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Supporting Information

Asymmetric catalytic nitrooxylation and azidation of β-keto amides/esters with hypervalent iodine reagents

Changqiang He, Zhikun Wu, Yuqiao Zhou, Weidi Cao* and Xiaoming Feng*

Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064.

E-mail: xmfeng@scu.edu.cn; wdcao@scu.edu.cn

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1. General remarks

^{1}H NMR spectra were recorded on Bruker AMX-400 (400 MHz) or Bruker AMX-600 (600 MHz). The chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26). Data were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, tt = triplet of triplets), coupling constants (Hz), integration and assignment. ^{13}C NMR data were collected on Bruker AMX-400 (101 MHz) or Bruker AMX-600 (151 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.00). ^{19}F NMR spectra were collected on on Bruker AMX-400 (376 MHz) or Bruker AMX-600 (565 MHz) with complete proton decoupling. Enantiomeric excesses (ee) were determined by HPLC analysis using the corresponding commercial chiralpak column as stated in the experimental procedures at 25 ºC. Melting points (Mp) were determined using OptiMelt automated melting point system. Optical rotations were reported as follows: $[\alpha]_{\lambda}^{T}$ = (*c* = g/100 mL, in solvent). ESI-HRMS spectra were recorded as thin-films on a Perkin-Elmer Spectrum One FT-IR instrument. X-ray crystallographic data were collected by a Bruker D8 Venture Photon II. All reactions were performed in sealed oven-dried glass tubes under an atmosphere of air unless otherwise noted. All the solvents were purified by usual methods before use. Metal salts obtained from commercial sources were used without further purification. The chiral *N*,*N*'-dioxide ligands were synthesized by the same procedure in the literature.[1] The cyclic hypervalent iodine(III) reagents **2** and **4** were synthesized by the same procedure in the literature.[2, 3]

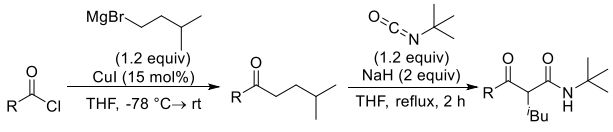
2. Synthesis of substrates

2.1 General procedures for the synthesis of the substituted indanonecarboxamides and indanonecarboxesters

Following a reported procedure,[4] NaH (60% dispersion, 2.0 equiv) was suspended in dry THF under nitrogen in an oven-dried flask. A solution of the appropriate 1-indanone (1.0 equiv) in dry THF was added dropwise. After stirring for 10 minutes, a solution of the isocyanate in dry THF was added dropwise and the mixture was heated to reflux for 2 h. After cooling to 0 °C, 1 N HCl was added cautiously until the solid had completely dissolved. The solution was extracted with Et_2O (2 x 20 mL) and the organic phase was washed with sat $NaHCO_3$ (20 mL), brine (20 mL). The combined organic layers were dried (MgSO4), filtered and evaporated. The crude was purified by column chromatography on silica gel.

To a flask equipped with a Dean-Stark trap and reflux condenser was added β-ketomethyl ester, corresponding alcohol, the transesterification catalyst ZnO and solvent (toluene or cyclohexane). The mixture was heated to reflux, distilling the methanol formed during the reaction. The mixture was refluxed for 10-24 h until complete conversion was observed by TLC, then concentrated under reduced pressure and the crude residue was purified by column chromatography.

2.2 General procedures for the synthesis of acyclic β-keto amides



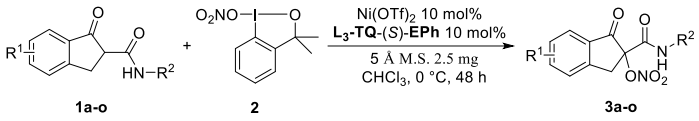
Following a reported procedure,[5] a dry Schlenk tube was charged with CuI (0.15 equiv), THF (0.1 M) and the acid chloride (1.0 equiv). The mixture was cooled to –78 °C and *i*-pentylmagnesium bromide (1.2 equiv) was added dropwise. The mixture was warmed to room temperature overnight. The mixture was diluted with NH_4Cl and EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were dried ($MgSO_4$), filtered and evaporated. The crude was purified by column chromatography on silica gel.

NaH (60% dispersion, 2.0 equiv) was suspended in dry THF under nitrogen in an oven-dried flask. A solution of the appropriate ketone (1.0 equiv) in dry THF was added dropwise. After stirring for 10 minutes, a solution of the isocyanate in dry THF was added dropwise and the mixture was heated to reflux for 2 h. After cooling to 0 °C, 1 N HCl was added cautiously until the solid had completely dissolved. The solution was extracted with Et_2O (2 x 20 mL) and the organic phase was washed with sat $NaHCO_3$ (20 mL), brine (20 mL). The combined organic layers were dried (MgSO4), filtered and evaporated. The crude was purified by column chromatography on silica gel.

3.Typical procedure for the catalytic asymmetric reaction

The corresponding racemic products were obtained by using racemic *N*,*N*'-dioxide (±)-**L_3-PiEt$_2$** as the ligand under the respective catalytic reaction conditions.

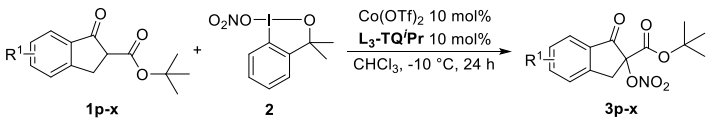
3.1 General procedure (A) for the reaction of indanonecarboxamides 1a-o and nitratobenziodoxole 2:



1a-o **2** **3a-o**

To an oven-dried tube was added $Ni(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%), **L_3-TQ**-(*S*)-**EPh** (6.3 mg, 0.01 mmol, 10 mol%), indanonecarboxamides **1a-o** (0.10 mmol) and 5 Å molecular sieves (2.5 mg) under Ar atmosphere. Anhydrous $CHCl_3$ (0.5 mL) was added and the mixture was stirred at 30 °C for 15 minutes. Subsequently, the reaction was cooled to 0 °C, a solution of the nitratobenziodoxole **2** (42.0 mg, 0.13 mmol) in $CHCl_3$ (1.0 mL) was added. The reaction was performed at 0 °C for 48 hours and directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane/ethyl acetate = 20:10:1) to afford the corresponding product **3a-o**.

3.2 General procedure (B) for the reaction of indanonecarboxesters 1p-x and nitratobenziodoxole 2:

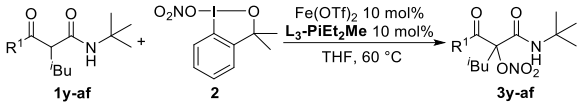


1p-x **2** **3p-x**

To an oven-dried tube was added $Co(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%), **L_3-TQ^{i}Pr** (5.1 mg, 0.01 mmol, 10 mol%), indanonecarboxesters **1p-x** (0.10 mmol) and nitratobenziodoxole **2** (42.0 mg, 0.13 mmol) under Ar

atmosphere. The mixture was cooled to -10 °C and anhydrous $CHCl_3$ (1.0 mL) was added. The reaction was performed at -10 °C for 24 hours and directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to afford the corresponding product **3p-x**.

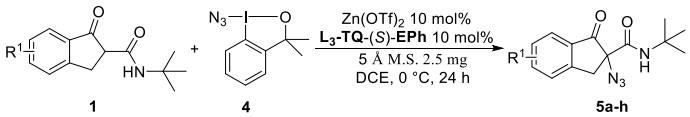
3.3 General procedure (C) for the reaction of acyclic β-keto amides 1y-af and nitratobenziodoxole 2:



1y-af 2 3y-af

To an oven-dried tube was added $Fe(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%), **L_3-PiEt$_2$Me** (6.2 mg, 0.01 mmol, 10 mol%) and acyclic β-keto amides **1y-af** (0.10 mmol) under Ar atmosphere. Anhydrous THF (1.0 mL) was added and the mixture was stirred at 30 °C for 15 minutes. Subsequently, the nitratobenziodoxole **2** (35.5 mg, 0.11 mmol) was added and the reaction was performed at 60 °C. The reaction mixture was directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20:1) to afford the corresponding product **3y-af**.

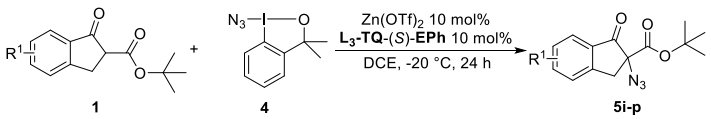
3.4 General procedure (D) for the reaction of indanonecarboxamides and azidoiodinane 4:



1 4 5a-h

To an oven-dried tube was added $Zn(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%), **L_3-TQ**-(*S*)-**EPh** (6.3 mg, 0.01 mmol, 10 mol%), 5 Å molecular sieves (2.5 mg), indanonecarboxamides **1** (0.10 mmol) and azidoiodinane **4** (39.4 mg, 0.13 mmol) under Ar atmosphere. The mixture was cooled to 0 °C and anhydrous DCE (1.0 mL) was added. The reaction was performed at 0 °C for 24 hours and directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane/ethyl acetate = 20:10:1) to afford the corresponding product **5a-h**.

3.5 General procedure (E) for the reaction of indanonecarboxesters and azidoiodinane 4:



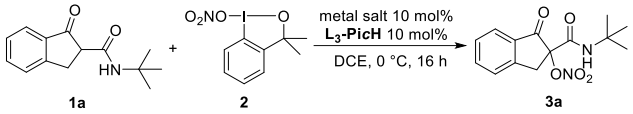
1 4 5i-p

To an oven-dried tube was added $Zn(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%), **L_3-TQ**-(*S*)-**EPh** (6.3 mg, 0.01 mmol, 10 mol%), indanonecarboxesters **1** (0.10 mmol) and azidoiodinane **4** (39.4 mg, 0.13 mmol) under Ar atmosphere. The mixture was cooled to -20 °C and anhydrous DCE (1.0 mL) was added. The reaction was performed at -20 °C for 24 hours and directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 20:1) to afford the corresponding product **5i-p**.

4. Optimization of reaction conditions

4.1. The reaction of indanonecarboxamide and nitratobenziodoxole 2

Table S1. Screening of the metal salts[a]

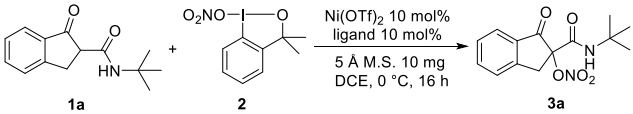


1a 2 3a

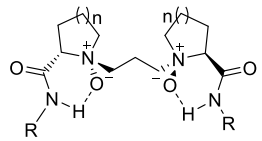
Entry	Metal salt	Yield (%)[b]	ee (%)[c]
1	$Sc(OTf)_3$	64	5
2	$Mg(OTf)_2$	68	12
3	$Co(BF_4)_2{\cdot}6H_2O$	67	72
4	$Co(OTf)_2$	69	67
5	$Ni(OTf)_2$	68	76
6	$Ni(BF_4)_2{\cdot}6H_2O$	74	68
7	$Ni(ClO_4)_2{\cdot}6H_2O$	64	55
8	$Ni(acac)_2$	63	48
9	$Ni(OTs)_2{\cdot}6H_2O$	73	39
10[d]	$Ni(OTf)_2$	76	68
11[e]	$Ni(OTf)_2$	85	53
12[f]	$Ni(OTf)_2$	61	68
13[g]	$Ni(OTf)_2$	75	80

[a]Unless otherwise noted, all reactions were carried out with metal salt (0.01 mmol, 10 mol%), *N,N'*-dioxide **L$_3$-PicH** (4.9 mg, 0.01 mmol, 10 mol%), indanonecarboxamide **1a** (23.1 mg, 0.10 mmol) and nitratobenziodoxole **2** (42.0 mg, 0.13 mmol) in DCE (1.0 mL) at 0 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]The reaction was performed at 10 °C. [e]The reaction was performed at 20 °C. [f]The reaction was performed at -10 °C. [g]5 Å molecular sieves (10.0 mg) was added.

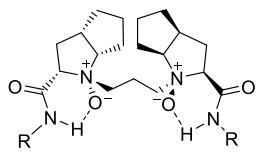
Table S2. Screening of the ligands[a]



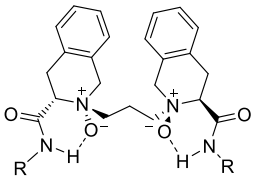
1a 2 3a



L$_3$-PicH: R = cyclohexyl, n = 2
L$_3$-PicP: R = cyclopentyl, n = 2
L$_3$-PrcP: R = cyclopentyl, n = 1



L$_3$-RacP: R = cyclopentyl



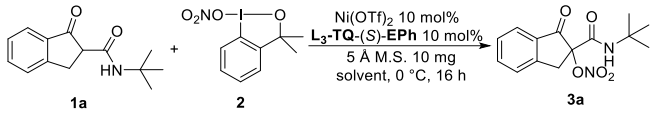
L$_3$-TQBn: R = Bn
L$_3$-TQ^{i}Pr: R = ^{i}Pr
L$_3$-TQcH: R = cyclohexyl
L$_3$-TQ-(*S*)-**EPh**: R = (*S*)-2-phenylethyl
L$_3$-TQ-(*R*)-**EPh**: R = (*R*)-2-phenylethyl
L$_3$-TQCHPh$_2$: R = Ph_2CH
L$_3$-TQ^{t}Bu: R = ^{t}Bu

Entry	**Ligand**	Yield (%)[b]	ee (%)[c]
1	**L$_3$-PicH**	75	80
2	**L$_3$-PicP**	75	57

3	**L_3-PrcP**	70	20
4	**L_3-RacP**	64	12
5	**L_3-TQBn**	74	64
6	**L_3-TQ^{i}Pr**	72	82
7	**L_3-TQcH**	74	84
8	**L_3-TQ**-(*S*)-**EPh**	70	87
9	**L_3-TQ**-(*R*)-**EPh**	52	80
10	**L_3-TQ^{t}Bu**	60	30

[a]Unless otherwise noted, all reactions were carried out with $Ni(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%), ligand (0.01 mmol, 10 mol%), 5 Å molecular sieves (10.0 mg) , indanonecarboxamide **1a** (23.1 mg, 0.10 mmol) and nitratobenziodoxole **2** (42.0 mg, 0.13 mmol) in DCE (1.0 mL) at 0 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase.

Table S3. Screening of the solvents[a]

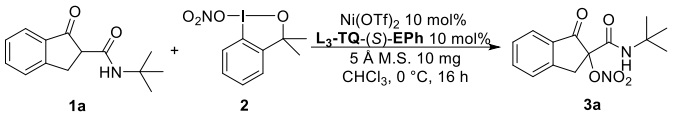


1a **2** **3a**

Entry	Solvent	Yield (%)[b]	ee (%)[c]
1	CH_2Cl_2	84	82
2	$CHCl_3$	80	90
3	CH_2ClCH_2Cl	70	87
4	$Cl_2CHCHCl_2$	72	68
5	THF	83	8
6	Et_2O	48	0
7	Toluene	58	13

[a]Unless otherwise noted, all reactions were carried out with $Ni(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%), **L_3-TQ**-(*S*)-**EPh** (6.3 mg, 0.01 mmol, 10 mol%), 5 Å molecular sieves (10.0 mg) , indanonecarboxamide **1a** (23.1 mg, 0.10 mmol) and nitratobenziodoxole **2** (42.0 mg, 0.13 mmol) in solvent (1.0 mL) at 0 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase.

Table S4. Screening of the quantities of 5 Å molecular sieves[a]

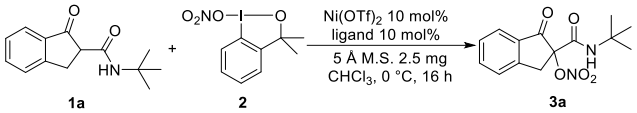


1a **2** **3a**

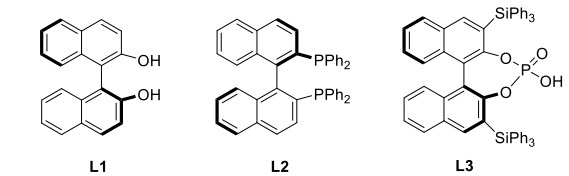
Entry	5 Å MS	Yield (%)[b]	ee (%)[c]
1	10.0 mg	80	90
2	5.0 mg	81	90
3	2.5 mg	81	92
4	0 mg	72	76
5[d]	2.5 mg	83	92

[a]Unless otherwise noted, all reactions were carried out with $Ni(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%), **L_3-TQ**-(*S*)-**EPh** (6.3 mg, 0.01 mmol, 10 mol%), 5 Å molecular sieves, indanonecarboxamide **1a** (23.1 mg, 0.10 mmol) and nitratobenziodoxole **2** (42.0 mg, 0.13 mmol) in $CHCl_3$ (1.0 mL) at 0 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]The reaction was performed in $CHCl_3$ (1.5 mL) for 48 h.

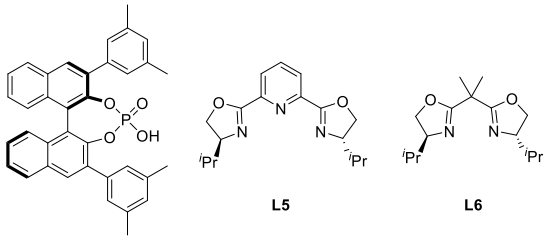
Table S5. Screen of other ligands[a]



1a 2 3a



L1 L2 L3



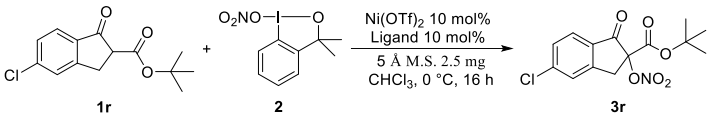
L4 L5 L6

Entry	**Ligand**	Yield (%)[b]	ee (%)[c]
1	**L1**	39	-20
2	**L2**	51	-22
3	**L3**	74	0
4	**L4**	36	0
5	**L5**	50	0
6	**L6**	58	30

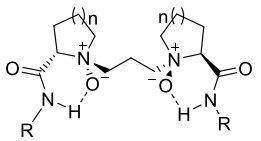
[a]Unless otherwise noted, all reactions were carried out with $Ni(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%), ligand (0.01 mmol, 10 mol%), 5 Å molecular sieves (2.5 mg), indanonecarboxamide **1a** (23.1 mg, 0.10 mmol) and nitratobenziodoxole **2** (42.0 mg, 0.13 mmol) in $CHCl_3$ (1.5 mL) at 0 °C under Ar atmosphere 48 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase.

4.2 The reaction of indanonecarboxesters and nitratobenziodoxole 2

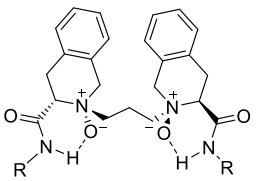
Table S6. Screening of the ligands[a]



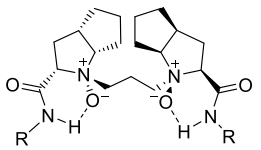
1r 2 3r



L_3-PicH: R = cyclohexyl, n = 2
L_3-PrcH: R = cyclohexyl, n = 1



L_3-TQBn: R = Bn
L_3-TQ^{i}Pr: R = ^{i}Pr
L_3-TQcH: R = cyclohexyl
L_3-TQ-(*S*)-EPh: R = (*S*)-2-phenylethyl
L_3-TQ-1-Ad: R = 1-adamantyl



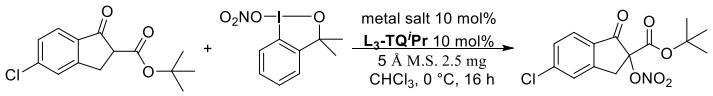
L_3-RacH: R = cyclohexyl

Entry	**Ligand**	Yield (%)[b]	ee (%)[c]
1	**L_3-PicH**	83	20

2	**L_3-PrcH**	62	0
3	**L_3-RacH**	68	0
4	**L_3-TQBn**	72	16
5	**L_3-TQ^{i}Pr**	77	40
6	**L_3-TQcH**	64	26
7	**L_3-TQ**-(*S*)-**EPh**	78	10
8	**L_3-TQ-1-Ad**	73	20

[a]Unless otherwise noted, all reactions were carried out with $Ni(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%), ligand (0.01 mmol, 10 mol%), 5 Å molecular sieves (2.5 mg), indanonecarboxester **1r** (26.7 mg, 0.10 mmol) and nitratobenziodoxole **2** (42.0 mg, 0.13 mmol) in $CHCl_3$ (1.0 mL) at 0 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase.

Table S7. Screening of the metal salts[a]



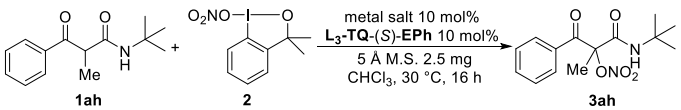
1r **2** **3r**

Entry	Metal salt	Yield (%)[b]	ee (%)[c]
1	$Mg(OTf)_2$	60	6
2	$Fe(OTf)_2$	61	0
3	$Co(OTf)_2$	78	84
4	$Ni(OTf)_2$	68	50
5	$Cu(OTf)_2$	73	14
6	$Zn(OTf)_2$	84	64
7	$Sc(OTf)_3$	78	0
8	$Gd(OTf)_3$	72	20
9[d]	$Co(OTf)_2$	78	88
10[d, e]	$Co(OTf)_2$	76	90
11[d, e, f]	$Co(OTf)_2$	81	90

[a]Unless otherwise noted, all reactions were carried out with metal salt (0.01 mmol, 10 mol%), **L_3-TQ^{i}Pr** (5.1 mg, 0.01 mmol, 10 mol%), 5 Å molecular sieves (2.5 mg), indanonecarboxester **1r** (26.7 mg, 0.10 mmol) and nitratobenziodoxole **2** (42.0 mg, 0.13 mmol) in $CHCl_3$ (1.0 mL) at 0 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Without 5 Å molecular sieves. [e]The reaction was performed at -10 °C. [f]The reaction was performed for 24 h.

4.3 The reaction of acyclic β-keto amides and nitratobenziodoxole 2:

Table S8. Screening of the metal salts[a]

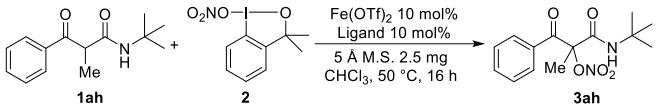


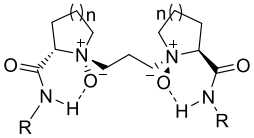
1ah **2** **3ah**

Entry	Metal salt	Yield (%)[b]	ee (%)[c]
1	$Mg(OTf)_2$	trace	8
2	$Fe(OTf)_2$	trace	30
3	$Co(OTf)_2$	trace	7
4	$Ni(OTf)_2$	trace	10
5	$Cu(OTf)_2$	trace	0
6	$Zn(OTf)_2$	trace	14
7	$Sc(OTf)_3$	trace	7
8[d]	$Fe(OTf)_2$	50	14

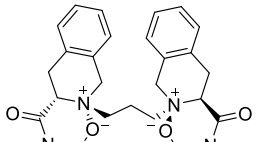
[a]Unless otherwise noted, all reactions were carried out with metal salt (0.01 mmol, 10 mol%), **L_3-TQ**-(*S*)-**EPh** (6.3 mg, 0.01 mmol, 10 mol%), 5 Å molecular sieves (2.5 mg), acyclic β-keto amide **1ah** (23.3 mg, 0.10 mmol) and nitratobenziodoxole **2** (42.0 mg, 0.13 mmol) in $CHCl_3$ (1.0 mL) at 30 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]The reaction was performed at 50 °C.

Table S9. Screening of the ligands[a]

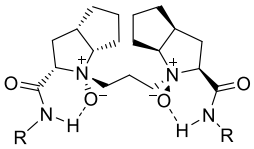




L_3-PrPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 1
L_3-PiPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 2
L_3-PiEt$_2$Me: R = 2,6-Et$_{2\text{-}4}$-Me-C$_6$H$_2$, n = 2
L_3-PiEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$, n = 2
L_3-PiMe$_3$: R = 2,4,6-Me$_3$C$_6$H$_2$, n = 2
L_3-PiMe$_2$: R = 2,6-Me$_2$C$_6$H$_3$, n = 2
L_3-PiAd: R = adamantyl, n = 2
L_3-PicH: R = cyclohexyl, n = 2



L_3-TQ^{i}Pr: R = ^{i}Pr
L_3-TQ-(*S*)-**EPh**: R = (*S*)-2-phenylethyl

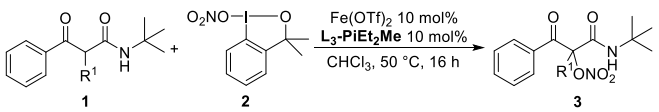


L_3-RaPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$

Entry	**Ligand**	Yield (%)[b]	ee (%)[c]
1	**L_3-TQ*s*EPh**	50	14
2	**L_3-TQ^{i}Pr**	46	5
3	**L_3-RaPr$_2$**	55	18
4	**L_3-PrPr$_2$**	51	28
5	**L_3-PiPr$_2$**	52	35
6	**L_3-PiEt$_2$Me**	52	45
7	**L_3-PiEt$_2$**	52	30
8	**L_3-PiMe$_3$**	55	22
9	**L_3-PiMe$_2$**	51	17
10	**L_3-PiAd**	46	30
11	**L_3-PicH**	46	7
12[d]	**L_3-PiEt$_2$Me**	51	46

[a]Unless otherwise noted, all reactions were carried out with $Fe(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%), ligand (0.01 mmol, 10 mol%), 5 Å molecular sieves (2.5 mg), acyclic β-keto amide **1ah** (23.3 mg, 0.10 mmol) and nitratobenziodoxole **2** (42.0 mg, 0.13 mmol) in $CHCl_3$ (1.0 mL) at 50 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Without 5 Å molecular sieves.

Table S10. Screening of the acyclic β-keto amides[a]

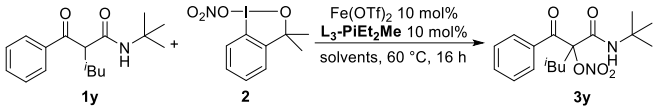


Entry	R^1	Yield (%)[b]	ee (%)[c]
1	Me	51	46
2	Et	58	77

3[d]	Et	58	80
4[d]	^{i}Pr	N.R.	--
5[d]	^{i}Bu	41	93
6[d]	F	N.R.	--
7[d]	Cl	N.R.	--
8[d, e]	^{i}Bu	44	93

[a]Unless otherwise noted, all reactions were carried out with $Fe(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%), **L_3-PiEt$_2$Me** (6.2 mg, 0.01 mmol, 10 mol%), acyclic β-keto amide **1** (0.10 mmol) and nitratobenziodoxole **2** (42.0 mg, 0.13 mmol) in $CHCl_3$ (1.0 mL) at 50 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Nitratobenziodoxole **2** (35.5 mg, 0.11 mmol) was added. [e]The reaction was performed at 60 °C.

Table S11. Screening of the solvents[a]



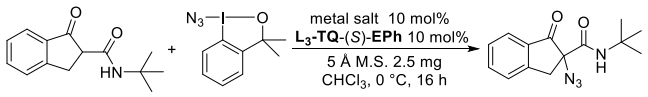
1y **2** **3y**

Entry	Solvent	Yield (%)[b]	ee (%)[c]
1	$CHCl_3$	44	93
2	EtOAc	21	75
3	MeCN	45	80
4	Et_2O	N.R.	--
5	Toluene	20	75
6	THF	70	92
7[d]	THF	82	92

[a]Unless otherwise noted, all reactions were carried out with $Fe(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%), **L_3-PiEt$_2$Me** (6.2 mg, 0.01 mmol, 10 mol%), acyclic β-keto amide **1y** (27.5 mg, 0.10 mmol) and nitratobenziodoxole **2** (35.5 mg, 0.11 mmol) in solvent (1.0 mL) at 60 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]The reaction was performed for 24 h.

4.4 The reaction of indanonecarboxamides and azidoiodinane 4:

Table S12. Screening of the metal salts[a]

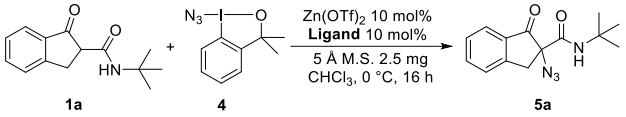


1a **4** **5a**

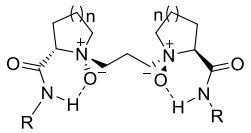
Entry	Metal salt	Yield (%)[b]	ee (%)[c]
1	$Mg(OTf)_2$	trace	16
2	$Fe(OTf)_2$	78	30
3	$Co(OTf)_2$	trace	30
4	$Ni(OTf)_2$	trace	0
5	$Cu(OTf)_2$	trace	0
6	$Zn(OTf)_2$	84	75
7	$Sc(OTf)_3$	trace	7

[a]Unless otherwise noted, all reactions were carried out with metal salt (0.01 mmol, 10 mol%), **L_3-TQ**-(*S*)-**EPh** (6.3 mg, 0.01 mmol, 10 mol%), 5 Å molecular sieves (2.5 mg), indanonecarboxamides **1a** (0.10 mmol) and azidoiodinane **4** (39.4 mg, 0.13 mmol) in $CHCl_3$ (1.0 mL) at 0 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase.

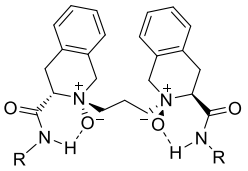
Table S13. Screening of the ligands[a]



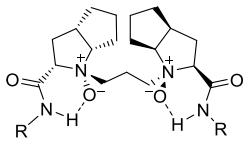
1a 4 5a



L_3-$PrPr_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 1
L_3-$PiPr_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 2



L_3-TQBn: R = Bn
L_3-TQ^{i}Pr: R = ^{i}Pr
L_3-TQ*c*H: R = cyclohexyl
L_3-TQ-(*S*)-**EPh**: R = (*S*)-2-phenylethyl
L_3-$TQCHPh_2$: R = CHPh$_2$

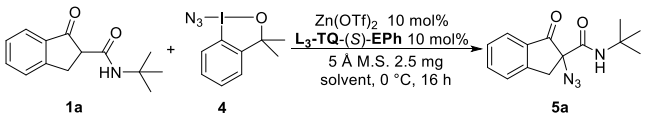


L_3-$RaPr_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$

Entry	**Ligand**	Yield (%)[b]	ee (%)[c]
1	**L_3-$PrPr_2$**	58	0
2	**L_3-$PiPr_2$**	67	60
3	**L_3-$RaPr_2$**	64	0
4	**L_3-TQ^{i}Pr**	54	73
5	**L_3-TQ*c*H**	58	66
6	**L_3-TQ**-(*S*)-**EPh**	84	75
7	**L_3-$TQCHPh_2$**	83	60

[a]Unless otherwise noted, all reactions were carried out with Zn(OTf)$_2$ (3.6 mg, 0.01 mmol, 10 mol%), ligand (0.01 mmol, 10 mol%), 5 Å molecular sieves (2.5 mg), indanonecarboxamides **1a** (0.10 mmol) and azidoiodinane **4** (39.4 mg, 0.13 mmol) in $CHCl_3$ (1.0 mL) at 0 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase.

Table S14. Screening of the solvents[a]



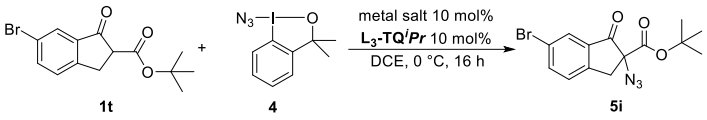
1a 4 5a

Entry	Solvent	Yield (%)[b]	ee (%)[c]
1	DCM	37	63
2	$CHCl_3$	84	75
3	DCE	78	90
4	EtOAc	40	51
5	Toluene	22	38
6	THF	53	11
7[d]	DCE	84	90

[a]Unless otherwise noted, all reactions were carried out with Zn(OTf)$_2$ (3.6 mg, 0.01 mmol, 10 mol%), **L_3-TQ**-(*S*)-**EPh** (0.01 mmol, 10 mol%), 5 Å molecular sieves (2.5 mg), indanonecarboxamides **1a** (0.10 mmol) and azidoiodinane **4** (39.4 mg, 0.13 mmol) in solvent (1.0 mL) at 0 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]The reaction was performed for 24 h.

4.5 The reaction of indanonecarboxesters and azidoiodinane 4:

Table S15. Screening of the metal salts[a]

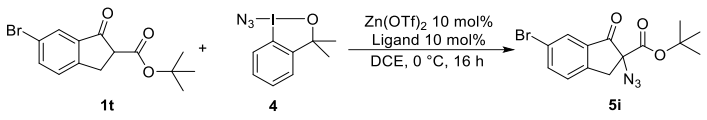


1t 4 5i

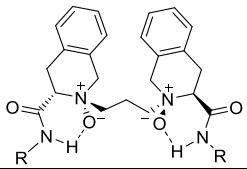
Entry	Metal salt	Yield (%)[b]	ee (%)[c]
1	$Mg(OTf)_2$	33	78
2	$Fe(OTf)_2$	38	-16
3	$Co(OTf)_2$	42	72
4	$Ni(OTf)_2$	48	53
5	$Zn(OTf)_2$	64	92

[a]Unless otherwise noted, all reactions were carried out with metal salt (0.01 mmol, 10 mol%), **L_3-TQ^{i}Pr** (5.1 mg, 0.01 mmol, 10 mol%), indanonecarboxesters **1t** (0.10 mmol) and azidoiodinane **4** (39.4 mg, 0.13 mmol) in DCE (1.0 mL) at 0 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase.

Table S16. Screening of the ligands[a]



1t 4 5i



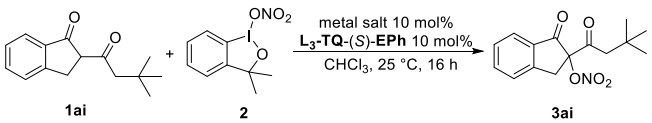
L_3-TQ^{i}Pr: R = ^{i}Pr
L_3-TQ*c*H: R = cyclohexyl
L_3-TQ-(*S*)-**EPh**: R = (*S*)-2-phenylethyl

Entry	**Ligand**	Yield (%)[b]	ee (%)[c]
1	**L_3-TQ^{i}Pr**	64	92
2	**L_3-TQ*c*H**	82	30
3	**L_3-TQ**-(*S*)-**EPh**	72	91
4[d]	**L_3-TQ**-(*S*)-**EPh**	78	92
5[e]	**L_3-TQ**-(*S*)-**EPh**	78	94
6[f]	**L_3-TQ**-(*S*)-**EPh**	76	92

[a]Unless otherwise noted, all reactions were carried out with $Zn(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%), ligand (0.01 mmol, 10 mol%), indanonecarboxesters **1t** (0.10 mmol) and azidoiodinane **4** (39.4 mg, 0.13 mmol) in DCE (1.0 mL) at 0 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]The reaction was performed at -10 °C for 24 hours. [e]The reaction was performed at -20 °C for 24 hours. [f]The reaction was performed at -30 °C for 24 hours.

4.6 The reaction of 1,3-diketones and nitratobenziodoxole 2:

Table S17. Screening of the metal salts[a]



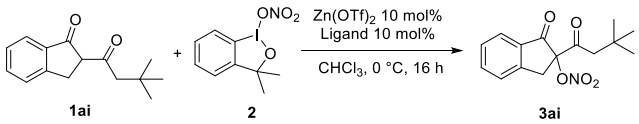
1ai 2 3ai

Entry	Metal salt	Yield (%)[b]	ee (%)[c]
1	$Sc(OTf)_3$	85	0

2	$Gd(OTf)_3$	72	0
3	$Mg(OTf)_2$	71	-6
4	$Fe(OTf)_2$	N.R.	--
5	$Fe(OTf)_3$	N.R.	--
6	$Co(OTf)_2$	70	10
7	$Ni(OTf)_2$	70	0
8	$Cu(OTf)_2$	77	0
9	$Zn(OTf)_2$	76	11
10[d]	$Zn(OTf)_2$	89	36

[a]Unless otherwise noted, all reactions were carried out with metal salt (0.01 mmol, 10 mol%), **L_3-TQ**-(*S*)-**EPh** (6.3 mg, 0.01 mmol, 10 mol%), 1,3-diketones **1ai** (0.10 mmol) and nitratobenziodoxole **2** (42.0 mg, 0.13 mmol) in $CHCl_3$ (1.0 mL) at 25 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]The reaction was performed at 0 °C for 16 hours

Table S18. Screening of the ligands[a]

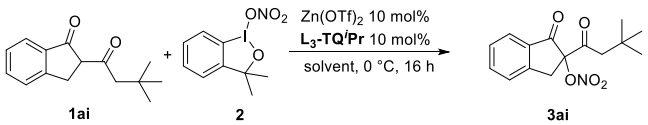


1ai 2 3ai

Entry	**Ligand**	Yield (%)[b]	ee (%)[c]
1	**L_3-TQBn**	84	22
2	**L_3-TQCHPh$_2$**	78	18
3	**L_3-TQ^{i}Pr**	87	56
4	**L_3-TQ*c*H**	93	50
5	**L_3-TQ**-(*S*)-**EPh**	89	36
6	**L_3-PiMe$_2$**	84	25
7	**L_3-PiMe$_2$^{t}Bu**	87	28
8	**L_3-PiEt$_2$**	88	28
9	**L_3-PiPr$_2$**	69	10
10	**L_3-PiEt$_2$Me**	85	30
11[d]	**L_3-TQ^{i}Pr**	79	46

[a]Unless otherwise noted, all reactions were carried out with $Zn(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%), ligand (0.01 mmol, 10 mol%), 1,3-diketones **1ai** (0.10 mmol) and nitratobenziodoxole **2** (42.0 mg, 0.13 mmol) in $CHCl_3$ (1.0 mL) at 0 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]The reaction was performed at -10 °C for 36 hours.

Table S19. Screening of the solvents[a]

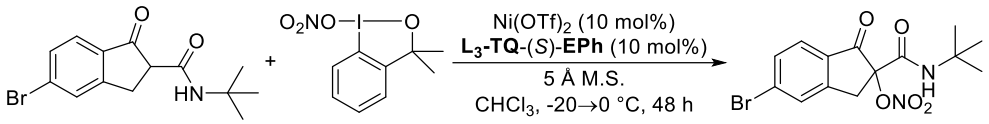


1ai 2 3ai

Entry	solvent	Yield (%)[b]	ee (%)[c]
1	DCM	89	22
2	$CHCl_3$	87	56
3	DCE	91	22
4	EtOAc	92	34
5	Toluene	27	0
6	THF	52	0
7	Et_2O	26	0

[a]Unless otherwise noted, all reactions were carried out with $Zn(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%), **L_3-TQ^{i}Pr** (5.1 mg, 0.01 mmol, 10 mol%), 1,3-diketones **1ai** (0.10 mmol) and nitratobenziodoxole **2** (42.0 mg, 0.13 mmol) in solvent (1.0 mL) at 0 °C under Ar atmosphere for 16 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase.

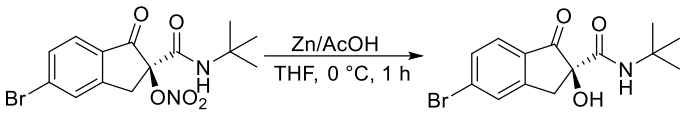
5. Typical procedure for the gram-scale synthesis of product



1f (3.5 mmol, 1.09 g) **2** **3f** (1.06 g, 82% yield, 92% ee)
After recrystallization: (0.80 g, 62% yield, 99% ee)

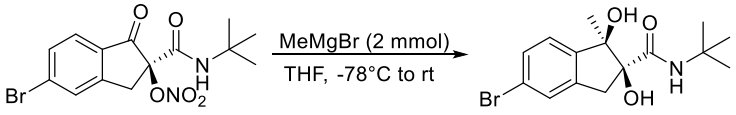
To an oven-dried round bottomed flask was added $Ni(OTf)_2$ (124.9 mg, 0.35 mmol, 10 mol%), **L_3-TQ**-(*S*)-**EPh** (221.5 mg, 0.35 mmol, 10 mol%), indanonecarboxamides **1f** (1085.7 mg, 3.5 mmol) and 5 Å molecular sieves (87.5 mg) under Ar atmosphere. Anhydrous $CHCl_3$ (17.5 mL) was added and the mixture was stirred at 30 °C for 2 h. Then the reaction was cooled to -20 °C, a solution of the nitratobenziodoxole **2** (1470.0 mg, 4.55 mmol) in $CHCl_3$ (35 mL) was added dropwise. The reaction was performed at -20 °C for 30 mins. Subsequently, the reaction is allowed to warm to 0 °C for 48 hours. The reaction was directly subjected to flash column chromatography on silica gel (eluent: petroleum ether/dichloromethane/ethyl acetate = 20:10:1) to afford the corresponding product **3f** as white amorphous solid (1.06 g, 82% yield, 92% ee). **3f** could be obtained in 62% yield with 99% ee after recrystallization.

6. Transformations of the product



3f (0.1 mmol, 99% ee) **6** (93% yield, 99% ee)

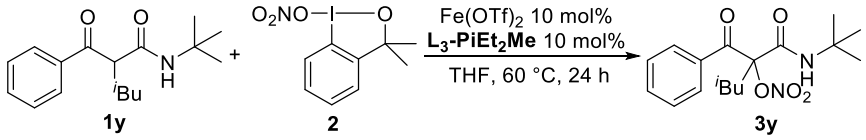
Synthesis of molecule **6**: Following a reported procedure,[2] a solution of **3f** (37.1 mg, 0.1 mmol, 1 equiv) in THF (1.0 mL) was cooled to 0 °C before addition of Zn powder (65.4 mg, 1.0 mmol, 10 equiv) and AcOH (0.5 mL). The reaction was left to stir for 1 hour before filtration over Celite. Solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography on silica (eluent: petroleum ether/ethyl acetate = 20:1)**.**



3f (0.1 mmol, 99% ee) **7** (63% yield, >19:1 d.r., 99% ee)

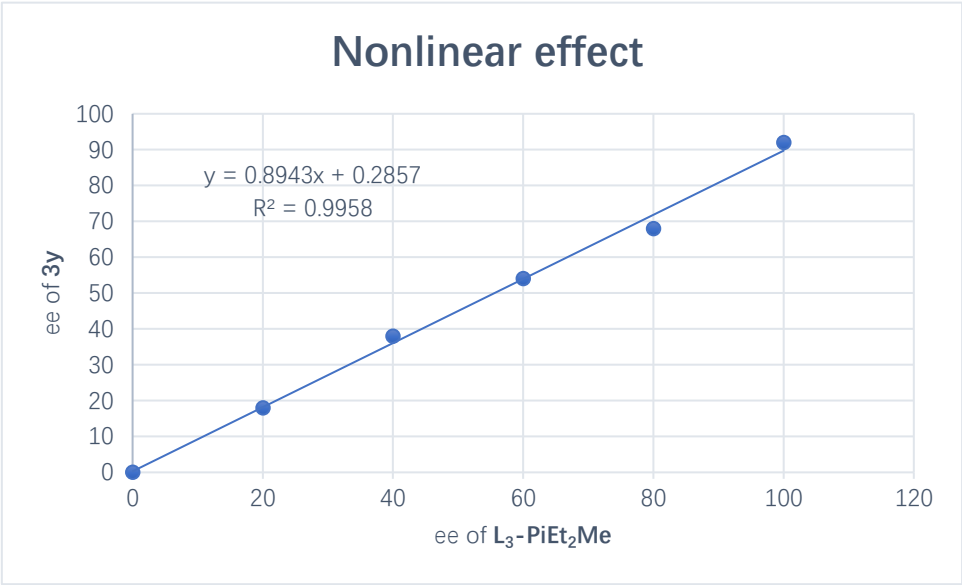
Synthesis of molecule **7**: Following a reported procedure,[6] to a solution of **3f** (37.1 mg, 0.1 mmol, 1 equiv.) in THF (1.0 mL, 0.1 M) was added MeMgBr (3 M solution in Et_2O, 0.66 mL, 2 mmol, 20.0 equiv.) under nitrogen at -78 °C. Then the reaction was allowed to warm up to room temperature overnight and quenched with a saturated aqueous solution of NH_4Cl, extracted with EtOAc (3 x 20 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Purification by flash column chromatography (SiO_2, eluent: petroleum ether/ ethyl acetate = 4:1) affords the compound **7** (21.6 mg, 63% yield, > 19:1 d.r., 99% ee).

7. The nonlinear effect between the ee value of the ligand L_3-$PiEt_2Me$ and the product 3y

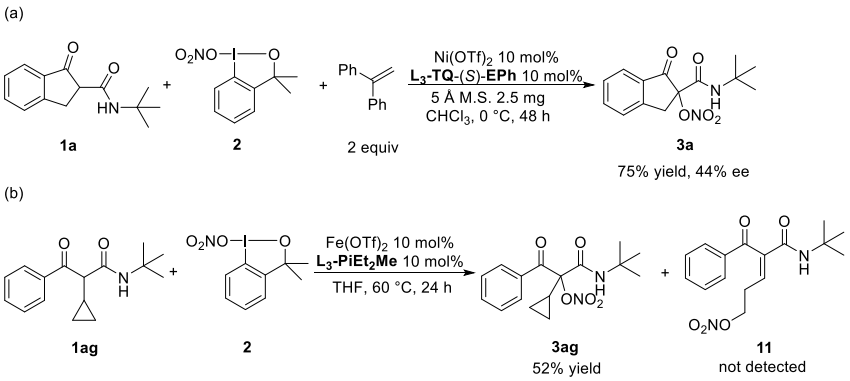


A dry reaction tube was charged with prepared catalyst **L_3-$PiEt_2Me$**/$Fe(OTf)_2$ (x mg), ***ent*-L_3-$PiEt_2Me$**/$Fe(OTf)_2$ (y mg) under an inert atmosphere. Anhydrous tetrahydrofuran (0.5 mL) was added and the resulting solution was stirred at 30 °C for 0.5 h. After the solvent was removed in vacuo, acyclic β-keto amides **1y** (0.10 mmol) and nitratobenziodoxole **2** (0.10 mmol) were added. Tetrahydrofuran (1.0 mL) was added and the reaction mixture was stirred at 60 °C for 24 h. The product **3y** was purified by flash chromatography.

Entry	x/y (mg)	ee of **L_3-$PiEt_2Me$**	ee of **3y**
1	3.1/3.1	0	0
2	3.7/2.5	20	18
3	4.4/1.8	40	38
4	5.0/1.2	60	54
5	5.6/0.6	80	68
6	6.3/0	100	92



8. Control experiments



Scheme 1. (a) Radical trap experiment with 1,1-diphenylethene. (b) Radical clock experiment.

When the radical inhibitor 1,1-diphenylethene was added to the reaction mixture of **1a** and **2**, the reaction could still be carried out to provide the corresponding product **3a** in 75% yield with 44% ee (Scheme 1a). Moreover, a radical clock reaction of **1ag** under the conditions C was carried out, affording the racemic product **3ag** in 52% yield, while the product **11** was not detected (Scheme 1b). These results indicated that the reaction pathway probably did not involve a radical process.

9. Unsuccessful substrate scope

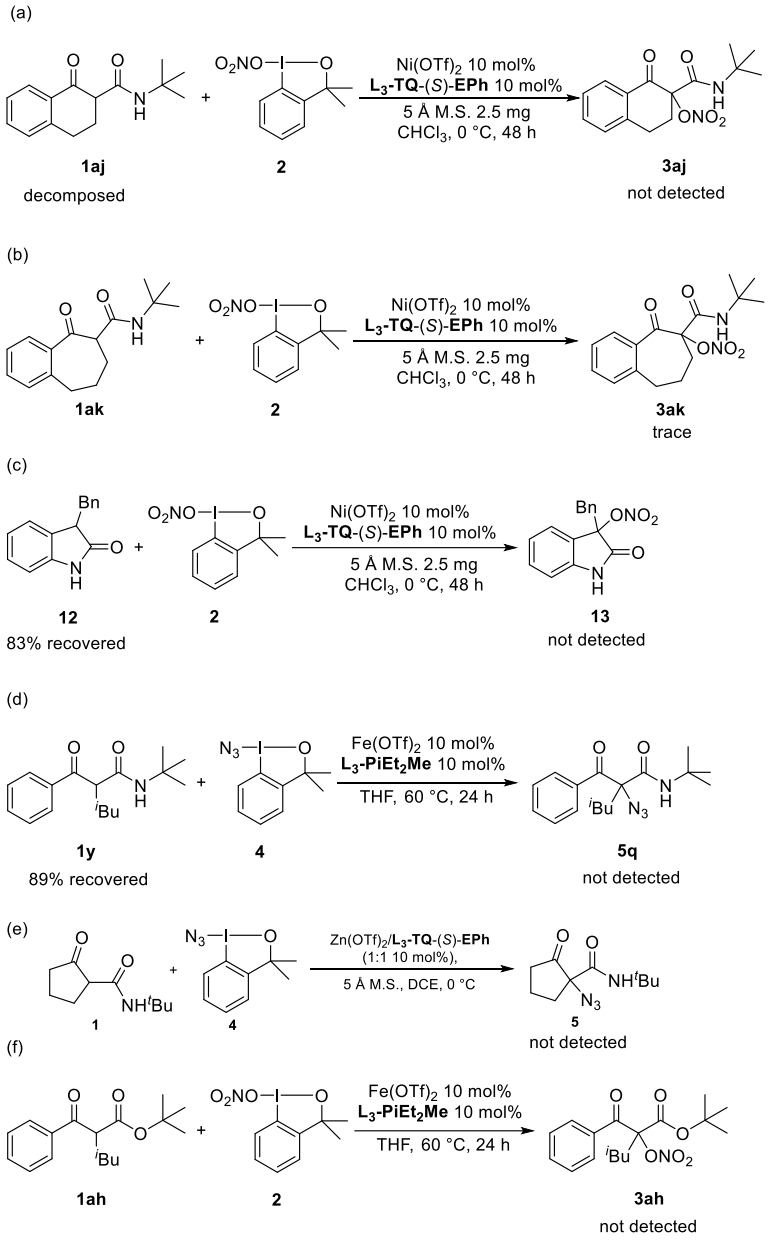
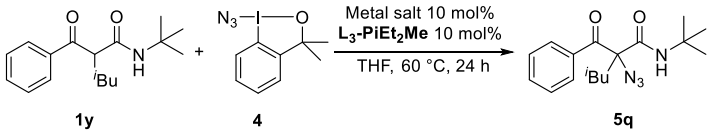


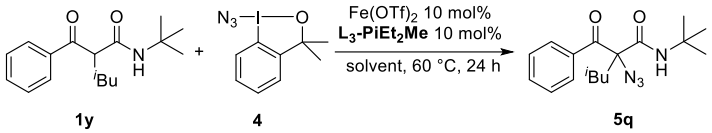
Table S20. Screening of the metal salts[a]



Entry	Metal salt	Yield (%)[b]	ee (%)[c]
1	$Mg(OTf)_2$	N.R.	-
2	$Fe(OTf)_2$	N.R.	-
3	$Co(OTf)_2$	N.R.	-
4	$Ni(OTf)_2$	N.R.	-
5	$Cu(OTf)_2$	N.R.	-
6	$Zn(OTf)_2$	N.R.	-
7	$Sc(OTf)_3$	N.R.	-

[a]Unless otherwise noted, all reactions were carried out with metal salt (0.01 mmol, 10 mol%), **L_3-PiEt$_2$Me** (6.2 mg, 0.01 mmol, 10 mol%), acyclic β-keto amide **1y** (0.10 mmol) and azidoiodinane **4** (33.3 mg, 0.11 mmol) in THF (1.0 mL) at 60 °C under Ar atmosphere for 24 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase.

Table S21. Screening of the solvents[a]

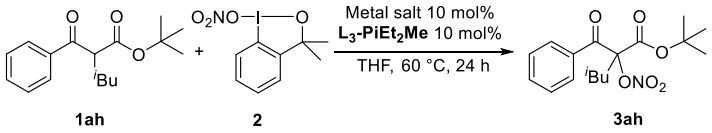


1y **4** **5q**

Entry	solvent	Yield (%)[b]	ee (%)[c]
1	THF	N.R.	-
2	$CHCl_3$	N.R.	-
3	DCE	N.R.	-
4	EtOAc	N.R.	-
5	Toluene	N.R.	-
6[d]	Toluene	N.R.	-

[a]Unless otherwise noted, all reactions were carried out with $Fe(OTf)_2$ (3.6 mg, 0.01 mmol, 10 mol%), **L_3-PiEt$_2$Me** (3.2 mg, 0.01 mmol, 10 mol%), acyclic β-keto amide **1y** (0.10 mmol) and azidoiodinane **4** (33.3 mg, 0.11 mmol) in solvent (1.0 mL) at 60 °C under Ar atmosphere for 24 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]The reaction was performed at 90 °C.

Table S22. Screening of the metal salts[a]

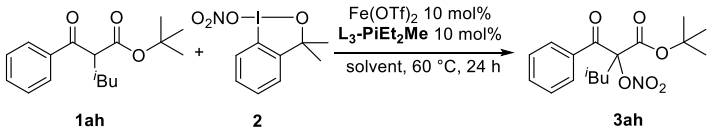


1ah **2** **3ah**

Entry	Metal salt	Yield (%)[b]	ee (%)[c]
1	$Mg(OTf)_2$	N.R.	-
2	$Fe(OTf)_2$	N.R.	-
3	$Co(OTf)_2$	N.R.	-
4	$Ni(OTf)_2$	N.R.	-
5	$Cu(OTf)_2$	N.R.	-
6	$Zn(OTf)_2$	N.R.	-
7	$Sc(OTf)_3$	N.R.	-

[a]Unless otherwise noted, all reactions were carried out with metal salt (0.01 mmol, 10 mol%), **L_3-PiEt$_2$Me** (6.2 mg, 0.01 mmol, 10 mol%), acyclic β-keto ester **1ah** (0.10 mmol) and nitratobenziodoxole **2** (35.5 mg, 0.11 mmol) in THF (1.0 mL) at 60 °C under Ar atmosphere for 24 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase.

Table S23. Screening of the solvents[a]



1ah **2** **3ah**

Entry	solvent	Yield (%)[b]	ee (%)[c]
1	THF	N.R.	-
2	$CHCl_3$	N.R.	-
3	DCE	N.R.	-
4	EtOAc	N.R.	-

5	Toluene	N.R.	-
6[d]	Toluene	N.R.	-

[a]Unless otherwise noted, all reactions were carried out with $Fe(OTf)_2$ (0.01 mmol, 10 mol%), **L_3-PiEt$_2$Me** (6.2 mg, 0.01 mmol, 10 mol%), acyclic β-keto ester **1ah** (0.10 mmol) and nitratobenziodoxole **2** (35.5 mg, 0.11 mmol) in solvent (1.0 mL) at 60 °C under Ar atmosphere for 24 hours. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]The reaction was performed at 90 °C.

10. Computational studies

Computational Methods

All computations were carried out using the Gaussian 09 D.01 software package[7]. The calculation of geometry optimization, frequency and Gibbs energy corrections were carried out for 1f at the temperature of 298.15K. All calculations were performed at M06-2X[8] level of theory with Grimme's D3 empirical dispersion correction[9] with def2-TZVP[10] and SMD (trichloromethane) implicit solvation model[11]. The Mulliken population and atomic charges of 1f was analyzed by Multiwfn (version 3.8)[12] and CYLview[13] was used as the visualizer.

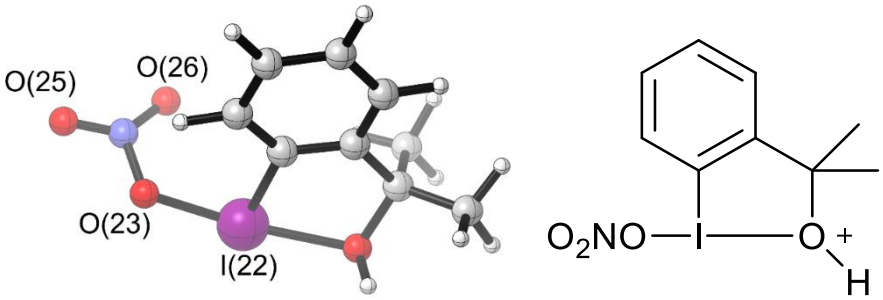


Fig1. Optimized configuration of **2**+H$^+$ with I(22), O(23), O(25) and O(26) labeled.

Mulliken population and atomic charges of 2+H$^+$

Atom	C(1)	Population:	5.85275492	Net charge:	0.14724508
Atom	C(2)	Population:	6.19831710	Net charge:	-0.19831710
Atom	C(3)	Population:	6.14685940	Net charge:	-0.14685940
Atom	C(4)	Population:	6.15314274	Net charge:	-0.15314274
Atom	C(5)	Population:	6.17149975	Net charge:	-0.17149975
Atom	C(6)	Population:	6.00256064	Net charge:	-0.00256064
Atom	H(7)	Population:	0.77217121	Net charge:	0.22782879
Atom	H(8)	Population:	0.80655584	Net charge:	0.19344416
Atom	H(9)	Population:	0.80997827	Net charge:	0.19002173
Atom	H(10)	Population:	0.79467495	Net charge:	0.20532505
Atom	C(11)	Population:	5.92695627	Net charge:	0.07304373
Atom	C(12)	Population:	6.38716464	Net charge:	-0.38716464
Atom	H(13)	Population:	0.81559950	Net charge:	0.18440050
Atom	H(14)	Population:	0.81512745	Net charge:	0.18487255
Atom	H(15)	Population:	0.82753479	Net charge:	0.17246521
Atom	C(16)	Population:	6.46740600	Net charge:	-0.46740600
Atom	H(17)	Population:	0.81056550	Net charge:	0.18943450
Atom	H(18)	Population:	0.80109608	Net charge:	0.19890392
Atom	H(19)	Population:	0.81287890	Net charge:	0.18712110
Atom	O(20)	Population:	8.49088658	Net charge:	-0.49088658
Atom	H(21)	Population:	0.57940408	Net charge:	0.42059592
Atom	I(22)	Population:	24.18426853	Net charge:	0.81573147
Atom	O(23)	Population:	8.35382716	Net charge:	-0.35382716

Atom N(24) Population: 6.43470487 Net charge: 0.56529513

Atom O(25) Population: 8.27840939 Net charge: -0.27840939

Atom O(26) Population: 8.30565546 Net charge: -0.30565546

Total net charge: 1.00000000

Energies and coordinates of 2+H$^+$

C	-0.387800	0.769600	-0.301800
C	0.258400	1.960200	-0.562800
C	-0.489800	3.126100	-0.463300
C	-1.830900	3.067200	-0.114500
C	-2.445400	1.847700	0.129900
C	-1.725700	0.660700	0.036000
H	1.299600	2.001200	-0.851600
H	-0.014100	4.076700	-0.664900
H	-2.407400	3.979600	-0.037400
H	-3.493200	1.817200	0.400200
C	-2.340500	-0.693300	0.341800
C	-2.226600	-1.014100	1.820600
H	-2.779400	-0.266800	2.389800
H	-2.644400	-2.000600	2.021500
H	-1.185500	-0.989200	2.148100
C	-3.754700	-0.848900	-0.178000
H	-3.819400	-0.592500	-1.237400
H	-4.084700	-1.877400	-0.029100
H	-4.428700	-0.197700	0.376600
O	-1.504400	-1.687700	-0.351900
H	-1.845200	-1.832300	-1.253300
I	0.664500	-1.052800	-0.391300
O	2.436500	-0.108500	-0.554000
N	2.998100	0.415000	0.601600
O	4.078200	0.875300	0.428700
O	2.346600	0.361300	1.604700

Zero-point correction = 0.197650

Thermal correction to Enthalpy = 0.213227

Thermal correction to Gibbs Free Energy = 0.155149

11. Crystal data

The absolute configuration of compound **6** was determined to be *S* by X-ray chromatography analysis. Single crystal of **6** [$C_{14}H_{16}BrNO_3$] was obtained by slow evaporation in petroleum ether/CH_2Cl_2 at 25 °C. CCDC: 2100120.

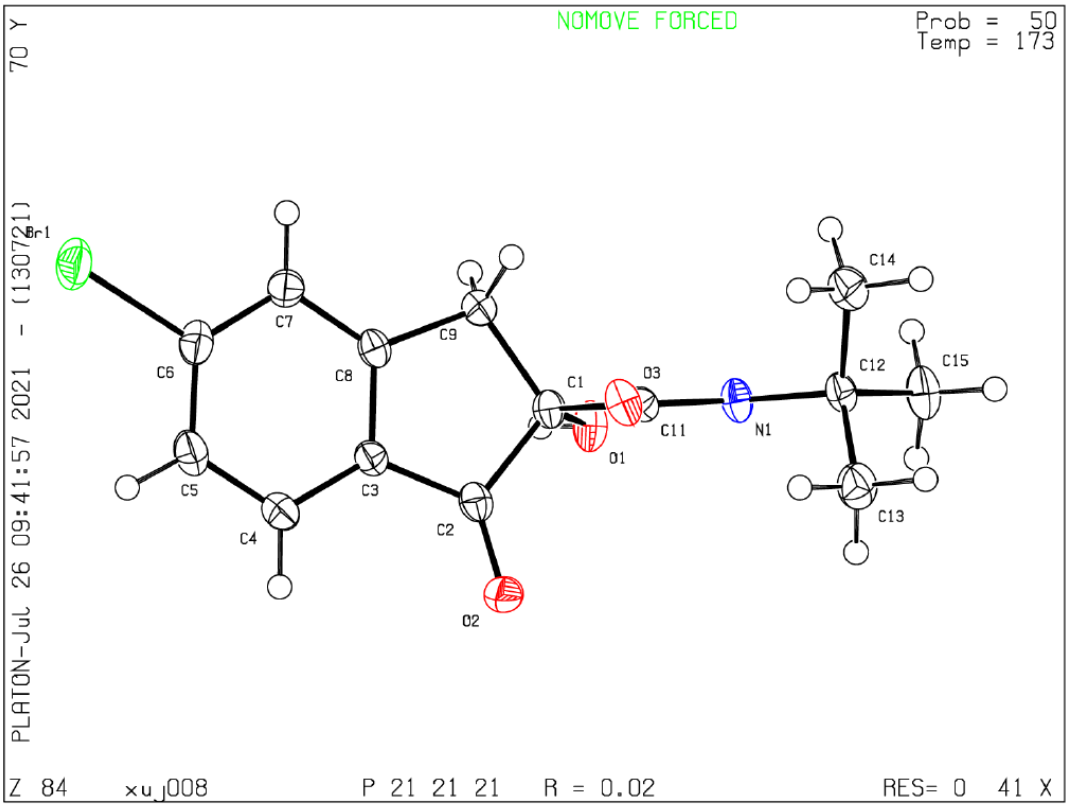
The colourless crystal in block-shape, with approximate dimensions of 0.262 × 0.272 × 0.328 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Mo radiation source (K_α = 0.71073Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package[a, b, c, d]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[e].

Crystallographic Data for $C_{14}H_{16}BrNO_3$.

Formula	$C_{14}H_{16}BrNO_3$
Formula mass (amu)	326.19
Space group	P 21 21 21
a (Å)	9.8997(3)
b (Å)	10.1961(3)
c (Å)	14.3871(5)
α (deg)	90
β (deg)	90
γ (deg)	90
V ($Å^3$)	1452.21(8)
Z	4
λ (Å)	0.71073
T (K)	173 K
ρ_{calcd} (g cm^{-3})	1.492
μ (mm^{-1})	2.834
Transmission factors	0.438,0.642
$2\theta_{max}$ (deg)	27.521
No. of unique data, including $F_o^2 < 0$	3175
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	3048
No. of variables	183
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [a]	0.0188
$R_w(F_o^2)$ [b]	0.0484
Goodness of fit	1.064

[a] $R(F) = \sum||F_o| - |F_c|| / \sum|F_o|$.

[b] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2,0) + 2F_c^2] / 3$.



12. References

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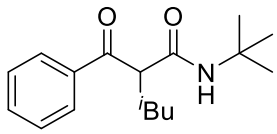
13. Spectral characterization data for the reaction substrates 1y-1af

2-Benzoyl-*N*-(*tert*-butyl)-4-methylpentanamide (1y)



White amorphous solid, 78% yield.

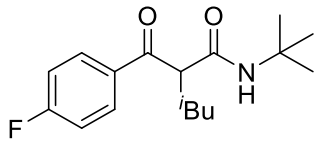
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08–7.97 (m, 2H), 7.64–7.55 (m, 1H), 7.52–7.44 (m, 2H), 6.10 (s, 1H), 4.30 (t, *J* = 9.6 Hz, 1H), 1.95–1.70 (m, 2H), 1.66–1.53 (m, 1H), 1.29 (s, 9H), 0.95–0.87 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 168.1, 136.7, 133.7, 128.8, 128.6, 55.8, 51.2, 41.5, 28.5, 26.6, 22.6, 22.5.

IR (film, cm^{-1}) :3295, 2961, 1688, 1641, 1545, 1452, 1326, 1228, 689;

HRMS (ESI$^+$) m/z calcd for $C_{17}H_{25}NNaO_2^+$ ([M]+Na^+) = 298.1778, found 298.1776.

***N*-(*tert*-Butyl)-2-(4-fluorobenzoyl)-4-methylpentanamide (1z)**



White amorphous solid, 71% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–8.00 (m, 2H), 7.20–7.08 (m, 2H), 6.00 (s, 1H), 4.24 (t, *J* = 7.2 Hz, 1H), 1.93–1.70 (m, 2H), 1.64–1.52 (m, 1H), 1.28 (s, 9H), 0.94–0.86 (m, 6H).

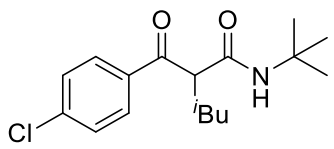
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 167.9, 166.2 (d, *J* = 254.6 Hz), 133.0 (d, *J* = 2,9 Hz), 131.4 (d, *J* = 9.4 Hz), 116.0 (d, *J* = 21.8 Hz), 55.9, 51.3, 41.1, 28.5, 26.5, 22.6, 22.4.

^{19}F NMR (376 MHz, $CDCl_3$) δ -103.9.

IR (film, cm^{-1}) :3284, 2960, 1689, 1639, 1598, 1549, 1456, 1327, 1232, 855, 607;

HRMS (ESI$^+$) m/z calcd for $C_{17}H_{24}FNNaO_2^+$ ([M]+Na^+) = 316.1683, found 316.1685.

***N*-(*tert*-Butyl)-2-(4-chlorobenzoyl)-4-methylpentanamide (1aa)**



White amorphous solid, 70% yield.

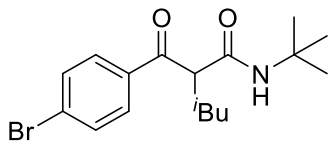
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.92 (m, 2H), 7.52–7.40 (m, 2H), 5.97 (s, 1H), 4.23 (t, *J* = 7.2 Hz, 1H), 1.93–1.68 (m, 2H), 1.64–1.50 (m, 1H), 1.28 (s, 9H), 0.96–0.84 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 167.8, 140.4, 134.9, 130.1, 129.2, 55.0, 51.4, 41.1, 28.5, 26.6, 22.5, 22.4.

IR (film, cm^{-1}) :3310, 2960, 1688, 1645, 1540, 1224, 1094;

HRMS (ESI$^+$) m/z calcd for $C_{17}H_{24}Cl^{34.9689}NNaO_2^+$ ([M]+Na^+) = 332.1388, found 332.1384 and $C_{17}H_{24}Cl^{36.9659}NNaO_2^+$ ([M]+Na^+) = 334.1358, found 334.1350.

2-(4-Bromobenzoyl)-*N*-(*tert*-butyl)-4-methylpentanamide (1ab)



White amorphous solid, 72% yield.

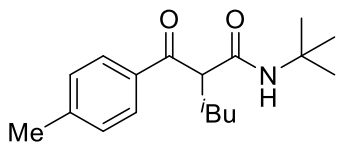
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.82 (m, 2H), 7.66–7.56 (m, 2H), 5.97 (s, 1H), 4.22 (t, *J* = 7.2 Hz, 1H), 1.90–1.70 (m, 2H), 1.64–1.54 (m, 1H), 1.28 (s, 9H), 0.95–0.82 (m, 6H).

^{13}C NMR (101MHz, $CDCl_3$) δ 198.8, 167.8, 140.4, 134.9, 130.1, 129.2, 55.0, 51.4, 41.1, 28.5, 26.6, 22.5, 22.4.

IR (film, cm^{-1}) :3312, 2960, 1688, 1644, 1540, 1224, 1070;

HRMS (ESI$^+$) m/z calcd for $C_{17}H_{24}Br^{78.9183}NNaO_2^+$ ([M]+Na^+) = 376.0883, found 376.0880 and $C_{17}H_{24}Br^{80.9163}NNaO_2^+$ ([M]+Na^+) = 378.0862, found 378.0859.

***N*-(*tert*-Butyl)-4-methyl-2-(4-methylbenzoyl)pentanamide (1ac)**



White amorphous solid, 76% yield.

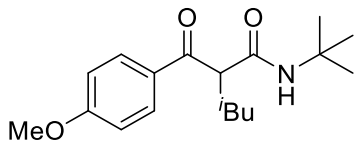
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.87 (m, 2H), 7.30–7.26 (m, 2H), 6.14 (s, 1H), 4.28 (t, *J* = 7.2 Hz, 1H), 2.42 (s, 3H), 1.93–1.70 (m, 2H), 1.65–1.52 (m, 1H), 1.28 (s, 9H), 0.95–0.82 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 168.3, 144.8, 134.2, 129.5, 128.8, 55.5, 51.2, 41.6, 28.5, 26.6, 22.6, 22.5, 21.7.

IR (film, cm^{-1}) :3304, 2960, 1684, 1645, 1541, 1229;

HRMS (ESI$^+$) m/z calcd for $C_{18}H_{27}NNaO_2^+$ ([M]+Na$^+$) = 312.1934, found 312.1935.

_N_-(_tert_-Butyl)-2-(4-methoxybenzoyl)-4-methylpentanamide (1ad)



White amorphous solid, 75% yield.

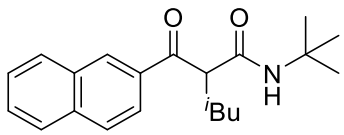
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–7.98 (m, 2H), 7.00–6.90 (m, 2H), 6.18 (s, 1H), 4.25 (t, *J* = 7.2 Hz, 1H), 3.88 (s, 3H), 1.90–1.70 (m, 2H), 1.65–1.52 (m, 1H), 1.28 (s, 9H), 0.95–0.85 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 168.4, 164.1, 131.1, 129.6, 114.0, 55.5, 55.2, 51.1, 41.7, 28.5, 26.5, 22.6, 22.5.

IR (film, cm^{-1}) :3328, 2960, 1651, 1599, 1534, 1255, 1172, 1030;

HRMS (ESI$^+$) m/z calcd for $C_{18}H_{27}NNaO_3^+$ ([M]+Na$^+$) = 328.1883, found 328.1882.

2-(2-Naphthoyl)-_N_-(_tert_-butyl)-4-methylpentanamide (1ae)



White amorphous solid, 76% yield.

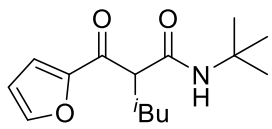
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.11–7.97 (m, 2H), 7.94–7.84 (m, 2H), 7.66–7.52 (m, 2H), 6.19 (s, 1H), 4.48 (t, *J* = 7.2 Hz, 1H), 1.99–1.77 (m, 2H), 1.70–1.55 (m, 1H), 1.30 (s, 9H), 0.98–0.87 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 168.2, 135.9, 134.0, 132.5, 130.9, 130.0, 129.0, 128.8, 127.8, 127.0, 123.9, 55.8, 51.3, 41.8, 28.6, 26.7, 22.59, 22.57.

IR (film, cm^{-1}) :3291, 2960, 1683, 1642, 1544, 1225;

HRMS (ESI$^+$) m/z calcd for $C_{21}H_{27}NNaO_2^+$ ([M]+Na$^+$) = 348.1934, found 348.1935.

_N_-(_tert_-Butyl)-2-(furan-2-carbonyl)-4-methylpentanamide (1af)



White amorphous solid, 65% yield.

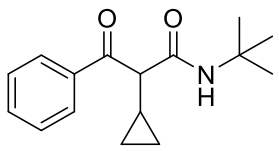
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.60 (m, 1H), 7.38–7.32 (m, 1H), 6.60–6.53 (m, 1H), 6.25 (s, 1H), 4.05 (t, *J* = 7.2 Hz, 1H), 1.90–1.70 (m, 2H), 1.64–1.52 (m, 1H), 1.29 (s, 9H), 0.95–0.87 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.2, 167.6, 152.0, 147.7, 119.7, 112.7, 55.4, 51.2, 41.4, 28.5, 26.4, 22.5, 22.4.

IR (film, cm^{-1}) :3308, 2962, 1674, 1645, 1537, 1463, 1225, 765;

HRMS (ESI$^+$) m/z calcd for $C_{15}H_{23}NNaO_3^+$ ([M]+Na$^+$) = 288.1570, found 288.1569.

_N_-(_tert_-Butyl)-2-cyclopropyl-3-oxo-3-phenylpropanamide (1ag)



White amorphous solid, 36% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.94 (m, 2H), 7.64–7.55 (m, 1H), 7.52–7.44 (m, 2H), 6.40 (s, 1H), 4.50 (d, *J* = 9.6 Hz, 1H), 1.43–1.35 (m, 1H), 1.33 (s, 9H), 0.72–0.62 (m, 1H), 0.61–0.45 (m, 2H), 0.27–0.17 (m, 1H),

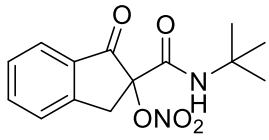
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 167.8, 136.6, 133.7, 128.76, 128.75, 60.7, 51.3, 28.6, 13.2, 4.7, 3.4.

IR (film, cm^{-1}) :3293, 2976, 1689, 1635, 1552, 1226;

HRMS (ESI$^+$) m/z calcd for $C_{16}H_{21}NNaO_2^+$ ([M]+Na$^+$) = 282.1465, found 282.1463.

14. Spectral characterization data and HPLC conditions for products.

(*S*)-2-(*tert*-Butylcarbamoyl)-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate (3a)



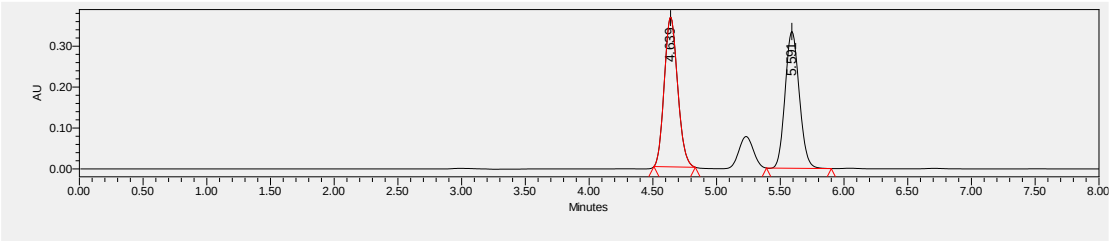
White amorphous solid, 24.3 mg, 83% yield, 92% ee, m.p. 96–99 °C. $[\alpha]_D^{25}$ = 132.0 (*c* = 0.18, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 4.62 min, $t_{(major)}$ = 5.57 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.74 (m, 1H), 7.71–7.63 (m, 1H), 7.54–7.48 (m, 1H), 7.45–7.37 (m, 1H), 6.28 (s, 1H), 4.31 (d, *J* = 17.2 Hz, 1H), 3.26 (d, *J* = 17.2 Hz, 1H), 1.33 (s, 9H).

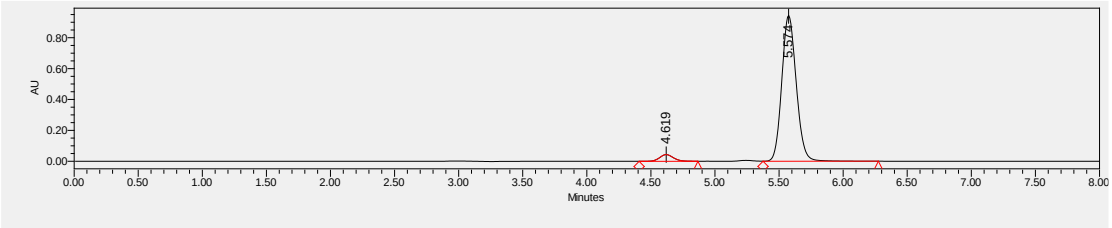
^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0, 161.3, 151.9, 136.8, 132.7, 128.3, 126.4, 125.3, 91.1, 52.3, 35.3, 28.3.

IR (film, cm^{-1}) :3370, 2973, 1729, 1657, 1522, 1294, 1219, 840;

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{16}N_2NaO_5^+$ ([M]+Na$^+$) = 315.0951, found 315.0950.

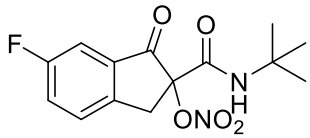


	Retention Time	Area	% Area
1	4.639	2666074	50.78
2	5.591	2584652	49.22



	Retention Time	Area	% Area
1	4.619	323962	4.20
2	5.574	7381642	95.80

(*S*)-2-(*tert*-Butylcarbamoyl)-6-fluoro-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate (3b)



White amorphous solid, 26.3 mg, 85% yield, 92% ee, m.p. 93–97 °C. $[\alpha]_D^{25}$ = 115.5 (*c* = 0.32, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 5.26 min, $t_{(major)}$ = 5.73 min;

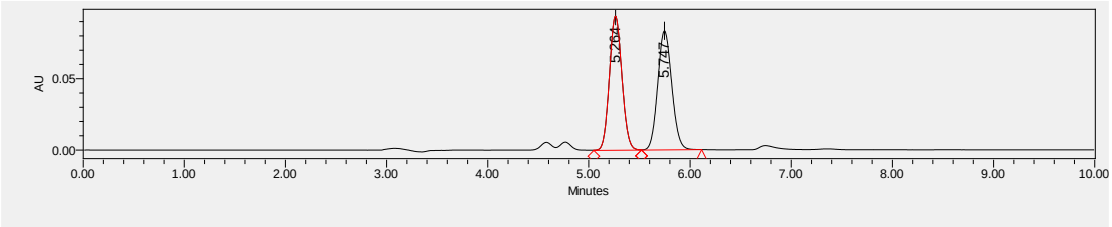
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.48 (m, 1H), 7.44–7.36 (m, 2H), 6.23 (s, 1H), 4.25 (d, *J* = 17.2 Hz, 1H), 3.23 (d, *J* = 17.2 Hz, 1H), 1.34 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 162.5 (*J* = 248.4 Hz), 160.9, 147.4 (*J* = 2.1 Hz), 134.4 (*J* = 7.9 Hz), 127.9 (*J* = 7.9 Hz), 124.5 (*J* = 23.5 Hz), 111.1 (*J* = 22.4 Hz), 91.5, 52.5, 34.9, 28.3.

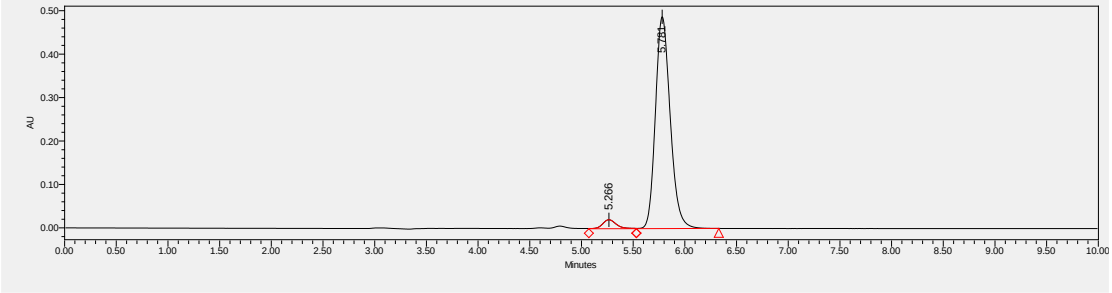
^{19}F NMR (376 MHz, $CDCl_3$) δ -112.4.

IR (film, cm^{-1}) :3373, 2974, 1733, 1659, 1522, 1487, 1293, 1268, 1224, 837;

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{15}FN_2NaO_5^+$ ([M]+Na$^+$) = 338.0857, found 338.0861.

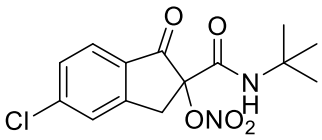


	Retention Time	Area	% Area
1	5.264	806223	50.06
2	5.747	804284	49.94



	Retention Time	Area	% Area
1	5.266	188425	3.74
2	5.781	4844274	96.26

(*S*)-2-(*tert*-Butylcarbamoyl)-5-chloro-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate (3c)



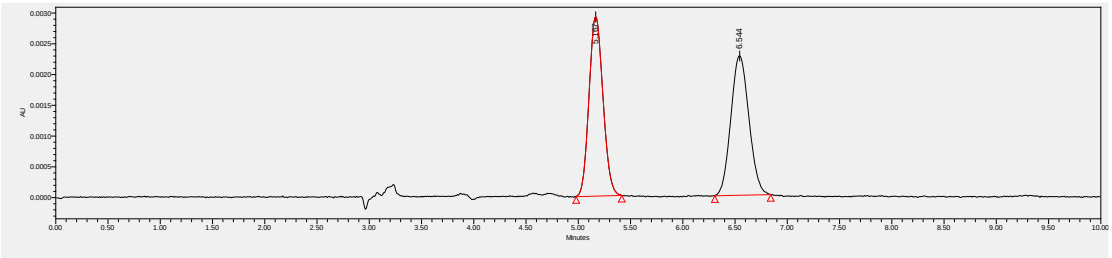
White amorphous solid, 28.1 mg, 86% yield, 94% ee, m.p. 97–99 °C. $[\alpha]_D^{25}$ = 129.8 (*c* = 0.24, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 5.11 min, $t_{(major)}$ = 6.52 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.68 (m, 1H), 7.56–7.47 (m, 1H), 7.44–7.37 (m, 1H), 6.23 (s, 1H), 4.22 (d, *J* = 17.6 Hz, 1H), 3.21 (d, *J* = 17.6 Hz, 1H), 1.33 (s, 9H).

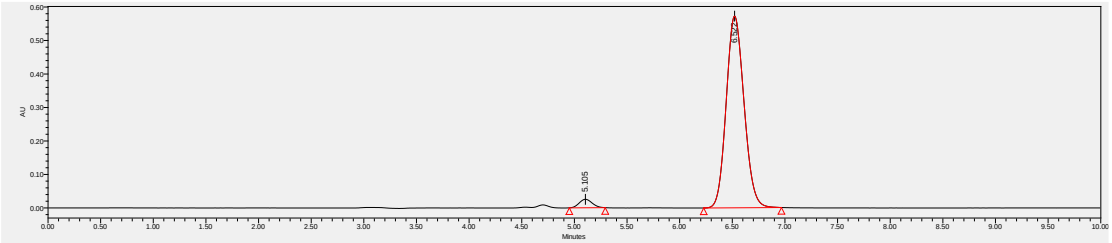
^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 161.0, 153.1, 143.6, 131.2, 129.2, 126.7, 126.4, 91.0, 52.5, 35.1, 28.3.

IR (film, cm^{-1}) :3372, 2973, 1731, 1659, 1522, 1292, 1214, 829;

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{15}Cl^{34.9689}N_2NaO_5^+$ ([M]+Na$^+$) = 349.0562, found 349.0565 and $C_{14}H_{15}Cl^{36.9659}N_2NaO_5^+$ ([M]+Na$^+$) = 351.0532, found 351.0536.

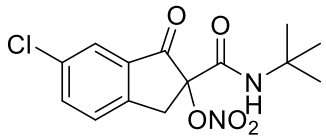


	Retention Time	Area	% Area
1	5.167	27103	49.84
2	6.544	27281	50.16



	Retention Time	Area	% Area
1	5.105	215733	3.10
2	6.522	6735775	96.90

(*S*)-2-(*tert*-Butylcarbamoyl)-6-chloro-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate (3d)

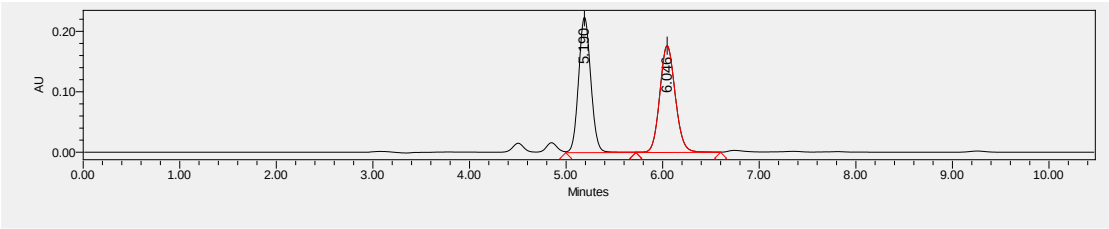


White amorphous solid, 28.7 mg, 88% yield, 93% ee, m.p. 104–107 °C. $[\alpha]_D^{25}$ = 112.7 (*c* = 0.36, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 5.19 min, $t_{(major)}$ = 6.03 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.73 (m, 1H), 7.67–7.62 (m, 1H), 7.53–7.43 (m, 1H), 6.22 (s, 1H), 4.24 (d, *J* = 17.2 Hz, 1H), 3.23 (d, *J* = 17.2 Hz, 1H), 1.33 (s, 9H).

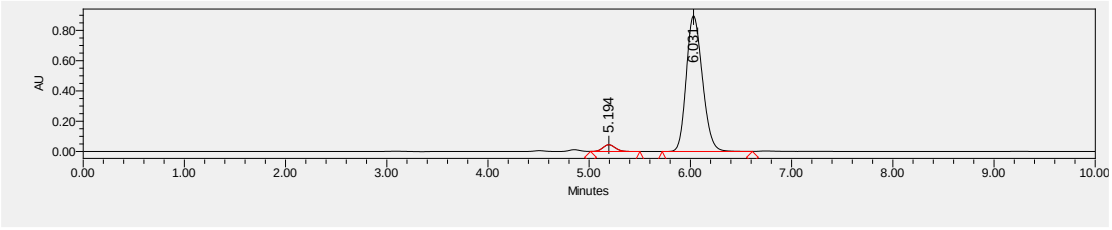
^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 160.8, 149.9, 136.7, 134.7, 134.2, 127.6, 125.0, 91.2, 52.5, 35.0, 28.3.

IR (film, cm^{-1}) :3374, 2973, 1733, 1659, 1522, 1293, 1209, 836;

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{15}Cl^{34.9689}N_2NaO_5^+$ ([M+Na$^+$) = 365.0301, found 365.0304 and $C_{14}H_{15}Cl^{36.9659}N_2NaO_5^+$ ([M]+Na$^+$) = 367.0272, found 367.0276.

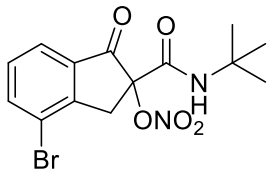


	Retention Time	Area	% Area
1	5.190	1972684	50.07
2	6.046	1966850	49.93



	Retention Time	Area	% Area
1	5.194	376025	3.65
2	6.031	9914165	96.35

(*S*)-4-Bromo-2-(*tert*-butylcarbamoyl)-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate (3e)



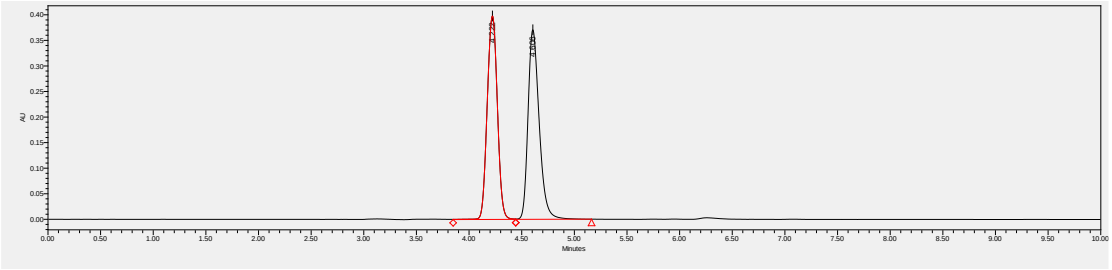
Colorless oil, 31.4 mg, 85% yield, 92% ee, $[\alpha]_D^{25}$ = 118.2 (*c* = 0.34, CH_2Cl_2); HPLC (Daicel chiralcel ID, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 4.21 min, $t_{(major)}$ = 4.60 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.84 (m, 1H), 7.75–7.73 (m, 1H), 7.36–7.32 (m, 1H), 6.24 (s, 1H), 4.26 (d, *J* = 17.6 Hz, 1H), 3.18 (d, *J* = 17.6 Hz, 1H), 1.35 (s, 9H).

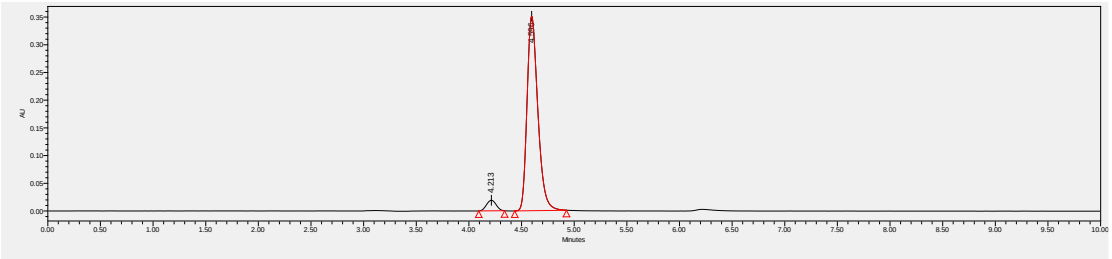
^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 161.0, 151.6, 139.4, 134.7, 129.9, 124.1, 121.7, 90.6, 52.5, 36.6, 28.4.

IR (film, cm^{-1}) :3376, 2973, 1736, 1660, 1521, 1294, 1216, 820;

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{15}Br^{78.9183}N_2NaO_5^+$ ([M+Na$^+$) = 393.0057, found 393.0053 and $C_{14}H_{15}Br^{80.9163}N_2NaO_5^+$ ([M+Na$^+$) = 395.0036, found 395.0040.

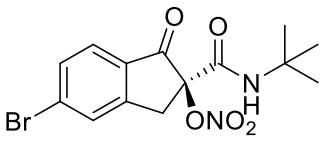


	Retention Time	Area	% Area
1	4.222	2669002	49.49
2	4.606	2723707	50.51



	Retention Time	Area	% Area
1	4.213	121310	4.61
2	4.596	2508090	95.39

(*S*)-5-Bromo-2-(*tert*-butylcarbamoyl)-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate (3f)



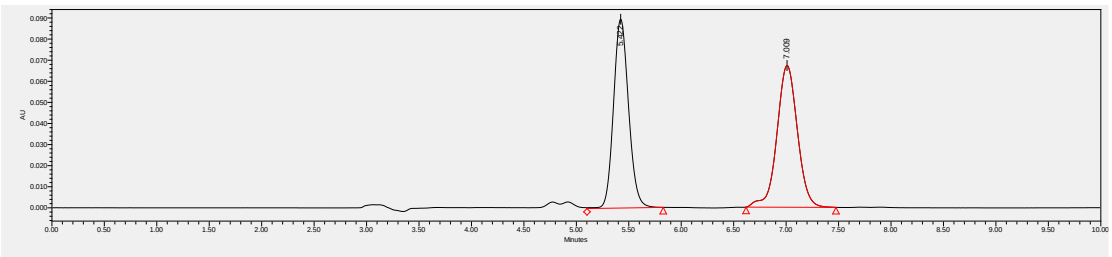
White amorphous solid, 31.2 mg, 84% yield, 93% ee, m.p. 109–112 °C. $[\alpha]_D^{25}$ = 129.8 (*c* = 0.42, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 5.34 min, $t_{(major)}$ = 6.95 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.70 (m, 1H), 7.65–7.63 (m, 1H), 7.60–7.55 (m, 1H), 6.23 (s, 1H), 4.26 (d, *J* = 17.2 Hz, 1H), 3.25 (d, *J* = 17.2 Hz, 1H), 1.33 (s, 9H).

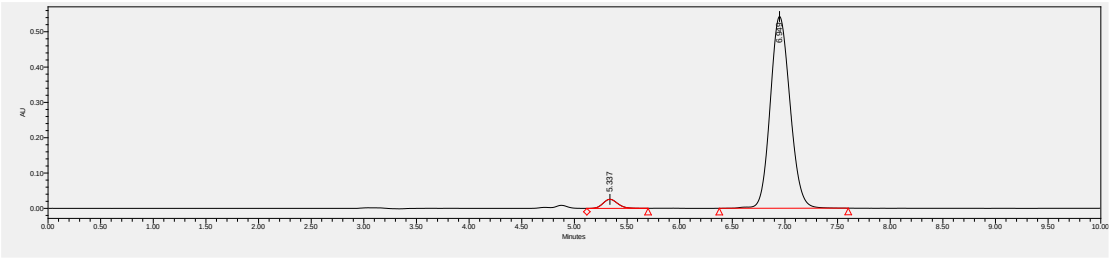
^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 161.0, 153.2, 132.6, 132.1, 131.6, 129.8, 126.4, 90.9, 52.5, 35.0, 28.3.

IR (film, cm^{-1}) :3372, 2973, 1731, 1659, 1522, 1292, 1213, 827;

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{15}Br^{78.9183}N_2NaO_5^+$ ([M+Na$^+$) = 393.0057, found 393.0058 and $C_{14}H_{15}Br^{80.9163}N_2NaO_5^+$ ([M+Na$^+$) = 395.0036, found 395.0042.

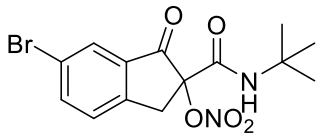


	Retention Time	Area	% Area
1	5.422	892503	49.44
2	7.009	912720	50.56



	Retention Time	Area	% Area
1	5.337	249939	3.41
2	6.949	7088978	96.59

(*S*)-6-Bromo-2-(*tert*-butylcarbamoyl)-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate (3g)



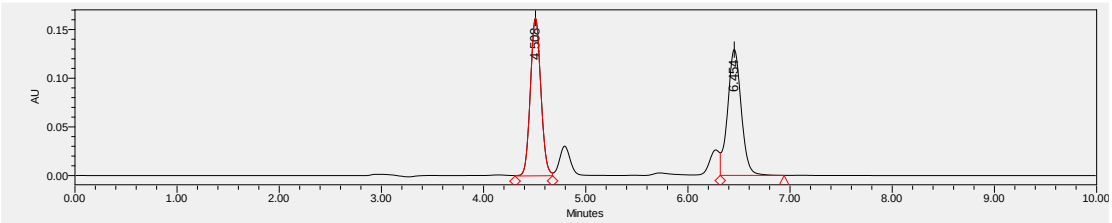
White amorphous solid, 27.5 mg, 74% yield, 89% ee, m.p. 93–97 °C. $[\alpha]_D^{25}$ = 95.7 (*c* = 0.28, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 4.51 min, $t_{(major)}$ = 6.45 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.90 (m, 1H), 7.82–7.75 (m, 1H), 7.45–7.37 (m, 1H), 6.22 (s, 1H), 4.22 (d, *J* = 17.6 Hz, 1H), 3.21 (d, *J* = 17.6 Hz, 1H), 1.33 (s, 9H).

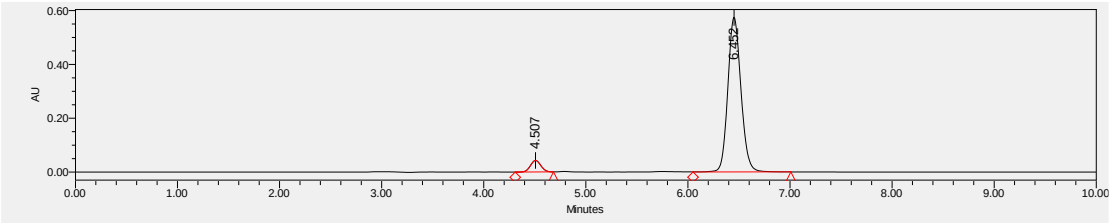
^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 160.9, 150.4, 139.5, 134.5, 128.1, 127.9, 122.4, 91.1, 52.5, 35.1, 28.3.

IR (film, cm^{-1}) :3374, 2973, 1733, 1659, 1522, 1294, 1208, 824;

HRMS (ESI^+) m/z calcd for $C_{14}H_{15}Br^{78.9183}N_2NaO_5^+$ ([M+Na^+]) = 393.0057, found 393.0059 and $C_{14}H_{15}Br^{80.9163}N_2NaO_5^+$ ([M+Na^+]) = 395.0036, found 395.0044.

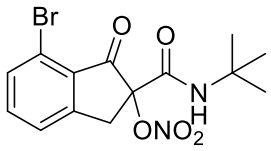


	Retention Time	Area	% Area
1	4.508	1154427	49.15
2	6.454	1194169	50.85



	Retention Time	Area	% Area
1	4.507	302783	5.58
2	6.452	5126355	94.42

(*S*)-7-Bromo-2-(*tert*-butylcarbamoyl)-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate (3h)



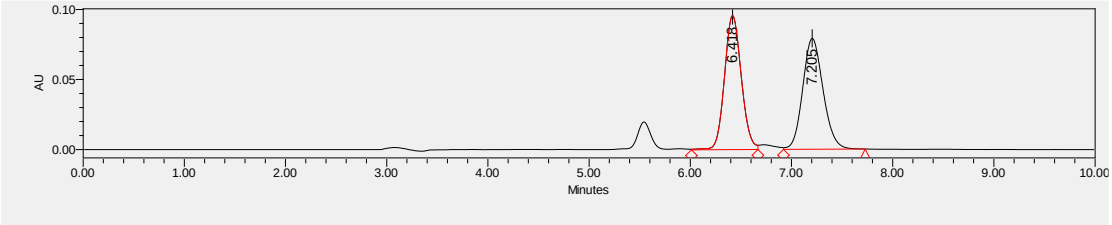
Colorless oil, 27.8 mg, 75% yield, 85% ee, $[\alpha]_D^{25}$ = 134.2 (*c* = 0.08, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 6.42 min, $t_{(major)}$ = 7.20 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64–7.56 (m, 1H), 7.54–7.44 (m, 2H), 6.26 (s, 1H), 4.27 (d, *J* = 17.2 Hz, 1H), 3.25 (d, *J* = 17.2 Hz, 1H), 1.34 (s, 9H).

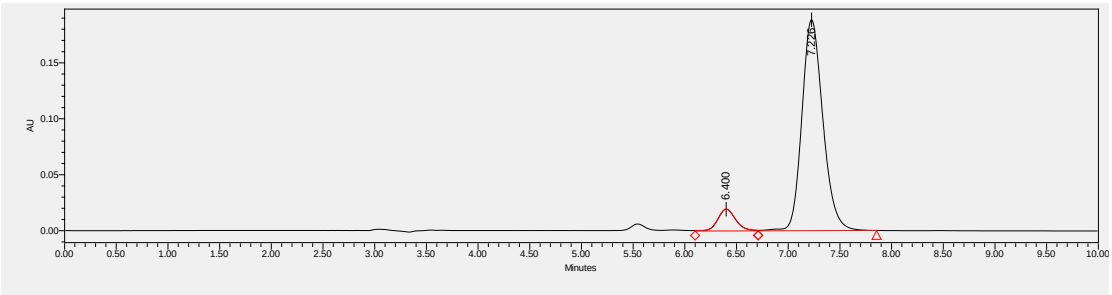
^{13}C NMR (101 MHz, $CDCl_3$) δ 192.5, 161.0, 154.5, 137.0, 133.3, 130.7, 125.3, 121.2, 91.2, 52.5, 34.5, 28.3.

IR (film, cm^{-1}) :3375, 2972, 1732, 1659, 1522, 1291, 1215, 830;

HRMS (ESI^+) m/z calcd for $C_{14}H_{15}Br^{78.9183}N_2NaO_5^+$ ([M+Na$^+$]) = 393.0057, found 393.0058 and $C_{14}H_{15}Br^{80.9163}N_2NaO_5^+$ ([M+Na$^+$]) = 395.0036, found 395.0043.

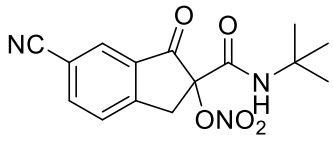


	Retention Time	Area	% Area
1	6.418	1102788	49.92
2	7.205	1106370	50.08



	Retention Time	Area	% Area
1	6.400	210877	7.46
2	7.226	2615017	92.54

(*S*)-2-(*tert*-Butylcarbamoyl)-6-cyano-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate (3i)



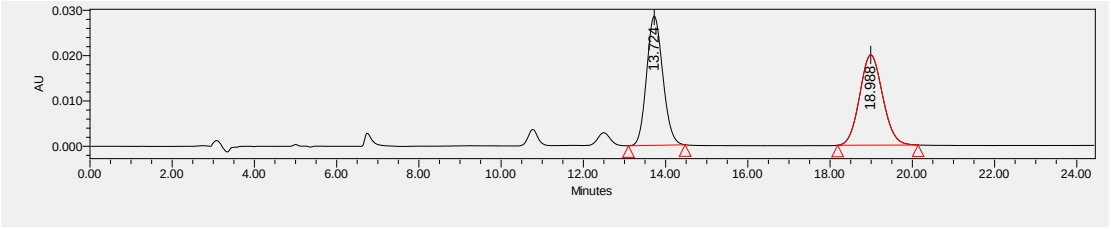
White amorphous solid, 27.0 mg, 85% yield, 72% ee, m.p. 83–87 °C. $[\alpha]_D^{25}$ = 63.4 (*c* = 0.40, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 13.71 min, $t_{(major)}$ = 18.93 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–8.00 (m, 1H), 7.97–7.90 (m, 1H), 7.70–7.64 (m, 1H), 6.22 (s, 1H), 4.31 (d, *J* = 17.6 Hz, 1H), 3.35 (d, *J* = 17.6 Hz, 1H), 1.33 (s, 9H).

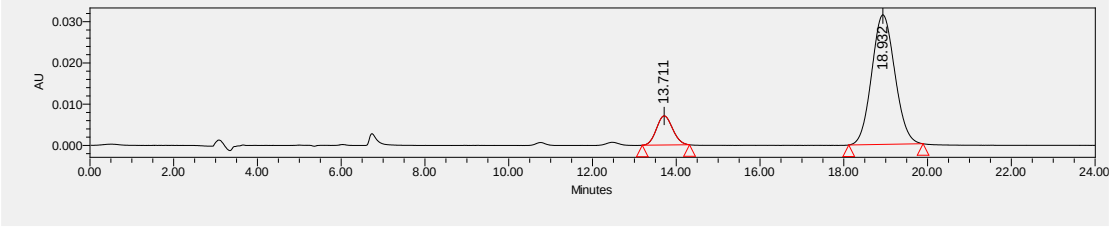
^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 160.5, 155.5, 138.9, 133.6, 129.3, 127.6, 117.3, 112.8, 90.6, 52.7, 35.8, 28.3.

IR (film, cm^{-1}) :3374, 2975, 1741, 1660, 1524, 1294, 1218, 836;

HRMS (ESI^+) m/z calcd for $C_{15}H_{15}N_3NaO_5^+$ ([M+Na$^+$]) = 340.0904, found 340.0909.

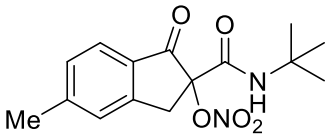


	Retention Time	Area	% Area
1	13.724	779923	50.27
2	18.988	771438	49.73



	Retention Time	Area	% Area
1	13.711	189664	13.60
2	18.932	1205268	86.40

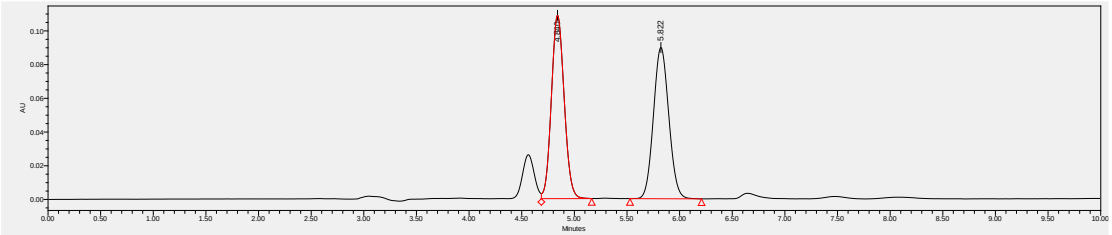
(*S*)-2-(*tert*-Butylcarbamoyl)-5-methyl-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate (3j)



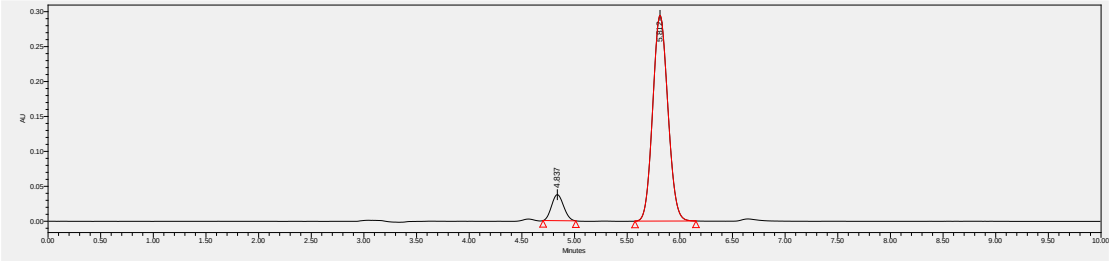
White amorphous solid, 19.1 mg, 62% yield, 82% ee, m.p. 90–94 °C. $[\alpha]_D^{25}$ = 132.3 (*c* = 0.22, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 4.84 min, $t_{(major)}$ = 5.81 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.63 (m, 1H), 7.35–7.27 (m, 1H), 7.26–7.20 (m, 1H), 6.26 (s, 1H), 4.27 (d, *J* = 16.8 Hz, 1H), 3.21 (d, *J* = 16.8 Hz, 1H), 2.46 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 161.5, 152.3, 148.7, 130.4, 129.7, 126.8, 125.2, 91.4, 52.3, 35.1, 28.4, 22.4.

IR (film, cm^{-1}) :3368, 2972, 1725, 1657, 1523, 1293, 830;

HRMS (ESI$^+$) m/z calcd for $C_{15}H_{18}N_2NaO_5^+$ ([M]+Na$^+$) = 329.1108, found 329.1109.



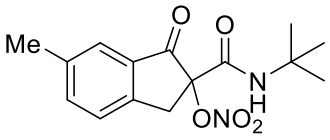
	Retention Time	Area	% Area
1	4.840	916810	50.19
2	5.822	909777	49.81



	Retention Time	Area	% Area

1	4.837	295498	9.08
2	5.812	2957458	90.92

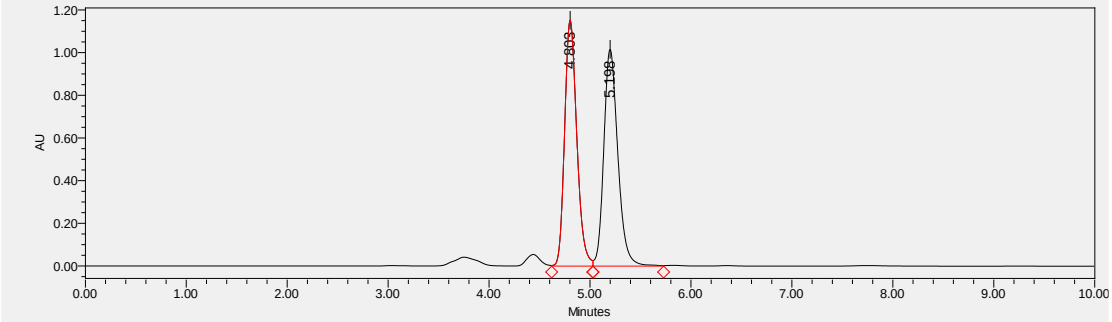
(*S*)-2-(*tert*-Butylcarbamoyl)-6-methyl-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate (3k)



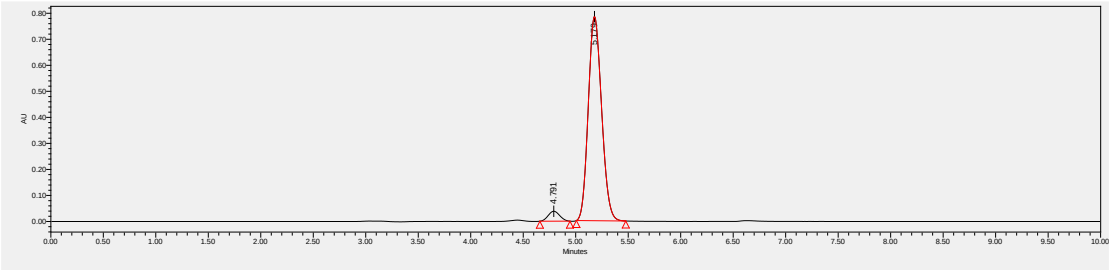
White amorphous solid, 25.4 mg, 83% yield, 92% ee, m.p. 90–94 °C. $[\alpha]_D^{25}$ = 127.7 (*c* = 0.33, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 4.79 min, $t_{(major)}$ = 5.18 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.54 (m, 1H), 7.53–7.47 (m, 1H), 7.44–7.37 (m, 1H), 6.25 (s, 1H), 4.26 (d, *J* = 17.2 Hz, 1H), 3.21 (d, *J* = 17.2 Hz, 1H), 2.40 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0, 161.4, 149.3, 138.5, 138.1, 132.8, 126.1, 125.2, 91.5, 52.3, 35.0, 28.4, 21.1.

IR (film, cm^{-1}) :3370, 2972, 1726, 1656, 1522, 1291, 1222, 825;

HRMS (ESI^+) m/z calcd for $C_{15}H_{18}N_2NaO_5^+$ ([M]+Na^+) = 329.1108, found 329.1107.

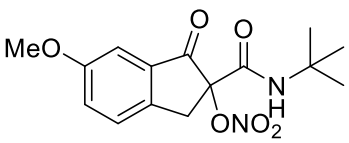


	Retention Time	Area	% Area
1	4.803	9634809	49.56
2	5.198	9804439	50.44



	Retention Time	Area	% Area
1	4.791	290889	4.03
2	5.179	6923964	95.97

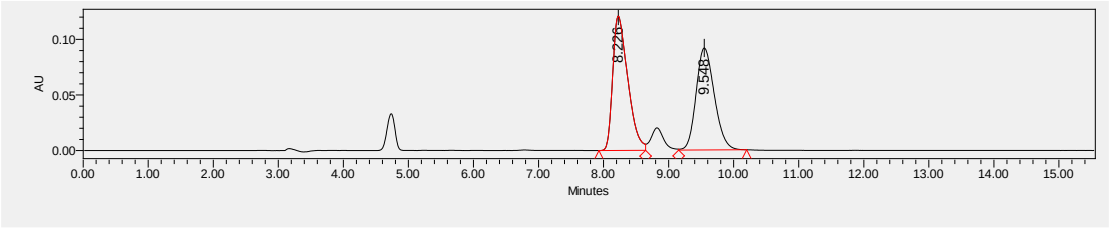
(*S*)-2-(*tert*-Butylcarbamoyl)-6-methoxy-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate (3l)



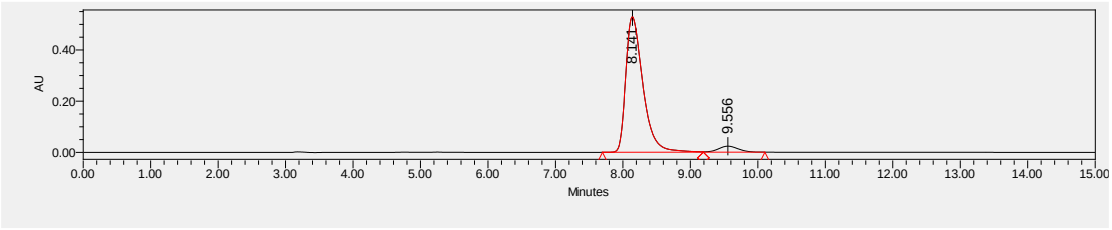
White amorphous solid, 26.0 mg, 80% yield, 90% ee, m.p. 117–121 °C. $[\alpha]_D^{25}$ = 92.1 (*c* = 0.13, CH_2Cl_2); HPLC (Daicel chiralcel ID, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(major)}$ = 8.14 min, $t_{(minor)}$ = 9.56 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.36 (m, 1H), 7.32–7.25 (m, 1H), 7.22–7.15 (m, 1H), 6.25 (s, 1H), 4.23 (d, *J* = 16.8 Hz, 1H), 3.84 (s, 3H), 3.19 (d, *J* = 16.8 Hz, 1H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0, 161.3, 159.9, 145.0, 133.8, 127.2, 126.4, 106.2, 91.7, 55.6, 52.4, 34.7, 28.4.

IR (film, cm^{-1}) :3371, 2970, 1724, 1657, 1494, 1286, 1229, 840;

HRMS (ESI^+) m/z calcd for $C_{15}H_{18}N_2NaO_6^+$ ([M]+Na^+) = 345.1057, found 345.1059.

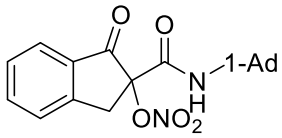


	Retention Time	Area	% Area
1	8.226	1893757	51.44
2	9.548	1787507	48.56



	Retention Time	Area	% Area
1	8.141	9332492	95.10
2	9.556	481095	4.90

(*S*)-2-(((3r)-Adamantan-1-yl)carbamoyl)-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate (3m)



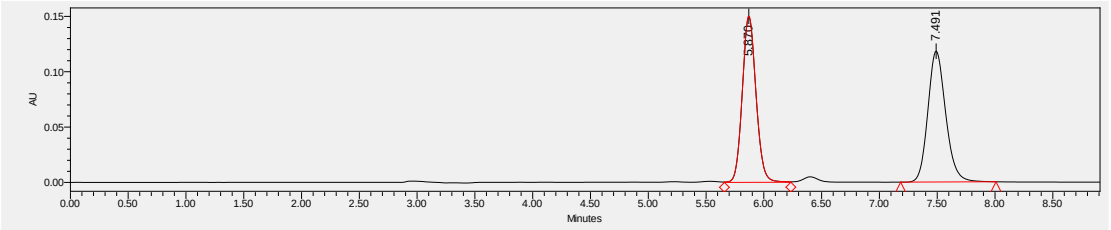
White amorphous solid, 29.0 mg, 78% yield, 76% ee, m.p. 111–114 °C. $[\alpha]_D^{25}$ = 104.6 (*c* = 0.30, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 5.80 min, $t_{(major)}$ = 7.41 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.75 (m, 1H), 7.73–7.65 (m, 1H), 7.55–7.48 (m, 1H), 7.45–7.38 (m, 1H), 6.12 (s, 1H), 4.30 (d, *J* = 17.2 Hz, 1H), 3.26 (d, *J* = 17.2 Hz, 1H), 2.12–2.02 (m, 3H), 2.00–1.91 (m, 6H), 1.68–1.60 (m, 6H).

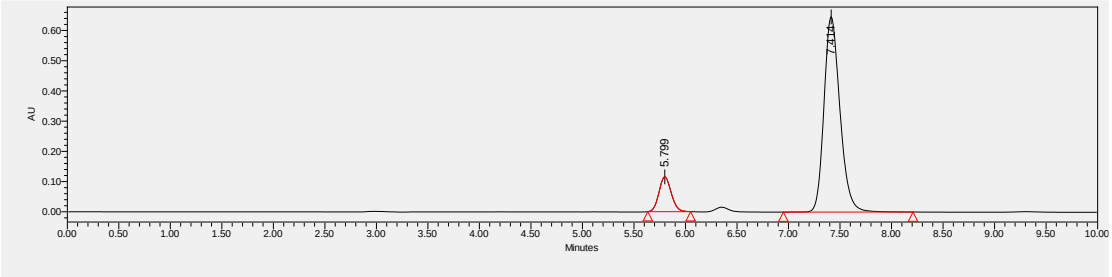
^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0, 161.0, 151.9, 136.8, 132.8, 128.3, 126.4, 125.4, 91.2, 53.1, 41.1, 36.1, 35.3, 29.3.

IR (film, cm^{-1}) :3363, 2910, 1728, 1666, 1520, 1294, 831;

HRMS (ESI$^+$) m/z calcd for $C_{20}H_{22}N_2NaO_5^+$ ([M]+Na$^+$) = 393.1421, found 393.1423.

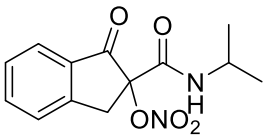


	Retention Time	Area	% Area
1	5.870	1236915	49.34
2	7.491	1270089	50.66



	Retention Time	Area	% Area
1	5.799	947888	11.96
2	7.414	6977375	88.04

(*S*)-2-(Isopropylcarbamoyl)-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate (3n)



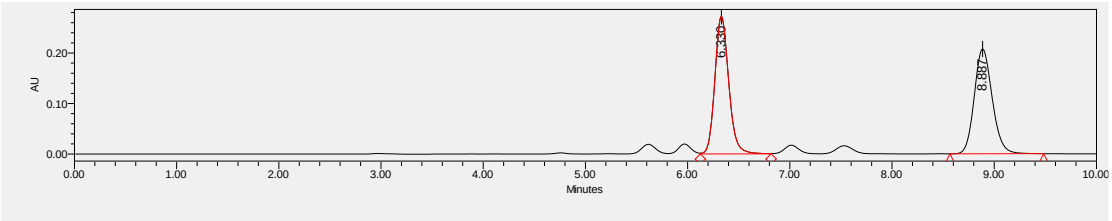
White amorphous solid, 22.2 mg, 80% yield, 82% ee, m.p. 73–75 °C. $[\alpha]_D^{25}$ = 98.9 (*c* = 0.09, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 6.30 min, $t_{(major)}$ = 8.95 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.75 (m, 1H), 7.73–7.65 (m, 1H), 7.55–7.48 (m, 1H), 7.46–7.39 (m, 1H), 6.31 (s, 1H), 4.34 (d, *J* = 17.2 Hz, 1H), 4.10–3.90 (m, 1H), 3.30 (d, *J* = 17.2 Hz, 1H), 1.22–1.14 (m, 6H).

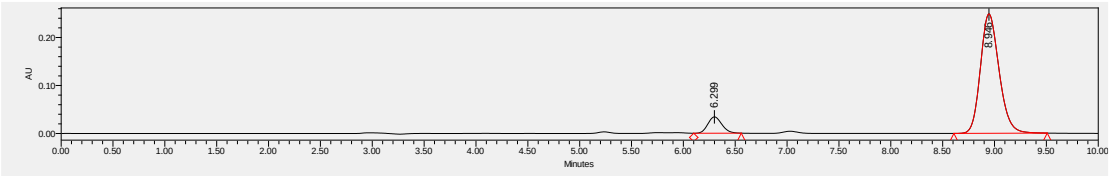
^{13}C NMR (101 MHz, $CDCl_3$) δ 194.8, 161.6, 151.9, 136.9, 132.7, 128.3, 126.6, 125.4, 90.9, 42.7, 35.4, 22.4, 22.1.

IR (film, cm^{-1}) :3362, 2976, 1730, 1657, 1527, 1295, 839;

HRMS (ESI$^+$) m/z calcd for $C_{13}H_{14}N_2NaO_5^+$ ([M]+Na$^+$) = 301.0795, found 301.0797.

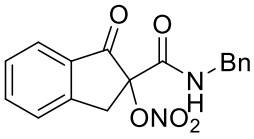


	Retention Time	Area	% Area
1	6.330	2563149	50.36
2	8.887	2526856	49.64



	Retention Time	Area	% Area
1	6.299	320142	9.35
2	8.946	3105466	90.65

(*S*)-2-(Benzylcarbamoyl)-1-oxo-2,3-dihydro-1*H*-inden-2-yl nitrate (3o)



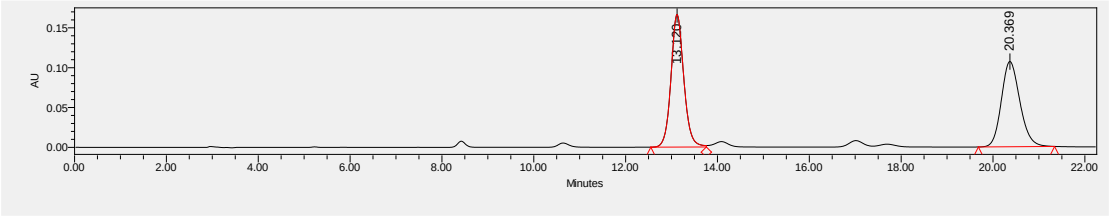
Colorless oil, 24.3 mg, 75% yield, 78% ee, $[\alpha]_D^{25}$ = 100.0 (*c* = 0.06, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 13.08 min, $t_{(major)}$ = 20.48 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.78 (m, 1H), 7.75–7.67 (m, 1H), 7.59–7.52 (m, 1H), 7.50–7.41 (m, 1H), 7.40–7.19 (m, 5H), 6.82 (s, 1H), 4.57–4.37 (m, 3H), 3.35 (d, *J* = 16.8 Hz, 1H).

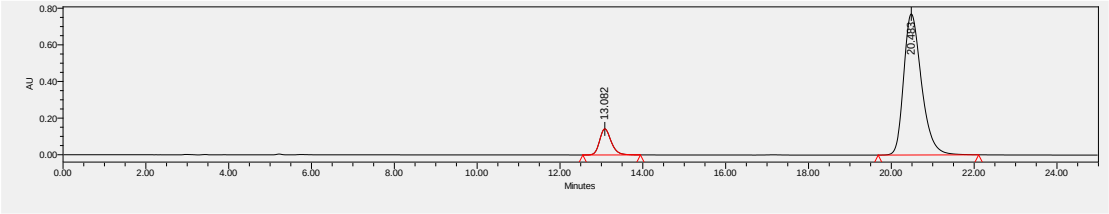
^{13}C NMR (101 MHz, $CDCl_3$) δ 194.5, 162.6, 151.8, 137.0, 136.9, 132.6, 128.8, 128.5, 127.8, 127.6, 126.5, 125.5, 90.9, 44.2, 35.6.

IR (film, cm^{-1}) :3358, 2928, 1729, 1657, 1527, 1294, 836;

HRMS (ESI$^+$) m/z calcd for $C_{17}H_{14}N_2NaO_5^+$ ([M]+Na$^+$) = 349.0795, found 349.0797.

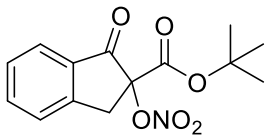


	Retention Time	Area	% Area
1	13.120	3232179	51.91
2	20.369	2994498	48.09



	Retention Time	Area	% Area
1	13.082	2760601	10.72
2	20.483	22998813	89.28

(*S*)-*tert*-Butyl-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3p)



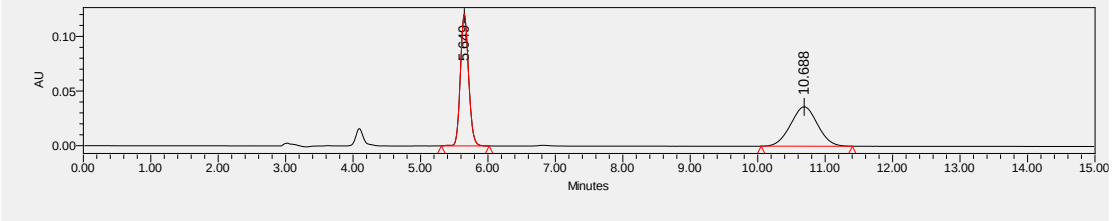
Colorless oil, 23.7 mg, 81% yield, 84% ee, $[\alpha]_D^{25}$ = 138.4 (*c* = 0.44, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 5.65 min, $t_{(major)}$ = 10.66 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85–7.80 (m, 1H), 7.75–7.67 (m, 1H), 7.55–7.50 (m, 1H), 7.49–7.42 (m, 1H), 4.23 (d, *J* = 17.6 Hz, 1H), 3.41 (d, *J* = 17.6 Hz, 1H), 1.44 (s, 9H).

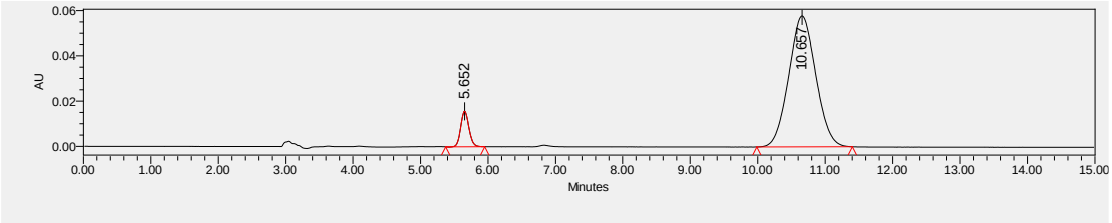
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 163.9, 151.7, 136.9, 132.6, 128.6, 126.3, 125.8, 89.0, 85.0, 38.3, 27.6.

IR (film, cm^{-1}) : 2982, 1729, 1656, 1296, 1153, 840;

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{15}NNaO_6^+$ ([M]+Na$^+$) = 316.0792, found 316.0794.

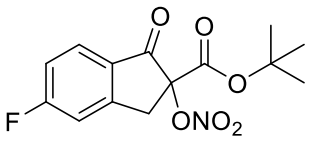


	Retention Time	Area	% Area
1	5.649	1021626	50.48
2	10.688	1002056	49.52



	Retention Time	Area	% Area
1	5.652	132971	7.64
2	10.657	1608156	92.36

(*S*)-*tert*-Butyl-5-fluoro-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3q)



Colorless oil, 25.2 mg, 81% yield, 91% ee, $[\alpha]_D^{25}$ = 132.5 (*c* = 0.46, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 6.26 min, $t_{(major)}$ = 13.86 min;

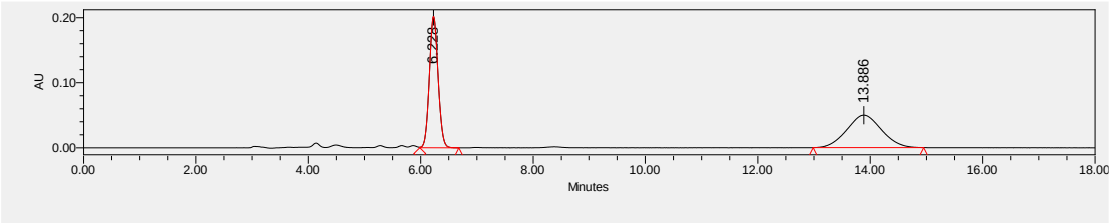
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.75 (m, 1H), 7.25–7.10 (m, 2H), 4.22 (d, *J* = 18.0 Hz, 1H), 3.39 (d, *J* = 18.0 Hz, 1H), 1.44 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4, 168.3 (*J* = 259 Hz), 163.7, 154.7 (*J* = 10.8 Hz), 129.1 (*J* = 1.7 Hz), 128.3 (*J* = 10.8 Hz), 117.2 (*J* = 23.8 Hz), 113.3 (*J* = 22.9 Hz), 89.0, 85.3, 38.2 (*J* = 1.9 Hz), 27.6.

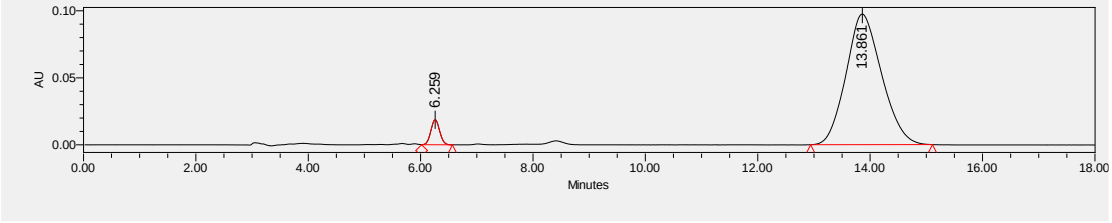
^{19}F NMR (376 MHz, $CDCl_3$) δ -97.8.

IR (film, cm^{-1}) : 2983, 1731, 1658, 1259, 1153, 834;

HRMS (ESI^+) m/z calcd for $C_{14}H_{14}FNNaO_6^+$ ([M]+Na^+) = 334.0697, found 334.0697.

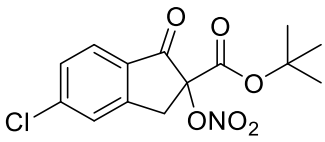


	Retention Time	Area	% Area
1	6.228	2182525	50.44
2	13.886	2144565	49.56



	Retention Time	Area	% Area
1	6.259	202335	4.51
2	13.861	4285804	95.49

(*S*)-*tert*-Butyl-5-chloro-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3r)



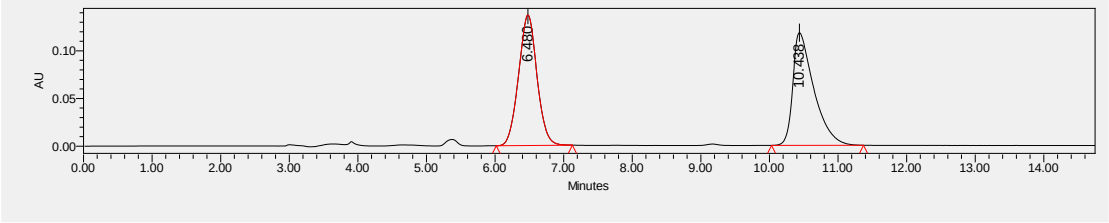
Colorless oil, 26.7 mg, 81% yield, 90% ee, $[\alpha]_D^{25}$ = 147.5 (*c* = 0.67, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 6.32 min, $t_{(major)}$ = 10.96 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.71 (m, 1H), 7.55–7.50 (m, 1H), 7.47–7.40 (m, 1H), 4.19 (d, *J* = 17.6 Hz, 1H), 3.38 (d, *J* = 17.6 Hz, 1H), 1.43 (s, 9H).

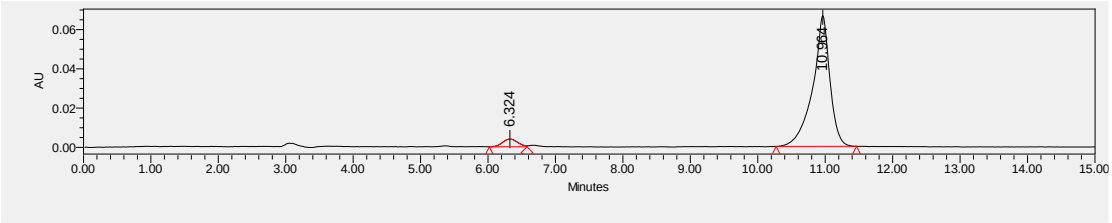
^{13}C NMR (101 MHz, $CDCl_3$) δ 189.9, 163.6, 153.0, 143.7, 131.1, 129.5, 126.8, 126.6, 88.9, 85.3, 38.0, 27.6.

IR (film, cm^{-1}) : 2982, 1730, 1658, 1296, 1153, 832;

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{14}Cl^{34.9689}NNaO_6^+$ ([M]+Na$^+$) = 350.0402, found 350.0406 and $C_{14}H_{14}Cl^{36.9659}NNaO_6^+$ ([M]+Na$^+$) = 352.0372, found 352.0375.

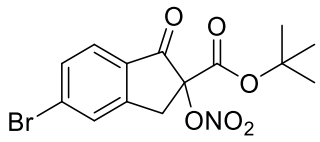


	Retention Time	Area	% Area
1	6.480	2546466	50.36
2	10.438	2510115	49.64



	Retention Time	Area	% Area
1	6.324	61179	4.95
2	10.964	1175112	95.05

(*S*)-*tert*-Butyl-5-bromo-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3s)



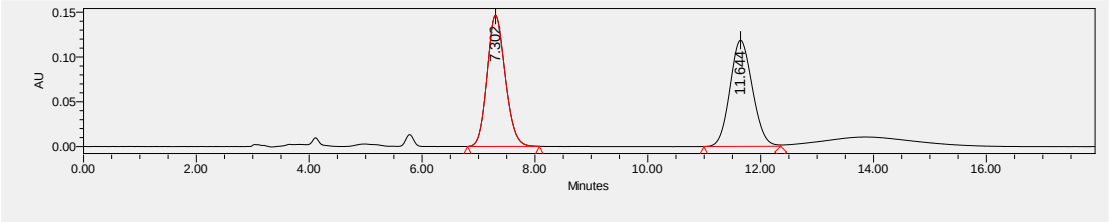
White amorphous solid, 33.6 mg, 90% yield, 90% ee, m.p. 70–74 °C. $[\alpha]_D^{25}$ = 137.3 (*c* = 0.47, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ =7.35 min, $t_{(major)}$ = 11.73 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.55 (m, 1H), 4.20 (d, *J* = 18.0 Hz, 1H), 3.38 (d, *J* = 18.0 Hz, 1H), 1.44 (s, 9H).

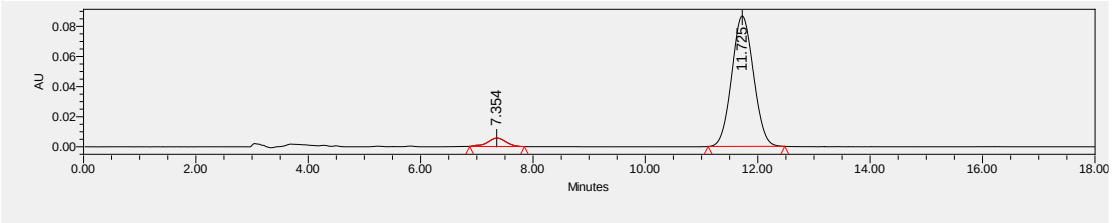
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 163.5, 153.0, 132.7, 132.4, 131.5, 129.7, 126.8, 88.8, 85.3, 37.9, 27.6.

IR (film, cm^{-1}) : 2981, 1730, 1658, 1296, 1153, 832;

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{14}Br^{78.9183}NNaO_6^+$ ([M]+Na$^+$) = 393.9897, found 393.9899 and $C_{14}H_{14}Br^{80.9163}NNaO_6^+$ ([M]+Na$^+$) = 395.9876, found 395.9878.

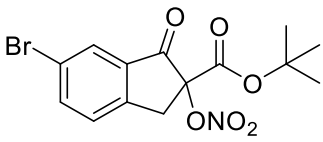


	Retention Time	Area	% Area
1	7.302	3259470	49.94
2	11.644	3267084	50.06



	Retention Time	Area	% Area
1	7.354	126550	5.16
2	11.725	2326373	94.84

(*S*)-*tert*-Butyl-6-bromo-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3t)



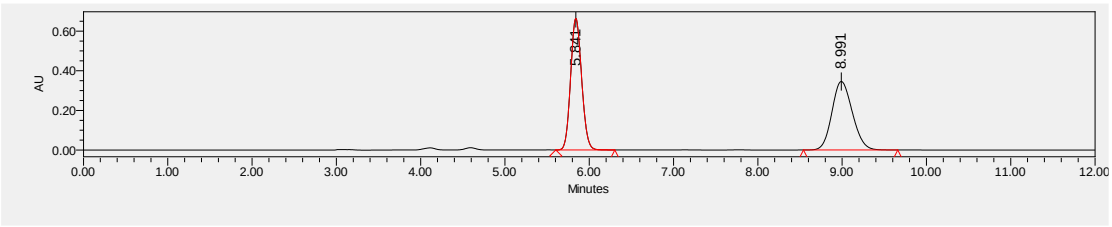
Colorless oil, 30.7 mg, 82% yield, 89% ee, $[\alpha]_D^{25}$ = 144.6 (*c* = 0.45, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 5.82 min, $t_{(major)}$ = 8.96 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.90 (m, 1H), 7.85–7.75 (m, 1H), 7.45–7.37 (m, 1H), 4.16 (d, *J* = 18.0 Hz, 1H), 3.34 (d, *J* = 18.0 Hz, 1H), 1.44 (s, 9H).

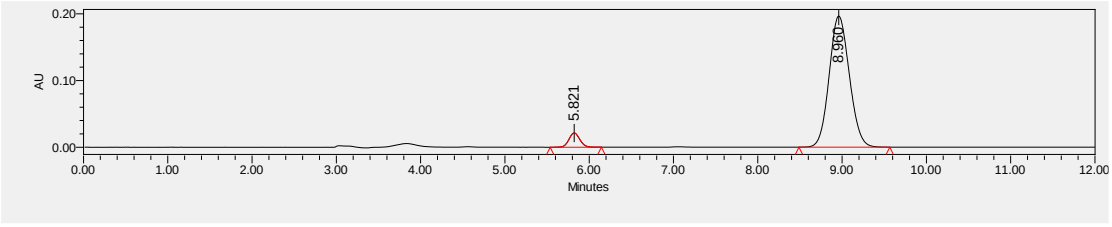
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 163.5, 150.2, 139.7, 134.4, 128.5, 127.8, 122.7, 89.1, 85.4, 38.0, 27.6.

IR (film, cm^{-1}) : 2981, 1729, 1655, 1298, 1152, 839;

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{14}Br^{78.9183}NNaO_6^+$ ([M]+Na$^+$) = 393.9897, found 393.9896 and $C_{14}H_{14}Br^{80.9163}NNaO_6^+$ ([M]+Na$^+$) = 395.9876, found 395.9877.

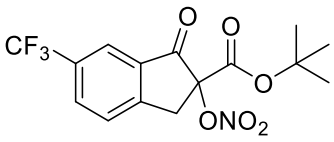


	Retention Time	Area	% Area
1	5.841	6015995	50.83
2	8.991	5819941	49.17



	Retention Time	Area	% Area
1	5.821	193598	5.59
2	8.960	3267831	94.41

(*S*)-*tert*-Butyl-2-(nitrooxy)-1-oxo-6-(trifluoromethyl)-2,3-dihydro-1*H*-indene-2-carboxylate (3u)



Colorless oil, 20.1 mg, 67% yield, 78% ee, $[\alpha]_D^{25}$ = 107.7 (*c* = 0.38, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 4.70 min, $t_{(major)}$ = 5.91 min;

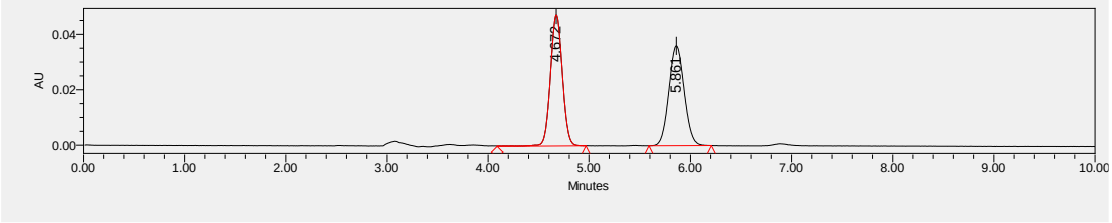
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15–8.05 (m, 1H), 8.00–7.90 (m, 1H), 7.73–7.64 (m, 1H), 4.29 (d, *J* = 18.0 Hz, 1H), 3.47 (d, *J* = 18.0 Hz, 1H), 1.45 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 163.4, 154.7, 133.2 (q, *J* = 3.0 Hz), 131.6 (q, *J* = 33.0 Hz), 127.2, 123.3 (q, *J* = 271 Hz), 122.9 (q, *J* = 4.0 Hz), 88.9, 85.6, 38.4, 27.6.

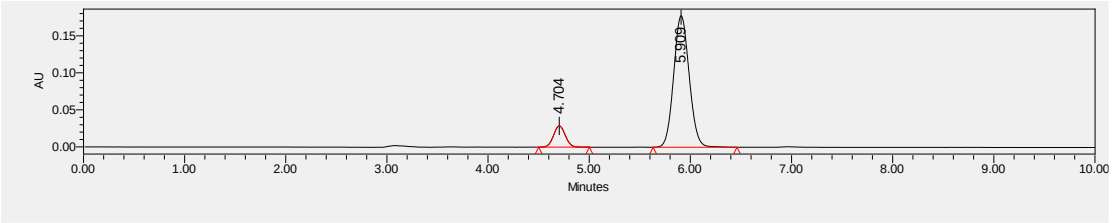
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8.

IR (film, cm^{-1}) : 2982, 1731, 1658, 1297, 1151, 835;

HRMS (ESI^+) m/z calcd for $C_{15}H_{14}F_3NKO_6^+$ ([M]+K^+) = 400.0406, found 400.0406.

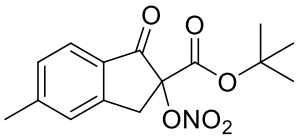


	Retention Time	Area	% Area
1	4.672	387507	50.56
2	5.861	378876	49.44



	Retention Time	Area	% Area
1	4.704	231669	10.91
2	5.909	1891031	89.09

(*S*)-*tert*-Butyl-5-methyl-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3v)



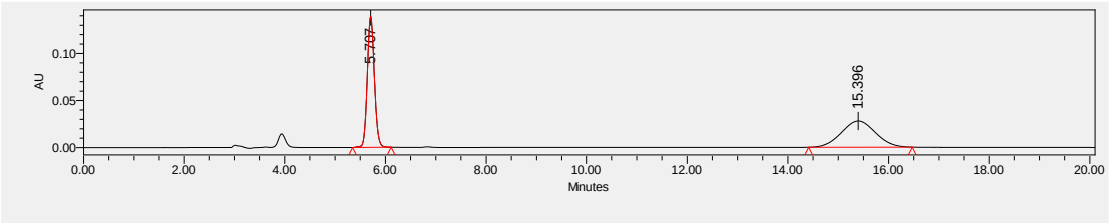
Colorless oil, 25.0 mg, 81% yield, 88% ee, $[\alpha]_D^{25}$ = 93.1 (*c* = 0.32, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 5.71 min, $t_{(major)}$ = 15.39 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.60 (m, 1H), 7.28–7.15 (m, 2H), 4.10 (d, *J* = 17.6 Hz, 1H), 3.27 (d, *J* = 17.6 Hz, 1H), 2.41 (s, 3H), 1.37 (s, 9H).

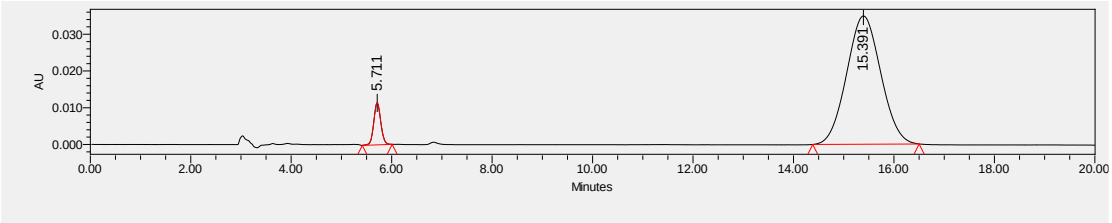
^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 164.1, 152.2, 148.8, 130.4, 129.9, 126.6, 125.6, 89.3, 84.9, 38.1, 27.6, 22.3.

IR (film, cm^{-1}) : 2984, 1735, 1661, 1298, 1141, 837;

HRMS (ESI^+) m/z calcd for $C_{15}H_{17}NNaO_6^+$ ([M]+Na^+) = 330.0948, found 330.0949.

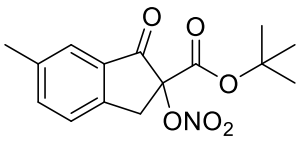


	Retention Time	Area	% Area
1	5.707	1352543	50.80
2	15.396	1310096	49.20



	Retention Time	Area	% Area
1	5.711	112276	6.39
2	15.391	1645363	93.61

(*S*)-*tert*-Butyl-6-methyl-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3w)



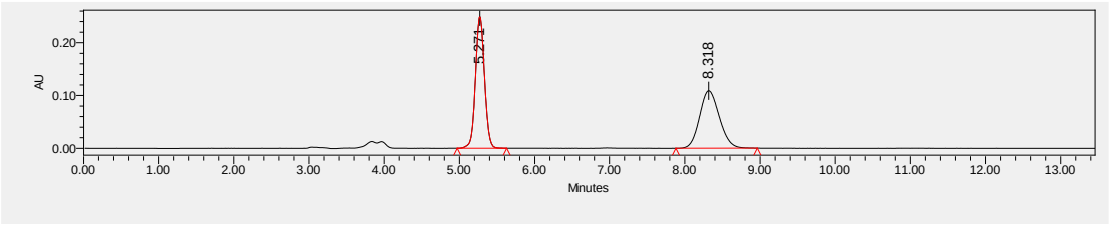
Colorless oil, 24.1 mg, 79% yield, 93% ee, $[\alpha]_D^{25}$ = 162.4 (*c* = 0.43, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 5.30 min, $t_{(major)}$ = 8.37 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65–7.58 (m, 1H), 7.55–7.47 (m, 1H), 7.43–7.37 (m, 1H), 4.17 (d, *J* = 17.6 Hz, 1H), 3.34 (d, *J* = 17.6 Hz, 1H), 2.42 (s, 3H), 1.44 (s, 9H).

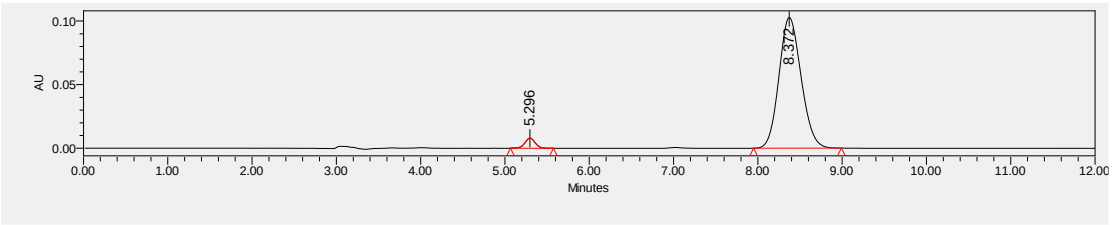
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 164.0, 149.1, 138.8, 138.2, 132.8, 126.0, 125.6, 89.4, 84.9, 38.0, 27.6, 21.1.

IR (film, cm^{-1}) : 2982, 1727, 1655, 1297, 1152, 834;

HRMS (ESI$^+$) m/z calcd for $C_{15}H_{17}NNaO_6^+$ ([M]+Na$^+$) = 330.0948, found 330.0947.

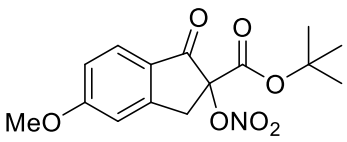


	Retention Time	Area	% Area
1	5.271	2078580	51.19
2	8.318	1982161	48.81



	Retention Time	Area	% Area
1	5.296	67243	3.46
2	8.372	1873595	96.54

(*S*)-*tert*-Butyl-5-methoxy-2-(nitrooxy)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (3x)



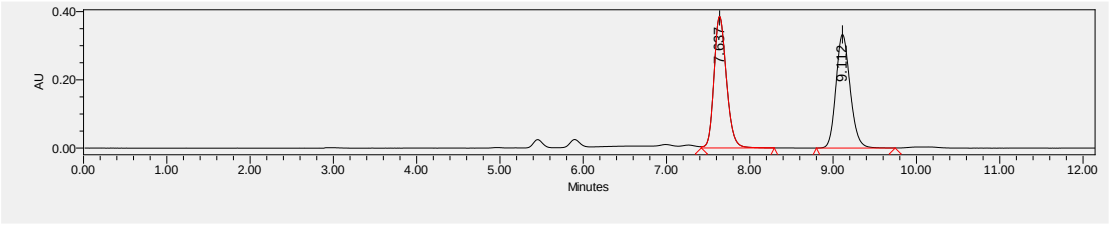
Colorless oil, 29.8 mg, 92% yield, 84% ee, $[\alpha]_D^{25}$ = 194.6 (*c* = 0.41, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 7.64 min, $t_{(major)}$ = 9.10 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.65 (m, 1H), 7.03–6.86 (m, 2H), 4.18 (d, *J* = 17.6 Hz, 1H), 3.92 (s, 3H), 3.33 (d, *J* = 17.6 Hz, 1H), 1.45 (s, 9H).

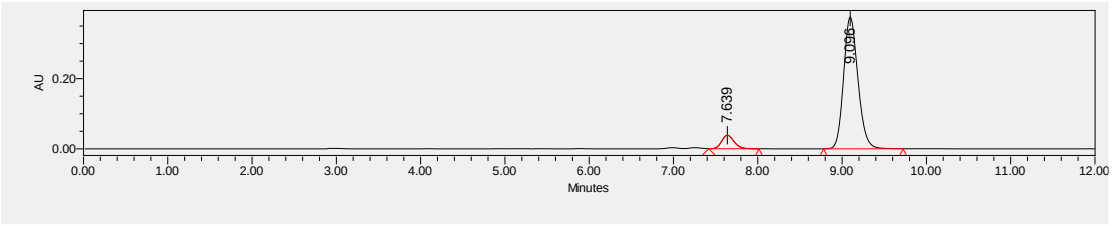
^{13}C NMR (101 MHz, $CDCl_3$) δ 188.9, 167.0, 164.2, 154.9, 127.6, 125.7, 116.9, 109.4, 89.4, 84.8, 55.9, 38.3, 27.7.

IR (film, cm^{-1}) : 2981, 1721, 1655, 1299, 1265, 1154, 838;

HRMS (ESI^+) m/z calcd for $C_{15}H_{17}NNaO_7^+$ ([M]+Na^+) = 346.0897, found 346.0896.

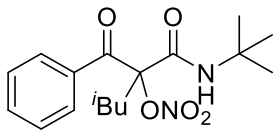


	Retention Time	Area	% Area
1	7.637	3988068	50.35
2	9.112	3932793	49.65



	Retention Time	Area	% Area
1	7.639	395197	8.19
2	9.096	4430042	91.81

(*S*)-2-Benzoyl-1-(*tert*-butylamino)-4-methyl-1-oxopentan-2-yl nitrate (3y)



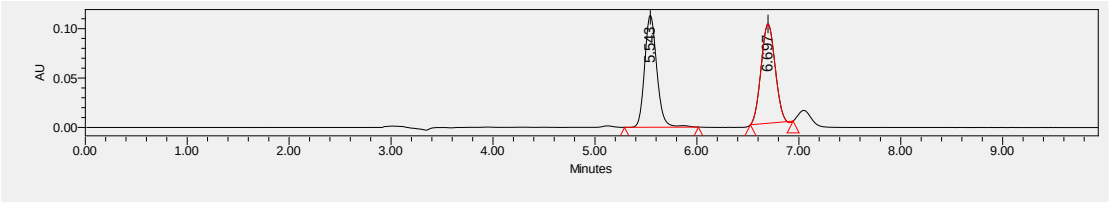
White amorphous solid, 27.6 mg, 82% yield, 92% ee, m.p. 96–99 °C. $[\alpha]_\lambda^{25}$ = 207.3 (*c* = 0.47, CH_2Cl_2, λ = 365 nm); HPLC (Daicel chiralcel IG, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 5.62 min, $t_{(major)}$ = 6.80 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.83–7.75 (m, 2H), 7.61–7.51 (m, 1H), 7.46–7.37 (m, 2H), 2.65–2.45 (m, 2H), 1.81–1.73 (m, 1H), 1.40 (s, 9H), 0.98–0.89 (m, 6H).

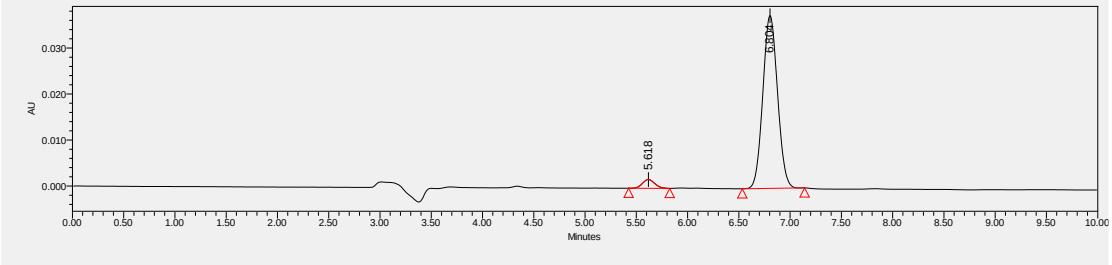
^{13}C NMR (101 MHz, $CDCl_3$) δ 187.3, 162.5, 133.9, 133.8, 128.7, 128.2, 98.3, 52.5, 45.3, 28.3, 24.3, 23.7, 23.5.

IR (film, cm^{-1}) :3395, 2967, 1680, 1515, 1225;

HRMS (ESI^+) m/z calcd for $C_{17}H_{25}N_2O_5^+$ ([M]+H^+) = 337.1758, found 337.1754.

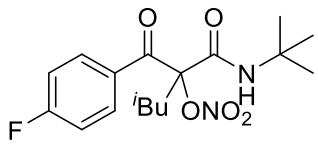


	Retention Time	Area	% Area
1	5.543	942474	49.54
2	6.697	959996	50.46



	Retention Time	Area	% Area
1	5.618	15943	4.09
2	6.804	373897	95.91

(*S*)-1-(*tert*-Butylamino)-2-(4-fluorobenzoyl)-4-methyl-1-oxopentan-2-yl nitrate (3z)



Colorless oil, 25.5 mg, 72% yield, 82% ee, $[\alpha]_{\lambda}^{25}$ = 164.4 (*c* = 0.15, CH_2Cl_2, λ = 365 nm); HPLC (Daicel chiralcel IG, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 4.99 min, $t_{(major)}$ = 6.09 min;

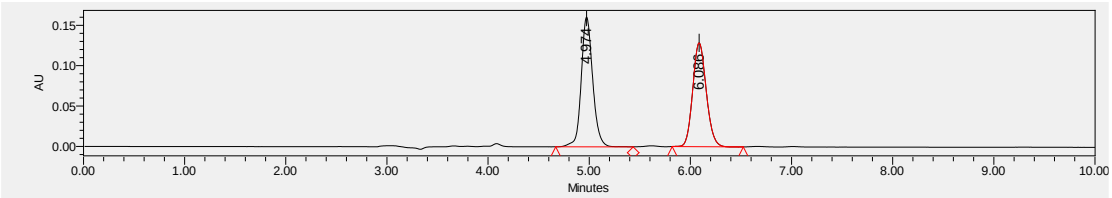
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.87–7.77 (m, 2H), 7.15–7.05 (m, 2H), 2.62–2.43 (m, 2H), 1.80–1.74 (m, 1H), 1.40 (s, 9H), 0.98–0.90 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 185.6, 165.9 (*J* = 215.4 Hz), 162.5, 131.0 (*J* = 9.5 Hz), 130.3 (*J* = 3.2 Hz), 116.1 (*J* = 22.1 Hz), 98.2, 52.6, 45.4, 28.3, 24.3, 23.7, 23.6.

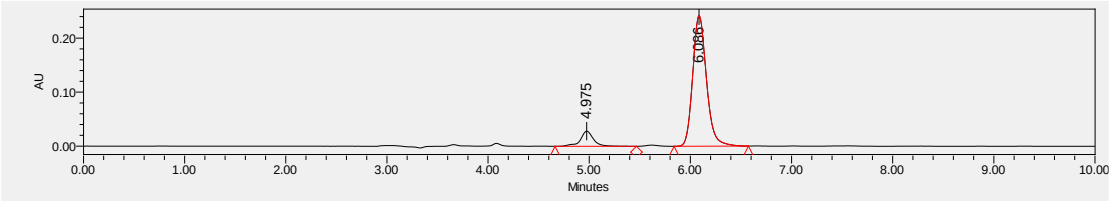
^{19}F NMR (376 MHz, $CDCl_3$) δ -103.2.

IR (film, cm^{-1}) :3395, 2965, 1707, 1681, 1513, 1239, 1162, 849;

HRMS (ESI^+) m/z calcd for $C_{17}H_{24}FN_2O_5^+$ ($[M]+H^+$) = 355.1664, found 355.1661.

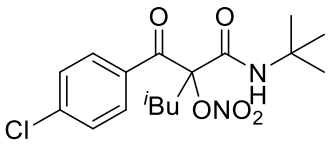


	Retention Time	Area	% Area
1	4.974	1268369	51.60
2	6.086	1189522	48.40



	Retention Time	Area	% Area
1	4.994	2420812	8.96
2	6.087	24586681	91.04

(*S*)-1-(*tert*-Butylamino)-2-(4-chlorobenzoyl)-4-methyl-1-oxopentan-2-yl nitrate (3aa)



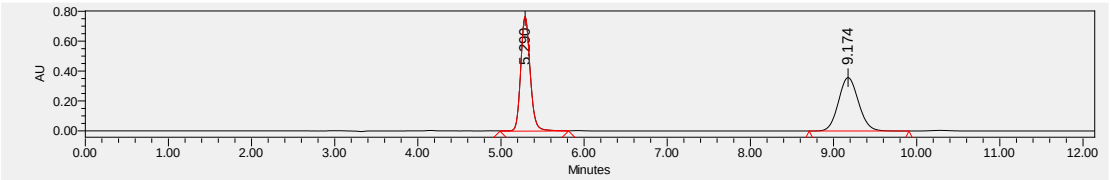
Colorless oil, 26.9 mg, 73% yield, 82% ee, $[\alpha]_{\lambda}^{25}$ = 207.5 (*c* = 0.28, CH_2Cl_2, λ = 365 nm); HPLC (Daicel chiralcel IG, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 5.31 min, $t_{(major)}$ = 9.17 min;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.78–7.65 (m, 2H), 7.45–7.35 (m, 2H), 2.60–2.43 (m, 2H), 1.80–1.74 (m, 1H), 1.40 (s, 9H), 0.97–0.91 (m, 6H).

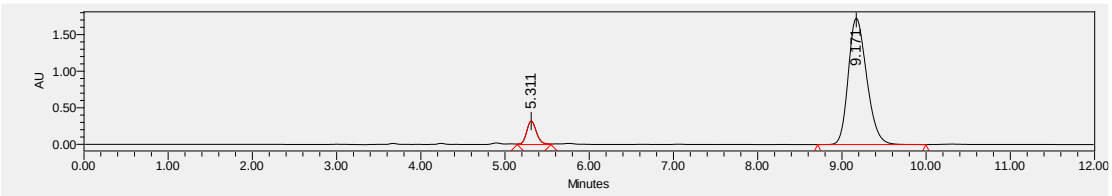
^{13}C NMR (151 MHz, $CDCl_3$) δ 185.7, 162.4, 140.3, 132.3, 129.6, 129.1, 98.0, 52.6, 45.4, 28.3, 24.3, 23.62, 23.56.

IR (film, cm^{-1}) :3395, 2966, 1708, 1681, 1514, 1222, 1095, 844;

HRMS (ESI$^+$) m/z calcd for $C_{17}H_{24}Cl^{34.9689}N_2O_5^+$ ([M]+H$^+$) = 371.1368, found 371.1364 and $C_{17}H_{24}Cl^{36.9659}N_2O_5^+$ ([M]+Na$^+$) = 373.1339, found 373.1336.

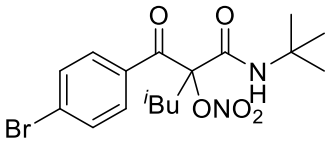


	Retention Time	Area	% Area
1	5.290	6070018	50.42
2	9.174	5969028	49.58



	Retention Time	Area	% Area
1	5.311	2641932	9.16
2	9.171	26201400	90.84

(*S*)-2-(4-Bromobenzoyl)-1-(*tert*-butylamino)-4-methyl-1-oxopentan-2-yl nitrate (3ab)



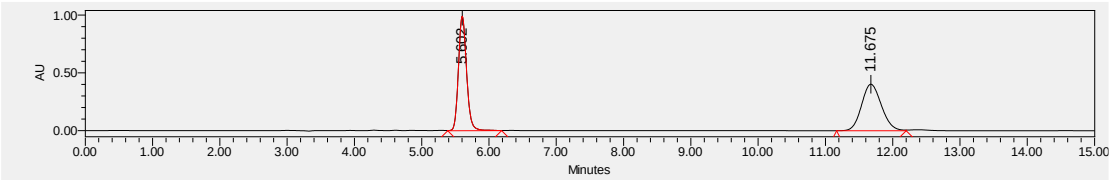
Colorless oil, 25.0 mg, 60% yield, 79% ee, $[\alpha]_{\lambda}^{25}$ = 245.0 (*c* = 0.12, CH_2Cl_2, λ = 365 nm); HPLC (Daicel chiralcel IG, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 5.61 min, $t_{(major)}$ = 11.54 min;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.71–7.61 (m, 2H), 7.60–7.50 (m, 2H), 2.60–2.43 (m, 2H), 1.80–1.73 (m, 1H), 1.40 (s, 9H), 0.99–0.91 (m, 6H).

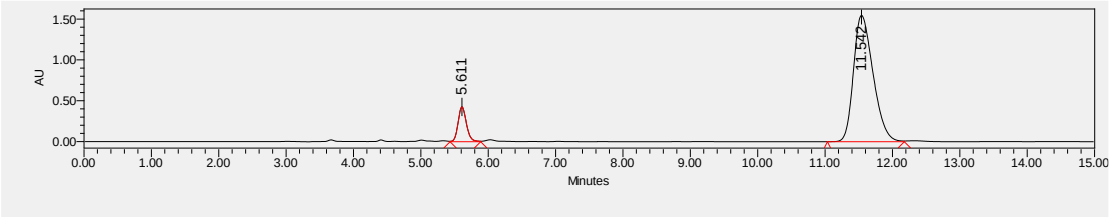
^{13}C NMR (151 MHz, $CDCl_3$) δ 185.9, 162.4, 132.7, 132.1, 129.6, 129.1, 98.0, 52.6, 45.4, 28.3, 24.3, 23.62, 23.56.

IR (film, cm^{-1}) :3395, 2965, 1709, 1681, 1514, 1221, 842;

HRMS (ESI$^+$) m/z calcd for $C_{17}H_{24}Br^{78.9183}N_2O_5^+$ ([M]+H$^+$) = 415.0863, found 415.0856 and $C_{17}H_{24}Br^{80.9163}N_2O_5^+$ ([M]+Na$^+$) = 417.0843, found 417.0851.

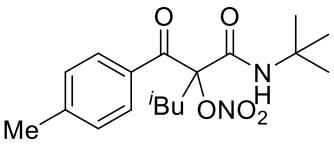


	Retention Time	Area	% Area
1	5.602	8333841	50.35
2	11.675	8218342	49.65



	Retention Time	Area	% Area
1	5.611	3693074	10.56
2	11.542	31264185	89.44

(*S*)-1-(*tert*-Butylamino)-4-methyl-2-(4-methylbenzoyl)-1-oxopentan-2-yl nitrate (3ac)



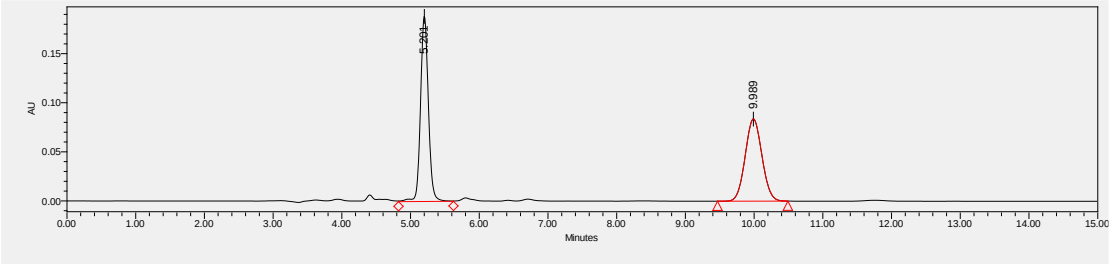
Colorless oil, 27.7 mg, 79% yield, 91% ee, $[\alpha]_{\lambda}^{25}$ = 216.2 (*c* = 0.26, CH_2Cl_2, λ = 365 nm); HPLC (Daicel chiralcel IG, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 5.23 min, $t_{(major)}$ = 10.17 min;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.75–7.66 (m, 2H), 7.25–7.18 (m, 2H), 2.65–2.45 (m, 2H), 2.38 (s, 3H), 1.79–1.71 (m, 1H), 1.40 (s, 9H), 0.97–0.88 (m, 6H).

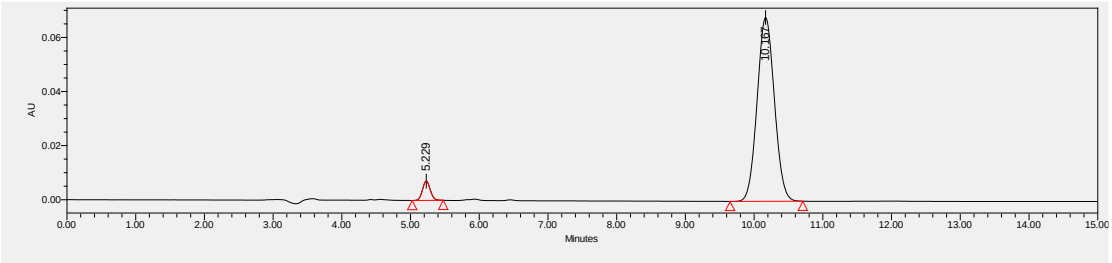
^{13}C NMR (151 MHz, $CDCl_3$) δ 187.3, 162.5, 145.0, 131.3, 129.5, 128.4, 98.5, 52.4, 45.2, 28.3, 24.3, 23.7, 23.5, 21.6.

IR (film, cm^{-1}) :3395, 2966, 1704, 1515, 1224, 835;

HRMS (ESI^+) m/z calcd for $C_{18}H_{27}N_2O_5^+$ ([M]+H^+) = 351.1914, found 351.1916.

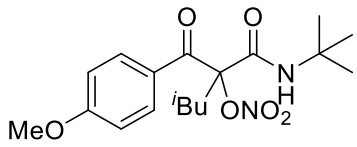


	Retention Time	Area	% Area
1	5.201	1502104	51.46
2	9.989	1416895	48.54



	Retention Time	Area	% Area
1	5.229	56162	4.52
2	10.167	1186862	95.48

(*S*)-1-(*tert*-Butylamino)-2-(4-methoxybenzoyl)-4-methyl-1-oxopentan-2-yl nitrate (3ad)



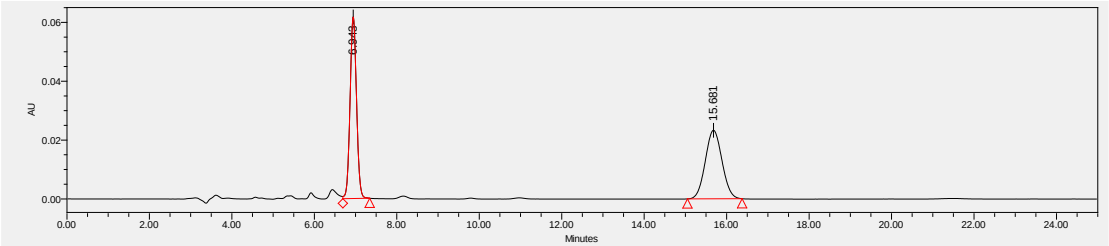
Colorless oil, 32.6 mg, 89% yield, 90% ee, $[\alpha]_{\lambda}^{25}$ = 200.6 (*c* = 0.52, CH_2Cl_2, λ = 365 nm); HPLC (Daicel chiralcel IG, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ =6.89 min, $t_{(major)}$ = 15.80 min;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.87–7.73 (m, 2H), 7.92–7.85 (m, 2H), 3.84 (s, 3H), 2.70–2.44 (m, 2H), 1.75–1.67 (m, 1H), 1.40 (s, 9H), 0.97–0.85 (m, 6H).

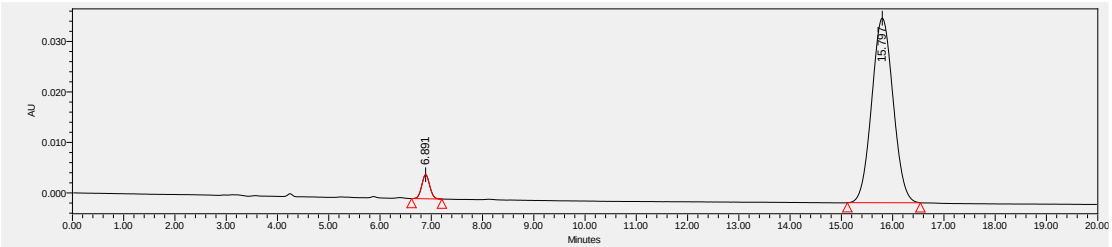
^{13}C NMR (151 MHz, $CDCl_3$) δ 186.7, 164.1, 162.6, 130.8, 126.5, 114.0, 98.6, 55.5, 52.4, 45.1, 28.3, 24.2, 23.7, 23.4.

IR (film, cm^{-1}) :3394, 2966, 1698, 1600, 1513, 1268, 1177, 1025, 844;

HRMS (ESI^+) m/z calcd for $C_{18}H_{27}N_2O_6^+$ ([M]+H^+) = 367.1864, found 367.1855.

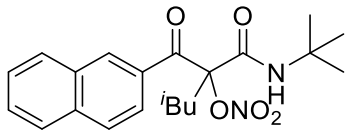


	Retention Time	Area	% Area
1	6.943	670471	50.58
2	15.681	655060	49.42



	Retention Time	Area	% Area
1	6.891	51671	4.64
2	15.797	1060822	95.36

(*S*)-2-(2-Naphthoyl)-1-(*tert*-butylamino)-4-methyl-1-oxopentan-2-yl nitrate (3ae)



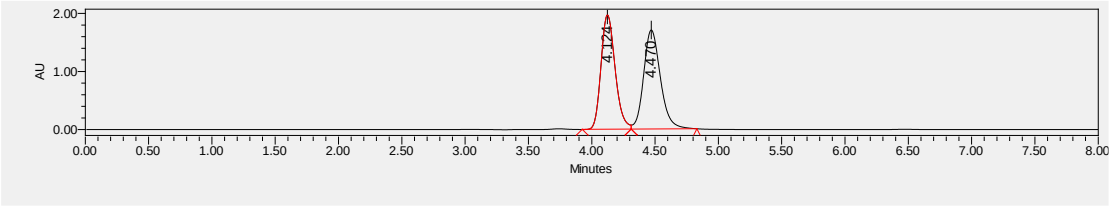
White amorphous solid, 28.7 mg, 74% yield, 86% ee, m.p. 86–89 °C. $[\alpha]_{\lambda}^{25}$ = 61.3 (*c* = 0.15, CH_2Cl_2, λ = 405 nm); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 4.13 min, $t_{(major)}$ = 4.48 min;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.13 (s, 1H), 7.91–7.82 (m, 4H), 7.64–7.52 (m, 2H), 2.70–2.55 (m, 2H), 1.86–1.78 (m, 1H), 1.43 (s, 9H), 0.99–0.93 (m, 6H).

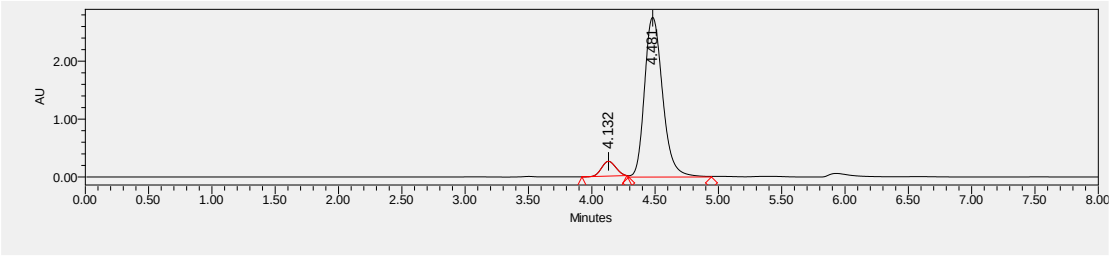
^{13}C NMR (151 MHz, $CDCl_3$) δ 187.2, 162.6, 135.7, 132.2, 131.2, 129.9, 129.7, 129.1, 128.7, 127.7, 127.1, 123.8, 98.5, 52.6, 45.5, 28.3, 24.3, 23.7, 23.6.

IR (film, cm^{-1}) :3394, 2966, 1680, 1515, 1220;

HRMS (ESI^+) m/z calcd for $C_{21}H_{27}N_2O_5^+$ ([M]+H^+) = 387.1914, found 387.1906.

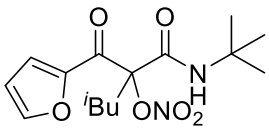


	Retention Time	Area	% Area
1	4.124	15229233	49.28
2	4.470	15673074	50.72



	Retention Time	Area	% Area
1	4.132	1983242	6.74
2	4.481	27461000	93.26

(*S*)-1-(*tert*-Butylamino)-2-(furan-2-carbonyl)-4-methyl-1-oxopentan-2-yl nitrate (3af)



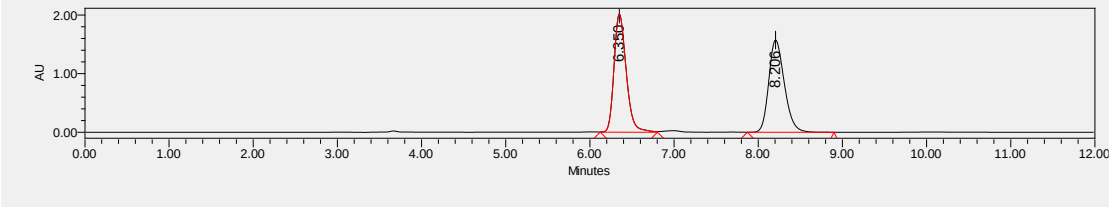
Colorless oil, 27.2 mg, 83% yield, 81% ee, $[\alpha]_{\lambda}^{25}$ = 104.6 (*c* = 0.28, CH_2Cl_2, λ = 365 nm); HPLC (Daicel chiralcel IG, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 6.41 min, $t_{(major)}$ = 8.26 min;

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.55–7.47 (m, 1H), 7.43–7.32 (m, 1H), 6.60–6.50 (m, 1H), 2.67–2.37 (m, 2H), 1.75–1.65 (m, 1H), 1.39 (s, 9H), 0.98–0.86 (m, 6H).

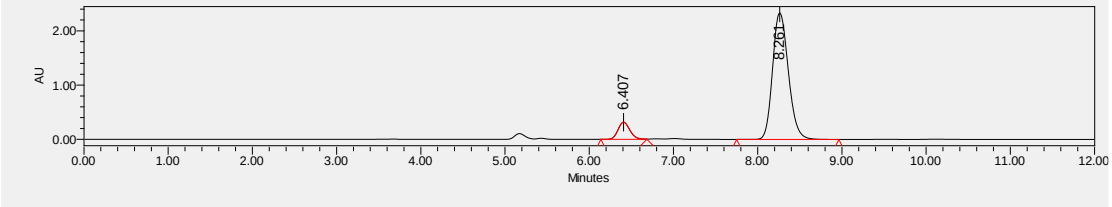
^{13}C NMR (151 MHz, $CDCl_3$) δ 177.5, 161.9, 150.0, 146.9, 120.2, 113.1, 97.3, 52.4, 43.7, 28.3, 24.2, 23.5, 23.4.

IR (film, cm^{-1}) :3399, 2967, 1701, 1519, 1458, 767;

HRMS (ESI$^+$) m/z calcd for $C_{15}H_{23}N_2O_6^+$ ([M]+H$^+$) = 327.1551, found 327.1551.



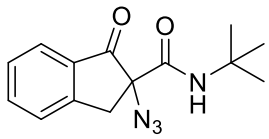
	Retention Time	Area	% Area
1	6.350	20289917	50.14
2	8.206	20178380	49.86



	Retention Time	Area	% Area
1	6.407	3130712	9.36

2	8.261	30329403	90.64

(*S*)-2-Azido-*N*-(*tert*-butyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxamide (5a)



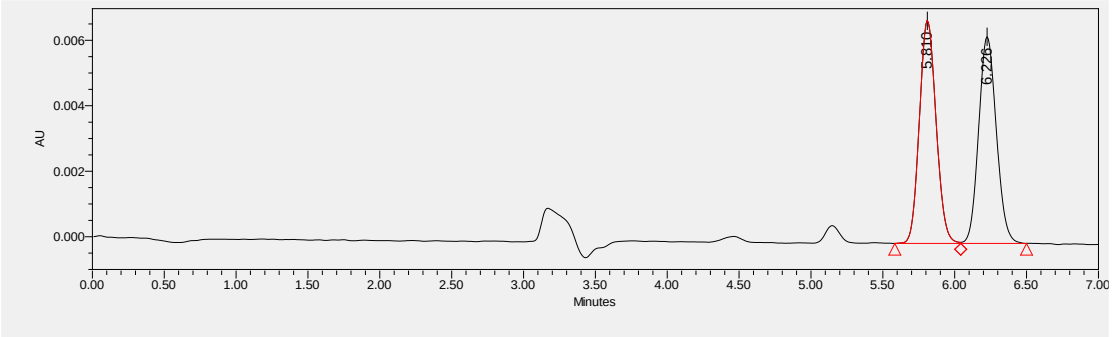
White amorphous solid, 22.9 mg, 84% yield, 90% ee, m.p. 70–72 °C. $[\alpha]_{\lambda}^{25}$ = -158.2 (*c* = 0.33, CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(major)}$ = 5.97 min, $t_{(minor)}$ = 6.44 min;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82–7.77 (m, 1H), 7.70–7.65 (m, 1H), 7.52–7.48 (m, 1H), 7.45–7.40 (m, 1H), 6.61 (s, 1H), 3.99 (d, *J* = 17.4 Hz, 1H), 3.18 (d, *J* = 17.4 Hz, 1H), 1.37 (s, 9H).

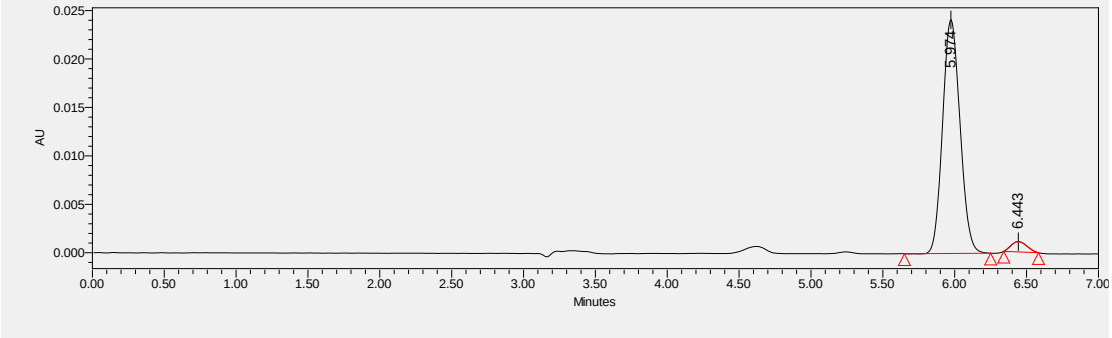
^{13}C NMR (151 MHz, $CDCl_3$) δ 198.8, 164.9, 152.5, 136.6, 133.5, 128.3, 126.4, 125.4, 72.8, 52.0, 37.4, 28.5.

IR (film, cm^{-1}) :3405, 2972, 2110, 1720, 1675, 1519, 1221;

HRMS (ESI^+) m/z calcd for $C_{14}H_{16}N_4NaO_2^+$ ([M]+Na^+) = 295.1165, found 295.1166.

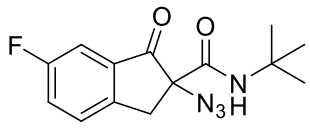


	Retention Time	Area	% Area
1	5.810	55015	50.48
2	6.226	53978	49.52



	Retention Time	Area	% Area
1	5.974	1025127	94.65
2	6.443	57919	5.35

(*S*)-2-Azido-*N*-(*tert*-butyl)-6-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxamide (5b)



Colorless oil, 23.5 mg, 81% yield, 90% ee, $[\alpha]_{\lambda}^{25}$ = -235.5 (*c* = 0.21, CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(major)}$ = 5.34 min, $t_{(minor)}$ = 5.62 min;

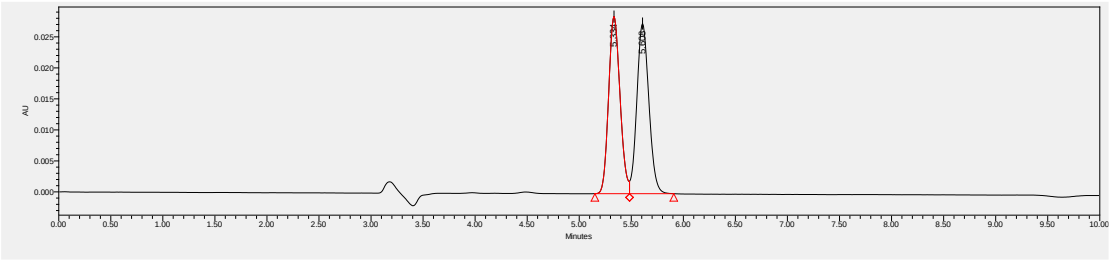
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50–7.46 (m, 1H), 7.45–7.41 (m, 1H), 7.41–7.36 (m, 1H), 6.57 (s, 1H), 3.94 (d, *J* = 16.8 Hz, 1H), 3.14 (d, *J* = 16.8 Hz, 1H), 1.36 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 197.9, 164.6, 162.6 (*J* = 260.6 Hz), 148.1 (*J* = 3.0 Hz), 135.2 (*J* = 9.1 Hz), 127.8 (*J* = 8.2 Hz), 124.3 (*J* = 23.9 Hz), 111.1 (*J* = 22.7 Hz), 73.6, 52.1, 37.0, 28.5.

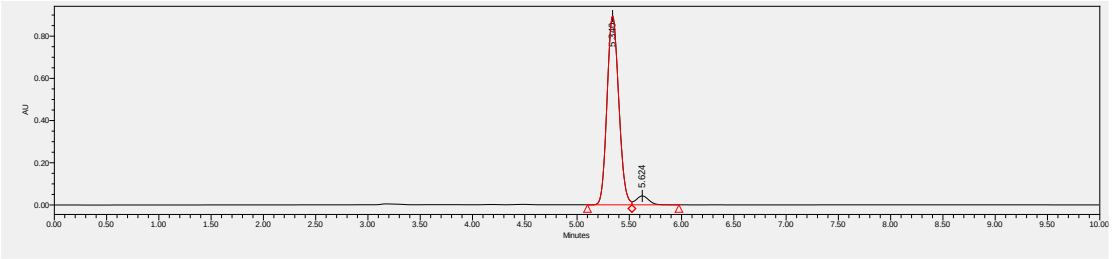
^{19}F NMR (565 MHz, $CDCl_3$) δ -112.7.

IR (film, cm^{-1}) :3407, 2972, 2112, 1726, 1678, 1519, 1487, 1265;

HRMS (ESI^+) m/z calcd for $C_{14}H_{15}FN_4NaO_2^+$ ([M]+Na^+) = 313.1071, found 313.1068.

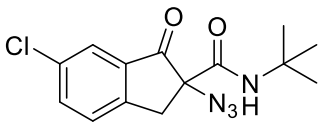


	Retention Time	Area	% Area
1	5.334	217767	49.70
2	5.608	220424	50.30



	Retention Time	Area	% Area
1	5.340	6965675	95.15
2	5.624	354788	4.85

(*S*)-2-Azido-*N*-(*tert*-butyl)-6-chloro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxamide (5c)



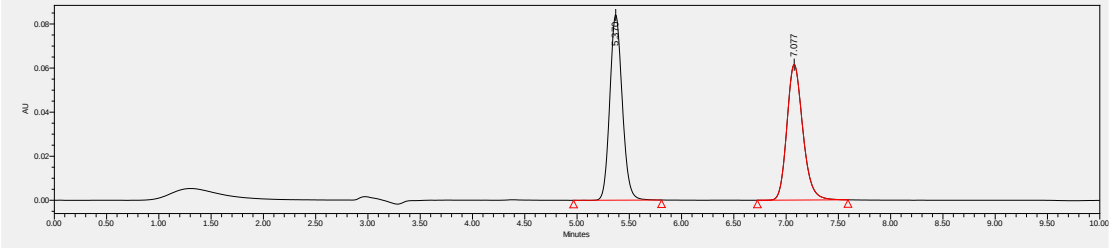
White amorphous solid, 25.5 mg, 83% yield, 93% ee, m.p. 84–86 °C. $[\alpha]_\lambda^{25}$ = -224.0 (*c* = 0.20, CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 5.41 min, $t_{(major)}$ = 7.11 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.73 (m, 1H), 7.66–7.60 (m, 1H), 7.47–7.42 (m, 1H), 6.56 (s, 1H), 3.95 (d, *J* = 17.6 Hz, 1H), 3.14 (d, *J* = 17.6 Hz, 1H), 1.36 (s, 9H).

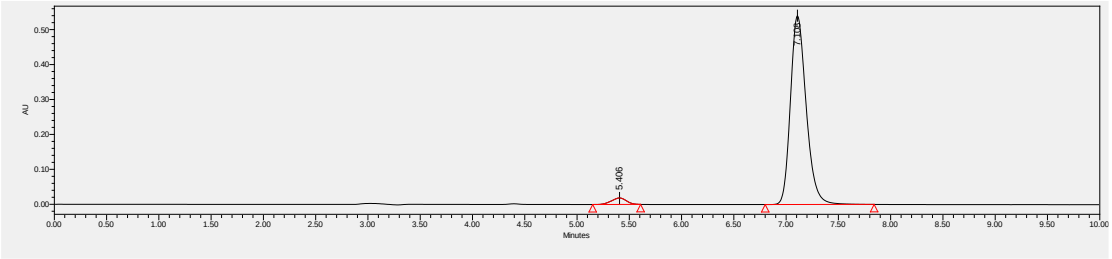
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 164.6, 150.6, 136.5, 135.0, 134.8, 127.6, 125.0, 73.4, 52.2, 37.1, 28.5.

IR (film, cm^{-1}) :3405, 2971, 2111, 1725, 1678, 1518, 1252;

HRMS (ESI^+) m/z calcd for $C_{14}H_{15}Cl^{34.9689}N_4NaO_2^+$ ([M]+Na^+) = 329.0776, found 329.0776 and $C_{14}H_{15}Cl^{36.9659}N_4NaO_2^+$ ([M]+Na^+) = 331.0746, found 331.0744.

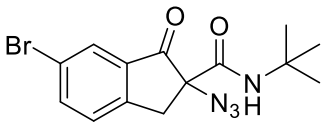


	Retention Time	Area	% Area
1	5.370	695713	51.63
2	7.077	651725	48.37



	Retention Time	Area	% Area
1	5.406	184279	3.15
2	7.108	5661442	96.85

(*S*)-2-Azido-6-bromo-*N*-(*tert*-butyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxamide (5d)



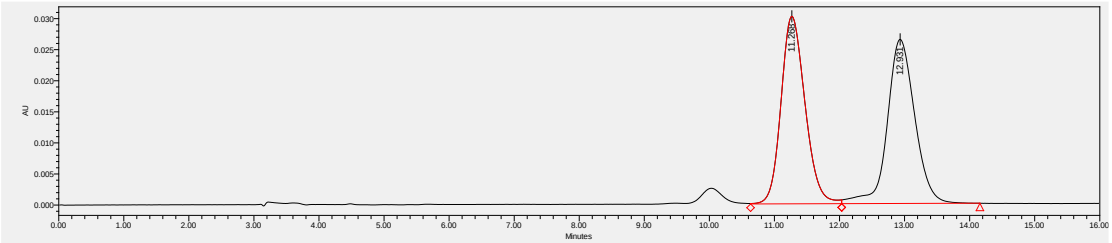
White amorphous solid, 28.4 mg, 81% yield, 95% ee, m.p. 98–101 °C. $[\alpha]_{\lambda}^{25}$ = -142.7 (*c* = 0.31, CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel ODH, *n*-hexane/*i*-PrOH 98/2, 1.0 mL/min, λ = 254 nm) $t_{(major)}$ = 11.62 min, $t_{(minor)}$ = 13.27 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.88 (m, 1H), 7.82–7.72 (m, 1H), 7.42–7.35 (m, 1H), 6.56 (s, 1H), 3.93 (d, *J* = 17.2 Hz, 1H), 3.11 (d, *J* = 17.2 Hz, 1H), 1.36 (s, 9H).

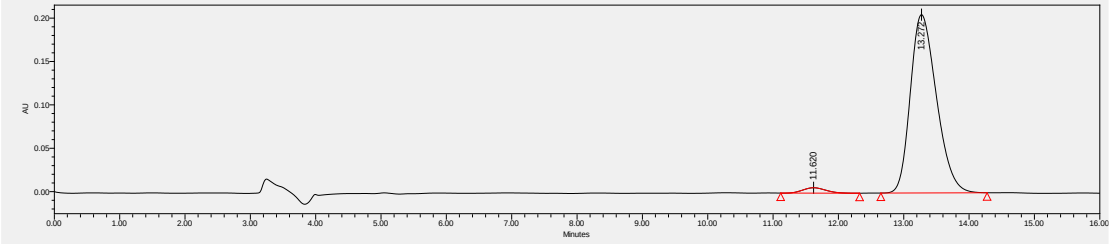
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 164.5, 151.1, 139.3, 135.3, 128.1, 127.9, 122.4, 73.2, 52.2, 37.2, 28.5.

IR (film, cm^{-1}) :3404, 2971, 2110, 1725, 1677, 1518, 1253;

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{15}Br^{78.9183}N_4NaO_2^+$ ([M]+Na$^+$) = 373.0271, found 373.0272 and $C_{14}H_{15}Br^{80.9163}N_4NaO_2^+$ ([M]+Na$^+$) = 375.0250, found 375.0251.

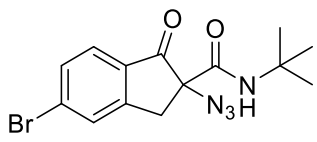


	Retention Time	Area	% Area
1	11.268	3575568	50.73
2	12.931	3473332	49.27



	Retention Time	Area	% Area
1	11.620	143025	2.45
2	13.272	5702816	97.55

(*S*)-2-Azido-5-bromo-*N*-(*tert*-butyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxamide (5e)



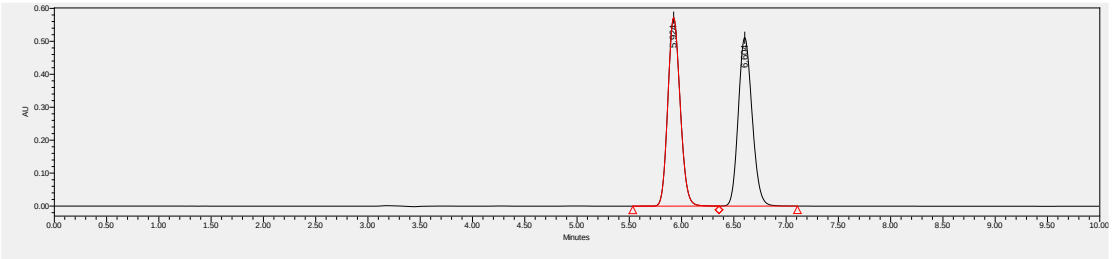
White amorphous solid, 28.0 mg, 80% yield, 93% ee, m.p. 80–83 °C. $[\alpha]_{\lambda}^{25}$ = -231.0 (*c* = 0.23, CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(major)}$ = 5.94 min, $t_{(minor)}$ = 6.62 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.53 (m, 3H), 6.57 (s, 1H), 3.96 (d, *J* = 17.2 Hz, 1H), 3.15 (d, *J* = 17.2 Hz, 1H), 1.36 (s, 9H).

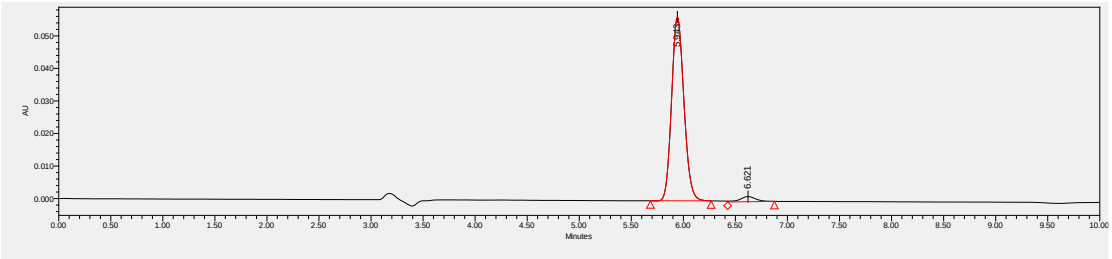
^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 164.6, 153.9, 132.38, 132.37, 132.1, 129.8, 126.4, 73.0, 52.2, 37.2, 28.5.

IR (film, cm^{-1}) :3404, 2971, 2110, 1723, 1678, 1518, 1260, 1216;

HRMS (ESI^+) m/z calcd for $C_{14}H_{15}Br^{78.9183}N_4NaO_2^+$ ([M+Na^+]) = 373.0271, found 373.0272 and $C_{14}H_{15}Br^{80.9163}N_4NaO_2^+$ ([M+Na^+]) = 375.0250, found 375.0251.

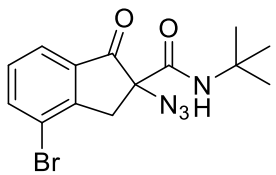


	Retention Time	Area	% Area
1	5.924	4709282	50.01
2	6.604	4707355	49.99



	Retention Time	Area	% Area
1	5.943	465270	96.57
2	6.621	16531	3.43

(*S*)-2-Azido-4-bromo-*N*-(*tert*-butyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxamide (5f)



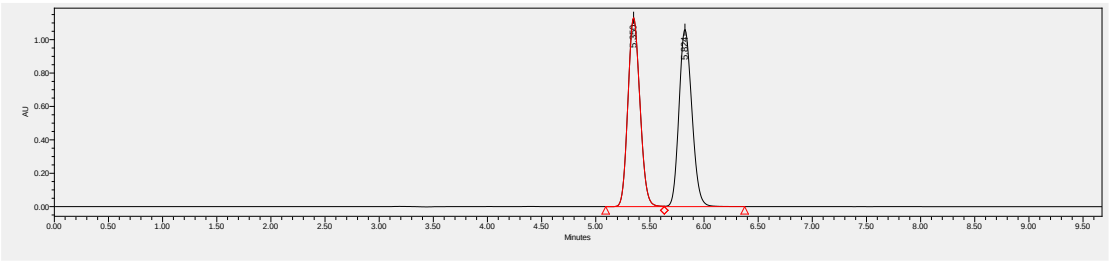
Colorless oil, 28.1 mg, 80% yield, 84% ee, $[\alpha]_{\lambda}^{25}$ = -230.3 (*c* = 0.28, CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(major)}$ = 5.37 min, $t_{(minor)}$ = 5.86 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88–7.81 (m, 1H), 7.78–7.71 (m, 1H), 7.37–7.30 (m, 1H), 6.58 (s, 1H), 3.92 (d, *J* = 18.0 Hz, 1H), 3.11 (d, *J* = 18.0 Hz, 1H), 1.37 (s, 9H).

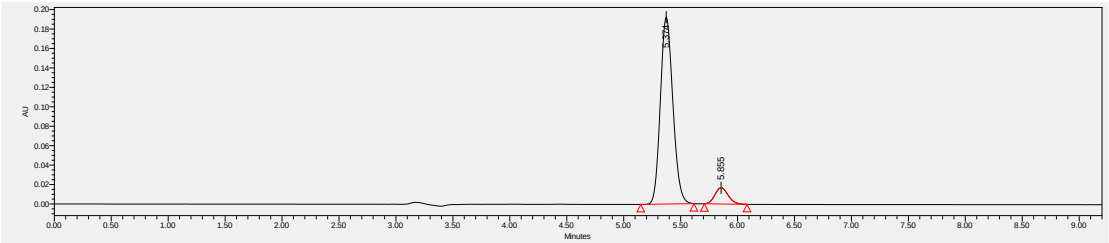
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2, 164.7, 152.4, 139.2, 135.6, 130.0, 124.1, 121.7, 72.6, 52.2, 38.7, 28.5.

IR (film, cm^{-1}) :3404, 2971, 2110, 1729, 1678, 1518, 1263;

HRMS (ESI^+) m/z calcd for $C_{14}H_{15}Br^{78.9183}N_4NaO_2^+$ ([M+Na^+]) = 373.0271, found 373.0270 and $C_{14}H_{15}Br^{80.9163}N_4NaO_2^+$ ([M+Na^+]) = 375.0250, found 375.0250.

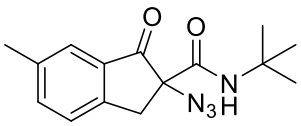


	Retention Time	Area	% Area
1	5.350	8750682	49.93
2	5.824	8774990	50.07



	Retention Time	Area	% Area
1	5.374	1467693	91.62
2	5.855	134172	8.38

(*S*)-2-Azido-*N*-(*tert*-butyl)-6-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxamide (5g)



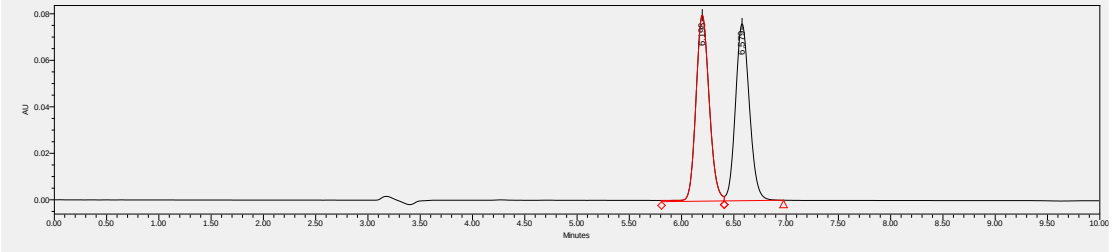
White amorphous solid, 24.3 mg, 85% yield, 74% ee, m.p. 75–79 °C. $[\alpha]_{\lambda}^{25}$ = -161.9 (*c* = 0.45, CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel OXH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(major)}$ = 6.17 min, $t_{(minor)}$ = 6.57 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61–7.56 (m, 1H), 7.52–7.45 (m, 1H), 7.41–7.34 (m, 1H), 6.60 (s, 1H), 3.93 (d, *J* = 17.2 Hz, 1H), 3.13 (d, *J* = 17.2 Hz, 1H), 2.40 (s, 3H), 1.36 (s, 9H).

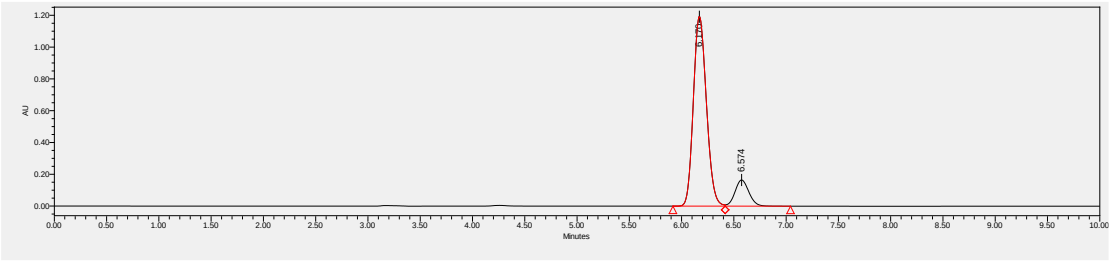
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 165.0, 150.0, 138.4, 137.9, 133.6, 126.0, 125.2, 73.2, 52.0, 37.0, 28.5, 21.0.

IR (film, cm^{-1}) :3408, 2970, 2110, 1719, 1678, 1519, 1276, 1225;

HRMS (ESI^+) m/z calcd for $C_{15}H_{18}N_4NaO_2^+$ ([M]+Na^+) = 309.1322, found 309.1323.

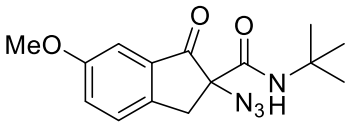


	Retention Time	Area	% Area
1	6.198	709894	50.19
2	6.579	704654	49.81



	Retention Time	Area	% Area
1	6.170	10347264	87.20
2	6.574	1519141	12.80

(*S*)-2-Azido-*N*-(*tert*-butyl)-6-methoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxamide (5h)



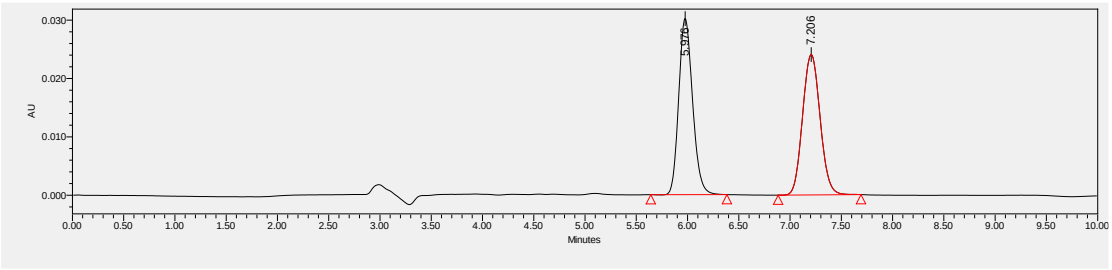
White amorphous solid, 25.9 mg, 86% yield, 54% ee, m.p. 69–72 °C. $[\alpha]_{\lambda}^{25}$ = -137.4 (*c* = 0.34, CH_2Cl_2, λ = 436 nm); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 6.05 min, $t_{(major)}$ = 7.25 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.35 (m, 1H), 7.28–7.23 (m, 1H), 7.21–7.19 (m, 1H), 6.59 (s, 1H), 3.89 (d, *J* = 17.2 Hz, 1H), 3.83 (s, 3H), 3.10 (d, *J* = 17.2 Hz, 1H), 1.36 (s, 9H).

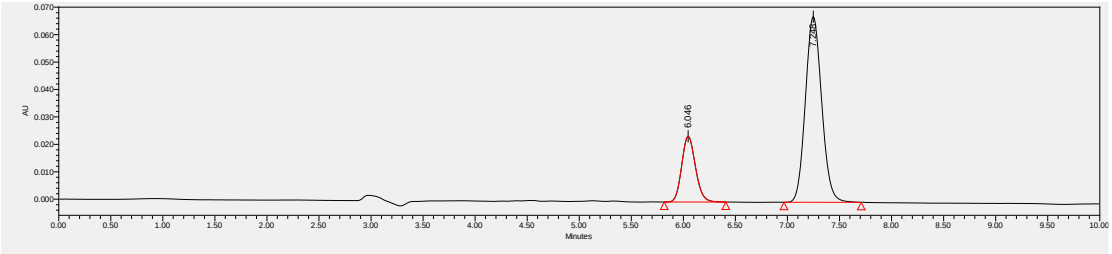
^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 165.0, 159.9, 145.6, 134.7, 127.1, 126.2, 106.1, 73.6, 55.6, 52.0, 36.9, 28.5.

IR (film, cm^{-1}) :3406, 2969, 2110, 1717, 1677, 1458, 1276, 1231;

HRMS (ESI$^+$) m/z calcd for $C_{15}H_{18}N_4NaO_3^+$ ([M]+Na$^+$) = 325.1271, found 325.1272.

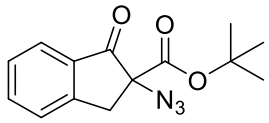


	Retention Time	Area	% Area
1	5.976	284437	49.98
2	7.206	284656	50.02



	Retention Time	Area	% Area
1	6.046	220023	22.97
2	7.248	737852	77.03

(*S*)-*tert*-Butyl-2-azido-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (5i)



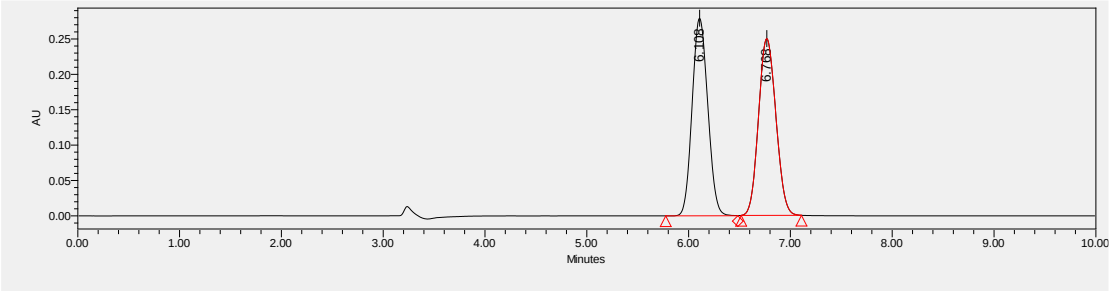
Colorless oil, 24.0 mg, 88% yield, 97% ee, $[\alpha]_D^{25}$ = -209.5 (*c* = 0.37, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 98/2, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 6.14 min, $t_{(major)}$ = 6.75 min;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86–7.75 (m, 1H), 7.69–7.61 (m, 1H), 7.52–7.36 (m, 2H), 3.63 (d, *J* = 16.8 Hz, 1H), 2.99 (d, *J* = 16.8 Hz, 1H), 1.45 (s, 9H).

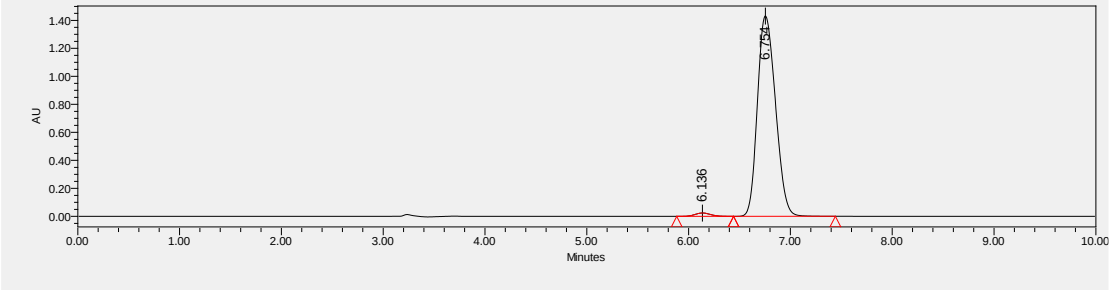
^{13}C NMR (151 MHz, $CDCl_3$) δ 197.9, 167.3, 152.2, 136.2, 133.2, 128.2, 126.3, 125.4, 84.4, 70.4, 38.5, 27.8.

IR (film, cm^{-1}) :2981, 2114, 1741, 1719, 1608, 1250, 1152;

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{15}FN_3NaO_3^+$ ([M]+Na$^+$) = 273.1113, found 273.1115.

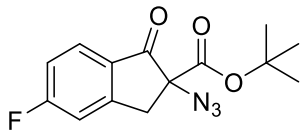


	Retention Time	Area	% Area
1	6.108	2984304	50.22
2	6.768	2958257	49.78



	Retention Time	Area	% Area
1	6.136	249022	1.39
2	6.754	17631236	98.61

(*S*)-*tert*-Butyl-2-azido-5-fluoro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (5j)



Colorless oil, 23.3 mg, 80% yield, 97% ee, $[\alpha]_D^{25}$ = -235.7 (*c* = 0.25, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 92/8, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 4.86 min, $t_{(major)}$ = 5.14 min;

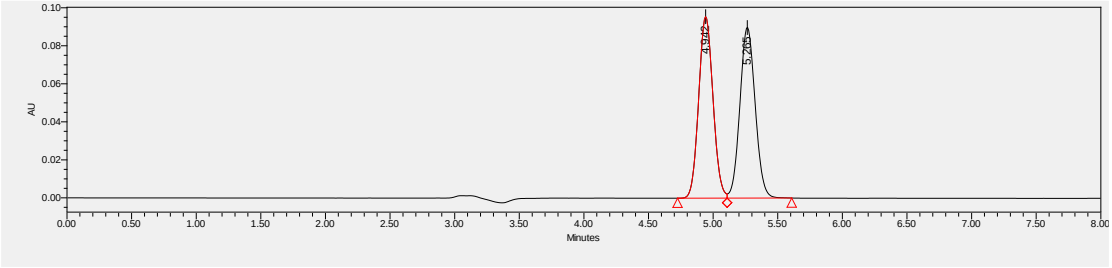
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88–7.76 (m, 1H), 7.21–7.06 (m, 2H), 3.61 (d, *J* = 17.4 Hz, 1H), 2.96 (d, *J* = 17.4 Hz, 1H), 1.46 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.1, 167.9 (*J* = 259.8 Hz), 167.0, 155.2 (*J* = 10.6 Hz), 129.5 (*J* = 1.4 Hz), 127.9 (*J* = 10.7 Hz), 116.8 (*J* = 23.9 Hz), 113.2 (*J* = 22.8 Hz), 84.7, 70.6, 38.3, 27.8.

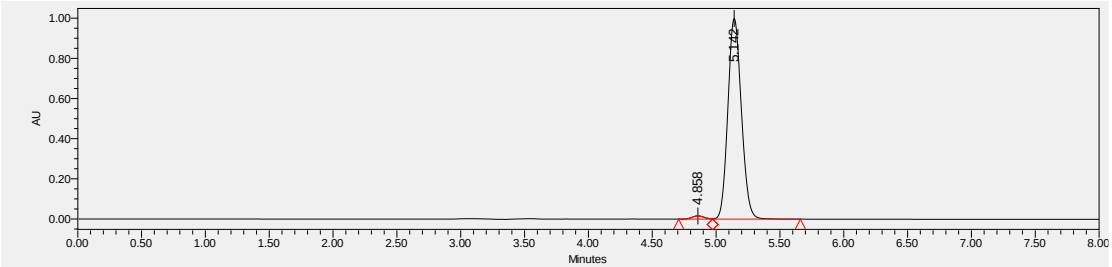
^{19}F NMR (565 MHz, $CDCl_3$) δ -99.4.

IR (film, cm^{-1}) :2982, 2113, 1727, 1612, 1598, 1258, 1153;

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{14}FN_3NaO_3^+$ ([M]+Na$^+$) = 314.0911, found 314.0915.

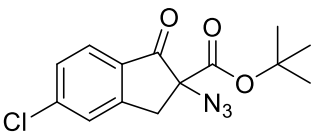


	Retention Time	Area	% Area
1	4.942	733622	49.84
2	5.265	738275	50.16



	Retention Time	Area	% Area
1	4.858	109238	1.46
2	5.142	7349262	98.54

(*S*)-*tert*-Butyl-2-azido-5-chloro-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (5k)



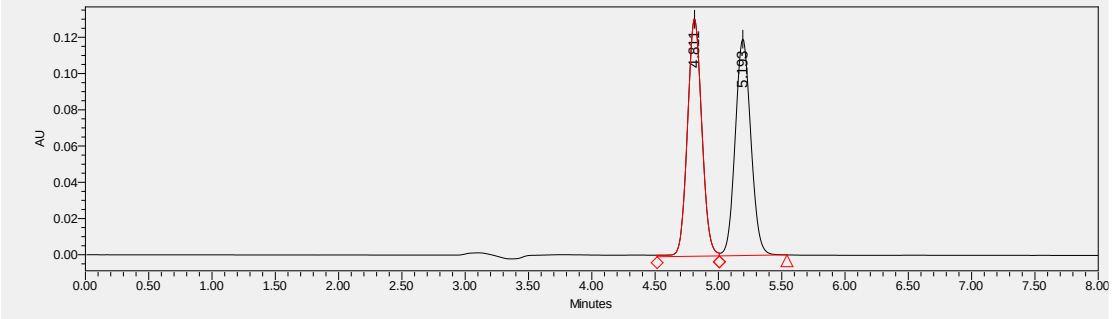
Colorless oil, 25.5 mg, 83% yield, 94% ee, $[\alpha]_D^{25}$ = -247.0 (*c* = 0.46, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 4.81 min, $t_{(major)}$ = 5.19 min;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78–7.70 (m, 1H), 7.49–7.44 (m, 1H), 7.44–7.39 (m, 1H), 3.60 (d, *J* = 17.4 Hz, 1H), 2.95 (d, *J* = 17.4 Hz, 1H), 1.45 (s, 9H).

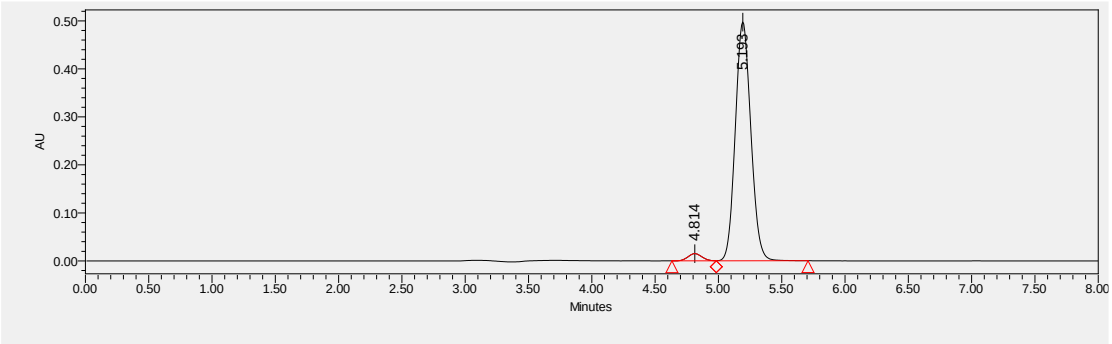
^{13}C NMR (151 MHz, $CDCl_3$) δ 196.6, 166.9, 153.6, 142.9, 131.6, 129.1, 126.6, 126.5, 84.8, 70.4, 38.2, 27.8.

IR (film, cm^{-1}) :2981, 2113, 1725, 1599, 1253, 1152;

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{14}Cl^{34.9689}N_3NaO_3^+$ ([M]+Na$^+$) = 330.0616, found 330.0613 and $C_{14}H_{14}Cl^{36.9659}N_3NaO_3^+$ ([M]+Na$^+$) = 332.0586, found 332.0581.

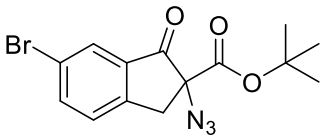


	Retention Time	Area	% Area
1	4.811	1033786	50.23
2	5.193	1024236	49.77



	Retention Time	Area	% Area
1	4.814	114710	2.63
2	5.193	4245150	97.37

(*S*)-*tert*-Butyl-2-azido-6-bromo-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (5l)



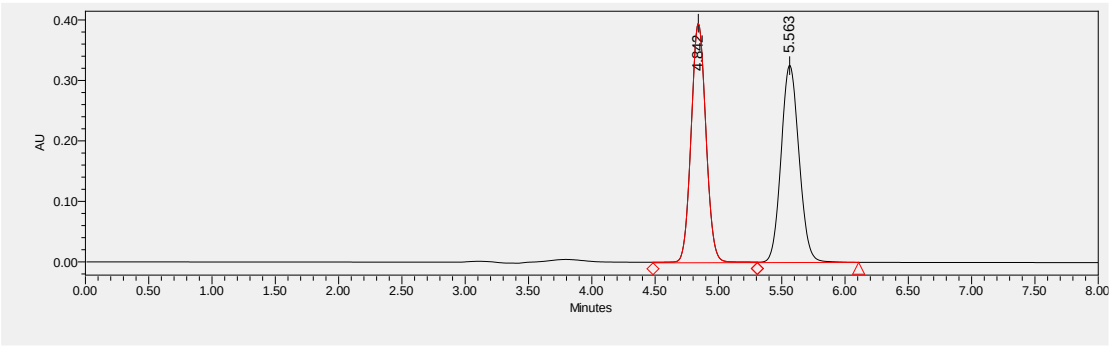
White amorphous solid, 27.6 mg, 78% yield, 94% ee, m.p. 69–71 °C. $[\alpha]_D^{25}$ = -215.8 (*c* = 0.48, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 4.78 min, $t_{(major)}$ = 5.41 min;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96–7.89 (m, 1H), 7.80–7.72 (m, 1H), 7.38–7.32 (m, 1H), 3.57 (d, *J* = 17.4 Hz, 1H), 2.92 (d, *J* = 17.4 Hz, 1H), 1.45 (s, 9H).

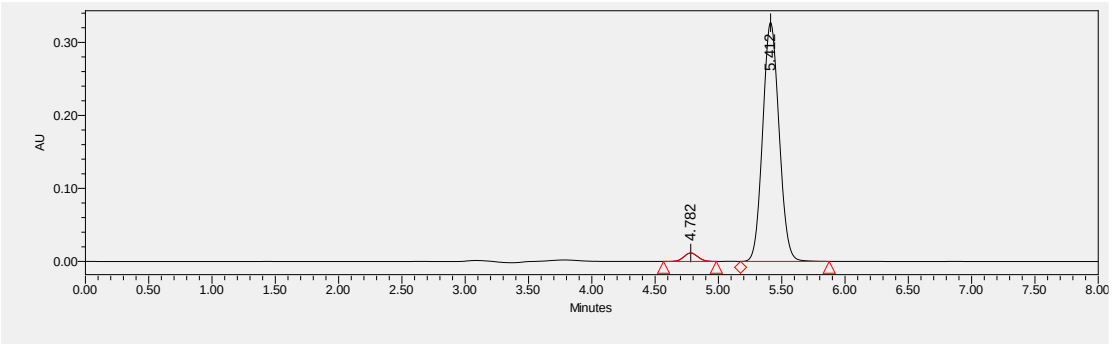
^{13}C NMR (151 MHz, $CDCl_3$) δ 196.7, 166.8, 150.7, 138.9, 135.0, 128.2, 127.8, 122.3, 84.8, 70.7, 38.2, 27.8.

IR (film, cm^{-1}) :2980, 2113, 1743, 1722, 1250, 1152;

HRMS (ESI^+) m/z calcd for $C_{14}H_{14}Br^{78.9183}N_3NaO_3^+$ ([M+Na$^+$]) = 374.0111, found 374.0108 and $C_{14}H_{14}Br^{80.9163}N_3NaO_3^+$ ([M+Na$^+$]) = 376.0090, found 376.0088.

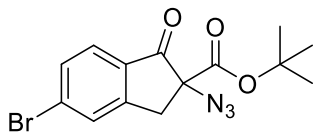


	Retention Time	Area	% Area
1	4.842	3228342	50.11
2	5.563	3214210	49.89



	Retention Time	Area	% Area
1	4.782	88886	2.93
2	5.412	2943410	97.07

(*S*)-*tert*-Butyl-2-azido-5-bromo-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (5m)



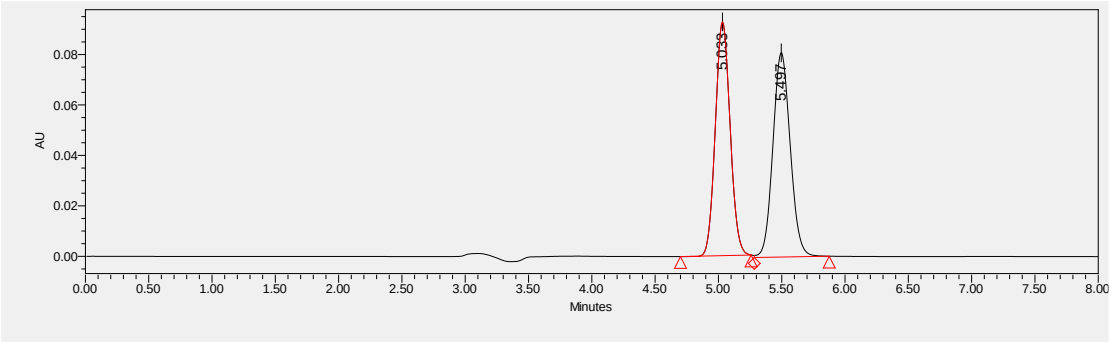
White amorphous solid, 31.4 mg, 89% yield, 94% ee, m.p. 78–80 °C. $[\alpha]_D^{25}$ = -202.6 (*c* = 0.61, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 5.03 min, $t_{(major)}$ = 5.49 min;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69–7.66 (m, 1H), 7.65–7.62 (m, 1H), 7.60–7.55 (m, 1H), 3.60 (d, *J* = 17.4 Hz, 1H), 2.96 (d, *J* = 17.4 Hz, 1H), 1.46 (s, 9H).

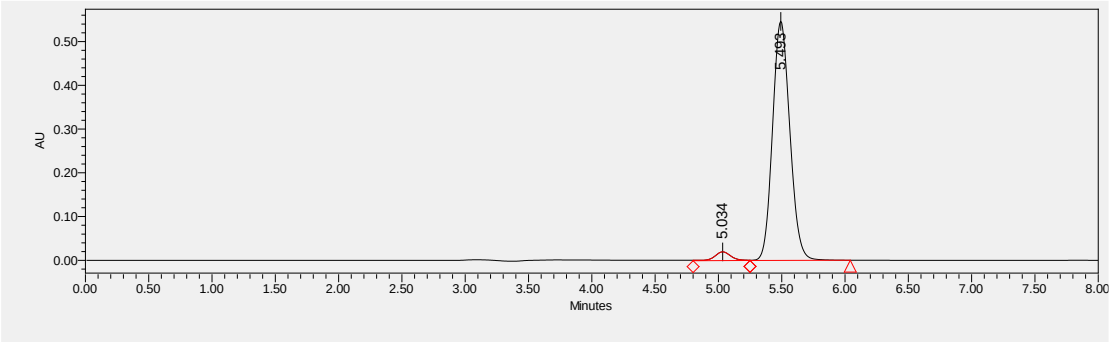
^{13}C NMR (151 MHz, $CDCl_3$) δ 196.8, 166.9, 153.6, 132.01, 131.97, 131.8, 129.7, 126.5, 84.8, 70.4, 38.1, 27.8.

IR (film, cm^{-1}) :2980, 2113, 1721, 1593, 1253, 1152;

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{14}Br^{78.9183}N_3NaO_3^+$ ([M+Na$^+$) = 374.0111, found 374.0110 and $C_{14}H_{14}Br^{80.9163}N_3NaO_3^+$ ([M]+Na$^+$) = 376.0090, found 376.0089.

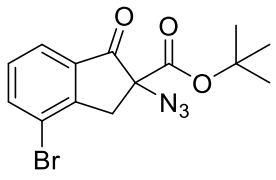


	Retention Time	Area	% Area
1	5.033	753169	49.47
2	5.497	769344	50.53



	Retention Time	Area	% Area
1	5.034	175426	3.27
2	5.493	5193400	96.73

(*S*)-*tert*-Butyl-2-azido-4-bromo-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (5n)



Colorless oil, 28.6 mg, 81% yield, 90% ee, $[\alpha]_D^{25}$ = -206.3 (*c* = 0.48, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(major)}$ = 4.06 min, $t_{(minor)}$ = 4.62 min;

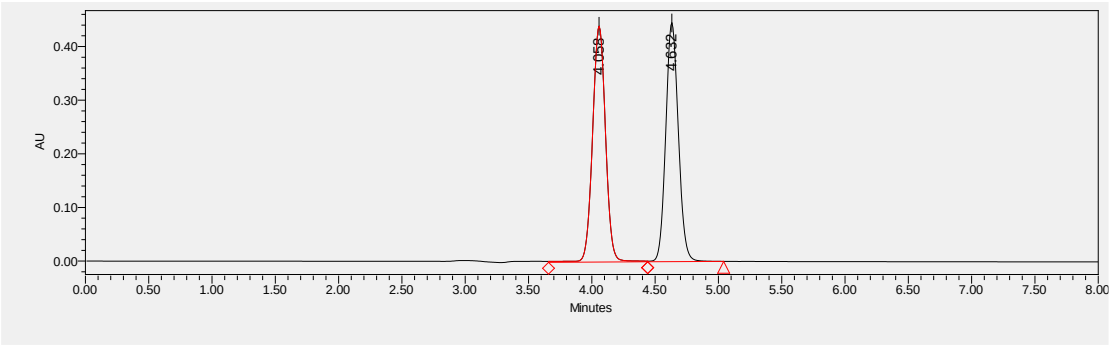
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86–7.81 (m, 1H), 7.79–7.71 (m, 1H), 7.38–7.32

(m, 1H), 3.55 (d, *J* = 17.4 Hz, 1H), 2.92 (d, *J* = 17.4 Hz, 1H), 1.47 (s, 9H).

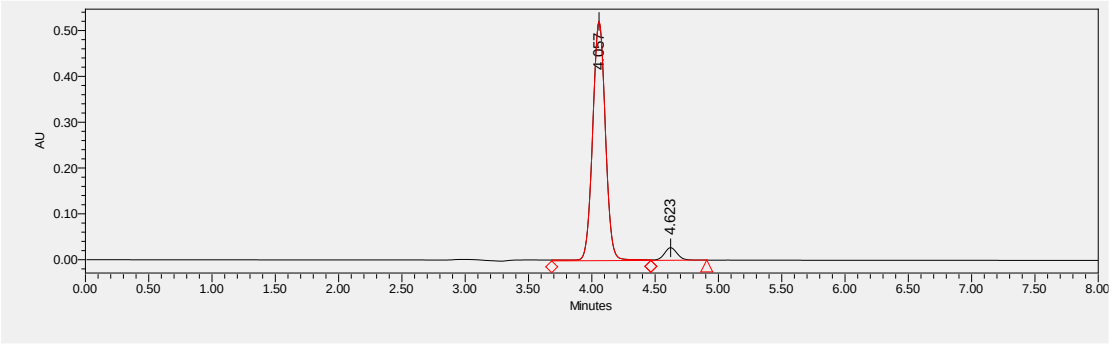
^{13}C NMR (151 MHz, $CDCl_3$) δ 197.3, 166.8, 151.9, 138.9, 135.1, 130.0, 124.2, 121.6, 84.9, 70.3, 39.6, 27.8.S

IR (film, cm^{-1}) :2980, 2115, 1725, 1257, 1152;

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{14}Br^{78.9183}N_3NaO_3^+$ ([M+Na$^+$]) = 374.0111, found 374.0108 and $C_{14}H_{14}Br^{80.9163}N_3NaO_3^+$ ([M+Na$^+$]) = 376.0090, found 376.0087.

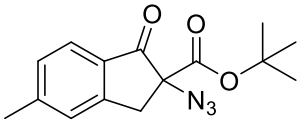


	Retention Time	Area	% Area
1	4.058	3137768	50.44
2	4.632	3082892	49.56



	Retention Time	Area	% Area
1	4.057	3654678	94.94
2	4.623	194911	5.06

(*S*)-*tert*-Butyl-2-azido-5-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (5o)



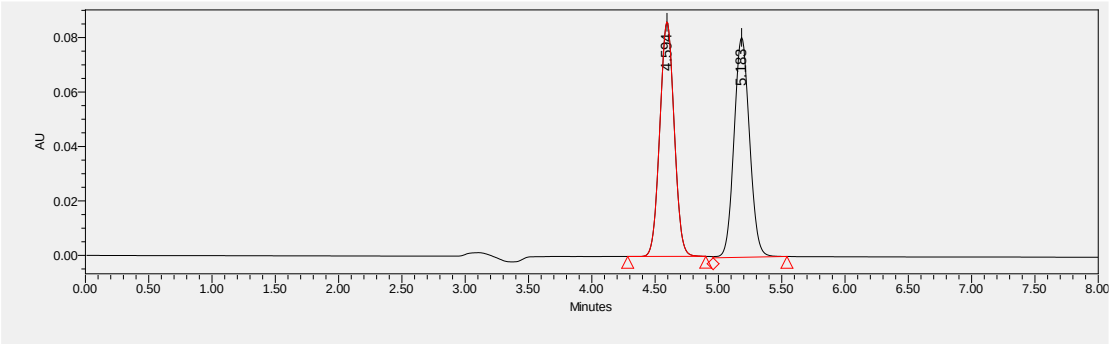
Colorless oil, 24.2 mg, 84% yield, 97% ee, $[\alpha]_D^{25}$ = -274.2 (*c* = 0.39, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 4.59 min, $t_{(major)}$ = 5.18 min;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72–7.66 (m, 1H), 7.25–7.21 (m, 2H), 3.67 (d, *J* = 17.4 Hz, 1H), 2.92 (d, *J* = 17.4 Hz, 1H), 2.46 (s, 3H), 1.46 (s, 9H).

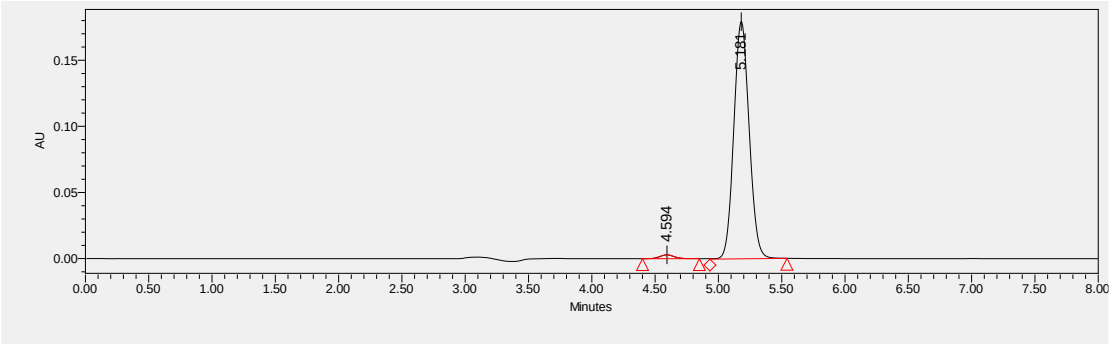
^{13}C NMR (151 MHz, $CDCl_3$) δ 197.3, 167.4, 152.7, 147.8, 130.9, 129.5, 126.6, 125.3, 84.3, 70.7, 38.3, 27.8, 22.2.

IR (film, cm^{-1}) :2980, 2110, 1740, 1717, 1609, 1246, 1153;

HRMS (ESI$^+$) m/z calcd for $C_{15}H_{17}N_3NaO_3^+$ ([M+Na$^+$]) = 310.1162, found 310.1163

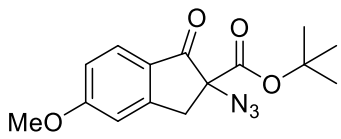


	Retention Time	Area	% Area
1	4.594	679625	49.70
2	5.183	687964	50.30



	Retention Time	Area	% Area
1	4.594	22456	1.46
2	5.181	1511263	98.54

(*S*)-*tert*-Butyl-2-azido-5-methoxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (5p)



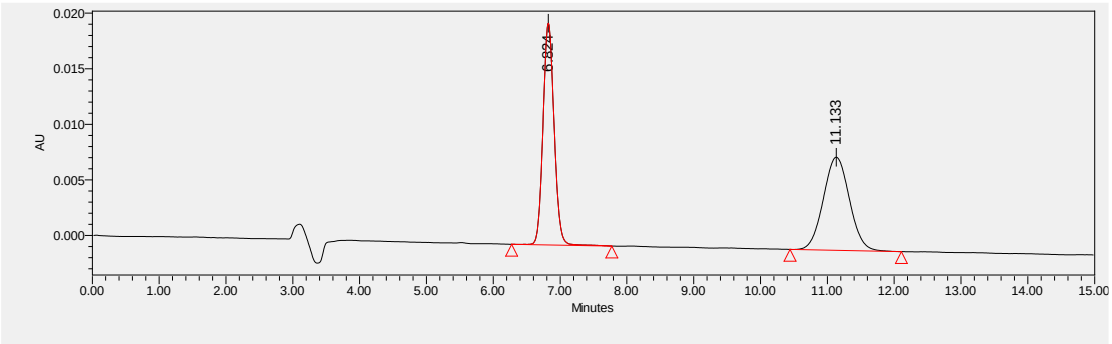
Colorless oil, 23.9 mg, 79% yield, 92% ee, $[\alpha]_D^{25}$ = 229.5 (*c* = 0.41, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 6.83 min, $t_{(major)}$ = 11.1 min;

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78–7.70 (m, 1H), 6.98–6.91 (m, 1H), 6.89–6.83 (m, 1H), 3.90 (s, 3H), 3.57 (d, *J* = 17.4 Hz, 1H), 2.91 (d, *J* = 17.4 Hz, 1H), 1.46 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.8, 167.6, 166.5, 155.3, 127.2, 126.2, 116.3, 109.5, 84.3, 70.7, 55.8, 38.4, 27.8.

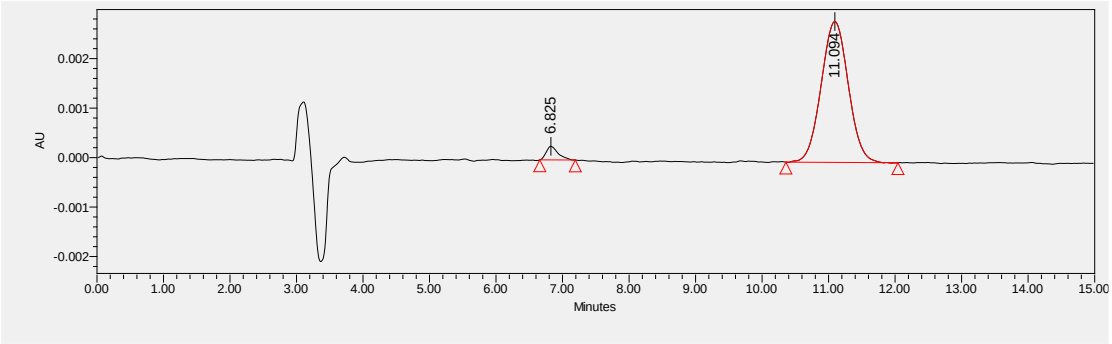
IR (film, cm^{-1}) :2980, 2111, 1739, 1711, 1600, 1264, 1153;

HRMS (ESI^+) m/z calcd for $C_{15}H_{17}N_3NaO_4^+$ ([M]+Na^+) = 326.1111, found 326.1111



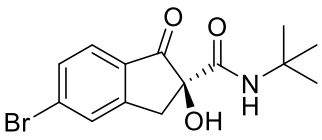
	Retention Time	Area	% Area

1	6.824	229632	50.23
2	11.133	227520	49.77



	Retention Time	Area	% Area
1	6.825	3416	4.06
2	11.094	80660	95.94

(*S*)-5-Bromo-*N*-(*tert*-butyl)-2-hydroxy-1-oxo-2,3-dihydro-1*H*-indene-2-carboxamide (6)

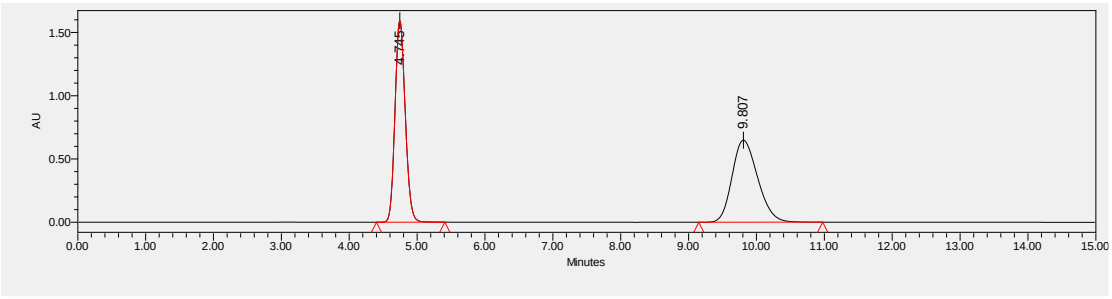


White amorphous solid, 30.5 mg, 93% yield, 99% ee, m.p. 161–165 °C. $[\alpha]_D^{25}$ = -10.6 (*c* = 0.48, CH_2Cl_2); HPLC (Daicel chiralcel ASH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 254 nm) $t_{(minor)}$ = 4.74 min, $t_{(major)}$ = 9.84 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67–7.47 (m, 3H), 6.77 (s, 1H), 4.04 (s, 1H), 3.64 (d, *J* = 16.8 Hz, 1H), 3.00 (d, *J* = 16.8 Hz, 1H), 1.30 (s, 9H).

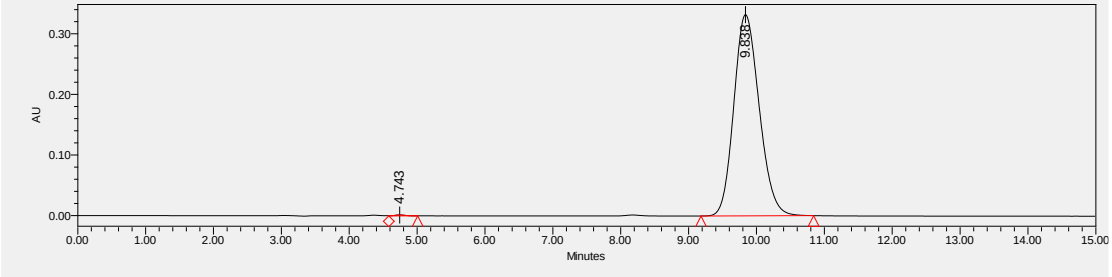
^{13}C NMR (101 MHz, $CDCl_3$) δ 202.7, 169.2, 154.5, 132.8, 131.8, 131.5, 129.6, 126.0, 82.3, 51.4, 40.3, 28.5.

IR (film, cm^{-1}) :3384, 2969, 1725, 1651, 1595, 1528, 1214, 929;

HRMS (ESI$^+$) m/z calcd for $C_{14}H_{16}Br^{78.9183}NNaO_3^+$ ([M]+Na$^+$) = 348.0206, found 348.0203 and $C_{14}H_{16}Br^{80.9163}NNaO_3^+$ ([M]+Na$^+$) = 350.0185, found 350.0180.

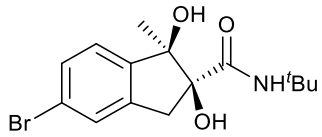


	Retention Time	Area	% Area
1	4.745	16673420	49.46
2	9.807	17040559	50.54



	Retention Time	Area	% Area
1	4.743	17461	0.20
2	9.838	8623379	99.80

(*R*)-5-Bromo-2-((*R*)-1-(*tert*-butylamino)-1-hydroxyethyl)-2-hydroxy-2,3-dihydro-1*H*-inden-1-one (7)



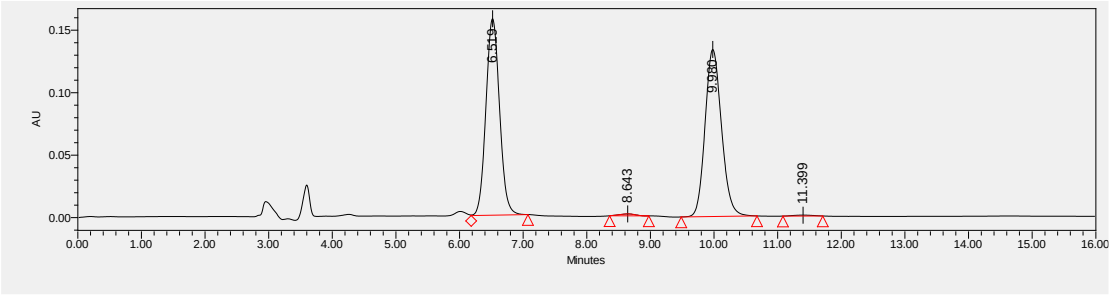
White amorphous solid, 20.5 mg, 63% yield, > 19:1 d.r., 99% ee, m.p. 128–132 °C. $[\alpha]_D^{25}$ = 24.2 (*c* = 0.26, CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, λ = 215 nm) $t_{(minor)}$ = 6.56 min, $t_{(major)}$ = 9.99 min;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.34 (m, 2H), 7.23–7.16 (m, 1H), 6.47 (s, 1H), 4.04 (s, 1H), 3.53 (d, *J* = 16.4 Hz, 1H), 2.97 (d, *J* = 16.4 Hz, 1H), 2.85 (s, 1H), 1.45 (s, 3H), 1.32 (s, 9H).

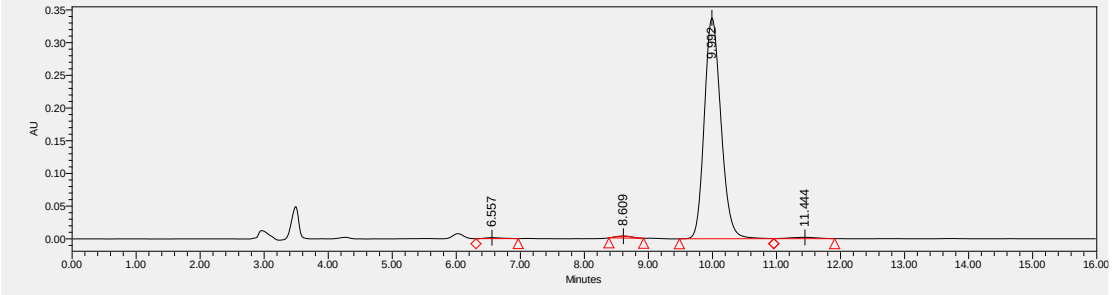
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 144.0, 142.1, 130.6, 128.2, 124.9, 122.9, 85.2, 81.9, 51.1, 41.2, 28.6, 22.6.

IR (film, cm^{-1}) :3395, 2969, 1652, 1532, 1367, 1225, 1094, 1041;

HRMS (ESI$^+$) m/z calcd for $C_{15}H_{20}Br^{78.9183}NNaO_3^+$ ([M+Na$^+$]) = 364.0519, found 364.0514 and $C_{15}H_{20}Br^{80.9163}NNaO_3^+$ ([M+Na$^+$]) = 366.0498, found 366.0494.



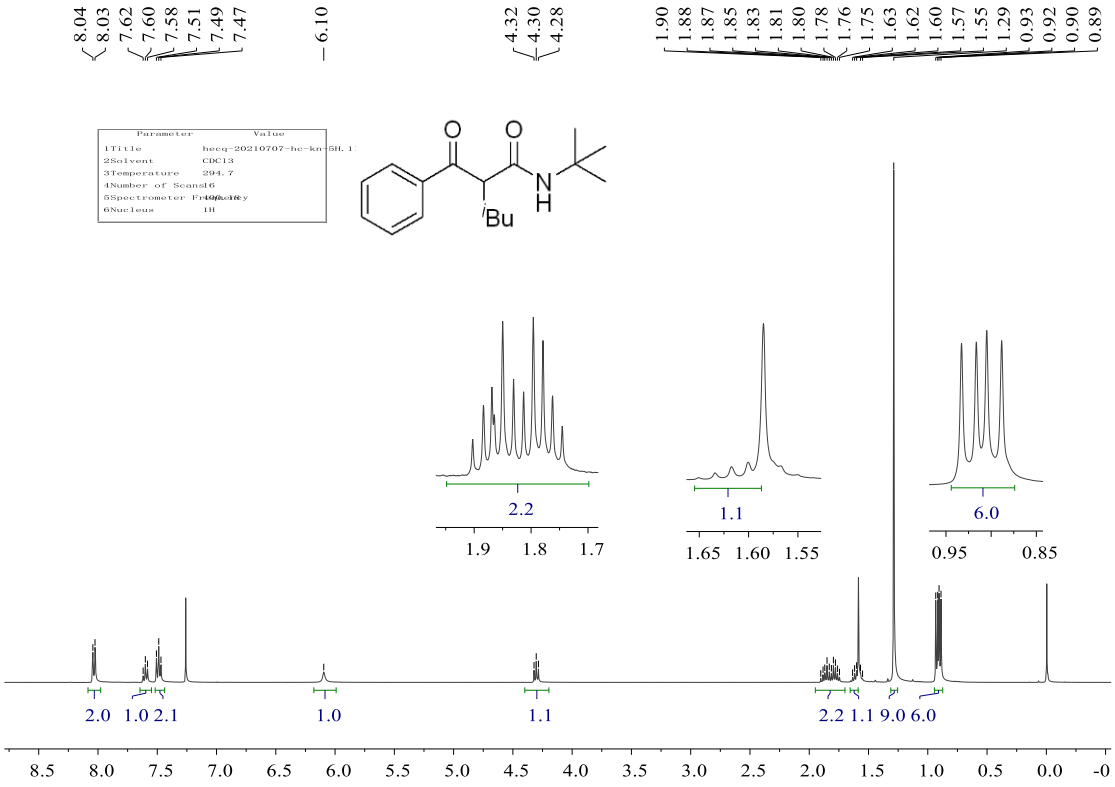
	Retention Time	Area	% Area
1	6.519	2337246	48.91
2	8.643	27101	0.57
3	9.980	2398774	50.20
4	11.399	15459	0.32



	Retention Time	Area	% Area
1	6.557	27822	0.45
2	8.609	49037	0.79
3	9.992	6088192	97.79
4	11.444	60565	0.97

15. Copies of NMR Spectra for the Reaction Substrates and Products

1y



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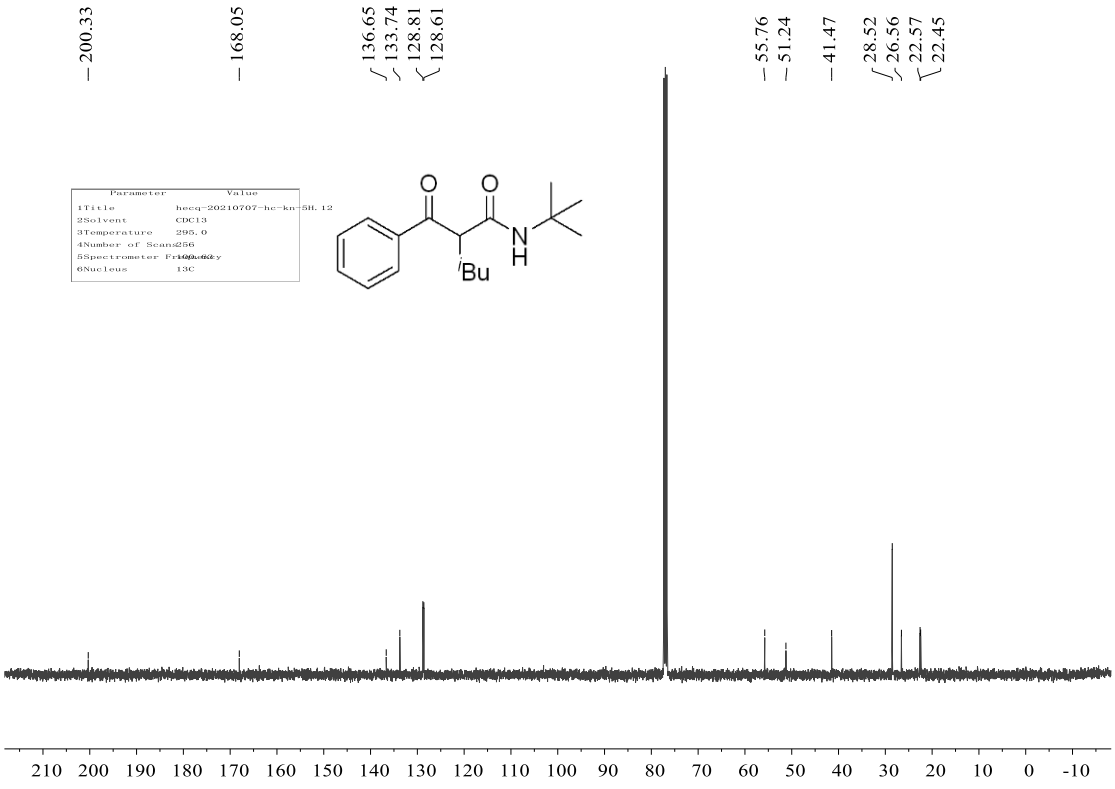
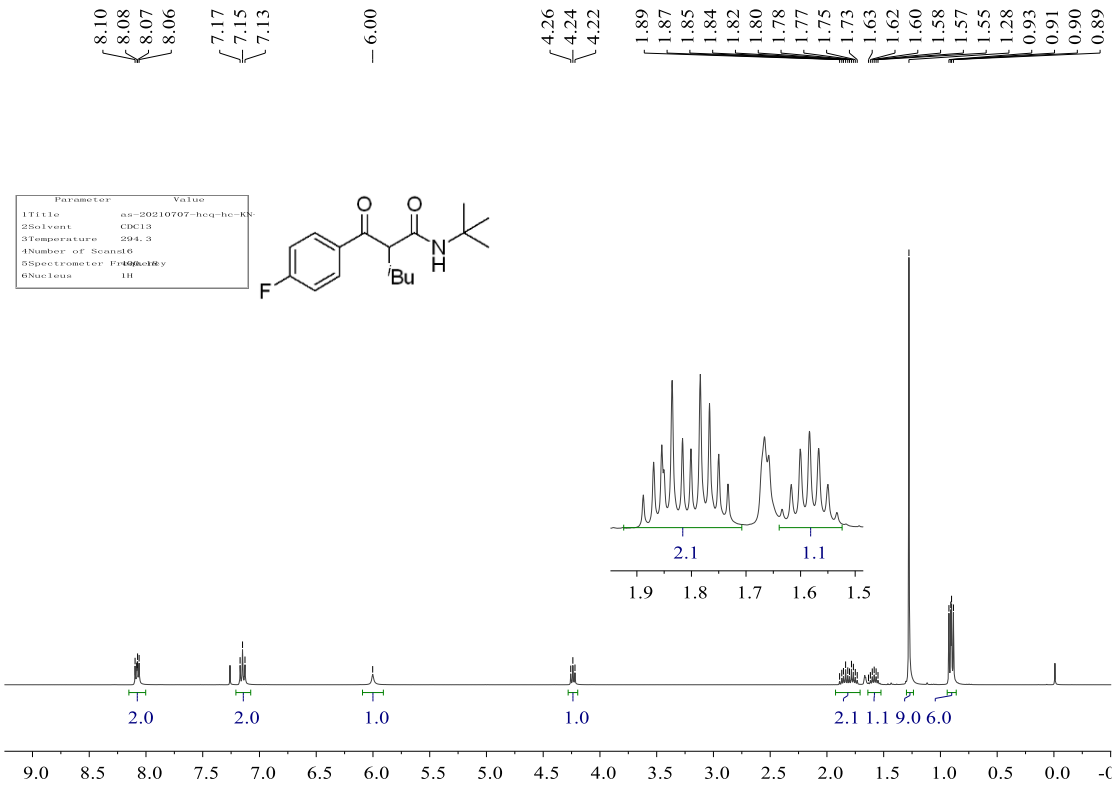


1z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8.07
8.06
7.17
7.15
7.13
6.00
4.26
4.24
4.22
1.89
1.87
1.85
1.84
1.82
1.80
1.78
1.77
1.75
1.73
1.63
1.62
1.60
1.58
1.57
1.55
1.28
0.93
0.91
0.90
0.89
Parameter Value
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2Solvent CDCl3
3Temperature 294.3
4Number of Scans 16
5Spectrometer Frequency
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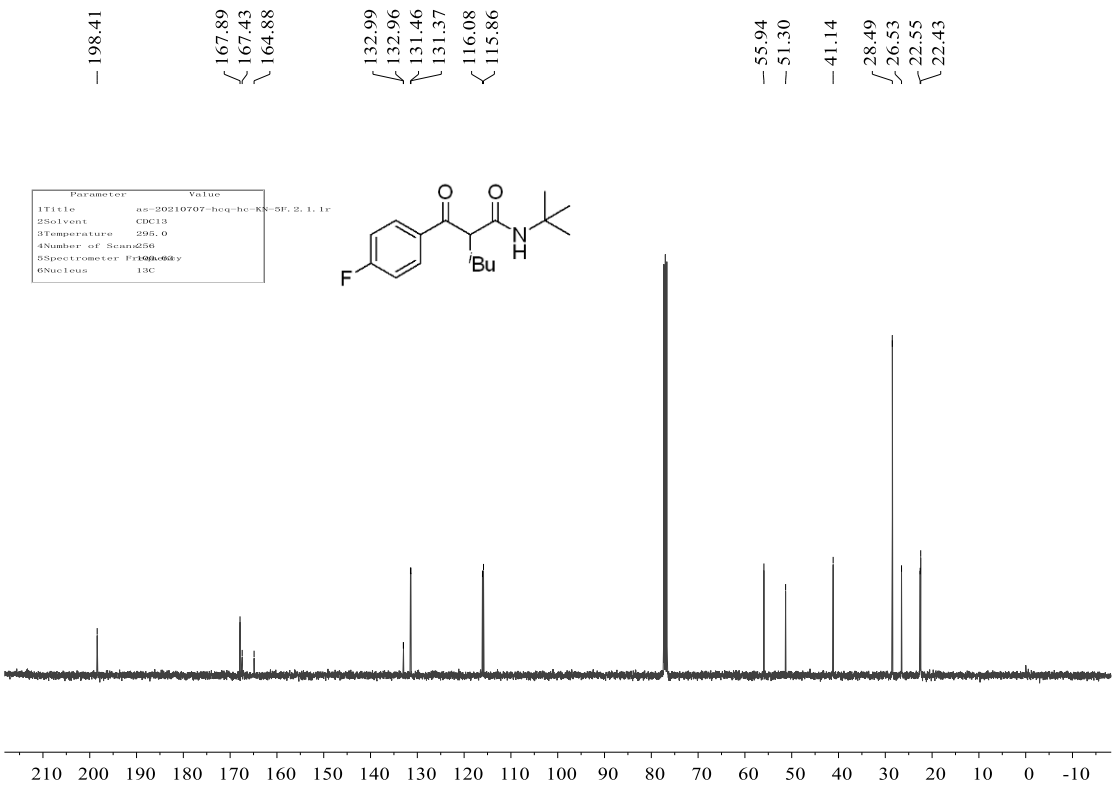
O
O
N
H
F
tBu
2.1
1.1
1.9 1.8 1.7 1.6 1.5
2.0 2.0 1.0 1.0 2.1 1.1 9.0 6.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

1z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55.94
51.30
41.14
28.49
26.53
22.55
22.43
Parameter Value
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2Solvent CDCl3
3Temperature 295.0
4Number of Scans 256
5Spectrometer Frequency
6Nucleus 13C
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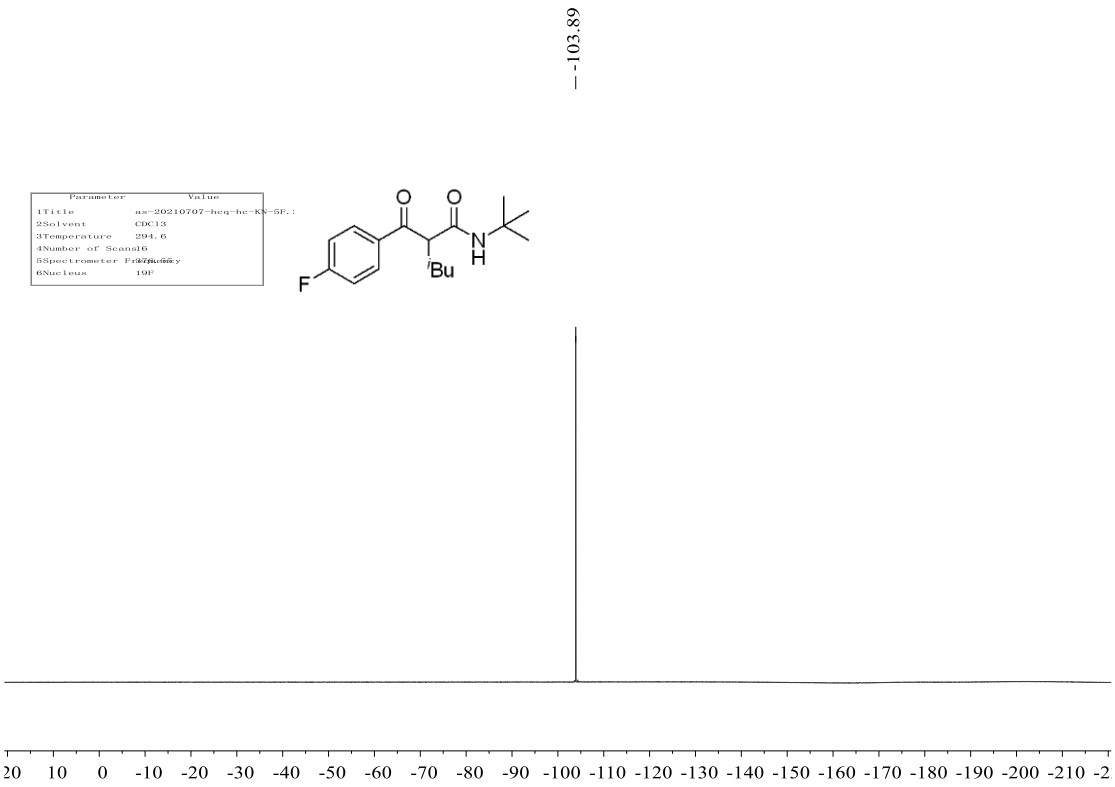
O
N
H
F
tBu
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

1z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O
N
H
F
tBu
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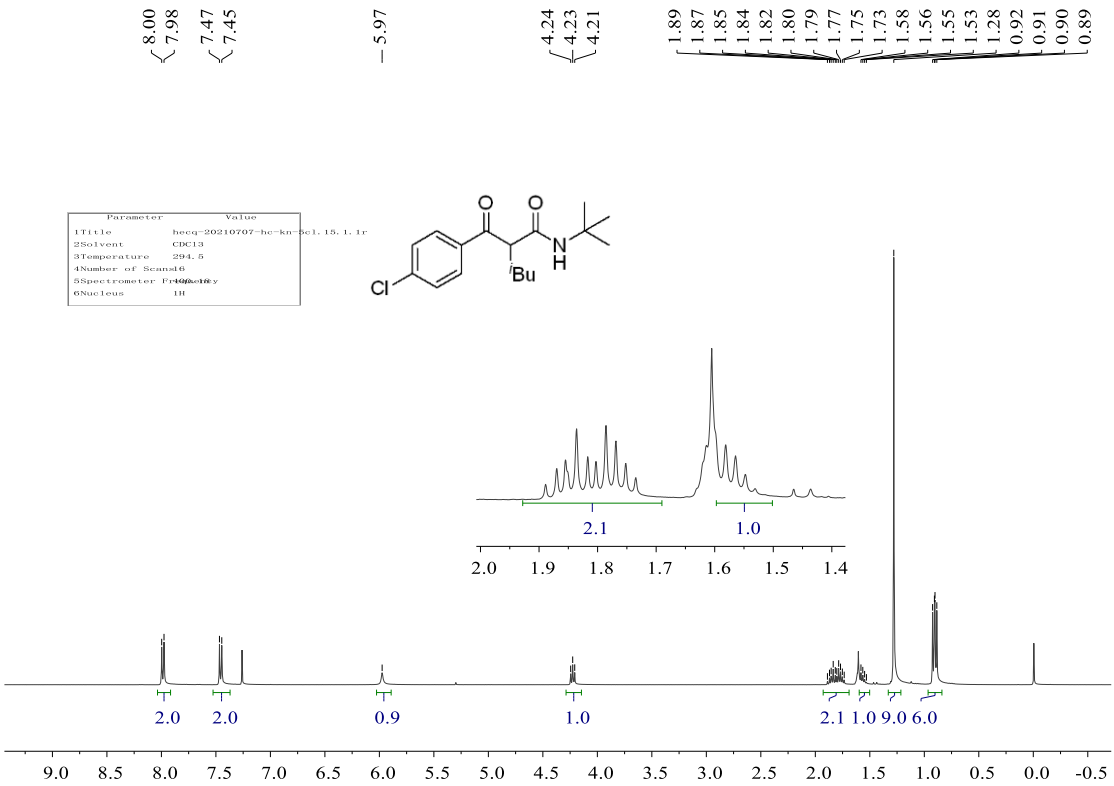
1aa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4.23
4.21
1.89
1.87
1.85
1.84
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1.80
1.79
1.77
1.75
1.73
1.58
1.56
1.55
1.53
1.28
0.92
0.91
0.90
0.89
Parameter Value
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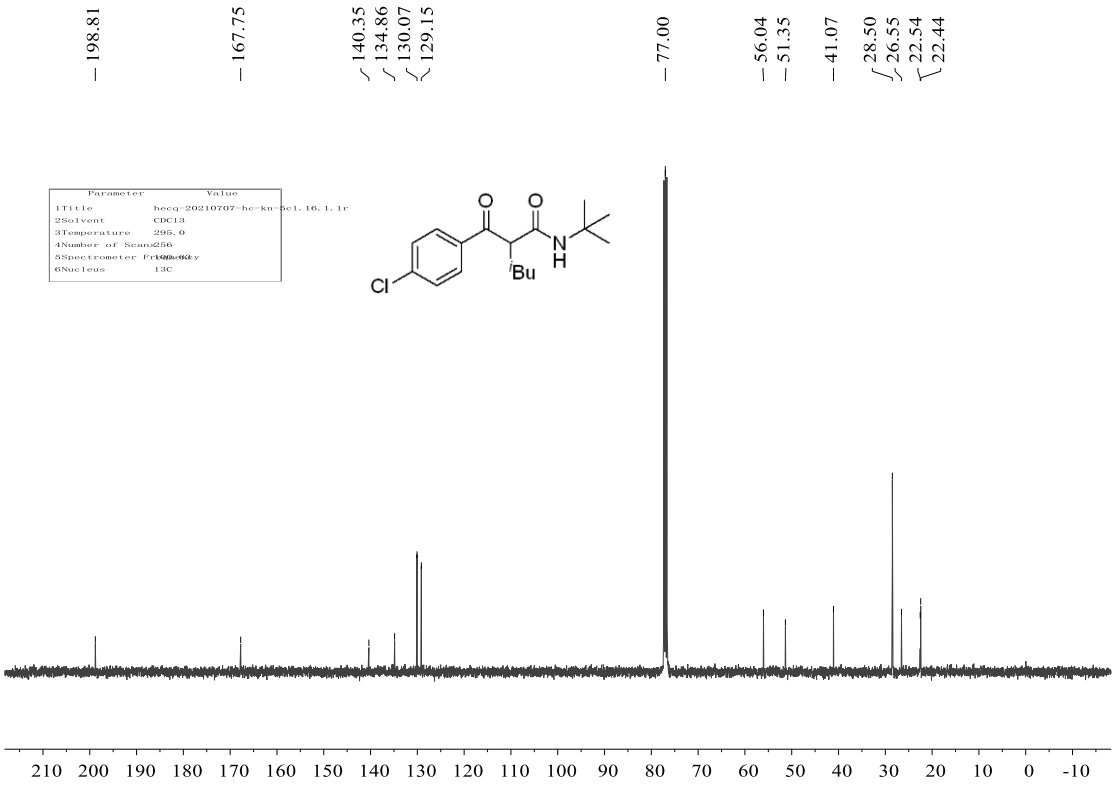
3Temperature 294.5
4Number of Scans16
5Spectrometer Pr
6Nucleus 1H
Cl
O
O
N
H
tBu
2.1
1.0
2.0 1.9 1.8 1.7 1.6 1.5 1.4
2.0 2.0 0.9 1.0 2.1 1.0 9.0 6.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

1aa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77.00
56.04
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41.07
28.50
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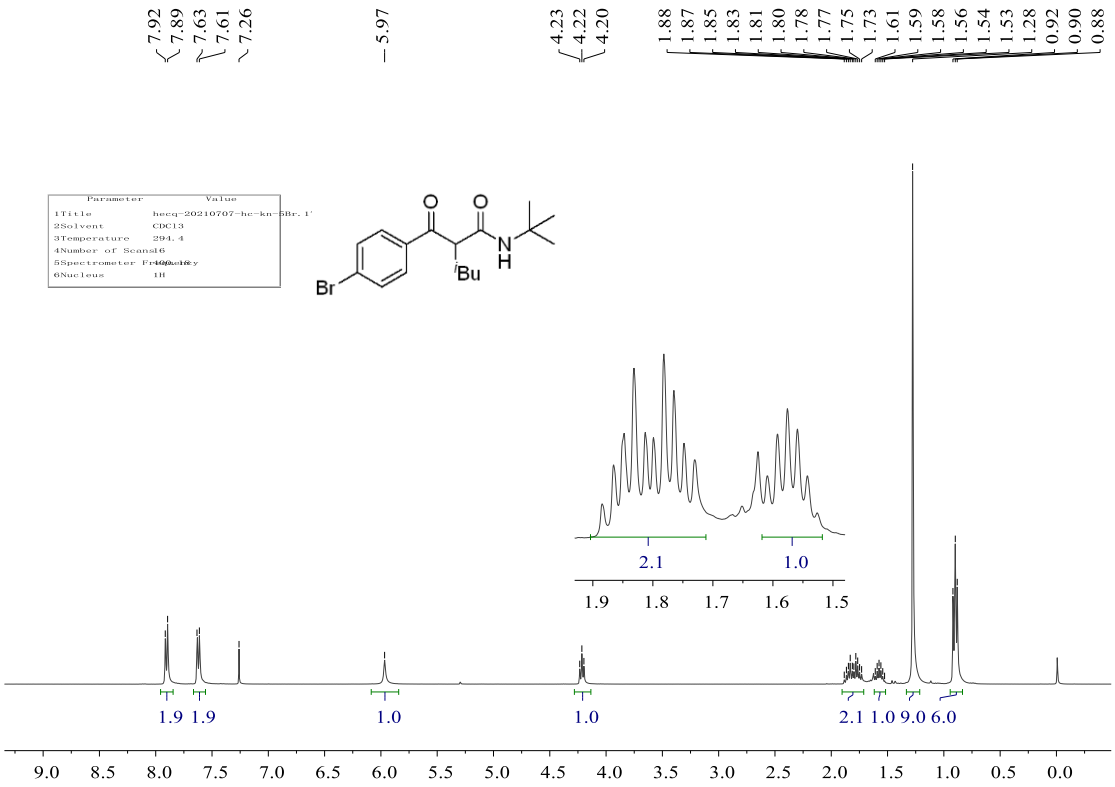
22.54
22.44
Parameter Value
1Title hecq-20210707-hc-kn-5cl.16.1.1r
2Solvent CDCl3
3Temperature 295.0
4Number of Scans256
5Spectrometer Fr
6Nucleus 13C
Cl
O
O
N
H
tBu
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

1ab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7.61
7.26
5.97
4.23
4.22
4.20
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1.87
1.85
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1.81
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1.78
1.77
1.75
1.73
1.61
1.59
1.58
1.56
1.54
1.53
1.28
0.92
0.90
0.88
Parameter Value
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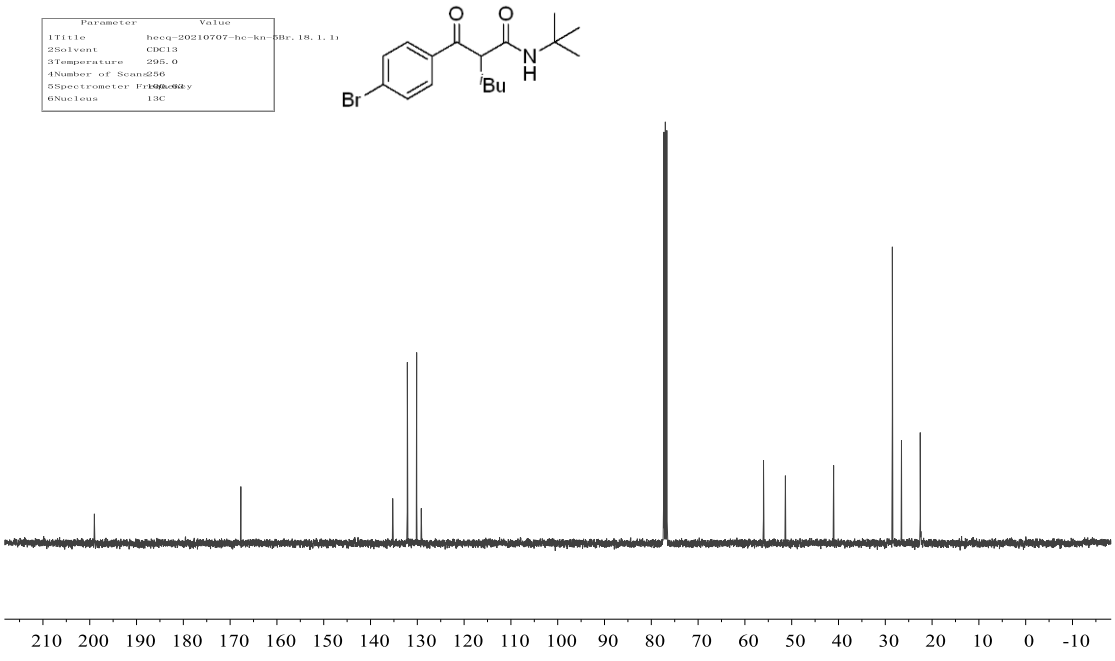
2Solvent CDCl3
3Temperature 294.4
4Number of Scans16
5Spectrometer Fr
6Nucleus 1H
Br
O
O
N
H
tBu
2.1
1.0
1.9 1.8 1.7 1.6 1.5
1.9 1.9
1.0
1.0
2.1 1.0 9.0 6.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

1ab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4Number of Scans256
5Spectrometer Fr
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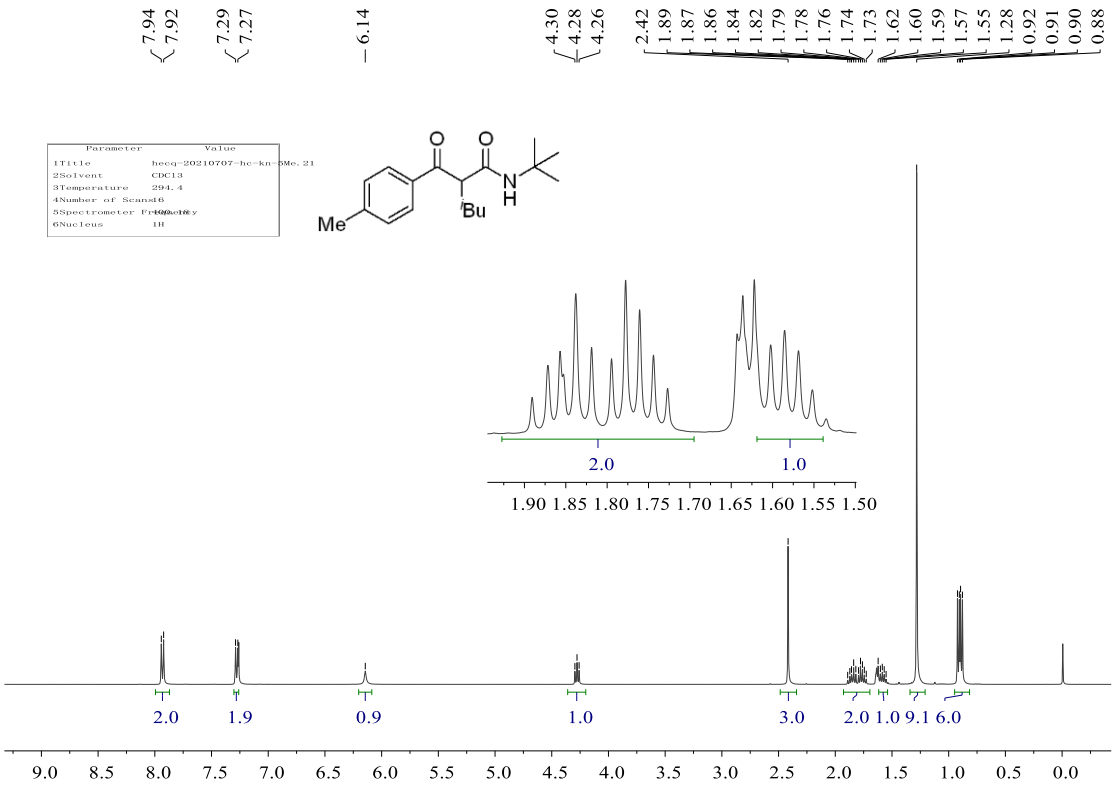
Br
O
O
N
H
tBu
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

1ac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6.14
4.30
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1.87
1.86
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1.79
1.78
1.76
1.74
1.73
1.62
1.60
1.59
1.57
1.55
1.28
0.92
0.91
0.90
0.88
Parameter Value
1Title hecq-20210707-hc-kn-5Me.21
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3Temperature 294.4
4Number of Scans 16
5Spectrometer Frequency
6Nucleus 1H
Me
tBu
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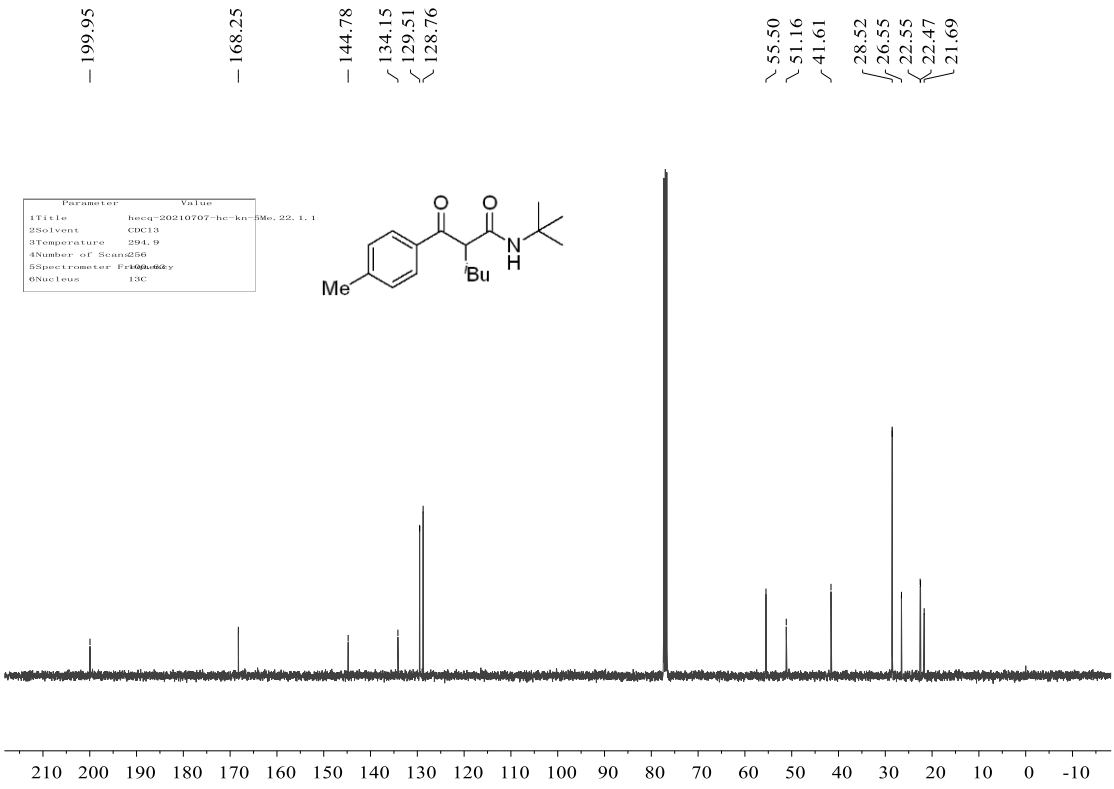
1.0
1.90 1.85 1.80 1.75 1.70 1.65 1.60 1.55 1.50
2.0 1.9 0.9 1.0 3.0 2.0 1.0 9.1 6.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

1ac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51.16
41.61
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26.55
22.55
22.47
21.69
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2Solvent CDCl3
3Temperature 294.9
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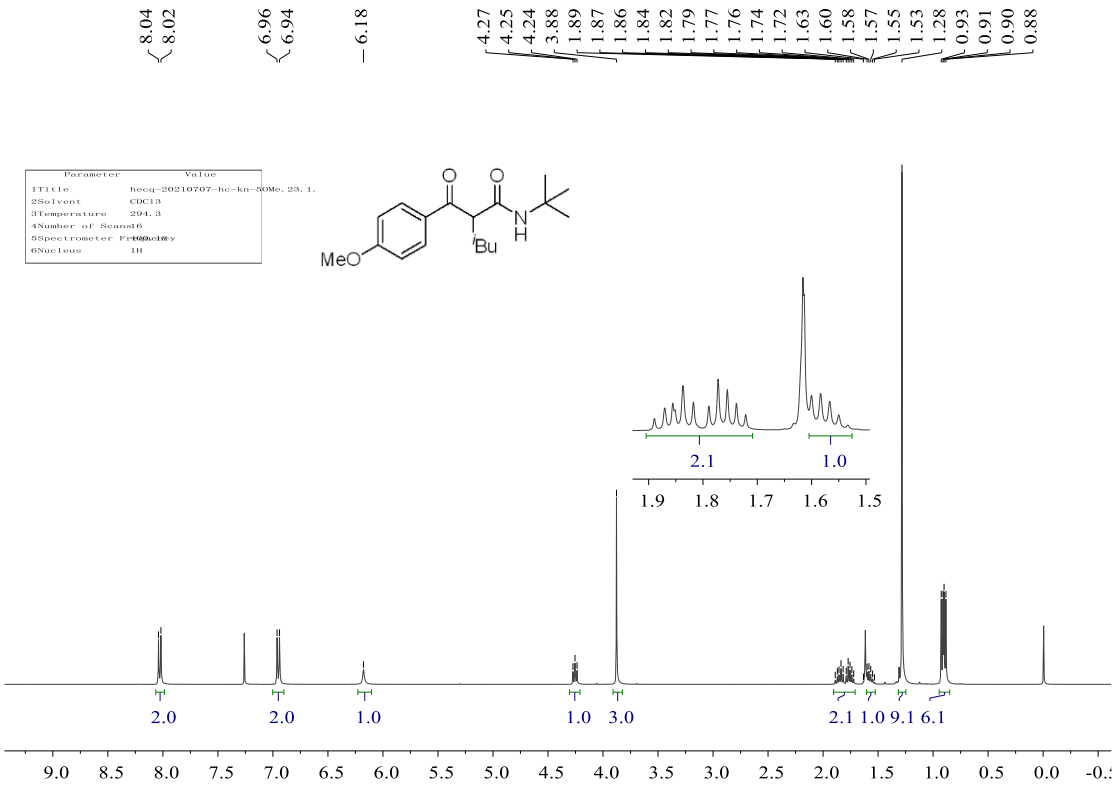
5Spectrometer Frequency
6Nucleus 13C
Me
tBu
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

1ad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8.02
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4.24
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1.89
1.87
1.86
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1.82
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1.77
1.76
1.74
1.72
1.63
1.60
1.58
1.57
1.55
1.53
1.28
0.93
0.91
0.90
0.88
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3Temperature 294.3
4Number of Scans16
5Spectrometer Fr
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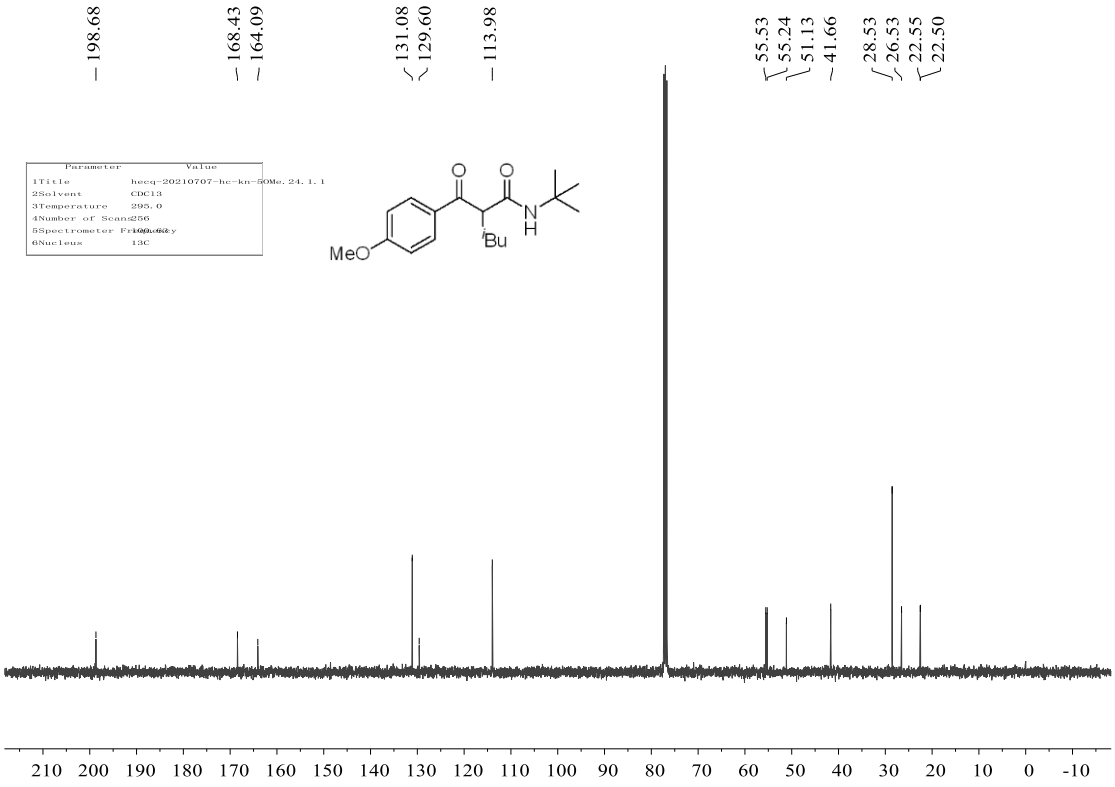
tBu
N
H
O
2.1
1.0
1.9 1.8 1.7 1.6 1.5
2.0 2.0 1.0 1.0 3.0 2.1 1.0 9.1 6.1
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

1ad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22.55
22.50
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MeO
tBu
N
H
O
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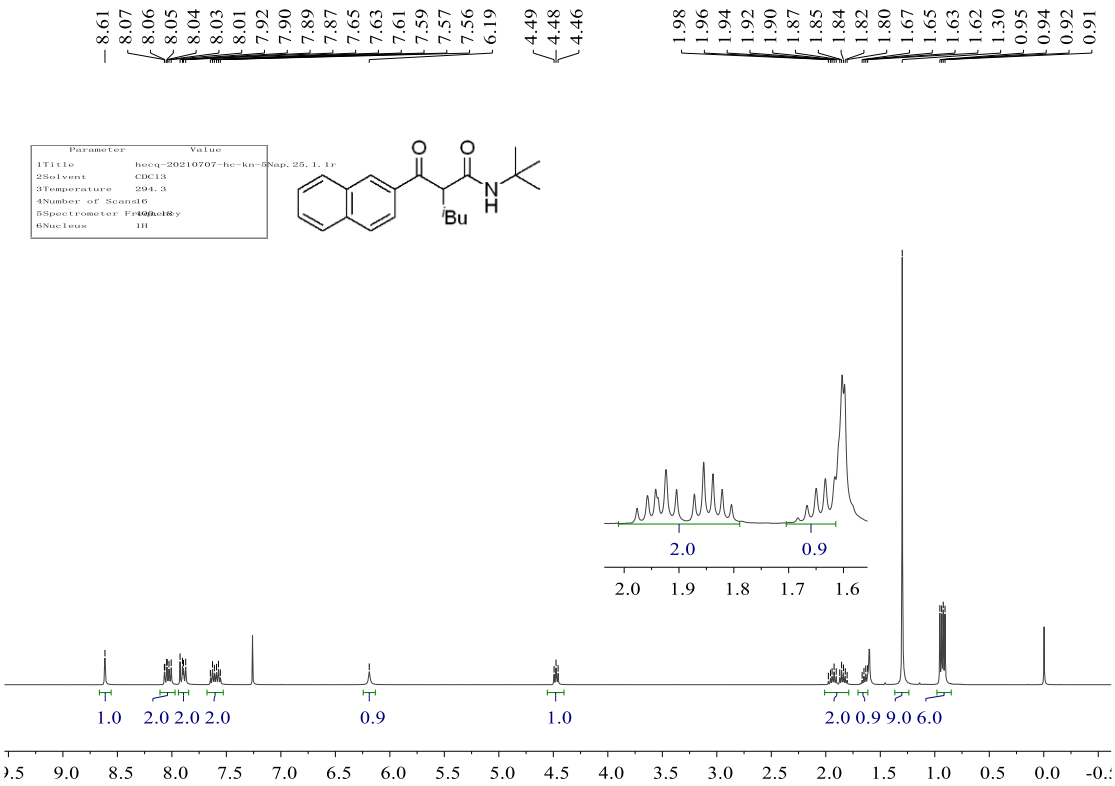
1ae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7.59
7.57
7.56
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1.94
1.92
1.90
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1.85
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1.65
1.63
1.62
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O
N
H
tBu
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1.0 2.0 2.0 2.0 0.9 1.0 2.0 0.9 9.0 6.0
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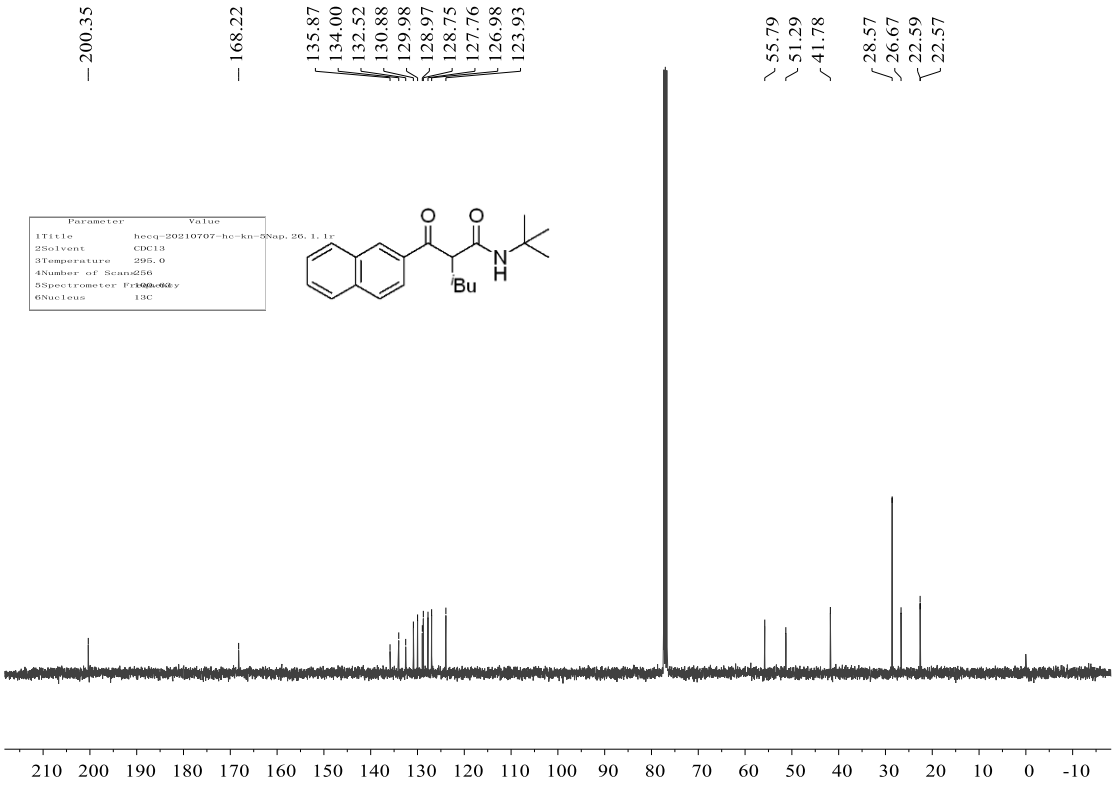
1ae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26.67
22.59
22.57
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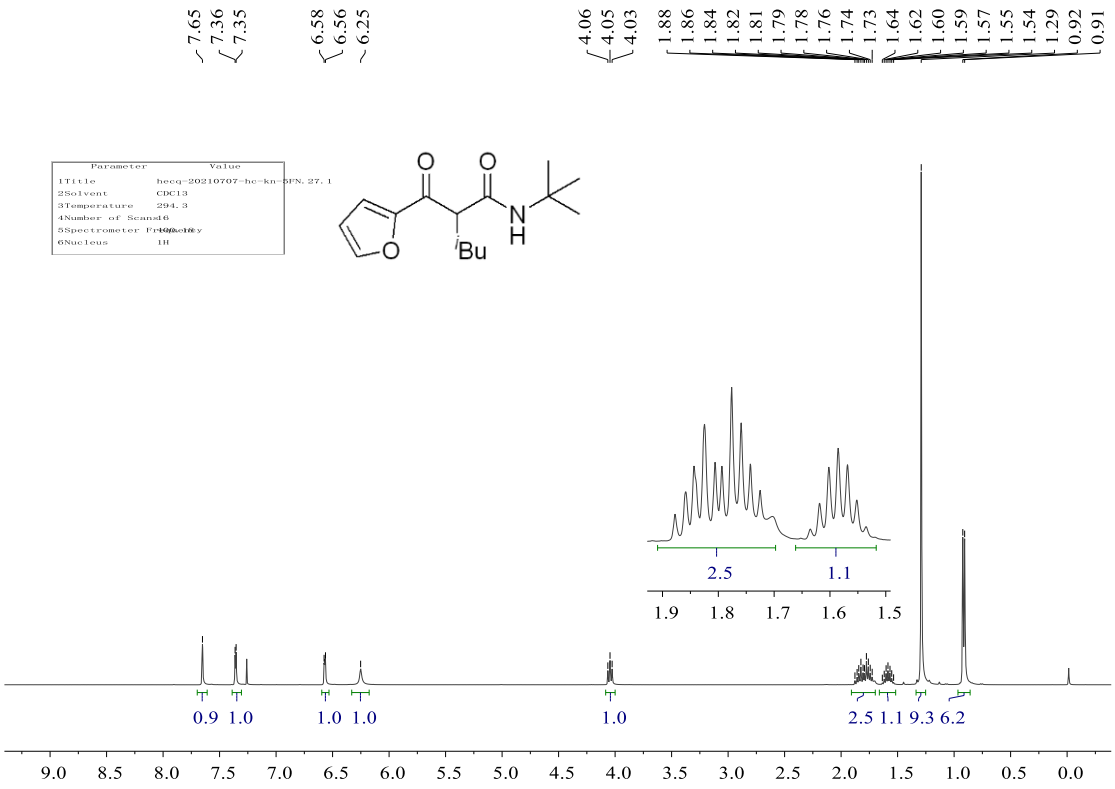
1af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1.76
1.74
1.73
1.64
1.62
1.60
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1.57
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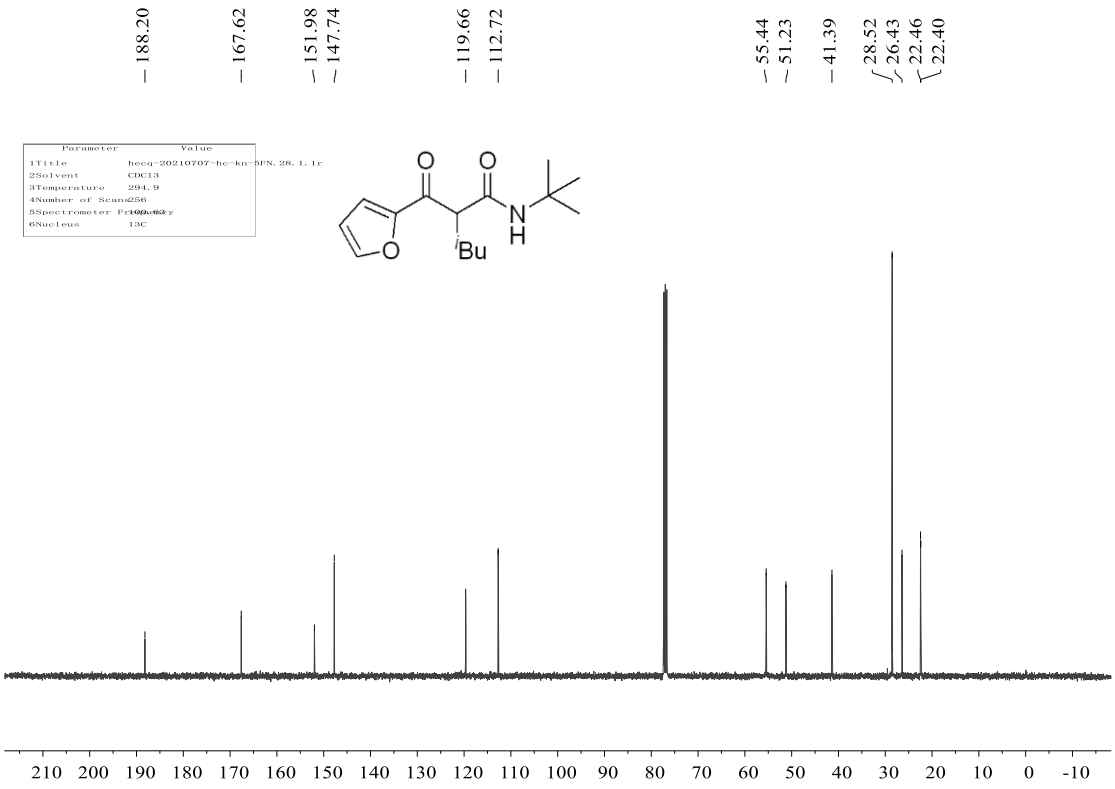
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5Spectrometer Frequency
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O
iBu
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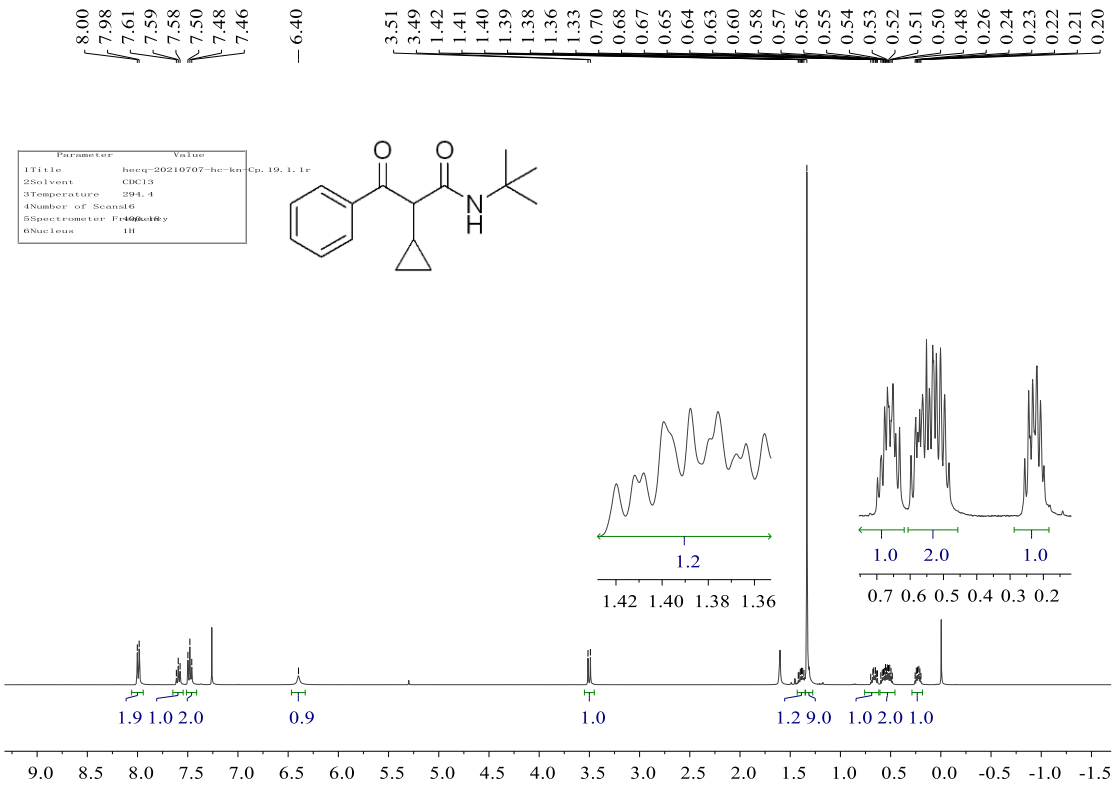
1ag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3.51 3.49 1.42 1.41 1.40 1.39 1.38 1.36 1.33 0.70 0.68 0.67 0.65 0.64 0.63 0.60 0.58 0.57 0.56 0.55 0.54 0.53 0.52 0.51 0.50 0.48 0.26 0.24 0.23 0.22 0.21 0.20
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4Number of Scans16
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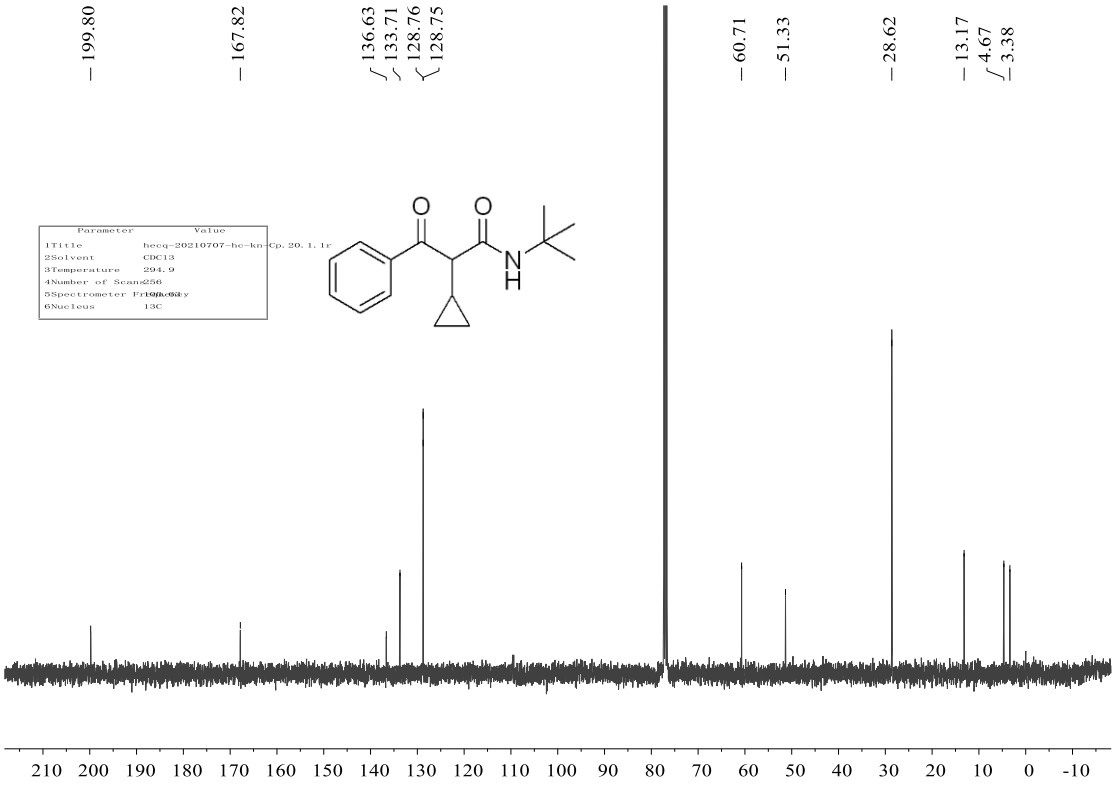
O
N
H
1.2
1.42 1.40 1.38 1.36
1.0 2.0 1.0
0.7 0.6 0.5 0.4 0.3 0.2
1.9 1.0 2.0
0.9
1.0
1.2 9.0
1.0 2.0 1.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5

1ag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Parameter Value
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3Temperature 294. 9
4Number of Scans256
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O
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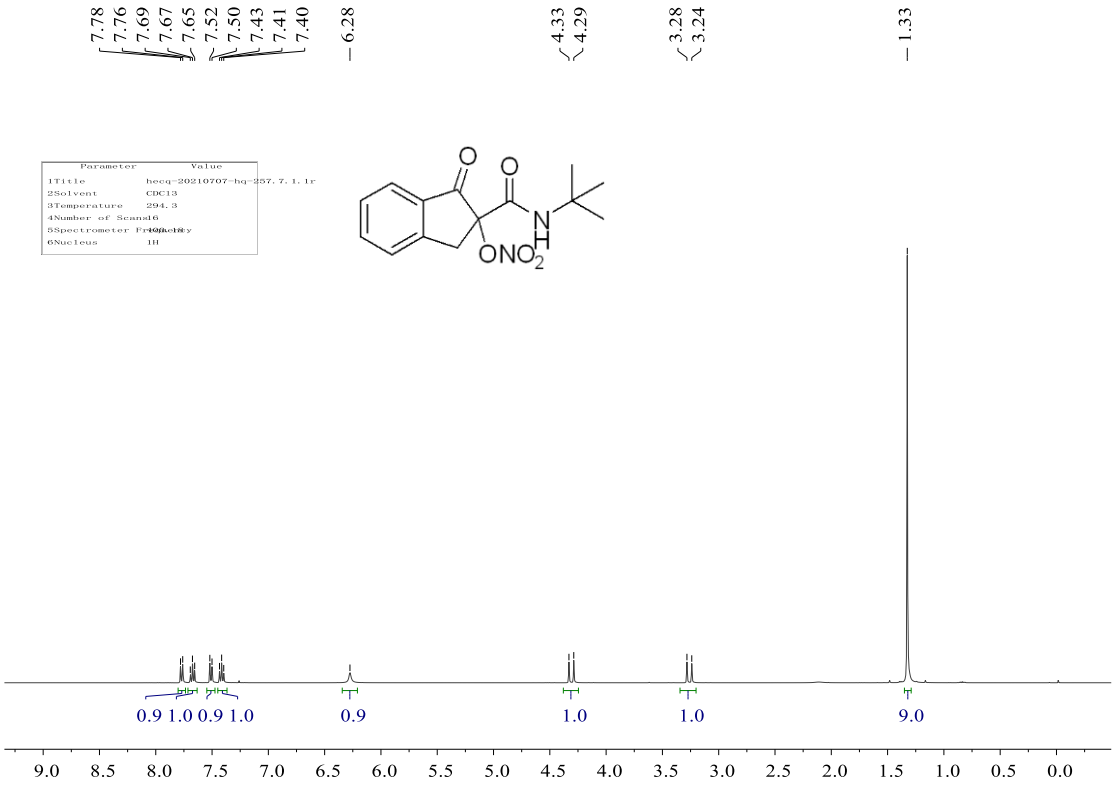
3a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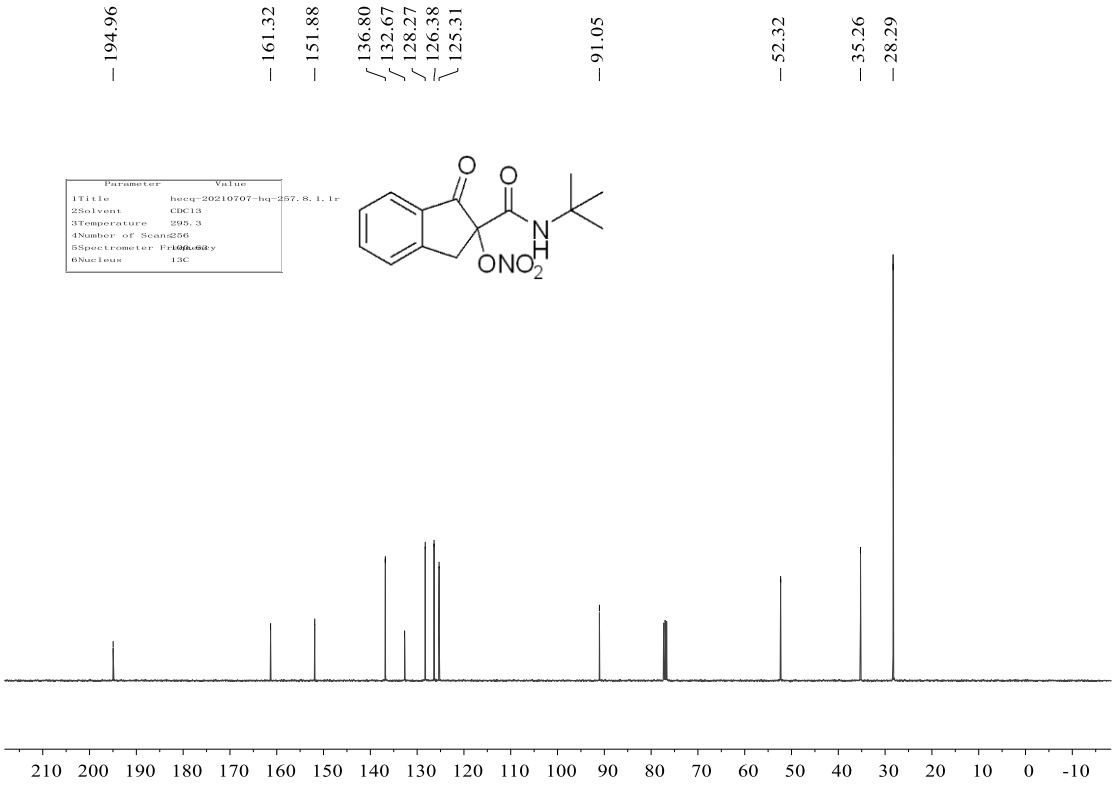
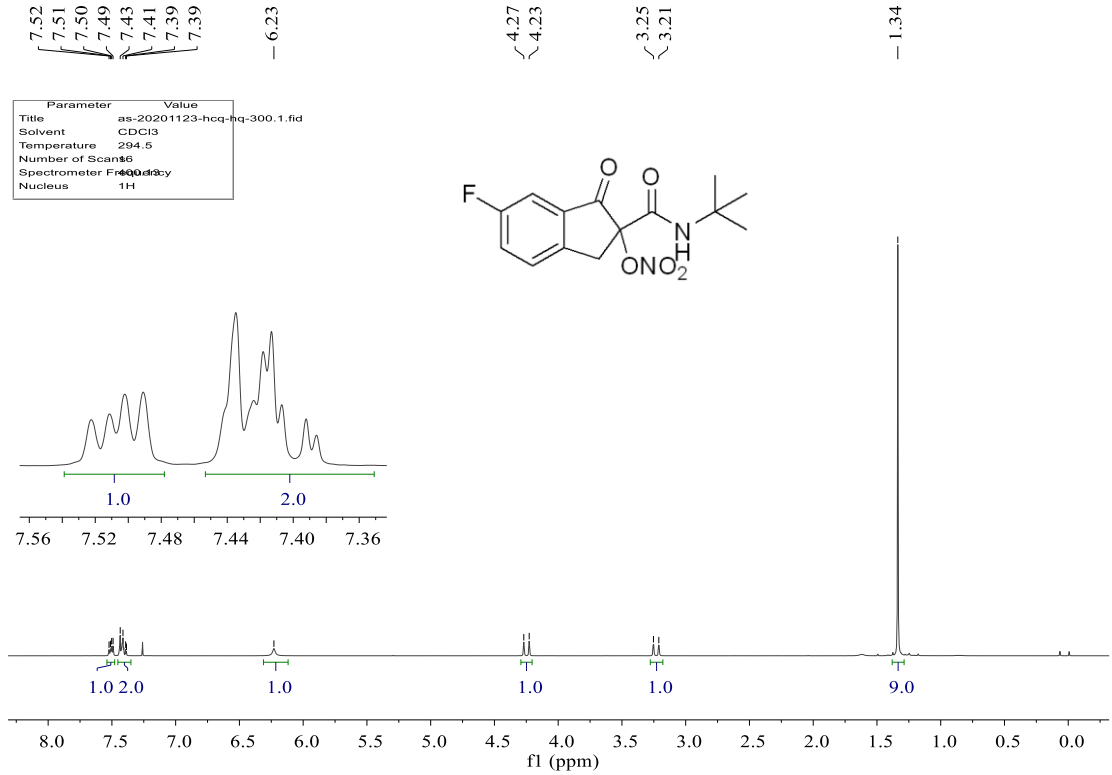
7.43
7.41
7.40
6.28
4.33
4.29
3.28
3.24
1.33
Parameter Value
1Title hecq-20210707-hq-257.7.1.1r
2Solvent CDCl3
3Temperature 294.3
4Number of Scans 16
5Spectrometer Frequency
6Nucleus 1H
O
O
N
H
ONO2
0.9 1.0 0.9 1.0
0.9
1.0
1.0
9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

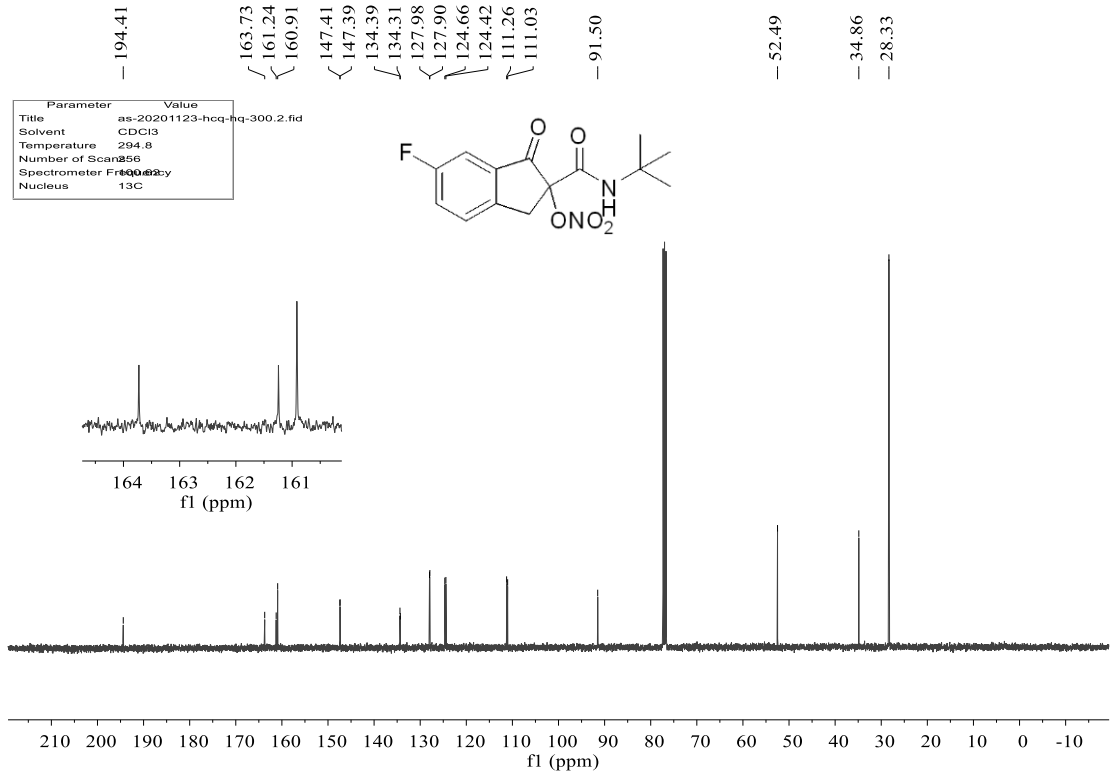
3a


194.96
161.32
151.88
136.80
132.67
128.27
126.38
125.31
91.05
52.32
35.26
28.29
Parameter Value
1Title hecq-20210707-hq-257.8.1.1r
2Solvent CDCl3
3Temperature 295.3
4Number of Scans 256
5Spectrometer Frequency
6Nucleus 13C
O
O
N
H
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

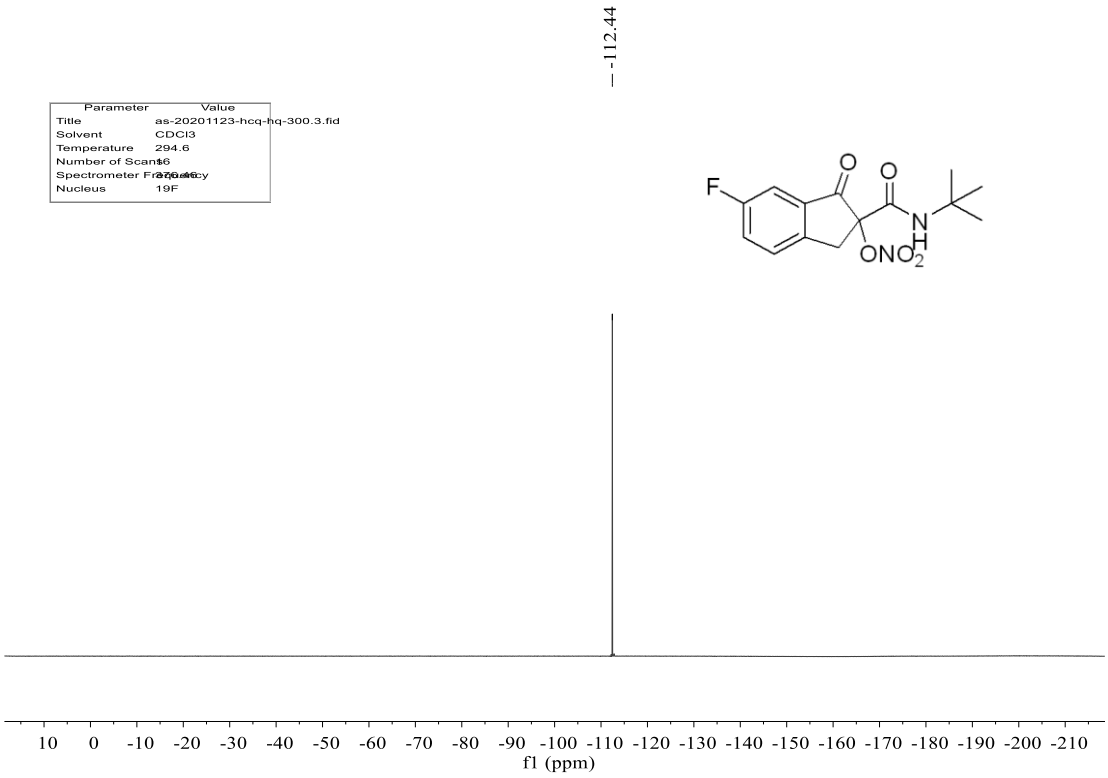
3b


7.52
7.51
7.50
7.49
7.43
7.41
7.39
7.39
6.23
4.27
4.23
3.25
3.21
1.34
Parameter Value
Title as-20201123-hcq-hq-300.1.fid
Solvent CDCl3
Temperature 294.5
Number of Scans 16
Nucleus 1H
F
O
O
N
H
ONO2
1.0
2.0
7.56 7.52 7.48 7.44 7.40 7.36
1.0 2.0
1.0
1.0
1.0
9.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

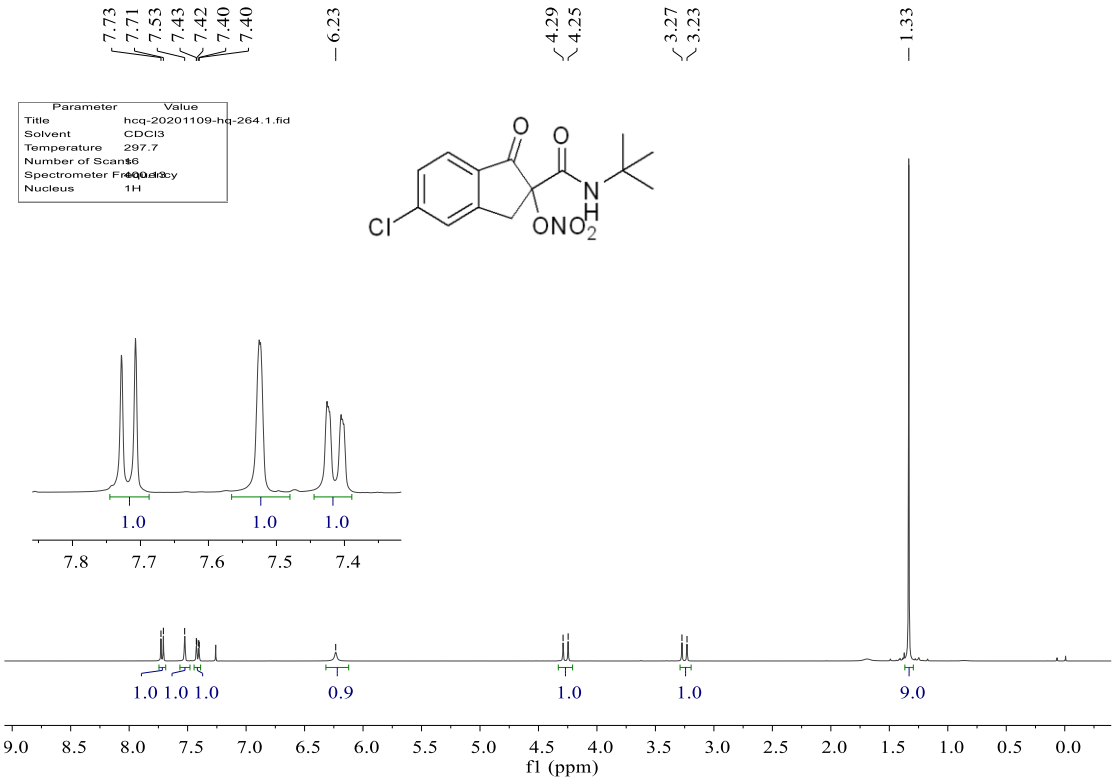
3b


194.41
163.73
161.24
160.91
147.41
147.39
134.39
134.31
127.98
127.90
124.66
124.42
111.26
111.03
91.50
52.49
34.86
28.33
Parameter Value
Title as-20201123-hcq-hq-300.2.fid
Solvent CDCl3
Temperature 294.8
Number of Scans 256
Nucleus 13C
F
O
O
N
H
ONO2
164 163 162 161
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

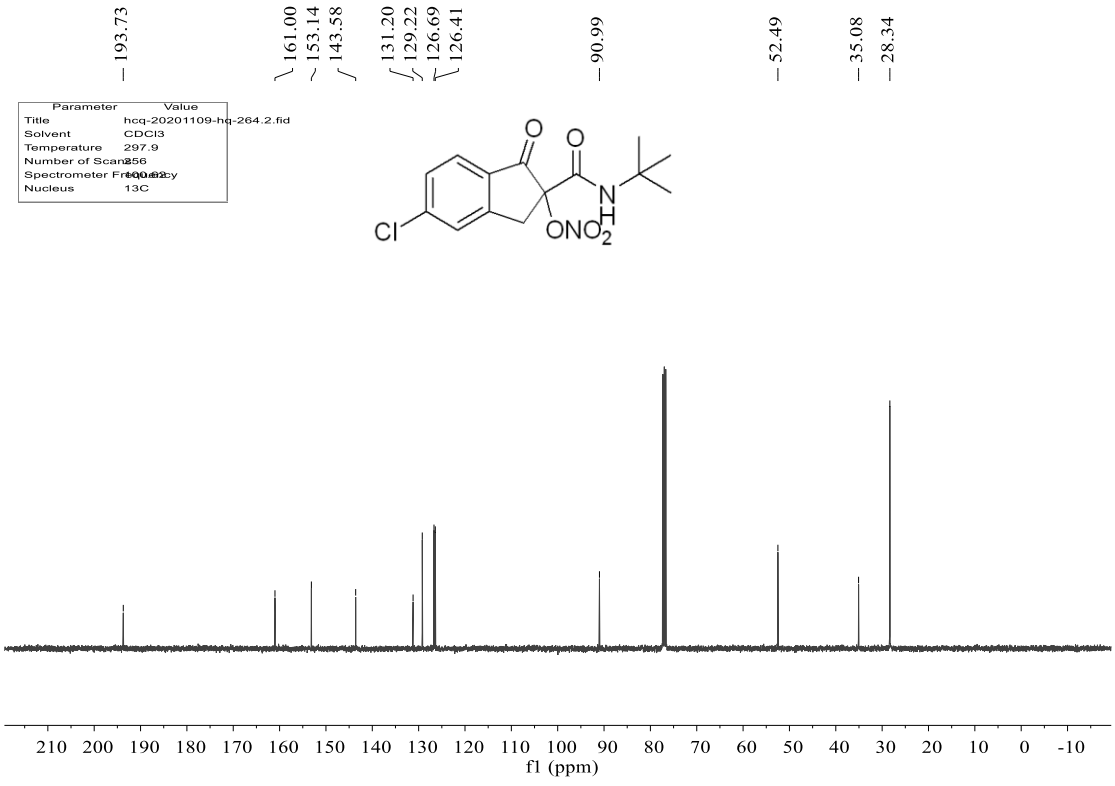
3b


-112.44
Parameter Value
Title as-20201123-hcq-hq-300.3.fid
Solvent CDCl3
Temperature 294.6
Number of Scans 16
Nucleus 19F
F
O
O
N
H
ONO2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

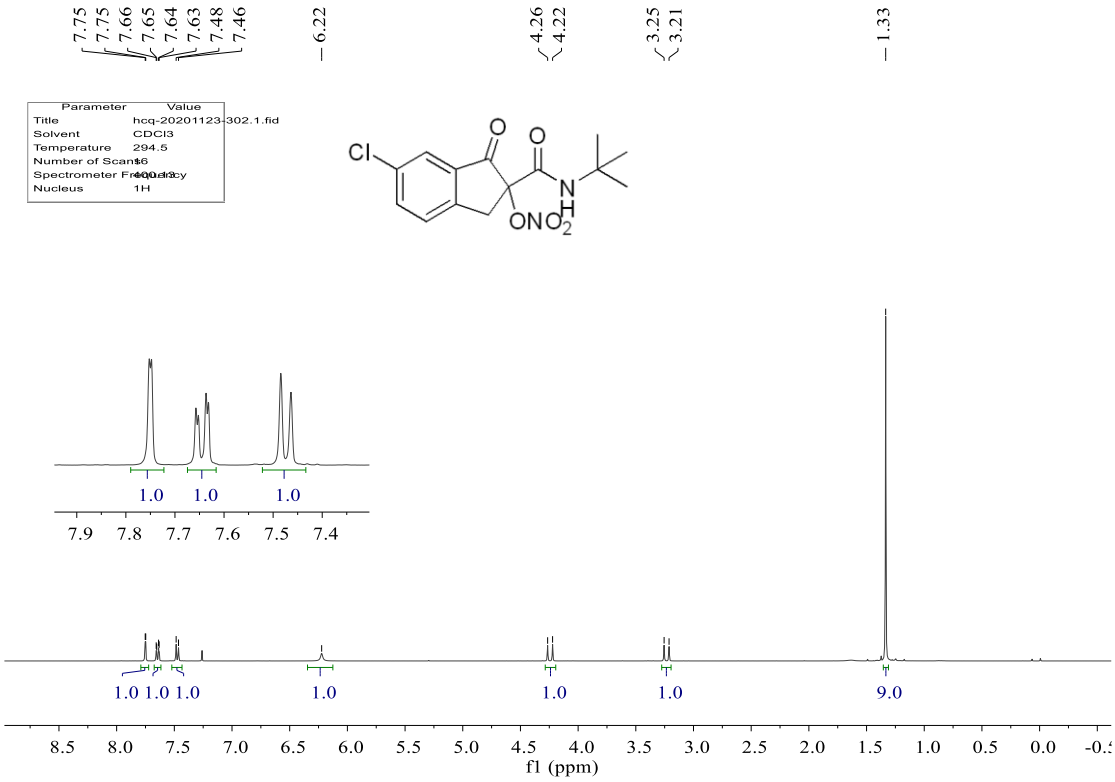
3c


7.73
7.71
7.53
7.43
7.42
7.40
7.40
6.23
4.29
4.25
3.27
3.23
1.33
Parameter Value
Title hcq-20201109-hq-264.1.fid
Solvent CDCl3
Temperature 297.7
Number of Scans 16
Nucleus 1H
Cl
O
O
N
H
ONO2
1.0 1.0 1.0
0.9
1.0
1.0
9.0
f1 (ppm)

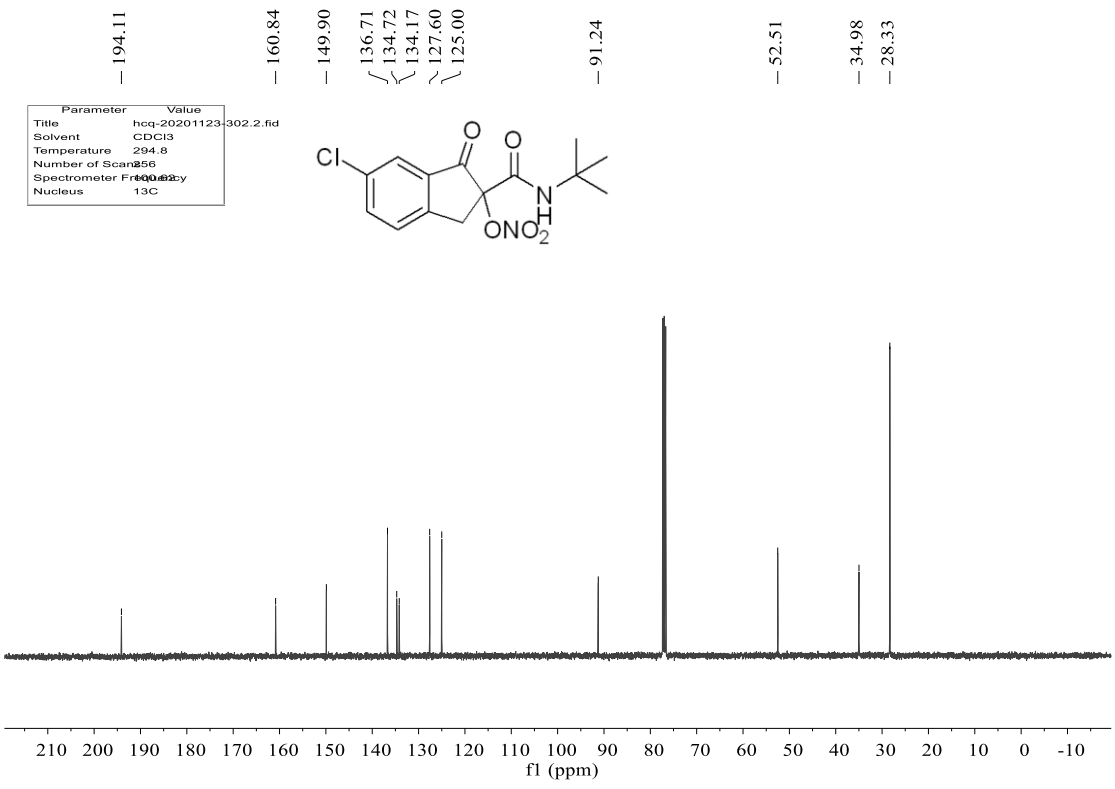
3c


193.73
161.00
153.14
143.58
131.20
129.22
126.69
126.41
90.99
52.49
35.08
28.34
Parameter Value
Title hcq-20201109-hq-264.2.fid
Solvent CDCl3
Temperature 297.9
Number of Scans 256
Nucleus 13C
Cl
O
O
N
H
ONO2
f1 (ppm)

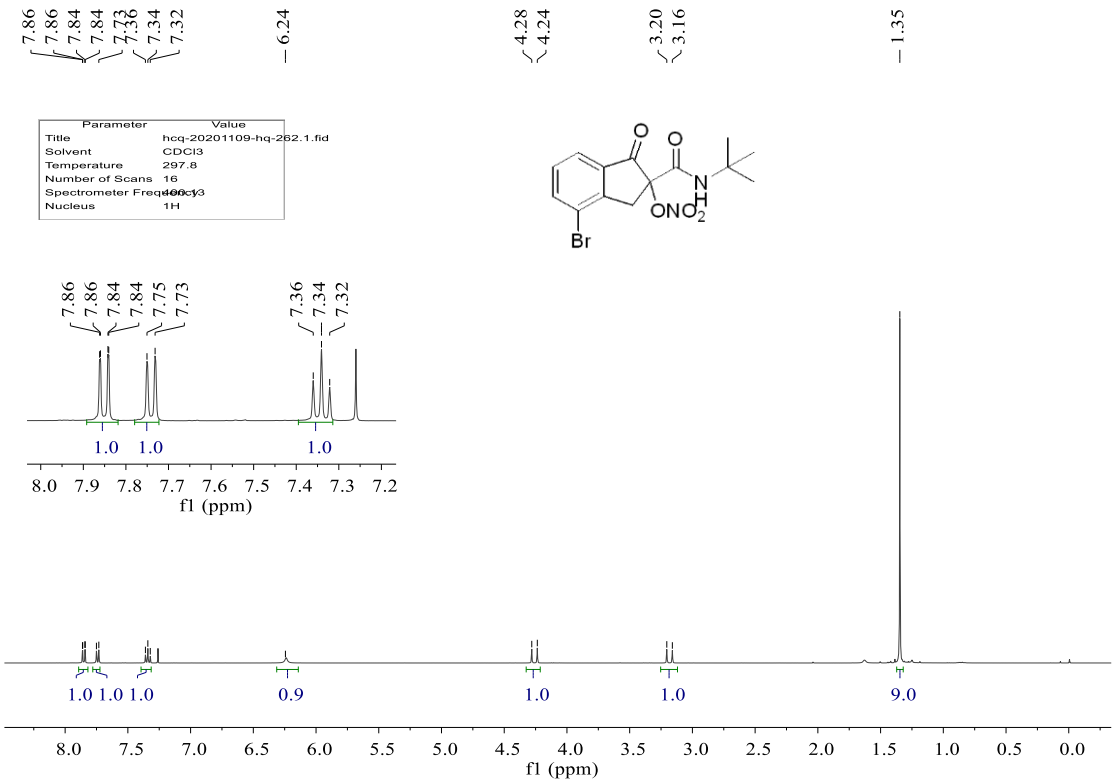
3d


7.75
7.75
7.66
7.65
7.64
7.63
7.48
7.46
6.22
4.26
4.22
3.25
3.21
1.33
Parameter Value
Title hcq-20201123-302.1.fid
Solvent CDCl3
Temperature 294.5
Number of Scans 16
Nucleus 1H
Cl
O
O
N
H
ONO2
1.0 1.0 1.0
7.9 7.8 7.7 7.6 7.5 7.4
1.0 1.0 1.0 1.0 1.0 9.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

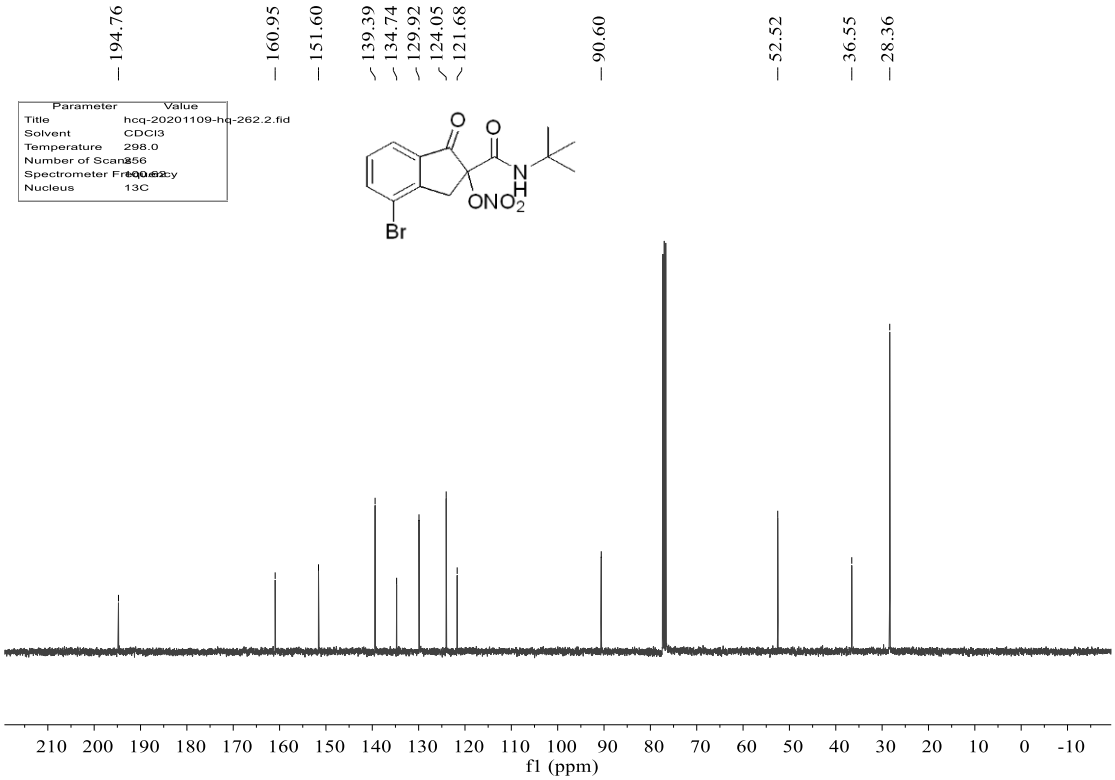
3d


194.11
160.84
149.90
136.71
134.72
134.17
127.60
125.00
91.24
52.51
34.98
28.33
Parameter Value
Title hcq-20201123-302.2.fid
Solvent CDCl3
Temperature 294.8
Number of Scans 256
Nucleus 13C
Cl
O
O
N
H
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

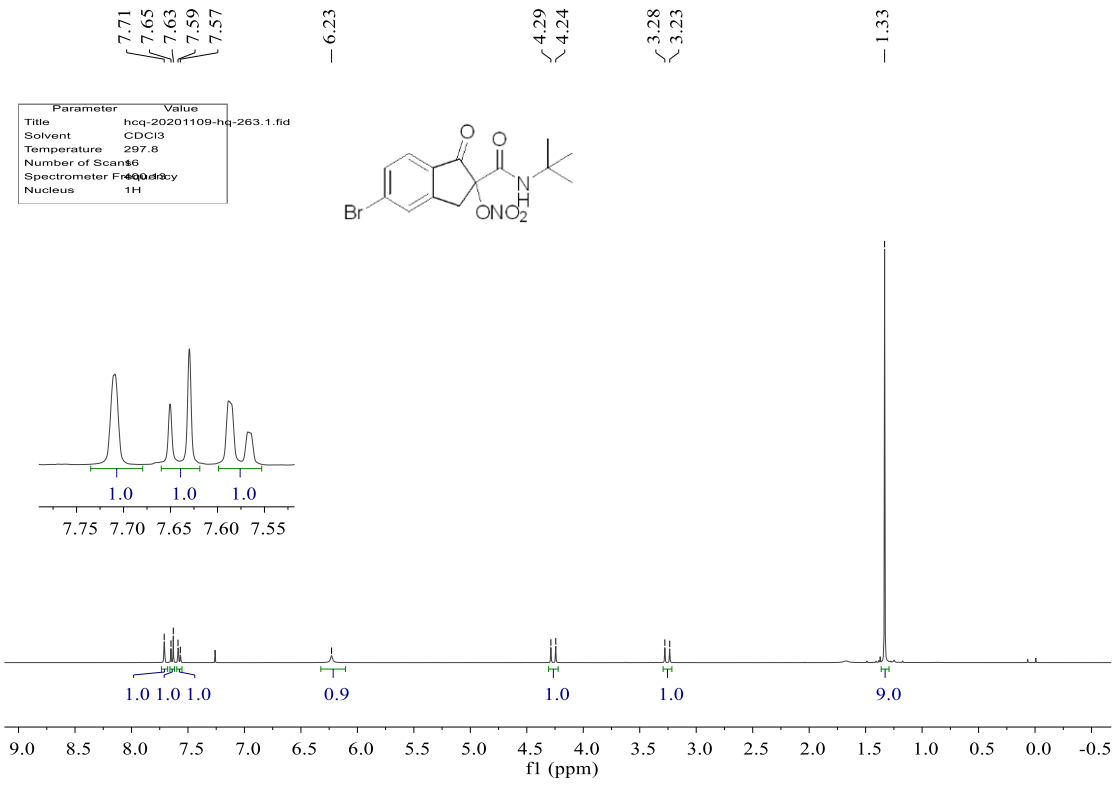
3e


7.86
7.86
7.84
7.84
7.73
7.36
7.34
7.32
6.24
4.28
4.24
3.20
3.16
1.35
Parameter Value
Title hcq-20201109-hq-262.1.fid
Solvent CDCl3
Temperature 297.8
Number of Scans 16
Nucleus 1H
O
O
N
H
ONO2
Br
1.0 1.0 1.0
0.9
1.0
1.0
9.0
f1 (ppm)

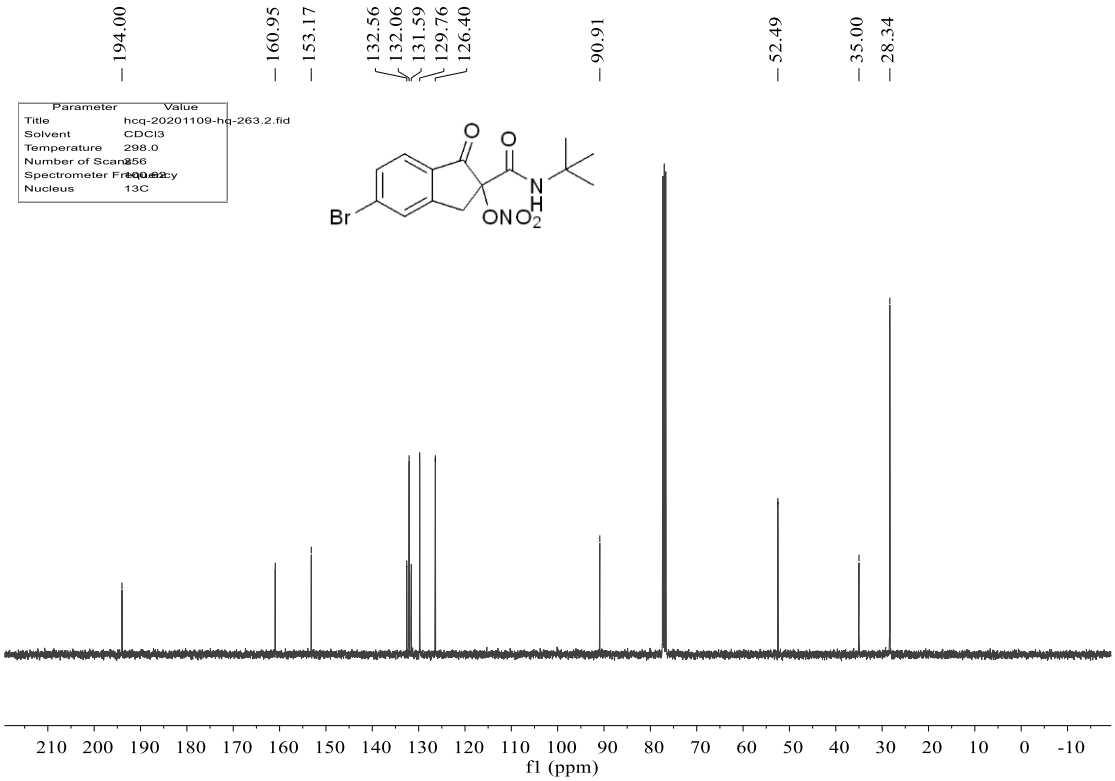
3e


194.76
160.95
151.60
139.39
134.74
129.92
124.05
121.68
90.60
52.52
36.55
28.36
Parameter Value
Title hcq-20201109-hq-262.2.fid
Solvent CDCl3
Temperature 298.0
Number of Scans 256
Nucleus 13C
O
O
N
H
ONO2
Br
f1 (ppm)

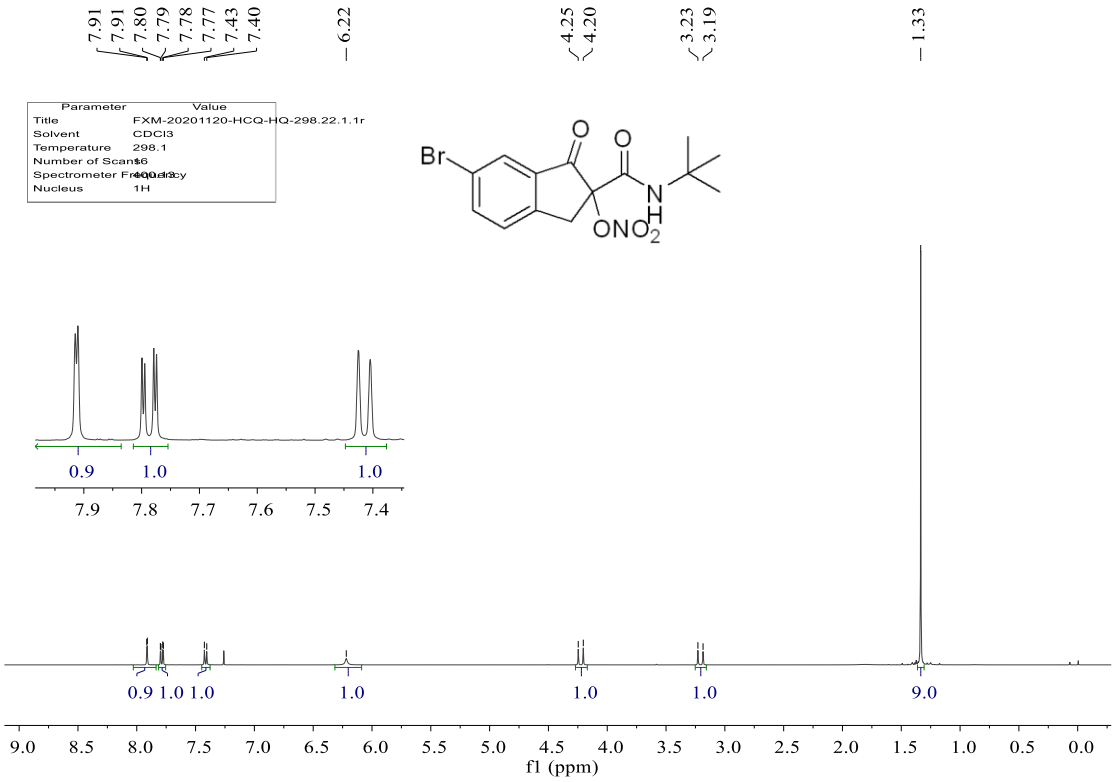
3f


7.71
7.65
7.63
7.59
7.57
6.23
4.29
4.24
3.28
3.23
1.33
Parameter Value
Title hcq-20201109-hq-263.1.fid
Solvent CDCl3
Temperature 297.8
Number of Scans 16
Nucleus 1H
Br
ONO2
1.0 1.0 1.0
7.75 7.70 7.65 7.60 7.55
1.0 1.0 1.0 0.9 1.0 1.0 9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

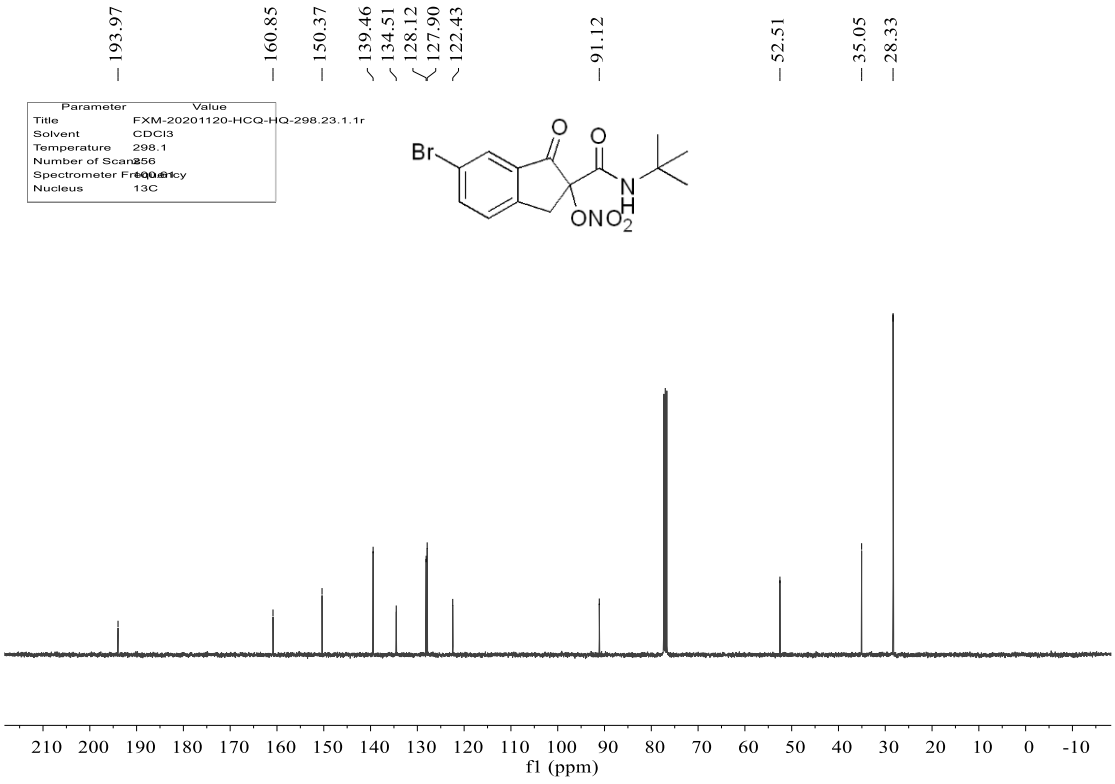
3f


194.00
160.95
153.17
132.56
132.06
131.59
129.76
126.40
90.91
52.49
35.00
28.34
Parameter Value
Title hcq-20201109-hq-263.2.fid
Solvent CDCl3
Temperature 298.0
Number of Scans 256
Nucleus 13C
Br
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

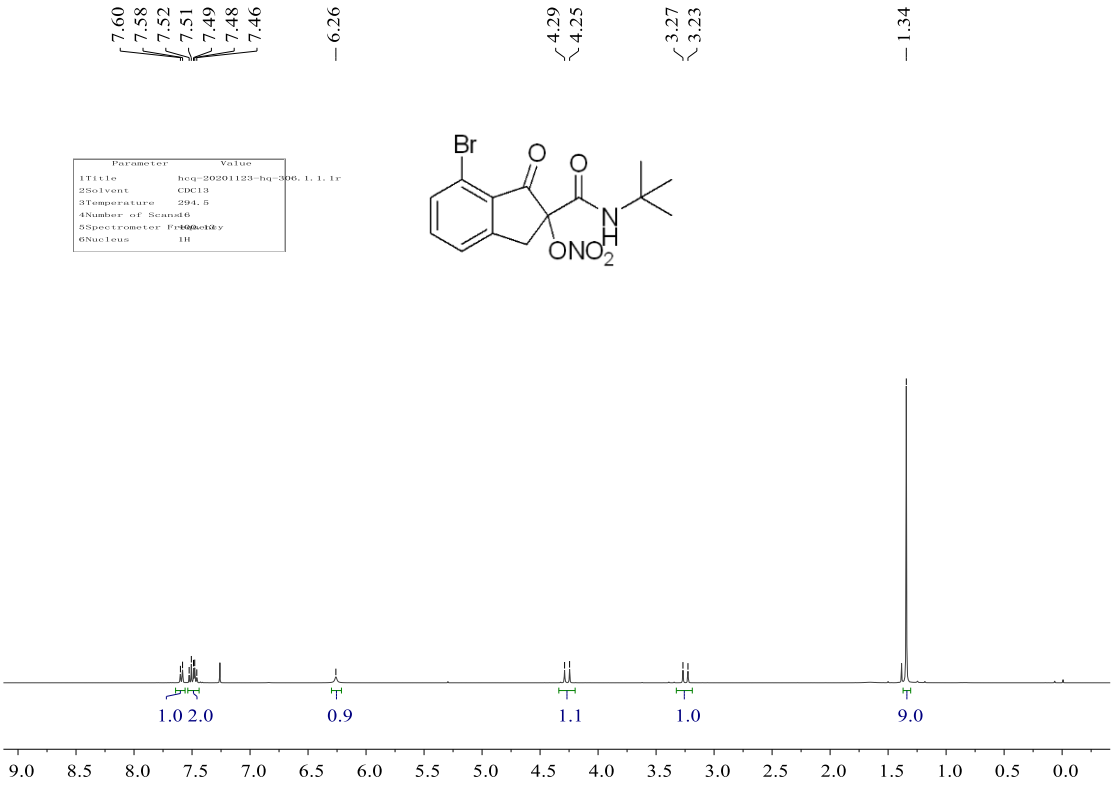
3g


7.91
7.91
7.80
7.79
7.78
7.77
7.43
7.40
6.22
4.25
4.20
3.23
3.19
1.33
Parameter Value
Title FXM-20201120-HCQ-HQ-298.22.1.1r
Solvent CDCl3
Temperature 298.1
Number of Scans 16
Nucleus 1H
Br
O
O
N
H
ONO2
0.9 1.0 1.0
0.9 1.0 1.0 1.0 1.0 1.0 9.0
f1 (ppm)

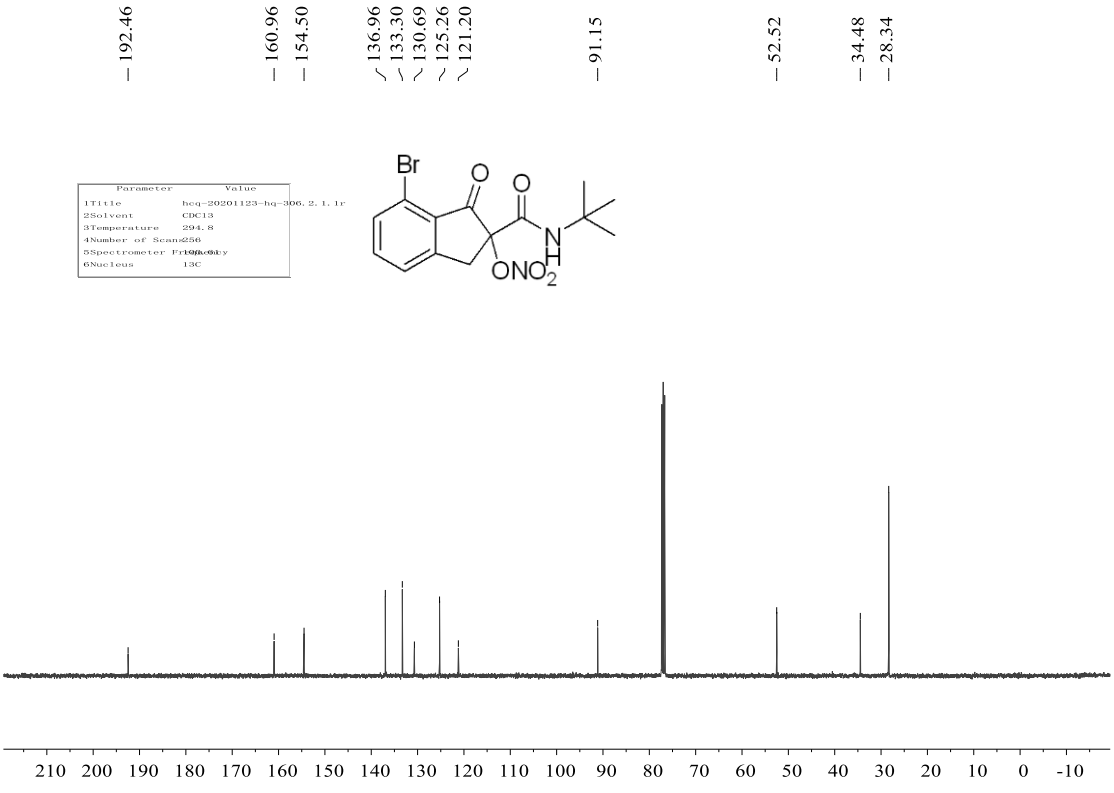
3g


193.97
160.85
150.37
139.46
134.51
128.12
127.90
122.43
91.12
52.51
35.05
28.33
Parameter Value
Title FXM-20201120-HCQ-HQ-298.23.1.1r
Solvent CDCl3
Temperature 298.1
Number of Scans 256
Nucleus 13C
Br
O
O
N
H
ONO2
f1 (ppm)

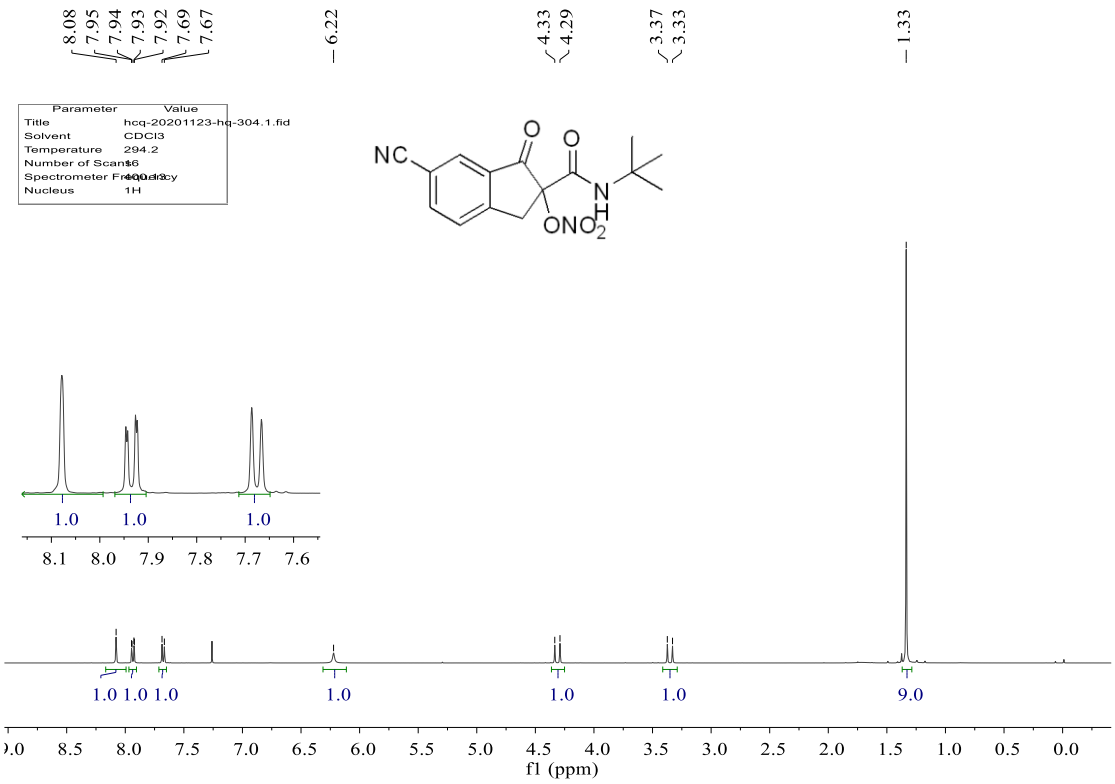
3h


7.60
7.58
7.52
7.51
7.49
7.48
7.46
6.26
4.29
4.25
3.27
3.23
1.34
Parameter Value
1Title hcq-20201123-hq-306, 1, 1, 1r
2Solvent CDCl3
3Temperature 294.5
4Number of Scans 16
6Nucleus 1H
Br
O
O
N
H
ONO2
1.0 2.0
0.9
1.1
1.0
9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

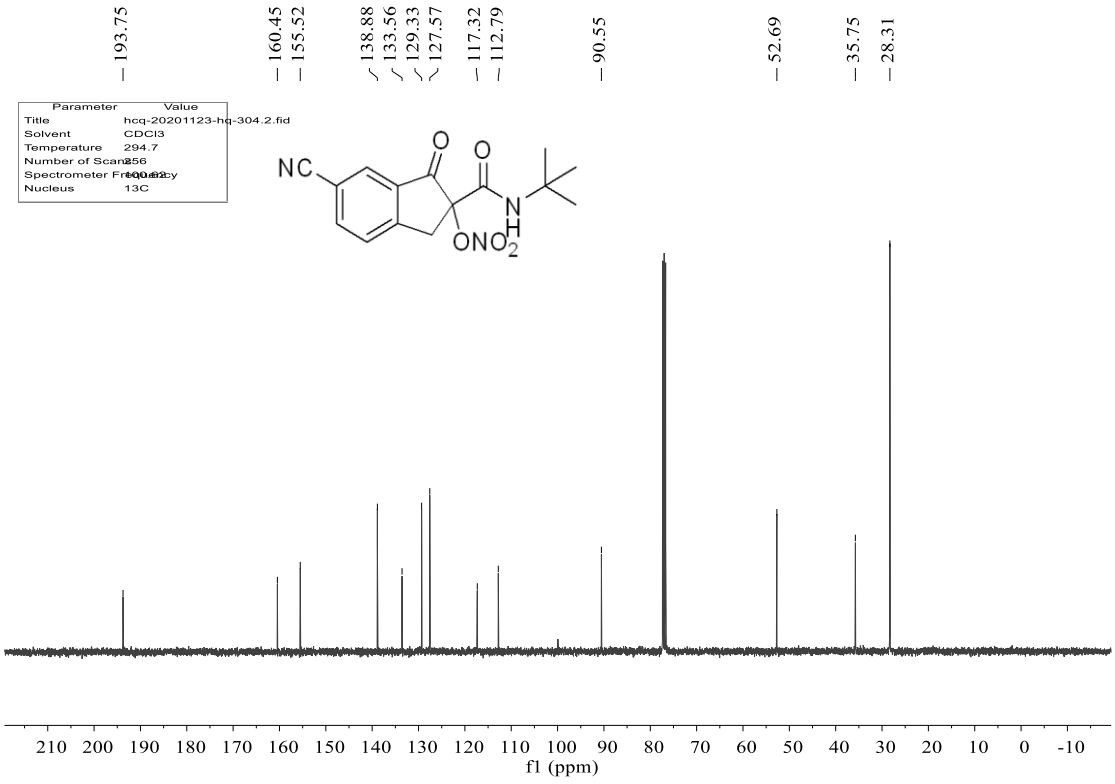
3h


192.46
160.96
154.50
136.96
133.30
130.69
125.26
121.20
91.15
52.52
34.48
28.34
Parameter Value
1Title hcq-20201123-hq-306, 2, 1, 1r
2Solvent CDCl3
3Temperature 294.8
4Number of Scans 256
6Nucleus 13C
Br
O
O
N
H
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

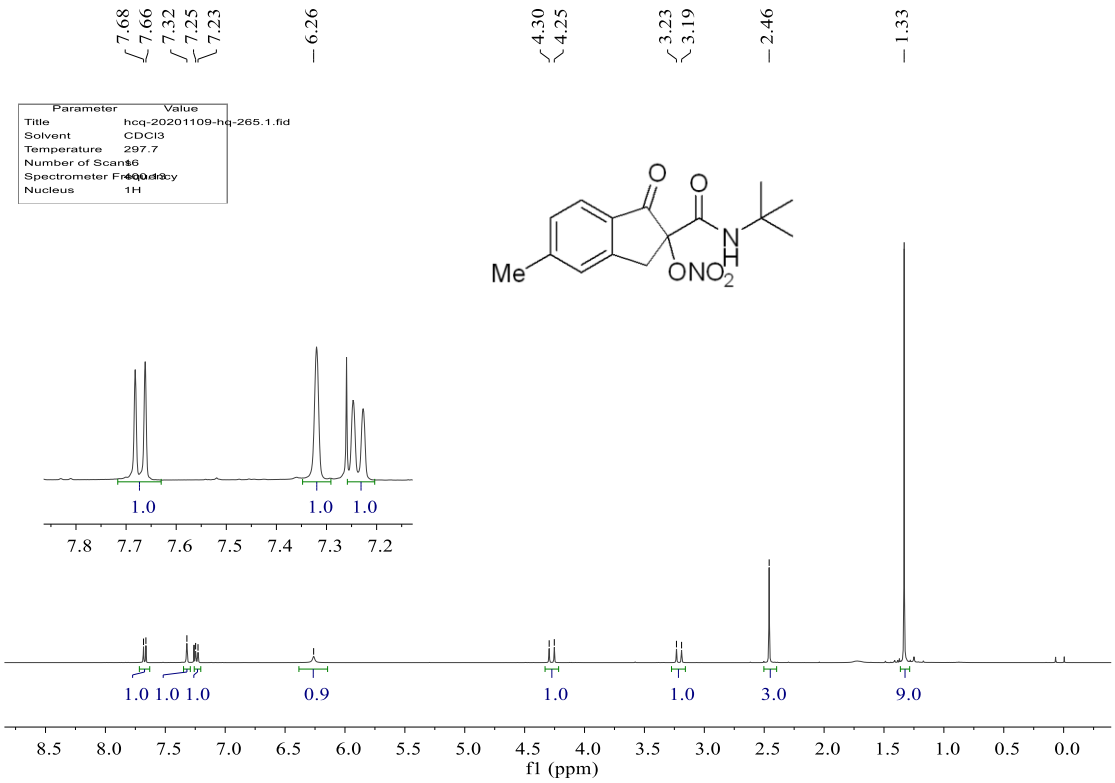
3i


8.08
7.95
7.94
7.93
7.92
7.69
7.67
6.22
4.33
4.29
3.37
3.33
1.33
Parameter Value
Title hcq-20201123-hq-304.1.fid
Solvent CDCl3
Temperature 294.2
Number of Scans 16
Nucleus 1H
NC
O
O
N
H
ONO2
1.0 1.0 1.0
8.1 8.0 7.9 7.8 7.7 7.6
1.0 1.0 1.0 1.0 1.0 9.0
f1 (ppm)

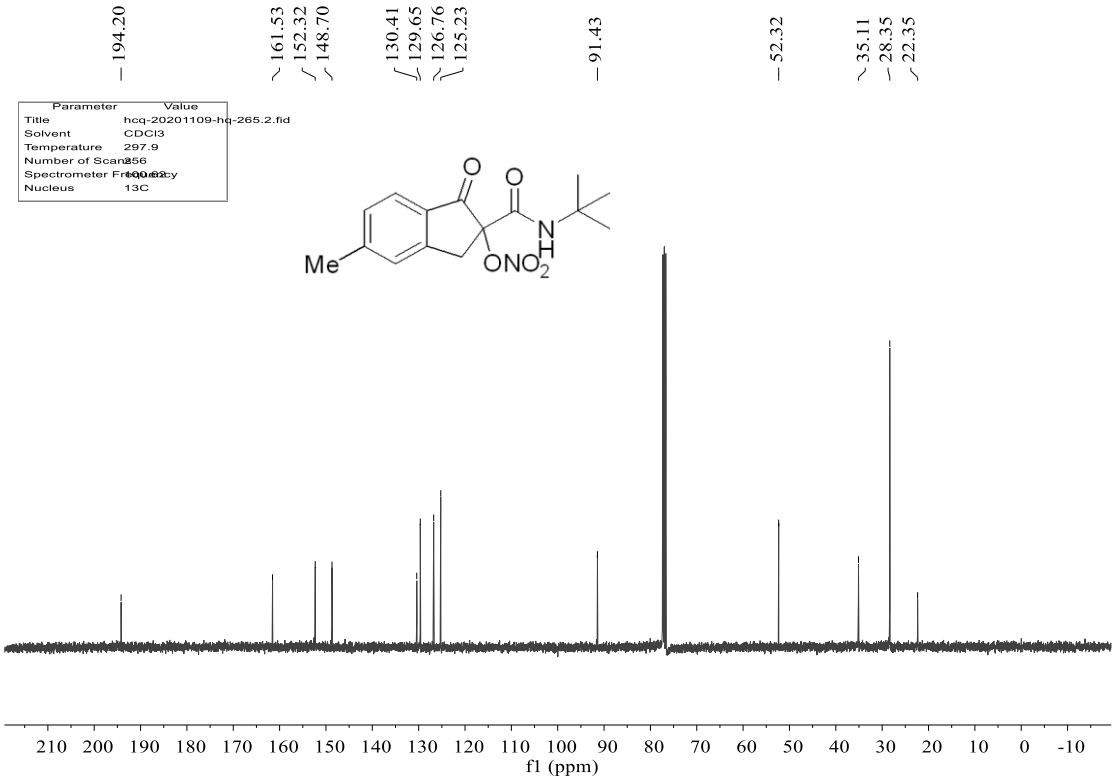
3i


193.75
160.45
155.52
138.88
133.56
129.33
127.57
117.32
112.79
90.55
52.69
35.75
28.31
Parameter Value
Title hcq-20201123-hq-304.2.fid
Solvent CDCl3
Temperature 294.7
Number of Scans 256
Nucleus 13C
NC
O
O
N
H
ONO2
f1 (ppm)

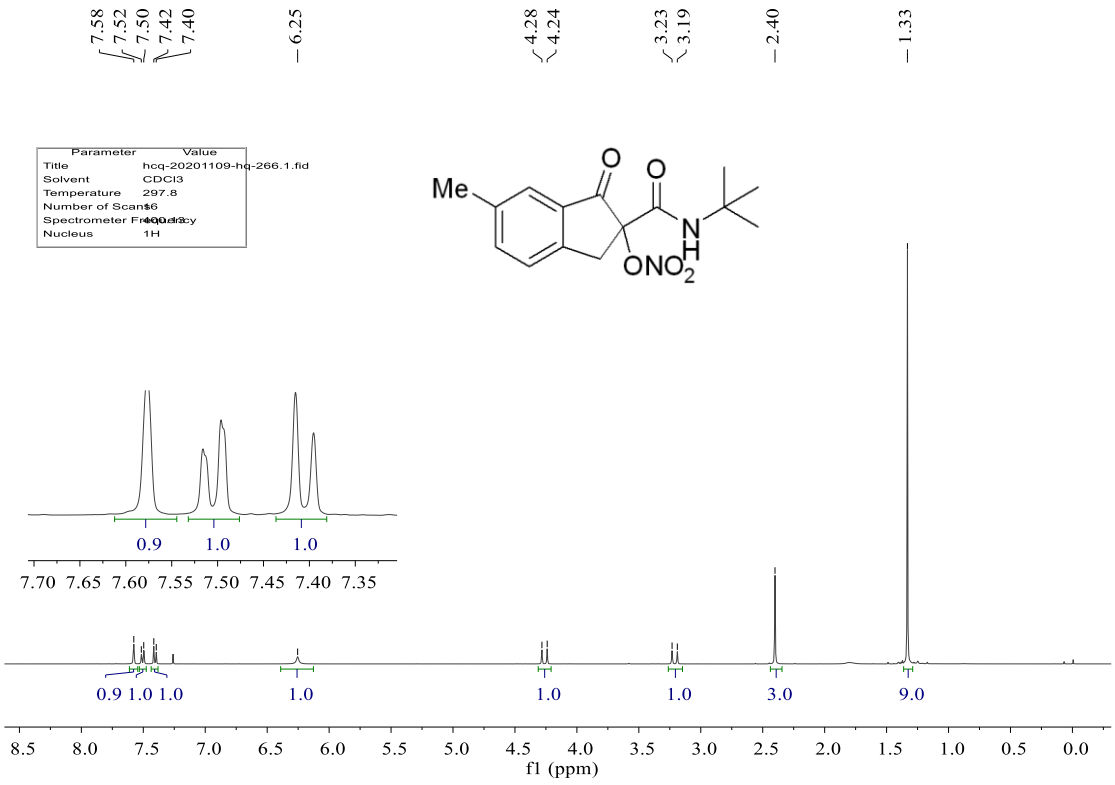
3j


7.68
7.66
7.32
7.25
7.23
6.26
4.30
4.25
3.23
3.19
2.46
1.33
Parameter Value
Title hcq-20201109-hq-265.1.fid
Solvent CDCl3
Temperature 297.7
Number of Scans 16
Nucleus 1H
Me
O
O
N
H
ONO2
1.0
1.0 1.0
7.8 7.7 7.6 7.5 7.4 7.3 7.2
1.0 1.0 1.0 0.9 1.0 1.0 3.0 9.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

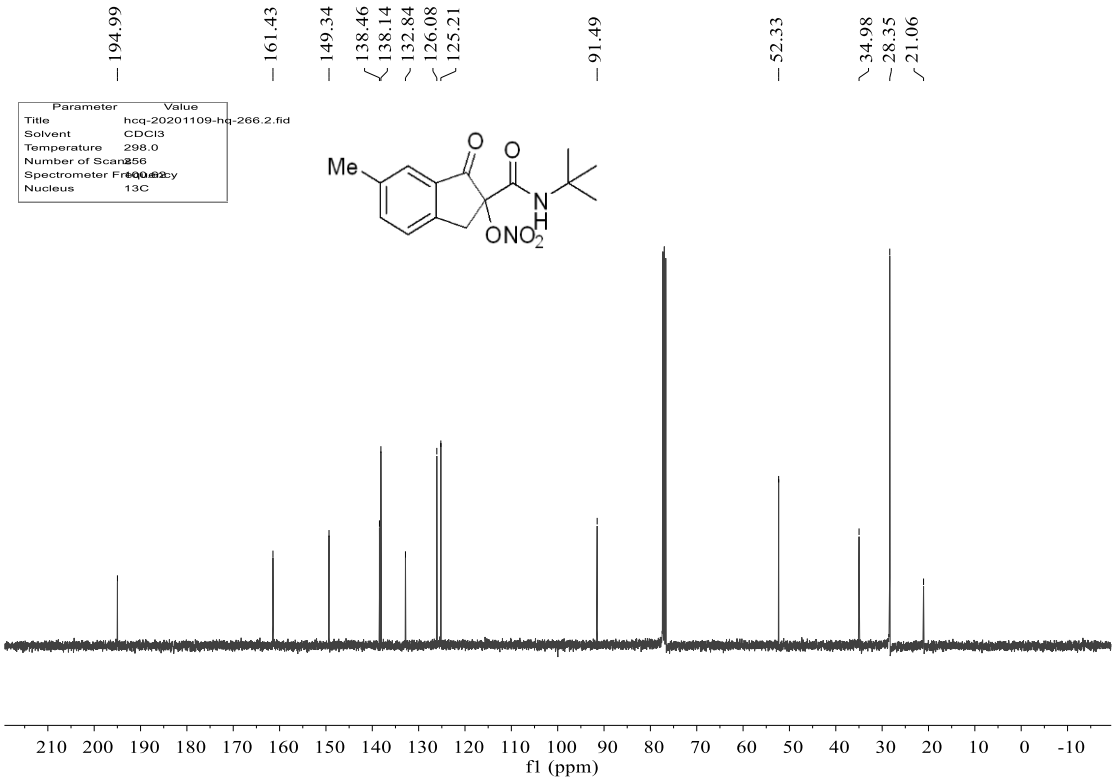
3j


194.20
161.53
152.32
148.70
130.41
129.65
126.76
125.23
91.43
52.32
35.11
28.35
22.35
Parameter Value
Title hcq-20201109-hq-265.2.fid
Solvent CDCl3
Temperature 297.9
Number of Scans 256
Nucleus 13C
Me
O
O
N
H
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

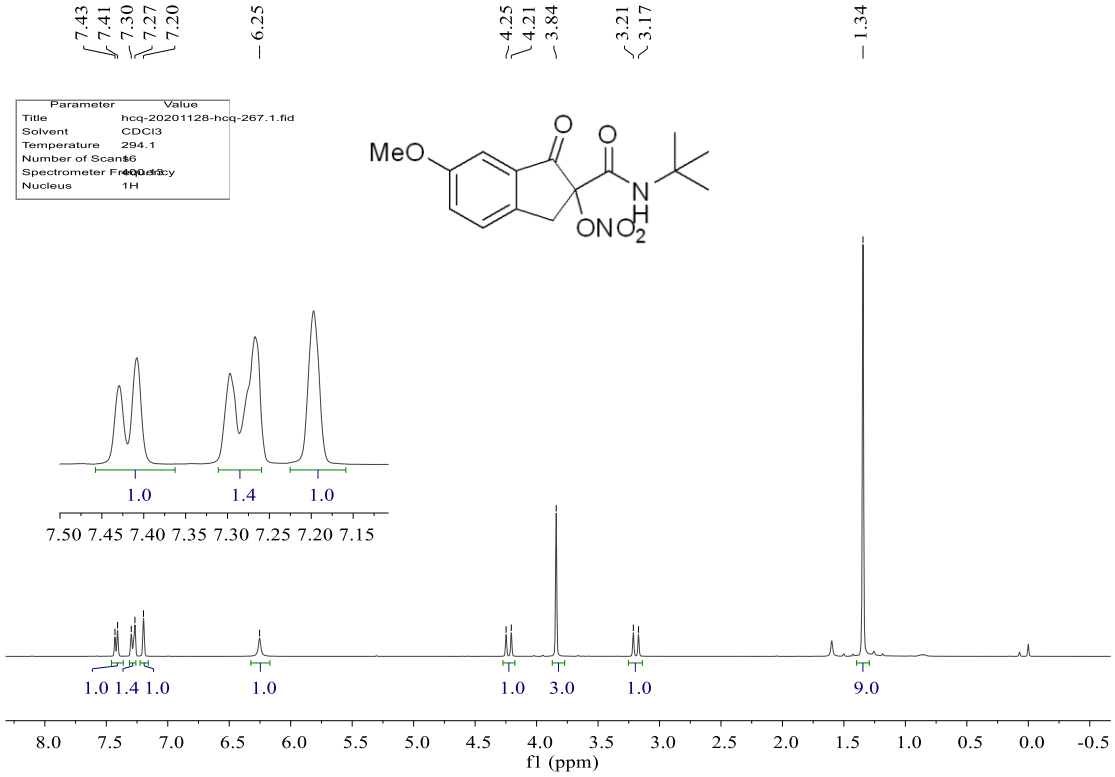
3k


7.58
7.52
7.50
7.42
7.40
6.25
4.28
4.24
3.23
3.19
2.40
1.33
Parameter Value
Title hcq-20201109-hq-266.1.fid
Solvent CDCl3
Temperature 297.8
Number of Scans 16
Nucleus 1H
Me
O
O
N
H
ONO2
0.9 1.0 1.0
7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35
0.9 1.0 1.0 1.0 1.0 1.0 3.0 9.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

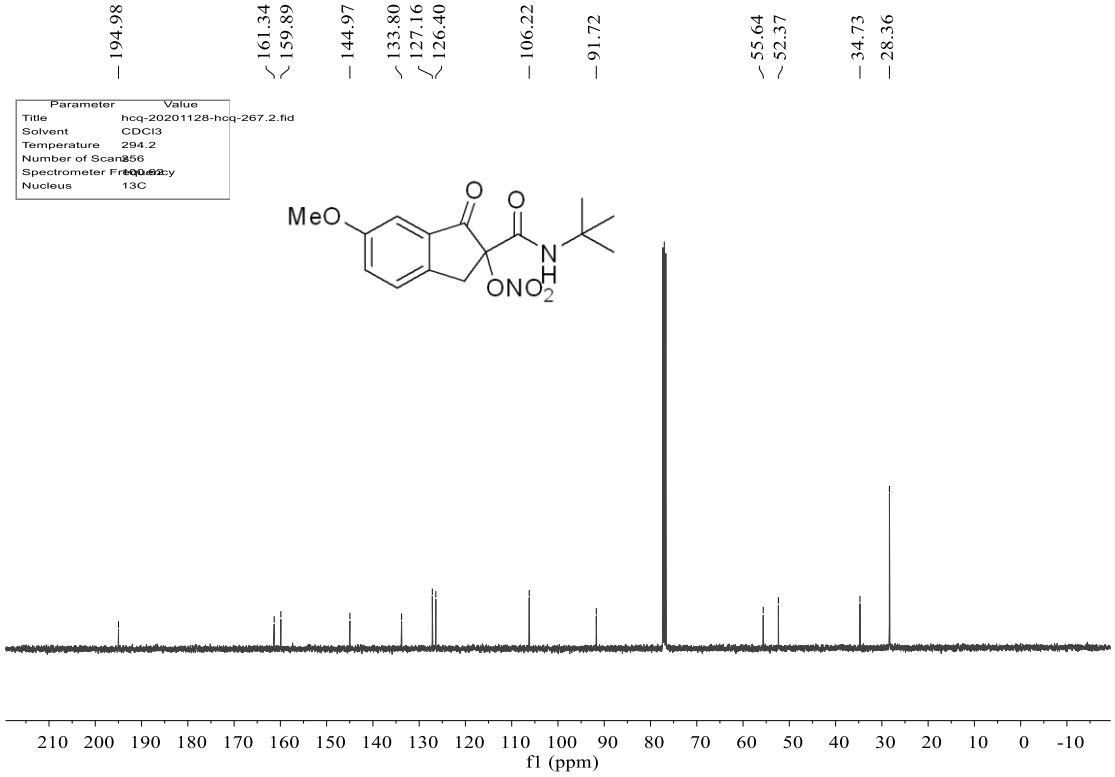
3k


194.99
161.43
149.34
138.46
138.14
132.84
126.08
125.21
91.49
52.33
34.98
28.35
21.06
Parameter Value
Title hcq-20201109-hq-266.2.fid
Solvent CDCl3
Temperature 298.0
Number of Scans 256
Nucleus 13C
Me
O
O
N
H
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

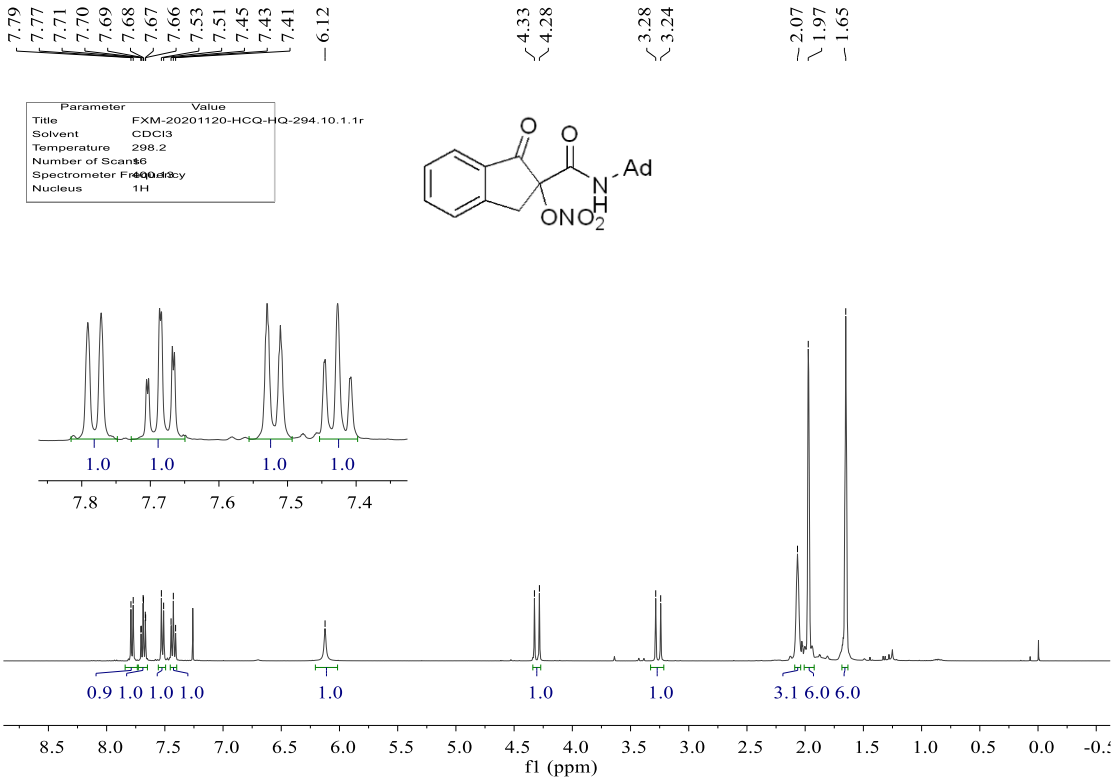
3l


7.43
7.41
7.30
7.27
7.20
6.25
4.25
4.21
3.84
3.21
3.17
1.34
Parameter Value
Title hcq-20201128-hcq-267.1.fid
Solvent CDCl3
Temperature 294.1
Number of Scans 16
Nucleus 1H
MeO
O
O
N
H
ONO2
1.0 1.4 1.0
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15
1.0 1.4 1.0 1.0 1.0 3.0 1.0 9.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

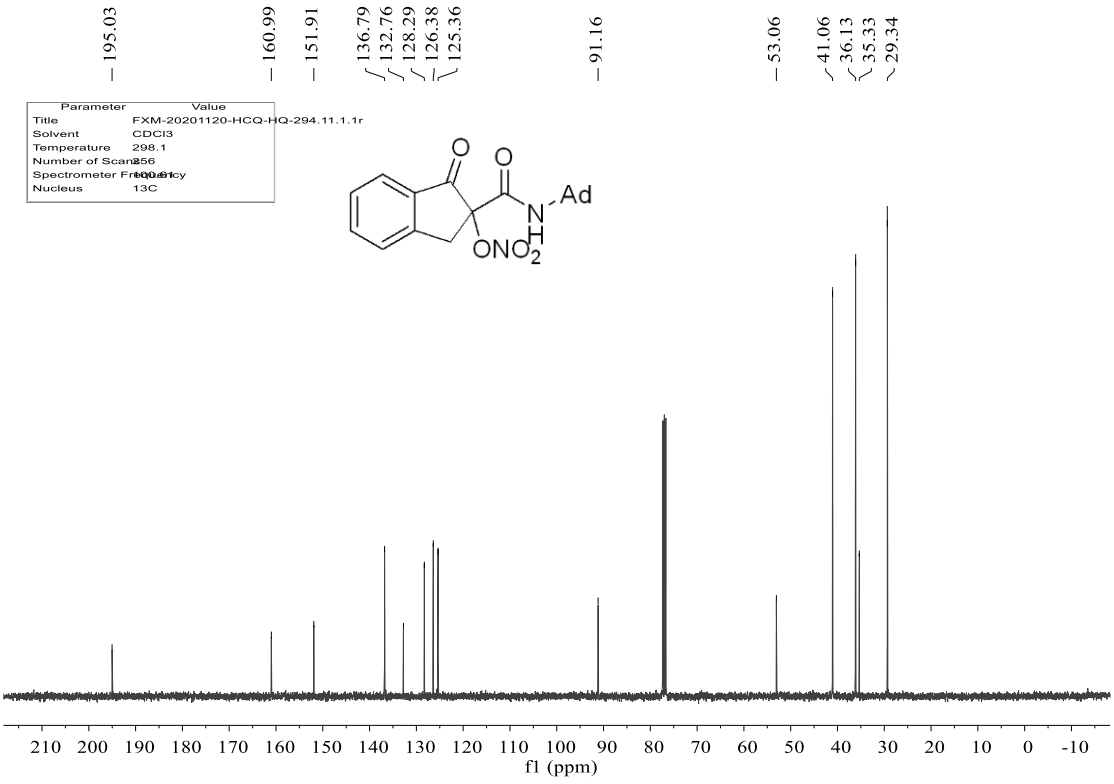
3l


194.98
161.34
159.89
144.97
133.80
127.16
126.40
106.22
91.72
55.64
52.37
34.73
28.36
Parameter Value
Title hcq-20201128-hcq-267.2.fid
Solvent CDCl3
Temperature 294.2
Number of Scans 256
Nucleus 13C
MeO
O
O
N
H
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

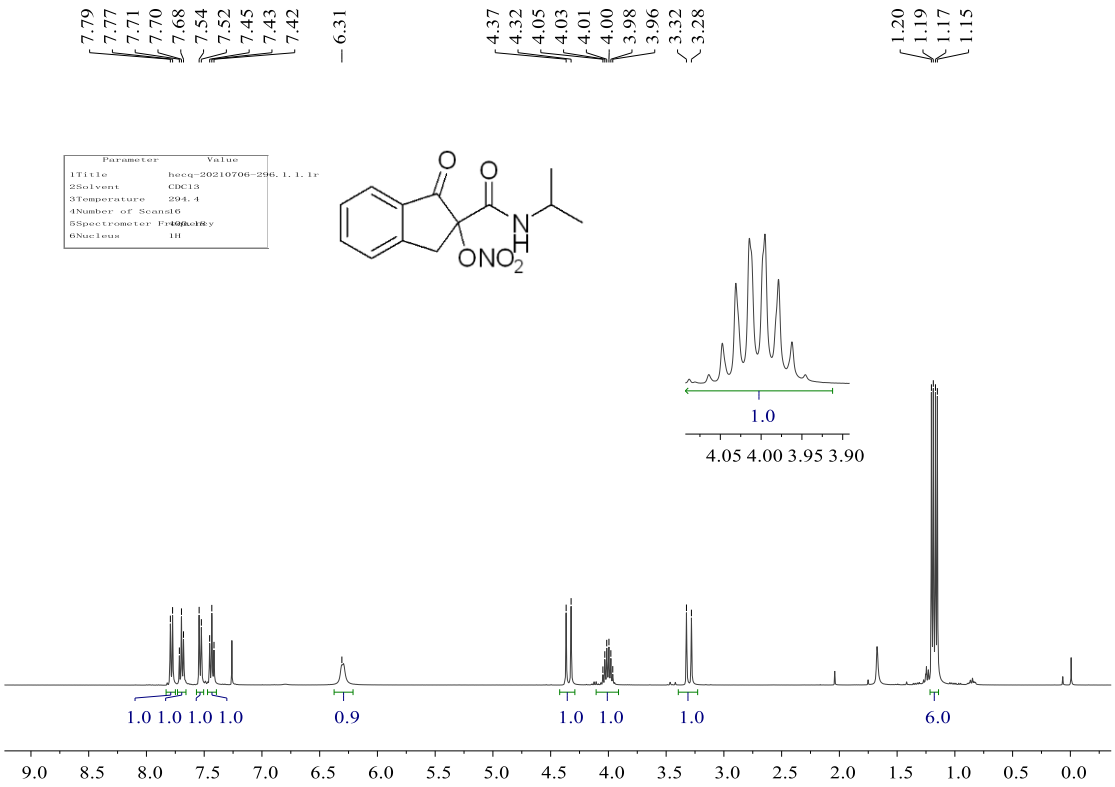
3m


7.79
7.77
7.71
7.70
7.69
7.68
7.67
7.66
7.53
7.51
7.45
7.43
7.41
6.12
4.33
4.28
3.28
3.24
2.07
1.97
1.65
Parameter Value
Title FXM-20201120-HCQ-HQ-294.10.1.1r
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Nucleus 1H
O
O
N
Ad
H
ONO2
1.0 1.0 1.0 1.0
7.8 7.7 7.6 7.5 7.4
0.9 1.0 1.0 1.0
1.0
1.0
1.0
3.1 6.0 6.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

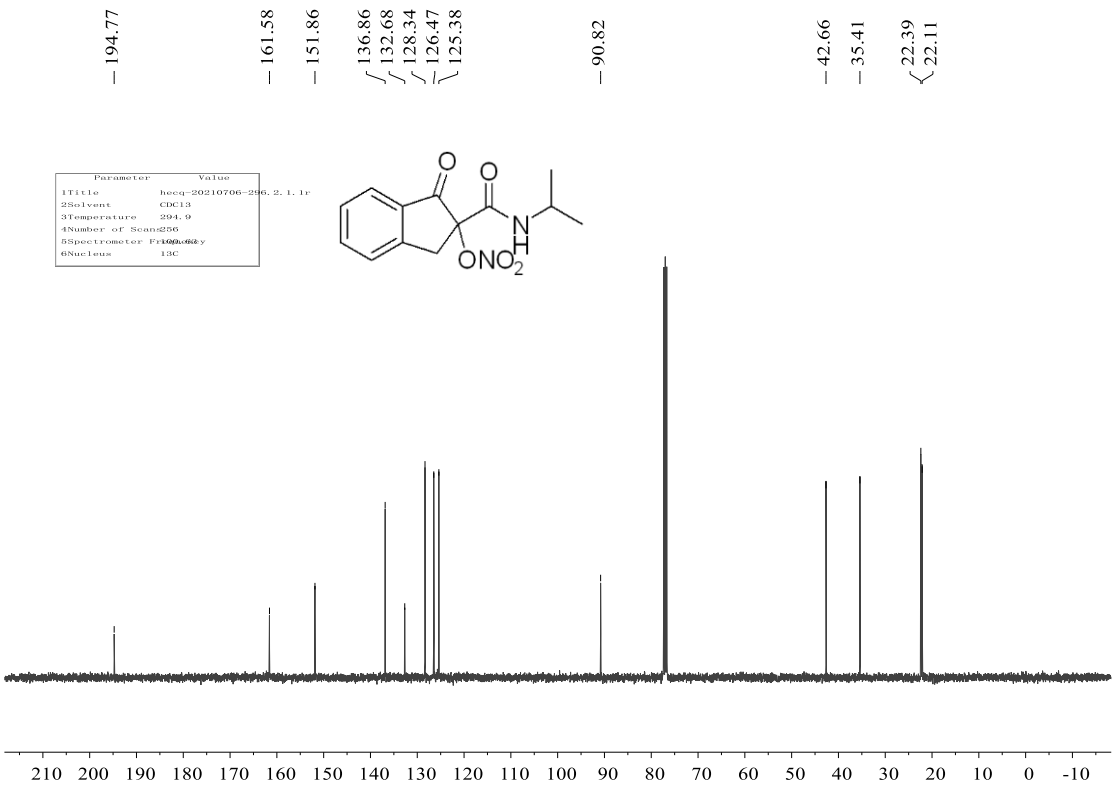
3m


195.03
160.99
151.91
136.79
132.76
128.29
126.38
125.36
91.16
53.06
41.06
36.13
35.33
29.34
Parameter Value
Title FXM-20201120-HCQ-HQ-294.11.1.1r
Solvent CDCl3
Temperature 298.1
Number of Scans 256
Nucleus 13C
O
O
N
Ad
H
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

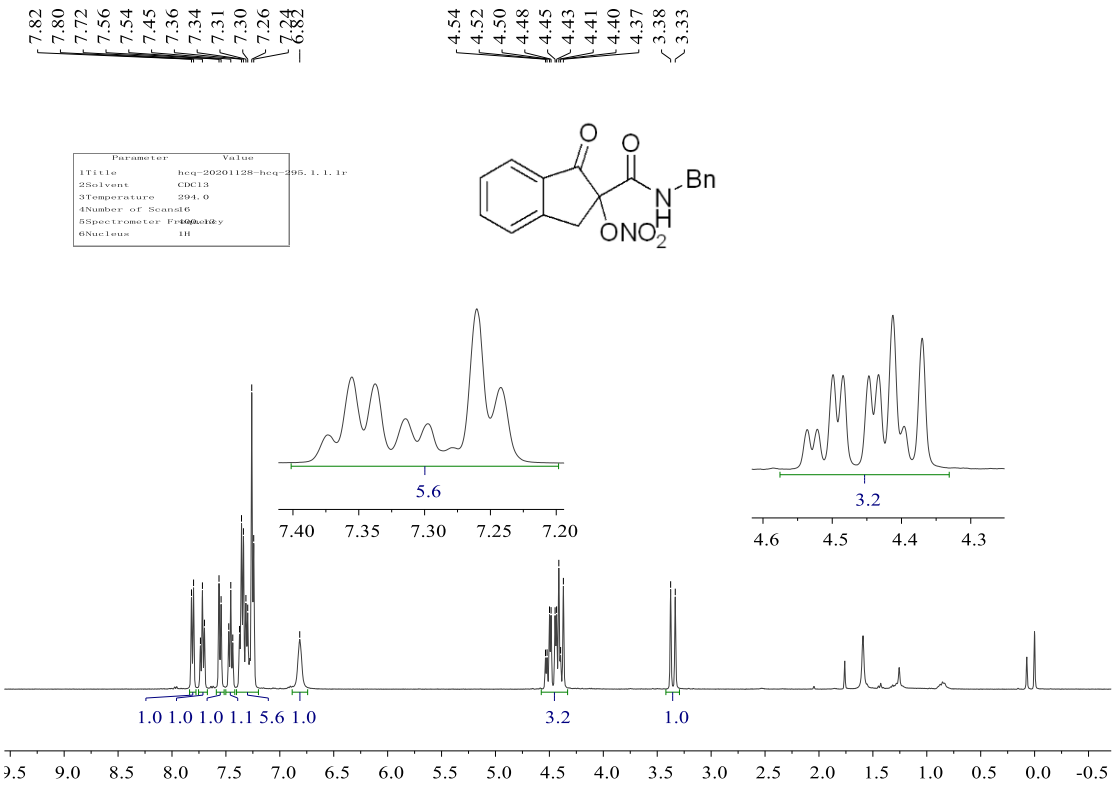
3n


7.79
7.77
7.71
7.70
7.68
7.54
7.52
7.45
7.43
7.42
6.31
4.37
4.32
4.05
4.03
4.01
4.00
3.98
3.96
3.32
3.28
1.20
1.19
1.17
1.15
Parameter Value
1Title hecq-20210706-296. 1. 1. 1r
2Solvent CDCl3
3Temperature 294. 4
4Number of Scans 16
6Nucleus 1H
ONO2
1.0
4.05 4.00 3.95 3.90
1.0 1.0 1.0 1.0
0.9
1.0 1.0
1.0
6.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

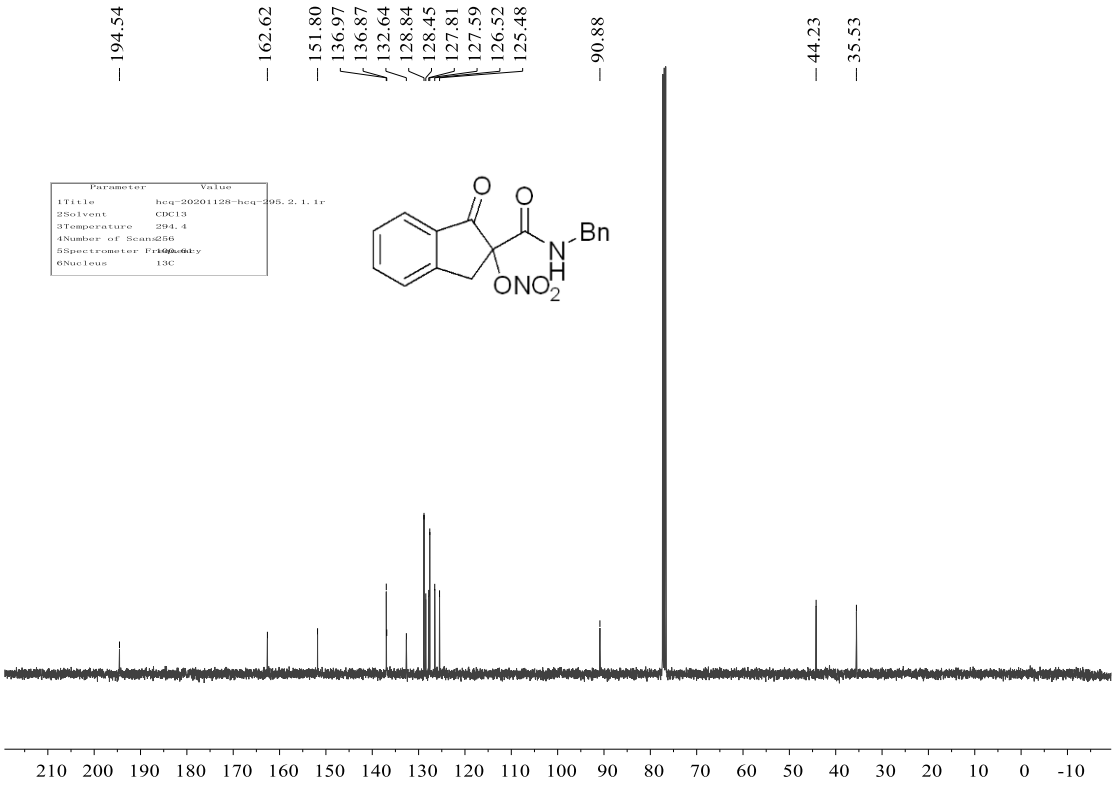
3n


194.77
161.58
151.86
136.86
132.68
128.34
126.47
125.38
90.82
42.66
35.41
22.39
22.11
Parameter Value
1Title hecq-20210706-296. 2. 1. 1r
2Solvent CDCl3
3Temperature 294. 9
4Number of Scans 256
6Nucleus 13C
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

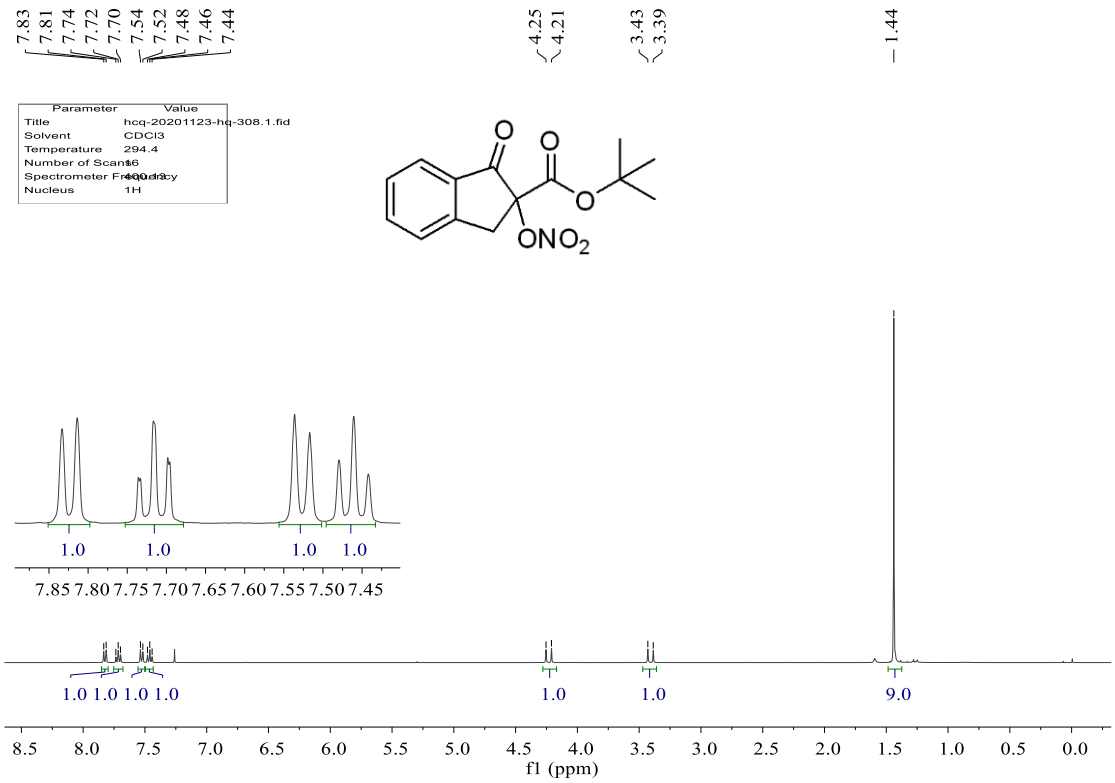
3o


7.82
7.80
7.72
7.56
7.54
7.45
7.36
7.34
7.31
7.30
7.26
7.24
6.82
4.54
4.52
4.50
4.48
4.45
4.43
4.41
4.40
4.37
3.38
3.33
Parameter Value
1Title hcq-20201128-hcq-295.1.1.1r
2Solvent CDCl3
3Temperature 294.0
4Number of Scans16
5Spectrometer Frequency
6Nucleus 1H
O
O
N
H
Bn
ONO2
5.6
7.40 7.35 7.30 7.25 7.20
3.2
4.6 4.5 4.4 4.3
1.0 1.0 1.0 1.1 5.6 1.0
3.2
1.0
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

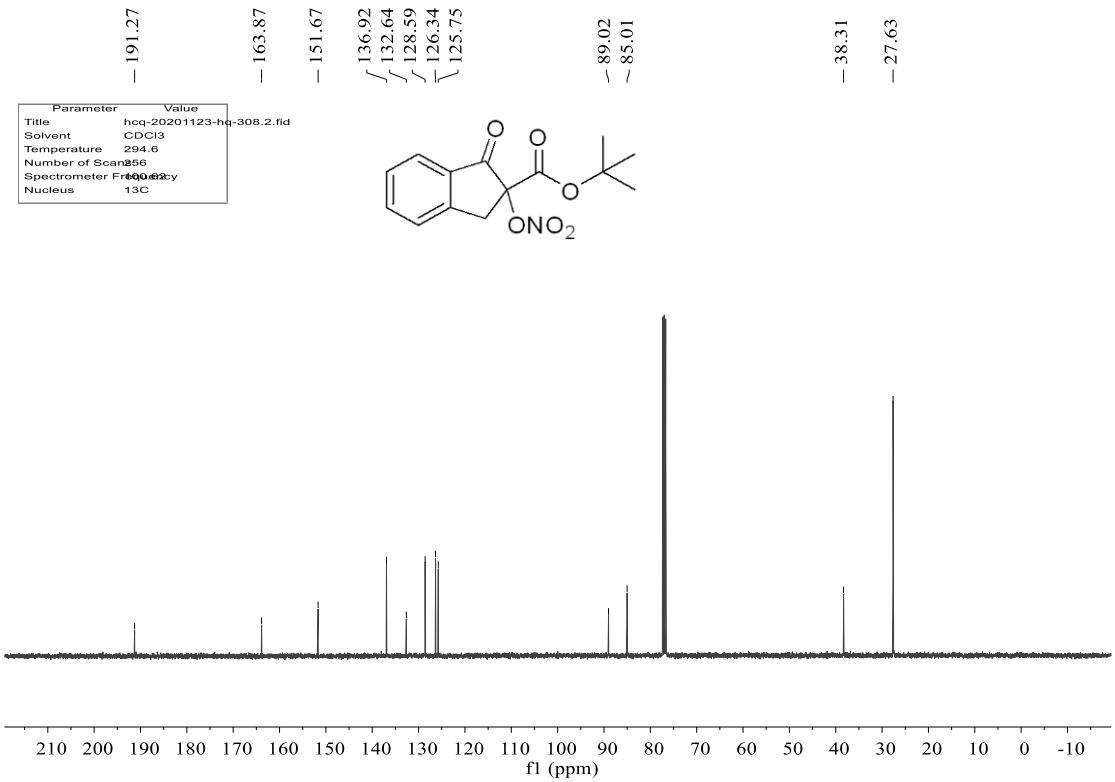
3o


194.54
162.62
151.80
136.97
136.87
132.64
128.84
128.45
127.81
127.59
126.52
125.48
90.88
44.23
35.53
Parameter Value
1Title hcq-20201128-hcq-295.2.1.1r
2Solvent CDCl3
3Temperature 294.4
4Number of Scans256
5Spectrometer Frequency
6Nucleus 13C
O
O
N
H
Bn
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

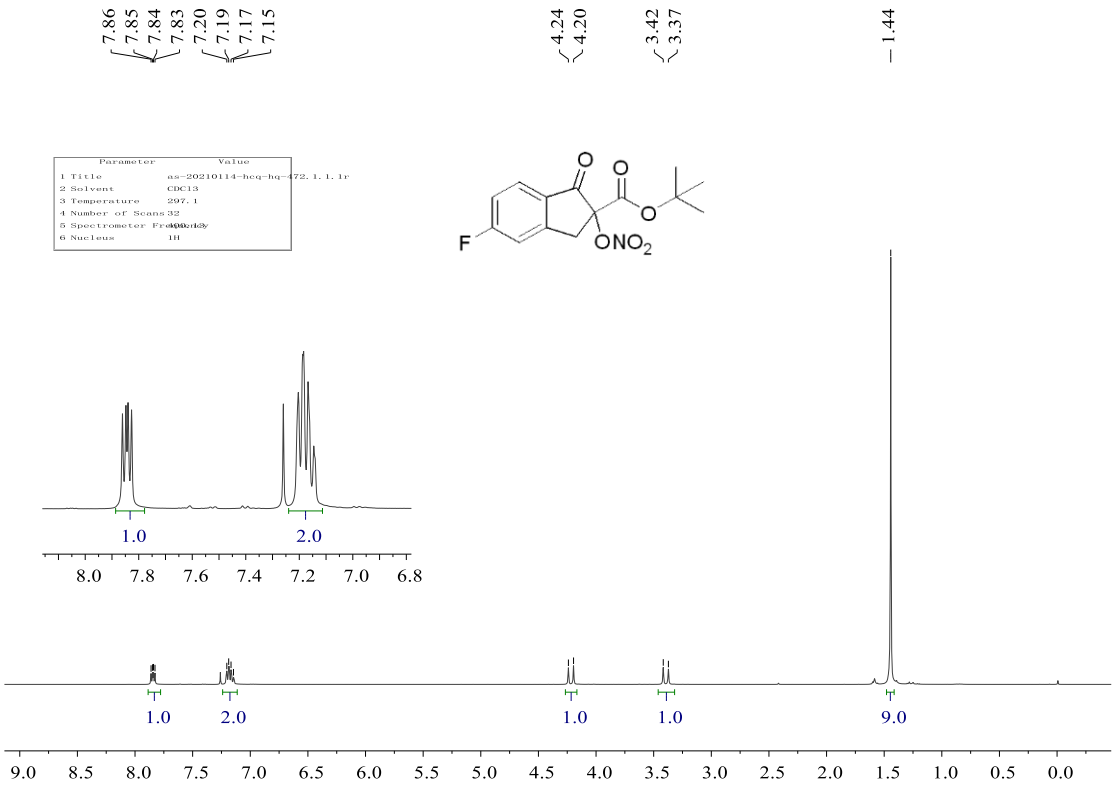
3p


7.83
7.81
7.74
7.72
7.70
7.54
7.52
7.48
7.46
7.44
4.25
4.21
3.43
3.39
1.44
Parameter Value
Title hcq-20201123-hq-308.1.fid
Solvent CDCl3
Temperature 294.4
Number of Scans 16
Nucleus 1H
O
O
O
ONO2
1.0 1.0 1.0 1.0
7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45
1.0 1.0 1.0 1.0 1.0 9.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

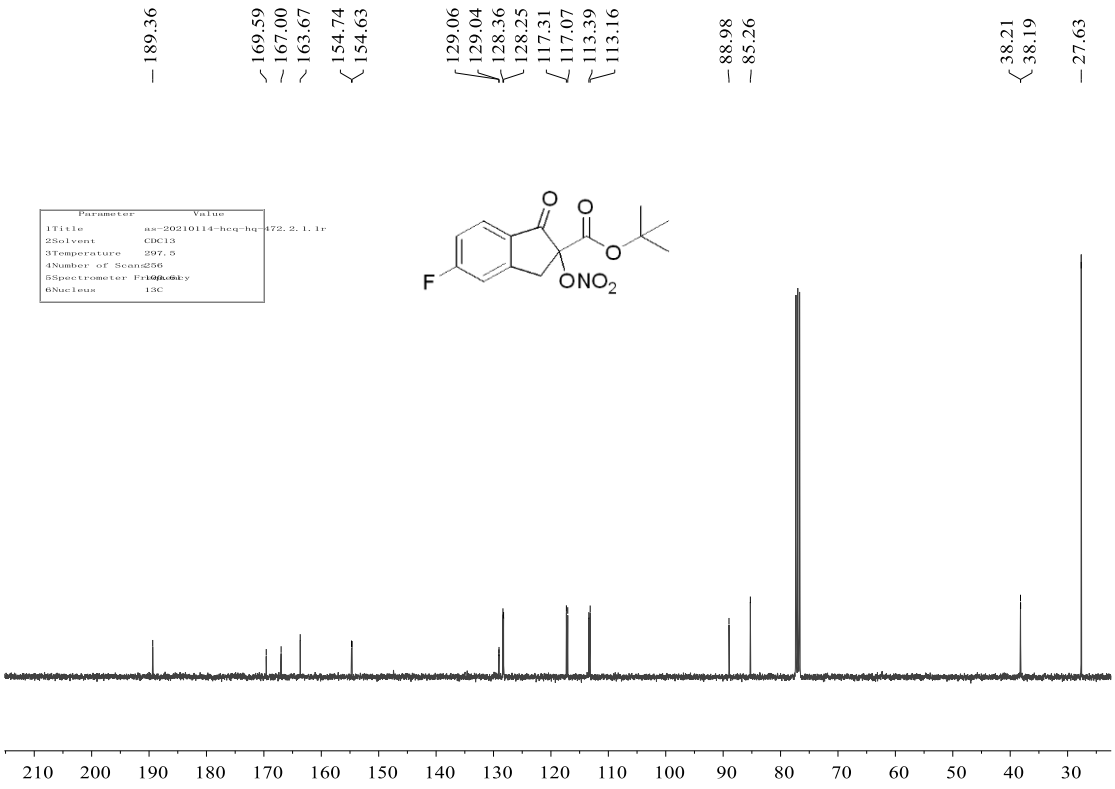
3p


191.27
163.87
151.67
136.92
132.64
128.59
126.34
125.75
89.02
85.01
38.31
27.63
Parameter Value
Title hcq-20201123-hq-308.2.fid
Solvent CDCl3
Temperature 294.6
Number of Scans 256
Nucleus 13C
O
O
O
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

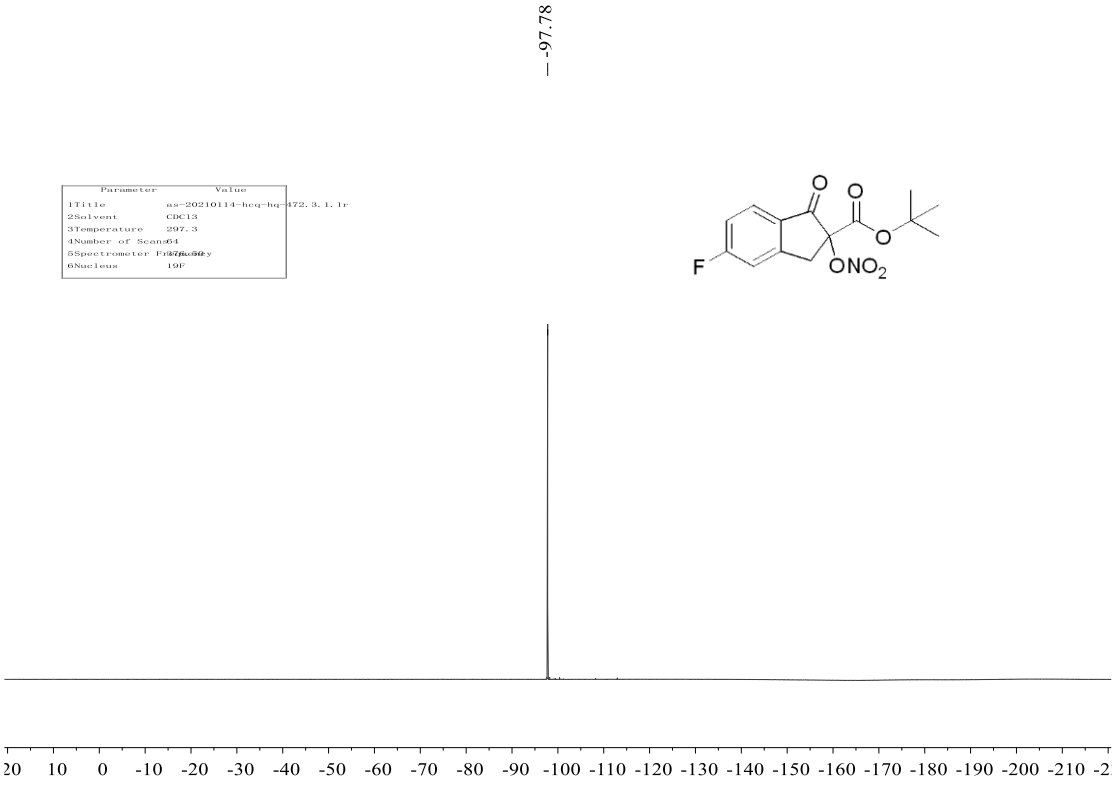
3q


7.86
7.85
7.84
7.83
7.20
7.19
7.17
7.15
4.24
4.20
3.42
3.37
1.44
Parameter Value
1 Title as-20210114-hcq-hq-472.1.1.1r
2 Solvent CDCl3
3 Temperature 297.1
4 Number of Scans 32
5 Spectrometer Frequency
6 Nucleus 1H
O
O
O
F
ONO2
1.0
2.0
8.0 7.8 7.6 7.4 7.2 7.0 6.8
1.0 2.0 1.0 1.0 9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

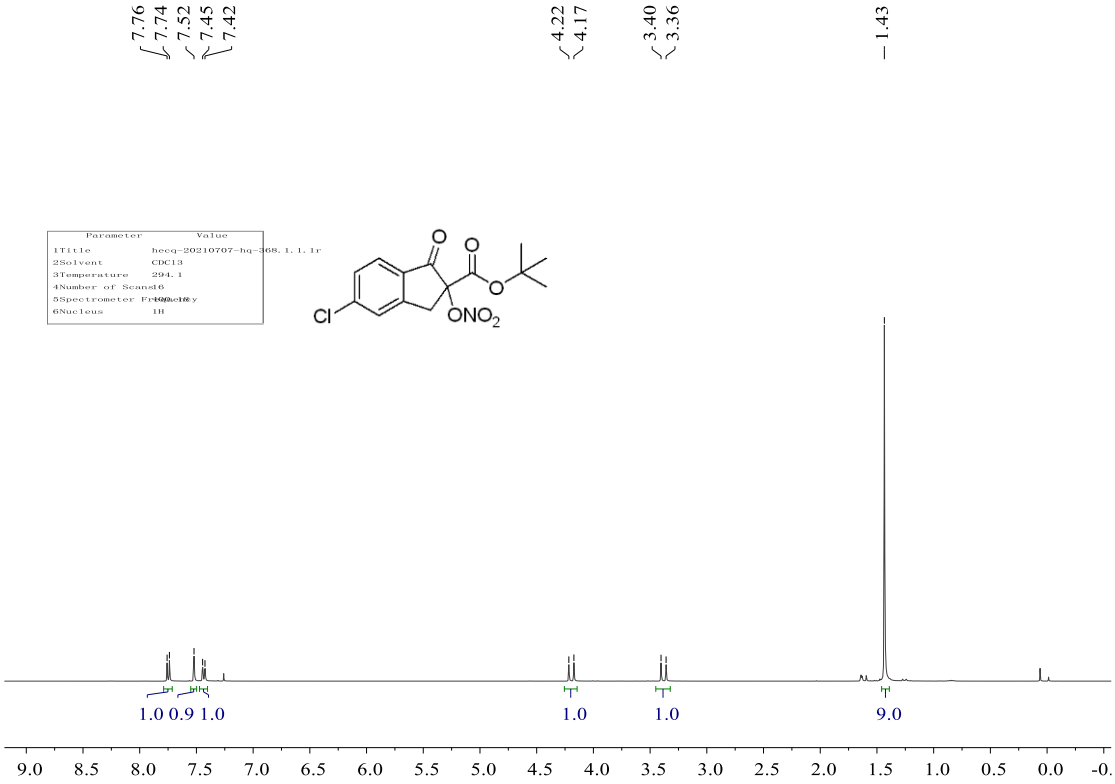
3q


189.36
169.59
167.00
163.67
154.74
154.63
129.06
129.04
128.36
128.25
117.31
117.07
113.39
113.16
88.98
85.26
38.21
38.19
27.63
Parameter Value
1Title as-20210114-hcq-hq-472.2.1.1r
2Solvent CDCl3
3Temperature 297.5
4Number of Scans 256
5Spectrometer Frequency
6Nucleus 13C
O
O
O
F
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30

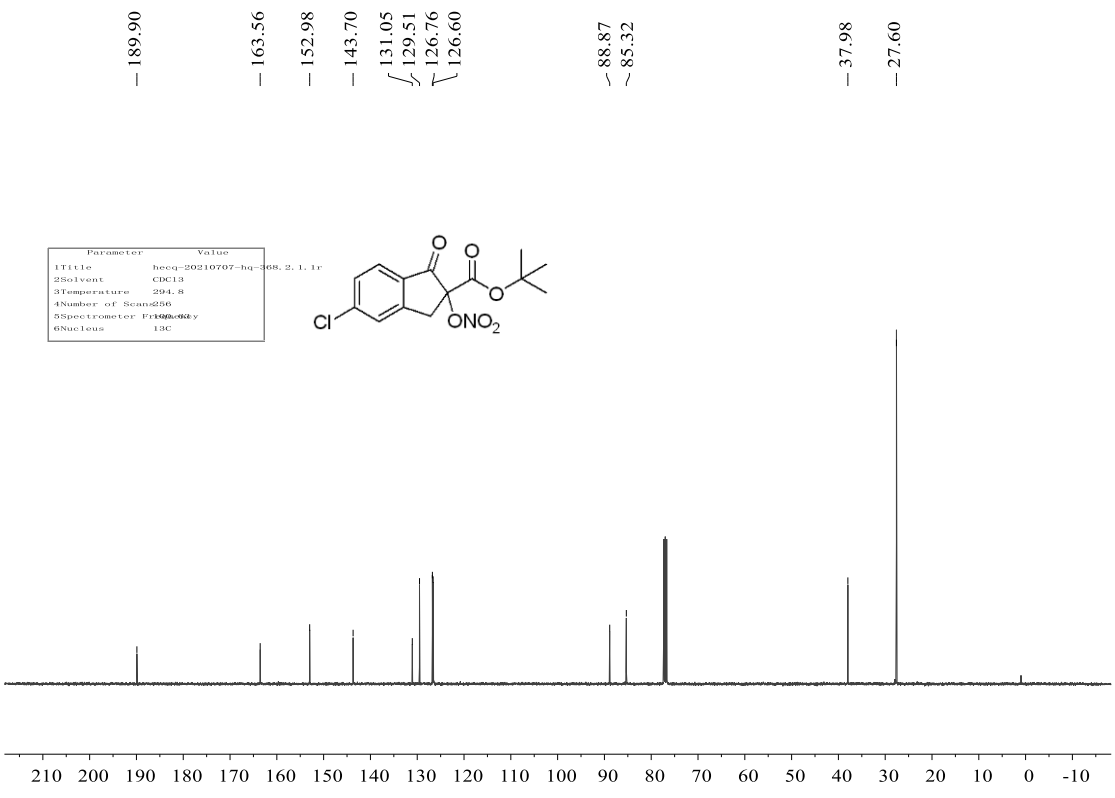
3q


-97.78
Parameter Value
1Title as-20210114-hcq-hq-472.3.1.1r
2Solvent CDCl3
3Temperature 297.3
4Number of Scans 64
6Nucleus 19F
O
O
O
F
ONO2
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

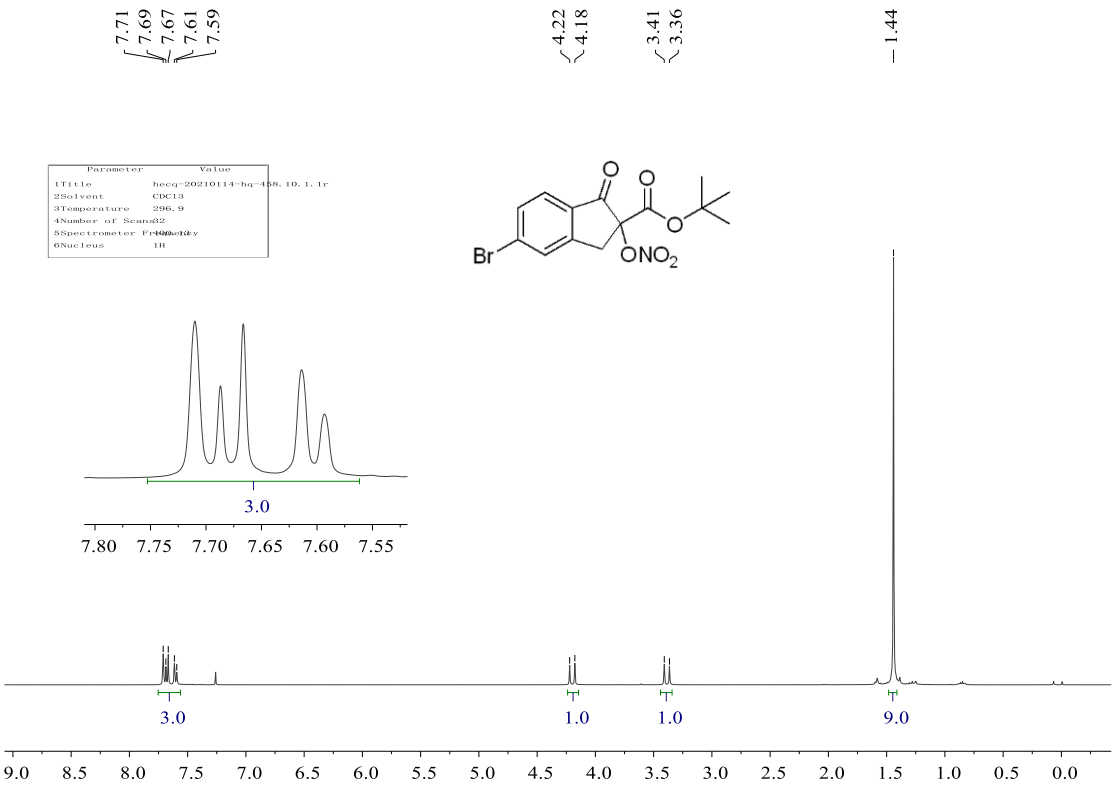
3r


7.76
7.74
7.52
7.45
7.42
4.22
4.17
3.40
3.36
1.43
Parameter Value
1Title hecq-20210707-hq-368. 1. 1. 1r
2Solvent CDC13
3Temperature 294. 1
4Number of Scans16
6Nucleus 1H
Cl
ONO2
1.0 0.9 1.0
1.0
1.0
9.0

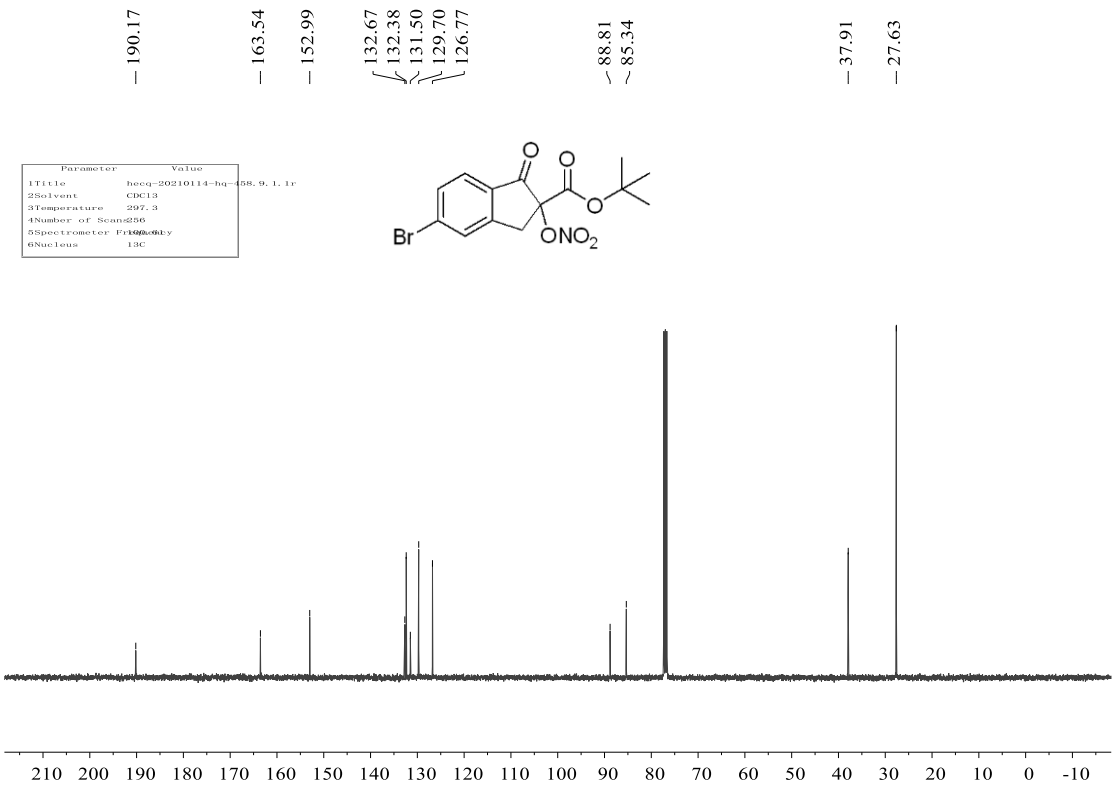
3r


189.90
163.56
152.98
143.70
131.05
129.51
126.76
126.60
88.87
85.32
37.98
27.60
Parameter Value
1Title hecq-20210707-hq-368. 2. 1. 1r
2Solvent CDC13
3Temperature 294. 8
4Number of Scans256
6Nucleus 13C
Cl
ONO2

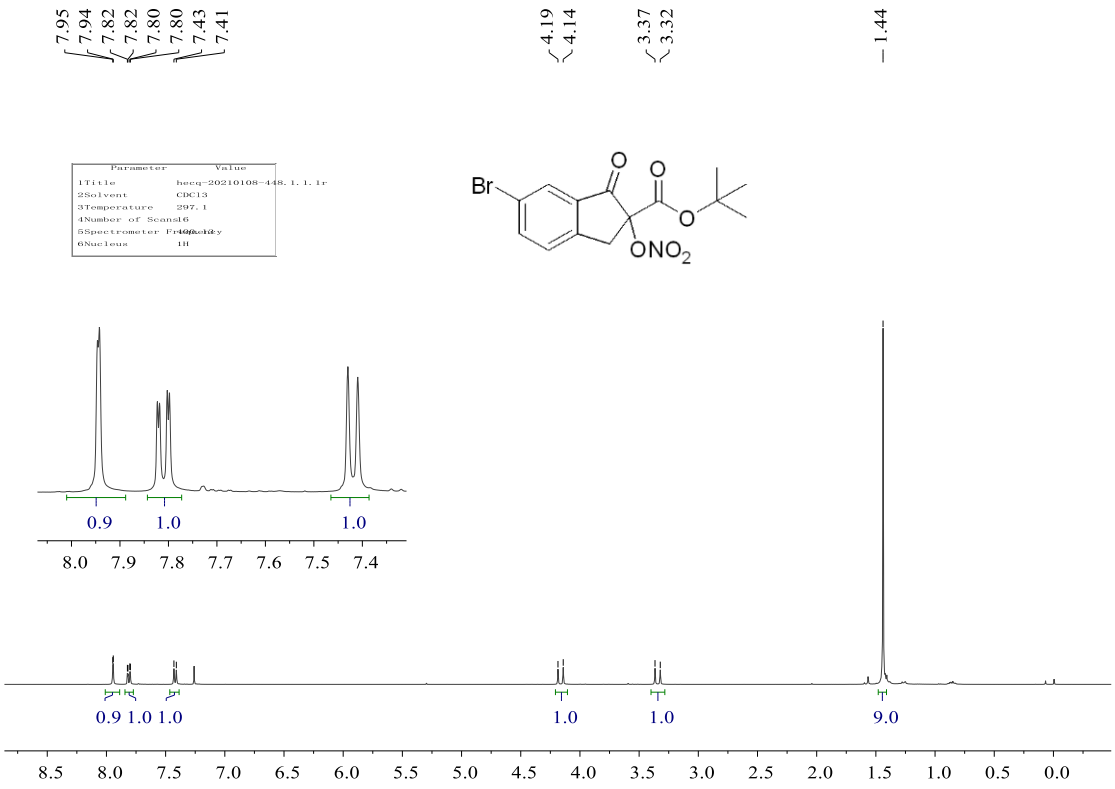
3s


7.71
7.69
7.67
7.61
7.59
4.22
4.18
3.41
3.36
1.44
Parameter Value
1Title hecq-20210114-hq-458.10.1.1r
2Solvent CDCl3
3Temperature 296.9
4Number of Scans32
5Spectrometer Frequency
6Nucleus 1H
Br
ONO2
3.0
7.80 7.75 7.70 7.65 7.60 7.55
3.0
1.0
1.0
9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

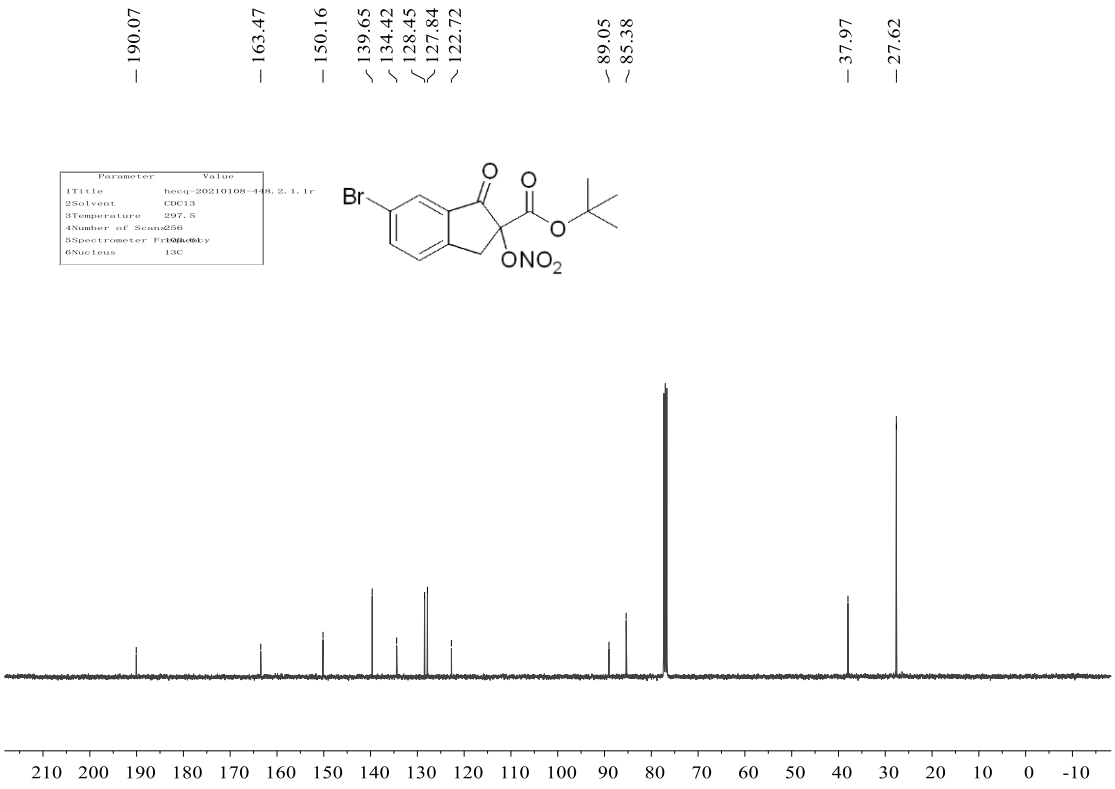
3s


190.17
163.54
152.99
132.67
132.38
131.50
129.70
126.77
88.81
85.34
37.91
27.63
Parameter Value
1Title hecq-20210114-hq-458.9.1.1r
2Solvent CDCl3
3Temperature 297.3
4Number of Scans256
5Spectrometer Frequency
6Nucleus 13C
Br
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

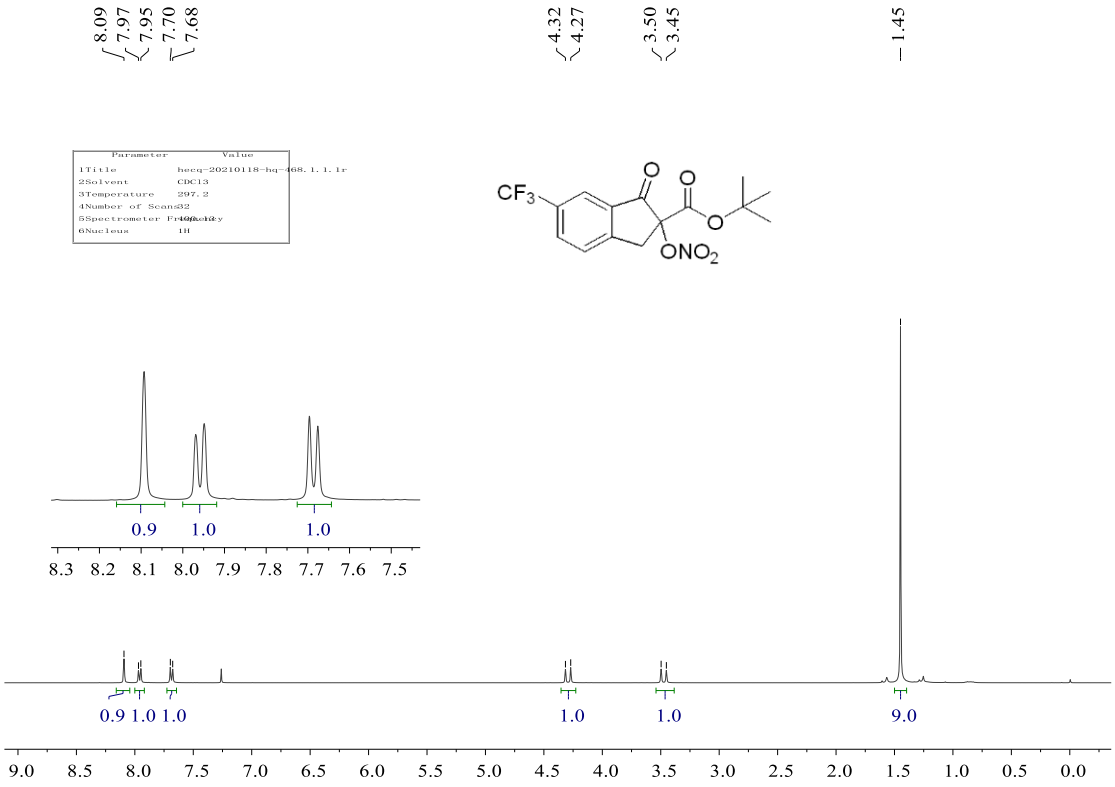
3t


7.95
7.94
7.82
7.82
7.80
7.80
7.43
7.41
4.19
4.14
3.37
3.32
1.44
Parameter Value
1Title hecq-20210108-448.1.1.1r
2Solvent CDCl3
3Temperature 297.1
4Number of Scans16
5Spectrometer Frequency
6Nucleus 1H
Br
O
O
O
ONO2
0.9 1.0 1.0
8.0 7.9 7.8 7.7 7.6 7.5 7.4
0.9 1.0 1.0 1.0 1.0 9.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

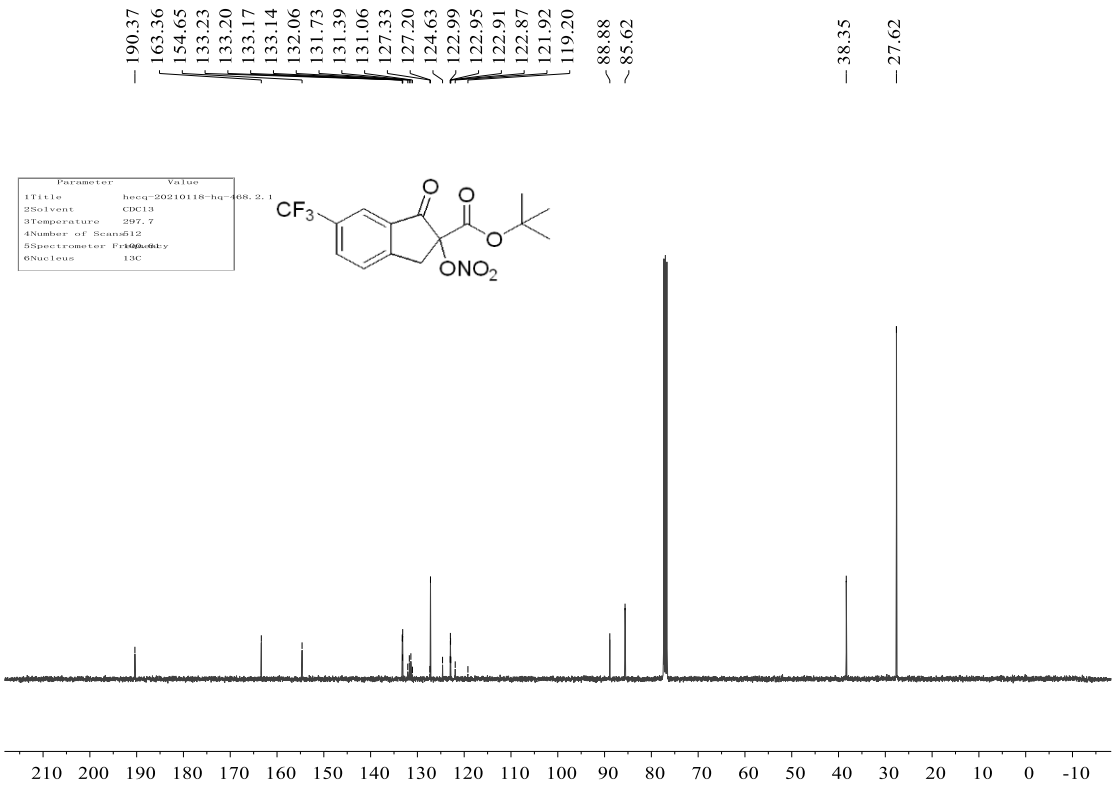
3t


190.07
163.47
150.16
139.65
134.42
128.45
127.84
122.72
89.05
85.38
37.97
27.62
Parameter Value
1Title hecq-20210108-448.2.1.1r
2Solvent CDCl3
3Temperature 297.5
4Number of Scans256
5Spectrometer Frequency
6Nucleus 13C
Br
O
O
O
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

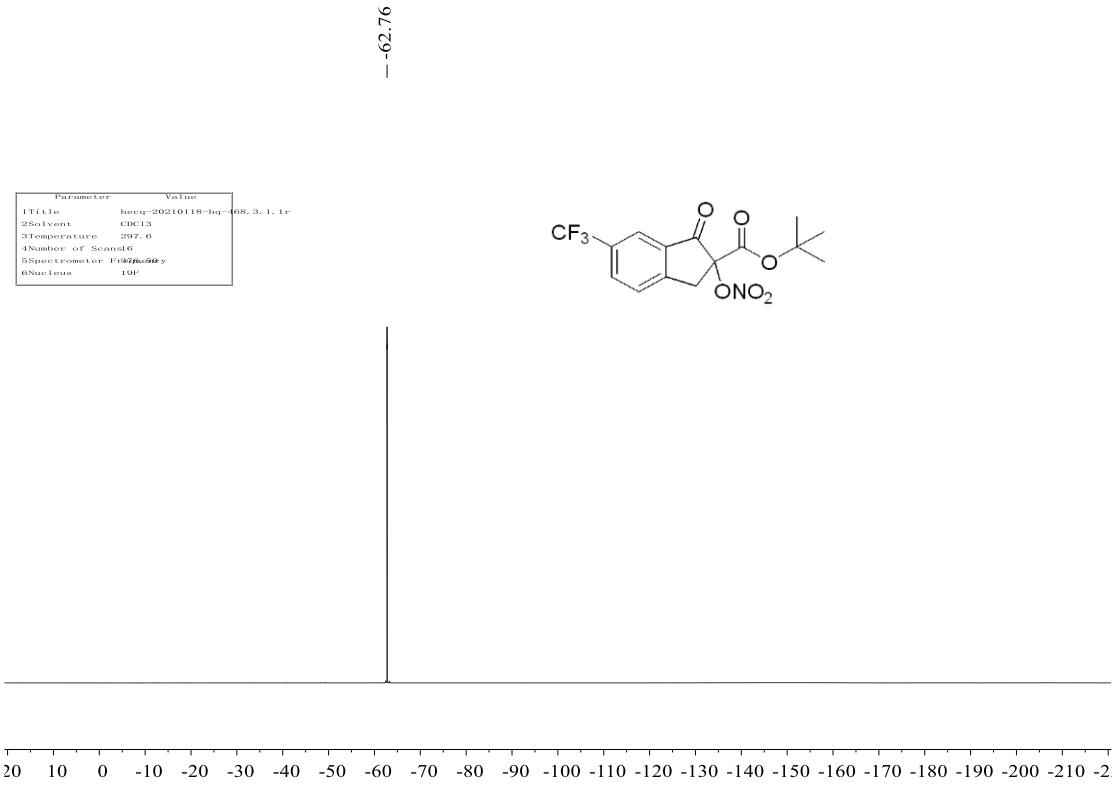
3u


8.09
7.97
7.95
7.70
7.68
4.32
4.27
3.50
3.45
1.45
Parameter Value
1Title hecq-20210118-hq-468.1.1.1r
2Solvent CDCl3
3Temperature 297.2
4Number of Scans32
6Nucleus 1H
CF3
O
O
O
ONO2
0.9 1.0 1.0
8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5
0.9 1.0 1.0 1.0 1.0 9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

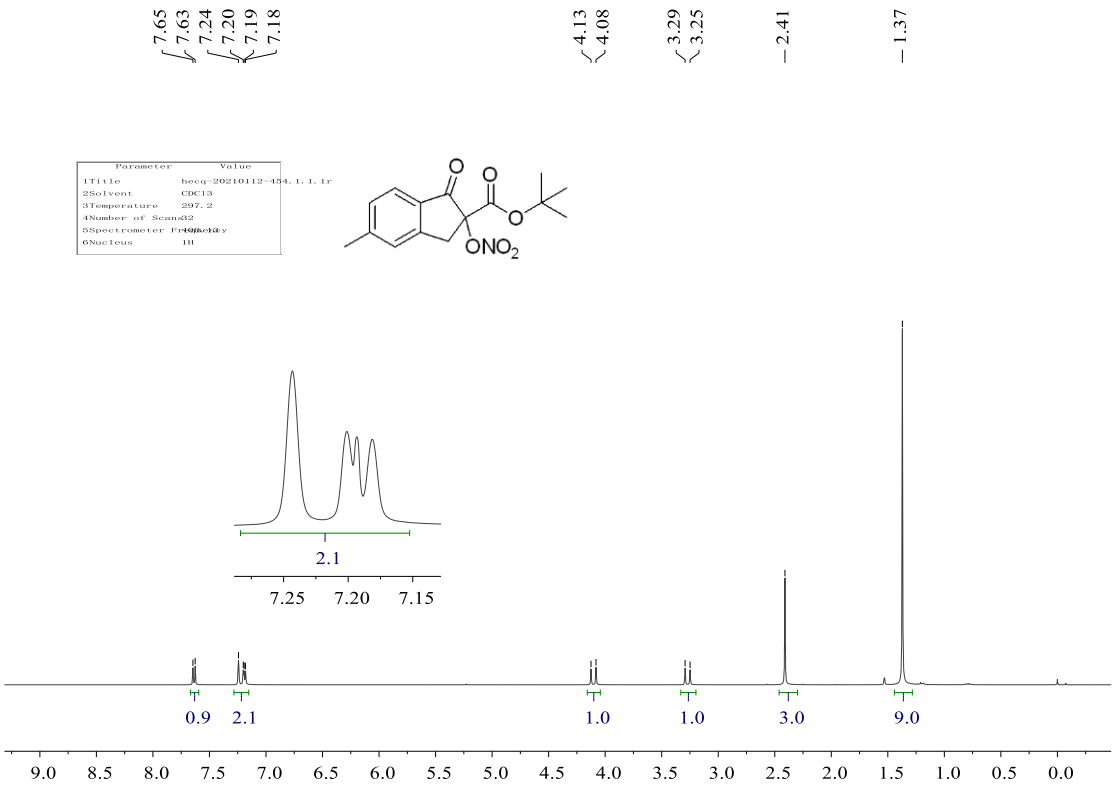
3u


190.37
163.36
154.65
133.23
133.20
133.17
133.14
132.06
131.73
131.39
131.06
127.33
127.20
124.63
122.99
122.95
122.91
122.87
121.92
119.20
88.88
85.62
38.35
27.62
Parameter Value
1Title hecq-20210118-hq-468.2.1
2Solvent CDCl3
3Temperature 297.7
4Number of Scans512
6Nucleus 13C
CF3
O
O
O
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

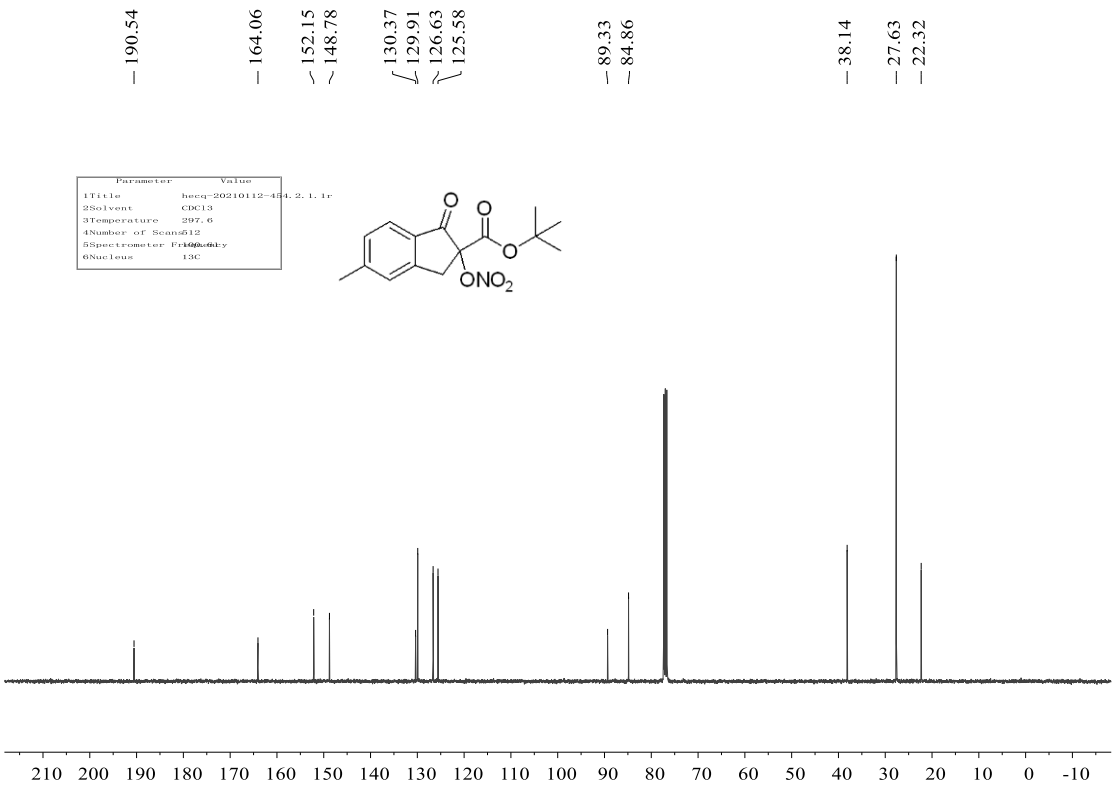
3u


-62.76
Parameter Value
1Title hecq-20210118-hq-468.3.1.1r
2Solvent CDCl3
3Temperature 297.6
4Number of Scans16
6Nucleus 19F
CF3
O
O
O
ONO2
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

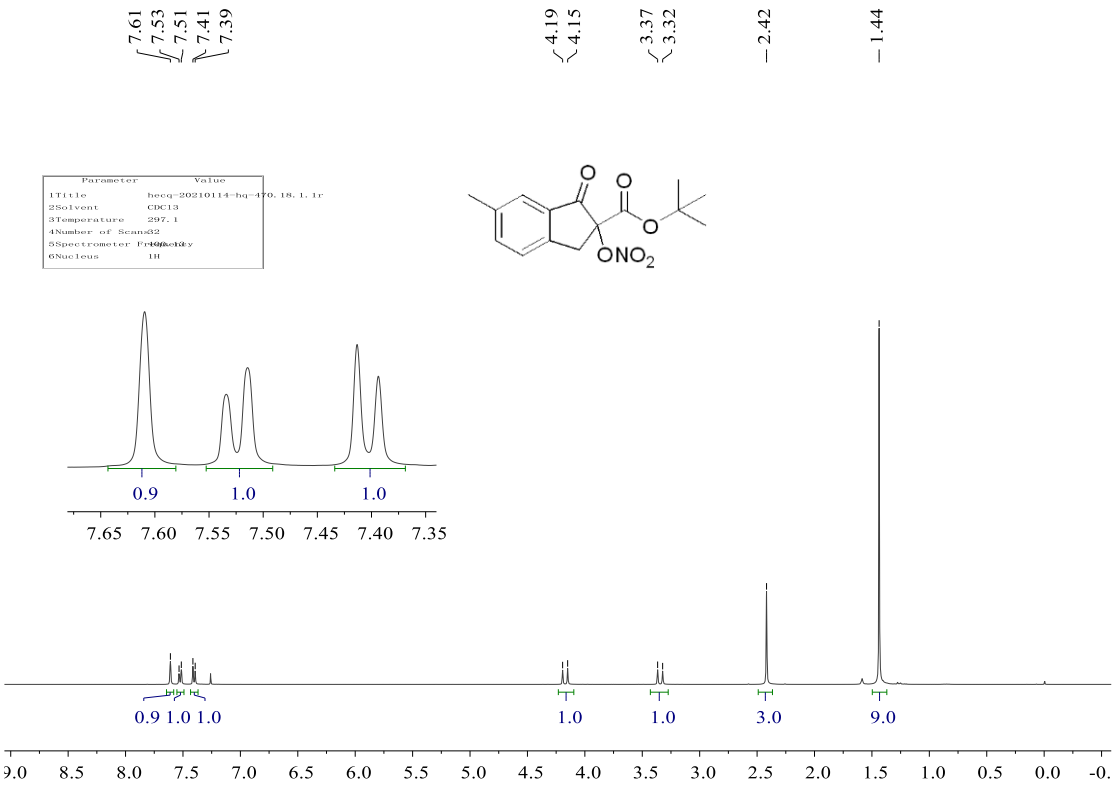
3v


7.65
7.63
7.24
7.20
7.19
7.18
4.13
4.08
3.29
3.25
2.41
1.37
Parameter Value
1Title hecq-20210112-454.1.1.1r
2Solvent CDCl3
3Temperature 297.2
4Number of Scans 32
5Spectrometer Frequency
6Nucleus 1H
ONO2
2.1
7.25 7.20 7.15
0.9 2.1 1.0 1.0 3.0 9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

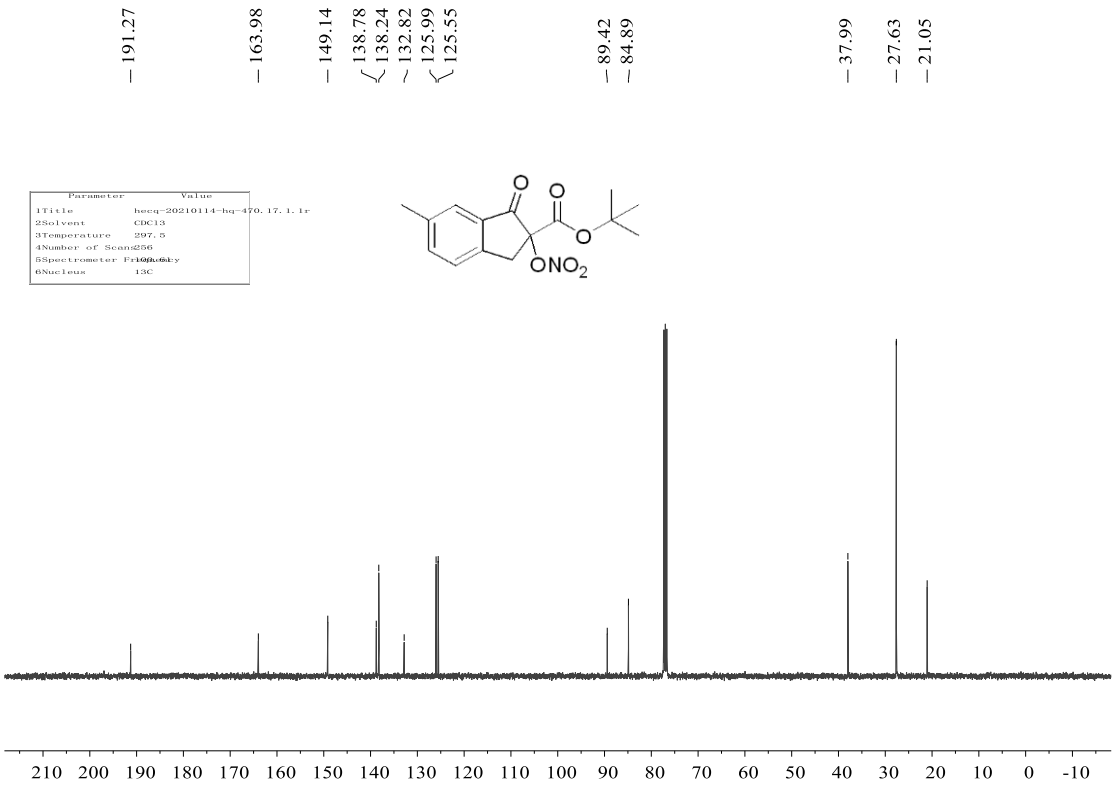
3v


190.54
164.06
152.15
148.78
130.37
129.91
126.63
125.58
89.33
84.86
38.14
27.63
22.32
Parameter Value
1Title hecq-20210112-454.2.1.1r
2Solvent CDCl3
3Temperature 297.6
4Number of Scans 512
5Spectrometer Frequency
6Nucleus 13C
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

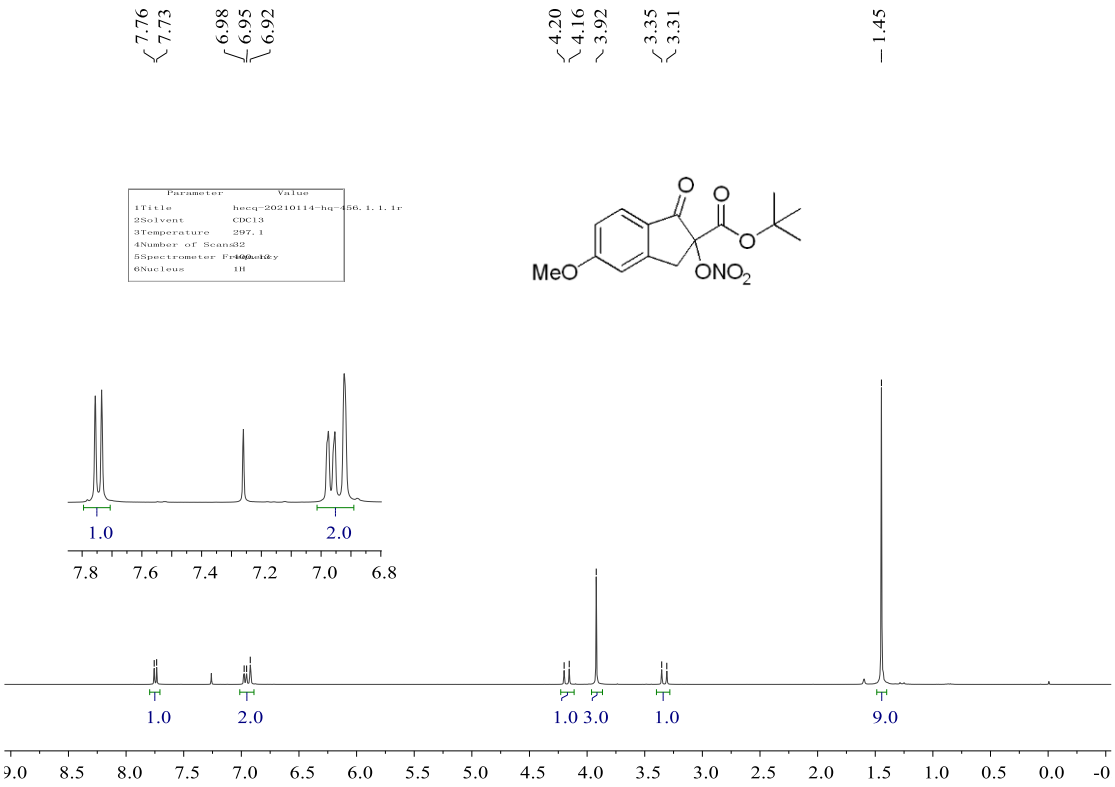
3w


7.61
7.53
7.51
7.41
7.39
4.19
4.15
3.37
3.32
2.42
1.44
Parameter Value
1Title hecq-20210114-hq-470.18.1.1r
2Solvent CDCl3
3Temperature 297.1
4Number of Scans 32
6Nucleus 1H
ONO2
0.9 1.0 1.0
7.65 7.60 7.55 7.50 7.45 7.40 7.35
0.9 1.0 1.0 1.0 1.0 3.0 9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.

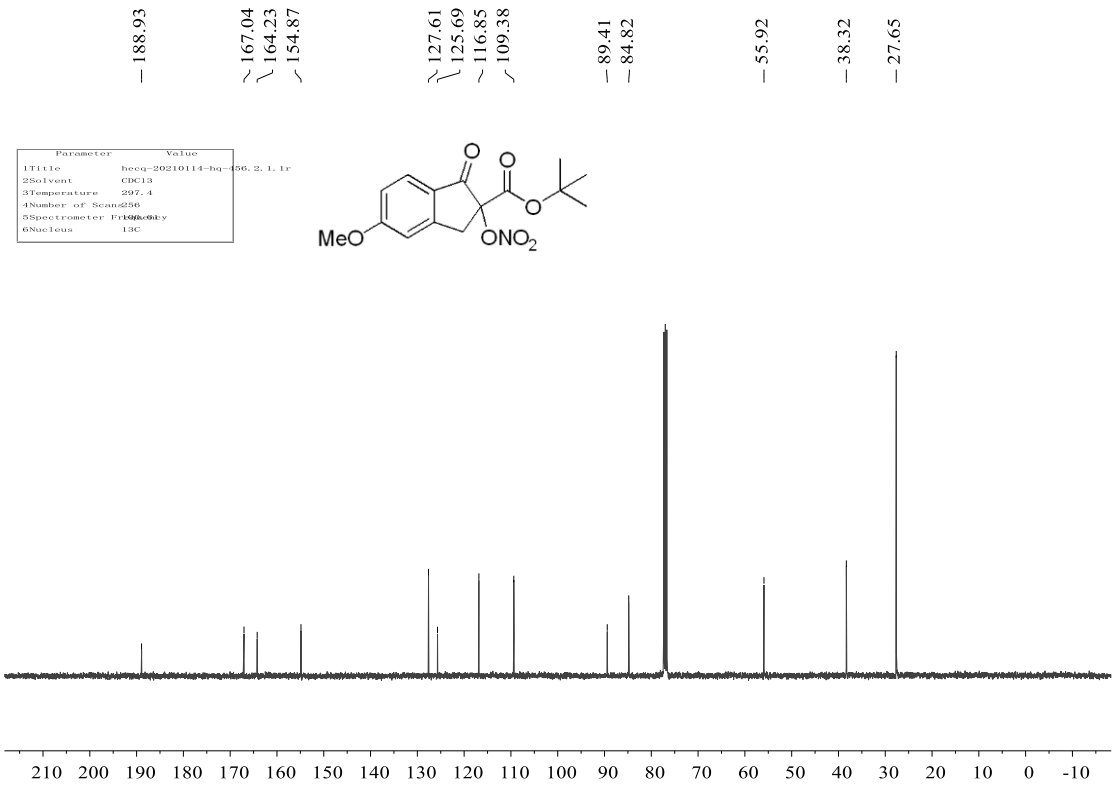
3w


191.27
163.98
149.14
138.78
138.24
132.82
125.99
125.55
89.42
84.89
37.99
27.63
21.05
Parameter Value
1Title hecq-20210114-hq-470.17.1.1r
2Solvent CDCl3
3Temperature 297.5
4Number of Scans 256
6Nucleus 13C
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

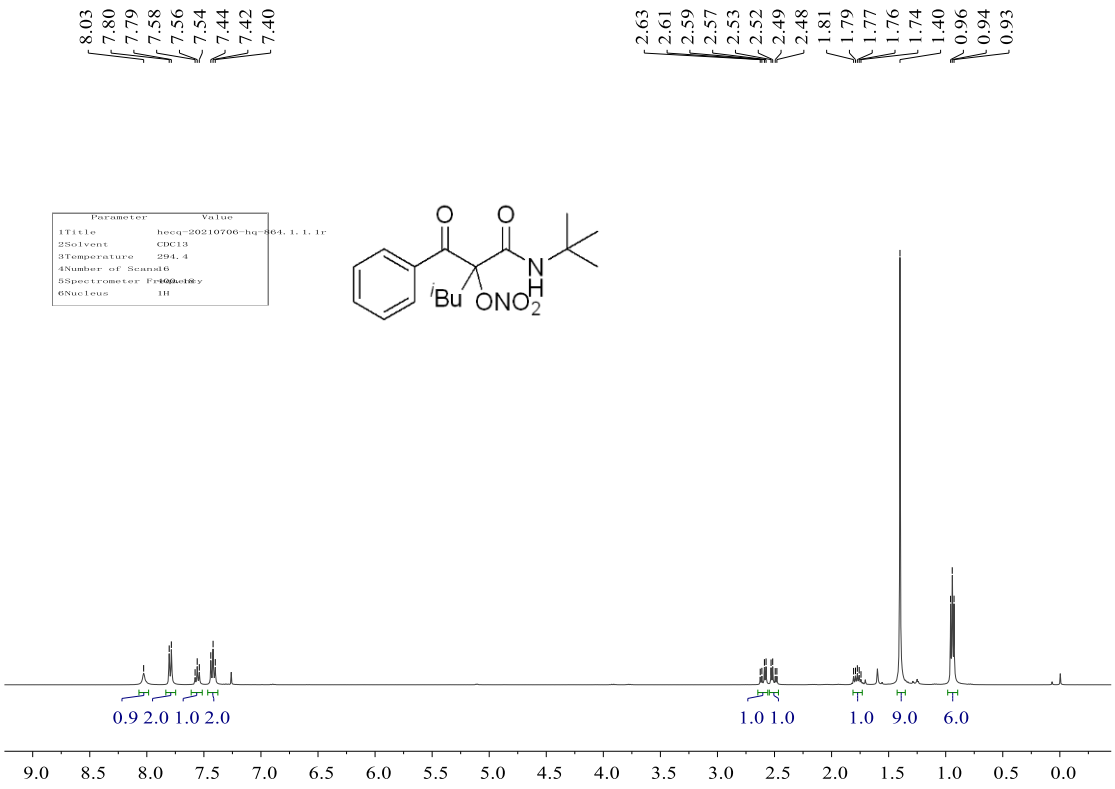
3x


7.76
7.73
6.98
6.95
6.92
4.20
4.16
3.92
3.35
3.31
1.45
Parameter Value
1Title hecq-20210114-hq-456.1.1.1r
2Solvent CDCl3
3Temperature 297.1
4Number of Scans 32
6Nucleus 1H
MeO
ONO2
1.0
2.0
7.8 7.6 7.4 7.2 7.0 6.8
1.0 2.0 1.0 3.0 1.0 9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

3x


188.93
167.04
164.23
154.87
127.61
125.69
116.85
109.38
89.41
84.82
55.92
38.32
27.65
Parameter Value
1Title hecq-20210114-hq-456.2.1.1r
2Solvent CDCl3
3Temperature 297.4
4Number of Scans 256
6Nucleus 13C
MeO
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

3y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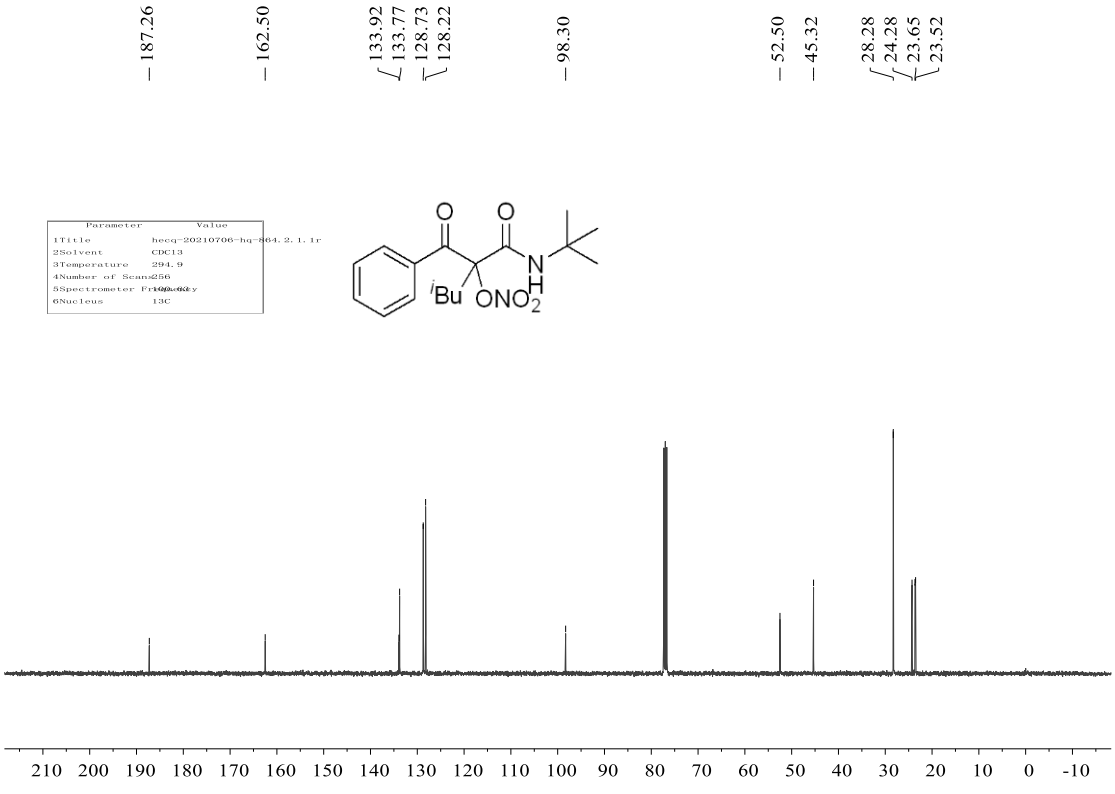
7.80
7.79
7.58
7.56
7.54
7.44
7.42
7.40
2.63
2.61
2.59
2.57
2.53
2.52
2.49
2.48
1.81
1.79
1.77
1.76
1.74
1.40
0.96
0.94
0.93
Parameter Value
1Title hecq-20210706-hq-864.1.1.1r
2Solvent CDCl3
3Temperature 294.4
4Number of Scans16
5Spectrometer Pr
6Nucleus 1H
O
O
N
H
iBu
ONO2
0.9 2.0 1.0 2.0
1.0 1.0
1.0
9.0
6.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

3y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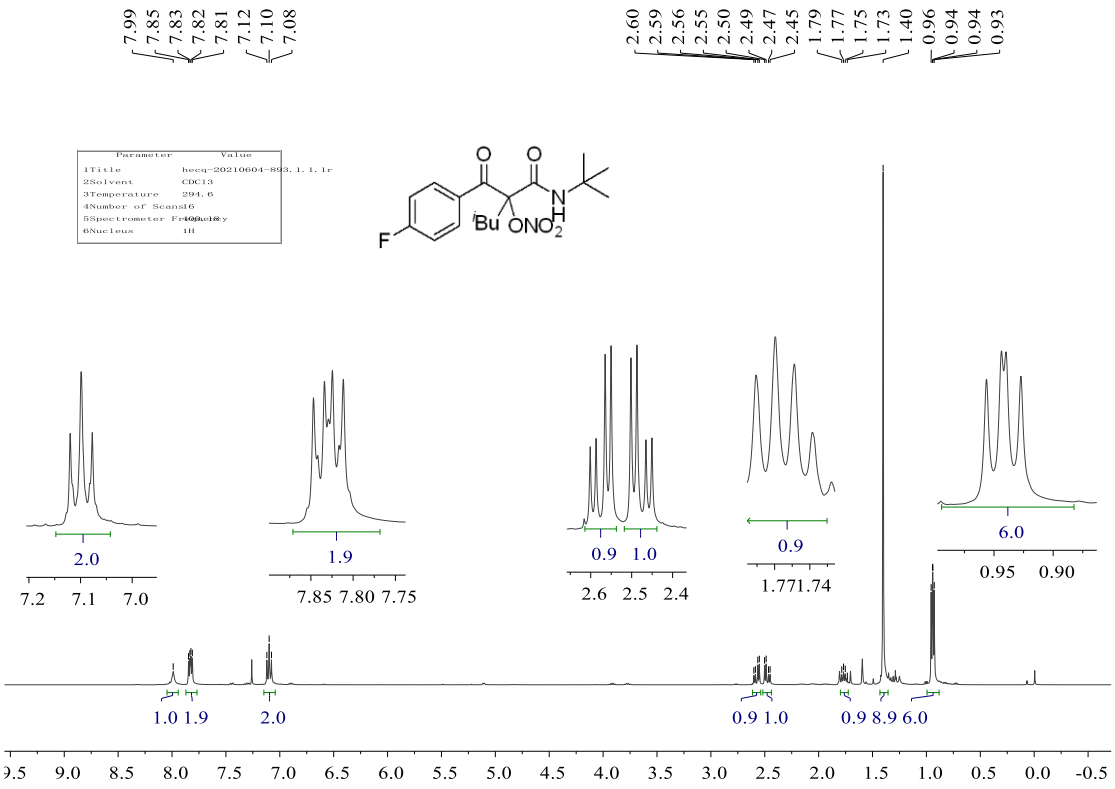
162.50
133.92
133.77
128.73
128.22
98.30
52.50
45.32
28.28
24.28
23.65
23.52
Parameter Value
1Title hecq-20210706-hq-864.2.1.1r
2Solvent CDCl3
3Temperature 294.9
4Number of Scans256
5Spectrometer Pr
6Nucleus 13C
O
O
N
H
iBu
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

3z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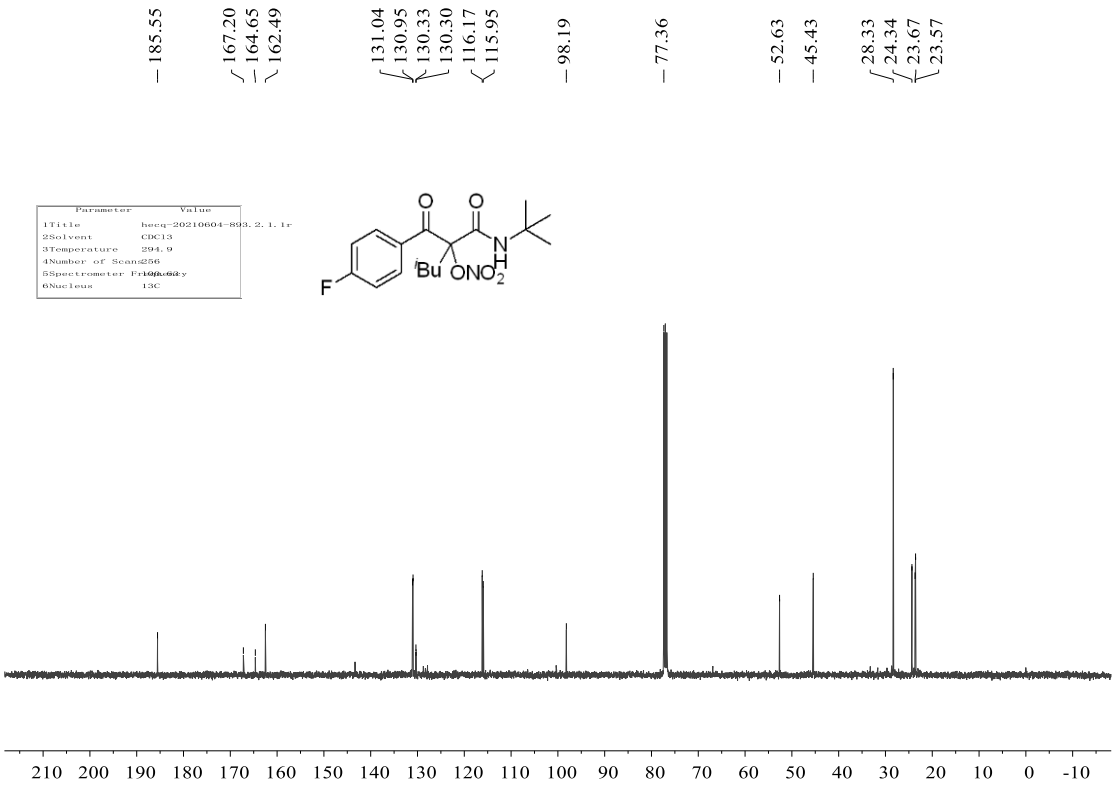
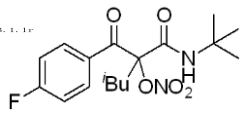
7.85
7.83
7.82
7.81
7.12
7.10
7.08
2.60
2.59
2.56
2.55
2.50
2.49
2.47
2.45
1.79
1.77
1.75
1.73
1.40
0.96
0.94
0.94
0.93
Parameter Value
1Title heeq-20210604-893.1.1.1r
2Solvent CDCl3
3Temperature 294.6
4Number of Scans 16
6Nucleus 1H
F
iBu
ONO2
2.0
1.9
0.9 1.0
0.9
6.0
7.2 7.1 7.0
7.85 7.80 7.75
2.6 2.5 2.4
1.771.74
0.95 0.90
1.0 1.9 2.0
0.9 1.0 0.9 8.9 6.0

3z

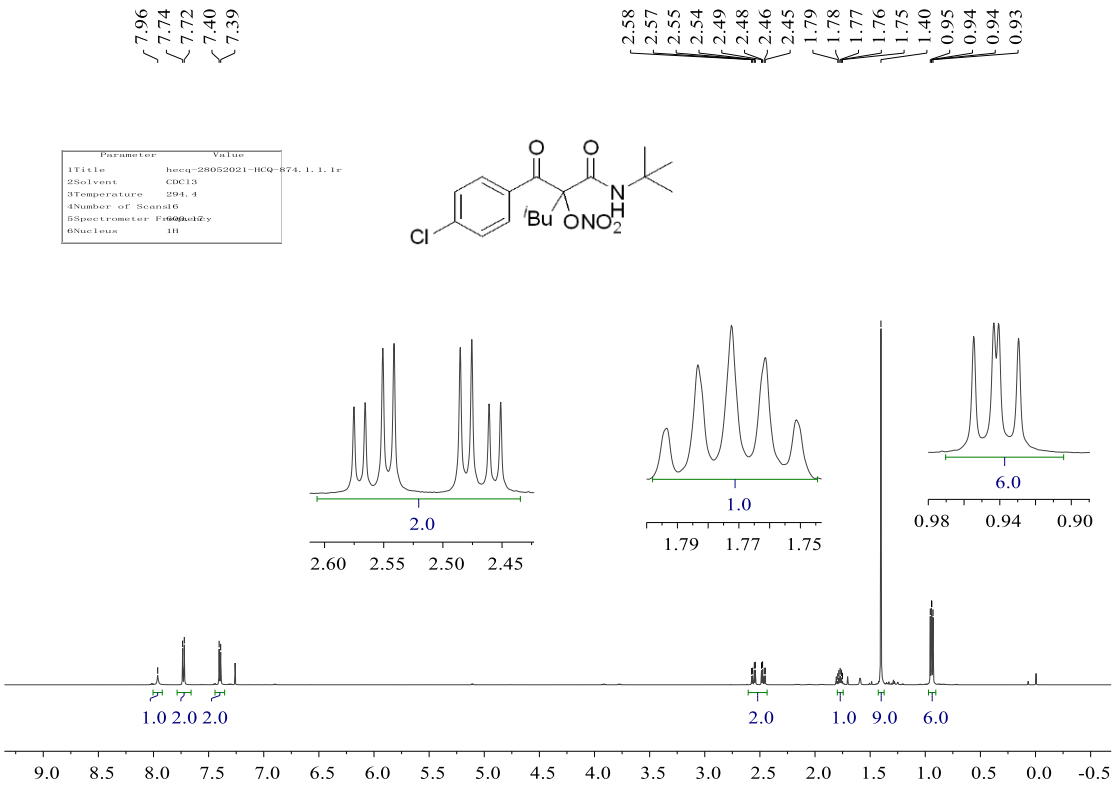

185.55
167.20
164.65
162.49
131.04
130.95
130.33
130.30
116.17
115.95
98.19
77.36
52.63
45.43
28.33
24.34
23.67
23.57
Parameter Value
1Title heeq-20210604-893.2.1.1r
2Solvent CDCl3
3Temperature 294.9
4Number of Scans 256
6Nucleus 13C
F
iBu
ONO2

3z

Parameter	Value
1Title	as-20210707-hcq-hq-893.3.1.1r
2Solvent	CDCl3
3Temperature	294.6
4Number of Scans	16
5Spectrometer Frequency	[illegible]
6Nucleus	19F



3aa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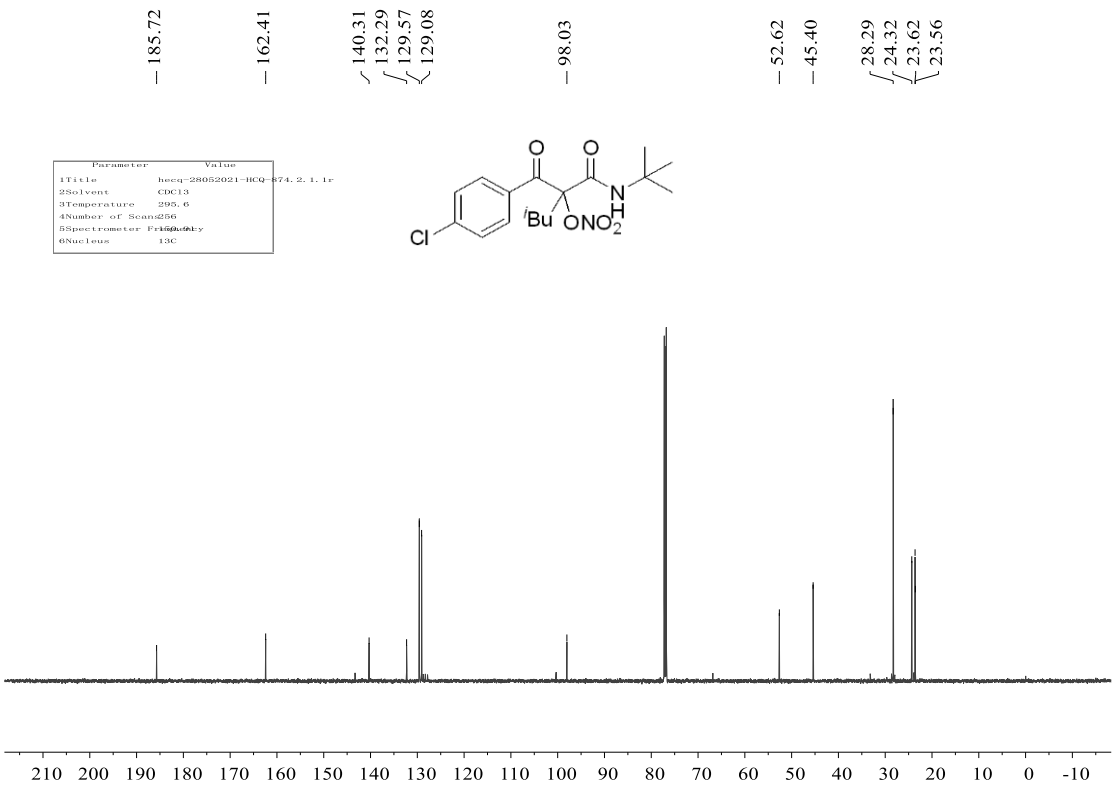
7.74
7.72
7.40
7.39
2.58
2.57
2.55
2.54
2.49
2.48
2.46
2.45
1.79
1.78
1.77
1.76
1.75
1.40
0.95
0.94
0.94
0.93
Parameter Value
1Title hecq-28052021-HCQ-874.1.1.1r
2Solvent CDCl3
3Temperature 294.4
4Number of Scans 16
5Spectrometer Frequency
6Nucleus 1H
Cl
O
O
N
H
tBu
ONO2
2.0
1.0
6.0
1.0 2.0 2.0
2.0
1.0 9.0 6.0

3aa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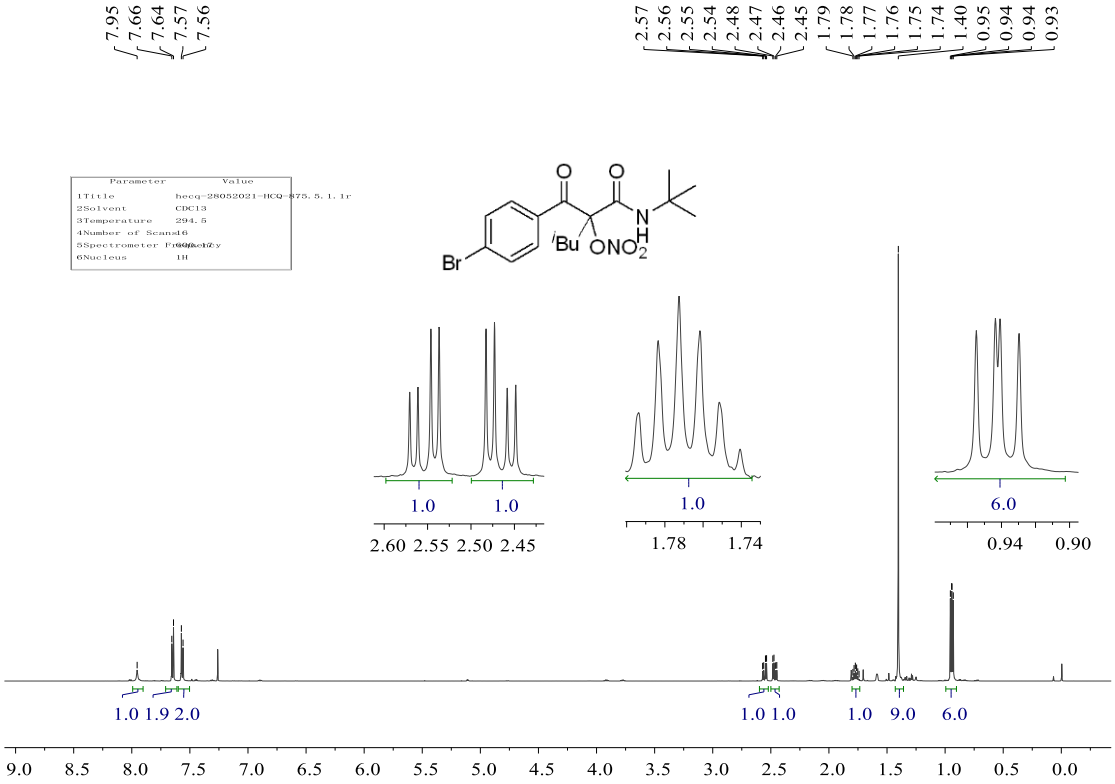
162.41
140.31
132.29
129.57
129.08
98.03
52.62
45.40
28.29
24.32
23.62
23.56
Parameter Value
1Title hecq-28052021-HCQ-874.2.1.1r
2Solvent CDCl3
3Temperature 295.6
4Number of Scans 256
5Spectrometer Frequency
6Nucleus 13C
Cl
O
O
N
H
tBu
ONO2

3ab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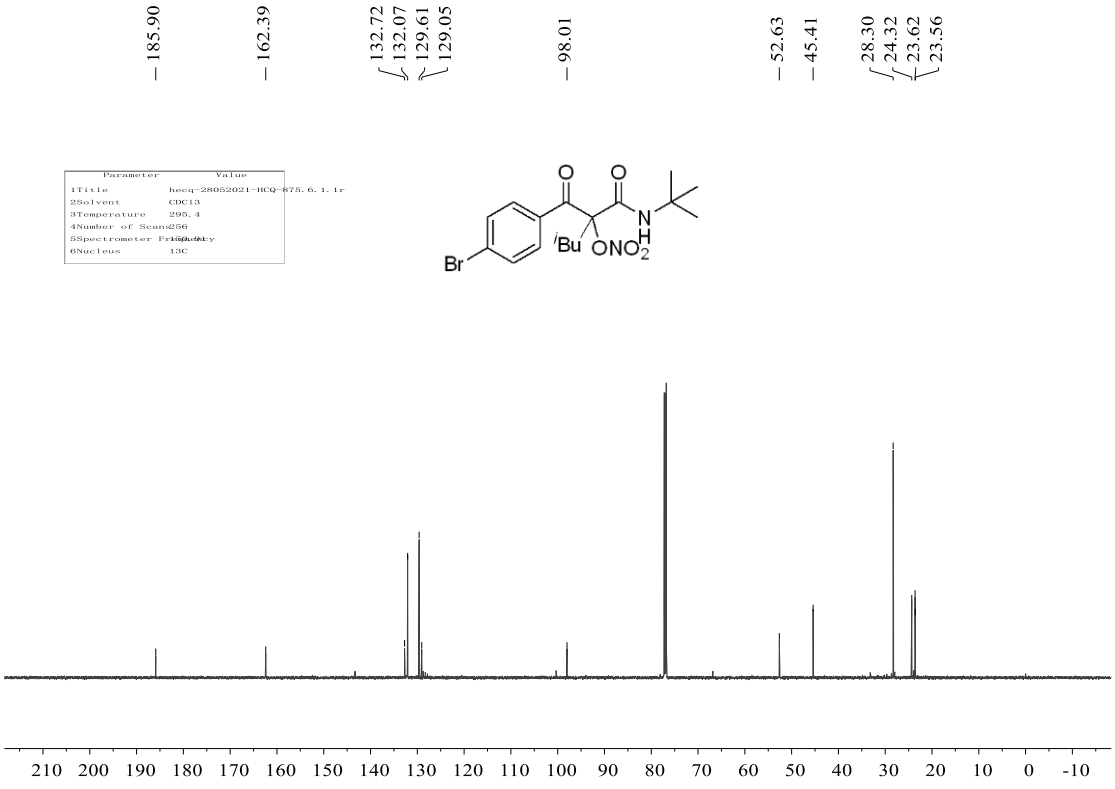
7.66
7.64
7.57
7.56
2.57
2.56
2.55
2.54
2.48
2.47
2.46
2.45
1.79
1.78
1.77
1.76
1.75
1.74
1.40
0.95
0.94
0.94
0.93
Parameter Value
1Title hecq-28052021-HCQ-875.5.1.1r
2Solvent CDCl3
3Temperature 294.5
4Number of Scans 16
6Nucleus 1H
Br
tBu
ONO2
1.0 1.0
2.60 2.55 2.50 2.45
1.0
1.78 1.74
6.0
0.94 0.90
1.0 1.9 2.0
1.0 1.0
1.0 9.0 6.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

3ab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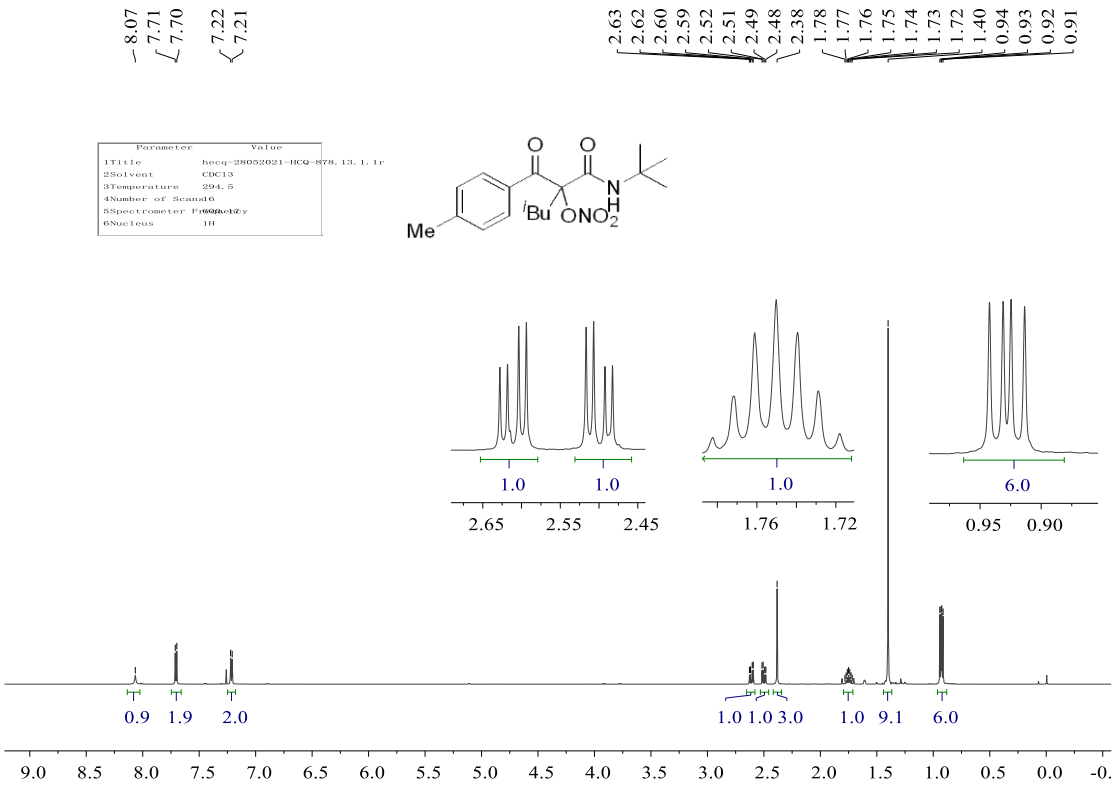
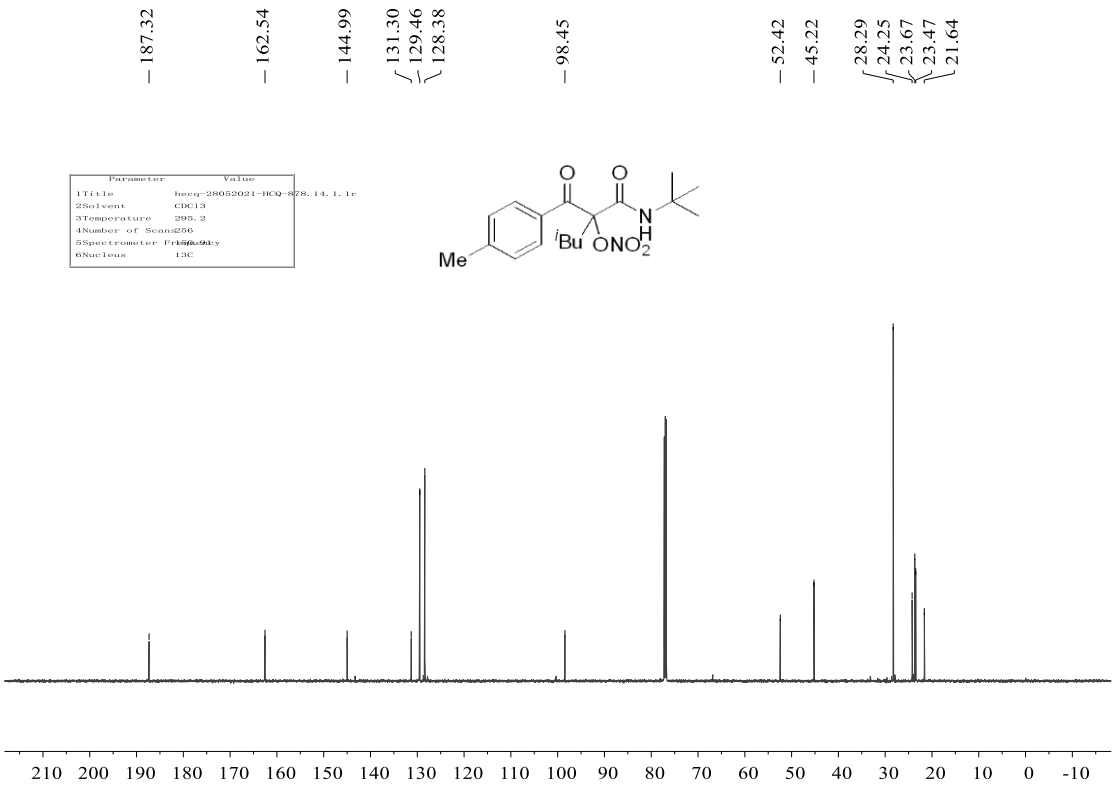
162.39
132.72
132.07
129.61
129.05
98.01
52.63
45.41
28.30
24.32
23.62
23.56
Parameter Value
1Title hecq-28052021-HCQ-875.6.1.1r
2Solvent CDCl3
3Temperature 295.4
4Number of Scans 256
6Nucleus 13C
Br
tBu
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

3ac


8.07
7.71
7.70
7.22
7.21
2.63
2.62
2.60
2.59
2.52
2.51
2.49
2.48
2.38
1.78
1.77
1.76
1.75
1.74
1.73
1.72
1.40
0.94
0.93
0.92
0.91
Parameter Value
1Title hecq-28052021-HCQ-878.13.1.1r
2Solvent CDCl3
3Temperature 294.5
4Number of Scans16
6Nucleus 1H
Me
tBu
ONO2
1.0
1.0
1.0
6.0
0.9
1.9
2.0
1.0
1.0
3.0
1.0
9.1
6.0

3ac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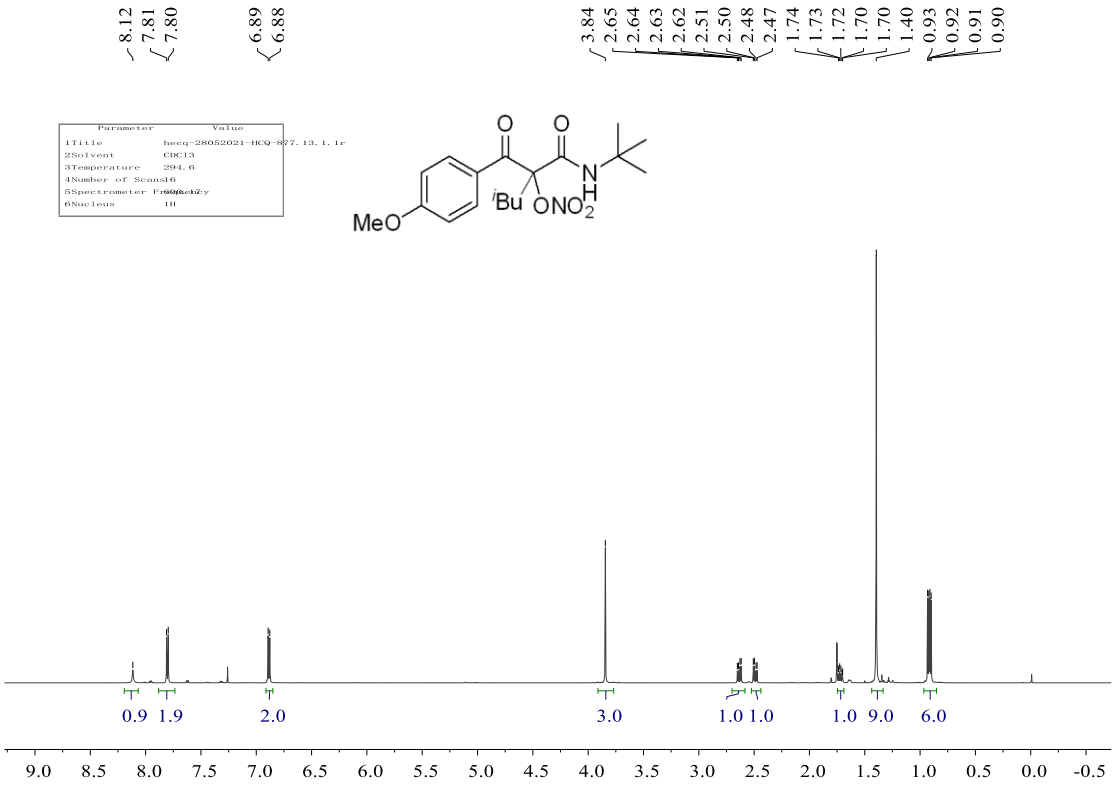
144.99
131.30
129.46
128.38
98.45
52.42
45.22
28.29
24.25
23.67
23.47
21.64
Parameter Value
1Title hecq-28052021-HCQ-878.14.1.1r
2Solvent CDCl3
3Temperature 295.2
4Number of Scans256
6Nucleus 13C
Me
tBu
ONO2

3ad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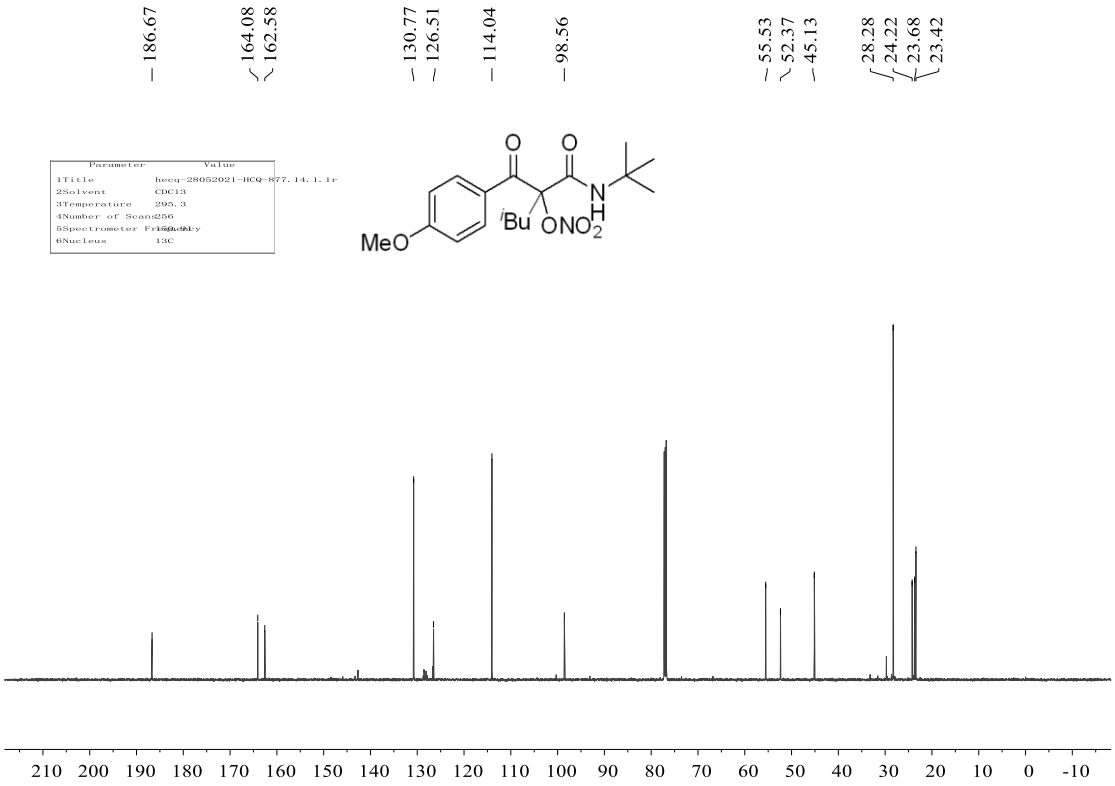
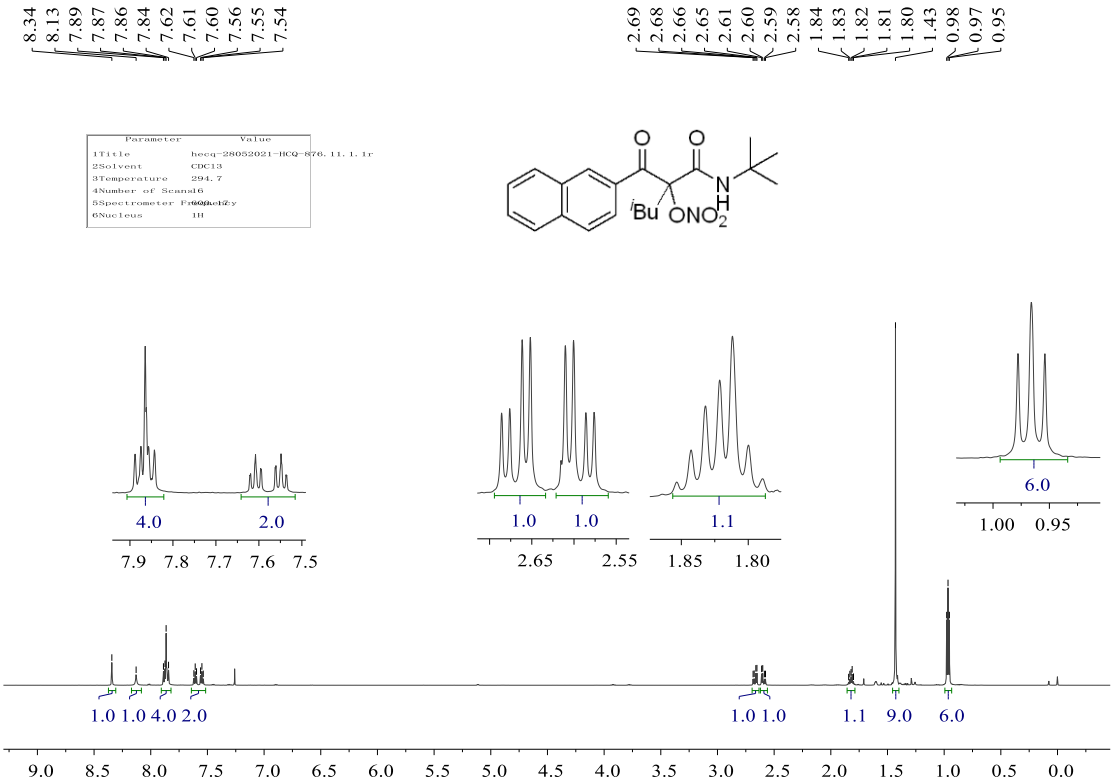
7.81
7.80
6.89
6.88
3.84
2.65
2.64
2.63
2.62
2.51
2.50
2.48
2.47
1.74
1.73
1.72
1.70
1.70
1.40
0.93
0.92
0.91
0.90
Parameter Value
1Title hecq-28052021-HCQ-877.13.1.1r
2Solvent CDCl3
3Temperature 294.6
4Number of Scans16
6Nucleus 1H
MeO
tBu
ONO2
0.9 1.9 2.0 3.0 1.0 1.0 1.0 9.0 6.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

3ad


186.67
164.08
162.58
130.77
126.51
114.04
98.56
55.53
52.37
45.13
28.28
24.22
23.68
23.42
Parameter Value
1Title hecq-28052021-HCQ-877.14.1.1r
2Solvent CDCl3
3Temperature 295.3
4Number of Scans256
6Nucleus 13C
MeO
tBu
ONO2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

3ae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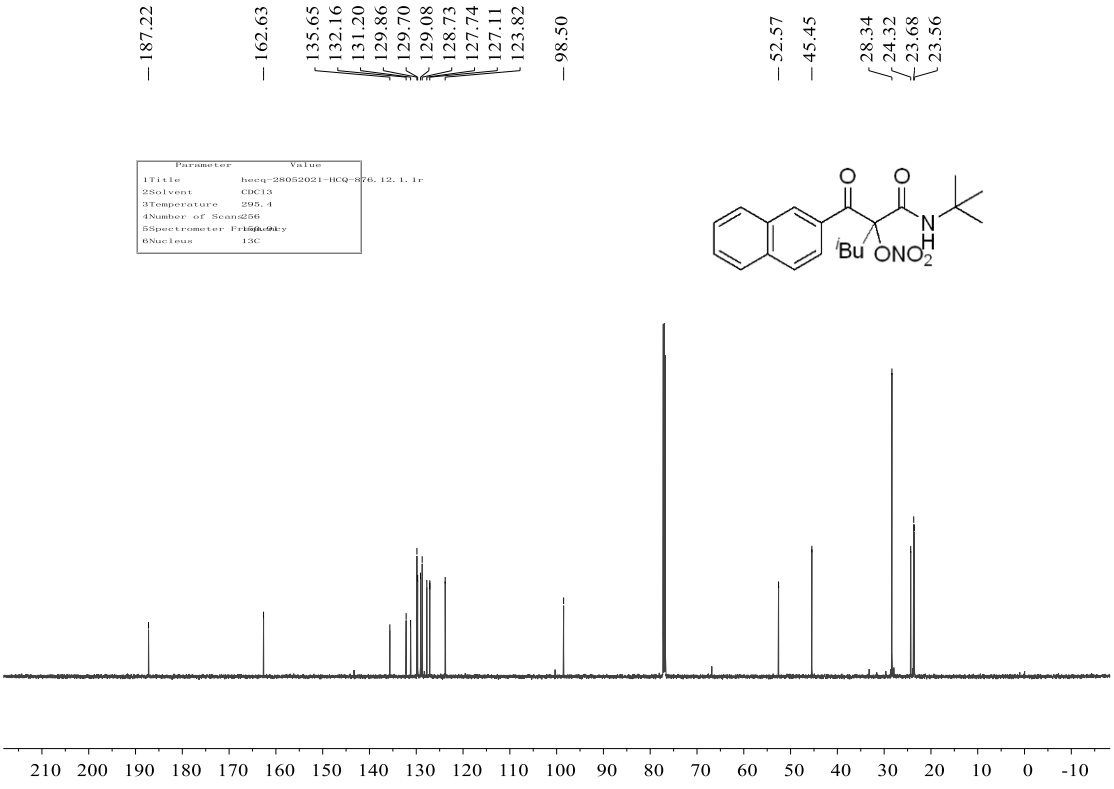
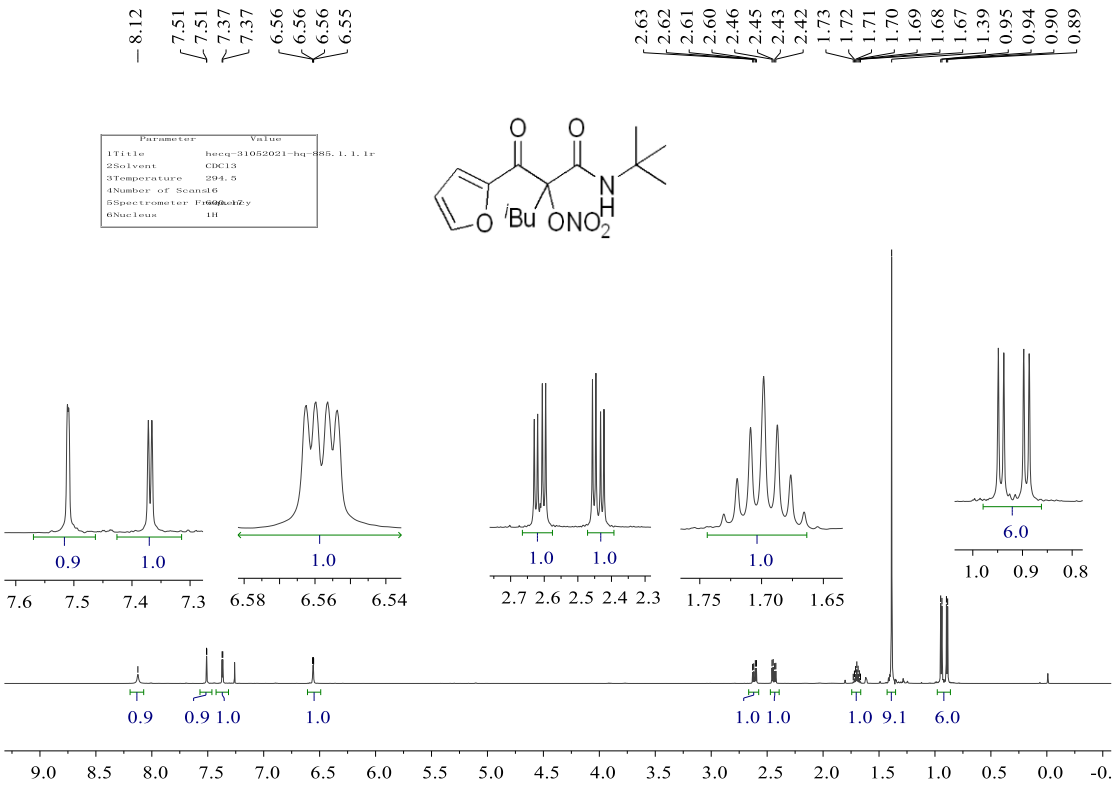
2.69 2.68 2.66 2.65 2.61 2.60 2.59 2.58 1.84 1.83 1.82 1.81 1.80 1.43 0.98 0.97 0.95
Parameter Value
1Title hecq-28052021-HCQ-876.11.1.1r
2Solvent CDCl3
3Temperature 294.7
4Number of Scans 16
6Nucleus 1H
tBu ONO2
4.0 2.0
1.0 1.0
1.1
6.0
1.0 1.0 4.0 2.0
1.0 1.0
1.1 9.0 6.0

3ae


187.22 162.63 135.65 132.16 131.20 129.86 129.70 129.08 128.73 127.74 127.11 123.82 98.50 52.57 45.45 28.34 24.32 23.68 23.56
Parameter Value
1Title hecq-28052021-HCQ-876.12.1.1r
2Solvent CDCl3
3Temperature 295.4
4Number of Scans 256
6Nucleus 13C
tBu ONO2

3af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7.51
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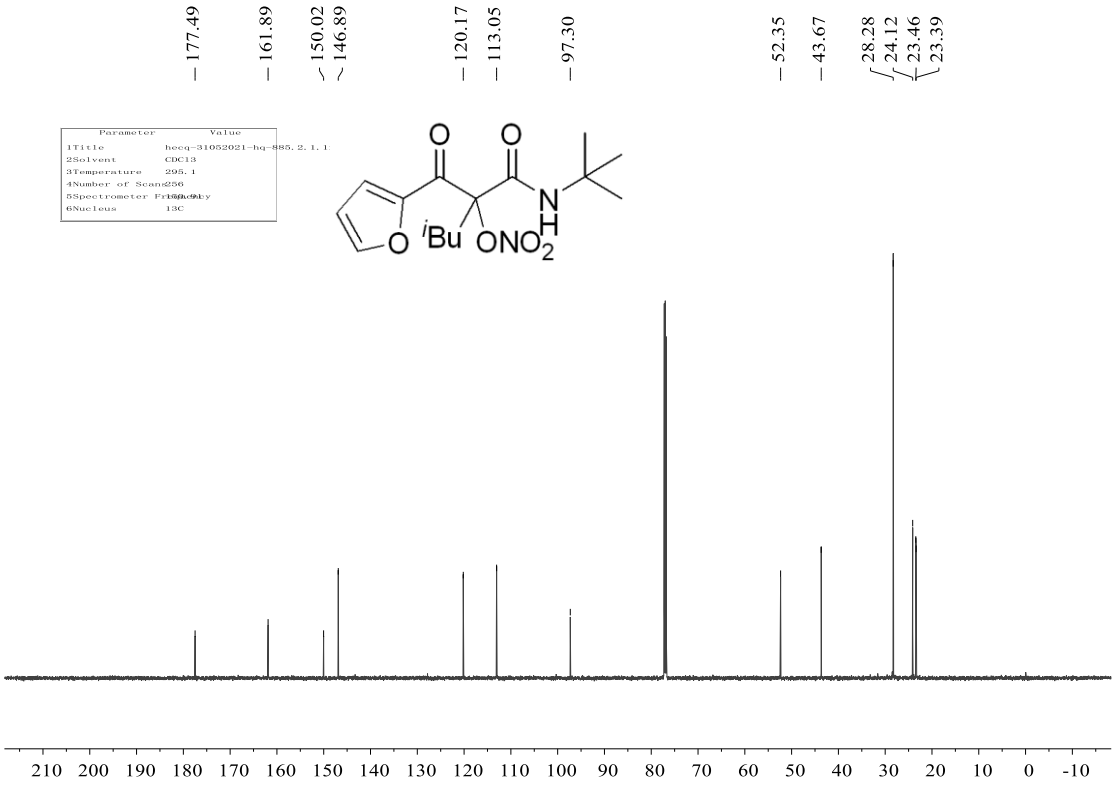
6.56
6.56
6.56
6.55
2.63
2.62
2.61
2.60
2.46
2.45
2.43
2.42
1.73
1.72
1.71
1.70
1.69
1.68
1.67
1.39
0.95
0.94
0.90
0.89
Parameter Value
1Title hecq-31052021-hq-885.1.1.1r
2Solvent CDCl3
3Temperature 294.5
4Number of Scans 16
6Nucleus 1H
O
O
N
H
O
tBu
ONO2
0.9
1.0
1.0
1.0
1.0
1.0
6.0
0.9 0.9 1.0
1.0
1.0 1.0
1.0 9.1
6.0

3af


177.49
161.89
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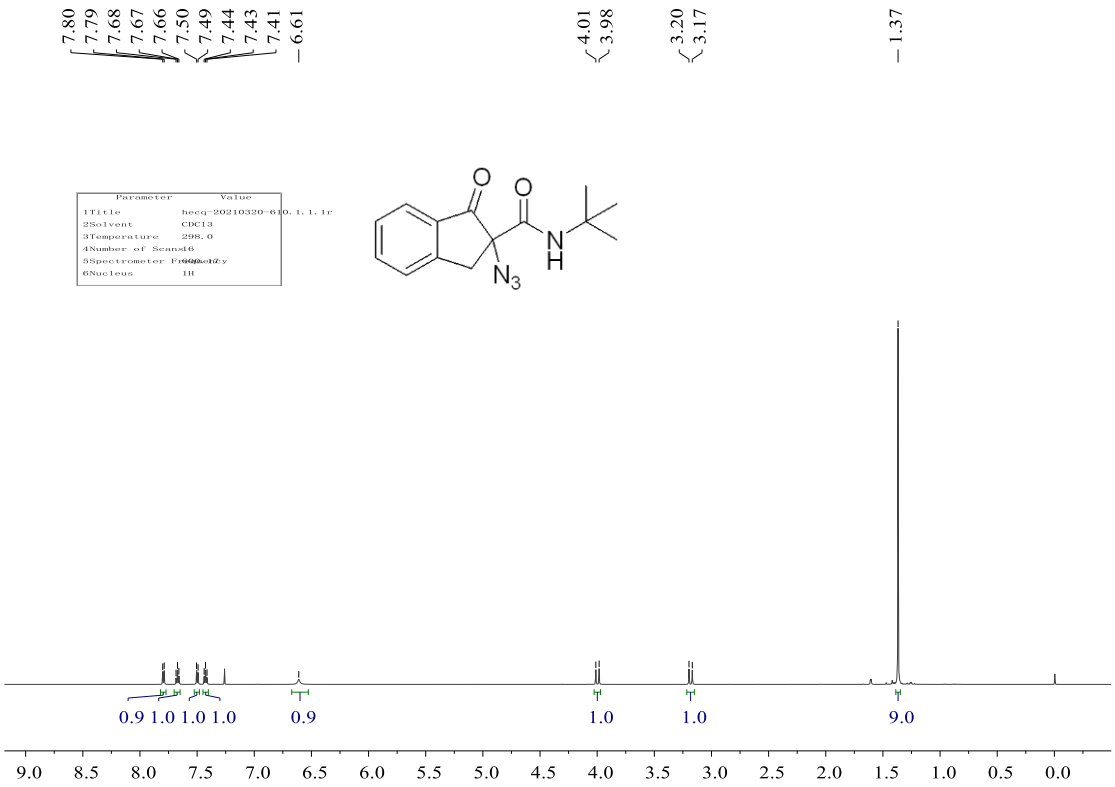
146.89
120.17
113.05
97.30
52.35
43.67
28.28
24.12
23.46
23.39
Parameter Value
1Title hecq-31052021-hq-885.2.1.1
2Solvent CDCl3
3Temperature 295.1
4Number of Scans 256
6Nucleus 13C
O
O
N
H
O
tBu
ONO2

5a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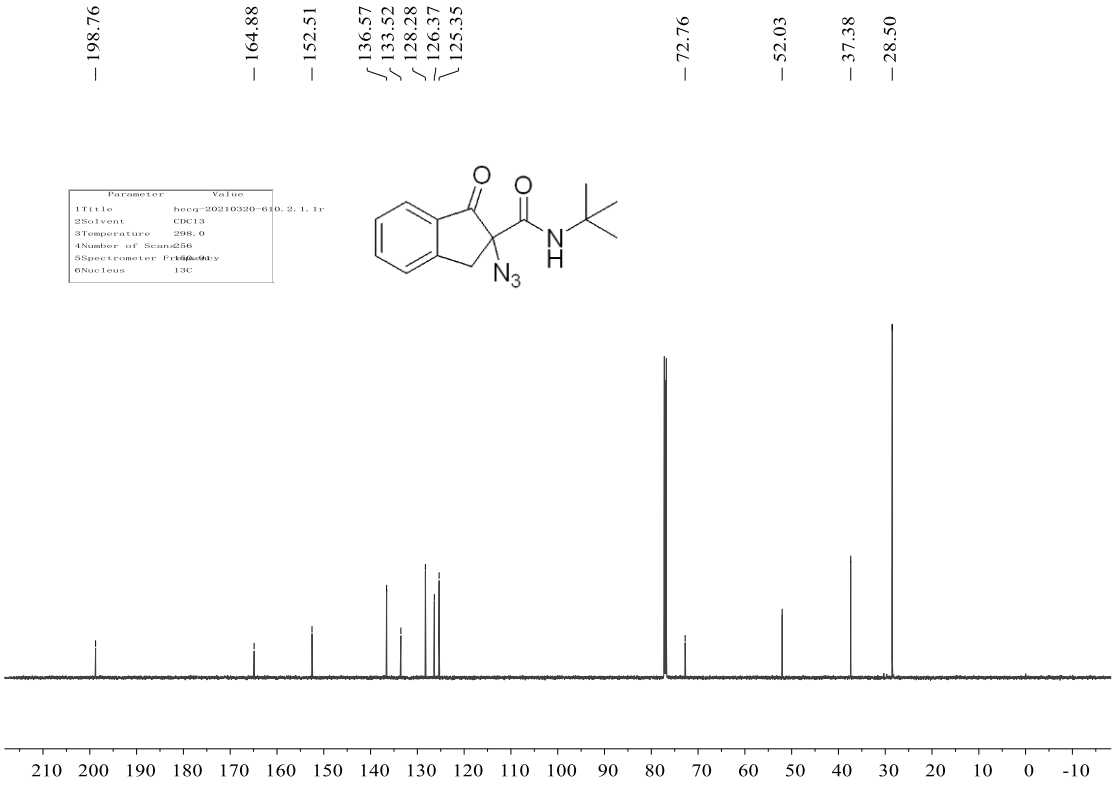
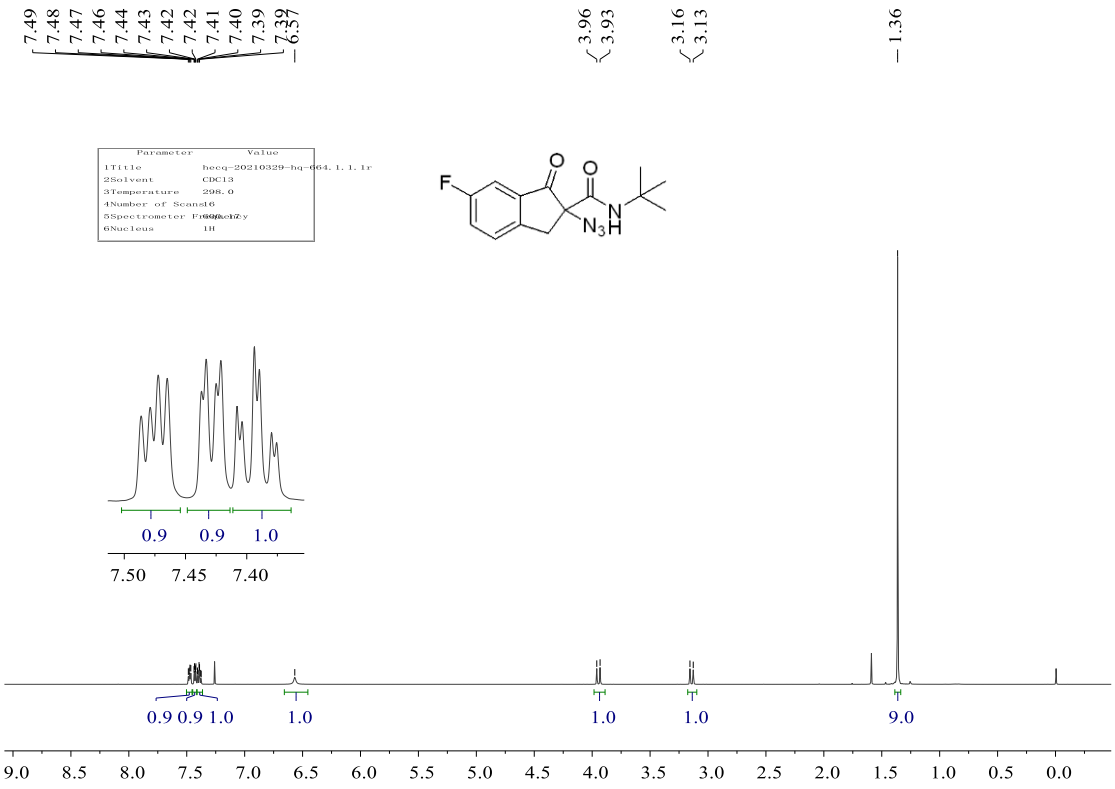
7.67
7.66
7.50
7.49
7.44
7.43
7.41
6.61
4.01
3.98
3.20
3.17
1.37
Parameter Value
1Title hecq-20210320-610.1.1.1r
2Solvent CDCl3
3Temperature 298.0
4Number of Scans 16
6Nucleus 1H
O
O
N
H
N3
0.9 1.0 1.0 1.0 0.9 1.0 1.0 9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

5a


198.76
164.88
152.51
136.57
133.52
128.28
126.37
125.35
72.76
52.03
37.38
28.50
Parameter Value
1Title hecq-20210320-610.2.1.1r
2Solvent CDCl3
3Temperature 298.0
4Number of Scans 256
6Nucleus 13C
O
O
N
H
N3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

5b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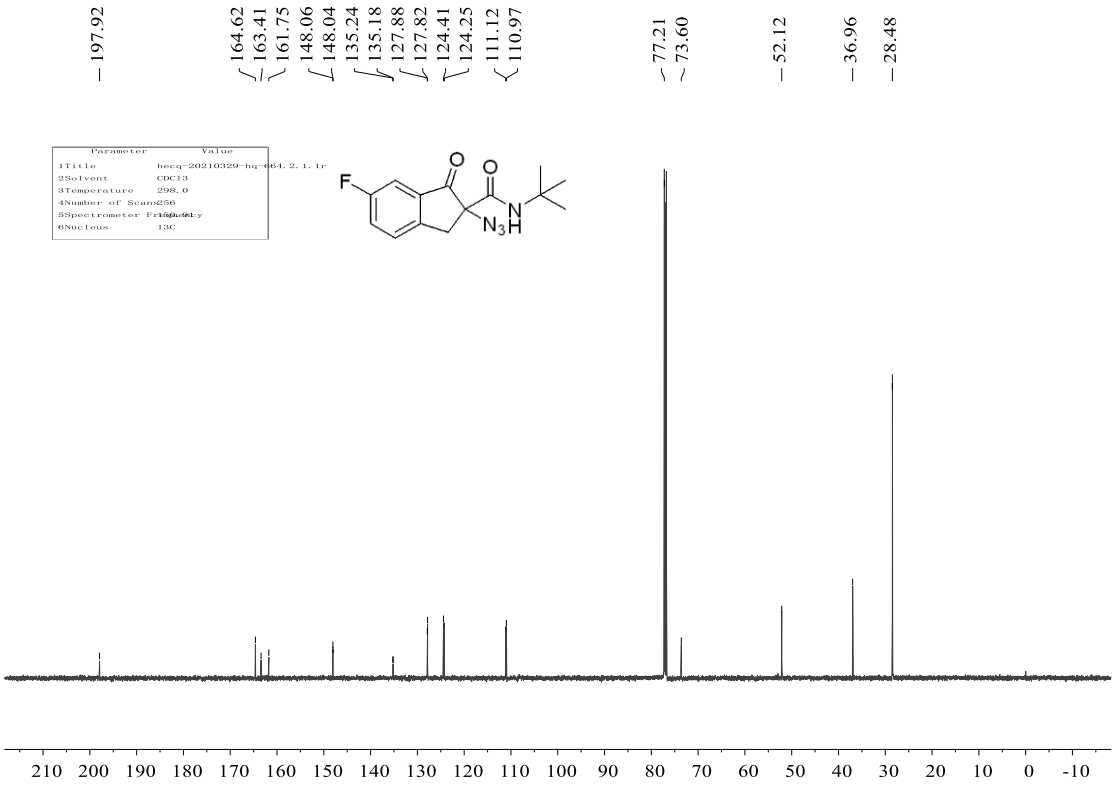
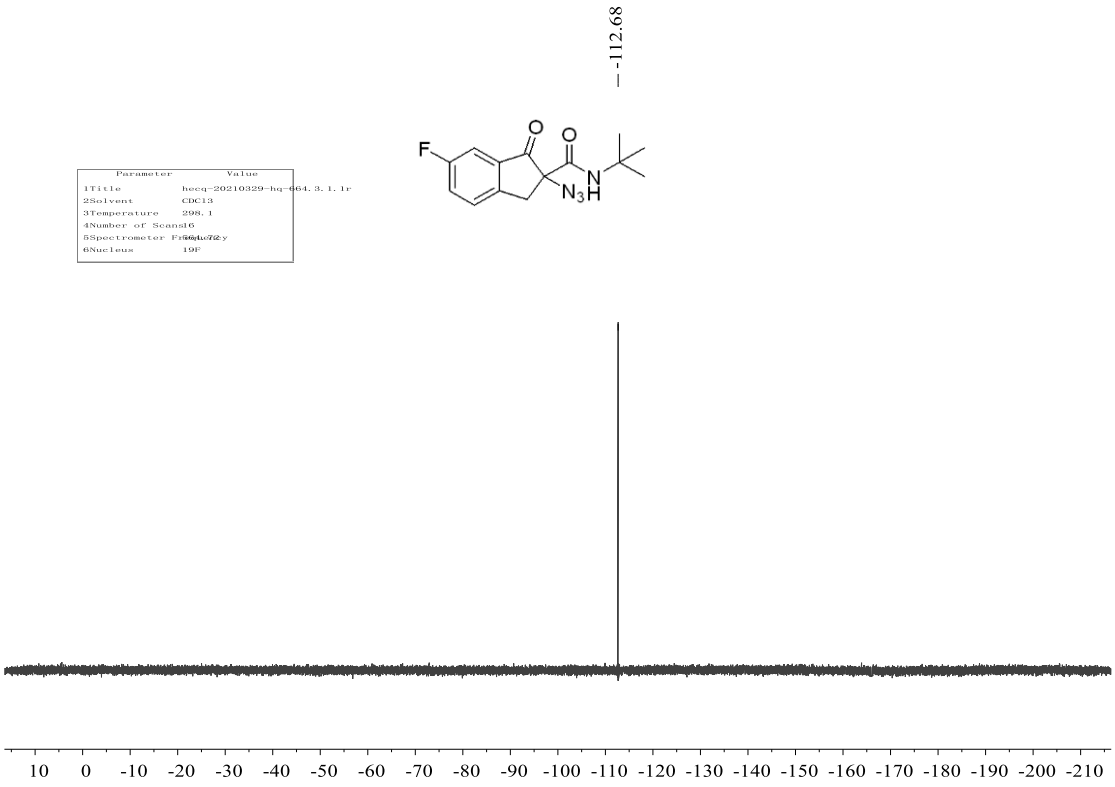
7.48
7.47
7.46
7.44
7.43
7.42
7.42
7.41
7.40
7.39
7.37
6.57
3.96
3.93
3.16
3.13
1.36
Parameter Value
1Title hecq-20210329-hq-664.1.1.1r
2Solvent CDCl3
3Temperature 298.0
4Number of Scans16
5Spectrometer Fr
6Nucleus 1H
F
O
O
N
N3H
0.9 0.9 1.0
7.50 7.45 7.40
0.9 0.9 1.0 1.0 1.0 1.0 9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

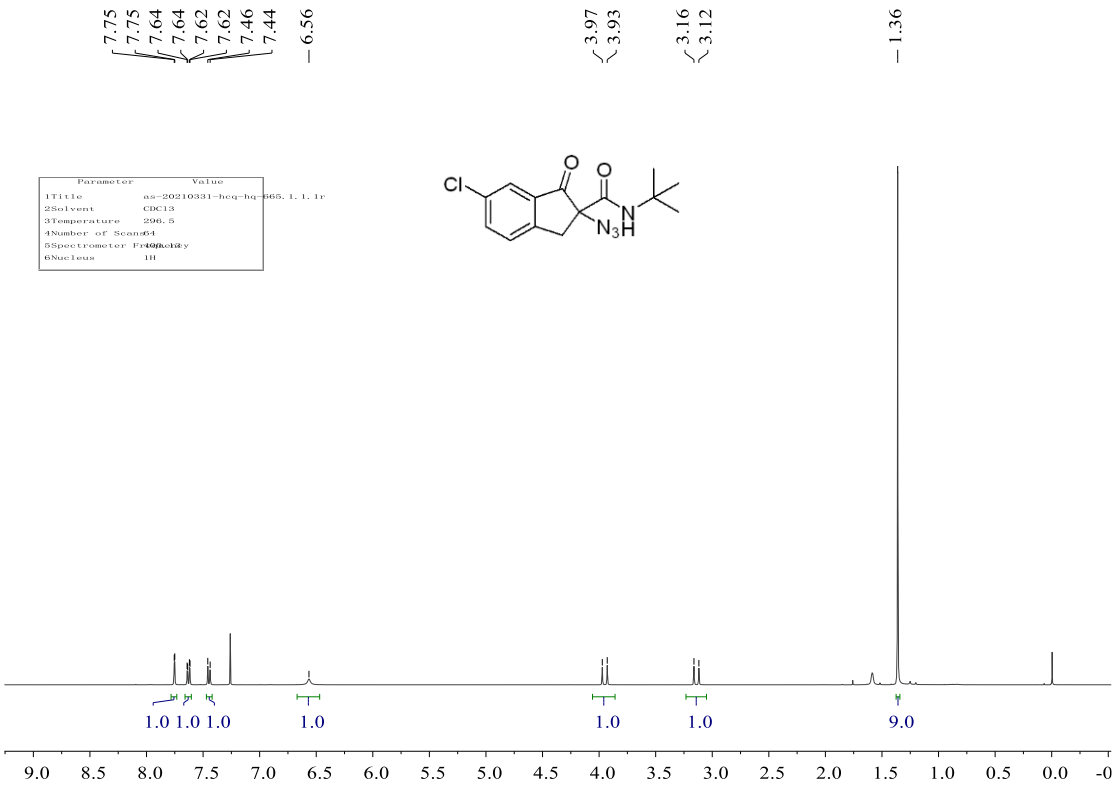
5b


197.92
164.62
163.41
161.75
148.06
148.04
135.24
135.18
127.88
127.82
124.41
124.25
111.12
110.97
77.21
73.60
52.12
36.96
28.48
Parameter Value
1Title hecq-20210329-hq-664.2.1.1r
2Solvent CDCl3
3Temperature 298.0
4Number of Scans256
5Spectrometer Fr
6Nucleus 13C
F
O
O
N
N3H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

5b


-112.68
F
O
O
N
N3H
Parameter Value
1Title hecq-20210329-hq-664.3.1.1r
2Solvent CDCl3
3Temperature 298.1
4Number of Scans16
5Spectrometer Frequency
6Nucleus 19F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

5c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7.75
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7.64
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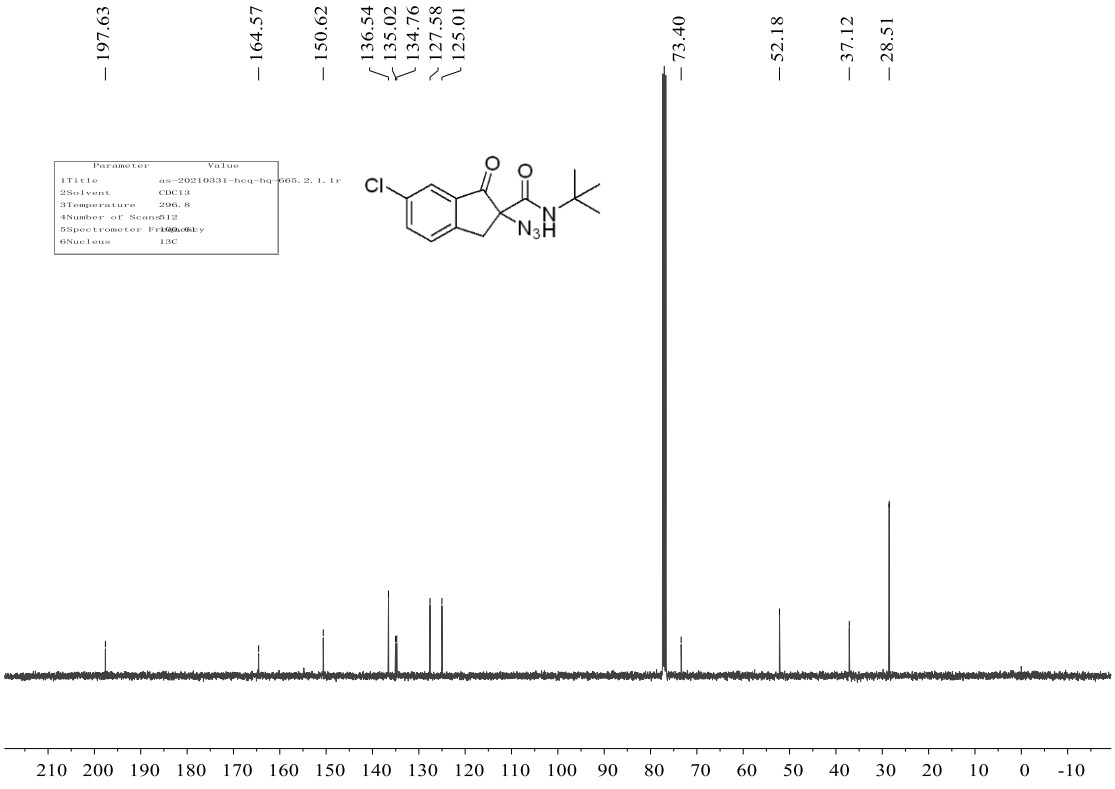
7.62
7.46
7.44
6.56
3.97
3.93
3.16
3.12
1.36
Parameter Value
1Title as-20210331-hcq-hq-565.1.1.1r
2Solvent CDCl3
3Temperature 296.5
4Number of Scans 64
6Nucleus 1H
Cl
O
O
N
N3H
1.0 1.0 1.0 1.0 1.0 1.0 9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

5c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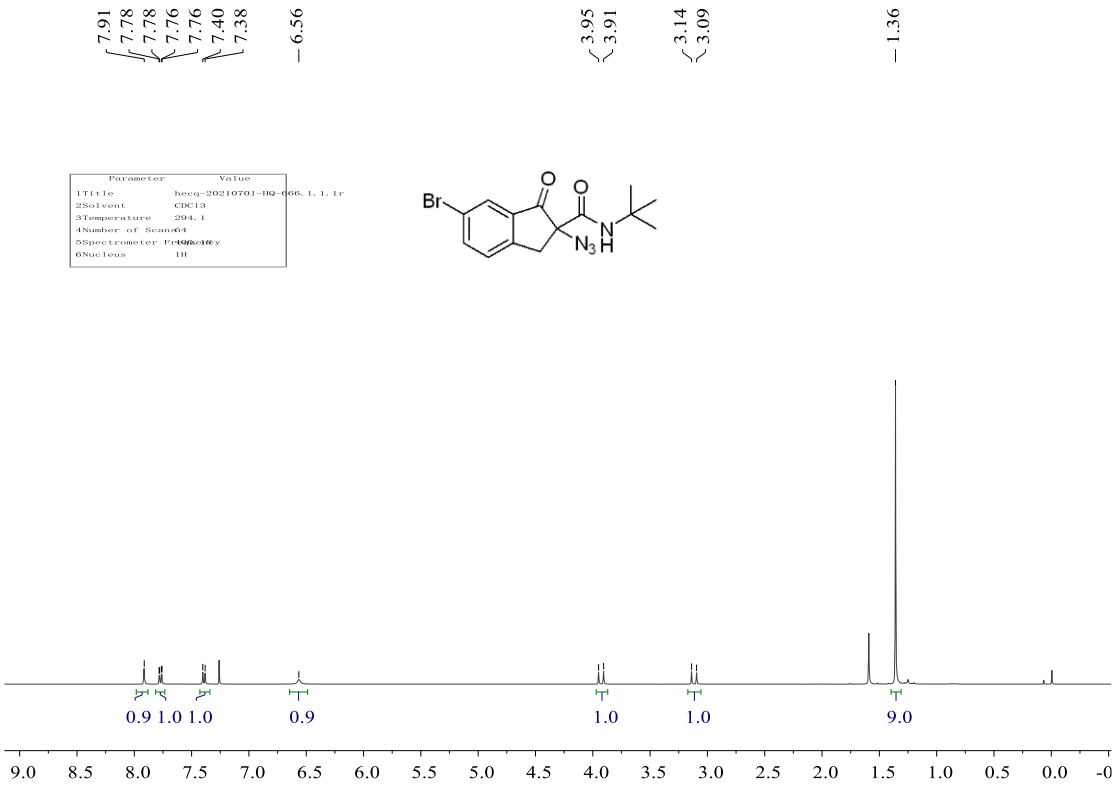
136.54
135.02
134.76
127.58
125.01
73.40
52.18
37.12
28.51
Parameter Value
1Title as-20210331-hcq-hq-565.2.1.1r
2Solvent CDCl3
3Temperature 296.8
4Number of Scans 512
6Nucleus 13C
Cl
O
O
N
N3H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

5d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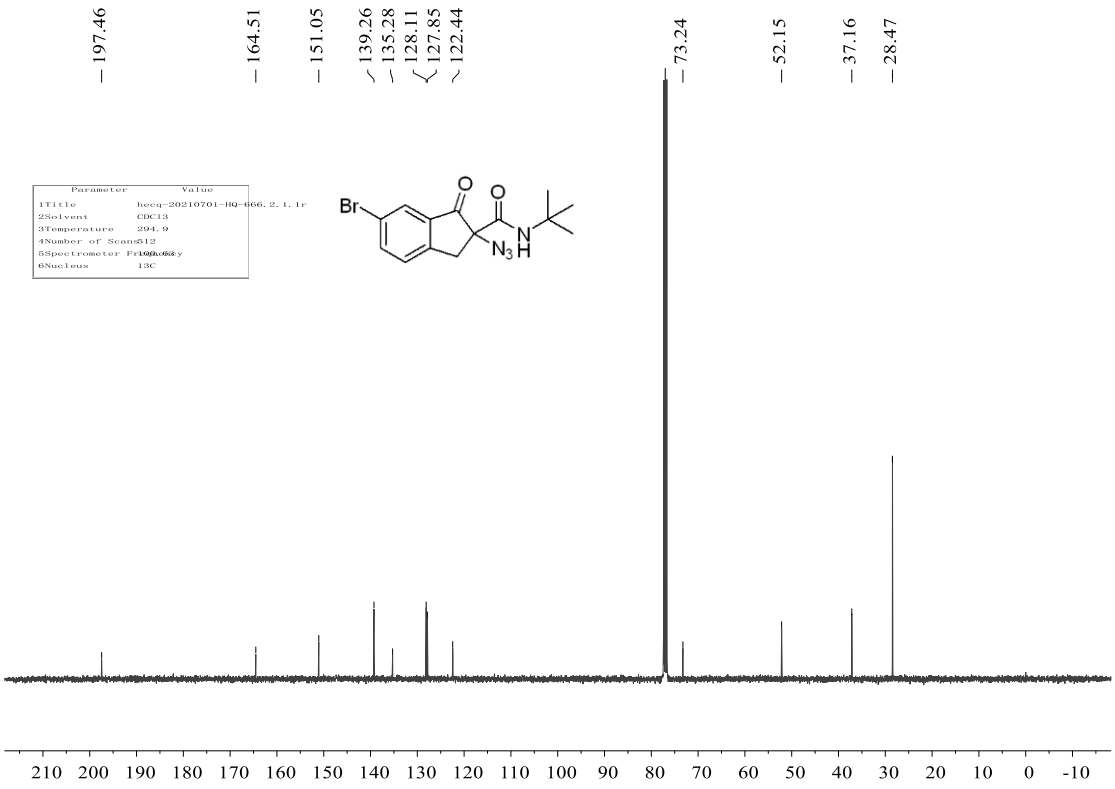
7.76
7.76
7.40
7.38
6.56
3.95
3.91
3.14
3.09
1.36
Parameter Value
1Title hecq-20210701-HQ-666.1.1.1r
2Solvent CDCl3
3Temperature 294.1
4Number of Scans 64
6Nucleus 1H
Br
O
O
N
H
N3
0.9 1.0 1.0 0.9 1.0 1.0 9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

5d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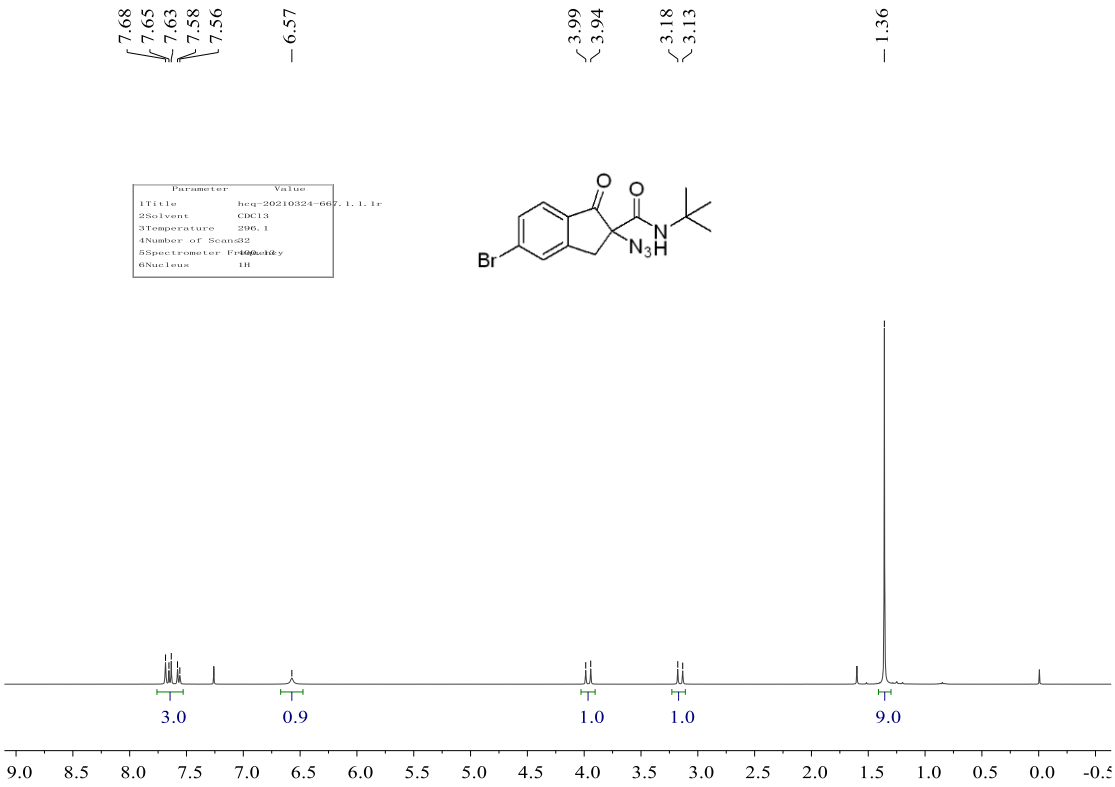
164.51
151.05
139.26
135.28
128.11
127.85
122.44
73.24
52.15
37.16
28.47
Parameter Value
1Title hecq-20210701-HQ-666.2.1.1r
2Solvent CDCl3
3Temperature 294.9
4Number of Scans 512
6Nucleus 13C
Br
O
O
N
H
N3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

5e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7.65
7.63
7.58
7.56
6.57
3.99
3.94
3.18
3.13
1.36
Parameter Value
1Title hcq-20210324-667.1.1.1r
2Solvent CDCl3
3Temperature 296.1
4Number of Scans32
6Nucleus 1H
Br
O
O
N
N3H
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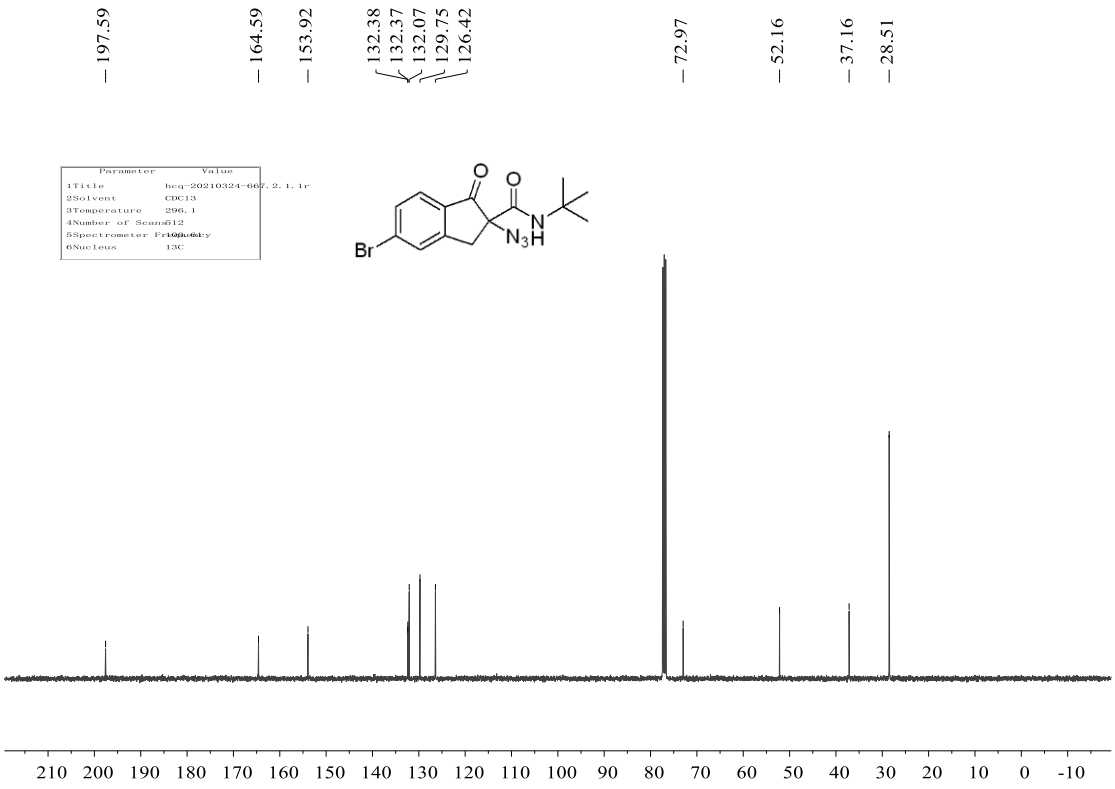
0.9
1.0
1.0
9.0

5e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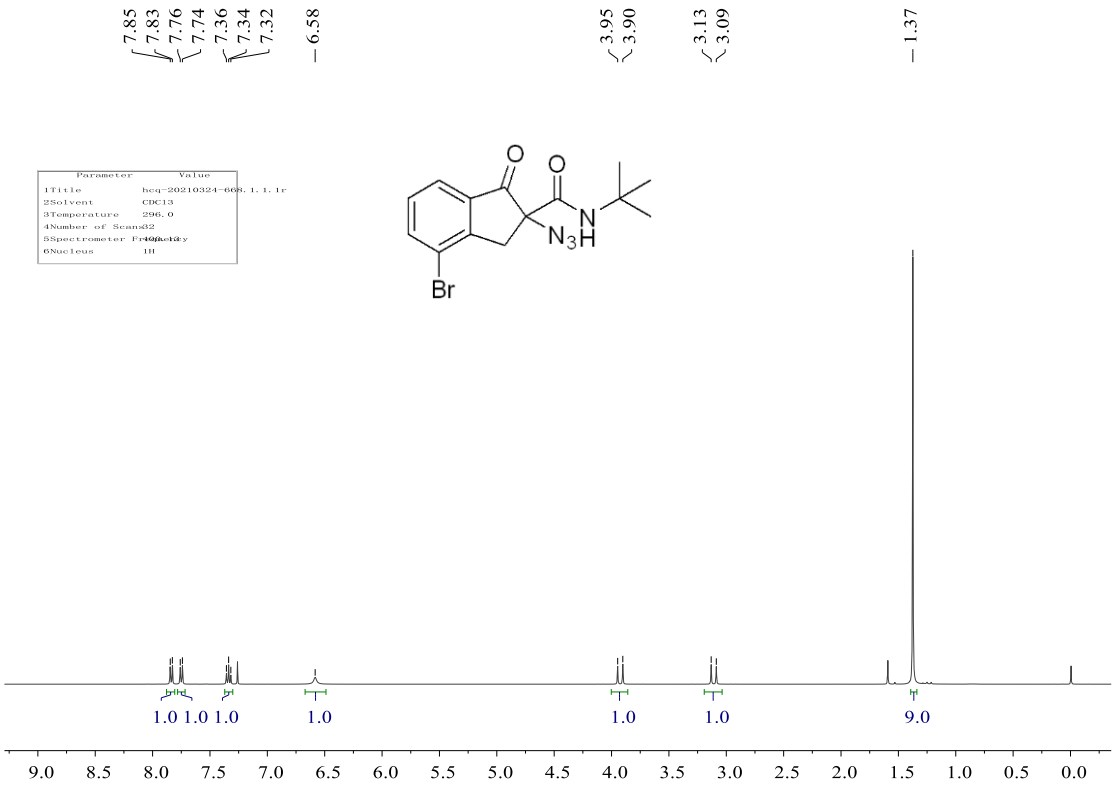
132.07
129.75
126.42
72.97
52.16
37.16
28.51
Parameter Value
1Title hcq-20210324-667.2.1.1r
2Solvent CDCl3
3Temperature 296.1
4Number of Scans612
6Nucleus 13C
Br
O
O
N
N3H

5f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7.74
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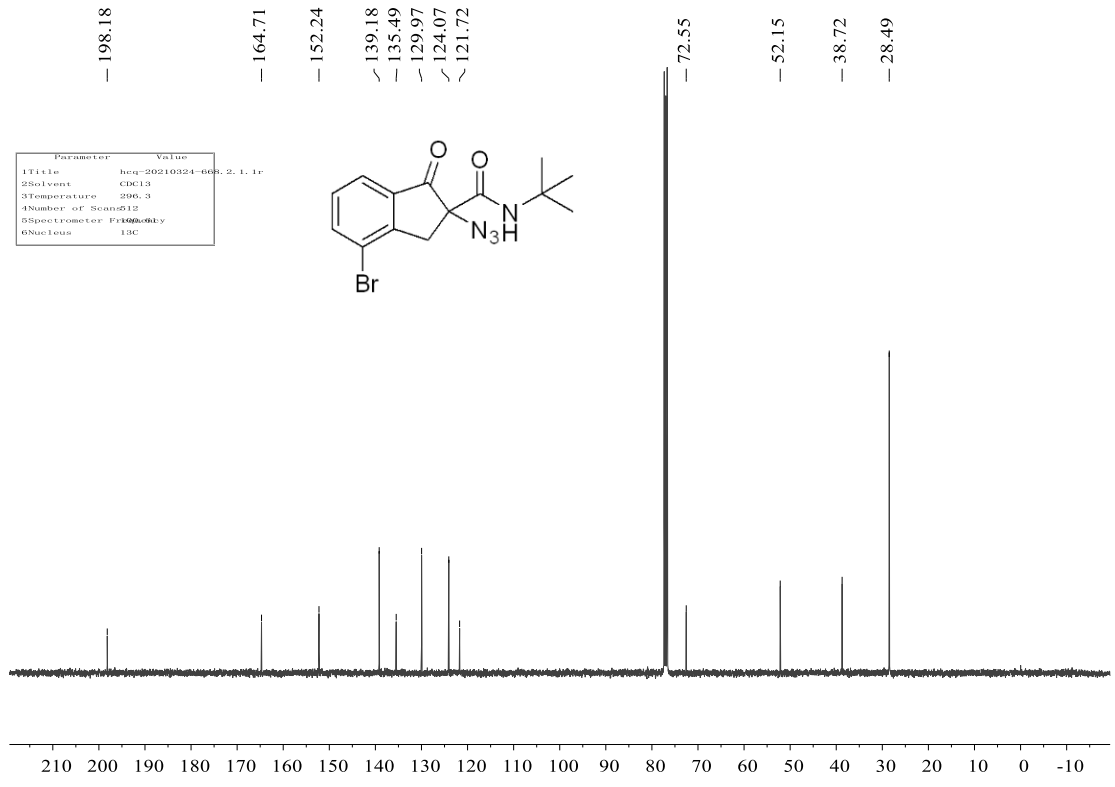
7.34
7.32
6.58
3.95
3.90
3.13
3.09
1.37
Parameter Value
1Title hcq-20210324-668.1.1.1r
2Solvent CDCl3
3Temperature 296.0
4Number of Scans32
6Nucleus 1H
O
O
N
N3H
Br
1.0 1.0 1.0 1.0 1.0 1.0 9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

5f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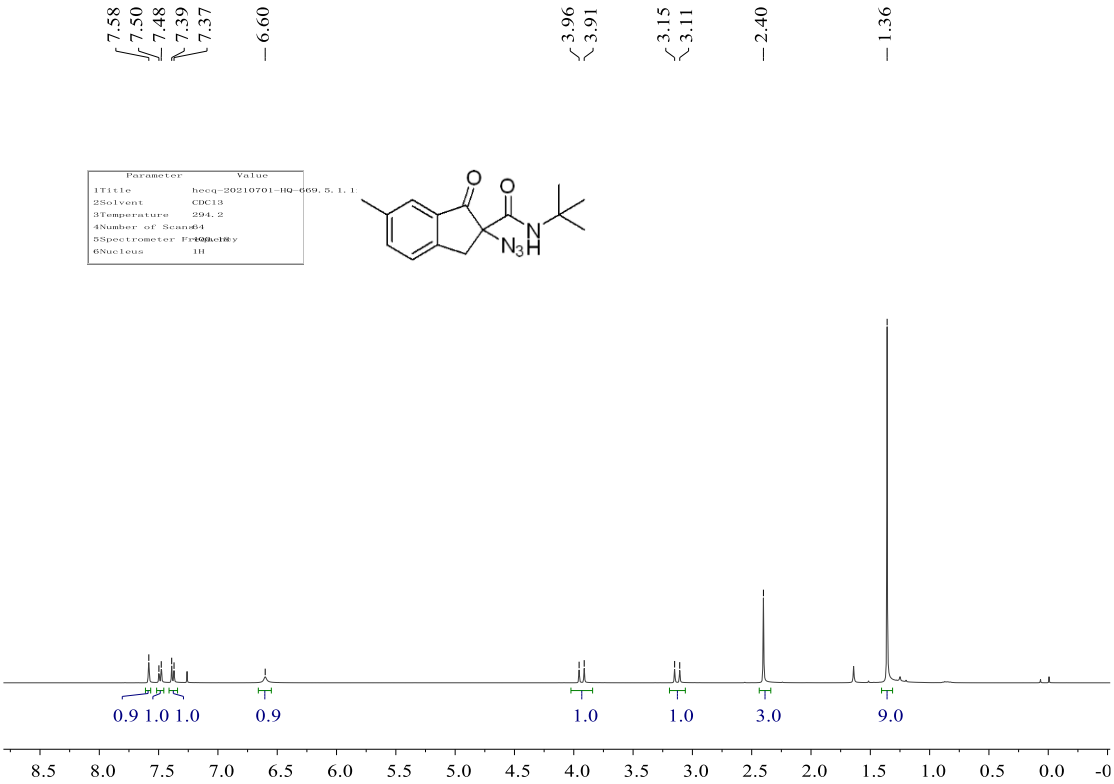
152.24
139.18
135.49
129.97
124.07
121.72
72.55
52.15
38.72
28.49
Parameter Value
1Title hcq-20210324-668.2.1.1r
2Solvent CDCl3
3Temperature 296.3
4Number of Scans512
6Nucleus 13C
O
O
N
N3H
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

5g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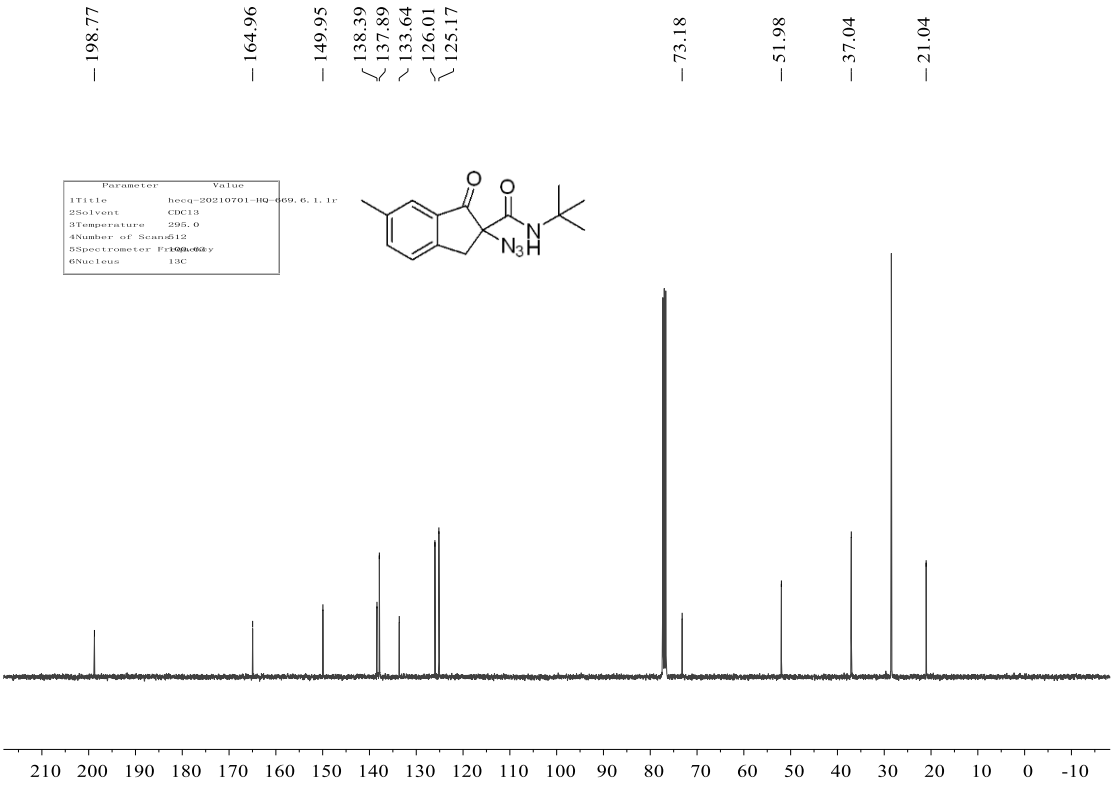
7.37
6.60
3.96
3.91
3.15
3.11
2.40
1.36
Parameter Value
1Title hecq-20210701-HQ-669.5.1.1
2Solvent CDCl3
3Temperature 294.2
4Number of Scans 64
5Spectrometer Fr
6Nucleus 1H
O
O
N3H
0.9 1.0 1.0 0.9 1.0 1.0 3.0 9.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

5g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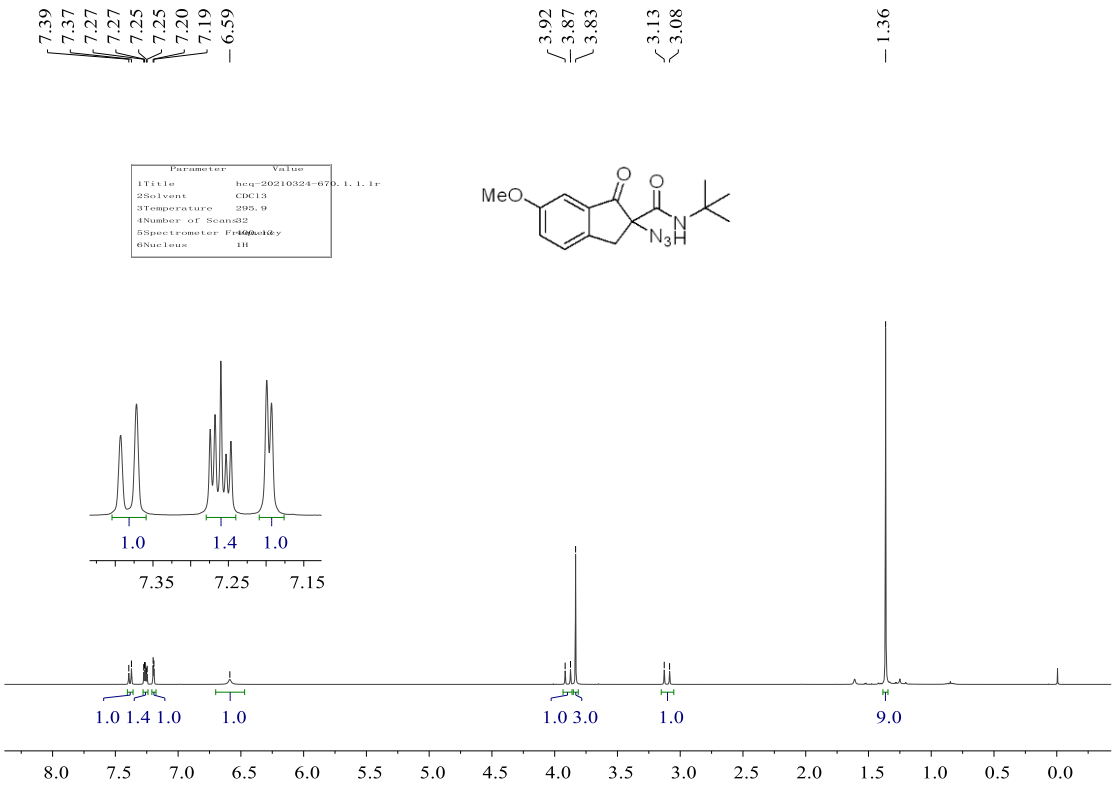
137.89
133.64
126.01
125.17
73.18
51.98
37.04
21.04
Parameter Value
1Title hecq-20210701-HQ-669.6.1.1r
2Solvent CDCl3
3Temperature 295.0
4Number of Scans 612
5Spectrometer Fr
6Nucleus 13C
O
O
N3H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

5h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7.20
7.19
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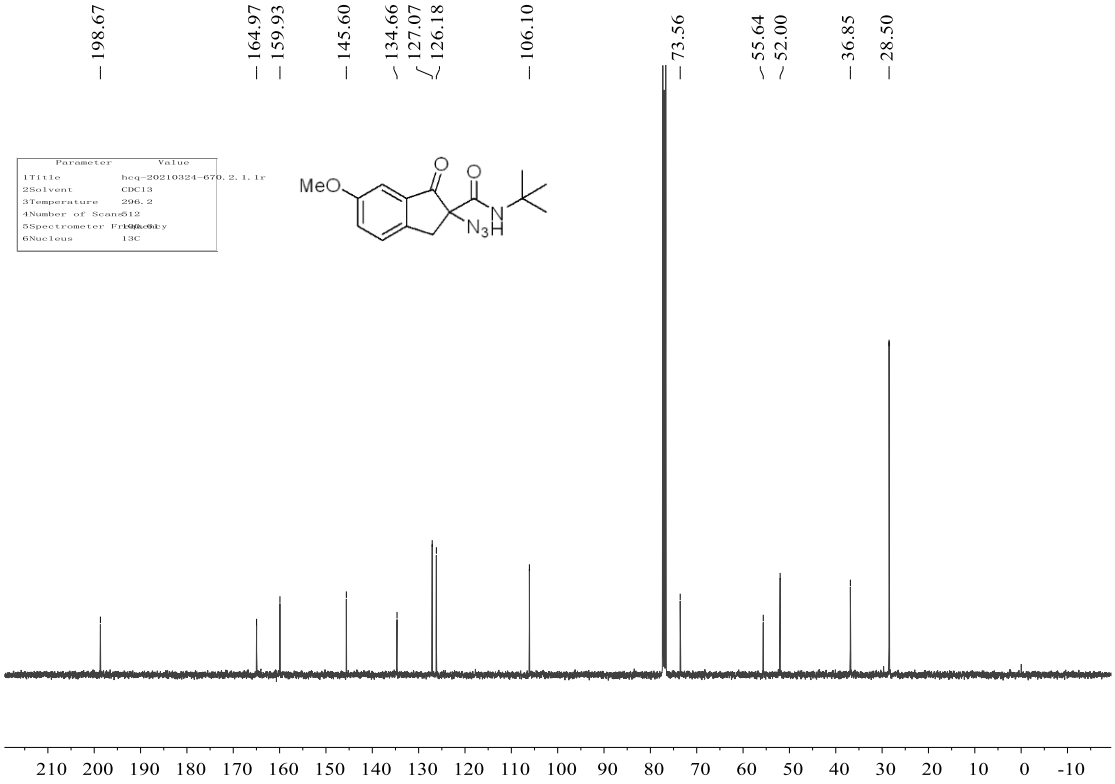
3.87
3.83
3.13
3.08
1.36
MeO
O
O
N
N3H
1.0
1.4
1.0
7.35
7.25
7.15
1.0 1.4 1.0
1.0
1.0 3.0
1.0
9.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

5h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145.60
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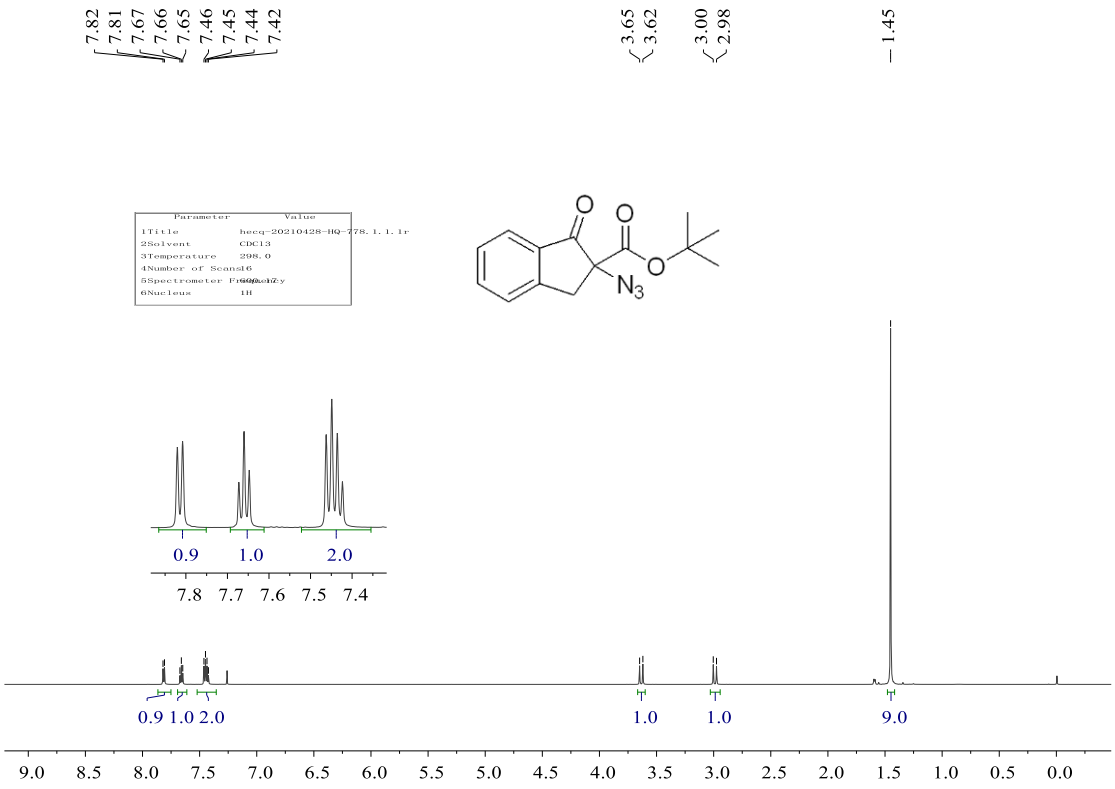
127.07
126.18
106.10
73.56
55.64
52.00
36.85
28.50
MeO
O
O
N
N3H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

5i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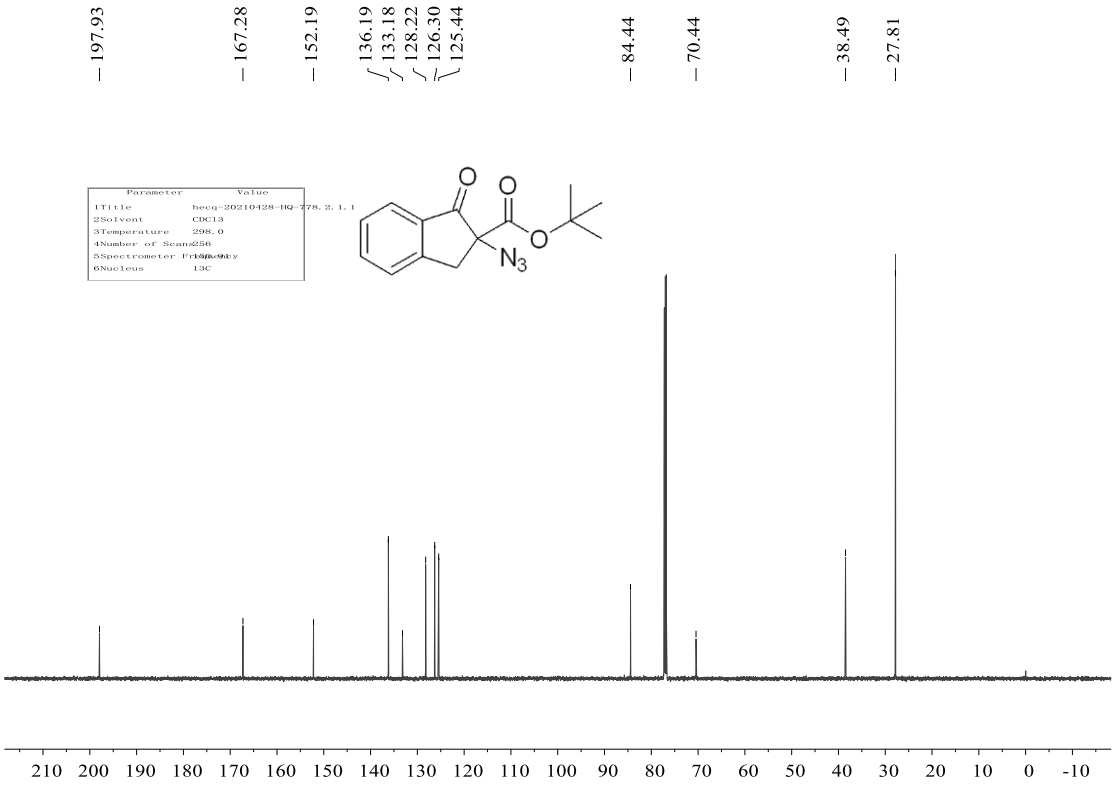
7.46
7.45
7.44
7.42
3.65
3.62
3.00
2.98
1.45
Parameter Value
1Title hecq-20210428-HQ-778.1.1.1r
2Solvent CDCl3
3Temperature 298.0
4Number of Scans16
5Spectrometer Frequency
6Nucleus 1H
O
O
O
N3
0.9 1.0 2.0
7.8 7.7 7.6 7.5 7.4
0.9 1.0 2.0
1.0
1.0
9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

5i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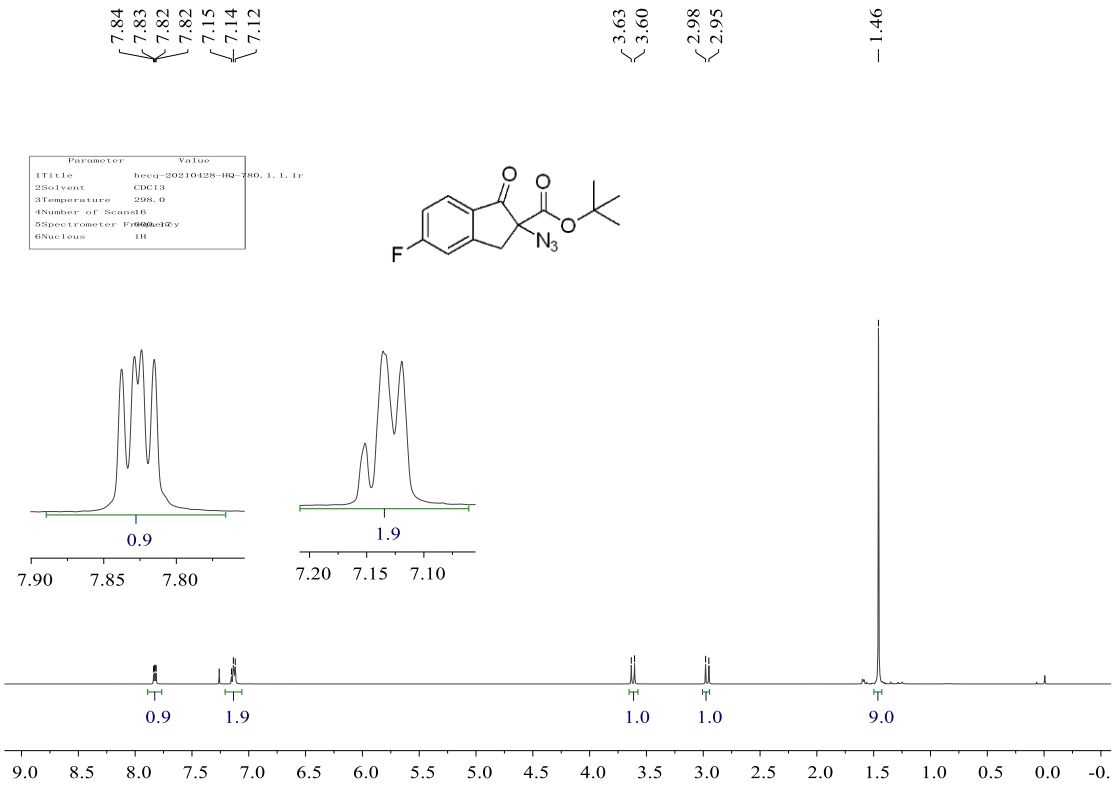
152.19
136.19
133.18
128.22
126.30
125.44
84.44
70.44
38.49
27.81
Parameter Value
1Title hecq-20210428-HQ-778.2.1.1
2Solvent CDCl3
3Temperature 298.0
4Number of Scans256
5Spectrometer Frequency
6Nucleus 13C
O
O
O
N3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

5j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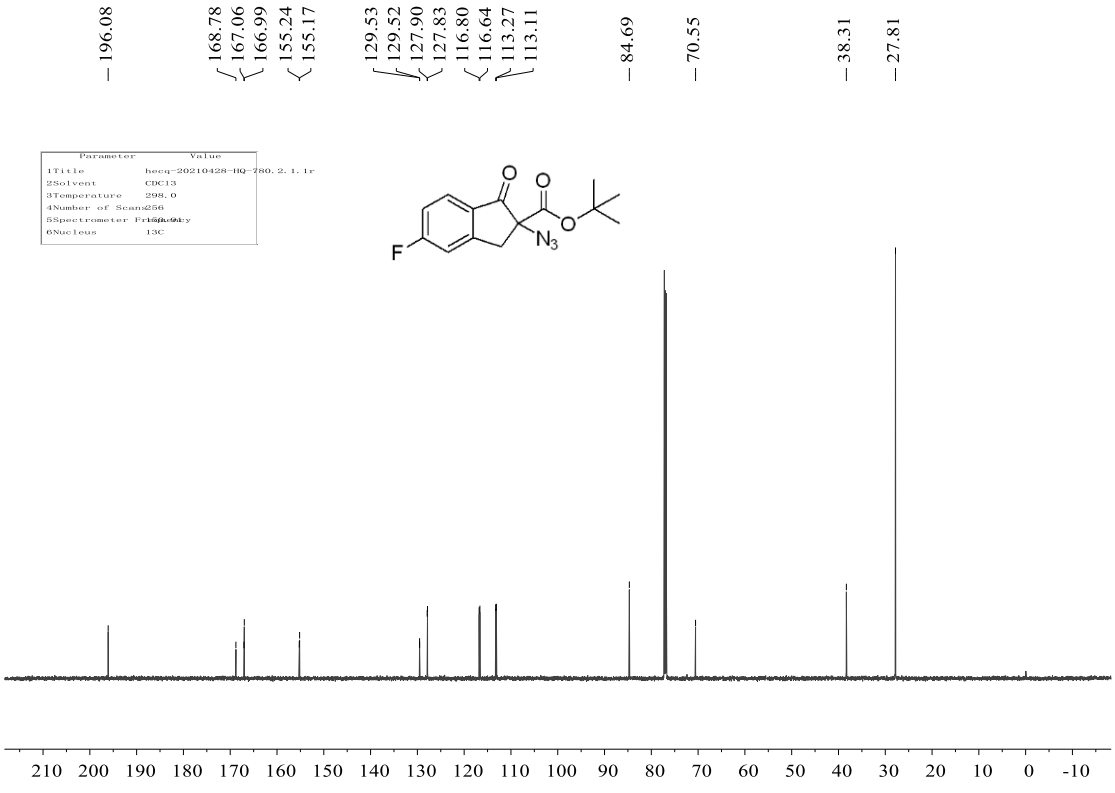
7.83
7.82
7.82
7.15
7.14
7.12
3.63
3.60
2.98
2.95
1.46
Parameter Value
1Title hecq-20210428-HQ-780. 1. 1. 1r
2Solvent CDCl3
3Temperature 298. 0
4Number of Scans16
6Nucleus 1H
F
O
O
O
N3
0.9
1.9
7.90 7.85 7.80
7.20 7.15 7.10
0.9 1.9 1.0 1.0 9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.

5j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155.17
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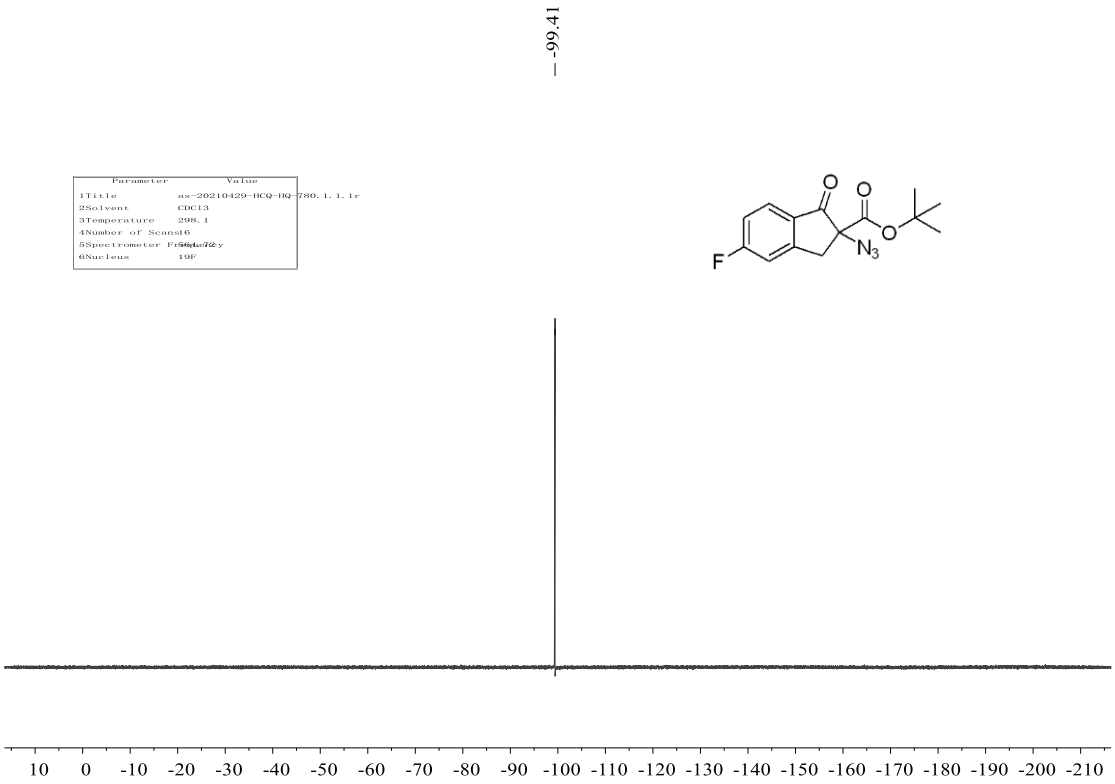
129.52
127.90
127.83
116.80
116.64
113.27
113.11
84.69
70.55
38.31
27.81
Parameter Value
1Title hecq-20210428-HQ-780. 2. 1. 1r
2Solvent CDCl3
3Temperature 298. 0
4Number of Scans256
6Nucleus 13C
F
O
O
O
N3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

5j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3Temperature 298.1
4Number of Scans16
5Spectrometer Frequency
6Nucleus 19F
O
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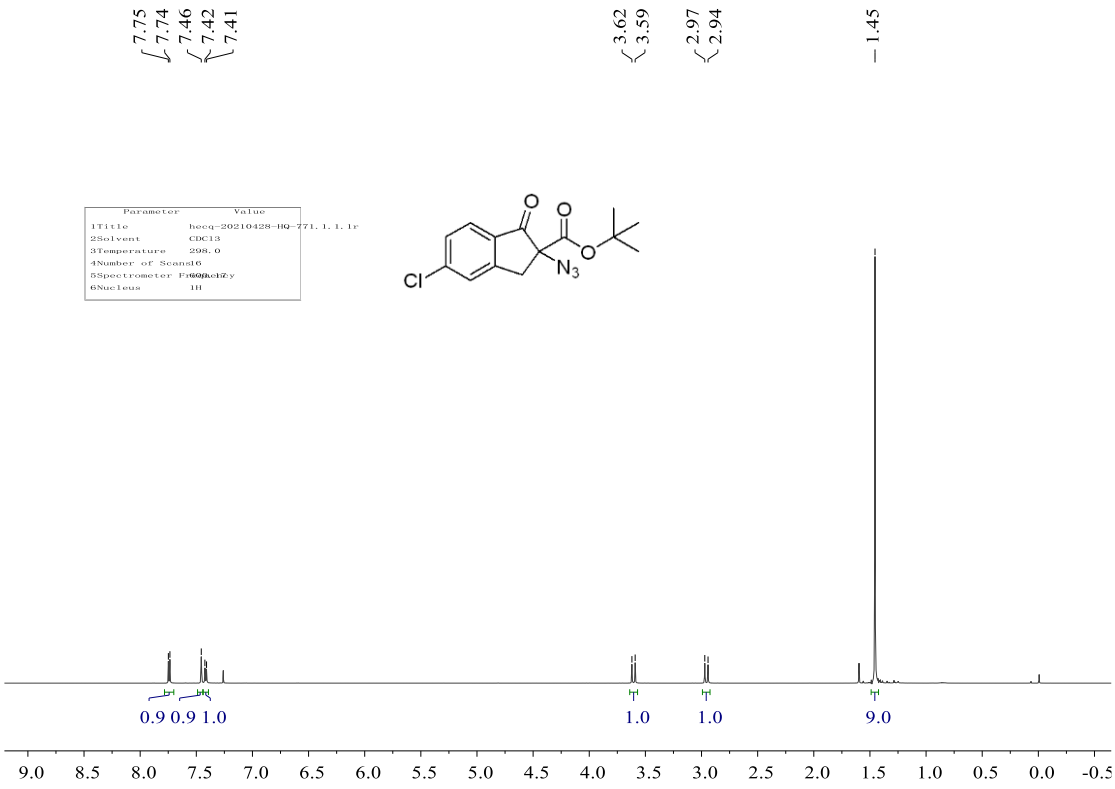
O
N3
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

5k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3.59
2.97
2.94
1.45
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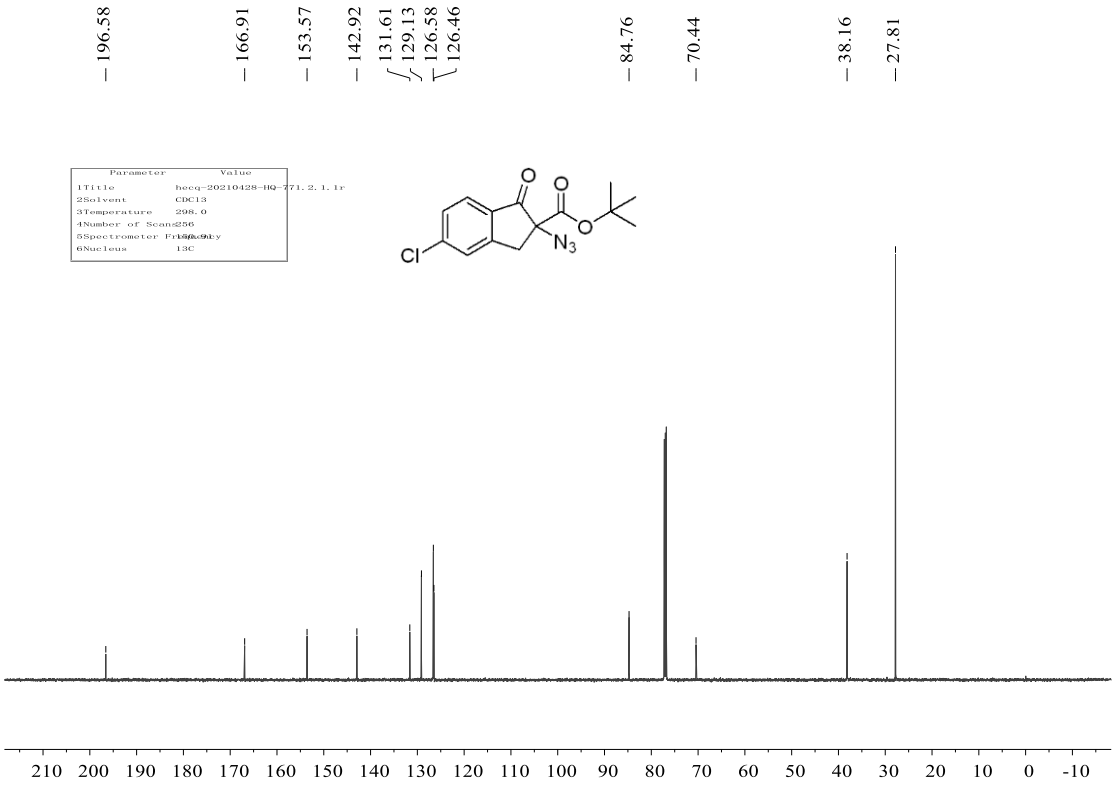
2Solvent CDCl3
3Temperature 298.0
4Number of Scans 16
6Nucleus 1H
Cl
N3
0.9 0.9 1.0
1.0
1.0
9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

5k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126.46
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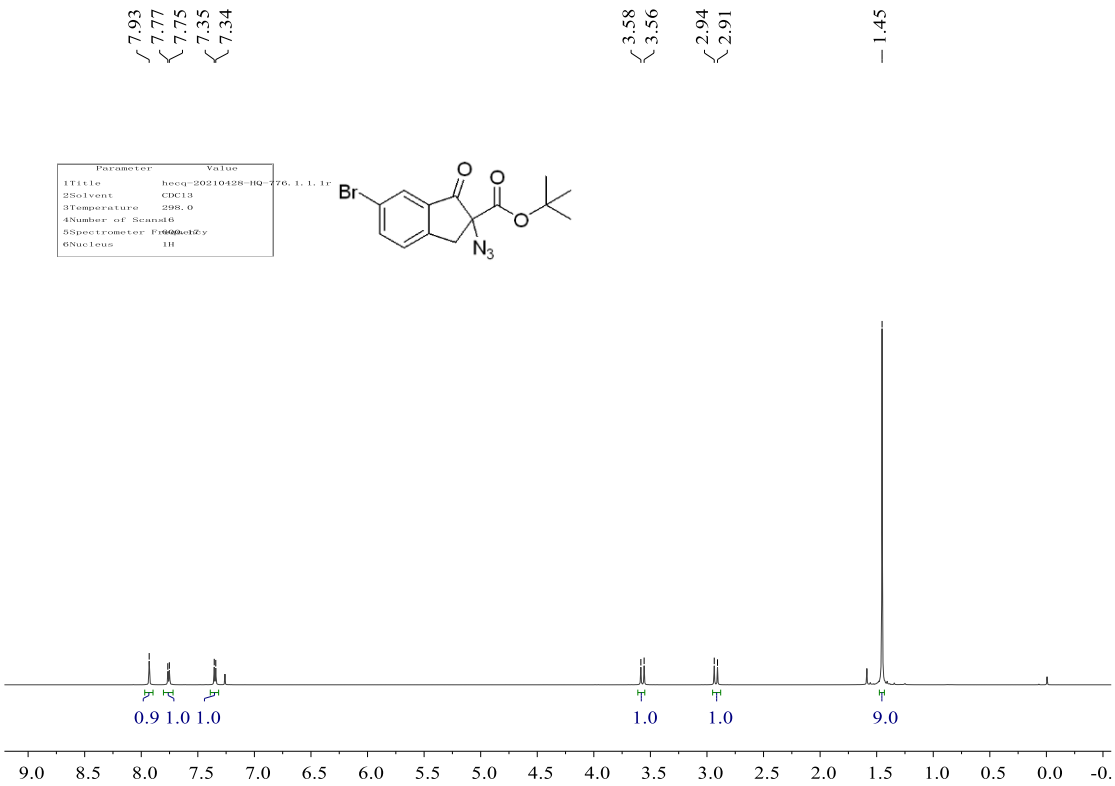
70.44
38.16
27.81
Parameter Value
1Title hecq-20210428-HQ-771.2.1.1r
2Solvent CDCl3
3Temperature 298.0
4Number of Scans 256
6Nucleus 13C
Cl
N3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

5l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3.56
2.94
2.91
1.45
Parameter Value
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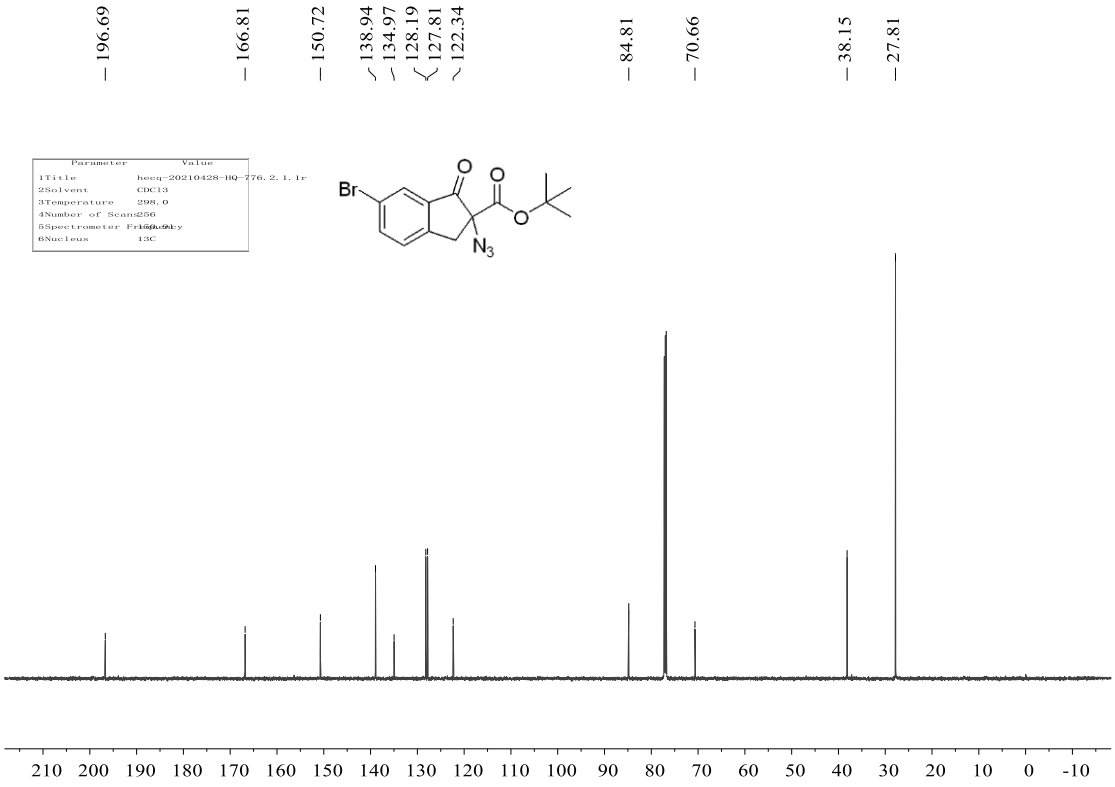
2Solvent CDCl3
3Temperature 298.0
4Number of Scans 16
6Nucleus 1H
Br
O
O
N3
0.9 1.0 1.0
1.0
1.0
9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.

5l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128.19
127.81
122.34
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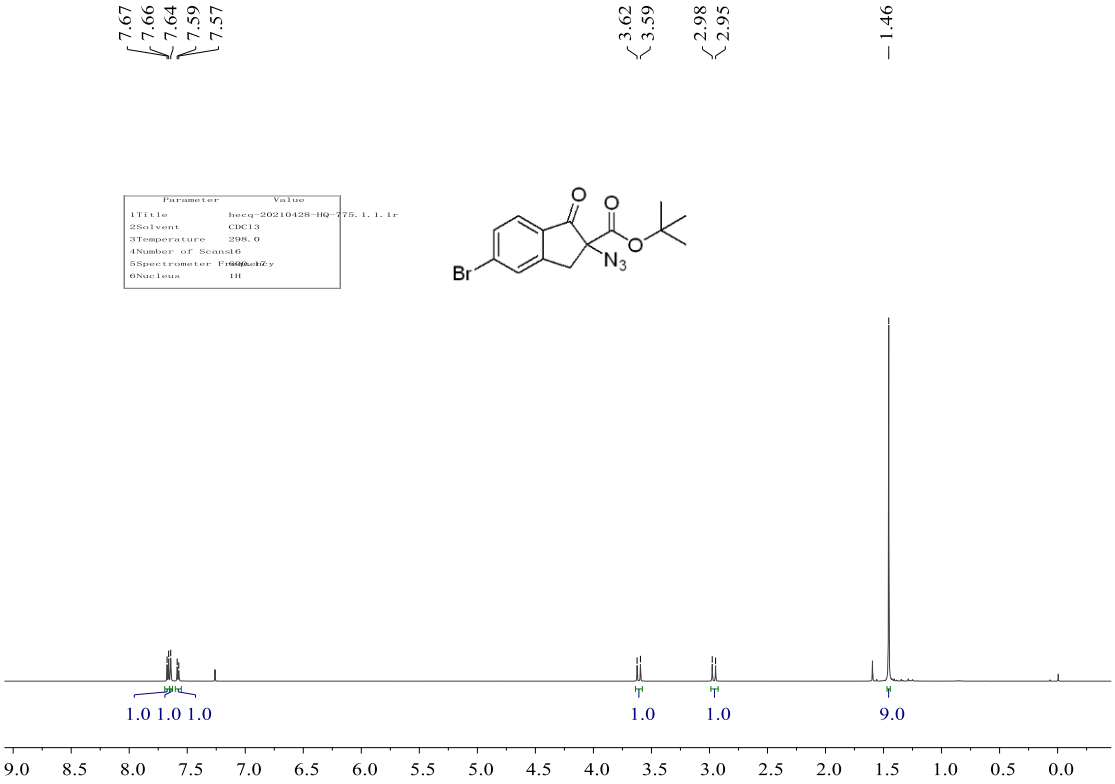
70.66
38.15
27.81
Parameter Value
1Title hecq-20210428-HQ-776.2.1.1r
2Solvent CDCl3
3Temperature 298.0
4Number of Scans 256
6Nucleus 13C
Br
O
O
N3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

5m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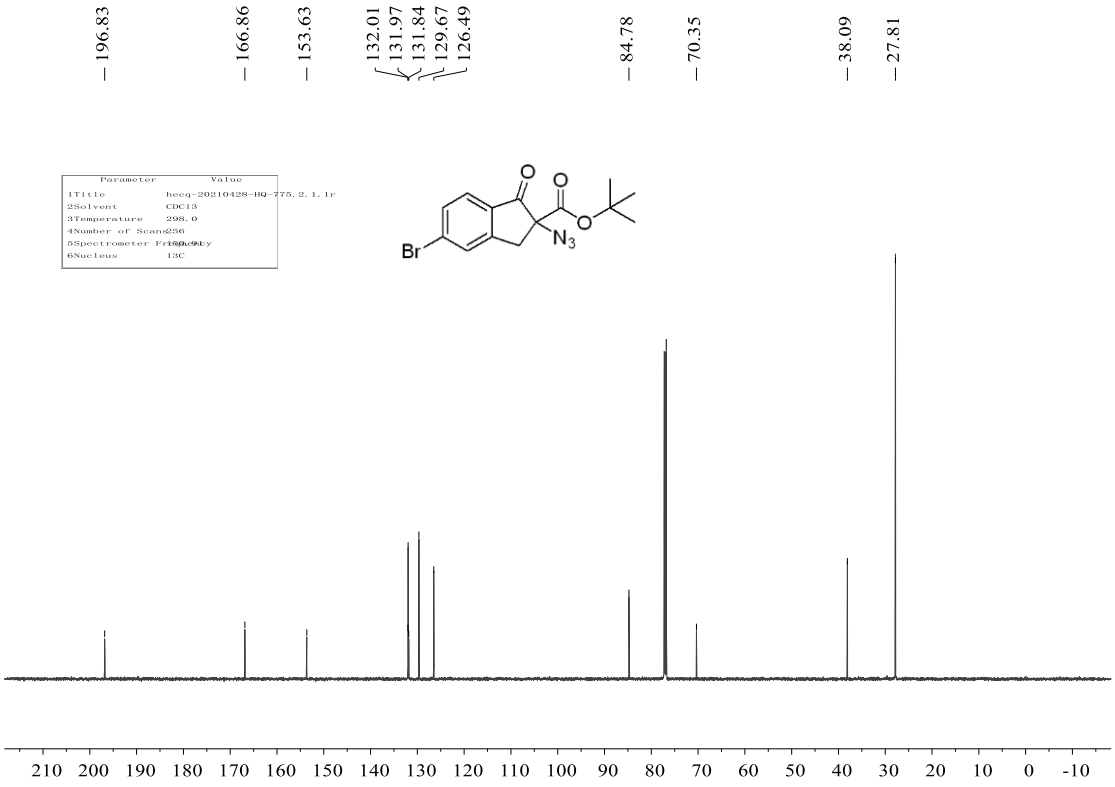
7.57
3.62
3.59
2.98
2.95
1.46
Parameter Value
1Title hecq-20210428-HQ-775.1.1.1r
2Solvent CDCl3
3Temperature 298.0
4Number of Scans16
5Spectrometer Fr
6Nucleus 1H
O
O
O
N3
Br
1.0 1.0 1.0
1.0
1.0
9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

5m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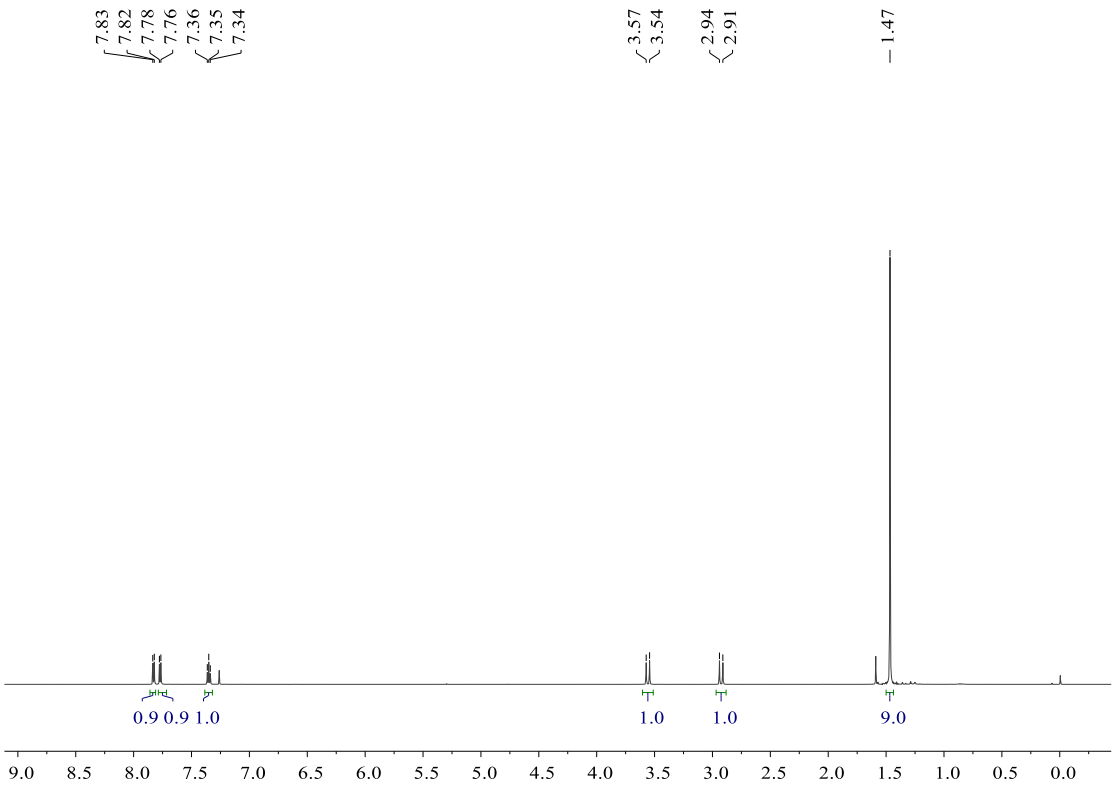
132.01
131.97
131.84
129.67
126.49
84.78
70.35
38.09
27.81
Parameter Value
1Title hecq-20210428-HQ-775.2.1.1r
2Solvent CDCl3
3Temperature 298.0
4Number of Scans256
5Spectrometer Fr
6Nucleus 13C
O
O
O
N3
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

5n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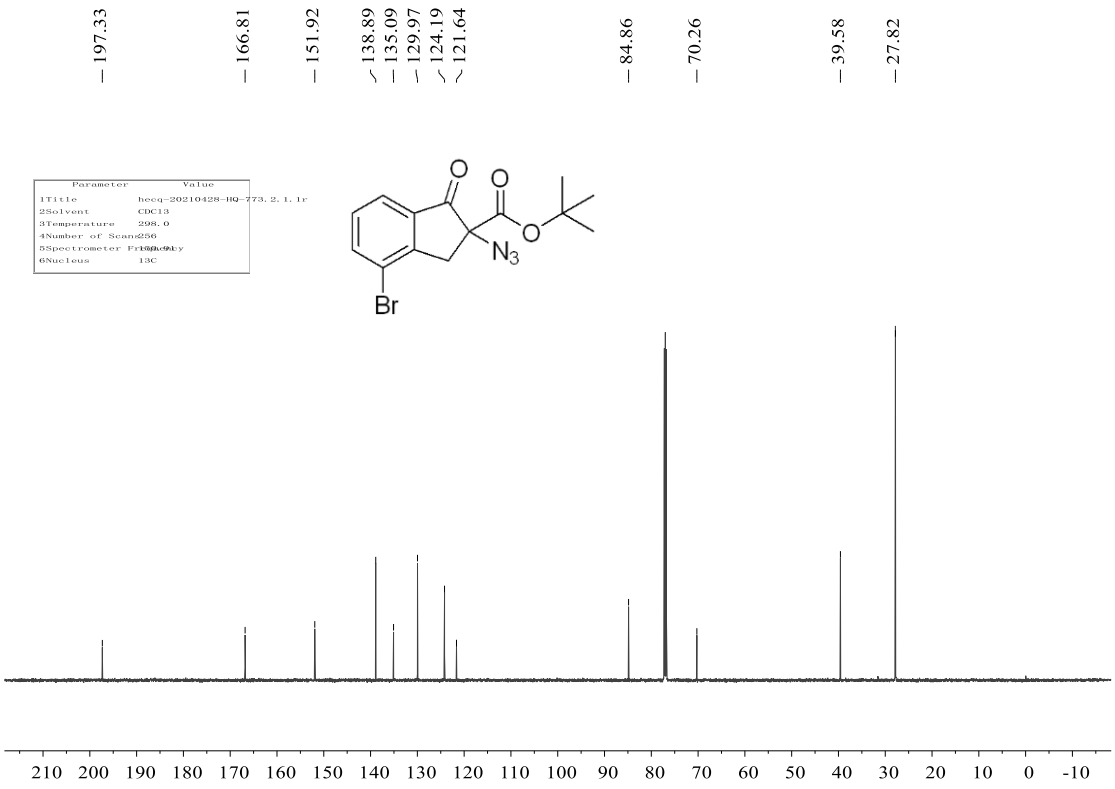
7.82
7.78
7.76
7.36
7.35
7.34
3.57
3.54
2.94
2.91
1.47
0.9 0.9 1.0
1.0
1.0
9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

5n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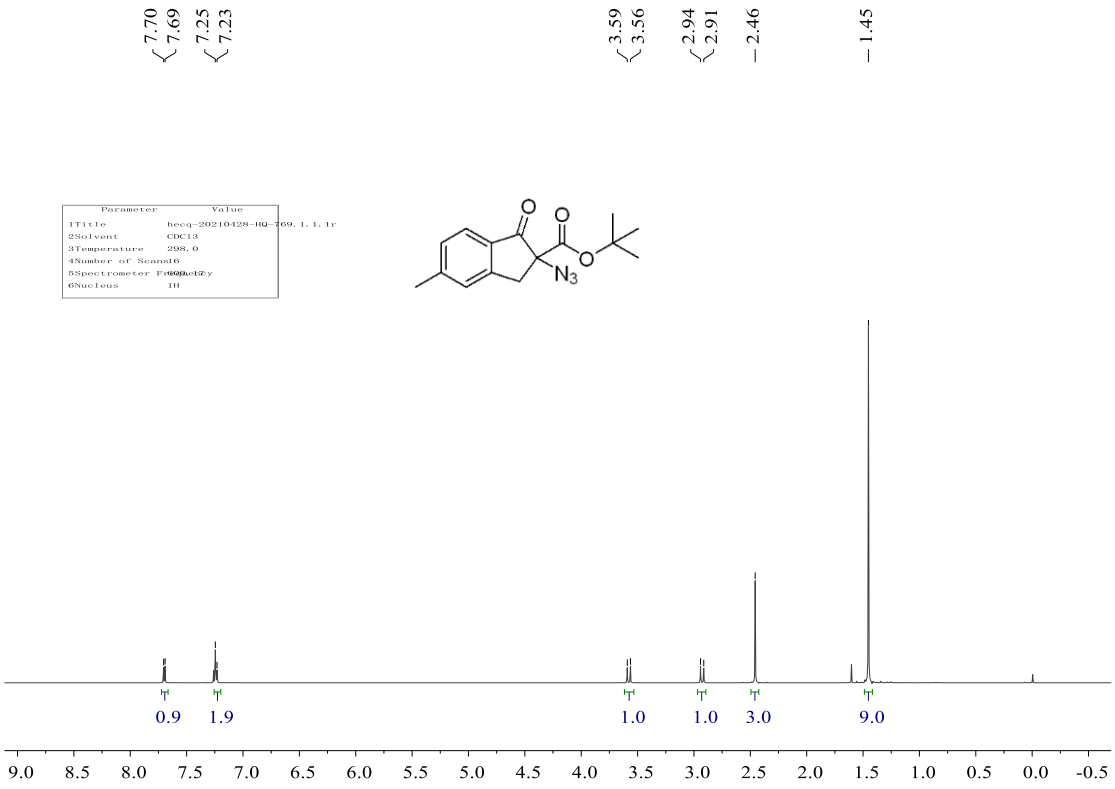
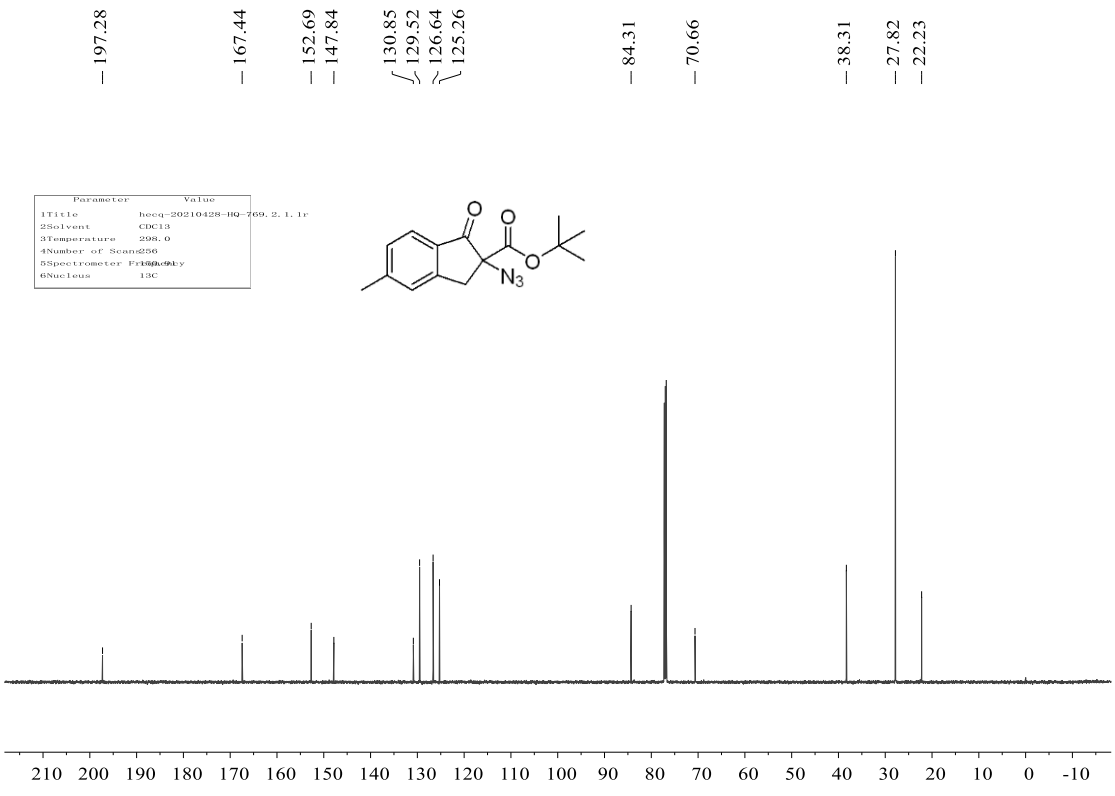
166.81
151.92
138.89
135.09
129.97
124.19
121.64
84.86
70.26
39.58
27.82
Parameter Value
1Title hecq-20210428-HQ-773.2.1.1r
2Solvent CDCl3
3Temperature 298.0
4Number of Scans 256
5Spectrometer Prob
6Nucleus 13C
O
O
O
N3
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

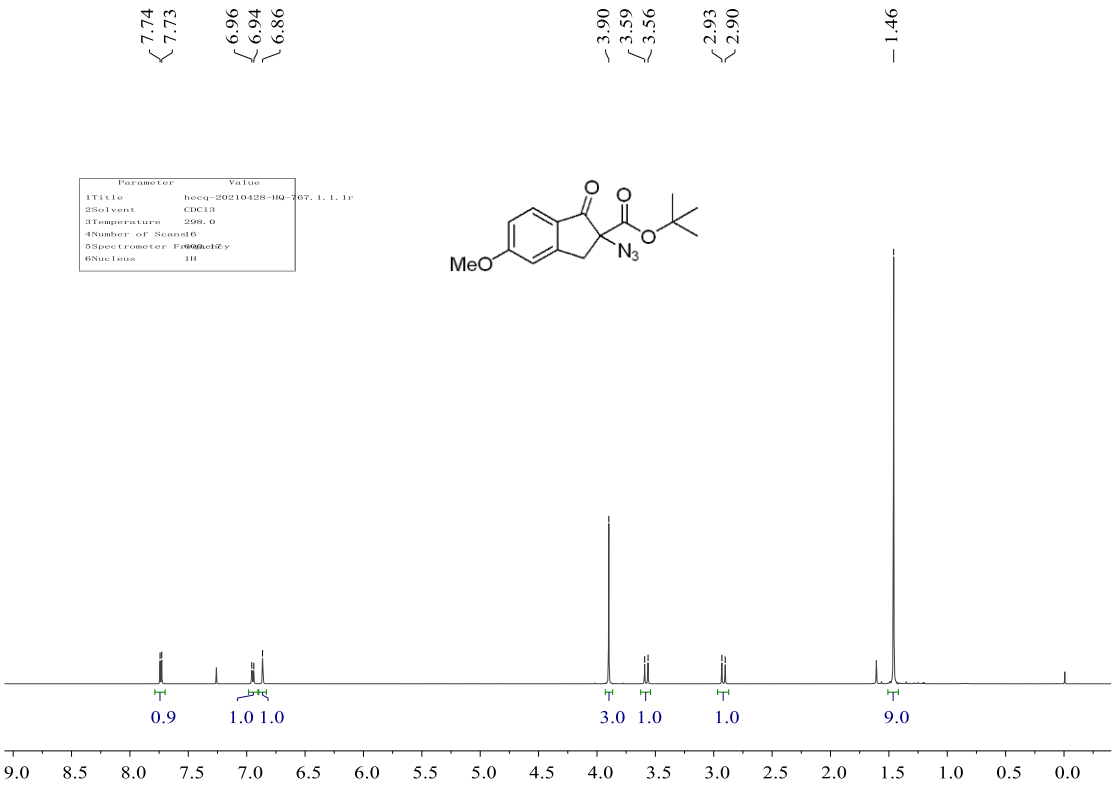
5o


7.70
7.69
7.25
7.23
3.59
3.56
2.94
2.91
2.46
1.45
Parameter Value
1Title hecq-20210428-HQ-769, 1, 1, 1r
2Solvent CDCl3
3Temperature 298.0
4Number of Scans 16
5Spectrometer Frequency
6Nucleus 1H
O
O
O
N3
0.9
1.9
1.0
1.0
3.0
9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

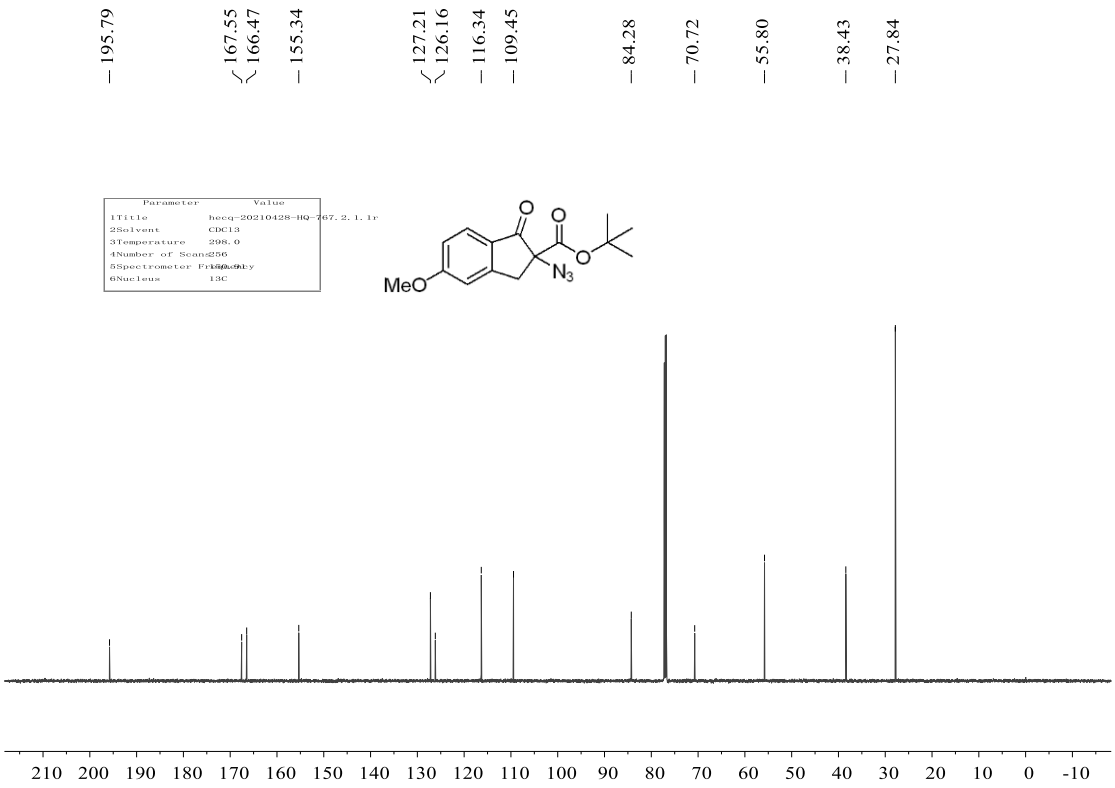
5o


197.28
167.44
152.69
147.84
130.85
129.52
126.64
125.26
84.31
70.66
38.31
27.82
22.23
Parameter Value
1Title hecq-20210428-HQ-769, 2, 1, 1r
2Solvent CDCl3
3Temperature 298.0
4Number of Scans 256
5Spectrometer Frequency
6Nucleus 13C
O
O
O
N3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

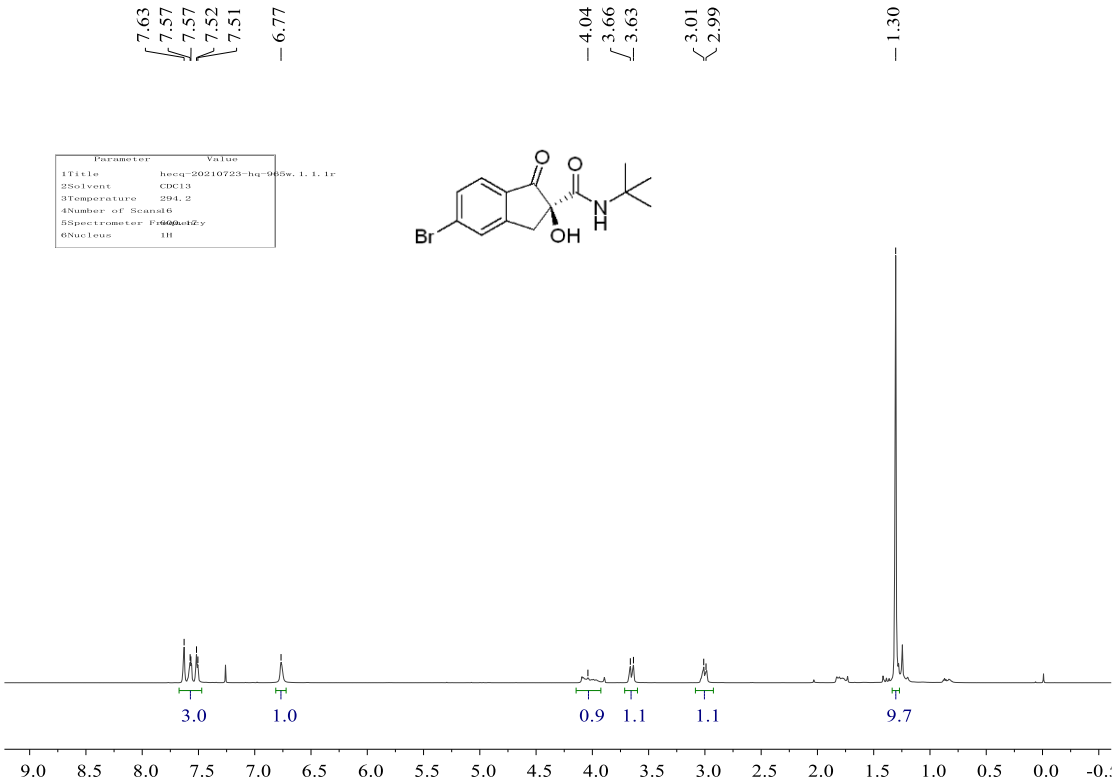
5p


7.74
7.73
6.96
6.94
6.86
3.90
3.59
3.56
2.93
2.90
1.46
Parameter Value
1Title hecq-20210428-HQ-767.1.1.1r
2Solvent CDCl3
3Temperature 298.0
4Number of Scans16
5Spectrometer Frequency
6Nucleus 1H
MeO
N3
0.9
1.0 1.0
3.0 1.0
1.0
9.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

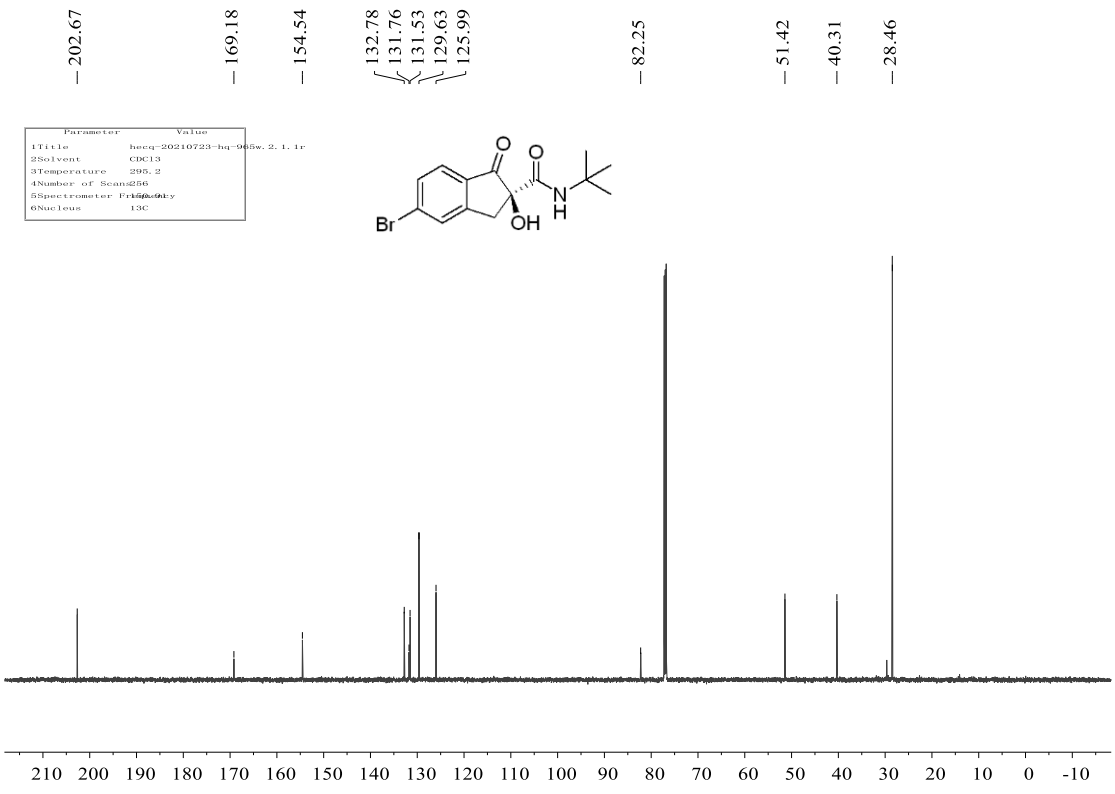
5p


195.79
167.55
166.47
155.34
127.21
126.16
116.34
109.45
84.28
70.72
55.80
38.43
27.84
Parameter Value
1Title hecq-20210428-HQ-767.2.1.1r
2Solvent CDCl3
3Temperature 298.0
4Number of Scans256
5Spectrometer Frequency
6Nucleus 13C
MeO
N3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

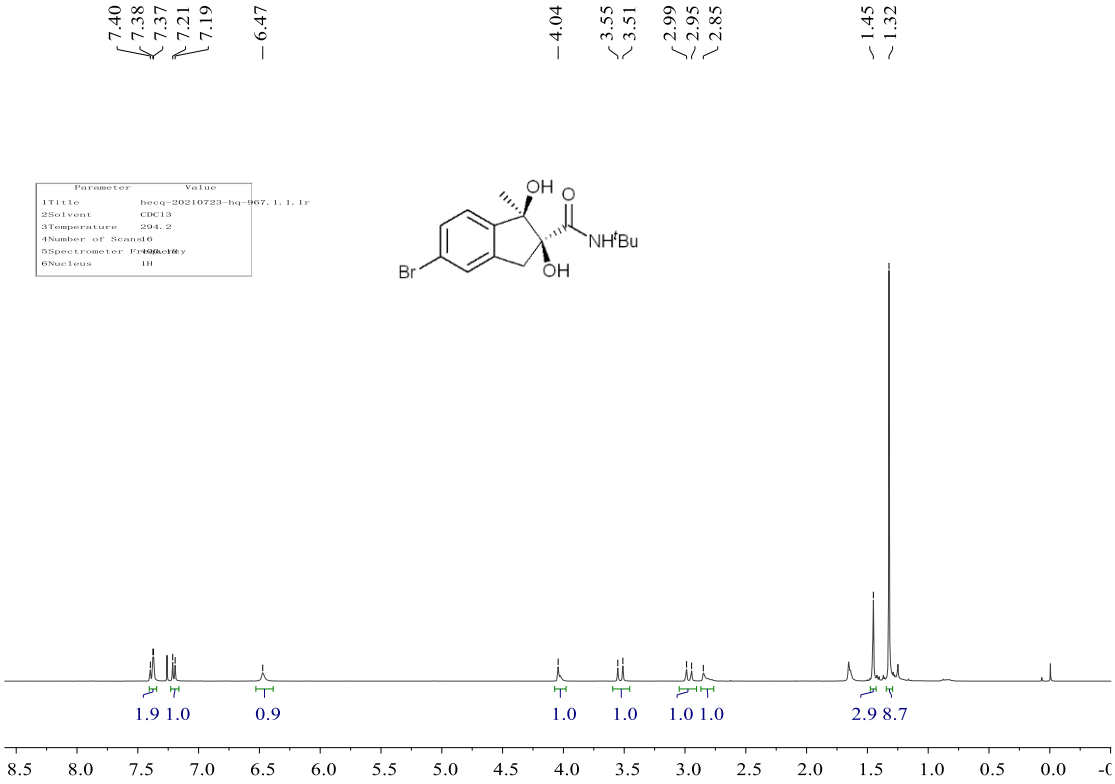
6


7.63
7.57
7.57
7.52
7.51
6.77
4.04
3.66
3.63
3.01
2.99
1.30
Parameter Value
1Title hecq-20210723-hq-965w.1.1.1r
2Solvent CDCl3
3Temperature 294.2
4Number of Scans 16
6Nucleus 1H
Br
OH
N
H
O
3.0
1.0
0.9
1.1
1.1
9.7
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

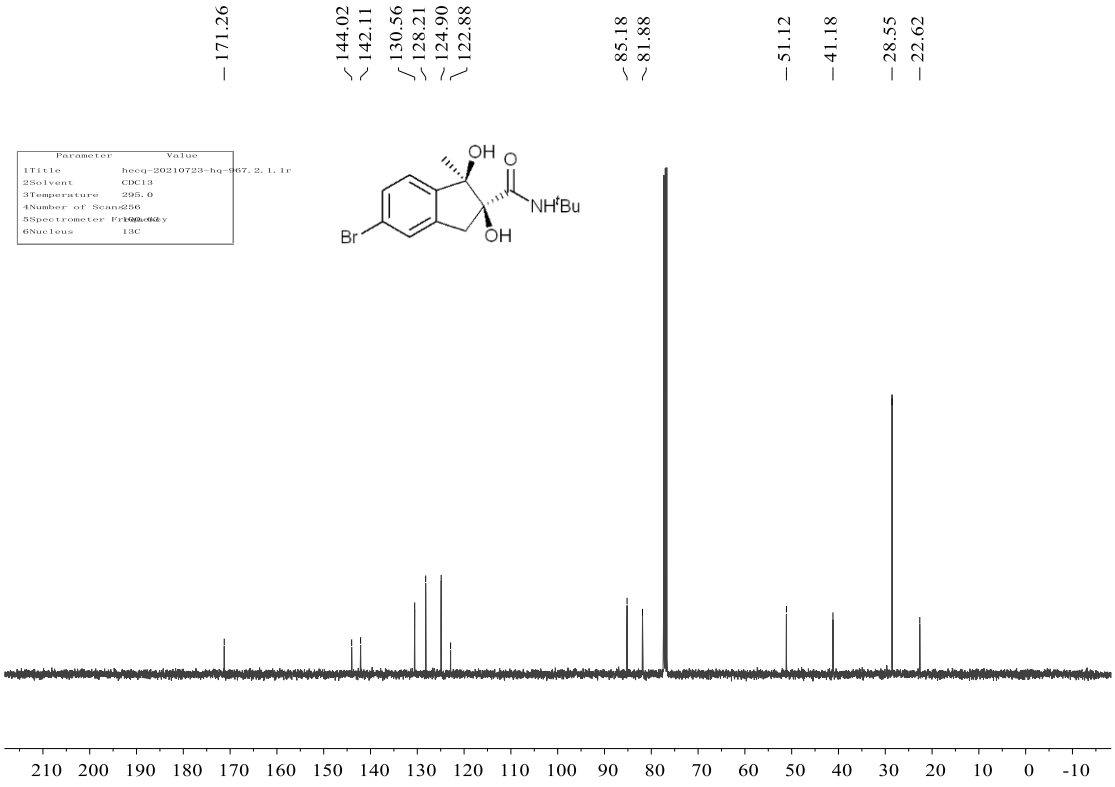
6


202.67
169.18
154.54
132.78
131.76
131.53
129.63
125.99
82.25
51.42
40.31
28.46
Parameter Value
1Title hecq-20210723-hq-965w.2.1.1r
2Solvent CDCl3
3Temperature 295.2
4Number of Scans 256
6Nucleus 13C
Br
OH
N
H
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

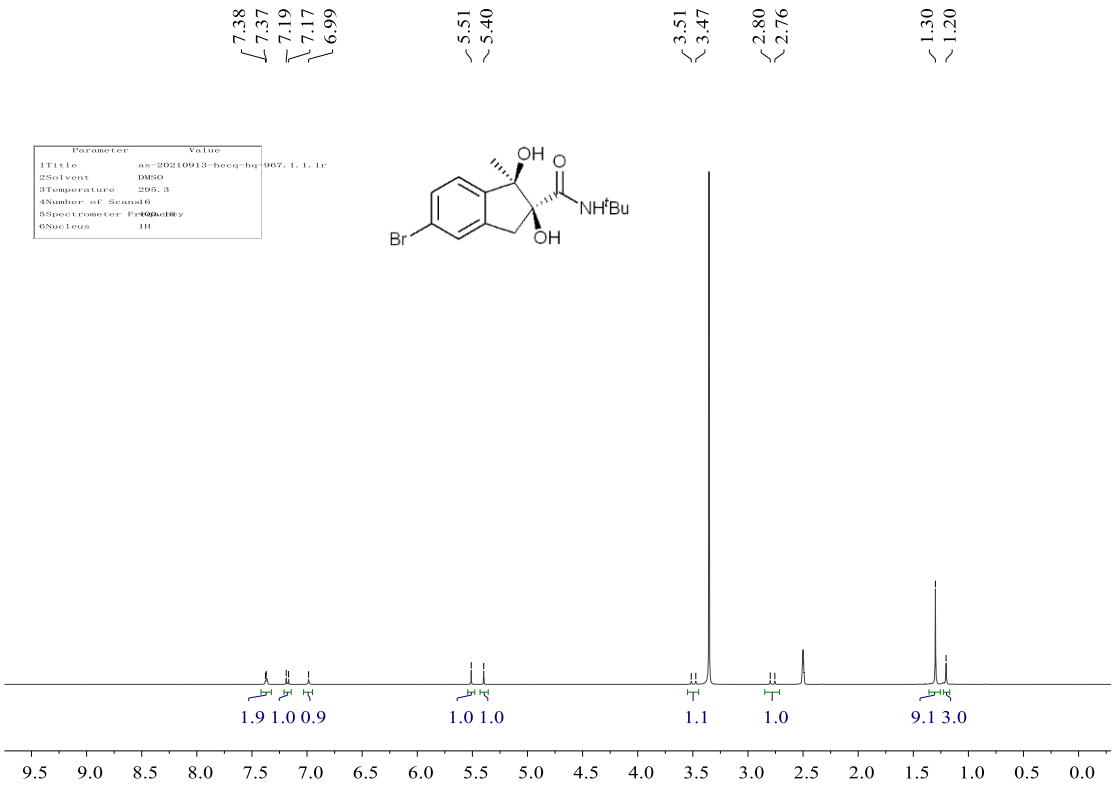
7 (in $CDCl_3$)



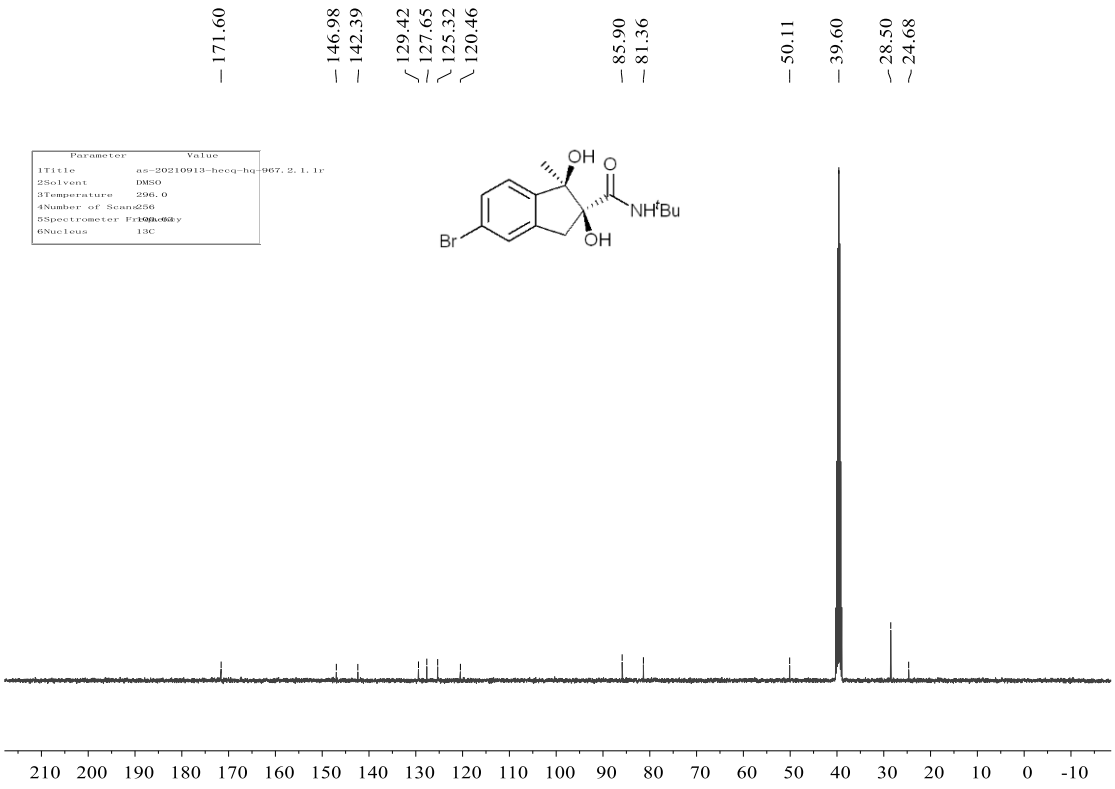
7 (in $CDCl_3$)



7 (in d_6-DMSO)

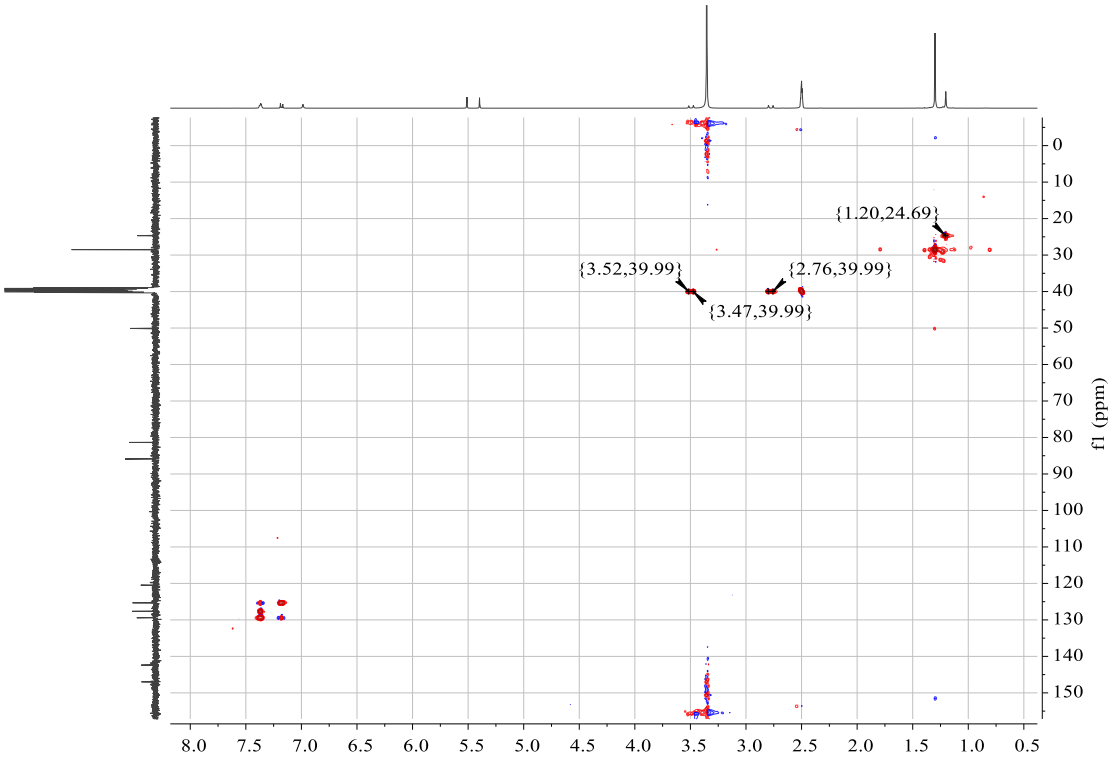


7 (in d_6-DMSO)



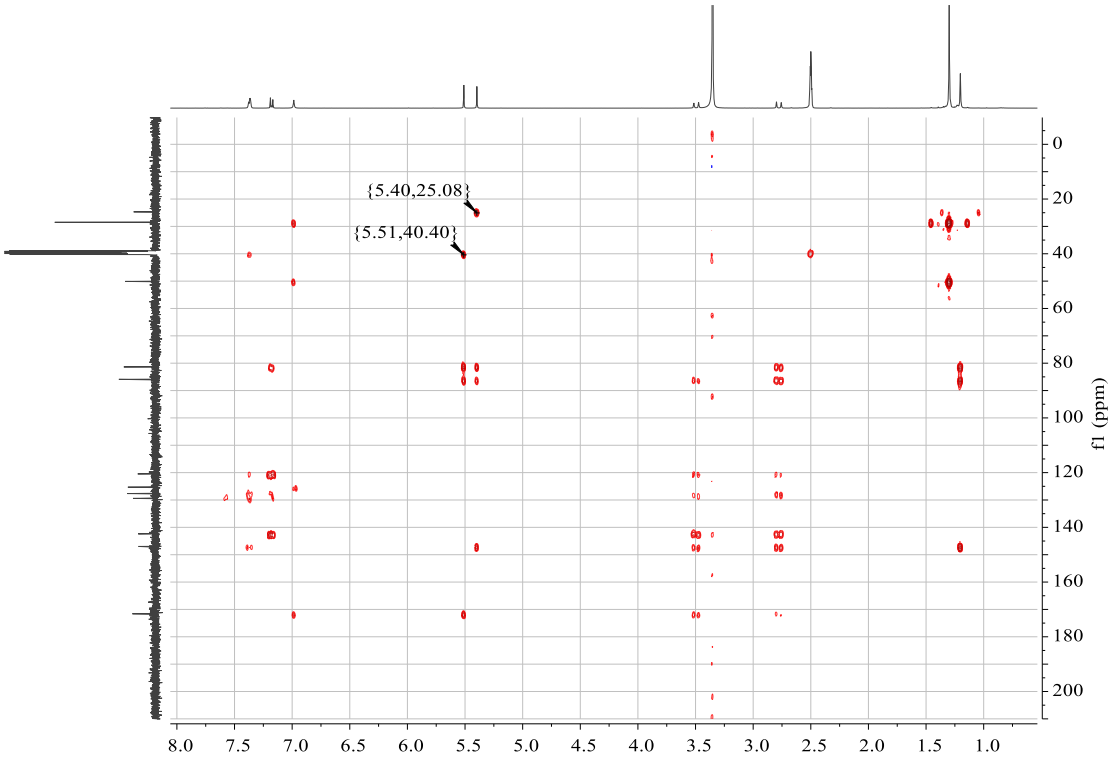
7 (in d_6-DMSO)

as-20210913-hecq-hq-967.5.1.2rr — HSQCGP DMSO {D:\data} as 46

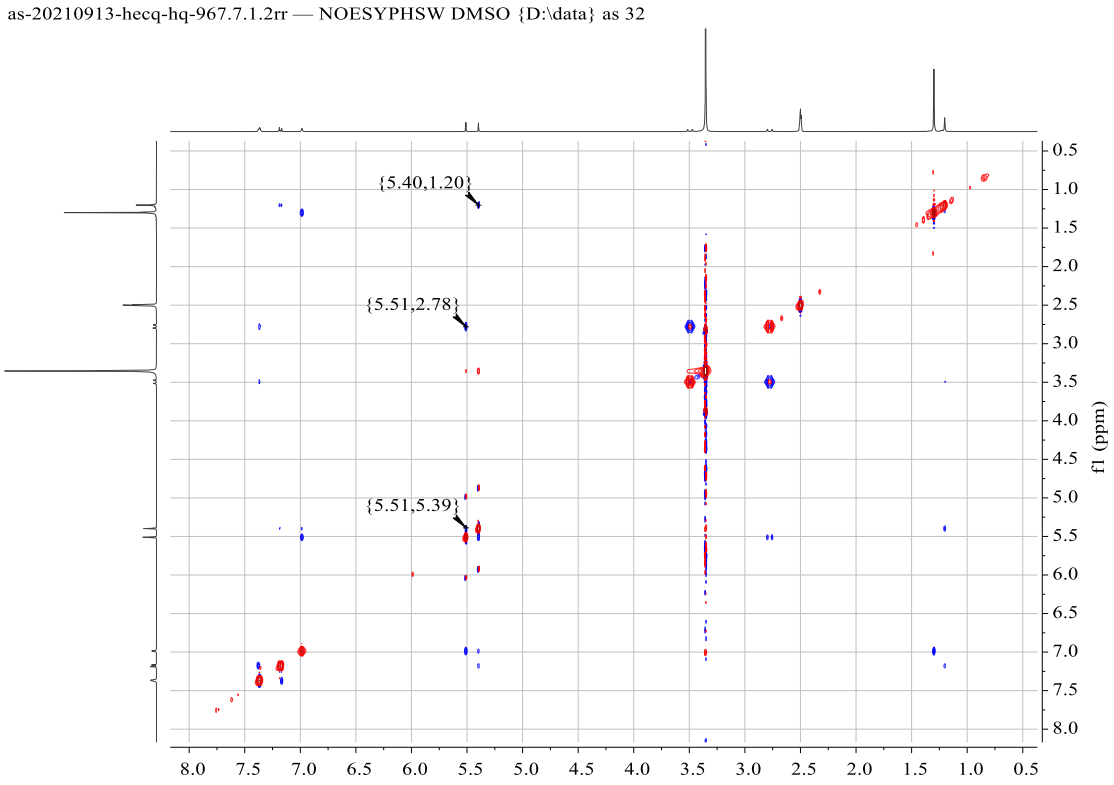


7 (in d_6-DMSO)

as-20210913-hecq-hq-967.4.1.2rr — HMBCGP DMSO {D:\data} as 46



7 (in d_6-DMSO)



7 (in d_6-DMSO)