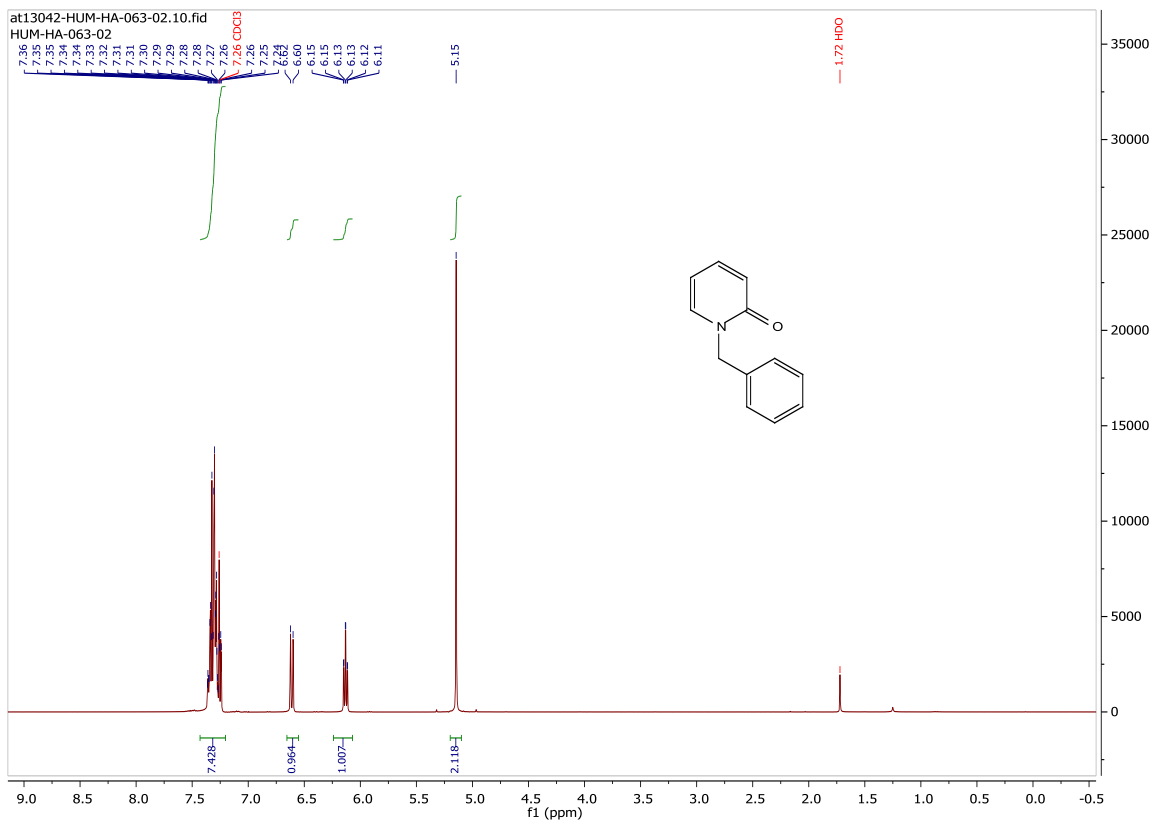


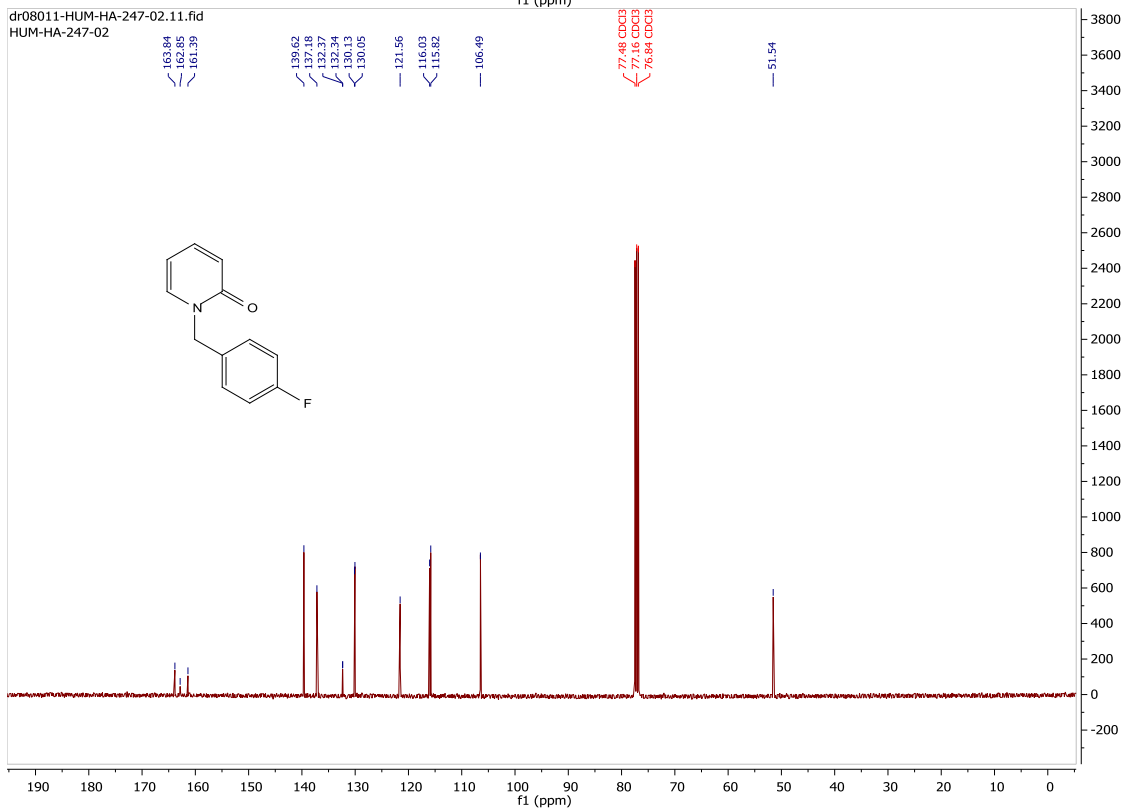
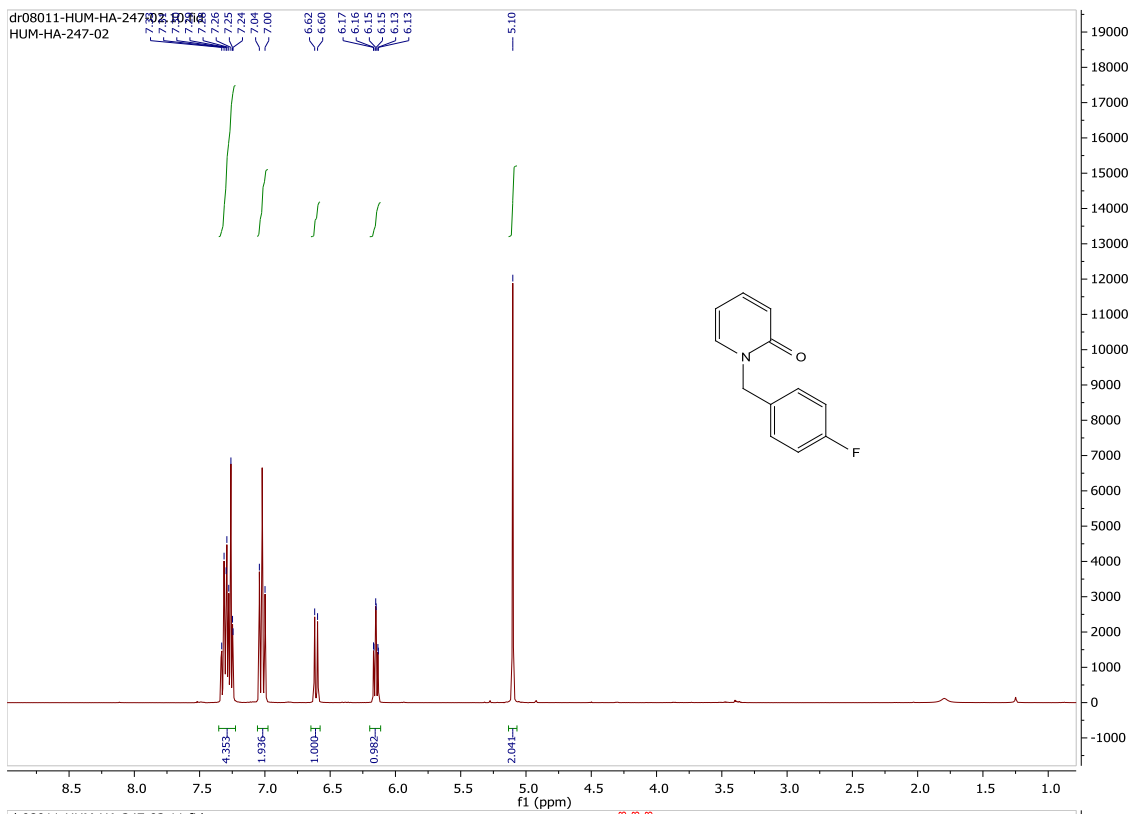
m. p. (decomp.) = 183.4-184.7 °C. ¹H NMR (400 MHz, CD₂Cl₂) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.20 – 6.10 (m, 1H), 5.76 – 5.68 (m, 1H), 5.22 (dt, *J* = 5.4, 2.6 Hz, 1H), 2.89 (dt, *J* = 6.9, 2.3 Hz, 1H), 2.43 (s, 3H). ¹³C NMR (101 MHz, CD₂Cl₂) δ 207.7, 170.3, 145.9, 135.5, 130.1, 128.6, 90.3, 77.1, 66.3, 53.8, 22.0. IR (film, cm⁻¹): 3079, 2922, 2064,

1992, 1698, 1594, 1347, 1158, 1084, 608, 546. HRMS (Exact): m/z : calcd for $C_{15}H_{11}FeNO_6Na [M+Na^+]$: 411.95487, found: 411.95461. Single crystals suitable for X-ray diffraction were grown by slowly lowering the temperature of a saturated solution of this product in EtOAc/pentane from 20 °C to –30 °C.

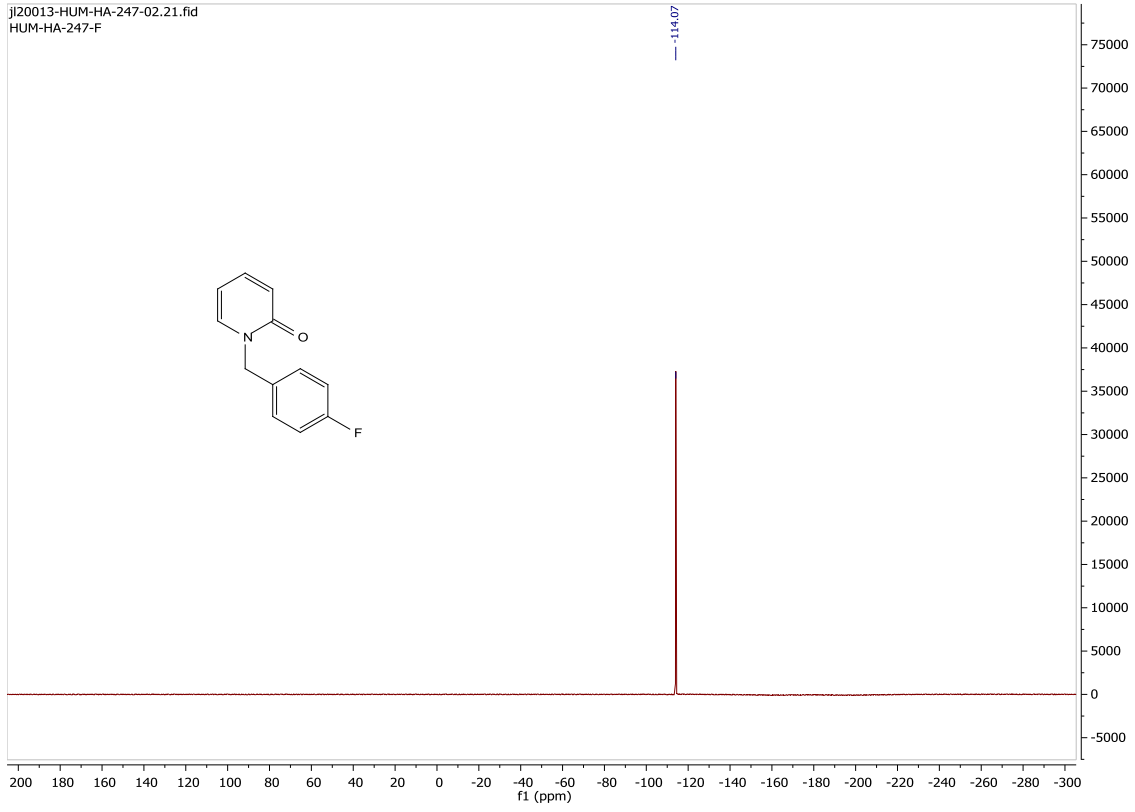
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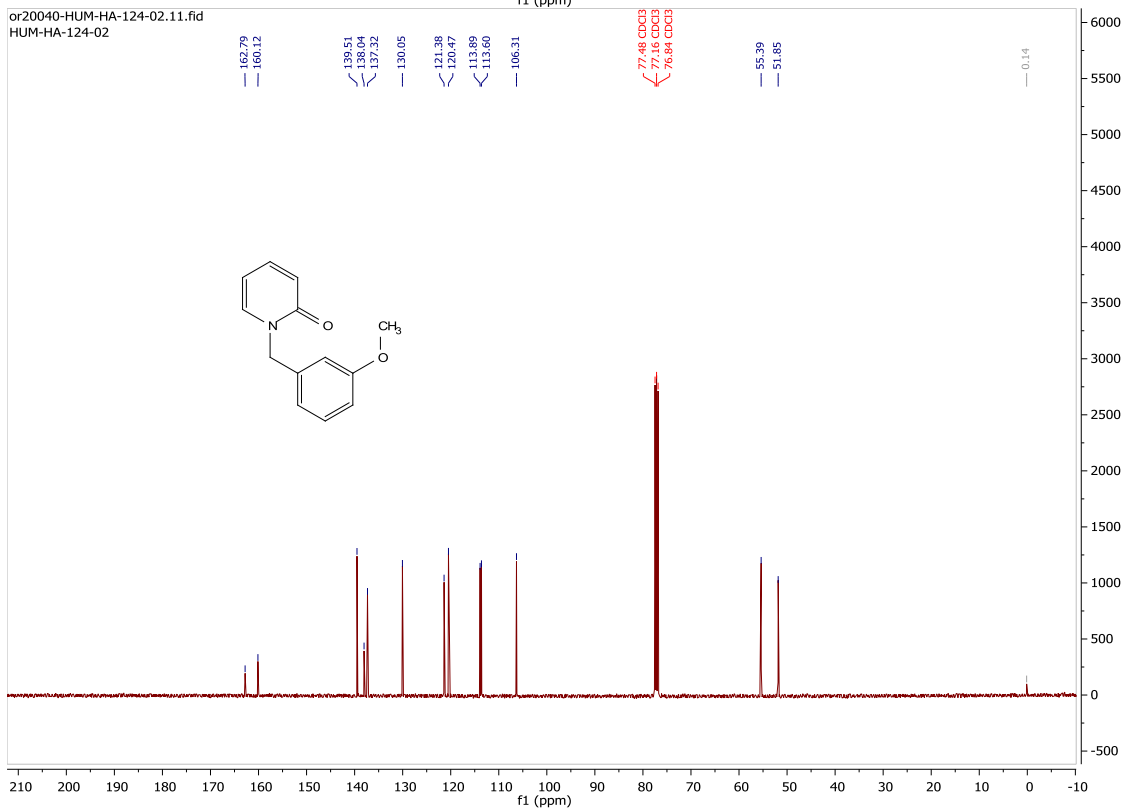
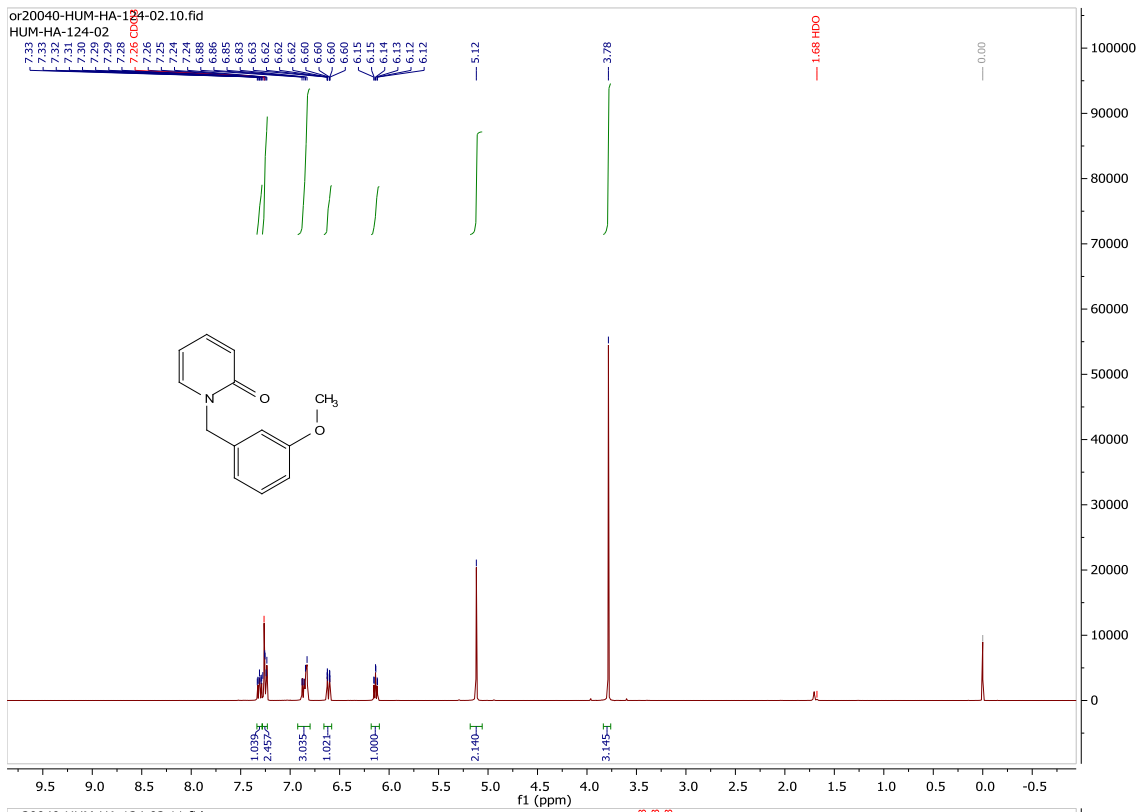
- (1) Falb, E.; Ulanenko, K.; Tor, A.; Gottesfeld, R.; Weitman, M.; Afri, M.; Gottlieb, H.; Hassner, A. *Green Chem.* **2017**, *19*, 5046.
- (2) Sugahara, M.; Ukita, T. *Chem. Pharm. Bull.* **1997**, *45*, 719.
- (3) Sun, C.-L.; Fürstner, A. *Angew. Chem. Int. Ed.* **2013**, *52*, 13071.

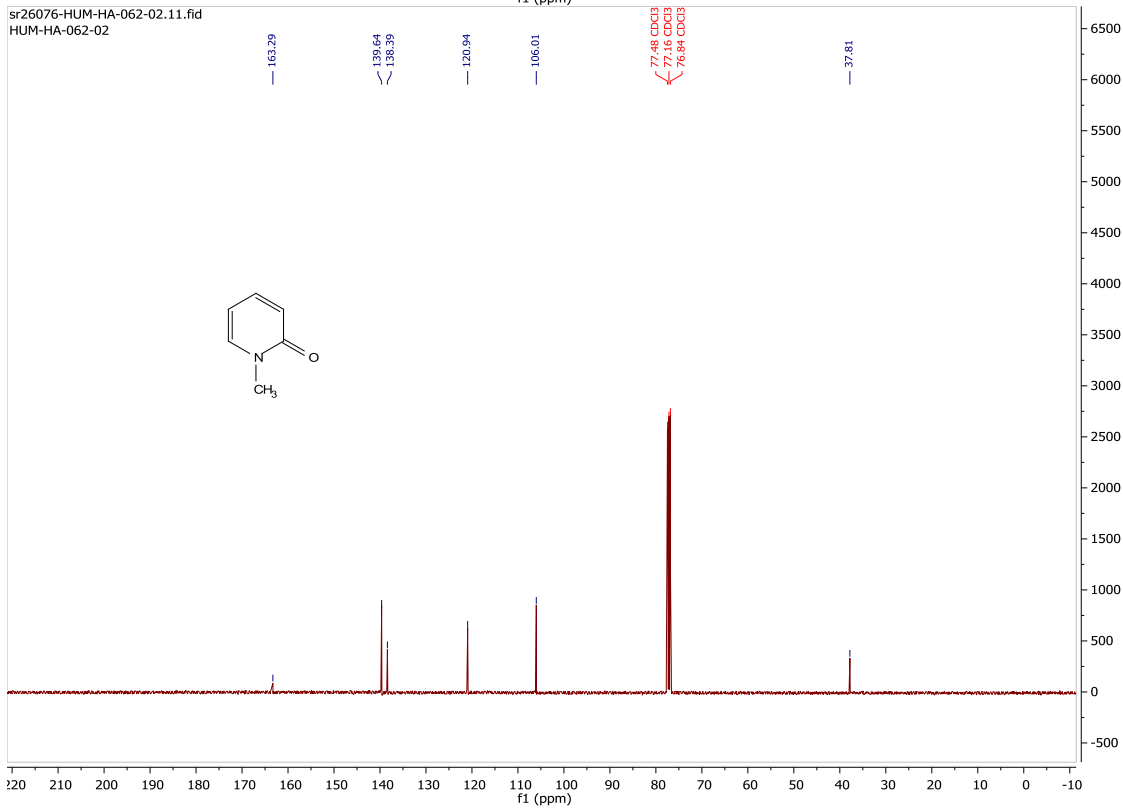
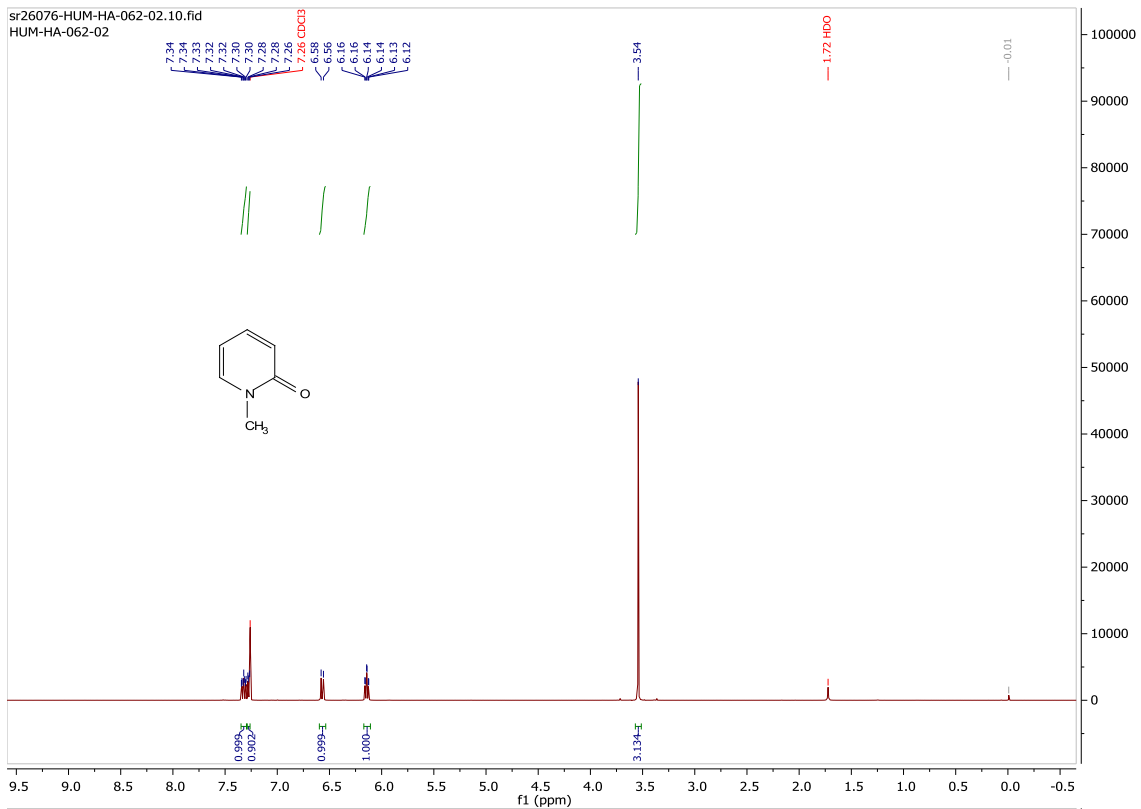


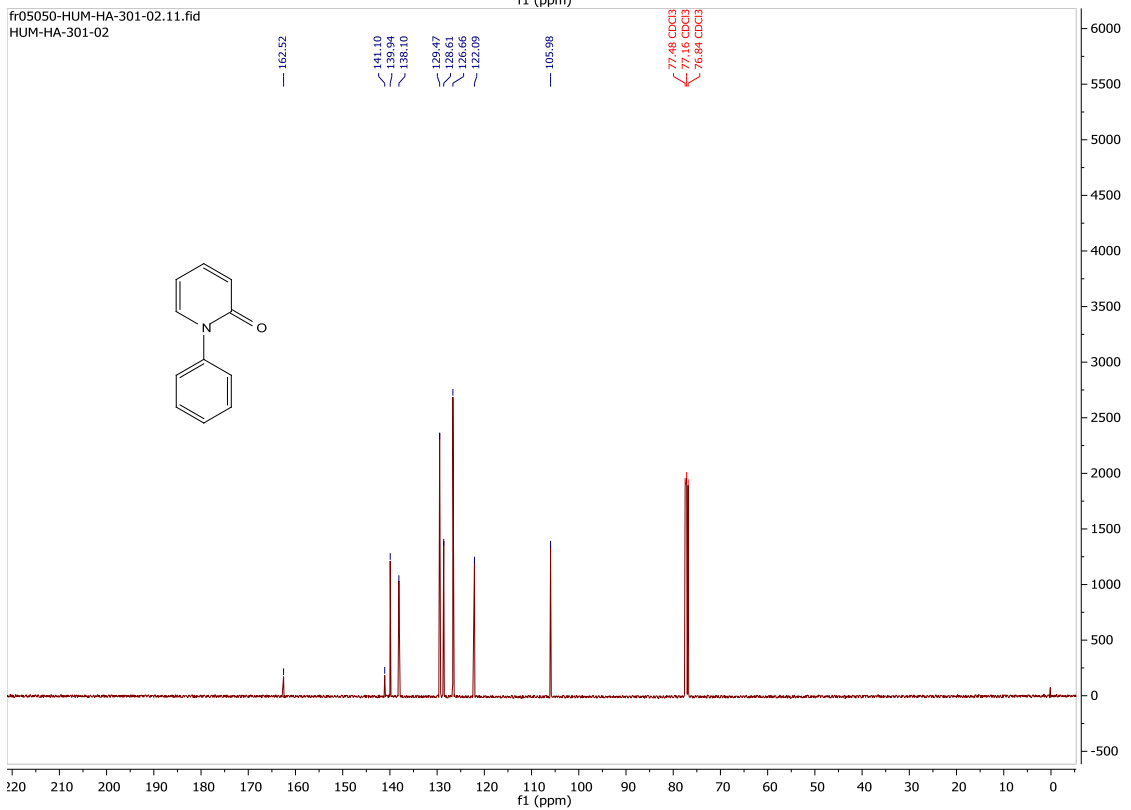
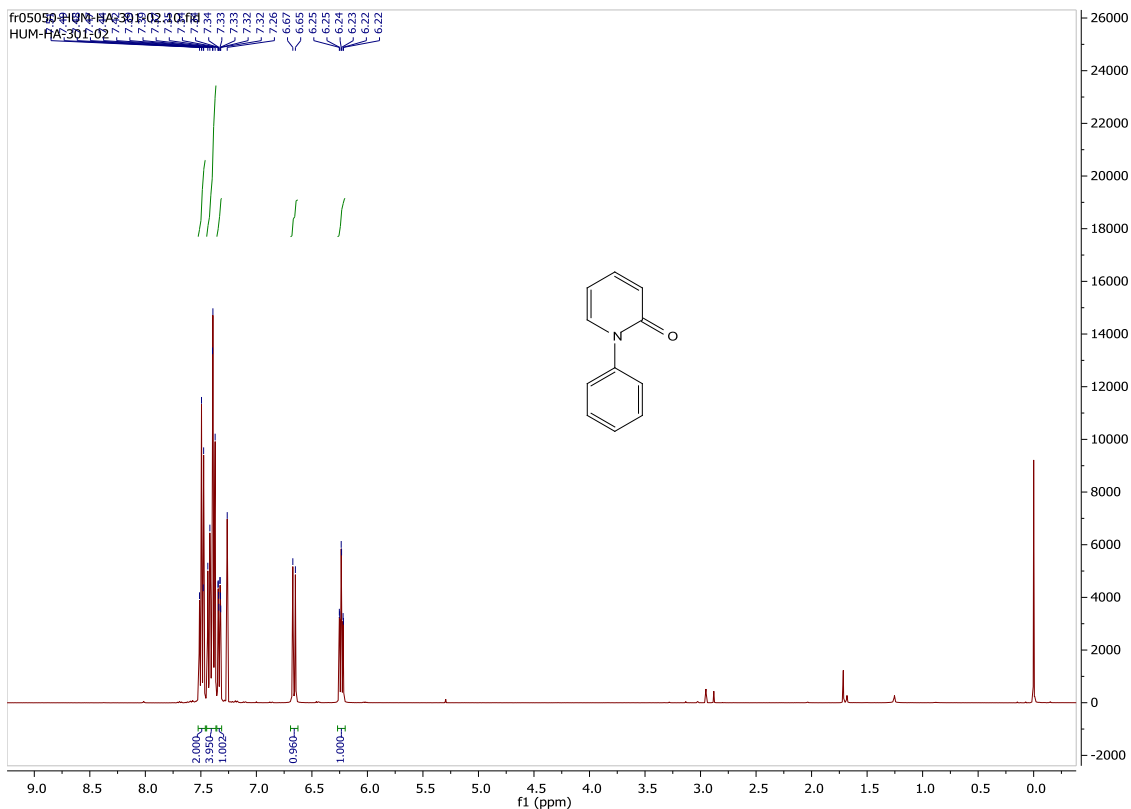


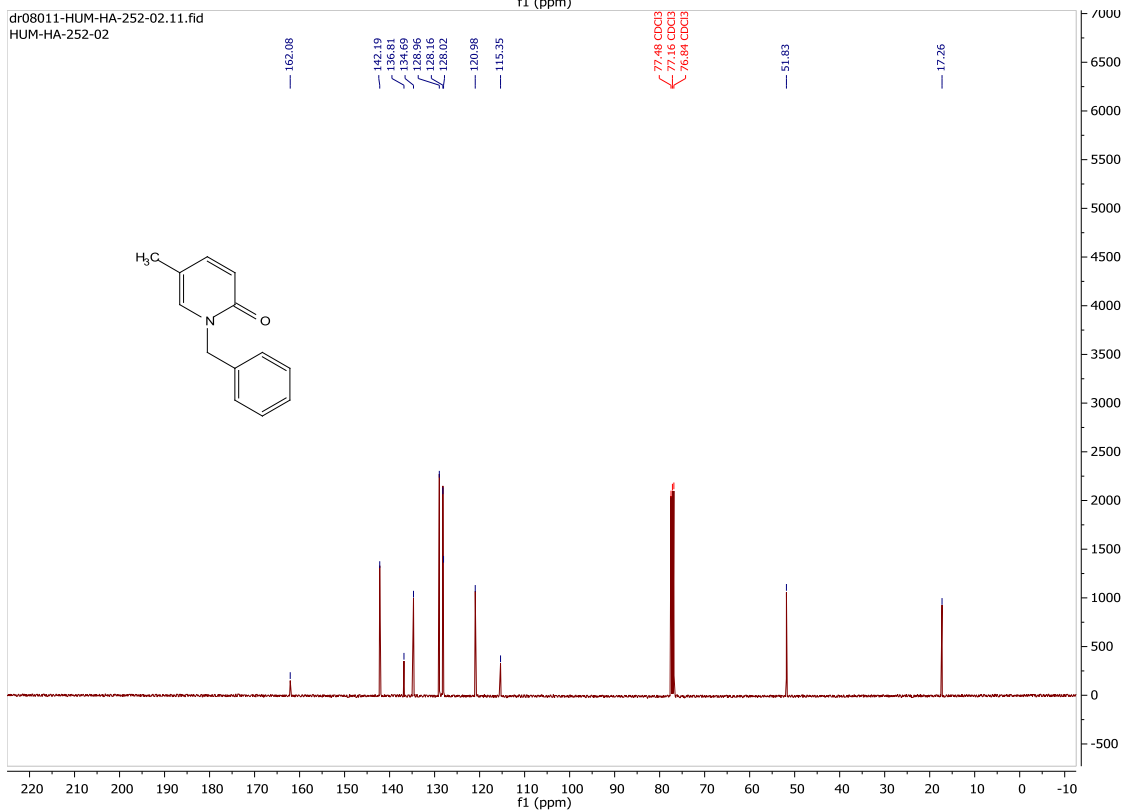
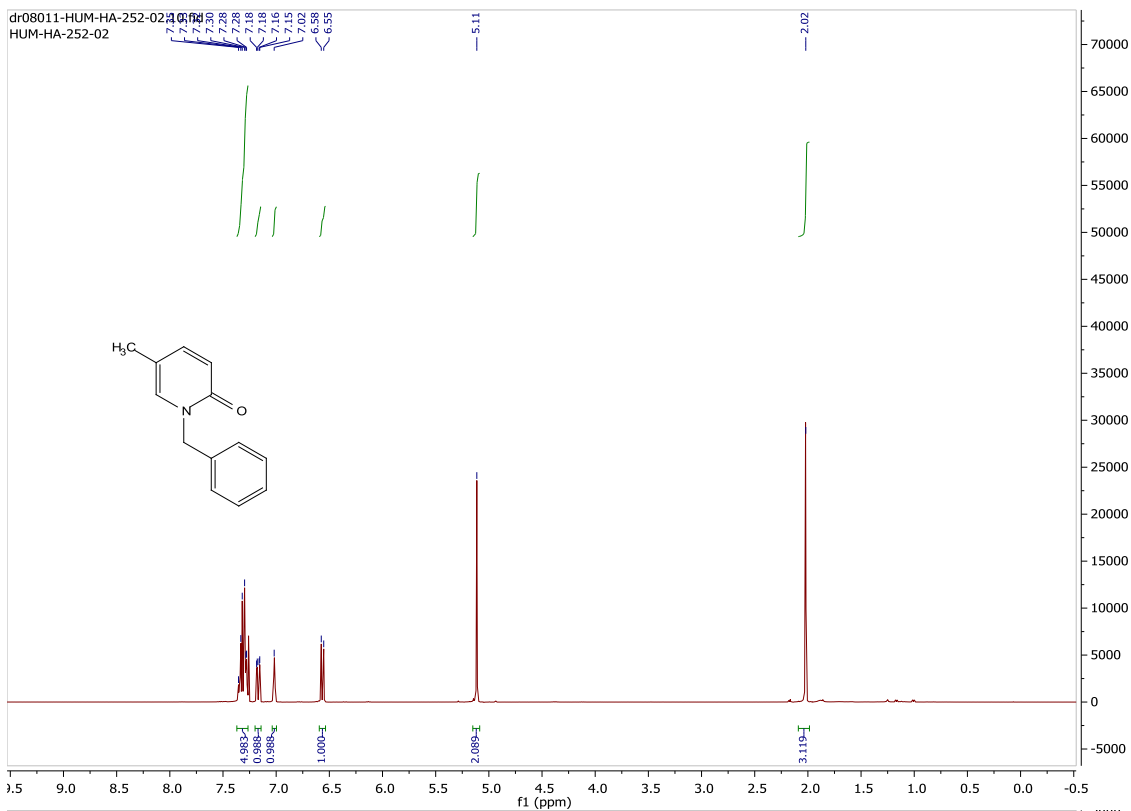
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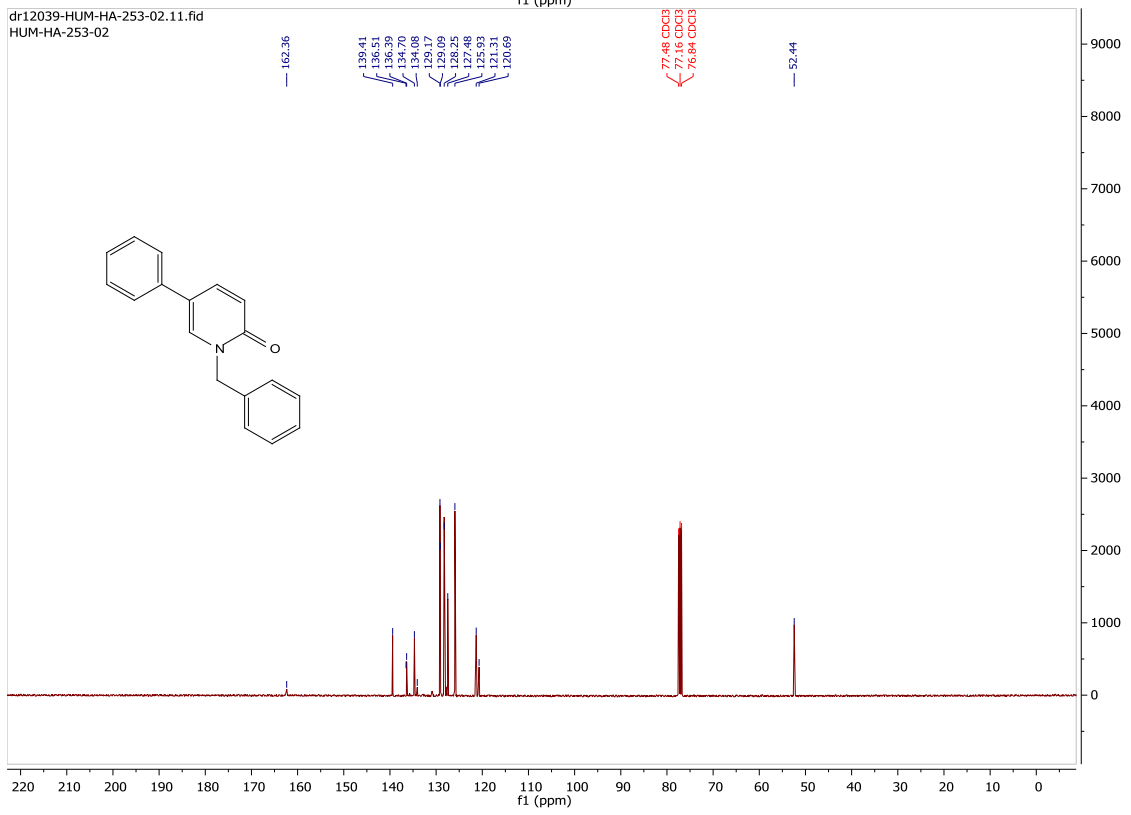
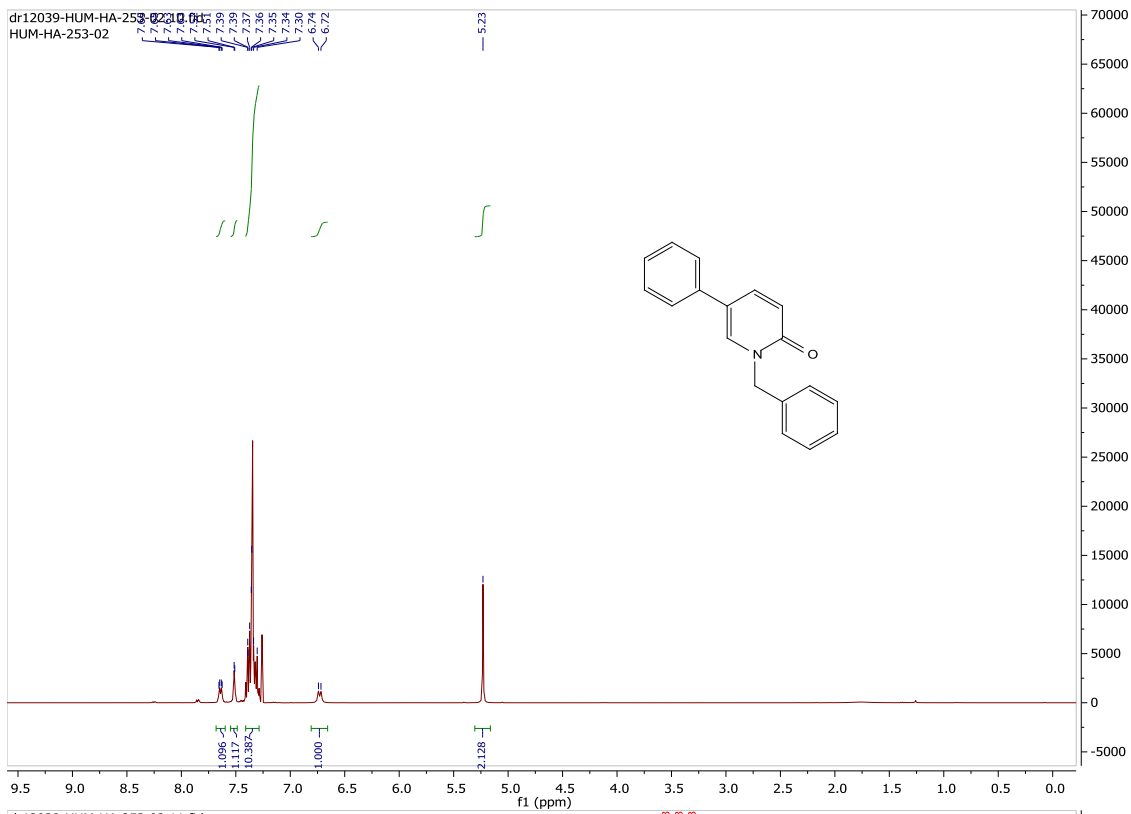


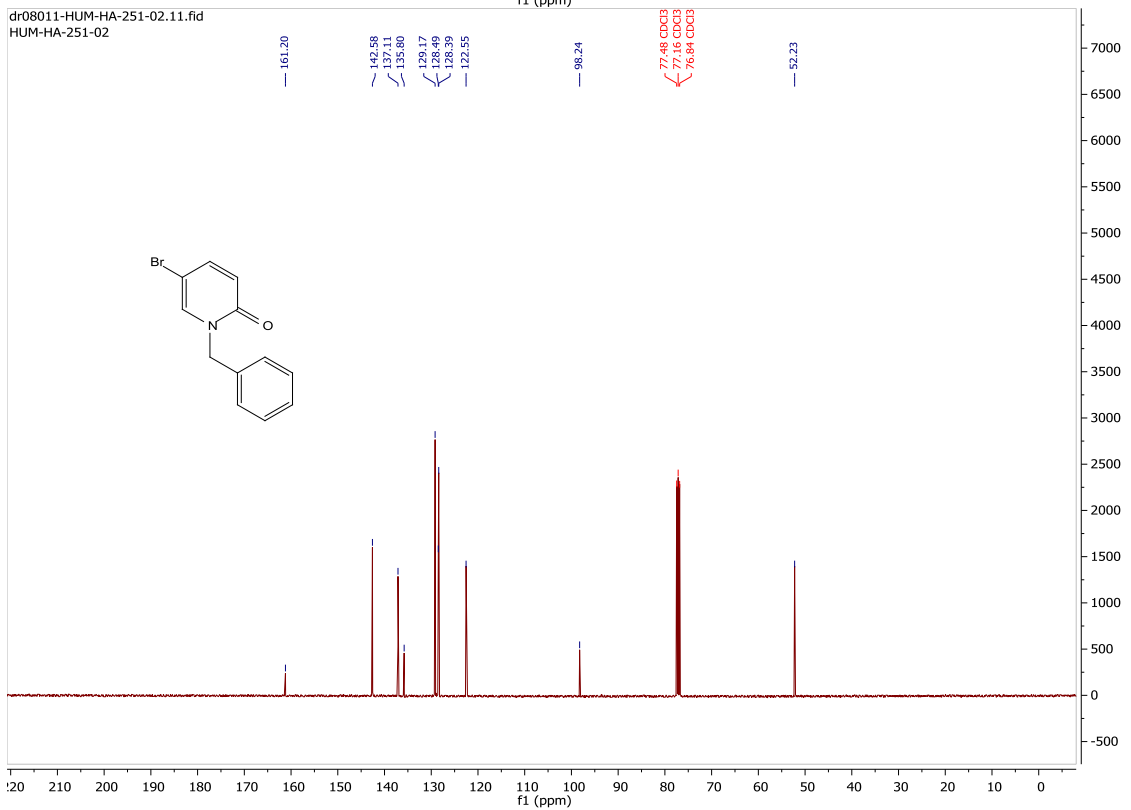
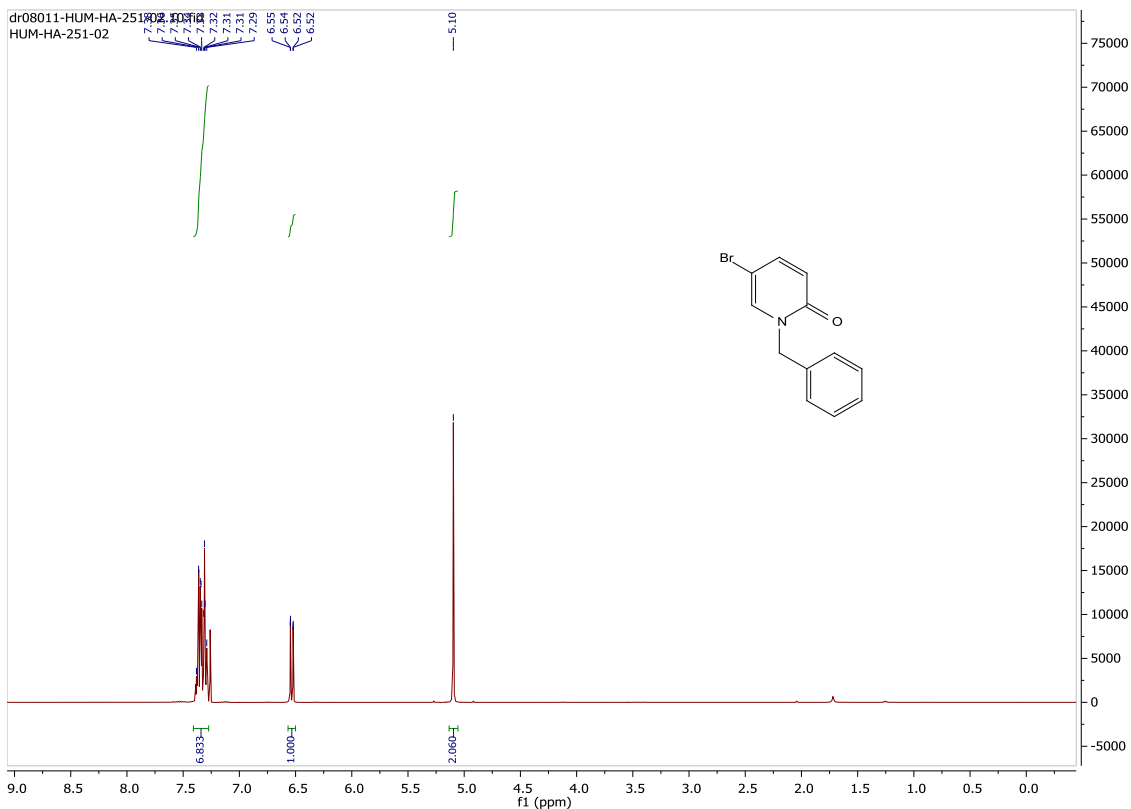


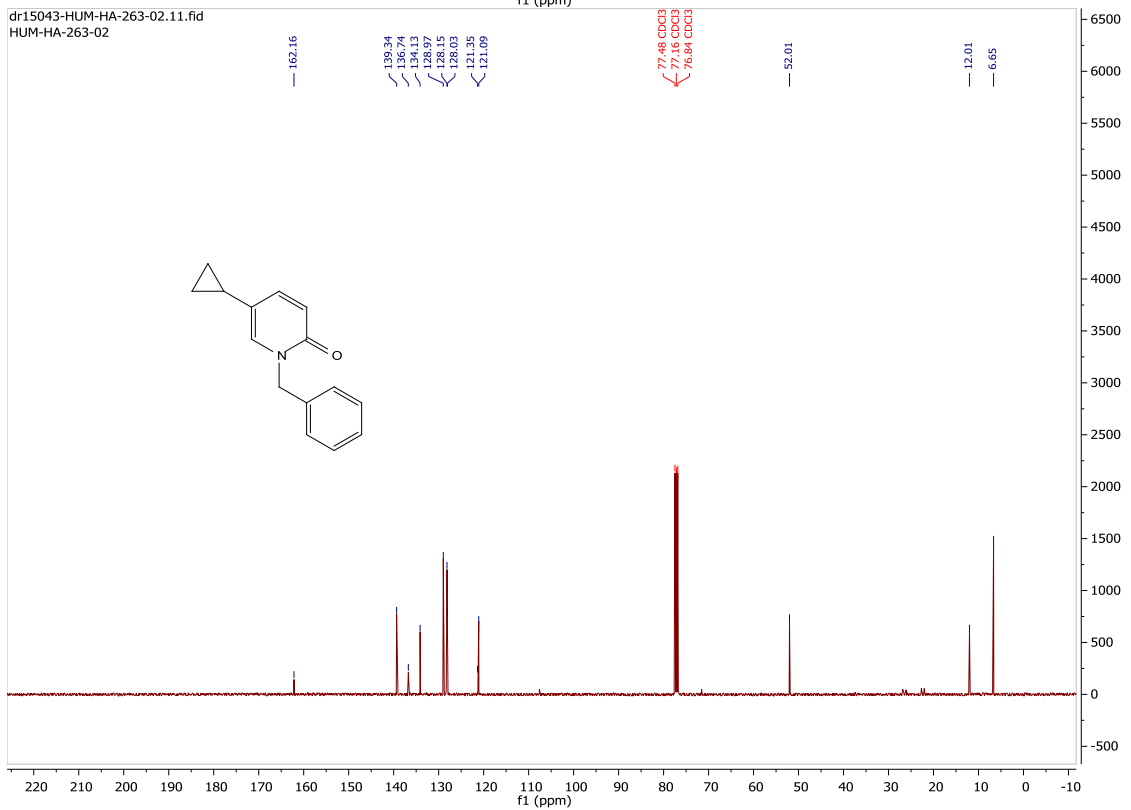
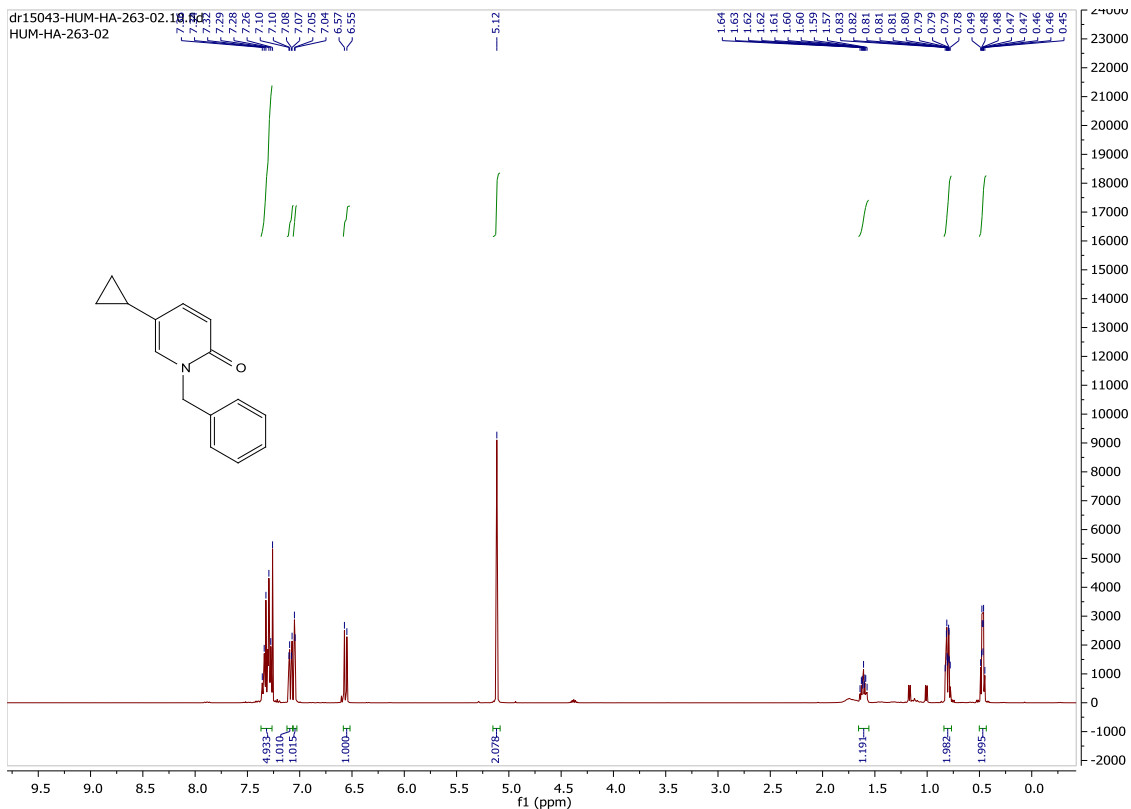


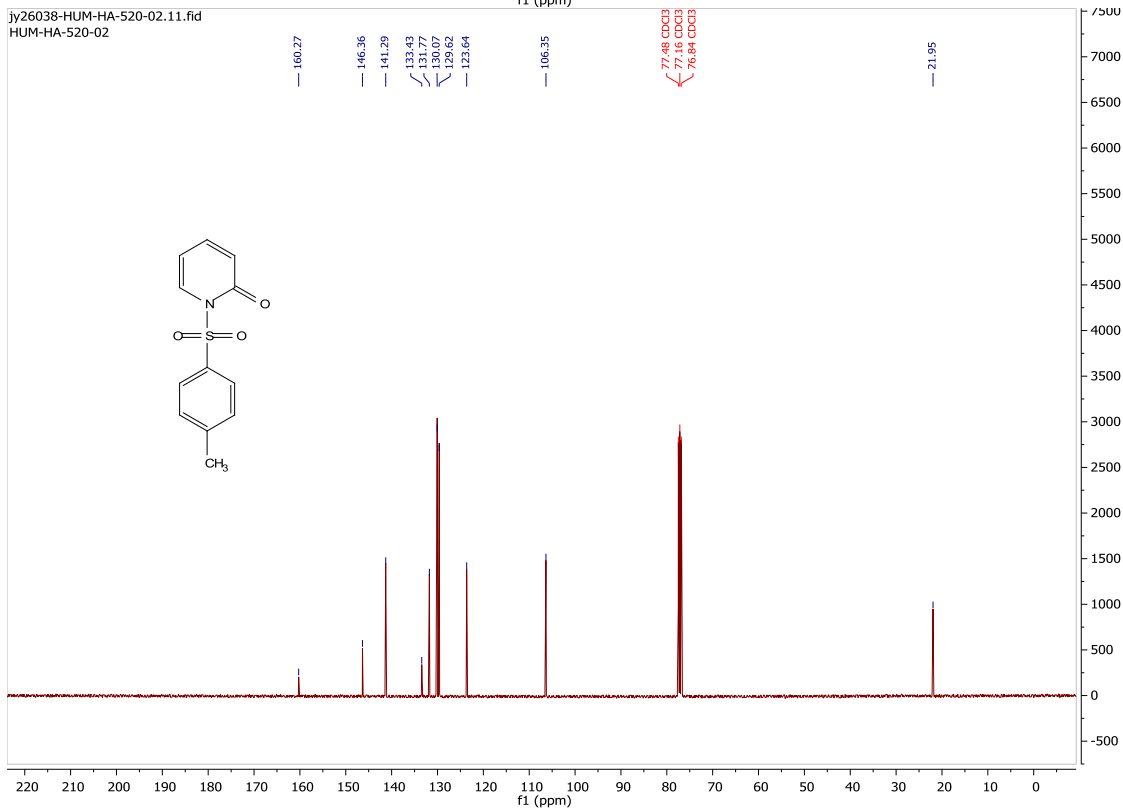
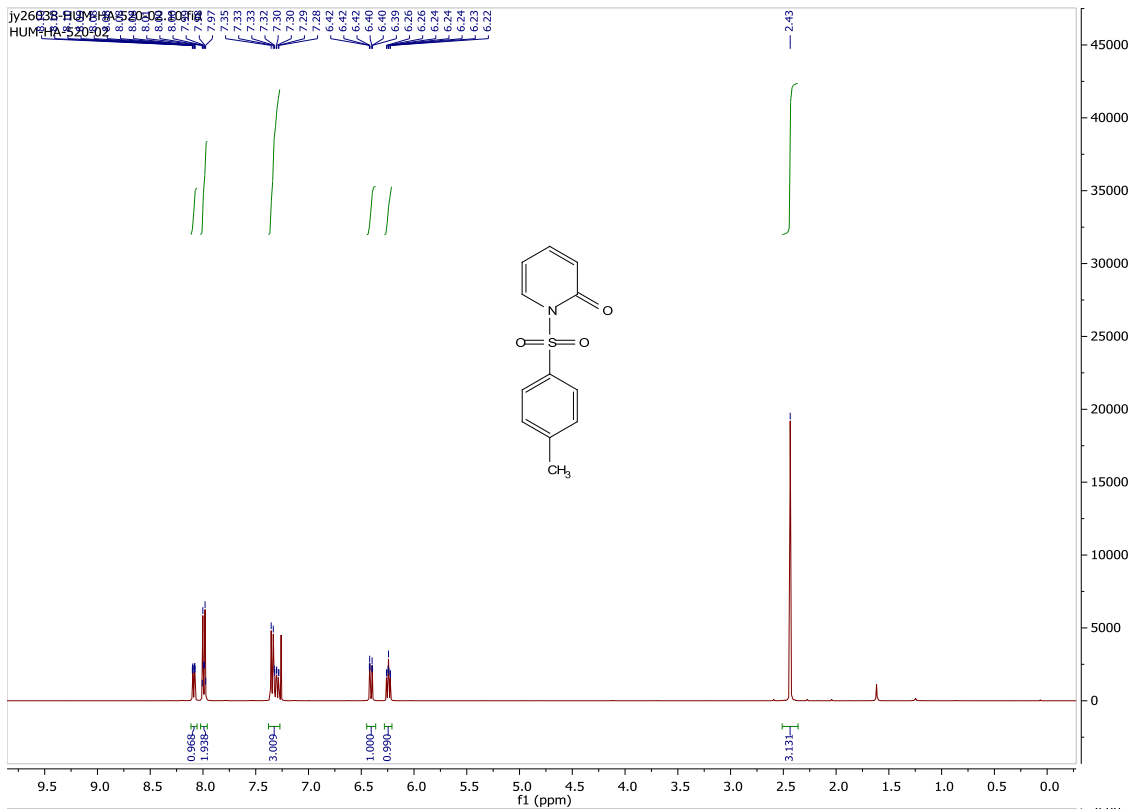


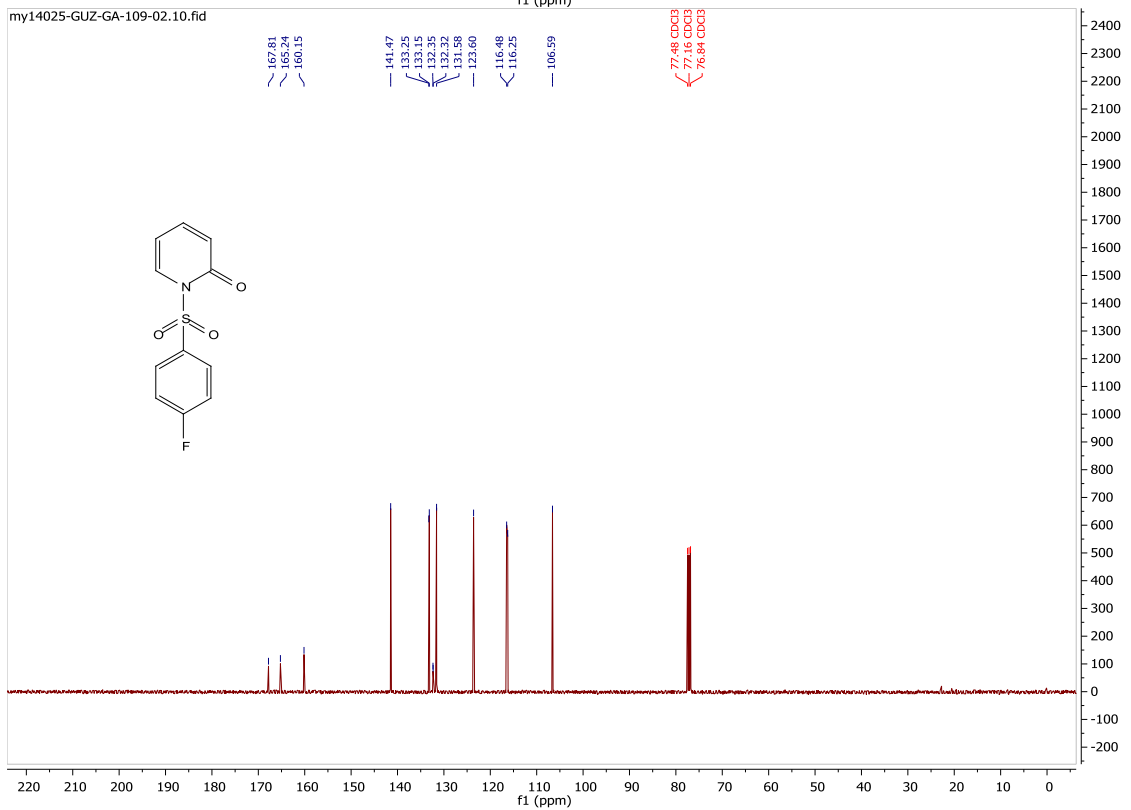
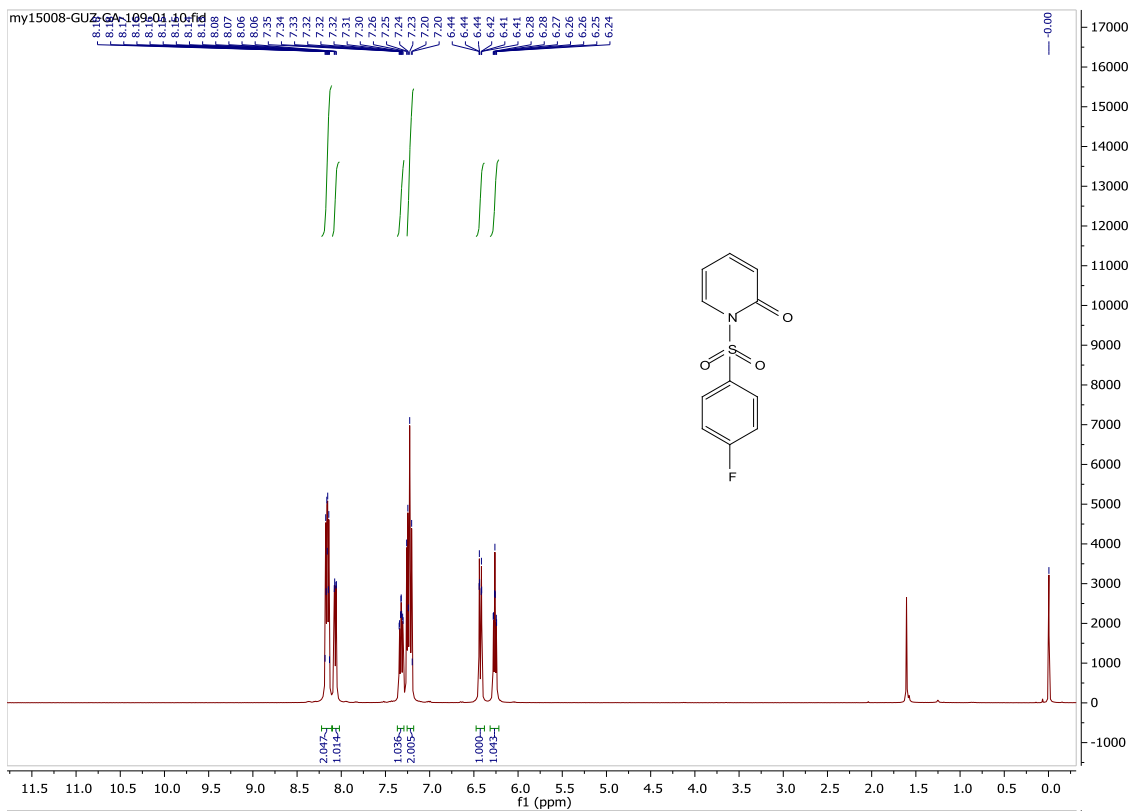




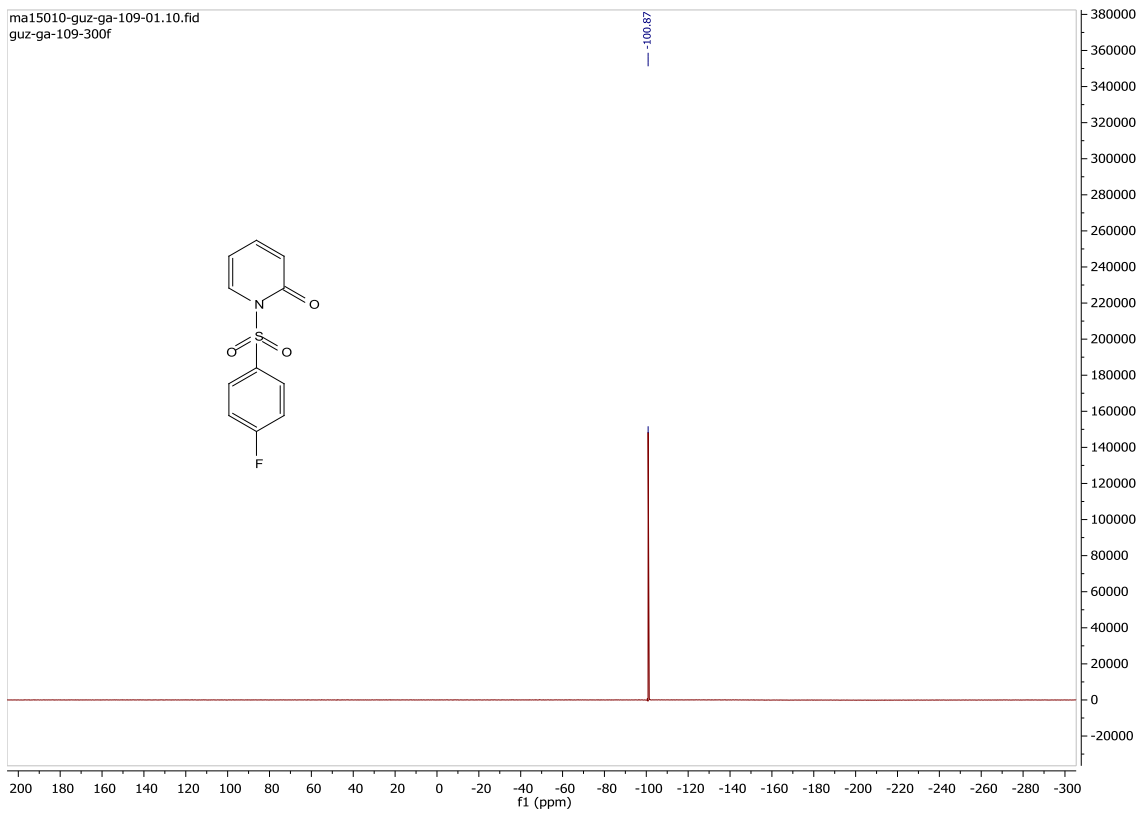


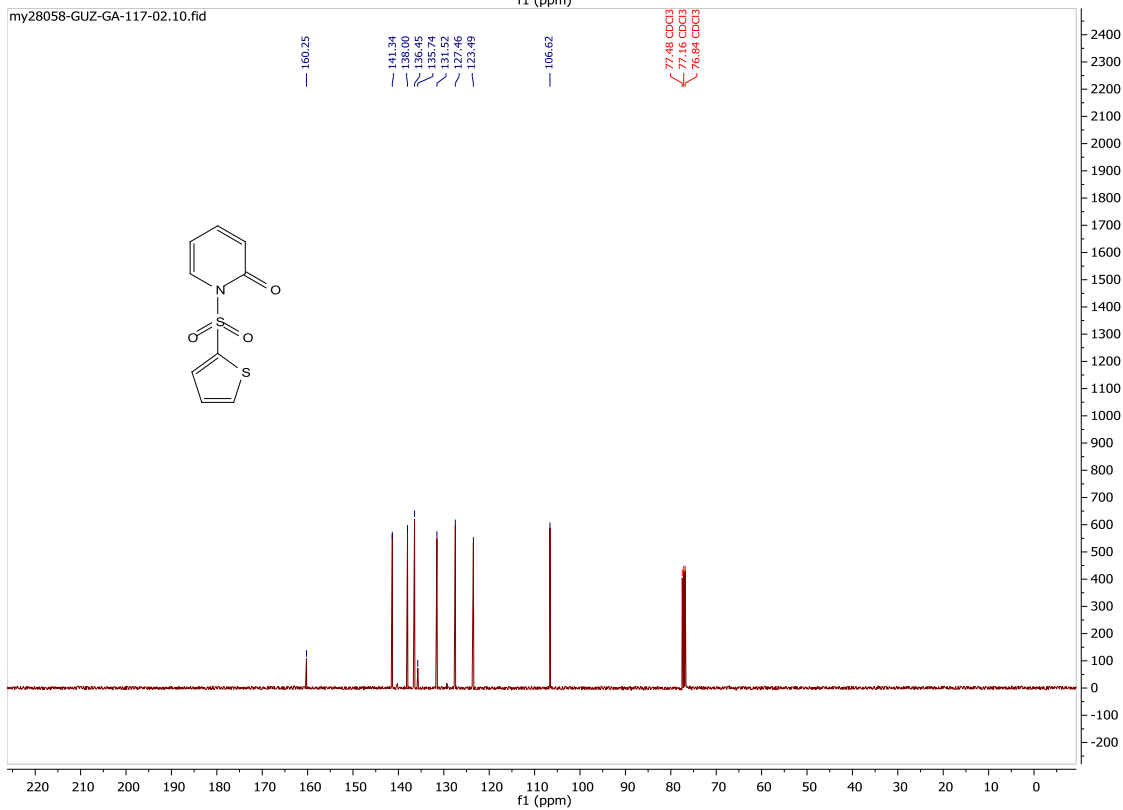
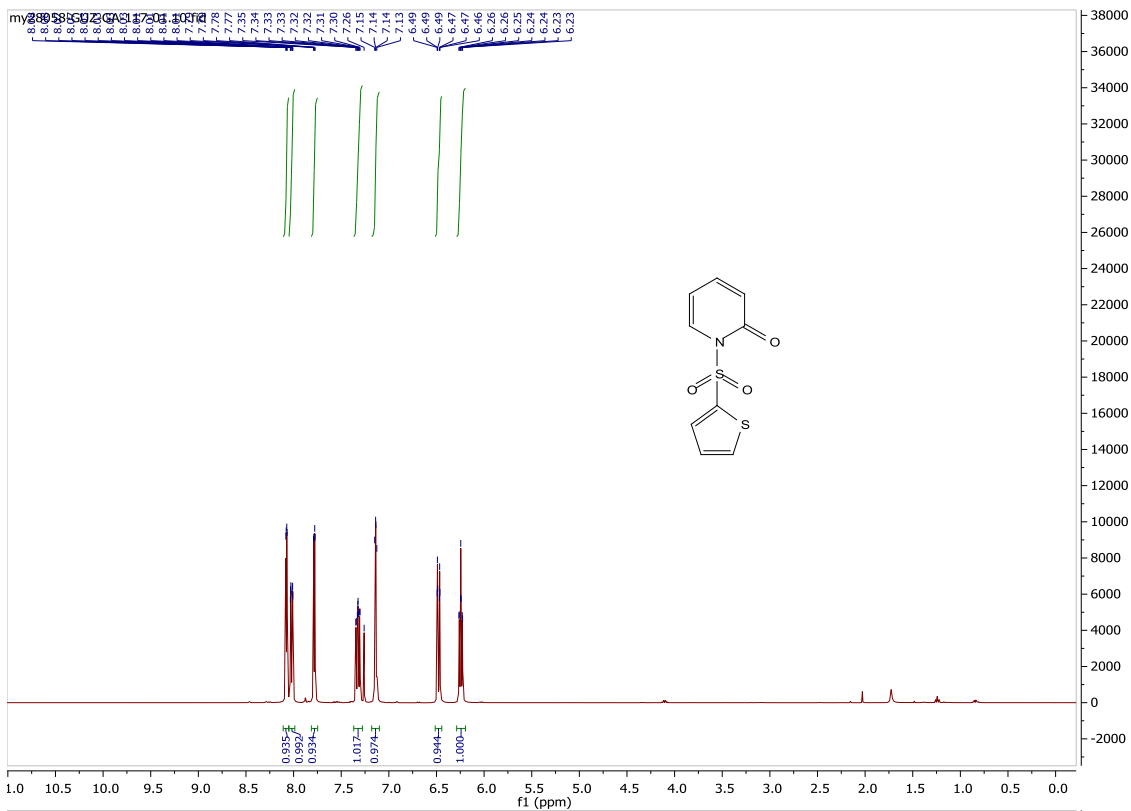


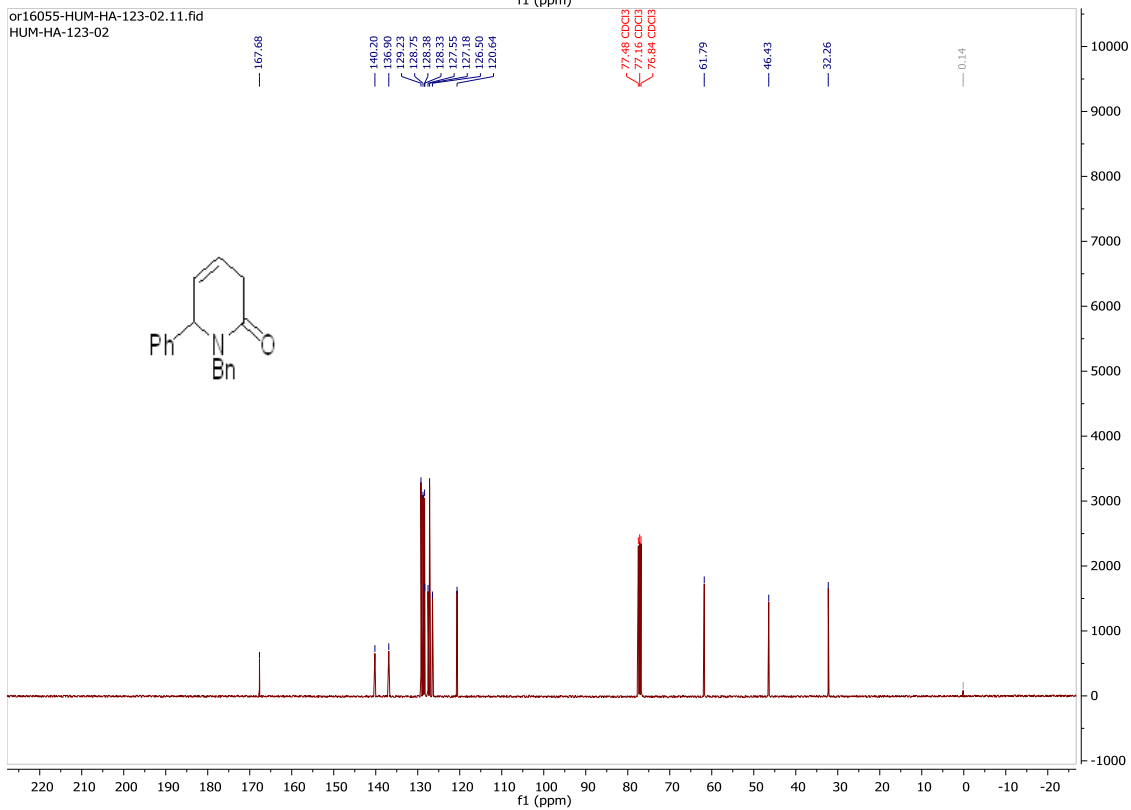
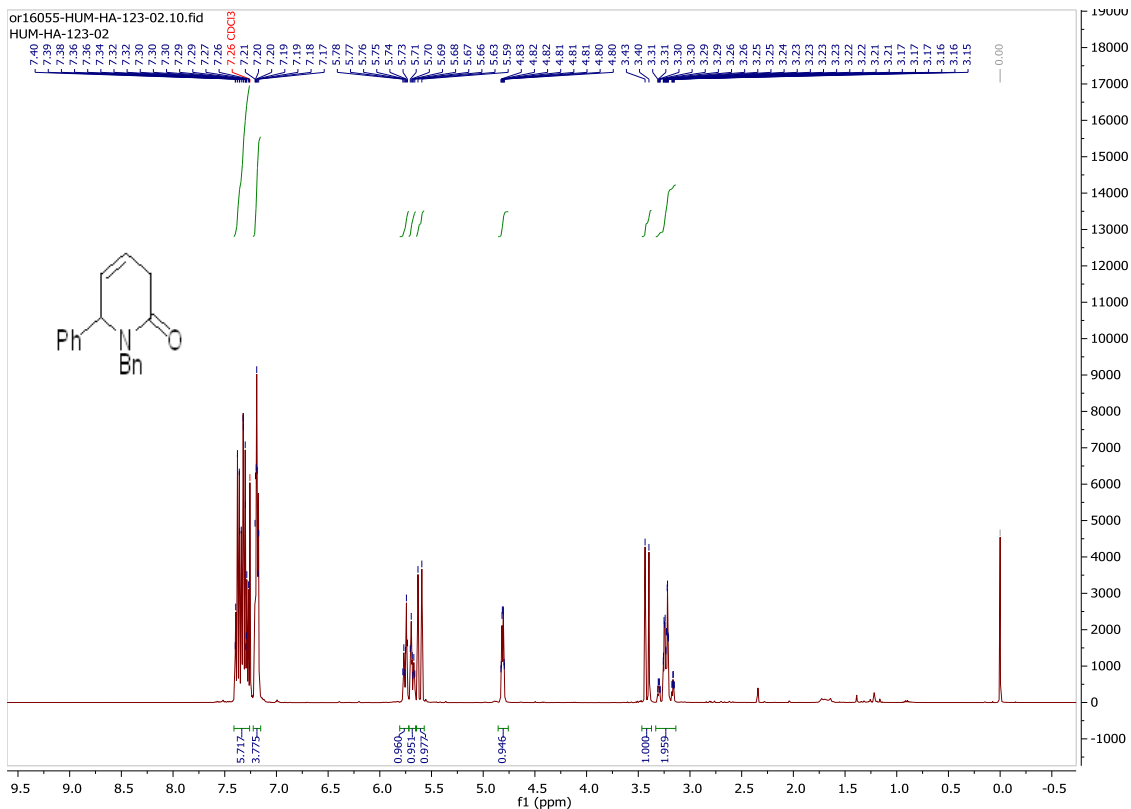


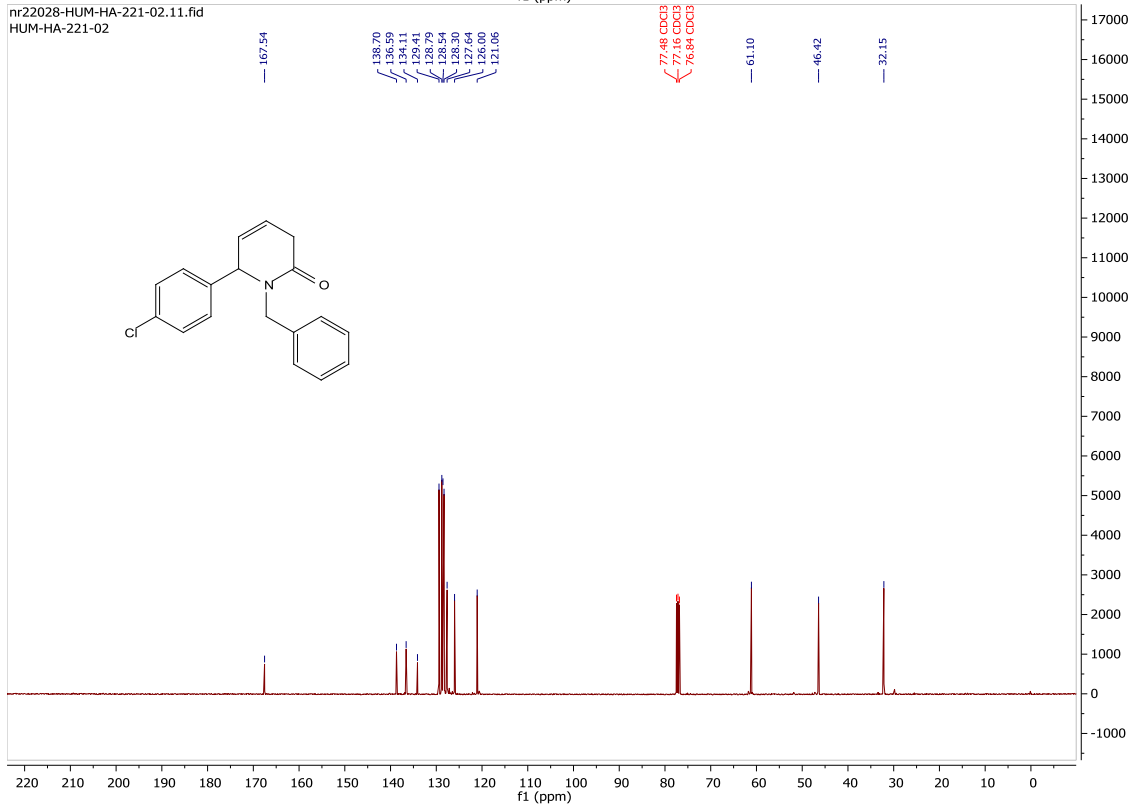
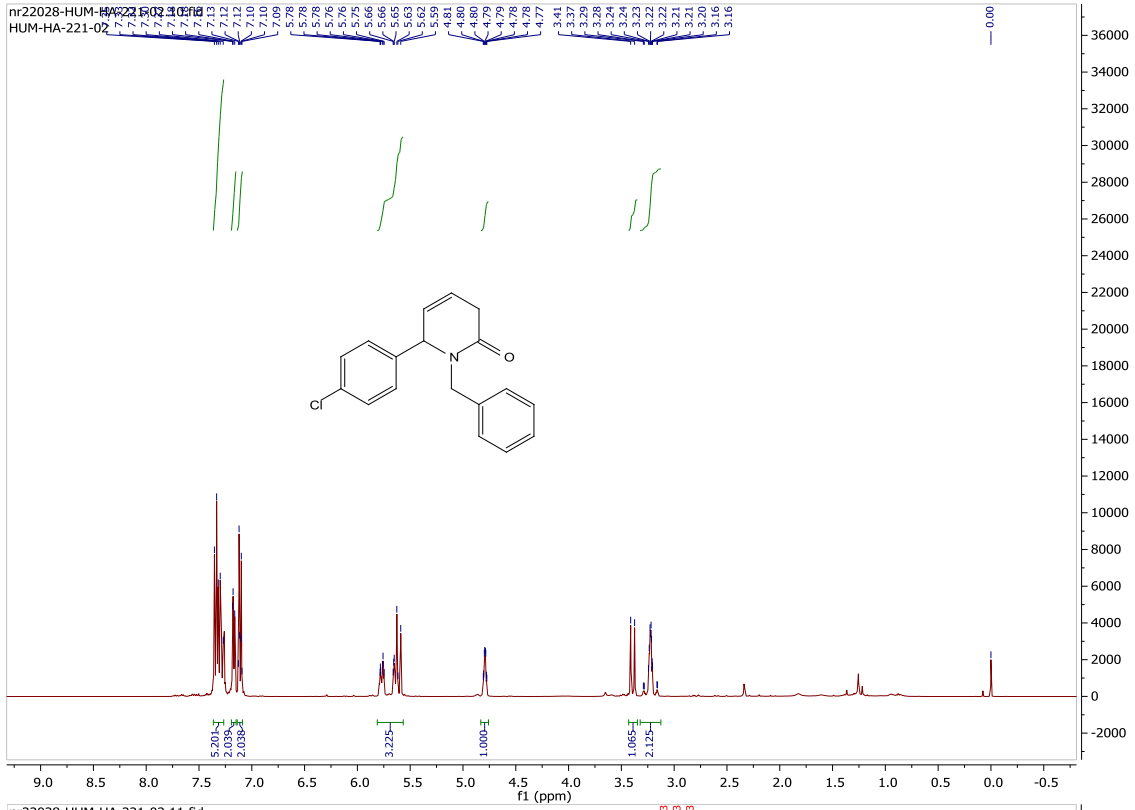


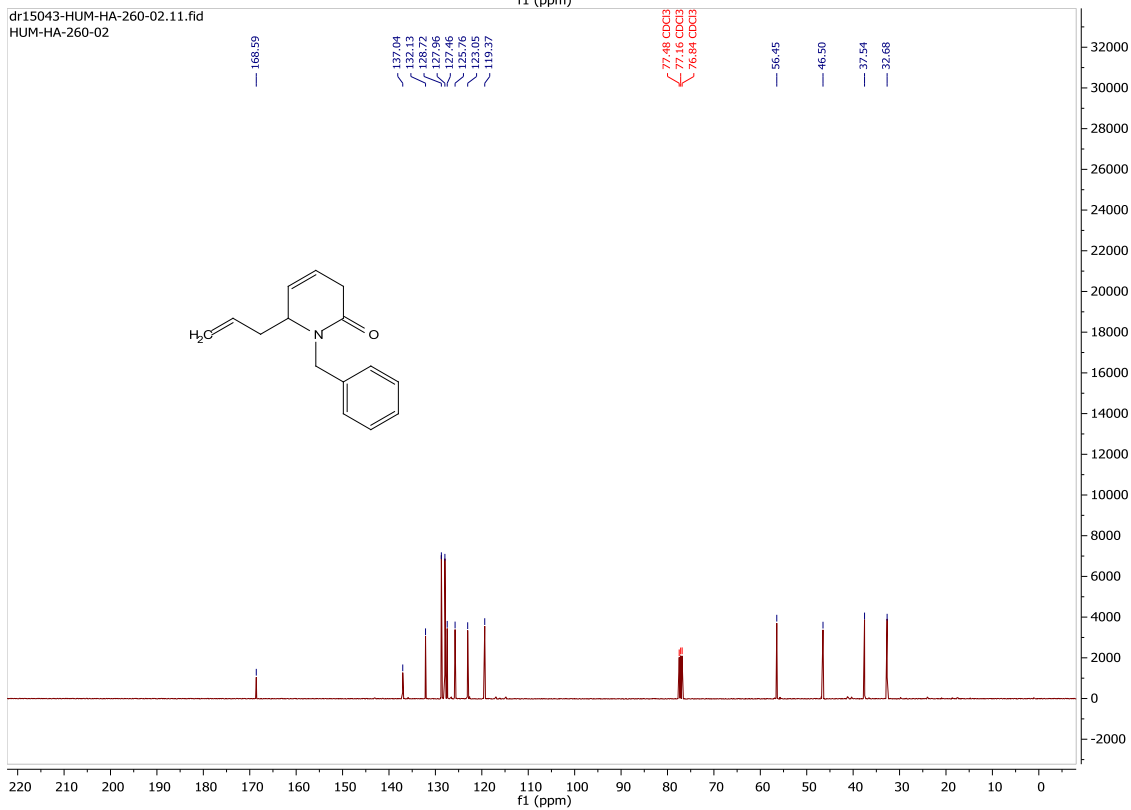
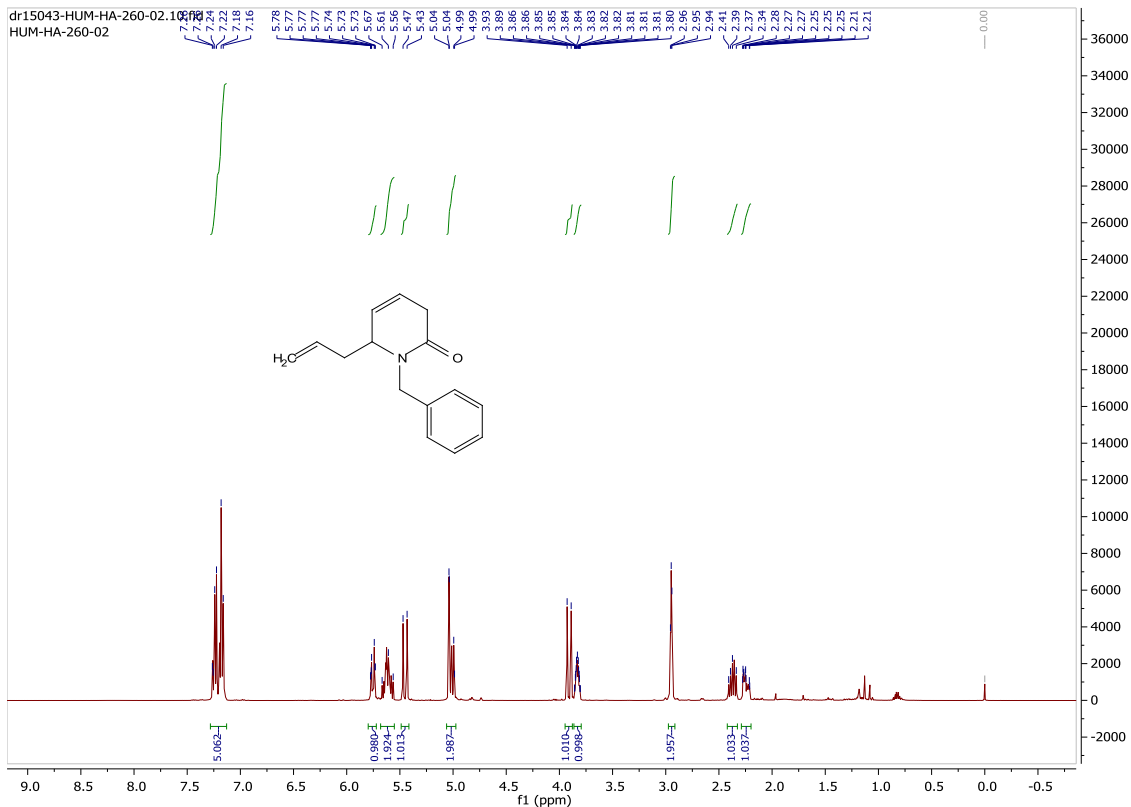
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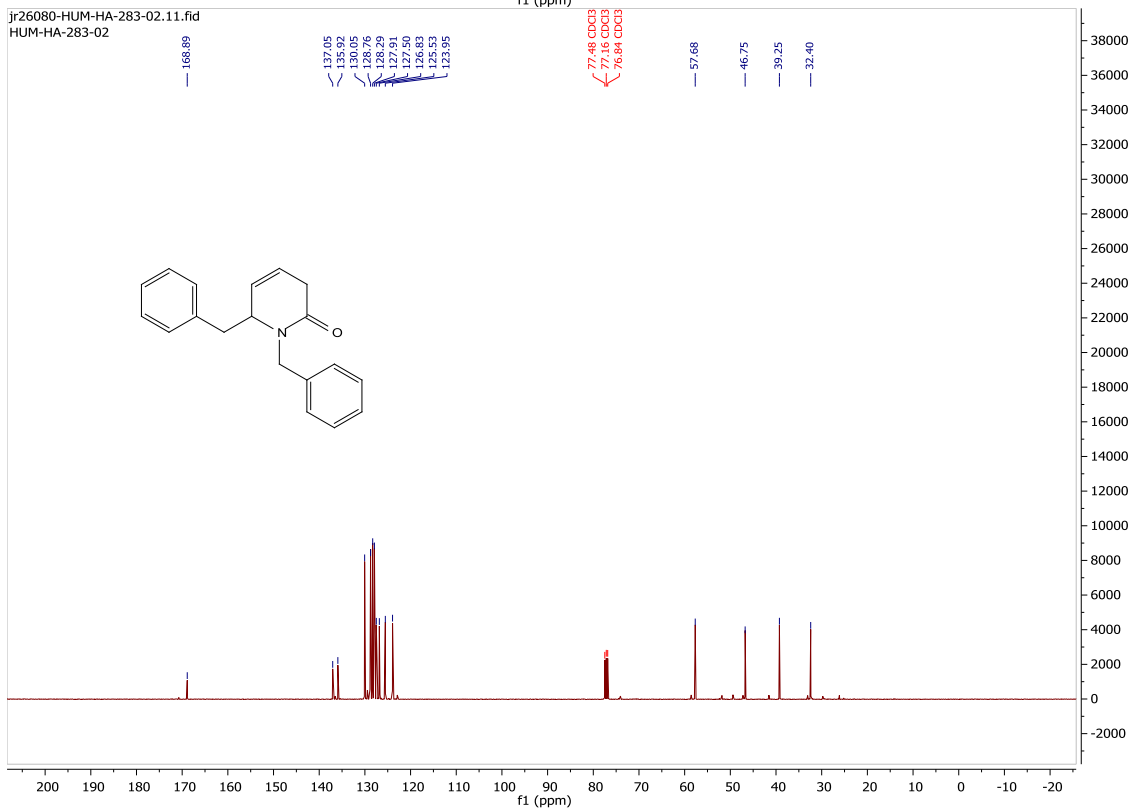
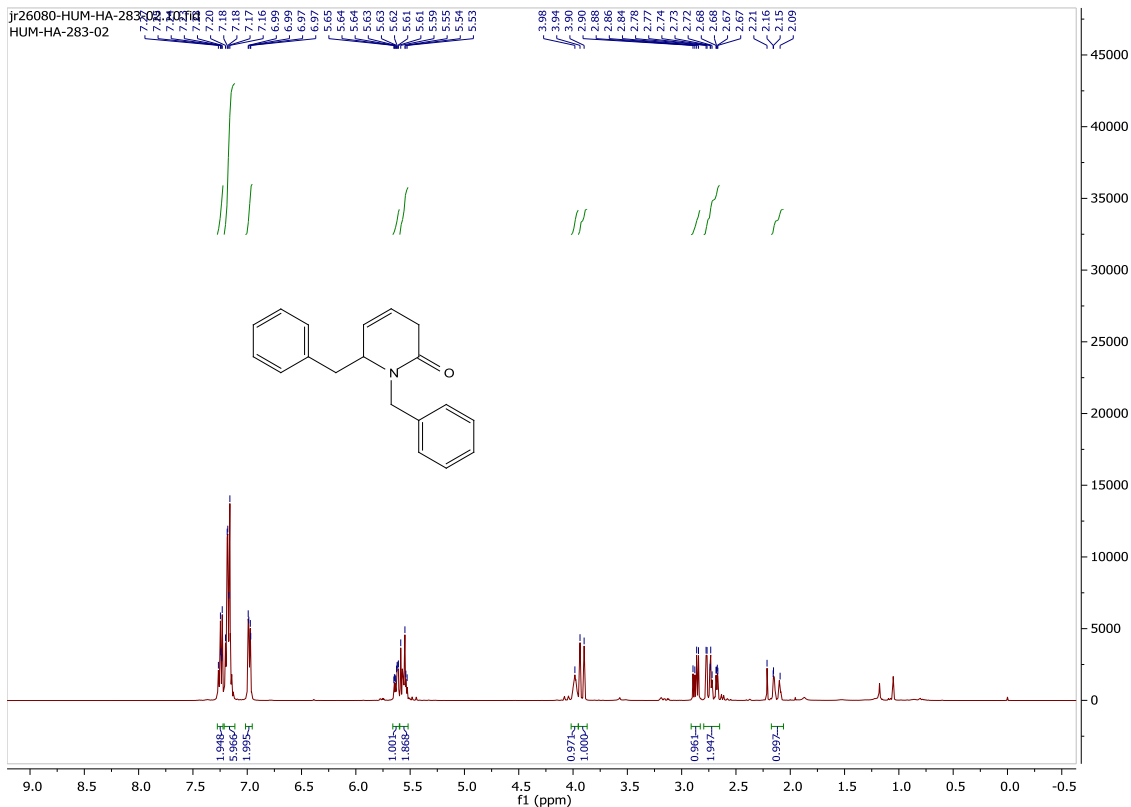


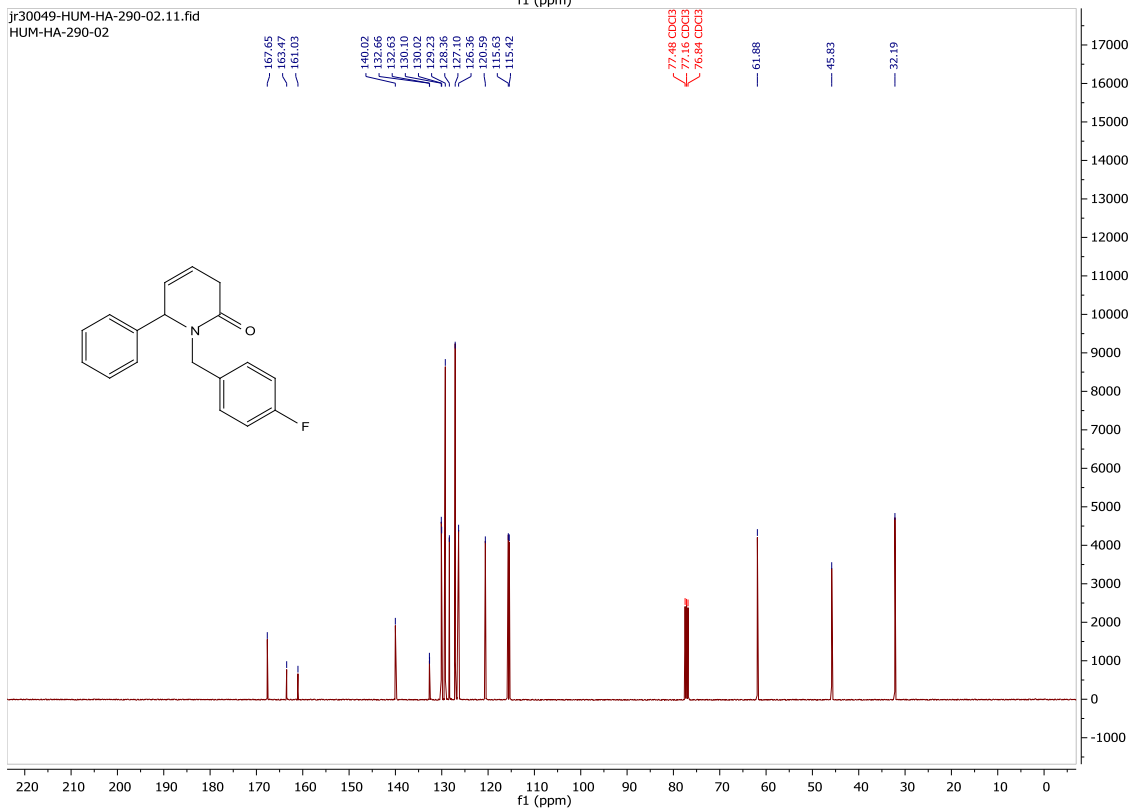
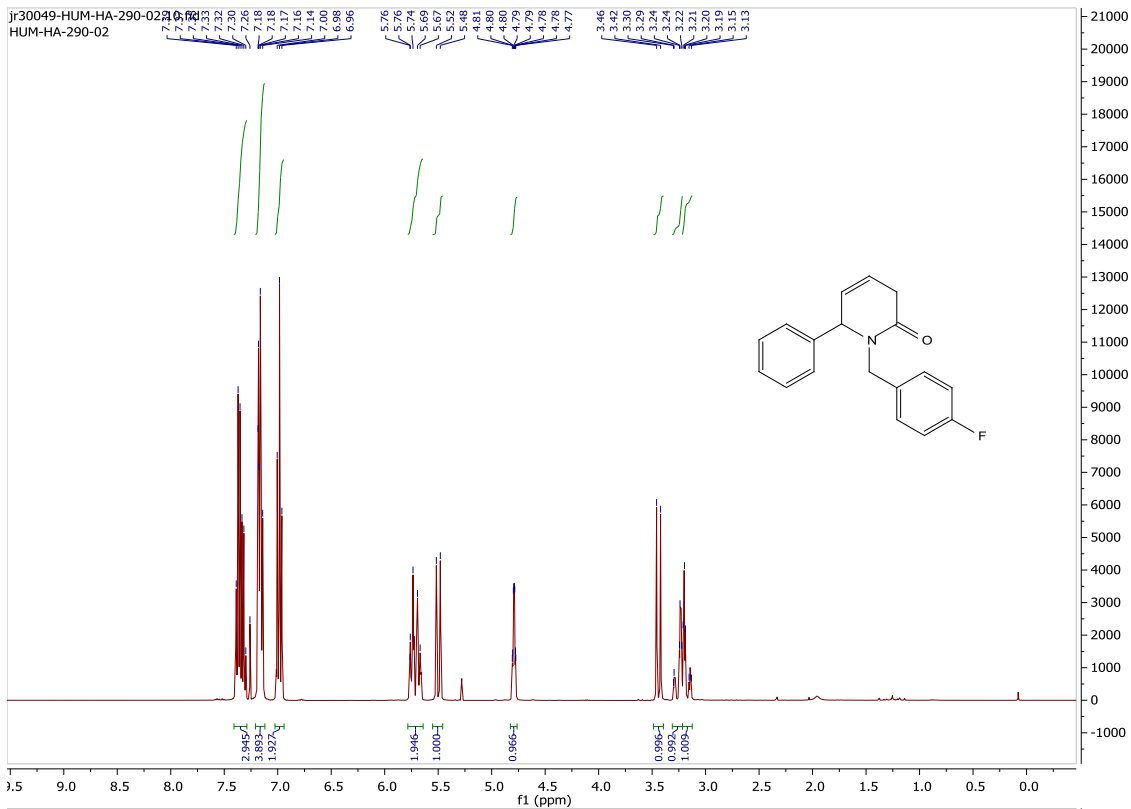




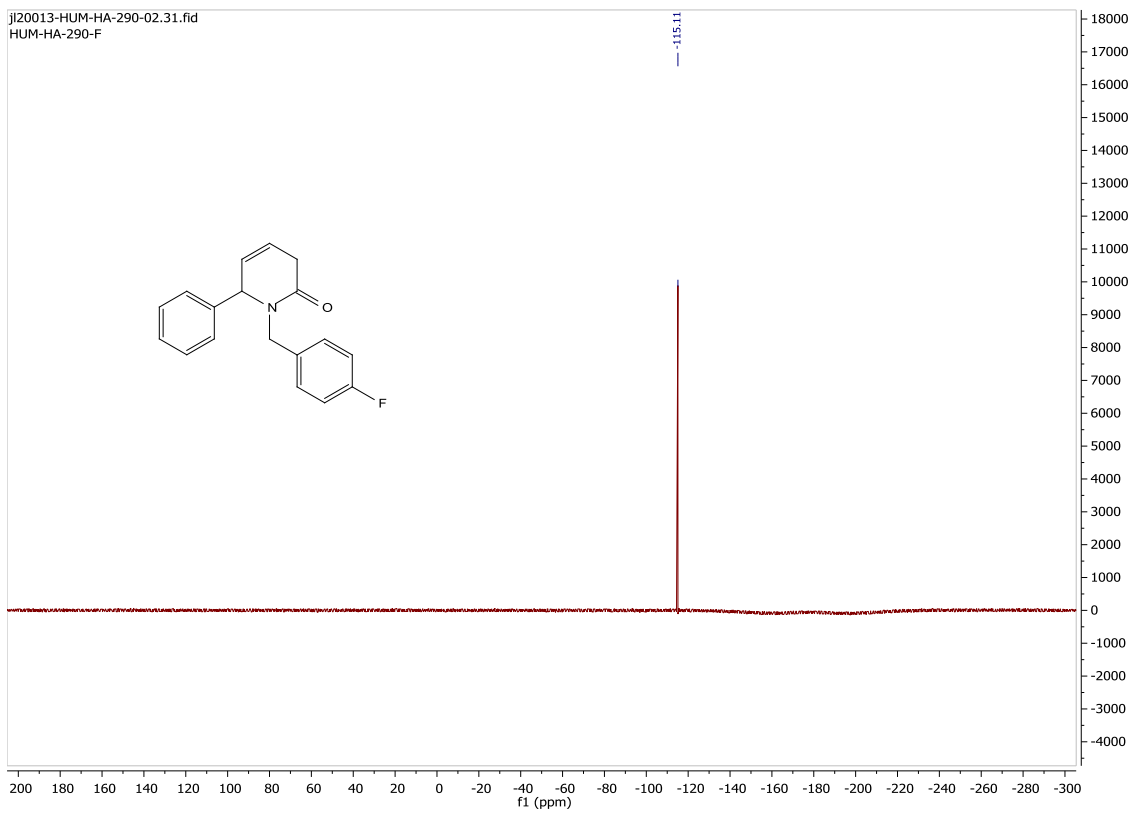


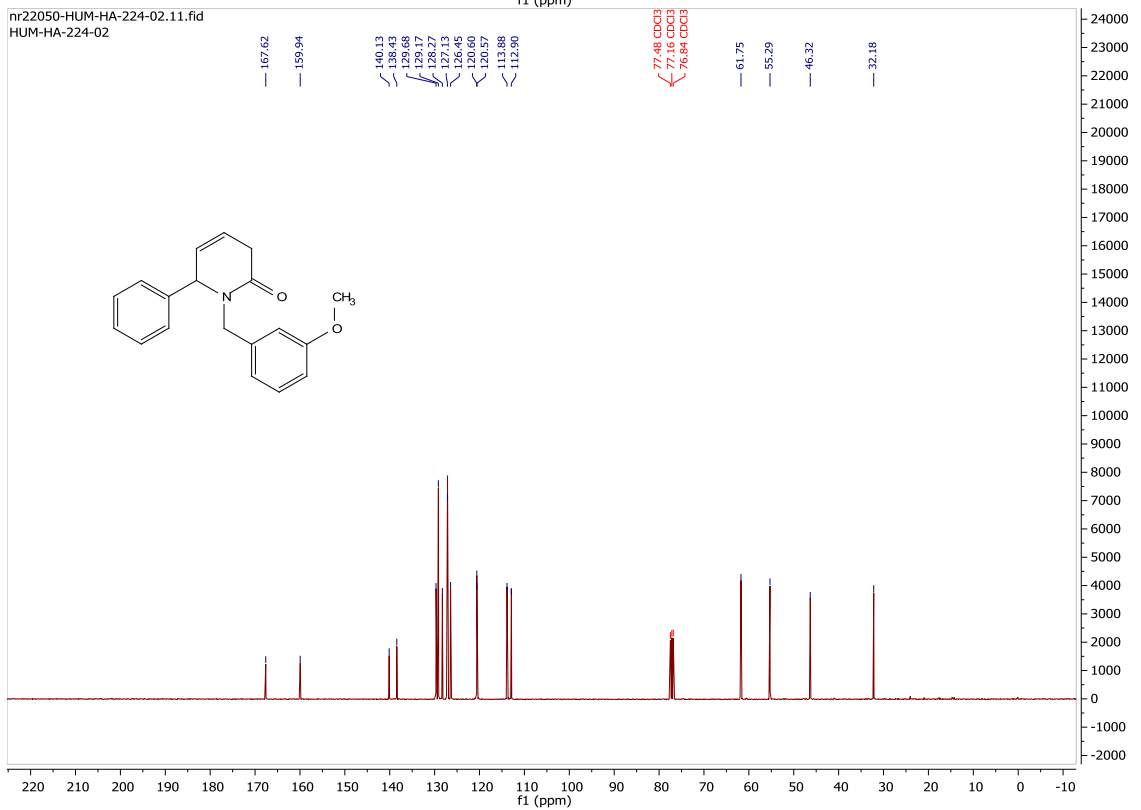
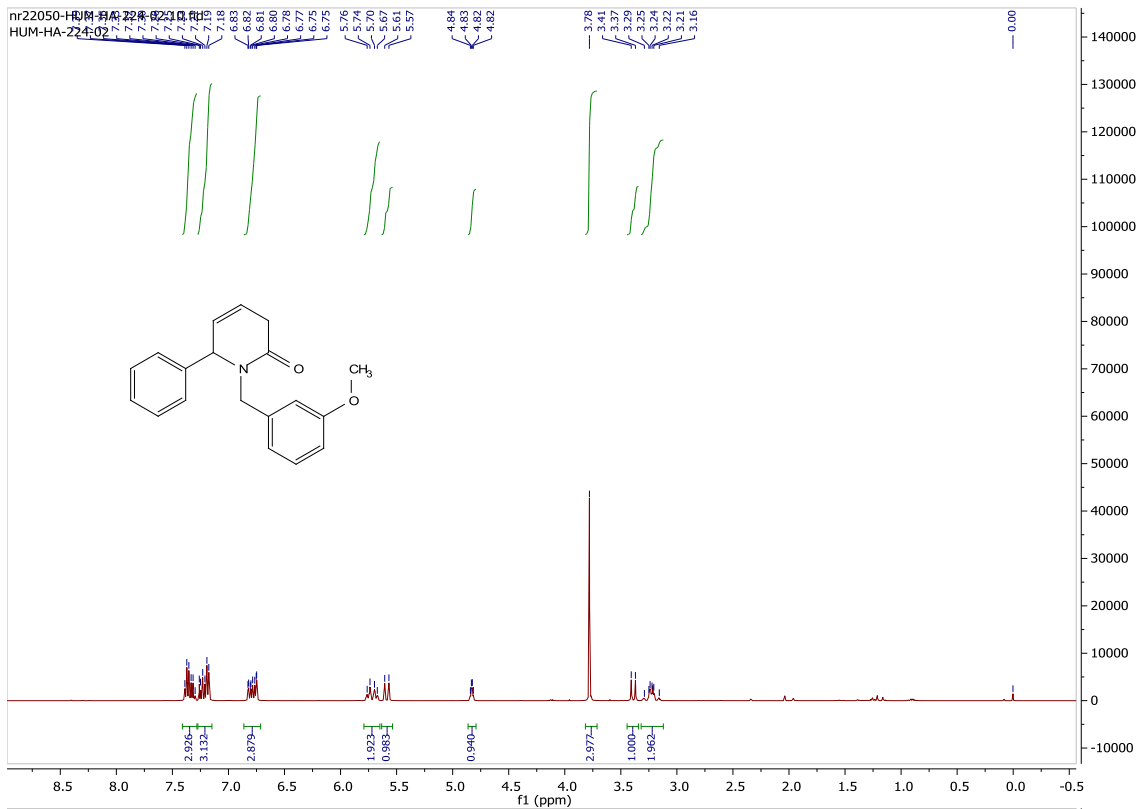


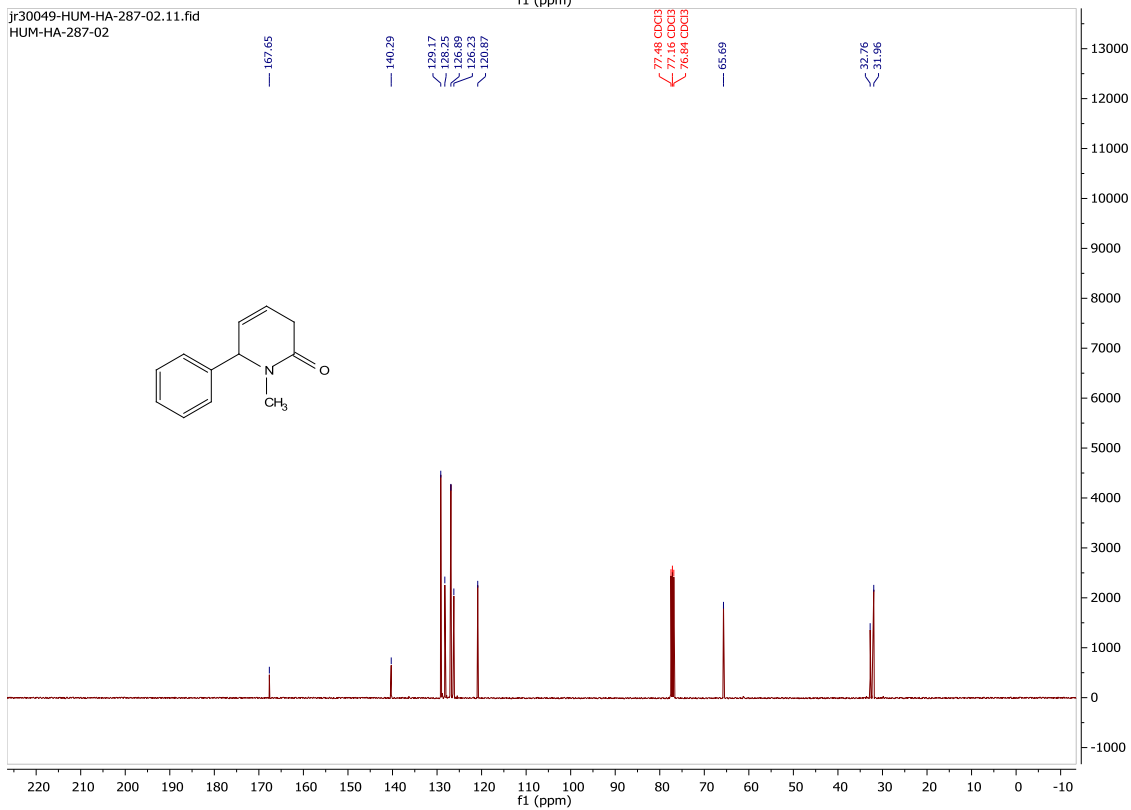
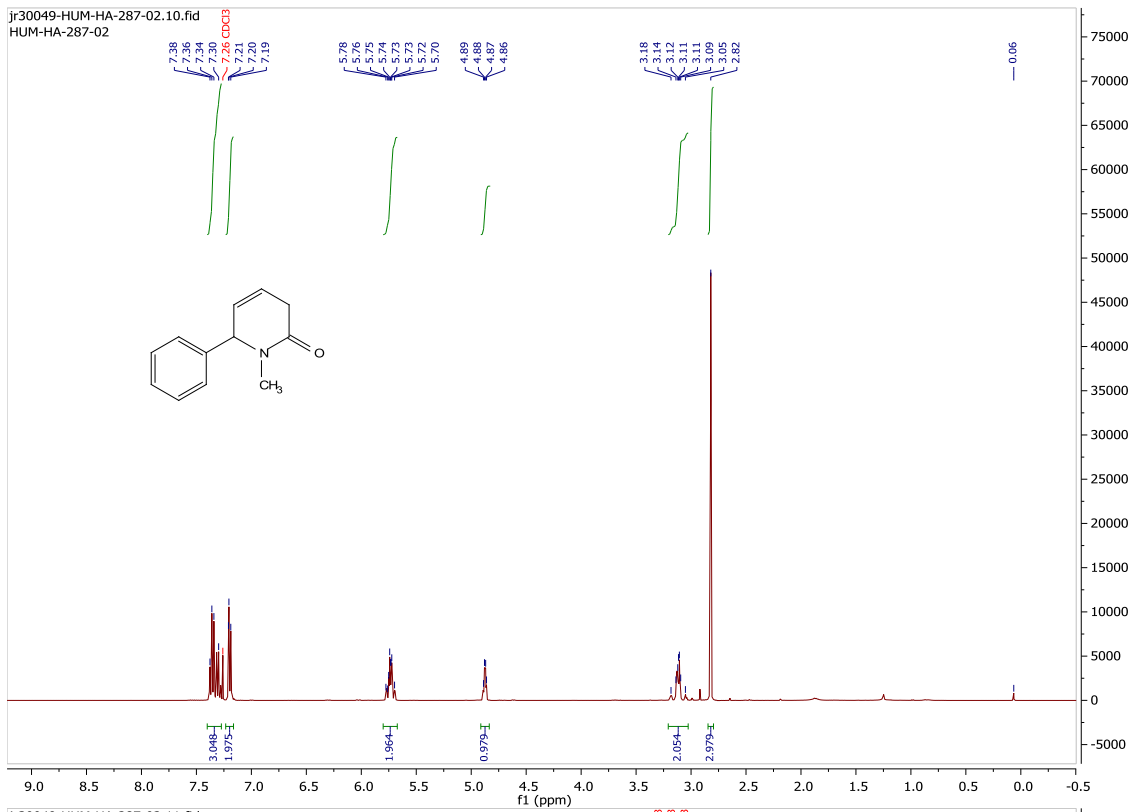


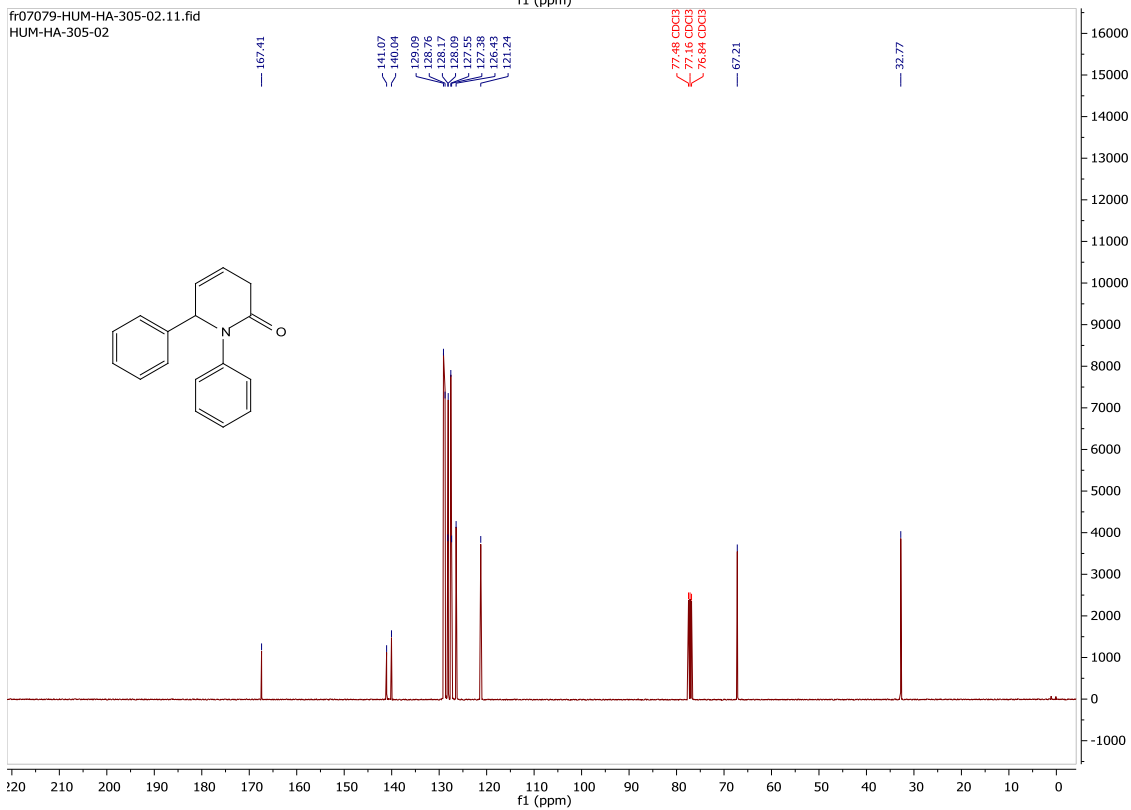
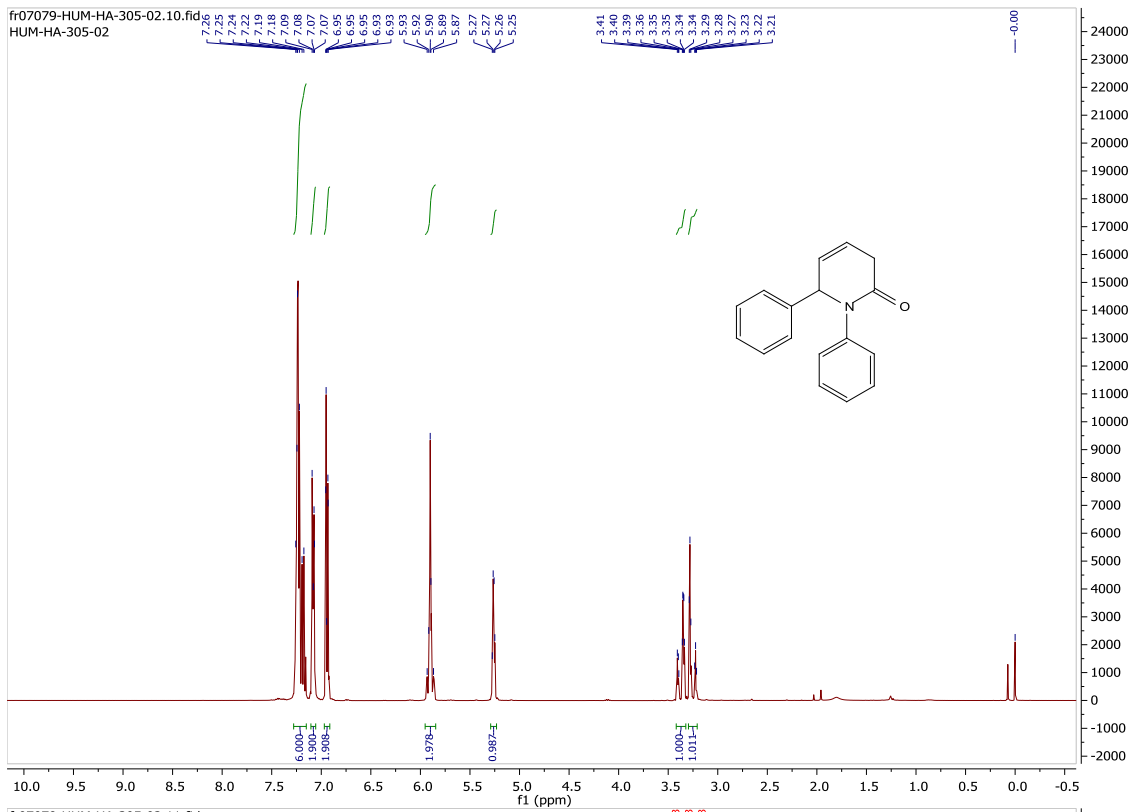


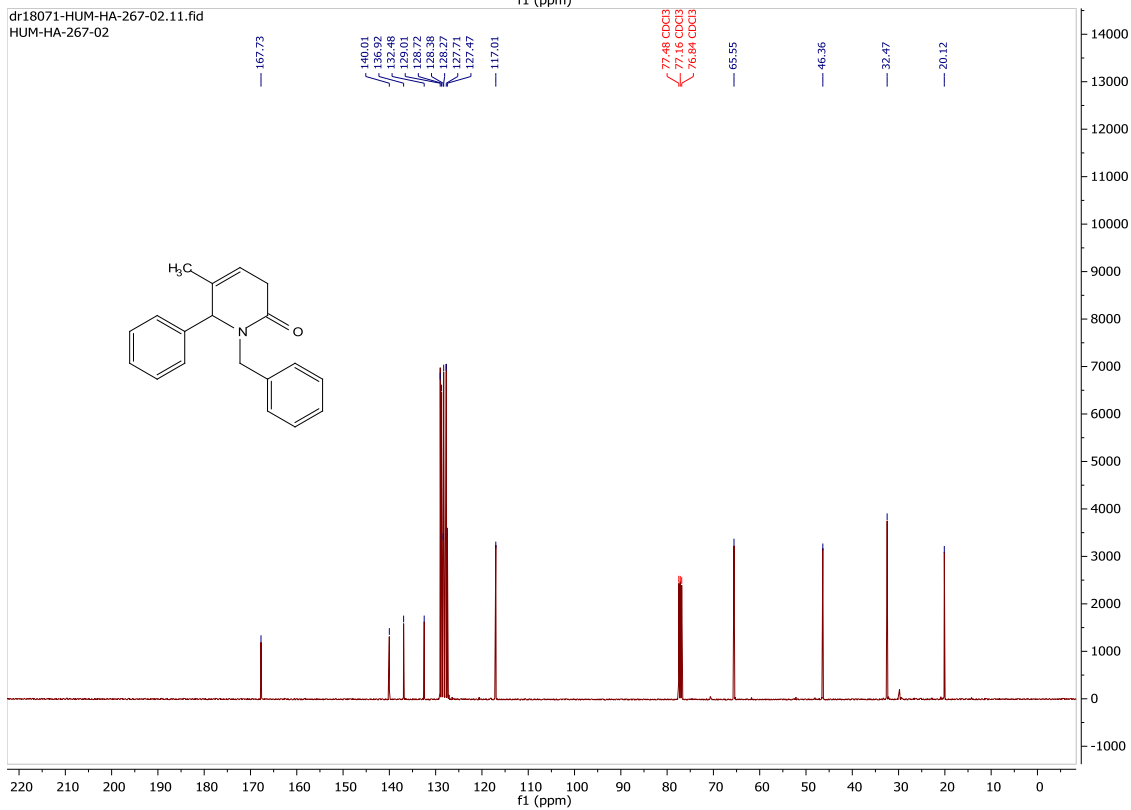
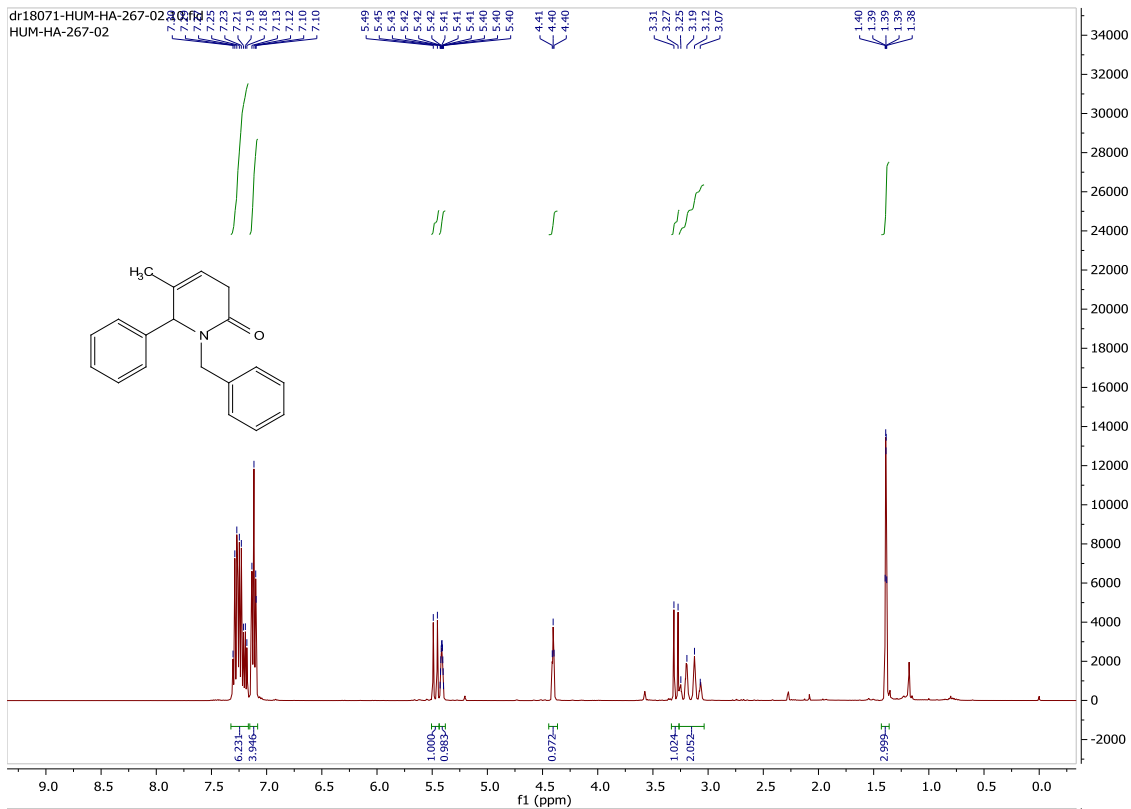
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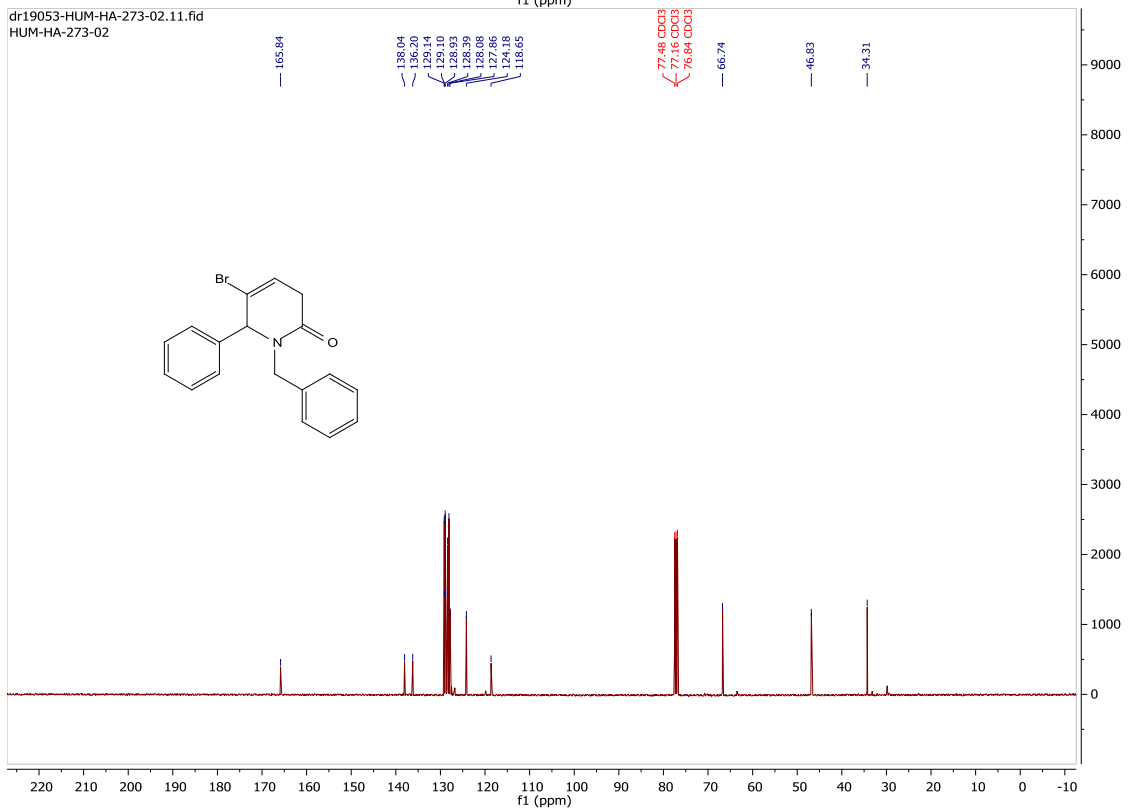
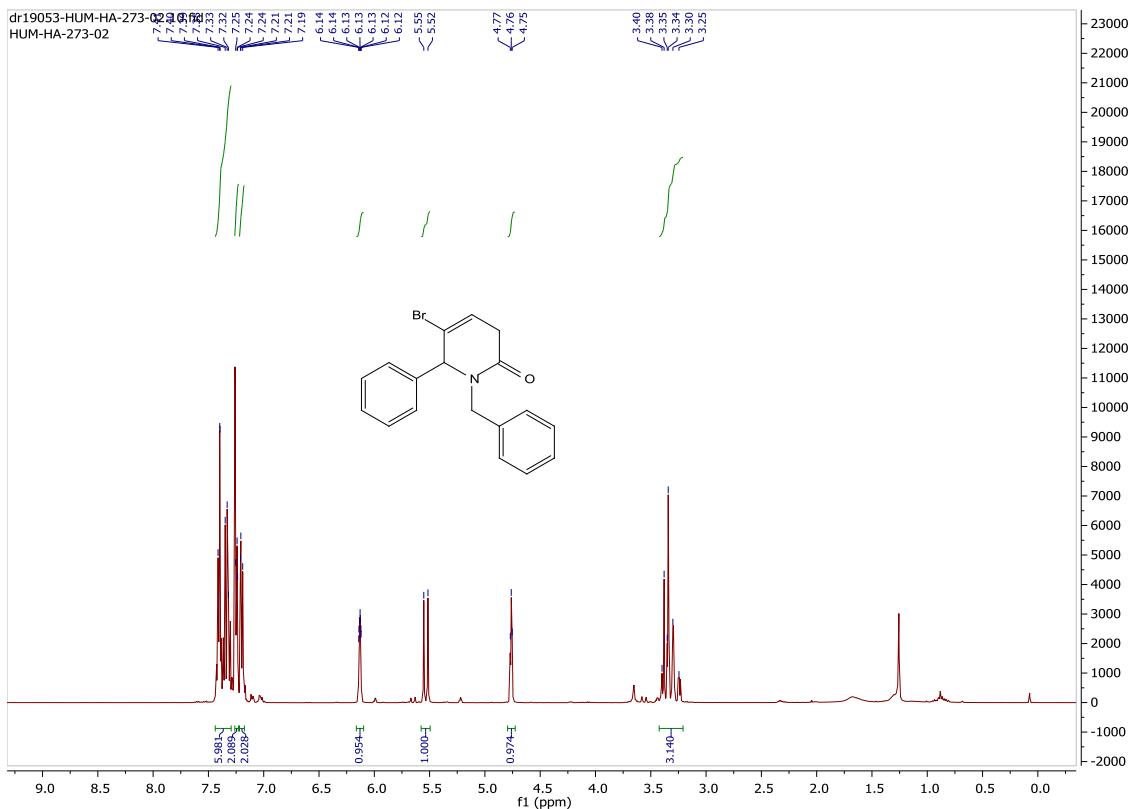


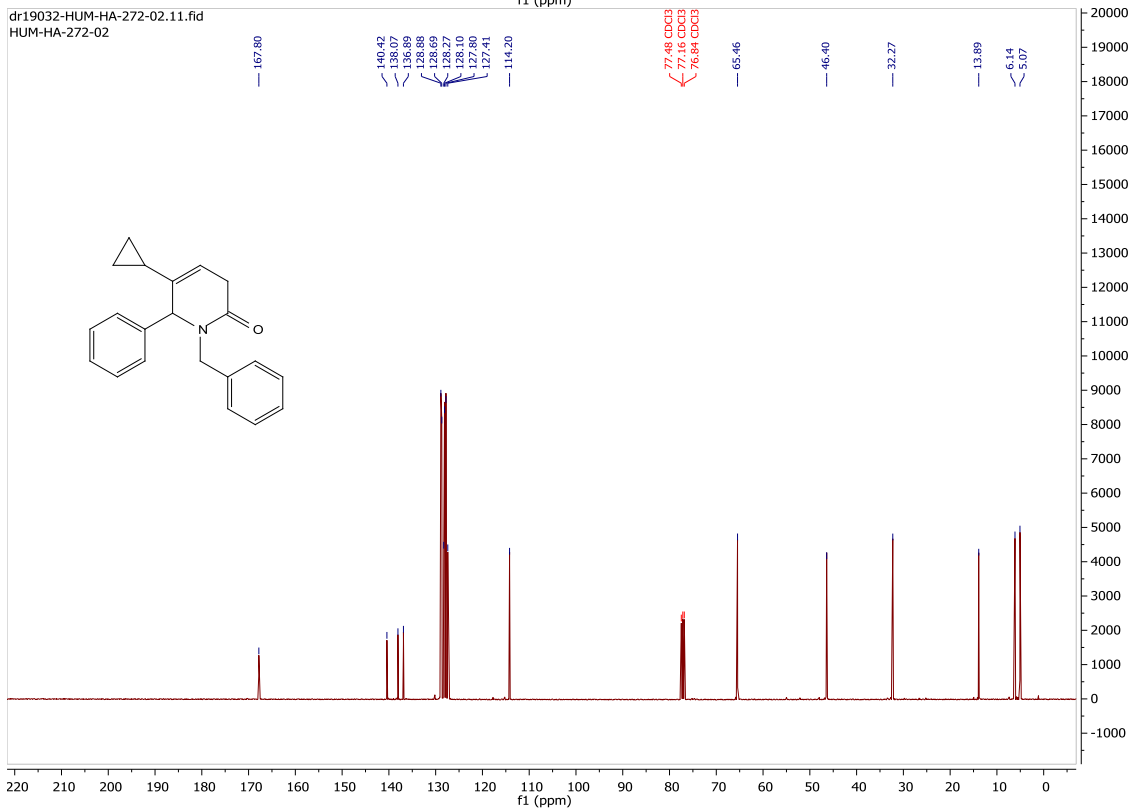
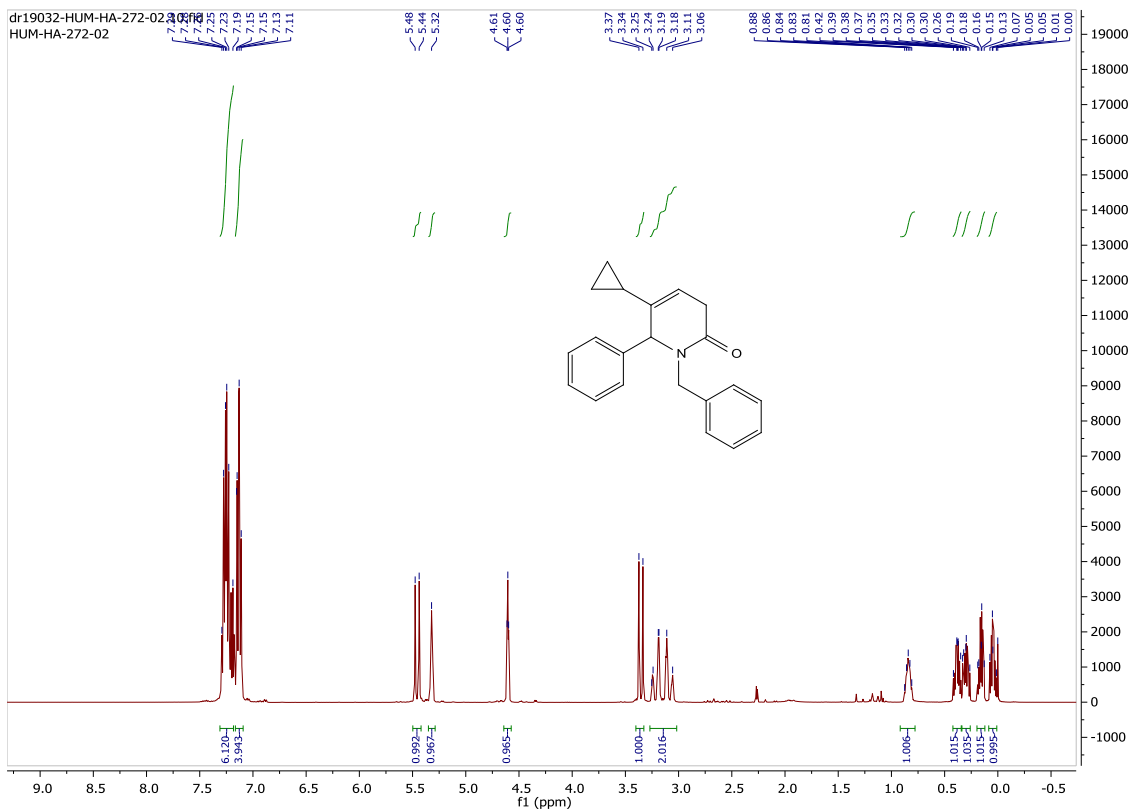


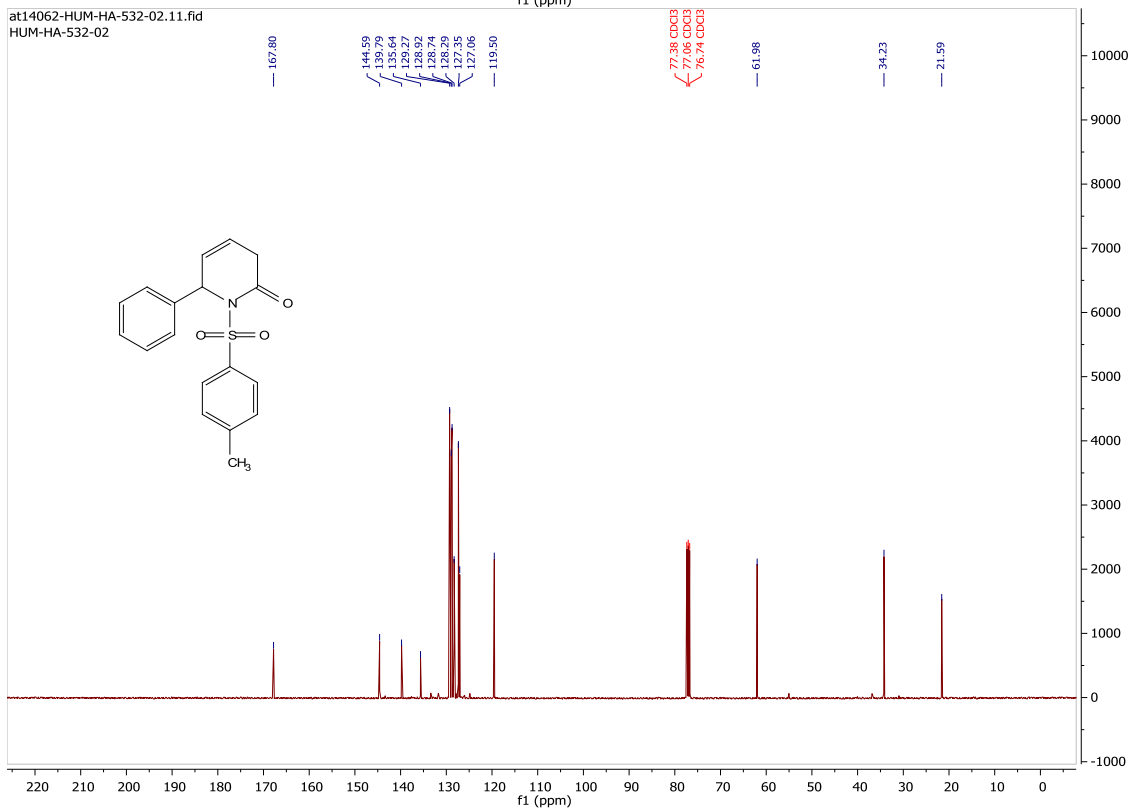
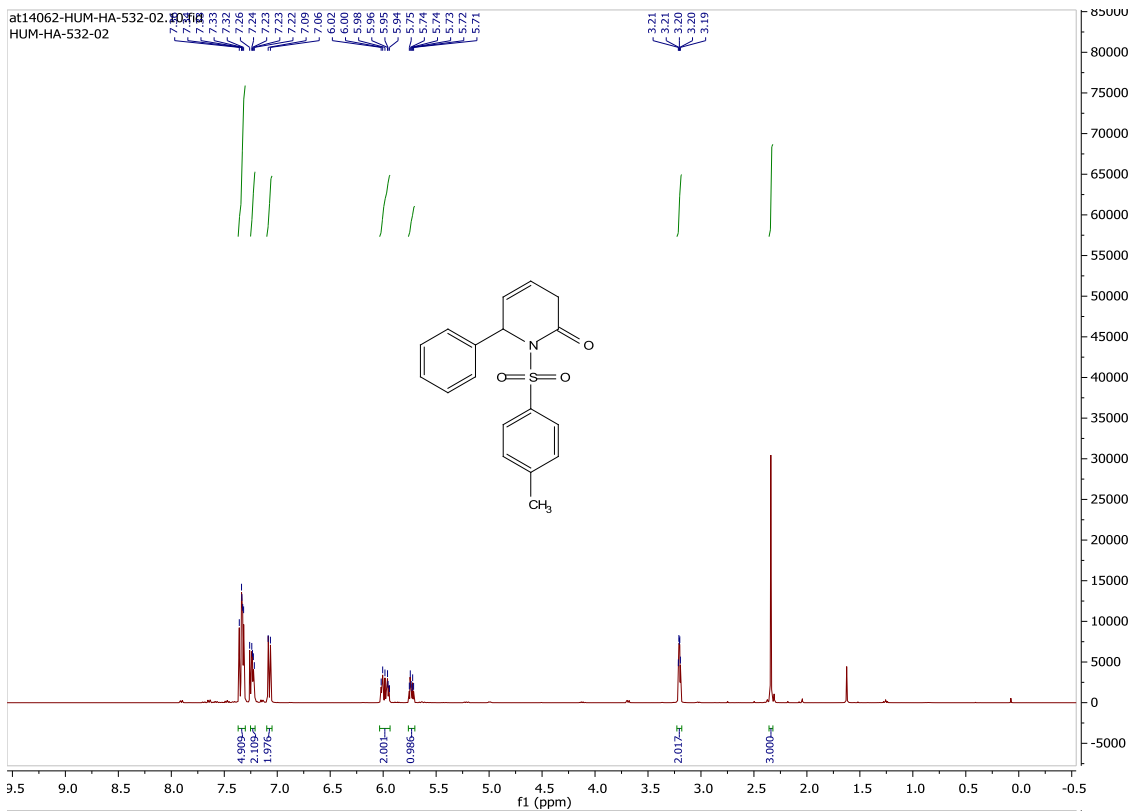


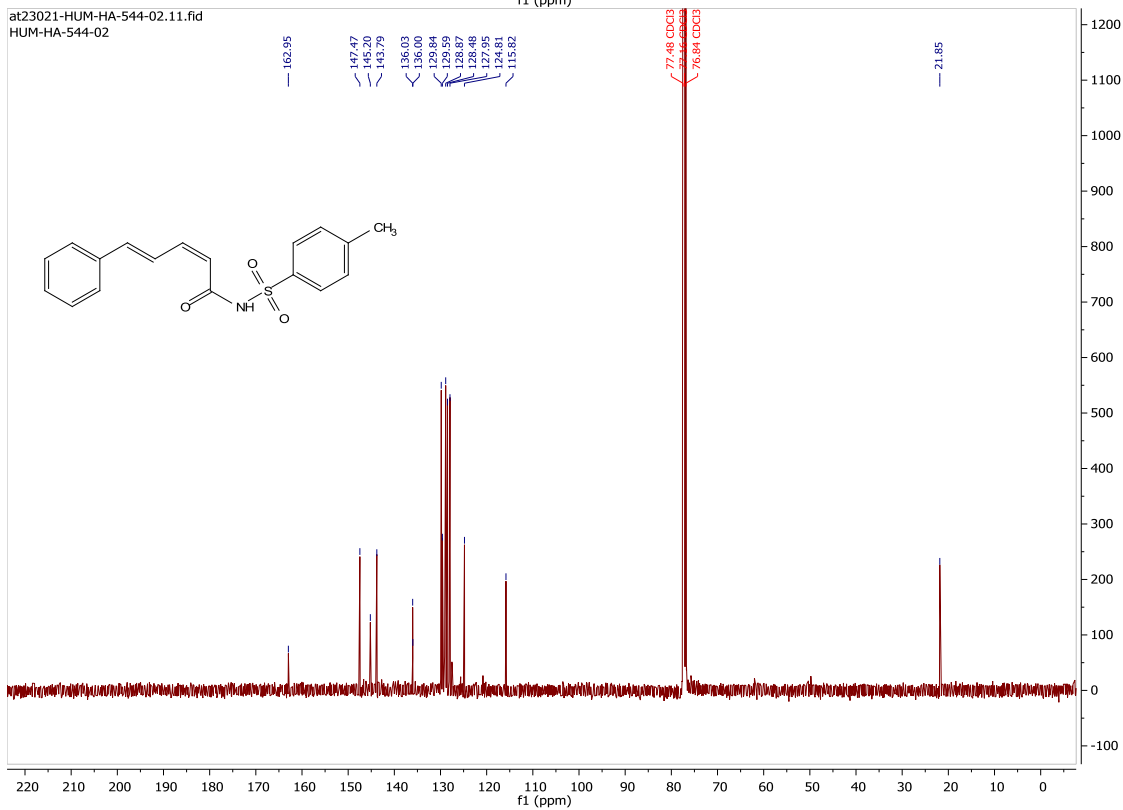
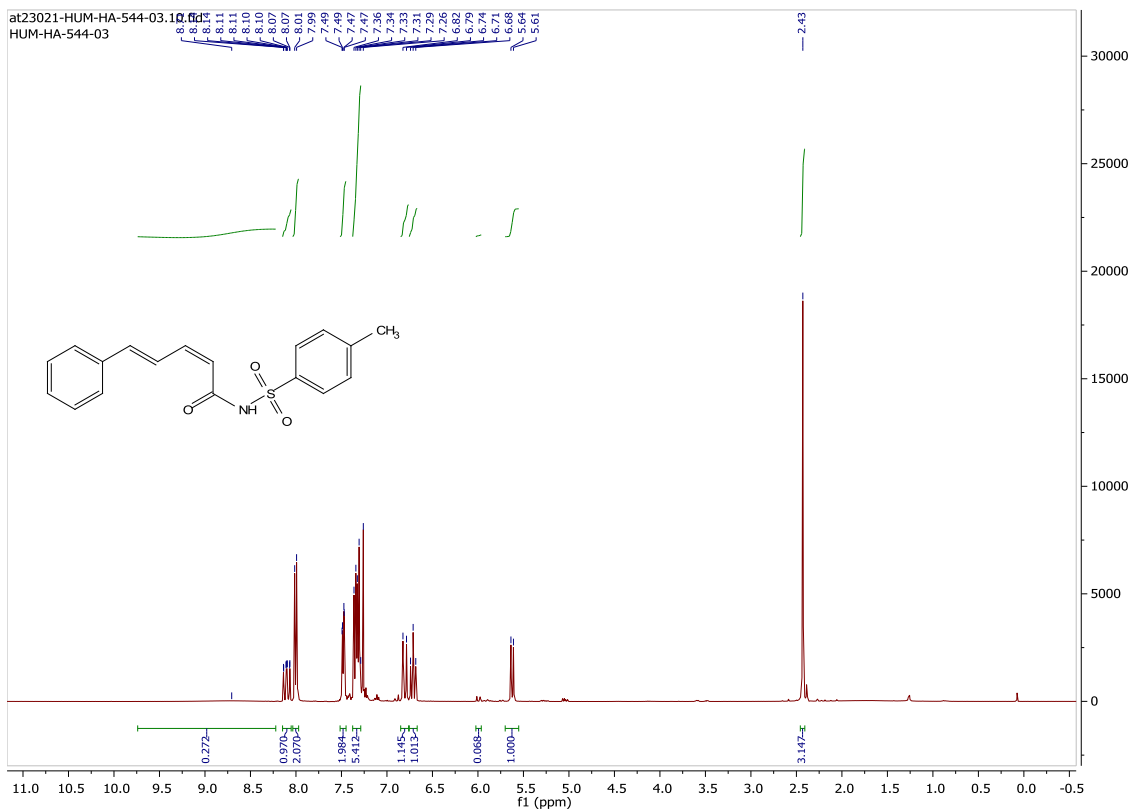


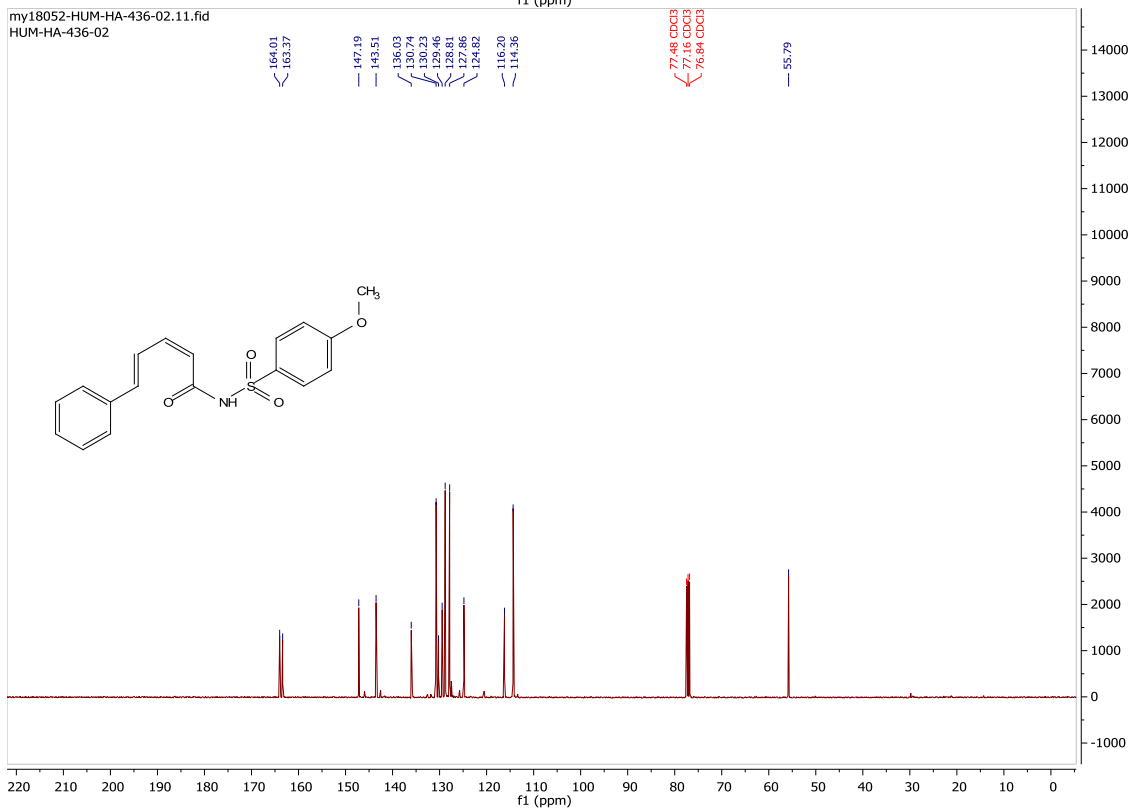
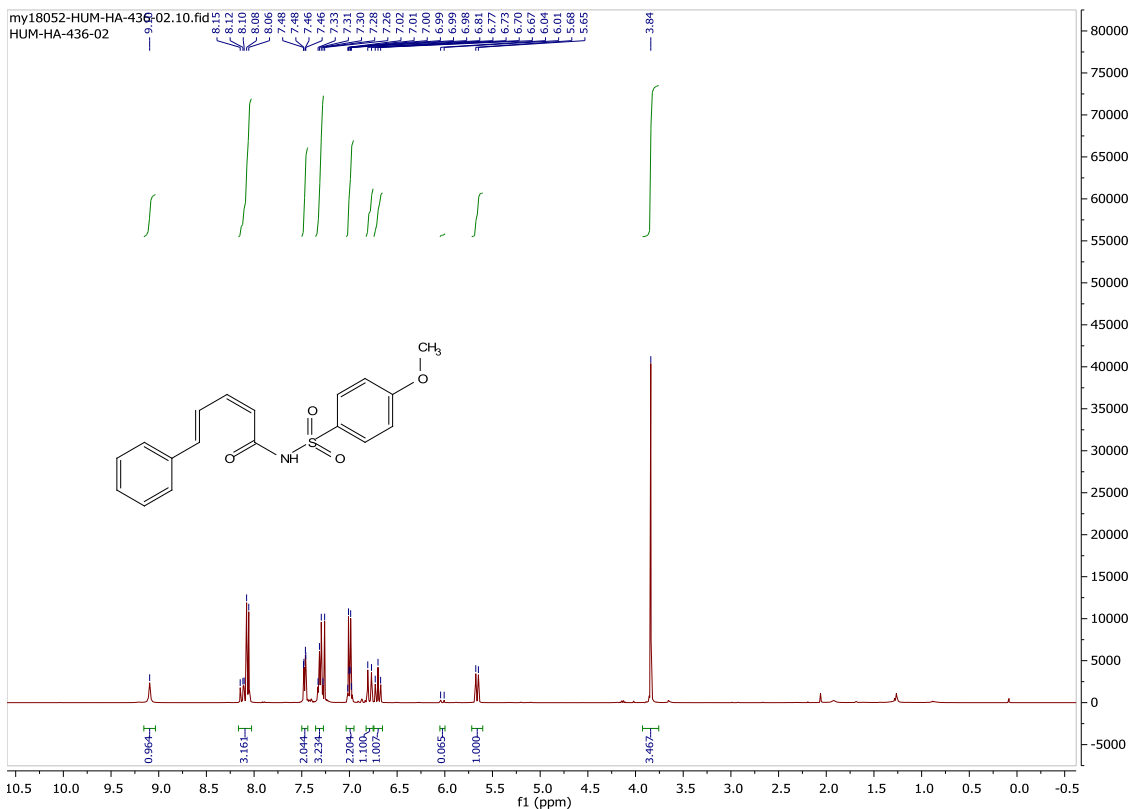


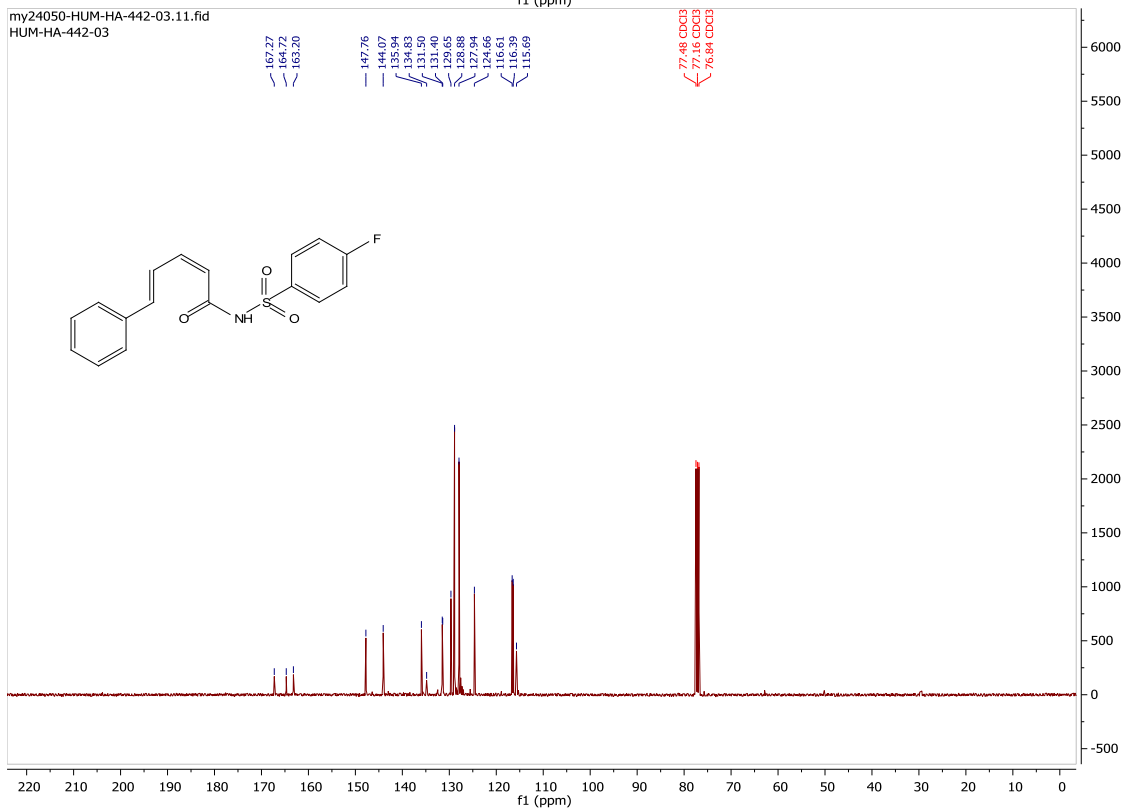
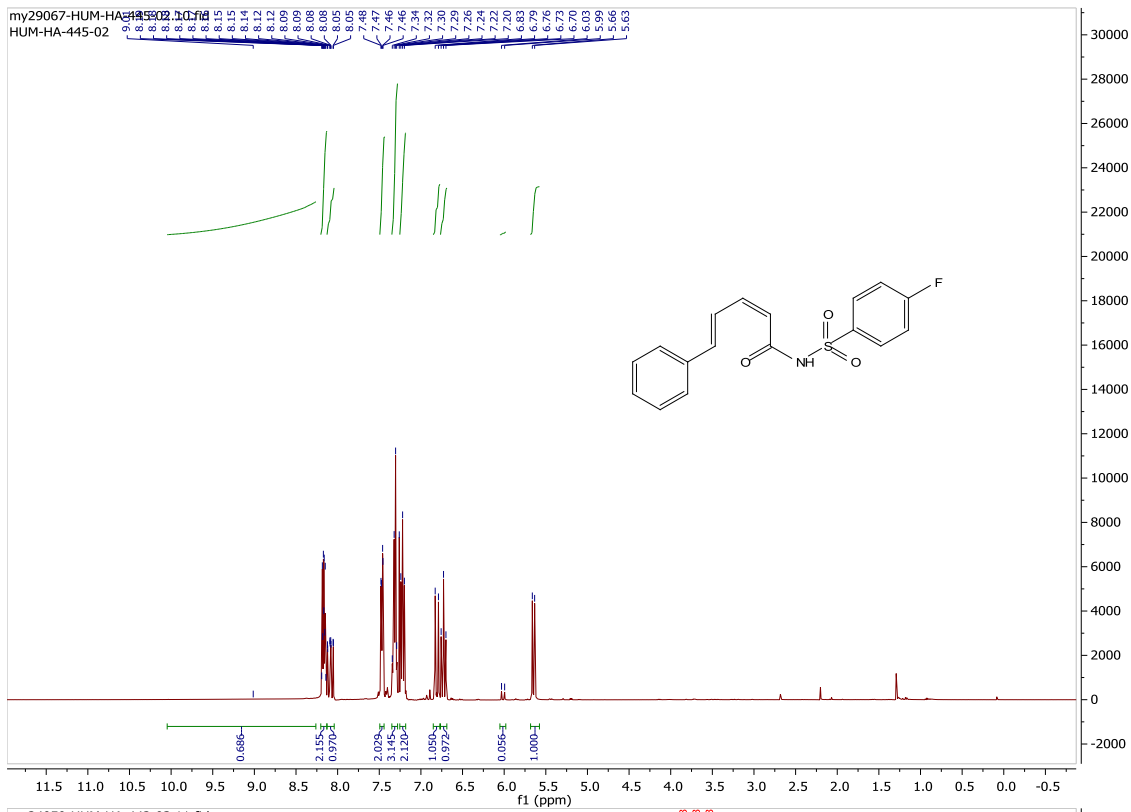




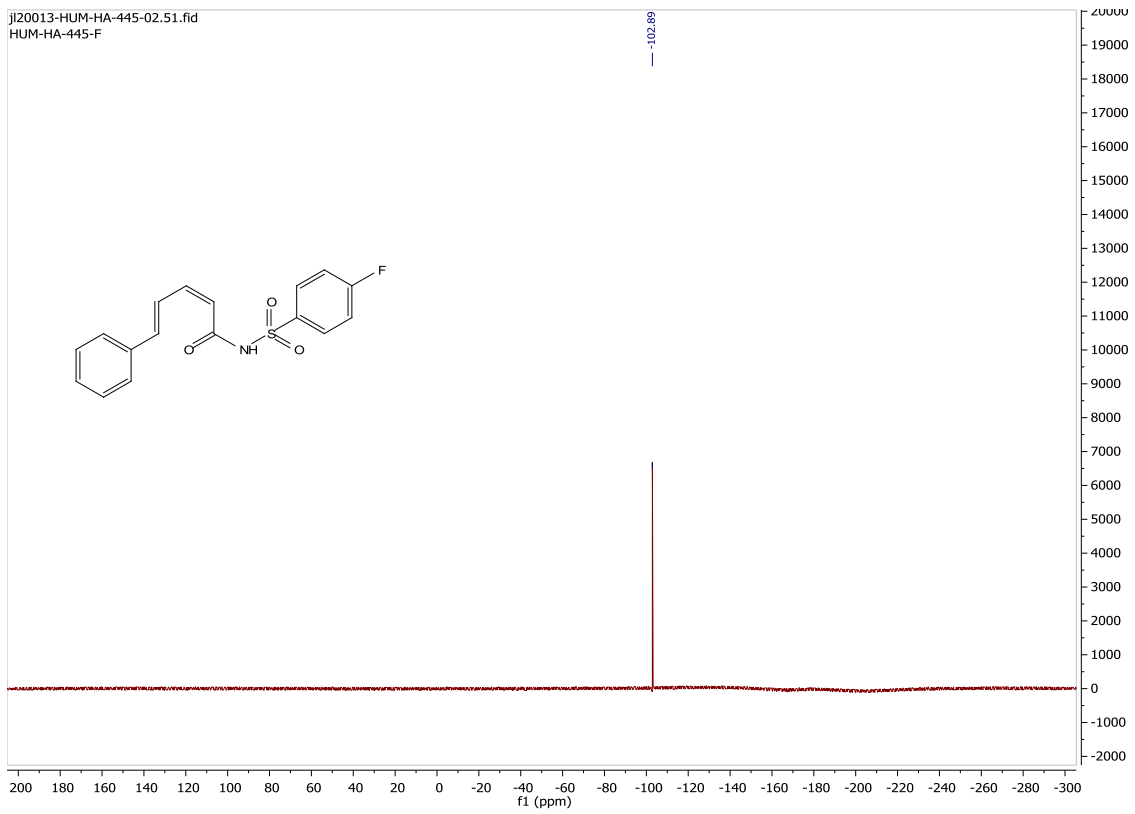


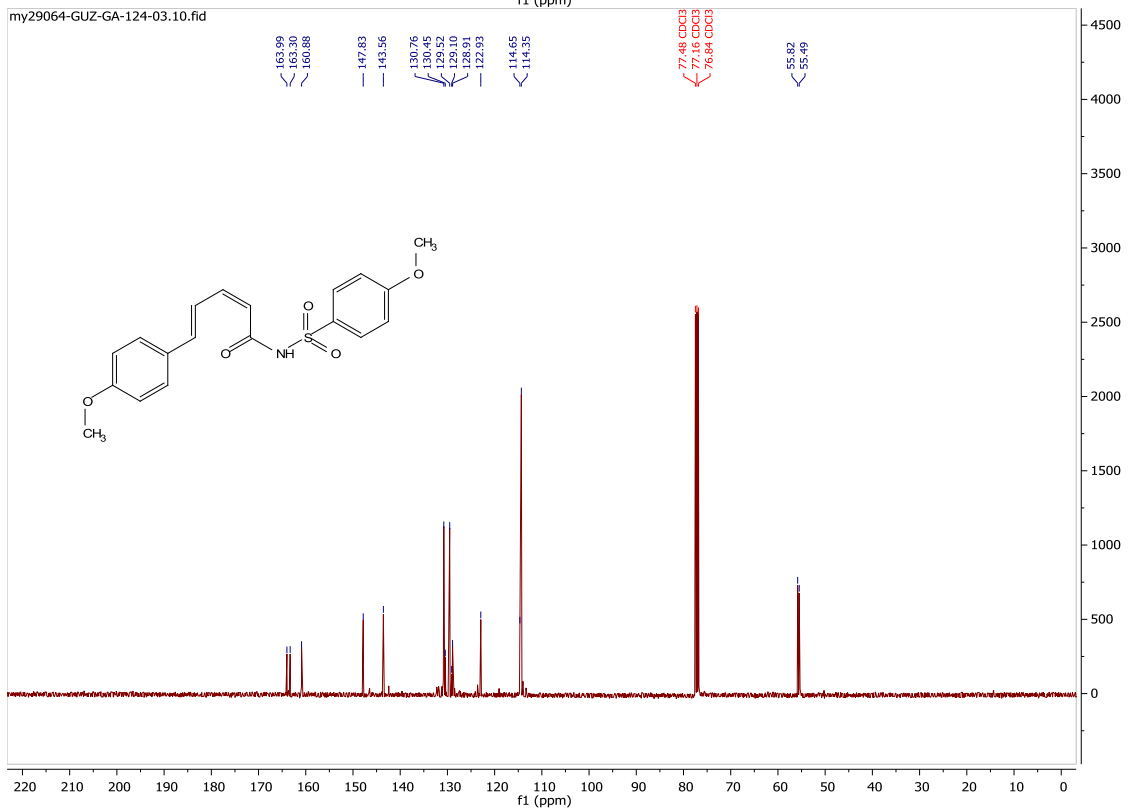
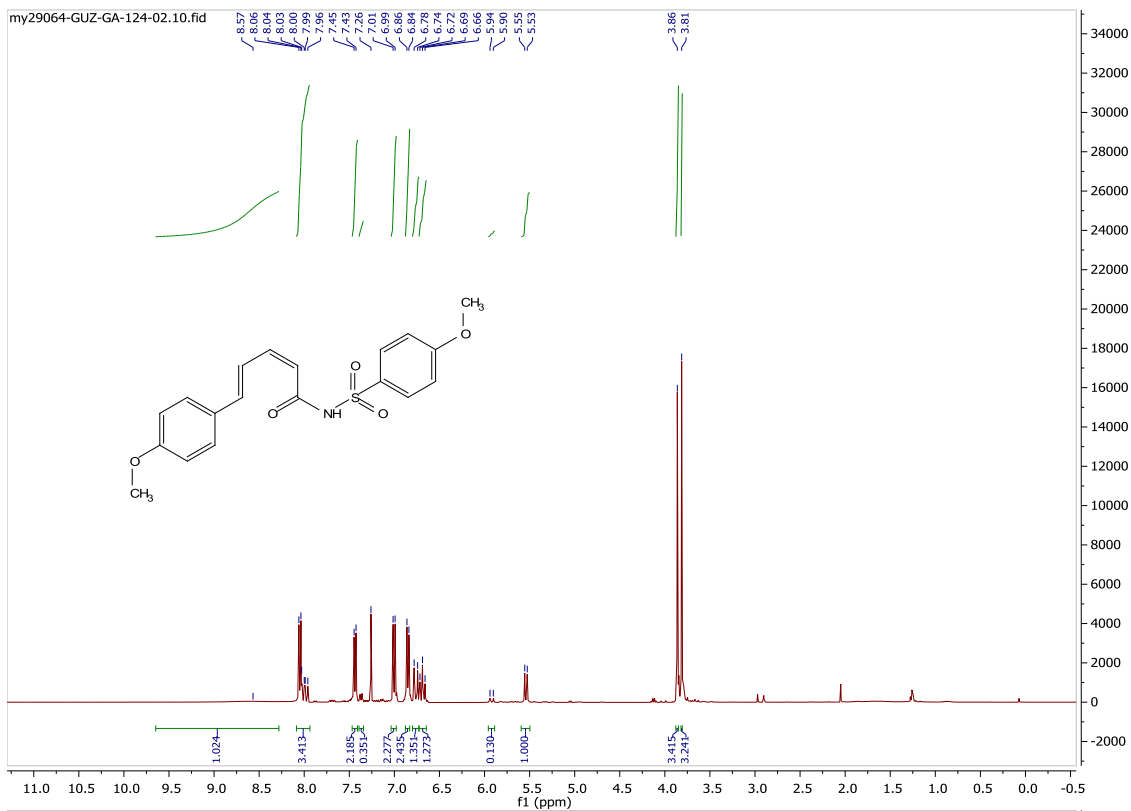


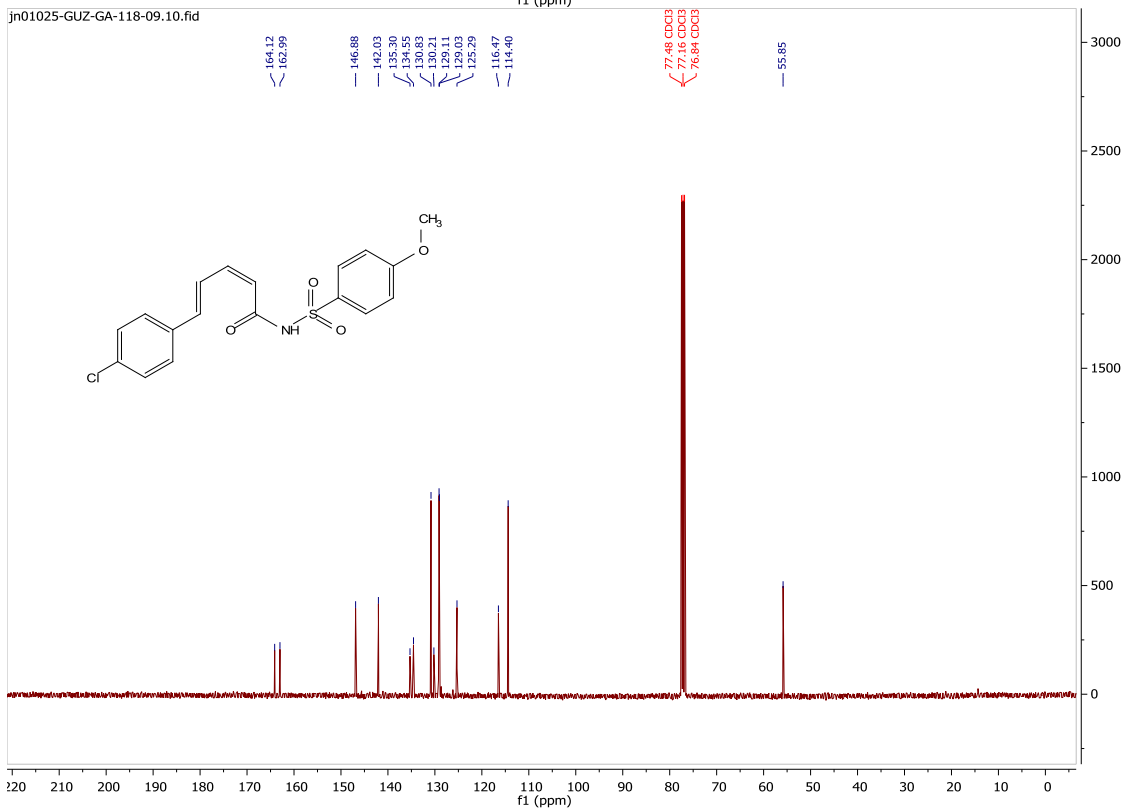
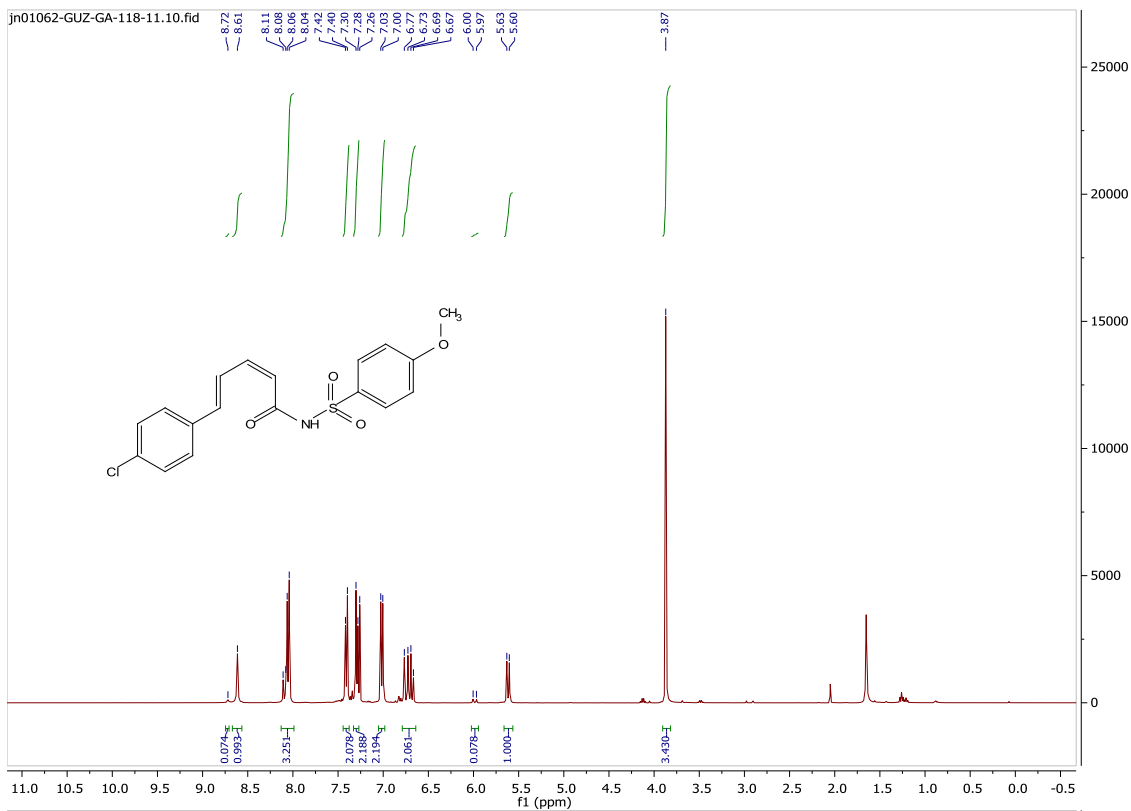


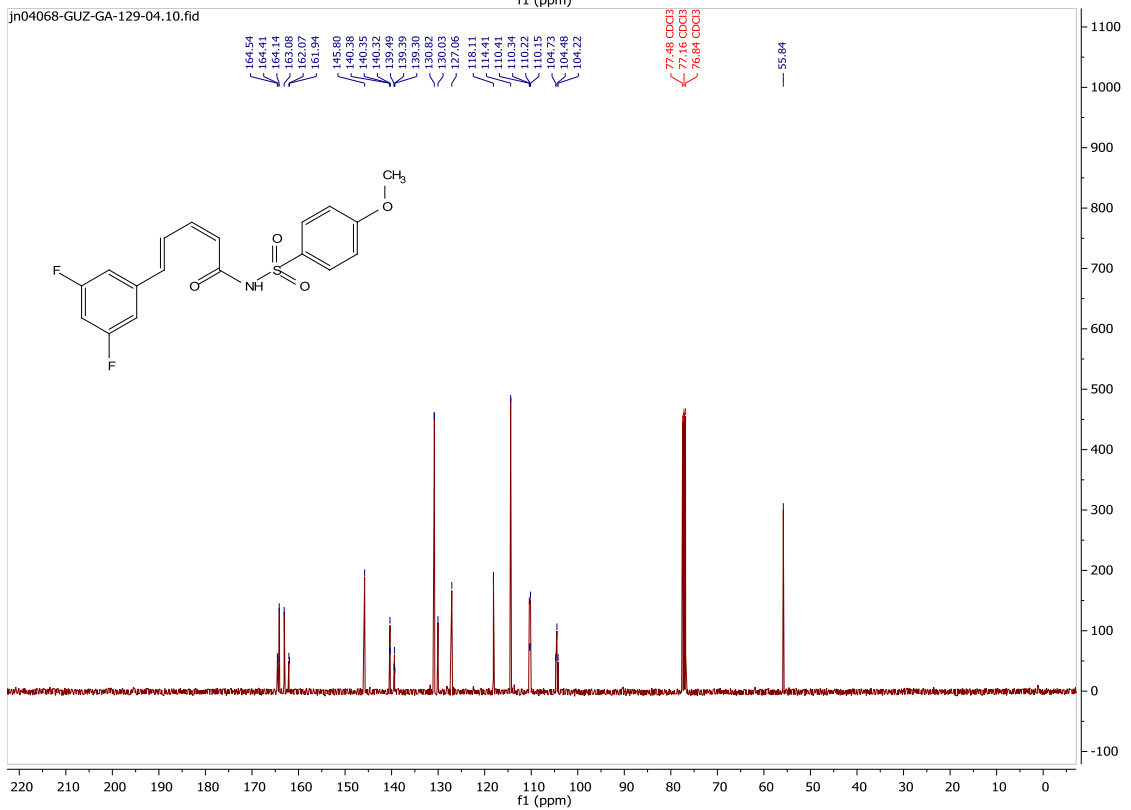
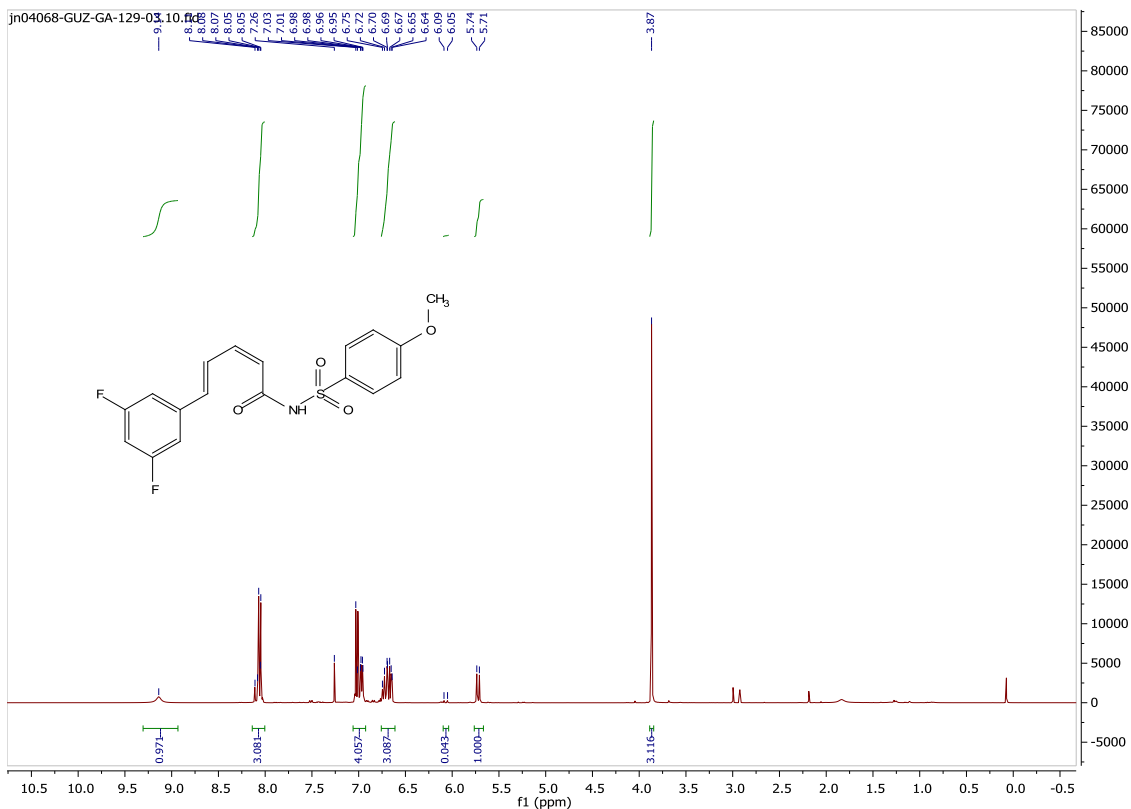


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