Supporting Information

Sai Ruan, Xia Zhong, Quangang Chen, Xiaoming Feng, and Xiaohua Liu*

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

E-mail: liuxh@scu.edu.cn

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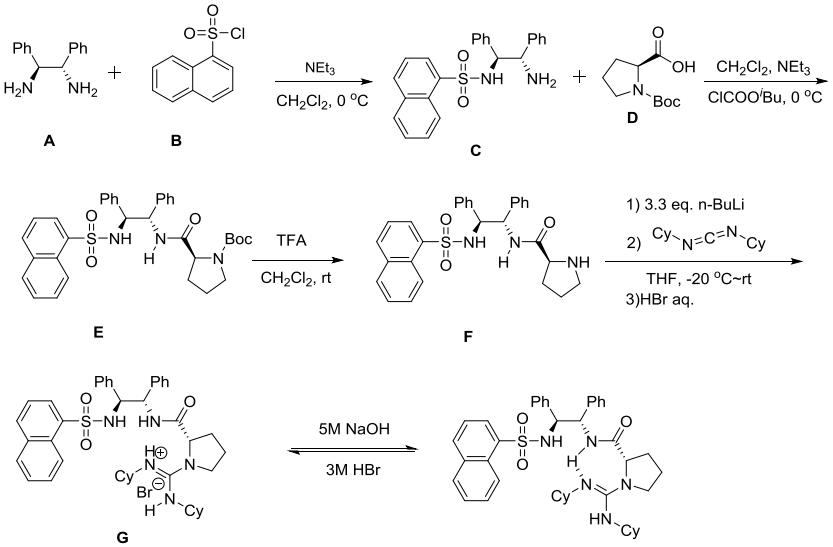
1. General information

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26), and spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}CNMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Enantiomeric excesses (*ee*) were determined by HPLC or UPC^2 analysis using the corresponding commercial chiralpak column as stated in the experimental procedures at 35 ℃. Optical rotations were reported as follows: $[\alpha]_D^{18}$ (*c*: g/100 mL, in solvent). HRMS was recorded on a commercial apparatus (ESI Source). All catalytic reactions were run in dried glassware. THF, toluene and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl. Ethyl acetate, CH_2Cl_2 was distilled over CaH_2.

2. Typical procedure for guanidines preparation



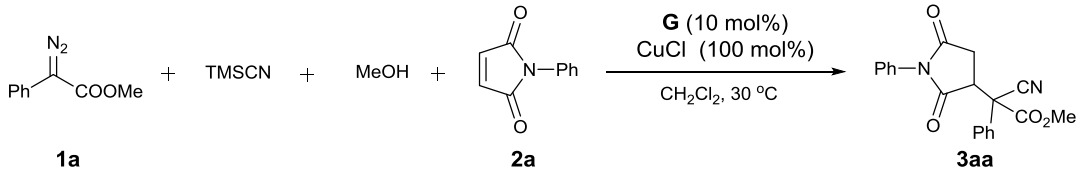
A solution of sulfonyl chloride **B** (10 mmol) was slowly added to a stirred solution of diamine **A** (10 mmol), NEt_3 (11 mmol) in dichloromethane (25 mL). The resulting mixture was stirred for another 2 hours, washed twice with water (25 mL) and dried over Na_2SO_4. The solvent was removed *in vacuo* to give a white solid **C**. To a solution of *N*-Boc protected *L*-Proline **D** in CH_2Cl_2 (40 mL) was added NEt_3 (11 mmol), isobutyl carbonochloridate (11 mmol) at 0 ℃ under stirring. After 10 min, **C** was added. The reaction was allowed to warm to room temperature for another 2 hours. The mixture was washed with 1 N $KHSO_4$ solution, saturated $NaHCO_3$ solution, and brine, dried over anhydrous Na_2SO_4 and concentrated to get a white solid **E**. Then, TFA (10 mL) was added to the CH_2Cl_2 (10 mL) solution of **E**, and stirred until the reaction finished (1-2 h). The pH value of the mixture was brought into the range of 10–12 by the addition of 2 N NaOH solution. 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 concentrated and purified through flash chromatograph as a white solid **F** (40% yield).

*n*BuLi (2.4 M in *n*-hexane, 3.3 eq., 13.2 mmol) was injected into a solution of **F** (4.0 mmol) in THF (30 mL) dropwise over 10 min under nitrogen atmosphere at −20 ℃ with well stirring. After additional 10 min, a solution of *N*,*N*-dicyclohexylcarbodiimide (1.2 eq., 4.8 mmol) in 10 mL of THF was added

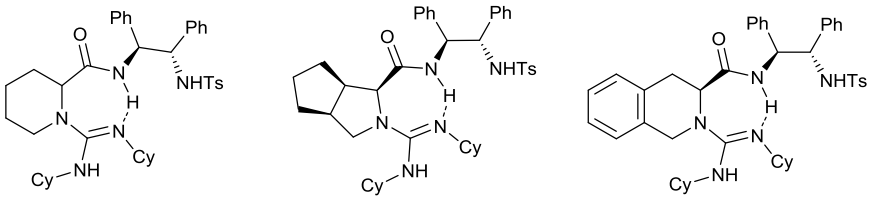
dropwise within 10 min. The reaction was allowed to warm to room temperature and detected by TLC. After 16 h, the mixture was evaporated under reduced pressure to get rid of THF, and the pH value of the mixture was brought into the range of 0–1 by the addition of 3 M HBr. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL), washed with water, dried over anhydrous Na_2SO_4 and evaporated in vacuum, and purified through flash chromatograph on silica gel to produce guanidinium salt **G**. The purified guanidinium salt **G** (46% yield) can be given through recrystallization in $CHCl_3$ and n-Hexane. Then, guanidinium salt **G** in CH_2Cl_2 (20 mL) was added 5 M NaOH (20 mL) and stirred until the basification finished (10 mins). The pH value of the mixture was kept in the range of 11–12. The aqueous phase was extracted with CH_2Cl_2 (5 × 20 mL). The combined organic phase was washed with 5 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. For other catalysts, the synthesis method could be found in the literature.[1]

3. Optimization of the reaction conditions

Table 1: Screening of guanidines[a]

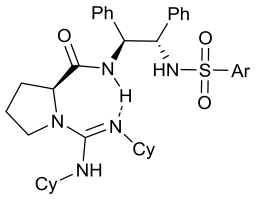


1a **2a** **3aa**

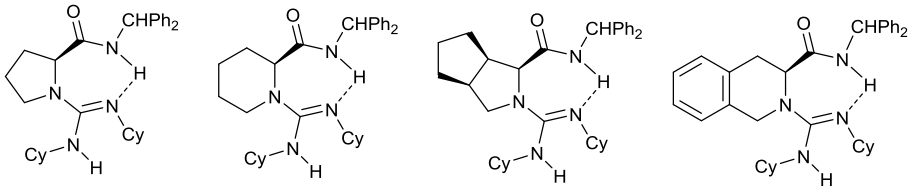


G-1 **G-2** **G-3**

(Cy = Cyclohexyl)



G-4: Ar = 4-MeC_6H_4
G-5: Ar = 1-naphthyl
G-6: Ar = C_6H_5
G-7: Ar = 4-$MeOC_6H_4$
G-8: Ar = 4-*i*PrC_6H_4
G-9: Ar = 2,4,6-trimethylC_6H_2
G-10: Ar = 2,4,6-triisopropylC_6H_2

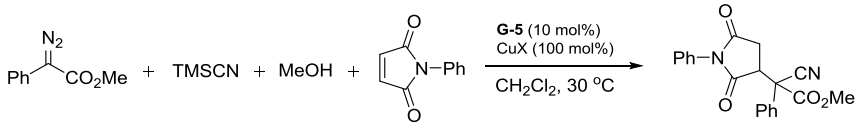


G-11 **G-12** **G-13** **G-14**

entry	cat	yield (%)[b]	dr[c]	ee (%)[c]
1	**G-1**	21	94:6	8/5
2	**G-2**	18	>19:1	31
3	**G-3**	13	84:16	5/11
4	**G-4**	40	88:12	49/33
5	**G-5**	46	88:12	67/43
6	**G-6**	51	88:12	50/22
7	**G-7**	39	91:9	48/17
8	**G-8**	42	86:14	53/30
9	**G-9**	55	88:12	52/27
10	**G-10**	49	88:12	45/17
11	**G-11**	26	90:10	5/5
12	**G-12**	15	91::9	9/5
13	**G-13**	29	83:17	0/0
14	**G-14**	19	87:13	13/5

[a] Unless otherwise noted, all reactions were carried out with guanidine (10 mol%), CuCl(100 mol%), **1a** (0.10 mmol), TMSCN (0.10 mmol) and MeOH (0.10 mmol) in CH_2Cl_2 (0.5 mL) at 30 ℃ for 2 h, then **2a** (0.10 mmol) was added at 30 ℃ and reacted at 30 ℃ for 12 h. [b] Isolated yield. [c] Determined by HPLC analysis.

Table 2: Screening of the copper salt[a]

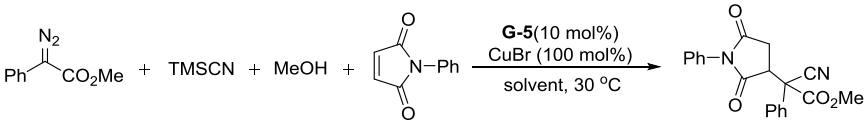


1a **2a** **3aa**

entry	CuX	yield (%)[b]	dr[c]	ee (%)[c]
1	CuCl	46	88:12	67/43
2	CuBr	60	88:12	73/47
3	CuI	5	80:20	0/0
4	CuBr•SMe_2	trace	nd	nd
5	$Cu(MeCN)_4PF_6$	trace	nd	nd
6	$Cu(MeCN)_4BF_4$	trace	nd	nd

[a] Unless otherwise noted, all reactions were carried out with **G-5** (10 mol%), copper salts (100 mol%), **1a** (0.10 mmol), TMSCN (0.10 mmol) and MeOH (0.10 mmol) in CH_2Cl_2 (0.5 mL) at 30 ℃ for 2 h, then **2a** (0.10 mmol) was added at 30 ℃ and reacted at 30 ℃ for 12 h. [b] Isolated yield. [c] Determined by HPLC analysis. nd: not detected.

Table 3: Screening of the solvents[a]



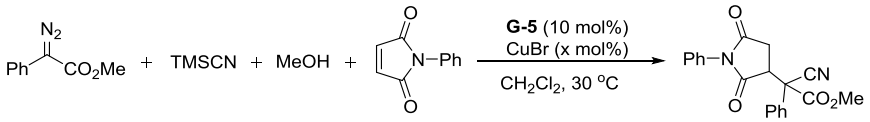
1a **2a** **3aa**

entry	solvent	yield (%)[b]	dr[c]	ee (%)[c]
1	Toluene	trace	nd	nd
2	THF	trace	nd	nd

3	CH_2Cl_2	60	88:12	73/47
3	$CHCl_3$	43	86:14	65/43
4	AcOEt	nr	nd	nd
5	CH_3CN	nr	nd	nd
6	Et_2O	trace	nd	nd

[a] Unless otherwise noted, all reactions were carried out with **G-5** (10 mol%), CuBr (100 mol%), **1a** (0.10 mmol), TMSCN (0.10 mmol) and MeOH (0.10 mmol) in solvent (0.5 mL) at 30 ℃ for 2 h, then **2a** (0.10 mmol) was added at 30 ℃ and reacted at 30 ℃ for 12 h. [b] Isolated yield. [c] Determined by HPLC analysis. nd: not detected, nr: no reaction.

Table 4: Screening the amount of copper salt and additives [a]

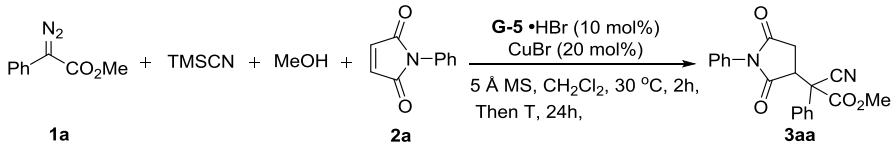


1a **2a** **3aa**

entry	CuBr [x mol%]	Additive [mg]	yield (%)[b]	dr[c]	ee (%)[c]
1	100	-	60	88:12	73/47
2[d]	50	-	65	89:11	73/49
3[e]	50	-	71	88:12	74/49
4[e]	40	-	66	88:12	74/49
5[e]	30	-	trace	nd	nd
6[e]	30	5 Å MS (20)	83	89:11	73/49
7[e]	20	5 Å MS (20)	85	88:12	74/47
8[e]	20	4 Å MS (20)	trace	nd	nd
9[e]	20	3 Å MS (20)	trace	nd	nd
10[e]	15	5 Å MS (20)	trace	nd	nd
11[e]	10	5 Å MS (20)	trace	nd	nd
12[f]	15	5 Å MS (20)+YB_3 (1.7)	trace	nd	nd
13[g]	15	5 Å MS (20)+HBr (5 mol%)	trace	nd	nd

[a] Unless otherwise noted, all reactions were carried out with **G-5** (10 mol%), CuBr (x mol%), **1a** (0.10 mmol), TMSCN (0.10 mmol) and MeOH (0.10 mmol) in CH_2Cl_2 (0.5 mL) at 30 ℃ for 2 h, then **2a** (0.10 mmol) was added at 30 ℃ for 12 h. [b] Isolated yield. [c] Determined by HPLC analysis. [d] **G-5**·HCl (10 mol%). [e] **G-5**·HBr (10 mol%).[f] YB_3 (5 mol%: 1.7 mg). [g] HBr (5 mol%: 1.0 M, 5.0 uL).

Table 5: Screening of the temperature[a]

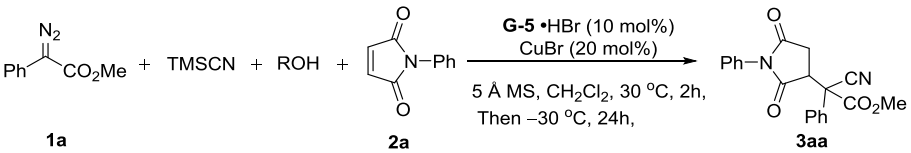


1a 2a 3aa

entry	T (℃)	yield (%)[b]	dr[c]	ee (%)[c]
1	0	67	95:5	87
2	–10	62	96:4	90
3	–20	61	96:4	92
4	–30	65	96:4	95
5	–40	62	96:4	96

[a] Unless otherwise noted, all reactions were carried out with **G-5**·HBr (10 mol%), CuBr (20 mol%), 5 Å MS (20 mg), **1a** (0.10 mmol), TMSCN (0.10 mmol) and MeOH (0.10 mmol) in CH_2Cl_2 (0.5 mL) at 30 ℃ for 2 h, then **2a** (0.10 mmol) was added at the corresponding temperature and reacted for 24 h. [b] Isolated yield. [c] Determined by HPLC analysis.

Table 6: Screening of the alcohols[a]

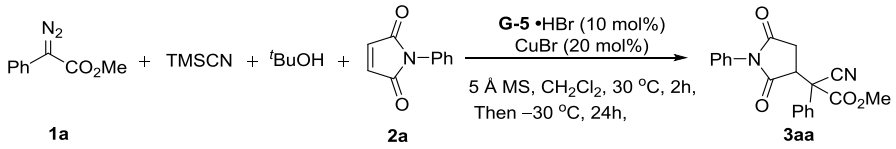


1a 2a 3aa

entry	ROH	yield (%)[b]	dr[c]	ee (%)[c]
1	MeOH	65	96:4	95
2	^{i}PrOH	60	96:4	95
3	^{t}BuOH	80	96:4	95
4	CF_3CH_2OH	trace	nd	nd
5	H_2O	60	95:5	95
6	HFIP	trace	nd	nd
7	Benzoic Acid	nr	—	—
8	Phenol	nr	—	—
9	—	nr	—	—

[a] Unless otherwise noted, all reactions were carried out with **G-5**·HBr (10 mol%), CuBr (20 mol%), 5 Å MS (20 mg)，**1a** (0.10 mmol), TMSCN (0.10 mmol) and alcohol (0.10 mmol) in CH_2Cl_2 (0.5 mL) at 30 ℃ for 2 h, then **2a** (0.10 mmol) was added at –30 ℃ and reacted at –30 ℃ for 24 h. [b] Isolated yield. [c] Determined by HPLC analysis. HFIP: Hexafluoroisopropanol.

Table 7: Screening of the substrate ratio[a]

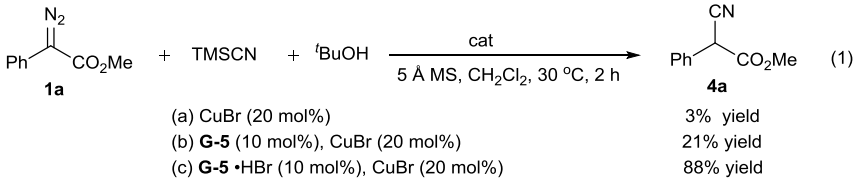


1a 2a 3aa

entry	**1a**:TMSCN:^{t}BuOH:**2a**	yield (%)[b]	dr[c]	ee (%)[c]
1	1:1:1:1	80	96:4	95
2	1.2:1.2:1.2:1	86	96:4	95
3	1.4:1.4:1.4:1	87	96:4	95
4[d]	1.2:1.2:1.2:1	77	97:3	95

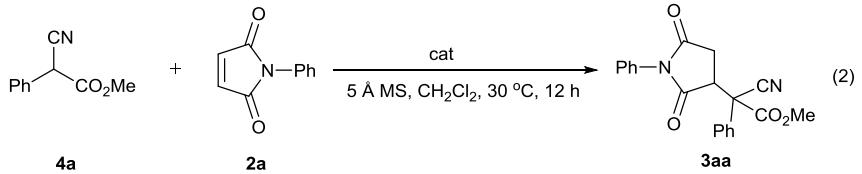
[a] Unless otherwise noted, all reactions were carried out with **G-5**·HBr (10 mol%), CuBr (20 mol%), 5 Å MS (20 mg), **1a**, TMSCN, and ^{t}BuOH in CH_2Cl_2 (0.5 mL) at 30 ℃ for 2 h, then **2a** (0.10 mmol) was added at –30 ℃ and reacted at –30 ℃ for 24 h. [b] Isolated yield. [c] Determined by HPLC analysis. [d] CH_2Cl_2 (1.0 mL).

Table 8: Control experiments A[a]



1a 4a

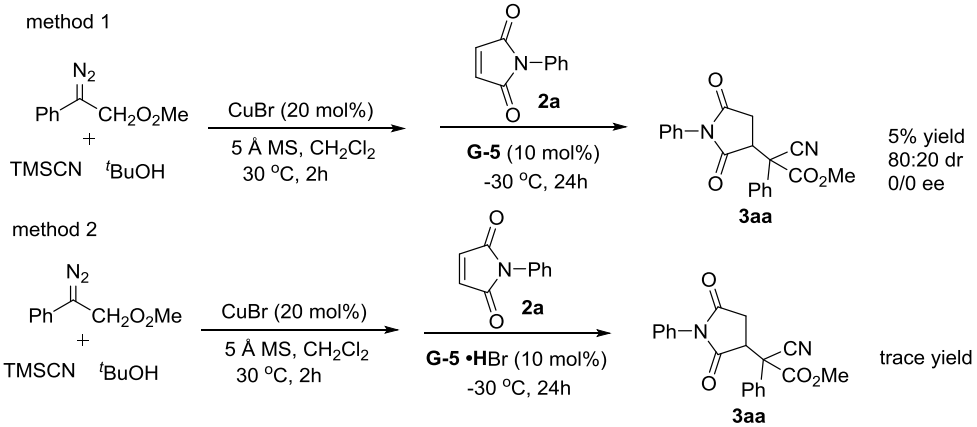
(a) CuBr (20 mol%) — 3% yield
(b) **G-5** (10 mol%), CuBr (20 mol%) — 21% yield
(c) **G-5** •HBr (10 mol%), CuBr (20 mol%) — 88% yield



4a 2a 3aa

(d) **G-5** •HBr (10 mol%), CuBr (20 mol%) — no reaction
(e) **G-5** •HBr (10 mol%) — trace, 9:1 dr, 0/0% ee
(f) **G-5** (10 mol%) — 76% yield, >19:1 dr, 91% ee
(g) **G-5** •HBr (10 mol%), CuBr (20 mol%), TMSCN/*t*BuOH (1.0 equiv) — 10% yield, 86:14 dr, 0/0% ee

Table 9: Control experiments B



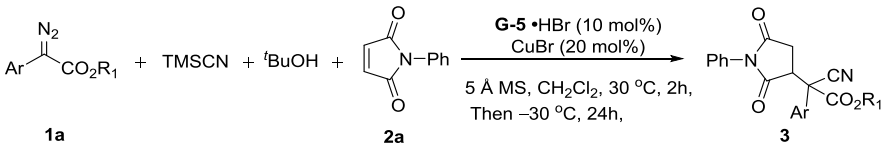
Method 1: CuBr (20 mol%) and 5 Å MS (20 mg) were added into the test tube, then under the protection of nitrogen, CH_2Cl_2 (0.5 mL) was added. Then the ^{t}BuOH (0.12 mmol), TMSCN (0.12

mmol) and α-diazoester **1a** (0.12 mmol) were added in sequence to the reaction which were stirred at 30 ℃ for 2 h. Subsequently, the reaction mixture was stirred at –30 °C for 5 min, *N*-phenyl maleimide **2a** (0.10 mmol) and catalyst **G-5** (10 mol%) dissolved in 0.2 mL of CH_2Cl_2 were added to the reaction. After the mixture was stirred at –30 ℃ for 24 h. Isolated yield. Ee and dr values were determined by UPC^2 analysis.

Method 2：The reactions were carried out with CuBr (20 mol%) and 5 Å MS (20 mg) were added into the test tube, then under the protection of nitrogen, CH_2Cl_2 (0.5 mL) was added. Then the ^{t}BuOH (0.12 mmol), TMSCN (0.12 mmol) and α-diazoester **1a** (0.12 mmol) were added in sequence to the reaction which were stirred at 30 ℃ for 2 h. Subsequently, the reaction mixture was stirred at –30 °C for 5 min, *N*-phenyl maleimide **2a** (0.10 mmol) and catalyst **G-5**·HBr (10 mol%) dissolved in 0.2 mL of CH_2Cl_2 were added to the reaction. After the mixture was stirred at –30 ℃ for 24 h. Isolated yield. Ee and dr values were determined by UPC^2 analysis.

4. Substrate scope

Table 9: Substrate scope of α-aryl diazoacetates **1**[a]

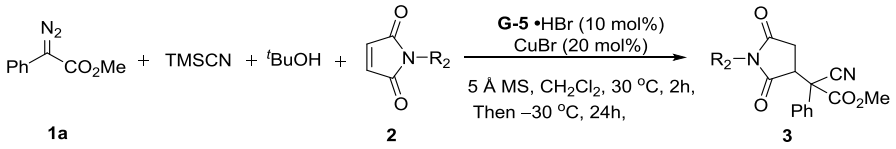


1a **2a** **3**

entry	**1**: Ar	R_1	Additives	Yield (%)[b]	dr[c]	ee (%)[c]
1	**1a**: Ph	Me	5 Å MS (20 mg)	86 (**3aa**)	13:1	95
2	**1b**: Ph	Et	5 Å MS (20 mg)	81 (**3ba**)	13:1	96
3	**1c**: Ph	^{i}Pr	5 Å MS (20 mg)	68 (**3ca**)	13:1	96
4	**1d**: Ph	^{t}Bu	5 Å MS (20 mg)	trace (**3da**)	nd	nd
5	**1e**: 2-FC_6H_4	Me	DABCO (50 mol%)	75 (**3ea**)	2:1	85/70
6[a]	**1f**: 3-MeC_6H_4	Me	DABCO (30 mol%)	87 (**3fa**)	13:1	89
7	**1g**: 4-MeC_6H_4	Me	5 Å MS (20 mg)	71 (**3ga**)	13:1	95
8	**1h**: 4-$MeOC_6H_4$	Me	DABCO (30 mol%)	68 (**3ha**)	13:1	93
9	**1i**: 4-FC_6H_4	Me	5 Å MS (20 mg)	80 (**3ia**)	>19:1	93
10[e]	**1j**: 4-ClC_6H_4	Me	DABCO (30 mol%)	74(90)[f] (**3ja**)	>19:1	78(91)[f]
11[e]	**1k**: 4-BrC_6H_4	Me	DABCO (30 mol%)	69(74)[f] (**3ka**)	>19:1	72(92)[f]
12[e]	**1l**: 4-IC_6H_4	Me	DABCO (30 mol%)	59(70)[f] (**3la**)	>19:1	70(88)[f]
13[g]	**1m**: 2-naphthyl	Me	DABCO (30 mol%)	99 (**3ma**)	15:1	92

[a] unless otherwise noted, all reactions were carried out with **G-5 HBr** (10 mol%), CuBr (20 mol%), 5 Å MS, **1** (1.2 equiv), TMSCN (1.2 equiv) and ^{t}BuOH (1.2 equiv) in CH_2Cl_2 (0.5 mL) at 30 ℃ for 2 h, then **2a** (0.10 mmol) and DABCO were added at –30 ℃ and reacted at –30 ℃ for 24 h. [b] Isolated yield. [c] Determined by UPC[2] and NMR analysis. [d] CuBr•SMe_2 (20 mol%). [e] **1a**/TMSCN/^{t}BuOH/**2a** (1.4/1.4/1.4/1), CuBr (40 mol%); [f] Date in parentheses was used CuBr (100 mol%), and DABCO (0.5 equiv). [g] CuBr (50 mol%), and at –30 ℃ for 12 h.

Table 10: Substrate scope of *N*-substituted maleimides **2**[a]

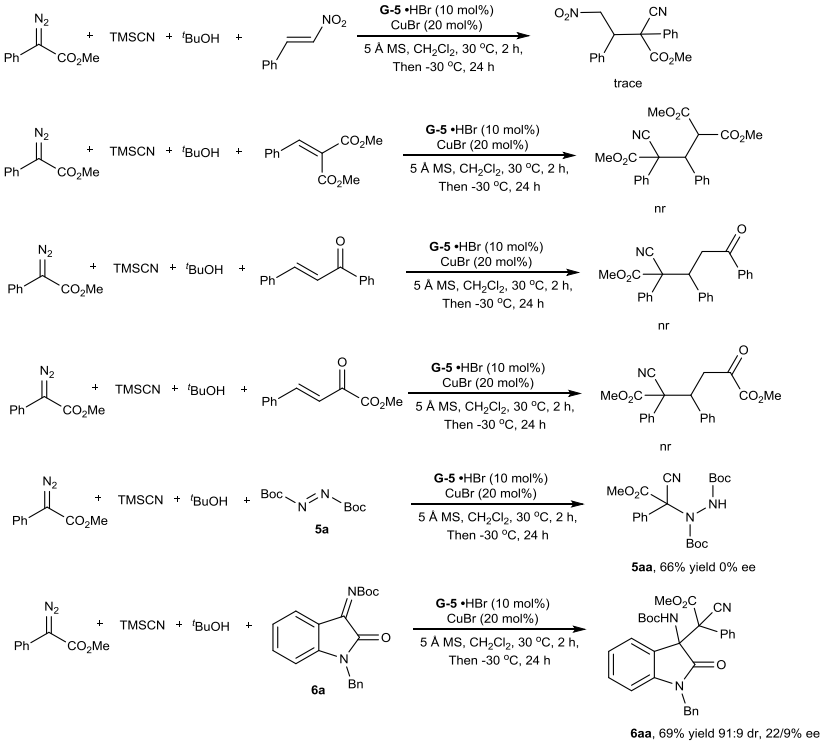


1a **2** **3**

entry	**2**: R_2	yield (%)[b]	dr[c]	ee (%)[c]
1	4-MeC_6H_4	62 (**3ab**)	>19:1	92
2	4-$MeOC_6H_4$	70 (**3ac**)	16:1	92
3	4-EtC_6H_4	73 (**3ad**)	>19:1	93
4	4-$EtOC_6H_4$	65 (**3ae**)	>19:1	93
5	4-*i*PrC_6H_4	72 (**3af**)	>19:1	92
6	4-FC_6H_4	78 (**3ag**)	19:1	92
7	4-ClC_6H_4	68 (**3ah**)	16:1	93
8	4-BrC_6H_4	65 (**3ai**)	16:1	93
9	4-IC_6H_4	78 (**3aj**)	16:1	93
10	2-FC_6H_4	73 (**3ak**)	11:1	93
11	2-MeC_6H_4	85 (**3al**)	60:40	92
12	3-FC_6H_4	65 (**3am**)	16:1	91
13	Bn	36 (**3an**)	7:1	72
14	Me	54 (**3ao**)	5:1	50
15	H	nr (**3ap**)	—	—

[a] Unless otherwise noted, the reactions were carried out **G-5**·HBr (10 mol%), 5 Å MS (20 mg), **1a** (0.12 mmol), TMSCN (0.12 mmol) and ^{t}BuOH (0.12 mmol) in CH_2Cl_2 (0.5 mL) at 30 ℃ for 2 h, then **2** (0.10 mmol) was added at –30 ℃ and reacted at –30 ℃ for 24 h. [b] Isolated yield. [c] Determined by UPC[2] and NMR analysis .

5. Attempts of other Electrophiles

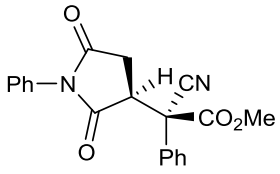


6. Typical procedure for the reaction

CuBr (2.9 mg, 20 mol%), catalyst **G-5**·HBr (7.8 mg, 10 mol%) and 5 Å MS (20 mg) were added into the test tube, then under the protection of nitrogen, CH_2Cl_2 (0.5 mL) was added. Then the ^tBuOH (0.12 mmol, 12.0 uL), TMSCN (0.12 mmol, 16.0 uL) and α-diazoester **1a** (0.12 mmol, 20.5 uL) were added in sequence to the reaction which were stirred at 30 ℃ for 2 h. Subsequently, the reaction mixture was stirred at –30 °C for 5 min, *N*-phenyl maleimide **2a** (0.10 mmol, 17.3 mg) and DABCO (0-50 mol%) dissolved in 0.2 mL of CH_2Cl_2 were added to the reaction. After the mixture was stirred at –30 ℃ for 24 h, it was purified by silica gel column chromatography (ethyl acetate/petroleum ether/CH_2Cl_2 1/4/1) to afford the desired product. Then the purified product was used for HPLC or UPC[2] analysis.

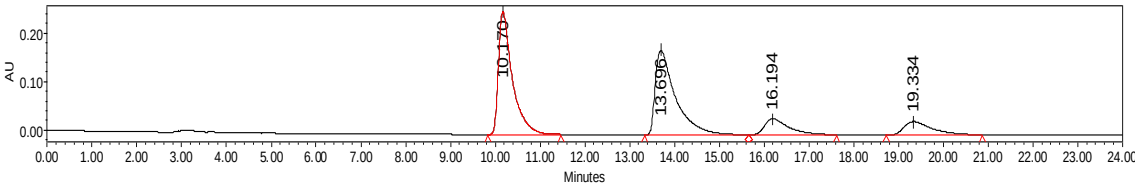
7. The analytical and spectral characterization data of the product

Methyl (*R*)-2-cyano-2-[(*S*)-2,5-dioxo-1-phenylpyrrolidin-3-yl]-2-phenylacetate (3aa)

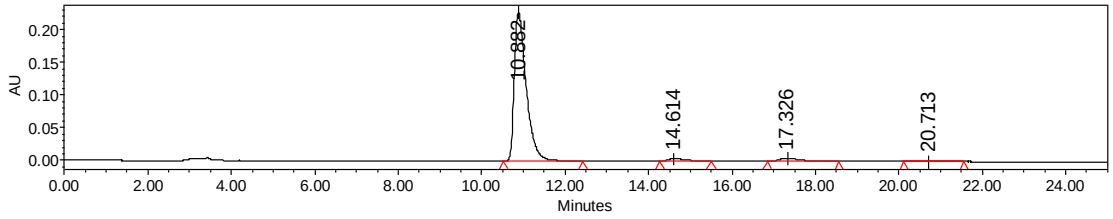


3aa

White solid, 85% yield, 13:1 dr, 95% ee, mp: 125-129 ℃. $[\alpha]_D^{23}$ = –54.5 (*c*: 0.54, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralcel IB, *n*-Hexane/^{i}PrOH = 70/30, 1.0 mL/min, λ = 230.0 nm, t (major$_{isomer}$) = 10.88 min, 14.61 min; t (minor$_{isomer}$) = 17.33, 20.71 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.59 (m, 2H), 7.53 – 7.38 (m, 6H), 7.35 – 7.28 (m, 2H), 4.41 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.88 (s, 3H), 2.82 (dd, *J* = 18.8, 9.6 Hz,1H), 2.55 (dd, *J* = 18.4, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 172.8, 166.6, 131.2, 131.1, 130.0, 129.8, 129.3, 129.1, 126.5, 115.8, 55.3, 54.7, 47.1, 31.6. HRMS (ESI-FT) caled for **$C_{20}H_{16}N_2O_4K^+$ (M+K)$^+$**, m/z: 387.0742, observed: 387.0737. IR: 1750, 1715, 1500, 1387, 1244, 1193, 695, 623 cm^{-1}.

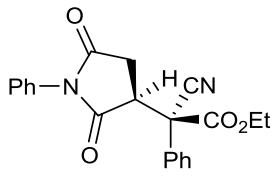


	Retention Time	Area	% Area
1	10.170	5462740	40.76
2	13.696	5469977	40.81
3	16.194	1242043	9.27
4	19.334	1228520	9.17



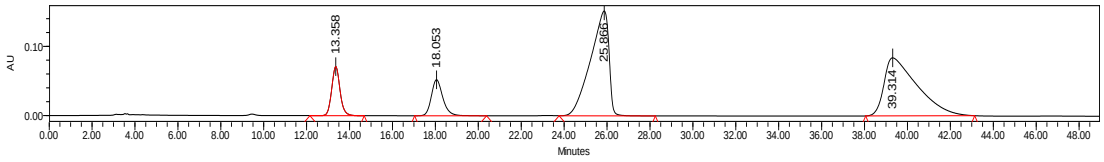
	Retention Time	Area	% Area
1	10.882	4487906	93.76
2	14.614	114802	2.40
3	17.326	162423	3.39
4	20.713	21366	0.45

Ethyl 2-cyano-2-[2,5-dioxo-1-phenylpyrrolidin-3-yl]-2-phenylacetate (3ba)

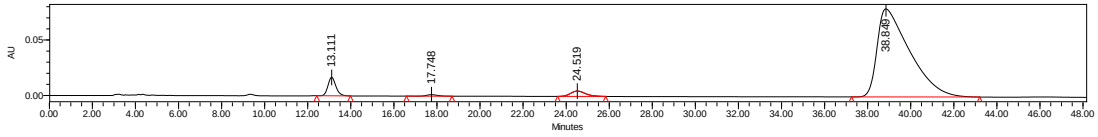


3ba

Colorless oily, 81% yield, 13:1 dr, 96% ee, $[\alpha]_D^{23} = -52.3$ (*c*: 0.53, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralcel ADH, *n*-Hexane/^{i}PrOH = 70/30, 1.0 mL/min, $\lambda = 254.0$ nm, t (major$_{isomer}$) = 24.52 min, 38.85 min; t (minor$_{isomer}$) = 13.11, 17.75 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.61 (m, 2H), 7.51 – 7.38 (m, 6H), 7.35 – 7.27 (m, 2H), 4.43 – 4.34 (m, 2H), 4.31 – 4.23 (m, 1H), 2.80 (dd, *J* = 18.8, 9.6 Hz, 1H), 2.65 (dd, *J* = 18.4, 6.4 Hz, 1H), 1.31 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 172.9, 166.0, 131.2, 129.9, 129.7, 129.3, 129.1, 126.6, 126.5, 115.9, 64.2, 55.5, 47.0, 31.7, 13.8. HRMS (ESI-FT) caled for **$C_{21}H_{18}N_2O_4Na^+$ (M+Na)$^+$**, m/z: 385.1159, observed: 385.1169. IR: 1745, 1717, 1499, 1386, 1237, 1191, 1023, 730, 694 cm^{-1}.

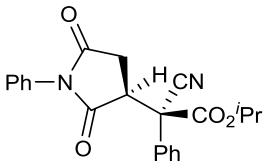


	Retention Time	Area	% Area
1	13.358	1911979	8.74
2	18.053	1927429	8.85
3	25.866	9058756	41.40
4	39.314	8972201	41.01



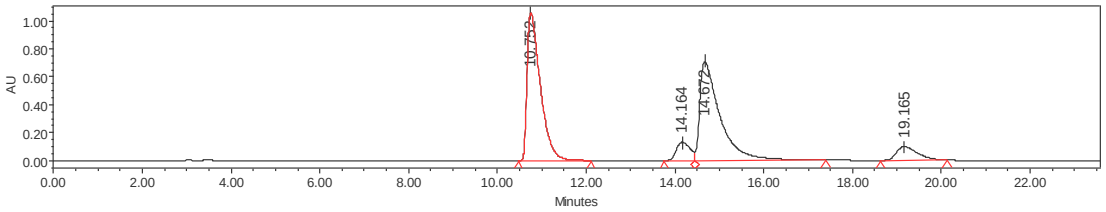
	Retention Time	Area	% Area
1	13.111	426616	4.72
2	17.748	47087	0.52
3	24.519	233550	2.58
4	38.849	8333312	92.18

Isopropyl 2-cyano-2-[2,5-dioxo-1-phenylpyrrolidin-3-yl]-2-phenylacetate (3ca)

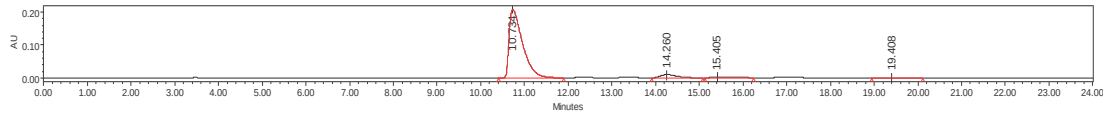


3ca

Colorless oily, 68% yield, 13:1 dr, 96% ee, $[\alpha]_D^{23}$ = –45.2 (*c*: 0.46, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralcel IB, *n*-Hexane /^{i}PrOH = 75/25, 1.0 mL/min, λ = 254 nm, t (major$_{isomer}$) = 10.73, 15.40 min, t (minor$_{isomer}$) = 14.26, 19.41 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 2H), 7.51 – 7.39 (m, 6H) , 7.34 – 7.28 (m, 2H), 5.19– 5.05 (m, 1H), 4.50 – 4.28 (m, 1H), 2.86 – 2.73 (dd, *J* = 18.4, 9.2 Hz, 1H), 2.61 – 2.45 (dd, *J* = 18.8, 6.8 Hz, 1H), 1.36 (d, *J* = 6.4 Hz, 2H), 1.21 (d, *J* = 6.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 172.9, 165.4, 131.4, 131.3, 129.9, 129.7, 129.3, 129.1, 126.6, 126.5, 116.0, 72.5, 55.7, 46.8, 31.7, 21.4, 21.3. HRMS (ESI-FT) caled for **$C_{22}H_{20}N_2O_4Na^+$ (M+Na)$^+$**, m/z: 399.1315, observed: 399.1309. IR: 1749, 1715, 1490, 1386, 1244, 1179, 1070, 1014, 826, 731, 695 cm^{-1}.

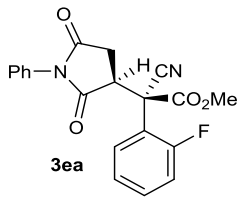


	Retention Time	Area	% Area
1	10.752	21862603	43.63
2	14.164	2794838	5.58
3	14.672	22251187	44.41
4	19.165	3196963	6.38



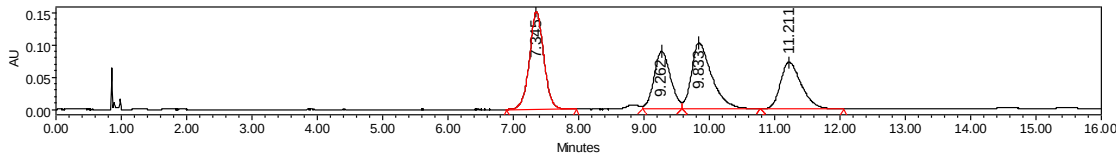
	Retention Time	Area	% Area
1	10.734	4419091	92.21
2	14.260	261732	5.46
3	15.405	87786	1.83
4	19.408	23611	0.49

Methyl 2-cyano-2-(2,5-dioxo-1-phenylpyrrolidin-3-yl)-2-(2-fluorophenyl)acetate (3ea)

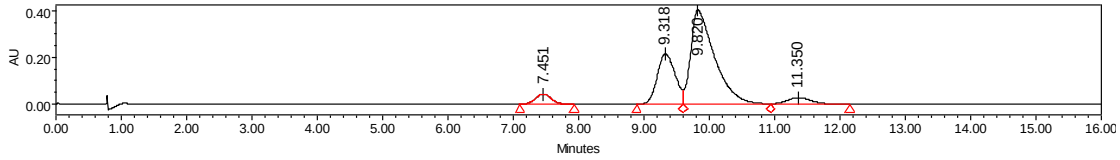


3ea

Colorless oily, 75% yield, 2:1 dr, 85/70% ee, $[\alpha]_D^{25}$ = –22.3 (*c*: 0.89, CH_2Cl_2); Determined by UPC[2] analysis [Daicel chiralcel OX-3, $scCO_2$/^{i}PrOH = 90/10, 1.5 mL/min, λ = 229.0 nm, t ($major_{isomer}$) = 7.45, 9.82, t ($minor_{isomer}$) = 9.32, 11.35 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.37 (m, 5H), 7.31 – 7.25 (m, 3H), 7.22 – 7.12 (m, 1H), 4.50 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.90 (s, 3H), 3.13 (dd, *J* = 18.4, 9.6 Hz, 1H), 2.71 (dd, *J* = 18.4, 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 173.0, 165.5, 161.1 (*J* = 249.6 Hz, 1C), 158.6, 132.3 (*J* = 22.9 Hz, 1C), 131.3, 129.9 (*J* = 2.2 Hz, 1C), 129.3 (*J* = 2.2 Hz, 1C), 126.5, 125.4, 119.0 (*J* = 7.8 Hz, 1C), 117.6 (*J* = 22.4 Hz, 1C), 115.7, 54.8, 52.9, 44.9, 32.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.4 (s, 1F). HRMS (ESI-FT) calcd for **[M+Na]$^+$ $C_{20}H_{15}FN_2O_4Na^+$**, m/z: 389.0908, observed: 389.0904. IR: 1754, 1720, 1494, 1389, 1264, 1193, 896, 732, 703 cm^{-1}.

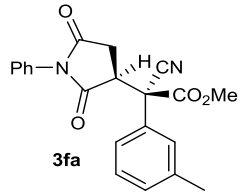


	Retention Time	Area	% Area
1	7.345	2306081	29.87
2	9.262	1579427	20.46
3	9.833	2225581	28.83
4	11.211	1608789	20.84



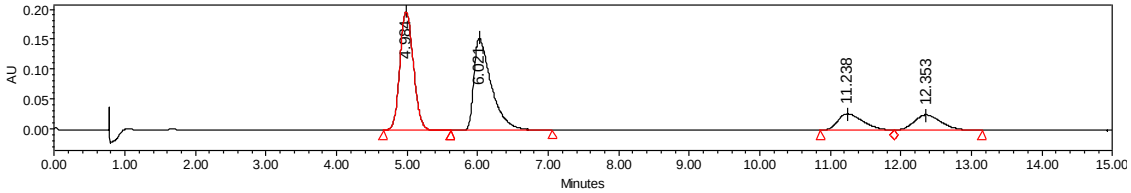
	Retention Time	Area	% Area
1	7.451	744249	4.66
2	9.318	4144402	25.95
3	9.820	10327444	64.66
4	11.350	756454	4.74

Methyl 2-cyano-2-[2,5-dioxo-1-phenylpyrrolidin-3-yl]-2-(3-methyphenyl)acetate (3fa)

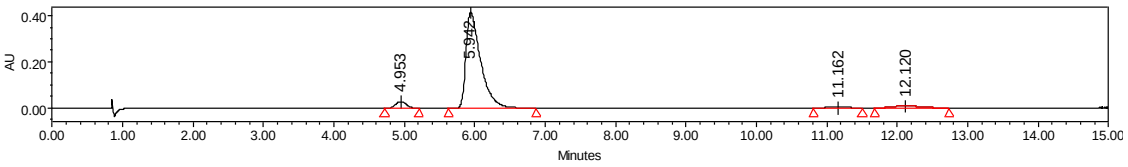


3fa

White solid, 87% yield, 13:1 dr, 90% ee, mp: 82-84 ℃. $[\alpha]_D^{24}$ = –55.9 (*c*: 0.54, CH_2Cl_2); Determined by UPC[2] analysis [Daicel chiralcel OX-3, $scCO_2$/^{i}PrOH = 90/10, 1.5 mL/min, λ = 233.0 nm, t ($major_{isomer}$) = 5.04, 5.95 min, t ($minor_{isomer}$) = 11.42, 12.43 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.37 (m, 5H), 7.36 – 7.24 (m, 4H), 4.40 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.88 (s, 3H), 2.82 (dd, *J* = 18.8, 9.6 Hz, 1H), 2.55 (dd, *J* = 18.8, 6.4 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 172.9, 166.6, 139.8, 131.2, 130.9, 130.8, 129.6, 129.3, 129.1, 127.1, 126.5, 123.5, 115.9, 55.2, 54.6, 47.7, 31.7, 21.6. HRMS (ESI-FT) calcd for **[M+Na]$^+$ $C_{21}H_{18}N_2O_4Na^+$**, m/z: 385.1159, observed: 385.1157. IR: 1750, 1716, 1500, 1387, 1263, 1191, 734, 699 cm^{-1}.

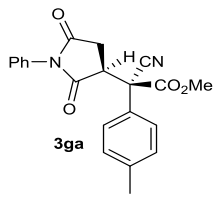


	Retention Time	Area	% Area
1	4.984	2645648	39.35
2	6.021	2666564	39.66
3	11.238	701030	10.43
4	12.353	710731	10.57



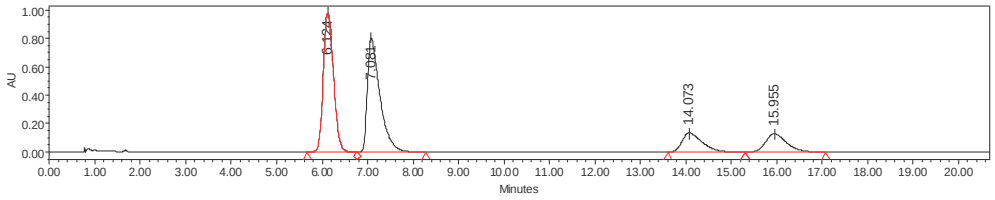
	Retention Time	Area	% Area
1	4.953	328087	4.89
2	5.942	6076977	90.63
3	11.162	72050	1.07
4	12.120	228006	3.40

Methyl -2-cyano-2-(2,5-dioxo-1-phenylpyrrolidin-3-yl)-2-(p-tolyl)acetate (3ga)

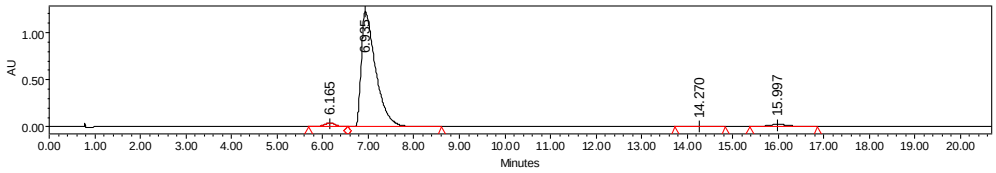


3ga

White solid, 71% yield, 13:1 dr, 95% ee, mp: 150-154 ℃. $[\alpha]_D^{16}$ = –89.7 (*c*: 0.14, CH_2Cl_2); Determined by UPC[2] analysis [Daicel chiralcel OX-3, $scCO_2$/^{i}PrOH = 90/10, 1.5 mL/min, λ = 218.0 nm, t ($major_{isomer}$) = 6.16, 6.94 min, t ($minor_{isomer}$) = 14.27, 16.00 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.38 (m, 5H), 7.33 – 7.25 (m, 4H), 4.38 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.87 (s, 3H), 2.82 (dd, *J* = 18.8, 9.6 Hz, 1H), 2.55 (dd, *J* = 18.4, 6.4 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 172.9, 166.8, 140.2, 131.2, 130.4, 129.3, 129.1, 128.1, 126.5, 126.4, 115.9, 55.0, 54.6, 47.0, 31.6, 21.1. HRMS (ESI-FT) calcd for **[M+Na]$^+$ $C_{21}H_{18}N_2O_4Na^+$**, m/z: 385.1159, observed: 385.1163. IR: 1748, 1713, 1501, 1388, 1243, 1193, 1019, 694 cm^{-1}.

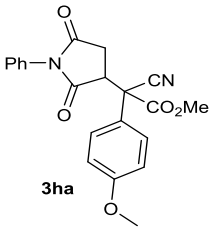


	Retention Time	Area	% Area
1	6.124	15289599	39.32
2	7.081	15333483	39.44
3	14.073	4139311	10.65
4	15.955	4118060	10.59

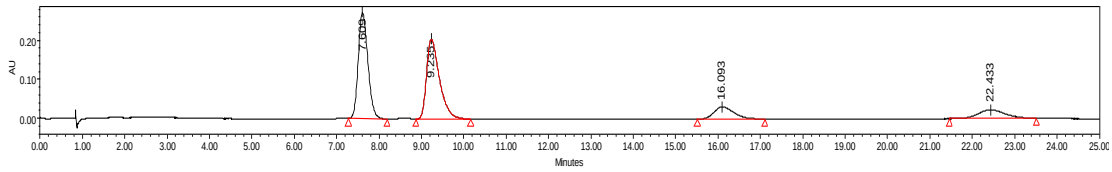


	Retention Time	Area	% Area
1	6.165	715219	2.50
2	6.935	26891083	93.88
3	14.270	174932	0.61
4	15.997	864105	3.02

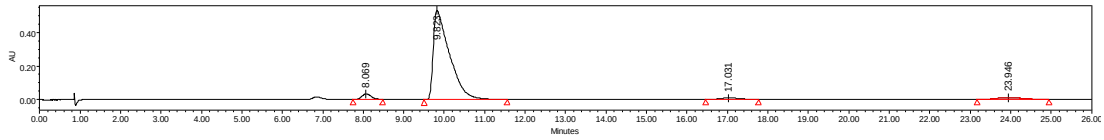
Methyl -2-cyano-2-(2,5-dioxo-1-phenylpyrrolidin-3-yl)-2-(4-methoxyphenyl)acetate (3ha)



White solid, 68% yield, 13:1 dr, 93% ee, mp: 145-147 ℃. $[\alpha]_D^{24}$ = –68.0 (*c*: 0.53, CH_2Cl_2); Determined by UPC[2] analysis [Daicel chiralcel OX-3, $scCO_2$/^{i}PrOH = 90/10, 1.5 mL/min, λ = 234.0 nm, t (major$_{isomer}$) = 8.07, 9.82 min, t (minor$_{isomer}$) = 17.03, 23.95 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.38 (m, 5H), 7.33 – 7.28 (m, 2H), 7.02 – 6.92 (m, 2H), 4.36 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 2.82 (dd, *J* = 18.8, 9.6 Hz, 1H), 2.55 (dd, *J* = 18.8, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 172.9, 166.9, 160.7, 131.2, 129.3, 129.1, 127.8, 126.5, 122.8, 116.0, 115.0, 55.5, 54.7, 54.5, 47.1, 31.6. HRMS (ESI-FT) calcd for **[M+Na]$^+$ $C_{21}H_{18}N_2O_5Na^+$**, m/z: 401.1108, observed: 401.1107. IR: 1748, 1714, 1608, 1511, 1389, 1260, 1186, 1029, 747, 697 cm^{-1}.

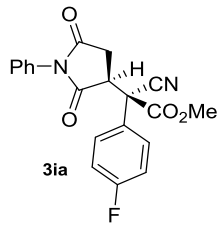


	Retention Time	Area	% Area
1	7.609	4306811	40.51
2	9.235	4317786	40.61
3	16.093	1039100	9.77
4	22.433	967979	9.10



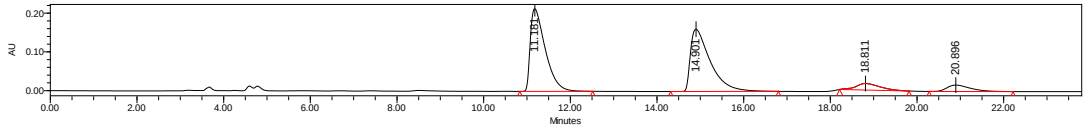
	Retention Time	Area	% Area
1	8.069	513137	3.19
2	9.823	14753883	91.81
3	17.031	315565	1.96
4	23.946	487872	3.04

Methyl 2-cyano-2-[2,5-dioxo-1-phenylpyrrolidin-3-yl]-2-(4-fluorophenyl)acetate (3ia)

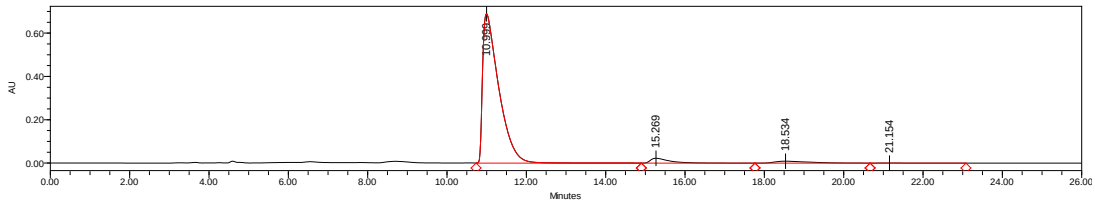


3ia

White solid, 80% yield, >19:1 dr, 93% ee, mp: 160-162 ℃. $[\alpha]_D^{16}$ = –46.2 (*c*: 0.42, CH_2Cl_2); Determined by HPLC analysis [Daicel chiralcel IB, *n*-Hexane/^{i}PrOH = 70/30, 1.0 mL/min, λ = 254 nm, t (major$_{isomer}$) = 9.91, 14.38 min, t (minor$_{isomer}$) = 17.04, 18.85 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.60 (m, 2H), 7.53 – 7.39 (m, 3H), 7.35 – 7.28 (m, 2H), 7.23 – 7.13 (m, 2H), 4.35 (dd, *J* = 9.6, 6.8Hz, 1H), 3.89 (s, 3H), 2.83 (dd, *J* = 18.4, 9.6 Hz, 1H), 2.54 (dd, *J* = 18.4, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 172.6, 166.5, 164.7 (*J* = 249.8 Hz, 1C), 131.1, 129.3 (*J* = 8.2 Hz, 1C), 129.2, 128.7 (*J* = 8.5 Hz, 1C), 126.9 (*J* = 3.3 Hz, 1C), 126.5, 117.0 (*J* = 22 Hz, 1C), 115.7, 54.7, 54.7, 47.2, 31.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.4 (s, 1F). HRMS (ESI-FT) calcd for **[M+Na]$^+$ $C_{20}H_{15}FN_2O_4Na^+$**, m/z: 389.0908, observed: 389.0907. IR: 2360, 2341, 1752, 1717, 1509, 1390, 1263, 734, 700 cm^{-1}.

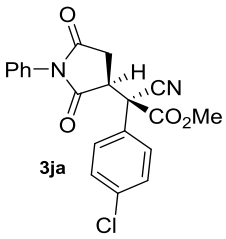


	Retention Time	Area	% Area
1	11.181	5130085	44.57
2	14.901	5105901	44.36
3	18.811	653612	5.68
4	20.896	621565	5.40



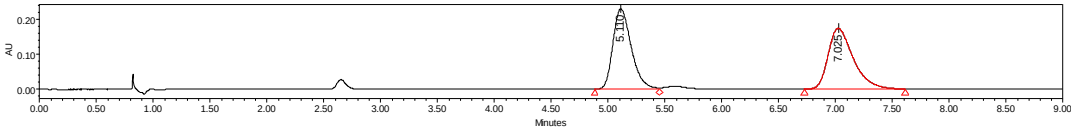
	Retention Time	Area	% Area
1	10.999	19283257	93.89
2	15.269	731013	3.56
3	18.534	512041	2.49
4	21.155	11380	0.06

Methyl 2-cyano-2-[2,5-dioxo-1-phenylpyrrolidin-3-yl]-2-(4-chlorophenyl)acetate (3ja)

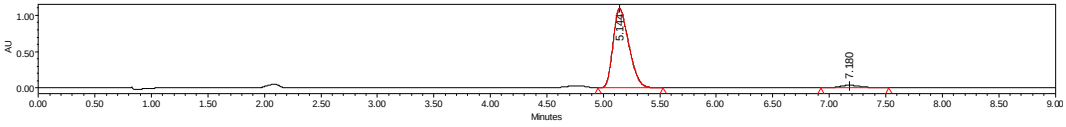


3ja

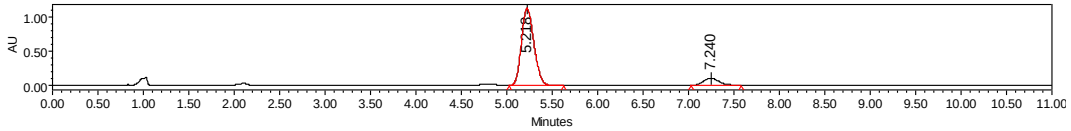
White solid, 90% yield, >19:1 dr, 91% ee, mp: 75-78 ℃. $[\alpha]_D^{24}$ = –60.7 (*c*: 0.57, CH_2Cl_2); Determined by UPC[2] analysis [Daicel chiralcel OJ-3, $scCO_2$/MeOH = 90/10, 1.5 mL/min, λ = 233.0 nm, t ($major_{isomer}$) = 5.14 min, t ($minor_{isomer}$) = 7.18 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.55 (m, 2H), 7.51 – 7.39 (m, 5H), 7.34 – 7.27 (m, 2H), 4.35 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.88 (s, 3H), 2.82 (dd, *J* = 18.4, 9.6 Hz, 1H), 2.52 (dd, *J* = 18.8, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 172.6, 166.4, 136.5, 131.1, 130.0, 129.6, 129.4, 129.2, 128.0, 126.5, 115.5, 54.8, 47.1, 31.5. HRMS (ESI-FT) calcd for **[M+Na]$^+$ $C_{20}H_{15}ClN_2O_4Na^+$**, m/z: 405.0613, 407.0583, observed: 405.0612, 407.0580. IR: 1750, 1714, 1495, 1388, 1263, 1195, 1097, 1015, 734, 699 cm^{-1}.



	Retention Time	Area	% Area
1	5.110	2575251	49.22
2	7.025	2657138	50.78

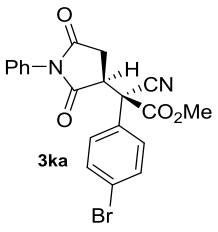


	Retention Time	Area	% Area
1	5.144	10545906	95.67
2	7.180	476811	4.33



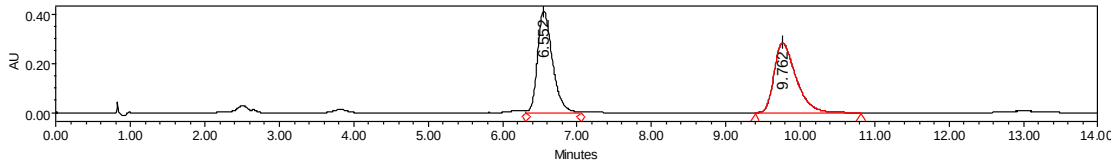
	Retention Time	Area	% Area
1	5.218	10695785	89.07
2	7.240	1312694	10.93

Methyl 2-cyano-2-[2,5-dioxo-1-phenylpyrrolidin-3-yl]-2-(4-bromophenyl)acetate (3ka)

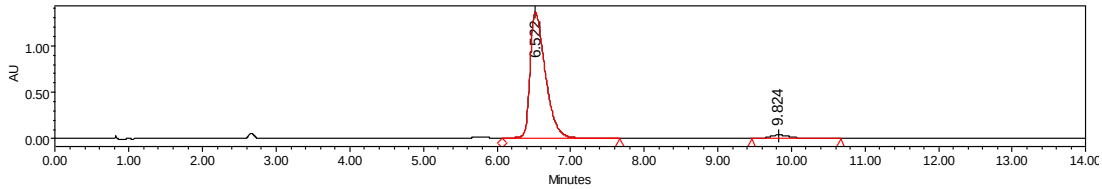


3ka

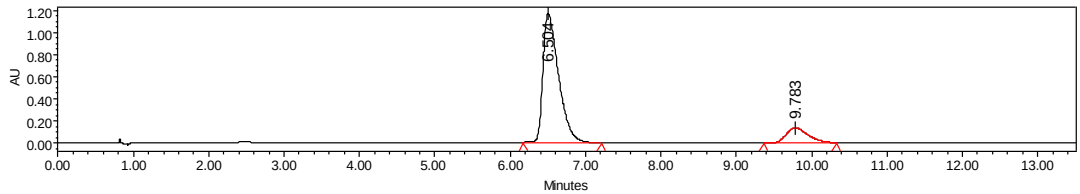
Colorless oily, 74% yield, >19:1 dr, 92% ee, $[\alpha]_D^{24} = -62.8$ (*c*: 0.37, CH_2Cl_2); Determined by UPC[2] analysis [Daicel chiralcel OJ-3, $scCO_2$/MeOH = 90/10, 1.5 mL/min, λ = 235.0 nm, t ($major_{isomer}$) = 6.52 min, t ($minor_{isomer}$) = 9.82 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.58 (m, 2H), 7.56 – 7.39 (m, 5H), 7.35 – 7.27 (m, 2H), 4.34 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.89 (s, 3H), 2.82 (dd, *J* = 18.8, 9.6 Hz, 1H), 2.52 (dd, *J* = 18.8, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 172.5, 166.3, 133.0, 131.1, 130.1, 129.4, 129.2, 128.2, 126.5, 124.6, 115.4, 54.9, 54.8, 47.1, 31.5. HRMS (ESI-FT) calcd for **[M+Na]$^+$ $C_{20}H_{15}BrN_2O_4Na^+$**, m/z: 449.0107, 451.0087, observed: 449.0114, 451.0092. IR: 1750, 1715, 1492, 1389, 1261, 1197, 733, 698 cm^{-1}.



	Retention Time	Area	% Area
1	6.552	5729941	49.88
2	9.762	5756762	50.12

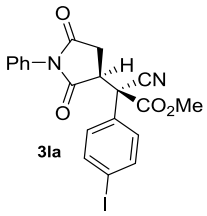


	Retention Time	Area	% Area
1	6.522	19823378	96.12
2	9.824	800139	3.88



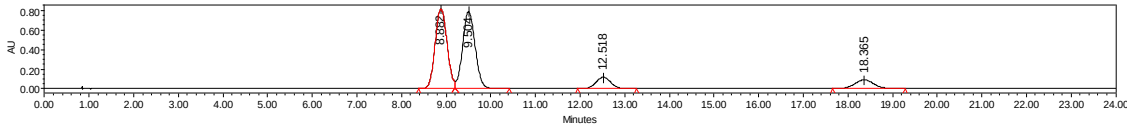
	Retention Time	Area	% Area
1	6.504	16738518	86.17
2	9.783	2686045	13.83

Methyl -2-cyano-2-(2,5-dioxo-1-phenylpyrrolidin-3-yl)-2-(4-iodophenyl)acetate (3la)

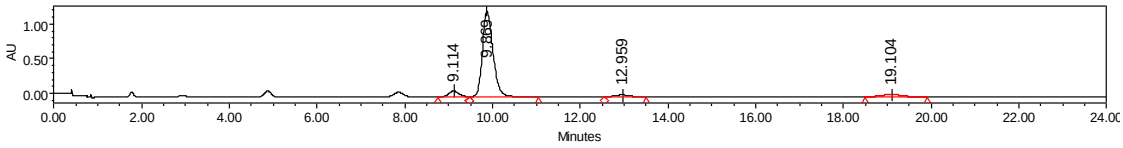


3la

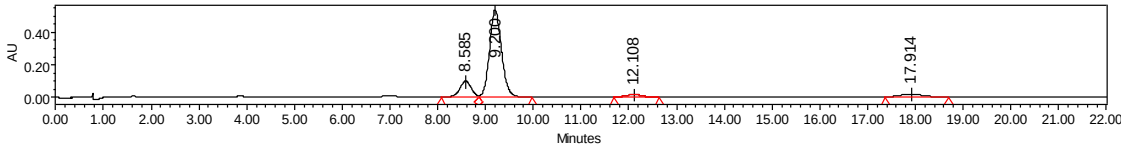
Colorless oily, 70% yield, >19:1 dr, 88% ee, $[\alpha]_D^{25}$ = –63.5 (*c*: 0.38, CH_2Cl_2); Determined by UPC[2] analysis [Daicel chiralcel OJ-3, $scCO_2$/MeOH = 90/10, 1.5 mL/min, λ = 235.0 nm, t ($major_{isomer}$) = 9.11,9.87 min, t ($minor_{isomer}$) = 12.96, 19.10 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.75 (m, 2H), 7.98 – 7.84 (m, 5H), 7.63 – 7.54 (m, 2H), 7.51 – 7.38 (m, 3H), 7.37 – 7.28 (m, 2H), 4.54 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.88 (s, 3H), 2.81 (dd, *J* = 18.8, 9.6 Hz, 1H), 2.58 (dd, *J* = 18.4, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 172.5, 166.2, 138.9, 131.1, 130.8, 129.3, 129.2, 128.3, 126.5, 115.4, 96.4, 55.0, 54.8, 47.0, 31.5. HRMS (ESI-FT) calcd for **$[M+Na]^+$ $C_{20}H_{15}IN_2O_4Na^+$**, m/z: 496.9969, observed: 496.9969. IR: 1750, 1715, 1500, 1389, 1262, 1196, 1007, 735, 698 cm^{-1}.



	Retention Time	Area	% Area
1	8.882	15103086	42.20
2	9.504	15308544	42.77
3	12.518	2700167	7.54
4	18.365	2679439	7.49

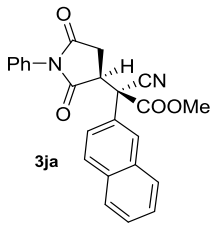


	Retention Time	Area	% Area
1	9.114	1240865	5.38
2	9.869	20465604	88.70
3	12.959	486425	2.11
4	19.104	880061	3.81

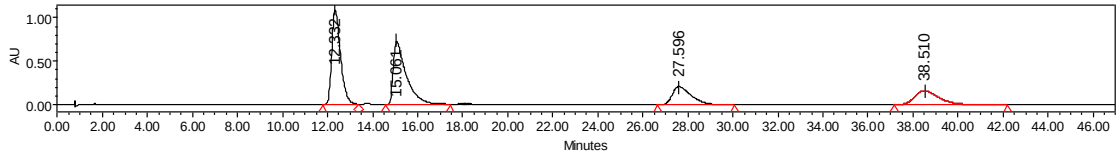


	Retention Time	Area	% Area
1	8.585	1613971	13.68
2	9.200	9334372	79.10
3	12.108	321235	2.72
4	17.914	530998	4.50

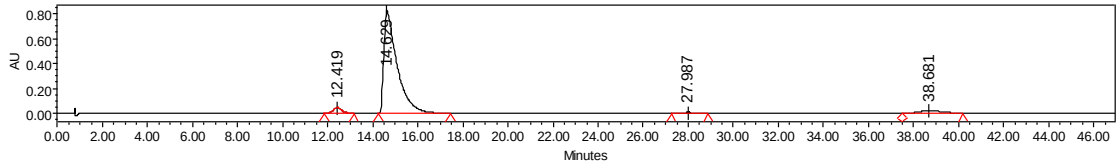
Methyl 2-cyano-2-[2,5-dioxo-1-phenylpyrrolidin-3-yl]-2-(2-naphthyl)acetate (3ja)



White solid, 99% yield, 15:1 dr, 92% ee, mp: 76-78 ℃. $[\alpha]_D^{25}$ = –90.5 (*c*: 0.55, CH_2Cl_2); Determined by UPC[2] analysis [Daicel chiralcel OX-3, $scCO_2$/^{i}PrOH = 90/10, 1.5 mL/min, λ = 235.0 nm, t ($major_{isomer}$) = 12.42, 12.63 min, t ($minor_{isomer}$) = 27.99, 38.68 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 1.2 Hz, 1H), 7.98 – 7.81 (m, 3H), 7.68 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.51 – 7.38 (m, 3H), 7.37 – 7.27 (m, 2H), 4.54 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.88 (s, 3H), 2.81 (dd, *J* = 18.8, 9.6 Hz, 1H), 2.58 (dd, *J* = 18.4, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 172.8, 166.6, 133.4, 133.0, 131.2, 130.0, 129.3, 129.2, 129.1, 128.5, 128.2, 127.8, 127.7, 127.5, 127.1, 126.5, 122.4, 115.9, 55.5, 54.7, 47.1, 31.6. HRMS (ESI-FT) calcd for **[M+Na]$^+$** **$C_{24}H_{18}N_2O_4Na^+$**, m/z: 421.1159, observed: 421.1153. IR: 1752, 1721, 1264, 1194, 817, 731, 703 cm^{-1}.

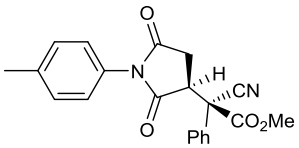


	Retention Time	Area	% Area
1	12.332	29549603	35.59
2	15.061	28956816	34.88
3	27.596	12262460	14.77
4	38.510	12251330	14.76



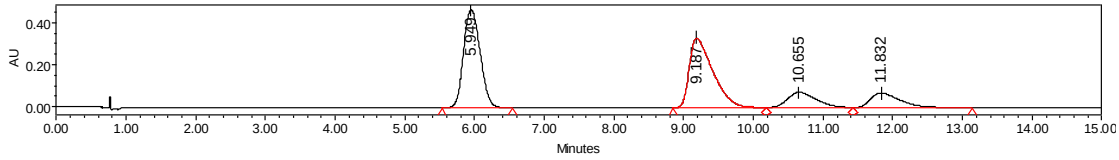
	Retention Time	Area	% Area
1	12.419	1234498	3.39
2	14.629	33419784	91.86
3	27.987	252423	0.69
4	38.681	1474426	4.05

Methyl 2-cyano-2-[1-(p-tolyl)-2,5-dioxopyrrolidin-3-yl]-2-phenylacetate (3ab)

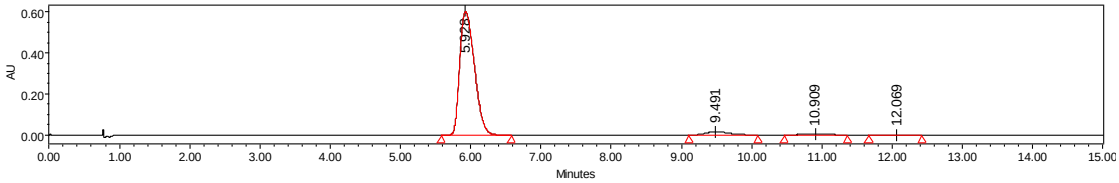


3ab

White solid, 62% yield, >19:1 dr, 92% ee, mp: 126-130 ℃. $[\alpha]_D^{16}$ = –64.9 (*c*: 0.60, CH_2Cl_2); Determined by UPC^2 analysis [Daicel chiralcel OD-3, $scCO_2$/^{i}PrOH = 90/10, 1.5 mL/min, λ = 232.0 nm, t (major$_{isomer}$) = 5.93, 9.49 min, t (minor$_{isomer}$) = 10.91, 12.07 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.61 (m, 2H), 7.52 – 7.43 (m, 3H), 7.31 – 7.26 (d, *J* = 8.4 Hz, 2H), 7.22 – 7.14 (m, 2H), 4.39 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.88 (s, 3H), 2.80 (dd, *J* = 18.4, 9.2 Hz, 1H), 2.53 (dd, *J* = 18.4, 6.4 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1, 173.0, 166.6, 139.2, 131.1, 130.0, 129.9, 129.8, 128.5, 126.5, 126.3, 115.8, 55.3, 54.6, 47.1, 31.6, 21.3. HRMS (ESI-TOF) calcd for **[M+Na]$^+$ $C_{21}H_{18}N_2O_4Na^+$**, m/z: 385.1159, observed: 385.1163. IR: 2360, 1751, 1715, 1514, 1245, 1197, 731, 698 cm^{-1}.

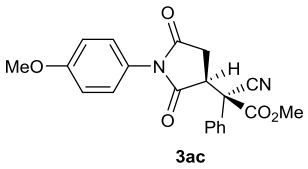


	Retention Time	Area	% Area
1	5.949	7711751	39.29
2	9.187	7743878	39.46
3	10.655	2104209	10.72
4	11.832	2066402	10.53



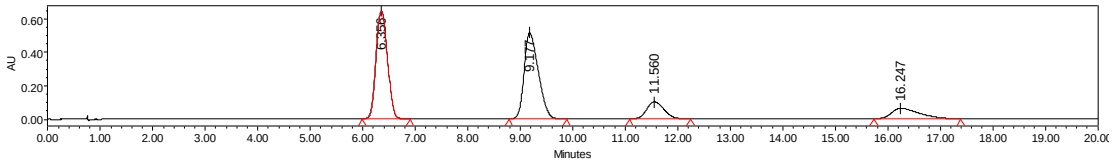
	Retention Time	Area	% Area
1	5.928	8633167	94.42
2	9.491	355083	3.88
3	10.909	129443	1.42
4	12.069	25311	0.28

Methyl 2-cyano-2-[1-(4-methoxyphenyl)-2,5-dioxopyrrolidin-3-yl]-2-phenylacetate (3ac)

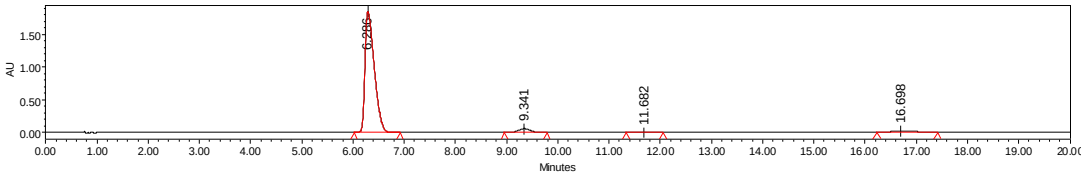


3ac

White solid, 70% yield, 16:1 dr, 92% ee, mp: 126-130 ℃. $[\alpha]_D^{15}$ = –64.9 (*c*: 0.60, CH_2Cl_2); Determined by UPC^2 analysis [Daicel chiralcel OD-3, $scCO_2$/MeOH = 90/10, 1.5 mL/min, λ = 229.0 nm, t ($major_{isomer}$) = 6.29, 9.39 min, t ($minor_{isomer}$) = 11.68, 16.70 min]; ^{1}H NMR (400 MHz, CDCl3) δ 7.72 – 7.60 (m, 2H), 7.52 – 7.42 (m, 3H), 7.25 – 7.22 (m, 2H), 7.02 – 6.93 (m, 2H), 4.39 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 2.80 (dd, *J* = 18.4, 9.2 Hz, 1H), 2.52 (dd, *J* = 18.4, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 173.1, 166.6, 159.8, 131.1, 130.0, 129.8, 127.8, 126.5, 123.8, 115.8, 114.6, 55.5, 55.3, 54.6, 47.0, 31.5. HRMS (ESI-FT) calcd for **[M+Na]$^+$ $C_{21}H_{18}N_2O_5Na^+$**, m/z: 401.1108, observed: 401.1113. IR: 2361, 1753, 1721, 1514, 1264, 896, 731, 703 cm^{-1}.

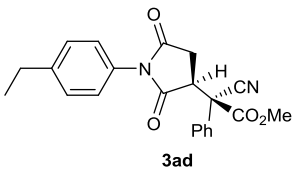


	Retention Time	Area	% Area
1	6.356	9692246	40.56
2	9.177	9683538	40.52
3	11.560	2269478	9.50
4	16.247	2253353	9.43



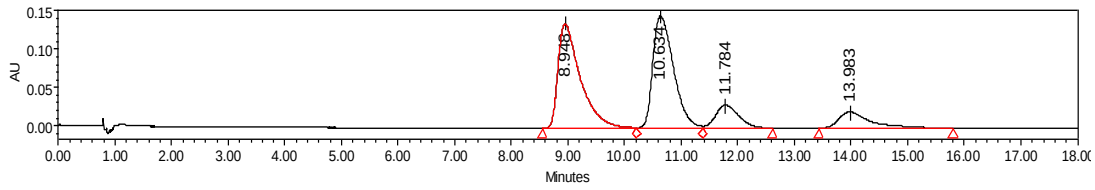
	Retention Time	Area	% Area
1	6.286	23467367	92.70
2	9.341	949059	3.75
3	11.682	124468	0.49
4	16.698	773564	3.06

Methyl 2-cyano-2-[1-(4-ethylphenyl)-2,5-dioxopyrrolidin-3-yl]-2-phenylacetate (3ad)

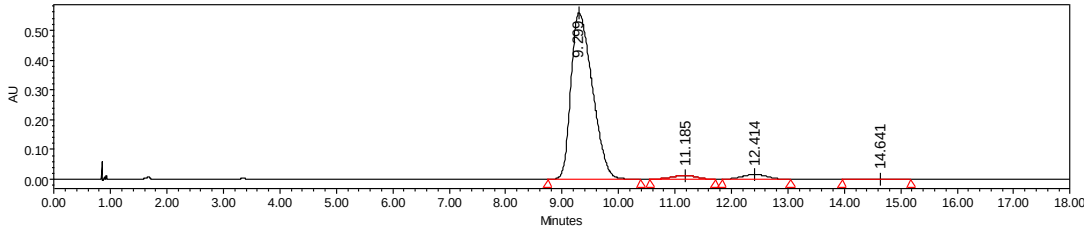


3ad

White solid, 73% yield, >19:1 dr, 93% ee, mp: 132-135 ℃. $[\alpha]_D^{17}$ = –55.6 (*c*: 0.54, CH_2Cl_2); Determined by UPC[2] analysis [Daicel chiralcel OJ-3, $scCO_2$/^{i}PrOH = 95/5, 1.5 mL/min, λ = 237.0 nm, t ($major_{isomer}$) = 9.30, 11.18 min, t ($minor_{isomer}$) = 12.41, 14.64 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.61 (m, 2H), 7.52 – 7.44 (m, 3H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.39 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.87 (s, 3H), 2.80 (dd, *J* = 18.4, 9.2 Hz, 1H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.53 (dd, *J* = 18.8, 6.4 Hz, 1H), 1.24 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 173.1, 166.6, 159.8, 131.1, 130.0, 129.8, 127.8, 126.5, 123.8, 115.8, 114.6, 55.3, 54.6, 47.1, 31.6, 28.6, 15.4. HRMS (ESI-TOF) calcd for **$[M+Na]^+$ $C_{22}H_{20}N_2O_4Na^+$**, m/z: 399.1315, observed: 399.1314. IR: 2360, 1753, 1721, 1515, 1390, 1264, 731, 703 cm^{-1}.

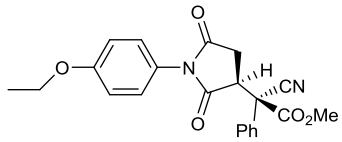


	Retention Time	Area	% Area
1	8.947	4907363	40.95
2	10.635	4880129	40.72
3	11.790	1125910	9.39
4	13.969	1071735	8.94



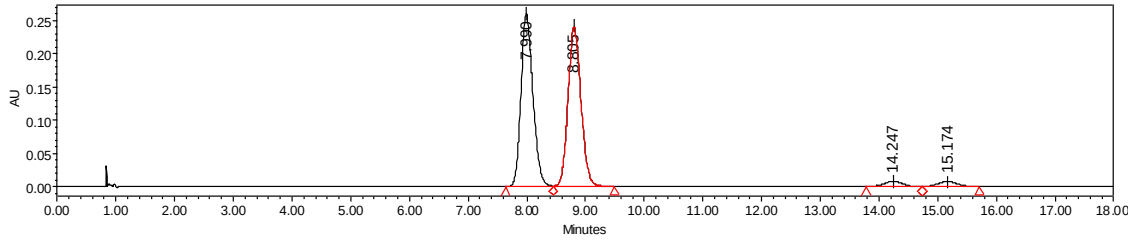
	Retention Time	Area	% Area
1	9.299	368282	94.19
2	11.185	14638092	2.37
3	12.414	482305	3.10
4	14.641	52437	0.34

Methyl 2-cyano-2-[1-(4-ethoxyphenyl)-2,5-dioxopyrrolidin-3-yl]-2-phenylacetate (3ae)

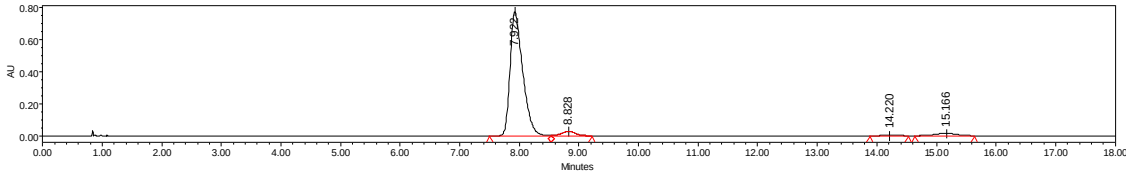


3ae

White solid, 65% yield, >19:1 dr, 93% ee, mp: 94-98 ℃. $[\alpha]_D^{20}$ = –56.1 (*c*: 0.54, CH_2Cl_2); Determined by UPC[2] analysis [Daicel chiralcel OJ-3, scCO_2/MeOH = 90/10, 1.5 mL/min, λ = 235.0 nm, t (major$_{isomer}$) = 7.92, 8.83 min, t (minor$_{isomer}$) = 14.22, 15.17 min; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.47 (m, 2H), 7.45 – 7.31 (m, 3H), 7.17 – 7.05 (m, 2H), 6.94 – 6.79 (m, 2H), 4.31 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.97 (q, *J* = 7.2 Hz, 1H), 3.80 (s, 3H), 2.72 (dd, *J* = 18.8, 9.6 Hz, 1H), 2.44 (dd, *J* = 18.8, 6.4 Hz, 1H), 1.34 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 173.1, 166.6, 159.2, 131.1, 130.0, 129.8, 127.7, 126.5, 123.6, 115.8, 115.1, 63.8, 55.3, 54.6, 47.0, 31.5, 14.7. HRMS (ESI-TOF) calcd for **[M+Na]$^+$ $C_{22}H_{20}N_2O_5Na^+$**, m/z: 415.1264, observed: 415.1263. IR: 1719, 1521, 1264, 731, 702 cm^{-1}.

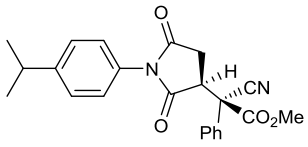


	Retention Time	Area	% Area
1	7.990	3690318	47.46
2	8.805	3703534	47.63
3	14.247	192994	2.48
4	15.174	188458	2.42



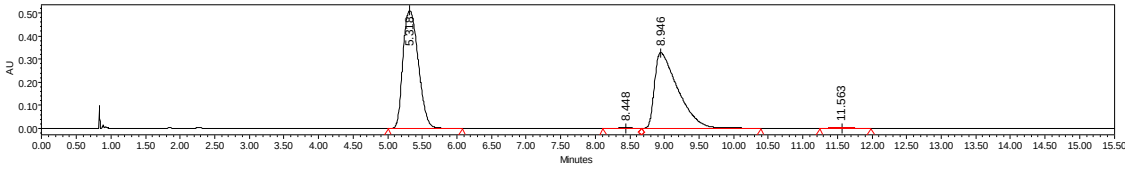
	Retention Time	Area	% Area
1	7.922	11100691	93.58
2	8.828	372677	3.14
3	14.220	38197	0.32
4	15.166	350948	2.96

Methyl 2-cyano-2-[1-(4-isopropylphenyl)-2,5-dioxopyrrolidin-3-yl]-2-phenylacetate (3af)

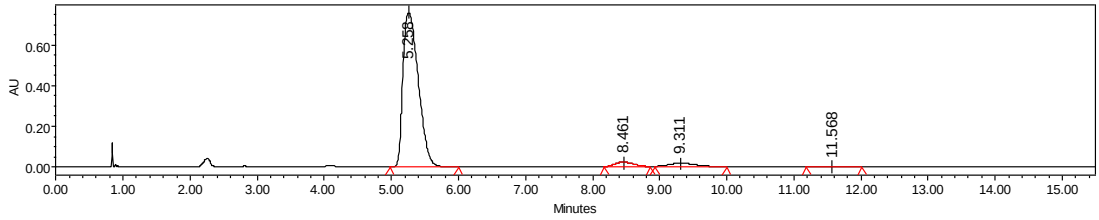


3af

White solid, 72% yield, >19:1 dr, 92% ee, mp: 165-170 ℃. $[\alpha]_D^{16}$ = –51.5 (*c*: 0.52, CH_2Cl_2); Determined by UPC[2] analysis [Daicel chiralcel OD-3, scCO_2/^{i}PrOH = 90/10, 1.5 mL/min, λ = 244.0 nm, t (major$_{isomer}$) = 5.26, 9.31 min, t (minor$_{isomer}$) = 8.46, 11.57 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H), 7.52 – 7.44 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.18 (m, 2H), 4.39 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.87 (s, 3H), 3.00 – 2.88 (m, 1H), 2.80 (dd, *J* = 18.8, 9.6 Hz, 1H), 2.53 (dd, *J* = 18.8, 6.4 Hz, 1H), 1.25 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 173.0, 166.6, 150.0, 131.1, 130.0, 129.8, 128.7, 127.4, 126.5, 126.3, 115.8, 55.3, 54.6, 54.6, 47.1, 34.0, 31.6, 23.9. HRMS (ESI-FT) calcd for **[M+Na]$^+$ $C_{23}H_{22}N_2O_4Na^+$**, m/z: 413.1472, observed: 413.1476. IR: 2961, 1751, 1716, 1514, 1391, 1245, 734, 700 cm^{-1}.

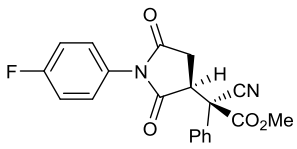


	Retention Time	Area	% Area
1	5.318	7845279	50.21
2	8.448	40555	0.26
3	8.946	7693338	49.23
4	11.563	47147	0.30



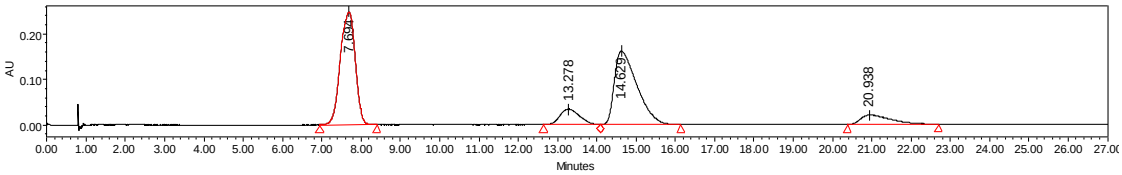
	Retention Time	Area	% Area
1	5.258	12081664	93.12
2	8.461	412056	3.18
3	9.311	440869	3.40
4	11.568	39094	0.30

Methyl 2-cyano-2-[1-(4-fluorophenyl)-2,5-dioxopyrrolidin-3-yl]-2-phenylacetate (3ag)

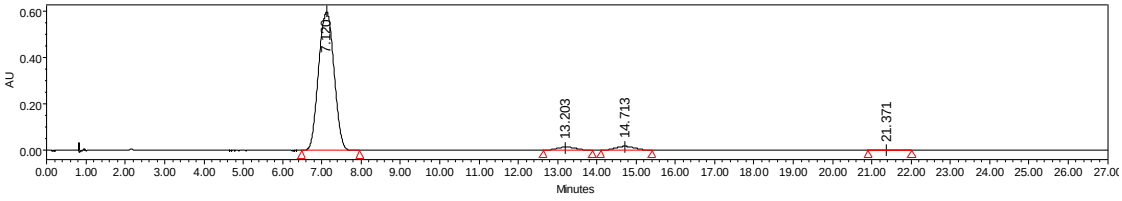


3ag

White solid, 78% yield, 19:1 dr, 92% ee, mp: 96-98 ℃. $[\alpha]_D^{16}$ = –47.9 (*c*: 0.24, CH_2Cl_2); Determined by UPC[2] analysis [Daicel chiralcel OD-3, scCO_2/^{i}PrOH = 94/6, 1.5 mL/min, λ = 227.0 nm, t (major$_{isomer}$) = 7.12, 14.71 min, t (minor$_{isomer}$) = 13.20, 21.37 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.60 (m, 2H), 7.53 – 7.43 (m, 3H), 7.35 – 7.27 (m, 2H), 7.21 – 7.11 (m, 2H), 4.41 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.89 (s, 3H), 2.82 (dd, *J* = 18.4, 9.2 Hz, 1H), 2.54 (dd, *J* = 18.4, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 172.7, 166.6, 163.7 (*J* = 247.7 Hz, 1C), 130.9, 130.1, 129.8, 128.5 (*J* = 8.8 Hz, 1C), 127.1 (*J* = 3.2 Hz, 1C), 126.5, 116.5 (*J* = 22.9 Hz, 1C), 115.8, 55.3, 54.7, 47.0, 31.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.5 (s, 1F). HRMS (ESI-FT) calcd for **[M+Na]$^+$** **$C_{20}H_{15}FN_2O_4Na^+$**, m/z: 389.0908, observed: 389.0898. IR: 1750, 1717, 1510, 1392, 1241, 1193, 1017, 969, 837, 730, 698 cm^{-1}.

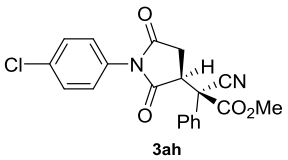


	Retention Time	Area	% Area
1	7.694	6604763	42.97
2	13.278	1197234	7.79
3	14.629	6418296	41.76
4	20.938	1149061	7.48



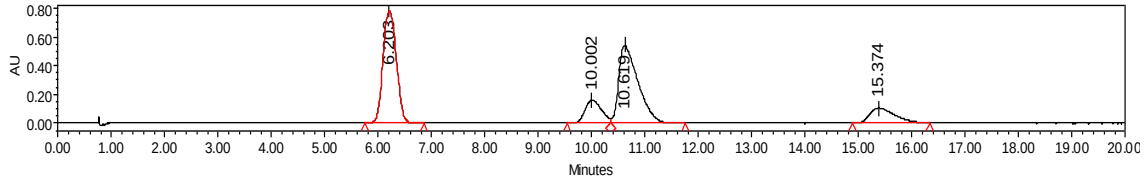
	Retention Time	Area	% Area
1	7.120	16181493	93.55
2	13.203	475743	2.75
3	14.713	593126	3.43
4	21.371	46098	0.27

Methyl 2-[1-(4-chlorophenyl)-2,5-dioxopyrrolidin-3-yl]-2-cyano-2-phenylacetate (3ah)

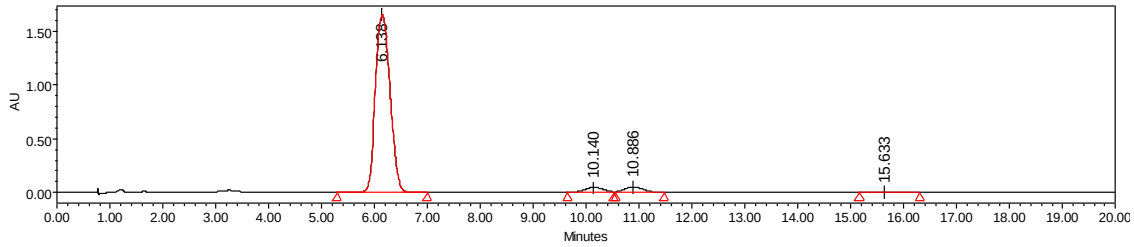


3ah

White solid, 68% yield, 16:1 dr, 93% ee, mp: 59-62 ℃. $[\alpha]_D^{16} = -56.4$ (*c*: 0.39, CH_2Cl_2); Determined by UPC[2] analysis [Daicel chiralcel OD-3, $scCO_2/^iPrOH$ = 90/10, 1.5 mL/min, λ = 232.0 nm, t ($major_{isomer}$) = 6.14, 10.87 min, t ($minor_{isomer}$) = 10.14, 15.63 min]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 2H), 7.51 – 7.42 (m, 5H), 7.30 – 7.24 (m, 2H), 4.40 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.89 (s, 3H), 2.82 (dd, *J* = 18.8, 9.6 Hz, 1H), 2.54 (dd, *J* = 18.8, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 172.5, 166.5, 135.0, 130.9, 130.1, 129.8, 129.6, 129.5, 127.8, 126.5, 125.7, 115.8, 55.3, 54.7, 47.1, 31.6. HRMS (ESI-FT) calcd for **$[M+Na]^+$ $C_{20}H_{15}ClN_2O_4Na^+$**, m/z: 405.0613, 407.0585; observed: 405.0615, 407.0585. IR: 1749, 1710, 1493, 1388, 1244, 1192, 1092, 1017, 830, 730, 696 cm^{-1}.

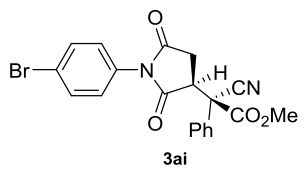


	Retention Time	Area	% Area
1	6.203	13525704	39.71
2	10.002	3471574	10.19
3	10.619	13582259	39.87
4	15.374	3484799	10.23



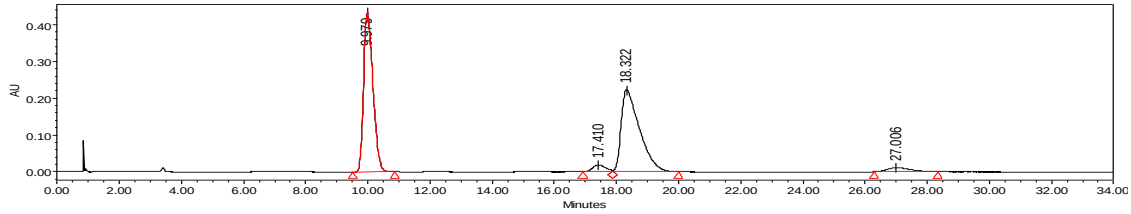
	Retention Time	Area	% Area
1	6.138	31880220	93.26
2	10.140	1000078	2.93
3	10.886	1105004	3.23
4	15.633	197396	0.58

Methyl 2-[1-(4-bromophenyl)-2,5-dioxopyrrolidin-3-yl]-2-cyano-2-phenylacetate (3ai)

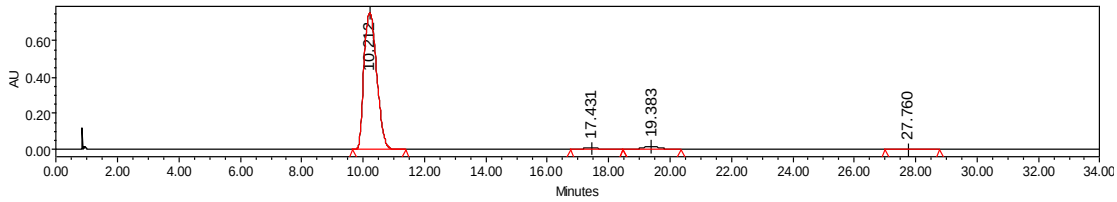


3ai

White solid, 65% yield, 16:1 dr, 93% ee, mp: 55-58 ℃. $[\alpha]_D^{16}$ = –44.0 (*c*: 0.54, CH_2Cl_2); Determined by UPC^2 analysis [Daicel chiralcel OD-3, $scCO_2$/^{i}PrOH = 92/8, 1.5 mL/min, λ = 231.0 nm, t (major$_{isomer}$) = 10.21, 19.38 min, t (minor$_{isomer}$) = 17.43, 27.76 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.57 (m, 4H), 7.52 – 7.44 (m, 3H), 7.25 – 7.17 (m, 2H), 4.40 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.89 (s, 3H), 2.81 (dd, *J* = 18.8, 9.6 Hz, 1H), 2.54 (dd, *J* = 18.4, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 172.4, 166.5, 132.5, 130.9, 130.2, 130.1, 129.8, 128.0, 126.5, 123.0, 115.8, 55.3, 54.7, 47.1, 31.6. HRMS (ESI-FT) calcd for **[M+Na]$^+$ $C_{20}H_{15}BrN_2O_4Na^+$**, m/z: 449.0107, 451.0087; observed: 449.0114, 451.0095. IR: 1749, 1715, 1490, 1386, 1244, 1179, 1070, 1014, 969, 826, 731, 695 cm^{-1}.

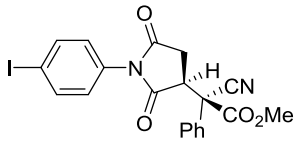


	Retention Time	Area	% Area
1	9.979	9102482	47.13
2	17.410	546893	2.83
3	18.322	9098166	47.11
4	27.006	566656	2.93



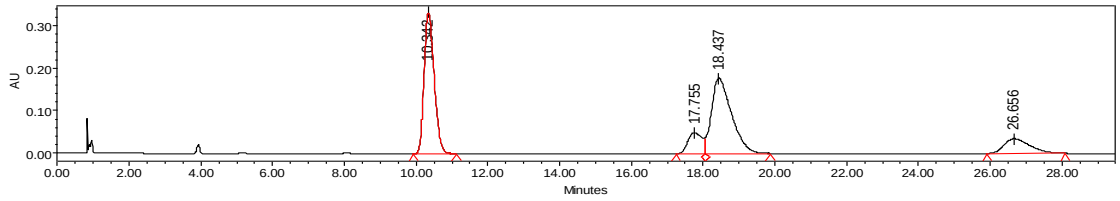
	Retention Time	Area	% Area
1	10.212	21753915	94.85
2	17.431	357193	1.56
3	19.383	756187	3.30
4	27.760	68318	0.30

Methyl 2-[1-(4-iodophenyl)-2,5-dioxopyrrolidin-3-yl]-2-cyano-2-phenylacetate (3aj)

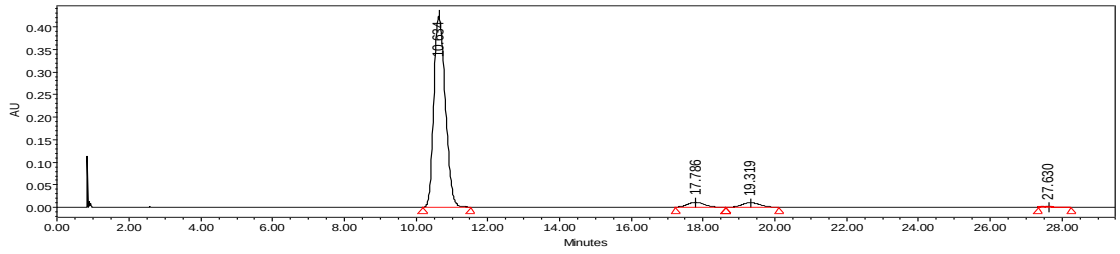


3aj

White solid, 78% yield, 16:1 dr, 93% ee, mp: 76-79 ℃. $[\alpha]_D^{18} = -34.6$ (*c*: 0.18, CH_2Cl_2); Determined by UPC[2] analysis [Daicel chiralcel OD-3, $scCO_2/^iPrOH = 90/10$, 1.5 mL/min, $\lambda = 227.0$ nm, t ($major_{isomer}$) = 10.63, 19.32 min, t ($minor_{isomer}$) = 17.79, 27.63 min]; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 2H), 7.70 – 7.57 (m, 2H), 7.51 – 7.43 (m, 3H), 7.14 – 7.00 (m, 2H), 4.40 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.88 (s, 3H), 2.80 (dd, *J* = 18.8, 9.6 Hz, 1H), 2.52 (dd, *J* = 18.4, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 172.4, 166.5, 138.5, 130.9, 130.9, 130.1, 129.8, 128.2, 126.5, 115.8, 94.7, 55.3, 54.7, 47.1, 31.6. HRMS (ESI-FT) calcd for **[M+Na]$^+$ $C_{20}H_{15}IN_2O_4Na^+$**, m/z: 496.9969; observed: 496.9974. IR: 2360, 1752, 1722, 1487, 1386, 1264, 1194, 731, 703 cm^{-1}.

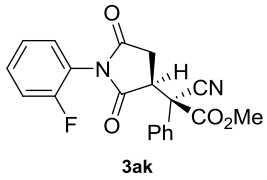


	Retention Time	Area	% Area
1	10.342	6521672	39.47
2	17.755	1395249	8.44
3	18.437	6860454	41.52
4	26.656	1744743	10.56



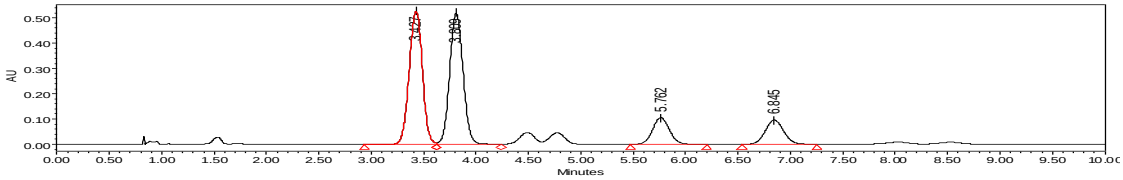
	Retention Time	Area	% Area
1	10.634	9366577	92.72
2	17.786	365453	3.62
3	19.319	347651	3.44
4	27.630	22396	0.22

Methyl 2-cyano-2-[1-(2-fluorophenyl)-2,5-dioxopyrrolidin-3-yl]-2-phenylacetate (3ak)

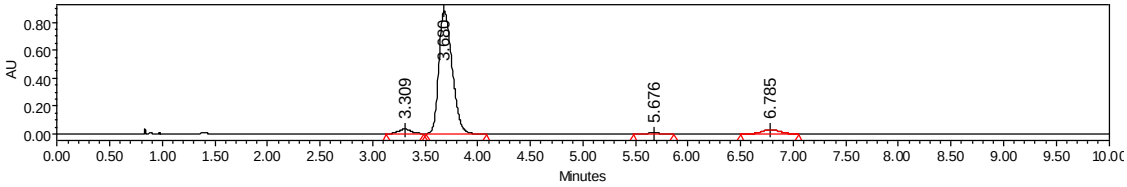


3ak

White solid, 73% yield, 11:1 dr, 93% ee, mp: 148-152 ℃. $[\alpha]_D^{15} = -50.2$ (*c*: 0.51, CH_2Cl_2); Determined by UPC[2] analysis [Daicel chiralcel OX-3, $scCO_2$/MeOH = 90/10, 1.5 mL/min, λ = 230.0 nm, t ($major_{isomer}$) = 3.31, 3.68 min, t ($minor_{isomer}$) = 5.68, 6.78 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.60 (m, 2H), 7.52 – 7.40 (m, 4H), 7.32 – 7.20 (m, 3H), 4.55 – 4.36 (m, 1H), 3.88 (s, 3H), 3.00 – 2.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 171.9, 166.5, 164.0, 158.6 (*J* = 250.0 Hz, 1C), 131.5 (*J* = 8.0 Hz, 1C), 131.1, 130.0, 129.8 (*J* = 22.9 Hz, 1C), 126.5, 124.9, 119.0 (*J* = 13.2 Hz, 1C), 116.8, 116.7, 54.7, 54.6, 47.3, 31.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.8，-119.9 (d, 1F). HRMS (ESI-FT) calcd for **$[M+Na]^+$ $C_{20}H_{15}FN_2O_4Na^+$**, m/z: 389.0908, observed: 389.0890. IR: 1750, 1721, 1504, 1388, 1240, 1194, 817, 761, 730, 680 cm^{-1}.

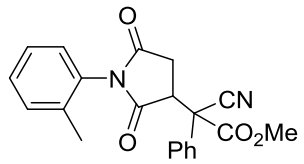


	Retention Time	Area	% Area
1	3.427	4598266	39.77
2	3.809	4628572	40.04
3	5.762	1171740	10.14
4	6.845	1162164	10.05



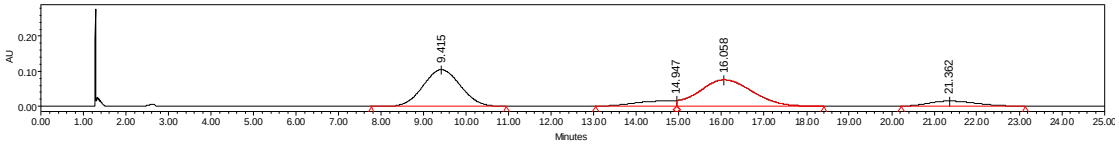
	Retention Time	Area	% Area
1	3.309	270453	3.23
2	3.680	7685474	91.78
3	5.676	57154	0.68
4	6.785	360956	4.31

Methyl 2-cyano-2-(2,5-dioxo-1-(o-tolyl)pyrrolidin-3-yl)-2-phenylacetate (3al)

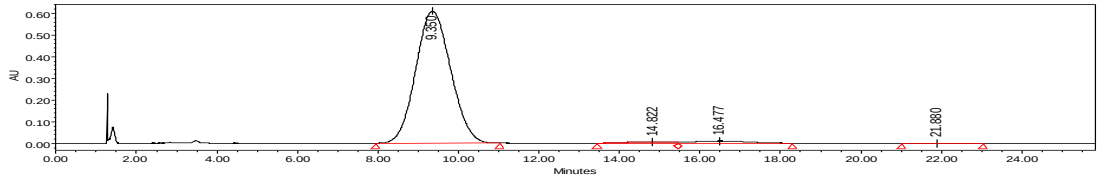


3al

White solid, 85% yield, >19:1 dr, 93% ee, mp: 152-155 ℃. $[\alpha]_D^{19}$ = –51.5 (*c*: 0.39, CH_2Cl_2); Determined by UPC^2 analysis [Daicel chiralcel OD-3, $scCO_2/^iPrOH$ = 92/8, 1.0 mL/min, λ = 219.0 nm, t (major$_{isomer}$)) = 9.35, 16.48 min, t (minor$_{isomer}$)) = 14.82, 21.88 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.61 (m, 2H), 7.55 – 7.42 (m, 3H), 7.38 – 7.27 (m, 3H), 7.21 – 7.00 (m, 1H), 4.52 – 4.36 (m, 1H, rotamer), 3.87 (s, 3H), 2.93 – 2.74 (m, 1H, rotamer), 2.66 – 2.49 (m, 1H, rotamer), 2.25 and 2.16 (s, 3H, rotamer). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0 and 173.9 (rotamer), 172.8 and 172.7 (rotamer), 166.6, 136.2, 135.3, 131.4, 131.1, 130.3 and 130.3 (rotamer), 130.0 and 130.0 (rotamer), 129.9 and 129.8 (rotamer), 128.2 and 127.7 (rotamer), 127.3 and 126.9 (rotamer), 126.6 and 126.5 (rotamer), 116.1 and 115.8 (rotamer), 55.5 and 55.1 (rotamer), 54.6, 47.7 and 47.1 (rotamer), 31.8 and 31.7 (rotamer), 17.9 and 17.7 (rotamer). HRMS (ESI-FT) calcd for **[M+Na]$^+$ $C_{21}H_{18}N_2O_4Na^+$**, m/z: 385.1159, observed: 385.1164. IR: 1721, 1264, 896, 731, 703 cm^{-1}.

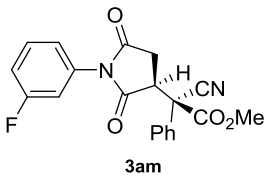


	Retention Time	Area	% Area
1	9.415	6440618	42.37
2	14.947	997951	6.57
3	16.058	6594736	43.38
4	21.362	1167692	7.68



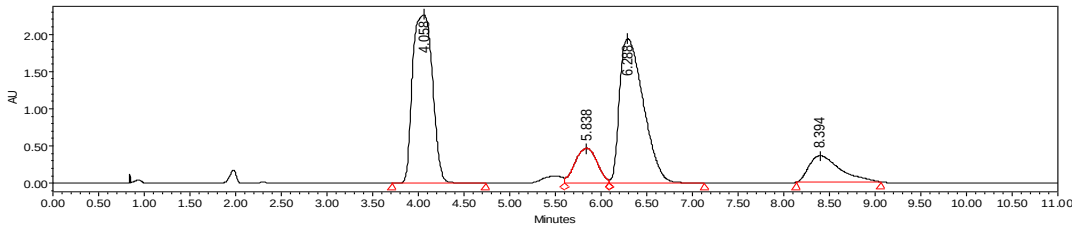
	Retention Time	Area	% Area
1	9.350	36869712	95.46
2	14.822	578301	1.50
3	16.477	1103569	2.86
4	21.880	71150	0.18

Methyl 2-cyano-2-[1-(3-fluorophenyl)-2,5-dioxopyrrolidin-3-yl]-2-phenylacetate (3am)

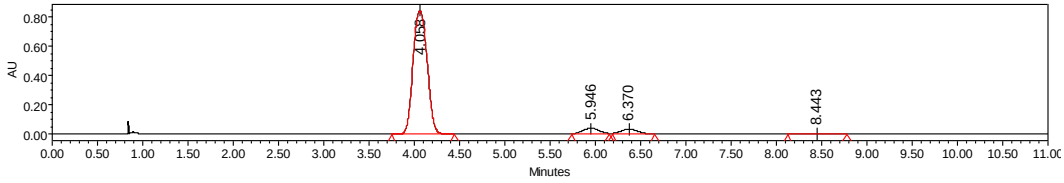


3am

White solid, 65% yield, 16:1 dr, 91% ee, mp: 119-122 ℃. $[\alpha]_D^{16}$ = –72.5 (*c*: 0.34, CH_2Cl_2); Determined by UPC[2] analysis [Daicel chiralcel OD-3, $scCO_2$/^{i}PrOH = 90/10, 1.5 mL/min, λ = 235.0 nm, t ($major_{isomer}$)) = 4.06, 6.37 min, t ($minor_{isomer}$)) = 5.95, 8.44 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.61 (m, 2H), 7.53 – 7.39 (m, 4H), 7.18 – 7.06 (m, 3H), 4.41 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.89 (s, 3H), 2.83 (dd, *J* = 18.8, 9.6 Hz, 1H), 2.55 (dd, *J* = 18.4, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 172.3, 166.5, 163.9 (*J* = 246.5 Hz, 1C), 132.4 (*J* = 10.1 Hz, 1C), 130.9, 130.5 (*J* = 8.8 Hz, 1C), 130.1, 129.8, 126.5, 122.2 (*J* = 3.3 Hz, 1C), 116.3 (*J* = 20.6 Hz, 1C), 115.8, 114.2 (*J* = 24.4 Hz, 1C), 55.3, 54.7, 47.1, 31.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.7 (s, 1F). HRMS (ESI-FT) calcd for **[M+Na]$^+$ $C_{20}H_{15}FN_2O_4Na^+$**, m/z: 389.0908, observed: 389.0898. IR: 1750, 1719, 1599, 1492, 1452, 1384, 1237, 1177, 843, 775, 730, 704 cm^{-1}.

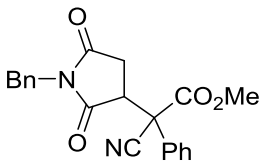


	Retention Time	Area	% Area
1	4.058	7868603	39.94
2	5.838	34203507	9.19
3	6.288	35086322	40.97
4	8.394	8487091	9.91



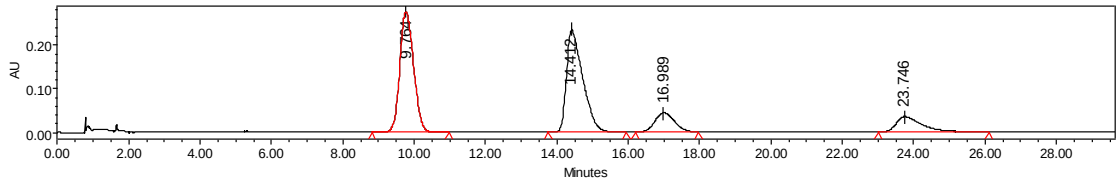
	Retention Time	Area	% Area
1	4.058	9099367	90.66
2	5.946	457321	4.56
3	6.370	408199	4.07
4	8.443	72159	0.72

Methyl 2-(1-benzyl-2,5-dioxopyrrolidin-3-yl)-2-cyano-2-phenylacetate (3an)

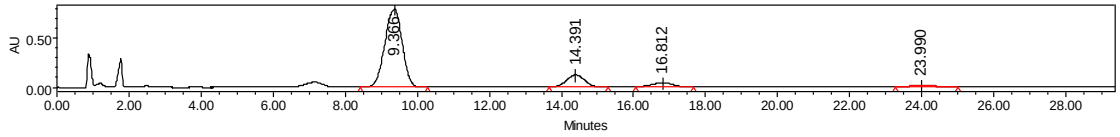


3an

Colorless oily, 36% yield, 7:1 dr, 72% ee, $[\alpha]_D^{19} = -11.6$ (*c*: 0.63, CH_2Cl_2); Determined by UPC[2] analysis [Daicel chiralcel OX-3, $scCO_2$/MeOH = 95/5, 1.5 mL/min, λ = 214.0 nm, t ($major_{isomer}$) = 9.37, 14.39 min, t ($minor_{isomer}$) = 16.81, 23.99 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.54 (m, 2H), 7.46 – 7.41 (m, 3H), 7.39 – 7.34 (m, 2H), 7.33 – 7.27 (m, 3H), 4.70 (dd, *J* = 14.0, 30.4 Hz, 2H), 4.22 (dd, *J* = 9.2, 7.6 Hz, 1H), 3.89 (s, 3H), 2.61 (dd, *J* = 18.4, 9.6 Hz, 1H), 2.36 (dd, *J* = 18.4, 6.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 173.4, 166.6, 135.0, 131.1, 129.9, 129.7, 128.7, 128.7, 128.2, 126.4, 115.7, 54.8, 54.6, 47.0, 42.9, 31.5. HRMS (ESI-FT) calcd for **[M+Na]$^+$ $C_{21}H_{18}N_2O_4Na^+$**, m/z: 385.1159, observed: 385.1162. IR: 1751, 1711, 1399, 1264, 1169, 817, 731, 701 cm^{-1}.

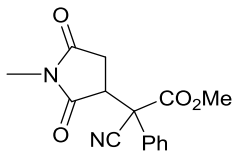


	Retention Time	Area	% Area
1	9.764	7334510	40.88
2	14.412	7326609	40.83
3	16.989	1630771	9.09
4	23.746	1651163	9.20



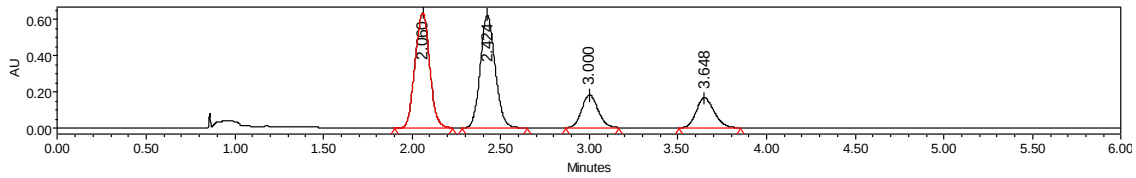
	Retention Time	Area	% Area
1	9.366	26410074	80.15
2	14.391	4247999	12.89
3	16.812	1636591	4.97
4	23.990	654148	1.99

Methyl 2-cyano-2-(1-methyl-2,5-dioxopyrrolidin-3-yl)-2-phenylacetate (3ao)

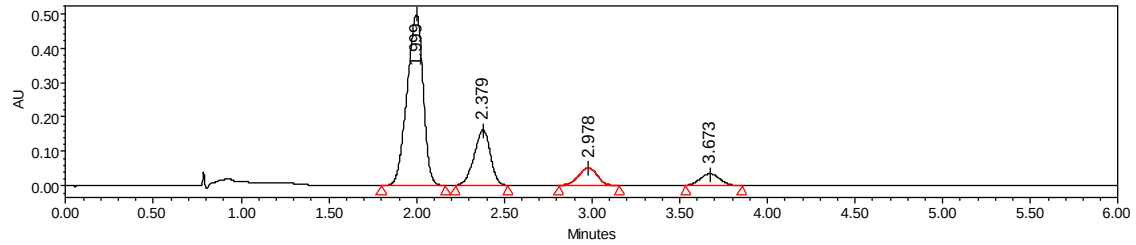


3ao

Colorless oily, 54% yield, 5:1 dr, 50% ee, $[\alpha]_D^{19}$ = –11.1 (*c*: 0.21, CH_2Cl_2); Determined by UPC^2 analysis [Daicel chiralcel OX-3, $scCO_2$/^{i}PrOH = 85/15, 1.5 mL/min, λ = 224.0 nm, t (major$_{isomer}$) = 2.00, 2.38 min, t (minor$_{isomer}$) = 2.98, 3.67 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.32 (m, 5H), 4.15 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.83 (s, 3H), 2.99 (s, 3H), 2.57 (dd, *J* = 18.4, 9.2 Hz, 1H), 2.30 (dd, *J* = 18.4, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.8, 172.7, 165.6, 130.1, 128.9, 128.7, 125.4, 114.7, 53.9, 53.6, 46.1, 30.4, 24.2. HRMS (ESI-FT) calcd for **[M+Na]$^+$ $C_{15}H_{14}N_2O_4Na^+$**, m/z: 309.0846, observed: 309.0845. IR: 1747, 1701, 1436, 1384, 1284, 1241, 1118, 978, 731, 695 cm^{-1}.

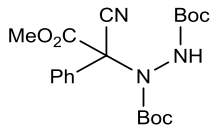


	Retention Time	Area	% Area
1	2.060	3633845	37.84
2	2.424	3638673	37.89
3	3.000	1159924	12.08
4	3.648	1171882	12.20



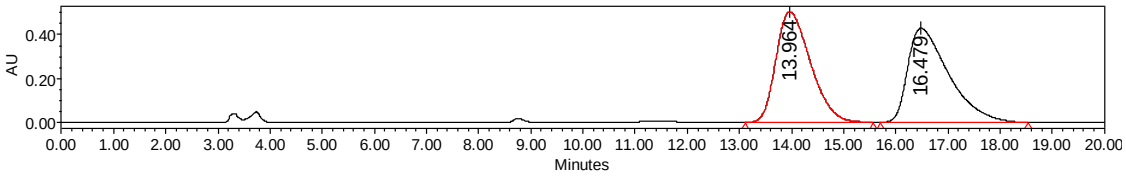
	Retention Time	Area	% Area
1	1.999	3150944	65.26
2	2.379	1035094	21.44
3	2.978	377262	7.81
4	3.673	264909	5.49

Di-tert-butyl 1-(1-cyano-2-methoxy-2-oxo-1-phenylethyl)hydrazine-1,2-dicarboxylate (5aa)

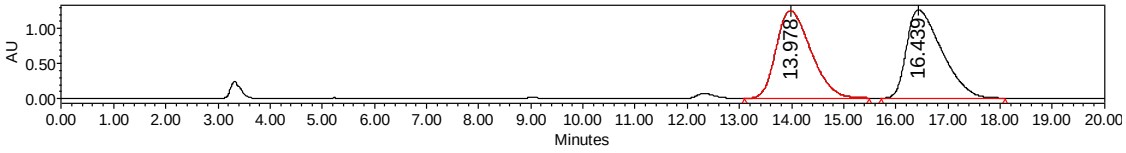


5aa

Colorless oily, 66% yield, 0% ee; Determined by HPLC analysis [Daicel chiralcel IB, *n*-Hexane /^{i}PrOH = 95/5, 1.0 mL/min, λ = 220 nm, t_1 = 13.98 min, t_2 = 16.44 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.55 (m, 2H), 7.48 – 7.33 (m, 3H), 6.30 – 5.87 (m, 1H), 3.88 – 3.75 (m, 3H), 1.58 – 1.23 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 164.7, 153.0, 129.6/129.2(rotamer), 129.1/129.0(rotamer), 128.4, 128.2/127.9 (rotamer), 127.2/127.0(rotamer), 114.6, 82.2, 80.6, 76.3, 53.3, 27.1, 27.0, 26.9. HRMS (ESI-FT) calcd for **[M+Na]$^{+}$ $C_{20}H_{27}N_3O_6Na^{+}$**, m/z: 428.1792, observed: 428.1797. IR: 1739, 1264, 1153, 907, 731, 705 cm^{-1}.

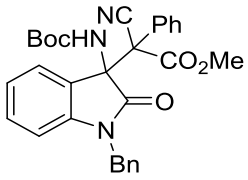


	Retention Time	Area	% Area
1	13.964	23149540	49.85
2	16.479	23285563	50.15



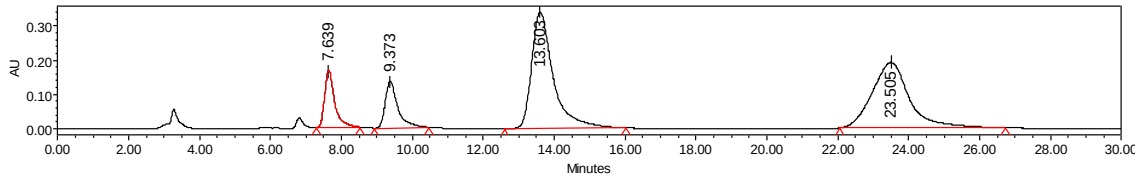
	Retention Time	Area	% Area
1	13.978	57670214	49.40
2	16.439	59078987	50.60

Methyl 2-(1-benzyl-3-((tert-butoxycarbonyl)amino)-2-oxoindolin-3-yl)-2-cyano-2-phenylacetate (6aa)

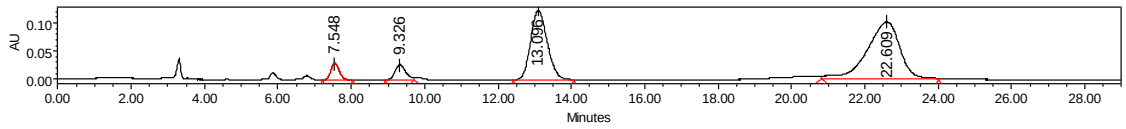


6aa

Colorless oily, 69% yield, 10:1 dr, 22% ee; Determined by HPLC analysis [Daicel chiralcel ADH, *n*-Hexane /^{i}PrOH = 80/20, 1.0 mL/min, λ = 228 nm, t (major$_{isomer}$) = 13.10, 22.61 min, t (minor$_{isomer}$) = 7.55, 9.33 min]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.32 (m, 1H), 7.27 – 7.21 (m, 2H), 7.20 – 7.06 (m, 6H), 6.97 – 6.83 (m, 1H), 6.79 (t, J = 7.6 Hz, 1H), 6.57 (s, 1H), 6.50 (d, J = 7.6 Hz, 1H), 4.92 – 4.76 (m, 1H), 4.72 – 4.55 (m, 1H), 3.83 (s, 3H), 1.17 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ173.2, 166.6, 153.9, 144.2, 135.1, 130.3, 129.8, 129.0, 128.6, 128.3, 128.0, 127.5, 127.4, 125.8, 124.5, 122.3, 115.0, 109.5, 80.9, 65.8, 57.9, 54.7, 44.6, 28.0. HRMS (ESI-FT) calcd for **[M+Na]$^{+}$ $C_{30}H_{29}N_3O_5Na^{+}$**, m/z: 534.1999, observed: 534.1993. IR: 1724, 1611, 1486, 1263, 1241, 1162, 906, 731, 703 cm^{-1}.



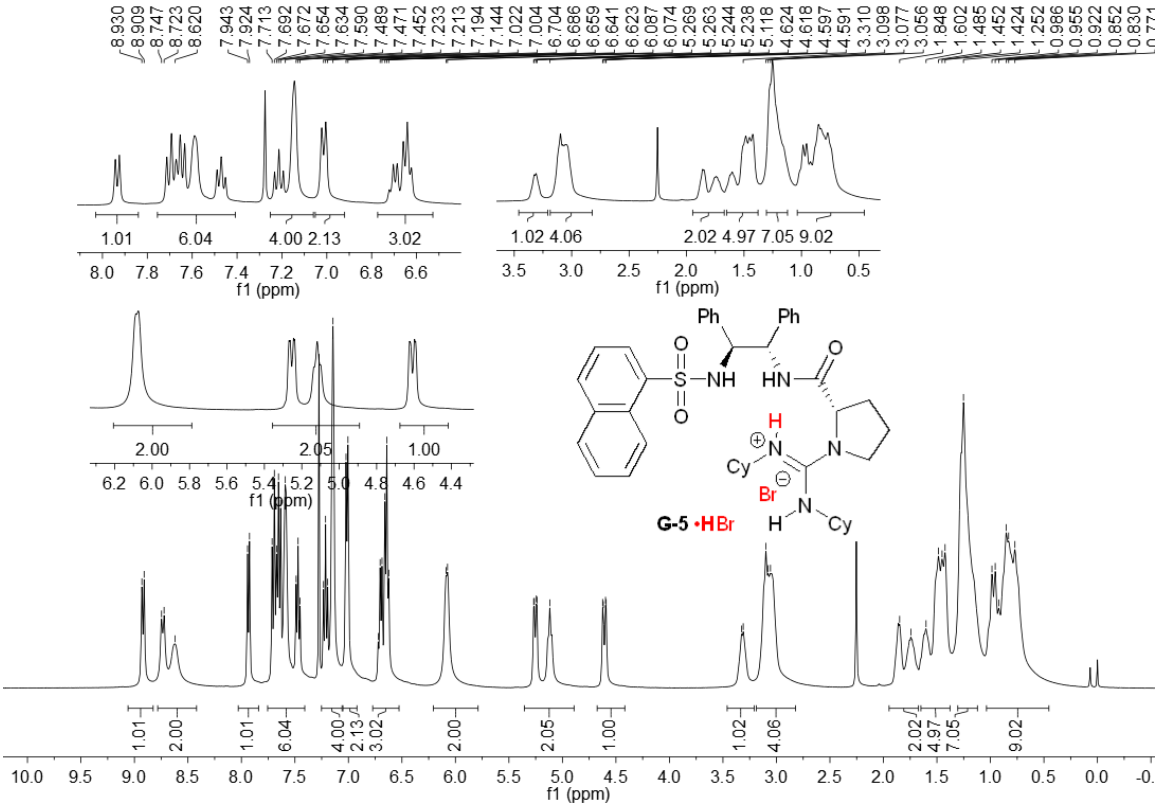
	Retention Time	Area	% Area
1	7.639	3266876	9.33
2	9.373	3331704	9.51
3	13.603	14410318	41.15
4	23.505	14011513	40.01

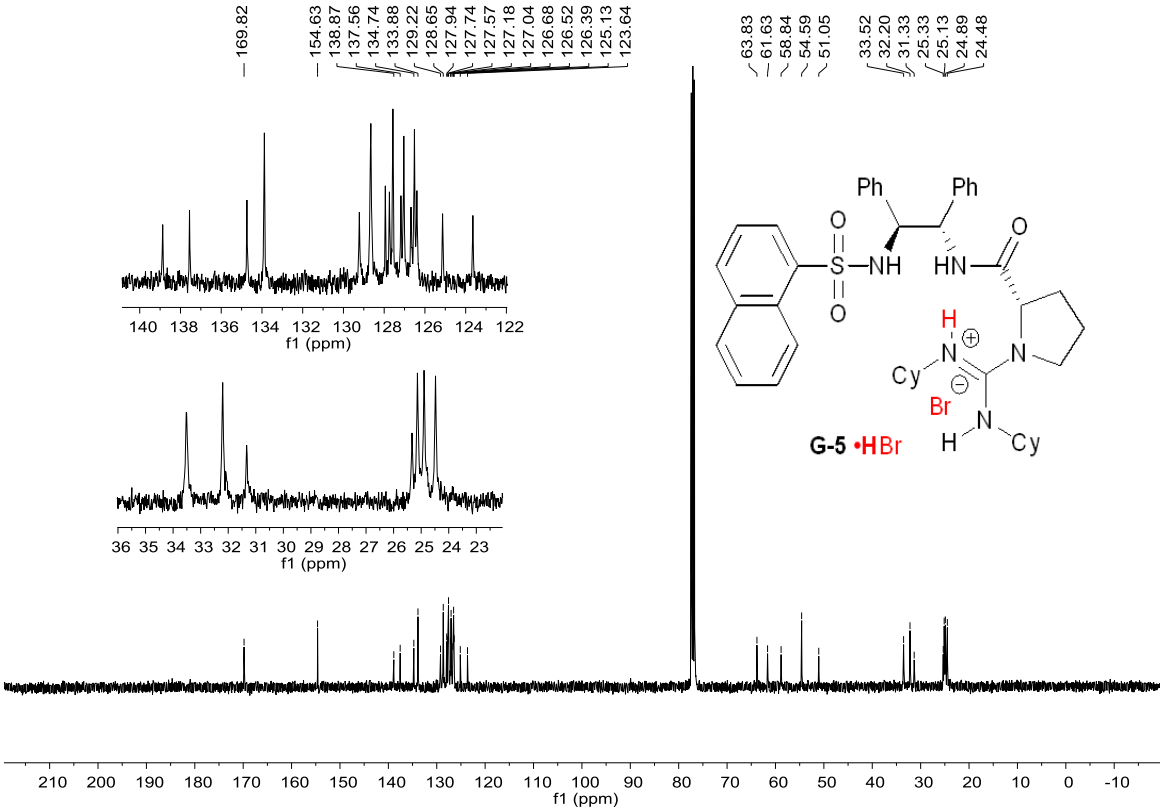


	Retention Time	Area	% Area
1	7.548	468756	4.25
2	9.326	562038	5.10
3	13.096	3862692	35.03
4	22.609	6133507	55.62

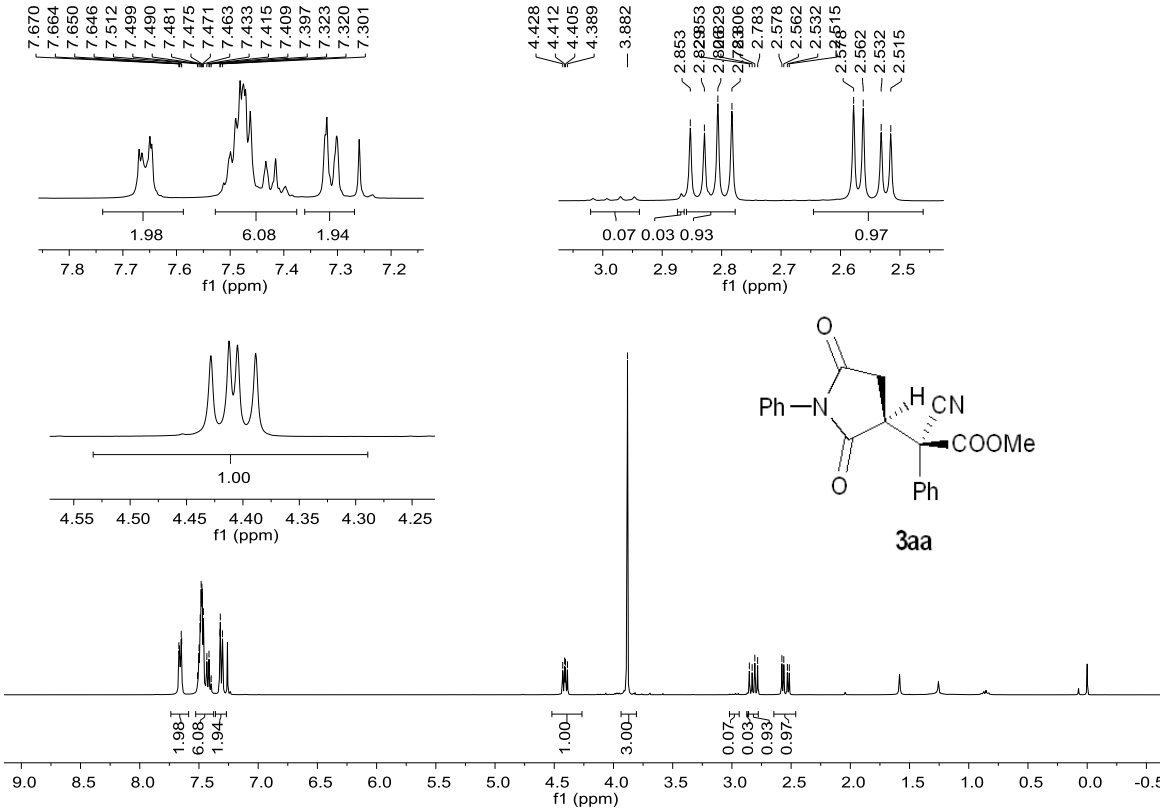
8. NMR spectra

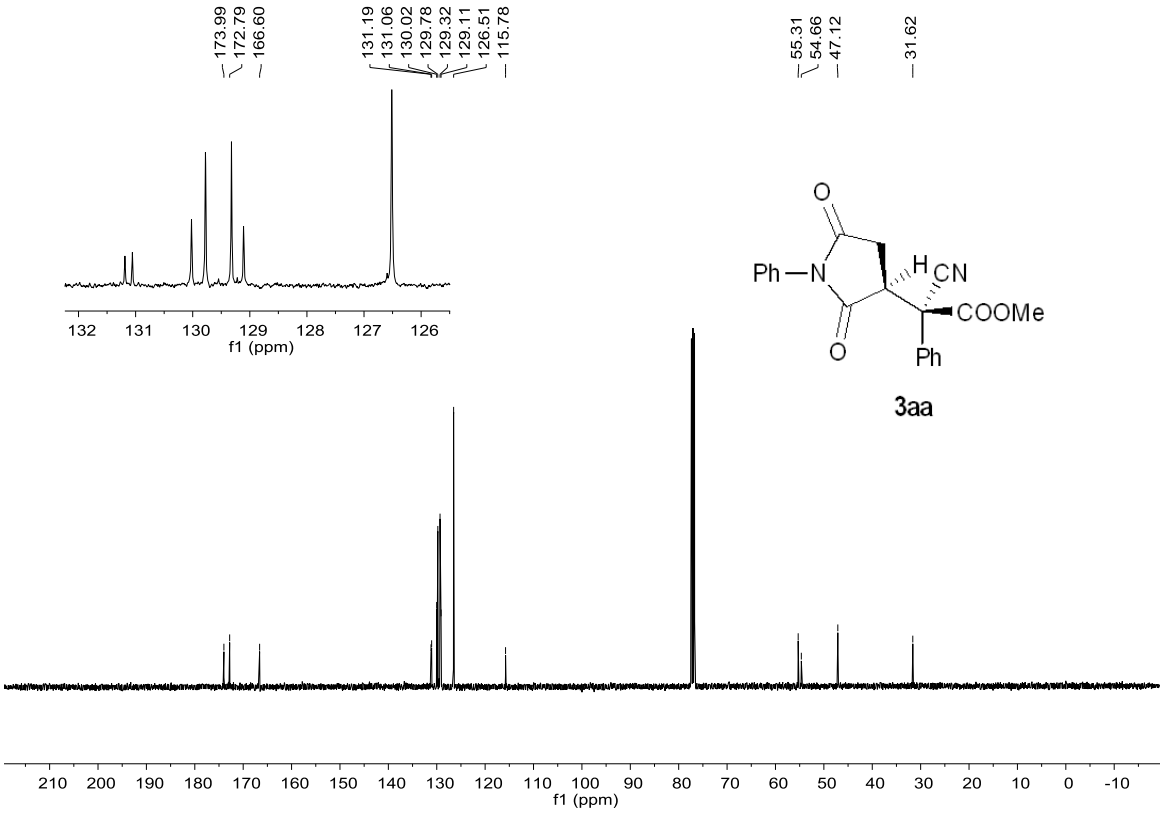
G-5 • HBr



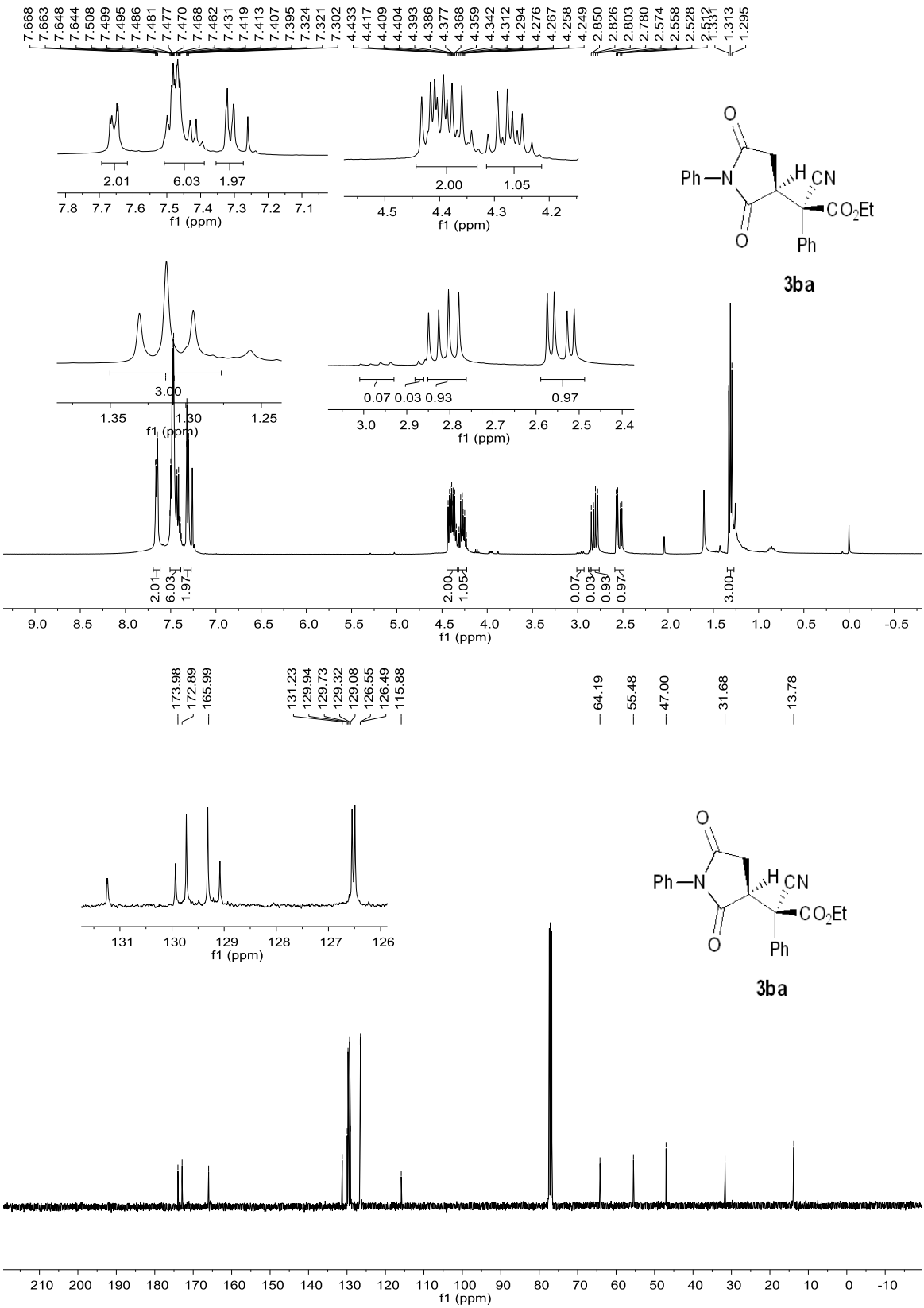


3aa


7.670
7.664
7.650
7.646
7.512
7.499
7.490
7.481
7.475
7.471
7.463
7.433
7.415
7.409
7.397
7.323
7.320
7.301
1.98
6.08
1.94
f1 (ppm)
4.428
4.412
4.405
4.389
3.882
2.853
2.783
2.578
2.562
2.532
2.515
0.07 0.03 0.93
0.97
f1 (ppm)
1.00
f1 (ppm)
Ph—N
H
CN
COOMe
Ph
O
3aa
1.98
6.08
1.94
1.00
3.00
0.07
0.03
0.93
0.97
f1 (ppm)


173.99
172.79
166.60
131.19
131.06
130.02
129.78
129.32
129.11
126.51
115.78
55.31
54.66
47.12
31.62
f1 (ppm)
Ph—N
H
CN
COOMe
Ph
O
3aa
f1 (ppm)

3ba


7.668 7.663 7.648 7.644 7.508 7.499 7.495 7.486 7.481 7.477 7.470 7.468 7.462 7.431 7.419 7.413 7.407 7.395 7.324 7.321 7.302
4.433 4.417 4.409 4.404 4.393 4.386 4.377 4.368 4.359 4.342 4.312 4.294 4.276 4.267 4.258 4.249
2.850 2.826 2.803 2.780 2.574 2.558 2.528 2.511 1.331 1.313 1.295
2.01 6.03 1.97
2.00 1.05
f1 (ppm)
Ph—N
H
CN
CO2Et
Ph
3ba
3.00
0.07 0.03 0.93 0.97
2.01 6.03 1.97 2.00 1.05 0.07 0.03 0.93 0.97 3.00
f1 (ppm)
173.98 172.89 165.99 131.23 129.94 129.73 129.32 129.08 126.55 126.49 115.88 64.19 55.48 47.00 31.68 13.78
f1 (ppm)
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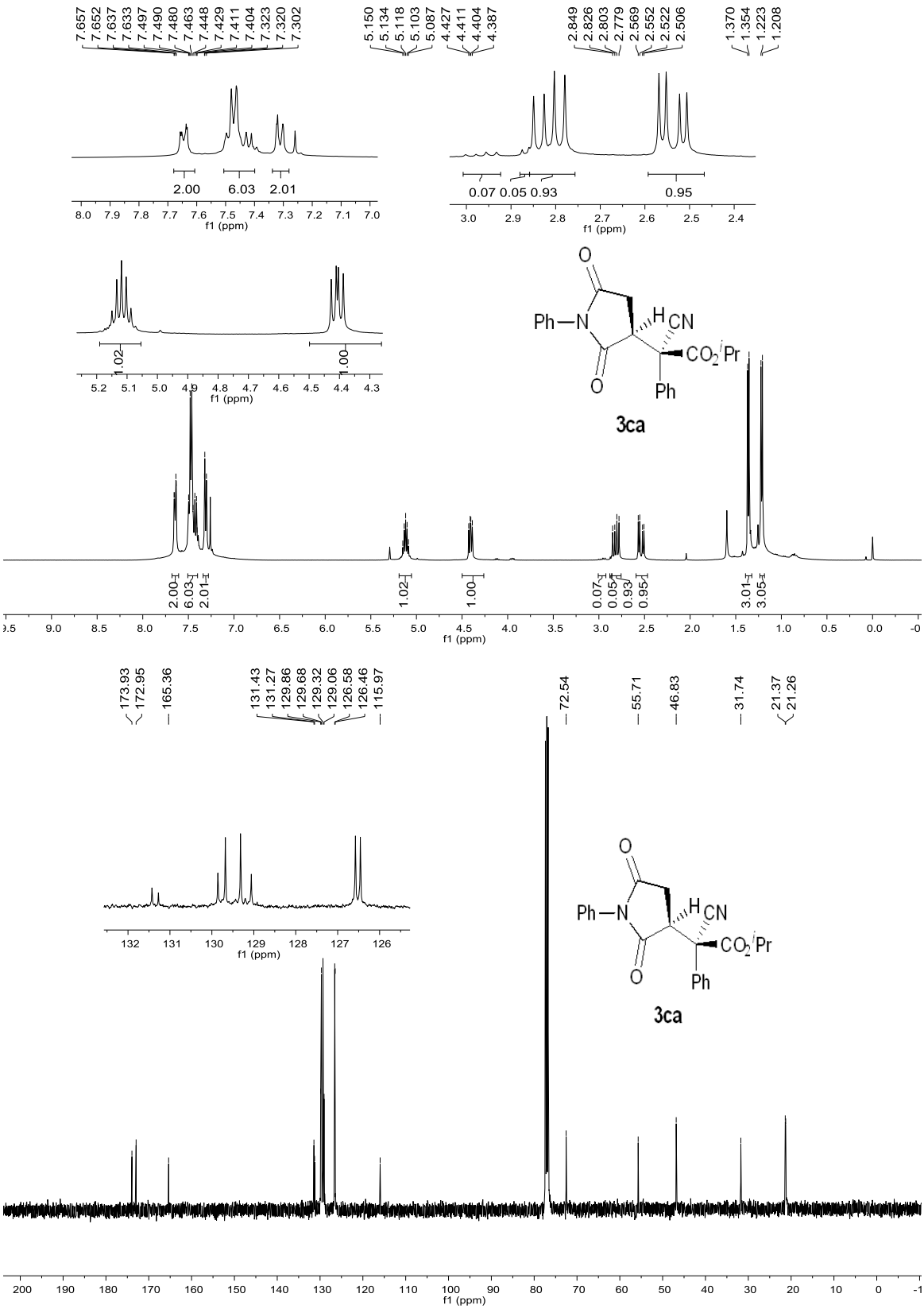
H
CN
CO2Et
Ph
3ba
f1 (ppm)

3ca


7.657
7.652
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7.404
7.323
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5.150
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5.103
5.087
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4.404
4.387
2.849
2.826
2.803
2.779
2.569
2.552
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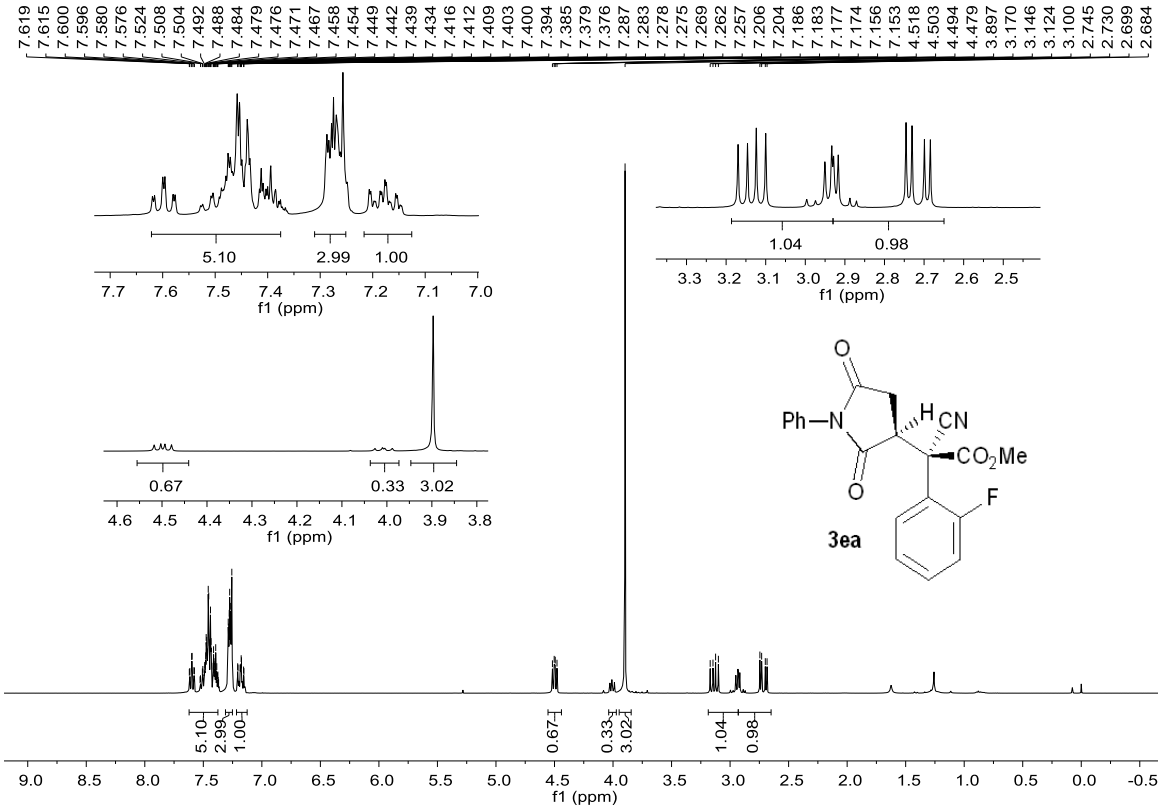
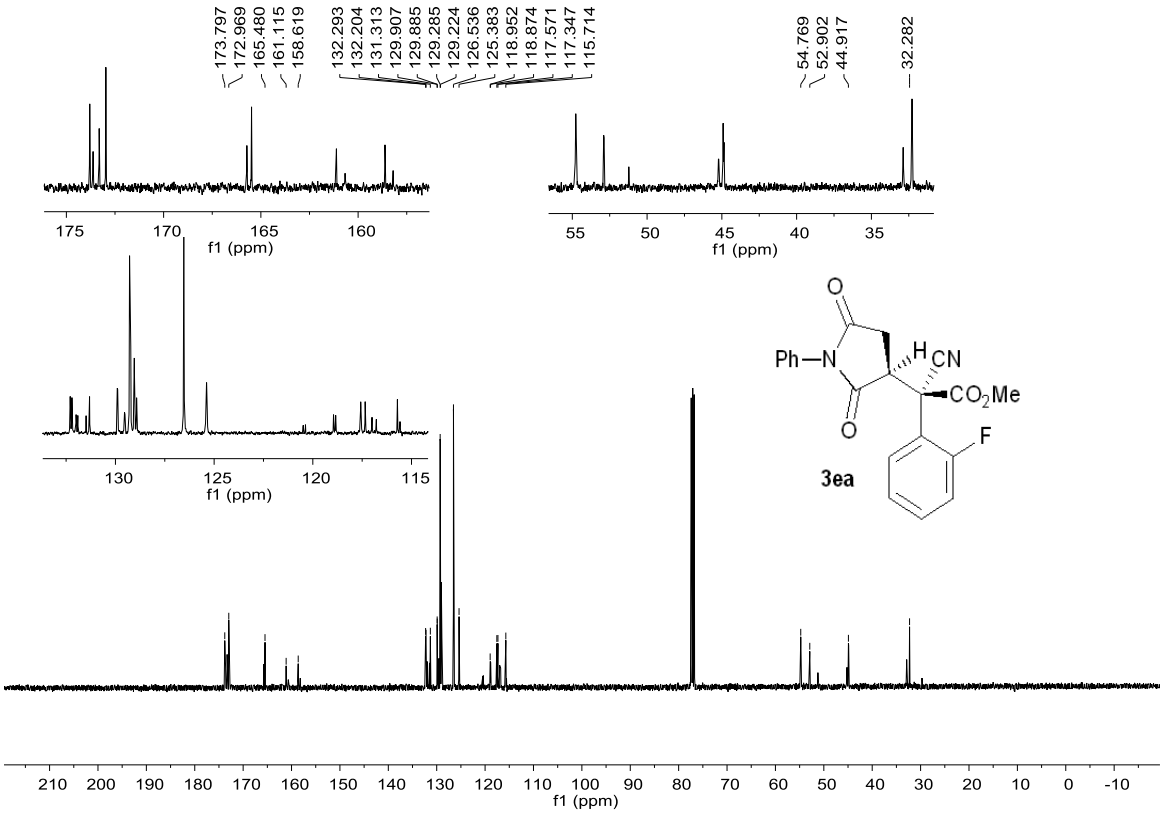
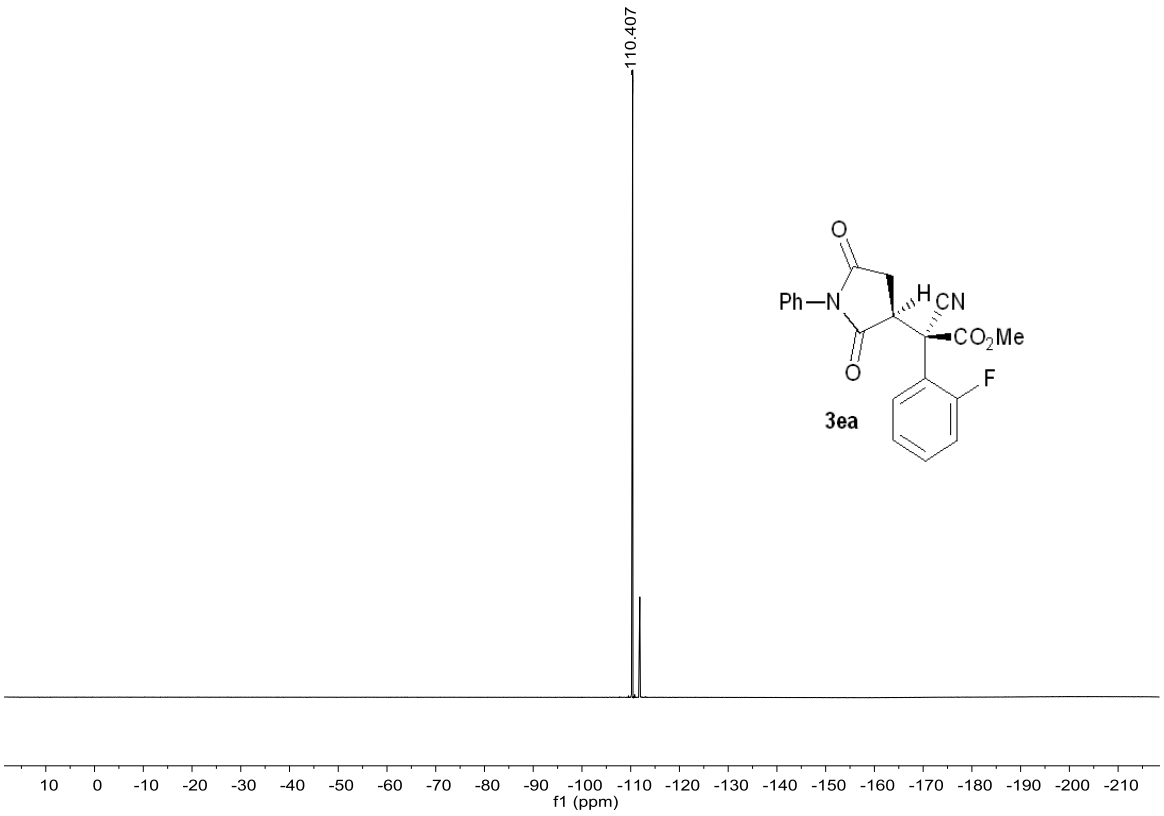
1.354
1.223
1.208
2.00
6.03
2.01
0.07 0.05 0.93
0.95
1.02
1.00
f1 (ppm)
Ph—N
H
CN
CO2iPr
Ph
3ca
2.00
6.03
2.01
1.02
1.00
0.07
0.05
0.93
0.95
3.01
3.05
173.93
172.95
165.36
131.43
131.27
129.86
129.68
129.32
129.06
126.58
126.46
115.97
72.54
55.71
46.83
31.74
21.37
21.26

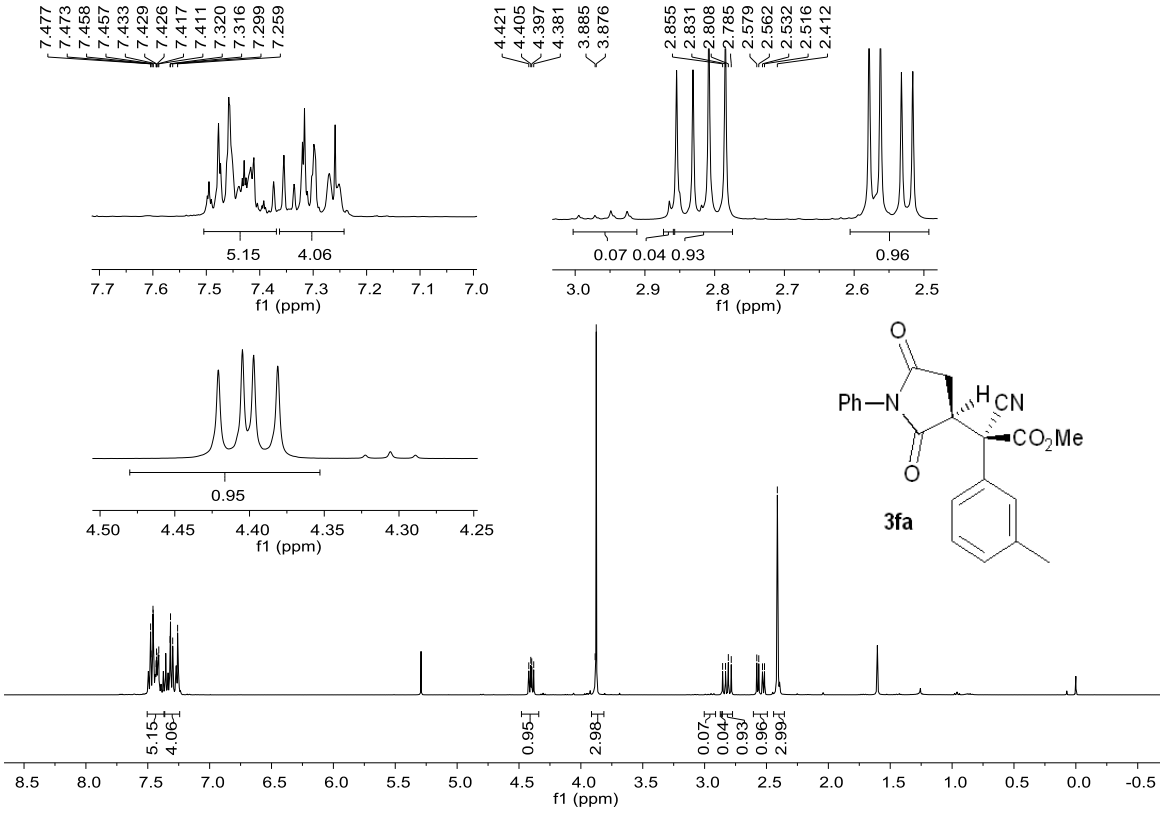
3ea

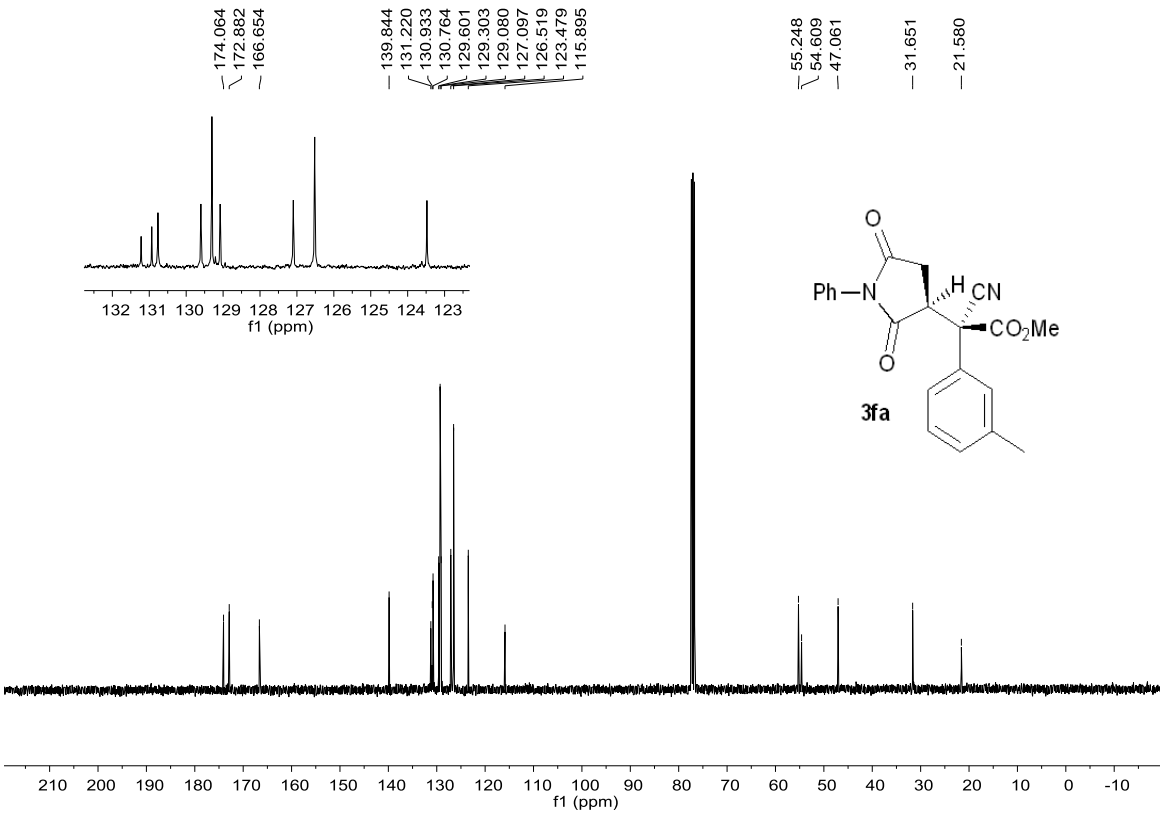

7.619 7.615 7.600 7.596 7.580 7.576 7.524 7.508 7.504 7.492 7.488 7.484 7.479 7.476 7.471 7.467 7.458 7.454 7.449 7.442 7.439 7.434 7.416 7.412 7.409 7.403 7.400 7.394 7.385 7.379 7.376 7.287 7.283 7.278 7.275 7.269 7.262 7.257 7.206 7.204 7.186 7.183 7.177 7.174 7.156 7.153 4.518 4.503 4.494 4.479 3.897 3.170 3.146 3.124 3.100 2.745 2.730 2.699 2.684
5.10 2.99 1.00
1.04 0.98
0.67 0.33 3.02
f1 (ppm)
Ph—N
H
CN
CO2Me
F
O
3ea


173.797 172.969 165.480 161.115 158.619 132.293 132.204 131.313 129.907 129.885 129.285 129.224 126.536 125.383 118.952 118.874 117.571 117.347 115.714 54.769 52.902 44.917 32.282
f1 (ppm)
Ph—N
H
CN
CO2Me
F
O
3ea

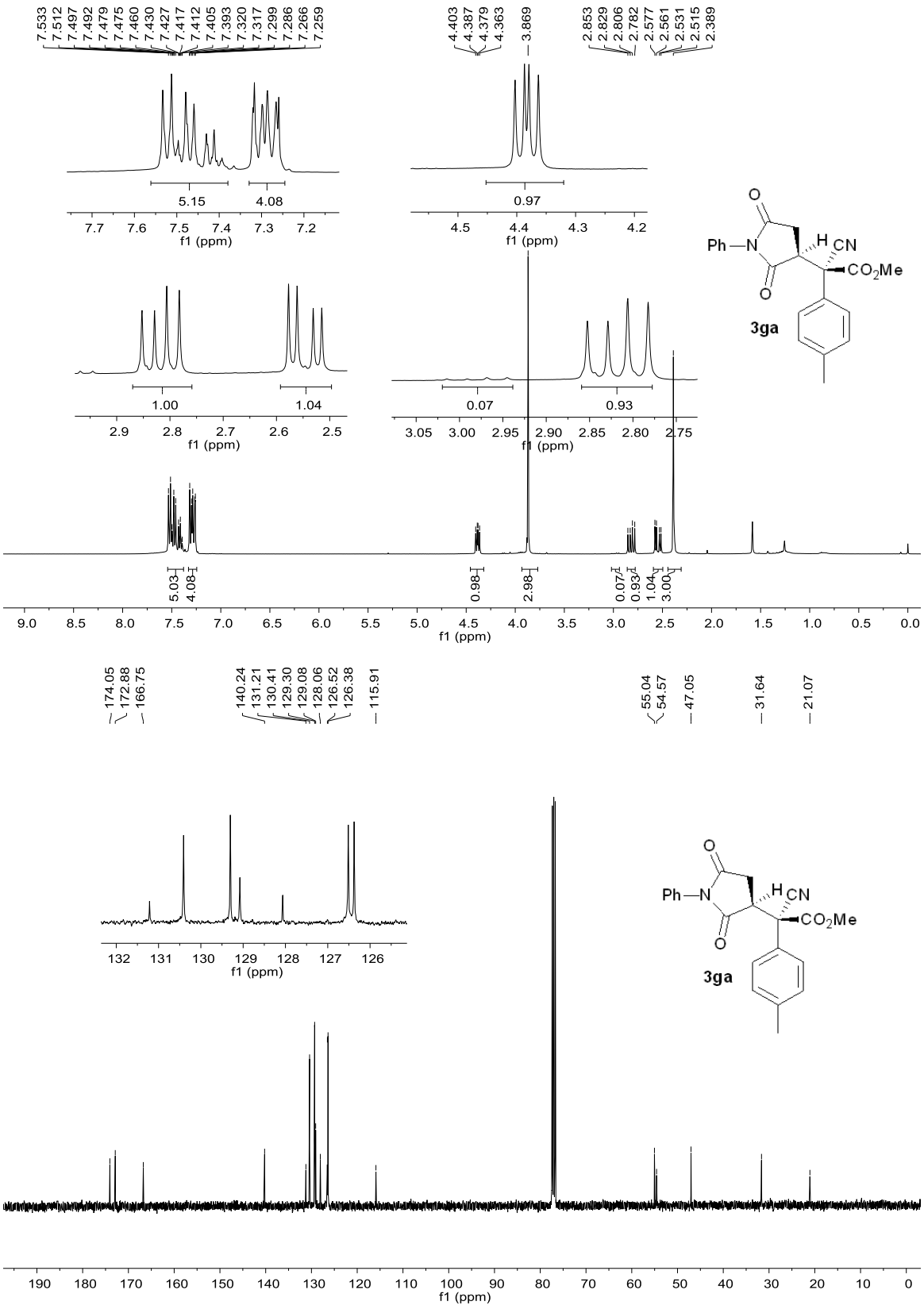

110.407
O
Ph—N
O
H
CN
CO2Me
F
3ea
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

3fa

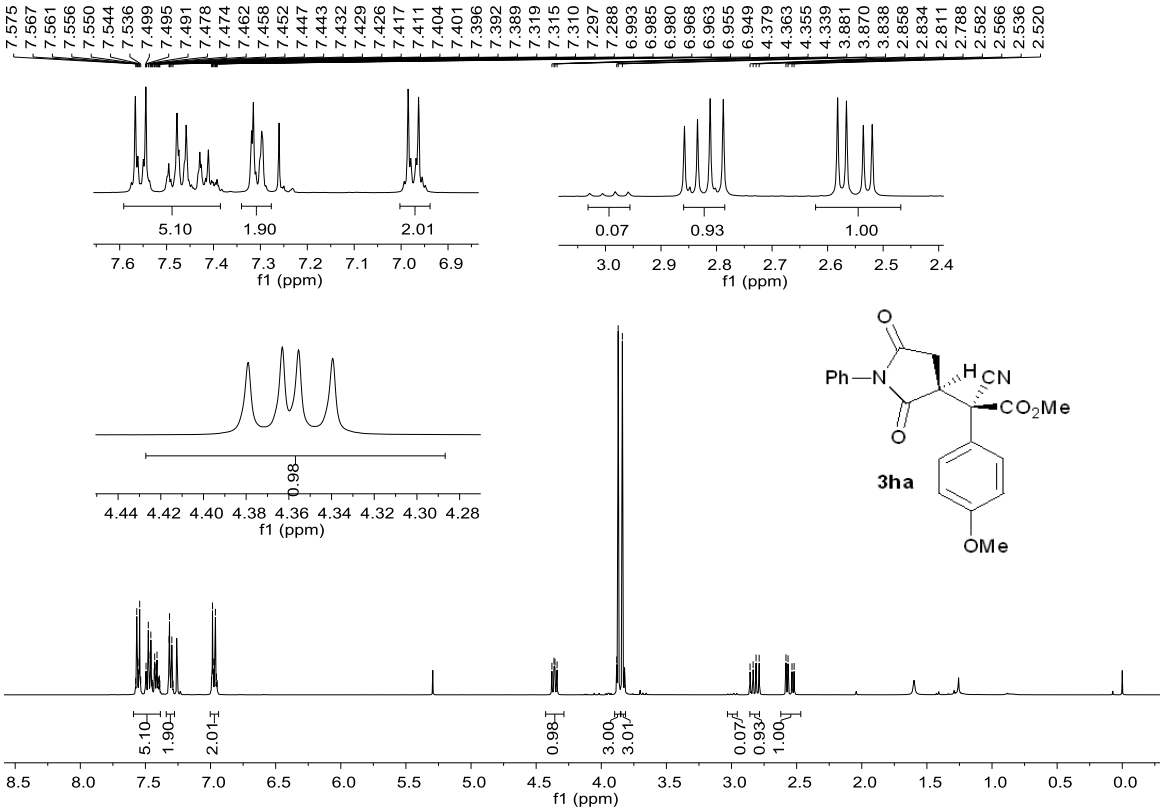

7.477
7.473
7.458
7.457
7.433
7.429
7.426
7.417
7.411
7.320
7.316
7.299
7.259
4.421
4.405
4.397
4.381
3.885
3.876
2.855
2.831
2.808
2.785
2.579
2.562
2.532
2.516
2.412
5.15
4.06
0.07 0.04 0.93
0.96
0.95
f1 (ppm)
Ph—N
H
CN
CO2Me
3fa
5.15
4.06
0.95
2.98
0.07
0.04
0.93
0.96
2.99

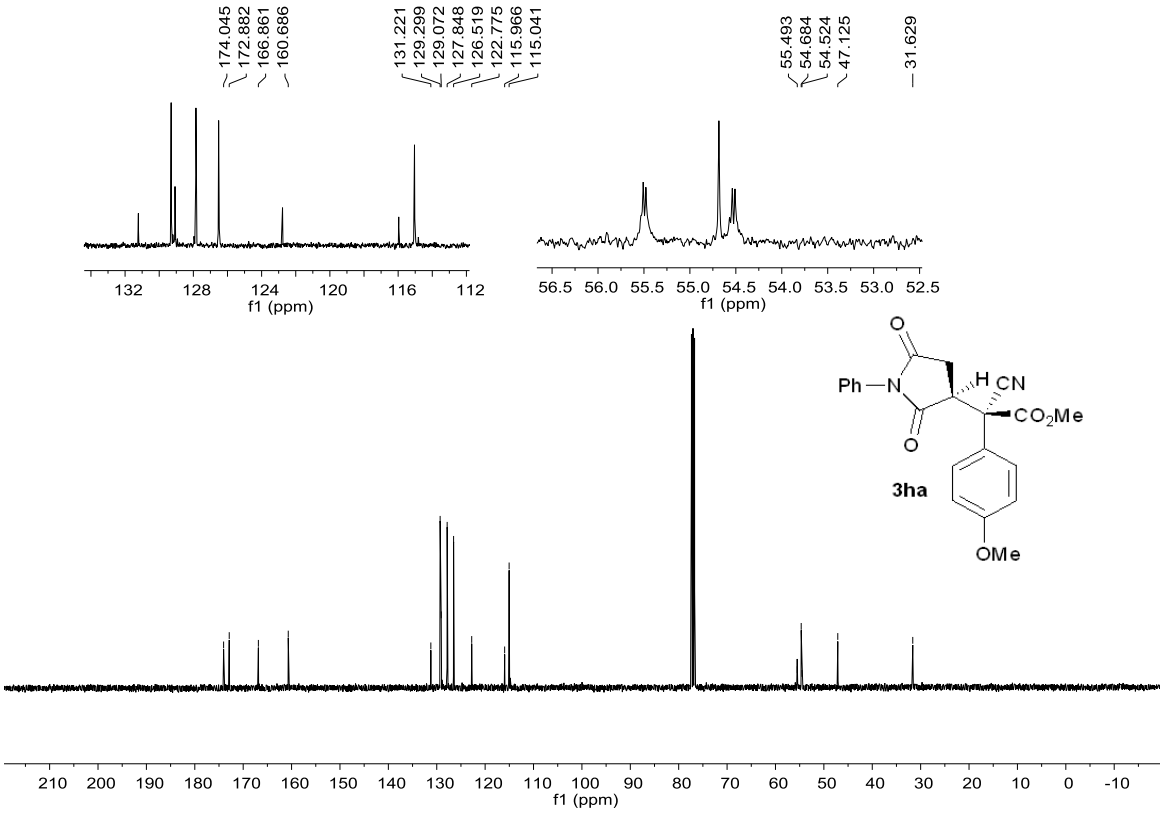

174.064
172.882
166.654
139.844
131.220
130.933
130.764
129.601
129.303
129.080
127.097
126.519
123.479
115.895
55.248
54.609
47.061
31.651
21.580
f1 (ppm)
Ph—N
H
CN
CO2Me
3fa

3ga

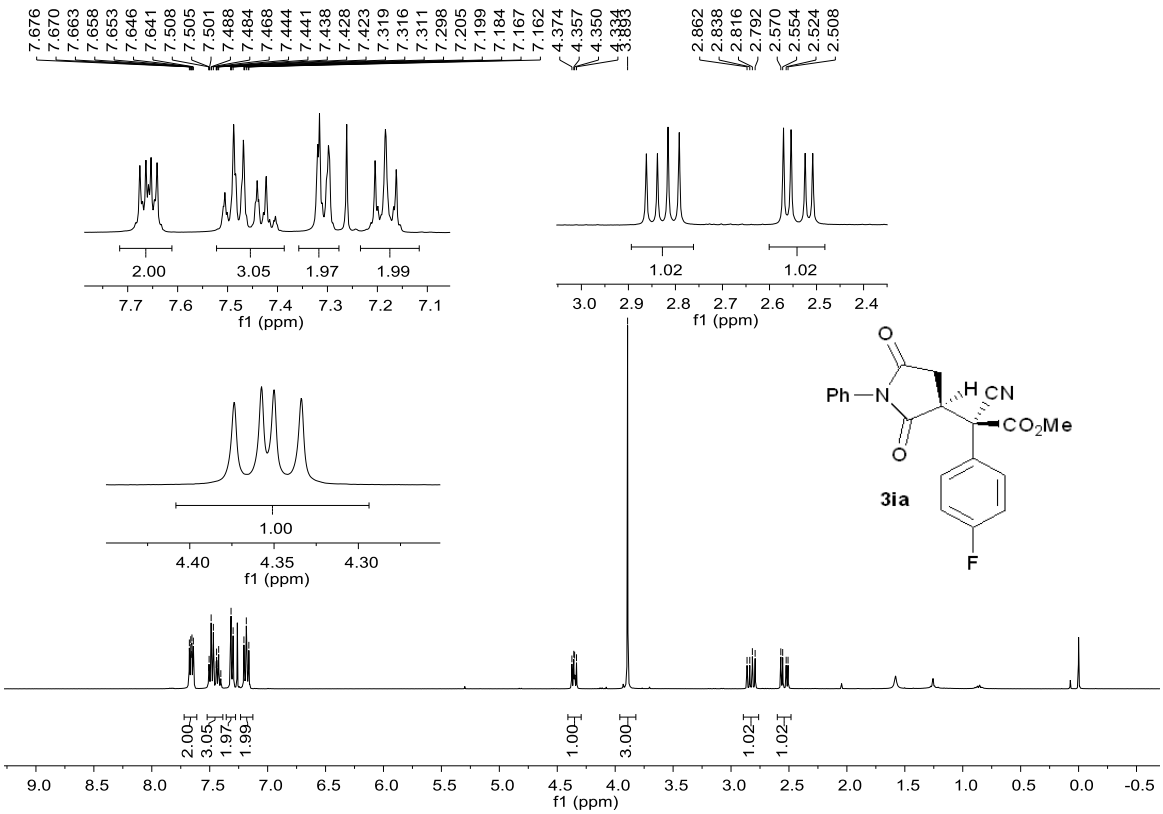

7.533
7.512
7.497
7.492
7.479
7.475
7.460
7.430
7.427
7.417
7.412
7.405
7.393
7.320
7.317
7.299
7.286
7.266
7.259
4.403
4.387
4.379
4.363
3.869
2.853
2.829
2.806
2.782
2.577
2.561
2.531
2.515
2.389
5.15
4.08
0.97
1.00
1.04
0.07
0.93
f1 (ppm)
Ph—N
H
CN
CO2Me
3ga
5.03
4.08
0.98
2.98
0.07
0.93
1.04
3.00
174.05
172.88
166.75
140.24
131.21
130.41
129.30
129.08
128.06
126.52
126.38
115.91
55.04
54.57
47.05
31.64
21.07

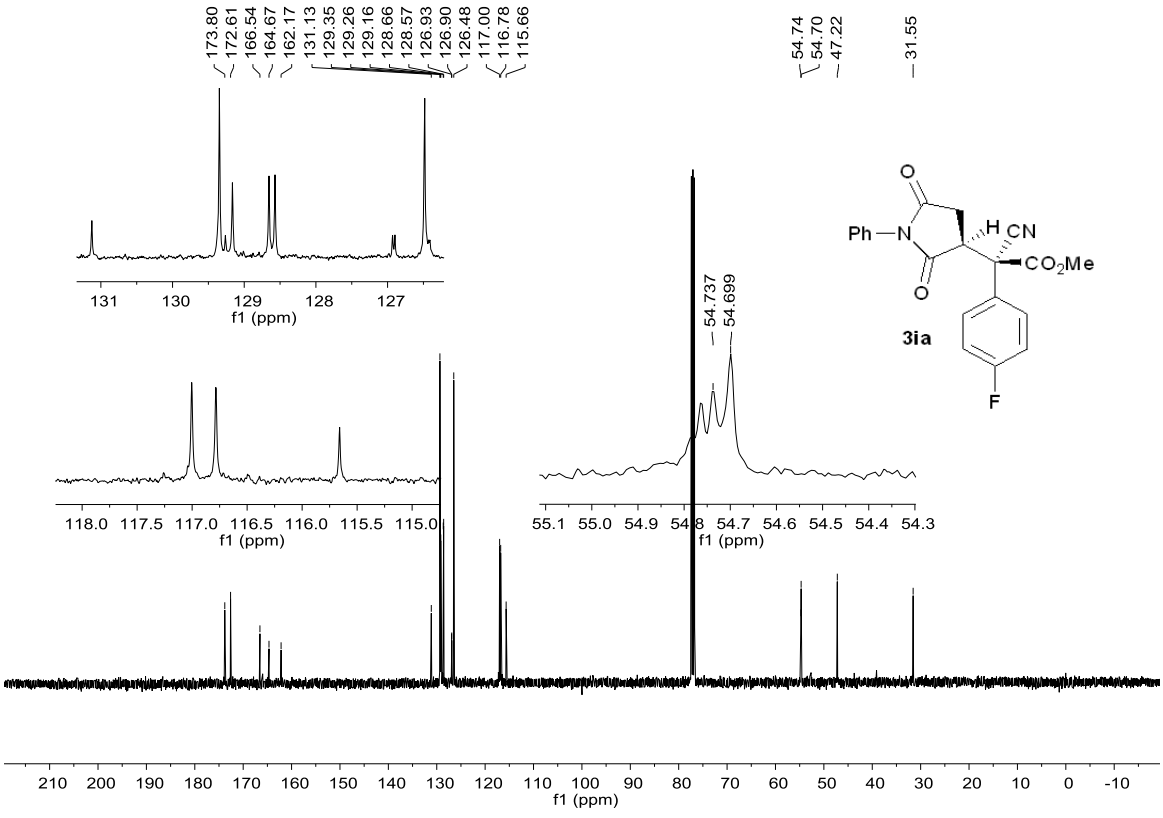
3ha

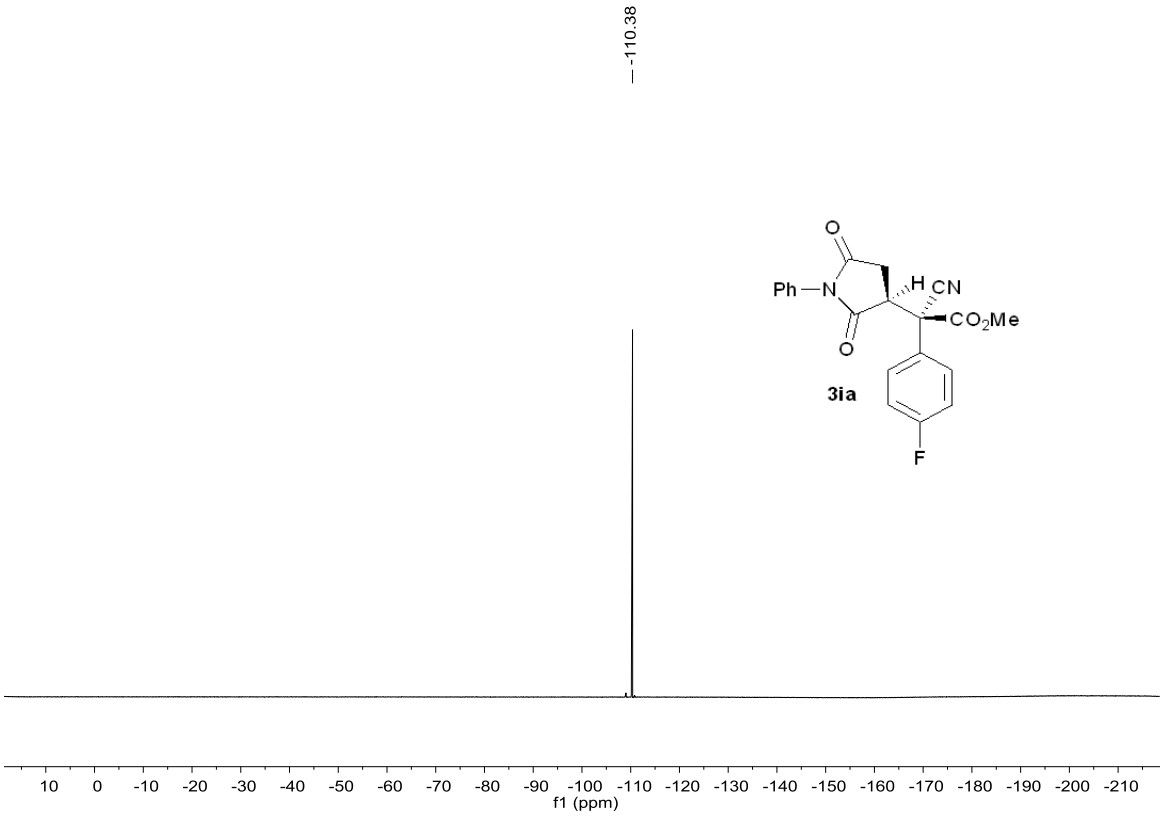

7.575 7.567 7.561 7.556 7.550 7.544 7.536 7.499 7.495 7.491 7.478 7.474 7.462 7.458 7.452 7.447 7.443 7.432 7.429 7.426 7.417 7.411 7.404 7.401 7.396 7.392 7.389 7.319 7.315 7.310 7.297 7.288 6.993 6.985 6.980 6.968 6.963 6.955 6.949 4.379 4.363 4.355 4.339 3.881 3.870 3.838 2.858 2.834 2.811 2.788 2.582 2.566 2.536 2.520
5.10 1.90 2.01
0.07 0.93 1.00
0.98
f1 (ppm)
Ph—N
H CN
CO2Me
O
3ha
OMe
5.10 1.90 2.01 0.98 3.00 3.01 0.07 0.93 1.00


174.045 172.882 166.861 160.686 131.221 129.299 129.072 127.848 126.519 122.775 115.966 115.041 55.493 54.684 54.524 47.125 31.629
f1 (ppm)
Ph—N
H CN
CO2Me
O
3ha
OMe

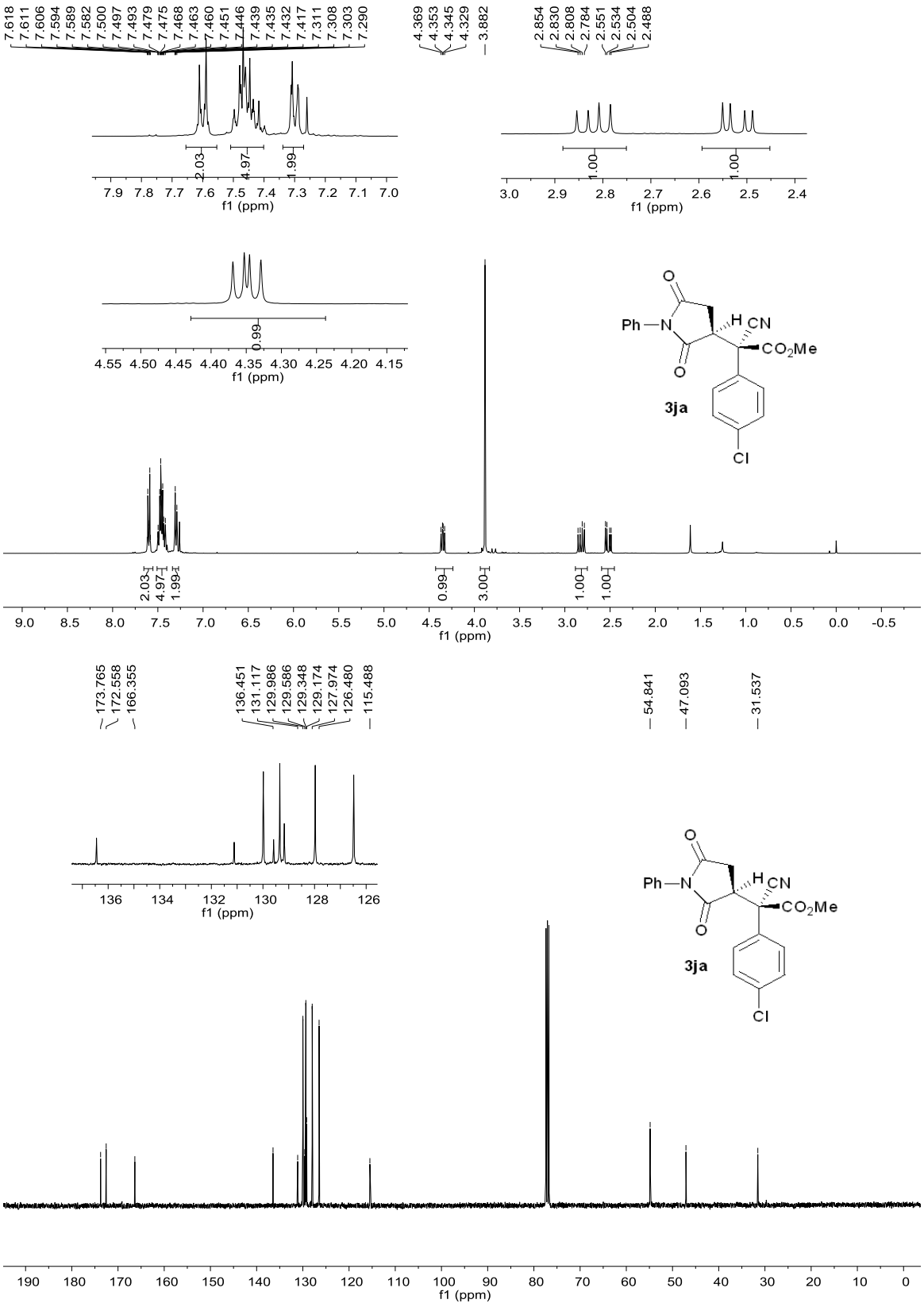
3ia


7.676
7.670
7.663
7.658
7.653
7.646
7.641
7.508
7.505
7.501
7.488
7.484
7.468
7.444
7.441
7.438
7.428
7.423
7.319
7.316
7.311
7.298
7.205
7.199
7.184
7.167
7.162
4.374
4.357
4.350
3.893
2.862
2.838
2.816
2.792
2.570
2.554
2.524
2.508
2.00
3.05
1.97
1.99
1.02
1.02
1.00
f1 (ppm)
Ph—N
H
CN
CO2Me
3ia
F

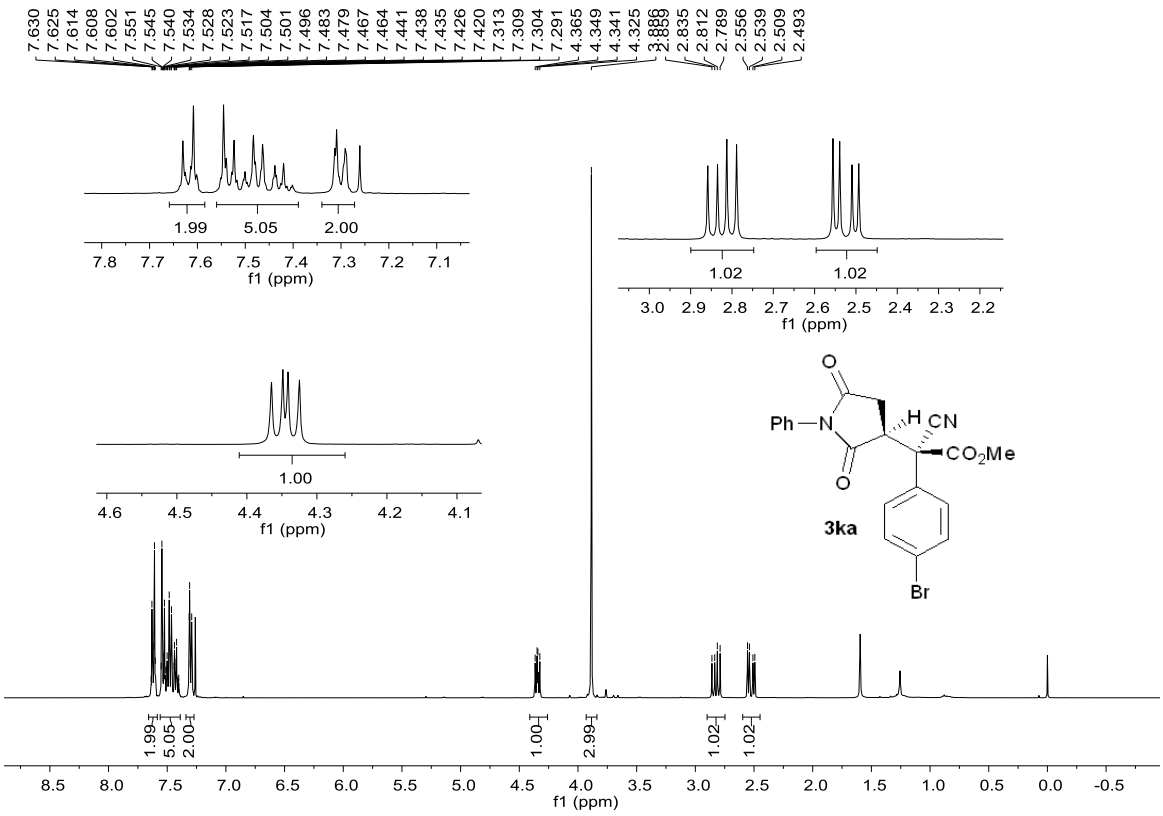

173.80
172.61
166.54
164.67
162.17
131.13
129.35
129.26
129.16
128.66
128.57
126.93
126.90
126.48
117.00
116.78
115.66
54.74
54.70
47.22
31.55
54.737
54.699
f1 (ppm)
Ph—N
H
CN
CO2Me
3ia
F

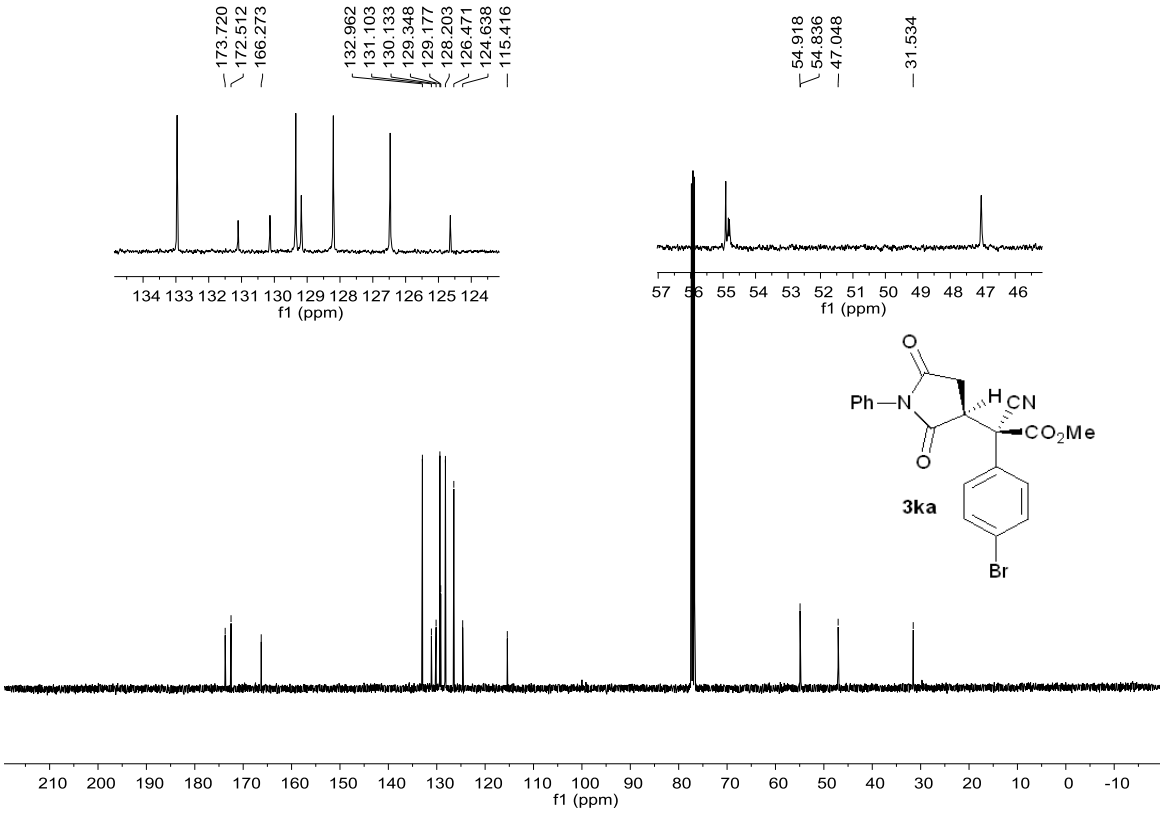

-110.38
O
Ph—N
O
H
CN
CO2Me
3ia
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

3ja

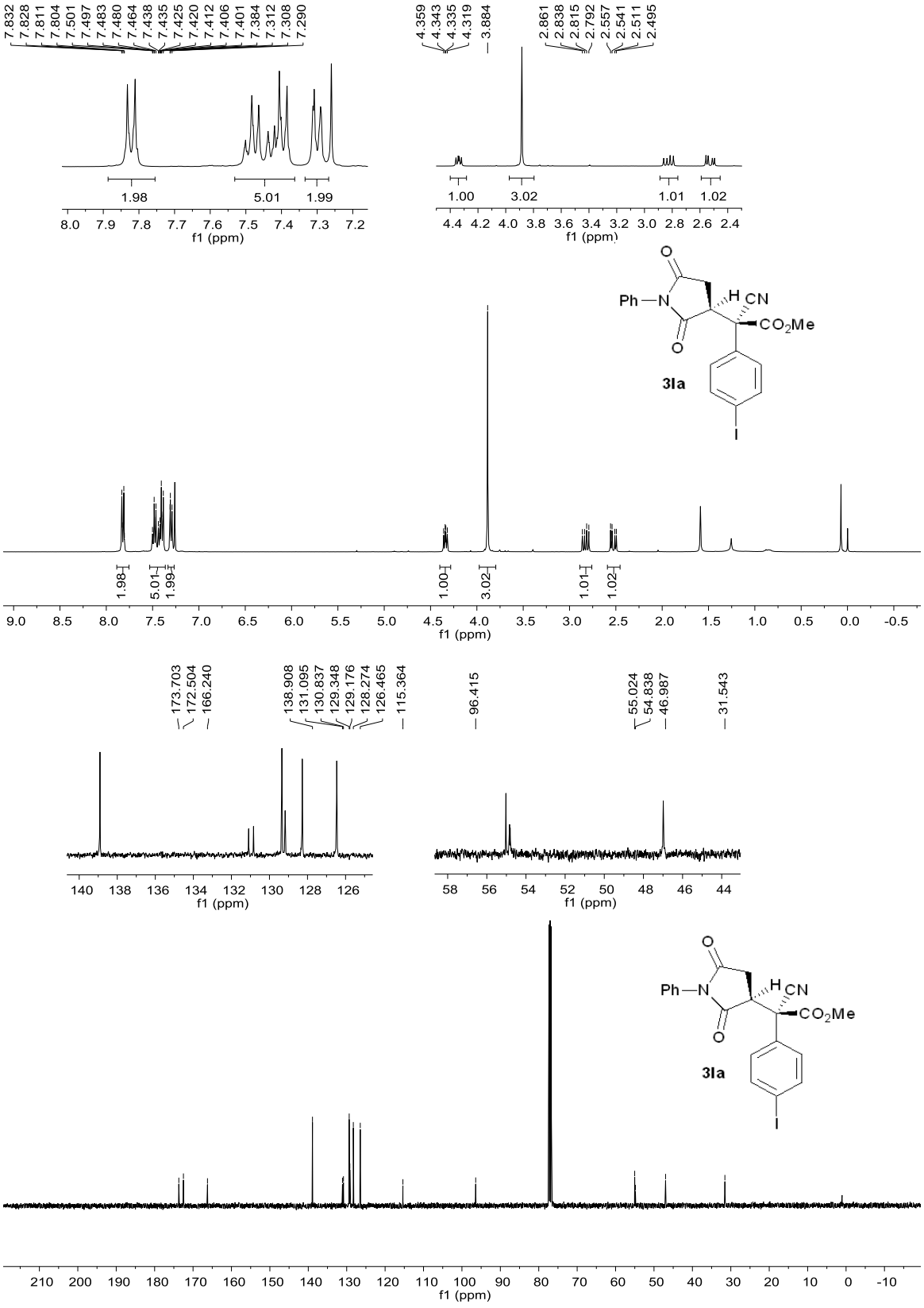

7.618
7.611
7.606
7.594
7.589
7.582
7.500
7.497
7.493
7.479
7.475
7.468
7.463
7.460
7.451
7.446
7.439
7.435
7.432
7.417
7.311
7.308
7.303
7.290
4.369
4.353
4.345
4.329
3.882
2.854
2.830
2.808
2.784
2.551
2.534
2.504
2.488
2.03
4.97
1.99
1.00
1.00
0.99
f1 (ppm)
Ph—N
H
CN
CO2Me
O
3ja
Cl
2.03
4.97
1.99
0.99
3.00
1.00
1.00
173.765
172.558
166.355
136.451
131.117
129.986
129.586
129.348
129.174
127.974
126.480
115.488
54.841
47.093
31.537

3ka

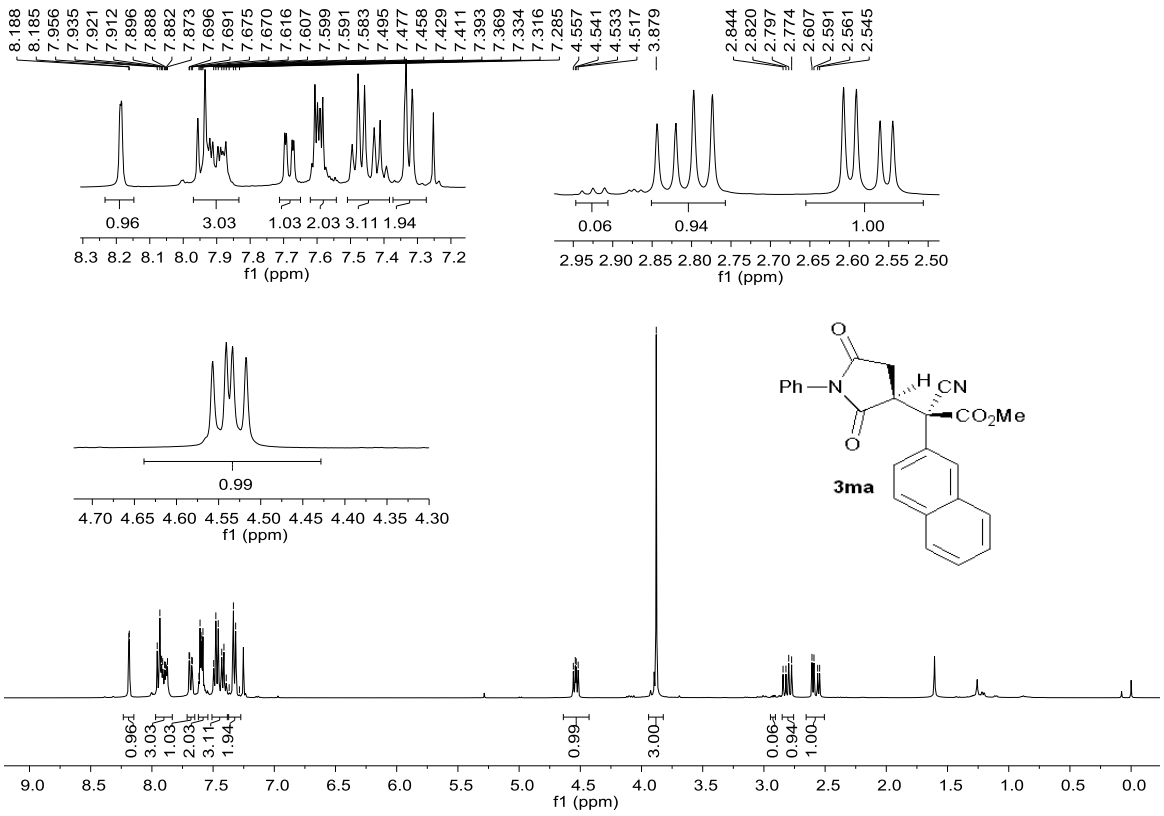

7.630
7.625
7.614
7.608
7.602
7.551
7.545
7.540
7.534
7.528
7.523
7.517
7.504
7.501
7.496
7.483
7.479
7.467
7.464
7.441
7.438
7.435
7.426
7.420
7.313
7.309
7.304
7.291
4.365
4.349
4.341
4.325
2.835
2.812
2.789
2.556
2.539
2.509
2.493
1.99
5.05
2.00
1.02
1.02
1.00
f1 (ppm)
Ph—N
H
CN
CO2Me
3ka
Br
1.99
5.05
2.00
1.00
2.99
1.02
1.02

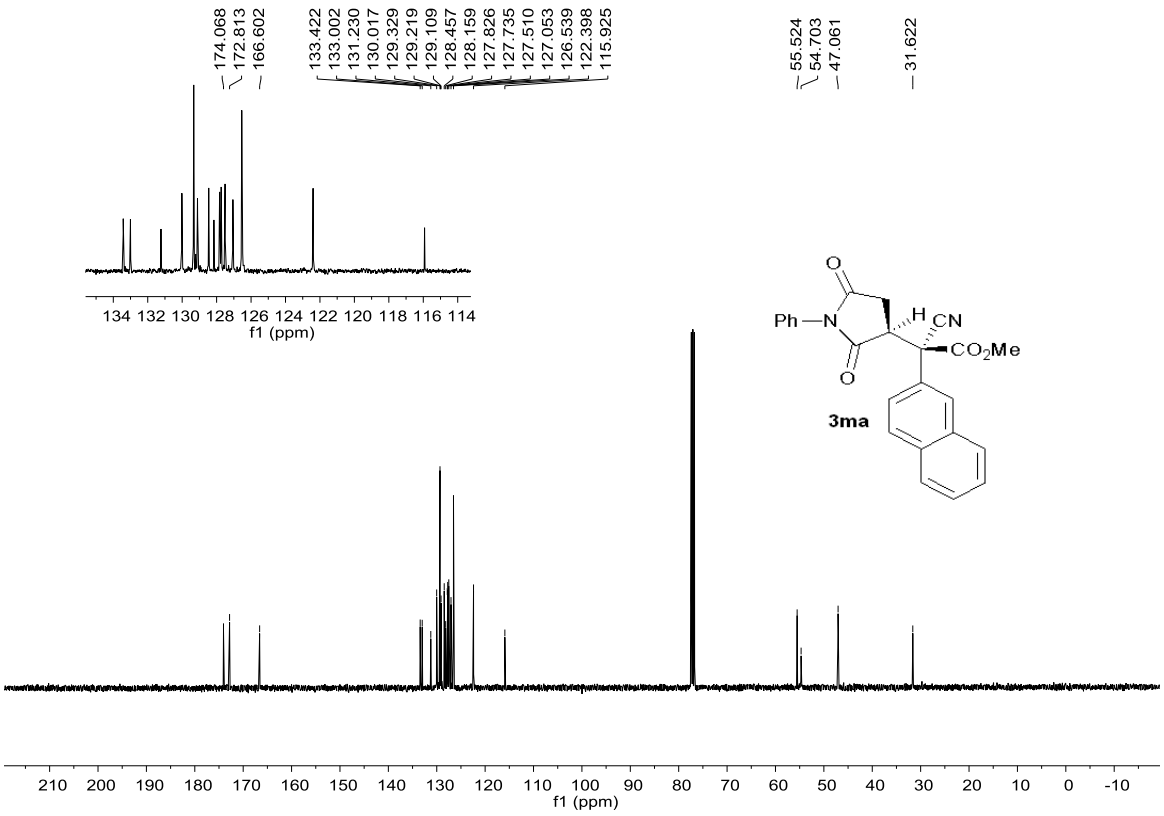

173.720
172.512
166.273
132.962
131.103
130.133
129.348
129.177
128.203
126.471
124.638
115.416
54.918
54.836
47.048
31.534
f1 (ppm)
Ph—N
H
CN
CO2Me
3ka
Br

3la

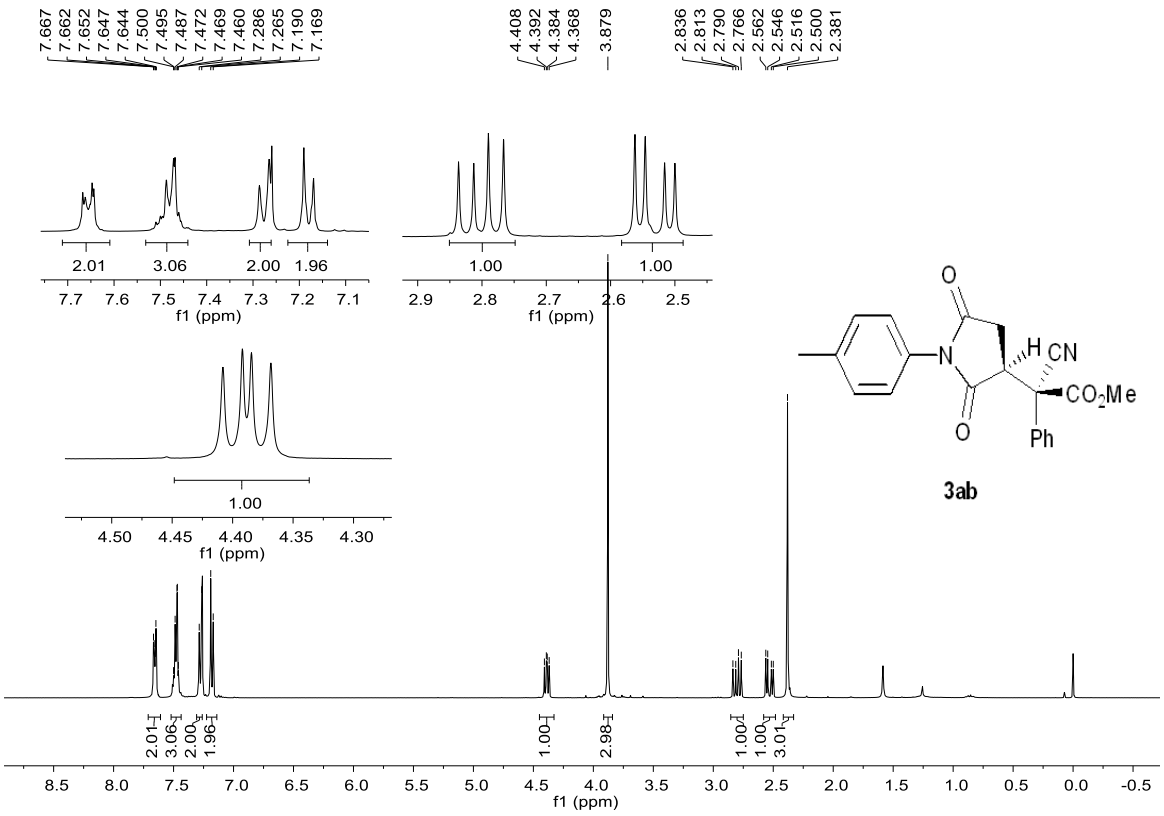

7.832
7.828
7.811
7.804
7.501
7.497
7.483
7.480
7.464
7.438
7.435
7.425
7.420
7.412
7.406
7.401
7.384
7.312
7.308
7.290
4.359
4.343
4.335
4.319
3.884
2.861
2.838
2.815
2.792
2.557
2.541
2.511
2.495
1.98
5.01
1.99
1.00
3.02
1.01
1.02
f1 (ppm)
Ph—N
H
CN
CO2Me
3la
I
173.703
172.504
166.240
138.908
131.095
130.837
129.348
129.176
128.274
126.465
115.364
96.415
55.024
54.838
46.987
31.543

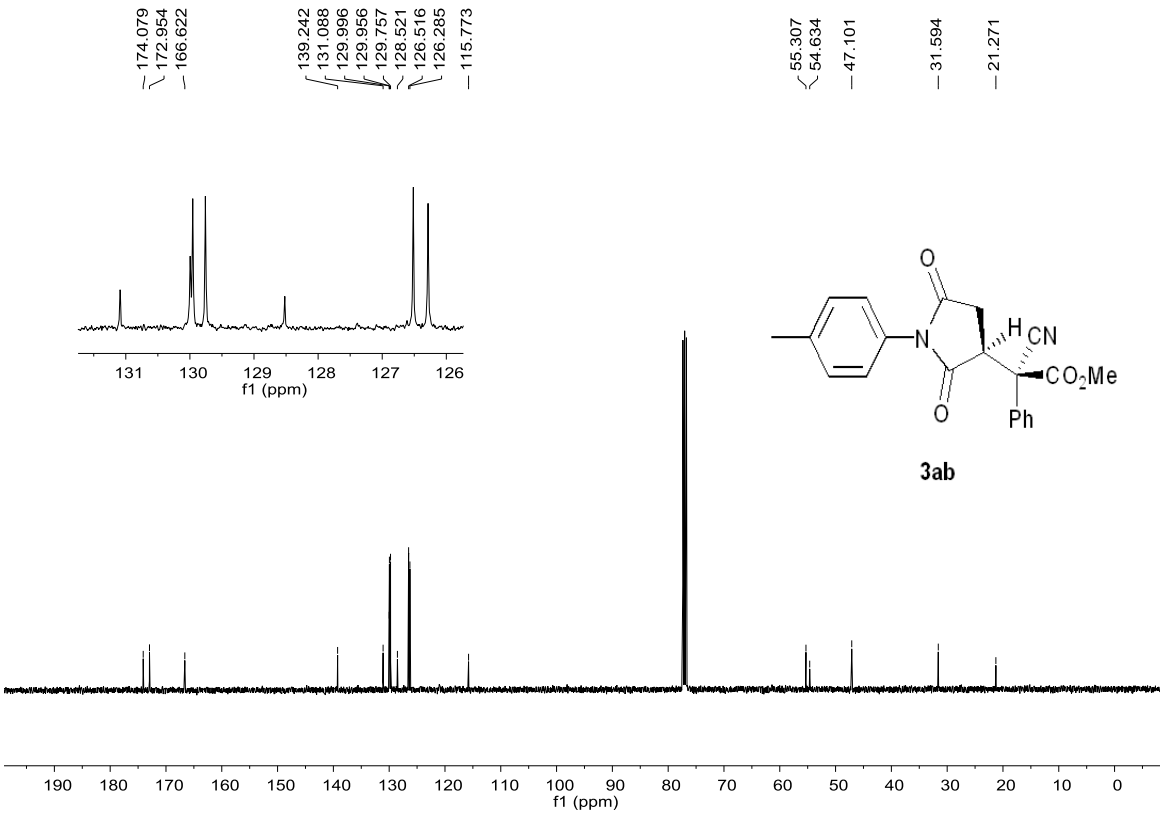
3ma


8.188
8.185
7.956
7.935
7.921
7.912
7.896
7.888
7.882
7.873
7.696
7.691
7.675
7.670
7.616
7.607
7.599
7.591
7.583
7.495
7.477
7.458
7.429
7.411
7.393
7.369
7.334
7.316
7.285
4.557
4.541
4.533
4.517
3.879
2.844
2.820
2.797
2.774
2.607
2.591
2.561
2.545
0.96
3.03
1.03 2.03 3.11 1.94
0.06
0.94
1.00
f1 (ppm)
0.99
Ph—N
H
CN
CO2Me
3ma
0.96
3.03
1.03
2.03
3.11
1.94
0.99
3.00
0.06
0.94
1.00

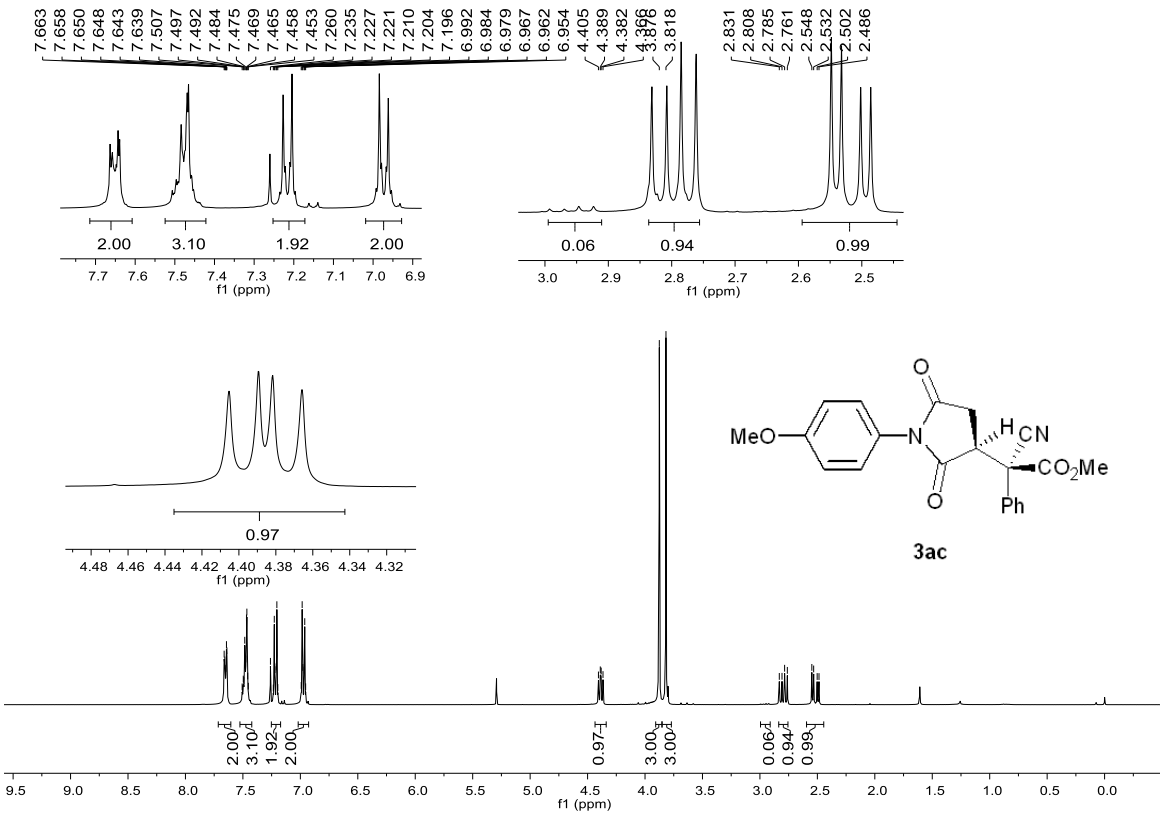

174.068
172.813
166.602
133.422
133.002
131.230
130.017
129.329
129.219
129.109
128.457
128.159
127.826
127.735
127.510
127.053
126.539
122.398
115.925
55.524
54.703
47.061
31.622
f1 (ppm)
Ph—N
H
CN
CO2Me
3ma

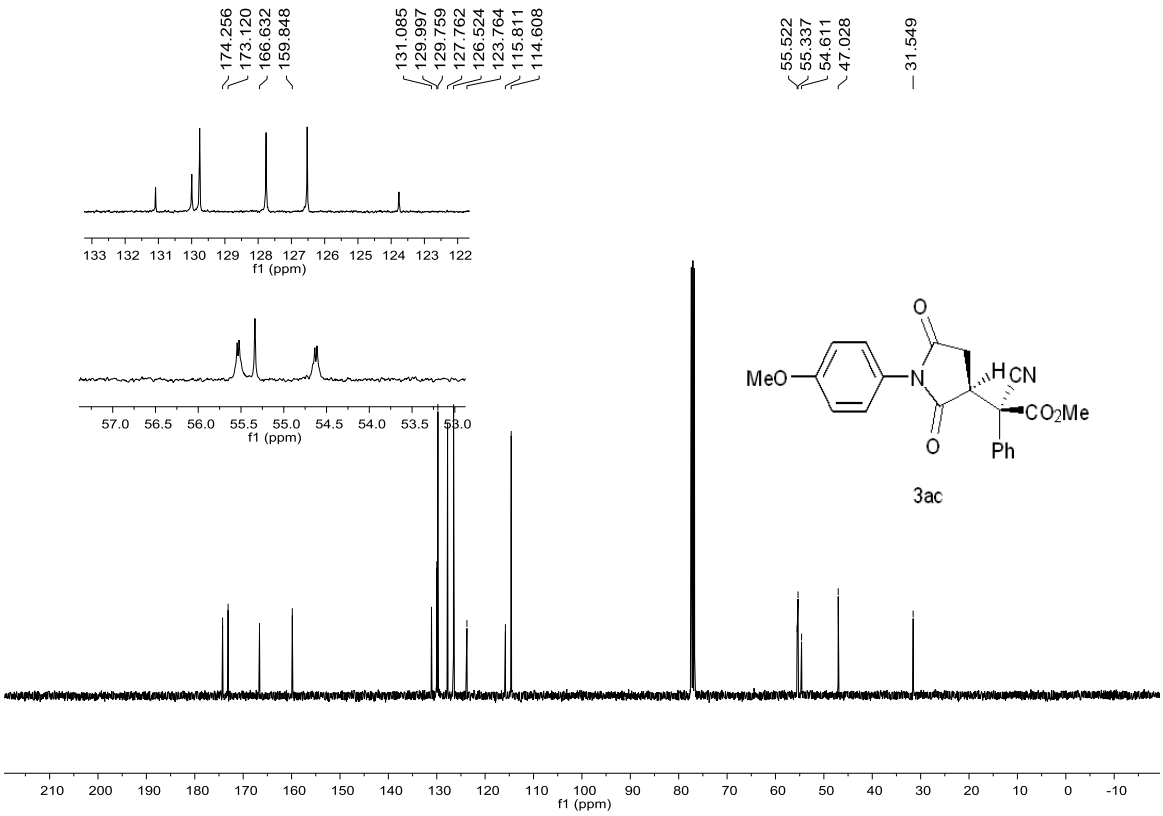
3ab


7.667
7.662
7.652
7.647
7.644
7.500
7.495
7.487
7.472
7.469
7.460
7.286
7.265
7.190
7.169
4.408
4.392
4.384
4.368
3.879
2.836
2.813
2.790
2.766
2.562
2.546
2.516
2.500
2.381
2.01
3.06
2.00
1.96
1.00
1.00
1.00
f1 (ppm)
O
N
H
CN
CO2Me
O
Ph
3ab
2.01
3.06
2.00
1.96
1.00
2.98
1.00
1.00
3.01
f1 (ppm)

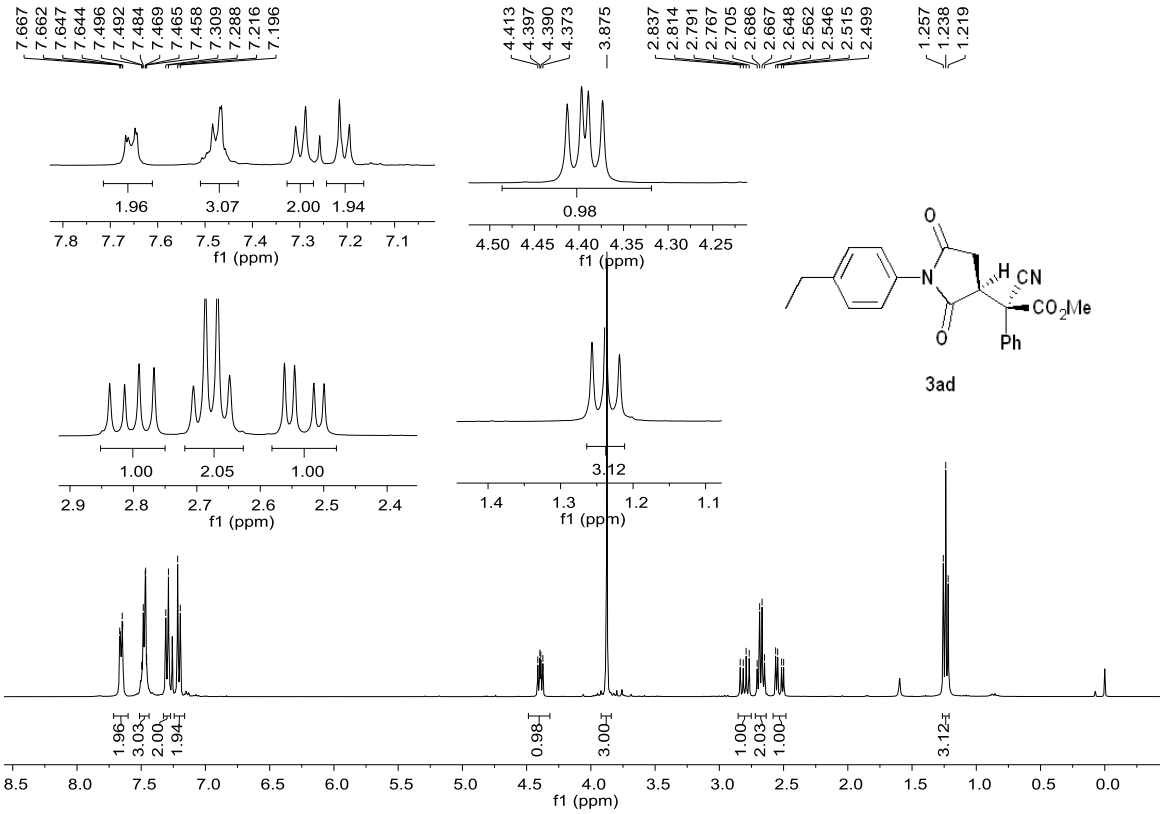

174.079
172.954
166.622
139.242
131.088
129.996
129.956
129.757
128.521
126.516
126.285
115.773
55.307
54.634
47.101
31.594
21.271
f1 (ppm)
O
N
H
CN
CO2Me
O
Ph
3ab
f1 (ppm)

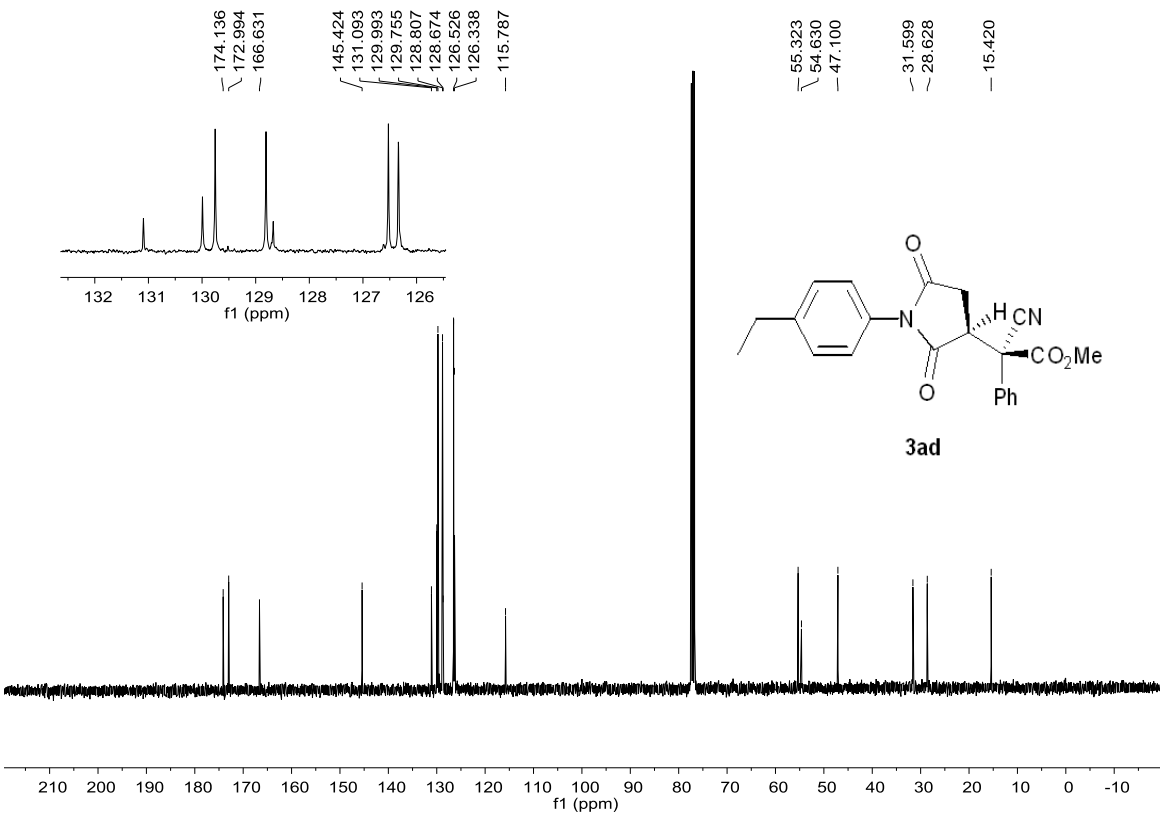
3ac


7.663 7.658 7.650 7.648 7.643 7.639 7.507 7.497 7.492 7.484 7.475 7.469 7.465 7.458 7.453 7.260 7.235 7.227 7.221 7.210 7.204 7.196 6.992 6.984 6.979 6.967 6.962 6.954 4.405 4.389 4.382 4.366 3.818 2.831 2.808 2.785 2.761 2.548 2.532 2.502 2.486
2.00 3.10 1.92 2.00
0.06 0.94 0.99
f1 (ppm)
0.97
MeO
N
H
CN
CO2Me
Ph
O
3ac
2.00 3.10 1.92 2.00 0.97 3.00 3.00 0.06 0.94 0.99
f1 (ppm)

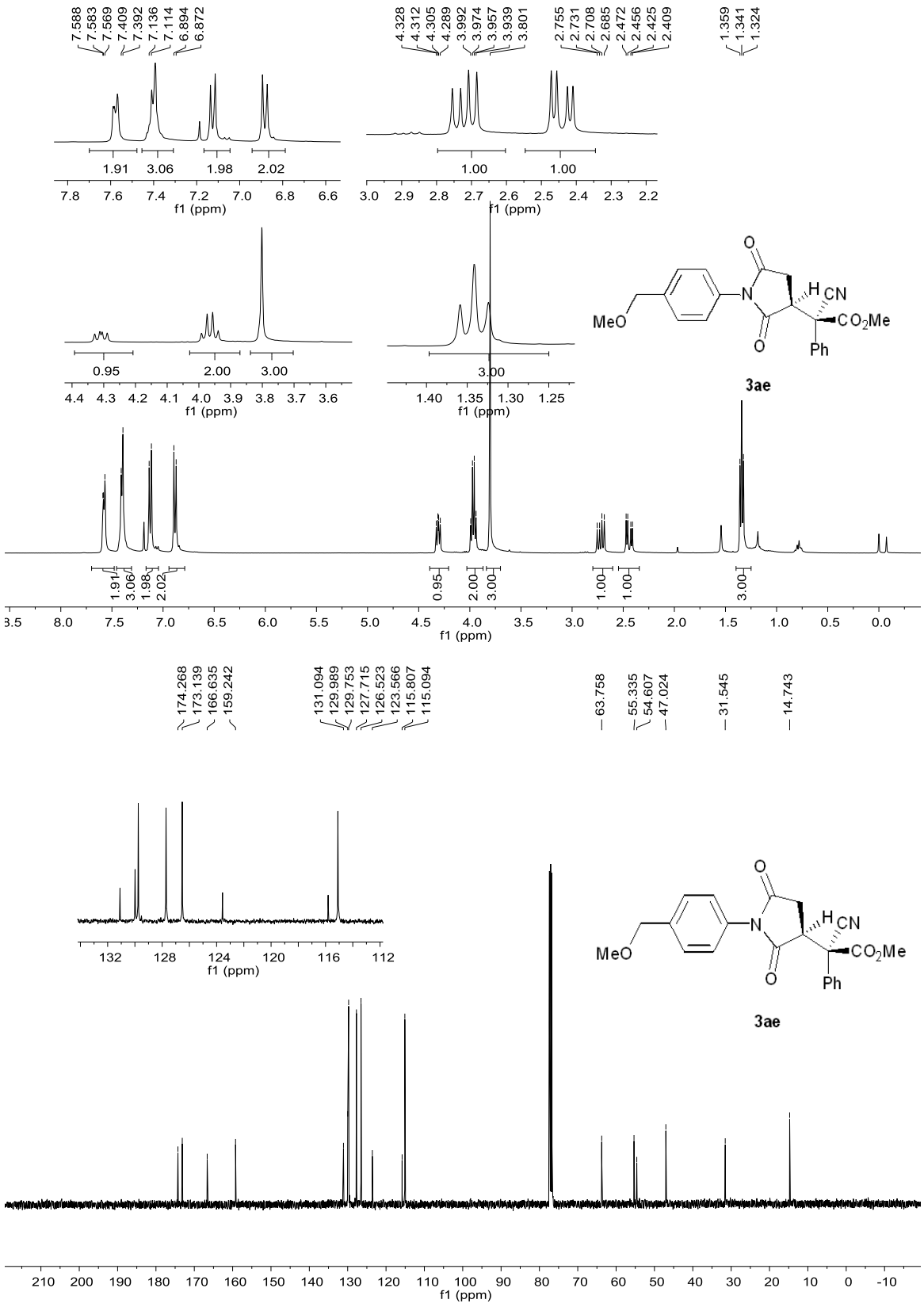

174.256 173.120 166.632 159.848 131.085 129.997 129.759 127.762 126.524 123.764 115.811 114.608 55.522 55.337 54.611 47.028 31.549
f1 (ppm)
MeO
N
H
CN
CO2Me
Ph
O
3ac
f1 (ppm)

3ad


7.667
7.662
7.647
7.644
7.496
7.492
7.484
7.469
7.465
7.458
7.309
7.288
7.216
7.196
4.413
4.397
4.390
4.373
3.875
2.837
2.814
2.791
2.767
2.705
2.686
2.667
2.648
2.562
2.546
2.515
2.499
1.257
1.238
1.219
1.96
3.07
2.00
1.94
0.98
1.00
2.05
1.00
3.12
f1 (ppm)
3ad

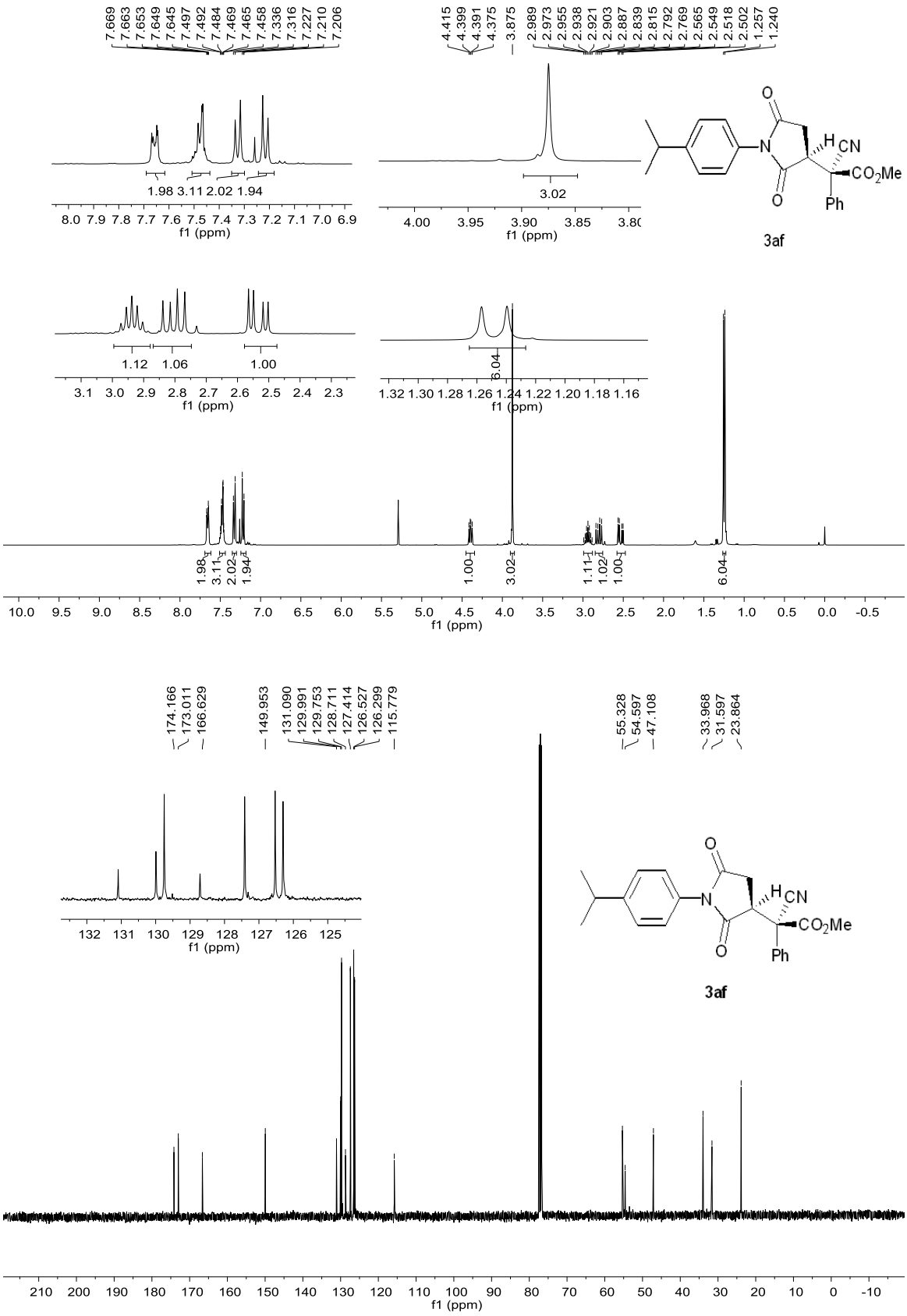

174.136
172.994
166.631
145.424
131.093
129.993
129.755
128.807
128.674
126.526
126.338
115.787
55.323
54.630
47.100
31.599
28.628
15.420
f1 (ppm)
3ad

3ae

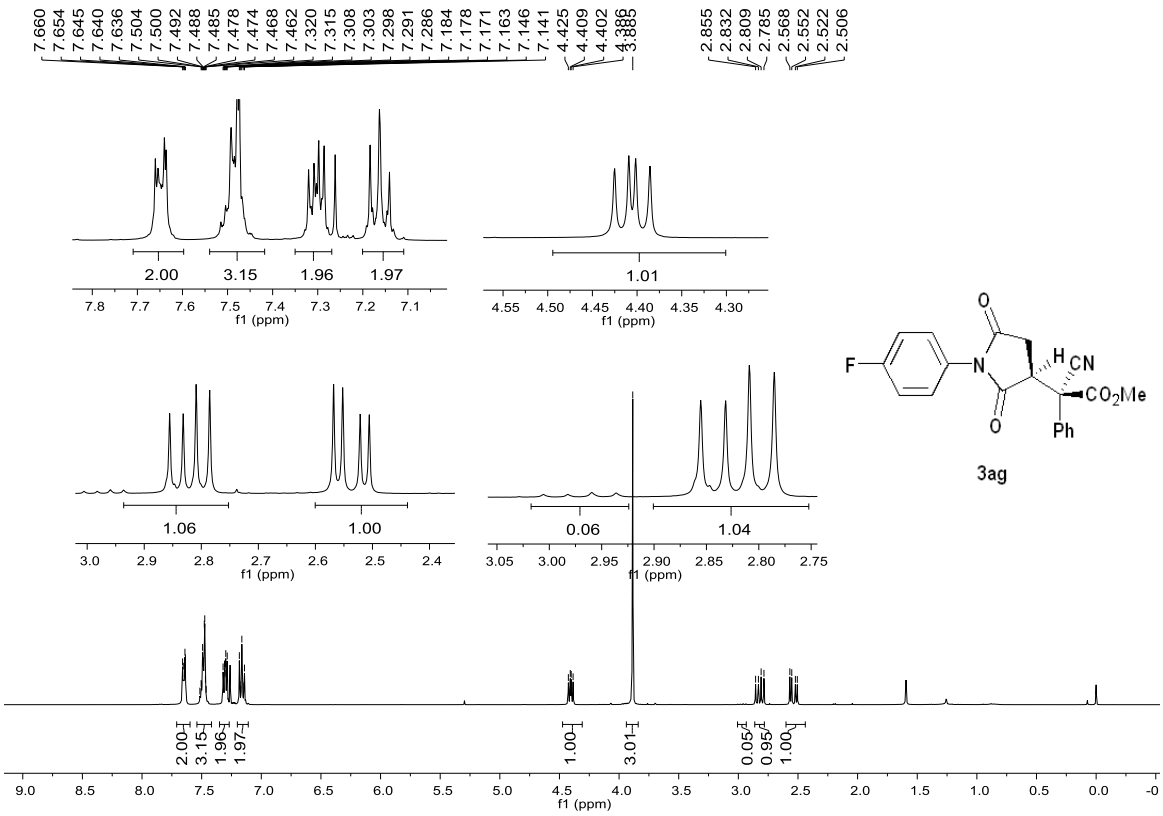

7.588
7.583
7.569
7.409
7.392
7.136
7.114
6.894
6.872
4.328
4.312
4.305
4.289
3.992
3.974
3.957
3.939
3.801
2.755
2.731
2.708
2.685
2.472
2.456
2.425
2.409
1.359
1.341
1.324
1.91
3.06
1.98
2.02
1.00
1.00
0.95
2.00
3.00
3.00
MeO
H
CN
CO2Me
Ph
3ae
f1 (ppm)

174.268
173.139
166.635
159.242
131.094
129.989
129.753
127.715
126.523
123.566
115.807
115.094
63.758
55.335
54.607
47.024
31.545
14.743
MeO
H
CN
CO2Me
Ph
3ae
f1 (ppm)

3af


7.669
7.663
7.653
7.649
7.645
7.497
7.492
7.484
7.469
7.465
7.458
7.336
7.316
7.227
7.210
7.206
1.98 3.11 2.02 1.94
f1 (ppm)
4.415
4.399
4.391
4.375
3.875
2.989
2.973
2.955
2.938
2.921
2.903
2.887
2.839
2.815
2.792
2.769
2.565
2.549
2.518
2.502
1.257
1.240
3.02
f1 (ppm)
O
N
H
CN
CO2Me
O
Ph
3af
1.12
1.06
1.00
f1 (ppm)
6.04
f1 (ppm)
1.98
3.11
2.02
1.94
1.00
3.02
1.11
1.02
1.00
6.04
f1 (ppm)
174.166
173.011
166.629
149.953
131.090
129.991
129.753
128.711
127.414
126.527
126.299
115.779
55.328
54.597
47.108
33.968
31.597
23.864
f1 (ppm)
O
N
H
CN
CO2Me
O
Ph
3af
f1 (ppm)

3ag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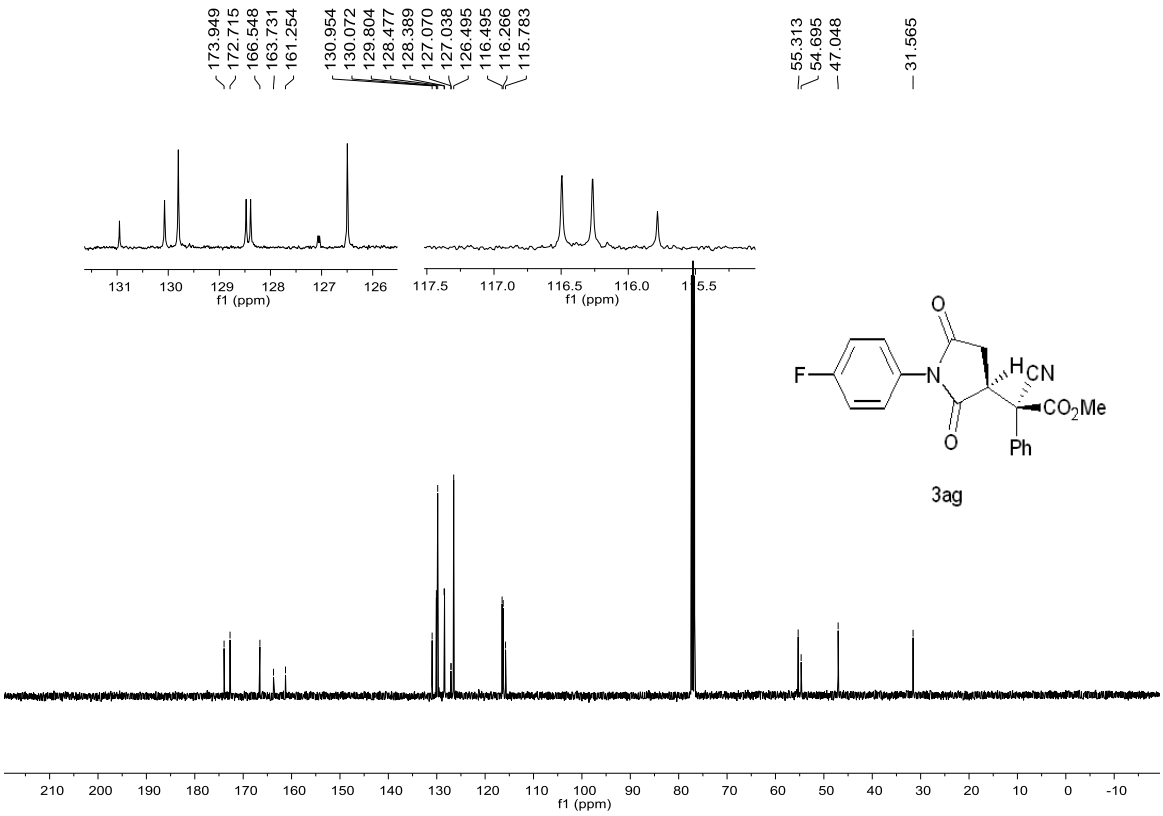
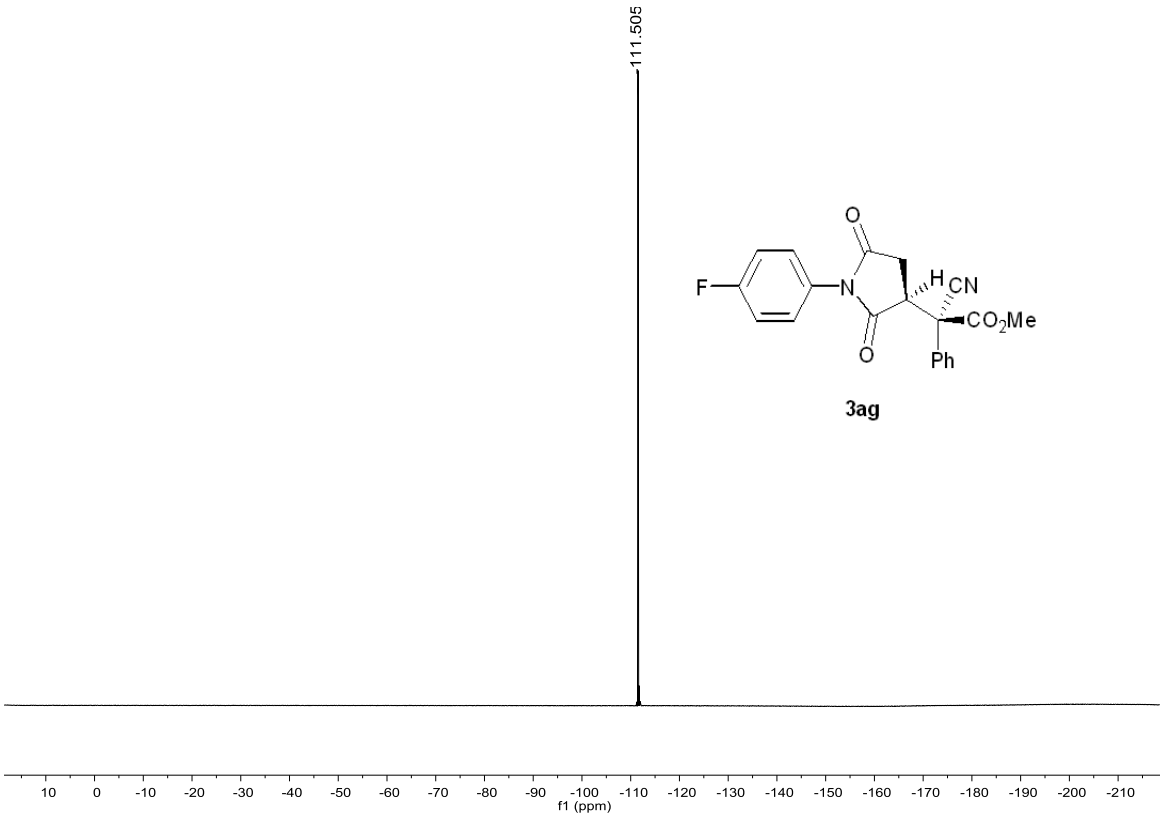
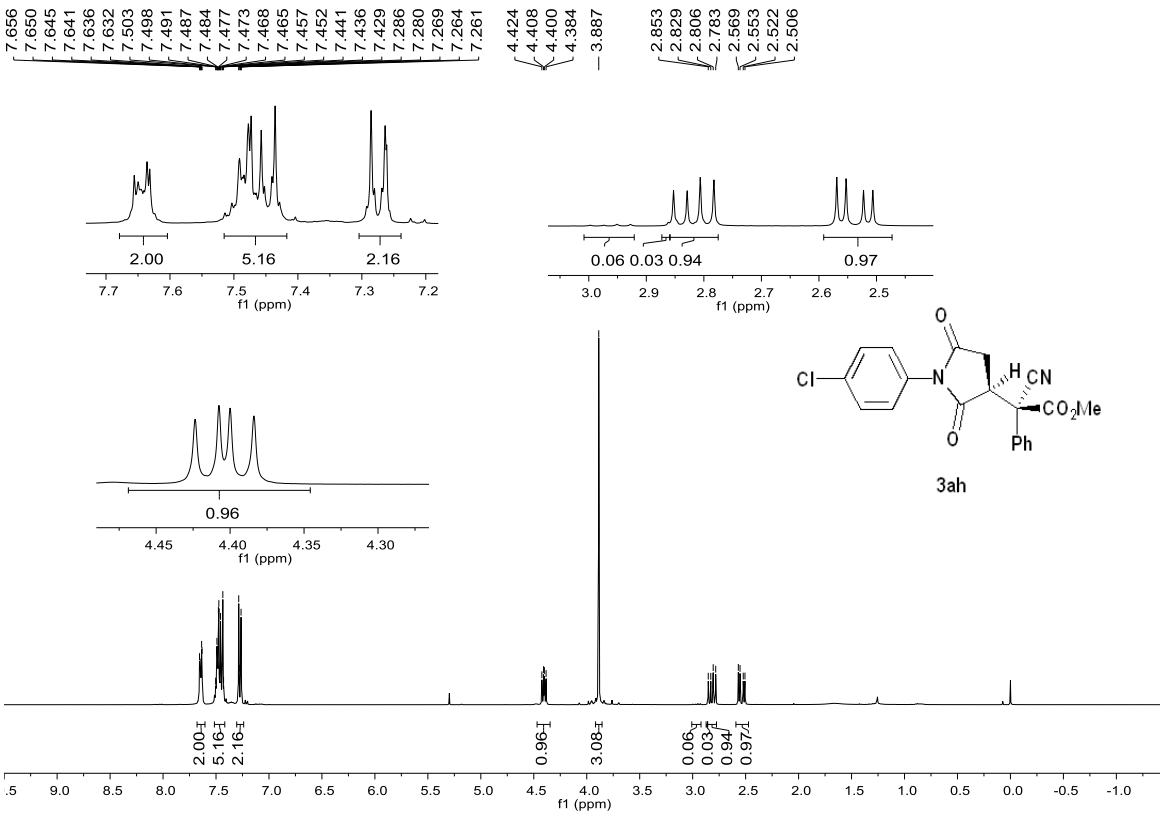
7.654
7.645
7.640
7.636
7.504
7.500
7.492
7.488
7.485
7.478
7.474
7.468
7.462
7.320
7.315
7.308
7.303
7.298
7.291
7.286
7.184
7.178
7.171
7.163
7.146
7.141
4.425
4.409
4.402
4.386
3.885
2.855
2.832
2.809
2.785
2.568
2.552
2.522
2.506
2.00
3.15
1.96
1.97
1.01
1.06
1.00
0.06
1.04
f1 (ppm)
F
N
O
H
CN
CO2Me
Ph
3ag

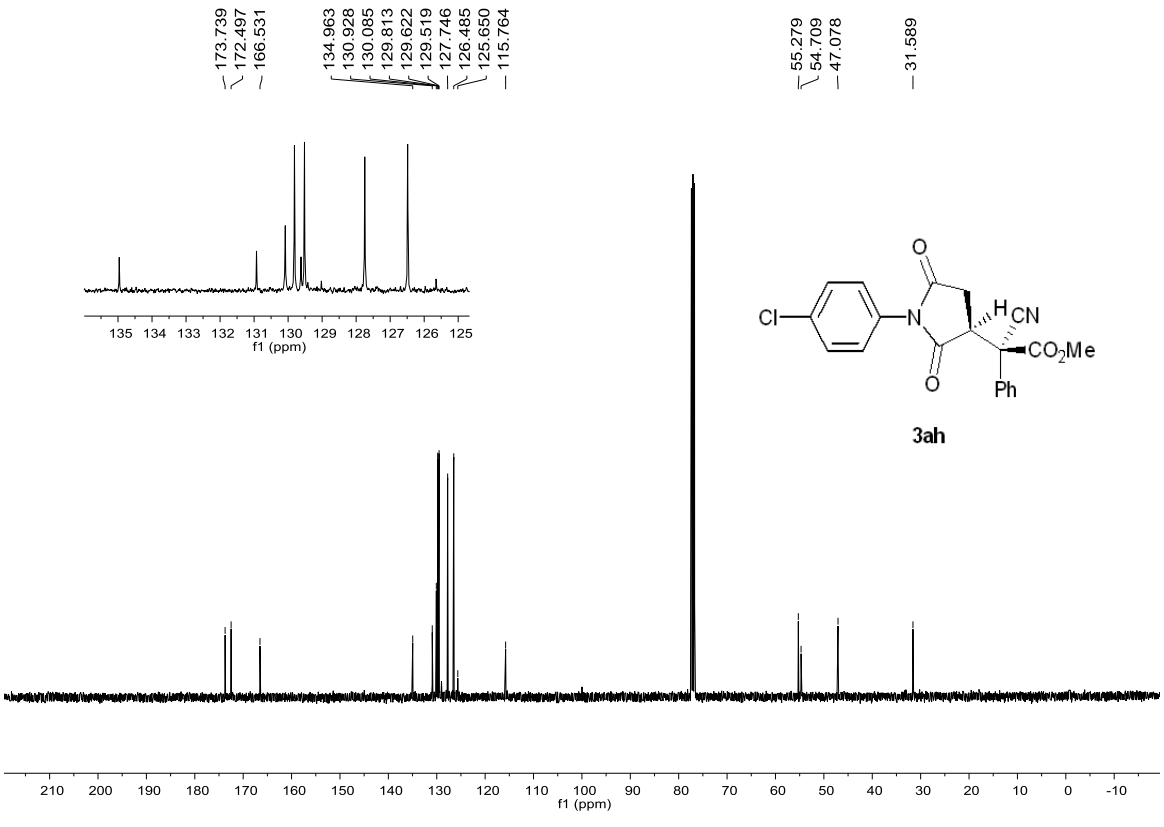

173.949
172.715
166.548
163.731
161.254
130.954
130.072
129.804
128.477
128.389
127.070
127.038
126.495
116.495
116.266
115.783
55.313
54.695
47.048
31.565
f1 (ppm)
F
N
O
H
CN
CO2Me
Ph
3ag


111.505
O
F
N
H
CN
CO2Me
Ph
O
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

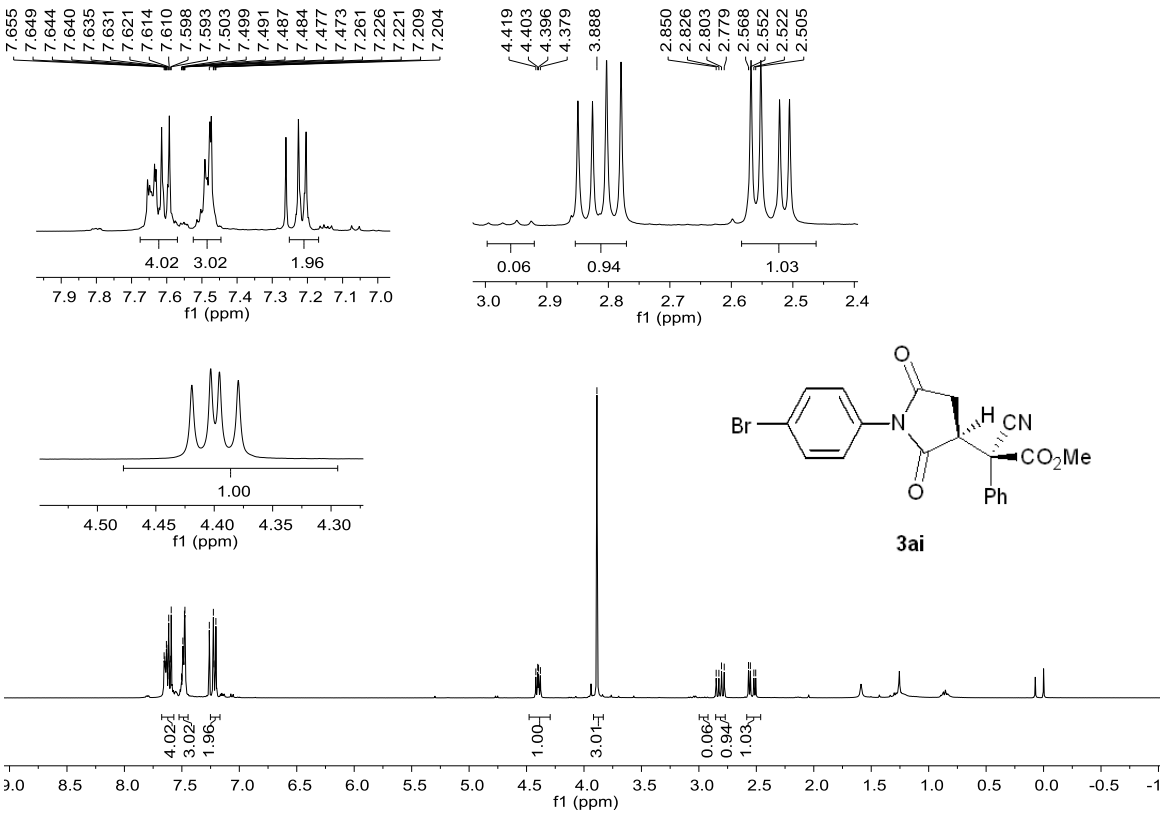
3ag

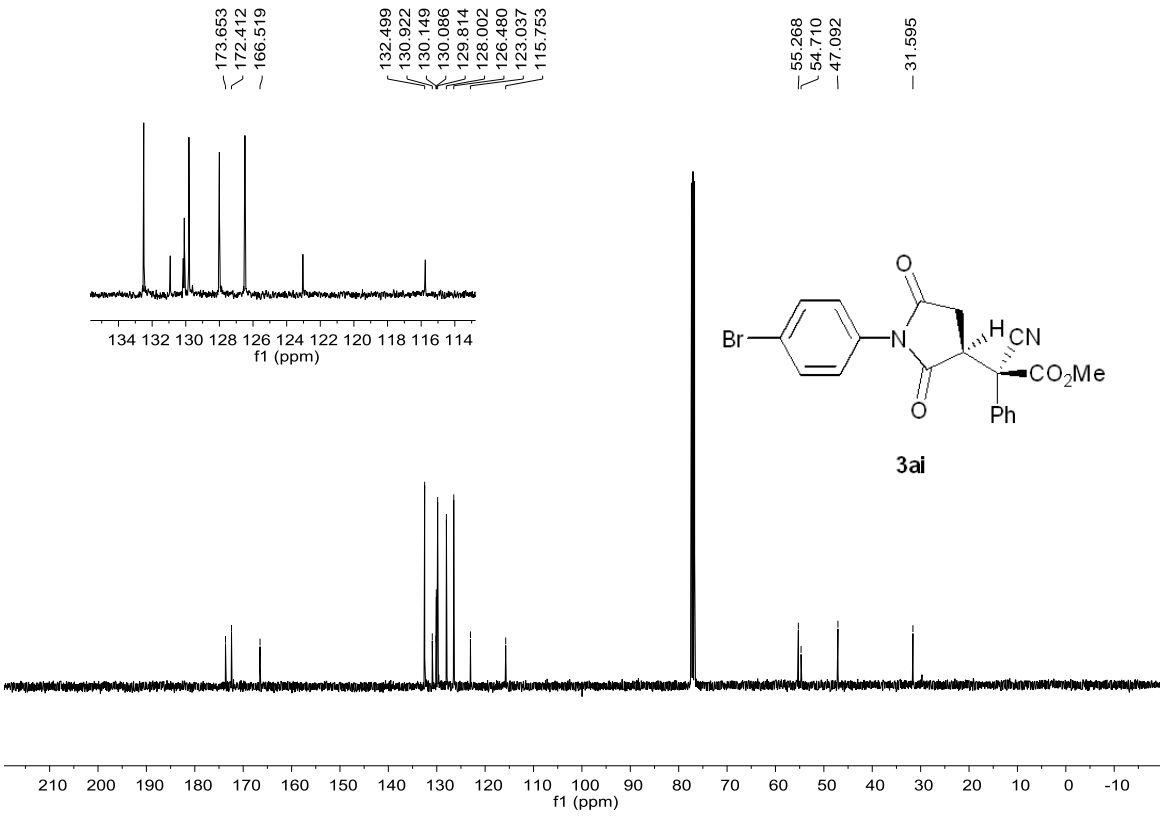
3ah


7.656
7.650
7.645
7.641
7.636
7.632
7.503
7.498
7.491
7.487
7.484
7.477
7.473
7.468
7.465
7.457
7.452
7.441
7.436
7.429
7.286
7.280
7.269
7.264
7.261
4.424
4.408
4.400
4.384
3.887
2.853
2.829
2.806
2.783
2.569
2.553
2.522
2.506
2.00
5.16
2.16
0.06 0.03 0.94
0.97
0.96
f1 (ppm)
Cl
N
O
H
CN
CO2Me
Ph
3ah
2.00
5.16
2.16
0.96
3.08
0.06
0.03
0.94
0.97

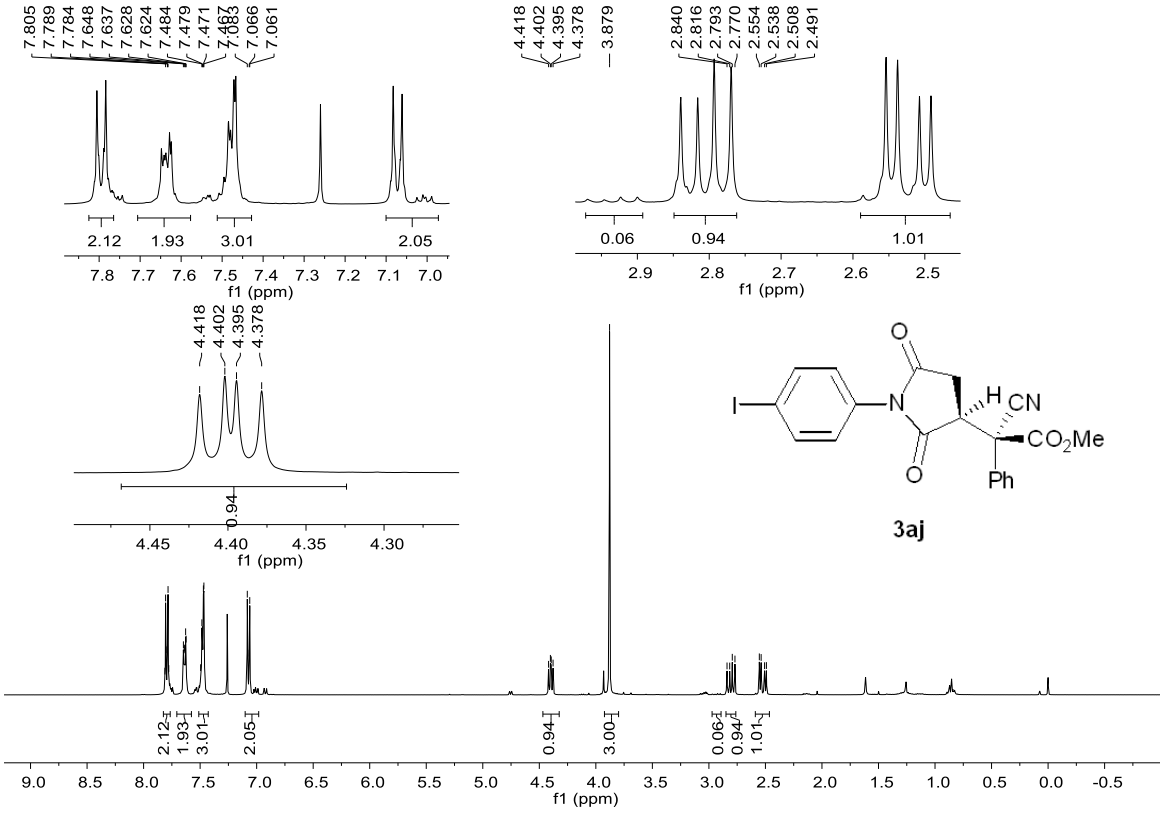

173.739
172.497
166.531
134.963
130.928
130.085
129.813
129.622
129.519
127.746
126.485
125.650
115.764
55.279
54.709
47.078
31.589
f1 (ppm)
Cl
N
O
H
CN
CO2Me
Ph
3ah

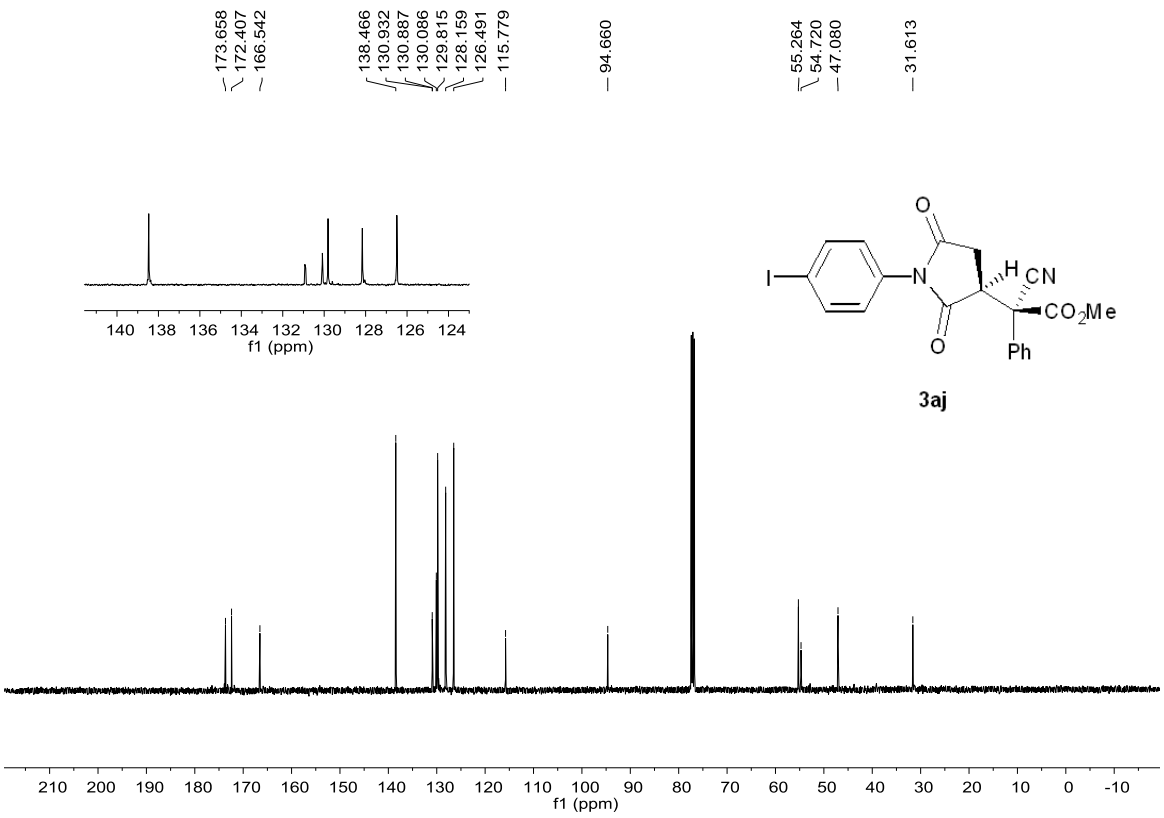
3ai


7.655 7.649 7.644 7.640 7.635 7.631 7.621 7.614 7.610 7.598 7.593 7.503 7.499 7.491 7.487 7.484 7.477 7.473 7.261 7.226 7.221 7.209 7.204
4.419 4.403 4.396 4.379 3.888 2.850 2.826 2.803 2.779 2.568 2.552 2.522 2.505
4.02 3.02 1.96
0.06 0.94 1.03
1.00
f1 (ppm)
Br
N
O
H
CN
CO2Me
Ph
3ai

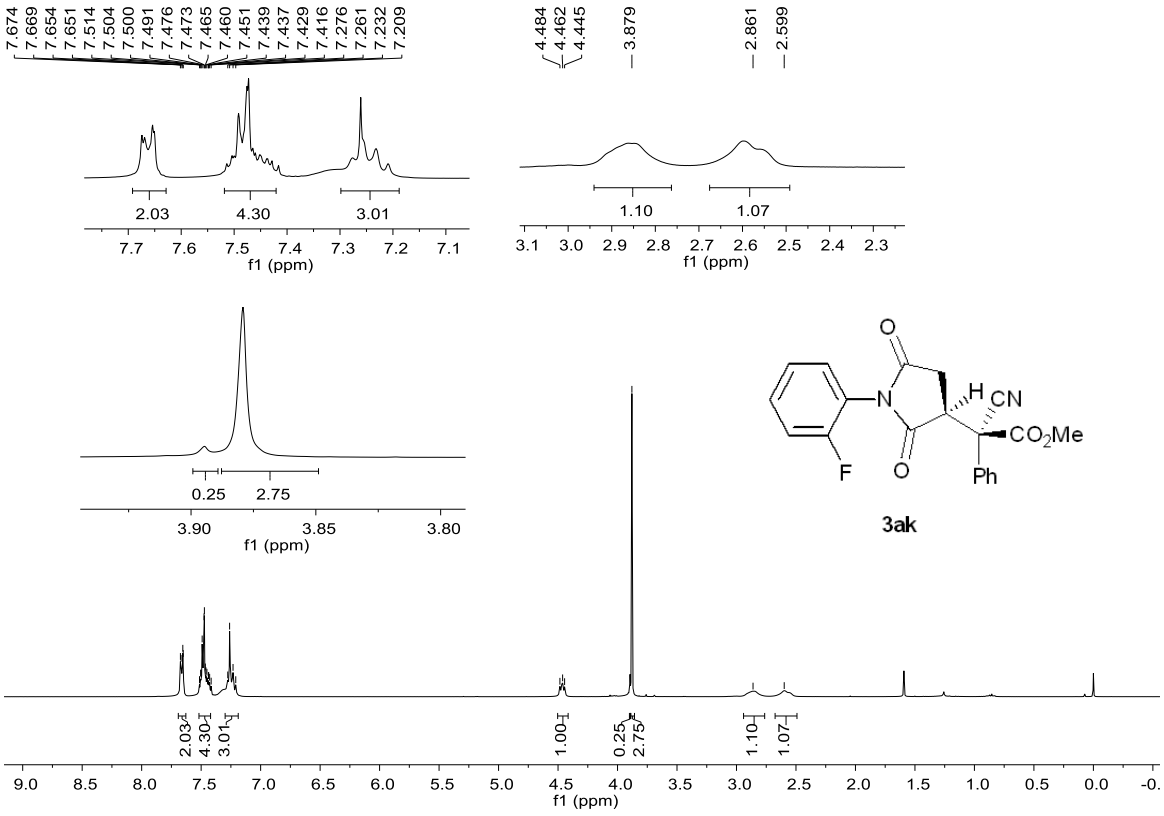

173.653 172.412 166.519 132.499 130.922 130.149 130.086 129.814 128.002 126.480 123.037 115.753 55.268 54.710 47.092 31.595
f1 (ppm)
Br
N
O
H
CN
CO2Me
Ph
3ai

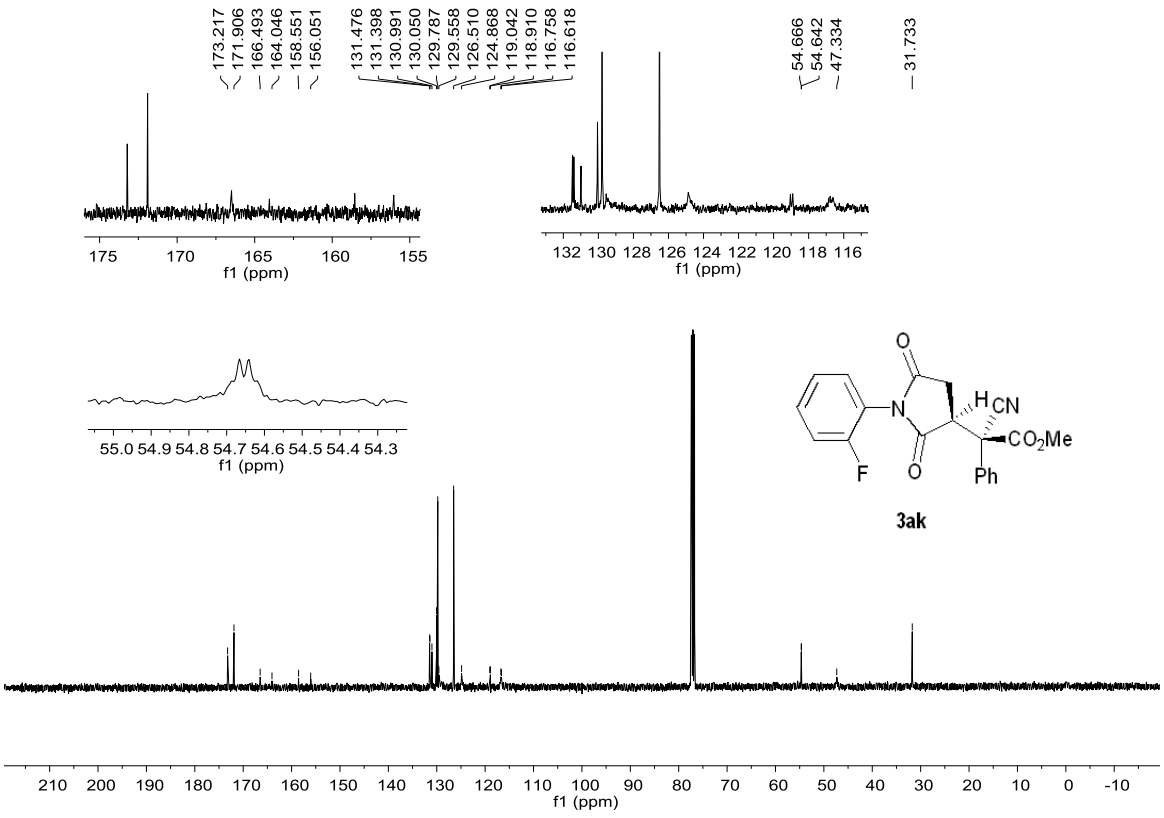
3aj

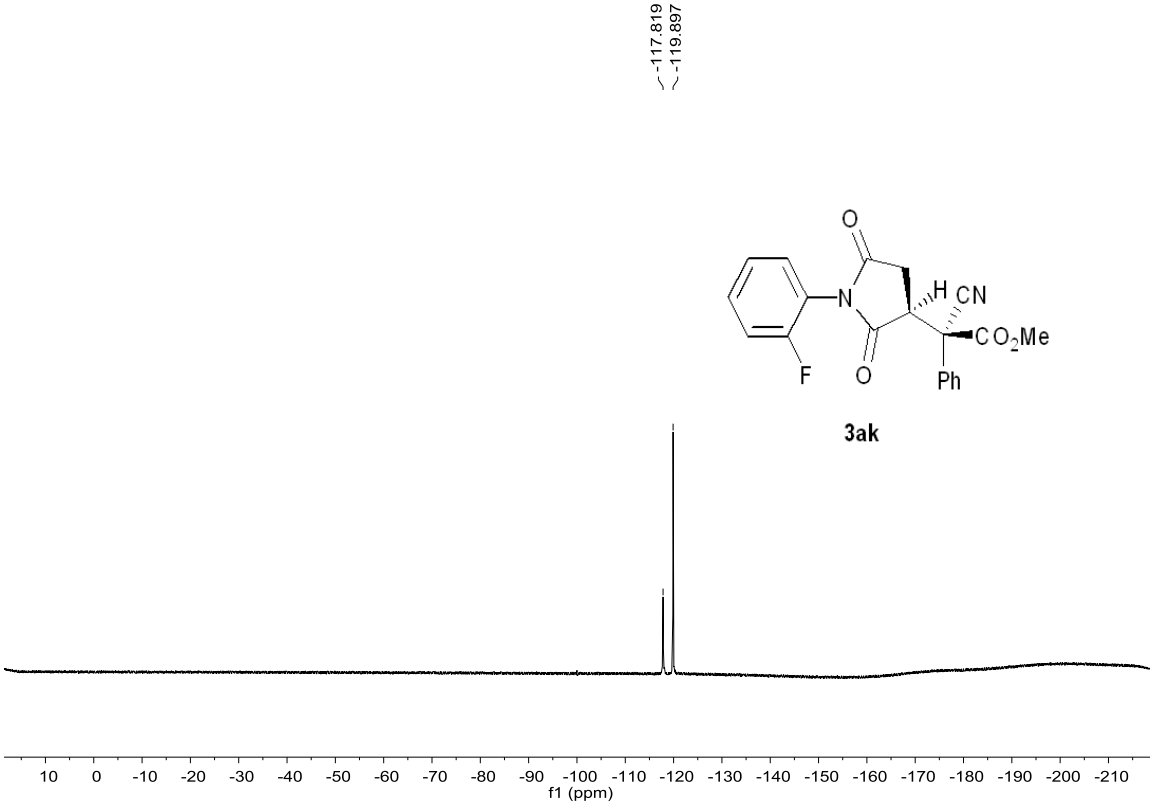

7.805
7.789
7.784
7.648
7.637
7.628
7.624
7.484
7.479
7.471
7.066
7.061
2.12
1.93
3.01
2.05
f1 (ppm)
4.418
4.402
4.395
4.378
3.879
2.840
2.816
2.793
2.770
2.554
2.538
2.508
2.491
0.06
0.94
1.01
f1 (ppm)
4.418
4.402
4.395
4.378
0.94
f1 (ppm)
I
N
O
O
H
CN
CO2Me
Ph
3aj
2.12
1.93
3.01
2.05
0.94
3.00
0.06
0.94
1.01
f1 (ppm)


173.658
172.407
166.542
138.466
130.932
130.887
130.086
129.815
128.159
126.491
115.779
94.660
55.264
54.720
47.080
31.613
f1 (ppm)
I
N
O
O
H
CN
CO2Me
Ph
3aj
f1 (ppm)

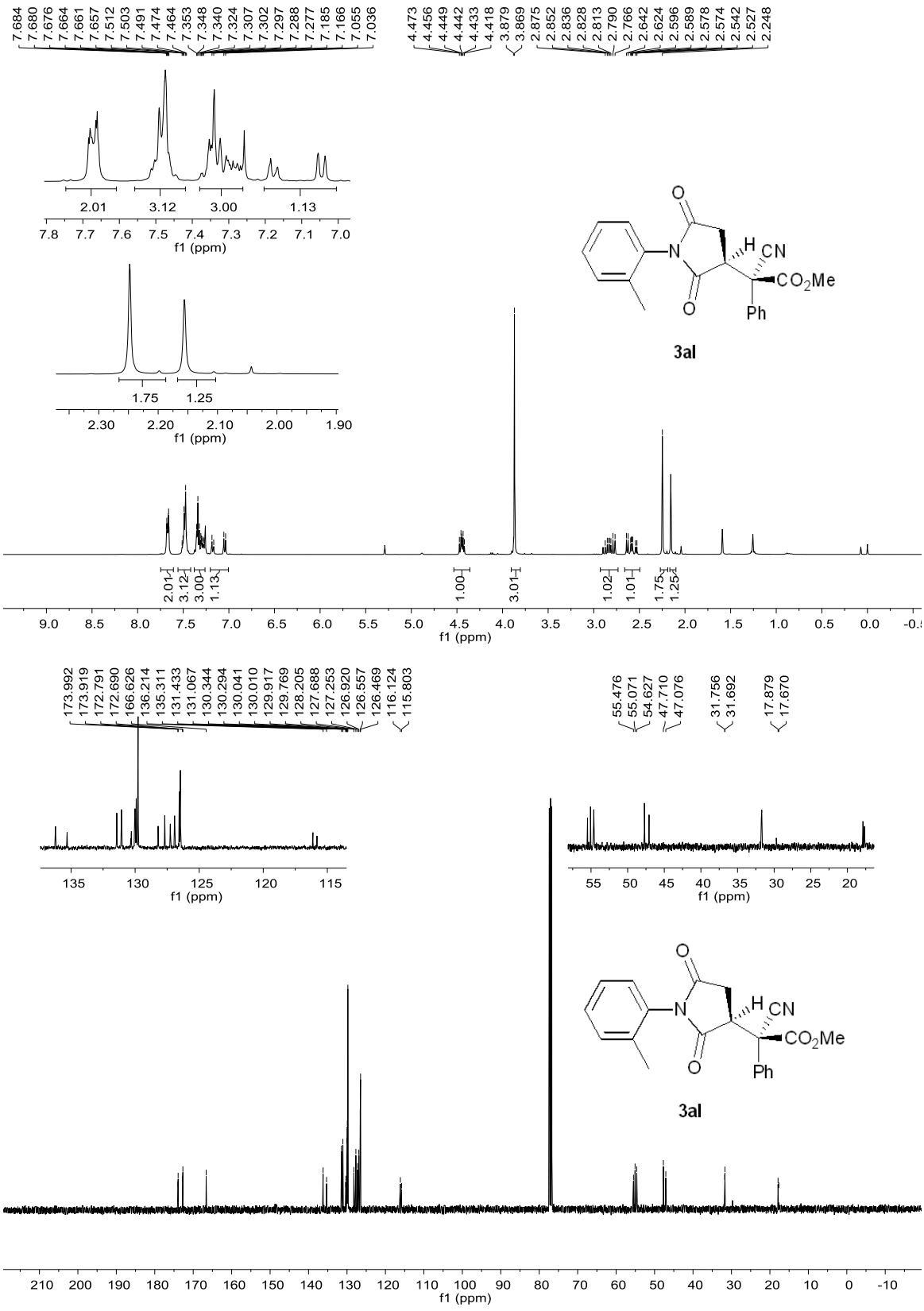
3ak


7.674
7.669
7.654
7.651
7.514
7.504
7.500
7.491
7.476
7.473
7.465
7.460
7.451
7.439
7.437
7.429
7.416
7.276
7.261
7.232
7.209
2.03
4.30
3.01
f1 (ppm)
4.484
4.462
4.445
3.879
2.861
2.599
1.10
1.07
f1 (ppm)
0.25
2.75
f1 (ppm)
3ak
2.03
4.30
3.01
1.00
0.25
2.75
1.10
1.07
f1 (ppm)

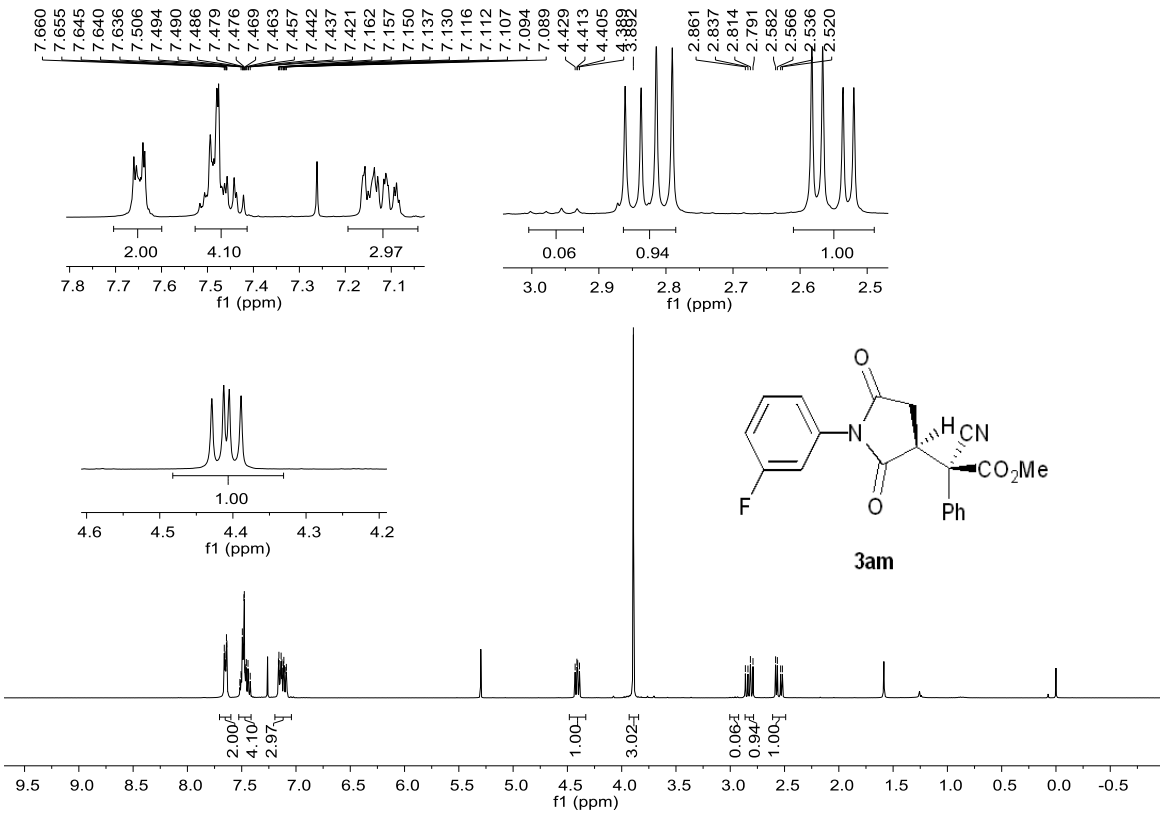

173.217
171.906
166.493
164.046
158.551
156.051
131.476
131.398
130.991
130.050
129.787
129.558
126.510
124.868
119.042
118.910
116.758
116.618
54.666
54.642
47.334
31.733
f1 (ppm)
f1 (ppm)
55.0 54.9 54.8 54.7 54.6 54.5 54.4 54.3
f1 (ppm)
3ak
f1 (ppm)

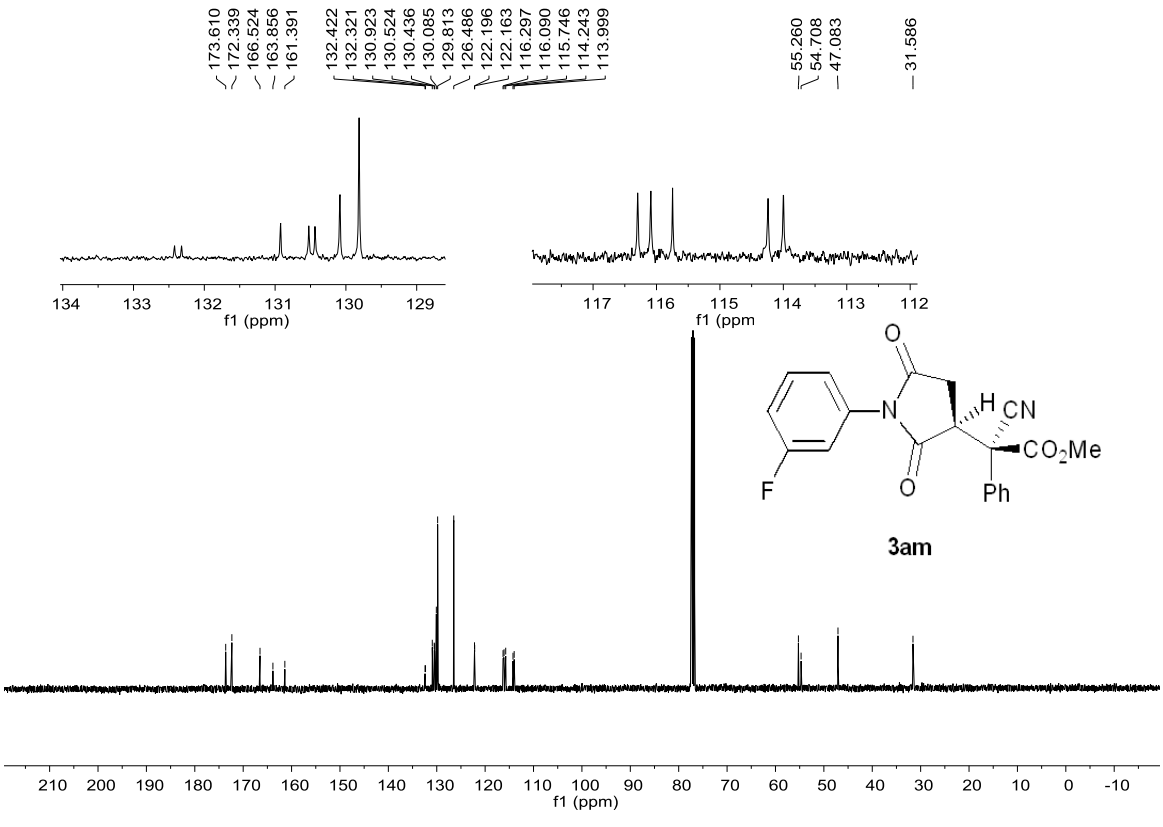

-117.819
-119.897
O
N
H
CN
CO2Me
F
O
Ph
3ak
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

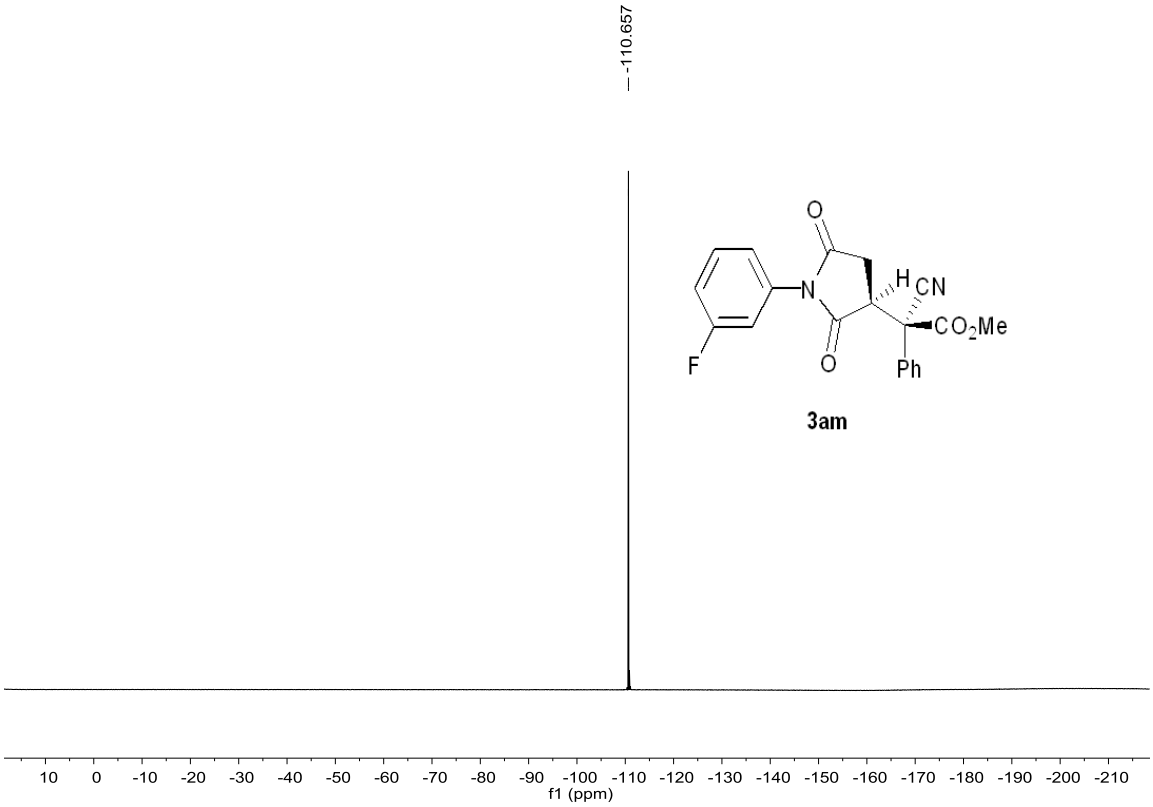
3al


7.684 7.680 7.676 7.664 7.661 7.657 7.512 7.503 7.491 7.474 7.464 7.353 7.348 7.340 7.324 7.307 7.302 7.297 7.288 7.277 7.185 7.166 7.055 7.036
4.473 4.456 4.449 4.442 4.433 4.418 3.879 3.869 2.875 2.852 2.836 2.828 2.813 2.790 2.766 2.642 2.624 2.596 2.589 2.578 2.574 2.542 2.527 2.248
2.01 3.12 3.00 1.13
1.75 1.25
f1 (ppm)
3al
2.01 3.12 3.00 1.13 1.00 3.01 1.02 1.01 1.75 1.25
173.992 173.919 172.791 172.690 166.626 136.214 135.311 131.433 131.067 130.344 130.294 130.041 130.010 129.917 129.769 128.205 127.688 127.253 126.920 126.557 126.469 116.124 115.803
55.476 55.071 54.627 47.710 47.076 31.756 31.692 17.879 17.670
3al

3am

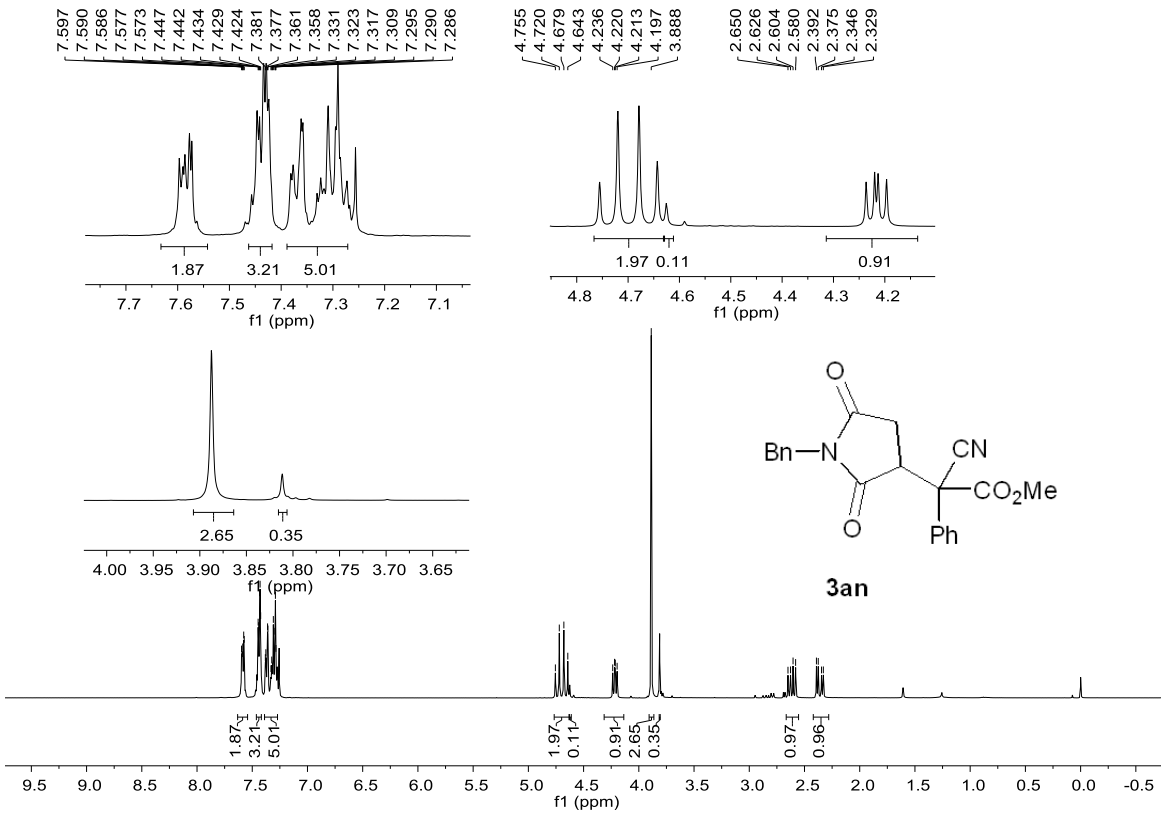

7.660 7.655 7.645 7.640 7.636 7.506 7.494 7.490 7.486 7.479 7.476 7.469 7.463 7.457 7.442 7.437 7.421 7.162 7.157 7.150 7.137 7.130 7.116 7.112 7.107 7.094 7.089 4.429 4.413 4.405 4.389 3.882 2.861 2.837 2.814 2.791 2.582 2.566 2.536 2.520
2.00 4.10 2.97
0.06 0.94 1.00
f1 (ppm)
1.00
f1 (ppm)
O
N
H
CN
CO2Me
F
O
Ph
3am
2.00 4.10 2.97 1.00 3.02 0.06 0.94 1.00
f1 (ppm)


173.610 172.339 166.524 163.856 161.391 132.422 132.321 130.923 130.524 130.436 130.085 129.813 126.486 122.196 122.163 116.297 116.090 115.746 114.243 113.999 55.260 54.708 47.083 31.586
f1 (ppm)
f1 (ppm)
O
N
H
CN
CO2Me
F
O
Ph
3am
f1 (ppm)


-110.657
O
N
H
CN
CO2Me
Ph
O
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

3am

3an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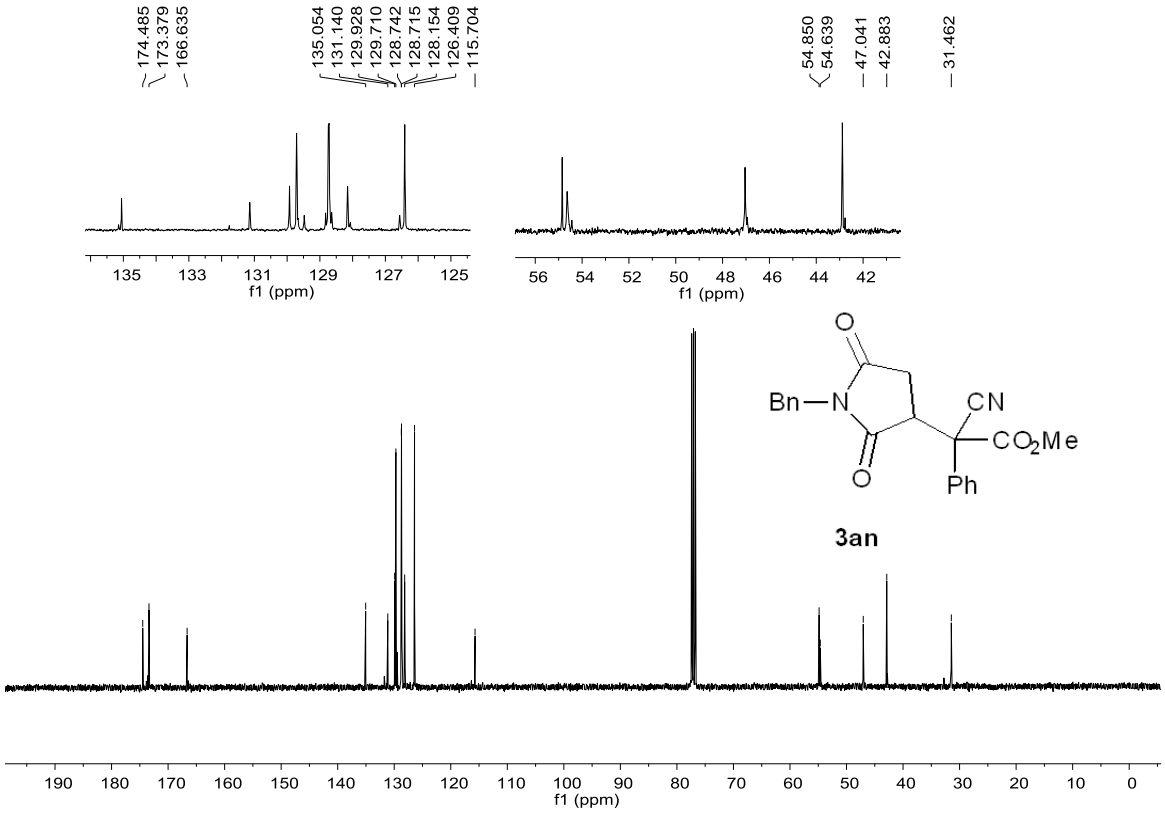
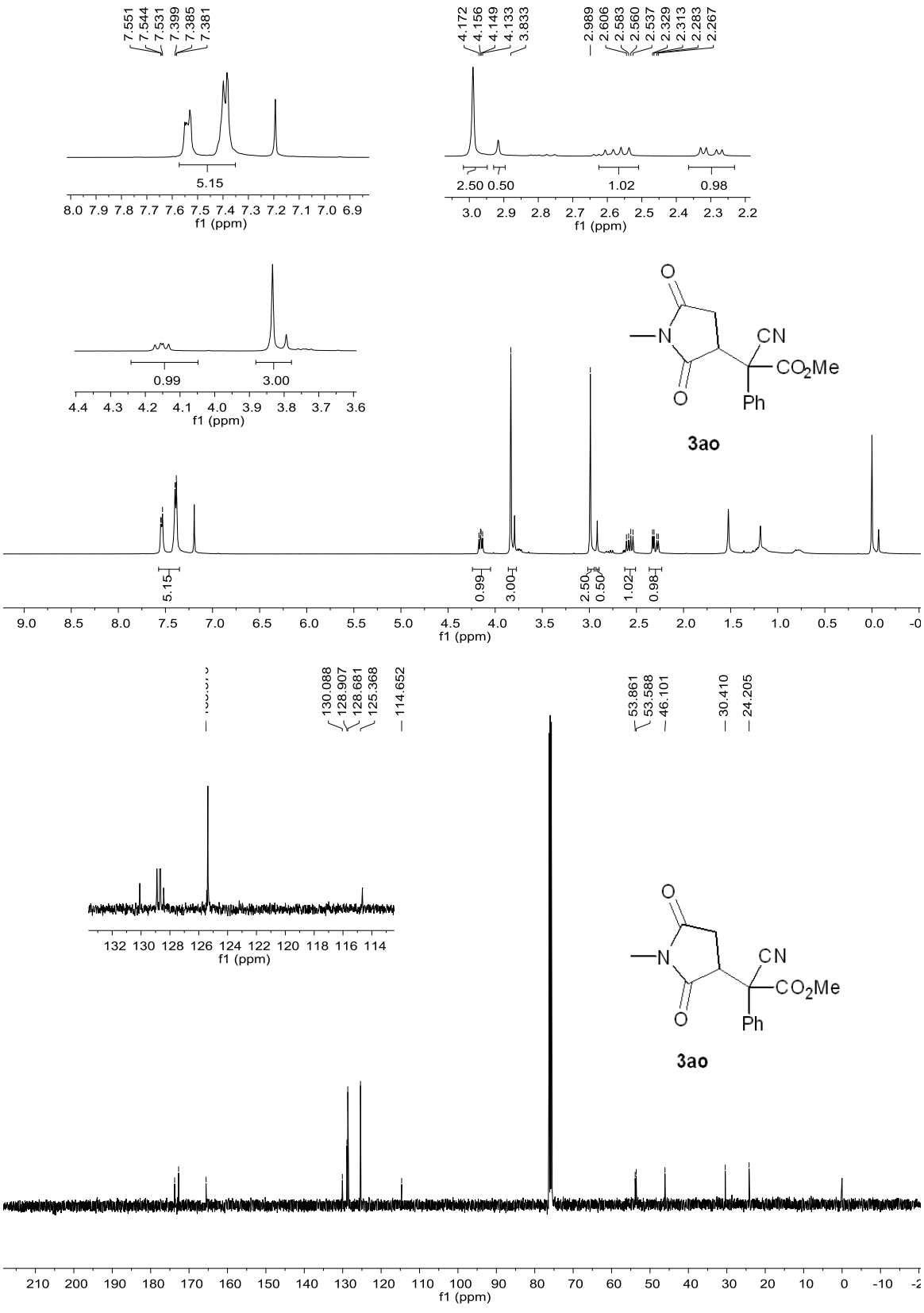
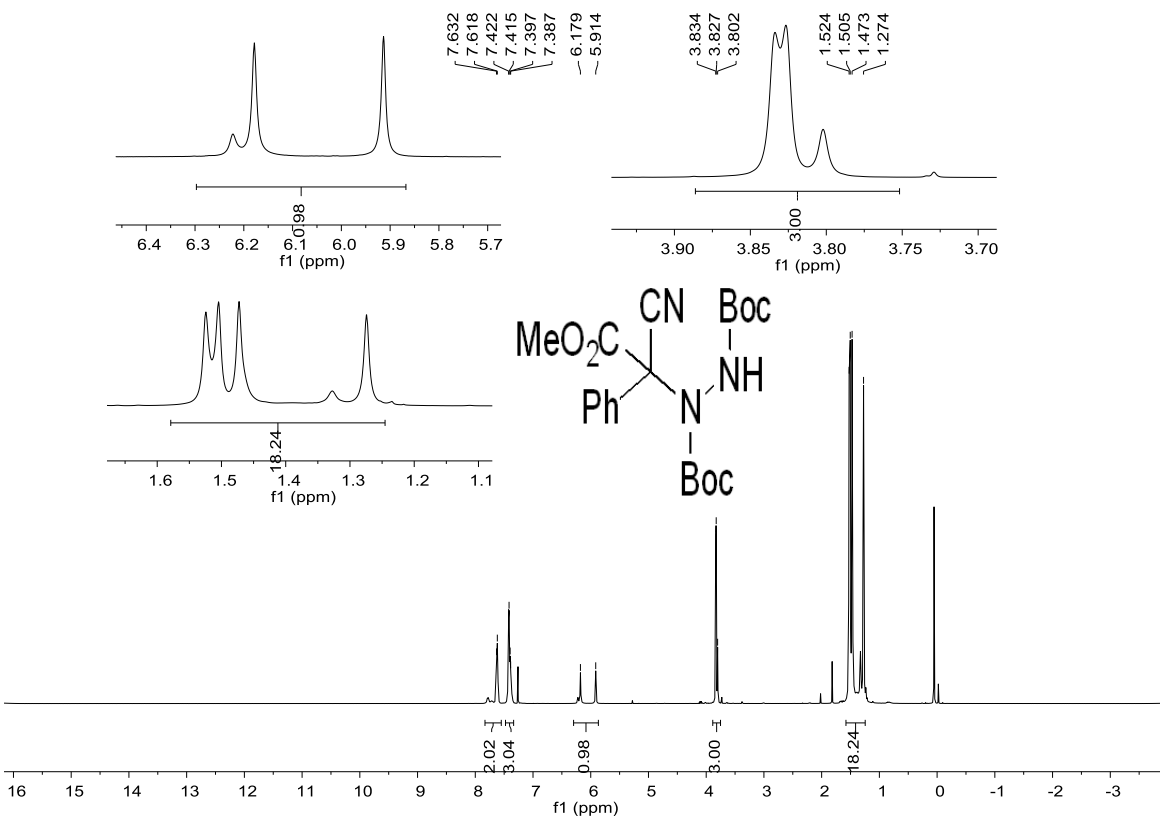
7.590
7.586
7.577
7.573
7.447
7.442
7.434
7.429
7.424
7.381
7.377
7.361
7.358
7.331
7.323
7.317
7.309
7.295
7.290
7.286
4.755
4.720
4.679
4.643
4.236
4.220
4.213
4.197
3.888
2.650
2.626
2.604
2.580
2.392
2.375
2.346
2.329
1.87
3.21
5.01
1.97
0.11
0.91
2.65
0.35
0.97
0.96
f1 (ppm)
Bn—N
CN
CO2Me
Ph
O
3an

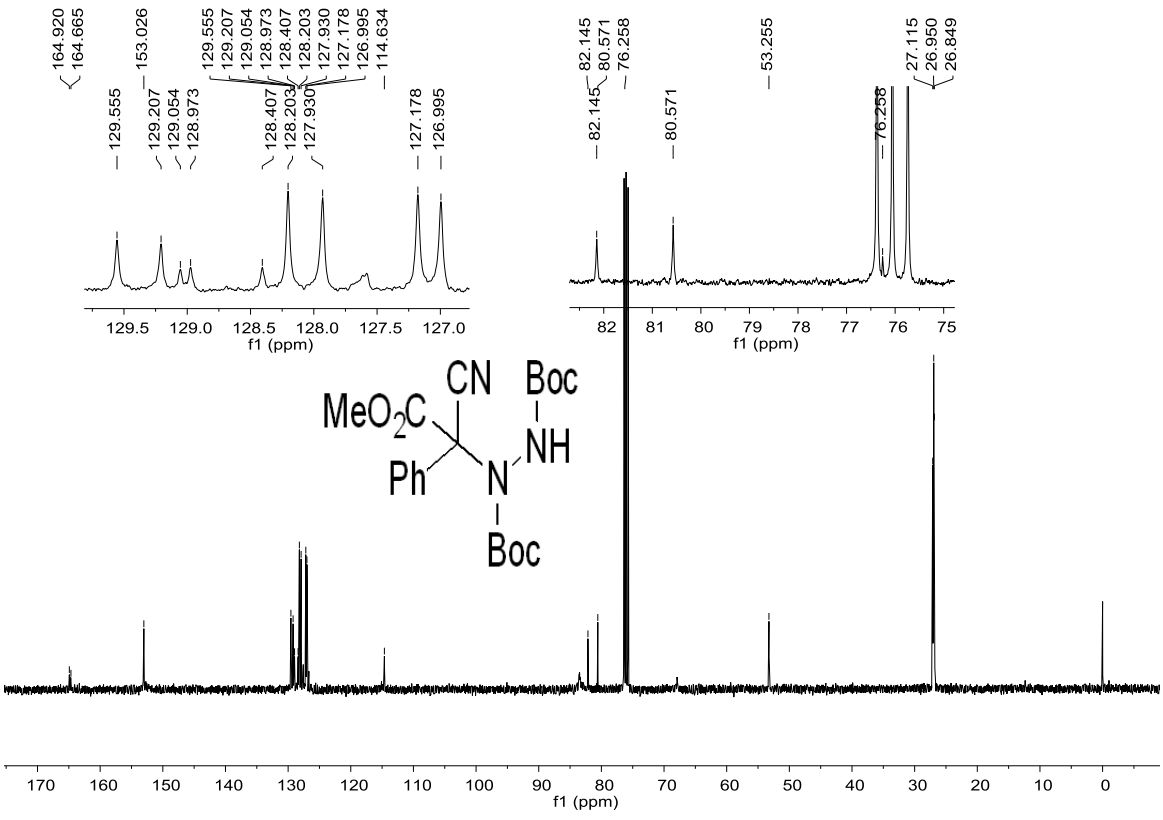

174.485
173.379
166.635
135.054
131.140
129.928
129.710
128.742
128.715
128.154
126.409
115.704
54.850
54.639
47.041
42.883
31.462
f1 (ppm)
Bn—N
CN
CO2Me
Ph
O
3an

3ao

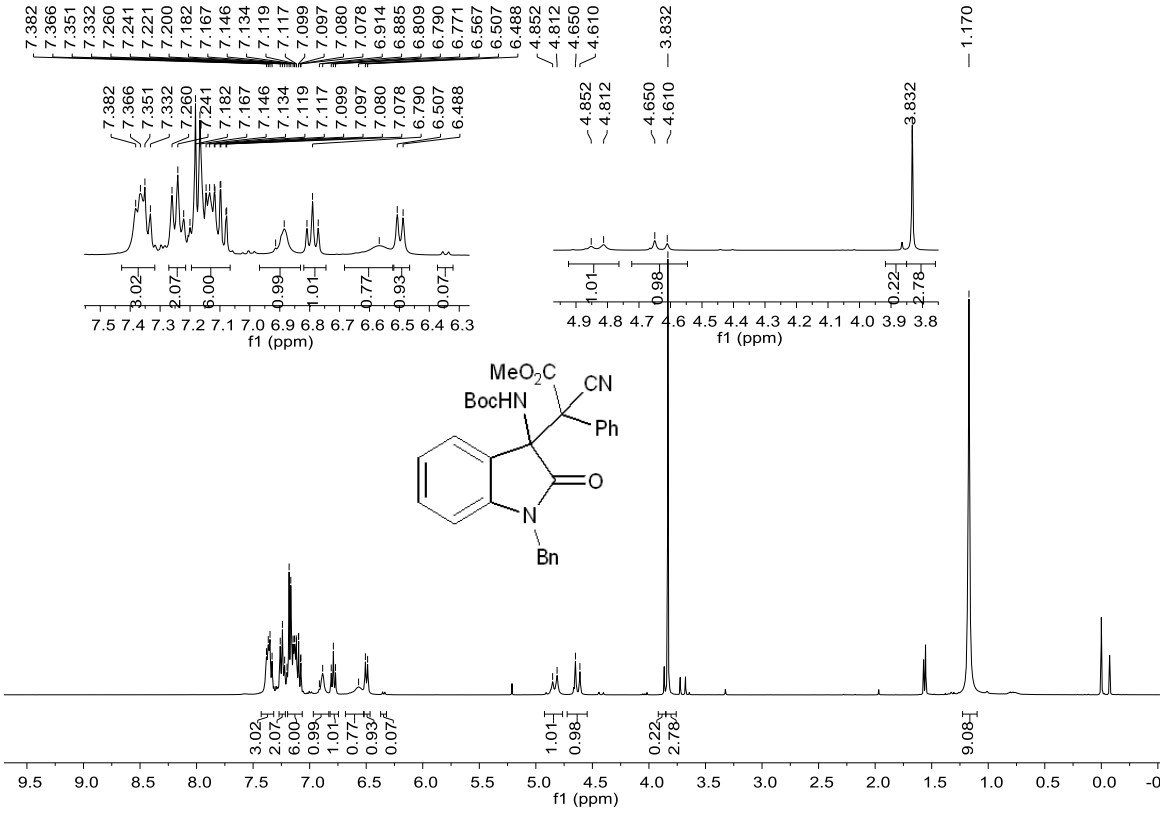

7.551
7.544
7.531
7.399
7.385
7.381
5.15
f1 (ppm)
4.172
4.156
4.149
4.133
3.833
2.989
2.606
2.583
2.560
2.537
2.329
2.313
2.283
2.267
2.50 0.50
1.02
0.98
f1 (ppm)
0.99
3.00
f1 (ppm)
O
N
CN
CO2Me
Ph
O
3ao
5.15
0.99
3.00
2.50
0.50
1.02
0.98
f1 (ppm)
130.088
128.907
128.681
125.368
114.652
53.861
53.588
46.101
30.410
24.205
f1 (ppm)
O
N
CN
CO2Me
Ph
O
3ao
f1 (ppm)

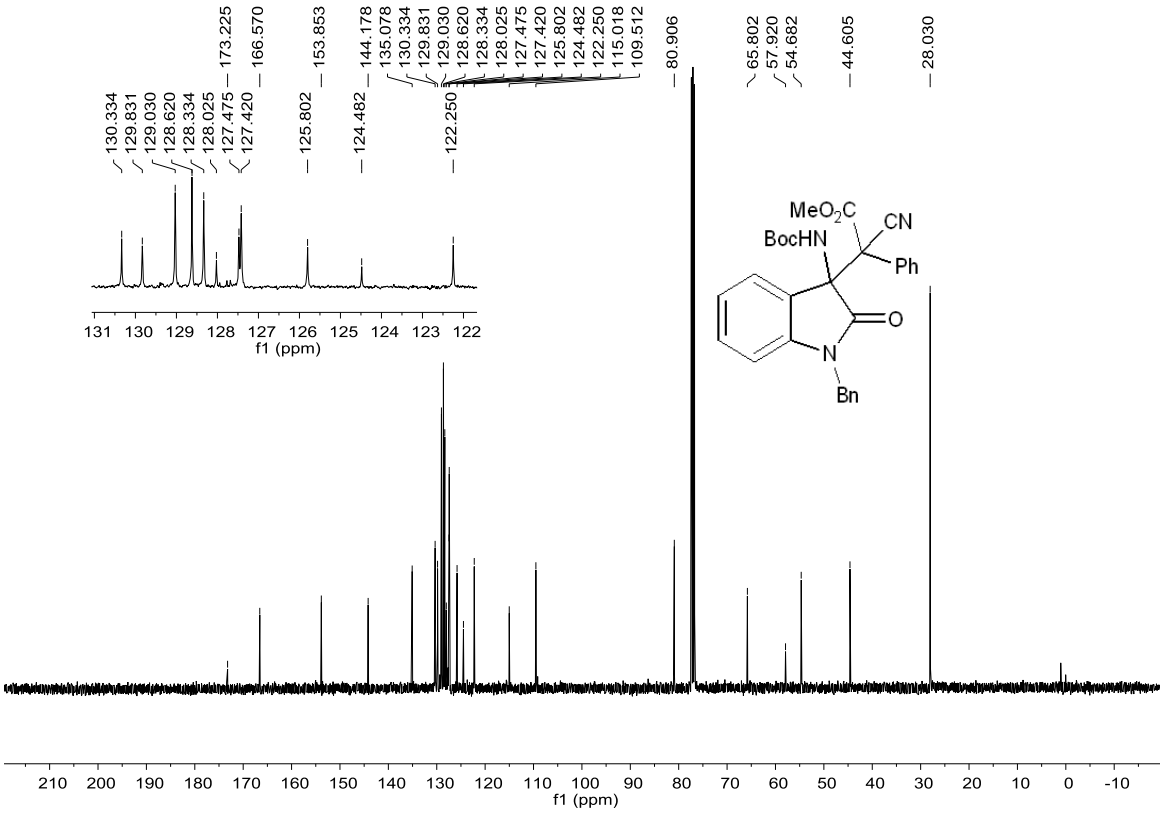
5aa


7.632
7.618
7.422
7.415
7.397
7.387
6.179
5.914
3.834
3.827
3.802
1.524
1.505
1.473
1.274
0.98
3.00
18.24
f1 (ppm)
MeO2C
CN
Boc
NH
Ph
N
Boc
2.02
3.04
0.98
3.00
18.24


164.920
164.665
153.026
129.555
129.207
129.054
128.973
128.407
128.203
127.930
127.178
126.995
114.634
82.145
80.571
76.258
53.255
27.115
26.950
26.849
f1 (ppm)
MeO2C
CN
Boc
NH
Ph
N
Boc

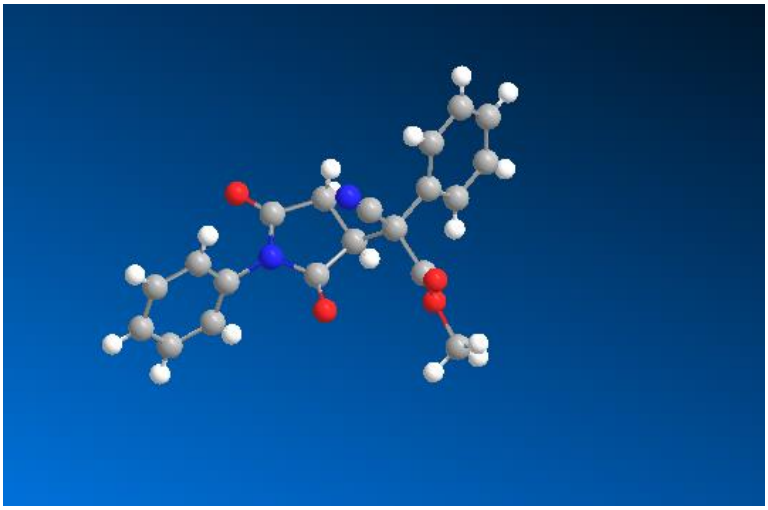
6aa

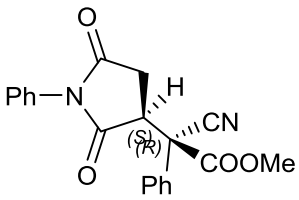




9. X-ray crystal structure of the product 3aa

The colourless and block-shape crystals were selected and mounted for the single-crystal X-ray diffraction. The data set was collected by a Bruker D8 Venture Photon II at 241K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). The structure solution was solved and refinement was processed by SHELXTL (version 6.14) program package[2a, 2b]. The structure was analyzed by ADDSYM routine in PLATON suite and no higher symmetry was suggested[2c].



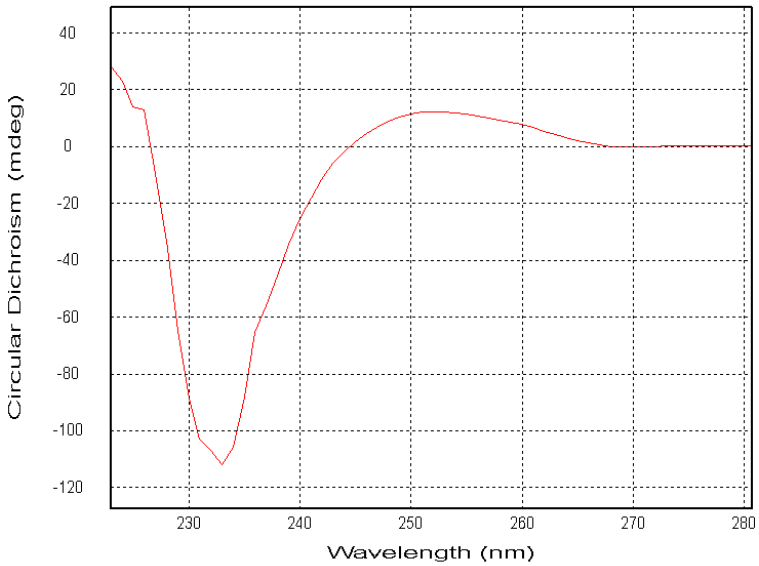


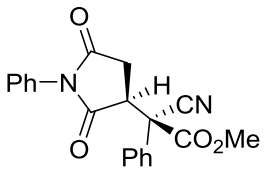
3aa

CCDC: 1901489

10. Copies of the CD spectra of the products 3

(*S*,*R*)-3aa (standard)





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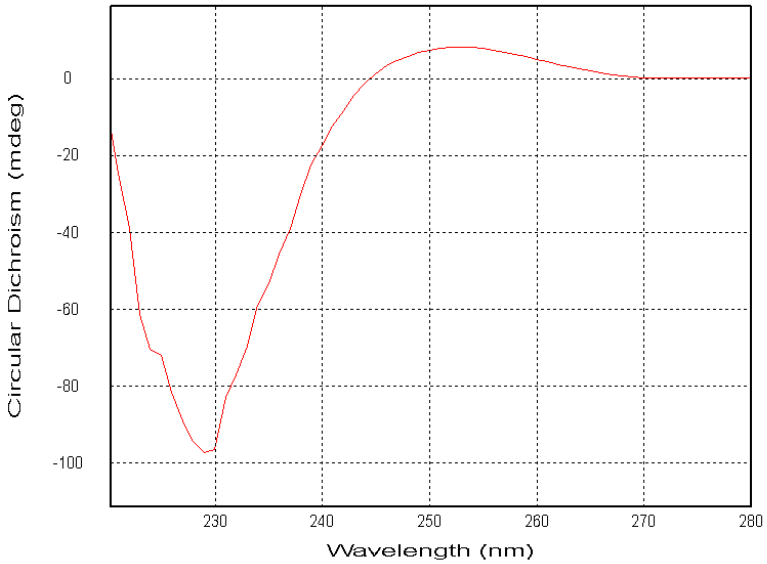
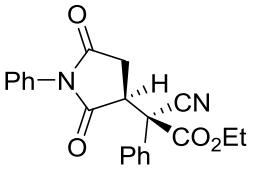
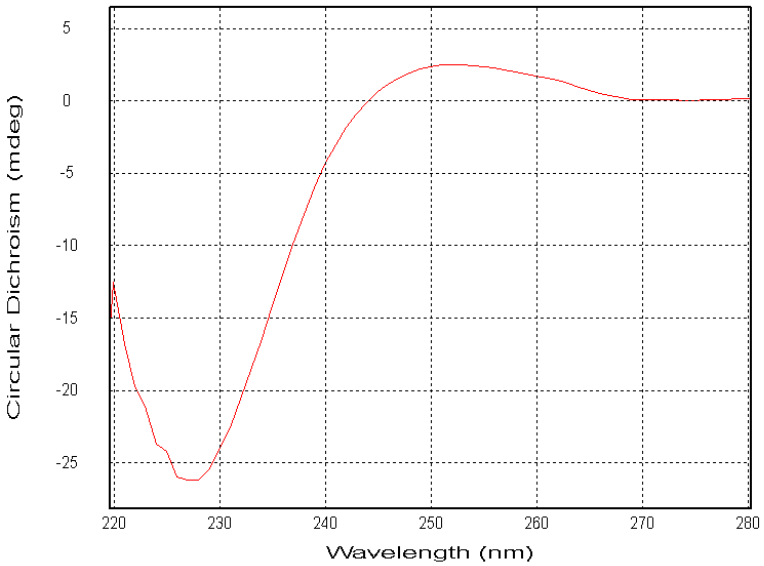




3ba


Circular Dichroism (mdeg)
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-10
-15
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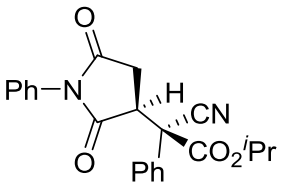
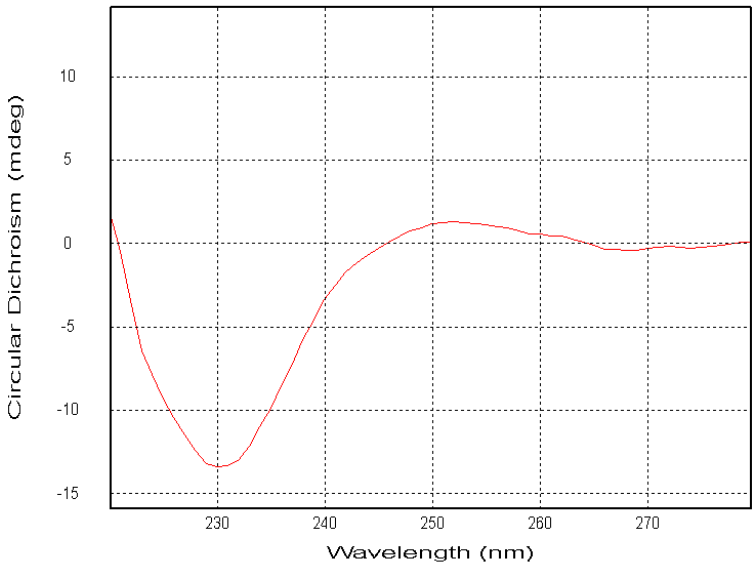
-25
220
230
240
250
260
270
280
Wavelength (nm)


O
Ph—N
H
CN
O
Ph
CO2iPr

3ca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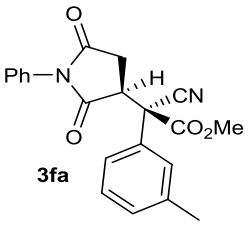
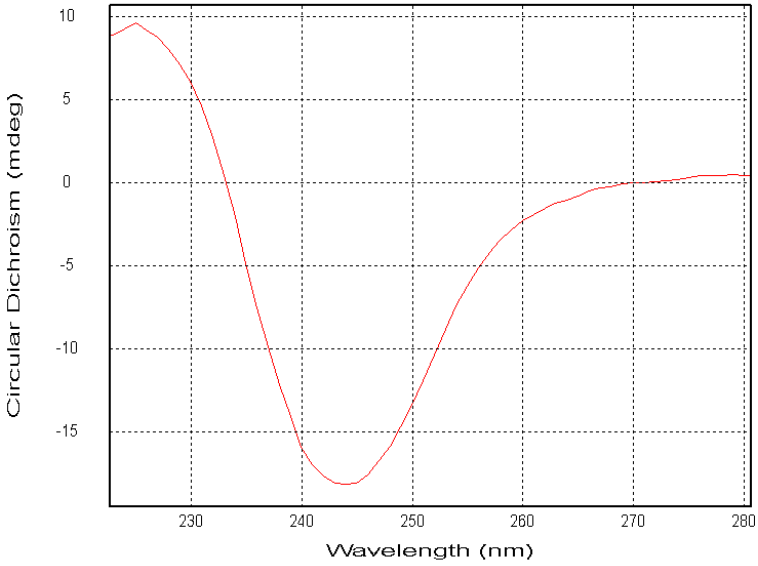
-15
230
240
250
260
270
Wavelength (nm)


O
Ph—N
H
CN
O
CO2Me

3fa


Circular Dichroism (mdeg)
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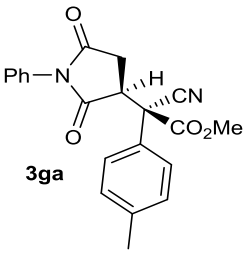
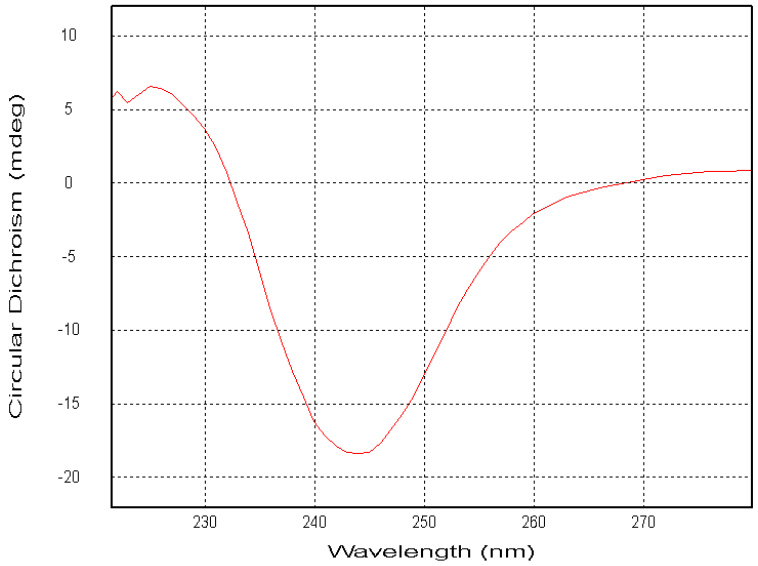
-10
-15
230
240
250
260
270
280
Wavelength (nm)


O
Ph—N
H
CN
CO2Me
O

3ga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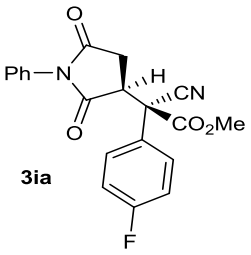
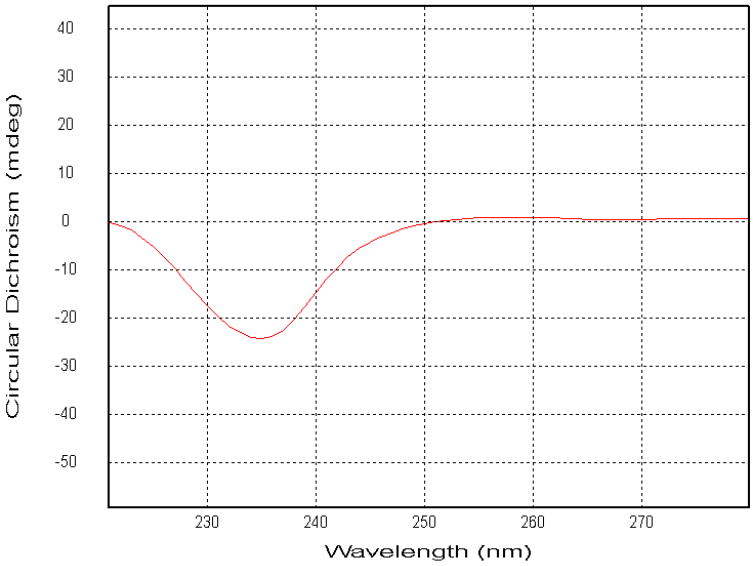
230
240
250
260
270
Wavelength (nm)


O
Ph—N
H
CN
CO2Me
O
F

3ia


Circular Dichroism (mdeg)
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20
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0
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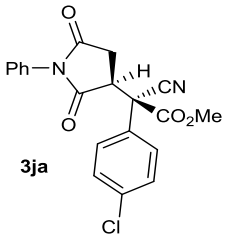
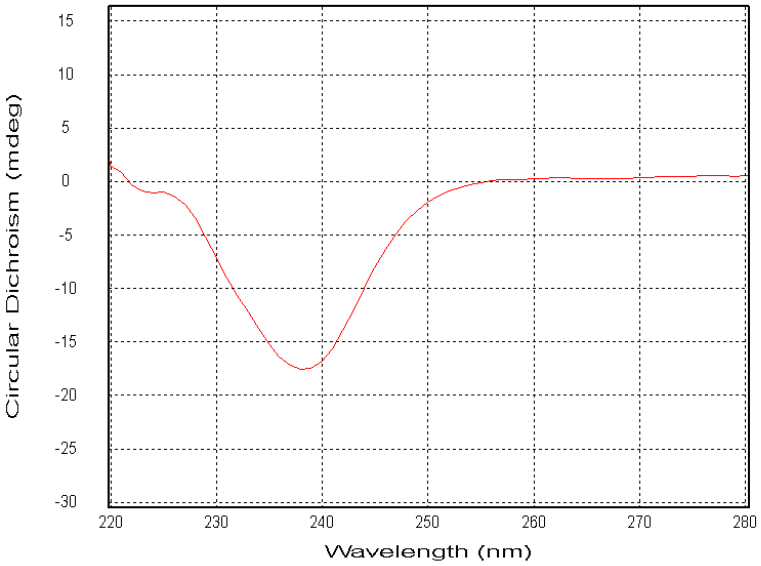
-40
-50
230
240
250
260
270
Wavelength (nm)


O
Ph—N
H
CN
CO2Me
O
Cl

3ja


Circular Dichroism (mdeg)
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10
5
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-20
-25
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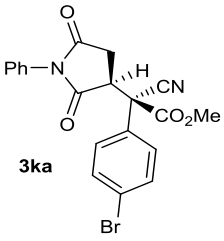
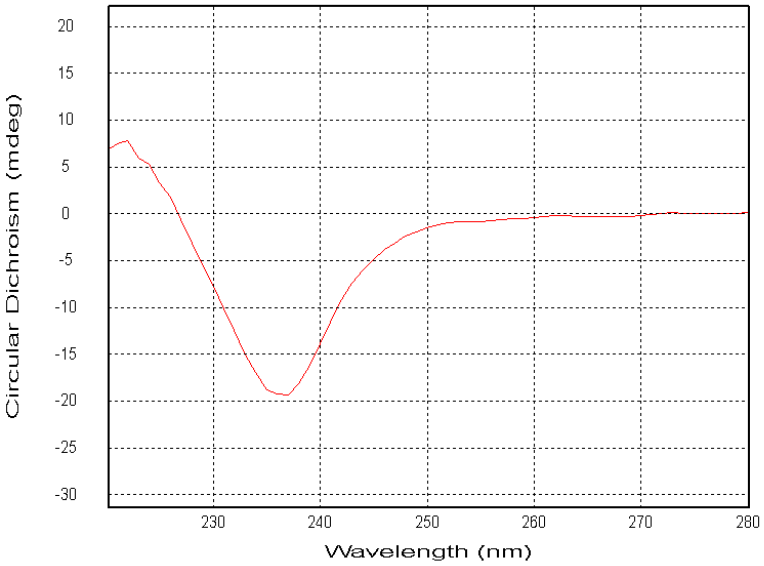
220
230
240
250
260
270
280
Wavelength (nm)


O
Ph—N
H
CN
CO2Me
O
Br

3ka


Circular Dichroism (mdeg)
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15
10
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-10
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-20
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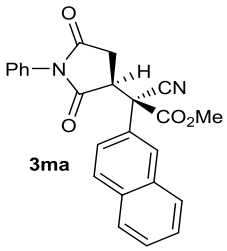
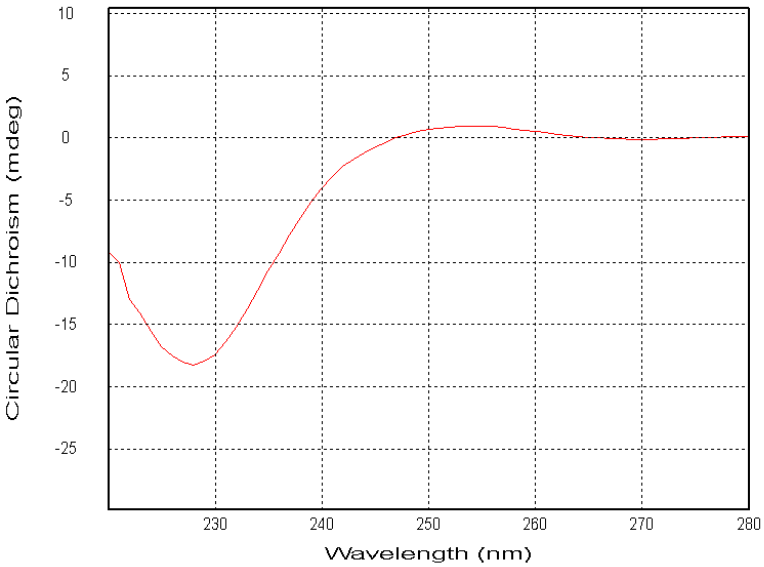
230
240
250
260
270
280
Wavelength (nm)


O
Ph—N
H
CN
CO2Me
O

3ma


Circular Dichroism (mdeg)
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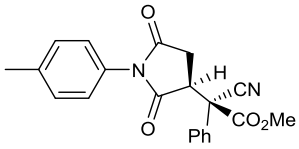
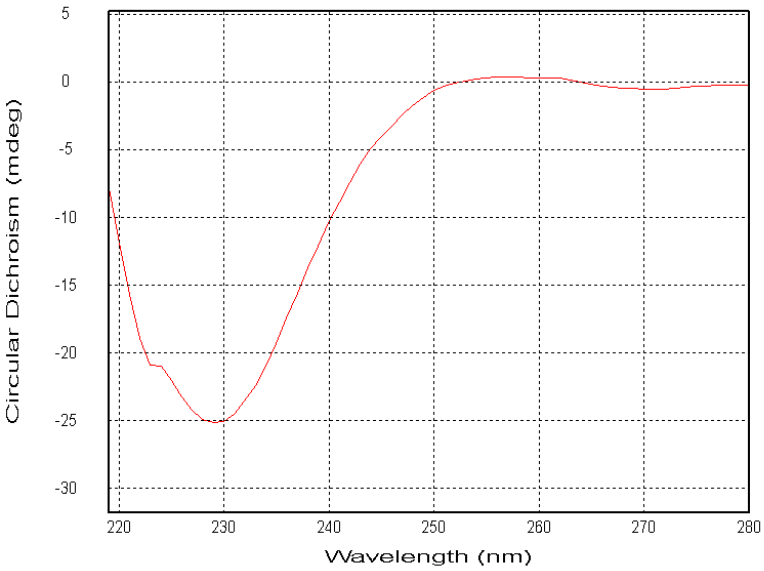
0
-5
-10
-15
-20
-25
230
240
250
260
270
280
Wavelength (nm)


O
N
H
CN
CO2Me
O
Ph

3ab


Circular Dichroism (mdeg)
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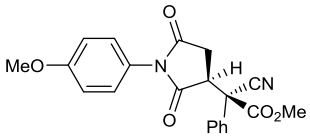
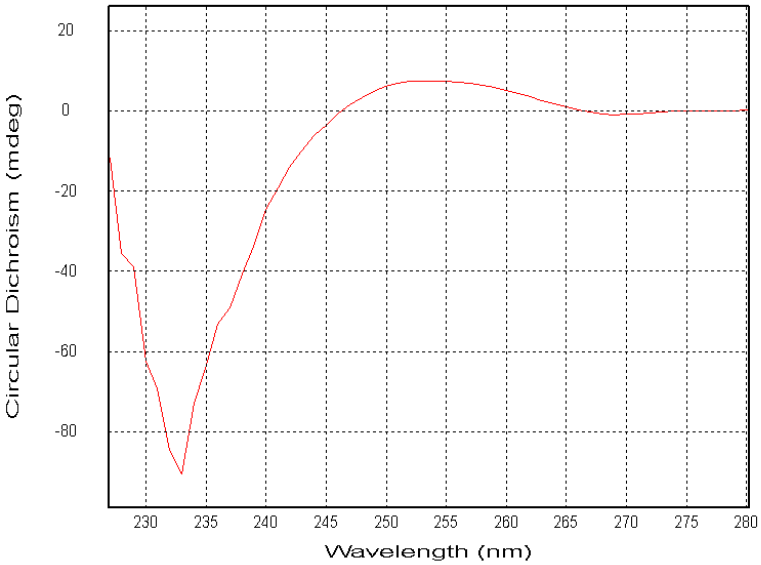
0
-5
-10
-15
-20
-25
-30
220
230
240
250
260
270
280
Wavelength (nm)


MeO
N
O
O
H
CN
CO2Me
Ph

3ac


Circular Dichroism (mdeg)
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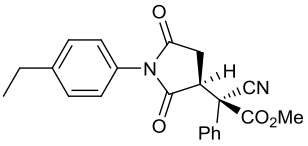
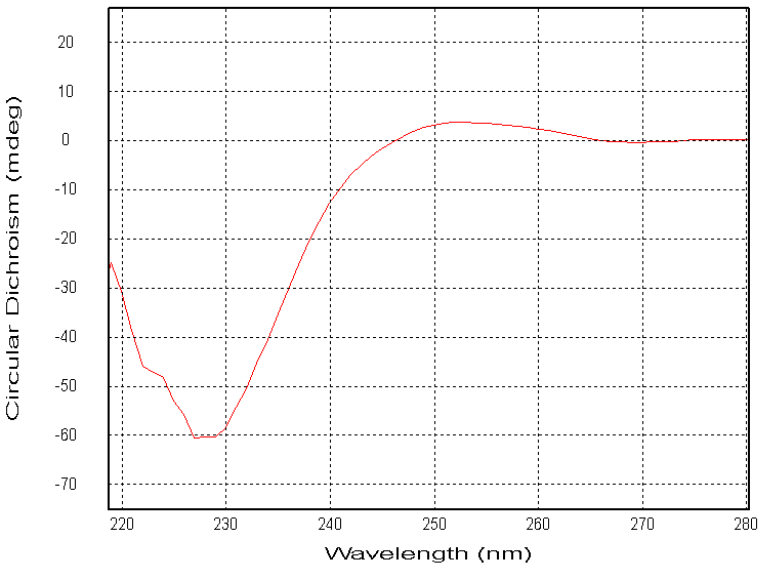
-60
-80
230
235
240
245
250
255
260
265
270
275
280
Wavelength (nm)


N
O
O
H
CN
CO2Me
Ph

3ad


Circular Dichroism (mdeg)
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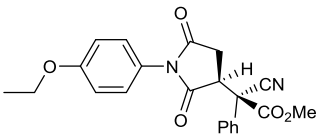
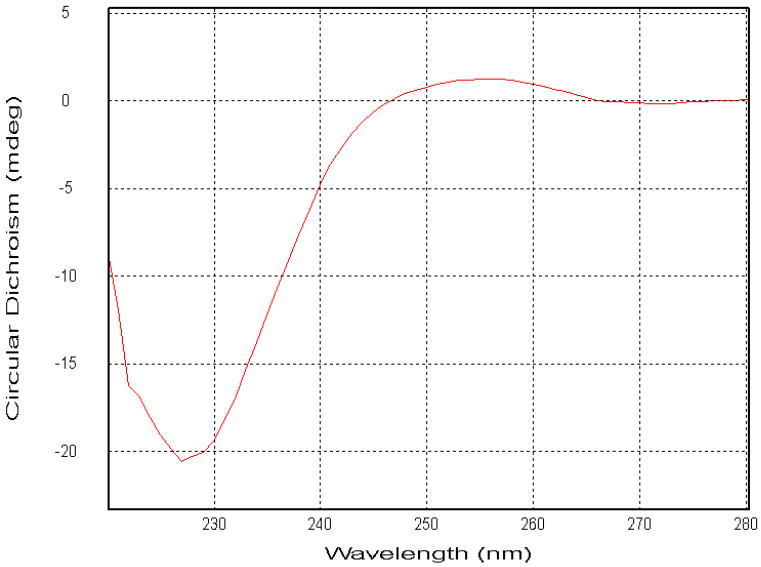
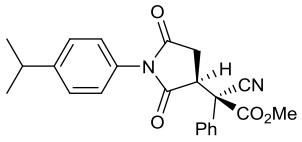
-10
-20
-30
-40
-50
-60
-70
220
230
240
250
260
270
280
Wavelength (nm)

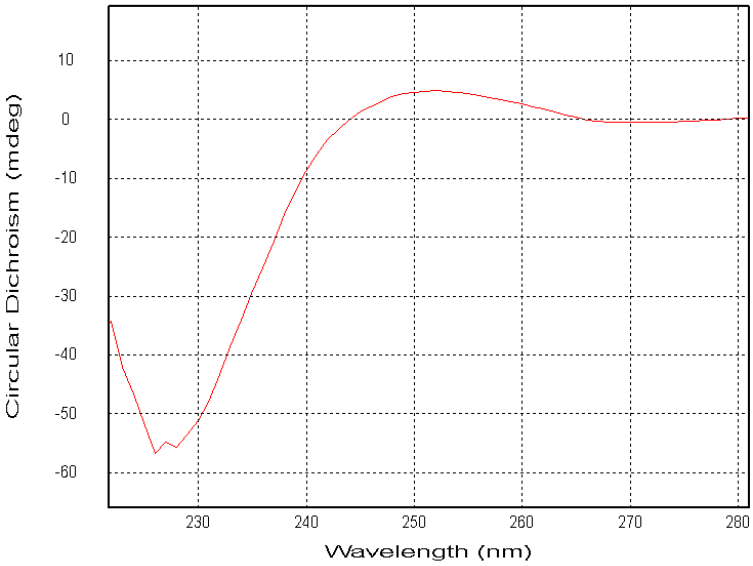

O
O
N
O
H
CN
CO2Me
Ph

3ae


Circular Dichroism (mdeg)
5
0
-5
-10
-15
-20
230
240
250
260
270
280
Wavelength (nm)


O
O
N
O
H
CN
CO2Me
Ph

3af


Circular Dichroism (mdeg)
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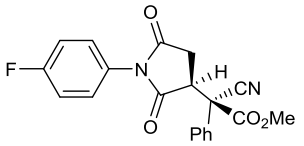
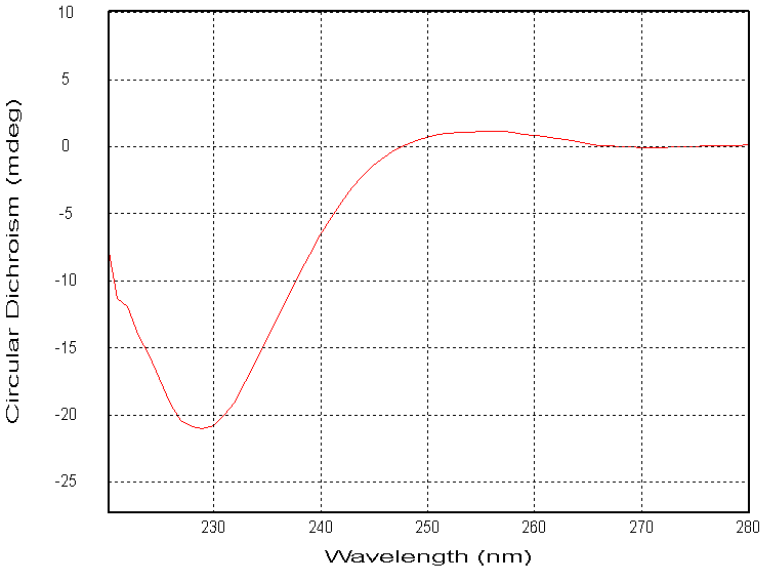
-10
-20
-30
-40
-50
-60
230
240
250
260
270
280
Wavelength (nm)


F
N
O
O
H
CN
CO2Me
Ph

3ag


Circular Dichroism (mdeg)
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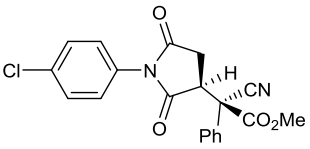
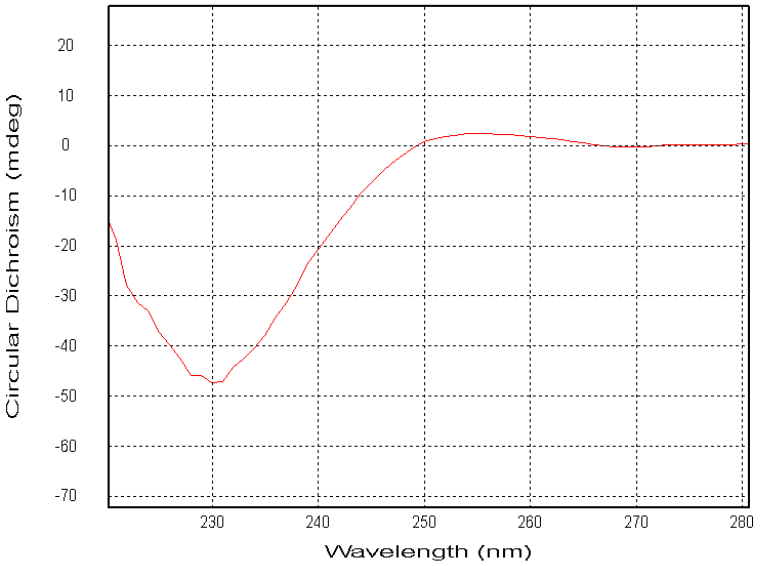
-5
-10
-15
-20
-25
230
240
250
260
270
280
Wavelength (nm)


Cl
N
O
O
H
CN
CO2Me
Ph

3ah


Circular Dichroism (mdeg)
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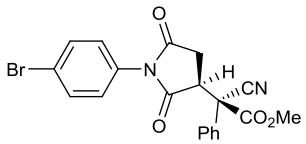
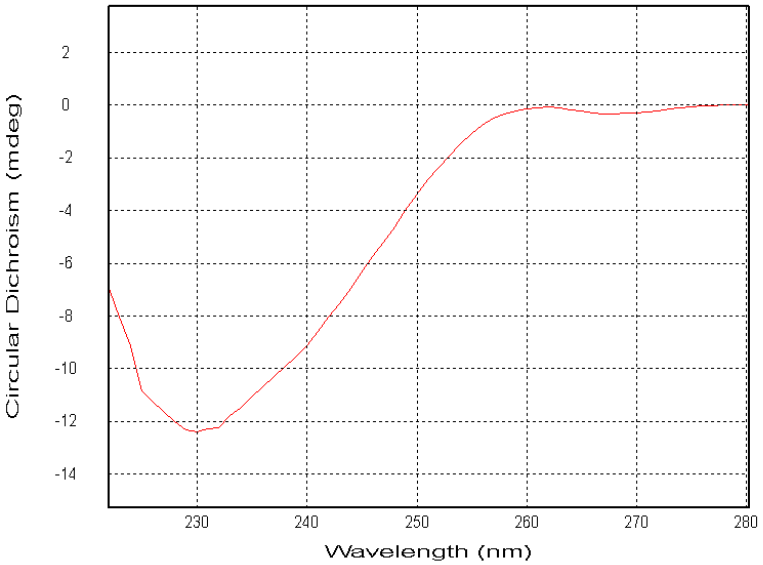
-20
-30
-40
-50
-60
-70
230
240
250
260
270
280
Wavelength (nm)


Br
N
O
O
H
CN
CO2Me
Ph

3ai


Circular Dichroism (mdeg)
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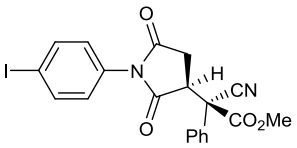
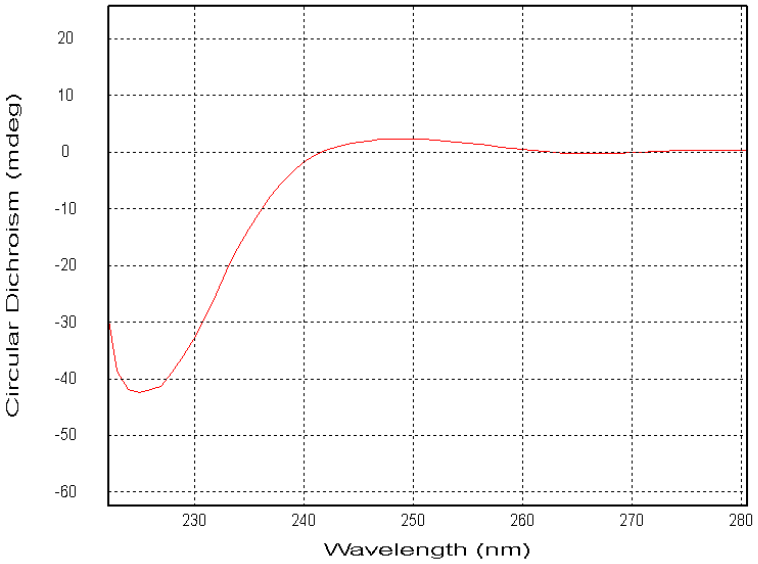
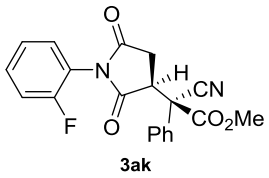
-10
-12
-14
230
240
250
260
270
280
Wavelength (nm)

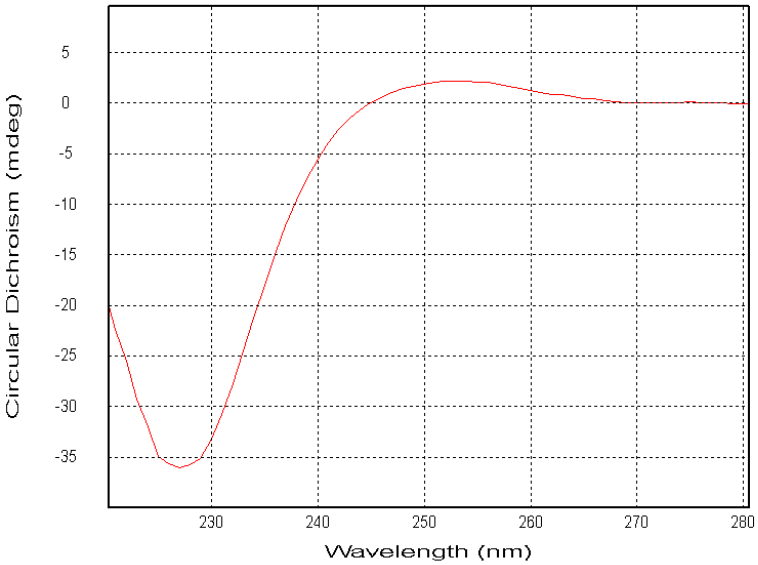

I
N
O
O
H
CN
CO2Me
Ph

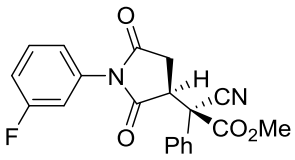
3aj





3ak





3ab

11. References

1. (a) Z. P. Yu, X. H. Liu, L. Zhou, L. L. Lin and X. M. Feng, *Angew. Chem. Int. Ed.*, 2009, **48**, 5195; (b) S. X. Dong, X. H. Liu, X. H. Chen, F. Mei, Y. L. Zhang, B. Gao, L. L. Lin and X. M. Feng, *J. Am. Chem. Soc.*, 2010, **132**, 10650; (c) S. X. Dong, X. H. Liu, Y. L. Zhang, L. L. Lin and X. M. Feng, *Org. Lett.*, 2011, **13**, 5060; (d) S. Ruan, X. B. Lin, L. H. Xie, L. L. Lin, X. M. Feng and X. H. Liu, *Org. Chem. Front.*, 2018, **5**, 32.
2. (a) G. M. Sheldrick, *Acta Cryst.*, 2008, A**64**, 112; (b) G. M. Sheldrick, *Acta Cryst.*, 2015, A**71**, 3; (c) A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7.