Electronic Supplementary Information

Visible-light induced C_{sp3}–H functionalization of glycine derivatives by cerium catalysis

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1. Experiment Information

1.1 General information

Unless otherwise noted, all reagents were purchased from commercial sources and used as received without further purification. *N*-arylglycine derivatives[1,2] were prepared according to literature procedures. Unless otherwise indicated, all experiments were carried out under air atmosphere. Irradiation of photochemical reactions was carried out using 18 W blue LED bulb or 5 W LED waveband light source. The silica gel (200−300 meshes) was used for column chromatography and TLC inspections were taken on silica gel GF254 plates. Liquid ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. High resolution mass spectra (HRMS) were obtained on a mass spectrometer by using electrospray ionization (ESI) analyzed by quadrupole time-of-flight (QTof).

1.2 General procedure for the visible-light-induced oxidative dehydrogenative coupling/aromatization tandem reaction of glycine derivatives and alkenes.

To a solution of *N*-arylglycine derivative **1** (0.2 mmol, 1 eq) and $Ce(OTf)_3$ (30 mol%) in dry CH_3CN (4.0 mL) was added styrene derivative (1.0 mmol, 5 eq). The solution was irradiated with 18 W blue LED under air atmosphere at room temperature. After completion of the reaction as monitored by TLC, the solvent was removed under vacuo, and the residue was separated by silica gel column chromatography (with petroleum ether/EtOAc = 8/1 to 4/1 as eluent) to afford the product.

1.3 Substrate limitation

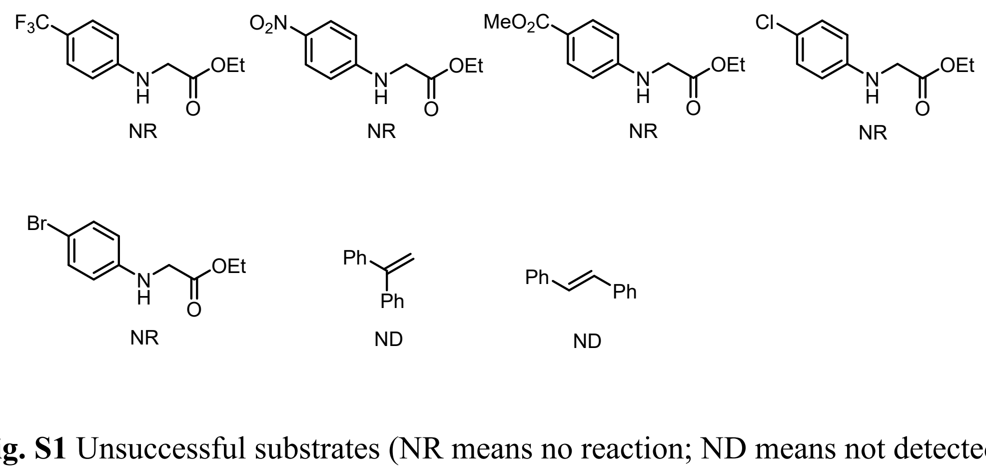


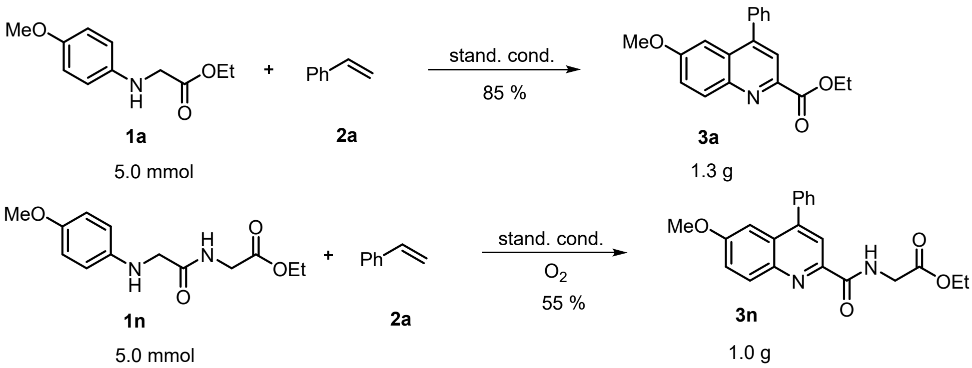
Fig. S1 Unsuccessful substrates (NR means no reaction; ND means not detected).

1.4 General procedure for the visible-light-induced post-modification of oligopeptides containing glycine residues.

Glycine derived peptide **1** (0.2 mmol, 1 eq) and Ce(OTf)$_3$ (30 mol%) in dry CH_3CN (4.0 mL) was added styrene derivative (1.0 mmol, 5 eq). The solution was irradiated with 18 W blue LED under O_2 atmosphere at room temperature. After completion of the reaction as monitored by TLC, the solvent was removed under vacuo, and the residue was separated by silica gel column chromatography (with PE/EA = 4/1 to 2/1 as eluent) to afford the product. ***Note: The reaction can also be carried out under air atmosphere, but the reaction rate is relatively slow.***

Fig. S2 Picture of photoreaction device.

1.5 Gram-scale synthesis and coupling of glycine ester with other nucleophiles



Scheme S1 Gram scale experiment.

To a solution of **1a** (1.05 g, 5.0 mmol, 1 eq) and Ce(OTf)$_3$ (0.88 g, 30 mol%) in dry CH_3CN (100 mL) was added **2a** (2.60 g, 25.0 mmol, 5 eq). The mixed solution was irradiated with 18 W blue LED under air atmosphere at room temperature. After completion of the reaction as monitored by TLC, the solvent was removed under vacuo, and the residue was separated by silica gel column chromatography (with petroleum ether/EtOAc = 8/1 to 4/1 as eluent) to afford the product **3a** (1.30 g, 85 % yield) as a white solid.

To a solution of **1n** (1.33 g, 5.0 mmol, 1 eq) and Ce(OTf)$_3$ (0.88 g, 30 mol%) in dry CH_3CN (100 mL) was added **2a** (2.60 g, 25.0 mmol, 5 eq). The mixed solution was irradiated with 18 W blue LED under O_2 atmosphere at room temperature. After completion of the reaction as monitored by TLC, the solvent was removed under vacuo, and the residue was separated by silica gel column chromatography (with petroleum ether/EtOAc = 4/1 to 2/1 as eluent) to afford the product **3n** (1.00 g, 55 % yield) as a white solid.

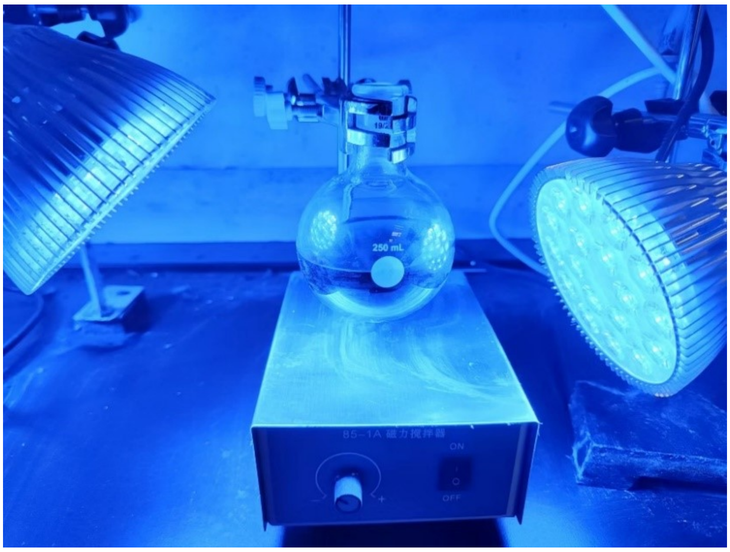
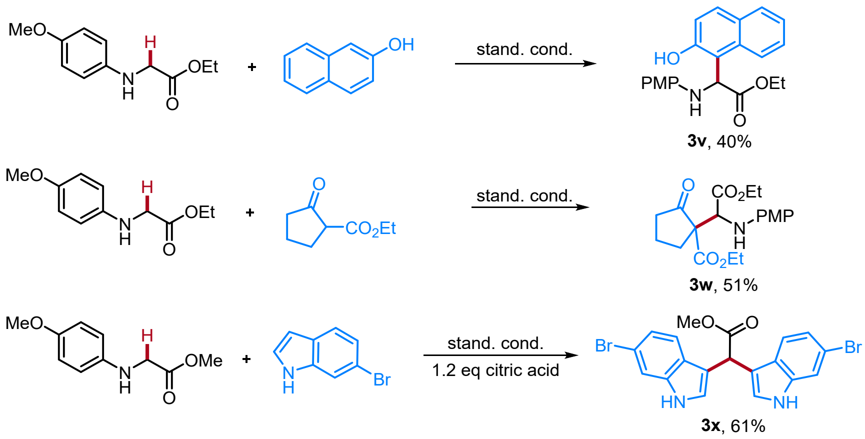


Fig. S3 Picture of set-up for the gram scale reaction.

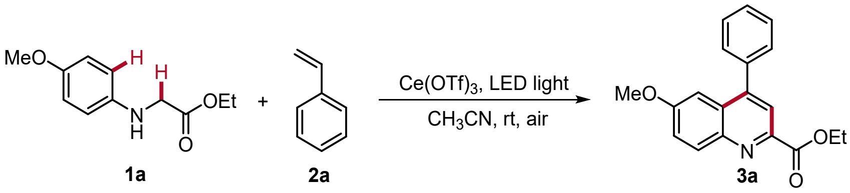


Scheme S2 Reactions of **1** with other nucleophiles.

To a solution of *N*-arylglycine derivative **1** (0.2 mmol, 1 eq) in dry CH_3CN (4.0 mL) were added $Ce(OTf)_3$ (30 mol%). The mixed solution was irradiated with 18 W blue LED under air atmosphere at room temperature. After **1** completely transformed into imine **5** as monitored by TLC, other nucleophiles (2-naphthol, 1,3-dicarbonyl compound and indole) were added. After completion of the reaction as monitored by TLC, the solvent was removed under vacuo, and the residue was separated by silica gel column chromatography to afford the corresponding coupling product.

2. Optimization of Reaction Conditions

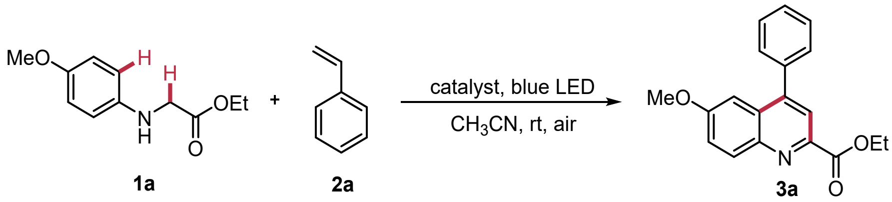
Table S1. Screening of light sources [a]



Entry	Light Source	Yield (%) [b]
1	365-375 nm	67
2	380-385 nm	85
3	390-400 nm	82
4	**Blue LED**	**95**
5	White LED	82
6	Green LED	65
7	dark	trace

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), $Ce(OTf)_3$ (30 mol%), CH_3CN (2.0 mL), LED light irradiation under air at room temperature. [b] Yields were determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

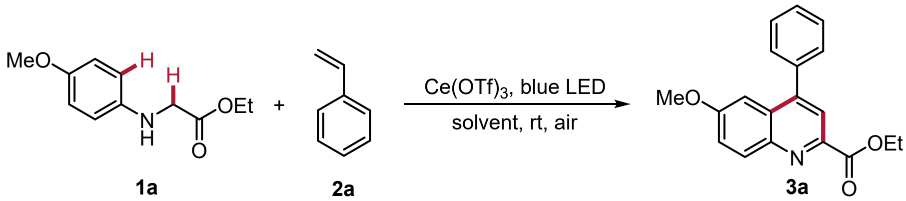
Table S2. Screening of catalysts [a]



Entry	Catalyst	Yield (%) [b]
1	$Ho(OTf)_3$	58
2	$Tm(OTf)_3$	62
3	$Gd(OTf)_3$	80
4	$Lu(OTf)_3$	75
5	$In(OTf)_3$	37
6	$Sn(OTf)_2$	NR
7	AgOTf	43
8	$CeCl_3$	80
9 [c]	$Ce(OTf)_3$	71
10 [d]	$Ce(OTf)_3$	68

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), catalyst (30 mol%), CH_3CN (2 mL), blue LED light irradiation under air at room temperature. [b] Yields were determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c] 15 mol% $Ce(OTf)_3$ was used. [d] 40 mol% $Ce(OTf)_3$ was used.

Table S3. Screening of solvents [a]



Entry	Solvent	Yield (%) [b]
1	CH_3OH	trace
2	THF	82
3	DMF	trace
4	DMSO	trace
5	$CHCl_3$	66
6	DCM	78
7	DCE	87
8	1,4-Dioxane	53
9	Toluene	61
10	Et_2O	trace
11	EtOAc	trace
12 [c]	CH_3CN	75
13 [d]	CH_3CN	86

[a] Reaction conditions: **1a** (0.1 mmol), **2a** (0.5 mmol), $Ce(OTf)_3$ (30 mol%), solvent (2.0 mL), blue LED light irradiation under air at room temperature. [b] Yields were determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c] 1.0 mL CH_3CN was used. [d] 0.5 mL CH_3CN was used.

3. Mechanistic Investigation

3.1 UV/Vis absorption spectra

The UV/Vis absorption spectra were recorded in 1 cm path quartz cuvettes by using a Varian Cary 300 Conc UV/Vis spectrometer. The concentrations of **1a** and Ce(OTf)$_3$ were 0.03 M and 0.015 M, respectively. The obtained bathochromic shift in UV/vis absorption spectra (partial spectrum) were shown in **Fig. S4**.

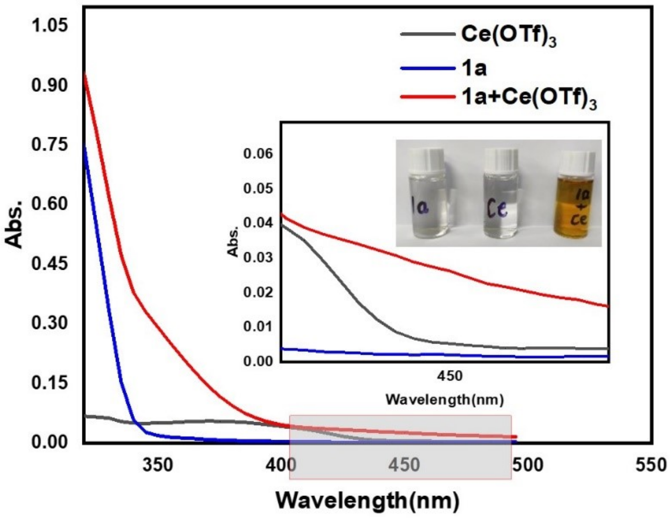
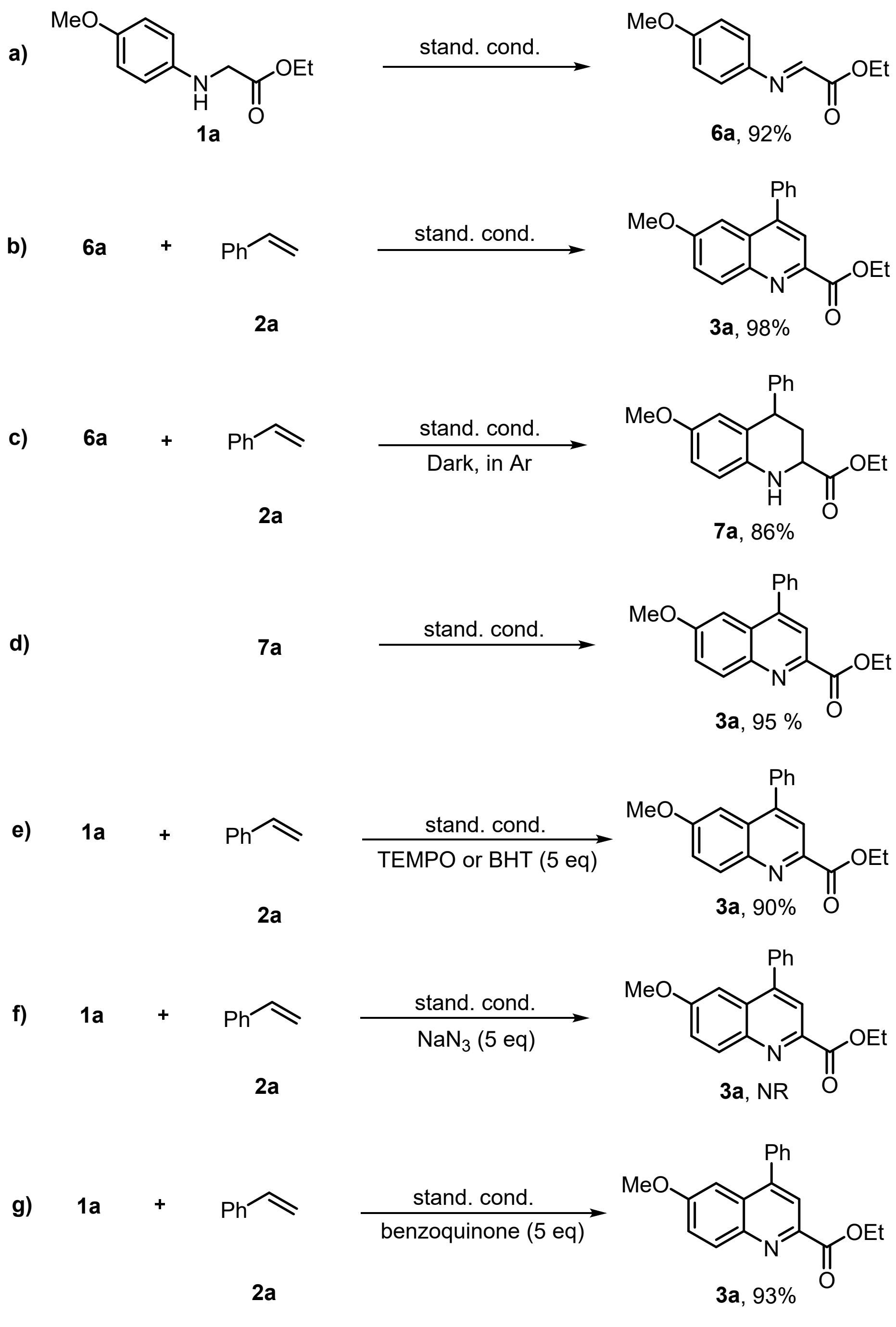


Fig. S4. The UV-Vis spectrum of **1a**, Ce(OTf)$_3$ and **1a** + Ce(OTf)$_3$ in CH_3CN.

3.2 Control experiments



Scheme S3 Control experiments.

3.3 EPR spectra

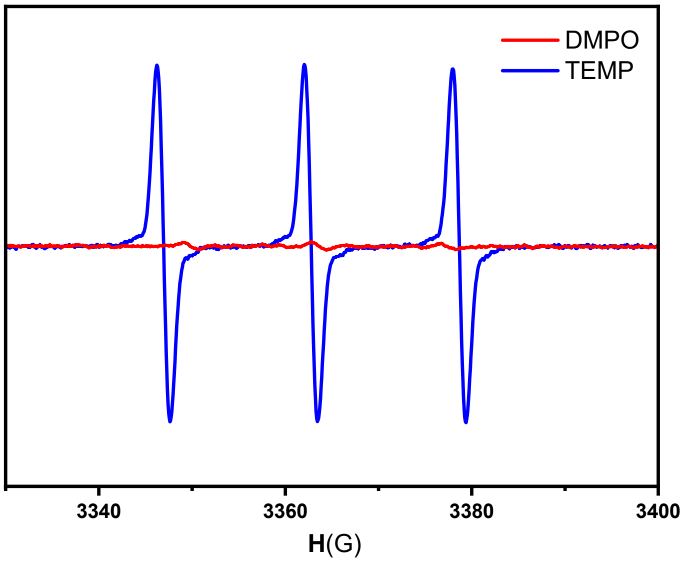


Fig. S5. EPR spectra of **1a** (0.05 mol/L), $Ce(OTf)_3$ (0.015 mol/L) and DMPO (red) or TEMP (blue) in air-saturated CH_3CN upon irradiation with blue LED for 10 min.

3.4 Quantum yield determination

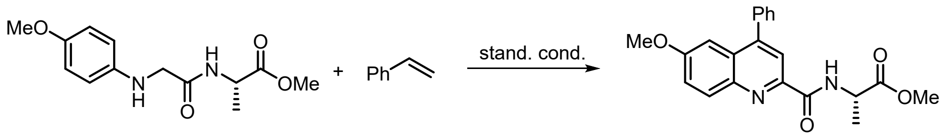
To a solution of **1a** (0.2 mmol, 1 eq) and $Ce(OTf)_3$ (30 mol%) in dry CH_3CN (4.0 mL) were added **2a** (1.0 mmol, 5 eq). The mixed solution was irradiated with 30 W blue LED under air atmosphere at room temperature for 8 h. The yield of product **3a** was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. The quantum yield is calcd using the following equation：

$$\phi = \frac{n\ of\ 3a}{flux * S * t}$$

Where, Φ is quantum yield, S (m^2) is the irradiation area and t (s) is the photoreaction time. Experiment: the unit photon flux was 357 $\mu mol \cdot s^{-1} \cdot m^{-2}$, the irradiation area was 1.66×10^{-3} m^2, and the product yield was 41% after 8 h.

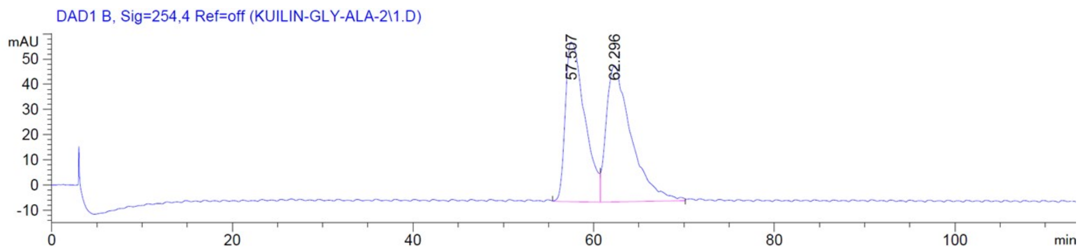
Quantum yield: 0.0048

3.5 Enantiomeric purity study of product 3o



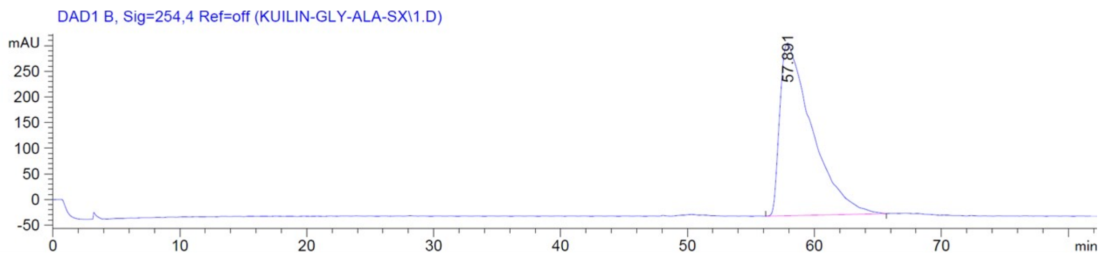
Scheme S4 Enantiomeric purity study of product **3o**. The high ee value of product **3o** indicates that our reaction maintains the enantiomeric purity of the derived alanine.

Racemic product



	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	57.507	MM	2.4880	9463.74609	63.39716	47.5469
2	62.296	MM	3.2139	1.04403e4	54.14102	52.4531

Chiral product



	Retention Time/min	Int Type	Width/min	Area/mAU	Height/mAU	Area/%
1	57.891	BB	2.3037	5.95935e4	336.89441	100.0000

4. Computational Study

4.1 Computational methods

All calculations were carried out with the Gaussian 09 D.01programs.[3] Ground state geometry were fully optimized by using density functional theory (DFT)[4] and the B3LYP[5] method with the 6-31G* basic set for C, H, O and N. For Ce atom, MWB28 basic set was used. Frequency calculations have been performed to verify the optimized structures as local minima and to obtain zero-point energy (ZPE) at 298 K. The 3D molecular structures were generated using the CYL-View.[6] Using this geometry, single point time dependent density functional theory (TD-DFT) calculation was then performed with the CAM-B3LYP/(6-31G*, MWB28) level of theory. The effect of solvent is considered from Truhlar and co-workers' universal solvation model (SMD-CH_3CN).[7,8] The first 10 excited states of the complex B is reported below.

4.2 Optimized structure and binding energy of 1a-Ce(III) complex

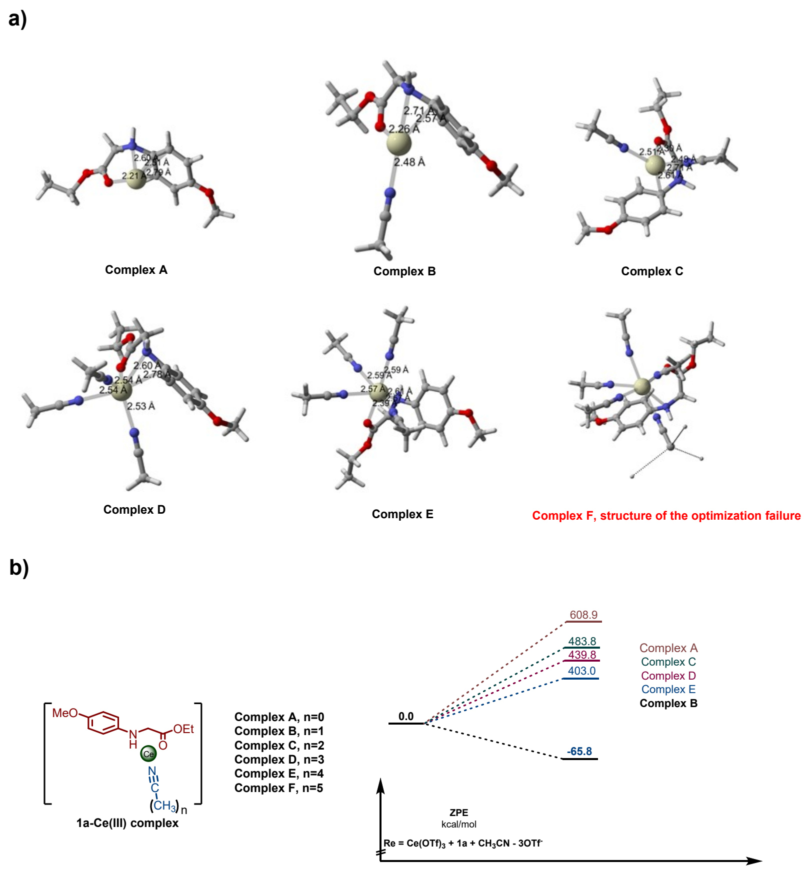


Fig. S6. a) Optimized structure and b) formation energy of **1a**-Ce(III) complex.

The formation energy shows that only ***complex B (5a)*** with one CH_3CN molecule coordination has a favorable formation energy is -65.8 kcal/mol. For complexes with other quantities of CH_3CN molecule coordination (0, 2, 3 and 4) have very unfavorable formation energies (608.9 kcal/mol, 483.8 kcal/mol, 439.8 kcal/mol and 403.0 kcal/mol). Therefore, we speculate that ***complex B (5a)*** may be the structure of **1a**-Ce(III) complex.

4.3 UV-Vis spectra predicted by TD-DFT of 1a-Ce(III) complex

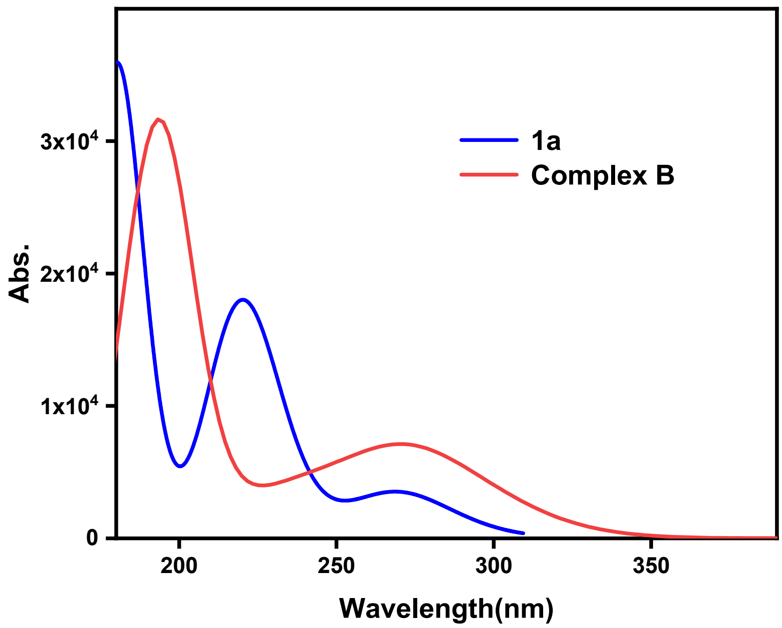


Fig. S7. UV-Vis absorption spectra predicted by TD-DFT.

4.4 Mulliken spin population analysis

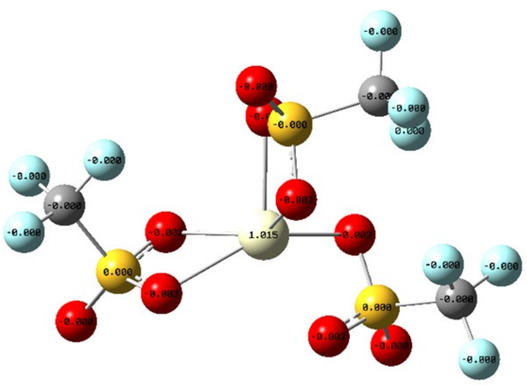


Fig. S8. Mulliken spin population analysis of $Ce(OTf)_3$: Ce=1.015.

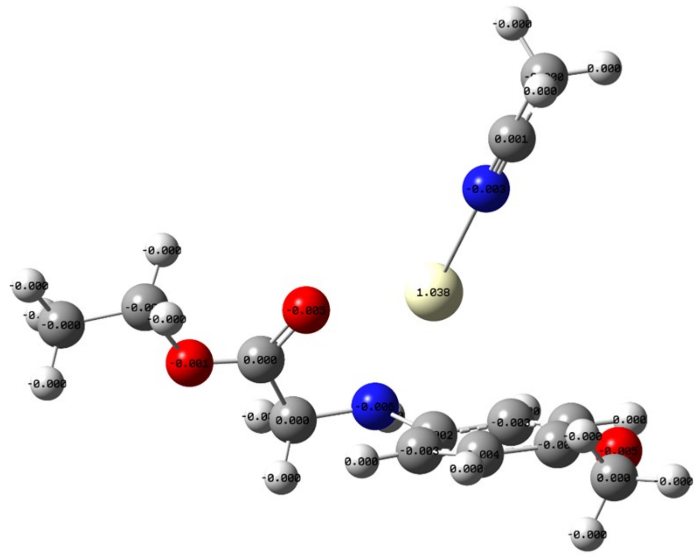


Fig. S9. Mulliken spin population analysis of complex B: Ce=1.038.

4.5 Excited state of Complex B

Complex B

Excited State 1: 2.001-A 0.2281 eV 5436.33 nm f=0.0000 <S**2>=0.751

80A -> 82A -0.15459

80A -> 83A 0.13349

80A -> 87A -0.20460

80A -> 88A -0.29170

80A -> 89A -0.70555

80A -> 90A 0.90412

80A <- 87A -0.12344

80A <- 88A -0.17105

80A <- 89A -0.41058

80A <- 90A 0.53746

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-DFT) = -1315.79091250

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: 2.001-A 0.2550 eV 4862.30 nm f=0.0000 <S**2>=0.751

80A -> 82A 0.25183

80A -> 83A 0.21106

80A -> 85A 0.27470

80A -> 86A 0.18890

80A -> 88A -0.10495

80A -> 89A -0.62074

80A -> 90A -0.52942

80A -> 91A 0.68683

80A <- 82A 0.13692

80A <- 83A 0.10110

80A <- 85A 0.10492

80A <- 86A 0.13002

80A <- 89A -0.33191

80A <- 90A -0.29375

80A <- 91A 0.38241

Excited State 3: 2.001-A 0.3345 eV 3706.41 nm f=0.0000 <S**2>=0.751

80A -> 83A -0.27781

80A -> 84A -0.15518

80A -> 85A 0.14013

80A -> 86A 0.21675

80A -> 87A 0.23960

80A -> 88A 0.66728

80A -> 89A -0.46845

80A -> 91A -0.35734

80A -> 93A -0.46999

80A <- 87A 0.10721

80A <- 88A 0.33336

80A <- 89A -0.23908

80A <- 91A -0.18617

80A <- 93A -0.21181

Excited State 4: 2.001-A 0.6678 eV 1856.71 nm f=0.0000 <S**2>=0.751

80A -> 84A 0.36250 80A -> 85A 0.84949

80A -> 86A -0.22799

80A -> 87A -0.21548

80A -> 89A 0.11216

80A -> 92A 0.10732

80A <- 85A -0.12735

Excited State 5: 2.001-A 0.6840 eV 1812.55 nm f=0.0000 <S**2>=0.751

80A -> 82A 0.30675

80A -> 83A -0.20094

80A -> 84A 0.56264

80A -> 85A -0.31245

80A -> 86A 0.35679

80A -> 87A -0.50964

80A -> 88A 0.16394

80A -> 92A 0.15515

Excited State 6: 2.000-A 0.7438 eV 1666.87 nm f=0.0000 <S**2>=0.750

80A -> 82A -0.10017

80A -> 83A -0.54989

80A -> 84A -0.26387

80A -> 85A 0.19567

80A -> 86A 0.55575

80A -> 88A -0.37142

80A -> 89A 0.21510

80A -> 90A 0.13013

80A -> 91A 0.21576

80A -> 93A -0.13623

Excited State 7: 3.460-A 3.1641 eV 391.84 nm f=0.0000 <S**2>=2.743

79A -> 82A -0.25997

81A -> 83A 0.49132

81A -> 84A 0.20129

81A -> 86A 0.12359

81A -> 88A -0.23018

81A -> 91A -0.10030

81A -> 93A -0.20719

79B -> 81B 0.26829

80B -> 82B -0.46811

80B -> 83B -0.26125

80B -> 84B 0.13617

80B -> 85B 0.18829

80B -> 92B -0.16172

Excited State 8: 3.452-A 3.2792 eV 378.09 nm f=0.0000 <S**2>=2.730

81A -> 82A 0.68533

81A -> 92A -0.14900

80B -> 81B -0.66929

Excited State 9: 2.037-A 4.1219 eV 300.79 nm f=0.0232 80A -> 82A 0.53062

80A -> 83A -0.10036

80A -> 84A -0.19773

80A -> 86A -0.15746

80A -> 90A 0.16499

80A -> 92A 0.18013

80A -> 94A 0.12216

80A -> 96A -0.14386

80A -> 97A 0.18241

81A -> 82A -0.47374

80B -> 81B -0.47443

Excited State 10: 2.029-A 4.1964 eV 295.45 nm f=0.0257 <S**2>=0.779

80A -> 82A 0.50445

80A -> 83A -0.15815

80A -> 84A -0.17913

80A -> 86A -0.21724

80A -> 90A 0.12940

80A -> 92A 0.17757

80A -> 94A 0.11575

80A -> 96A -0.12681

80A -> 97A 0.17207

81A -> 82A 0.47589

80B -> 81B 0.47676

4.6 The Cartesian coordinates of 1a-Ce(III) complex

Complex A

3 2

C	3.18148100	0.63565100	0.21631600
C	3.03876400	-0.63726700	0.86330100
C	1.84601400	-0.99747300	1.47986500
C	0.72165400	-0.11767500	1.47771800
C	0.84348900	1.12530300	0.82102200
C	2.03496800	1.48652100	0.16887100
H	3.90626200	-1.29273400	0.90346400
H	1.78861900	-1.95778400	1.99548000
H	0.02160500	1.83671400	0.80624500
H	2.09781400	2.46221100	-0.30362400
N	-0.55856700	-0.73131400	1.69433600
H	-0.51367800	-1.46987100	2.40055100
O	4.35658300	0.89810100	-0.27088100
C	4.71409800	2.19501800	-0.85955300
H	5.77191900	2.10067500	-1.09633000
H	4.13093800	2.35713300	-1.76966200
H	4.55428000	2.98386900	-0.12073500
C	-1.80044800	0.06693700	1.84724000
H	-1.63295600	1.01120300	2.38131500
H	-2.51448700	-0.50558800	2.44939000
C	-2.42841400	0.34538800	0.48441500

O	-1.77745400	-0.02053200	-0.57333800
O	-3.54079000	0.92105500	0.48885200
C	-4.40656000	1.28980300	-0.75635500
H	-4.17715100	2.34944000	-0.87892500
H	-4.00743100	0.69516800	-1.57794100
C	-5.83914000	1.00939700	-0.39771800
H	-6.16158200	1.58669800	0.47246300
H	-6.44716800	1.33106000	-1.25350500
H	-6.02802500	-0.05494300	-0.23586800
Ce	0.16170400	-1.05366700	-0.78035300

Complex B

3 2

C	2.67313300	-1.69360900	0.53522000
C	2.55535600	-1.75145200	-0.88802300
C	1.31179400	-1.87994700	-1.49863400
C	0.11664000	-1.94564200	-0.72573500
C	0.22430200	-1.85209300	0.67526700
C	1.47545200	-1.70774600	1.30018900
H	3.46729300	-1.74732800	-1.47999500
H	1.26391800	-1.96565300	-2.58526500
H	-0.65535700	-1.90723400	1.31030900
H	1.51659000	-1.67488700	2.38401700
N	-1.10153400	-1.65975700	-1.41525100

H	-1.12365700	-2.07320300	-2.34842600
O	3.89218900	-1.63734800	1.00840500
C	4.17417300	-1.72993600	2.43738800
H	5.26031700	-1.73616800	2.50341900
H	3.76710700	-0.85738200	2.95597400
H	3.76491700	-2.66250000	2.83416600
C	-2.41511300	-1.77618700	-0.75100700
H	-2.47751900	-2.63447600	-0.06918100
H	-3.18239200	-1.93708100	-1.51574200
C	-2.75915300	-0.49715700	0.00650400
O	-1.89502800	0.44636500	0.08495300
O	-3.91102700	-0.46516500	0.52203000
C	-4.47346800	0.73029400	1.30905900
H	-3.85505300	0.78124500	2.20713400
H	-4.30229400	1.59767800	0.66942600
C	-5.92439300	0.43447000	1.57663600
H	-6.05037600	-0.46863900	2.17924800
H	-6.33195700	1.27842700	2.14599000
H	-6.49899700	0.34600400	0.65107700
Ce	0.19438900	0.62372400	-0.75525200
C	2.63374300	4.92205600	0.48724900
H	2.84552100	4.96313000	1.56352200
H	3.57819400	4.96339100	-0.07078400
H	2.01367600	5.78451200	0.20932200

C	1.93281100	3.69630600	0.17229200
N	1.37078500	2.70650100	-0.08204800

Complex C

3 2

C	3.03319000	1.67937000	0.55199200
C	2.83223000	0.73029000	1.59458600
C	1.57100300	0.53475400	2.14924300
C	0.44632200	1.26822600	1.68260400
C	0.63325400	2.17502500	0.62377800
C	1.90344700	2.37921800	0.06199300
H	3.69884700	0.20341900	1.98415100
H	1.46167600	-0.15907900	2.98283300
H	-0.19414500	2.76336600	0.23750200
H	2.01358800	3.11891500	-0.72342500
N	-0.84477100	0.77373400	2.05474200
H	-0.86124000	0.44199500	3.01840500
O	4.27385000	1.82362500	0.13577600
C	4.63793700	2.86341600	-0.81118000
H	5.71945400	2.78806100	-0.90607900
H	4.16142500	2.67833400	-1.77855900
H	4.36259600	3.84412400	-0.41380400
C	-2.07473300	1.51080200	1.72399300
H	-1.95714800	2.60031900	1.78646800

H	-2.85192000	1.24606200	2.44825400
C	-2.57509600	1.13295500	0.33347100
O	-1.89989300	0.34248400	-0.39848900
O	-3.67811100	1.66726900	-0.00018400
C	-4.35418800	1.40639500	-1.33748100
H	-3.64788000	1.75903900	-2.09166400
H	-4.46796500	0.32251800	-1.39990600
C	-5.66019000	2.15821800	-1.32575300
H	-5.50548500	3.23516600	-1.22035200
H	-6.15832100	1.98068600	-2.28562300
H	-6.32274400	1.80368600	-0.53191200
Ce	0.11816900	-0.69349300	-0.01316600
C	-0.49776700	-5.28957600	2.12162300
H	-1.45059800	-5.71742400	1.78567600
H	-0.49624000	-5.22895200	3.21704500
H	0.32409500	-5.93932700	1.79590100
C	-0.32926700	-3.96625600	1.55608600
N	-0.19355300	-2.90231400	1.10224700
C	1.45379600	-2.11677700	-4.75148100
H	1.44817400	-1.26000800	-5.43636300
H	2.45558600	-2.56358600	-4.74070500
H	0.73048700	-2.86279900	-5.10303700
C	1.09726700	-1.68023700	-3.41609600
N	0.81175000	-1.33054300	-2.34303100

Complex D

3 2

C	-3.89703700	0.33124900	-0.27455200
C	-3.28119600	-0.64107200	-1.09929200
C	-2.02786100	-0.40892600	-1.65014200
C	-1.34354600	0.80451100	-1.39176200
C	-1.93092700	1.74928300	-0.53575200
C	-3.19746900	1.52209100	0.00817600
H	-3.83458200	-1.54517200	-1.33232800
H	-1.62187200	-1.12681800	-2.36275600
H	-1.44795100	2.69829400	-0.32417500
H	-3.64356300	2.28944900	0.62993600
N	-0.01964700	0.95067700	-1.96985200
H	-0.01608600	0.58725300	-2.92336900
O	-5.10926000	0.02451000	0.17269700
C	-5.90288300	1.00809400	0.87328800
H	-6.86254700	0.52556400	1.05035000
H	-5.43638100	1.27196800	1.82806500
H	-6.04252800	1.89722400	0.25135800
C	0.62726700	2.27668800	-1.94526900
H	-0.06791700	3.09992700	-2.14598800
H	1.38908500	2.30987900	-2.73250500
C	1.32723900	2.49258500	-0.61256900

O	1.43548500	1.53744800	0.20786000
O	1.78321400	3.67053200	-0.43105200
C	2.55762500	4.04970500	0.80981200
H	1.88052500	3.87276200	1.64801600
H	3.40095900	3.35783000	0.85683900
C	2.96595200	5.49332800	0.65405700
H	2.09647500	6.15095600	0.57282900
H	3.52921600	5.78578600	1.54704400
H	3.61270800	5.63657900	-0.21554600
Ce	0.58045700	-0.63363400	0.00262400
C	1.52762900	-4.38122000	-3.39935500
H	2.56395300	-4.30391600	-3.74911100
H	0.85307200	-4.33227700	-4.26242700
H	1.38966000	-5.34286400	-2.89090300
C	1.23549700	-3.29462500	-2.48239600
N	0.99932200	-2.42290200	-1.74948900
C	-2.17872400	-2.31711700	3.99762700
H	-2.29175500	-1.53209400	4.75456400
H	-3.17070500	-2.65638200	3.67714900
H	-1.63583100	-3.16255300	4.43638500
C	-1.44382000	-1.79944600	2.85806300
N	-0.85506200	-1.38545800	1.94516800
C	4.87975800	-2.26183700	2.33387900
H	5.04870700	-1.66107800	3.23523200

H	5.73619700	-2.14581700	1.65935400
H	4.78602100	-3.31660800	2.61760000
C	3.66674600	-1.82085000	1.66946900
N	2.69504200	-1.46827000	1.13795500

Complex E

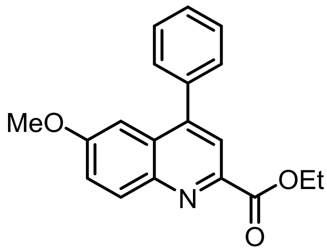
3 2

C	4.06068400	-0.18174500	-0.67930100
C	3.28715800	0.78835100	-1.35501700
C	1.99623000	0.49360000	-1.77219900
C	1.43369500	-0.77991500	-1.52198600
C	2.18399300	-1.72914400	-0.81284900
C	3.48635200	-1.43880800	-0.40479200
H	3.74513800	1.74468300	-1.58476500
H	1.45952100	1.22041500	-2.38334300
H	1.79390900	-2.72189900	-0.61180300
H	4.05747600	-2.20645900	0.10398000
N	0.07614000	-0.99951800	-1.98407100
H	-0.03571100	-0.61425000	-2.92194700
O	5.29782200	0.18903800	-0.35165500
C	6.23094600	-0.77794900	0.17038400
H	7.17261000	-0.24102500	0.27300200
H	5.90472700	-1.14456300	1.14965100
H	6.35262700	-1.61015400	-0.52971100

C	-0.47092900	-2.36695200	-1.95111500
H	0.25362800	-3.12961900	-2.25763200
H	-1.30698300	-2.42440500	-2.65692100
C	-1.01692100	-2.68331400	-0.56698300
O	-1.16492700	-1.77263200	0.28480400
O	-1.31470800	-3.91828400	-0.38805900
C	-1.92516100	-4.39513000	0.89824000
H	-1.21304700	-4.13946000	1.68582500
H	-2.84385000	-3.81954900	1.03038000
C	-2.16013500	-5.87964600	0.75713200
H	-1.22394500	-6.42011900	0.59365000
H	-2.60644000	-6.24784300	1.68709700
H	-2.85138200	-6.09991800	-0.06071700
Ce	-0.57819300	0.53314600	0.03094600
C	0.27896100	5.59250700	-0.86173500
H	0.31840000	5.80320700	-1.93645300
H	1.22925800	5.88945200	-0.40399700
H	-0.53240000	6.17580300	-0.41206300
C	0.04744800	4.17396000	-0.64404400
N	-0.13568300	3.04007600	-0.47205900
C	-4.10361800	1.49698300	3.70188100
H	-3.89500800	0.87225200	4.57762300
H	-4.07140900	2.55152800	3.99794100
H	-5.10513600	1.26106400	3.32517000

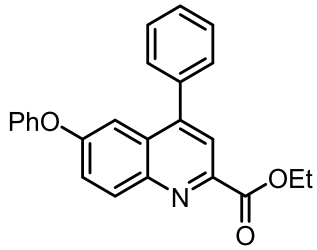
C	-3.11394100	1.24358300	2.66786300
N	-2.32333400	1.04167800	1.84223000
C	-4.64650800	1.55492800	-3.04831300
H	-5.37784400	0.74052800	-2.99583700
H	-4.33394400	1.68819700	-4.09016500
H	-5.11596400	2.47987900	-2.69519300
C	-3.49313200	1.23849200	-2.22101600
N	-2.57109100	0.98385900	-1.56255800
C	2.57315000	0.87285800	4.13354900
H	2.09346900	1.52524400	4.87172100
H	3.53798200	1.30667000	3.84836400
H	2.73976400	-0.11245100	4.58300000
C	1.72293800	0.74440400	2.96131600
N	1.04211400	0.64289800	2.02666900

5. Product Data



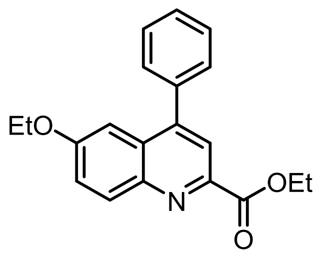
3a

***Ethyl 6-methoxy-4-phenylquinoline-2-carboxylate* (3a).**[9] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). White solid, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 9.3 Hz,1H), 8.10 (s, 1H), 7.61-7.47 (m, 5H), 7.44 (dd, J = 9.3, 2.8 Hz, 1H), 7.22 (d, J = 2.7 Hz, 1H), 4.56 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 1.49 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 159.5, 148.0, 145.4, 144.3, 137.9, 132.7, 129.3, 129.2, 128.8, 128.6, 122.8, 121.8, 103.3, 62.1, 55.5, 14.4.



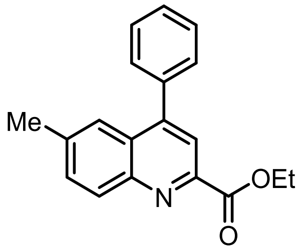
3b

***Ethyl 6-phenoxy-4-phenylquinoline-2-carboxylate* (3b).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). White solid, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 9.0 Hz, 1H), 8.11 (s, 1H), 7.54-7.38 (m, 7H), 7.36-7.28 (m, 2H), 7.15-7.05 (m, 1H), 7.05-6.93 (m, 2H), 4.54 (q, J = 7.1 Hz, 2H), 1.46 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 157.2, 156.0, 148.6, 146.5, 145.0, 137.3, 133.1, 129.9, 129.3, 128.9, 128.7, 128.7, 124.2, 123.2, 121.7, 119.4, 111.4, 62.2, 14.4. HRMS (ESI) calcd for $C_{24}H_{20}NO_3$ (M+H$^+$) 370.1438, found 370.1434.



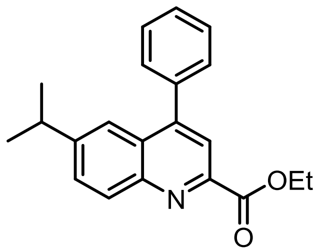
3c

***Ethyl 6-ethoxy-4-phenylquinoline-2-carboxylate* (3c).**[10] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). White solid, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 9.3 Hz, 1H), 8.09 (s, 1H), 7.59-7.48 (m, 5H), 7.43 (dd, *J* = 9.3, 2.8 Hz, 1H), 7.20 (d, *J* = 2.8 Hz, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 4.01 (q, *J* = 7.0 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H), 1.42 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 158.8, 147.9, 145.2, 144.2, 137.9, 132.6, 129.3, 129.1, 128.7, 128.5, 122.9, 121.7, 103.9, 63.7, 62.0, 14.5, 14.3.



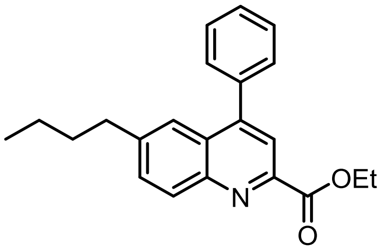
3d

***Ethyl 6-methyl-4-phenylquinoline-2-carboxylate* (3d).**[9] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). White solid, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.7 Hz, 1H), 8.08 (s, 1H), 7.69 (s, 1H), 7.59 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.56-7.45 (m, 5H), 4.54 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 149.0, 147.0, 146.9, 139.0, 137.8, 132.4, 130.9, 129.6, 128.7, 128.6, 127.8, 124.4, 121.5, 62.2, 22.1, 14.5.



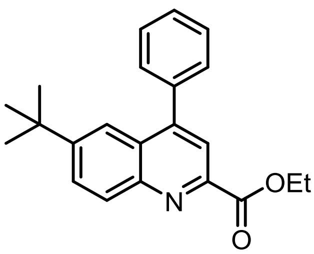
3e

***Ethyl 6-isopropyl-4-phenylquinoline-2-carboxylate* (3e).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). White solid, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.7 Hz, 1H), 8.12 (s, 1H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.71 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.58-7.46 (m, 5H), 4.56 (q, *J* = 7.1 Hz, 2H), 3.04 (p, *J* = 6.9 Hz, 1H), 1.48 (t, *J* = 7.1 Hz, 3H), 1.28 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.44, 149.34, 149.01, 147.00, 146.79, 137.61, 130.95, 129.46, 129.36, 128.48, 128.44, 127.59, 121.67, 121.21, 61.97, 34.29, 23.53, 14.23. HRMS (ESI) calcd for $C_{21}H_{22}NO_2$ $(M+H^+)$ 320.1645, found 320.1643.



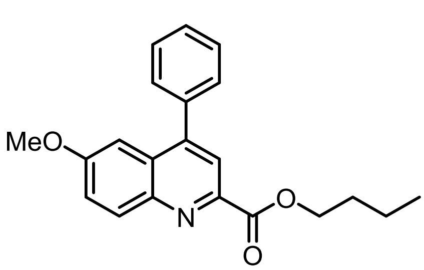
3f

Ethyl 6-butyl-4-phenylquinoline-2-carboxylate **(3f).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). White solid, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.7 Hz, 1H), 8.10 (s, 1H), 7.70 (d, *J* = 1.9 Hz, 1H), 7.64 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.58-7.49 (m, 5H), 4.56 (q, *J* = 7.1 Hz, 2H), 2.80–2.68 (m, 2H), 1.67–1.58 (m, 2H), 1.48 (t, *J* = 7.1 Hz, 3H), 1.40-1.31 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 149.2, 147.2, 147.0, 144.0, 138.0, 131.7, 131.1, 129.7, 128.8, 128.7, 127.9, 123.9, 121.5, 62.3, 36.1, 33.4, 22.5, 14.5, 14.0. HRMS (ESI) calcd for $C_{22}H_{24}NO_2$ (M+H$^+$) 334.1802, found 334.1801.



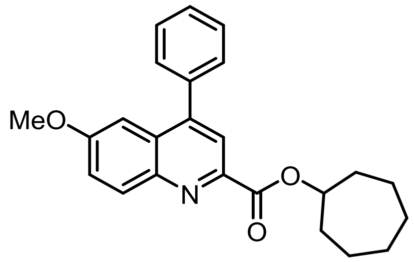
3g

Ethyl 6-(tert-butyl)-4-phenylquinoline-2-carboxylate **(3g).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). White solid, 81% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.9 Hz, 1H), 8.11 (s, 1H), 7.94–7.85 (m, 2H), 7.60–7.48 (m, 5H), 4.56 (q, *J* = 7.1 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 151.8, 149.6, 147.2, 146.9, 137.9, 130.8, 129.7, 129.1, 128.8, 127.5, 121.5, 120.6, 62.3, 35.4, 31.1, 14.5. HRMS (ESI) calcd for $C_{22}H_{24}NO_2$ (M+H$^+$) 334.1802, found 334.1800.



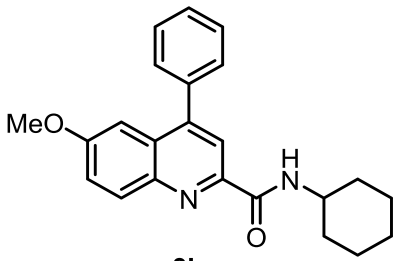
3h

Benzyl 6-methoxy-4-phenylquinoline-2-carboxylate **(3h).**[11] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). White solid, 97% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 9.2 Hz, 1H), 8.07 (s, 1H), 7.58 – 7.47 (m, 5H), 7.43 (ddd, *J* = 9.3, 2.9, 1.3 Hz, 1H), 7.21 (d, *J* = 2.7 Hz, 1H), 4.48 (t, *J* = 6.9 Hz, 2H), 3.79 (s, 3H), 1.90-1.77 (m, 2H), 1.56-1.42 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 159.4, 147.9, 145.2, 144.2, 137.8, 132.6, 129.2, 129.0, 128.7, 128.5, 122.7, 121.6, 103.1, 65.8, 55.4, 30.6, 19.1, 13.7.



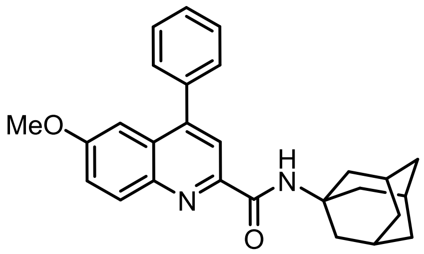
3i

Cycloheptyl 6-methoxy-4-phenylquinoline-2-carboxylate **(3i).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). Colorless oily liquid, 90% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 9.3 Hz, 1H), 8.02 (s, 1H), 7.58-7.47 (m, 5H), 7.41 (dd, *J* = 9.3, 2.8 Hz, 1H), 7.18 (d, *J* = 2.8 Hz, 1H), 5.33-5.27 (m, 1H), 3.79 (s, 3H), 2.15-2.07 (m, 2H), 1.94-1.85 (m, 2H), 1.79-1.69 (m, 2H), 1.66-1.46 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 159.5, 148.0, 146.0, 144.5, 138.2, 133.0, 129.4, 129.1, 128.9, 128.7, 122.7, 121.8, 103.3, 77.2, 55.6, 33.9, 28.3, 23.1. HRMS (ESI) calcd for $C_{24}H_{26}NO_3$ (M+H$^+$) 376.1907, found 376.1907.



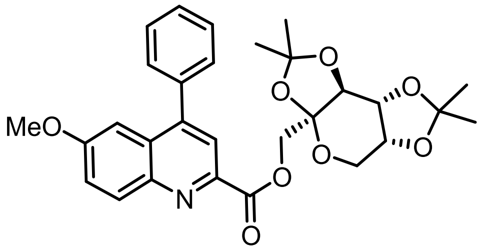
3j

N-cyclohexyl-6-methoxy-4-phenylquinoline-2-carboxamide **(3j).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). White solid, 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.15 (d, *J* = 8.6 Hz, 1H), 8.07 (d, *J* = 9.2 Hz, 1H), 7.58-7.45 (m, 5H), 7.41 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.23 (d, *J* = 2.8 Hz, 1H), 4.14-3.95 (m, 1H), 3.80 (s, 3H), 2.13-2.03 (m, 2H), 1.84-1.78 (m, 2H), 1.74-1.64 (m, 1H), 1.54-1.34 (m, 4H), 1.33-1.24 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9, 159.0, 148.4, 147.6, 143.3, 138.3, 131.7, 129.5, 129.0, 128.8, 128.6, 122.7, 119.7, 103.7, 55.6, 48.4, 33.3, 25.8, 25.1. HRMS (ESI) calcd for $C_{23}H_{25}N_2O_2$ ($M+H^+$) 361.1911, found 361.1907.



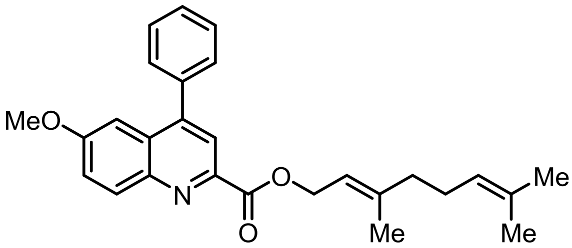
3k

***N-((3s,5s,7s)-adamantan-1-yl)-6-methoxy-4-phenylquinoline-2-carboxamide* (3k).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). White solid, 30% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.09 (s, 1H), 8.05 (d, J = 9.2 Hz, 1H), 7.55-7.46 (m, 5H), 7.40 (dd, J = 9.3, 2.8 Hz, 1H), 7.23 (d, J = 2.8 Hz, 1H), 3.80 (s, 3H), 2.23 (d, J = 2.8 Hz, 6H), 2.18-2.14 (m, 3H), 1.83-1.67 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 159.0, 148.4, 148.3, 143.1, 138.4, 131.6, 129.5, 128.9, 128.8, 128.6, 122.6, 119.3, 103.7, 55.6, 51.8, 41.7, 36.6, 29.7. HRMS (ESI) calcd for $C_{27}H_{29}N_2O_2$ ($M+H^+$) 413.2224, found 413.2222.



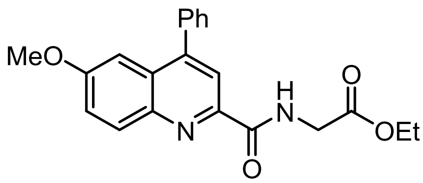
3l

***((3aS,5aR,8aR,8bS)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methyl 6-methoxy-4-phenylquinoline-2-carboxylate* (3l).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). White solid, 48% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 9.3 Hz, 1H), 8.09 (s, 1H), 7.56-7.47 (m, 5H), 7.41 (dd, J = 9.2, 2.8 Hz, 1H), 7.20 (d, J = 2.8 Hz, 1H), 4.78 (d, J = 11.7 Hz, 1H), 4.67-4.57 (m, 2H), 4.43 (d, J = 11.7 Hz, 1H), 4.27-4.25 (m, 1H), 3.98-3.95 (m, 1H), 3.83-3.77 (m, 4H), 1.55 (d, J = 2.9 Hz, 6H), 1.44 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 159.7, 148.0, 144.9, 144.5, 137.9, 132.8, 129.4, 129.3, 128.9, 128.8, 123.0, 121.9, 109.3, 109.2, 103.3, 101.9, 71.0, 70.5, 70.2, 65.9, 61.5, 55.6, 26.7, 26.0, 25.6, 24.2. HRMS (ESI) calcd for $C_{29}H_{32}NO_8$ ($M+H^+$) 522.2122, found 522.2123.



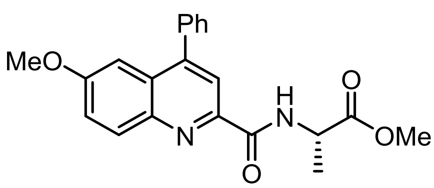
3m

***(E)-3,7-dimethylocta-2,6-dien-1-yl 6-methoxy-4-phenylquinoline-2-carboxylate* (3m).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). White solid, 40% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.27 (d, J = 9.3 Hz, 1H), 8.09 (s, 1H), 7.58-7.48 (m, 5H), 7.43 (dd, J = 9.2, 2.8 Hz, 1H), 7.21 (d, J = 2.8 Hz, 1H), 5.57-5.53 (m, 1H), 5.11-5.07 (m, 1H), 5.01 (d, J = 7.1 Hz, 2H), 3.80 (s, 3H), 2.15-2.03 (m, 4H), 1.79 (d, J = 1.3 Hz, 3H), 1.66 (d, J = 1.4 Hz, 3H), 1.59 (d, J = 1.3 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 165.8, 159.6, 148.1, 145.6, 144.5, 142.6, 138.1, 132.9, 132.0, 129.5, 129.3, 128.9, 128.8, 123.9, 122.9, 122.0, 118.4, 103.4, 63.2, 55.7, 39.8, 26.4, 25.8, 17.8, 16.8. HRMS (ESI) calcd for $C_{27}H_{29}NO_3H$ (M+H$^+$) 416.2220, found 416.2214.



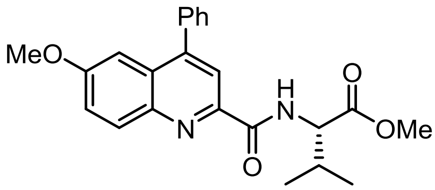
3n

***Ethyl (6-methoxy-4-phenylquinoline-2-carbonyl)glycinate* (3n).**[9] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 4/1 to 2/1 as eluent). Pale yellow solid, 62% yield. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.69 (t, J = 5.7 Hz, 1H), 8.18 (s, 1H), 8.06 (d, J = 9.2 Hz, 1H), 7.55-7.45 (m, 5H), 7.39 (dd, J = 9.2, 2.8 Hz, 1H), 7.21 (d, J = 2.8 Hz, 1H), 4.32 (d, J = 5.7 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.0, 165.2, 159.2, 148.3, 146.5, 143.3, 138.1, 131.8, 129.4, 129.1, 128.8, 128.6, 122.8, 119.5, 103.5, 61.6, 55.6, 41.6, 14.3.



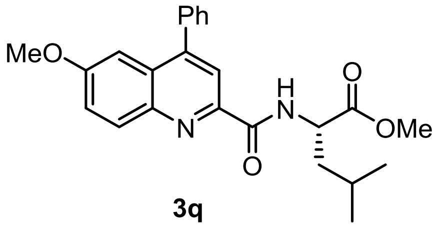
3o

***Methyl (6-methoxy-4-phenylquinoline-2-carbonyl)-L-alaninate* (3o).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 4/1 to 2/1 as eluent). Pale yellow solid, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 8.0 Hz, 1H), 8.19 (s, 1H), 8.11 (d, *J* = 9.3 Hz, 1H), 7.57 – 7.48 (m, 5H), 7.43 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.24 (d, *J* = 2.8 Hz, 1H), 4.88 (p, *J* = 7.3 Hz, 1H), 3.81 (s, 6H), 1.62 (d, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.57, 164.55, 159.20, 148.42, 146.61, 143.37, 138.18, 131.89, 129.48, 129.22, 128.85, 128.68, 122.85, 119.64, 103.58, 55.66, 52.67, 48.32, 18.70. HRMS (ESI) calcd for $C_{21}H_{21}N_2O_4$ (M+H$^+$) 365.1496, found 365.1495.



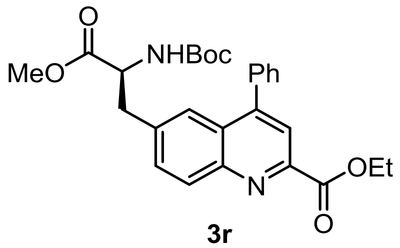
3p

***Methyl (6-methoxy-4-phenylquinoline-2-carbonyl)-L-valinate* (3p).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 4/1 to 2/1 as eluent). Pale yellow solid, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 9.3 Hz, 1H), 8.19 (s, 1H), 8.12 (d, *J* = 9.2 Hz, 1H), 7.55–7.46 (m, 5H), 7.42 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.23 (d, *J* = 2.8 Hz, 1H), 4.81 (dd, *J* = 9.3, 5.3 Hz, 1H), 3.79 (s, 6H), 2.40-2.33 (m, 1H), 1.07 (dd, *J* = 6.9, 2.0 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 164.8, 159.2, 148.4, 146.7, 143.3, 138.2, 132.0, 129.4, 129.2, 128.8, 128.6, 122.7, 119.7, 103.5, 57.5, 55.6, 52.3, 31.7, 19.3, 18.1. HRMS (ESI) calcd for $C_{23}H_{24}N_2O_4$ (M+H$^+$) 393.1809, found 393.1806.



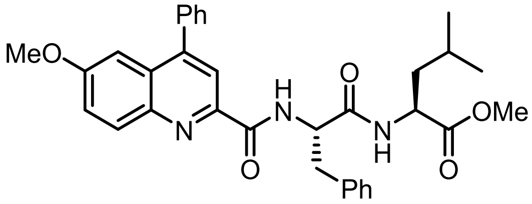
3q

***Methyl (6-methoxy-4-phenylquinoline-2-carbonyl)-L-leucinate* (3q).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 4/1 to 2/1 as eluent). Pale yellow solid, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.8 Hz, 1H), 8.19 (s, 1H), 8.11 (d, *J* = 9.2 Hz, 1H), 7.56–7.45 (m, 5H), 7.42 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.23 (d, *J* = 2.8 Hz, 1H), 4.94-4.89 (m, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 1.88–1.76 (m, 3H), 1.05–0.97 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 164.7, 159.2, 148.4, 146.6, 143.3, 138.2, 131.9, 129.4, 129.2, 128.8, 128.6, 122.8, 119.7, 103.6, 55.6, 52.4, 51.0, 41.9, 25.1, 23.1, 22.0. HRMS (ESI) calcd for $C_{24}H_{27}N_2O_4$ ($M+H^+$) 407.1965, found 407.1963.



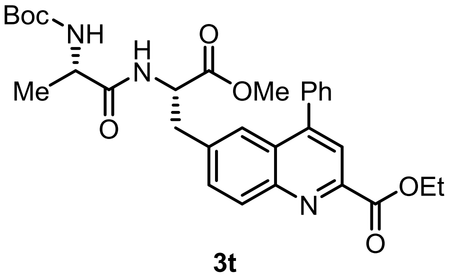
3r

***Ethyl (S)-6-(2-((tert-butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)-4-phenylquinoline-2-carboxylate* (3r).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 4/1 to 2/1 as eluent). Pale yellow solid, 60% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.7 Hz, 1H), 8.10 (s, 1H), 7.67 (d, *J* = 2.0 Hz, 1H), 7.61–7.47 (m, 6H), 4.98 (d, *J* = 8.2 Hz, 1H), 4.65-4.60 (m, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 3.60 (s, 3H), 3.03-3.14 (m, 2H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 165.6, 155.0, 149.4, 147.7, 147.5, 137.6, 137.1, 131.9, 131.4, 129.6, 128.9, 127.7, 125.8, 121.7, 80.1, 62.4, 54.3, 52.4, 38.7, 28.3, 14.5. HRMS (ESI) calcd for $C_{27}H_{31}N_2O_6$ ($M+H^+$) 479.2177, found 479.2176.



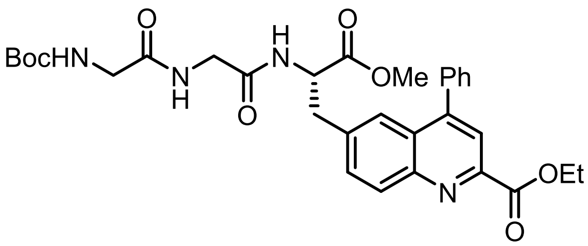
3s

***Methyl (6-methoxy-4-phenylquinoline-2-carbonyl)-L-phenylalanyl-L-leucinate* (3s).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 4/1 to 2/1 as eluent). Pale yellow solid, 60% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.80 (d, *J* = 8.6 Hz, 1H), 8.12 (s, 1H), 8.04 (d, *J* = 9.2 Hz, 1H), 7.55-7.44 (m, 5H), 7.39 (dd, *J* = 9.2, 2.8 Hz, 1H), 7.34-7.29 (m, 2H), 7.27 (s, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.19 (q, *J* = 2.4 Hz, 2H), 6.92 (d, *J* = 9.3 Hz, 1H), 5.07-5.06 m, 1H), 4.59-4.57 (m, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 3.37-3.22 (m, 2H), 1.61-1.41 (m, 3H), 0.81 (dd, *J* = 10.2, 5.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 170.8, 164.9, 159.2, 148.3, 146.3, 143.2, 138.0, 136.7, 131.8, 129.6, 129.4, 129.1, 128.7, 128.60, 128.57, 126.9, 122.8, 119.4, 103.5, 55.5, 54.5, 52.2, 51.0, 41.3, 38.3, 24.8, 22.7, 22.0; HRMS (ESI) calcd for $C_{33}H_{36}N_3O_5$ (M+H$^+$) 554.2650, found 554.2650.



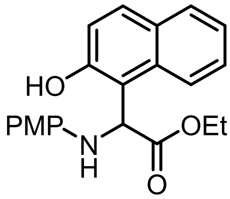
3t

***Ethyl 6-((S)-2-((S)-2-((tert-butoxycarbonyl)amino)propanamido)-3-methoxy-3-oxopropyl)-4-phenylquinoline-2-carboxylate* (3t).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 4/1 to 2/1 as eluent). White solid, 45% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.6 Hz, 1H), 8.07 (s, 1H), 7.61 (d, J = 1.9 Hz, 1H), 7.56–7.45 (m, 6H), 6.78 (d, J = 7.2 Hz, 1H), 4.85-4.80 (m, 2H), 4.51 (q, J = 7.1 Hz, 2H), 4.08-4.03 (m, 1H), 3.55 (s, 3H), 3.31 (dd, J = 14.0, 5.8 Hz, 1H), 3.18 (dd, J = 14.0, 5.9 Hz, 1H), 1.44 (t, J = 7.1 Hz, 3H), 1.29 (s, 9H), 1.16 (d, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 171.4, 165.4, 155.4, 149.4, 147.6, 147.4, 137.5, 137.0, 131.9, 131.3, 129.6, 128.9, 127.6, 125.6, 121.6, 80.2, 62.3, 53.1, 52.4, 50.1, 37.9, 28.2, 18.0, 14.4. HRMS (ESI) calcd for $C_{30}H_{35}N_3O_7Na$ (M+Na$^+$) 572.2367, found 572.2372.



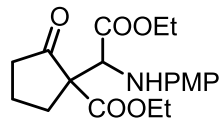
3u

***Ethyl (S)-6-(12-(methoxycarbonyl)-2,2-dimethyl-4,7,10-trioxo-3-oxa-5,8,11-triazatridecan-13-yl)-4-phenylquinoline-2-carboxylate* (3u).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 4/1 to 2/1 as eluent). White solid, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (t, J = 5.7 Hz, 1H), 8.21 (s, 1H), 8.11 (d, J = 8.6 Hz, 1H), 7.63 (d, J = 1.8 Hz, 1H), 7.58-7.46 (m, 6H), 6.59 (d, J = 7.5 Hz, 1H), 4.96 (s, 1H), 4.92-4.88 (m, 1H), 4.35-4.24 (m, 4H), 3.76-3.64 (m, 2H), 3.58 (s, 3H), 3.38-3.16 (m, 2H), 1.37 (s, 9H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 169.9, 169.2, 164.9, 156.0, 149.7, 148.7, 146.5, 137.7, 136.2, 131.8, 130.7, 129.7, 128.9, 127.8, 125.9, 119.4, 80.5, 61.7, 53.2, 52.5, 44.4, 41.7, 38.0, 28.3, 14.3. HRMS (ESI) calcd for $C_{31}H_{36}N_4O_8Na$ (M+Na$^+$) 615.2425, found 615.2424.



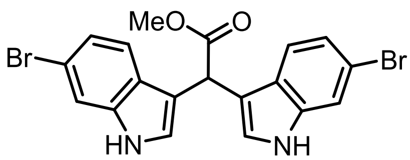
3v

***Ethyl 2-(2-hydroxynaphthalen-1-yl)-2-((4-methoxyphenyl)amino)acetate* (3v).**[12] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 16/1 to 8/1 as eluent). Pale red oil, 40% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, J = 8.8 Hz, 1H), 7.83 (d, J = 7.8Hz, 1H), 7.75 (d, J = 8.8 Hz, 1H), 7.59-7.53 (m, 1H), 7.43-7.37 (m, 1H), 7.08 (d, J = 8.8 Hz, 1H), 6.80-6.56 (m, 4H), 5.82 (s, 1H), 4.35-4.20 (m, 1H), 4.15-4.00 (m, 1H), 3.67 (s, 3H), 1.10 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3 156.2, 154.9, 138.9, 132.6, 130.7, 129.3, 129.1, 127.0, 123.1, 122.0, 119.9, 117.9, 114.9, 111.4, 62.6, 58.2, 55.6, 14.0.



3w

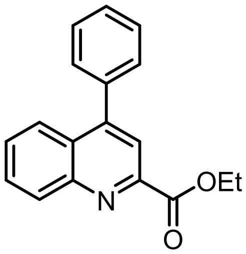
***Ethyl 1-(2-ethoxy-1-(4-methoxyphenylamino)-2-oxoethyl)-2-oxocyclopentanecarboxylatepale* (3w).**[13] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 16/1 to 8/1 as eluent). Colourless oil, 51% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81-6.67 (m, 4H), 4.69 (d, J = 30.7 Hz, 1H), 4.22-4.06 (m, 4H), 3.73 (d, J = 1.7 Hz, 3H), 2.62-2.36 (m, 2H), 2.33-2.04 (m, 2H), 2.03-1.87 (m, 2H), 1.27-1.15 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 212.5, 171.8, 169.0, 153.7, 141.0, 117.0, 116.1, 114.8, 114.7, 62.6 (62.64, 62.61), 61.9, 61.6, 55.7, 38.9, 30.0, 19.9, 14.2, 14.1.



3x

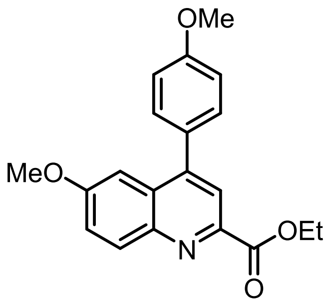
***Methyl 2,2-bis(6-bromo-1H-indol-3-yl)acetate* (3x).**[14] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 4/1 as eluent). Yellow solid, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 2H), 7.51 (d, J = 1.7 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H), 7.19 (dd, J = 8.7, 1.8 Hz, 2H), 7.11 (d, J = 2.7 Hz, 2H), 5.43 (s, 1H), 3.75

(s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 137.3, 125.6, 124.0, 123.2, 120.7, 116.1, 114.3, 113.7, 52.5, 40.5.



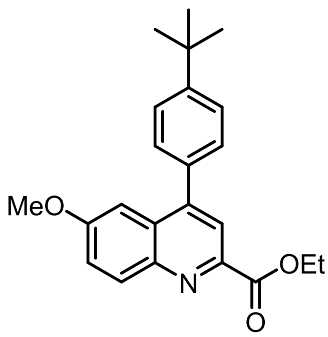
3y

***Ethyl 4-phenylquinoline-2-carboxylate* (3y).**[16] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). Colorless oily liquid, 18% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.5 Hz, 1H), 8.14 (s, 1H), 7.98 (dd, J = 8.5, 1.4 Hz, 1H), 7.79 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.60 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H), 7.56-7.50 (m, 5H), 4.57 (q, J = 7.1 Hz, 2H), 1.49 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 150.0, 148.3, 147.9, 137.7, 131.4, 130.1, 129.7, 128.9, 128.8, 128.7, 127.9, 125.9, 121.4, 62.5, 14.6.



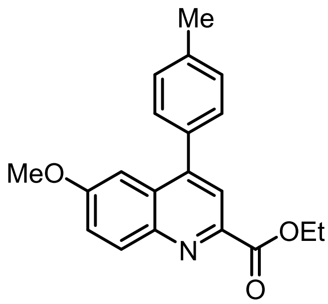
4a

***Ethyl 6-methoxy-4-(p-tolyl)quinoline-2-carboxylate* (4a).**[9] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). White solid, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 9.3 Hz, 1H), 8.06 (s, 1H), 7.51-7.45 (m, 2H), 7.40 (dd, J = 9.3, 2.8 Hz, 1H), 7.24 (d, J = 2.8 Hz, 1H), 7.09-7.04 (m, 2H), 4.53 (q, J = 7.1 Hz, 2H), 3.89 (s, 3H), 3.80 (s, 3H), 1.46 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 160.0, 159.5, 147.8, 145.5, 144.4, 132.8, 130.7, 130.2, 129.4, 122.8, 121.8, 114.3, 103.4, 62.1, 55.6, 55.5, 14.5.



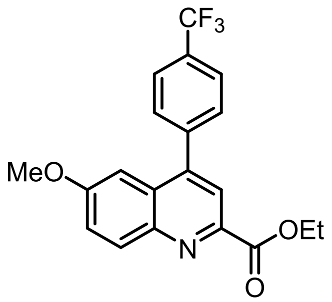
4b

***Ethyl 4-(4-(tert-butyl)phenyl)-6-methoxyquinoline-2-carboxylate* (4b).**[15] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). White solid, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 9.3 Hz, 1H), 8.08 (s, 1H), 7.59-7.52 (m, 2H), 7.51-7.46 (m, 2H), 7.40 (dd, J = 9.3, 2.8 Hz, 1H), 7.29 (d, J = 2.9 Hz, 1H), 4.52 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 1.45 (t, J = 7.1 Hz, 3H), 1.40 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 159.5, 151.8, 148.1, 145.4, 144.4, 135.0, 132.7, 129.3, 129.1, 125.8, 122.6, 121.9, 103.6, 62.1, 55.6, 34.8, 31.4, 14.5.



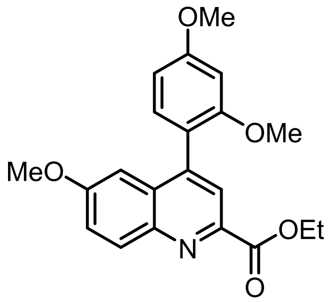
4c

***Ethyl 4-([1,1'-biphenyl]-4-yl)-6-methoxyquinoline-2-carboxylate* (4c).**[15] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). White solid, 95% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 9.3 Hz, 1H), 8.08 (s, 1H), 7.47-7.40 (m, 3H), 7.37-7.34 (m, 2H), 7.25 (d, J = 2.8 Hz, 1H), 4.54 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 2.47 (s, 3H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 159.6, 148.3, 145.5, 144.5, 138.7, 135.1, 132.8, 129.6, 129.4, 122.9, 121.9, 103.5, 62.2, 55.7, 21.5, 14.6.



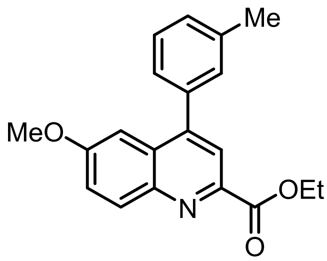
4d

***Ethyl 4-(4-fluorophenyl)-6-methoxyquinoline-2-carboxylate* (4d).**[9] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). Brown solid, 88% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 9.3 Hz, 1H), 8.06 (s, 1H), 7.81 (d, J = 8.1 Hz, 2H), 7.70-7.63 (m, 2H), 7.44 (dd, J = 9.3, 2.8 Hz, 1H), 7.07 (d, J = 2.8 Hz, 1H), 4.54 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 159.9, 146.4, 145.4, 144.4, 141.7 (d, J = 1.4 Hz), 133.0, 130.8 (q, J = 32.5 Hz), 129.8, 128.8, 126.2 (q, J = 2.5 Hz), 125.8 (q, J = 3.8 Hz), 124.1 (q, J = 272.3 Hz), 123.1, 121.9, 102.9, 62.3, 55.7, 14.5.



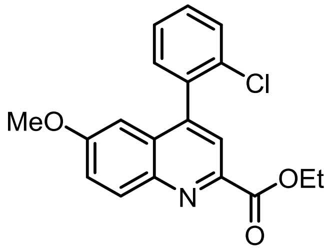
4e

***Ethyl 4-(2,4-dimethoxyphenyl)-6-methoxyquinoline-2-carboxylate* (4e).**[9] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). Pale yellow solid, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 9.2 Hz, 1H), 8.05 (s, 1H), 7.38 (dd, J = 9.3, 2.8 Hz, 1H), 7.24-7.17 (m, 1H), 6.91 (d, J = 2.8 Hz, 1H), 6.67-6.61 (m, 2H), 4.53 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 3.77 (s, 3H), 3.70 (s, 3H), 1.46 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 161.6, 159.2, 157.9, 145.5, 145.4, 144.2, 132.6, 131.9, 130.4, 123.0, 122.7, 119.4, 104.9, 103.9, 99.0, 62.1, 55.6, 55.5, 14.5.



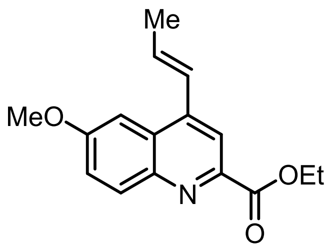
4f

***Ethyl 6-methoxy-4-(m-tolyl)quinoline-2-carboxylate* (4f).**[15] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). White solid, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 9.3 Hz, 1H), 8.08 (s, 1H), 7.46-7.40 (m, 2H), 7.37-7.29 (m, 3H), 7.23 (d, J = 2.8 Hz, 1H), 4.55 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 2.46 (s, 3H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 159.6, 148.3, 145.5, 144.5, 138.7, 138.0, 132.8, 130.1, 129.5, 129.4, 128.7, 126.5, 122.8, 121.9, 103.5, 62.2, 55.6, 21.6, 14.5.



4g

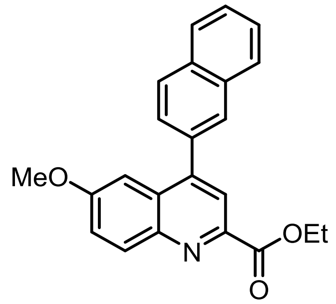
***Ethyl 4-(3-chlorophenyl)-6-methoxyquinoline-2-carboxylate* (4g).**[9] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). Yellow solid, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 9.3 Hz, 1H), 8.06 (s, 1H), 7.59-7.56 (m, 1H), 7.48-7.40 (m, 3H), 7.38-7.35 (m, 1H), 6.75 (d, J = 2.8 Hz, 1H), 4.57-4.51 (m, 2H), 3.76 (s, 3H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 159.7, 145.5, 145.4, 144.2, 136.6, 133.3, 132.8, 131.4, 130.2, 130.1, 129.4, 127.2, 123.1, 122.4, 103.4, 62.2, 55.7, 14.5.



4h

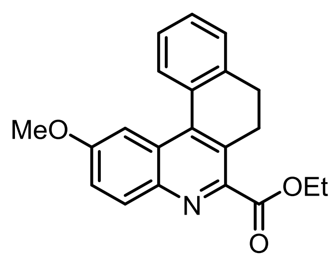
***Ethyl (E)-6-methoxy-4-(prop-1-en-1-yl)quinoline-2-carboxylate* (4h).**[9] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent).

White solid, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.16 (m, 2H), 7.40 (dd, J = 9.3, 2.8 Hz, 1H), 7.29 (d, J = 2.8 Hz, 1H), 7.03-6.96 (m, 1H), 6.64-6.55 (m, 1H), 4.55 (q, J = 7.1 Hz, 2H), 3.97 (s, 3H), 2.06 (dd, J = 6.7, 1.8 Hz, 3H), 1.49 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 159.3, 145.6, 144.2, 143.3, 133.8, 132.8, 128.5, 125.7, 122.7, 117.8, 101.3, 62.1, 55.7, 19.3, 14.5.



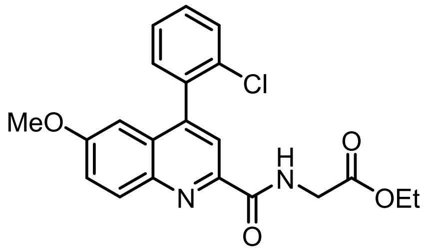
4i

***Ethyl 6-methoxy-4-(naphthalen-1-yl)quinoline-2-carboxylate* (4i).**[9] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). Pale yellow solid, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 9.3 Hz, 1H), 8.19 (s, 1H), 8.04-7.96 (m, 2H), 7.88-7.94 (m, 2H), 7.63 (dd, J = 8.4, 1.8 Hz, 1H), 7.60-7.52 (m, 2H), 7.43 (dd, J = 9.3, 2.8 Hz, 1H), 7.23 (d, J = 2.8 Hz, 1H), 4.55 (q, J = 7.1 Hz, 2H), 3.73 (s, 3H), 1.48 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.7, 159.6, 148.0, 145.4, 144.4, 135.4, 133.4, 133.1, 132.8, 129.3, 128.7, 128.4, 128.3, 127.9, 127.0, 126.9, 126.8, 122.9, 122.1, 103.3, 62.1, 55.5, 14.5.



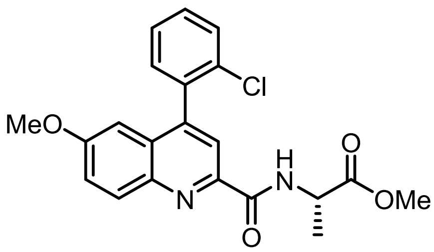
4j

***Ethyl 2-methoxy-7,8-dihydrobenzo[k]phenanthridine-6-carboxylate* (4j).**[9] Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 8/1 to 4/1 as eluent). Pale yellow solid, 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 9.2 Hz, 1H), 7.99-7.92 (m, 1H), 7.77 (d, J = 2.8 Hz, 1H), 7.44-7.33 (m, 4H), 4.53 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 2.97-2.94 (m, 2H), 2.86–2.76 (m, 2H), 1.47 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 159.3, 146.7, 143.5, 140.4, 140.3, 132.4, 132.1, 130.6, 129.0, 128.5, 128.2, 126.42, 126.40, 121.6, 103.5, 62.0, 55.6, 28.9, 25.8, 14.4.



4k

***Ethyl (4-(2-chlorophenyl)-6-methoxyquinoline-2-carbonyl)glycinate* (4k).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 4/1 to 2/1 as eluent). Yellow solid, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (t, J = 5.5 Hz, 1H), 8.15 (s, 1H), 8.09 (d, J = 9.2 Hz, 1H), 7.57 (dd, J = 7.5, 1.9 Hz, 1H), 7.49-7.38 (m, 3H), 7.35 (dd, J = 7.1, 2.2 Hz, 1H), 6.76 (d, J = 2.8 Hz, 1H), 4.38-4.19 (m, 4H), 3.77 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 165.1, 159.4, 146.5, 145.9, 143.1, 136.8, 133.3, 131.9, 131.4, 130.1, 130.0, 129.4, 127.1, 123.1, 120.2, 103.6, 61.7, 55.7, 41.7, 14.4. HRMS (ESI) calcd for $C_{21}H_{19}ClN_2O_4Na$ ($M+Na^+$) 421.0926, found 421.0928.



4l

***Methyl (4-(2-chlorophenyl)-6-methoxyquinoline-2-carbonyl)-L-alaninate* (4l).** Purified by flash column chromatography (silica gel, petroleum ether/EtOAc = 4/1 to 2/1 as eluent). Yellow solid, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, J = 8.1 Hz, 1H), 8.18-8.08 (m, 2H), 7.56 (dd, J = 7.3, 2.0 Hz, 1H), 7.49-7.37 (m, 3H), 7.37-7.33 (m, 1H), 6.76 (t, J = 2.3 Hz, 1H), 4.95-4.81 (m, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 1.61 (d, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 164.4, 159.3, 146.6, 145.9, 143.0, 136.8, 131.9, 131.4, 130.10, 130.03, 130.00, 129.4, 127.1, 123.1, 120.2, 103.6, 55.7, 52.6, 48.3, 18.7. HRMS (ESI) calcd for $C_{21}H_{19}ClN_2O_4K$ ($M+K^+$) 437.0665, found 437.0670.

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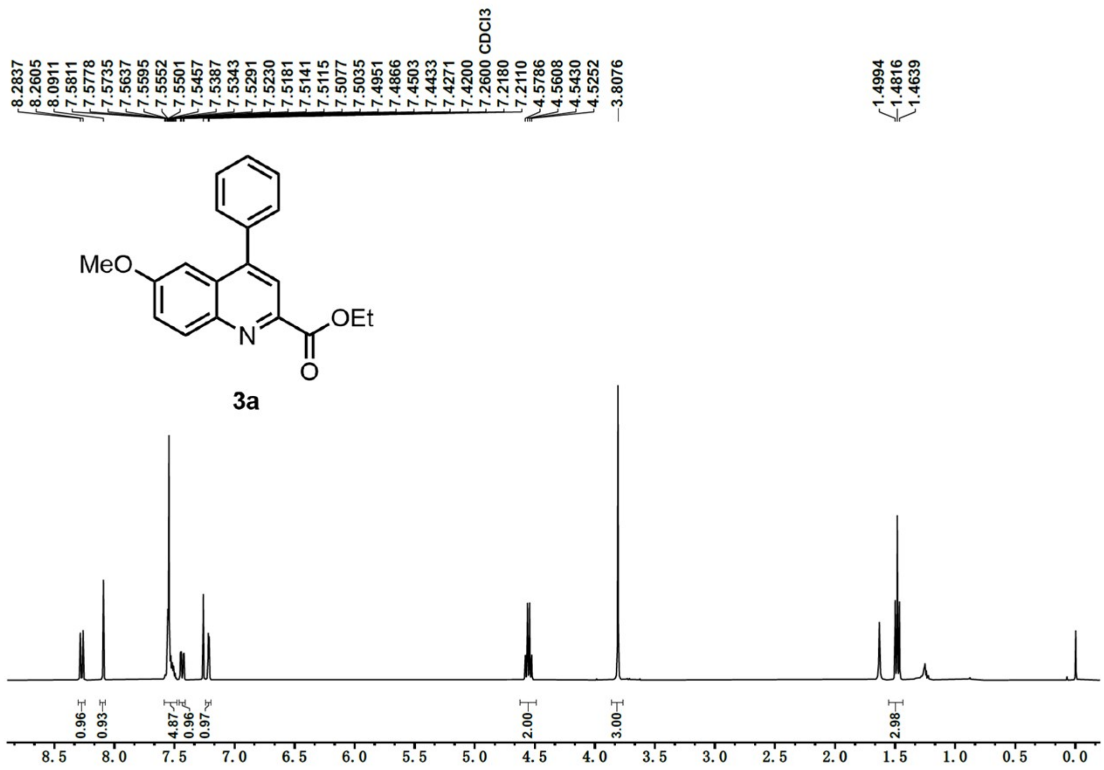
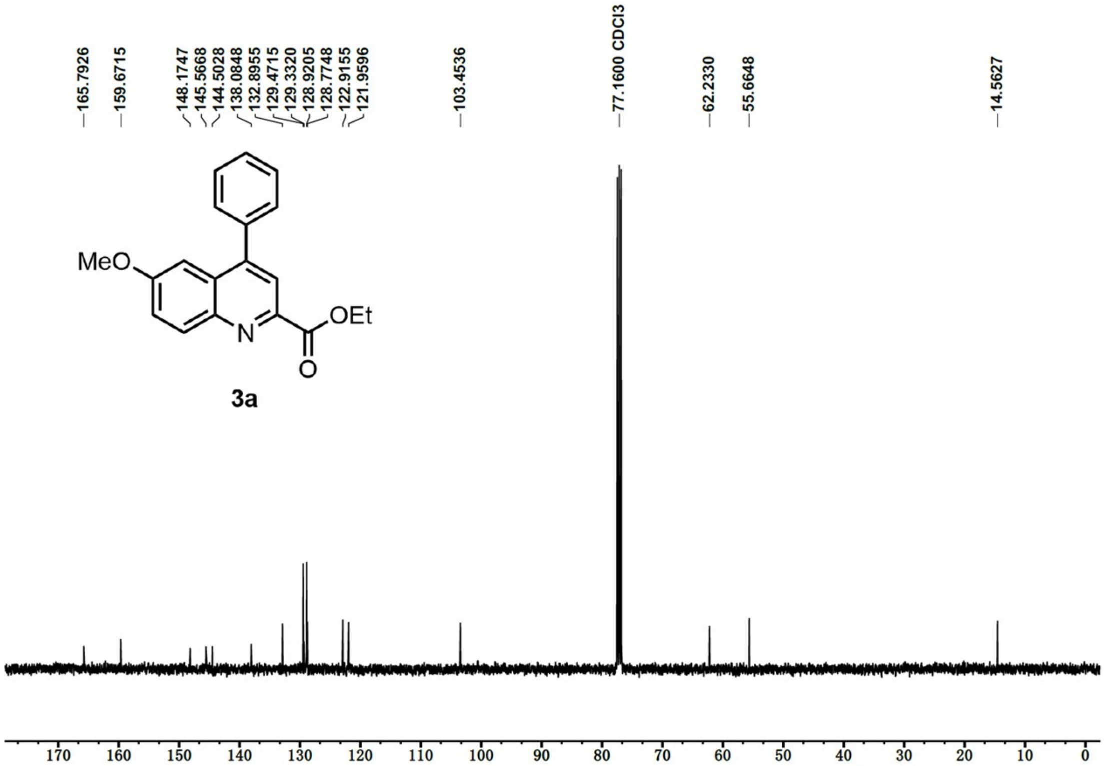
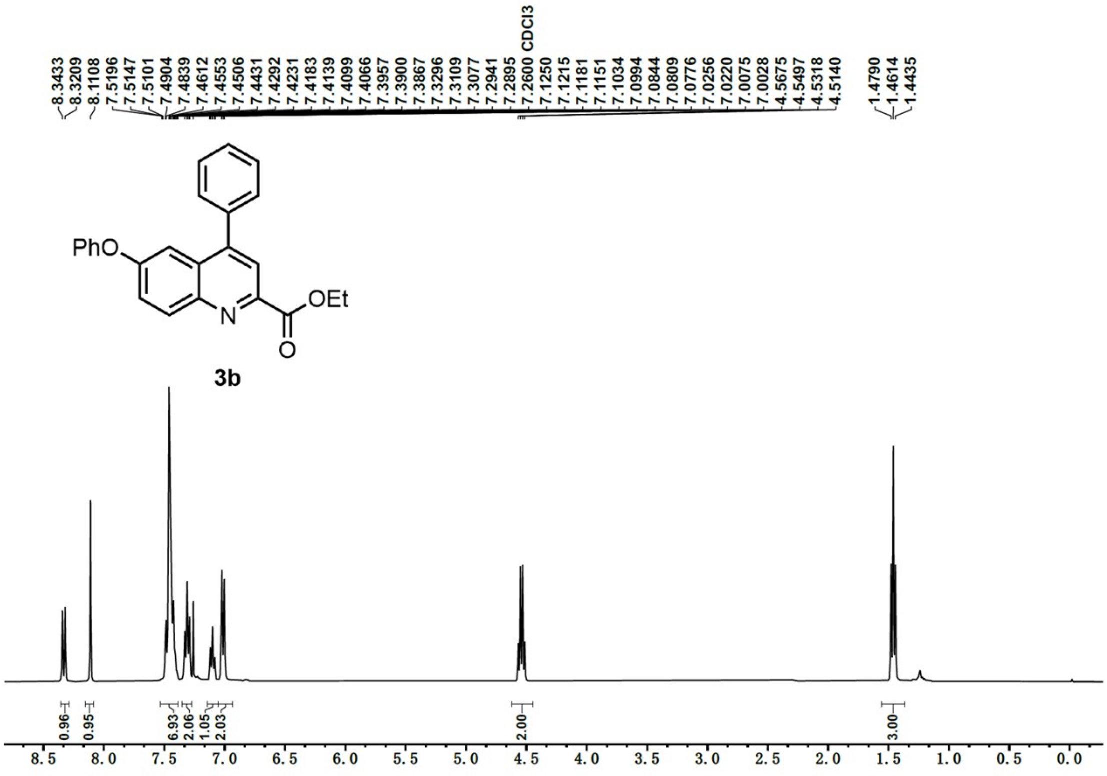
7. Copies of ^1H and ^{13}C NMR Spectra







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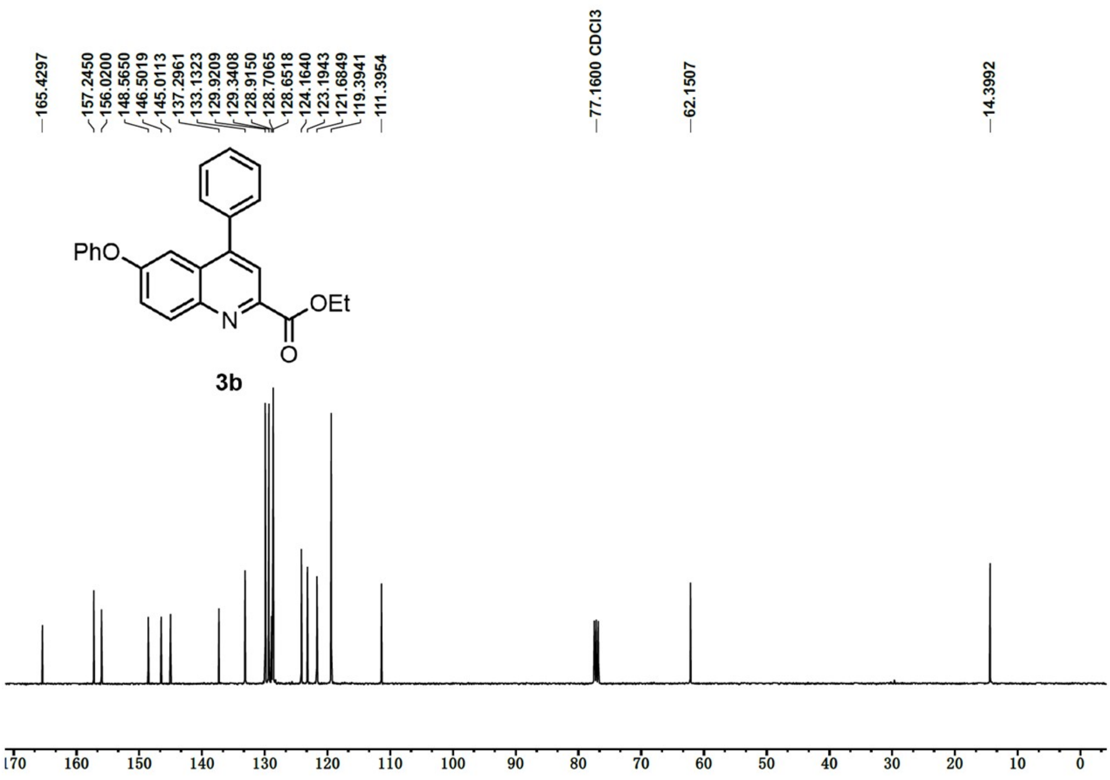

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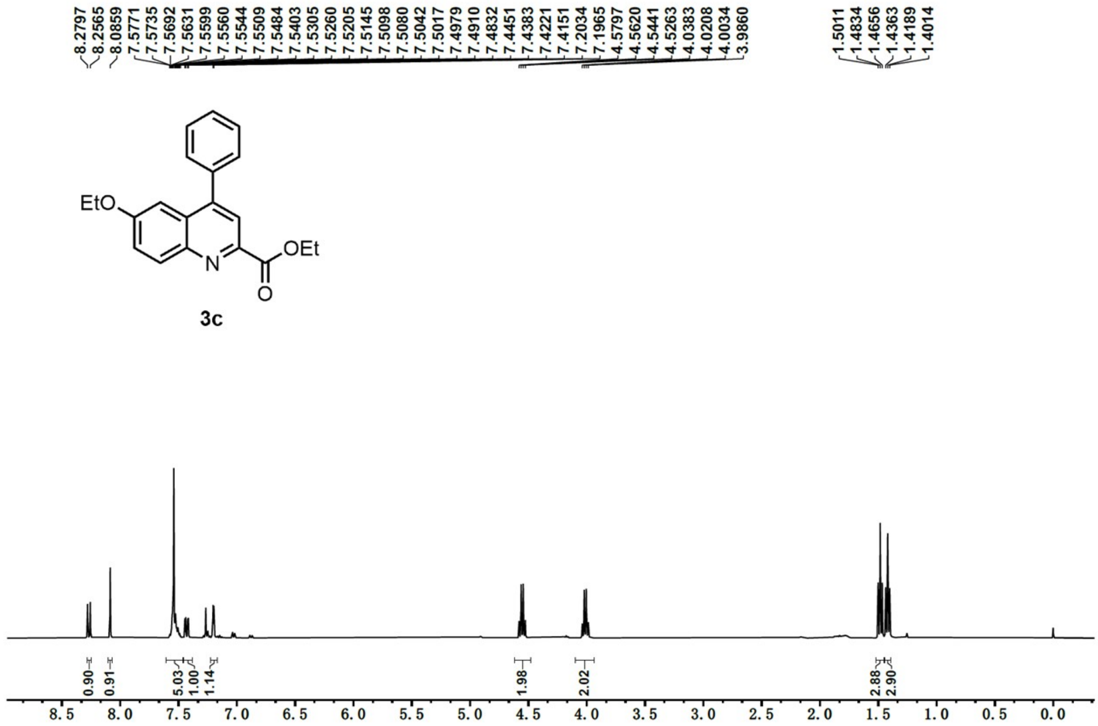

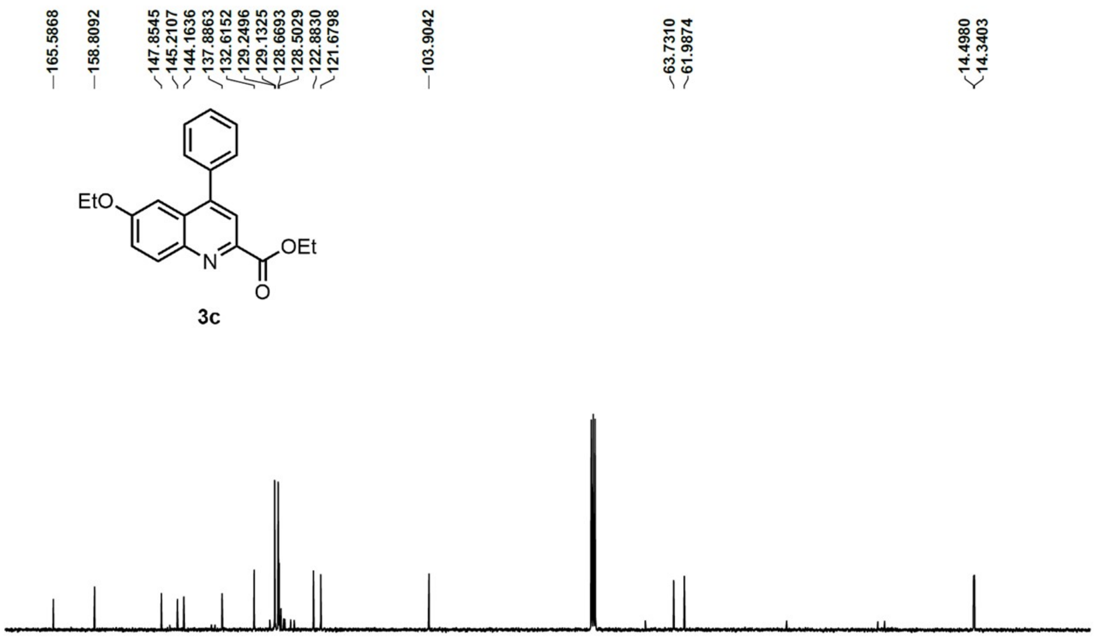

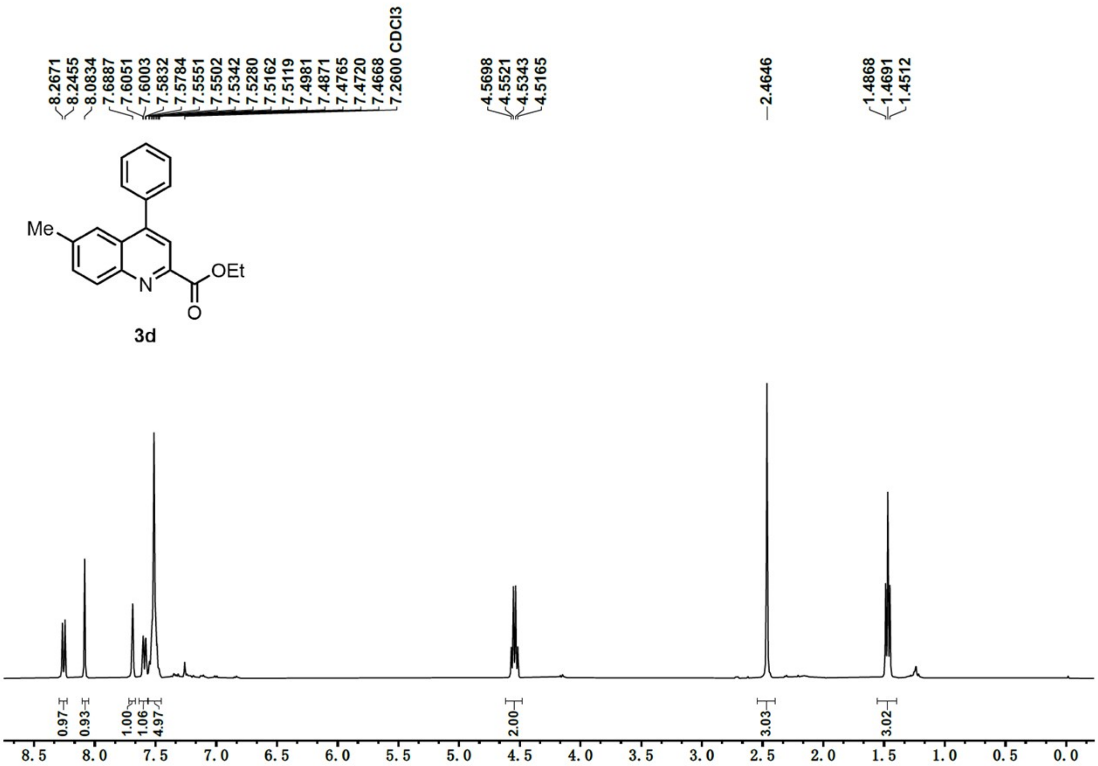

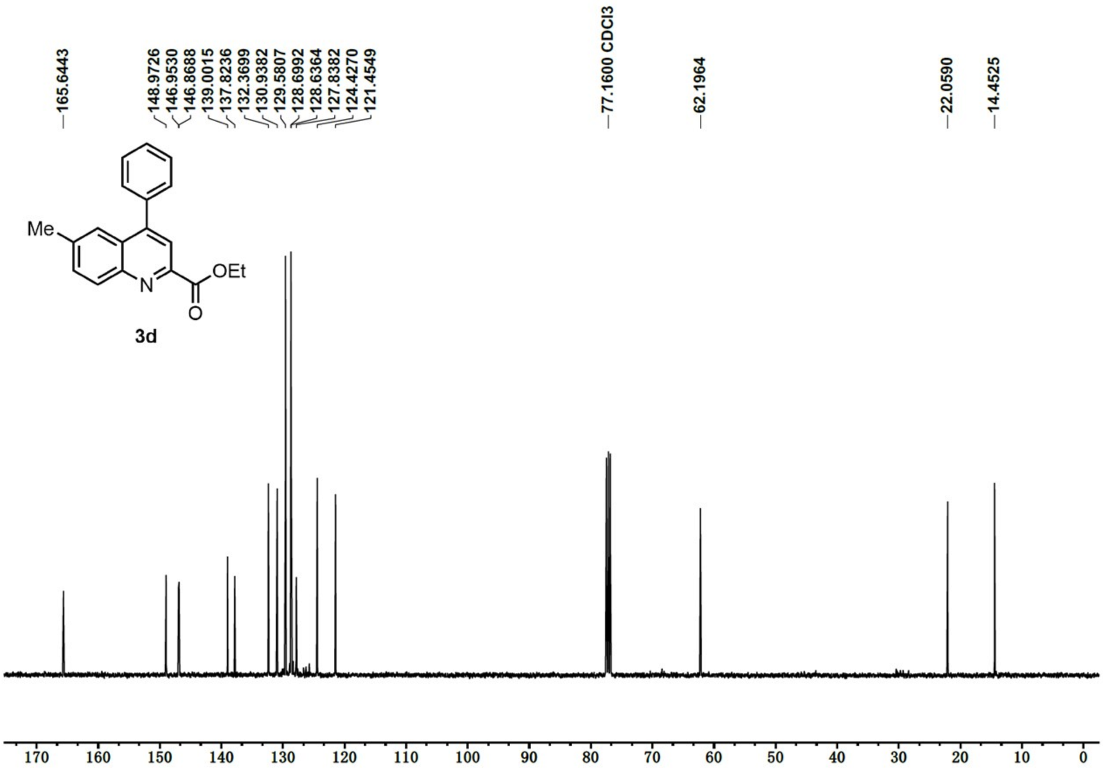

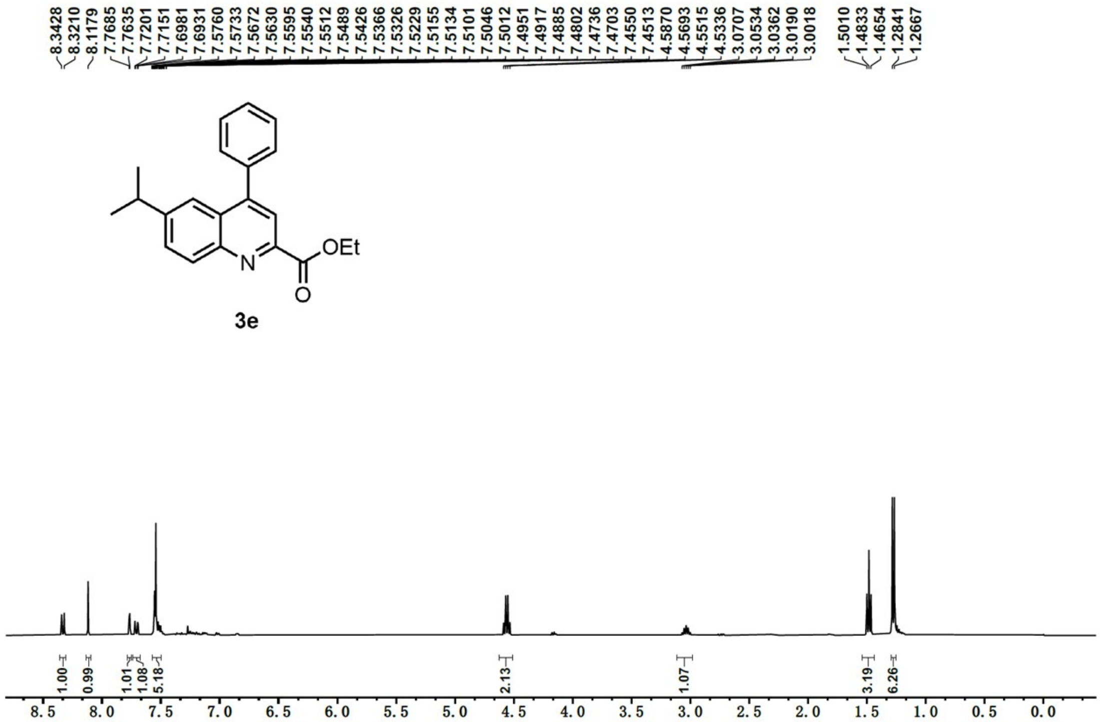
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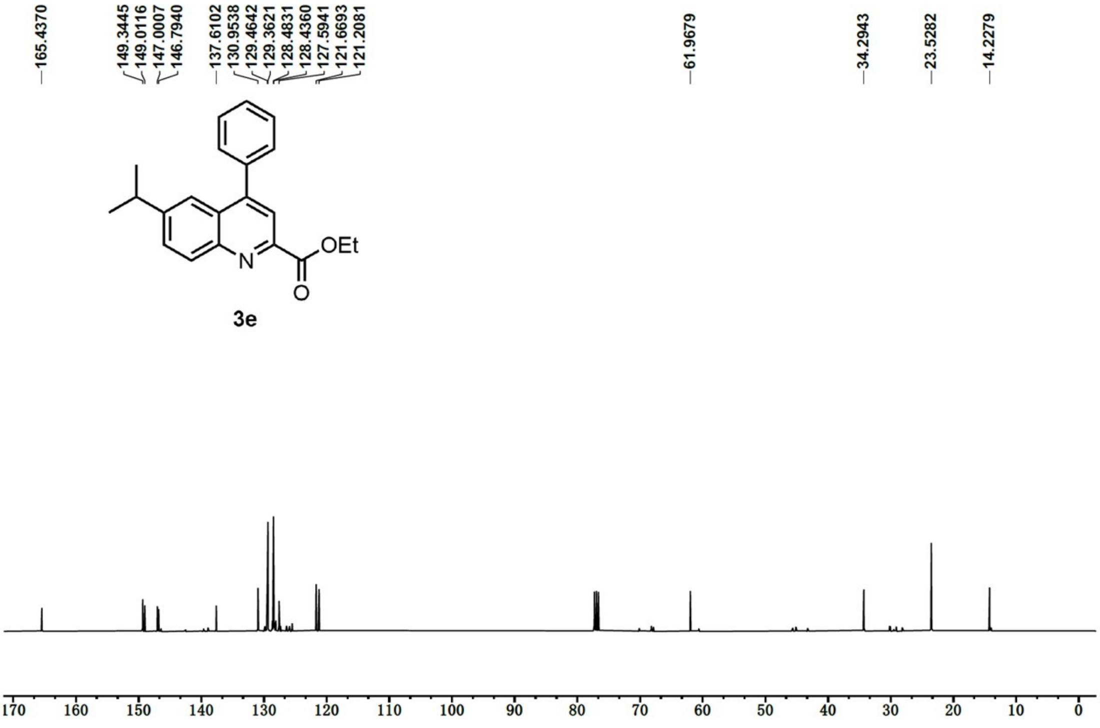
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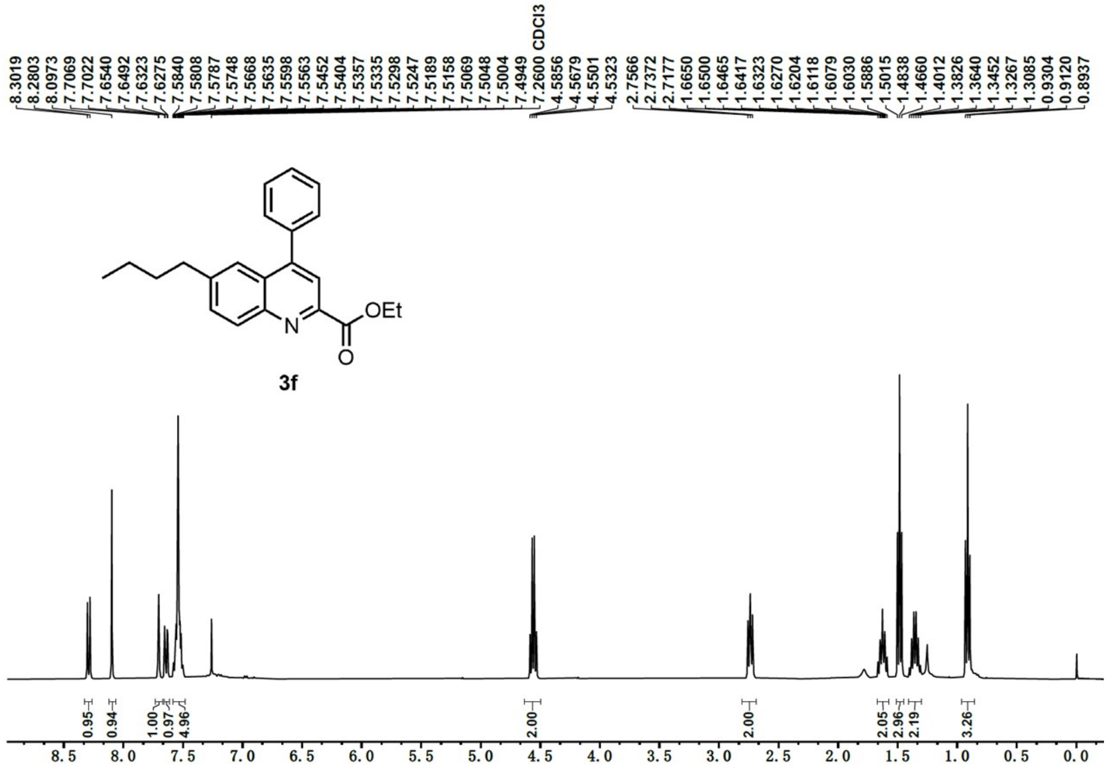
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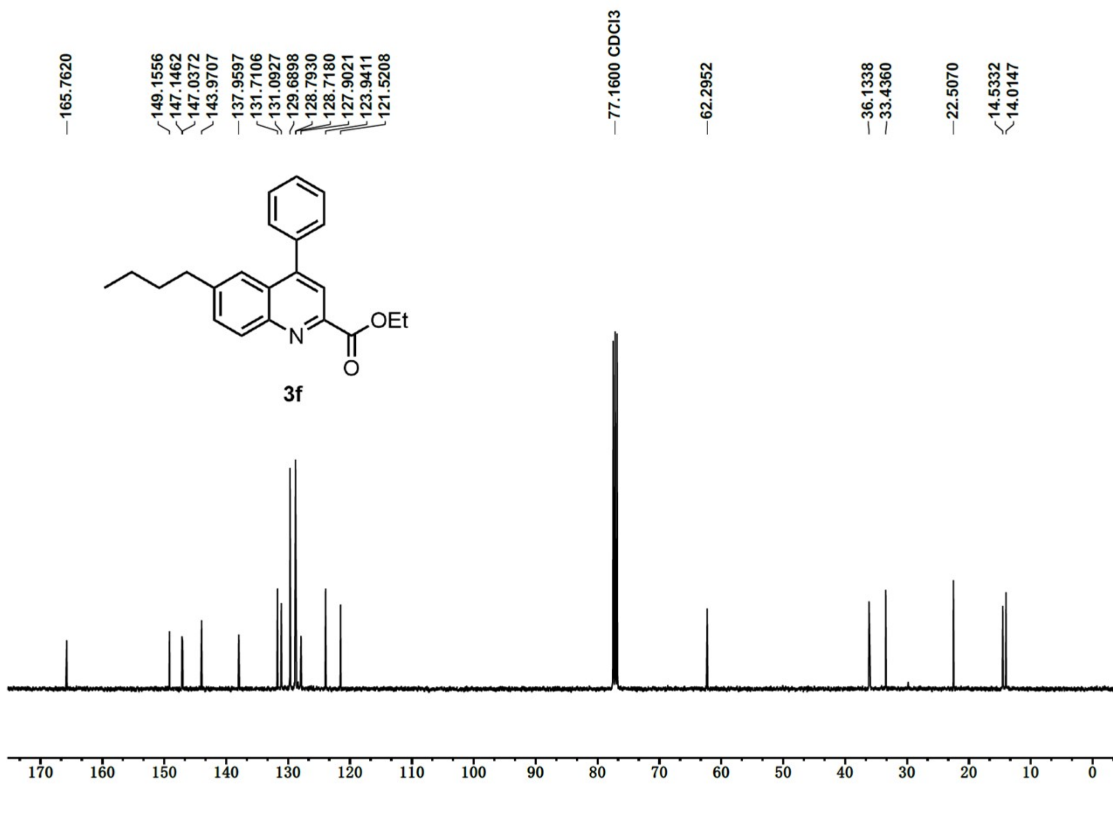
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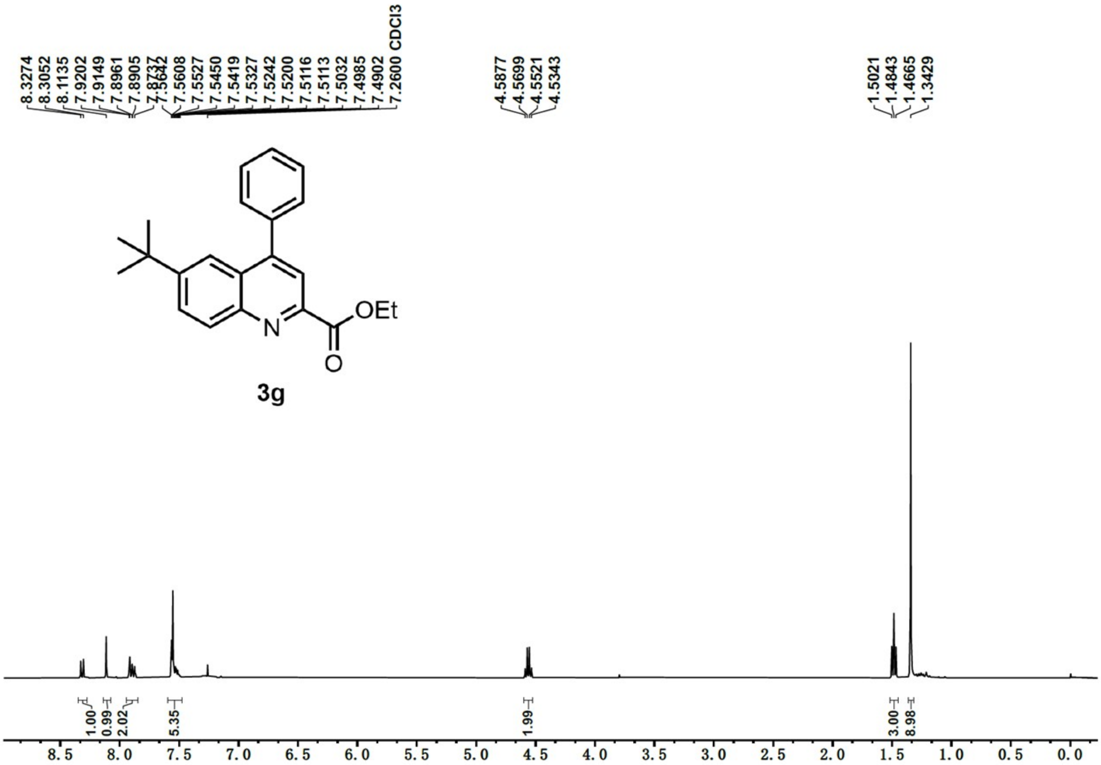
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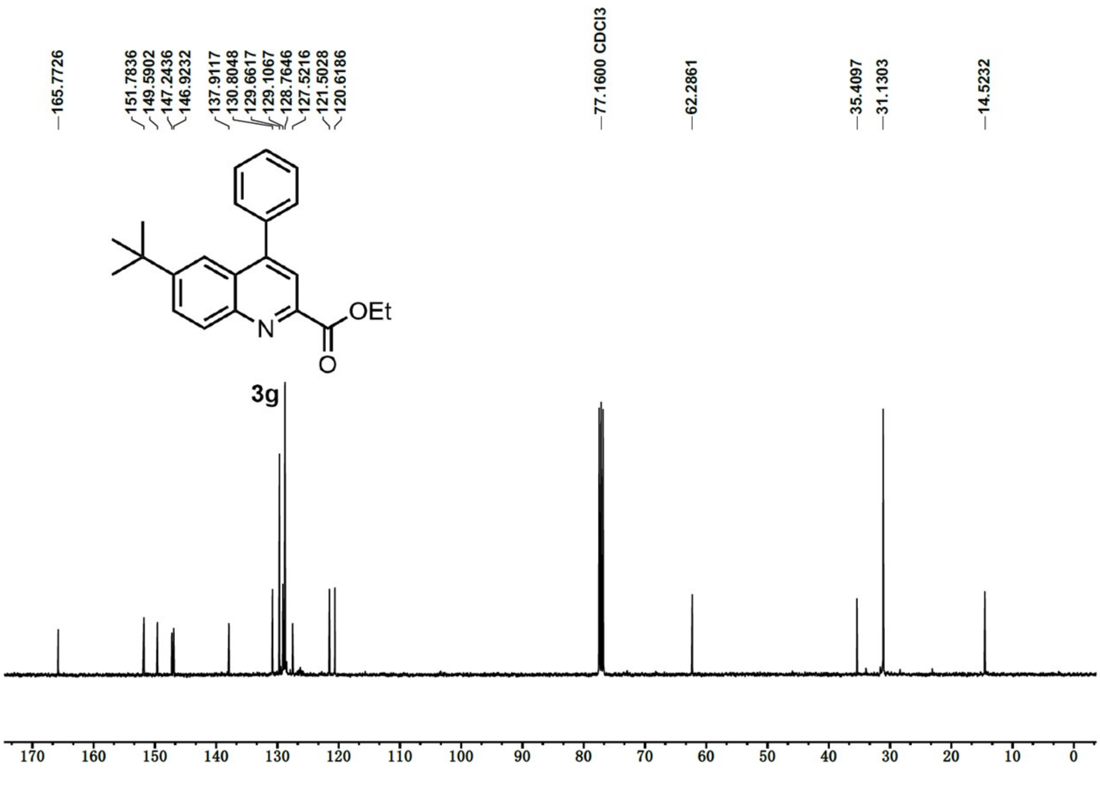
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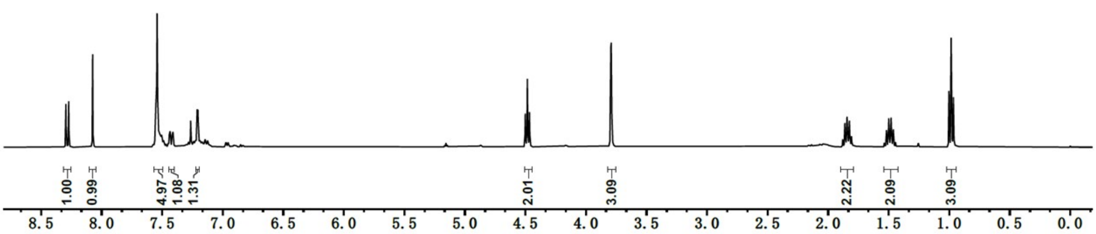
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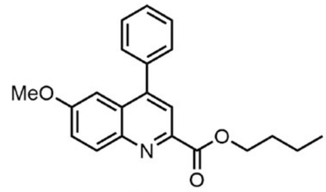
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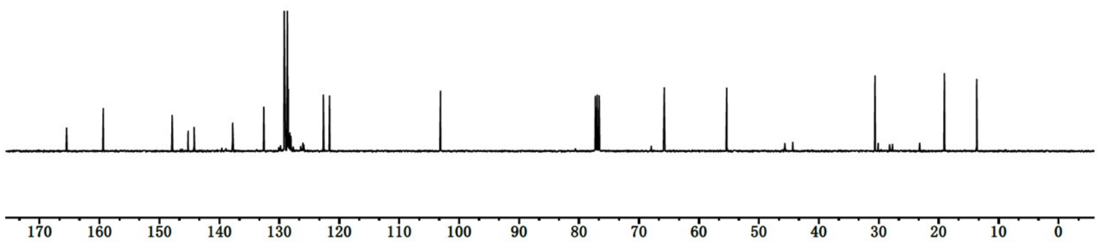
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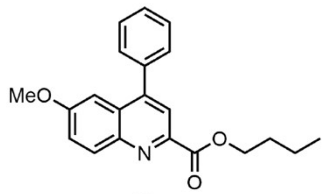
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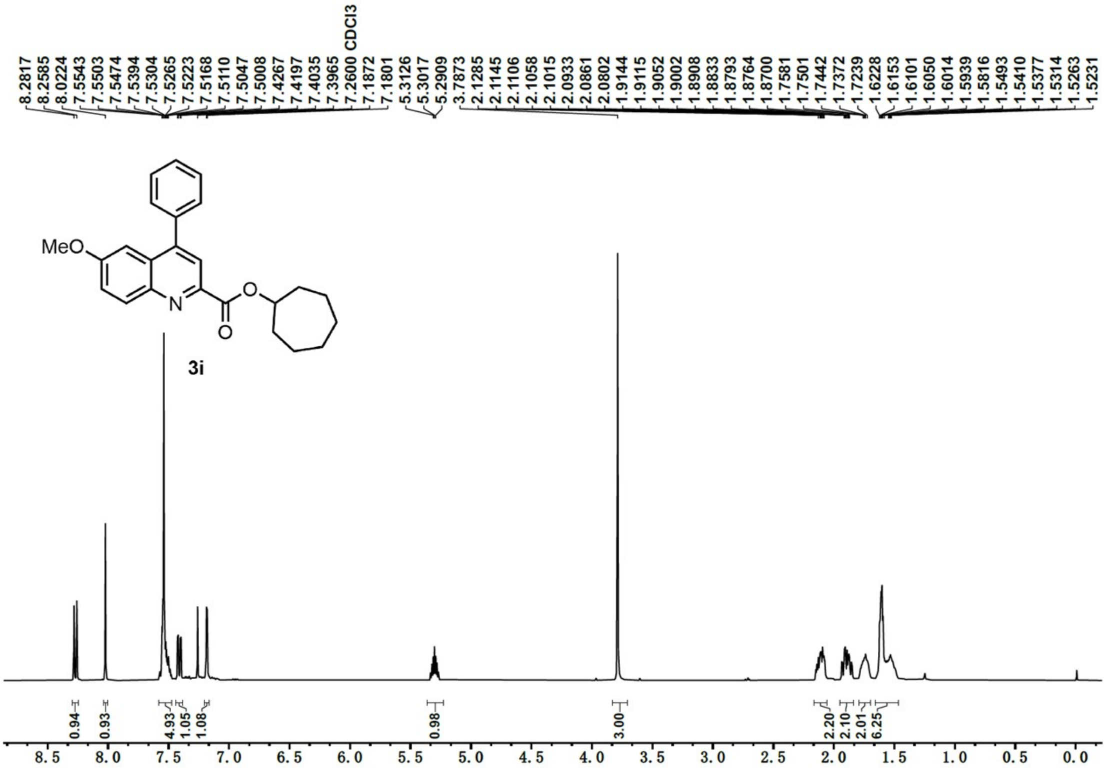
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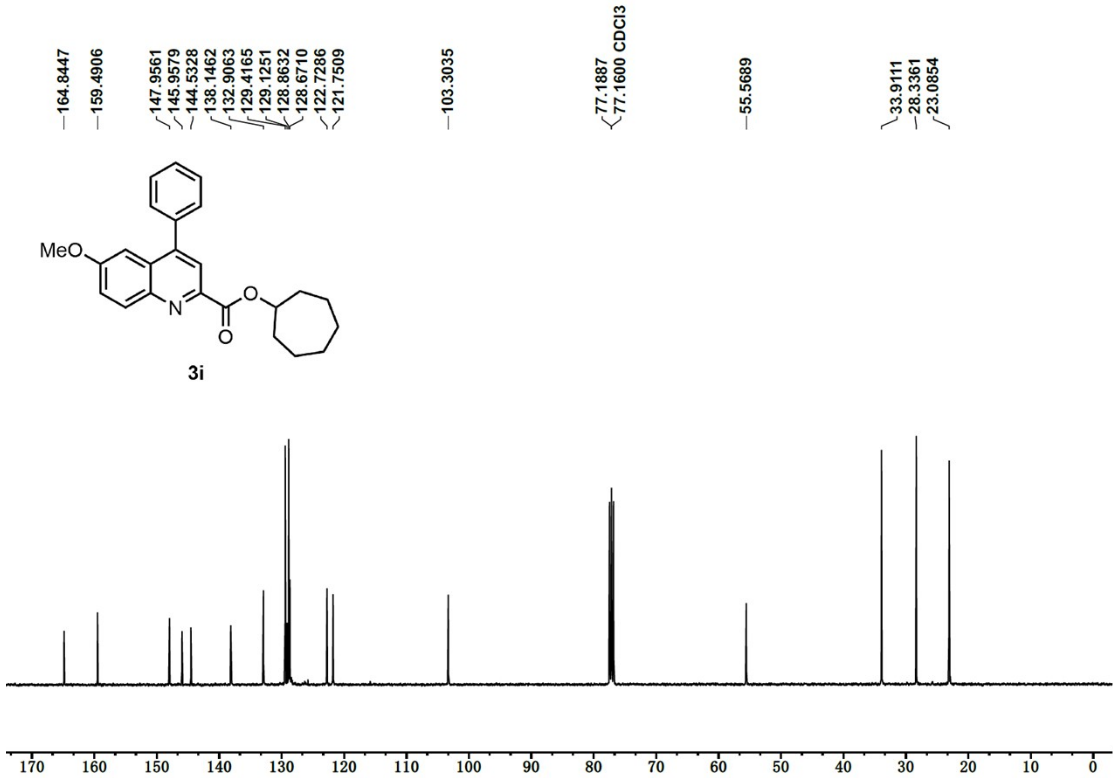
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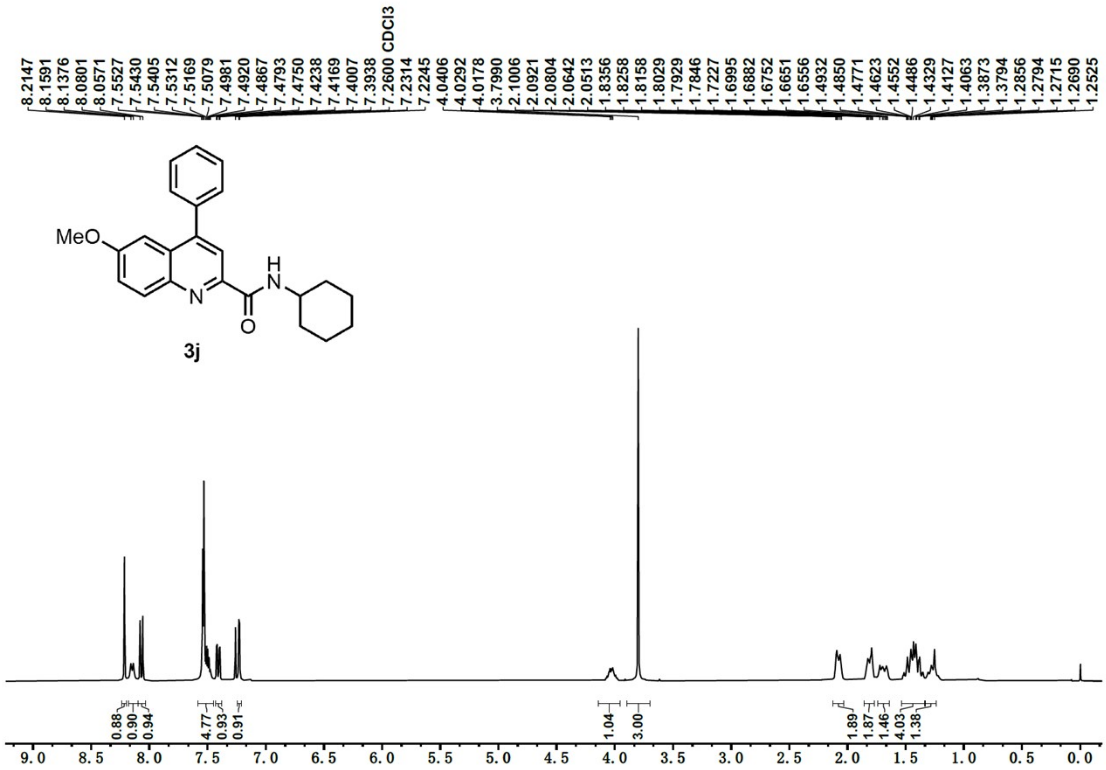

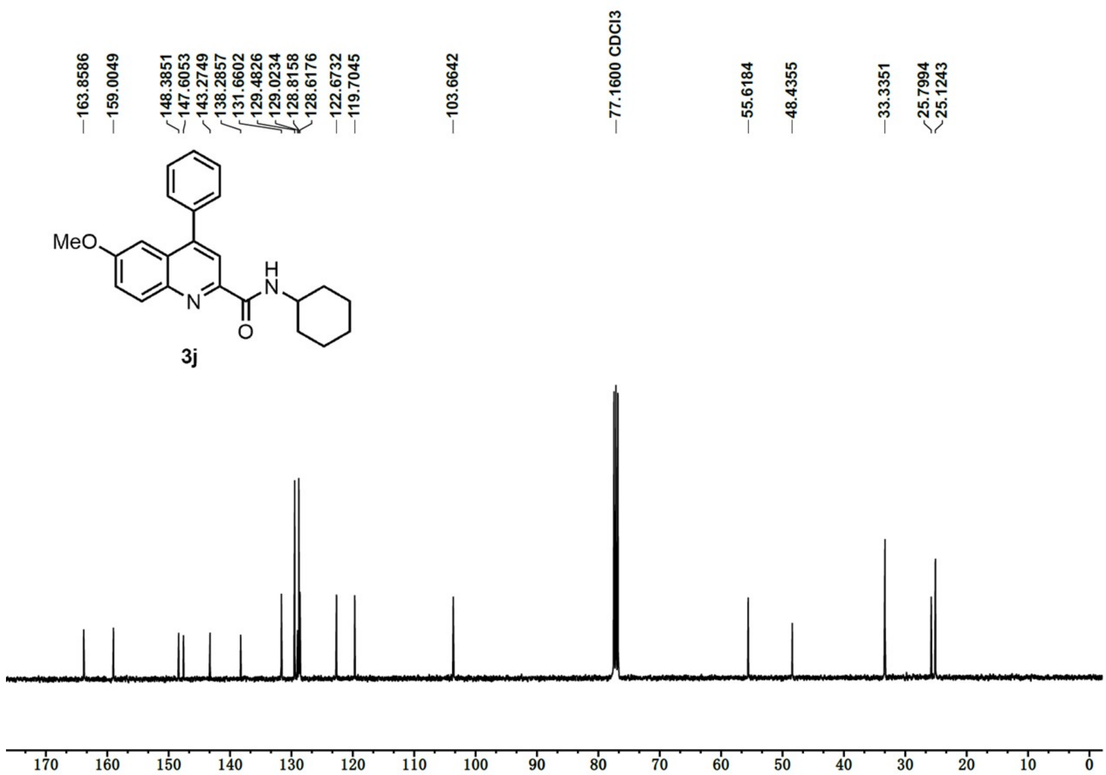

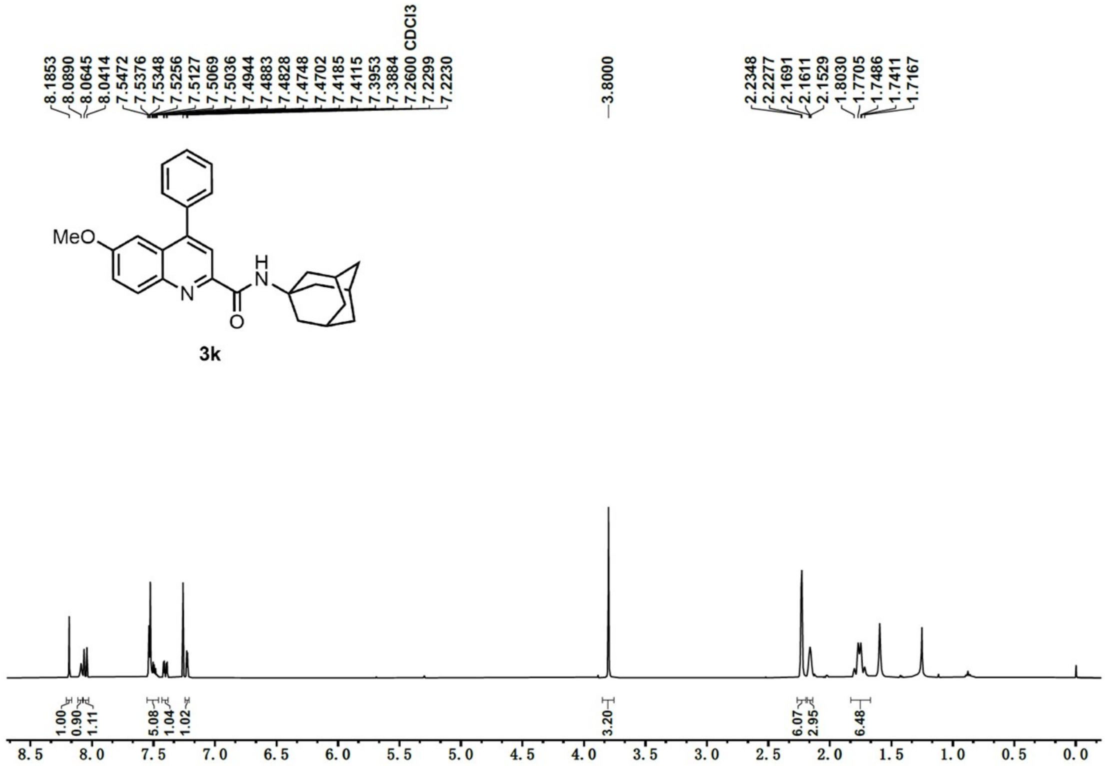
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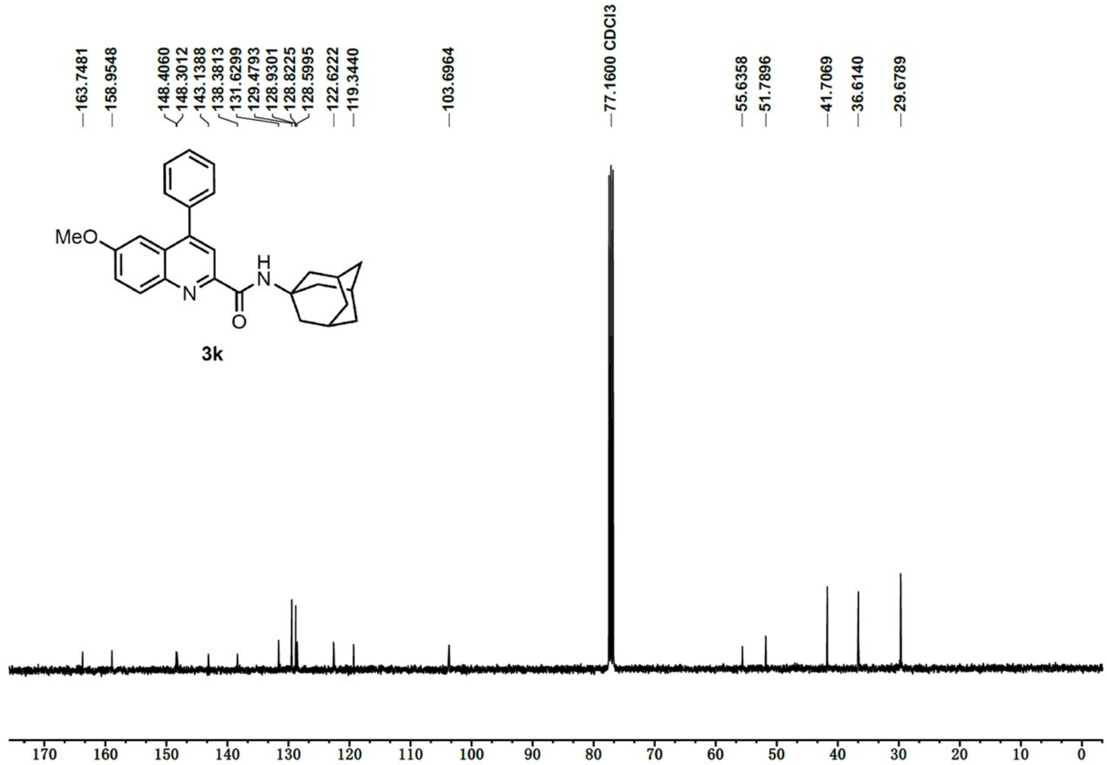
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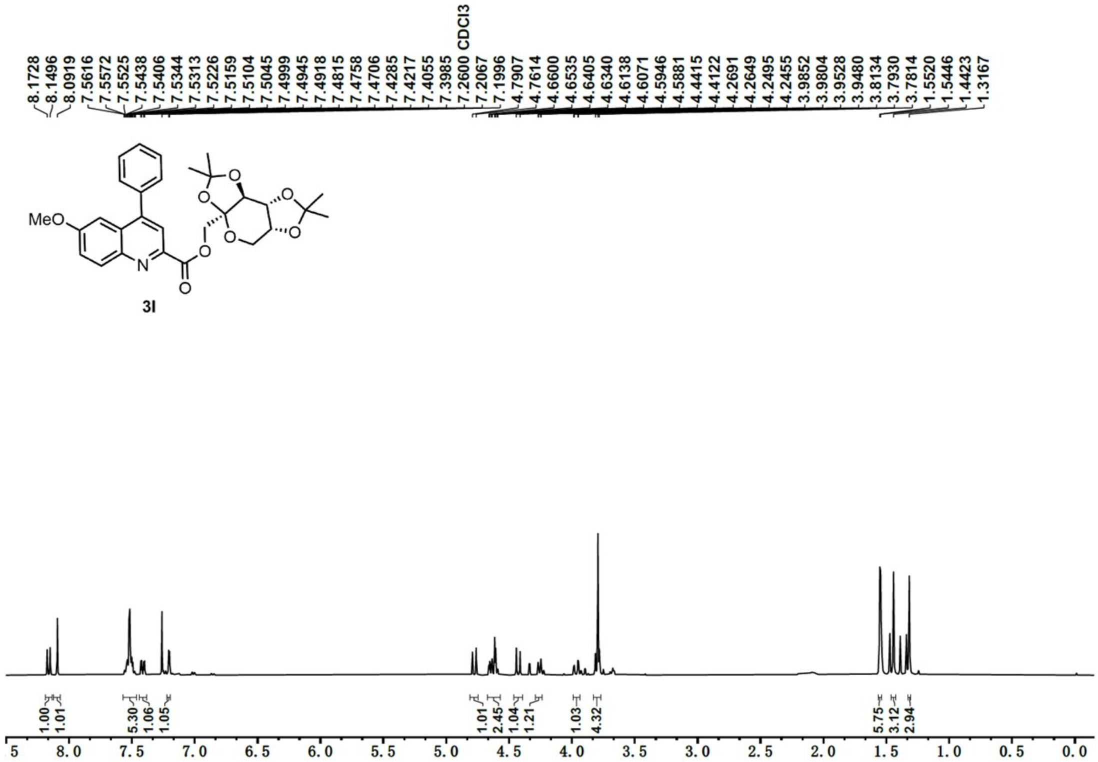

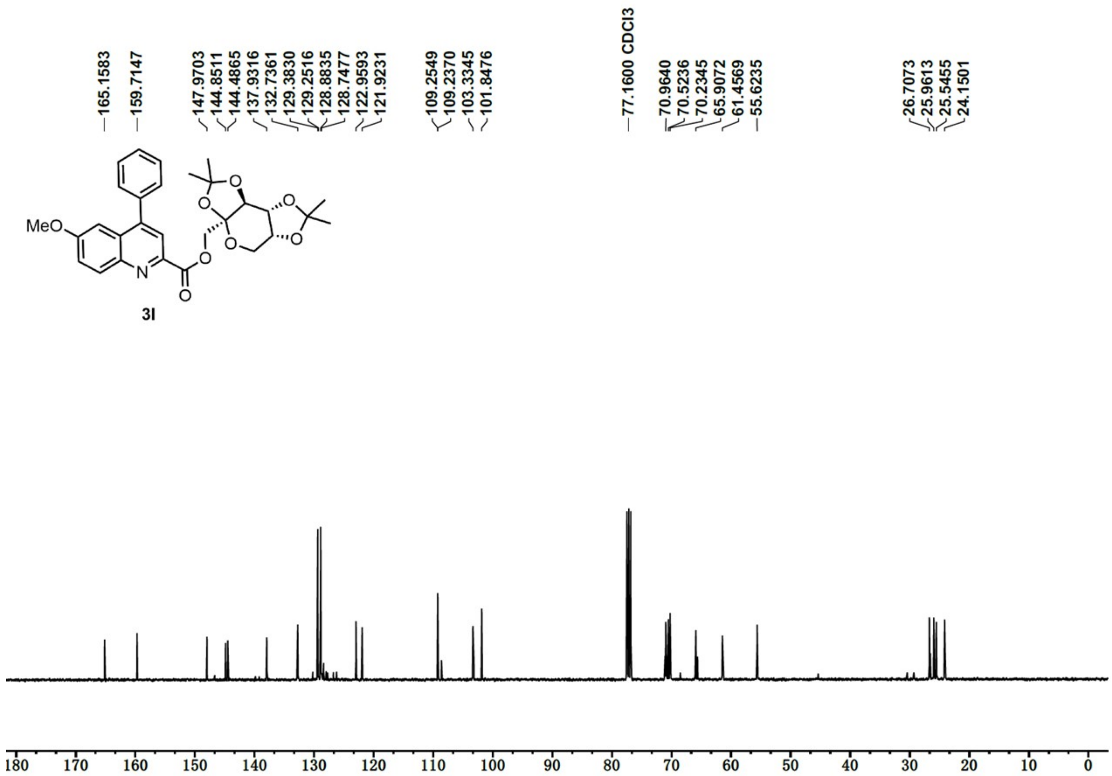

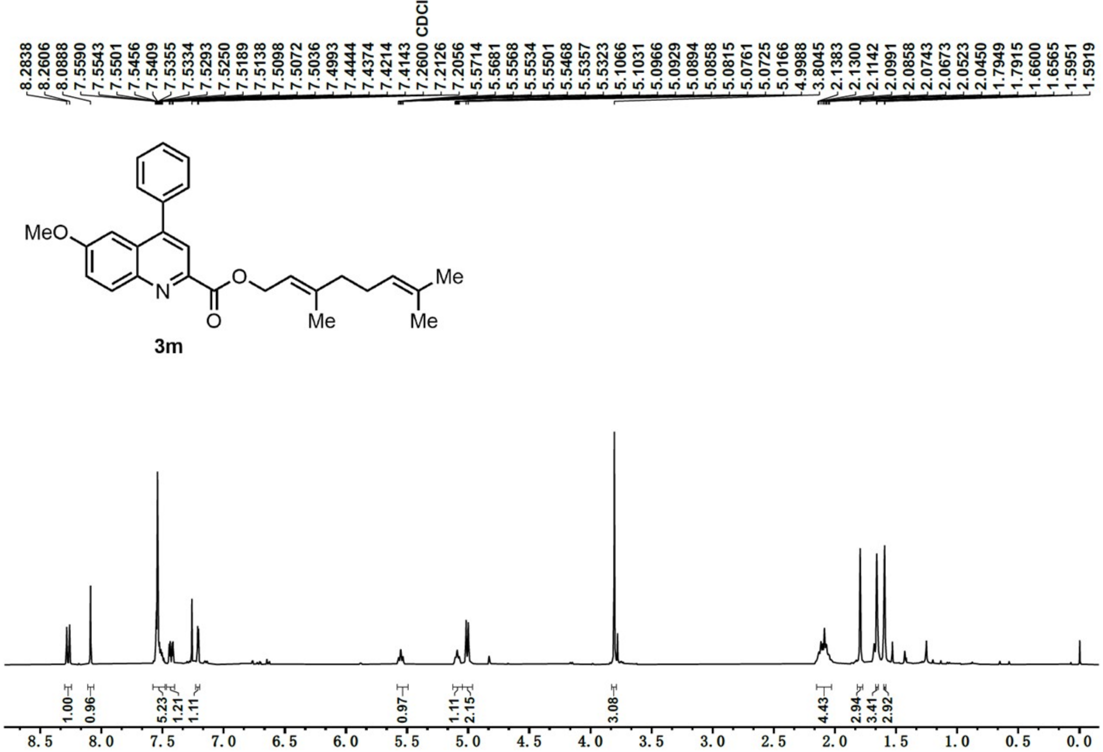

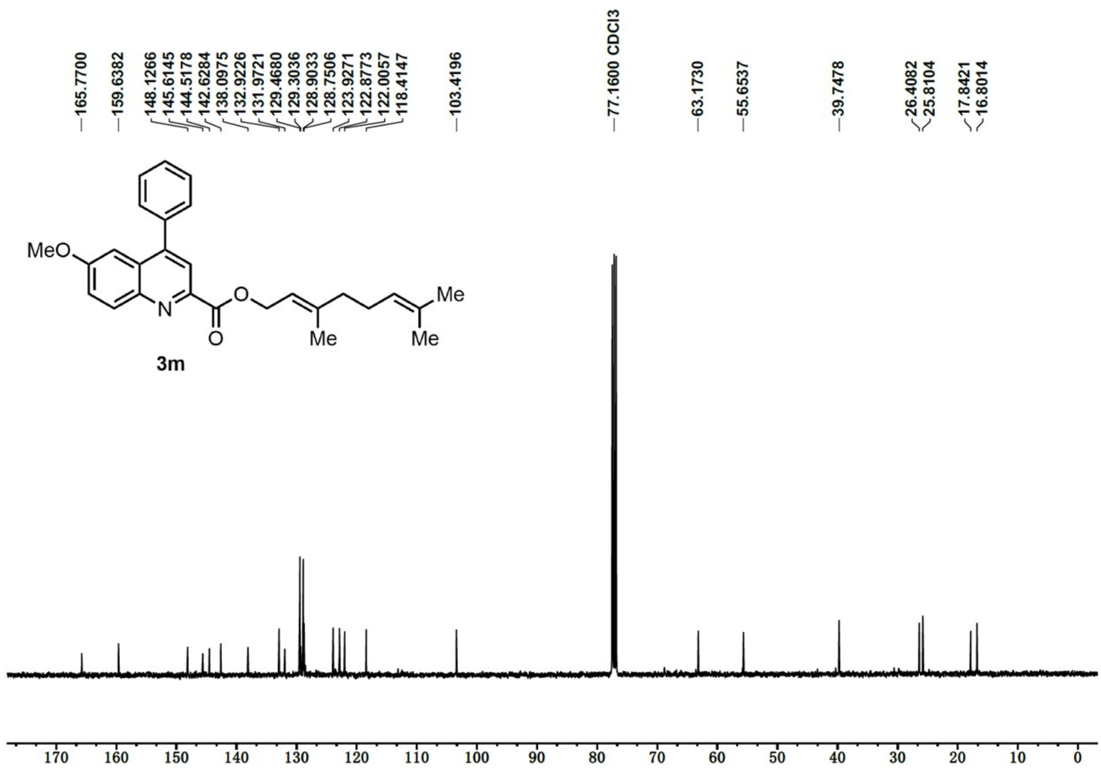

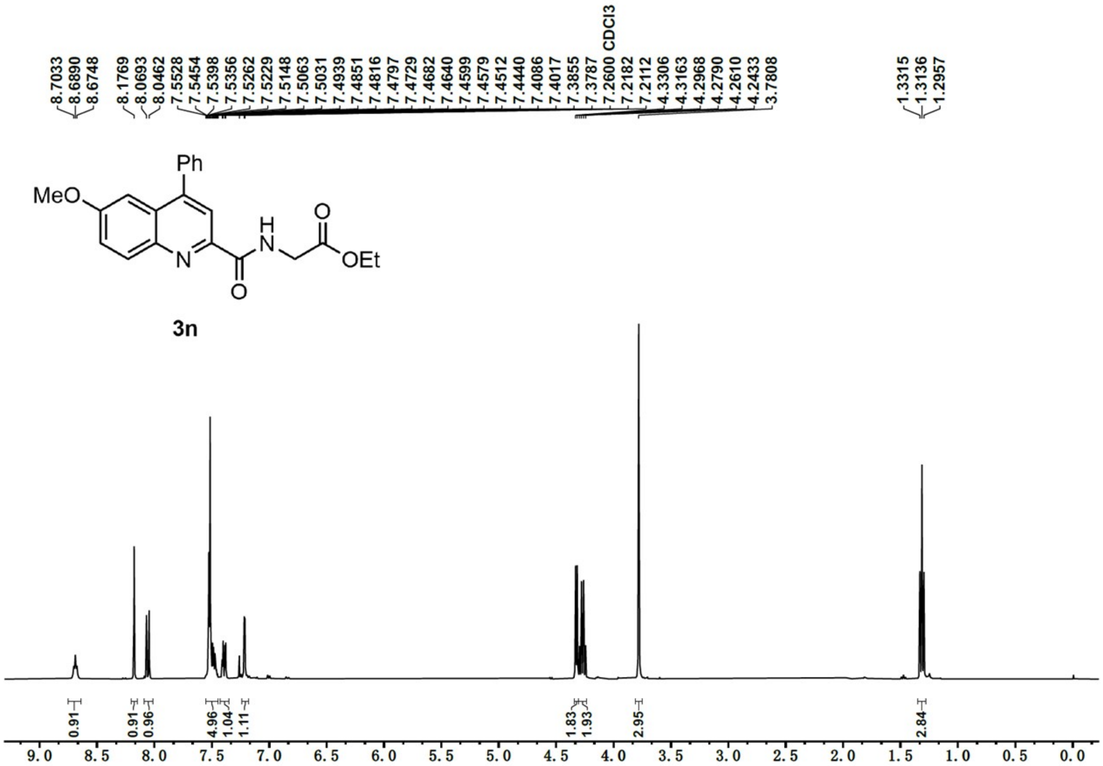
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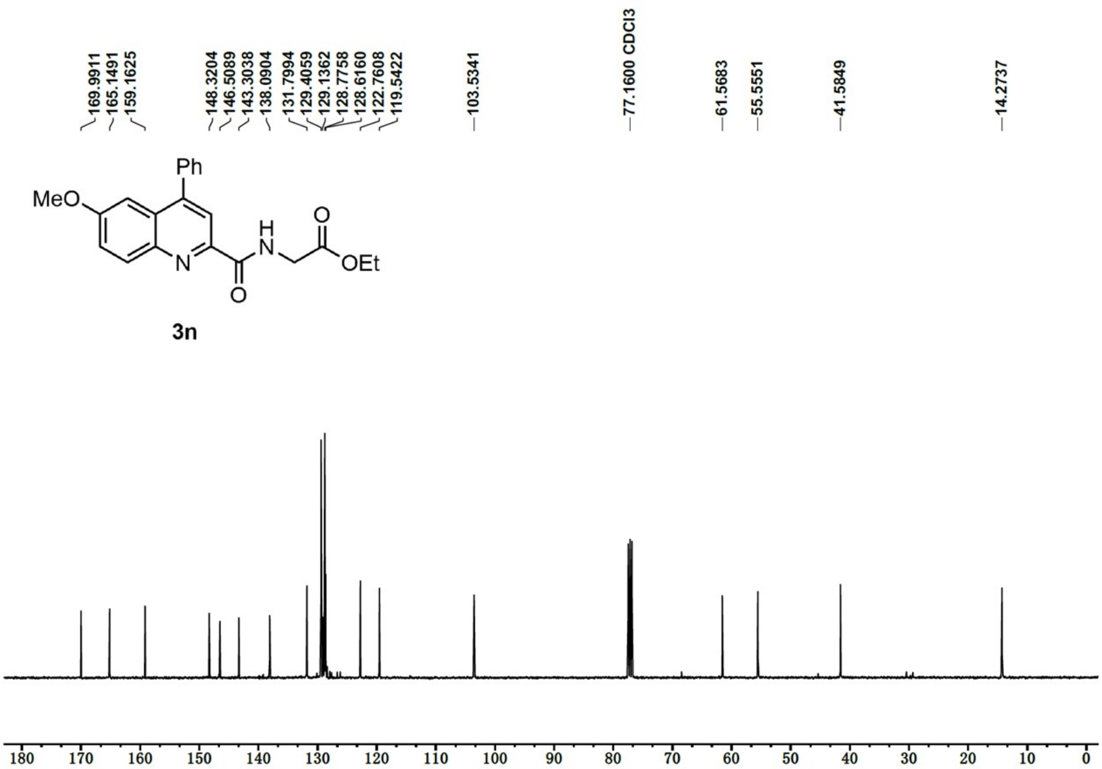
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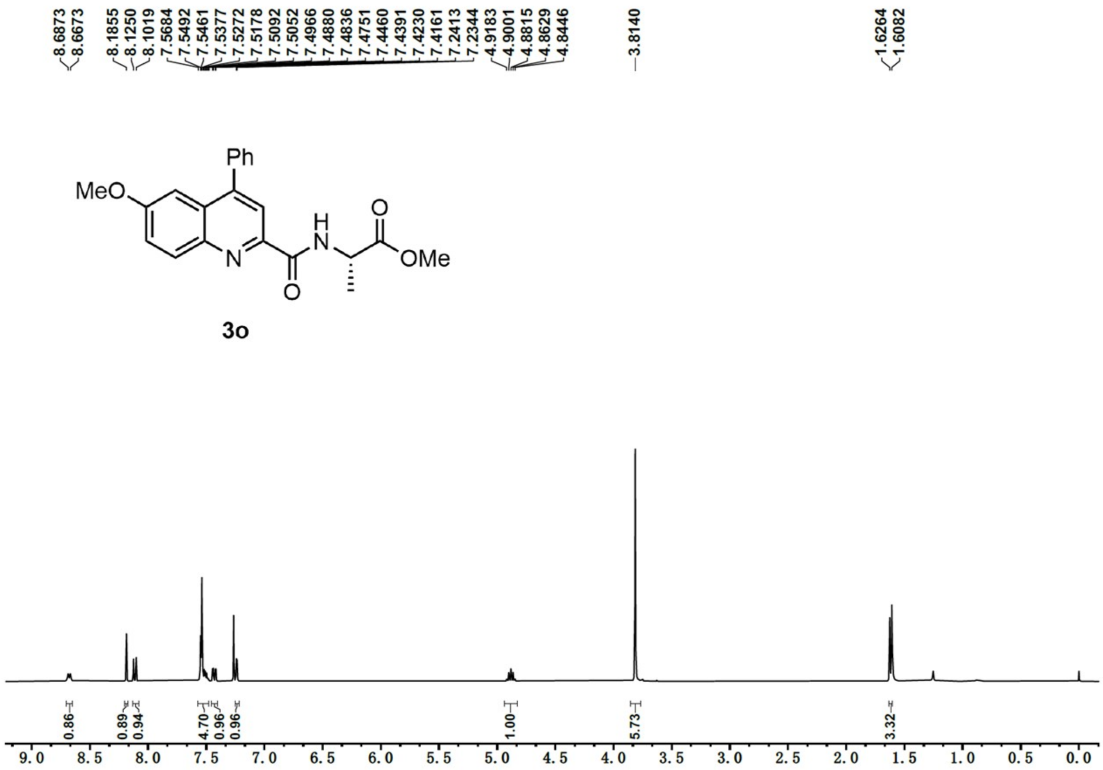

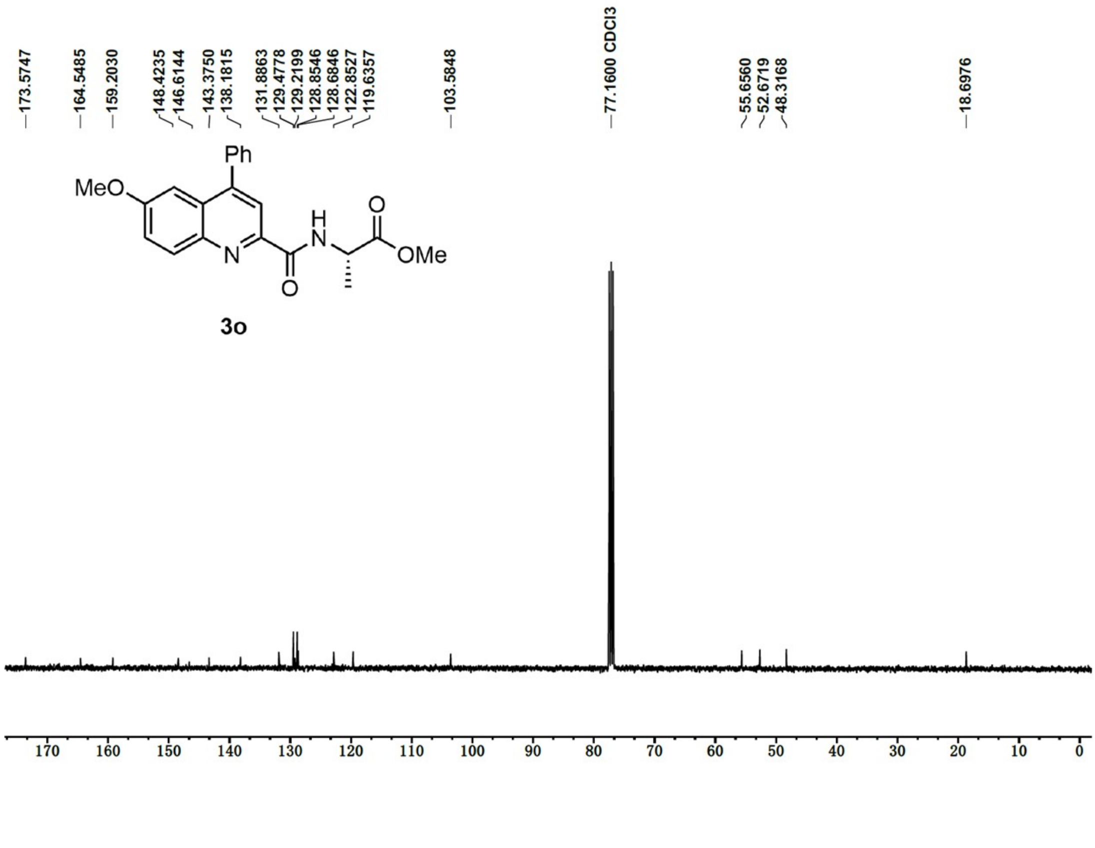

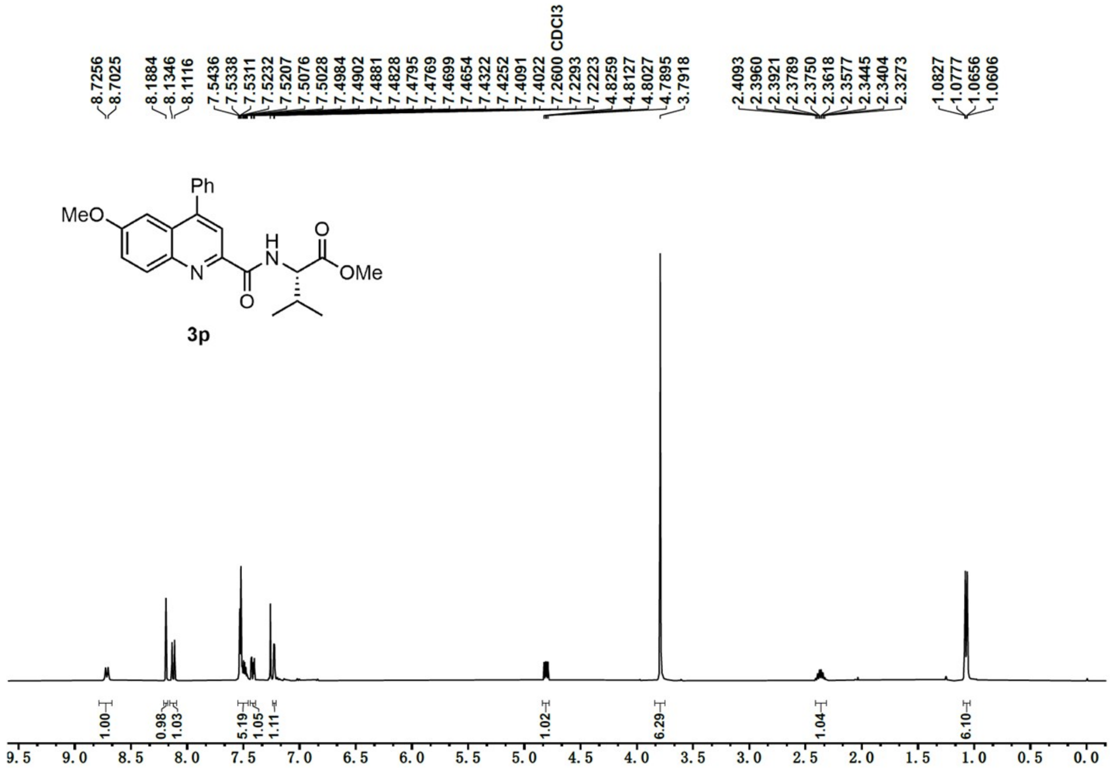
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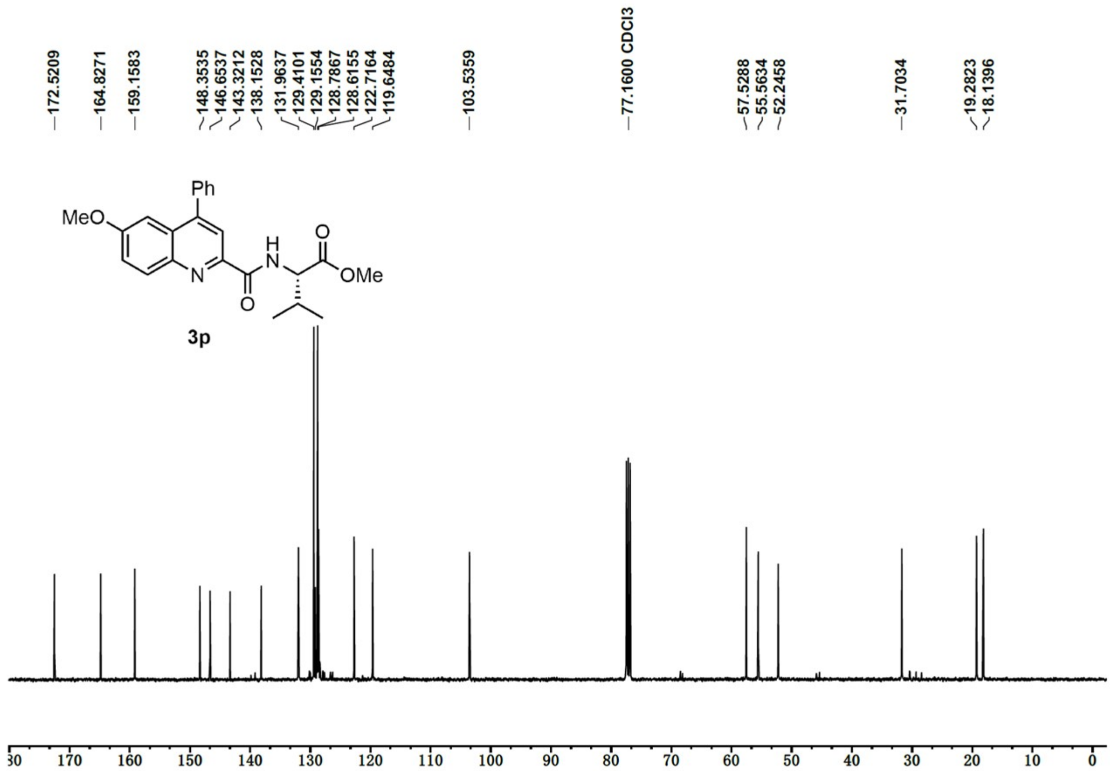
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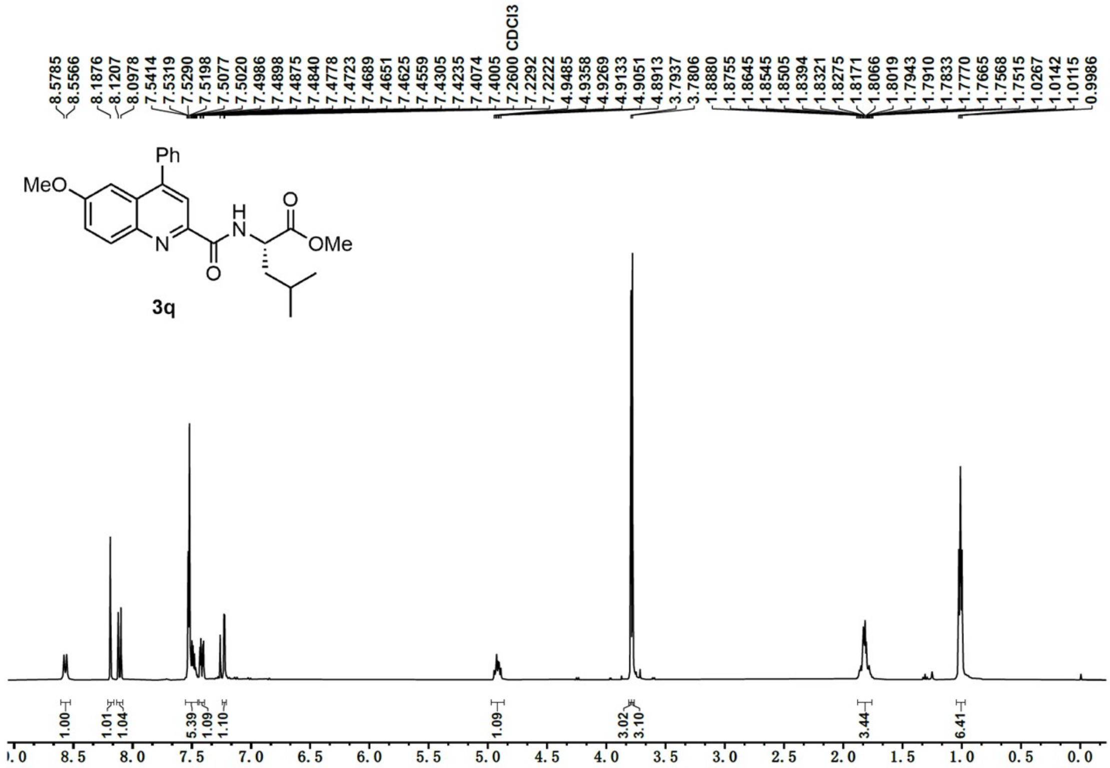

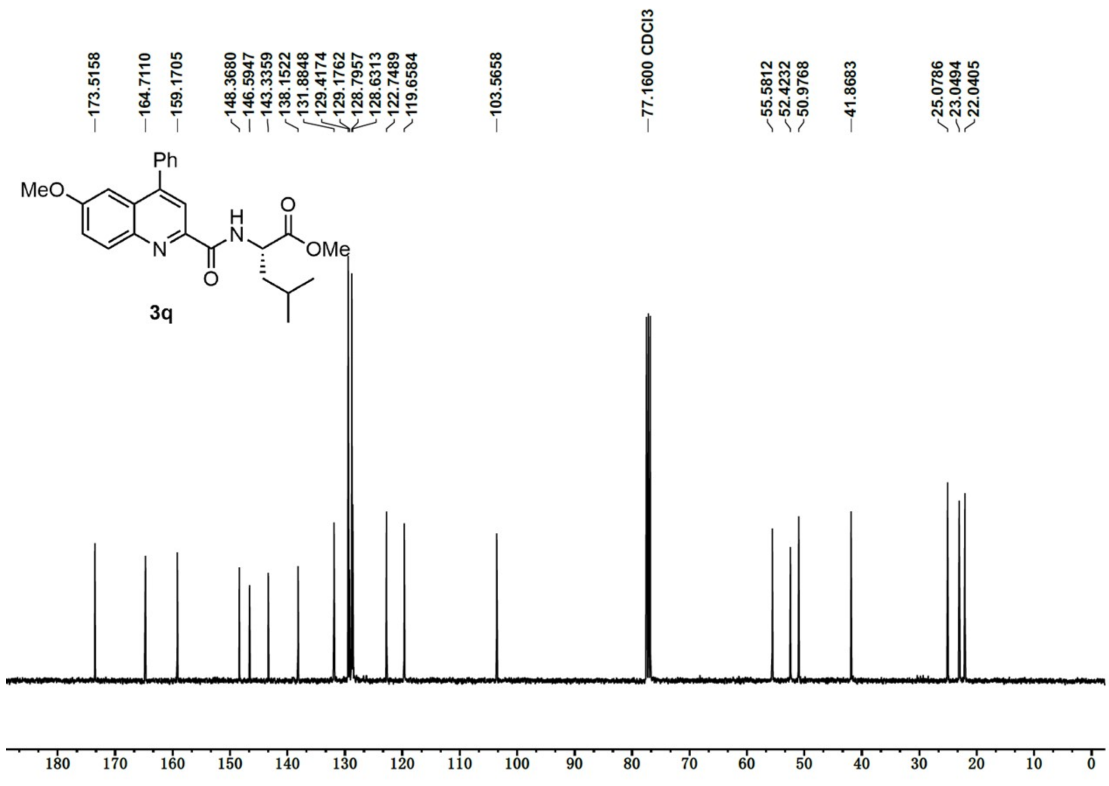

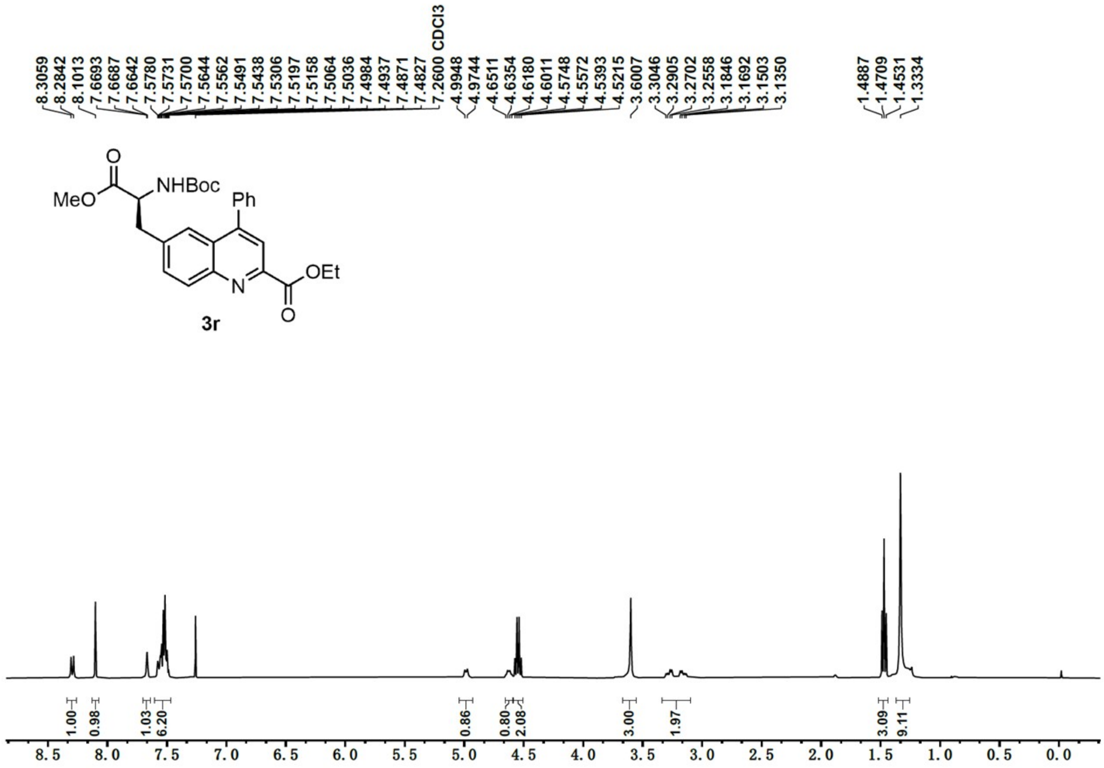
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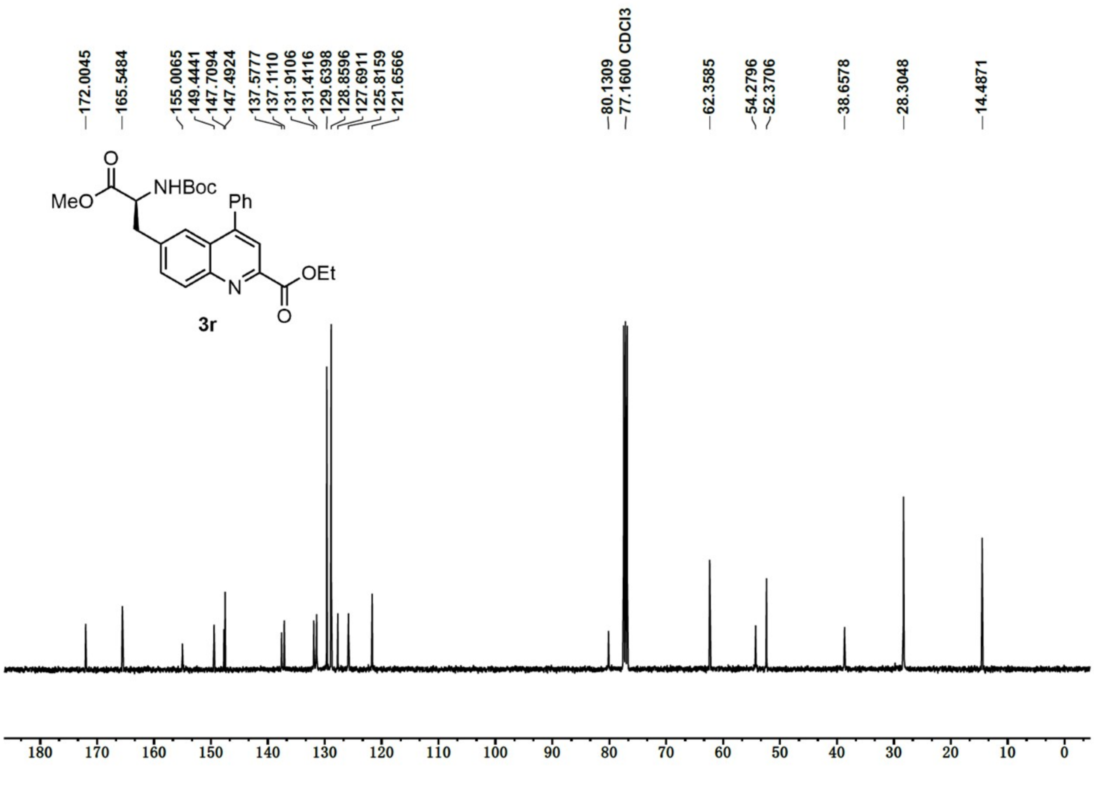
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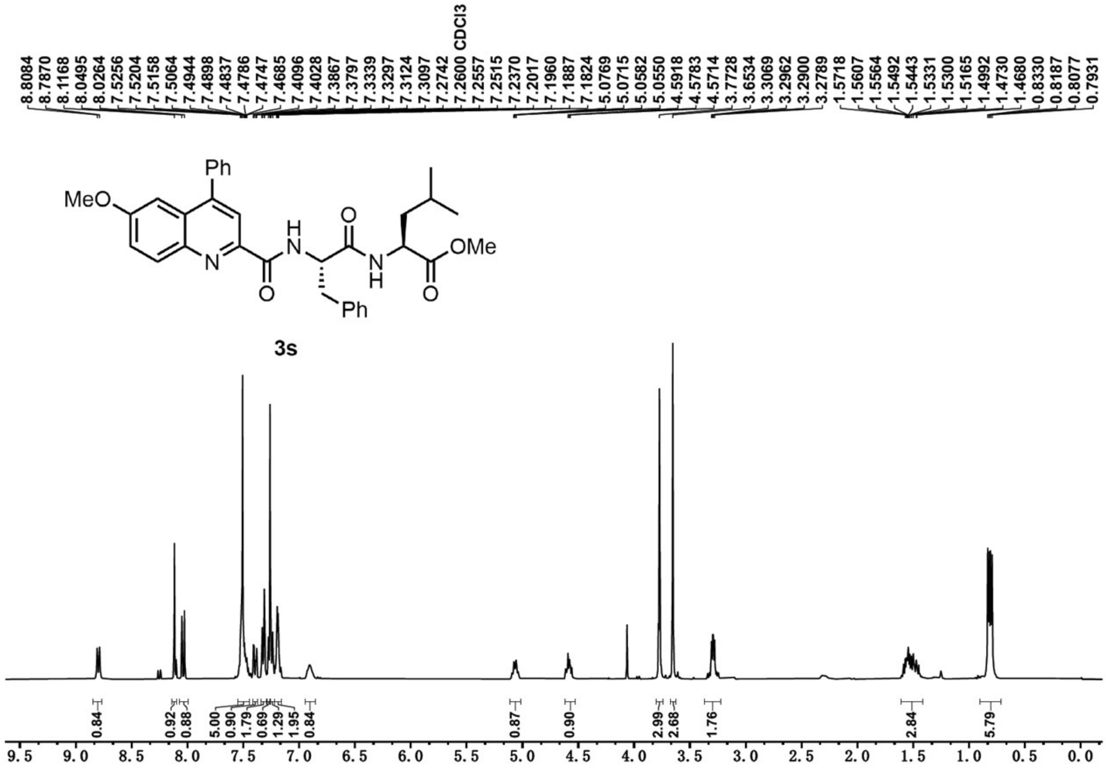
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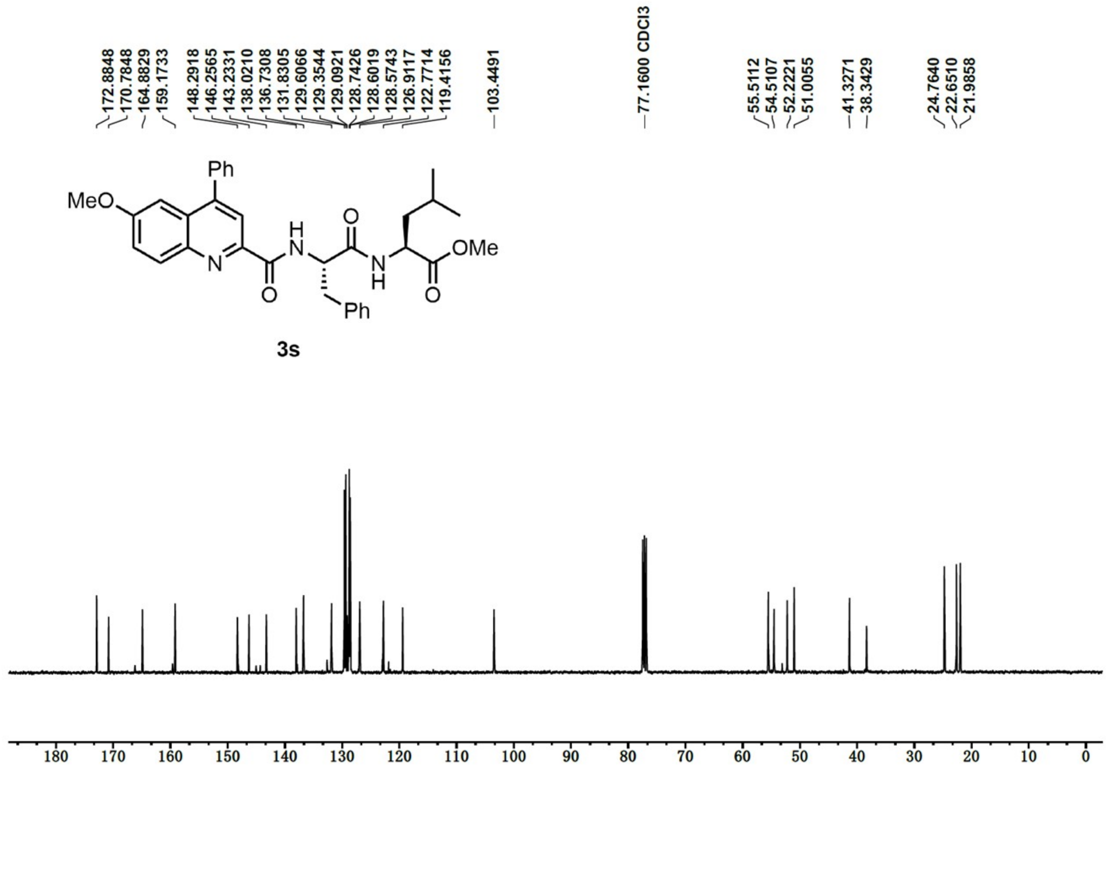
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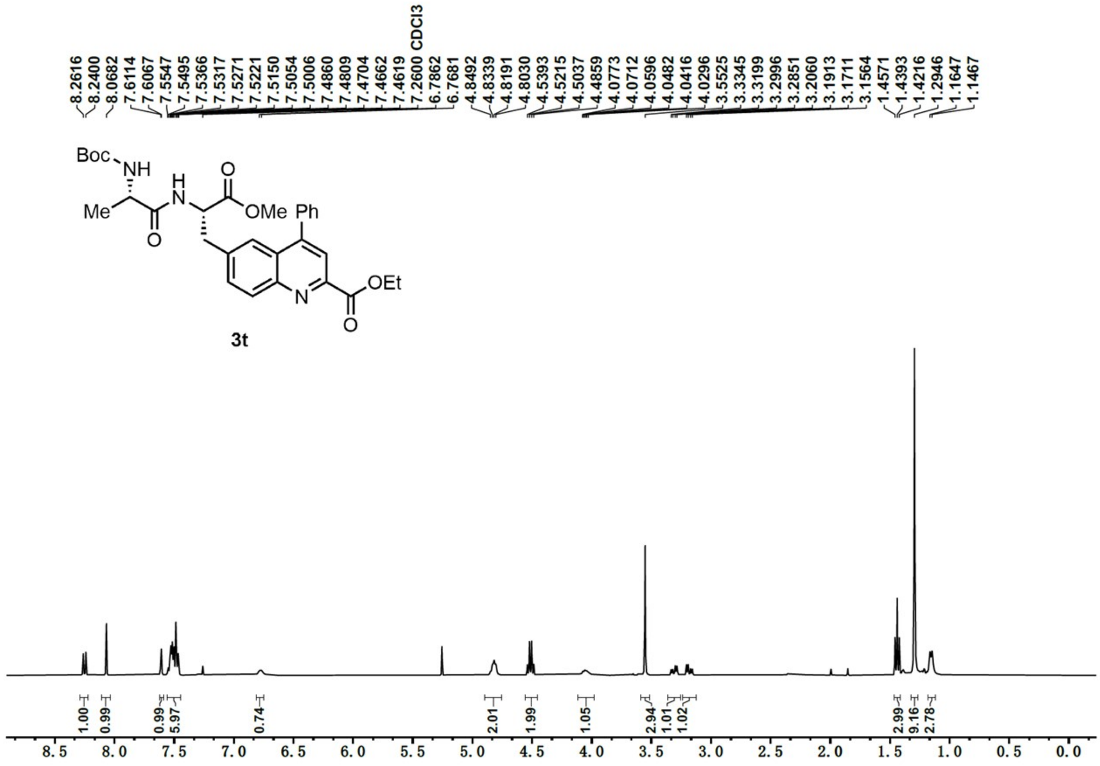

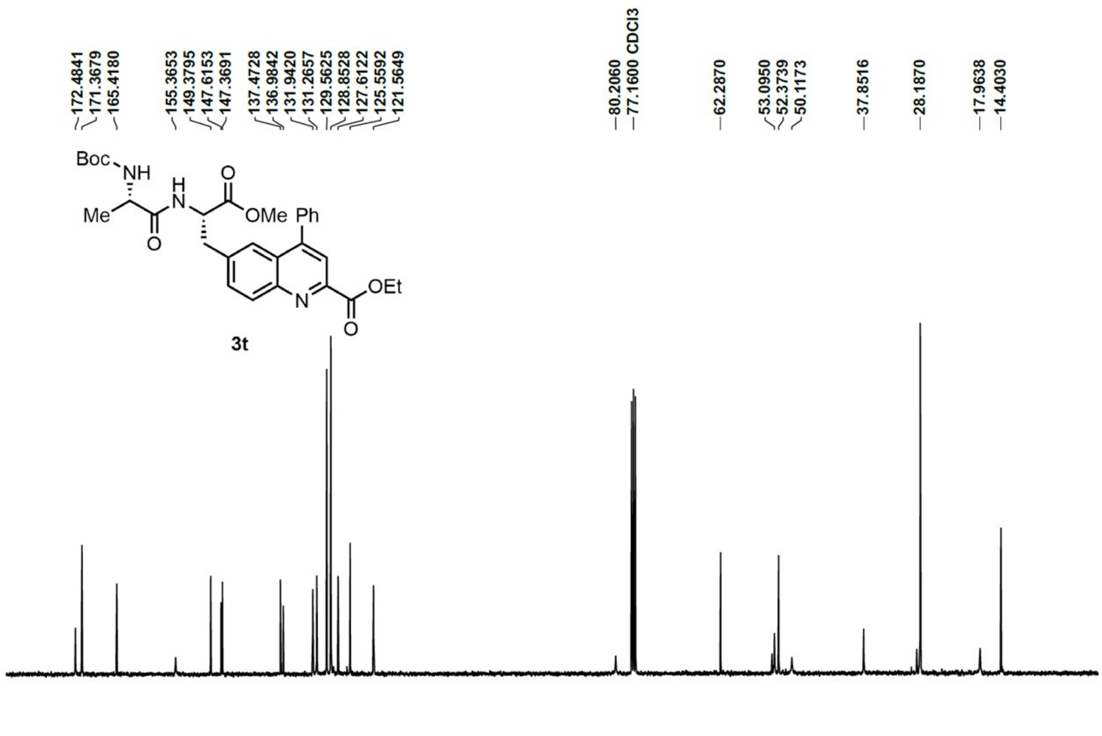

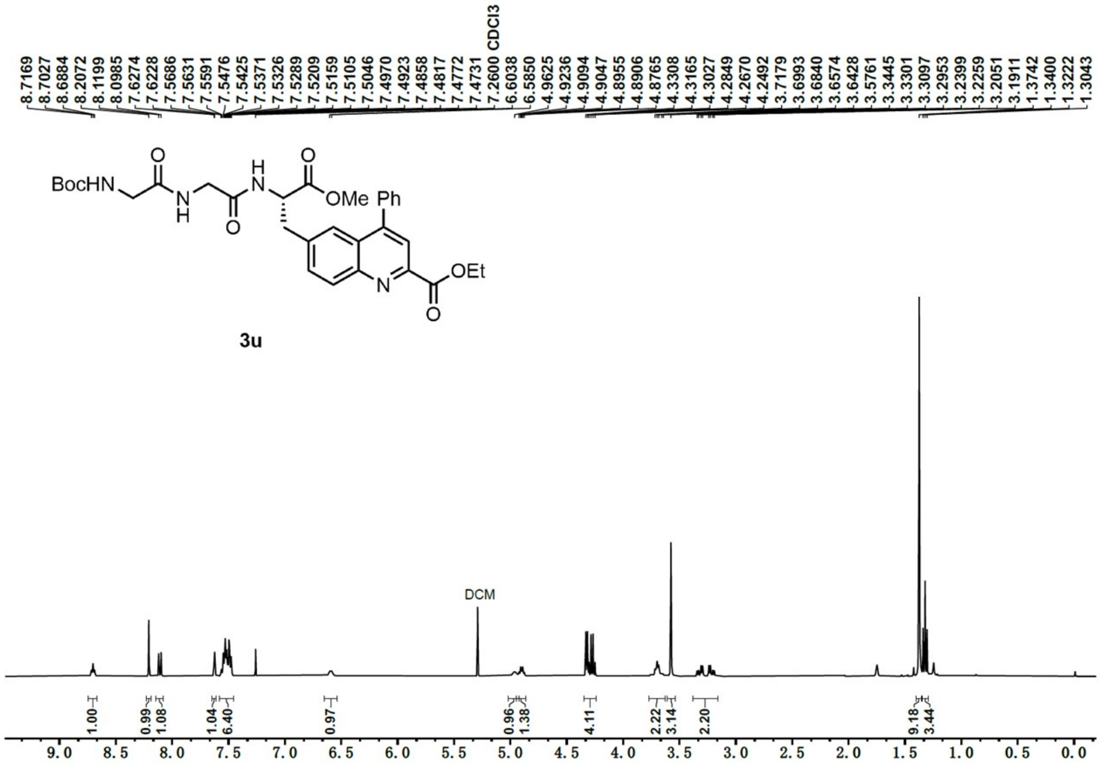
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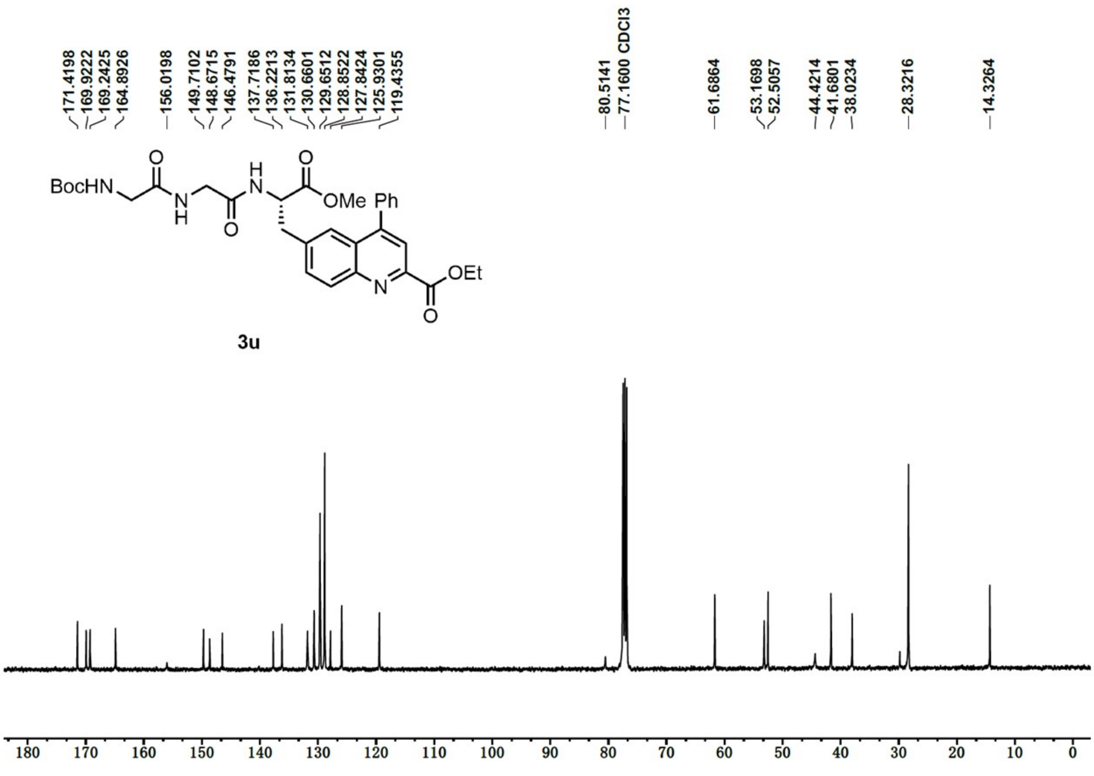
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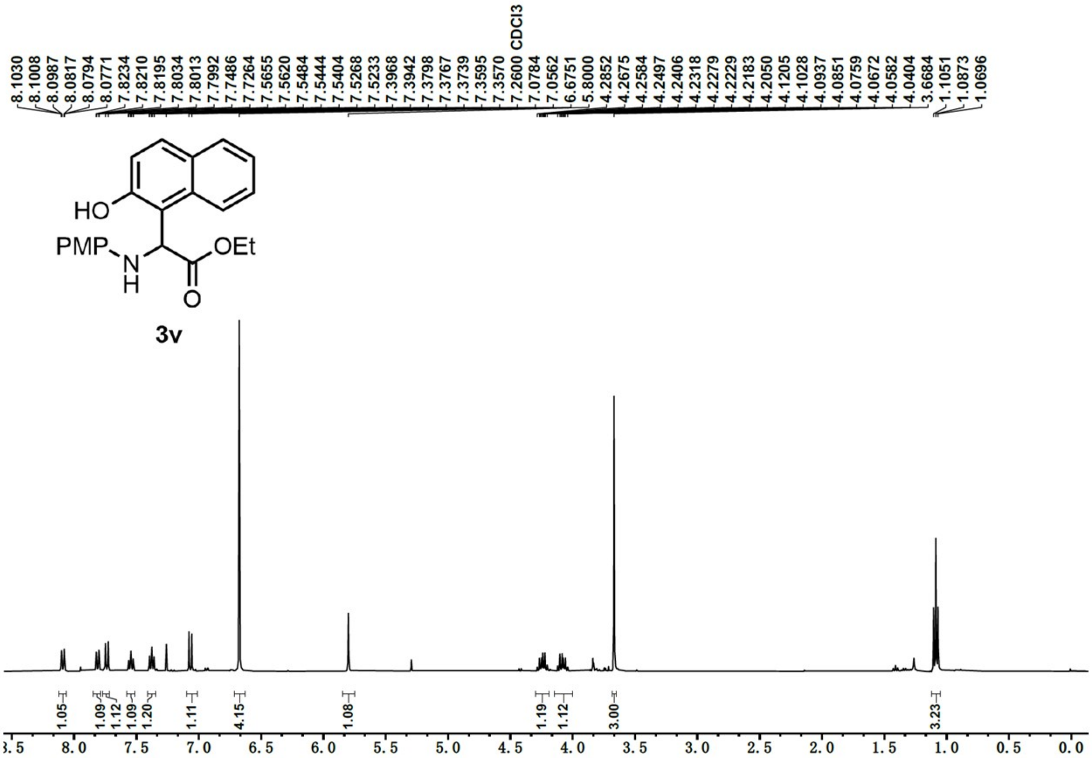

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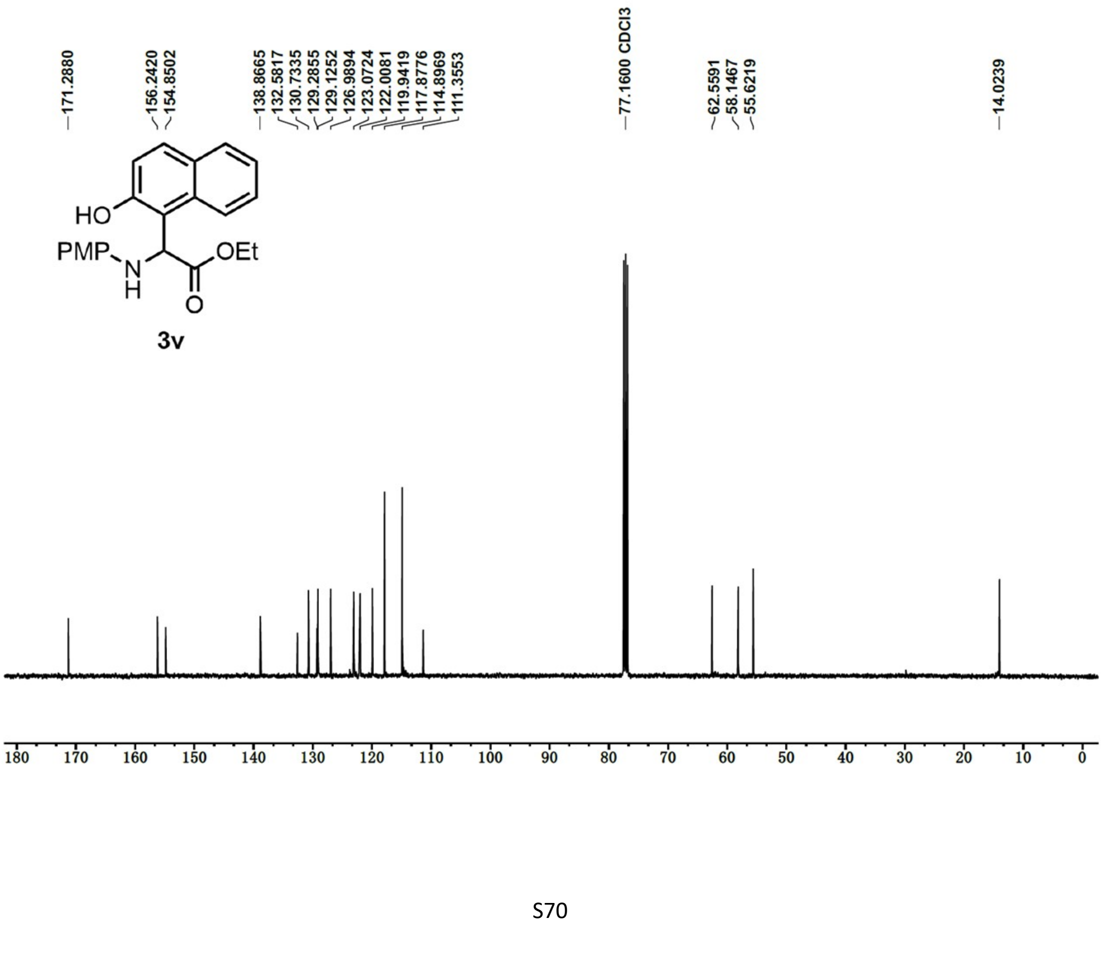

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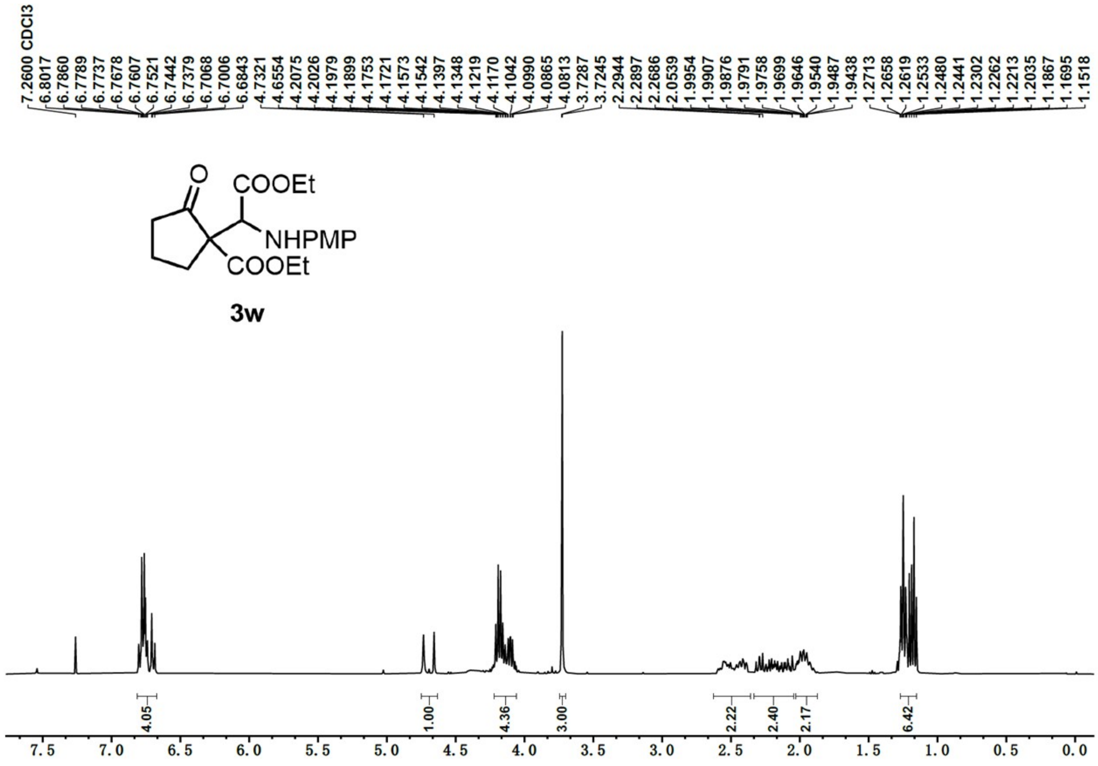
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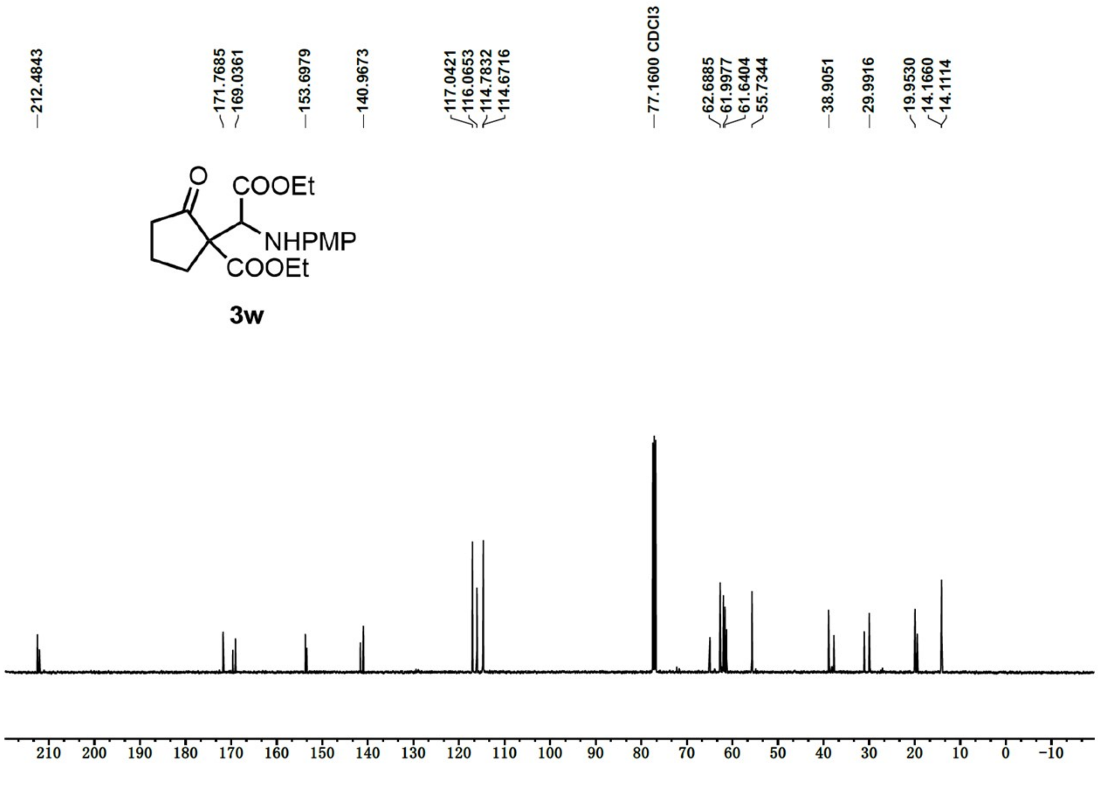
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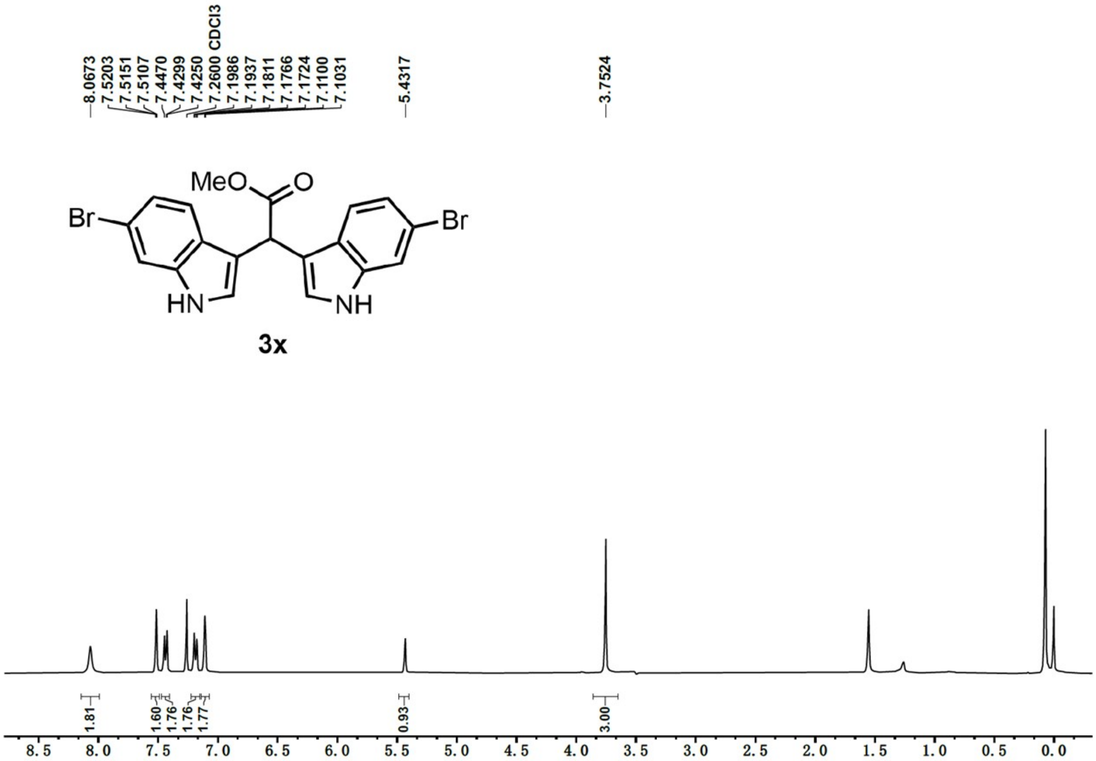

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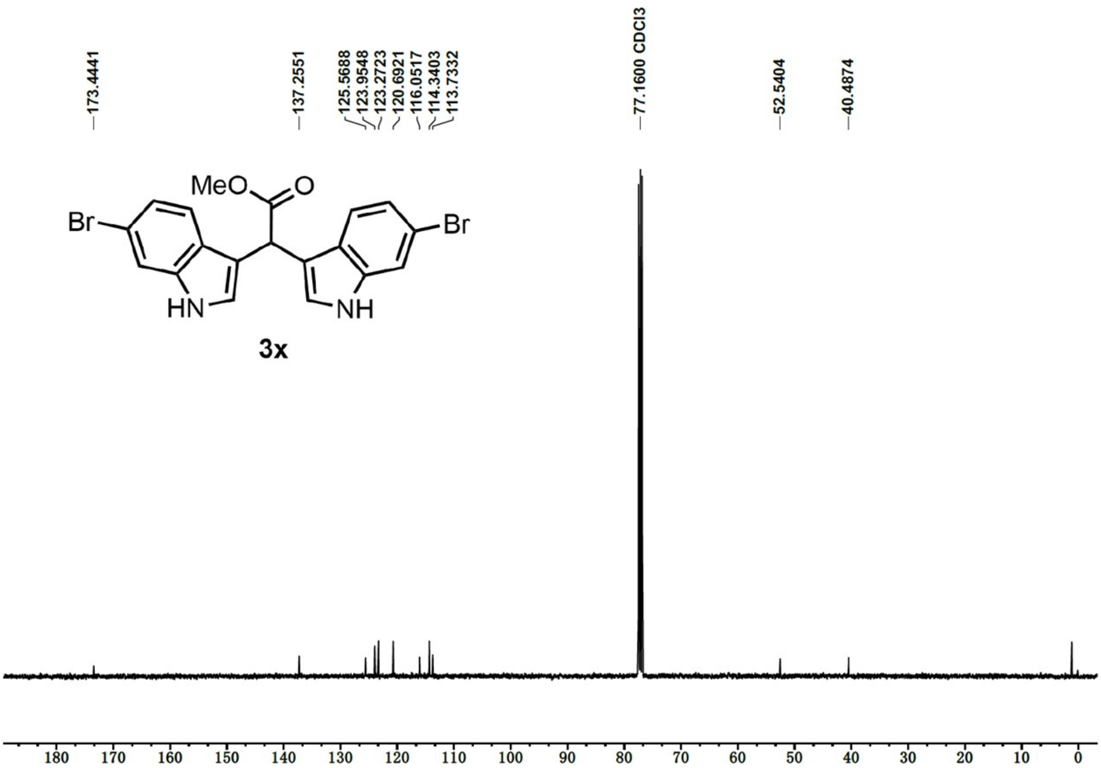

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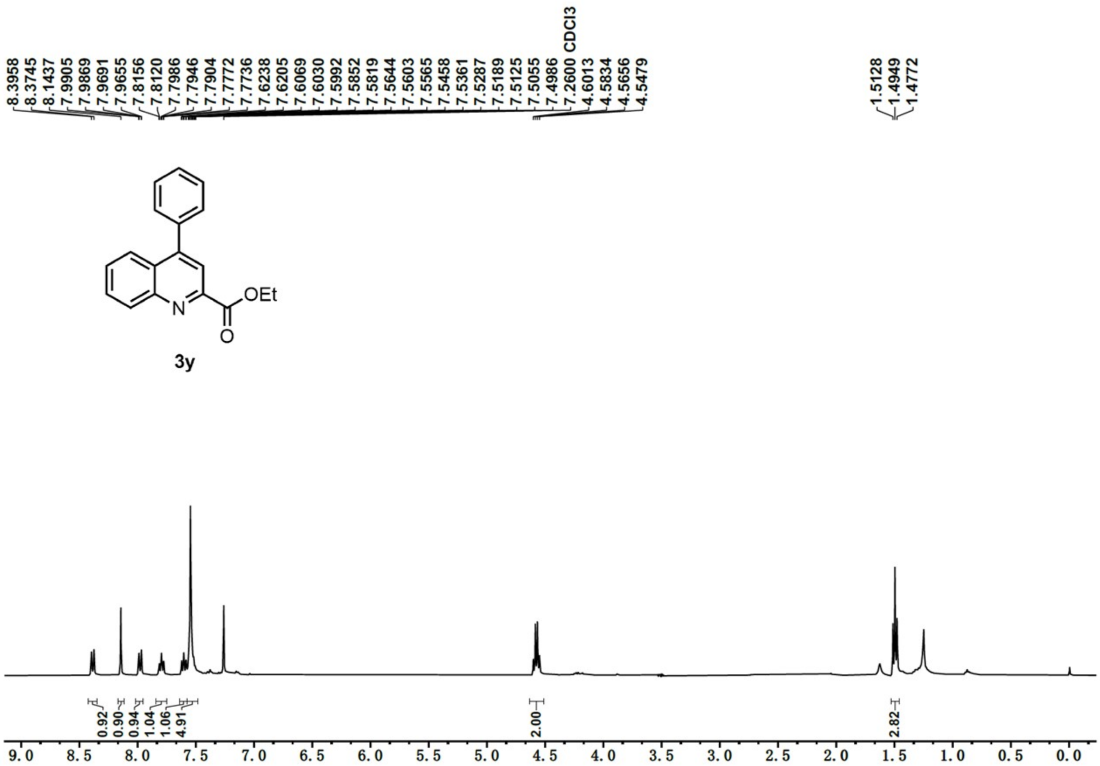

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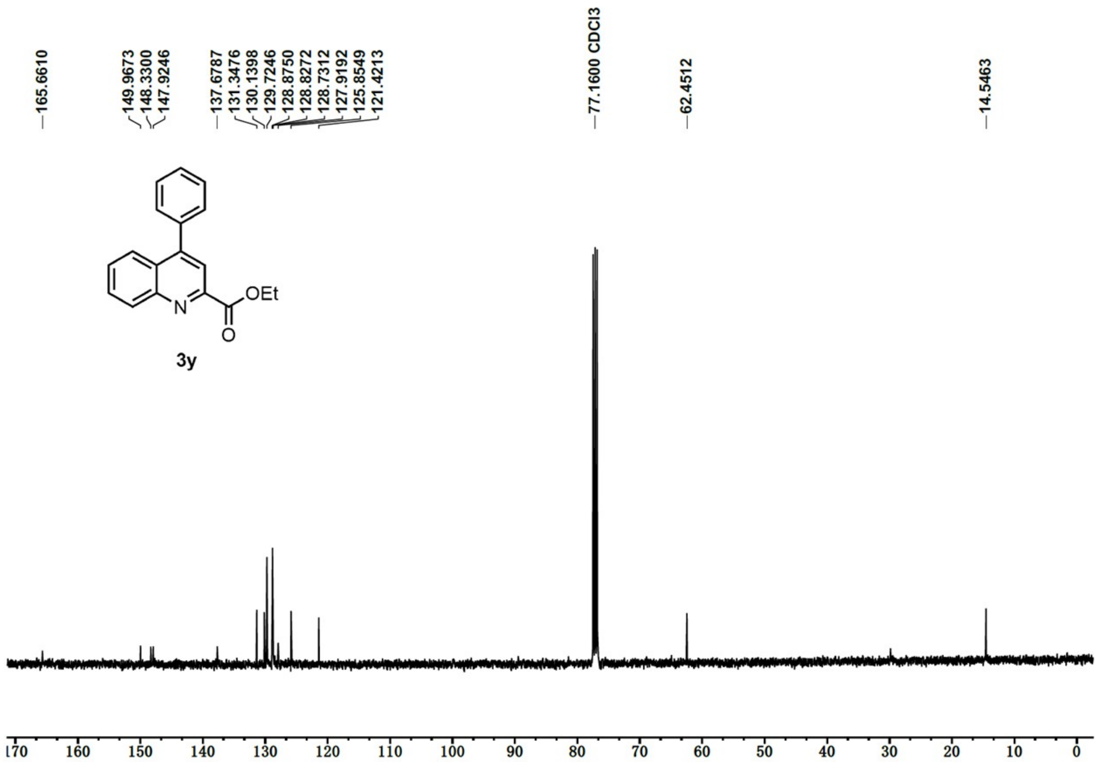

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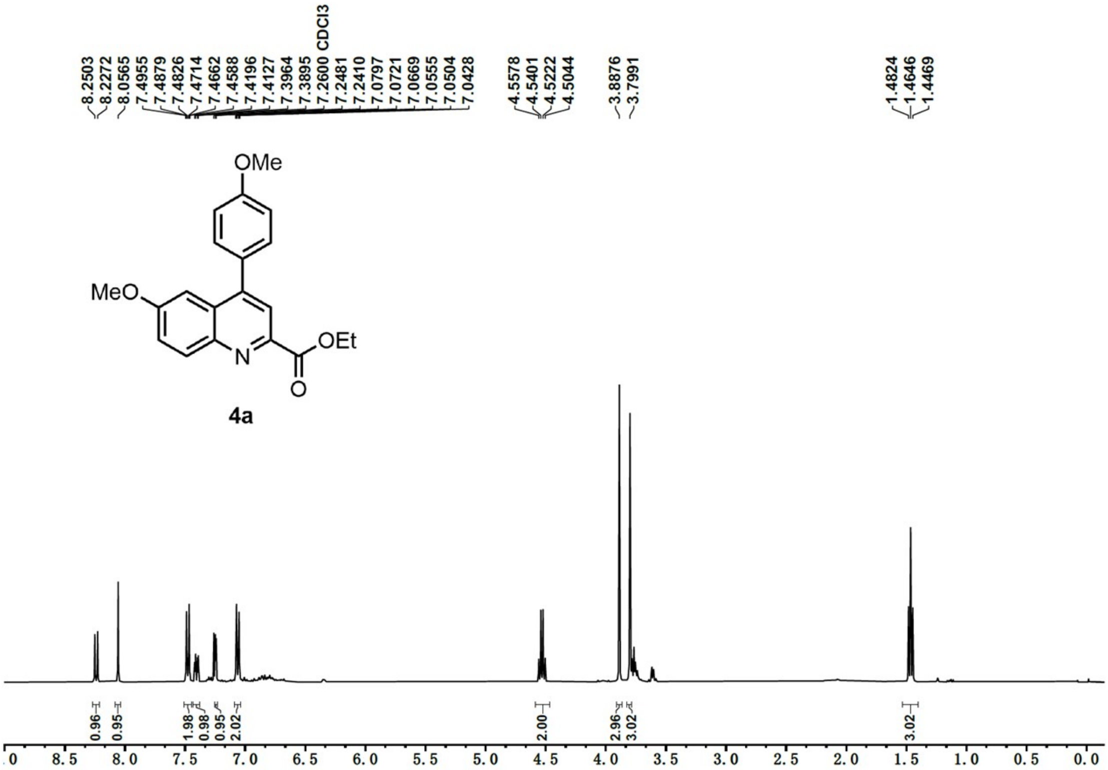
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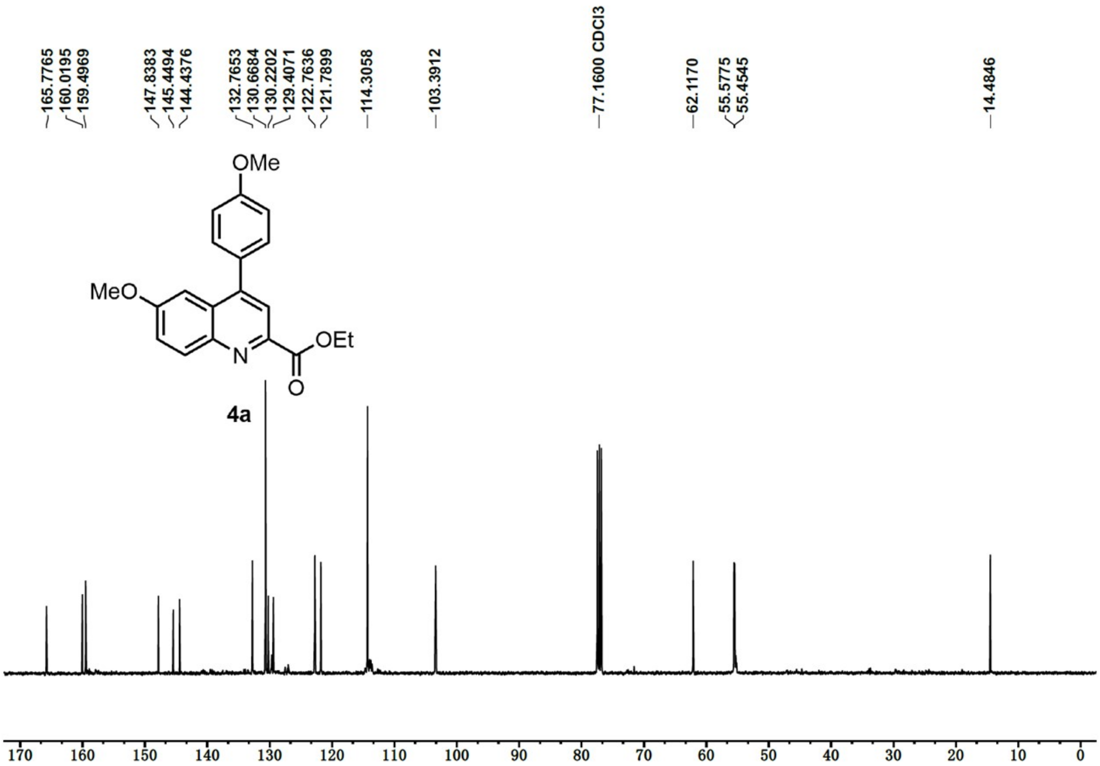
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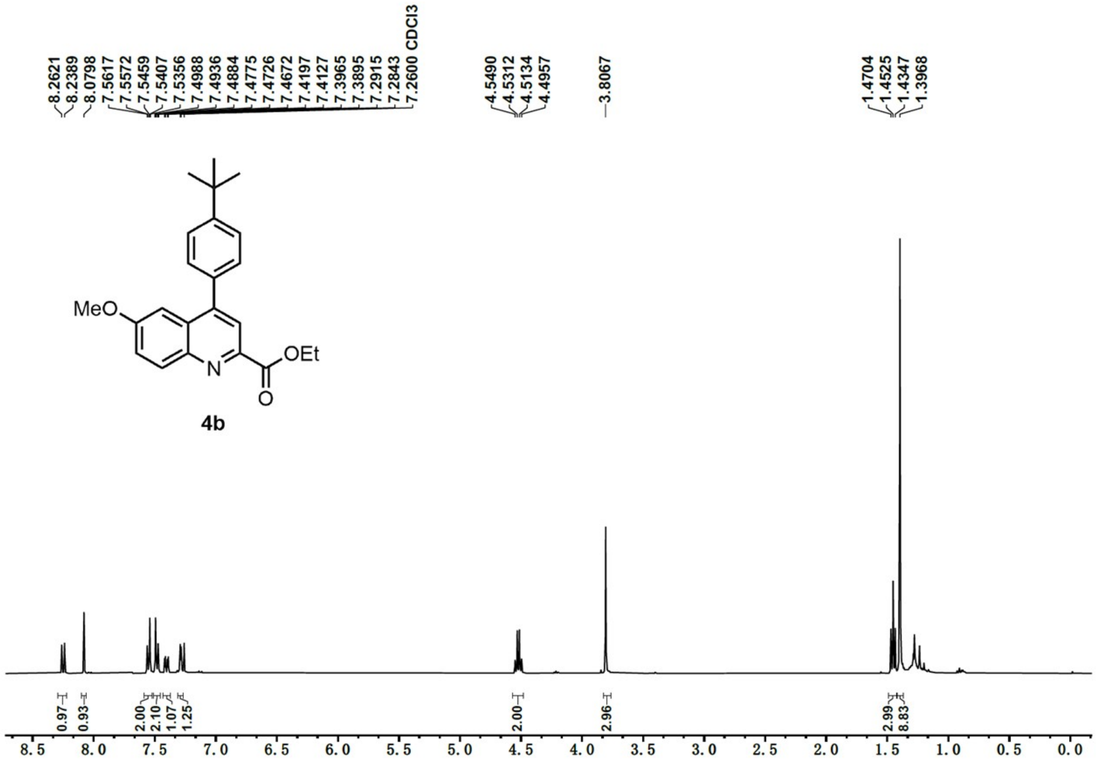
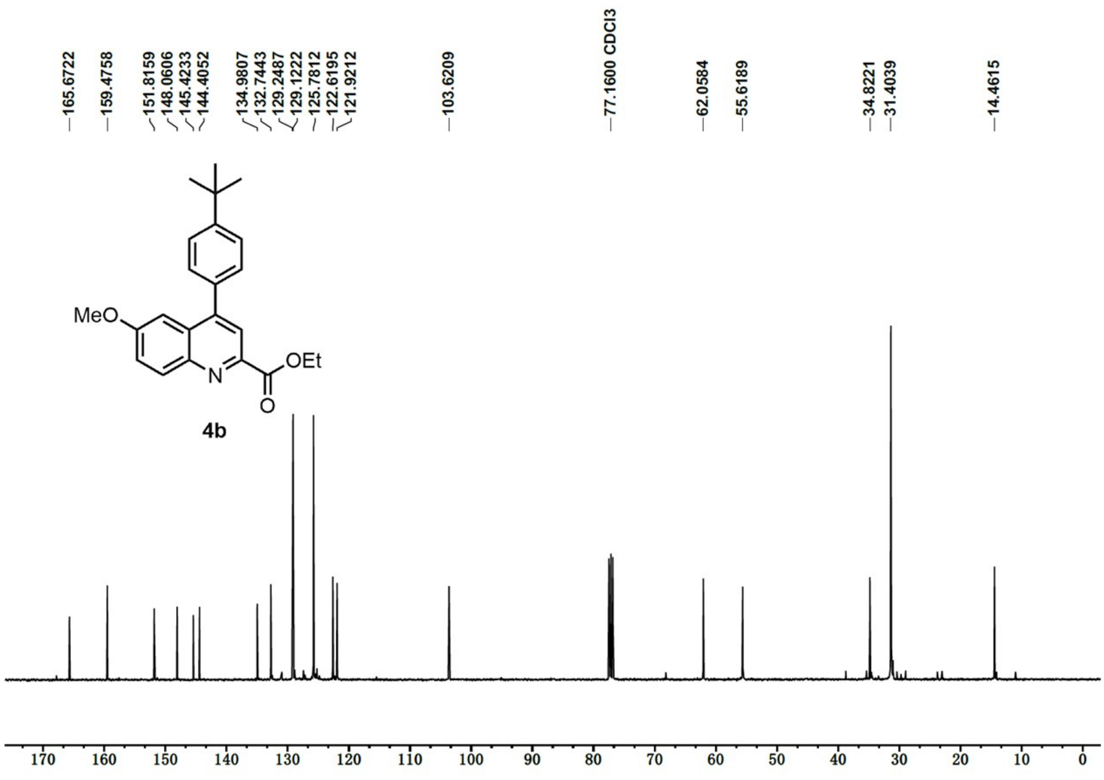
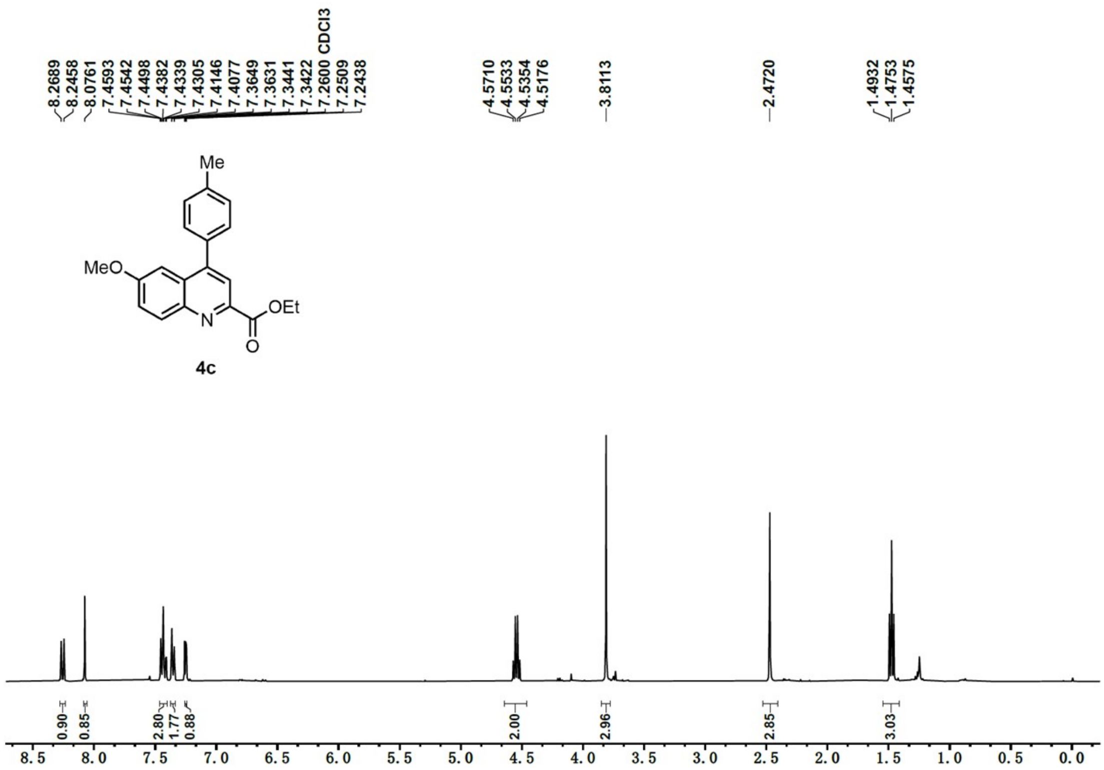
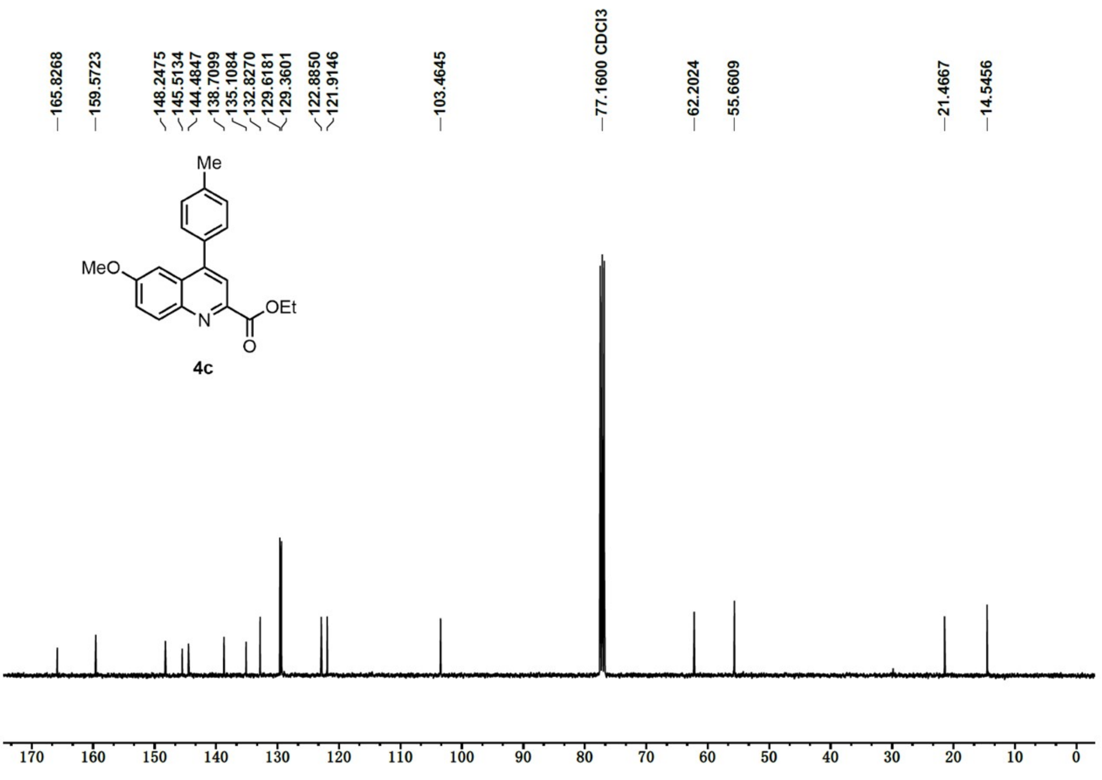
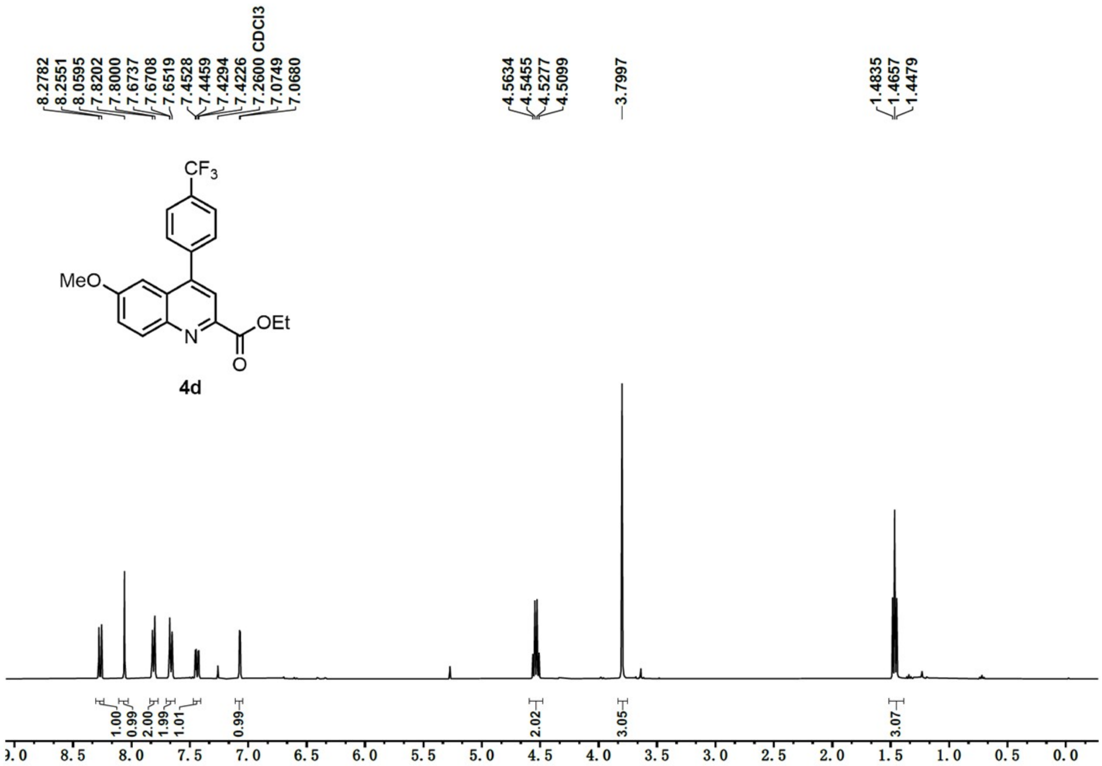
4a







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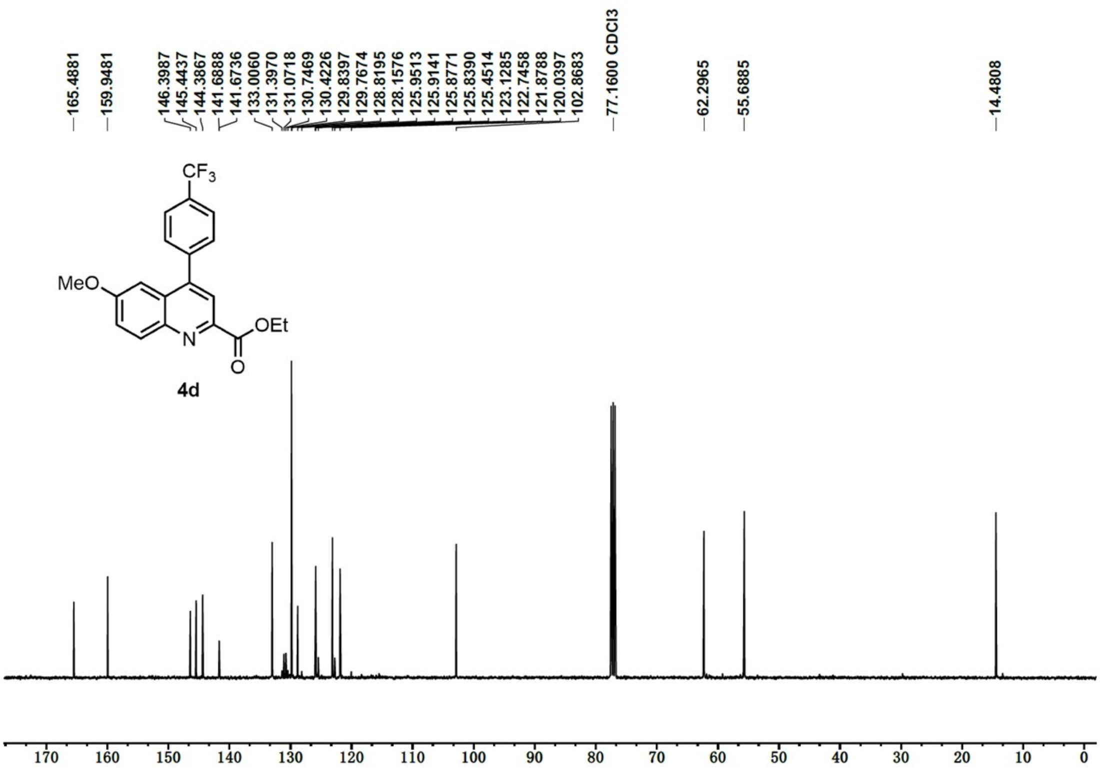
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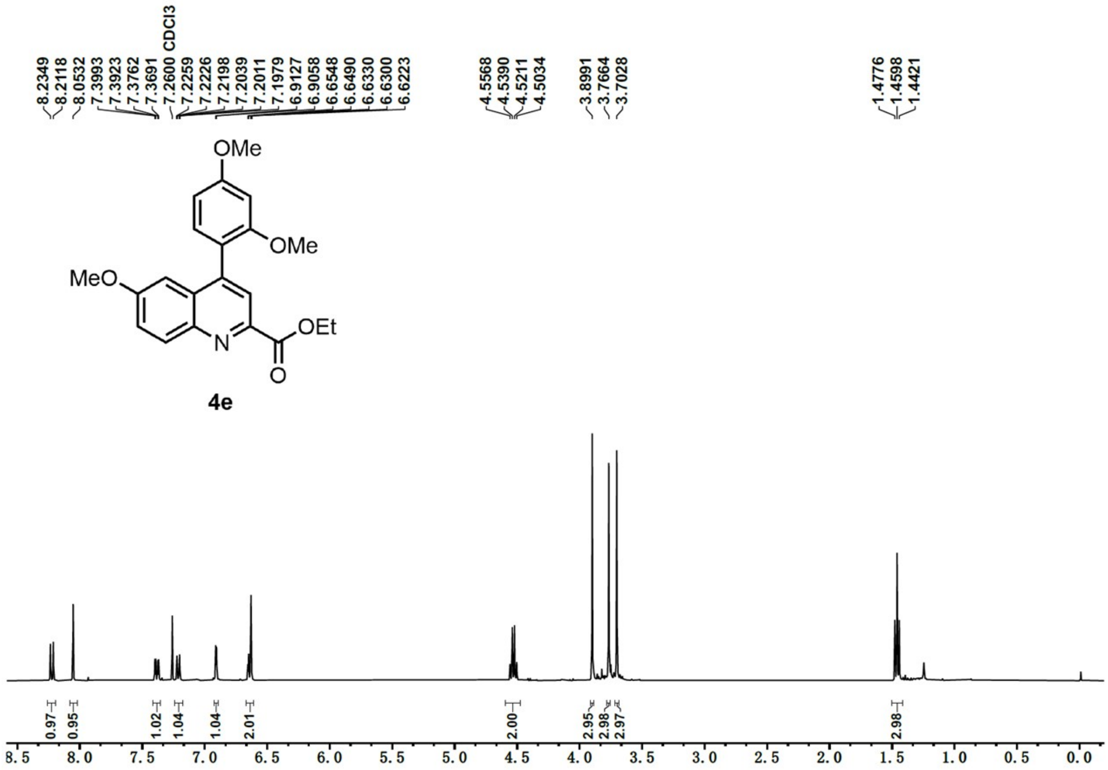
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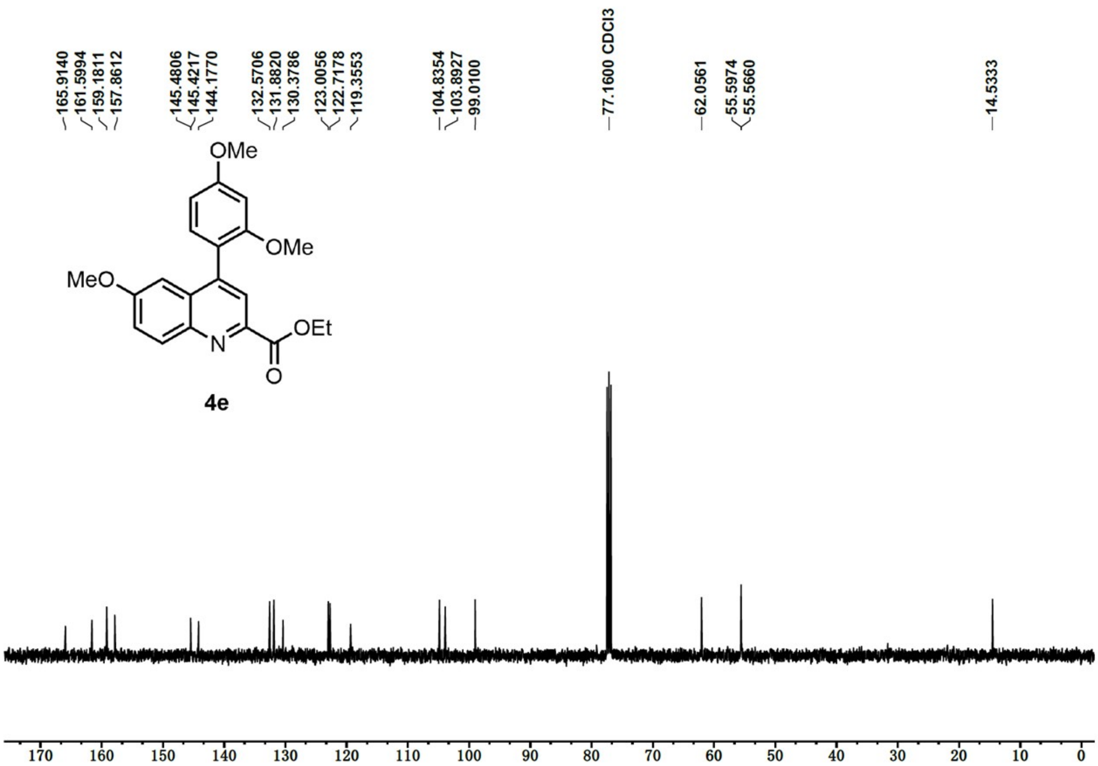
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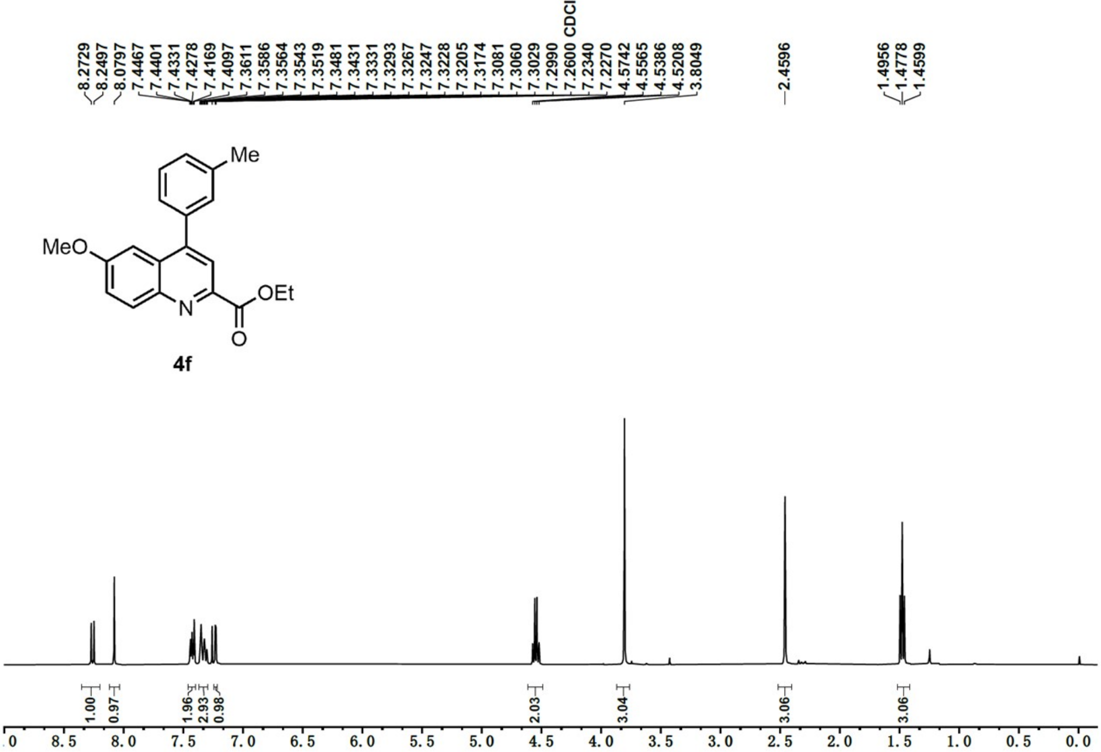
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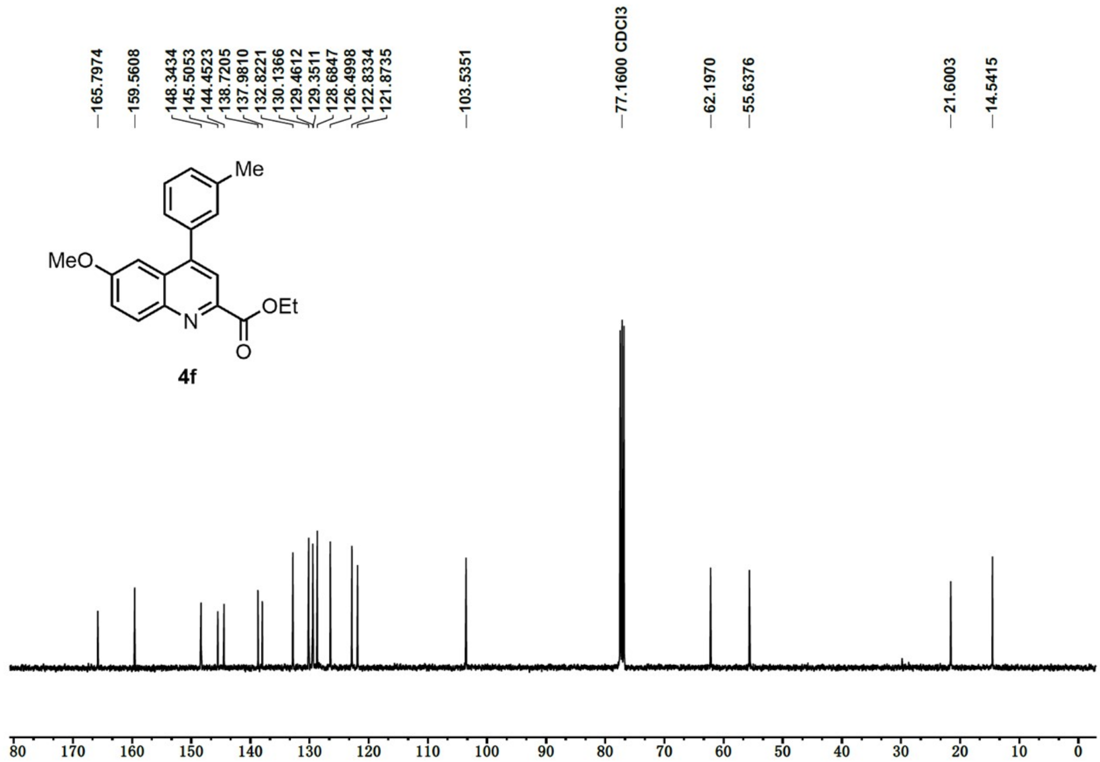
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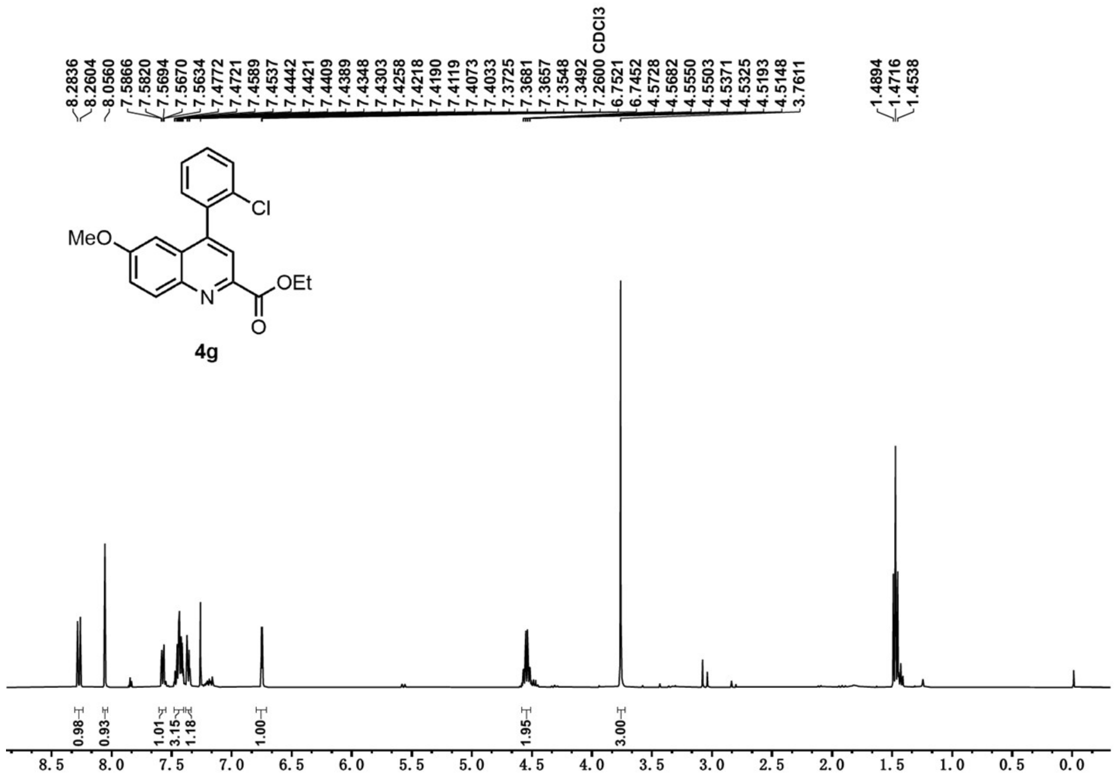

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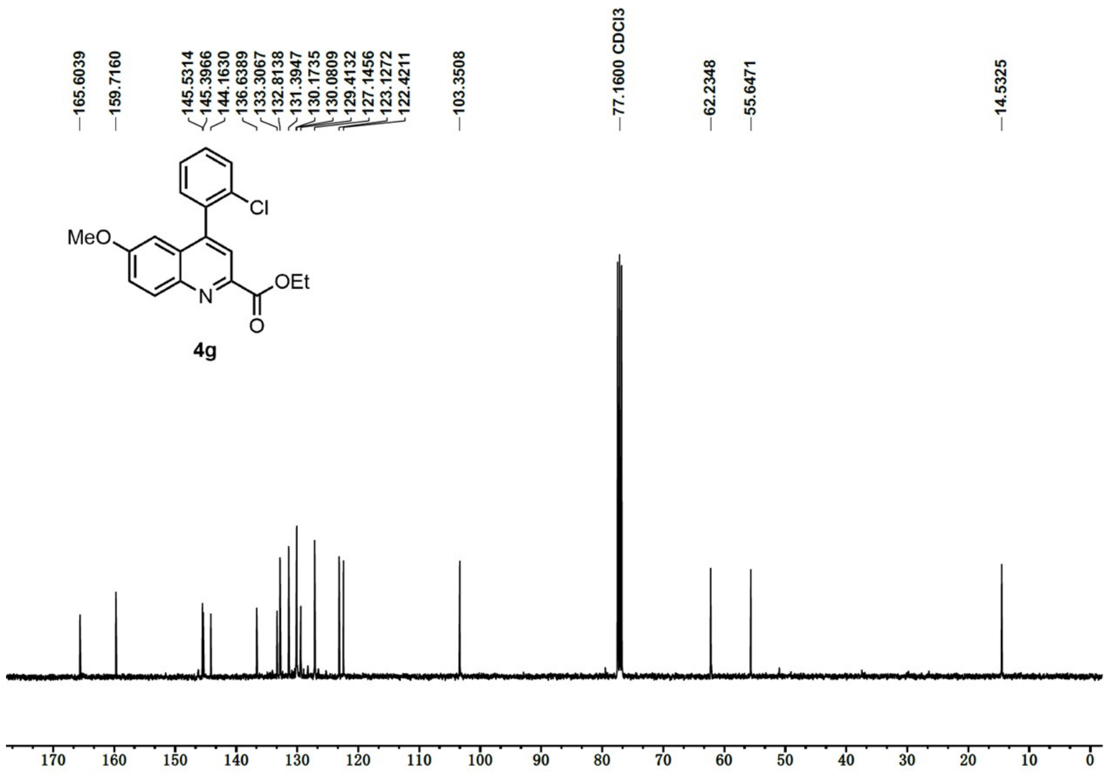

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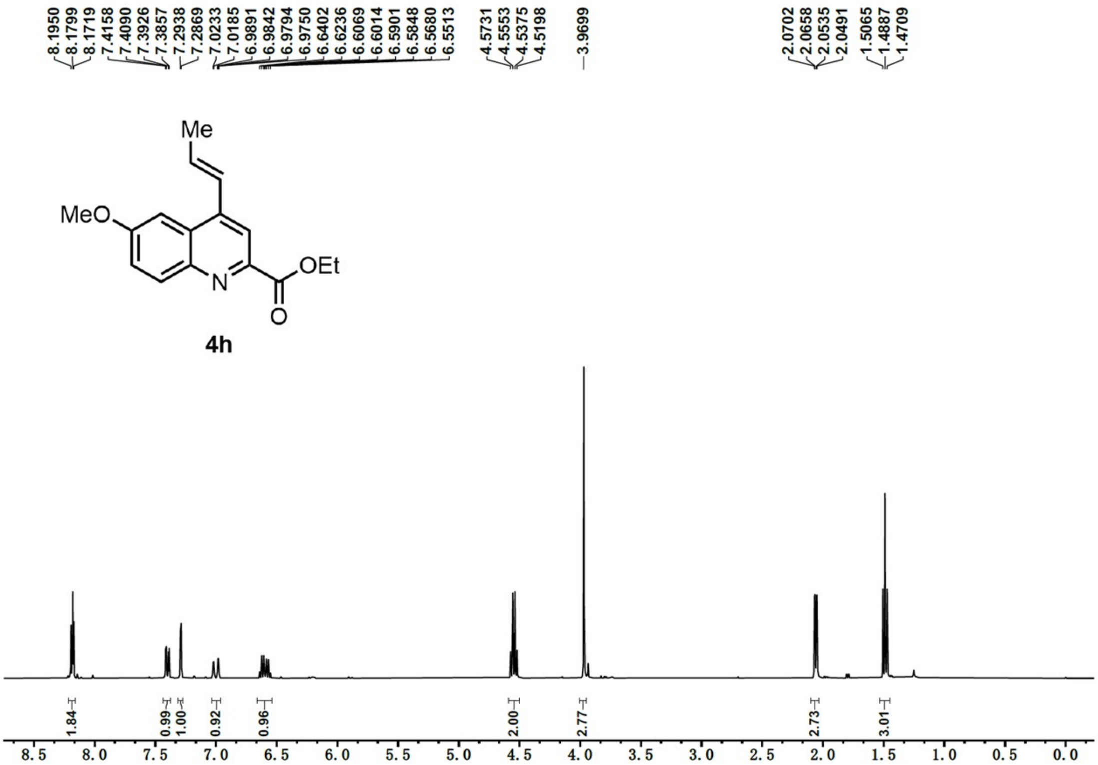
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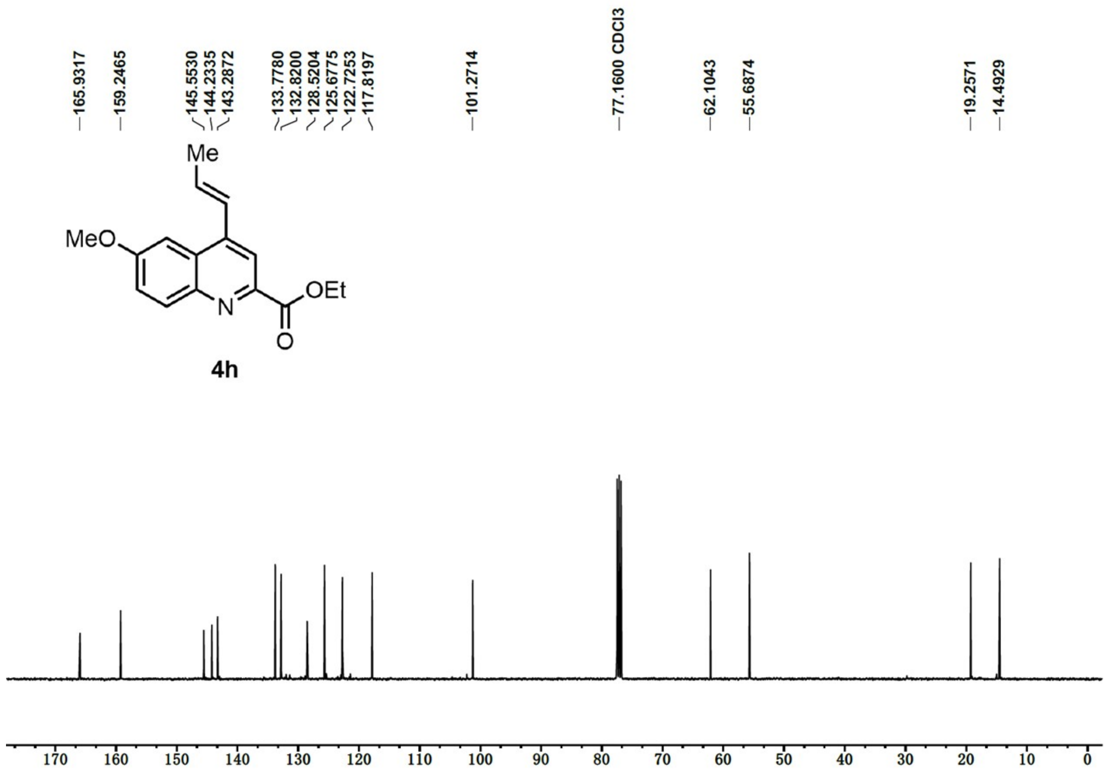
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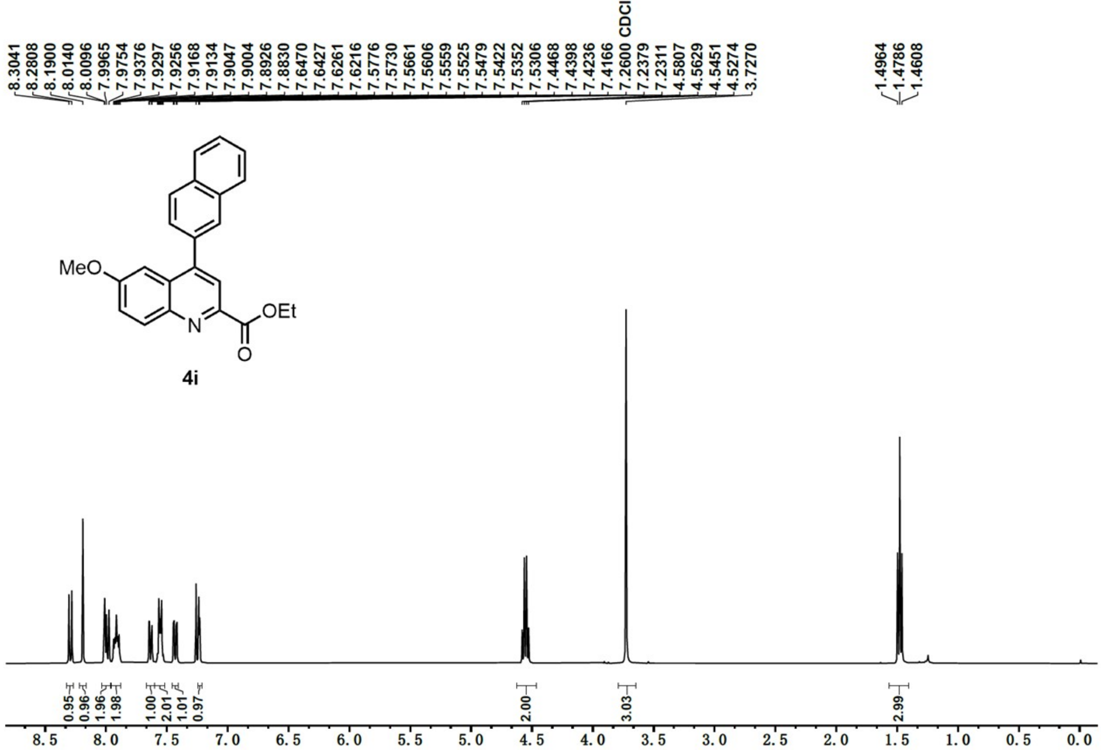
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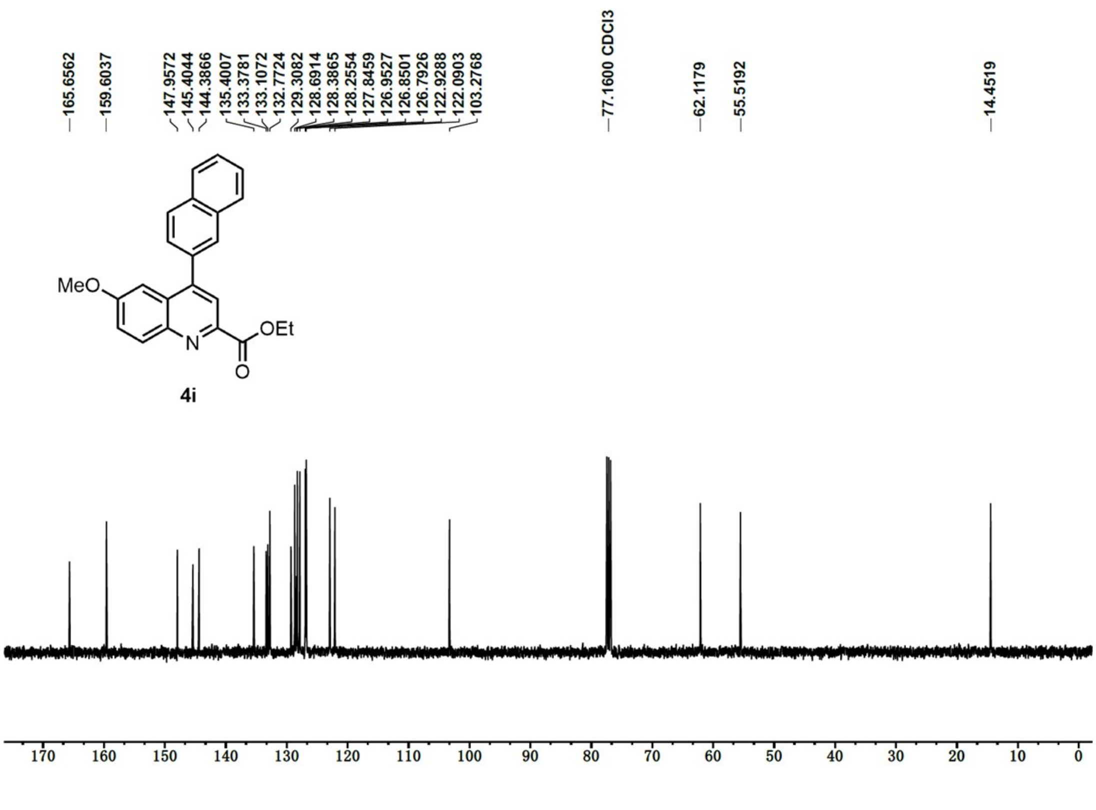
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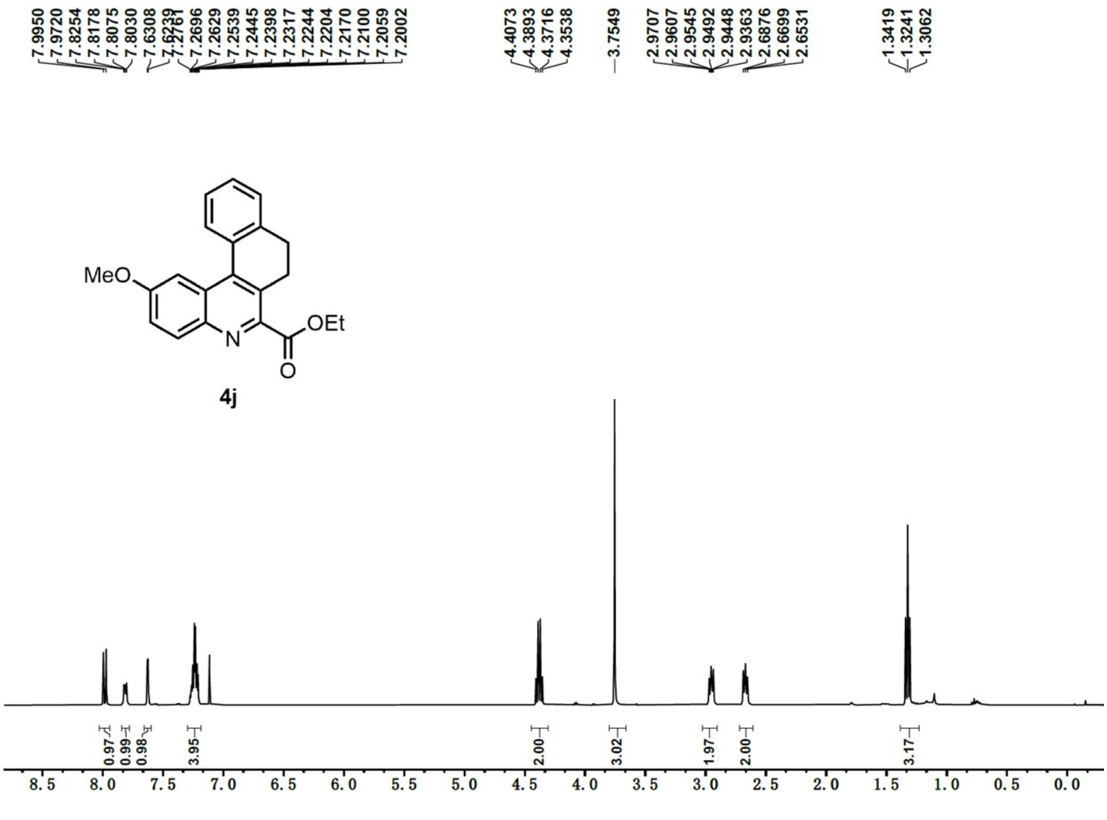

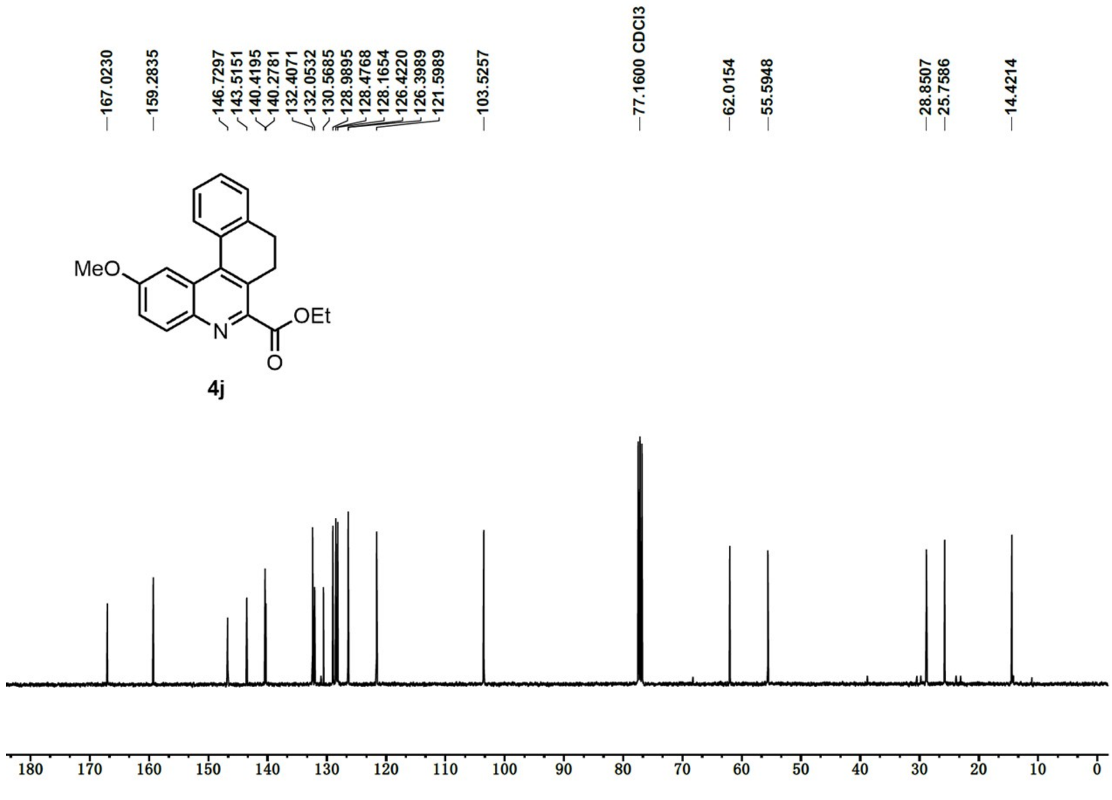

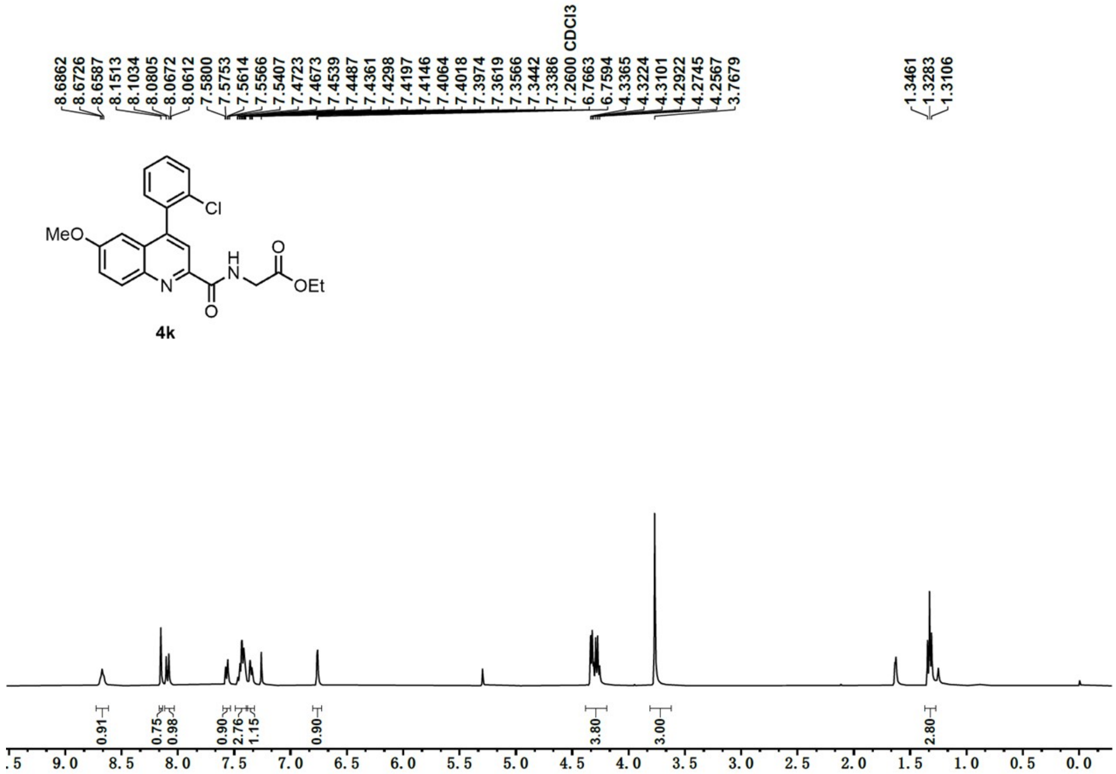

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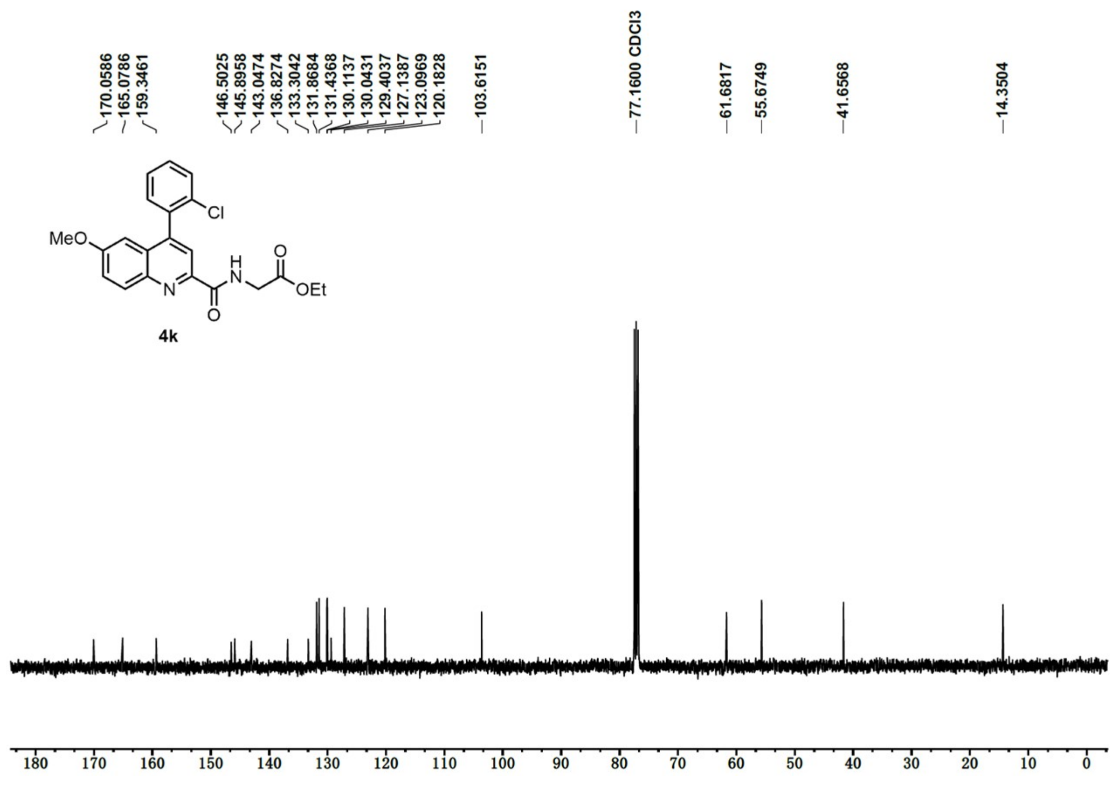

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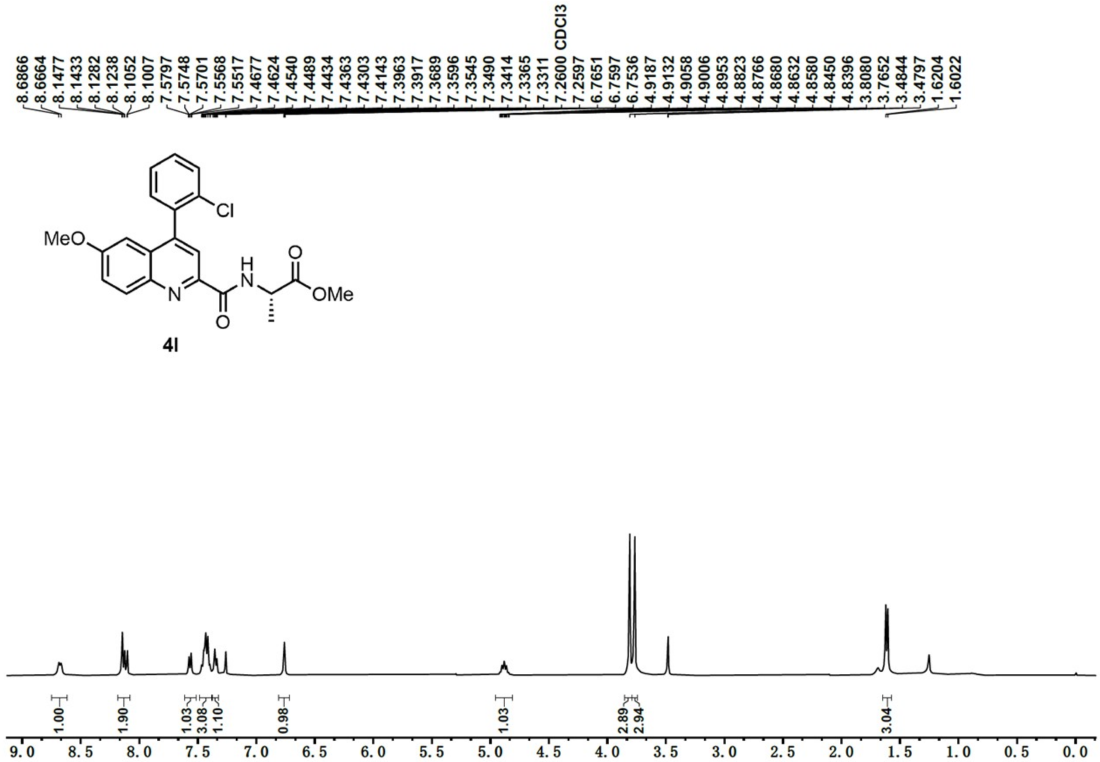

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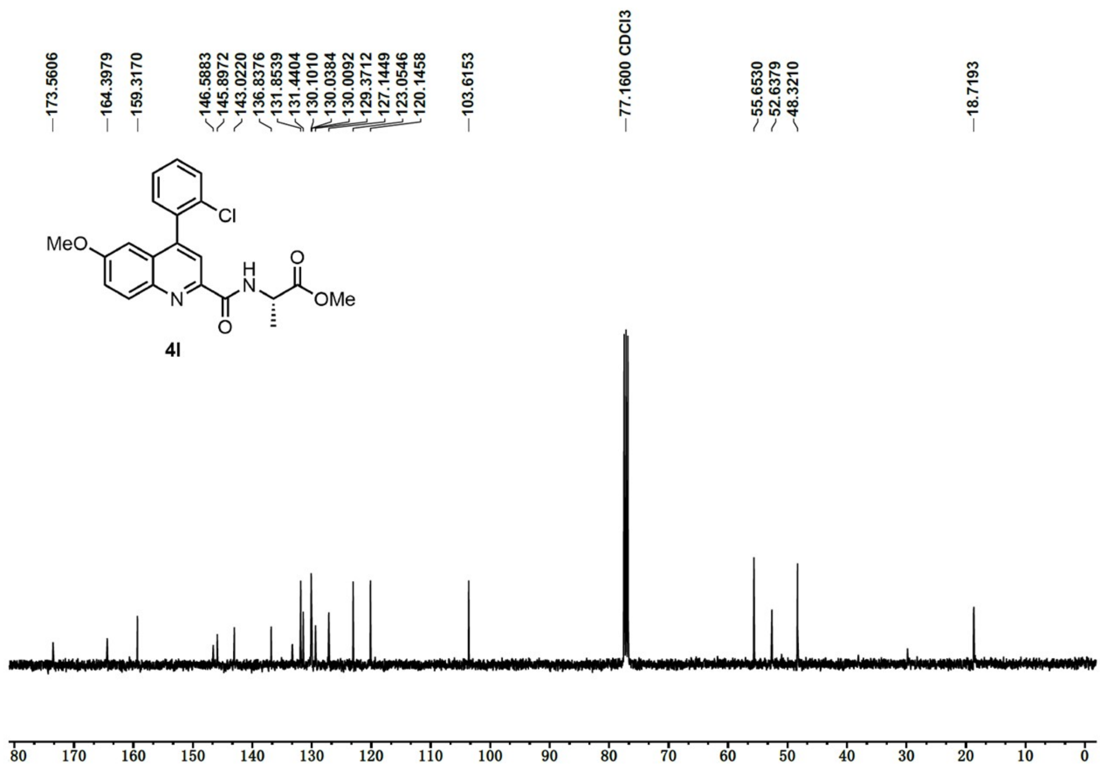

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