Electronic Supplementary Information

Highly selective $AlCl_3$ initiated intramolecular α-alkylation of α,β-unsaturated lactams and lactones

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Experimental Section

General experimental methods

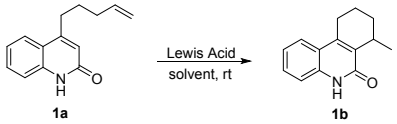
^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were acquired on a Bruker Avance Ultrashield 400 MHz and a Bruker DPX 400 MHz spectrometer. Mass Spectroscopy (MS) and High Resolution Mass Spectroscopy (HR-MS) was performed on a Thermo Scientific LTQ-FT Ultra (ESI). IR spectra were recorded on a Varian FTIR-670 spectrometer using a GladiATR accessory with a diamond ATR element. Melting points were determined on a MPM-H2 apparatus. Anhydrous CH_2Cl_2, THF was obtained from a M. Braun SPS purification system. The following compounds were synthesized according to literature procedures. Pent-4-en-1-ylzinc(II) bromide,[1] 1-methyl-2-oxo-1,2-dihydroquinolin-4-yl trifluoromethane sulfonate,[1] (*E*)-5-bromopent-2-ene,[2] 5,7-dimethoxy-4-methylquinolin-2(1*H*)-one,[3] **1a**,[4] **3a**,[1] **5a**,[5] **6a**,[5] **10a**,[5] **11a**.[5]

Crystal structure determination details:

A clear, colorless fragment-like specimen of $C_{15}H_{17}NO$, approximate dimensions 0.186 mm x 0.209 mm x 0.317 mm, was used for the X-ray crystallographic analysis. The crystal was mounted on a microsampler with perfluorinated ether and transferred to the diffractometer. The X-ray intensity data were measured on a Bruker D8 Kappa Apex II system equipped with a Triumph monochromator and a Mo fine-focus sealed tube (λ = 0.71073 Å). A total of 1199 frames were collected. The total exposure time was 19.98 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 14663 reflections to a maximum θ angle of 25.02° (0.84 Å resolution), of which 2068 were independent (average redundancy 7.090, completeness = 99.9%, Rint = 4.52%, Rsig = 2.82%) and 2002 (96.81%) were greater than 2σ(F2). The final cell constants of a = 7.1064(12) Å, b = 10.3163(18) Å, c = 15.973(2) Å, volume = 1171.0(3) Å3, are based upon the refinement of the XYZ-centroids of 122 reflections above 20 σ(I) with 13.10° < 2θ < 50.61°. Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9750 and 0.9850. The final anisotropic full-matrix least-squares refinement on F2 with 205 variables converged at R1 = 2.79%, for the observed data and wR2 = 7.36% for all data. The goodness-of-fit was 1.083. The largest peak in the final difference electron density synthesis was 0.120 e-/Å3 and the largest hole was -0.157 $e^-/Å^3$ with an RMS deviation of 0.032 e^-

/Å^3. On the basis of the final model, the calculated density was 1.289 g/cm^3 and F(000), 488 e$^-$.

Table S1 Optimization of reaction conditions[a]



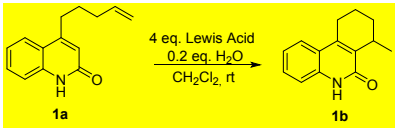
Entry	Initiator	Solvent	Equiv.	T (h)	Yield[b]
1	$CuCl_2$	CH_2Cl_2	2	2	0 (98)[c]
2	$ZnCl_2$	CH_2Cl_2	2	2	0 (99)[c]
3	$FeCl_3$	CH_2Cl_2	2	2	0 (93)[c]
4	$Cu(OTf)_2$	CH_2Cl_2	2	2	0 (98)[c]
5	$Nd(OTf)_3$	CH_2Cl_2	2	2	0 (98)[c]
6	$Sc(OTf)_3$	CH_2Cl_2	2	2	0 (98)[c]
7	BF_3•OEt_2	CH_2Cl_2	2	2	0 (93)[c]
8	BCl_3	CH_2Cl_2	2	2	0 (99)[c]
9	BBr_3	CH_2Cl_2	2	2	0 (99)[c]
10	$AlMe_3$	CH_2Cl_2	2	2	0 (99)[c]
11	$AlMe_2Cl$	CH_2Cl_2	2	2	0 (99)[c]
12	$AlEtCl_2$	CH_2Cl_2	2	2	15
13	$AlCl_3$	CH_2Cl_2	2	2	99
14	$AlBr_3$	CH_2Cl_2	2	2	86
15	HCl (aq)	CH_2Cl_2	2	2	0 (99)[c]
16	$AlCl_3$	CH_2Cl_2	1.5	4	96
17	$AlCl_3$	CH_2Cl_2	1.3	8	97
18	$AlCl_3$	CH_2Cl_2	1.1	24	96
19	$AlCl_3$	CH_2Cl_2	≦1	24	0 (99)[c]
20	$AlCl_3$	MeCN	2	24	0 (98)[c]
21	$AlCl_3$	MeOH	2	2	0 (99)[c]
22	$AlCl_3$	THF	2	2	0 (98)[c]
23	$AlCl_3$	Et_2O	2	2	0 (98)[c]
24	$AlCl_3$	$CHCl_3$	2	2	95

[a] All reactions were carried out using **1a** (0.2 mmol) and a Lewis acid (0.4 mmol) in anhydrous solvents (10 mL) at room temperature under an argon atmosphere. [b] Isolated

yields were reported. [c] Recovered yield of **1a**.

Commonly used Lewis acids, such as $CuCl_2$, $ZnCl_2$ and $FeCl_3$, did not afford any product (Table S1, entries 1-3). The same results were obtained when using $Cu(OTf)_2$, $Nd(OTf)_3$, and $Sc(OTf)_3$ bearing OTf^- as a counter anion (Table S1, entries 4-6). Applying the boron-based Lewis acids, BF_3•OEt, BCl_3, and BBr_3, the reaction did not afford any product either, despite of their strong Lewis acidity (Table S1, entries 7-9). Subsequently, a series of aluminum-centered Lewis acids were examined (Table S1, entries 10-14). While $AlMe_3$ and $AlMe_2Cl$ did not give any desired products (Table S1, entries 10-11), mono ethyl substituted aluminum chloride $AlEtCl_2$ performed the targeted transformation, however with very low yield (Table S1, entry 12). In contrast, full conversion was achieved with the aluminum halides $AlCl_3$ and $AlBr_3$ (Table S1, entries 13-14). However, due to the excessive Lewis acidity of $AlBr_3$,[6] substrate **1a** underwent partial decomposition, thus lowering the yield. Protic acid HCl was also checked for this reaction and no reaction product was detected (Table S1, entry 15). Therefore, $AlCl_3$ was chosen as the best available Lewis acid for this reaction. The results of a screening with different loadings of $AlCl_3$ demonstrated that a lower loading did not significantly affect reaction yields and the reaction did not take place with less than one equivalent of $AlCl_3$ (Table S1, entries 16-19). Although, understandably, the reactions proceeded faster with more equivalents of $AlCl_3$. As the reaction was completed within 24 h with a loading of 1.1 equivalent of $AlCl_3$, it thus indicated that the first equivalent of $AlCl_3$ acted as the reaction initiator, while the following portion of $AlCl_3$ served as the actual catalyst (*vide infra*). Considering that $AlCl_3$ was cheap and the reaction was completed within two hours when two equivalents of $AlCl_3$ were applied, this amount was chosen as the standard loading for all following reactions. In a next step, different solvents were evaluated for their applicability in the transformation. The reaction did not work in coordinating solvents like MeCN, MeOH, THF or Et_2O, with most of the starting material being recycled (Table S1, entries 20-23). It was assumed that this behavior was a result of solvent coordination to $AlCl_3$ and hence a weakened activity of the adduct. Chloroform was proven to be an effective solvent, affording the desired product in an excellent yield (Table S1, entry 24). Nonetheless, due to its comparatively high toxicity, chemically similar but less toxic dichloromethane was selected as the optimal solvent for this α-alkylation.

Table S2 Effect of water on the reaction[a]



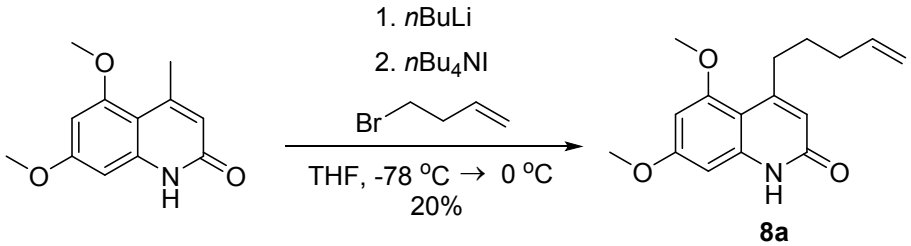
Entry	Initiator	T (h)	Yield[b]
1	$CuCl_2$	2	0 (99)[c]
2	$ZnCl_2$	2	0 (99)[c]
3	$FeCl_3$	2	0 (90)[c]
4	$Cu(OTf)_2$	2	0 (98)[c]
5	$Nd(OTf)_3$	2	0 (98)[c]
6	$Sc(OTf)_3$	2	0 (98)[c]
7	$BF_3•OEt_2$	2	0 (85)[c]
8	BCl_3	2	0 (80)[c]
9	BBr_3	2	0 (82)[c]
10	$AlMe_3$	2	0 (62)[c]
11	$AlMe_2Cl$	2	0 (50)[c]
12	$AlEtCl_2$	2	17
13	$AlCl_3$	2	95

[a] All reactions were carried out using **1a** (0.2 mmol), Lewis acid (0.8 mmol) and H_2O (0.04 mmol) in anhydrous CH_2Cl_2 (10 mL) at room temperature under an argon atmosphere. [b] Isolated yields were reported. [c] Recovered yield of **1a**.

The effect of water on the reaction was investigated by adding 0.2 equiv. of water to the reaction medium (Table S2). Lewis acids other than $AlCl_3$ and $AlEtCl_2$ do not give any product (entries 1-11), while $AlCl_3$ still produces the product in excellent yield (entry 13). In this way, the significance of $AlCl_3$ is supported.

General Procedure I for the synthesis of substrates

Synthesis of 5,7-dimethoxy-4-(pent-4-en-1-yl)quinolin-2(1*H*)-one (8a)



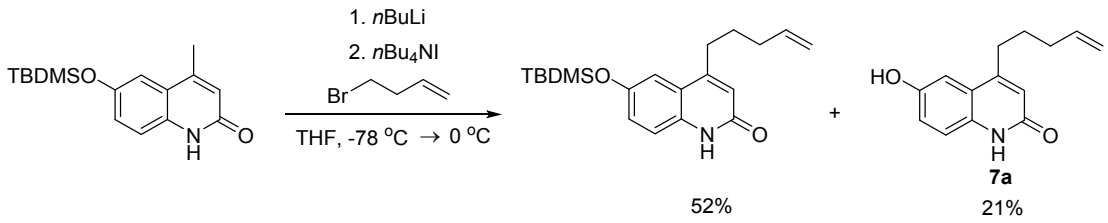
8a

To a 100 mL Schlenk flask is added 5,7-dimethoxy-4-methylquinolin-2(1*H*)-one[3] (765 mg, 3.5 mmol), and dry THF (20 mL). The reaction mixture is cooled to 0 °C under

argon atmosphere and treated dropwise with *n*-butyl lithium (2.5 M in *n*-hexane, 2.8 mL, 7.0 mmol). The dark red solution is stirred at room temperature for 3 h, cooled to -78 °C and treated with tetrabutylammonium iodide (nBu$_4$NI) (970 mg, 2.6 mmol) and 4-bromobut-1-ene (0.7 mL, 7.0 mmol) is added subsequently. The yellow solution is stirred at room temperature overnight and then cooled to 0 °C, treated with 10 mL 1 N HCl. The solvent is evaporated and the residue is extracted with ethyl acetate (3 × 30 mL). The combined organic layers are washed with brine (15 mL), dried over $MgSO_4$, filtered, and evaporated. The crude product is purified by column chromatography (hexane/ethyl acetate = 1:1) to give the product **8a** as a solid (191 mg, 20%); mp 156.1-156.8 °C (hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.89 (s, 1 H), 6.44 (d, J = 1.6 Hz, 1 H), 6.28 (s, 1 H), 6.24 (d, J = 2.0 Hz, 1 H), 5.95-5.75 (m, 1 H), 5.10-4.90 (m, 1 H), 3.90 (s, 3 H), 3.87 (s, 3 H), 2.98 (t, J = 7.6 Hz, 3 H), 2.22-2.10 (m, 2 H), 1.80-1.60 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.1, 161.8, 158.9, 154.7, 142.3, 138.6, 117.4, 114.8, 105.6, 94.6, 91.4, 55.7, 55.5, 36.6, 33.8, 29.8; IR (neat) 1591, 1500, 1477, 1463, 1452, 1442, 1428 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{20}NO_3^+$: 274.1438, found: 274.1437.

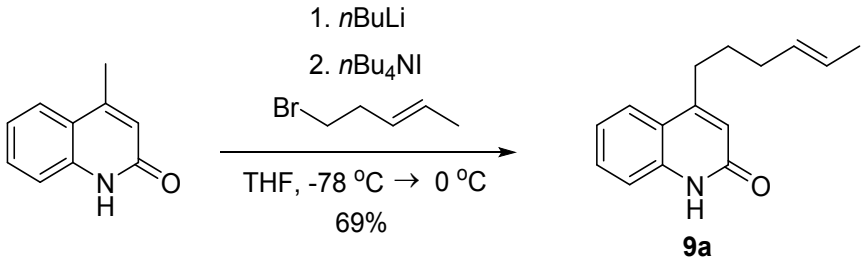
The following compounds were prepared according to General Procedure I

(1) 6-((*tert*-Butyldimethylsilyl)oxy)-4-(pent-4-en-1-yl)quinolin-2(1*H*)-one (7a)



The reaction of 6-((*tert*-butyldimethylsilyl)oxy)-4-methylquinolin-2(1*H*)-one (1.096 g, 3.8 mmol), *n*-butyl lithium (2.5 M in *n*-hexane, 3 mL, 7.6 mmol), nBu$_4$NI (1.054 g, 2.9 mmol), and 4-bromobut-1-ene (1 mL, 7.6 mmol) in THF (20 mL) affords **7a** as a solid (182 mg, 21%); mp 238.8-239.3 °C (methanol); ^{1}H NMR (400 MHz, DMSO) δ 11.40 (s, 1 H), 9.37 (s, 1 H), 7.16 (d, J = 8.8 Hz, 1 H), 7.06-6.94 (m, 2 H), 6.30 (s, 1 H), 5.93-5.80 (m, 1 H), 5.11-4.95 (m, 2 H), 2.70 (t, J = 7.8 Hz, 2 H), 2.18-2.08 (m, 2 H), 1.75-1.63 (m, 2 H); ^{13}C NMR (100 MHz, MeOD) δ 164.5, 154.6, 154.4, 139.1, 133.2, 122.0, 121.4, 119.9, 118.6, 115.9, 109.3, 34.5, 32.7, 29.3; IR (neat) 2942, 1638, 1624, 1576, 1502, 1453 cm^{-1}; HRMS m/z (ESI): m/z calcd for $C_{14}H_{16}NO_2^+$: 230.1176, found: 230.1175.

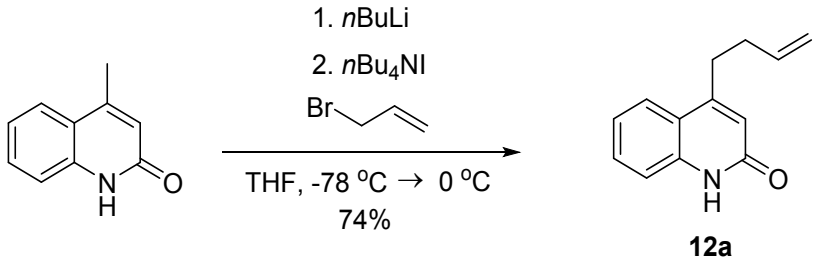
(2) (*E*)-4-(Hex-4-en-1-yl)quinolin-2(*1H*)-one (9a)



9a

The reaction of 4-methylquinolin-2(1*H*)-one (2.387 g, 15.0 mmol), *n*-butyl lithium (2.5 M in *n*-hexane, 12.0 mL, 12 mmol), nBu$_4$NI (4.155 g, 11.3 mmol), and (*E*)-5-bromopent-2-ene[2] (4.478 g, 30 mmol) in THF (50 mL) affords **9a** as a solid (2.351 g, 69%); mp 145.7-146.4 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.43 (s, 1 H), 7.71 (d, J = 8.0 Hz, 1 H), 7.55-7.39 (m, 2 H), 7.23 (t, J = 8.0 Hz, 1 H), 6.60 (s, 1 H), 5.59-5.38 (m, 2 H), 2.86 (t, J = 7.6 Hz, 2 H), 2.20-2.07 (m, 2 H), 1.87-1.74 (m, 2 H), 1.68 (d, J = 5.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 153.2, 138.6, 130.31, 130.26, 126.0, 124.2, 122.4, 119.8, 119.5, 116.8, 32.2, 31.6, 28.6, 17.9; IR (neat) 1647, 1611, 1554, 1508, 1439 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{18}NO^+$: 228.1383, found: 228.1382.

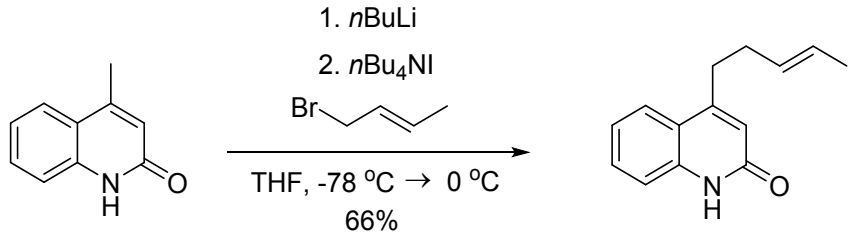
(3) 4-(*but*-3-En-1-yl)quinolin-2(1*H*)-one (12a)



12a

The reaction of 4-methylquinolin-2(1*H*)-one (2.441 g, 15.0 mmol), *n*-butyl lithium (2.5 M in *n*-hexane, 12 mL, 30.0 mmol), nBu$_4$NI (4.15 g, 11.3 mmol), and 3-bromobut-1-ene (2.8 mL, 32.3 mmol) in THF (50 mL) affords **12a** as a solid (2.259 g, 74%); mp 118.3-118.9 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.58 (s, 1 H), 7.72 (d, J = 7.6 Hz, 1 H), 7.56-7.44 (m, 2 H), 7.29-7.19 (m, 1 H), 6.61 (s, 1 H), 6.01-5.80 (m, 1 H), 5.18-5.01 (m, 2 H), 2.97 (t, J = 8.0 Hz, 2 H), 2.57-2.40 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 152.4, 138.5, 136.9, 130.4, 124.0, 122.5, 119.7, 119.4, 117.0, 115.9, 32.7, 31.5; IR (neat) 1645, 1555, 1508, 1433, 1398 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{14}NO^+$: 200.1070, found: 200.1070.

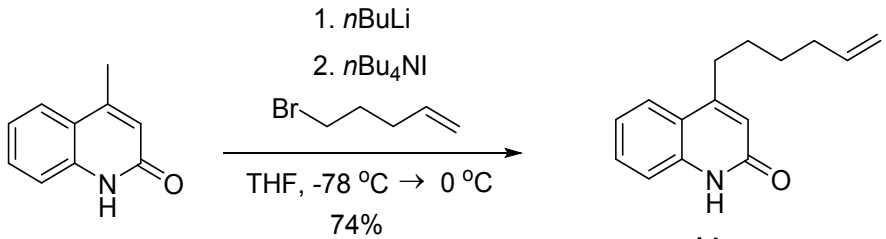
(4) 4-(Hex-4-en-1-yl)quinolin-2(1*H*)-one (13a)



13a

The reaction of 4-methylquinolin-2(1*H*)-one (1.592 g, 10.0 mmol), *n*-butyl lithium (2.5 M in hexane, 8.0 mL, 20.0 mmol), nBu$_4$NI (2.772 g, 7.5 mmol), and 1-bromobut-2-ene (2.700 g, 20.0 mmol) in THF (60 mL) affords **13a** as a solid (1.408 g, 66%); mp 167.9-170.3 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.76 (s, 1 H), 7.71 (d, J = 8.4 Hz, 1 H), 7.53-7.46 (m, 2 H), 7.26-7.19 (m, 1 H), 6.60 (s, 1 H), 5.60-5.44 (m, 2 H), 2.92 (t, J = 7.6 Hz, 2 H), 2.46-2.33 (m, 2 H), 1.72-1.60 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 152.6, 138.6, 130.3, 129.5, 126.4, 124.1, 122.4, 119.8, 119.5, 116.9, 32.3, 31.6, 17.9; IR (neat) 1648, 1611, 1557, 1506, 1438, 1401 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{16}NO^+$: 214.1226, found: 214.1226.

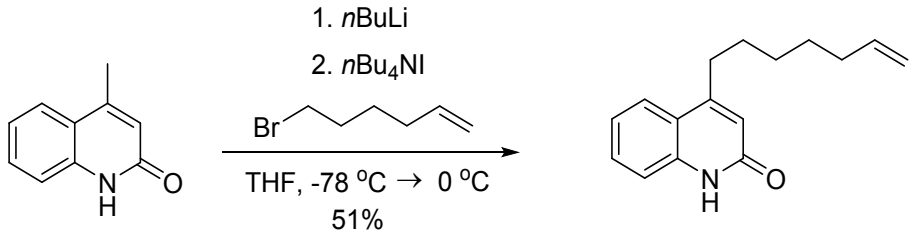
(5) 4-(Hex-5-en-1-yl)quinolin-2(1*H*)-one (14a)



14a

The reaction of 4-methylquinolin-2(1*H*)-one (1.593 g, 10.0 mmol), *n*-butyl lithium (2.5 M in *n*-hexane, 8 mL, 20 mmol), nBu$_4$NI (2.775 g, 7.5 mmol), and 5-bromobut-1-ene (2.4 mL, 20.0 mmol) in THF (40 mL) affords **14a** as a solid (1.800 g, 74%); mp 115.7-116.3 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.91 (s, 1 H), 7.71 (d, J = 8.0 Hz, 1 H), 7.55-7.44 (m, 2 H), 7.29-7.15 (m, 1 H), 6.60 (s, 1 H), 5.90-5.70 (m, 1 H), 5.10-4.90 (m, 2 H), 2.86 (t, J = 7.6 Hz, 2 H), 2.20-2.05 (m, 2 H), 1.85-1.65 (m, 2 H), 1.61-1.45 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 153.2, 138.6, 138.3, 130.3, 124.0, 122.4, 119.8, 119.3, 116.9, 114.8, 33.5, 32.0, 28.7, 28.2; IR (neat) 1651, 1555, 1466, 1434, 1396 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{18}NO^+$: 228.1383, found: 228.1382.

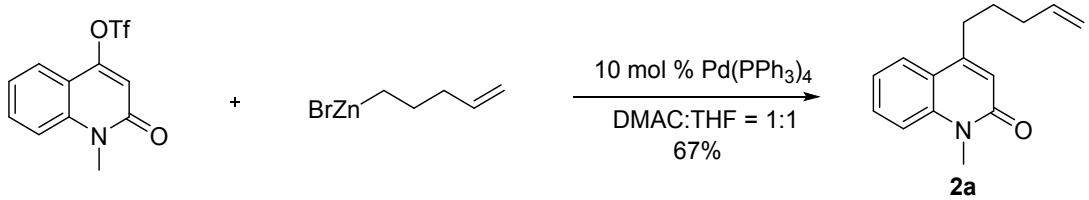
(6) 4-(Hept-6-en-1-yl)quinolin-2(1*H*)-one (15a)



15a

The reaction of 4-methylquinolin-2(1*H*)-one (955 mg, 6.0 mmol), *n*-butyl lithium (2.5 M in *n*-hexane, 4.8 mL, 12.0 mmol), nBu$_4$NI (1.848 g, 5.0 mmol), and 6-bromobut-1-ene (1.5 mL, 11.0 mmol) in THF (30 mL) affords **15a** as a solid (738 mg, 51%); mp 105.1-105.9 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.80 (s, 1 H), 7.71 (d, J = 8.0 Hz, 1 H), 7.52-7.46 (m, 2 H), 7.25-7.18 (m, 1 H), 6.60 (s, 1 H), 5.89-5.71 (m, 1 H), 5.07-4.87 (m, 2 H), 2.86 (t, J = 7.8 Hz, 2 H), 2.13-2.00 (m, 2 H), 1.80-1.66 (m, 2 H), 1.53-1.40 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 153.4, 138.7, 138.5, 130.3, 124.1, 122.5, 119.9, 119.3, 116.9, 114.5, 33.6, 32.2, 29.0, 28.7; IR (neat) 1650, 1553 1471, 1431, 1394 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{20}NO^+$: 242.1539, found: 242.1539.

Synthesis of 1-methyl-4-(pent-4-en-1-yl)quinolin-2(1*H*)-one (2a)

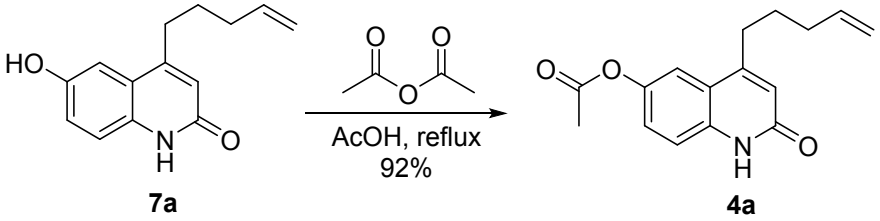


2a

Under argon atmosphere, pent-4-en-1-ylzinc(II) bromide[1] (8.6 mL, 13 mmol, 1.5 M in DMAC), 1-methyl-2-oxo-1,2-dihydroquinolin-4-yl trifluoromethanesulfonate[1] (2.000 g, 6.51 mmol), and Pd(PPh$_3$)$_4$ (690 mg, 0.65 mmol) are added to dry THF (10 mL) at rt. The resulting mixture is stirred at 50 °C under argon atmosphere. The coupling reaction is completed after 4 h as monitored by TLC (*n*-hexane/ethyl acetate = 5:1). The reaction is quenched with 1 N HCl (10 mL) and extracted with ethyl acetate (20 mL x 4). The combined organic layers are washed with brine (30 mL x 3), dried over Na_2SO_4, filtered, and evaporated. The residue is purified by flash chromatography on silica gel (eluent: *n*-hexane/ethyl acetate = 5:1) to afford product **2a** as a solid (991 mg, 67%); mp 44.8-45.4 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 8.0, 1.2 Hz, 1 H), 7.53 (td, J = 7.2, 1.2 Hz, 1 H), 7.35 (d, J = 8.4 Hz, 1 H), 7.22 (t, J = 8.4 Hz, 1 H), 6.57 (s, 1 H), 5.90-5.75 (m, 1 H), 5.10-4.95 (m, 2 H), 3.68 (s, 3 H), 2.79 (t, J = 7.8 Hz, 2 H), 2.25-2.10 (m, 2 H), 1.85-1.73 (m, 2 H); ^{13}C NMR

($CDCl_3$, 100 MHz) δ 162.0, 149.9, 140.0, 137.7, 130.2, 124.8, 121.7, 120.5, 120.0, 115.4, 114.5, 33.3, 31.2, 29.1, 27.8; IR (neat) 1655, 1643, 1588, 1453, 1417 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{18}NO^+$: 228.1383, found: 228.1382.

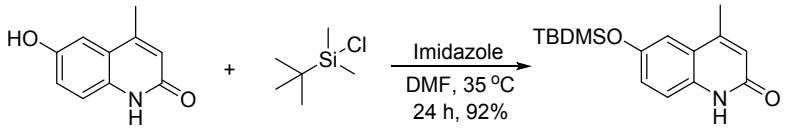
Synthesis of 6-acetoxy -4-(pent-4-en-1-yl)quinolin-2(1*H*)-one (4a)



7a **4a**

To a three necked bottle **7a** (138 mg, 0.6 mmol), acetic anhydride (1 mL), and acetic acid (4 mL) are added. The mixture is then refluxed overnight. The mixture is diluted with 10 mL water and extracted with ethyl acetate (10 mL x 3). The combined organic layers are washed with brine and dried over $MgSO_4$, filtered, evaporated. The residue is purified by column chromatography (*n*-hexane/ethyl acetate = 1:1) to give the product **4a** as a solid (150 mg, 92%); mp 154.2-155.0 ^oC (*n*-hexane/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 12.51 (s, 1 H), 7.49-7.40 (m, 2 H), 7.28-7.23 (m, 1 H), 6.62 (s, 1 H), 5.92-5.76 (m, 1 H), 5.16-5.00 (m, 2 H), 2.82 (t, J = 7.8 Hz, 2 H), 2.34 (s, 3 H), 2.26-2.16 (m, 2 H), 1.89-1.78 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 164.1, 152.5, 145.6, 137.6, 136.3, 124.5, 120.3, 120.1, 117.7, 116.4, 115.6, 33.2, 31.4, 27.5, 21.1; IR (neat) 1760, 1663, 1504, 1426 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{18}NO_3^+$: 272.1281, found: 272.1282.

Synthesis of 6-((tert-butyldimethylsilyl)oxy)-4-methylquinolin-2(1*H*)-one

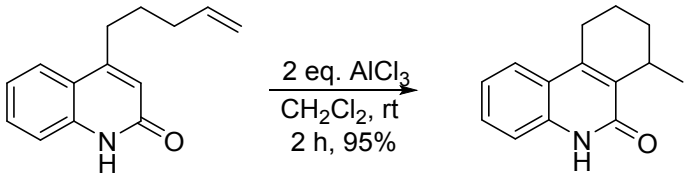


To a 10 mL Schlenk flask 6-hydroxy-4-methylquinolin-2(1*H*)-one (175 mg, 1.0 mmol), *tert*-butylchlorodimethylsilane (TBDMSCl) (181 mg, 1.2 mmol), imidazole (171 mg, 2.5 mmol), and DMF (2 ml) are added. The mixture is stirred at 35 ^oC for 24 h. The mixture is washed with 15 mL water and extracted with ethyl acetate (10 mL x 3). The combined organic layers are washed with brine and dried over $MgSO_4$, filtered, evaporated. The residue is purified by column chromatography (ethyl acetate) to give the product 6-((*tert*-butyldimethylsilyl)oxy)-4-methylquinolin-2(1*H*)-one as a solid (266 mg, 92%); mp 173.7-175.0 ^oC (*n*-hexane/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 12.57 (s, 1 H), 7.34 (d, J = 8.8 Hz, 1 H), 7.10-7.01 (m, 2 H), 6.58 (s, 1 H),

2.46 (s, 3 H), 1.00 (s, 9 H), 0.21 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 150.8, 148.4, 133.2, 124.0, 121.3, 120.7, 117.6, 113.7, 25.7, 19.2, 18.2, -4.4; IR (neat) 1656, 1619, 1473, 1424 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{23}NO_2Si^+$: 289.1498, found: 289.1498.

General procedure II for the α-alkylation reaction

Synthesis of 7-methyl-7,8,9,10-tetrahydrophenanthridin-6(5*H*)-one (1b)

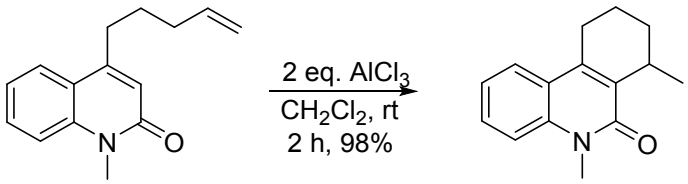


1a **1b**

To a 25 mL Schlenk flask **1a** (43 mg, 0.2 mmol), $AlCl_3$ (53 mg, 0.4 mmol), and CH_2Cl_2 (10 mL) are added. The mixture is stirred at room temperature under argon atmosphere. The reaction is completed after 2 h as monitored by TLC (hexane/ethyl acetate = 1:1). The solvent is removed and the residue is purified by column chromatography (*n*-hexane/ethyl acetate = 3:1) to give the product **1b** as a solid (41 mg, 95%); mp 207.5-208.5 ^{o}C (*n*-hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.79 (s, 1 H), 7.67 (d, J = 8.0 Hz, 1 H), 7.44 (t, J = 8.0 Hz, 1 H), 7.36 (d, J = 7.6 Hz, 1 H), 7.19 (t, J = 7.2 Hz, 1 H), 3.37-3.20 (m, 1 H), 3.10-2.96 (m, 1 H), 2.82-2.65 (m, 1 H), 2.05-1.73 (m, 4 H), 1.33 (d, J = 6.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 143.6, 136.6, 133.0, 129.0, 123.2, 122.0, 120.5, 115.9, 29.1, 27.3, 25.7, 19.7, 17.1; IR (neat) 1644, 1609, 1561, 1505, 1433 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{16}NO^+$: 214.1226, found: 214.1226.

The following reactions were conducted according to general procedure IV.

(1) 5,7-Dimethyl-7,8,9,10-tetrahydrophenanthridin-6(5*H*)-one (2b)

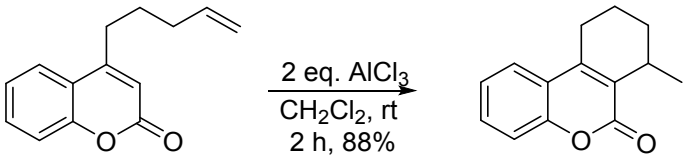


2a **2b**

The reaction of **2a** (45 mg, 0.2 mmol), $AlCl_3$ (53 mg, 0.4 mmol), and CH_2Cl_2 (10 mL) affords **2b** as a solid (44 mg, 98%); mp 88.8-89.8 ^{o}C (*n*-hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 9.2 Hz, 1 H), 7.49 (t, J = 8.2 Hz, 1 H), 7.34 (d, J = 8.4 Hz, 1 H), 7.22 (t, J = 8.2 Hz, 1 H), 3.73 (s, 3 H), 3.28-3.15 (m, 1 H), 3.03-2.90 (m, 1 H), 2.80-2.63 (m, 1 H), 1.96-1.83 (m, 2 H), 1.81-1.66 (m, 2 H), 1.26 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 141.3, 138.2, 133.2, 129.0, 123.8, 121.6,

121.2, 114.0, 29.5, 29.2, 27.9, 25.5, 19.6, 17.1; IR (neat) 1626, 1592, 1571, 1453, 1411 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{18}NO^+$: 228.1383, found: 228.1382.

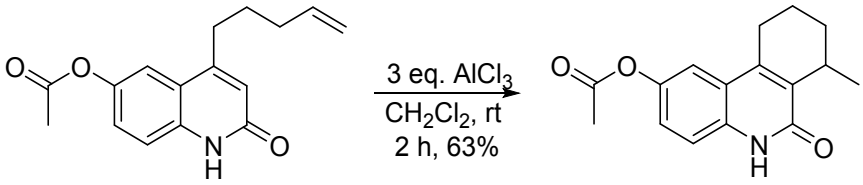
(2) 7-Methyl-7,8,9,10-tetrahydro-6*H*-benzo[*c*]chromen-6-one (3b)



3a **3b**

The reaction of **3a** (43 mg, 0.2 mmol), $AlCl_3$ (53 mg, 0.4 mmol), and CH_2Cl_2 (10 mL) affords **3b** as a solid (38 mg, 88%); mp 89.0-91.0 ^oC (*n*-hexane/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.0 Hz, 1 H), 7.45 (t, J = 8.4 Hz, 1 H), 7.33-7.24 (m, 2 H), 3.15-3.01 (m, 1 H), 2.97-2.84 (m, 1 H), 2.73-2.60 (m, 1 H), 1.96-1.68 (m, 4 H), 1.27 (d, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2, 152.1, 146.7, 130.3, 128.5, 123.9, 123.3, 120.2, 116.7, 28.9, 27.8, 25.4, 19.4, 16.8; IR (neat) 1705, 1621, 1606, 1572, 1448 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{15}O_2^+$: 215.1067, found: 215.1067.

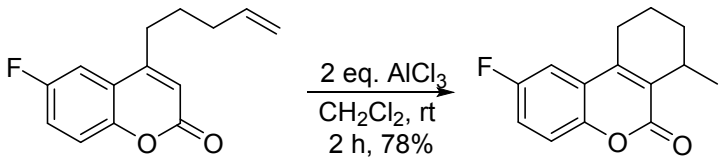
(3) 2-Acetoxy-7-methyl-7,8,9,10-tetrahydrophenanthridin-6(5*H*)-one (4b)



4a **4b**

The reaction of **4a** (54 mg, 0.2 mmol), $AlCl_3$ (81 mg, 0.6 mmol), and CH_2Cl_2 (10 mL) affords **4b** as a solid (34 mg, 63%); mp 203.0-203.9 ^oC (*n*-hexane/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 12.26 (s, 1 H), 7.45-7.31 (m, 2 H), 7.17 (dd, J = 8.4, 2.2 Hz, 1 H), 3.31-3.18 (m, 1 H), 3.00-2.85 (m, 1 H), 2.78-2.62 (m, 1 H), 2.33 (s, 3 H), 1.99-1.68 (m, 4 H), 1.31 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 163.5, 145.3, 143.1, 134.5, 133.8, 122.9, 121.1, 116.9, 115.6, 29.0, 27.3, 25.7, 21.1, 19.7, 17.0; IR (neat) 1753, 1643, 1624, 1501, 1428, 1415 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{18}NO_3^+$: 272.1281, found: 272.1282.

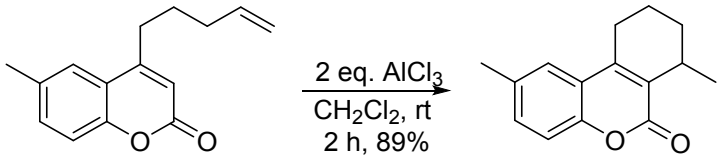
(4) 2-Fluoro-7-methyl-7,8,9,10-tetrahydro-6*H*-benzo[*c*]chromen-6-one (5b)



5a **5b**

The reaction of **5a** (46 mg, 0.2 mmol), $AlCl_3$ (53 mg, 0.4 mmol), and CH_2Cl_2 (10 mL) affords **5b** as a solid (36 mg, 78%); mp 116.2-116.9 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.10 (m, 3 H), 3.12-3.00 (m, 1 H), 2.89-2.75 (m, 1 H), 2.69-2.53 (m, 1 H), 1.98-1.68 (m, 4 H), 1.27 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 160.0, 157.6, 148.2, 145.9, 129.6, 121.2, 121.1, 118.1, 118.0, 117.6, 117.4, 109.3, 109.1, 28.8, 27.9, 25.4, 19.3, 16.6; IR (neat) 1711, 1579, 1493, 1434 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{14}FO_2^+$: 233.0972, found: 233.0971.

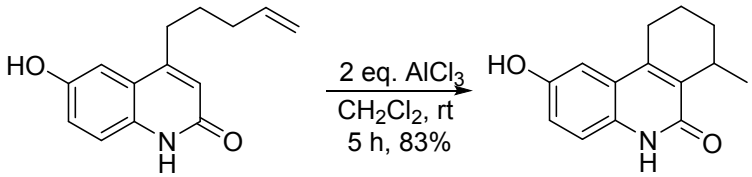
(5) 2,7-Dimethyl-7,8,9,10-tetrahydro-6*H*-benzo[*c*]chromen-6-one (6b)



6a **6b**

The reaction of **6a** (45 mg, 0.2 mmol), $AlCl_3$ (53 mg, 0.4 mmol), and CH_2Cl_2 (10 mL) affords **6b** as a solid (40 mg, 89%); mp 119.6-120.3 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1 H), 7.25 (dd, J = 8.0, 2.0 Hz, 1 H), 7.19 (d, J = 8.4 Hz, 1 H), 3.12-3.00 (m, 1 H), 2.94-2.82 (m, 1 H), 2.72-2.58 (m, 1 H), 2.41 (s, 3 H), 1.95-1.69 (m, 4 H), 1.26 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 150.1, 146.7, 133.4, 131.2, 128.3, 123.3, 119.9, 116.4, 28.9, 27.8, 25.4, 21.1, 19.4, 16.8; IR (neat) 1705, 1618, 1577, 1457, 1431, 1413 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{17}O_2^+$: 229.1223, found: 229.1223.

(6) 2-Hydroxy-7-methyl-7,8,9,10-tetrahydrophenanthridin-6(5*H*)-one (7b)

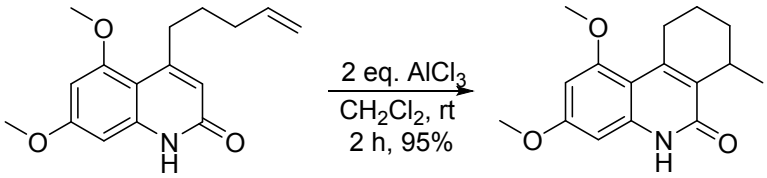


7a **7b**

The reaction of **7a** (46 mg, 0.2 mmol), $AlCl_3$ (53 mg, 0.4 mmol), and CH_2Cl_2 (10 mL) affords **7b** as a solid (38 mg, 83%); mp 268.0-268.9 °C (ethanol/ethyl acetate); ^{1}H NMR (400 MHz, DMSO) δ 11.34 (s, 1 H), 7.11 (d, J = 8.8 Hz, 1 H), 6.97 (d, J = 2.4 Hz, 1 H), 6.92 (dd, J = 8.8, 2.4 Hz, 1 H), 3.03-2.91 (m, 1 H), 2.86-2.73 (m, 1 H), 2.63-2.52

(m, 1 H), 1.86-1.58 (m, 4 H), 1.14 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, MeOD) δ 163.6, 154.1, 145.1, 133.6, 131.3, 122.8, 119.8, 117.7, 108.6, 30.1, 28.5, 26.7, 20.1, 18.0; IR (neat) 2930, 1650, 1619, 1502, 1429, 1417 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{16}NO_2^+$: 230.1176, found: 230.1175.

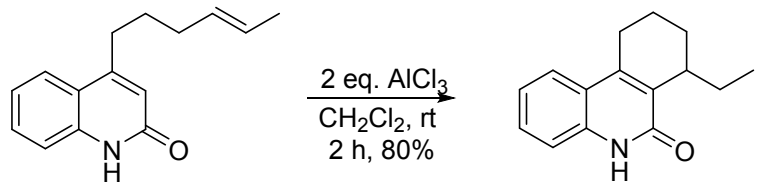
(7) 1,3-Dimethoxy-7-methyl-7,8,9,10-tetrahydrophenanthridin-6(5*H*)-one (8b)



8a **8b**

The reaction of **8a** (55 mg, 0.2 mmol), $AlCl_3$ (53 mg, 0.4 mmol), and CH_2Cl_2 (10 mL) affords **8b** as a solid (52 mg, 95%); mp 214.6-215.5 ^{o}C (*n*-hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.19 (s, 1 H), 6.47 (d, J = 2.4 Hz, 1 H), 6.20 (d, J = 2.4 Hz, 1 H), 3.86 (s, 3 H), 3.82 (s, 3 H), 3.41-3.29 (m, 1 H), 3.26-3.16 (m, 1 H), 3.04-2.89 (m, 1 H), 1.86-1.61 (m, 4 H), 1.30 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 160.6, 159.3, 146.8, 140.1, 128.7, 106.4, 94.4, 90.9, 55.4, 30.2, 28.9, 27.7, 20.2, 18.3; IR (neat) 1653, 1602, 1551, 1460, 1439, 1407 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{20}NO_3^+$: 274.1438, found: 274.1437.

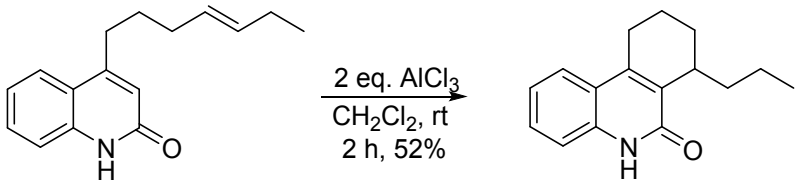
(8) 7-Ethyl-7,8,9,10-tetrahydrophenanthridin-6(5*H*)-one (9b)



9a **9b**

The reaction of **9a** (45 mg, 0.2 mmol), $AlCl_3$ (53 mg, 0.4 mmol), and CH_2Cl_2 (10 mL) affords **9b** as a solid (36 mg, 80%); mp 193.2-193.8 ^{o}C (*n*-hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.79 (s, 1 H), 7.66 (d, J = 8.0 Hz, 1 H), 7.44 (t, J = 8.2 Hz, 1 H), 7.34 (d, J = 8.8 Hz, 1 H), 7.19 (t, J = 8.2 Hz, 1 H), 3.09-2.92 (m, 2 H), 2.85-2.66 (m, 1 H), 2.07-1.80 (m, 4 H), 1.70-1.56 (m, 1 H), 1.43-1.28 (m, 1 H), 1.08 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 143.5, 136.6, 132.8, 128.9, 123.2, 122.0, 120.5, 115.8, 33.9, 25.6, 25.5, 24.1, 17.1, 12.6; IR (neat) 1644, 1610, 1561, 1433, 1397 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{18}NO^+$: 228.1383, found: 228.1382.

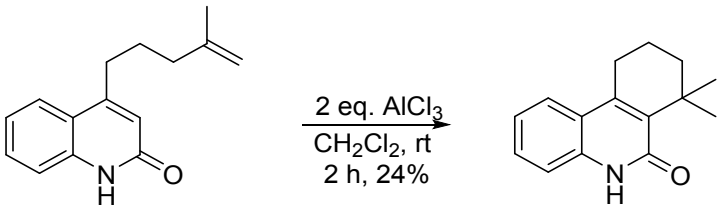
(9) 7-Propyl-7,8,9,10-tetrahydrophenanthridin-6(5*H*)-one (10b)



10a **10b**

The reaction of **10a** (48 mg, 0.2 mmol), $AlCl_3$ (53 mg, 0.4 mmol), and CH_2Cl_2 (10 mL) affords **10b** as a solid (25 mg, 52%); mp 180.0-180.9 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.15 (s, 1 H), 7.67 (d, J = 8.0 Hz, 1 H), 7.43 (t, J = 8.0 Hz, 1 H), 7.29 (d, J = 7.6 Hz, 1 H), 7.20 (t, J = 8.0 Hz, 1 H), 3.14-3.06 (m, 1 H), 3.03-2.94 (m, 1 H), 2.81 -2.68 (m, 1 H), 2.00-1.77 (m, 4 H), 1.67-1.41 (m, 3 H), 1.40-1.27 (m, 1 H), 1.00 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 143.4, 136.5, 133.0, 128.9, 123.2, 122.0, 120.6, 115.6, 35.0, 32.1, 25.5, 24.7, 21.2, 17.1, 14.3; IR (neat) 1645, 1609, 1563, 1505, 1456, 1433 cm^{-1}; HRMS (ESI): calcd for $C_{16}H_{20}NO^+$: 242.1539, found: 242.1539.

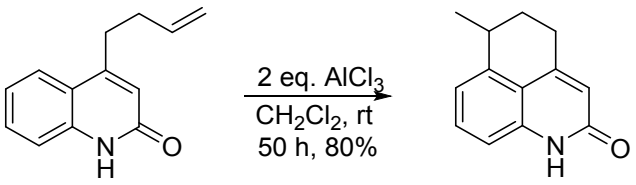
(10) 7,7-Dimethyl-7,8,9,10-tetrahydrophenanthridin-6(5*H*)-one (11b)



11a **11b**

The reaction of **11a** (45 mg, 0.2 mmol), $AlCl_3$ (53 mg, 0.4 mmol), and CH_2Cl_2 (10 mL) affords **11b** as a solid (11 mg, 24%); mp 179.2-180.0 °C (*n*-hexane/ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.63 (s, 1 H), 7.67 (d, J = 8.0 Hz, 1 H), 7.42 (t, J = 8.2 Hz, 1 H), 7.23-7.13 (m, 2 H), 2.89 (t, J = 6.2 Hz, 2 H), 1.93-1.80 (m, 2 H), 1.72-1.62 (m, 2 H), 1.52 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 144.5, 136.7, 135.5, 129.1, 123.8, 121.9, 120.6, 115.0, 40.9, 34.1, 27.5, 27.4, 18.5; IR (neat) 1639, 1604, 1553, 1503, 1432 cm^{-1}; HRMS (ESI): calcd for $C_{15}H_{18}NO^+$: 228.1383, found: 228.1382.

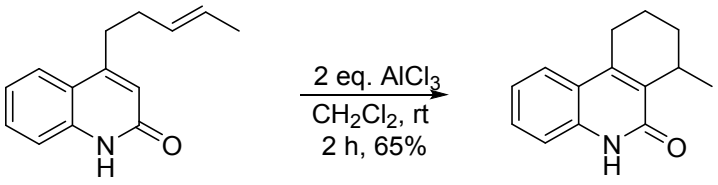
(11) 6-Methyl-5,6-dihydro-1*H*-benzo[*de*]quinolin-2(4*H*)-one (12b)



12a **12b**

The reaction of **12a** (40 mg, 0.2 mmol), $AlCl_3$ (53 mg, 0.4 mmol), and CH_2Cl_2 (10 mL) affords **12b** as a solid (32 mg, 80%); mp 195.2-196.2 ^oC (*n*-hexane/ethyl acetate); ^1H NMR (400 MHz, $CDCl_3$) δ 12.71 (s, 1 H), 7.42 (t, J = 7.8 Hz, 1 H), 7.30 (d, J = 8.0 Hz, 1 H), 7.06 (d, J = 7.4 Hz, 1 H), 6.47 (s, 1 H), 3.15-2.94 (m, 2 H), 2.93-2.79 (m, 1 H), 2.14-2.00 (m, 1 H), 1.84-1.71 (m, 1 H), 1.36 (d, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 150.8, 142.4, 138.5, 130.4, 120.2, 116.9, 116.8, 114.1, 33.0, 30.0, 27.8, 20.9; IR (neat) 1643, 1617, 1557, 1436, 1384 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{14}NO^+$: 200.1070, found: 200.1069.

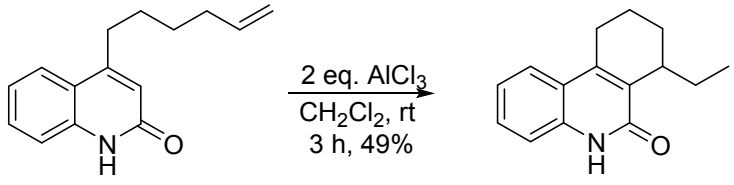
(12) 7-Methyl-7,8,9,10-tetrahydrophenanthridin-6(5*H*)-one (1b)



13a **1b**

The reaction of **13a** (43 mg, 0.2 mmol), $AlCl_3$ (53 mg, 0.4 mmol), and CH_2Cl_2 (10 mL) affords **1b** as a solid (28 mg, 65%); ^1H NMR (400 MHz, $CDCl_3$) δ 11.58 (s, 1 H), 7.67 (d, J = 8.0 Hz, 1 H), 7.44 (t, J = 8.0 Hz, 1 H), 7.34 (d, J = 8.0 Hz, 1 H), 7.20 (t, J = 8.2 Hz, 1 H), 3.37-3.20 (m, 1 H), 3.09-2.95 (m, 1 H), 2.83-2.67 (m, 1 H), 2.02-1.86 (m, 2 H), 1.84-1.74 (m, 2 H), 1.33 (d, J = 6.8 Hz, 3 H).

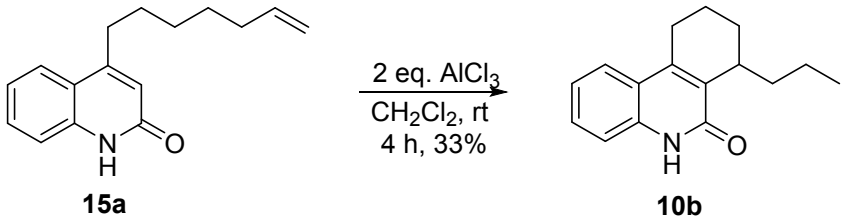
(13) 7-Ethyl-7,8,9,10-tetrahydrophenanthridin-6(5*H*)-one (9b)



14a **9b**

The reaction of **14a** (45 mg, 0.2 mmol), $AlCl_3$ (53 mg, 0.4 mmol), and CH_2Cl_2 (10 mL) affords **9b** as a solid (22 mg, 49%); ^1H NMR (400 MHz, $CDCl_3$) δ 11.64 (s, 1 H), 7.66 (d, J = 8.8 Hz, 1 H), 7.44 (t, J = 8.2 Hz, 1 H), 7.33 (d, J = 8.4 Hz, 1 H), 7.19 (t, J = 8.2 Hz, 1 H), 3.05-2.91 (m, 2 H), 2.84-2.68 (m, 1 H), 2.08-1.81 (m, 4 H), 1.70-1.54 (m, 1 H), 1.43-1.28 (m, 1 H), 1.08 (t, J = 7.2 Hz, 3 H).

(14) 7-Propyl-7,8,9,10-tetrahydrophenanthridin-6(5*H*)-one (10b)



The reaction of **15a** (48 mg, 0.2 mmol), $AlCl_3$ (53 mg, 0.4 mmol), and CH_2Cl_2 (10 mL) affords **10b** as a solid (16 mg, 33%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.07 (s, 1 H), 7.66 (d, J = 8.0 Hz, 1 H), 7.43 (t, J = 8.2 Hz, 1 H), 7.28 (d, J = 8.4 Hz, 1 H), 7.19 (t, J = 8.2 Hz, 1 H), 3.14-2.93 (m, 2 H), 2.83-2.68 (m, 1 H), 2.01-1.70 (m, 4 H), 1.65-1.41 (m, 3 H), 1.39-1.25 (m, 1 H), 1.00 (t, J = 7.4 Hz, 3 H).

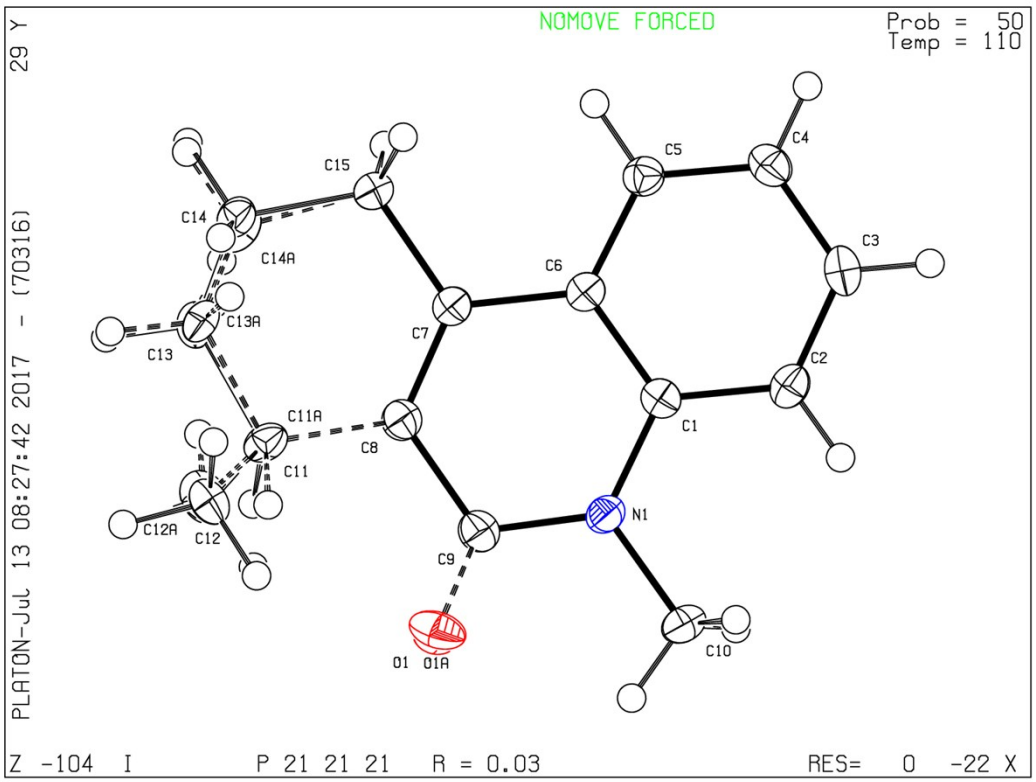


Figure S1. ORTEP-style representation of the X-ray crystal structure of **2b**. Ellipsoids are depicted at 50% probability level, hydrogen atoms with an arbitrary radius. Disorder in the alkyl part of the structure (C11 – C15) omitted for clarity.

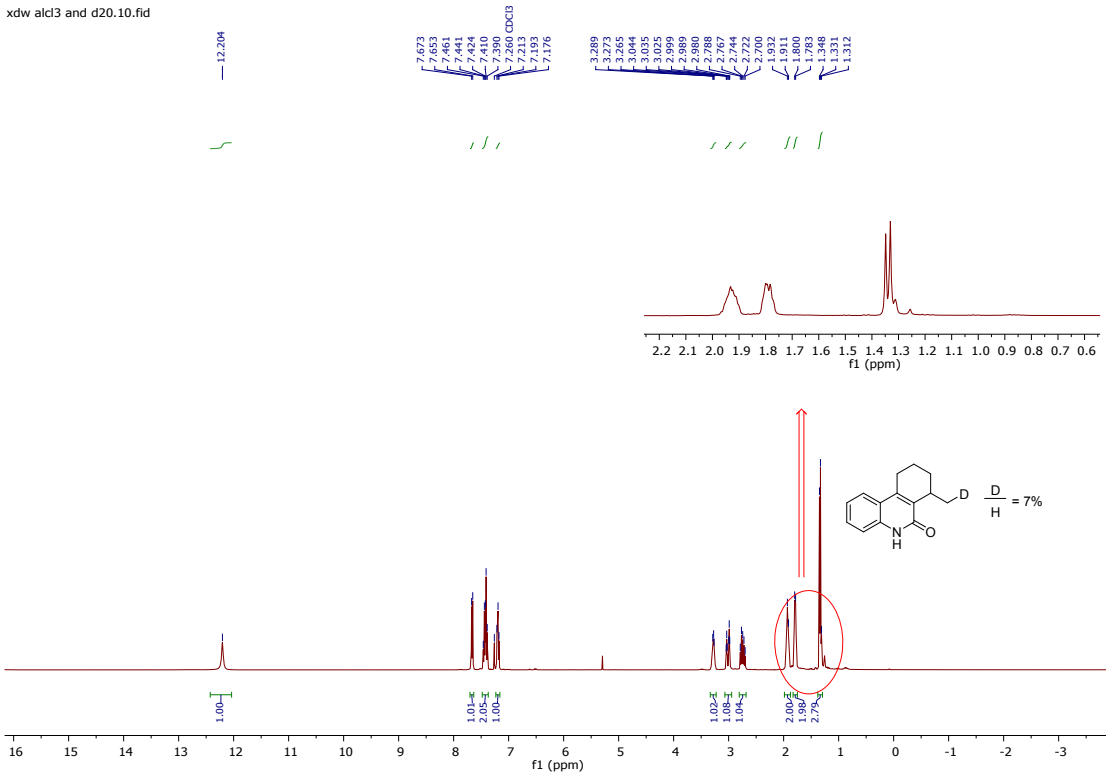


Figure S2. Deuterium labeling experiment

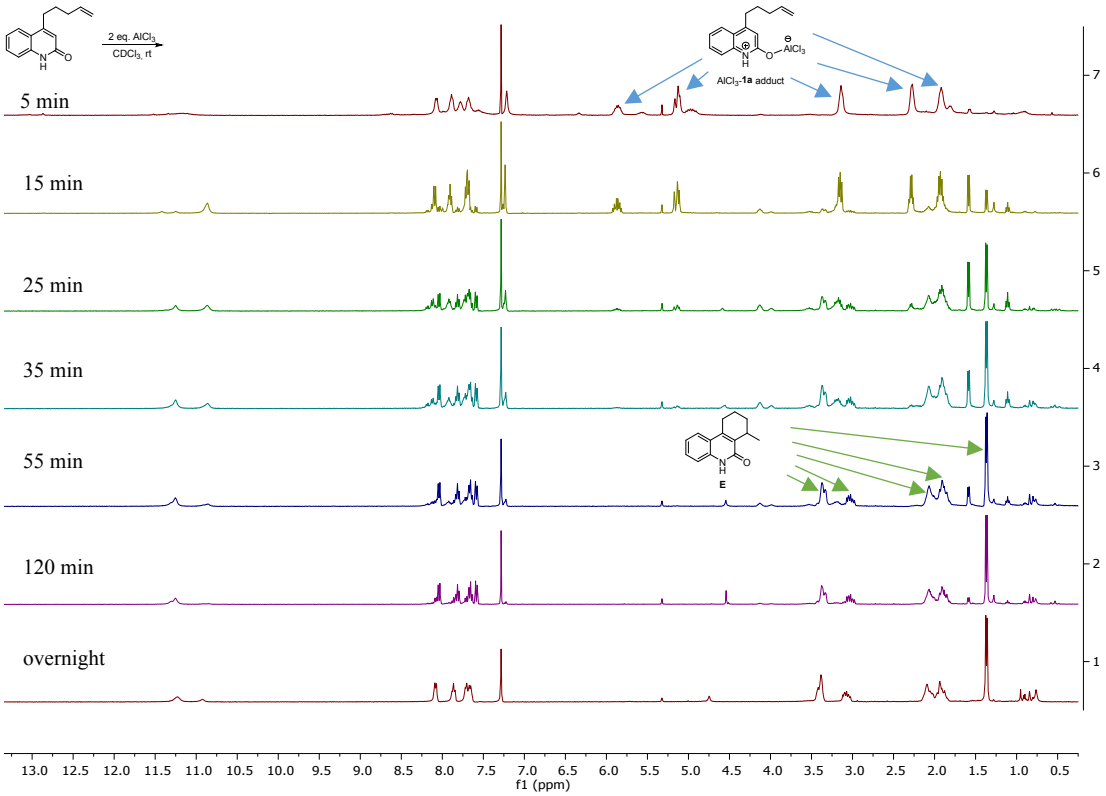
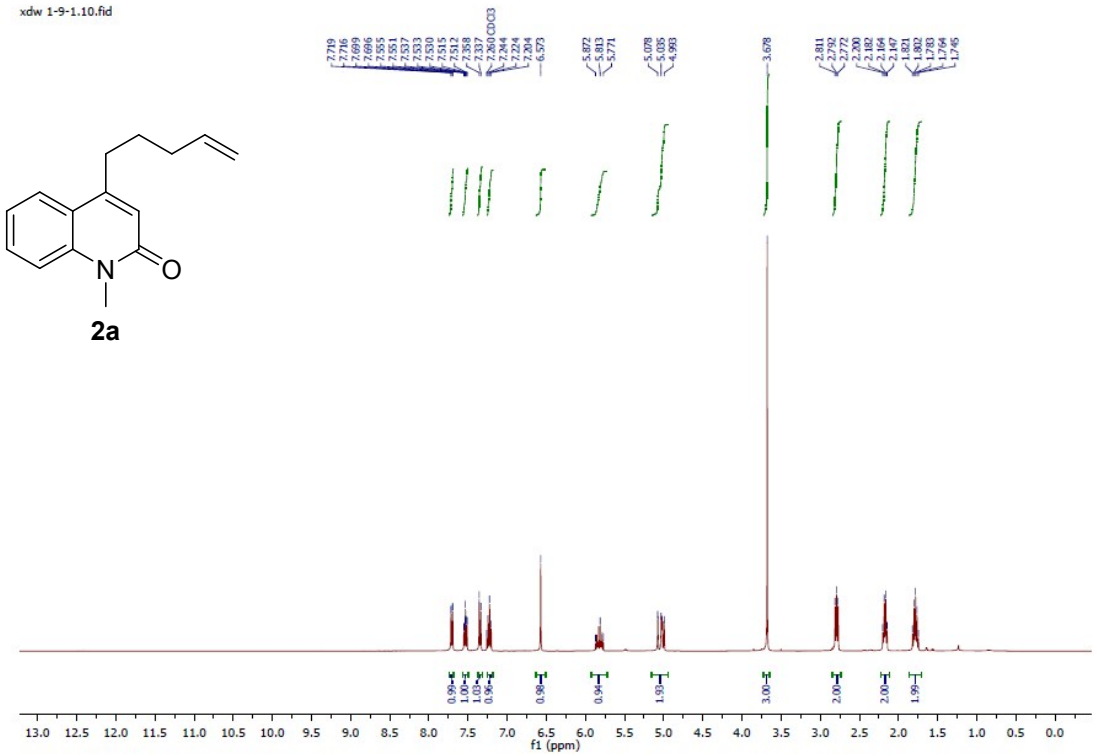
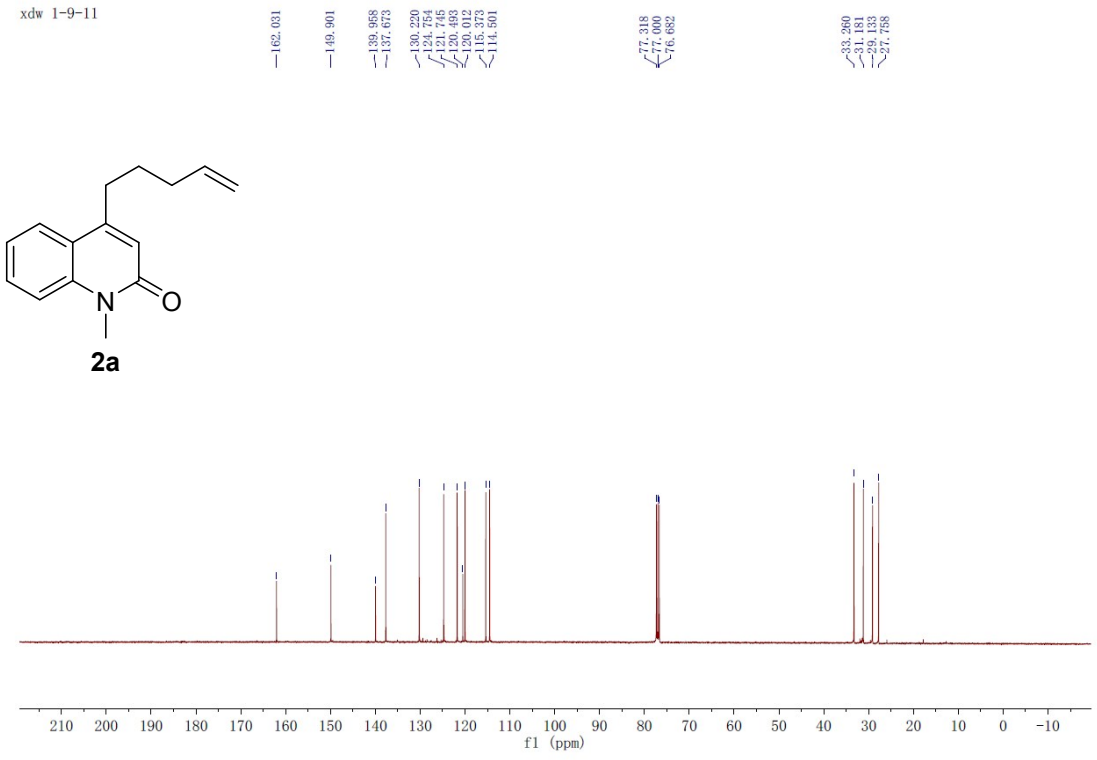
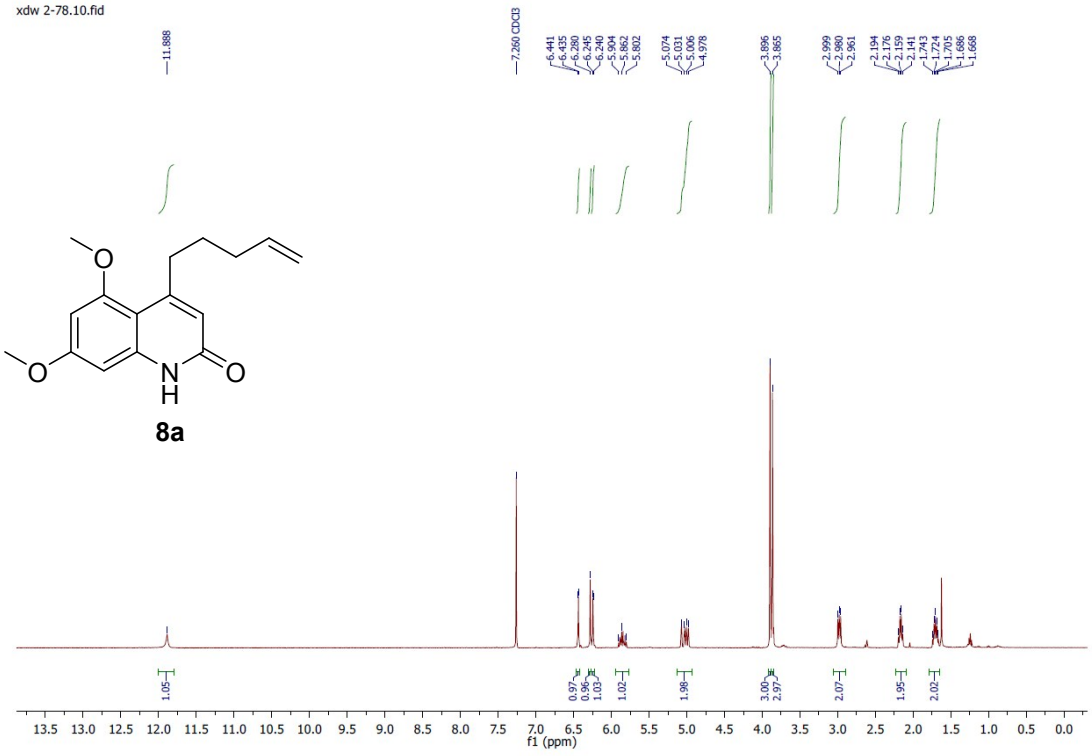


Figure S3.Intermediate trapping experiment

NMR Spectra



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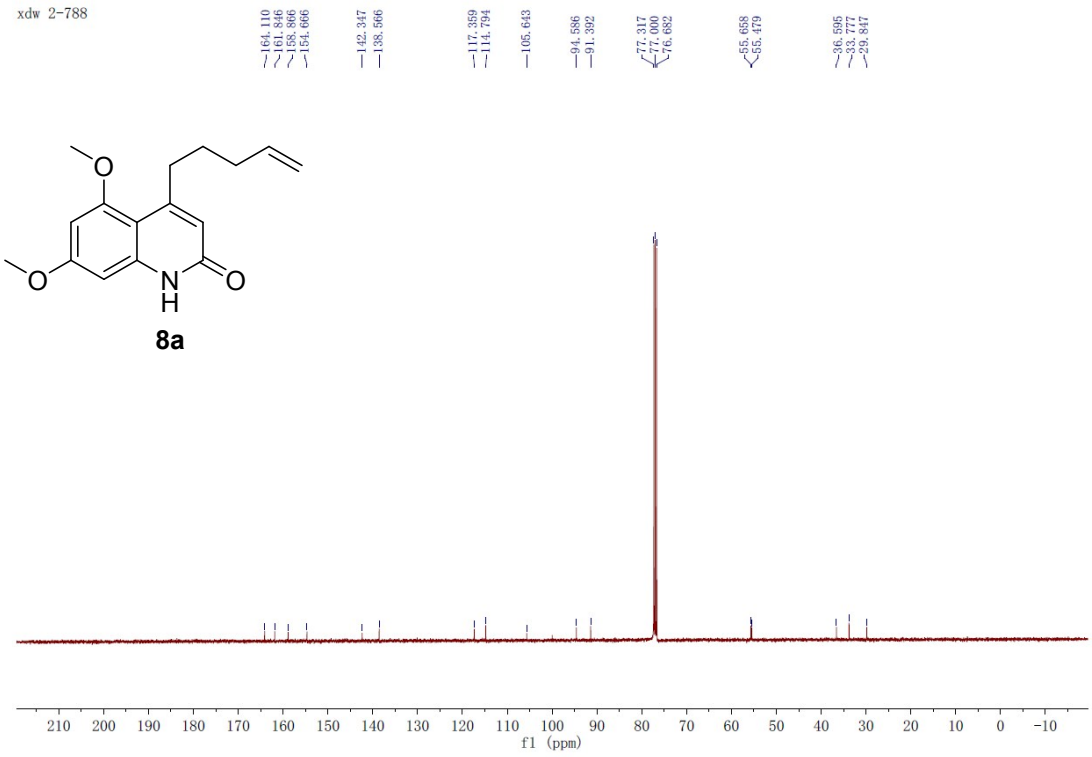
5.804
5.802
5.802
5.074
5.031
5.006
4.978
3.896
3.865
2.999
2.980
2.961
2.194
2.176
2.159
2.141
1.743
1.724
1.705
1.686
1.668
O
O
N
H
O
8a
1.05
0.97
0.96
1.03
1.02
1.98
3.00
2.97
2.07
1.95
2.02
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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142.347
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114.794
105.643
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91.392
77.317
77.000
76.682
55.658
55.479
36.595
33.177
29.847
O
O
N
H
O
8a
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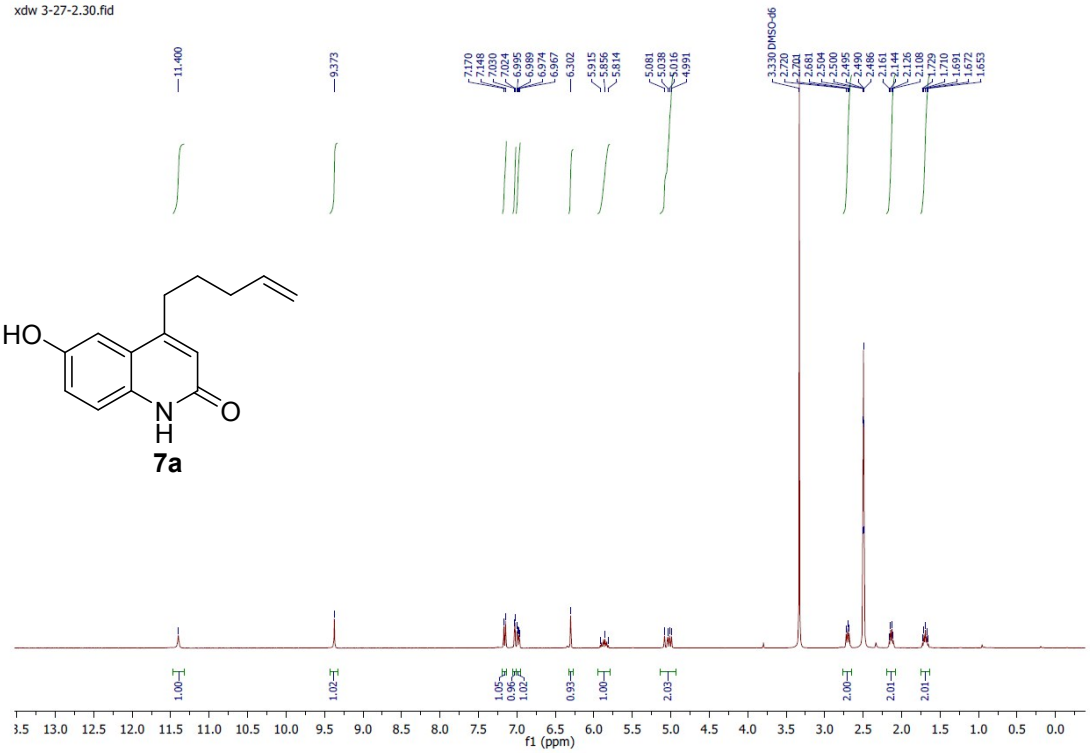
f1 (ppm)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7.148
7.030
7.024
6.995
6.989
6.974
6.967
6.302
5.915
5.856
5.814
5.081
5.038
5.016
4.991
3.330 DMSO-d6
2.720
2.701
2.681
2.504
2.500
2.495
2.490
2.486
2.161
2.144
2.126
2.108
1.729
1.710
1.691
1.672
1.653
HO
N
H
O
7a
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1.02
0.93
1.00
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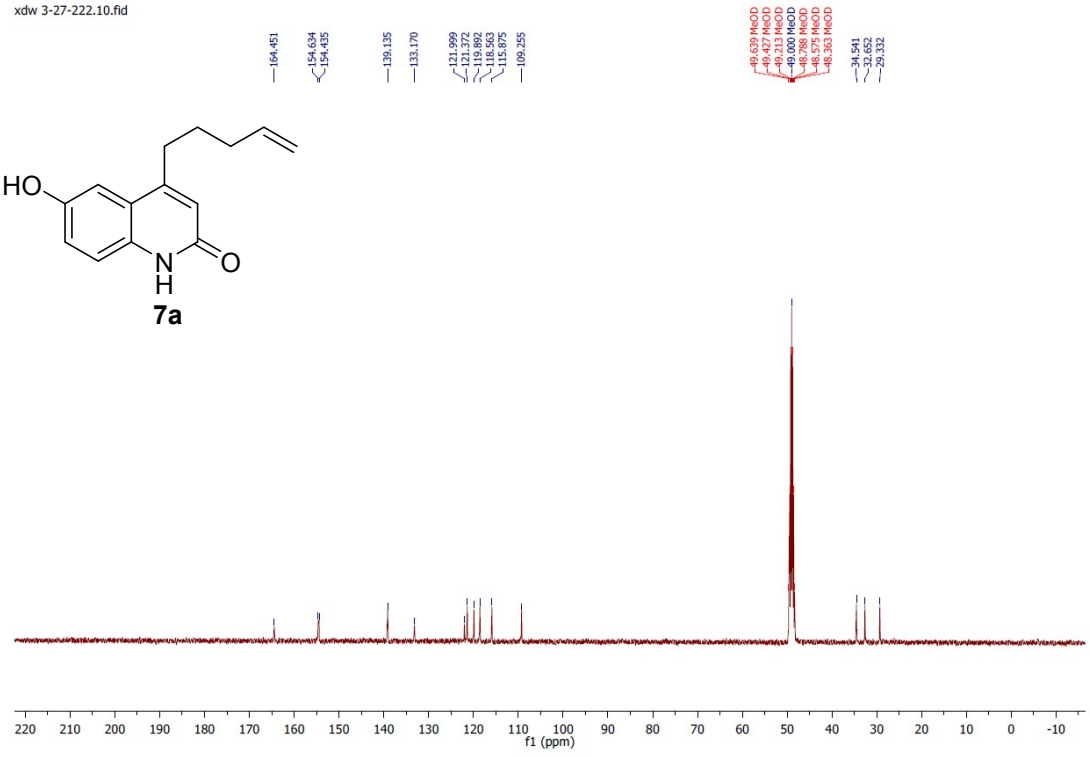
2.00
2.01
2.01
f1 (ppm)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133.170
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109.255
49.639 MeOD
49.427 MeOD
49.213 MeOD
49.000 MeOD
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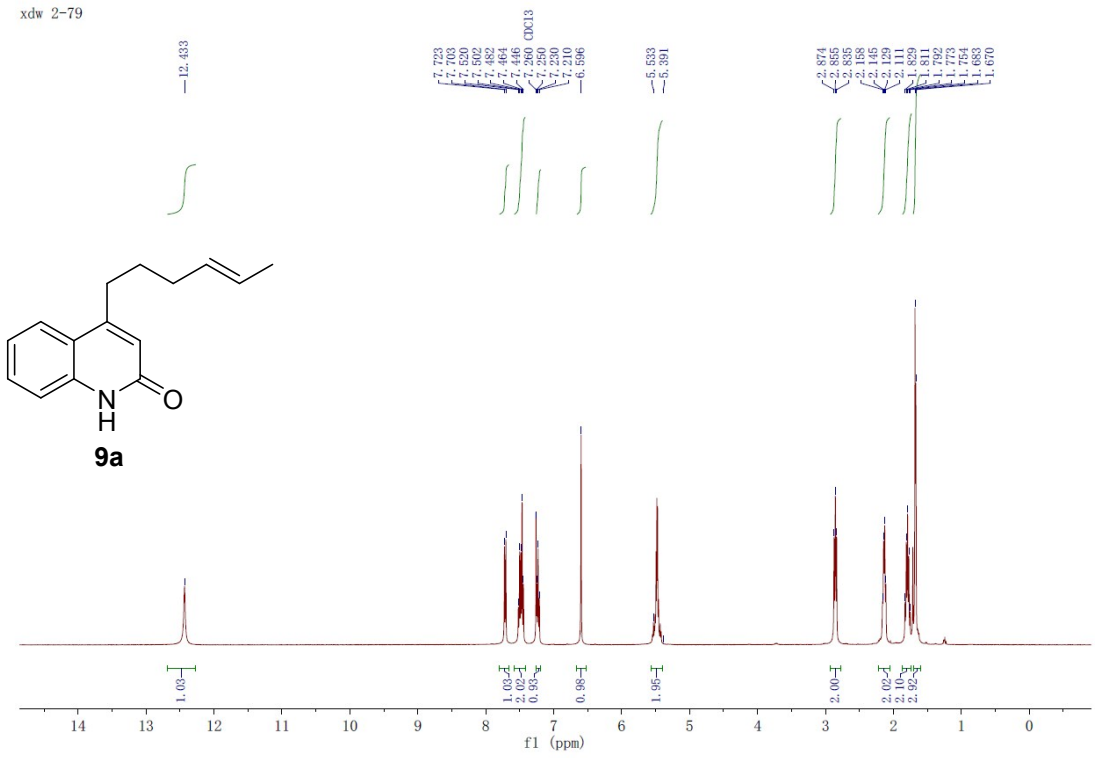
34.541
32.652
29.332
HO
N
H
O
7a
f1 (ppm)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7.250
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7.210
6.596
5.533
5.391
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2.855
2.835
2.158
2.145
2.129
2.111
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1.811
1.792
1.773
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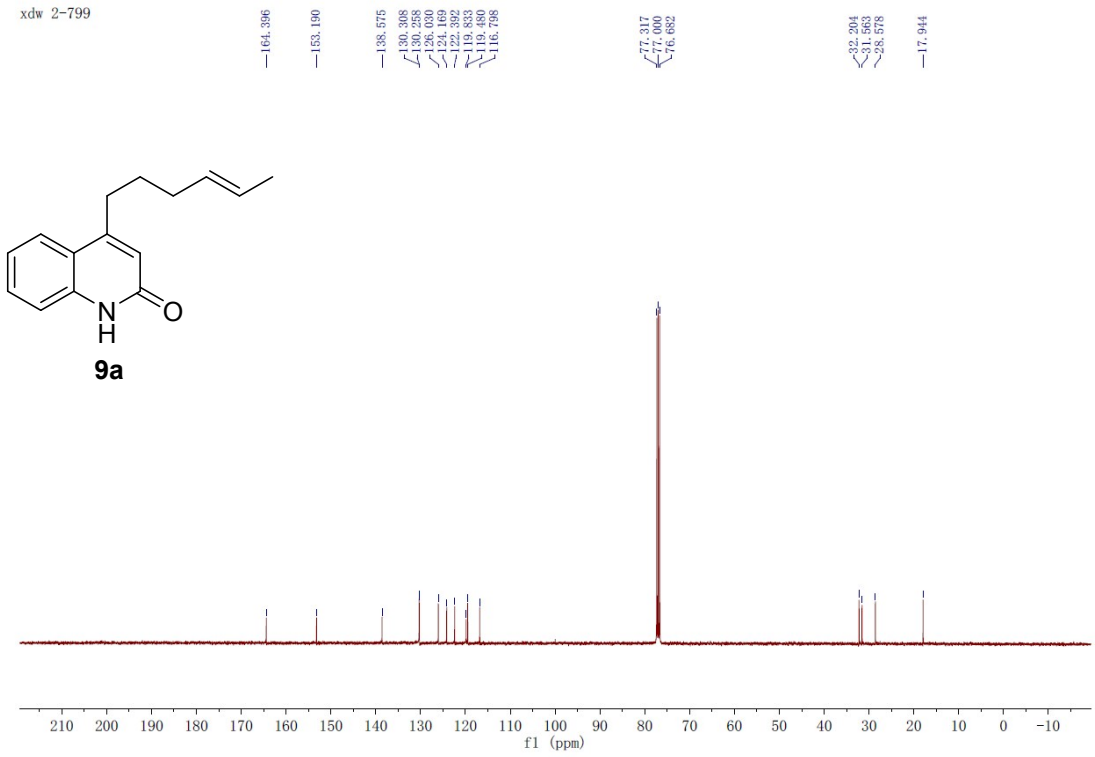
1.683
1.670
N
H
O
9a
1.03
1.03
2.02
0.93
0.98
1.95
2.00
2.02
2.10
2.92
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)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122.392
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116.798
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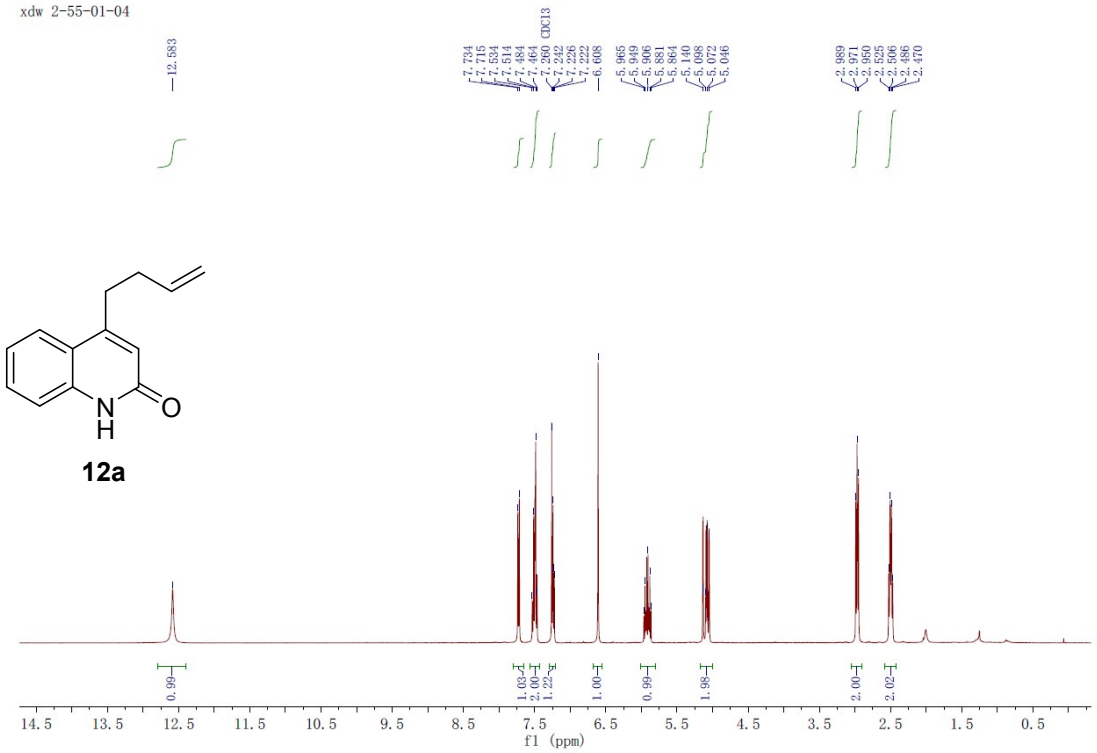
77.000
76.682
32.204
31.563
28.578
17.944
N
H
O
9a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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0.99
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12.5
11.5
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5.5
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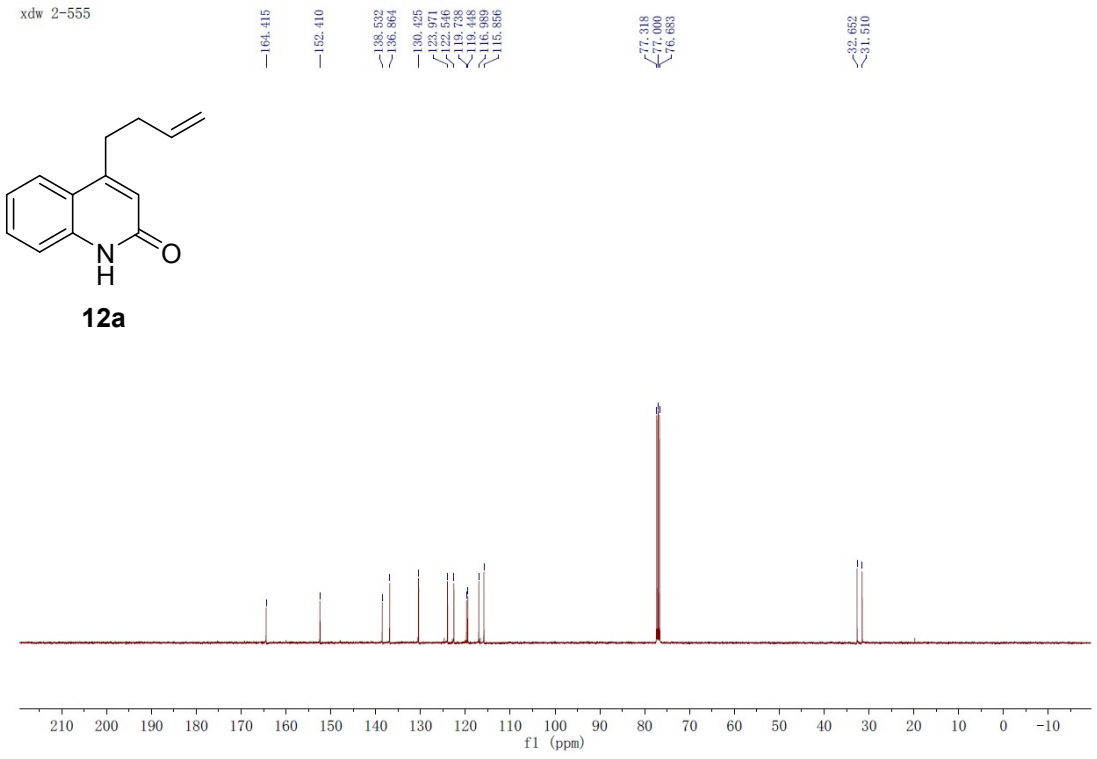
3.5
2.5
1.5
0.5
f1 (ppm)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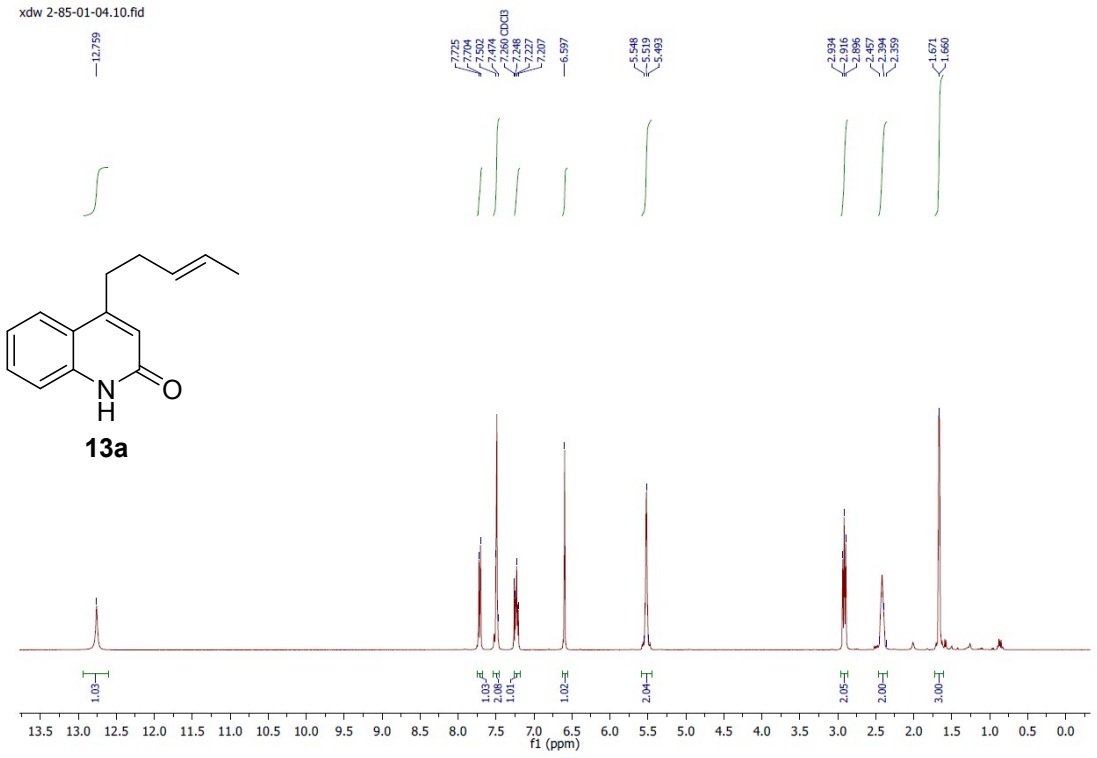
77.000
76.683
32.662
31.510
N
H
O
12a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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2.934
2.916
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2.394
2.359
1.671
1.660
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2.08
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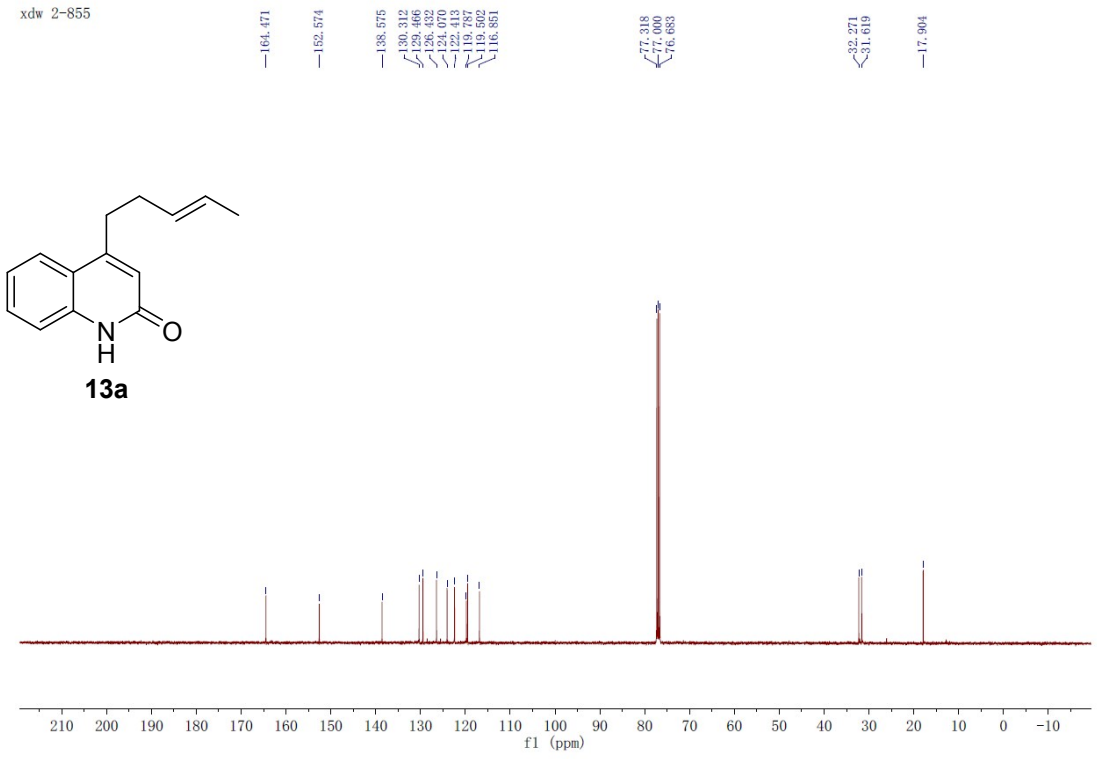
2.05
2.00
3.00
f1 (ppm)

13a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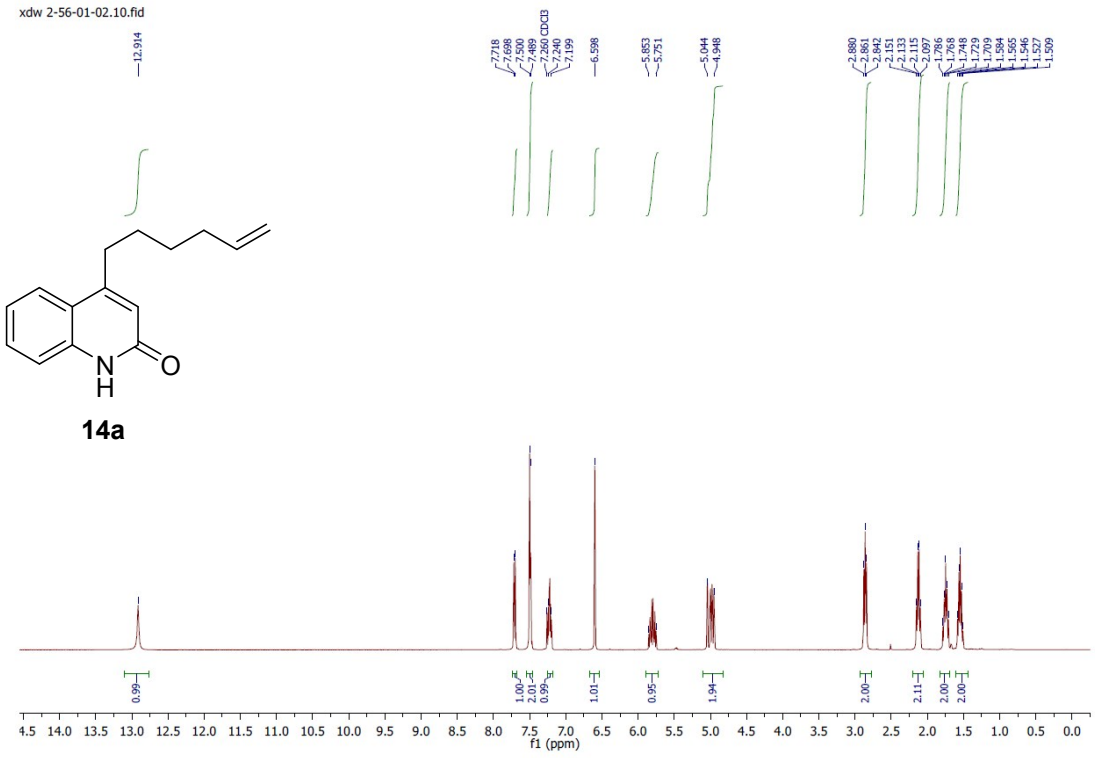
f1 (ppm)

13a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5.044
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2.861
2.842
2.151
2.133
2.115
2.097
1.786
1.768
1.748
1.729
1.709
1.584
1.565
1.546
1.527
1.509
0.99
1.00
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1.01
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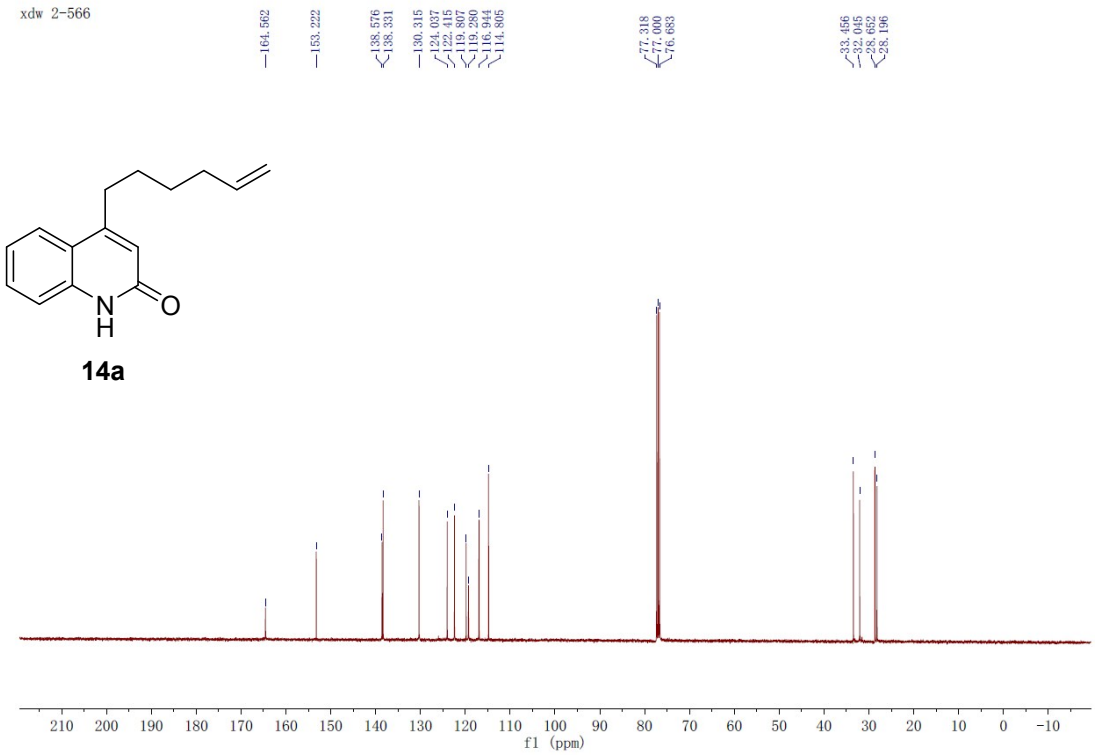
1.94
2.00
2.11
2.00
2.00
f1 (ppm)

14a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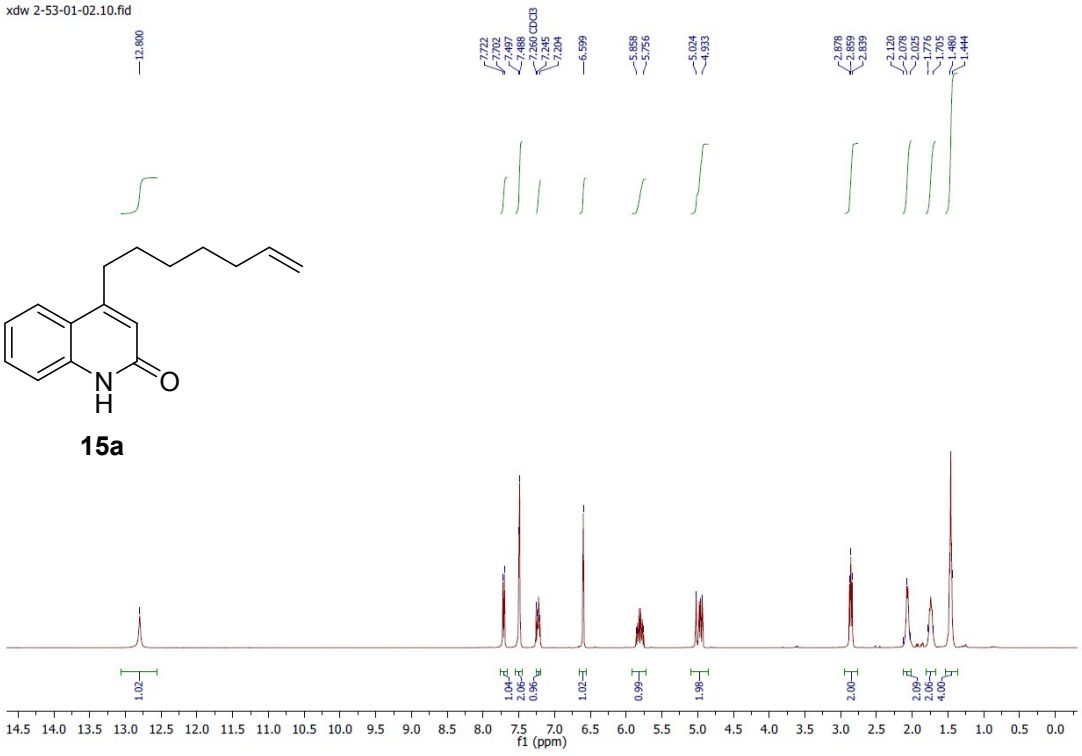
28.196
f1 (ppm)

14a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2.859
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1.776
1.705
1.490
1.444
N
H
O
15a
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1.04
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0.99
1.98
2.00
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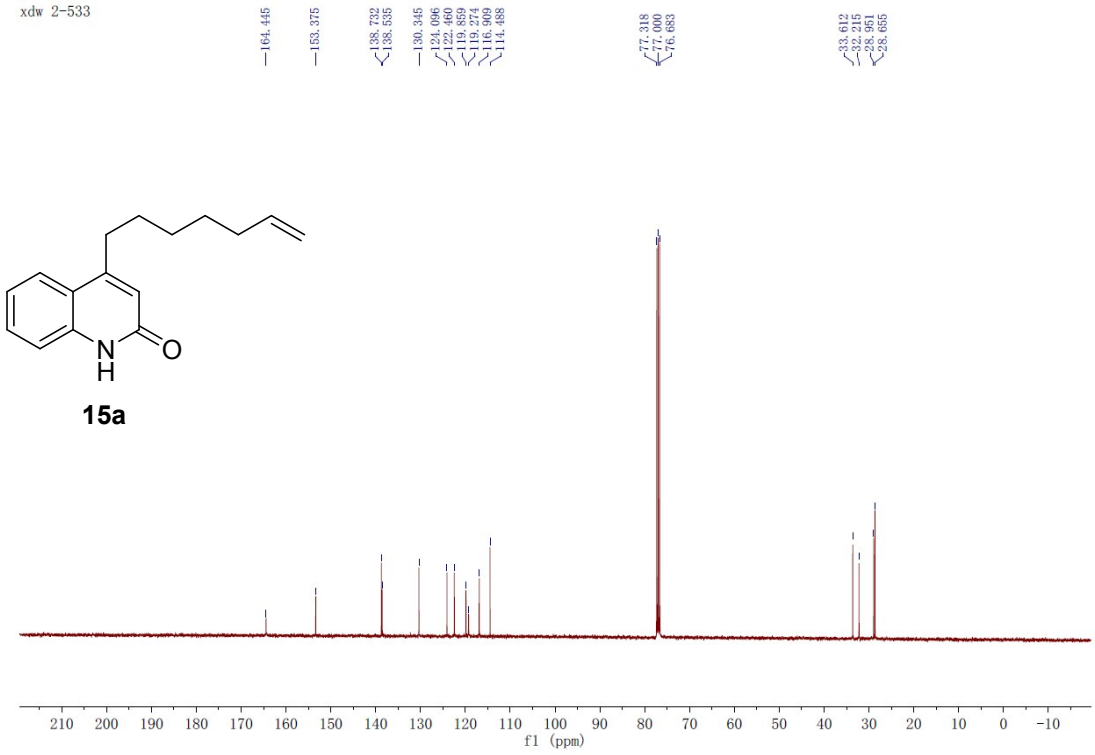
2.06
4.00
f1 (ppm)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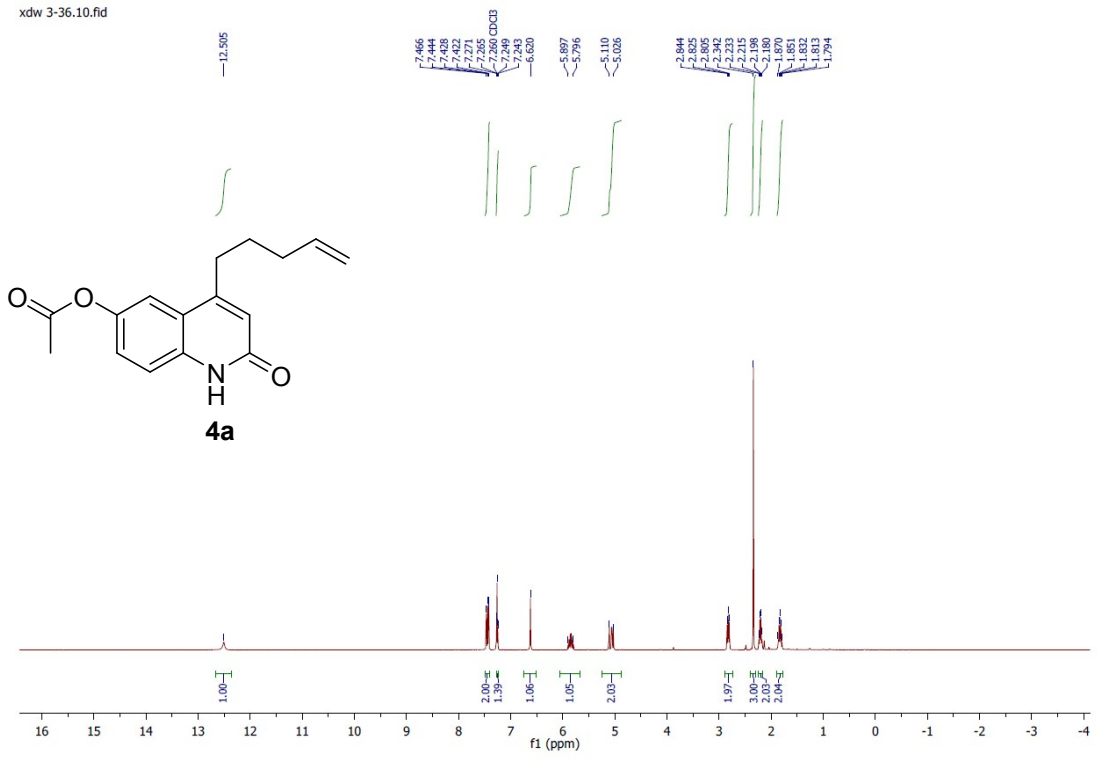
26.655
N
H
O
15a
f1 (ppm)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2.342
2.233
2.215
2.198
2.180
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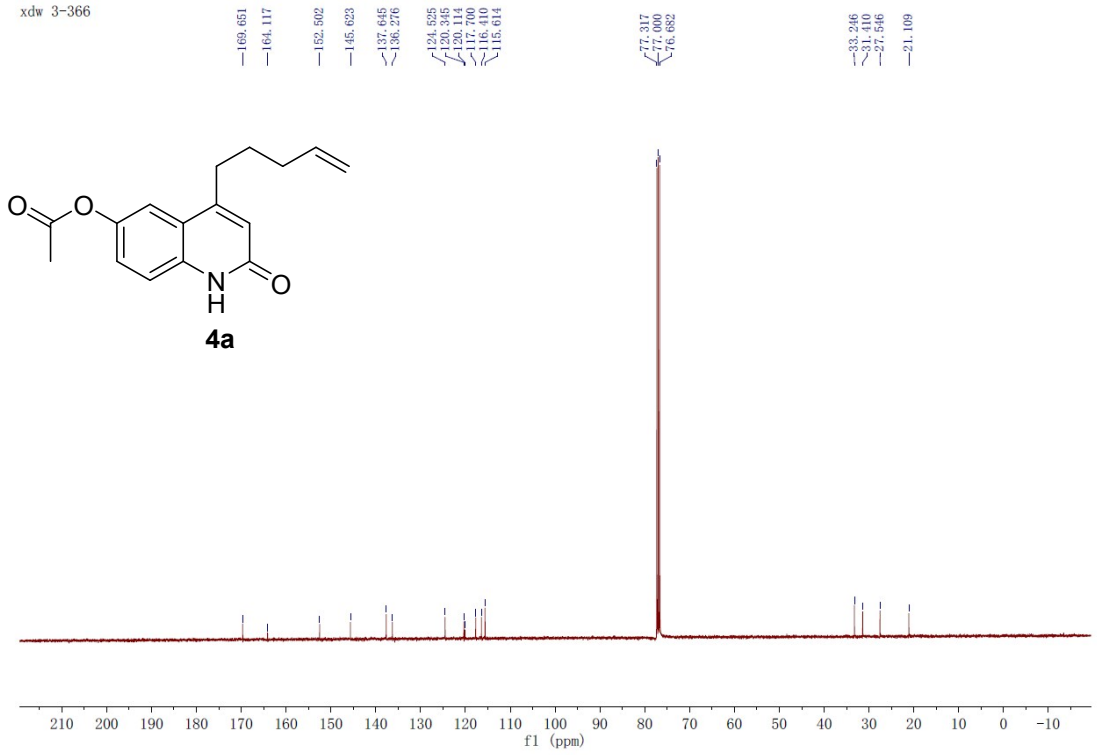
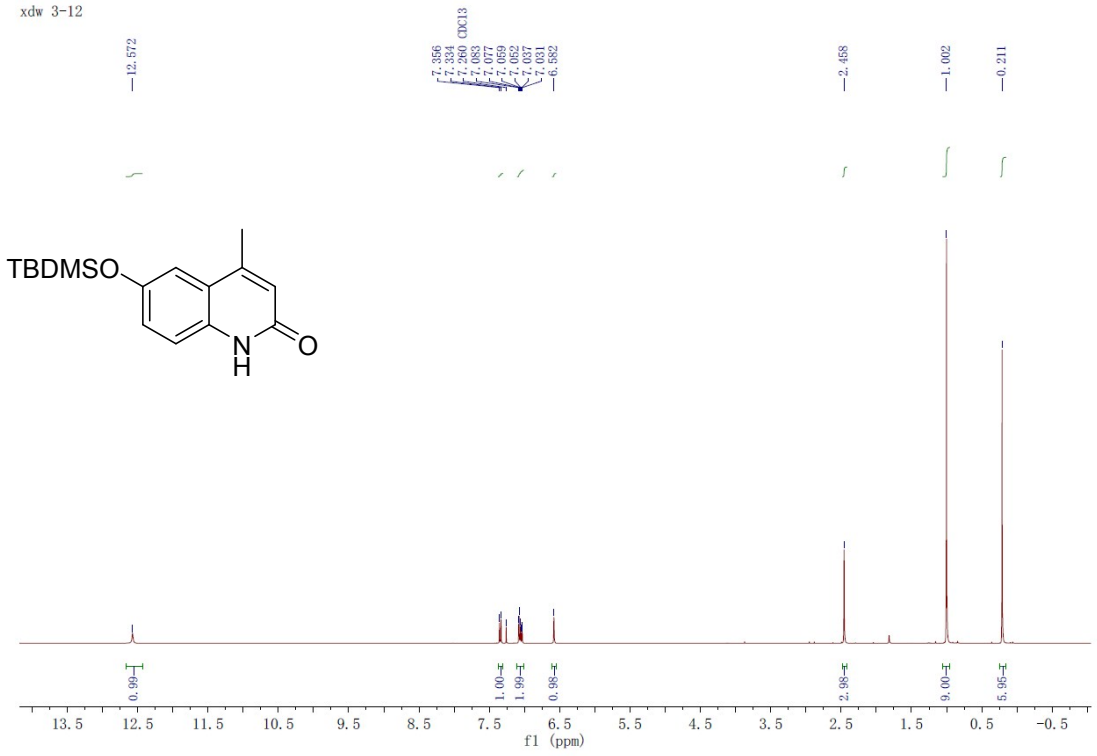
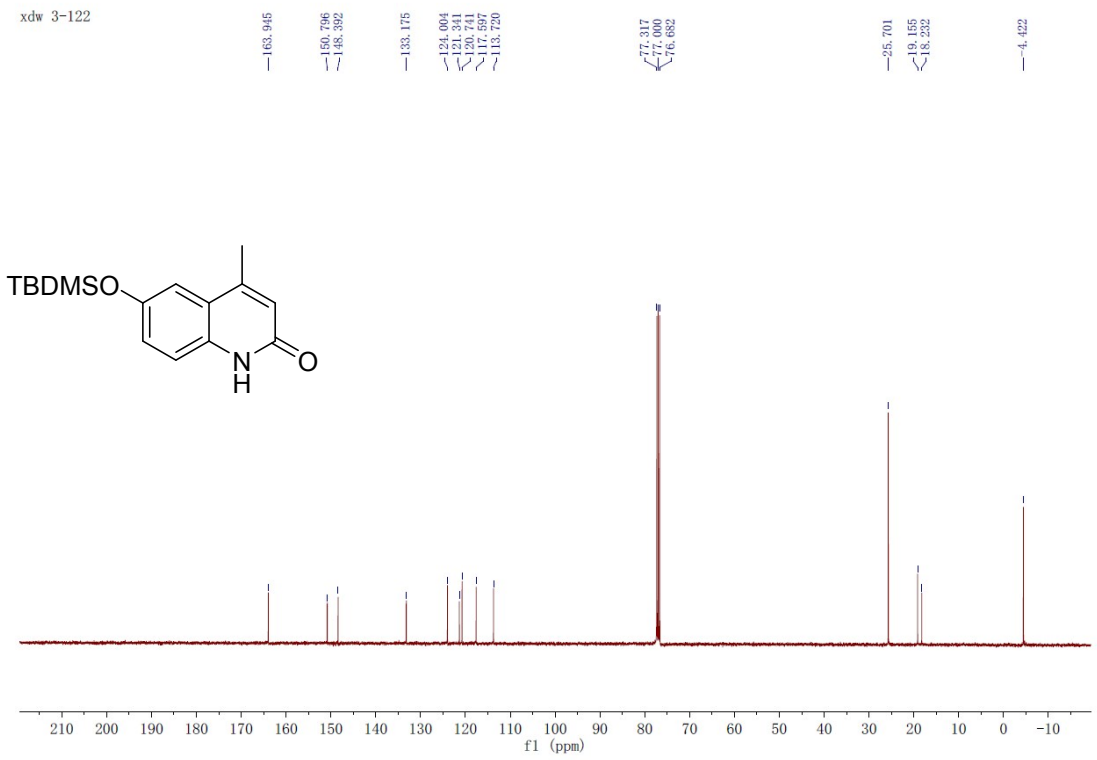
1.851
1.832
1.813
1.794
O
O
N
H
O
4a
1.00
2.00
1.39
1.06
1.05
2.03
1.97
3.00
2.03
2.04
f1 (ppm)

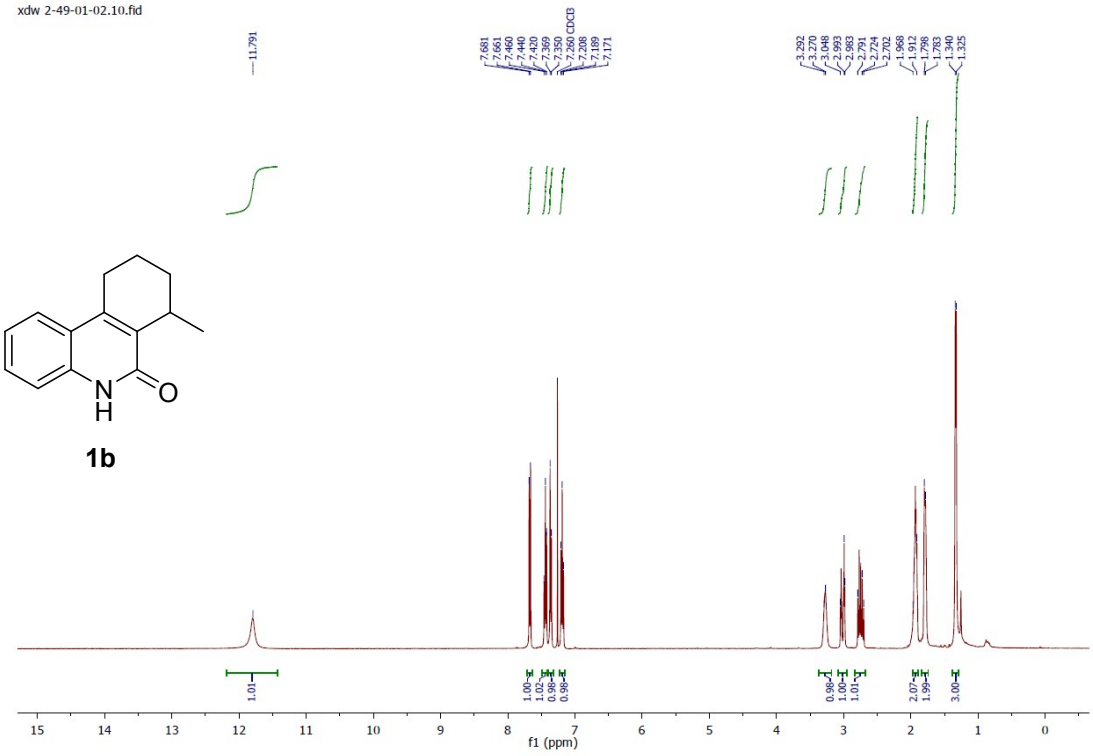

xdw 3-366
169.651
164.117
152.502
145.623
137.645
136.276
124.525
120.345
120.114
117.700
116.410
115.614
77.317
77.000
76.682
33.246
31.410
27.546
21.109
O
O
N
H
O
4a
f1 (ppm)

xdw 3-12

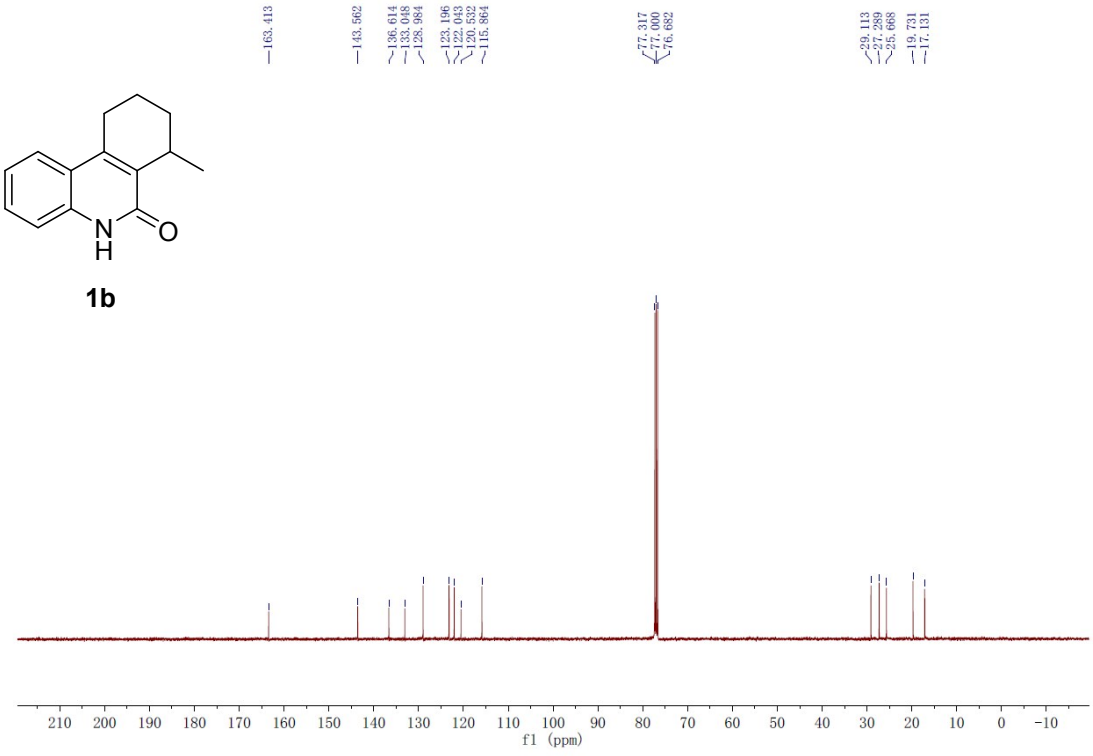


xdw 3-122

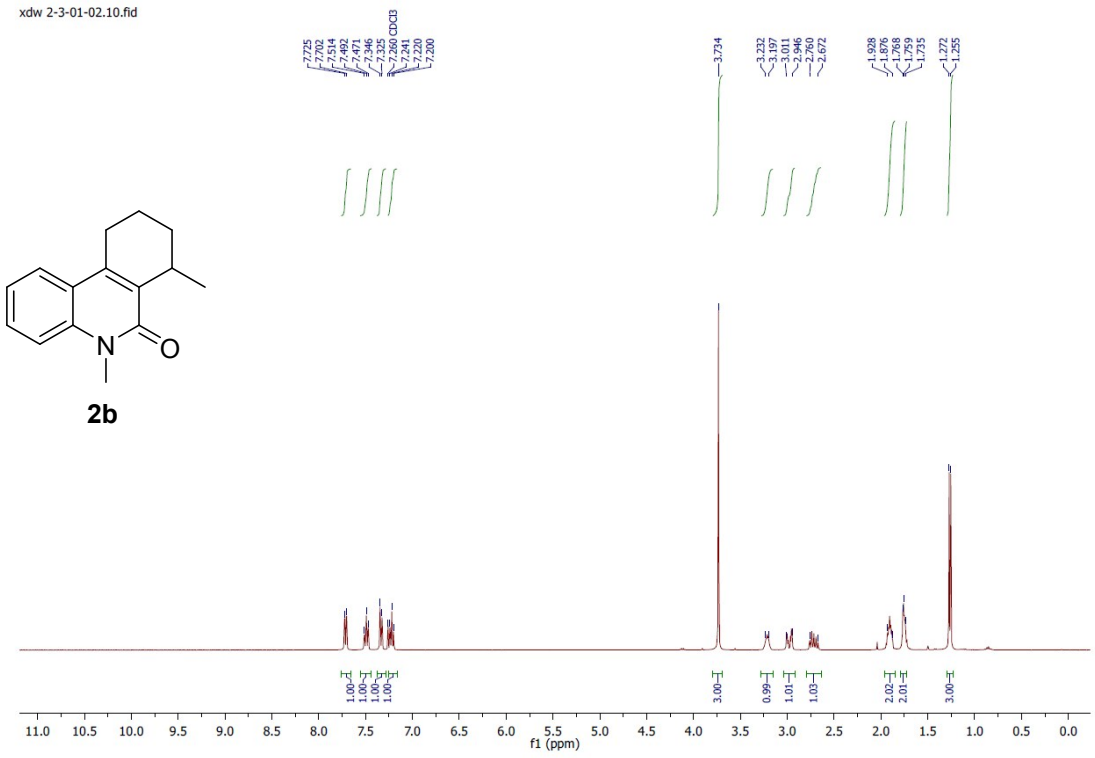



xdw 2-49-01-02.10.fid
11.791
7.681
7.661
7.460
7.440
7.420
7.369
7.350
7.260
CDCl3
7.208
7.189
7.171
3.292
3.270
3.048
2.993
2.963
2.791
2.724
2.702
1.968
1.912
1.798
1.783
1.340
1.325
1.01
1.00
1.02
0.98
0.98
0.98
1.00
1.01
2.07
1.99
3.00
f1 (ppm)

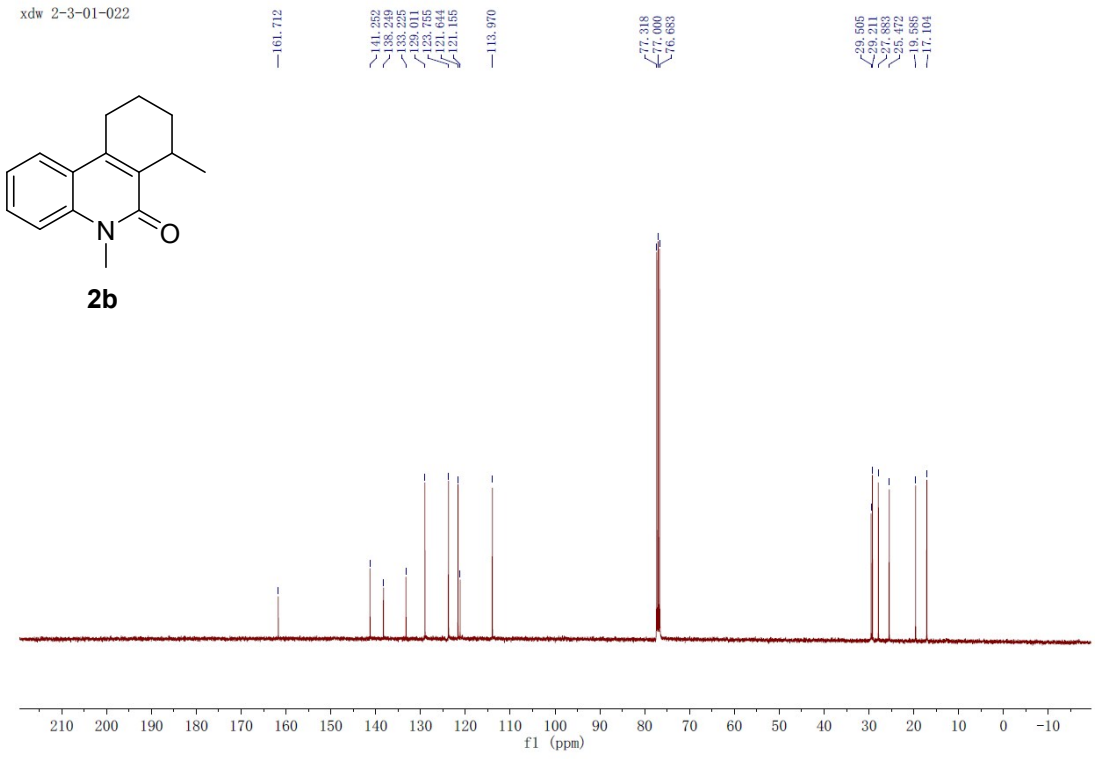
1b


163.413
143.562
136.614
133.048
128.984
123.196
122.043
120.532
115.864
77.317
77.000
76.682
29.113
27.289
25.668
19.731
17.131
f1 (ppm)

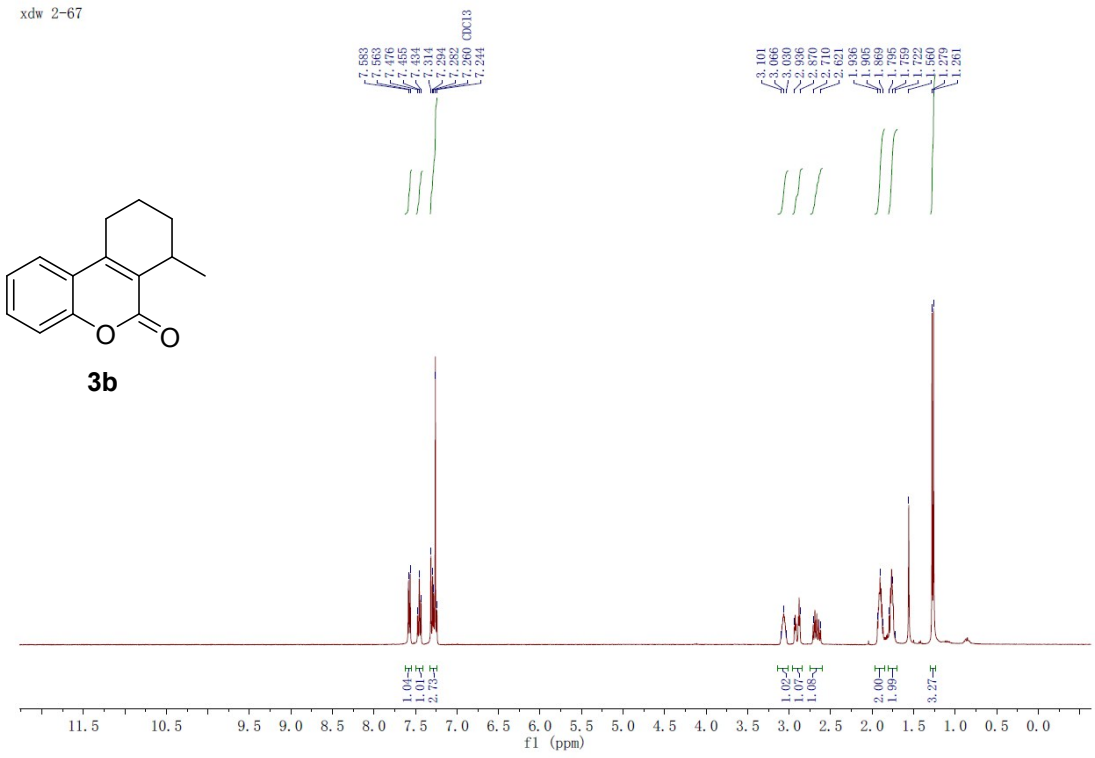
1b


xdw 2-3-01-02.10.fid
7.725
7.702
7.514
7.492
7.471
7.346
7.325
7.260 CDCl3
7.241
7.220
7.200
3.734
3.232
3.197
3.011
2.946
2.930
2.672
1.928
1.876
1.768
1.759
1.735
1.272
1.255
1.00
1.00
1.00
1.00
3.00
0.99
1.01
1.03
2.02
2.01
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
N
O

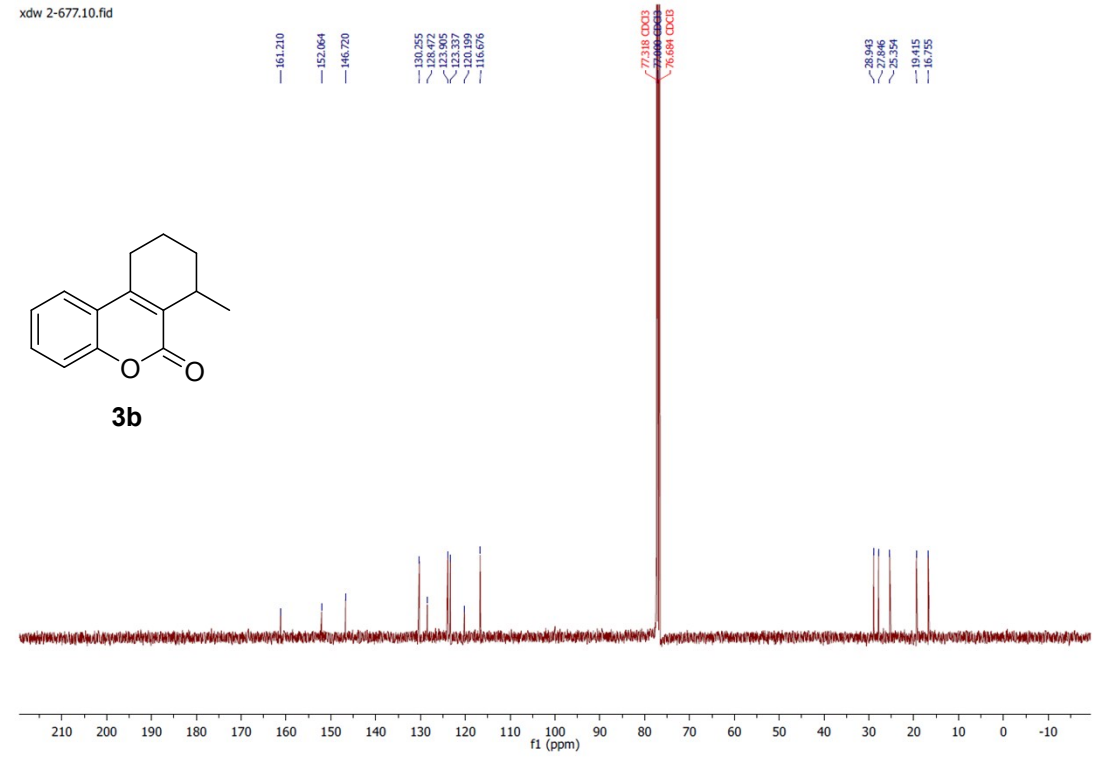
2b


xdw 2-3-01-022
161.712
141.252
138.249
133.225
129.011
123.755
121.644
121.155
113.970
77.318
77.000
76.683
29.505
29.211
27.883
26.472
19.585
17.104
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
N
O

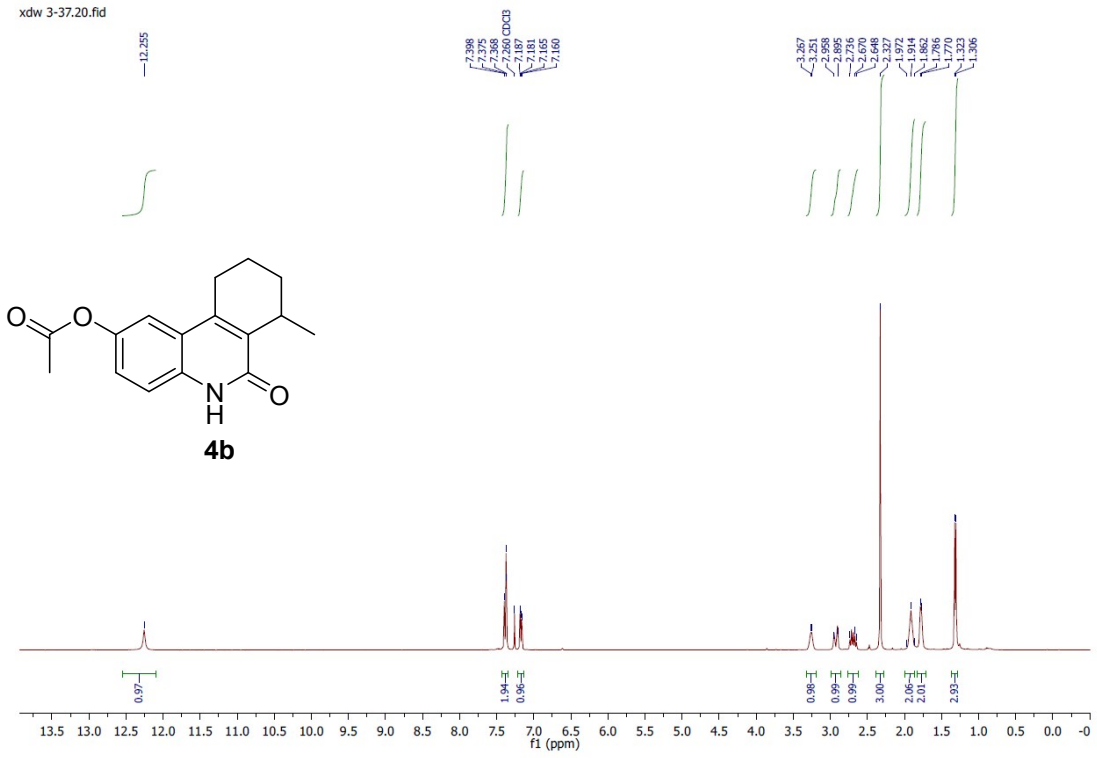
2b

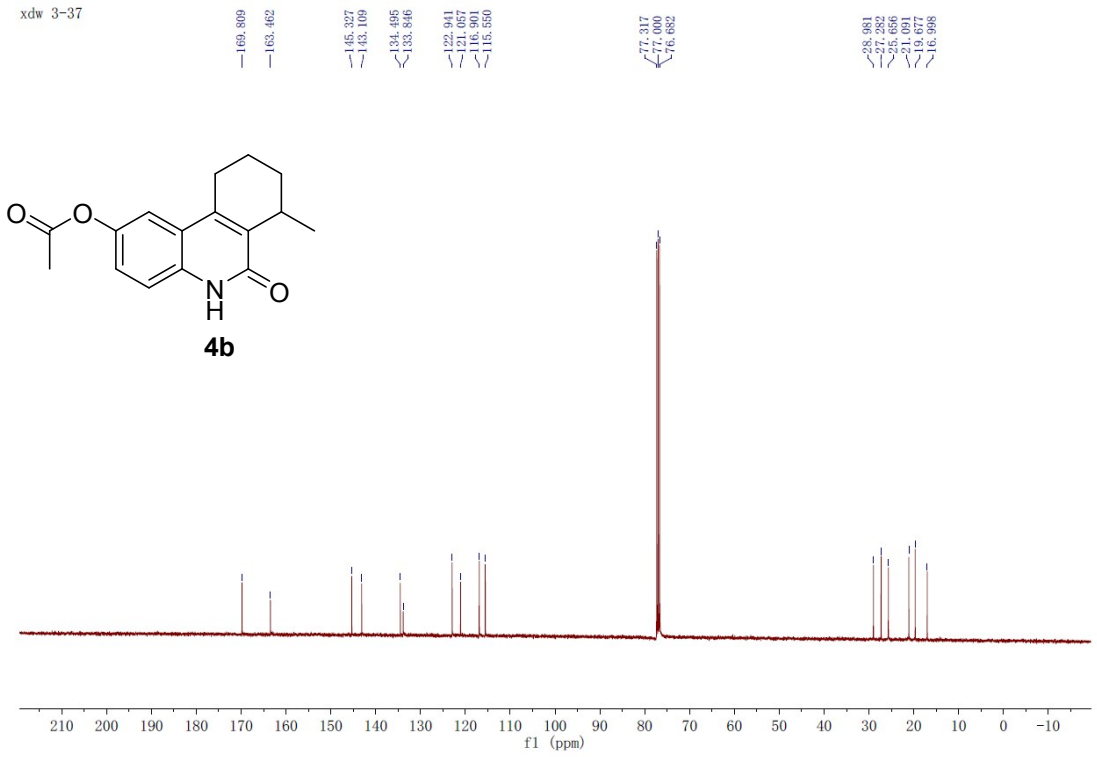

xdw 2-67
7.583
7.563
7.476
7.455
7.434
7.314
7.294
7.282
7.260 CDCl3
7.244
3.101
3.066
3.030
2.936
2.870
2.710
2.671
1.926
1.905
1.869
1.795
1.759
1.722
1.560
1.279
1.261
1.04
1.01
2.73
1.02
1.07
1.08
2.00
1.99
3.27
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
O

3b

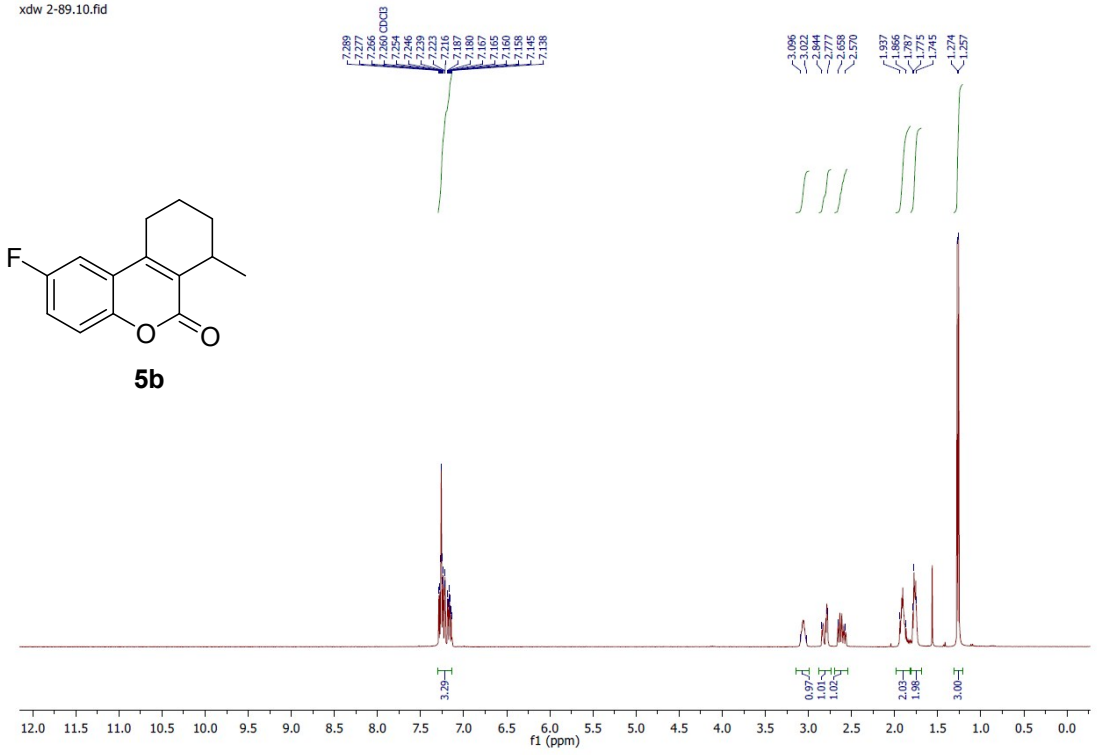

xdw 2-677.10.fid
161.210
152.064
146.720
130.255
128.472
123.905
123.337
120.199
116.676
77.318 CDCl3
76.681 CDCl3
28.943
27.046
25.354
19.415
16.755
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
O
O

3b


xdw 3-37.20.fid
12.255
7.398
7.375
7.368
7.260 CDCl3
7.187
7.181
7.165
7.160
3.267
3.251
2.958
2.895
2.736
2.670
2.648
2.327
1.972
1.914
1.862
1.806
1.770
1.323
1.306
O
O
N
H
O
4b
0.97
1.94
0.96
0.98
0.99
0.99
3.00
2.06
2.01
2.93
f1 (ppm)

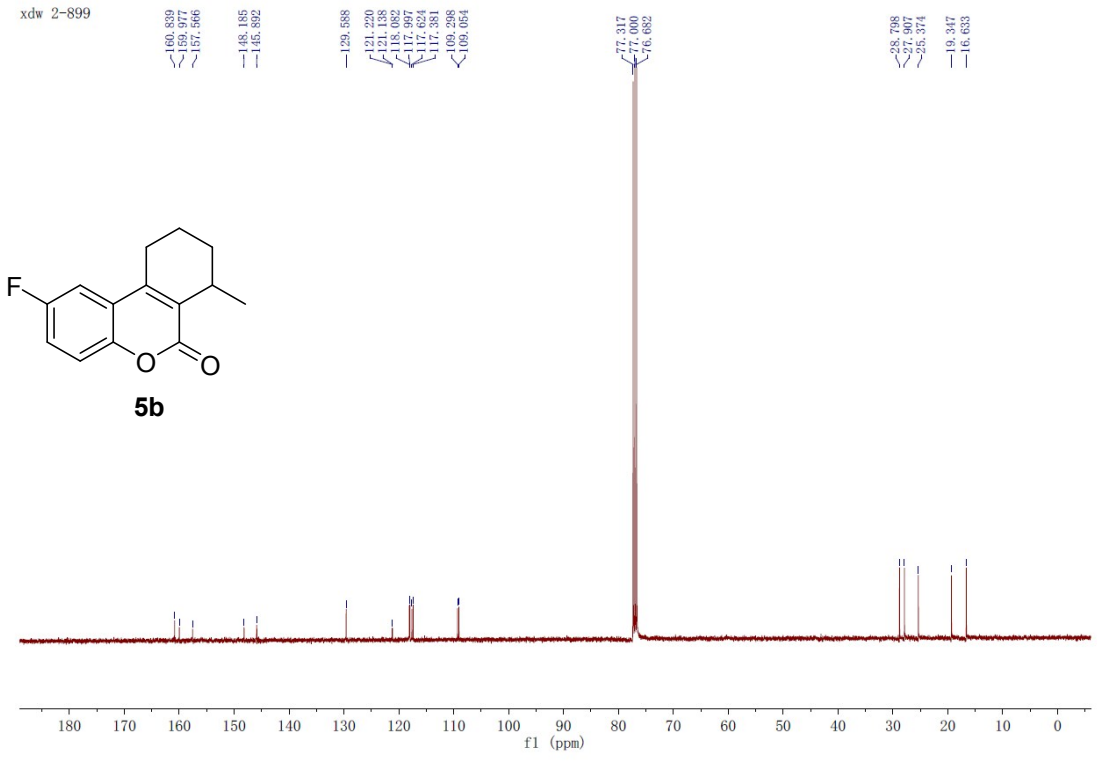

xdw 3-37
169.809
163.462
145.327
143.109
134.495
133.846
122.941
121.957
116.901
115.550
77.317
77.000
76.682
28.981
27.282
25.656
21.091
19.677
16.998
O
O
N
H
O
4b
f1 (ppm)

xdw 2-89.10.fid



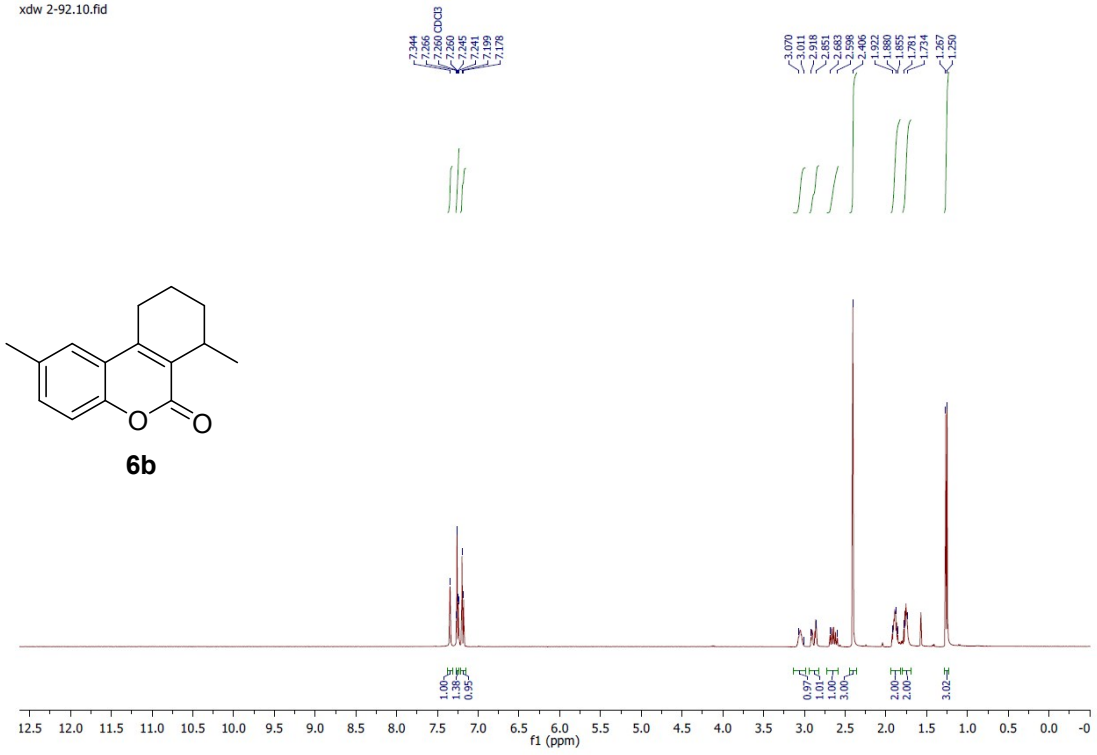
5b

xdw 2-899



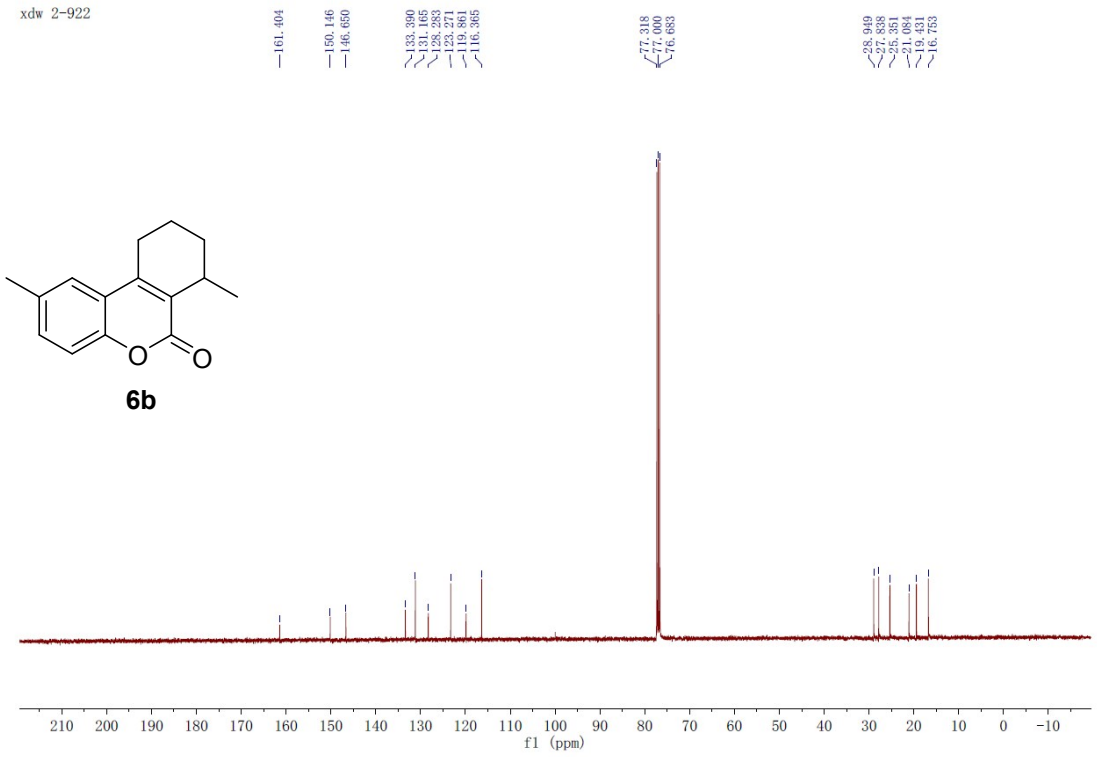
5b

xdw 2-92.10.fid

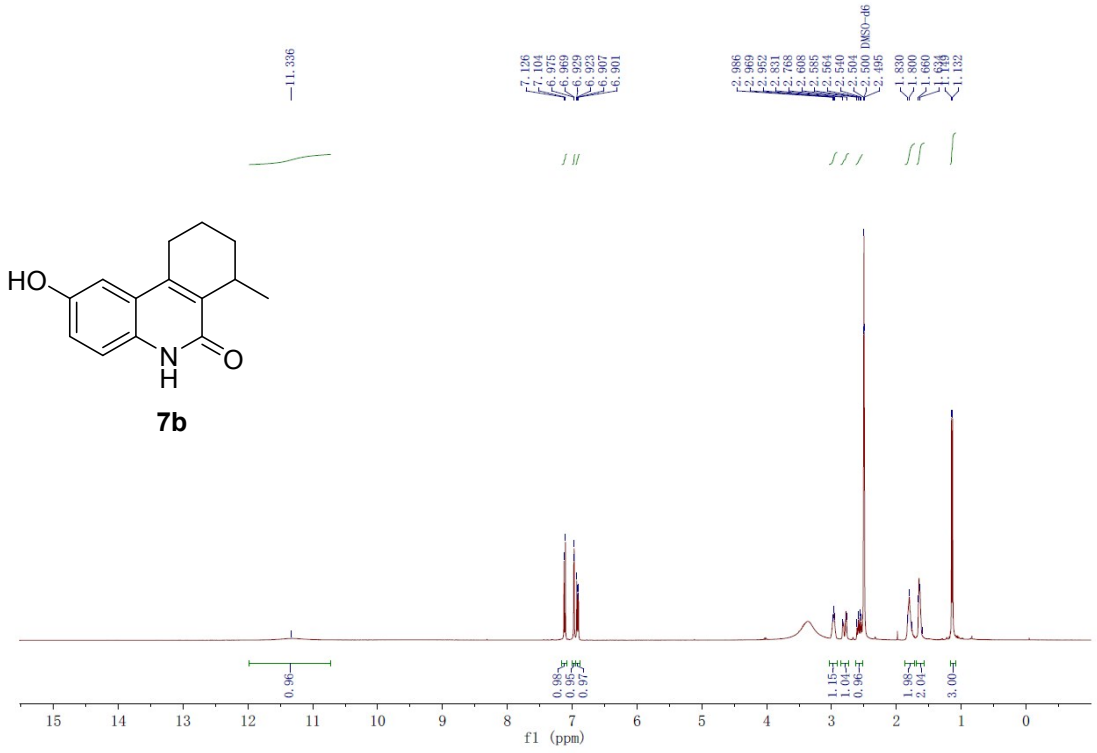


6b

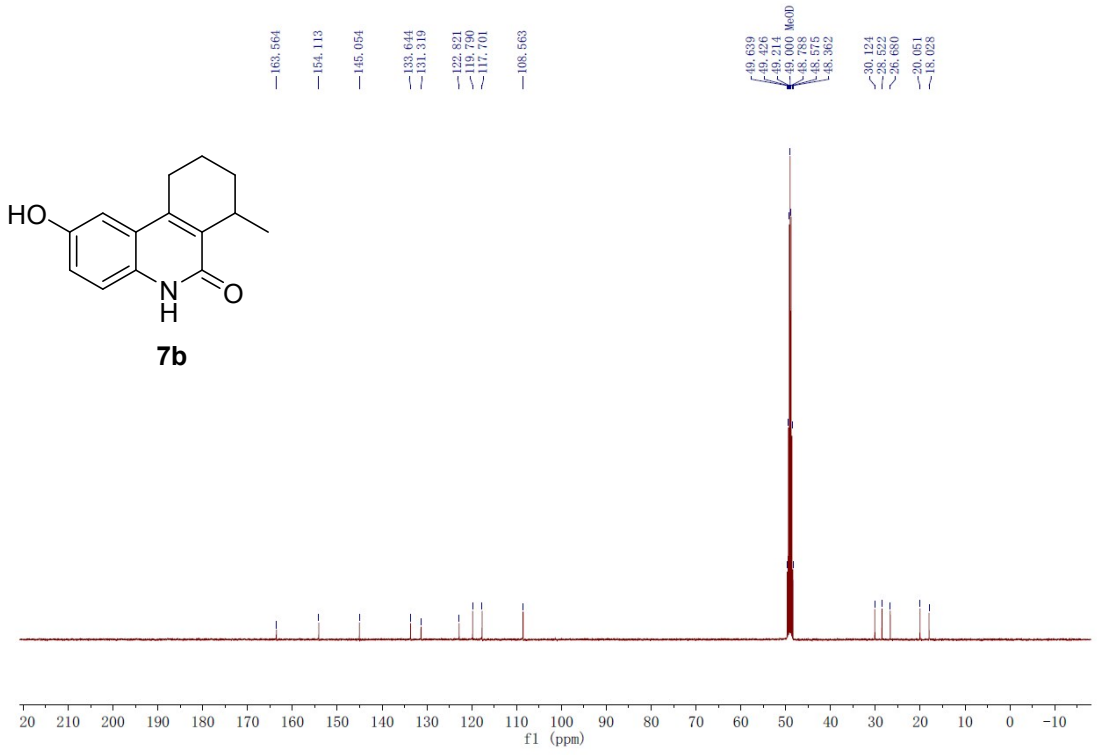
xdw 2-922



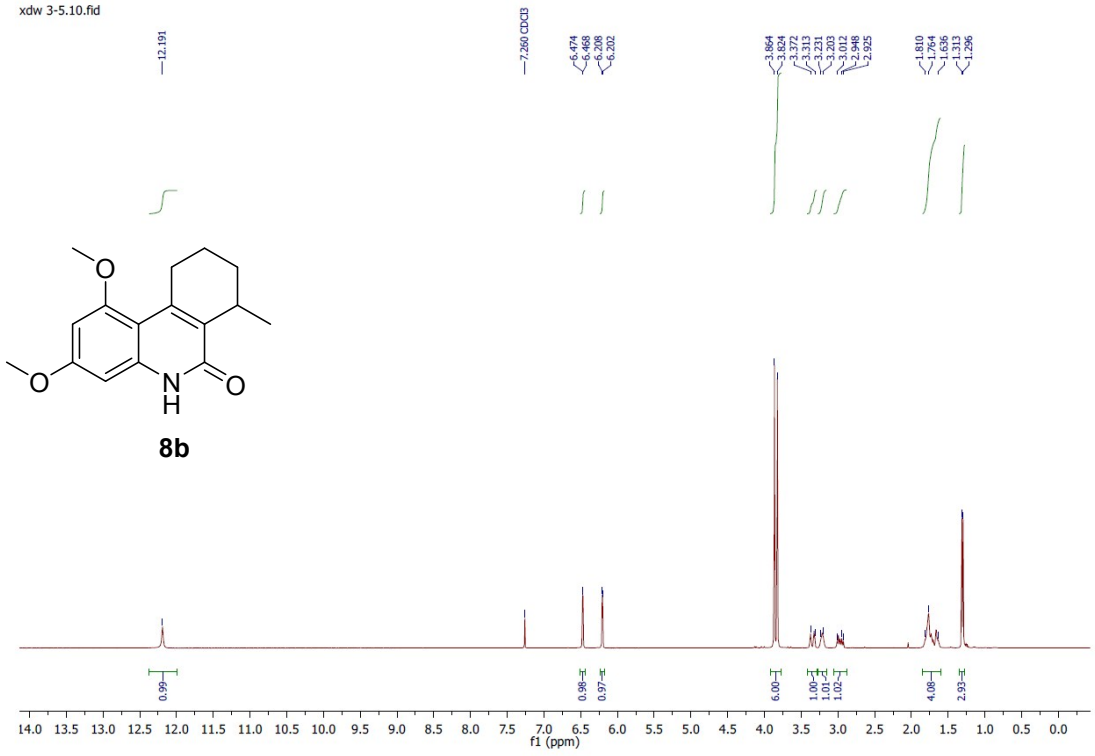
6b


11.336
7.126
7.104
6.975
6.969
6.929
6.923
6.907
6.901
2.986
2.969
2.962
2.831
2.768
2.608
2.585
2.564
2.540
2.504
2.500
2.495
DMSO-d6
1.830
1.800
1.660
1.644
1.628
1.132
HO
N
H
O
0.96
0.98
0.95
0.97
1.15
1.04
0.96
1.98
2.04
3.00
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

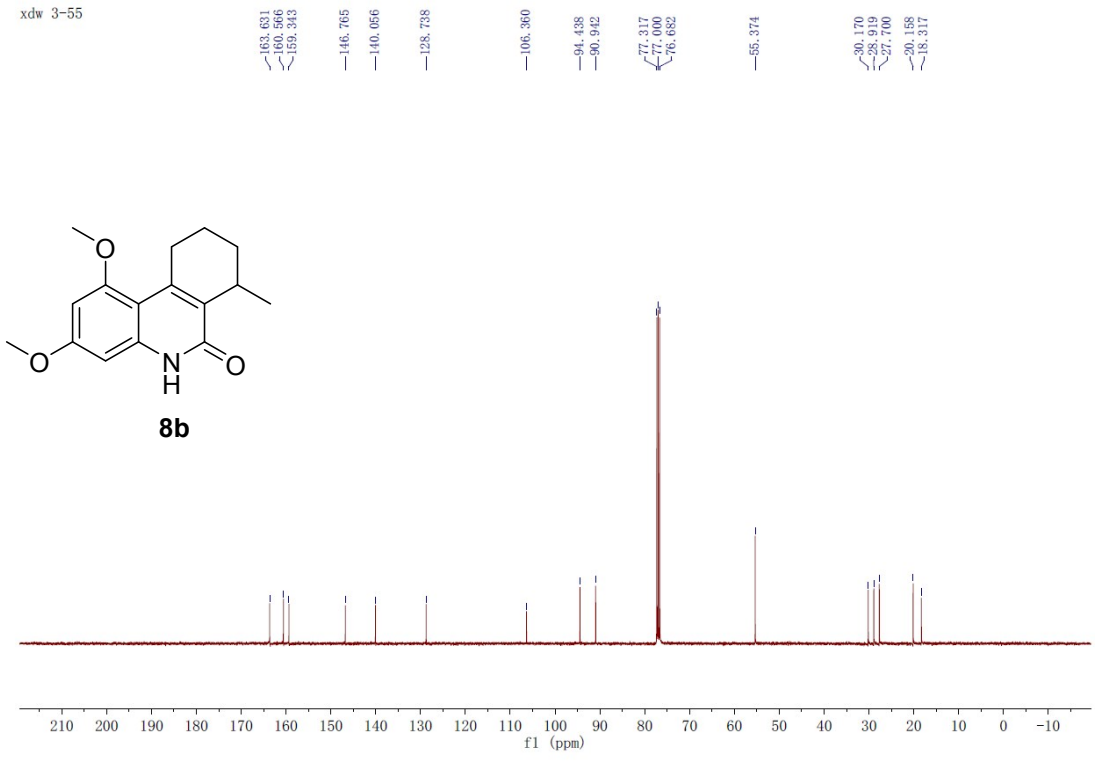
7b


163.564
154.113
145.054
133.644
131.319
122.821
119.790
117.701
108.563
49.639
49.426
49.214
49.000
48.788
48.575
48.362
MeOD
30.124
28.622
26.680
20.051
18.028
HO
N
H
O
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

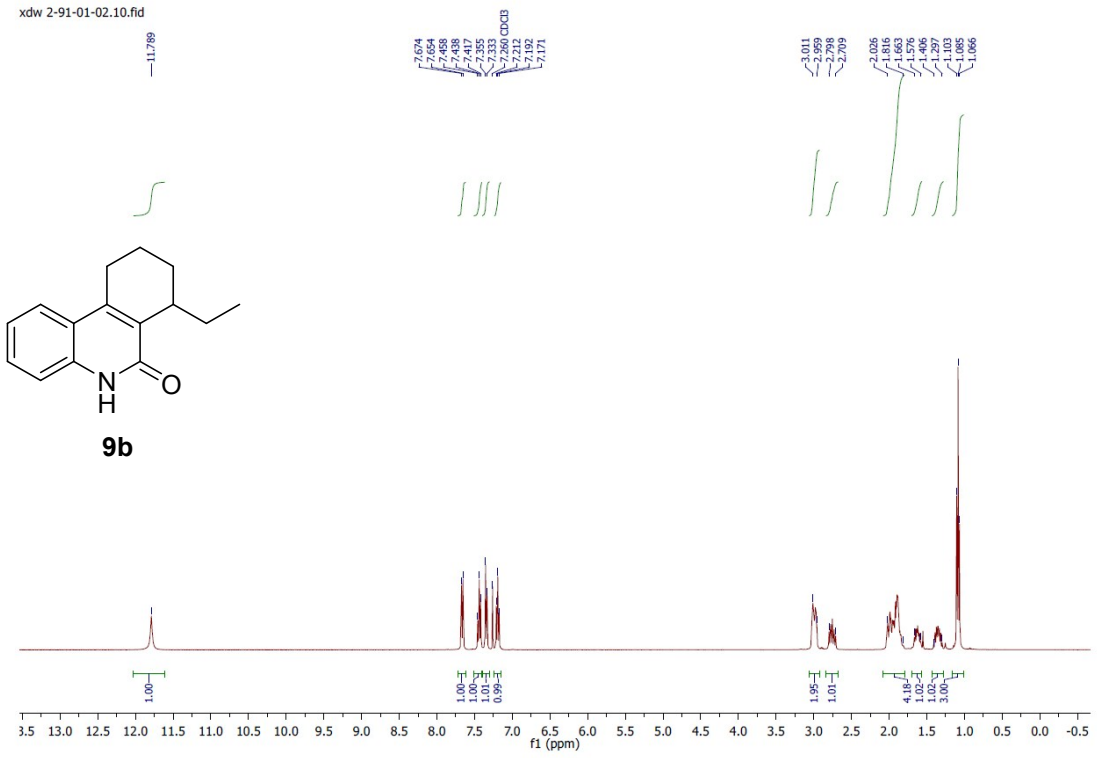
7b


xdw 3-5.10.fid
12.191
7.260 CDCl3
6.474
6.468
6.208
6.202
3.864
3.824
3.372
3.313
3.231
3.203
3.012
2.948
2.925
1.810
1.764
1.636
1.313
1.296
O
O
N
H
O
0.99
0.98
0.97
6.00
1.00
1.01
1.02
4.08
2.93
f1 (ppm)

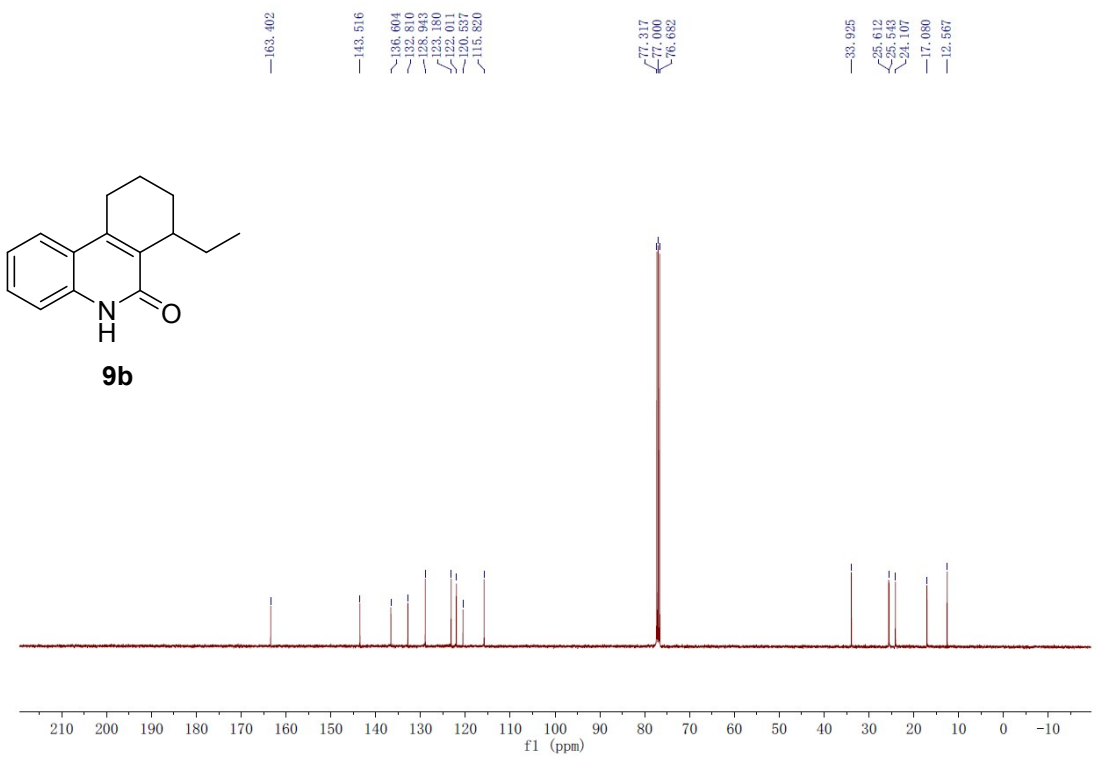
8b


xdw 3-55
163.631
160.566
159.343
146.765
140.056
128.738
106.360
94.438
90.942
77.317
77.000
76.682
55.374
30.170
28.919
27.700
20.158
18.317
O
O
N
H
O
f1 (ppm)

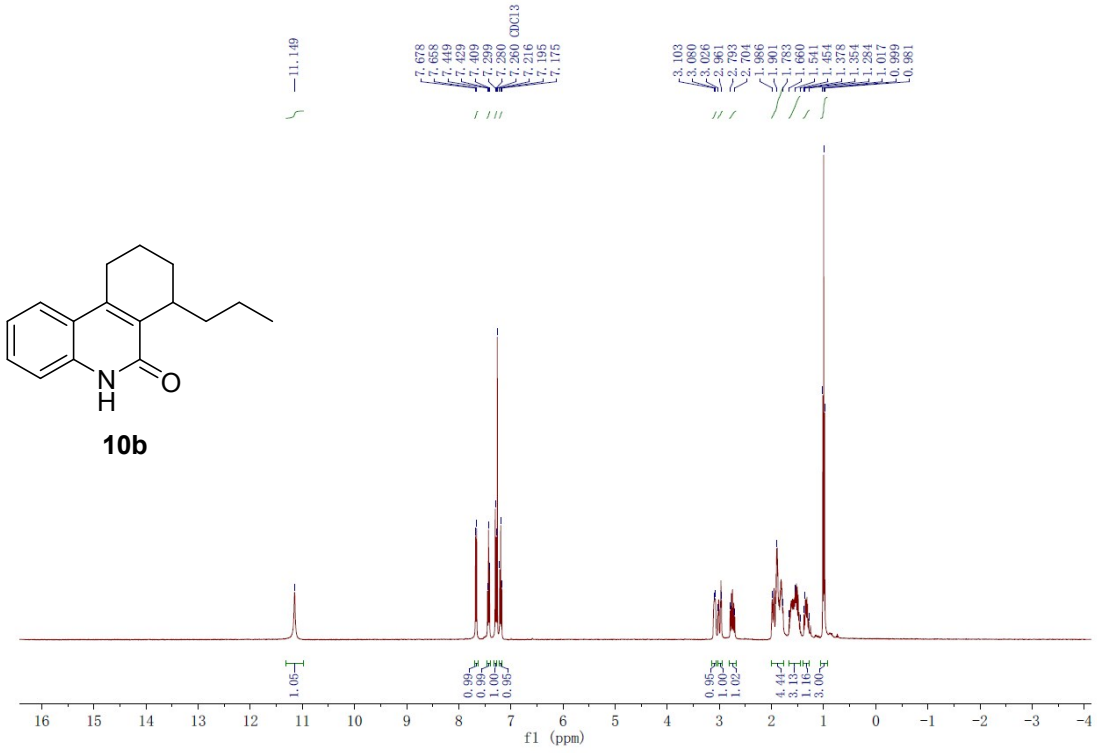
8b


xdw 2-91-01-02.10.fid
11.789
7.674
7.654
7.458
7.438
7.417
7.355
7.333
7.260 CDCl3
7.212
7.192
7.171
3.011
2.999
2.798
2.709
2.026
1.816
1.663
1.576
1.496
1.297
1.103
1.085
1.066
1.00
1.00
1.01
0.99
1.95
1.01
4.18
1.02
1.02
3.00
f1 (ppm)

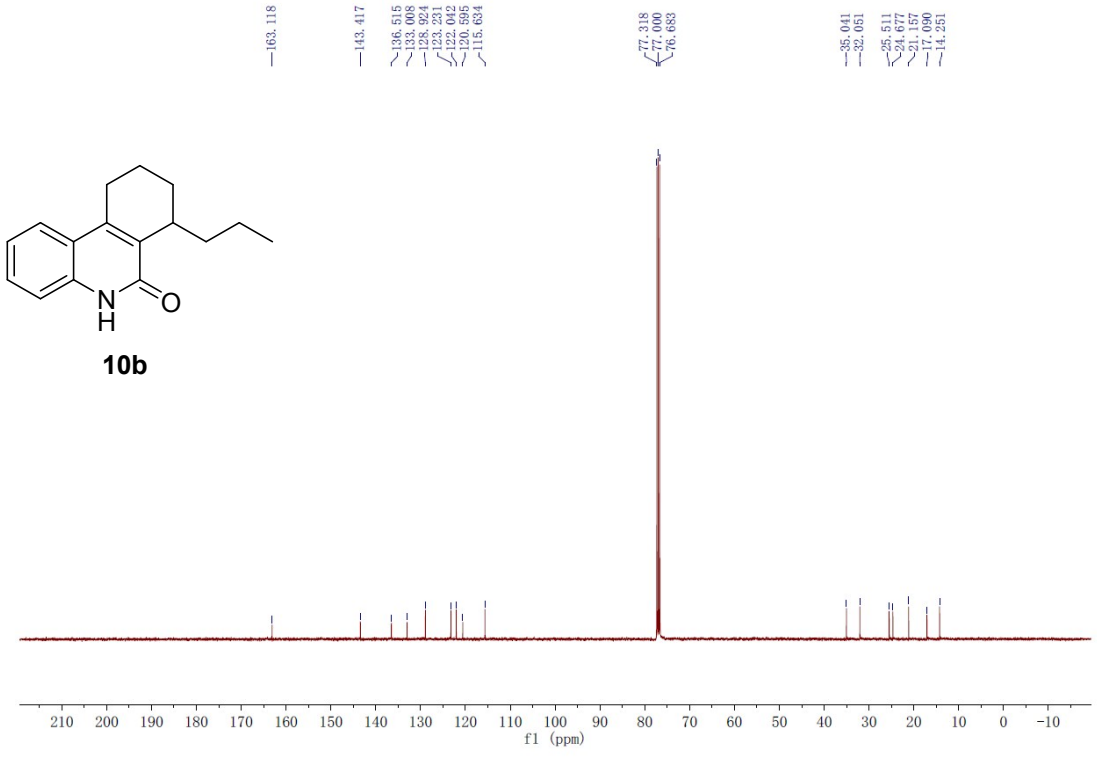
9b


163.402
143.516
136.604
132.810
128.943
123.180
122.011
120.537
115.820
77.317
77.000
76.682
33.925
25.612
25.543
24.107
17.080
12.567
f1 (ppm)

9b

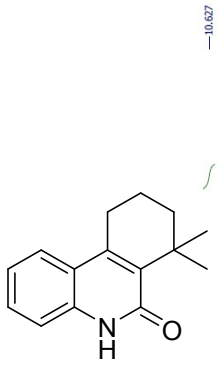

11.149
7.678
7.658
7.449
7.429
7.409
7.299
7.280
CDCl3
7.260
7.216
7.195
7.175
3.103
3.080
3.026
2.961
2.793
2.704
1.986
1.901
1.783
1.660
1.541
1.454
1.378
1.354
1.284
1.077
0.999
0.981
1.05
0.99
0.99
1.00
0.95
0.95
1.00
1.02
4.44
3.13
1.16
3.00
f1 (ppm)

10b


163.118
143.417
136.515
133.008
128.924
123.231
122.042
120.595
115.634
77.318
77.000
76.683
35.041
32.051
25.511
24.677
21.157
17.090
14.251
f1 (ppm)

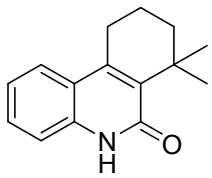
10b

xdw 2-88.10.fid

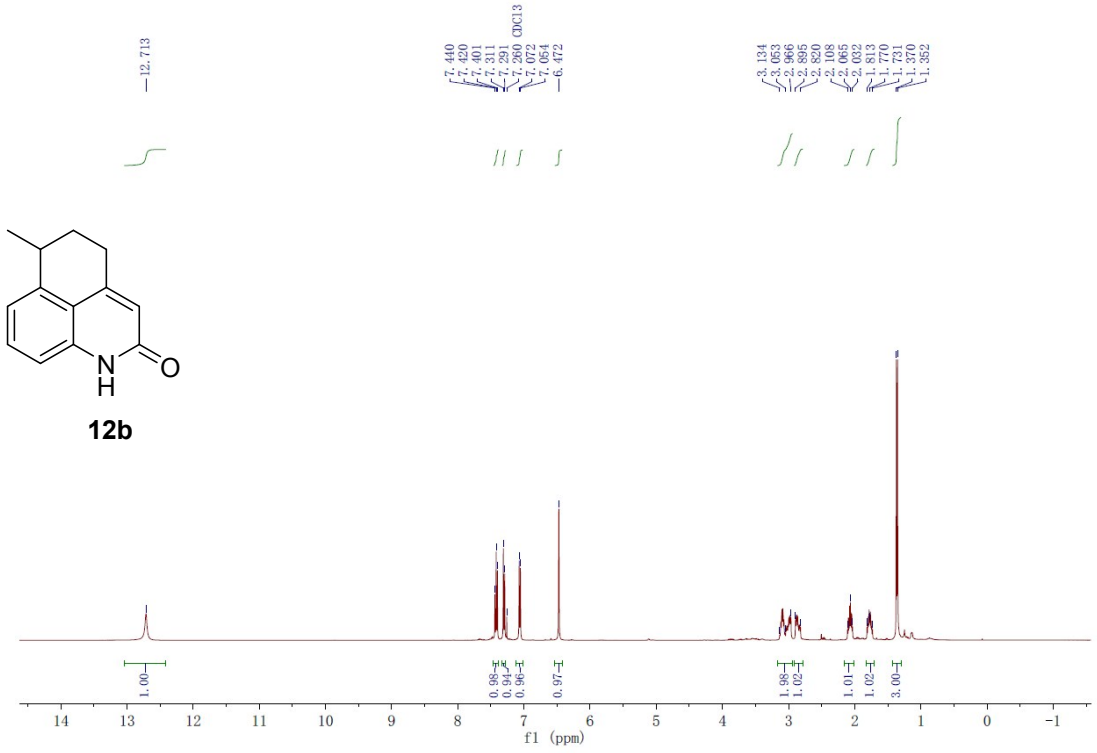


11b

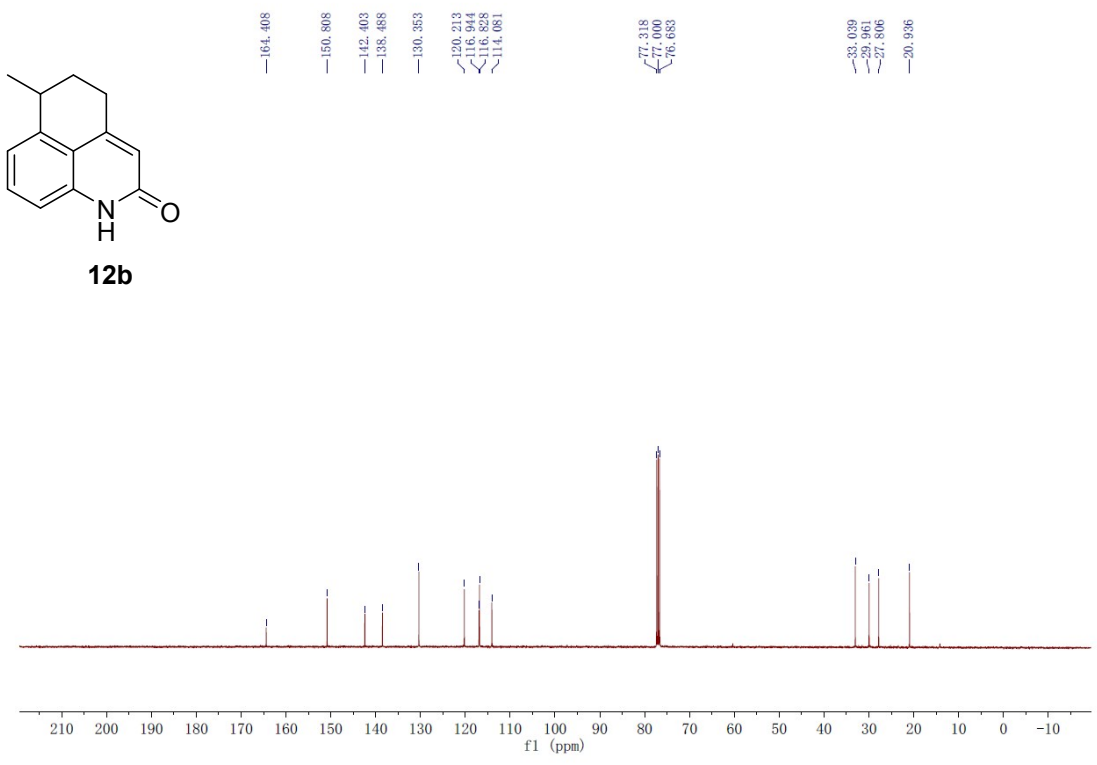
xdw 2-888.10.fid



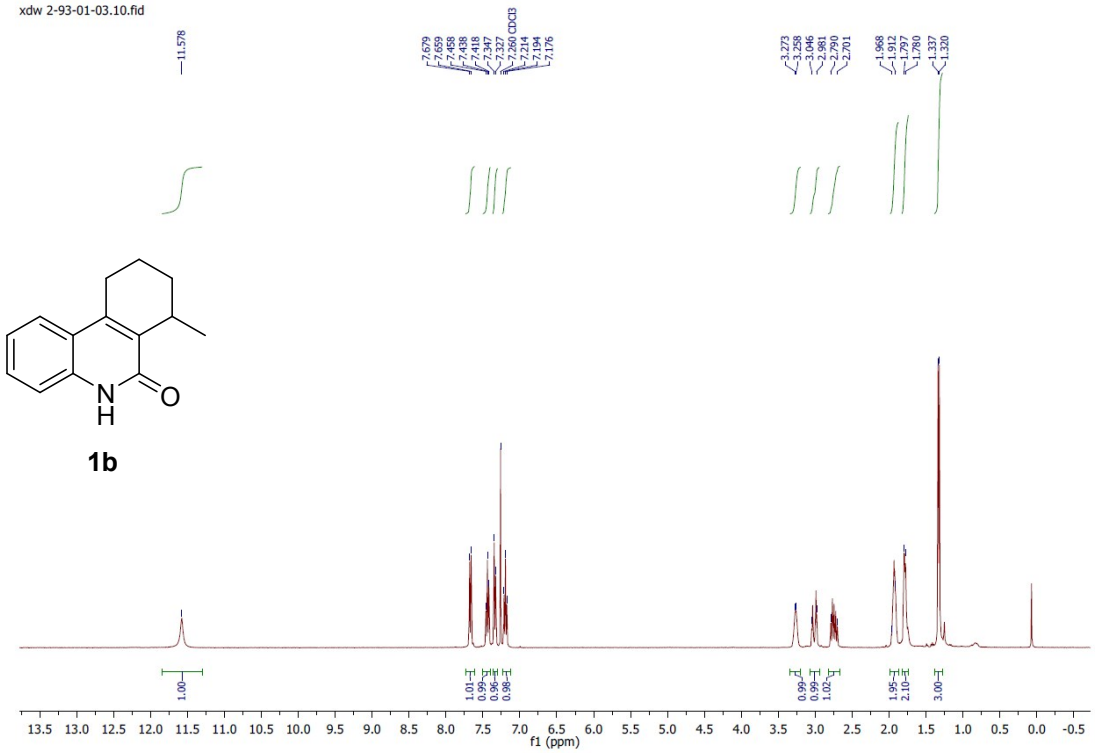
11b


12.713
7.440
7.420
7.401
7.311
7.291
7.269
CDCl3
7.072
7.054
6.472
3.134
3.053
2.966
2.895
2.820
2.108
2.065
2.032
1.813
1.770
1.731
1.370
1.352
N
H
O
1.00
0.98
0.94
0.96
0.97
1.98
1.02
1.01
1.02
3.00
f1 (ppm)

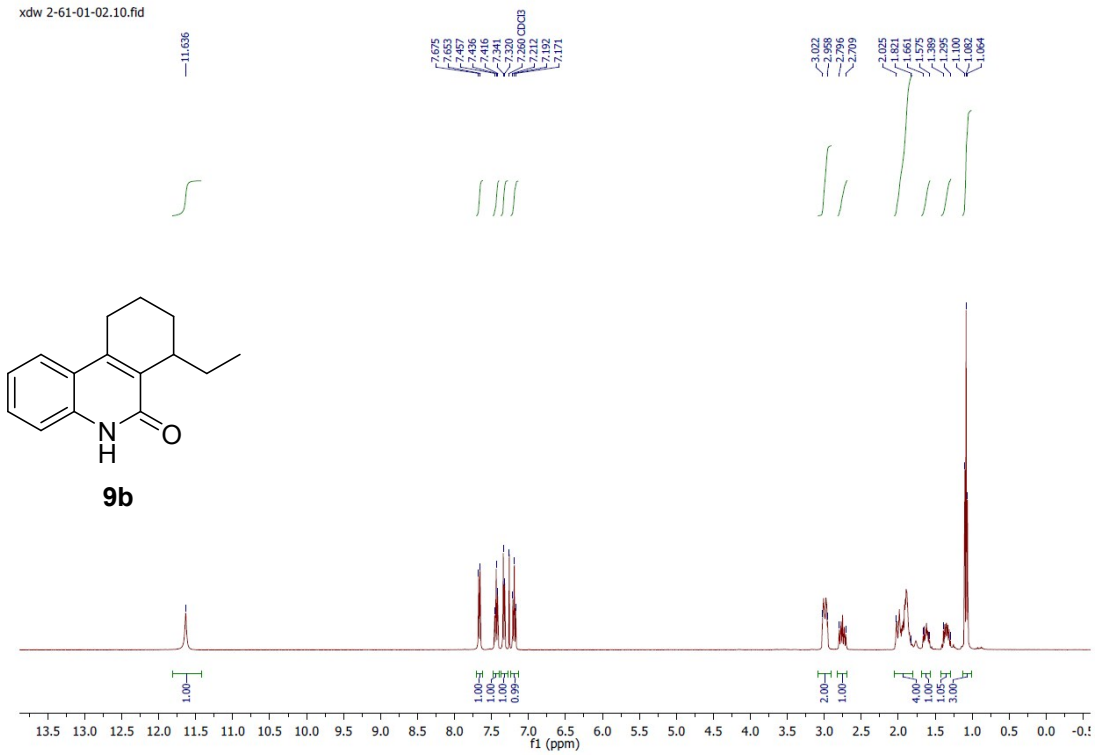
12b


164.408
150.808
142.403
138.488
130.353
120.213
116.944
116.828
114.081
77.318
77.000
76.683
33.039
29.961
27.806
20.936
N
H
O
f1 (ppm)

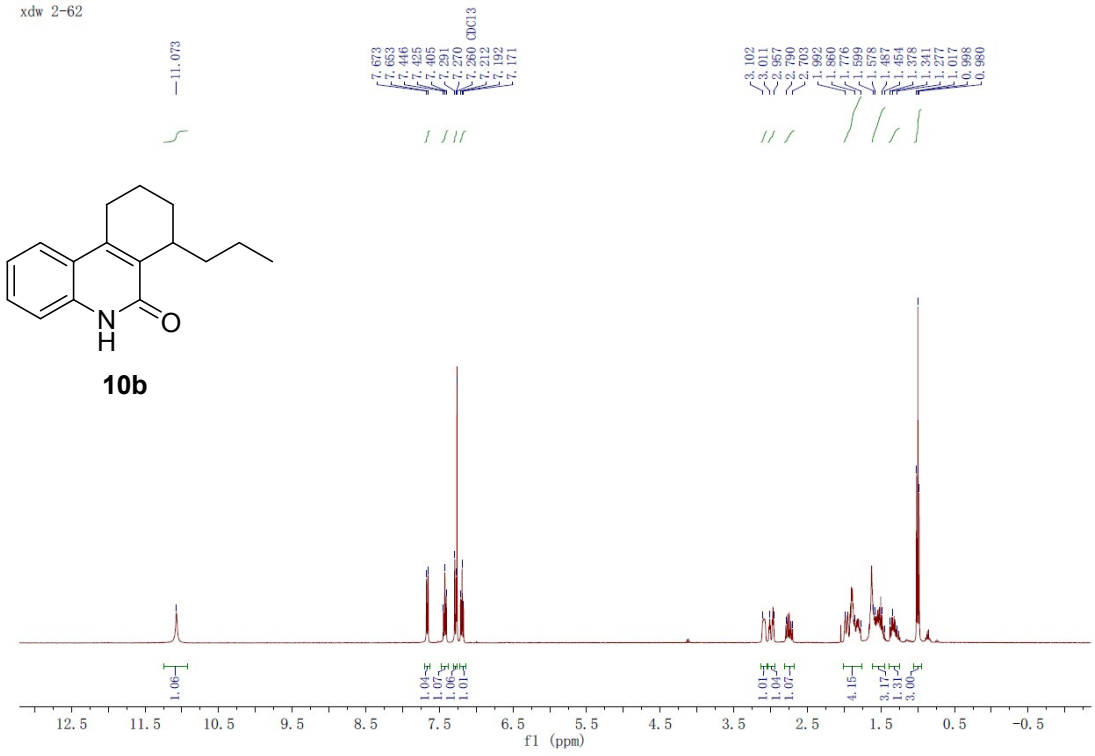
12b


xdw 2-93-01-03.10.fid
11.578
7.679
7.659
7.458
7.438
7.418
7.347
7.327
7.260 CDCl3
7.214
7.194
7.176
3.273
3.258
3.046
2.981
2.790
2.701
1.968
1.912
1.797
1.780
1.337
1.320
1.00
1.01
0.99
0.96
0.98
0.99
0.99
1.02
1.95
2.10
3.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

1b


xdw 2-61-01-02.10.fid
11.636
7.675
7.653
7.457
7.436
7.416
7.341
7.320
7.260 CDCl3
7.212
7.192
7.171
3.022
2.958
2.796
2.709
2.025
1.921
1.661
1.575
1.389
1.295
1.100
1.082
1.064
1.00
1.00
1.00
1.05
0.99
2.00
1.00
4.00
1.00
1.05
3.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

9b


xdw 2-62
11.073
7.673
7.653
7.446
7.425
7.405
7.291
7.270
CDCl3
7.260
7.212
7.192
7.171
3.102
3.011
2.957
2.790
2.703
1.992
1.860
1.776
1.599
1.578
1.487
1.454
1.378
1.341
1.277
1.017
0.998
0.980
N
H
O
10b
1.06
1.04
1.07
1.06
1.01
1.01
1.04
1.07
4.15
3.17
1.31
3.00
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

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