# Supplementary Information

## Ru(II)-catalyzed C–H addition and oxidative cyclization of 2-aryl quinazolinones with activated aldehydes

**Jin Ho Choi,[a,†] Kunyoung Kim,[a,†] Harin Oh,[a] Sangil Han,[a] Neeraj Kumar Mishra[a,*] and In Su Kim[a,*]**

[a] *School of Pharmacy, Sungkyunkwan University, Suwon 16419, Republic of Korea*

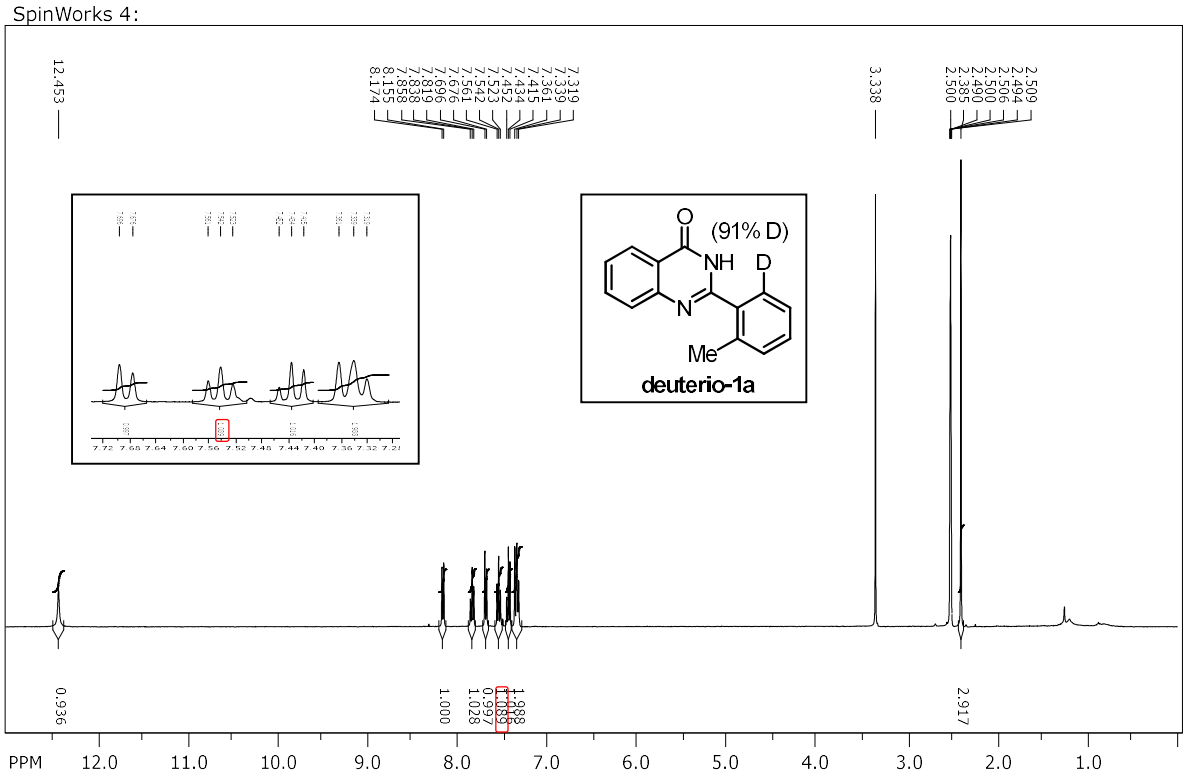
* Corresponding authors. E-mails: neerajchemistry@gmail.com (N.K.Mishra), insukim@skku.edu (I.S.Kim)

**List of the Contents**

**Experimental procedure and characterization data for the synthesis of deuterio-1a**

To an oven-dried sealed tube charged with **1a** (47.3 mg, 0.2 mmol, 100 mol %), [Ru(*p*-cymene)$Cl_2$]$_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), NaOAc (8.2 mg, 0.1 mmol, 50 mol %) and DCE (1 mL) was added $CD_3CO_2D$ (0.11 mL, 2.0 mmol, 10 equiv.) under air at room temperature. The reaction mixture was stirred at 80 °C for 20 h. The reaction mixture was diluted with EtOAc (3 mL) and concentrated in vacuo. The residue was purified by flash column chromatography (*n*-hexanes/EtOAc = 3:1) to afford **deuterio-1a** (37.8 mg, 80%) with 91% deuterium incorporation at *ortho*-position of aryl ring.

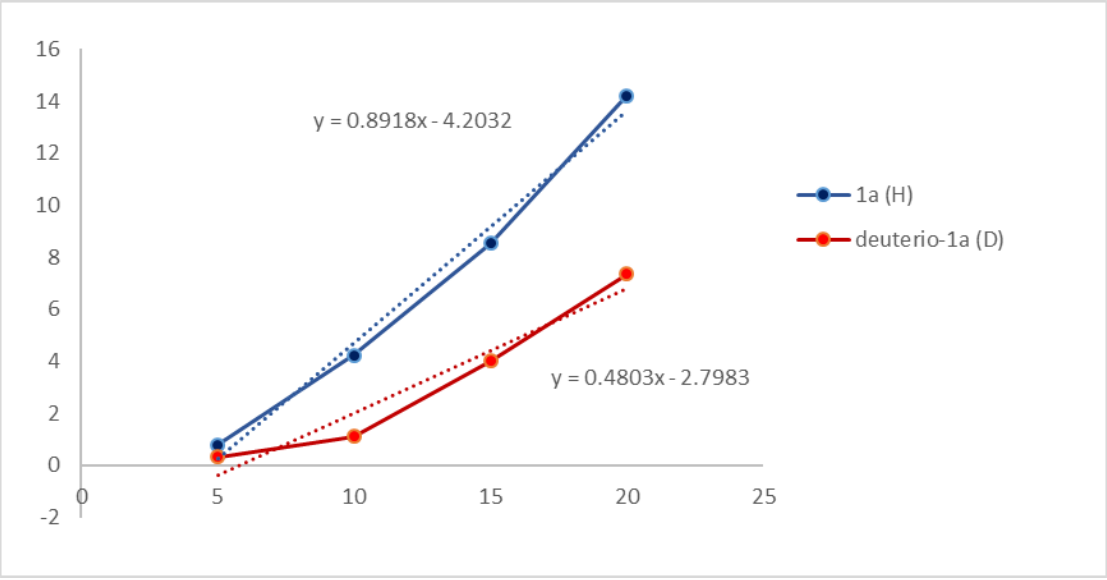
**2-(2-Deuterio-6-methylphenyl)quinazolin-4(3*H*)-one (deuterio-1a):** $^1$H NMR (400 MHz, $CDCl_3$) δ 12.45 (s, 1H), 8.16 (d, *J* = 7.6 Hz, 1H), 7.83 (t, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1.09H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.36–7.31 (m, 2H), 3.38 (s, 3H).



**Experimental procedure of kinetic isotope effect (KIE) experiment**

To an oven-dried sealed tube charged with **1a** (47.3 mg, 0.2 mmol, 100 mol %), [Ru(*p*-cymene)$Cl_2$]$_2$ (3.1 mg, 0.005 mmol, 2.5 mol %), NaOAc (8.2 mg, 0.1 mmol, 50 mol %) and ethyl 2-oxoacetate (~50% in toluene) (**2a**) (81.7 mg, 0.4 mmol, 200 mol %) in DCE (1 mL) was added bromobenzene (78.5 mg, 0.5 mmol, 250 mol %) as an internal standard. In another reaction tube, **deuterio-1a** (47.5 mg, 0.2 mmol, 100 mol %, 91% D) was used instead of **1a**. The two reactions were allowed to stir at 80 °C. An aliquot of each reaction mixture was taken at the time of 5 min, 10 min, 15 min, and 20 min. The corresponding yield of each product **3a** was determined by GC-MS (bromobenzene as an internal standard). A kinetic isotope effect value ($k_H/k_D$) of 1.85 was observed.

| starting material | relative yield (%) of **3a** based on bromobenzene | | | |
|---|---|---|---|---|
| | 5 min | 10 min | 15 min | 20 min |
| **1a** (H) | 0.78618551 | 4.23468618 | 8.54236322 | 14.21351523 |
| **deuterio-1a** (D) | 0.33251588 | 1.10362542 | 4.02012145 | 7.36522214 |



**Crystal structure determination**

The X-ray diffraction data for **4a** were collected on a Bruker APX-II diffractometer equipped with a monochromator in the Mo Kα (λ = 0.71073 A) incident beam. Each crystal was mounted on a glass fibre. The CCDC data were integrated and scaled using the Bruker-SAINT software package, and the structure was solved and refined using SHEXL-2014. All hydrogen atoms were placed in the calculated positions. The crystallographic data of **4a** are listed in Table S1-Table S6. Structural information was deposited at the Cambridge Crystallographic Data Centre. The CCDC reference numbers are 2013547 for **4a**.

**X-ray crystallographic data of compound 4a (CCDC 2013547)**

**Table S1.** Crystal data and structure refinement for **4a**.

| | | |
|---|---|---|
| Identification code | 20200612_0m | |
| Empirical formula | C19 H16 N2 O4 | |
| Formula weight | 336.34 | |
| Temperature | 296(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P n a 21 | |
| Unit cell dimensions | a = 7.67620(10) Å | a= 90°. |
| | b = 12.3159(2) Å | b= 90°. |
| | c = 17.1409(3) Å | g = 90°. |
| Volume | 1620.49(4) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.379 $Mg/m^3$ | |
| Absorption coefficient | 0.098 mm-1 | |
| F(000) | 704 | |
| Crystal size | 0.280 x 0.160 x 0.040 $mm^3$ | |
| Theta range for data collection | 2.036 to 28.326°. | |
| Index ranges | 0<=h<=10, 0<=k<=16, 0<=l<=22 | |
| Reflections collected | 2082 | |
| Independent reflections | 2082 [R(int) = 0.0000] | |
| Completeness to theta = 25.242° | 100.0 % | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2082 / 2 / 226 | |
| Goodness-of-fit on F2 | 1.004 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0549, wR2 = 0.1498 | |
| R indices (all data) | R1 = 0.0694, wR2 = 0.1613 | |
| Absolute structure parameter | 1.4(18) | |
| Extinction coefficient | n/a | |
| Largest diff. peak and hole | 0.330 and -0.213 e.$Å^{-3}$ | |

**Table S2.** Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for **4a**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 2469(4) | 3983(2) | 4714(2) | 66(1) |
| O(2) | 2756(3) | 4108(2) | 2954(1) | 54(1) |
| O(3) | -288(4) | 3073(2) | 3243(2) | 73(1) |
| O(4) | -1312(3) | 4518(2) | 3889(2) | 71(1) |
| N(1) | 1895(3) | 5403(2) | 3925(1) | 43(1) |
| N(2) | 2038(4) | 7257(2) | 4296(2) | 49(1) |
| C(1) | 2418(4) | 4974(3) | 4628(2) | 49(1) |
| C(2) | 1378(4) | 4724(2) | 3246(2) | 44(1) |
| C(3) | 830(4) | 5600(3) | 2676(2) | 46(1) |
| C(4) | 226(5) | 5451(3) | 1921(2) | 56(1) |
| C(5) | -231(5) | 6385(3) | 1502(2) | 65(1) |
| C(6) | -49(5) | 7406(3) | 1836(2) | 60(1) |
| C(7) | 586(4) | 7571(3) | 2583(2) | 51(1) |
| C(8) | 1013(4) | 6626(2) | 2999(2) | 44(1) |
| C(9) | 1697(4) | 6513(2) | 3795(2) | 44(1) |
| C(10) | 2666(4) | 6897(3) | 5018(2) | 51(1) |
| C(11) | 3071(6) | 7676(3) | 5585(2) | 69(1) |
| C(12) | 3675(6) | 7357(4) | 6312(3) | 79(1) |
| C(13) | 3908(6) | 6261(4) | 6480(2) | 73(1) |
| C(14) | 3507(5) | 5491(3) | 5939(2) | 64(1) |
| C(15) | 2877(4) | 5797(3) | 5202(2) | 50(1) |
| C(16) | -164(5) | 3990(2) | 3466(2) | 50(1) |
| C(17) | -2920(7) | 3955(5) | 4101(3) | 96(2) |
| C(18) | -3003(11) | 3798(8) | 4940(4) | 136(3) |
| C(19) | 827(6) | 8680(3) | 2909(3) | 64(1) |

**Table S3.** Bond lengths [Å] and angles [°] for **4a**.

| | |
|---|---|
| O(1)-C(1) | 1.230(4) |
| O(2)-C(2) | 1.395(4) |
| O(2)-H(2A) | 0.8200 |
| O(3)-C(16) | 1.196(4) |
| O(4)-C(16) | 1.314(4) |
| O(4)-C(17) | 1.462(5) |
| N(1)-C(1) | 1.376(4) |
| N(1)-C(9) | 1.393(4) |
| N(1)-C(2) | 1.487(4) |
| N(2)-C(9) | 1.282(4) |
| N(2)-C(10) | 1.400(5) |
| C(1)-C(15) | 1.456(5) |
| C(2)-C(3) | 1.515(4) |
| C(2)-C(16) | 1.537(4) |
| C(3)-C(8) | 1.386(5) |
| C(3)-C(4) | 1.387(4) |
| C(4)-C(5) | 1.400(5) |
| C(4)-H(4A) | 0.9300 |
| C(5)-C(6) | 1.388(6) |
| C(5)-H(5A) | 0.9300 |
| C(6)-C(7) | 1.385(5) |
| C(6)-H(6A) | 0.9300 |
| C(7)-C(8) | 1.404(4) |
| C(7)-C(19) | 1.487(5) |
| C(8)-C(9) | 1.470(5) |
| C(10)-C(15) | 1.400(5) |
| C(10)-C(11) | 1.400(5) |
| C(11)-C(12) | 1.388(6) |
| C(11)-H(11A) | 0.9300 |
| C(12)-C(13) | 1.392(6) |
| C(12)-H(12A) | 0.9300 |
| C(13)-C(14) | 1.362(6) |
| C(13)-H(13A) | 0.9300 |
| C(14)-C(15) | 1.405(5) |

| | |
|---|---|
| C(14)-H(14A) | 0.9300 |
| C(17)-C(18) | 1.451(7) |
| C(17)-H(17A) | 0.9700 |
| C(17)-H(17B) | 0.9700 |
| C(18)-H(18A) | 0.9600 |
| C(18)-H(18B) | 0.9600 |
| C(18)-H(18C) | 0.9600 |
| C(19)-H(19A) | 0.9600 |
| C(19)-H(19B) | 0.9600 |
| C(19)-H(19C) | 0.9600 |

| | |
|---|---|
| C(2)-O(2)-H(2A) | 109.5 |
| C(16)-O(4)-C(17) | 117.9(3) |
| C(1)-N(1)-C(9) | 123.3(3) |
| C(1)-N(1)-C(2) | 123.2(2) |
| C(9)-N(1)-C(2) | 113.5(2) |
| C(9)-N(2)-C(10) | 115.8(3) |
| O(1)-C(1)-N(1) | 119.7(3) |
| O(1)-C(1)-C(15) | 127.0(3) |
| N(1)-C(1)-C(15) | 113.3(3) |
| O(2)-C(2)-N(1) | 112.6(2) |
| O(2)-C(2)-C(3) | 111.5(2) |
| N(1)-C(2)-C(3) | 100.3(2) |
| O(2)-C(2)-C(16) | 110.6(2) |
| N(1)-C(2)-C(16) | 110.1(2) |
| C(3)-C(2)-C(16) | 111.3(2) |
| C(8)-C(3)-C(4) | 121.8(3) |
| C(8)-C(3)-C(2) | 111.3(3) |
| C(4)-C(3)-C(2) | 126.9(3) |
| C(3)-C(4)-C(5) | 116.9(3) |
| C(3)-C(4)-H(4A) | 121.5 |
| C(5)-C(4)-H(4A) | 121.5 |
| C(6)-C(5)-C(4) | 120.5(3) |
| C(6)-C(5)-H(5A) | 119.7 |
| C(4)-C(5)-H(5A) | 119.7 |
| C(7)-C(6)-C(5) | 123.3(3) |

| | |
|---|---|
| C(7)-C(6)-H(6A) | 118.3 |
| C(5)-C(6)-H(6A) | 118.3 |
| C(6)-C(7)-C(8) | 115.5(3) |
| C(6)-C(7)-C(19) | 121.8(3) |
| C(8)-C(7)-C(19) | 122.8(3) |
| C(3)-C(8)-C(7) | 121.9(3) |
| C(3)-C(8)-C(9) | 108.7(2) |
| C(7)-C(8)-C(9) | 129.3(3) |
| N(2)-C(9)-N(1) | 124.9(3) |
| N(2)-C(9)-C(8) | 128.8(3) |
| N(1)-C(9)-C(8) | 106.2(2) |
| C(15)-C(10)-N(2) | 123.1(3) |
| C(15)-C(10)-C(11) | 118.8(3) |
| N(2)-C(10)-C(11) | 118.2(3) |
| C(12)-C(11)-C(10) | 120.2(4) |
| C(12)-C(11)-H(11A) | 119.9 |
| C(10)-C(11)-H(11A) | 119.9 |
| C(11)-C(12)-C(13) | 120.2(3) |
| C(11)-C(12)-H(12A) | 119.9 |
| C(13)-C(12)-H(12A) | 119.9 |
| C(14)-C(13)-C(12) | 120.3(4) |
| C(14)-C(13)-H(13A) | 119.8 |
| C(12)-C(13)-H(13A) | 119.8 |
| C(13)-C(14)-C(15) | 120.3(4) |
| C(13)-C(14)-H(14A) | 119.9 |
| C(15)-C(14)-H(14A) | 119.9 |
| C(10)-C(15)-C(14) | 120.1(3) |
| C(10)-C(15)-C(1) | 119.6(3) |
| C(14)-C(15)-C(1) | 120.3(3) |
| O(3)-C(16)-O(4) | 126.2(3) |
| O(3)-C(16)-C(2) | 122.6(3) |
| O(4)-C(16)-C(2) | 111.1(3) |
| C(18)-C(17)-O(4) | 110.3(5) |
| C(18)-C(17)-H(17A) | 109.6 |
| O(4)-C(17)-H(17A) | 109.6 |
| C(18)-C(17)-H(17B) | 109.6 |

| | |
|---|---|
| O(4)-C(17)-H(17B) | 109.6 |
| H(17A)-C(17)-H(17B) | 108.1 |
| C(17)-C(18)-H(18A) | 109.5 |
| C(17)-C(18)-H(18B) | 109.5 |
| H(18A)-C(18)-H(18B) | 109.5 |
| C(17)-C(18)-H(18C) | 109.5 |
| H(18A)-C(18)-H(18C) | 109.5 |
| H(18B)-C(18)-H(18C) | 109.5 |
| C(7)-C(19)-H(19A) | 109.5 |
| C(7)-C(19)-H(19B) | 109.5 |
| H(19A)-C(19)-H(19B) | 109.5 |
| C(7)-C(19)-H(19C) | 109.5 |
| H(19A)-C(19)-H(19C) | 109.5 |
| H(19B)-C(19)-H(19C) | 109.5 |

Symmetry transformations used to generate equivalent atoms:

**Table S4.** Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2\ a^{*2}U^{11} + .....+ 2\ h\ k\ a^*\ b^*\ U^{12}]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| O(1) | 96(2) | 47(1) | 56(1) | 6(1) | -14(1) | -5(1) |
| O(2) | 57(1) | 50(1) | 55(1) | -4(1) | 5(1) | 2(1) |
| O(3) | 86(2) | 50(1) | 82(2) | -6(1) | -1(2) | -20(1) |
| O(4) | 65(2) | 66(2) | 82(2) | -11(1) | 20(1) | -20(1) |
| N(1) | 50(1) | 38(1) | 41(1) | 0(1) | 0(1) | -5(1) |
| N(2) | 58(1) | 39(1) | 51(1) | -2(1) | -1(1) | 0(1) |
| C(1) | 59(2) | 45(2) | 42(2) | 7(1) | 0(1) | -2(1) |
| C(2) | 51(2) | 42(1) | 40(1) | 1(1) | -1(1) | -1(1) |
| C(3) | 45(1) | 49(2) | 43(1) | 3(1) | 1(1) | -4(1) |
| C(4) | 63(2) | 59(2) | 48(2) | -2(2) | -3(2) | -5(2) |
| C(5) | 67(2) | 80(2) | 47(2) | 10(2) | -7(2) | -3(2) |
| C(6) | 56(2) | 64(2) | 61(2) | 23(2) | -5(2) | -3(2) |
| C(7) | 42(1) | 49(2) | 62(2) | 14(1) | 7(1) | 0(1) |
| C(8) | 42(1) | 45(1) | 47(2) | 5(1) | 4(1) | -3(1) |
| C(9) | 41(1) | 40(1) | 49(2) | 3(1) | 7(1) | -2(1) |
| C(10) | 55(2) | 48(2) | 50(2) | -6(1) | 1(1) | -4(1) |
| C(11) | 84(3) | 60(2) | 62(2) | -14(2) | -5(2) | -8(2) |
| C(12) | 102(3) | 77(3) | 57(2) | -18(2) | -10(2) | -20(2) |
| C(13) | 90(3) | 78(3) | 51(2) | 1(2) | -13(2) | -13(2) |
| C(14) | 77(2) | 66(2) | 50(2) | 4(2) | -6(2) | -13(2) |
| C(15) | 55(2) | 50(2) | 45(2) | -1(1) | 0(1) | -7(1) |
| C(16) | 58(2) | 49(2) | 43(2) | 3(1) | -4(1) | -8(1) |
| C(17) | 81(3) | 117(4) | 89(3) | 0(3) | 21(3) | -44(3) |
| C(18) | 112(5) | 205(9) | 91(4) | 7(5) | 16(4) | -73(6) |
| C(19) | 63(2) | 48(2) | 80(2) | 12(2) | 2(2) | 2(2) |

**Table S5.** Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters (Å$^2$x $10^3$) for **4a**.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(2A) | 3568 | 4510 | 2840 | 81 |
| H(4A) | 129 | 4762 | 1702 | 68 |
| H(5A) | -659 | 6321 | 997 | 78 |
| H(6A) | -370 | 8009 | 1543 | 72 |
| H(11A) | 2934 | 8410 | 5473 | 82 |
| H(12A) | 3925 | 7877 | 6689 | 94 |
| H(13A) | 4340 | 6053 | 6965 | 88 |
| H(14A) | 3652 | 4759 | 6058 | 77 |
| H(17A) | -3916 | 4378 | 3930 | 115 |
| H(17B) | -2963 | 3256 | 3841 | 115 |
| H(18A) | -4059 | 3423 | 5071 | 204 |
| H(18B) | -2985 | 4492 | 5195 | 204 |
| H(18C) | -2020 | 3377 | 5107 | 204 |
| H(19A) | 448 | 9208 | 2534 | 95 |
| H(19B) | 2036 | 8794 | 3026 | 95 |
| H(19C) | 151 | 8753 | 3377 | 95 |

**Table S6.** Torsion angles [°] for **4a**.

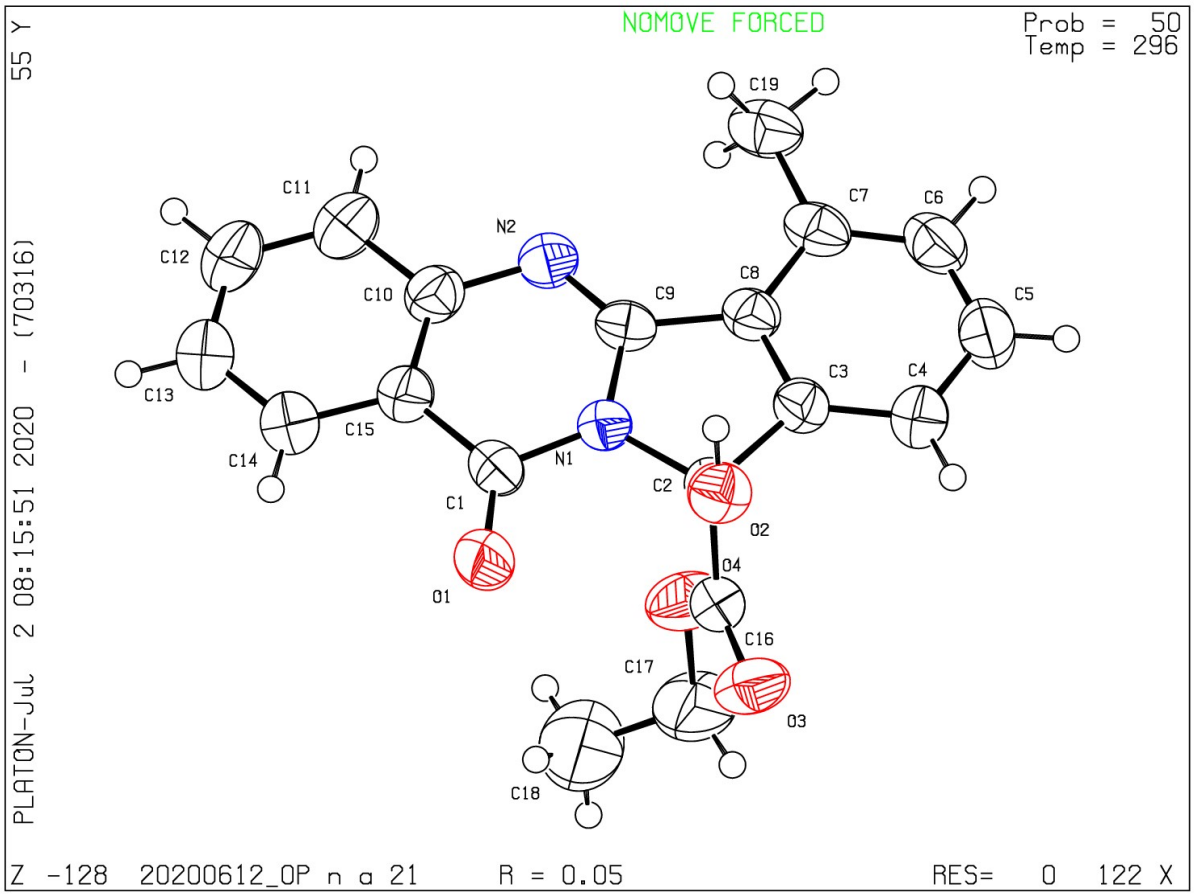
| | |
|---|---|
| C(9)-N(1)-C(1)-O(1) | 175.9(3) |
| C(2)-N(1)-C(1)-O(1) | -0.1(5) |
| C(9)-N(1)-C(1)-C(15) | -4.7(4) |
| C(2)-N(1)-C(1)-C(15) | 179.4(3) |
| C(1)-N(1)-C(2)-O(2) | -65.0(4) |
| C(9)-N(1)-C(2)-O(2) | 118.7(3) |
| C(1)-N(1)-C(2)-C(3) | 176.3(3) |
| C(9)-N(1)-C(2)-C(3) | 0.1(3) |
| C(1)-N(1)-C(2)-C(16) | 58.9(4) |
| C(9)-N(1)-C(2)-C(16) | -117.3(3) |
| O(2)-C(2)-C(3)-C(8) | -119.6(3) |
| N(1)-C(2)-C(3)-C(8) | -0.2(3) |
| C(16)-C(2)-C(3)-C(8) | 116.3(3) |
| O(2)-C(2)-C(3)-C(4) | 59.9(4) |
| N(1)-C(2)-C(3)-C(4) | 179.3(3) |
| C(16)-C(2)-C(3)-C(4) | -64.2(4) |
| C(8)-C(3)-C(4)-C(5) | -1.5(5) |
| C(2)-C(3)-C(4)-C(5) | 179.1(3) |
| C(3)-C(4)-C(5)-C(6) | 1.0(6) |
| C(4)-C(5)-C(6)-C(7) | 0.4(6) |
| C(5)-C(6)-C(7)-C(8) | -1.3(5) |
| C(5)-C(6)-C(7)-C(19) | 177.6(4) |
| C(4)-C(3)-C(8)-C(7) | 0.5(5) |
| C(2)-C(3)-C(8)-C(7) | -179.9(3) |
| C(4)-C(3)-C(8)-C(9) | -179.2(3) |
| C(2)-C(3)-C(8)-C(9) | 0.3(3) |
| C(6)-C(7)-C(8)-C(3) | 0.8(4) |
| C(19)-C(7)-C(8)-C(3) | -178.0(3) |
| C(6)-C(7)-C(8)-C(9) | -179.5(3) |
| C(19)-C(7)-C(8)-C(9) | 1.7(5) |
| C(10)-N(2)-C(9)-N(1) | 0.5(4) |
| C(10)-N(2)-C(9)-C(8) | 179.4(3) |
| C(1)-N(1)-C(9)-N(2) | 2.9(5) |
| C(2)-N(1)-C(9)-N(2) | 179.2(3) |

| | |
|---|---|
| C(1)-N(1)-C(9)-C(8) | -176.2(3) |
| C(2)-N(1)-C(9)-C(8) | 0.1(3) |
| C(3)-C(8)-C(9)-N(2) | -179.3(3) |
| C(7)-C(8)-C(9)-N(2) | 1.0(5) |
| C(3)-C(8)-C(9)-N(1) | -0.2(3) |
| C(7)-C(8)-C(9)-N(1) | -180.0(3) |
| C(9)-N(2)-C(10)-C(15) | -1.6(5) |
| C(9)-N(2)-C(10)-C(11) | 179.6(3) |
| C(15)-C(10)-C(11)-C(12) | 0.3(6) |
| N(2)-C(10)-C(11)-C(12) | 179.1(4) |
| C(10)-C(11)-C(12)-C(13) | 1.0(7) |
| C(11)-C(12)-C(13)-C(14) | -1.5(7) |
| C(12)-C(13)-C(14)-C(15) | 0.9(7) |
| N(2)-C(10)-C(15)-C(14) | -179.7(3) |
| C(11)-C(10)-C(15)-C(14) | -0.9(5) |
| N(2)-C(10)-C(15)-C(1) | -0.5(5) |
| C(11)-C(10)-C(15)-C(1) | 178.3(3) |
| C(13)-C(14)-C(15)-C(10) | 0.4(6) |
| C(13)-C(14)-C(15)-C(1) | -178.9(4) |
| O(1)-C(1)-C(15)-C(10) | -177.1(3) |
| N(1)-C(1)-C(15)-C(10) | 3.5(4) |
| O(1)-C(1)-C(15)-C(14) | 2.1(5) |
| N(1)-C(1)-C(15)-C(14) | -177.3(3) |
| C(17)-O(4)-C(16)-O(3) | -1.3(6) |
| C(17)-O(4)-C(16)-C(2) | 175.8(4) |
| O(2)-C(2)-C(16)-O(3) | -16.2(4) |
| N(1)-C(2)-C(16)-O(3) | -141.3(3) |
| C(3)-C(2)-C(16)-O(3) | 108.5(4) |
| O(2)-C(2)-C(16)-O(4) | 166.6(3) |
| N(1)-C(2)-C(16)-O(4) | 41.5(4) |
| C(3)-C(2)-C(16)-O(4) | -68.7(4) |
| C(16)-O(4)-C(17)-C(18) | 114.8(7) |

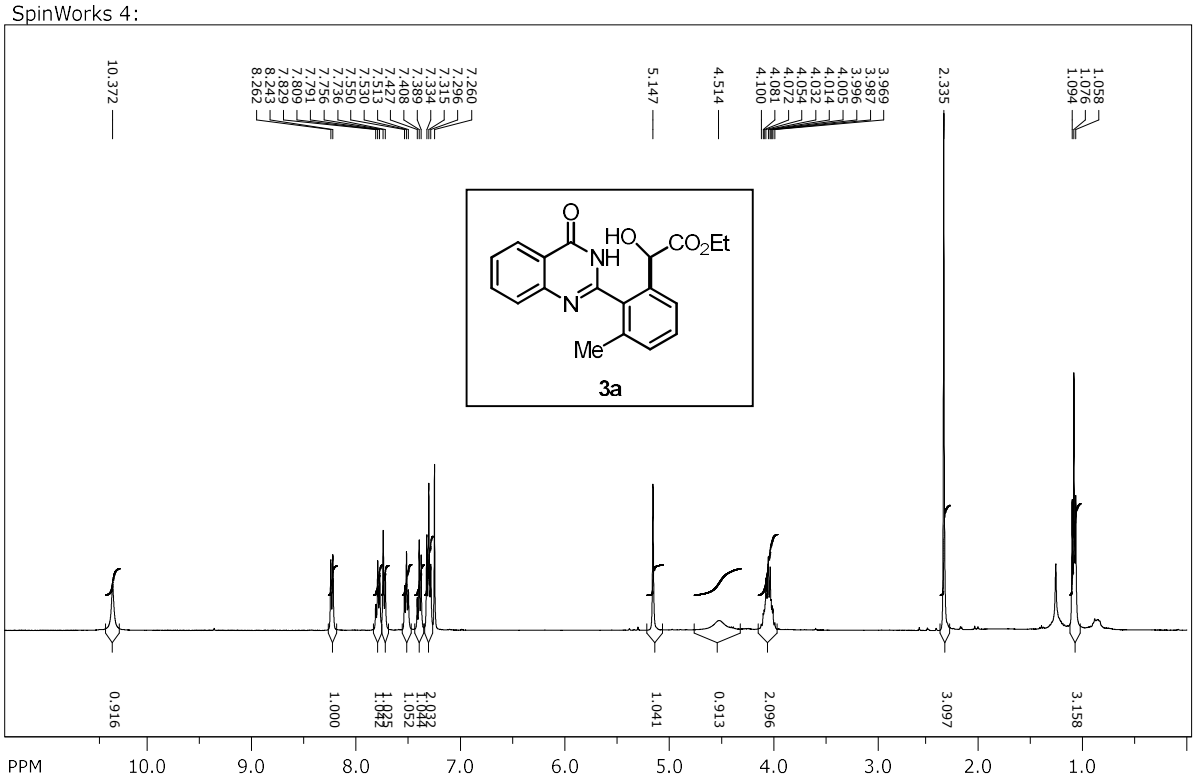
Symmetry transformations used to generate equivalent atoms:

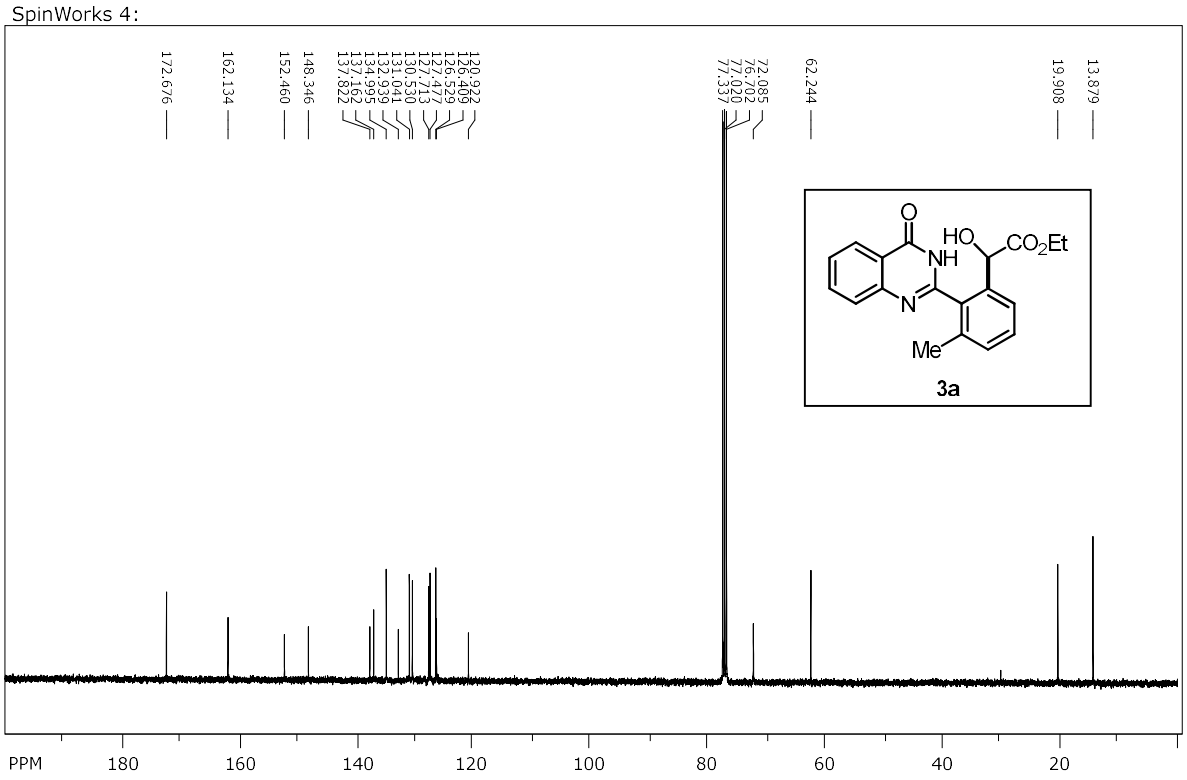
**X-ray crystallographic structure of compound 4a (CCDC 2013547)**

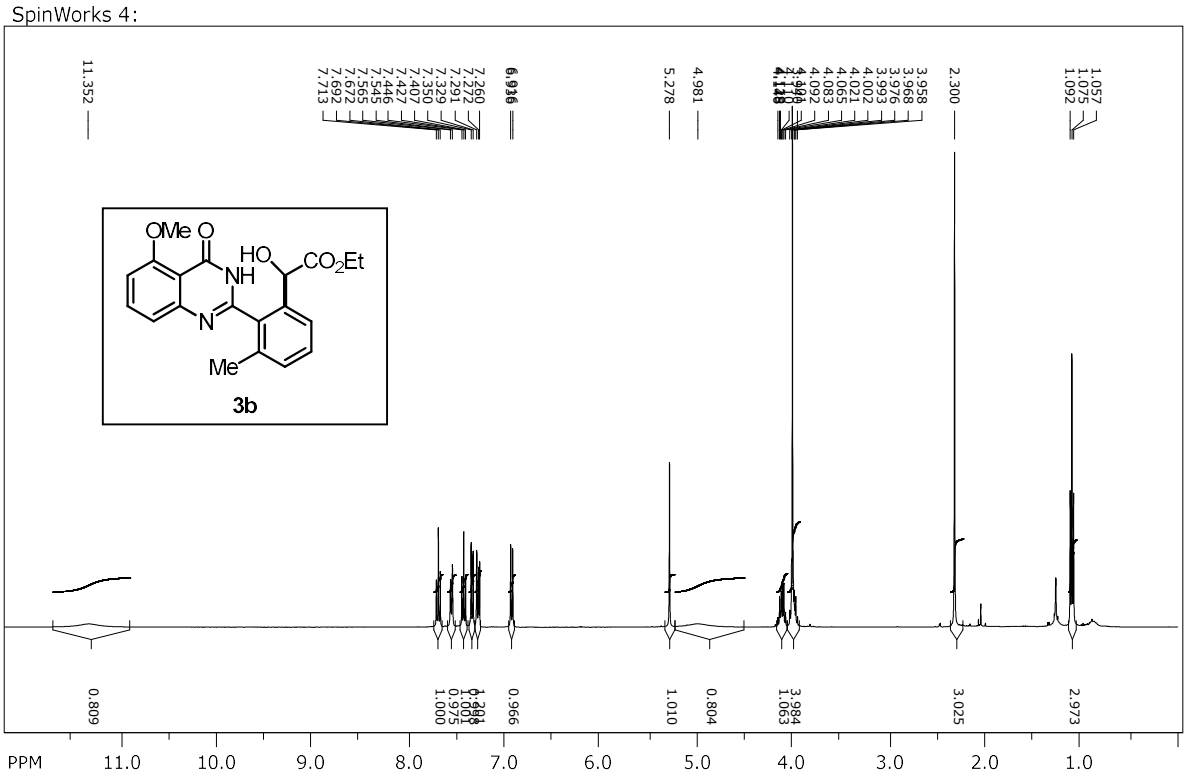
**Sample preparation (vapor diffusion)**: compound **4a** (5.1 mg) was dissolved with 1.5 mL of $CHCl_3$ in opened inner vessel, and pentane (6 mL) as an anti-solvent has been employed in closed outer vessel. After vapor diffusion for 10 days, the single crystals of compound **4a** were obtained.

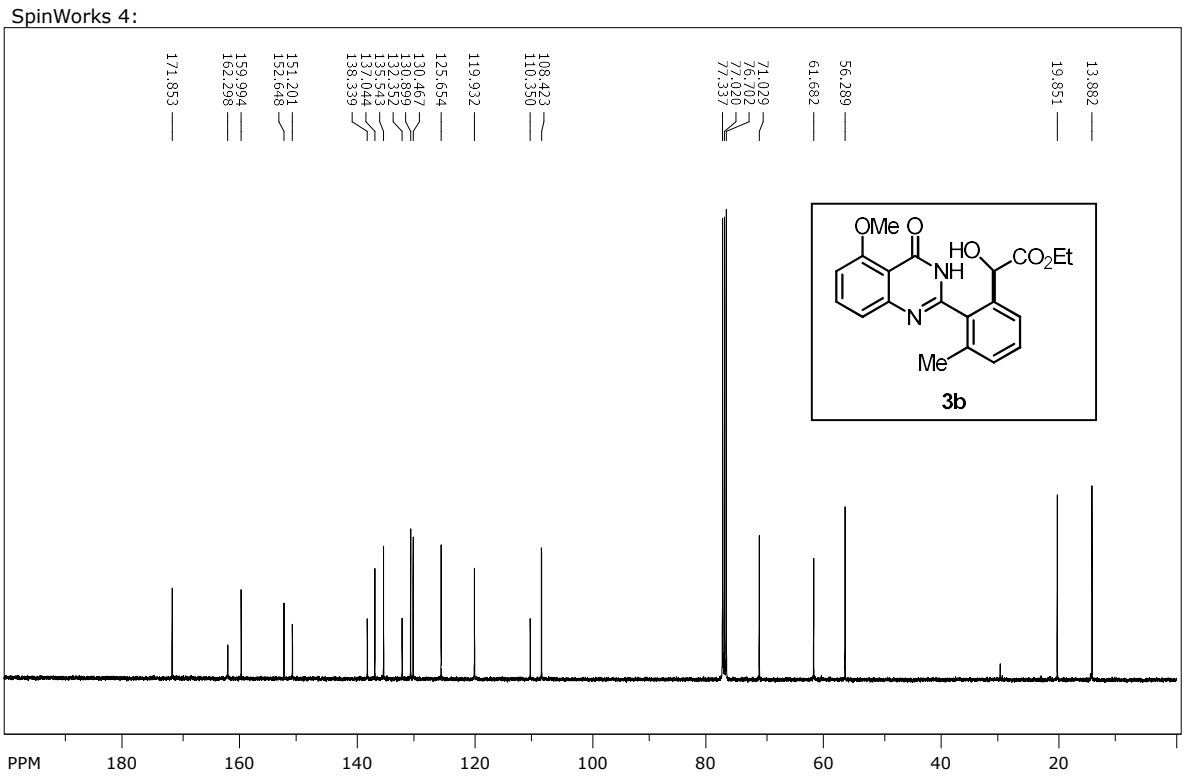


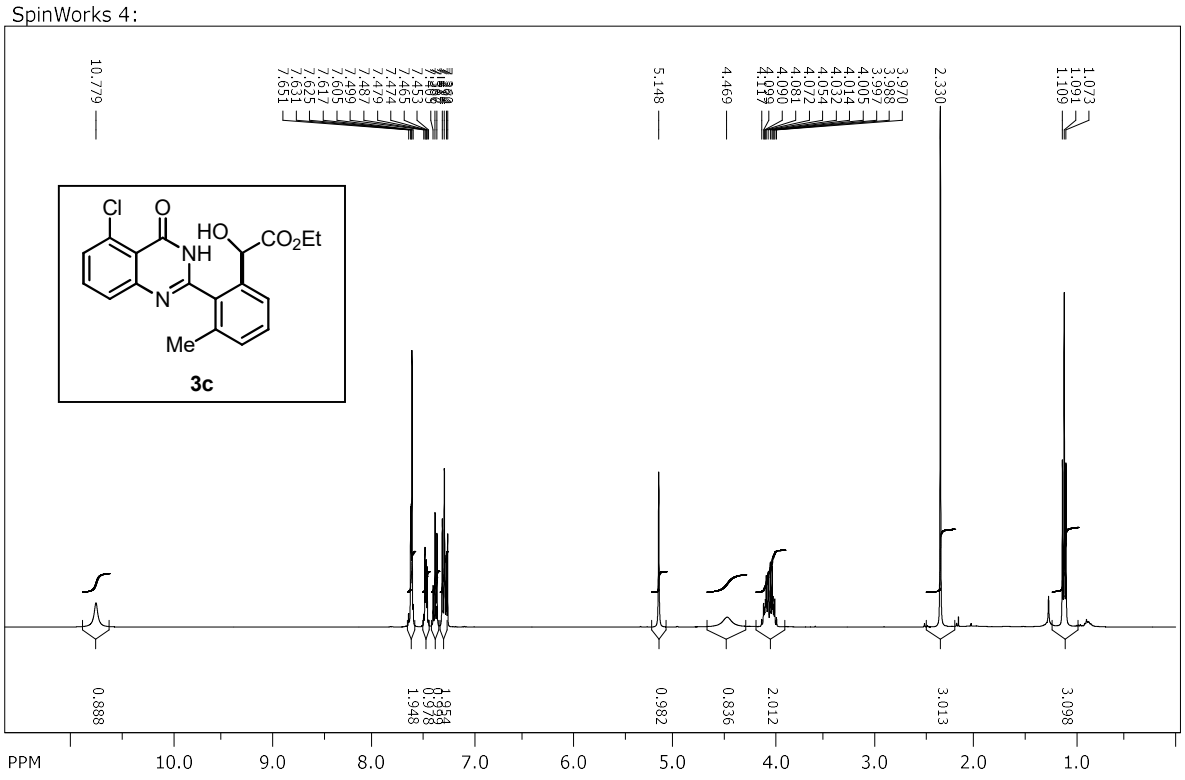
## $^{1}$H NMR and $^{13}$C NMR spectra of all products

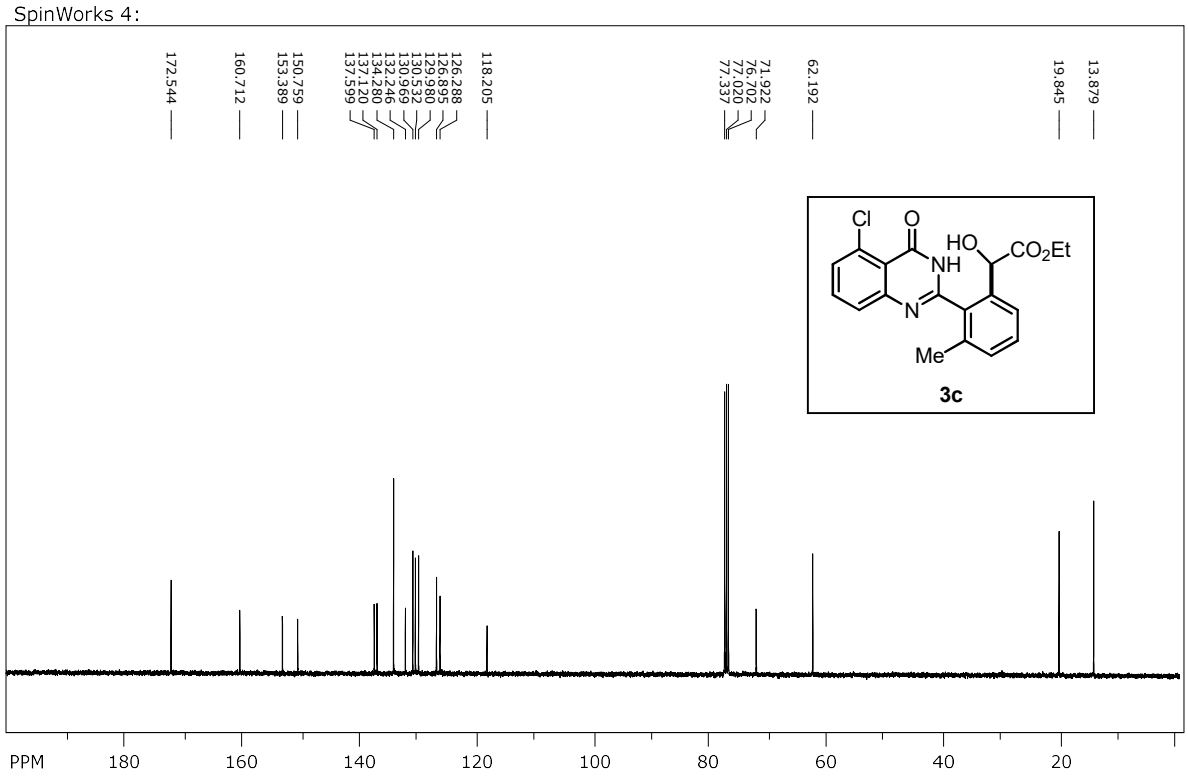


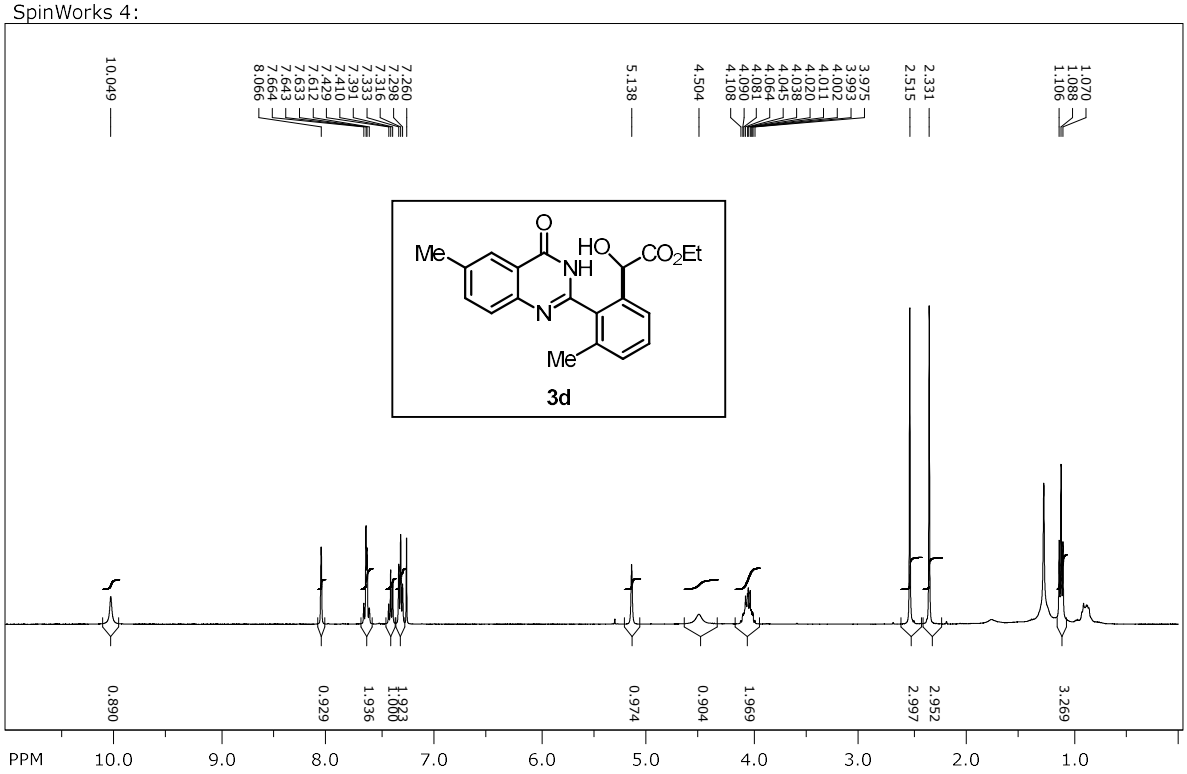

SpinWorks 4:
11.352
7.713
7.692
7.672
7.565
7.545
7.446
7.427
7.407
7.350
7.329
7.291
7.260
6.916
5.278
4.981
4.148
4.092
4.083
4.065
4.021
4.002
3.993
3.976
3.968
3.958
2.300
1.092
1.075
1.057
OMe O
HO
NH
CO2Et
N
Me
3b
0.809
1.000
0.966
1.010
0.804
1.063
3.025
2.973
PPM
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


SpinWorks 4:
171.853
162.298
159.994
152.648
151.201
138.339
137.044
135.543
132.352
130.899
130.467
125.654
119.932
110.350
108.423
77.337
77.020
76.702
71.029
61.682
56.289
19.851
13.882
OMe O
HO
NH
CO2Et
N
Me
3b
PPM
180
160
140
120
100
80
60
40
20

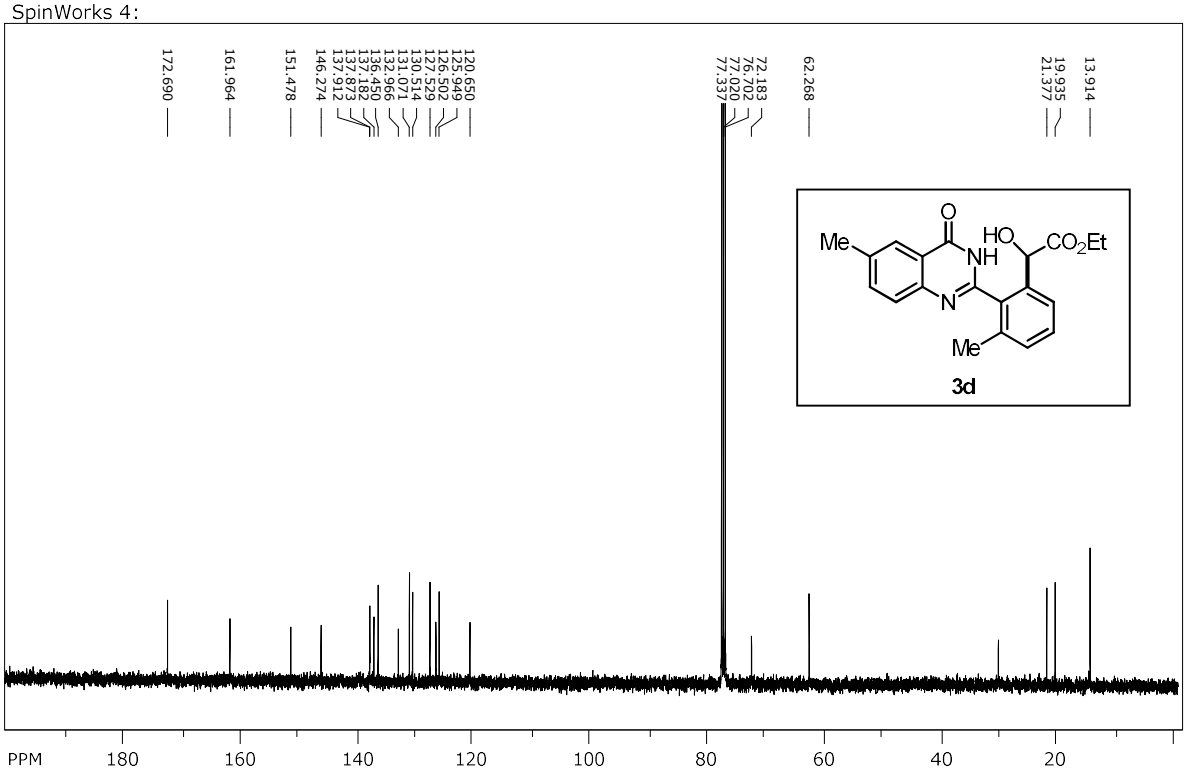

SpinWorks 4:
10.779
7.651
7.631
7.625
7.617
7.605
7.499
7.487
7.479
7.474
7.465
7.453
5.148
4.469
4.117
4.099
4.090
4.081
4.072
4.054
4.032
4.014
4.005
3.970
3.988
2.330
1.109
1.091
1.073
Cl
O
HO
CO2Et
NH
N
Me
3c
0.888
1.954
0.978
1.948
0.982
0.836
2.012
3.013
3.098
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0


SpinWorks 4:
172.544
160.712
153.389
150.759
137.599
137.120
134.280
132.246
130.969
130.592
129.980
126.885
126.288
118.205
77.337
77.020
76.702
71.922
62.192
19.845
13.879
Cl
O
HO
CO2Et
NH
N
Me
3c
PPM
180
160
140
120
100
80
60
40
20

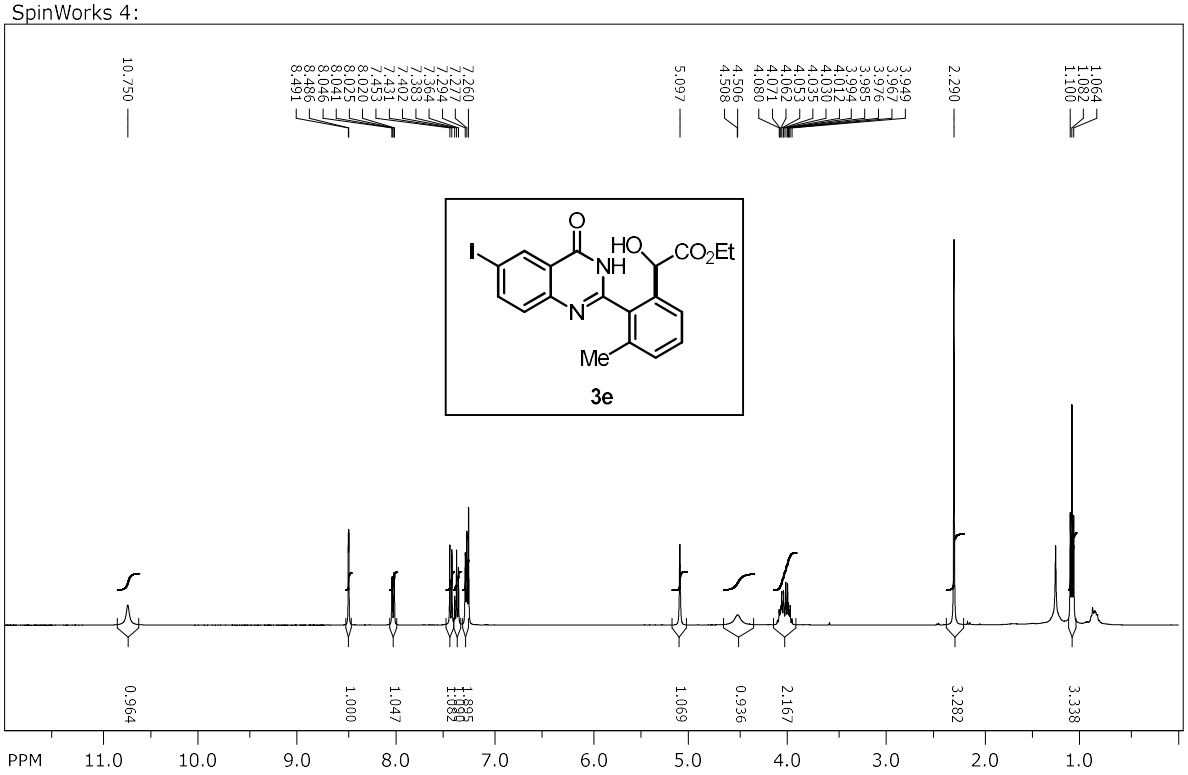
SpinWorks 4:



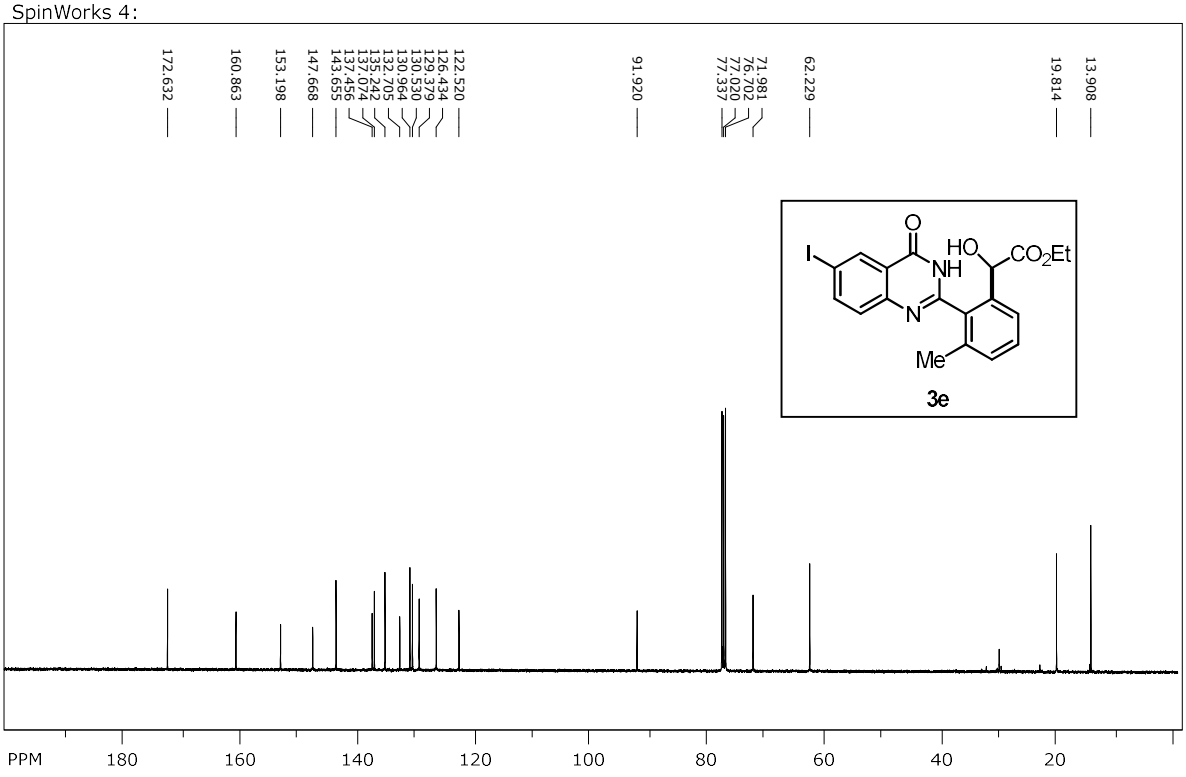

SpinWorks 4:



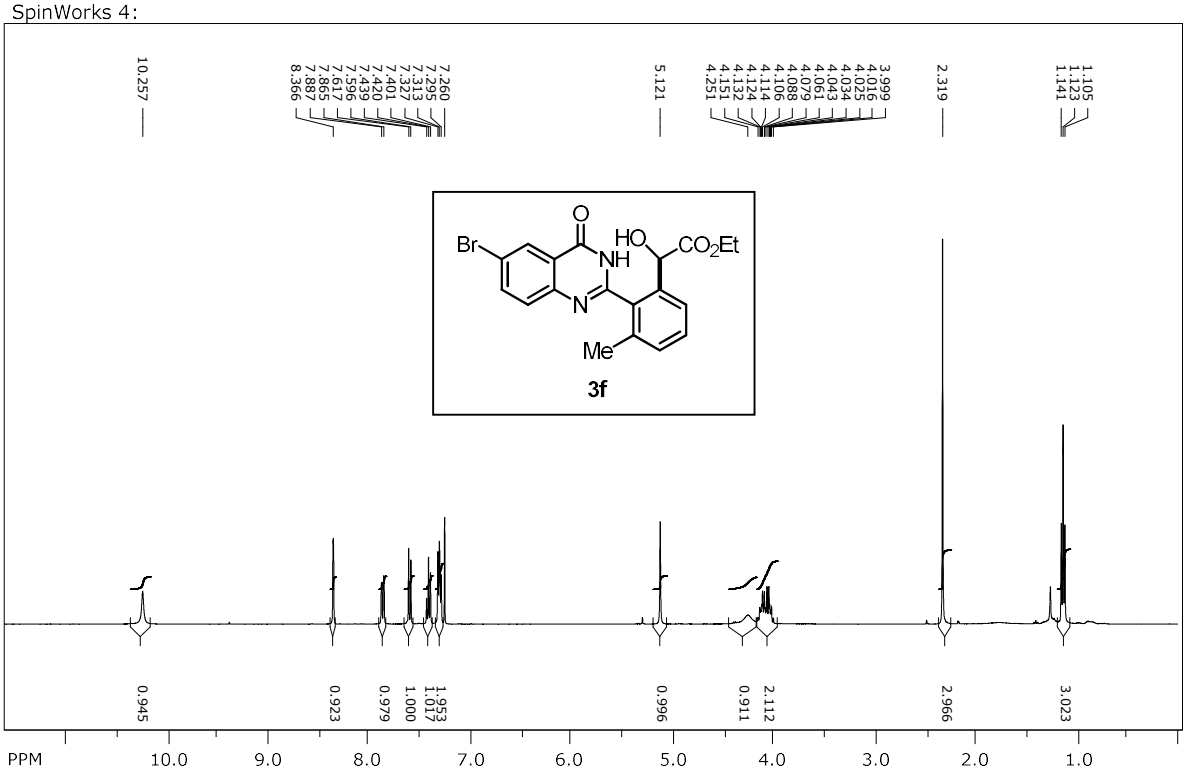
SpinWorks 4:



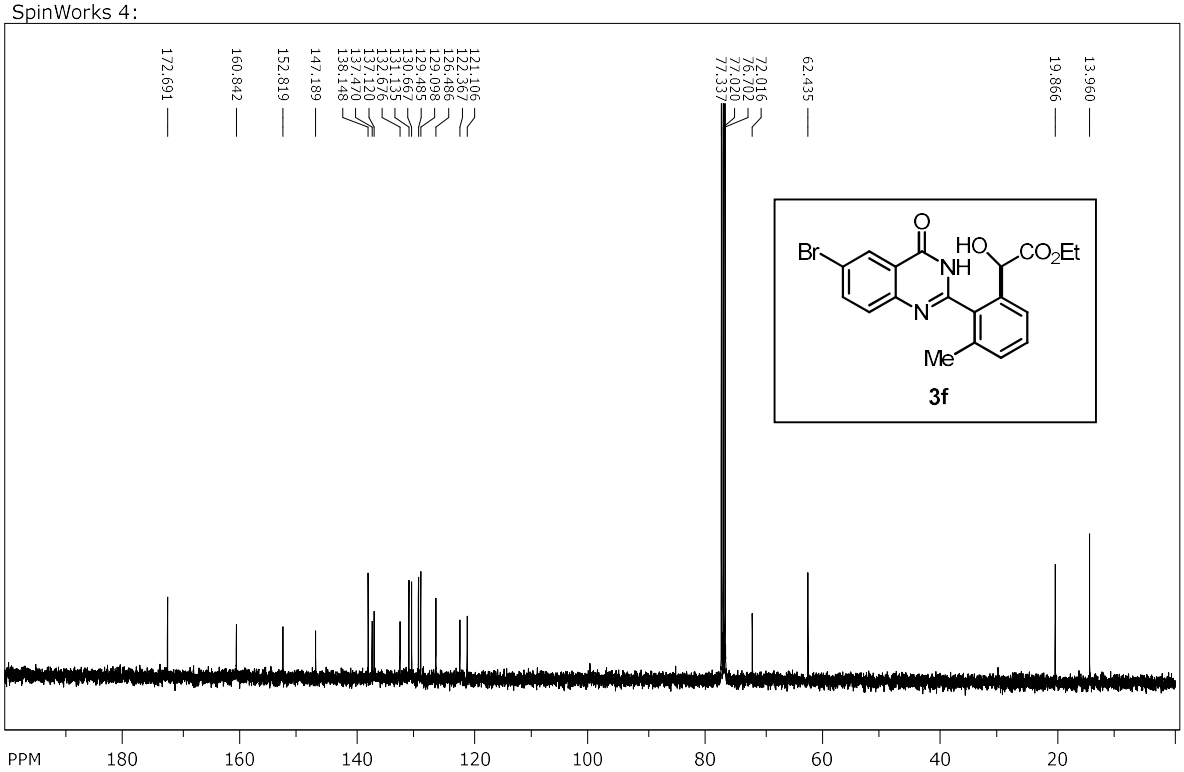

SpinWorks 4:



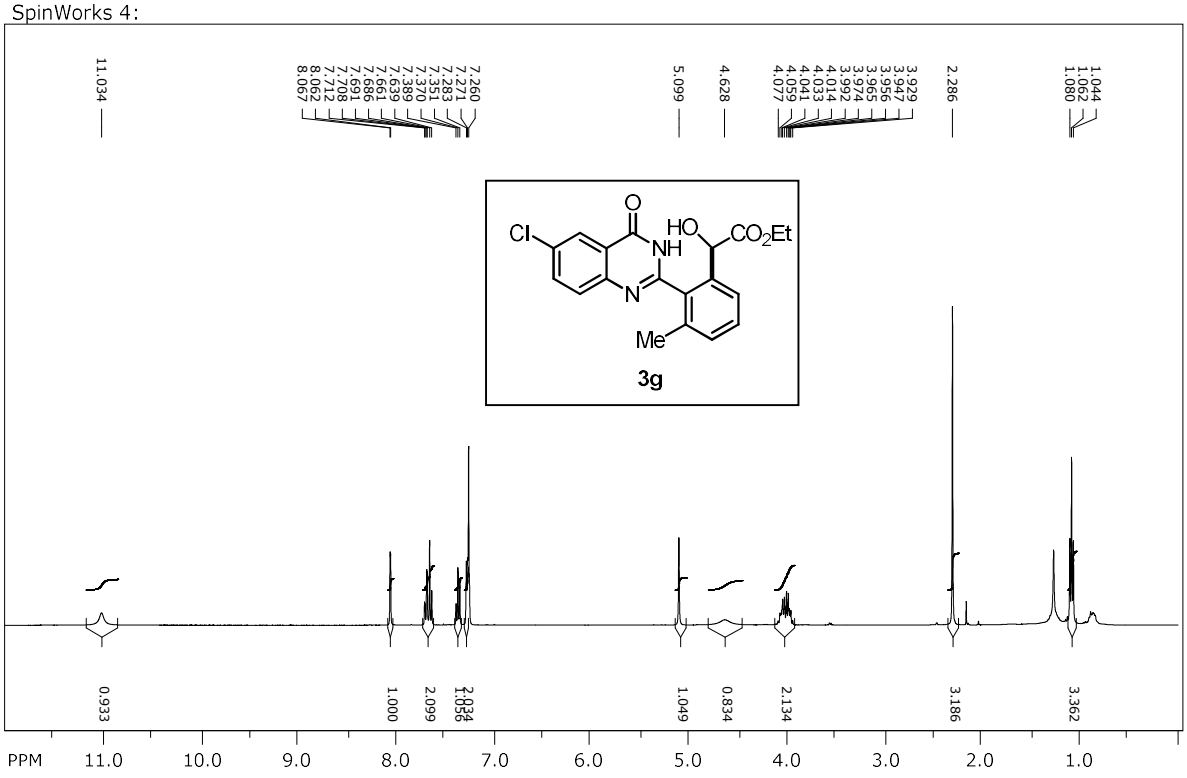
SpinWorks 4:



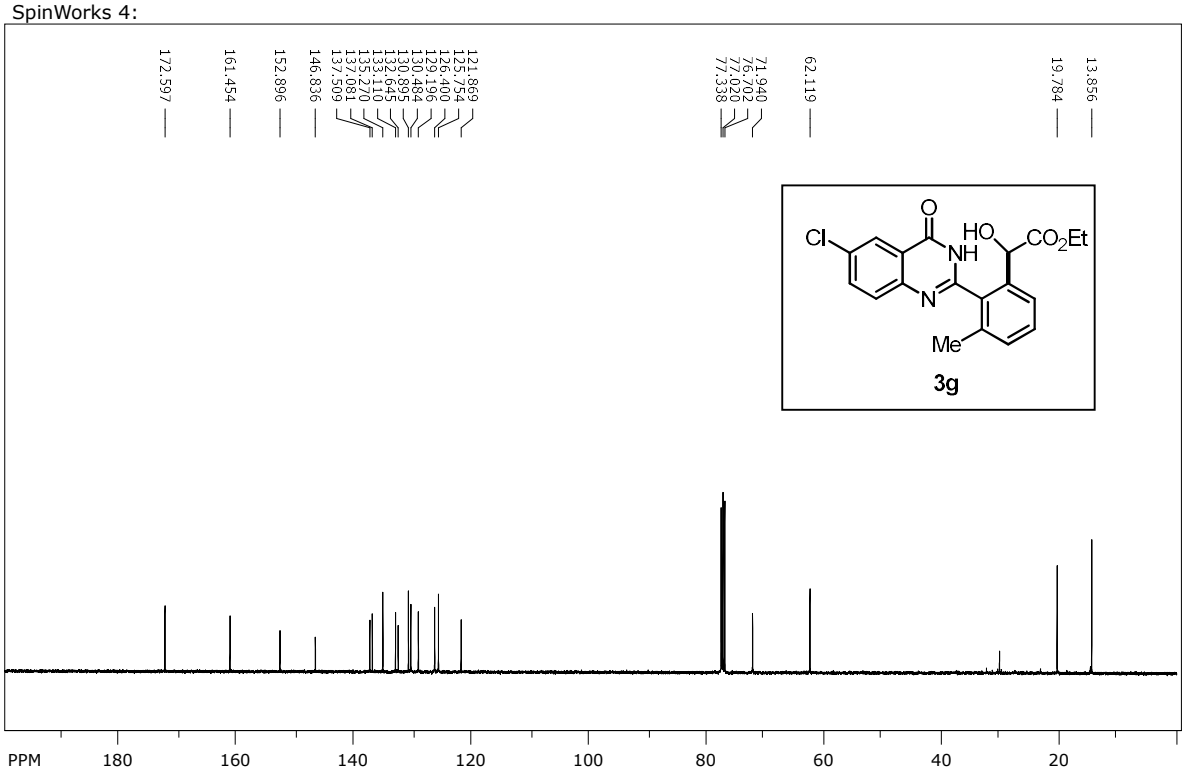

SpinWorks 4:

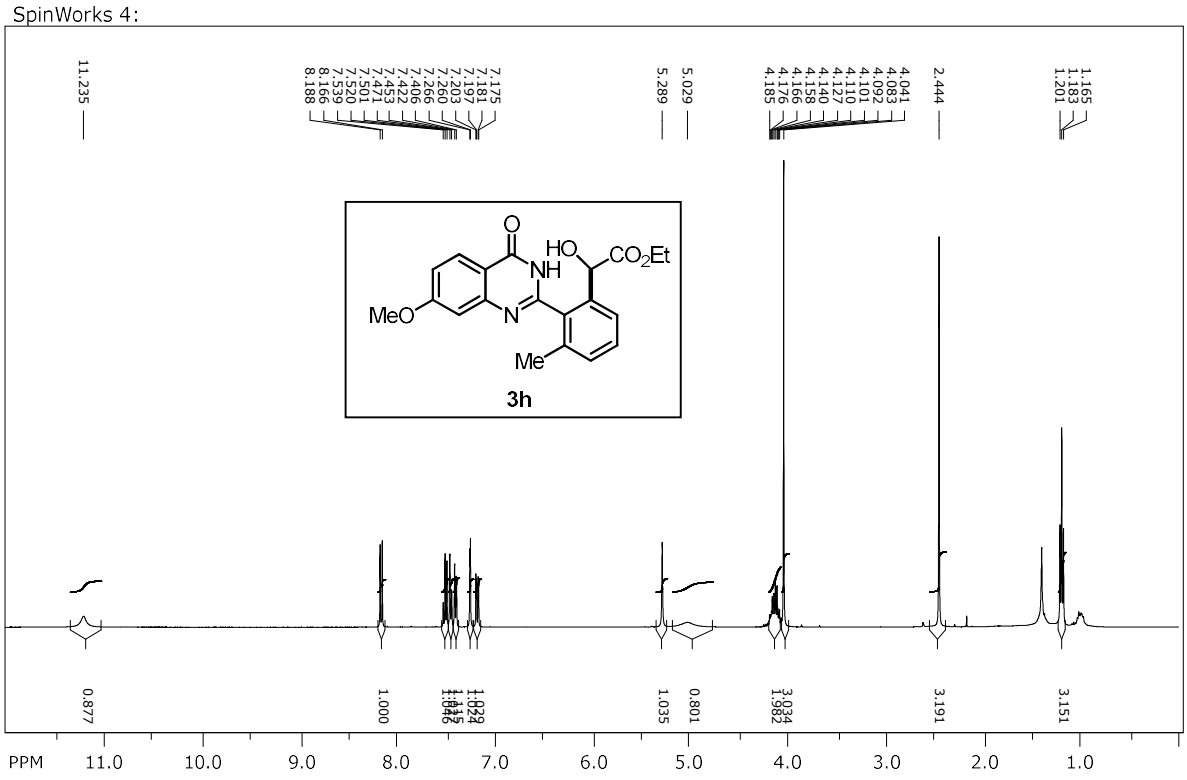


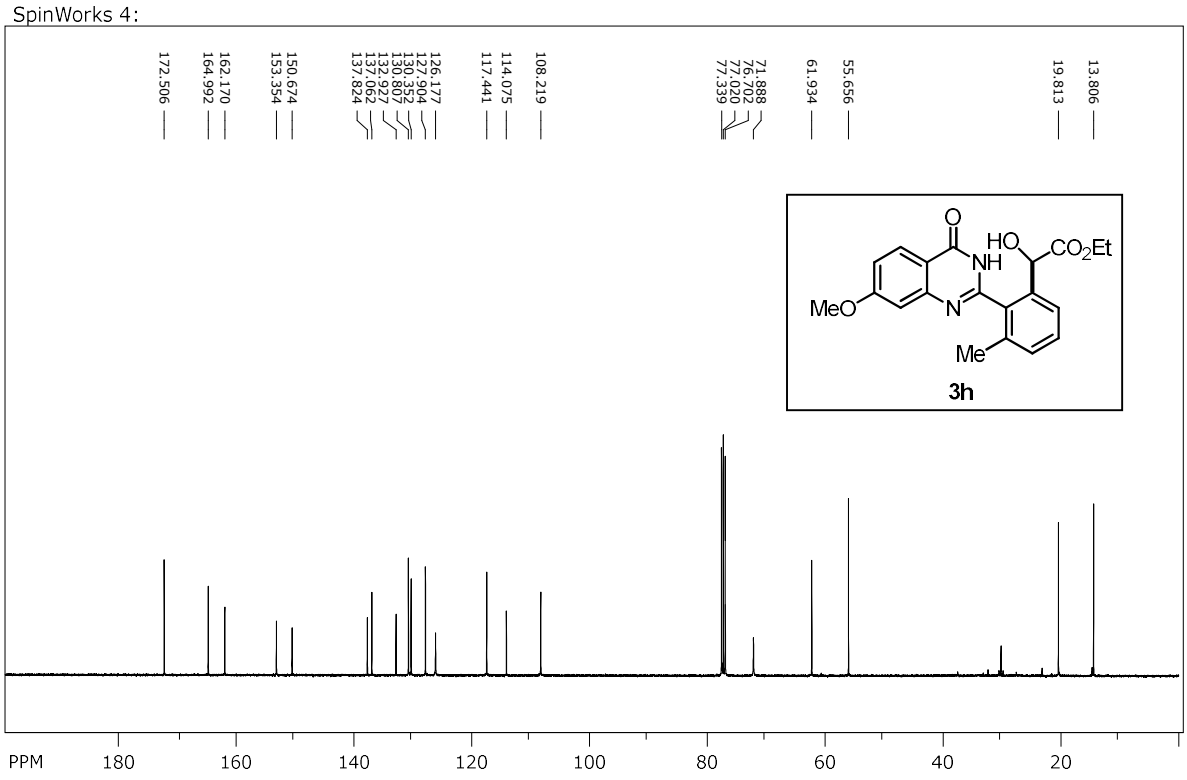
SpinWorks 4:



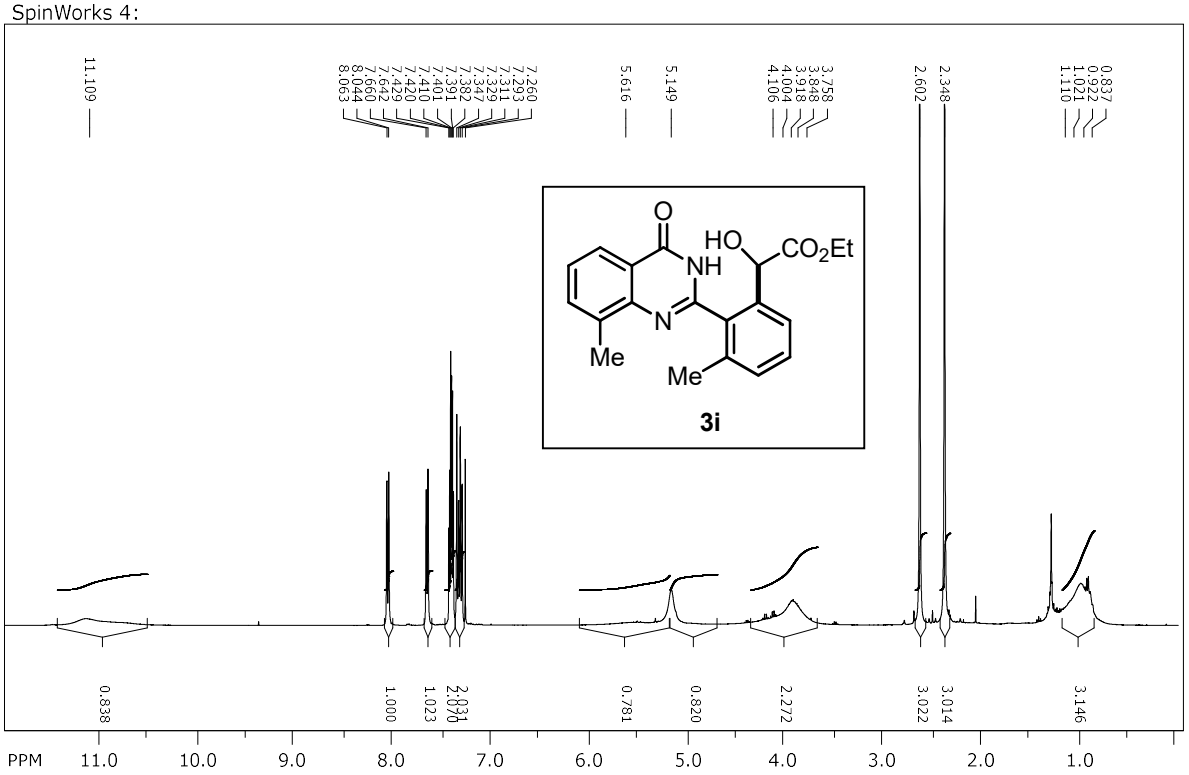

SpinWorks 4:



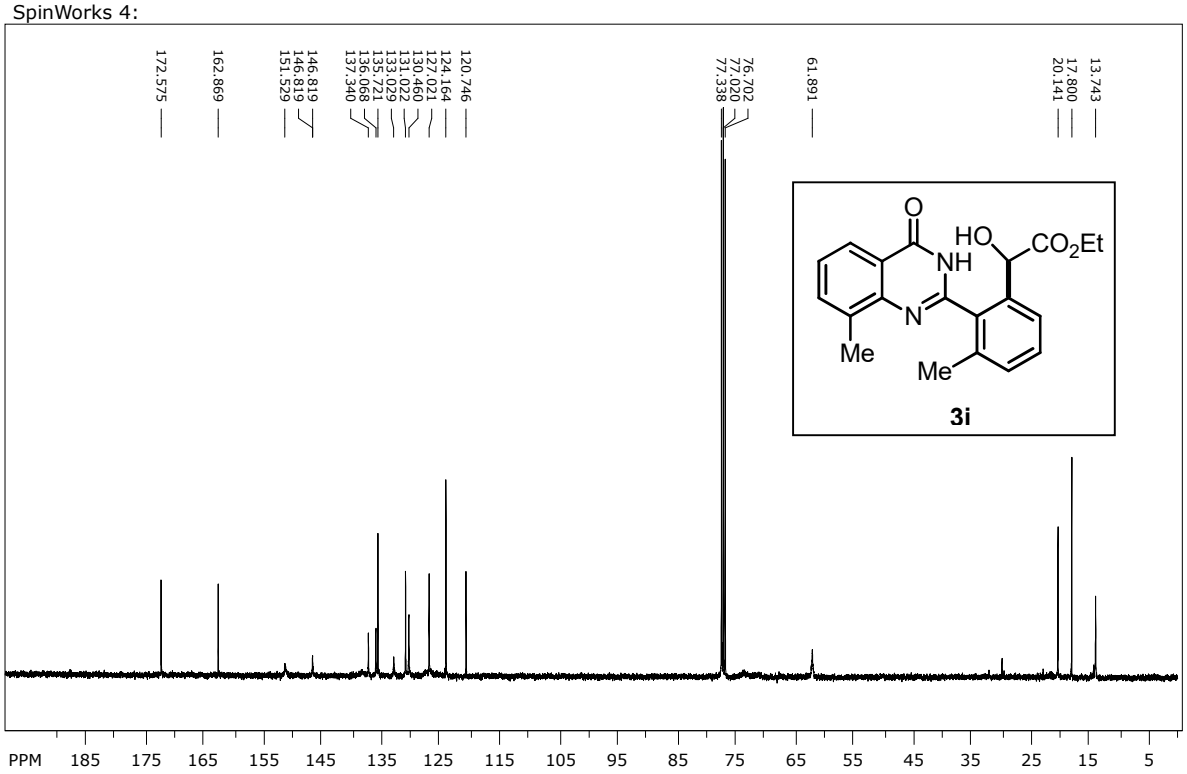

SpinWorks 4:
11.235
8.188
8.166
7.539
7.520
7.501
7.471
7.453
7.422
7.406
7.266
7.260
7.193
7.181
7.175
5.289
5.029
4.185
4.176
4.166
4.158
4.140
4.127
4.110
4.101
4.092
4.083
4.041
2.444
1.201
1.183
1.165
0.877
1.000
1.035
0.801
3.034
1.982
3.191
3.151
PPM
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
O
HO
CO2Et
NH
MeO
N
Me
3h


SpinWorks 4:
172.506
164.992
162.170
153.354
150.674
137.824
137.062
132.927
130.807
130.352
127.904
126.177
117.441
114.075
108.219
77.339
77.020
76.702
71.888
61.934
55.656
19.813
13.806
PPM
180
160
140
120
100
80
60
40
20
O
HO
CO2Et
NH
MeO
N
Me
3h

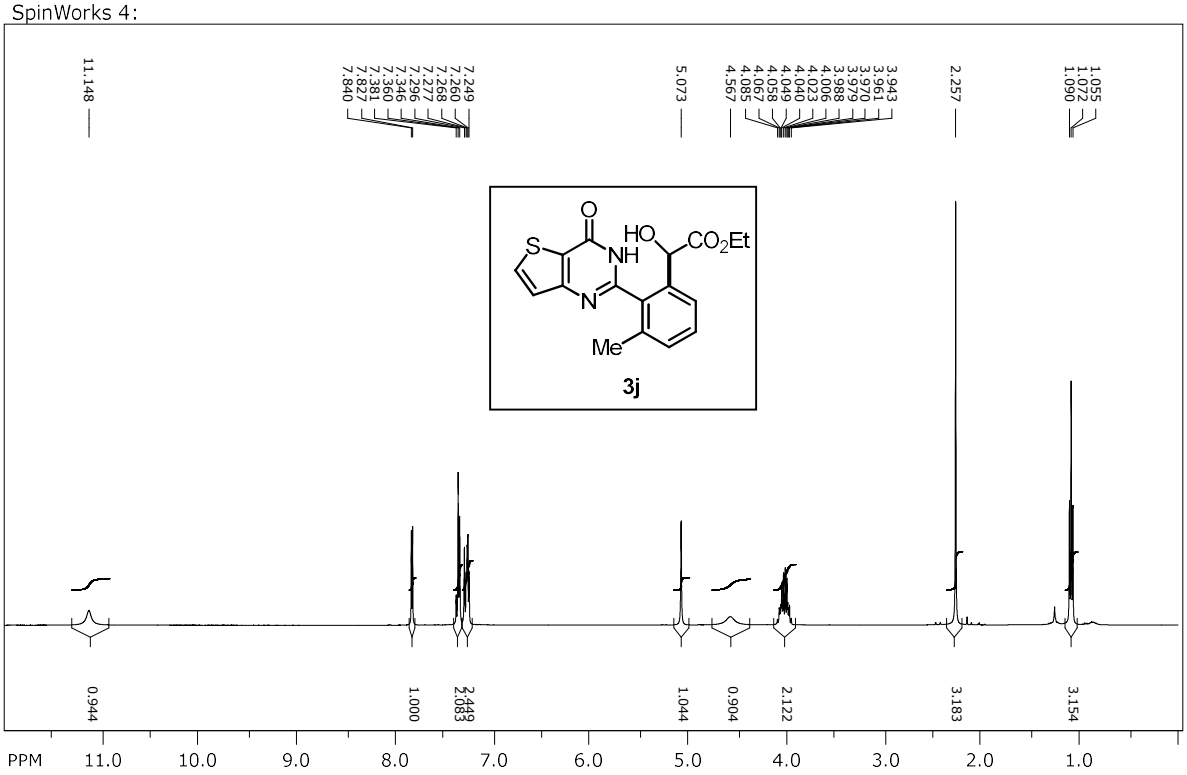
SpinWorks 4:



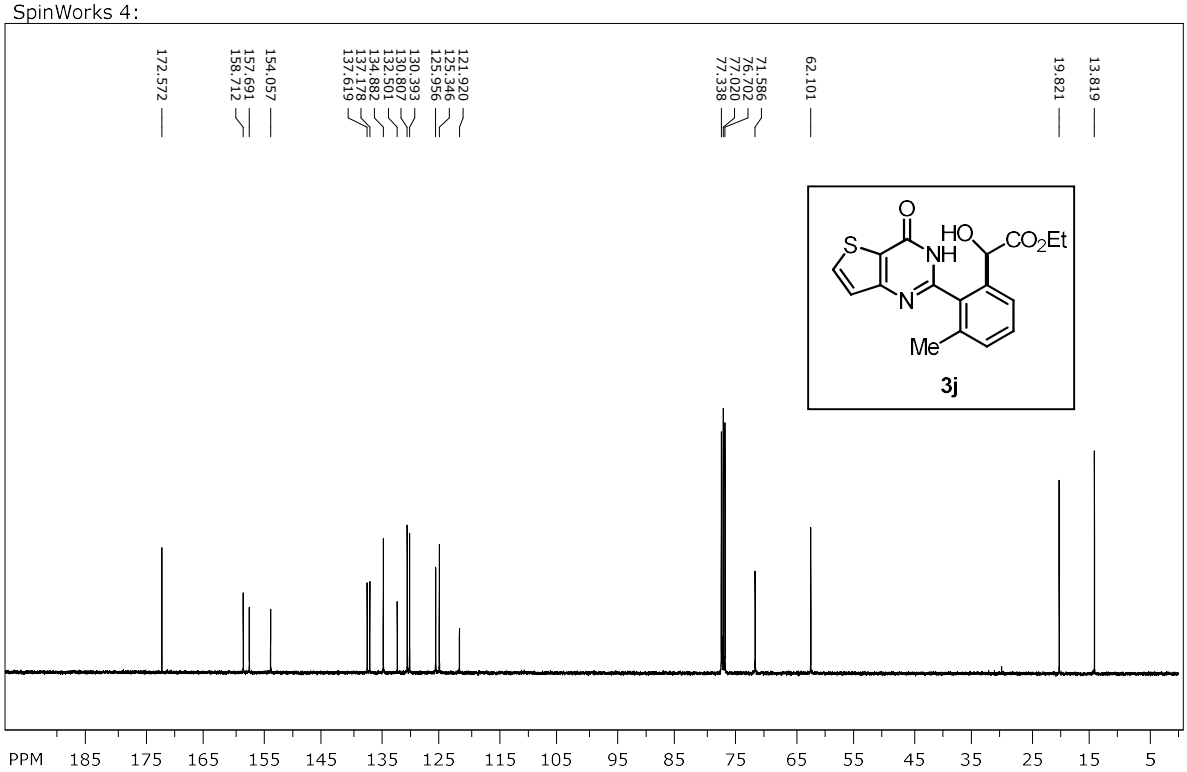

SpinWorks 4:



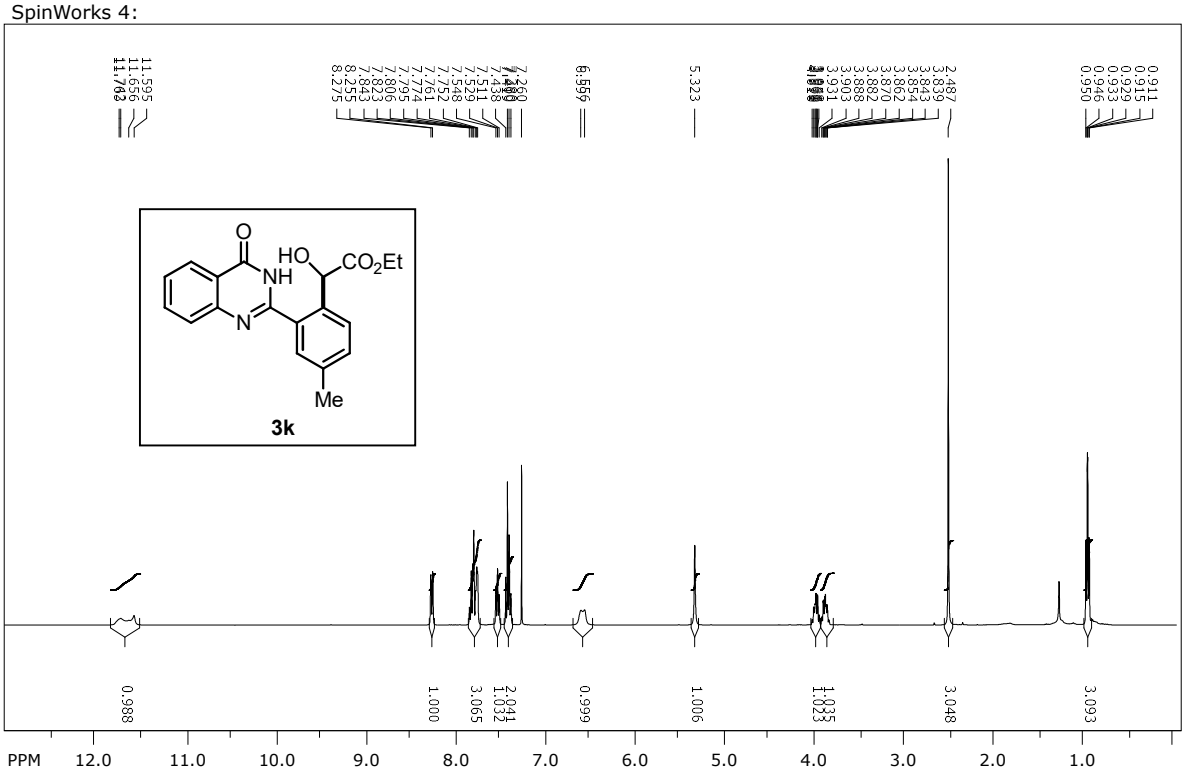
SpinWorks 4:



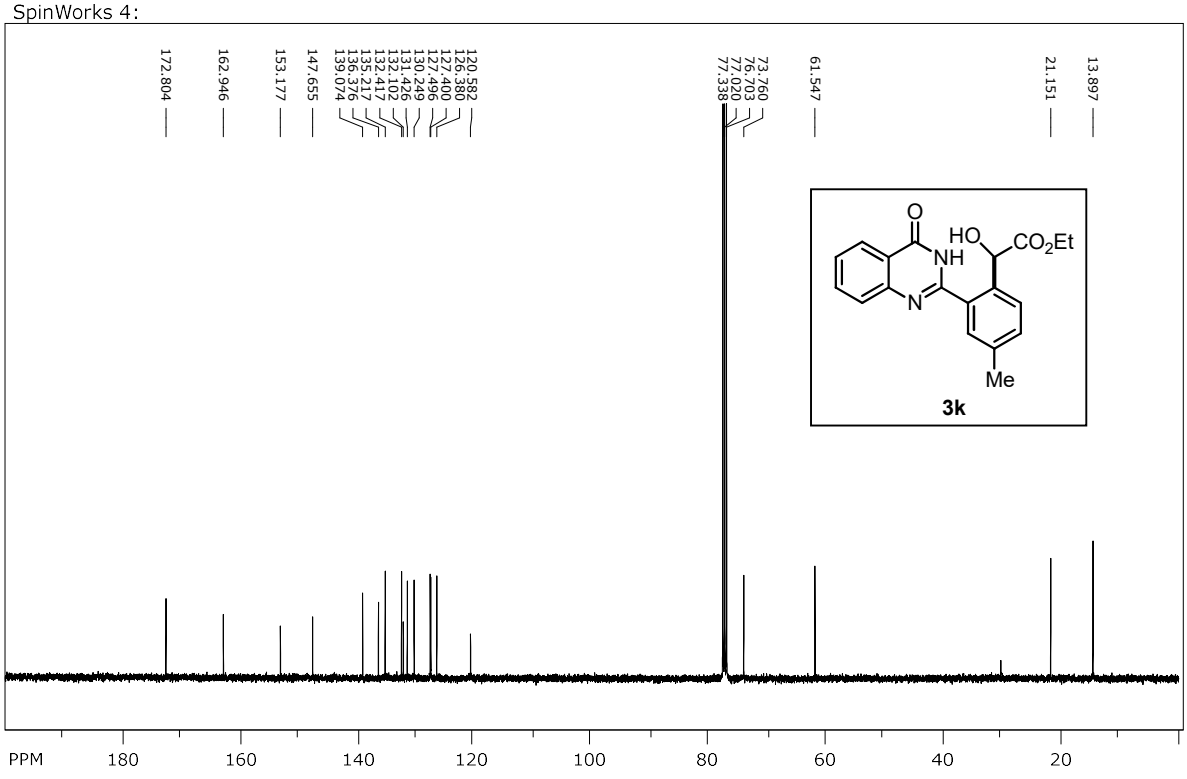

SpinWorks 4:

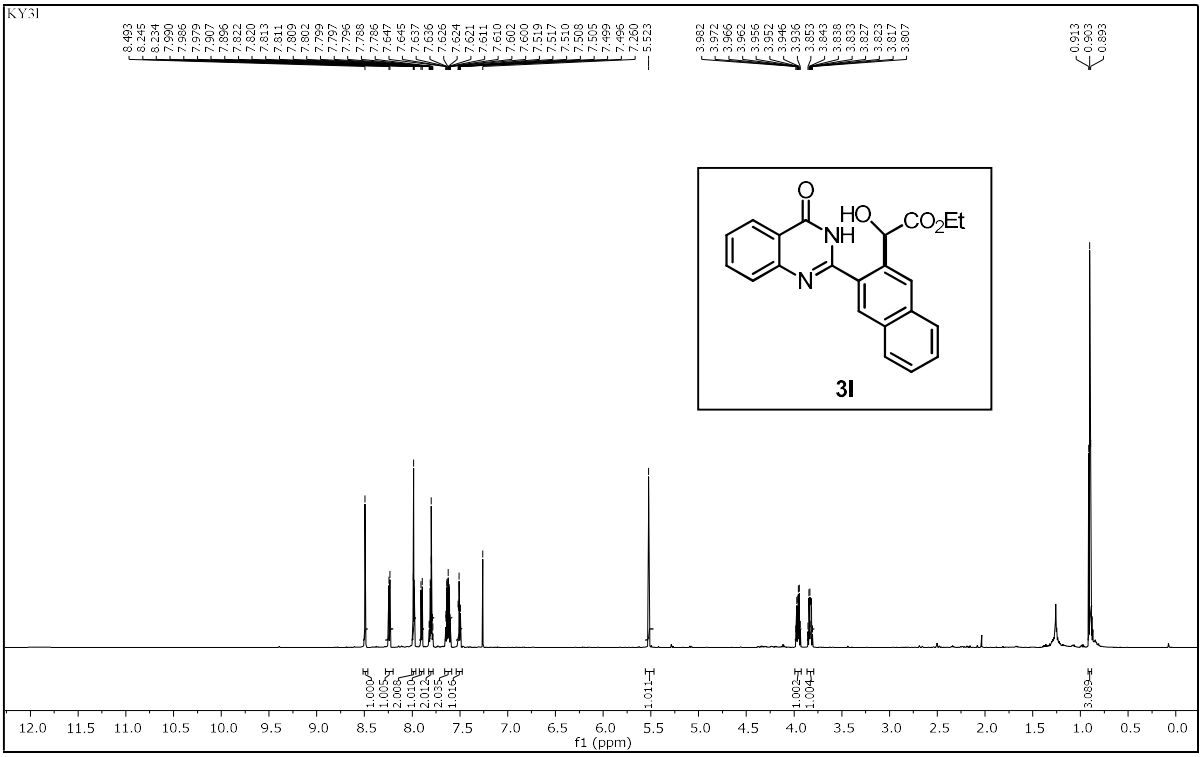


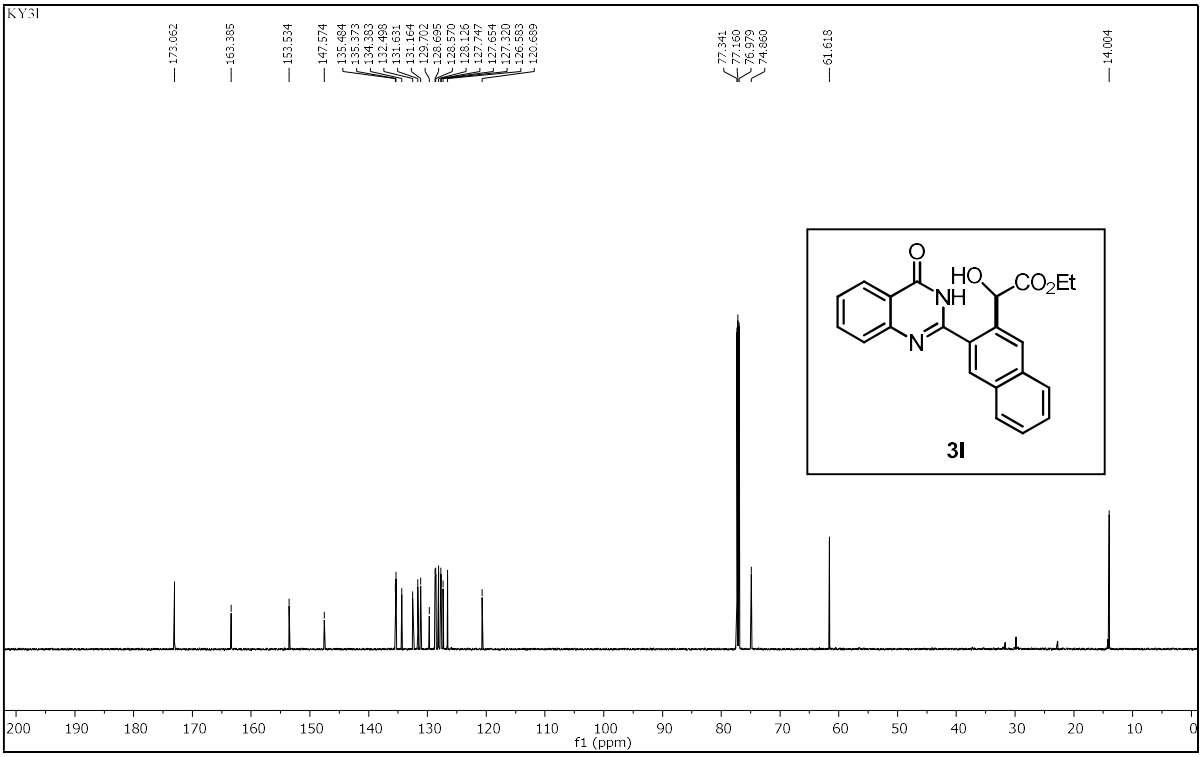
SpinWorks 4:



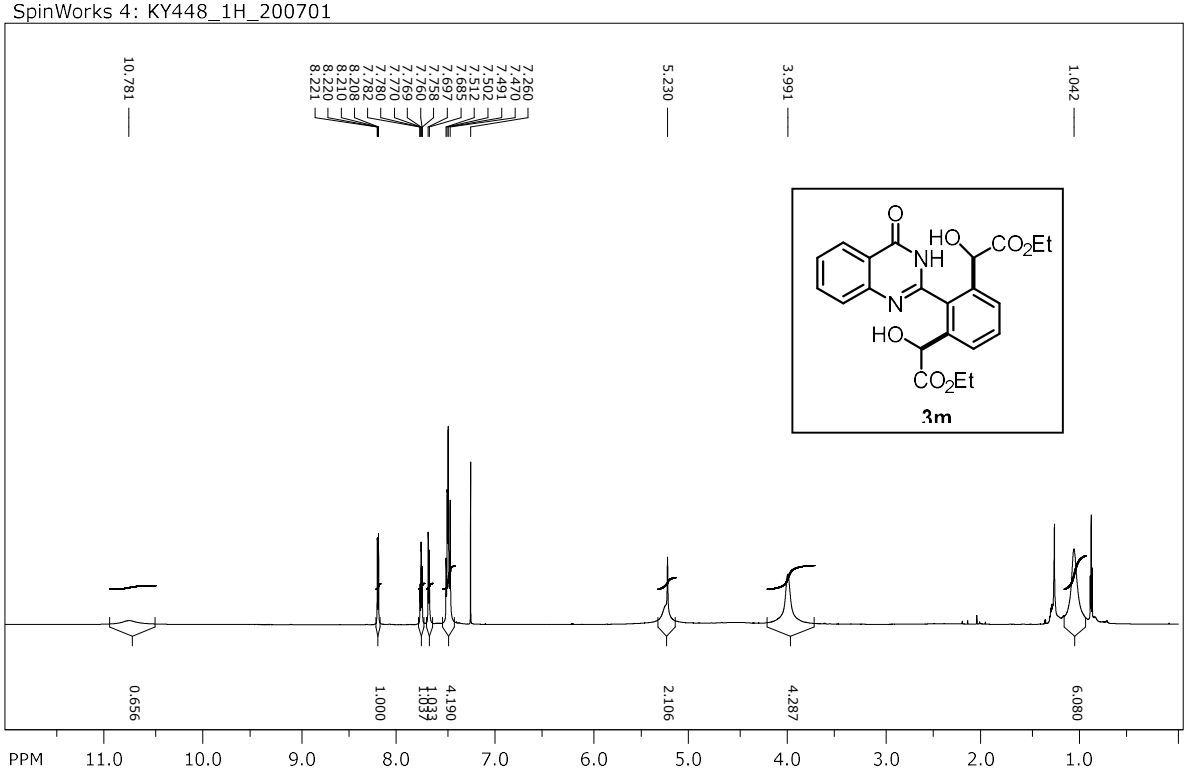

SpinWorks 4:



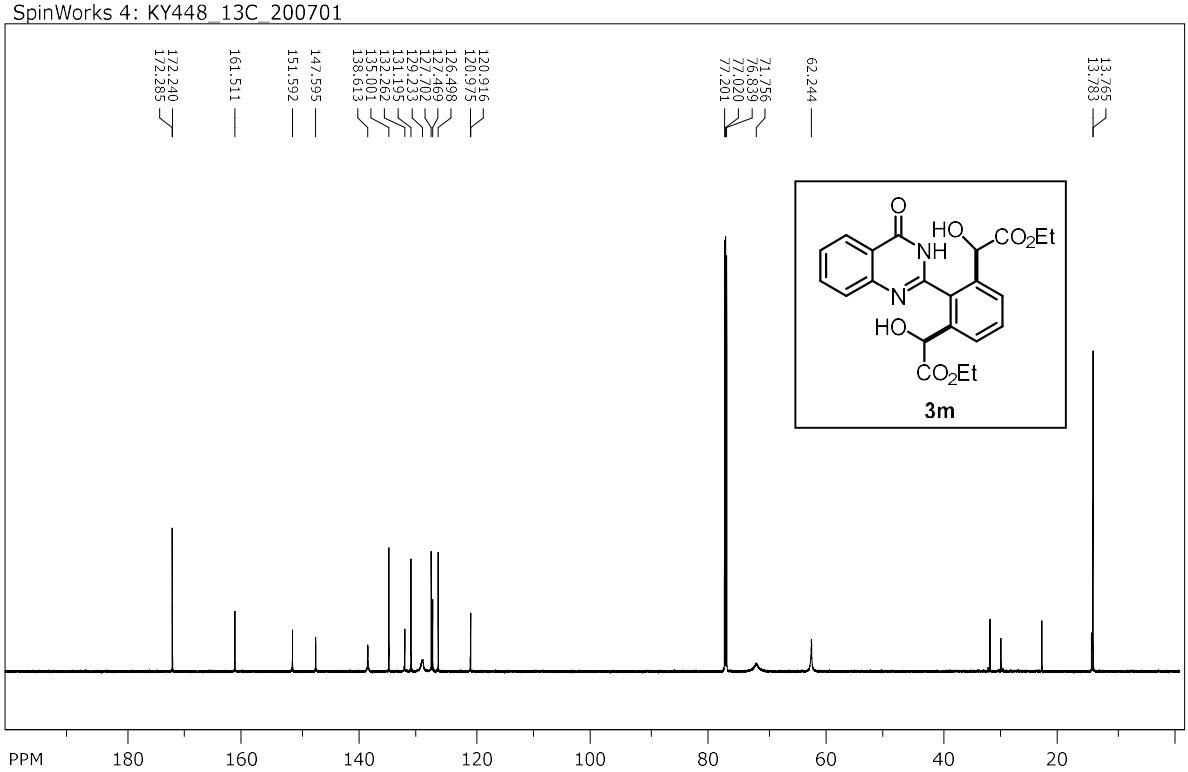

KY3I
8.493
8.245
8.234
7.990
7.986
7.979
7.907
7.896
7.822
7.820
7.813
7.811
7.809
7.802
7.799
7.797
7.796
7.788
7.786
7.647
7.645
7.637
7.636
7.626
7.624
7.621
7.611
7.610
7.602
7.600
7.519
7.517
7.510
7.508
7.505
7.499
7.496
7.260
5.523
3.982
3.972
3.966
3.962
3.956
3.952
3.946
3.896
3.853
3.848
3.838
3.833
3.827
3.823
3.817
3.807
0.913
0.903
0.893
O
HO
NH
N
CO2Et
3I
1.000
1.005
2.008
1.010
2.012
2.035
1.016
1.011
1.002
1.004
3.089
f1 (ppm)

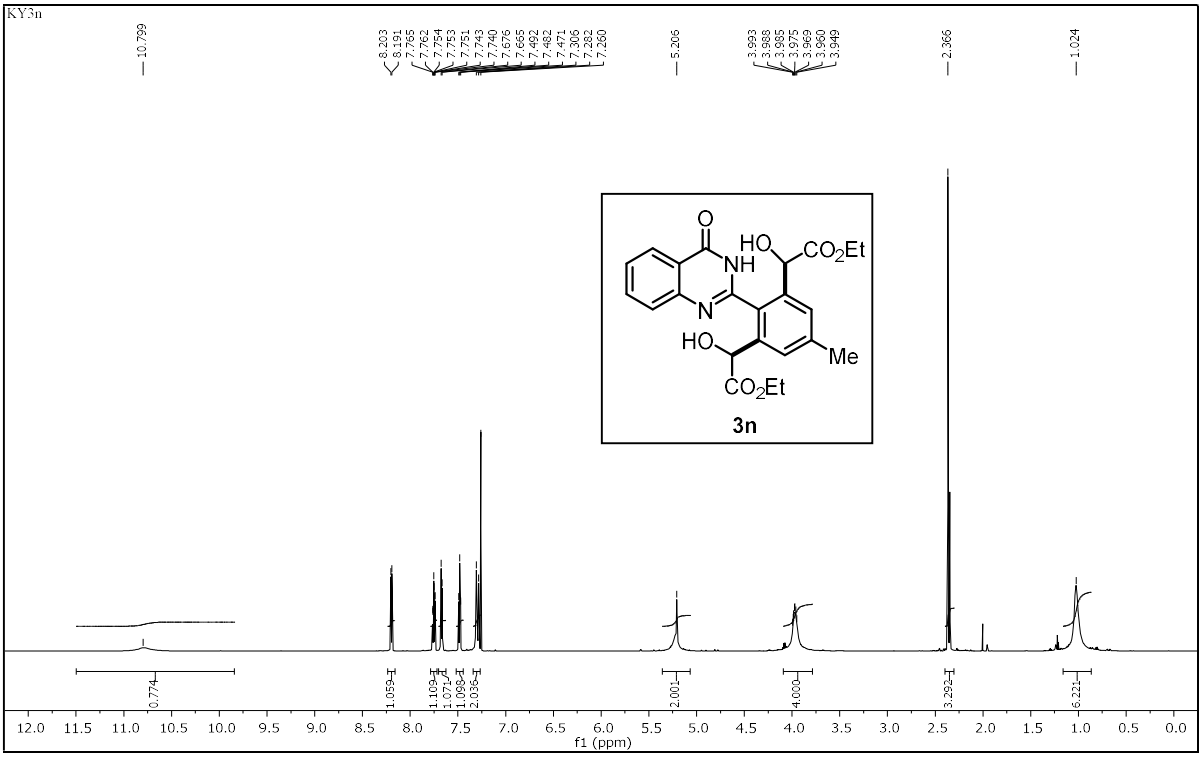

KY3I
173.062
163.385
153.534
147.574
135.484
135.373
134.383
132.498
131.631
131.164
129.702
128.695
128.570
128.126
127.747
127.654
127.320
126.583
120.689
77.341
77.160
76.979
74.860
61.618
14.004
O
HO
NH
N
CO2Et
3I
f1 (ppm)

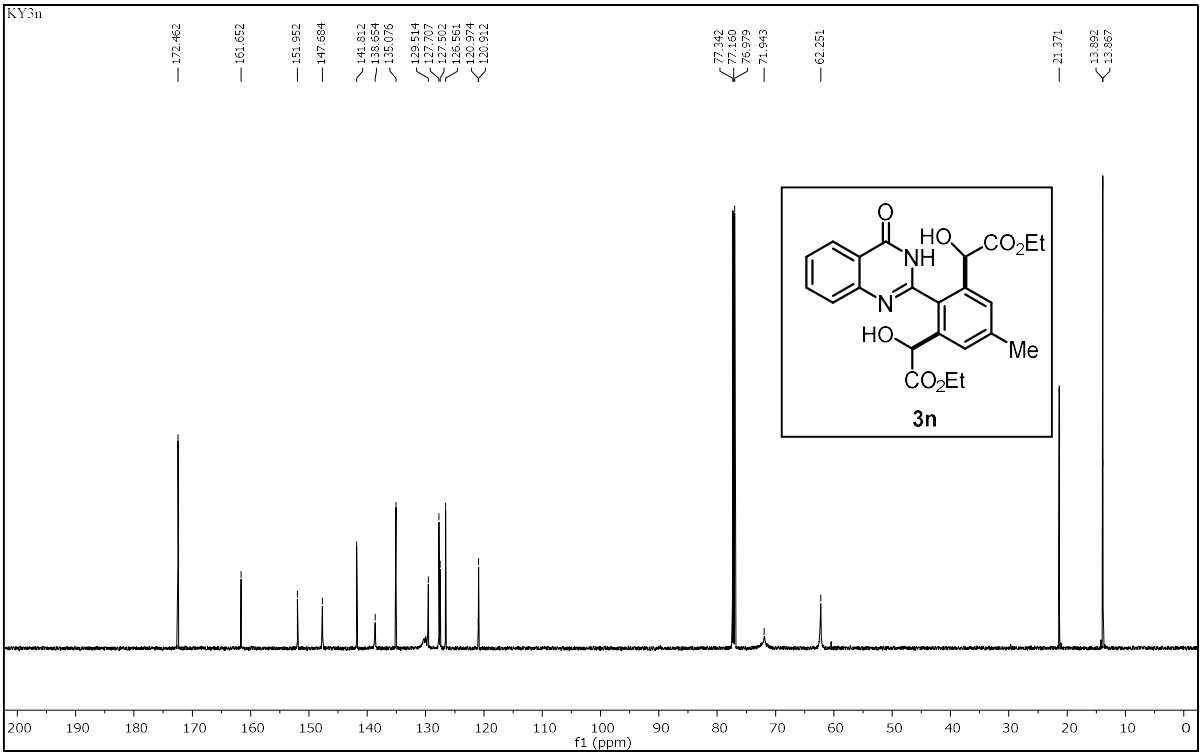
SpinWorks 4: KY448_1H_200701



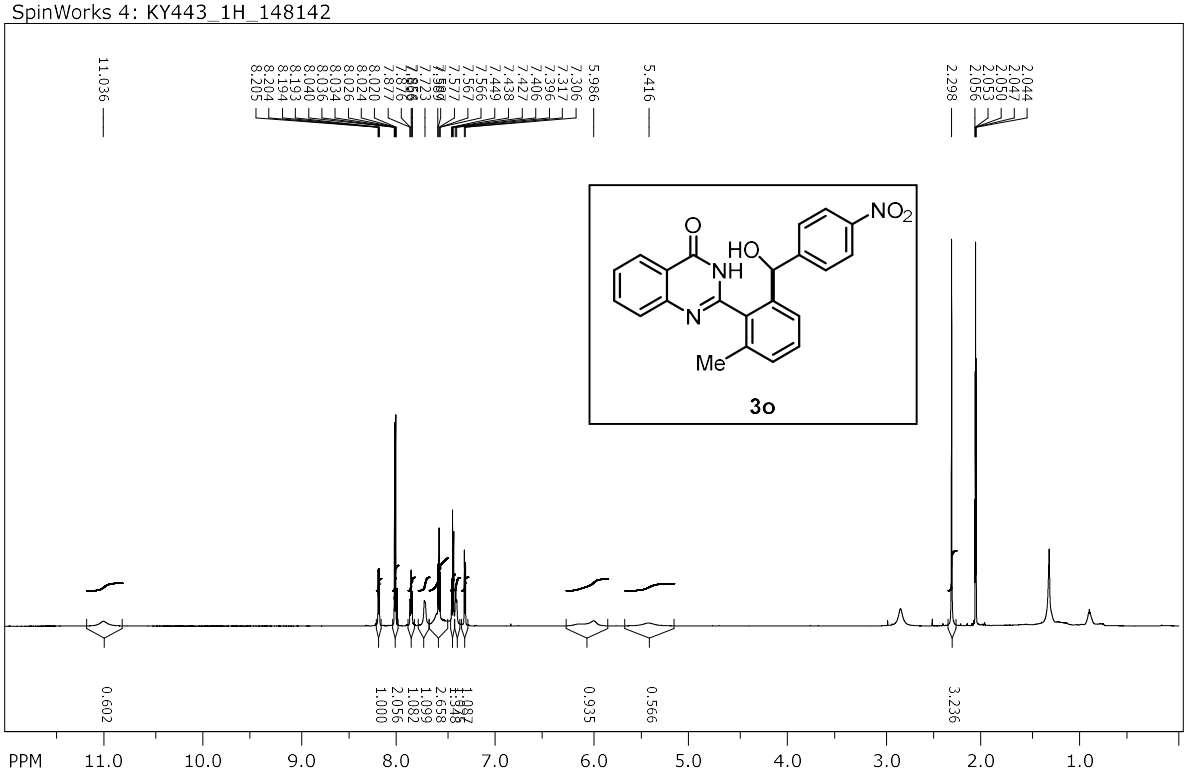

SpinWorks 4: KY448_13C_200701



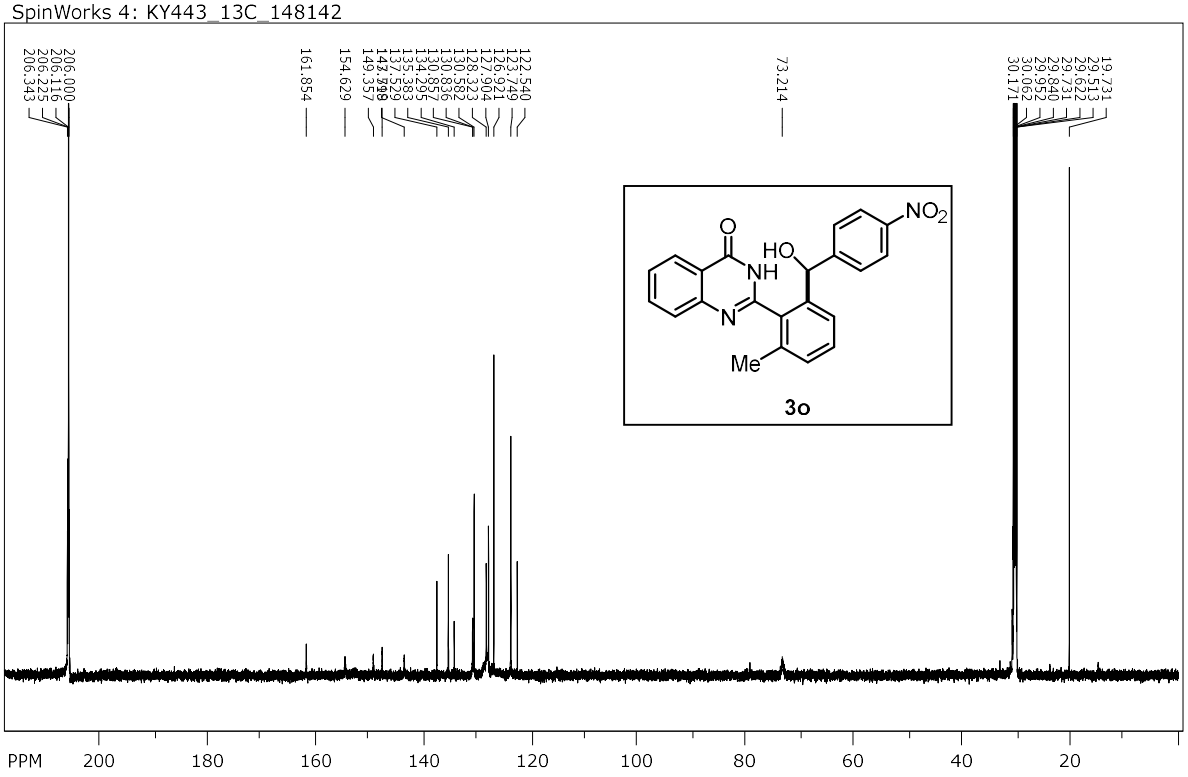

KY3n
10.799
8.203
8.191
7.765
7.762
7.754
7.753
7.751
7.743
7.740
7.676
7.665
7.492
7.482
7.471
7.306
7.282
7.260
5.206
3.993
3.988
3.985
3.975
3.969
3.960
3.949
2.366
1.024
HO
CO2Et
NH
N
HO
Me
CO2Et
3n
0.774
1.059
1.109
1.077
1.098
2.036
2.001
4.000
3.292
6.221
f1 (ppm)


KY3n
172.462
161.652
151.952
147.684
141.812
138.654
135.076
129.514
127.707
127.502
126.561
120.974
120.912
77.342
77.160
76.979
71.943
62.251
21.371
13.892
13.867
HO
CO2Et
NH
N
HO
Me
CO2Et
3n
f1 (ppm)

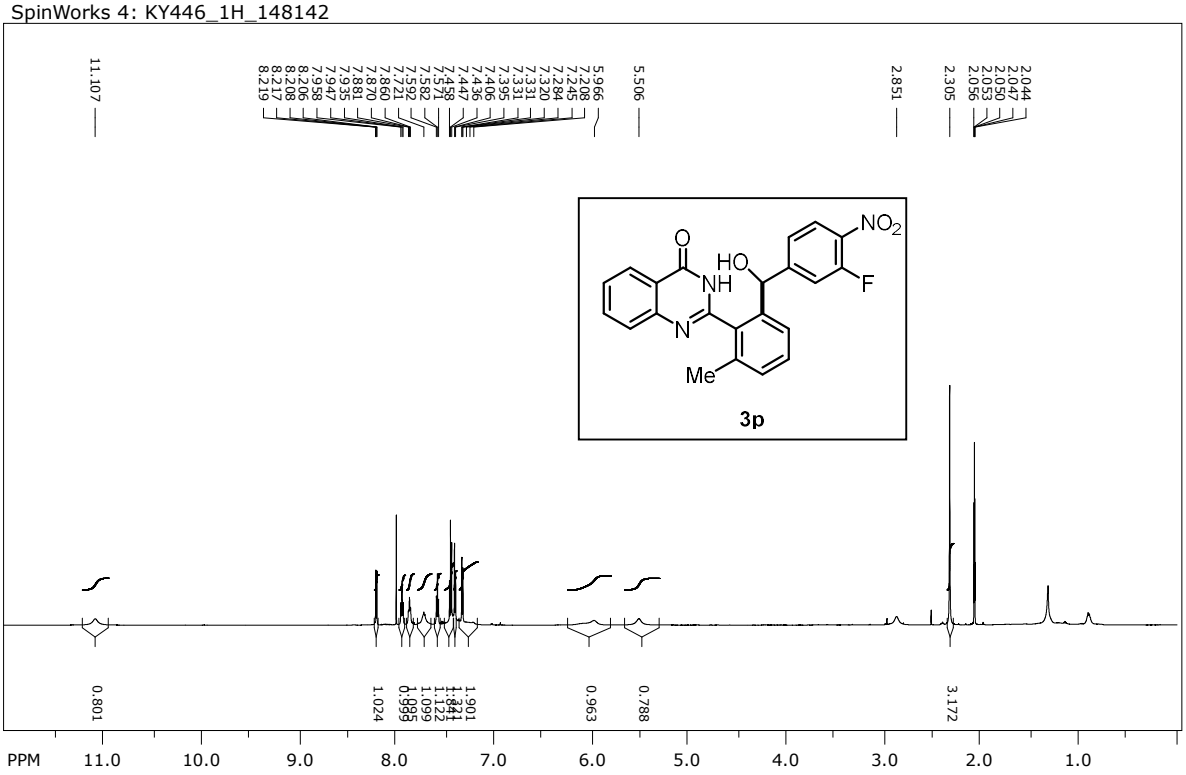
SpinWorks 4: KY443_1H_148142

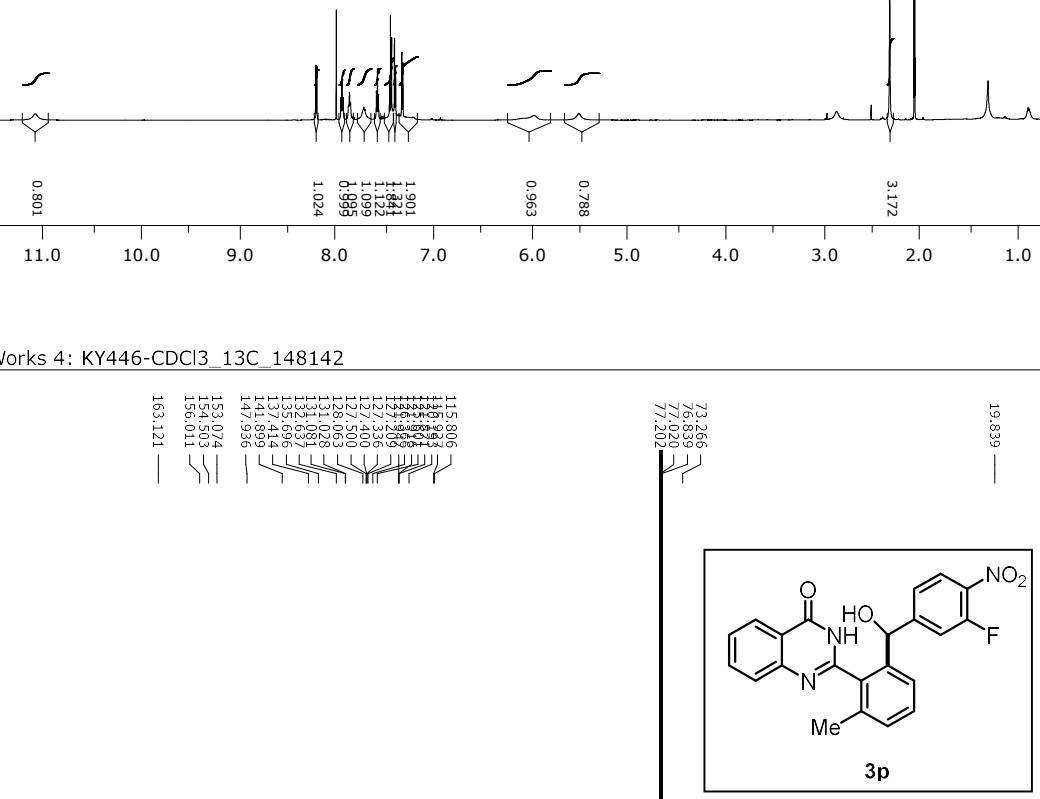



SpinWorks 4: KY443_13C_148142



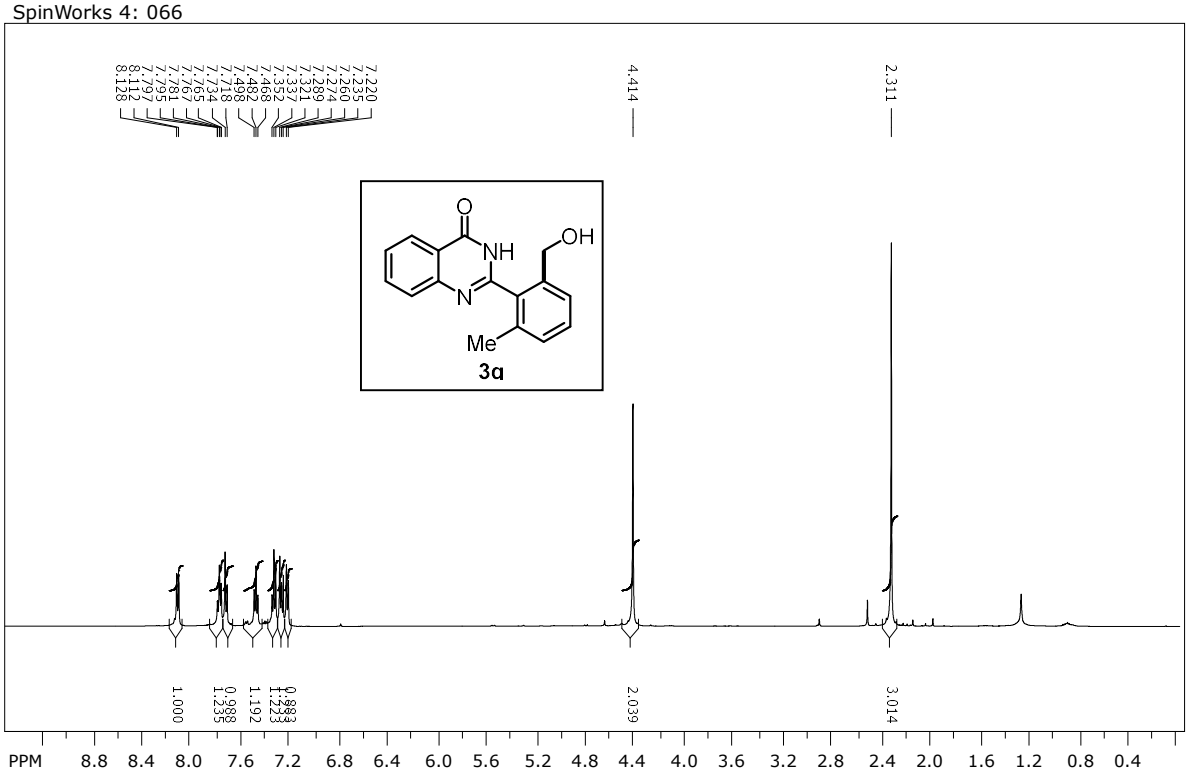
SpinWorks 4: KY446_1H_148142



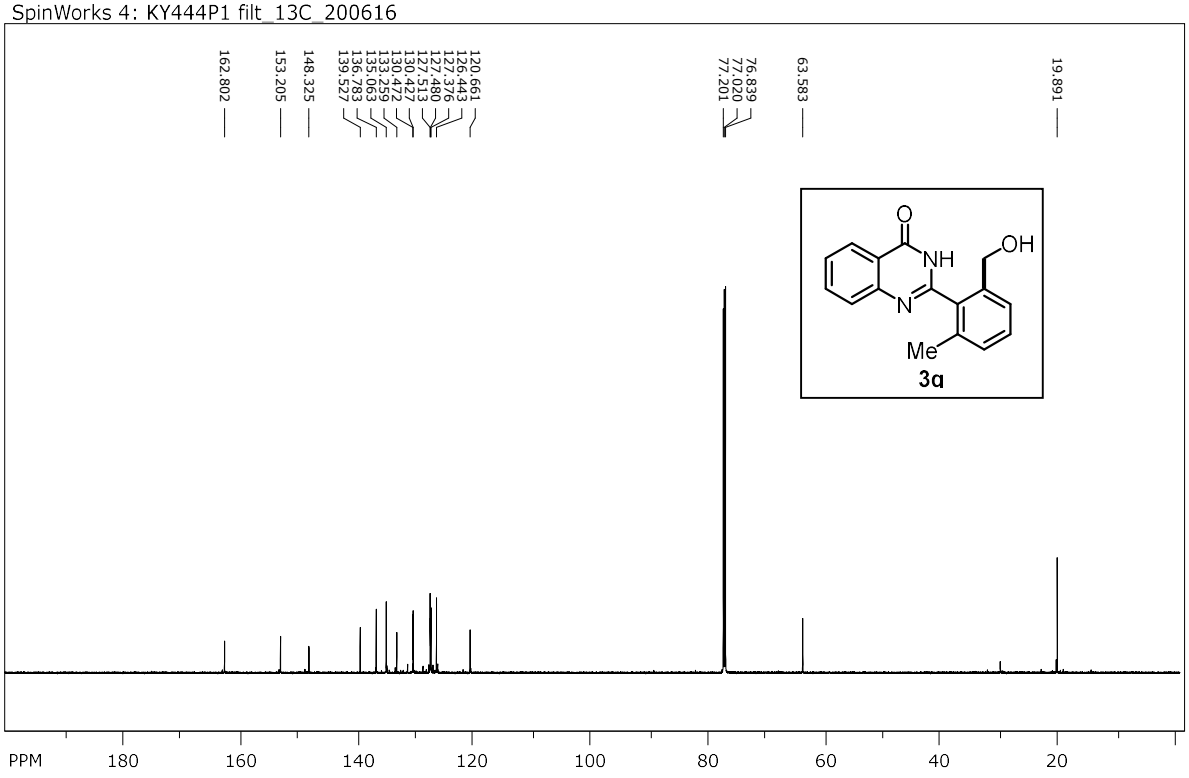




SpinWorks 4: KY446-CDCl3_13C_148142

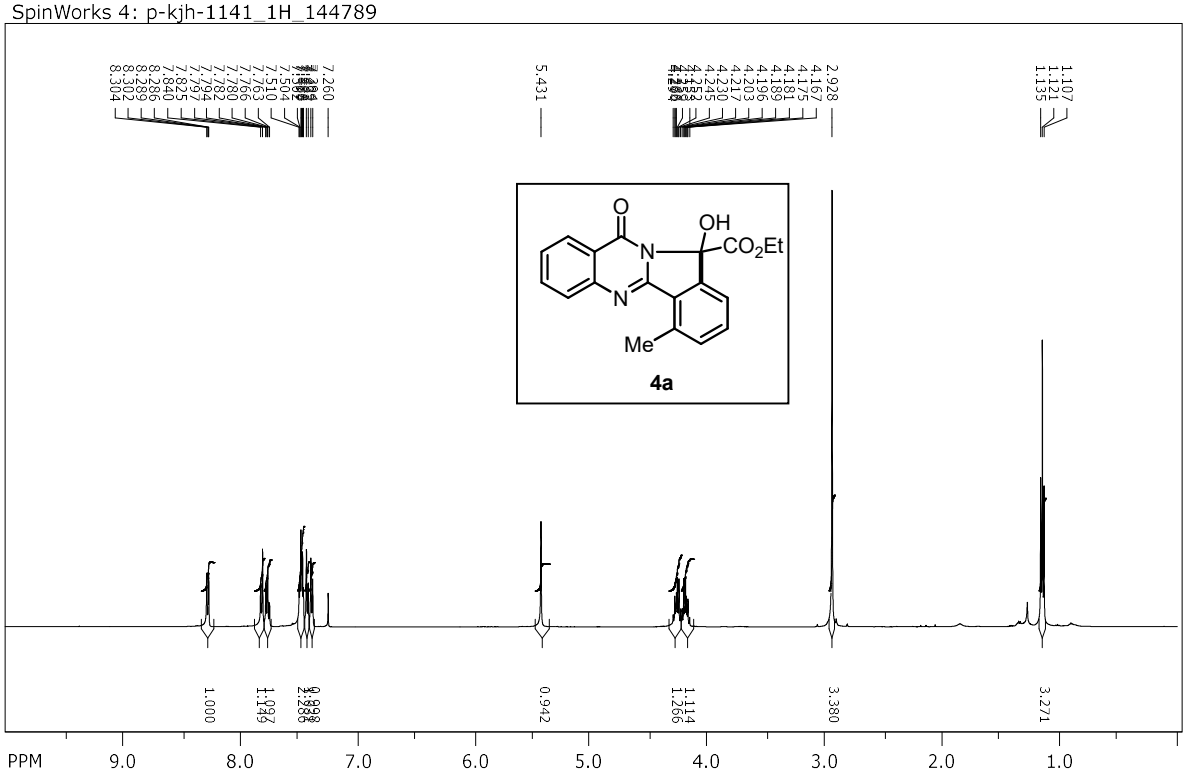
SpinWorks 4: 066



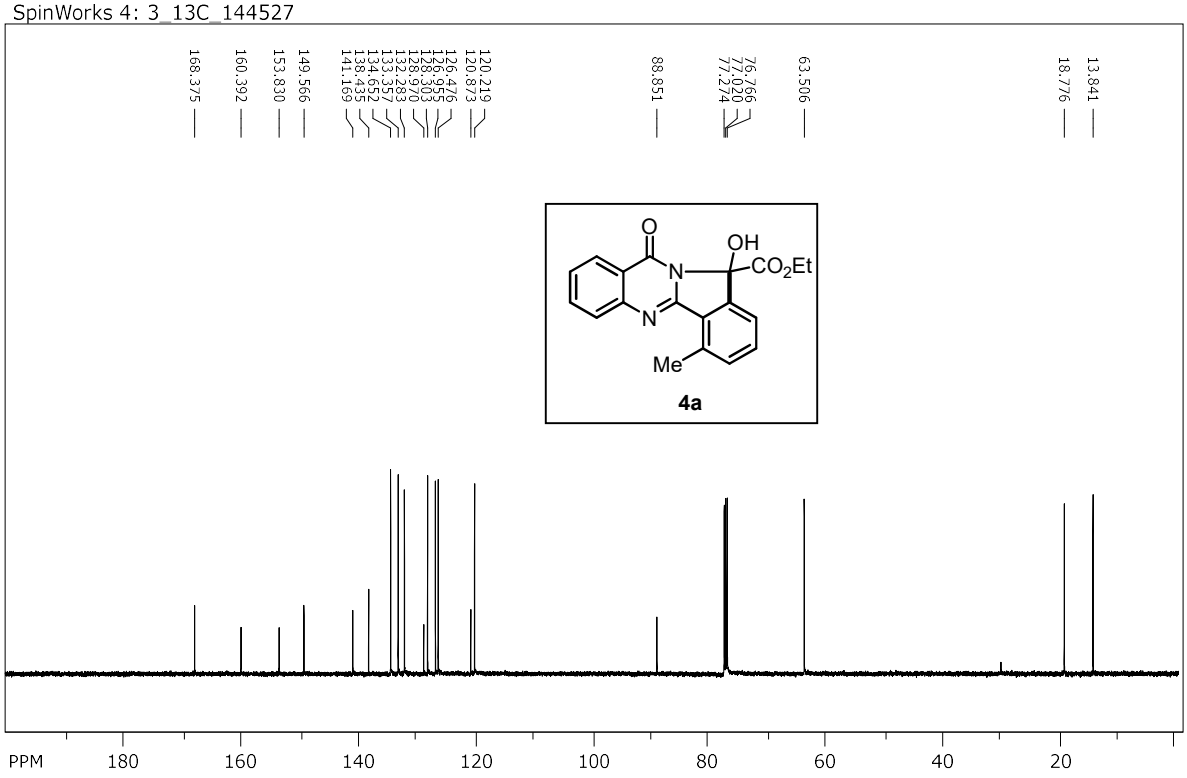

SpinWorks 4: KY444P1 filt_13C_200616



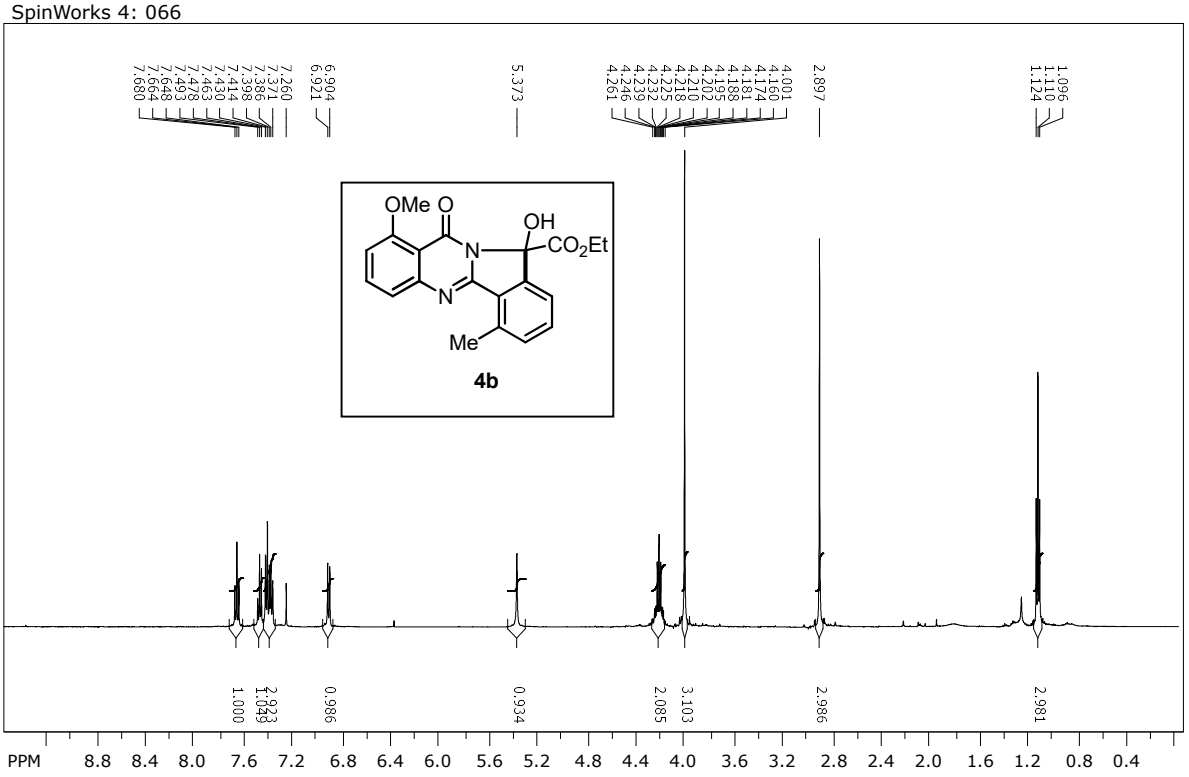
SpinWorks 4: p-kjh-1141_1H_144789



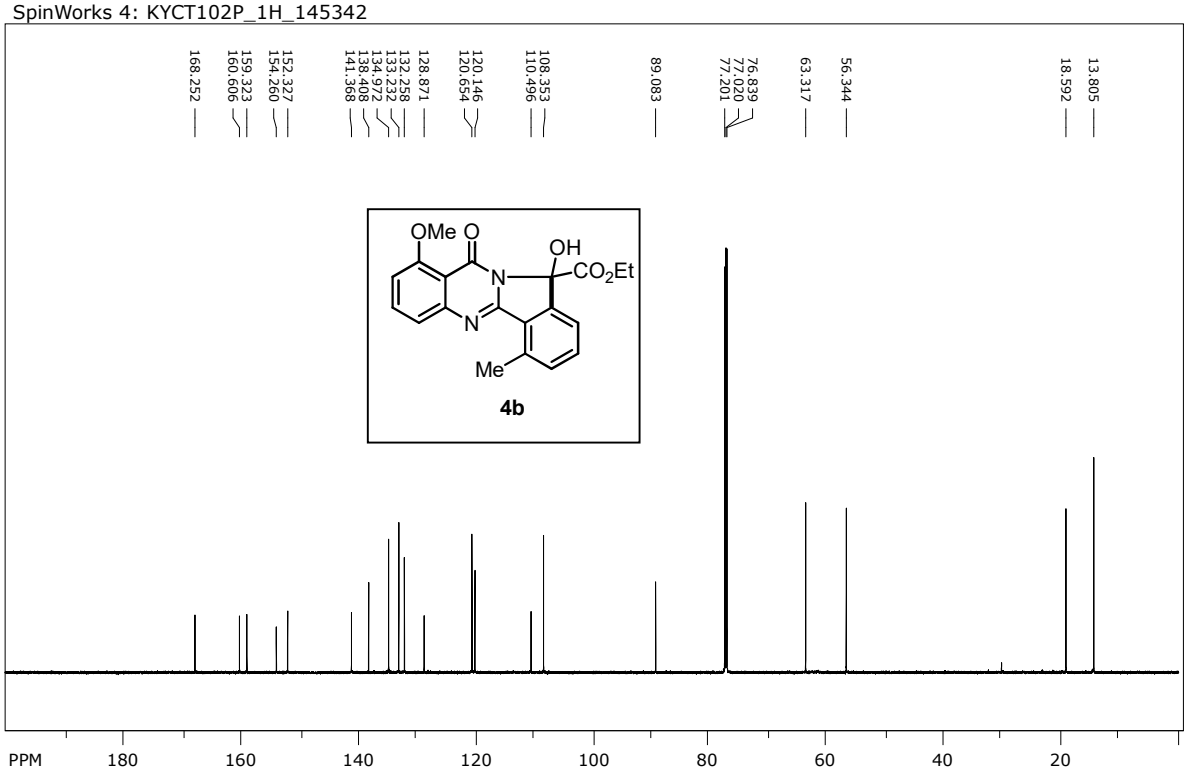

SpinWorks 4: 3_13C_144527



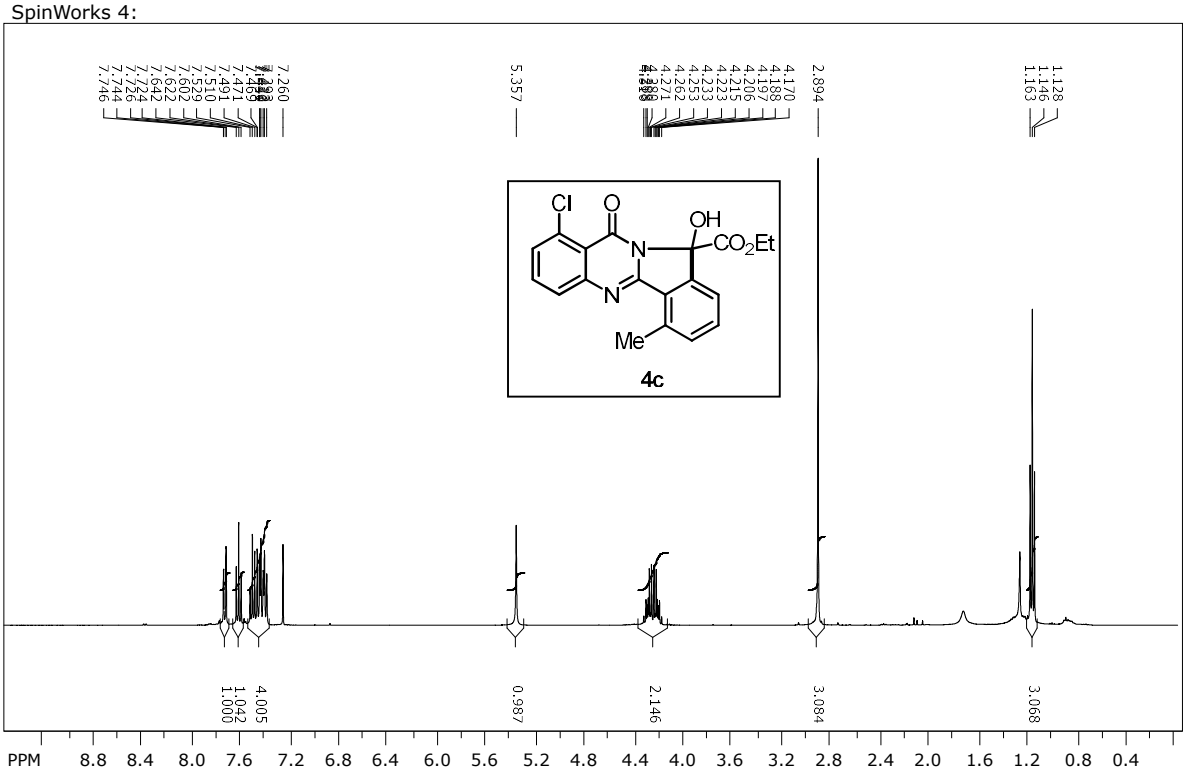
SpinWorks 4: 066



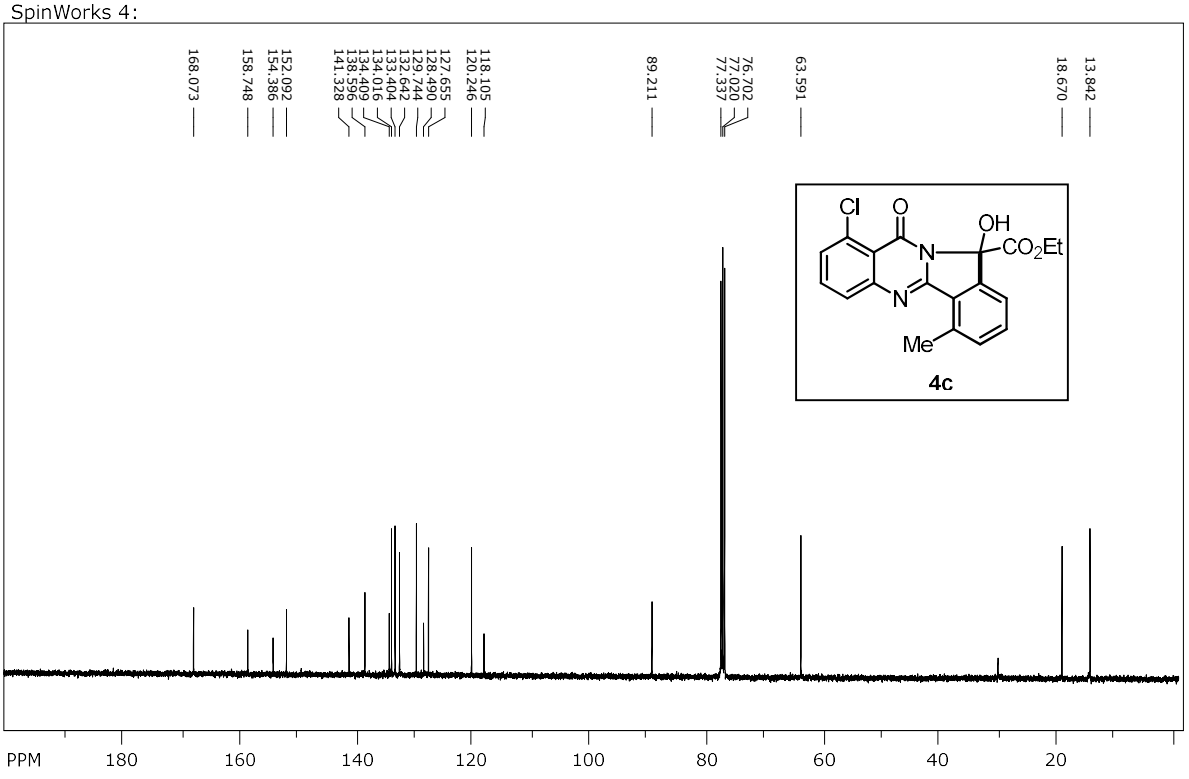

SpinWorks 4: KYCT102P_1H_145342



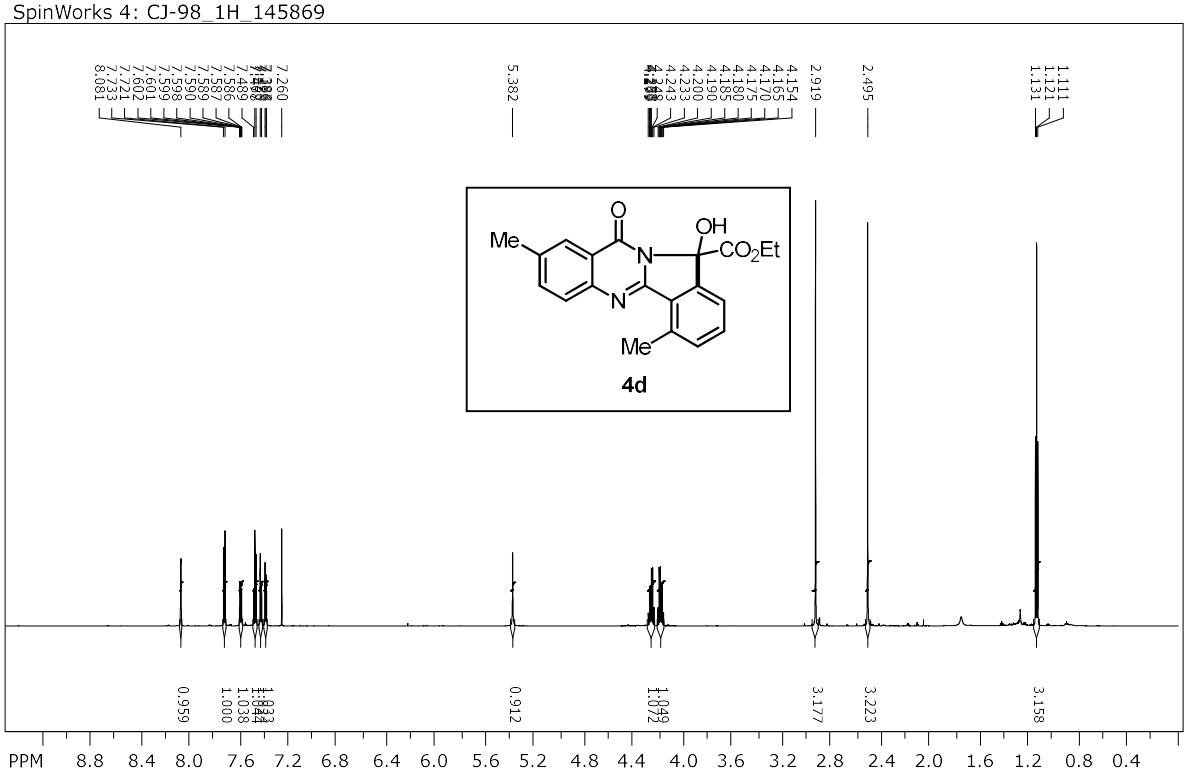
SpinWorks 4:



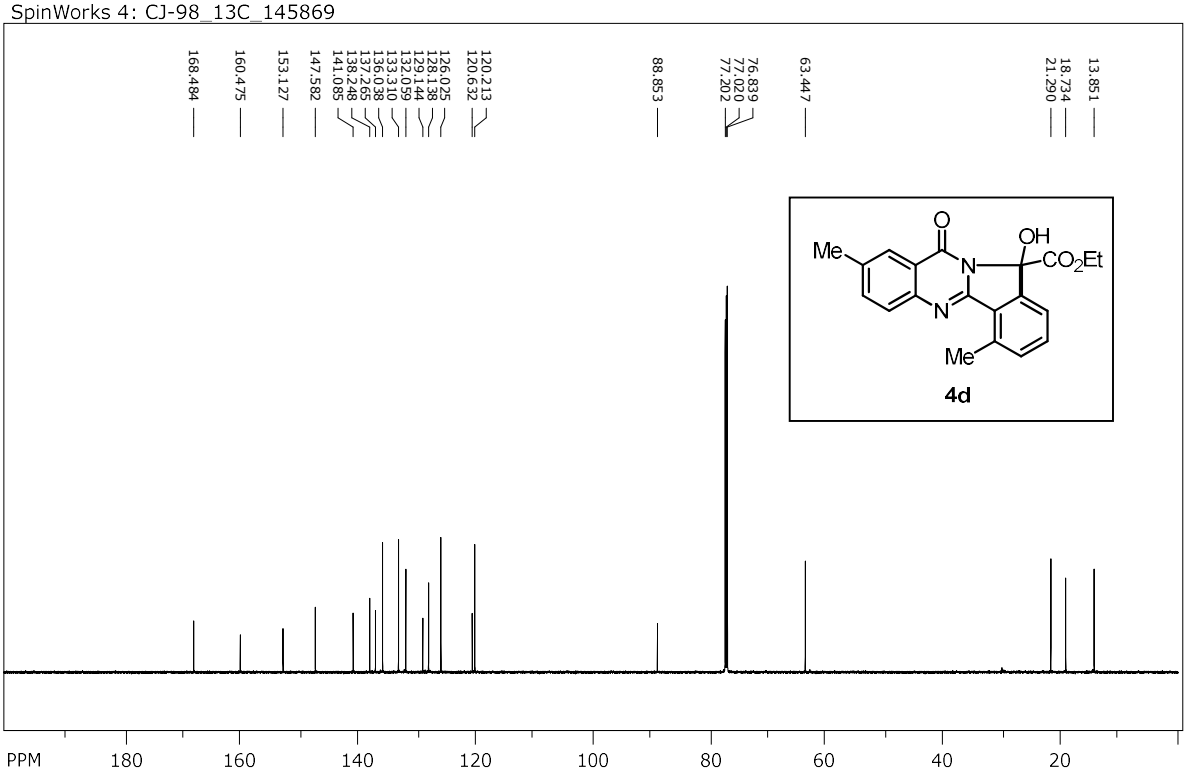

SpinWorks 4:



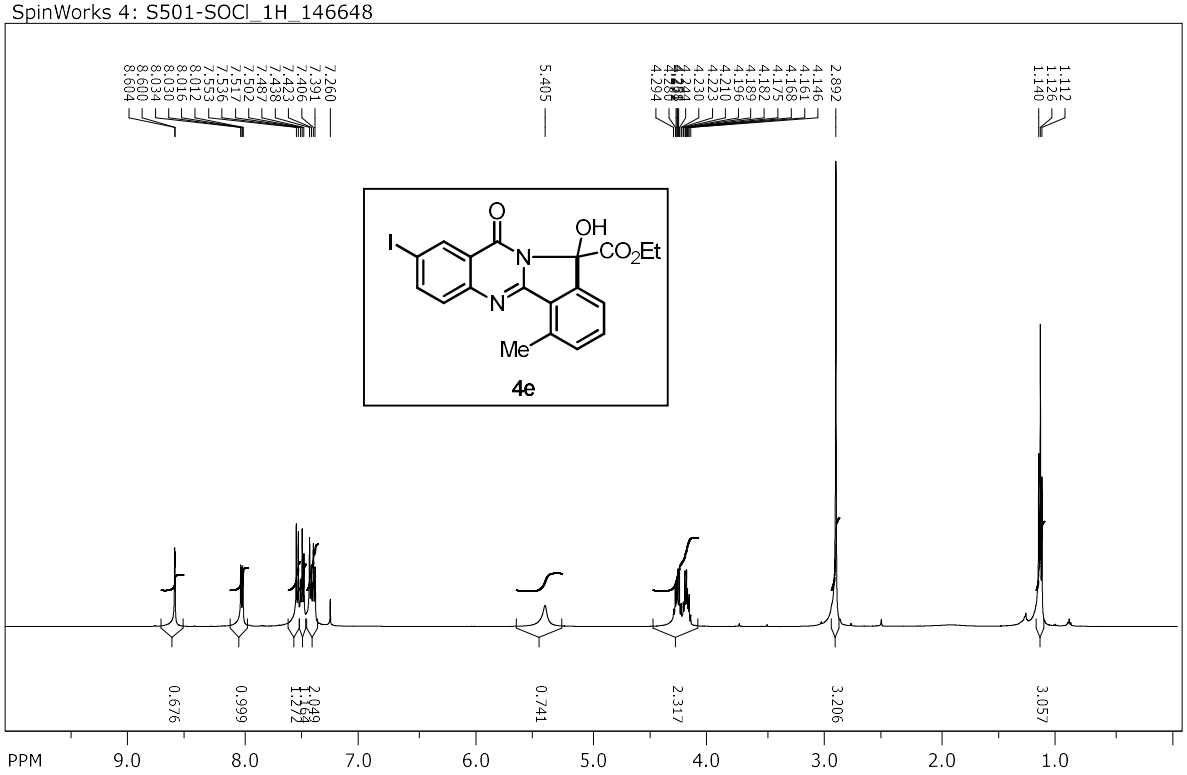
SpinWorks 4: CJ-98_1H_145869



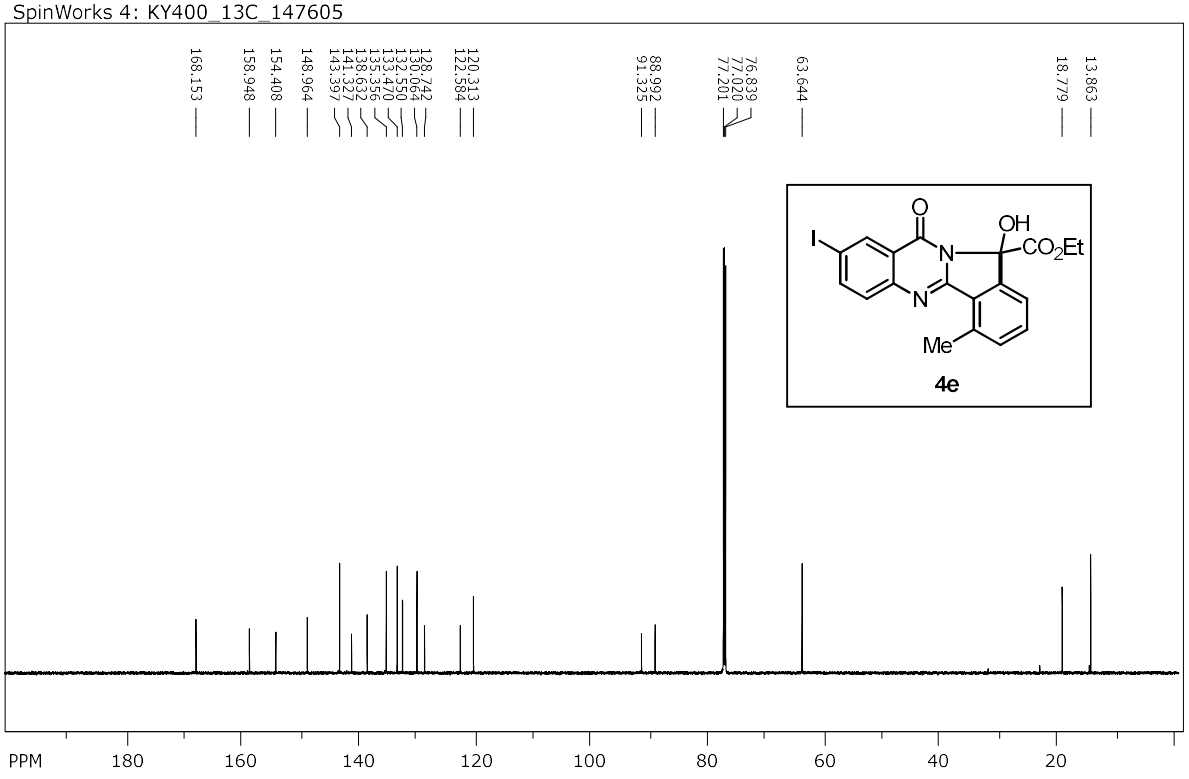

SpinWorks 4: CJ-98_13C_145869



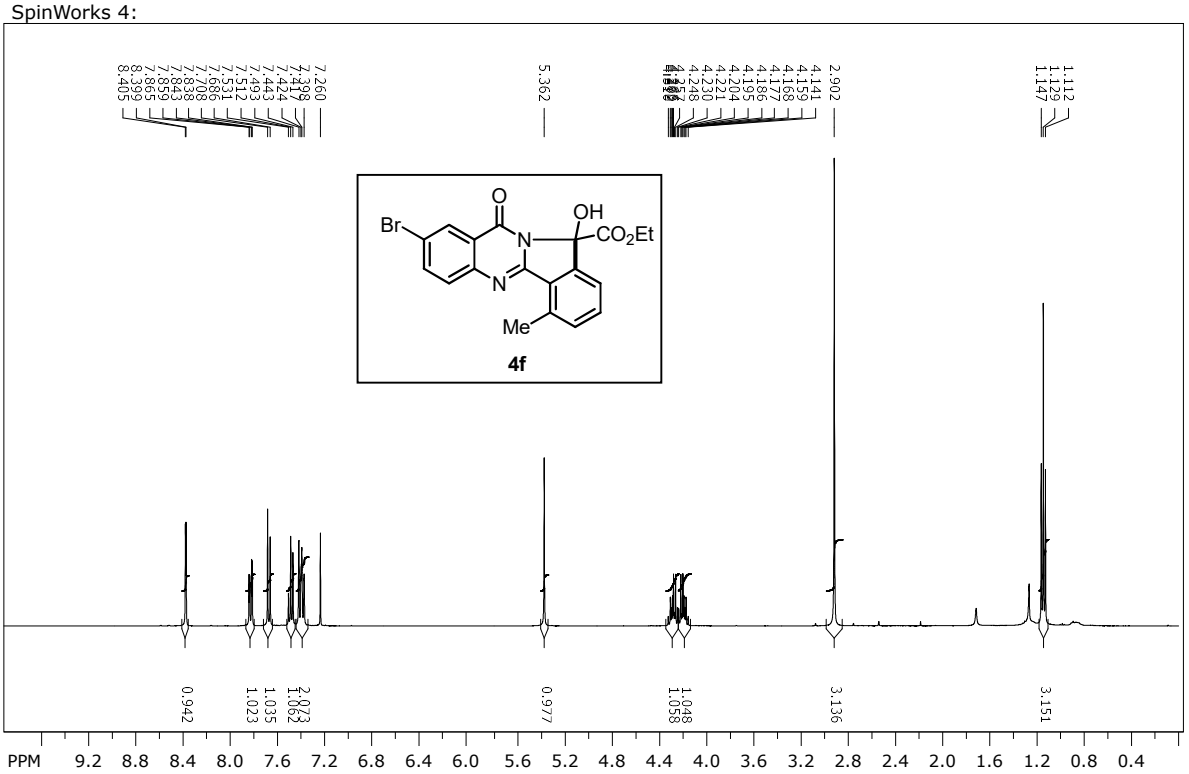
SpinWorks 4: S501-SOCl_1H_146648



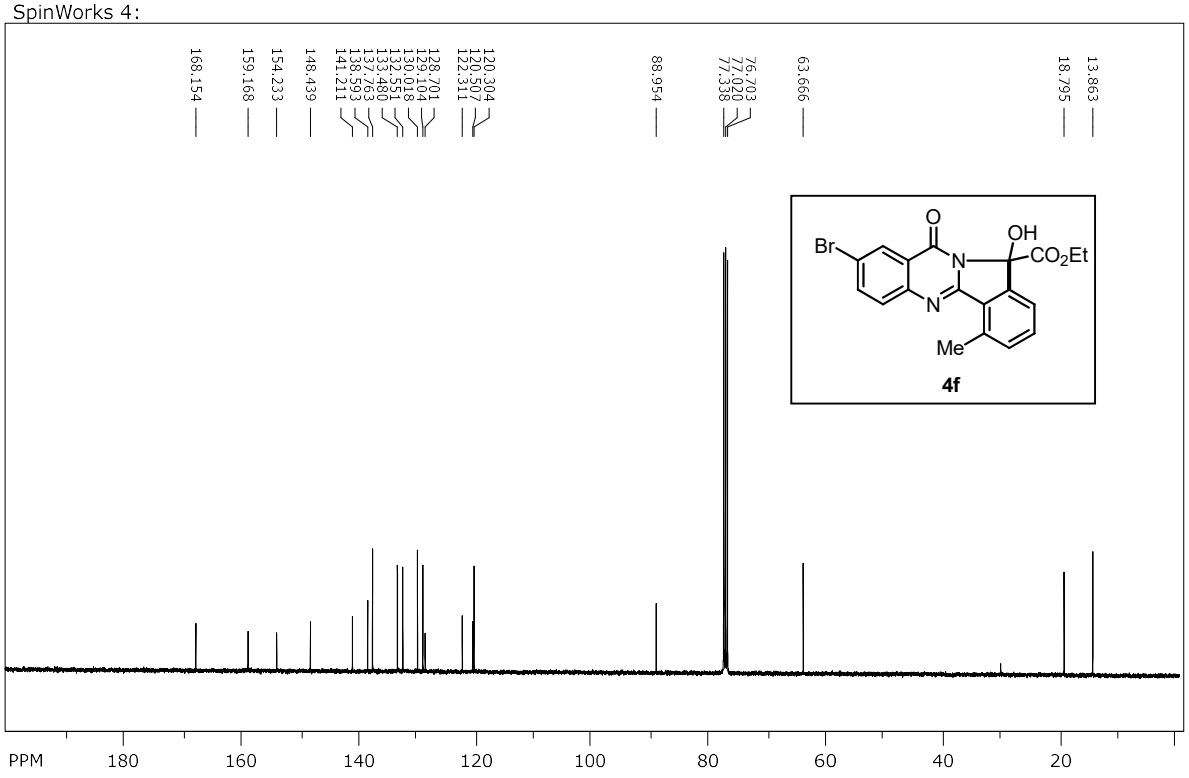

SpinWorks 4: KY400_13C_147605



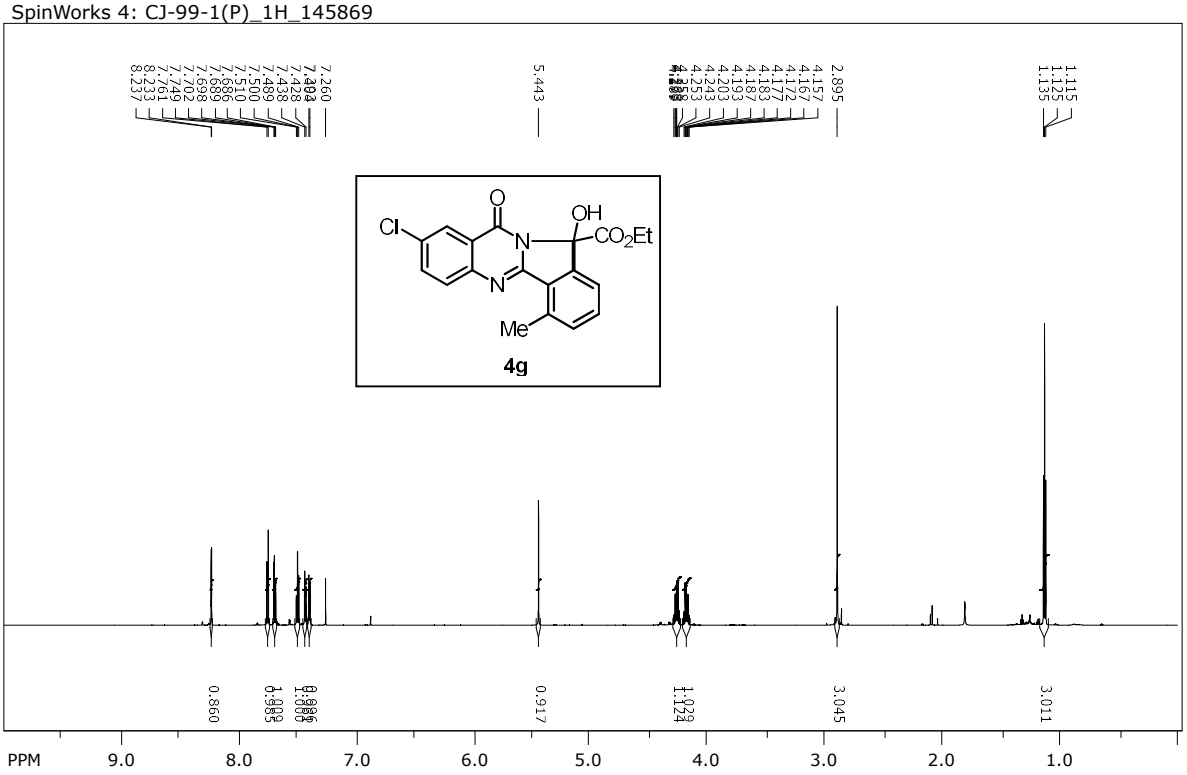
SpinWorks 4:



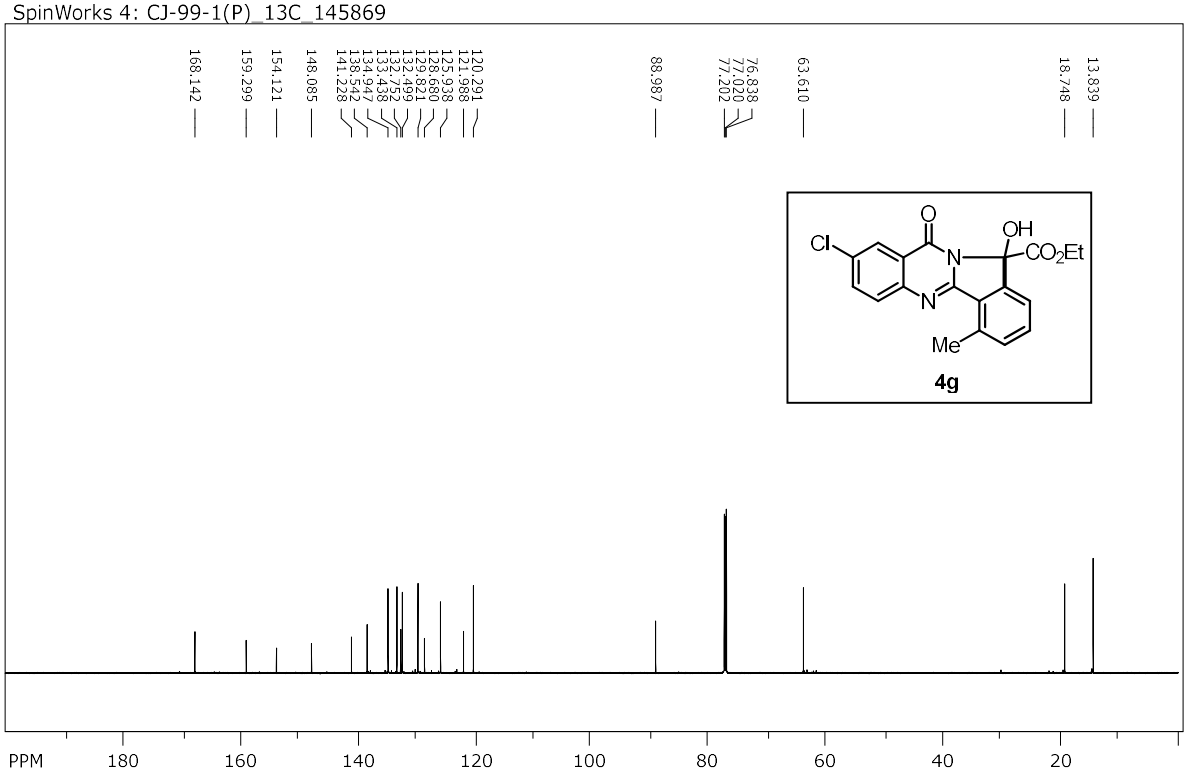

SpinWorks 4:



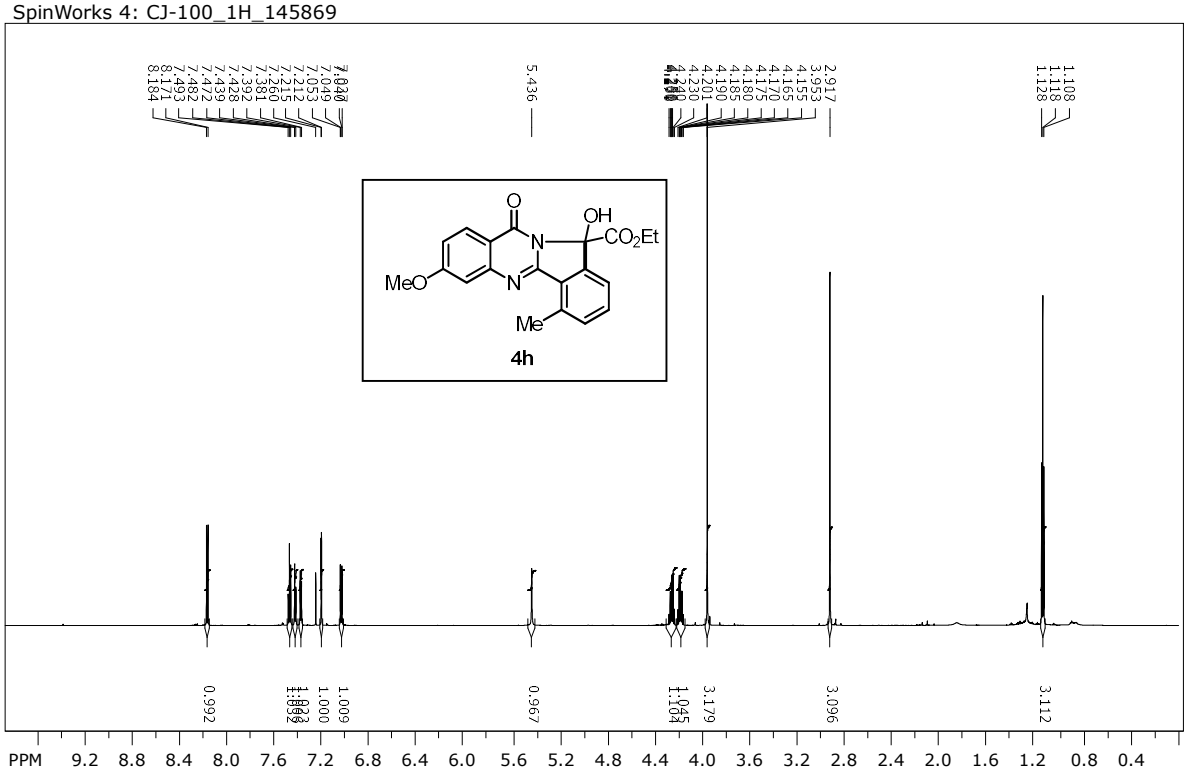
SpinWorks 4: CJ-99-1(P)_1H_145869



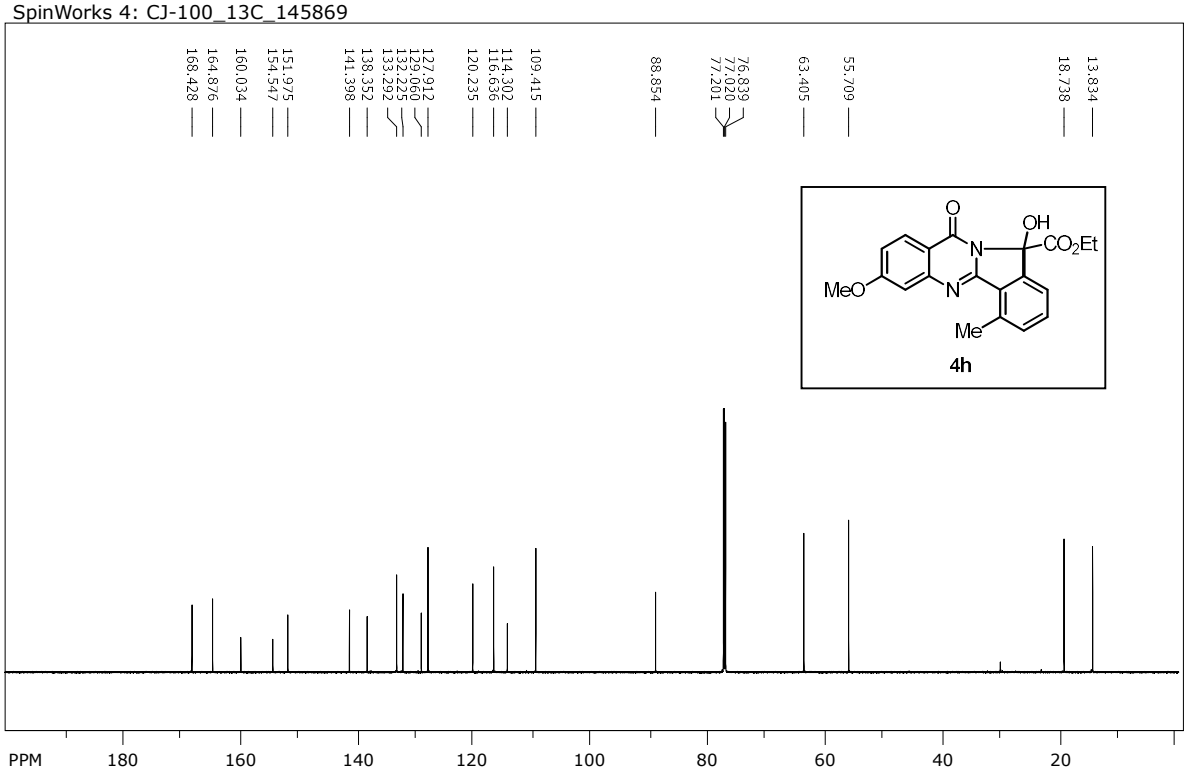

SpinWorks 4: CJ-99-1(P)_13C_145869



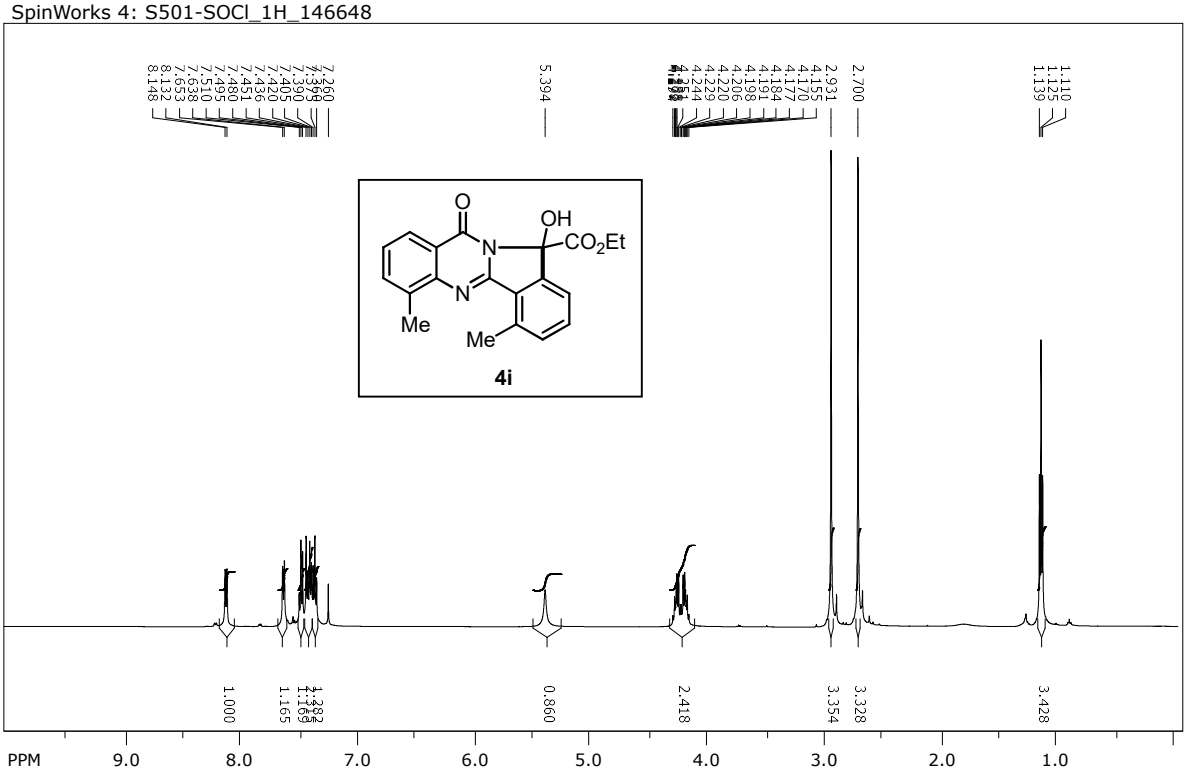
SpinWorks 4: CJ-100_1H_145869



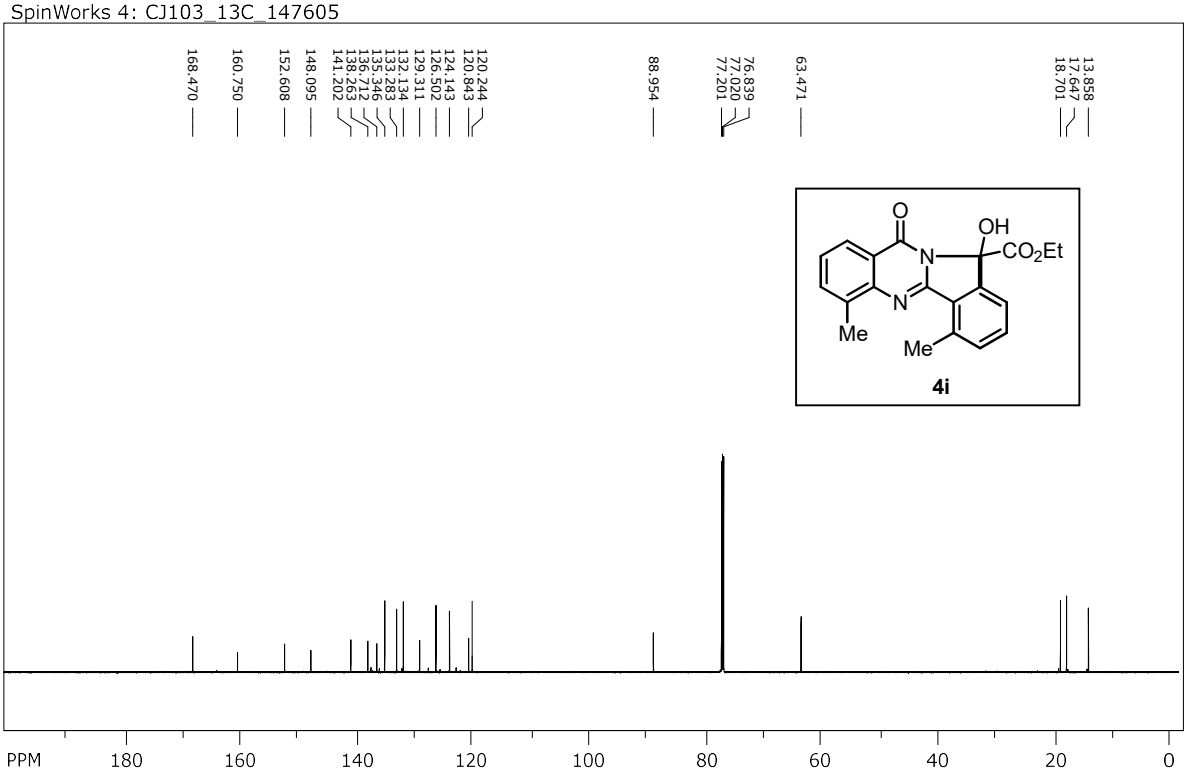

SpinWorks 4: CJ-100_13C_145869



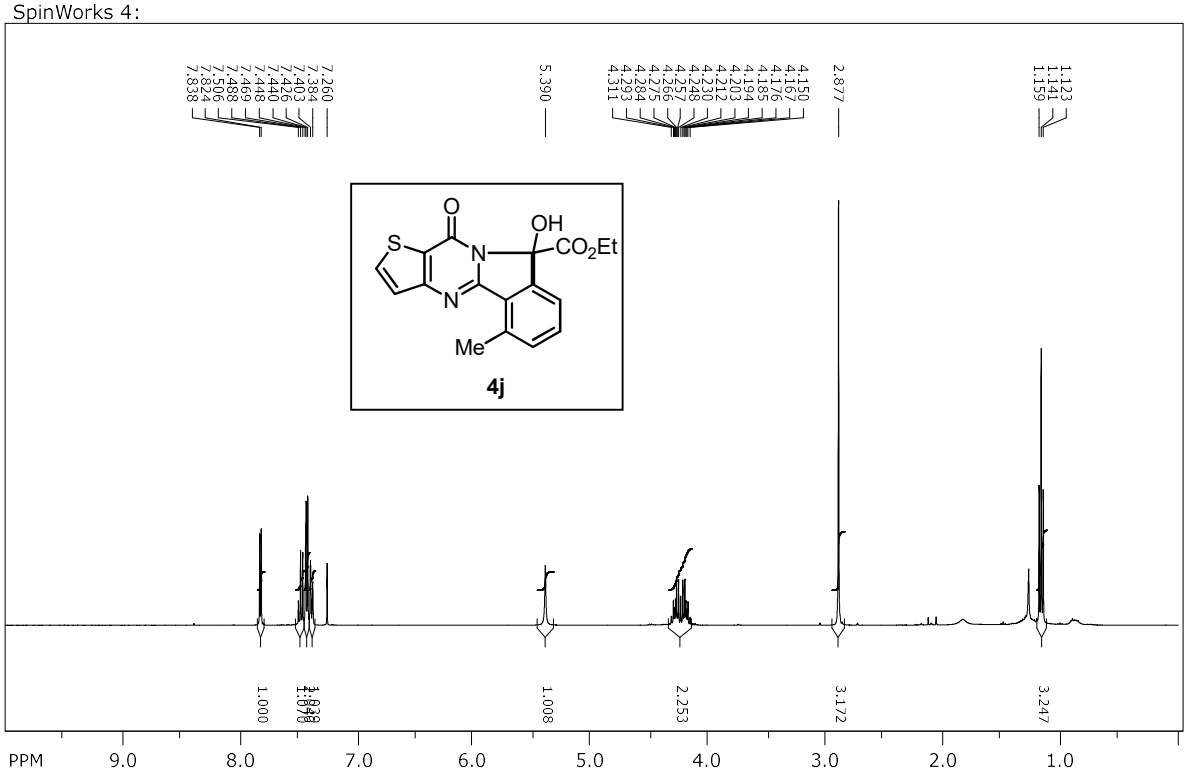
SpinWorks 4: S501-SOCl_1H_146648



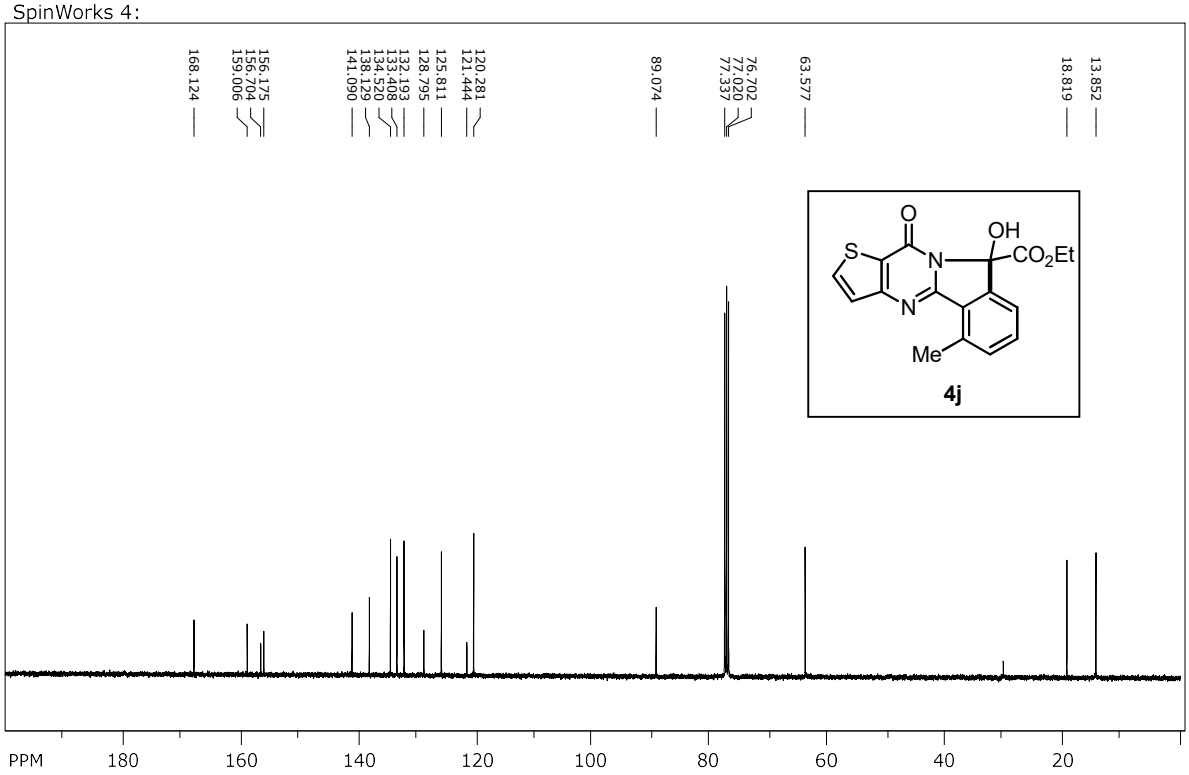

SpinWorks 4: CJ103_13C_147605



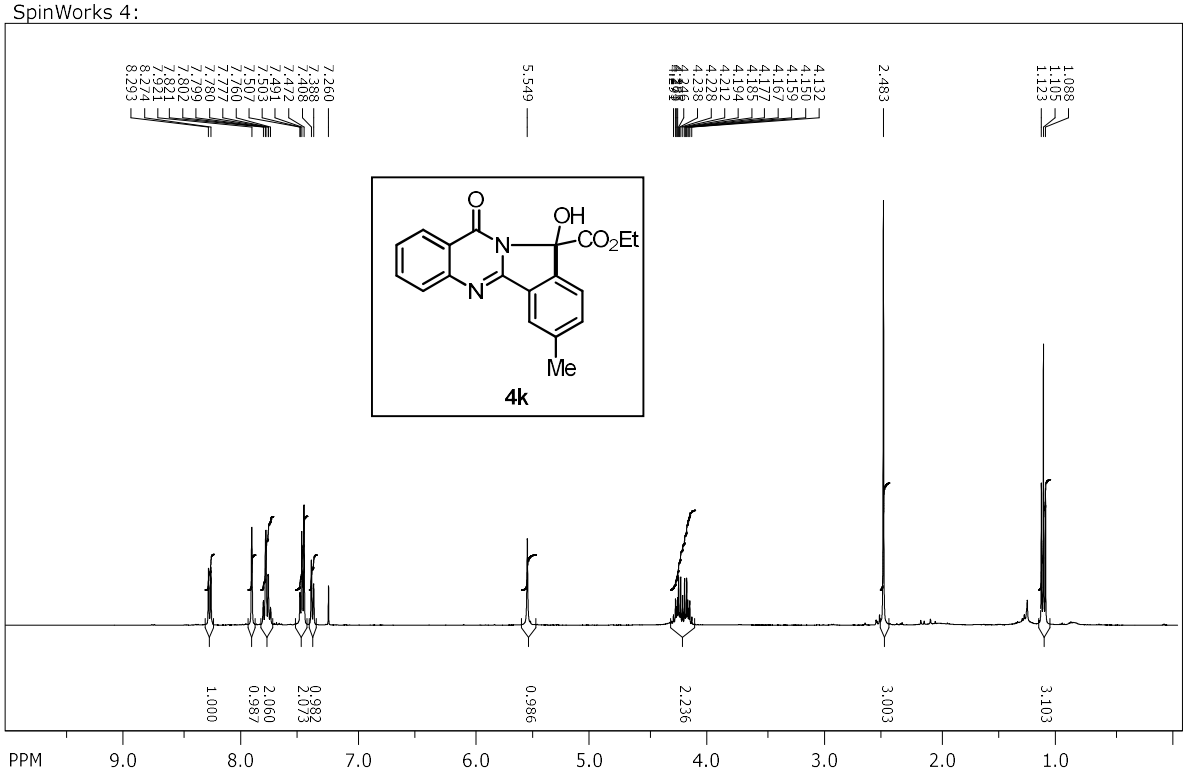
SpinWorks 4:



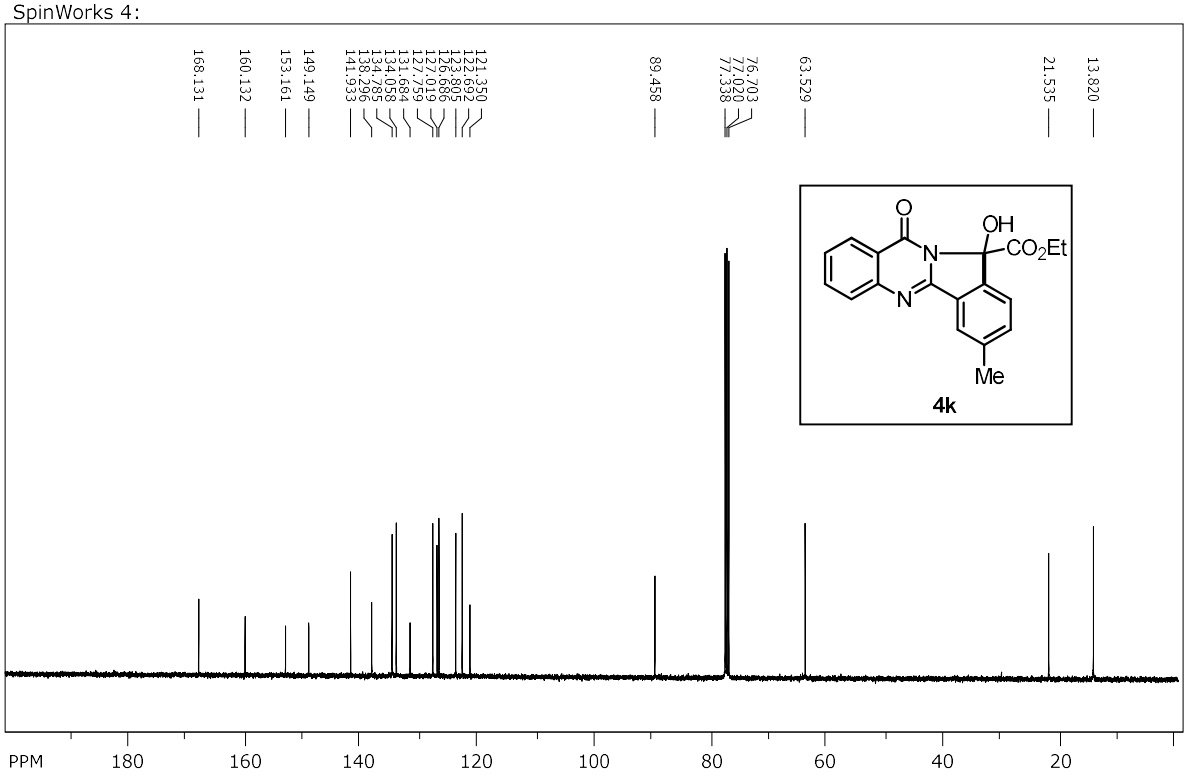

SpinWorks 4:

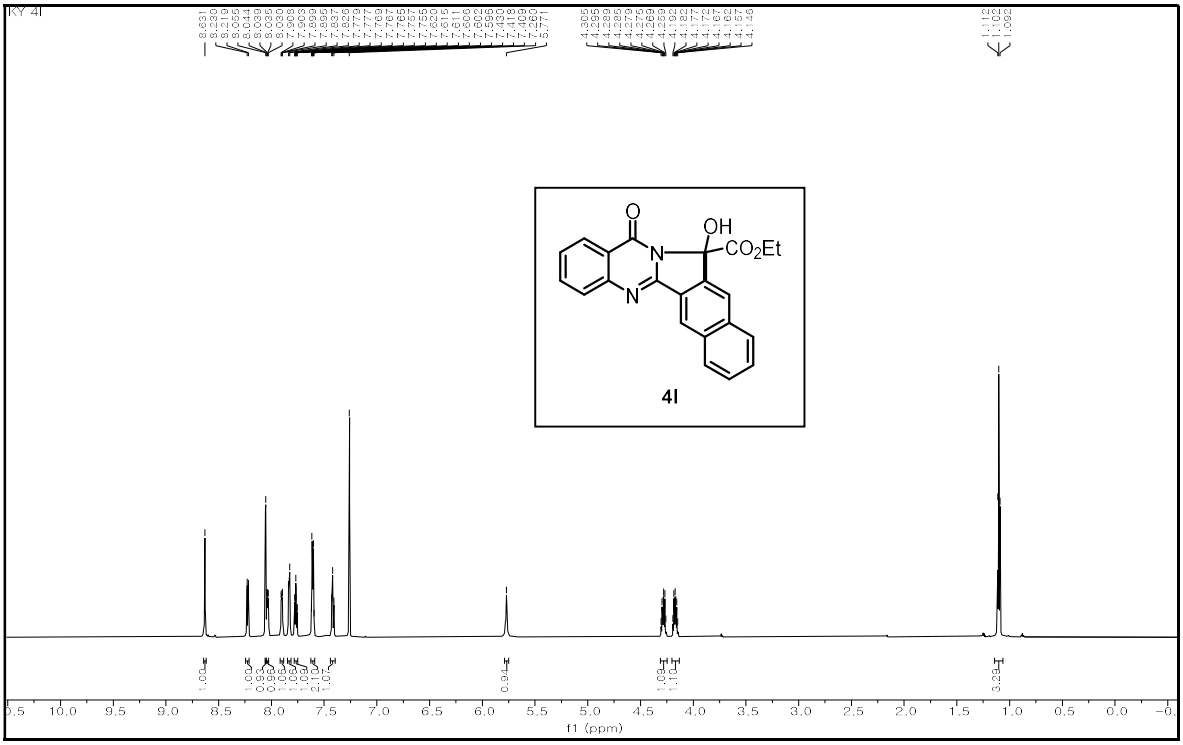


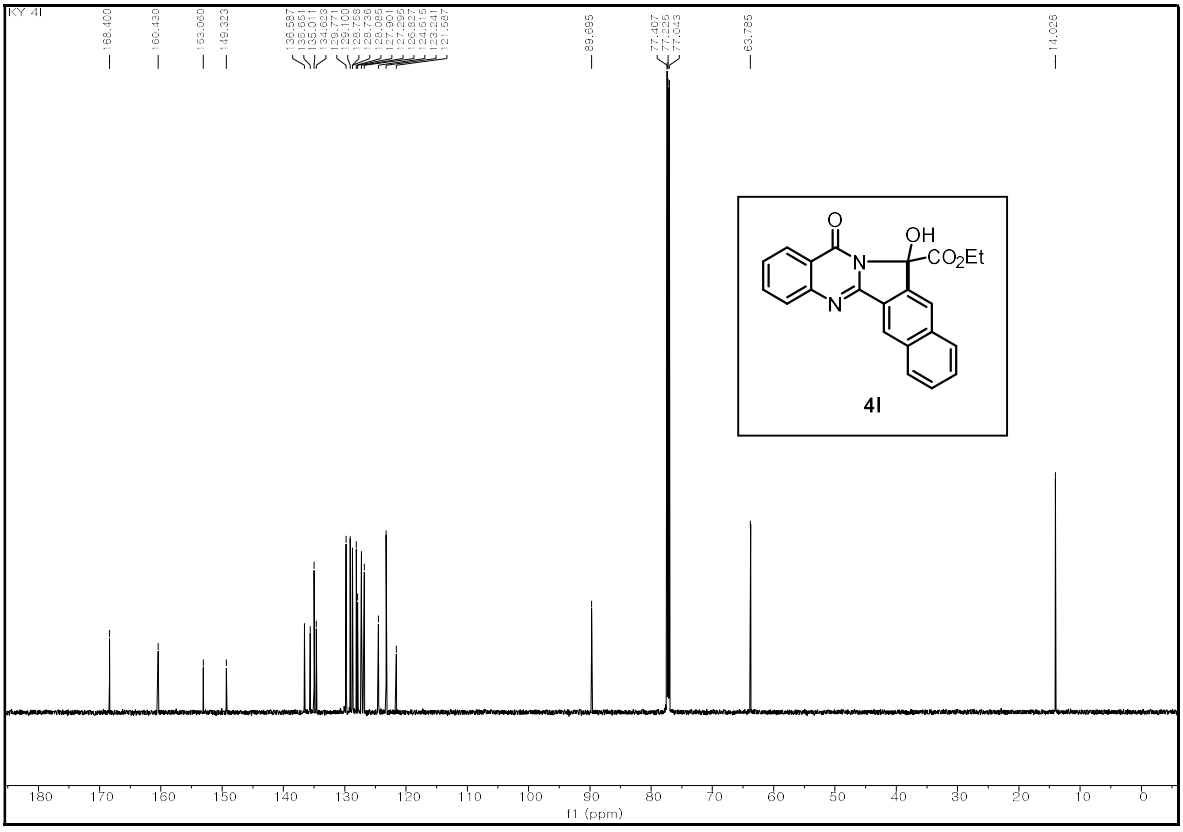
SpinWorks 4:

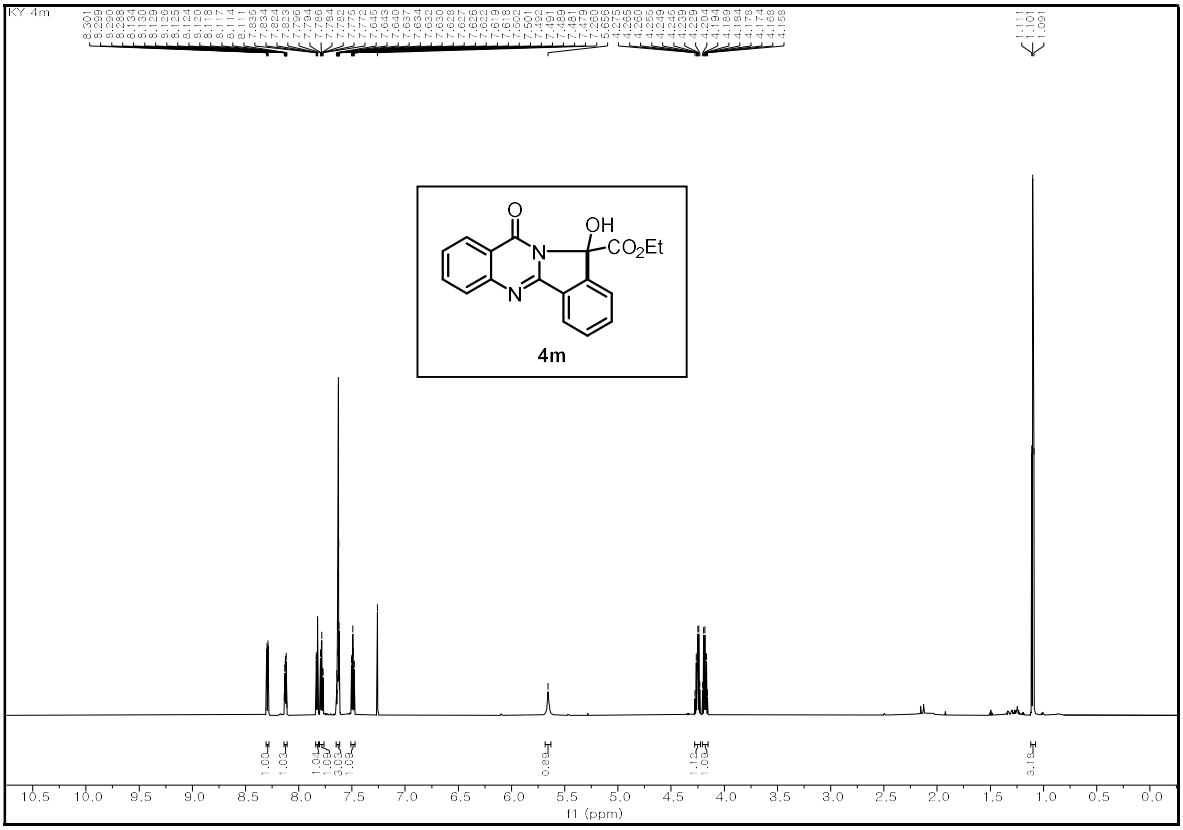


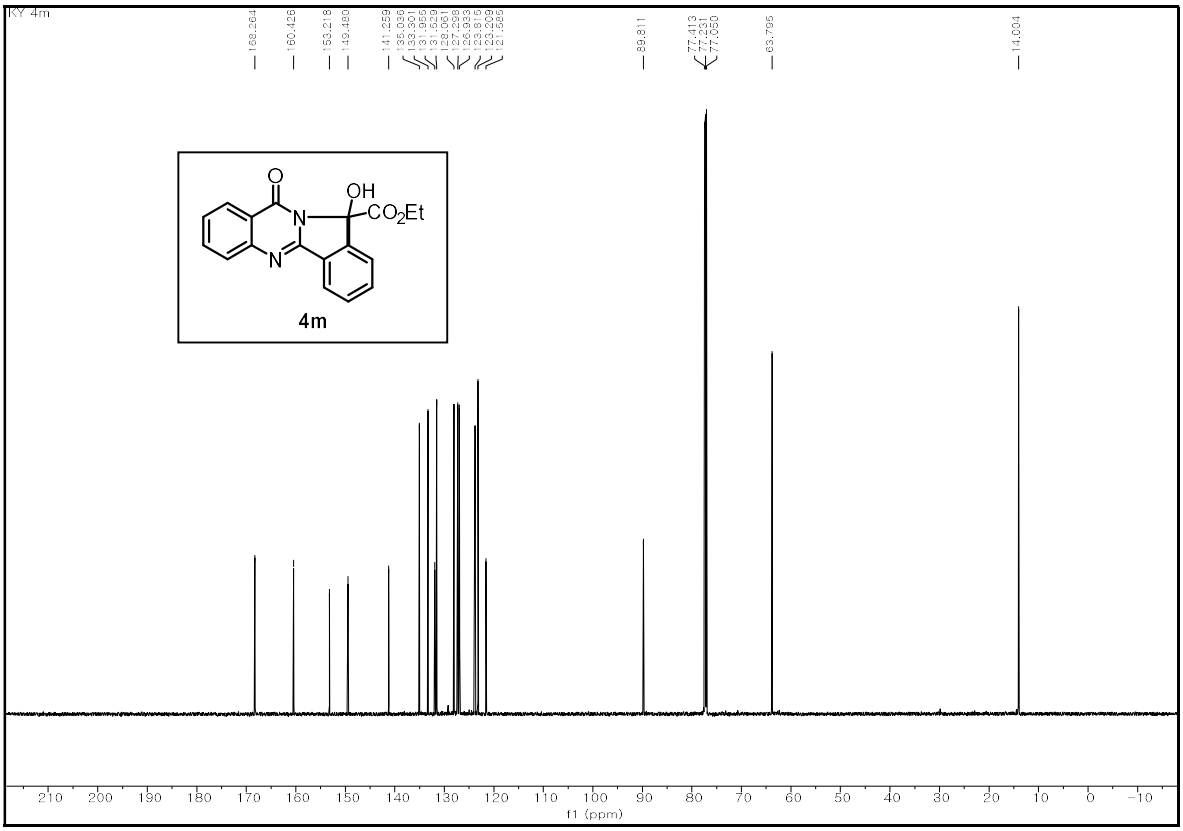

SpinWorks 4:



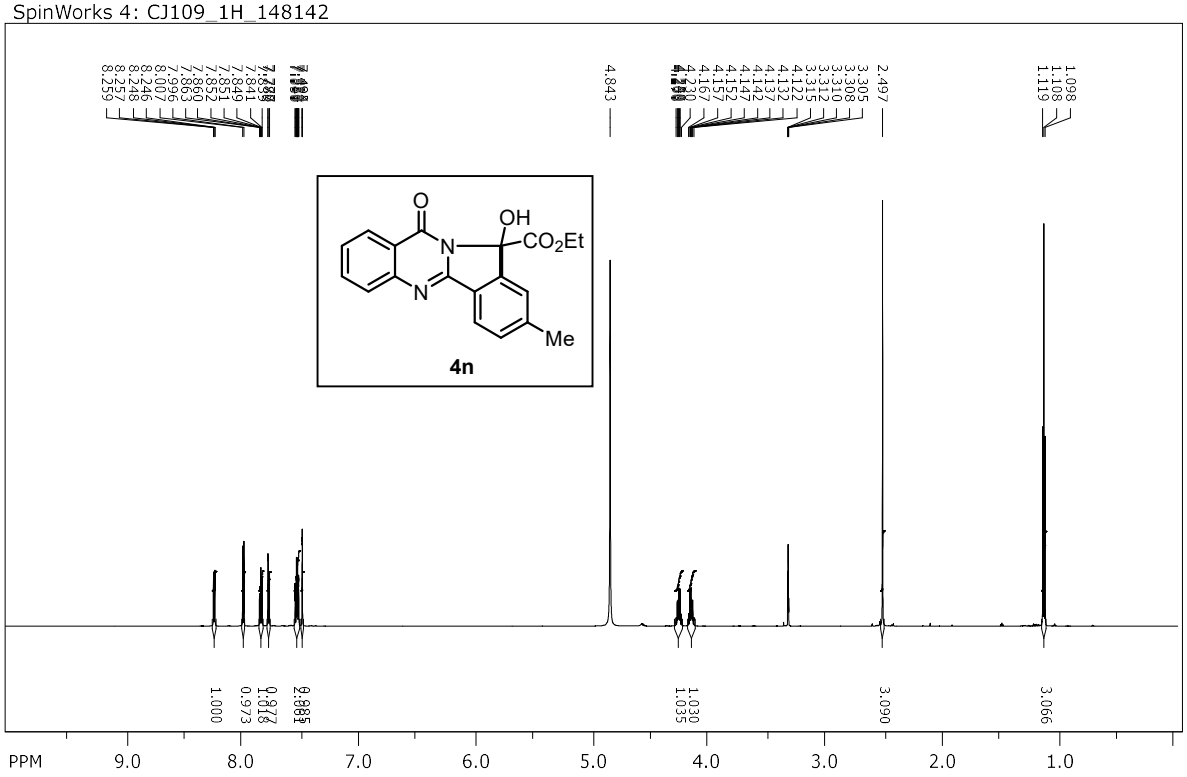

KY 4I
O
OH
N
N
CO2Et
4l
f1 (ppm)


KY 4I
O
OH
N
N
CO2Et
4l
f1 (ppm)

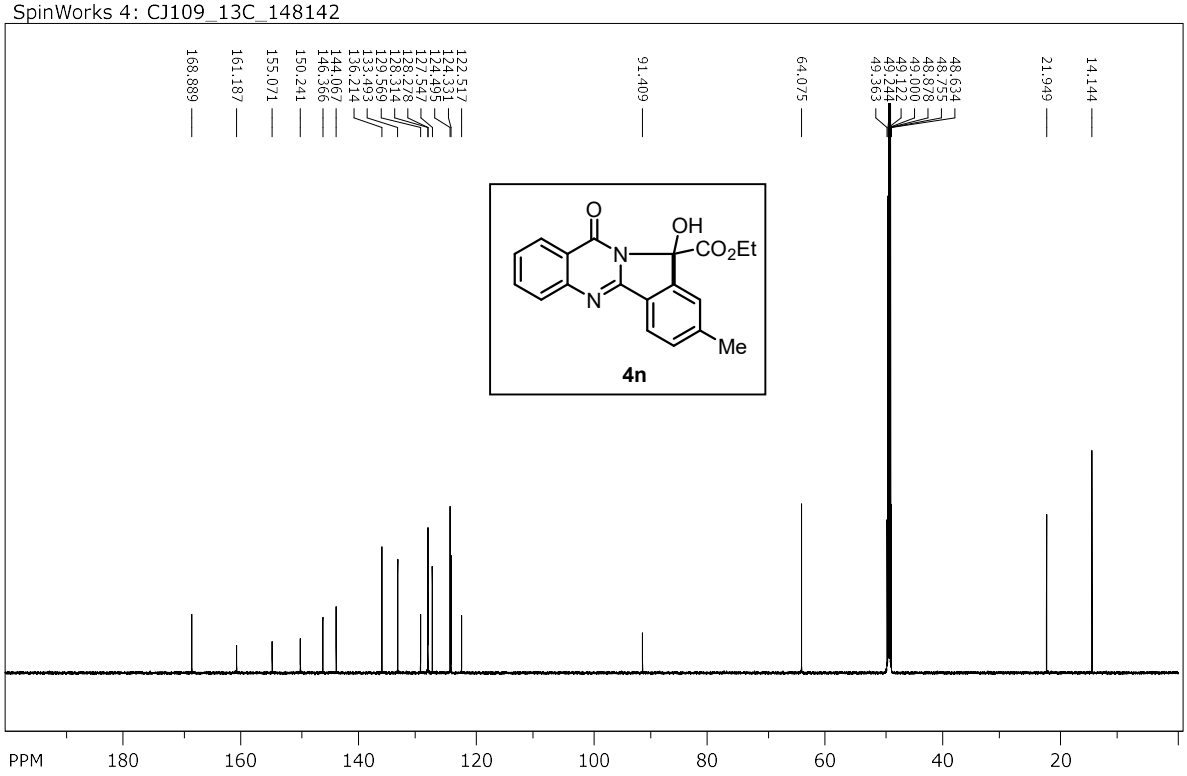

KY 4m
4m
f1 (ppm)

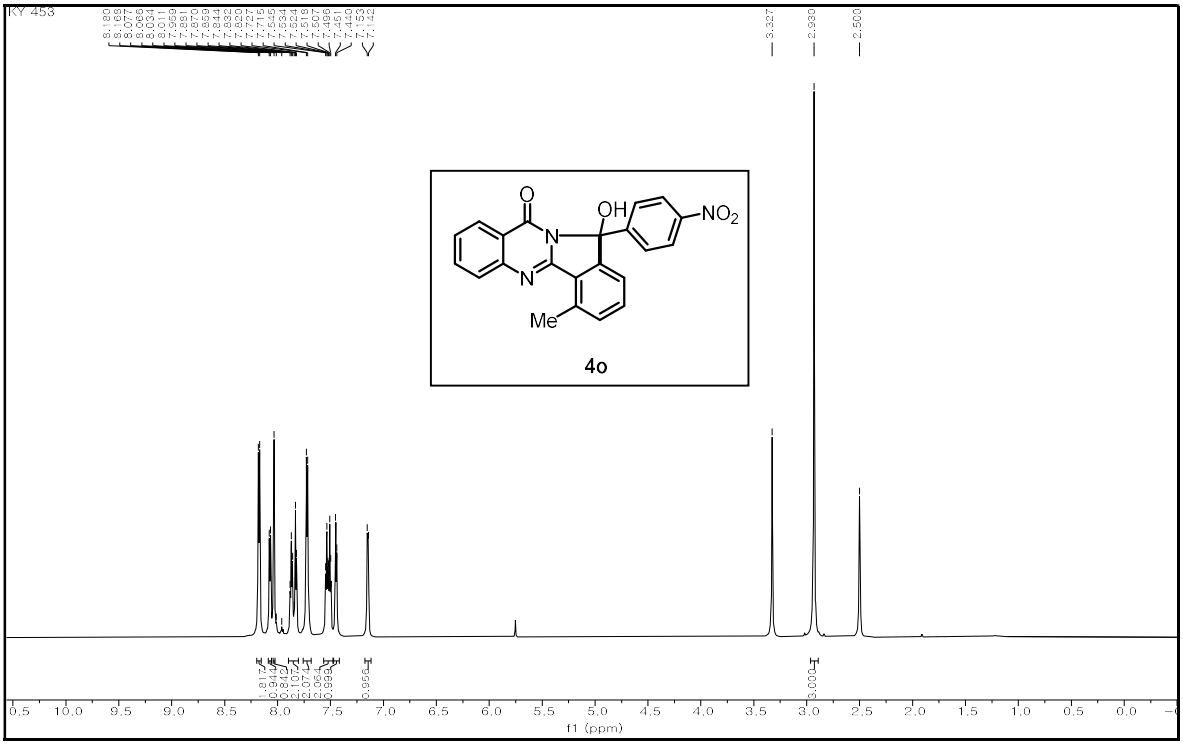

KY 4m
4m
f1 (ppm)

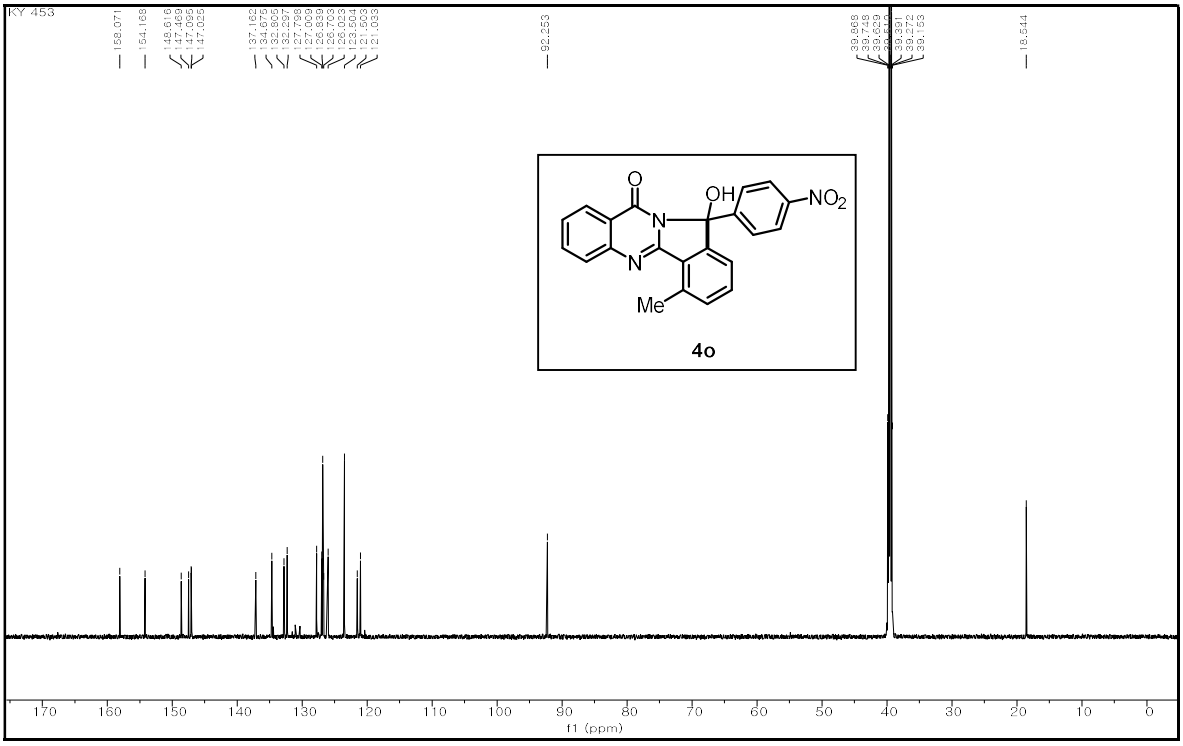
SpinWorks 4: CJ109_1H_148142

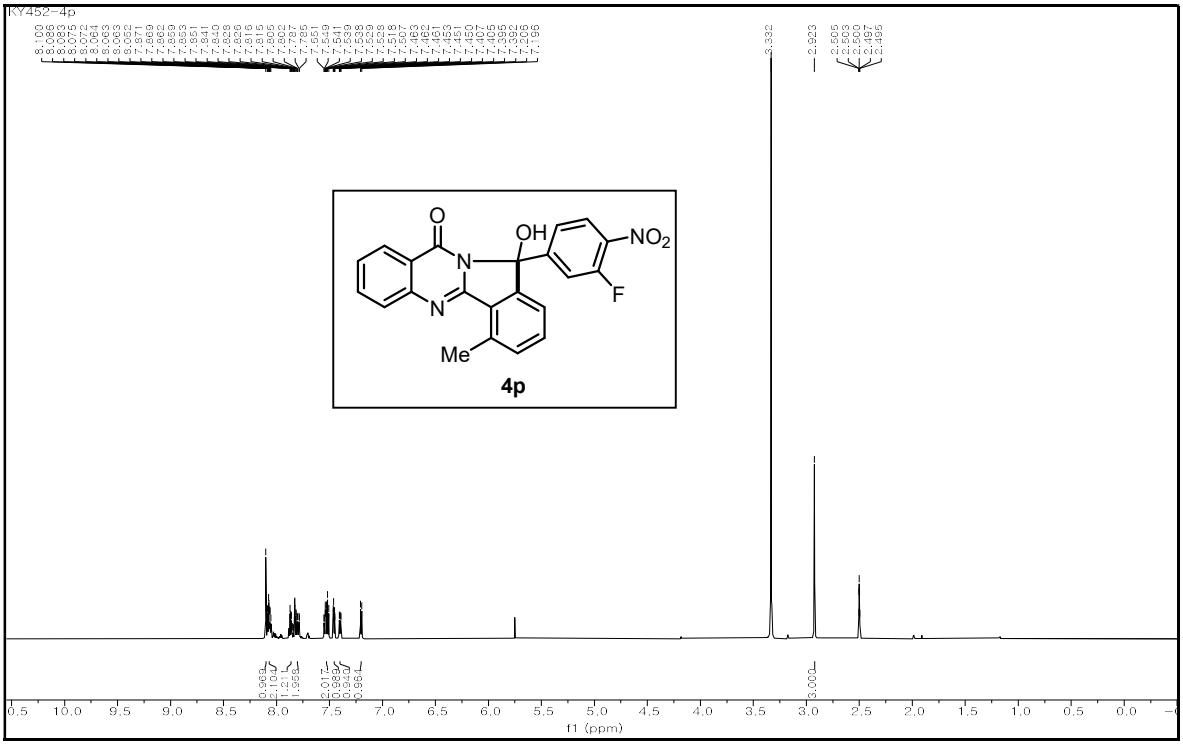


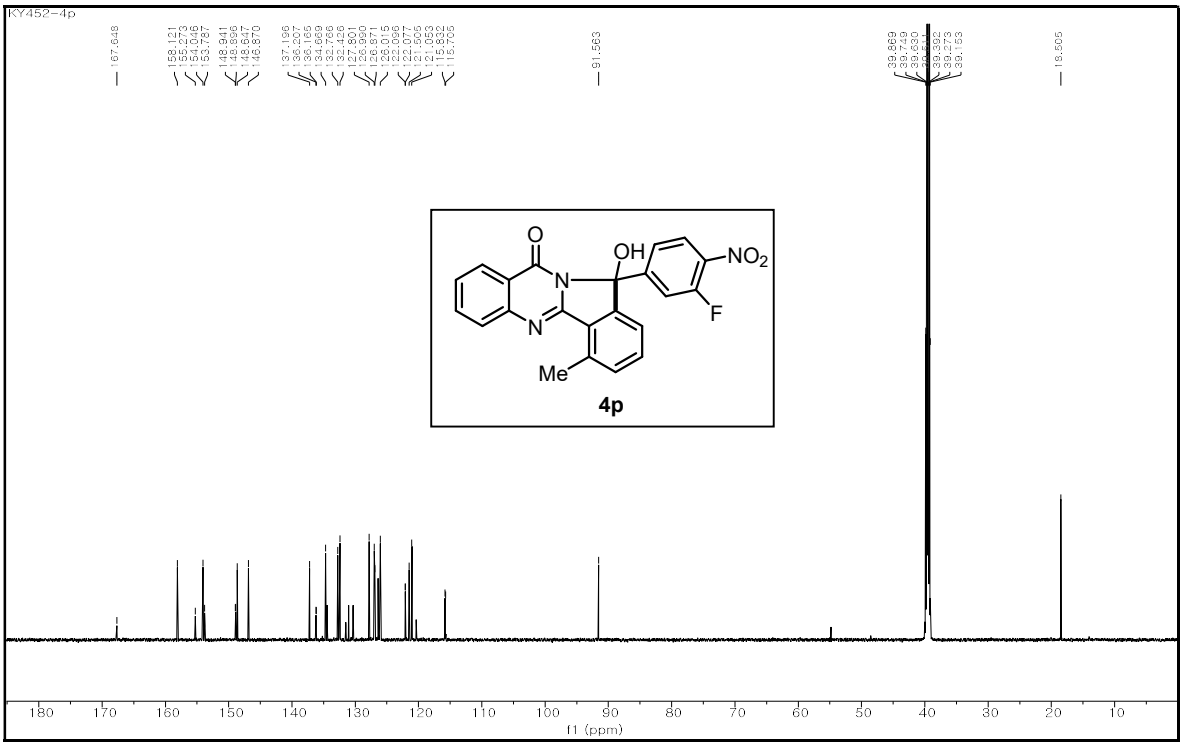

SpinWorks 4: CJ109_13C_148142



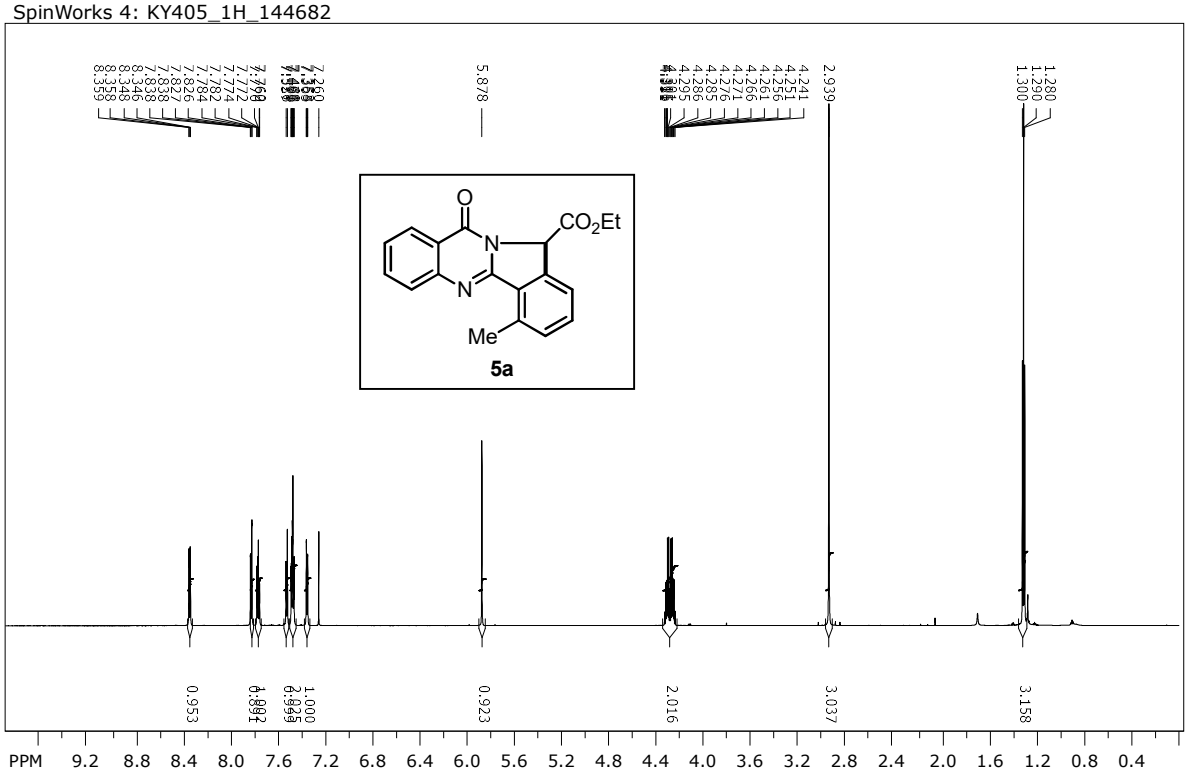

KY 453
O
OH
NO2
N
N
Me
4o
f1 (ppm)


KY 453
O
OH
NO2
N
N
Me
4o
f1 (ppm)

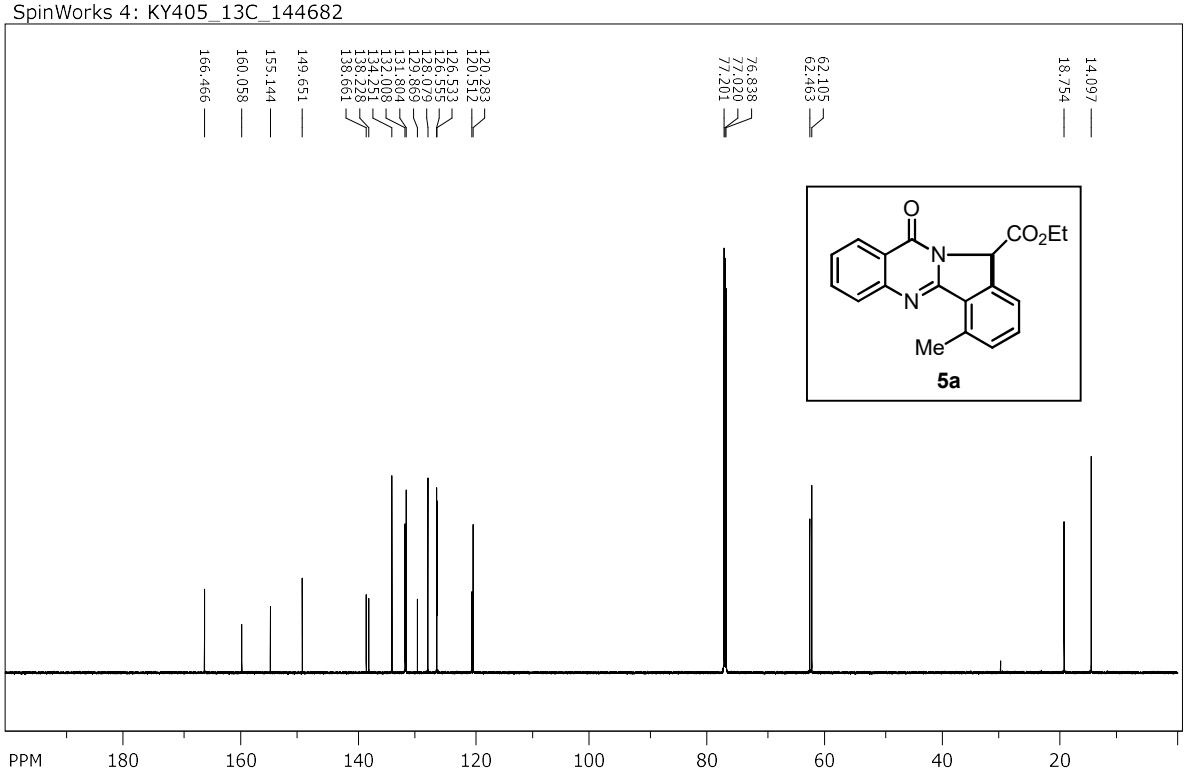

KY452-4p
O
OH
NO2
N
N
F
Me
4p
f1 (ppm)


KY452-4p
O
OH
NO2
N
N
F
Me
4p
f1 (ppm)

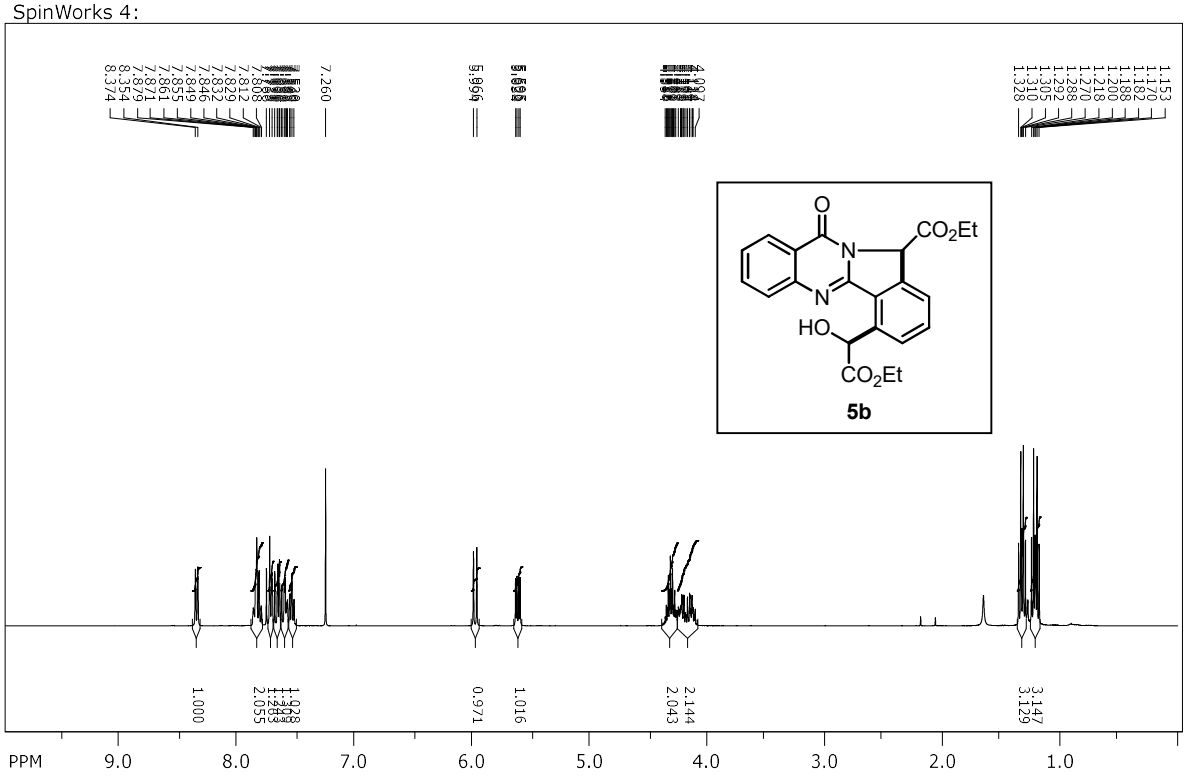
SpinWorks 4: KY405_1H_144682



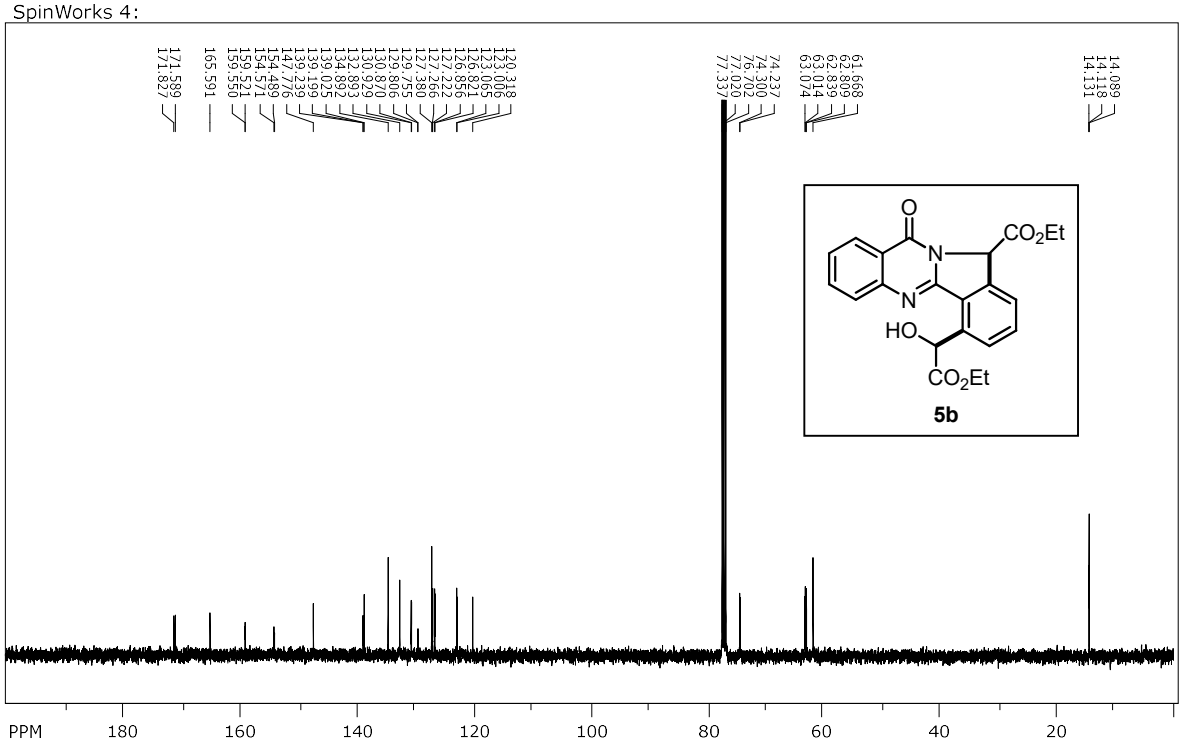

SpinWorks 4: KY405_13C_144682

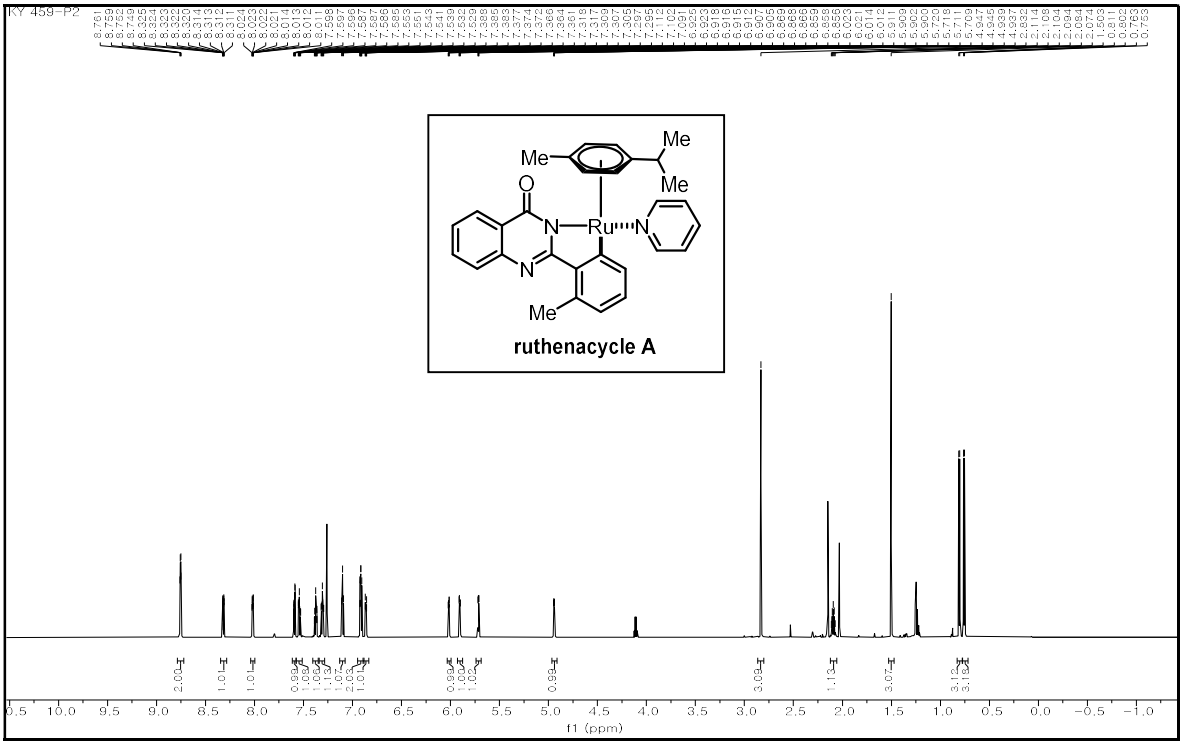


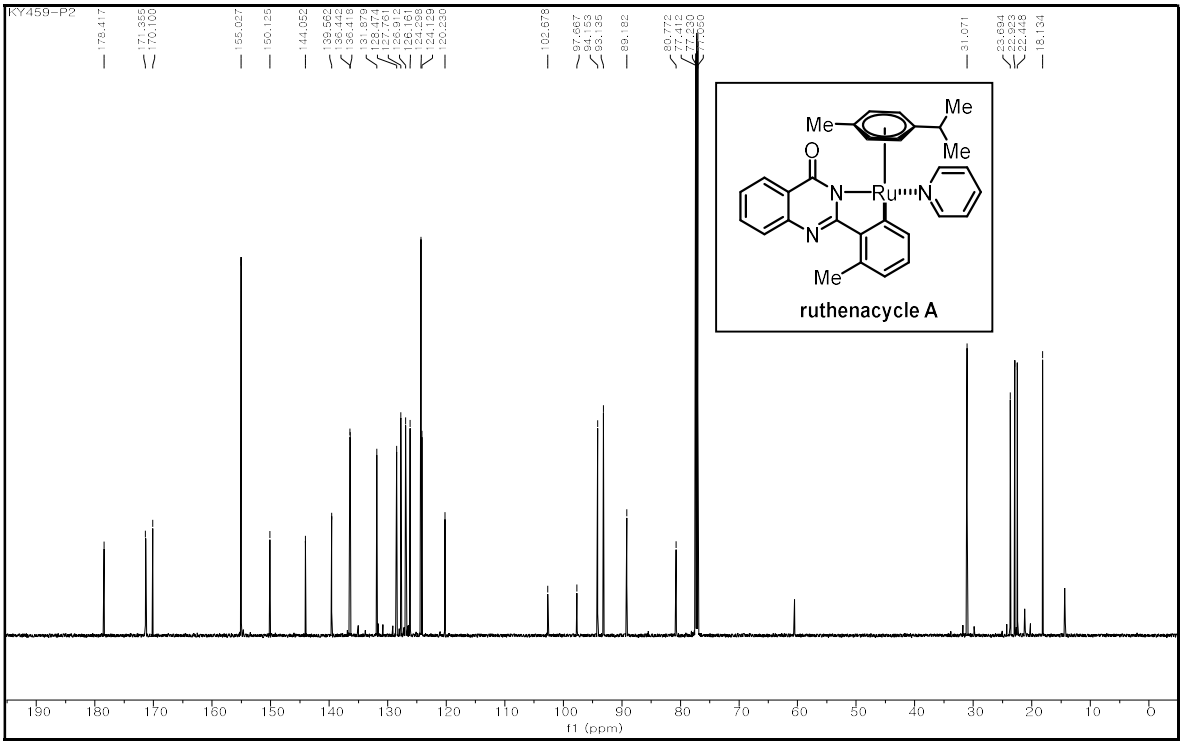
SpinWorks 4:




SpinWorks 4:




KY 459-P2
Me
Me
Me
O
N
Ru
N
N
Me
ruthenacycle A
f1 (ppm)


KY459-P2
Me
Me
Me
O
N
Ru
N
N
Me
ruthenacycle A
f1 (ppm)

## $^{19}$F NMR spectra of compounds 3p and 4p