Electronic Supplementary Material (ESI) for Chemical Science.

Enantioselective carbene insertion into N–H bond of benzophenone imine

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CONTENTS:

1. General remarks 2

2. General procedure for the synthesis of chiral guanidines..... 2

3. General procedure for the synthesis of the benzophenone imines and *α*-diazoesters..... 3

4. Typical procedure for the catalytic asymmetric reactions..... 4

5. General procedure for the preparation of the racemic products 5

6. Optimization of the asymmetric reaction conditions (*α*-aryl *α*-diazoesters) 6

7. Optimization of the asymmetric reaction conditions (*α*-alkyl *α*-diazoesters)..... 10

8. Scaled-up version of the asymmetric reaction and further transformations. 13

9. The analytical and spectral characterization data of products..... 18

10. X-ray crystal structure of product 7ba and G1 44

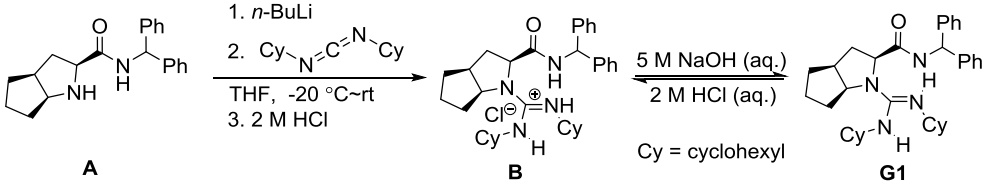
11. Copies of NMR spectra for the products..... 46

12. References 99

1. General remarks

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.260). Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets), coupling constants (Hz), integration. ^{13}C {^{1}H} NMR data were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.160). Enantiomeric excesses were determined by chiral HPLC analysis on Daicel Chiral IA, IC, IE, and IF at 23 °C with UV detector at 254 nm in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]_D^T$ (*c*: g/100 mL, in CH_2Cl_2). HRMS were recorded on a commercial apparatus (FTMS+c ESI). All the solvents were purified by usual methods before use. Silica gel for Thin-layer chromatography (HG/T2354-92) made in Qingdao Haiyang Chemical Co., Ltd.

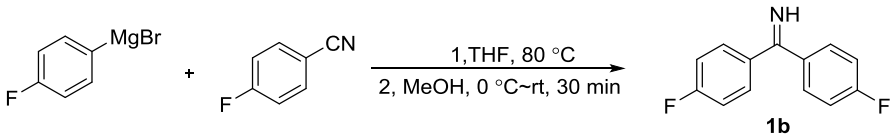
2. General procedure for the synthesis of chiral guanidines.



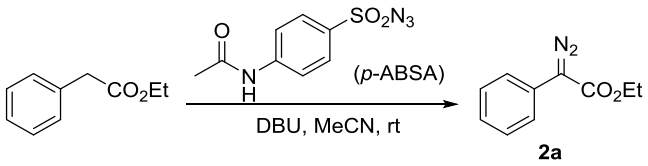
2.4 M *n*-BuLi in *n*-hexane (2.2 equiv, 3.7 mL, 8.8 mmol) was injected into a solution of *L*-ramipril-derived amide **A** (4.0 mmol) in THF (40 mL) dropwise over 5 minutes under nitrogen atmosphere at -20 ℃ with well stirring. After additional 10 minutes, a solution of *N*,*N*′-dicyclohexylcarbodiimide (1.2 equiv, 4.8 mmol) in 10 mL of THF was added dropwise within 5 minutes. The reaction was allowed to warm to room temperature and detected by TLC. After 12 h, the mixture was evaporated under reduced pressure to get rid of THF, and the pH value of the mixture was brought into the range of 0–1 by the addition of 2 M HCl. The aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phase was washed with brine, dried over

anhydrous Na_2SO_4 and evaporated in vacuum and purified through flash chromatograph on silica gel (EtOAc:MeOH = 35:1) to produce **B**. The white foam **B** can be recrystallized in CH_2Cl_2 and petroleum ether to get white crystal. Then, **B** in CH_2Cl_2 (10 mL) was added 4 M NaOH (15 mL) and stirred until the basification was finished (10 minutes). The pH value of the mixture was kept in the range of 11–12. The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was washed with 4 M NaOH, dried over anhydrous Na_2SO_4 and evaporated in vacuum. Finally a white solid was obtained. Then it was dissolved in CH_2Cl_2 and filtration through celite to remove the silicone gel, concentrate to get a kind of white foam (71% yield). For other guanidine catalysts, this synthesis method could be applied.[1]

3. General procedure for the synthesis of the benzophenone imines and *α*-diazoesters

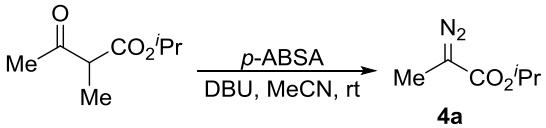


To a round flask were added the 4-fluorophenyl Grignard reagent (36 mmol) and 15 mL THF under N_2 atmosphere. Then, the corresponding 4-fluorophenylnitrile (30 mmol) was dissolved in 5 mL THF and added dropwise with well stirring, The mixture was then transferred to an oil bath (85 ℃) and detected by TLC. After stirred for 24 h. The reaction mixture was cooled to room temperature and dropwise addition of dry MeOH at 0 ℃. The resulting mixture was stirred at room temperature for 30 min, Then filtered through celite and the filter cake washed with THF. The filtrate was concentrated under reduced pressure and purified *via* fractionating vacuum distillation to obtain the title compound **1b** as a colorless oil (66% yield, 0.07 mmHg, 140–145 ˚C). The other benzophenone imines were prepared by the similar procedure.[2]



2a

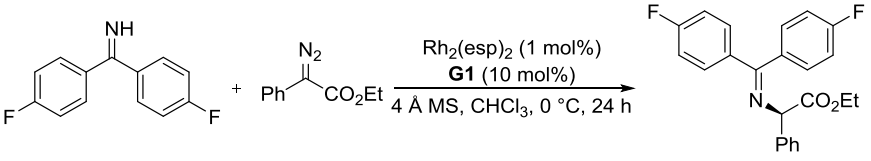
To a solution of ethyl 2-phenylacetate (1.34 g, 10 mmol) and *p*-ABSA (3.12 g, 13 mmol) in dry CH_3CN (20 mL) was added DBU (1.94 mL, 13 mmol) dropwise at 0 ℃. Then the mixture was stirred overnight at room temperature. The reaction was then quenched with 10 w% NH_4Cl, followed by extraction with Et_2O (2×20 mL). The combined organic extracts were anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The yellow crude product was purified by silica gel column chromatography (petroleum ether:Et_2O = 30:1) to give the product **2a** as a yellow oil (1.50 g, 93% yield). The other α-aryl α-diazoesters were prepared by the similar procedure.[3]



4a

To a solution of isopropyl 2-methyl-3-oxobutanoate (1.58 g, 10 mmol) and *p*-ABSA (3.12 g, 13 mmol) in dry CH_3CN (20 mL) was added DBU (1.94 mL, 13 mmol) dropwise at 0 ℃. Then the mixture was stirred overnight at room temperature. The reaction was then quenched with 10 w% NH_4Cl, followed by extraction with Et_2O (2×20 mL). The combined organic extracts were anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The yellow crude product was purified by silica gel column chromatography (petroleum ether:Et_2O = 20:1) to give the product **4a** as a yellow oil (1.50 g, 51% yield). The other α-alkyl α-diazoesters were prepared by the similar procedure.[4]

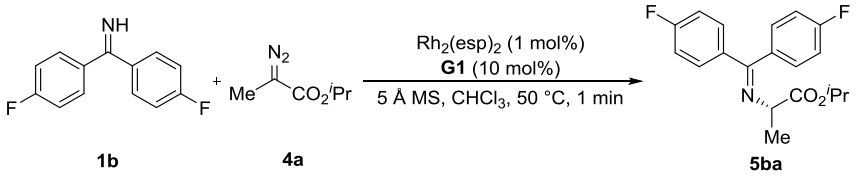
4. Typical procedure for the catalytic asymmetric reactions



1b **2a** **3ba**

Typical Procedure: To an oven-dried reaction tube under nitrogen atmosphere was

added the $Rh_2(esp)_2$ (0.8 mg, 1 mol%), **G1** (5.3 mg, 10 mol%), 4 Å MS (30 mg), and $CHCl_3$ (0.5 mL). The reaction mixture was stirred at 30 ℃ for 30 min. Subsequently, bis(4-fluorophenyl)methanimine **1b** (19.5 μL, 0.1 mmol) was added, then the reaction mixture was stirred at 0 ℃ for 10 min, ethyl 2-diazo-2-phenylacetate **2a** (20 μL, 0.12 mmol) was added and the reaction mixture was stirred at 0 ℃ for 24 h, then directly purified by flash column chromatography (petroleum ether:Et_2O = 10:1) to afford the desired product **3ba**.



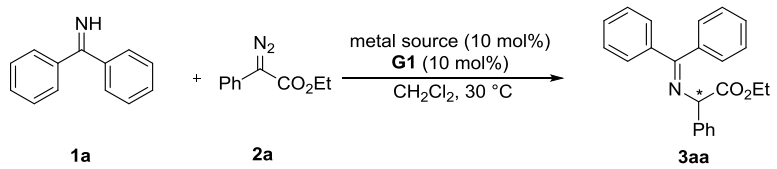
Typical Procedure: To an oven-dried reaction tube under nitrogen atmosphere was added the $Rh_2(esp)_2$ (0.8 mg, 1 mol%), **G1** (5.3 mg, 10 mol%), 5 Å MS (30 mg), and $CHCl_3$ (0.5 mL). The reaction mixture was stirred at 30 ℃ for 30 min. Subsequently, bis(4-fluorophenyl)methanimine **1b** (19.5 μL, 0.1 mmol) was added, then the reaction mixture was stirred at 50 ℃ for 10 min, isopropyl 2-diazopropanoate **4a** (30 μL, 0.2 mmol) was added and the reaction mixture was stirred at 50 ℃ for 1 min, then directly purified by flash column chromatography (petroleum ether:Et_2O = 10:1) to afford the desired product **5ba**.

5. General procedure for the preparation of the racemic products

The corresponding racemic products were obtained by the no using of chiral guanidine under the same reaction conditions.

6. Optimization of the asymmetric reaction conditions (*α*-aryl *α*-diazoesters)

Table 1. Screening of the metal sources[a]

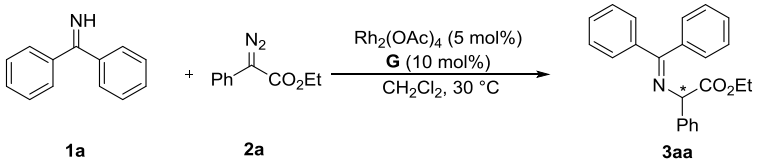


1a 2a 3aa

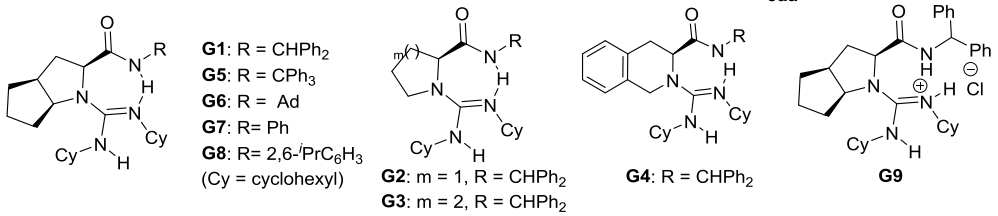
entry	metal source	yield[b] (%)	er[c]
1[d]	$Rh_2(OAc)_4$	84	75:25
2	$Cu(OTf)_2$	25	70:30
3	$Cu(OTf)•C_6H_6$	N.R.	-
4	CuCl	N.R.	-
5	$Pd(OAc)_2$	N.R.	-
6	$Pd_2(dba)_3$	N.R.	-
7	$Fe(ClO_4)_2•H_2O$	N.R.	-
8[e]	$AgNTf_2$	N.R.	50:50
9	AgOTf	N.R.	-

[a]Unless otherwise noted, all reactions were carried out with metal source (10 mol%), **G1** (10 mol%), **1a** (0.1 mmol), and **2a** (0.12 mmol) in CH_2Cl_2 (0.5 mL) at 30 ℃ for 5 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]$Rh_2(OAc)_4$ (5 mol %). [e]Reaction time: 3 days.

Table 2. Screening of chiral guanidines[a]



1a 2a 3aa

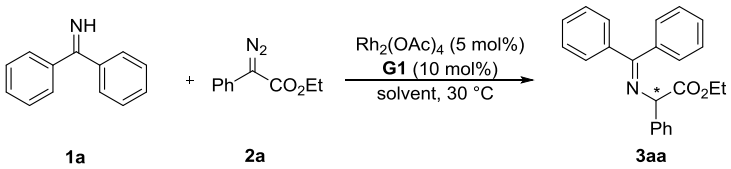


entry	**G**	yield[b] (%)	er[c]
1	**G1**	84	75:25
2	**G2**	82	50:50
3	**G3**	88	50:50

4	**G4**	89	50:50
5	**G5**	86	59:41
6	**G6**	84	59:41
7	**G7**	78	62:38
8	**G8**	84	57:43
9	**G9**	81	50:50

[a]Unless otherwise noted, all reactions were carried out with $Rh_2(OAc)_4$ (5 mol%), **G** (10 mol%)**,** **1a** (0.1 mmol), and **2a** (0.12 mmol) in CH_2Cl_2 (0.5 mL) at 30 ℃ for 5 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis.

Table 3. Screening of the solvents[a]

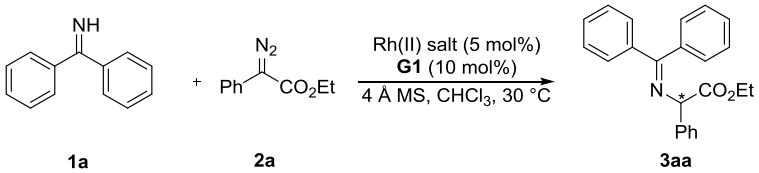


1a **2a** **3aa**

entry	solvent	yield[b] (%)	er[c] (%)
1	THF	84	65:35
2	Et_2O	25	73:27
3	Toluene	54	70:30
5	AcOEt	75	63:37
6	MeCN	67	60:40
7	CH_2Cl_2	84	75:25
8[d]	CH_2Cl_2	96	75:25
9[e]	CH_2Cl_2	81	73:27
10[d]	CH_2ClCH_2Cl	93	77:21
11[d]	$CHCl_3$	87	82:18

[a]Unless otherwise noted, all reactions were carried out with $Rh_2(OAc)_4$ (5 mol%), **G1** (10 mol%), **1a** (0.1 mmol), and **2a** (0.12 mmol) in solvent (0.5 mL) at 30 ℃ for 5 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]4 Å MS (30 mg) was added. [e]$MgSO_4$ (30 mg) was added.

Table 4. Screening of different Rh(II) salts[a]



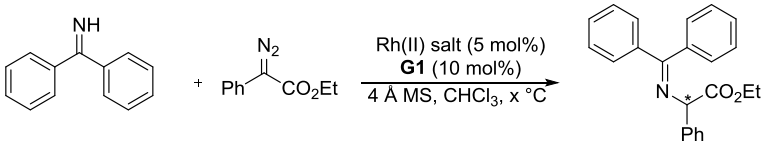
1a **2a** **3aa**

entry	Rh(II) salt	yield[b] (%)	er[c] (%)

1	$Rh_2(OAc)_4$	87	82:18
2	$Rh_2(oct)_4$	88	74:26
3	$Rh_2(TFA)_4$	N.R.	-
4	$Rh_2(TPA)_4 \bullet CH_2Cl_2$	N.R.	-
5[d]	$Rh_2(esp)_2$	90	74:26

[a]Unless otherwise noted, all reactions were carried out with Rh(II) salt (5 mol%), **G1** (10 mol%), 4 Å MS (30 mg), **1a** (0.1 mmol), and **2a** (0.12 mmol) in $CHCl_3$ (0.5 mL) at 30 ℃ for 5 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]Reaction time: 10 min.

Table 5. Screening of reaction temperature[a]

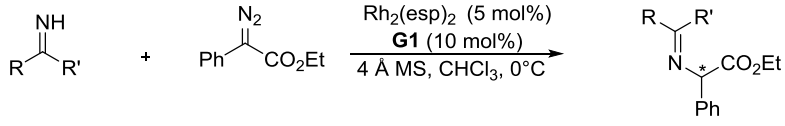


1a **2a** **3aa**

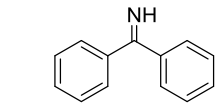
entry	Rh(II) salt	x	yield[b] (%)	er[d] (%)
1	$Rh_2(OAc)_4$	30	87	82:18
2	$Rh_2(OAc)_4$	0	37	76:24
3[d]	$Rh_2(esp)_2$	30	90	74:26
4[e]	$Rh_2(esp)_2$	0	93	82:18
5[f]	$Rh_2(esp)_2$	-10	83	86:14
6[f]	$Rh_2(esp)_2$	-20	32	70:30

[a]Unless otherwise noted, all reactions were carried out with Rh(II) salt (5 mol%), **G1** (10 mol%), 4 Å MS (30 mg), **1a** (0.1 mmol), and **2a** (0.12 mmol) in $CHCl_3$ (0.5 mL) at x ℃ for 5 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]Reaction time: 10 min. [e]Reaction time: 8 h. [f]Reaction time: 24 h.

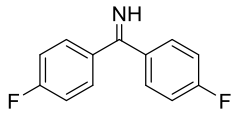
Table 6. Screening of different benzophenone imines[a]



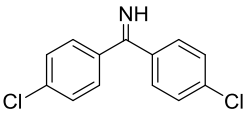
1 **2a** **3**



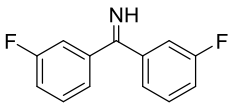
1a: 83% yield[b], 86:14 er[c] -10 °C



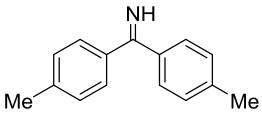
1b: 96% yield, 90:10 er



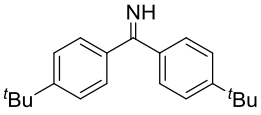
1c: 92% yield, 86:14 er



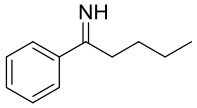
1d: 90% yield, 88:12 er



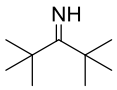
1e: 80% yield, 70:30 er



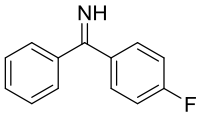
1f: 84% yield, 72:28 er



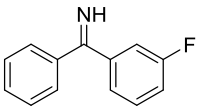
1g: N.R.



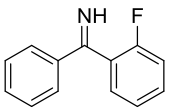
1h: N.R.



1i: 88% yield, *E/Z*[d] 60/40 77:23 er/80:20 er



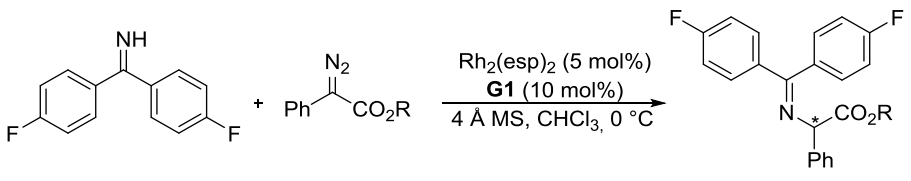
1j: 99% yield, *E/Z* 66/34 89:11 er/90:10 er



1k: 99% yield, *E/Z* 87/13 83:17 er/83:17 er

[a]Unless otherwise noted, all reactions were carried out with $Rh_2(esp)_2$ (5 mol%), **G1** (10 mol%), 4 Å MS (30 mg), **1** (0.1 mmol), and **2a** (0.12 mmol) in $CHCl_3$ (0.5 mL) at 0 ℃ for 8 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]Determined by chiral HPLC analysis.

Table 7. Screening of ester groups of the *α*-aryl *α*-diazoesters[a]



1b **2** **3**

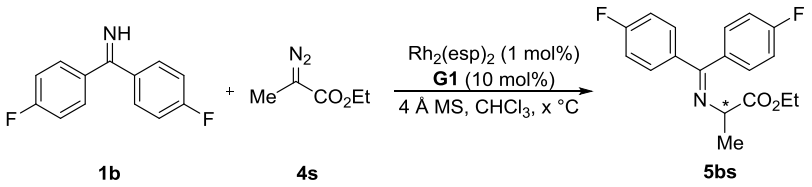
entry	R	yield[b] (%)	er[c] (%)
1	Et	96	90:10
2[d]	Et	96	90:10
3	Me	91	75:25
4	^{i}Pr	78	85:15
5	^{i}Bu	77	77:23
6	^{t}Bu	83	70:30
7	Bn	76	80:20
8	CH_2CF_3	99	77:23

9	CH_2CCl_3	89	68:32

[a]Unless otherwise noted, all reactions were carried out with $Rh_2(esp)_2$ (5 mol%), **G1** (10 mol%), 4 Å MS (30 mg), **1b** (0.1 mmol), and **2** (0.12 mmol) in $CHCl_3$ (0.5 mL) at 0 ℃ for 8 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d] $Rh_2(esp)_2$ (1 mol %), reaction time: 24 h.

7. Optimization of the asymmetric reaction conditions (*α*-alkyl *α*-diazoesters)

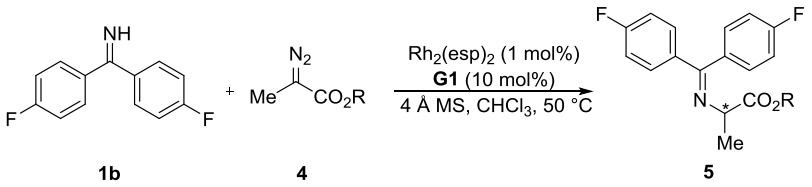
Table 1. Screening of reaction temperature[a]



entry	Temp (^oC)	yield[b] (%)	er[c] (%)
1[d]	0	48	72:28
2	20	88	69:31
3	30	89	72:28
4	40	94	77:23
5	50	90	79:21
6	60	85	79:21
7	70	92	79:21

[a]Unless otherwise noted, all reactions were carried out with $Rh_2(esp)_2$ (5 mol%), **G1** (10 mol%), 4 Å MS (30 mg), **1b** (0.1 mmol), and **4s** (0.2 mmol) in $CHCl_3$ (0.5 mL) at x ℃ for 1 min. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d] Reaction time: 3 h.

Table 2. Screening of ester groups of the *α*-alkyl *α*-diazoesters[a]

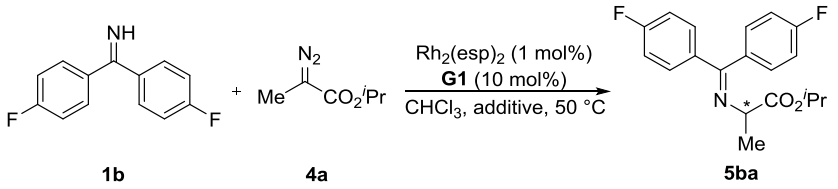


entry	R	yield[b] (%)	er[c] (%)
1	Me	97	64:36
2	Et	90	79:21
3	^{i}Pr	96	93:7
4	^{t}Bu	85	68:32

5	Bn	91	72:28

[a]Unless otherwise noted, all reactions were carried out with $Rh_2(esp)_2$ (1 mol%), **G1** (10 mol%), 4 Å MS (30 mg), **1b** (0.1 mmol), and **4** (0.2 mmol) in $CHCl_3$ (0.5 mL) at 50 ℃ for 1 min. [b]Isolated yield. [c]Determined by chiral HPLC analysis.

Table 3. Screening of the additives[a]

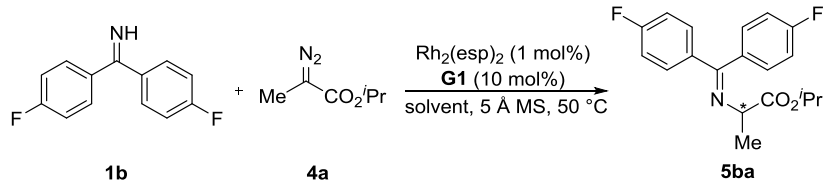


1b **4a** **5ba**

Entry	additive	yield[b] (%)	er[c] (%)
1	-	99	92:8
2	3 Å MS (30 mg)	99	93:7
3	4 Å MS (30 mg)	96	93:7
4	5 Å MS (30 mg)	96	94:6

[a]Unless otherwise noted, all reactions were carried out with $Rh_2(esp)_2$ (1 mol%), **G1** (10 mol%), additive (30 mg), **1b** (0.1 mmol), and **4a** (0.2 mmol) in $CHCl_3$ (0.5 mL) at 50 ℃ for 1 min. [b]Isolated yield. [c]Determined by chiral HPLC analysis.

Table 4. Screening of the solvents[a]

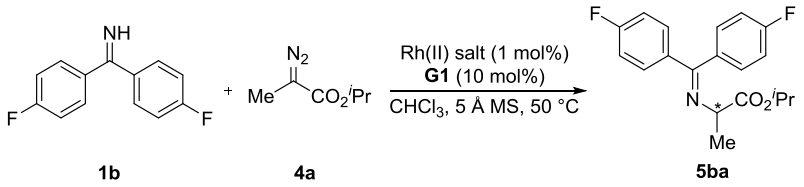


1b **4a** **5ba**

Entry	solvent	yield[b] (%)	er[c] (%)
1	CH_2Cl_2	99	93:7
2	$CHCl_3$	96	94:6
3	THF	99	93:7
4	Et_2O	94	94:6
5	Toluene	83	94:6
6	AcOEt	86	76:24

[a]Unless otherwise noted, all reactions were carried out with $Rh_2(esp)_2$ (1 mol%), **G1** (10 mol%), 5 Å MS (30 mg), **1b** (0.1 mmol), and **4a** (0.2 mmol) in solvent (0.5 mL) at 50 ℃ for 1 min. [b]Isolated yield. [c]Determined by chiral HPLC analysis.

Table 5. Screening of different Rh(II) salts[a]

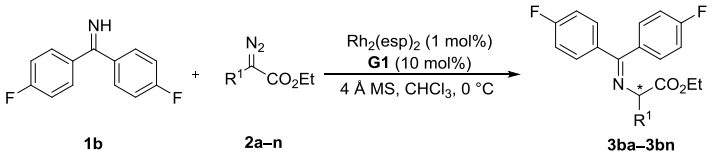


1b 4a 5ba

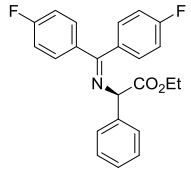
entry	Rh(II) salt	yield[b] (%)	er[c] (%)
1[d]	$Rh_2(OAc)_4$	57	90:10
2[d]	$Rh_2(oct)_4$	91	93:7
3[d]	$Rh_2(TFA)_4$	N.R.	-
4[d]	$Rh_2(TPA)_4 \bullet CH_2Cl_2$	93	94:6
5	$Rh_2(esp)_2$	96	94:6
5[f]	$Rh_2(esp)_2$	90	92:8

[a]Unless otherwise noted, all reactions were carried out with Rh(II) salt (1 mol%), **G1** (10 mol%), 5 Å MS (30 mg), **1b** (0.1 mmol), and **4a** (0.2 mmol) in $CHCl_3$ (0.5 mL) at 50 ℃ for 1 min. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]Reaction time: 10min. [f]**G1** (5 mol%).

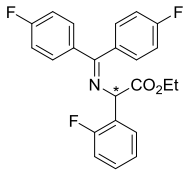
Table 6. Full list of the *α*-diazoesters insertion products



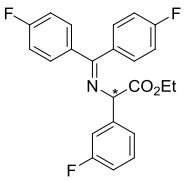
1b 2a–n 3ba–3bn



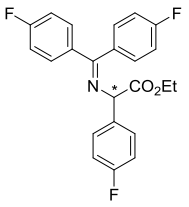
(*R*)-**3ba**[a], 24 h
96% yield[b], 90:10 er[c]



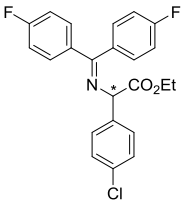
3bb, 24 h
99% yield, 67:33 er



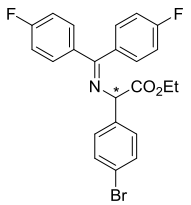
3bc, 24 h
99% yield, 88:12 er



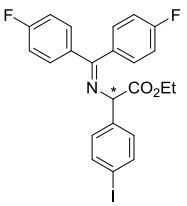
3bd, 20 h
97% yield, 85: 15 er



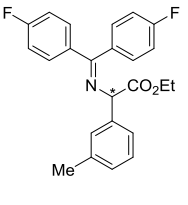
3be, 24 h
99% yield, 86:14 er



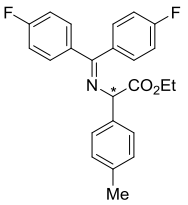
3bf, 24 h
96% yield, 88:12 er



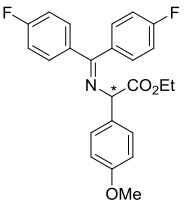
3bg, 24 h
99% yield, 90:10 er



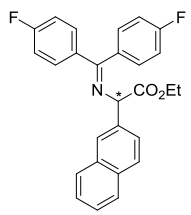
3bh, 36 h
98% yield, 88:12 er



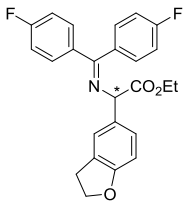
3bi, 24 h
99% yield, 88:12 er



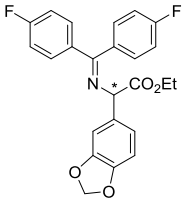
3bj, 24 h
98% yield, 84:16 er



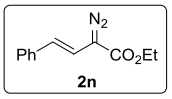
3bk, 24 h
99% yield, 90:10 er



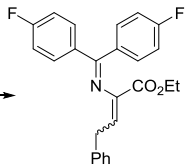
3bl, 5 h
93% yield, 78:22 er



3bm, 5 h
93% yield, 84.5:15.5 er



2n

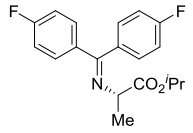


3bn, 36 h
59% yield

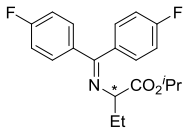
[a]Unless otherwise noted, all reactions were carried out with $Rh_2(esp)_2$ (1 mol%), **G1** (10 mol%), 4

Å MS (30 mg), **1b** (0.1 mmol), and **2** (0.12 mmol) in $CHCl_3$ (0.5 mL) at 0 ℃ for 24 h. [b]Isolated yield. [c]Determined by chiral HPLC analysis.

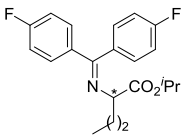
1b **4a–r** **5ba–5br**



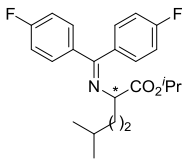
(*S*)-**5ba**[a]
96% yield[b], 94:6 er[c]



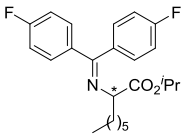
5bb
64% yield, 95:5 er



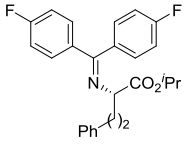
5bc
85% yield, 95.5:4.5 er



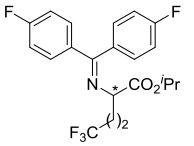
5bd
36% yield, 93:7 er



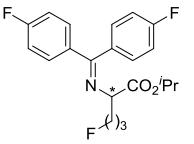
5be
30% yield, 94:6 er



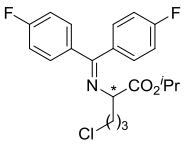
(*S*)-**5bf**
90% yield, 94.5:5.5 er



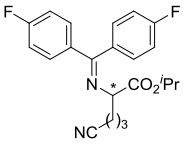
5bg
99% yield, 94:6 er



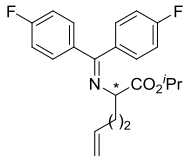
5bh
99% yield, 94:6 er



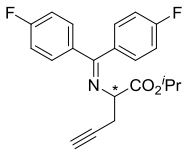
5bi
79% yield, 95:5 er



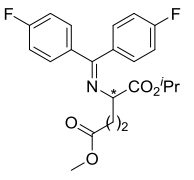
5bj
91% yield, 94:6 er



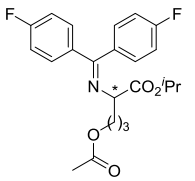
5bk
99% yield, 95:5 er



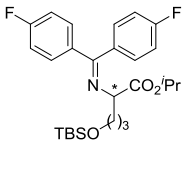
5bl
73% yield, 85:15 er



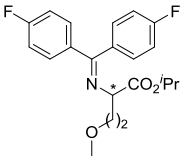
5bm
93% yield, 95:5 er



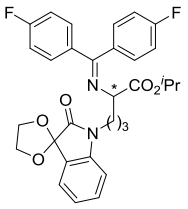
5bn
83% yield, 94:6 er



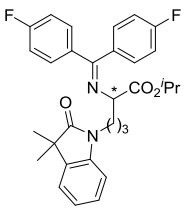
5bo
67% yield, 95:5 er



5bp[d]
35% yield, 93:7 er



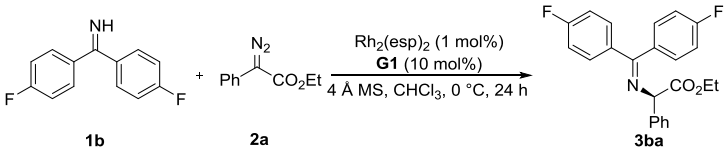
5bq
99% yield, 95.5:4.5 er



5br
99% yield, 95:5 er

[a]Unless otherwise noted, all reactions were carried out with $Rh_2(esp)_2$ (1 mol%), **G1** (10 mol%), 5 Å MS (30 mg), **1b** (0.1 mmol), and **4** (0.2 mmol) in $CHCl_3$ (0.5 mL) at 50 ℃ for 1 min. [b]Isolated yield. [c]Determined by chiral HPLC analysis. [d]**4p** (0.4 mmol) was added.

8. Scaled-up version of the asymmetric reaction and further transformations.

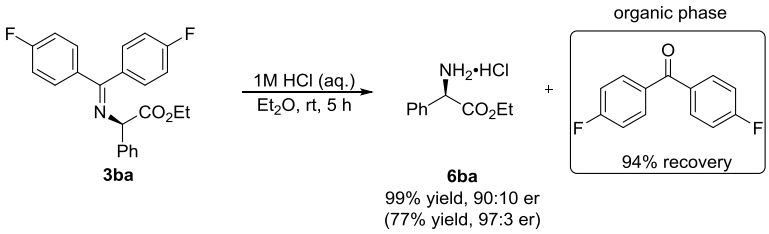


1b 2 mmol, 0.43 g

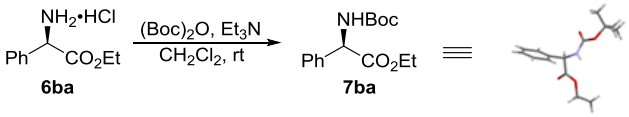
2a 2.4 mmol, 0.38 g

3ba
99% yield, 90:10 er
0.75 g

To a round flask under nitrogen atmosphere was added the $Rh_2(esp)_2$ (16 mg, 1 mol%), **G1** (0.11g, 10 mol%), 4 Å MS (0.60 g), and $CHCl_3$ (10 mL). The reaction mixture was stirred at 30 ℃ for 30 min. Subsequently, bis(4-fluorophenyl)methanimine **1b** (0.39 mL, 2 mmol) was added, then the reaction mixture was stirred at 0 ℃ for 10 min, ethyl 2-diazo-2-phenylacetate **2a** (0.40 mL, 2.4 mmol) was added and the reaction mixture was stirred at 0 ℃ for 24 h, then directly purified by flash column chromatography (petroleum ether:Et_2O = 10:1) to afford the desired product **3ba**.

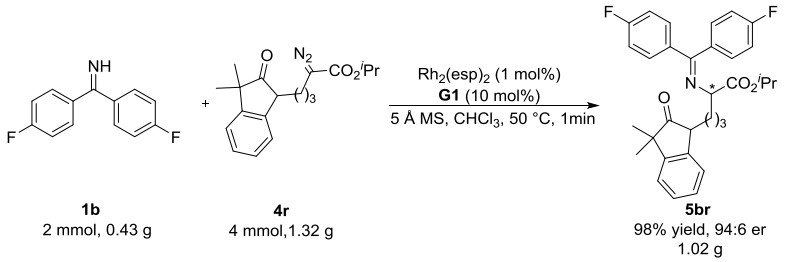


To a round flask was added the **3ba** (0.62 g), then 1M HCl (5 mL) and Et_2O (10 mL) were added. The reaction mixture was stirred at rt for 5 h. Subsequently, the aqueous phase was separated and was evaporated to afford the desired product α-amino ester **6ba** as a white solid with retained enantiopurity. The **6ba** was recrystallized from mixed solvents of MeOH and Et_2O, which significantly improved enantiopurity. The benzophenone could be recovered in 96% yield from the organic phase. Er was determined by chiral HPLC analysis of the corresponding *N*-Boc protected amines **7ba**.

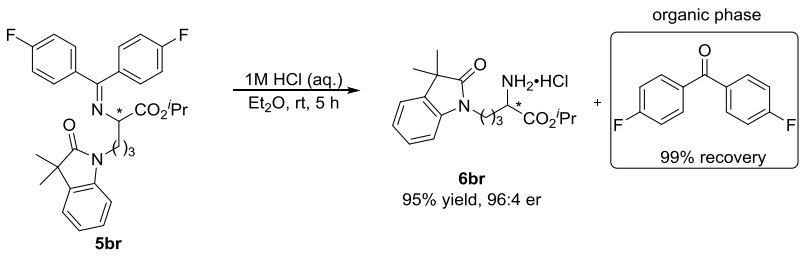


To a solution of **6ba** (0.27 g, 1.26 mmol) in CH_2Cl_2 (5 mL) was added Et_3N (0.42 mL, 3.02 mmol) dropwise at 0 ℃, followed by added $(Boc)_2O$ (0.33g, 1.51 mmol) after stirred 10 minutes, Then the mixture was stirred overnight at room temperature. Next, The mixture was washed with 1 M $KHSO_4$ solution, saturated $NaHCO_3$ solution, brine, dried over anhydrous Na_2SO_4, concentrated in vacuo to afford desired product **7ba** (99% yield). The absolute configuration of **7ba** was assigned as *R* based on X-ray crystal analysis. Therefore, **3ba** was assigned as

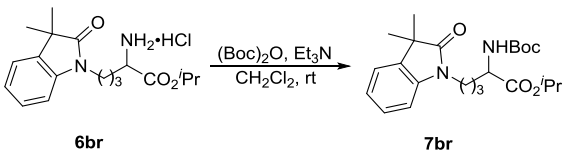
R-isomer.



To a round flask under nitrogen atmosphere was added the $Rh_2(esp)_2$ (16 mg, 1 mol%), **G1** (0.11g, 10 mol%), 5 Å MS (0.60 g), and $CHCl_3$ (10 mL). The reaction mixture was stirred at 30 ℃ for 30 min. Subsequently, bis(4-fluorophenyl)methanimine **1b** (0.39 mL, 2 mmol) was added, then the reaction mixture was stirred at 50 ℃ for 10 min, **4r** (1.32 g, 4 mmol) was added and the reaction mixture was stirred at 50 ℃ for 1 min, then directly purified by flash column chromatography (petroleum ether:Et_2O = 5:1) to afford the desired product **5br**.

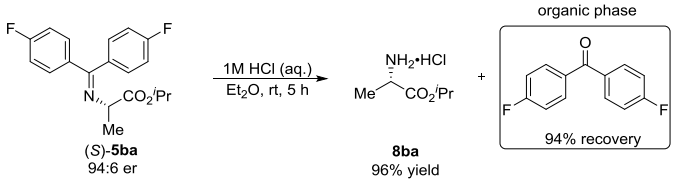


To a round flask was added the **5br** (0.60 g), then 1M HCl (5 mL) and Et_2O (10 mL) were added. The reaction mixture was stirred at rt for 5 h. Subsequently, the aqueous phase was separated and was evaporated to afford the desired product α-amino ester **6br** (0.39 g) as a white solid with retained enantiopurity. The benzophenone could be recovered in 99% yield (0.25 g) from the organic phase. Er was determined by chiral HPLC analysis of the corresponding *N*-Boc protected amines **7br**.

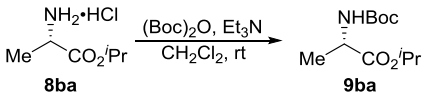


To a solution of **6br** (0.39 g, 1.23 mmol) in CH_2Cl_2 (5 mL) was added Et_3N (0.41 mL, 2.95 mmol) dropwise at 0 ℃, followed by added $(Boc)_2O$ (0.32 g, 1.48 mmol) after stirred 10 minutes, Then the mixture was stirred overnight at room

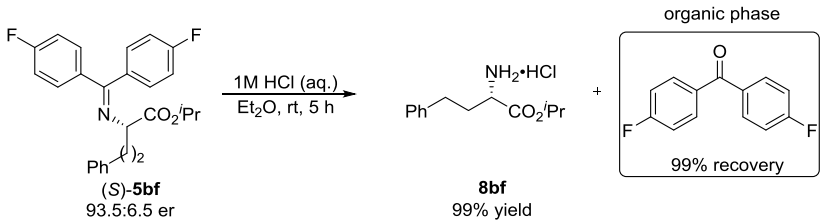
temperature. Next, The mixture was washed with 1 M $KHSO_4$ solution, saturated $NaHCO_3$ solution, brine, dried over anhydrous Na_2SO_4, concentrated in vacuo to afford desired product **7br** (99% yield).



To a round flask was added the **5ba** (0.132 g, 0.40 mmol), then 1M HCl (5 mL) and Et_2O (5 mL) were added. The reaction mixture was stirred at rt for 5 h. Subsequently, the aqueous phase was separated and was evaporated to afford the desired product *α*-amino ester **8ba** as a colorless oil. The benzophenone could be recovered in 94% yield from the organic phase.

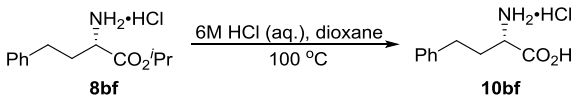


To a solution of **8ba** (0.064 g, 0.383 mmol) in CH_2Cl_2 (5 mL) was added Et_3N (0.13 mL, 0.919 mmol) dropwise at 0 ℃, followed by added $(Boc)_2O$ (0.10 g, 0.46 mmol) after stirred 10 minutes. Then the mixture was stirred overnight at room temperature. Next, the mixture was washed with 1 M $KHSO_4$ solution, saturated $NaHCO_3$ solution, brine, dried over anhydrous Na_2SO_4, concentrated in vacuo to afford desired product **9ba** (99% yield). The absolute configuration of **9ba** {$[\alpha]_D^{26}$ = -35.2 (*c* = 1.19, in MeOH)} was determined to be *S* by comparison of the optical rotation with that given in literature[5] {$[\alpha]_D^{20}$ = -31.0 (*c* = 1.0, in MeOH); *S*-isomer}. Therefore, the absolute configuration of **5ba** was assigned *S*-isomer.



To a round flask was added the **5bf** (0.23 g, 5.5 mmol), then 1M HCl (5 mL) and Et_2O (5 mL) were added. The reaction mixture was stirred at rt for 5 h. Subsequently, the aqueous phase was separated and was evaporated to afford the desired product

α-amino ester **8bf** as a colorless oil. The benzophenone could be recovered in 99% yield from the organic phase.

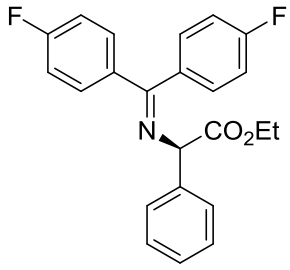


8bf **10bf**

To a round flask was added the **8bf** (0.1435 g, 5.5 mmol), then 6M HCl (10 mL) and dioxane (0.5 mL) were added. The reaction mixture was stirred at 100 ℃ for 12 h. The reaction mixture was cooled to rt and washed with Et_2O (3x5 mL). Subsequently, the aqueous phase was separated and was evaporated to afford the desired product amino acid hydrochloride **10bf** as a white solid (0.1271 g, 99% yield). The absolute configuration of **10bf** {$[\alpha]_D^{30}$ = +26.6 (*c* = 1.35, in 3M HCl)} was determined to be *S* by comparison of the optical rotation with that given in literature[6] {$[\alpha]_D^{20}$ = −46.0 (*c* = 1.0, in 3M HCl); *R*-isomer}. Therefore, the absolute configuration of **5bf** was assigned as *S*-isomer.

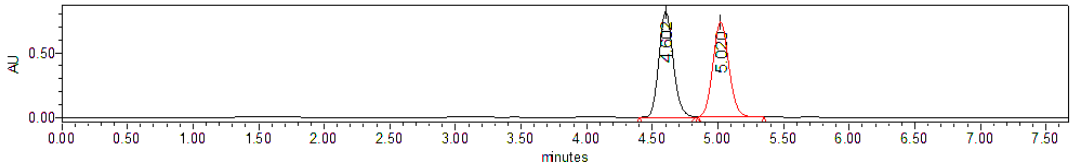
9. The analytical and spectral characterization data of products

Ethyl (*R*)-2-((bis(4-fluorophenyl)methylene)amino)-2-phenylacetate (3ba)

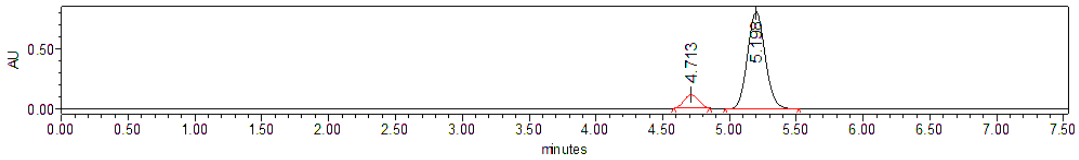


(**$C_{23}H_{19}F_2NO_2$**) colorless oil. 96% yield (36.3 mg), 90:10 er, HPLC (Chiral IA cloumn), *i*-PrOH/*n*-Hexane = 10/90, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (major) = 5.20 min, *t* (minor) = 4.71 min. $[\alpha]_{436}^{23}$ = +91.3 (*c* = 0.29, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 2H), 7.45 – 7.39 (m, 2H), 7.36 – 7.26 (m, 3H), 7.15 (t, *J* = 8.8 Hz, 2H), 7.11 – 6.98 (m, 4H), 5.06 (s, 1H), 4.20 – 4.07 (m, 2H), 1.18 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.4, 168.1, 164.5 (d, *J* = 249.7 Hz), 163.0 (d, *J* = 247.5 Hz), 139.1, 135.7 (d, *J* = 3.0 Hz) , 131.8 (d, *J* = 3.6 Hz), 131.2 (d, *J* = 8.6 Hz), 129.8 (d, *J* = 8.1 Hz), 128.7, 128.0, 116.0 (d, *J* = 21.5 Hz), 115.2 (d, *J* = 21.6 Hz), 69.9, 61.4, 14.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.0, -111.5.

HRMS (FTMS+c ESI): Calcd for $C_{23}H_{20}F_2NO_2^+$ [M+H$^+$] 380.1457, found 380.1454.

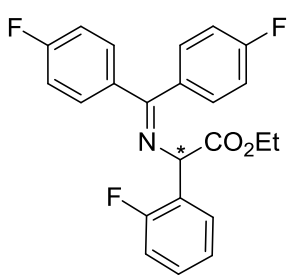


	Retention Time	Area	% Area
1	4.602	6246511	50.16
2	5.020	6206413	49.84



	Retention Time	Area	% Area
1	4.713	838319	10.15
2	5.198	7424872	89.85

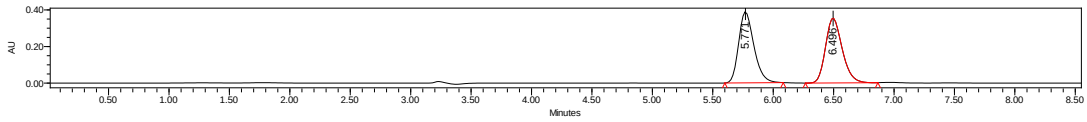
Ethyl 2-((bis(4-fluorophenyl)methylene)amino)-2-(2-fluorophenyl)acetate (3bb)



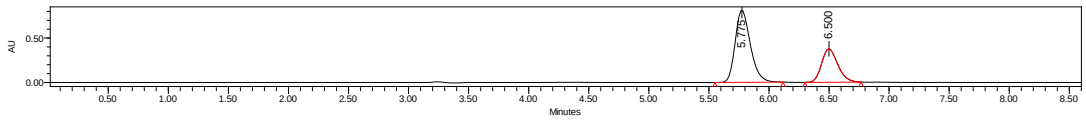
(**$C_{23}H_{18}F_3NO_2$**) colorless oil. 99% yield (39.5 mg), 67:33 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (major) = 5.78 min, *t* (minor) = 6.50 min. $[\alpha]_{436}^{24}$ = +39.9 (*c* = 0.56, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.62 (m, 3H), 7.30 – 7.24 (m, 1H), 7.21 – 7.08 (m, 5H), 7.07 – 6.96 (m, 3H), 5.40 (s, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.6, 169.3, 164.6 (d, *J* = 249.8 Hz), 163.0 (d, *J* = 247.6 Hz), 160.1 (d, *J* = 245.9 Hz), 135.6 (d, *J* = 3.0 Hz) , 131.7 (d, *J* = 3.6 Hz), 131.2 (d, *J* = 8.7 Hz) , 129.9 (d, *J* = 3.7 Hz) , 129.8 (d, *J* = 8.1 Hz), 129.5 (d, *J* = 8.2 Hz), 126.4

(d, *J* = 13.8 Hz) , 124.5 (d, *J* = 3.4 Hz), 116.0 (d, *J* = 21.5 Hz), 115.4 (d, *J* = 21.6 Hz), 115. 2 (d, *J* = 21.5 Hz), 62.8, 61.6, 14.2. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -109.8, -111.4, -118.2.

HRMS (FTMS+c ESI): Calcd for $C_{23}H_{19}F_3NO_2^+$ [M+H$^+$] 398.1364, found 398.1362.

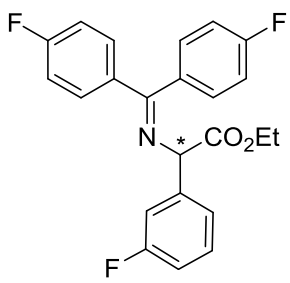


	Retention Time	Area	% Area
1	5.771	3402634	50.17
2	6.496	3379549	49.83



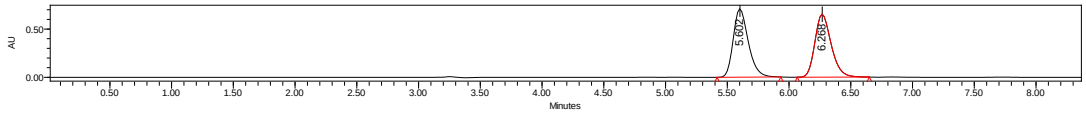
	Retention Time	Area	% Area
1	5.775	7139117	67.05
2	6.500	3508604	32.95

Ethyl 2-((bis(4-fluorophenyl)methylene)amino)-2-(3-fluorophenyl)acetate (3bc)

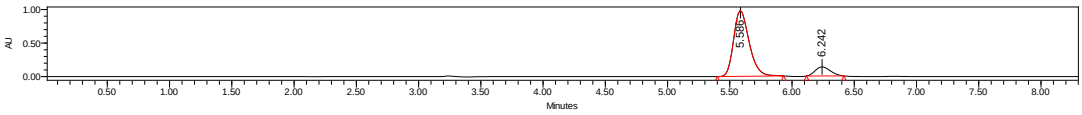


(**$C_{23}H_{18}F_3NO_2$**) colorless oil. 99% yield (39.4 mg), 88:12 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (major) = 5.59 min, *t* (minor) = 6.24 min. $[\alpha]_{436}^{22}$ = +91.9 (*c* = 0.66, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 2H), 7.33 – 7.26 (m, 1H), 7.23 (dt, *J* = 9.8, 2.2 Hz, 1H), 7.20 – 7.13 (m, 3H), 7.11 – 6.95 (m, 5H), 5.05 (s, 1H), 4.24 – 4.05 (m, 2H), 1.19 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.8, 168.7, 164.6 (d, *J* = 250.1 Hz), 163.0 (d, *J* = 247.9 Hz), 162.9 (d, *J* = 244.4 Hz), 141.4 (d, *J* = 7.3 Hz), 135.5 (d, *J* = 3.1 Hz), 131.7 (d, *J* = 3.6 Hz), 131.2 (d, *J* = 8.7 Hz), 130.1 (d, *J* = 8.2 Hz), 129.7 (d, *J* = 8.1 Hz), 123.6 (d, *J* = 2.8 Hz), 116.0 (d, *J* = 14.5 Hz), 115.3 (d, *J* = 21.5 Hz), 115.1 (d, *J* = 22.1 Hz), 115.0 (d, *J* = 21.1 Hz), 69.2, 61.6, 14.2. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -109.7, -111.2, -112.6.

HRMS (FTMS+c ESI): Calcd for $C_{23}H_{19}F_3NO_2^+$ [M+H$^+$] 398.1364, found 398.1361.

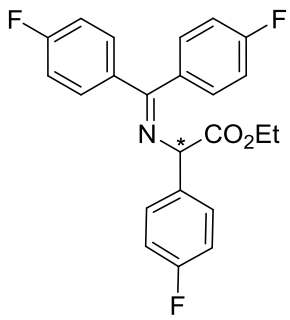


	Retention Time	Area	% Area
1	5.602	5997516	50.13
2	6.268	5965380	49.87



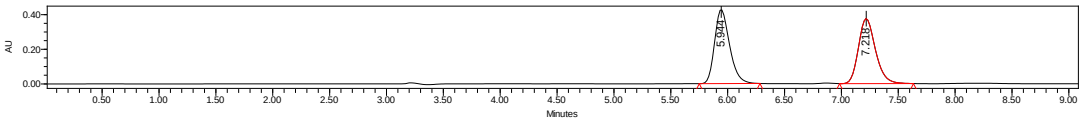
	Retention Time	Area	% Area
1	5.586	8482371	88.09
2	6.242	1147024	11.91

Ethyl 2-((bis(4-fluorophenyl)methylene)amino)-2-(4-fluorophenyl)acetate (3bd)

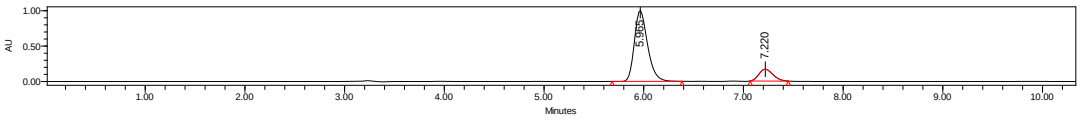


(**$C_{23}H_{18}F_3NO_2$**) colorless oil. 97% yield (38.5 mg), 85:15 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (major) = 5.97 min, *t* (minor) = 7.22 min. $[\alpha]_{436}^{23}$ = +98.5 (*c* = 0.72, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.65 (m, 2H), 7.45 – 7.36 (m, 2H), 7.16 (t, *J* = 8.8 Hz, 2H), 7.12 – 6.96 (m, 6H), 5.04 (s, 1H), 4.24 – 4.04 (m, 2H), 1.19 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.2, 168.4, 164.6 (d, *J* = 249.9Hz), 163.0 (d, *J* = 247.7 Hz), 162.5 (d, *J* = 244.8 Hz), 135.5 (d, *J* = 2.9 Hz), 134.9 (d, *J* = 3.1 Hz), 131.8 (d, *J* = 3.6 Hz), 131.1 (d, *J* = 8.7 Hz), 129.7 (d, *J* = 8.1 Hz), 129.6 (d, *J* = 8.0 Hz), 116.0 (d, *J* = 21.4 Hz), 115.5 (d, *J* = 21.4 Hz), 115.3 (d, *J* = 21.6 Hz), 69.0, 61.5, 14.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -109.8, -111.3, -114.4.

HRMS (FTMS+c ESI): Calcd for $C_{23}H_{19}F_3NO_2^+$ [M+H$^+$] 398.1364, found 398.1363.

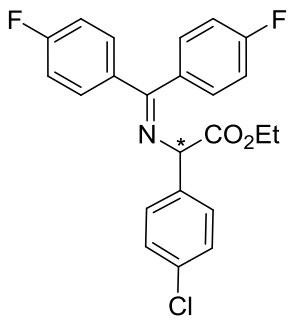


	Retention Time	Area	% Area
1	5.944	3913596	50.12
2	7.218	3894798	49.88



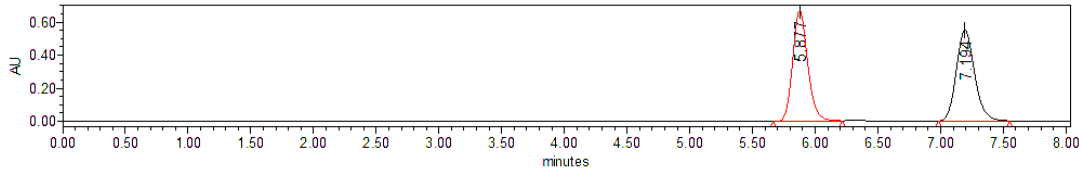
	Retention Time	Area	% Area
1	5.965	9216889	84.96
2	7.220	1631494	15.04

Ethyl 2-((bis(4-fluorophenyl)methylene)amino)-2-(4-chlorophenyl)acetate (3be)

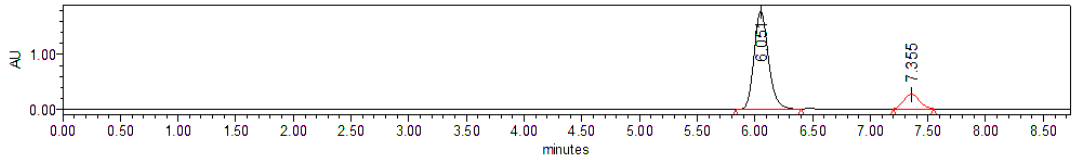


(**$C_{23}H_{18}ClF_2NO_2$**) colorless oil. 99% yield (41.2 mg), 86:14 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (major) = 6.05 min, *t* (minor) = 7.36 min. $[\alpha]_{436}^{25}$ = +52.7 (*c* = 0.77, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.64 (m, 2H), 7.40 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.16 (t, *J* = 8.6 Hz, 2H), 7.12 – 6.97 (m, 4H), 5.03 (s, 1H), 4.21 – 4.05 (m, 2H), 1.19 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.0, 168.6, 164.6 (d, *J* = 249.9 Hz), 163.0 (d, *J* = 247.9 Hz), 137.6, 135.5 (d, *J* = 2.8 Hz), 133.8, 131.7 (d, *J* = 3.6 Hz), 131.1 (d, *J* = 8.7 Hz), 129.1 (d, *J* = 8.1 Hz), 129.4, 128.8, 116.1 (d, *J* = 21.5 Hz), 115.3 (d, *J* = 21.6 Hz), 69.1, 61.6, 14.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -109.7, -111.2.

HRMS (FTMS+c ESI): Calcd for $C_{23}H_{19}{}^{34.9689}ClF_2NO_2^+$ [M+H$^+$] 414.1067, found 141.1067. HRMS (FTMS+c ESI): Calcd for $C_{23}H_{19}{}^{36.9659}ClF_2NO_2^+$ [M+H$^+$] 416.1037, found 416.1038.

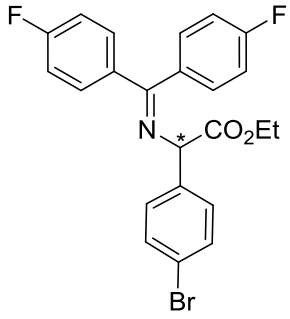


	Retention Time	Area	% Area
1	5.877	5565643	49.99
2	7.194	5567313	50.01



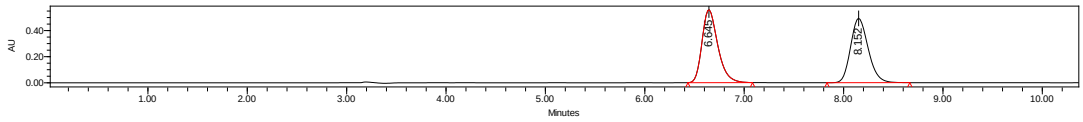
	Retention Time	Area	% Area
1	6.051	15416937	85.98
2	7.355	2514580	14.02

Ethyl 2-((bis(4-fluorophenyl)methylene)amino)-2-(4-bromophenyl)acetate (3bf)

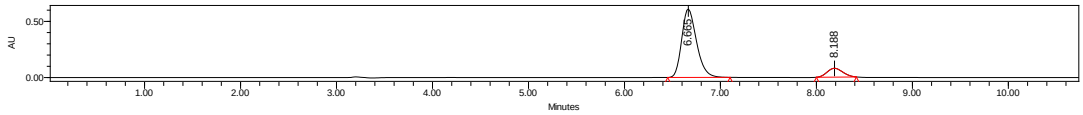


(**$C_{23}H_{18}BrF_2NO_2$**) colorless oil. 96% yield (43.9 mg), 88:12 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (major) = 6.67 min, *t* (minor) = 8.19 min. $[\alpha]_{436}^{24}$ = +31.4 (*c* = 0.92, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.63 (m, 2H), 7.50 – 7.43 (m, 2H), 7.35 – 7.29 (m, 2H), 7.16 (t, *J* = 8.6 Hz, 2H), 7.11 – 6.96 (m, 4H), 5.01 (s, 1H), 4.24 – 4.04 (m, 2H), 1.19 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.9, 168.6, 164.6 (d, *J* = 250.0 Hz), 163.0 (d, *J* = 247.9 Hz), 138.1, 135.4 (d, *J* = 2.9 Hz), 131.8, 131.7 (d, *J* = 3.6 Hz) , 131.1 (d, *J* = 8.7 Hz), 129.8, 129.7,

122.0, 116.1 (d, J = 21.5 Hz), 115.3 (d, J = 21.6 Hz), 69.14, 61.60, 14.20. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -109.6, -111.2.
HRMS (FTMS+c ESI): Calcd for $C_{23}H_{19}{}^{78.9183}BrF_2NO_2{}^{+}$ [M+H^{+}] 458.0562, found 458.0553. HRMS (FTMS+c ESI): Calcd for $C_{23}H_{19}{}^{80.9167}BrF_2NO_2{}^{+}$ [M+H^{+}] 460.0541, found 460.0532.

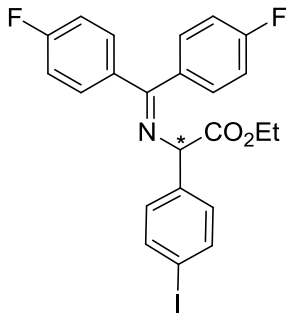


	Retention Time	Area	% Area
1	6.645	6140646	50.35
2	8.152	6054424	49.65

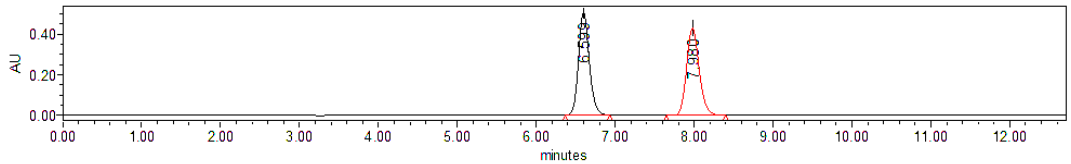


	Retention Time	Area	% Area
1	6.665	6527720	87.97
2	8.188	892695	12.03

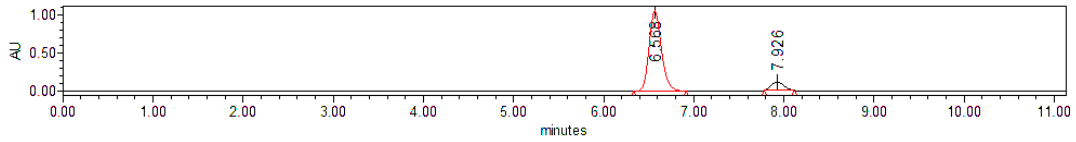
Ethyl 2-((bis(4-fluorophenyl)methylene)amino)-2-(4-iodophenyl)acetate (3bg)



(**$C_{23}H_{18}IF_2NO_2$**) colorless oil. 99% yield (50.3 mg), 90:10 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (major) = 6.57 min, *t* (minor) = 7.93 min. $[\alpha]_{405}{}^{23}$ = +16.8 (*c* = 0.85, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.63 (m, 4H), 7.22 – 7.12 (m, 4H), 7.10 – 6.97 (m, 4H), 4.99 (s, 1H), 4.22 – 4.05 (m, 2H), 1.19 (t, J = 7.2 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.8, 168.6, 164.6 (d, J = 250.0 Hz), 163.0 (d, J = 247.9 Hz), 138.8, 137.7, 135.4 (d, J = 3.0 Hz), 131.7 (d, J = 3.7 Hz). 131.1 (d, J = 8.7 Hz). 129.9, 129.7 (d, J = 8.1 Hz), 116.1 (d, J = 21.5 Hz), 115.3 (d, J = 21.6 Hz), 93.8, 69.3, 61.6, 14.2. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -109.6, -111.1.
HRMS (FTMS+c ESI): Calcd for $C_{23}H_{19}IF_2NO_2{}^{+}$ [M+H^{+}] 506.0423, found 506.0429.

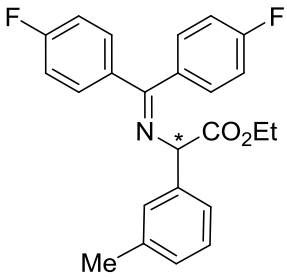


	Retention Time	Area	% Area
1	6.599	4789878	50.16
2	7.980	4759944	49.84

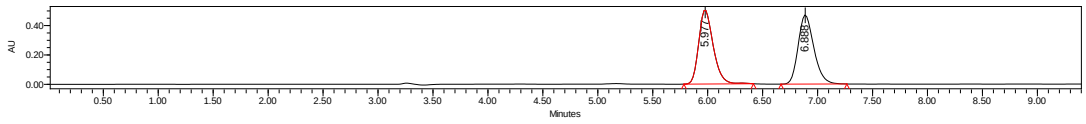


	Retention Time	Area	% Area
1	6.568	9994407	90.17
2	7.926	1089400	9.83

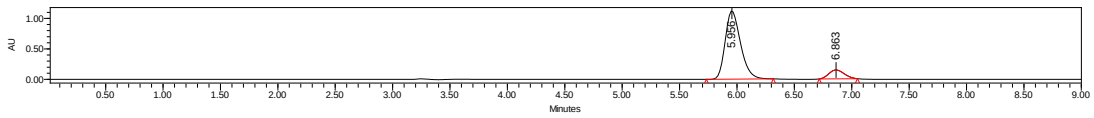
Ethyl 2-((bis(4-fluorophenyl)methylene)amino)-2-(m-tolyl)acetate (3bh)



(**$C_{24}H_{21}F_2NO_2$**) colorless oil. 98% yield (38.5 mg), 88:12 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (major) = 5.96 min, *t* (minor) = 6.86 min. $[\alpha]_{436}^{24}$ = +80.5 (*c* = 0.72, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.64 (m, 2H), 7.25 – 6.98 (m, 10H), 5.03 (s, 1H), 4.24 – 4.03 (m, 2H), 2.34 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.5, 168.0, 164.5 (d, *J* = 249.5 Hz), 163.0 (d, *J* = 247.5 Hz), 139.0, 138.3, 135.7 (d, *J* = 3.1 Hz), 131.9 (d, *J* = 3.7 Hz), 131.1 (d, *J* = 8.5 Hz), 129.8 (d, *J* = 8.1 Hz), 128.8, 128.6, 128.5, 125.0, 115.9 (d, *J* = 21.4 Hz),115.2 (d, *J* = 21.6 Hz), 69.9, 61.4, 21.6, 14.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.1, -111.5.
HRMS (FTMS+c ESI): Calcd for $C_{24}H_{22}F_2NO_2^+$ [M+H$^+$] 394.1613, found 394.1601.

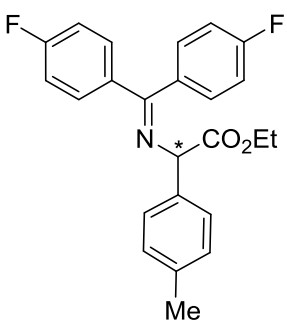


	Retention Time	Area	% Area
1	5.977	4619917	49.72
2	6.888	4671989	50.28



	Retention Time	Area	% Area
1	5.956	10390692	88.44
2	6.863	1358311	11.56

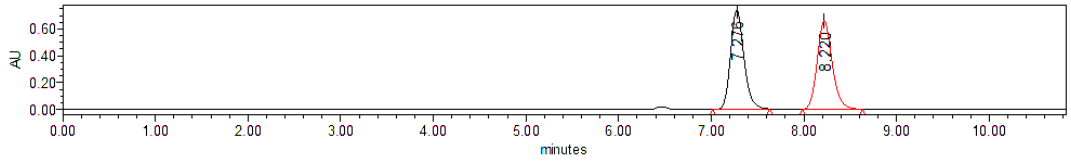
Ethyl 2-((bis(4-fluorophenyl)methylene)amino)-2-(p-tolyl)acetate(3bi)



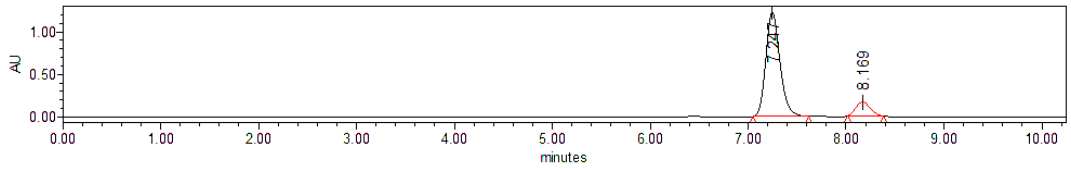
(**$C_{24}H_{21}F_2NO_2$**) colorless oil. 99% yield (39.1 mg), 88:12 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (major) = 7.25 min, *t* (minor) = 8.17 min. $[\alpha]_{436}^{22}$ = +52.5 (*c* = 0.71, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.62 (m, 2H), 7.33 – 7.27 (m, 2H), 7.19 – 7.11 (m, 4H), 7.10 – 7.04 (m, 2H), 7.04 – 6.97 (m, 2H), 5.03 (s, 1H), 4.21 – 4.05 (m, 2H), 2.33 (s, 3H), 1.19 (t, *J*

= 7.2 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 171.6, 167.9, 164.5 (d, *J* = 249.6 Hz), 163.0 (d, *J* = 247.5 Hz), 137.7, 136.2, 135.7 (d, *J* = 3.0 Hz), 131.9 (d, *J* = 3.6 Hz), 131.1 (d, *J* = 8.6 Hz), 129.8 (d, *J* = 8.1 Hz), 129.4, 127.8, 115.9 (d, *J* = 21.4 Hz), 115.2 (d, *J* = 21.4 Hz), 69.6, 61.4, 21.3, 14.2. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -110.2, -111.5.

HRMS (FTMS+c ESI): Calcd for $C_{24}H_{22}F_2NO_2^+$ [M+H$^+$] 394.1613, found 394.1600.

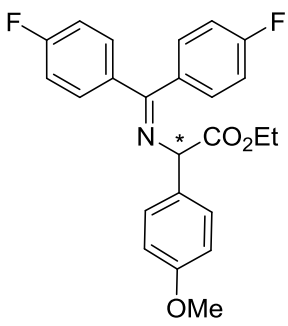


	Retention Time	Area	% Area
1	7.276	7420361	50.07
2	8.220	7398829	49.93



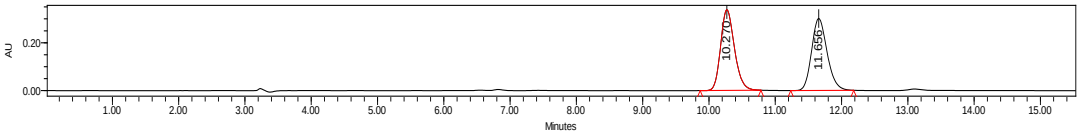
	Retention Time	Area	% Area
1	7.247	12306375	88.03
2	8.169	1673982	11.97

Ethyl 2-((bis(4-fluorophenyl)methylene)amino)-2-(4-methoxyphenyl)acetate (3bj)

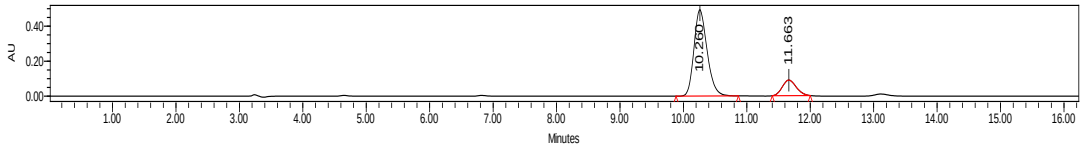


(**$C_{24}H_{21}F_2NO_3$**) colorless oil. 98% yield (40.3 mg), 84:16 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (major) = 10.26 min, *t* (minor) = 11.66 min. $[\alpha]_{436}^{23}$ = +43.2 (*c* = 0.62, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.63 (m, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.15 (t, *J* = 8.8 Hz, 2H), 7.10 – 6.97 (m, 4H), 6.90 – 6.83 (m, 2H), 5.01 (s, 1H), 4.20 – 40.6 (m, 2H), 3.79 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 171.7, 167.8, 164.5 (d, *J* = 249.6 Hz), 162.9 (d, *J* = 247.5 Hz), 159.3, 135.7 (d, *J* = 3.1 Hz), 131.9 (d, *J* = 3.6 Hz), 131.4, 131.1 (d, *J* = 8.7 Hz), 129.8 (d, *J* = 8.1 Hz), 129.1, 115.9 (d, *J* = 21.5 Hz), 115.2 (d, *J* = 21.5 Hz), 114.0, 69.2, 61.3, 55.4, 14.2. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -110.1, -111.5.

HRMS (FTMS+c ESI): Calcd for $C_{24}H_{22}F_2NO_3^+$ [M+H$^+$] 410.1562, found 410.1553.

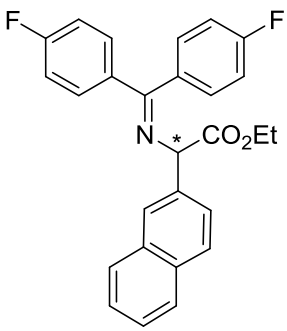


	Retention Time	Area	% Area
1	10.270	4882935	50.02
2	11.656	4879511	49.98



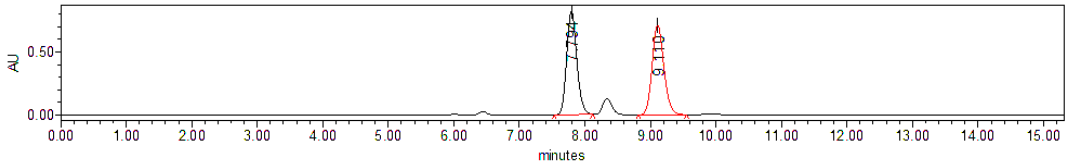
	Retention Time	Area	% Area
1	10.260	7115027	83.93
2	11.663	1362436	16.07

Ethyl 2-((bis(4-fluorophenyl)methylene)amino)-2-(naphthalen-2-yl)acetate (3bk)

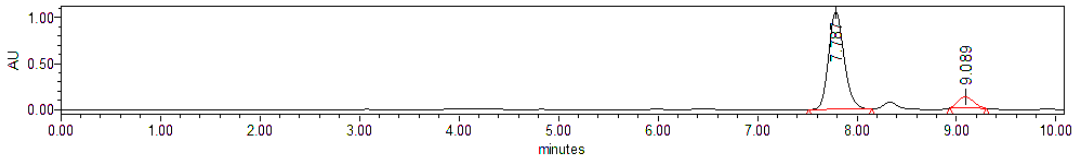


(**$C_{27}H_{21}F_2NO_2$**) colorless oil. 99% yield (42.3 mg), 90:10 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (major) = 7.78 min, *t* (minor) = 9.01 min. $[\alpha]_{436}^{24}$ = +41.4 (*c* = 0.81, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.77 (m, 4H), 7.77 – 7.67 (m, 2H), 7.61 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.51 – 7.42 (m, 2H), 7.16 (t, *J* = 8.4 Hz, 2H), 7.12 – 6.96 (m, 4H), 5.23 (s, 1H), 4.25 – 4.05 (m, 2H), 1.18 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.4, 168.4, 164.6 (d, *J* = 249.7 Hz), 163.0 (d, *J* = 247.6 Hz), 136.6, 135.7 (d, *J* = 3.0 Hz), 133.4, 133.2, 131.9 (d, *J* = 3.7 Hz), 131.2 (d, *J* = 8.1 Hz), 129.9 (d, *J* = 8.2 Hz), 128.4, 128.2, 127.8, 126.9, 126.2, 126.2, 125.9, 116.0 (d, *J* = 21.5 Hz), 115.2 (d, *J* = 21.6 Hz), 70.0 (d, *J* = 2.0 Hz), 61.5, 14.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -109.9, -111.1.

HRMS (FTMS+c ESI): Calcd for $C_{27}H_{22}F_2NO_2^+$ [M+H$^+$] 430.1613, found 430.1615.



	Retention Time	Area	% Area
1	7.794	8827775	49.85
2	9.110	8881653	50.15

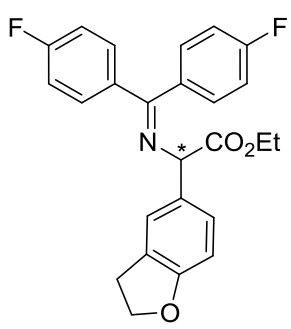


	Retention Time	Area	% Area
1	7.787	11497168	89.53
2	9.089	1343887	10.47

Ethyl

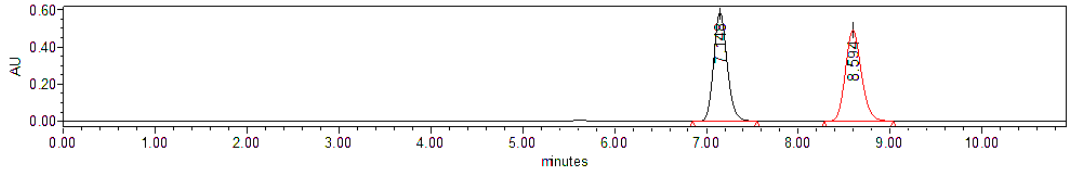
2-((bis(4-fluorophenyl)methylene)amino)-2-(2,3-dihydrobenzofuran-6-yl)acetate

(3bl)

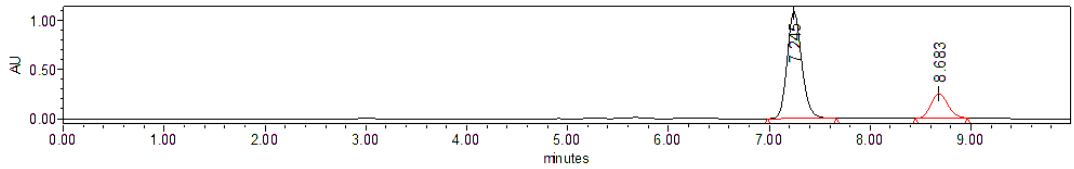


(**$C_{25}H_{21}F_2NO_3$**) colorless oil. 93% yield (39.1 mg), 78:22 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (major) = 7.25 min, *t* (minor) = 8.7 min. $[\alpha]_{436}^{24}$ = +24.8 (*c* = 0.67, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.63 (m, 2H), 7.33 (s, 1H), 7.16 (t, *J* = 8.6 Hz, 2H), 7.11 – 6.95 (m, 5H), 6.71 (d, *J* = 8.4 Hz, 1H), 4.99 (s, 1H), 4.56 (t, *J* = 8.8 Hz, 2H), 4.22 – 4.05 (m, 2H), 3.20 (t, *J* = 8.6 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.8, 167.7, 164.5 (d, *J* = 249.6 Hz), 162.9 (d, *J* = 247.5 Hz), 159.9, 135.7 (d, *J* = 2.9 Hz), 131.9 (d, *J* = 3.7 Hz), 131.2, 131.1 (d, *J* = 8.6 Hz), 129.8 (d, *J* = 8.0 Hz), 127.8, 127.5, 124.6, 115.9 (d, *J* = 21.5 Hz), 115.2 (d, *J* = 21.5 Hz), 109.2, 71.5, 69.5, 61.3, 29.8, 14.3. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.2, -111.6.

HRMS (FTMS+c ESI): Calcd for $C_{25}H_{22}F_2NO_3^+$ [M+H$^+$] 422.1562, found 422.1555.



	Retention Time	Area	% Area
1	7.148	5956764	50.12
2	8.594	5929092	49.88

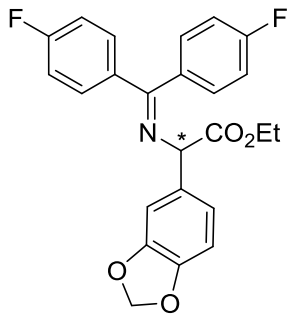


	Retention Time	Area	% Area
1	7.245	10990061	78.67
2	8.683	2980055	21.33

Ethyl

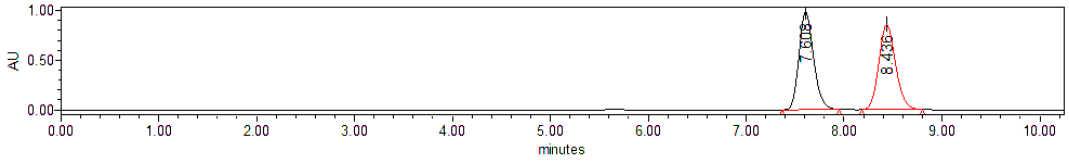
2-(benzo[*d*][1,3]dioxol-5-yl)-2-((bis(4-fluorophenyl)methylene)amino)acetate

(3bm)

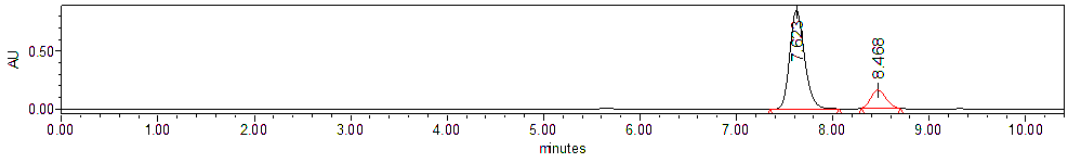


(**$C_{24}H_{19}F_2NO_4$**) colorless oil. 93% yield (39.4 mg), 84.5:15.5 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (major) = 7.62 min, *t* (minor) = 8.47 min. $[\alpha]_{436}^{26}$ = +30.8 (*c* = 0.62, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.62 (m, 2H), 7.16 (t, *J* = 8.6 Hz, 2H), 7.13 – 6.96 (m, 5H), 6.83 – 6.70 (m, 2H), 5.95 (s, 2H), 4.97 (s, 1H), 4.24 – 4.04 (m, 2H), 1.20 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.4, 168.0, 164.5 (d, *J* = 249.7 Hz), 163.0 (d, *J* = 247.6 Hz), 147.9, 147.4, 135.6 (d, *J* = 3.0 Hz), 132.9, 131.8 (d, *J* = 3.5 Hz), 131.1 (d, *J* = 8.6 Hz), 129.8 (d, *J* = 8.1 Hz), 121.3, 115.9 (d, *J* = 21.5 Hz), 115.2 (d, *J* = 21.5 Hz), 108.5, 108.3, 101.2, 69.4, 61.4, 14.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.0, -111.4.

HRMS (FTMS+c ESI): Calcd for $C_{24}H_{20}F_2NO_4^+$ [M+H$^+$] 424.1355, found 424.1351.

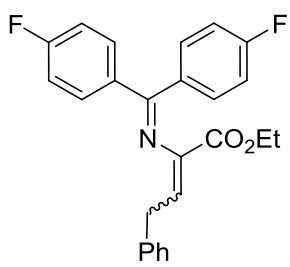


	Retention Time	Area	% Area
1	7.608	10180712	50.00
2	8.436	10181416	50.00



	Retention Time	Area	% Area
1	7.623	9047290	84.46
2	8.468	1664211	15.54

Ethyl 2-((bis(4-fluorophenyl)methylene)amino)-4-phenylbut-2-enoate (3bn)

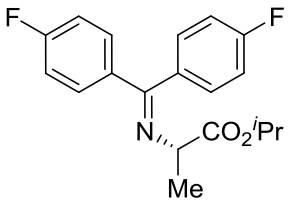


(**$C_{25}H_{21}F_2NO_2$**) colorless oil. 59% yield (23.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.68 (m, 2H), 7.28 – 7.23 (m, 2H), 7.21 – 7.17 (m, 1H), 7.14 – 6.99 (m, 8H), 6.25 (t, *J* = 7.6 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.39 (d, *J* = 7.6 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.0, 164.8 (d, *J* = 250.7 Hz), 163.9, 163.1 (d, *J* = 248.3 Hz), 140.3, 139.3, 135.1 (d, *J* = 3.1 Hz), 131.8 (d, *J* = 3.5 Hz), 131.7 (d, *J* = 8.6 Hz), 130.3 (d, *J* = 8.3 Hz), 128.7, 128.9, 126.4, 124.6, 115.4 (d, *J* = 21.5 Hz), 115.4 (d, *J* = 21.7 Hz), 61.1, 33.7, 14.3. ^{19}F{^{1}H} NMR (376 MHz,

$CDCl_3$) δ -109.0, -110.8.

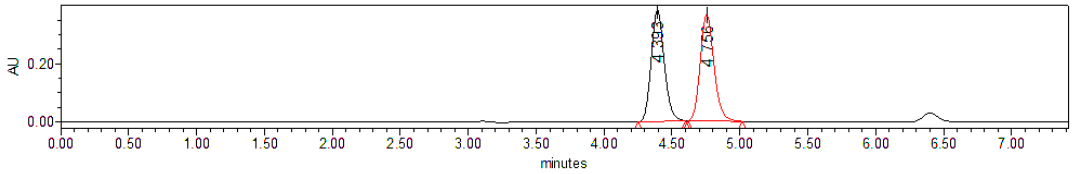
HRMS (FTMS+c ESI): Calcd for $C_{25}H_{22}F_2NO_2^+$ [M+H$^+$] 406.1613, found 406.1604.

Isopropyl (*S*)-2-((bis(4-fluorophenyl)methylene)amino)propanoate (5ba)

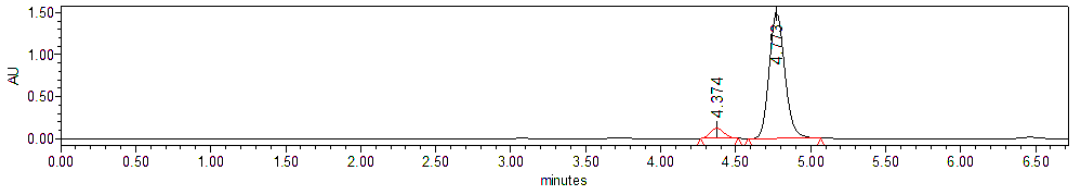


(**$C_{19}H_{19}F_2NO_2$**) colorless oil. 96% yield (33.4 mg), 94:6 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 4.37 min, *t* (major) = 4.77 min. $[\alpha]_{436}^{22}$ = -151.8 (*c* = 0.60, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.58 (m, 2H), 7.21 – 7.13 (m, 4H), 7.04 – 6.97 (m, 2H), 5.08 – 4.97 (m, 1H), 4.06 (q, *J* = 6.8 Hz, 1H), 1.43 (d, *J* = 6.8 Hz, 3H), 1.23 (dd, *J* = 6.4, 5.6 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.2, 167.5, 164.3 (d, *J* = 249.3 Hz), 162.8 (d, *J* = 247.2 Hz), 135.8 (d, *J* = 3.0 Hz), 132.0 (d, *J* = 3.6 Hz), 130.8 (d, *J* = 8.6 Hz), 129.8 (d, *J* = 8.1 Hz), 115.9 (d, *J* = 21.5 Hz), 115.1 (d, *J* = 21.5 Hz), 68.4, 60.8, 21.8, 19.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.4, -111.9.

HRMS (FTMS+c ESI): Calcd for $C_{19}H_{20}F_2NO_2^+$ [M+H$^+$] 332.1457, found 332.1458.

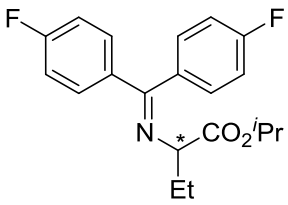


	Retention Time	Area	% Area
1	4.393	2569108	49.98
2	4.756	2570703	50.02



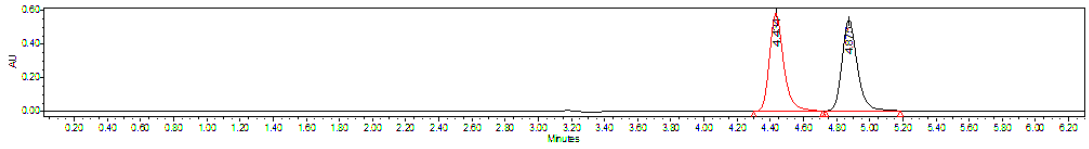
	Retention Time	Area	% Area
1	4.374	759759	6.55
2	4.773	10841719	93.45

Isopropyl 2-((bis(4-fluorophenyl)methylene)amino)butanoate (5bb)

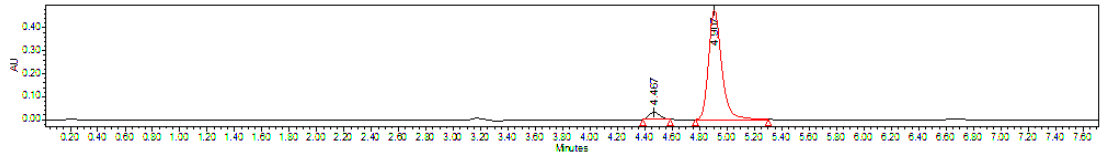


(**$C_{20}H_{21}F_2NO_2$**) colorless oil. 64% yield (22.2 mg), 95:5 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 4.47 min, *t* (major) = 4.91 min. $[\alpha]_{436}^{22}$ = -268.1 (*c* = 0.37, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.57 (m, 2H), 7.15 (d, *J* = 6.8 Hz, 4H), 7.06 – 6.96 (m, 2H), 5.10 – 4.96 (m, 2H), 3.87 (dd, *J* = 8.0 Hz, *J* = 5.2 Hz, 1H), 2.02 – 1.81 (m, 2H), 1.23 (dd, *J* = 7.3, 6.4 Hz, 6H), 0.86 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.7, 168.2, 164.4 (d, *J* = 249.2 Hz), 162.8 (d, *J* = 247.1 Hz), 135.9 (d, *J* = 3.1 Hz), 132.3 (d, *J* = 3.6 Hz), 130.9 (d, *J* = 8.5 Hz), 129.9 (d, *J* = 8.0 Hz), 115.9 (d, *J* = 21.4 Hz), 115.2 (d, *J* = 21.5 Hz), 68.3, 67.1, 27.0, 22.0, 21.9, 10.7. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.5, -112.0.

HRMS (FTMS+c ESI): Calcd for $C_{20}H_{22}F_2NO_2^+$ [M+H$^+$] 346.1613, found 346.1612.

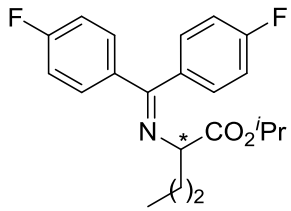


	Retention Time	Area	% Area
1	4.434	3441688	50.08
2	4.875	3430118	49.92



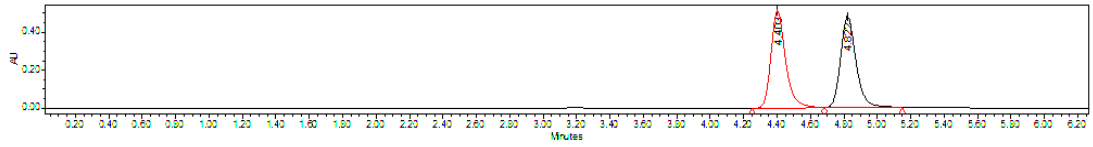
	Retention Time	Area	% Area
1	4.467	172171	5.16
2	4.907	3165284	94.84

Isopropyl 2-((bis(4-fluorophenyl)methylene)amino)pentanoate (5bc)

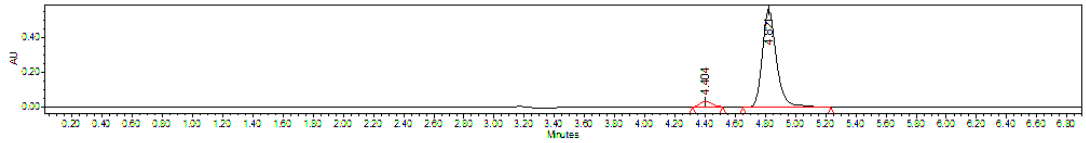


(**$C_{21}H_{23}F_2NO_2$**) colorless oil. 85% yield (30.5 mg), 95.5:4.5 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 4.40 min, *t* (major) = 4.82 min. $[\alpha]_{436}^{22}$ = -272.7 (*c* = 0.46, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.58 (m, 2H), 7.15 (d, *J* = 7.2 Hz, 4H), 7.05 – 6.94 (m, 2H), 5.09 – 4.97 (m, 1H), 3.93 (t, *J* = 6.6 Hz, 1H), 1.95 – 1.81 (m, 2H), 1.37 – 1.15 (m, 8H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.9, 168.1, 164.4 (d, *J* = 249.2 Hz), 162.8 (d, *J* = 247.1 Hz), 135.9 (d, *J* = 3.1 Hz), 132.3 (d, *J* = 3.8 Hz), 130.9 (d, *J* = 8.6 Hz), 129.9 (d, *J* = 8.0 Hz), 115.8 (d, *J* = 21.4 Hz), 115.2 (d, *J* = 21.5 Hz), 68.3, 65.6, 35.9, 21.9, 21.9, 19.4, 14.0. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.5, -112.0.

HRMS (FTMS+c ESI): Calcd for $C_{21}H_{24}F_2NO_2^+$ [M+H$^+$] 360.1770, found 360.1768.

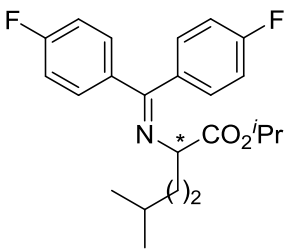


	Retention Time	Area	% Area
1	4.403	3123710	50.09
2	4.822	3112996	49.91



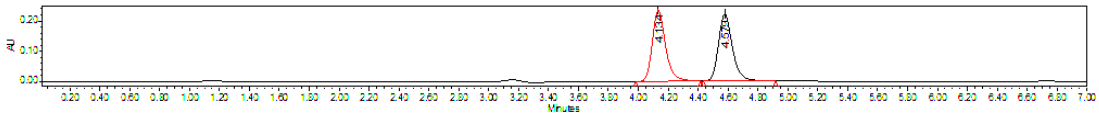
	Retention Time	Area	% Area
1	4.404	175745	4.59
2	4.821	3651203	95.41

Isopropyl 2-((bis(4-fluorophenyl)methylene)amino)-5-methylhexanoate (5bd)

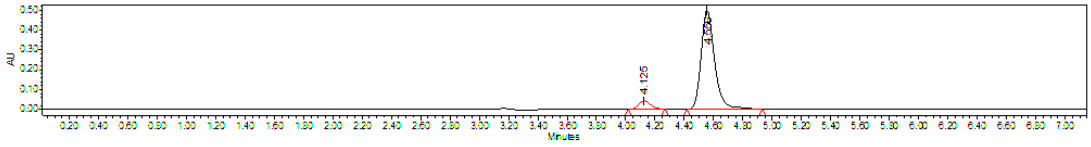


(**$C_{23}H_{27}NO_2$**) colorless oil. 36% yield (14.1 mg), 93:7 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 4.13 min, *t* (major) = 4.56 min. $[\alpha]_{436}^{22}$ = -364.6 (*c* = 0.34, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.56 (m, 2H), 7.15 (d, *J* = 7.2 Hz, 4H), 7.06 – 6.97 (m, 2H), 5.01 – 4.97 (m, 1H), 3.90 (dd, *J* = 7.6, 5.2 Hz, 1H), 1.99 – 1.78 (m, 2H), 1.54 – 1.41 (m, 1H), 1.23 (dd, *J* = 7.2, 6.8 Hz, 6H), 1.18 – 1.02 (m, 2H), 0.85 (dd, *J* = 6.6, 3.0 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.9, 168.0, 164.4 (d, *J* = 249.2 Hz), 162.8 (d, *J* = 247.1 Hz), 135.9 (d, *J* = 3.0 Hz), 132.3 (d, *J* = 3.6 Hz), 130.9 (d, *J* = 8.6 Hz), 129.9 (d, *J* = 7.6 Hz), 115.9 (d, *J* = 21.5 Hz), 115.2 (d, *J* = 21.5 Hz), 68.3, 66.1, 35.3, 31.7, 28.0, 22.7, 22.6, 22.0, 21.9. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.5, -112.0.

HRMS (FTMS+c ESI): Calcd for $C_{23}H_{28}F_2NO_2^+$ [M+H$^+$] 388.2080, found 388.2067.

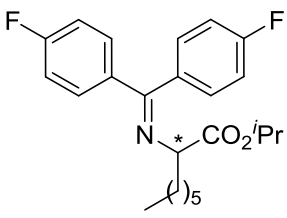


	Retention Time	Area	% Area
1	4.134	1439857	49.94
2	4.579	1443416	50.06



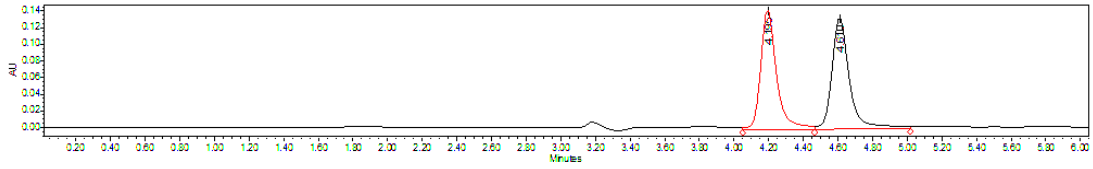
	Retention Time	Area	% Area
1	4.125	241535	7.02
2	4.556	3200742	92.98

Isopropyl 2-((bis(4-fluorophenyl)methylene)amino)octanoate (5be)

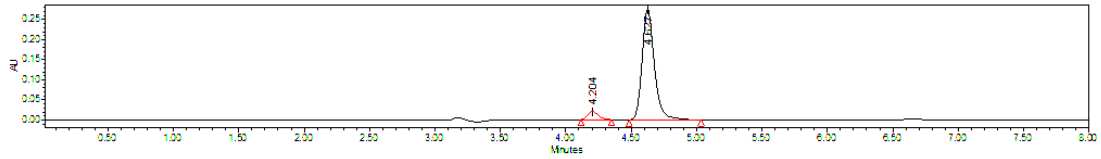


(**$C_{24}H_{29}F_2NO_2$**) colorless oil. 30% yield (12.2 mg), 94:6 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 4.20 min, *t* (major) = 4.63 min. $[\alpha]_{436}^{22}$ = -224.1 (*c* = 0.21, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.56 (m, 2H), 7.15 (d, *J* = 6.8 Hz, 4H), 7.06 – 6.95 (m, 2H), 5.08 – 4.98 (m, 1H), 3.92 (dd, *J* = 7.6, 5.6 Hz, 1H), 1.97 – 1.80 (m, 2H), 1.31 – 1.14 (m, 14H), 0.89 – 0.79 (m, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.9, 168.1, 164.4 (d, *J* = 249.2 Hz), 162.8 (d, *J* = 247.1 Hz), 135.9 (d, *J* = 3.1 Hz), 132.3 (d, *J* = 3.7 Hz), 130.9 (d, *J* = 8.6 Hz), 129.9 (d, *J* = 8.0 Hz), 115.9 (d, *J* = 21.3 Hz), 115.2 (d, *J* = 21.5 Hz), 68.3, 65.8, 33.8, 31.8, 29.2, 26.1, 22.7, 22.0, 21.9, 14.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.5, -112.0.

HRMS (FTMS+c ESI): Calcd for $C_{24}H_{30}F_2NO_2^+$ [M+H$^+$] 402.2239, found 402.2237.

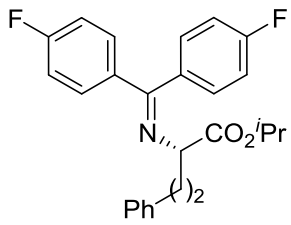


	Retention Time	Area	% Area
1	4.195	919857	49.46
2	4.610	939961	50.54



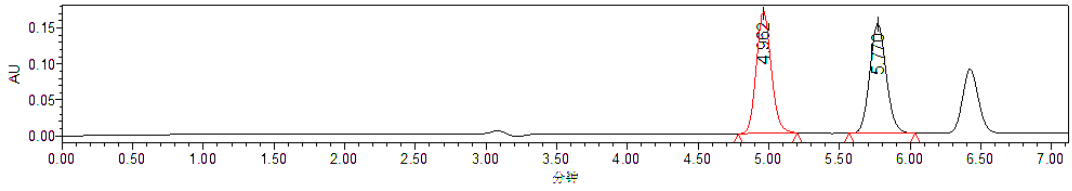
	Retention Time	Area	% Area
1	4.204	112994	5.92
2	4.627	1795259	94.08

Isopropyl (*S*)-2-((bis(4-fluorophenyl)methylene)amino)-4-phenylbutanoate (5bf)

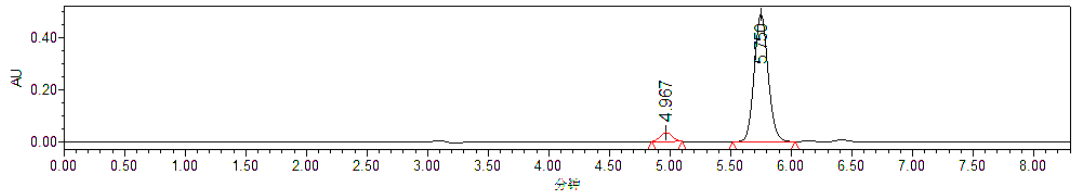


(**$C_{26}H_{25}F_2NO_2$**) colorless oil. 90% yield (37.9 mg), 94.5:5.5 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 4.97 min, *t* (major) = 5.75 min. $[\alpha]_{436}^{21}$ = -229.8 (*c* = 0.57, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.59 (m, 2H), 7.26 – 7.22 (m, 2H), 7.20 – 7.15 (m, 1H), 7.14 – 7.05 (m, 6H), 7.05 – 6.99 (m, 2H), 5.10 – 4.98 (m, *J* = 6.3 Hz, 1H), 3.98 (dd, *J* = 8.0, 5.2 Hz, 1H), 2.71 – 2.51 (m, 2H), 2.34 – 2.13 (m, 2H), 1.23 (dd, *J* = 9.2, 6.2 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.6, 168.6, 164.4 (d, *J* = 249.4 Hz), 162.8 (d, *J* = 247.2 Hz), 141.5, 135.8 (d, *J* = 3.0 Hz), 132.1 (d, *J* = 3.6 Hz), 130.9 (d, *J* = 8.6 Hz), 129.8 (d, *J* = 8.0 Hz), 128.5, 128.5, 126.0, 115.8 (d, *J* = 21.4 Hz), 115.2 (d, *J* = 21.5 Hz), 68.5, 65.1, 35.3, 32.4, 22.0, 21.9. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.3, -111.9.

HRMS (FTMS+c ESI): Calcd for $C_{26}H_{26}F_2NO_2^+$ [M+H$^+$] 422.1926, found 422.1924.



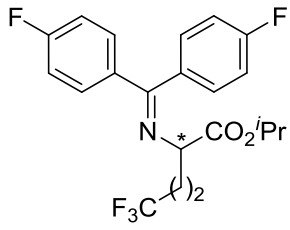
	Retention Time	Area	% Area
1	4.962	1234934	50.09
2	5.770	1230411	49.91



	Retention Time	Area	% Area
1	4.967	231184	5.60
2	5.750	3895120	94.40

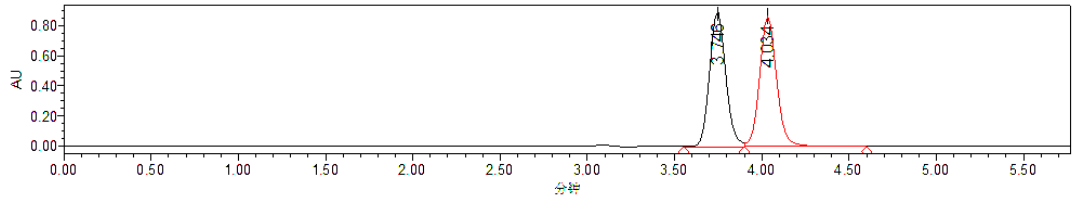
Isopropyl

2-((bis(4-fluorophenyl)methylene)amino)-5,5,5-trifluoropentanoate(5bg)

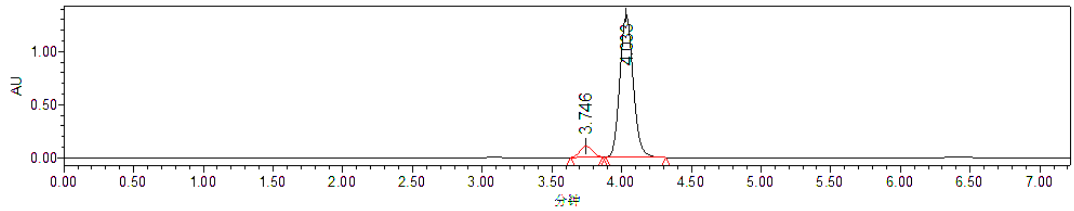


(**$C_{21}H_{20}F_5NO_2$**) colorless oil. 99% yield (40.9 mg), 93:7 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 3.75 min, *t* (major) = 4.03 min. $[\alpha]_{436}^{21}$ = -179.3 (*c* = 0.70, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.58 (m, 2H), 7.17 (d, *J* = 7.6 Hz, 4H), 7.07 – 6.98 (m, 2H), 5.09 – 4.97 (m, 1H), 4.07 – 3.95 (m, 1H), 2.23 – 2.07 (m, 4H), 1.23 (dd, *J* = 11.0, 6.4 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.6, 169.5, 164.6 (d, *J* = 250.1 Hz), 163.0 (d, *J* = 247.8 Hz), 135.4 (d, *J* = 3.0 Hz), 131.8 (d, *J* = 3.6 Hz), 131.0 (d, *J* = 8.6 Hz), 129.8 (d, *J* = 8.0 Hz), 127.2 (q, *J* = 274.5 Hz), 116.1 (d, *J* = 21.5 Hz), 115.3 (d, *J* = 21.6 Hz), 69.0, 63.7, 30.4 (q, *J* = 29.0 Hz), 26.1, 21.9, 21.8. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -66.3, -109.7, -111.4.

HRMS (FTMS+c ESI): Calcd for $C_{21}H_{21}F_5NO_2^+$ [M+H$^+$] 414.1487, found 414.1485.

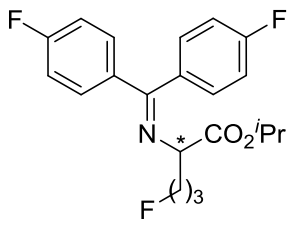


	Retention Time	Area	% Area
1	3.746	5778609	49.57
2	4.034	5878987	50.43



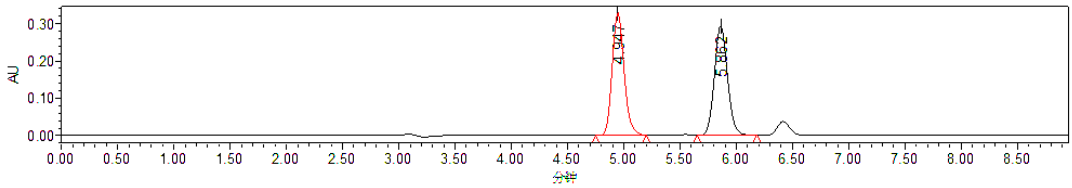
	Retention Time	Area	% Area
1	3.746	638913	6.70
2	4.033	8900935	93.30

Isopropyl 2-((bis(4-fluorophenyl)methylene)amino)-5-fluoropentanoate (5bh)

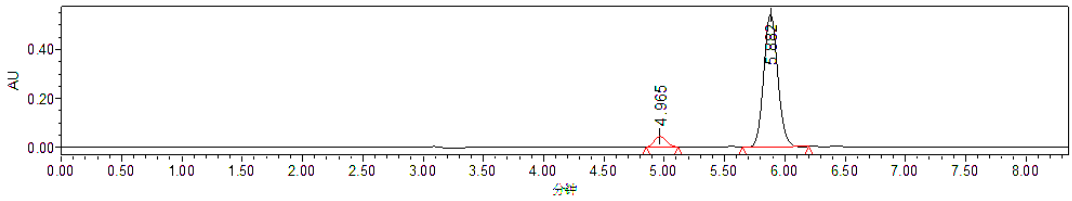


(**$C_{21}H_{22}F_3NO_2$**) colorless oil. 99% yield (37.5 mg), 94:6 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 10/90, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 4.97 min, *t* (major) = 5.88 min. $[\alpha]_{436}^{21}$ = -229.5 (*c* = 0.70, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.56 (m, 2H), 7.16 (d, *J* = 6.8 Hz, 4H), 7.07 – 6.94 (m, 2H), 5.09 – 4.98 (m, 1H), 4.47 (t, *J* = 6.4 Hz, 1H), 4.35 (t, *J* = 6.4 Hz, 1H), 3.98 (t, *J* = 6.4 Hz, 1H), 2.09 – 1.96 (m, 2H), 1.75 – 1.62 (m, 2H), 1.23 (dd, *J* = 8.6, 6.2 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.3, 168.7, 164.5 (d, *J* = 249.4 Hz), 162.9 (d, *J* = 247.5 Hz), 135.7 (d, *J* = 2.9 Hz), 132.1 (d, *J* = 3.7 Hz), 130.9 (d, *J* = 8.6 Hz), 129.9 (d, *J* = 8.0 Hz), 116.0 (d, *J* = 21.4 Hz), 115.2 (d, *J* = 21.5 Hz), 83.8 (d, *J* = 164.2 Hz), 68.6, 65.4, 29.4 (d, *J* = 5.3 Hz), 27.1 (d, *J* = 19.8 Hz), 21.9, 21.9. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.2, -111.7, 218.2.

HRMS (FTMS+c ESI): Calcd for $C_{21}H_{23}F_3NO_2^+$ [M+H$^+$] 378.1675, found 378.1665.

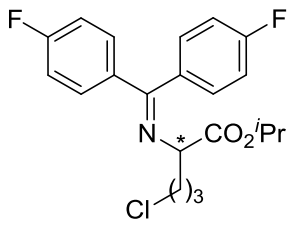


	Retention Time	Area	% Area
1	4.947	2408394	50.59
2	5.862	2352026	49.41



	Retention Time	Area	% Area
1	4.965	302202	6.47
2	5.882	4368050	93.53

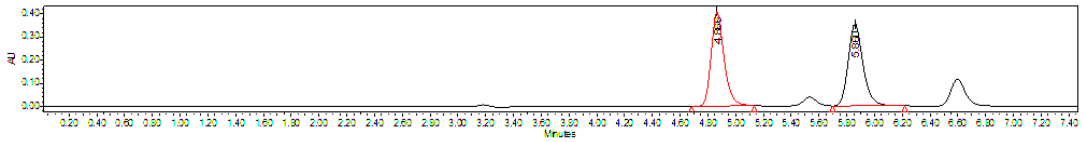
Isopropyl 2-((bis(4-fluorophenyl)methylene)amino)-5-chloropentanoate (5bi)



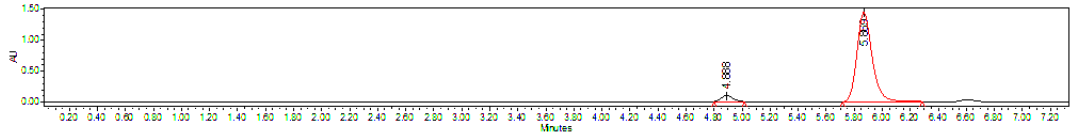
(**$C_{21}H_{22}ClF_2NO_2$**) colorless oil. 79% yield (31.1 mg), 95:5 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 4.89, *t* (major) = 5.87 min. $[\alpha]_{436}^{21}$ = -140.8 (*c* = 0.41, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 2H), 7.16 (d, *J* = 7.2 Hz, 4H), 7.07 – 6.96 (m, 2H), 5.08 – 4.98 (m, 1H), 3.96 (t, *J* = 6.4 Hz, 1H), 3.55 – 3.44 (m, 2H), 2.08 – 1.98 (m, 2H), 1.87 – 1.68 (m, 2H), 1.23 (dd, *J* = 8.8, 6.4 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.3, 168.7, 164.5 (d, *J* = 249.8 Hz), 162.9 (d, *J* = 247.4 Hz), 135.6 (d, *J* = 2.9 Hz), 132.1 (d, *J* = 3.6 Hz), 130.9 (d, *J* = 8.6 Hz), 129.8 (d, *J* = 8.1 Hz), 116.0 (d, *J* = 21.5 Hz), 115.3 (d, *J* = 21.5 Hz), 68.7, 64.9, 44.8, 31.0, 29.3, 21.9, 21.9. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.1,

-111.6.

HRMS (FTMS+c ESI): Calcd for $C_{21}H_{23}{}^{34.9689}ClF_2NO_2{}^+$ [M+H$^+$] 394.1380, found 394.1381. HRMS (FTMS+c ESI): Calcd for $C_{21}H_{23}{}^{36.9659}ClF_2NO_2{}^+$ [M+H$^+$] 396.1350, found 396.1349.

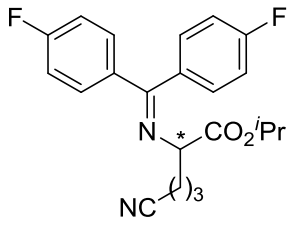


	Retention Time	Area	% Area
1	4.866	2629413	50.13
2	5.860	2616029	49.87



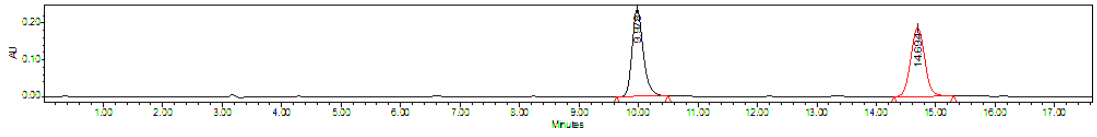
	Retention Time	Area	% Area
1	4.888	578065	5.03
2	5.869	10917634	94.97

Isopropyl 2-((bis(4-fluorophenyl)methylene)amino)-5-cyanopentanoate (5bj)

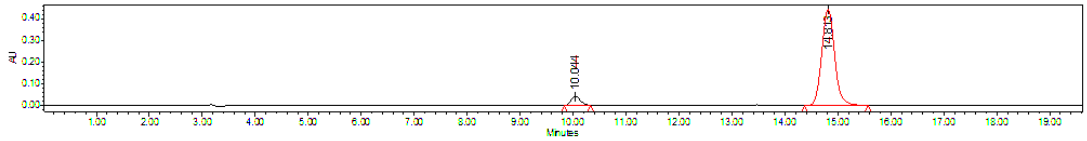


(**$C_{22}H_{22}F_2N_2O_2$**) colorless oil. 91% yield (43.9 mg), 94:6 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 10/90, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 10.04 min, *t* (major) = 14.81 min. $[\alpha]_{436}{}^{22}$ = -221.8 (*c* = 0.61, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 2H), 7.22 – 7.13 (m, 4H), 7.07 – 6.98 (m, 2H), 5.10 – 4.95 (m, 1H), 3.98 (dd, *J* = 7.2, 5.2 Hz, 1H), 2.41 – 2.27 (m, 2H), 2.12 – 1.95 (m, 2H), 1.76 – 1.66 (m, 2H), 1.23 (dd, *J* = 9.6, 6.4 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.9, 169.0, 164.5 (d, *J* = 249.8 Hz), 162.9 (d, *J* = 247.7 Hz), 135.4 (d, *J* = 2.9 Hz), 131.9 (d, *J* = 3.6 Hz), 130.9 (d, *J* = 8.7 Hz), 129.8 (d, *J* = 8.1 Hz), 119.5, 116.1 (d, *J* = 21.4 Hz), 115.3 (d, *J* = 21.6 Hz), 68.9, 64.6, 32.5, 22.3, 21.9, 21.9, 17.3. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -109.7, -111.4.

HRMS (FTMS+c ESI): Calcd for $C_{22}H_{23}F_2N_2O_2{}^+$ [M+H$^+$] 385.1722, found 385.1721.



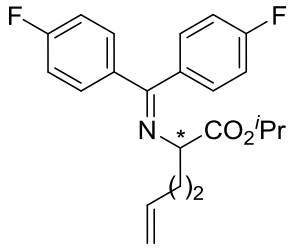
	Retention Time	Area	% Area
1	9.978	3063289	50.13
2	14.694	3047030	49.87



	Retention Time	Area	% Area

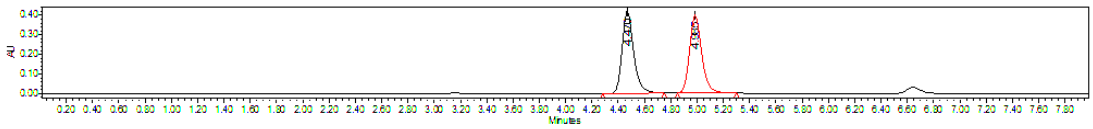
1	10.044	523332	6.54
2	14.813	7477973	93.46

Isopropyl 2-((bis(4-fluorophenyl)methylene)amino)hex-5-enoate (5bk)

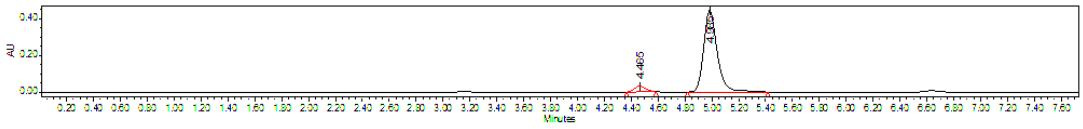


(**$C_{22}H_{23}F_2NO_2$**). colorless oil. 99% yield (37.4 mg), 95:5 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 4.67 min, *t* (major) = 4.99 min. $[\alpha]_{436}^{21}$ = -117.6 (*c* = 0.62, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.59 (m, 2H), 7.15 (d, *J* = 6.8 Hz, 4H), 7.06 – 6.96 (m, 2H), 5.79 – 5.65 (m, 1H), 5.10 – 5.00 (m, 1H), 5.00 – 4.88 (m, 2H), 4.02 – 3.87 (m, 1H), 2.12 – 1.93 (m, 4H), 1.23 (dd, *J* = 8.4, 6.2 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.7, 168.5, 164.4 (d, *J* = 249.4 Hz), 162.9 (d, *J* = 247.3 Hz), 137.8, 135.8 (d, *J* = 2.9 Hz), 132.2 (d, *J* = 3.6 Hz), 130.9 (d, *J* = 8.6 Hz), 129.9 (d, *J* = 8.0 Hz), 115.8 (d, *J* = 21.4 Hz), 115.2 (d, *J* = 21.5 Hz), 115.2, 68.5, 65.1, 33.0, 30.3, 21.9, 21.8. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.4, -111.9.

HRMS (FTMS+c ESI): Calcd for $C_{22}H_{24}F_2NO_2^+$ [M+H$^+$] 372.1770, found 372.1765.

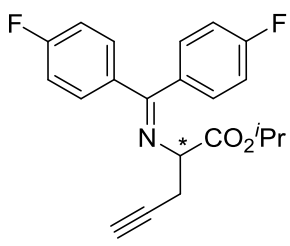


	Retention Time	Area	% Area
1	4.470	2559033	50.07
2	4.985	2551859	49.93



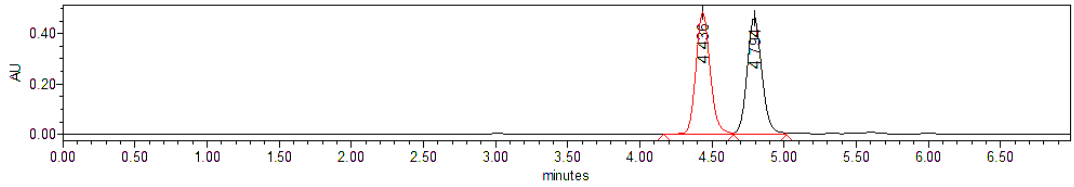
	Retention Time	Area	% Area
1	4.465	180868	5.51
2	4.985	3102669	94.49

Isopropyl 2-((bis(4-fluorophenyl)methylene)amino)pent-4-ynoate (5bl)

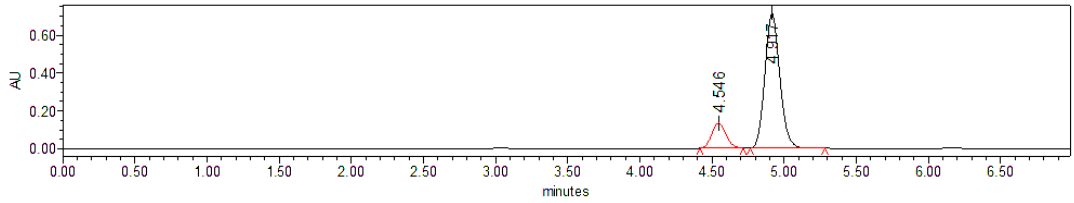


(**$C_{21}H_{19}F_2NO_2$**) colorless oil. 73% yield (28.5 mg), 85:15 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 4.55 min, *t* (major) = 4.92 min. $[\alpha]_{436}^{22}$ = -218.3 (*c* = 0.33, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.56 (m, 2H), 7.26 – 7.22 (m, 2H), 7.20 – 7.12 (m, 2H), 7.07 – 6.98 (m, 2H), 5.09 – 4.97 (m, 1H), 4.18 (dd, *J* = 8.2, 5.2 Hz, 1H), 2.92 – 2.70 (m, 2H), 1.95 (t, *J* = 2.6 Hz, 1H), 1.24 (t, *J* = 6.0 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.9, 169.8, 164.5 (d, *J* = 249.7 Hz), 163.0 (d, *J* = 247.7 Hz), 135.7 (d, *J* = 2.9 Hz), 131.8 (d, *J* = 3.6 Hz), 131.2 (d, *J* = 8.6 Hz), 131.4 (d, *J* = 8.0 Hz), 115.8 (d, *J* = 21.4 Hz), 115.2 (d, *J* = 21.6 Hz), 81.1, 70.4, 69.1, 64.3, 23.4, 21.9, 21.8. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.1, -111.7.

HRMS (FTMS+c ESI): Calcd for $C_{21}H_{20}F_2NO_2^+$ [M+H$^+$] 356.1457, found 356.1450.

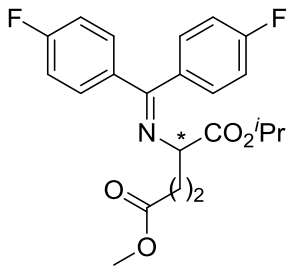


	Retention Time	Area	% Area
1	4.436	3343534	50.26
2	4.794	3309169	49.74



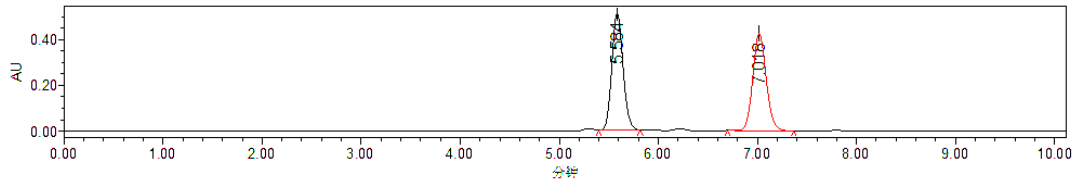
	Retention Time	Area	% Area
1	4.546	900599	14.91
2	4.917	5140247	85.09

1-isopropyl 4-methyl 2-((bis(4-fluorophenyl)methylene)amino)succinate (5bm)

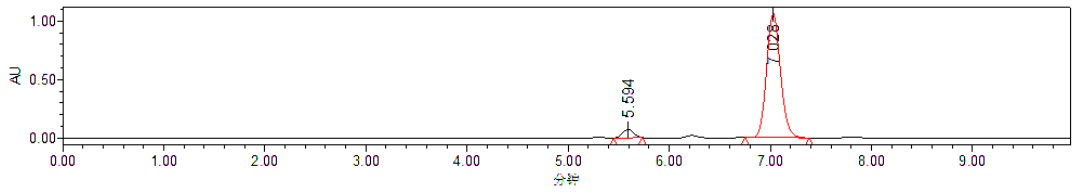


(**$C_{22}H_{23}F_2NO_4$**) colorless oil. 93% yield (37.3 mg), 95:5 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 10/90, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 5.59 min, *t* (major) = 7.03 min. $[\alpha]_{436}^{22}$ = -251.2 (*c* = 0.67, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.57 (m, 2H), 7.23 – 7.11 (m, 4H), 7.06 – 6.96 (m, 2H), 5.08 – 4.96 (m, 1H), 3.99 (t, *J* = 6.2 Hz, 1H), 3.59 (s, 3H), 2.44 – 2.30 (m, 2H), 2.28 – 2.20 (m, 2H), 1.23 (dd, *J* = 10.4, 6.4 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.5, 171.0, 169.0, 164.5 (d, *J* = 249.7 Hz), 162.9 (d, *J* = 247.4 Hz), 135.6 (d, *J* = 3.0 Hz), 132.0 (d, *J* = 3.6 Hz), 131.0 (d, *J* = 8.6 Hz), 129.9 (d, *J* = 8.1 Hz), 115.9 (d, *J* = 21.4 Hz), 115.2 (d, *J* = 21.5 Hz), 68.7, 64.4, 51.7, 30.5, 28.6, 21.9, 21.9. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.1, -111.7.

HRMS (FTMS+c ESI): Calcd for $C_{22}H_{24}F_2NO_4^+$ [M+H$^+$] 404.1668, found 404.1668.

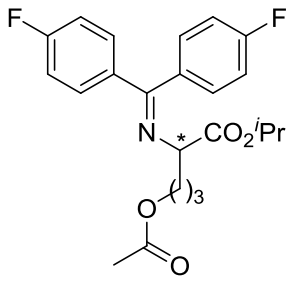


	Retention Time	Area	% Area
1	5.584	4029886	50.23
2	7.018	3993570	49.77

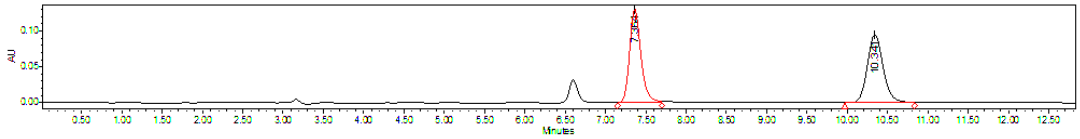


	Retention Time	Area	% Area
1	5.594	541383	5.11
2	7.028	10056359	94.89

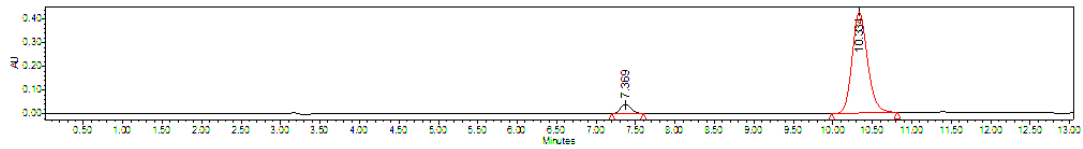
Isopropyl 3-acetoxy-2-((bis(4-fluorophenyl)methylene)amino)propanoate (5bn)



(**$C_{23}H_{25}F_2NO_4$**) colorless oil. 83% yield (34.6 mg), 94:6 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 10/90, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 7.37 min, *t* (major) = 10.33 min. $[\alpha]_{436}^{21}$ = -219.2 (*c* = 0.43, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.57 (m, 2H), 7.16 (d, *J* = 7.2 Hz, 4H), 7.07 – 6.98 (m, 2H), 5.09 – 4.96 (m, 1H), 4.02 (t, *J* = 6.4 Hz, 2H), 3.96 (t, *J* = 6.4 Hz, 1H), 2.02 (s, 3H), 2.00 – 1.92 (m, 2H), 1.68 – 1.49 (m, 2H), 1.23 (dd, *J* = 8.0, 6.4 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.3, 171.2, 168.7, 164.5 (d, *J* = 249.6 Hz), 162.9 (d, *J* = 247.5 Hz), 135.6 (d, *J* = 2.9 Hz), 132.1 (d, *J* = 3.7 Hz), 130.9 (d, *J* = 8.6 Hz), 129.9 (d, *J* = 8.0 Hz), 116.0 (d, *J* = 21.4 Hz), 115.2 (d, *J* = 21.6 Hz), 68.6, 65.2, 64.3, 30.2, 25.4, 21.9, 21.9, 21.1. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.2, -111.7. HRMS (FTMS+c ESI): Calcd for $C_{23}H_{26}F_2NO_4^+$ [M+H$^+$] 418.1824, found 418.1825.

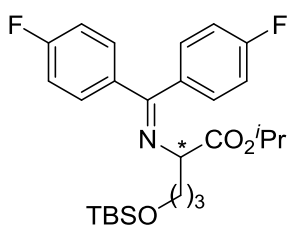


	Retention Time	Area	% Area
1	7.364	1273872	49.70
2	10.341	1289070	50.30



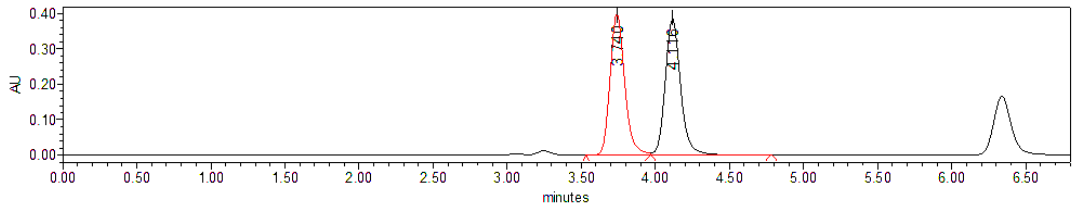
	Retention Time	Area	% Area
1	7.369	360239	5.88
2	10.334	5764025	94.12

Isopropyl 2-((bis(4-fluorophenyl)methylene)amino)-5-((tert-butyldimethylsilyl)oxy)pentanoate (5bo)

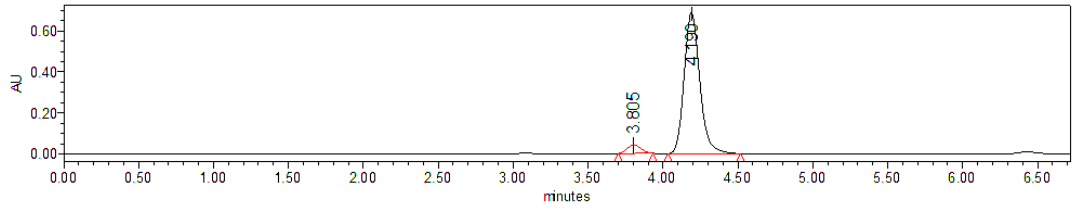


(**$C_{27}H_{37}F_2NO_3Si$**) colorless oil. 67% yield (32.6 mg), 95:5 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 3.81 min, *t* (major) = 4.19 min. $[\alpha]_{436}^{22}$ = -199.6 (*c* = 0.56, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.54 (m, 2H), 7.14 (d, *J* = 7.2 Hz, 4H), 7.05 – 6.94 (m, 2H), 5.09 – 4.95 (m, 1H), 3.92 (dd, *J* = 8.4, 4.8 Hz, 1H), 3.62 – 3.47 (m, 2H), 2.05 – 1.83 (m, 2H), 1.56 – 1.36 (m, 2H), 1.21 (dd, *J* = 7.6, 6.0 Hz, 6H), 0.86 (s, 9H), 0.00 (d, *J* = 2.4 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.7, 168.2, 164.4 (d, *J* = 249.4 Hz), 162.9 (d, *J* = 247.4 Hz), 135.8 (d, *J* = 3.0 Hz), 132.3 (d, *J* = 3.6 Hz), 130.9 (d, *J* = 8.6 Hz), 129.9 (d, *J* = 8.0 Hz), 115.9 (d, *J* = 21.4 Hz), 115.2 (d, *J* = 21.6 Hz), 68.4, 65.5, 62.9, 30.2, 29.4, 26.1, 21.9, 21.9, 18.5, -5.2. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.4, -111.9.

HRMS (FTMS+c ESI): Calcd for $C_{27}H_{38}F_2NO_3Si^+$ [M+H$^+$] 490.2584, found 490.2566.

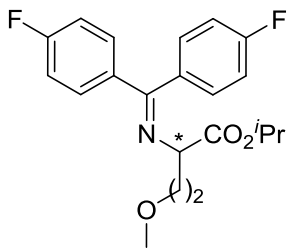


	Retention Time	Area	% Area
1	3.740	2723125	49.62
2	4.116	2764470	50.38



	Retention Time	Area	% Area
1	3.805	264637	5.03
2	4.190	4995431	94.97

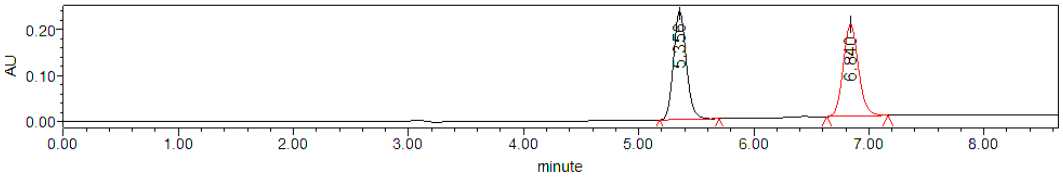
Isopropyl 2-((bis(4-fluorophenyl)methylene)amino)-4-methoxybutanoate (5bp)



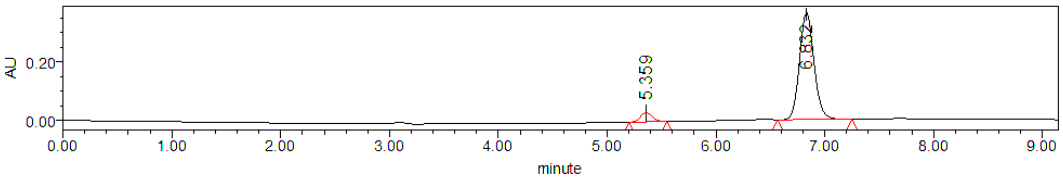
(**$C_{21}H_{23}F_2NO_3$**) colorless oil. 36% yield (13.3 mg), 93:7 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 95/5, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 5.34 min, *t* (major) = 6.83 min. $[\alpha]_{436}^{22}$ = -205.2 (*c* = 0.25, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H), 7.20 – 7.10 (m, 4H), 7.05 – 6.97 (m, 2H), 5.07 – 4.95 (m, 1H), 4.12 (dd, *J* = 8.6, 4.4 Hz, 1H), 3.46 – 3.29 (m, 2H), 3.23 (s, 3H), 2.29 – 2.10 (m, 2H), 1.22 (dd, *J* = 8.4, 6.4 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ

171.5, 169.0, 164.4 (d, *J* = 249.5 Hz), 162.9 (d, *J* = 247.1 Hz), 135.9 (d, *J* = 3.0 Hz), 132.1 (d, *J* = 3.7 Hz), 130.9 (d, *J* = 8.6 Hz), 129.9 (d, *J* = 8.1 Hz), 115.7 (d, *J* = 21.6 Hz), 115.2 (d, *J* = 21.5 Hz), 69.0, 68.5, 62.5, 58.6, 33.4, 21.9, 21.9. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -110.4, -112.0.

HRMS (FTMS+c ESI): Calcd for $C_{21}H_{24}F_2NO_3^+$ [M+H$^+$] 376.1719, found 376.1720.

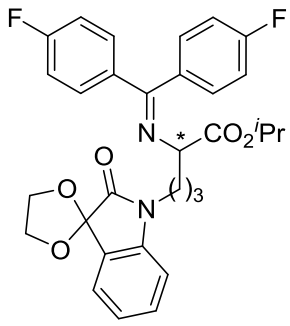


	Retention Time	Area	% Area
1	5.356	1822638	49.89
2	6.840	1831034	50.11



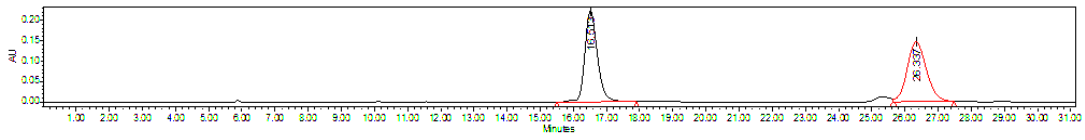
	Retention Time	Area	% Area
1	5.359	242059	6.67
2	6.832	3384613	93.33

Isopropyl 2-((bis(4-fluorophenyl)methylene)amino)-5-(2-oxospiro[indoline-3,2'-[1,3]dioxolan]-1-yl)pentanoate (5bq)

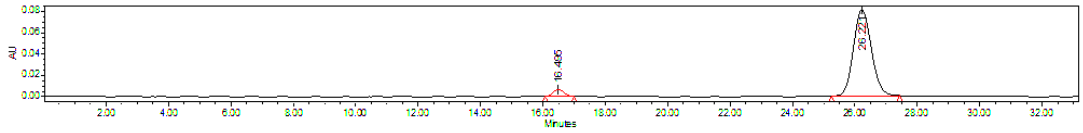


(**$C_{31}H_{30}F_2N_2O_5$**) colorless oil. 99% yield (54.4 mg), 95.5:4.5 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 10/90, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 16.50 min, *t* (major) = 26.22 min. $[\alpha]_{436}^{22}$ = -164.9 (*c* = 0.98, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.53 (m, 2H), 7.39 – 7.34 (m, 1H), 7.33 – 7.27 (m, 1H), 7.13 (d, *J* = 7.2 Hz, 4H), 7.08 – 7.04 (m, 1H), 7.03 – 6.95 (m, 2H), 6.77 (d, *J* = 7.6 Hz, 1H), 5.05 – 4.94 (m, 1H), 4.60 – 4.51 (m, 2H), 4.35 – 4.25 (m, 2H), 3.95 (dd, *J* = 7.2, 5.6 Hz, 1H), 3.60 (t, *J* =7.2, Hz, 2H), 2.05 – 1.86 (m, 2H), 1.74 – 1.62 (m, 2H), 1.19 (dd, *J* = 6.0, 1.2 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 173.3, 171.3, 168.7, 164.4 (d, *J* = 249.5 Hz), 162.8 (d, *J* = 247.4 Hz), 144.1, 135.6 (d, *J* = 3.0 Hz), 132.0 (d, *J* = 3.7 Hz), 131.7, 130.9 (d, *J* = 8.6 Hz), 129.8 (d, *J* = 8.1 Hz), 125.0, 124.2, 123.2, 115.9 (d, *J* = 21.4 Hz), 115.2 (d, *J* = 21.5 Hz), 109.0, 102.2, 68.6, 65.9, 65.0, 39.2, 31.0, 23.7, 21.8. $^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ -110.2, -111.7.

HRMS (FTMS+c ESI): Calcd for $C_{31}H_{31}F_2N_2O_5^+$ [M+H$^+$] 549.2196, found 549.2195.

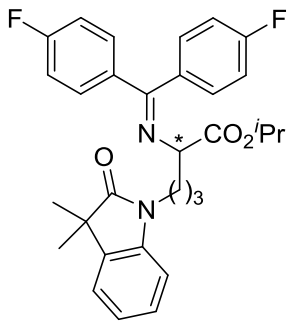


	Retention Time	Area	% Area
1	16.513	5842979	49.86
2	26.337	5876666	50.14



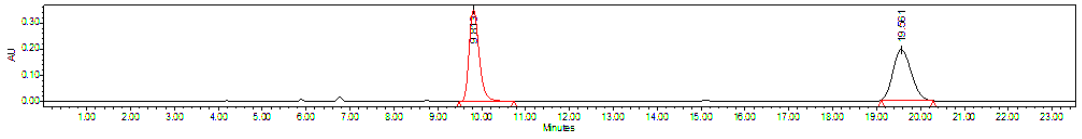
	Retention Time	Area	% Area
1	16.495	151519	4.52
2	26.221	3200624	95.48

Isopropyl 2-((bis(4-fluorophenyl)methylene)amino)-5-(3,3-dimethyl-2-oxoindolin-1-yl)pentanoate (5br)

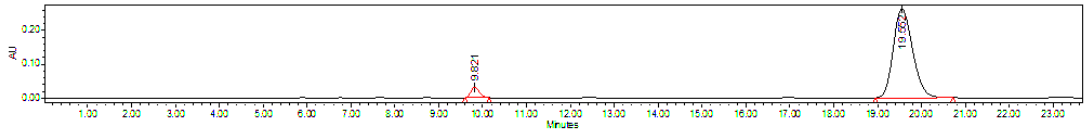


(**$C_{31}H_{32}F_2N_2O_3$**) colorless oil. 99% yield (51.5 mg), 95:5 er, HPLC (Chiral IF cloumn), *i*-PrOH/*n*-Hexane = 10/90, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (minor) = 9.82 min, *t* (major) = 19.55 min. $[\alpha]_{436}^{21}$ = -166.1 (*c* = 0.94, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.53 (m, 2H), 7.23 – 7.18 (m, 2H), 7.12 (d, *J* = 6.8 Hz, 4H), 7.06 – 6.95 (m, 3H), 6.85 – 6.80 (m, 1H), 5.06 – 4.92 (m, 1H), 3.96 (dd, *J* = 7.2, 5.2 Hz, 1H), 3.76 – 3.63 (m, 2H), 2.03 – 1.86 (m, 2H), 1.77 – 1.66 (m, 2H), 1.35 (d, *J* = 3.2 Hz, 6H), 1.17 (d, *J* = 6.0 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 181.3, 171.3, 168.7, 164.4 (d, *J* = 249.5 Hz), 162.9 (d, *J* = 247.4 Hz), 141.9, 136.1, 135.7 (d, *J* = 2.9 Hz), 132.0 (d, *J* = 3.7 Hz), 130.9 (d, *J* = 8.6 Hz), 129.9 (d, *J* = 8.1 Hz), 127.7, 122.6, 122.4, 115.9 (d, *J* = 21.5 Hz), 115.2 (d, *J* = 21.6 Hz), 108.4, 68.6, 65.9, 44.2, 39.6, 31.0, 24.6, 24.6, 23.9, 21.8. ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ -110.2, -111.7.

HRMS (FTMS+c ESI): Calcd for $C_{31}H_{33}F_2N_2O_3^+$ [M+H$^+$] 519.2454, found 519.2455.

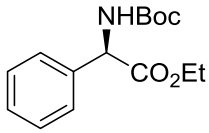


	Retention Time	Area	% Area
1	9.813	5544332	49.87
2	19.561	5572959	50.13

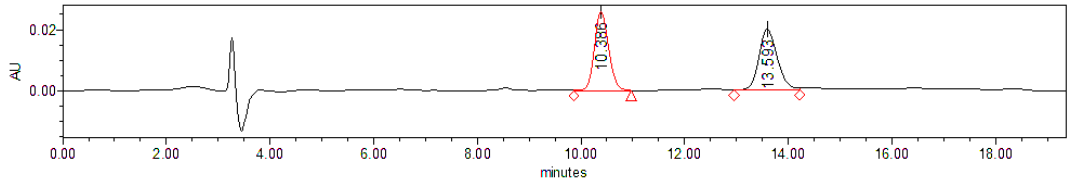


	Retention Time	Area	% Area
1	9.821	423996	5.02
2	19.552	8023546	94.98

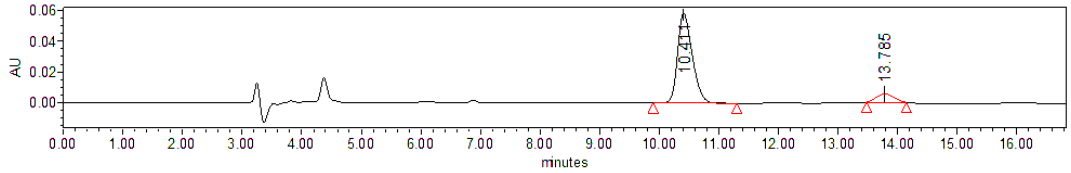
Ethyl (*R*)-2-((tert-butoxycarbonyl)amino)-2-phenylacetate (7ba)



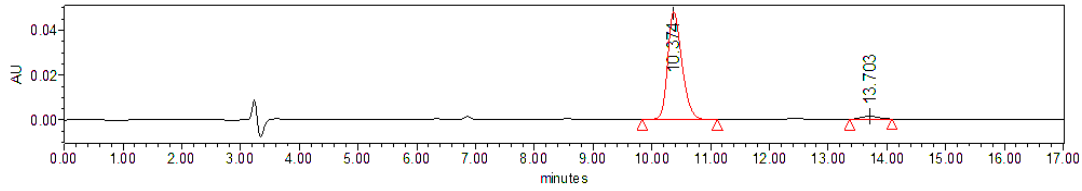
(**$C_{15}H_{21}NO_4$**) white solid. Melting point: 45–47 ^{o}C. 90:10 er (recrystallized 97:3 er), HPLC (Chiral IC cloumn), *i*-PrOH/*n*-Hexane = 5/95, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (major) = 10.41 min, *t* (minor) = 13.79 min. $[\alpha]_{436}^{19}$ = -196.6 (*c* = 1.58, in CH_2Cl_2).(recrystallized $[\alpha]_{436}^{22}$ = -227.4 (*c* = 0.79, in CH_2Cl_2)) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.27 (m, 5H), 5.59 (d, *J* = 7.6 Hz, 1H), 5.30 (d, *J* = 7.6 Hz, 1H), 4.27 – 4.02 (m, 2H), 1.43 (s, 9H), 1.20 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.2, 154.9, 128.9, 137.2, 128.9, 128.4, 127.2, 80.1, 61.8, 57.8, 28.4, 14.1. HRMS (FTMS+c ESI): Calcd for $C_{15}H_{22}NO_4^+$ [M+Na$^+$] 302.1363, found 302.1353.



	Retention Time	Area	% Area
1	10.386	489109	49.98
2	13.593	489457	50.02

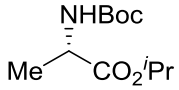


	Retention Time	Area	% Area
1	10.411	992034	89.97
2	13.785	110543	10.03



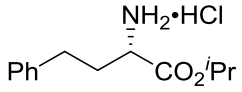
	Retention Time	Area	% Area
1	10.374	803225	97.00
2	13.703	24856	3.00

Isopropyl (tert-butoxycarbonyl)-(*S*)-alaninate (9ba)



(**$C_{11}H_{21}NO_4$**) colorless oil. $[\alpha]_D^{26}$ = -35.2 (*c* = 1.19, in MeOH). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 – 4.76 (m, 2H), 4.36 – 4.03 (m, 1H), 1.45 (s, 9H), 1.37 (d, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 6.8 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 173.0, 155.2, 79.8, 68.9, 49.5, 28.4, 21.8, 21.8, 18.8.
HRMS (FTMS+c ESI): Calcd for $C_{11}H_{21}NO_4^+$ [M+Na$^+$] 254.1360, found 254.1363. {$[\alpha]_D^{20}$ = -31.0 (*c* = 1.0, in MeOH); *S*-isomer}[5]

Isopropyl (*S*)-2-amino-4-phenylbutanoate hydrochloride (10bf)

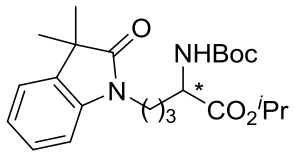


(**$C_{13}H_{20}ClNO_2$**) white solid. Melting point: 252–254 ℃. $[\alpha]_D^{30}$ = +26.6 (*c* = 1.35, in 3M HCl). ^{1}H NMR (400 MHz, CD_3OD) δ 7.35 – 7.21 (m, 5H), 4.01 (t, *J* = 6.2 Hz, 1H), 2.91 – 2.74 (m, 2H), 2.33 – 2.13 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD) δ 171.6, 141.1, 129.5, 129.2, 127.3, 53.4, 33.4, 31.9.
HRMS (FTMS+c ESI): Calcd for $C_{13}H_{20}NO_2^+$ [M+H$^+$] 180.1020, found 180.1019. {$[\alpha]_D^{20}$ = −46.0 (*c* = 1.0, in 3M HCl); *R*-isomer}[6]

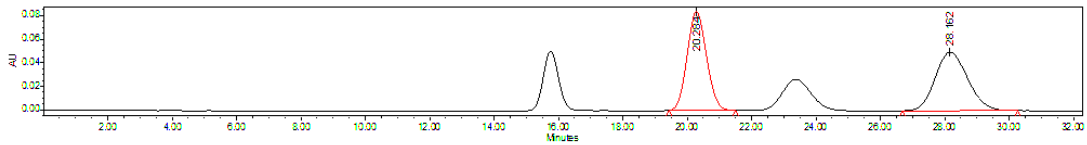
Isopropyl

2-((tert-butoxycarbonyl)amino)-5-(3,3-dimethyl-2-oxoindolin-1-yl)pentanoate

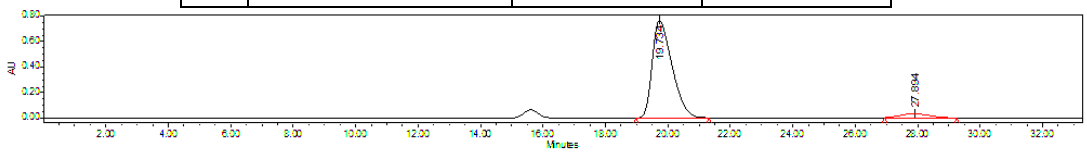
(7br)



(**$C_{23}H_{34}N_2O_5$**) colorless oil. 94:6 er, HPLC (Chiral IE cloumn), *i*-PrOH/*n*-Hexane = 20/80, Flow rate: 1.0 mL/min, λ = 254 nm, *t* (major) = 19.73 min, *t* (minor) = 27.89 min. $[\alpha]_{436}^{27}$ =+19.8 (*c* = 2.00, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.16 (m, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 5.11 (d, *J* = 8.0 Hz, 1H), 5.05 – 4.95 (m, 1H), 4.37 – 4.18 (m, 1H), 3.74 (t, *J* = 6.8 Hz, 2H), 1.91 – 1.63 (m, 4H), 1.43 (s, 9H), 1.36 (s, 6H), 1.22 (d, *J* = 6.4 Hz, 3H), 1.17 (d, *J* = 6.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 181.4, 172.0, 155.5, 141.8, 136.0, 127.7, 122.5, 122.5, 108.4, 79.9, 69.2, 53.3, 44.2, 39.3, 30.3, 28.4, 24.6, 24.5, 23.5, 21.8, 21.8.
HRMS (FTMS+c ESI): Calcd for $C_{23}H_{34}N_2O_5Na^+$ [M+Na$^+$] 441.2360, found 441.2359



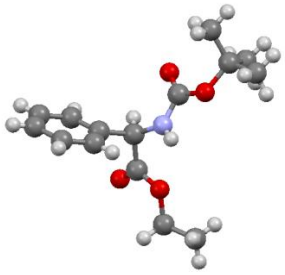
	Retention Time	Area	% Area
1	20.284	3486262	50.04
2	28.162	3481068	49.96



	Retention Time	Area	% Area

1	19.734	33471956	94.17
2	27.894	2071544	5.83

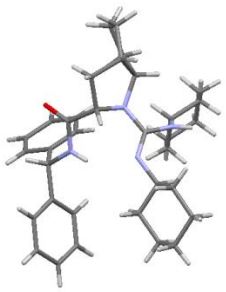
10. X-ray crystal structure of product 7ba and G1



Identification code	cu_20190514_YJ_01_0m_a
Empirical formula	$C_{15}H_{21}NO_4$
Formula weight	279.33
Temperature/K	300(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.3689(3)
b/Å	10.4011(6)
c/Å	27.4980(15)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1535.56(15)
Z	4
ρ_{calc}g/cm^3	1.208
μ/mm^{-1}	0.717
F(000)	600.0
Crystal size/mm^3	0.200 × 0.140 × 0.130
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.428 to 129.956
Index ranges	-6 ≤ h ≤ 6, -10 ≤ k ≤ 12, -32 ≤ l ≤ 32
Reflections collected	8783
Independent reflections	2611 [R_{int} = 0.0302, R_{sigma} = 0.0280]
Data/restraints/parameters	2611/0/189
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0342, wR_2 = 0.0860
Final R indexes [all data]	R_1 = 0.0352, wR_2 = 0.0868
Largest diff. peak/hole / e Å^{-3}	0.11/-0.18
Flack parameter	0.08(6)

Single crystal of ($C_{15}H_{21}NO_2$) **7ba** was recrystallized from mixed solvents of CH_2Cl_2 and *n*-hexane. The absolute configuration of the product **7ba** was determined to be (*R*)

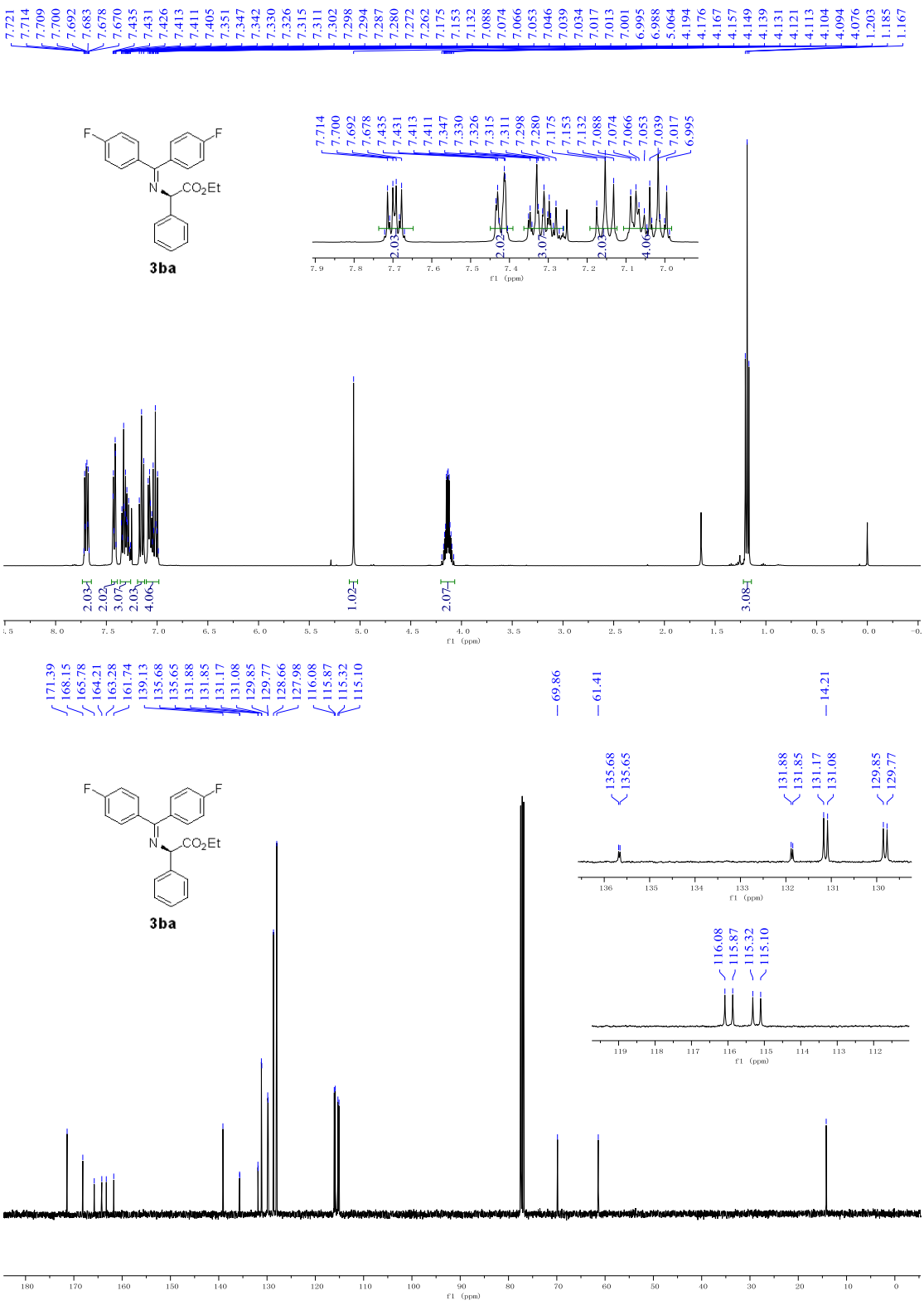
according to X-ray crystal structural analysis. (CCDC 1915990)

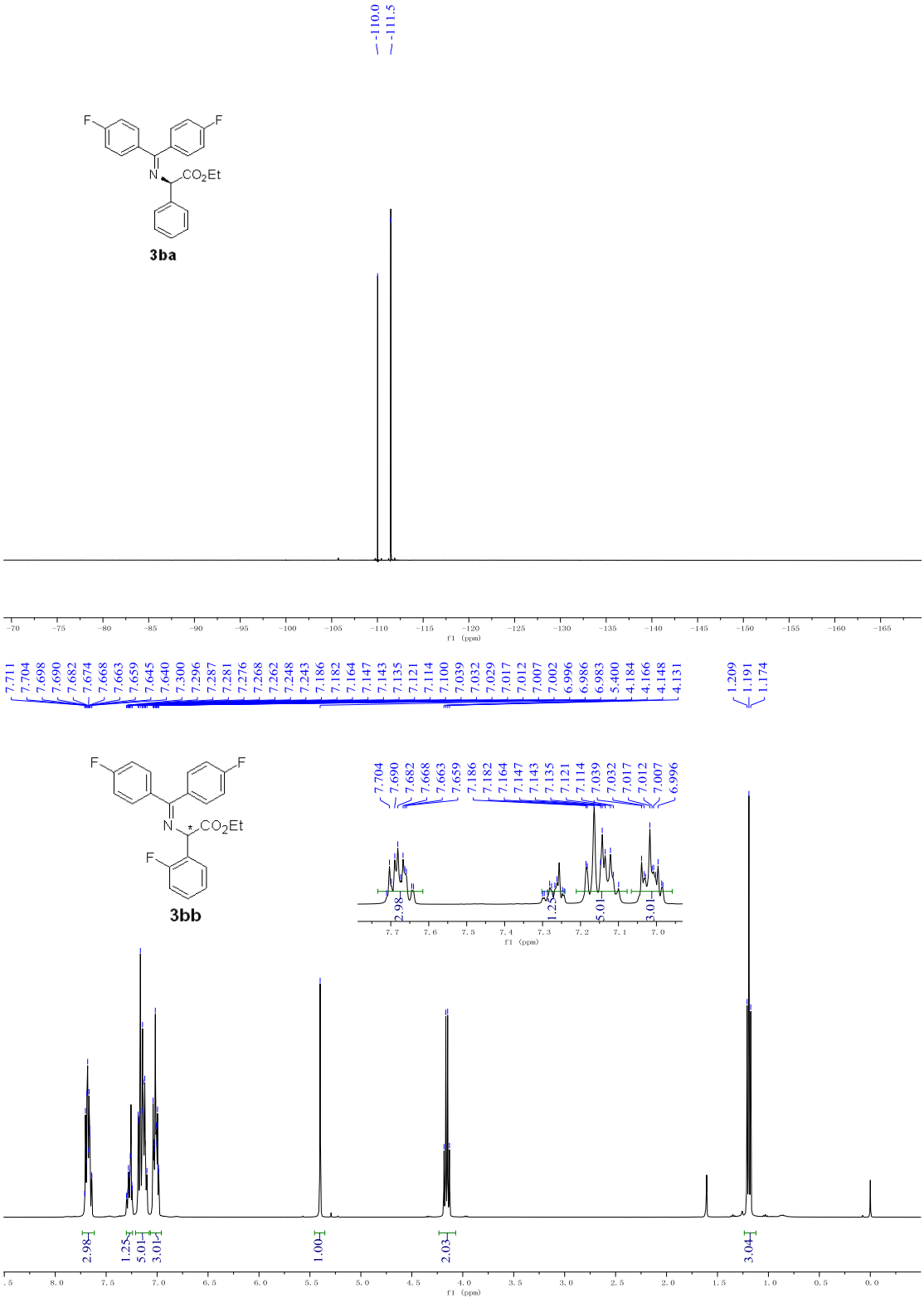


Identification code	cu_20190617_YJ_01_0m_a
Empirical formula	$C_{34}H_{46}N_4O$
Formula weight	526.75
Temperature/K	300(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	11.3578(2)
b/Å	16.0040(2)
c/Å	16.8541(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3063.57(8)
Z	4
ρ_{calc}g/cm^3	1.142
μ/mm^{-1}	0.533
F(000)	1144.0
Crystal size/mm^3	0.240 × 0.150 × 0.080
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.618 to 130.286
Index ranges	$-13 \le h \le 11$, $-18 \le k \le 18$, $-19 \le l \le 19$
Reflections collected	17635
Independent reflections	5169 [R_{int} = 0.0300, R_{sigma} = 0.0262]
Data/restraints/parameters	5169/0/356
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0418, wR_2 = 0.1071
Final R indexes [all data]	R_1 = 0.0433, wR_2 = 0.1101
Largest diff. peak/hole / e Å^{-3}	0.16/-0.35
Flack parameter	-0.02(9)

Single crystal of ($C_{34}H_{46}N_4O$) **G1** was recrystallized from mixed solvents of CH_2Cl_2 and petroleum ether. (CCDC 1935053)

11. Copies of NMR spectra for the products

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F
F
N
CO2Et
3ba
f1 (ppm)
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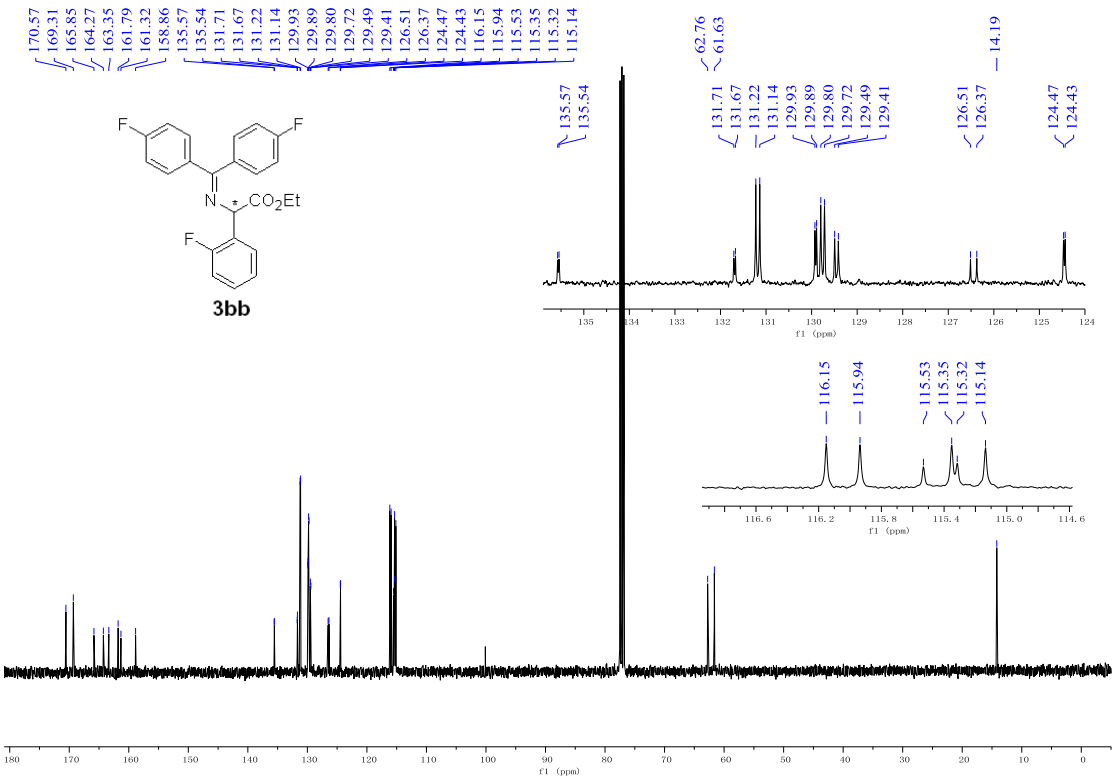
7.704
7.698
7.690
7.682
7.674
7.668
7.663
7.659
7.645
7.640
7.300
7.296
7.287
7.281
7.276
7.268
7.262
7.248
7.243
7.186
7.182
7.164
7.147
7.143
7.135
7.121
7.114
7.100
7.039
7.032
7.029
7.017
7.012
7.007
7.002
6.996
6.986
6.983
5.400
4.184
4.166
4.148
4.131
1.209
1.191
1.174
F
F
N
CO2Et
F
3bb
2.98
1.25
5.01
3.01
1.00
2.03
3.04
f1 (ppm)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164.27
163.35
161.79
161.32
158.86
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131.22
131.14
129.93
129.89
129.80
129.72
129.49
129.41
126.51
126.37
124.47
124.43
116.15
115.94
115.53
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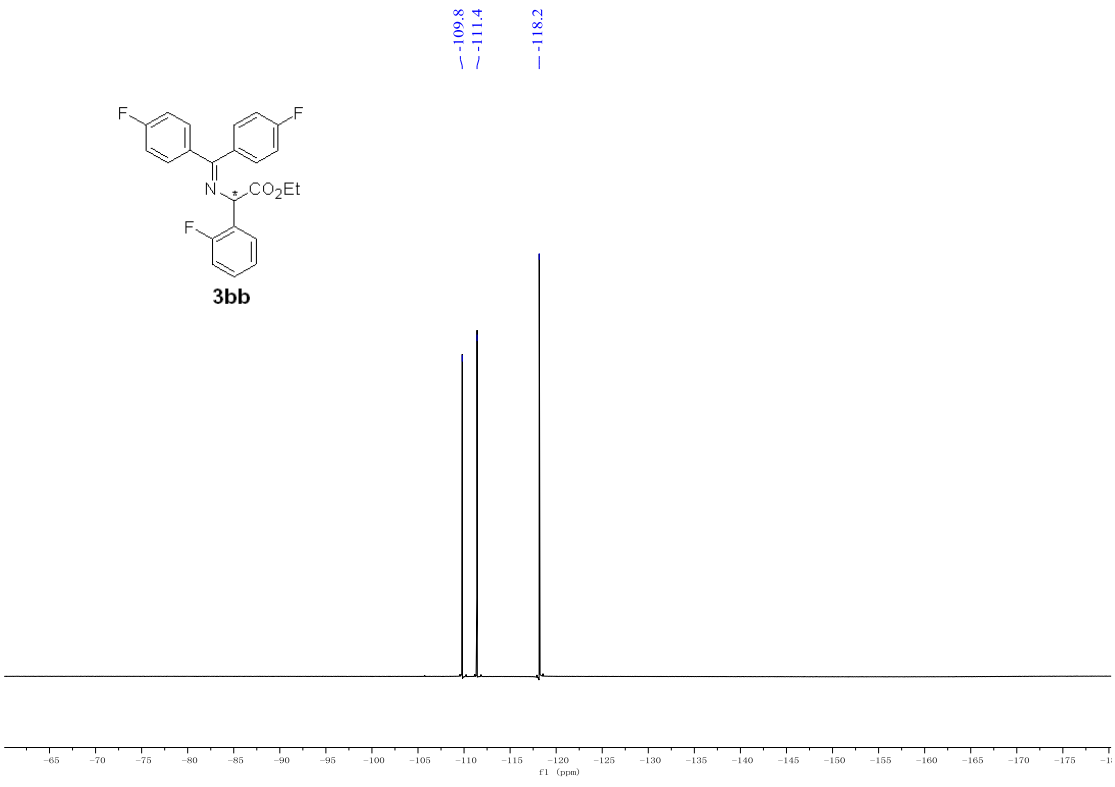
115.32
115.14
62.76
61.63
14.19
F
F
N
CO2Et
F
3bb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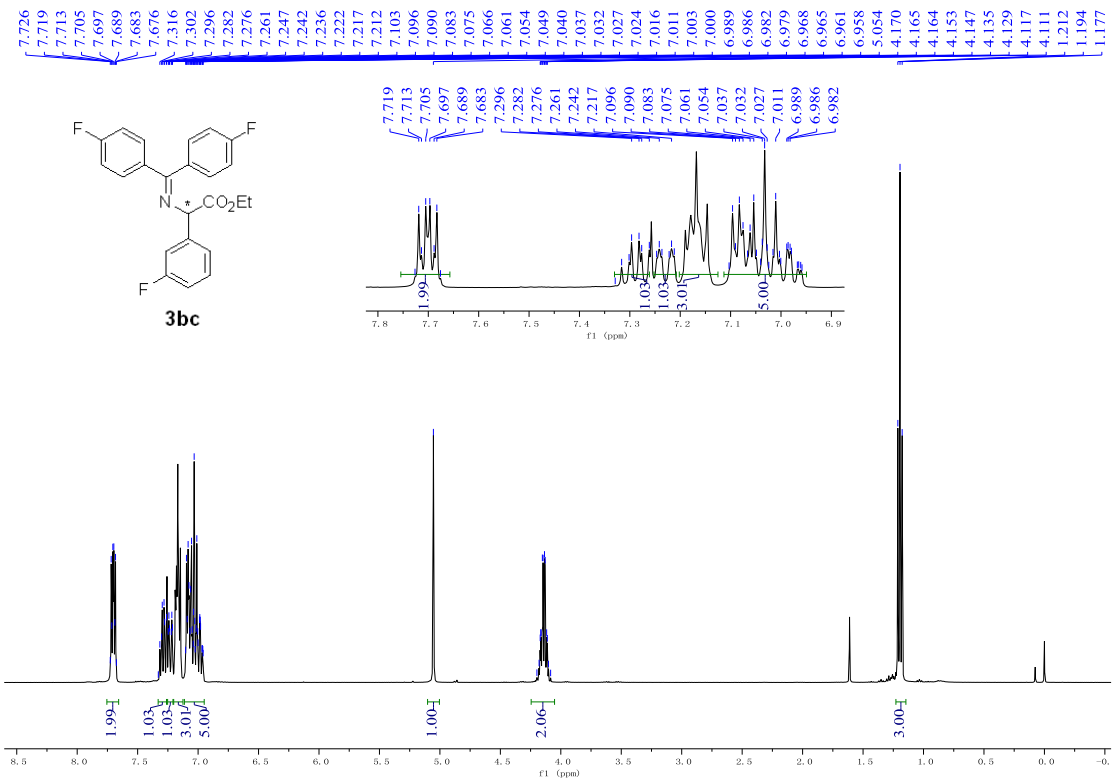
F
F
N
CO2Et
F
3bb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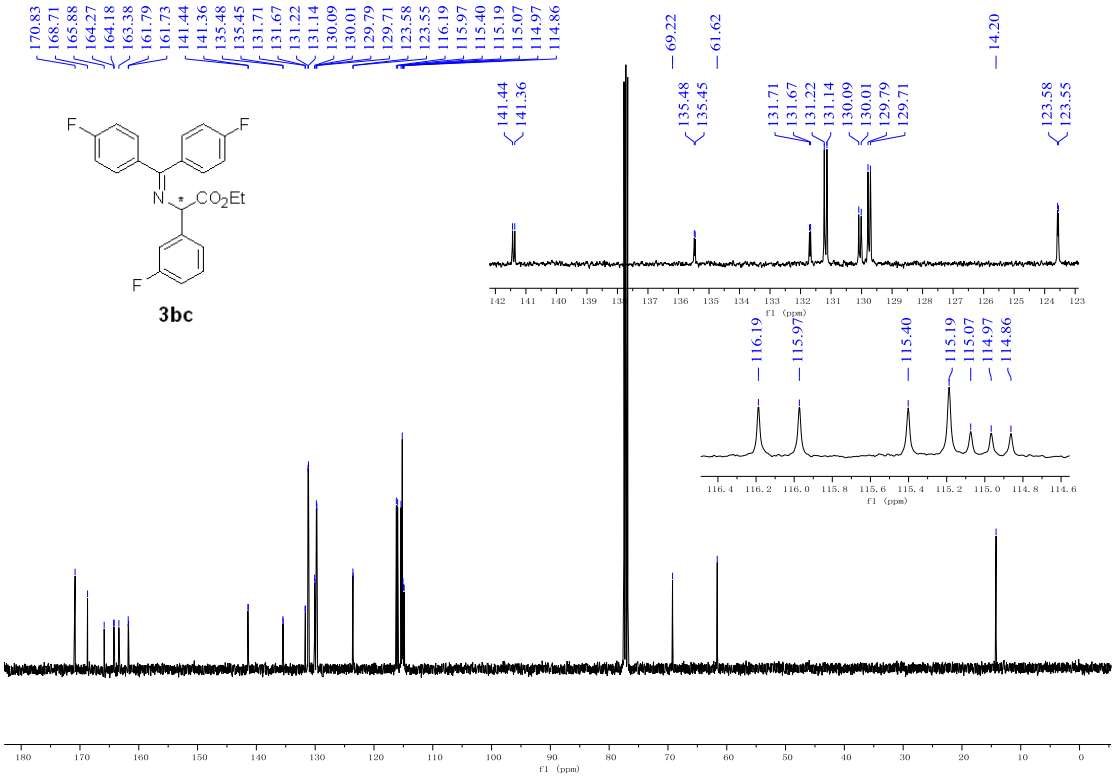
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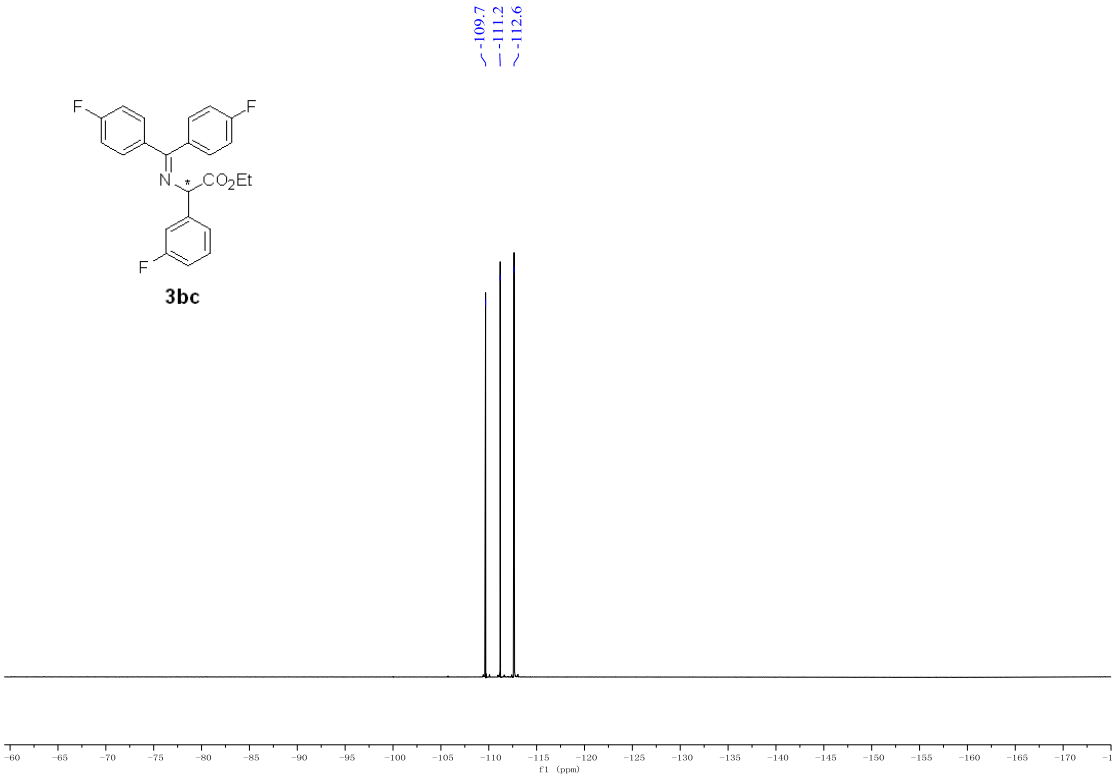
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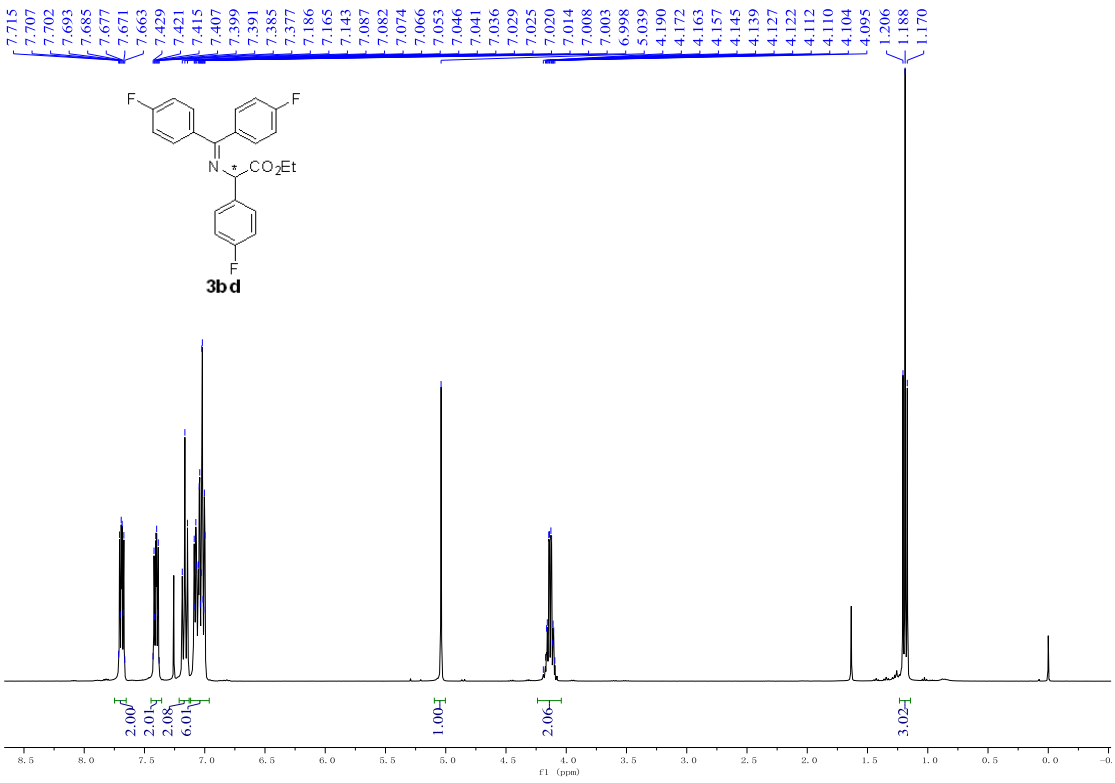
-111.2
-112.6
F
F
N
*
CO2Et
F
3bc
f1 (ppm)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7.663
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7.415
7.407
7.399
7.391
7.385
7.377
7.186
7.165
7.143
7.087
7.082
7.074
7.066
7.053
7.046
7.041
7.036
7.029
7.025
7.020
7.014
7.008
7.003
6.998
5.039
4.190
4.172
4.163
4.157
4.145
4.139
4.127
4.122
4.112
4.110
4.104
4.095
1.206
1.188
1.170
F
F
N
*
CO2Et
F
3bd
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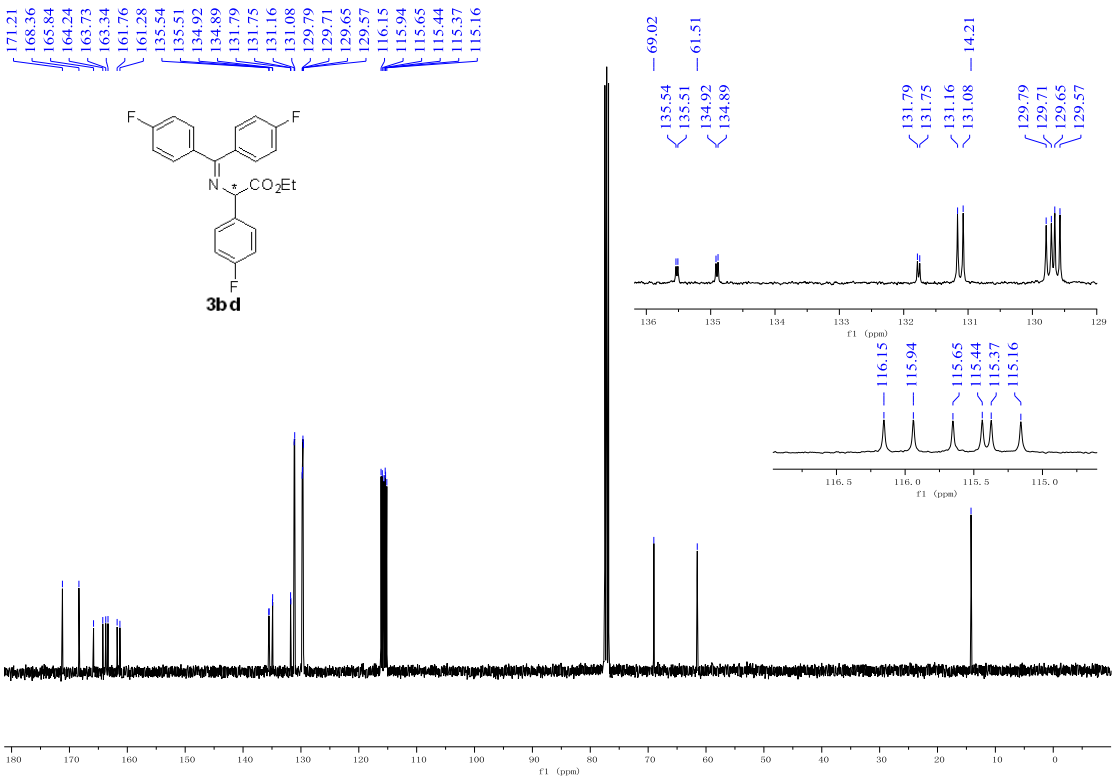
2.01
2.08
6.01
1.00
2.06
3.02
f1 (ppm)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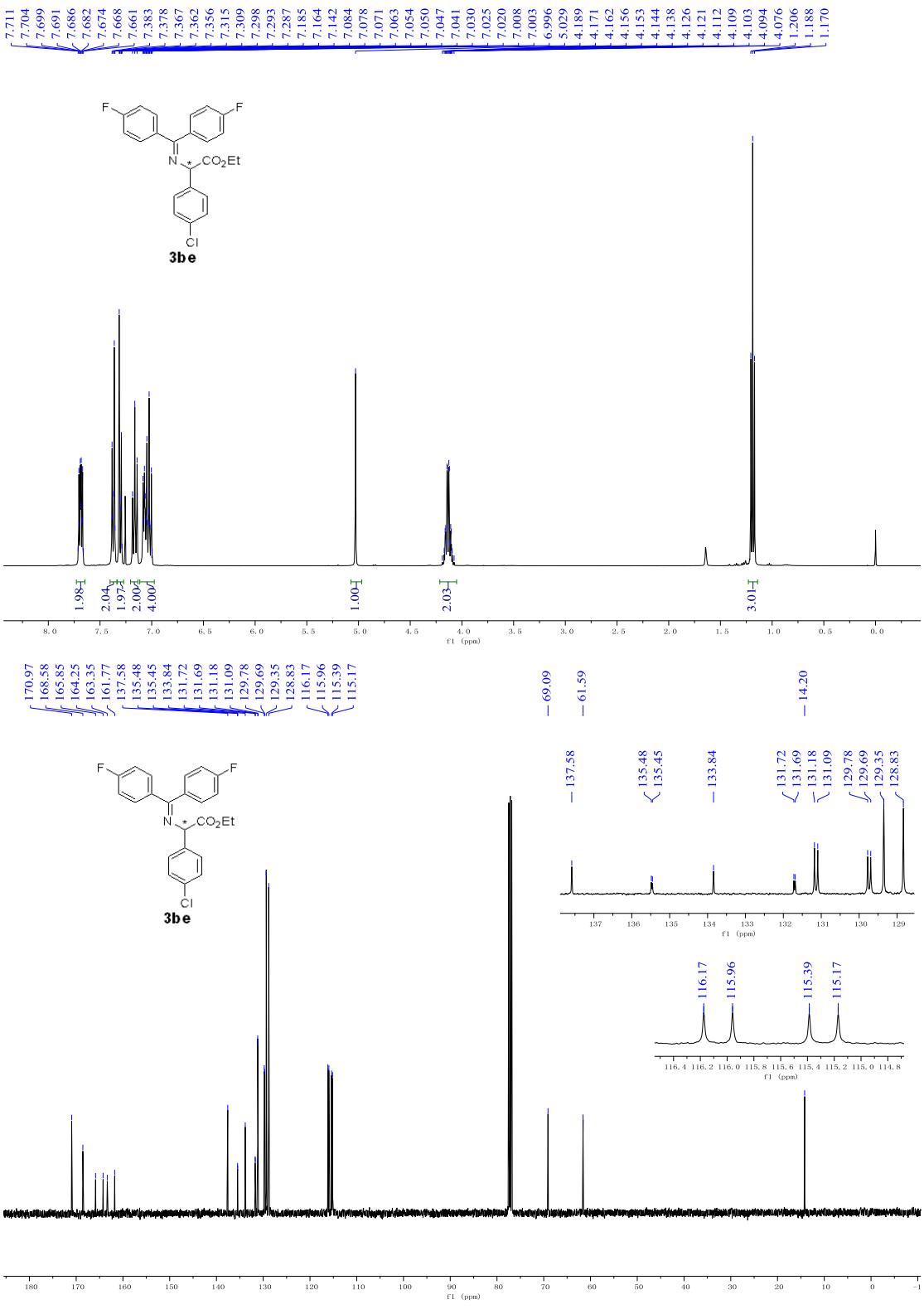
131.79
131.75
131.16
131.08
129.79
129.71
129.65
129.57
116.15
115.94
115.65
115.44
115.37
115.16
69.02
61.51
14.21
F
F
N
*
CO2Et
F
3bd
f1 (ppm)


-109.8
-111.3
-114.4
F
F
N
*
CO2Et
F
3bd
f1 (ppm)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7.362
7.356
7.315
7.309
7.298
7.293
7.287
7.185
7.164
7.142
7.084
7.078
7.071
7.063
7.054
7.050
7.047
7.041
7.030
7.025
7.020
7.008
7.003
6.996
5.029
4.189
4.171
4.162
4.156
4.153
4.144
4.138
4.126
4.121
4.112
4.109
4.103
4.094
4.076
1.206
1.188
1.170
F
F
N
CO2Et
Cl
3be
1.98
2.04
1.97
2.00
4.00
1.00
2.03
3.01
f1 (ppm)
170.97
168.58
165.85
164.25
163.35
161.77
137.58
135.48
135.45
133.84
131.72
131.69
131.18
131.09
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129.35
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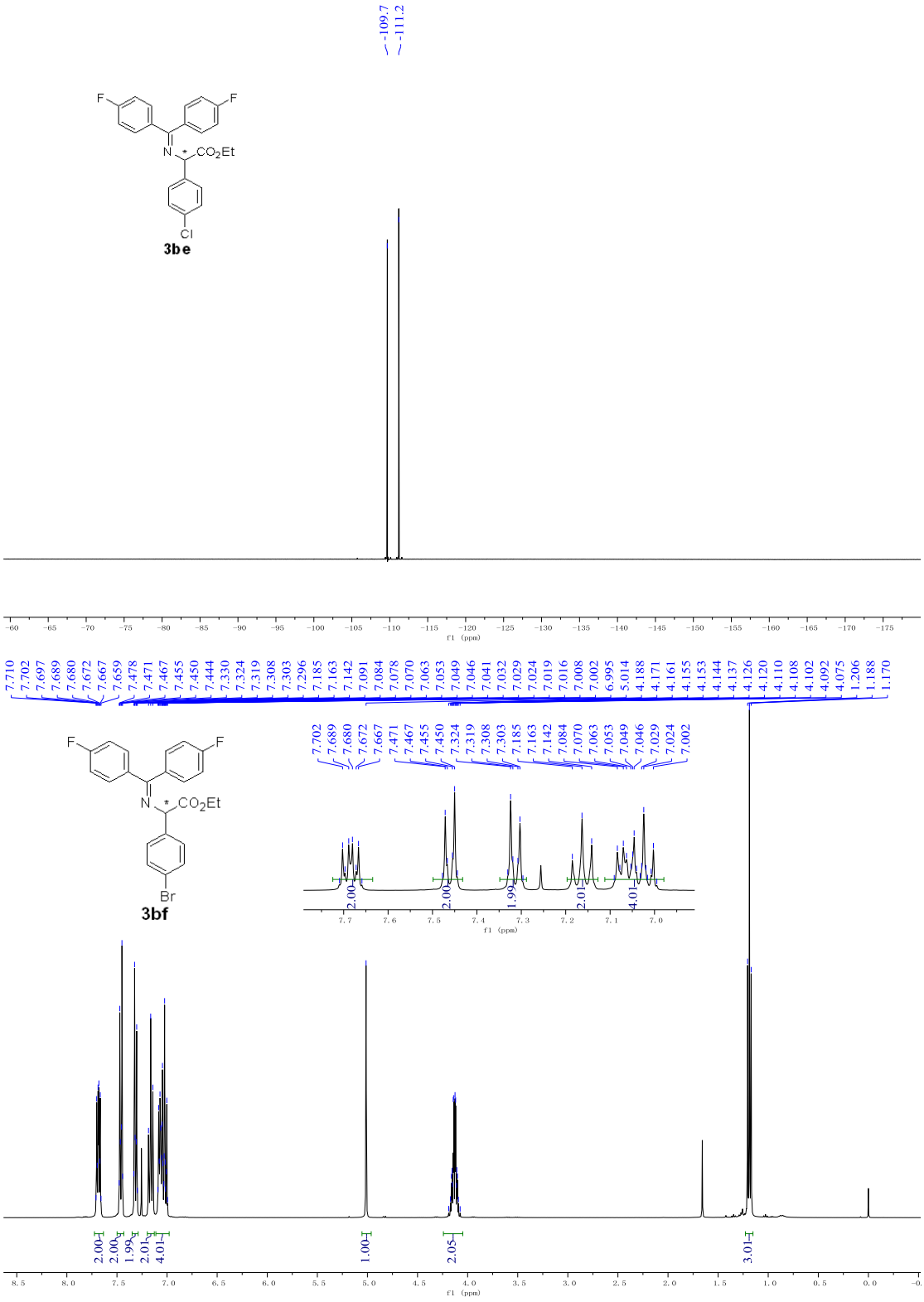
115.17
69.09
61.59
14.20
f1 (ppm)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-111.2
F
F
N
CO2Et
Cl
3be
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7.667
7.659
7.478
7.471
7.467
7.455
7.450
7.444
7.330
7.324
7.319
7.308
7.303
7.296
7.185
7.163
7.142
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7.084
7.078
7.070
7.063
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7.041
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7.024
7.019
7.016
7.008
7.002
6.995
5.014
4.188
4.171
4.161
4.155
4.153
4.144
4.137
4.126
4.120
4.110
4.108
4.102
4.092
4.075
1.206
1.188
1.170
F
F
N
CO2Et
Br
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1.99
2.01
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1.00
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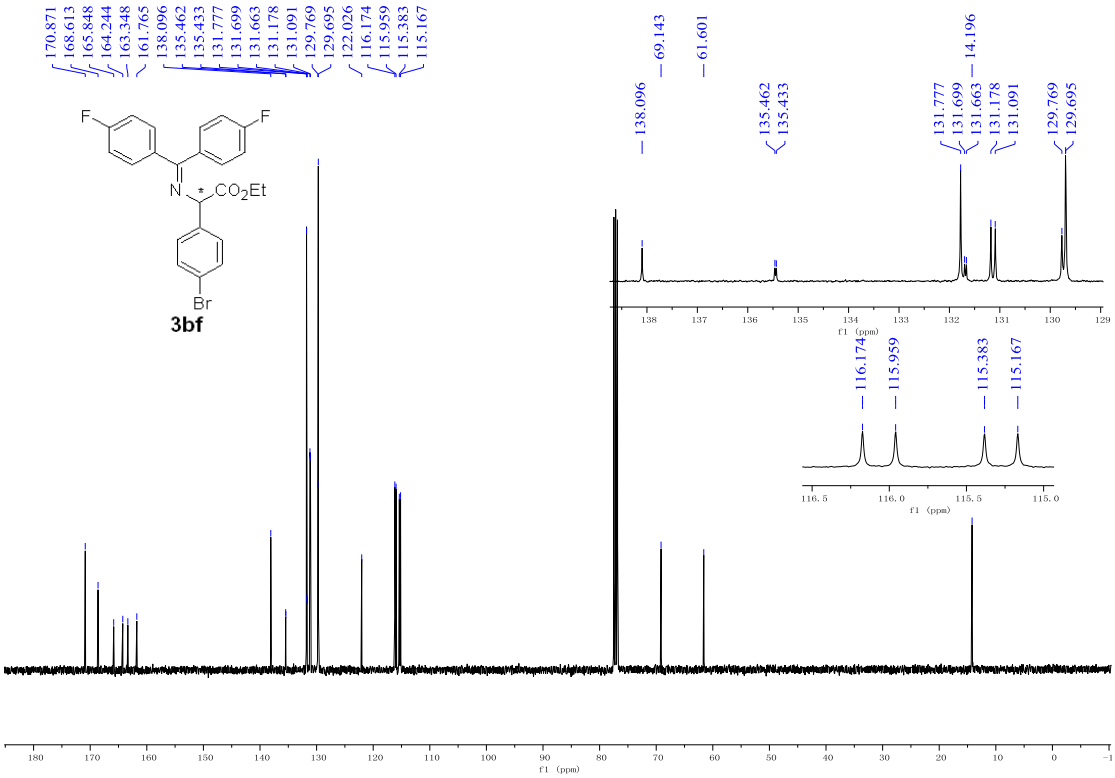
3.01
f1 (ppm)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131.091
129.769
129.695
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115.383
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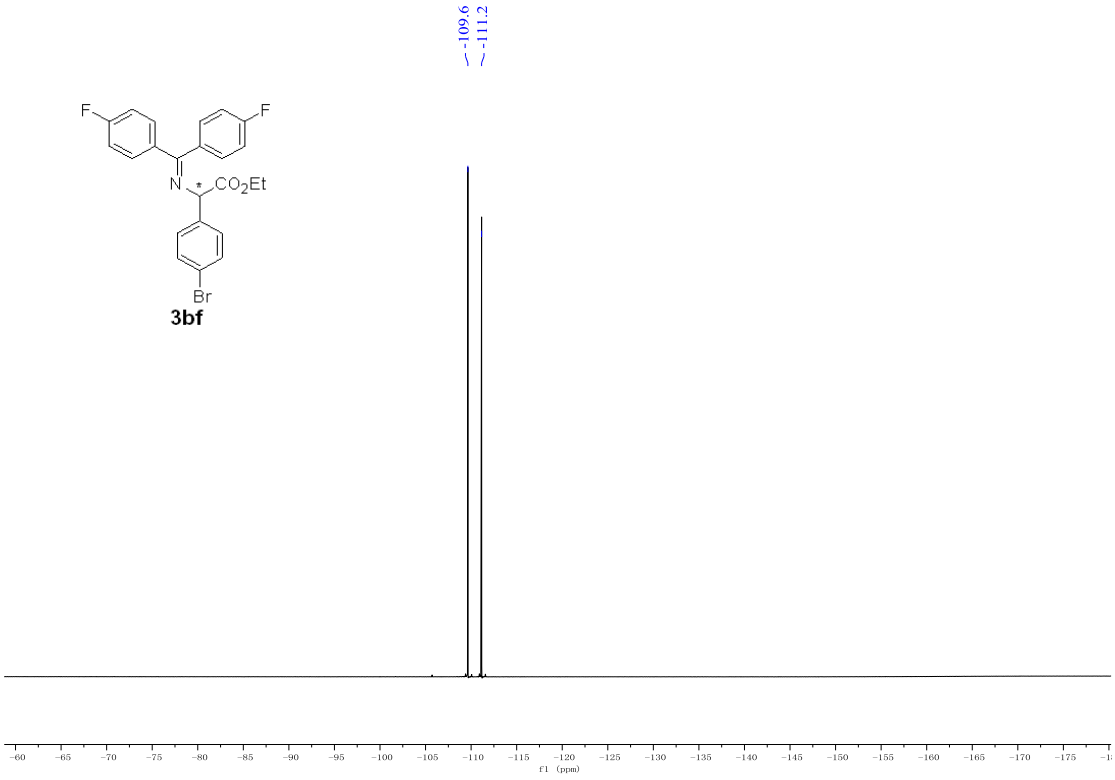
69.143
61.601
14.196
F
F
N
CO2Et
Br
3bf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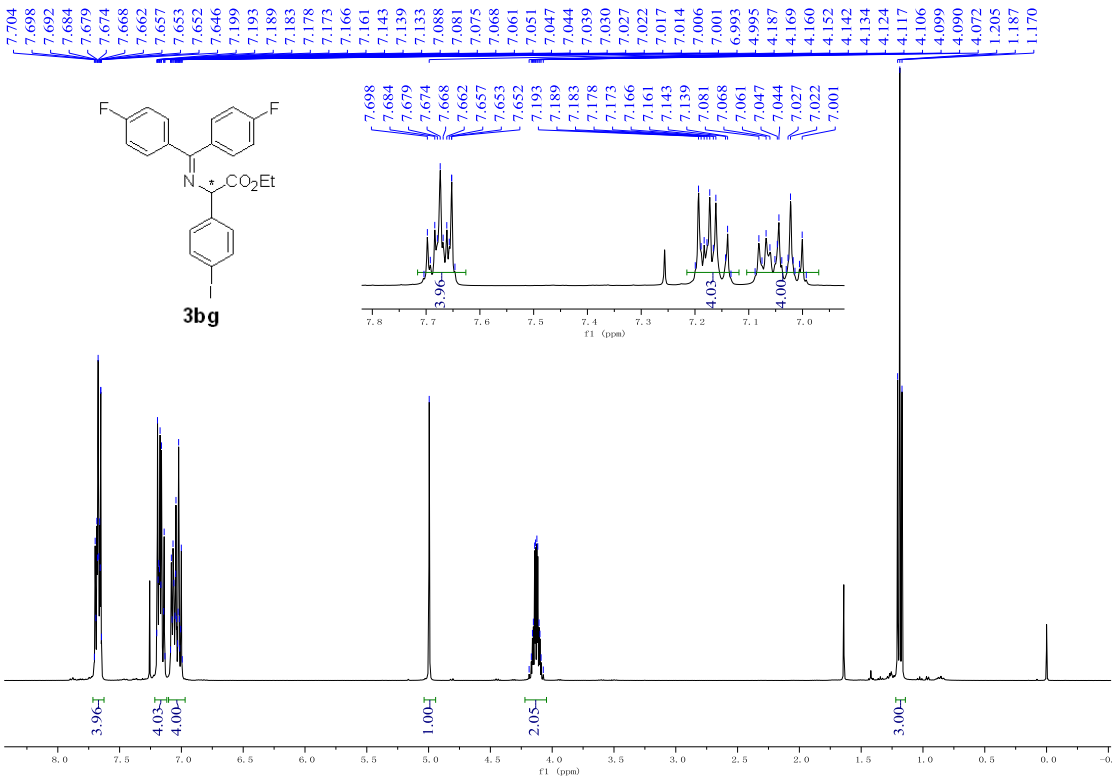
-111.2
F
F
N
CO2Et
Br
3bf


3bg
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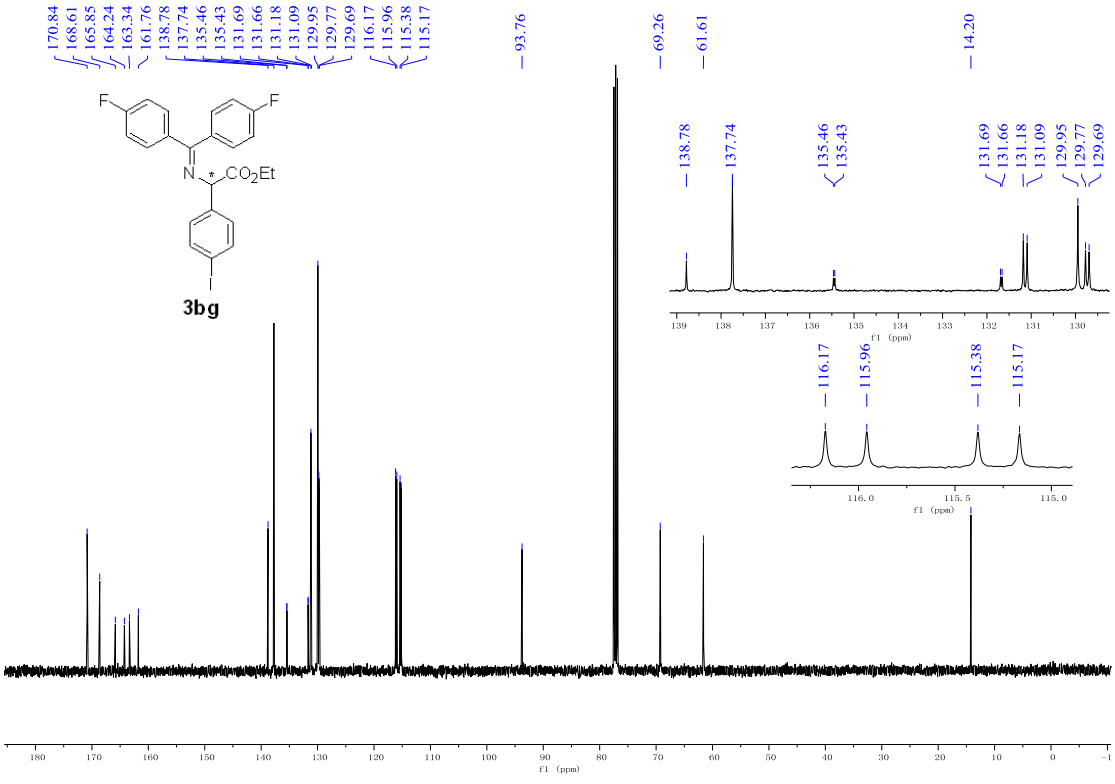
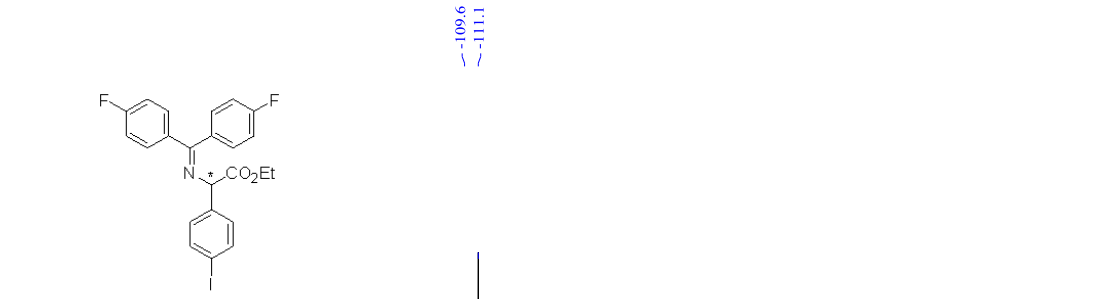
4.00
1.00
2.05
3.00
f1 (ppm)


3bg
f1 (ppm)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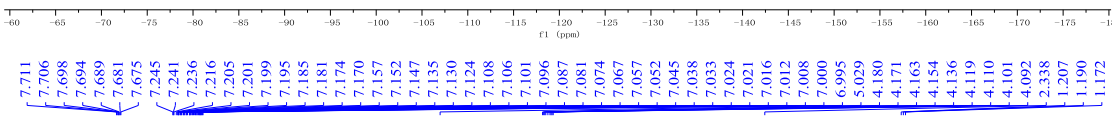
-111.1
F
F
N
*
CO2Et
I

3bg


f1 (ppm)

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7.681
7.675
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7.216
7.205
7.201
7.199
7.195
7.185
7.181
7.174
7.170
7.157
7.152
7.147
7.135
7.130
7.124
7.108
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7.067
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7.016
7.012
7.008
7.000
6.995
5.029
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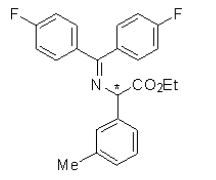
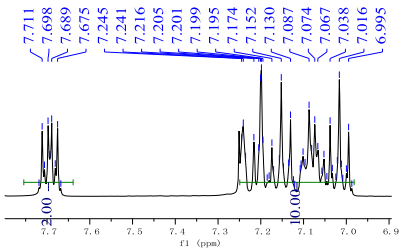
1.172


F
F
N
*
CO2Et
Me

3bh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7.205
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7.199
7.195
7.174
7.152
7.130
7.087
7.074
7.067
7.038
7.016
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10.00
f1 (ppm)

2.00
10.00
1.00
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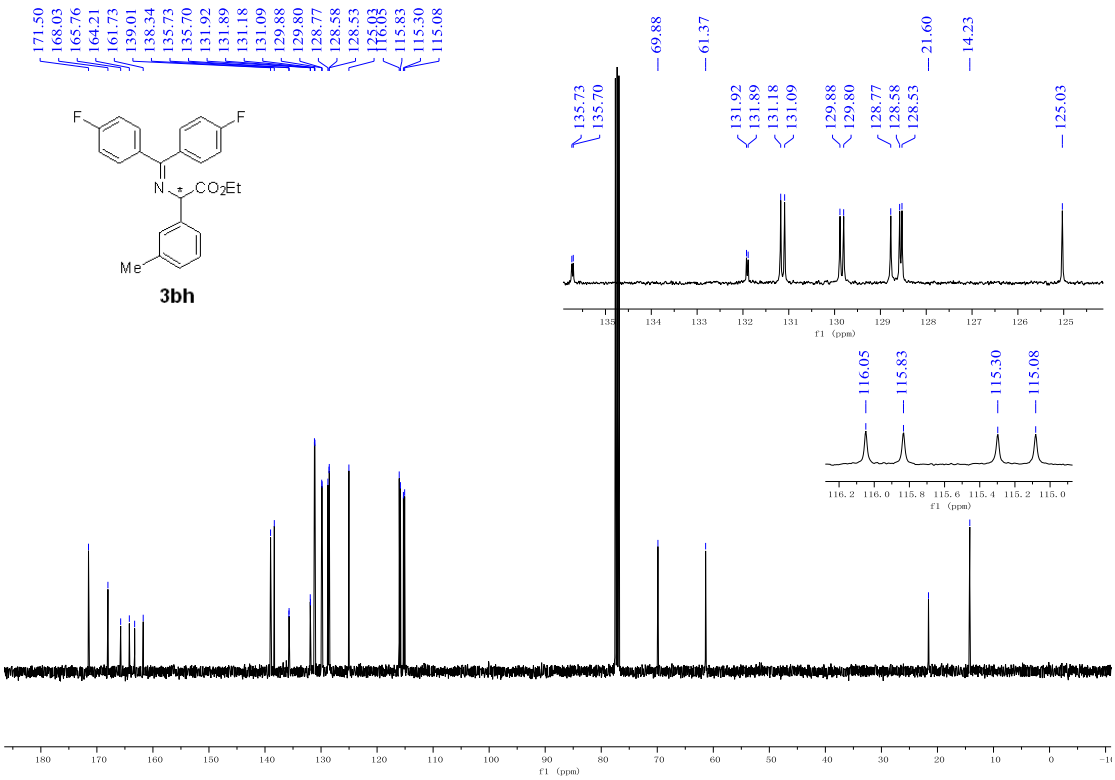
3.05
3.00
f1 (ppm)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129.80
128.77
128.58
128.53
125.03
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115.08
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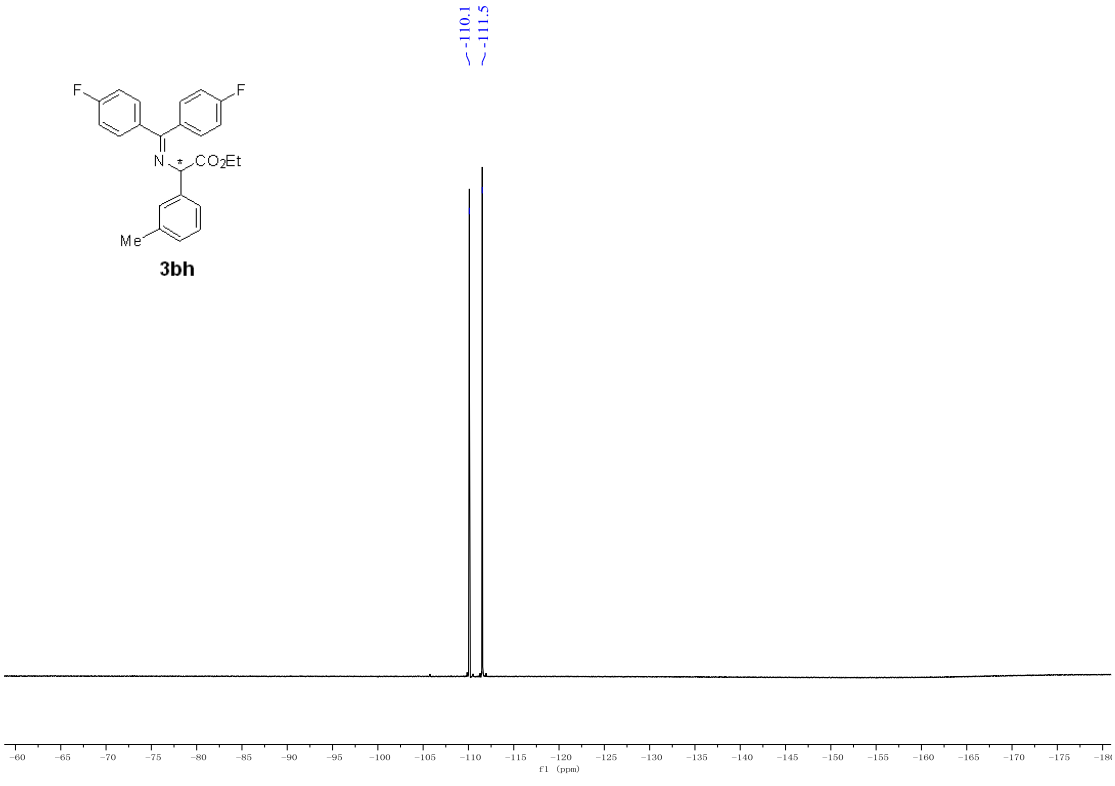
14.23
F
F
N
CO2Et
Me
3bh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F
F
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CO2Et
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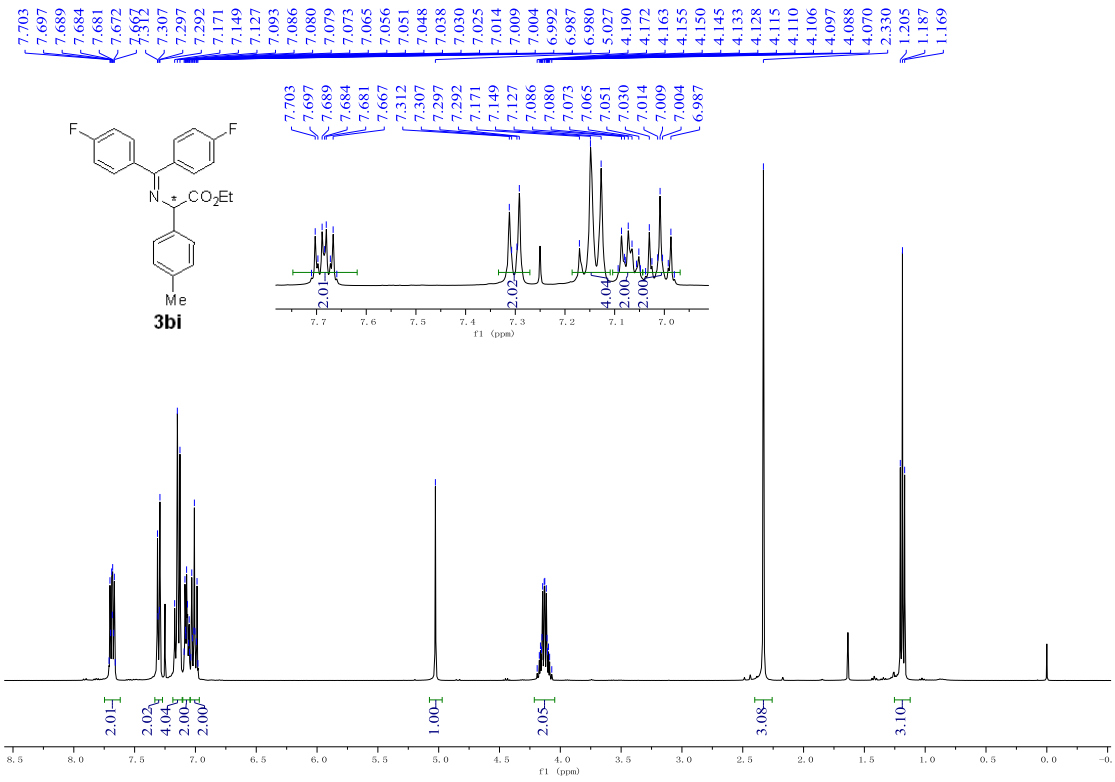
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7.127
7.093
7.086
7.080
7.079
7.073
7.065
7.056
7.051
7.048
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7.030
7.025
7.014
7.009
7.004
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6.987
6.980
5.027
4.190
4.172
4.163
4.155
4.150
4.145
4.133
4.128
4.115
4.110
4.106
4.097
4.088
4.070
2.330
1.205
1.187
1.169
F
F
N
*
CO2Et
Me
3bi
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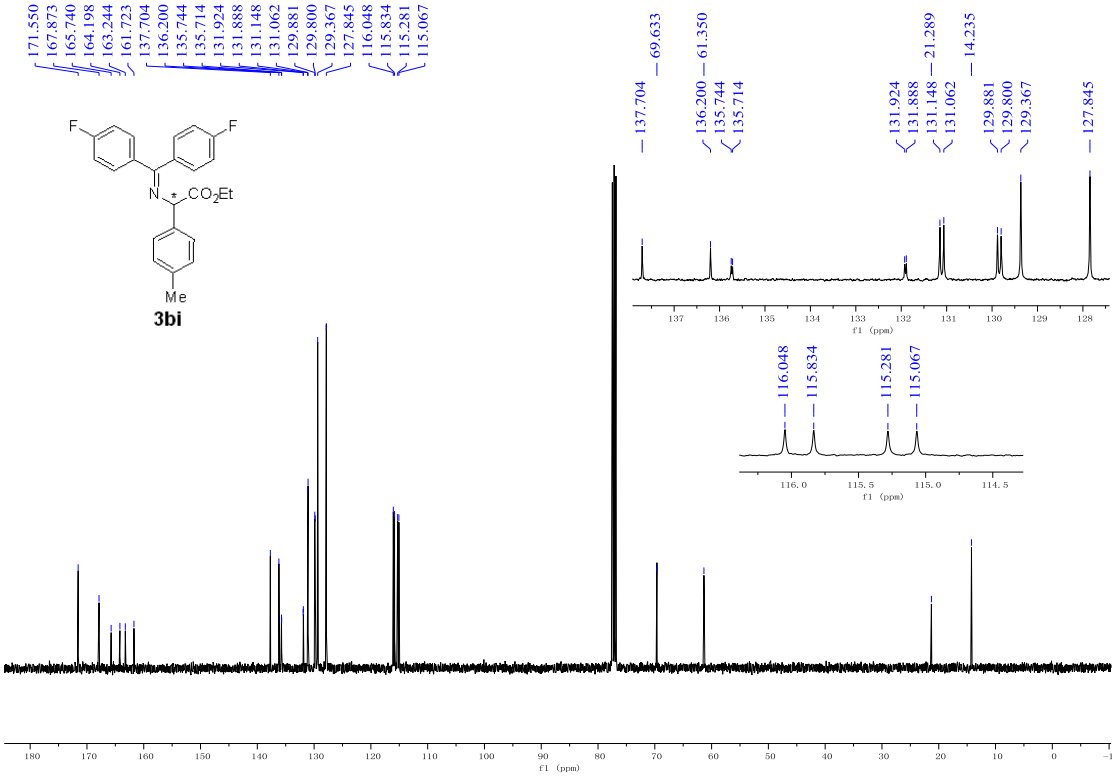
2.02
4.04
2.00
2.00
1.00
2.05
3.08
3.10
f1 (ppm)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131.062
129.881
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129.367
127.845
116.048
115.834
115.281
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69.633
61.350
21.289
14.235
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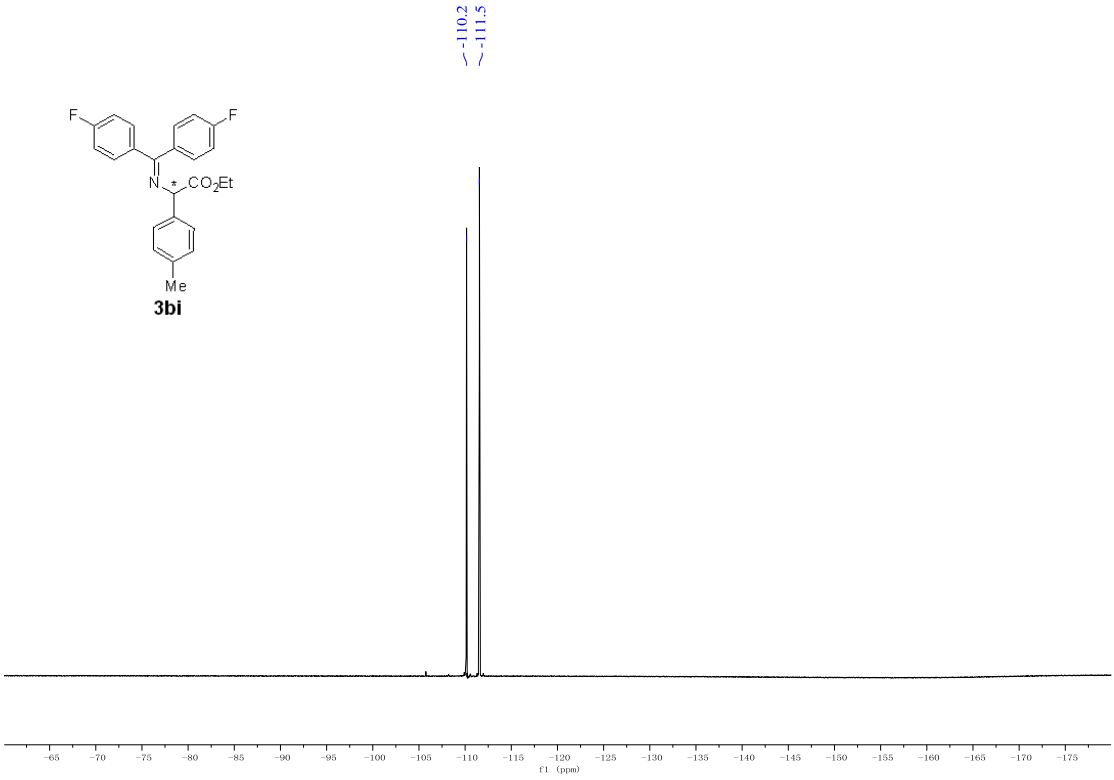
F
N
*
CO2Et
Me
3bi
f1 (ppm)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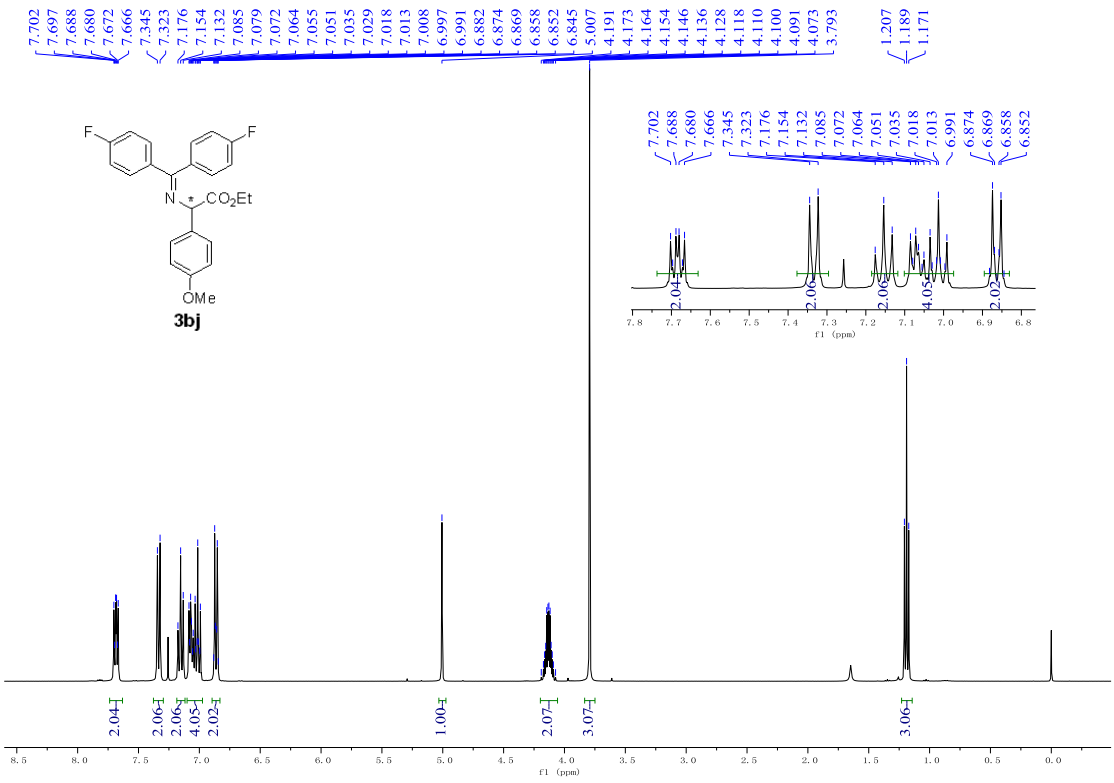
F
F
N
*
CO2Et
Me
3bi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7.013
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6.845
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4.154
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4.136
4.128
4.118
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4.091
4.073
3.793
1.207
1.189
1.171
F
F
N
*
CO2Et
OMe
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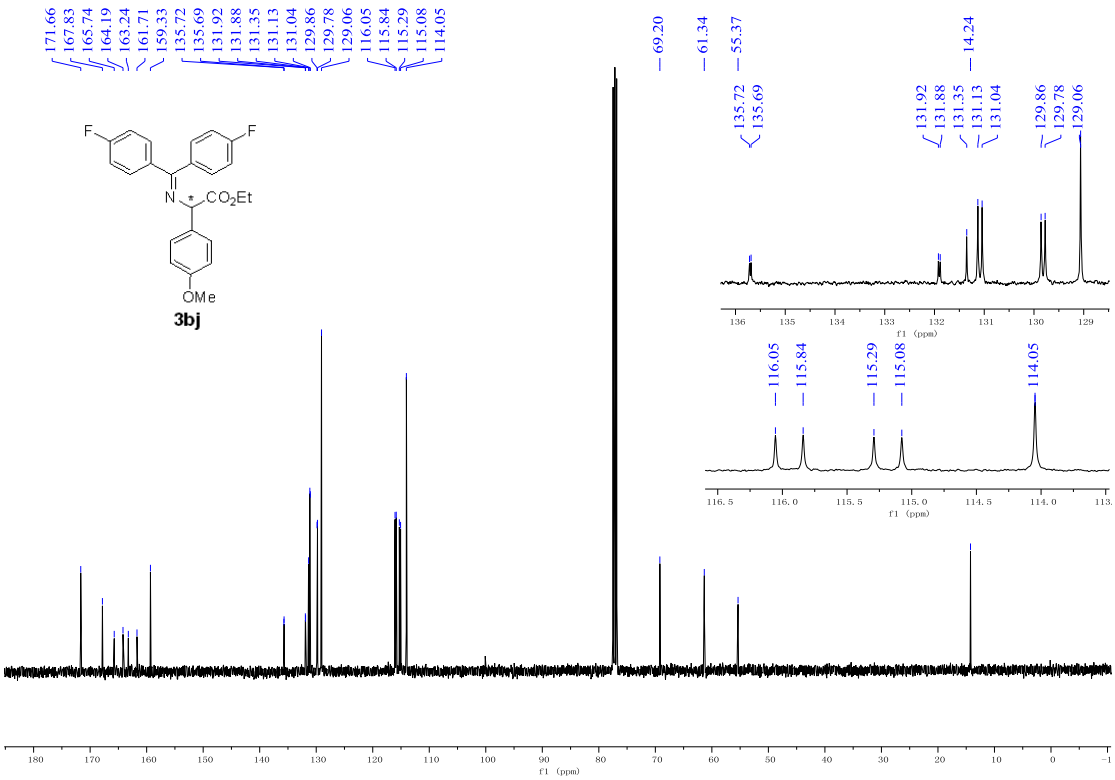
2.06
4.05
2.02
1.00
2.07
3.07
3.06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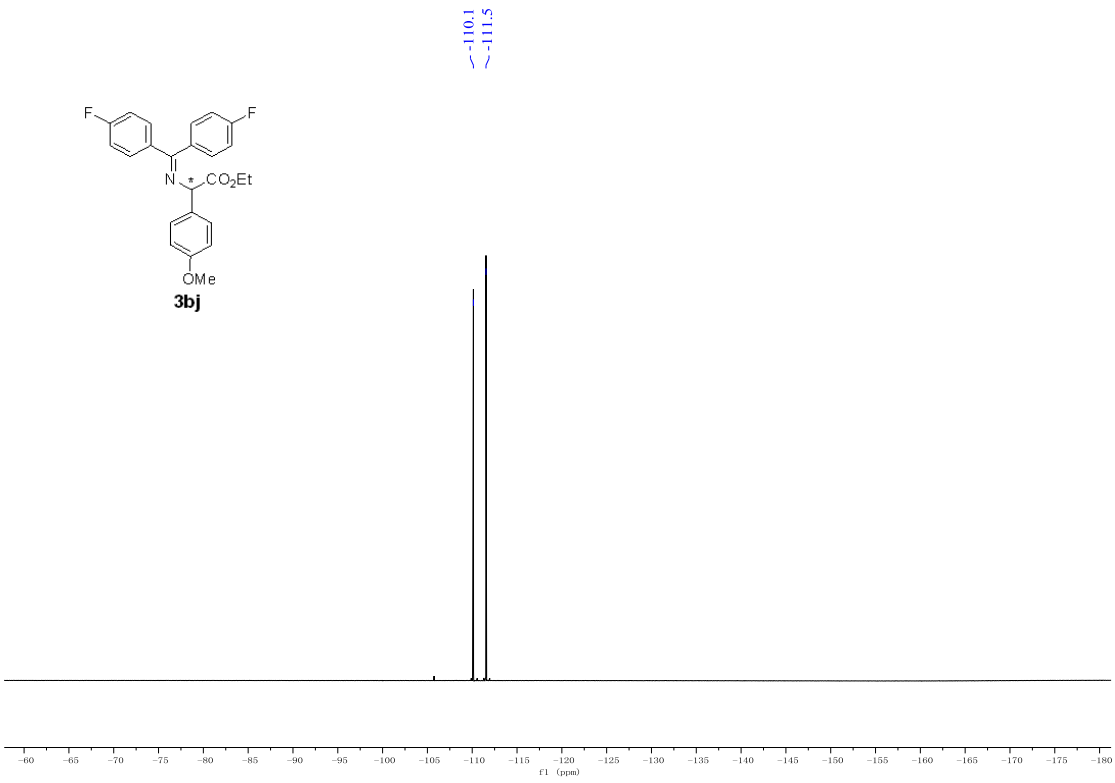
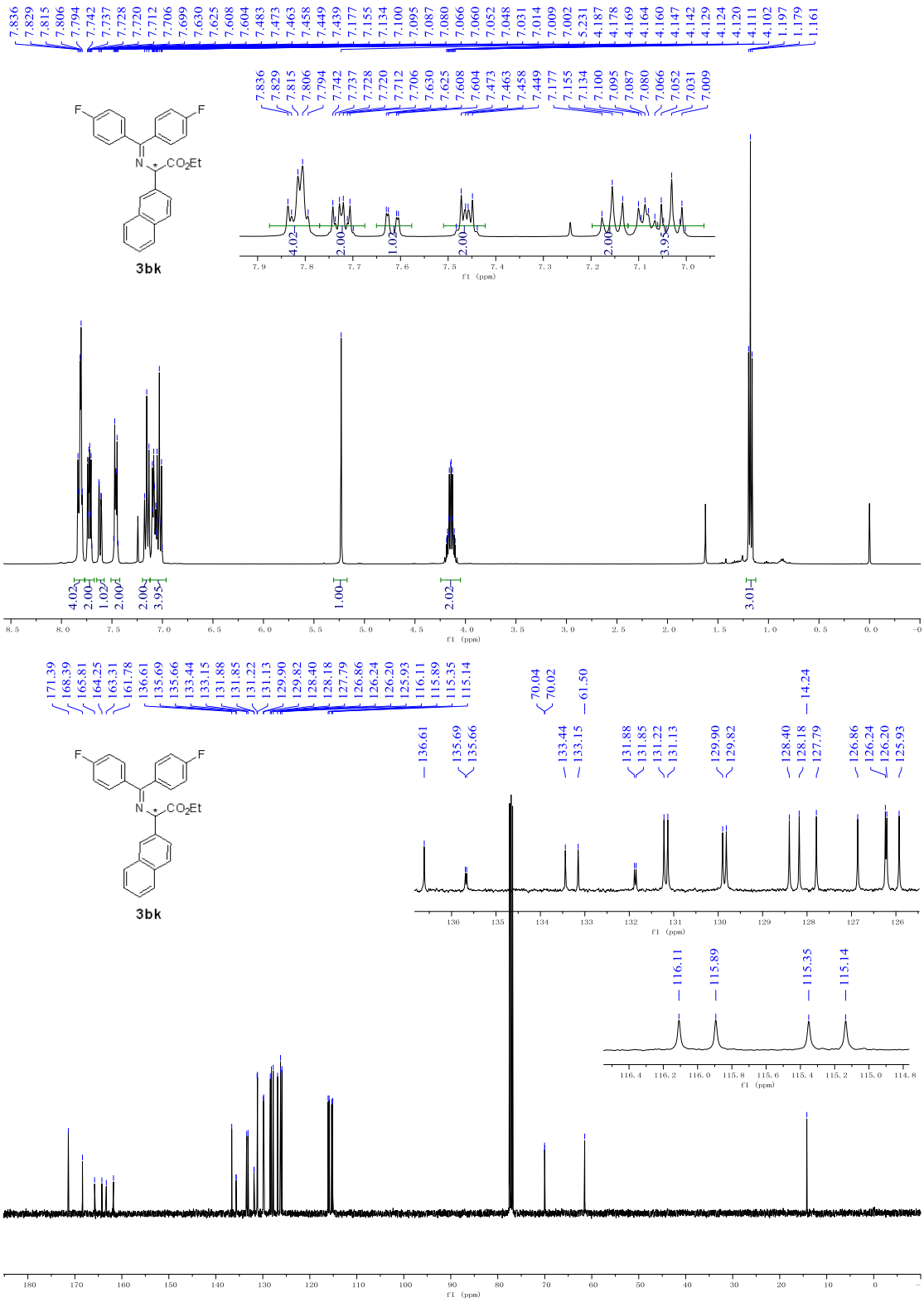
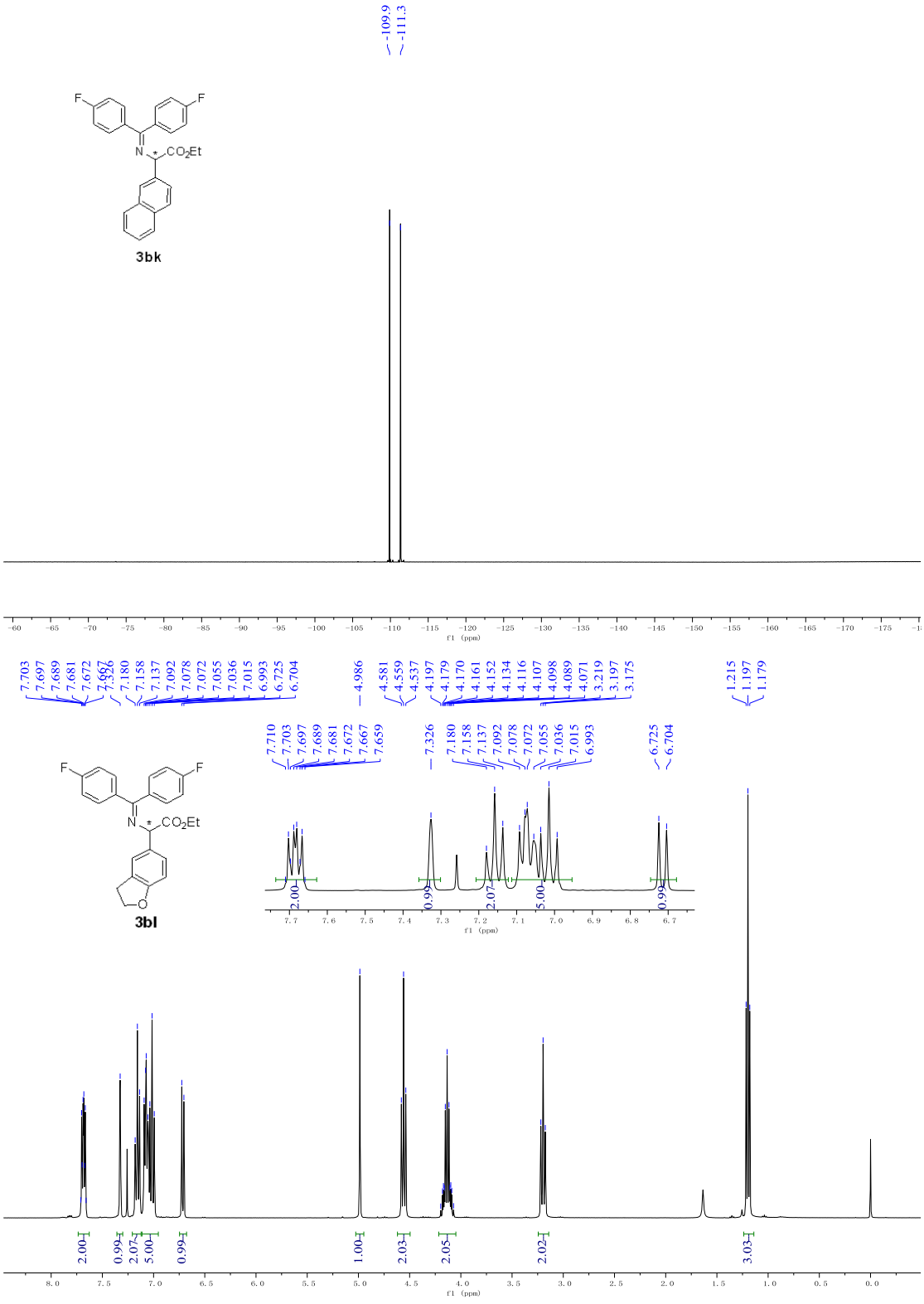
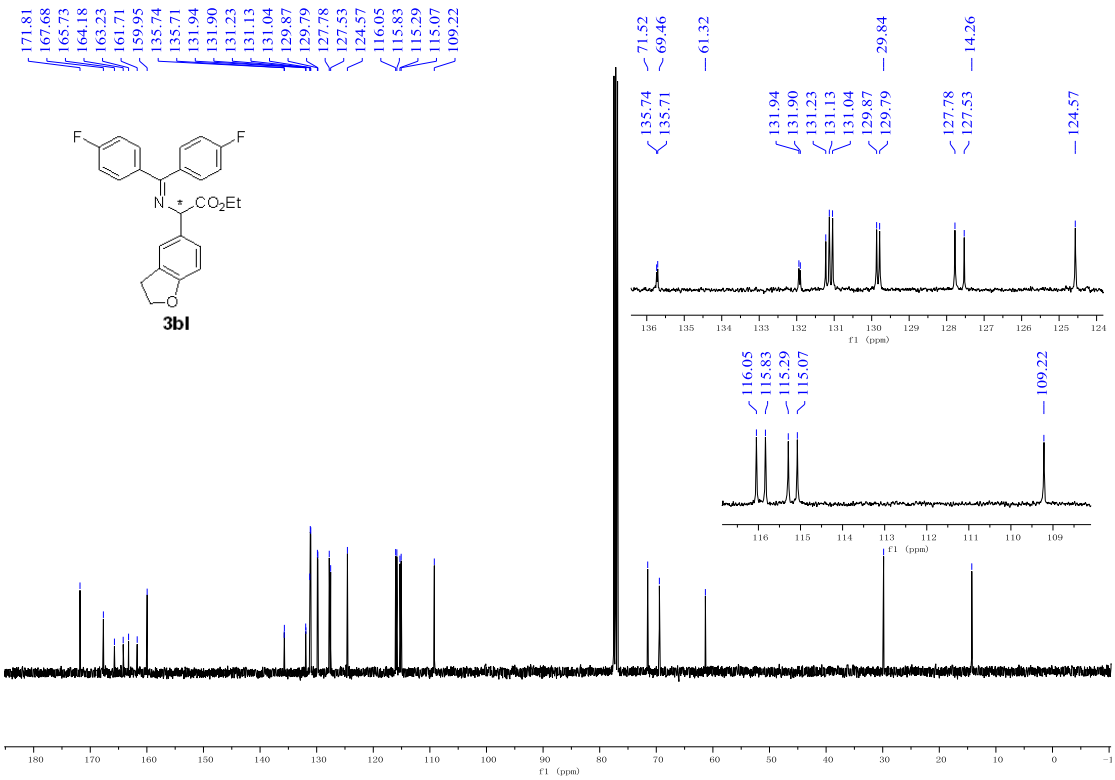
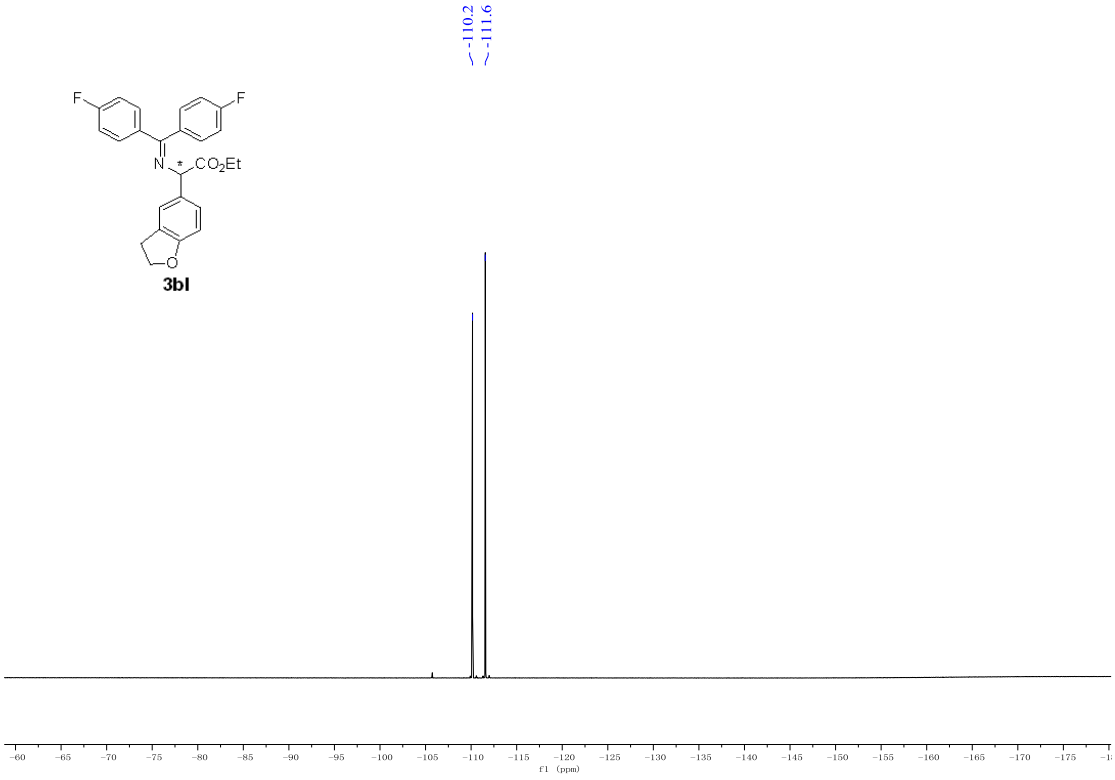
131.13
131.04
129.86
129.78
129.06
116.05
115.84
115.29
115.08
114.05
69.20
61.34
55.37
14.24
F
F
N
*
CO2Et
OMe
3bj
f1 (ppm)

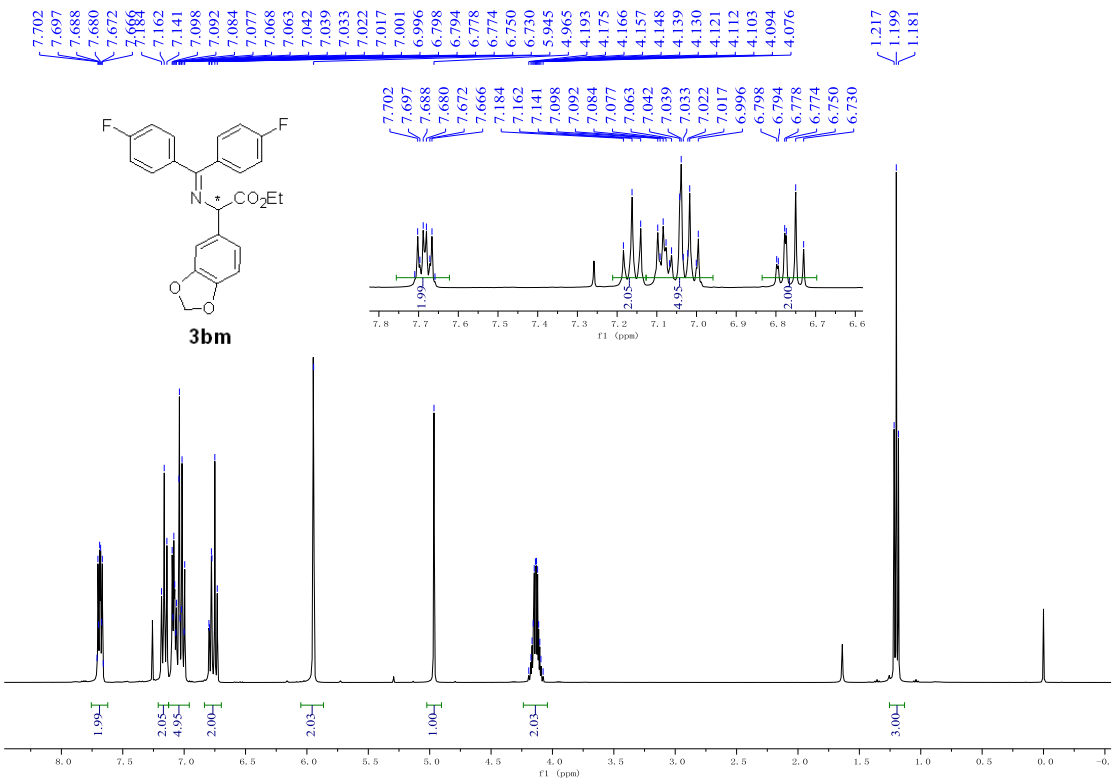

-110.1
-111.5
F
F
N
*
CO2Et
OMe
3bj
f1 (ppm)

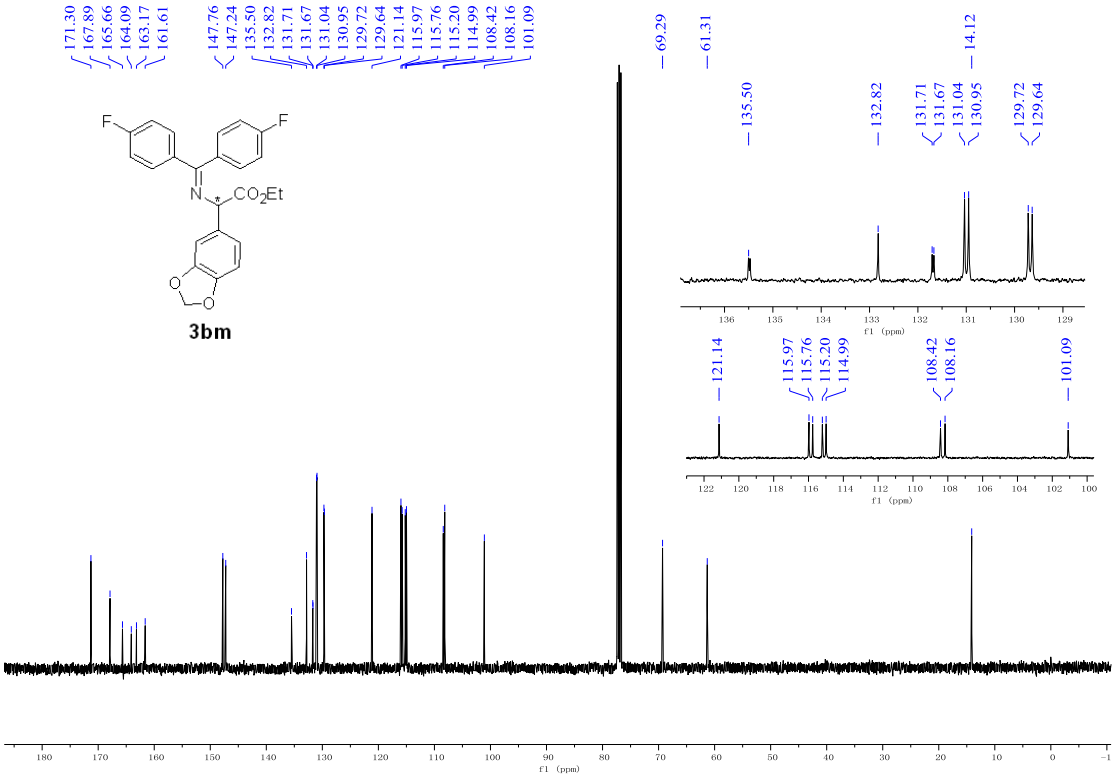

3bk
3bk

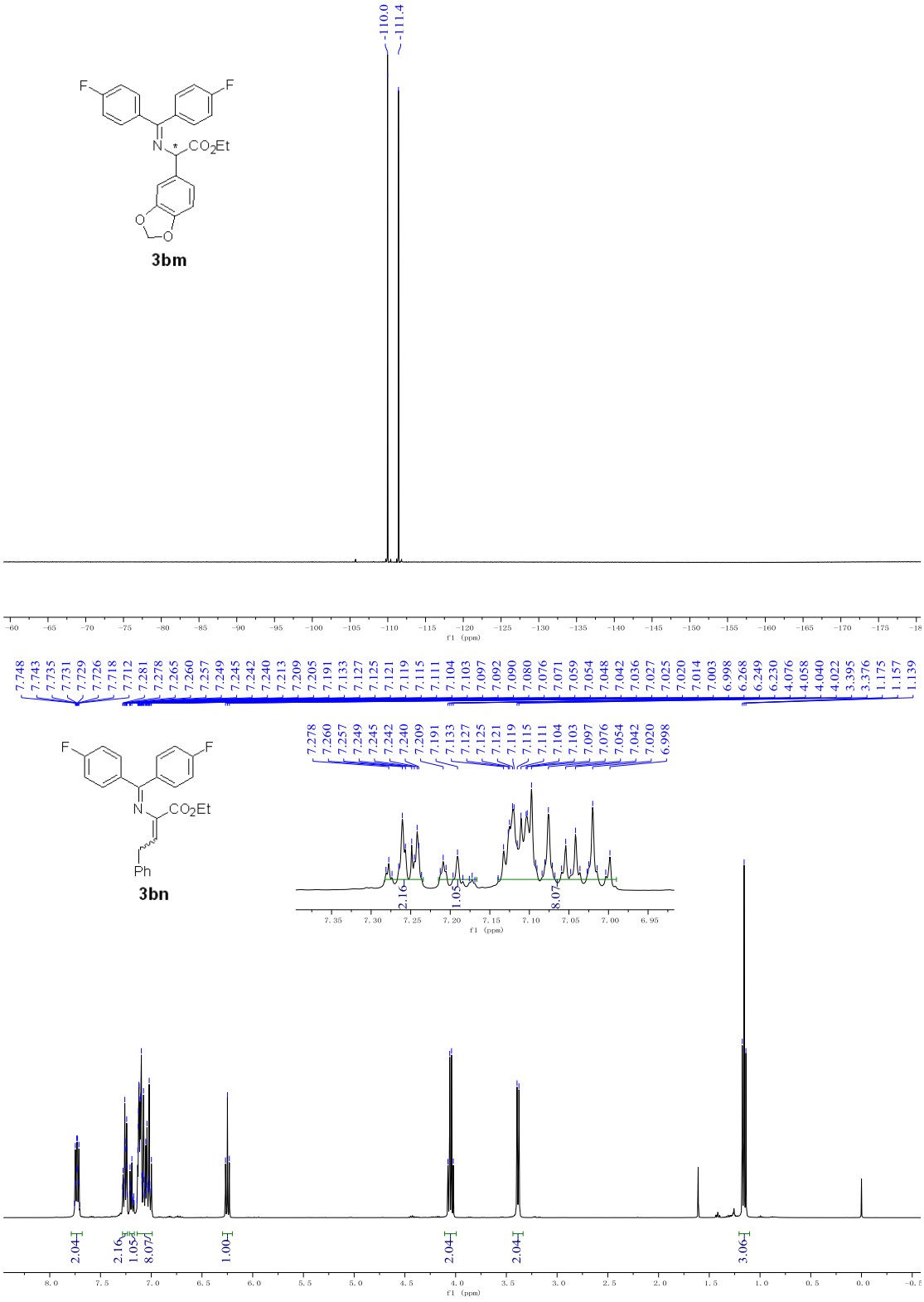

-109.9
-111.3
F
F
N
*
CO2Et
3bk
f1 (ppm)
7.703
7.697
7.689
7.681
7.672
7.667
7.326
7.180
7.158
7.137
7.092
7.078
7.072
7.055
7.036
7.015
6.993
6.725
6.704
4.986
4.581
4.559
4.537
4.197
4.179
4.170
4.161
4.152
4.134
4.116
4.107
4.098
4.089
4.071
3.219
3.197
3.175
1.215
1.197
1.179
3bl
2.00
0.99
2.07
5.00
0.99
1.00
2.03
2.05
2.02
3.03

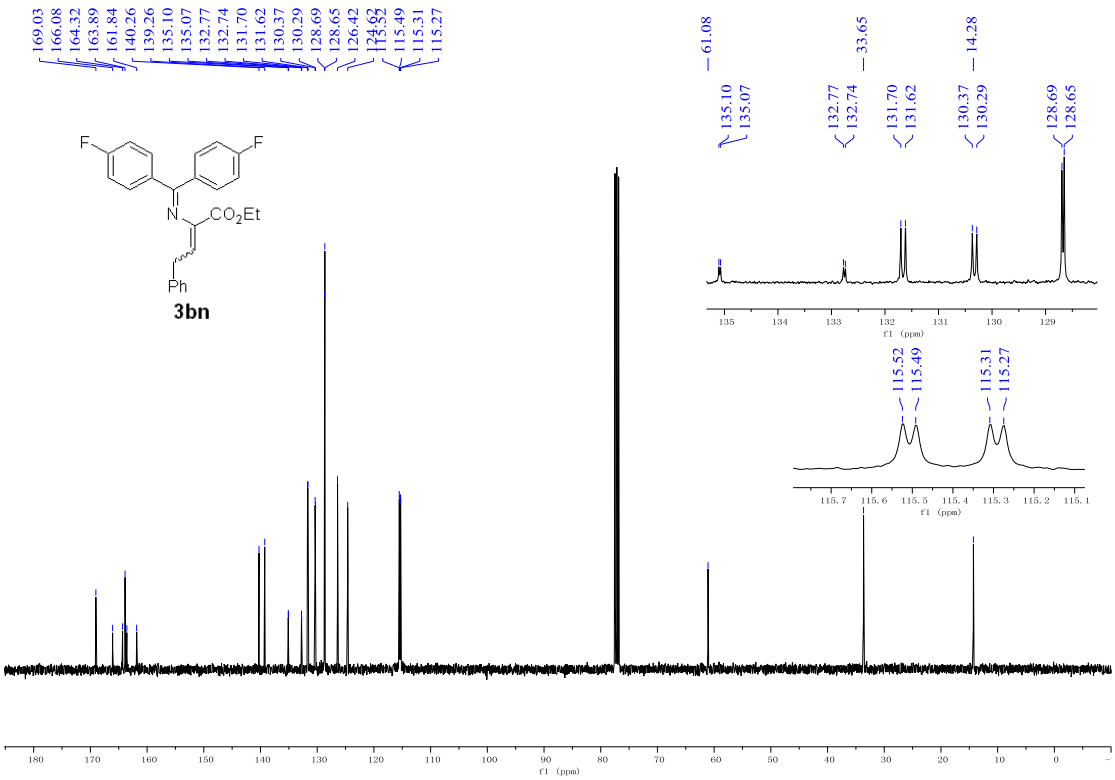

171.81
167.68
165.73
164.18
163.23
161.71
159.95
135.74
135.71
131.94
131.90
131.23
131.13
131.04
129.87
129.79
127.78
127.53
124.57
116.05
115.83
115.29
115.07
109.22
71.52
69.46
61.32
29.84
14.26
F
F
N
CO2Et
O
3bl
f1 (ppm)

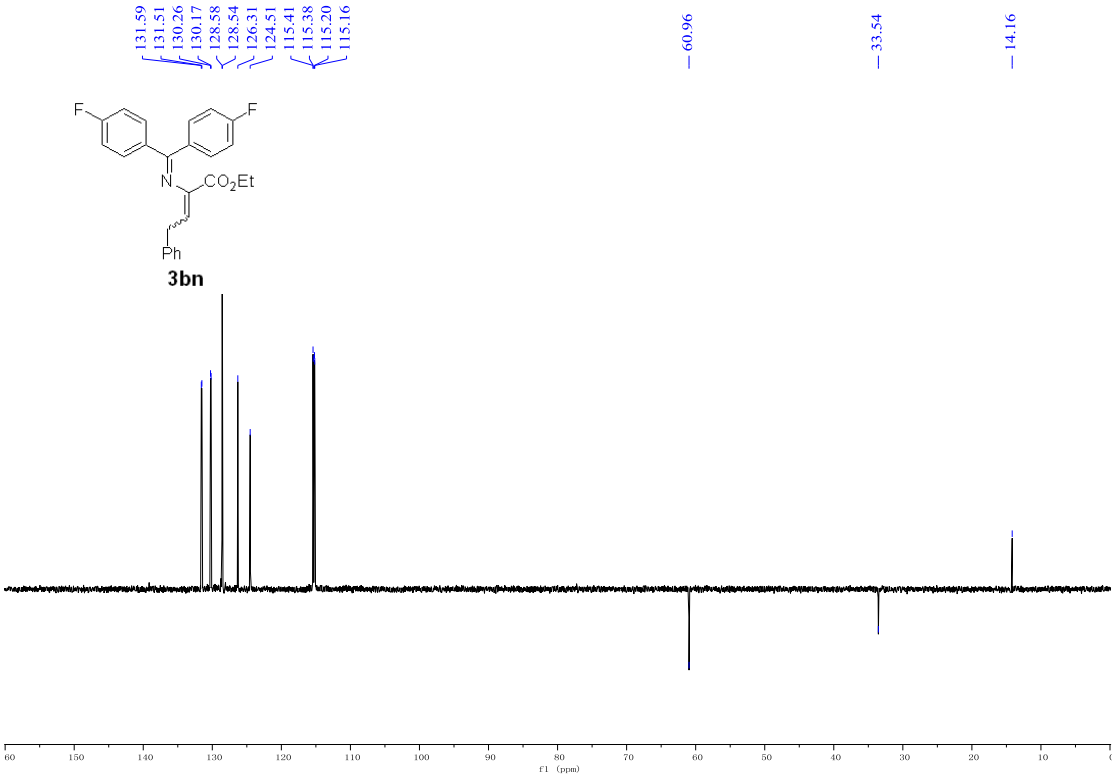

-110.2
-111.6
F
F
N
CO2Et
O
3bl
f1 (ppm)

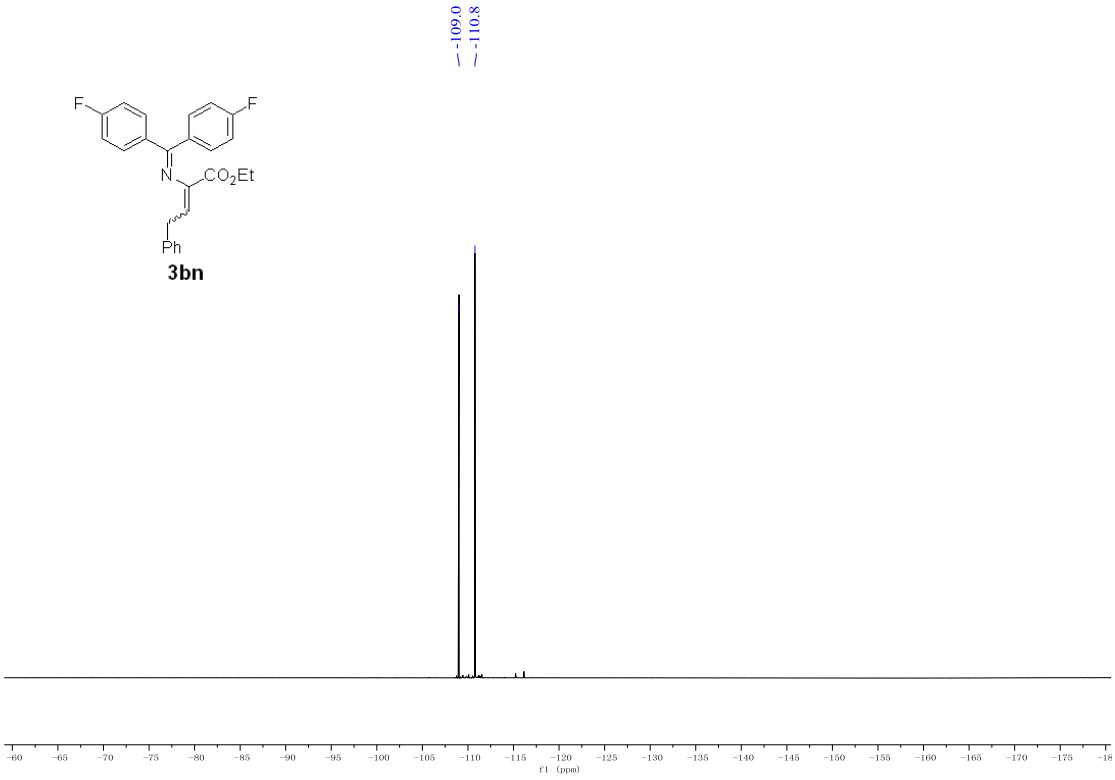

7.702
7.697
7.688
7.680
7.672
7.666
7.184
7.162
7.141
7.098
7.092
7.084
7.077
7.068
7.063
7.042
7.039
7.033
7.022
7.017
7.001
6.996
6.798
6.794
6.778
6.774
6.750
6.730
5.945
4.965
4.193
4.175
4.166
4.157
4.148
4.139
4.130
4.121
4.112
4.103
4.094
4.076
1.217
1.199
1.181
F
F
N
CO2Et
O
O
O
3bm
1.99
2.05
4.95
2.00
2.03
1.00
2.03
3.00
f1 (ppm)

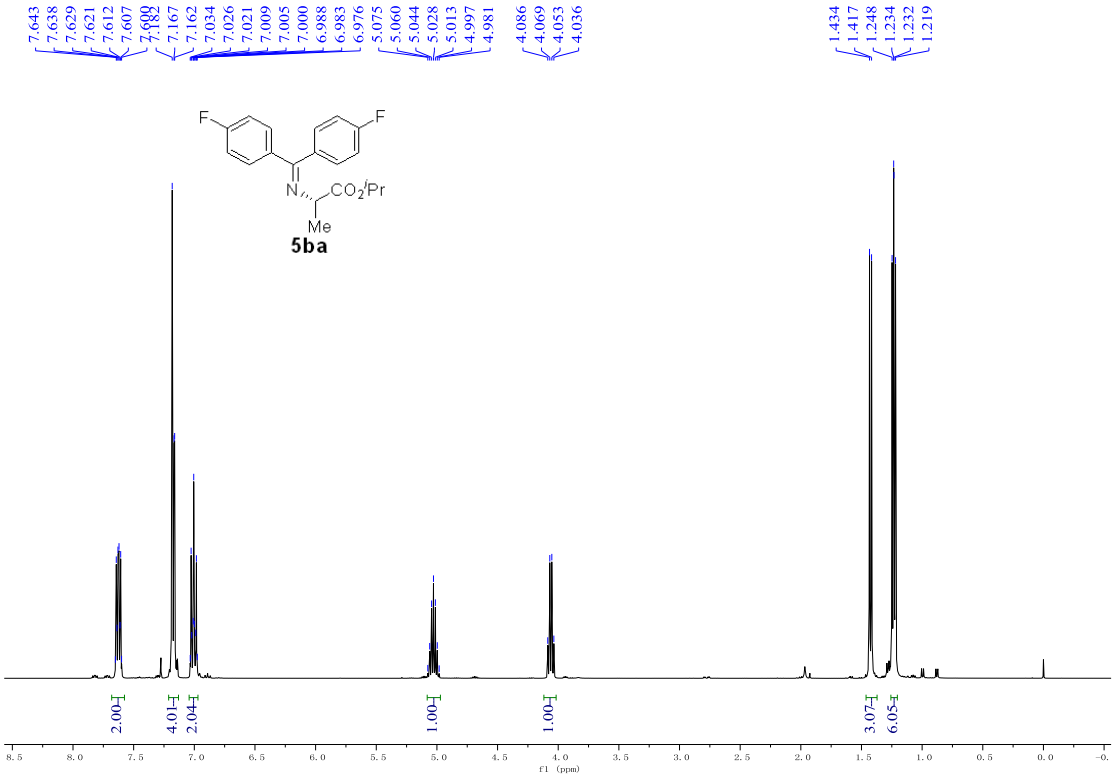

171.30
167.89
165.66
164.09
163.17
161.61
147.76
147.24
135.50
132.82
131.71
131.67
131.04
130.95
129.72
129.64
121.14
115.97
115.76
115.20
114.99
108.42
108.16
101.09
69.29
61.31
14.12
F
F
N
CO2Et
O
O
O
3bm
f1 (ppm)

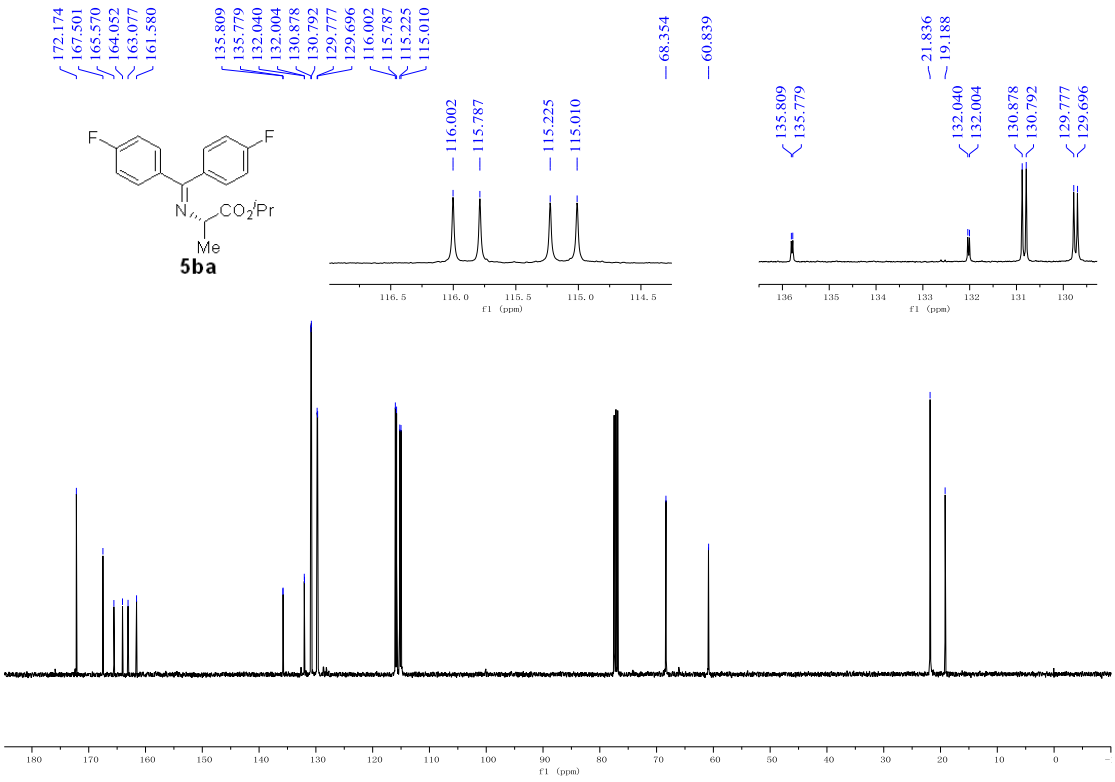

-110.0
-111.4
F
F
N
CO2Et
O
O
O
3bm
7.748
7.743
7.735
7.731
7.729
7.726
7.718
7.712
7.281
7.278
7.265
7.260
7.257
7.249
7.245
7.242
7.240
7.213
7.209
7.205
7.191
7.133
7.127
7.125
7.121
7.119
7.115
7.111
7.104
7.103
7.097
7.092
7.090
7.080
7.076
7.071
7.059
7.054
7.048
7.042
7.036
7.027
7.025
7.020
7.014
7.003
6.998
6.268
6.249
6.230
4.076
4.058
4.040
4.022
3.395
3.376
1.175
1.157
1.139
F
F
N
CO2Et
Ph
3bn
7.278
7.260
7.257
7.249
7.245
7.242
7.240
7.209
7.191
7.133
7.127
7.125
7.121
7.119
7.115
7.111
7.104
7.103
7.097
7.076
7.054
7.042
7.020
6.998
2.16
1.05
8.07
2.04
2.16
1.05
8.07
1.00
2.04
2.04
3.06
f1 (ppm)

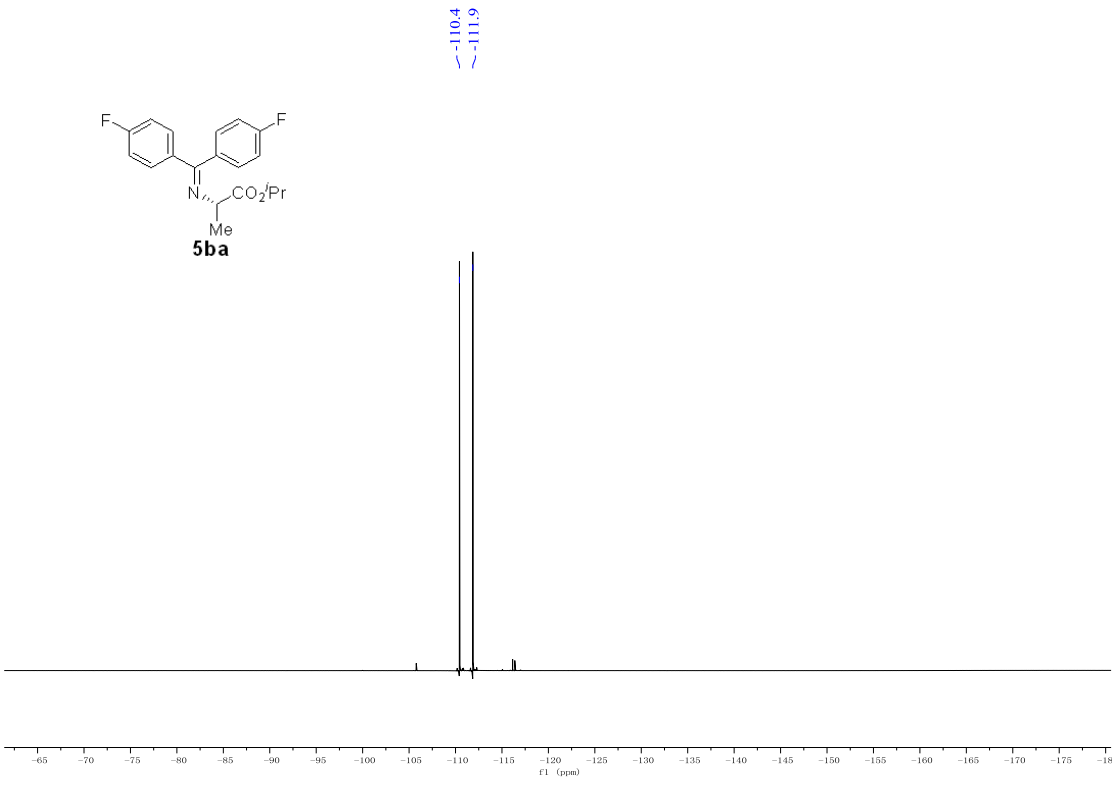

169.03
166.08
164.32
163.89
161.84
140.26
139.26
135.10
135.07
132.77
132.74
131.70
131.62
130.37
130.29
128.69
128.65
126.42
124.62
115.52
115.49
115.31
115.27
61.08
33.65
14.28
F
F
N
CO2Et
Ph
3bn
f1 (ppm)

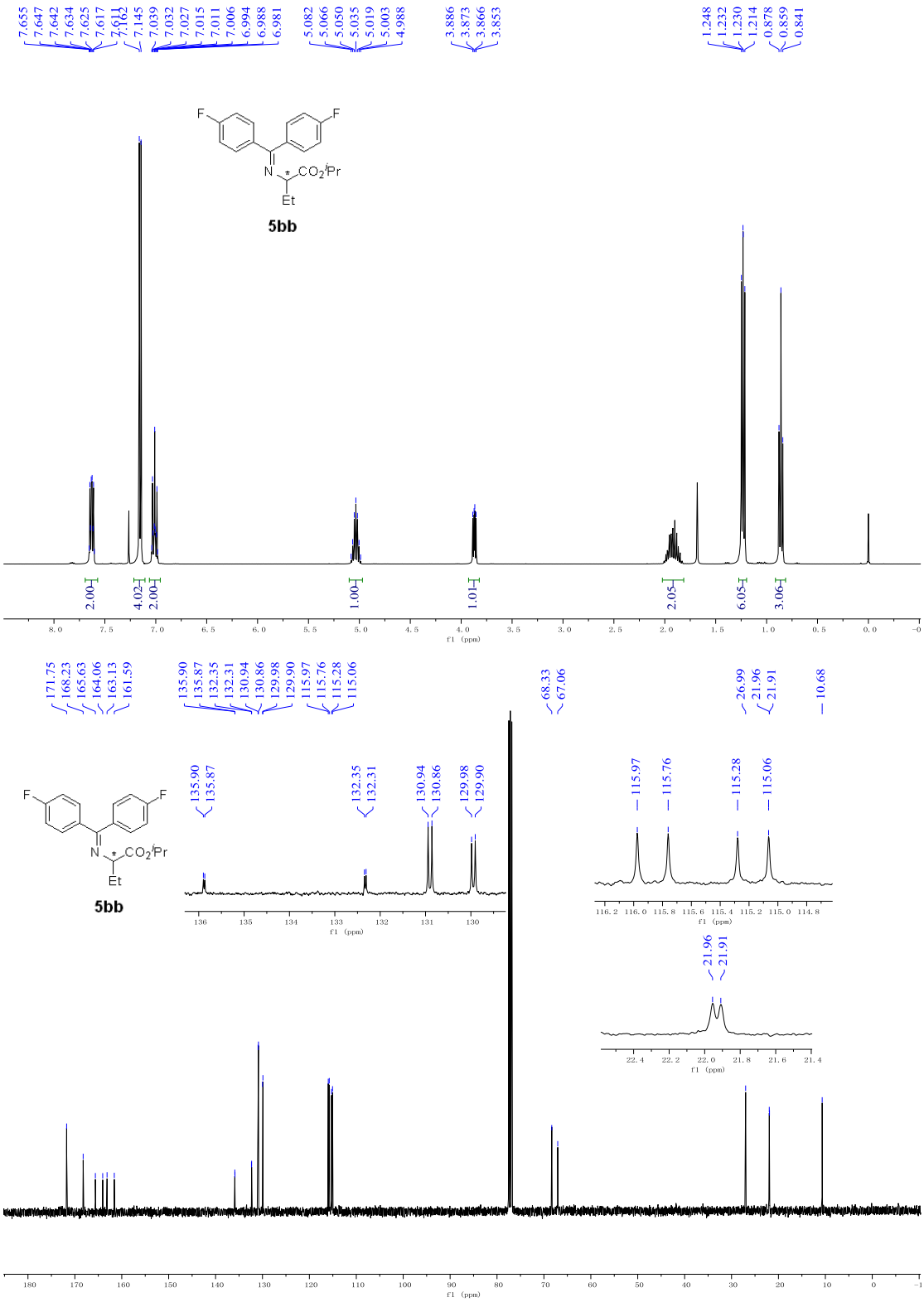

131.59
131.51
130.26
130.17
128.58
128.54
126.31
124.51
115.41
115.38
115.20
115.16
60.96
33.54
14.16
F
F
N
CO2Et
Ph
3bn
f1 (ppm)

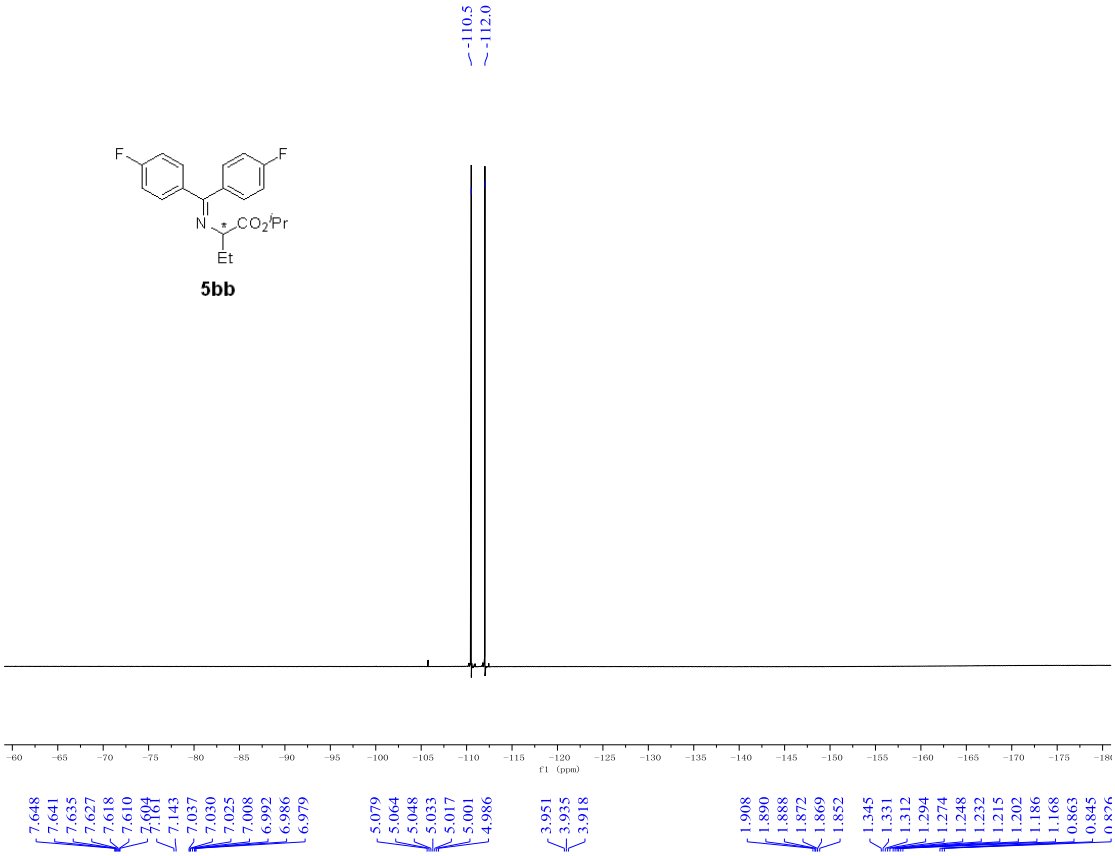

-109.0
-110.8
F
F
N
CO2Et
Ph
3bn
-60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -18
f1 (ppm)

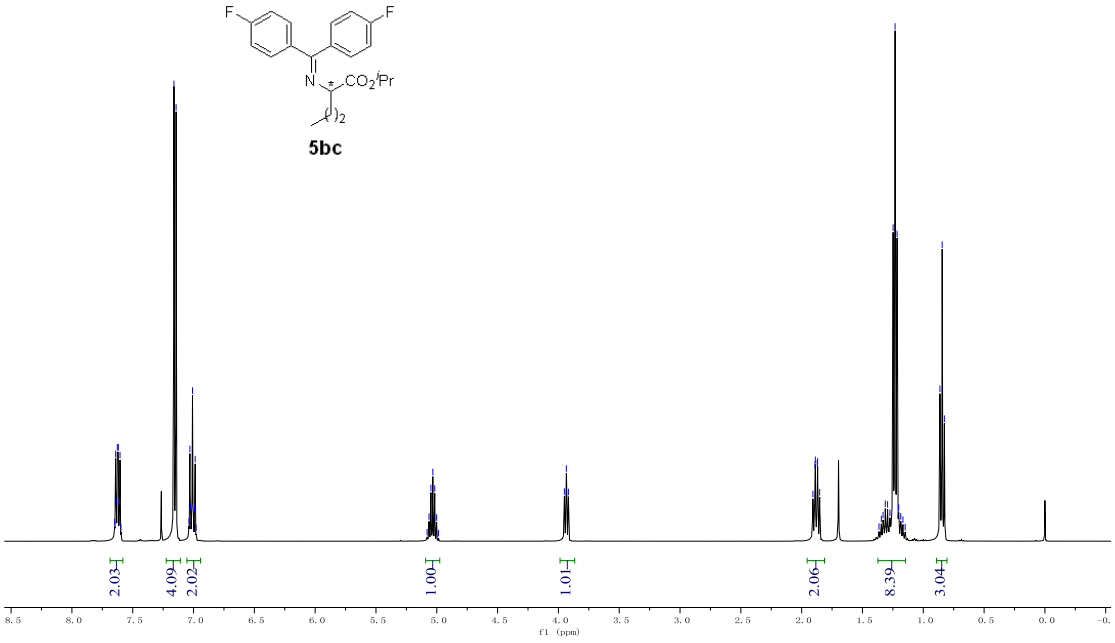

7.643
7.638
7.629
7.621
7.612
7.607
7.102
7.167
7.162
7.034
7.026
7.021
7.009
7.005
7.000
6.988
6.983
6.976
5.075
5.060
5.044
5.028
5.013
4.997
4.981
4.086
4.069
4.053
4.036
1.434
1.417
1.248
1.234
1.232
1.219
F
F
N
CO2iPr
Me
5ba
2.00
4.01
2.04
1.00
1.00
3.07
6.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

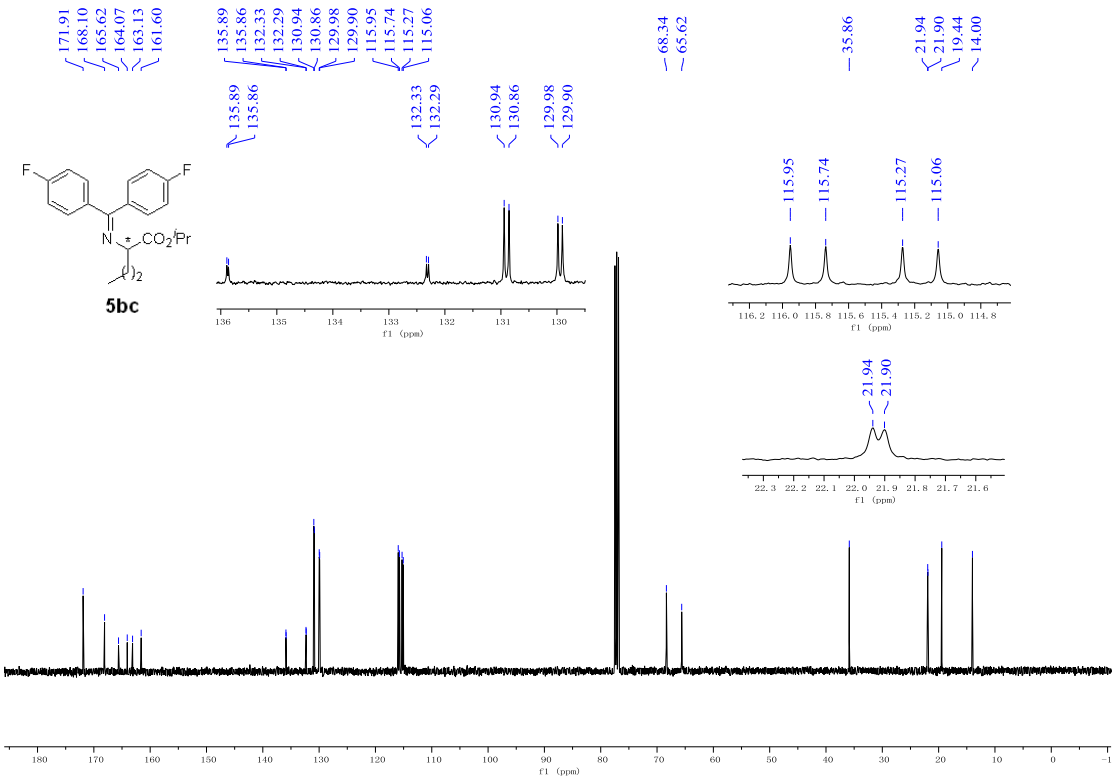

172.174
167.501
165.570
164.052
163.077
161.580
135.809
135.779
132.040
132.004
130.878
130.792
129.777
129.696
116.002
115.787
115.225
115.010
68.354
60.839
21.836
19.188
F
F
N
CO2iPr
Me
5ba
f1 (ppm)

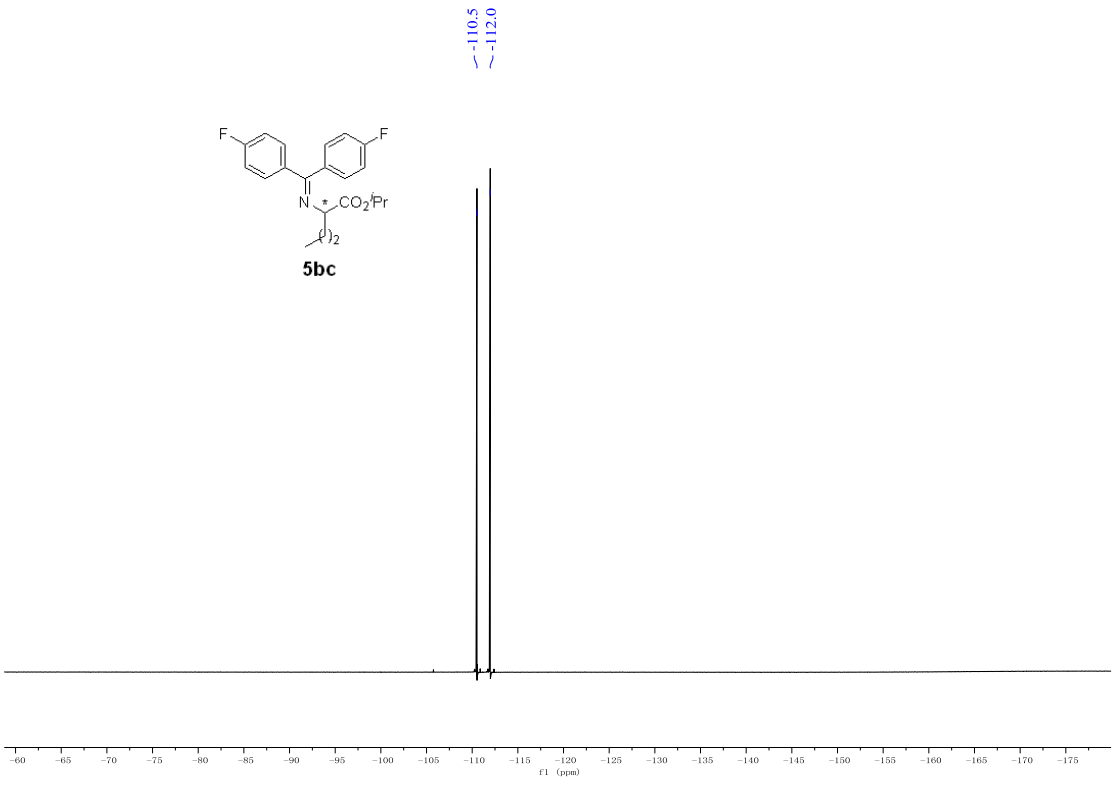

-110.4
-111.9
F
F
N
CO2iPr
Me
5ba
f1 (ppm)

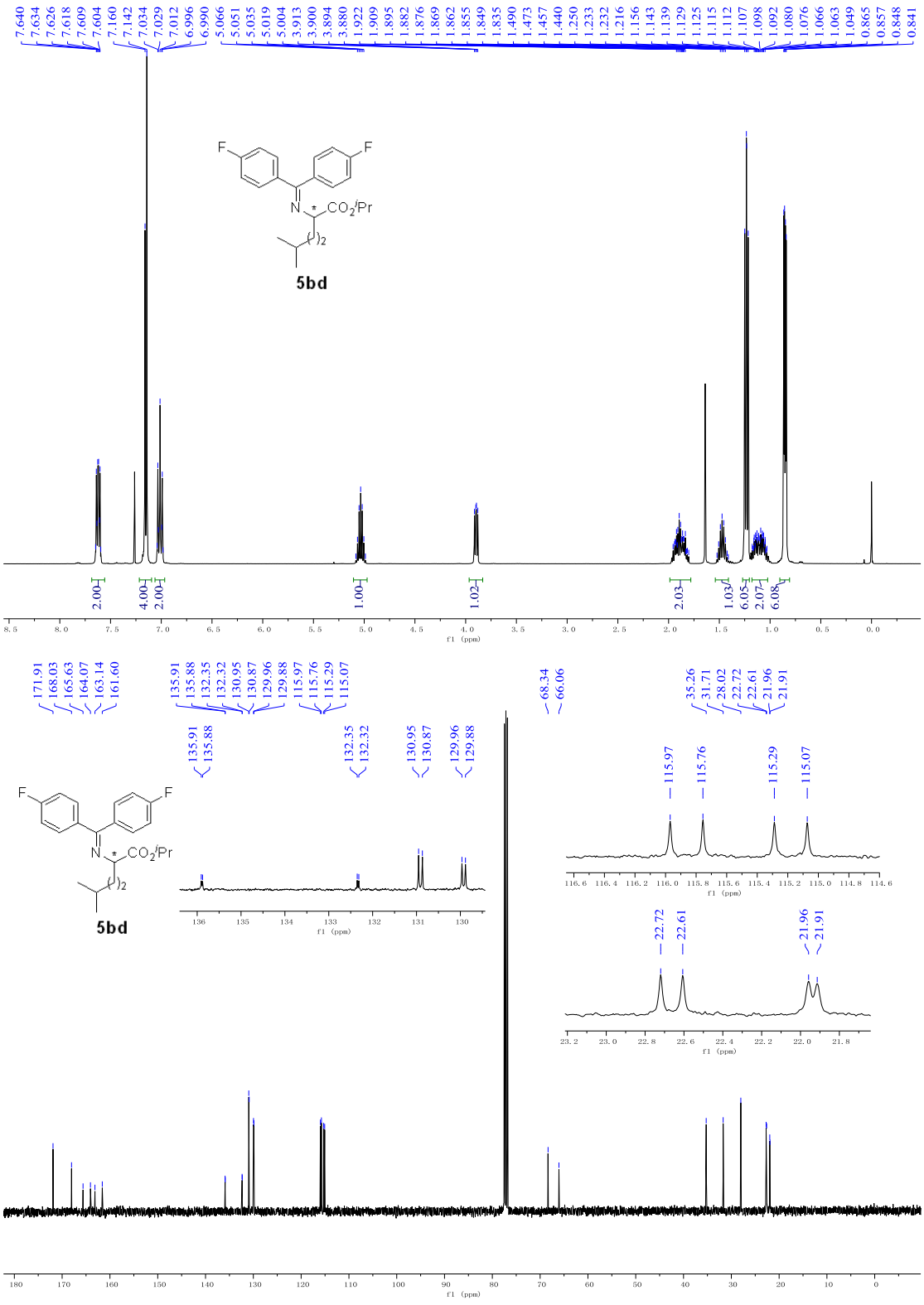

7.655
7.647
7.642
7.634
7.625
7.617
7.611
7.162
7.145
7.039
7.032
7.027
7.015
7.011
7.006
6.994
6.988
6.981
5.082
5.066
5.050
5.035
5.019
5.003
4.988
3.886
3.873
3.866
3.853
1.248
1.232
1.230
1.214
0.878
0.859
0.841
F
F
N
CO2iPr
Et
5bb
2.00
4.02
2.00
1.00
1.01
2.05
6.05
3.06
f1 (ppm)
171.75
168.23
165.63
164.06
163.13
161.59
135.90
135.87
132.35
132.31
130.94
130.86
129.98
129.90
115.97
115.76
115.28
115.06
68.33
67.06
26.99
21.96
21.91
10.68
f1 (ppm)

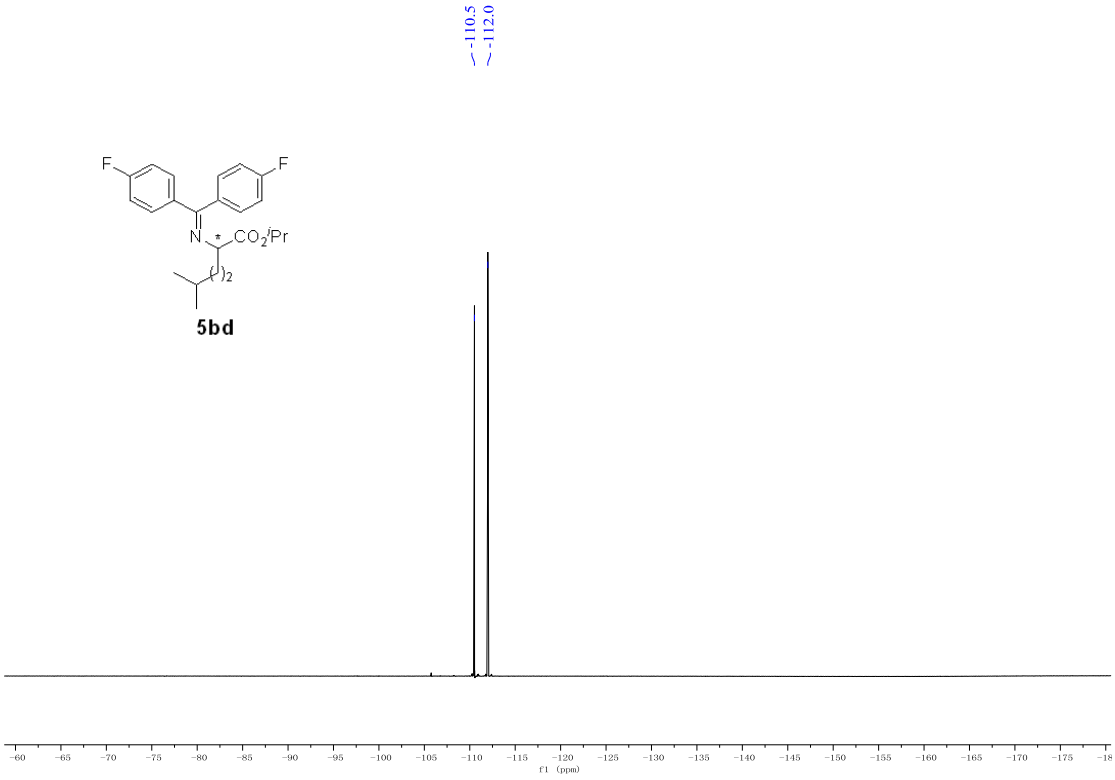

-110.5
-112.0
F
F
N
CO2iPr
Et
5bb
f1 (ppm)
7.648
7.641
7.635
7.627
7.618
7.610
7.604
7.181
7.143
7.037
7.030
7.025
7.008
6.992
6.986
6.979
5.079
5.064
5.048
5.033
5.017
5.001
4.986
3.951
3.935
3.918
1.908
1.890
1.888
1.872
1.869
1.852
1.345
1.331
1.312
1.294
1.274
1.248
1.232
1.215
1.202
1.186
1.168
0.863
0.845


F
F
N
CO2iPr
5bc
2.03
4.09
2.02
1.00
1.01
2.06
8.39
3.04
f1 (ppm)

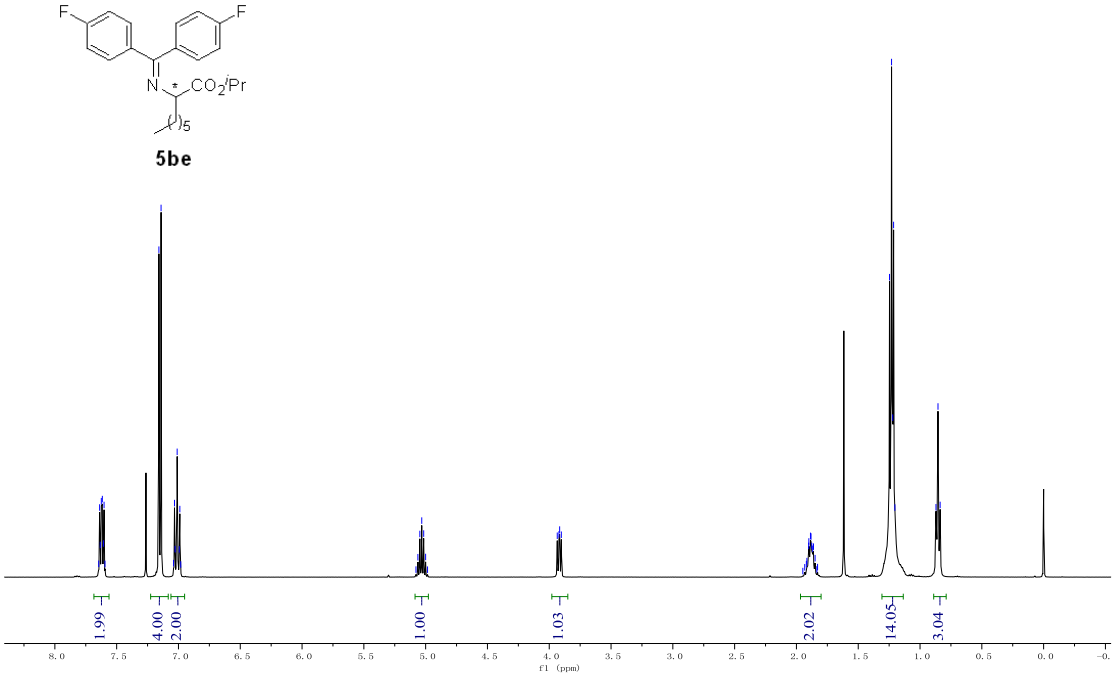

171.91
168.10
165.62
164.07
163.13
161.60
135.89
135.86
132.33
132.29
130.94
130.86
129.98
129.90
115.95
115.74
115.27
115.06
68.34
65.62
35.86
21.94
21.90
19.44
14.00
F
F
N
CO2iPr
5bc
f1 (ppm)

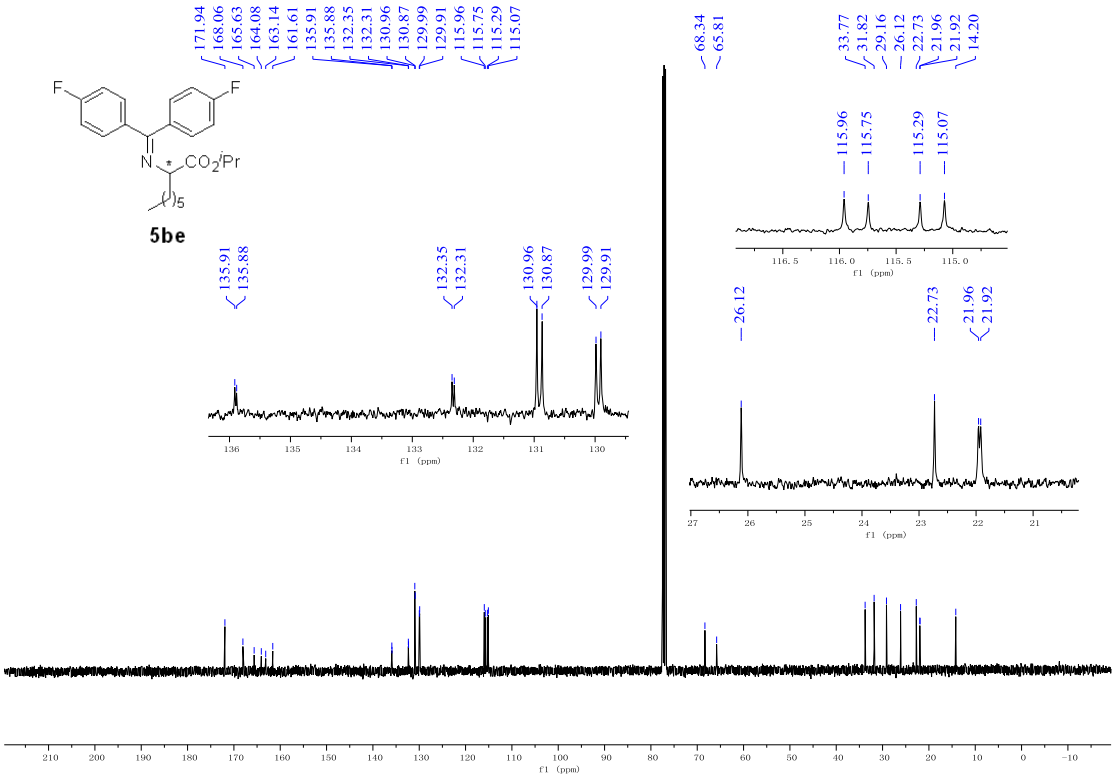

-110.5
-112.0
F
F
N
CO2iPr
5bc
f1 (ppm)


5bd
5bd



7.638 7.633 7.624 7.616 7.607 7.141 7.039 7.032 7.027 7.011 6.994 6.981 5.078 5.063 5.047 5.031 5.016 5.000 4.985 3.935 3.921 3.916 3.902 1.948 1.933 1.920 1.915 1.901 1.900 1.886 1.882 1.876 1.868 1.862 1.849 1.835 1.829 1.247 1.230 1.221 1.214 1.204 0.871 0.855 0.837

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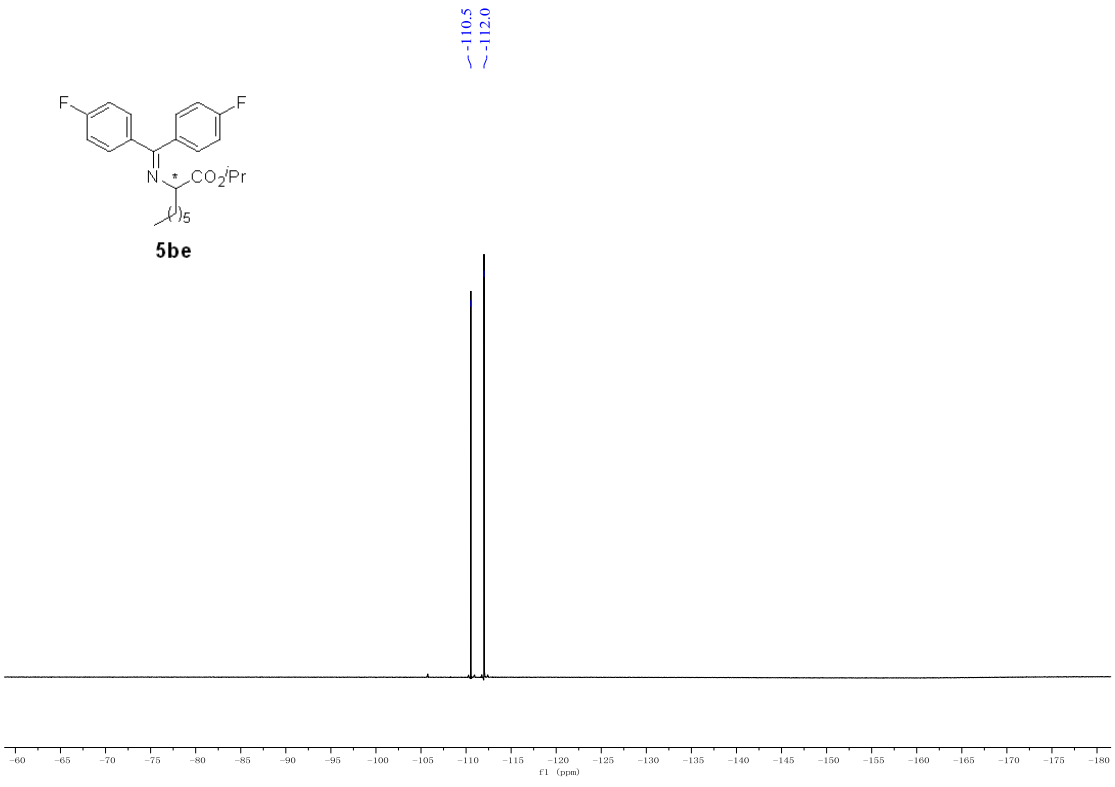
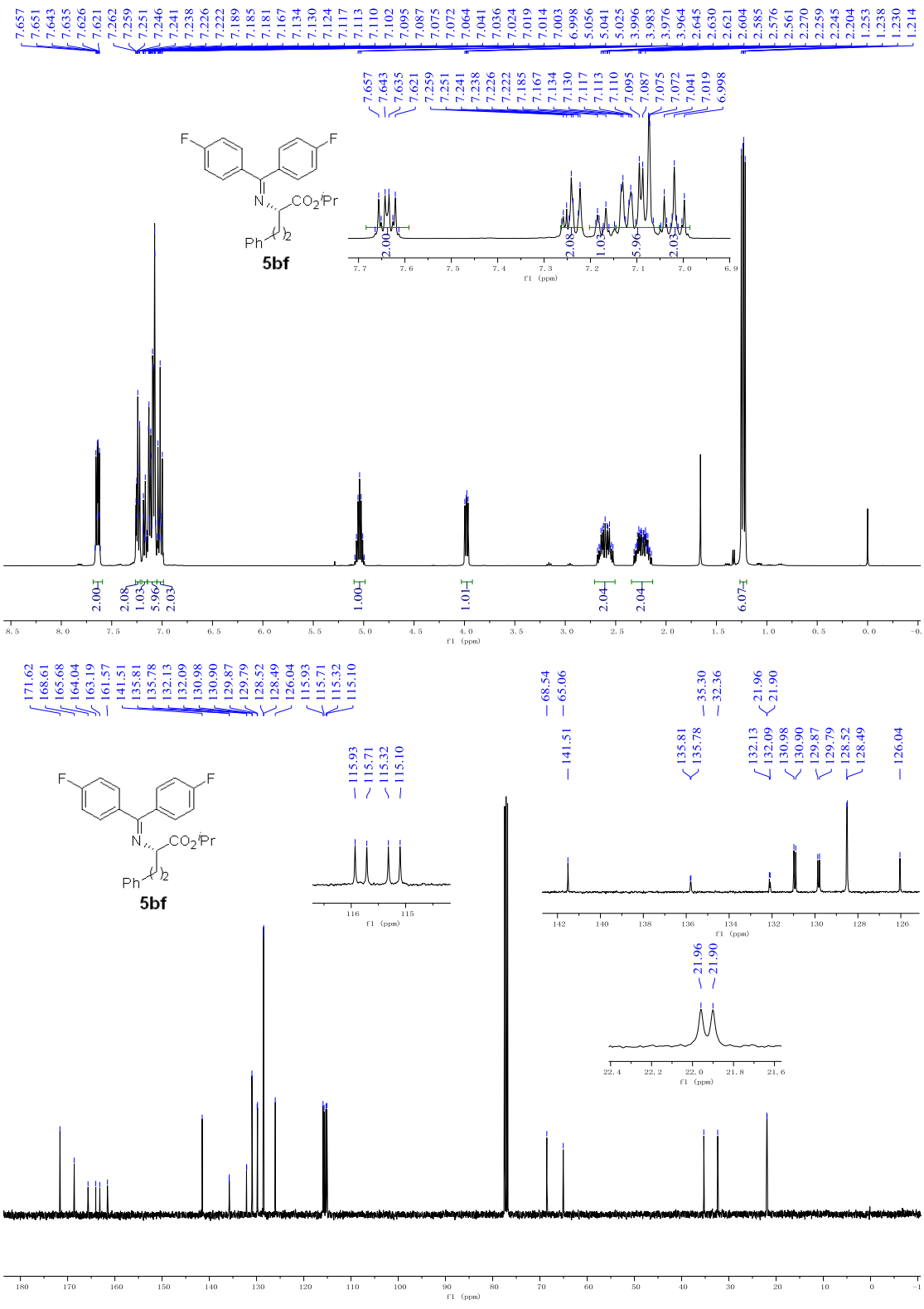
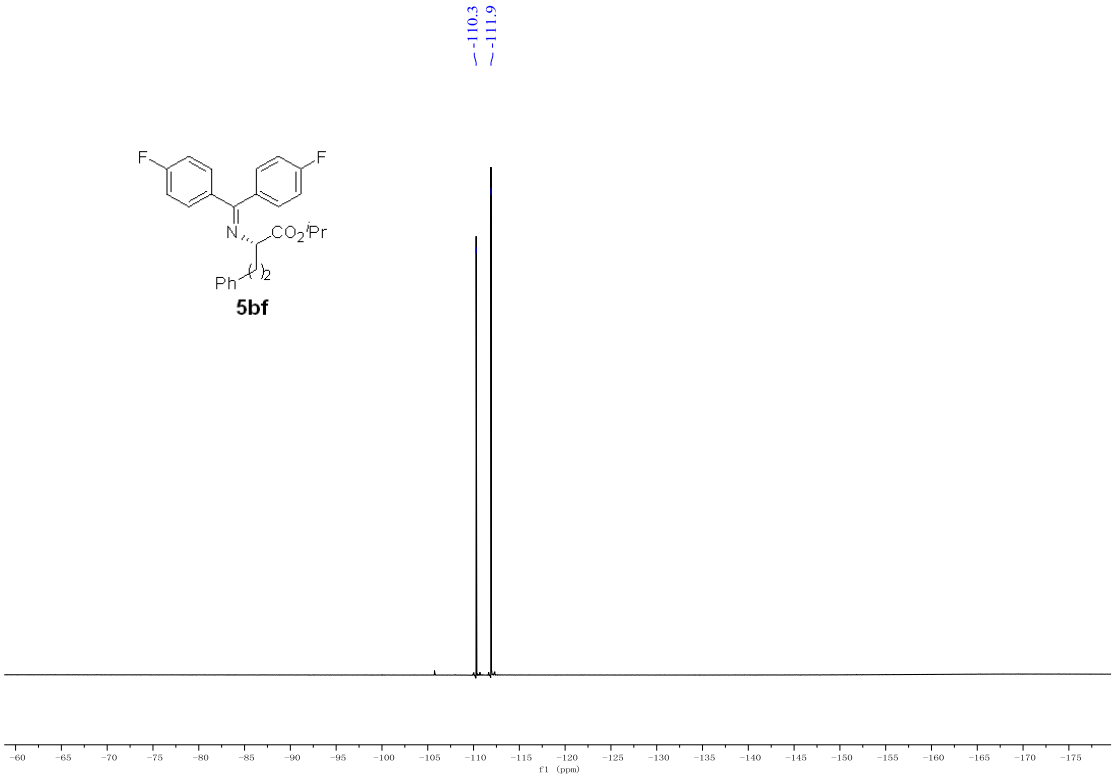
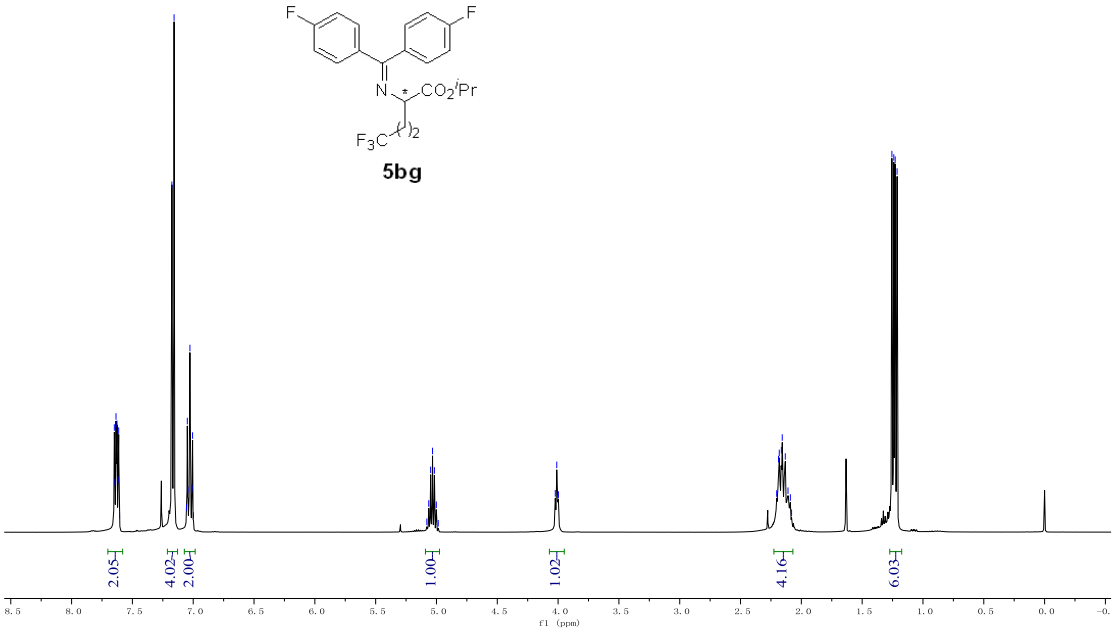
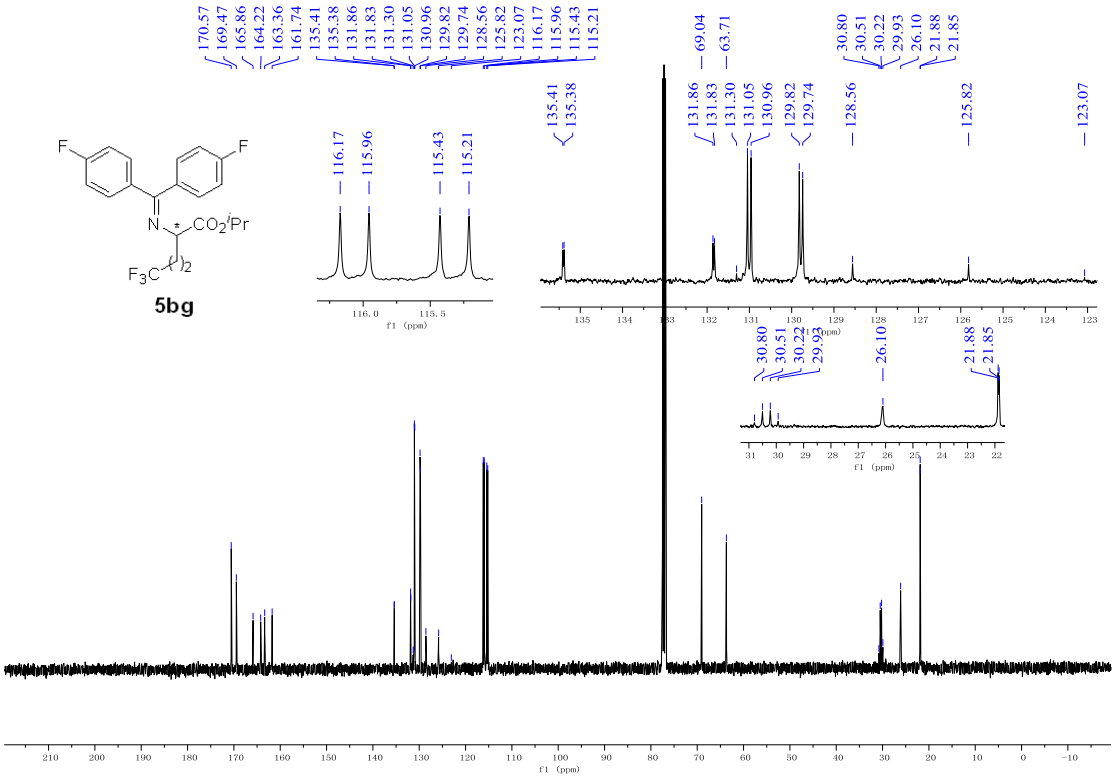
168.06
165.63
164.08
163.14
161.61
135.91
135.88
132.35
132.31
130.96
130.87
129.99
129.91
115.96
115.75
115.29
115.07
68.34
65.81
33.77
31.82
29.16
26.12
22.73
21.96
21.92
14.20
F
F
N
CO2iPr
5
5be

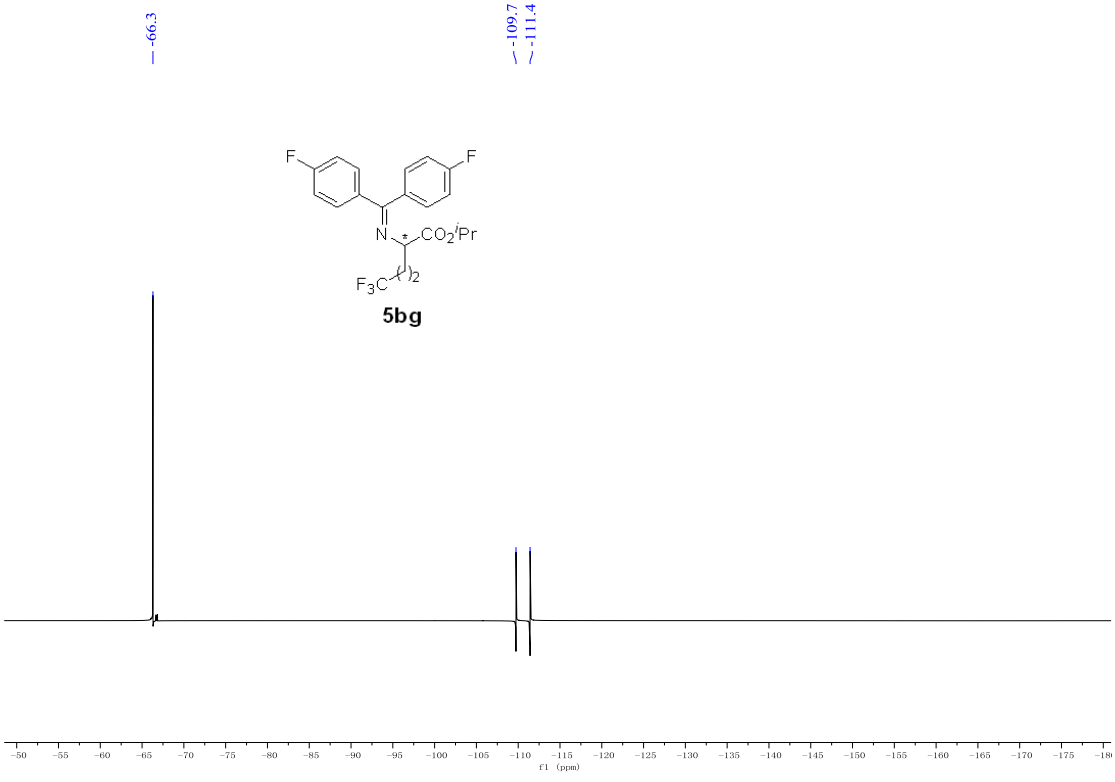

-110.5
-112.0
F
F
N
CO2iPr
5
5be

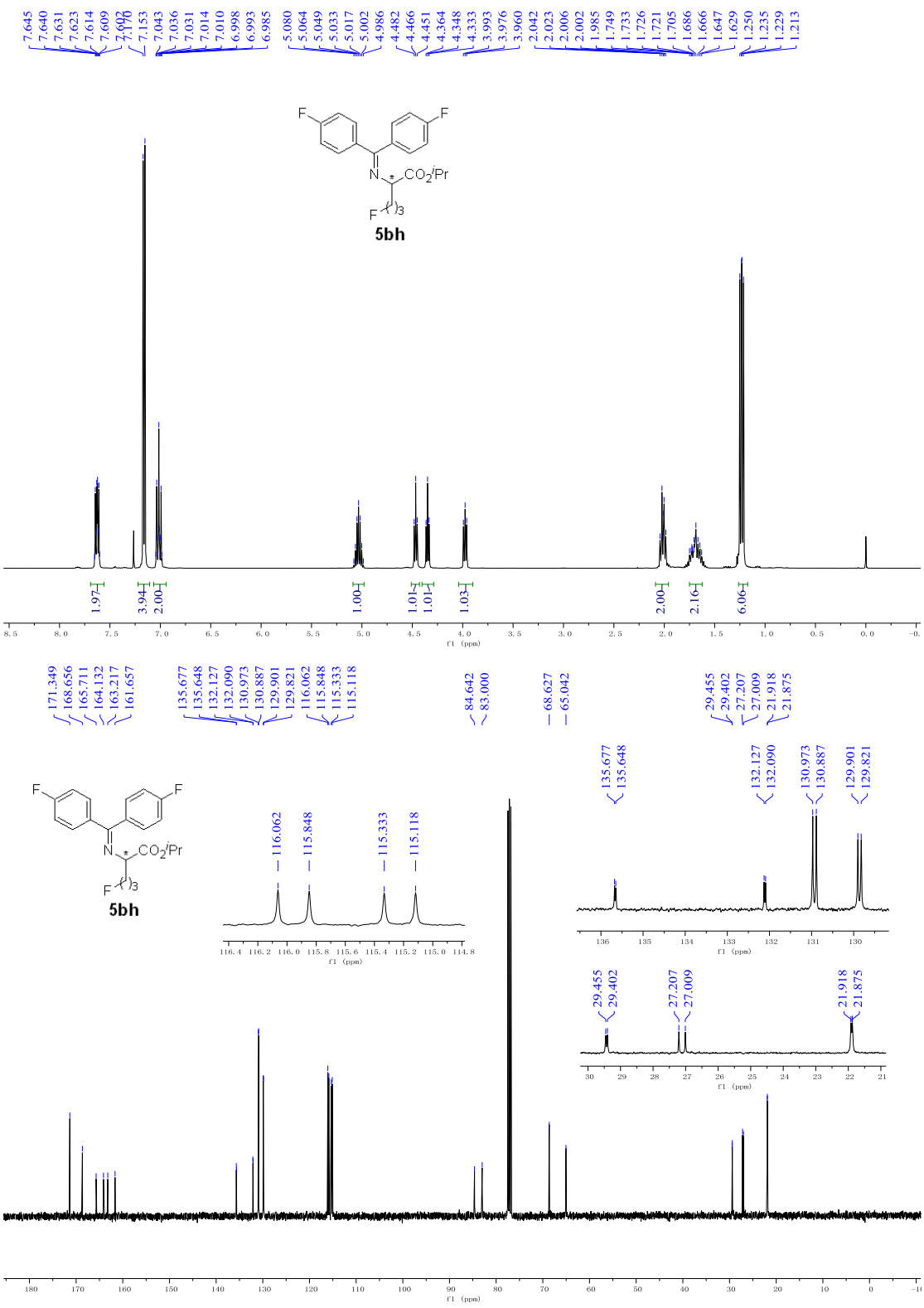

5bf
5bf


-110.3
-111.9
F
F
N
CO2iPr
Ph
2
5bf
f1 (ppm)
7.649
7.643
7.635
7.627
7.618
7.613
7.606
7.176
7.157
7.055
7.049
7.043
7.027
7.010
7.005
6.998
5.079
5.064
5.048
5.032
5.017
5.001
4.985
4.023
4.011
3.997
2.203
2.188
2.181
2.164
2.157
2.132
2.110
2.090
2.080
1.256
1.240
1.228
1.213


F
F
N
CO2iPr
F3C
2
5bg
2.05
4.02
2.00
1.00
1.02
4.16
6.03
f1 (ppm)


170.57
169.47
165.86
164.22
163.36
161.74
135.41
135.38
131.86
131.83
131.30
131.05
130.96
129.82
129.74
128.56
125.82
123.07
116.17
115.96
115.43
115.21
69.04
63.71
30.80
30.51
30.22
29.93
26.10
21.88
21.85
F
F
N
CO2iPr
F3C
2
5bg
f1 (ppm)


-66.3
-109.7
-111.4
F
F
N
CO2iPr
F3C
2
5bg
f1 (ppm)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7.014
7.010
6.998
6.993
6.985
5.080
5.064
5.049
5.033
5.017
5.002
4.986
4.482
4.466
4.451
4.364
4.348
4.333
3.993
3.976
3.960
2.042
2.023
2.006
2.002
1.985
1.749
1.733
1.726
1.721
1.705
1.686
1.666
1.647
1.629
1.250
1.235
1.229
1.213
F
F
N
CO2iPr
F
3
5bh
1.97
3.94
2.00
1.00
1.01
1.01
1.03
2.00
2.16
6.06
f1 (ppm)
171.349
168.656
165.711
164.132
163.217
161.657
135.677
135.648
132.127
132.090
130.973
130.887
129.901
129.821
116.062
115.848
115.333
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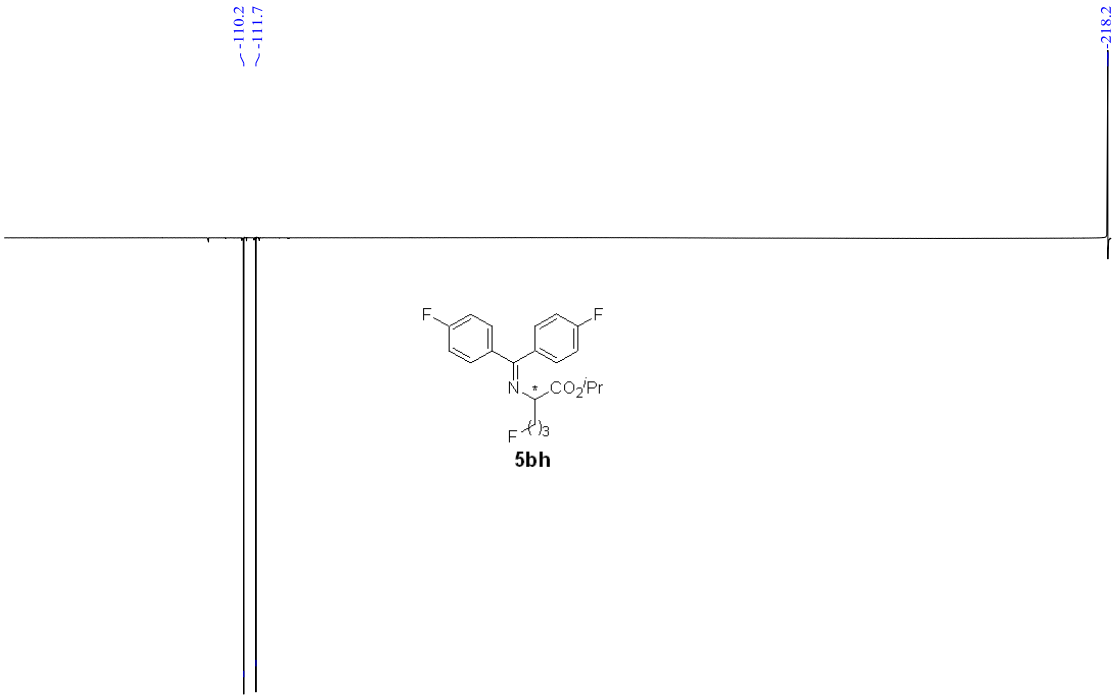
29.402
27.207
27.009
21.918
21.875
f1 (ppm)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218.2
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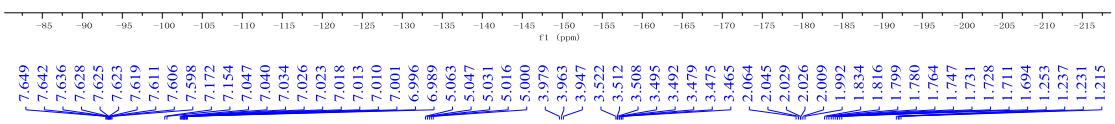
F
N
CO2iPr
F
3
5bh


f1 (ppm)

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7.047
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7.034
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7.018
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7.010
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3.508
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3.492
3.479
3.475
3.465
2.064
2.045
2.029
2.026
2.009
1.992
1.834
1.816
1.799
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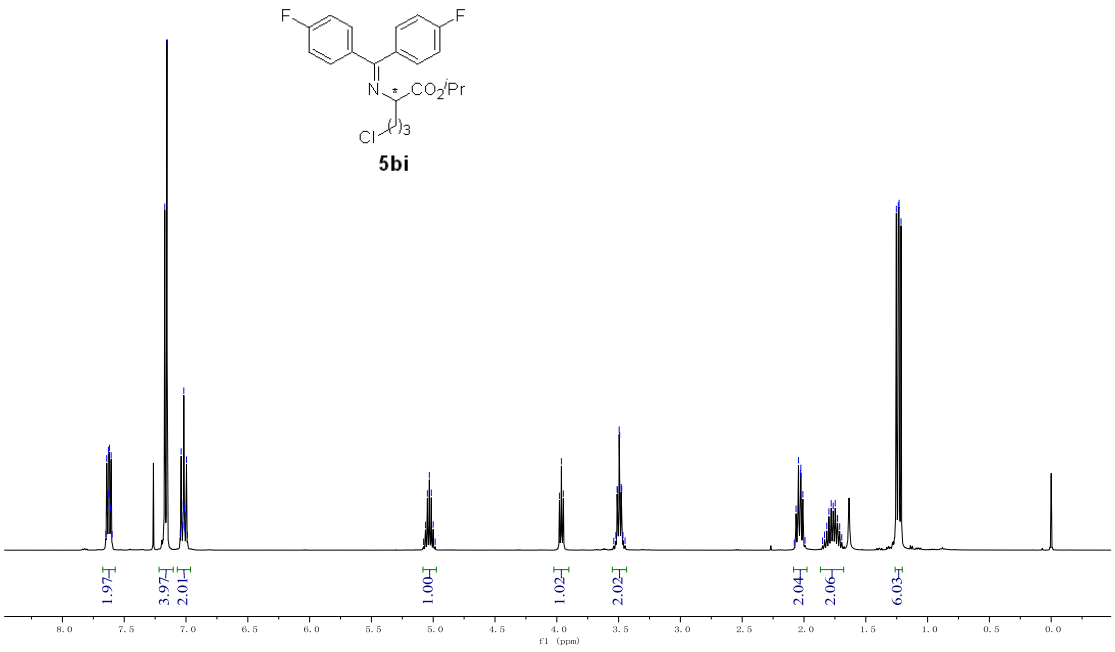
1.215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F
N
CO2iPr
Cl
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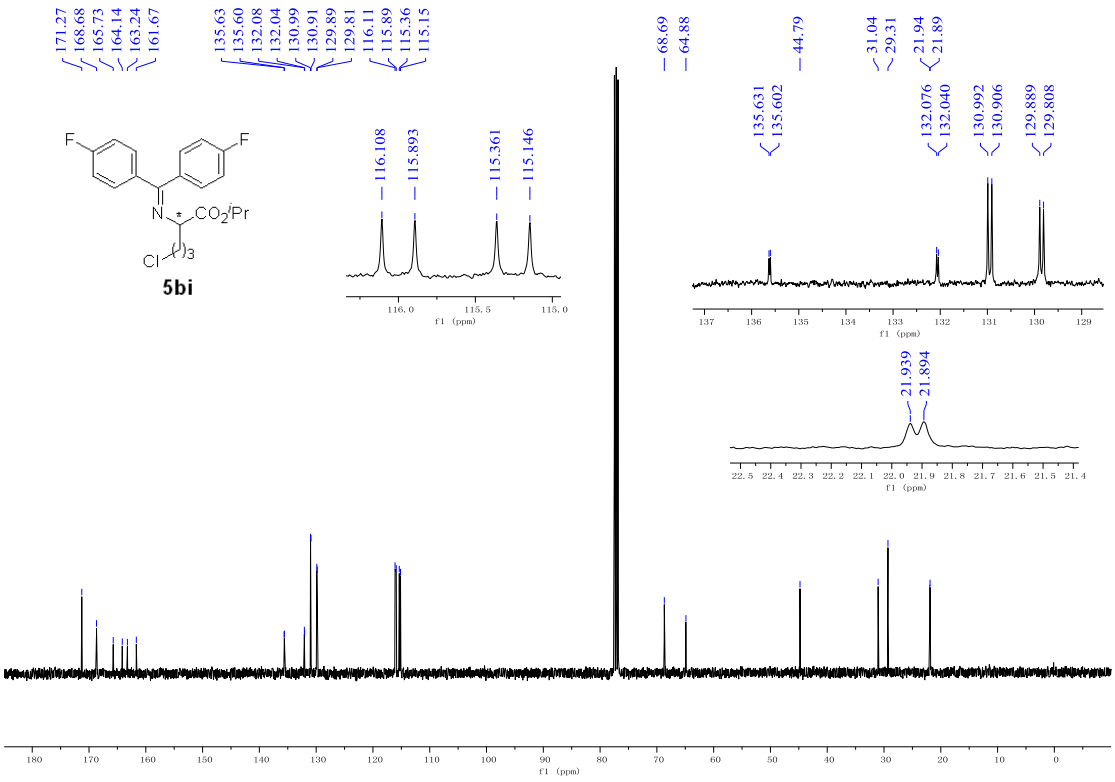
3.97
2.01
1.00
1.02
2.02
2.04
2.06
6.03
f1 (ppm)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129.81
116.11
115.89
115.36
115.15
68.69
64.88
44.79
31.04
29.31
21.94
21.89
F
F
N
CO2iPr
Cl
3
5bi
116.108
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115.361
115.146
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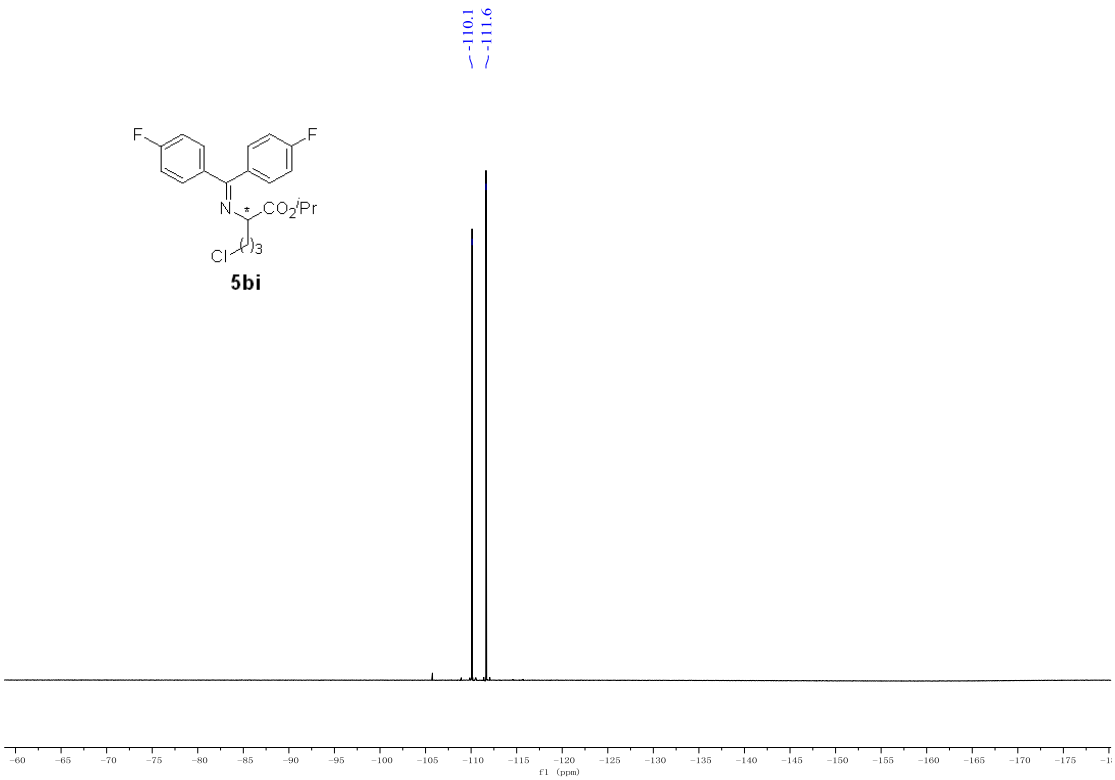
f1 (ppm)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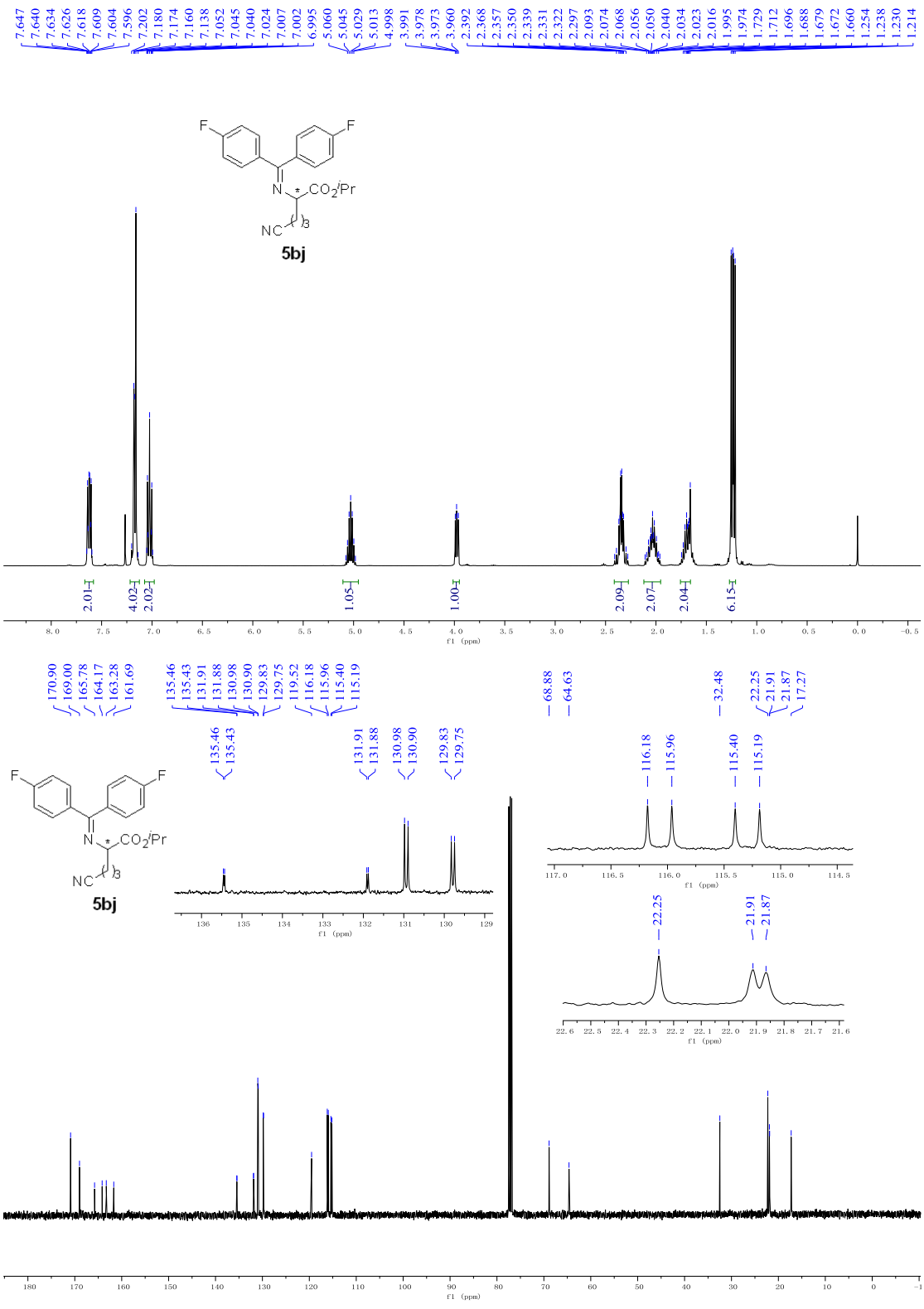
Cl
3
5bi
f1 (ppm)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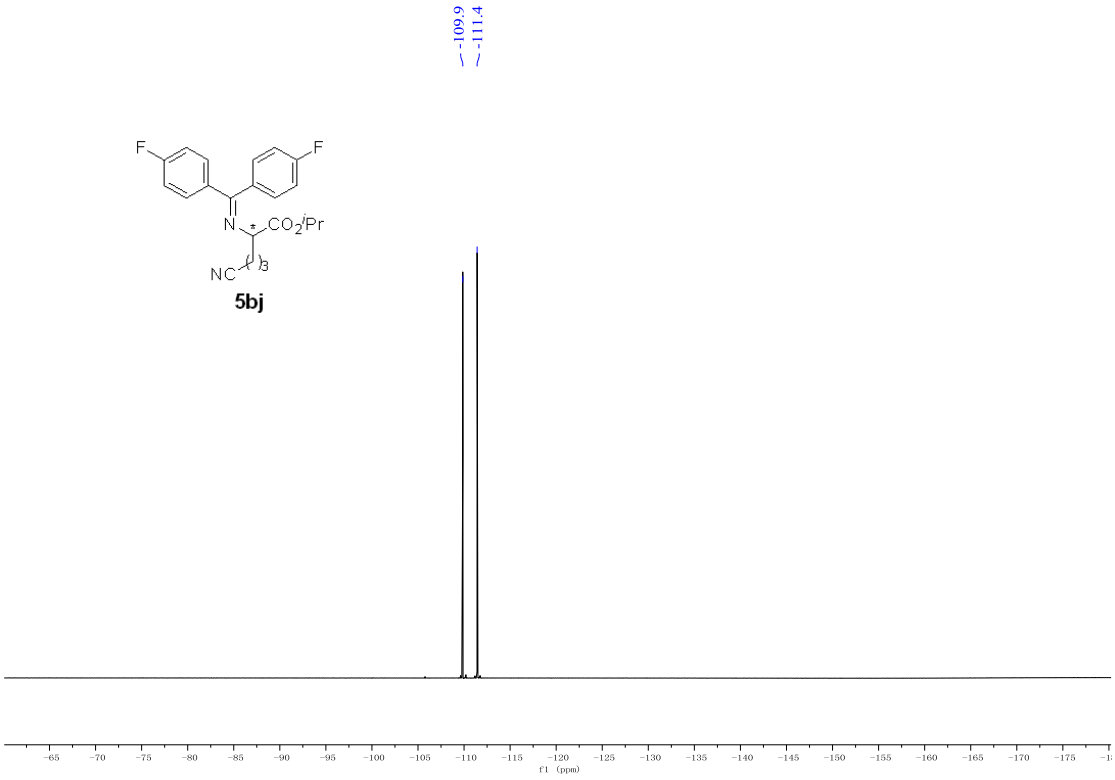
F
F
N
CO2iPr
NC
3
5bj
2.01
4.02
2.02
1.05
1.00
2.09
2.07
2.04
6.15
f1 (ppm)
170.90 169.00 165.78 164.17 163.28 161.69
135.46 135.43 131.91 131.88 130.98 130.90 129.83 129.75 119.52 116.18 115.96 115.40 115.19
68.88 64.63 32.48 22.25 21.91 21.87 17.27
f1 (ppm)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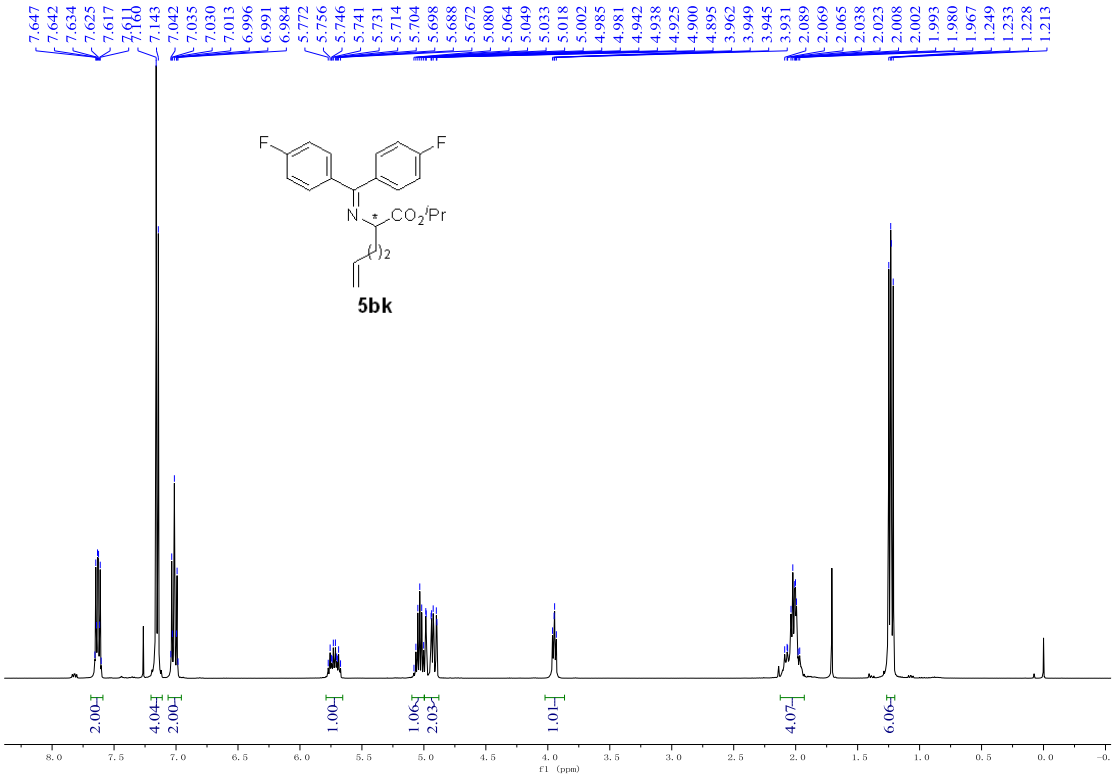
F
N
CO2iPr
NC
3
5bj
f1 (ppm)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7.030
7.013
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6.991
6.984
5.772
5.756
5.746
5.741
5.731
5.714
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5.698
5.688
5.672
5.080
5.064
5.049
5.033
5.018
5.002
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4.981
4.942
4.938
4.925
4.900
4.895
3.962
3.949
3.945
3.931
2.089
2.069
2.065
2.038
2.023
2.008
2.002
1.993
1.980
1.967
1.249
1.233
1.228
1.213
F
F
N
CO2iPr
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5bk
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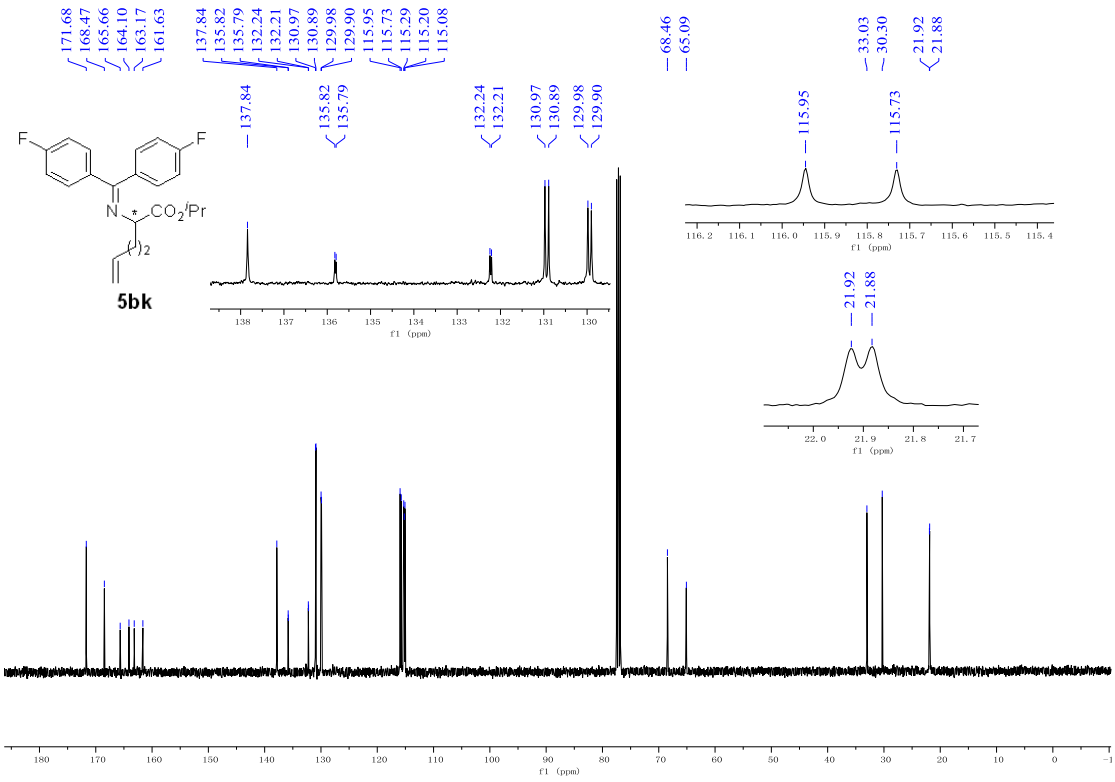
4.04
2.00
1.00
1.06
2.03
1.01
4.07
6.06
f1 (ppm)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132.24
132.21
130.97
130.89
129.98
129.90
115.95
115.73
115.29
115.20
115.08
68.46
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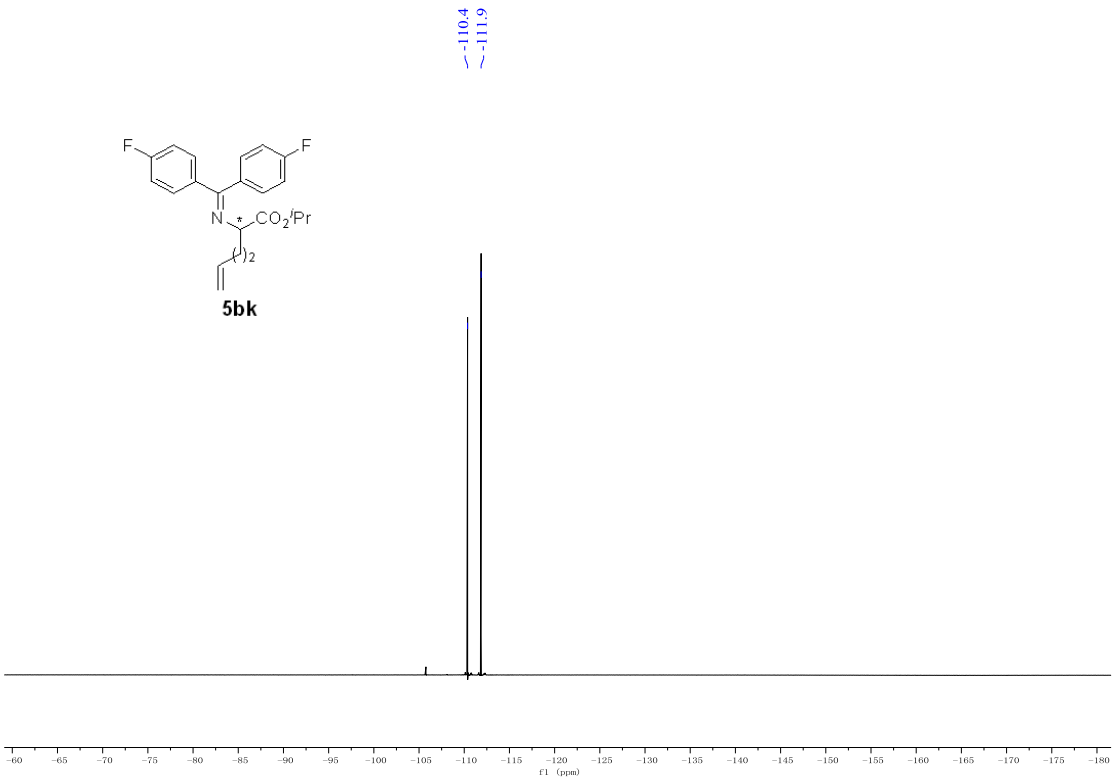
33.03
30.30
21.92
21.88
F
F
N
CO2iPr
5bk
f1 (ppm)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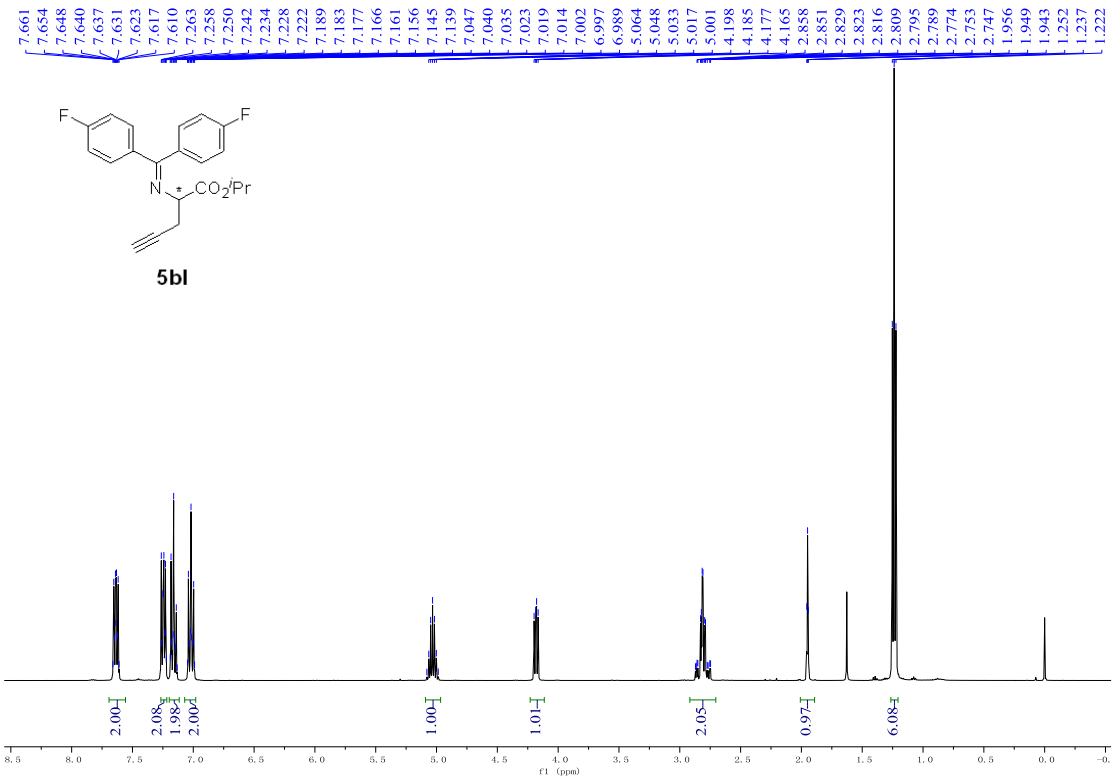
-111.9
F
F
N
CO2iPr
5bk
f1 (ppm)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7.250
7.242
7.234
7.228
7.222
7.189
7.183
7.177
7.166
7.161
7.156
7.145
7.139
7.047
7.040
7.035
7.023
7.019
7.014
7.002
6.997
6.989
5.064
5.048
5.033
5.017
5.001
4.198
4.185
4.177
4.165
2.858
2.851
2.829
2.823
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2.809
2.795
2.789
2.774
2.753
2.747
1.956
1.949
1.943
1.252
1.237
1.222
F
F
N
*
CO2iPr
5bl
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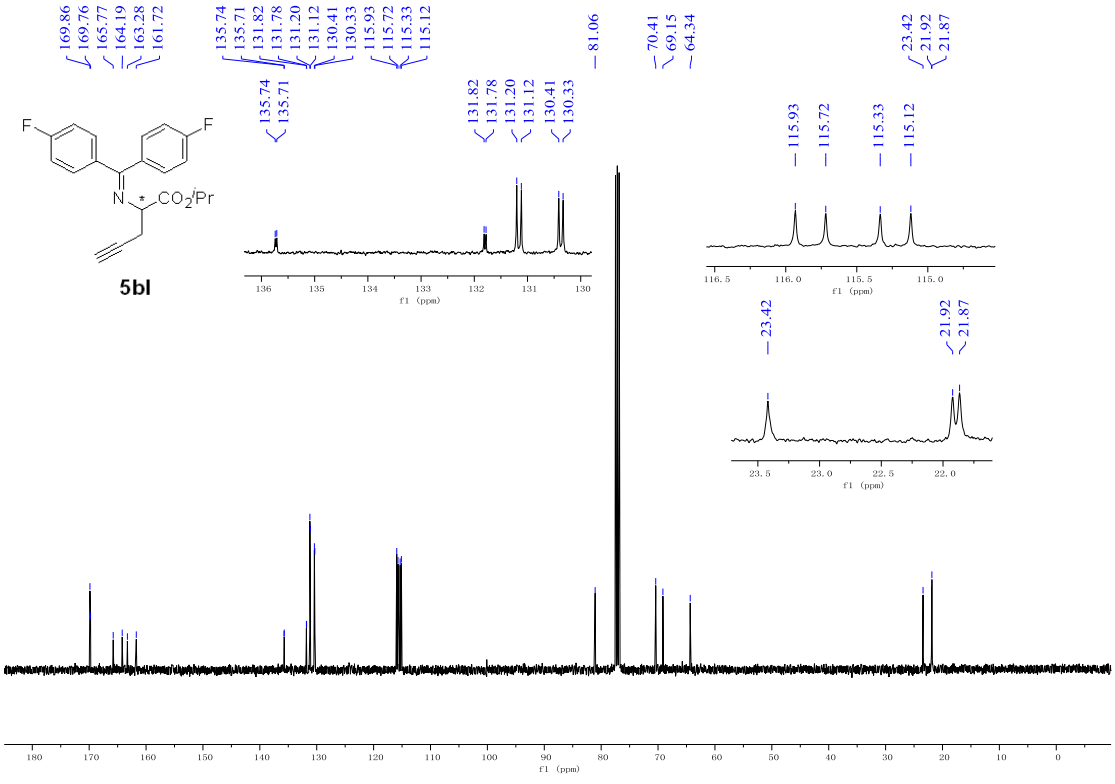
2.08
1.98
2.00
1.00
1.01
2.05
0.97
6.08
f1 (ppm)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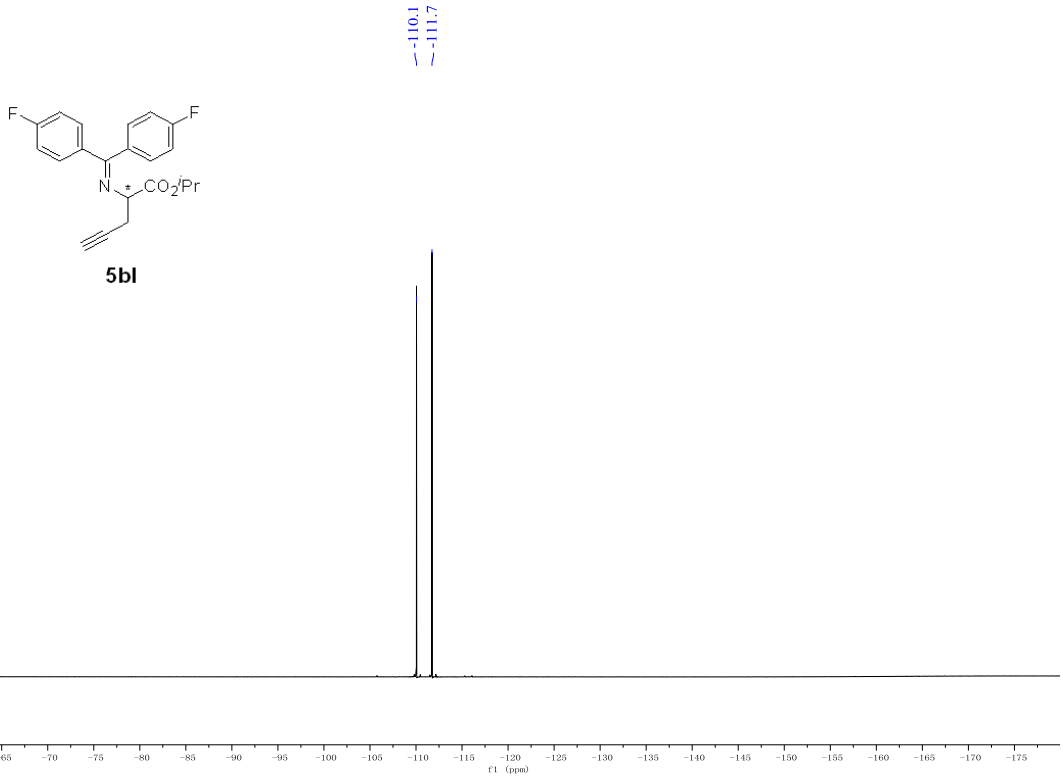
131.20
131.12
130.41
130.33
115.93
115.72
115.33
115.12
81.06
70.41
69.15
64.34
23.42
21.92
21.87
F
F
N
*
CO2iPr
5bl
f1 (ppm)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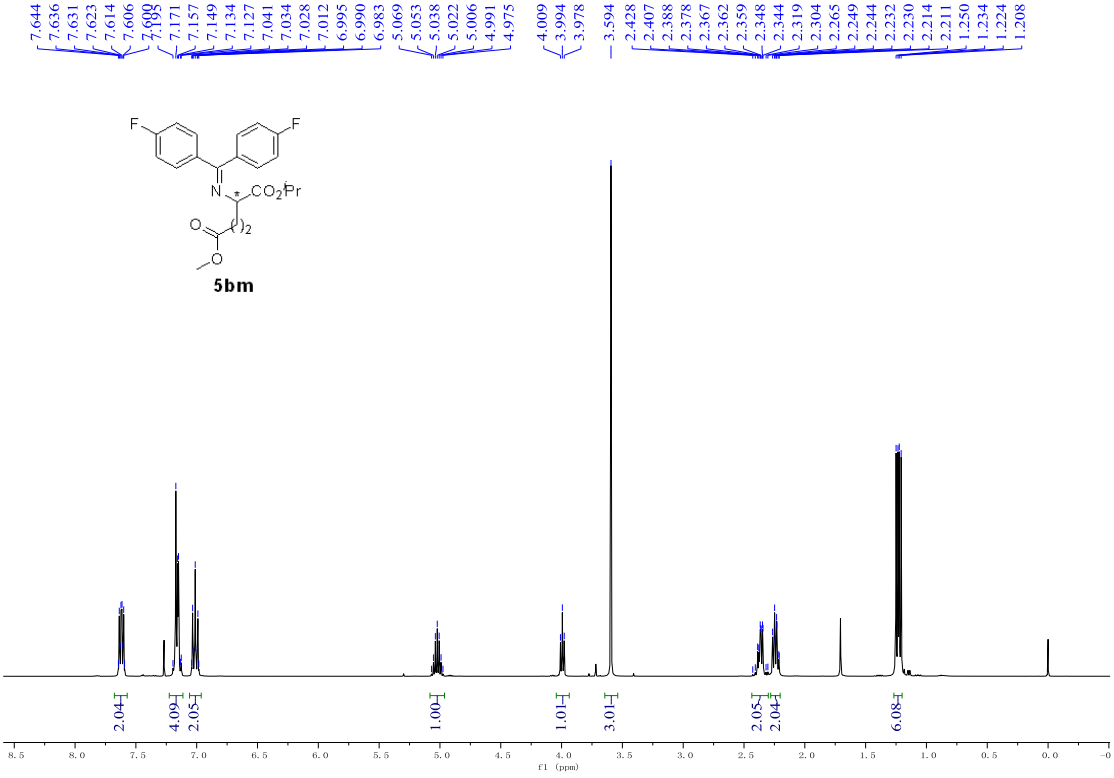
F
F
N
CO2iPr
f1 (ppm)

5bl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7.127
7.041
7.034
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7.012
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6.983
5.069
5.053
5.038
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5.006
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4.009
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3.978
3.594
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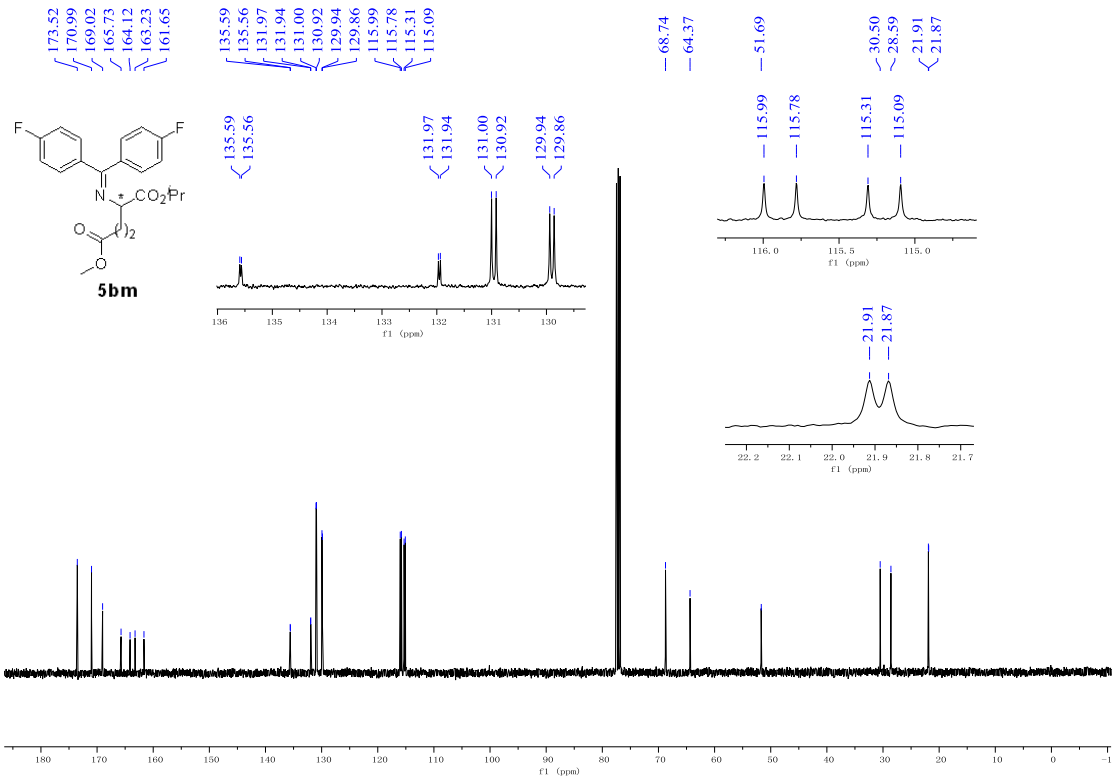
2.407
2.388
2.378
2.367
2.362
2.359
2.348
2.344
2.319
2.304
2.265
2.249
2.244
2.232
2.230
2.214
2.211
1.250
1.234
1.224
1.208
F
F
N
CO2iPr
O
O
O
2.04
4.09
2.05
1.00
1.01
3.01
2.05
2.04
6.08
f1 (ppm)

5bm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129.94
129.86
115.99
115.78
115.31
115.09
68.74
64.37
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30.50
28.59
21.91
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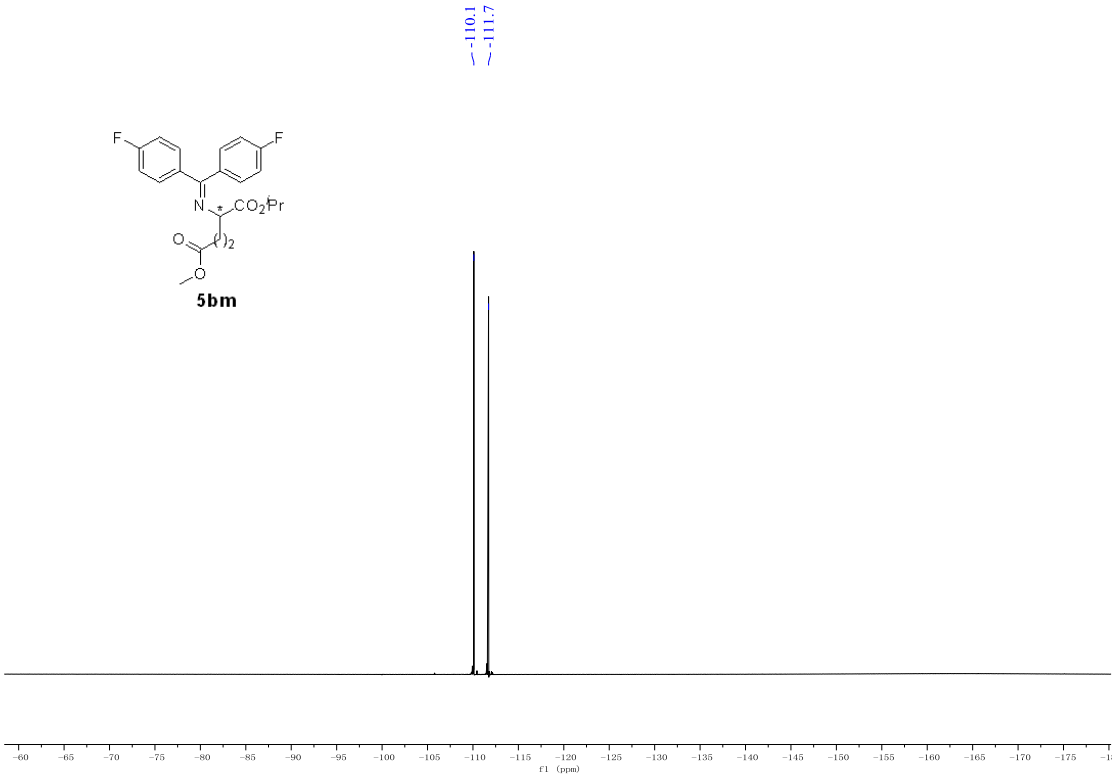
F
F
N
CO2iPr
O
O
O
5bm
f1 (ppm)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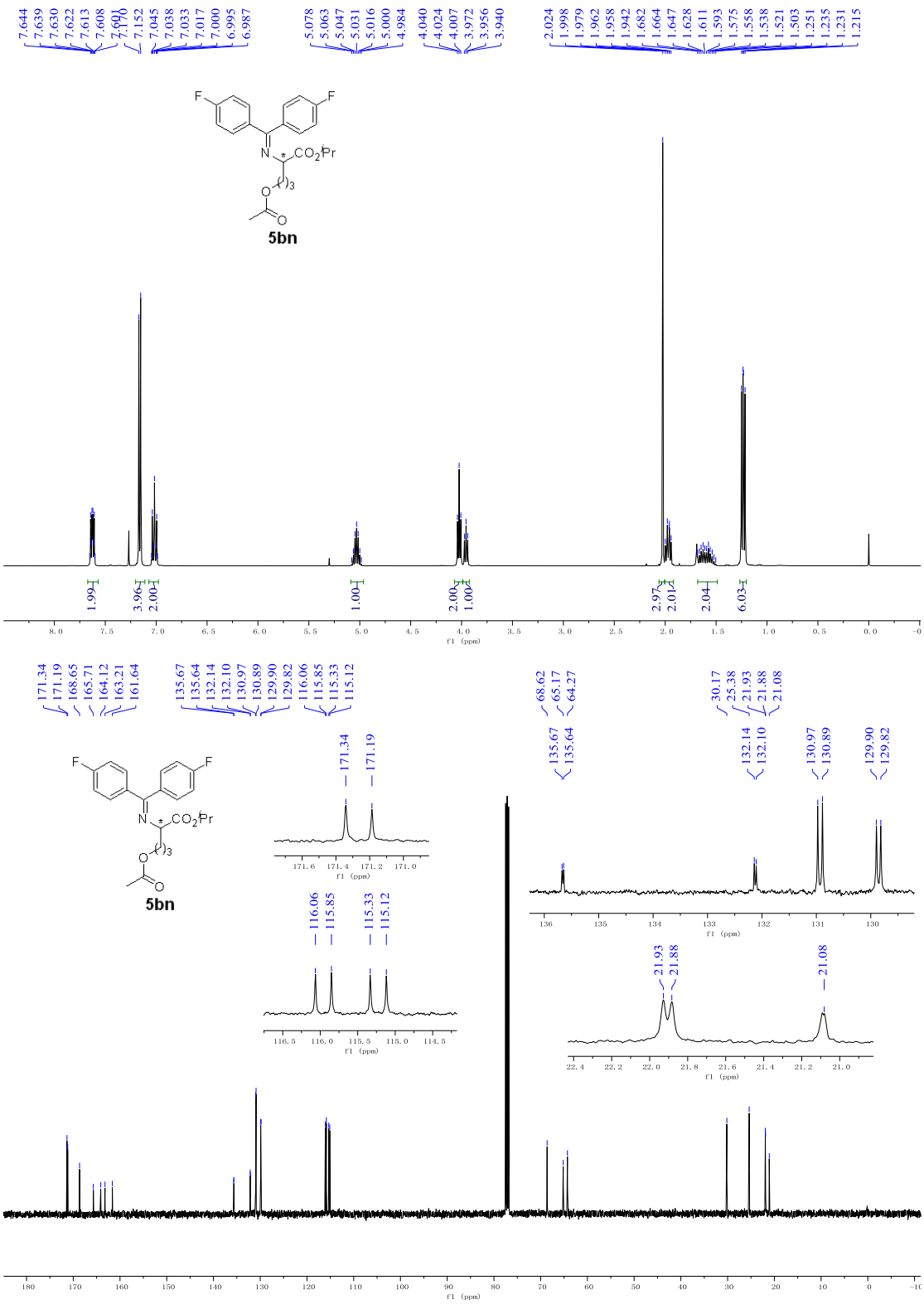
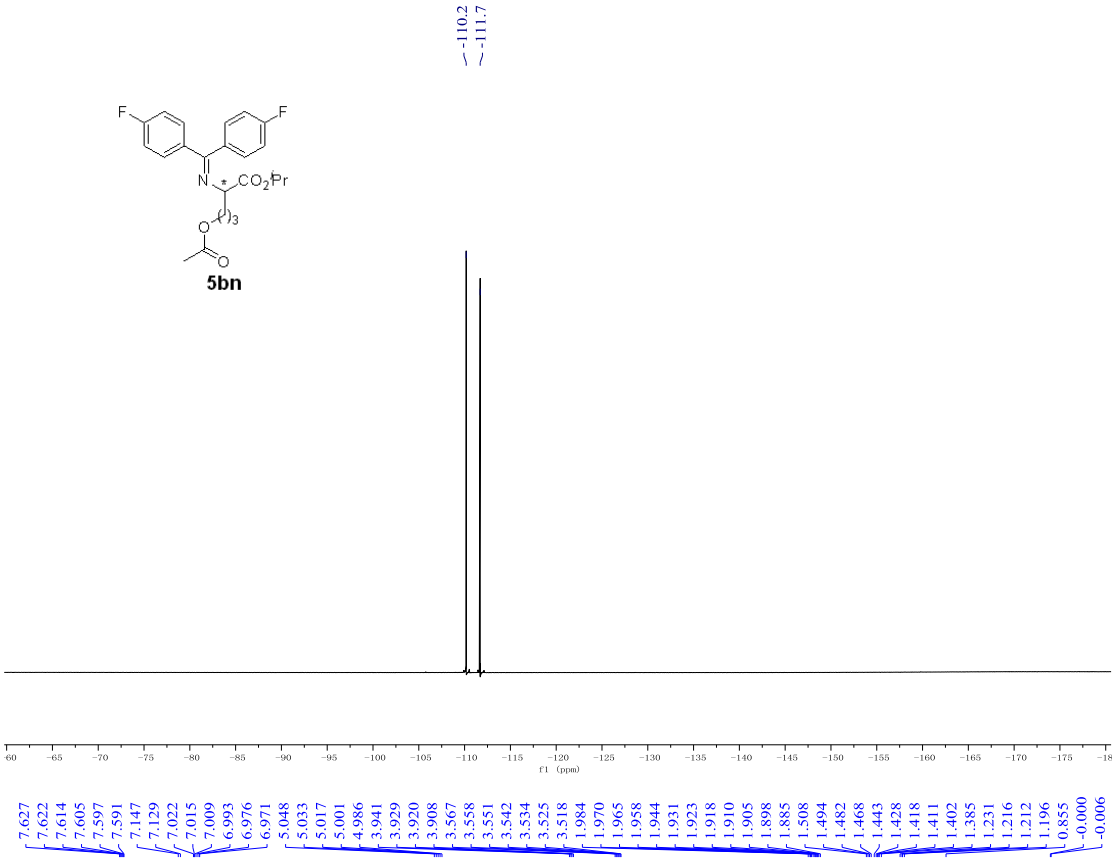
F
F
N
CO2iPr
O
O
O
5bm
f1 (ppm)


5bn
5bn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-111.7
F
F
N
CO2iPr
O
O
5bn
f1 (ppm)
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7.597
7.591
7.147
7.129
7.022
7.015
7.009
6.993
6.976
6.971
5.048
5.033
5.017
5.001
4.986
3.941
3.929
3.920
3.908
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3.542
3.534
3.525
3.518
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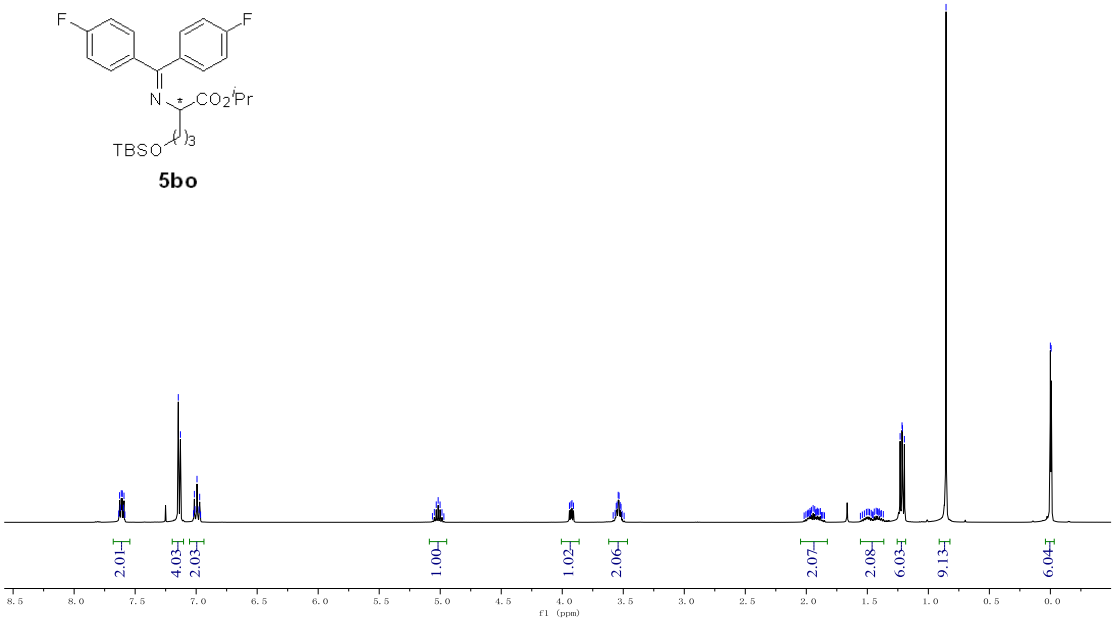
F
F
N
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TBSO
5bo
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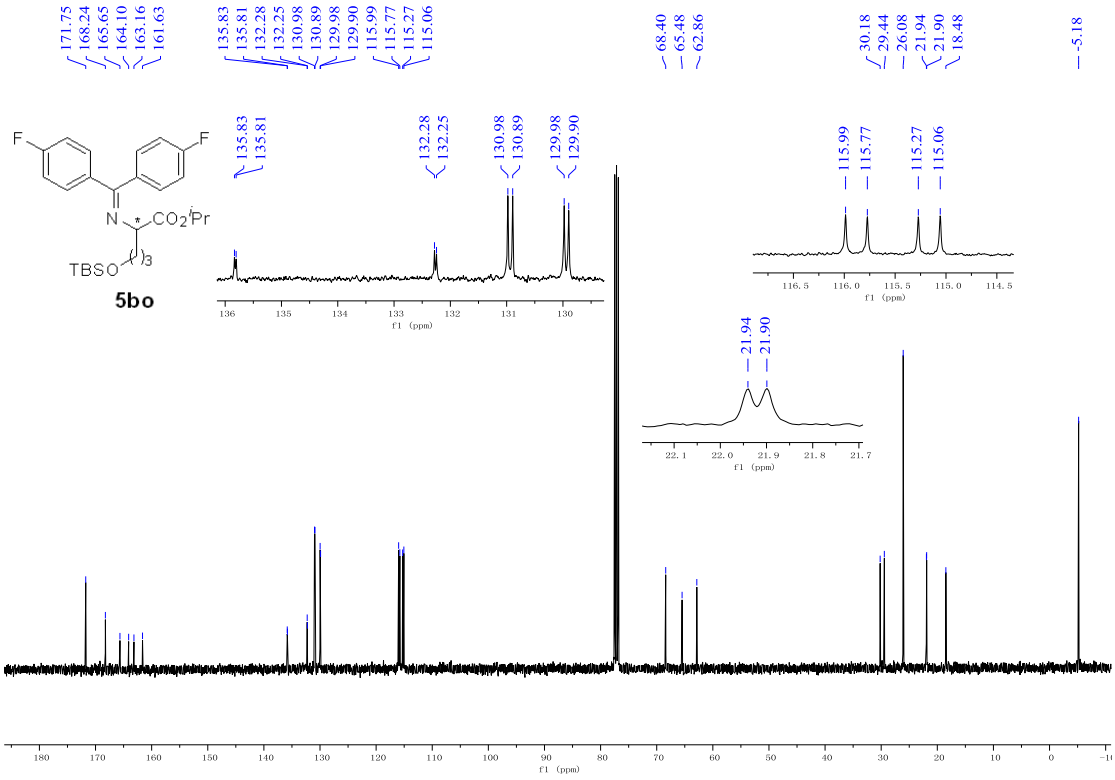
2.06
2.07
2.08
6.03
9.13
6.04
f1 (ppm)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115.77
115.27
115.06
68.40
65.48
62.86
30.18
29.44
26.08
21.94
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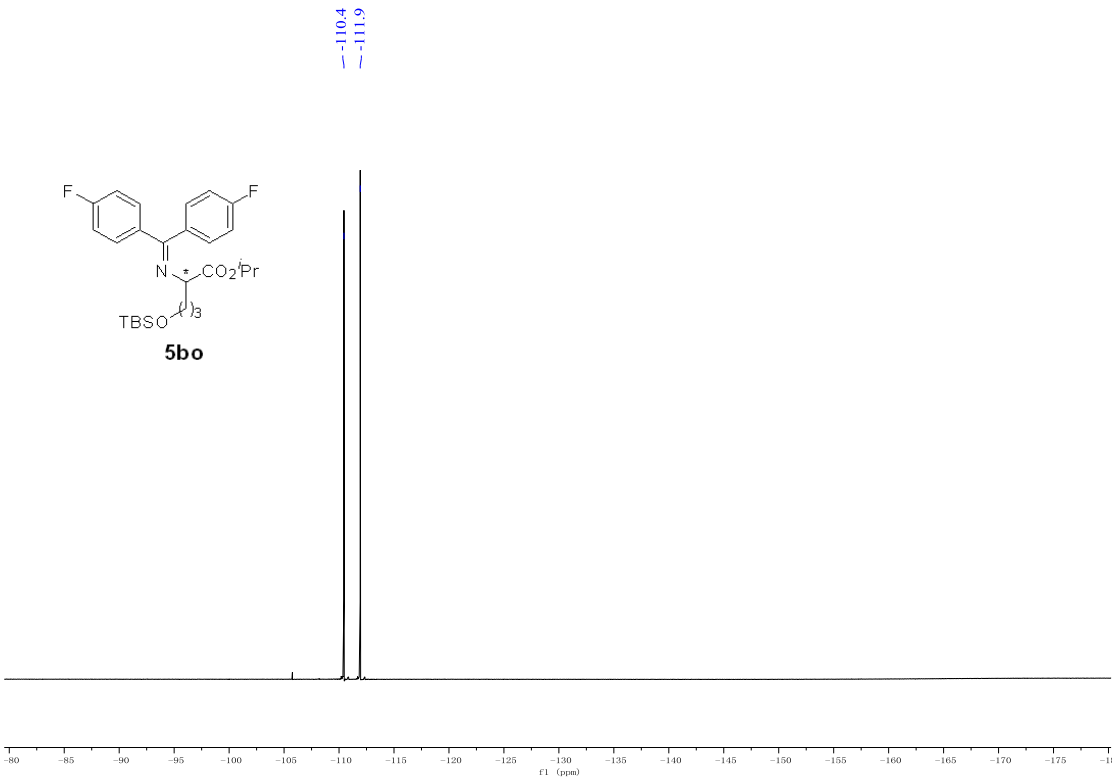
F
F
N
CO2iPr
TBSO
3
5bo
21.94
21.90
f1 (ppm)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F
F
N
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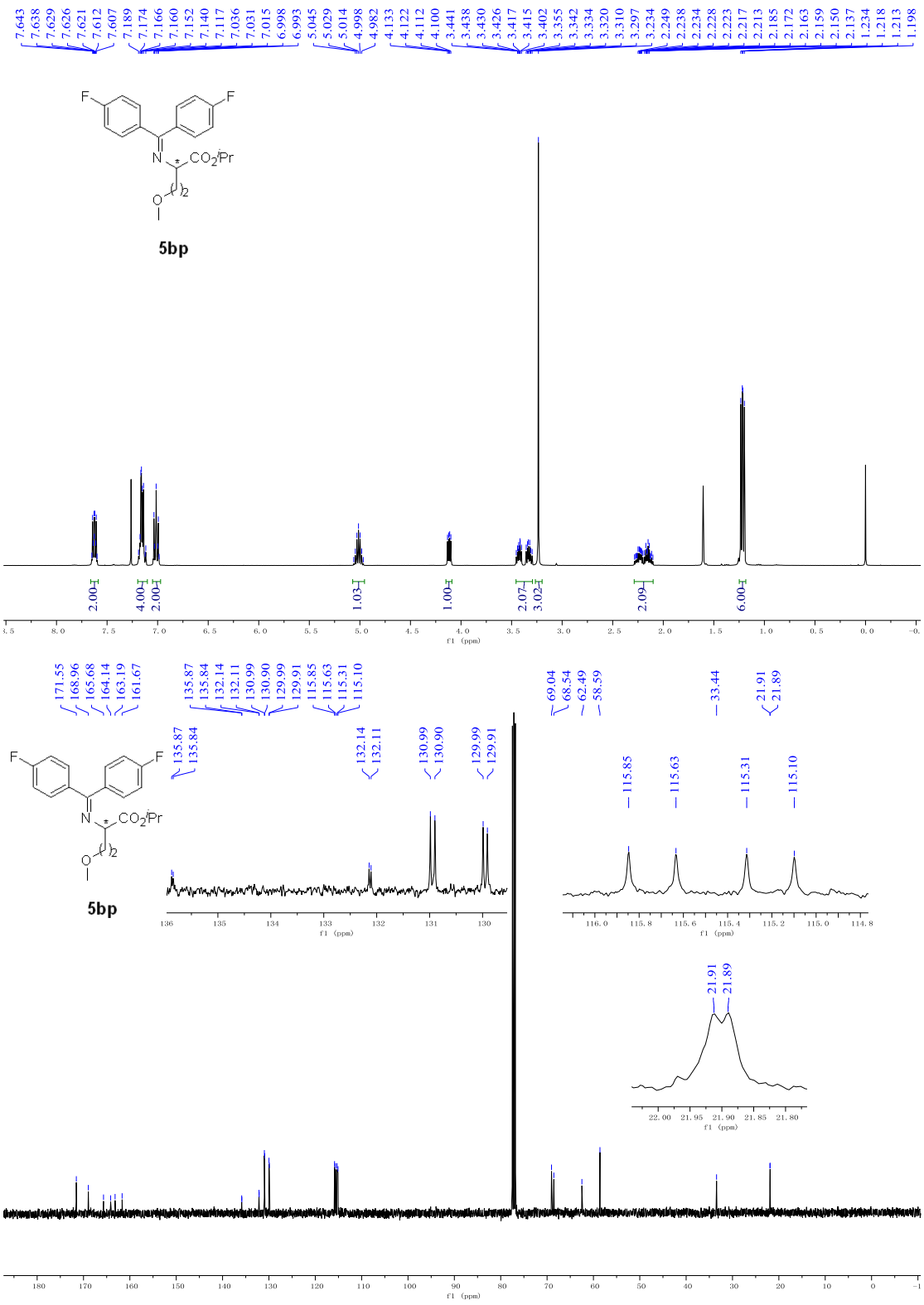
TBSO
3
5bo
f1 (ppm)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7.140
7.117
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7.015
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6.993
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5.029
5.014
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3.438
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3.402
3.355
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2.228
2.223
2.217
2.213
2.185
2.172
2.163
2.159
2.150
2.137
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1.218
1.213
1.198
F
F
N
CO2iPr
O
2
5bp
2.00
4.00
2.00
1.03
1.00
2.07
3.02
2.09
6.00
f1 (ppm)
171.55
168.96
165.68
164.14
163.19
161.67
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135.84
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115.10
69.04
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33.44
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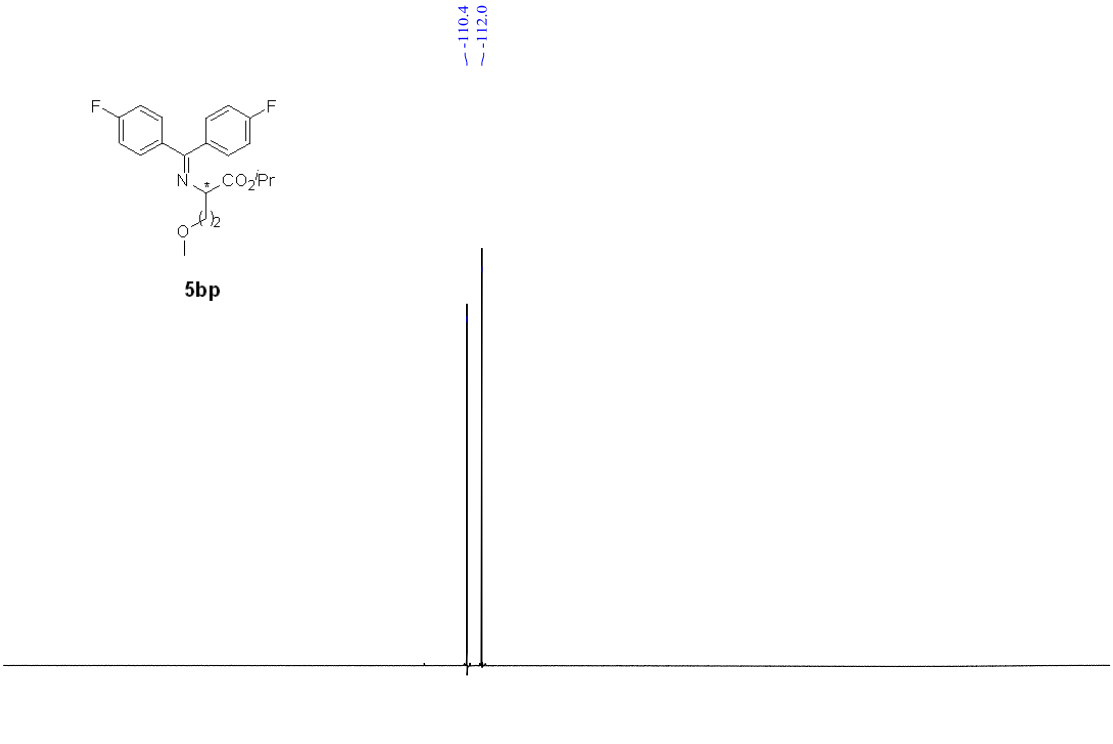
21.89
5bp
f1 (ppm)
f1 (ppm)
f1 (ppm)
f1 (ppm)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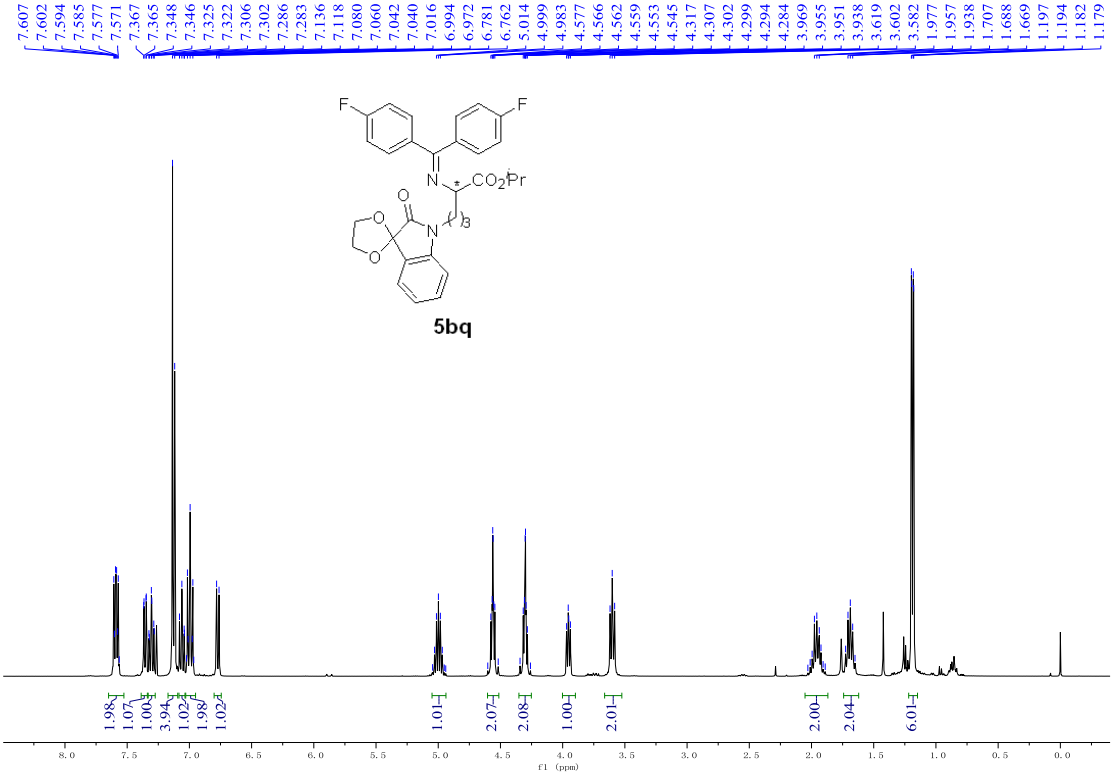
F
F
N
CO2iPr
O
2
5bp
f1 (ppm)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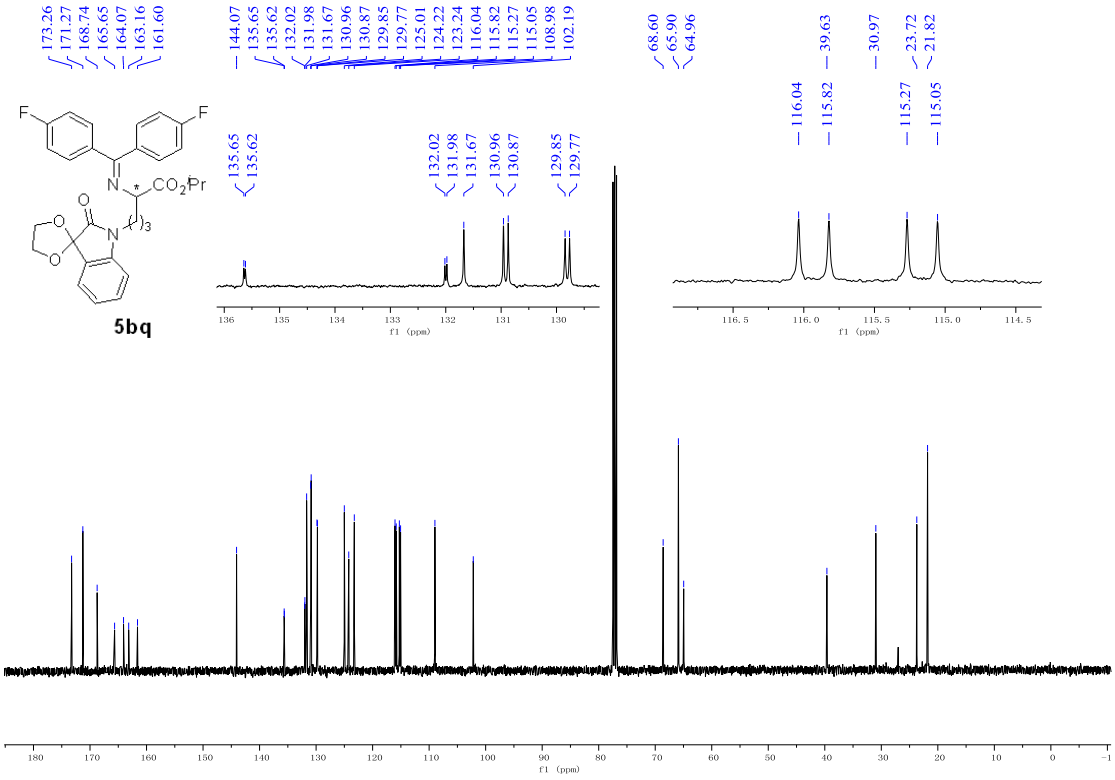
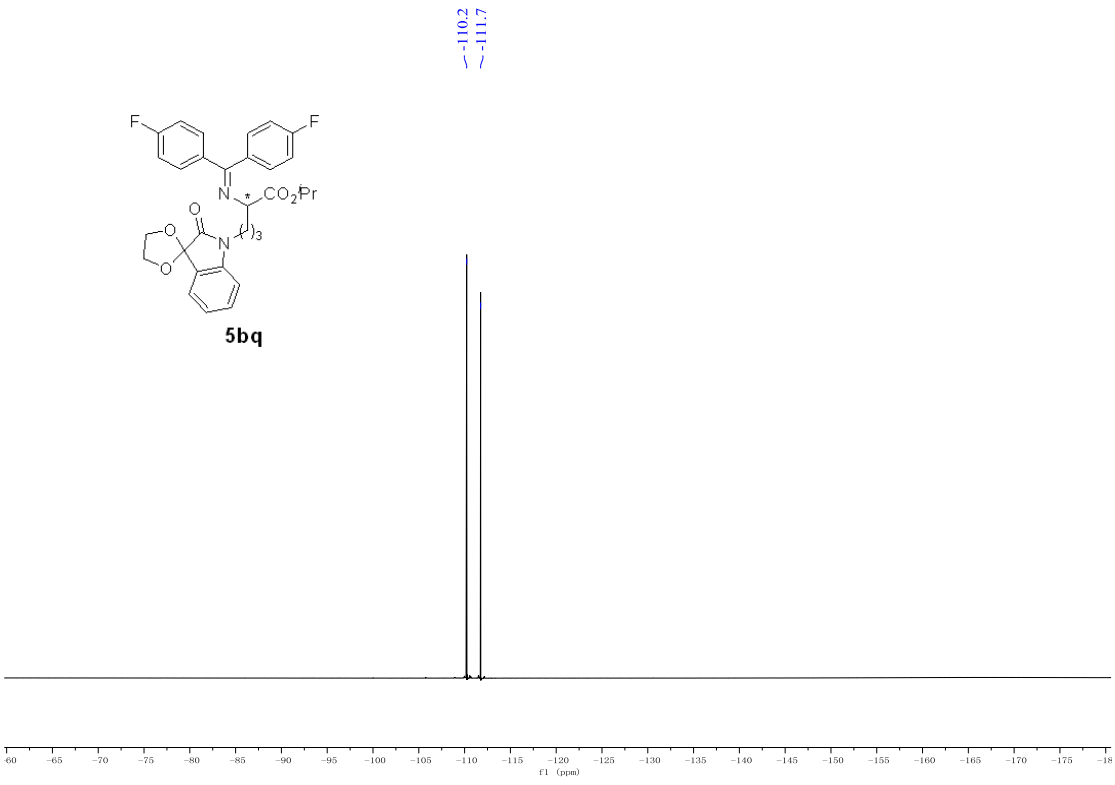
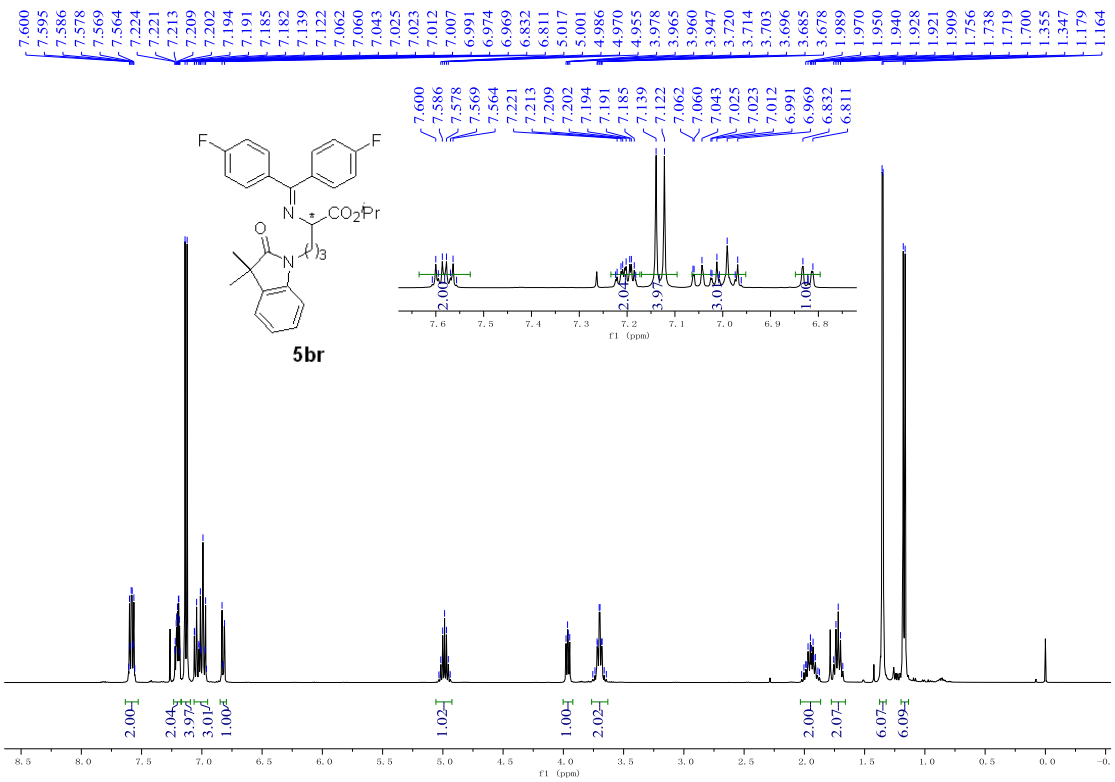
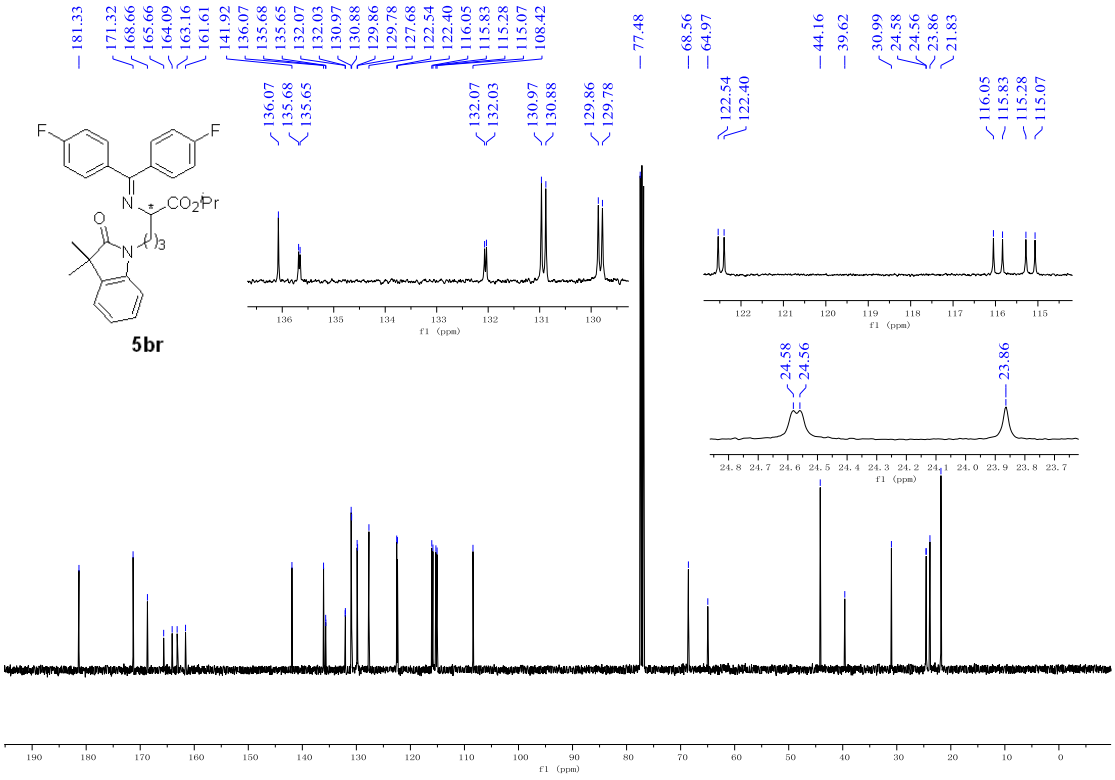
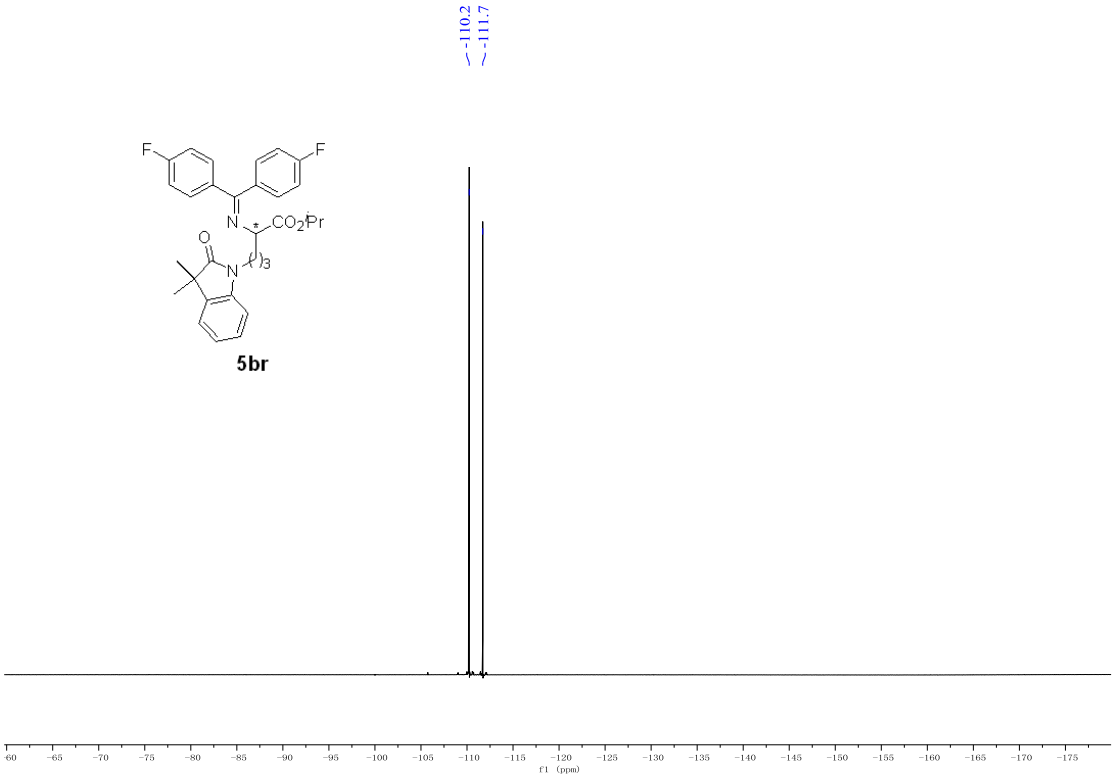
1.957
1.938
1.707
1.688
1.669
1.197
1.194
1.182
1.179
F
F
N
CO2iPr
O
O
O
N
3
5bq
1.98
1.07
1.00
3.94
1.02
1.98
1.02
1.01
2.07
2.08
1.00
2.01
2.00
2.04
6.01
f1 (ppm)

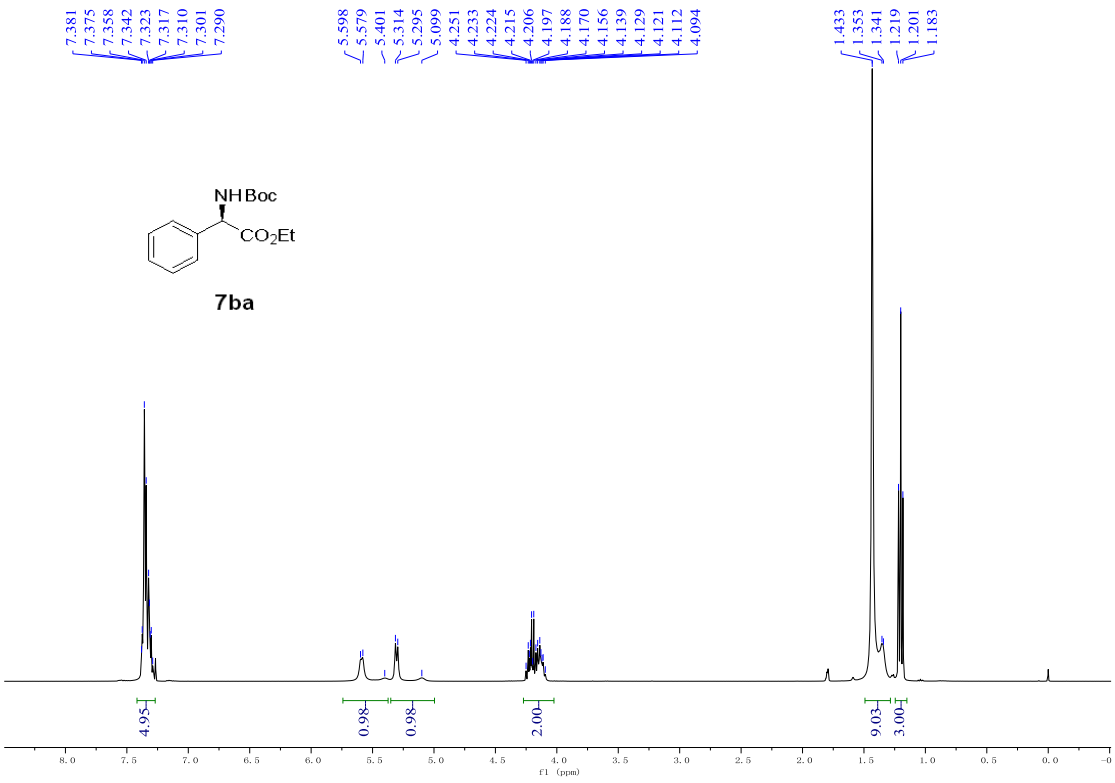

173.26
171.27
168.74
165.65
164.07
163.16
161.60
144.07
135.65
135.62
132.02
131.98
131.67
130.96
130.87
129.85
129.77
125.01
124.22
123.24
116.04
115.82
115.27
115.05
108.98
102.19
68.60
65.90
64.96
39.63
30.97
23.72
21.82
F
F
N
CO2iPr
O
O
O
N
3
5bq

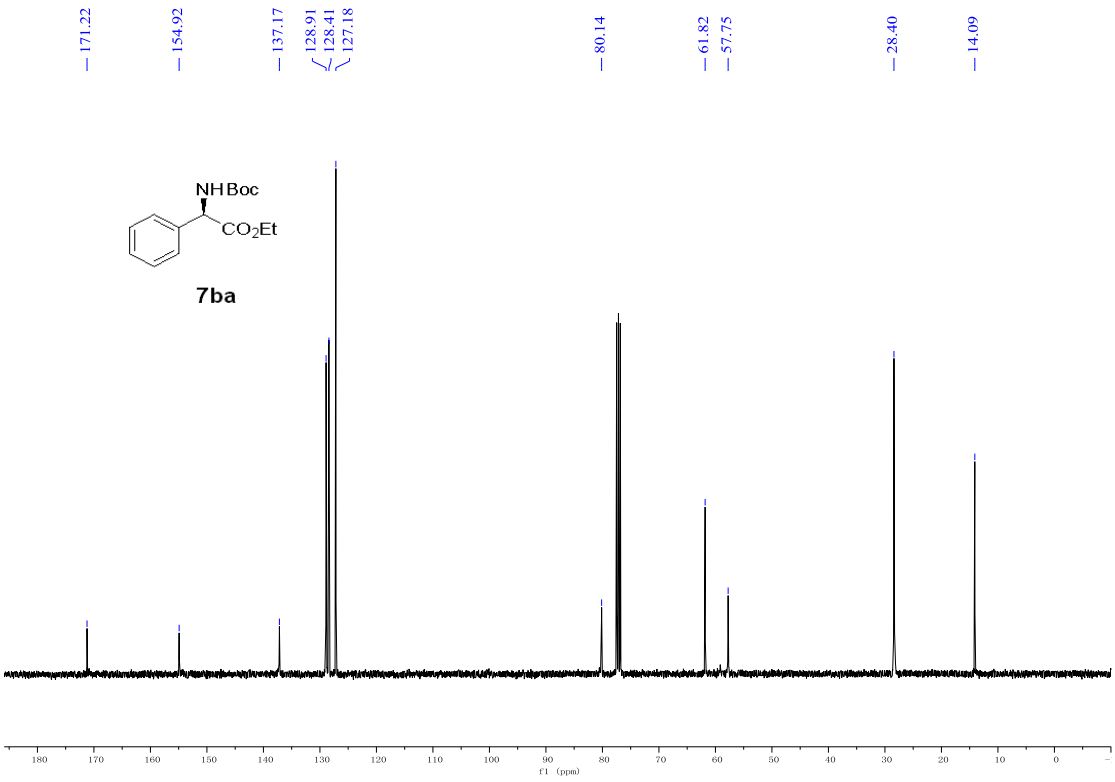

-110.2
-111.7
F
F
N
CO2iPr
O
O
O
N
3
5bq


5br

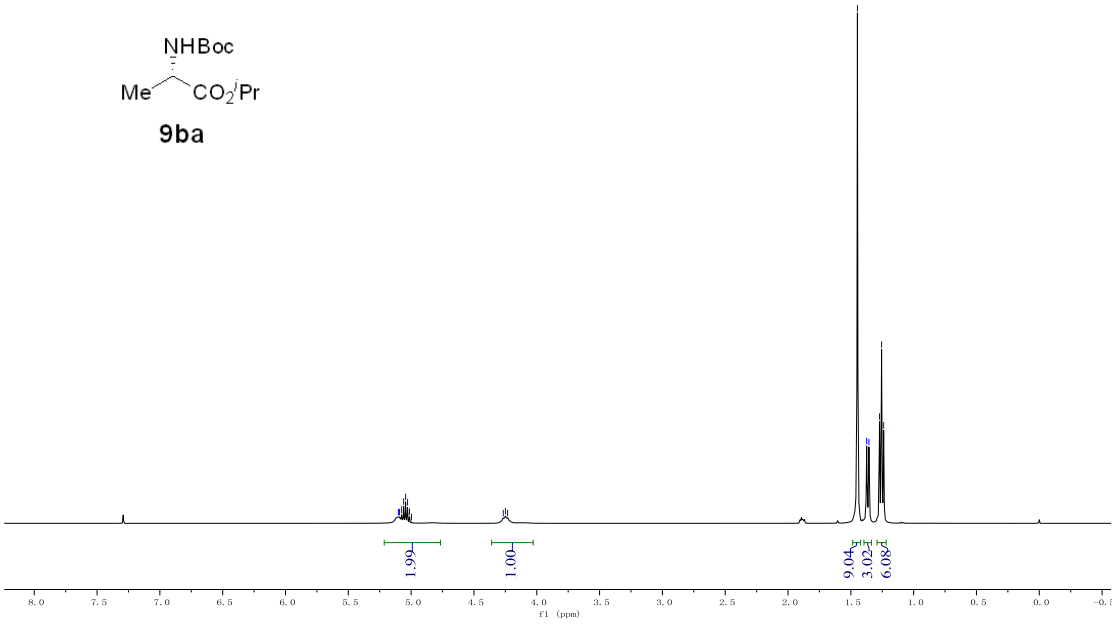

5br

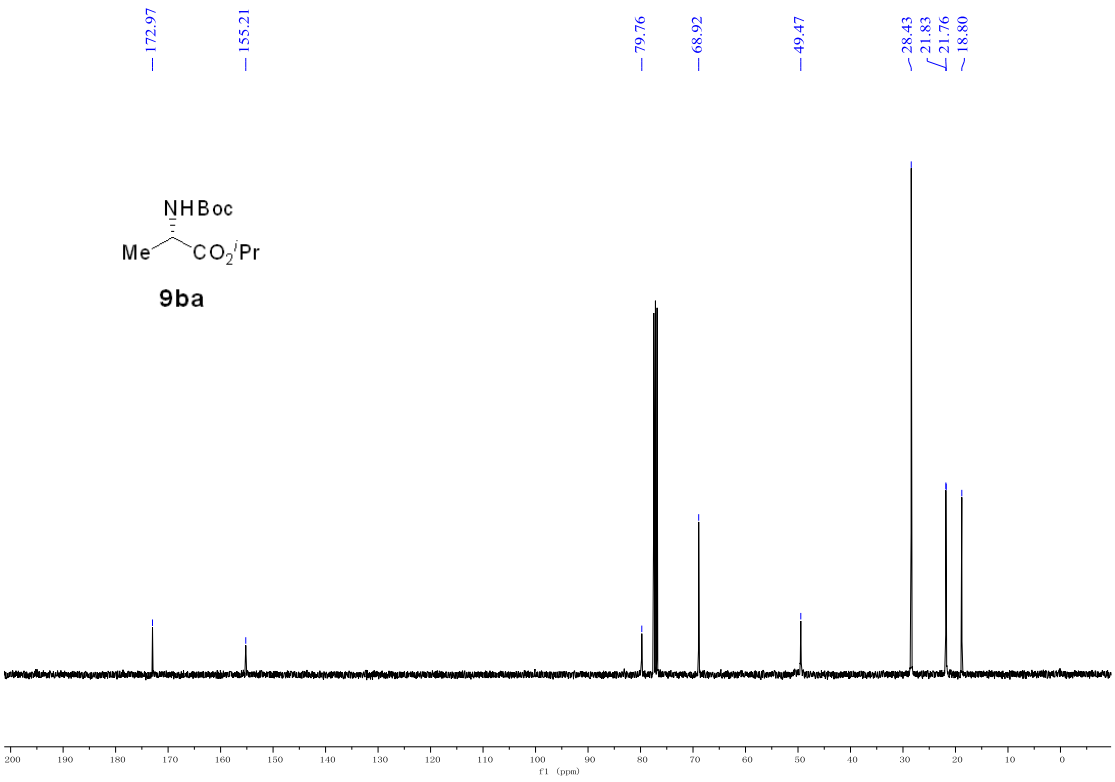

-110.2
-111.7
F
F
N
CO2iPr
O
N
3
5br
f1 (ppm)

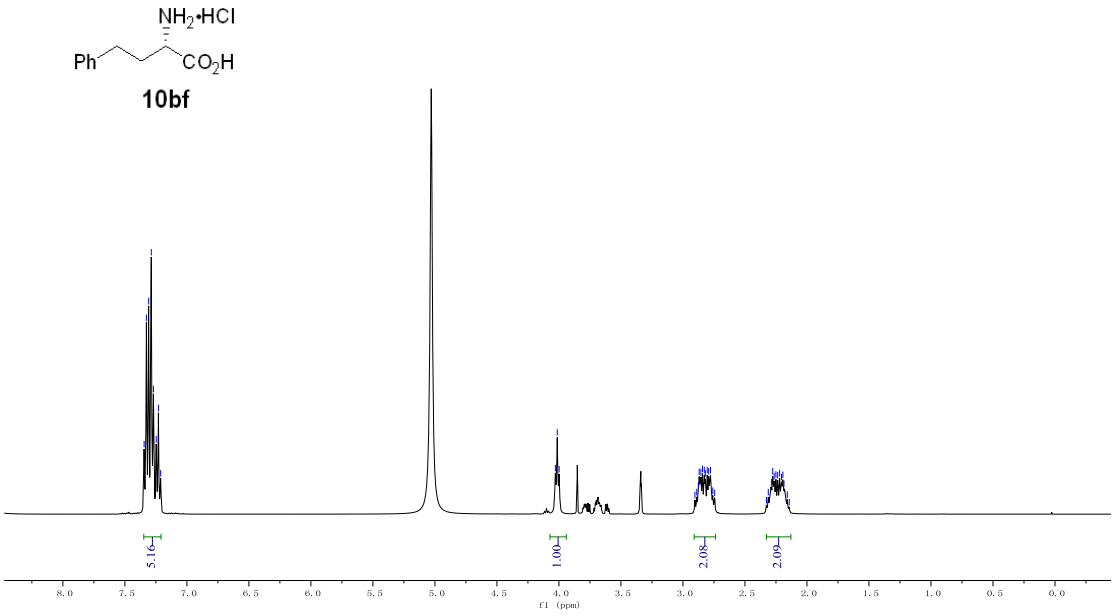

7.381
7.375
7.358
7.342
7.323
7.317
7.310
7.301
7.290
5.598
5.579
5.401
5.314
5.295
5.099
4.251
4.233
4.224
4.215
4.206
4.197
4.188
4.170
4.156
4.139
4.129
4.121
4.112
4.094
1.433
1.353
1.341
1.219
1.201
1.183
NHBoc
CO2Et
7ba
4.95
0.98
0.98
2.00
9.03
3.00
f1 (ppm)

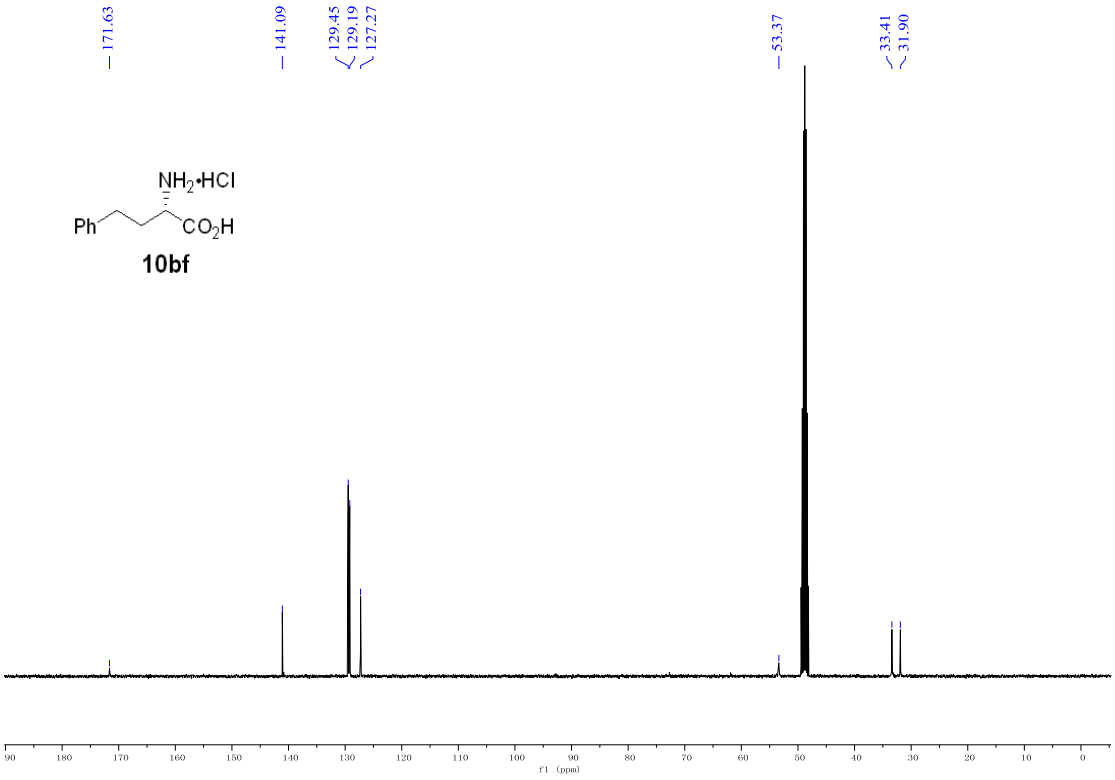

171.22
154.92
137.17
128.91
128.41
127.18
80.14
61.82
57.75
28.40
14.09
NHBoc
CO2Et
7ba
f1 (ppm)

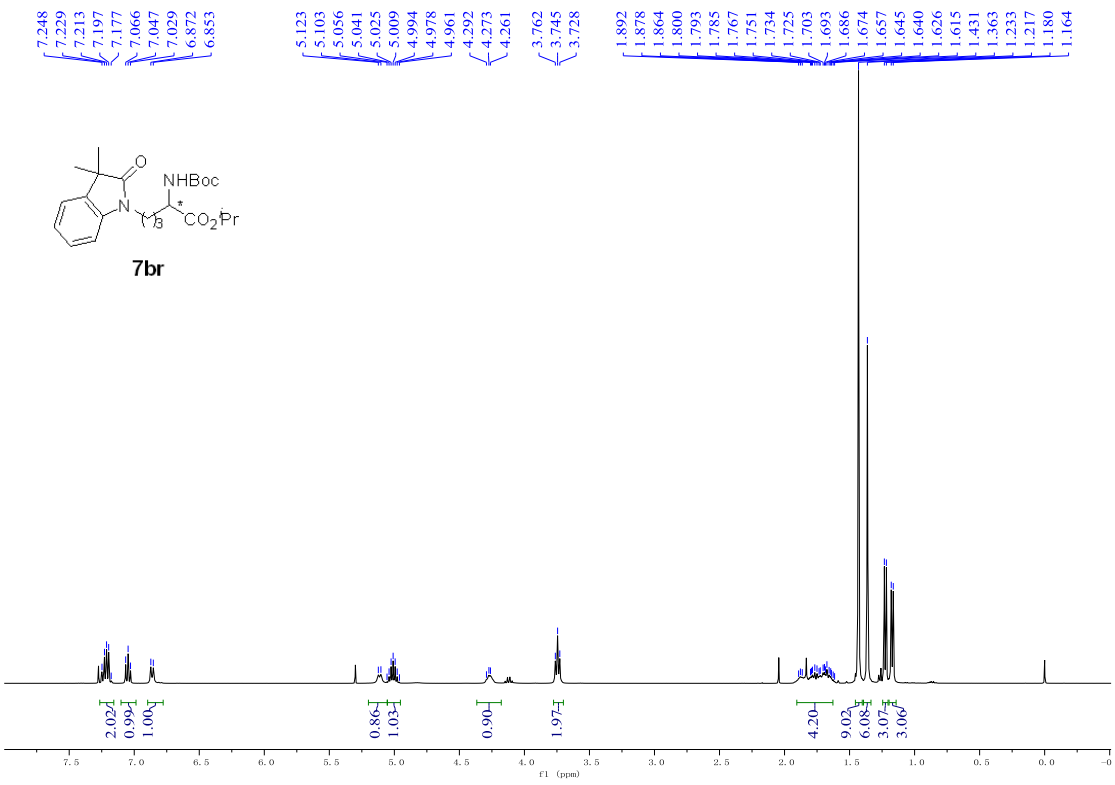

5.102
5.092
5.075
5.060
5.044
5.028
5.013
4.997
4.266
4.249
4.232
1.448
1.374
1.356
1.272
1.255
1.239

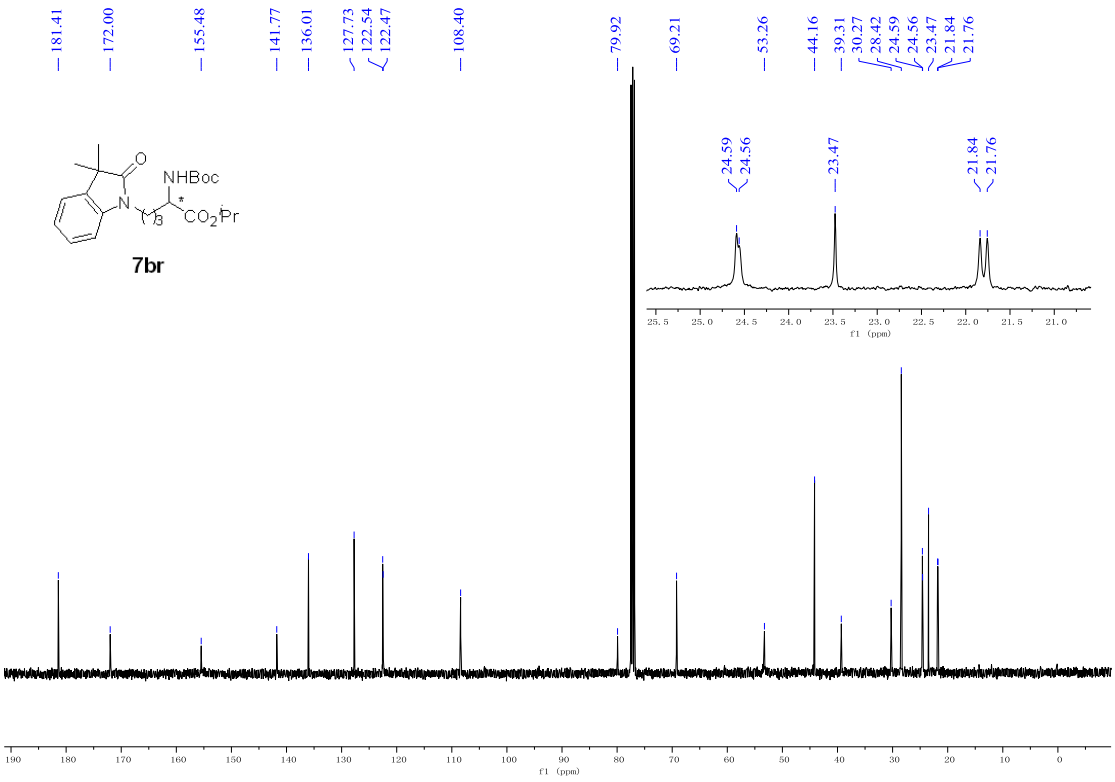

NHBoc
Me
CO2iPr
9ba
1.99
1.00
9.04
3.02
6.08
f1 (ppm)


172.97
155.21
79.76
68.92
49.47
28.43
21.83
21.76
18.80
NHBoc
Me
CO2iPr
9ba
f1 (ppm)
7.345
7.327
7.308
7.287
7.270
7.247
7.229
7.212
4.029
4.014
3.998
2.903
2.889
2.876
2.869
2.855
2.843
2.828
2.820
2.804
2.793
2.778
2.759
2.744
2.327
2.312
2.287
2.276
2.265
2.250
2.236
2.221
2.205
2.194
2.185
2.159
2.143


NH2•HCl
Ph
CO2H
10bf
5.16
1.00
2.08
2.09
f1 (ppm)


171.63
141.09
129.45
129.19
127.27
53.37
33.41
31.90
NH2•HCl
Ph
CO2H
10bf


7.248
7.229
7.213
7.197
7.177
7.066
7.047
7.029
6.872
6.853
5.123
5.103
5.056
5.041
5.025
5.009
4.994
4.978
4.961
4.292
4.273
4.261
3.762
3.745
3.728
1.892
1.878
1.864
1.800
1.793
1.785
1.767
1.751
1.734
1.725
1.703
1.693
1.686
1.674
1.657
1.645
1.640
1.626
1.615
1.431
1.363
1.233
1.217
1.180
1.164
O
NHBoc
N
CO2iPr
7br
2.02
0.99
1.00
0.86
1.03
0.90
1.97
4.20
9.02
6.08
3.07
3.06


181.41
172.00
155.48
141.77
136.01
127.73
122.54
122.47
108.40
79.92
69.21
53.26
44.16
39.31
30.27
28.42
24.59
24.56
23.47
21.84
21.76
NHBoc
CO2iPr
7br
f1 (ppm)

12. References

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