

Supporting information for

Electrochemically Cooperative Halogen Cation Delivery Enables Modular Electrophilic Haloesterification of Both Activated and Unactivated Alkenes

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1. General information

Anhydrous DCM and DMF was purchased from Energy. Other solvents and commercially available reagents were used without purification. Flash column chromatography was performed with silica gel (200–300 mesh). Cyclic voltammograms were recorded on a CHI 760E potentiostat. NMR spectra were recorded on Bruker AV-400 and Bruker AV-600 instruments. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) for ^1H and CDCl_3 (77.2 ppm) for ^{13}C . The abbreviations used for explaining the multiplicities were as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High resolution mass spectra (ESI) were recorded by the instrumentation center of Department of Chemistry, Henan Normal University, on a Micromass QTOF2 Quadruple/Time-of-Flight Tandem mass spectrometer.

2. General procedure for the electrolysis

Electrochemically cooperative halogen cations delivery enables modular intermolecular chloroesterification of alkenes. A 10-mL three-necked round-bottomed flask (Fig. S1A) was charged with the alkene substrate (0.1 mmol, 1 equiv), and Et_4NPF_6 (0.1 mmol, 1 equiv). The flask was equipped with a syringe needle, a carbon rod anode (ϕ 0.6 cm x 10 cm), and an aluminum plat (1.0 cm x 2.5 cm) cathode (Fig. S1B). Anhydrous *N, N*-dimethylformamide (4 mL) and anhydrous dichloromethane (2 mL) was added. The constant current (5 mA) electrolysis was carried out under air at 15°C until complete consumption of the substrate (monitored by TLC or ^1H NMR). The reaction mixture was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with dichloromethane / petroleum ether to give the product. However, some electrolysis compounds, such as 3, 4, 6, 16, 17, 56, 60, 60', 61, 62, 67, 68 etc., is observed metamorphic phenomenon when these compounds were gradient chromatographed through silica gel eluting with dichloromethane / petroleum ether. The corresponding residue is purified through flash chromatography with eluent of appropriate polarity to remove the impurity and maintain the product.

The 1.76 g scale electrolysis of compound **R1** was conducted in a 500-mL beaker-type cell (Fig. S1C) with four carbon rods anode (ϕ 0.6 cm x 23 cm), an aluminum plat (6 cm x 5 cm) cathode, and a constant current of 100 mA (12 h, 1.49 F mol $^{-1}$). The reaction mixture consisted DCM/DMF (300 mL, v/v = 1:2) and Et_4NBF_4 (2.75 g, 10 mmol). The residue was chromatographed through silica gel eluting with dichloromethane / petroleum ether to give the product **29** in 60% yield.

Electrochemically cooperative halogen cations delivery enables modular intermolecular bromoesterification of alkenes. A 10-mL three-necked round-bottomed flask (Fig. S1A) was charged with the alkene substrate (0.1 mmol, 1 equiv), and Et_4NPF_6 (0.1 mmol, 1 equiv). The flask was equipped with a syringe needle, a carbon rod anode (ϕ 0.6 cm x 10 cm), and an aluminum plat (1.0 cm x 2.5 cm) cathode (Fig. S1B). Anhydrous *N, N*-dimethylformamide (4 mL) and anhydrous dibromomethane (2 mL) was added. The constant current (5 mA) electrolysis was carried out under air at 15°C until complete consumption of the substrate (monitored by TLC or ^1H NMR). The reaction mixture was concentrated

under reduced pressure. The residue was chromatographed through silica gel eluting with dichloromethane / petroleum ether to give the product.

Electrochemically cooperative halogen cations delivery enables chlorination of aromatic ring. A 10-mL three-necked round-bottomed flask (Fig. S1A) was charged with the alkene substrate (0.1 mmol, 1 equiv), and Et_4NPF_6 (0.1 mmol, 1 equiv). The flask was equipped with a syringe needle, a carbon rod anode (ϕ 0.6 cm x 10 cm), and an aluminum plat (1.0 cm x 2.5 cm) cathode (Fig. S1B). Anhydrous *N,N*-dimethylformamide (4 mL) and anhydrous trichloromethane (2 mL) was added. The constant current (5 mA) electrolysis was carried out under air at 15°C until complete consumption of the substrate (monitored by TLC or ^1H NMR). The reaction mixture was concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with dichloromethane / petroleum ether to give the product.

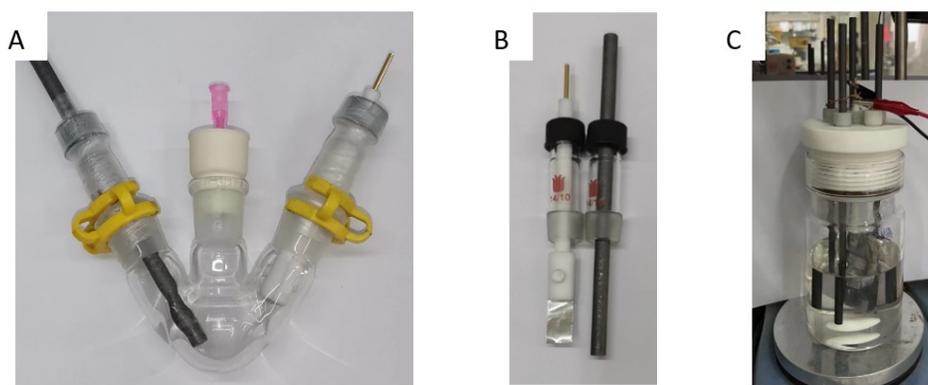
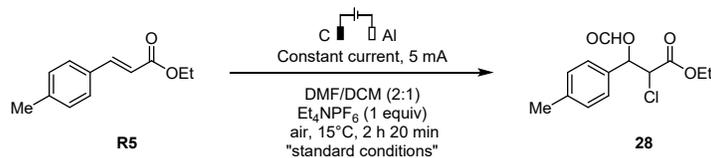


Fig. S1. The electrolysis setup.

3. Optimization of reaction conditions

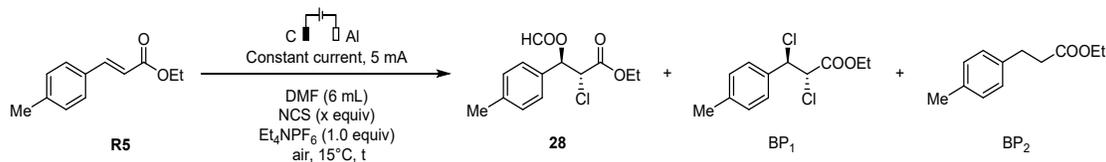
Table S1. Optimization of reaction conditions of **R5**.^a



Entry	Deviation from standard conditions	Yield [%] ^b
1	None	85 ^c
2	No DCM	ND
3	No DMF	ND
4	CHCl ₃ , DCE instead of DCM	85 ^c , 80 ^c
5	NCS (1.5 equiv, 2.0equiv) instead of DCM	53 ^c (28 ^c), 40 ^c (22 ^c)
6	DMF/DCM = 1:2, 3:1	51 ^c , 71 ^c
7	Reaction at 6 V, 9 V, 12 V	9 ^c (64 ^c), 48 ^c (25 ^c), 49 ^c
8	Reaction at 3 mA, 10 mA	69 ^c , 67 ^c (14 ^c)
9	Reaction at 30°C	66 ^c (16 ^c)
10	Reaction at 50°C	34 ^c (41 ^c)
11	Reaction at 100°C	41 ^c (58 ^c)
12	<i>n</i> Bu ₄ NPF ₆ , Me ₄ NPF ₆ , Et ₄ NBF ₄ as electrolyte	81 ^c , 80 ^c , 40 ^c
13	Copper plate (1 cm × 1 cm) as cathode	36 ^c (43 ^c)
14	Foam nickel (1 cm × 1 cm) as cathode	17 ^c (73 ^c)
15	Carbon rod (ϕ 0.6 cm) as cathode	17 ^c (49 ^c)

a) Reaction conditions: carbon rod anode (ϕ 0.6 cm × 10 cm), aluminum plate cathode (1.0 cm × 2.5 cm), alkene **R5** (0.1 mmol), solvent (6 mL), air, 2 h 20 min. b) Yield of the major diastereomer determined by ¹H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard. c) Isolated yield, unreacted **R5** in brackets. DMF, *N,N*-dimethylformamide; DCM, dichloromethane; DCE, 1,2-dichloroethane; ND, no detection; NCS, *N*-chlorosuccinimide.

Table S2. Optimization of reaction conditions of NCS and NBS of **R5**.^a

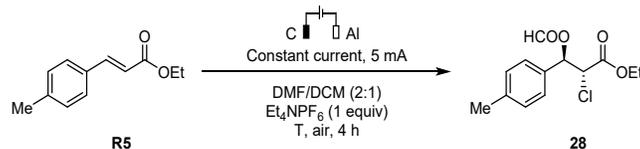


Entry	Deviation from standard conditions	Yield [%] ^b	28	D.R.
1	None	85 ^c		11:1
2	NCS (1.0 equiv), 2.3 h	-	100 RSM	-
3	NCS (1.5 equiv), 2.3 h	53 ^c	28 ^c	11:1
4	NCS (2.0 equiv), 2.3 h	22 ^c	40 ^c	14:1
5	NBS (1.5 equiv), 2.3 h		1/2/BP ₁ /BP ₂ =3:1:0.2:1.4	7.7:1

6	NBS (2.0 equiv), 2.3 h	1/2/BP ₁ /BP ₂ =1:1:0.4:0.5	14:1
7	NCS (1.0 equiv) without electrolysis, 12 h	N.R.	
8	NCS (1.5 equiv) without electrolysis, 12 h	N.R.	
9	NCS (2.0 equiv) without electrolysis, 12 h	N.R.	
10	NBS (1.0 equiv) without electrolysis, 12 h	N.R.	
11	NBS (1.5 equiv) without electrolysis, 12 h	49 NMR%	
12	NBS (2.0 equiv) without electrolysis, 12 h	52 NMR%	

a) Reaction conditions: carbon rod anode (ϕ 0.6 cm \times 10 cm), aluminum plate cathode (1.0 cm \times 2.5 cm), alkene **R5** (0.1 mmol), solvent (6 mL), air, 2 h 20 min. b) Yield of the major diastereomer determined by ¹H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard. c) Isolated yield; NBS, N-bromosuccinimide; N.R., No Reaction.

Table S3. Optimization of reaction conditions of voltage and current of **R5**.^a



Entry	Deviation from standard conditions	Yield [%] ^b	28	D.R.
1	none	85 ^c	-	11:1
2	80	48 ^c	36 ^c	4.8:1
3	100	41 ^c	58 ^c	5:1
4	3 v	-	67 ^c	-
5	6 v	9 ^c	64 ^c	7.7:1
6	9 v	48 ^c	29 ^c	10:1
7	12v	48 ^c	-	10:1

a) Reaction conditions: carbon rod anode (ϕ 0.6 cm \times 10 cm), aluminum plate cathode (1.0 cm \times 2.5 cm), alkene **R5** (0.1 mmol), solvent (6 mL), air, 2 h 20 min. b) Yield of the major diastereomer determined by ¹H NMR analysis with 1,3,5-trimethoxybenzene as the internal standard. c) Isolated yield.

4. X-ray crystallography

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated solution of 52-Br (n-hexane/CH₂Cl₂) in a loosely capped vial.

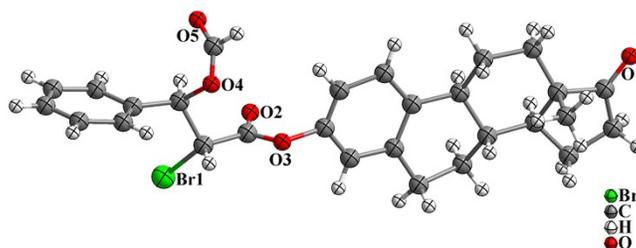


Table S4. Crystal data and structure refinement for 52-Br

Empirical formula	C ₂₈ H ₂₉ BrO ₅
Formula weight	525.42
Temperature/K	170(2)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	9.7657(4)
b/Å	10.2109(4)
c/Å	12.7242(7)
α/°	90
β/°	102.499(5)
γ/°	90
Volume/Å ³	1238.74(10)
Z	2
ρ _{calc} /cm ³	1.409

μ/mm^{-1}	2.560
F(000)	544.0
Crystal size/ mm^3	0.1mm \times 0.1mm \times 0.2mm
Radiation	CuK α ($\lambda = 1.54184$)
2Θ range for data collection/ $^\circ$	7.116 to 119.99
Index ranges	$-10 \leq h \leq 8, -11 \leq k \leq 11, -14 \leq l \leq 14$
Reflections collected	6243
Independent reflections	2992 [$R_{\text{int}} = 0.0523, R_{\text{sigma}} = 0.0597$]
Data/restraints/parameters	2992/319/308
Goodness-of-fit on F^2	1.662
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.1362, wR_2 = 0.3908$
Final R indexes [all data]	$R_1 = 0.1558, wR_2 = 0.4017$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	1.64/-0.56
Flack parameter	0.18(3)

5. Deuterium labeling study

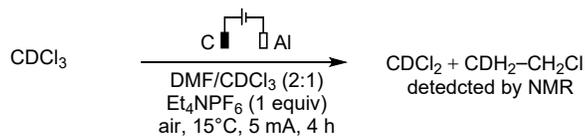


Fig. S2. Deuterium labeling experiments

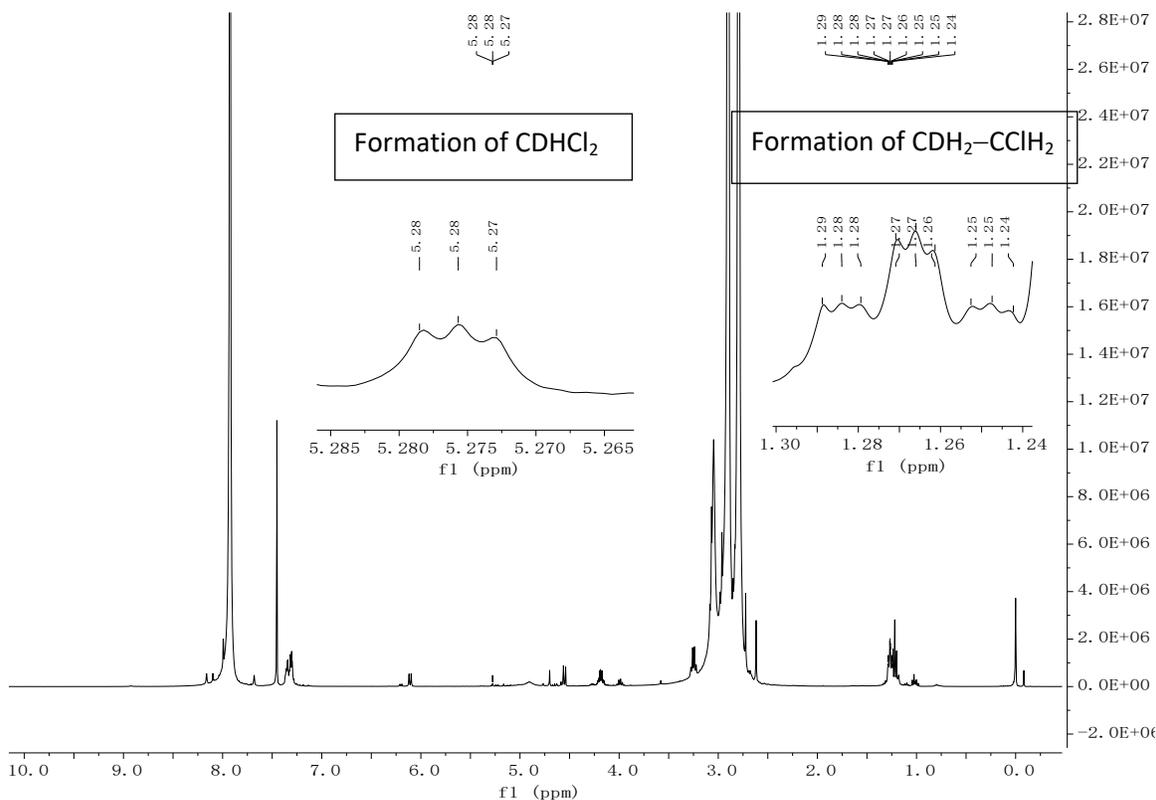


Fig. S3. ^1H NMR of the crude reaction mixture using CDCl_3

The deuterium labeling studies were performed by using CDCl_3 instead of CH_2Cl_2 and DMF under optimized conditions (Fig. S2). After 4 h the CDCl_2 and $\text{CDH}_2\text{-CClH}_2$ was observed in the ^1H NMR spectrum (Fig. S3). This result supported the CDCl_3 as the chlorine source.

6. Cyclic voltammetry studies

The cyclic voltammograms were recorded in an electrolyte solution of Et_4NPF_6 (0.1 M) in different solvent (6 mL) using a metal plate working electrode ($1.0 \text{ cm} \times 2.5 \text{ cm}$) or using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and an Ag/AgCl reference electrode. The scan rate was 100 mV/s.

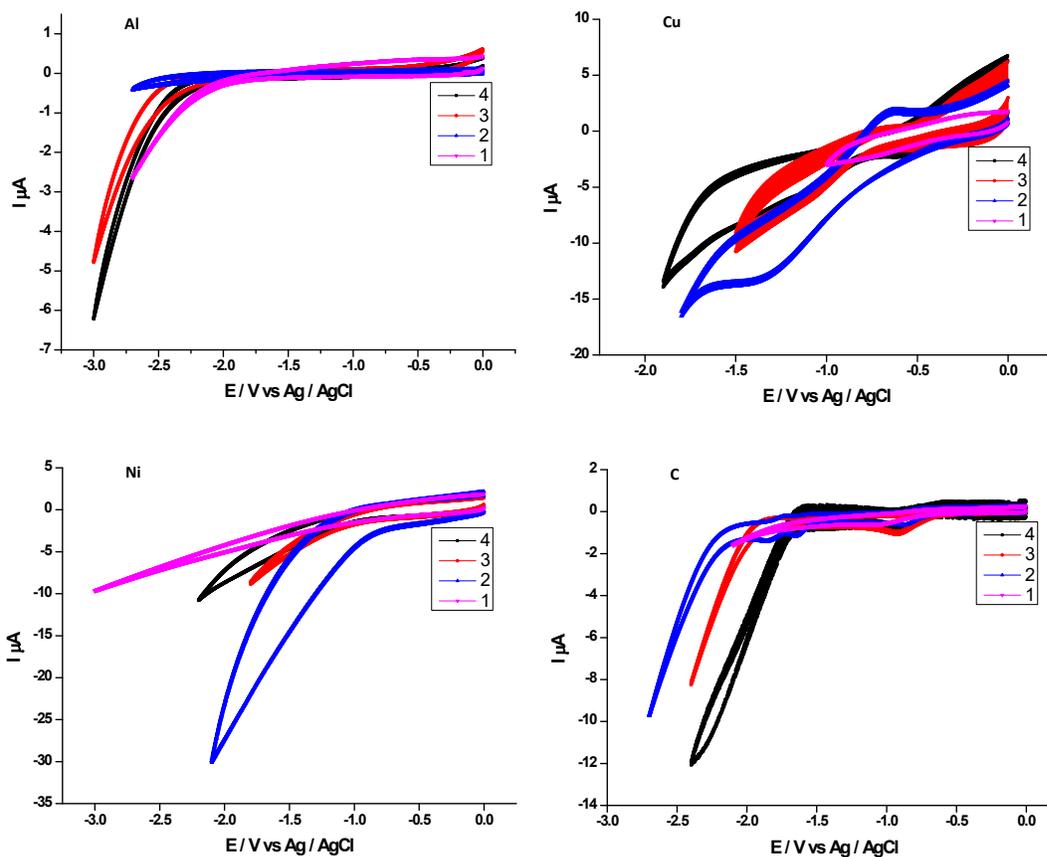


Fig. S4. Cyclic voltammograms for the reduction potential of different solvent on different electrode. (1) DCM (6 mL); (2) DMF (6 mL); (3) DMF (4 mL) + DCM (2 mL); (4) DMF (4 mL) + DCM (2 mL) +alkene **R1** (5 mM).

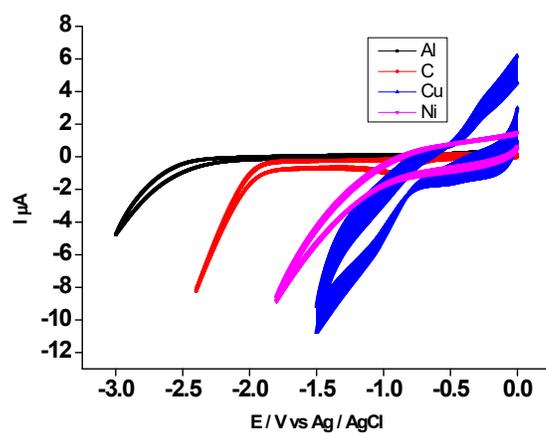


Fig. S5. Cyclic voltammograms for the reduction potential of CH_2Cl_2 on different electrode in DMF/DCM (2:1).

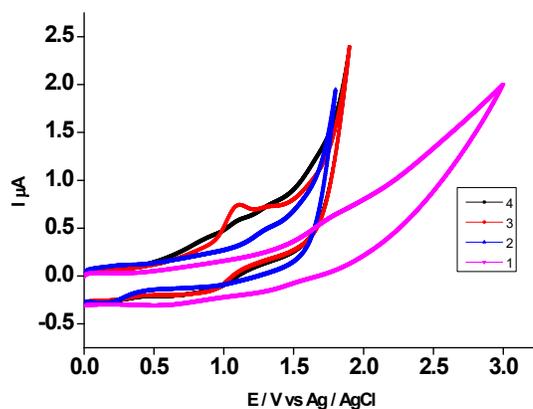
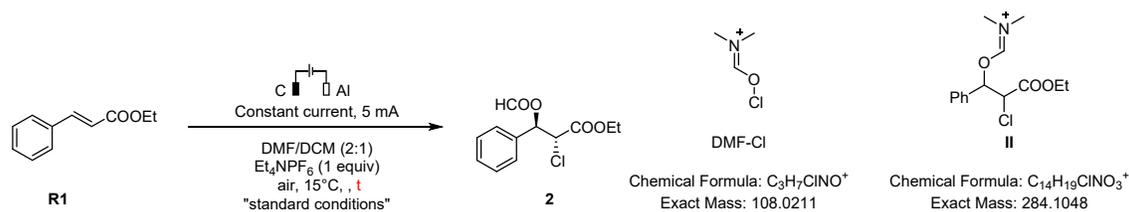


Fig. S6. Cyclic voltammograms for the oxidation potential of different solvent on glassy carbon disk electrode. (1) DCM (6 mL); (2) DMF (6 mL); (3) DMF (4 mL) + DCM (2 mL); (4) DMF (4 mL) + DCM (2 mL) + alkene **R1** (5 mM).

7. HR-MS used for monitoring reactions



HR-MS used for monitoring DMF-Cl and intermediate II of alkene **R1** in standard condition in different times (1.0 h, 2.0 h, 2.5 h, 3.5 h). DMF-Cl and intermediate II can be detected in in different times (**Fig. S7 Fig. S10**). The concentration of the DMF-Cl and intermediate II is increase following the reaction. And it reaches its peak in 2.5 hours.

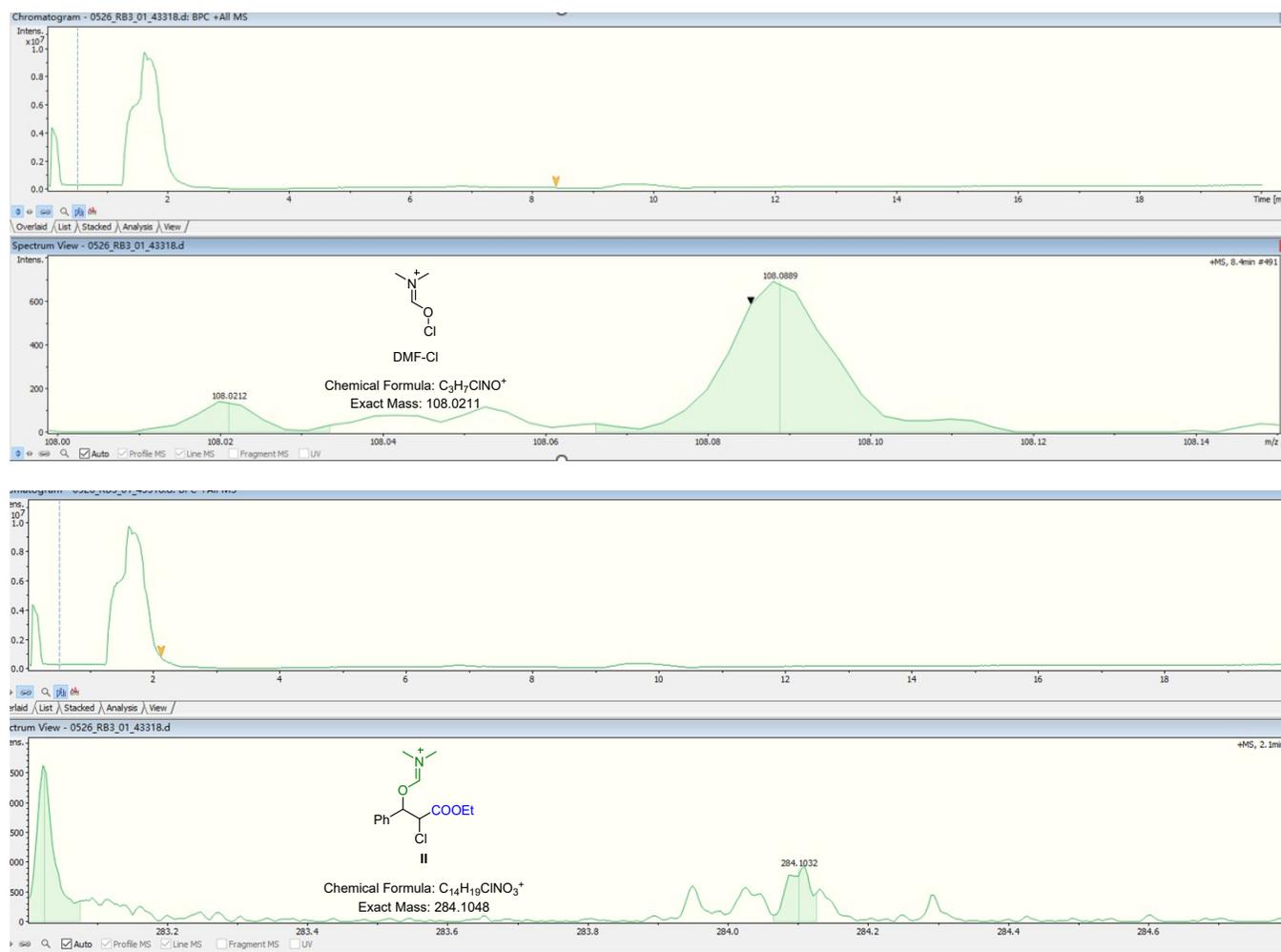


Fig. S7. HR-MS for monitoring DMF-Cl and intermediate II in 1.0 h

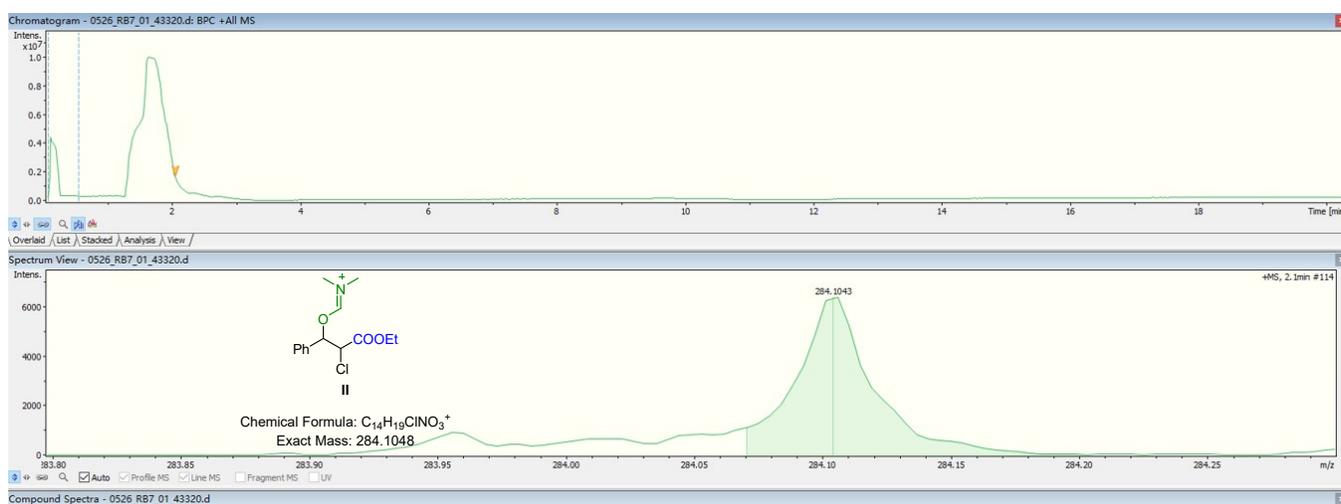
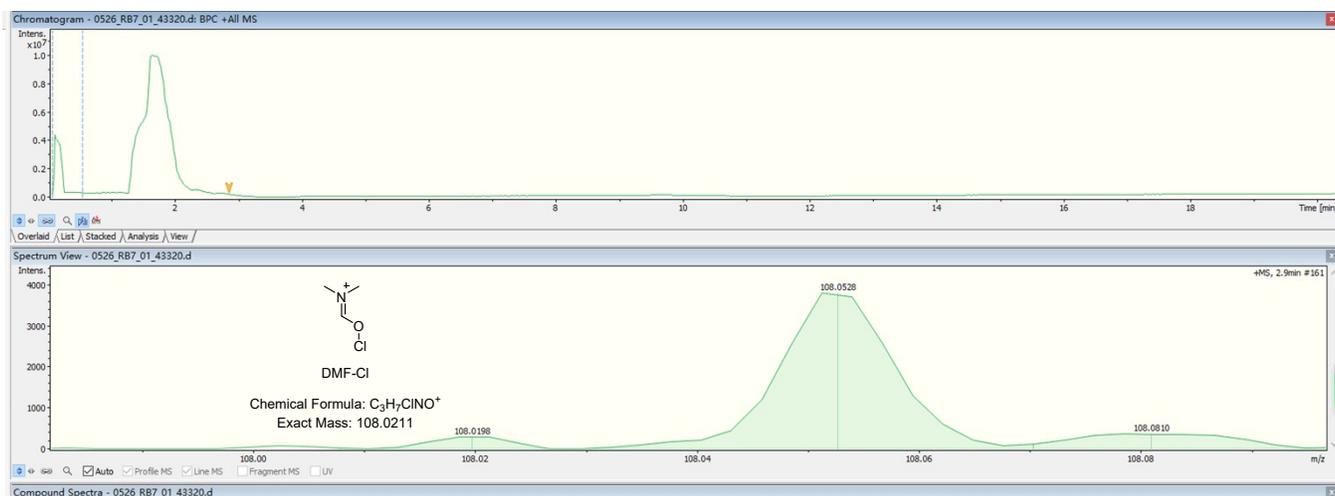
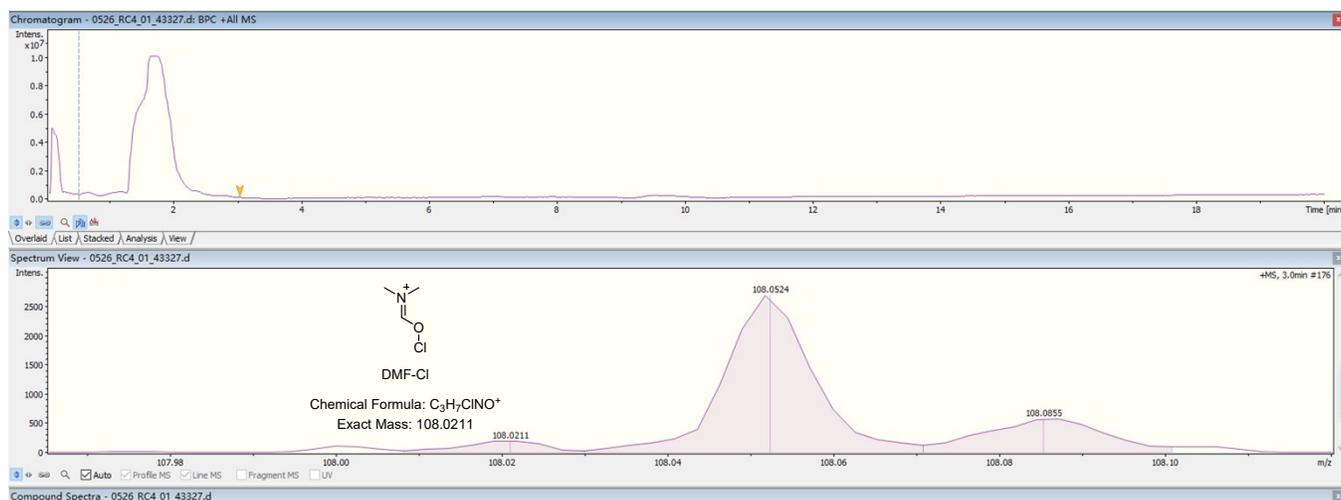


Fig. S8. HR-MS for monitoring DMF-Cl and intermediate II in 2.0 h



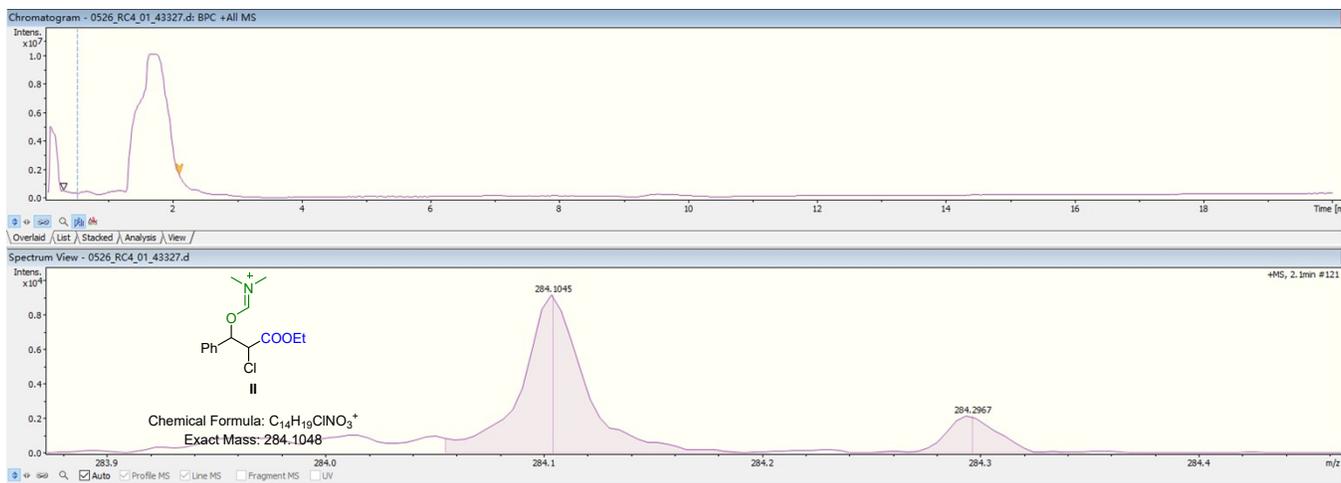


Fig. S9. HR-MS for monitoring DMF-Cl and intermediate II in 2.5 h

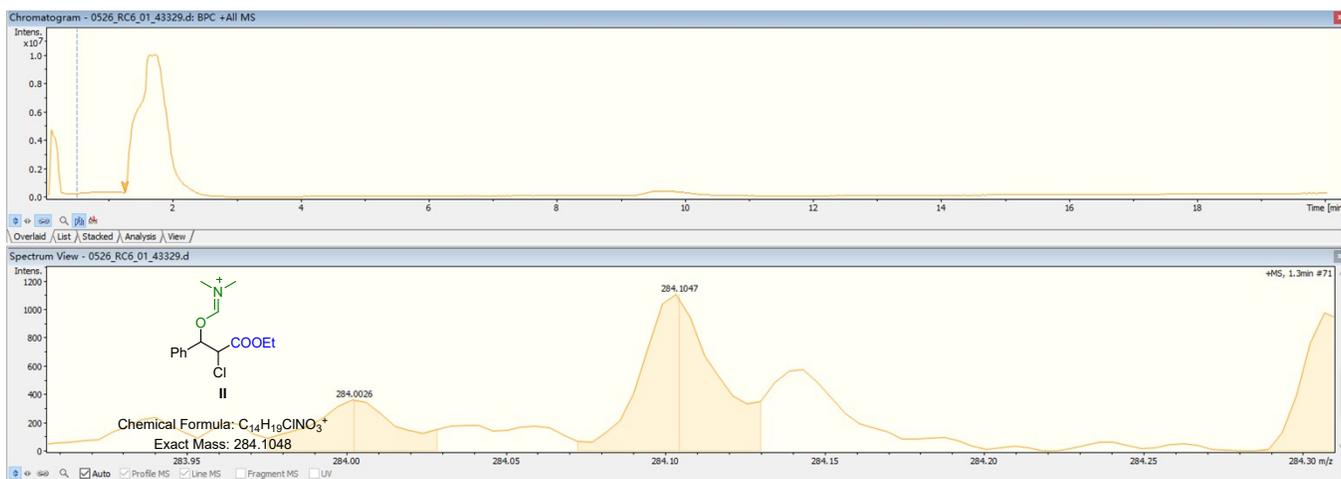
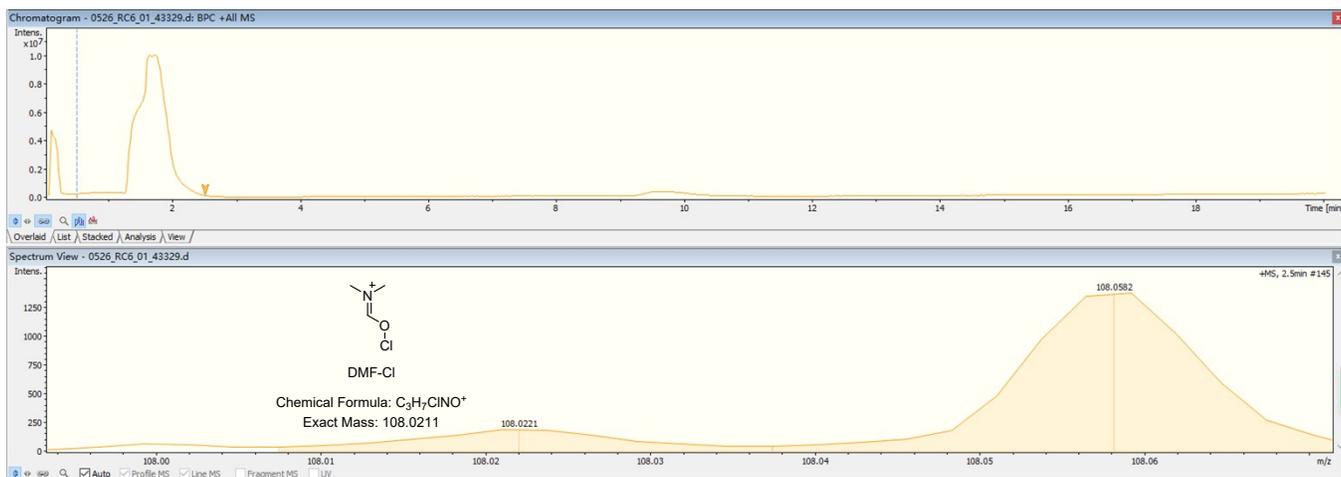
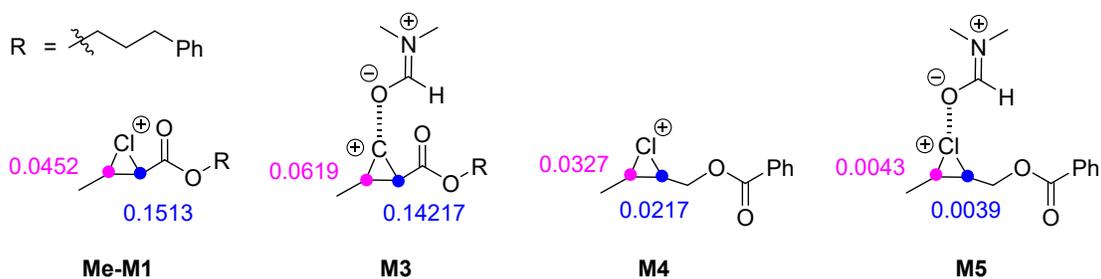


Fig. S10. HR-MS for monitoring DMF-Cl and intermediate II in 3.5 h

8. Computational details

All calculations were performed using Gaussian 16^[1]. Without any special indication, all calculations were performed using the solvent of DMF/DCM (4 mL /2 mL). Structures were optimized at the M06-2X/6-31+G(d,p) level of theory in dimethylformamide (DMF) and dichloromethane (DCM) using the IEF-PCM solvation model. Frequency analyses confirmed that all reactants, products, and intermediates possess no imaginary frequencies, while each transition state exhibits a single imaginary frequency, confirming its nature as a first-order saddle point. The Gibbs free energies reported in the discussion were obtained at the M06-2X/6-311++G(d,p)/IEF-PCM(DMF/DCM) level, based on the optimized geometries from the M06-2X/6-31+G(d,p)/IEF-PCM(DMF/DCM) level in each solvent. Fukui f^+ values were calculated using the finite difference approach based on Hirshfeld charges and generated with Multiwfn^[2]. The 3D-structures were rendered using the CYLView software^[3].

a. Fukui function



b. NBO charge

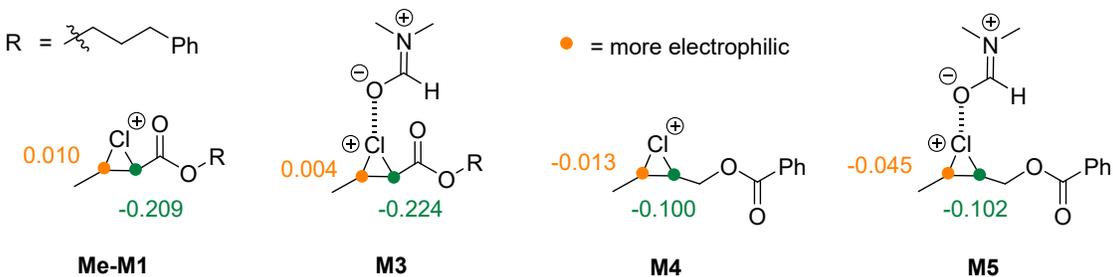


Fig. S11. (a) Fukui function f^+ for nucleophilic reactivity at alkene carbons of different intermediates. (b) Natural Bond Orbital (NBO) charge to establish regioselectivity of nucleophile attack.

8.1 Summary of absolute SPE, GFEC, and GFE of the optimized structures

Table S5. The single-point energies (SPE) at M062X/6-311++G(d, p)/IEF-PCM(DMF/DCM) level, Gibbs free energy corrections (GFEC) at M06-2X/6-31+G(d, p)/IEF-PCM(DMF/DCM) level, and Gibbs free energies (GFE = SPE + GFEC) of the stationary points involved in the reaction models.

	SPE (a.u.)	GFEC (a.u.)	GFE (a.u.)
DMF	-248.480439	0.074269	-248.406170
DMF-CL	-708.406700	0.074269	-708.332431
NH₂(Me)₂⁺	-135.586838	0.083423	-135.503415
H₂O	-76.428656	0.003851	-76.424805
R1	-576.763735	0.165419	-576.598316
TS1S	-1285.180237	0.259362	-1284.920875
M1S	-1036.730475	0.164772	-1036.565703
TS2SS	-1285.228614	0.263790	-1284.964824
TS2SR	-1285.223460	0.262712	-1284.960748
M2SS	-1285.277522	0.267038	-1285.010484
M2SR	-1285.276620	0.265527	-1285.011093
PSS	-1226.130303	0.188595	-1225.941708
TS2SS'	-1533.713609	0.351441	-1533.362168
TS2SR'	-1533.711531	0.359043	-1533.352488
Me-R1	-655.368832	0.218321	-655.150511
Me-TS1	-1363.785279	0.312547	-1363.472732
Me-TS1'	-1363.785162	0.312764	-1363.472398
Me_M1	-1115.323318	0.220125	-1115.103193
Me_M1'	-1115.323313	0.219991	-1115.103322
Me_TS2_SS	-1363.822876	0.316219	-1363.506657
Me_TS2_RR	-1363.821877	0.314698	-1363.507179
Me_M2SS	-1363.889721	0.319804	-1363.569917
Me_M2RR	-1363.889358	0.318866	-1363.570492
Me_M2SR	-1363.888365	0.319258	-1363.569107
Me_PSS	-1304.741601	0.241521	-1304.500080
Me_TS3	-1612.331558	0.412785	-1611.918773
M3	-1363.811091	0.309425	-1363.501666
M4	-1036.7288	0.167314	-1036.561486
M5	-1285.221545	0.261947	-1284.959598
M6	-1285.2148	0.255585	-1284.959215

Part 3 The energies, cartesian coordinates, and frequencies of the stationary points

DMF

Thermal energies (Hartree):

Zero-point correction = 0.10348900

Thermal correction to energy = 0.10958500

Thermal correction to enthalpy = 0.11052900

Thermal correction to Gibbs free energy = 0.07426900

Sum of electronic and zero-point energies = -248.31526100

Sum of electronic and thermal energies = -248.30916500

Sum of electronic and thermal enthalpies = -248.30822100

Sum of electronic and thermal free energies = -248.34448100

Final optimized coordinates (Angstrom):

C	0.855482	-0.646099	-0.000006
H	0.764209	-1.743951	0.000001
O	1.952813	-0.089290	-0.000073
N	-0.336104	-0.022740	-0.000095
C	-0.428937	1.426231	-0.000007
H	-0.969011	1.765713	-0.889379
H	-0.967768	1.765736	0.890119
H	0.576075	1.845076	-0.000710
C	-1.585076	-0.762810	0.000125
H	-2.171783	-0.514329	-0.889604
H	-1.378924	-1.834201	-0.000011
H	-2.171385	-0.514476	0.890164

Frequencies (cm⁻¹):

97.4948	167.3288	247.9651
328.0219	342.9740	403.2119
668.3553	891.3886	1040.3899
1089.4314	1117.9807	1127.7686
1177.0990	1305.9545	1431.4779
1443.7393	1456.9111	1476.8468
1477.6940	1494.8604	1506.4918
1554.6504	1741.2475	3057.9773
3066.0605	3070.2202	3129.0663
3135.0361	3176.1561	3202.7538

DMF-CI

Thermal energies (Hartree):

Zero-point correction = 0.10673400

Thermal correction to energy = 0.11422400

Thermal correction to enthalpy = 0.11516900

Thermal correction to Gibbs free energy = 0.07419900

Sum of electronic and zero-point energies = -708.21023400

Sum of electronic and thermal energies = -708.20274400

Sum of electronic and thermal enthalpies = -708.20180000

Sum of electronic and thermal free energies = -708.24277000

Final optimized coordinates (Angstrom):

N	-1.325678	-0.060576	-0.009856
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C	-1.723308	1.355916	-0.009220
H	-0.874321	1.983173	-0.268200
H	-2.519866	1.474593	-0.742804
H	-2.093437	1.607307	0.986114
C	-2.413399	-1.050911	-0.000642
H	-2.993525	-0.928312	-0.915216
H	-1.999193	-2.055632	0.051753
H	-3.039896	-0.858102	0.870405
C	-0.100542	-0.438704	0.009465
H	0.169578	-1.491309	0.010097
O	0.848568	0.481522	0.032983
Cl	2.427374	-0.138686	-0.010861

Frequencies (cm⁻¹):

62.4245	90.0426	166.8701
188.8067	274.6732	329.3912
420.7024	453.6226	528.2700
832.6237	899.2176	1003.9429
1077.9580	1124.2828	1170.1179
1180.5530	1269.3820	1307.0814
1440.4663	1452.3214	1465.7307
1471.3472	1489.8564	1495.6131
1522.8404	1798.5307	3109.4361
3110.9920	3201.2880	3203.7412
3223.8610	3236.6326	3248.2234

NH₂(Me)₂⁺

Thermal energies (Hartree):

Zero-point correction = 0.10920800

Thermal correction to energy = 0.11368800

Thermal correction to enthalpy = 0.11463200

Thermal correction to Gibbs free energy = 0.08342300

Sum of electronic and zero-point energies = -135.44710000

Sum of electronic and thermal energies = -135.44262000

Sum of electronic and thermal enthalpies = -135.44167600

Sum of electronic and thermal free energies = -135.47288500

Final optimized coordinates (Angstrom):

N	0.000008	0.542525	-0.000001
C	-1.248413	-0.276387	-0.000001
H	-1.246845	-0.897685	-0.893380
H	-1.247231	-0.897088	0.893790
H	-2.105297	0.393385	-0.000407
C	1.248400	-0.276402	0.000000
H	1.247197	-0.897133	-0.893768
H	2.105286	0.393376	0.000292
H	1.246912	-0.897558	0.893475
H	0.000009	1.160890	-0.815971
H	-0.000002	1.160874	0.815981

Frequencies (cm^{-1}):

154.3037	294.2903	411.2924
815.8398	906.9546	1040.3048
1041.7796	1104.0555	1262.8992
1277.6085	1401.5874	1442.5000
1452.7615	1490.5169	1495.1456
1498.4006	1509.7203	1520.1209
1655.8369	3122.9218	3126.5345
3229.2493	3232.6307	3234.9308
3235.6990	3463.1510	3515.6604

H₂O

Thermal energies (Hartree):

Zero-point correction = 0.02149800

Thermal correction to energy = 0.02433400

Thermal correction to enthalpy = 0.02527800

Thermal correction to Gibbs free energy = 0.00385100

Sum of electronic and zero-point energies = -76.38161000

Sum of electronic and thermal energies = -76.37877400

Sum of electronic and thermal enthalpies = -76.37783000

Sum of electronic and thermal free energies = -76.39925600

Final optimized coordinates (Angstrom):

O	-0.000000	0.000000	0.116986
H	-0.000000	0.765920	-0.467944

H -0.000000 -0.765920 -0.467944

Frequencies (cm⁻¹):

1600.3878 3864.8347 3971.2375

R1

Thermal energies (Hartree):

Zero-point correction = 0.20681100

Thermal correction to energy = 0.21923500

Thermal correction to enthalpy = 0.22017900

Thermal correction to Gibbs free energy = 0.16541900

Sum of electronic and zero-point energies = -576.42662700

Sum of electronic and thermal energies = -576.41420300

Sum of electronic and thermal enthalpies = -576.41325900

Sum of electronic and thermal free energies = -576.46802000

Final optimized coordinates (Angstrom):

C -0.609701 0.116189 -0.000437

H -0.584276 1.200554 -0.000460

C 0.489198 -0.652102 -0.000243

H 0.340747 -1.731598 -0.000231

C 1.884638 -0.196978 -0.000054

C 2.901478 -1.162391 0.000216

C 2.242867 1.161101 -0.000130

C 4.243157 -0.786403 0.000414

H	2.633582	-2.215522	0.000273
C	3.581231	1.536458	0.000066
H	1.475359	1.928624	-0.000346
C	4.585944	0.564512	0.000339
H	5.017659	-1.546487	0.000625
H	3.844540	2.589297	0.000003
H	5.629644	0.862157	0.000491
C	-1.946786	-0.513772	-0.000664
O	-2.166795	-1.710978	-0.000204
O	-2.919107	0.407819	-0.000300
C	-4.271734	-0.087923	0.000109
H	-4.411938	-0.712810	0.886385
H	-4.412558	-0.712545	-0.886256
C	-5.192897	1.111254	0.000608
H	-6.231795	0.772744	0.000906
H	-5.028756	1.725456	0.889311
H	-5.029357	1.725733	-0.888014

Frequencies (cm⁻¹):

10.7632	58.0196	71.9869
73.8951	98.8960	175.2787
185.9736	236.5127	261.8707
286.2433	325.4137	395.0187
409.8714	494.3982	514.3925
581.0076	627.2816	693.8937

730.4923	755.8349	788.3795
814.9308	860.6632	866.9261
902.9454	915.9132	952.1996
1008.7278	1013.5865	1020.0546
1024.4230	1032.7196	1062.3956
1090.8303	1114.0678	1146.6737
1175.5322	1178.9426	1202.6038
1228.7462	1242.6118	1303.0559
1323.7733	1348.1177	1360.8356
1363.6255	1400.9727	1435.2726
1482.4056	1491.9179	1493.6768
1517.8739	1544.4333	1655.9994
1681.8088	1728.6377	1790.3872
3082.9548	3094.7794	3141.4029
3166.8043	3169.3270	3189.4179
3213.1094	3219.8962	3227.1213
3234.2214	3242.1543	3244.7611

TS1S

Thermal energies (Hartree):

Zero-point correction = 0.31412800

Thermal correction to energy = 0.33519300

Thermal correction to enthalpy = 0.33613700

Thermal correction to Gibbs free energy = 0.25936200

Sum of electronic and zero-point energies = -1284.64428000

Sum of electronic and thermal energies = -1284.62321500

Sum of electronic and thermal enthalpies = -1284.62227100

Sum of electronic and thermal free energies = -1284.69904600

Final optimized coordinates (Angstrom):

C	-1.730150	0.657167	0.201416
C	-1.115703	1.588826	-0.580130
H	-1.384083	1.586429	-1.636743
C	-0.134861	2.578863	-0.162366
C	0.387984	3.441852	-1.138765
C	0.307183	2.697121	1.167814
C	1.330375	4.407041	-0.796614
H	0.049084	3.350369	-2.166780
C	1.249856	3.658566	1.505232
H	-0.083113	2.039415	1.937973
C	1.761709	4.515172	0.524836
H	1.727038	5.070854	-1.557180
H	1.587501	3.745921	2.532407
H	2.496864	5.266341	0.795172
C	-2.794387	-0.199320	-0.390545
O	-3.082051	-0.226089	-1.569682
O	-3.383362	-0.944455	0.542411
C	-4.429667	-1.830919	0.087480
H	-4.002715	-2.510194	-0.655016
H	-5.202364	-1.228572	-0.397145

C	-4.955173	-2.565926	1.299060
H	-5.750553	-3.248826	0.991570
H	-4.161975	-3.149035	1.772880
H	-5.364260	-1.864726	2.030217
H	-1.605948	0.609479	1.277976
Cl	0.199040	-0.757485	-0.366550
C	2.548459	-1.775558	0.148402
H	2.580271	-0.907930	0.805200
O	1.495555	-1.996223	-0.581343
N	3.560805	-2.576552	0.101859
C	3.590271	-3.766081	-0.756183
H	4.431327	-3.671207	-1.444478
H	3.731100	-4.642271	-0.121684
H	2.658400	-3.847879	-1.309456
C	4.752692	-2.328515	0.920937
H	5.612550	-2.223391	0.258443
H	4.619146	-1.418302	1.502785
H	4.899751	-3.178961	1.587654

Frequencies (cm⁻¹):

-163.1967	16.0589	23.2760
27.7106	38.4468	45.6861
57.2334	68.1187	78.1008
81.4801	95.6337	125.6522
156.1651	172.9022	181.8959

193.6922	220.2581	237.1203
263.2129	290.8363	301.6118
315.9901	322.6899	393.9681
407.8529	419.7812	435.8108
468.0945	499.6176	515.4873
579.5047	624.8889	689.1265
707.1159	744.3013	757.1770
786.7454	813.4602	863.2157
866.6534	891.9900	911.8755
915.3394	960.7333	1012.6250
1013.3825	1015.5849	1027.1265
1034.2297	1041.6287	1060.1291
1080.2036	1082.8147	1116.0407
1127.2611	1146.7360	1171.0633
1177.9920	1178.4012	1184.9607
1201.5808	1234.0447	1249.5799
1276.3426	1303.8008	1323.4833
1330.3941	1352.5275	1362.3525
1369.7004	1403.4466	1435.9905
1451.1371	1454.4948	1469.0548
1472.8350	1483.1911	1491.5884
1493.7834	1494.0809	1496.7089
1516.5320	1523.7693	1541.8442
1649.3196	1669.5457	1678.0578
1765.9245	1805.1642	3083.9801

3098.2532	3105.3398	3107.9943
3146.4208	3168.9765	3171.6136
3190.7343	3193.1639	3195.7641
3217.9253	3217.9792	3223.4486
3228.8322	3229.4614	3234.9365
3239.4168	3245.6014	3249.5396

M1S

Thermal energies (Hartree):

Zero-point correction = 0.20962300

Thermal correction to energy = 0.22362500

Thermal correction to enthalpy = 0.22456900

Thermal correction to Gibbs free energy = 0.16477200

Sum of electronic and zero-point energies = -1036.35839000

Sum of electronic and thermal energies = -1036.34438800

Sum of electronic and thermal enthalpies = -1036.34344400

Sum of electronic and thermal free energies = -1036.40324100

Final optimized coordinates (Angstrom):

C	0.531080	0.371500	-0.041652
C	-0.684238	-0.230171	-0.654621
H	-0.515292	-0.709350	-1.618269
C	-1.961462	-0.201687	-0.142127
C	-2.998031	-0.820413	-0.919925
C	-2.289048	0.411238	1.114174

C	-4.293948	-0.828326	-0.459653
H	-2.738764	-1.279677	-1.868578
C	-3.588976	0.397918	1.555199
H	-1.520177	0.889363	1.709845
C	-4.582803	-0.220517	0.771949
H	-5.084328	-1.293549	-1.035574
H	-3.854860	0.858240	2.498837
H	-5.606404	-0.225115	1.133619
C	1.751411	-0.527093	-0.257552
O	1.731525	-1.494906	-0.980592
O	2.778781	-0.093065	0.440761
C	4.016640	-0.841191	0.300586
H	4.292544	-0.834906	-0.756312
H	3.821506	-1.870503	0.610048
C	5.047341	-0.162427	1.170442
H	5.994049	-0.701380	1.089880
H	5.207158	0.869202	0.849227
H	4.734506	-0.165971	2.216912
H	0.436981	0.627522	1.011638
Cl	0.768402	1.908642	-0.949620

Frequencies (cm⁻¹):

6.8593	29.4690	53.3258
69.3762	92.7791	100.6625
145.4094	163.1394	202.8833

254.0784	281.6134	321.5717
331.2857	388.0336	398.1687
451.3153	510.6738	564.5071
607.0624	633.3528	662.2364
751.1926	792.2824	810.5162
825.7076	847.1418	859.5481
902.1985	972.8569	1002.4903
1003.3716	1018.7854	1033.8935
1041.6807	1059.4048	1062.4903
1116.6997	1145.6689	1173.8191
1178.4417	1193.0368	1211.0457
1229.5762	1262.4891	1293.5137
1306.8572	1364.3675	1383.6938
1412.6366	1435.4475	1442.3212
1480.1506	1483.0410	1491.8487
1503.3291	1515.8496	1611.4291
1624.5016	1670.8926	1836.3272
3086.9431	3108.0882	3158.1515
3172.0538	3178.9163	3200.5752
3219.4328	3239.4433	3244.3882
3255.5399	3264.2353	3267.8392

TS2SS

Thermal energies (Hartree):

Zero-point correction = 0.31511200

Thermal correction to energy = 0.33553700

Thermal correction to enthalpy = 0.33648200

Thermal correction to Gibbs free energy = 0.26379000

Sum of electronic and zero-point energies = -1284.68870100

Sum of electronic and thermal energies = -1284.66827600

Sum of electronic and thermal enthalpies = -1284.66733200

Sum of electronic and thermal free energies = -1284.74002300

Final optimized coordinates (Angstrom):

C	-0.300087	1.234750	0.034547
C	-1.207439	0.253692	-0.625108
C	-2.457852	-0.140206	-0.143289
C	-3.251969	-0.968714	-0.981941
C	-2.945685	0.252113	1.133968
C	-4.496098	-1.392537	-0.555319
H	-2.867767	-1.260835	-1.954423
C	-4.190547	-0.173104	1.545718
H	-2.349732	0.885820	1.781859
C	-4.959020	-0.993739	0.703685
H	-5.108746	-2.024687	-1.186805
H	-4.576802	0.120882	2.514418
H	-5.936718	-1.325478	1.038974
C	1.124955	1.117179	-0.503826
O	1.379786	0.921363	-1.667046
O	2.003108	1.266950	0.471470

C	3.402596	1.217311	0.091612
H	3.600044	2.064079	-0.570100
H	3.566566	0.292504	-0.468328
C	4.211776	1.276558	1.365366
H	5.274853	1.220173	1.120405
H	4.026580	2.211394	1.898813
H	3.962685	0.440304	2.023805
H	-0.309895	1.185054	1.121650
Cl	-0.939248	2.849406	-0.450827
H	-0.918299	-0.029888	-1.634877
O	0.146787	-1.482578	-0.042916
C	1.205492	-1.674927	0.585265
H	1.257445	-1.548860	1.675208
N	2.355126	-2.038338	0.020411
C	2.454223	-2.260204	-1.416989
C	3.525678	-2.370866	0.820410
H	3.361465	-1.778607	-1.790873
H	2.509681	-3.332961	-1.624585
H	1.581984	-1.830179	-1.905503
H	4.374740	-1.754436	0.510338
H	3.315575	-2.191785	1.875517
H	3.784106	-3.423740	0.679021

Frequencies (cm⁻¹):

-73.4255 21.0546 32.9399

48.7159	54.9319	64.3947
72.7996	92.4046	105.2467
109.0271	133.5272	152.3862
160.2845	166.7085	191.6677
196.0995	208.7562	256.5844
282.5681	287.0969	321.5256
332.8757	342.3378	384.4856
394.2736	401.9553	408.6732
480.6289	515.7503	565.2777
614.9469	661.8603	666.7405
700.3932	758.7931	791.8157
810.3358	824.2157	858.1461
871.7623	884.2069	907.3381
980.7118	999.1149	1008.5195
1011.1747	1027.3688	1044.1495
1051.8833	1053.7414	1068.1705
1084.7069	1117.3564	1126.4851
1132.1271	1145.3616	1170.1595
1176.7972	1178.8646	1187.6410
1208.2869	1224.7908	1255.8039
1280.0450	1294.8684	1304.4660
1367.1408	1379.7053	1403.5098
1412.6677	1421.0822	1440.4962
1447.8438	1460.7224	1472.8854
1475.8561	1481.8574	1483.5852

1490.5394	1496.1456	1504.8771
1509.2634	1517.7069	1551.0236
1579.2074	1629.3098	1659.5920
1697.9507	1851.4378	3073.9276
3079.2768	3084.4829	3102.9718
3110.0601	3144.9792	3150.8531
3155.1666	3170.5850	3176.3393
3186.9288	3200.0899	3212.8762
3233.2934	3234.5705	3237.6572
3245.1844	3256.4294	3259.9913

TS2SR

Thermal energies (Hartree):

Zero-point correction = 0.41959700

Thermal correction to energy = 0.44764600

Thermal correction to enthalpy = 0.44859000

Thermal correction to Gibbs free energy = 0.35904300

Sum of electronic and zero-point energies = -1533.00567600

Sum of electronic and thermal energies = -1532.97762700

Sum of electronic and thermal enthalpies = -1532.97668300

Sum of electronic and thermal free energies = -1533.06623000

Final optimized coordinates (Angstrom):

C 0.829537 -1.224466 0.668598

C 1.916595 -0.209345 0.526940

H	1.628562	0.819253	0.727116
C	3.226431	-0.463945	0.173871
C	4.089690	0.669921	0.034015
C	3.745660	-1.783288	-0.032224
C	5.417498	0.489445	-0.287805
H	3.663820	1.660466	0.160576
C	5.072265	-1.945182	-0.348658
H	3.098175	-2.647587	0.070696
C	5.900754	-0.812469	-0.475502
H	6.080860	1.338287	-0.399908
H	5.486106	-2.934780	-0.499557
H	6.946854	-0.955109	-0.728541
C	-0.413651	-0.606559	1.318803
O	-0.394382	0.493528	1.817501
O	-1.421756	-1.454134	1.343687
C	-2.640661	-0.968412	1.959260
H	-2.924668	-0.047921	1.441372
H	-2.422754	-0.732902	3.003983
C	-3.676118	-2.059364	1.820461
H	-4.625158	-1.713281	2.237416
H	-3.829861	-2.311919	0.767964
H	-3.369051	-2.959909	2.357172
H	1.152801	-2.056303	1.303786
Cl	0.474597	-1.924477	-0.945461
C	-2.634686	-0.438240	-1.303489

H	-2.249562	-1.341508	-1.802994
O	-1.879815	0.428527	-0.861718
N	-3.976612	-0.410254	-1.225765
C	-4.673353	0.699411	-0.598702
H	-5.339997	1.179902	-1.321369
H	-5.272070	0.334944	0.243323
H	-3.939272	1.421836	-0.243120
C	-4.798351	-1.465582	-1.791851
H	-5.422923	-1.069740	-2.598438
H	-4.160002	-2.255943	-2.189999
H	-5.448990	-1.889149	-1.020051
C	0.286788	2.412130	-1.044057
H	-0.457617	2.204516	-1.822664
O	1.460950	2.028765	-1.144837
N	-0.204214	3.103564	-0.007837
C	0.630661	3.471065	1.122959
H	0.420828	4.506908	1.402333
H	0.421845	2.818722	1.977107
H	1.678947	3.381734	0.837769
C	-1.625418	3.373502	0.112924
H	-1.789102	4.440981	0.286334
H	-2.131968	3.065831	-0.802132
H	-2.039983	2.800397	0.949544

Frequencies (cm⁻¹):

-41.8415	22.3850	31.1563
40.9231	49.5768	55.7432
59.2477	67.2286	73.1752
78.0525	82.7186	96.0919
108.3595	116.9832	121.1681
126.8904	137.2654	153.2083
158.6962	171.6117	176.8311
186.9464	197.7182	202.5606
223.3612	253.0100	256.5430
276.1146	290.2850	326.5677
336.5290	339.2855	344.5560
355.8442	385.5533	389.4468
405.1647	407.9159	417.6027
450.2962	507.1645	568.6740
604.6492	626.5371	637.9738
670.1996	671.6277	763.1322
786.6015	803.6365	819.6780
849.4975	864.0771	892.6132
893.9726	908.6246	959.6742
1002.8280	1005.6476	1012.8953
1026.5795	1030.6632	1037.4792
1043.9515	1056.4389	1069.4846
1086.2595	1090.1071	1112.4586
1119.5388	1126.3151	1127.9307
1129.7294	1145.8304	1153.7973

1176.1600	1177.2232	1179.2051
1193.4587	1206.6435	1221.1405
1252.5579	1285.2993	1303.7847
1304.9096	1306.5746	1362.5751
1377.7762	1407.4184	1427.0560
1427.6004	1427.9116	1440.0077
1441.4717	1441.6891	1456.6054
1458.7230	1471.7488	1474.9677
1476.0849	1477.6060	1480.2831
1482.9039	1494.4969	1495.4426
1496.7361	1503.1033	1506.3967
1507.5675	1517.6452	1553.6860
1556.6455	1609.0776	1614.7724
1667.9735	1715.2482	1745.9349
1842.5748	3061.5161	3063.5026
3064.8237	3069.7507	3075.3647
3084.0233	3106.8357	3113.7425
3116.1594	3128.0693	3132.1710
3134.0977	3145.9285	3154.2640
3168.1292	3174.4109	3178.1049
3186.9009	3191.0734	3195.9494
3235.9768	3242.1900	3243.6054
3246.0658	3260.3692	3263.2393

M2SS

Thermal energies (Hartree):

Zero-point correction = 0.31876800

Thermal correction to energy = 0.33896600

Thermal correction to enthalpy = 0.33991100

Thermal correction to Gibbs free energy = 0.26703800

Sum of electronic and zero-point energies = -1284.73590300

Sum of electronic and thermal energies = -1284.71570500

Sum of electronic and thermal enthalpies = -1284.71476100

Sum of electronic and thermal free energies = -1284.78763400

Final optimized coordinates (Angstrom):

C	0.280726	-1.067735	-0.093868
C	-0.665035	0.004244	0.454196
C	-2.110503	-0.219046	0.099154
C	-3.032401	-0.519444	1.101479
C	-2.525709	-0.143100	-1.233770
C	-4.368008	-0.751626	0.772845
H	-2.707953	-0.576776	2.136799
C	-3.860688	-0.367258	-1.558575
H	-1.812297	0.102684	-2.016026
C	-4.782226	-0.674842	-0.555616
H	-5.082055	-0.987691	1.554806
H	-4.181847	-0.303007	-2.592929
H	-5.821974	-0.851874	-0.810983
C	1.732005	-0.757694	0.262613

O	2.044278	0.088764	1.073672
O	2.572905	-1.516415	-0.410491
C	3.983834	-1.336715	-0.122199
H	4.135100	-1.522432	0.943760
H	4.241668	-0.297413	-0.339166
C	4.743544	-2.311866	-0.989958
H	5.813708	-2.205014	-0.798658
H	4.451773	-3.339912	-0.763908
H	4.559044	-2.114130	-2.048291
H	0.174261	-1.167281	-1.176250
Cl	-0.145785	-2.650182	0.627508
H	-0.532899	0.084092	1.537266
O	-0.225793	1.245234	-0.169585
C	0.314378	2.158608	0.584683
H	0.353216	2.017775	1.661800
N	0.790977	3.236929	0.063457
C	0.786737	3.492982	-1.381102
C	1.381728	4.279543	0.910048
H	0.251264	4.426265	-1.559382
H	1.821159	3.593180	-1.713209
H	0.299573	2.674192	-1.903154
H	0.819327	5.202933	0.767419
H	1.340443	3.975793	1.954387
H	2.418570	4.426232	0.605533

Frequencies (cm⁻¹):

24.3316	37.1540	40.3203
43.8792	53.6104	63.0872
85.8629	88.9681	99.4852
103.8403	147.0616	175.6334
192.0535	207.3985	223.8858
244.3619	255.6418	273.3643
288.3927	317.3271	345.8319
391.0434	413.9886	424.3490
427.9430	447.1351	494.2722
554.4401	604.9659	626.4657
648.3277	686.9011	715.7852
767.1075	793.3316	814.3170
862.5673	869.9926	877.0321
891.7878	912.2984	956.7202
1001.5213	1004.8660	1013.1641
1014.9010	1027.6715	1034.8936
1060.5377	1065.4150	1081.2410
1111.8239	1126.8454	1141.6567
1147.0594	1174.3063	1176.3292
1179.0194	1185.6746	1203.2789
1221.2580	1244.1258	1250.6281
1284.1852	1307.4795	1326.7976
1353.1947	1356.4550	1368.3991
1394.1365	1401.4902	1418.8703

1446.9098	1453.3770	1463.7983
1470.0652	1473.3844	1482.6975
1492.8250	1496.2254	1496.9454
1501.5846	1517.1034	1529.4297
1546.0067	1669.1182	1686.8378
1792.8741	1816.3095	3086.1438
3105.8480	3106.0598	3108.4817
3131.2363	3155.4645	3155.5859
3171.8383	3176.8709	3190.7102
3195.4853	3211.9036	3214.9409
3218.8592	3225.8819	3235.2287
3239.3298	3243.9333	3244.3930

M2SR

Thermal energies (Hartree):

Zero-point correction = 0.31838800

Thermal correction to energy = 0.33876000

Thermal correction to enthalpy = 0.33970400

Thermal correction to Gibbs free energy = 0.26552700

Sum of electronic and zero-point energies = -1284.73526000

Sum of electronic and thermal energies = -1284.71488900

Sum of electronic and thermal enthalpies = -1284.71394500

Sum of electronic and thermal free energies = -1284.78812200

Final optimized coordinates (Angstrom):

C	0.284543	-0.914972	-0.230743
C	-0.471635	0.218531	0.463030
H	-0.560434	-0.000659	1.531154
C	0.217384	1.540181	0.238345
C	0.214858	2.124843	-1.032289
C	0.888380	2.160365	1.293051
C	0.879238	3.330361	-1.241837
H	-0.315732	1.648008	-1.852285
C	1.558738	3.363767	1.077784
H	0.891501	1.700129	2.276882
C	1.553693	3.948799	-0.187731
H	0.871498	3.785635	-2.226568
H	2.079810	3.844073	1.899241
H	2.073212	4.887020	-0.353510
C	1.647209	-1.099985	0.431188
O	1.820091	-0.972531	1.621606
O	2.572120	-1.431093	-0.451428
C	3.900331	-1.683409	0.074567
H	3.822103	-2.481532	0.816794
H	4.243360	-0.772981	0.571874
C	4.778164	-2.067232	-1.093084
H	5.790030	-2.265147	-0.732142
H	4.401507	-2.969208	-1.580738
H	4.823557	-1.258692	-1.826172
H	0.393297	-0.722605	-1.298537

Cl	-0.604420	-2.470411	-0.067806
O	-1.793251	0.293409	-0.127385
C	-2.784868	-0.278117	0.492694
H	-2.638013	-0.682683	1.492242
N	-3.947912	-0.349837	-0.058131
C	-5.075131	-0.964268	0.653078
C	-4.224286	0.168436	-1.402900
H	-5.861969	-0.218057	0.767875
H	-5.442088	-1.802881	0.060467
H	-4.749193	-1.314949	1.630749
H	-4.976151	0.954557	-1.318629
H	-3.313271	0.564189	-1.843273
H	-4.613883	-0.650445	-2.009058

Frequencies (cm⁻¹):

11.8482	32.0532	39.7602
43.7578	47.8367	65.3408
75.9453	82.5318	95.5770
112.5035	141.7300	157.8214
185.4754	204.5111	215.5922
248.8496	263.3139	272.3674
293.6747	305.6790	329.7230
384.5404	412.5677	423.5207
425.1270	437.1662	489.3786
548.0161	617.7262	626.5226

641.1030	706.3114	715.4041
770.2017	786.8545	812.4435
840.3213	865.1852	875.1217
897.8464	908.8120	959.0560
1001.1260	1010.6480	1012.9893
1015.4824	1034.7195	1040.4488
1061.9487	1064.4937	1081.5457
1109.7852	1124.3471	1128.3866
1146.6408	1172.5809	1175.5868
1179.4148	1184.6255	1201.0547
1216.9480	1237.7193	1254.0109
1283.6151	1306.5342	1326.8451
1348.2711	1354.8699	1365.6795
1383.4530	1404.6069	1413.0535
1442.1133	1451.5065	1462.4119
1469.1893	1472.2025	1482.9324
1492.3065	1493.4710	1496.1580
1500.7708	1517.0198	1525.7657
1543.6206	1668.0221	1684.8583
1794.6356	1833.8541	3085.7518
3104.7201	3104.7405	3108.0477
3129.5773	3154.2562	3171.1822
3174.6976	3176.0315	3191.2021
3195.7900	3212.1860	3214.8583
3219.0630	3226.2166	3226.6148

3236.3755 3239.4021 3244.2851

M3SS

Thermal energies (Hartree):

Zero-point correction = 0.23596500

Thermal correction to energy = 0.25274100

Thermal correction to enthalpy = 0.25368500

Thermal correction to Gibbs free energy = 0.18859500

Sum of electronic and zero-point energies = -1225.67714300

Sum of electronic and thermal energies = -1225.66036700

Sum of electronic and thermal enthalpies = -1225.65942300

Sum of electronic and thermal free energies = -1225.72451300

Final optimized coordinates (Angstrom):

C	-0.486188	-0.534546	0.074607
C	0.568949	0.476767	-0.382311
C	1.978249	0.063799	-0.038102
C	2.856790	-0.333540	-1.046099
C	2.401992	0.058686	1.294194
C	4.152174	-0.740918	-0.726191
H	2.528602	-0.327002	-2.082108
C	3.696772	-0.343446	1.612576
H	1.724180	0.380470	2.080308
C	4.572868	-0.746090	0.602651
H	4.830867	-1.048994	-1.514869

H	4.022691	-0.342047	2.647664
H	5.581438	-1.059720	0.852343
C	-1.888625	-0.058251	-0.288275
O	-2.107457	0.761101	-1.153485
O	-2.811128	-0.658795	0.443518
C	-4.189340	-0.320995	0.149024
H	-4.379403	-0.562349	-0.899705
H	-4.310810	0.755849	0.288762
C	-5.057165	-1.123835	1.089517
H	-6.107408	-0.893968	0.895674
H	-4.903238	-2.194890	0.939466
H	-4.834205	-0.875164	2.129626
H	-0.415385	-0.715695	1.148794
Cl	-0.225651	-2.110882	-0.742601
H	0.465830	0.625135	-1.462969
O	0.239155	1.691686	0.309193
C	-0.129846	2.755851	-0.423331
H	-0.089265	2.595196	-1.509616
O	-0.462772	3.784419	0.100935

Frequencies (cm⁻¹):

23.6144	36.1569	40.9465
58.4480	66.0904	86.8526
106.9518	113.8916	154.9299
180.6636	200.9395	218.2604

245.4672	273.4324	293.3103
329.7022	337.7703	355.5542
394.6704	412.9861	494.1048
559.6532	613.6891	626.2120
673.8184	709.5340	716.1852
763.2987	792.8247	813.3429
867.3206	875.4802	878.8318
909.8883	953.4177	1004.7927
1011.4910	1015.4453	1031.8171
1051.5652	1059.4908	1066.6252
1082.3190	1112.0175	1140.7056
1147.2976	1174.1260	1179.0456
1199.9064	1209.6410	1219.9413
1239.2697	1255.9992	1306.6064
1327.5599	1354.3211	1359.0264
1389.3037	1393.8568	1417.3155
1444.3394	1448.5243	1483.4412
1492.7118	1499.6053	1517.4884
1544.8948	1668.6141	1686.8928
1824.9576	1848.9449	3084.7857
3104.5212	3105.4953	3110.3067
3153.3500	3159.8205	3170.4764
3174.9514	3211.8363	3214.6066
3223.3086	3233.3558	3241.5529

TS2SS'

Thermal energies (Hartree):

Zero-point correction = 0.41899500

Thermal correction to energy = 0.44789200

Thermal correction to enthalpy = 0.44883600

Thermal correction to Gibbs free energy = 0.35144100

Sum of electronic and zero-point energies = -1533.00782500

Sum of electronic and thermal energies = -1532.97892800

Sum of electronic and thermal enthalpies = -1532.97798400

Sum of electronic and thermal free energies = -1533.07537900

Final optimized coordinates (Angstrom):

C	0.098264	0.050521	-0.286087
C	0.504221	1.128371	0.652776
C	0.941276	2.402463	0.301821
C	1.189929	3.324255	1.359796
C	1.142847	2.805791	-1.050932
C	1.633668	4.599525	1.074882
H	1.030295	3.006577	2.385353
C	1.580930	4.083621	-1.320650
H	0.943777	2.119959	-1.867309
C	1.827136	4.972903	-0.260986
H	1.828888	5.306199	1.872380
H	1.734587	4.405511	-2.343608
H	2.174184	5.976727	-0.485192

C	0.326252	-1.322587	0.343797
O	-0.036416	-1.604174	1.459434
O	0.957668	-2.120139	-0.498989
C	1.354956	-3.410786	0.023711
H	0.452094	-3.977040	0.264463
H	1.914485	-3.234489	0.947359
C	2.192568	-4.080520	-1.039825
H	2.545342	-5.046464	-0.671019
H	1.608957	-4.246194	-1.948121
H	3.060319	-3.462946	-1.288864
H	0.559220	0.105965	-1.269725
Cl	-1.674941	0.322405	-0.485640
H	0.320683	0.907336	1.704639
O	2.641953	-0.185076	0.947424
C	3.437838	-0.360415	0.012827
H	3.417078	0.270967	-0.888885
N	4.383874	-1.301011	-0.016703
C	4.593461	-2.202923	1.105943
C	5.315769	-1.411277	-1.129139
H	4.476917	-3.239845	0.773974
H	5.606048	-2.071884	1.497863
H	3.867167	-1.977839	1.885242
H	5.302745	-2.431544	-1.522419
H	5.028020	-0.720396	-1.922157
H	6.329544	-1.174975	-0.793862

C	-4.928233	-0.403482	-0.113314
H	-4.253719	-1.129375	0.369811
O	-4.489621	0.545553	-0.765269
N	-6.226563	-0.674522	0.093294
C	-7.270967	0.166701	-0.465007
H	-7.889582	-0.414185	-1.156132
H	-7.906595	0.552092	0.337917
H	-6.809237	0.996649	-0.997102
C	-6.652096	-1.825061	0.870743
H	-7.265315	-2.489699	0.254838
H	-5.778216	-2.374862	1.223348
H	-7.240445	-1.500299	1.734018

Frequencies (cm⁻¹):

-32.3164	4.7302	10.6989
17.7674	28.0057	32.2366
40.0309	48.9835	57.6206
65.0046	71.7129	75.4913
79.7008	85.4206	91.5895
116.0376	122.6636	133.8861
147.8799	160.7144	162.7463
164.0623	184.9553	190.0845
211.8818	246.1706	265.5932
269.4875	278.6887	319.5267
330.3481	335.0332	344.5783

345.7565	373.5279	394.7126
401.6064	402.5878	407.8171
465.5153	502.4084	564.9153
612.7770	655.9570	668.6279
671.1043	704.3220	757.5284
790.5473	807.3327	820.9700
856.8044	869.5715	891.0493
892.3133	908.8874	977.5044
999.1250	1007.7327	1014.6165
1029.9917	1041.4275	1043.5180
1049.7207	1054.6309	1071.9562
1086.0742	1086.5806	1117.2371
1119.6675	1127.4195	1128.3519
1131.5524	1145.4443	1170.7793
1175.6193	1177.4633	1177.5478
1190.2805	1208.4758	1236.9981
1256.6391	1287.1958	1300.3601
1300.7502	1304.8304	1364.9427
1378.1640	1409.0027	1412.3743
1430.3363	1435.0185	1440.4144
1441.6734	1451.9037	1458.2683
1463.1054	1474.0933	1474.3551
1476.5556	1477.8439	1480.8301
1482.4672	1493.1074	1493.1188
1494.4819	1504.2496	1504.8990

1507.4667	1514.4126	1555.6326
1558.3327	1585.4987	1624.5916
1662.0183	1721.8358	1739.5179
1850.1283	3053.4321	3066.4591
3068.7963	3071.9230	3072.4962
3076.7887	3083.0843	3099.6231
3132.4923	3138.6127	3139.3944
3146.5709	3148.6984	3167.8208
3172.9911	3178.5523	3186.4876
3202.7088	3205.2422	3205.2609
3214.4725	3235.7891	3239.3918
3246.7301	3260.3863	3263.0899

TS2SR'

Thermal energies (Hartree):

Zero-point correction = 0.31433500

Thermal correction to energy = 0.33481000

Thermal correction to enthalpy = 0.33575400

Thermal correction to Gibbs free energy = 0.26271200

Sum of electronic and zero-point energies = -1284.68463000

Sum of electronic and thermal energies = -1284.66415500

Sum of electronic and thermal enthalpies = -1284.66321100

Sum of electronic and thermal free energies = -1284.73625300

Final optimized coordinates (Angstrom):

C	0.557810	-0.520406	-0.527613
C	-0.153906	0.449952	0.353956
H	-0.555698	0.041406	1.276877
C	-0.130376	1.839611	0.205543
C	0.327341	2.480595	-0.978470
C	-0.602208	2.622641	1.297029
C	0.329593	3.858515	-1.050592
H	0.657675	1.890203	-1.826607
C	-0.582881	4.000989	1.215675
H	-0.960480	2.125986	2.192575
C	-0.119040	4.612249	0.042292
H	0.670471	4.357710	-1.950836
H	-0.929530	4.606627	2.044374
H	-0.113254	5.696009	-0.024306
C	2.093452	-0.350195	-0.330415
O	2.620659	0.709414	-0.566821
O	2.693498	-1.444179	0.071108
C	4.137217	-1.356974	0.233347
H	4.342620	-0.562961	0.956643
H	4.562799	-1.072219	-0.734454
C	4.614393	-2.711636	0.702920
H	5.698233	-2.679372	0.837920
H	4.154568	-2.976603	1.659127
H	4.378569	-3.483309	-0.036373
H	0.361844	-0.299583	-1.579750

Cl	-0.010743	-2.179773	-0.223736
O	-2.147219	0.135137	-0.765648
C	-2.850939	-0.879648	-0.934999
H	-3.074928	-1.237669	-1.949100
N	-3.398842	-1.604876	0.030974
C	-4.103910	-2.847596	-0.253423
C	-3.214013	-1.252690	1.430602
H	-3.584062	-3.683012	0.223030
H	-5.123625	-2.793598	0.132352
H	-4.132608	-3.014433	-1.328885
H	-2.391967	-1.832845	1.867158
H	-3.004504	-0.188253	1.506929
H	-4.132314	-1.479226	1.975796

Frequencies (cm⁻¹):

-77.5268	24.5345	36.2614
43.3012	48.3697	57.6618
78.9893	84.6547	94.1036
97.7166	137.7504	142.2224
157.5274	163.1661	195.9464
206.7827	235.7515	266.2135
280.6023	292.0038	316.5927
334.5746	369.5464	380.4310
399.3034	413.9073	421.7901
444.9222	479.7125	585.1363

608.0126	625.1854	666.3358
668.4590	751.5291	792.5933
820.7086	843.1280	857.3127
870.3555	891.9345	908.3850
939.3703	984.9617	1003.6252
1009.5105	1025.5223	1039.6445
1051.7786	1053.0966	1061.9900
1084.9297	1110.4945	1124.4025
1132.8814	1143.4299	1152.9808
1175.8829	1181.2532	1189.4808
1198.3292	1209.4096	1257.9529
1282.5790	1299.5662	1310.1591
1325.1912	1367.2101	1402.0093
1403.9333	1421.8317	1437.7939
1444.2852	1457.7006	1468.8235
1477.6351	1479.5370	1483.9802
1493.8947	1495.4493	1503.2528
1512.2738	1517.0176	1547.7891
1565.1709	1628.4133	1659.0572
1703.7716	1834.0869	3068.0911
3074.8154	3084.6113	3091.9762
3097.0712	3142.2513	3144.2691
3151.2607	3160.0938	3162.4827
3166.0723	3201.4953	3219.1153
3230.4351	3238.4770	3241.7486

3245.9567 3251.8769 3258.1991

Me-R1

Thermal energies (Hartree):

Zero-point correction = 0.26362100

Thermal correction to energy = 0.27879300

Thermal correction to enthalpy = 0.27973700

Thermal correction to Gibbs free energy = 0.21832100

Sum of electronic and zero-point energies = -654.95841900

Sum of electronic and thermal energie = -654.94324700

Sum of electronic and thermal enthalpies = -654.94230200

Sum of electronic and thermal free energies = -655.00371800

Final optimized coordinates (Angstrom):

C	-4.108123	-0.661470	0.000148
H	-3.724183	-1.677320	0.000357
C	-5.417778	-0.394352	0.000098
H	-5.723915	0.651388	-0.000115
C	-3.115097	0.434496	-0.000077
O	-3.368463	1.624554	-0.000344
O	-1.861456	-0.042533	0.000035
C	-0.806496	0.933347	-0.000186
H	-0.910968	1.566755	0.886771
H	-0.910983	1.566367	-0.887418
C	0.510616	0.184185	-0.000034

H	0.562140	-0.462141	0.883702
H	0.562113	-0.462542	-0.883478
C	-6.496746	-1.426439	0.000310
H	-7.138390	-1.302652	0.878723
H	-7.138367	-1.303034	-0.878173
H	-6.087383	-2.438713	0.000533
C	1.699269	1.154583	-0.000267
H	1.638728	1.802555	0.881872
H	1.638711	1.802151	-0.882701
C	3.018128	0.419852	-0.000106
C	3.631145	0.052917	1.202845
C	3.630960	0.052076	-1.202897
C	4.827952	-0.663367	1.205888
H	3.166698	0.334812	2.145075
C	4.827765	-0.664208	-1.205625
H	3.166370	0.333316	-2.145253
C	5.430455	-1.024062	0.000212
H	5.291593	-0.936180	2.149080
H	5.291264	-0.937678	-2.148696
H	6.363617	-1.578599	0.000334

Frequencies (cm⁻¹):

23.8408	34.5224	40.5712
48.1165	94.7170	101.0354
112.0193	162.4857	179.2643

204.0869	214.5255	244.4169
297.8668	349.9815	379.1578
400.5394	415.3784	480.0572
534.4334	596.7047	629.1686
706.2569	716.0917	755.7277
756.0536	777.7782	834.8130
862.2719	870.9695	876.5363
926.6907	944.9328	1000.3681
1001.0857	1008.2680	1014.5294
1025.3299	1058.4920	1063.1229
1071.3886	1077.2882	1082.1250
1120.3717	1121.4549	1139.0310
1170.2721	1197.4674	1215.6043
1236.9928	1239.2506	1280.8757
1295.2634	1313.8850	1315.5762
1347.2252	1354.0500	1355.8532
1381.3003	1408.9572	1434.9870
1472.1948	1479.0489	1484.9151
1494.8203	1499.0900	1514.8074
1541.6656	1663.2204	1683.0367
1748.5670	1794.0844	3062.9162
3067.6621	3072.0517	3081.2719
3105.5655	3121.1512	3131.2248
3138.6374	3164.3192	3192.6534
3199.8020	3199.8814	3215.9831

3223.9967 3226.5292 3235.5722

Me-TS1

Thermal energies (Hartree):

Zero-point correction = 0.37121100

Thermal correction to energy = 0.39486300

Thermal correction to enthalpy = 0.39580700

Thermal correction to Gibbs free energy = 0.31254700

Sum of electronic and zero-point energies = -1363.17542800

Sum of electronic and thermal energies = -1363.15177600

Sum of electronic and thermal enthalpies = -1363.15083200

Sum of electronic and thermal free energies = -1363.23409200

Final optimized coordinates (Angstrom):

C	-1.517126	2.485098	-0.418609
C	-2.625249	3.187646	-0.061226
H	-2.882898	3.210090	0.997413
C	-0.652614	1.868911	0.630219
O	-0.954829	1.778003	1.801181
O	0.489646	1.428427	0.110027
C	1.416718	0.814410	1.028805
H	0.935391	-0.063459	1.471402
H	1.639053	1.528140	1.827858
C	2.657845	0.442863	0.244652
H	2.385156	-0.235335	-0.571842

H	3.086984	1.345202	-0.205374
C	-3.475609	3.959505	-1.003820
H	-4.528685	3.696360	-0.870288
H	-3.383237	5.024142	-0.760994
H	-3.182861	3.803223	-2.043045
C	3.699118	-0.229202	1.149802
H	3.265574	-1.133684	1.591964
H	3.952442	0.445980	1.975295
C	4.950731	-0.586388	0.384766
C	5.055722	-1.813035	-0.279972
C	6.010920	0.321040	0.287187
C	6.192375	-2.126925	-1.024861
H	4.240063	-2.529122	-0.209497
C	7.150016	0.011997	-0.456178
H	5.943376	1.276986	0.801532
C	7.243810	-1.214162	-1.115187
H	6.258543	-3.085136	-1.531234
H	7.964948	0.726852	-0.517626
H	8.130578	-1.457974	-1.691752
H	-1.152610	2.475581	-1.441638
Cl	-3.208884	0.762845	-0.579396
C	-4.155031	-1.574970	0.166243
H	-3.515660	-1.353883	1.020010
O	-4.222756	-0.741575	-0.823719
N	-4.838534	-2.673378	0.159080

C	-5.726403	-3.043142	-0.947687
H	-5.379087	-3.988767	-1.366744
H	-6.735852	-3.165548	-0.552116
H	-5.712275	-2.267067	-1.708491
C	-4.756116	-3.616789	1.278900
H	-4.400860	-4.576264	0.900926
H	-4.067548	-3.237221	2.031838
H	-5.750890	-3.733800	1.710457

Frequencies (cm⁻¹):

-161.0518	11.4349	19.7036
28.8748	38.6859	44.5996
49.4646	50.1315	71.2745
78.3288	100.7233	102.1311
116.4642	127.2629	157.9308
171.0148	180.9054	190.3938
196.6069	224.4232	234.1721
279.7021	292.6200	296.8305
308.4636	350.8241	378.7771
399.8514	415.0270	421.0986
436.9528	468.5198	484.0991
534.5362	596.7676	629.3072
704.5387	716.0964	733.1142
756.4227	758.7139	777.5421
835.2633	865.8439	876.2794

881.6953	893.2241	923.8582
945.3963	994.6726	1008.1274
1008.5316	1014.3584	1025.6475
1029.1974	1052.5941	1061.7719
1069.6572	1072.2316	1078.8721
1082.5409	1121.0448	1122.6066
1125.6583	1149.5039	1168.4970
1172.8910	1184.5052	1199.1362
1216.5037	1239.4048	1250.2215
1279.2607	1283.4481	1299.3675
1315.7487	1318.9330	1335.0726
1348.0566	1357.6353	1364.2679
1385.3253	1403.7429	1437.5914
1449.9628	1457.3580	1462.4789
1468.0783	1472.5786	1475.9637
1484.9988	1493.1859	1496.1694
1499.0074	1499.6831	1514.5129
1522.4014	1542.3857	1663.5278
1680.8778	1683.9028	1760.5806
1812.2304	3064.6770	3072.4611
3074.7519	3088.1053	3103.0634
3105.5098	3107.6833	3125.5147
3140.8413	3146.4361	3180.1347
3187.8785	3192.1843	3199.4632
3199.5196	3204.2789	3213.7243

3216.5138 3217.6598 3224.4672

3232.5329 3236.1319 3236.8232

Me-TS1'

Thermal energies (Hartree):

Zero-point correction = 0.37126900

Thermal correction to energy = 0.39487700

Thermal correction to enthalpy = 0.39582100

Thermal correction to Gibbs free energy = 0.31276400

Sum of electronic and zero-point energies = -1363.17524400

Sum of electronic and thermal energies = -1363.15163600

Sum of electronic and thermal enthalpies = -1363.15069200

Sum of electronic and thermal free energies = -1363.23374900

Final optimized coordinates (Angstrom):

C	1.472576	-2.302411	0.654400
C	2.573768	-3.068018	0.426371
H	2.692188	-3.487186	-0.572539
C	0.435972	-2.147803	-0.408766
O	0.553740	-2.555307	-1.544544
O	-0.628611	-1.497613	0.053027
C	-1.701747	-1.280551	-0.886261
H	-2.044174	-2.253083	-1.253150
H	-1.310458	-0.708109	-1.733015
C	-2.800322	-0.533203	-0.159740

H	-3.136355	-1.124009	0.699872
H	-2.404729	0.413701	0.224821
C	3.592645	-3.407561	1.452756
H	4.598139	-3.199842	1.076094
H	3.427626	-2.871512	2.388442
H	3.544127	-4.485595	1.643864
C	-3.986488	-0.257062	-1.093410
H	-4.371394	-1.207221	-1.481357
H	-3.642580	0.328960	-1.953435
C	-5.091528	0.486127	-0.382276
C	-6.089591	-0.209491	0.308801
C	-5.113951	1.884769	-0.362868
C	-7.087261	0.474697	1.002986
H	-6.085624	-1.297152	0.299081
C	-6.109419	2.573913	0.329828
H	-4.345829	2.437508	-0.899048
C	-7.099916	1.869925	1.015362
H	-7.856415	-0.081314	1.530439
H	-6.113765	3.659706	0.330628
H	-7.877487	2.404325	1.552097
H	1.245004	-1.908178	1.640515
Cl	3.026192	-0.618510	-0.087683
C	4.640070	1.425039	0.319304
H	4.684939	0.957415	1.302144
O	3.913182	0.898537	-0.614227

N	5.320107	2.504625	0.102850
C	5.312122	3.195361	-1.190317
H	4.963054	4.216748	-1.031487
H	6.331856	3.211760	-1.578107
H	4.654674	2.676804	-1.883227
C	6.151407	3.096280	1.155847
H	5.803692	4.112867	1.343864
H	6.074449	2.503614	2.065626
H	7.186533	3.117087	0.812385

Frequencies (cm⁻¹):

-166.8648	9.5594	21.2508
28.8893	37.7992	45.5989
53.5248	57.2787	69.8779
93.9869	99.4537	100.2071
115.4148	126.4401	166.0130
172.6894	178.9572	189.2433
196.3978	228.6153	237.6806
265.1405	293.4229	298.7031
315.4748	348.2184	377.4643
397.6487	414.6750	419.1073
433.5631	469.5787	481.1724
533.9618	596.7405	629.0510
704.1181	716.5885	733.8472
756.5024	757.4408	778.2228

835.3206	864.5422	877.0916
882.3296	894.1548	923.2368
946.2224	994.6302	1008.6875
1009.8225	1014.2177	1026.6986
1034.4911	1052.5945	1061.8803
1069.6933	1070.9314	1080.6155
1082.0520	1121.3986	1122.6482
1126.7106	1149.8893	1169.0121
1173.1643	1184.1473	1199.3877
1215.7370	1239.4972	1249.2191
1279.6714	1281.9956	1298.5070
1312.3919	1319.3510	1337.4528
1348.4871	1357.2352	1364.7084
1384.6592	1402.9048	1437.8078
1451.7544	1456.2153	1461.7367
1467.9752	1473.9952	1475.2022
1484.7661	1494.9720	1496.0830
1496.6524	1498.5209	1513.7985
1525.8092	1542.8070	1663.4329
1679.4413	1684.6252	1759.2012
1814.8619	3064.9691	3072.1893
3074.5331	3088.5620	3104.5733
3107.5664	3107.6484	3125.3213
3140.8076	3146.5743	3181.1212
3188.7941	3194.0491	3197.7573

3199.0399	3202.5708	3214.5778
3217.3993	3217.6314	3223.0614
3234.1966	3234.3459	3234.4408

Me-M1

Thermal energies (Hartree):

Zero-point correction = 0.26687000

Thermal correction to energy = 0.28305800

Thermal correction to enthalpy = 0.28400300

Thermal correction to Gibbs free energy = 0.22012500

Sum of electronic and zero-point energies = -1114.87635300

Sum of electronic and thermal energies = -1114.86016600

Sum of electronic and thermal enthalpies = -1114.85922100

Sum of electronic and thermal free energies = -1114.92309900

Final optimized coordinates (Angstrom):

C	-3.400838	-0.386626	0.402522
C	-4.634019	-0.803139	-0.262727
H	-4.798255	-0.373133	-1.250007
C	-2.379768	0.388213	-0.423296
O	-2.703827	1.136913	-1.309279
O	-1.165035	0.078990	-0.035146
C	-0.076177	0.702484	-0.768971
H	-0.176505	1.785821	-0.658627
H	-0.187657	0.439971	-1.824598

C	1.217393	0.181745	-0.181954
H	1.253687	0.418366	0.887070
H	1.249149	-0.908671	-0.282648
C	-5.407648	-1.999472	0.145916
H	-6.468248	-1.866052	-0.065594
H	-5.035560	-2.811754	-0.492020
H	-5.245894	-2.266478	1.190198
C	2.428369	0.803364	-0.891502
H	2.393167	1.893372	-0.783763
H	2.376108	0.580115	-1.963240
C	3.725614	0.277028	-0.325712
C	4.345910	0.915651	0.753206
C	4.305895	-0.887564	-0.839708
C	5.518964	0.403335	1.307524
H	3.907072	1.824034	1.159505
C	5.478491	-1.403910	-0.288934
H	3.835329	-1.391670	-1.680796
C	6.088555	-0.759286	0.787740
H	5.989366	0.914006	2.142260
H	5.917378	-2.306850	-0.702358
H	7.002848	-1.157892	1.215977
H	-3.032679	-0.967853	1.244003
Cl	-4.781933	0.698618	0.949142

Frequencies (cm⁻¹):

25.0049	36.7198	39.3092
45.4626	70.9661	101.5724
111.0363	144.2639	173.9824
196.5909	220.2296	234.4224
259.9931	303.1797	350.2074
366.9281	376.4823	415.4965
426.3126	469.6330	528.6439
590.8304	621.0275	629.1373
716.1304	744.3601	755.8362
776.3374	781.7178	834.5062
865.1883	875.6610	907.4691
943.5477	951.9371	993.9532
1007.5501	1014.5471	1026.2012
1030.4428	1060.9672	1065.0527
1071.0403	1093.9870	1116.0641
1120.2598	1122.0210	1171.1221
1176.5667	1198.4146	1216.4467
1228.9131	1239.0948	1277.3918
1284.8530	1299.3604	1322.6671
1348.2017	1357.3371	1367.2864
1385.5370	1402.5238	1433.5802
1450.8810	1476.7780	1486.1904
1496.4420	1498.9181	1503.9572
1513.5851	1542.9306	1663.7730
1685.0001	1861.0427	3067.4179

3072.7430	3078.9275	3098.8298
3111.9377	3131.7189	3160.3838
3167.1623	3199.3141	3200.6282
3212.4396	3217.1198	3223.0170
3224.7380	3236.6133	3238.5843

Me-M1'

Thermal energies (Hartree):

Zero-point correction = 0.26686900

Thermal correction to energy = 0.28306800

Thermal correction to enthalpy = 0.28401200

Thermal correction to Gibbs free energy = 0.21999100

Sum of electronic and zero-point energies = -1114.87634700

Sum of electronic and thermal energies = -1114.86014800

Sum of electronic and thermal enthalpies = -1114.85920400

Sum of electronic and thermal free energies = -1114.92322500

Final optimized coordinates (Angstrom):

C	3.402751	0.384939	-0.404597
C	4.637152	0.802415	0.257327
H	4.800395	0.378915	1.247561
C	2.379880	-0.381460	0.426818
O	2.701984	-1.120942	1.321177
O	1.165861	-0.077031	0.032586
C	0.076444	-0.694335	0.771175

H	0.186789	-0.421586	1.824343
H	0.177998	-1.778533	0.671328
C	-1.216989	-0.180347	0.178145
H	-1.248186	0.911249	0.265506
H	-1.254193	-0.429968	-0.887864
C	5.414874	1.993319	-0.159683
H	6.474928	1.858021	0.053273
H	5.254350	2.253284	-1.205881
H	5.045259	2.811597	0.471924
C	-2.427509	-0.792703	0.896610
H	-2.373410	-0.556636	1.965522
H	-2.393109	-1.883979	0.802343
C	-3.725629	-0.272588	0.326991
C	-4.305374	0.896935	0.830158
C	-4.348437	-0.922978	-0.743464
C	-5.480096	1.406486	0.277547
H	-3.833158	1.410191	1.664745
C	-5.523569	-0.417487	-1.299604
H	-3.910066	-1.835341	-1.141325
C	-6.092801	0.749987	-0.790320
H	-5.918650	2.313239	0.682870
H	-5.996002	-0.937401	-2.127466
H	-7.008848	1.143046	-1.219927
H	3.036661	0.960516	-1.250740
Cl	4.780722	-0.708584	-0.944056

Frequencies (cm⁻¹):

23.2559	35.4182	39.3441
44.3418	69.1200	102.0170
110.9011	143.9834	173.9710
197.1667	220.5231	234.5086
259.5227	303.7716	349.5691
367.9986	376.7257	415.4305
426.1234	469.7337	528.4389
590.8110	620.4357	629.1405
716.0406	744.7616	755.9552
776.2280	781.4956	834.5135
865.1963	875.5946	907.8205
943.5584	952.0611	993.7566
1007.5307	1014.5651	1026.1599
1030.1589	1060.8660	1064.8937
1070.8589	1094.1004	1115.8904
1120.5270	1121.8668	1171.1062
1176.6221	1198.2809	1216.3640
1230.0865	1239.0318	1277.8652
1284.8387	1299.1446	1322.5753
1347.9640	1357.1974	1367.2790
1385.5465	1402.7761	1433.6423
1450.9337	1478.2071	1486.2661
1496.1508	1498.9260	1504.5872

1513.4334	1542.7248	1663.5529
1684.7756	1861.3308	3067.2472
3073.2189	3078.8416	3098.7088
3111.6808	3131.5569	3160.2813
3167.6096	3199.6955	3200.5931
3212.7523	3217.2726	3223.2687
3225.0655	3236.7549	3239.5082

Me-TS2-SS

Thermal energies (Hartree):

Zero-point correction = 0.37128600

Thermal correction to energy = 0.39447400

Thermal correction to enthalpy = 0.39541800

Thermal correction to Gibbs free energy = 0.31621900

Sum of electronic and zero-point energies = -1363.20921800

Sum of electronic and thermal energies = -1363.18603000

Sum of electronic and thermal enthalpies = -1363.18508600

Sum of electronic and thermal free energies = -1363.26428500

Final optimized coordinates (Angstrom):

C	3.090700	-1.060903	0.523271
C	4.129620	-0.043739	0.639392
H	4.332728	0.527871	-0.263829
C	2.070013	-0.802324	-0.578293
O	2.383852	-0.418584	-1.676990
O	0.849677	-1.020291	-0.133882

C	-0.231414	-0.781205	-1.071363
H	-0.215540	-1.587376	-1.810598
H	-0.039572	0.167228	-1.582304
C	-1.518731	-0.755468	-0.276619
H	-1.623701	-1.694215	0.278001
H	-1.476079	0.055102	0.461176
C	4.899808	0.205500	1.858140
H	5.959713	0.329595	1.630154
H	4.527835	1.179964	2.207494
H	4.731922	-0.543605	2.630628
C	-2.732213	-0.557425	-1.194962
H	-2.782270	-1.385418	-1.911083
H	-2.608827	0.364020	-1.776245
C	-4.015206	-0.487331	-0.401918
C	-4.702183	-1.655551	-0.054531
C	-4.515516	0.741922	0.039731
C	-5.862639	-1.598055	0.716704
H	-4.325514	-2.617443	-0.394906
C	-5.675881	0.804691	0.811343
H	-3.994331	1.658326	-0.228128
C	-6.352874	-0.366397	1.152469
H	-6.385780	-2.513962	0.974105
H	-6.052833	1.767668	1.142125
H	-7.257763	-0.319440	1.750096
H	2.694543	-1.475158	1.447019

Cl	4.463060	-2.092320	-0.082374
C	1.242374	1.840763	0.906141
H	0.490094	1.720500	1.697612
O	2.420473	1.491155	1.093443
N	0.765337	2.377372	-0.217059
C	1.625984	2.682567	-1.353174
H	1.250927	2.179223	-2.248453
H	1.628905	3.762669	-1.523927
H	2.636892	2.340550	-1.141197
C	-0.622477	2.806439	-0.320799
H	-1.107208	2.299336	-1.161315
H	-1.155833	2.567805	0.600509
H	-0.665889	3.885446	-0.490925

Frequencies (cm⁻¹):

-212.2973	22.1541	35.1362
39.9689	49.6755	57.4218
62.7878	79.0843	85.4793
98.2066	103.8161	108.2908
140.9319	146.7092	163.2250
171.2107	183.9445	202.8013
207.2055	215.2636	249.2001
271.8911	287.9267	300.6859
329.5119	353.8503	371.5586
375.7505	388.7547	413.7559

414.5495	453.7981	529.0218
593.7921	629.0660	660.5750
674.8063	716.5673	752.2578
755.7246	776.5558	788.1160
834.7087	853.1599	863.9786
877.4082	884.9333	935.2249
947.6184	987.6911	1008.8577
1014.5391	1026.4069	1030.9541
1036.7225	1046.3582	1061.6961
1066.6816	1070.9613	1084.4657
1119.4556	1124.0198	1128.0911
1130.5385	1143.5841	1172.4501
1178.7331	1191.1313	1201.9671
1216.4470	1231.6160	1239.3521
1270.5355	1284.9392	1293.7480
1299.4739	1321.6729	1347.5961
1359.3428	1361.2035	1363.6915
1384.8119	1425.5574	1430.9283
1441.4600	1448.3685	1462.0130
1469.8249	1472.7796	1479.0281
1486.8380	1492.7293	1495.9910
1498.9301	1505.6812	1511.6124
1524.9987	1543.7579	1555.9554
1663.3038	1684.5001	1707.7709
1859.3440	3059.1203	3065.9788

3071.8274	3075.3280	3081.6803
3098.1884	3105.3597	3109.1779
3127.4526	3142.9887	3151.6123
3152.7356	3156.4313	3183.1606
3198.7854	3199.8219	3213.0500
3216.2729	3217.1908	3223.1701
3225.8287	3235.8450	3245.4759

Me-TS2-RR

Thermal energies (Hartree):

Zero-point correction = 0.37120800

Thermal correction to energy = 0.39454300

Thermal correction to enthalpy = 0.39548700

Thermal correction to Gibbs free energy = 0.31469800

Sum of electronic and zero-point energies = -1363.20821200

Sum of electronic and thermal energies = -1363.18487700

Sum of electronic and thermal enthalpies = -1363.18393300

Sum of electronic and thermal free energies = -1363.26472200

Final optimized coordinates (Angstrom):

C	3.196490	-0.619672	-0.605414
C	4.110376	0.346042	0.000391
H	4.314814	0.201676	1.058318
C	2.186173	-1.214265	0.367915
O	2.499259	-1.751630	1.398603

O	0.965557	-0.996121	-0.078529
C	-0.115443	-1.352068	0.818204
H	0.037163	-0.812300	1.759340
H	-0.061782	-2.426283	1.015462
C	-1.404417	-0.951179	0.135766
H	-1.352477	0.112918	-0.120765
H	-1.514420	-1.509295	-0.800492
C	4.781940	1.419976	-0.733266
H	5.847382	1.438302	-0.492857
H	4.611193	1.384111	-1.808530
H	4.355678	2.343126	-0.314375
C	-2.617156	-1.200470	1.041621
H	-2.481008	-0.661597	1.986355
H	-2.679905	-2.268012	1.281393
C	-3.895474	-0.746618	0.378686
C	-4.386156	0.546902	0.585643
C	-4.586043	-1.594360	-0.494165
C	-5.539156	0.986098	-0.065492
H	-3.863380	1.213392	1.268113
C	-5.739173	-1.160188	-1.147231
H	-4.217630	-2.604187	-0.659927
C	-6.218844	0.132994	-0.935033
H	-5.908454	1.991915	0.110039
H	-6.265075	-1.832381	-1.818354
H	-7.117961	0.471480	-1.440203

H	2.806484	-0.378259	-1.591589
Cl	4.684522	-1.642846	-0.773478
C	1.182292	1.930127	1.091985
H	0.747051	2.132907	2.079845
O	2.324588	1.448524	0.997925
N	0.386749	2.246305	0.072557
C	0.816855	2.078929	-1.307888
H	0.372092	1.177238	-1.740947
H	0.502215	2.949927	-1.886025
H	1.903485	2.006312	-1.339506
C	-0.924712	2.844707	0.289247
H	-1.681006	2.295459	-0.278073
H	-1.177975	2.804225	1.349348
H	-0.921136	3.885658	-0.045152

Frequencies (cm⁻¹):

-222.0254	10.7831	30.8726
34.9627	41.0501	43.0707
57.8211	69.1468	82.2980
92.9611	110.3851	113.4776
134.3734	147.1378	155.5179
178.5684	194.5671	206.6259
212.0842	214.5608	247.4375
259.5088	274.2779	292.0065
335.5666	348.7397	369.7926

371.1631	382.9329	415.0980
416.0683	448.1837	529.6021
593.4195	629.1372	661.4547
693.2003	716.6550	754.5876
755.5796	777.4588	787.7957
834.9135	864.6535	868.7859
877.1000	889.6493	928.4717
946.1895	988.9841	1008.4515
1014.3048	1026.2456	1034.7621
1039.4515	1046.8219	1060.7503
1067.9967	1073.9920	1087.4496
1120.7194	1122.1467	1126.0710
1130.4078	1148.3549	1172.2590
1175.1237	1198.6521	1198.9976
1215.2837	1226.7330	1239.5582
1270.8743	1283.7886	1298.0173
1299.8374	1320.5343	1347.8131
1357.5322	1358.3450	1365.3917
1385.6679	1428.9005	1430.1555
1443.5608	1447.9098	1461.9179
1465.1988	1473.3245	1482.5030
1483.9929	1495.2420	1497.5481
1500.8989	1509.6577	1511.6003
1523.4435	1542.6763	1553.8562
1662.8767	1683.8770	1713.1678

1864.2092	3060.5130	3067.5383
3075.7952	3079.3178	3082.6502
3090.0570	3105.8641	3112.3976
3133.2136	3145.4453	3148.7167
3153.9754	3158.3018	3186.0827
3197.5204	3197.7450	3199.9195
3210.1187	3215.9404	3221.0330
3224.2930	3235.4320	3251.9842

Me-TS2-SR

Me_M2SS

Thermal energies (Hartree):

Zero-point correction = 0.37639100

Thermal correction to energy = 0.39911100

Thermal correction to enthalpy = 0.40005600

Thermal correction to Gibbs free energy = 0.31980400

Sum of electronic and zero-point energies = -1363.27424300

Sum of electronic and thermal energies = -1363.25152200

Sum of electronic and thermal enthalpies = -1363.25057800

Sum of electronic and thermal free energies = -1363.33082900

Final optimized coordinates (Angstrom):

C	2.164298	-1.529619	0.406612
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C	3.651140	-1.255041	0.179120
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C	1.288041	-0.576012	-0.399930
O	1.722388	0.137621	-1.279165
O	0.025607	-0.632746	-0.022013
C	-0.904542	0.204667	-0.749143
H	-0.852411	-0.065430	-1.807900
H	-0.588169	1.245829	-0.636044
C	-2.281427	-0.037204	-0.168451
H	-2.535314	-1.098747	-0.264305
H	-2.274655	0.206047	0.899939
C	4.575776	-2.112680	1.014233
H	5.608688	-1.801914	0.848841
H	4.334953	-2.010958	2.075370
H	4.476535	-3.159522	0.724593
C	-3.337094	0.814563	-0.886701
H	-3.332615	0.572892	-1.955799
H	-3.075218	1.874676	-0.792058
C	-4.716196	0.579490	-0.318810
C	-5.529090	-0.442837	-0.820238
C	-5.189231	1.348617	0.749694
C	-6.785262	-0.692340	-0.267914
H	-5.174490	-1.046029	-1.652945
C	-6.444744	1.103243	1.305655
H	-4.568477	2.148652	1.146636
C	-7.246950	0.080855	0.797882
H	-7.404530	-1.487399	-0.672021

H	-6.797699	1.712577	2.132124
H	-8.225635	-0.109546	1.227032
H	1.914989	-1.456037	1.467530
Cl	1.777913	-3.202569	-0.109571
H	3.879127	-1.329249	-0.888478
O	3.848008	0.126307	0.602043
C	4.099771	1.023702	-0.305072
H	4.265536	0.720446	-1.335433
N	4.171714	2.271907	0.011708
C	4.493316	3.283017	-1.001140
C	3.951928	2.760136	1.377223
H	3.660671	3.984081	-1.068751
H	5.396927	3.809629	-0.692104
H	4.654078	2.802780	-1.964606
H	3.195430	3.544722	1.338855
H	3.618820	1.945353	2.014062
H	4.890512	3.172685	1.751168

Frequencies (cm⁻¹):

14.1721	20.9245	33.9085
36.7424	45.0078	48.8488
58.6874	70.5450	97.8214
103.5480	121.5122	147.1934
155.3859	164.2687	174.3901
195.9904	221.9485	239.5772

259.4466	268.0409	287.9711
309.1737	352.6630	364.8907
395.8335	405.0845	414.5760
415.3323	433.6993	486.6386
512.6821	541.6532	596.1134
614.6078	629.5315	664.1187
715.5378	759.6712	770.6181
784.1418	835.4889	856.5089
868.4010	873.8811	875.7042
927.8450	944.2588	954.9696
987.8706	1005.4998	1007.3231
1014.3431	1025.2523	1041.0796
1061.3927	1067.0936	1073.1699
1079.5255	1095.9118	1121.5908
1122.8690	1124.8723	1142.5605
1172.7611	1172.8388	1183.5605
1184.5723	1199.5576	1217.3752
1239.6939	1246.0346	1262.9105
1284.2214	1287.1145	1299.4356
1321.0271	1348.5460	1357.9147
1358.2151	1362.4701	1381.7450
1399.7822	1415.1616	1424.9869
1449.9614	1451.1406	1468.0531
1471.6278	1474.1322	1487.0033
1488.1042	1491.0466	1494.8982

1496.5027	1496.6146	1500.6194
1515.5812	1534.2228	1542.9975
1663.8649	1684.5411	1791.0966
1818.5448	3065.4620	3076.2657
3092.8687	3093.4529	3105.3761
3107.3077	3109.3294	3126.6692
3127.9702	3153.1772	3153.3519
3179.5711	3189.5254	3192.6142
3194.2793	3198.1045	3198.2042
3214.3746	3218.9339	3222.4237
3233.9049	3237.9524	3244.8488

Me-M2RR

Thermal energies (Hartree):

Zero-point correction = 0.37591500

Thermal correction to energy = 0.39866400

Thermal correction to enthalpy = 0.39960800

Thermal correction to Gibbs free energy = 0.31886600

Sum of electronic and zero-point energies = -1363.27403300

Sum of electronic and thermal energies = -1363.25128400

Sum of electronic and thermal enthalpies = -1363.25034000

Sum of electronic and thermal free energies = -1363.33108200

Final optimized coordinates (Angstrom):

C	2.003709	1.422628	0.586485
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C	2.523570	0.396126	1.603163
C	1.130307	0.746810	-0.469598
O	1.550466	0.210522	-1.466316
O	-0.142810	0.790038	-0.101335
C	-1.083216	0.098923	-0.956556
H	-0.760216	-0.942122	-1.053146
H	-1.055352	0.567782	-1.944605
C	-2.448163	0.210890	-0.311381
H	-2.417129	-0.242883	0.685754
H	-2.706551	1.268249	-0.185427
C	1.427808	-0.282564	2.397822
H	1.877144	-0.956727	3.128311
H	0.838158	0.468849	2.926671
H	0.765146	-0.854575	1.744660
C	-3.517062	-0.485256	-1.164752
H	-3.243518	-1.537520	-1.303319
H	-3.544875	-0.023451	-2.158418
C	-4.881211	-0.396423	-0.523869
C	-5.325587	-1.394096	0.350150
C	-5.708236	0.707913	-0.756466
C	-6.566910	-1.292742	0.978275
H	-4.693623	-2.259396	0.536702
C	-6.950129	0.814232	-0.130799
H	-5.376234	1.488983	-1.436701
C	-7.383264	-0.186892	0.739388

H	-6.897642	-2.078571	1.650569
H	-7.580857	1.676279	-0.325715
H	-8.350975	-0.107505	1.224650
Cl	3.381940	2.238577	-0.207476
H	3.243036	0.891330	2.262158
H	1.428997	2.183855	1.114580
O	3.209734	-0.640223	0.855753
C	4.492083	-0.535892	0.655889
H	5.091414	0.124520	1.279942
N	5.050200	-1.246420	-0.262959
C	6.505861	-1.248522	-0.439277
C	4.251408	-2.105944	-1.148197
H	6.867022	-2.271314	-0.324792
H	6.735696	-0.883562	-1.440764
H	6.968596	-0.607373	0.308893
H	4.787934	-2.199303	-2.090860
H	4.137093	-3.089236	-0.687741
H	3.277424	-1.645020	-1.310078

Frequencies (cm⁻¹):

12.2676	16.2419	20.4989
38.8713	44.0557	55.2148
67.0032	79.6268	82.8175
110.8537	113.1753	132.1007
158.7621	171.5219	175.9753

212.5549	224.4777	235.2609
247.1051	267.3820	278.6958
315.2223	345.9203	368.9086
380.5932	397.5541	414.7245
433.9923	446.1667	496.0758
517.2897	528.8158	593.9215
603.8952	628.8016	710.2665
715.4329	756.4179	773.5521
816.8967	830.1001	841.2925
860.5559	864.1327	874.7742
916.7402	943.4072	953.8673
975.8283	1006.7526	1008.7737
1014.2629	1025.0281	1032.4737
1060.3907	1061.0693	1067.4561
1070.6978	1087.2432	1117.4041
1121.8749	1123.3325	1138.2294
1162.8160	1171.3136	1176.1593
1180.4902	1197.9080	1215.6138
1237.0838	1239.3366	1276.9220
1283.2403	1286.1350	1297.7526
1319.2379	1325.3630	1347.9134
1353.4483	1356.6250	1374.0094
1383.6269	1407.2502	1426.7316
1442.0481	1452.4819	1463.4927
1465.5181	1474.2715	1481.7779

1484.1928	1490.7166	1493.4200
1494.6018	1495.9359	1497.8918
1513.0078	1517.9010	1542.5855
1663.2575	1684.6196	1789.1291
1843.7176	3064.8681	3074.6266
3091.3073	3095.5340	3101.8176
3104.1022	3108.3357	3122.0803
3126.5563	3151.0268	3175.6732
3183.7871	3188.0552	3193.4473
3195.7870	3199.4069	3199.6479
3215.5942	3216.4566	3218.1168
3223.8713	3227.2624	3236.0648

Me-M2SR

Thermal energies (Hartree):

Zero-point correction = 0.37613800

Thermal correction to energy = 0.39898800

Thermal correction to enthalpy = 0.39993300

Thermal correction to Gibbs free energy = 0.31925800

Sum of electronic and zero-point energies = -1363.27292100

Sum of electronic and thermal energies = -1363.25007100

Sum of electronic and thermal enthalpies = -1363.24912700

Sum of electronic and thermal free energies = -1363.32980200

Final optimized coordinates (Angstrom):

C	1.880058	-0.329121	-0.142573
C	3.133429	-1.199752	-0.134499
C	0.701984	-1.066698	0.485844
O	0.831810	-1.977855	1.270475
O	-0.450199	-0.560789	0.080024
C	-1.644722	-1.131841	0.662998
H	-1.566028	-1.056006	1.751505
H	-1.688630	-2.189721	0.387188
C	-2.826879	-0.354020	0.124923
H	-2.721539	0.701687	0.399004
H	-2.835088	-0.412262	-0.969257
C	3.002210	-2.411765	-1.034009
H	3.937950	-2.972819	-1.026379
H	2.205201	-3.059799	-0.666741
H	2.777653	-2.105197	-2.058429
C	-4.146545	-0.904566	0.682480
H	-4.121084	-0.869426	1.777716
H	-4.252123	-1.956629	0.393770
C	-5.331235	-0.116217	0.177820
C	-5.791655	1.004065	0.877882
C	-5.961870	-0.462238	-1.022102
C	-6.856822	1.762201	0.392139
H	-5.312180	1.281920	1.813721
C	-7.027595	0.292535	-1.512275
H	-5.615869	-1.332883	-1.574545

C	-7.478332	1.408060	-0.805782
H	-7.203512	2.626346	0.950655
H	-7.507973	0.007243	-2.443284
H	-8.309554	1.994770	-1.184066
H	1.633960	-0.002137	-1.154201
Cl	2.140578	1.163917	0.830977
H	3.378318	-1.486355	0.892413
C	5.042083	0.173177	0.158875
H	4.996840	-0.067114	1.219481
O	4.219260	-0.397784	-0.670469
N	5.929023	1.005569	-0.269363
C	6.047814	1.373831	-1.684690
H	6.157514	2.456674	-1.741955
H	6.936556	0.891469	-2.095841
H	5.160930	1.055301	-2.225920
C	6.898372	1.609737	0.651081
H	6.764640	2.691877	0.635194
H	6.739370	1.229685	1.658535
H	7.902921	1.354899	0.311464

Frequencies (cm⁻¹):

19.1673	20.3945	24.0045
35.8010	47.2223	48.6714
56.5660	64.8356	94.6872
104.7319	109.4846	145.0659

154.0254	158.9443	170.2646
202.2952	222.7406	225.4366
249.2775	260.7585	277.6784
318.3221	350.7571	364.6270
391.2532	393.8810	414.4596
418.5337	429.4676	488.4718
513.8032	539.6056	591.7840
609.3850	629.8042	684.2425
715.6995	756.1795	769.5947
783.2433	834.2508	837.6154
866.3205	872.5598	875.6163
929.9813	944.8347	971.0427
985.1148	1007.2729	1012.7676
1014.4755	1025.6068	1035.6600
1061.1508	1066.3490	1071.7779
1080.6656	1098.1491	1119.0951
1122.2974	1126.8496	1141.9149
1172.8977	1173.0924	1180.2628
1184.9206	1198.9282	1216.6885
1238.7796	1240.8884	1272.0050
1283.4308	1288.7661	1297.8972
1319.4126	1348.7000	1355.0691
1356.9233	1362.6780	1378.2776
1388.8929	1407.3066	1421.6012
1444.7961	1453.2827	1467.1090

1469.3551	1473.5377	1485.3274
1489.3058	1492.6503	1495.4543
1496.5894	1496.9308	1499.6466
1514.4823	1533.7600	1543.0703
1663.9612	1684.8148	1793.2395
1834.6930	3064.9214	3075.3485
3091.6727	3094.1241	3104.7402
3107.3119	3108.6095	3125.6559
3126.8451	3151.1603	3166.3563
3181.3077	3192.2300	3193.5232
3194.9856	3199.8754	3200.0355
3215.3661	3215.6243	3224.0886
3224.2321	3234.9551	3236.6833

Me-PSS

Thermal energies (Hartree):

Zero-point correction = 0.29353900

Thermal correction to energy = 0.31285300

Thermal correction to enthalpy = 0.31379700

Thermal correction to Gibbs free energy = 0.24152100

Sum of electronic and zero-point energies = -1304.21469200

Sum of electronic and thermal energies = -1304.19537800

Sum of electronic and thermal enthalpies = -1304.19443400

Sum of electronic and thermal free energies = -1304.26671000

Final optimized coordinates (Angstrom):

C	2.773578	-0.865856	0.424374
C	4.184575	-0.289975	0.308407
C	1.788673	-0.099658	-0.450583
O	2.123479	0.566052	-1.405387
O	0.541026	-0.270347	-0.043342
C	-0.487037	0.366886	-0.834458
H	-0.422698	-0.018221	-1.856721
H	-0.290831	1.443058	-0.852888
C	-1.819137	0.045343	-0.190611
H	-1.955190	-1.041486	-0.157877
H	-1.821196	0.409869	0.842802
C	5.196151	-0.967642	1.210905
H	6.160535	-0.465094	1.115126
H	4.870592	-0.913077	2.253281
H	5.319853	-2.014876	0.930443
C	-2.975109	0.688768	-0.968462
H	-2.961837	0.328022	-2.003402
H	-2.830395	1.774772	-1.001193
C	-4.309959	0.372761	-0.337772
C	-5.023424	-0.770936	-0.712078
C	-4.837058	1.192528	0.665964
C	-6.235162	-1.089539	-0.099127
H	-4.626085	-1.415294	-1.493002
C	-6.048265	0.878463	1.282173

H	-4.293774	2.086359	0.964106
C	-6.751404	-0.264790	0.900859
H	-6.777368	-1.979249	-0.404705
H	-6.444251	1.528141	2.056796
H	-7.695730	-0.509237	1.377054
H	2.434502	-0.862326	1.461928
Cl	2.750074	-2.576263	-0.127927
H	4.497691	-0.329213	-0.740922
O	4.061350	1.083251	0.718495
C	4.288280	2.042057	-0.191240
H	4.612829	1.669618	-1.172843
O	4.149631	3.205324	0.081067

Frequencies (cm⁻¹):

16.2724	22.5574	35.9988
40.1982	55.3488	65.6940
72.7307	105.6665	119.0228
144.7357	161.3119	180.2909
199.8984	213.8180	237.4836
243.0097	273.6807	314.1000
342.6579	350.2611	370.2136
398.4436	415.1821	478.3954
508.4954	540.9407	596.4969
629.7270	651.7540	683.8361
715.6963	757.7888	768.1175

780.3093	835.2435	854.1278
867.6797	875.5793	928.7961
944.4740	962.1880	993.1319
1007.2911	1014.4159	1025.3988
1046.1470	1051.1025	1061.7054
1067.9383	1072.3647	1119.1652
1122.4233	1128.8666	1135.7234
1172.4056	1182.2574	1198.8932
1216.5608	1222.6062	1239.3683
1245.0160	1264.2398	1283.6456
1298.7151	1319.8815	1348.8866
1354.7765	1357.2594	1377.8962
1386.0922	1409.3580	1422.6127
1446.4222	1449.4785	1485.5160
1488.9192	1493.0988	1496.5872
1499.0500	1514.2328	1542.9043
1663.7268	1685.0795	1827.3605
1844.4944	3065.3574	3075.6503
3087.5190	3089.4475	3105.6562
3108.5965	3109.7955	3126.4348
3148.7735	3158.7049	3171.9054
3185.8477	3198.9345	3199.3110
3216.1271	3223.5879	3235.8549

Me-TS3

Thermal energies (Hartree):

Zero-point correction = 0.47884300

Thermal correction to energy = 0.50899800

Thermal correction to enthalpy = 0.50994200

Thermal correction to Gibbs free energy = 0.41278500

Sum of electronic and zero-point energies = -1611.55071800

Sum of electronic and thermal energies = -1611.52056300

Sum of electronic and thermal enthalpies = -1611.51961900

Sum of electronic and thermal free energies = -1611.61677700

Final optimized coordinates (Angstrom):

C	-1.949216	-0.267612	1.161009
C	-2.871972	0.871890	0.758390
C	-0.969541	-0.522693	0.017133
O	-1.386923	-0.612575	-1.118706
O	0.292997	-0.615370	0.371976
C	1.247715	-0.794512	-0.700832
H	1.132458	0.041080	-1.400775
H	1.010134	-1.722649	-1.228148
C	2.626459	-0.825410	-0.076921
H	2.771217	0.076080	0.529754
H	2.705825	-1.687121	0.594850
C	-3.540837	1.735755	1.773337
H	-4.273557	2.380938	1.290310
H	-4.037174	1.105078	2.513310

H	-2.791646	2.341380	2.283524
C	3.715026	-0.901883	-1.155791
H	3.616848	-0.042874	-1.830659
H	3.570017	-1.805641	-1.758401
C	5.095818	-0.910665	-0.545516
C	5.741840	0.290984	-0.234731
C	5.734811	-2.115533	-0.235742
C	6.997482	0.290302	0.371747
H	5.255851	1.234669	-0.473537
C	6.990998	-2.121627	0.370987
H	5.244405	-3.056398	-0.474503
C	7.626071	-0.917756	0.676625
H	7.486360	1.231818	0.602808
H	7.474411	-3.066071	0.601597
H	8.604822	-0.920558	1.145944
H	-2.555004	-1.167846	1.275309
Cl	-1.178386	0.001210	2.744663
H	-3.030218	1.014571	-0.300223
O	-4.540382	-0.309162	0.577206
C	-4.715660	-0.848124	-0.541636
H	-3.960564	-0.750148	-1.333578
N	-5.776475	-1.566633	-0.860941
C	-5.910765	-2.182105	-2.175700
C	-6.860234	-1.794752	0.087341
H	-5.993966	-3.265878	-2.065654

H	-6.808146	-1.800626	-2.668288
H	-5.037045	-1.947602	-2.783570
H	-6.930612	-2.862568	0.309726
H	-6.660734	-1.239190	1.001041
H	-7.800704	-1.458262	-0.355357
C	-0.951035	2.394101	-0.693574
H	-1.693869	2.376928	-1.500935
O	-1.256328	2.078543	0.481845
N	0.268347	2.747652	-1.056752
C	1.359140	2.783257	-0.087462
H	2.255553	2.367328	-0.554294
H	1.560848	3.815011	0.213029
H	1.082029	2.192983	0.785778
C	0.565599	3.186977	-2.415796
H	1.336939	2.544251	-2.847252
H	-0.335368	3.130224	-3.026298
H	0.925238	4.218317	-2.396721

Frequencies (cm⁻¹):

-589.1900	16.9010	18.1920
26.4469	29.6260	32.3344
35.9456	43.7252	54.4069
56.8952	81.9290	85.0248
89.5240	99.3272	113.2705
118.2030	148.1223	152.7604

156.6498	159.2834	168.0160
174.5322	179.4404	182.8096
197.4757	220.2669	229.8151
242.5548	274.0110	277.2047
313.9615	327.6654	353.6591
364.6485	373.9476	377.5455
385.3697	396.6100	405.9088
414.2164	425.6153	428.5014
459.9541	519.4411	530.5445
587.8668	629.1360	629.3981
675.5717	683.7837	715.9232
761.3754	771.5308	783.9558
823.4471	836.4053	865.0344
875.7525	893.7397	895.8690
944.8344	948.3746	971.4415
1007.5124	1014.3514	1019.0390
1025.9243	1035.5557	1049.0803
1052.0890	1061.3713	1068.3877
1069.7066	1086.8359	1087.8650
1106.3128	1119.1063	1121.3925
1122.8472	1125.0851	1128.1354
1147.7026	1149.2183	1171.8550
1176.4384	1180.7943	1198.4156
1214.3394	1234.0159	1238.9177
1250.0013	1282.5855	1285.6029

1297.0004	1297.6766	1299.4401
1318.3763	1347.5958	1355.6056
1356.8408	1364.8040	1388.4089
1418.9567	1423.8252	1427.5560
1444.0029	1449.9215	1450.2667
1465.7799	1467.2814	1469.7785
1472.5255	1476.5488	1476.7396
1476.8786	1478.1240	1488.6735
1495.6896	1495.9112	1498.6421
1500.8492	1501.9519	1504.5153
1515.0574	1541.7238	1553.5359
1555.1089	1663.4338	1683.9401
1708.4299	1722.8704	1812.4889
3061.3618	3075.0421	3082.3470
3083.9628	3084.6896	3085.7858
3087.3039	3106.5649	3106.8314
3109.9551	3119.9483	3125.6636
3147.6155	3157.3915	3157.8249
3160.2355	3161.9580	3162.2413
3190.3556	3194.7347	3197.4765
3197.6811	3199.5391	3200.6600
3208.2508	3216.5459	3217.7365
3225.3168	3236.2152	3293.7326

M3

Thermal energies (Hartree):

Zero-point correction = 0.37138200

Thermal correction to energy = 0.39582700

Thermal correction to enthalpy = 0.39677100

Thermal correction to Gibbs free energy = 0.30963800

Sum of electronic and zero-point energies = -1363.19758000

Sum of electronic and thermal energies = -1363.17313500

Sum of electronic and thermal enthalpies = -1363.17219000

Sum of electronic and thermal free energies = -1363.25932300

Final optimized coordinates (Angstrom):

C	-1.228160	1.946617	-0.407410
C	-2.233164	2.903135	0.028256
H	-2.382143	2.969868	1.104825
C	-0.339299	1.316529	0.654890
O	-0.703741	1.160341	1.793164
O	0.832637	1.013811	0.143550
C	1.802099	0.435733	1.057409
H	1.368836	-0.478661	1.472466
H	1.968360	1.150041	1.868674
C	3.061909	0.164481	0.264580
H	2.832239	-0.517410	-0.561548
H	3.428180	1.101197	-0.169773
C	-2.739315	3.992310	-0.843155
H	-3.771909	4.238754	-0.596919

H	-2.117014	4.865298	-0.609546
H	-2.636642	3.757239	-1.902493
C	4.147326	-0.451171	1.158359
H	3.770195	-1.380551	1.600257
H	4.371030	0.234131	1.983831
C	5.407541	-0.734573	0.376430
C	5.568789	-1.949417	-0.298588
C	6.416193	0.229006	0.273079
C	6.710926	-2.197194	-1.059522
H	4.793154	-2.708258	-0.223667
C	7.560579	-0.013974	-0.486604
H	6.304368	1.176278	0.795609
C	7.710924	-1.228808	-1.155917
H	6.821549	-3.147002	-1.573828
H	8.335562	0.743595	-0.552751
H	8.601949	-1.420902	-1.745327
H	-0.830994	2.018787	-1.416278
Cl	-2.893865	1.142195	-0.447780
C	-5.235462	-1.289051	0.068473
H	-4.550664	-1.464138	0.912823
O	-5.051043	-0.363925	-0.730160
N	-6.247125	-2.163501	0.016440
C	-7.254683	-2.091119	-1.028797
H	-7.258594	-3.021041	-1.604928
H	-8.242666	-1.948231	-0.581411

H	-7.024323	-1.253803	-1.685033
C	-6.389426	-3.227310	0.996350
H	-6.358698	-4.201244	0.499448
H	-5.576282	-3.171981	1.721283
H	-7.343400	-3.127747	1.522001

Frequencies (cm⁻¹):

9.6157	21.8820	23.3019
25.9230	27.2366	37.2944
39.1505	49.2010	66.1298
80.5503	90.9843	93.9409
108.6361	118.0048	151.3448
165.7418	175.1444	201.5593
221.0094	239.5045	257.2234
263.8031	304.9074	347.0060
351.1024	354.3429	373.7248
378.2976	409.3439	415.8915
430.6814	471.2174	528.7816
586.9878	605.9108	628.8686
674.4768	716.6208	747.5936
758.0943	776.5195	780.7708
834.6333	865.9071	876.0677
892.4756	912.3868	944.4526
953.5538	996.6145	1008.1500
1014.5005	1026.4373	1032.7302

1044.7021	1060.8948	1065.3977
1071.4097	1088.7639	1094.1499
1113.0648	1121.2117	1121.9544
1127.4084	1127.6665	1171.5162
1177.5805	1178.6423	1199.0297
1216.6634	1237.4385	1239.6596
1277.6592	1284.7758	1299.7069
1304.4389	1321.8766	1348.3094
1357.7860	1366.6623	1385.7807
1404.4966	1432.3531	1434.7988
1446.6492	1452.5273	1461.1359
1477.3781	1478.8676	1485.1876
1486.4276	1495.8465	1495.9384
1499.5477	1505.7312	1509.9595
1516.5758	1542.9734	1557.9488
1663.3056	1684.9624	1728.9534
1855.1551	3067.4786	3068.0538
3072.4012	3076.1716	3077.4472
3078.7083	3098.6180	3111.6915
3131.2900	3137.4215	3143.6327
3159.7601	3168.0978	3182.5770
3198.4235	3199.9098	3206.9317
3211.6761	3216.3525	3223.4996
3225.4649	3235.9086	3239.0563

M4

Thermal energies (Hartree):

Zero-point correction = 0.20960800

Thermal correction to energy = 0.22299900

Thermal correction to enthalpy = 0.22394300

Thermal correction to Gibbs free energy = 0.16731400

Sum of electronic and zero-point energies = -1036.35555400

Sum of electronic and thermal energies = -1036.34216300

Sum of electronic and thermal enthalpies = -1036.34121800

Sum of electronic and thermal free energies = -1036.39784800

Final optimized coordinates (Angstrom):

C	-2.482764	-0.092812	0.480394
C	-3.860139	-0.285118	0.035490
H	-4.020904	-1.041341	-0.730441
C	-1.400853	-1.043879	0.077979
O	-0.179656	-0.327092	0.142222
C	-5.029647	0.153064	0.839919
H	-5.871012	0.406700	0.195457
H	-5.313190	-0.718784	1.442203
H	-4.786955	0.980325	1.506566
H	-2.326012	0.474004	1.396618
Cl	-2.931000	1.141949	-0.857404
C	0.931363	-1.075359	-0.053695
O	0.868050	-2.265807	-0.262198

C	2.181371	-0.278953	0.020501
C	2.164542	1.100465	0.251490
C	3.393788	-0.955123	-0.147434
C	3.366762	1.799968	0.314448
H	1.220616	1.618149	0.379917
C	4.591533	-0.250694	-0.082879
H	3.383766	-2.025307	-0.325789
C	4.577566	1.126205	0.148170
H	3.359327	2.869873	0.493302
H	5.533883	-0.772380	-0.211657
H	5.512471	1.675165	0.198954
H	-1.410796	-1.865178	0.805240
H	-1.562485	-1.457753	-0.921002

Frequencies (cm⁻¹):

27.2490	35.7885	58.2886
62.6370	119.7397	162.7513
198.6800	211.2103	250.0137
278.2214	316.7060	319.5262
412.1579	416.4762	447.6587
463.5215	478.1356	523.6769
563.1936	624.2976	690.2735
694.7668	724.5496	823.2971
859.9428	877.6247	924.3470
949.6669	974.5180	986.1825

1016.1036	1019.1008	1038.0271
1049.1350	1066.9667	1099.7117
1107.3529	1111.7054	1132.7352
1176.1048	1181.5049	1191.3583
1195.6159	1252.6153	1271.1208
1302.3540	1329.1162	1342.2176
1354.6848	1405.4986	1425.6462
1456.7399	1478.5988	1486.6209
1494.9715	1523.5273	1539.8294
1664.3433	1681.0095	1821.5588
3078.9099	3082.9623	3151.2041
3169.3612	3208.8086	3215.8434
3222.0595	3222.4227	3231.7285
3237.5358	3244.9856	3250.3380

M5

Thermal energies (Hartree):

Zero-point correction = 0.31458700

Thermal correction to energy = 0.33569700

Thermal correction to enthalpy = 0.33664100

Thermal correction to Gibbs free energy = 0.26194700

Sum of electronic and zero-point energies = -1284.68075500

Sum of electronic and thermal energies = -1284.65964500

Sum of electronic and thermal enthalpies = -1284.65870100

Sum of electronic and thermal free energies = -1284.73339600

Final optimized coordinates (Angstrom):

C	2.977840	0.809962	0.445148
C	4.256217	0.408980	-0.134280
H	4.378346	0.577655	-1.202471
C	1.964880	1.574671	-0.348459
O	0.692710	1.202413	0.159903
C	5.486166	0.236168	0.686554
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H	5.257883	-0.034246	1.717674
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Frequencies (cm⁻¹):

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414.3689	415.3528	449.0347
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1446.3561	1458.9411	1459.9595
1473.9534	1478.8096	1484.6631
1489.8024	1492.0983	1494.3496
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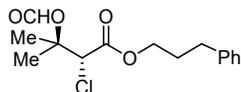
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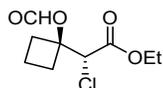
Reference

- [1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, F. Ding Williams, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford, CT, 2016.
- [2] Tian Lu, Feiwu Chen, *J. Comput. Chem.*, 33, 580-592 (2012).
- [3] C. Y. Legault, CYLview, 1.0b, Université de Sherbrooke, 2009, <http://www.cylview.org>.

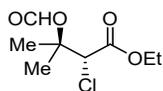
9. Characterization data for the electrolysis products



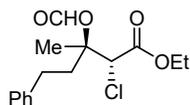
3-Phenylpropyl (R)-2-chloro-3-(formyloxy)-3-methylbutanoate (2). Yield = 90%, electricity = 2.30 F mol⁻¹, t = 6.0 h; Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.89 (s, 1H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.16–7.08 (m, 3H), 4.89 (s, 1H), 4.13 (t, *J* = 6.5 Hz, 2H), 2.63 (dd, *J* = 8.5, 6.8 Hz, 2H), 1.97–1.89 (m, 2H), 1.62 (s, 3H), 1.61 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 167.4, 159.8, 140.9, 128.7, 128.5, 126.3, 82.9, 65.6, 61.4, 32.1, 30.1, 23.7, 23.1; ESI HRMS *m/z* (M+Na)⁺ calcd 321.0864, obsd 321.0864.



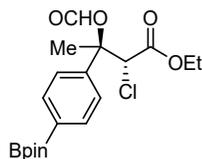
Ethyl 2-chloro-2-(1-(formyloxy)cyclobutyl)acetate (3). Yield = 41%, electricity = 2.02 F mol⁻¹, t = 4.0 h, t = 2.2 h; Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (s, 1H), 4.88 (s, 1H), 4.25 (qd, *J* = 7.1, 1.3 Hz, 2H), 2.84–2.69 (m, 2H), 2.56–2.40 (m, 2H), 1.99 (dtt, *J* = 11.7, 10.2, 4.8 Hz, 1H), 1.77 (dtt, *J* = 11.7, 9.3, 8.2 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 159.7, 83.2, 62.6, 58.8, 31.2, 31.2, 14.2, 14.1; ESI HRMS *m/z* (M+Na)⁺ calcd 243.0395, obsd 243.0395.



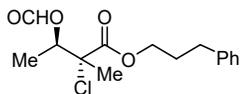
Ethyl 2-chloro-3-(formyloxy)-3-methylbutanoate (4). Yield = 42%, electricity = 1.86 F mol⁻¹, t = 2.0 h; Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (s, 1H), 4.94 (s, 1H), 4.26 (qd, *J* = 7.2, 1.0 Hz, 2H), 1.68 (d, *J* = 3.6 Hz, 6H), 1.31 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.4, 159.9, 83.0, 62.4, 61.4, 23.6, 23.1, 14.2; ESI HRMS *m/z* (M+Na)⁺ calcd 231.0395, obsd 231.0393.



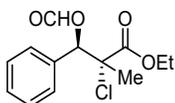
Ethyl 2-chloro-3-(formyloxy)-3-methyl-5-phenylpentanoate (5). Yield = 72%, electricity = 2.33 F mol⁻¹, t = 2.5 h; ¹H NMR (600 MHz, CDCl₃) δ 7.94 (s, 1H), 7.23–7.19 (m, 2H), 7.14–7.10 (m, 3H), 5.01 (s, 1H), 4.22–4.15 (m, 2H), 2.63–2.57 (m, 2H), 2.46–2.39 (m, 1H), 2.21–2.14 (m, 1H), 1.65 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 167.4, 159.7, 141.1, 128.7, 128.6, 126.3, 85.0, 62.5, 60.0, 37.6, 29.5, 20.6, 14.2; ESI HRMS *m/z* (M+Na)⁺ calcd 321.0864, obsd 321.0869.



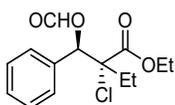
Ethyl 2-chloro-3-(formyloxy)-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)butanoate (6). Yield = 51%, electricity = 3.27 F mol⁻¹, t = 3.5 h; Colorless oil; Isolated as a 7.4:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 7.95 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.51 (s, 1H), 4.12 (qt, *J* = 7.3, 3.7 Hz, 2H), 2.11 (s, 3H), 1.27 (s, 12H), 1.17 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 167.1, 158.8, 142.6, 135.1, 125.2, 124.6, 84.4, 84.1, 63.3, 62.4, 25.0, 20.1, 14.1; ESI HRMS *m/z* (M+Na)⁺ calcd 419.1403, obsd 419.1404.



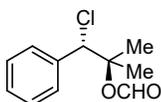
3-Phenylpropyl (3R)-2-chloro-3-(formyloxy)-2-methylbutanoate (8). Yield = 79%, electricity = 2.33 F mol⁻¹, t = 2.5 h; Colorless oil. Isolated as a 3.7:1 mixture of regioisomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 1H), 7.25–7.19 (m, 2H), 7.16–7.08 (m, 3H), 5.51 (q, *J* = 6.3 Hz, 1H), 4.11 (t, *J* = 6.4 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.97–1.88 (m, 2H), 1.69 (s, 3H), 1.35 (d, *J* = 6.2 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 169.5, 159.6, 140.9, 128.7, 128.6, 126.3, 83.0, 73.0, 65.9, 32.1, 30.1, 22.5, 15.0; ESI HRMS *m/z* (M+Na)⁺ calcd 321.0864, obsd 321.0866.



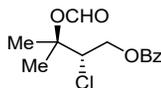
Ethyl 2-chloro-3-(formyloxy)-2-methyl-3-phenylpropanoate (9). Yield = 70%, electricity = 4.67 F mol⁻¹, t = 5.0 h; Colorless oil; Isolated as a 14:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 1.0 Hz, 1H), 7.46–7.41 (m, 2H), 7.38–7.33 (m, 3H), 6.40 (s, 1H), 4.34–4.19 (m, 2H), 1.72 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 169.3, 158.9, 134.1, 129.2, 128.7, 128.1, 77.6, 67.7, 62.8, 22.4, 14.1; ESI HRMS *m/z* (M+Na)⁺ calcd 293.0551, obsd 293.0551.



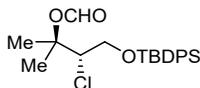
Ethyl 2-chloro-2-((formyloxy)(phenyl)methyl)butanoate (10). Yield = 66%, electricity = 4.67 F mol⁻¹, t = 5.0 h; Faint yellow oil; Isolated as a 3.7:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 0.9 Hz, 1H), 7.37–7.31 (m, 2H), 7.28–7.23 (m, 3H), 6.32 (s, 1H), 4.17–4.04 (m, 2H), 2.19 (dq, *J* = 14.3, 7.1 Hz, 1H), 1.95 (dq, *J* = 14.6, 7.4 Hz, 1H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 168.2, 159.4, 134.9, 129.3, 128.5, 128.2, 77.5, 76.9, 62.8, 32.1, 14.2, 9.3; ESI HRMS *m/z* (M+Na)⁺ calcd 307.0708, obsd 307.0710.



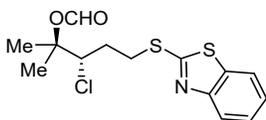
1-Chloro-2-methyl-1-phenylpropan-2-yl formate (11). Yield = 40%, electricity = 1.86 F mol⁻¹, t = 2.0 h; Colorless oil; Isolated as a 2:1 mixture of regioisomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 8.01 (s, 1H), 7.46–7.42 (m, 2H), 7.36–7.31 (m, 3H), 5.38 (s, 1H), 1.58 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 160.3, 137.4, 129.3, 128.8, 128.3, 84.8, 68.0, 23.8, 23.4; ESI HRMS *m/z* (M+Na)⁺ calcd 235.0496, obsd 235.0496.



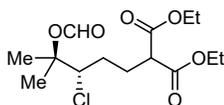
2-Chloro-3-(formyloxy)-3-methylbutyl benzoate (12). Yield = 46%, electricity = 0.93 F mol⁻¹, t = 1.0 h; Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 8.04–7.96 (m, 2H), 7.95–7.91 (m, 1H), 7.51 (dtd, *J* = 7.3, 4.3, 3.5, 1.8 Hz, 1H), 7.43–7.36 (m, 2H), 4.70 (dt, *J* = 11.8, 3.2 Hz, 1H), 4.61 (dt, *J* = 8.2, 3.1 Hz, 1H), 4.40 (ddt, *J* = 11.0, 7.6, 2.7 Hz, 1H), 1.64 (s, 3H), 1.63 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.3, 159.9, 133.5, 13.0, 129.7, 128.7, 83.6, 65.2, 63.7, 24.3, 23.2; ESI HRMS *m/z* (M+Na)⁺ calcd 293.0551, obsd 293.0554.



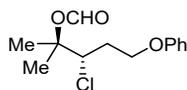
4-((*tert*-Butyldiphenylsilyloxy)-3-chloro-2-methylbutan-2-yl formate (13). Yield = 61%, electricity = 1.56 F mol⁻¹, t = 1.7 h; Colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.83 (s, 1H), 7.61 (dt, *J* = 7.9, 1.5 Hz, 4H), 7.39–7.35 (m, 2H), 7.35–7.30 (m, 4H), 4.37 (dd, *J* = 6.8, 4.2 Hz, 1H), 3.90 (dd, *J* = 11.4, 4.2 Hz, 1H), 3.77 (dd, *J* = 11.5, 6.8 Hz, 1H), 1.49 (s, 6H), 1.00 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 160.0, 135.8, 133.1 (d, *J* = 5.2 Hz, 1C), 130.1 (d, *J* = 2.2 Hz, 1C), 128.0, 83.9, 67.3, 64.9, 26.9, 24.2, 23.7, 19.4; ESI HRMS *m/z* (M+Na)⁺ calcd 427.1467, obsd 427.1471.



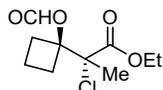
5-(Benzo[*d*]thiazol-2-ylthio)-3-chloro-2-methylpentan-2-yl formate (14). Yield = 54%, electricity = 1.56 F mol⁻¹, t = 1.7 h; Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.87 (s, 1H), 7.79 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.69 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.38–7.32 (m, 1H), 7.23 (td, *J* = 7.6, 1.2 Hz, 1H), 4.47 (dd, *J* = 11.2, 2.0 Hz, 1H), 3.63 (ddd, *J* = 13.6, 8.2, 4.3 Hz, 1H), 3.32 (dt, *J* = 13.6, 7.9 Hz, 1H), 2.44 (dtd, *J* = 14.4, 8.0, 2.0 Hz, 1H), 2.05 (dddd, *J* = 14.5, 11.2, 8.0, 4.3 Hz, 1H), 1.54 (s, 6H), 1.52 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.2, 160.0, 153.4, 135.5, 126.3, 124.5, 121.8, 121.2, 84.5, 66.1, 32.6, 31.2, 23.8, 22.9; ESI HRMS *m/z* (M+Na)⁺ calcd 352.0203, obsd 352.0206.



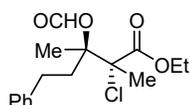
Diethyl 2-(3-chloro-4-(formyloxy)-4-methylpentyl)malonate (15). Yield = 46%, electricity = 1.56 F mol⁻¹, t = 1.7 h; Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (s, 1H), 4.22 (dd, *J* = 11.2, 2.0 Hz, 1H), 4.21–4.07 (m, 4H), 3.29 (dd, *J* = 7.8, 6.8 Hz, 1H), 2.29–2.17 (m, 1H), 1.88 (ttdd, *J* = 16.1, 7.8, 6.4, 3.9 Hz, 2H), 1.63–1.56 (m, 1H), 1.52 (s, 3H), 1.50 (s, 3H), 1.21 (tt, *J* = 7.1, 1.2 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 169.3, 169.2, 160.0, 84.7, 67.0, 61.7, 51.4, 30.2, 26.7, 23.8, 22.7, 14.3; ESI HRMS *m/z* (M+Na)⁺ calcd 345.1075, obsd 345.1074.



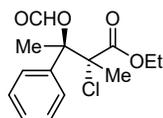
3-Chloro-2-methyl-5-phenoxy-pentan-2-yl formate (16). Yield = 59%, electricity = 1.56 F mol⁻¹, t = 1.7 h; Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 1H), 7.25–7.18 (m, 2H), 6.91–6.82 (m, 3H), 4.49 (dd, *J* = 11.4, 2.0 Hz, 1H), 4.14–4.07 (m, 2H), 2.35 (dddd, *J* = 16.0, 8.8, 6.8, 1.9 Hz, 1H), 1.93 (ddt, *J* = 18.5, 11.4, 4.2 Hz, 1H), 1.58 (s, 3H), 1.57 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 160.0, 129.7, 121.2, 116.1, 114.8, 84.5, 64.8, 64.0, 32.7, 23.8, 22.8; ESI HRMS *m/z* (M+Na)⁺ calcd 279.0758, obsd 279.0758.



Ethyl 2-chloro-2-(1-(formyloxy)cyclobutyl)propanoate (17). Yield = 59%, electricity = 1.40 F mol⁻¹, t = 1.5 h; Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 8.01 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.82 (dddd, *J* = 14.2, 7.4, 4.1, 1.4 Hz, 1H), 2.74–2.60 (m, 3H), 2.14 – 1.98 (m, 1H), 1.76 – 1.62 (m, 4H), 1.23 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 169.4, 159.7, 88.0, 71.3, 62.6, 30.2, 29.7, 23.0, 14.1, 13.4; ESI HRMS *m/z* (M+Na)⁺ calcd 257.0551, obsd 257.0550.

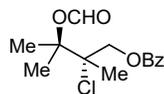


Ethyl 2-chloro-3-(formyloxy)-2,3-dimethyl-5-phenylpentanoate (18). Yield = 40%, electricity = 3.07 F mol⁻¹, t = 3.3 h; Colorless oil; Isolated as a 20:1 mixture of regioisomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 8.23 (s, 1H), 7.25–7.19 (m, 2H), 7.16–7.09 (m, 3H), 4.18 (qd, *J* = 7.1, 1.7 Hz, 2H), 2.73–2.58 (m, 1H), 2.35 (ddd, *J* = 14.2, 11.4, 5.4 Hz, 1H), 2.08–1.97 (m, 1H), 1.79 (s, 3H), 1.78 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 169.3, 160.3, 141.2, 128.8, 128.6, 126.4, 87.0, 75.5, 63.0, 38.5, 30.7, 25.0, 20.9, 14.1; ESI HRMS *m/z* (M+Na)⁺ calcd 335.1021, obsd 335.1019.

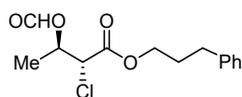


Ethyl 2-chloro-3-(formyloxy)-2-methyl-3-phenylbutanoate (19). Yield = 39%, electricity = 4.67 F mol⁻¹, t = 5.0 h; Colorless oil; Isolated as a 4.3:1 mixture of regioisomers and only the major isomer was

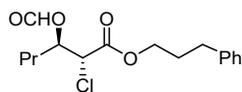
shown. ^1H NMR (400 MHz, CDCl_3) δ 8.13 (s, 1H), 7.37–7.28 (m, 5H), 4.19 (q, $J = 7.2$ Hz, 2H), 2.24 (s, 3H), 1.70 (s, 3H), 1.23 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.2, 159.1, 138.1, 128.4, 127.8, 127.4, 87.0, 73.9, 62.7, 25.1, 22.6, 14.0; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 307.0708, obsd 307.0705.



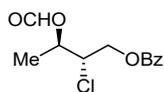
2-Chloro-3-(formyloxy)-2,3-dimethylbutyl benzoate (20). Yield = 42%, electricity = 1.55 F mol $^{-1}$, $t = 1.7$ h; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 8.05–7.95 (m, 3H), 7.56–7.49 (m, 1H), 7.44–7.36 (m, 2H), 4.65–4.54 (m, 2H), 1.76 (s, 3H), 1.74 (s, 3H), 1.67 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.3, 159.7, 133.5, 129.9, 129.9, 128.7, 86.4, 74.7, 68.4, 22.8, 22.3; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 307.0708, obsd 307.0708.



3-Phenylpropyl 2-chloro-3-(formyloxy)butanoate (21). Yield = 44%, electricity = 5.60 F mol $^{-1}$, $t = 6.0$ h; Colorless oil; Isolated as a 7.7:1 mixture of regioisomers and only the major isomer was shown. ^1H NMR (400 MHz, CDCl_3) δ 7.94 (s, 1H), 7.26–7.20 (m, 2H), 7.16–7.08 (m, 3H), 5.38 (pd, $J = 6.4, 1.0$ Hz, 1H), 4.37 (d, $J = 6.3$ Hz, 1H), 4.14 (td, $J = 6.5, 2.1$ Hz, 2H), 2.64 (t, $J = 7.6$ Hz, 2H), 1.98–1.89 (m, 2H), 1.37 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.1, 159.6, 140.9, 128.7, 128.6, 126.4, 70.3, 65.9, 59.1, 32.1, 30.1, 16.3; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 307.0708, obsd 307.0706.

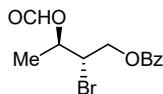


3-Phenylpropyl 2-chloro-3-(formyloxy)hexanoate (22). Yield = 45%, electricity = 5.60 F mol $^{-1}$, $t = 6.0$ h; Colorless oil; Isolated as a 11:1 mixture of regioisomers and only the major isomer was shown. ^1H NMR (400 MHz, CDCl_3) δ 8.10 (s, 1H), 7.35–7.29 (m, 2H), 7.26–7.18 (m, 3H), 5.48 (ddd, $J = 9.3, 6.1, 3.9$ Hz, 1H), 4.50 (d, $J = 6.2$ Hz, 1H), 4.23 (t, $J = 6.6$ Hz, 2H), 2.74 (t, $J = 7.6$ Hz, 2H), 2.03 (dq, $J = 8.7, 6.6$ Hz, 2H), 1.87–1.72 (m, 2H), 1.52–1.31 (m, 2H), 0.97 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 167.2, 160.0, 140.9, 128.7, 128.6, 126.4, 73.1, 65.9, 58.1, 32.4, 32.1, 30.1, 18.2, 13.9; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 335.1021, obsd 335.1021.

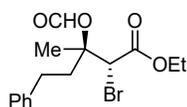


2-Chloro-3-(formyloxy)butyl benzoate (23). Yield = 60%, electricity = 1.87 F mol $^{-1}$, $t = 2.0$ h; Colorless oil; Isolated as a 4:1 mixture of regioisomers and only the major isomer was shown. ^1H NMR (400 MHz, CDCl_3) δ 8.12–8.01 (m, 3H), 7.63–7.55 (m, 1H), 7.52–7.41 (m, 2H), 5.43–5.34 (m, 1H), 4.56 (dtdd, $J = 15.0, 11.8, 7.4, 4.2$ Hz, 2H), 4.33 (qd, $J = 5.6, 2.9$ Hz, 1H), 1.50–1.43 (m, 3H); ^{13}C NMR (151 MHz,

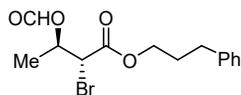
CDCl₃) δ 166.1, 159.9, 133.6, 129.9, 129.5, 128.7, 70.0, 64.7, 60.1, 16.4; ESI HRMS m/z (M+Na)⁺ calcd 279.0395, obsd 279.0393.



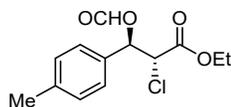
2-Bromo-3-(formyloxy)butyl benzoate (24). Yield = 65%, electricity = 3.73 F mol⁻¹, t = 4.0 h; Colorless oil; Isolated as a 5:1 mixture of regioisomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 8.11–7.99 (m, 3H), 7.62–7.56 (m, 1H), 7.50–7.41 (m, 2H), 5.41–5.32 (m, 1H), 4.62 (dd, J = 6.1, 1.3 Hz, 2H), 4.45–4.37 (m, 1H), 1.49 (dd, J = 6.4, 1.3 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 166.0, 159.9, 133.6, 129.9, 129.5, 128.7, 69.9, 64.9, 51.9, 17.4; ESI HRMS m/z (M+Na)⁺ calcd 322.9889, obsd 322.9889.



Ethyl 2-bromo-3-(formyloxy)-3-methyl-5-phenylpentanoate (25). Yield = 40%, electricity = 6.53 F mol⁻¹, t = 7.0 h; Colorless oil; Isolated as a 10:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, J = 3.3 Hz, 1H), 7.32–7.24 (m, 3H), 7.23–7.15 (m, 2H), 5.07 (d, J = 3.5 Hz, 1H), 4.24 (qd, J = 7.1, 3.7 Hz, 2H), 2.66 (td, J = 8.8, 7.8, 3.3 Hz, 2H), 2.50 (tt, J = 10.2, 7.9, 7.3, 4.3 Hz, 1H), 2.37 (ddt, J = 12.3, 5.6, 3.3 Hz, 1H), 1.80 (d, J = 3.2 Hz, 3H), 1.35–1.27 (m, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.4, 159.6, 140.9, 128.6, 128.4, 126.2, 84.7, 62.3, 49.6, 38.1, 29.4, 20.8, 14.0; ESI HRMS m/z (M+Na)⁺ calcd 365.0359, obsd 365.0364.

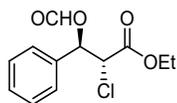


3-Phenylpropyl (2*R*,3*R*)-2-bromo-3-(formyloxy)butanoate (27). Yield = 61%, electricity = 7.46 F mol⁻¹, t = 8.0 h; Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (s, 1H), 7.22 (dd, J = 8.0, 6.8 Hz, 2H), 7.16–7.09 (m, 3H), 5.34 (dq, J = 7.4, 6.3, 1.0 Hz, 1H), 4.27 (d, J = 7.7 Hz, 1H), 4.18–4.07 (m, 2H), 2.63 (dd, J = 8.4, 6.9 Hz, 2H), 1.96–1.88 (m, 2H), 1.43 (d, J = 6.3 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 167.5, 159.5, 140.9, 128.7, 128.6, 126.3, 70.2, 65.7, 47.5, 32.1, 30.1, 17.6; ESI HRMS m/z (M+Na)⁺ calcd 351.0202, obsd 351.0202.

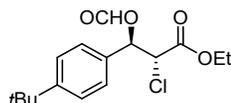


Ethyl 2-chloro-3-(formyloxy)-3-(p-tolyl)propanoate (28). Yield = 85%, electricity = 2.17 F mol⁻¹, t = 2.3 h; Faint yellow oil; Isolated as a 11:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, J = 1.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.17 (d, J = 8.9 Hz, 1H), 4.56 (d, J = 8.9 Hz, 1H), 4.26 (qt, J = 7.3, 3.7 Hz, 2H), 2.36 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ¹³C NMR (101

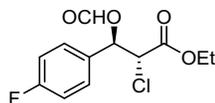
MHz, CDCl₃) δ 167.3, 158.9, 139.6, 132.1, 129.5, 127.9, 75.2, 62.7, 57.9, 21.4, 14.1; ESI HRMS *m/z* (M+Na)⁺ calcd 293.0551, ESI HRMS *m/z* (M+H)⁺ calcd 293.0551, obsd 293.0551.



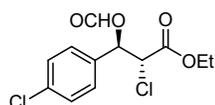
Ethyl 2-chloro-3-(formyloxy)-3-phenylpropanoate (29). Yield = 74%, electricity = 3.73 F mol⁻¹, t = 4.0 h; Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 1.0 Hz, 1H), 7.39–7.26 (m, 5H), 6.14 (dd, *J* = 8.7, 1.0 Hz, 1H), 4.51 (d, *J* = 8.8 Hz, 1H), 4.20 (qq, *J* = 7.3, 3.7 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 158.9, 135.0, 129.6, 128.8, 128.0, 75.3, 62.7, 57.9, 14.1; ESI HRMS *m/z* (M+Na)⁺ calcd 279.0395, obsd 279.0393.



Ethyl 3-(4-(*tert*-butyl)phenyl)-2-chloro-3-(formyloxy)propanoate (30). Yield = 80%, electricity = 3.73 F mol⁻¹, t = 4.0 h; Faint yellow oil; Isolated as a 17:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 0.9 Hz, 1H), 7.36–7.23 (m, 4H), 6.13 (dd, *J* = 8.8, 0.9 Hz, 1H), 4.51 (d, *J* = 8.8 Hz, 1H), 4.20 (qt, *J* = 7.1, 3.5 Hz, 2H), 1.26–1.20 (m, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 167.3, 159.0, 152.7, 131.9, 127.7, 125.7, 75.1, 62.7, 57.9, 34.9, 31.4, 14.1; ESI HRMS *m/z* (M+Na)⁺ calcd 335.1021, obsd 335.1021.

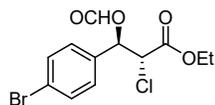


Ethyl 2-chloro-3-(4-fluorophenyl)-3-(formyloxy)propanoate (31). Yield = 72%, electricity = 3.73 F mol⁻¹, t = 4.0 h; Faint yellow oil; Isolated as a 17:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 1.0 Hz, 1H), 7.38–7.29 (m, 2H), 7.05–6.96 (m, 2H), 6.13 (dd, *J* = 8.8, 1.0 Hz, 1H), 4.48 (d, *J* = 8.8 Hz, 1H), 4.20 (qq, *J* = 7.3, 3.6 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 167.1, 163.4 (d, *J*_{C-F} = 248.7 Hz), 158.8, 130.9 (d, *J*_{C-F} = 3.3 Hz), 129.9 (d, *J*_{C-F} = 8.7 Hz), 115.9 (d, *J*_{C-F} = 22.0 Hz), 74.5, 62.8, 57.8, 14.1; ¹⁹F NMR (565 MHz, CDCl₃) δ -111.56 – -111.63 (m, 1F); ESI HRMS *m/z* (M+Na)⁺ calcd 297.0300, obsd 297.0300.

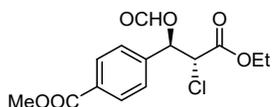


Ethyl 2-chloro-3-(4-chlorophenyl)-3-(formyloxy)propanoate (32). Yield = 72%, electricity = 6.84 F mol⁻¹, t = 7.3 h; Faint yellow oil; Isolated as a 25:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 1.0 Hz, 1H), 7.31–7.28 (m, 4H), 6.11 (dd, *J* = 8.8, 1.0 Hz, 1H), 4.47 (d, *J* = 8.7 Hz, 1H), 4.20 (qq, *J* = 7.1, 3.7 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H); ¹³C NMR

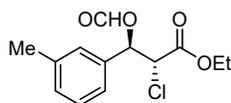
(101 MHz, CDCl₃) δ 167.0, 158.8, 135.6, 133.5, 129.4, 129.1, 74.5, 62.9, 57.7, 14.1; ESI HRMS m/z (M+Na)⁺ calcd 313.0005, obsd 313.0004.



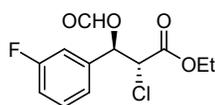
Ethyl 3-(4-bromophenyl)-2-chloro-3-(formyloxy)propanoate (33). Yield = 80%, electricity = 6.84 F mol⁻¹, t = 7.3 h; Pale yellow oil; Isolated as a 25:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 1.0 Hz, 1H), 7.50–7.41 (m, 2H), 7.27–7.19 (m, 2H), 6.10 (dd, J = 8.8, 1.0 Hz, 1H), 4.47 (d, J = 8.7 Hz, 1H), 4.20 (qq, J = 6.9, 3.6 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 158.7, 134.1, 132.0, 129.7, 123.8, 74.6, 62.9, 57.6, 14.1; ESI HRMS m/z (M+Na)⁺ calcd 356.9500, obsd 356.9499.



Methyl 4-(2-chloro-3-ethoxy-1-(formyloxy)-3-oxopropyl)benzoate (34). Yield = 54%, electricity = 6.84 F mol⁻¹, t = 7.3 h; Colorless oil; Isolated as a 25:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 8.09–8.02 (m, 3H), 7.52–7.47 (m, 2H), 6.25 (d, J = 8.6 Hz, 1H), 4.58 (d, J = 8.6 Hz, 1H), 4.28 (qd, J = 7.2, 3.2 Hz, 2H), 3.92 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.9, 166.6, 158.7, 139.7, 131.3, 130.0, 128.0, 74.7, 62.9, 57.6, 52.5, 14.1; ESI HRMS m/z (M+Na)⁺ calcd 337.0449, obsd 337.0448.

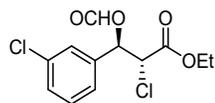


Ethyl 2-chloro-3-(formyloxy)-3-(m-tolyl)propanoate (35). Yield = 78%, electricity = 3.73 F mol⁻¹, t = 4.0 h; Faint yellow oil; Isolated as a 17:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, J = 1.0 Hz, 1H), 7.23–7.09 (m, 4H), 6.09 (dd, J = 8.9, 1.0 Hz, 1H), 4.49 (d, J = 8.9 Hz, 1H), 4.20 (qd, J = 7.1, 3.1 Hz, 2H), 2.30 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.3, 158.9, 138.5, 134.9, 130.4, 128.7, 128.6, 125.0, 75.4, 62.7, 57.8, 21.9, 14.1; ESI HRMS m/z (M+Na)⁺ calcd 293.0551, obsd 293.0547.

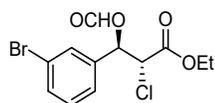


Ethyl 2-chloro-3-(3-fluorophenyl)-3-(formyloxy)propanoate (36). Yield = 48%, electricity = 6.84 F mol⁻¹, t = 7.3 h; Faint yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 7.96 (d, J = 1.0 Hz, 1H), 7.32–7.26 (m, 1H), 7.16–7.12 (m, 1H), 7.09–7.05 (m, 1H), 7.03–6.98 (m, 1H), 6.13 (d, J = 8.6 Hz, 1H), 4.48 (d, J = 8.7 Hz, 1H), 4.25–4.16 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.9, 162.8 (d, J_{C-F} = 247.1 Hz), 158.7, 137.4 (d, J_{C-F} = 7.7 Hz), 130.4 (d, J_{C-F} = 8.1 Hz), 123.8 (d, J_{C-F} = 3.2 Hz), 116.6 (d,

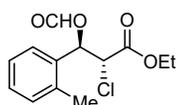
$J_{C-F} = 21.0$ Hz), 115.0 (d, $J_{C-F} = 22.8$ Hz), 74.5, 62.9, 57.7, 14.1; ^{19}F NMR (376 MHz, CDCl_3) δ -111.91 – -112.04 (m); ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 297.0300, obsd 297.0301.



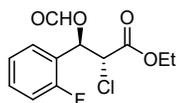
Ethyl 2-chloro-3-(3-chlorophenyl)-3-(formyloxy)propanoate (37). Yield = 63%, electricity = 6.84 F mol $^{-1}$, $t = 7.3$ h; Faint yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 1.0$ Hz, 1H), 7.37–7.33 (m, 1H), 7.31–7.22 (m, 3H), 6.10 (dd, $J = 8.7, 1.0$ Hz, 1H), 4.47 (d, $J = 8.6$ Hz, 1H), 4.20 (qd, $J = 7.2, 2.0$ Hz, 2H), 1.23 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.9, 158.7, 136.9, 134.8, 130.0, 129.8, 128.0, 126.3, 74.5, 62.9, 57.7, 14.1; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 313.0005, obsd 313.0001.



Ethyl 3-(3-bromophenyl)-2-chloro-3-(formyloxy)propanoate (38). Yield = 55%, electricity = 6.84 F mol $^{-1}$, $t = 7.3$ h; Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 1.0$ Hz, 1H), 7.51–7.49 (m, 1H), 7.47–7.41 (m, 1H), 7.32–7.27 (m, 1H), 7.22–7.17 (m, 1H), 6.09 (dd, $J = 8.7, 0.9$ Hz, 1H), 4.47 (d, $J = 8.7$ Hz, 1H), 4.21 (qd, $J = 7.2, 1.8$ Hz, 2H), 1.24 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.9, 158.7, 137.2, 132.7, 130.9, 130.3, 126.8, 122.82, 74.4, 62.9, 57.7, 14.1; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 356.9500, obsd 356.9496.

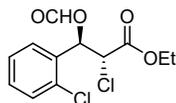


Ethyl 2-chloro-3-(formyloxy)-3-(o-tolyl)propanoate (39). Yield = 63%, electricity = 6.84 F mol $^{-1}$, $t = 7.3$ h; Faint yellow oil; Isolated as a 10:1 mixture of diastereomers and only the major isomer was shown. ^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, $J = 1.0$ Hz, 1H), 7.31–7.26 (m, 1H), 7.21–7.15 (m, 2H), 7.15–7.09 (m, 1H), 6.35 (dd, $J = 9.8, 1.0$ Hz, 1H), 4.48 (d, $J = 9.8$ Hz, 1H), 4.30–4.15 (m, 2H), 2.48 (s, 3H), 1.24 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.6, 158.8, 137.7, 134.1, 130.8, 129.3, 126.6, 126.6, 71.7, 62.7, 57.8, 19.7, 14.1; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 293.0551, obsd 293.0551.

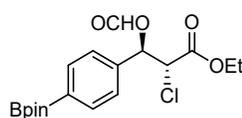


Ethyl 2-chloro-3-(2-fluorophenyl)-3-(formyloxy)propanoate (40). Yield = 71%, electricity = 6.84 F mol $^{-1}$, $t = 7.3$ h; Faint yellow oil; Isolated as a 25:1 mixture of diastereomers and only the major isomer was shown. ^1H NMR (400 MHz, CDCl_3) δ 7.96 (d, $J = 0.9$ Hz, 1H), 7.42–7.32 (m, 1H), 7.35–7.25 (m, 1H), 7.15–7.06 (m, 1H), 7.07–6.97 (m, 1H), 6.40 (dd, $J = 8.5, 0.9$ Hz, 1H), 4.67 (d, $J = 8.6$ Hz, 1H), 4.26–4.12 (m, 2H), 1.22 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.0, 160.8 (d, $J_{C-F} = 249.3$ Hz), 158.8, 131.4 (d, $J_{C-F} = 8.7$ Hz), 129.8 (d, $J_{C-F} = 3.6$ Hz), 124.5 (d, $J_{C-F} = 3.6$ Hz), 122.5 (d, $J_{C-F} = 13.0$

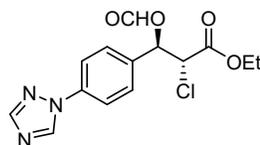
Hz), 116.0 (d, $J_{C-F} = 21.2$ Hz), 70.4, 62.8, 56.7 (d, $J_{C-F} = 2.4$ Hz), 14.1; ^{19}F NMR (565 MHz, CDCl_3) δ -116.06–-116.14 (m, 1F); ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 297.0300, obsd 297.0301.



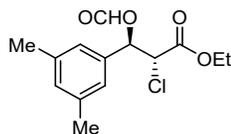
Ethyl 2-chloro-3-(2-chlorophenyl)-3-(formyloxy)propanoate (41). Yield = 46%, electricity = 6.84 F mol $^{-1}$, $t = 7.3$ h; Faint yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 0.9$ Hz, 1H), 7.41–7.31 (m, 2H), 7.28–7.21 (m, 2H), 6.58 (dd, $J = 7.5, 1.0$ Hz, 1H), 4.68 (d, $J = 7.5$ Hz, 1H), 4.15 (qq, $J = 10.8, 7.2$ Hz, 2H), 1.17 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.7, 158.8, 133.9, 133.1, 130.6, 130.1, 128.8, 127.3, 72.2, 62.7, 57.1, 14.1; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 313.0005, obsd 313.0009.



Ethyl 2-chloro-3-(formyloxy)-3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propanoate (42). Yield = 56%, electricity = 6.53 F mol $^{-1}$, $t = 7.0$ h; Colorless solid; ^1H NMR (400 MHz, CDCl_3) δ 7.95 (d, $J = 1.0$ Hz, 1H), 7.78–7.73 (m, 2H), 7.37–7.33 (m, 2H), 6.14 (d, $J = 8.7$ Hz, 1H), 4.50 (d, $J = 8.8$ Hz, 1H), 4.19 (qd, $J = 7.1, 3.0$ Hz, 2H), 1.26 (s, 12H), 1.23 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.1, 158.8, 137.8, 135.2, 127.2, 84.2, 75.3, 62.7, 57.7, 25.0, 14.1; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 405.1247, obsd 405.1248.

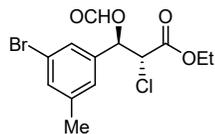


Ethyl 3-(4-(1H-1,2,4-triazol-1-yl)phenyl)-2-chloro-3-(formyloxy)propanoate (43). Yield = 72%, electricity = 5.59 F mol $^{-1}$, $t = 6.0$ h; Colorless oil; Isolated as a 7.1:1 mixture of diastereomers and only the major isomer was shown. ^1H NMR (400 MHz, CDCl_3) δ 8.52 (s, 1H), 8.03 (s, 1H), 8.00–7.96 (m, 1H), 7.69–7.61 (m, 2H), 7.54–7.47 (m, 3H), 6.19 (d, $J = 8.7$ Hz, 1H), 4.58–4.50 (m, 1H), 4.21 (qd, $J = 7.2, 2.8$ Hz, 2H), 1.24 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 166.8, 158.7, 152.9, 141.1, 137.7, 135.0, 129.5, 120.1, 74.4, 62.9, 57.6, 14.1; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 346.0565, obsd 346.0566.

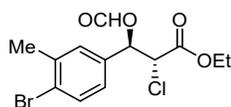


Ethyl 2-chloro-3-(3,5-dimethylphenyl)-3-(formyloxy)propanoate (44). Yield = 67%, electricity = 6.84 F mol $^{-1}$, $t = 7.3$ h; Colorless oil; Isolated as a 12.5:1 mixture of diastereomers and only the major isomer was shown. ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 0.9$ Hz, 1H), 6.94 (d, $J = 8.4$ Hz, 3H), 6.05 (dd, $J = 9.0, 0.9$ Hz, 1H), 4.48 (d, $J = 9.0$ Hz, 1H), 4.19 (qd, $J = 7.2, 2.1$ Hz, 2H), 2.25 (s, 6H), 1.23 (t, $J = 7.1$

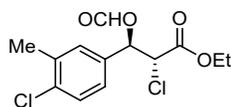
Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.3, 159.0, 138.4, 134.8, 131.3, 125.7, 75.4, 62.6, 57.8, 21.5, 14.1; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 307.0708, obsd 307.0709.



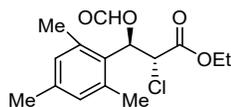
Ethyl 3-(3-bromo-5-methylphenyl)-2-chloro-3-(formyloxy)propanoate (45). Yield = 55%, electricity = 6.84 F mol^{-1} , $t = 7.3 \text{ h}$; Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, $J = 1.0 \text{ Hz}$, 1H), 7.37–7.32 (m, 2H), 7.15 (d, $J = 1.7 \text{ Hz}$, 1H), 6.11 (dd, $J = 8.7, 1.0 \text{ Hz}$, 1H), 4.52 (d, $J = 8.7 \text{ Hz}$, 1H), 4.27 (qd, $J = 7.2, 1.3 \text{ Hz}$, 2H), 2.35 (d, $J = 0.8 \text{ Hz}$, 3H), 1.31 (t, $J = 7.2 \text{ Hz}$, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.0, 158.7, 140.6, 136.9, 133.3, 127.9, 127.6, 122.6, 74.5, 62.8, 57.7, 21.3, 14.1; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 370.9656, obsd 370.9653.



Ethyl 3-(4-bromo-3-methylphenyl)-2-chloro-3-(formyloxy)propanoate (46). Yield = 73%, electricity = 3.74 F mol^{-1} , $t = 4.0 \text{ h}$; Colorless oil; Isolated as a 17:1 mixture of diastereomers and only the major isomer was shown. ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 1.0 \text{ Hz}$, 1H), 7.54 (d, $J = 8.2 \text{ Hz}$, 1H), 7.29 (d, $J = 2.2 \text{ Hz}$, 1H), 7.10 (dd, $J = 8.2, 2.3 \text{ Hz}$, 1H), 6.13 (d, $J = 8.8 \text{ Hz}$, 1H), 4.53 (d, $J = 8.8 \text{ Hz}$, 1H), 4.27 (qd, $J = 7.1, 2.7 \text{ Hz}$, 2H), 2.41 (s, 3H), 1.30 (t, $J = 7.1 \text{ Hz}$, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.0, 158.8, 138.5, 134.3, 132.8, 130.4, 126.8, 126.3, 74.7, 62.8, 57.6, 23.2, 14.1; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 370.9656, obsd 370.9654.

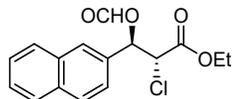


Ethyl 2-chloro-3-(4-chloro-3-methylphenyl)-3-(formyloxy)propanoate (47). Yield = 71%, electricity = 6.84 F mol^{-1} , $t = 7.3 \text{ h}$; Colorless oil; Isolated as a 17:1 mixture of diastereomers and only the major isomer was shown. ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, $J = 0.9 \text{ Hz}$, 1H), 7.35 (d, $J = 8.2 \text{ Hz}$, 1H), 7.29 (d, $J = 2.2 \text{ Hz}$, 1H), 7.19 (dd, $J = 8.2, 2.3 \text{ Hz}$, 1H), 6.14 (dd, $J = 8.9, 0.9 \text{ Hz}$, 1H), 4.54 (d, $J = 8.8 \text{ Hz}$, 1H), 4.27 (qd, $J = 7.1, 2.7 \text{ Hz}$, 2H), 2.39 (s, 3H), 1.31 (t, $J = 7.1 \text{ Hz}$, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.1, 158.8, 136.7, 135.7, 133.5, 130.5, 129.5, 126.6, 74.7, 62.8, 57.7, 20.3, 14.1; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 327.0161, obsd 327.0164.

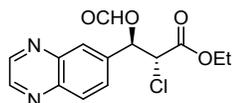


Ethyl 2-chloro-3-(formyloxy)-3-mesitylpropanoate (48). Yield = 50%, electricity = 4.6 F mol^{-1} , $t = 5.0 \text{ h}$; Colorless oil; Isolated as a 9:1 mixture of diastereomers and only the major isomer was shown. ^1H

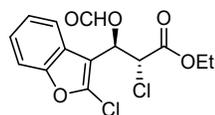
NMR (400 MHz, CDCl₃) δ 7.96 (d, J = 1.0 Hz, 1H), 7.26 (s, 1H), 6.96 (s, 1H), 6.75–6.56 (m, 1H), 4.82 (d, J = 10.9 Hz, 1H), 4.32 (qq, J = 10.7, 7.1 Hz, 2H), 2.71–2.42 (m, 6H), 2.34 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 167.8, 158.7, 137.6, 135.0, 134.7, 132.4, 130.9, 130.2, 72.0, 62.8, 55.7, 21.1, 20.9, 18.0, 14.2; ESI HRMS m/z (M+Na)⁺ calcd 321.0864, obsd 321.0862.



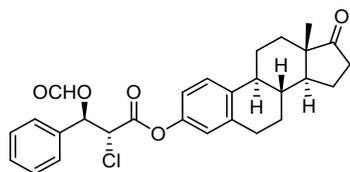
Ethyl 2-chloro-3-(formyloxy)-3-(naphthalen-2-yl)propanoate (49). Yield = 62%, electricity = 6.53 F mol⁻¹, t = 7.0 h; Pale yellow oil; Isolated as a 12.5:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 7.99 (s, 1H), 7.86–7.83 (m, 1H), 7.82–7.76 (m, 3H), 7.48–7.39 (m, 3H), 6.31 (d, J = 8.9 Hz, 1H), 4.61 (d, J = 8.9 Hz, 1H), 4.21 (qd, J = 7.2, 2.7 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.3, 158.9, 133.8, 133.0, 132.3, 128.8, 128.4, 128.3, 127.9, 127.1, 126.8, 124.5, 75.5, 62.8, 57.8, 14.1; ESI HRMS m/z (M+Na)⁺ calcd 329.0551, obsd 329.0550.



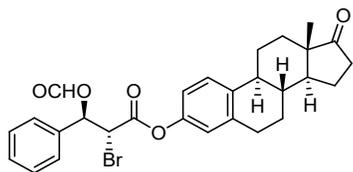
Ethyl 2-chloro-3-(formyloxy)-3-(quinoxalin-6-yl)propanoate (50). Yield = 47%, electricity = 12.12 F mol⁻¹, t = 13.0 h; Pale yellow oil; ¹H NMR (600 MHz, CDCl₃) δ 8.83–8.81 (m, 2H), 8.13 (d, J = 2.0 Hz, 1H), 8.09 (d, J = 8.6 Hz, 1H), 8.02 (d, J = 1.0 Hz, 1H), 7.77 (dd, J = 8.7, 2.0 Hz, 1H), 6.38 (d, J = 8.6 Hz, 1H), 4.62 (d, J = 8.6 Hz, 1H), 4.28–4.19 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 166.9, 158.8, 146.0, 145.8, 143.3, 142.7, 137.1, 130.2, 129.4, 129.2, 74.7, 63.0, 57.8, 14.2; ESI HRMS m/z (M+Na)⁺ calcd 331.0456, obsd 331.0453.



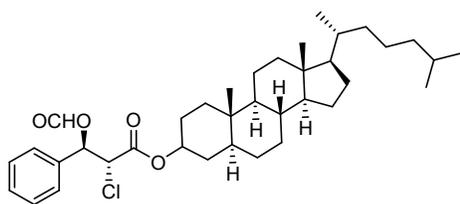
Ethyl (2*R*,3*R*)-2-chloro-3-(2-chlorobenzofuran-3-yl)-3-(formyloxy)propanoate (51). Yield = 38%, electricity = 3.42 F mol⁻¹, t = 3.7 h; Pale yellow oil; Isolated as a 17:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, J = 1.0 Hz, 1H), 7.61–7.56 (m, 1H), 7.40–7.37 (m, 1H), 7.24 (pd, J = 7.4, 1.5 Hz, 2H), 6.36 (dd, J = 9.7, 1.0 Hz, 1H), 4.76 (d, J = 9.7 Hz, 1H), 4.31–4.15 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 158.5, 153.7, 142.3, 126.0, 125.2, 124.1, 119.7, 111.6, 109.9, 68.5, 63.0, 55.5, 14.1; ESI HRMS m/z (M+Na)⁺ calcd 352.9954, obsd 352.9957.



(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthren-3-yl 2-chloro-3-(formyloxy)-3-phenylpropanoate (52). Yield = 68%, electricity = 6.98 F mol⁻¹, t = 7.5 h; Colorless solid; ¹H NMR (400 MHz, CDCl₃) δ 8.09 (s, 1H), 7.49 (dd, *J* = 6.8, 2.8 Hz, 2H), 7.42 (dd, *J* = 5.1, 2.0 Hz, 3H), 7.32–7.28 (m, 1H), 6.86 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.83–6.81 (m, 1H), 6.33 (d, *J* = 8.8 Hz, 1H), 4.79 (d, *J* = 8.8 Hz, 1H), 2.92 (dd, *J* = 9.0, 4.2 Hz, 2H), 2.51 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.40 (dt, *J* = 9.2, 2.9 Hz, 1H), 2.29 (td, *J* = 10.8, 4.2 Hz, 1H), 2.20–2.10 (m, 1H), 2.09–1.94 (m, 3H), 1.69–1.59 (m, 2H), 1.57–1.42 (m, 4H), 0.91 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 220.8, 166.0, 158.9, 148.2, 138.5, 138.4, 134.8, 129.8, 128.9, 128.1, 126.8, 121.1, 118.2, 75.2, 57.8, 50.6, 48.1, 44.3, 38.1, 36.0, 31.7, 29.6, 26.4, 25.9, 21.8, 14.0; ESI HRMS *m/z* (M+Na)⁺ calcd 503.1596, obsd 503.1596.

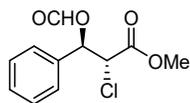


(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthren-3-yl 2-bromo-3-(formyloxy)-3-phenylpropanoate (52-Br). Yield = 65%, electricity = 10.3 F mol⁻¹, t = 11.0 h; Colorless solid; ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 1.0 Hz, 1H), 7.52–7.44 (m, 2H), 7.46–7.37 (m, 3H), 7.31 (d, *J* = 8.5 Hz, 1H), 6.89 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.88–6.82 (m, 1H), 6.34 (d, *J* = 10.0 Hz, 1H), 4.72 (d, *J* = 10.1 Hz, 1H), 2.93 (dd, *J* = 9.0, 4.3 Hz, 2H), 2.51 (dd, *J* = 18.8, 8.7 Hz, 1H), 2.47–2.36 (m, 1H), 2.30 (td, *J* = 10.7, 4.2 Hz, 1H), 2.22–2.10 (m, 1H), 2.13–1.93 (m, 3H), 1.61 (ddd, *J* = 9.6, 5.0, 2.7 Hz, 2H), 1.58–1.39 (m, 4H), 0.91 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 220.9, 166.4, 158.8, 148.3, 138.5, 138.3, 135.3, 129.8, 128.9, 128.2, 126.7, 121.0, 118.2, 75.4, 50.6, 48.1, 45.7, 44.3, 38.1, 36.0, 31.7, 29.6, 26.5, 25.9, 21.8, 14.0; ESI HRMS *m/z* (M+Na)⁺ calcd 547.1091, obsd 547.1096.

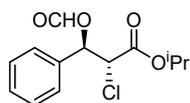


(5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[*a*]phenanthren-3-yl 2-chloro-3-(formyloxy)-3-phenylpropanoate (53). Yield = 75%, electricity = 6.84 F mol⁻¹, t = 11.0 h; Colorless solid; ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 1.1 Hz, 1H), 7.45–7.40 (m, 2H), 7.40–7.34 (m, 3H), 6.19 (dd, *J* = 8.9, 0.9 Hz, 1H), 4.79 (tt, *J* = 10.9, 5.0 Hz, 1H), 4.53 (d, *J* = 8.9 Hz, 1H), 1.97 (dt, *J* = 12.6, 3.4 Hz, 1H), 1.85–1.72 (m, 3H), 1.70–1.62 (m, 1H), 1.56–1.43 (m, 4H), 1.39–1.21 (m, 10H), 1.19–1.04 (m, 8H), 1.03–0.96 (m, 4H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 1.8 Hz, 3H), 0.85 (d, *J* = 1.8 Hz, 3H), 0.83 (s, 3H), 0.65 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.7, 158.9, 135.1, 129.6, 128.8, 128.1, 76.5, 75.3, 58.1, 56.6, 56.5, 54.3, 44.8, 42.8, 40.1, 39.7, 36.8,

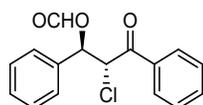
36.4, 36.0, 35.6, 33.8, 33.7, 32.1, 28.8, 28.4, 28.2, 27.3, 27.3, 24.4, 24.0, 23.0, 22.8, 21.4, 18.9, 12.4, 12.3; ESI HRMS m/z (M+H)⁺ calcd 599.3862, obsd 599.3860.



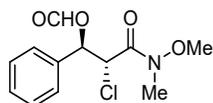
Methyl 2-chloro-3-(formyloxy)-3-phenylpropanoate (54). Yield = 65%, electricity = 6.84 F mol⁻¹, t = 7.3 h; Colorless oil; Isolated as a 25:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, J = 1.0 Hz, 1H), 7.46–7.34 (m, 5H), 6.21 (dd, J = 8.7, 1.0 Hz, 1H), 4.61 (d, J = 8.7 Hz, 1H), 3.82 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.7, 158.9, 134.9, 129.6, 128.8, 127.9, 75.2, 57.7, 53.5; ESI HRMS m/z (M+Na)⁺ calcd 265.0238, obsd 265.0238.



isoPropyl 2-chloro-3-(formyloxy)-3-phenylpropanoate (55). Yield = 50%, electricity = 6.84 F mol⁻¹, t = 7.3 h; Colorless oil; Isolated as a 17:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, J = 1.1 Hz, 1H), 7.45–7.41 (m, 2H), 7.38 (dd, J = 5.1, 2.1 Hz, 3H), 6.20 (dd, J = 9.0, 1.0 Hz, 1H), 5.10 (hept, J = 6.3 Hz, 1H), 4.54 (d, J = 8.9 Hz, 1H), 1.28 (dd, J = 7.6, 6.2 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 166.7, 158.9, 135.1, 129.6, 128.8, 128.0, 75.3, 70.7, 58.0, 21.7, 21.6; ESI HRMS m/z (M+Na)⁺ calcd 293.0551, obsd 293.0553.

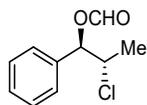


2-Chloro-3-oxo-1,3-diphenylpropyl formate (56). Yield = 47%, electricity = 3.72 F mol⁻¹, t = 4.0 h; Yellow oil; Isolated as a 13:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 8.07–8.02 (m, 2H), 7.93 (d, J = 0.9 Hz, 1H), 7.68–7.61 (m, 1H), 7.56–7.48 (m, 4H), 7.45–7.37 (m, 3H), 6.42 (d, J = 9.4 Hz, 1H), 5.41 (d, J = 9.4 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 191.3, 158.9, 135.7, 134.6, 134.4, 129.5, 129.2, 128.7, 128.2, 74.7, 56.3; ESI HRMS m/z (M+Na)⁺ calcd 311.0445, obsd 311.0449.

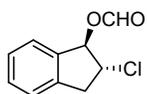


2-Chloro-3-(methoxy(methyl)amino)-3-oxo-1-phenylpropyl formate (57). Yield = 37%, electricity = 2.49 F mol⁻¹, t = 2.7 h; Colorless oil; Isolated as a 9:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 1.0 Hz, 1H), 7.42–7.38 (m, 2H), 7.36–7.30 (m, 3H), 6.13 (d, J = 9.9 Hz, 1H), 4.99 (d, J = 10.0 Hz, 1H), 3.76 (s, 3H), 3.22 (s, 3H); ¹³C NMR (151 MHz,

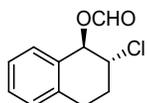
CDCl₃) δ 167.4, 158.9, 135.7, 129.4, 128.7, 128.3, 75.3, 62.2, 52.5, 32.6; ESI HRMS m/z (M+Na)⁺ calcd 294.0504, obsd 294.0500.



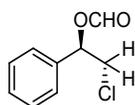
2-Chloro-1-phenylpropyl formate (60). Yield = 58%, electricity = 2.33 F mol⁻¹, t = 2.5 h; Yellow oil; Isolated as a 8:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, J = 0.9 Hz, 1H), 7.40–7.35 (m, 5H), 6.02 (dd, J = 5.1, 1.0 Hz, 1H), 4.32 (qd, J = 6.7, 5.0 Hz, 1H), 1.50 (d, J = 6.7 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 159.8, 136.3, 129.0, 128.6, 127.4, 78.1, 58.4, 20.0; ESI HRMS m/z (M+Na)⁺ calcd 221.0340, obsd 221.0340.



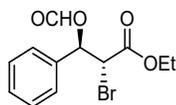
2-Chloro-2,3-dihydro-1H-inden-1-yl formate (61). Yield = 51%, electricity = 2.33 F mol⁻¹, t = 2.5 h; Yellow oil; Isolated as a 5:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, J = 1.0 Hz, 1H), 7.41–7.34 (m, 2H), 7.31–7.27 (m, 2H), 6.36 (d, J = 3.8 Hz, 1H), 4.58–4.51 (m, 1H), 3.64 (dd, J = 16.7, 6.8 Hz, 1H), 3.18 (dd, J = 16.6, 4.7 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 160.4, 140.9, 137.8, 130.1, 127.9, 126.0, 125.1, 83.4, 60.7, 40.9; ESI HRMS m/z (M+H)⁺ calcd 197.0364, obsd 197.0359.



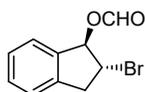
2-Chloro-1,2,3,4-tetrahydronaphthalen-1-yl formate (62). Yield = 66%, electricity = 2.33 F mol⁻¹, t = 2.5 h; Colorless oil; Isolated as a 25:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, J = 1.1 Hz, 1H), 7.32–7.20 (m, 3H), 7.18–7.14 (m, 1H), 6.19 (d, J = 5.0 Hz, 1H), 4.40 (td, J = 4.9, 2.5 Hz, 1H), 3.09 (ddd, J = 17.3, 8.9, 5.8 Hz, 1H), 2.90 (dt, J = 17.3, 5.6 Hz, 1H), 2.44 (dddd, J = 14.3, 8.7, 5.7, 2.9 Hz, 1H), 2.26–2.13 (m, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 160.3, 136.3, 131.1, 129.9, 129.1, 129.0, 126.9, 73.0, 57.1, 27.7, 25.4; ESI HRMS m/z (M+Na)⁺ calcd 233.0340, obsd 233.0336.



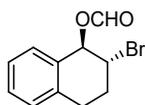
2-Chloro-1-phenylethyl formate (63). Yield = 60%, electricity = 1.87 F mol⁻¹, t = 2.0 h; Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 8.19 (s, 1H), 7.43–7.38 (m, 5H), 6.10 (ddd, J = 8.3, 4.4, 1.0 Hz, 1H), 3.86 (dd, J = 11.8, 8.2 Hz, 1H), 3.78 (dd, J = 11.8, 4.4 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 159.9, 136.7, 129.3, 129.0, 126.9, 75.1, 46.4; ESI HRMS m/z (M+Na)⁺ calcd 185.0364, obsd 185.0367.



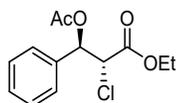
Ethyl 2-bromo-3-(formyloxy)-3-phenylpropanoate (66). Yield = 64%, electricity = 3.26 F mol⁻¹, t = 3.5 h; Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 0.9 Hz, 1H), 7.38–7.33 (m, 2H), 7.33–7.29 (m, 3H), 6.16 (dd, *J* = 10.1, 1.0 Hz, 1H), 4.44 (d, *J* = 10.0 Hz, 1H), 4.27–4.16 (m, 2H), 1.23 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 167.6, 158.8, 135.5, 129.6, 128.8, 128.1, 75.4, 62.6, 45.9, 14.1; ESI HRMS *m/z* (M+Na)⁺ calcd 322.9889, obsd 322.9885.



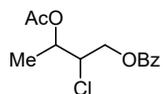
2-Bromo-2,3-dihydro-1H-inden-1-yl formate (67). Yield = 54%, electricity = 2.33 F mol⁻¹, t = 2.5 h; Yellow oil; Isolated as a 10:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 1.1 Hz, 1H), 7.36–7.33 (m, 1H), 7.31–7.27 (m, 1H), 7.25–7.20 (m, 2H), 6.38 (d, *J* = 3.5 Hz, 1H), 4.50–4.41 (m, 1H), 3.66 (dd, *J* = 17.0, 6.7 Hz, 1H), 3.23 (dd, *J* = 17.0, 4.4 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 160.3, 141.5, 137.9, 130.1, 127.9, 126.1, 125.1, 83.8, 49.6, 41.6; ESI HRMS *m/z* (M+H)⁺ calcd 240.9859, obsd 240.9875.



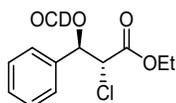
2-Bromo-1,2,3,4-tetrahydronaphthalen-1-yl formate (68). Yield = 53%, electricity = 3.26 F mol⁻¹, t = 3.5 h; Colorless oil; Isolated as a 25:1 mixture of diastereomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 1.0 Hz, 1H), 7.25–7.13 (m, 3H), 7.10 (d, *J* = 7.7 Hz, 1H), 6.21 (d, *J* = 4.6 Hz, 1H), 4.43 (ddd, *J* = 6.3, 4.5, 2.9 Hz, 1H), 3.02 (ddd, *J* = 17.3, 9.3, 5.7 Hz, 1H), 2.83 (dt, *J* = 17.4, 5.3 Hz, 1H), 2.41 (dddd, *J* = 14.8, 9.0, 5.7, 2.9 Hz, 1H), 2.17 (dq, *J* = 14.3, 5.6 Hz, 1H); ¹³C NMR (151 MHz, CDCl₃) δ 160.2, 136.3, 131.0, 130.2, 129.2, 129.1, 126.9, 73.1, 48.7, 27.7, 26.1; ESI HRMS *m/z* (M+Na)⁺ calcd 276.9835, obsd 276.9839.



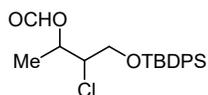
Ethyl 3-acetoxy-2-chloro-3-phenylpropanoate (69). Yield = 51%, electricity = 3.74 F mol⁻¹, t = 4.0 h; Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.38–7.25 (m, 5H), 6.03 (d, *J* = 8.7 Hz, 1H), 4.48 (d, *J* = 8.7 Hz, 1H), 4.25–4.13 (m, 2H), 1.99 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 169.0, 167.4, 135.7, 129.3, 128.7, 128.0, 75.6, 62.6, 58.4, 21.0, 14.2; ESI HRMS *m/z* (M+Na)⁺ calcd 293.0551, obsd 293.0551.



3-Acetoxy-2-chlorobutyl benzoate (70). Yield = 78%, electricity = 1.86 F mol⁻¹, t = 2.0 h; Colorless oil; Isolated as a 6.1:1 mixture of regioisomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 8.01–7.96 (m, 2H), 7.54–7.49 (m, 1H), 7.42–7.36 (m, 2H), 5.17 (p, *J* = 6.3 Hz, 1H), 4.51 – 4.45 (m, 2H), 4.26 (dq, *J* = 11.4, 5.6 Hz, 1H), 2.01 (s, 3H), 1.34 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 170.1, 166.2, 133.6, 129.9, 129.6, 128.7, 70.3, 64.9, 60.5, 21.2, 16.5; ESI HRMS *m/z* (M+Na)⁺ calcd 293.0551, obsd 293.0551.



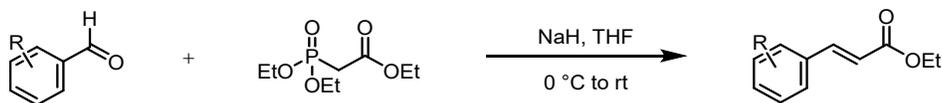
Ethyl 2-chloro-3-((formyl-d)oxy)-3-phenylpropanoate ([D]-29). Yield = 78%, electricity = 6.18 F mol⁻¹, t = 6.6 h; Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.45–7.34 (m, 5H), 6.21 (d, *J* = 8.8 Hz, 1H), 4.58 (d, *J* = 8.8 Hz, 1H), 4.27 (qt, *J* = 7.0, 3.5 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.2, 158.7 (t, *J*_{C-D} = 35.1 Hz), 135.0, 129.6, 128.8, 128.0, 75.2, 62.7, 57.8, 14.1; ESI HRMS *m/z* (M+Na)⁺ calcd 280.0457, obsd 280.0457.



4-(((*tert*-Butyldiphenylsilyl)oxy)methyl)-3-methyloxetan-2-ol (74). Yield = 43%, electricity = 0.93 F mol⁻¹, t = 1.0 h; Colorless oil; Isolated as a 2.2:1 mixture of regioisomers and only the major isomer was shown. ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 0.9 Hz, 1H), 7.61–7.56 (m, 4H), 7.38–7.31 (m, 6H), 5.47–5.35 (m, 1H), 4.04 (ddd, *J* = 6.9, 5.4, 4.5 Hz, 1H), 3.80 (dd, *J* = 11.0, 5.3 Hz, 1H), 3.70 (dd, *J* = 11.0, 6.8 Hz, 1H), 1.25 (d, *J* = 6.4 Hz, 3H), 1.00 (s, 6H), 0.98 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 160.1, 135.8, 132.9, 130.2, 128.0, 69.9, 64.7, 63.1, 26.9, 20.6, 19.4, 15.3; ESI HRMS *m/z* (M+Na)⁺ calcd 413.1310, obsd 413.1313.

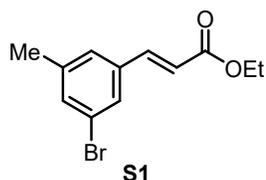
10. Synthesis and characterization of substrates

The known alkenes were obtained by Wittig reaction or Horner–Wadsworth–Emmons reaction¹⁻¹¹. The unknown alkenes were synthesised through the following method.

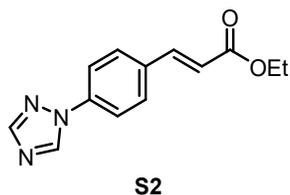


General Procedure: To a solution of NaH (6 mmol, 1.2 equiv) in THF (20 mL) was dropwise added ethyl 2-(diethoxyphosphoryl)acetate (6 mmol, 1.2 equiv) under N₂ at 0 °C. The reaction mixture was warmed to RT and stirred for 0.5 h. The aldehydes or ketones were dropwise added in DCM (10 mL). The reaction mixture was stirred overnight. The saturated NH₄Cl (30 mL) were added and the layers

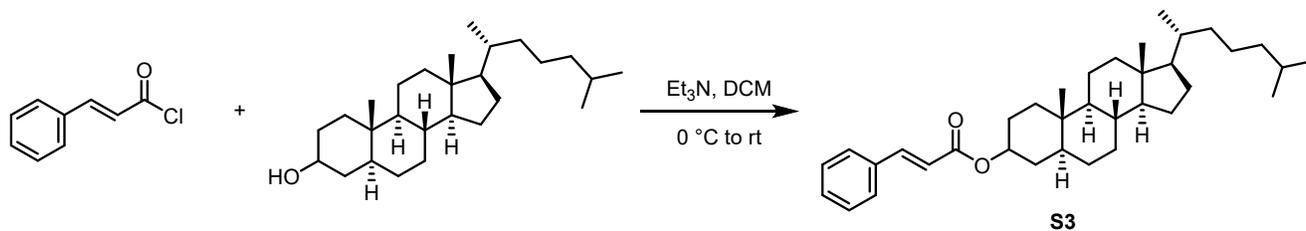
were separated. The aqueous phase was extracted twice with dichloromethane. The reaction solution was concentrated under reduced pressure. The residue extracted twice with DCM (20 mL) and H₂O (20 mL). The combined organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the product.



Ethyl (*E*)-3-(3-bromo-5-methylphenyl)acrylate (S1). The title compound was obtained as a colorless oil in 66% yield (0.60 g) starting from 3-bromo-5-methylbenzaldehyde and 2-(diethoxyphosphoryl)acetate by following the General Procedure. ¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 16.0 Hz, 1H), 7.47 (s, 1H), 7.34 (s, 1H), 7.24 (s, 1H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.8, 143.2, 140.8, 136.5, 133.8, 128.0, 127.7, 122.9, 119.7, 60.8, 21.2, 14.5; ESI HRMS *m/z* (M+Na)⁺ calcd 290.9991, obsd 290.9993.

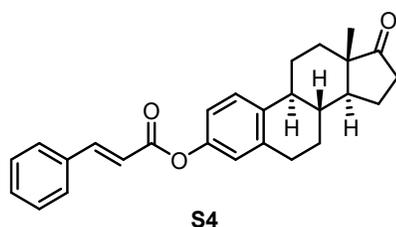


Ethyl (*E*)-3-(4-(1H-1,2,4-triazol-1-yl)phenyl)acrylate (S2). The title compound was obtained as a colorless solid in 88% yield (0.63 g) starting from 4-(1H-1,2,4-triazol-1-yl)benzaldehyde and 2-(diethoxyphosphoryl)acetate by following the General Procedure. ¹H NMR (400 MHz, CDCl₃) δ 8.61 (s, 1H), 8.12 (s, 1H), 7.75–7.70 (m, 2H), 7.69 (d, *J* = 18.7 Hz, 1H), 7.68–7.64 (m, 2H), 6.47 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.8, 153.0, 142.9, 141.0, 138.1, 134.6, 129.6, 120.3, 119.7, 60.9, 14.5; ESI HRMS *m/z* (M+Na)⁺ calcd 266.0900, obsd 266.0897.

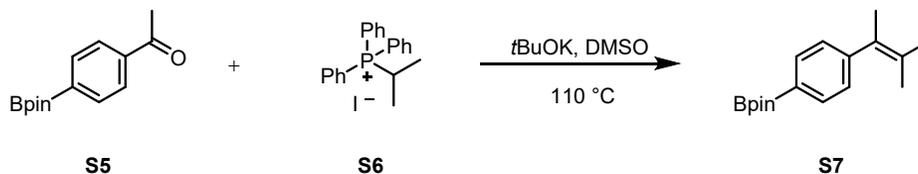


5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl cinnamate (S3). To a solution of dihydrocholesterol (3.0 mmol, 1.0 equiv) in DCM (10.0 mL) was added cinnamoyl chloride (4.5 mmol, 1.5 equiv) and triethylamine (4.5

mmol, 1.5 equiv) at 0 °C. The reaction was warmed to ambient temperature and stirred for 16 h. The saturation NaHCO₃ (30 mL) were added and the layers were separated. The aqueous phase was extracted twice with dichloromethane. The combined organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give **S3** as a colorless solid (0.40 g, 78% yield): ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.54–7.48 (m, 2H), 7.4–7.35 (m, 3H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.83 (tt, *J* = 11.3, 4.9 Hz, 1H), 1.97 (dt, *J* = 12.5, 3.4 Hz, 1H), 1.93–1.85 (m, 1H), 1.84–1.73 (m, 2H), 1.71–1.64 (m, 2H), 1.63–1.42 (m, 6H), 1.40–1.19 (m, 10H), 1.17–1.08 (m, 5H), 1.08–1.05 (m, 1H), 1.05–0.96 (m, 3H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 1.9 Hz, 3H), 0.86–0.84 (m, 6H), 0.65 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.7, 144.5, 134.8, 130.3, 129.0, 128.2, 119.0, 74.1, 56.6, 56.5, 54.4, 44.9, 42.8, 40.2, 39.7, 37.0, 36.4, 36.0, 35.7, 34.3, 32.2, 28.8, 28.4, 28.2, 27.8, 24.4, 24.0, 23.0, 22.8, 21.4, 18.9, 12.5, 12.3; ESI HRMS *m/z* (M+Na)⁺ calcd 519.4197, obsd 519.4197.

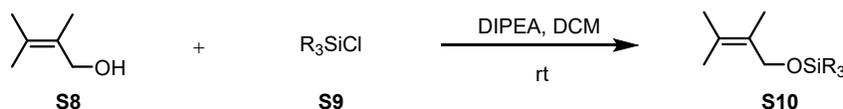


(8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl cinnamate (S4**).** The title compound was obtained as a colorless solid in 66% yield (0.97 g) starting from Estrone (3.7 mmol, 1.0 equiv) and cinnamoyl chloride (5.6 mmol, 1.5 equiv) by following the Procedure of **S2**. ¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 16.0 Hz, 1H), 7.60–7.55 (m, 2H), 7.45–7.39 (m, 3H), 7.32 (d, *J* = 8.5 Hz, 1H), 6.94 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.92–6.89 (m, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 2.96–2.91 (m, 2H), 2.51 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.45–2.38 (m, 1H), 2.30 (td, *J* = 10.8, 4.0 Hz, 1H), 2.20–1.94 (m, 4H), 1.70–1.40 (m, 6H), 0.92 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 165.8, 148.8, 146.6, 138.2, 137.5, 134.4, 130.8, 129.2, 128.4, 126.6, 121.8, 119.0, 117.6, 50.6, 48.1, 44.3, 38.2, 36.0, 31.7, 29.6, 26.5, 25.9, 21.8, 14.0; ESI HRMS *m/z* (M+Na)⁺ calcd 423.1931, obsd 423.1931.

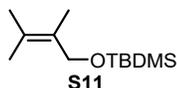


4,4,5,5-Tetraethyl-2-(4-(3-methylbut-2-en-2-yl)phenyl)-1,3,2-dioxaborolane (S7**).** To a solution of isopropyltriphenylphosphonium (6 mmol, 2 equiv) in DMSO (20 mL) added Potassium tert-butoxide (6 mmol, 2 equiv). after mixing, arylmethylketone (3 mmol, 1.0 equiv) in toluene was added under N₂. The reaction solution was heated to 110 °C and stirred until complete consumption of the substrate (monitored by TLC or ¹H NMR). The reaction solution was cooled to rt and extracted twice with petroleum ether (20 mL) and H₂O (20 mL). The combined organic phase was dried over MgSO₄, filtered and concentrated

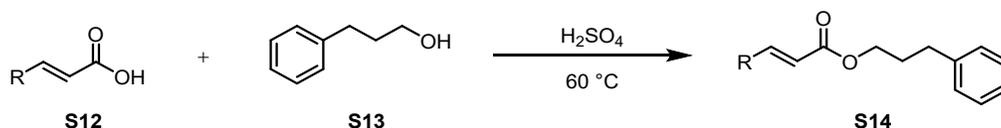
under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the product **S7** as a colorless oil in 46% yield (0.37 g). $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.71–7.66 (m, 2H), 7.09–7.04 (m, 2H), 1.88 (s, 3H), 1.73 (s, 3H), 1.51 (s, 3H), 1.27 (s, 12H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 148.7, 134.7, 130.2, 128.1, 127.7, 83.8, 25.1, 22.2, 20.8, 20.8; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 295.1840, obsd 295.1840.



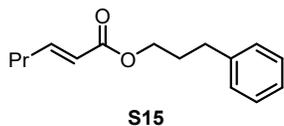
General Procedure: To a solution of 2,3-dimethylbut-2-en-1-ol (7 mmol, 1.0 equiv) in DCM (20 mL) was added Chlorotrialkylsilane (8.4 mmol, 1.2 equiv) and DIPEA (14 mmol, 2 equiv) under N_2 at rt. The reaction mixture was stirred until complete consumption of the substrate (monitored by TLC or $^1\text{H NMR}$). The reaction solution was concentrated under reduced pressure. The residue extracted twice with DCM (20 mL) and H_2O (20 mL). The combined organic phase was dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the product.



tert-Butyl((2,3-dimethylbut-2-en-1-yl)oxy)dimethylsilane (S11). The title compound was obtained as a colorless oil in 12% yield (0.13 g) starting from 2,3-dimethylbut-2-en-1-ol (4.3 mmol, 1.0 equiv) and TBDMSCl (5.16 mmol, 1.2 equiv) by following the General Procedure. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 4.15 (s, 2H), 1.69 (s, 6H), 1.66 (s, 3H), 0.91 (s, 9H), 0.07 (s, 6H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 127.7, 127.0, 64.1, 26.2, 21.1, 20.1, 18.7, 16.0, -5.0; ESI HRMS m/z ($\text{M}+\text{Na}$) $^+$ calcd 237.1645, obsd 237.1643.



General Procedure: To a solution of acrylic acid (5 mmol, 1.0 equiv) in 3-phenylpropan-1-ol (2 mL) was added 4-5 drops concentrated sulfuric acid at rt. The reaction mixture was heated to 60 $^\circ\text{C}$ and stirred overnight. The reaction solution was extracted twice with EA (20 mL) and H_2O (20 mL). The combined organic phase was dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was chromatographed through silica gel eluting with ethyl acetate/hexanes to give the product.



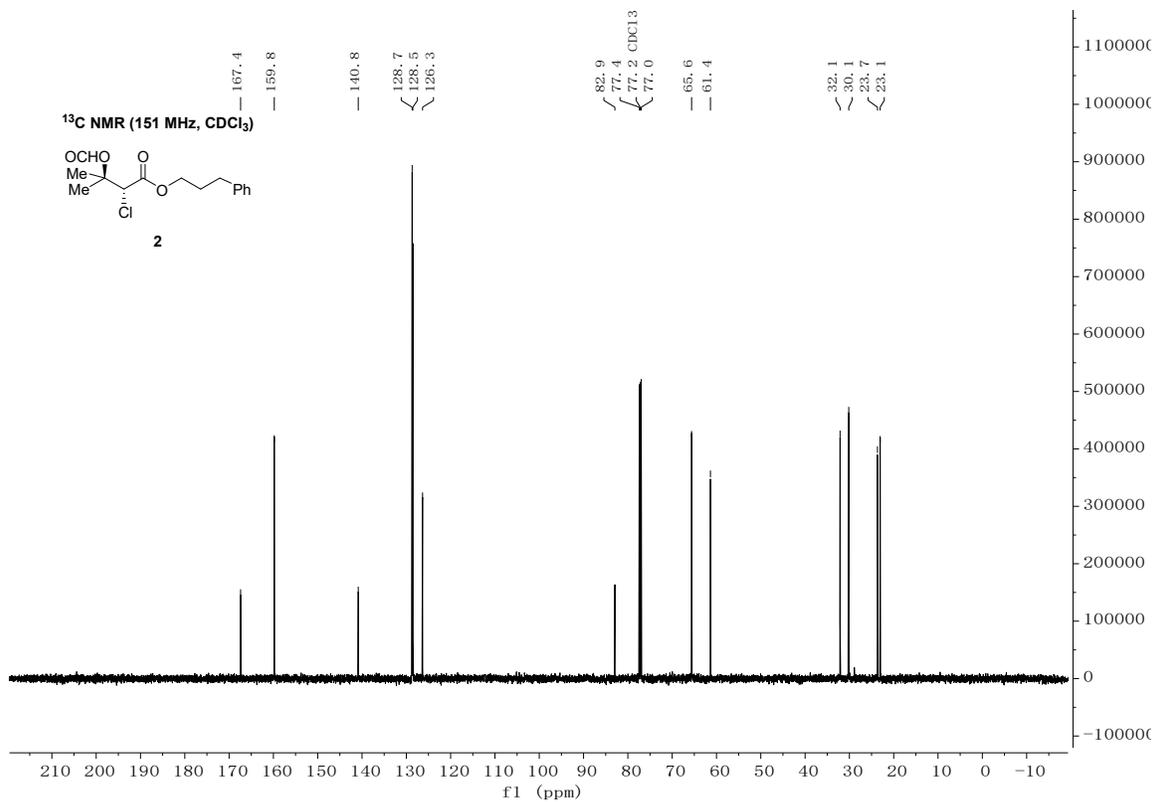
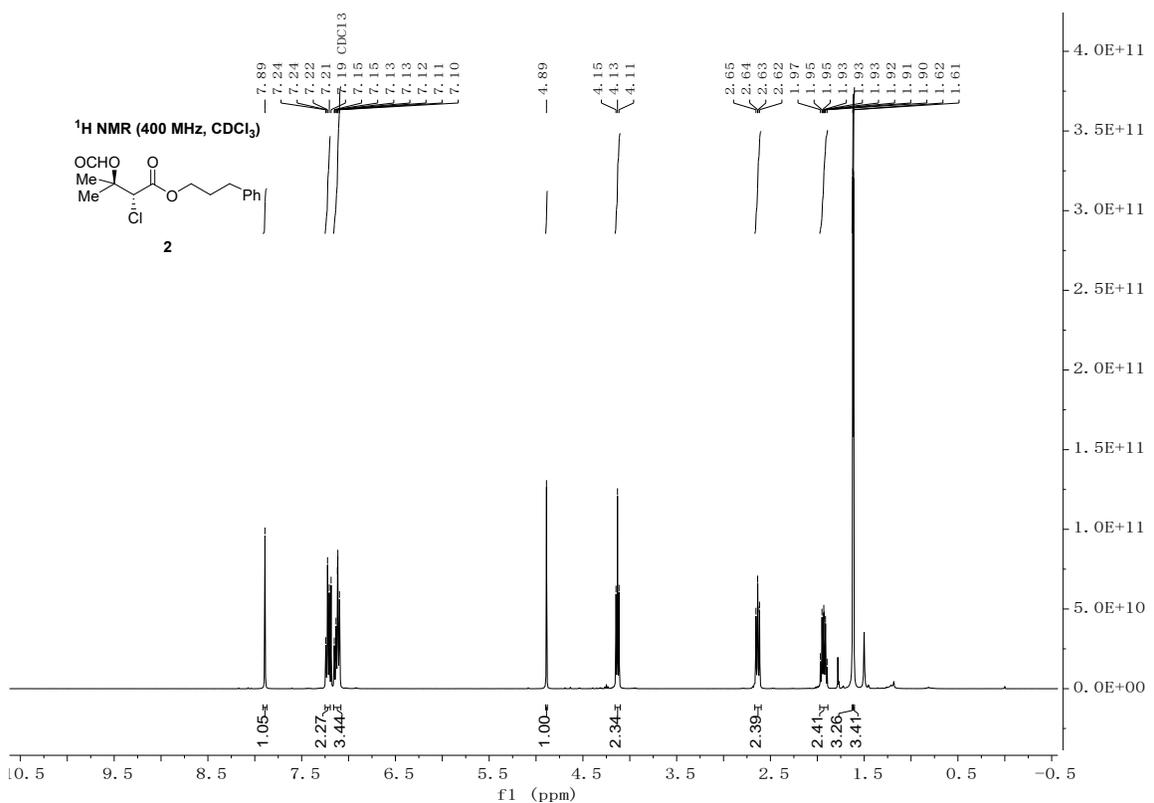
3-Phenylpropyl (E)-hex-2-enoate (S15). The title compound was obtained as a colorless oil in 70% yield (0.72 g) starting from 2,3-dimethylbut-2-en-1-ol (5 mmol, 1.0 equiv) and 3-phenylpropan-1-ol (2 mL) by

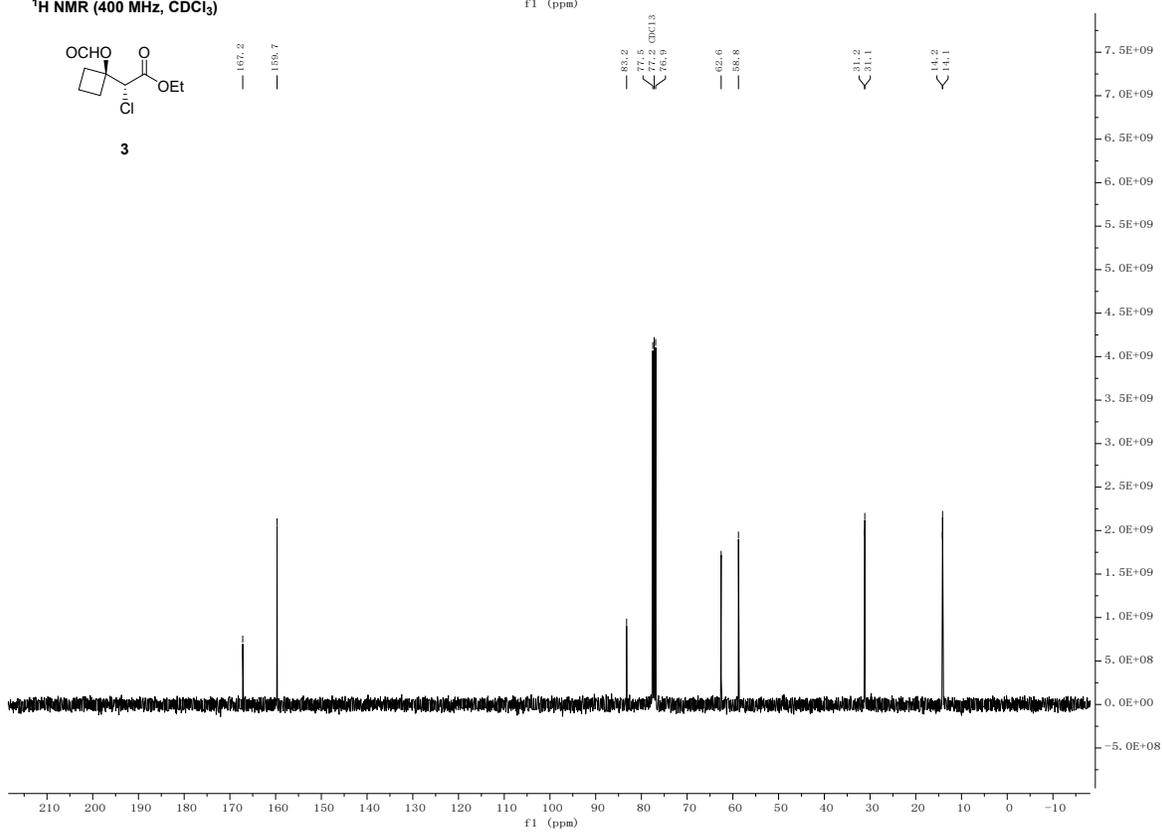
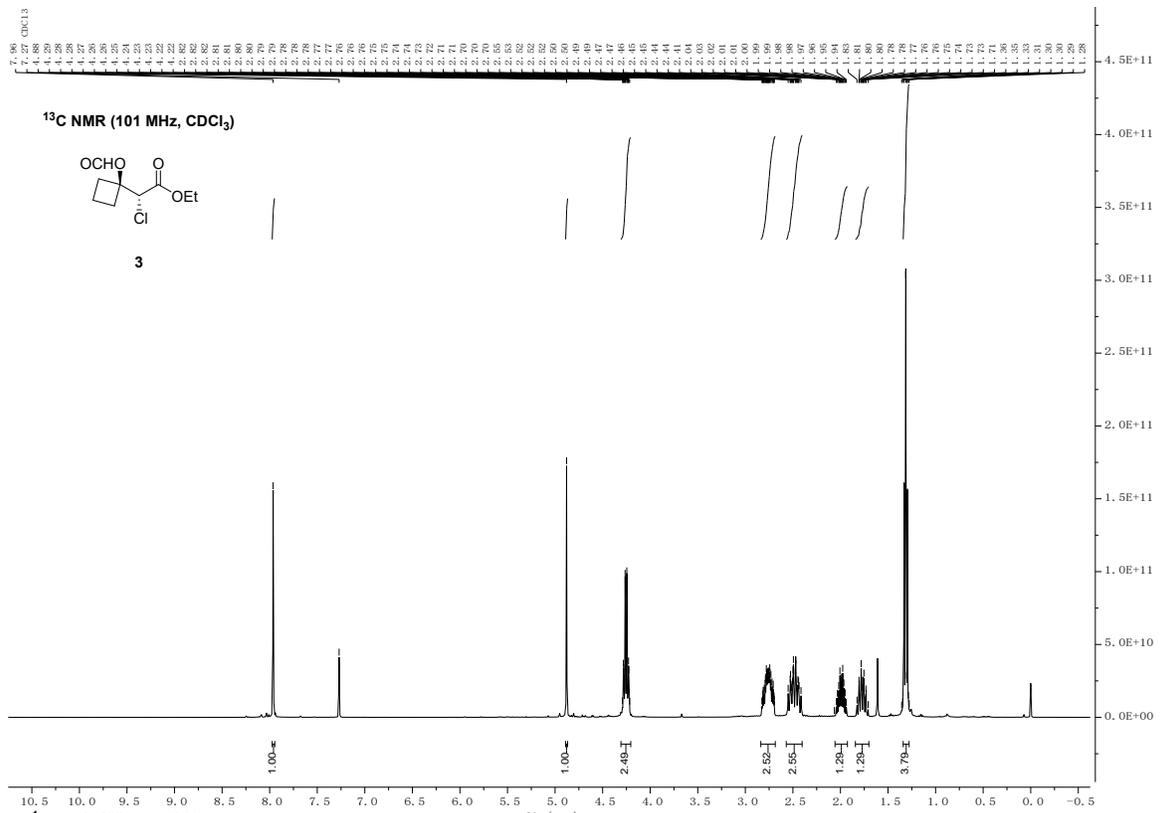
following the General Procedure. ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.27 (m, 2H), 7.22–7.16 (m, 3H), 6.96 (dt, *J* = 15.6, 7.0 Hz, 1H), 5.83 (dt, *J* = 15.7, 1.6 Hz, 1H), 4.15 (t, *J* = 6.5 Hz, 2H), 2.71 (dd, *J* = 8.6, 6.8 Hz, 2H), 2.19 (qd, *J* = 7.1, 1.6 Hz, 2H), 2.04–1.95 (m, 2H), 1.50 (h, *J* = 7.4 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 166.9, 149.5, 141.4, 128.6, 126.1, 121.4, 63.7, 34.4, 32.4, 30.5, 21.4, 13.8; ESI HRMS *m/z* (M+Na)⁺ calcd 255.1356, 255.1355.

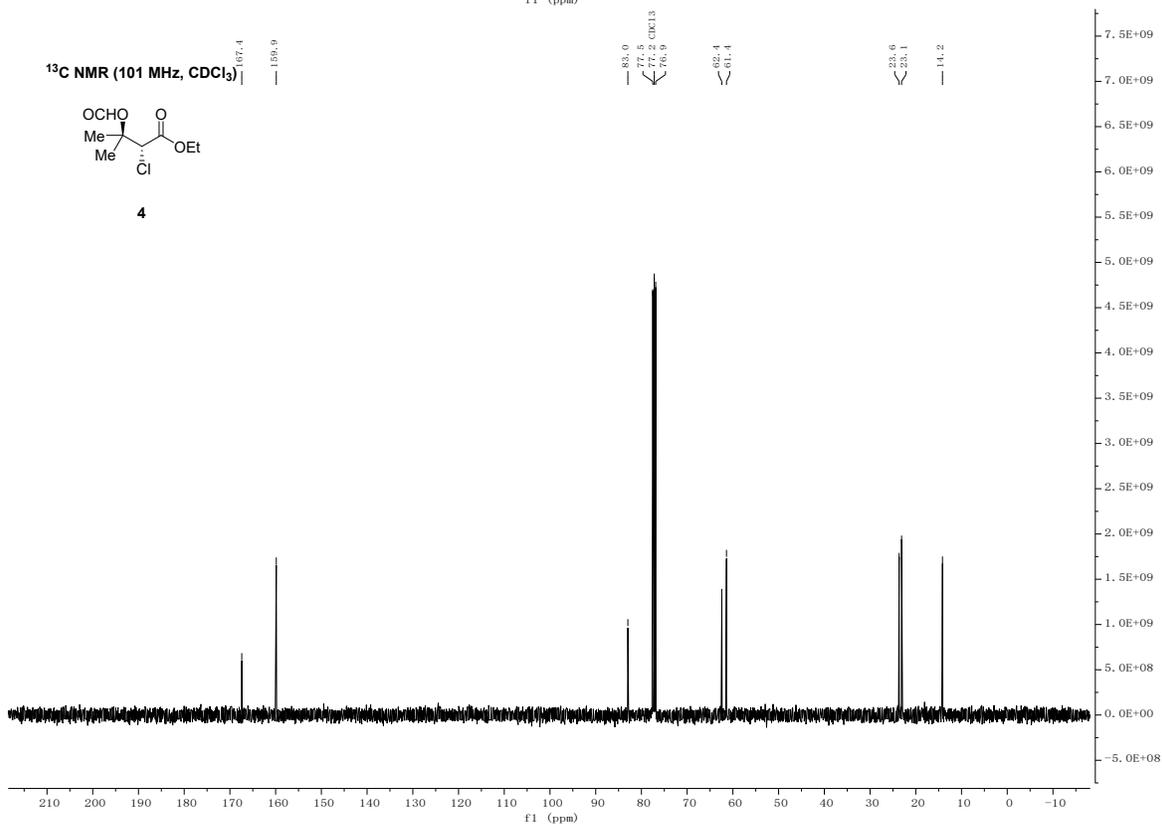
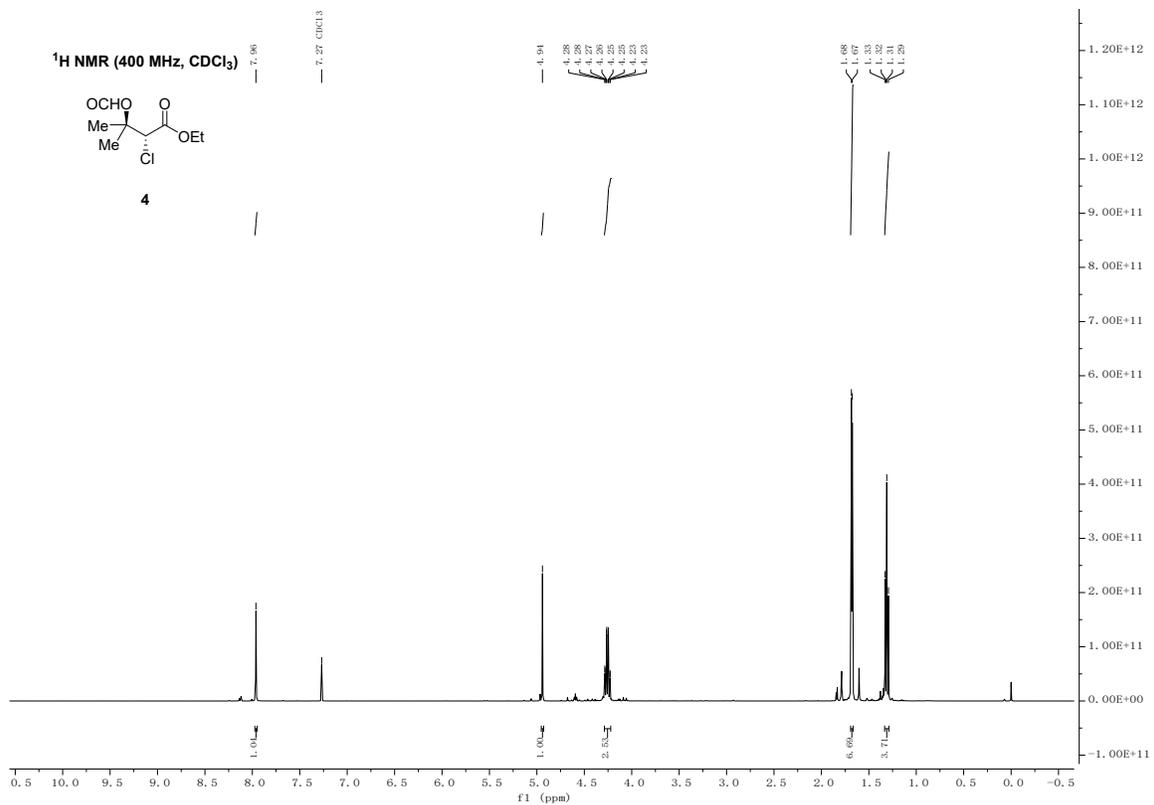
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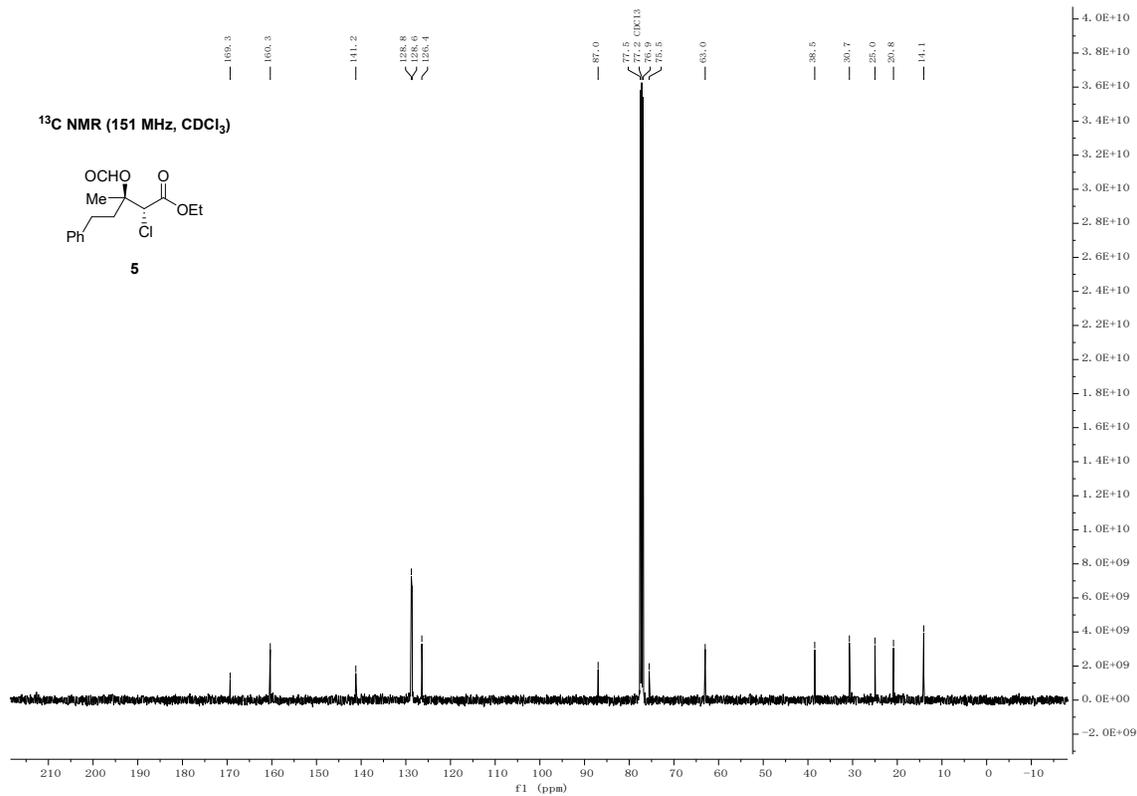
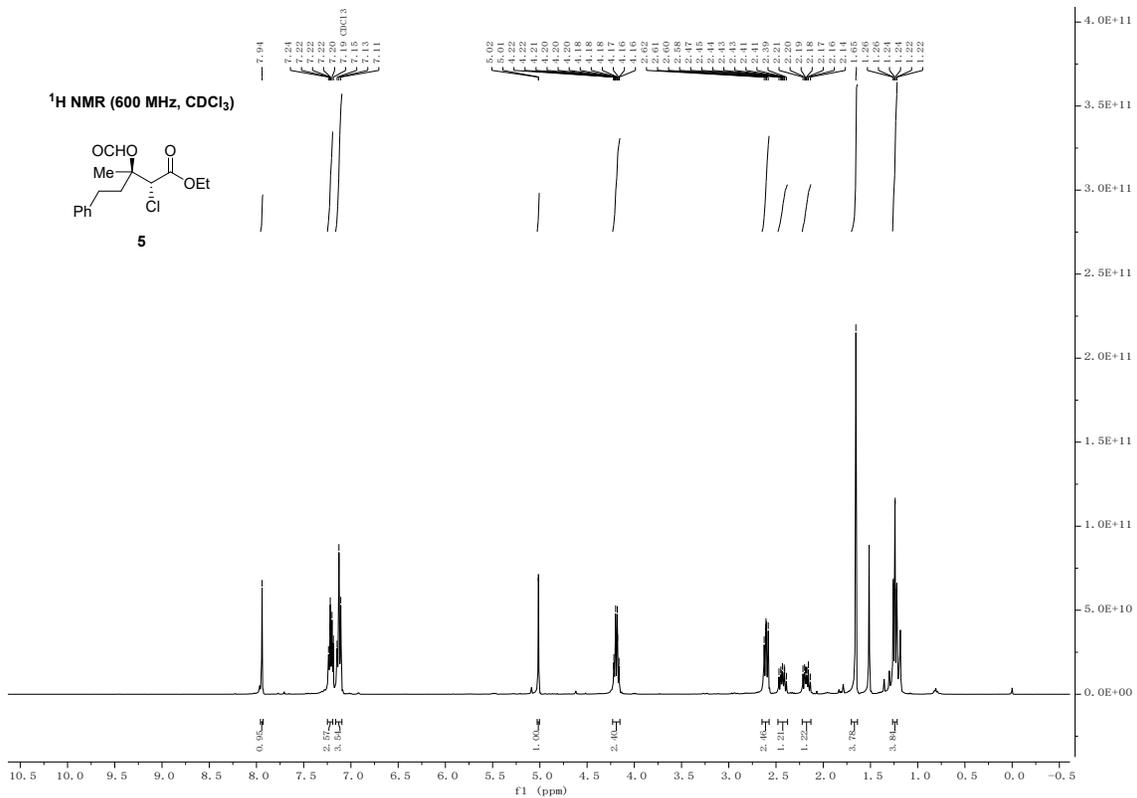
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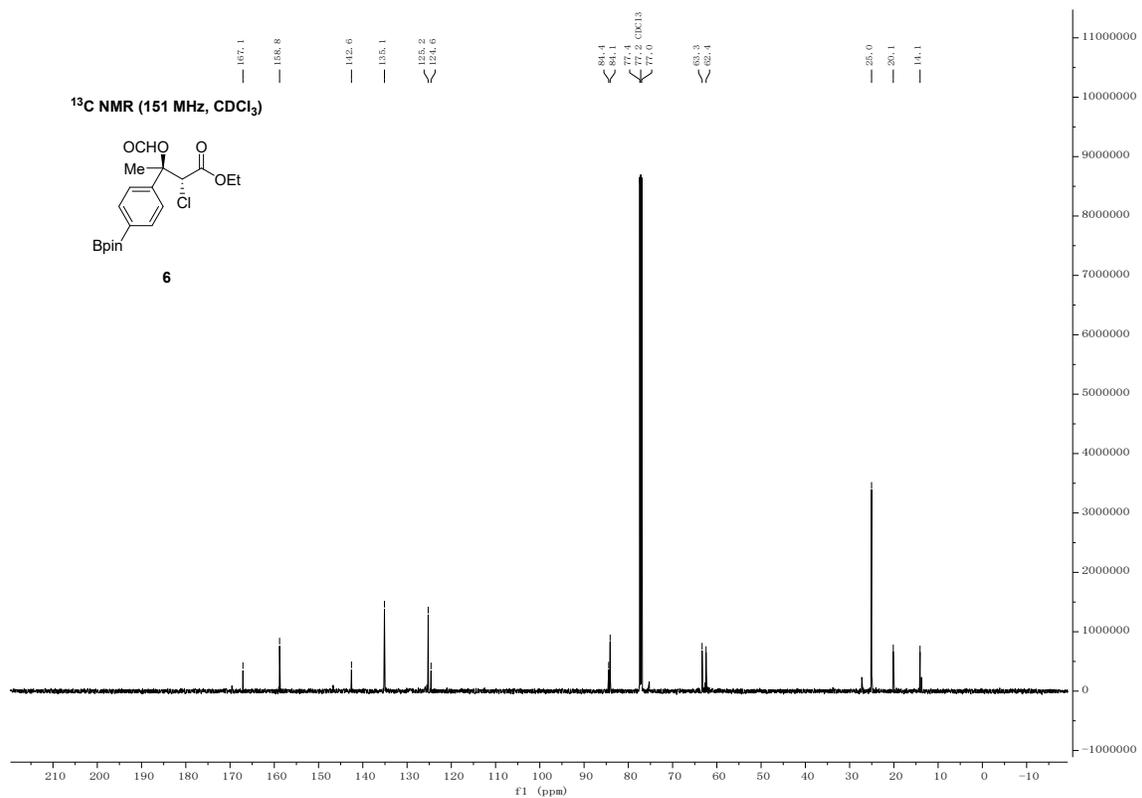
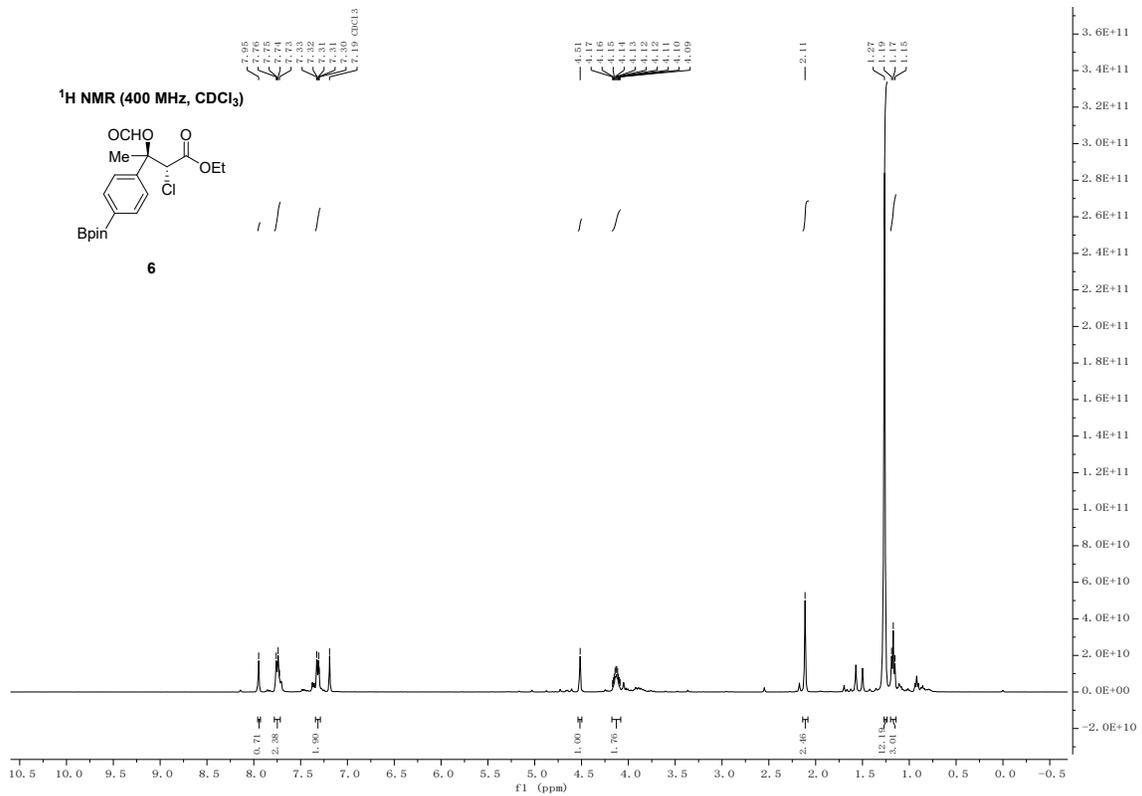
11. NMR spectra for new compounds

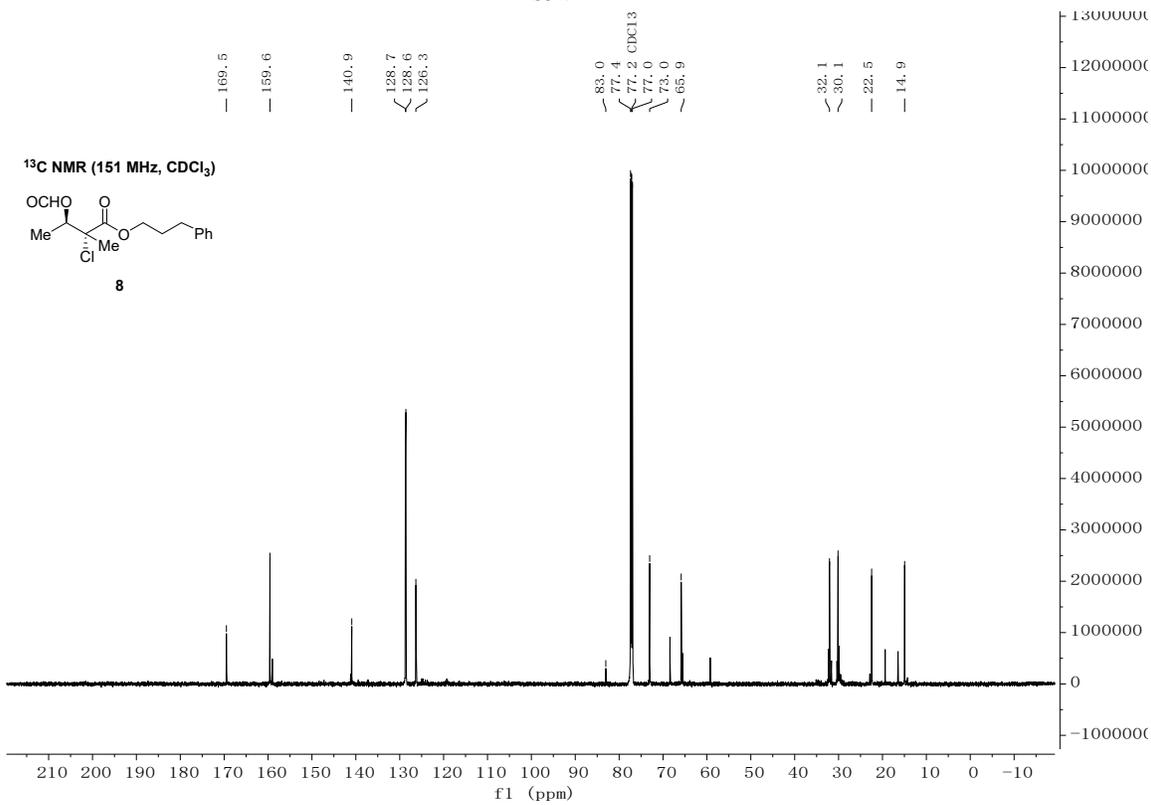
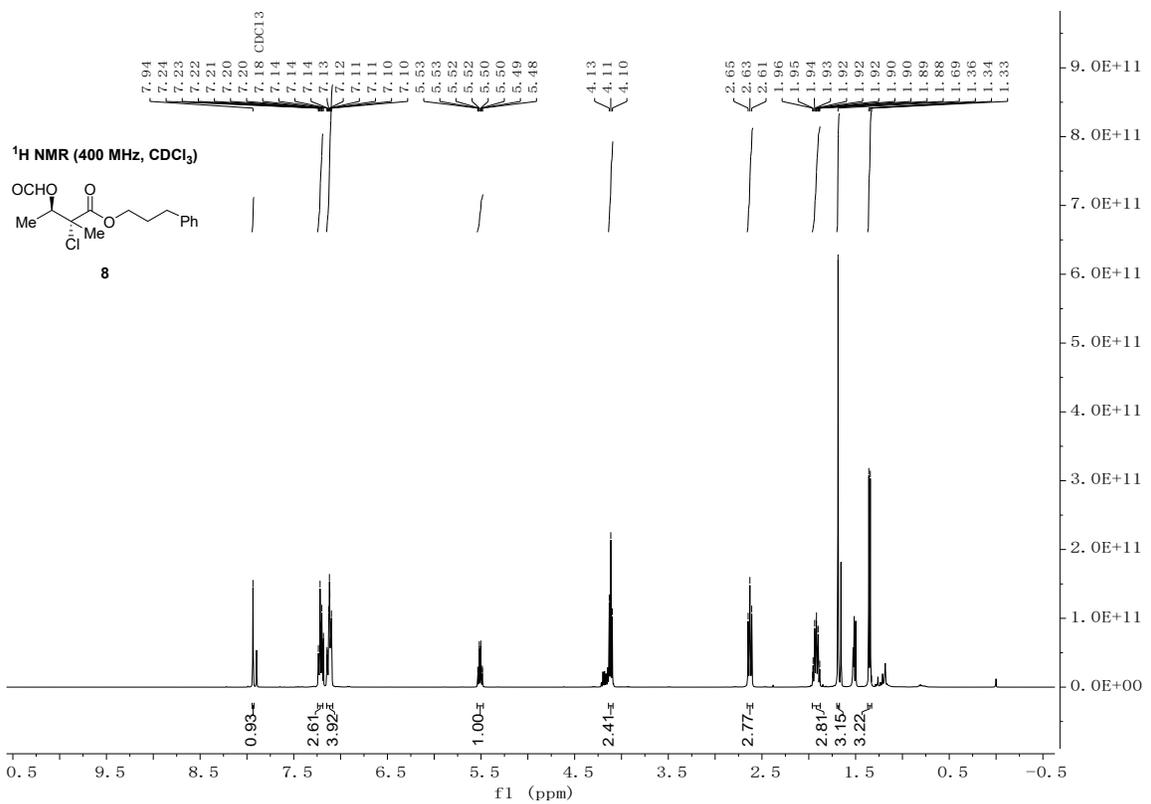


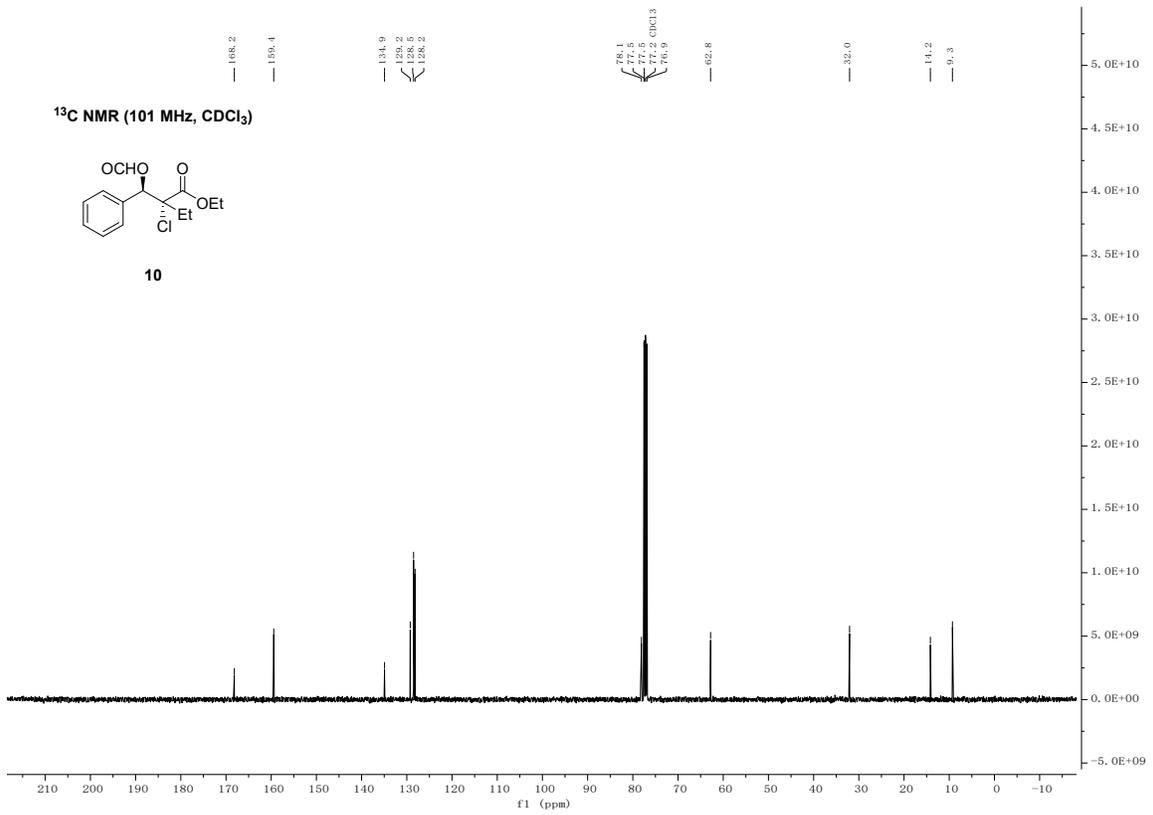
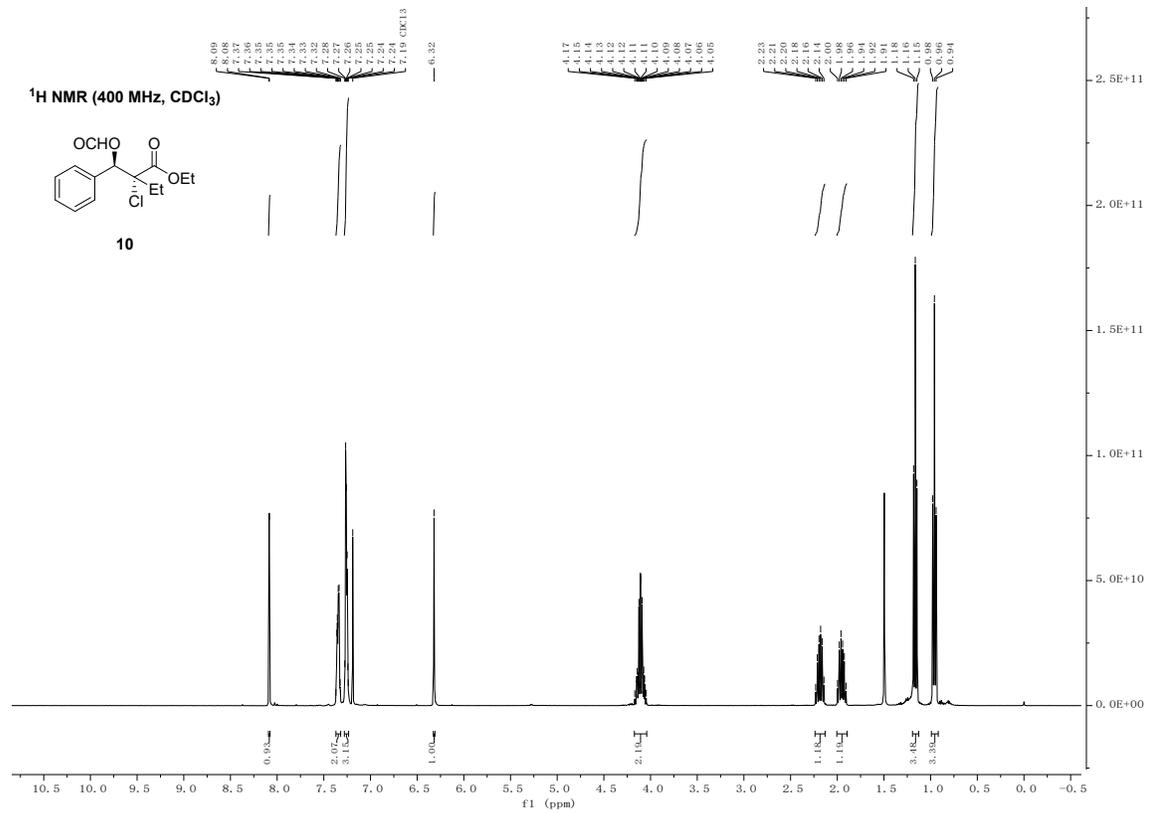


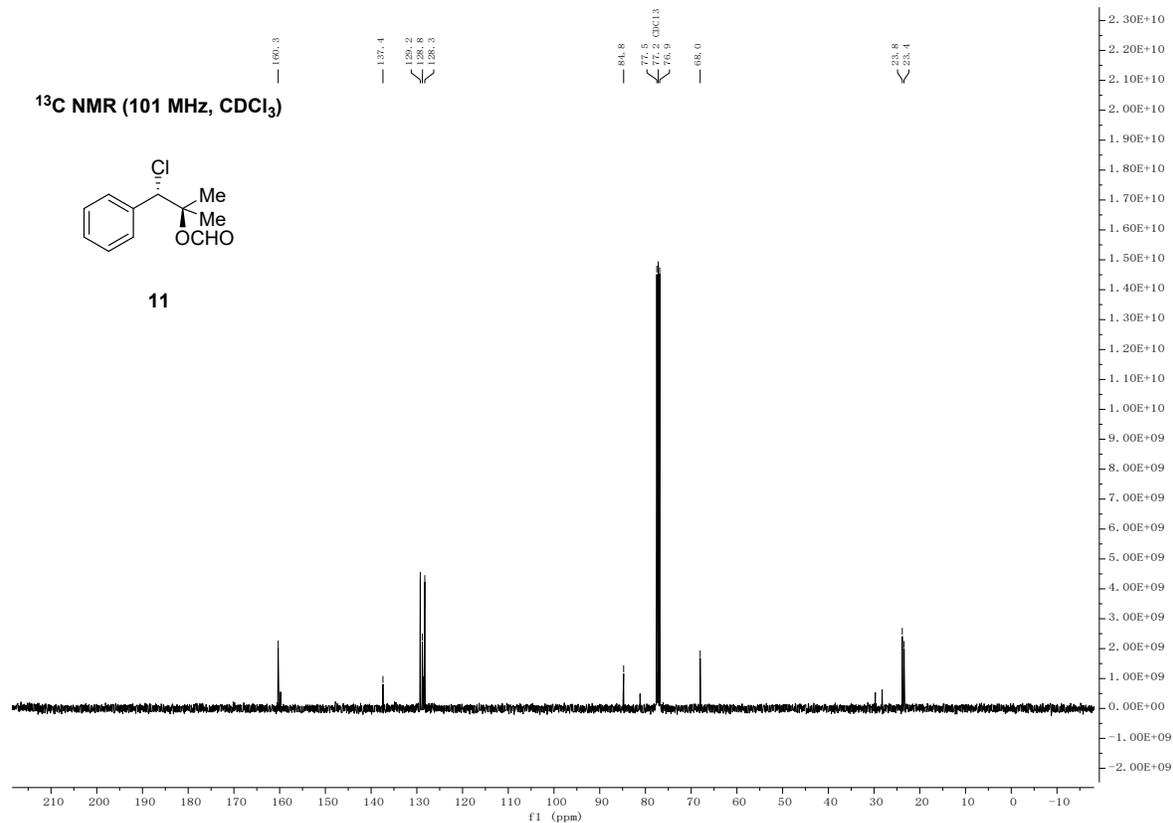
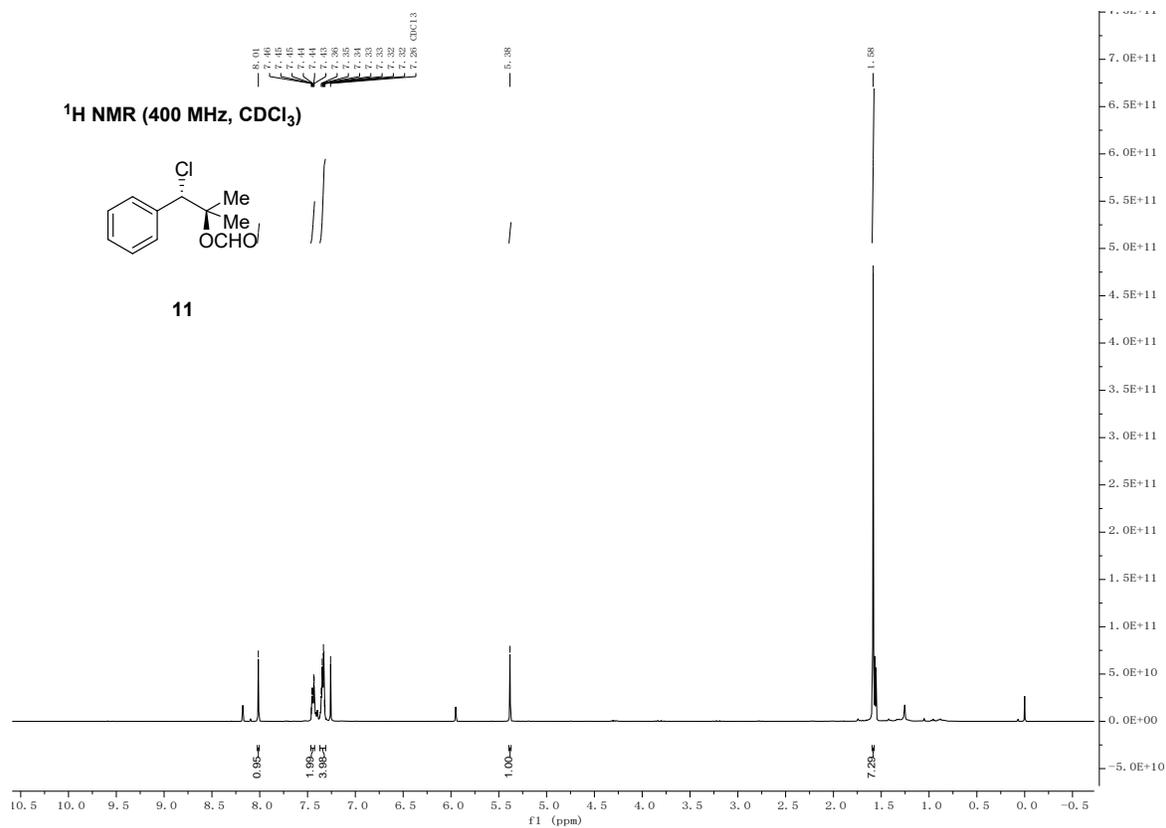


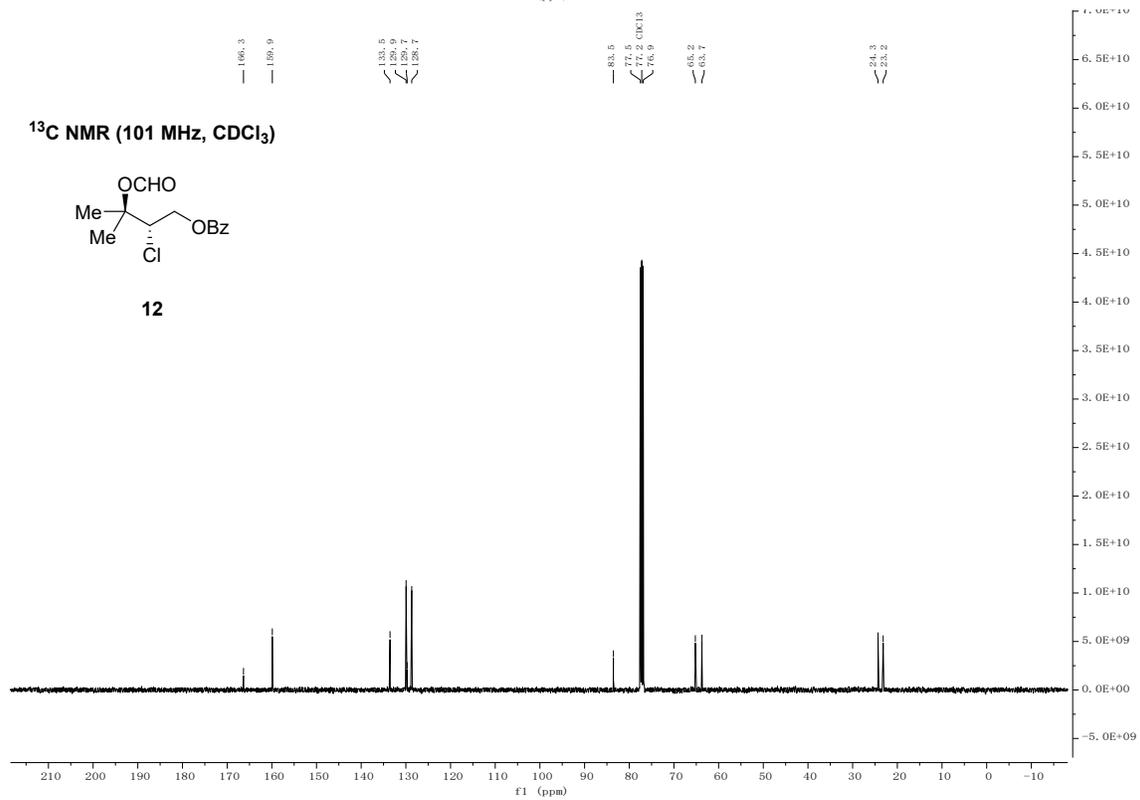
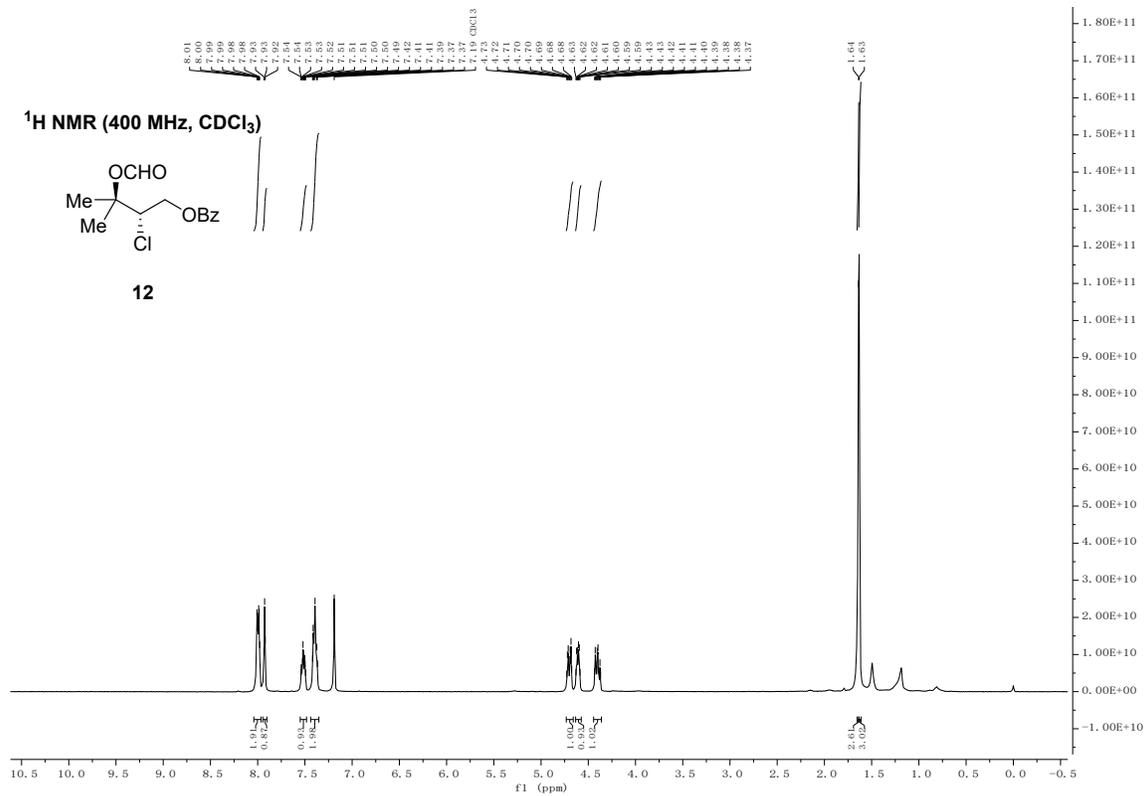


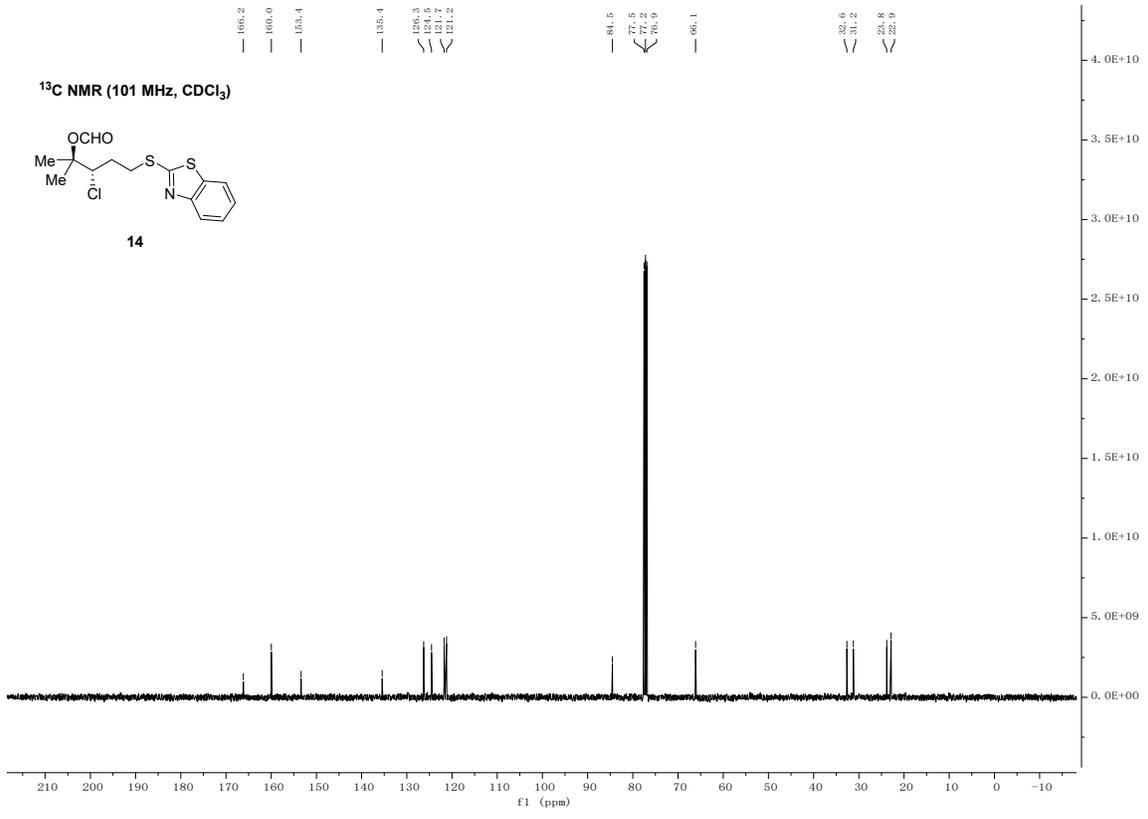
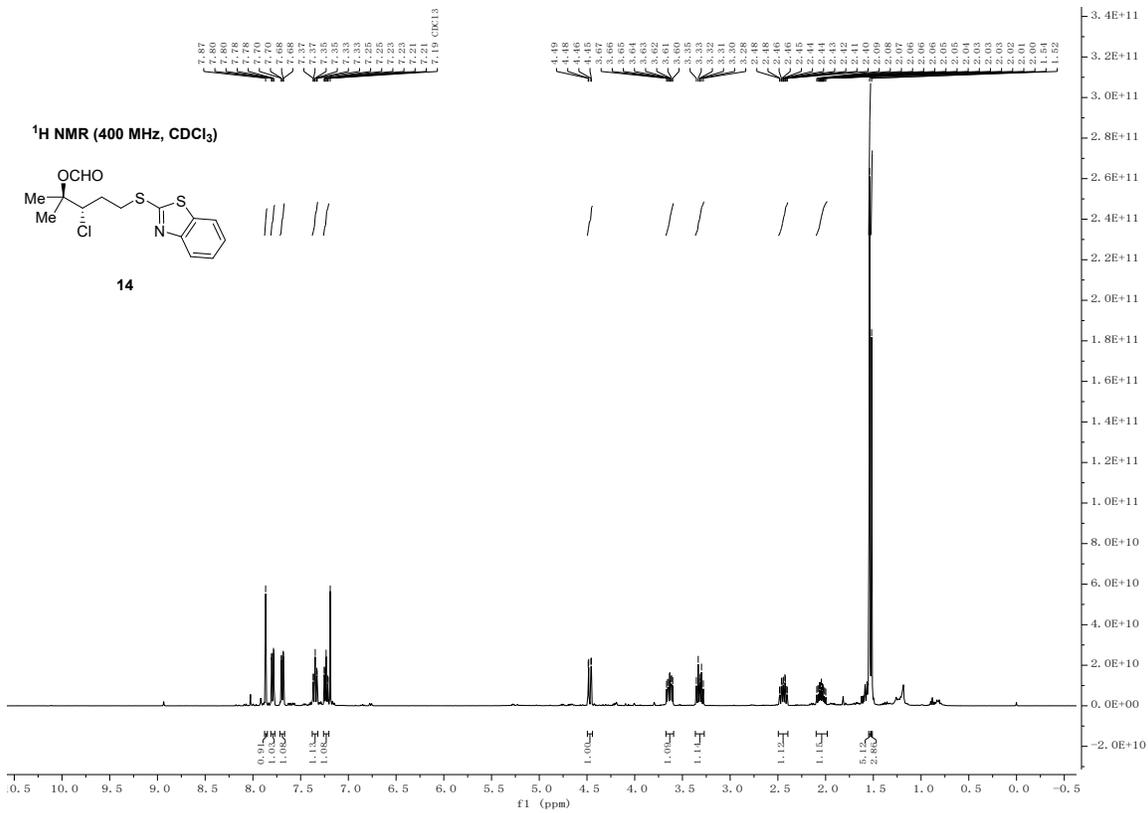


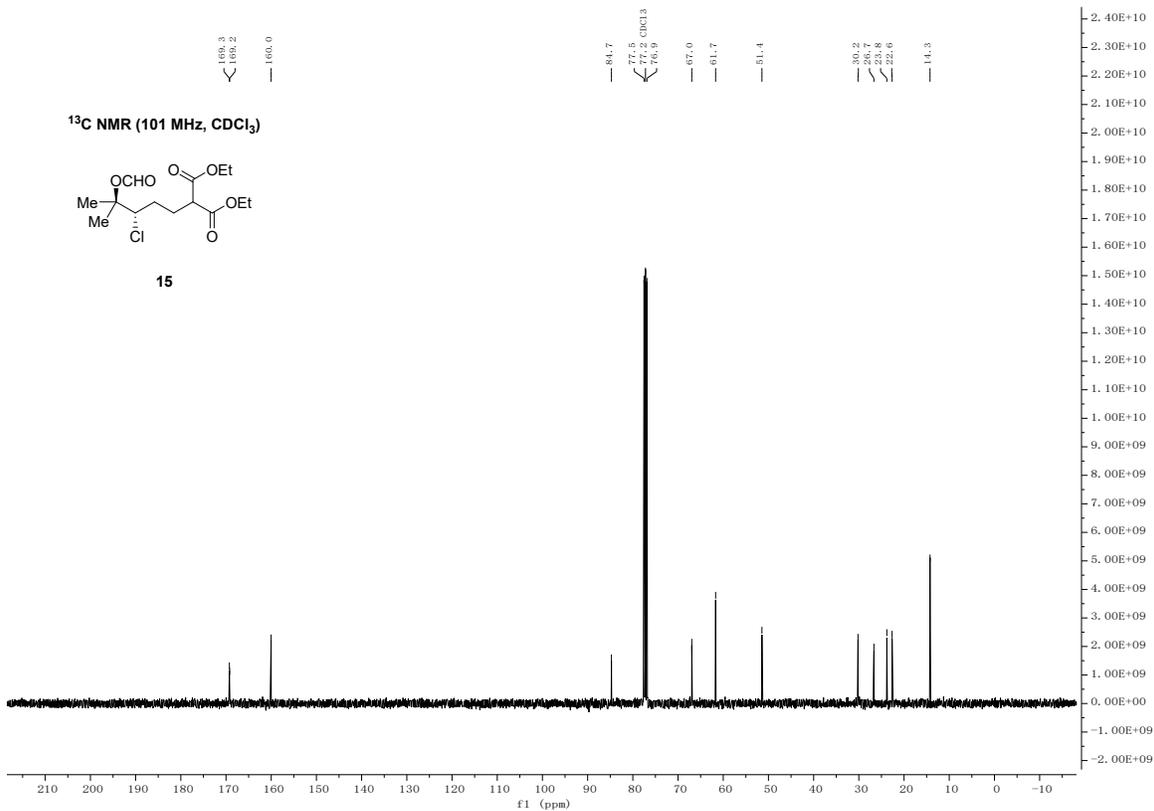
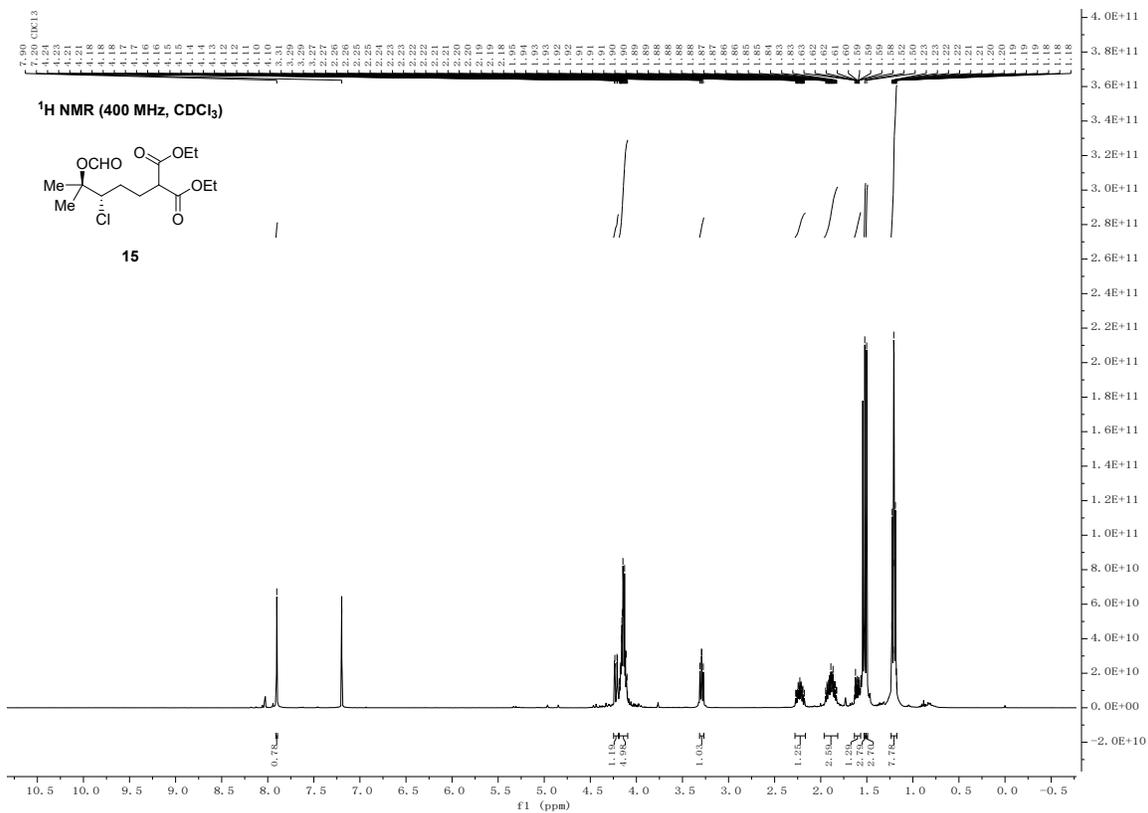


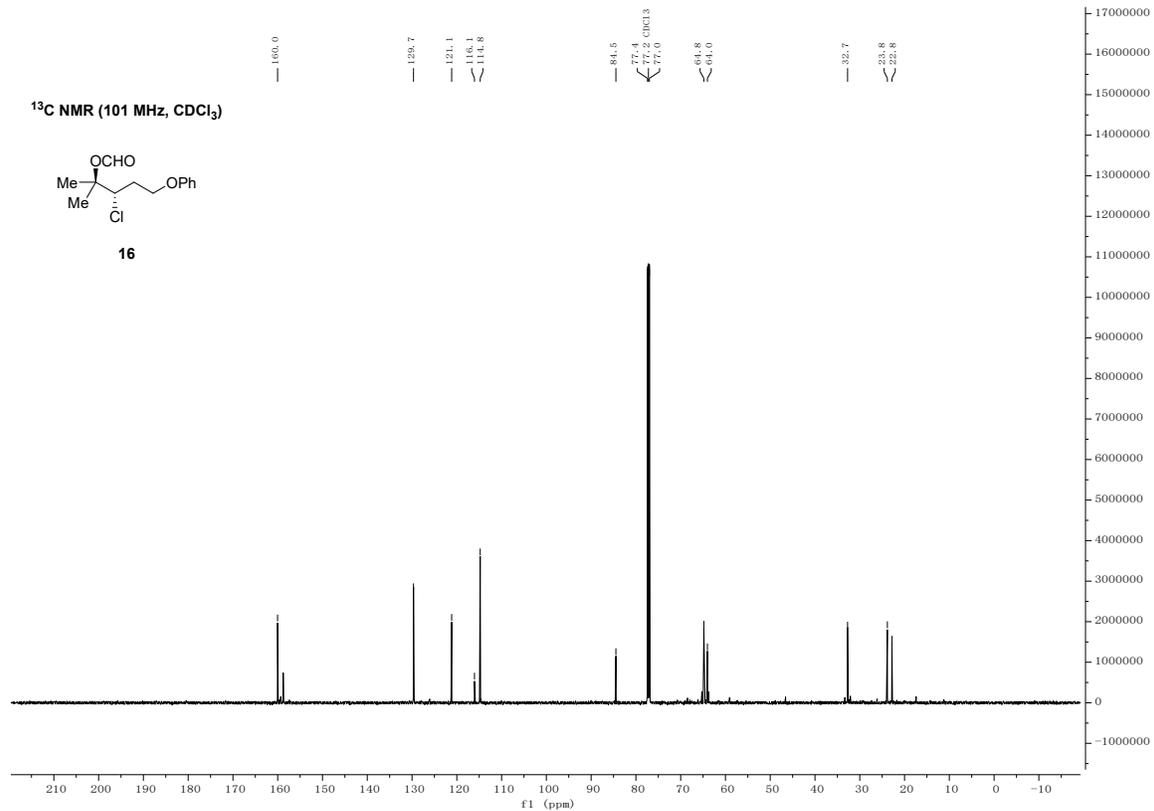
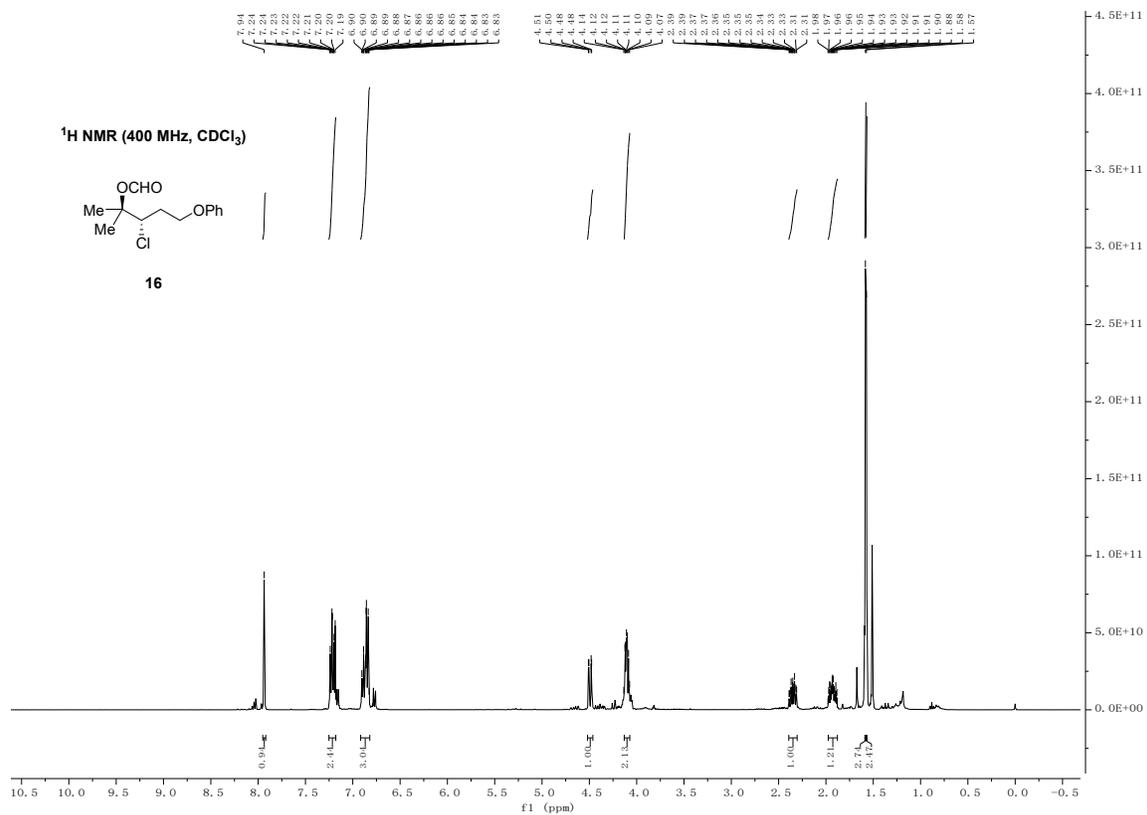


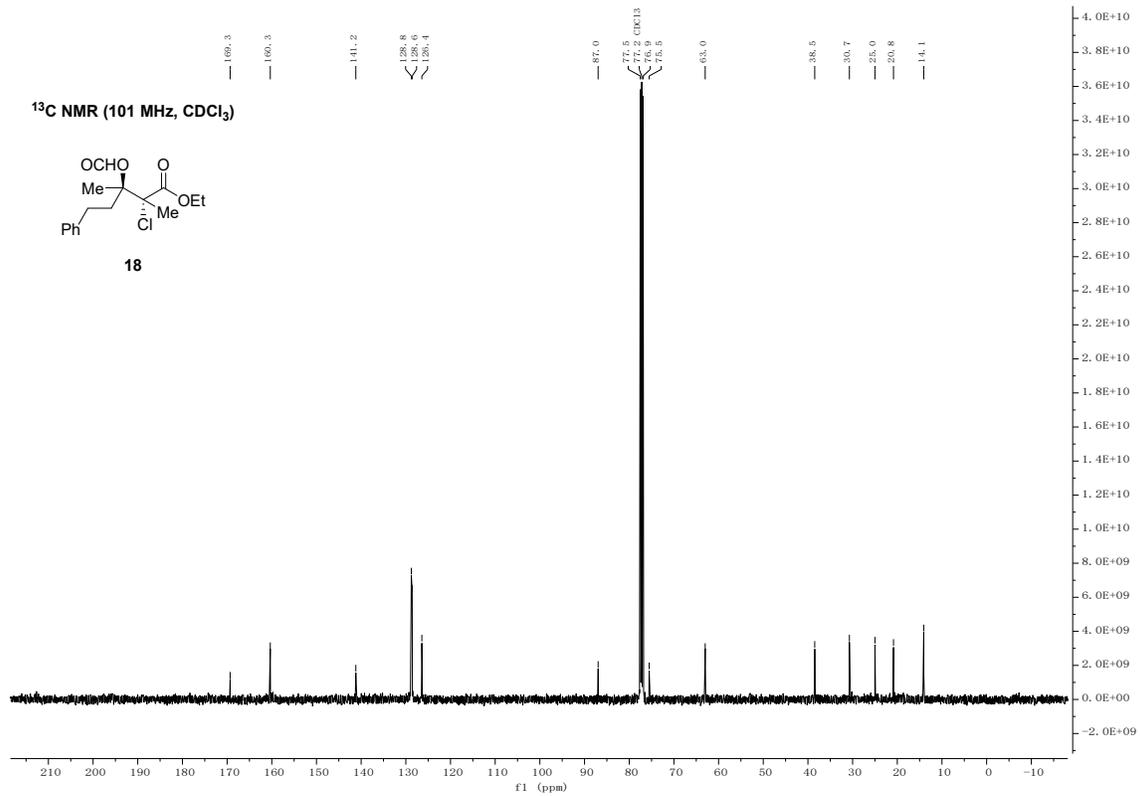
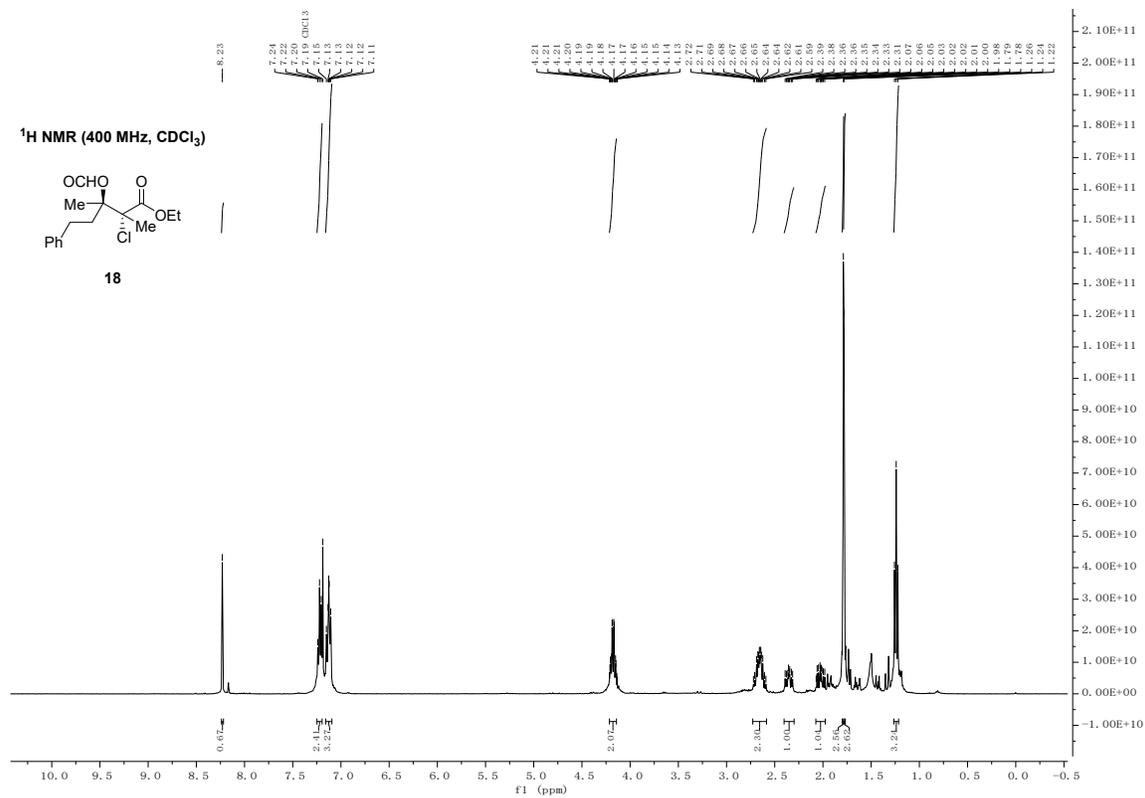


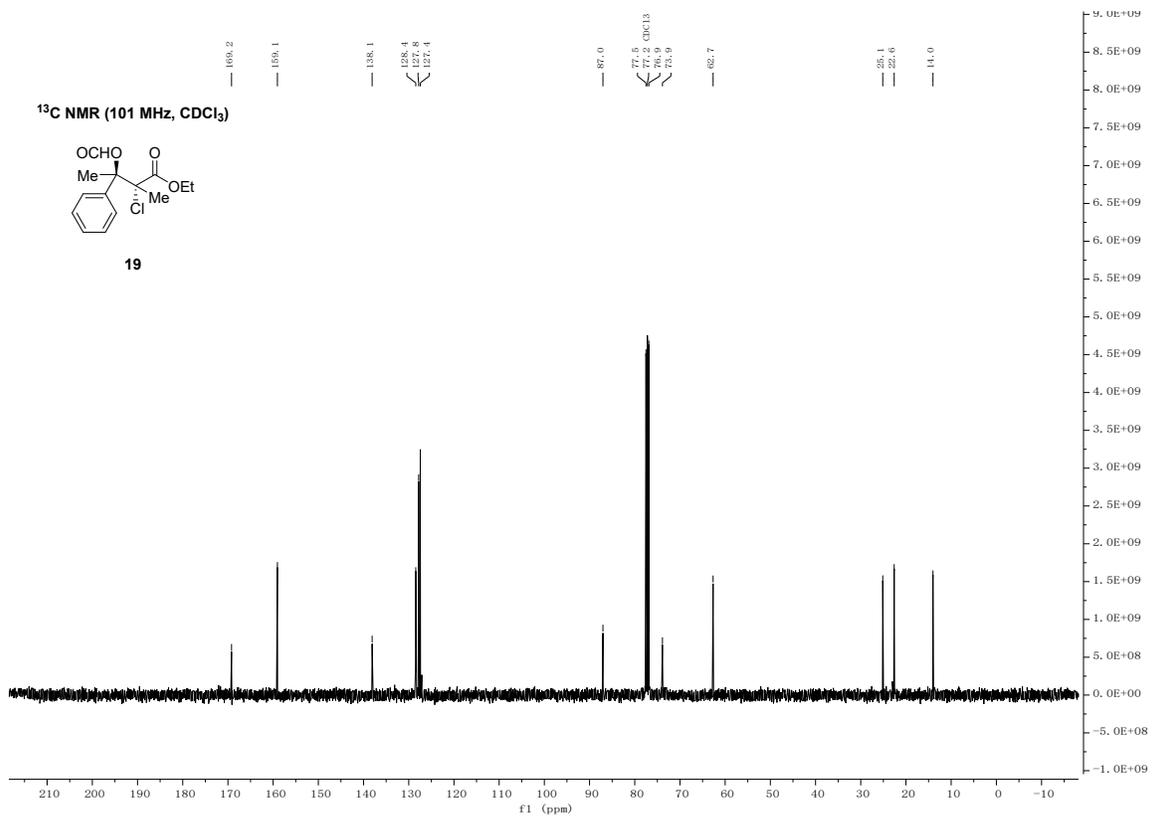
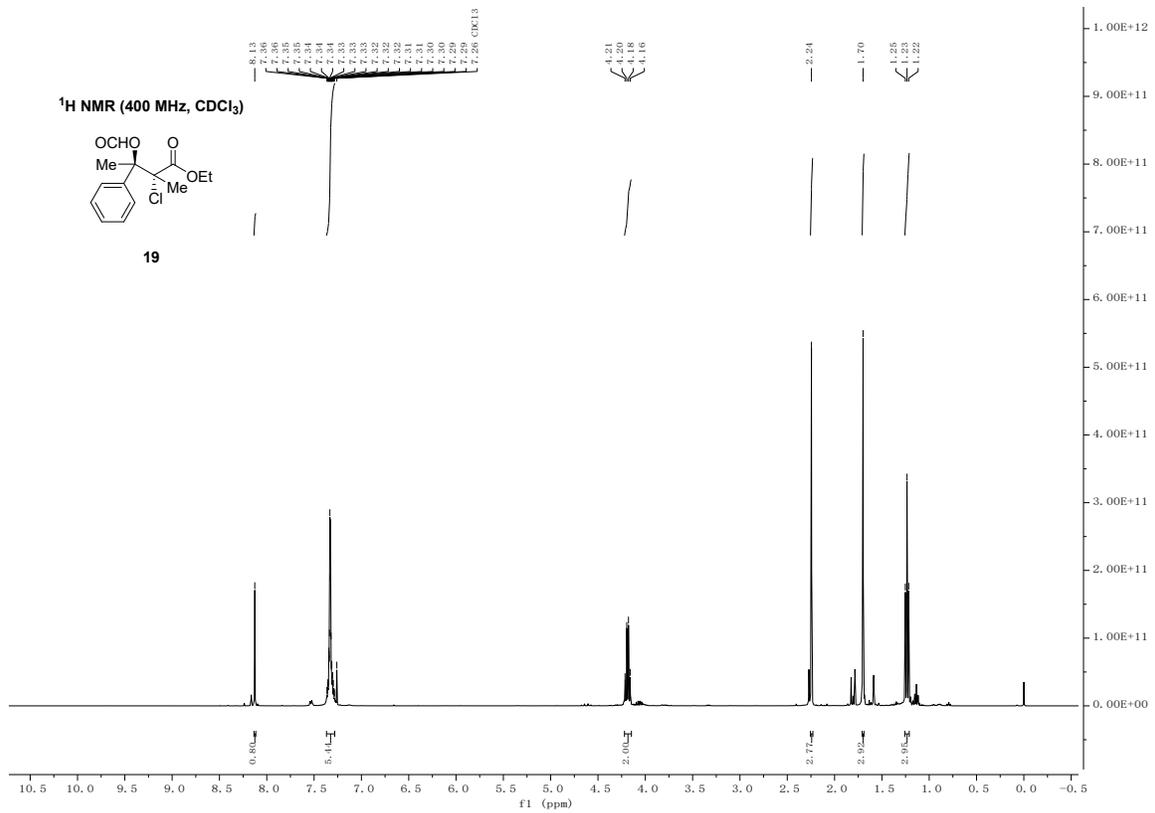


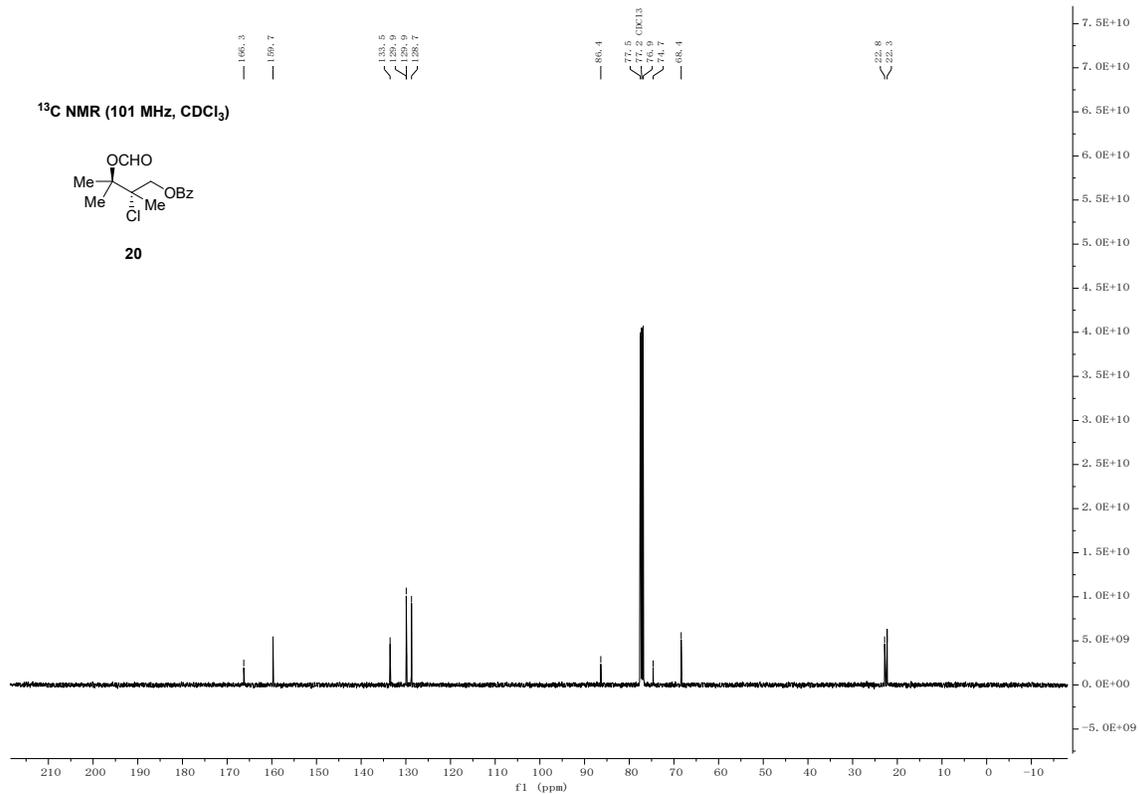
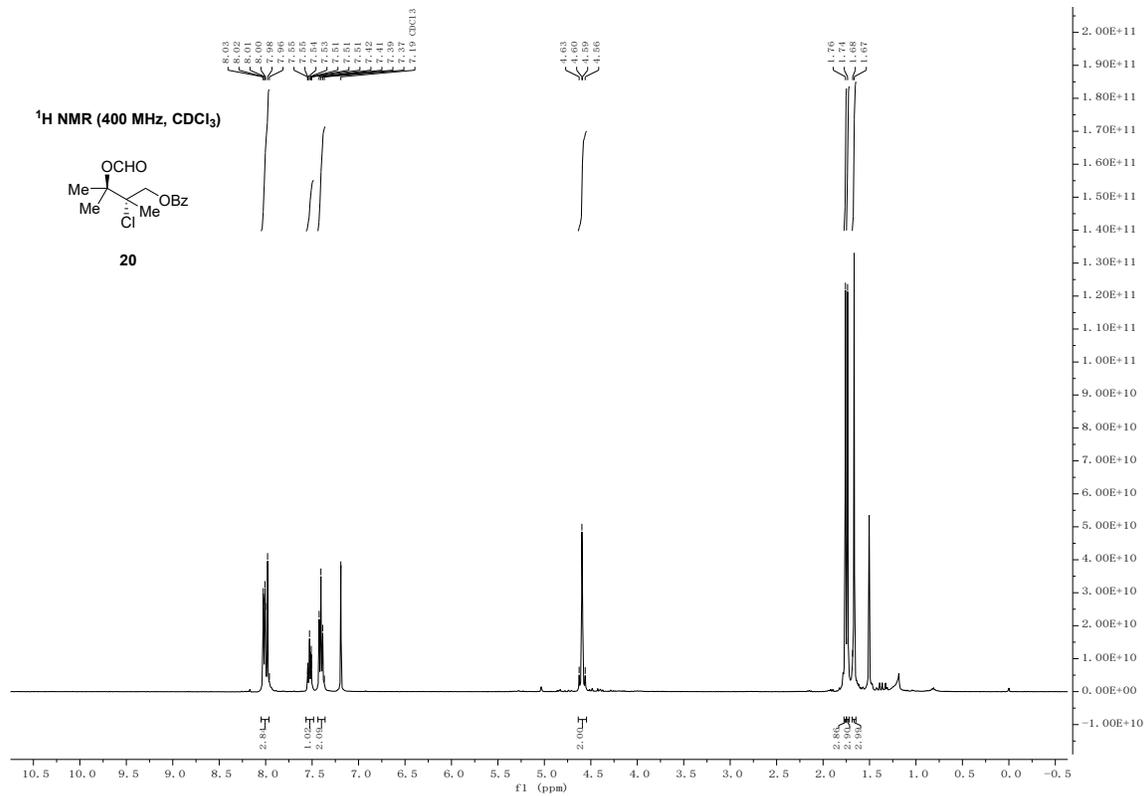


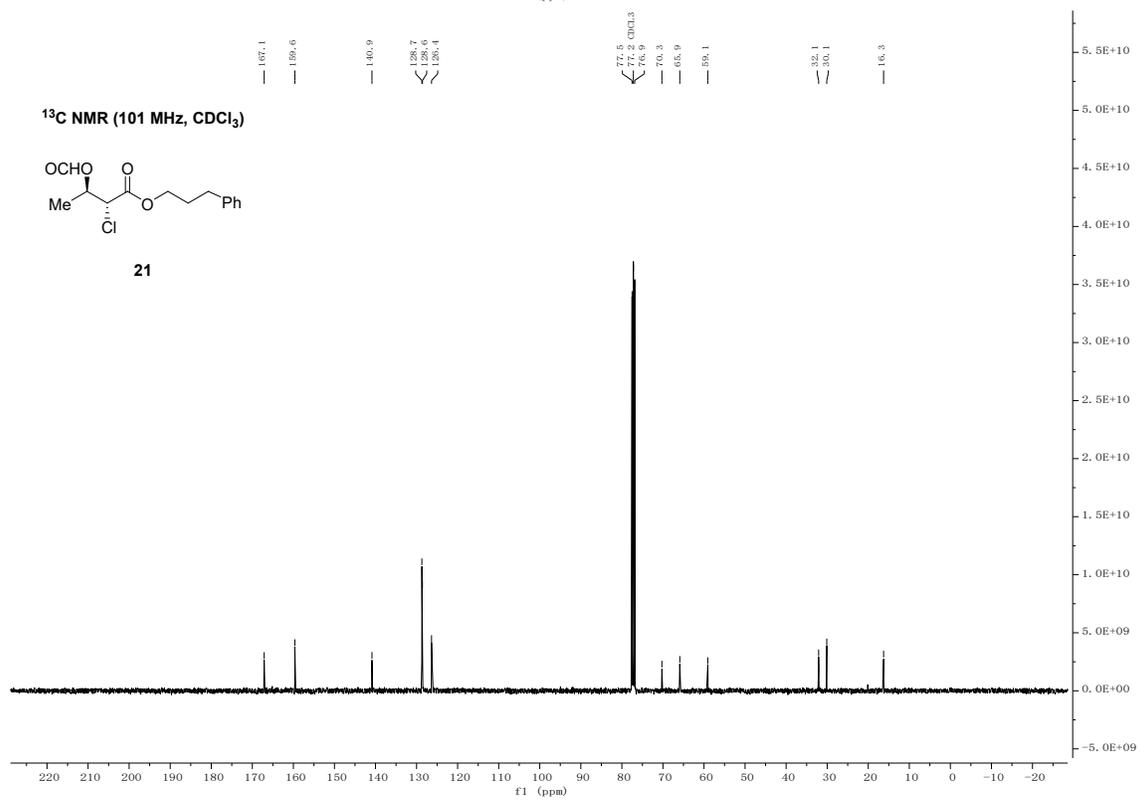
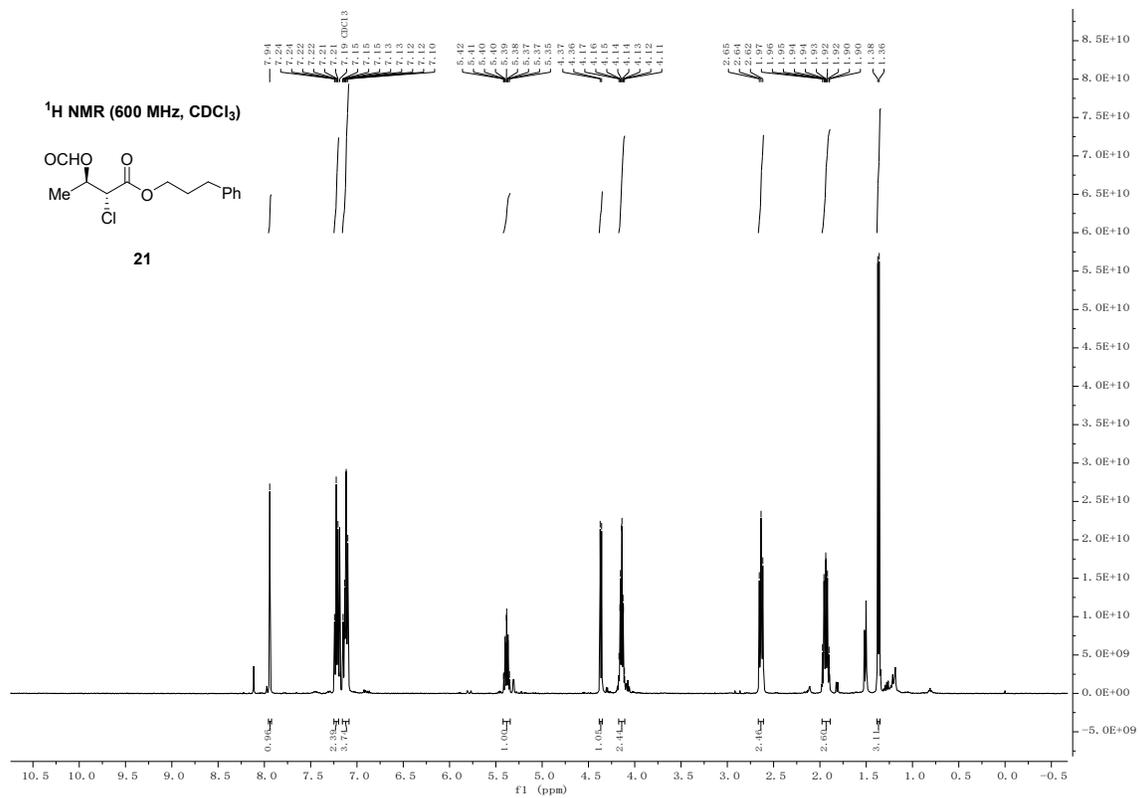


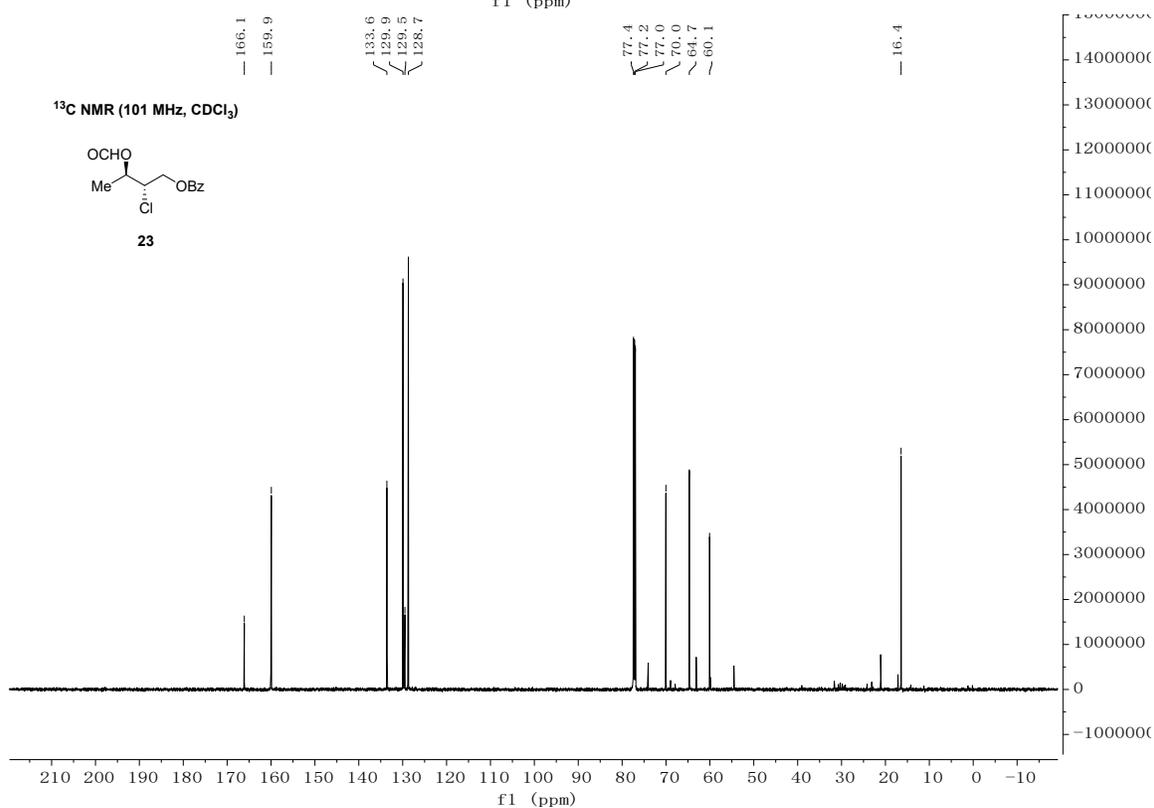
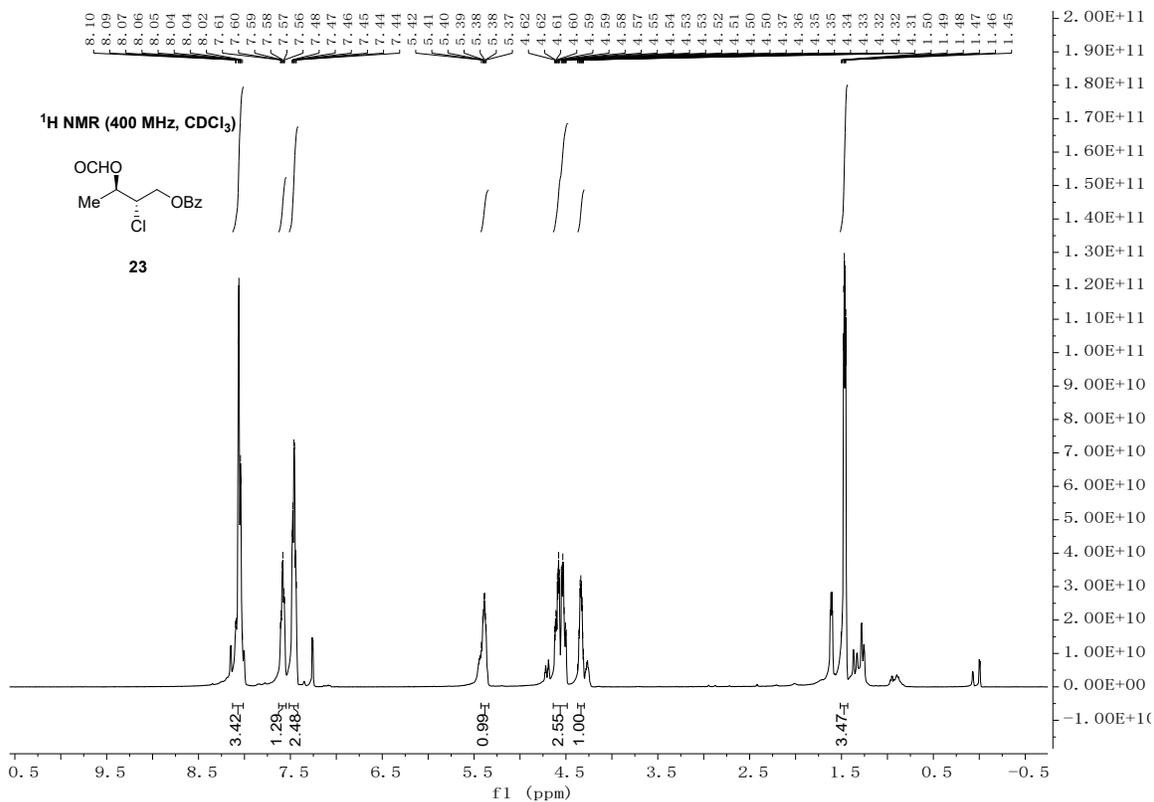


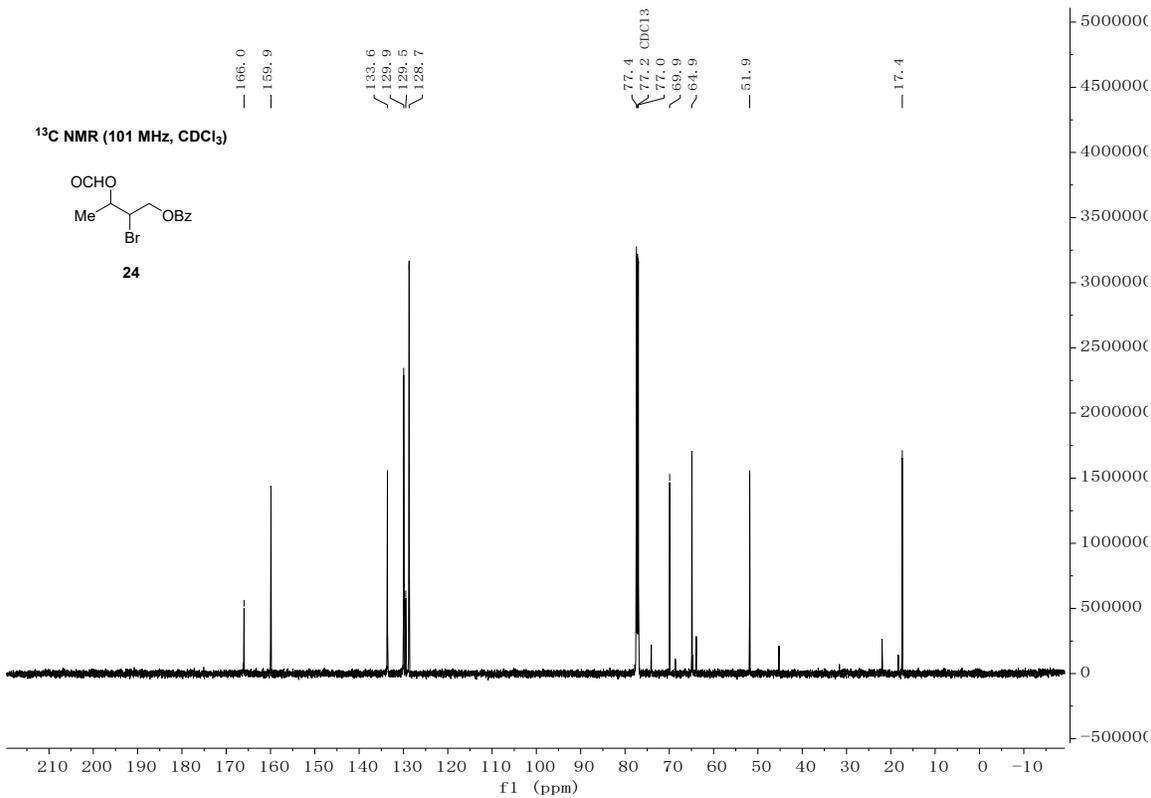
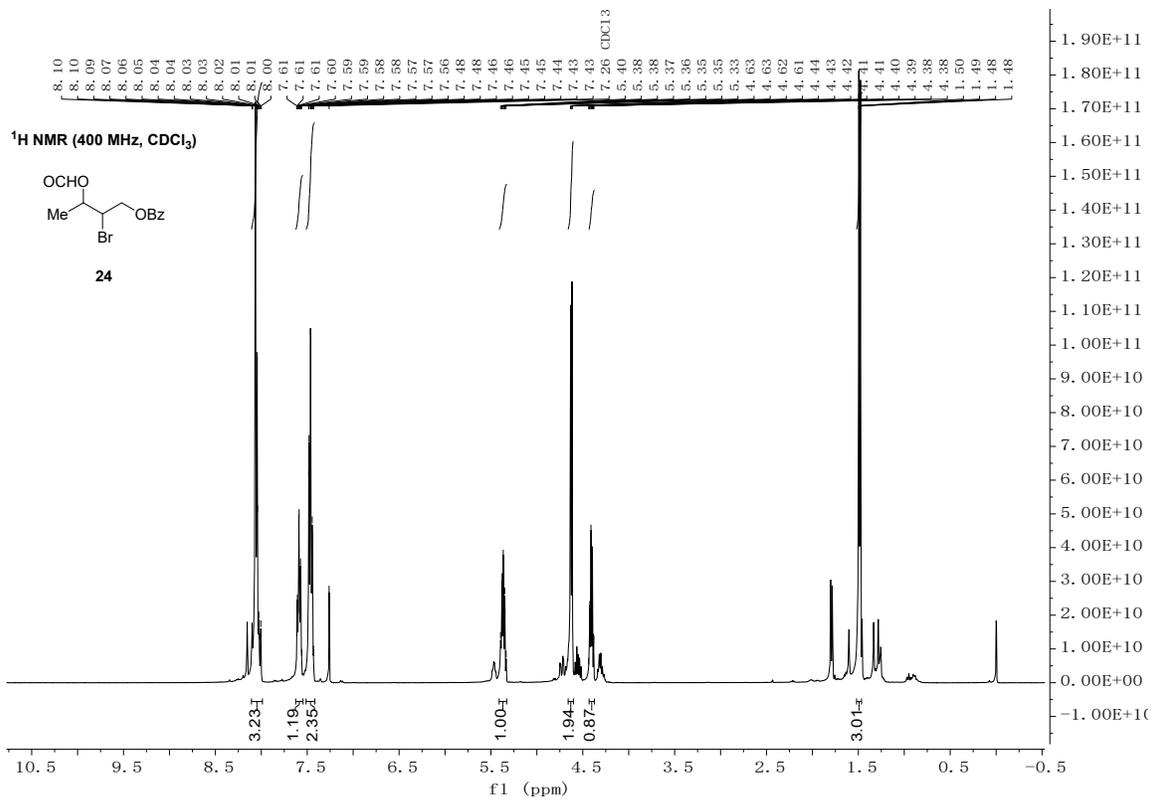


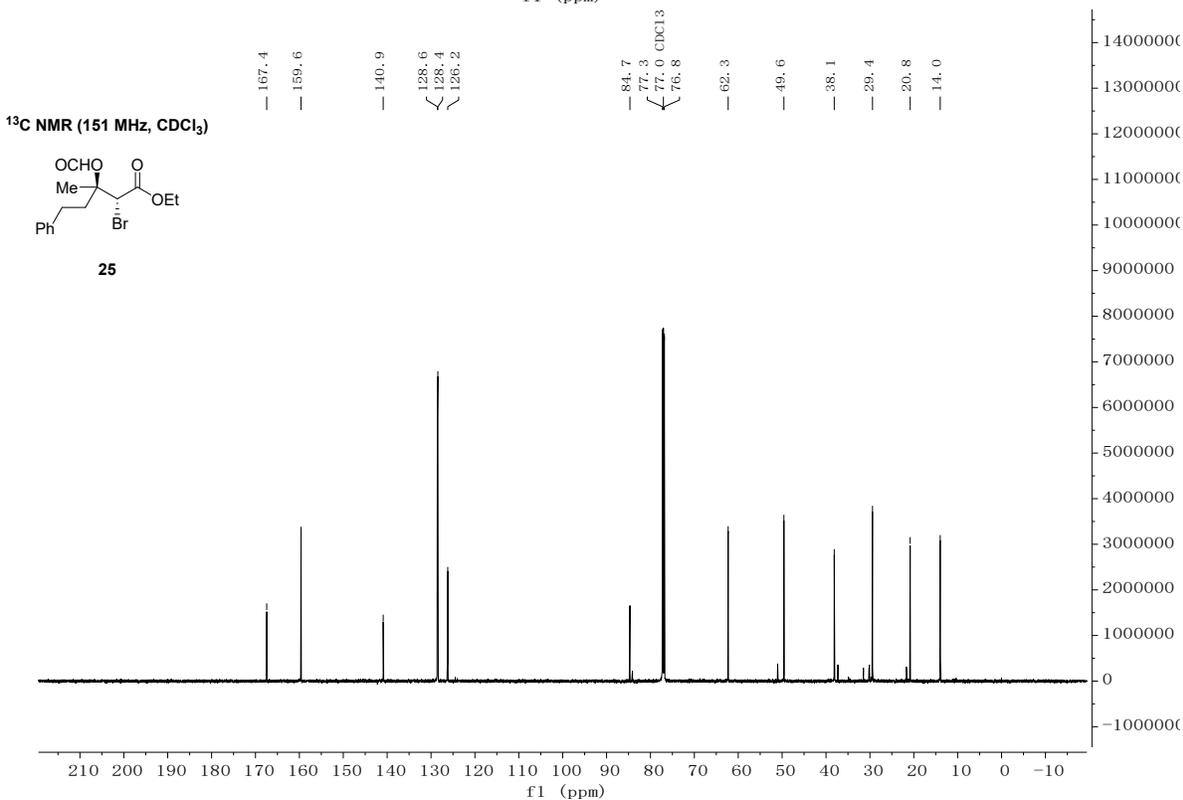
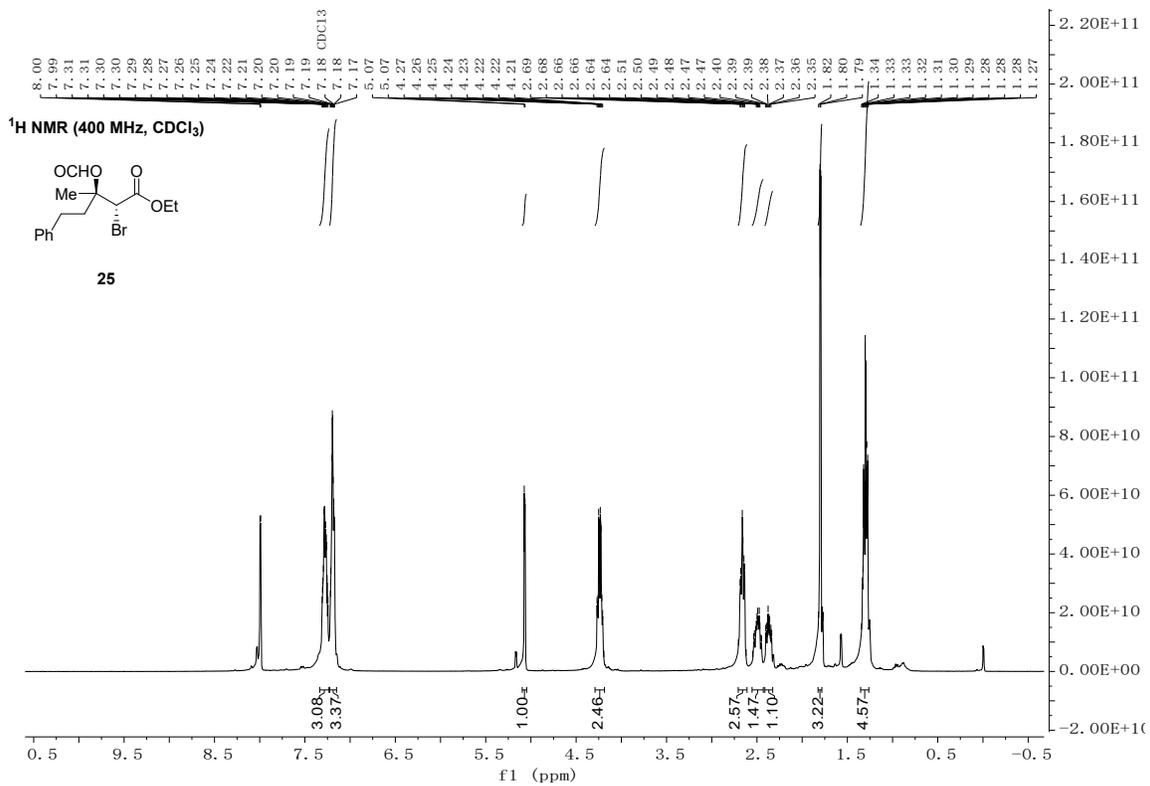


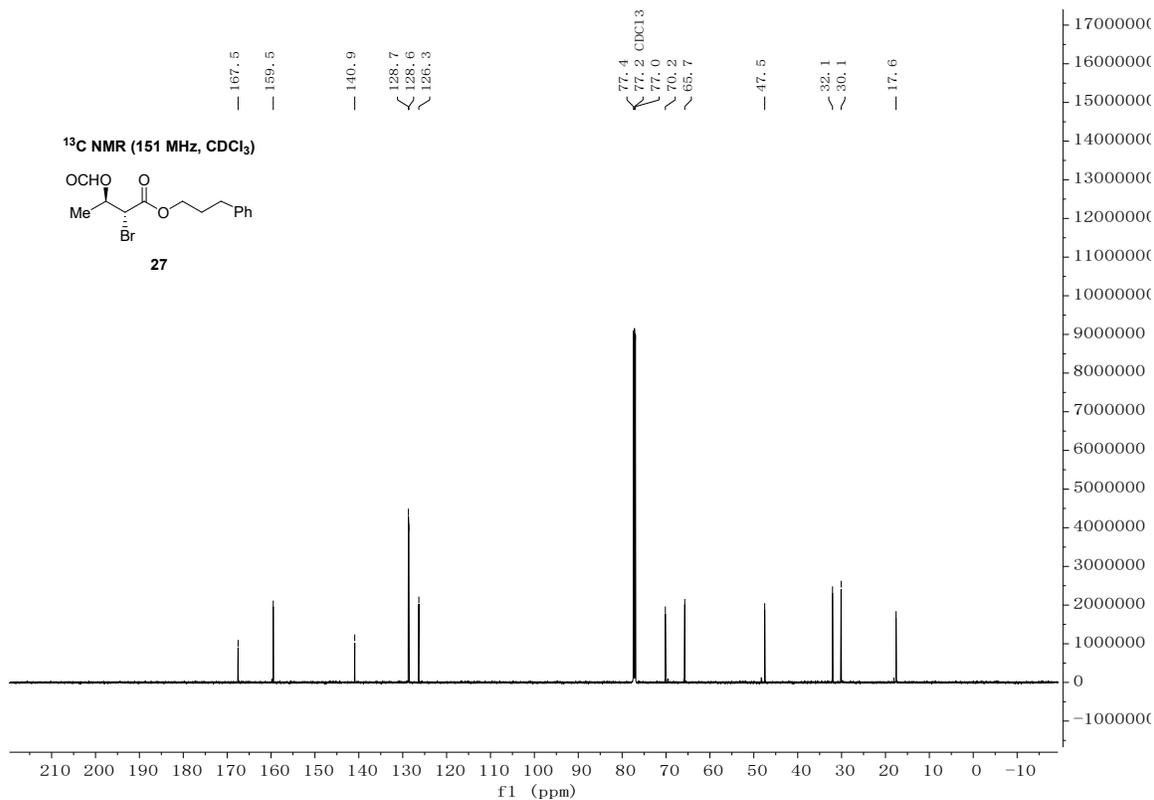
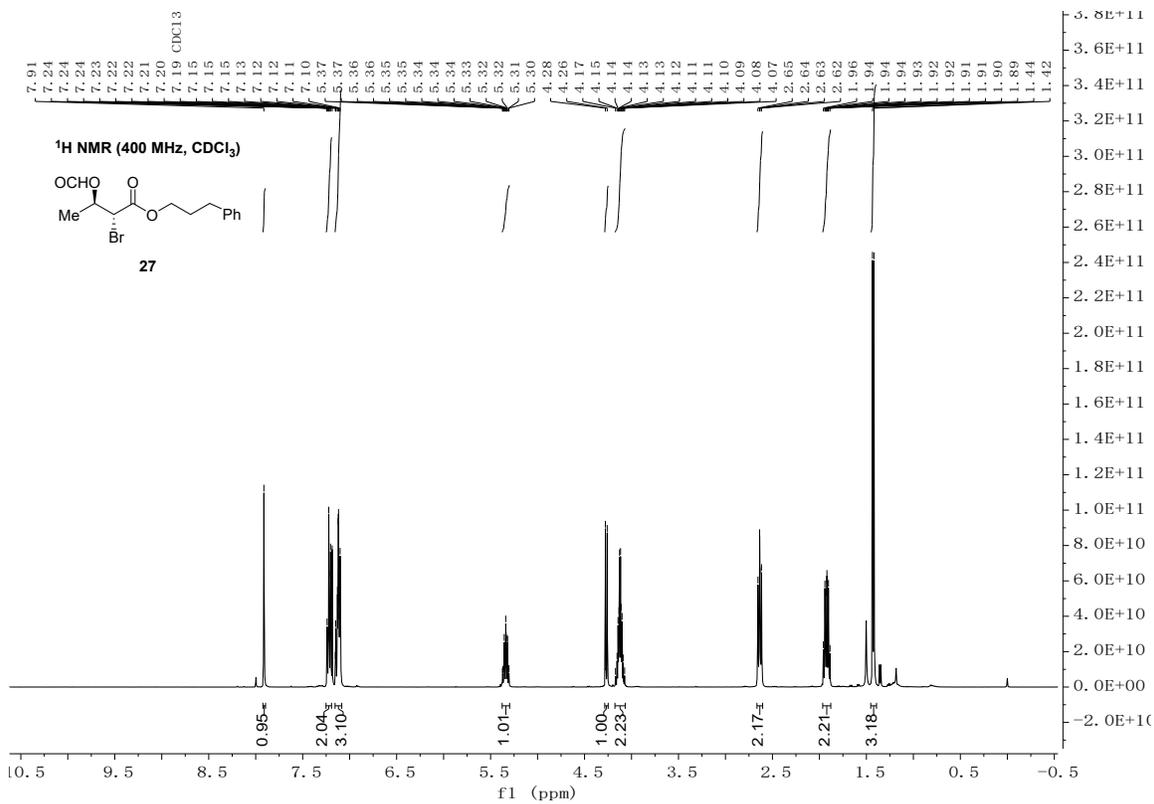


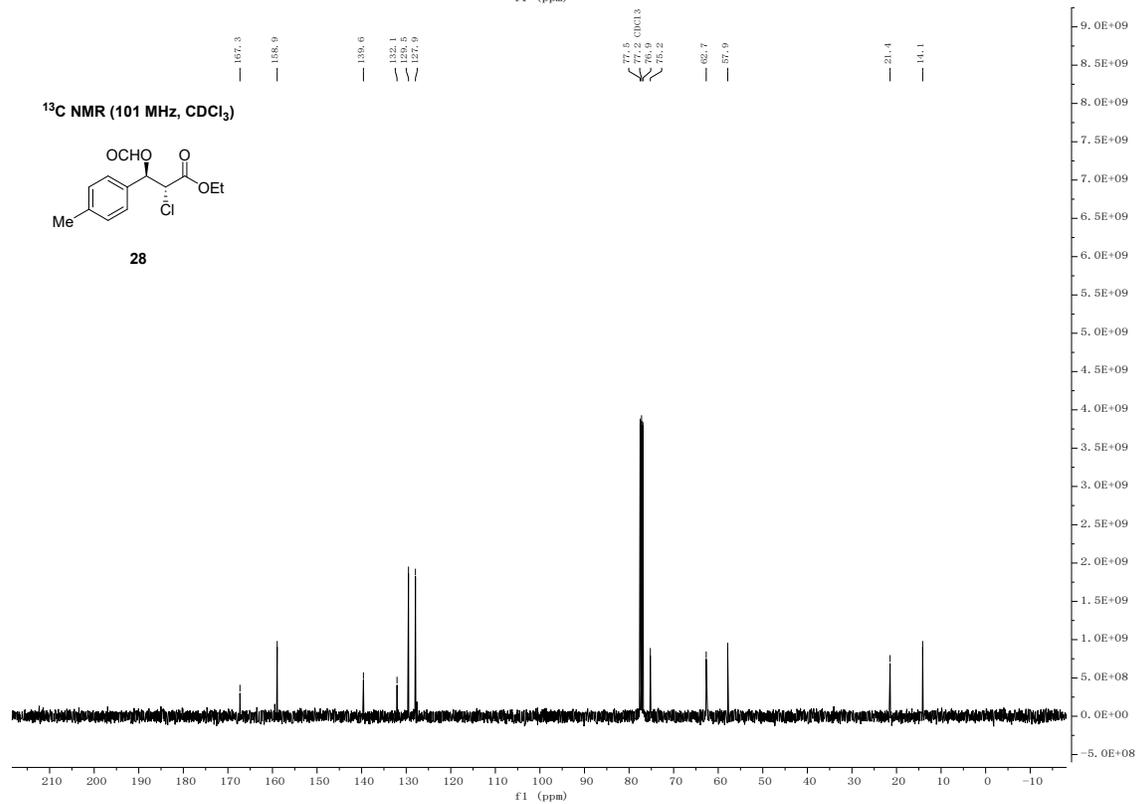
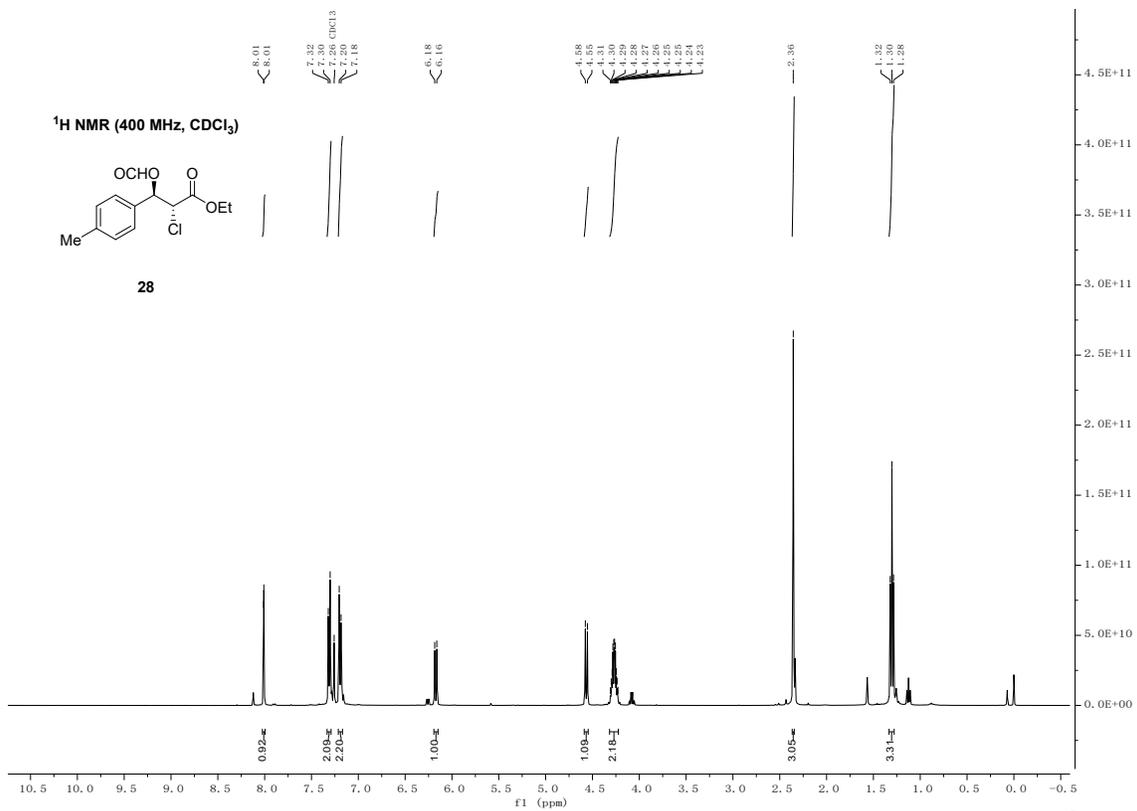


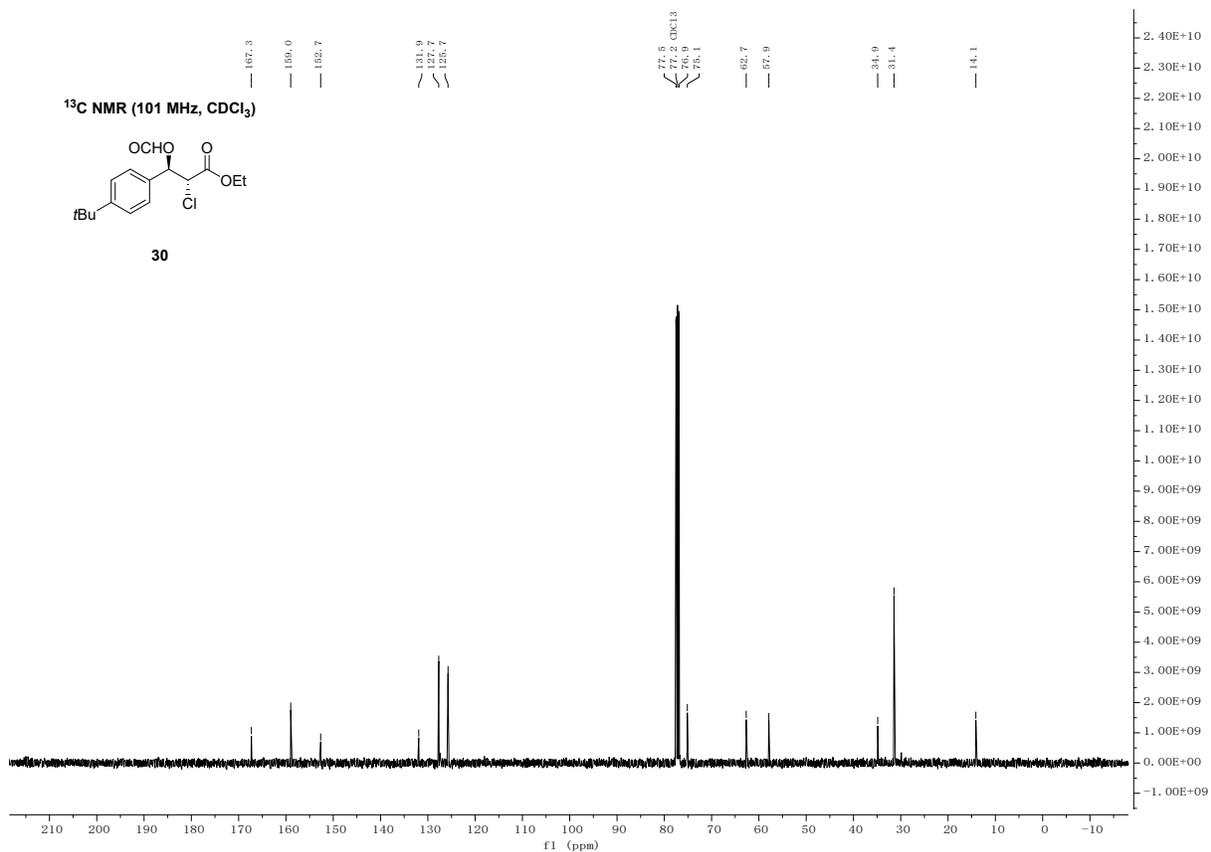
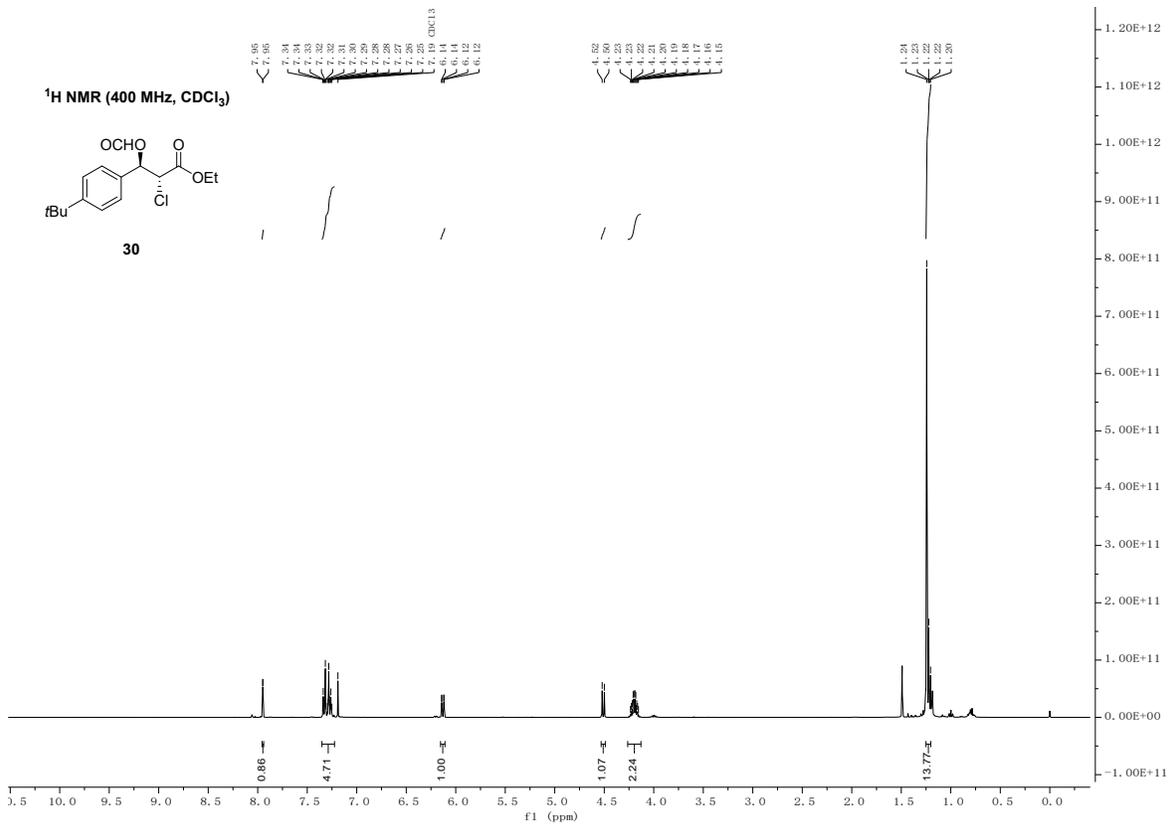


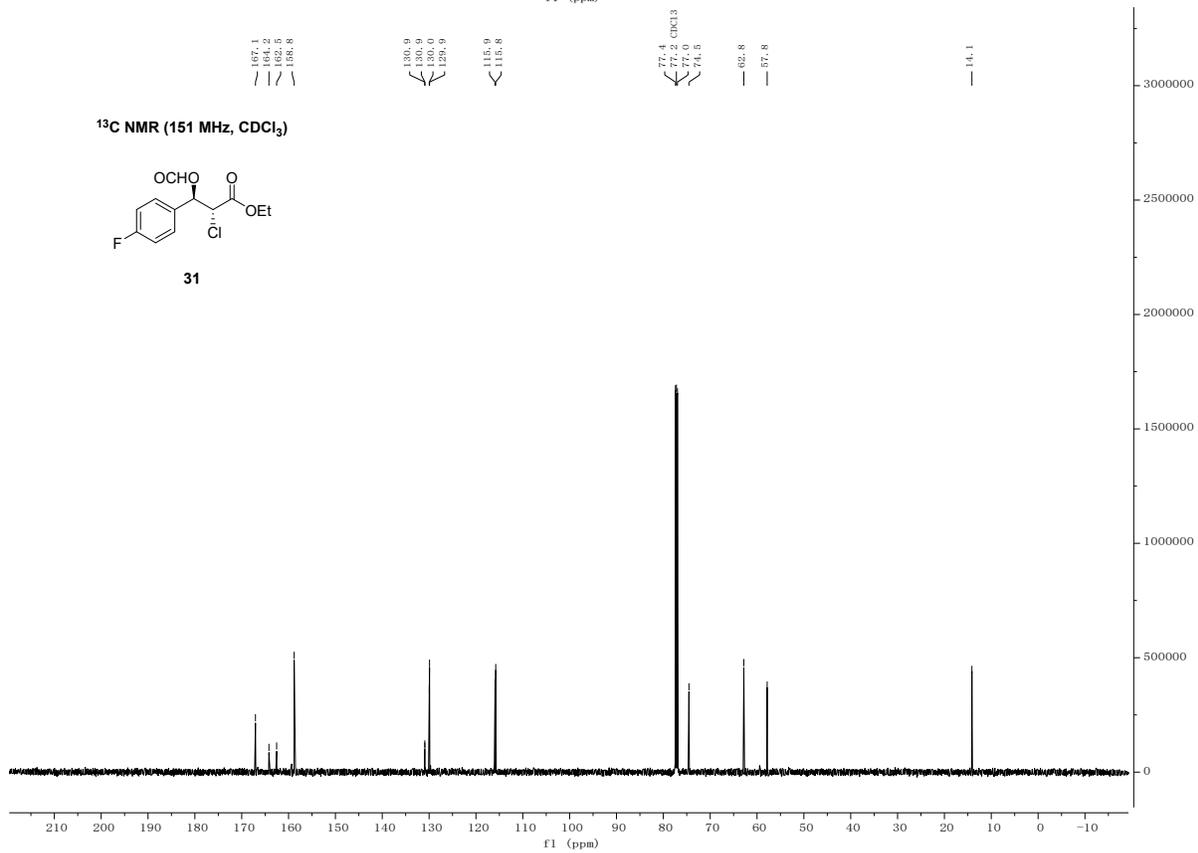
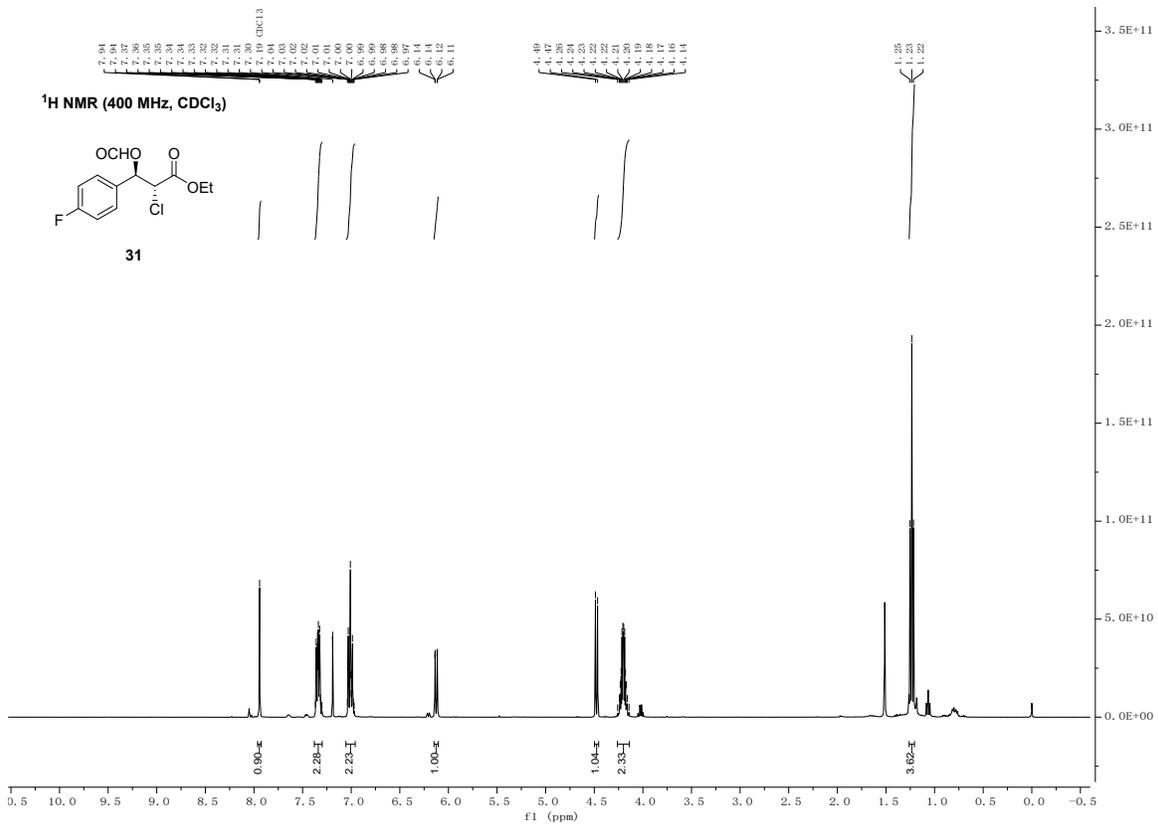


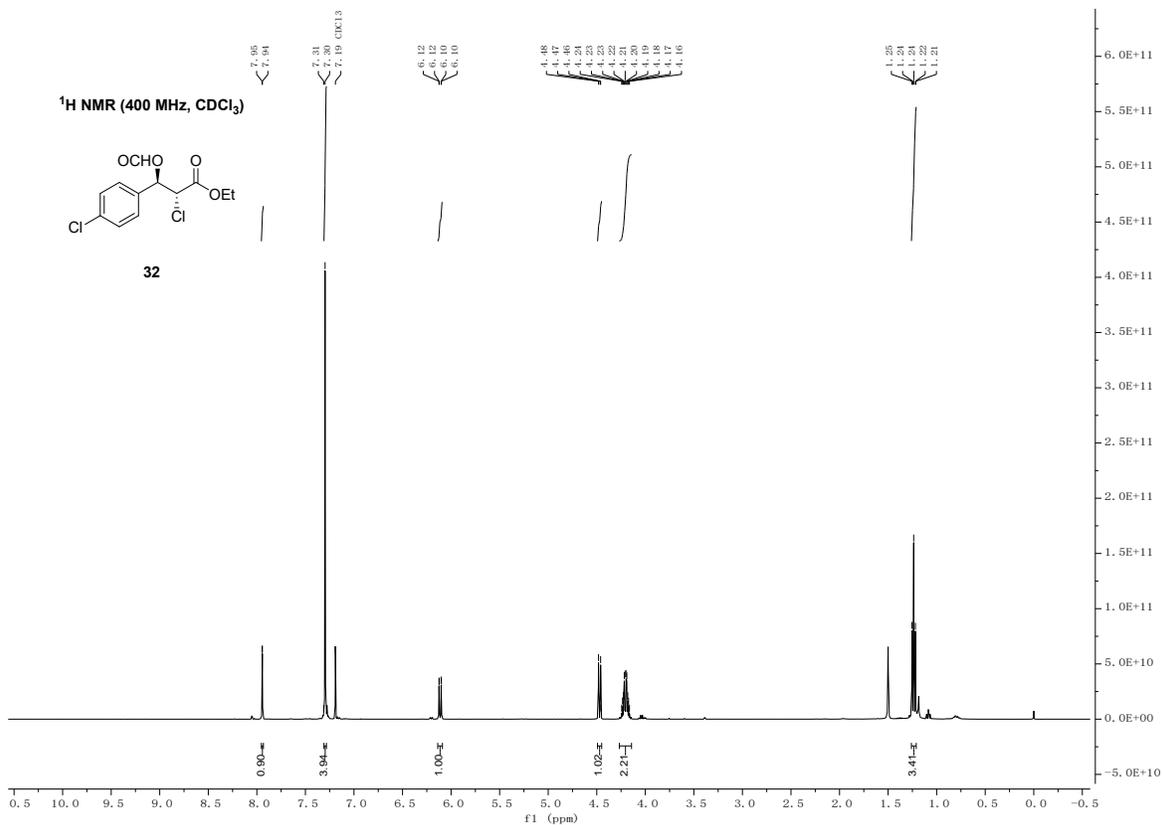
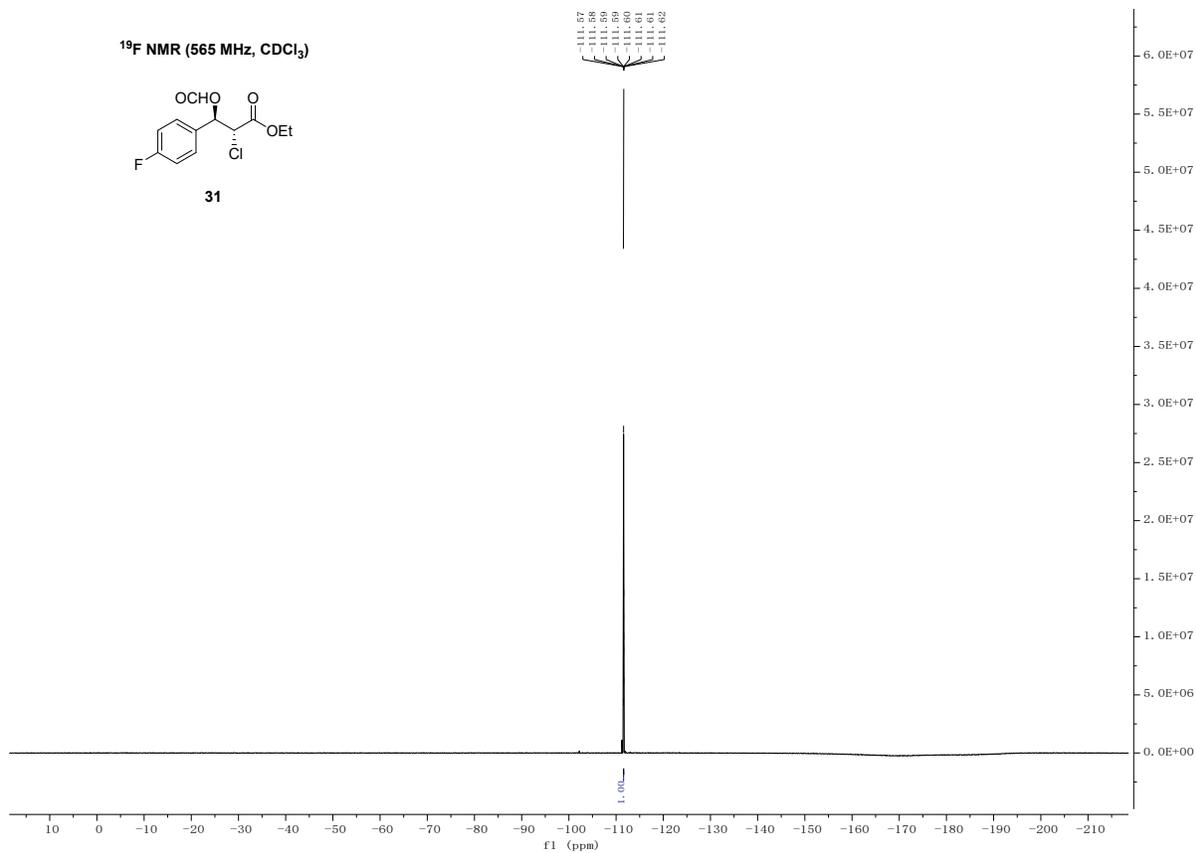


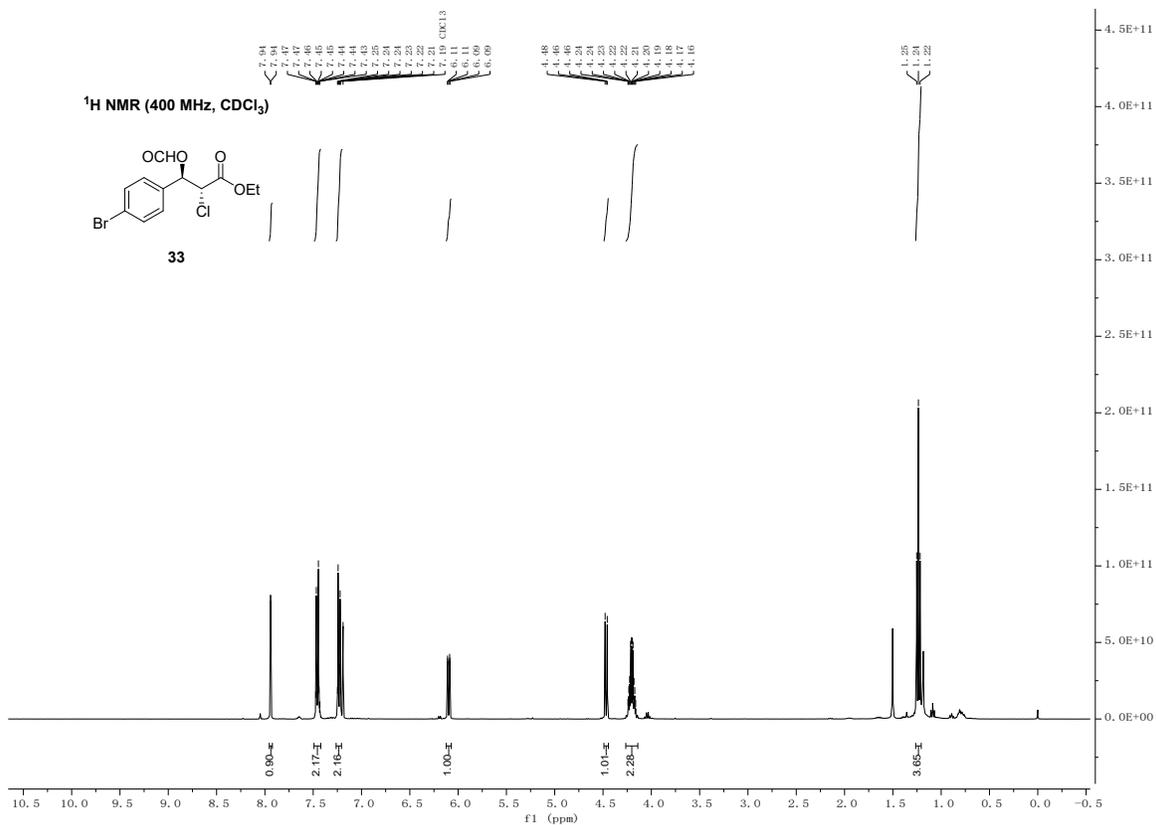
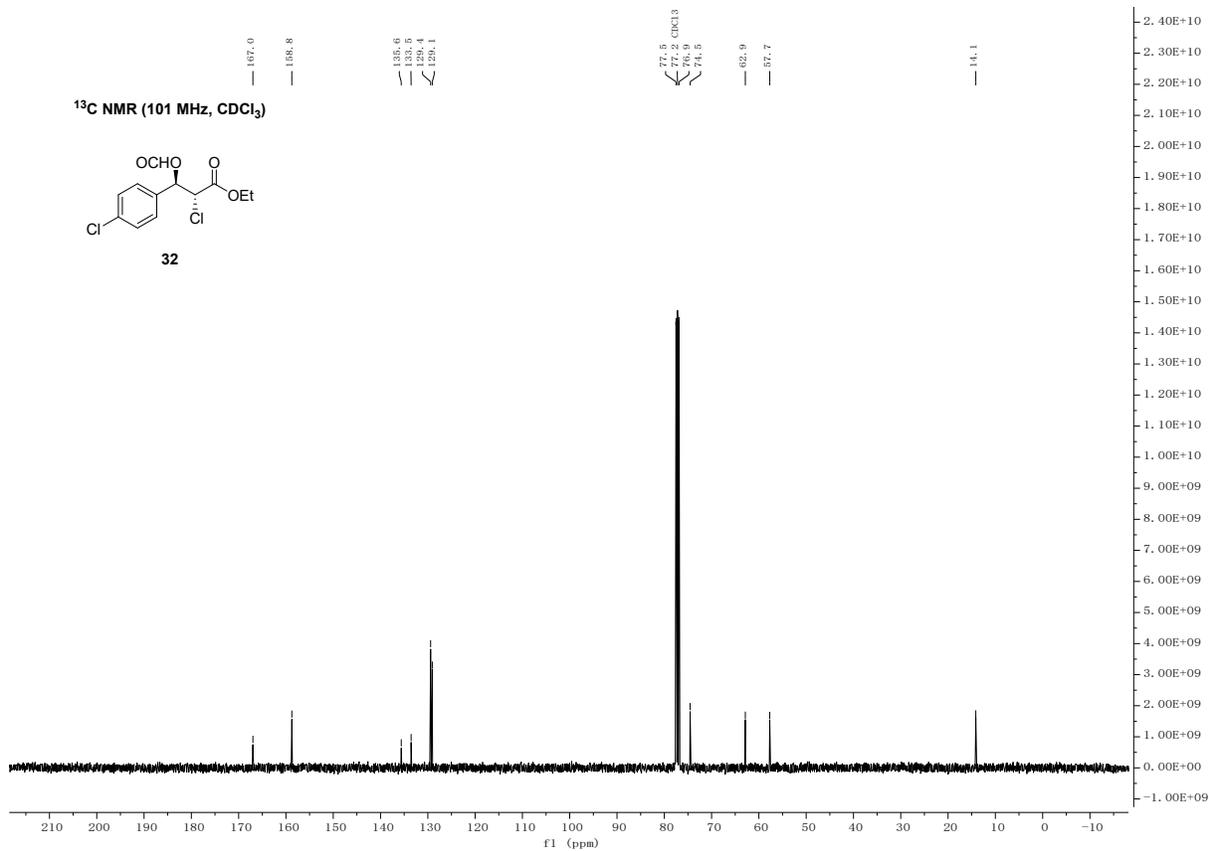


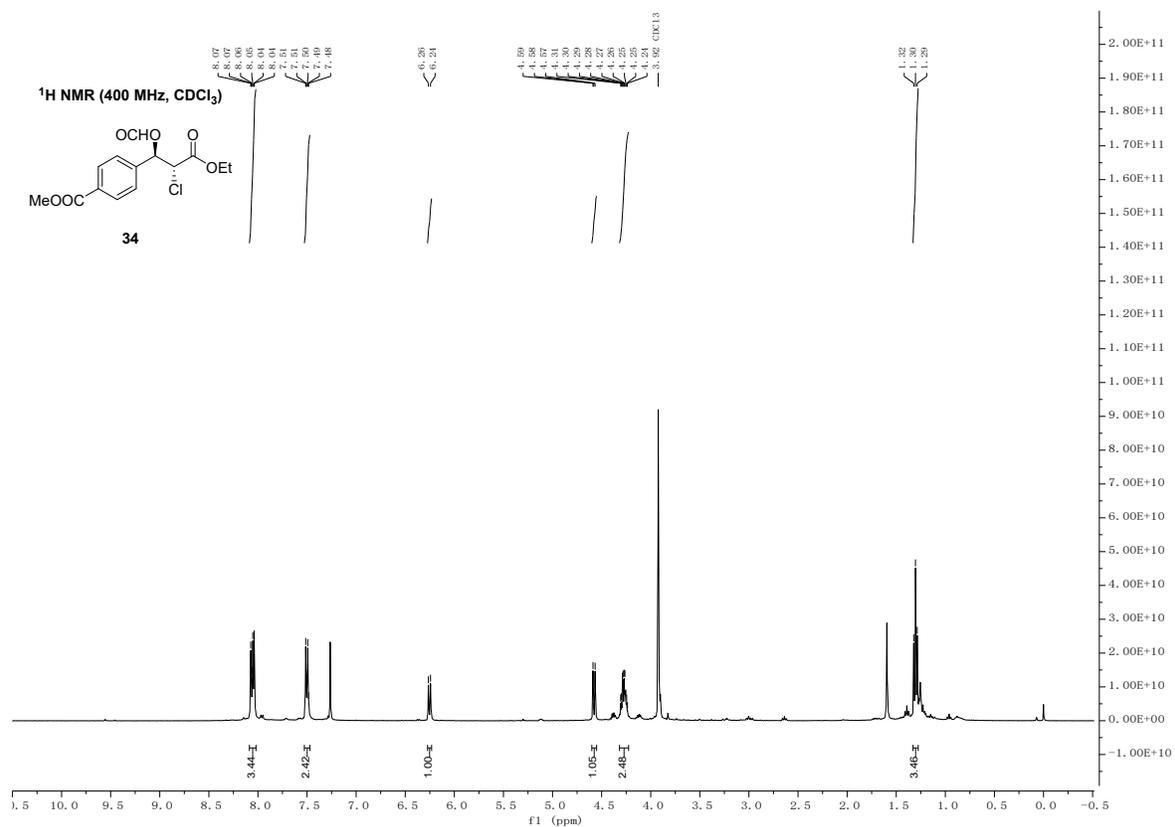
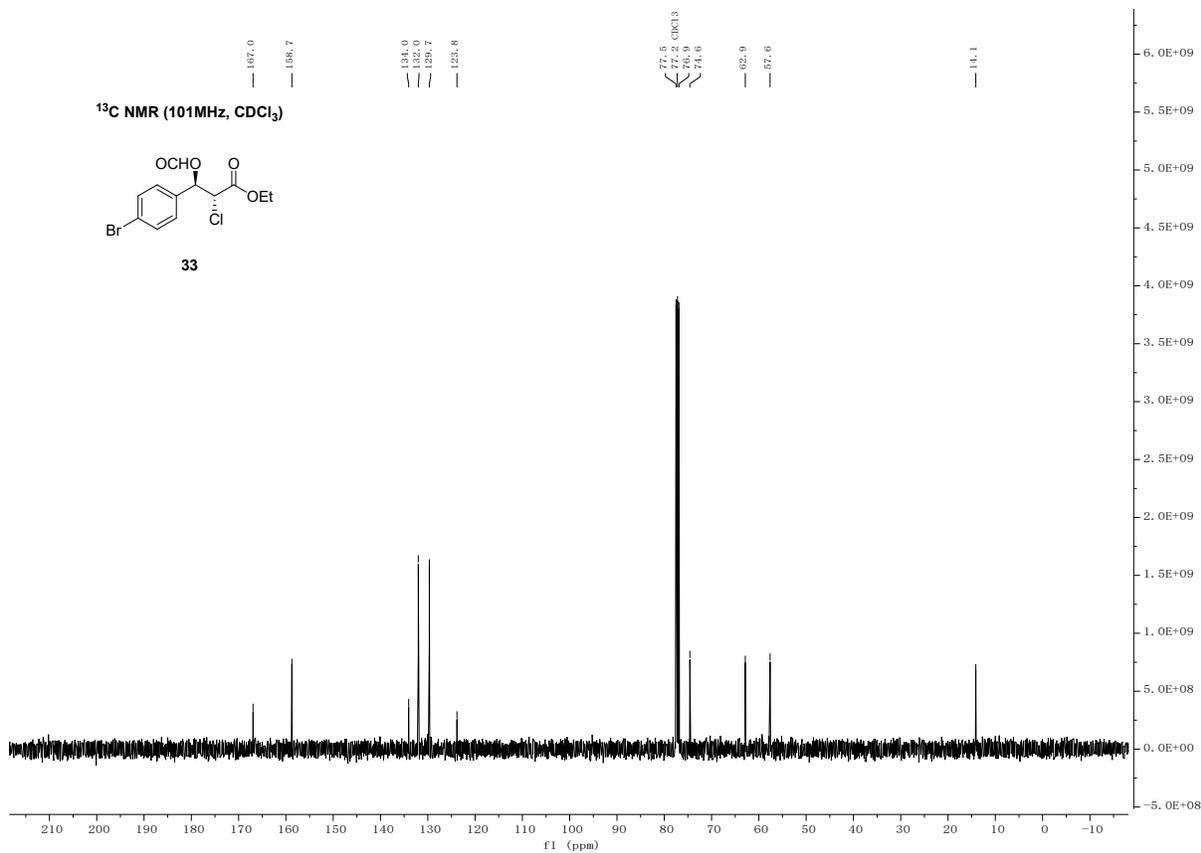


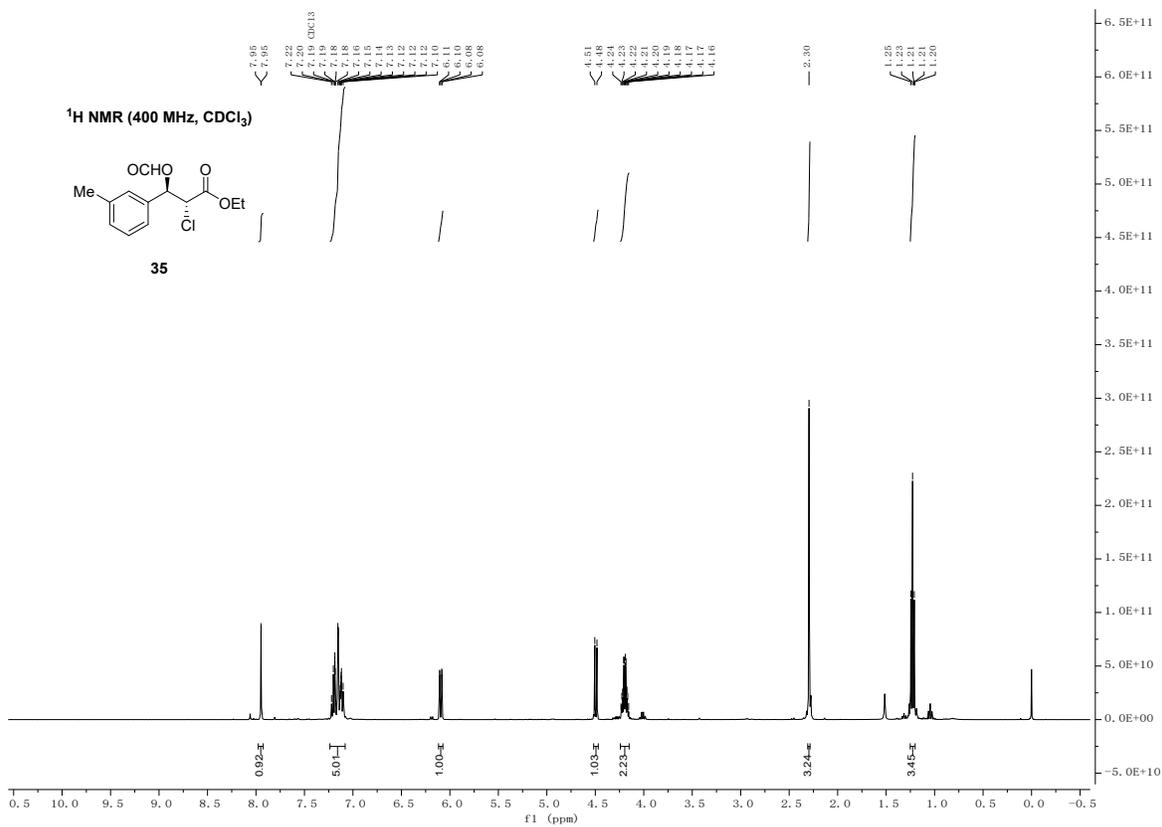
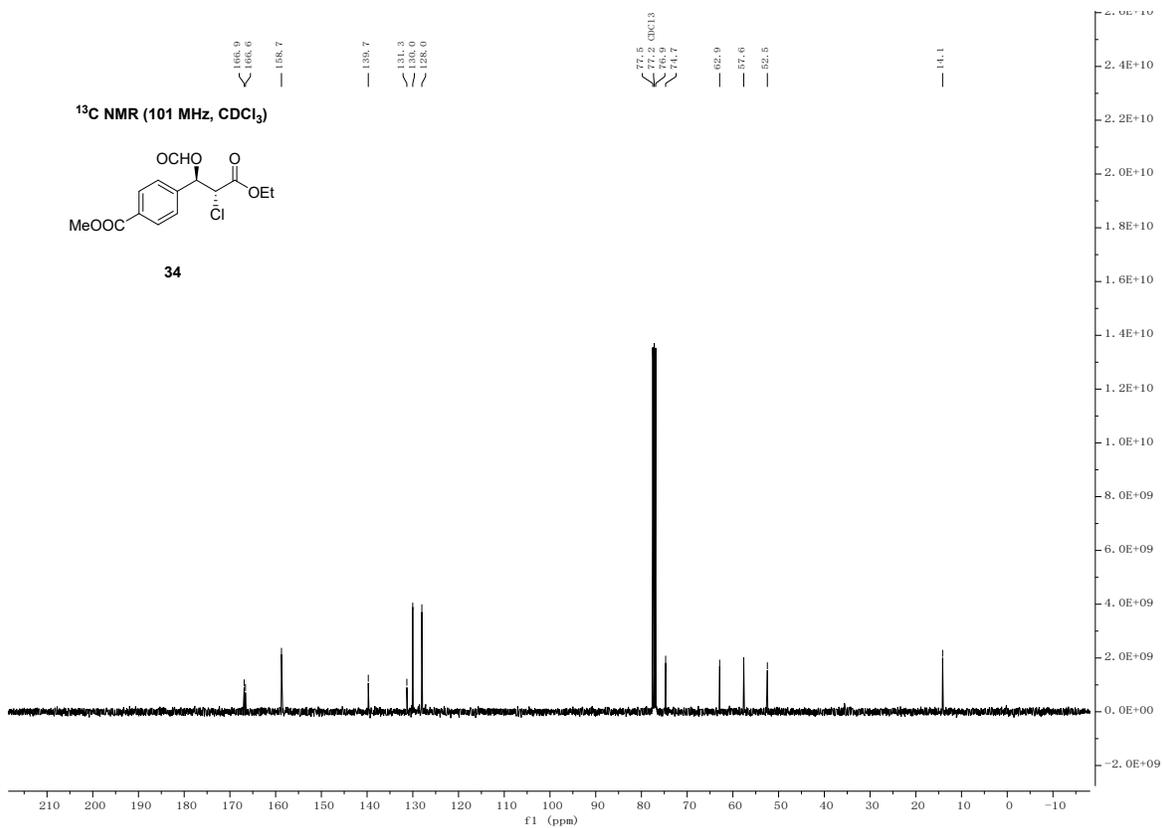


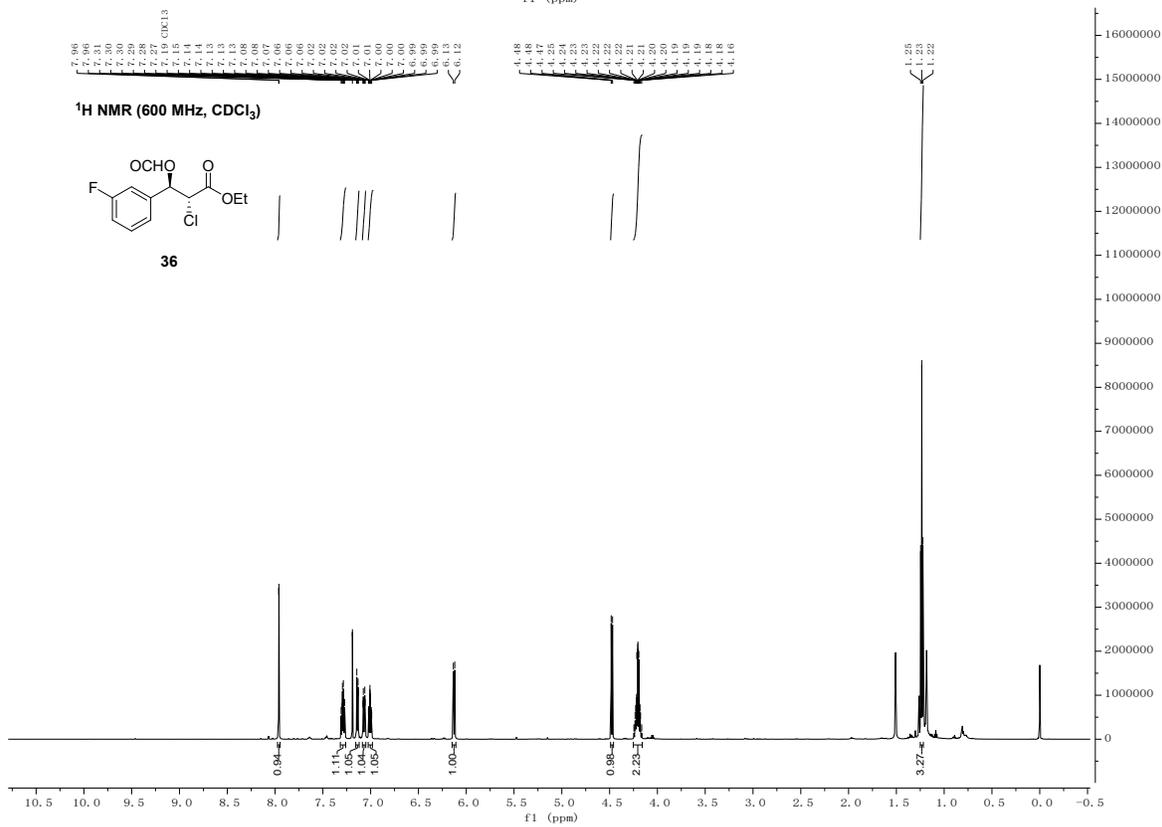
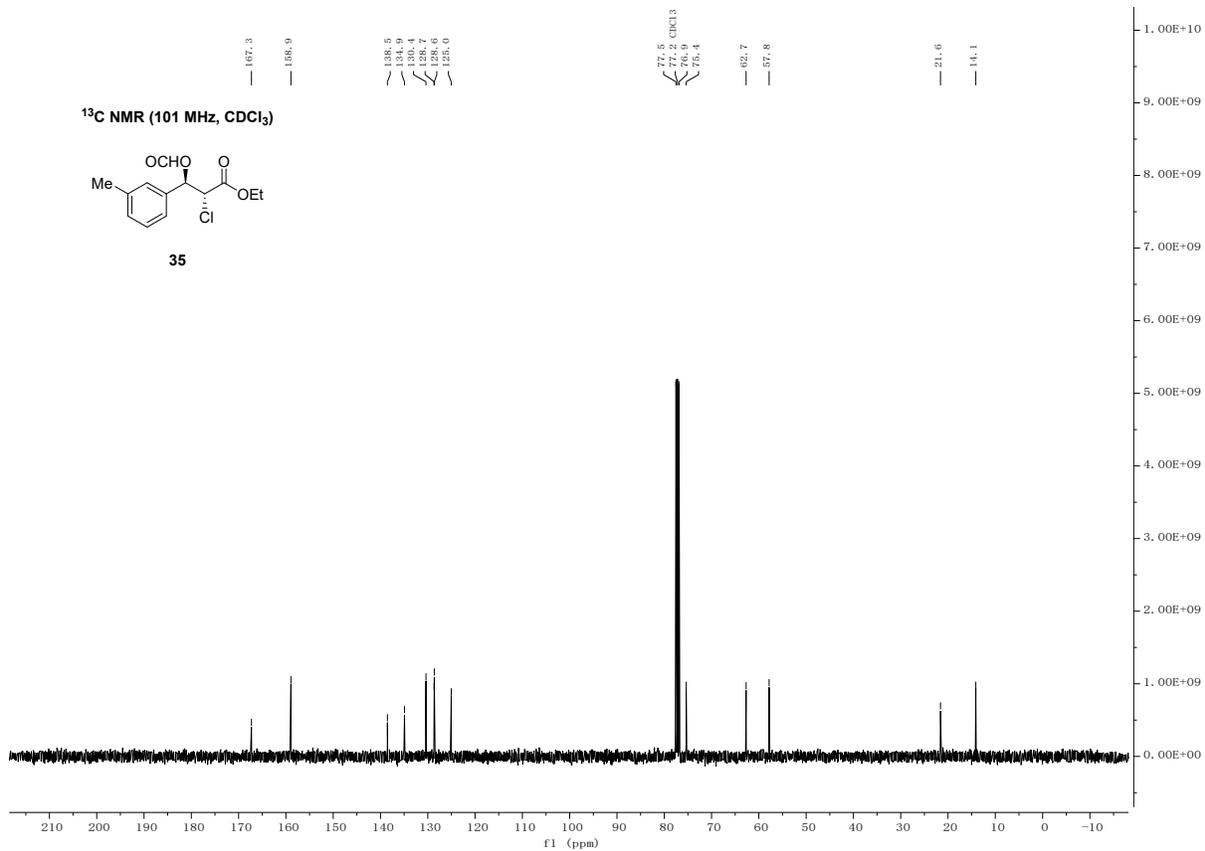


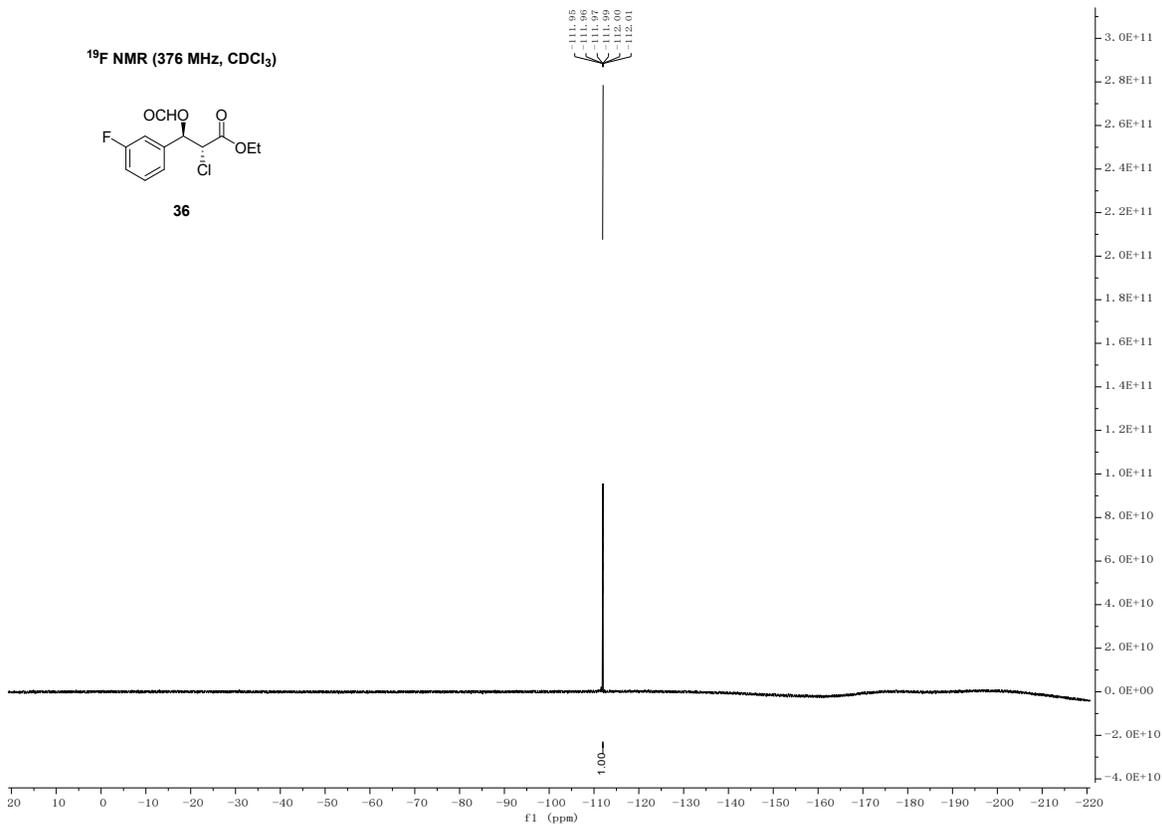
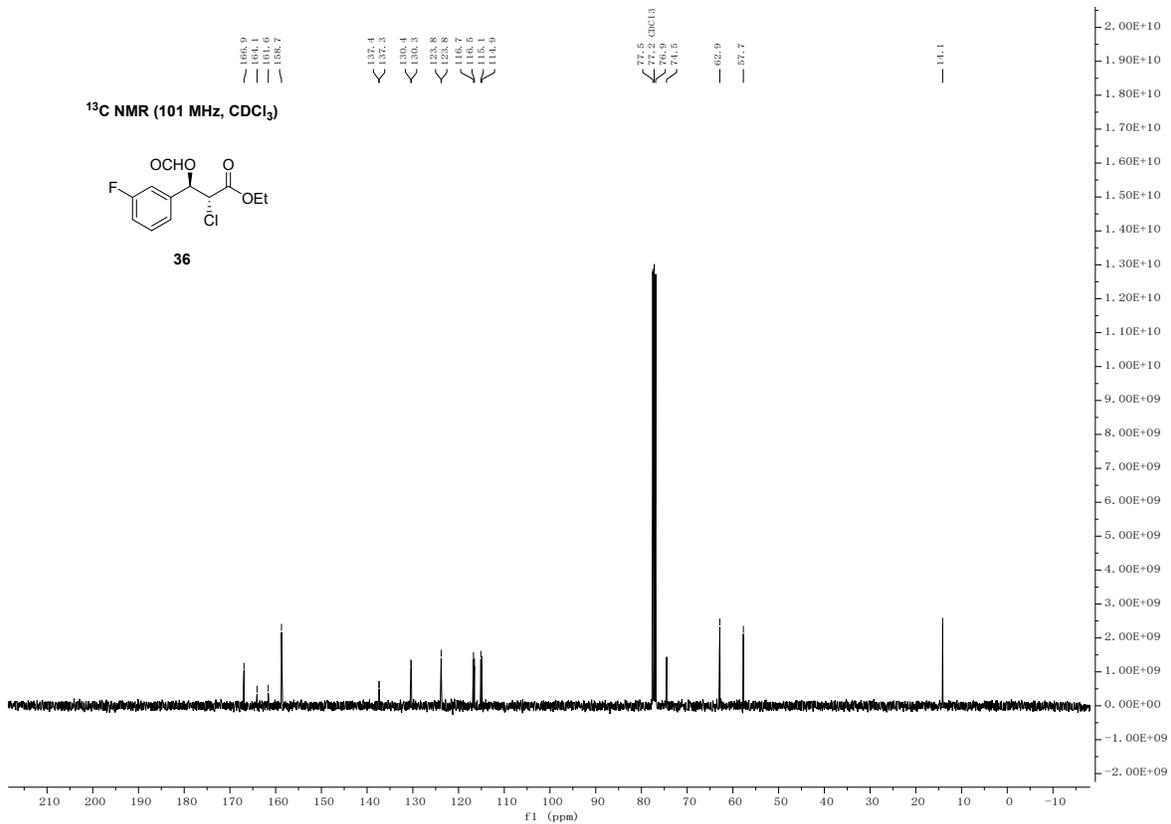


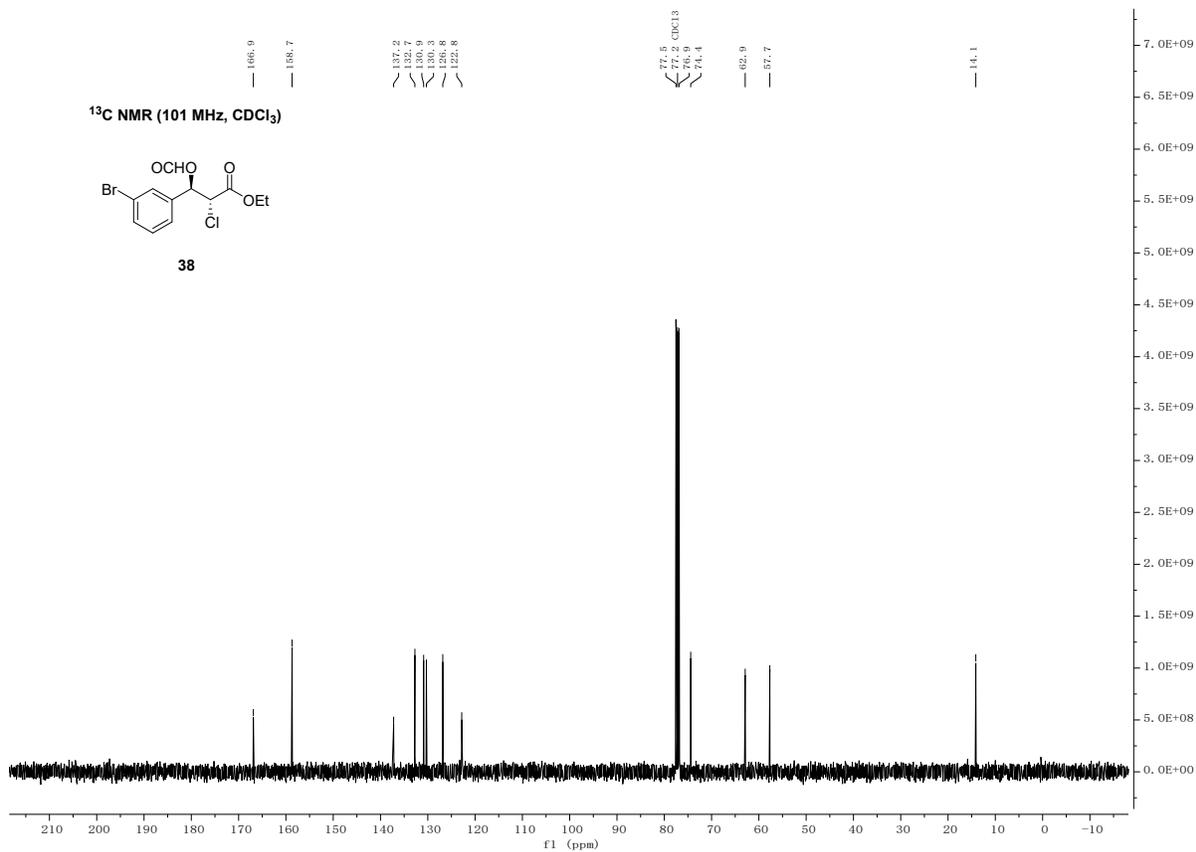
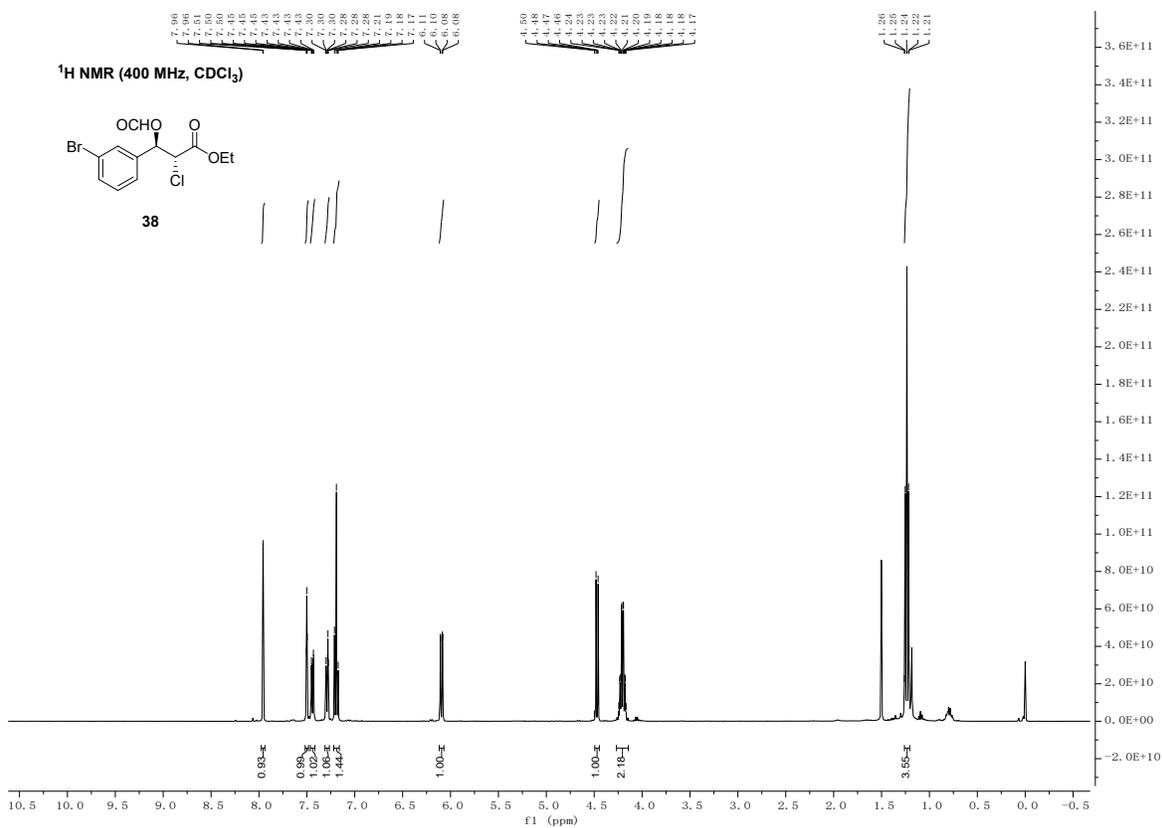


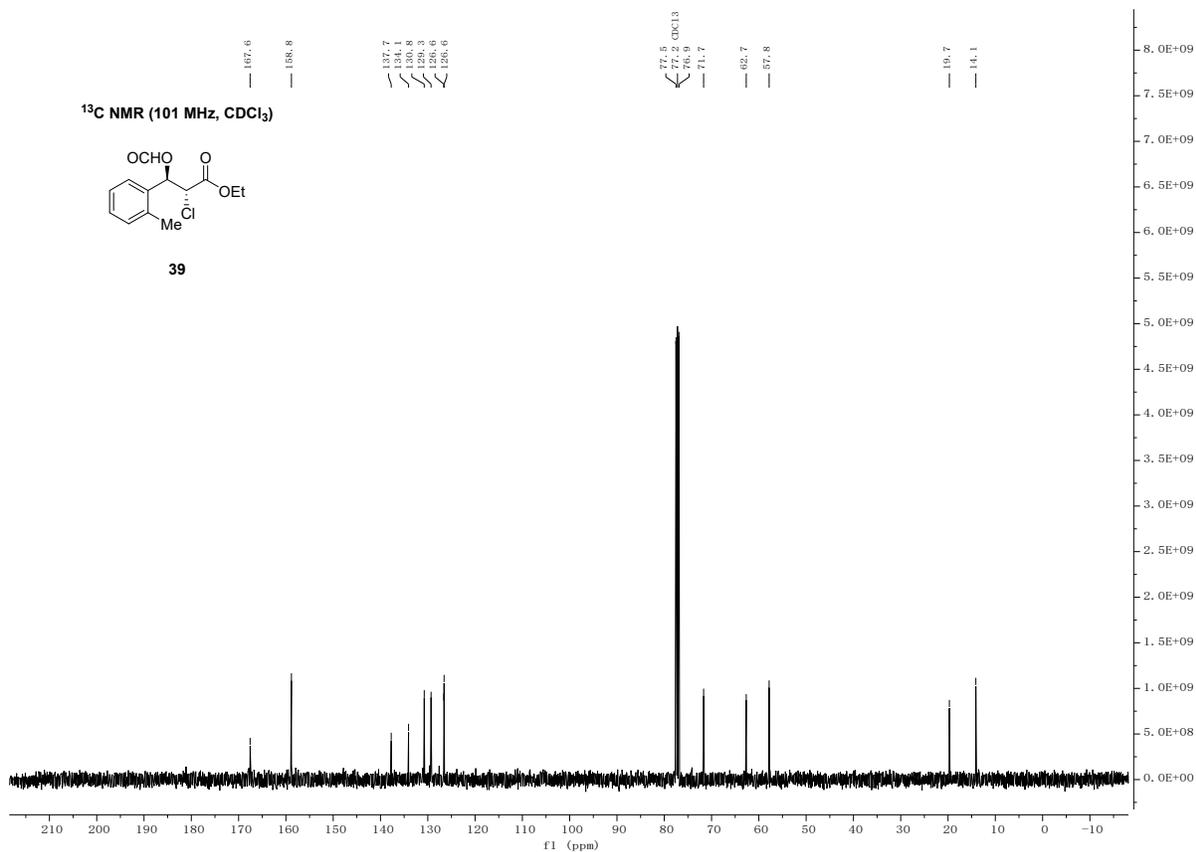
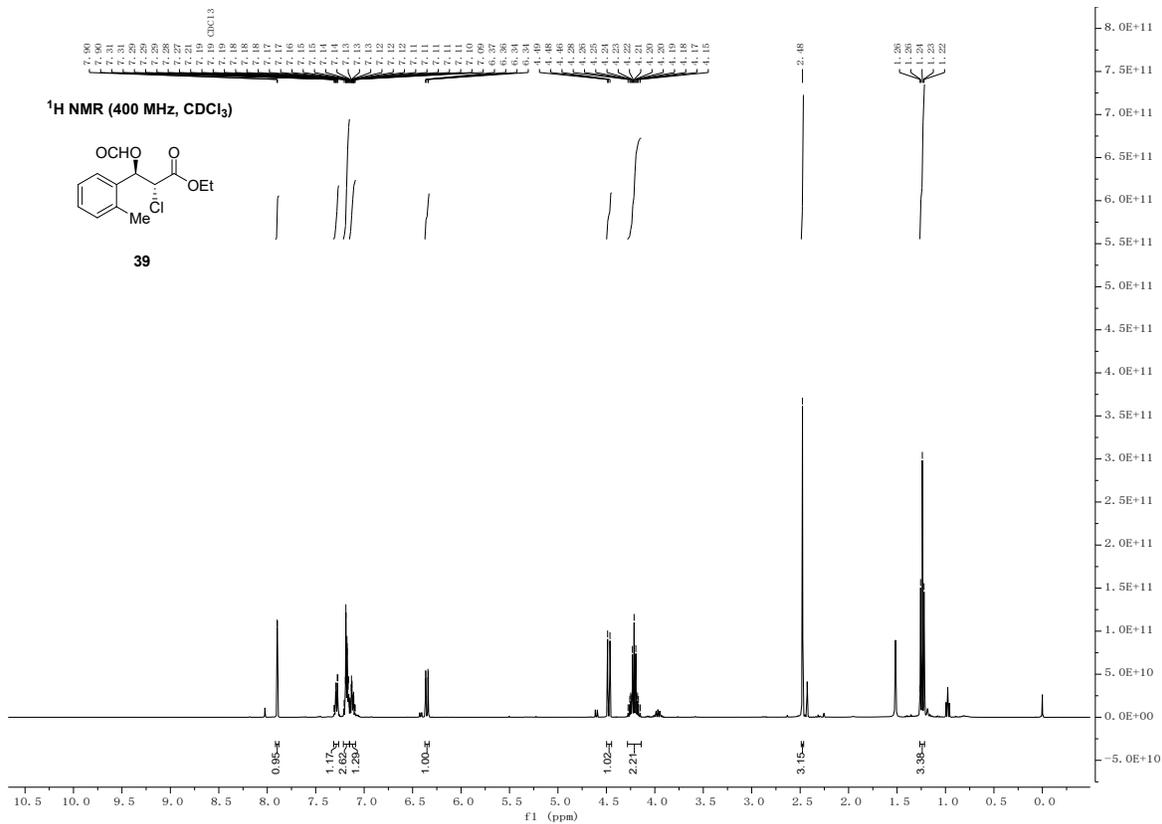




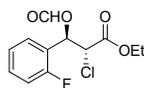




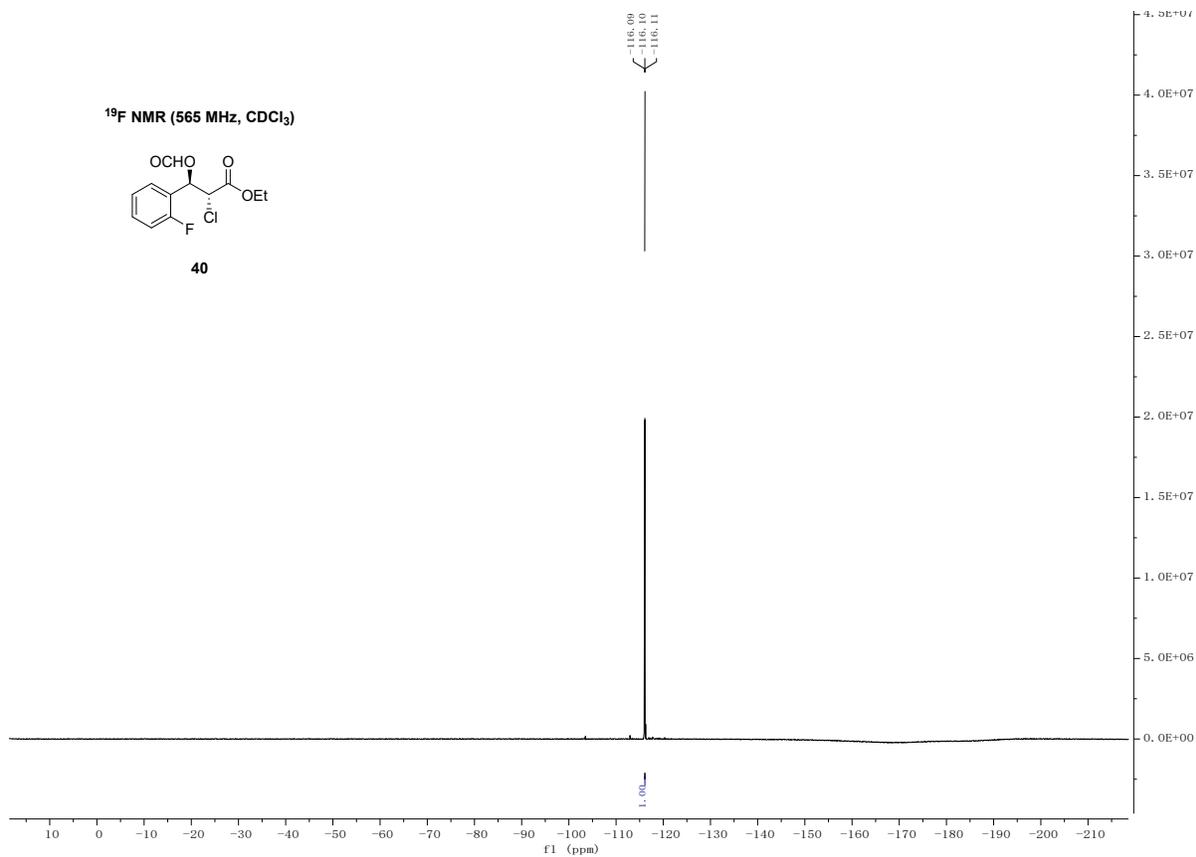




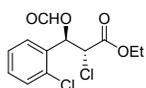
¹⁹F NMR (565 MHz, CDCl₃)



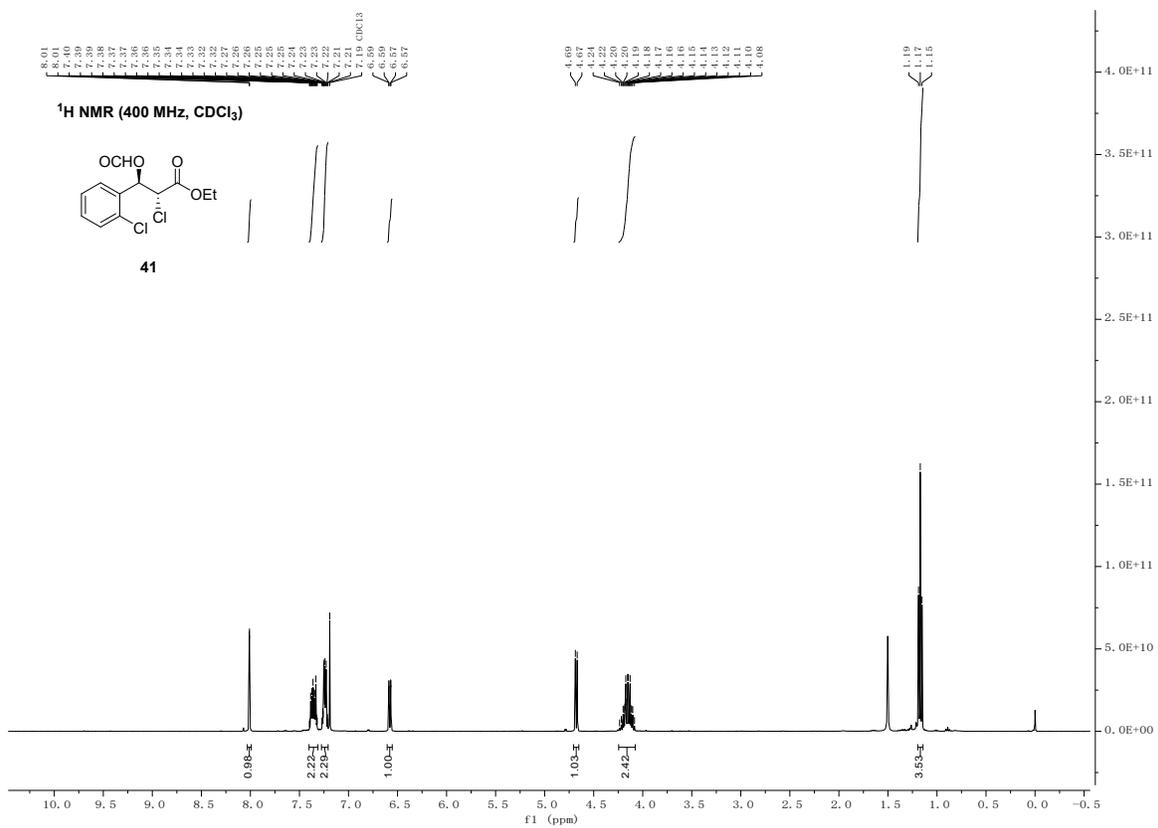
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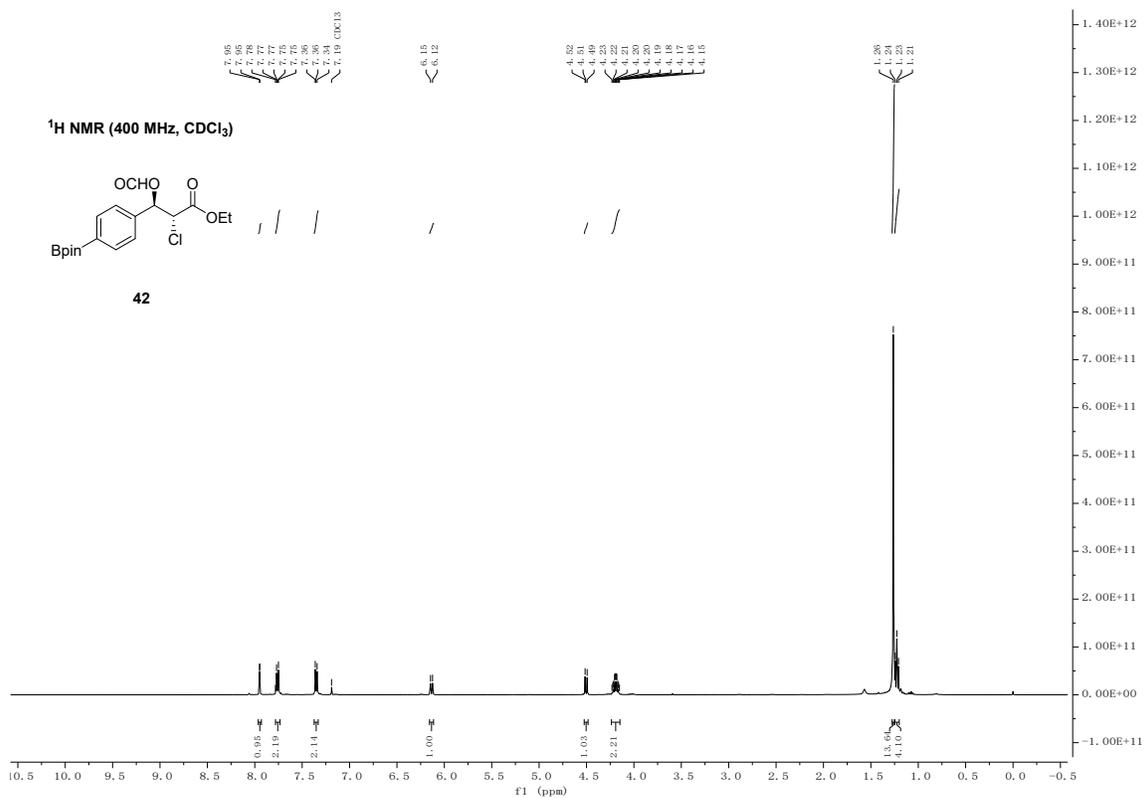
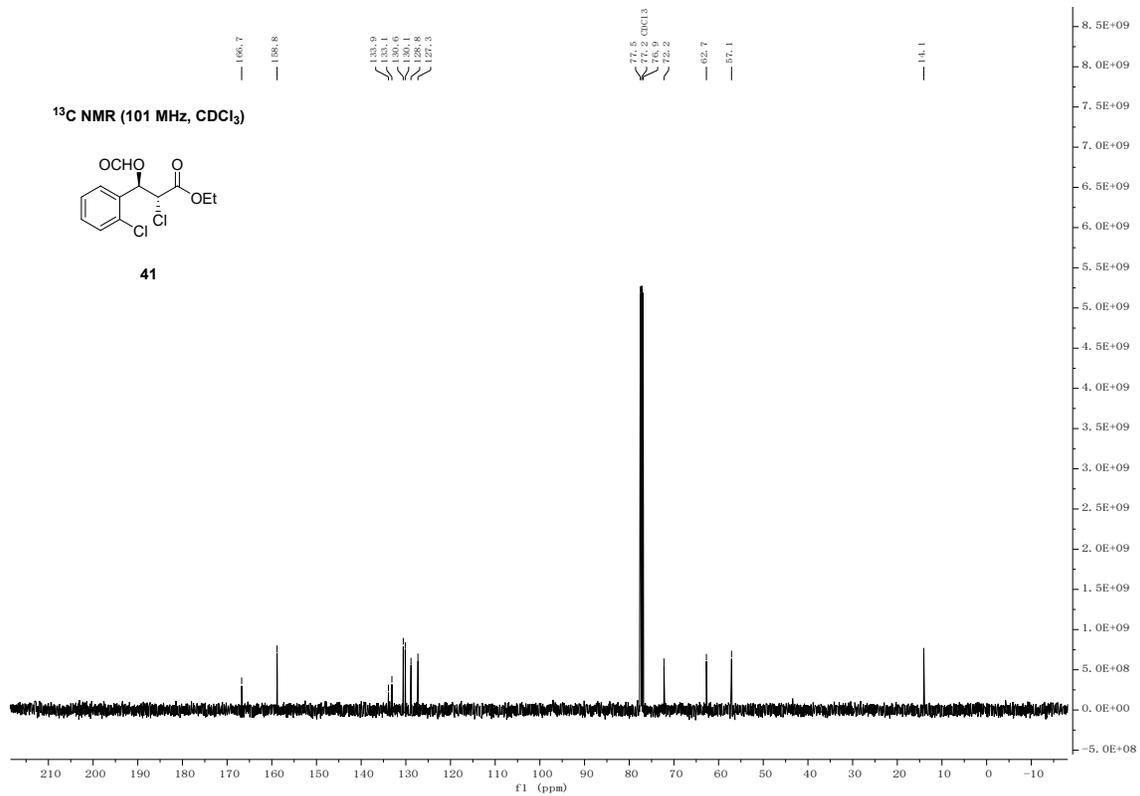


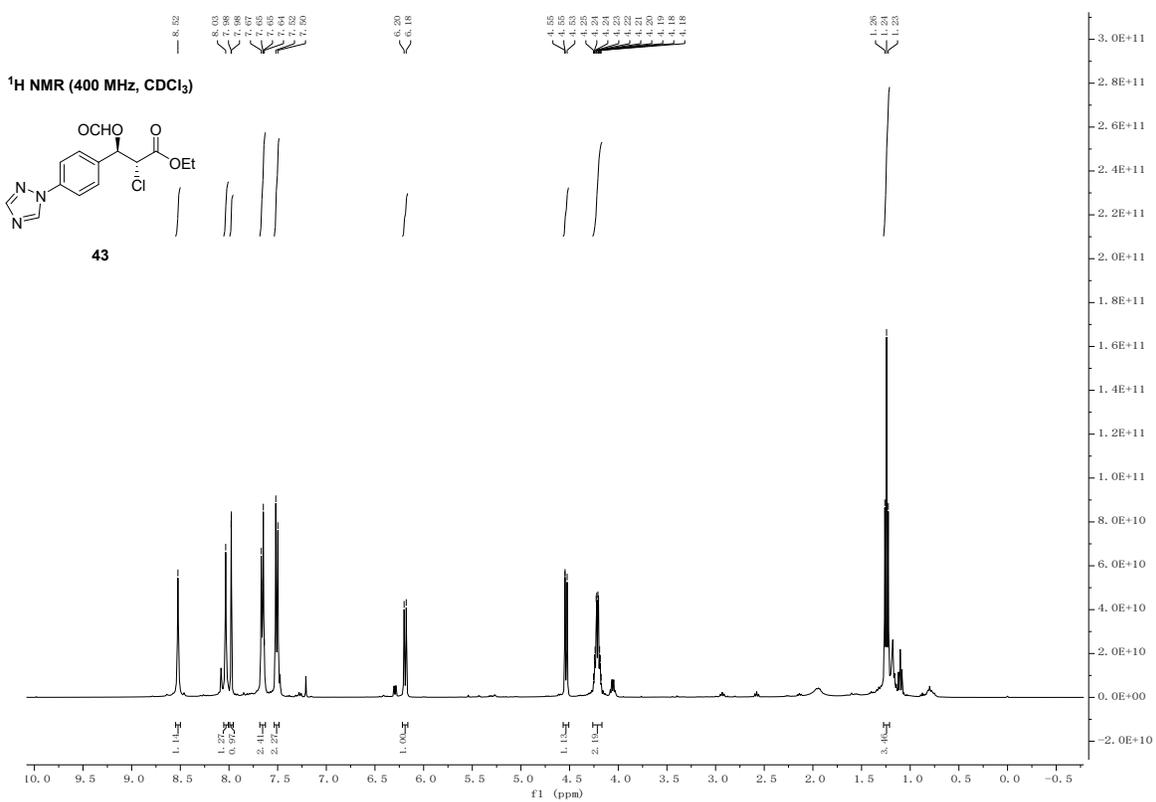
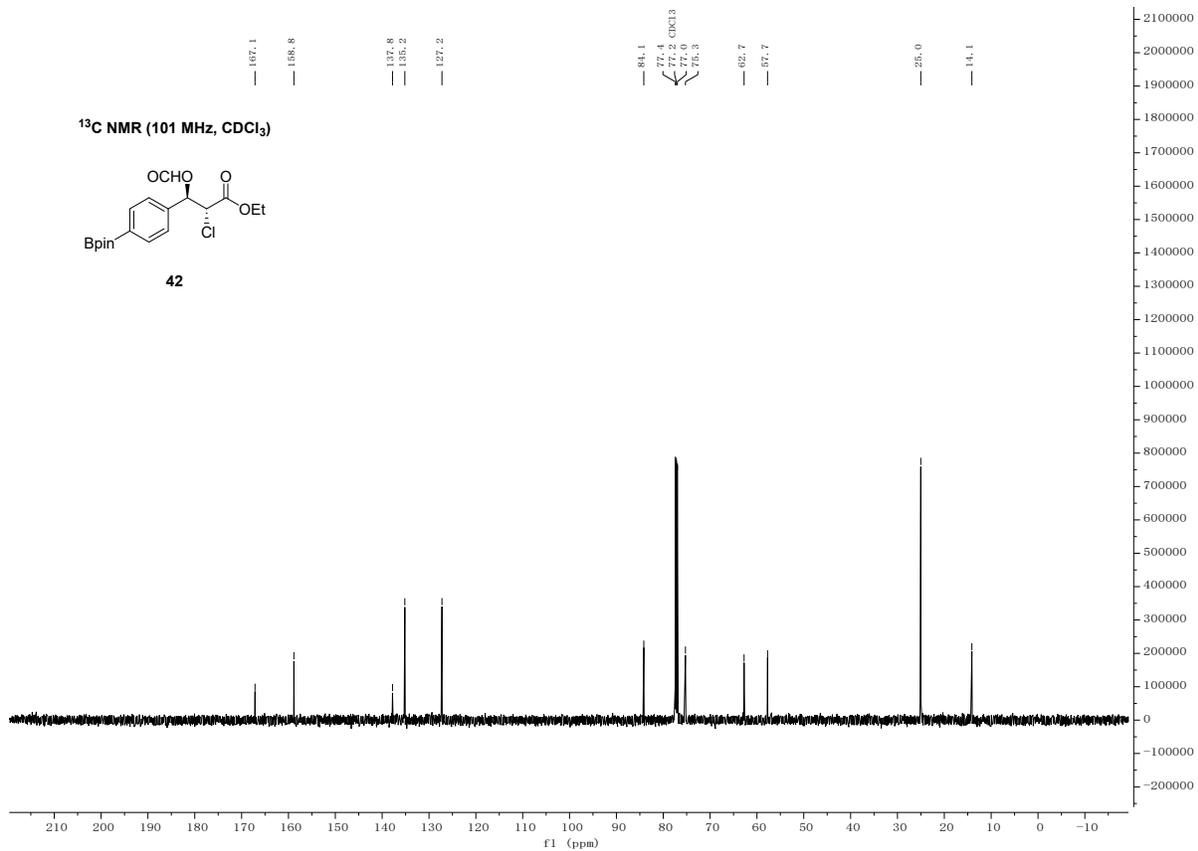
¹H NMR (400 MHz, CDCl₃)

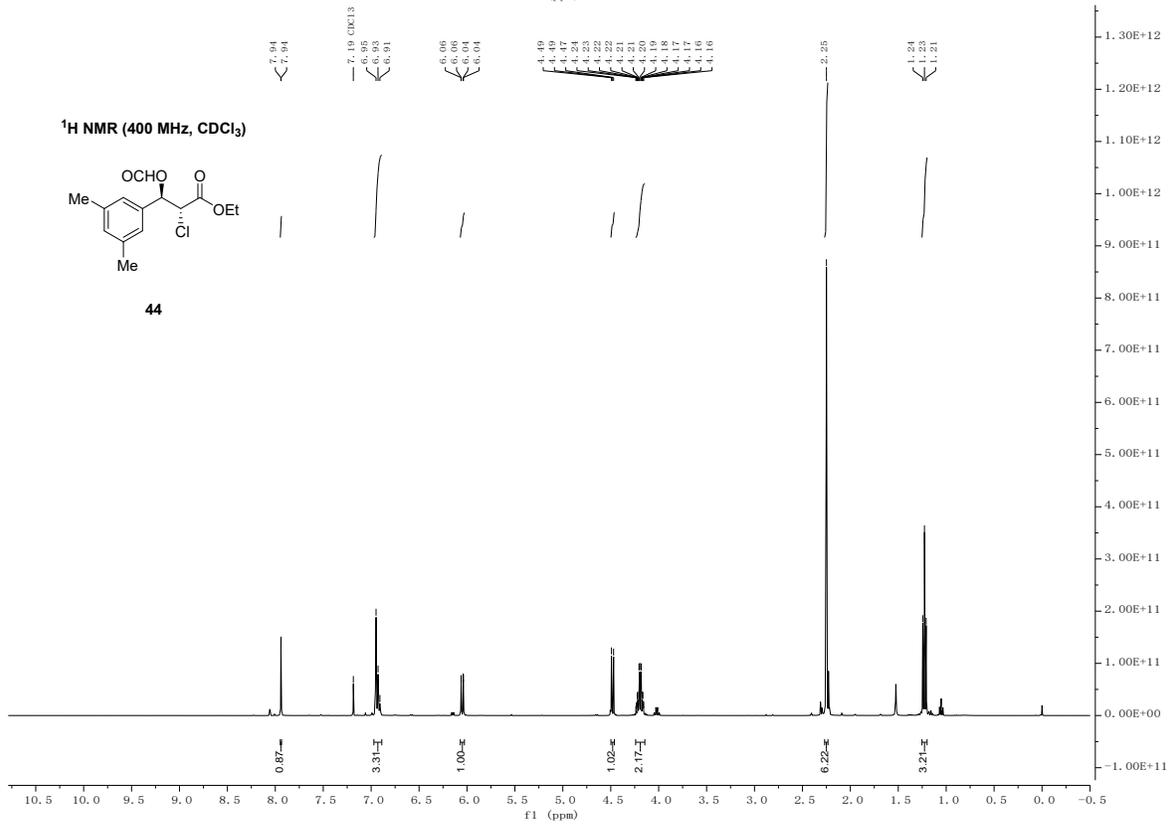
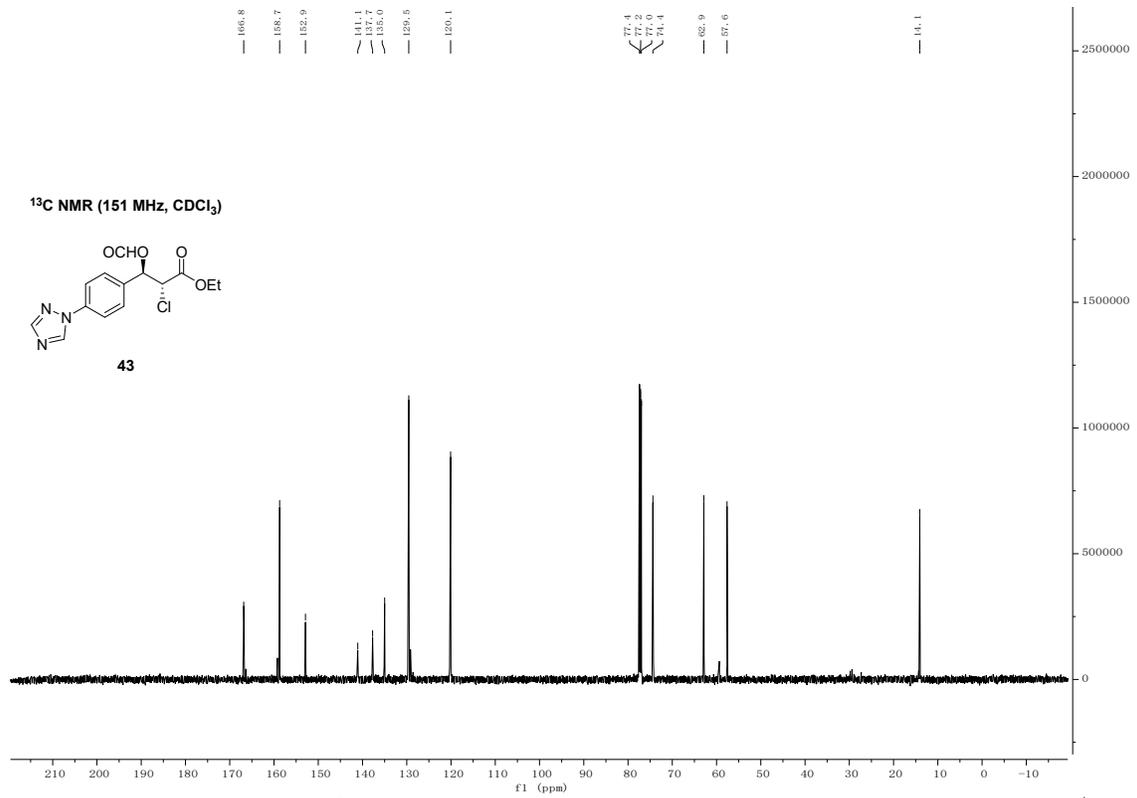


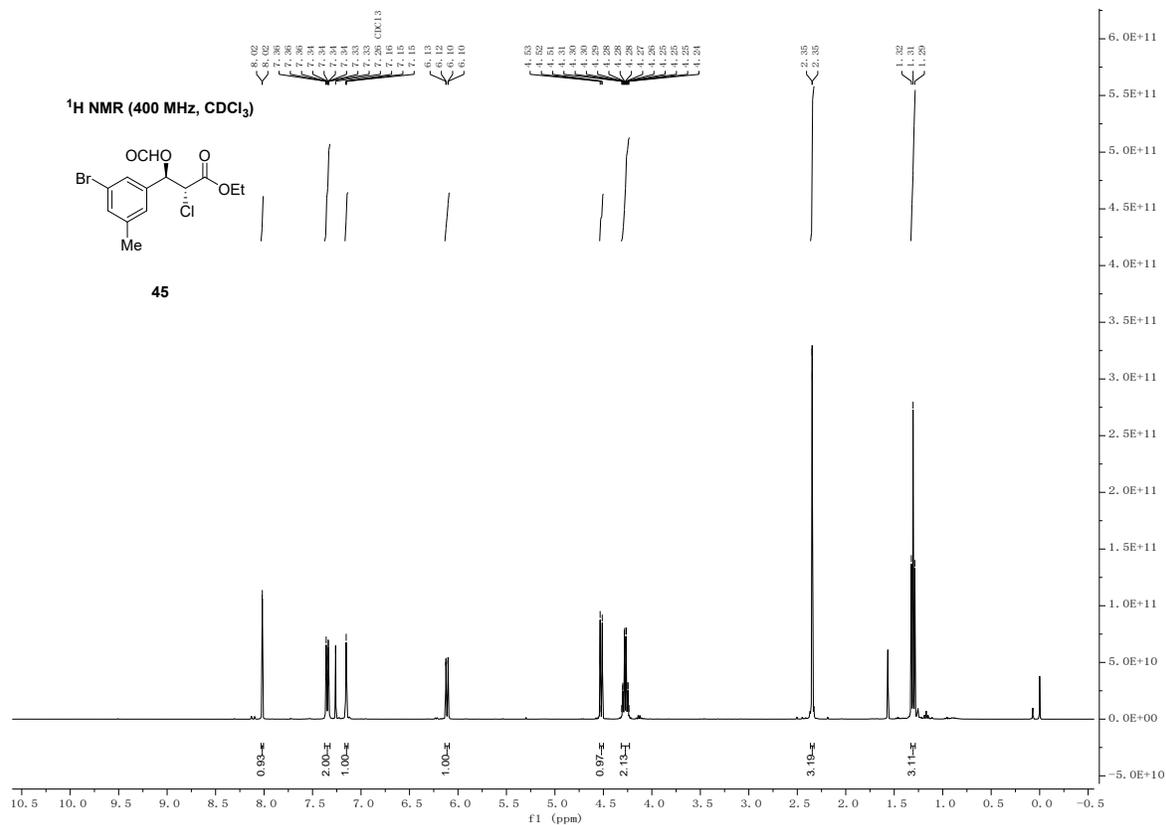
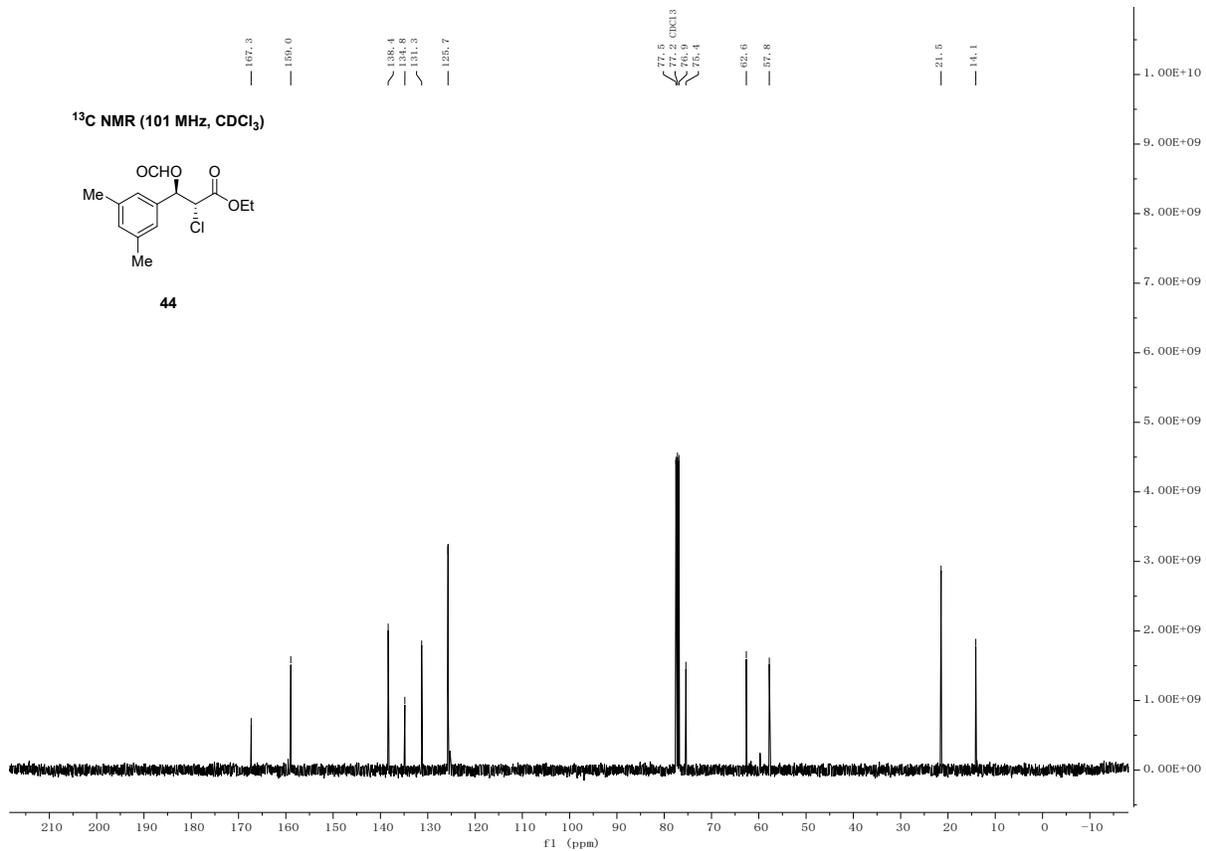
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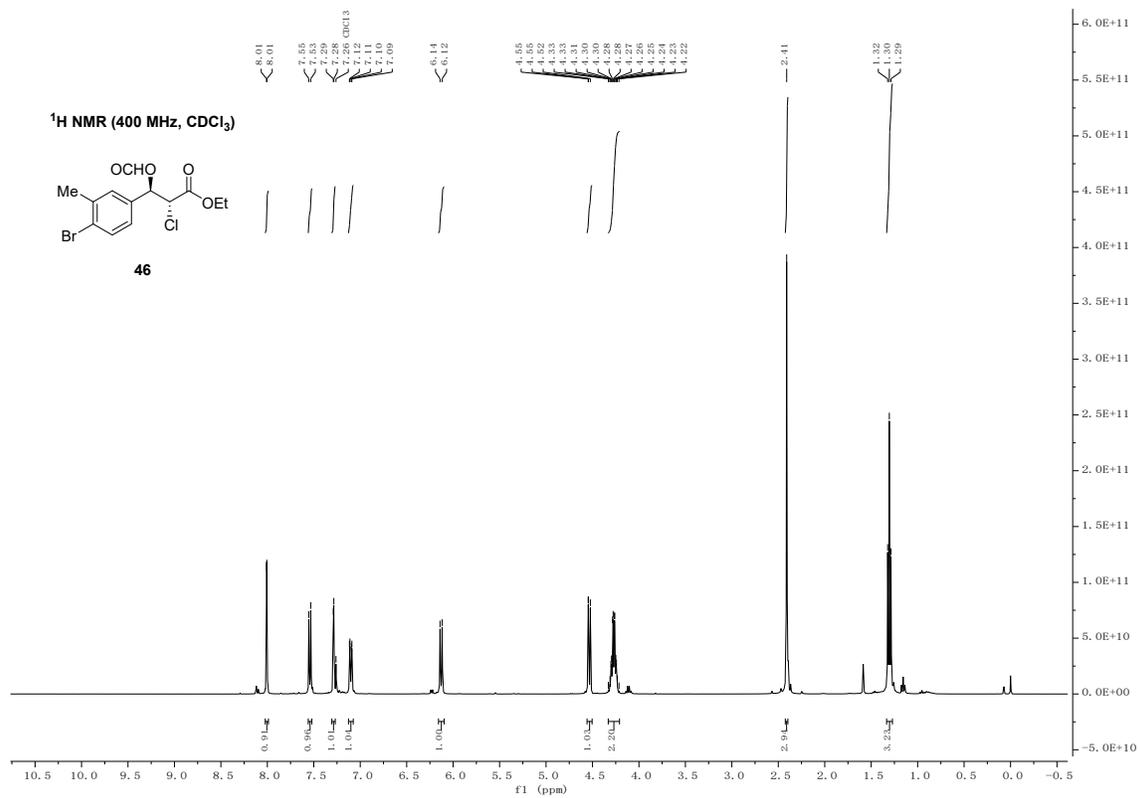
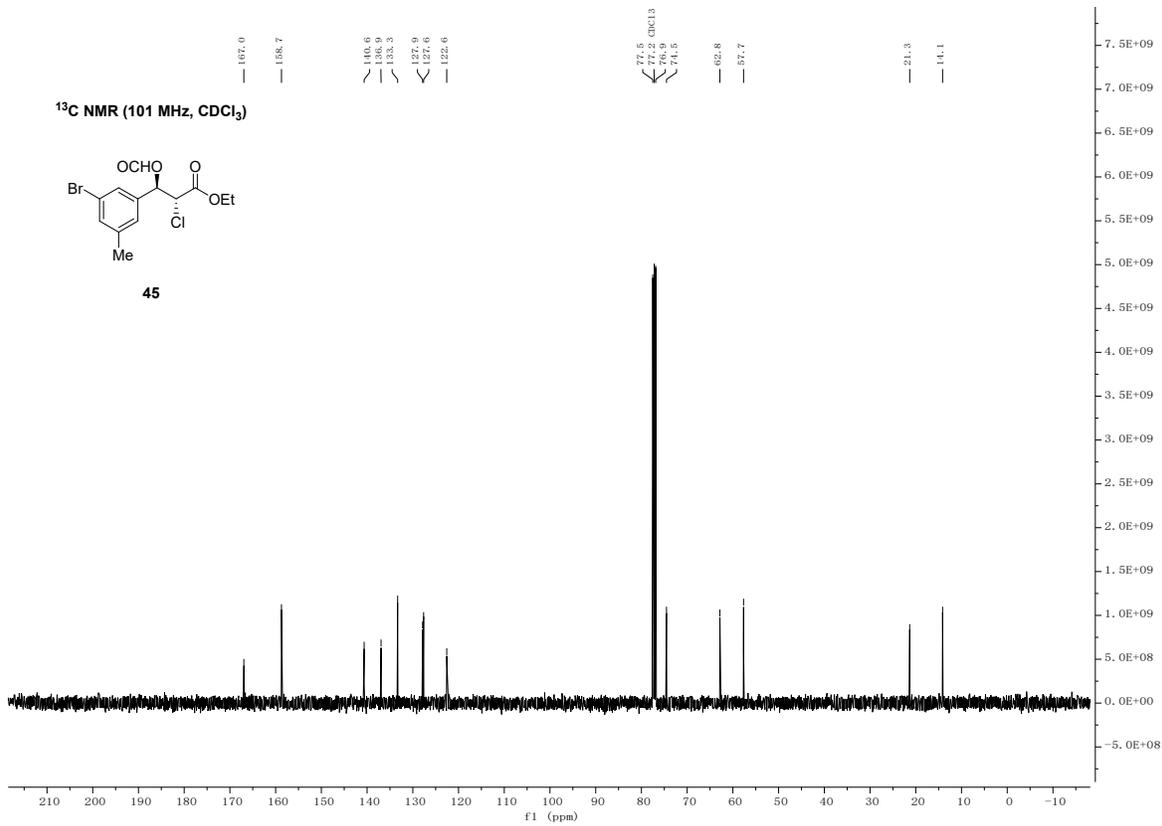


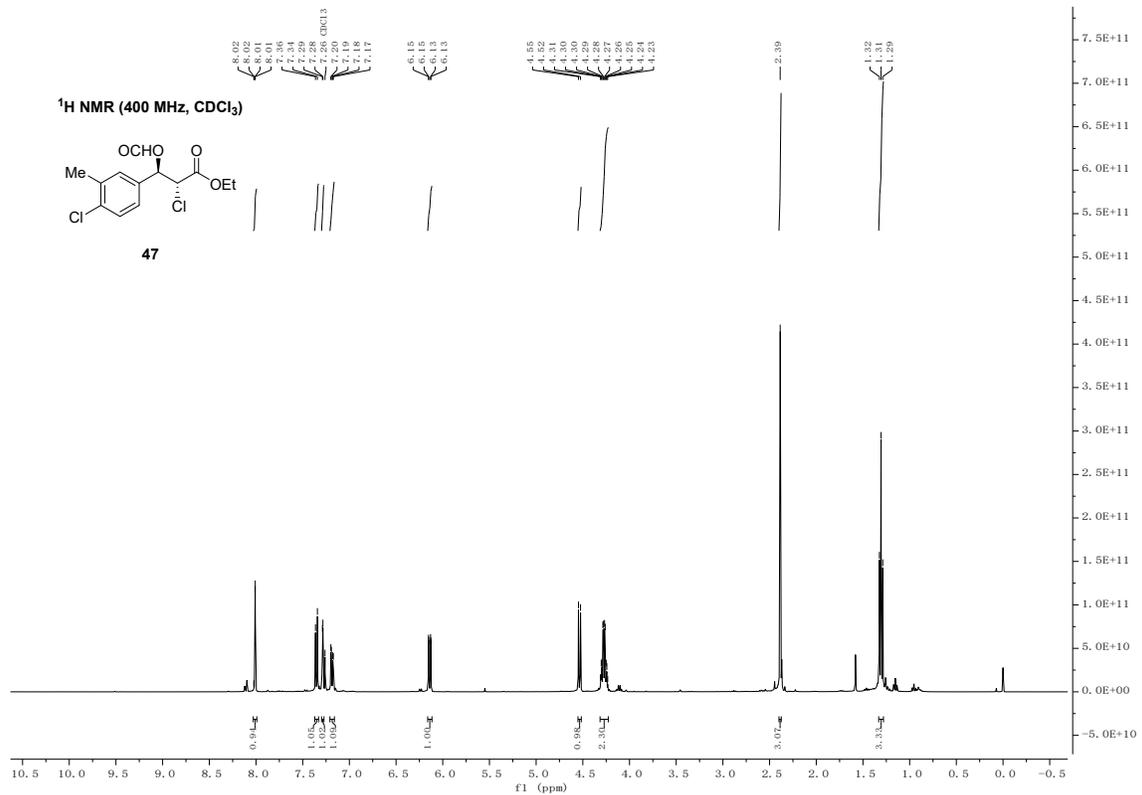
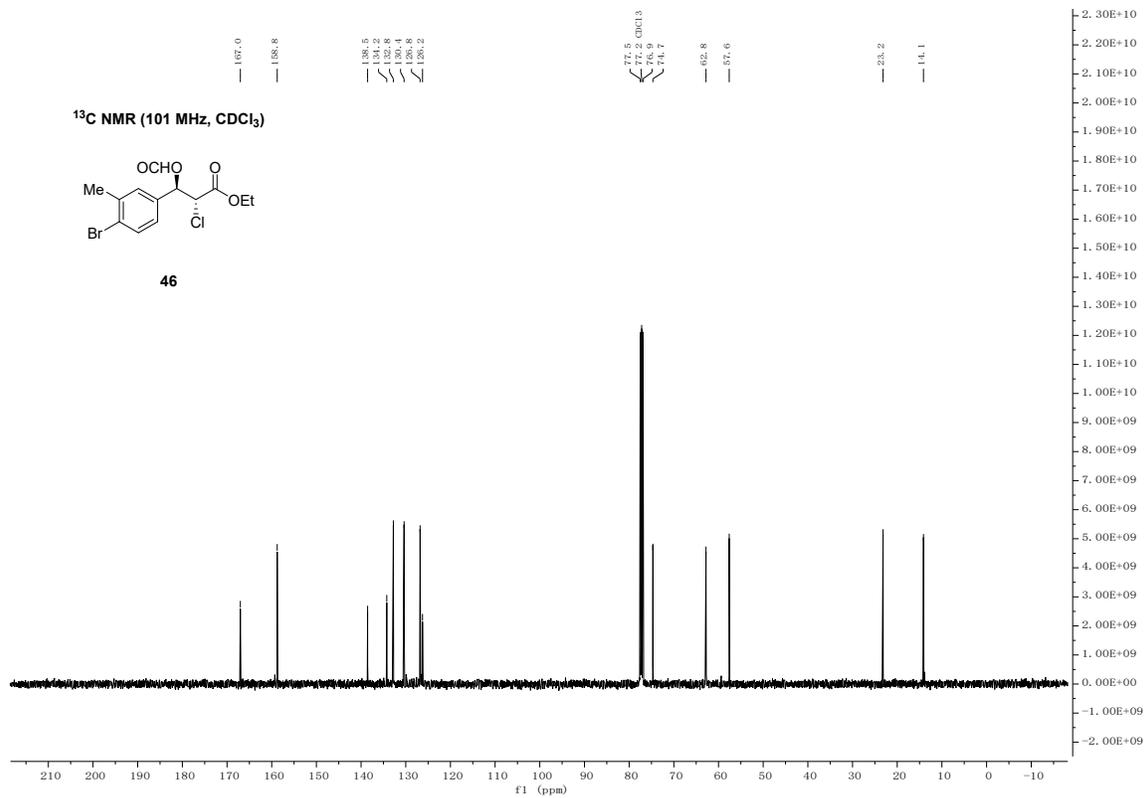


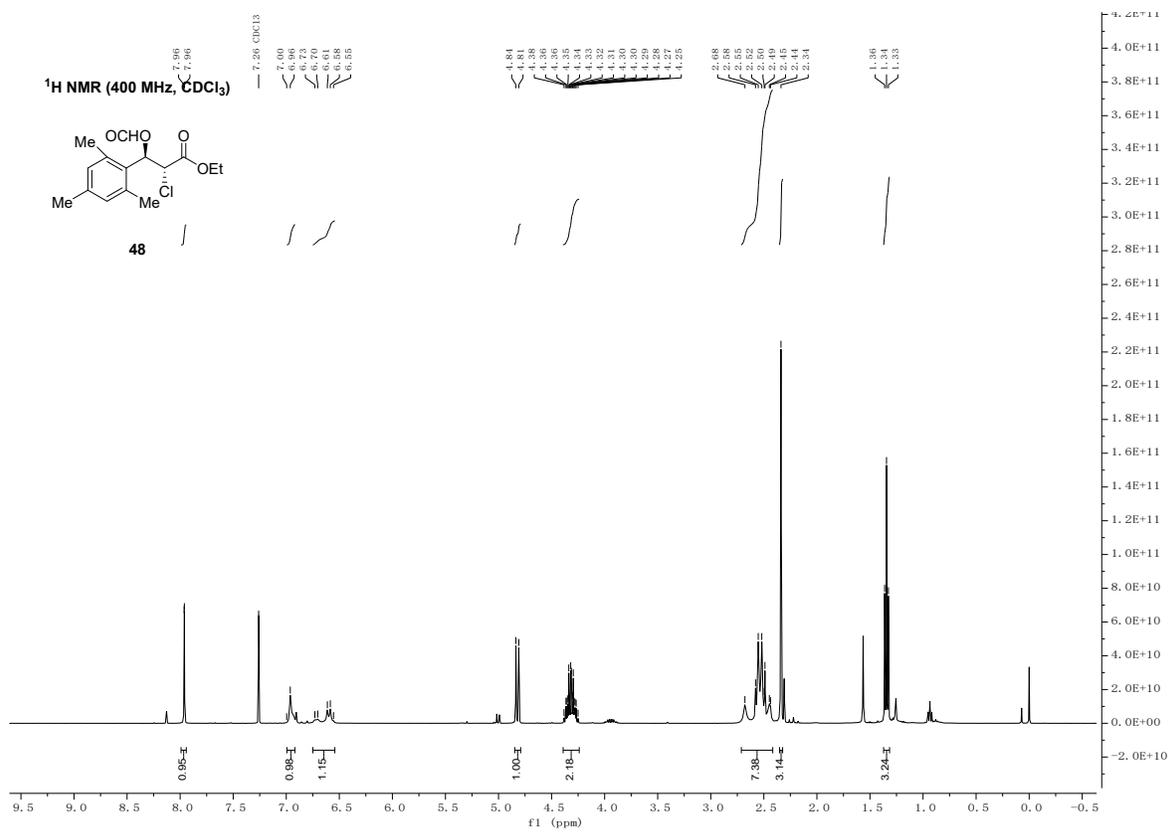
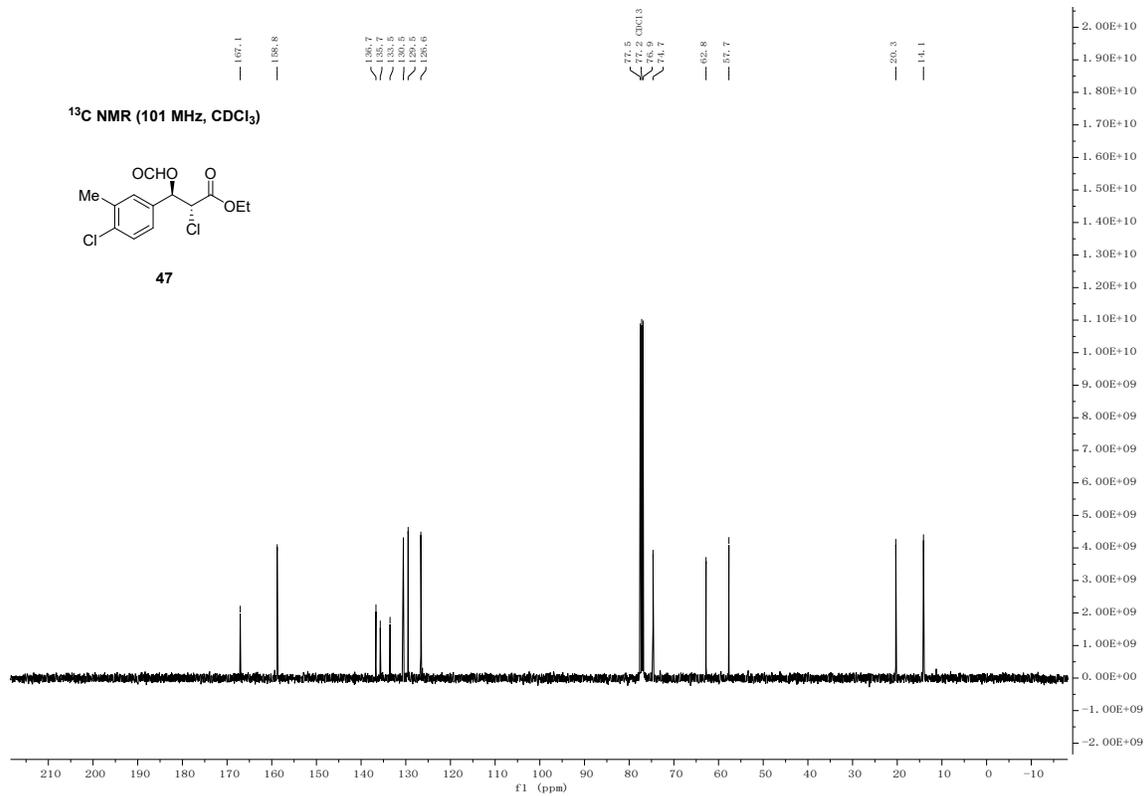


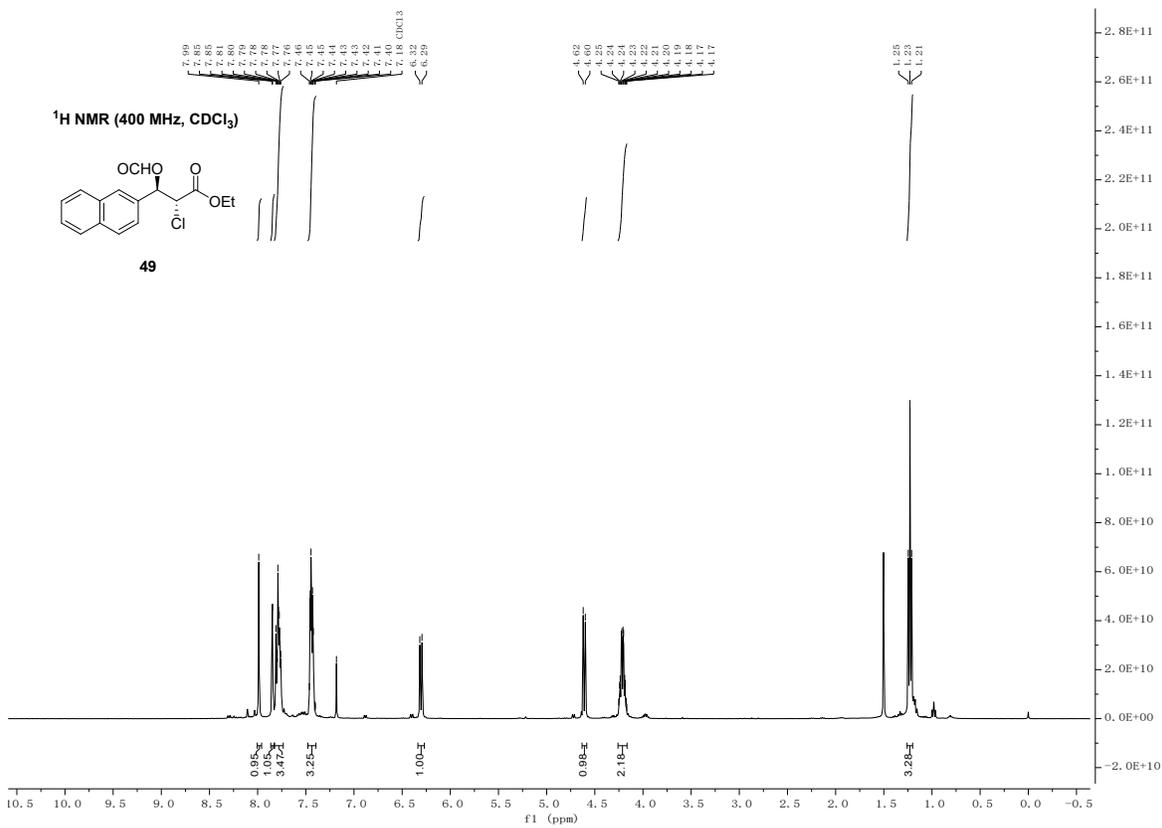
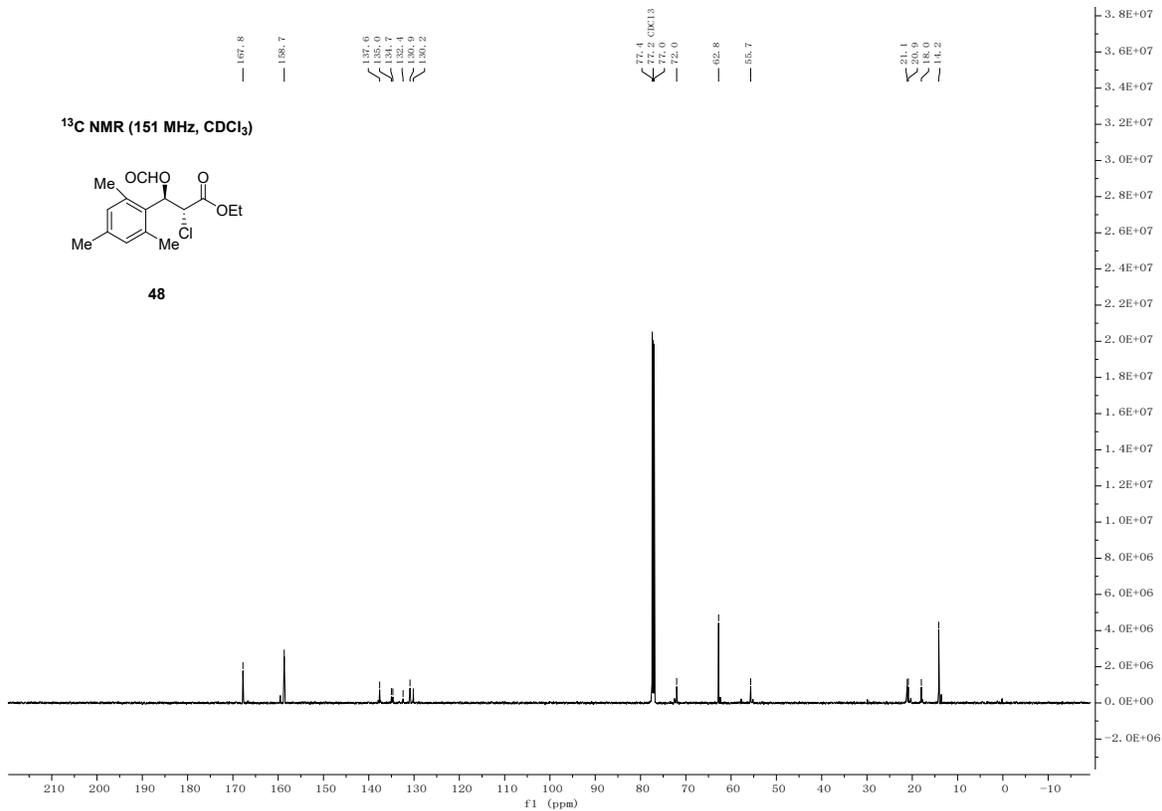


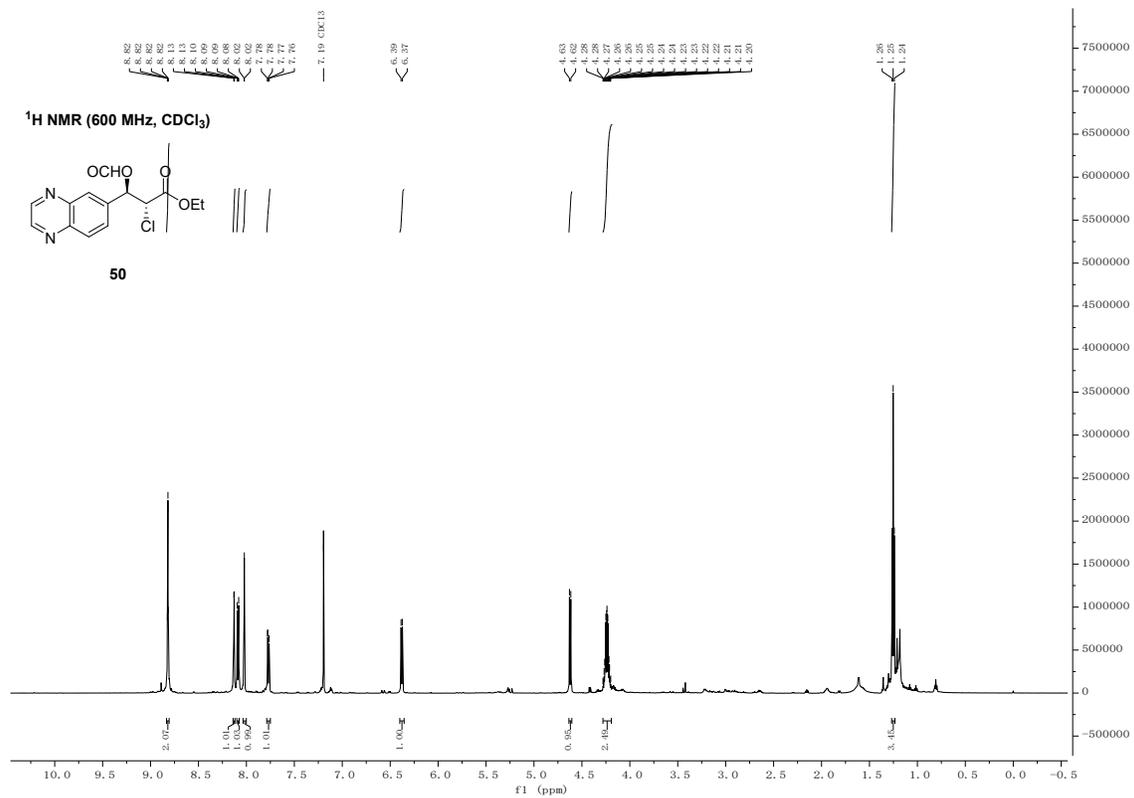
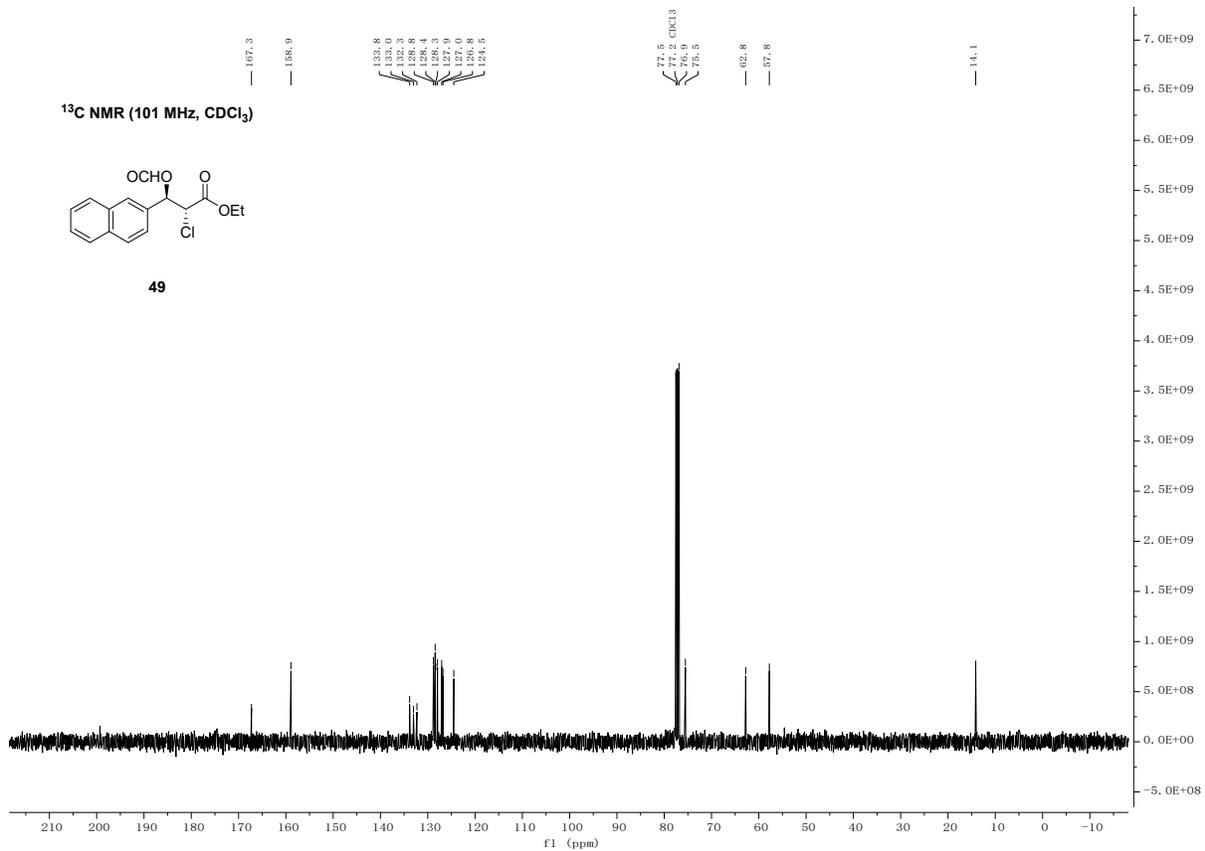


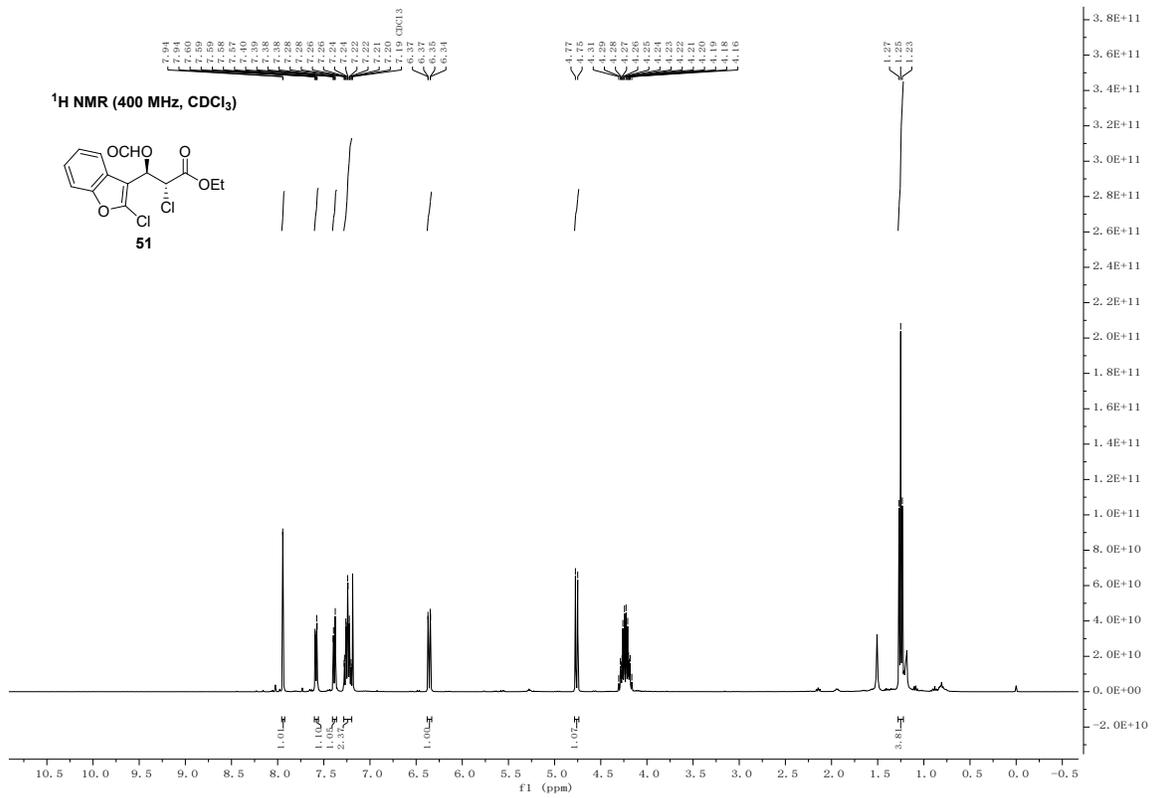
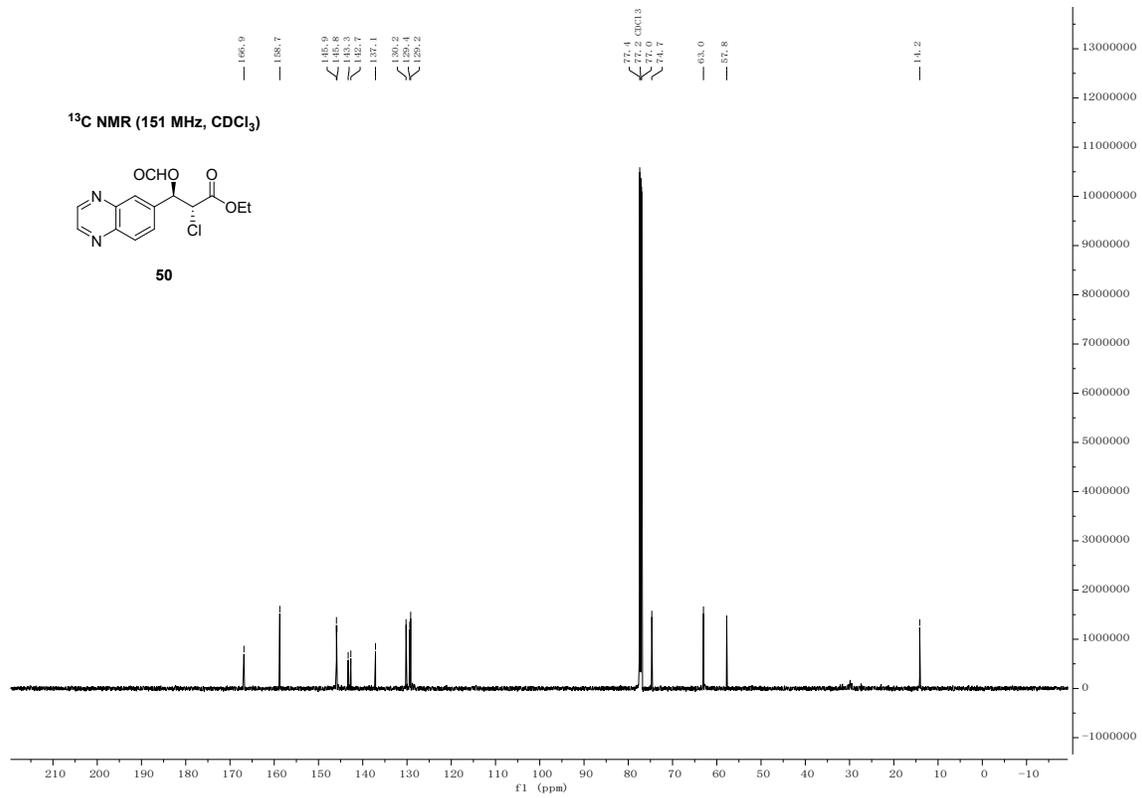


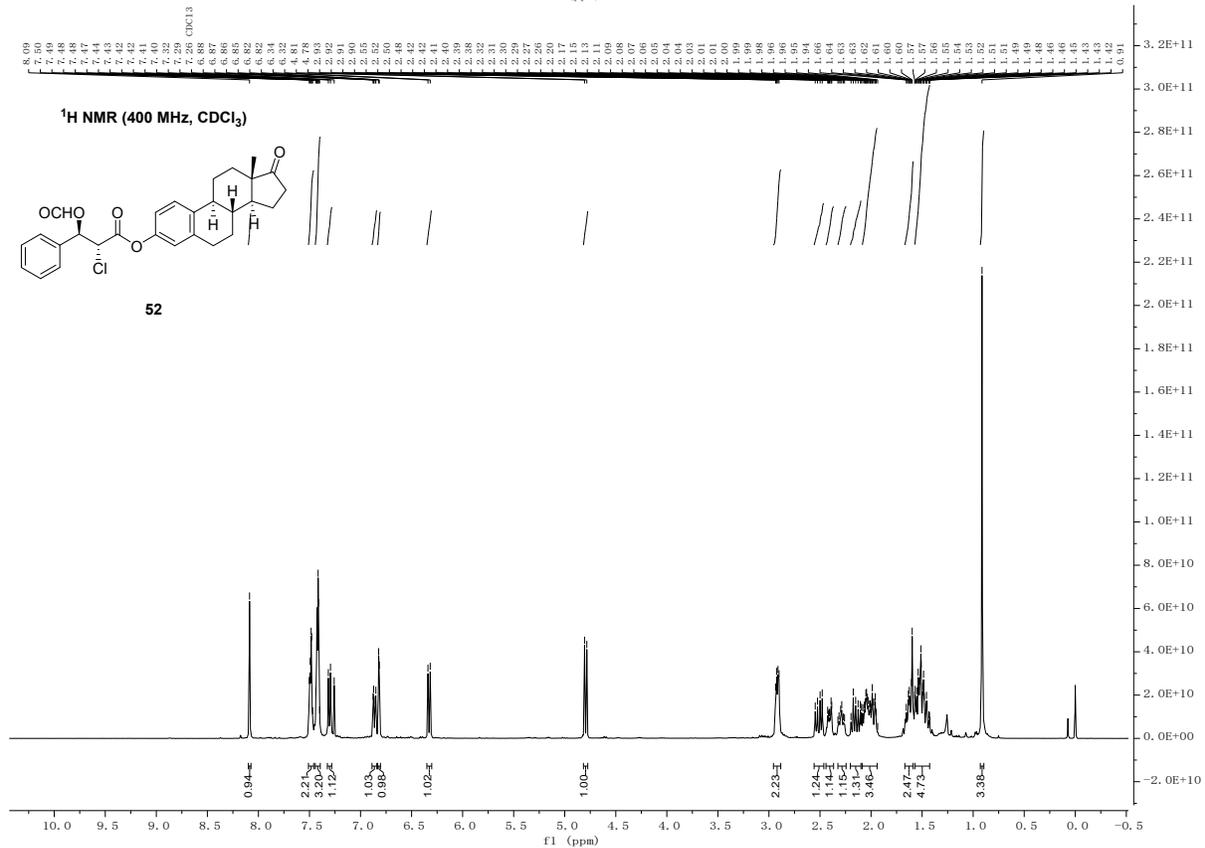
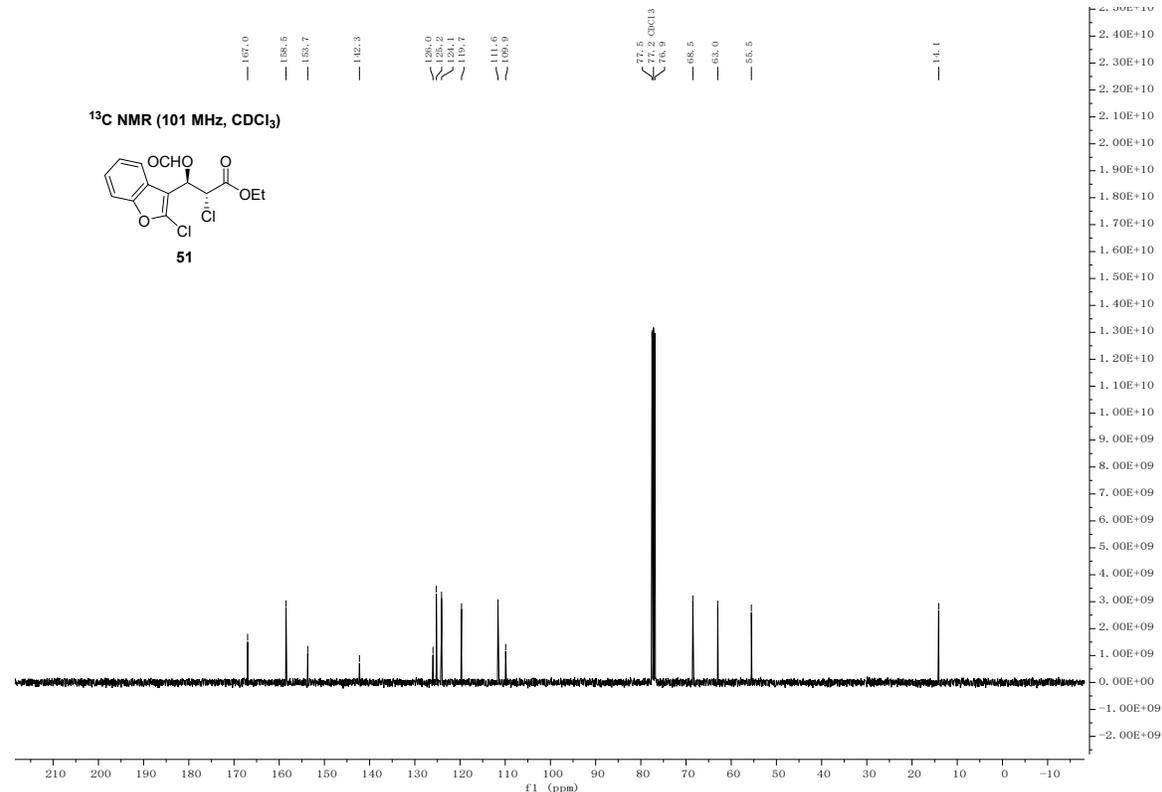


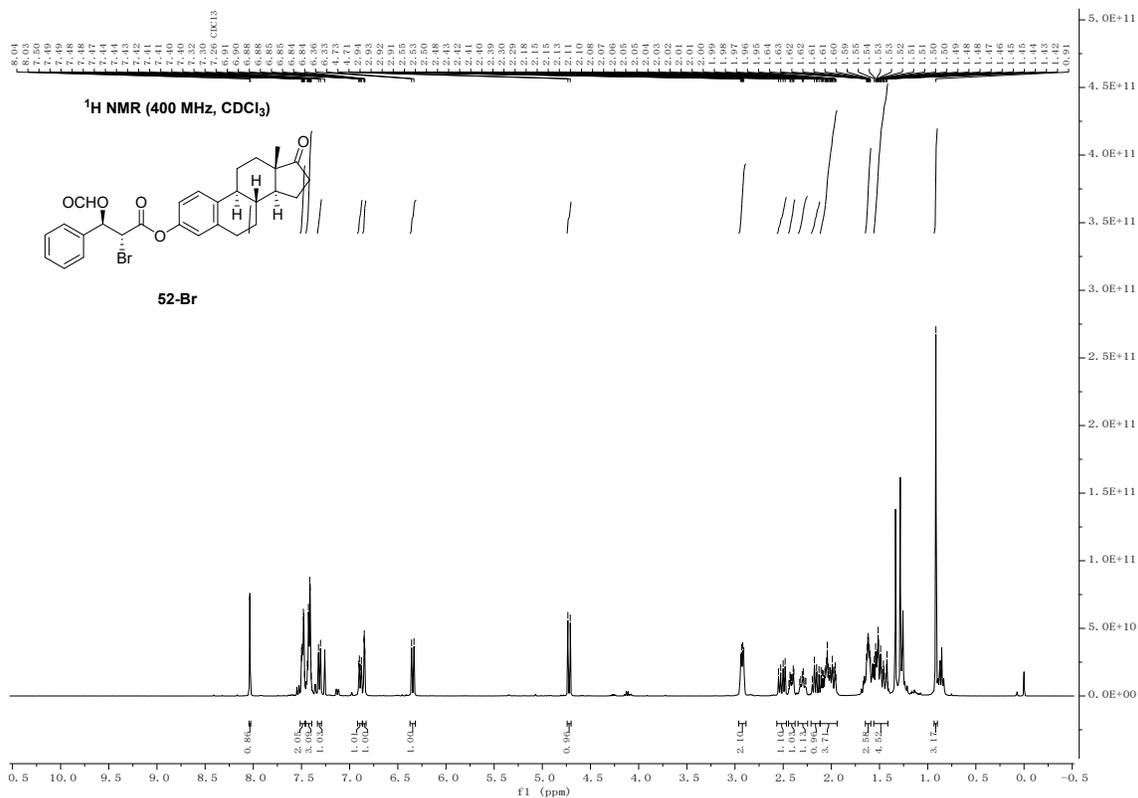
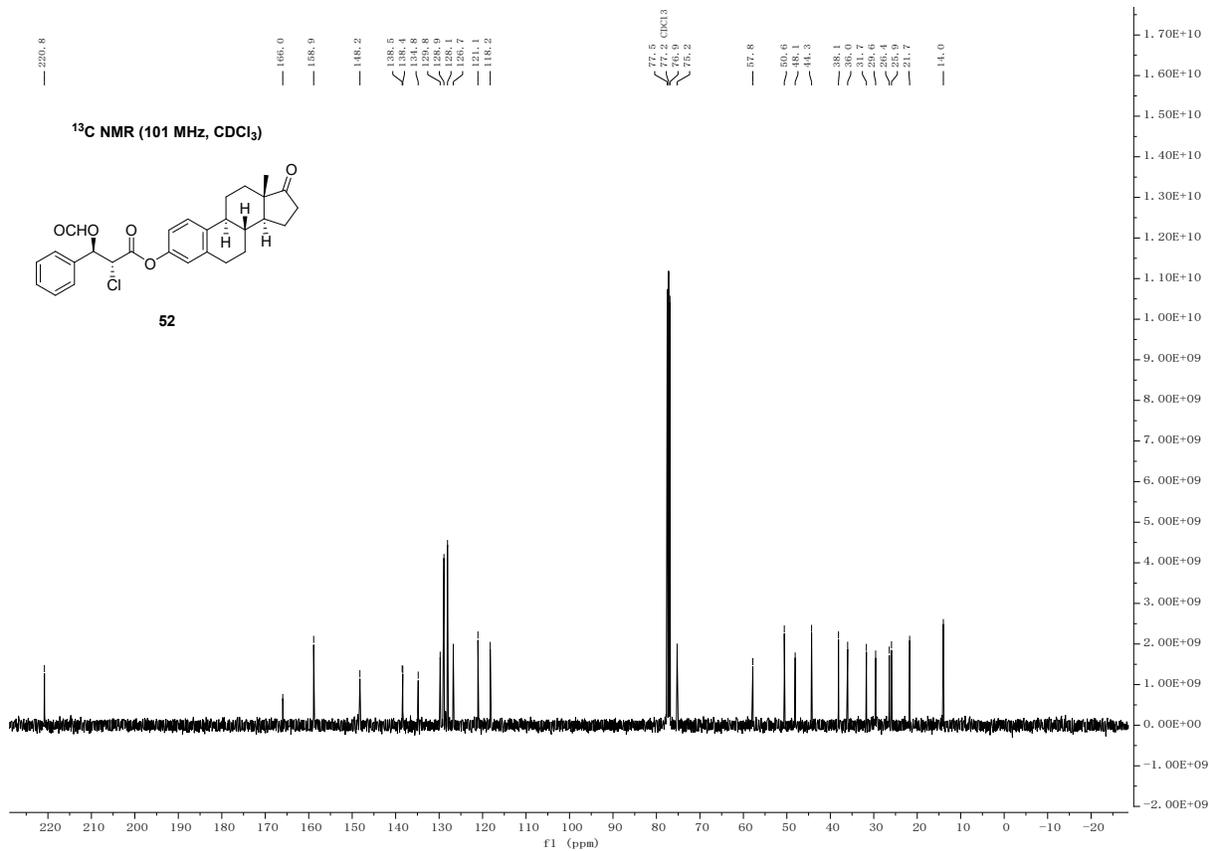


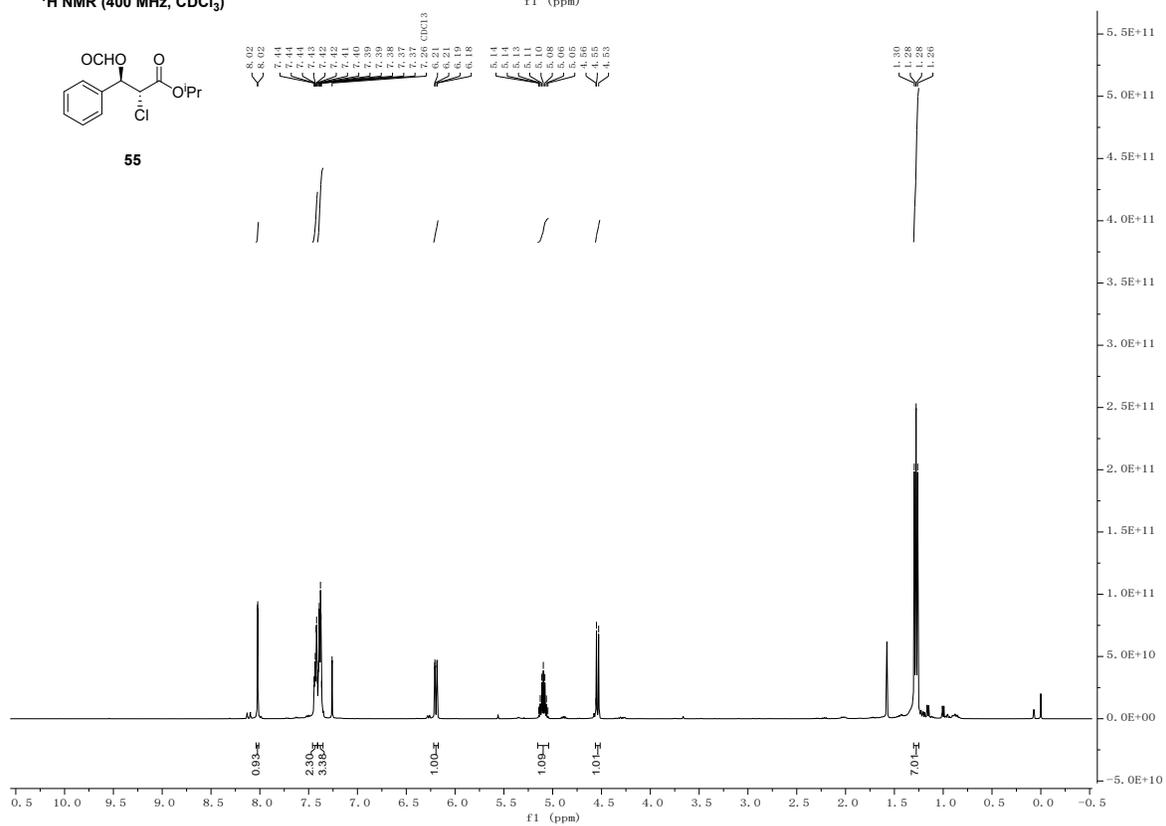
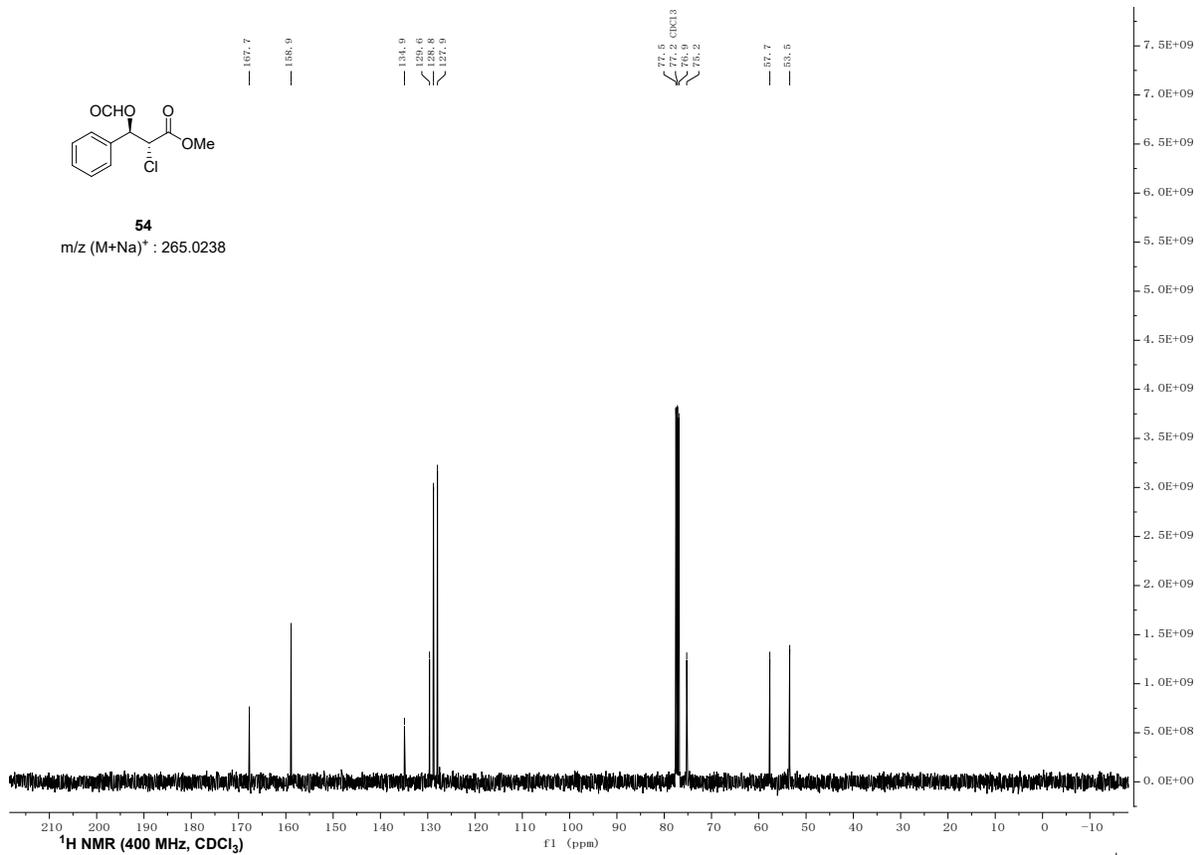


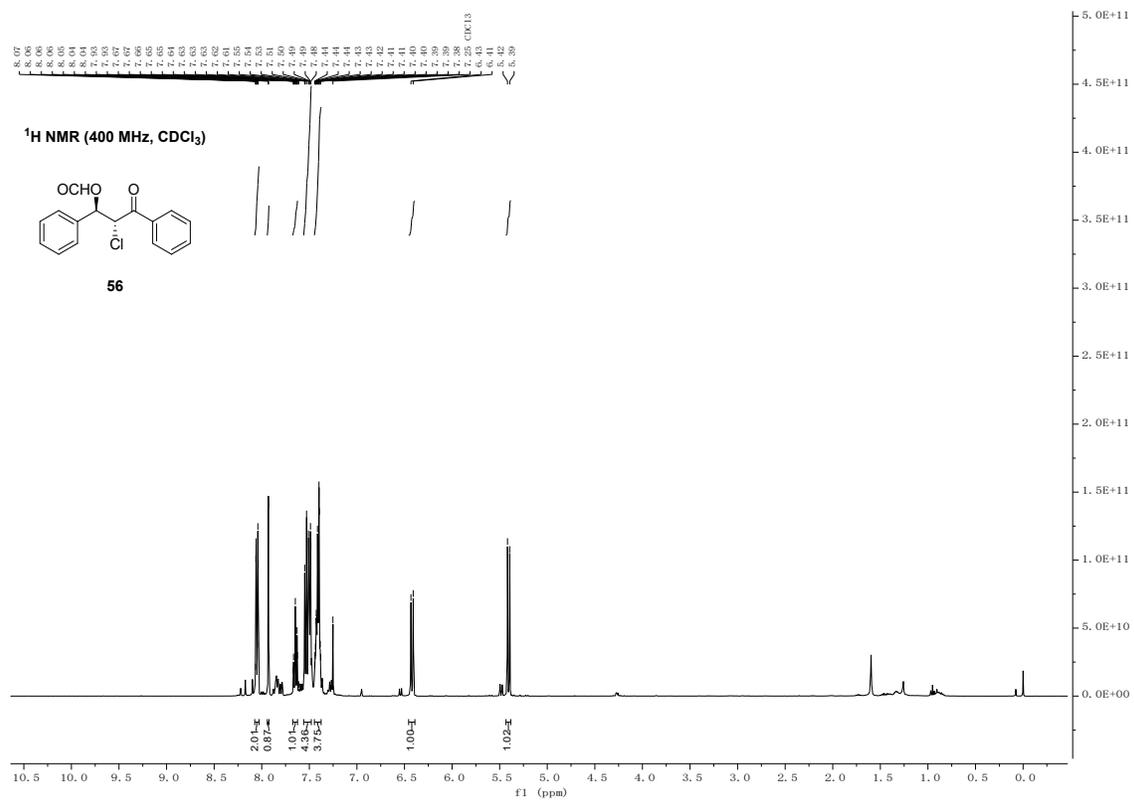
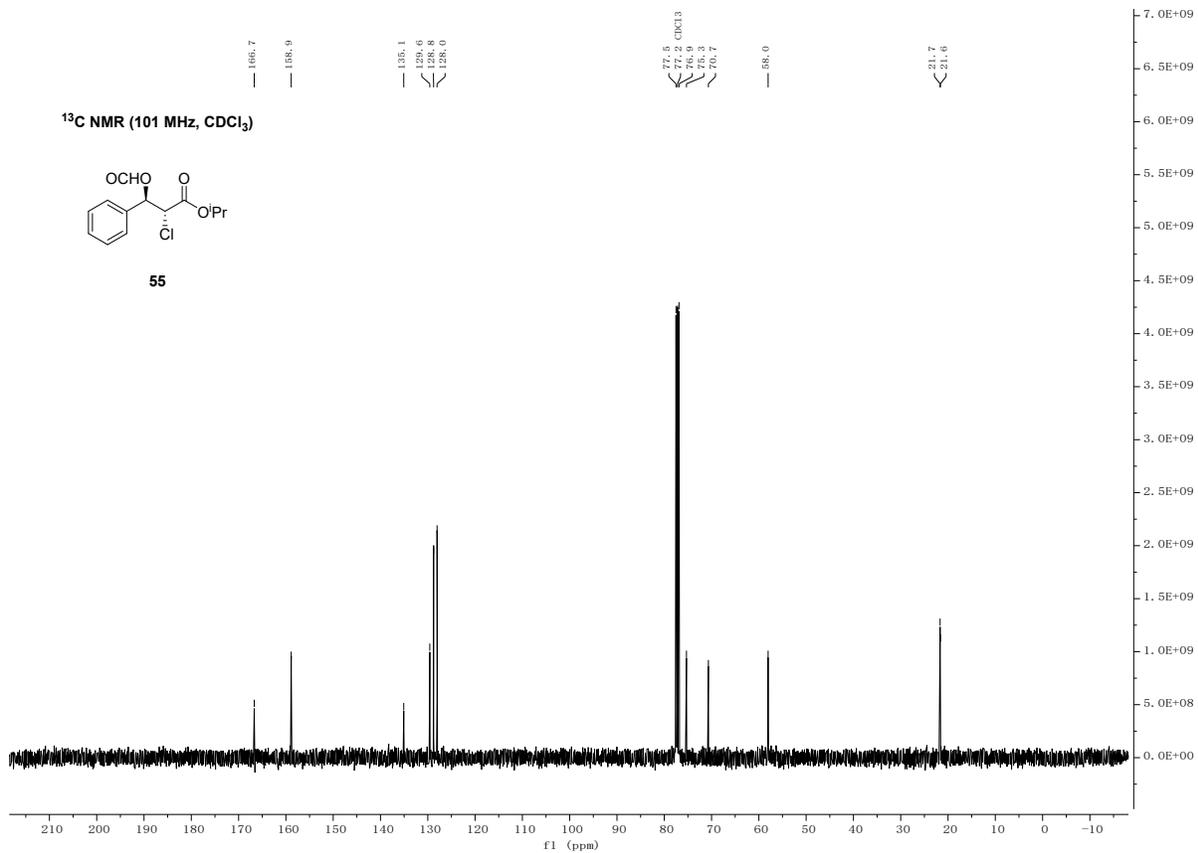


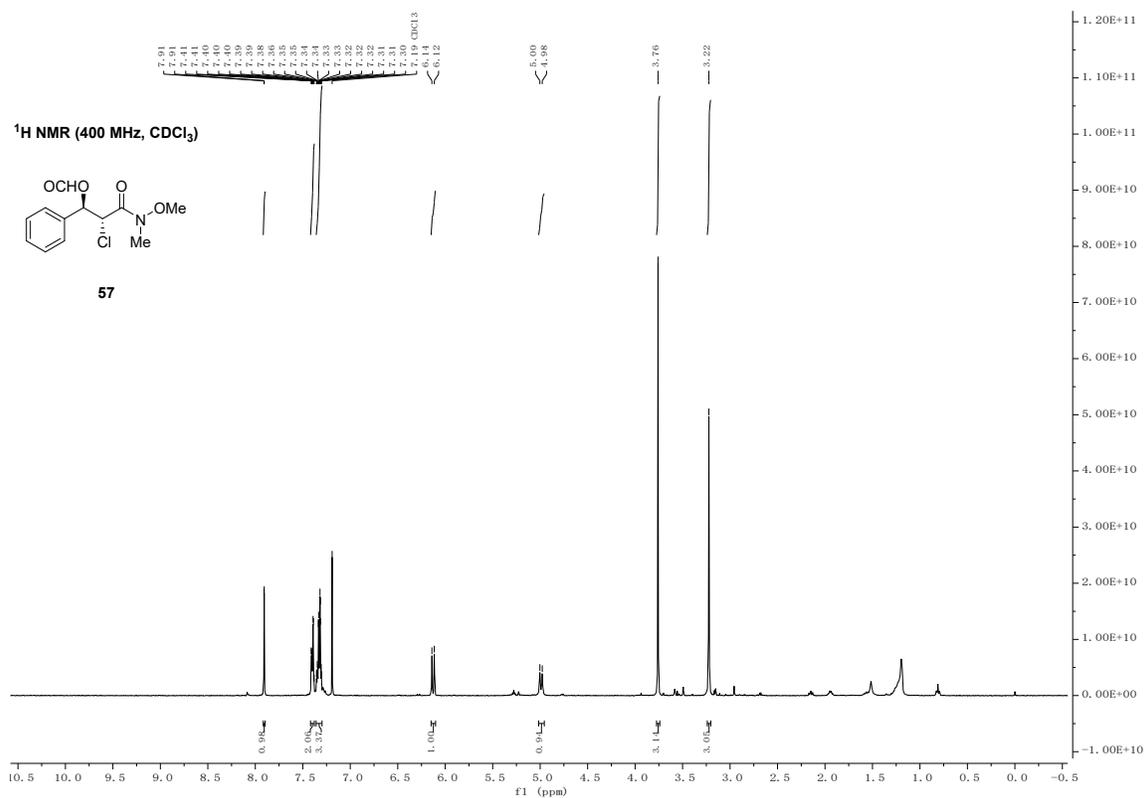
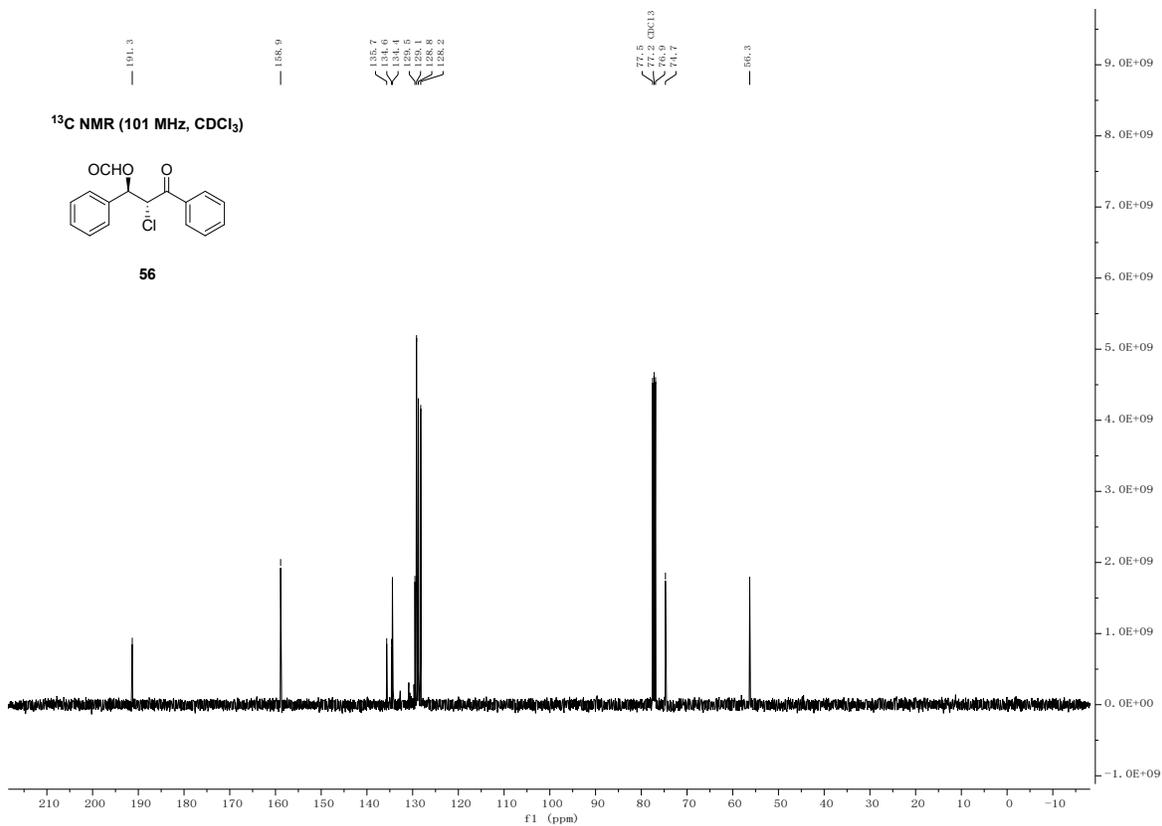


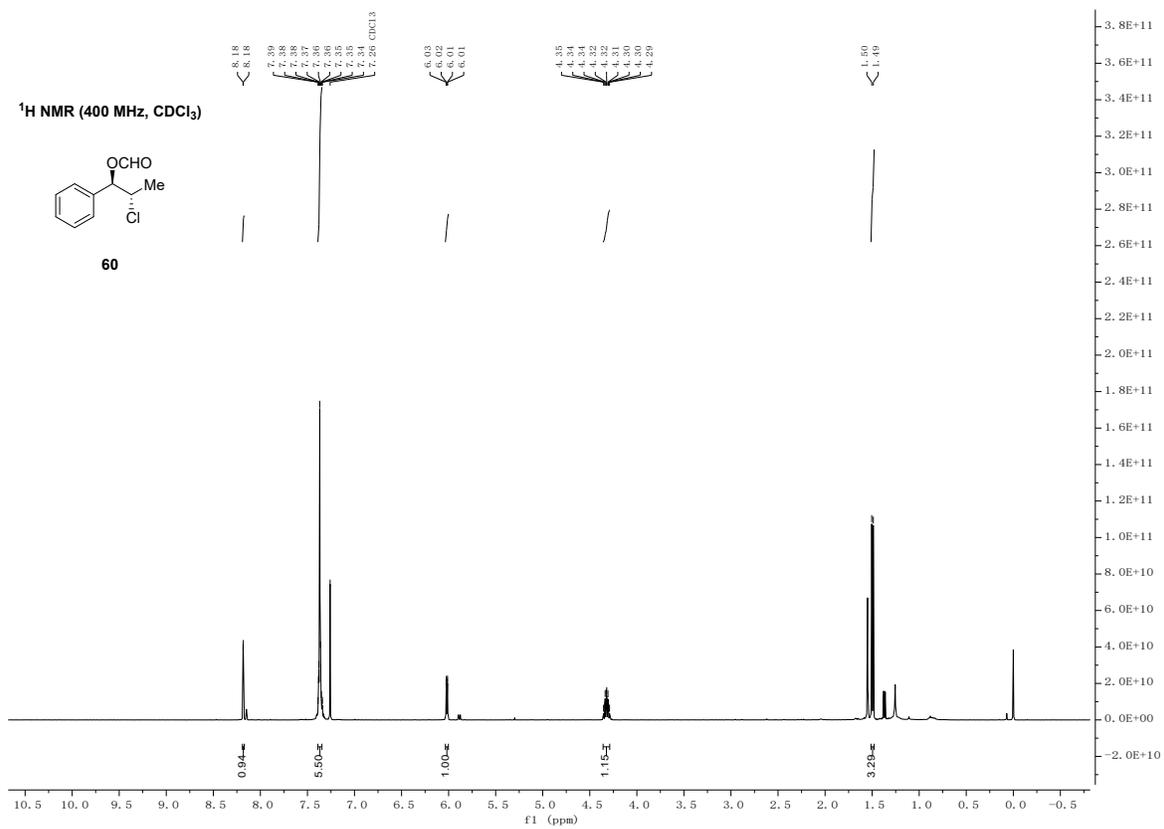
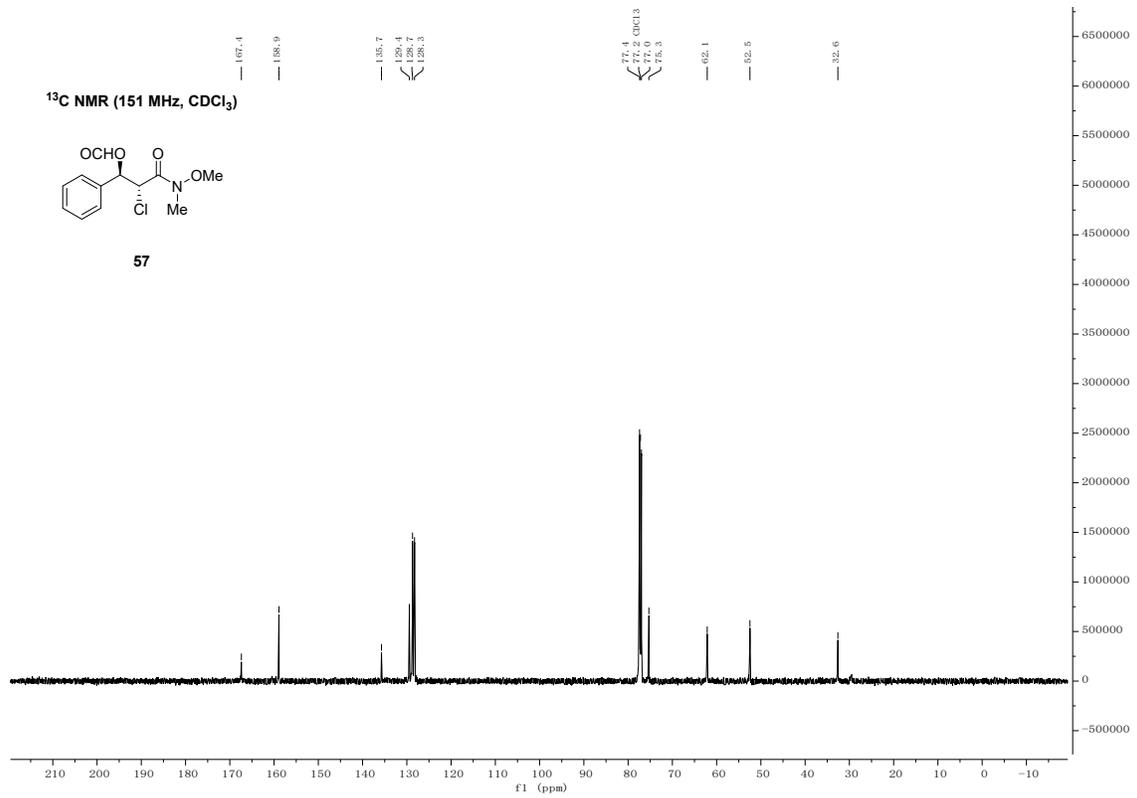


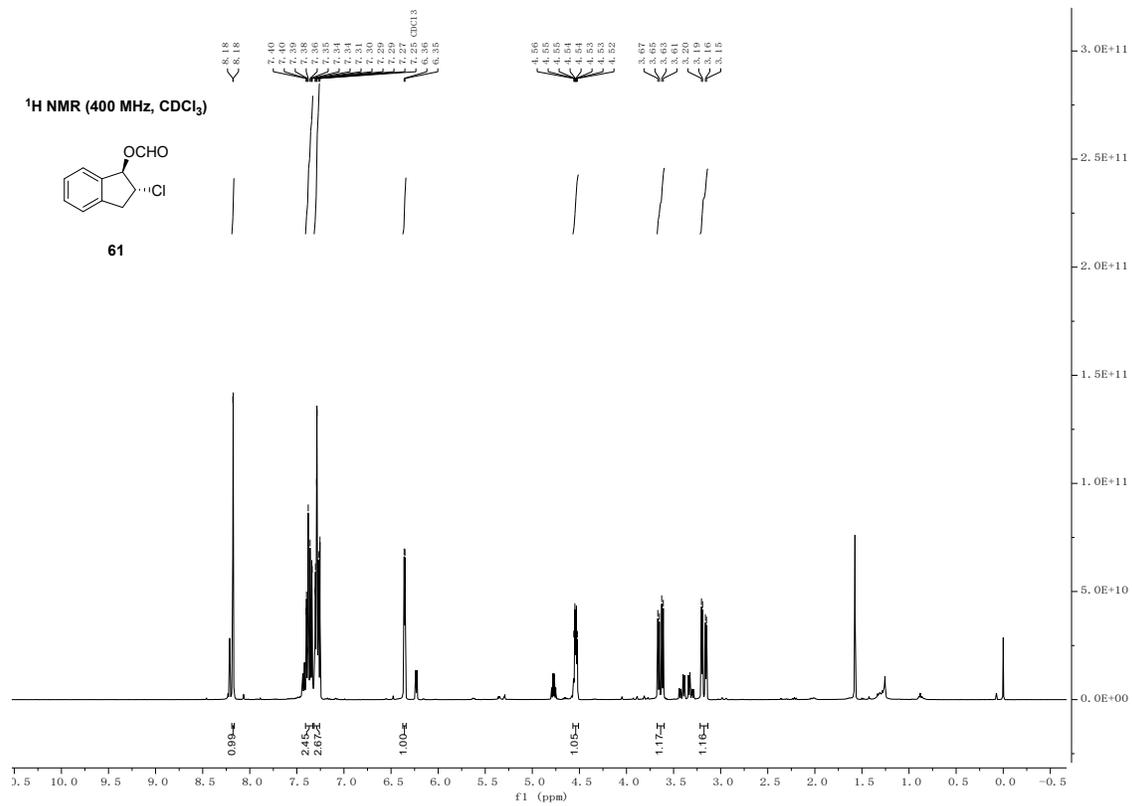
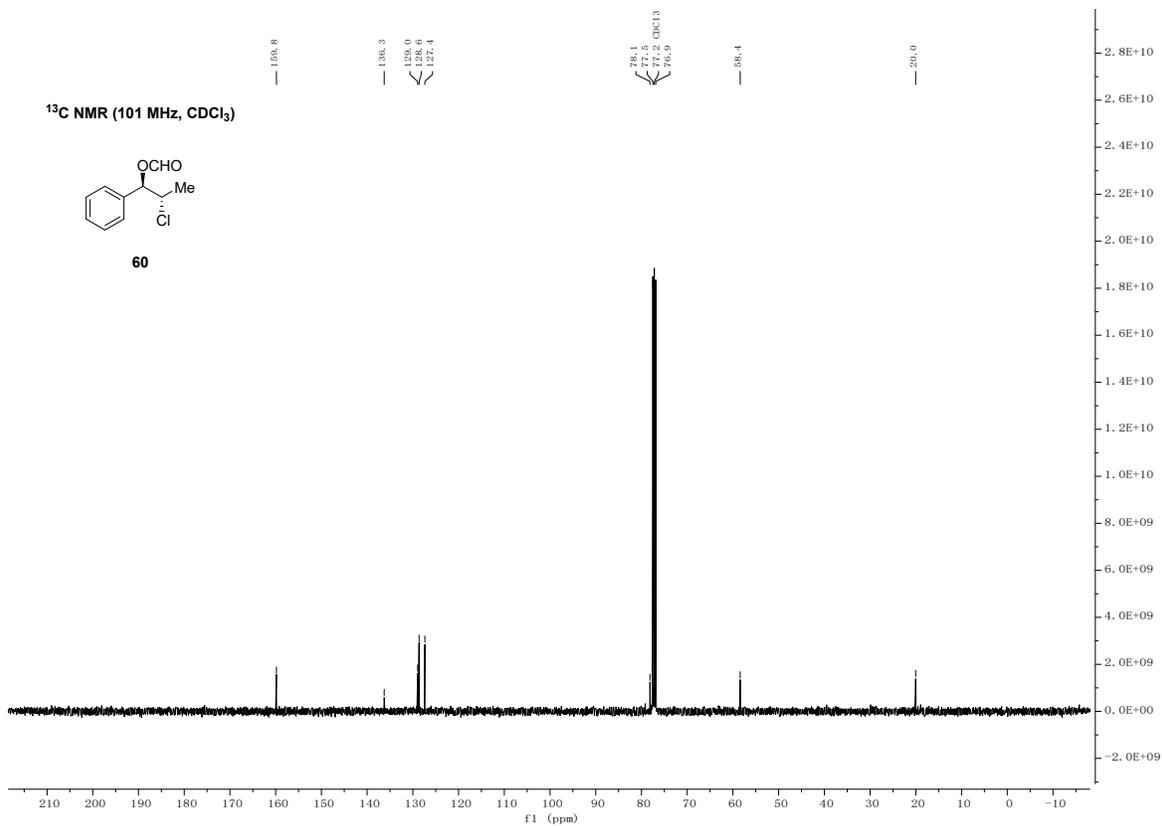


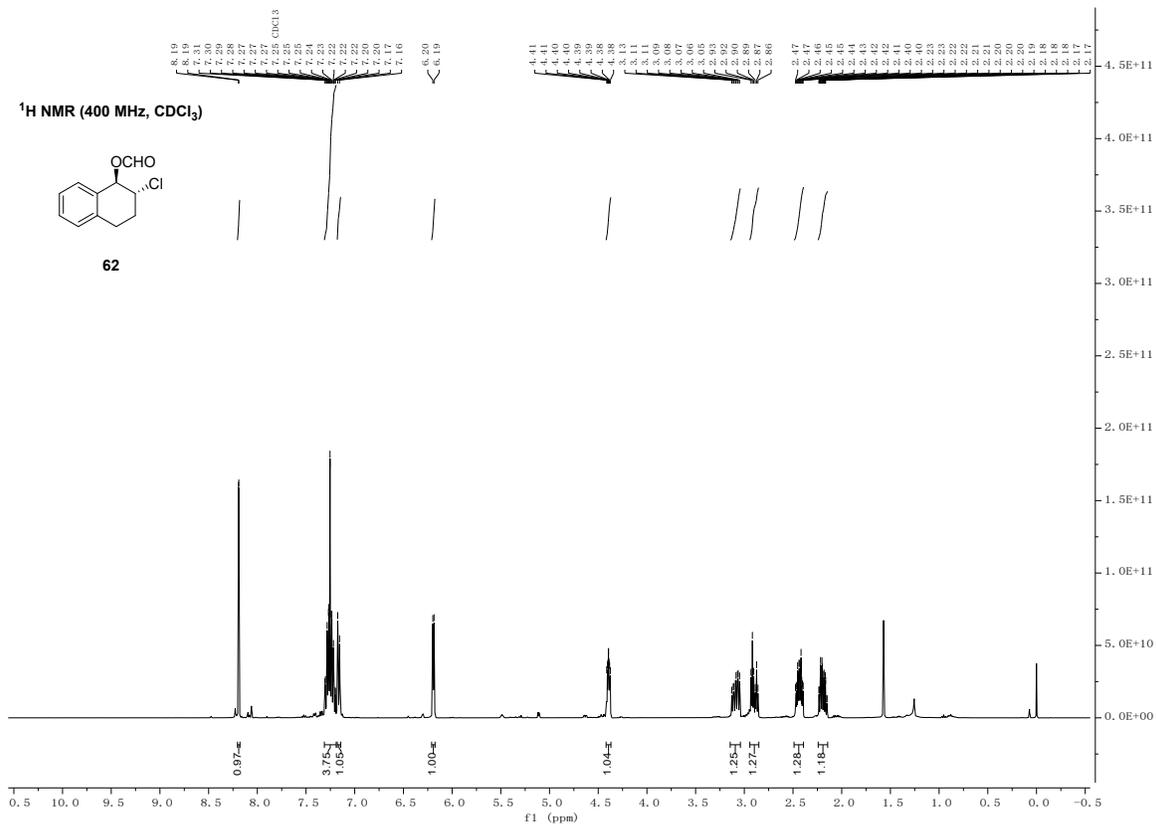
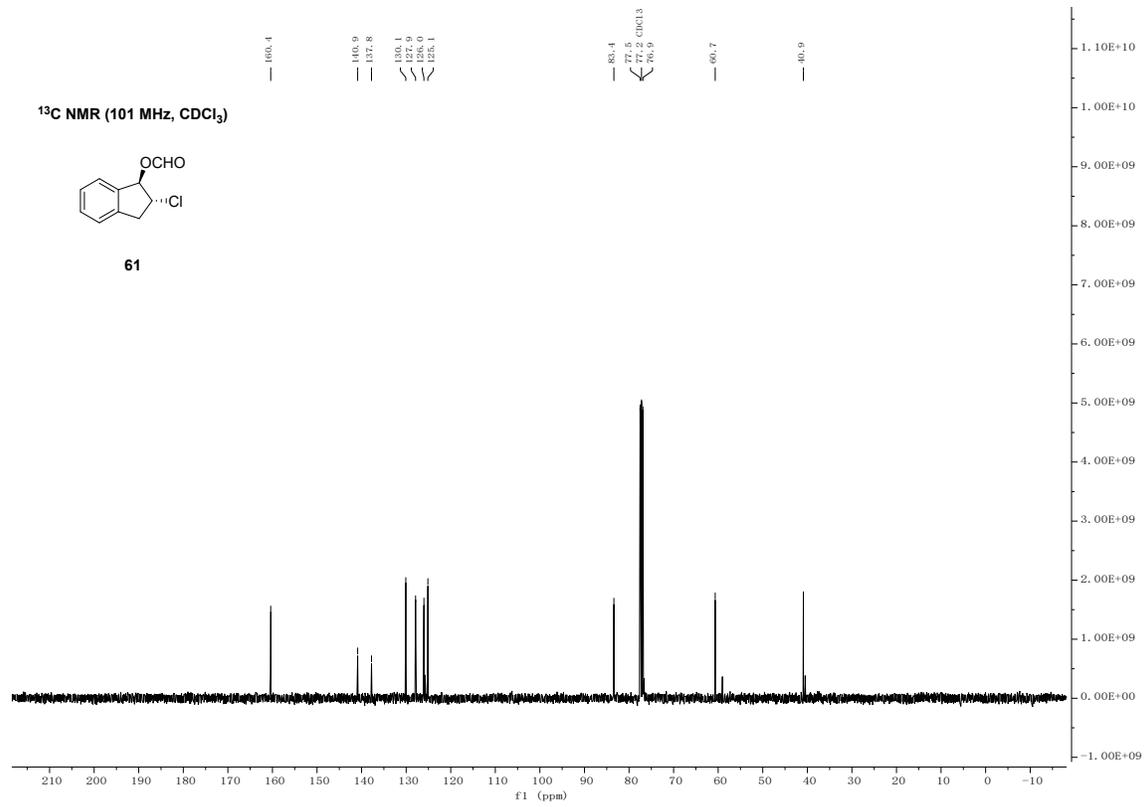


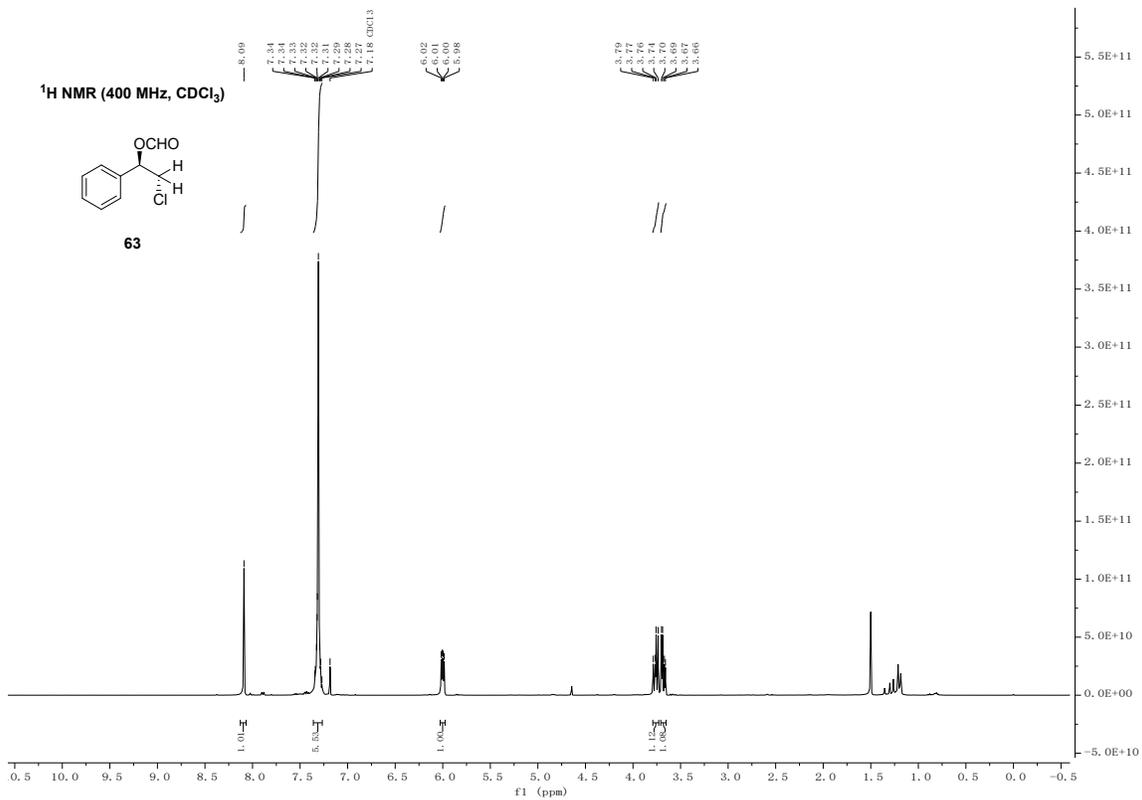
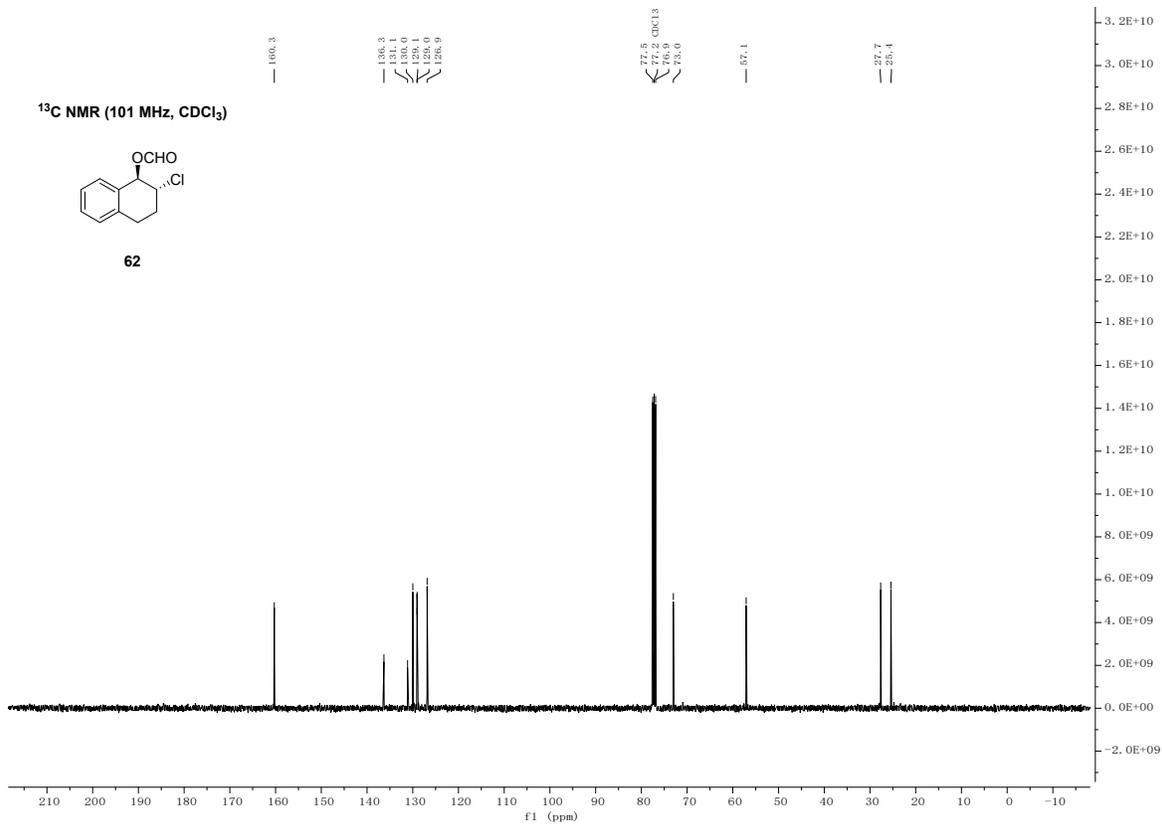




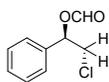




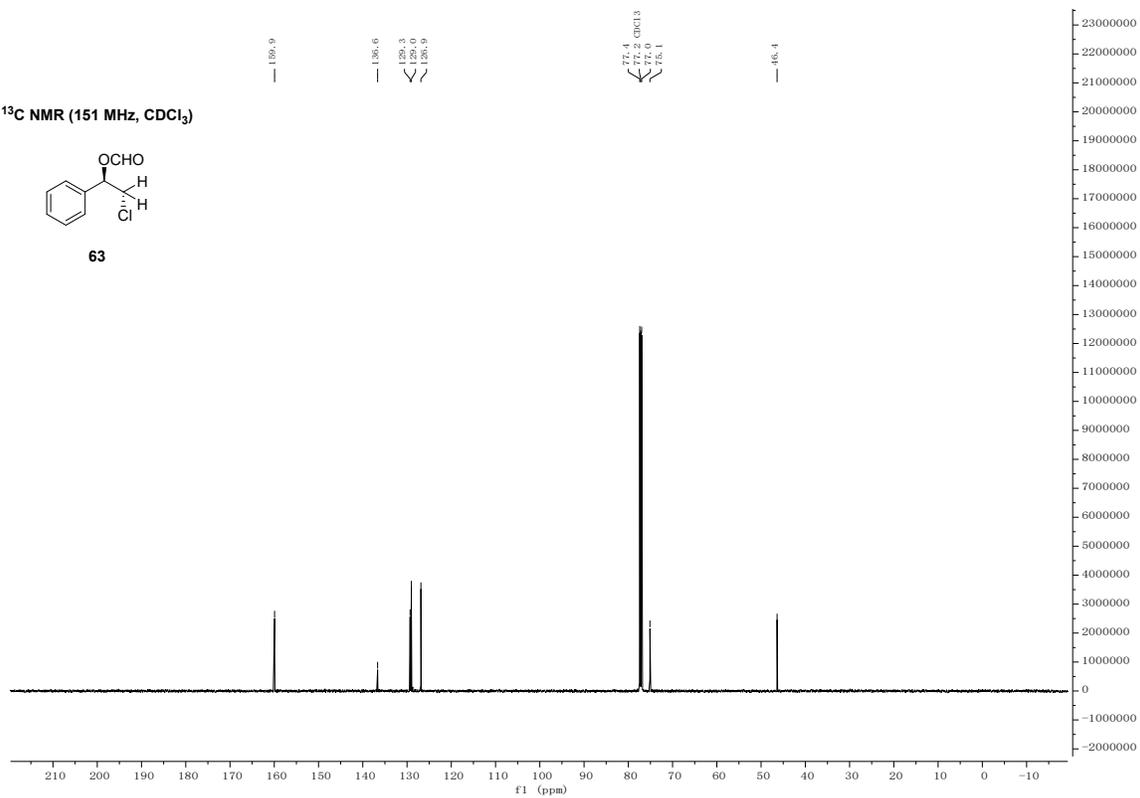




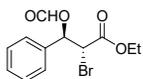
¹³C NMR (151 MHz, CDCl₃)



63



¹H NMR (400 MHz, CDCl₃)



66

