

Catalytic Synthesis of Seven-Membered Carbocycles via Ring Expansion of Cyclic β -Ketoesters

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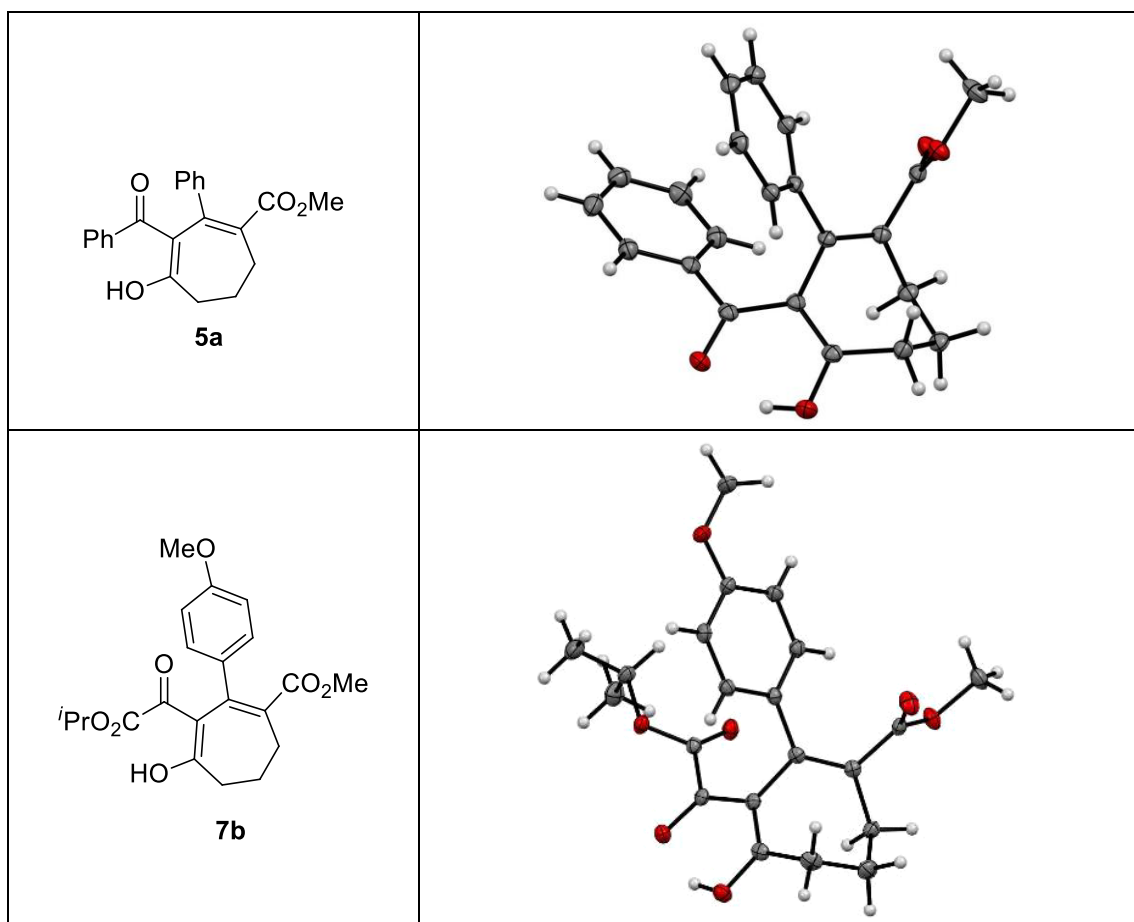
I. General Information.

Commercially available chemicals were directly used without further purification, unless otherwise mentioned, all experiments and manipulations involving air- or moisture-sensitive compounds were performed using standard Schlenk technique. All solvents were purified and dried using typical procedures. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker AVANCE III HD400 (400 MHz) and ECZ600S (600 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane ($\delta = 0.00$ ppm). ¹H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplet), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded on a Bruker AVANCE III HD400 (101

MHz) and ECZ600S (151 MHz) spectrometers. High resolution mass spectral analysis (HRMS) was performed on Thermo Fisher Scientific Q Exactive Plus Hybrid Quadrupole-Orbitrap Mass Spectrometer. X-ray crystallography analysis was performed on Agilent Super Nova X-ray diffractionmeter. Analytical thin-layer chromatography (TLC) was carried out on WFH-203 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp or 2,4-Dinitrophenylhydrazine or potassium permanganate stain or phosphomolybdic acid. All substrates of alkynyl diketones were prepared according to the literature reports.^[1-4]

II. X-ray crystallographic analysis

Method for single crystals cultivation: a pure solid sample (10–20 mg) was dissolved in dichloromethane/ethyl acetate/THF (1 mL) in a vial at room temperature, and petroleum ether/hexane (2 mL) was added into the above solution slowly while keeping the sample completely dissolved. The vial was properly sealed with parafilm and kept at room temperature to allow the slow evaporation of the solvents until a single crystal was obtained.



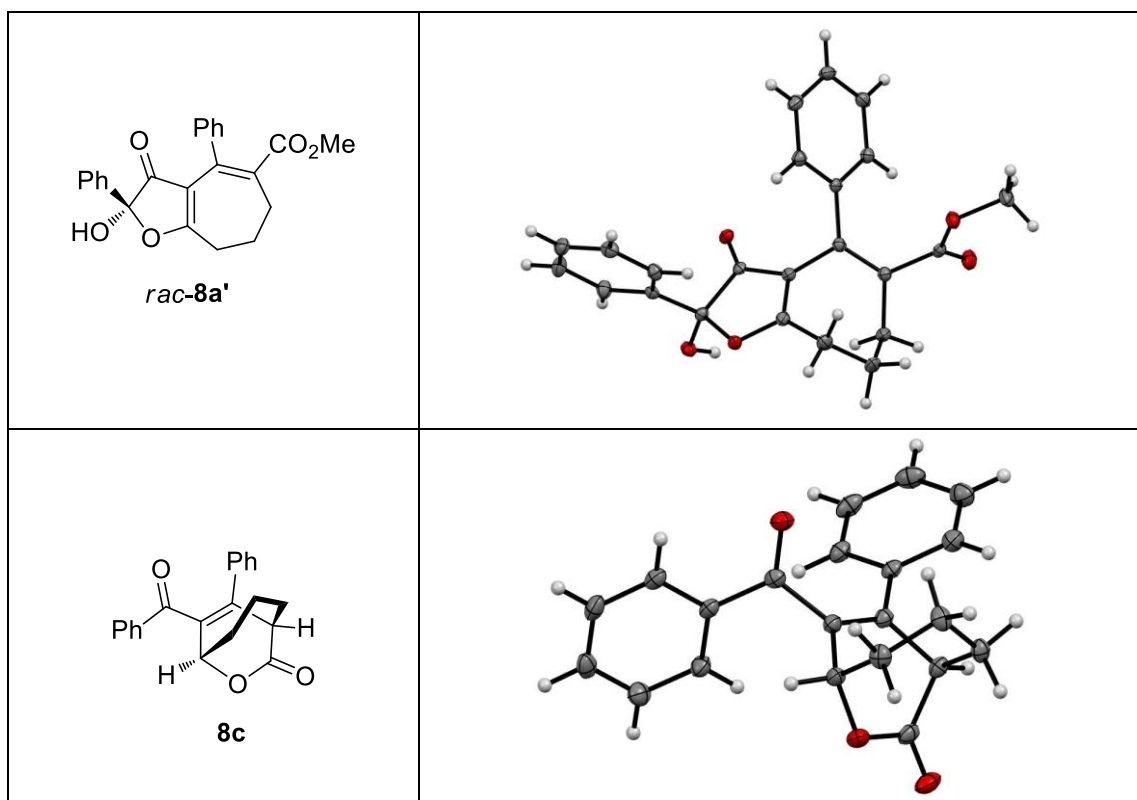


Table S1 Crystal data and structure refinement for 5a.

Identification code	5a
Empirical formula	C ₂₂ H ₂₀ O ₄
Formula weight	348.38
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	6.593
b/Å	15.25490(10)
c/Å	17.53070(10)
α/°	90
β/°	93.1820(10)
γ/°	90
Volume/Å ³	1760.335(15)
Z	4
ρ _{calc} /g/cm ³	1.315
μ/mm ⁻¹	0.464
F(000)	736.0
Crystal size/mm ³	0.1 × 0.1 × 0.1
Radiation	GaKα (λ = 1.3405)
2θ range for data collection/°	6.682 to 120.956
Index ranges	-8 ≤ h ≤ 8, -19 ≤ k ≤ 19, -22 ≤ l ≤ 22

Reflections collected	69133
Independent reflections	4034 [$R_{\text{int}} = 0.0873$, $R_{\text{sigma}} = 0.0250$]
Data/restraints/parameters	4034/0/237
Goodness-of-fit on F^2	1.037
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0378$, $wR_2 = 0.0962$
Final R indexes [all data]	$R_1 = 0.0445$, $wR_2 = 0.0989$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.32/-0.22

Table S2 Crystal data and structure refinement for 7b.

Identification code	7b
Empirical formula	$\text{C}_{21}\text{H}_{24}\text{O}_7$
Formula weight	388.40
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
$a/\text{\AA}$	17.1896(3)
$b/\text{\AA}$	5.80260(10)
$c/\text{\AA}$	20.7903(4)
$\alpha/^\circ$	90
$\beta/^\circ$	110.598(2)
$\gamma/^\circ$	90
Volume/ \AA^3	1941.15(7)
Z	4
$\rho_{\text{calc}}/\text{g/cm}^3$	1.329
μ/mm^{-1}	0.529
F(000)	824.0
Crystal size/ mm^3	$0.1 \times 0.1 \times 0.1$
Radiation	$\text{GaK}\alpha$ ($\lambda = 1.3405$)
2θ range for data collection/ $^\circ$	5.012 to 121.02
Index ranges	$-22 \leq h \leq 22$, $-5 \leq k \leq 7$, $-25 \leq l \leq 26$
Reflections collected	38963
Independent reflections	4411 [$R_{\text{int}} = 0.0901$, $R_{\text{sigma}} = 0.0444$]
Data/restraints/parameters	4411/0/258
Goodness-of-fit on F^2	1.102
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0397$, $wR_2 = 0.1072$
Final R indexes [all data]	$R_1 = 0.0464$, $wR_2 = 0.1116$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.31/-0.24

Table S3 Crystal data and structure refinement for cl-1_auto.

Identification code	cl-1_auto
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Empirical formula	C ₂₃ H ₂₀ O ₅
Formula weight	376.39
Temperature/K	100(2)
Crystal system	triclinic
Space group	P-1
a/Å	8.6573(7)
b/Å	10.0811(7)
c/Å	12.3197(11)
α/°	84.259(7)
β/°	69.811(8)
γ/°	69.254(7)
Volume/Å ³	943.40(15)
Z	2
ρ _{calc} /g/cm ³	1.325
μ/mm ⁻¹	0.486
F(000)	396.0
Crystal size/mm ³	0.1 × 0.1 × 0.1
Radiation	GaKα (λ = 1.3405)
2Θ range for data collection/°	8.156 to 120.668
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -11 ≤ l ≤ 15
Reflections collected	12253
Independent reflections	4188 [R _{int} = 0.0220, R _{sigma} = 0.0213]
Data/restraints/parameters	4188/0/256
Goodness-of-fit on F ²	1.052
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0339, wR ₂ = 0.0849
Final R indexes [all data]	R ₁ = 0.0355, wR ₂ = 0.0861
Largest diff. peak/hole / e Å ⁻³	0.36/-0.23

Table S4 Crystal data and structure refinement for 8c.

Identification code	8c
Empirical formula	C ₂₁ H ₁₈ NO ₃
Formula weight	318.35
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	9.44830(10)
b/Å	9.97000(10)
c/Å	9.7662(2)
α/°	90
β/°	118.501(2)

$\gamma/^\circ$	90
Volume/ \AA^3	808.48(2)
Z	2
$\rho_{\text{calc}}/\text{g/cm}^3$	1.308
μ/mm^{-1}	0.443
F(000)	336.0
Crystal size/ mm^3	$0.1 \times 0.1 \times 0.1$
Radiation	GaK α ($\lambda = 1.3405$)
2θ range for data collection/ $^\circ$	8.958 to 120.866
Index ranges	$-12 \leq h \leq 12, -12 \leq k \leq 12, -12 \leq l \leq 12$
Reflections collected	33268
Independent reflections	3678 [$R_{\text{int}} = 0.0995, R_{\text{sigma}} = 0.0364$]
Data/restraints/parameters	3678/1/217
Goodness-of-fit on F^2	1.042
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0335, wR_2 = 0.0804$
Final R indexes [all data]	$R_1 = 0.0352, wR_2 = 0.0813$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.18/-0.18
Flack parameter	-0.10(15)

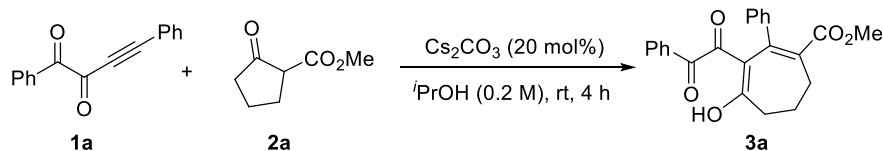
III. Procedures for the preparation of substrates.

Substrates **1a–1h** are known compounds and were prepared according to the literature reports.^[1-5]

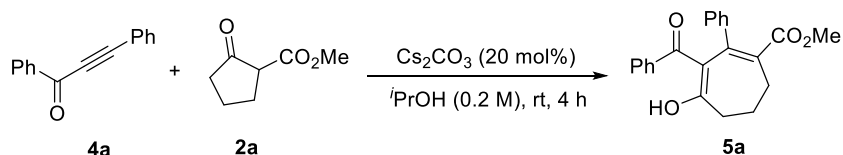
Substrates **4a–4i** are known compounds and were prepared according to the literature reports.^[6-7]

Substrates **6a, 6b** are known compounds and were prepared according to the literature reports.^[8-9]

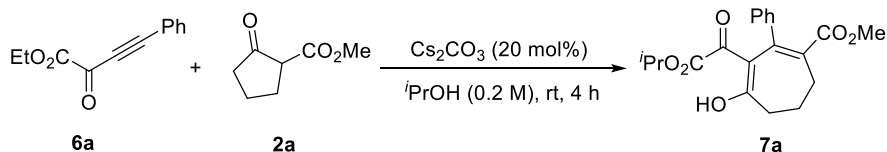
IV. Typical procedures for the ring expansion reactions.



1a (47 mg, 0.2 mmol), **2a** (48 μL , 0.4 mmol), and Cs_2CO_3 (13.1 mg, 0.04 mmol) was added to $i\text{PrOH}$ (1.0 mL) at room temperature. The reaction system was stirred for 4 h. the solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 3:1) to give the product **3a** (63 mg, 84% yield). Compounds **3b–3h** were synthesized using the same method.

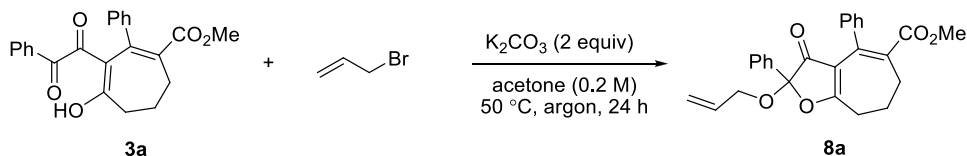


4a (206 mg, 1 mmol), **2a** (0.19 mL, 1.5 mmol), and Cs_2CO_3 (65 mg, 0.2 mmol) was added to *i*PrOH (5.0 mL) at room temperature. The reaction system was stirred for 4 h. the solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 5:1) to give the product **5a** (303 mg, 87% yield). Compounds **5b–5j** were synthesized using the same method.

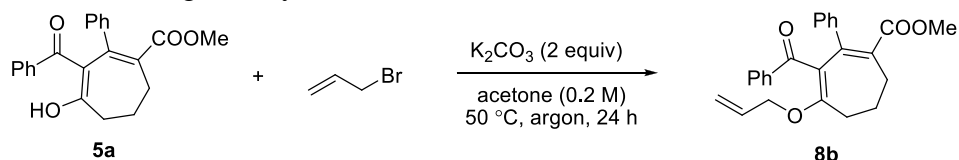


6a (40 mg, 0.2 mmol), **2a** (48 μL , 0.4 mmol), and Cs_2CO_3 (13 mg, 0.04 mmol) was added to *i*PrOH (1.0 mL) at room temperature. The reaction system was stirred for 4 h. the solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 5:1) to give the product **7a** (58 mg, 81% yield). Compounds **7b** was synthesized using the same method.

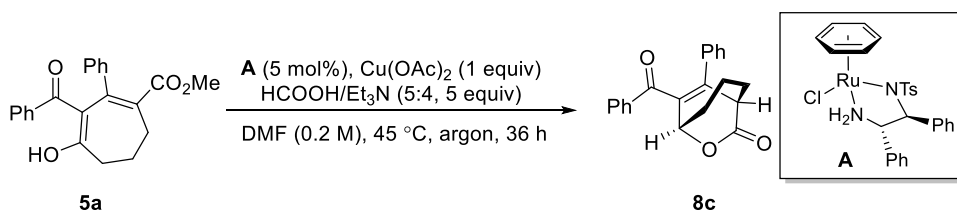
V. Procedures for the product derivatizations.



3a (38 mg, 0.1 mmol), allyl bromide (17 μL , 0.2 mmol), and K_2CO_3 (28 mg, 0.2 mmol) was added to acetone (0.5 mL) at 50 °C. The reaction system was stirred for 24 h. The mixture was quenched by aqueous NH_4Cl and extracted with ethyl acetate (3 \times 5 mL). The organic solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 3:1) to afford yellow oil **8a** (23 mg, 55% yield)

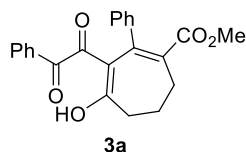


5a (105 mg, 0.3 mmol), allyl bromide (39 μL , 0.45 mmol), and K_2CO_3 (83 mg, 0.6 mmol) was add to acetone (1.5 mL) at 50 °C. The reaction system was stirred for 24 h. The mixture was quenched by aqueous NH_4Cl and extracted with ethyl acetate (3 \times 5 mL). The organic solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 5:1) to afford yellow solid **8b** (87 mg, 75% yield)



To a 10 mL flame-dry Schlenk tube equipped with a magnetic stir bar was added **5a** (70 mg, 0.2 mmol) and the catalyst **A** (6 mg, 0.01 mol), then formic acid/Et₃N azeotrope (127 mg, 5:4, 5.0 equiv) dissolved in DMF (1 mL) was added and the mixture was stirred at 50 °C under argon atmosphere. After completion of the reaction as indicated by TLC, it was quenched with water, extracted with ethyl acetate (3 × 10 mL), washed with brine, dried over anhydrous Na₂SO₄, filtered and concentrated. The residue was purified by chromatography (petroleum ether/ethyl acetate, v:v = 5:1) to give white solid **8c** (27 mg, 42% yield, 98% *ee*).

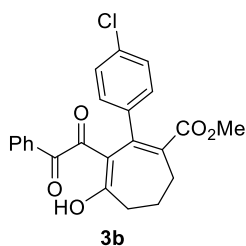
VI. Characterizations of new compounds



methyl

4-hydroxy-3-(2-oxo-2-phenylacetyl)-2-phenylcyclohepta-1,3-diene-1-carboxylate

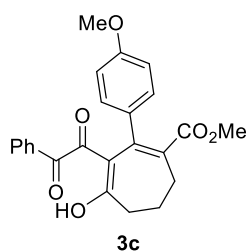
(3a): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), white solid, mp 148–150 °C, 63 mg, 84% yield. ¹H NMR (400 MHz, acetone-d₆) δ 7.64–7.62 (m, 2H), 7.47–7.43 (m, 3H), 7.38 (s, 1H), 7.25–7.24 (m, 3H), 7.13–7.10 (m, 2H), 3.43 (s, 3H), 3.13–3.05 (m, 1H), 3.02–2.94 (m, 1H), 2.65–2.62 (m, 2H), 2.41–2.34 (m, 2H); ¹³C NMR (101 MHz, acetone-d₆) δ 195.9, 193.3, 170.3, 138.8, 138.2, 136.8, 133.0, 129.4, 128.7, 128.5, 127.7, 127.7, 126.0, 111.9, 104.3, 51.1, 30.3, 30.0, 29.9. HRMS (MALDI-Quadrupole-Orbitrap) m/z: [M + Na]⁺ Calcd for C₂₃H₂₀O₅Na⁺ 399.1203; Found 399.1208. IR (KBr thin film, cm⁻¹): ν 3261, 2360, 2342, 1670, 1232, 764, 669. 655, 501.



methyl

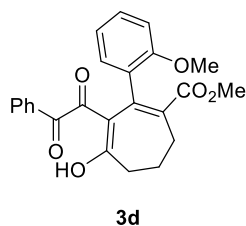
2-(4-chlorophenyl)-4-hydroxy-3-(2-oxo-2-phenylacetyl)cyclohepta-1,3-diene-1-ca

rboxylate (3b): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), white solid, mp 165–167 °C, 60 mg, 73% yield. ¹H NMR (400 MHz, DMSO-d₆) δ 8.57 (s, 1H), 7.48–7.43 (m, 5H), 7.34–7.32 (m, 2H), 7.07–7.05 (m, 2H), 3.44 (s, 3H), 3.11–3.03 (m, 1H), 2.97–2.89 (m, 1H), 2.59–2.57 (m, 2H), 2.31–2.24 (m, 2H); ¹³C NMR (151 MHz, DMSO-d₆) δ 197.2, 194.7, 170.3, 138.0, 137.4, 137.0, 133.4, 133.0, 130.7, 130.1, 129.4, 128.5, 126.5, 111.7, 105.3, 52.5, 30.6, 30.4, 30.2. HRMS (MALDI-Quadrupole-Orbitrap) m/z: [M + Na]⁺ Calcd for C₂₃H₁₉ClO₅Na⁺ 433.0813; Found 433.0813. IR (KBr thin film, cm⁻¹): ν 3734, 2360, 2342, 1717, 1264, 731, 702, 669.



methyl

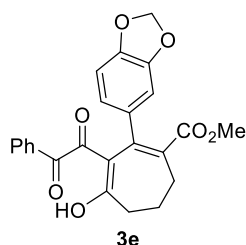
4-hydroxy-2-(4-methoxyphenyl)-3-(2-oxo-2-phenylacetyl)cyclohepta-1,3-diene-1-carboxylate (3c): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), white solid, mp 185–187 °C, 75 mg, 92% yield. ¹H NMR (400 MHz, DMSO-d₆) δ 8.57 (s, 1H), 7.51–7.48 (m, 2H), 7.47–7.44 (m, 3H), 7.00–6.96 (m, 2H), 6.84–6.81 (m, 2H), 3.76 (s, 3H), 3.46 (s, 3H), 3.06–2.98 (m, 1H), 2.91–2.83 (m, 1H), 2.55–2.52 (m, 2H), 2.34–2.27 (m, 2H); ¹³C NMR (101 MHz, DMSO-d₆) δ 197.0, 194.8, 171.1, 159.7, 138.3, 137.1, 131.8, 131.0, 130.2, 130.0, 129.4, 126.4, 114.0, 112.1, 105.5, 55.9, 52.4, 31.5, 30.4, 30.0. HRMS (MALDI-Quadrupole-Orbitrap) m/z: [M + Na]⁺ Calcd for C₂₄H₂₂O₆Na⁺ 429.1309; Found 429.1307. IR (KBr thin film, cm⁻¹): ν 3358, 2949, 2360, 2342, 1700, 1575, 1510, 1244, 1176, 1125, 1032, 832, 764, 669.



methyl

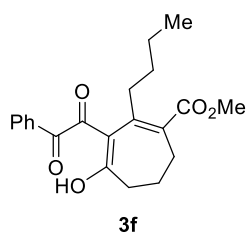
4-hydroxy-2-(2-methoxyphenyl)-3-(2-oxo-2-phenylacetyl)cyclohepta-1,3-diene-1-carboxylate (3d): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), white solid, mp 115–117 °C, 58 mg, 71% yield. ¹H NMR (400 MHz, DMSO-d₆) δ 8.38 (s, 1H), 7.36 (m, 5H), 7.14–7.10 (m, 1H), 6.83–6.71 (m, 3H), 3.43 (s, 3H), 3.29 (s, 3H), 3.01–2.92 (m, 1H), 2.84–2.76 (m, 1H), 2.58–

2.48 (m, 2H), 2.21–2.16 (m, 2H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 196.5, 192.5, 169.5, 156.7, 136.9, 135.2, 135.2, 132.6, 129.8, 129.5, 129.1, 128.8, 127.6, 126.0, 120.0, 112.2, 110.7, 55.4, 51.6, 30.1, 29.4, 29.3. HRMS (MALDI-Quadrupole-Orbitrap) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{24}\text{H}_{22}\text{O}_6\text{Na}^+$ 429.1309; Found 429.1311. IR (KBr thin film, cm^{-1}): ν 3373, 2949, 1705, 1560, 1434, 1244, 1124, 1023, 732, 700.



methyl

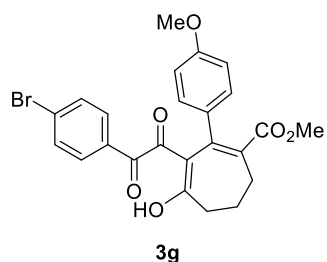
2-(benzo[d][1,3]dioxol-5-yl)-4-hydroxy-3-(2-oxo-2-phenylacetyl)cyclohepta-1,3-diene-1-carboxylate (3e): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), white solid, mp 208–210 °C, 67 mg, 80% yield. ^1H NMR (400 MHz, DMSO- d_6) δ 8.52 (s, 1H), 7.44–7.39 (m, 5H), 6.79–6.76 (m, 1H), 6.55–6.48 (m, 2H), 5.98 (s, 2H), 3.42 (s, 3H), 3.01–2.93 (m, 1H), 2.87–2.79 (m, 1H), 2.49–2.40 (m, 2H), 2.26–2.22 (m, 2H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 196.5, 194.3, 170.5, 147.3, 147.2, 136.6, 132.5, 131.9, 129.6, 128.9, 126.0, 122.1, 111.5, 108.9, 108.1, 101.5, 52.0, 30.6, 29.9, 29.8. HRMS (MALDI-Quadrupole-Orbitrap) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{24}\text{H}_{20}\text{O}_7\text{Na}^+$ 443.1101; Found 443.1104. IR (KBr thin film, cm^{-1}): ν 3735, 2360, 2342, 1700, 1235, 1036, 764, 669.



methyl

2-butyl-4-hydroxy-3-(2-oxo-2-phenylacetyl)cyclohepta-1,3-diene-1-carboxylate (3f): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow oil, 43 mg, 60% yield. ^1H NMR (400 MHz, DMSO- d_6) δ 8.49 (s, 1H), 7.40–7.35 (m, 5H), 3.65 (s, 3H), 2.88–2.79 (m, 1H), 2.76–2.70 (m, 1H), 2.62 (t, J = 6.4 Hz, 2H), 2.33–2.30 (m, 2H), 2.14–2.06 (m, 2H), 1.18–1.12 (m, 4H), 0.75–0.70 (m, 3H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 197.9, 193.3, 169.2, 142.0, 136.8, 130.0, 129.6, 128.9, 125.9, 111.7, 52.0, 31.6, 30.1, 29.7, 29.5, 28.9, 22.4, 14.3. HRMS (MALDI-Quadrupole-Orbitrap) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_5\text{Na}^+$ 379.1516;

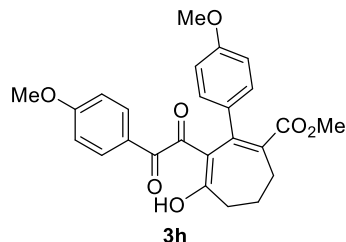
Found 379.1520. IR (KBr thin film, cm^{-1}): ν 3055, 1728, 1435, 1264, 1025, 896, 131, 702.



methyl

4-hydroxy-3-(2-oxo-2-phenylacetyl)-2-phenylcyclohepta-1,3-diene-1-carboxylate (3g):

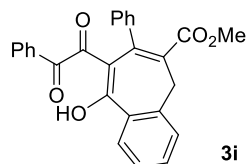
purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), white solid, mp 82–84 °C, 62 mg, 64% yield. ^1H NMR (400 MHz, acetone- d_6) δ 7.61–7.58 (m, 2H), 7.55–7.52 (m, 2H), 7.44 (s, 1H), 6.99–6.97 (m, 2H), 6.77–6.75 (m, 2H), 3.75 (s, 3H), 3.43 (s, 3H), 3.06–2.98 (m, 1H), 2.95–2.87 (m, 1H), 2.57–2.54 (m, 2H), 2.38–2.31 (m, 2H); ^{13}C NMR (101 MHz, acetone- d_6) δ 195.7, 193.8, 170.6, 159.8, 137.9, 136.4, 132.2, 131.9, 130.9, 129.9, 128.4, 123.3, 113.3, 112.2, 103.9, 55.0, 51.3, 31.0, 30.1, 29.8. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{24}\text{H}_{21}\text{BrO}_6\text{Na}^+$ 507.0414; Found 507.0411. IR (KBr thin film, cm^{-1}): ν 3734, 2360, 2342, 1700, 1508, 1264, 731, 702, 669.



methyl

4-hydroxy-2-(4-methoxyphenyl)-3-(2-(4-methoxyphenyl)-2-oxoacetyl)cyclohepta-1,3-diene-1-carboxylate (3h):

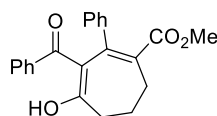
purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), white solid, mp 198–200 °C, 57 mg, 66% yield. ^1H NMR (400 MHz, DMSO- d_6) δ 8.41 (s, 1H) 7.37–7.35 (m, 2H), 6.96–6.92 (m, 4H), 6.80–6.77 (m, 2H), 3.76 (s, 3H), 3.72 (s, 3H), 3.41 (s, 3H), 2.97–2.90 (m, 1H), 2.84–2.76 (m, 1H), 2.48–2.46 (m, 2H), 2.32–2.21 (m, 2H); ^{13}C NMR (101 MHz, DMSO- d_6) δ 196.6, 194.1, 170.7, 160.3, 159.3, 131.1, 130.6, 129.8, 128.7, 127.5, 114.3, 113.5, 111.6, 55.7, 55.5, 51.9, 31.1, 30.0, 29.6. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{24}\text{O}_7\text{Na}^+$ 459.1414; Found 459.1422. IR (KBr thin film, cm^{-1}): ν 3735, 2360, 2342, 1700, 1509, 1247, 1176, 749, 734, 700, 669.



3i

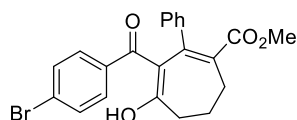
methyl

9-hydroxy-8-(2-oxo-2-phenylacetyl)-7-phenyl-5H-benzo[7]annulene-6-carboxylate (3i): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), white solid, mp 210–211 °C, 43 mg, 51% yield. ¹H NMR (400 MHz, acetone-d₆) δ 8.12–8.10 (m, 2H), 7.79–7.75 (m, 1H), 7.68–7.65 (m, 2H), 7.61–7.57 (m, 2H), 7.53–7.49 (m, 2H), 7.46–7.41 (m, 3H), 7.19–7.17 (m, 3H), 7.05–7.03 (m, 2H), 3.70 (brs, 2H), 3.37 (s, 3H); ¹³C NMR (101 MHz, acetone-d₆) δ 196.0, 181.6, 167.6, 140.2, 137.9, 137.8, 136.5, 134.5, 129.2, 128.6, 128.4, 128.1, 127.5, 127.3, 127.2, 126.1, 125.8, 123.4, 113.0, 50.8, 35.7. HRMS (MALDI-Quadrupole-Orbitrap) m/z: [M + Na]⁺ Calcd for C₂₇H₂₀O₅Na⁺ 447.1203; Found 447.1204. IR (KBr thin film, cm⁻¹): ν 3304, 2946, 1717, 1683, 1541, 1399, 1247, 1124, 763, 695.



5a

methyl 3-benzoyl-4-hydroxy-2-phenylcyclohepta-1,3-diene-1-carboxylate (5a): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), white solid, mp 139–141 °C, 303 mg, 87% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.22–7.18 (m, 3H), 7.12–7.08 (m, 2H), 6.95–6.90 (m, 3H), 6.81–6.78 (m, 2H), 3.45 (s, 3H), 2.90–2.63 (m, 3H), 2.58–2.45 (m, 1H), 2.38–2.24 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 195.4, 191.0, 170.9, 145.3, 140.2, 137.1, 131.0, 130.6, 128.7, 127.8, 127.8, 127.3, 127.2, 113.0, 51.7, 35.2, 31.0, 29.4. HRMS (MALDI-Quadrupole-Orbitrap) m/z: [M + Na]⁺ Calcd for C₂₂H₂₀O₄Na⁺ 371.1254; Found 371.1261. IR (KBr thin film, cm⁻¹): ν 3735, 2360, 2342, 1705, 1265, 731, 696, 669.

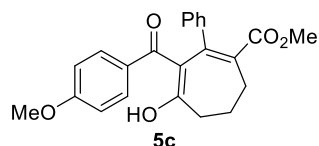


5b

methyl

3-(4-bromobenzoyl)-4-hydroxy-2-phenylcyclohepta-1,3-diene-1-carboxylate (5b): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), white solid, mp 131–133 °C, 397 mg, 93% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.25–7.23 (m, 2H), 7.09–7.07 (m, 2H), 7.00–6.95 (m, 3H), 6.80–6.78 (m, 2H), 3.46 (s,

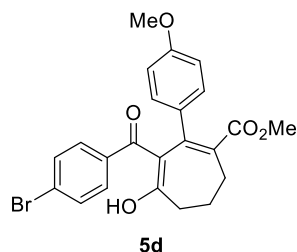
3H), 2.86–2.62 (m, 3H), 2.57–2.46 (m, 1H), 2.34–2.30 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 195.5, 189.9, 170.8, 144.7, 140.1, 136.0, 131.1, 131.0, 129.4, 128.7, 127.7, 127.5, 125.6, 113.0, 51.8, 35.2, 31.1, 29.4. HRMS (MALDI-Quadrupole-Orbitrap) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{19}\text{O}_4\text{Na}^+$ 449.0359; Found 449.0364. IR (KBr thin film, cm^{-1}): ν 3735, 2360, 2342, 1716, 1264, 1011, 731, 702, 669.



methyl

4-hydroxy-3-(4-methoxybenzoyl)-2-phenylcyclohepta-1,3-diene-1-carboxylate

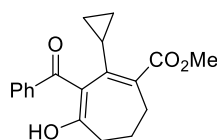
(5c): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, $v:v = 5:1$), white solid, mp 120–122 $^{\circ}\text{C}$, 269 mg, 71% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.31–7.29 (m, 2H), 6.98–6.96 (m, 3H), 6.88–6.86 (m, 2H), 6.64–6.61 (m, 2H), 3.73 (s, 3H), 3.47 (s, 3H), 2.85–2.64 (m, 3H), 2.60–2.44 (m, 1H), 2.37–2.21 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 194.8, 189.8, 171.1, 162.1, 145.5, 140.2, 130.5, 130.3, 129.6, 128.7, 127.5, 127.3, 113.2, 112.2, 55.4, 51.8, 35.2, 31.1, 29.5. HRMS (MALDI-Quadrupole-Orbitrap) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{22}\text{O}_5\text{Na}^+$ 401.1359; Found 401.1363. IR (KBr thin film, cm^{-1}): ν 3735, 2948, 2360, 2342, 1705, 1603, 1251, 1169, 1029, 839, 765, 613.



methyl

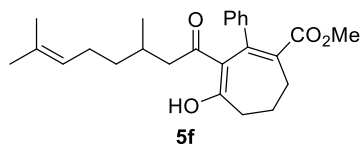
3-(4-bromobenzoyl)-4-hydroxy-2-(4-methoxyphenyl)cyclohepta-1,3-diene-1-carboxylate (5d)

(5d): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, $v:v = 5:1$), white solid, mp 141–143 $^{\circ}\text{C}$, 430 mg, 94% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.26–7.24 (m, 2H), 7.11–7.09 (m, 2H), 6.75–6.72 (m, 2H), 6.52–6.49 (m, 2H), 3.68 (s, 3H), 3.50 (s, 3H), 2.85–2.57 (m, 3H), 2.52–2.45 (m, 1H), 2.36–2.23 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 195.3, 190.0, 170.9, 159.0, 144.6, 136.1, 132.6, 131.1, 130.1, 129.6, 129.3, 125.6, 113.1, 112.9, 55.3, 51.8, 35.1, 31.2, 29.4. HRMS (MALDI-Quadrupole-Orbitrap) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{23}\text{H}_{21}\text{BrO}_5\text{Na}^+$ 479.0465; Found 479.0470. IR (KBr thin film, cm^{-1}): ν 3735, 2949, 2360, 2342, 1701, 1588, 1508, 1247, 1173, 1011, 831, 734, 678.



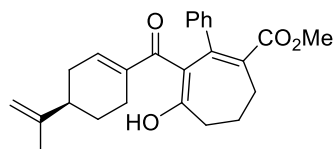
5e

methyl 3-benzoyl-2-cyclopropyl-4-hydroxycyclohepta-1,3-diene-1-carboxylate (5e): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), colorless oil, 181 mg, 58% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.69–7.65 (m, 2H), 7.48–7.36 (m, 3H), 3.80 (s, 3H), 2.74 (m, 1H), 2.45–2.42 (m, 2H), 2.27–2.20 (m, 3H), 2.09–2.00 (m, 1H), 0.82–0.78 (m, 1H), 0.15–0.11 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 196.4, 186.7, 168.8, 151.7, 137.4, 131.7, 129.6, 128.6, 128.3, 109.7, 51.5, 35.2, 30.6, 28.1, 16.6. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{20}\text{O}_4\text{Na}^+$ 335.1254; Found 335.1258. IR (KBr thin film, cm^{-1}): ν 3628, 2947, 2360, 2342, 1706, 1559, 1431, 1233, 1156, 1106, 1020, 762, 695, 677.



5f

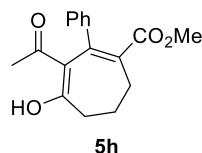
methyl 3-(3,7-dimethyloct-6-enoyl)-4-hydroxy-2-phenylcyclohepta-1,3-diene-1-carboxylate (5f): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), colorless oil, 305 mg, 77% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.33–7.27 (m, 3H), 7.20–7.17 (m, 2H), 5.01–4.96 (m, 1H), 3.50 (s, 3H), 2.77–2.63 (m, 2H), 2.44–2.34 (m, 2H), 2.27–2.15 (m, 2H), 1.87–1.70 (m, 4H), 1.67–1.65 (m, 4H), 1.56–1.52 (m, 3H), 1.06–0.84 (m, 2H), 0.74–0.59 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 197.5, 197.3, 195.1, 195.0, 171.1, 171.0, 143.2, 143.1, 140.9, 140.7, 132.0, 131.9, 131.6, 131.5, 128.4, 128.3, 128.3, 124.4, 124.3, 113.4, 113.1, 51.8, 44.7, 37.0, 36.8, 35.1, 35.0, 31.0, 30.3, 30.1, 29.1, 25.8, 25.3, 25.2, 19.4, 19.1, 17.7. HRMS (MALDI-Quadrupole-Orbitrap) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{32}\text{O}_4\text{Na}^+$ 419.2193; Found 419.2193. IR (KBr thin film, cm^{-1}): ν 3735, 2927, 2360, 2342, 1714, 1559, 1431, 1168, 1099, 764, 701, 680.



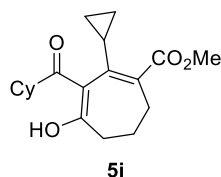
5g

methyl (R)-4-hydroxy-2-phenyl-3-(4-(prop-1-en-2-yl)cyclohex-1-ene-1-carbonyl)cyclohepta-1,3-diene-1-carboxylate (5g): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), white solid, mp 100–102 $^{\circ}\text{C}$, 287 mg, 73%

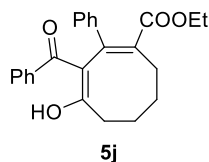
yield. ^1H NMR (400 MHz, CDCl_3) δ 7.25–7.20 (m, 3H), 7.03–7.01 (m, 2H), 5.88–5.87 (m, 1H), 4.65 (s, 1H), 4.55 (s, 1H), 3.48 (s, 3H), 2.79–2.45 (m, 4H), 2.28–2.21 (m, 3H), 2.03–1.96 (m, 1H), 1.79–1.72 (m, 1H), 1.60 (s, 5H), 1.45–1.41 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 196.6, 171.2, 149.2, 149.1, 146.0, 141.7, 135.2, 129.7, 128.7, 127.8, 127.6, 109.1, 51.8, 35.7, 31.1, 30.8, 29.5, 26.4. HRMS (MALDI-Quadrupole-Orbitrap) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{28}\text{O}_4\text{Na}^+$ 415.1880; Found 415.1884. IR (KBr thin film, cm^{-1}): ν 3735, 2360, 2342, 1559, 1264, 896, 731, 703, 669.



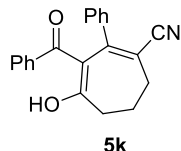
methyl 3-acetyl-4-hydroxy-2-phenylcyclohepta-1,3-diene-1-carboxylate (5h): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), white solid, mp 93–95 °C, 246 mg, 86% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.33–7.29 (m, 3H), 7.19–7.17 (m, 2H), 3.49 (s, 3H), 2.69–2.63 (m, 2H), 2.45–2.38 (m, 2H), 2.22–2.10 (m, 2H), 1.53 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 195.2, 194.7, 171.1, 143.0, 140.8, 131.9, 128.4, 128.4, 128.2, 113.0, 51.8, 34.9, 31.2, 29.1, 25.5. HRMS (MALDI-Quadrupole-Orbitrap) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{18}\text{O}_4\text{Na}^+$ 309.1097; Found 309.1105. IR (KBr thin film, cm^{-1}): ν 3735, 2360, 2341, 1715, 1266, 1171, 1101, 732, 702, 669.



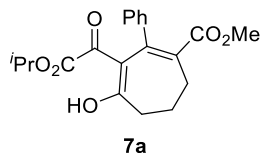
methyl 3-(cyclohexanecarbonyl)-2-cyclopropyl-4-hydroxycyclohepta-1,3-diene-1-carboxylate (5i): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), colorless oil, 175 mg, 55% yield. ^1H NMR (400 MHz, CDCl_3) δ 3.78 (s, 3H), 2.68–2.57 (m, 3H), 2.31–2.25 (m, 1H), 2.12–2.10 (m, 4H), 1.78–1.70 (m, 3H), 1.67–1.57 (m, 3H), 1.23–1.21 (m, 4H), 0.97–0.90 (m, 1H), 0.72–0.65 (m, 1H), 0.51–0.45 (m, 1H), 0.17–0.11 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 199.2, 192.9, 168.9, 150.3, 130.0, 108.5, 51.6, 45.5, 34.2, 30.8, 30.8, 27.7, 27.3, 26.4, 25.8, 25.4, 15.8, 8.2, 6.0. HRMS (MALDI-Quadrupole-Orbitrap) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{26}\text{O}_4\text{Na}^+$ 341.1723; Found 341.1728. IR (KBr thin film, cm^{-1}): ν 3735, 2930, 2855, 2360, 2342, 1706, 1576, 1448, 1297, 1167, 1104, 961, 764, 735, 669.



ethyl (1E,3Z)-3-benzoyl-4-hydroxy-2-phenylcycloocta-1,3-diene-1-carboxylate (5j): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), white solid, mp 101–103 °C, 132 mg, 35% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.26–7.22 (m, 3H), 7.16–7.12 (m, 2H), 7.00–6.91 (m, 3H), 6.74–6.72 (m, 2H), 3.96–3.81 (m, 2H), 3.16–3.11 (m, 1H), 2.72–2.58 (m, 2H), 2.45–2.38 (m, 1H), 2.12–2.04 (m, 1H), 1.97–1.90 (m, 1H), 1.69–1.60 (m, 1H), 1.41–1.30 (m, 1H), 0.78 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 194.4, 191.4, 171.2, 141.0, 140.8, 138.3, 133.8, 130.8, 128.3, 127.9, 127.4, 127.4, 127.2, 112.8, 60.8, 35.0, 32.1, 24.5, 24.4, 13.7. HRMS (MALDI-Quadrupole-Orbitrap) *m/z*: [M + Na]⁺ Calcd for C₂₄H₂₄O₄Na⁺ 399.1567; Found 399.1574. IR (KBr thin film, cm⁻¹): ν 3735, 2360, 2342, 1705, 1559, 1264, 1154, 1107, 732, 696, 669.

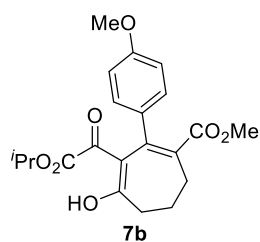


3-benzoyl-4-hydroxy-2-phenylcyclohepta-1,3-diene-1-carbonitrile (5k): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), white solid, mp 171–172 °C, 276 mg, 88% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.22–7.19 (m, 3H), 7.14–7.10 (m, 4H), 7.06–7.04 (m, 3H), 2.71–2.69 (m, 2H), 2.61–2.46 (m, 2H), 2.44–2.38 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 195.4, 191.0, 155.8, 138.0, 136.5, 131.4, 129.1, 128.9, 127.9, 127.9, 127.8, 120.3, 111.3, 108.4, 35.3, 31.0, 30.4. HRMS (MALDI-Quadrupole-Orbitrap) *m/z*: [M + Na]⁺ Calcd for C₂₁H₁₇NO₂Na⁺ 338.1151; Found 338.1153. IR (KBr thin film, cm⁻¹): ν 3051, 2969, 2197, 1562, 1441, 761, 691.



methyl 4-hydroxy-3-(2-isopropoxy-2-oxoacetyl)-2-phenylcyclohepta-1,3-diene-1-carboxylate (7a): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), brown oil, 87 mg, 81% yield. ¹H NMR (400 MHz, CDCl₃) δ 15.82 (s, 1H), 7.14–7.13 (m, 3H), 7.01–6.99 (m, 2H), 4.31–4.25 (m, 1H), 3.36 (s, 3H), 2.59–2.37 (m, 4H), 2.20–2.13 (m, 2H), 0.95–0.68 (m, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 195.5, 183.7, 170.4, 161.9, 142.5, 139.5, 131.3, 129.8, 128.5, 127.9, 112.1, 70.5, 51.8, 34.5,

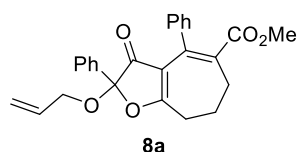
32.0, 29.0, 21.3. HRMS (MALDI-Quadrupole-Orbitrap) m/z : $[M + Na]^+$ Calcd for $C_{20}H_{22}O_6Na^+$ 381.1309; Found 381.1316 IR (KBr thin film, cm^{-1}): ν 3735, 2984, 2360, 2342, 1732, 1559, 1243, 1200, 1100, 948, 765, 733, 701, 669.



methyl

4-hydroxy-3-(2-isopropoxy-2-oxoacetyl)-2-(4-methoxyphenyl)cyclohepta-1,3-diene-1-carboxylate (7b):

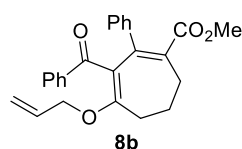
purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, $v:v = 5:1$), white solid, mp 95–97 °C, 56 mg, 72% yield. 1H NMR (400 MHz, $CDCl_3$) δ 15.86 (s, 1H), 7.06–7.03 (m, 2H), 6.80–6.77 (m, 2H), 4.48–4.42 (m, 1H), 3.78 (s, 3H), 3.52 (s, 3H), 2.72–2.47 (m, 4H), 2.30–2.26 (m, 2H), 1.09–0.84 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0, 184.3, 170.5, 162.0, 159.9, 142.6, 132.0, 131.3, 129.8, 113.3, 112.4, 70.5, 55.4, 51.8, 34.4, 32.3, 28.9, 21.3. HRMS (MALDI-Quadrupole-Orbitrap) m/z : $[M + Na]^+$ Calcd for $C_{21}H_{24}O_7Na^+$ 411.1414; Found 411.1419. IR (KBr thin film, cm^{-1}): ν 3734, 2983, 2360, 2342, 1732, 1508, 1248, 1175, 1100, 834, 733, 702.



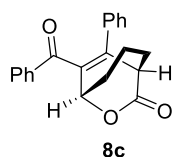
methyl

2-(allyloxy)-3-oxo-2,4-diphenyl-3,6,7,8-tetrahydro-2H-cyclohepta[b]furan-5-carboxylate (8a):

purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, $v:v = 3:1$), yellow oil, 23 mg, 55% yield. 1H NMR (400 MHz, $CDCl_3$) δ 7.95–7.92 (m, 2H), 7.61–7.57 (m, 1H), 7.51–7.47 (m, 2H), 7.36–7.27 (m, 5H), 5.09–5.00 (m, 1H), 4.86 (dd, $J = 10.4, 1.2$ Hz, 1H), 4.70 (dd, $J = 17.1, 1.5$ Hz, 1H), 3.93 (d, $J = 5.7$ Hz, 2H), 3.52 (s, 3H), 2.69–2.62 (m, 4H), 2.04–1.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 191.0, 170.3, 164.0, 142.4, 140.7, 135.3, 134.0, 131.8, 130.7, 129.2, 128.3, 127.9, 127.7, 121.4, 119.1, 77.4, 71.1, 51.9, 38.7, 28.8, 25.6. HRMS (MALDI-Quadrupole-Orbitrap) m/z : $[M + Na]^+$ Calcd for $C_{26}H_{24}O_5Na^+$ 439.1516; Found 439.1524. IR (KBr thin film, cm^{-1}): ν 2949, 1712, 1669, 1553, 1264, 1086, 731, 701.



methyl 4-(allyloxy)-3-benzoyl-2-phenylcyclohepta-1,3-diene-1-carboxylate (8b): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), white solid, mp 103–105 °C, 87 mg, 75% yield. ¹H NMR (600 MHz, CDCl₃) δ 7.42–7.40 (m, 2H), 7.30–7.26 (m, 1H), 7.17–7.14 (m, 2H), 6.97–6.96 (m, 3H), 6.84–6.83 (m, 2H), 5.67–5.61 (m, 1H), 5.04 (dd, *J* = 20.3, 17.6 Hz, 2H), 4.27 (d, *J* = 4.9 Hz, 2H), 3.30 (s, 3H), 2.59 (t, *J* = 14.3 Hz, 2H), 2.46 (t, *J* = 14.2 Hz, 2H), 2.34–2.29 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 195.1, 170.7, 169.8, 148.9, 139.6, 139.5, 132.6, 132.1, 131.9, 128.7, 128.4, 128.1, 127.6, 127.6, 120.4, 117.8, 71.1, 51.6, 37.9, 29.7, 28.7. HRMS (MALDI-Quadrupole-Orbitrap) *m/z*: [M + Na]⁺ Calcd for C₂₅H₂₄O₄Na⁺ 411.1567; Found 411.1574. IR (KBr thin film, cm⁻¹): ν 2360, 2342, 1705, 1234, 765, 669.



(1R,5S)-9-benzoyl-8-phenyl-6-oxabicyclo[3.2.2]non-8-en-7-one (8c): purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), white solid, mp 134–136 °C, 27 mg, 42% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.62–7.60 (m, 2H), 7.34–7.30 (m, 1H), 7.19–7.15 (m, 2H), 7.13–7.09 (m, 5H), 5.30 (dd, *J* = 5.0, 1.7 Hz, 1H), 3.74 (t, *J* = 4.0 Hz, 1H), 2.28–2.20 (m, 1H), 2.06–1.97 (m, 1H), 1.96–1.88 (m, 4H); ¹³C NMR (151 MHz, CDCl₃) δ 195.9, 175.0, 144.5, 135.9, 135.9, 133.6, 133.2, 129.4, 129.4, 128.6, 128.4, 128.3, 78.4, 48.0, 27.9, 23.7, 20.2. HRMS (MALDI-Quadrupole-Orbitrap) *m/z*: [M + Na]⁺ Calcd for C₂₁H₁₈O₃Na⁺ 341.1148; Found 341.1147. [α]_D²⁹: +133.4 (*c* 0.36, CHCl₃); HPLC analysis: 98% *ee* (Chiralcel OD-H, 5:95 ⁱPrOH/Hexane, 1 mL/min), R_t (major) = 10.5 min, R_t (minor) = 8.2 min. IR (KBr thin film, cm⁻¹): ν 3054, 1699, 1605, 1488, 1408, 1264, 1092, 1014, 734, 703.

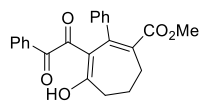
Reference

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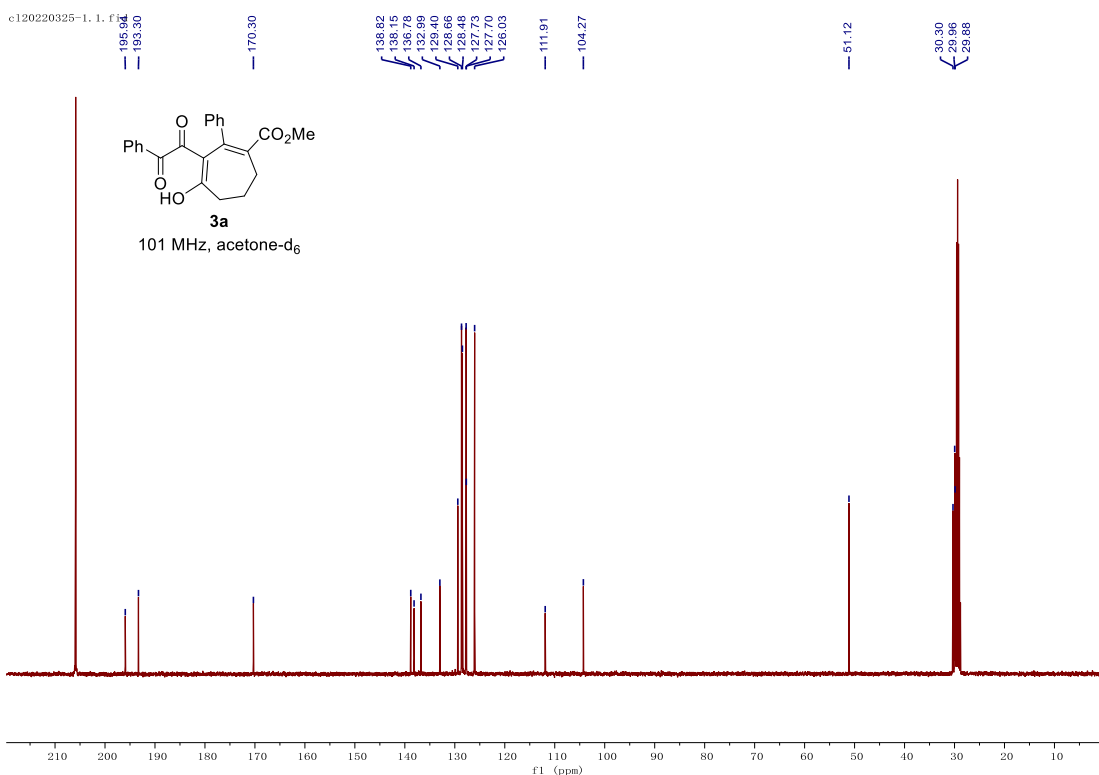
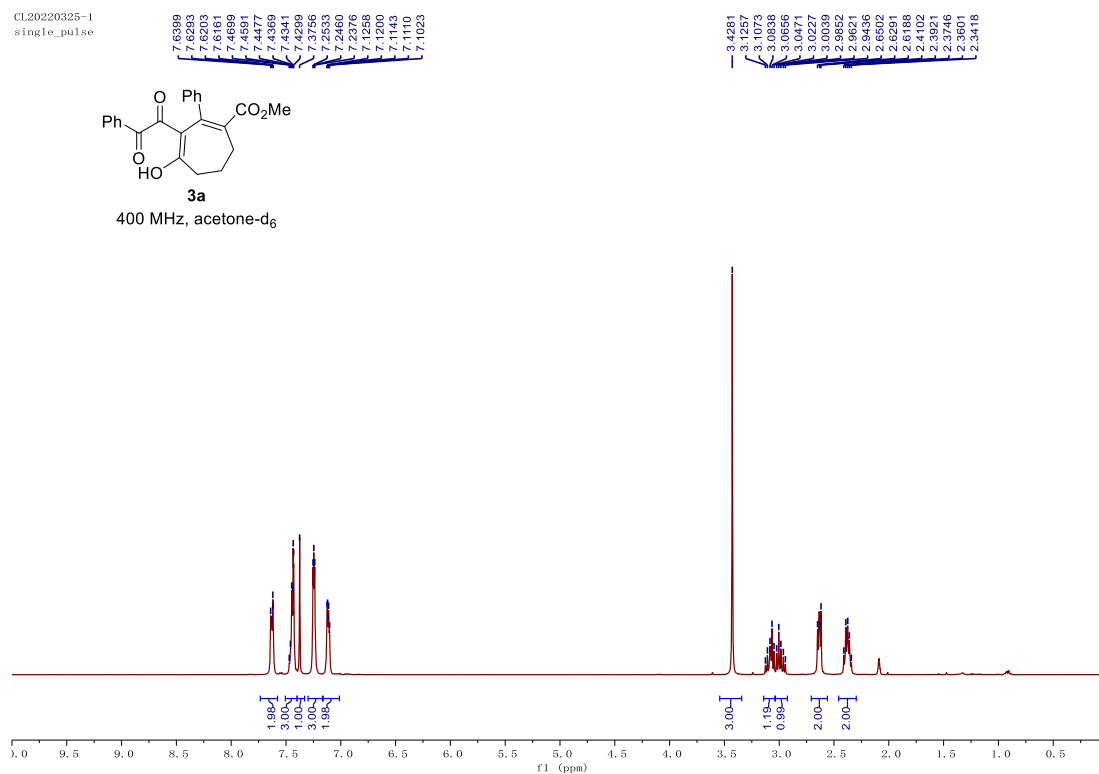
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VII. ¹H NMR and ¹³C NMR spectra of products

CL20220325-1
single_pulse



400 MHz, acetone-d₆

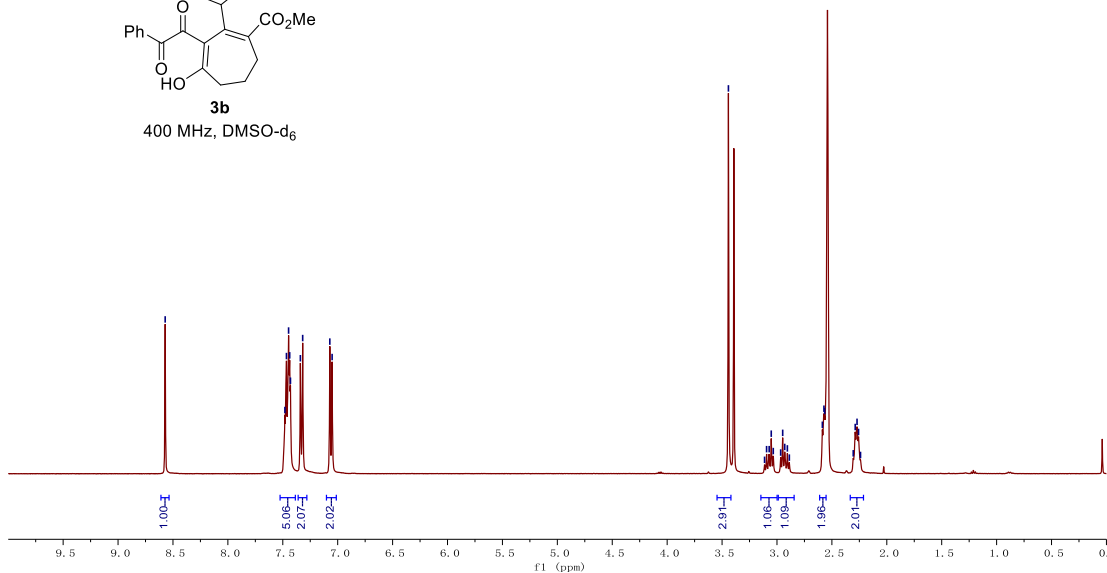
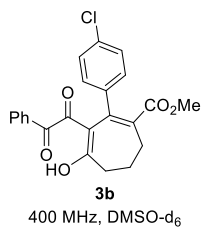


c120220516-Cl, 2, F1d

8.5709

7.4806
7.4665
7.4471
7.4371
7.3988
7.3910
7.0191
7.0508

3.4421
3.1130
3.0776
3.0776
3.0521
3.0337
2.9664
2.9480
2.9285
2.8664
2.8371
2.5867
2.5723
2.5656
2.3055
2.2876
2.2770
2.2572
2.2393



CL20220520-Cl

single pulse decoupled gated NOE

198.17
187.66

170.31

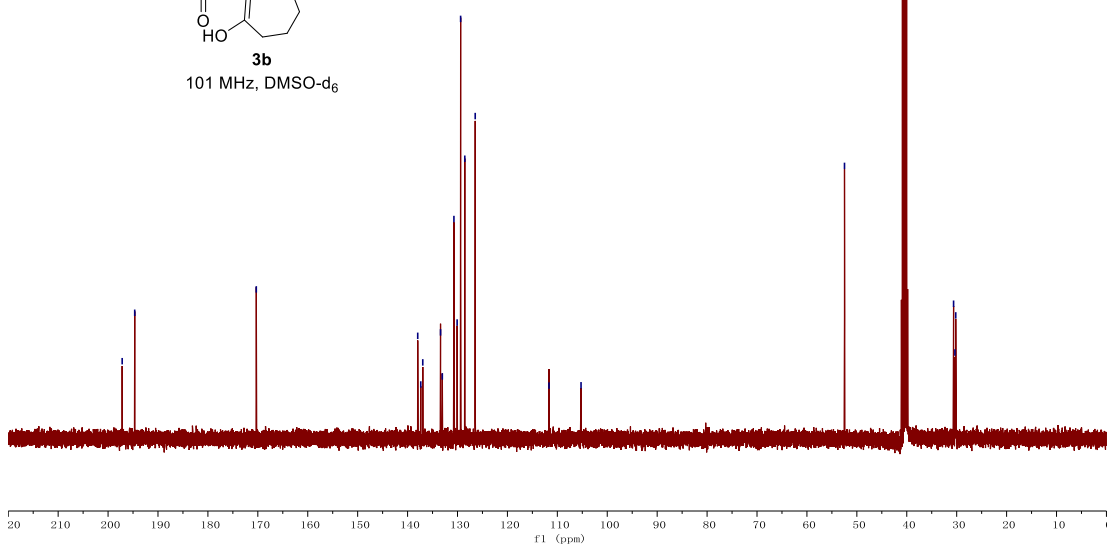
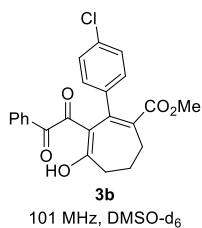
137.97
137.36
136.96
133.39
133.04
132.72
130.07
129.37
128.54
126.45

111.67

105.25

52.47

30.62
30.35
30.19

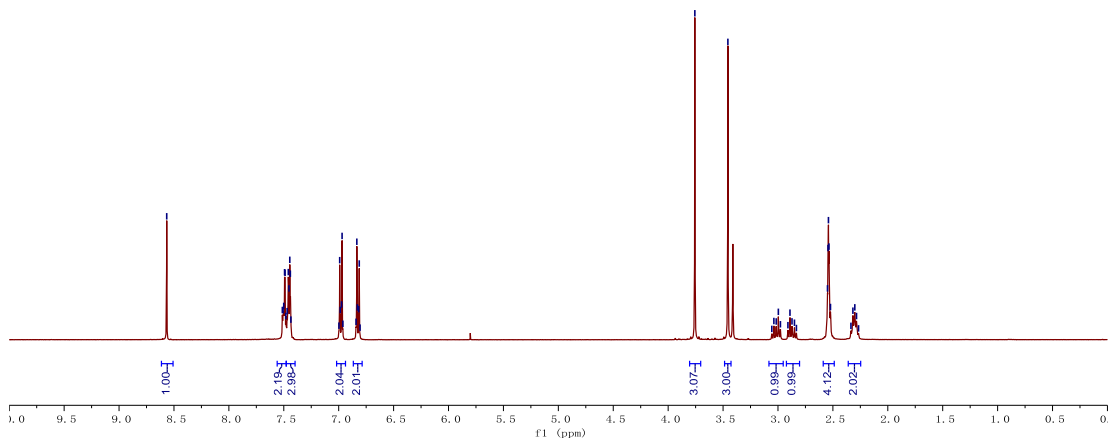
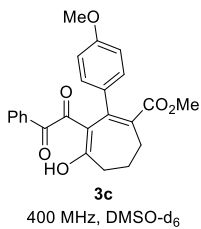


CL2022_05_16-0Me
single_pulse

8.56689
7.5131
7.5068
7.5004
7.4882
7.4813
7.4696
7.4588
7.4453
7.4352
6.9978
6.9908
6.9859
6.9740
6.9691
6.9647
6.8348
6.8298
6.8177
6.8129
6.8056

3.7570

3.4562
3.0592
3.0159
2.9965
2.9778
2.9608
2.9474
2.9321
2.5445
2.5403
2.5358
2.5310
2.3177
2.3004
2.2849
2.2663

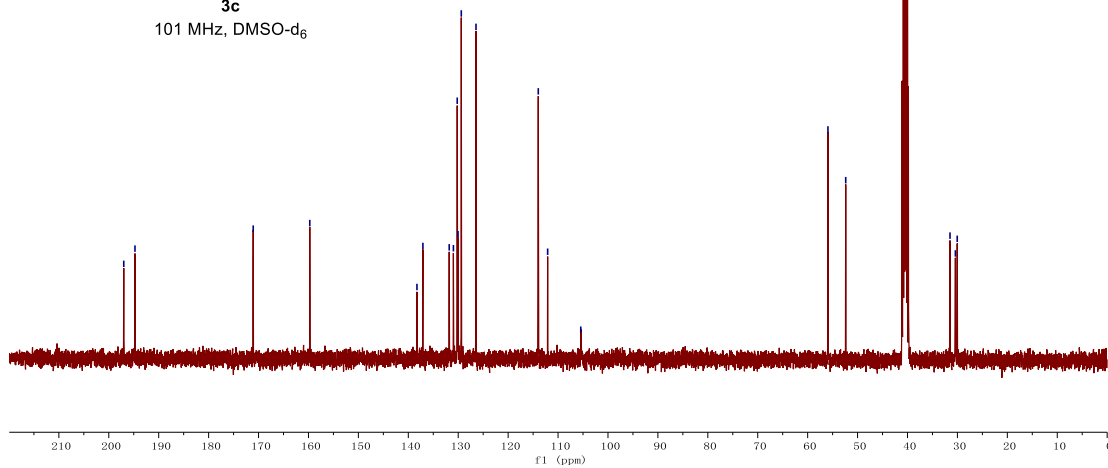
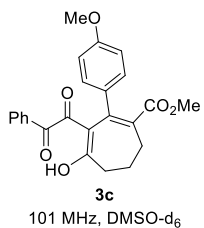


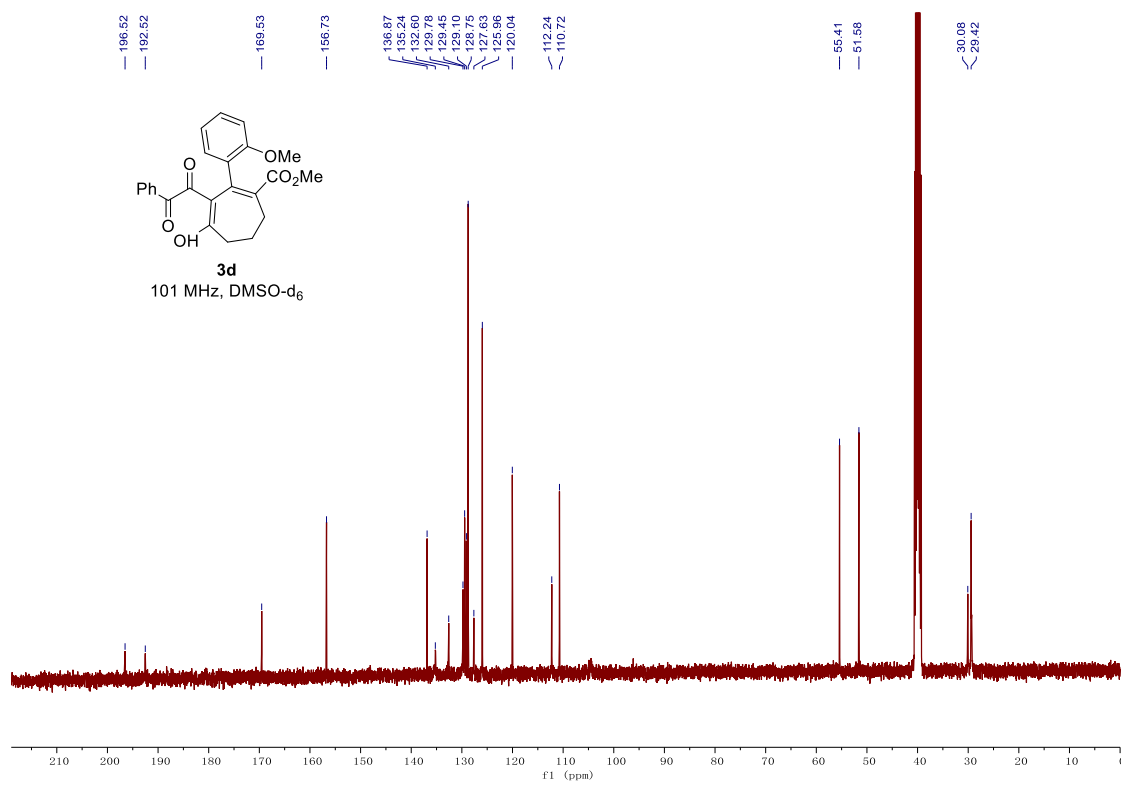
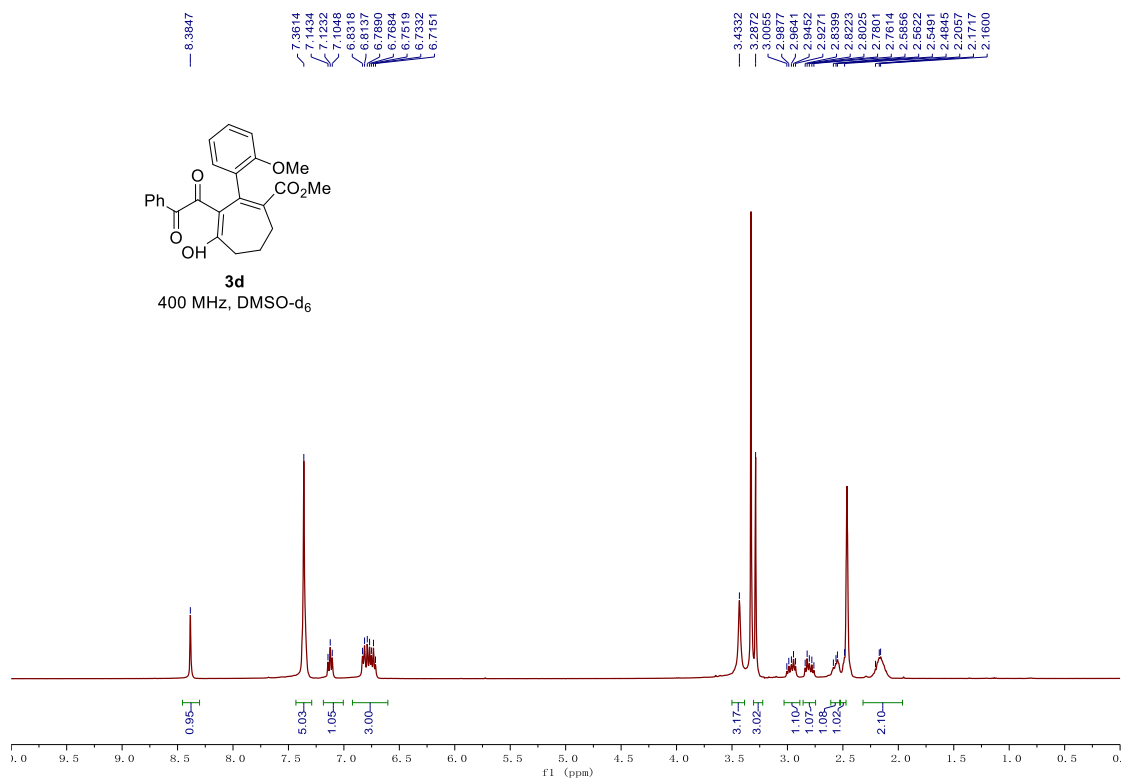
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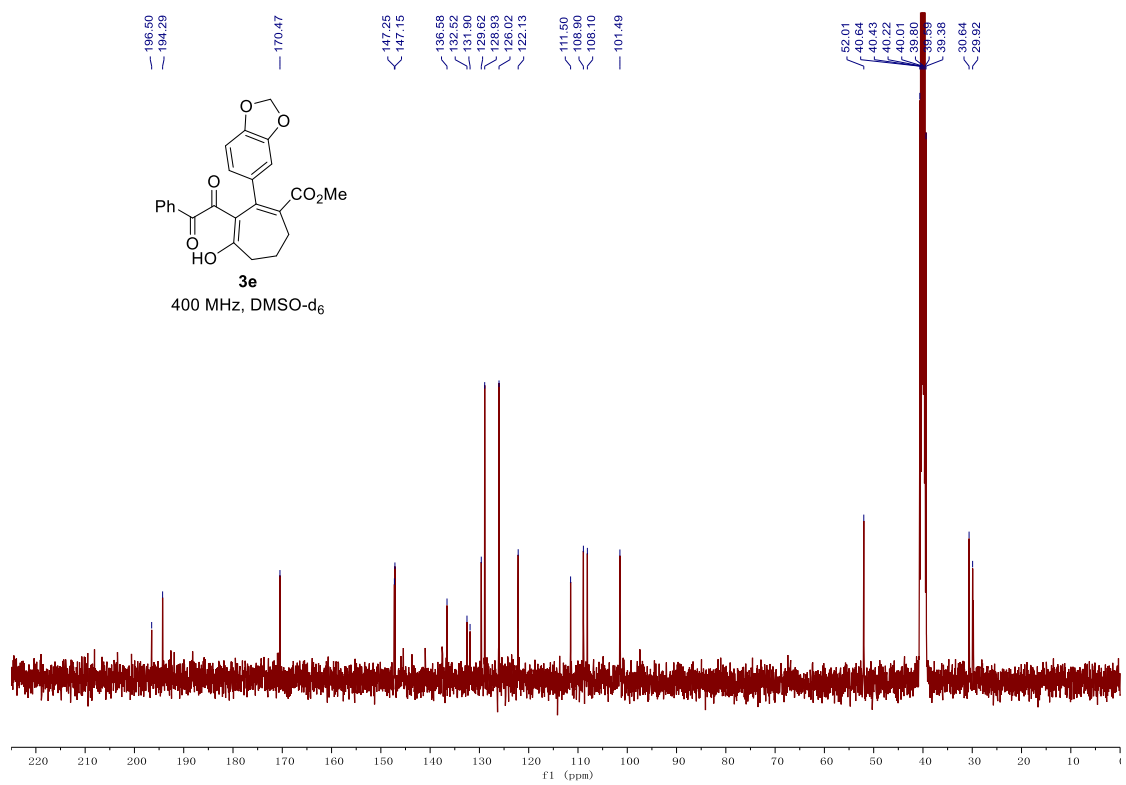
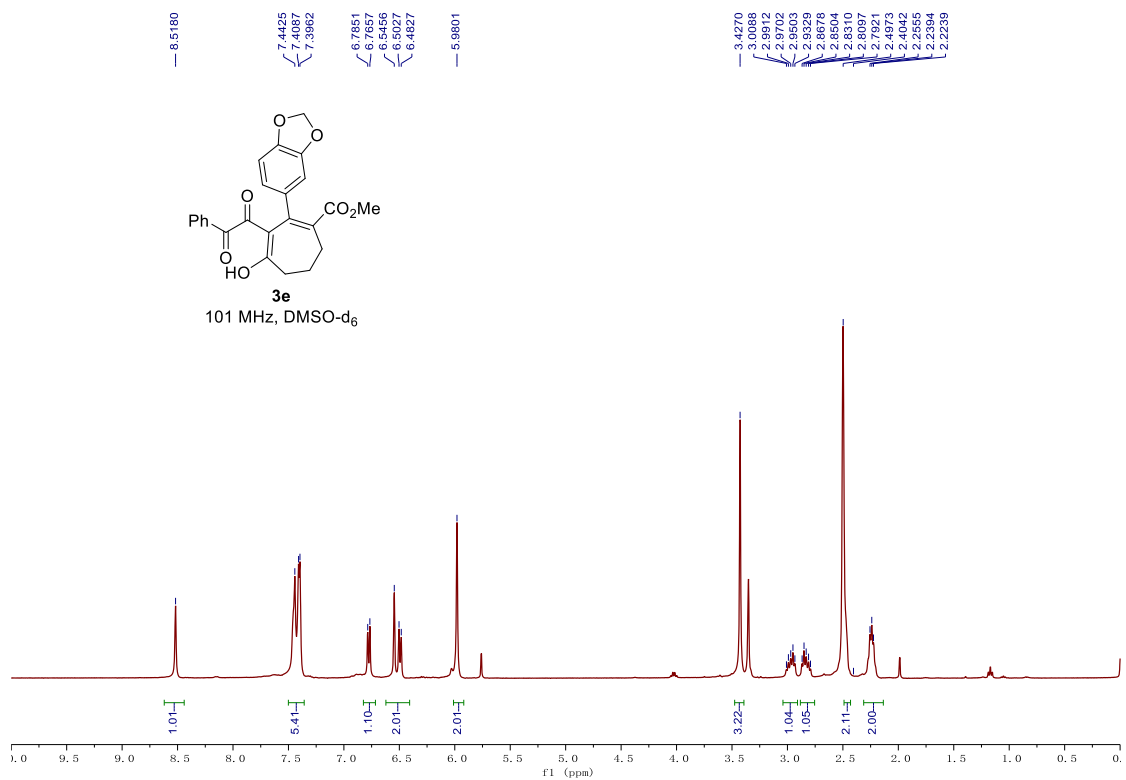
197.00
194.26
171.07
159.74
138.27
137.08
131.80
130.96
130.04
129.39
126.44
113.96
112.09
105.45

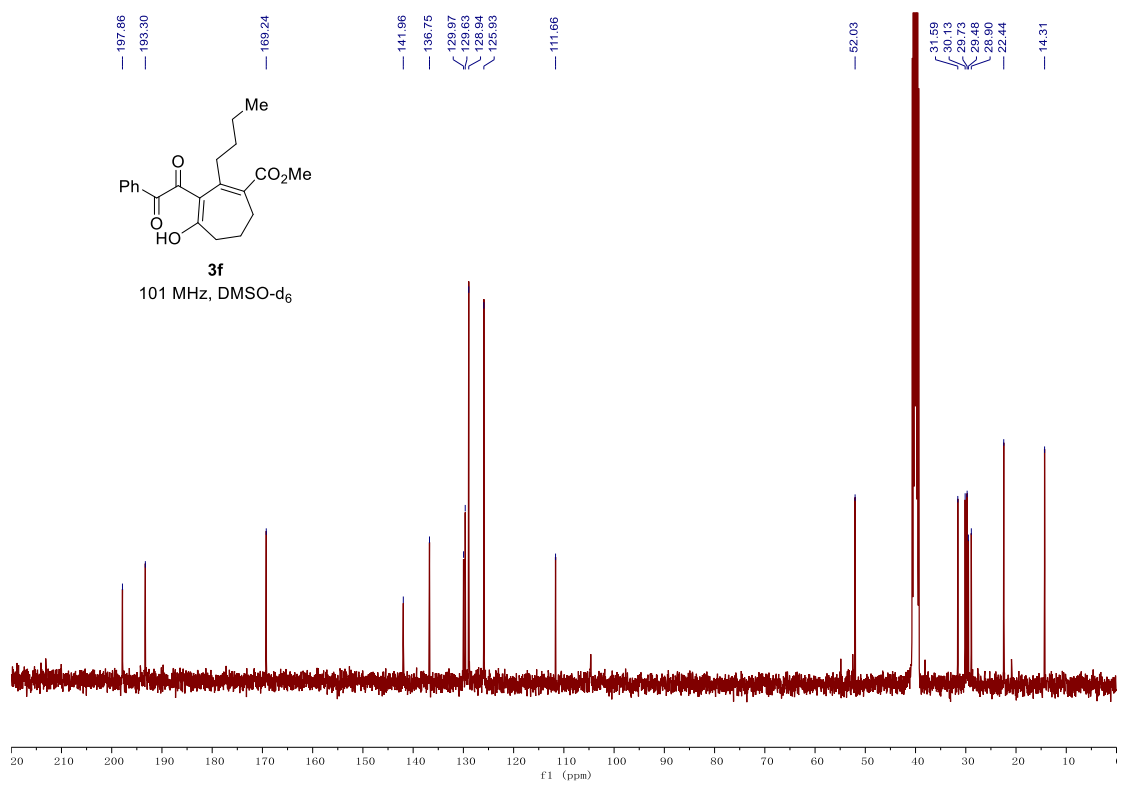
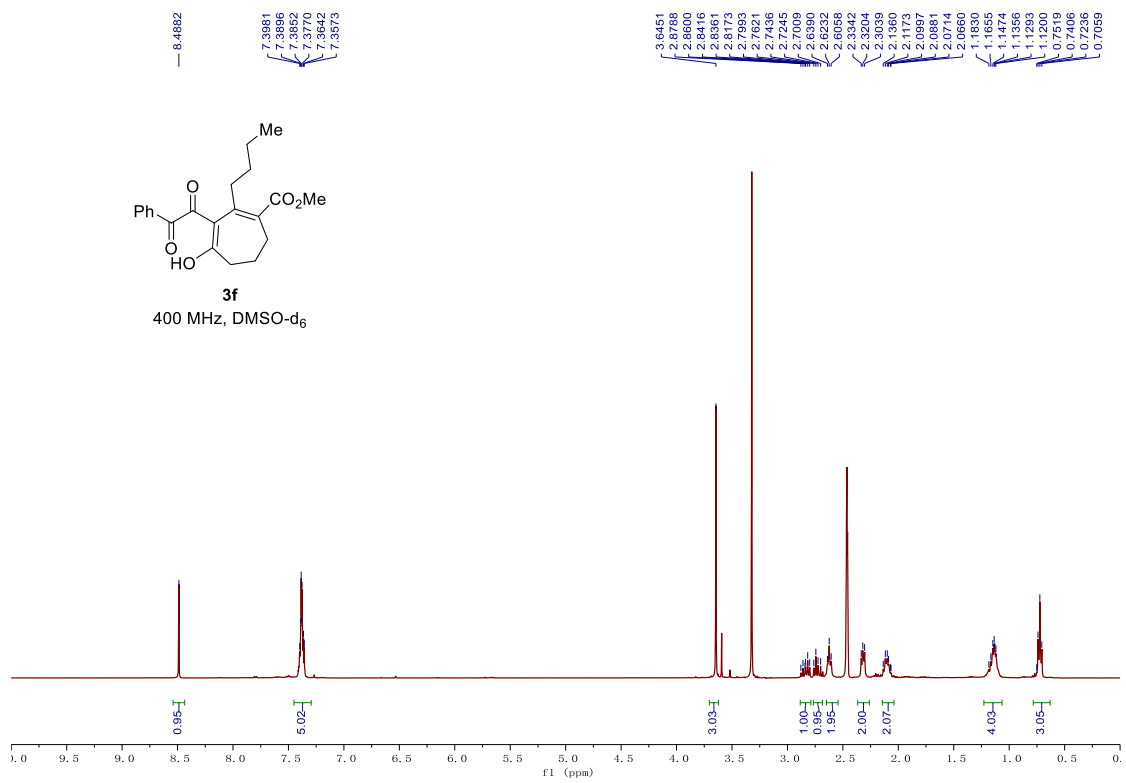
55.94
52.37

31.48
30.41
30.04

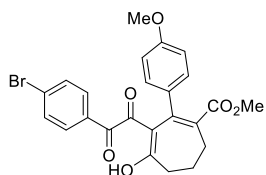






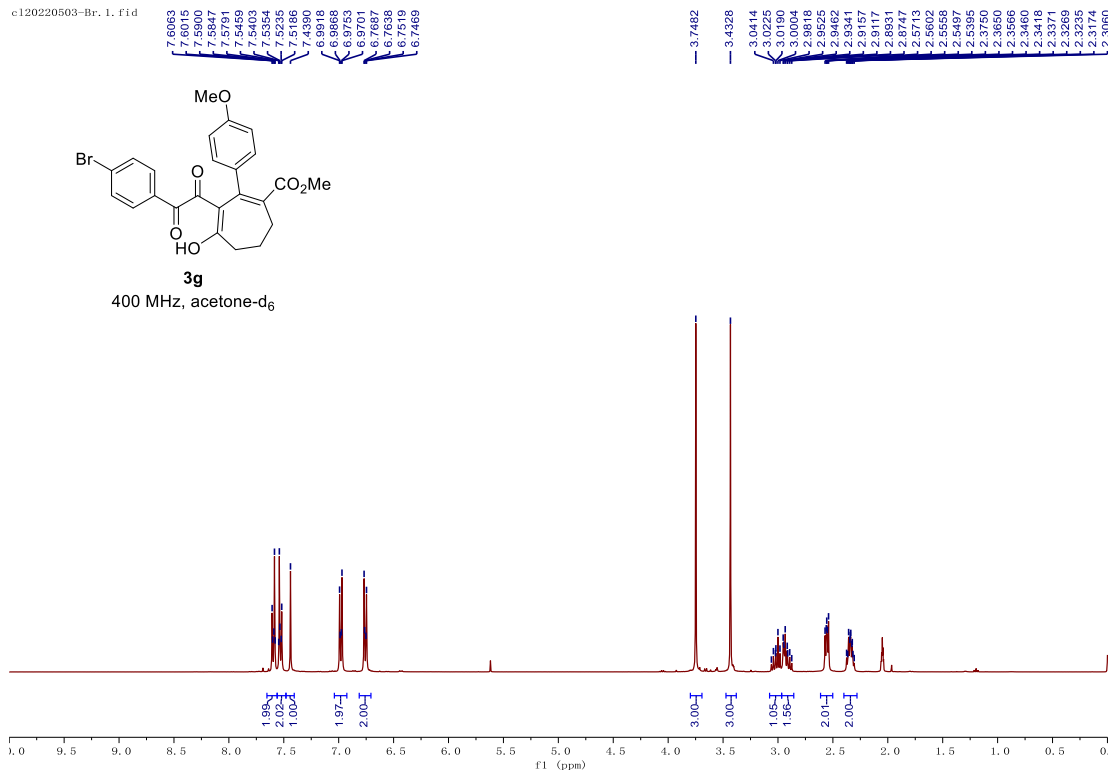


c120220503-Br, 1, f1d

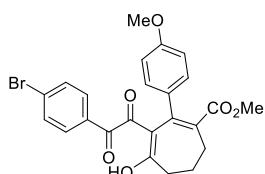


3g

400 MHz, acetone-d₆

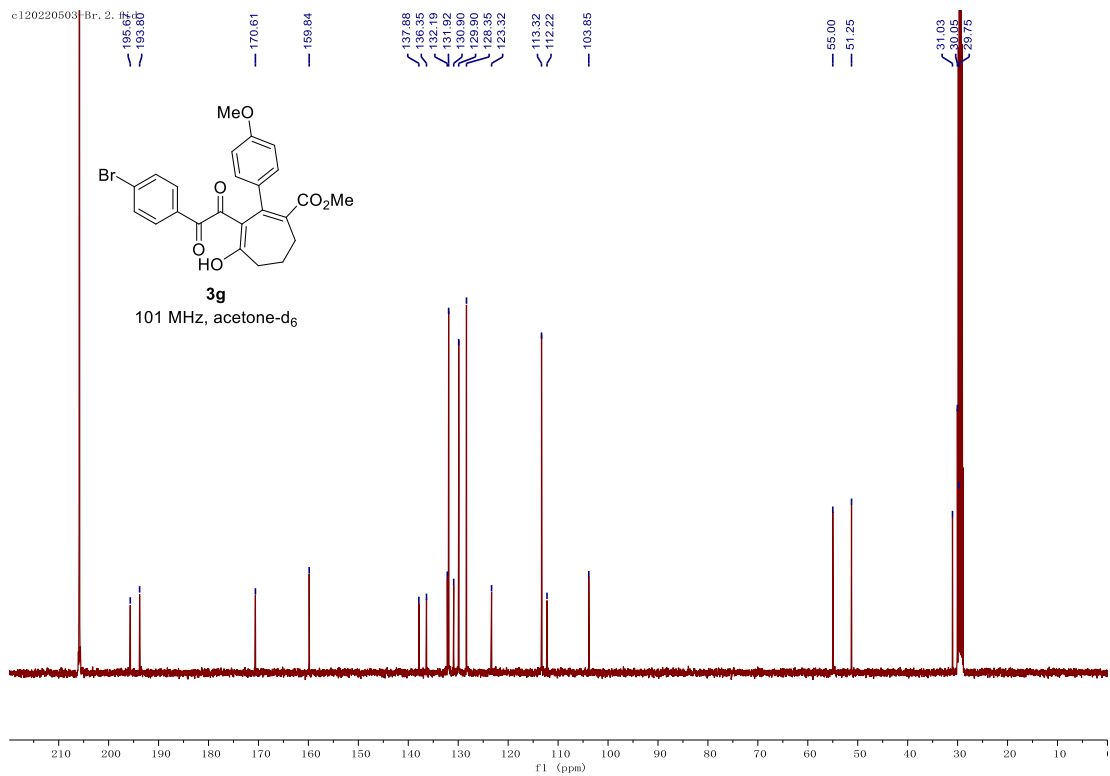


c120220503-Br, 2,

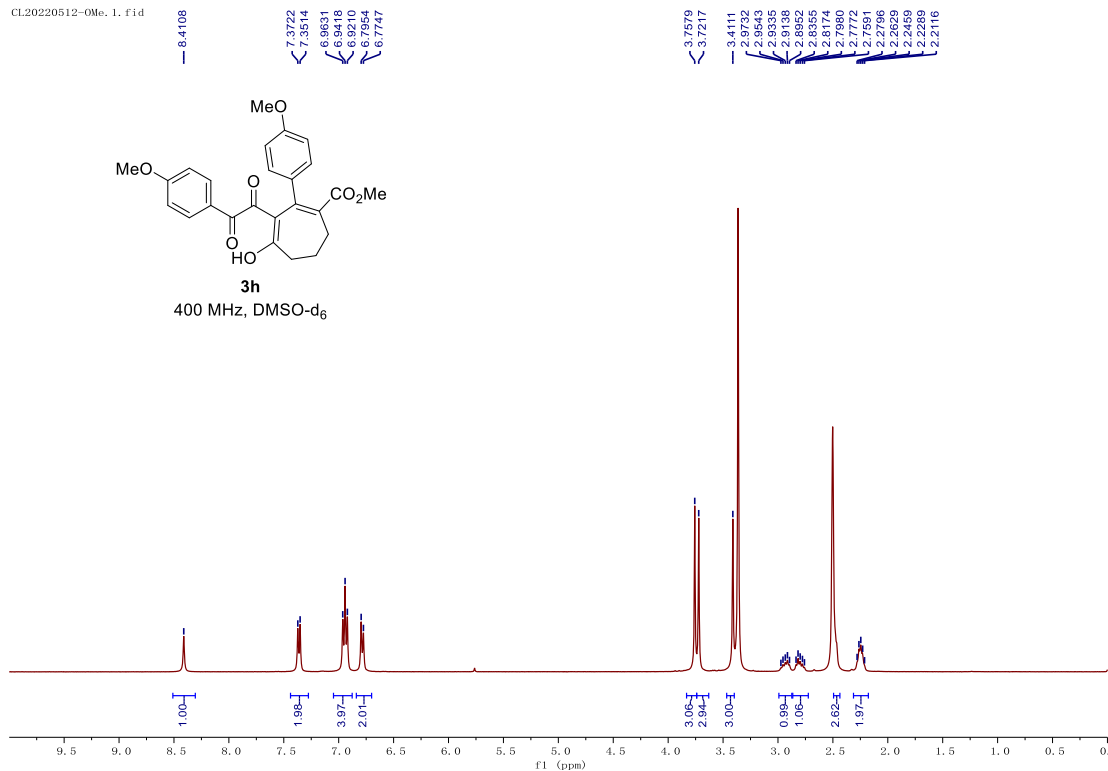


3g

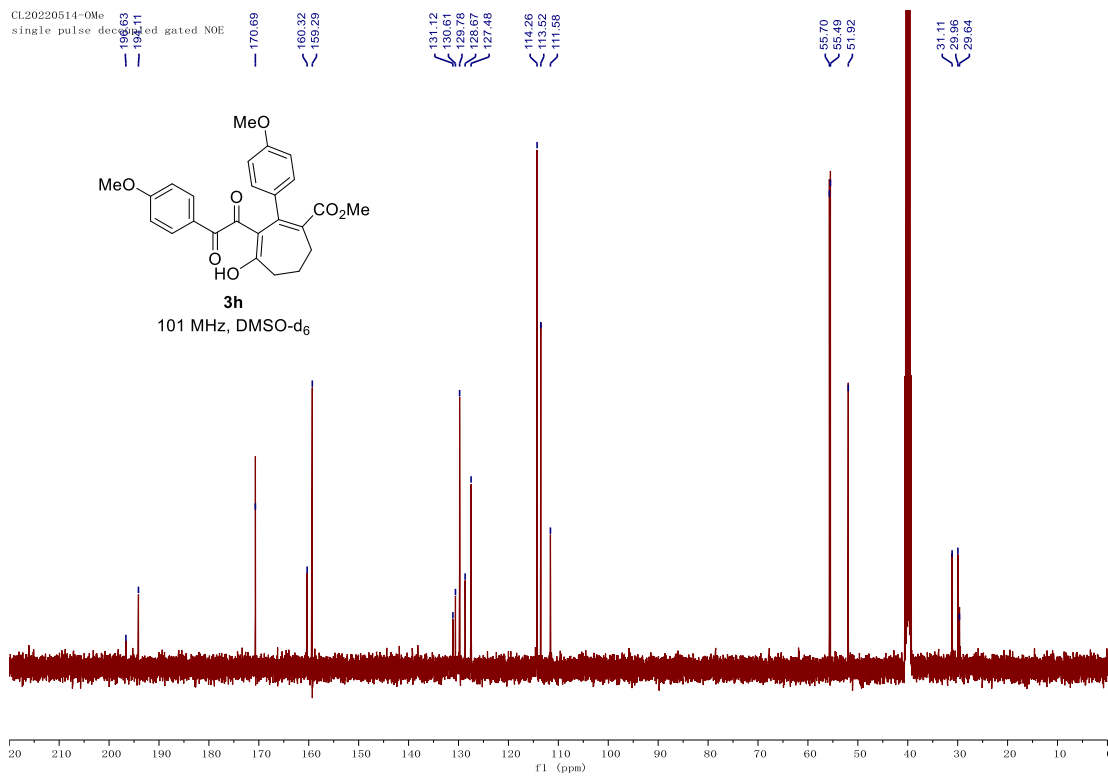
101 MHz, acetone-d₆

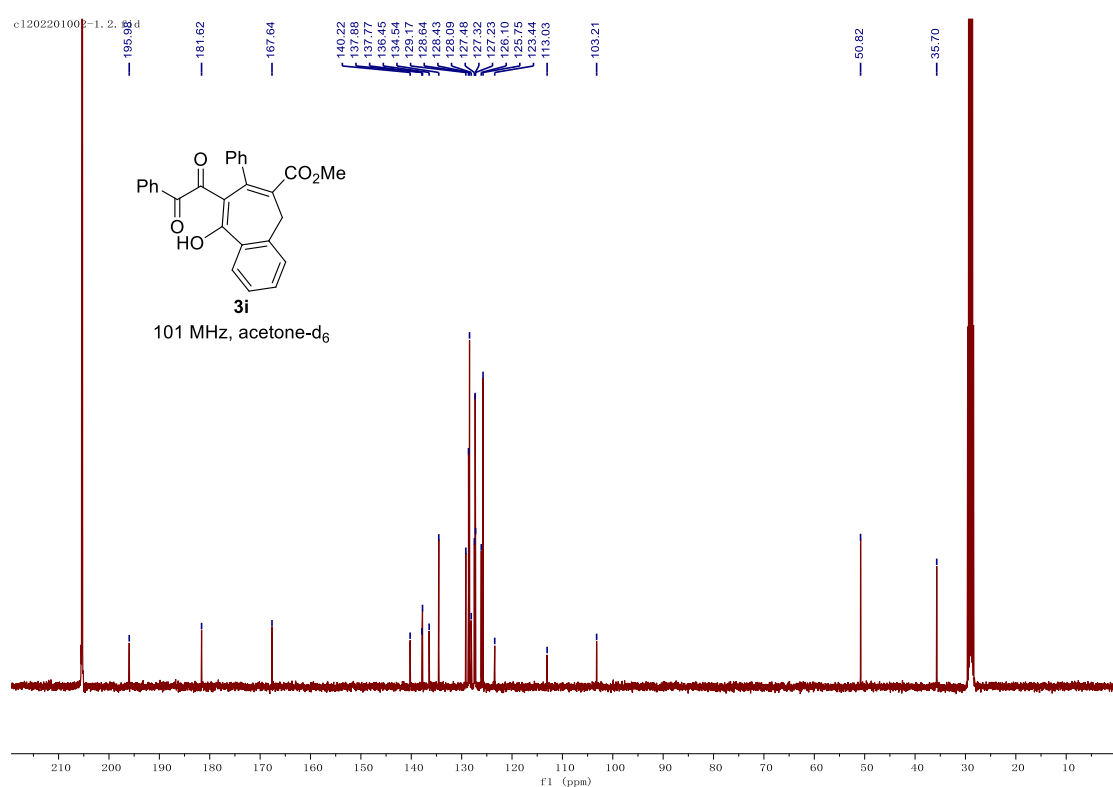
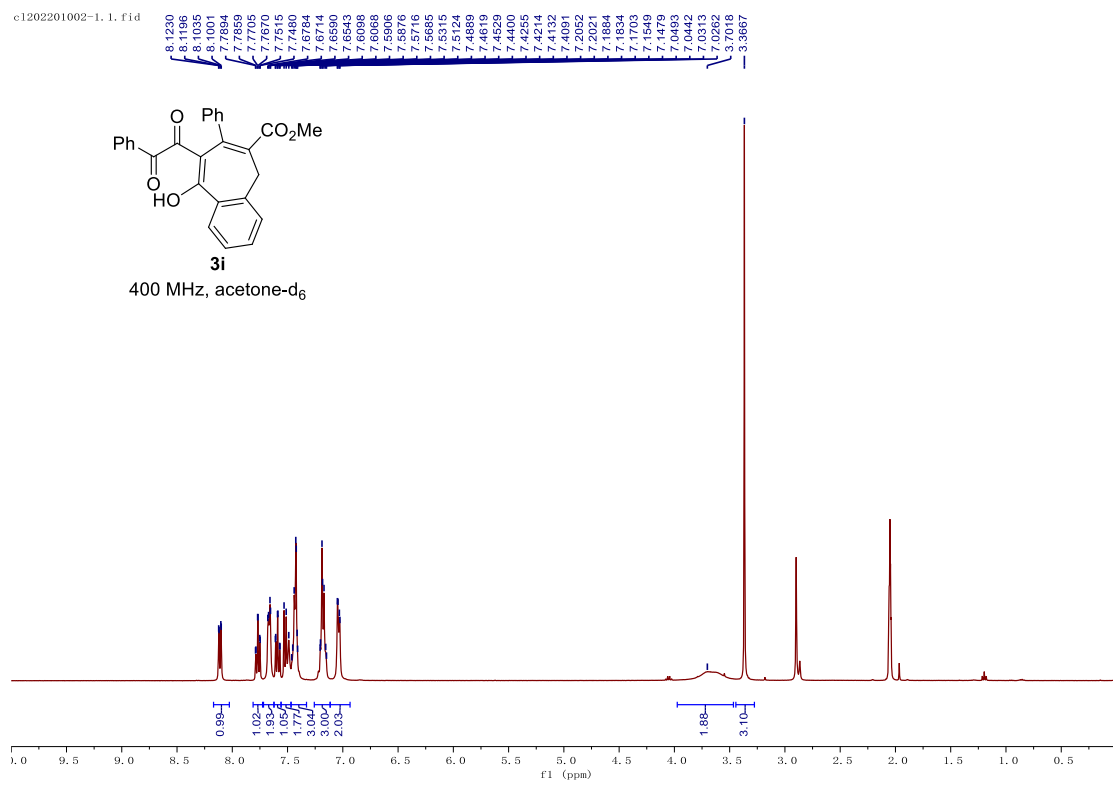


CL20220512-OMe. 1. f1d

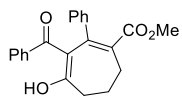


CL20220514-OMe
single pulse decoupled gated NOE

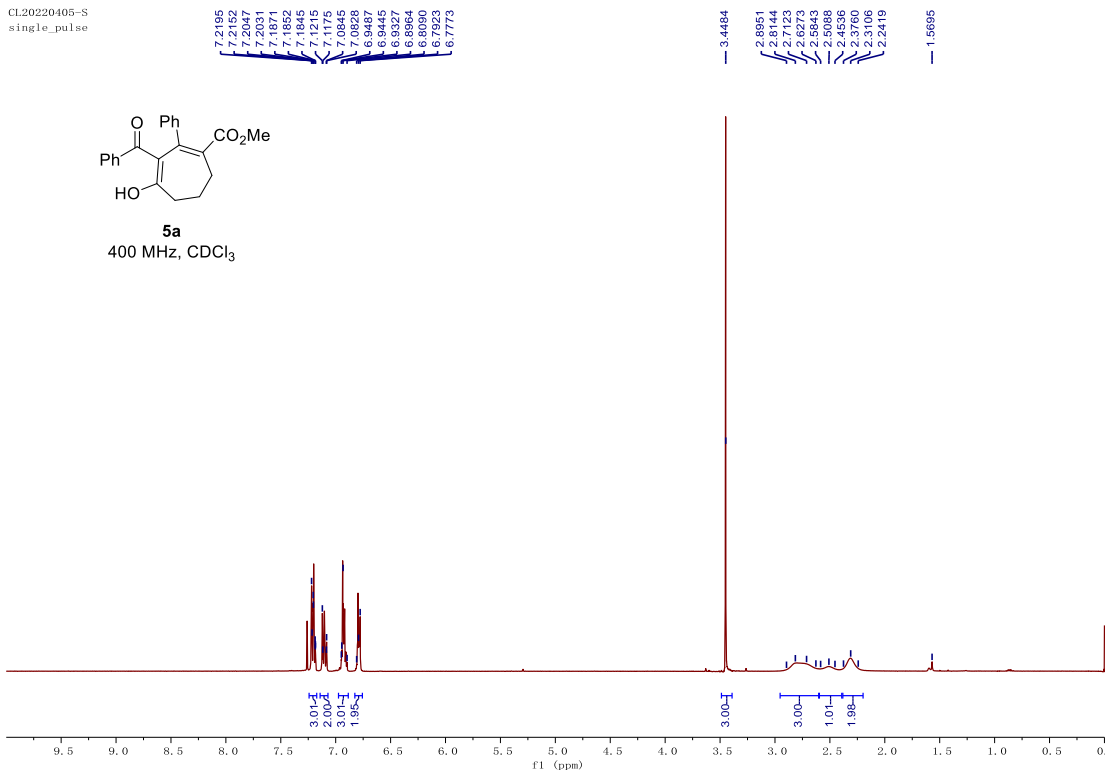




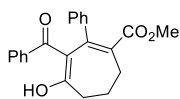
CL20220405-S
single_pulse



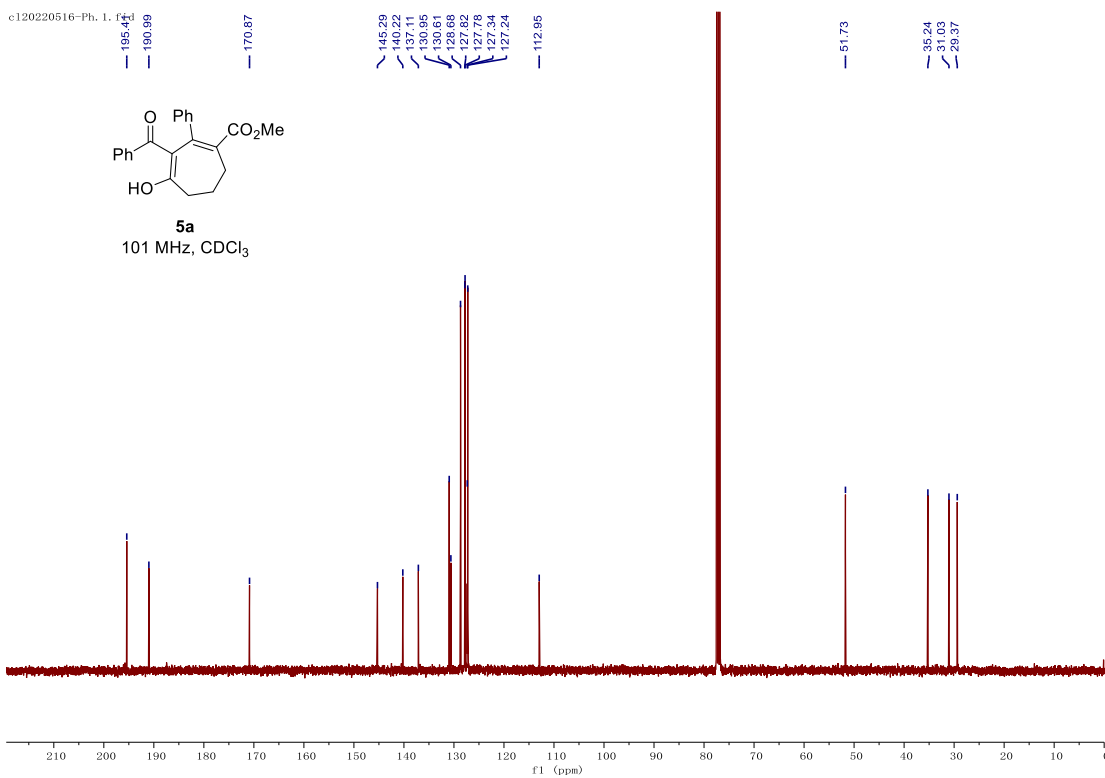
5a
400 MHz, CDCl₃



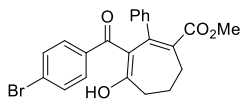
c120220516-Ph. 1.



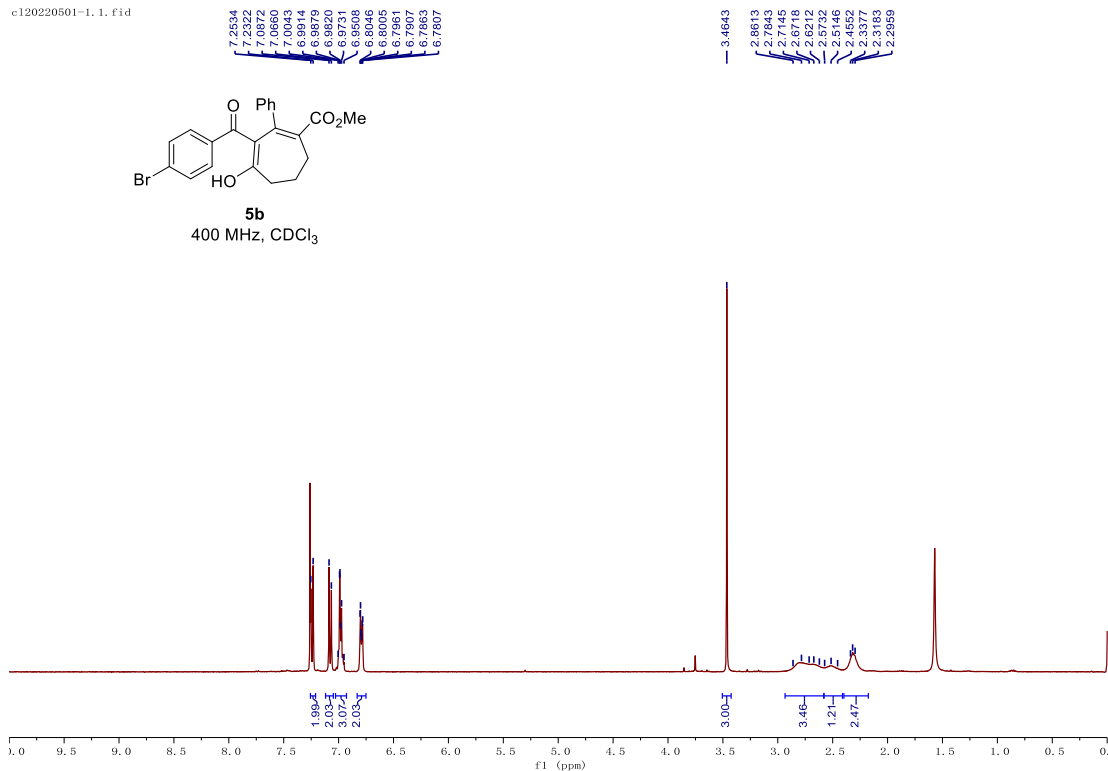
5a
101 MHz, CDCl₃



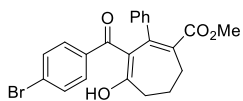
c120220501-1.1.fid



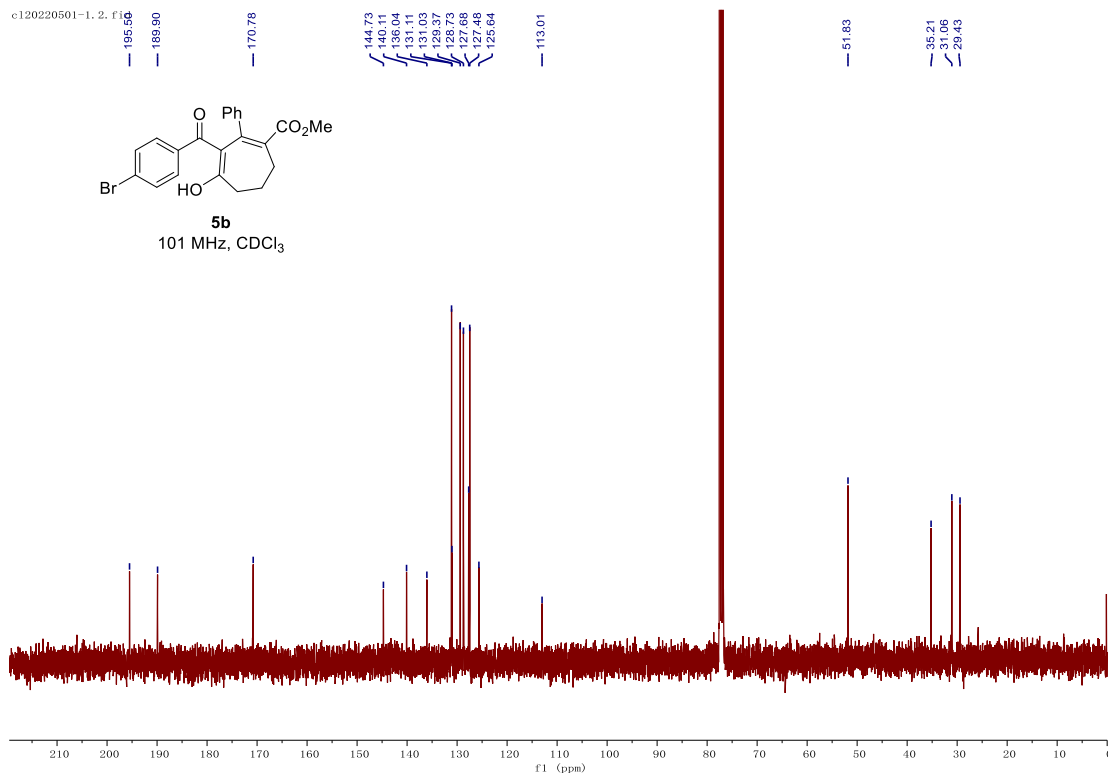
5b
400 MHz, CDCl₃



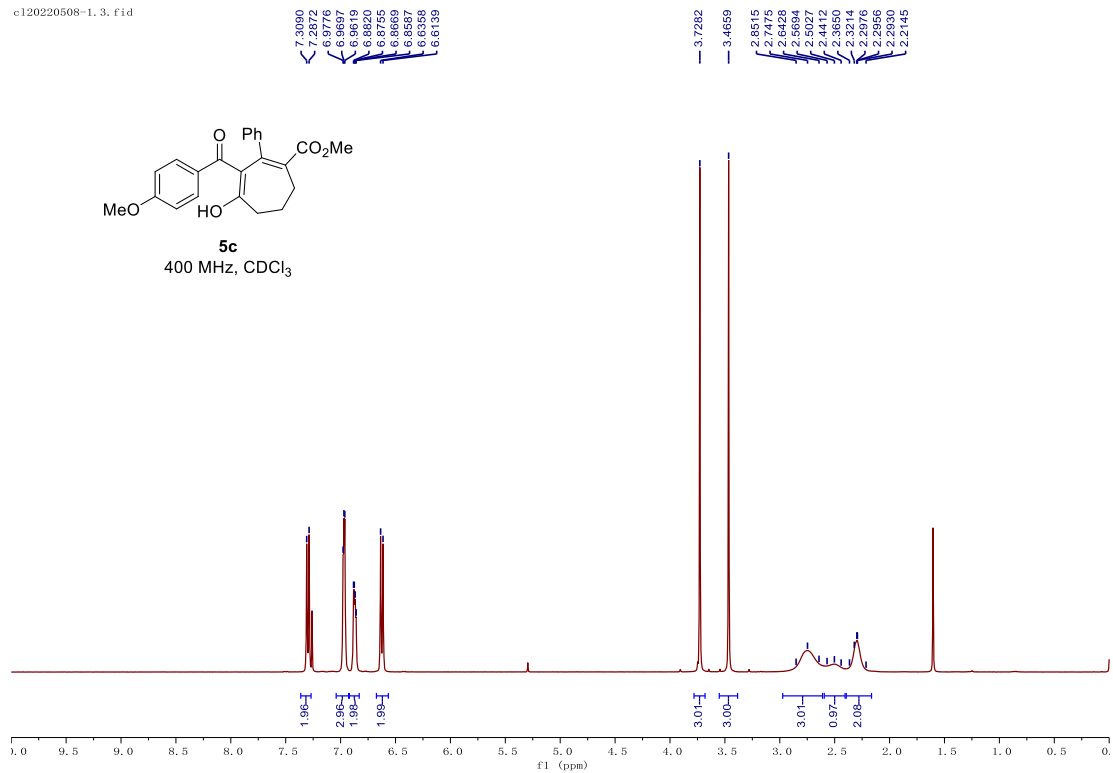
c120220501-1.2.fid



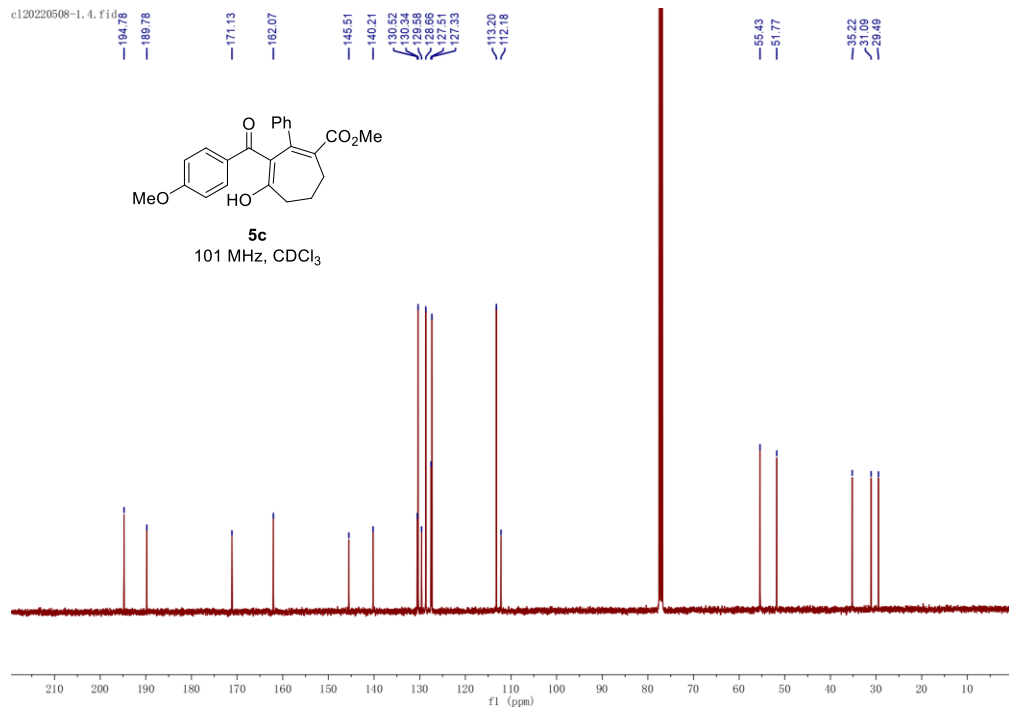
5b
101 MHz, CDCl₃



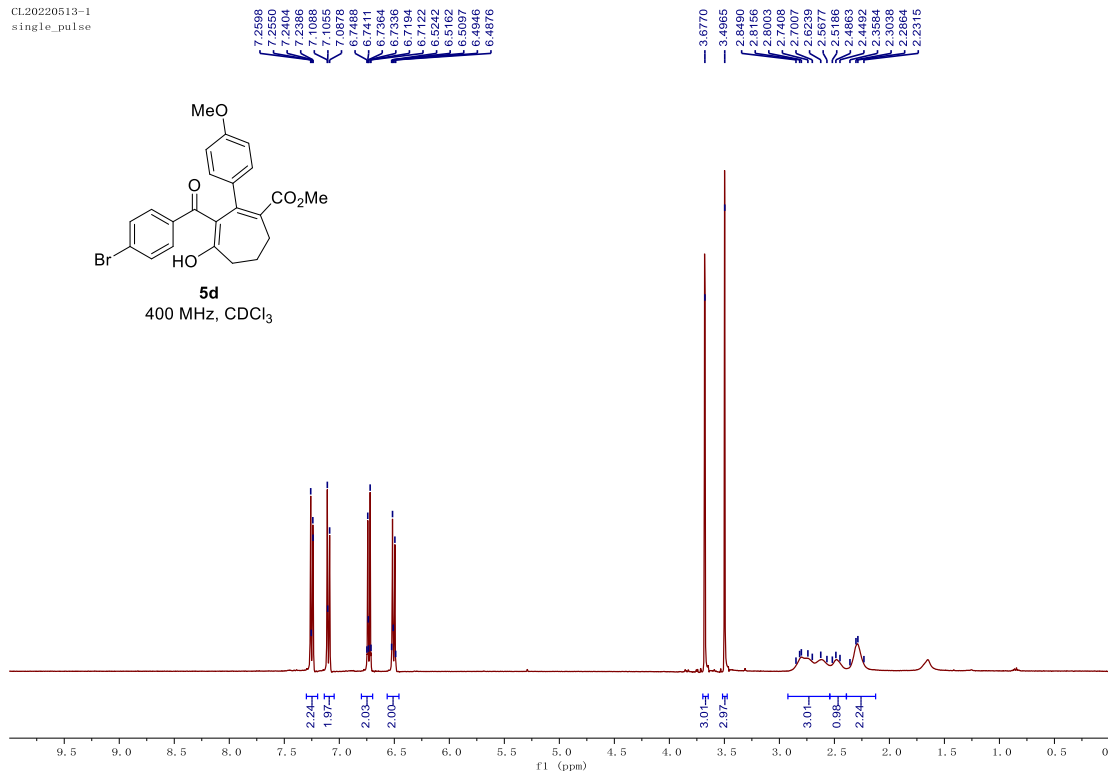
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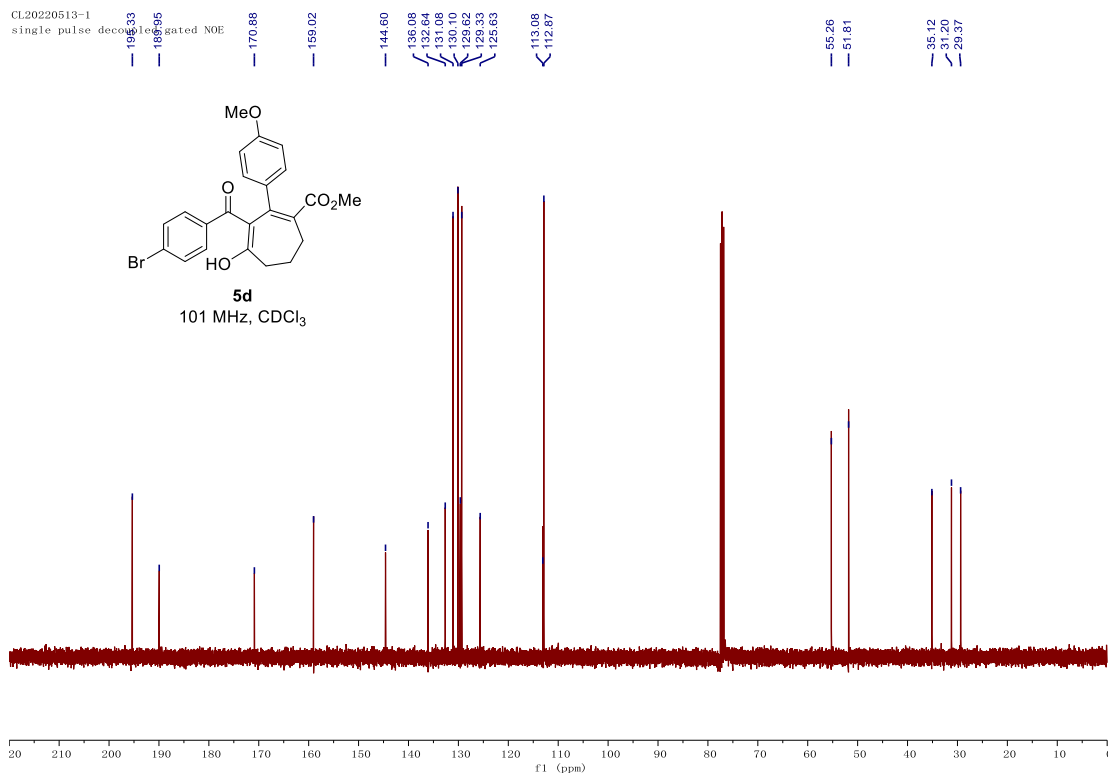
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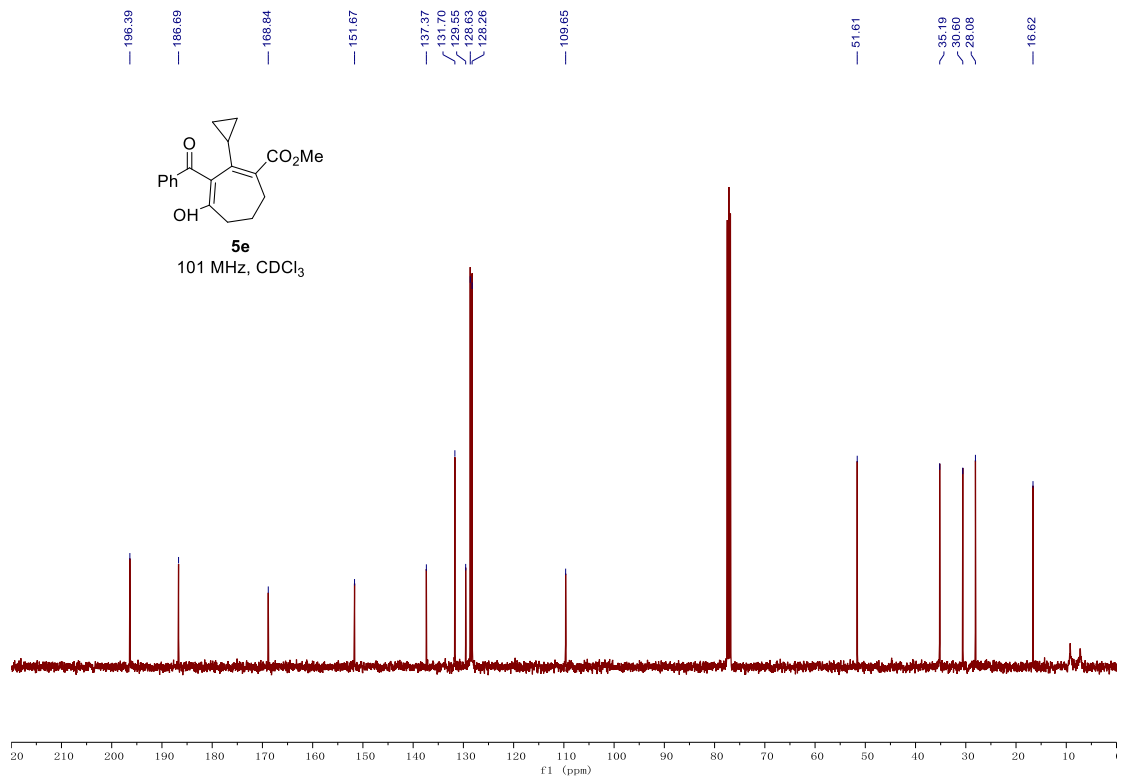
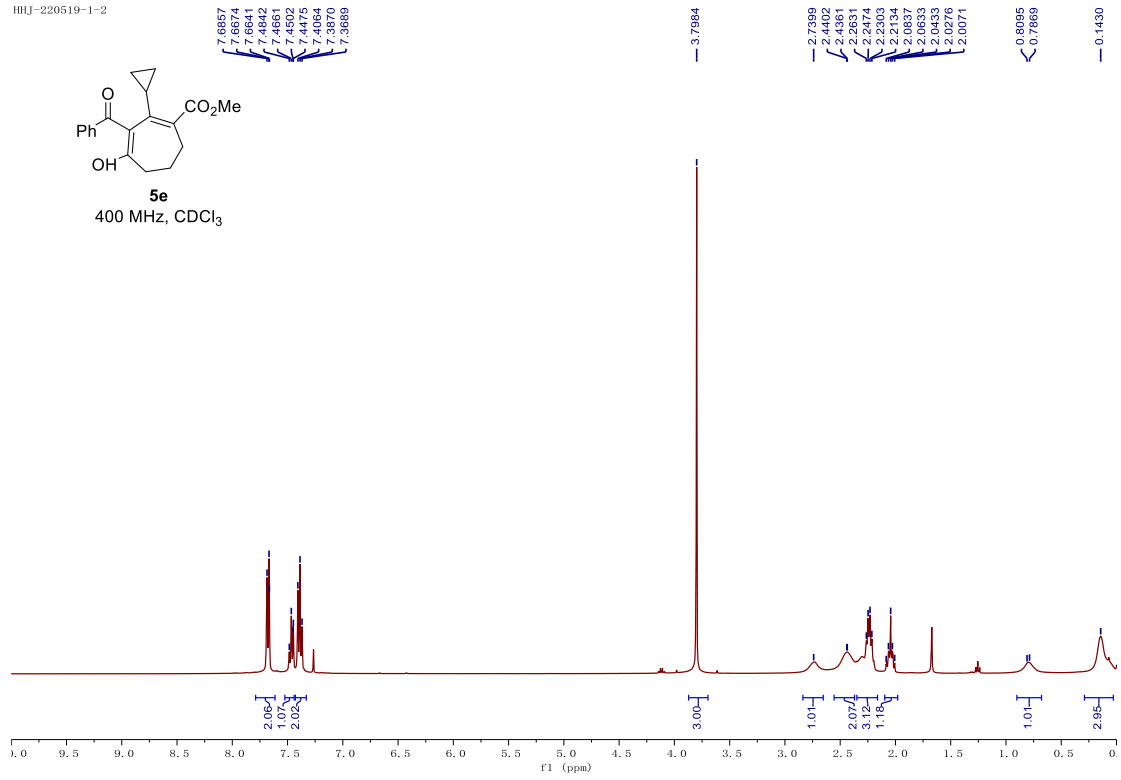
CL20220513-1
single_pulse



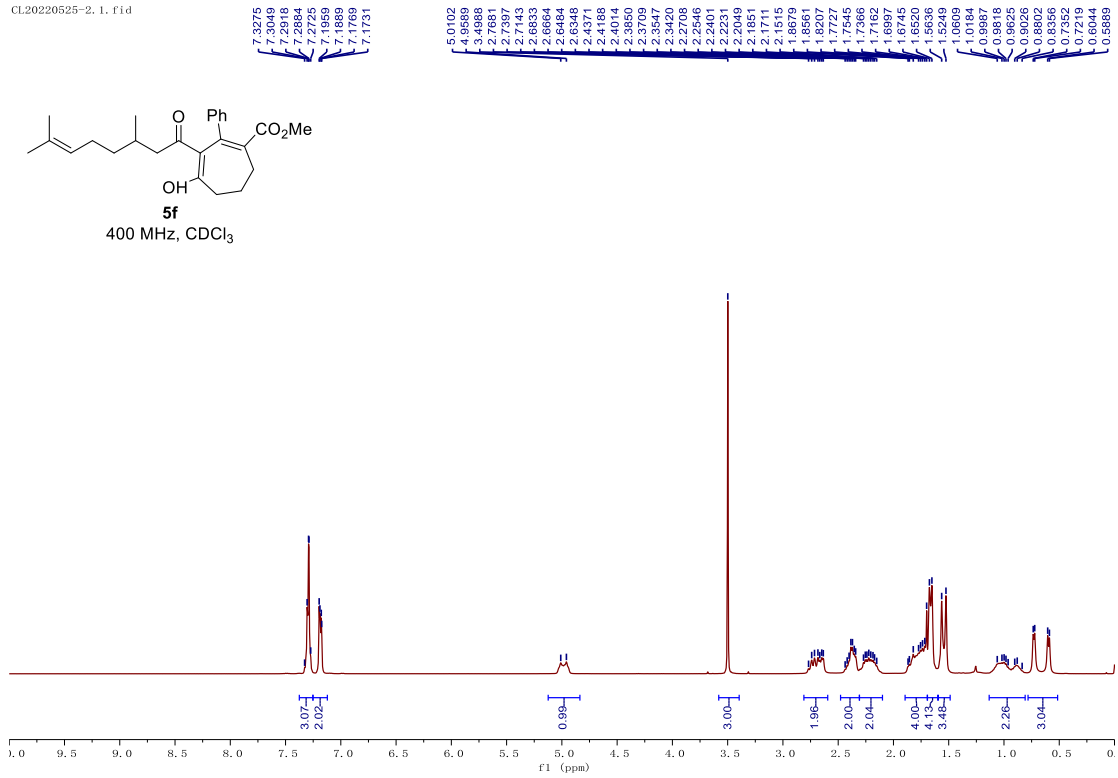
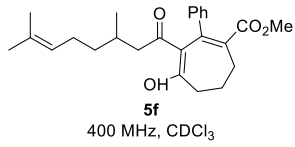
CL20220513-1
single_pulse decoupled



HLJ-220519-1-2



CL20220525-2. 1. f1.d



CL20220525-2

single pulse

gated NOE

136.46

132.26

132.00

131.98

171.05

170.99

143.15

143.00

140.70

131.96

131.91

131.59

131.49

128.43

128.25

124.37

124.33

113.35

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44.68

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36.75

35.09

34.94

30.98

30.32

30.06

29.06

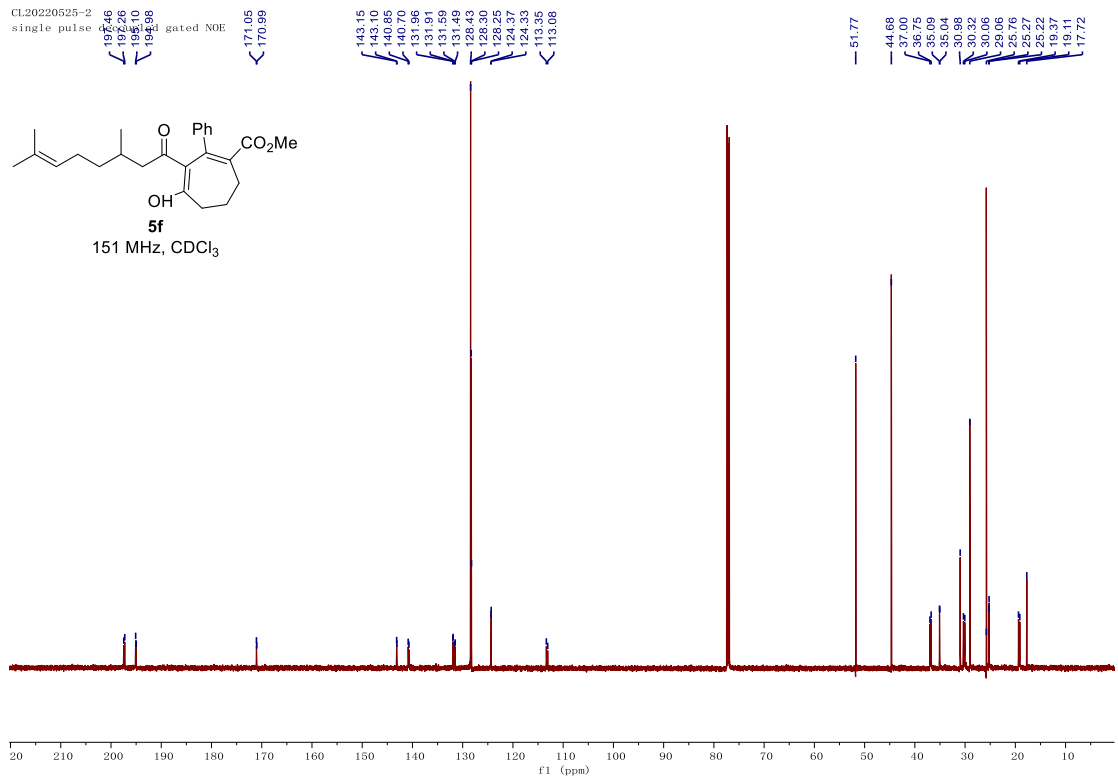
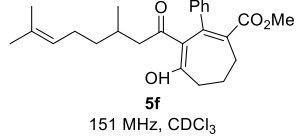
25.76

25.27

19.57

19.11

17.72



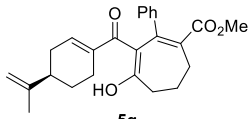
CL220607-1
single_pulse

7.2159
7.2322
7.2148
7.2028
7.0321
7.0264
7.0288
7.0086

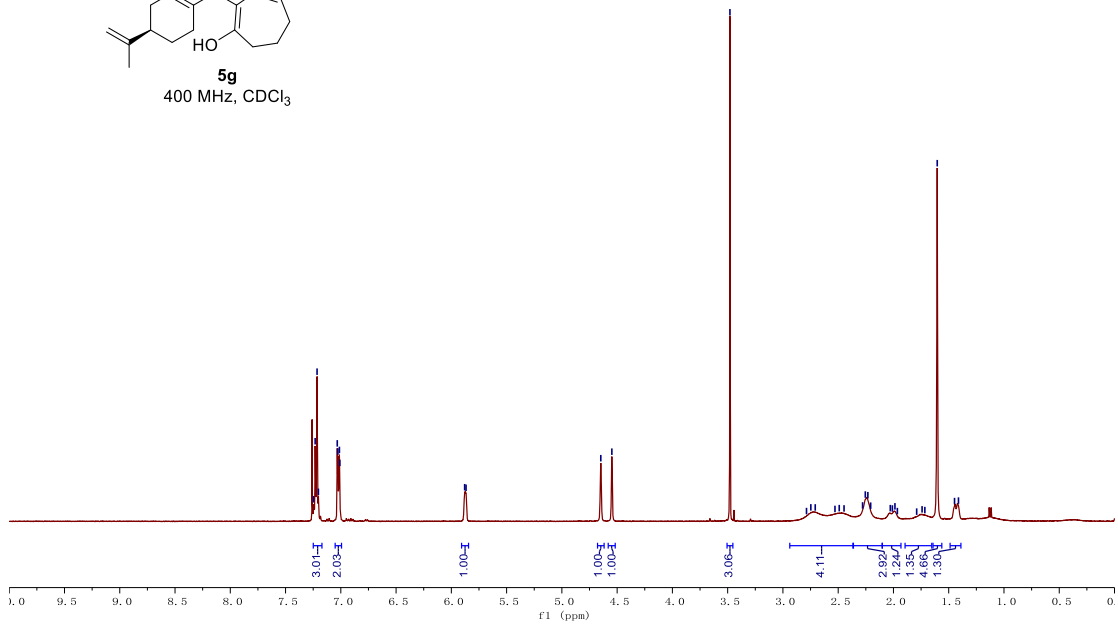
5.8795
5.8670

4.6478
4.5478

3.4794
2.7886
2.7474
2.7076
2.5291
2.4905
2.4470
2.4246
2.2315
2.2061
2.0286
2.0097
1.9885
1.7898
1.7409
1.7159
1.6039
1.4474
1.4118



5g
400 MHz, CDCl₃



CL20220607-1
single pulse decoupled gated NOE

163.83

171.16

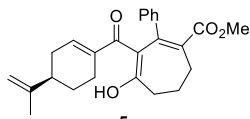
149.17
149.13
145.95
141.71
135.20
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128.70
127.63

109.05

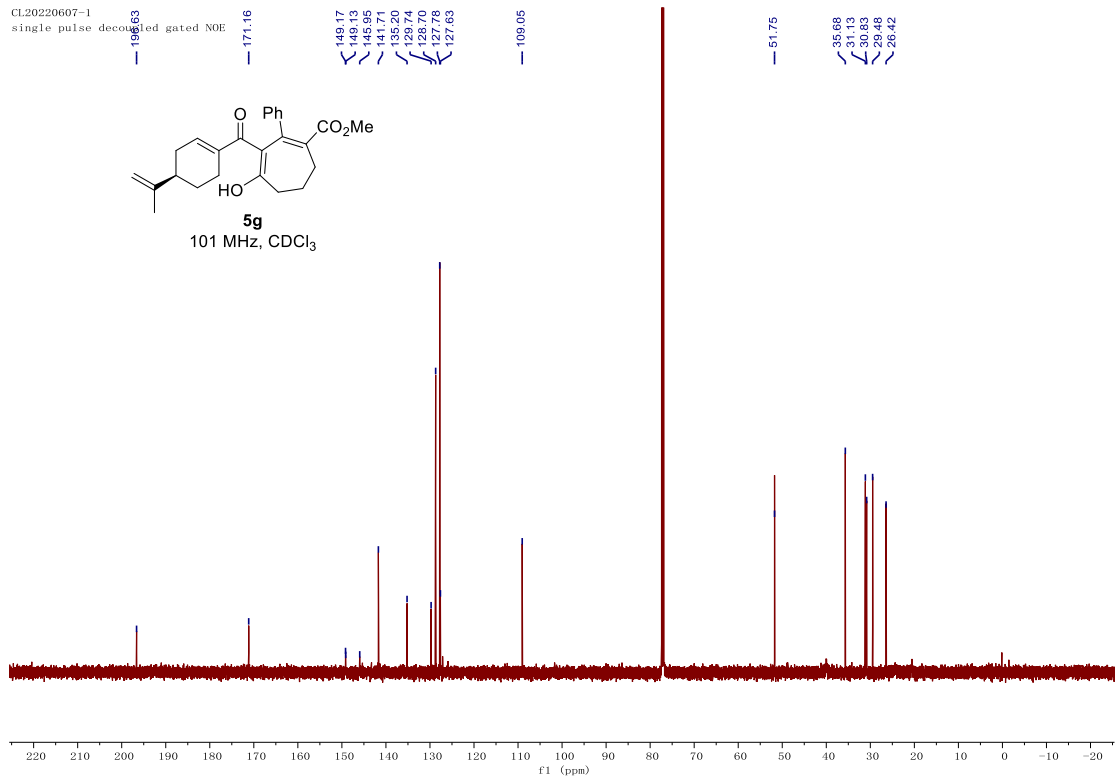
51.75

35.68
31.13
29.48

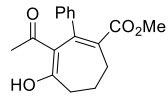
26.42



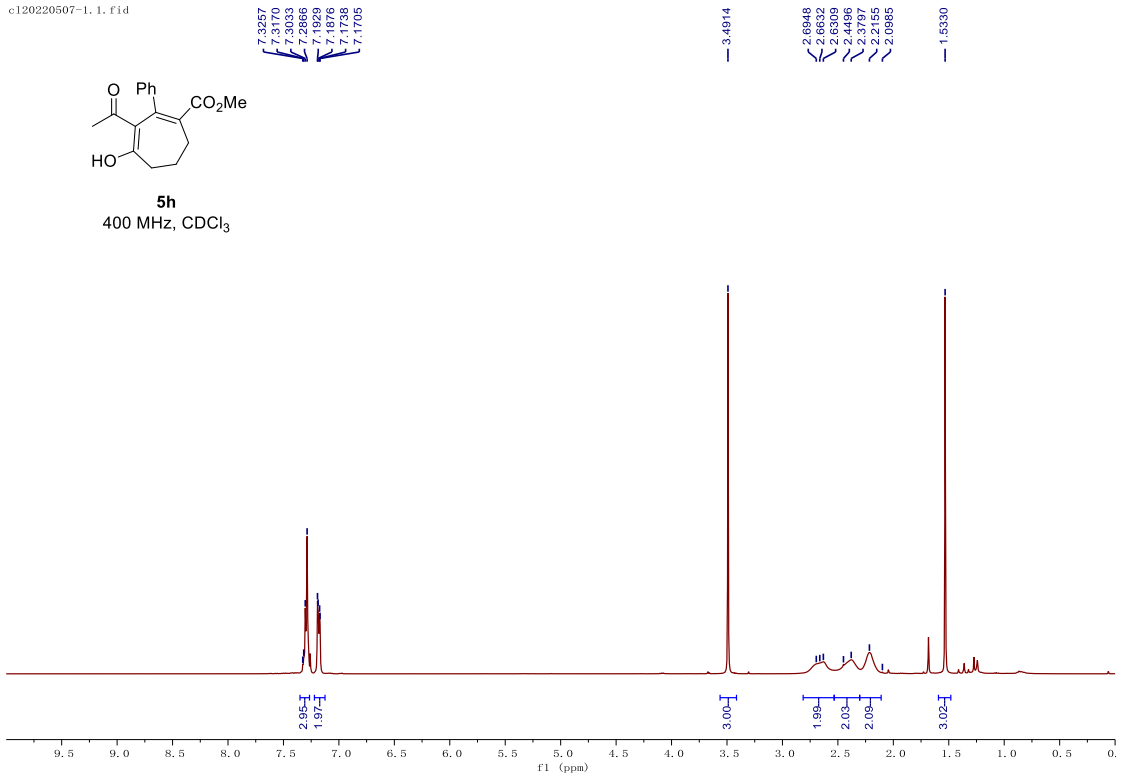
5g
101 MHz, CDCl₃



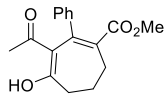
c120220507-1.1.fid



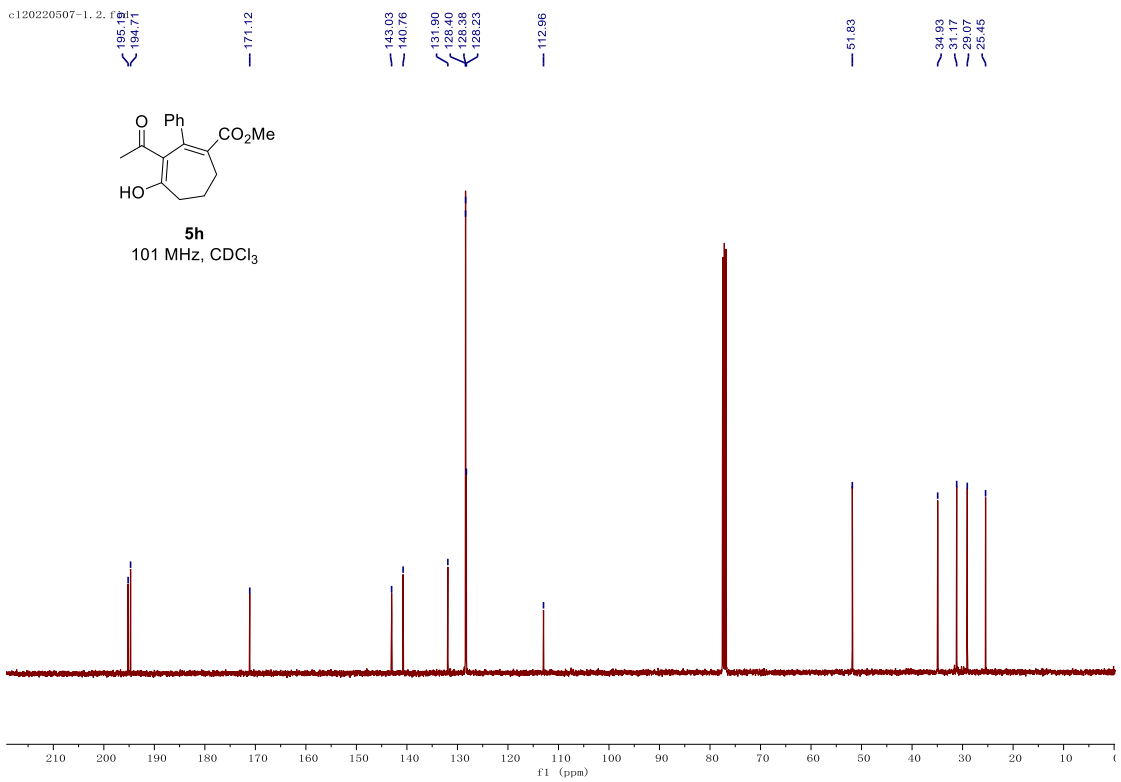
5h
400 MHz, CDCl₃



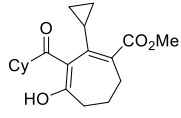
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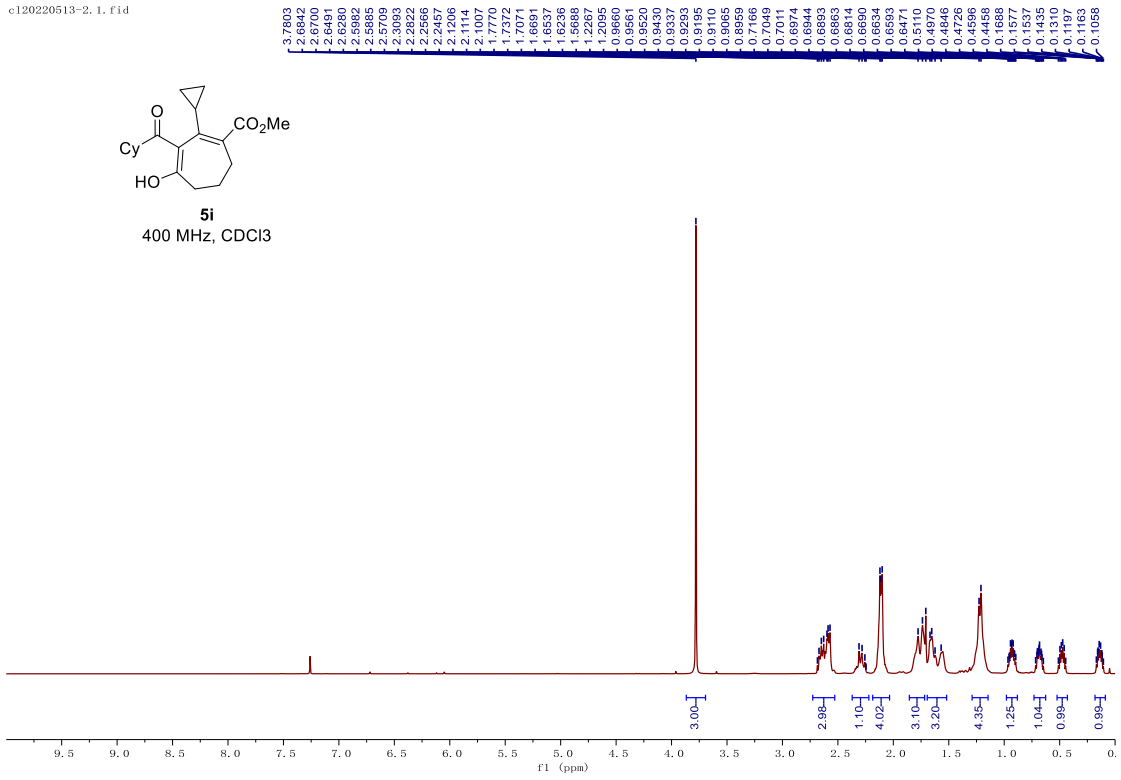
5h
101 MHz, CDCl₃



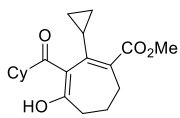
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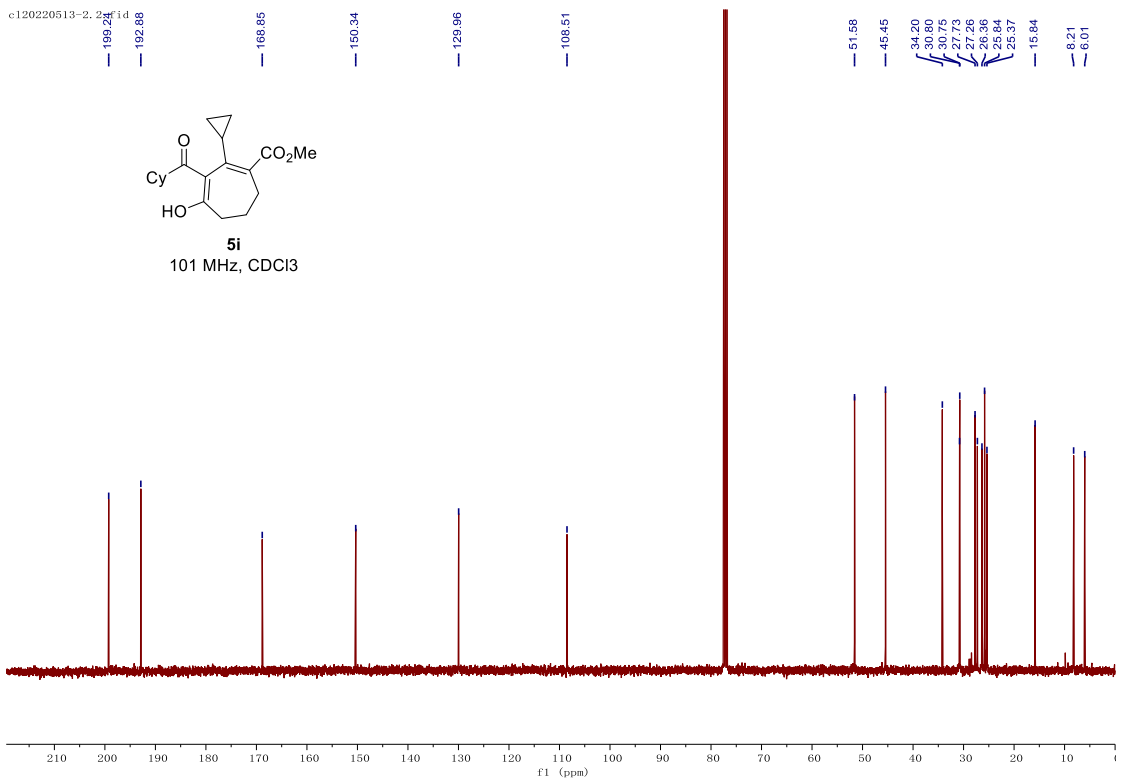
5i
400 MHz, CDCl₃

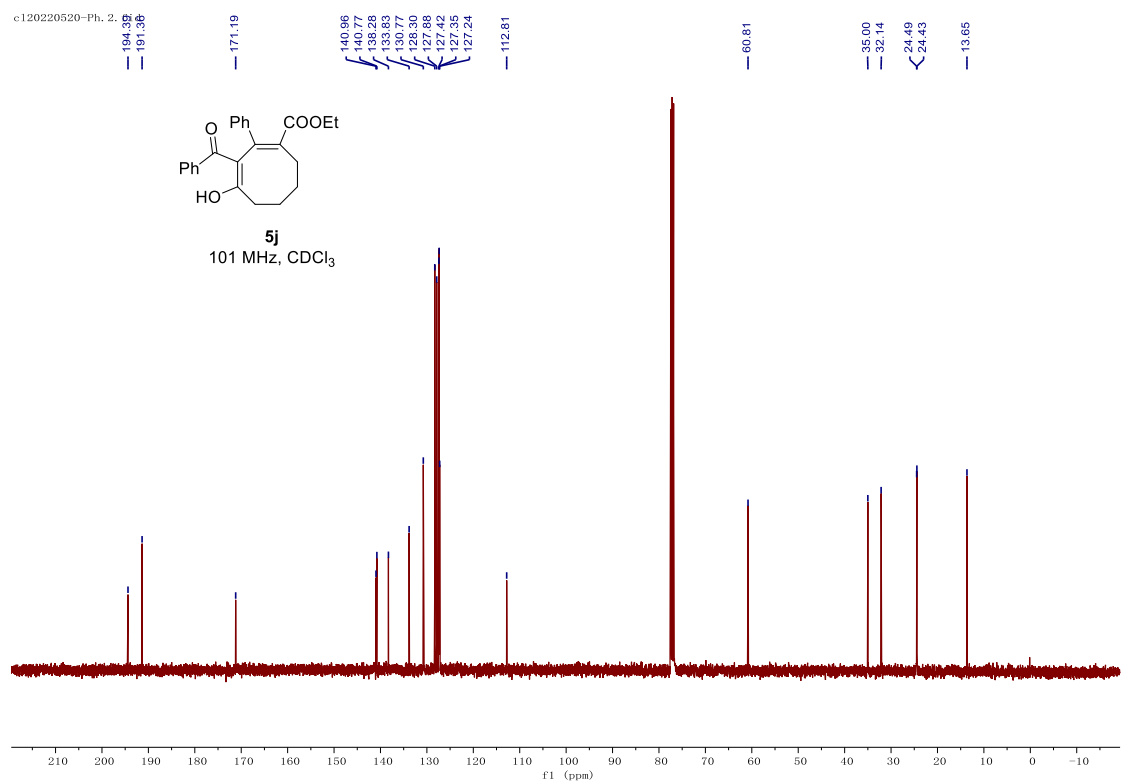
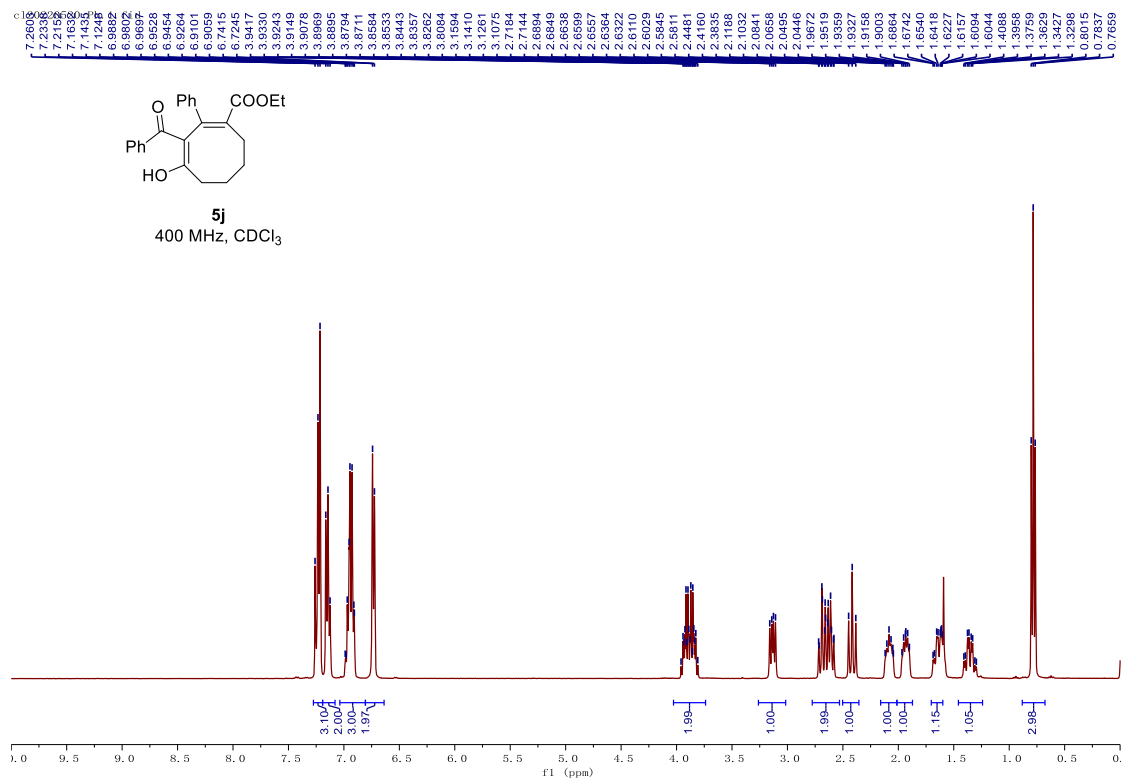


c120220513-2.2.fid



5i
101 MHz, CDCl₃

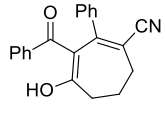




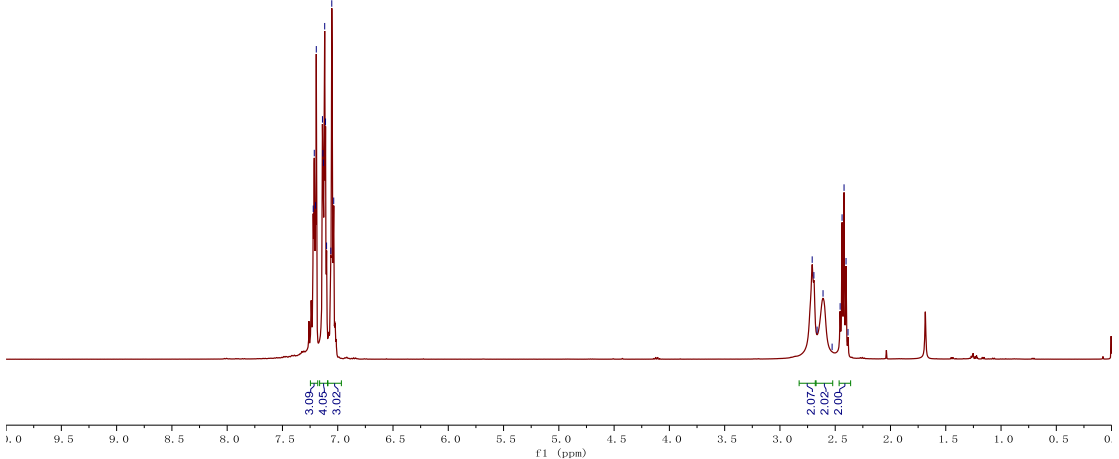
HHJ-220927-1-3H

7.2216
7.2121
7.2007
7.1940
7.1383
7.1341
7.1298
7.1178
7.1102
7.1008
7.0623
7.0538
7.0361

2.7083
2.6928
2.6840
2.6102
2.5281
2.4555
2.4380
2.4272
2.4022
2.3842



5k
400 MHz, CDCl₃



HHJ220927-1-3

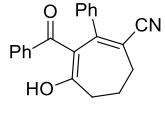
195.36
190.98

155.79

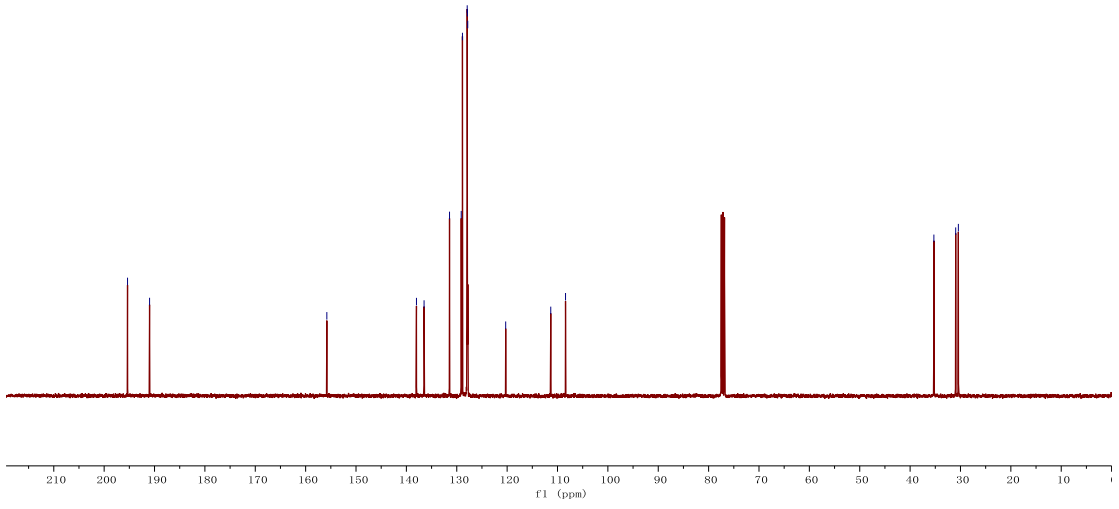
138.00
136.49
131.44
128.87
127.93
127.89
127.82
120.29

111.34
108.41

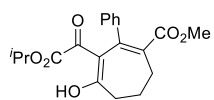
35.28
30.95
30.42



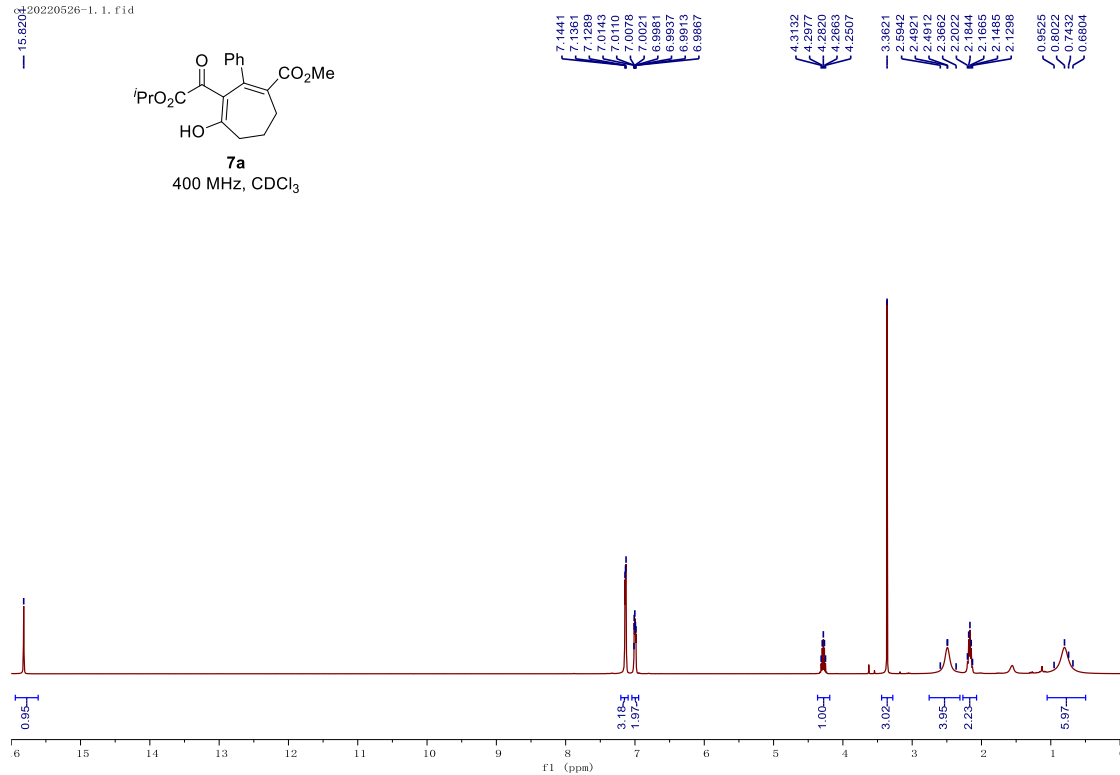
5k
101 MHz, CDCl₃



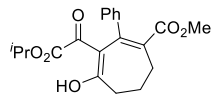
20220526-1.1.fid



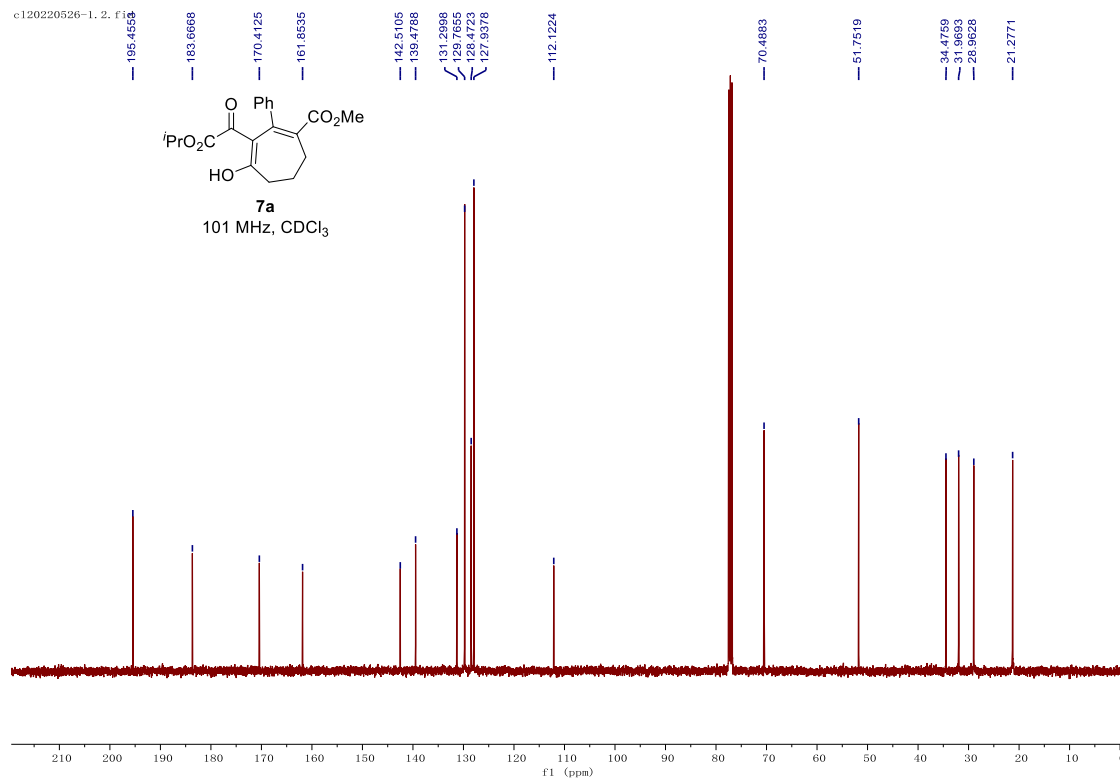
7a
400 MHz, CDCl₃



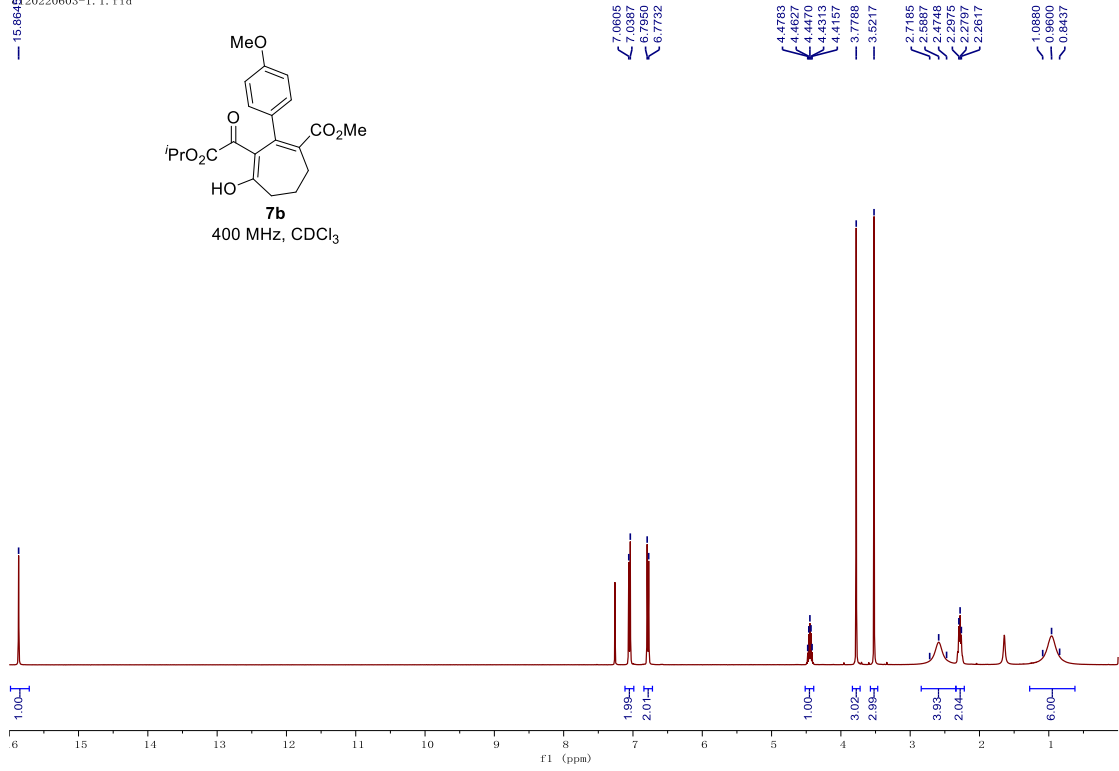
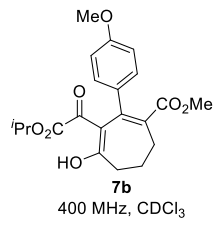
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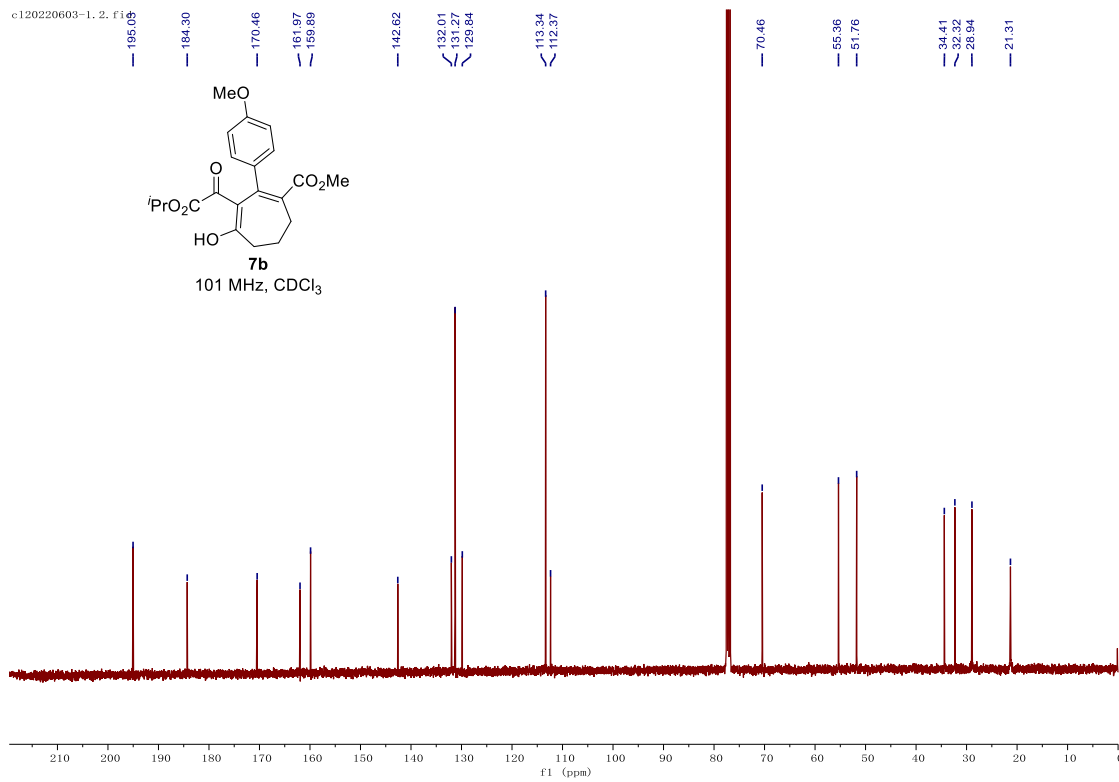
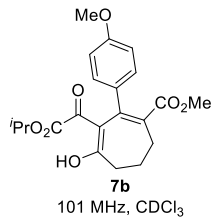
7a
101 MHz, CDCl₃

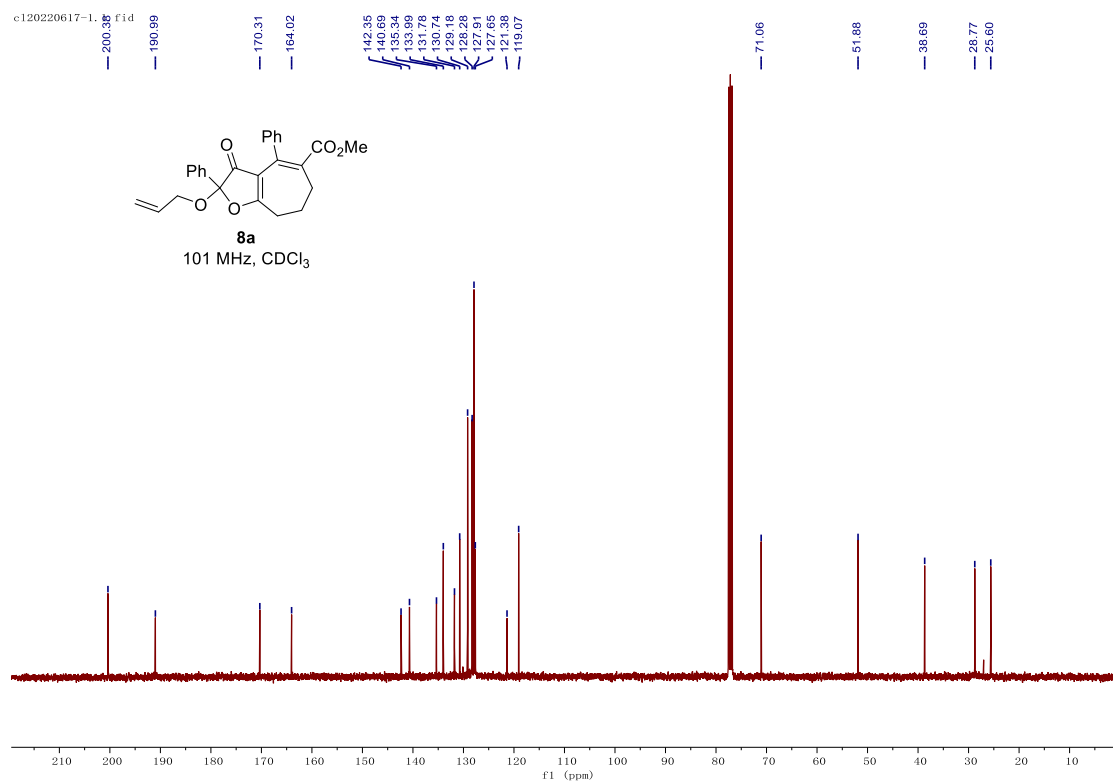
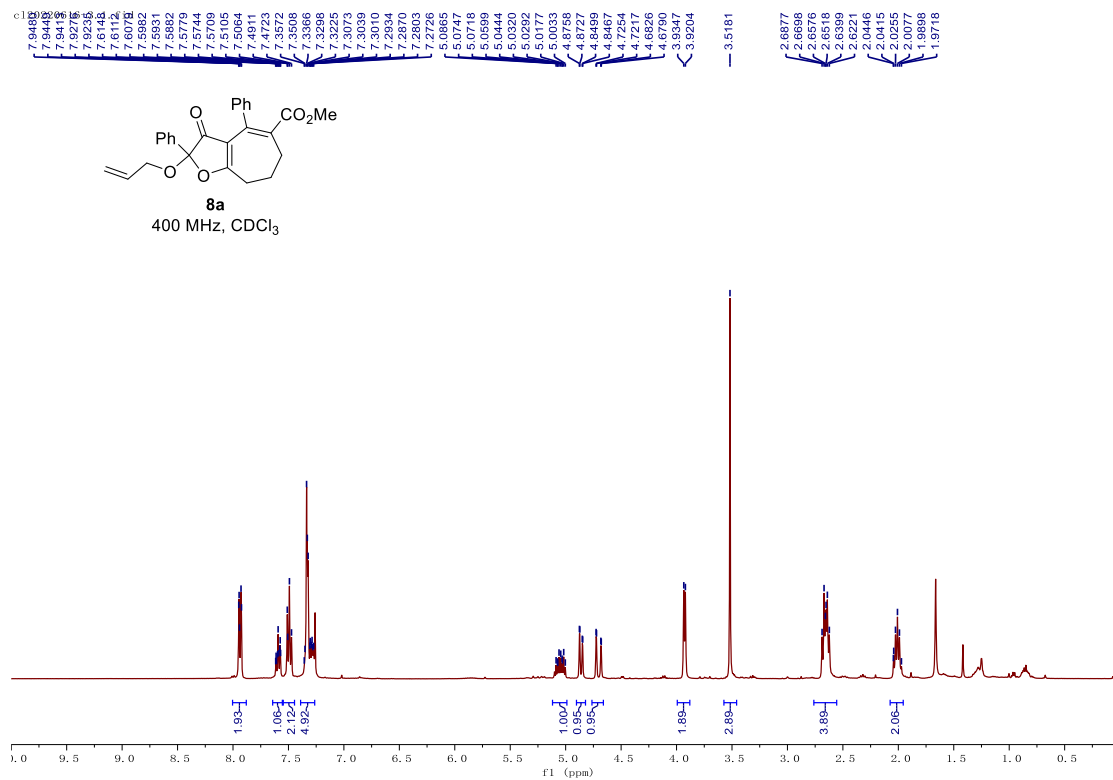


20220603-1. 1. f1.d

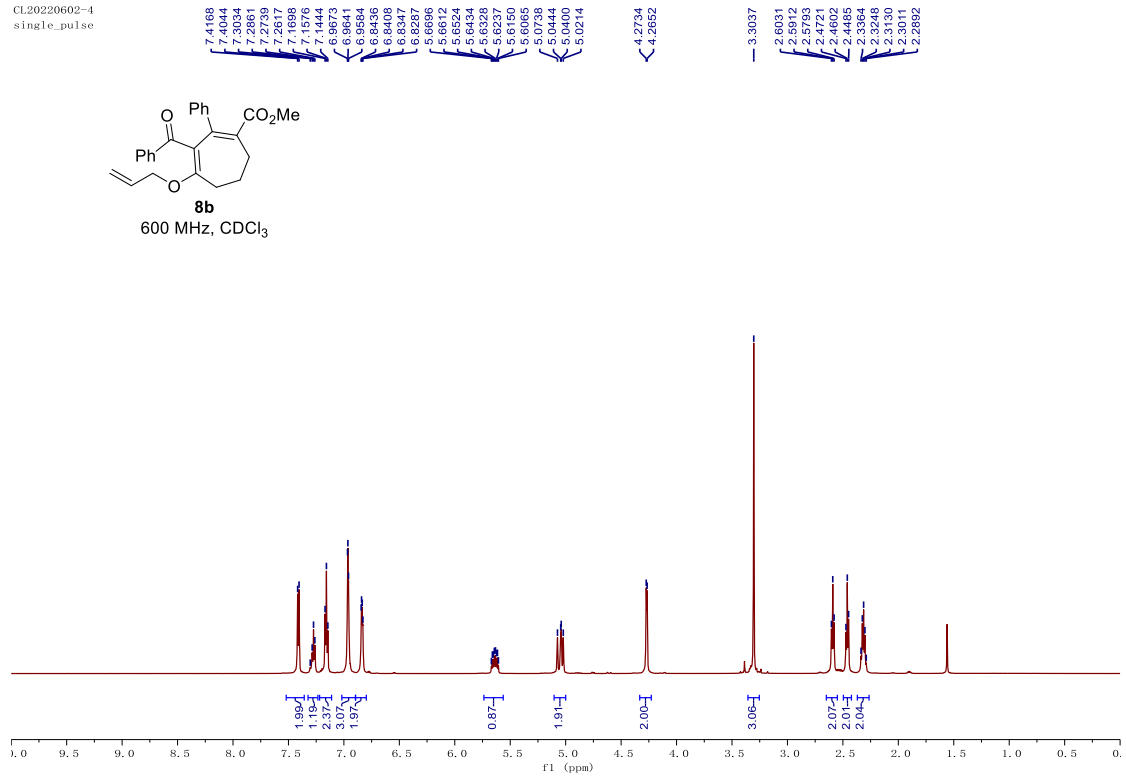
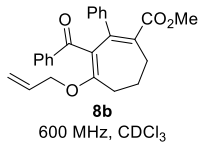


c120220603-1. 2. f1.d

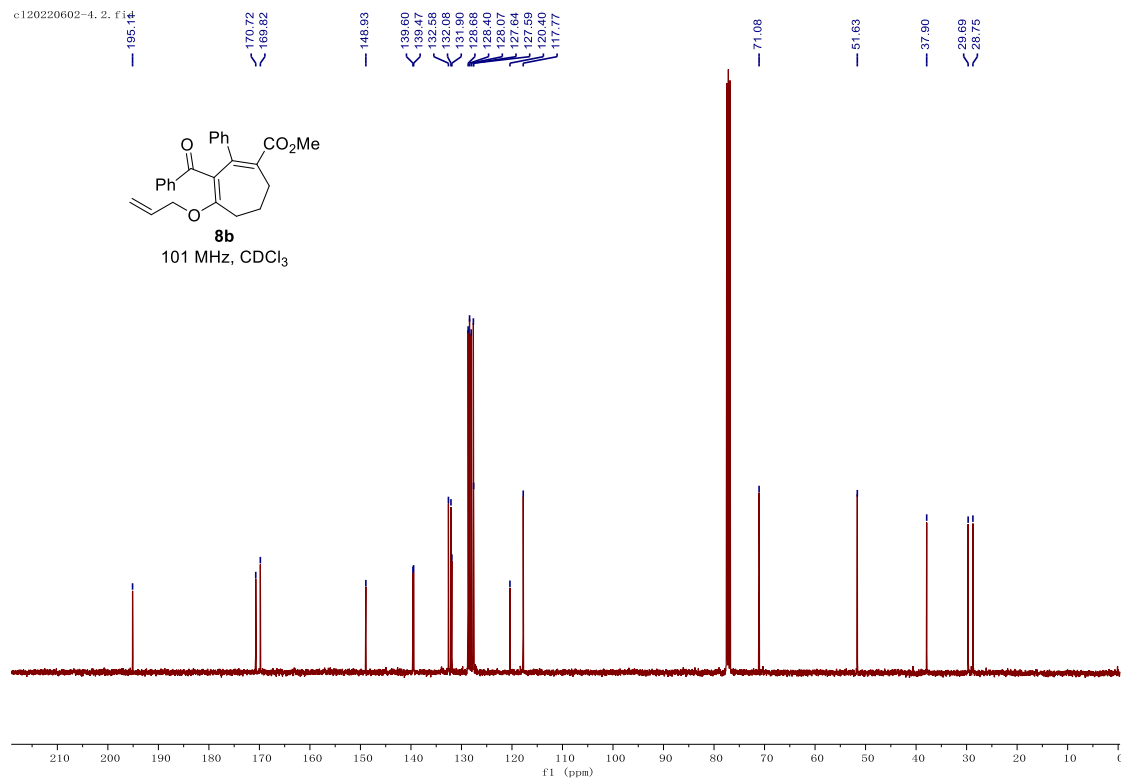
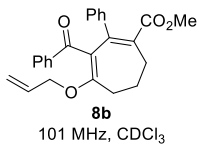




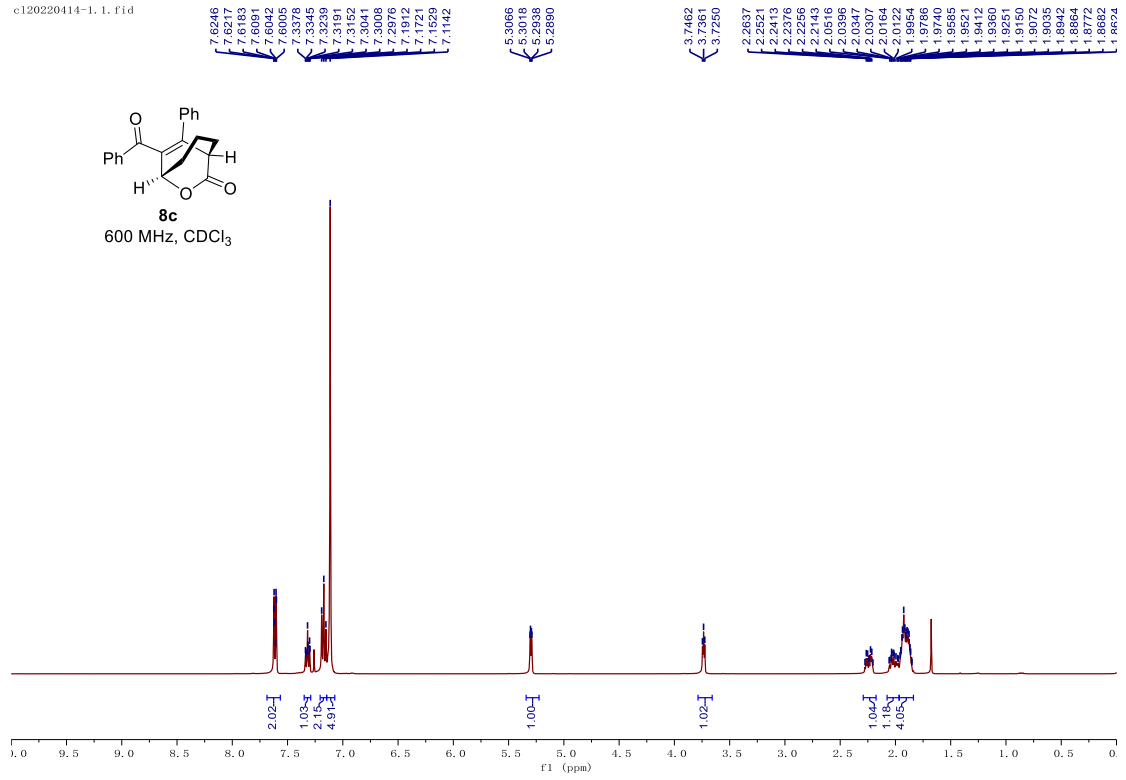
CL20220602-4
single_pulse



c120220602-4.2.f1

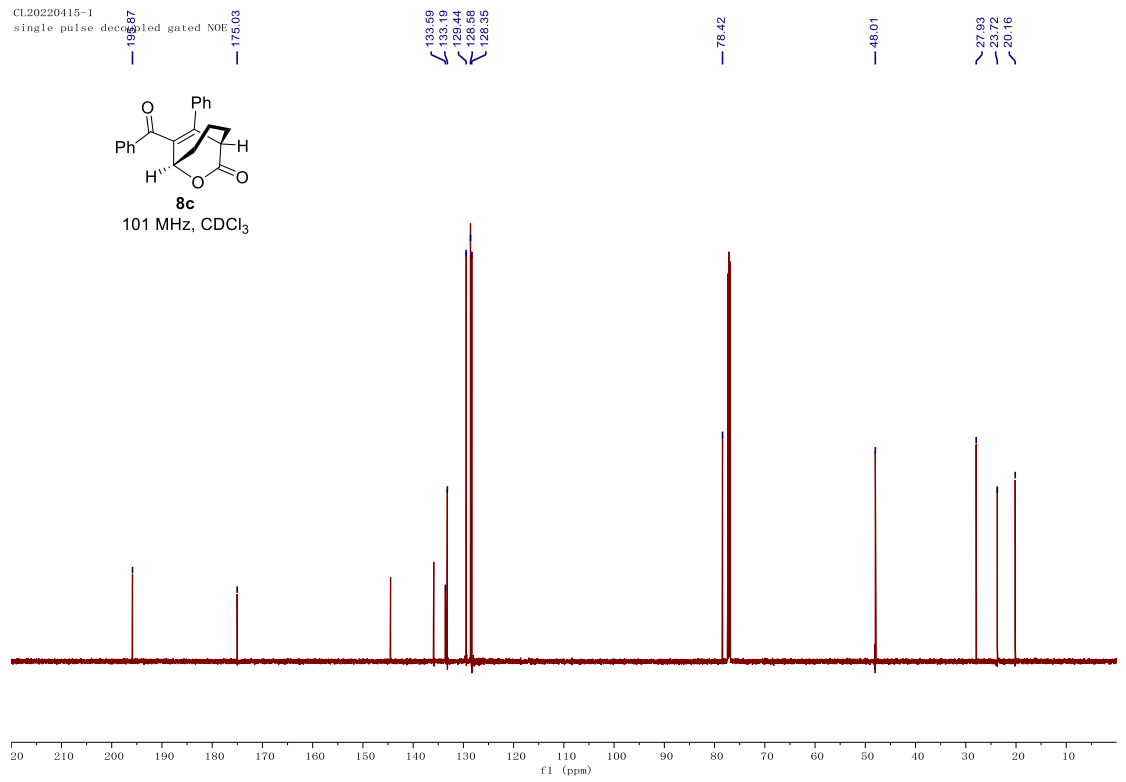


c120220414-1. 1. f1d

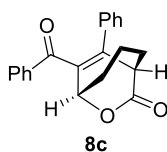


Cl20220415-1

single pulse decoupled gated NOE

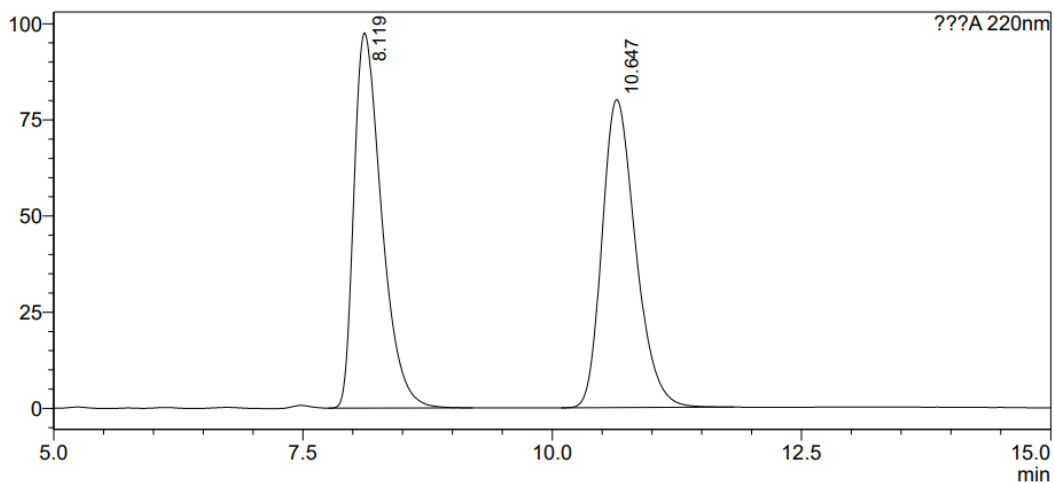


VIII. HPLC spectra for *ee* determination



<Chromatogram>

mV



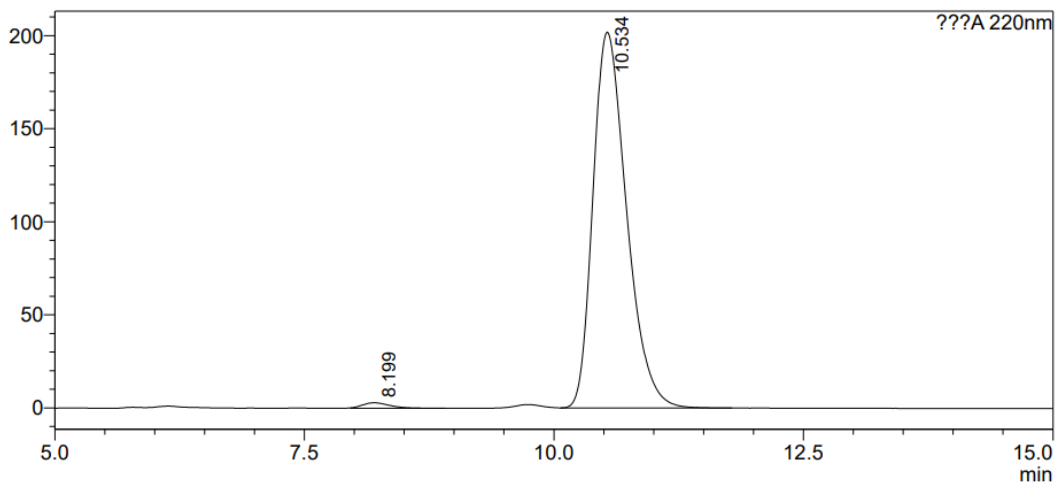
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.119	1879900	97493	50.014			
2	10.647	1878821	80081	49.986			
Total		3758721	177573				

<Chromatogram>

mV



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.199	54478	2911	1.140		M	
2	10.534	4725980	201840	98.860			
Total		4780458	204751				