Electronic Supplementary Information

Chiral Lewis acid-catalyzed enantioselective cyclopropanation and C-H insertion reactions of vinyl ketones with α-diazoesters

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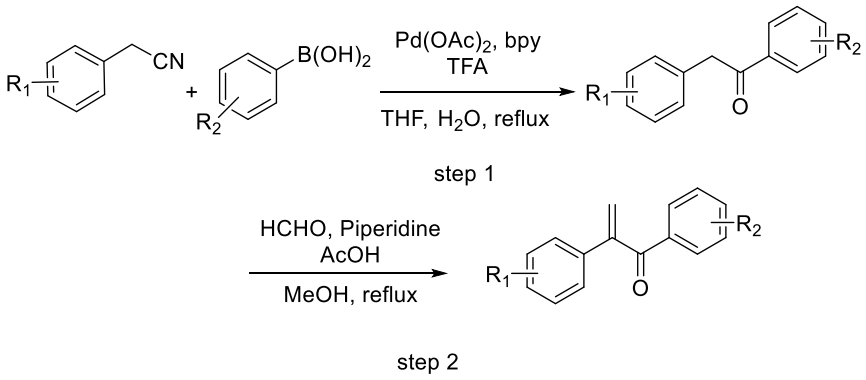
1. General remarks

Reactions were carried out using commercially available reagents in oven-dried apparatus. CH_2Cl_2 was dried over K_2CO_3 and distilled under nitrogen just before use. Enantiomeric excess (*ee*) were determined by HPLC analysis using the corresponding commercially chiral column as stated in the experimental procedures at 23 °C with UV detector at 254 nm. Optical rotations were reported as follows: $[\alpha]^T_D$ (c g/100 mL, in solvent). HRMS was recorded on a commercial apparatus (ESI source). ^{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. Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were collected on commercial instruments (101 MHz) with complete proton decoupling. ^{19}F NMR spectra were collected on commercial instruments (376 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. IR spectra was recorded on SHIMADZU UV-2600 UV-vis spectrophotometer in a 10.0 mm quartz cuvette. Chromatography: Silica gel (HG/T2354-2010) made in Qingdao Haiyang Chemical Co., Ltd.

2. Preparation of the starting materials

All the α-substituted vinyl ketones were prepared by the similar procedure in the literature: [1]



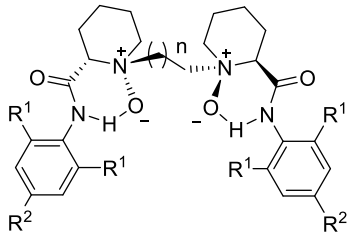
Experimental procedure of step 1: a mixture of substituted phenylacetonitrile and phenylboronic acid (2 equiv) and $Pd(OAc)_2$ (5 mol%), 2,2'-dipyridine (10 mol%), TFA (10 equiv), THF (0.5 M), and H_2O (0.4 mL/mmol) was reflux at 80 ℃ under nitrogen atmosphere for 36 h. The residue was dissolved in AcOEt and washed with water. The aqueous phase was washed with AcOEt and the organic layers were combined, washed with brine, dried over Na_2SO_4 and concentrated in vacuo, which was further purified by silica gel chromatography.

Experimental procedure of step 2: to a solution of the products from step 1 and formaldehyde

(4 equiv), piperidine (0.1 equiv), AcOH (0.2 equiv) and MeOH (5 M) was reflux for 6 h. After completion of this reaction, water was added after evaporation of MeOH. Then, the residue was washed with CH_2Cl_2 and the organic layer were combined, washed with brine, dried over Na_2SO_4 and concentrated in vacuo, which was further purified by silica gel chromatography. *α*-Alkyl-*α*-diazoesters synthesized according the previous report. [2]

3. General procedure for chiral *N,N′*-dioxides preparation

The *N,N'*-dioxide ligands were prepared by the similar procedure in the literature.[3]



L_3-PiEt$_2$Me: n = 2, R^1 = Et, R^2 = Me
L_3-PiMe$_2$: n = 2, R^1 = Me, R^2 = H
L_3-PiEt$_2$: n = 2, R^1 = Et, R^2 = H
L_3-PiMe$_3$: n = 2, R^1 = R^2 = Me
L_3-PiPr$_3$: n = 2, R^1 = R^2 = ^{i}Pr
L_2-PiPr$_3$: n = 1, R^1 = R^2 = ^{i}Pr
L_2-PiPh: n = 1, R^1 = R^2 = H

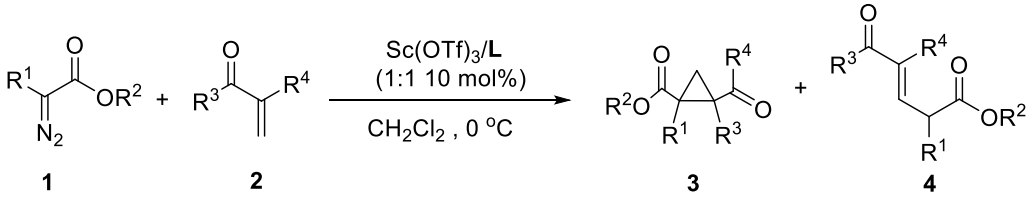
L_2-PiMe: n = 1, R^1 = H, R^2 = Me
L_2-PiBu: n = 1, R^1 = H, R^2 = ^{t}Bu
L_2-PiEt: n = 1, R^1 = H, R^2 = Et
L_2-PiPr: n = 1, R^1 = H, R^2 = ^{i}Pr
L_2-PiEt$_2$: n = 1, R^1 = Et, R^2 = H
L_2-PiMe$_2$: n = 1, R^1 = Me, R^2 = H
L_2-PiMe$_3$: n = 1, R^1 = R^2 = Me

Figure S1 Structures of *N,N′* -dioxide ligands.

4. General procedure for the preparation of the racemic products

To an oven-dried reaction tube were added $Sc(OTf)_3$ (10 mol %), rac-**L-PiMe$_3$** (10 mol %), and THF (0.5 mL). The suspensions were stirred at 30 ℃ for 0.5 h under nitrogen atmosphere. After the solvent had been removed under vacuum, enone (0.1 mmol), α-diazoester (0.15 mmol) and CH_2Cl_2 (0.5 mL) were added at 0 ℃. Then the solutions were stirred at 0 ℃ for 72 h. After the completion of the reaction, the suspensions were directly purified by flash chromatography on silica gel (Eluent: ether: petroleum ether = 1:15-1:40) to provide the desired products, respectively.

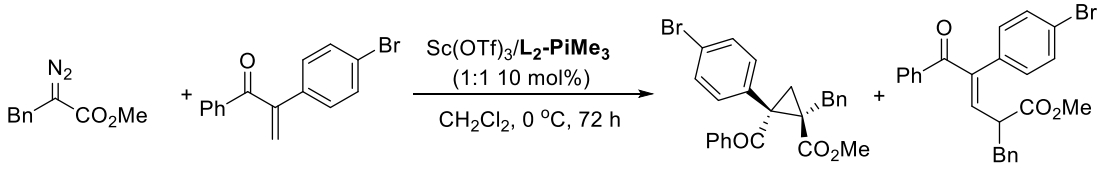
5. General procedure for the catalytic asymmetric transformation



1 **2** **3** **4**

General Procedure: To an oven-dried reaction tube were added $Sc(OTf)_3$ (10 mol %), **L_2-PiMe$_3$** (10 mol %), and THF (0.5 mL). The suspensions were stirred at 30 ℃ for 0.5 h under nitrogen atmosphere. After the solvent had been removed under vacuum, enone **2** (0.1 mmol), α-diazoester **1** (0.15 mmol) and CH_2Cl_2 (0.5 mL) were added at 0 ℃. Then the solutions were stirred at 0 ℃ for 72 h. After the completion of the reaction, the suspensions were directly purified by flash chromatography on silica gel (Eluent: ether: petroleum ether = 1:15-1:40) to afford the corresponding product **3** and **4**, respectively.

6. Experimental procedure for the gram-scale reaction



1a
1.6 mL
5.19 mmol

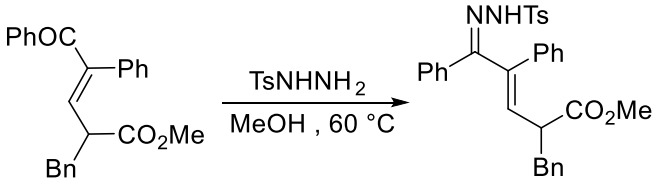
2i
0.995 g
3.46 mmol

3ai
0.830 g
53% yield

4ai
0.721 g
46% yield

To an oven-dried 50 mL round-bottomed flask were added $Sc(OTf)_3$ (10 mol%), **L_2-PiMe$_3$** (10 mol%), and THF (25 mL). The suspensions were stirred at 30 ℃ for 0.5 h under nitrogen atmosphere. After the solvent had been removed under vacuum, enone **2i** (3.46 mmol), α-diazoester **1** (5.19 mmol) and CH_2Cl_2 (25 mL) were added at 0 ℃. Then the solutions were stirred at 0 ℃ for 72 h. After the completion of the reaction, the suspensions were directly purified by flash chromatography on silica gel (Eluent: ether: petroleum ether = 1:15) to afford the corresponding product **3ai** and **4ai**, respectively.

7. Experimental procedure for the synthesis of 5aa



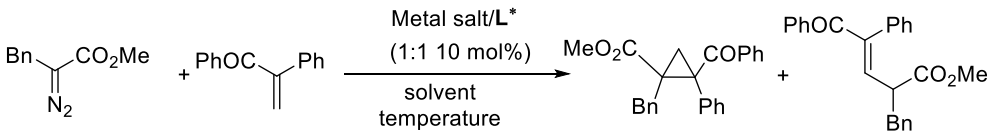
3aa, 90% ee

5aa
64% yield , 90% ee

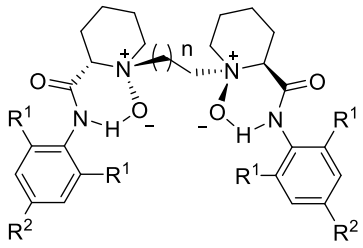
Experimental procedure for the synthesis of **5aa**: An oven-dried test tube was charged with **3aa** (0.10 mmol, 37.0 mg) and MeOH (1.0 mL). The tube was sealed with a stopper. Then, $TsNHNH_2$ (0.20 mmol, 37.2 mg) was added under stirring, and the mixture was stirred at the 60 ℃ for 3 h before it was directly purified by flash chromatography on silica gel (eluent : petroleum ether : EtOH= 5:1) to afford the desired product **5aa** in 64% yield.

8. Optimization of the conditions[a]

Table S1. Optimization of the conditions.



1a **2a** **3aa** **4aa**



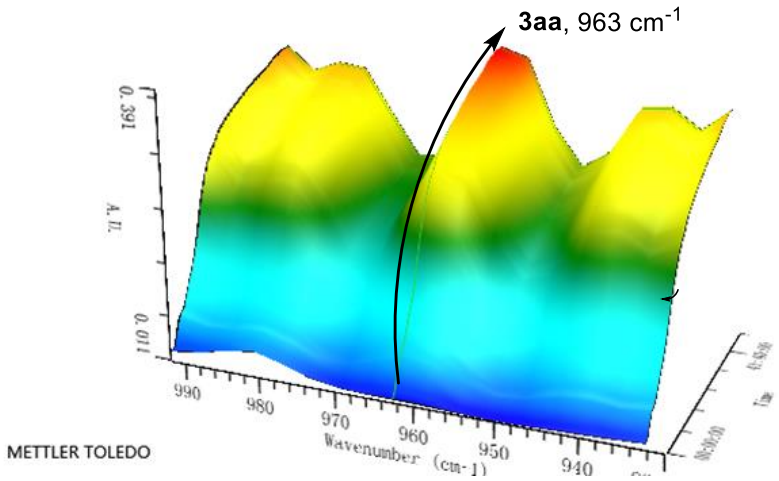
L_3-PiEt$_2$Me: n = 2, R^1 = Et, R^2 = Me
L_3-PiMe$_2$: n = 2, R^1 = Me, R^2 = H
L_3-PiEt$_2$: n = 2, R^1 = Et, R^2 = H
L_3-PiMe$_3$: n = 2, R^1 = R^2 = Me
L_3-PiPr$_3$: n = 2, R^1 = R^2 = ^{i}Pr
L_2-PiPr$_3$: n = 1, R^1 = R^2 = ^{i}Pr
L_2-PiPh: n = 1, R^1 = R^2 = H

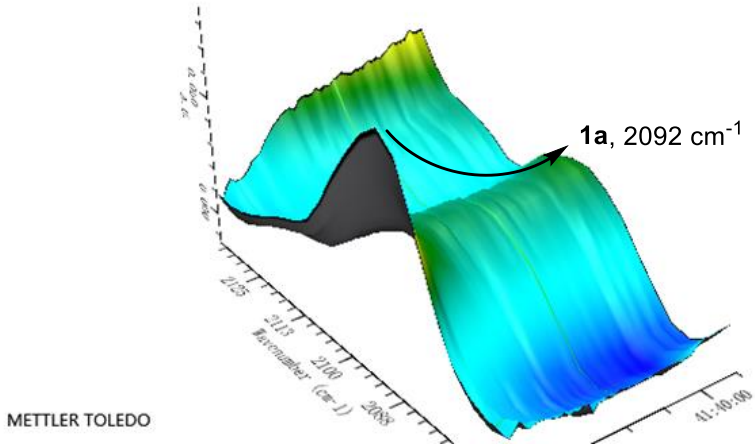
L_2-PiMe: n = 1, R^1 = H, R^2 = Me
L_2-PiBu: n = 1, R^1 = H, R^2 = ^{t}Bu
L_2-PiEt: n = 1, R^1 = H, R^2 = Et
L_2-PiPr: n = 1, R^1 = H, R^2 = ^{i}Pr
L_2-PiEt$_2$: n = 1, R^1 = Et, R^2 = H
L_2-PiMe$_2$: n = 1, R^1 = Me, R^2 = H
L_2-PiMe$_3$: n = 1, R^1 = R^2 = Me

entry	**L***	Metal salt	solvent	Temp. (℃)	Yield **3**/**4** (%)[b]	ee **3**/**4** (%)[c]
1	**L_3-PiEt$_2$Me**	$Sc(OTf)_3$	CH_2Cl_2	30	11/34	57/69
2	**L_3-PiMe$_2$**	$Sc(OTf)_3$	CH_2Cl_2	30	21/23	71/77
3	**L_3-PiEt$_2$**	$Sc(OTf)_3$	CH_2Cl_2	30	28/28	75/73
4	**L_3-PiMe$_3$**	$Sc(OTf)_3$	CH_2Cl_2	30	26/28	79/81
5	**L_3-PiPr$_3$**	$Sc(OTf)_3$	CH_2Cl_2	30	21/6	75/73
6	**L_2-PiPr$_3$**	$Sc(OTf)_3$	CH_2Cl_2	30	30/35	30/50
7	**L_2-PiPh**	$Sc(OTf)_3$	CH_2Cl_2	30	44/34	54/47
8	**L_2-PiMe**	$Sc(OTf)_3$	CH_2Cl_2	30	49/46	60/73
9	**L_2-PiBu**	$Sc(OTf)_3$	CH_2Cl_2	30	43/43	67/43
10	**L_2-PiEt**	$Sc(OTf)_3$	CH_2Cl_2	30	33/34	60/55
11	**L_2-PiPr**	$Sc(OTf)_3$	CH_2Cl_2	30	38/34	65/40
12	**L_2-PiEt$_2$**	$Sc(OTf)_3$	CH_2Cl_2	10	49/43	93/84
13	**L_2-PiMe$_2$**	$Sc(OTf)_3$	CH_2Cl_2	10	51/46	94/88
14	**L_2-PiMe$_3$**	$Sc(OTf)_3$	CH_2Cl_2	10	48/48	99/90
15	**L_2-PiMe$_3$**	$Sc(OTf)_3$	CH_2Cl_2	0	46/45	99/91
16	**L_2-PiMe$_3$**	$Sc(OTf)_3$	Ethyl	0	24/5	95/89
17	**L_2-PiMe$_3$**	$Sc(OTf)_3$	$CHCl_2CH$	0	34/15	95/89
18	**L_2-PiMe$_3$**	$Sc(OTf)_3$	$CHCl_3$	0	21/7	96/88
19	**L_2-PiMe$_3$**	$Sc(OTf)_3$	CH_3CN	0	31/11	90/95
20	**L_2-PiMe$_3$**	$La(OTf)_3$	CH_2Cl_2	30	16/trace	Race/-
21	**L_2-PiMe$_3$**	$Yb(OTf)_3$	CH_2Cl_2	30	18/trace	Race/-
22	**L_2-PiMe$_3$**	$In(OTf)_3$	CH_2Cl_2	30	27/trace	55/-
23	**L_2-PiMe$_3$**	$Mg(OTf)_2$	CH_2Cl_2	30	13/trace	Race/-
24	**L_2-PiMe$_3$**	$InBr_3$	CH_2Cl_2	30	14/trace	Race/-
25	**L_2-PiMe$_3$**	$ScCl_3 \cdot 6H_2O$	CH_2Cl_2	30	17/trace	Race/-

[a] Unless otherwise noted, the reactions were performed with 10 mol % metal salt, 10 mol% ligand, 1a (0.15 mmol) and 2a (0.1 mmol) in solvent (0.5 mL) under N_2 for 24 h. [b] Isolated yield by silica gel chromatography. [c] Determined by chiral HPLC analysis (Chiralcel IB).

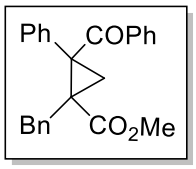
9. Operando IR experiments



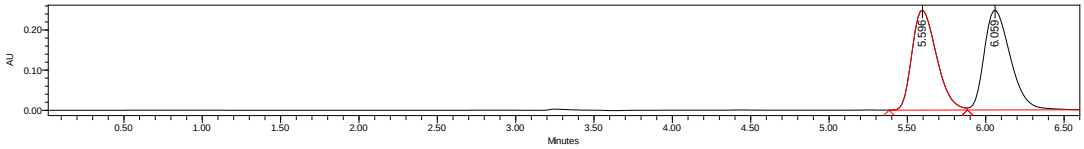


10. The analytical and spectral characterization data of the products

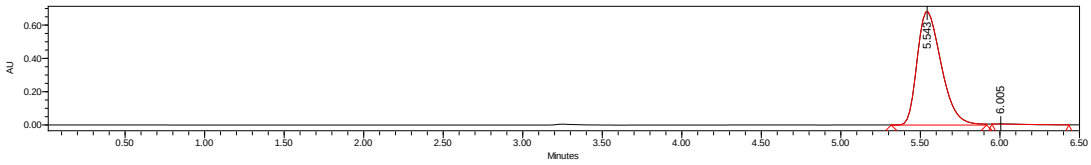
Methyl 2-benzoyl-1-benzyl-2-phenylcyclopropane-1-carboxylate(3a)



White powder, m.p. 86 - 90 ℃, 46% yield, ee = 99%, $[\alpha]^{16}_{D}$ = +29.9 (*c* = 0.68, in CH_2Cl_2). **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 5.54 min, t_R (minor) = 6.01 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.11 – 8.04 (m, 2H), 7.50 (ddd, *J* = 7.1, 3.5, 1.5 Hz, 3H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.27 – 7.15 (m, 8H), 3.94 (dd, *J* = 14.9, 1.4 Hz, 1H), 3.31 (s, 3H), 2.47 (dd, *J* = 5.5, 1.4 Hz, 1H), 2.23 (d, *J* = 14.9 Hz, 1H), 1.97 (d, *J* = 5.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$)δ 196.1, 170.7, 138.9, 135.8, 135.8, 133.2, 129.9, 129.6, 128.6, 128.5, 128.4, 127.6, 126.5, 51.8, 45.7, 38.1, 37.6, 21.8. **IR** (film): ν(cm^{-1}) 2968, 1726, 1669, 1448, 1282, 705. **HRMS** (FTMS + ESI) calcd for $C_{25}H_{22}NaO_3^+$ ([M]+Na^+) = 393.1461 found 393.1462.

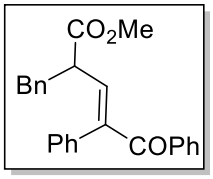


	Retention Time	Area	% Area
1	5.596	2711910	48.44
2	6.059	2886499	51.56

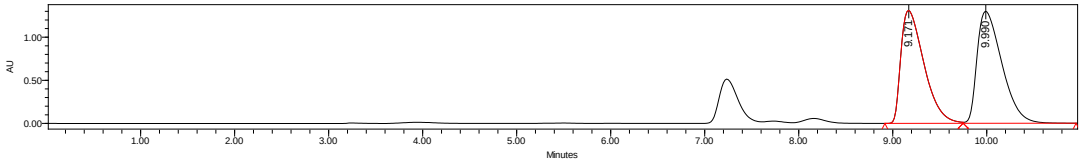


	Retention Time	Area	% Area
1	5.543	7197073	99.69
2	6.005	22263	0.31

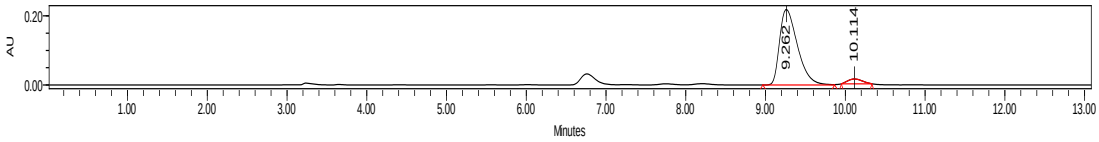
Methyl (E)-2-benzyl-5-oxo-4,5-diphenylpent-3-enoate (4aa)



Colorless oil, 45% yield, ee = 90%, $[\alpha]^{16}_{D}$ = −74.0 (*c* = 0.70, in CH_2Cl_2). **HPLC** (Chiral IB column) ^{i}PrOH/^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 9.26 min, t_R (minor) = 10.11 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 – 7.59 (m, 2H), 7.55 – 7.48 (m, 1H), 7.43 – 7.35 (m, 2H), 7.31 (d, *J* = 2.0 Hz, 3H), 7.28 (d, *J* = 1.7 Hz, 1H), 7.27 – 7.24 (m, 2H), 7.04 – 6.96 (m, 4H), 6.28 (d, *J* = 10.6 Hz, 1H), 3.73 – 3.66 (m, 1H), 3.69 (s, 3H), 3.16 (dd, *J* = 13.7, 6.1 Hz, 1H), 2.87 (dd, *J* = 13.7, 9.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.5, 172.9, 144.0, 138.2, 137.7, 137.5, 135.1, 132.4, 129.9, 129.2, 129.1, 128.5, 128.3, 128.3, 127.9, 126.8, 52.3, 47.4, 38.5, 29.7. **IR** (film): ν(cm^{-1}) 2936, 1740, 1634, 1354, 698. **HRMS** (FTMS + ESI) calcd for $C_{25}H_{22}NaO_3^+$ ([M]+Na^+) = 393.1461, found 393.1462.

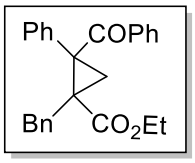


	Retention Time	Area	% Area
1	9.171	22275332	48.29
2	9.990	23851801	51.71

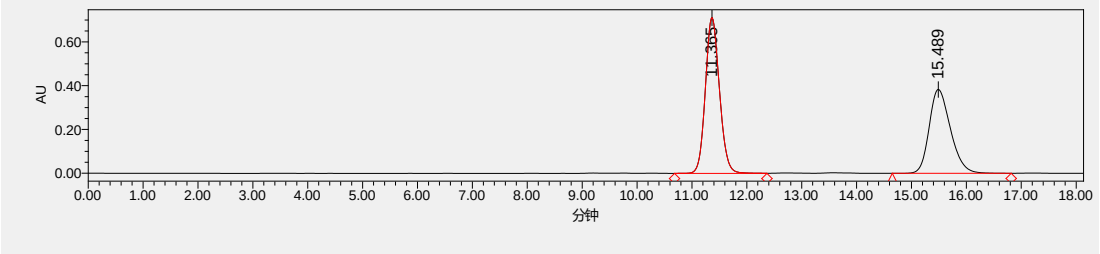


	Retention Time	Area	% Area
1	9.262	3406267	95.10
2	10.114	175414	4.90

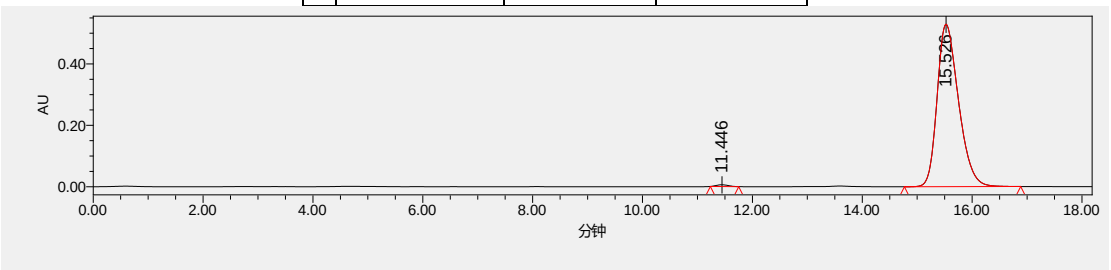
Ethyl 2-benzoyl-1-benzyl-2-phenylcyclopropane-1-carboxylate(3ba)



White powder, m.p.98 - 104 ℃, 53% yield, ee = 99%, $[\alpha]^{16}_{D}$ = +35.7 (*c* = 1.00, in CH_2Cl_2). **HPLC** (Chiral IC column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (minor) = 11.45 min, t_R (major) = 15.53 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 (dd, *J* = 7.3, 1.7 Hz, 2H), 7.59 – 7.48 (m, 3H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.19 (m, 6H), 7.18 – 7.10 (m, 2H), 3.95 (d, *J* = 14.9 Hz, 1H), 3.87 – 3.64 (m, 2H), 2.55 – 2.45 (m, 1H), 2.23 (d, *J* = 14.9 Hz, 1H), 1.95 (d, *J* = 5.5 Hz, 1H), 0.84 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.2, 170.1, 139.0, 135.9, 135.7, 133.1, 130.1, 129.6, 128.7, 128.5, 128.4, 128.3, 127.6, 126.4, 60.9, 45.6, 38.2, 37.4, 21.8, 13.7. **IR** (film): ν(cm^{-1}) 2910, 2378, 1726, 1649,1271, 694. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{24}NaO_3^+$ ([M]+Na^+) = 407.1618 found 407.1609.



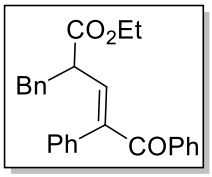
	Retention Time	Area	% Area
1	11.365	12678626	55.08
2	15.489	10340960	44.92



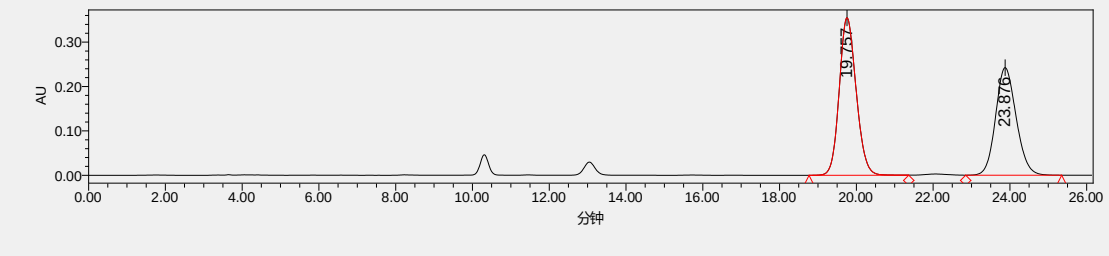
	Retention Time	Area	% Area
1	11.446	85540	0.60

2	15.526	14286613	99.40

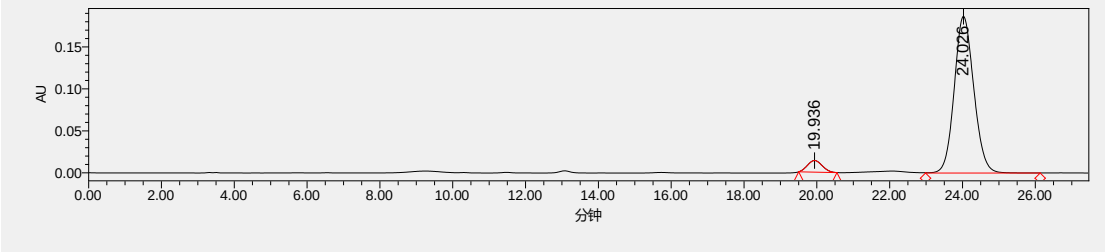
Ethyl (E)-2-benzyl-5-oxo-4,5-diphenylpent-3-enoate(4ba)



Colorless oil, 43% yield, ee = 90%, $[\alpha]^{16}_{D}$ = −90.1 (*c* = 0.64, in CH_2Cl_2). **HPLC** (Chiral IC column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (minor) = 19.94 min, t_R (major) = 24.03 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.72 – 7.60 (m, 2H), 7.52 (td, *J* = 7.4, 1.5 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.29 – 7.22 (m, 3H), 7.11 – 6.88 (m, 4H), 6.29 (d, *J* = 10.6 Hz, 1H), 4.14 (dt, *J* = 8.3, 6.6 Hz, 2H), 3.74 – 3.60 (m, 1H), 3.13 (d, *J* = 6.2 Hz, 1H), 2.87 (dd, *J* = 13.7, 9.0 Hz, 1H), 1.23 (td, *J* = 7.2, 1.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.6, 172.4, 143.8, 138.6, 137.7, 137.6, 135.1, 132.4, 129.9, 129.2, 129.2, 128.5, 128.3, 128.2, 127.9, 126.8, 61.2, 47.5, 38.5, 14.2. **IR** (film): ν(cm^{-1}) 2978, 1741, 1651, 1446, 1282, 1174, 711. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{24}NaO_3^+$ ([M]+Na$^+$) = 407.1618 found 407.1625.

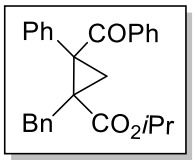


	Retention Time	Area	% Area
1	19.757	10854715	54.61
2	23.876	9021638	45.39

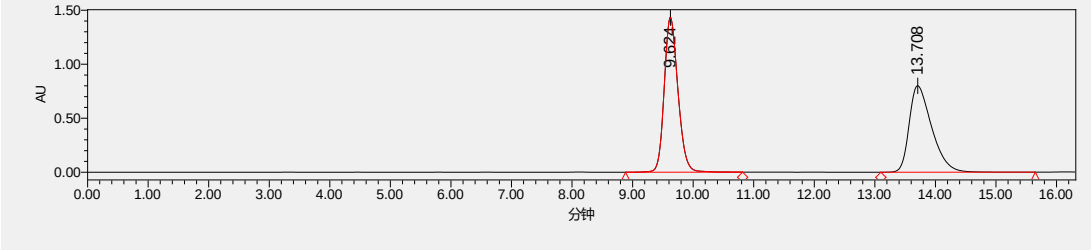


	Retention Time	Area	% Area
1	19.936	389458	5.31
2	24.026	6948941	94.69

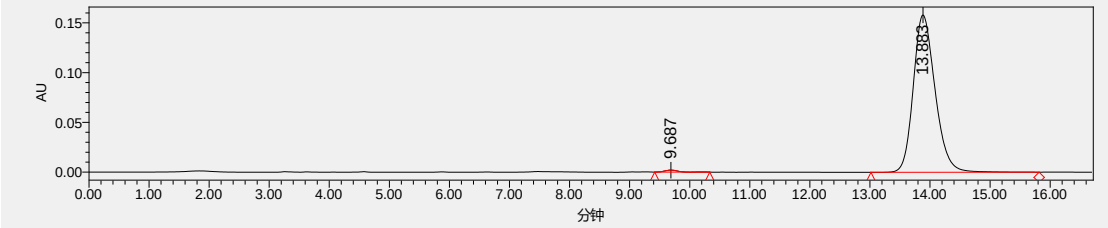
Isopropyl 2-benzoyl-1-benzyl-2-phenylcyclopropane-1-carboxylate (3ca)



White powder, m.p.103 - 108 ℃, 62% yield, ee = 99%, $[\alpha]^{16}_{D}$ = +44.3 (*c* = 0.45, in CH_2Cl_2). **HPLC** (Chiral IC column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (minor) = 9.69 min, t_R (major) = 13.89 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.14 – 8.01 (m, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.53 – 7.47 (m, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.22 (d, *J* = 4.6 Hz, 6H), 7.20 – 7.13 (m, 2H), 4.59 (p, *J* = 6.2 Hz, 1H), 3.94 (d, *J* = 14.9 Hz, 1H), 2.55 (d, *J* = 5.4 Hz, 1H), 2.24 (d, *J* = 14.9 Hz, 1H), 1.91 (d, *J* = 5.4 Hz, 1H), 0.95 (d, *J* = 6.3 Hz, 3H), 0.72 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.2, 169.5, 139.1, 135.9, 135.5, 133.1, 130.2, 129.6, 128.7, 128.5, 128.4, 128.3, 127.6, 126.4, 68.5, 45.2, 38.5, 37.4, 21.9, 21.7, 21.0. **IR** (film): ν(cm^{-1}) 2987, 1722, 1660, 1435, 1278, 1116. **HRMS** (FTMS + ESI) calcd for $C_{27}H_{26}NaO_3^+$ ([M]+Na$^+$) = 421.1774 found 421.1768.

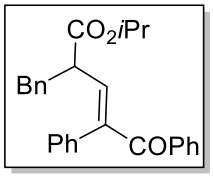


	Retention Time	Area	% Area
1	9.624	22561019	52.22
2	13.708	20645680	47.78



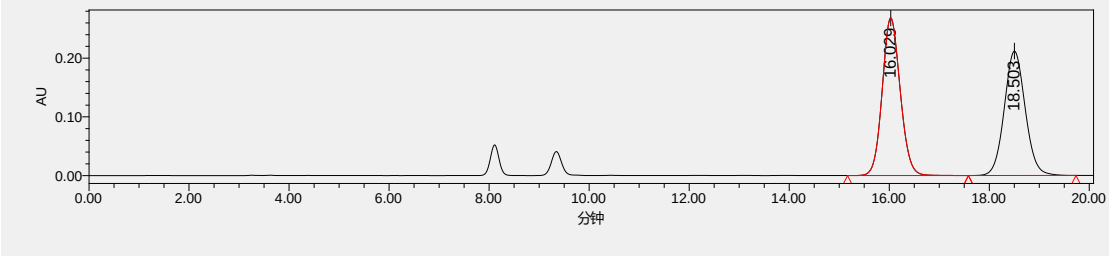
	Retention Time	Area	% Area
1	9.687	30085	0.75
2	13.883	3983860	99.25

Isopropyl (E)-2-benzyl-5-oxo-4,5-diphenylpent-3-enoate (4ca)

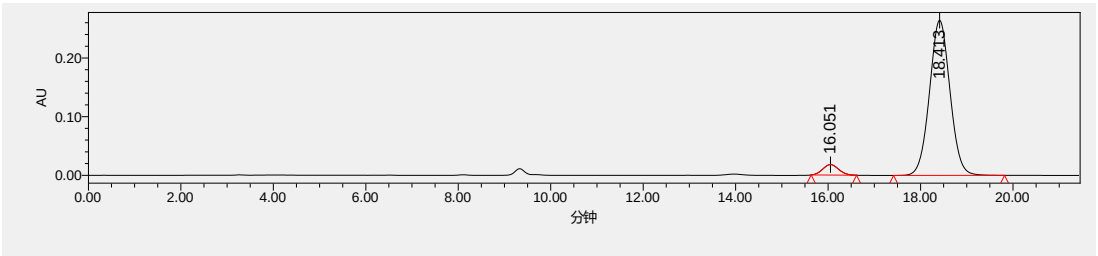


Colorless oil, 25% yield, ee = 90%, $[\alpha]^{16}_{D}$ = −95.6 (*c* = 0.37, in CH_2Cl_2). HPLC (Chiral IC column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (minor) = 16.05 min, t_R (major) = 18.41 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 – 7.63 (m, 2H), 7.55 – 7.50 (m, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.32 (dd, *J* = 5.2, 1.8 Hz, 3H), 7.25 (t, *J* = 4.7 Hz, 3H), 7.07 – 6.89 (m, 4H), 6.29 (d, *J* = 10.5 Hz, 1H), 5.01 (p, *J* = 6.3 Hz, 1H), 3.62 (ddd, *J* = 10.6, 8.9, 6.2 Hz, 1H), 3.13 (dd, *J* = 13.7, 6.3 Hz, 1H), 2.85 (dd, *J* = 13.7, 8.9 Hz,

1H), 1.24 (d, *J* = 6.2 Hz, 3H), 1.18 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.6, 171.9, 143.7, 138.9, 137.8, 137.6, 135.1, 132.4, 129.9, 129.2, 129.2, 128.4, 128.2, 127.8, 126.7, 68.6, 47.7, 38.4, 21.8, 21.7. **IR** (film): ν(cm^{-1}) 2978, 1728, 1647, 1261, 1163, 1087, 698. **HRMS** (FTMS + ESI) calcd for $C_{27}H_{26}NaO_3^+$ ([M]+Na^+) = 421.1774 found 421.1776.

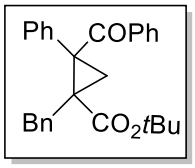


	Retention Time	Area	% Area
1	16.029	6705723	52.11
2	18.503	6162504	47.89

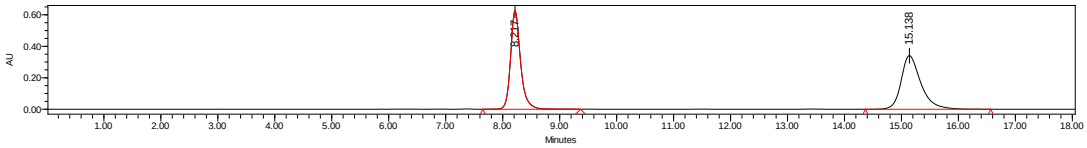


	Retention Time	Area	% Area
1	16.051	429798	5.02
2	18.413	8131851	94.98

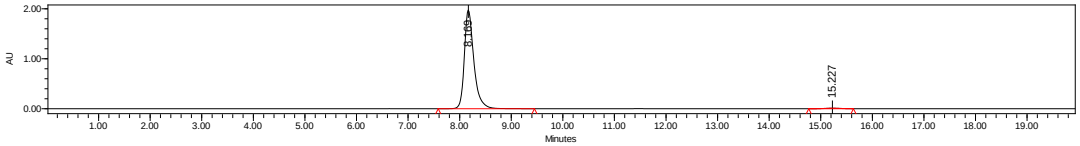
Tert-butyl 2-benzoyl-1-benzyl-2-phenylcyclopropane-1-carboxylate (3da)



White powder, m.p.126 - 130 ℃, 62% yield, ee = 98%, $[\alpha]^{16}_D$ = +61.9 (*c* = 1.15, in CH_2Cl_2). **HPLC** (Chiral IA column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 8.17 min, t_R (minor) = 15.23 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.19 – 7.92 (m, 2H), 7.71 – 7.56 (m, 2H), 7.55 – 7.46 (m, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.24 (t, *J* = 3.5 Hz, 6H), 7.21 – 7.09 (m, 2H), 3.89 (dd, *J* = 15.0, 1.3 Hz, 1H), 2.56 (dd, *J* = 5.4, 1.4 Hz, 1H), 2.24 (d, *J* = 15.0 Hz, 1H), 1.85 (d, *J* = 5.4 Hz, 1H), 1.02 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.3, 168.8, 139.4, 135.9, 135.4, 133.1, 130.3, 129.6, 128.7, 128.5, 128.3, 128.2, 127.5, 126.3, 81.0, 44.7, 38.9, 37.9, 27.5, 22.1. **IR** (film): ν(cm^{-1}) 2987, 2927, 1722,1668, 1161, 690. **HRMS** (FTMS + ESI) calcd for $C_{28}H_{28}NaO_3^+$ ([M]+Na^+) = 435.1921 found 435.1930.

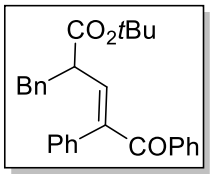


	Retention Time	Area	% Area
1	8.217	7621736	48.24
2	15.138	8176795	51.76

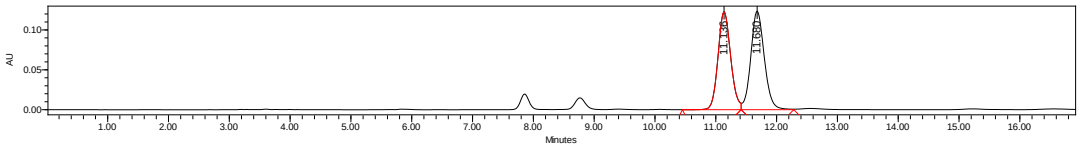


	Retention Time	Area	% Area
1	8.169	25209381	99.21
2	15.227	200284	0.79

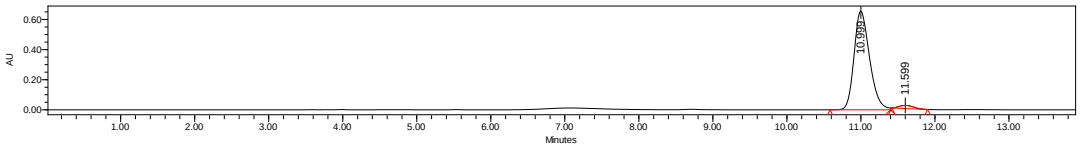
Tert-butyl (E)-2-benzyl-5-oxo-4,5-diphenylpent-3-enoate(4da)



Colorless oil, 26% yield, ee = 94%, $[\alpha]^{16}_{D} = -116.5$ (*c* = 0.16, in CH_2Cl_2). HPLC (Chiral IA column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (minor) = 11.00 min, t_R (major) = 11.60 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.68 – 7.63 (m, 2H), 7.53 – 7.49 (m, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.32 (d, *J* = 2.1 Hz, 1H), 7.31 (d, *J* = 1.9 Hz, 2H), 7.28 – 7.23 (m, 3H), 7.06 – 6.99 (m, 4H), 6.26 (d, *J* = 10.6 Hz, 1H), 3.62 – 3.52 (m, 1H), 3.10 (dd, *J* = 13.8, 6.3 Hz, 1H), 2.83 (dd, *J* = 13.8, 8.9 Hz, 1H), 1.43 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.6, 171.5, 143.5, 139.4, 138.0, 137.7, 135.2, 132.4, 129.9, 129.3, 129.2, 128.4, 128.2, 128.2, 127.8, 126.7, 81.6, 48.5, 38.4, 28.0. **IR** (film): ν(cm^{-1}) 2981,1724, 1676, 1446, 1367, 1276, 1155. **HRMS** (FTMS + ESI) calcd for $C_{28}H_{28}NaO_3^+$ ([M]+Na$^+$) = 435.1921 found 435.1931.

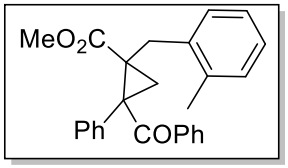


	Retention Time	Area	% Area
1	10.999	9531170	97.15
2	11.599	279585	2.85

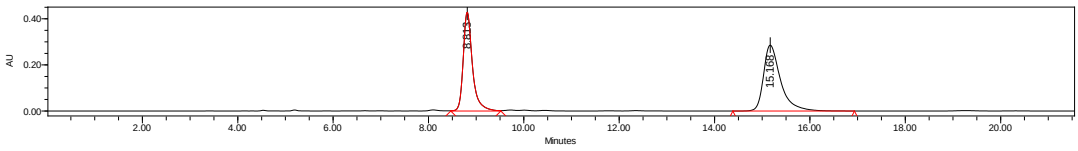


	Retention Time	Area	% Area
1	11.136	1768484	48.06
2	11.680	1911211	51.94

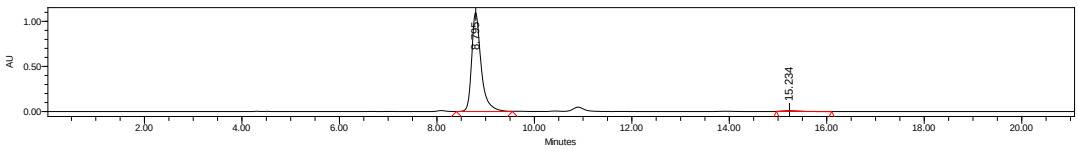
Methyl 2-benzoyl-1-(2-methylbenzyl)-2-phenylcyclopropane-1-carboxylate (3ea)



White powder, m.p.64 - 70 ℃, 45% yield, ee = 98%, $[\alpha]^{16}_D$ = +8.6 (*c* = 0.23, in CH_2Cl_2) **HPLC** (Chiral IA column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 8.80 min, t_R (minor) = 15.23 min, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 7.3 Hz, 2H), 7.50 (t, 1H), 7.43 (t, 2H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.22 (dd, *J* = 12.5, 6.2 Hz,5H), 7.04 (d, *J* = 8.0 Hz, 2H), 3.92 (d, *J* = 14.9 Hz, 1H), 3.35 (s, 3H), 2.43 (d, *J* = 5.3 Hz, 1H), 2.24 (s, 3H), 2.20 (s, 1H), 1.95 (d, *J* = 5.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.1, 170.8, 138.9, 137.4, 135.9, 133.1, 132.7, 129.8, 129.6, 129.2, 128.6, 128.5, 128.4, 126.5, 51.8, 45.5, 38.1, 37.5, 21.7, 21.1. **IR** (film): ν(cm^{-1}) 2951, 1762, 1668, 1475, 1286, 698. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{25}O_3^+$ ([M]+H^+) = 385.1798 found 385.1808.

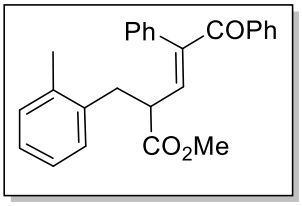


	Retention Time	Area	% Area
1	8.813	5751389	44.84
2	15.168	7074896	55.16



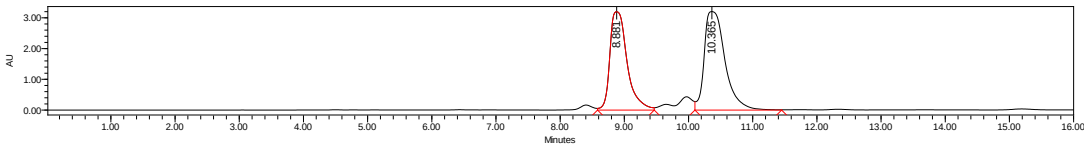
	Retention Time	Area	% Area
1	8.795	14826384	98.95
2	15.234	157436	1.05

Methyl (E)-2-(2-methylbenzyl)-5-oxo-4,5-diphenylpent-3-enoate (4ea)

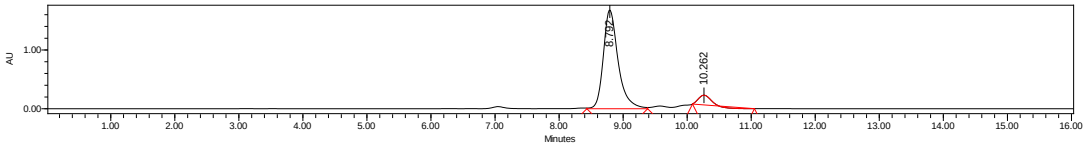


Colorless oil, 47% yield, ee = 82%, $[\alpha]^{16}_D$ = −88.6 (*c* = 0.22, in CH_2Cl_2) **HPLC** (Chiral IA column) ^{i}PrOH/ ^{n}Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, t_R (minor) = 8.79 min, t_R (major) = 10.26 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.50 (s, 1H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.12 (d, *J* = 7.7 Hz,

2H), 7.03 (d, *J* = 7.2 Hz, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 6.24 (d, *J* = 10.5 Hz, 1H), 3.78 – 3.70 (m, 1H), 3.68 (s, 3H), 3.15 (dd, *J* = 13.7, 6.1 Hz, 1H), 2.90 (dd, *J* = 8.9 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.8, 172.9, 144.0, 137.8, 137.7, 137.6, 137.6, 132.4, 132.1, 129.8, 129.2, 129.1, 128.5, 128.4, 128.2, 126.8, 52.2, 47.3, 38.6, 21.3. **IR** (film): ν(cm^{-1}) 2949, 1741, 1651, 1261, 1149, 715. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{24}NaO_3^+$ ([M]+Na^+) = 407.1618 found 407.1613.

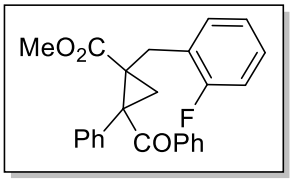


	Retention Time	Area	% Area
1	8.881	59669701	45.30
2	10.365	72059632	54.70

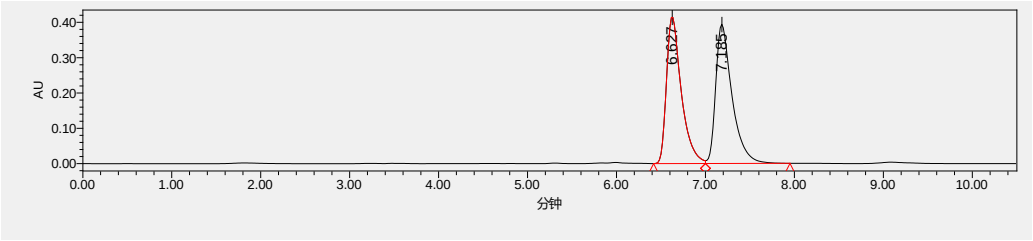


	Retention Time	Area	% Area
1	8.792	26944391	91.13
2	10.262	2621442	8.87

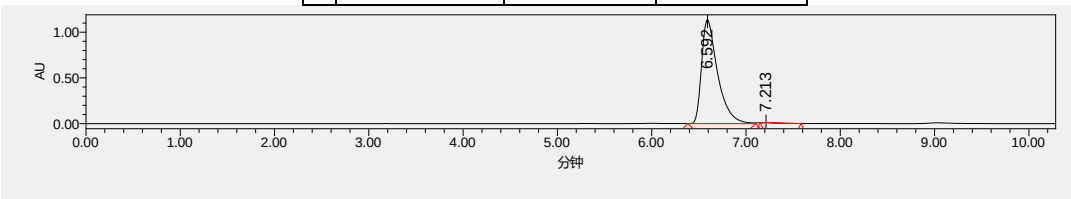
Methyl 2-benzoyl-1-(2-fluorobenzyl)-2-phenylcyclopropane-1-carboxylate (3fa)



White powder, m.p.80 - 84 ℃, 42% yield, ee = 97%, $[\alpha]^{16}_D$ = +37.8 (*c* = 0.25, in CH_2Cl_2) **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 2/98, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 6.59 min, t_R (minor) = 7.21 min, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.48 (m, 1H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.28 (m, 3H), 7.22 (d, *J* = 7.6 Hz,1H), 7.01 (m, 2H), 6.92 (m, 3H), 6.31 (d, *J* = 10.6 Hz, 1H), 3.72 (d, *J* = 3.0 Hz, 1H), 3.69 (s, 3H), 3.10 (dd, *J* = 6.0, 6.0 Hz, 1H), 2.96 (dd, *J* = 13.7, 9.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.4, 172.7, 144.2, 137.8, 137.5, 134.8, 132.4, 131.4 (d, *J* = 4.5 Hz), 131.4, 129.8, 129.1, 128.8, 128.7, 128.3, 127.9, 124.8, 124.6, 124.1, 124.0, 115.5, 115.3, 52.3, 46.0, 31.7, 29.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = −113.3 (s, 1F). **IR** (film): ν(cm^{-1}) 2935, 1741, 1664, 1500, 1257, 696. **HRMS** (FTMS + ESI) calcd for $C_{25}H_{21}NaFO_3^+$ ([M]+Na^+) = 411.1367 found 411.1378.

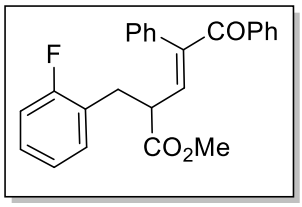


	Retention Time	Area	% Area
1	6.627	4797762	48.91
2	7.185	5012195	51.09

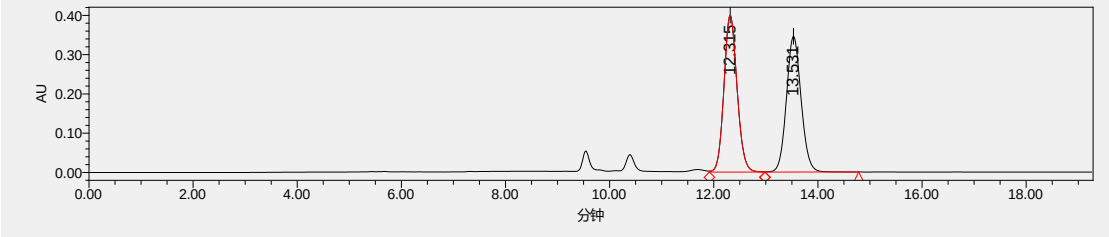


	Retention Time	Area	% Area
1	6.592	13379322	98.66
2	7.214	181595	1.34

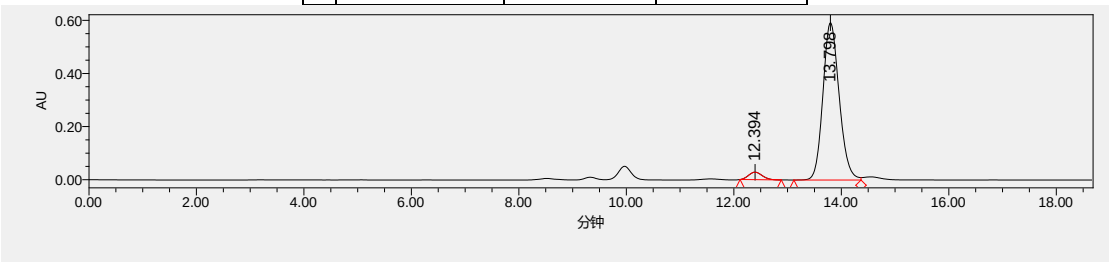
Methyl (E)-2-(2-fluorobenzyl)-5-oxo-4,5-diphenylpent-3-enoate (4fa)



Colorless oil, 46% yield, ee = 92%, $[\alpha]^{16}_{D}$ =−105.1 (*c* = 0.29, in CH_2Cl_2) **HPLC** (Chiral IC column) ^{i}PrOH/ ^{n}Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, t_R (minor) = 12.39 min, t_R (major) = 13.80 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.73 – 7.66 (m, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.32 – 7.28 (m, 3H), 7.25 – 7.19 (m, 1H), 7.03 (dd, *J* = 7.1, 1.7 Hz, 2H), 6.97 (dd, *J* = 6.6, 2.9 Hz, 2H), 6.32 (d, *J* = 10.6 Hz, 1H), 3.79 – 3.71 (m, 1H), 3.69 (s, 3H), 3.14 (dd, *J* = 13.7, 6.0 Hz, 1H), 2.96 (dd, *J* = 13.7, 9.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.4, 172.7, 161.2 (d, *J* = 245.8 Hz), 144.2, 137.8, 137.5, 134.8, 132.4, 131.4 (d, *J* = 4.5 Hz), 129.8, 129.1, 128.7 (d, *J* = 8.1 Hz), 128.3, 127.9, 124.7 (d, J = 15.5 Hz), 124.1 (d, *J* = 3.4 Hz), 115.4 (d, *J* = 21.9 Hz), 52.3, 46.1, 31.7, 29.7. **IR** (film): ν(cm^{-1}) 2927, 1757, 1639, 1502, 1392, 1261, 773. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = −117.3 (s, 1F). **HRMS** (FTMS + ESI) calcd for $C_{25}H_{21}NaFO_3^+$ ([M]+Na$^+$) = 411.1367 found 411.1361.

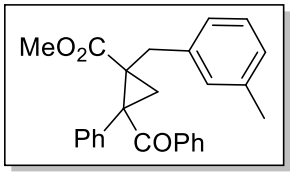


	Retention Time	Area	% Area
1	12.315	6976800	50.75
2	13.531	6771497	49.25

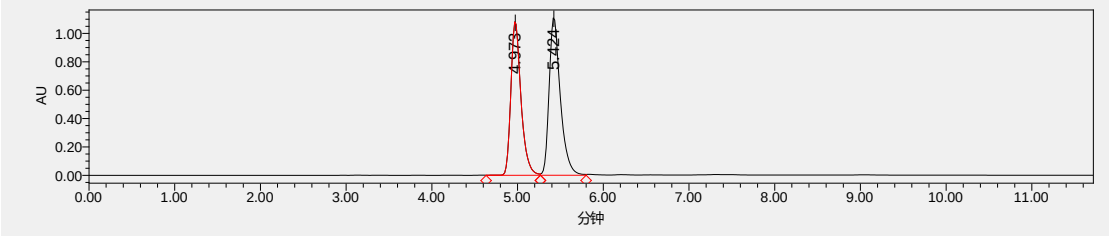


	Retention Time	Area	% Area
1	12.394	498155	3.85
2	13.798	12441825	96.15

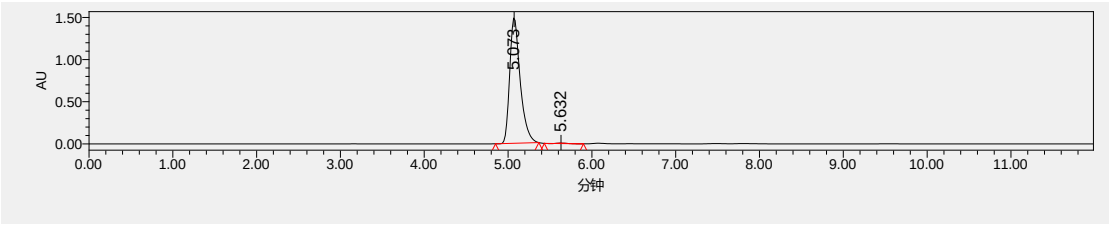
Methyl 2-benzoyl-1-(3-methylbenzyl)-2-phenylcyclopropane-1-carboxylate(3ga)



White powder, m.p.80 - 86 ℃, 49% yield, ee = 99%, $[\alpha]^{16}_{D}$ =+36.4 (*c* = 0.31, in CH_2Cl_2); **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 5.07 min, t_R (minor) = 5.63 min. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 3H), 7.43 (t, *J* = 7.3 Hz,2H), 7.28 – 7.20 (m, 2H), 7.20 – 7.08 (m, 2H), 7.04 – 6.94 (m, 3H), 3.90 (d, *J* = 14.9 Hz, 1H), 3.33 (s, 3H), 2.45 (d, *J* = 5.5 Hz, 1H), 2.28 (s, 3H), 2.19 (d, *J* = 14.9 Hz, 1H), 1.96 (d, *J* = 5.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.1, 170.8, 138.8, 137.9, 135.9, 135.9, 133.1, 130.0, 129.6, 129.5, 128.5, 128.4, 128.3, 127.6, 127.3, 125.6, 51.8, 45.8, 38.0, 37.6, 29.7, 21.7, 21.4. **IR** (film): ν(cm^{-1}) 2944, 1741, 1638, 1184, 1135, 711. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{24}NaO_3^+$ ([M]+Na^+) = 407.1618 found 407.1615.

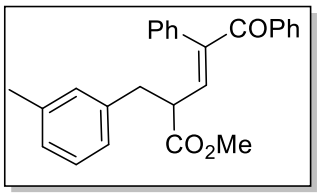


	Retention Time	Area	% Area
1	4.973	8906968	46.86
2	5.424	10099169	53.14

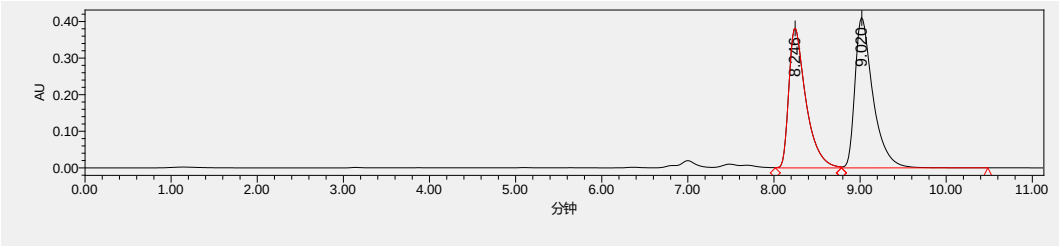


	Retention Time	Area	% Area
1	5.073	12961054	99.63
2	5.632	48180	0.37

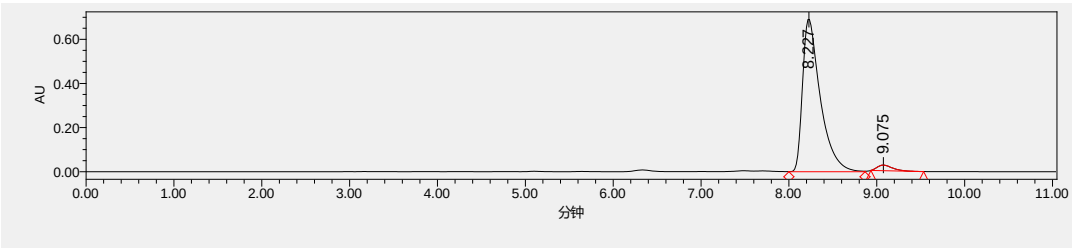
Methyl (E)-2-(3-methylbenzyl)-5-oxo-4,5-diphenylpent-3-enoate(4ga)



Colorless oil, 45% yield, ee = 92%, $[\alpha]^{16}_{D} = -48.2$ (c = 0.29, in CH_2Cl_2) **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 8.23 min, t_R (minor) = 9.08 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 7.1 Hz, 2H), 7.53 (s, 1H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.32 (dd, *J* = 5.0, 1.8 Hz, 3H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.97 (dd, *J* = 6.4, 3.1 Hz, 2H), 6.88 – 6.77 (m, 2H), 6.27 (d, *J* = 10.6 Hz, 1H), 3.70 (s, 3H), 3.14 (dd, *J* = 13.7, 5.7 Hz, 1H), 2.83 (dd, *J* = 13.7, 9.4 Hz, 1H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.6, 172.9, 143.9, 138.4, 138.1, 137.6, 137.6, 135.1, 132.4, 129.8, 129.2, 128.4, 128.2, 127.8, 127.6, 126.2, 52.3, 52.2, 47.3, 38.4, 21.4. **IR** (film): ν(cm^{-1}) 2945, 1732, 1653, 1206, 1164, 704. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{24}NaO_3^+$ ([M]+Na^+) = 407.1618 found 407.1614.



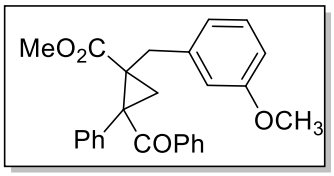
	Retention Time	Area	% Area
1	8.246	5255153	46.88
2	9.020	5955071	53.12



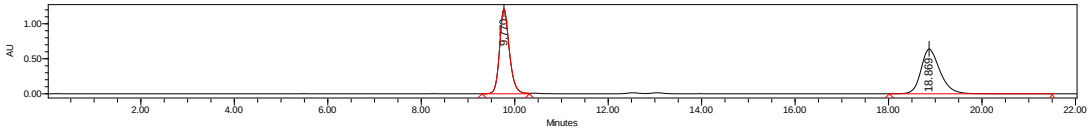
	Retention Time	Area	% Area

1	8.227	9707989	96.91
2	9.075	309180	3.09

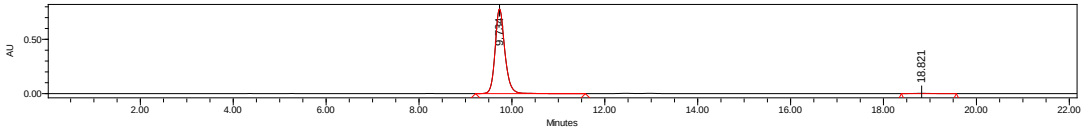
Methyl 2-benzoyl-1-(3-methoxybenzyl)-2-phenylcyclopropane-1-carboxylate(3ha)



White powder, 51% yield, ee = 99%, $[\alpha]^{16}_{D}$ = +48.4 (*c* = 0.27, in CH_2Cl_2) **HPLC** (Chiral IA column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 9.73 min, t_R (minor) = 18.82 min, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 3H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 7.1 Hz, 2H), 7.20 – 7.12 (m, 2H), 6.87 – 6.62 (m, 3H), 3.92 (d, *J* = 15.0 Hz, 1H), 3.76 (s, 3H), 3.33 (s, 3H), 2.48 (d, *J* = 5.5 Hz, 1H), 2.20 (d, *J* = 15.0 Hz, 1H), 1.96 (d, *J* = 5.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.1, 170.7, 159.6, 140.4, 135.8, 135.8, 133.2, 129.9, 129.6, 129.4, 128.5, 128.4, 127.6, 120.9, 114.4, 111.8, 55.1, 51.8, 45.7, 38.1, 37.4, 29.7, 21.8. **IR** (film): ν(cm^{-1}) 2924, 1730, 1452, 1271, 702. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{24}NaO_4^+$ ([M]+Na$^+$) = 423.1567 found 423.1563.

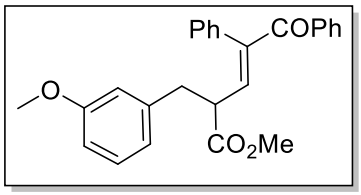


	Retention Time	Area	% Area
1	9.770	17656272	49.42
2	18.869	18073544	50.58



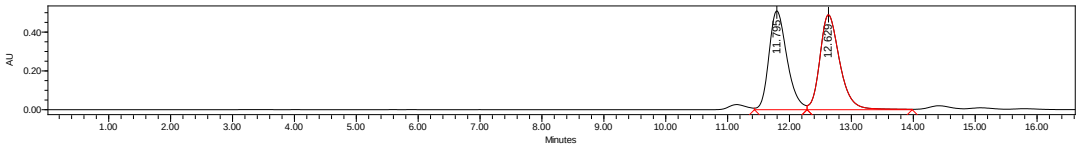
	Retention Time	Area	% Area
1	9.734	11302674	99.38
2	18.821	70625	0.62

Methyl (E)-2-(3-methoxybenzyl)-5-oxo-4,5-diphenylpent-3-enoate (4ha)

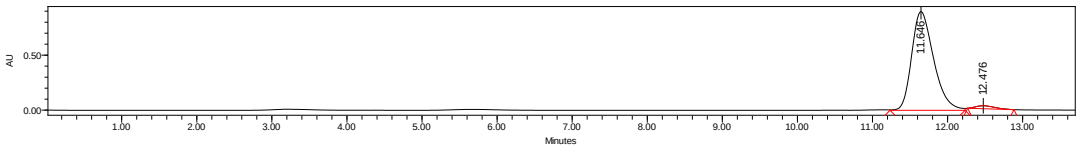


Colorless oil, 46% yield, ee = 95%, $[\alpha]^{16}_{D}$ = −88.2 (*c* = 0.26, in CH_2Cl_2) **HPLC** (Chiral ADH column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 11.65 min, t_R (minor) = 12.48 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 7.2 Hz, 2H), 7.51 (dd, *J* = 6.4, 2.4 Hz, 3H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.28 – 7.19 (m, 2H), 7.19 – 7.09 (m, 2H), 6.85 – 6.67 (m, 3H), 3.92 (d, *J* = 15.0 Hz, 1H), 3.75 (s, 3H), 3.32 (s, 3H), 2.48 (d, *J* = 6.4 Hz, 1H), 2.21 (d, *J* = 15.0 Hz, 1H), 1.96 (d, *J* = 5.5 Hz, 1H). **^{13}C NMR** (101

MHz, $CDCl_3$) δ 196.1, 170.7, 159.6, 140.5, 135.8, 135.8, 133.2, 129.9, 129.6, 129.4, 128.5, 128.4, 127.6, 120.9, 114.4, 111.8, 55.1, 55.1, 51.8, 45.7, 38.1, 37.4, 21.8. **IR** (film): ν(cm^{-1}) 2920, 1737, 1658, 1454, 1261, 1170. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{24}NaO_4^+$ ([M]+Na^+) = 423.1567 found 423.1575.

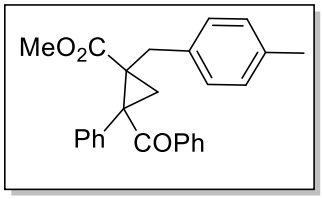


	Retention Time	Area	% Area
1	11.795	10300961	48.60
2	12.629	10896061	51.40

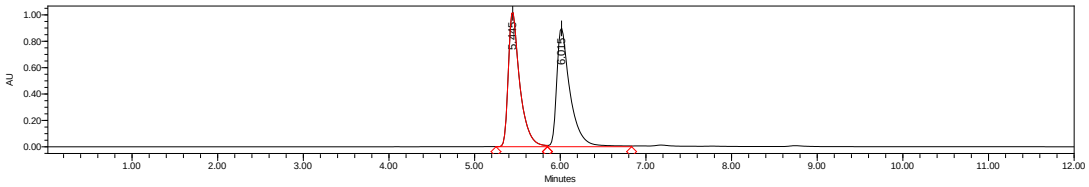


	Retention Time	Area	% Area
1	11.646	18219594	97.44
2	12.476	477828	2.56

Methyl 2-benzoyl-1-(4-methylbenzyl)-2-phenylcyclopropane-1-carboxylate (3ia)

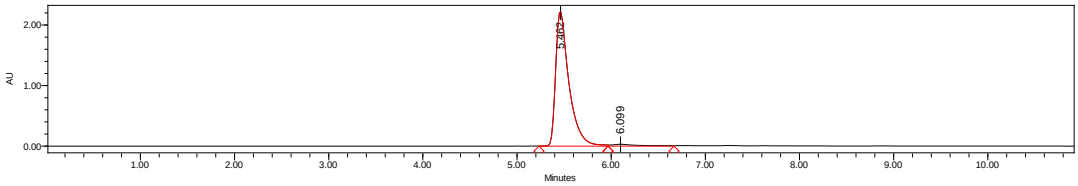


Colorless oil, 49% yield, ee = 94%, $[\alpha]^{16}_D$ = 28.4 (*c* = 0.37, in CH_2Cl_2). **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 5.46 min, t_R (minor) = 6.10 min,. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.6 Hz, 2H), 7.49 (td, *J* = 5.2, 4.7, 1.5 Hz, 3H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.26 – 7.20 (m, 2H), 7.19 – 7.13 (m, 1H), 7.12 – 7.01 (m, 4H), 3.90 (d, *J* = 14.8 Hz, 1H), 3.32 (s, 2H), 2.44 (d, *J* = 5.5 Hz, 1H), 2.27 (s, 3H), 2.18 (d, *J* = 14.9 Hz, 1H), 1.96 (d, *J* = 5.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ196.1, 170.8, 136.0, 135.9, 135.8, 133.1, 123.0, 129.6, 129.2, 129.1, 128.5, 128.5, 128.4, 127.6, 51.8, 45.8, 37.8, 21.7, 21.0.. **IR** (film): ν(cm^{-1}) 2980, 1726, 1097, 1060, 902. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{24}NaO_3^+$ ([M]+Na^+) = 407.1618 found 407.1616.



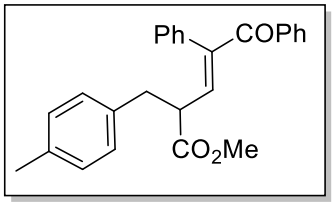
	Retention Time	Area	% Area
1	5.445	9497254	49.33

2	6.015	9753358	50.67

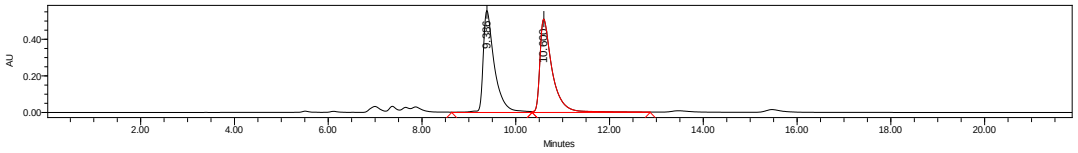


	Retention Time	Area	% Area
1	5.462	21784796	97.20
2	6.099	628217	2.80

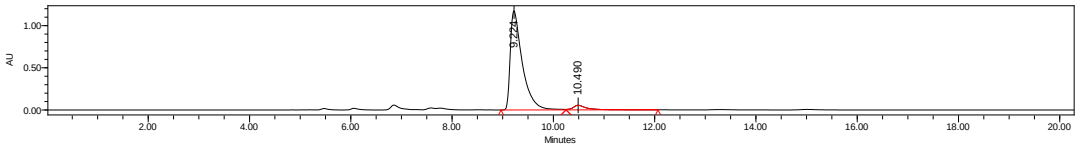
Methyl (E)-2-(4-methylbenzyl)-5-oxo-4,5-diphenylpent-3-enoate(4ia)



Colorless oil, 45% yield, ee = 90%, $[\alpha]^{16}_{D}$ = −57.0 (*c* = 0.36, in CH_2Cl_2). **HPLC** (Chiral IC column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 9.22 min, t_R (minor) = 10.49 min. **^{1}H NMR** (400 MHz, Chloroform-*d*)δ 7.68 – 7.63 (m, 2H), 7.53 – 7.49 (m, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.31 (dd, *J* = 5.3, 1.9 Hz, 3H), 7.08 (d, *J* = 7.7 Hz, 2H), 7.03 – 6.98 (m, 2H), 6.90 (d, *J* = 7.8 Hz, 2H), 6.29 (d, *J* = 10.5 Hz, 1H), 3.68 (s, 3H), 3.11 (dd, *J* = 13.7, 6.2 Hz, 1H), 2.84 (dd, *J* = 13.8, 8.8 Hz, 1H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ196.6, 172.9, 143.8, 138.4, 137.6, 136.4, 135.1, 134.5, 132.4, 129.9, 129.2, 129.2, 129.0, 128.3, 128.2, 127.9, 52.2, 47.5, 38.2, 21.1. **IR** (film): ν(cm^{-1}) 2941, 1745, 1662, 1446, 1257. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{24}NaO_3^+$ ([M]+Na$^+$) = 407.1618 found 407.1626.

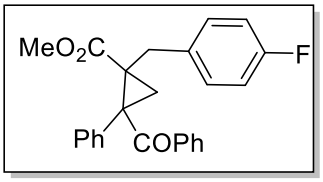


	Retention Time	Area	% Area
1	9.386	9267111	49.52
2	10.600	9446961	50.48

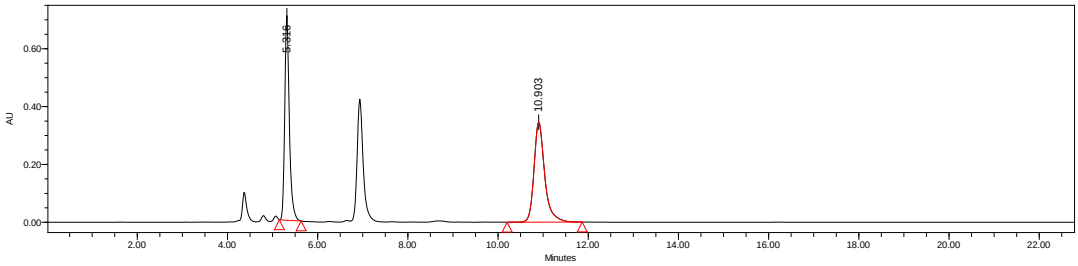


	Retention Time	Area	% Area
1	9.224	19415176	94.80
2	10.490	1065956	5.20

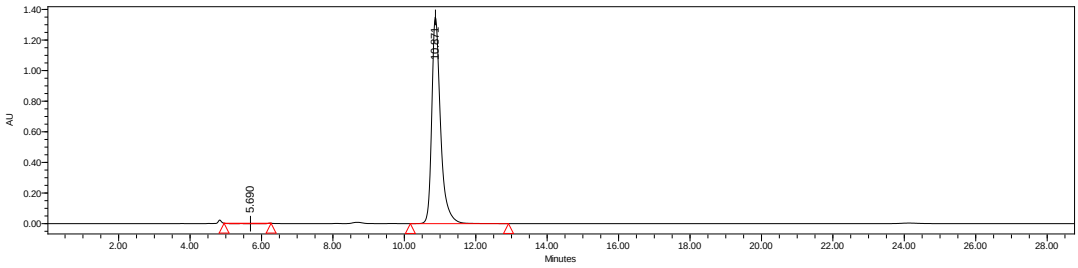
Methyl 2-benzoyl-1-(4-fluorobenzyl)-2-phenylcyclopropane-1-carboxylate(3ja)



White powder, m.p.80 - 88 °C, 48% yield, ee = 98%, $[\alpha]^{16}_D$ = +28.2 (*c* = 0.57, in CH_2Cl_2). **HPLC** (Chiral IA column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (minor) = 5.69 min, t_R (major) = 10.87 min, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 – 8.03 (m, 2H), 7.50 (d, *J* = 7.0 Hz, 3H), 7.45 (d, *J* = 7.7 Hz, 2H), 7.28 – 7.20 (m, 2H), 7.20 – 7.13 (m, 3H), 6.93 (t, *J* = 8.7 Hz, 2H), 3.91 (d, *J* = 14.9 Hz, 1H), 3.31 (s, 3H), 2.46 (d, *J* = 1.3 Hz, 1H), 2.19 (d, *J* = 14.9 Hz, 1H), 1.95 (d, *J* = 5.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.9, 170.6, 162.9, 160.4, 135.7 (d, *J* = 6.4 Hz), 134.5 (d, *J* = 3.2 Hz), 133.2, 130.1 (d, *J* = 7.9 Hz), 129.9, 129.6, 128.5 (d, *J* = 8.9 Hz), 127.7, 115.3, 115.1, 51.8, 45.7, 37.6, 37.4, 21.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = −116.6 (s, 1F). **IR** (film): ν(cm^{-1}) 2954, 1730, 1678, 1467, 1282, 786. **HRMS** (FTMS + ESI) calcd for $C_{25}H_{21}NaFO_3^+$ ([M]+Na^+) = 389.1547 found 389.1540.

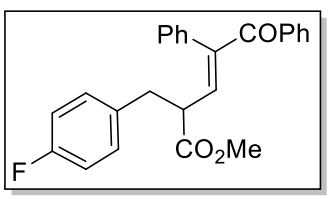


	Retention Time	Area	% Area
1	5.316	4997528	46.77
2	10.903	5688358	53.23



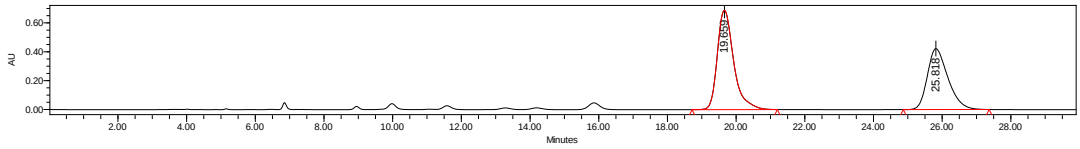
	Retention Time	Area	% Area
1	5.690	182197	0.79
2	10.871	22984111	99.21

Methyl (E)-2-(4-fluorobenzyl)-5-oxo-4,5-diphenylpent-3-enoate (4ja)

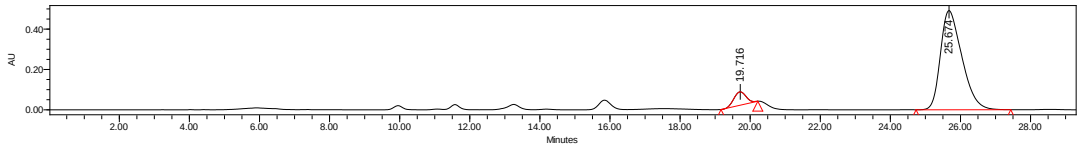


Colorless oil, 46% yield, ee = 86%, $[\alpha]^{16}_D$ = −123.7 (*c* = 0.38, in CH_2Cl_2). **HPLC** (Chiral IC column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (minor) = 19.72 min, t_R (major) = 25.67 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.71 – 7.63 (m, 2H), 7.57 – 7.48 (m, 1H), 7.45 – 7.37 (m, 2H), 7.35 – 7.30 (m, 3H), 7.03 (dd, *J* = 7.4,

2.2 Hz, 2H), 6.97 – 6.91 (m, 4H), 6.28 (d, *J* = 10.6 Hz, 1H), 3.69 (s, 3H), 3.68 – 3.61 (m, 1H), 3.11 (dd, *J* = 13.8, 6.2 Hz, 1H), 2.84 (dd, *J* = 13.8, 8.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.3, 172.7, 161.8 (d, *J* = 245.1 Hz), 144.1, 137.5 (d, *J* = 20.0 Hz), 135.0, 133.4 (d, *J* = 3.3 Hz), 132.6, 130.6, 130.5, 129.8, 129.1, 128.4, 128.3, 128.0, 115.3 (d, *J* = 21.3 Hz), 52.3, 47.4, 37.7, 29.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = −116.0 (s, 1F). **IR** (film): ν(cm^{-1}) 2920, 1735,1666,1519, 1224, 694. **HRMS** (FTMS + ESI) calcd for $C_{25}H_{21}NaFO_3^+$ ([M]+Na$^+$) = 411.1367 found 411.1372.

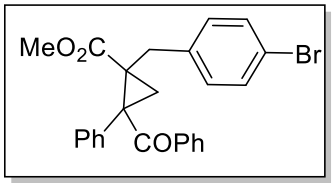


	Retention Time	Area	% Area
1	19.659	22704405	56.39
2	25.818	17558281	43.61

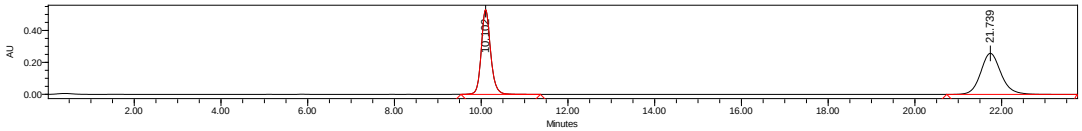


	Retention Time	Area	% Area
1	19.716	1600344	7.12
2	25.674	20869342	92.88

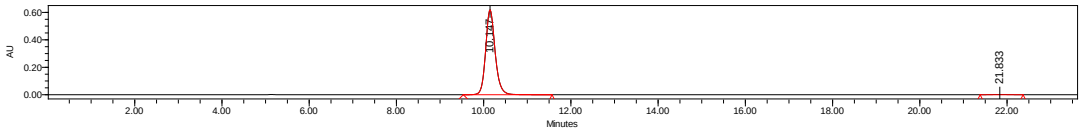
Methyl 2-benzoyl-1-(4-bromobenzyl)-2-phenylcyclopropane-1-carboxylate(3ka)



White powder, m.p.94 - 102 ℃, 50% yield, ee = 99%, $[\alpha]^{16}_D$ =+26.3 (*c* = 0.32, in CH_2Cl_2). **HPLC** (Chiral IA column) ^{i}PrOH/ ^{n}Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 10.15 min, t_R (minor) = 21.83 min, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 7.2 Hz, 2H), 7.53 – 7.47 (m, 4H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.22 (m, 3H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 2H), 3.89 (d, *J* = 14.9 Hz, 1H), 2.48 (d, *J* = 6.4 Hz, 1H), 2.17 (d, *J* = 15.0 Hz, 1H), 1.94 (d, *J* = 5.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.9, 170.5, 137.9, 135.7, 135.6, 133.2, 131.5, 130.4, 129.9, 129.6, 128.5, 128.4, 127.7, 120.4, 51.9, 45.6, 37.6, 37.3, 21.7. **IR** (film): ν(cm^{-1}) 2954, 1734, 1678, 1448, 1274, 1182. **HRMS** (FTMS + ESI) calcd for $C_{25}H_{21}NaBrO_3^+$ ([M]+Na$^+$) = 471.0566 and 473.0546 found 471.0563 and 473.0543.

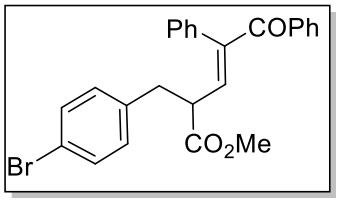


	Retention Time	Area	% Area
1	10.102	7911795	48.55
2	21.739	8384182	51.45

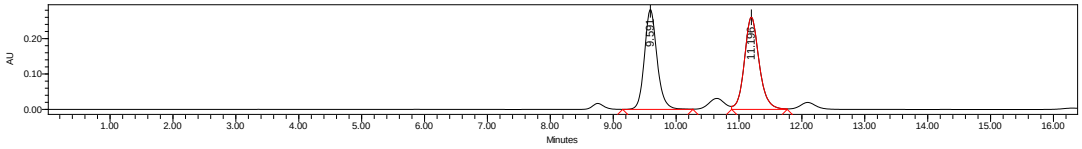


	Retention Time	Area	% Area
1	10.147	9297272	99.52
2	21.833	44477	0.48

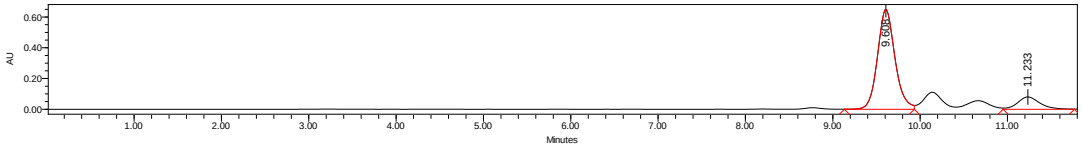
Methyl (E)-2-(4-bromobenzyl)-5-oxo-4,5-diphenylpent-3-enoate (4ka)



Colorless oil, 48% yield, ee = 72%, $[\alpha]^{16}_{D}$ = −46.4 (*c* = 0.27, in CH_2Cl_2) **HPLC** (Chiral IA column) ^{i}PrOH/ ^{n}Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 9.61 min, t_R (minor) = 11.23 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.63 (m, 2H), 7.54 – 7.49 (m, 1H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.39 – 7.36 (m, 2H), 7.35 – 7.31 (m, 2H), 7.29 (d, *J* = 4.4 Hz, 1H), 7.03 (dd, *J* = 7.4, 2.1 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.25 (d, *J* = 10.5 Hz, 1H), 3.70 (s, 3H), 3.68 – 3.63 (m, 1H), 3.09 (dd, *J* = 13.8, 6.2 Hz, 1H), 2.82 (dd, *J* = 13.8, 8.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.3, 172.6, 144.2, 137.3, 136.7, 134.9, 132.6, 131.6, 130.8, 129.8, 129.1, 128.4, 128.3, 128.0, 120.7, 52.4, 47.1, 37.8, 29.7. **IR** (film): ν(cm^{-1}) 2916, 1741, 1668, 1498, 1396, 1253, 1087, 702. **HRMS** (FTMS + ESI) calcd for $C_{25}H_{21}NaBrO_3^+$ ([M]+Na^+) = 471.0566 and 473.0546 found 471.0563 and 473.0548.



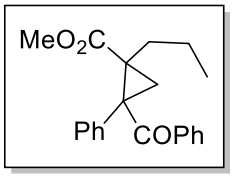
	Retention Time	Area	% Area
1	9.591	3948011	48.18
2	11.196	4245968	51.82



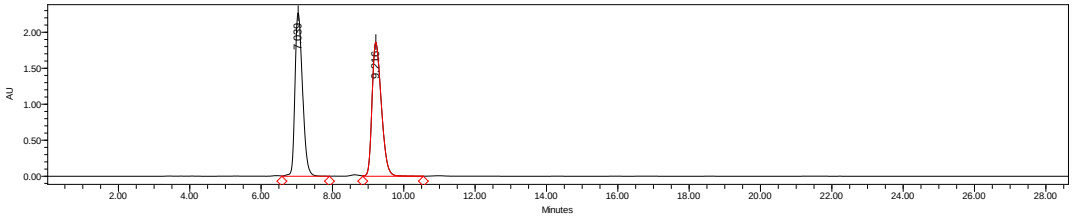
	Retention Time	Area	% Area
1	9.608	8978363	86.30

2	11.233	1425645	13.70

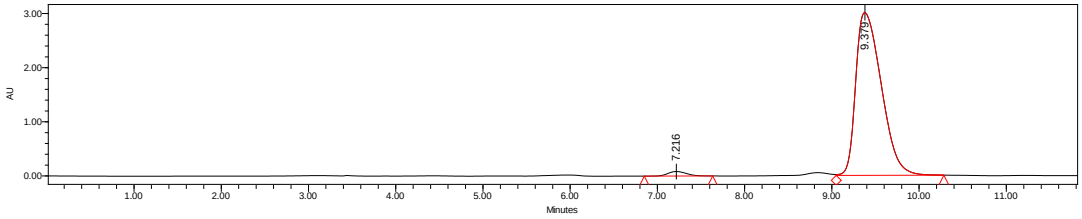
Methyl 2-benzoyl-2-phenyl-1-propylcyclopropane-1-carboxylate(3la)



Colorless oil, 61% yield, ee = 96%, $[\alpha]^{16}_D$ = +24.3 (*c* = 0.55, in CH_2Cl_2) **HPLC** (Chiral IC column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (minor) = 7.22 min, t_R (major) = 9.38 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.07 – 7.97 (m, 2H), 7.49 – 7.37 (m, 5H), 7.21 (dd, *J* = 8.3, 6.6 Hz, 2H), 7.17 – 7.11 (m, 1H), 3.42 (s, 3H), 2.64 – 2.52 (m, 1H), 2.29 (dd, *J* = 5.3, 1.5 Hz, 1H), 1.70 (d, *J* = 5.3 Hz, 1H), 1.47 – 1.32 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H), 0.82 – 0.75 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.3, 171.4, 136.1, 135.9, 132.9, 130.0, 129.6, 128.4, 128.3, 127.5, 51.8, 45.8, 37.0, 34.9, 21.3, 21.1, 14.0. **IR** (film): ν(cm^{-1}) 2960, 1741, 1672, 1436, 1261, 1170. **HRMS** (FTMS + ESI) calcd for $C_{21}H_{22}NaO_3^+$ ([M]+Na$^+$) = 345.1461 found 345.1456.

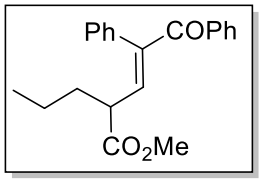


	Retention Time	Area	% Area
1	7.039	33357420	49.83
2	9.216	33581733	50.17



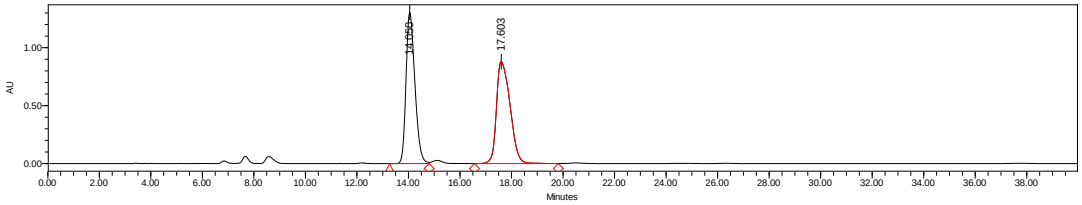
	Retention Time	Area	% Area
1	7.216	1236398	1.98
2	9.379	61098787	98.02

Methyl (E)-5-oxo-4,5-diphenyl-2-propylpent-3-enoate(4la)

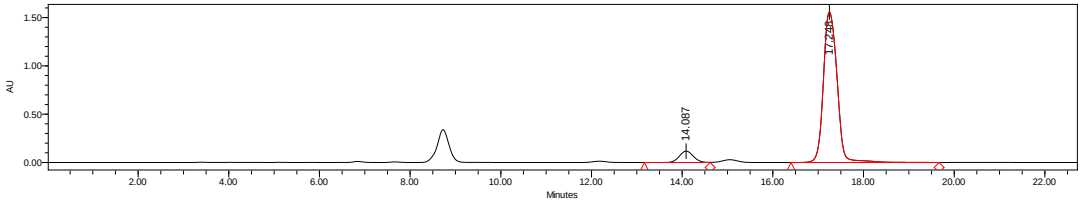


Colorless oil, 34% yield, ee = 85%, $[\alpha]^{16}_D$ = −101.1 (*c* = 0.37, in CH_2Cl_2) **HPLC** (Chiral IC column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (minor) = 14.09 min, t_R (major) = 17.25 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.1 Hz, 1H), 7.33 – 7.25 (m, 3H), 6.36 (d, *J* = 10.6 Hz, 1H), 3.72 (s, 3H), 3.35-3.45 (m, 7.6 Hz, 1H), 1.84 – 1.69 (m, 1H), 1.58 – 1.50 (m, 1H), 1.30 (dd, *J*

= 17.4, 7.4 Hz, 1H), 1.23 – 1.13 (m, 1H), 0.80 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.6, 173.7, 143.1, 139.7, 137.7, 135.3, 132.4, 129.9, 129.3, 128.4, 128.3, 127.9, 52.1, 52.1, 45.4, 34.8, 20.3, 13.7. **IR** (film): ν(cm^{-1}) 2964, 1737, 1651, 1450, 1388, 1276. **HRMS** (FTMS + ESI) calcd for $C_{21}H_{22}NaO_3^+$ ([M]+Na$^+$) = 359.1618 found 359.1627.

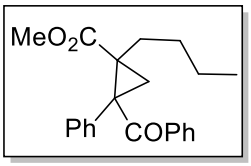


	Retention Time	Area	% Area
1	14.050	31148731	49.16
2	17.603	32212392	50.84

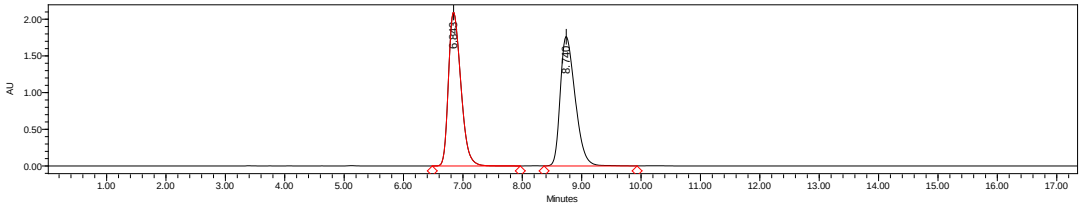


	Retention Time	Area	% Area
1	14.087	2545047	7.27
2	17.248	32478706	92.73

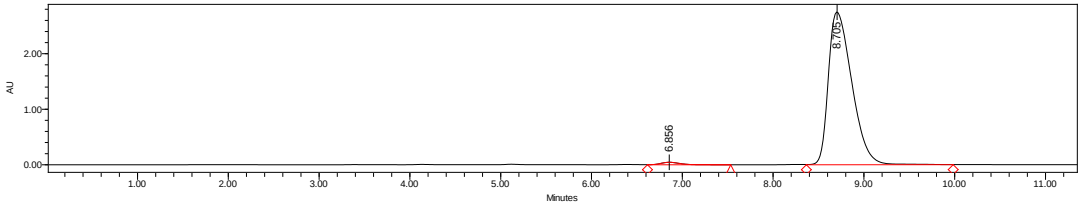
Methyl 2-benzoyl-1-butyl-2-phenylcyclopropane-1-carboxylate(3ma)



Colorless oil, 49% yield, ee = 98%, $[\alpha]^{16}_D$ = +20. 9 (*c* = 0.72, in CH_2Cl_2) **HPLC** (Chiral IC column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (minor) = 6.86 min, t_R (major) = 8.71 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 – 7.94 (m, 2H), 7.52 – 7.36 (m, 5H), 7.21 (dd, *J* = 8.2, 7.1 Hz, 2H), 7.17 – 7.09 (m, 1H), 3.42 (s, 3H), 2.65 – 2.52 (m, 1H), 2.29 (dt, *J* = 5.3, 1.3 Hz, 1H), 1.69 (dd, *J* = 5.2, 0.9 Hz, 1H), 1.44 – 1.20 (m, 4H), 0.91 – 0.74 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.3, 171.4, 136.1, 136.0, 132.9, 130.0, 129.5, 128.4, 128.3, 127.5, 51.8, 46.0, 37.2, 32.7, 30.1, 22.6, 21.2, 14.0. **IR** (film): ν(cm^{-1}) 2960, 2856, 1751, 1674, 1456, 1263, 704 **HRMS** (FTMS + ESI) calcd for $C_{22}H_{24}NaO_3^+$ ([M]+Na$^+$) = 359.1618 found 359.1614.

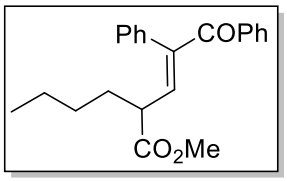


	Retention Time	Area	% Area
1	6.843	30321503	49.68
2	8.740	30715288	50.32

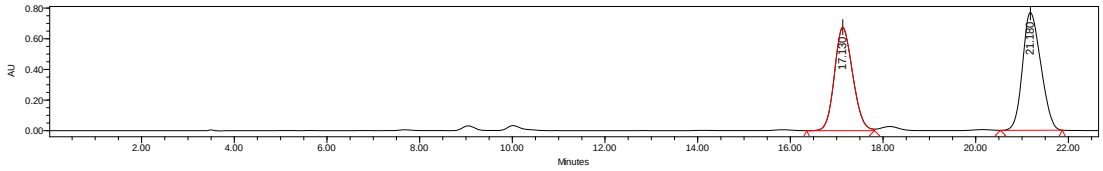


	Retention Time	Area	% Area
1	6.856	625651	1.25
2	8.705	49410835	98.75

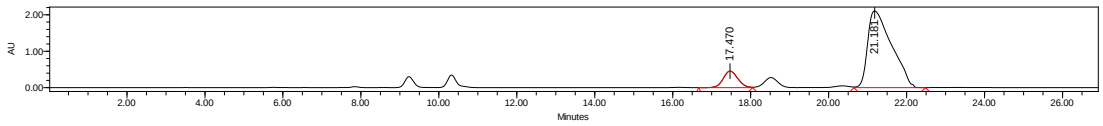
Methyl (E)-2-(3-oxo-2,3-diphenylprop-1-en-1-yl) hexanoate(4ma)



Colorless oil, 41% yield, ee = 77%, $[\alpha]^{16}_{D}$ = − 99.7 (*c* = 0.41, in CH_2Cl_2) **HPLC** (Chiral IC column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (minor) = 17.47 min, t_R (major) = 21.18 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 – 7.80 (m, 2H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 7.1 Hz, 1H), 7.31 – 7.25 (m, 2H), 6.36 (d, *J* = 10.6 Hz, 1H), 3.72 (s, 3H), 3.53 – 3.26 (m, 1H), 1.89 – 1.69 (m, 1H), 1.59 (s, 2H), 1.24-1.15 (m, 3H), 0.83 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.6, 173.7, 143.1, 139.8, 137.7, 135.3, 132.5, 129.9, 129.3, 128.4, 128.3, 127.9, 100.0, 52.1, 45.6, 32.4, 29.1, 22.3, 13.8. **IR** (film): ν(cm^{-1}) 2956, 1737, 1668, 1450, 1253, 723. **HRMS** (FTMS + ESI) calcd for $C_{22}H_{24}NaO_3^+$ ([M]+Na^+) = 359.1618 found 359.1619.



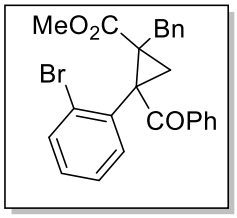
	Retention Time	Area	% Area
1	17.130	18365445	46.63
2	21.180	21023276	53.37



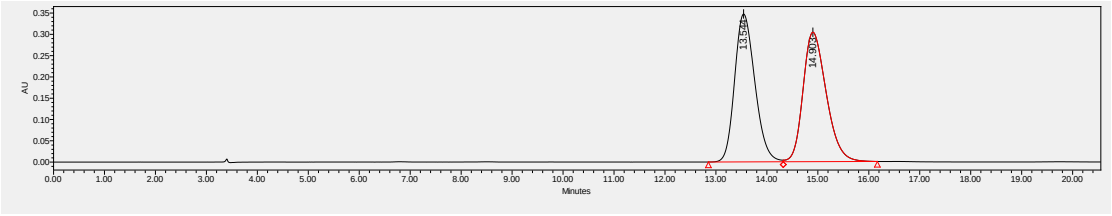
	Retention Time	Area	% Area
1	17.470	11860829	11.68

2	21.181	89714750	88.32

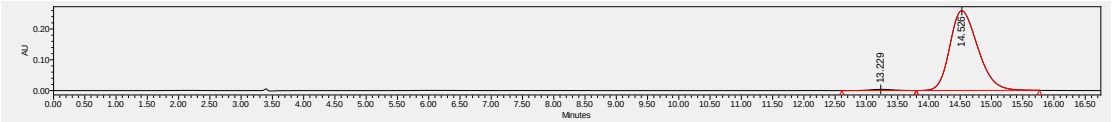
Methyl 2-benzoyl-1-benzyl-2-(2-bromophenyl) cyclopropane-1-carboxylate(3ab)



Colorless oil, 73% yield, ee = 98%, $[\alpha]^{16}_{D}$ = + 76.7(*c* = 0.99, in CH_2Cl_2) **HPLC** (Chiral IC column) ^{i}PrOH/ ^{n}Hexane = 2/98, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 13.23 min, t_R (minor) = 14.53 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.56 – 7.47 (m, 3H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.20 (m, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 2H), 3.89 (d, *J* = 15.0 Hz, 1H), 3.30 (s, 3H), 2.48 (d, *J* = 5.5 Hz, 1H), 2.17 (d, *J* = 15.0 Hz, 1H), 1.94 (d, *J* = 5.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.9, 170.5, 137.9, 135.7, 135.6, 133.2, 131.5, 130.4, 129.9, 129.6, 128.5, 128.4, 127.7, 120.4, 51.9, 45.6, 37.6, 21.7. **IR** (film): ν(cm^{-1}) 2951, 1739, 1666, 1436, 1257, 759,704. **HRMS** (FTMS + ESI) calcd for $C_{25}H_{21}NaBrO_3^+$ ([M]+Na^+) = 471.0566 and 473.0546 found 471.0563 and 473.0544.

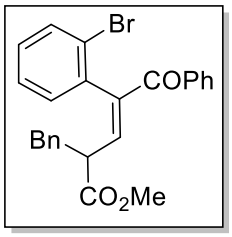


	Retention Time	Area	% Area
1	13.544	9571612	49.94
2	14.903	9595091	50.06



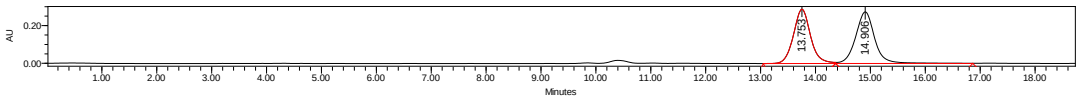
	Retention Time	Area	% Area
1	13.229	102601	1.26
2	14.526	8047853	98.74

Methyl (E)-2-benzyl-4-(2-bromophenyl)-5-oxo-5-phenylpent-3-enoate (4ab)

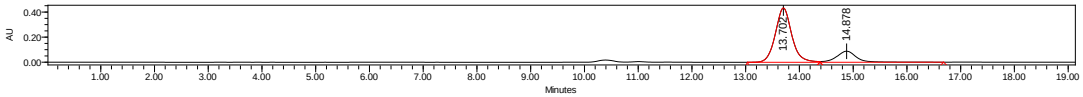


Colorless oil, 24% yield, ee = 60%, $[\alpha]^{16}_{D}$ = − 28.4 (*c* = 0.26, in CH_2Cl_2) **HPLC** (Chiral IA column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 13.70 min, t_R (minor) = 14.88 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 – 7.61 (m, 2H), 7.54 – 7.50 (m, 1H), 7.43 – 7.35 (m, 4H), 7.33 (d, *J* = 6.9 Hz, 3H), 7.03 (dd, *J* = 7.5, 2.0 Hz, 2H), 6.89 – 6.82 (m, 2H), 6.26 (d, *J* = 10.5 Hz, 1H), 3.78 – 3.71 (m, 1H), 3.70 (s, 3H), 3.09 (dd, *J* = 13.8, 6.2 Hz, 1H), 2.82 (dd, *J* = 13.8, 8.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.3, 172.6, 144.2, 141.9, 137.4, 137.3, 137.2, 136.7, 134.9, 132.6, 131.6, 131.6, 130.9, 130.8, 129.8, 129.1, 128.4, 128.3, 128.0, 120.7, 52.4,

47.1, 37.8. **IR** (film): ν(cm^{-1}) 2912, 1741, 1654, 1446, 1269, 1031. **HRMS** (FTMS + ESI) calcd for $C_{25}H_{21}NaBrO_3^+$ ([M]+Na$^+$) = 471.0566 and 473.0546 found 471.0559 and 473.0540.

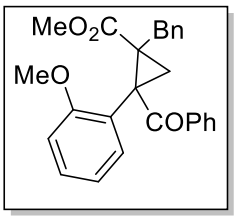


	Retention Time	Area	% Area
1	13.753	48.32	287687
2	14.906	51.68	274003

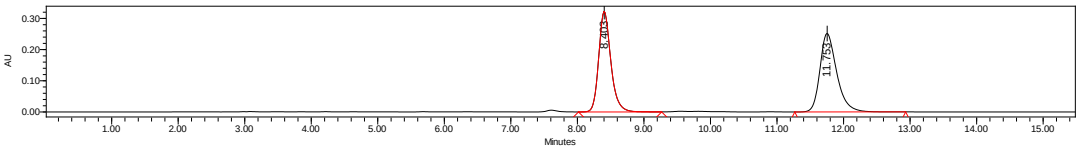


	Retention Time	Area	% Area
1	13.702	9152634	80.06
2	14.878	2279301	19.94

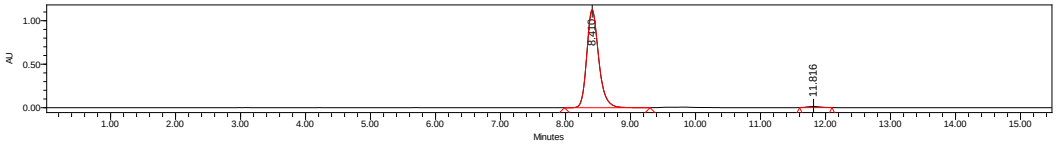
Methyl 2-benzoyl-1-benzyl-2-(2-methoxyphenyl) cyclopropane-1-carboxylate (3ac)



White powder, m.p.84 - 90 °C, 50% yield, ee = 97%, $[\alpha]^{16}_D$ = −76.6 (*c* = 0.86, in CH_2Cl_2) **HPLC** (Chiral IA column) ^{i}PrOH/ ^{n}Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 8.41 min, t_R (minor) = 11.42 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.46-7.38 (m, 7.9 Hz, 4H), 7.24 (d, *J* = 4.5 Hz, 4H), 7.21-7.10 (m, 2H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 8.3 Hz, 1H), 3.81 (d, 1H), 3.79 (s, 3H), 3.41 (s, 1H), 2.40 (d, *J* = 14.8 Hz, 1H), 2.25 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.6, 171.4, 158.6, 139.3, 137.5, 132.3, 131.6, 129.0, 12.0, 128.8, 128.30, 128.0, 126.3, 124.7, 120.3, 110.8, 55.1, 51.8, 42.8, 38.6, 36.5, 23.2. **IR** (film): ν(cm^{-1}) 2960, 1730, 1685, 1508, 1271, 754. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{24}NaO_4^+$ ([M]+Na$^+$) = 423.1567 found 423.1558.

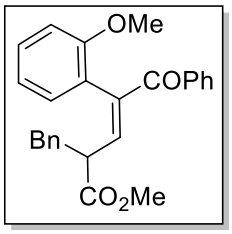


	Retention Time	Area	% Area
1	8.403	4082521	48.10
2	11.753	4405843	51.90

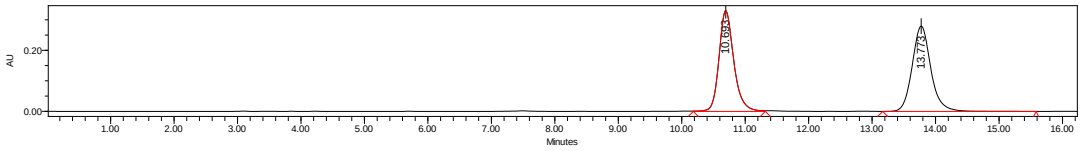


	Retention Time	Area	% Area
1	8.410	14345123	98.74
2	11.816	182593	1.26

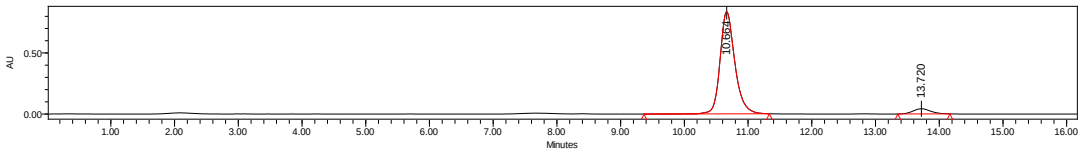
Methyl (E)-2-benzyl-4-(2-methoxyphenyl)-5-oxo-5-phenylpent-3-enoate (4ac)



Colorless oil. 44% yield, ee = 89%, $[\alpha]^{16}_{D} = -83.7$ ($c = 0.63$, in CH_2Cl_2) **HPLC** (Chiral IA column) ^{i}PrOH/ ^{n}Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 10.66 min, t_R (minor) = 13.72 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.66 – 7.57 (m, 2H), 7.48 (d, J = 7.4 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.26 – 7.21 (m, 3H), 7.05 – 6.94 (m, 4H), 6.82 (d, J = 8.2 Hz, 1H), 6.28 (d, J = 10.5 Hz, 1H), 3.77 – 3.70 (m, 1H), 3.67 (s, 3H), 3.55 (s, 3H), 3.14 (dd, J = 13.8, 6.4 Hz, 1H), 2.88 (dd, J = 13.8, 8.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 197.2, 173.0, 156.7, 141.2, 138.9, 138.1, 137.8, 131.9, 131.2, 129.9, 129.8, 129.0, 128.4, 127.9, 126.6, 124.8, 120.5, 110.7, 55.2, 52.1, 47.5, 38.6, 25.4. **IR** (film): ν(cm^{-1}) 2927, 1737, 1716, 1651, 1556, 1261. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{24}NaO_4^+$ ([M]+Na$^+$) = 423.1567 found 423.1558.

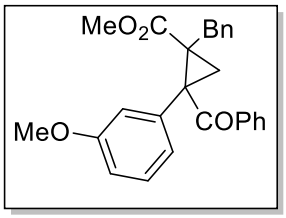


	Retention Time	Area	% Area
1	10.693	5347901	48.46
2	13.773	5687080	51.54

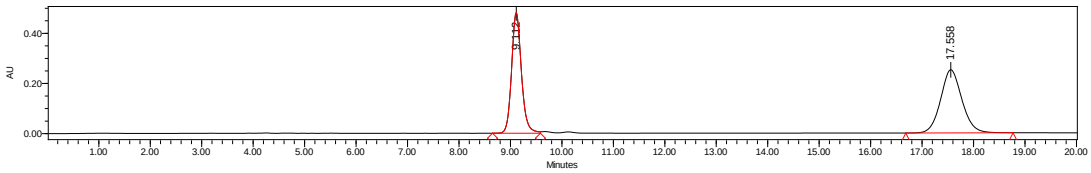


	Retention Time	Area	% Area
1	10.664	13446757	94.28
2	13.720	816245	5.72

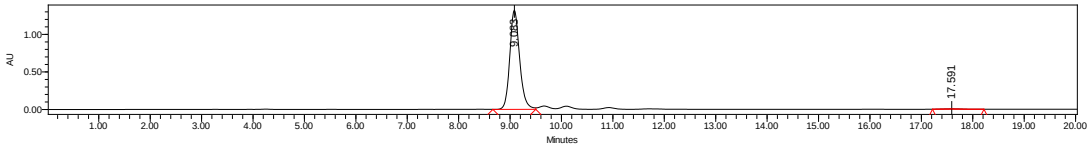
Methyl 2-benzoyl-1-benzyl-2-(3-methoxyphenyl) cyclopropane-1-carboxylate (3ad)



White powder, m.p.60 - 64 °C, 46% yield, ee = 98%, $[\alpha]^{16}_{D}$ = +24.3 (*c* = 0.40, in CH_2Cl_2). **HPLC** (Chiral IA column) ^{i}PrOH/ ^{n}Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 9.08 min, t_R (minor) = 17.59 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.12 – 8.02 (m, 2H), 7.54 – 7.48 (m, 3H), 7.43 (dd, *J* = 8.3, 6.6 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.20 – 7.12 (m, 2H), 6.82 – 6.70 (m, 3H), 3.92 (dd, *J* = 15.0, 1.3 Hz, 1H), 3.75 (s, 3H), 3.32 (s, 3H), 2.48 (dd, *J* = 5.5, 1.4 Hz, 1H), 2.21 (d, *J* = 14.9 Hz, 1H), 1.96 (d, *J* = 5.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.0, 170.7, 159.6, 140.5, 135.8, 135.8, 133.2, 129.9, 129.6, 129.4, 128.5, 128.4, 127.6, 120.9, 114.4, 111.8, 55.1, 51.8, 45.7, 38.1, 37.4, 21.8. **IR** (film): ν(cm^{-1}) 2974, 1737, 1683, 1589, 1269, 1097, 1055, 871.**HRMS** (FTMS + ESI) calcd for $C_{26}H_{24}NaO_4^+$ ([M]+Na$^+$) = 423.1567 found 423.1571.

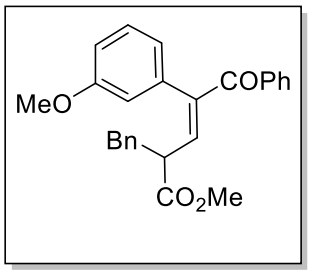


	Retention Time	Area	% Area
1	9.112	6384728	46.94
2	17.558	7216607	53.06



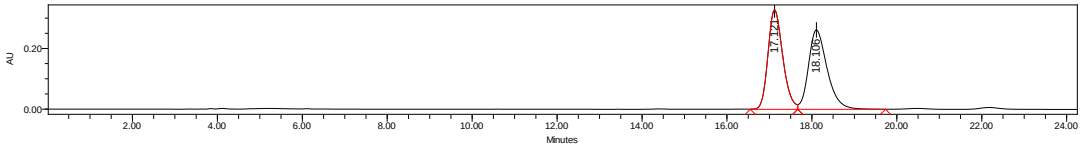
	Retention Time	Area	% Area
1	9.083	17559295	99.31
2	17.591	121675	0.69

Methyl (E)-2-benzyl-4-(3-methoxyphenyl)-5-oxo-5-phenylpent-3-enoate (4ad)

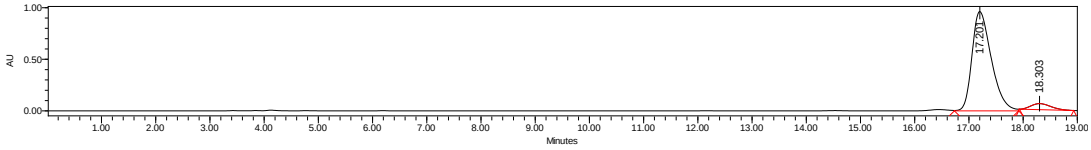


Colorless oil, 46% yield, ee = 88%, $[\alpha]^{16}_{D}$ = −39.2 (*c* = 0.33, in CH_2Cl_2) **HPLC** (Chiral ID column) ^{i}PrOH/ ^{n}Hexane = 15/85, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 17.20 min, t_R (minor) = 18.30 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.68 – 7.61 (m, 2H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.33 – 7.29 (m, 3H), 7.20 (t, *J* = 7.9 Hz, 1H), 7.03 – 6.95 (m, 2H), 6.79 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.62 (d, *J* = 7.5 Hz, 1H), 6.54 (t, *J* = 1.9 Hz, 1H), 6.27 (d, *J* = 10.6 Hz, 1H), 3.73 (s, 3H), 3.70 (s, 3H), 3.66 (q, *J* = 6.0 Hz, 1H), 3.14 (dd, *J* = 13.6, 5.9 Hz, 1H), 2.84 (dd, *J* = 13.6, 9.2 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.5, 172.8, 159.7, 144.0, 139.2, 138.1, 137.5, 135.08, 132.5, 129.9, 129.5, 129.2, 128.8, 128.6, 128.3,

128.3, 127.9, 121.5, 114.5, 112.5, 55.1, 52.3, 47.3, 38.6. **IR** (film): ν(cm^{-1}) 2993, 1741, 1643, 1363, 1244, 1182, 1031, 702. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{24}NaO_4^+$ ([M]+Na$^+$) = 423.1567 found 423.1570.

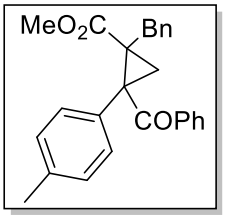


	Retention Time	Area	% Area
1	17.121	7921702	49.79
2	18.106	7988944	50.21

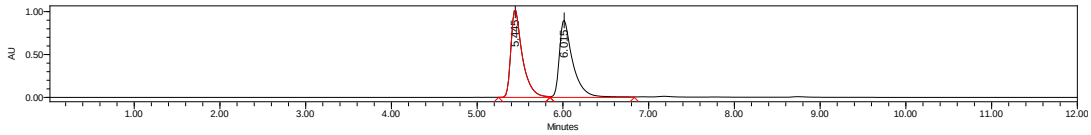


	Retention Time	Area	% Area
1	17.201	23817834	93.94
2	18.303	1535172	6.06

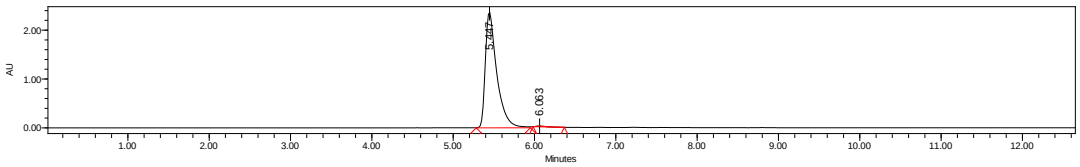
Methyl 2-benzoyl-1-benzyl-2-(p-tolyl)cyclopropane-1-carboxylate (3ae)



Colorless oil, 45% yield, ee = 99%, $[\alpha]^{16}_D$ = +39.4 (*c* = 0.21, in CH_2Cl_2) **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 5.45 min, t_R (minor) = 6.06 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) 8.10 – 8.05 (m, 2H), 7.51 – 7.47 (m, 1H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.27 – 7.17 (m, 5H), 7.04 (d, *J* = 7.9 Hz, 2H), 3.92 (d, *J* = 14.9 Hz, 1H),3.35 (s, 3H), 2.43 (d, *J* = 6.8 Hz, 1H), 2.23 (s, 3H), 1.95 (d, *J* = 5.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, 170.8, 138.9, 137.4, 135.9, 133.1, 132.7, 129.8, 129.6, 129.2, 128.6, 128.6, 128.5, 128.4, 126.5, 51.9, 45.5, 38.1, 37.5, 21.8, 21.1. **IR** (film): ν(cm^{-1}) 3021, 2947, 2735, 1761, 1631, 1358, 1084, 704. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{24}NaO_3^+$ ([M]+Na$^+$) = 407.1618 found 407.1619.

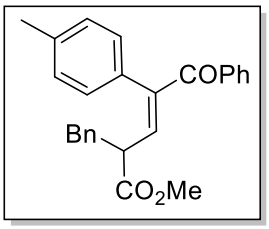


	Retention Time	Area	% Area
1	5.445	9497254	49.33
2	6.015	9753358	50.67

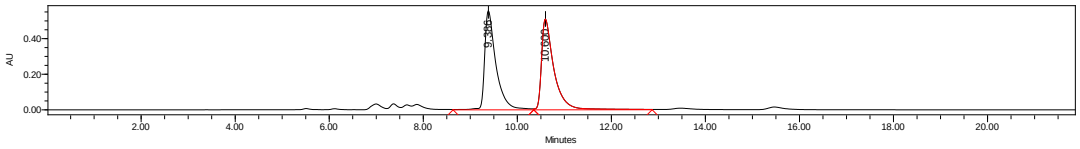


	Retention Time	Area	% Area
1	5.447	23129220	99.49
2	6.063	119608	0.51

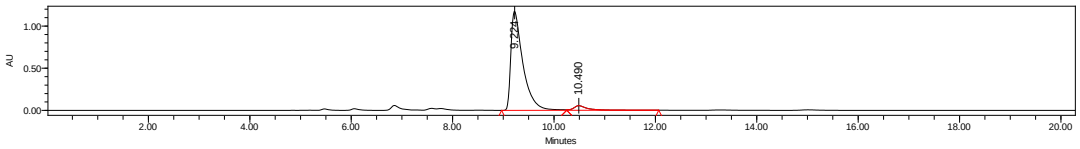
Methyl (E)-2-benzyl-5-oxo-5-phenyl-4-(p-tolyl)pent-3-enoate (4ae)



Colorless oil, 53% yield, ee = 99%, $[\alpha]^{16}_{D}$ = − 40.6 (*c* = 0.31, in CH_2Cl_2) **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 9.22 min, t_R (minor) = 10.49 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.51 – 7.48 (m, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.22 (m, 3H), 7.12 (d, *J* = 7.7 Hz, 2H), 7.06 – 7.01 (m, 2H), 6.88 (d, *J* = 7.7 Hz, 2H), 6.24 (d, *J* = 10.5 Hz, 1H), 3.68 (s, 3H), 3.15 (dd, *J* = 13.7, 6.1 Hz, 1H), 2.88 (dd, *J* = 13.7, 8.9 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.8, 172.9, 144.0, 137.8, 137.7, 137.6, 137.6, 133.1, 132.4, 132.1, 129.8, 129.2, 129.1, 128.5, 128.2, 126.8, 124.9, 52.2, 47.3, 38.6, 21.3. **IR** (film): ν(cm^{-1}) 3035, 1737, 1654, 1465, 1276. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{24}NaO_3^+$ ([M]+Na$^+$) = 407.1618 found 407.1612.

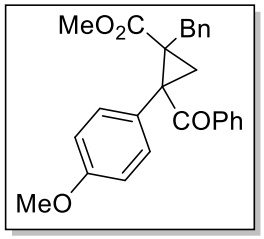


	Retention Time	Area	% Area
1	9.386	9267111	49.52
2	10.600	9446961	50.48

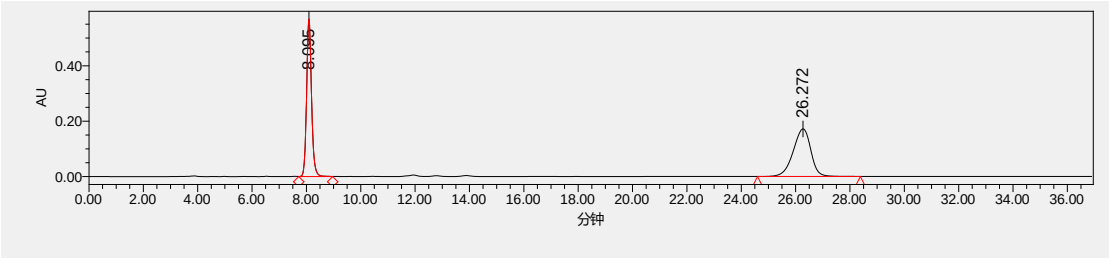


	Retention Time	Area	% Area
1	9.224	19415176	94.80
2	10.490	1065956	5.20

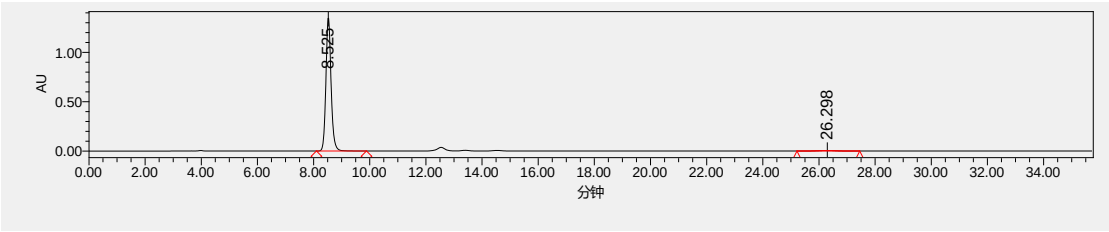
Methyl 2-benzoyl-1-benzyl-2-(4-methoxyphenyl) cyclopropane-1-carboxylate (3af)



Colorless oil, 42% yield, ee = 97%, $[\alpha]^{16}_{D}$ = −70.5 (*c* = 0.26, in CH_2Cl_2) **HPLC** (Chiral IA column) ^{i}PrOH/ ^{n}Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 8.53 min, t_R (minor) = 26.30 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.3 Hz, 2H), 7.55 – 7.48 (m, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.23 (m, 3H), 7.06 – 6.99 (m, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.88 – 6.80 (m, 2H), 6.23 (d, *J* = 10.5 Hz, 1H), 3.81 (s, 3H), 3.77 – 3.70 (m, 1H), 3.69 (s, 3H), 3.16 (dd, *J* = 13.7, 6.1 Hz, 1H), 2.87 (dd, *J* = 13.7, 9.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.9, 172.9, 159.2, 143.6, 137.7, 137.6, 132.4, 130.4, 129.8, 129.1, 128.5, 128.2, 127.4, 126.8, 113.8, 55.3, 55.2, 52.2, 47.4, 38.6. **IR** (film): ν(cm^{-1}) 2949, 1737, 1672, 1512, 1253, 1178. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{25}O_4^+$ ([M]+H$^+$) = 401.1747 found 401.1750.

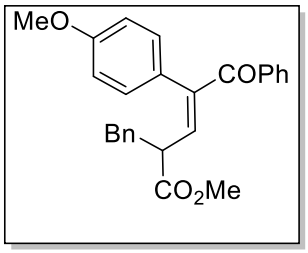


	Retention Time	Area	% Area
1	8.095	7161328	48.07
2	26.272	7737130	51.93



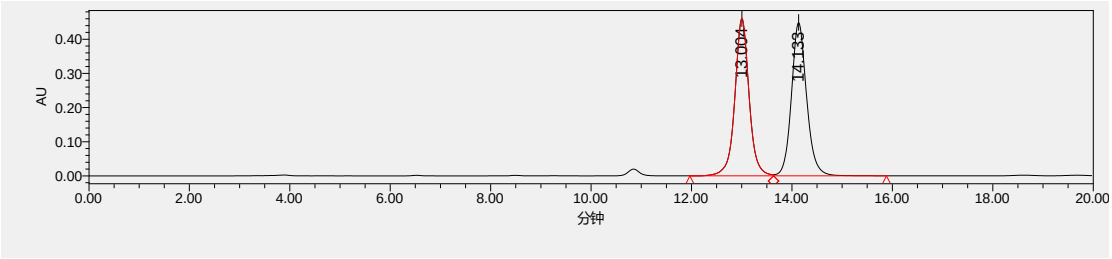
	Retention Time	Area	% Area
1	8.525	17280828	98.75
2	26.298	219091	1.25

Methyl (E)-2-benzyl-4-(4-methoxyphenyl)-5-oxo-5-phenylpent-3-enoate (4af)

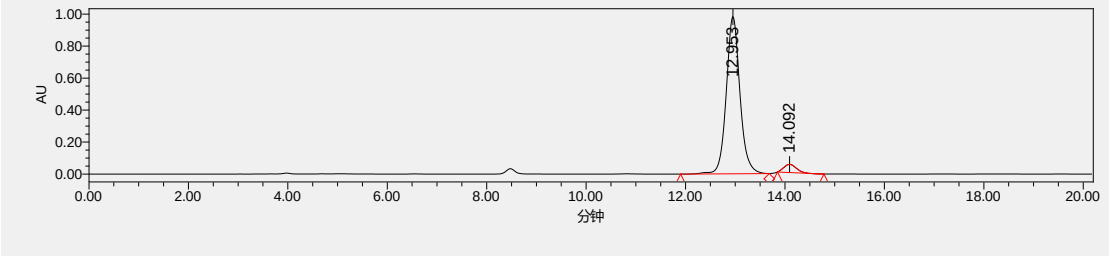


Colorless oil, 57% yield, ee = 91%, $[\alpha]^{16}_{D}$ = +161.0 (*c* = 0.29, in CH_2Cl_2) **HPLC** (Chiral IA column) ^{i}PrOH/ ^{n}Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 12.95 min, t_R (minor) = 14.09 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.08 – 8.04 (m, 2H), 7.54 – 7.48 (m, 1H), 7.43 (dd, *J* = 14.8, 8.1 Hz, 4H), 7.25 (d, 1H), 7.24-7.19 (m, 4H), 6.76 (d, *J* = 8.8 Hz, 2H), 3.92 (d, *J* = 14.9 Hz, 1H), 3.72 (s, 3H), 3.36 (s, 3H), 2.41 (d, *J* = 5.4 Hz, 1H), 2.21 (d, *J* = 14.9 Hz, 1H), 1.94 (d, *J* = 5.4 Hz, 1H). **^{13}C NMR** (101 MHz,

$CDCl_3$) δ 196.2, 170.8, 158.9, 1390, 135.9, 133.0, 131.1, 129.6, 128.6, 128.5, 128.4, 127.6, 126.5, 113.8, 55.1, 51.9, 45.0, 38.1, 37.6, 21.8. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{24}NaO_4^+$ ([M]+Na^+) = 423.1567 found 423.1564.

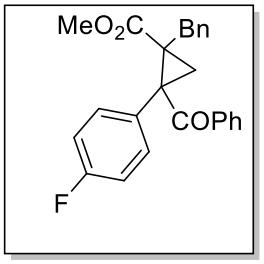


	Retention Time	Area	% Area
1	13.004	9066559	49.03
2	14.133	9424995	50.97

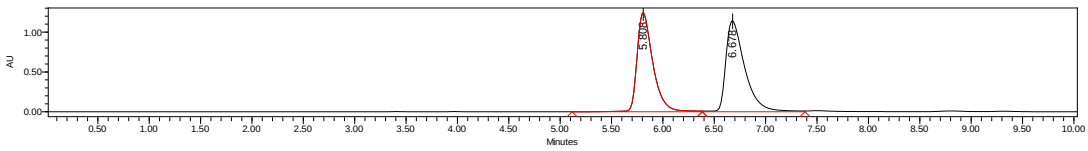


	Retention Time	Area	% Area
1	12.953	18805335	95.38
2	14.092	910726	4.62

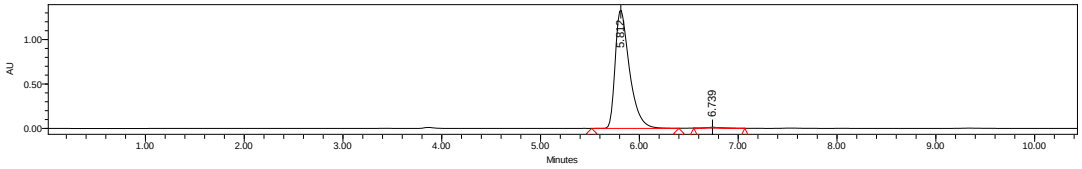
Methyl 2-benzoyl-1-benzyl-2-(4-fluorophenyl) cyclopropane-1-carboxylate (3ag)



White powder, m.p.70 - 78 ℃, 46% yield, ee = 98%, $[\alpha]^{16}_D$ = +30.0 (*c* = 0.32, in CH_2Cl_2) **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 5.81 min, t_R (minor) = 6.74 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 7.1 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.28 – 7.10 (m, 7H), 6.93 – 6.80 (m, 1H), 3.91 (d, *J* = 14.9 Hz, 1H), 3.37 (s, 3H), 2.46 (d, *J* = 4.6 Hz, 1H), 2.22 (d, *J* = 15.0 Hz, 1H), 1.98 (d, *J* = 5.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.6, 170.4, 163.7, 138.3 (d, *J* = 7.5 Hz), 138.3, 135.6, 133.4, 129.9 (d, *J* = 8.4 Hz), 128.6 (d, *J* = 3.6 Hz), 128.6, 128.4, 126.6, 125.6, 117.0 (d, *J* = 22.1 Hz), 114.9, 114.7, 52.0, 45.2, 37.9 (d, *J* = 28.6 Hz), 21.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = −113.9 (s, 1F). **IR** (film): ν(cm^{-1}) 2935, 1745, 1685, 1423, 1286, 1165. **HRMS** (FTMS + ESI) calcd for $C_{25}H_{21}NaFO_3^+$ ([M]+Na^+) = 411.1367 found 411.1366.

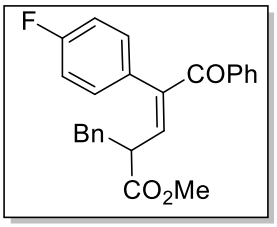


	Retention Time	Area	% Area
1	5.808	13300063	47.67
2	6.678	14599024	52.33

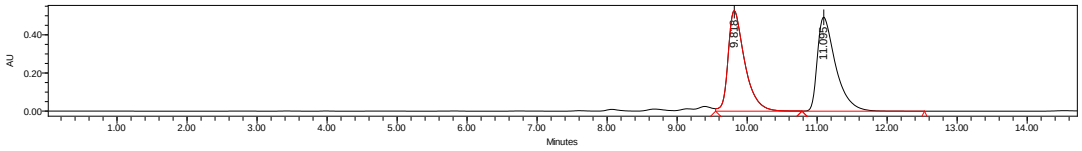


	Retention Time	Area	% Area
1	5.812	13395367	99.26
2	6.739	99531	0.74

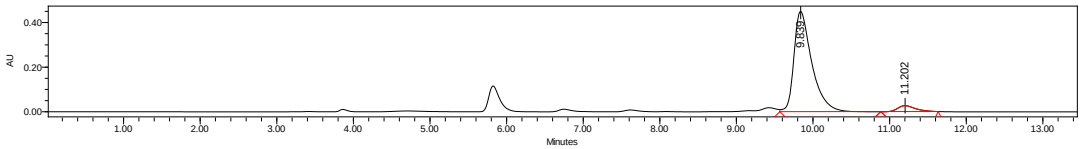
Methyl (E)-2-benzyl-4-(4-fluorophenyl)-5-oxo-5-phenylpent-3-enoate (4ag)



Colorless oil, 46% yield, ee = 89%, $[\alpha]^{16}_{D}$ = −13.9 (*c* = 0.07, in CH_2Cl_2) **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 5.81 min, t_R (minor) = 6.68min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.65 – 7.60 (m, 2H), 7.56 – 7.50 (m, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.27 (dd, *J* = 8.4, 6.7 Hz, 3H), 7.04 – 6.98 (m, 4H), 6.94 – 6.89 (m, 2H), 6.30 (d, *J* = 10.6 Hz, 1H), 3.70 (s, 3H), 3.63 (dd, *J* = 5.7, 1.2 Hz, 1H), 3.17 (dd, *J* = 13.7, 5.7 Hz, 1H), 2.85 (dd, *J* = 13.7, 9.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.3, 172.6, 140.9 (d, *J* = 422.2 Hz), 137.5 (d, *J* = 21.1 Hz) 132.5, 131.0 (d, *J* = 8.2 Hz), 129.80 129.5, 129.1, 128.6, 128.6, 128.4, 128.3, 126.9, 115.3 (d, *J* = 21.5 Hz), 52.3, 47.5, 38.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = −113.9 (s, 1F) **IR** (film): ν(cm^{-1}) 2953, 1741, 1654, 1593, 1512, 1454, 1220, 1141. **HRMS** (FTMS + ESI) calcd for $C_{25}H_{21}NaFO_3^+$ ([M]+Na^+) = 389.1547 found 389.1552.

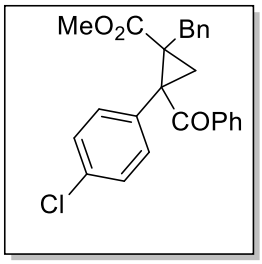


	Retention Time	Area	% Area
1	9.818	8666712	49.39
2	11.095	8882024	50.61

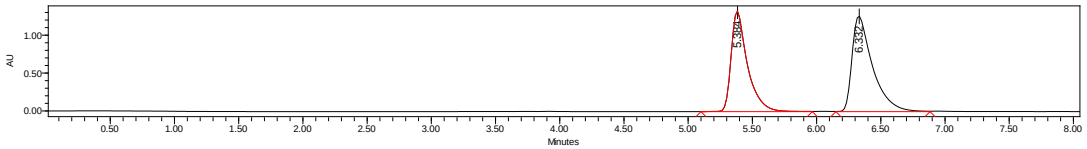


	Retention Time	Area	% Area
1	9.839	7259147	94.49
2	11.202	423195	5.51

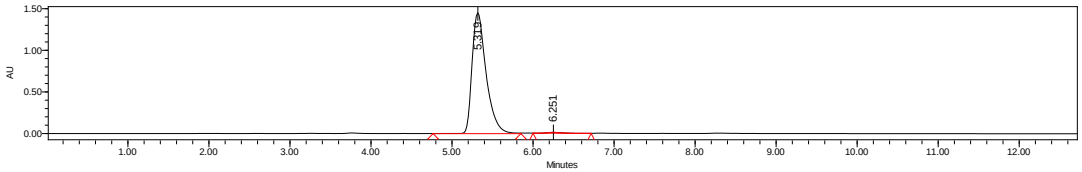
Methyl 2-benzoyl-1-benzyl-2-(4-chlorophenyl) cyclopropane-1-carboxylate (3ah)



Colorless oil, 45% yield, ee = 98%, $[\alpha]^{16}_{D}$ = +17.1 (*c* = 0.80, in CH_2Cl_2) **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 5.32 min, t_R (minor) = 6.25 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ8.06 – 8.00 (m, 2H), 7.54 – 7.50 (m, 1H), 7.48 – 7.42 (m, 4H), 7.25 – 7.24 (m, 1H), 7.22 (d, *J* = 1.7 Hz, 2H), 7.20 (d, *J* = 2.7 Hz, 3H), 7.18 (d, *J* = 1.6 Hz, 1H), 3.92 (d, *J* = 14.9 Hz, 1H), 3.36 (s, 3H), 2.44 (dd, *J* = 5.6, 1.4 Hz, 1H), 2.22 (d, *J* = 14.9 Hz, 1H), 1.98 (d, *J* = 5.6 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.7, 170.5, 138.6, 135.7, 134.4, 133.7, 133.3, 131.3, 129.5, 128.7, 128.6, 128.6, 128.5, 128.4 128.4, 126.6, 52.0, 45.0, 38.0, 37.7, 21.8. **IR** (film): ν(cm^{-1}) 2953, 1737, 1675, 1498, 1450, 1261, 1101, 694. **HRMS** (FTMS + ESI) calcd for $C_{25}H_{21}NaClO_3^+$ ([M]+Na$^+$) = 427.1071 and 429.1042 found 427.1079 and 429.1051.

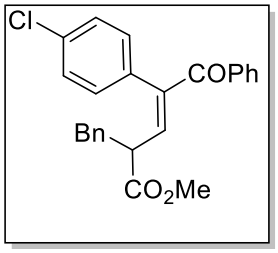


	Retention Time	Area	% Area
1	5.384	11691002	45.57
2	6.332	13965446	54.43

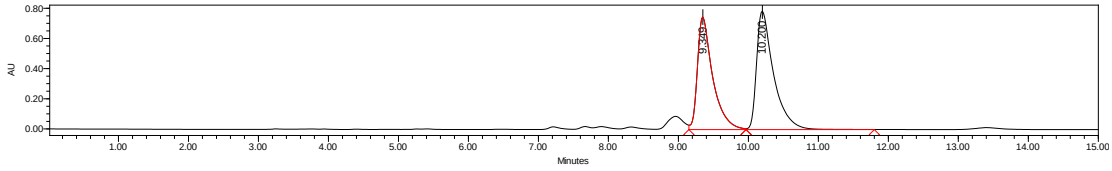


	Retention Time	Area	% Area
1	5.319	17522229	99.27
2	6.251	128086	0.73

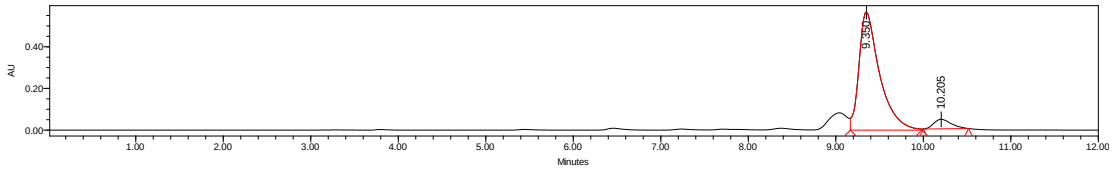
Methyl (E)-2-benzyl-4-(4-chlorophenyl)-5-oxo-5-phenylpent-3-enoate (4ah)



Colorless oil, 47% yield, ee = 87%, $[\alpha]^{16}_{D} = -50.7$ (c = 0.29, in CH_2Cl_2) **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 9.35 min, t_R (minor) = 10.21 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 (d, J = 7.0 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.31 – 7.24 (m, 5H), 7.02 (d, J = 6.2 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 6.31 (d, J = 10.7 Hz, 1H), 3.70 (s, 3H), 3.65 – 3.57 (m, 1H), 3.18 (dd, J = 13.7, 5.6 Hz, 1H), 2.86 (dd, J = 13.7, 9.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.1, 172.6, 142.9, 139.0, 137.5, 137.3, 134.0, 133.4, 132.6, 130.6, 129.8, 129.6, 129.4, 129.2, 128.7, 128.7, 128.6, 128.5, 128.3, 128.1, 126.9, 52.4, 47.6, 38.4. **IR** (film): ν(cm^{-1}) 2956, 1745, 1639, 1494, 1265, 1101. **HRMS** (FTMS + ESI) calcd for $C_{25}H_{21}NaClO_3^+$ ([M]+Na$^+$) = 427.1071 and 429.1042 found 427.1078 and 429.1049.

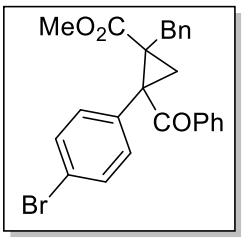


	Retention Time	Area	% Area
1	9.349	11267629	45.99
2	10.200	13231651	54.01



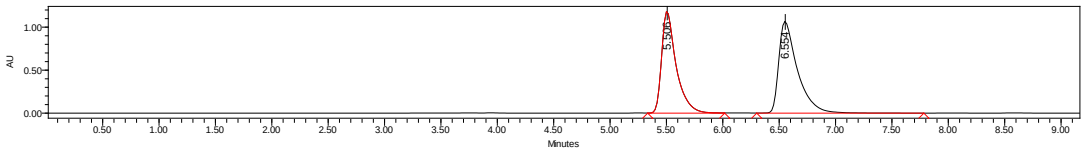
	Retention Time	Area	% Area
1	9.350	9263127	93.64
2	10.205	628963	6.36

Methyl 2-benzoyl-1-benzyl-2-(4-bromophenyl) cyclopropane-1-carboxylate (3ai)

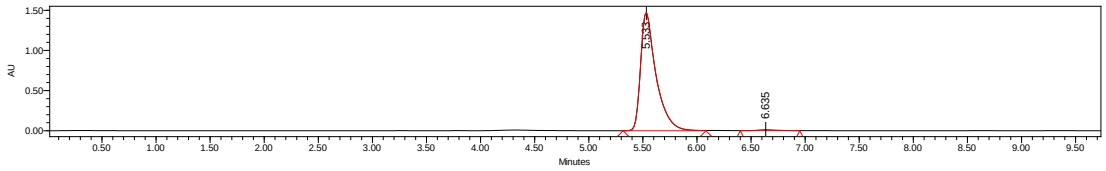


Colorless oil, 46% yield, ee = 98%, $[\alpha]^{16}_{D} = -12.8$ (c = 0.26, in CH_2Cl_2) **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 5.53 min, t_R (minor) = 6.64 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.58 (m, 2H), 7.55 – 7.49 (m, 1H), 7.44 – 7.38 (m, 4H), 7.29 – 7.23 (m, 3H), 7.04 – 7.00 (m, 2H), 6.82 – 6.78 (m, 2H), 6.31 (d, J = 10.7 Hz, 1H), 3.68 (s, 3H), 3.63 – 3.57 (m, 1H), 3.17 (dd, J = 13.7, 5.6 Hz, 1H), 2.85 (dd, J = 13.7, 9.5 Hz, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.6, 170.5, 138.6, 135.6, 134.9, 133.4, 131.6, 131.6, 129.5, 128.6, 128.6, 128.4, 126.6, 121.9, 52.0, 45.1, 38.0, 37.7, 21.8.

IR (film): ν(cm^{-1}) 2920, 1745, 1651, 1384, 1276, 1068. **HRMS** (FTMS + ESI) calcd for $C_{25}H_{21}NaBrO_3^+$ ([M]+H$^+$) = 471.0566 and 473.0546 found 471.0570 and 473.0551.

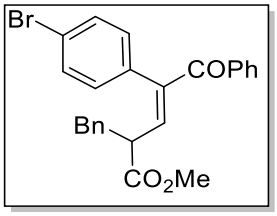


	Retention Time	Area	% Area
1	5.506	10602897	46.34
2	6.554	12279695	53.66

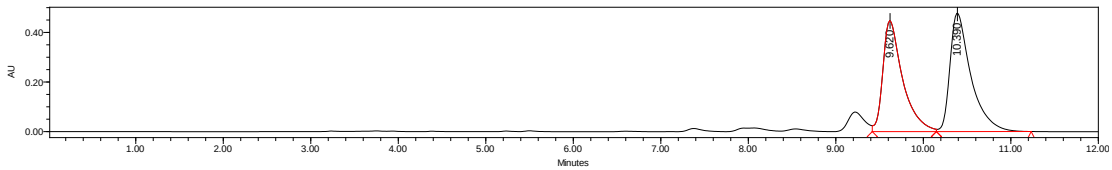


	Retention Time	Area	% Area
1	5.533	14551571	99.20
2	6.635	117626	0.80

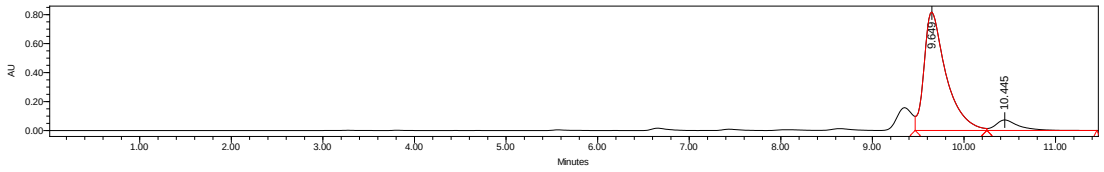
Methyl (E)-2-benzyl-4-(4-bromophenyl)-5-oxo-5-phenylpent-3-enoate (4ai)



Colorless oil, 46% yield, ee = 83%, $[\alpha]^{16}_D$ = −44.0 (*c* = 0.22, in CH_2Cl_2) **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 9.65 min, t_R (minor) = 10.45 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.65 – 7.58 (m, 2H), 7.56 – 7.51 (m, 1H), 7.42 (dd, *J* = 8.1, 6.2 Hz, 4H), 7.28 (dd, *J* = 9.0, 7.4 Hz, 3H), 7.05 – 6.99 (m, 2H), 6.79 (d, *J* = 8.1 Hz, 2H), 6.31 (d, *J* = 10.7 Hz, 1H), 3.70 (s, 3H), 3.65 – 3.55 (m, 1H), 3.17 (dd, *J* = 13.7, 5.5 Hz, 1H), 2.85 (dd, *J* = 13.7, 9.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.0, 172.6, 143.0, 139.0, 137.5, 137.3, 133.9, 132.6, 131.4, 130.9, 129.8, 129.2, 128.6, 128.3, 127.0, 122.2, 52.4, 47.6, 38.4, 36.6, 24.7. **IR** (film): ν(cm^{-1}) 2974, 1734, 1654, 1462, 1093, 1055, 891. **HRMS** (FTMS + ESI) calcd for $C_{25}H_{21}NaBrO_3^+$ ([M]+H$^+$) = 471.0566 and 473.0546 found 471.0562 and 473.0543.

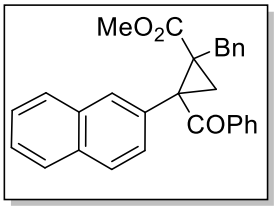


	Retention Time	Area	% Area
1	9.620	7025228	46.98
2	10.390	7929632	53.02

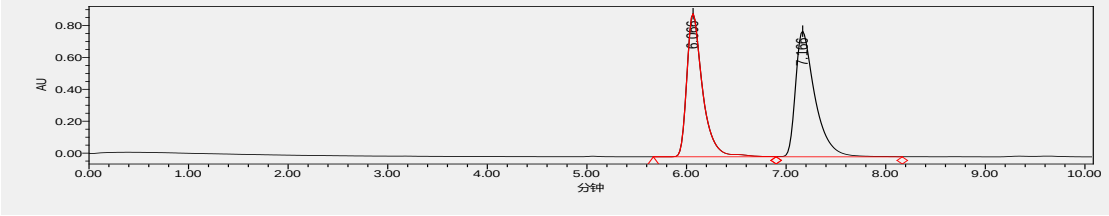


	Retention Time	Area	% Area
1	9.649	13581690	91.46
2	10.445	1267699	8.54

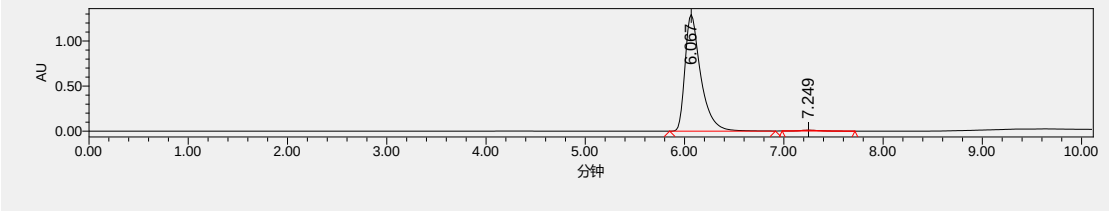
Methyl 2-benzoyl-1-benzyl-2-(naphthalen-2-yl) cyclopropane-1-carboxylate (3aj)



White powder, m.p.96 - 102 ℃, 50% yield, ee = 98%, $[\alpha]^{16}_{D}$ =+25.6 (*c* = 0.19, in CH_2Cl_2) **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 2/98, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 6.08 min, t_R (minor) = 7.25 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.17 – 8.08 (m, 2H), 7.97 (d, *J* = 1.9 Hz, 1H), 7.81 – 7.74 (m, 1H), 7.74 – 7.69 (m, 2H), 7.61 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.45 – 7.38 (m, 4H), 7.26 – 7.21 (m, 4H), 7.20 – 7.14 (m, 1H), 4.00 (dd, *J* = 14.9, 1.4 Hz, 1H), 3.27 (s, 3H), 2.57 (dd, *J* = 5.4, 1.4 Hz, 1H), 2.29 (d, *J* = 14.9 Hz, 1H), 2.07 (d, *J* = 5.4 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.0, 170.8, 138.8, 135.8, 133.3, 133.2, 133.2, 132.6, 129.6, 129.4, 128.6, 128.5, 128.4, 128.1, 127.9, 127.6, 127.2, 126.5, 126.3, 126.2, 100.0, 51.9, 45.9, 38.1, 37.7, 21.9. **IR** (film): ν(cm^{-1}) 2935, 1734, 1653, 1278, 742, 702. **HRMS** (FTMS + ESI) calcd for $C_{29}H_{25}O_3^+$ ([M]+H^+) =421.1798 found 421.1801.



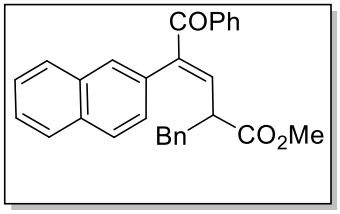
	Retention Time	Area	% Area
1	6.066	9855882	48.03
2	7.166	10663752	51.97



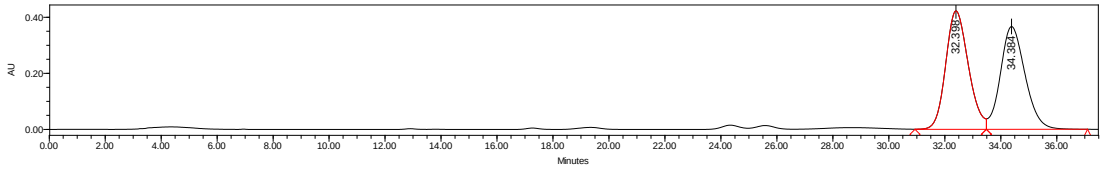
	Retention Time	Area	% Area

1	6.067	14257650	99.20
2	7.249	115397	0.80

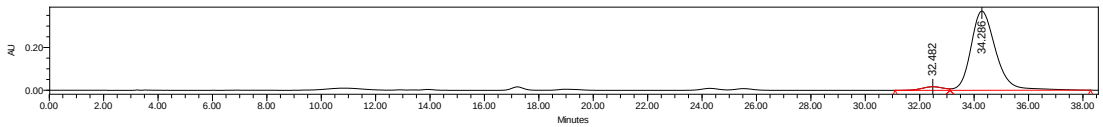
Methyl (E)-2-benzyl-4-(naphthalen-2-yl)-5-oxo-5-phenylpent-3-enoate(4aj)



Colorless oil, 45% yield, ee = 92%, $[\alpha]^{16}_D$ = −24.1 (*c* = 0.63, in CH_2Cl_2) **HPLC** (Chiral IC column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (minor) = 32.48 min, t_R (major) = 34.89 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.84 – 7.80 (m, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.53 – 7.50 (m, 1H), 7.48 (dd, *J* = 6.2, 3.3 Hz, 2H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.34 (s, 1H), 7.28 (d, *J* = 2.3 Hz, 2H), 7.23 – 7.13 (m, 2H), 7.10 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.03 (dd, *J* = 6.7, 2.9 Hz, 2H), 6.37 (d, *J* = 10.7 Hz, 1H), 3.81 – 3.72 (m, 1H), 3.70 (s, 3H), 3.16 (d, *J* = 5.7 Hz, 1H), 2.99 – 2.68 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.6, 172.8, 144.1, 138.4, 137.7, 137.5, 133.0, 132.8, 132.6, 132.5, 129.9, 129.3, 128.7, 128.6, 128.4, 128.3, 128.2, 127.9, 127.7, 126.9, 126.9, 126.3, 126.2, 52.3, 52.3, 47.5, 38.6, 29.7. **IR** (film): ν(cm^{-1}) 2949, 1741, 1662, 1446, 1261, 698. **HRMS** (FTMS + ESI) calcd for $C_{29}H_{24}NaO_3^+$ ([M]+Na^+) =443.1618 found 443.1615.

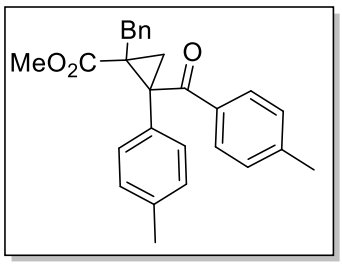


	Retention Time	Area	% Area
1	32.398	23738564	51.46
2	34.384	22392099	48.54



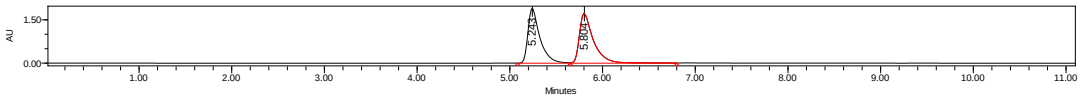
	Retention Time	Area	% Area
1	32.482	911431	3.75
2	34.286	23423287	96.25

Methyl 1-benzyl-2-(4-methylbenzoyl)-2-(p-tolyl) cyclopropane-1-carboxylate(3ak)

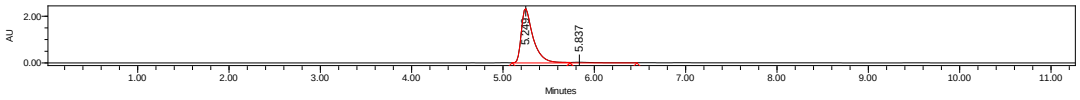


Colorless oil, 45% yield, ee = 95%, $[\alpha]^{16}_D$ = +12.8 (*c* = 0.88, in CH_2Cl_2) **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) =5.25 min, t_R (minor) = 5.84 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.15 (m, 7H), 7.03 (d, *J* = 8.0 Hz, 2H), 3.91 (d, *J* = 14.9 Hz, 1H), 3.35 (s, 3H), 2.44 – 2.39 (m, 1H), 2.36 (s, 3H),

2.23 (s, 3H), 2.19 (d, J = 15.0 Hz, 1H), 1.93 (d, J = 5.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.6, 170.9, 144.0, 139.0, 137.3, 133.2, 132.9, 130.0, 129.8, 129.7, 129.2, 129.2, 128.6, 128.4, 127.0, 126.4, 51.8, 45.5, 38.2, 37.3, 21.8, 21.7, 21.7, 21.1. **IR** (film): ν(cm^{-1}) 3030, 1741, 1658, 1600, 1446, 1276, 1170. **HRMS** (FTMS + ESI) calcd for $C_{27}H_{26}NaO_3^+$ ([M]+Na^+) = 421.1774 found 421.1766.

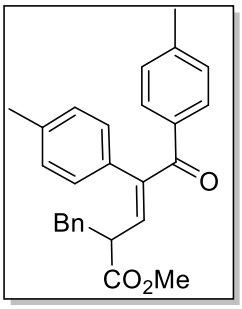


	Retention Time	Area	% Area
1	5.243	17018095	48.20
2	5.804	18290023	51.80

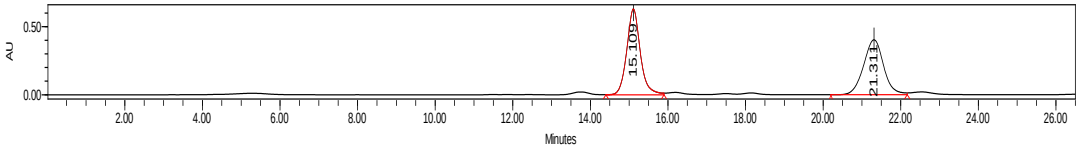


	Retention Time	Area	% Area
1	5.249	20995908	97.39
2	5.837	561659	2.61

Methyl (E)-2-benzyl-5-oxo-4,5-di-p-tolylpent-3-enoate(4ak)

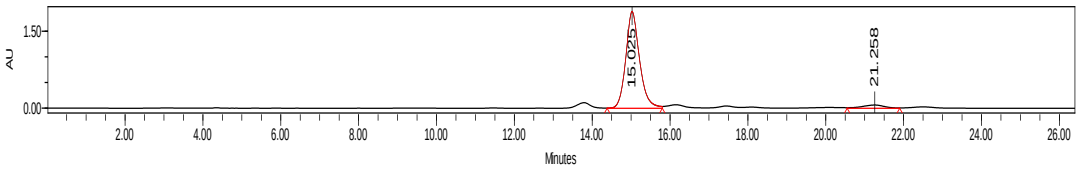


Colorless oil, 54% yield, ee = 90%, $[\alpha]^{16}_D$ = − 84.5 (c = 0.26, in CH_2Cl_2) **HPLC** (Chiral IA column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) =15.03 min, t_R (minor) = 21.26 min. **^{1}H NMR** (400 MHz, Chloroform-d) δ 7.55 (d, J = 8.1 Hz, 2H), 7.26 (q, J = 6.1, 4.9 Hz, 3H), 7.18 (d, J = 7.9 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 7.04 (d, J = 6.6 Hz, 2H), 6.89 (d, J = 8.0 Hz, 2H), 6.20 (d, J = 10.6 Hz, 1H), 3.72 (ddd, J = 10.6, 9.0, 6.3 Hz, 1H), 3.68 (s, 3H), 3.15 (dd, J = 13.7, 6.2 Hz, 1H), 2.88 (dd, J = 13.7, 8.9 Hz, 1H), 2.40 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.5, 173.0, 144.0, 143.2, 137.8, 137.6, 136.7, 134.8, 132.3, 130.1, 129.2, 129.0, 129.0, 128.9, 128.5, 126.8, 52.2, 47.3, 38.6, 21.6, 21.3. **IR** (film): ν(cm^{-1}) 3035, 1745, 1658, 1265, 1174, 759. **HRMS** (FTMS + ESI) calcd for $C_{27}H_{26}NaO_3^+$ ([M]+Na^+) = 421.1774 found 421.1770.



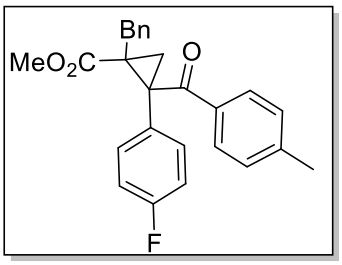
	Retention Time	Area	% Area
1	15.109	15234332	51.28

2	21.311	14476175	48.72

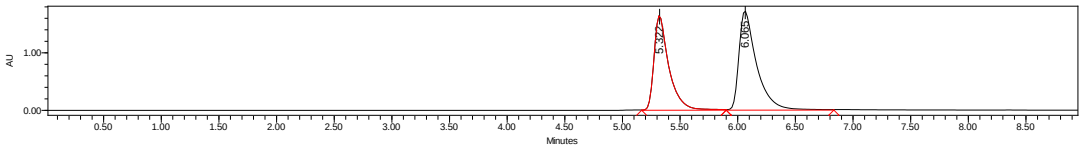


	Retention Time	Area	% Area
1	15.025	46361510	94.93
2	21.258	2473877	5.07

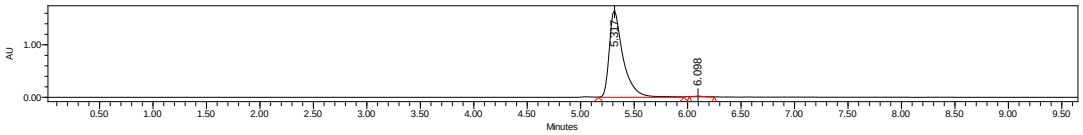
Methyl 1-benzyl-2-(4-fluorophenyl)-2-(4-methylbenzoyl) cyclopropane-1-carboxylate(3al)



Colorless oil, 43% yield, ee = 99%, $[\alpha]^{16}_{D}$ = +20.6 (*c* = 0.79, in CH_2Cl_2) **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) =5.32 min, t_R (minor) = 6.10 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.28 – 7.21 (m, 4H), 7.18 (d, *J* = 7.0 Hz, 3H), 6.92 (t, *J* = 8.7 Hz, 2H), 3.92 (dd, *J* = 15.0, 1.3 Hz, 1H), 3.34 (s, 3H), 2.44 (dd, *J* = 5.5, 1.4 Hz, 1H), 2.38 (s, 3H), 2.20 (d, *J* = 15.0 Hz, 1H), 1.95 (d, *J* = 5.5 Hz, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 195.4, 170.7, 162.0 (d, *J* = 247.2 Hz), 144.3, 138.8, 133.0, 131.8 (d, *J* = 3.2 Hz), 131.6 (d, *J* = 8.2 Hz), 129.7, 129.3, 128.6, 128.4, 126.5, 115.4 (d, *J* = 21.6 Hz), 51.9, 44.8, 38.2, 37.5, 22.0, 21.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = −114.1 (s, 1F). **IR** (film): ν(cm^{-1}) 2956, 1737, 1724, 1647, 1552, 1498. **HRMS** (FTMS + ESI) calcd for $C_{26}H_{24}FO_3^+$ ([M]+H^+) = 403.1704 found 403.1710.



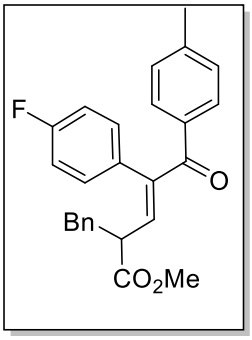
	Retention Time	Area	% Area
1	5.322	14777280	44.62
2	6.065	18339573	55.38



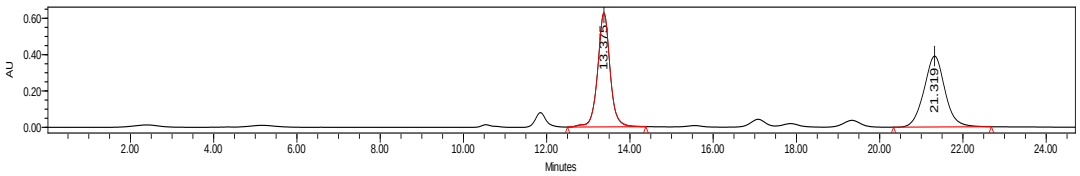
	Retention Time	Area	% Area
1	5.317	14893761	99.55

2	6.098	67366	0.45

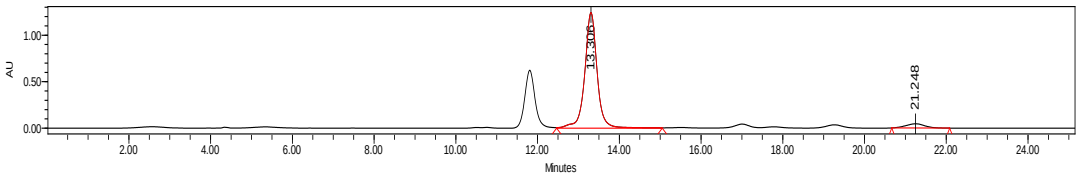
Methyl (E)-2-benzyl-4-(4-fluorophenyl)-5-oxo-5-(p-tolyl)pent-3-enoate（4al）



Colorless oil, 55% yield, ee = 90%, $[\alpha]^{16}_{D}$ = −61.5 (*c* = 0.64, in CH_2Cl_2) **HPLC** (Chiral IA column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 13.31 min, t_R (minor) = 21.25 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 – 7.51 (m, 2H), 7.28 (dd, *J* = 7.2, 2.2 Hz, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 7.07 – 6.99 (m, 3H), 6.96 (s, 2H), 6.93 (d, *J* = 2.4 Hz, 2H), 6.25 (d, *J* = 10.6 Hz, 1H), 3.70 (s, 3H), 3.66 – 3.61 (m, 1H), 3.16 (dd, *J* = 13.7, 5.7 Hz, 1H), 2.85 (dd, *J* = 13.7, 9.3 Hz, 1H), 2.41 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.0, 172.8, 162.4 (d, *J* = 247.0 Hz), 143.3 (d, *J* = 38.3 Hz), 137.7 (d, *J* = 13.1 Hz), 134.6, 131.6, 131.1, 132.0, 130.9, 130.3, 130.0, 129.7, 129.3, 129.1, 129.0, 128.8, 128.6, 128.5, 128.4, 127.2, 126.9, 116.3, 116.1, 115.3 (d, *J* = 21.3 Hz), 52.3, 47.4, 38.4, 21.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = −114.0 (s, 1F). **IR** (film): ν(cm^{-1}) 2953, 1737, 1668, 1610, 1508, 1224. **HRMS** (FTMS + c ESI) calcd for $C_{26}H_{23}NaFO_3^+$ ([M]+Na^+) =425.1523 found 425.1523.

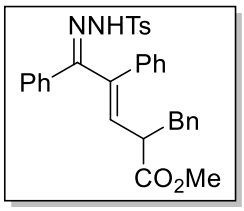


	Retention Time	Area	% Area
1	13.375	12937078	48.70
2	21.319	13627492	51.30

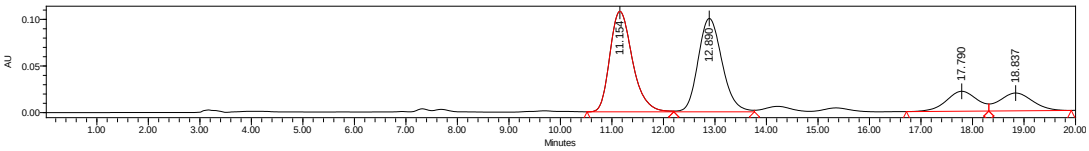


	Retention Time	Area	% Area
1	13.306	26220410	94.75
2	21.248	1453042	5.25

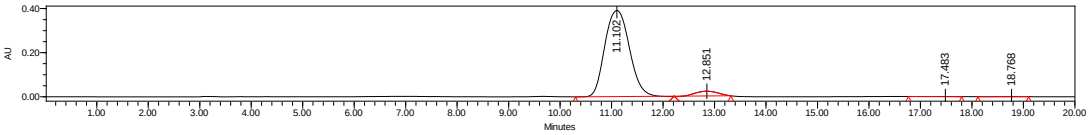
Methyl (3E,5Z)-2-benzyl-4,5-diphenyl-5-(2-tosylhydrazono) pent-3-enoate (5)



White powder, m.p.125 - 128 ℃, 64% yield, ee = 90%, $[\alpha]^{16}_{D}$ =-26.0 (*c* = 0.68, in CH_2Cl_2) **HPLC** (Chiral ADH column) ^{i}PrOH/ ^{n}Hexane = 10/90, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 11.10 min, t_R (minor) = 12.85 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.49 (dd, *J* = 5.2, 1.9 Hz, 3H), 7.38 – 7.28 (m, 4H), 7.25 – 7.15 (m, 4H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.07 – 6.99 (m, 2H), 6.83 (dd, *J* = 6.5, 3.0 Hz, 2H), 6.77 – 6.64 (m, 2H), 5.47 (d, *J* = 10.5 Hz, 1H), 3.57 (s, 3H), 3.43 – 3.27 (m, 1H), 2.92 (dd, *J* = 13.4, 6.0 Hz, 1H), 2.62 (dd, *J* = 13.5, 9.0 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.2, 156.3, 143.9, 143.7, 137.8, 136.0, 135.1, 134.9, 130.6, 123.0, 129.8, 129.6, 129.2, 128.3, 128.2, 128.0, 127.6, 127.1, 126.5, 52.0, 47.6, 38.6, 21.6. **IR** (film): ν(cm^{-1}) 1737, 1670, 1444, 1261, 1230, 1072. **HRMS** (FTMS + c ESI) calcd for $C_{32}H_{30}NaN_2O_4S^+$ ([M]+Na$^+$) =561.1818 found 561.1825.

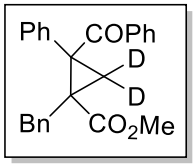


	Retention Time	Area	% Area
1	11.154	3279466	39.75
2	12.890	3227948	39.13
3	17.790	890972	10.80
4	18.837	851605	10.32



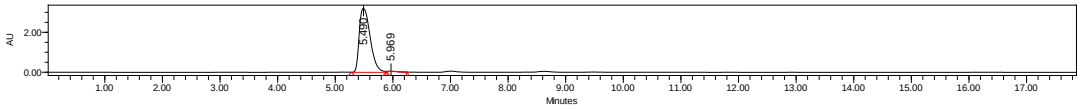
	Retention Time	Area	% Area
1	11.102	12941042	95.01
2	12.851	669034	4.91
3	17.483	2872	0.02
4	18.768	7892	0.06

Methyl 2-benzoyl-1-benzyl-2-phenylcyclopropane-1-carboxylate-3,3-d$_2$ (D-3aa)



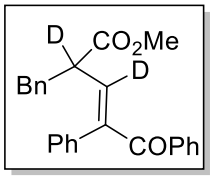
White powder, m.p.94 - 100 ℃, 45% yield, ee = 99%, $[\alpha]^{16}_{D}$ = +27.6 (*c* = 0.60, in CH_2Cl_2) **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 5.49 min, t_R (minor) = 5.97 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.13 – 8.00 (m, 2H), 7.50 (d, *J* = 7.6 Hz, 3H), 7.43 (dd, *J* = 8.2, 6.4 Hz, 2H), 7.30 – 7.08 (m, 84H), 3.93 (d, *J* = 14.9 Hz, 1H), 3.31 (s, 3H), 2.23 (d, *J* = 15.0 Hz, 1H). **^{13}C**

NMR (101 MHz, $CDCl_3$) δ 196.1, 170.7, 138.9, 135.9, 135.8, 133.1, 123.0, 129.6, 128.6, 128.5, 128.4, 127.6, 126.5, 51.8, 45.6, 38.0, 37.4. **IR** (film): ν(cm^{-1}) 1734, 1656, 1448, 1259. **HRMS** (FTMS + c ESI) calcd for $C_{32}H_{30}NaN_2O_4S^+$ ([M]+Na^+) =395.1587 found 395.1587.

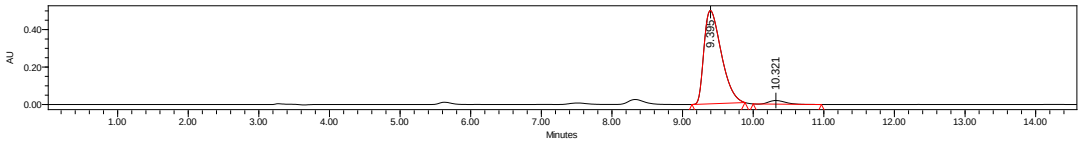


	Retention Time	Area	% Area
1	5.490	42291490	99.66
2	5.969	145963	0.34

Methyl (E)-2-benzyl-5-oxo-4,5-diphenylpent-3-enoate-2,3-d_2 (D-4aa)



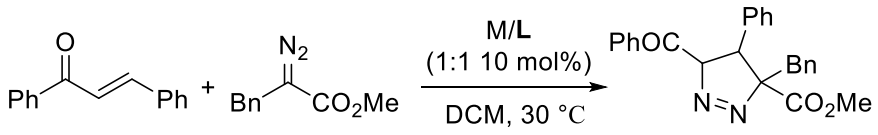
Colorless oil, 44% yield, ee = 93%, $[\alpha]^{16}_D$ = + 61 (*c* = 0.56, in CH_2Cl_2) **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 9.40 min, t_R (minor) = 10.32 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.64 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.55 – 7.48 (m, 0H), 7.39 (t, *J* = 7.7 Hz, 1H), 7.31 (td, *J* = 4.7, 1.5 Hz, 2H), 7.28 (s, 0H), 7.26 (d, *J* = 2.6 Hz, 1H), 7.06 – 6.93 (m, 2H), 3.68 (s, 2H), 3.15 (d, *J* = 13.7 Hz, 1H), 2.87 (d, *J* = 13.7 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 196.50, 172.85, 143.87, 137.65, 137.54, 135.04, 132.44, 129.84, 129.18, 129.12, 128.50, 128.29, 128.25, 127.88, 126.82, 126.28, 52.25, 38.45, 29.71. **IR** (film): ν(cm^{-1}) 1734, 1662, 1591, 1492, 1444,1261, 1230. **HRMS** (FTMS + c ESI) calcd for $C_{32}H_{30}NaN_2O_4S^+$ ([M]+Na^+) =395.1587 found 395.1582.



	Retention Time	Area	% Area
1	9.395	8479170	96.49
2	10.321	308773	3.51

11. Limitation of scope with cyclopropanation and C-H insertion reaction of enones

Table S2. Optimization of the conditions use chalcone as substrate [a]



2 1 3

entry	M	**L**	yield (%)[b]	dr[c]	ee (%)[c]
1	$Sc(OTf)_3$	**L_3-RaPr$_2$**	trace	nd	nd
2	$Y(OTf)_3$	**L_3-RaPr$_2$**	trace	nd	nd
3	$Ni(OTf)_2$	**L_3-RaPr$_2$**	trace	nd	nd
4	$Sc(OTf)_3$	**L_3-PrPr$_2$**	13	92:8	race
5	$Sc(OTf)_3$	**L_3-PiMe$_3$**	16	92:8	10
6	$Sc(OTf)_3$	**L_2-PiMe$_2$**	27	96:4	55
7	$Sc(OTf)_3$	**L_2-PiMe$_3$**	30	>20:1	69

[a] Unless otherwise noted, the reactions were performed with 10 mol % metal salt, 10 mol% ligand, 1 (0.10 mmol) and 2 (0.15 mmol) in solvent (0.5 mL) under N_2 for 24 h. [b] Isolated yield by silica gel chromatography. [c] Determined by chiral HPLC analysis.

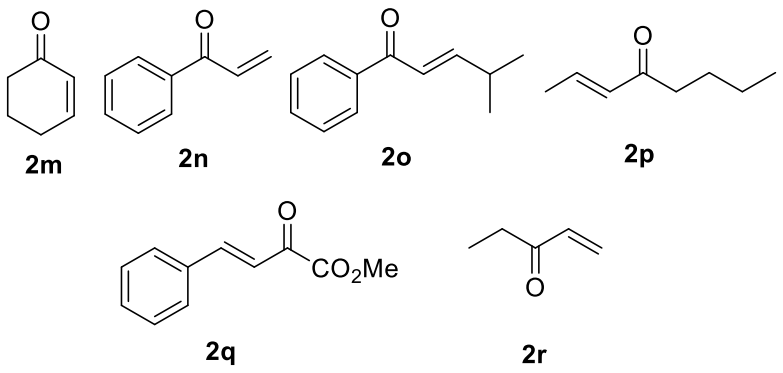
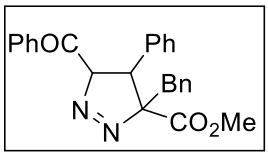
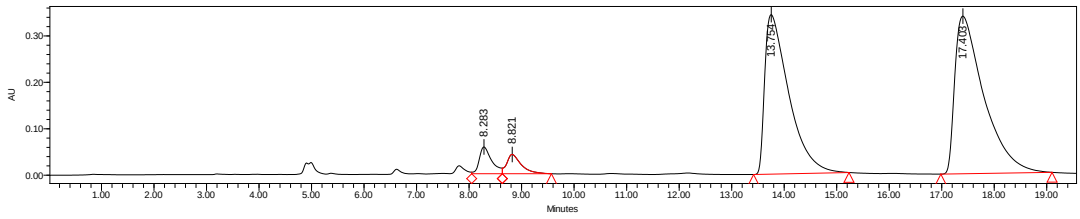


Figure S2 Structures of substrates with no reactions

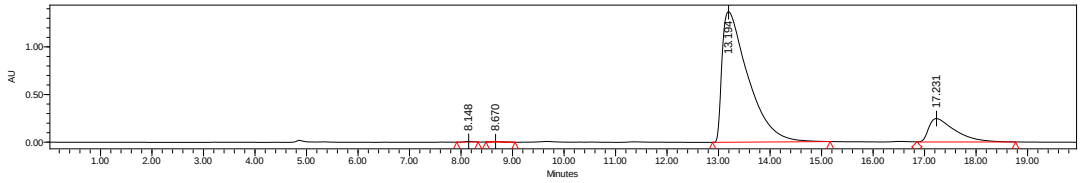
Methyl 5-benzoyl-3-benzyl-4-phenyl-4,5-dihydro-3H-pyrazole-3-carboxylate



Colorless oil, 30% yield, ee = 69%,dr > 20:1, **HPLC** (Chiral IB column) ^{i}PrOH/ ^{n}Hexane = 5/95, Flow rate: 1.0 mL/min, 254 nm, t_R (major) = 13.19 min, t_R (minor) = 17.23 min. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.15 – 8.08 (m, 2H), 7.55 – 7.52 (m, 1H), 7.47 – 7.42 (m, 2H), 7.31 – 7.25 (m, 7H), 7.23 – 7.19 (m, 3H), 7.17 – 7.09 (m, 2H), 6.68 (s, 1H), 4.59 (s, 1H), 3.46 (d, *J* = 13.3 Hz, 1H), 3.24 (s, 3H), 3.08 (d, *J* = 13.3 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.0, 151.04 135.8, 134.4, 132.6, 130.2, 130.0, 129.8, 129.0, 128.8, 128.6, 128.1, 128.1, 127.8, 127.7, 106.0, 59.5, 51.9, 43.6. **HRMS** (FTMS + c ESI) calcd for $C_{25}H_{22}NaN_2O_3^+$ ([M]+Na^+) =421.1523 found 421.1519.



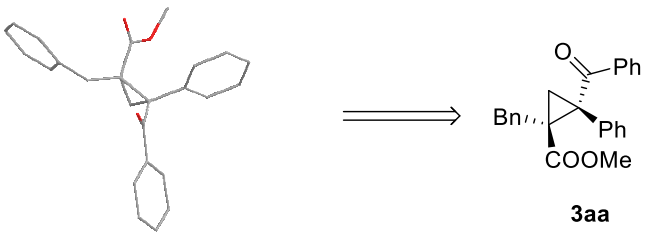
	Retention Time	Area	% Area
1	8.283	945918	3.68
2	8.821	791927	3.08
3	13.754	10931731	42.51
4	17.403	13043327	50.73



	Retention Time	Area	% Area
1	8.148	79164	0.14
2	8.670	68653	0.12
3	13.194	48060674	84.44
4	17.231	8705835	15.30

12. X-ray crystallography data

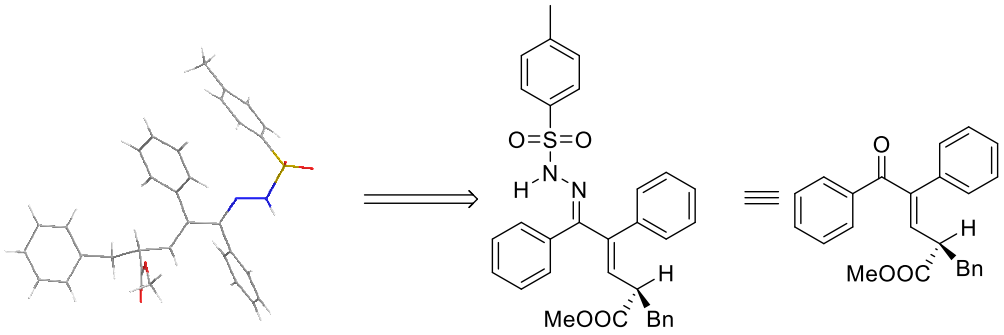
(a) The absolute configuration of **3aa** was determined by X-ray chromatography analysis.



3aa

Single crystal of the cyclopropanation product **3aa** [$C_{25}H_{22}O_3$] was obtained from the mixed solvents of petroleum ether, ethyl acetate. The absolute configuration of **3aa** is (1*S*, 2*R*). CCDC 1843744 contains

the supplementary crystallographic data which can be obtained free of charge from the Cambrige Crystallographic Data Centere via www.ccdc.cam.ac.uk/data_request/cif.



5aa **4aa**

(b) The absolute configuration of **5aa** was determined by X-ray chromatography analysis.

The carbon insertion product **4aa** can conversion to the product **5aa**. Single crystal of the product **5aa** [$C_{32}H_{30}N_2O_4S_1$] was obtained from the mixed solvents of petroleum ether, ethyl acetate. The absolute configuration of **5aa** is (*S*, *E*). CCDC 1843745 contains the supplementary crystallographic data which can be obtained free of charge from the Cambrige Crystallographic Data Centere via www.ccdc.cam.ac.uk/data_request/cif.

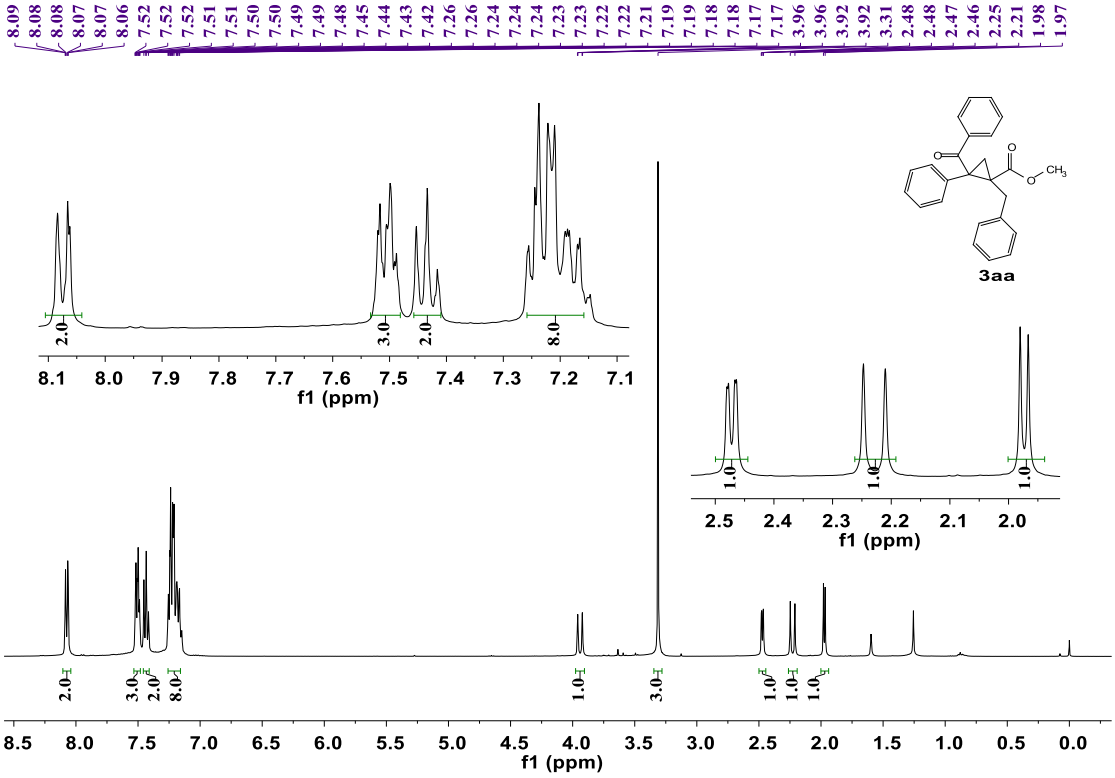
13. reference

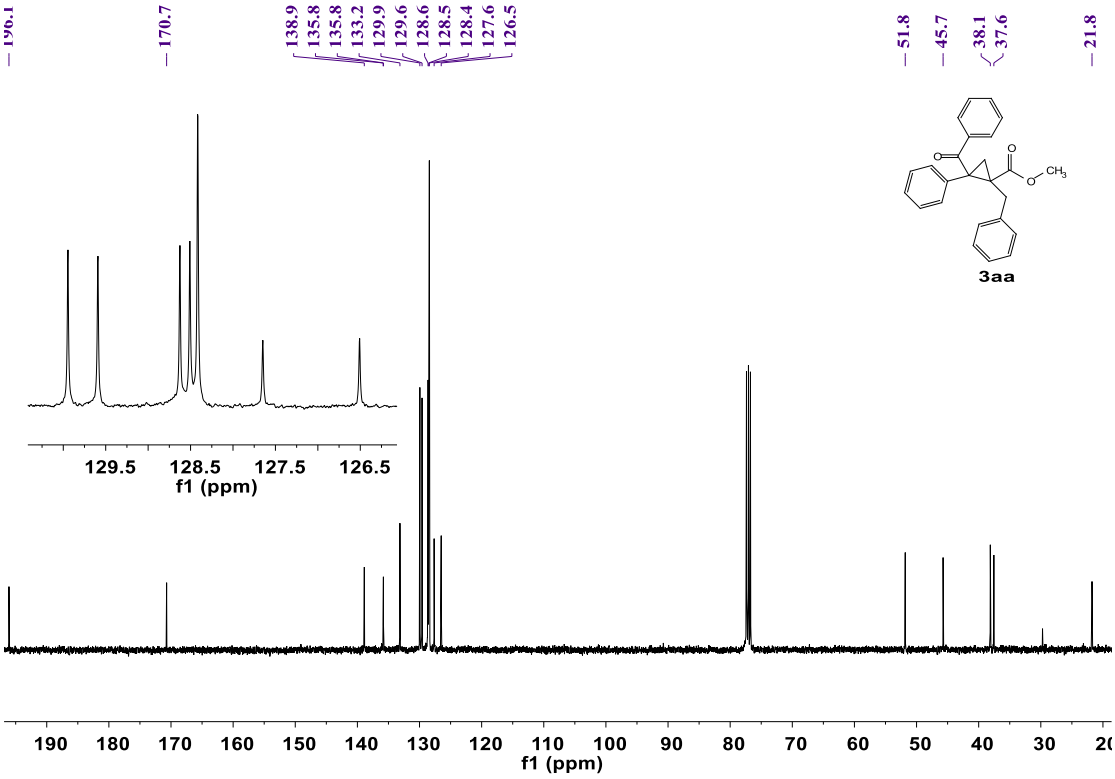
[1]. (a) V. Gembus, J.-J. Bonnet, F. Janin, P. Bohn, V. Levacher, J.-F. Brière, *Org. Biomol. Chem*. 2010, **8**, 3287.

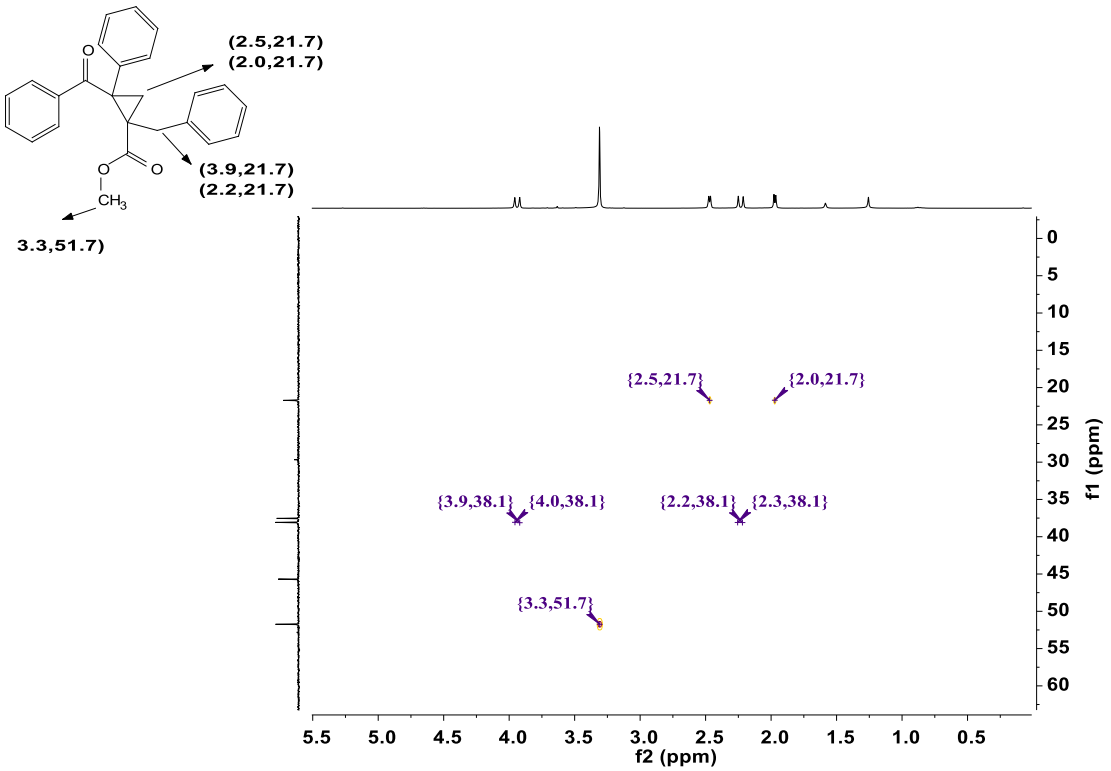
[2]. (a) C. Peng, Y. Wang, J. Wang, *J. Am. Chem. Soc*. 2008, **130**, 1566. (b) L. Gao, B. C. Kang, G.-S. Hwang, D. H. Ryu, *Angew. Chem. Int. Ed*. 2012, **51**, 8322. (c) W. Li, X. Liu, X. Y. Hao, Y. F. Cai, L. L. Lin, X. M. Feng, *Angew. Chem. Int. Ed*. 2012, **51**, 8644.

[3]. (a)Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin and X. M. Feng, *Synlett* 2005, **16**, 2445; (b) X. H. Liu, L. L. Lin and X. M. Feng, *Acc. Chem. Res.* 2011, **44**,574; (c) X. H. Liu, L. L. Lin and X. M. Feng, *Org. Chem. Front.* 2014, **1**, 298.

14. Copies of NMR spectra for substrates and products



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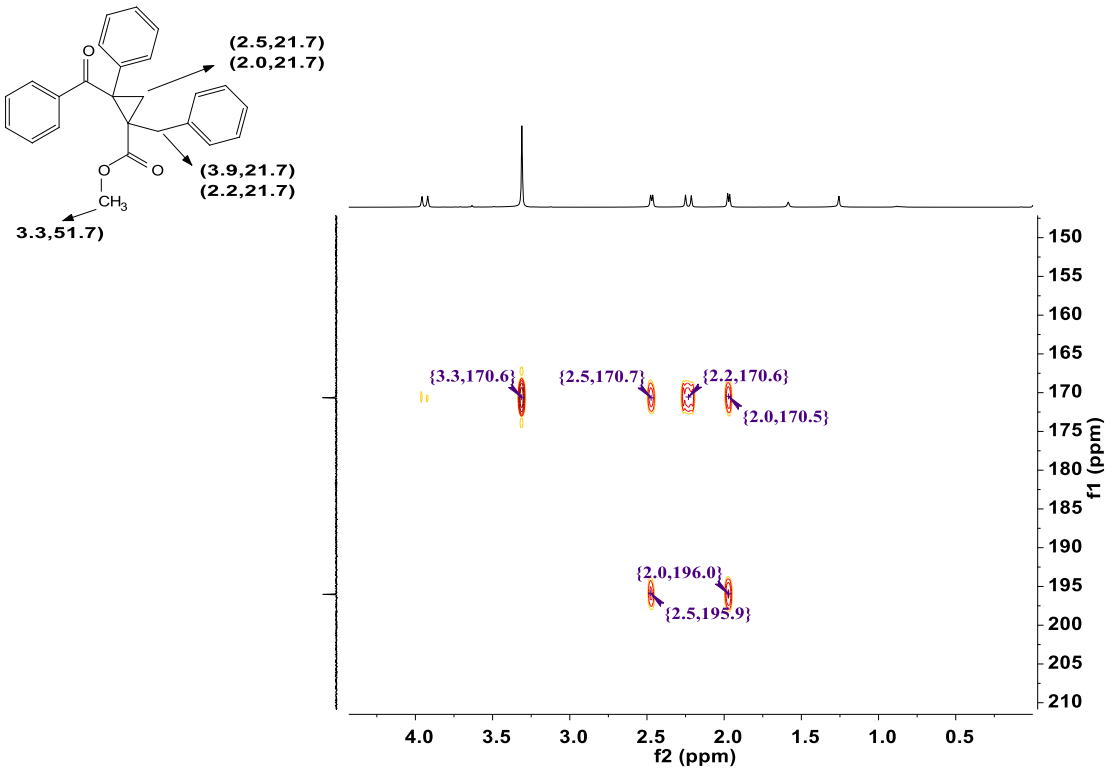
f2 (ppm)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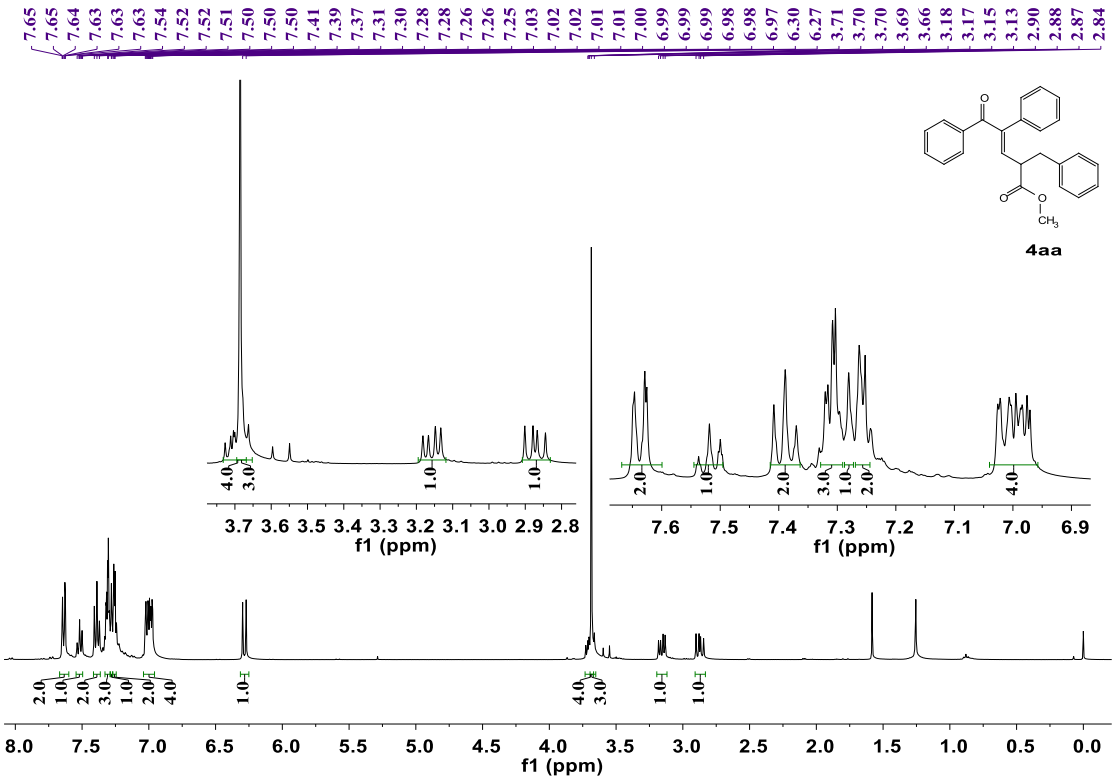
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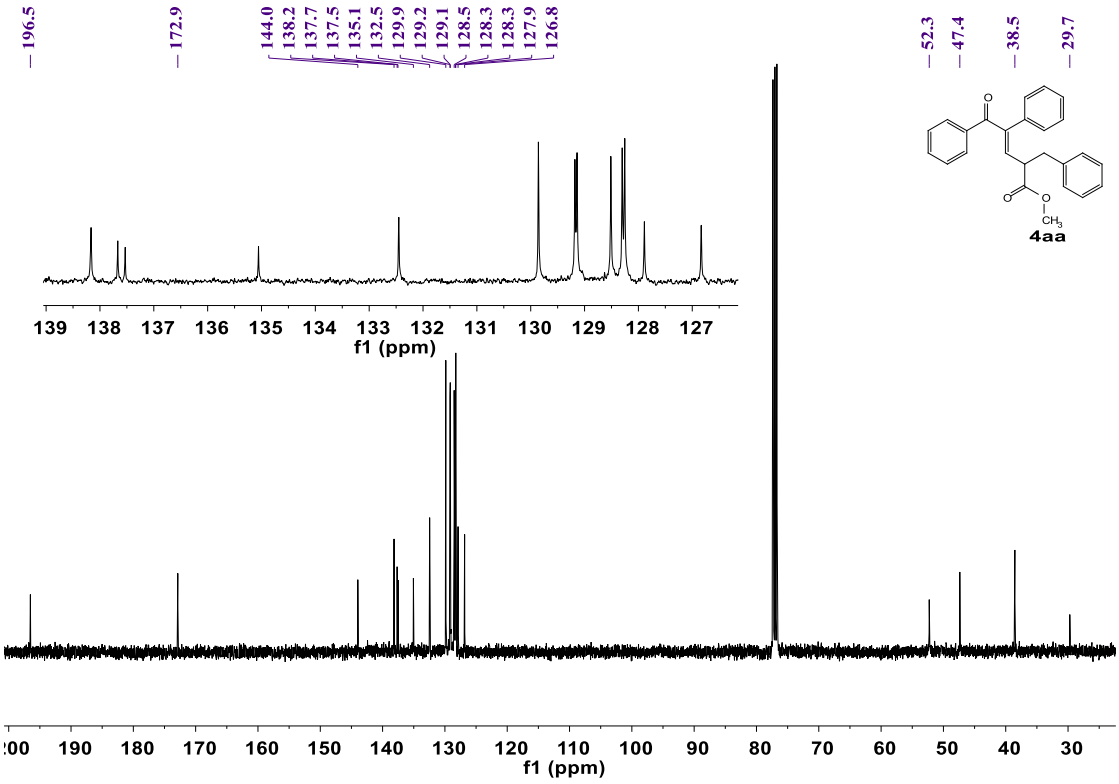
4aa
f1 (ppm)
f1 (ppm)
f1 (ppm)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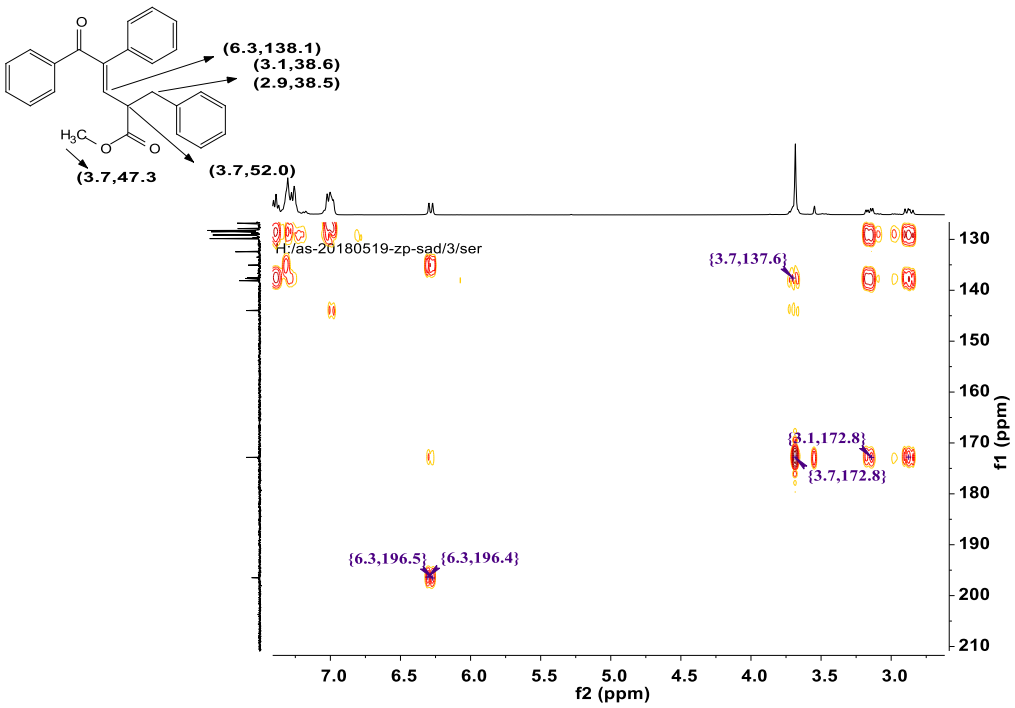
4aa
f1 (ppm)
f1 (ppm)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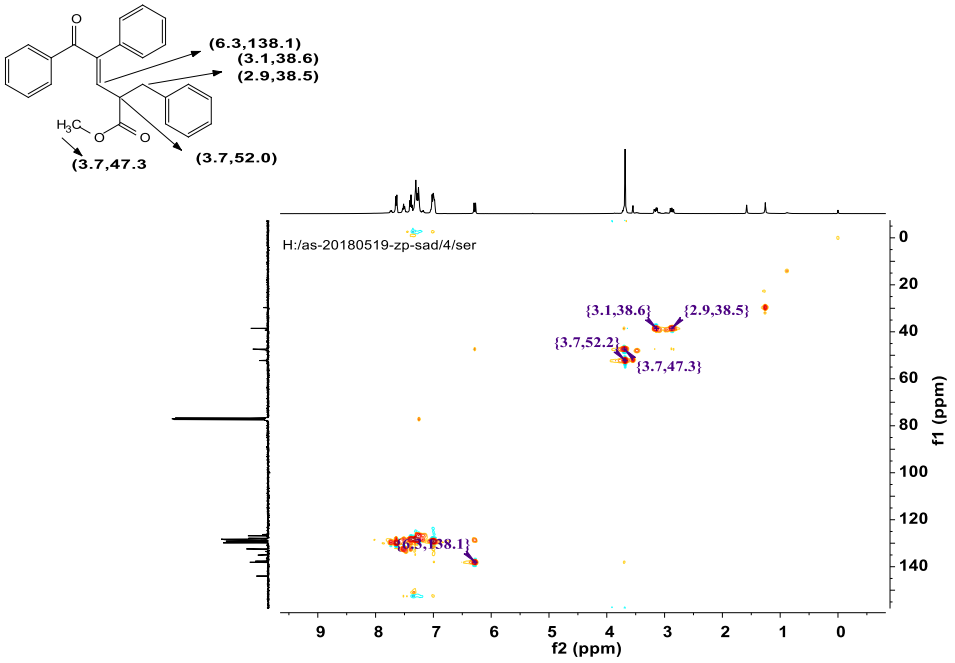
f1 (ppm)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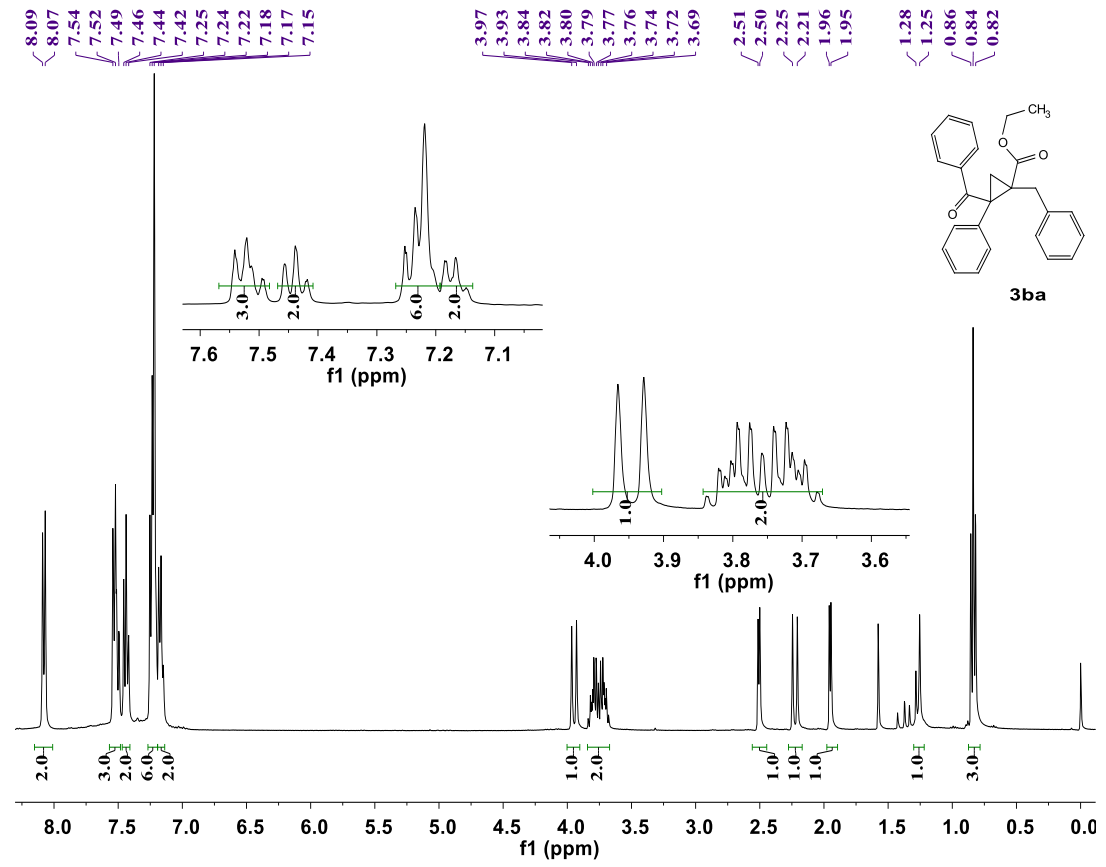
f1 (ppm)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1.95
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1.0
1.0
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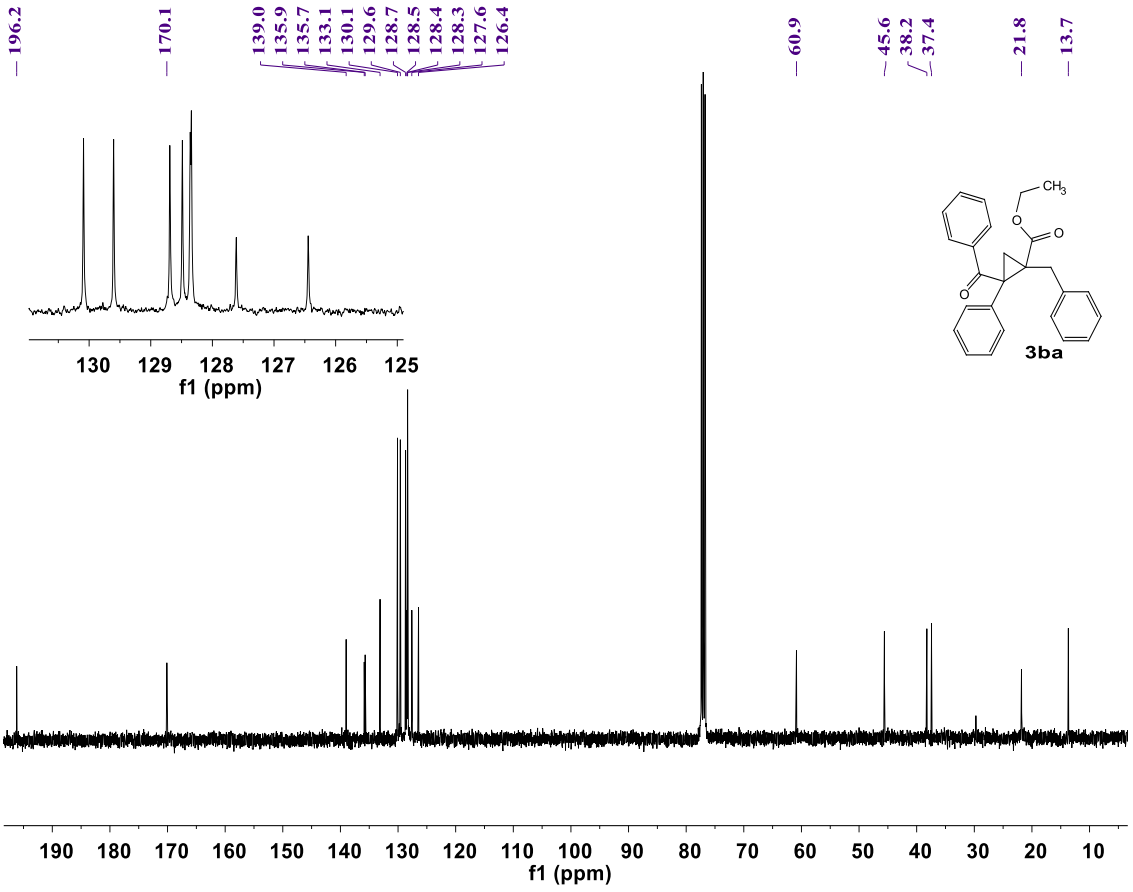
O
O
3ba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37.4
21.8
13.7
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f1 (ppm)
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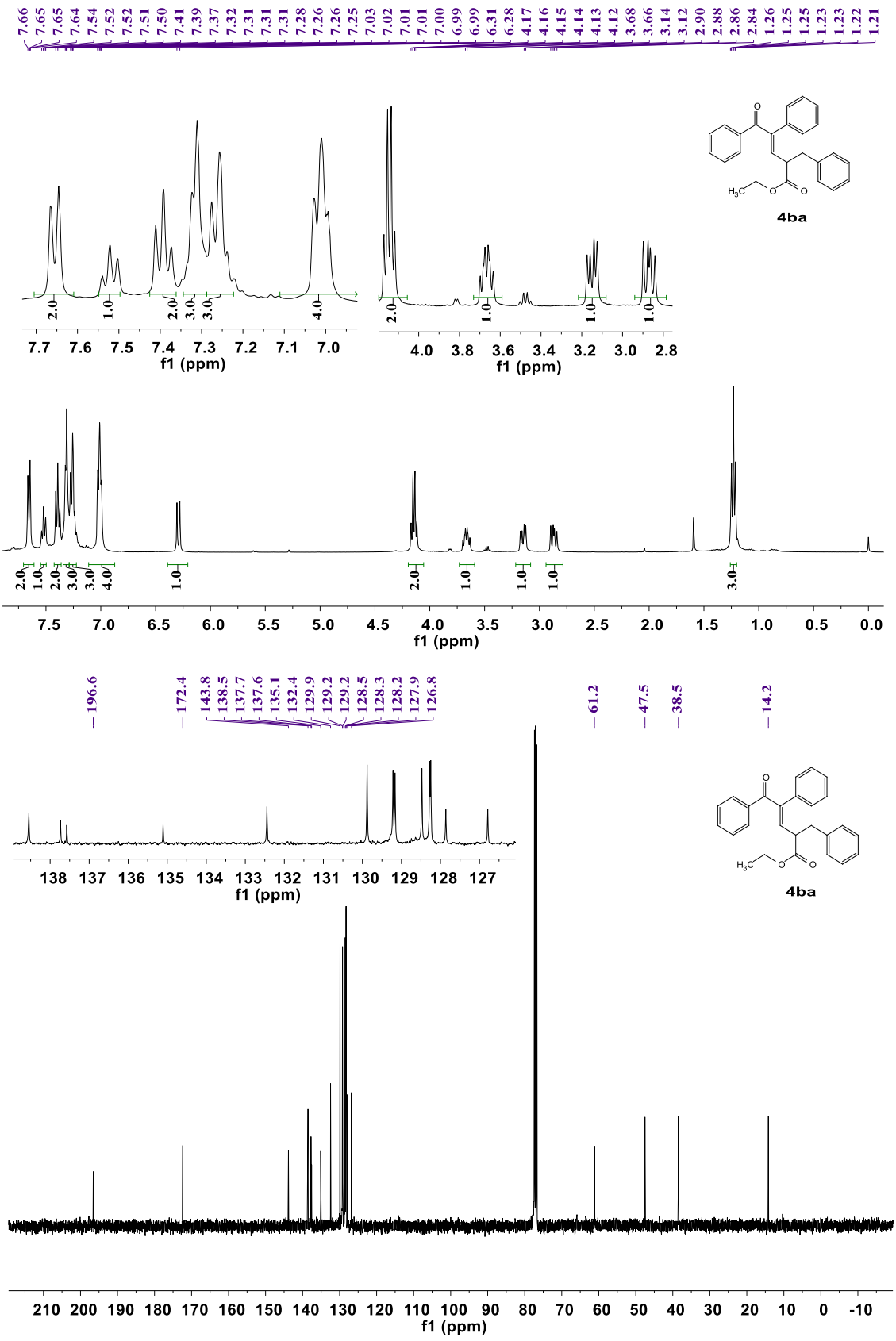
O
O
3ba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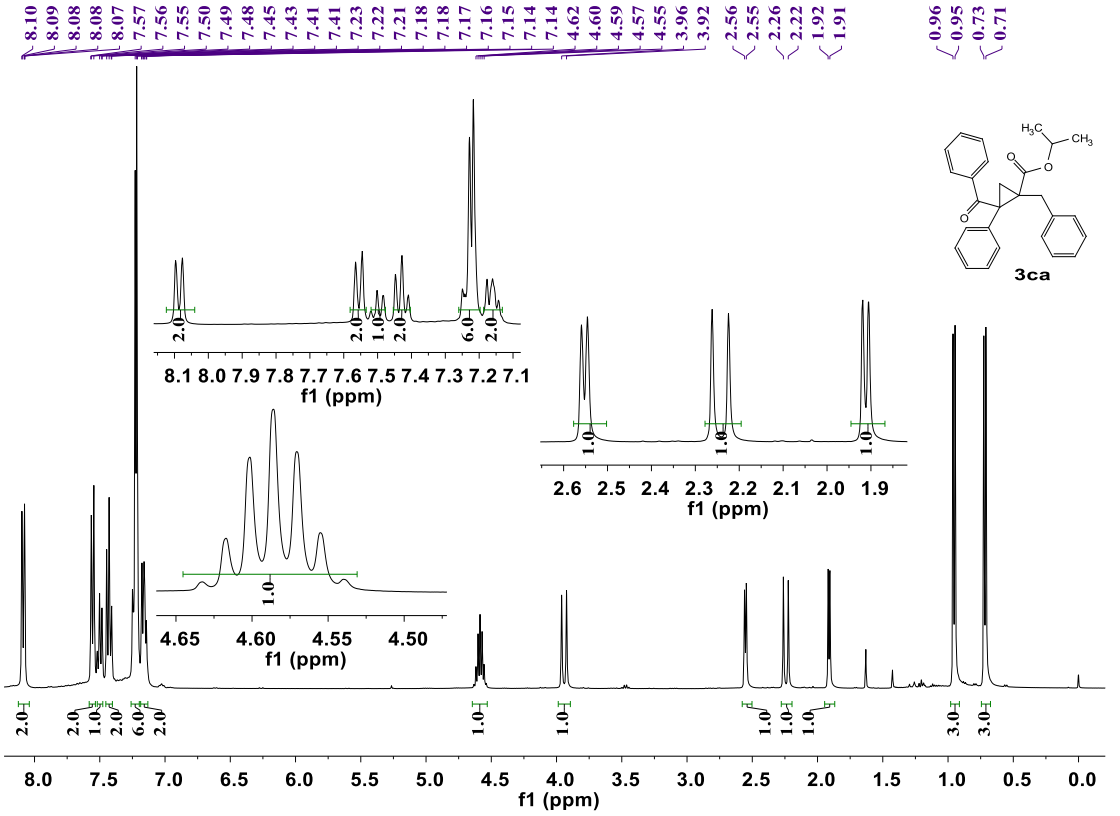
f1 (ppm)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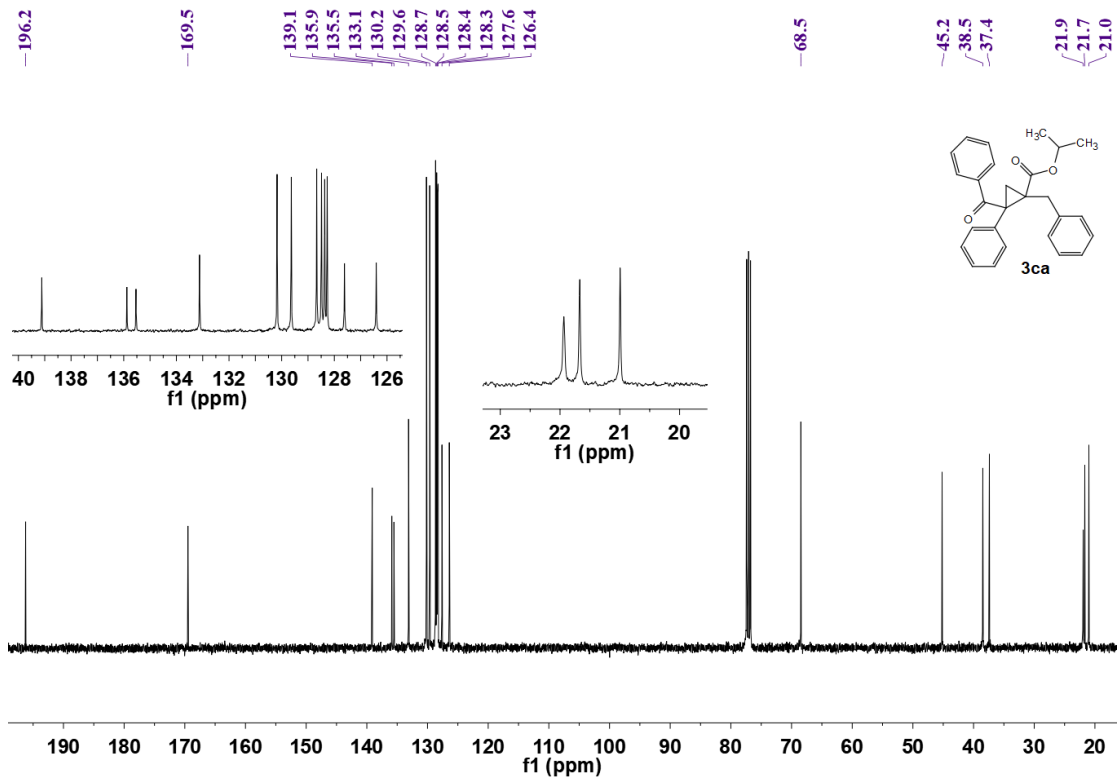
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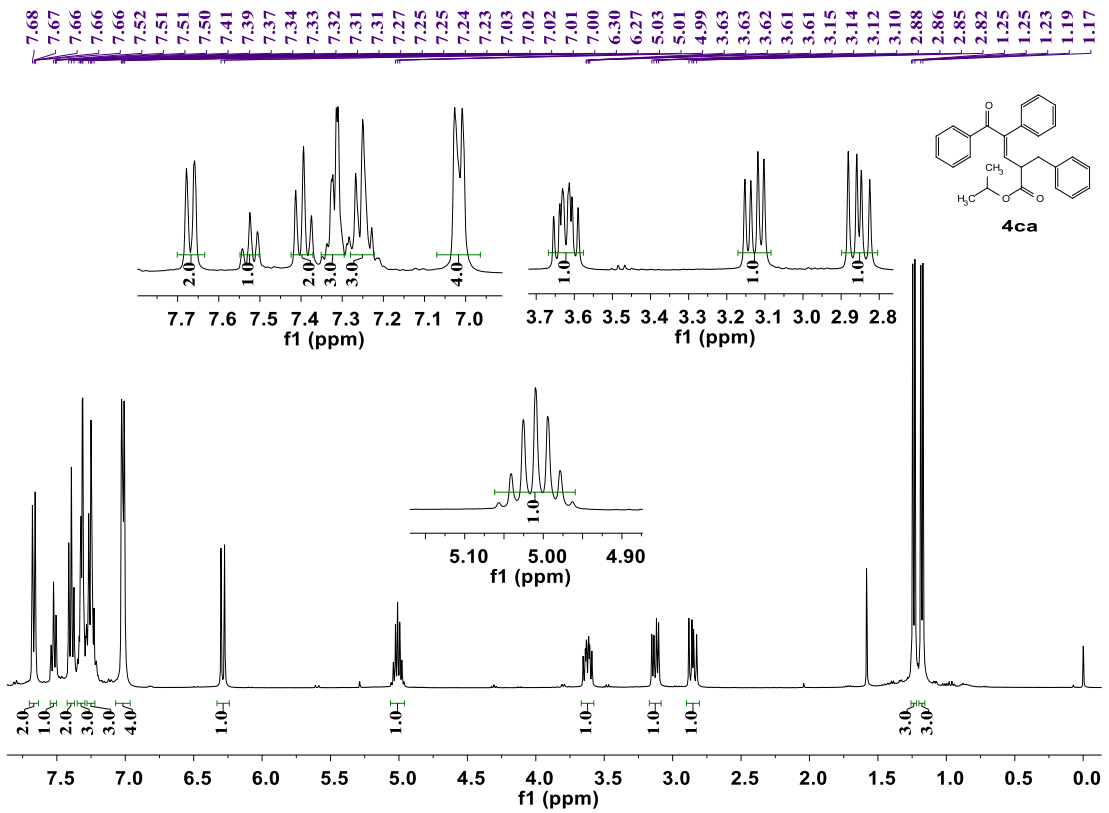
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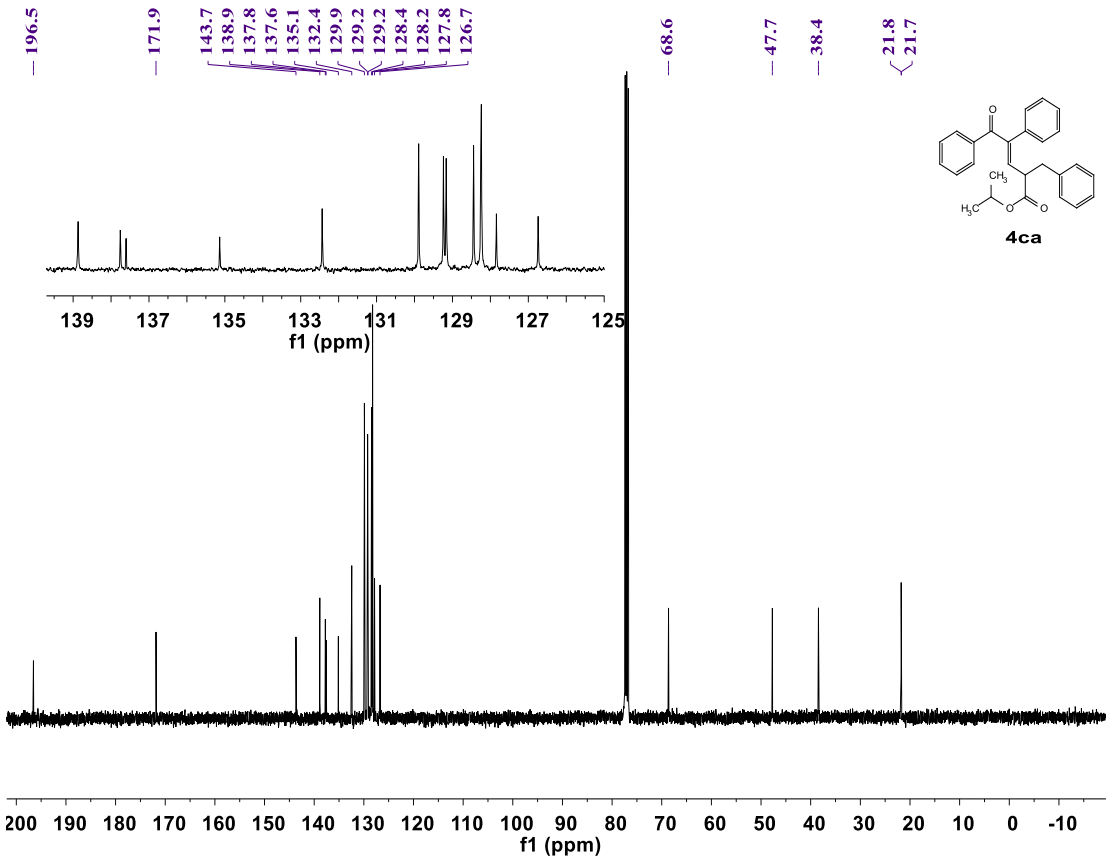
f1 (ppm)
f1 (ppm)
f1 (ppm)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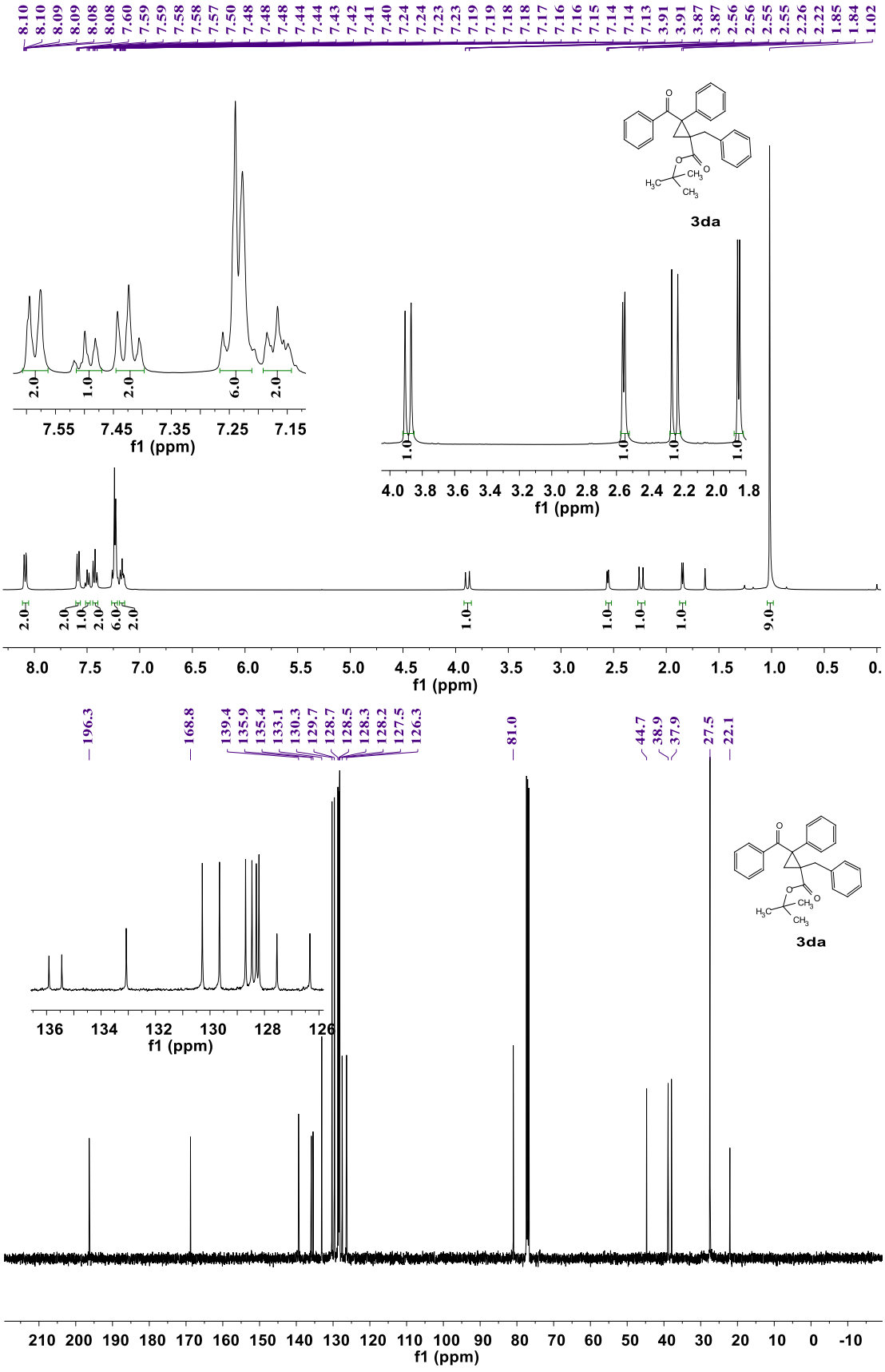
f1 (ppm)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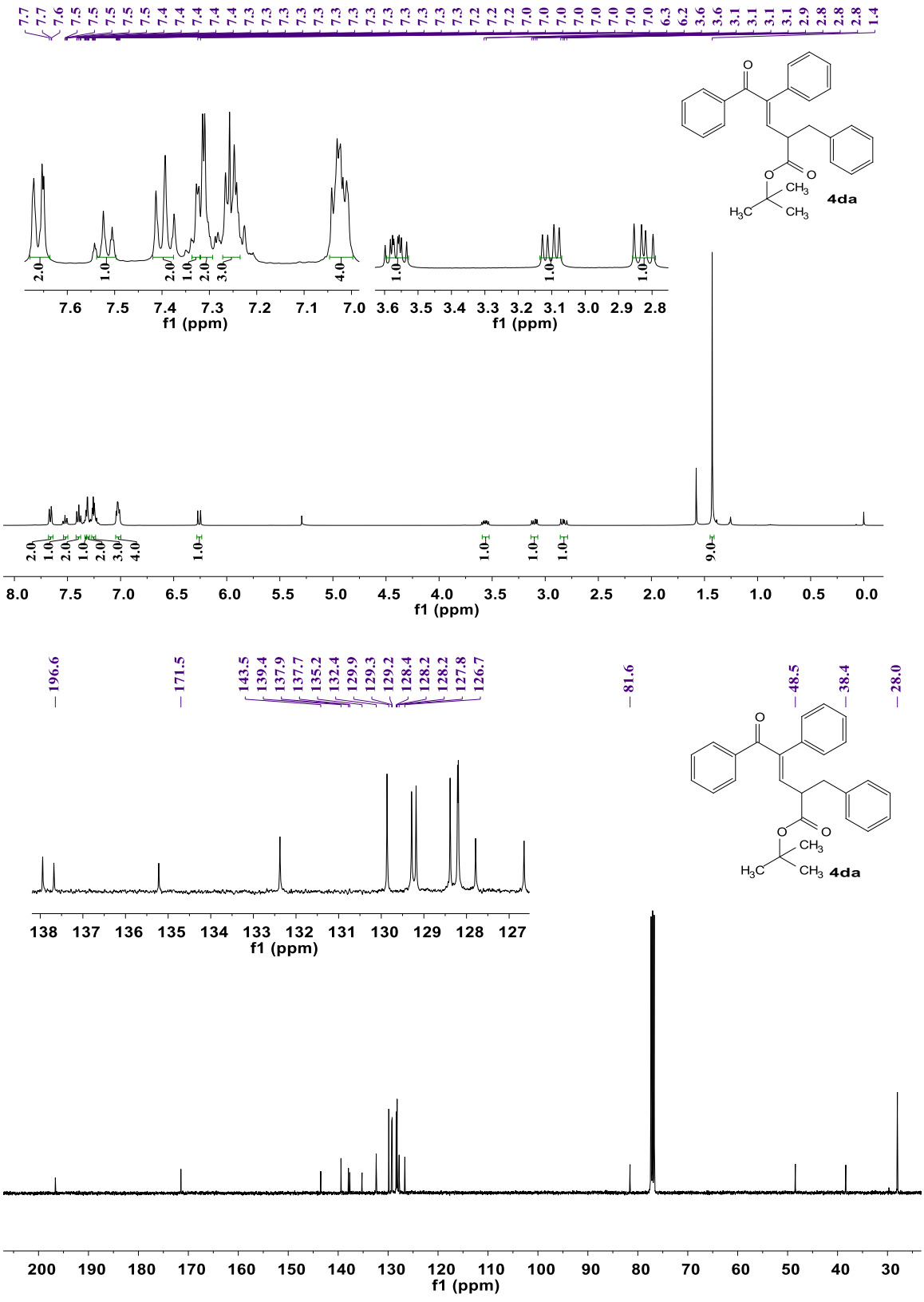
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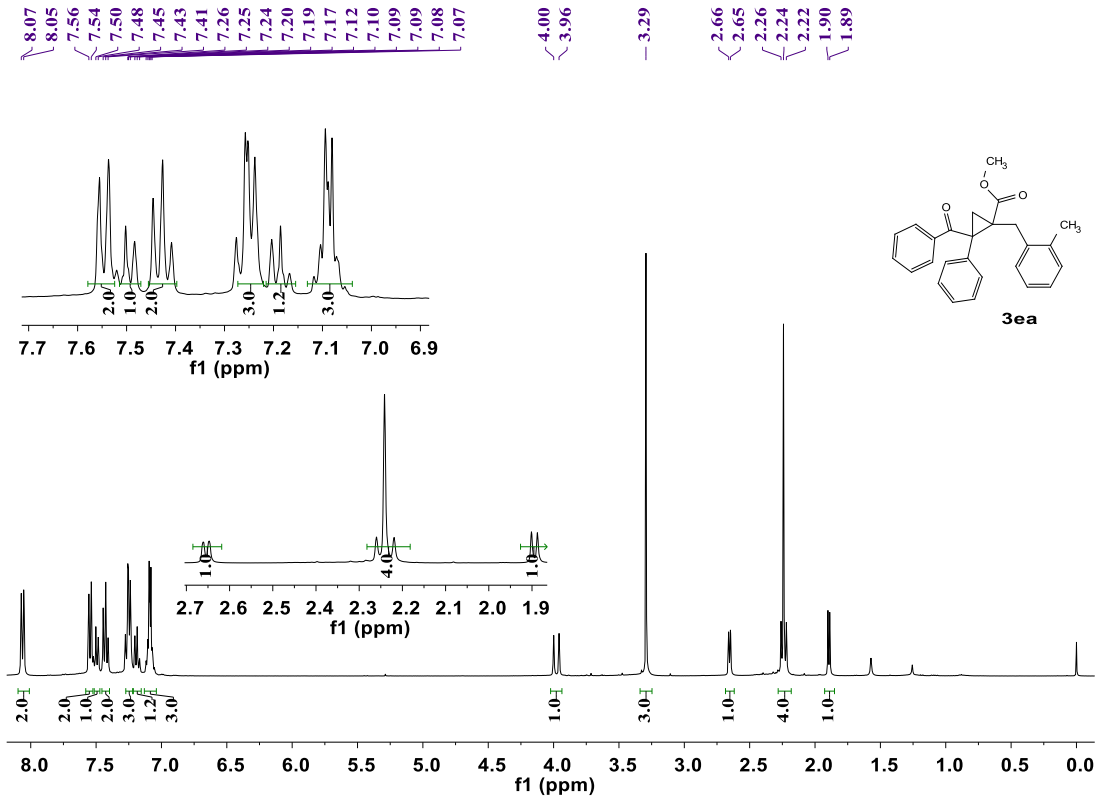
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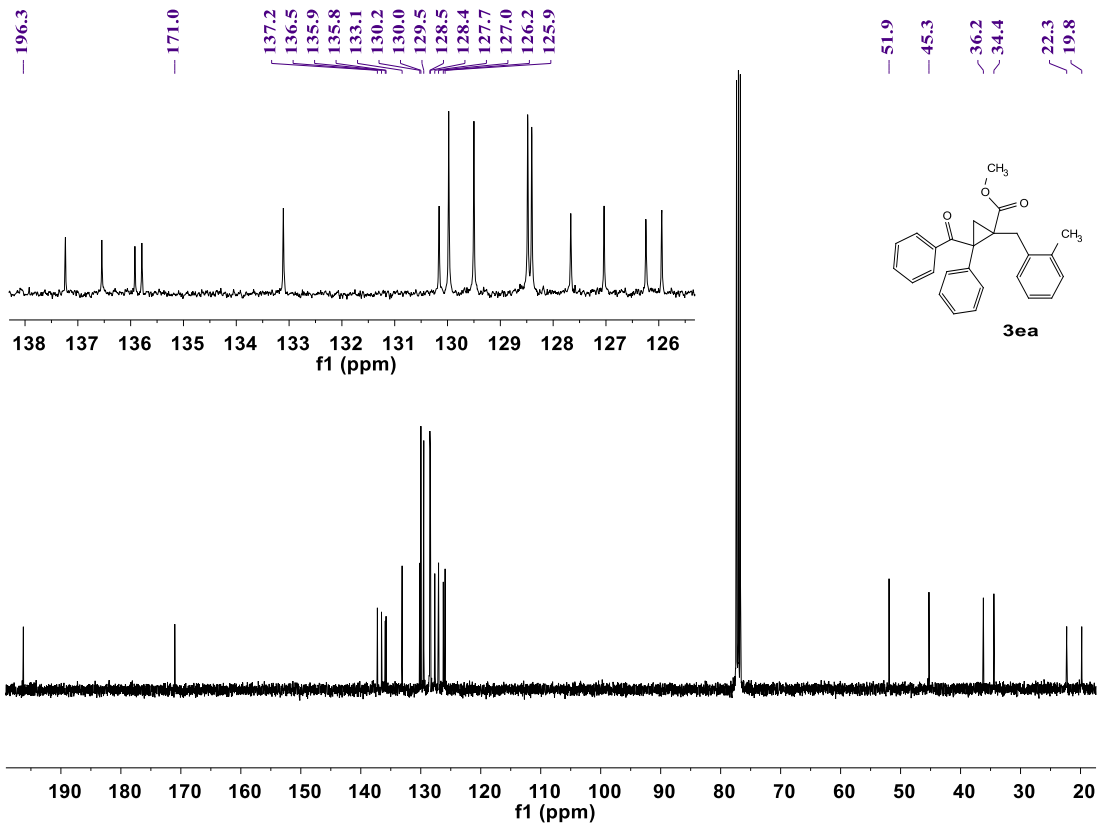
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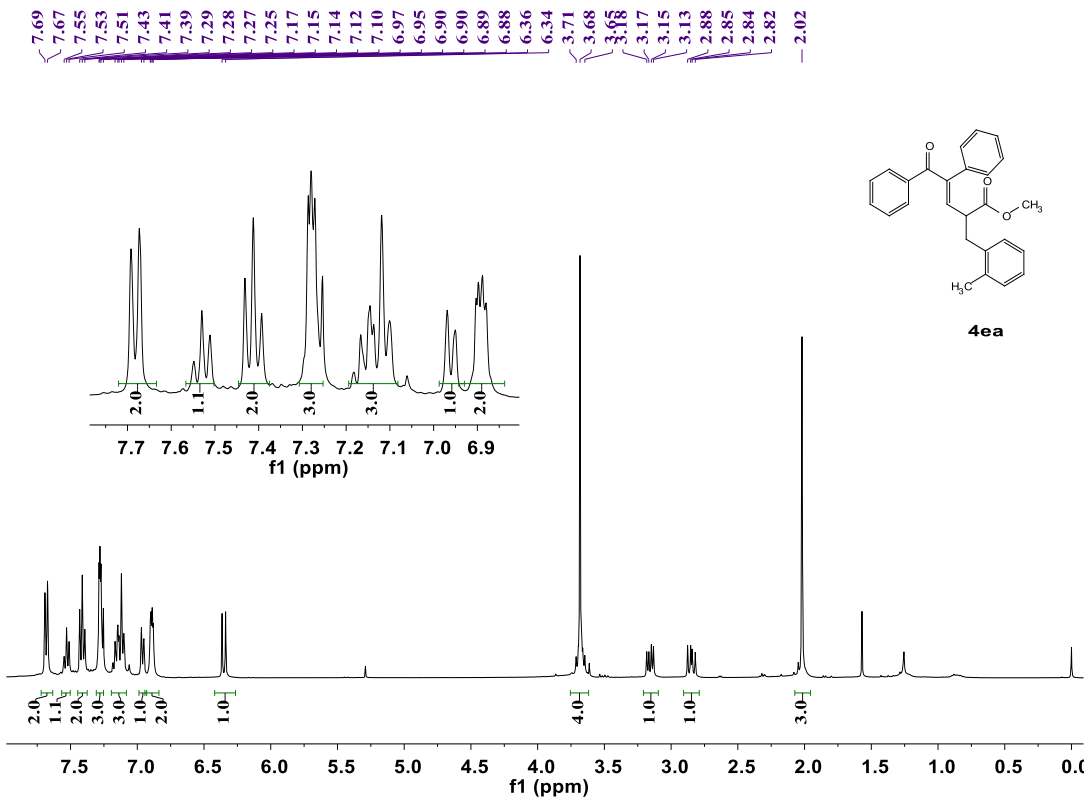
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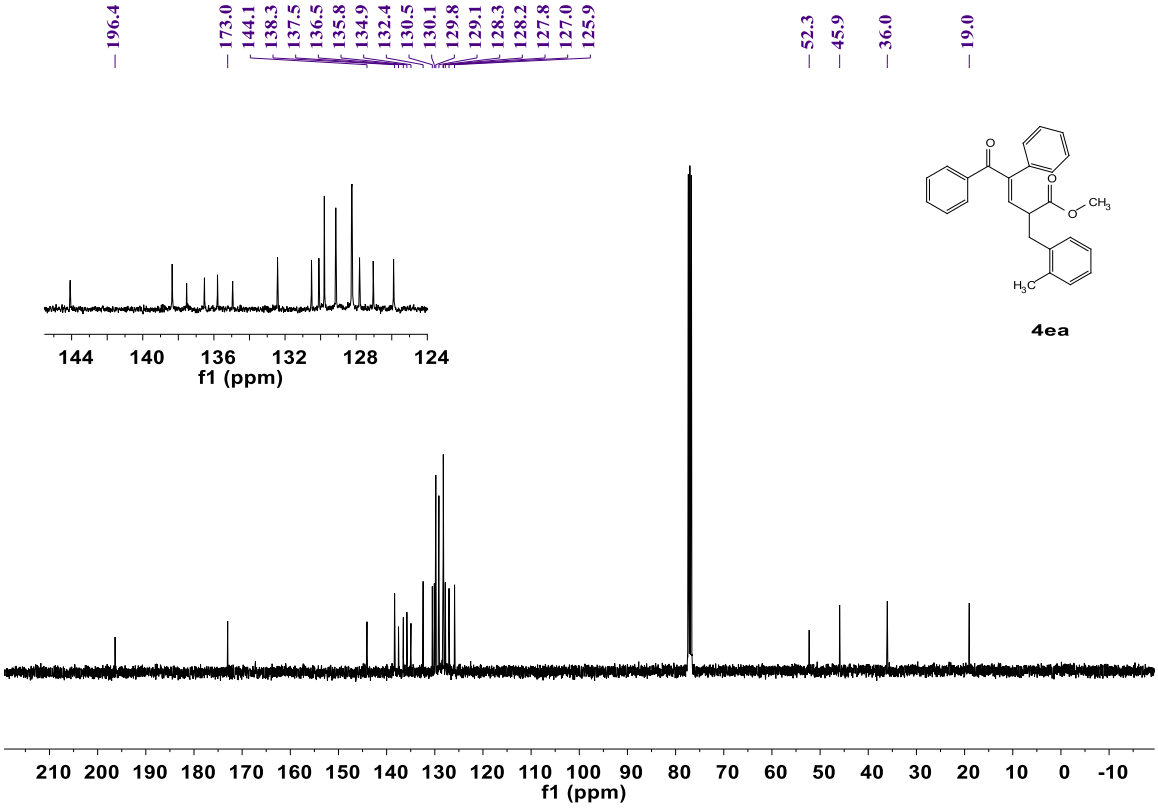
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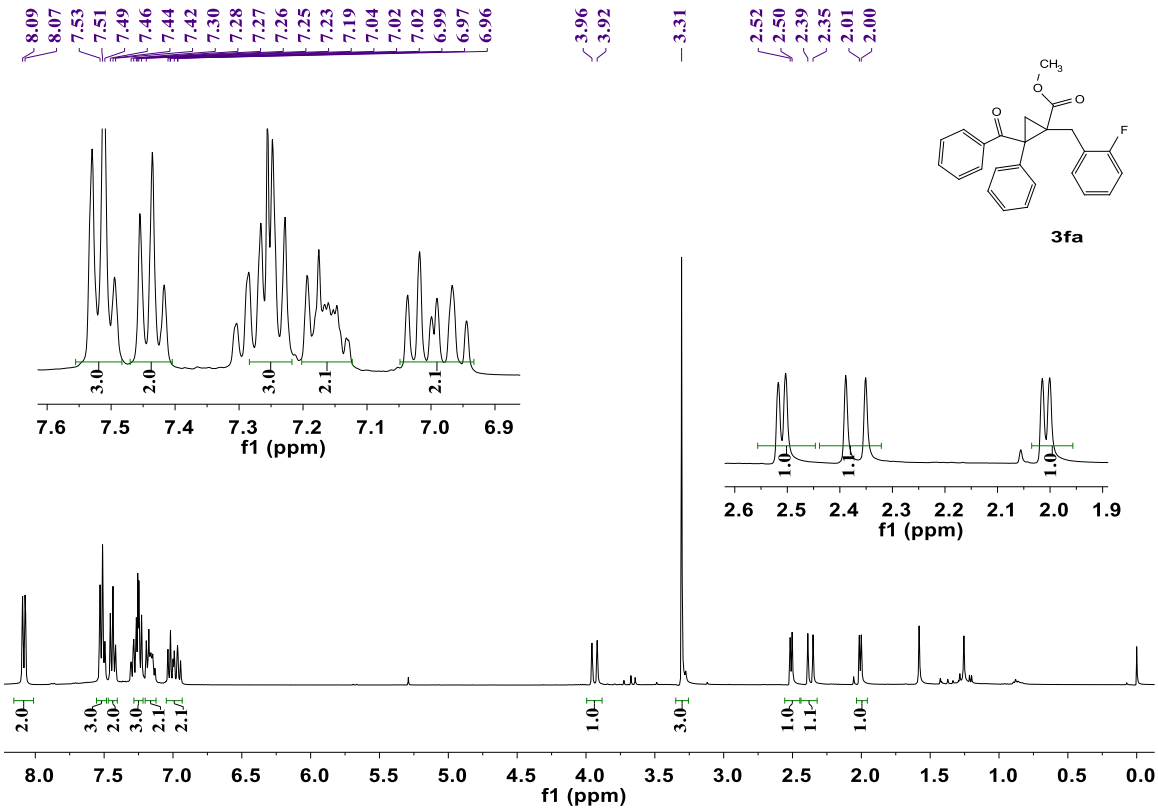
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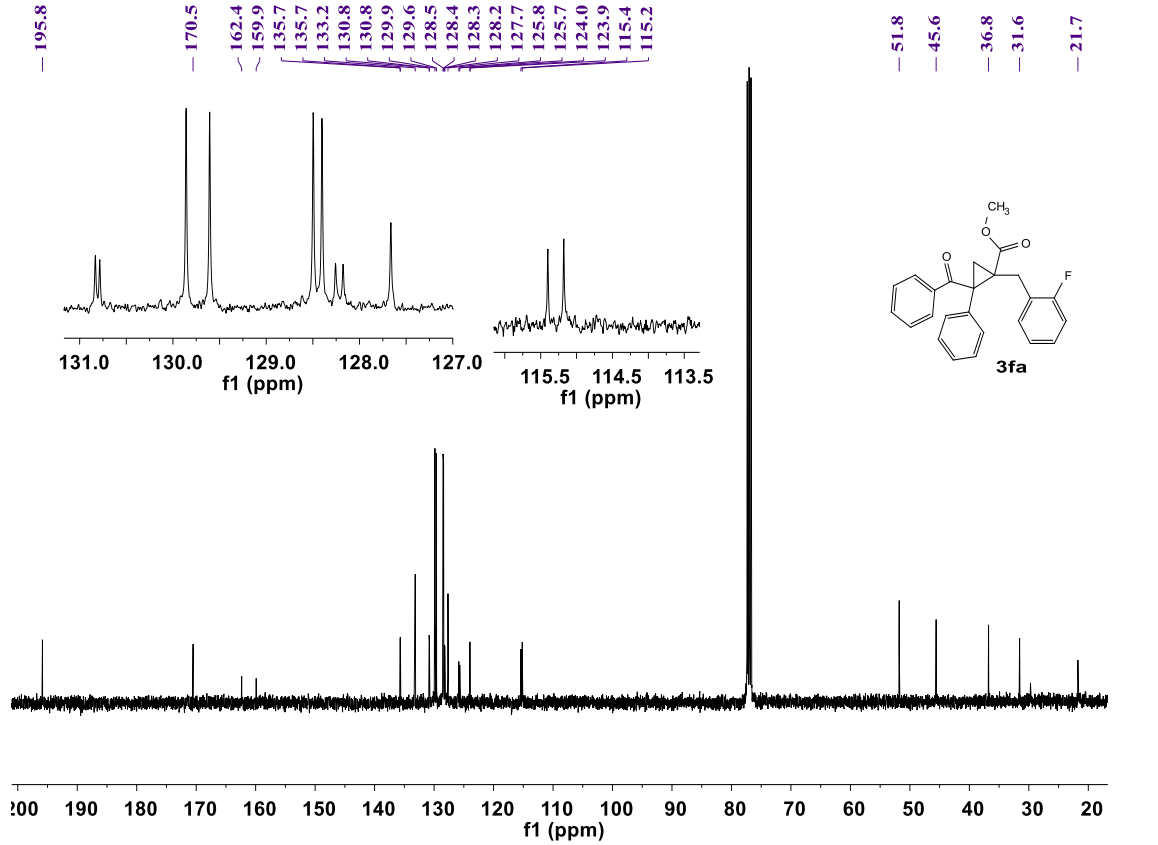
F
3fa
f1 (ppm)
f1 (ppm)
f1 (ppm)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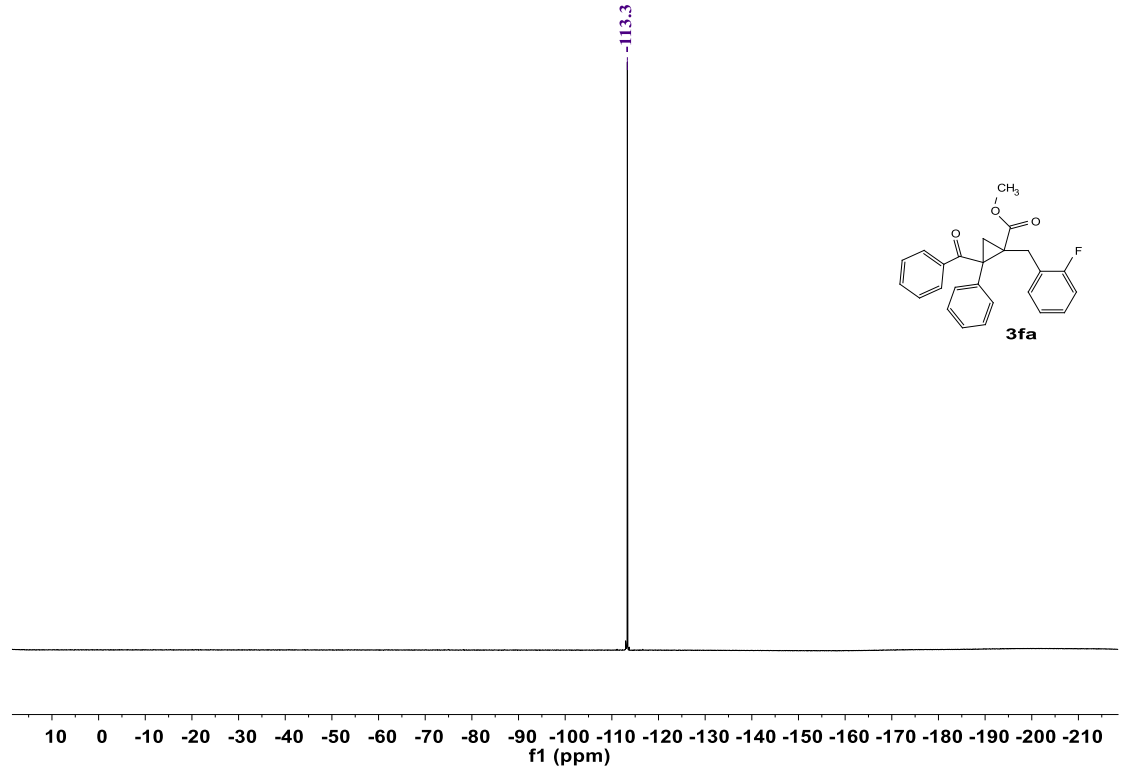
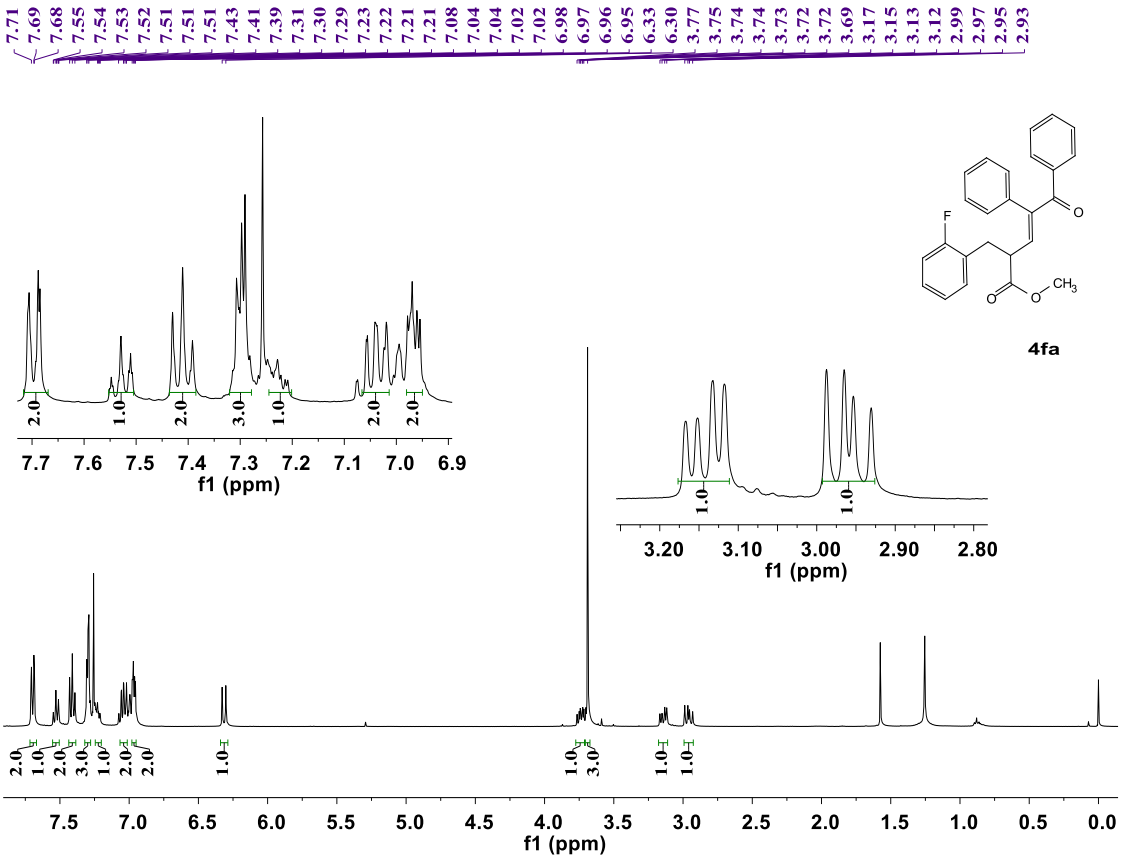
170.5
162.4
159.9
135.7
135.7
133.2
130.8
130.8
129.9
129.6
128.5
128.4
128.3
128.2
127.7
125.8
125.7
124.0
123.9
115.4
115.2
51.8
45.6
36.8
31.6
21.7
CH3
O
O
O
F
3fa
f1 (ppm)
f1 (ppm)
f1 (ppm)


-113.3
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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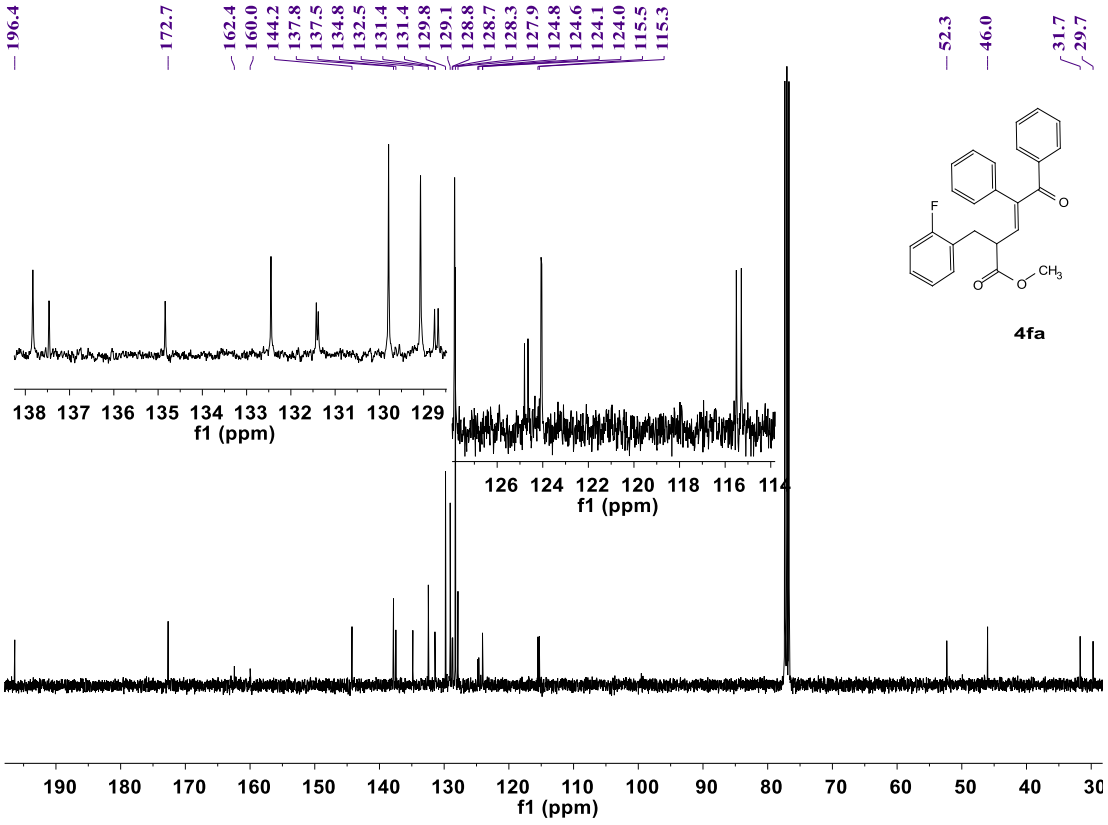
2.0 1.0 2.0 3.0 1.0 2.0 2.0
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.0 1.0
3.20 3.10 3.00 2.90 2.80
f1 (ppm)
2.0 1.0 2.0 3.0 1.0 2.0 2.0 1.0 1.0 3.0 1.0 1.0
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

4fa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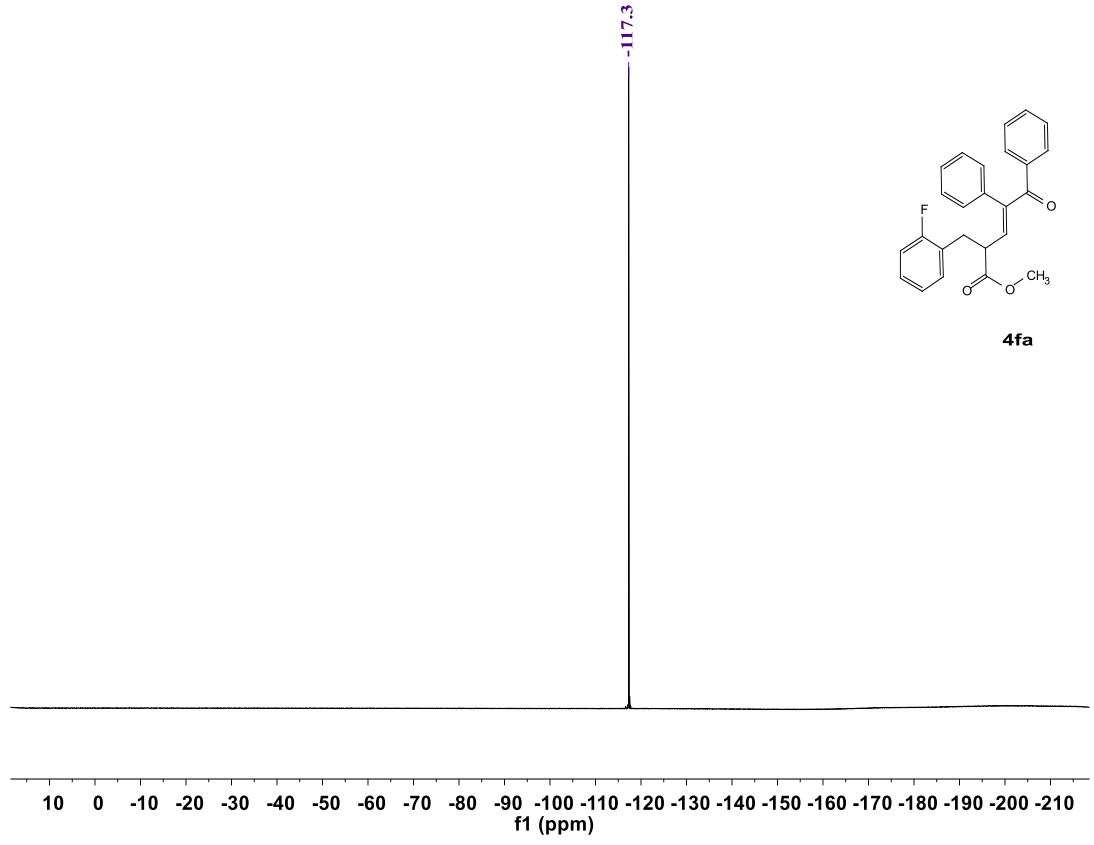
137.8
137.5
134.8
132.5
131.4
131.4
129.8
129.1
128.8
128.7
128.3
127.9
124.8
124.6
124.1
124.0
115.5
115.3
52.3
46.0
31.7
29.7
F
O
O
O
CH3
4fa
138 137 136 135 134 133 132 131 130 129
f1 (ppm)
126 124 122 120 118 116 114
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
f1 (ppm)


-117.3
F
O
O
O
CH3
4fa
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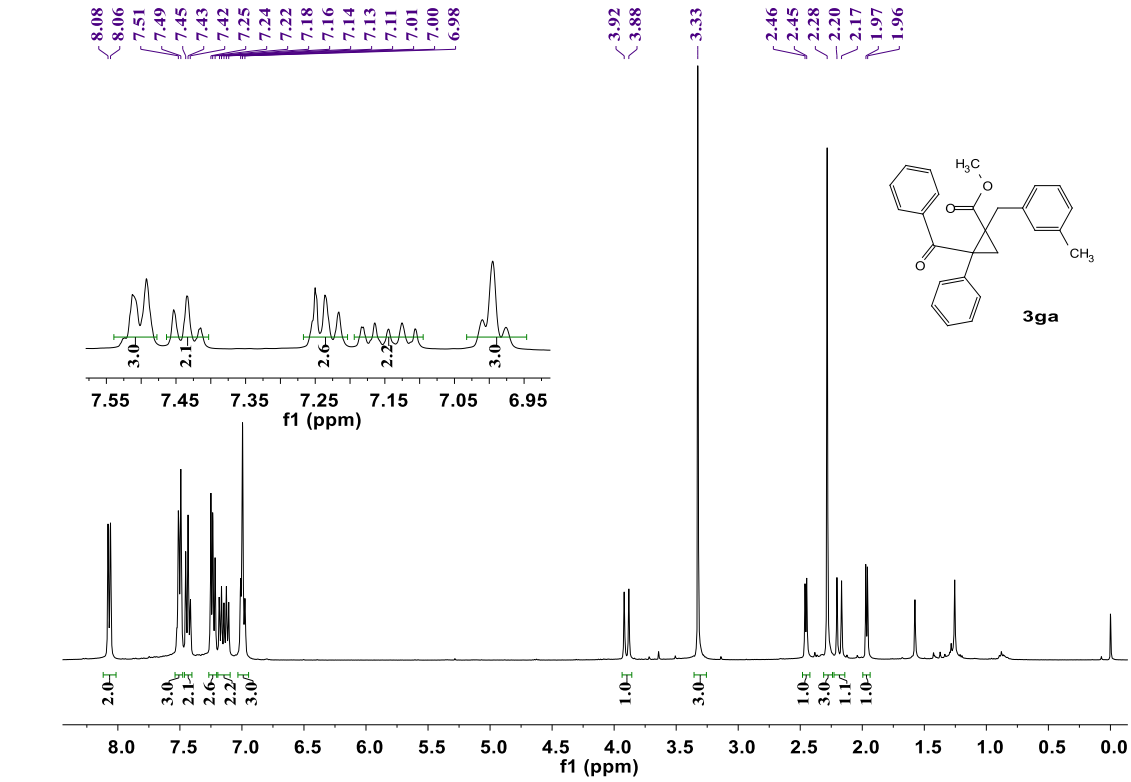
f1 (ppm)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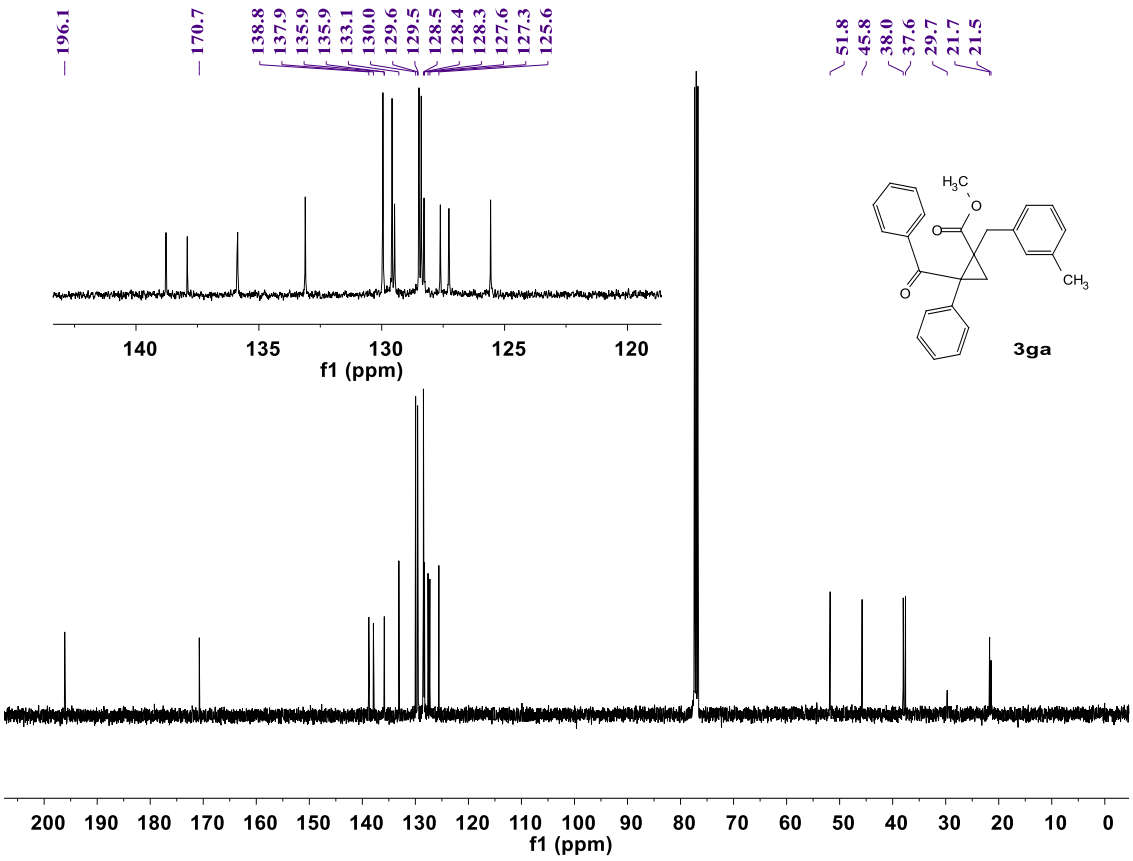
8.06
7.51
7.49
7.45
7.43
7.42
7.25
7.24
7.22
7.18
7.16
7.14
7.13
7.11
7.01
7.00
6.98
3.92
3.88
3.33
2.46
2.45
2.28
2.20
2.17
1.97
1.96
3.0
2.1
2.6
2.2
3.0
7.55 7.45 7.35 7.25 7.15 7.05 6.95
f1 (ppm)
2.0
3.0
2.1
2.6
2.2
3.0
1.0
3.0
1.0
3.0
1.1
1.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
H3C
O
O
O
CH3
3ga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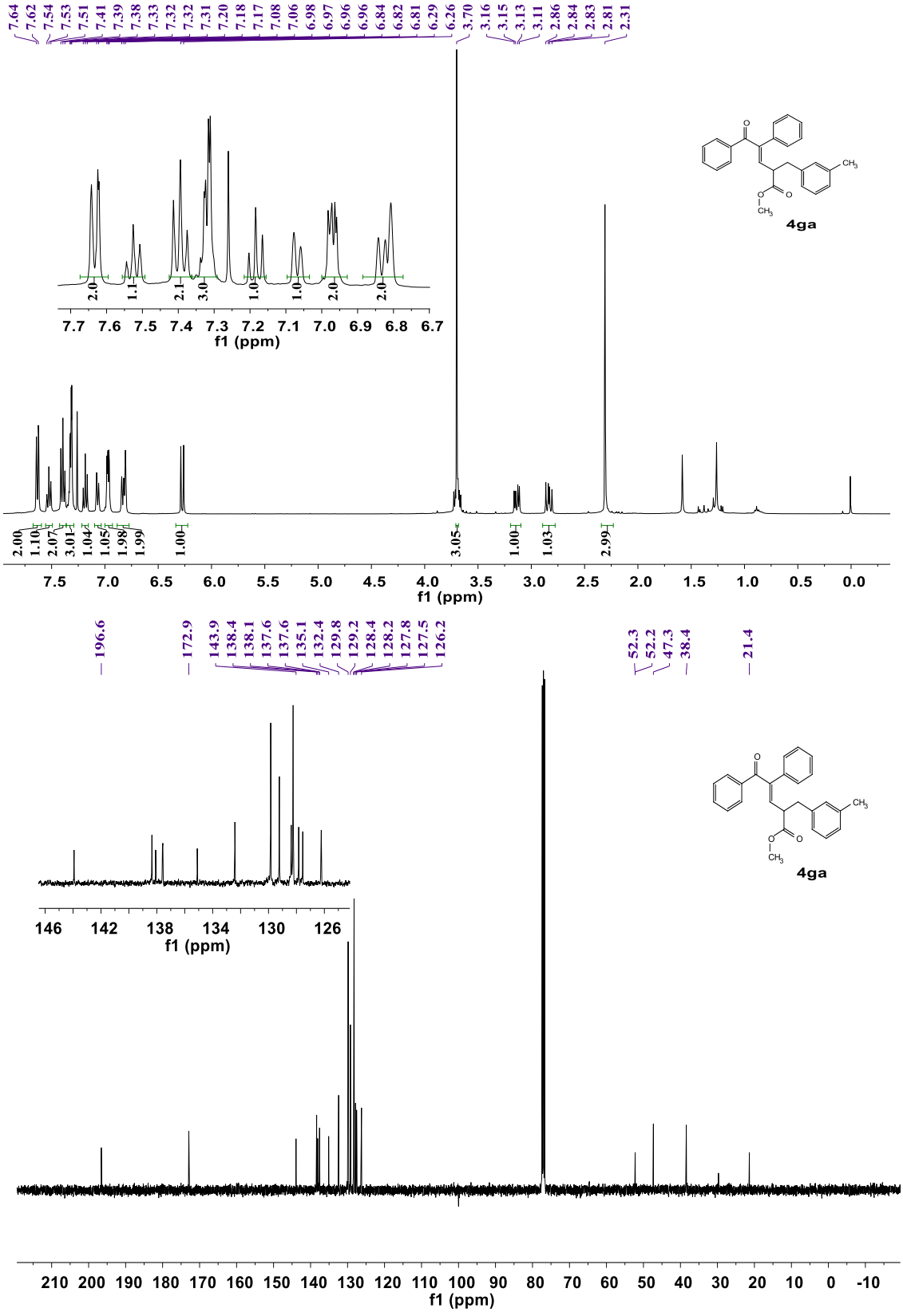
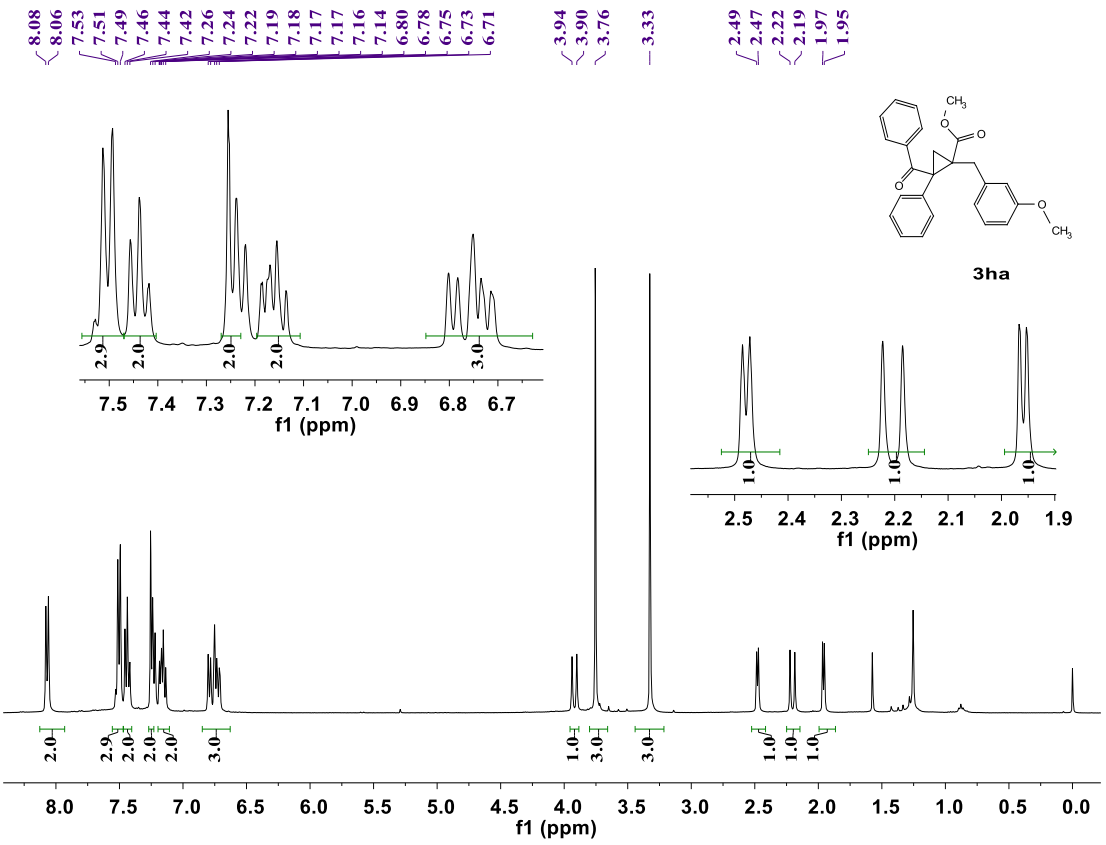
170.7
138.8
137.9
135.9
135.9
133.1
130.0
129.6
129.5
128.5
128.4
128.3
127.6
127.3
125.6
51.8
45.8
38.0
37.6
29.7
21.7
21.5
140 135 130 125 120
f1 (ppm)
H3C
O
O
O
CH3
3ga
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.64 7.62 7.54 7.53 7.51 7.41 7.39 7.38 7.33 7.32 7.32 7.31 7.20 7.18 7.17 7.08 7.06 6.98 6.97 6.96 6.96 6.84 6.82 6.81 6.29 6.26 3.70 3.16 3.15 3.13 3.11 2.86 2.84 2.83 2.81 2.31
2.00 1.10 2.07 3.01 1.04 1.05 1.98 1.99 1.00 3.05 1.00 1.03 2.99
f1 (ppm)
4ga
196.6 172.9 143.9 138.4 138.1 137.6 137.6 135.1 132.4 129.8 129.2 128.4 128.2 127.8 127.5 126.2 52.3 52.2 47.3 38.4 21.4
f1 (ppm)
4ga
f1 (ppm)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8.06
7.53
7.51
7.49
7.46
7.44
7.42
7.26
7.24
7.22
7.19
7.18
7.17
7.17
7.16
7.14
6.80
6.78
6.75
6.73
6.71
3.94
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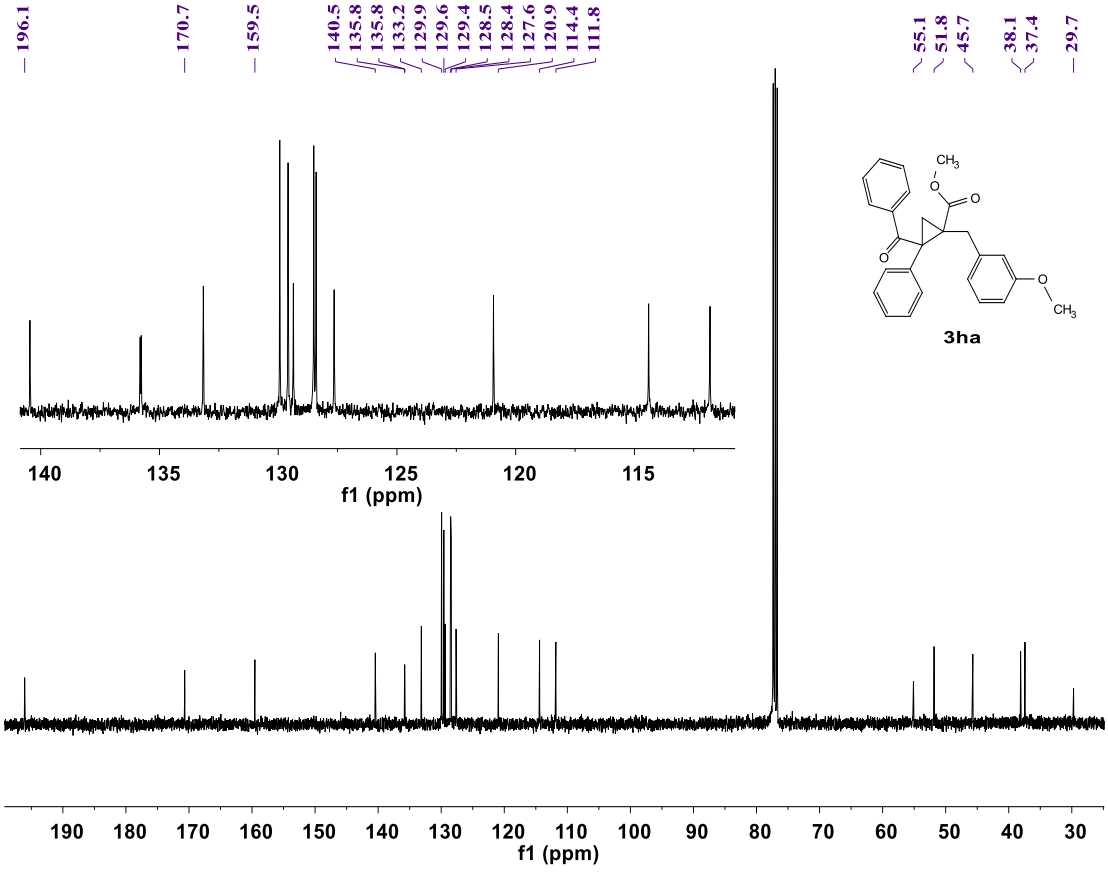
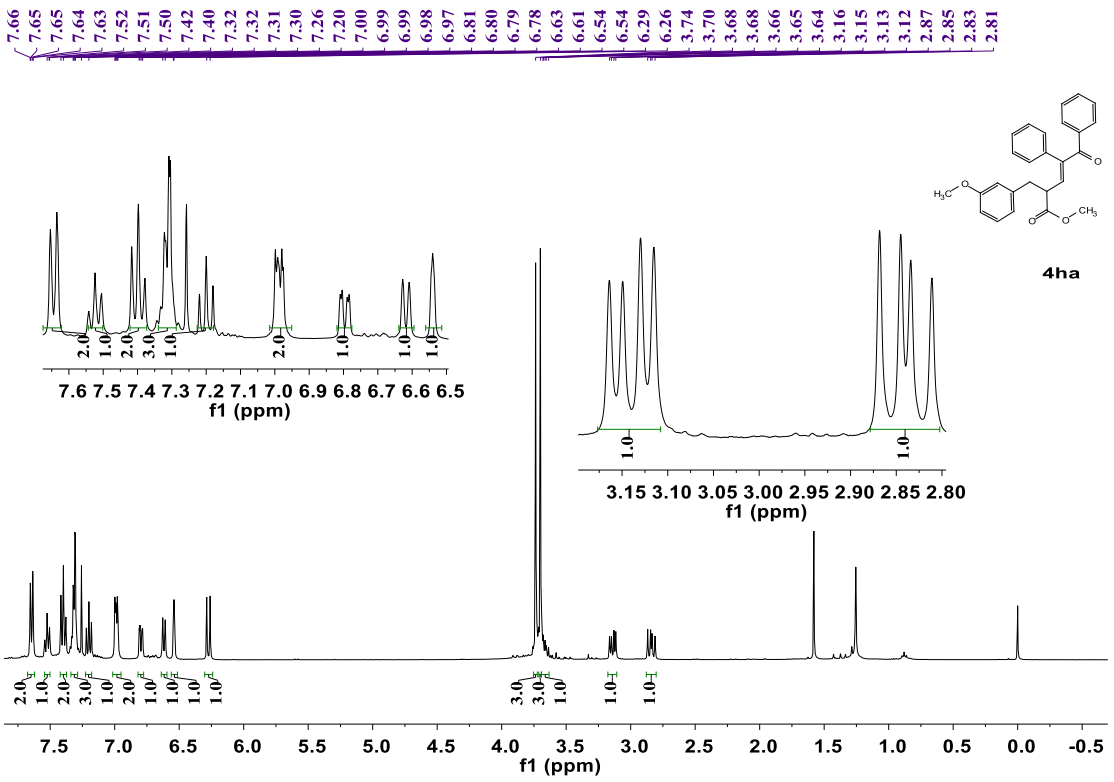
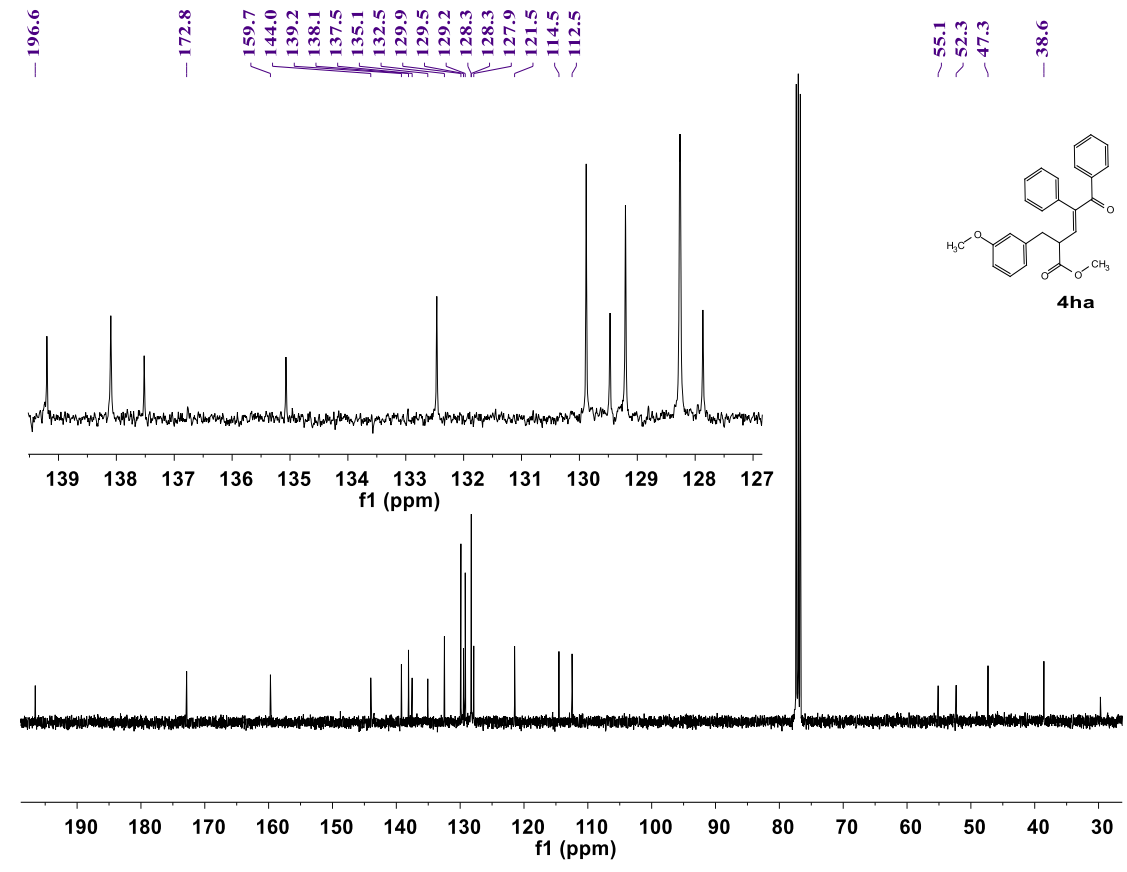
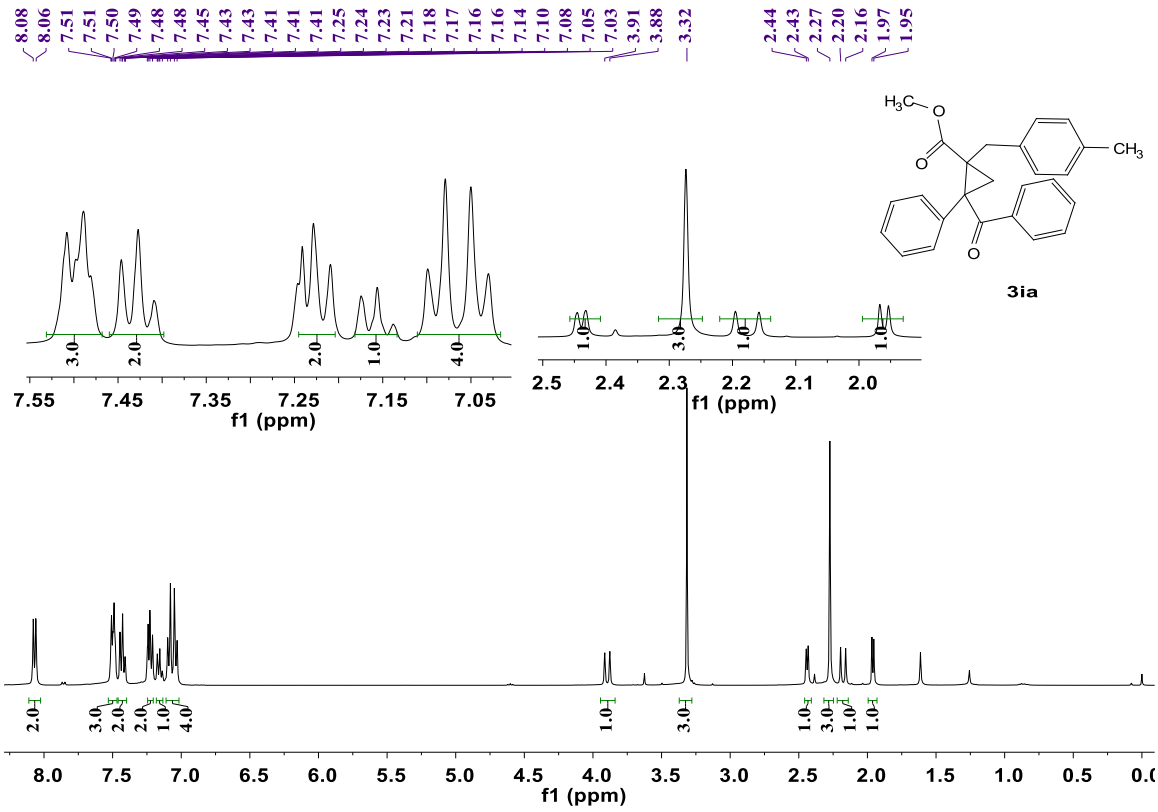
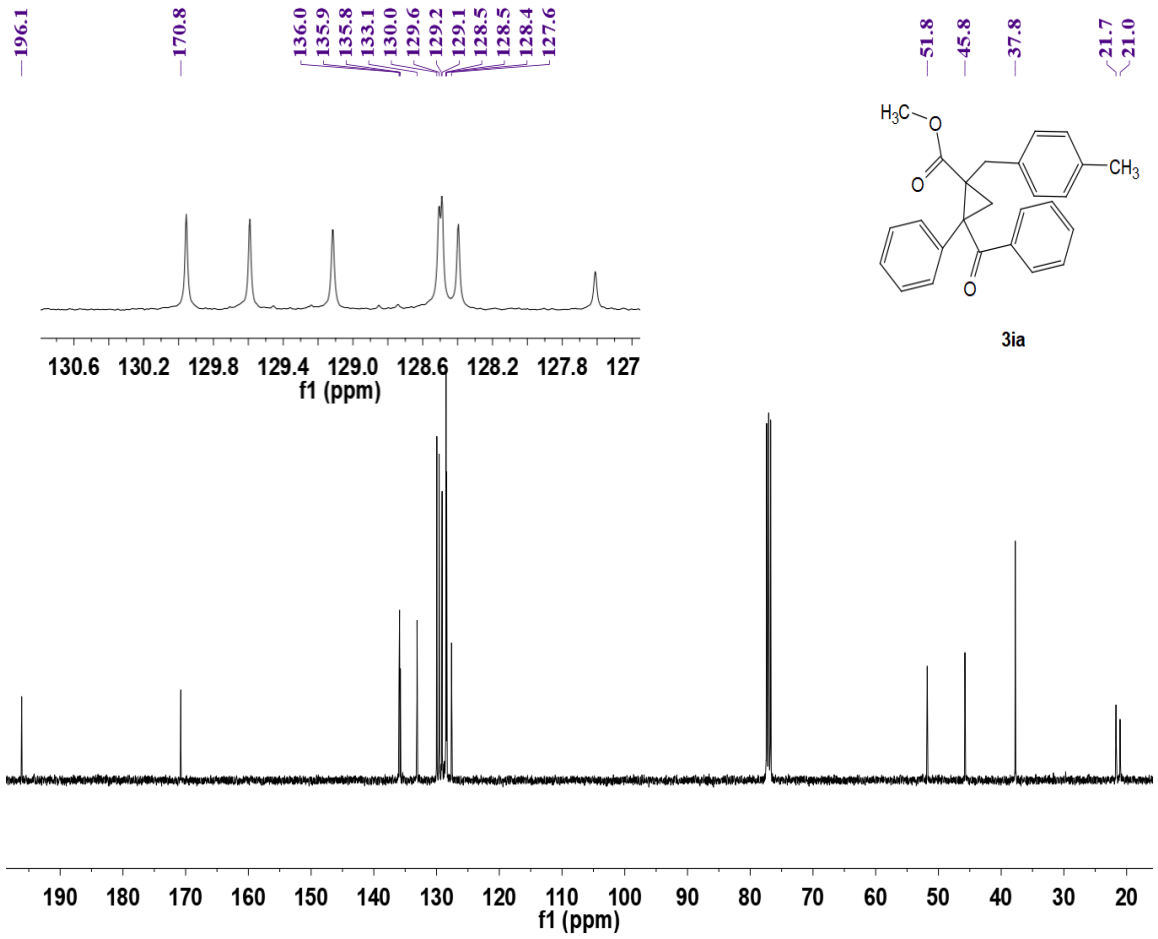
3.33
2.49
2.47
2.22
2.19
1.97
1.95
3ha
f1 (ppm)

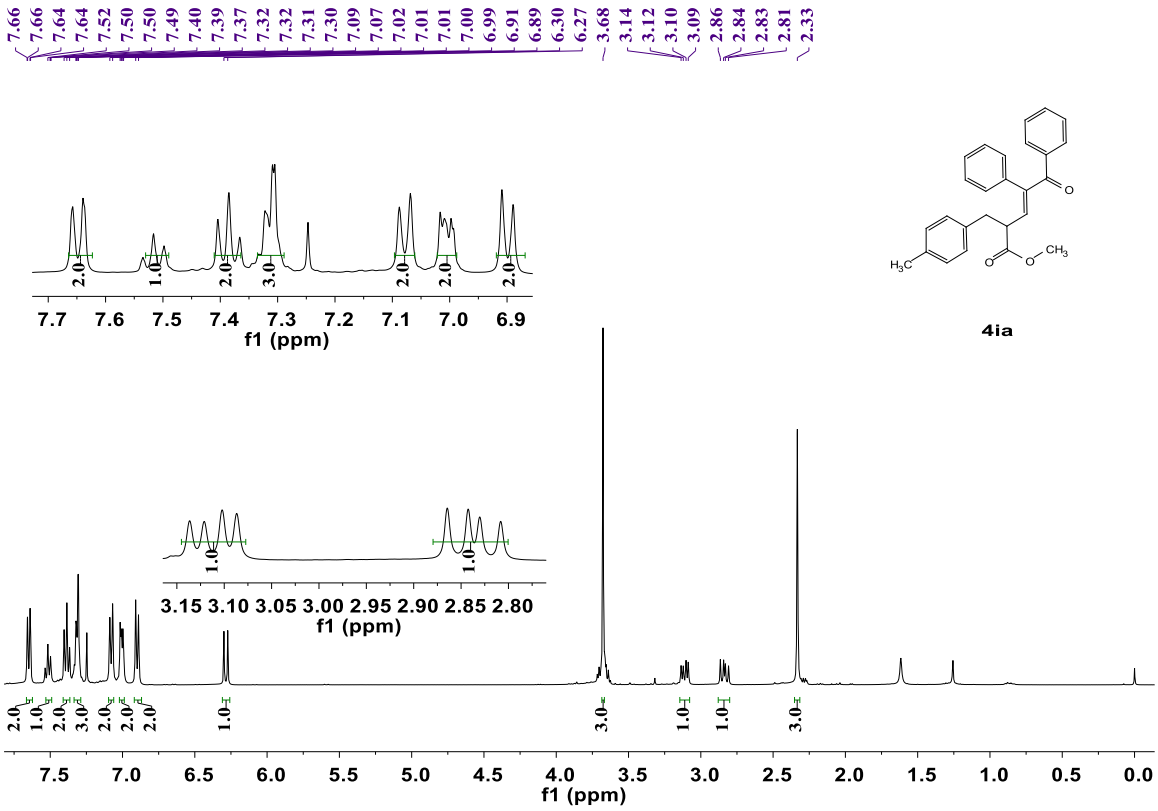

196.1
170.7
159.5
140.5
135.8
135.8
133.2
129.9
129.6
129.4
128.5
128.4
127.6
120.9
114.4
111.8
55.1
51.8
45.7
38.1
37.4
29.7
3ha
f1 (ppm)

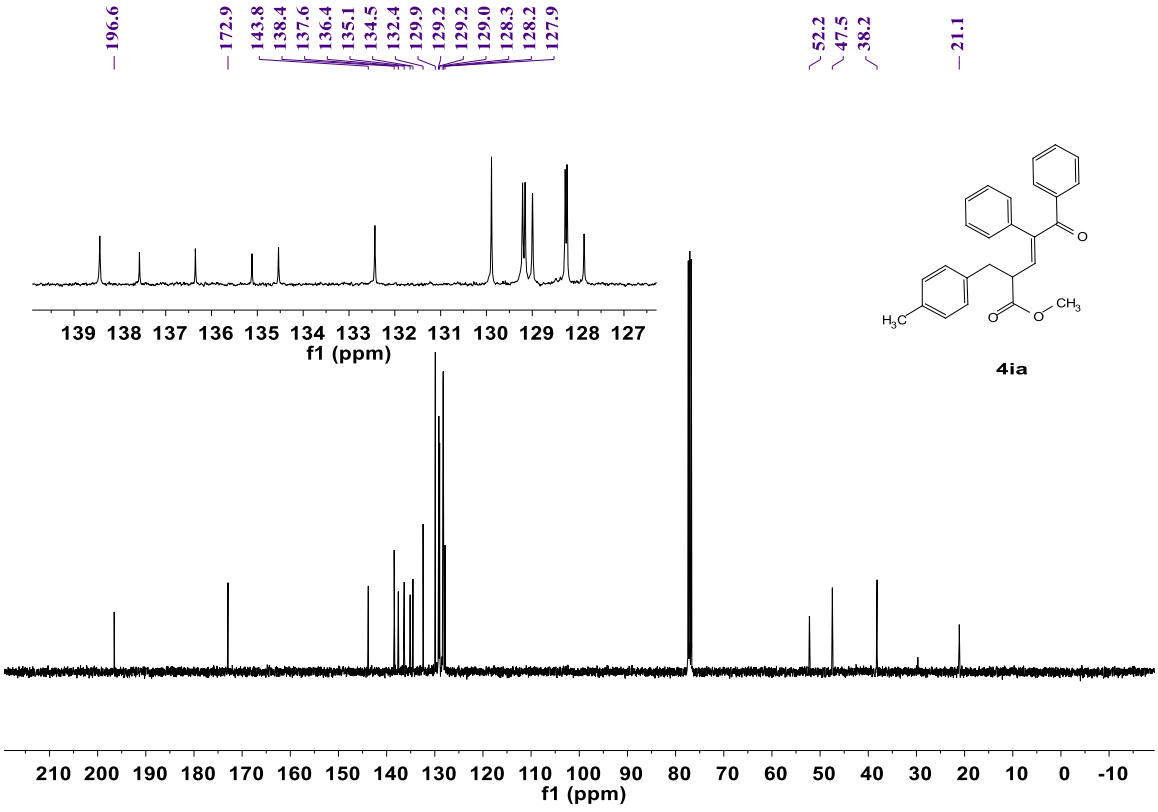

7.66 7.65 7.65 7.64 7.63 7.52 7.51 7.50 7.42 7.40 7.32 7.32 7.31 7.30 7.26 7.20 7.00 6.99 6.99 6.98 6.97 6.81 6.80 6.79 6.78 6.63 6.61 6.54 6.54 6.29 6.26 3.74 3.70 3.68 3.66 3.65 3.64 3.16 3.15 3.13 3.12 2.87 2.85 2.83 2.81
4ha
f1 (ppm)

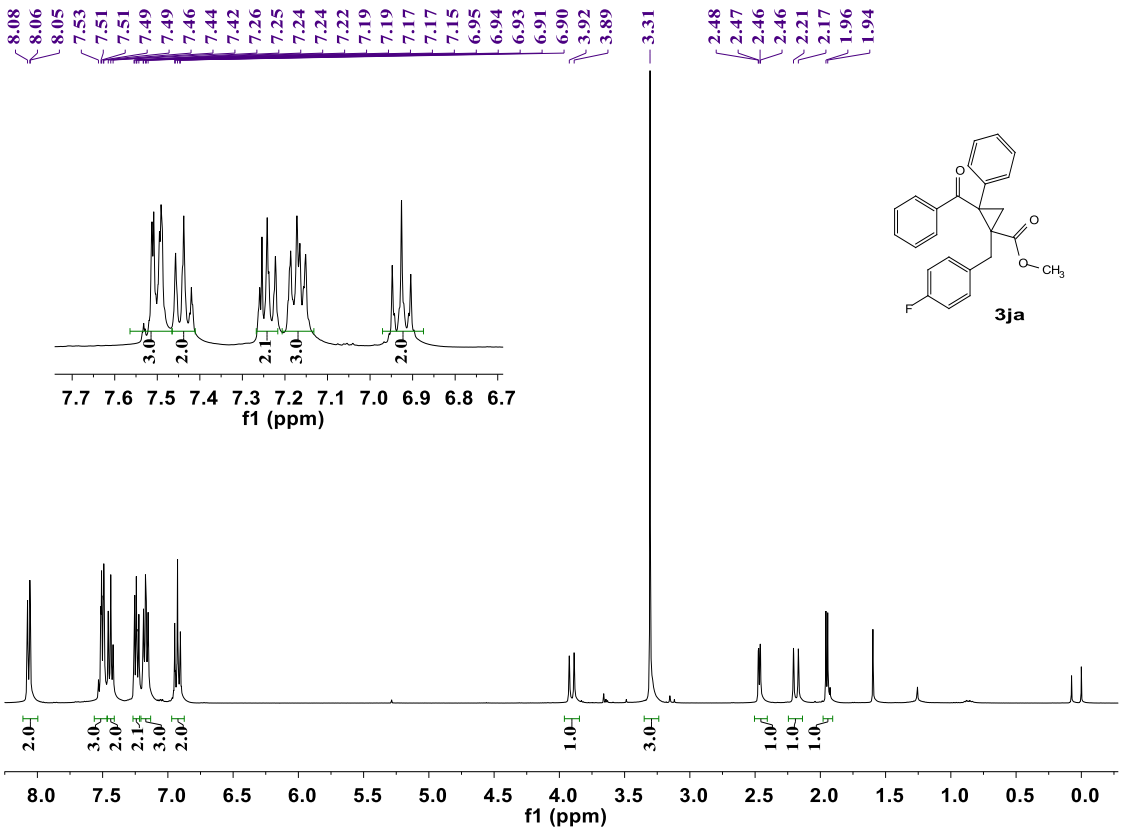

196.6 172.8 159.7 144.0 139.2 138.1 137.5 135.1 132.5 129.9 129.5 129.2 128.3 128.3 127.9 121.5 114.5 112.5 55.1 52.3 47.3 38.6
4ha
f1 (ppm)


8.08 8.06 7.51 7.51 7.50 7.49 7.48 7.48 7.45 7.43 7.43 7.41 7.41 7.41 7.25 7.24 7.23 7.21 7.18 7.17 7.16 7.16 7.14 7.10 7.08 7.05 7.03 3.91 3.88 3.32 2.44 2.43 2.27 2.20 2.16 1.97 1.95
H3C O O CH3 O
3ia
f1 (ppm)


196.1 170.8 136.0 135.9 135.8 133.1 130.0 129.6 129.2 129.1 128.5 128.5 128.4 127.6 51.8 45.8 37.8 21.7 21.0
H3C O O CH3 O
3ia
f1 (ppm)


7.66 7.66 7.64 7.64 7.52 7.50 7.50 7.49 7.40 7.39 7.37 7.32 7.32 7.31 7.30 7.09 7.07 7.02 7.01 7.01 7.00 6.99 6.91 6.89 6.30 6.27 3.68 3.14 3.12 3.10 3.09 2.86 2.84 2.83 2.81 2.33
2.0 1.0 2.0 3.0 2.0 2.0 2.0
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.0 1.0
3.15 3.10 3.05 3.00 2.95 2.90 2.85 2.80
f1 (ppm)
2.0 1.0 2.0 3.0 2.0 2.0 2.0 1.0 3.0 1.0 1.0 3.0
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
4ia


196.6 172.9 143.8 138.4 137.6 136.4 135.1 134.5 132.4 129.9 129.2 129.2 129.0 128.3 128.2 127.9 52.2 47.5 38.2 21.1
139 138 137 136 135 134 133 132 131 130 129 128 127
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
4ia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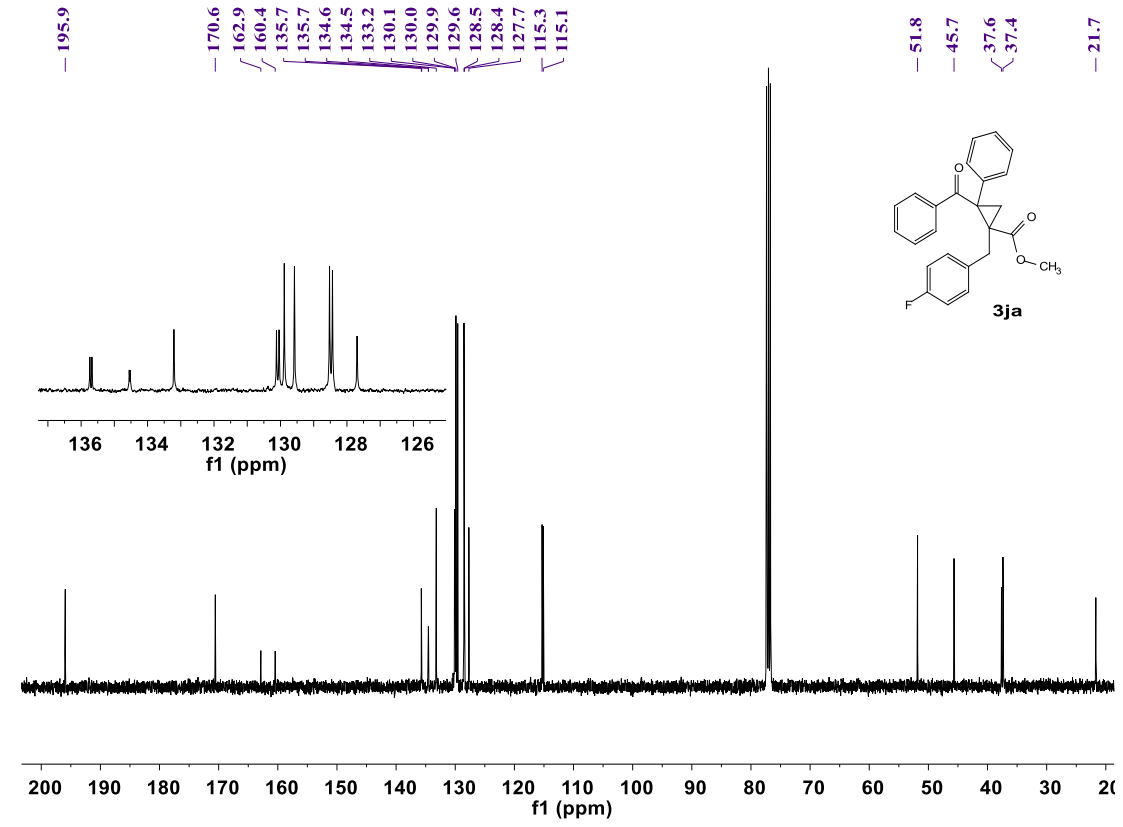
8.06
8.05
7.53
7.51
7.51
7.49
7.49
7.46
7.44
7.42
7.26
7.25
7.24
7.24
7.22
7.19
7.19
7.17
7.17
7.15
6.95
6.94
6.93
6.91
6.90
3.92
3.89
3.31
2.48
2.47
2.46
2.46
2.21
2.17
1.96
1.94
3.0
2.0
2.1
3.0
2.0
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
O
O
O
CH3
F
3ja
2.0
3.0
2.0
2.1
3.0
2.0
1.0
3.0
1.0
1.0
1.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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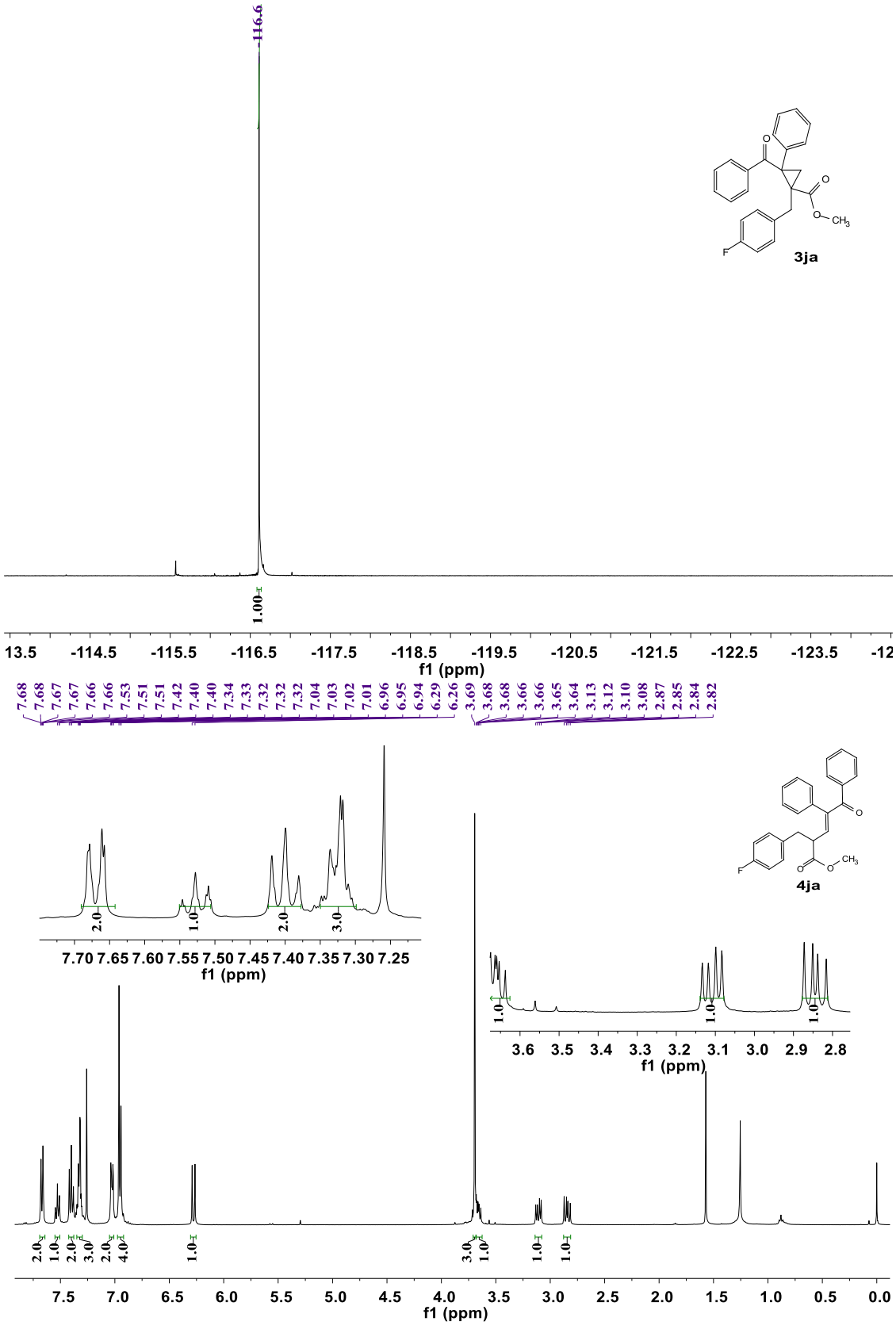
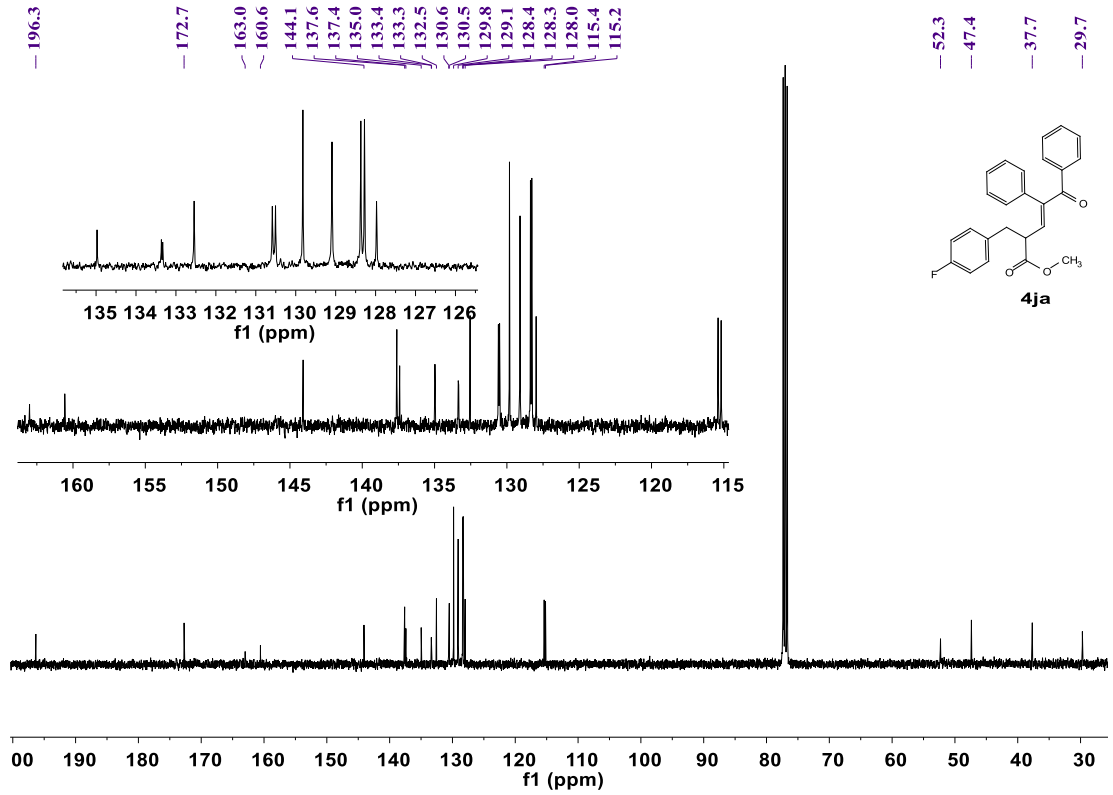
170.6
162.9
160.4
135.7
135.7
134.6
134.5
133.2
130.1
130.0
129.9
129.6
128.5
128.4
127.7
115.3
115.1
51.8
45.7
37.6
37.4
21.7
136 134 132 130 128 126
f1 (ppm)
O
O
O
CH3
F
3ja
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


-116.6
1.00
13.5 -114.5 -115.5 -116.5 -117.5 -118.5 -119.5 -120.5 -121.5 -122.5 -123.5 -12
f1 (ppm)
3ja
7.68 7.68 7.67 7.67 7.66 7.66 7.53 7.51 7.51 7.42 7.40 7.40 7.34 7.33 7.32 7.32 7.32 7.04 7.03 7.02 7.01 6.96 6.95 6.94 6.29 6.26
3.69 3.68 3.68 3.66 3.66 3.65 3.64 3.13 3.12 3.10 3.08 2.87 2.85 2.84 2.82
2.0 1.0 2.0 3.0
7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25
f1 (ppm)
4ja
1.0 1.0 1.0
3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8
f1 (ppm)
2.0 1.0 2.0 3.0 2.0 4.0 1.0 3.0 1.0 1.0 1.0
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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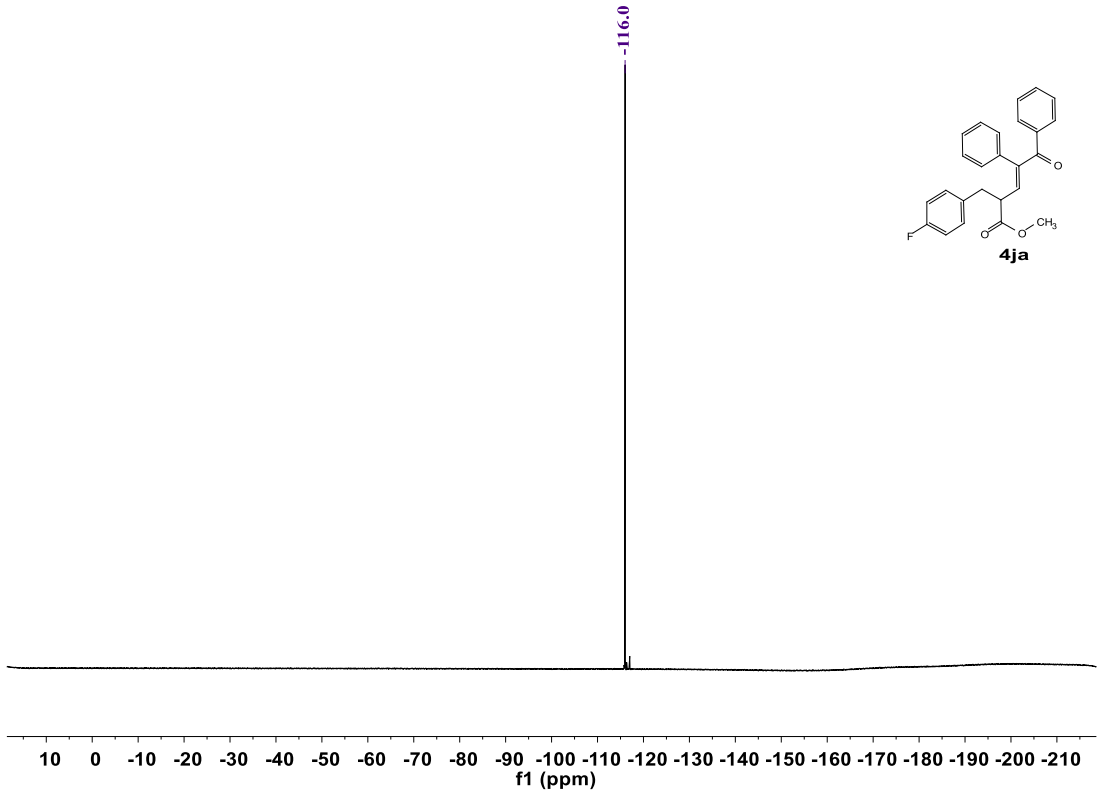
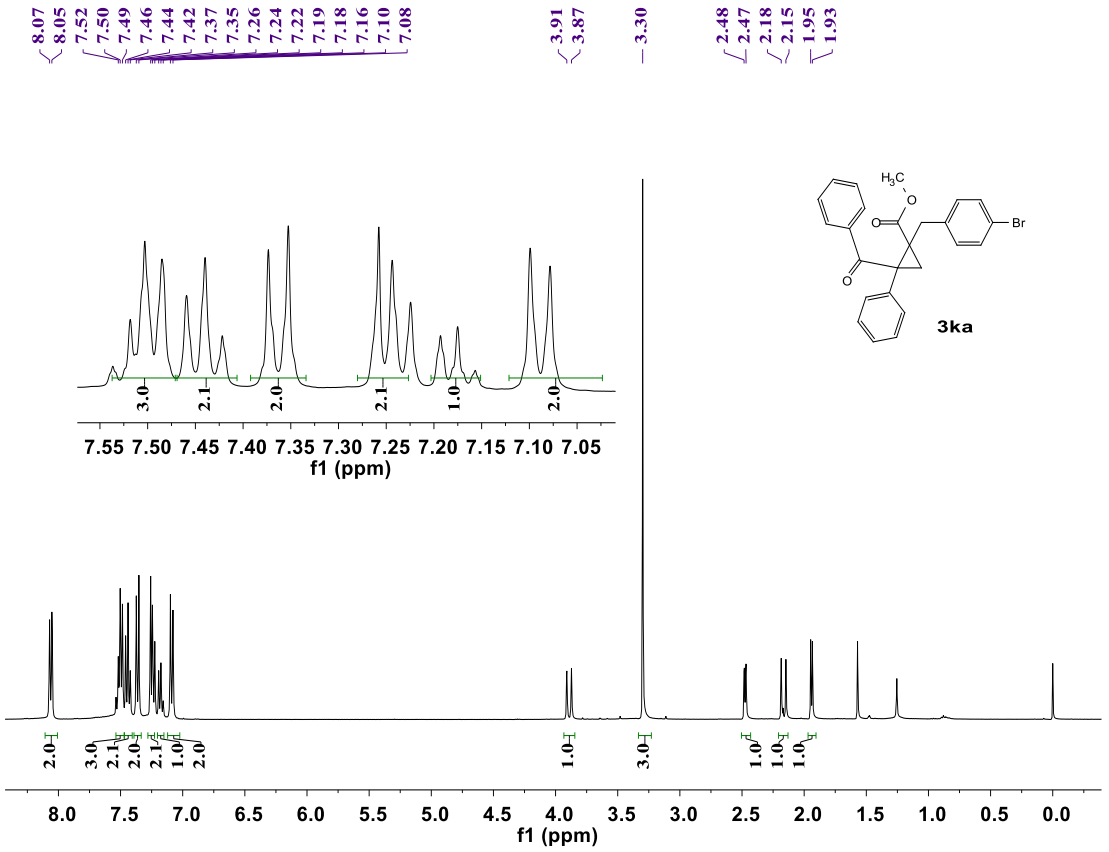
163.0
160.6
144.1
137.6
137.4
135.0
133.4
133.3
132.5
130.6
130.5
129.8
129.1
128.4
128.3
128.0
115.4
115.2
52.3
47.4
37.7
29.7
135 134 133 132 131 130 129 128 127 126
f1 (ppm)
160 155 150 145 140 135 130 125 120 115
f1 (ppm)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
f1 (ppm)
4ja


-116.0
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)
4ja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7.50
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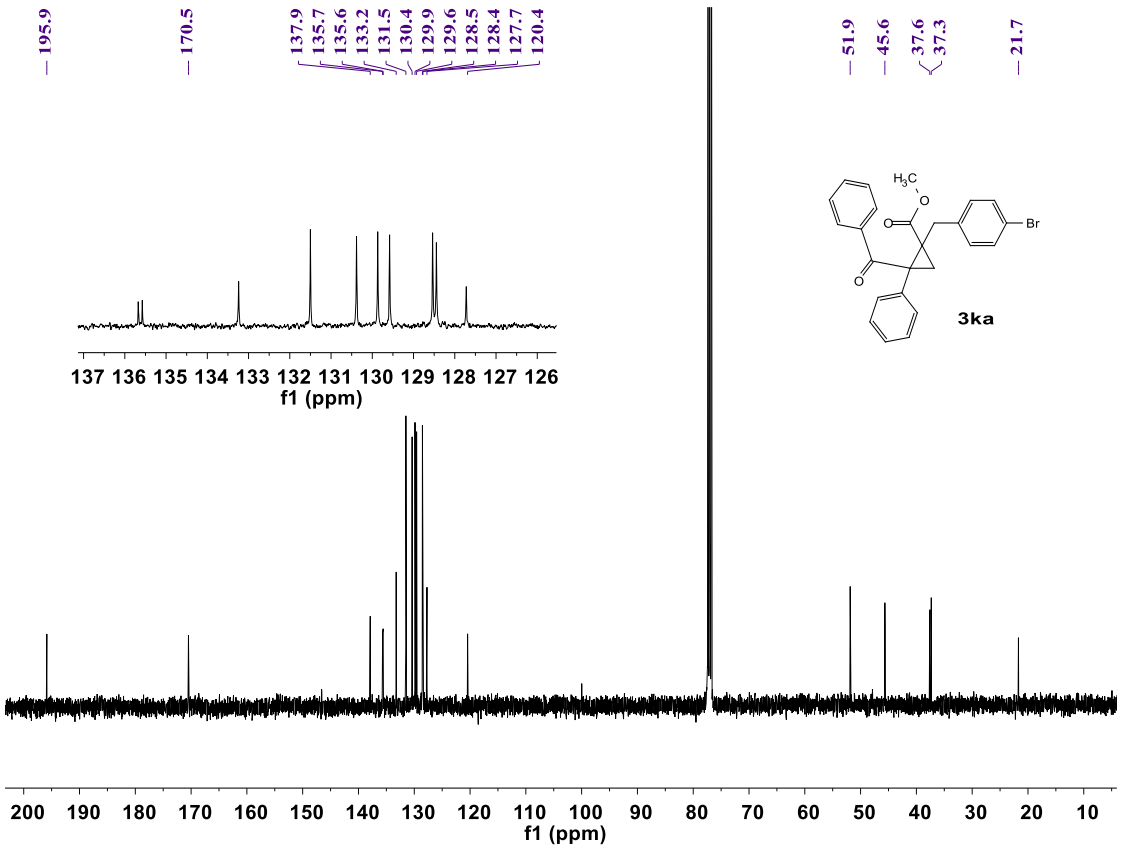
7.46
7.44
7.42
7.37
7.35
7.26
7.24
7.22
7.19
7.18
7.16
7.10
7.08
3.91
3.87
3.30
2.48
2.47
2.18
2.15
1.95
1.93
3ka
f1 (ppm)


195.9
170.5
137.9
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135.6
133.2
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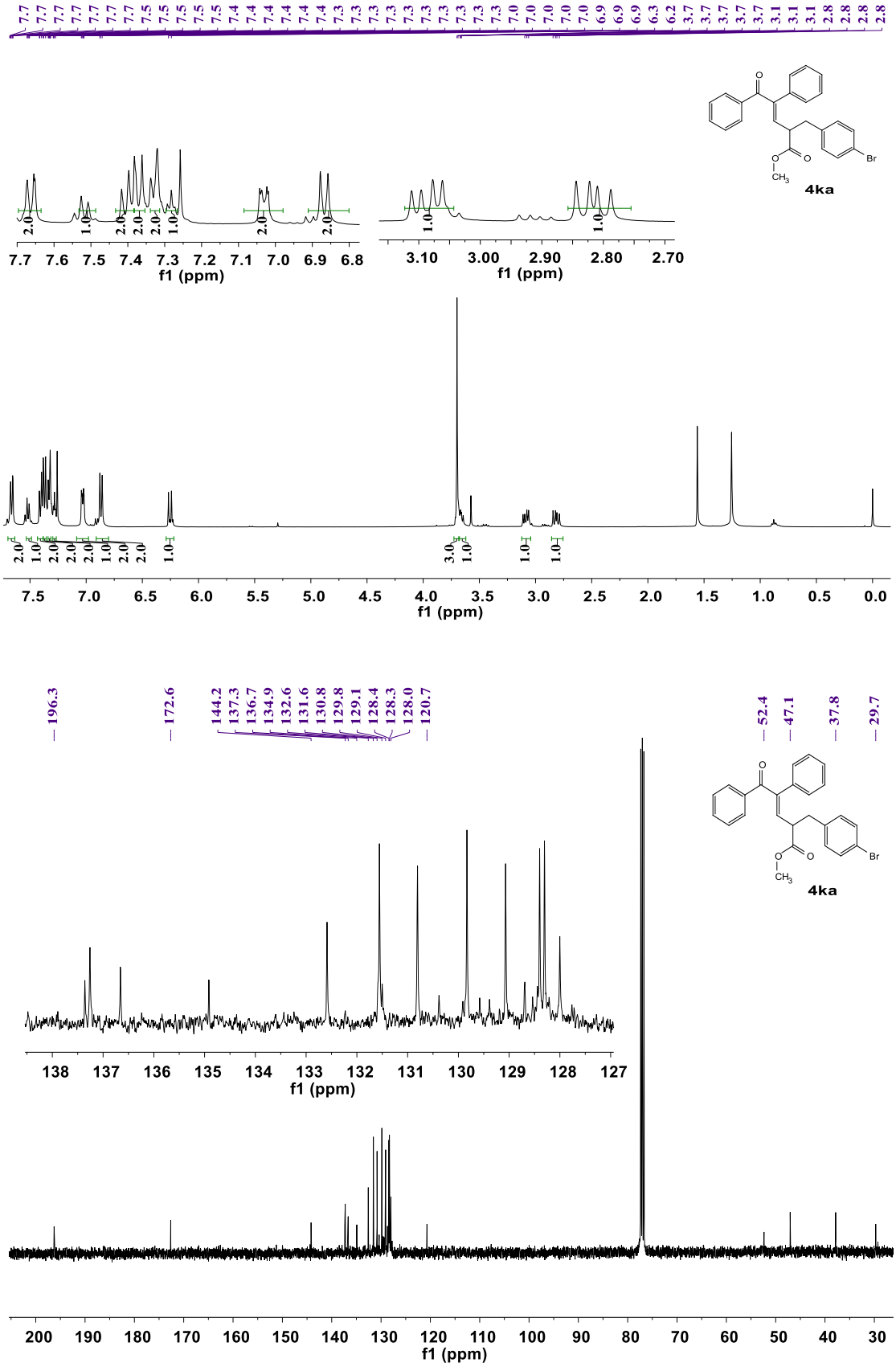
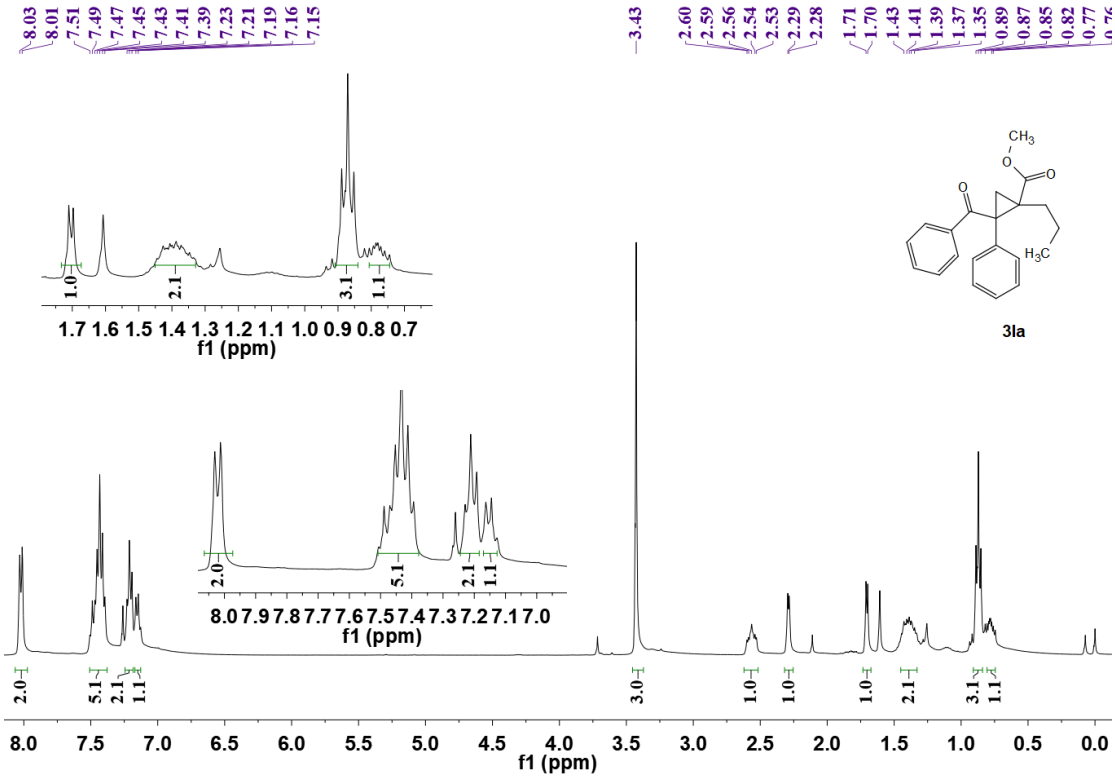
130.4
129.9
129.6
128.5
128.4
127.7
120.4
51.9
45.6
37.6
37.3
21.7
3ka
f1 (ppm)


4ka
f1 (ppm)

4ka
f1 (ppm)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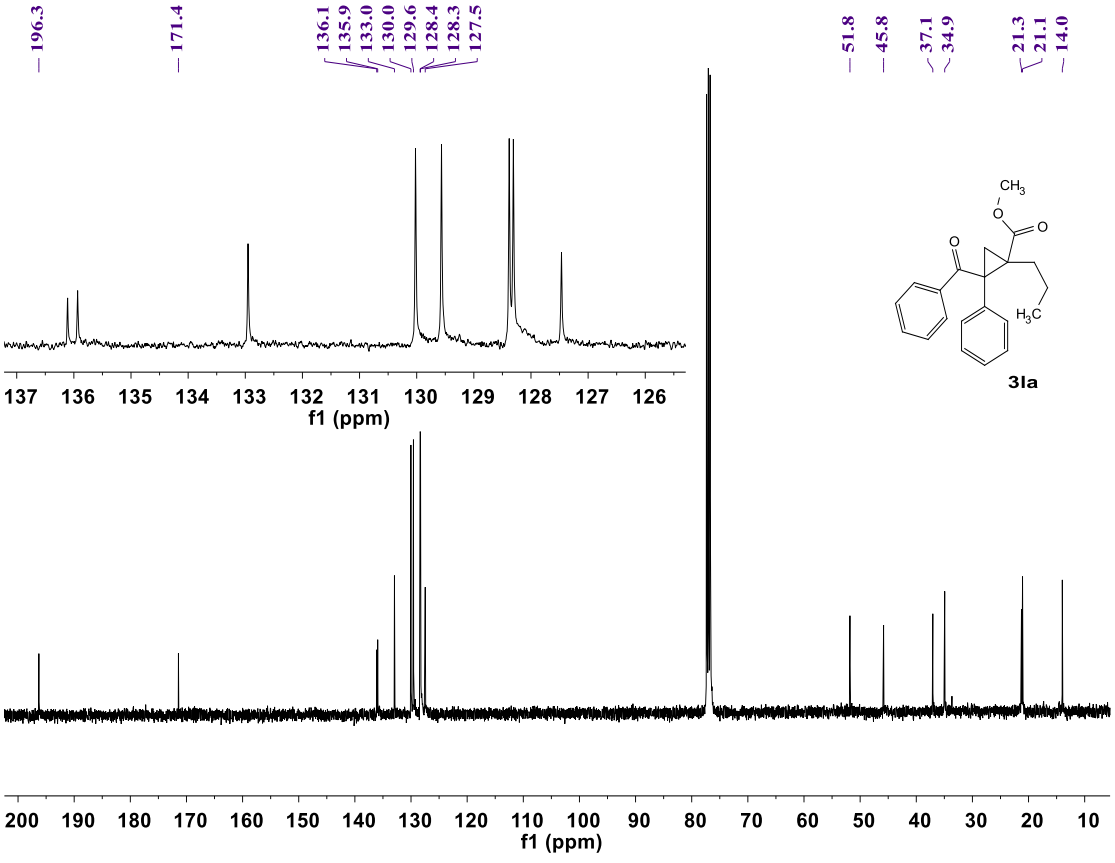
7.51
7.49
7.47
7.45
7.43
7.41
7.39
7.23
7.21
7.19
7.16
7.15
3.43
2.60
2.59
2.56
2.54
2.53
2.29
2.28
1.71
1.70
1.43
1.41
1.39
1.37
1.35
0.89
0.87
0.85
0.82
0.77
1.0
2.1
3.1
1.1
1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7
f1 (ppm)
2.0
5.1
2.1
1.1
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
2.0
5.1
2.1
1.1
3.0
1.0
1.0
1.0
2.1
3.1
1.1
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
CH3
O
O
O
H3C
3la


196.3
171.4
136.1
135.9
133.0
130.0
129.6
128.4
128.3
127.5
51.8
45.8
37.1
34.9
21.3
21.1
14.0
137 136 135 134 133 132 131 130 129 128 127 126
f1 (ppm)
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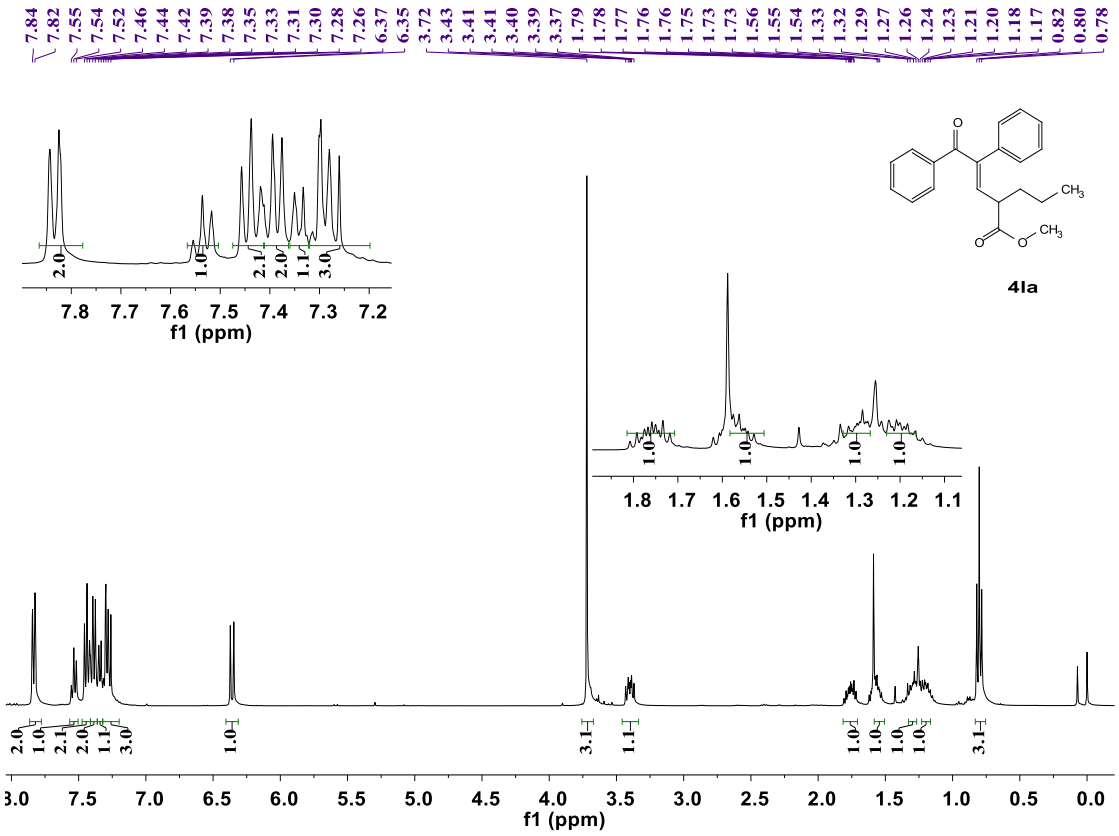
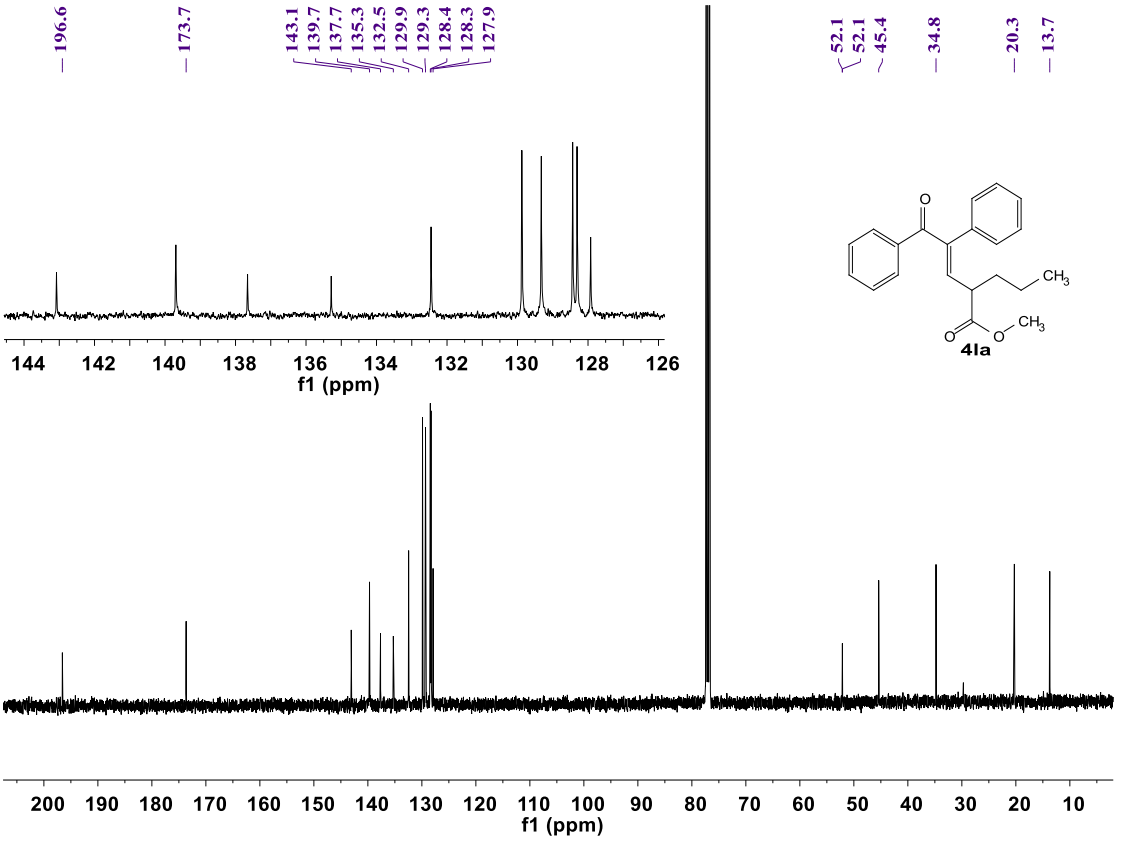
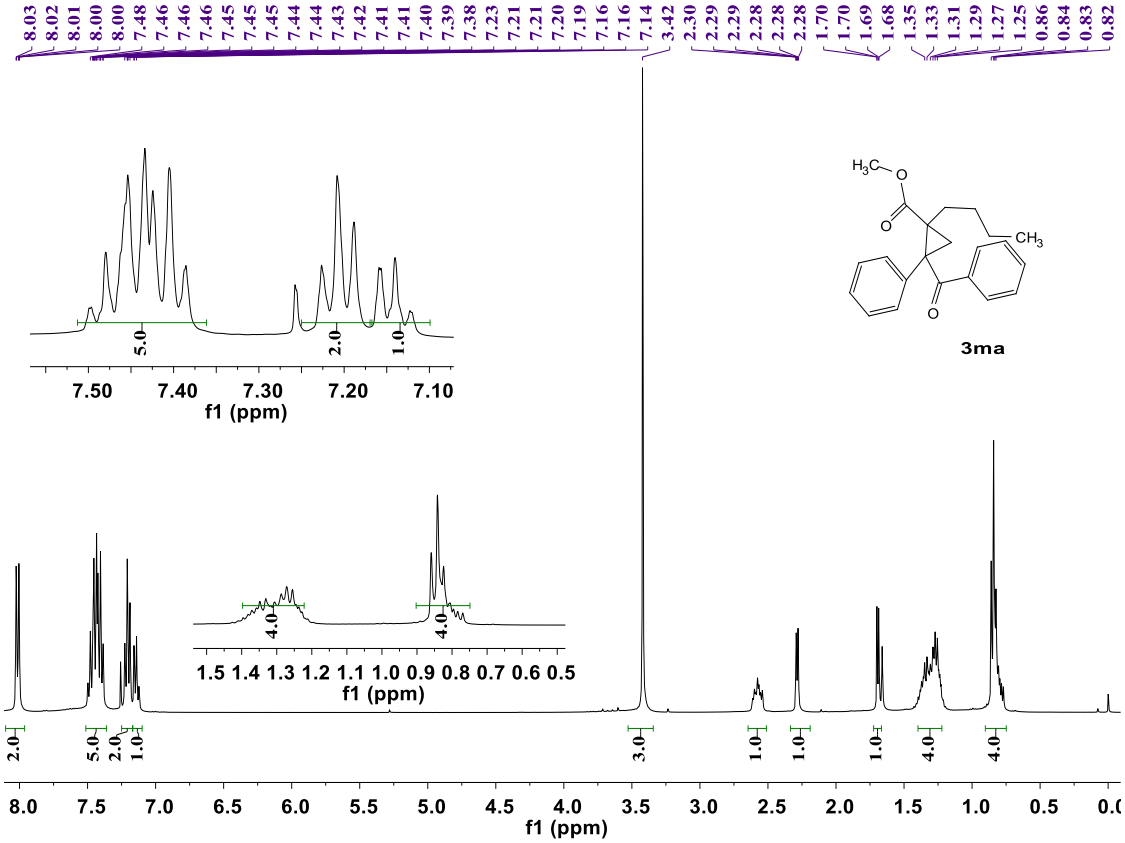
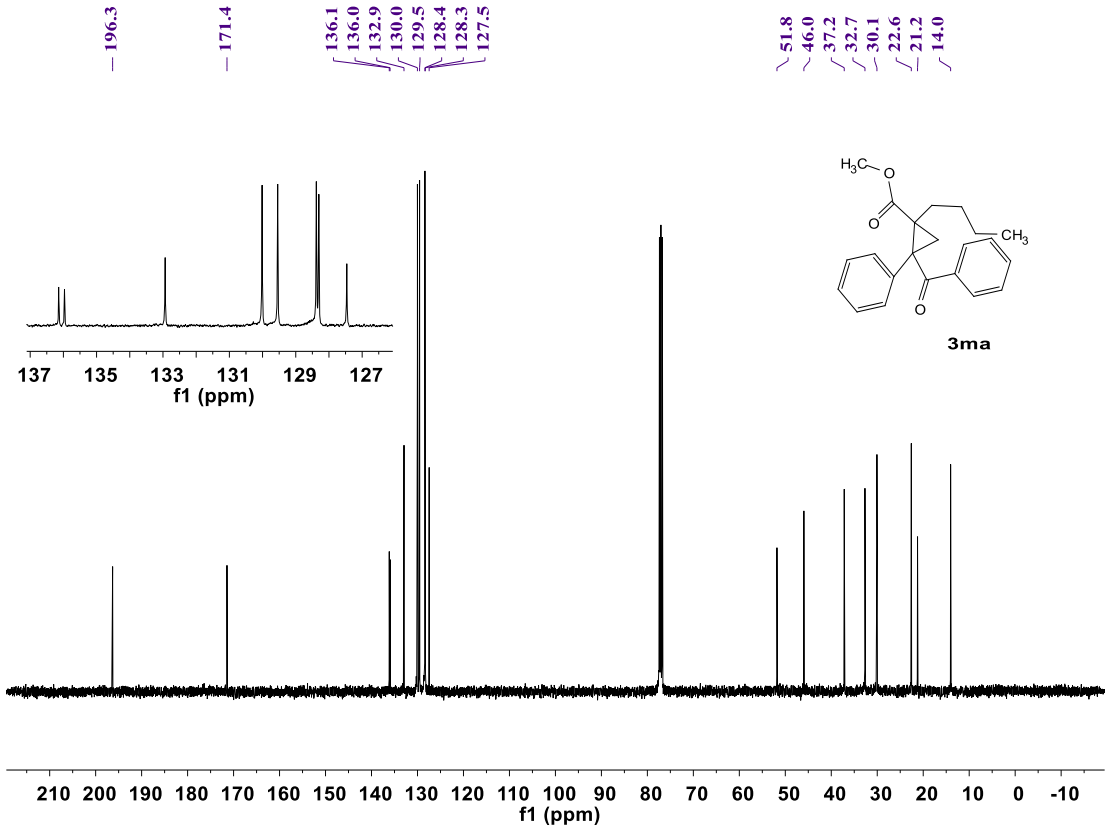
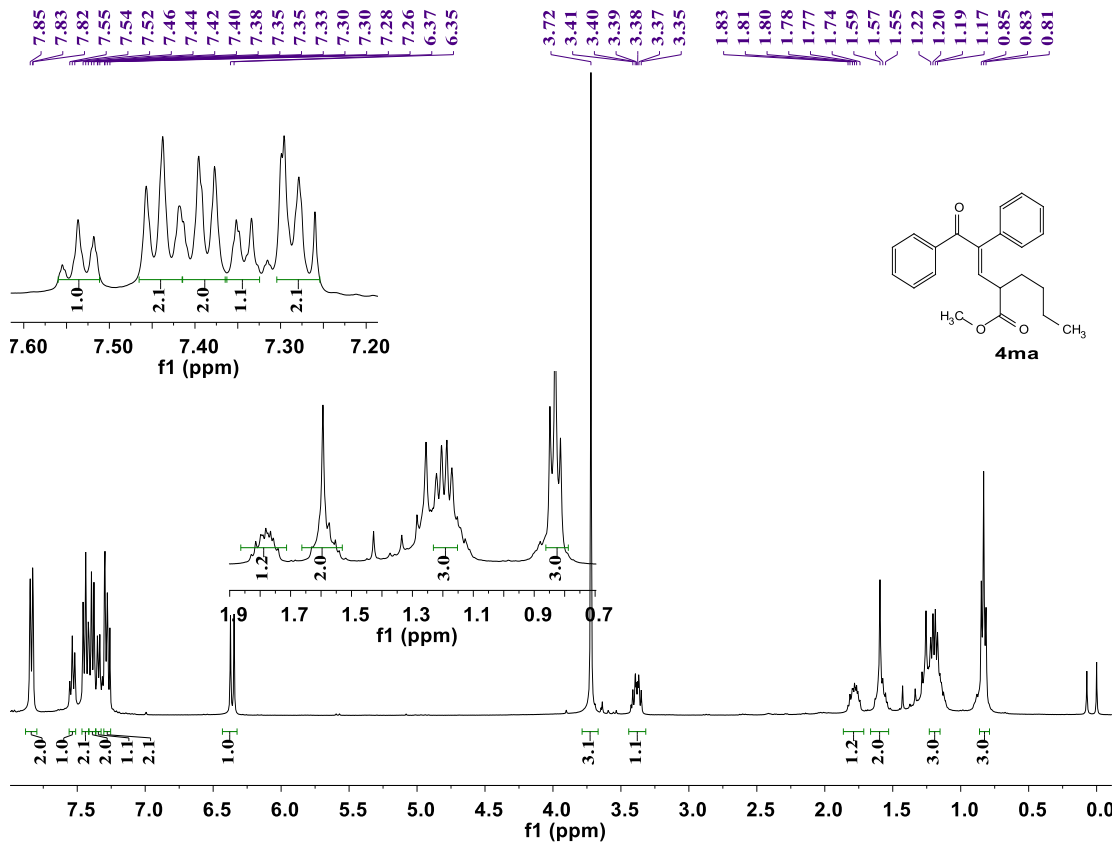
f1 (ppm)
CH3
O
O
O
H3C
3la

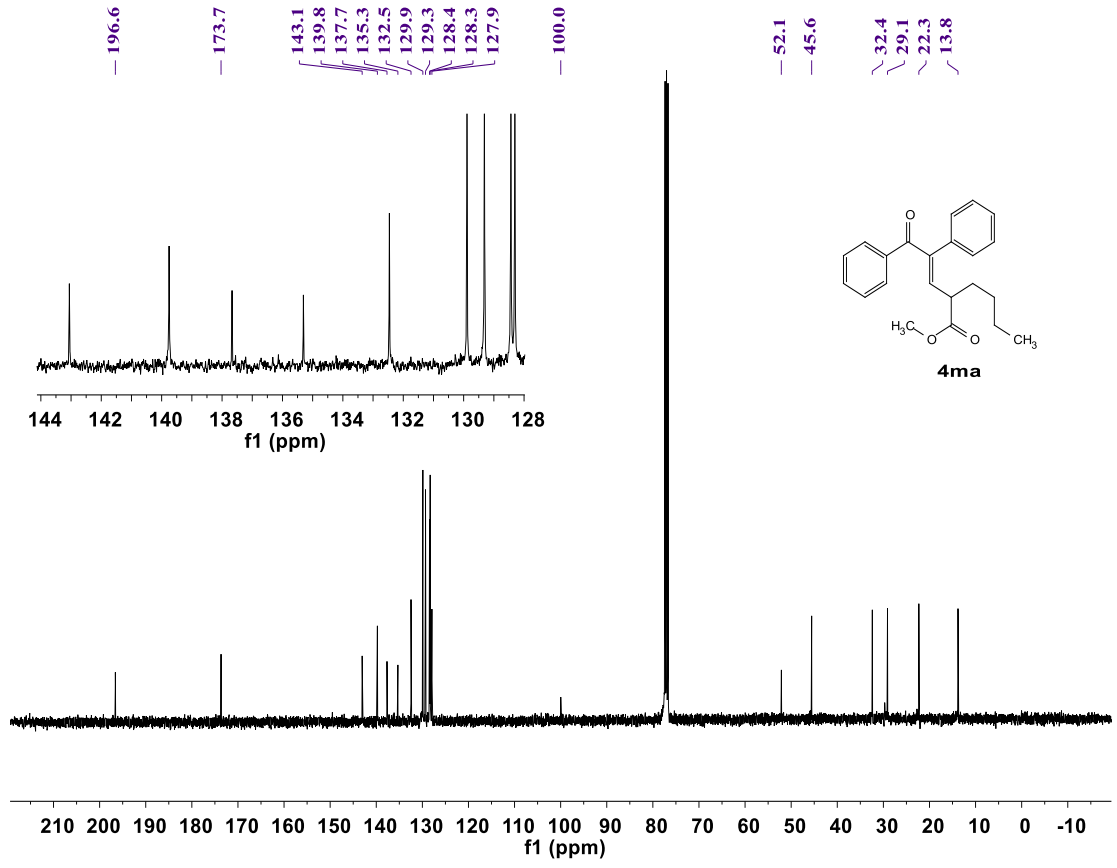

7.84 7.82 7.55 7.54 7.52 7.46 7.44 7.42 7.39 7.38 7.35 7.33 7.31 7.30 7.28 7.26 6.37 6.35
3.72 3.43 3.41 3.41 3.40 3.39 3.37 1.79 1.78 1.77 1.76 1.76 1.75 1.73 1.73 1.56 1.55 1.54 1.33 1.32 1.29 1.27 1.26 1.24 1.23 1.21 1.20 1.18 1.17 0.82 0.80 0.78
4la
f1 (ppm)

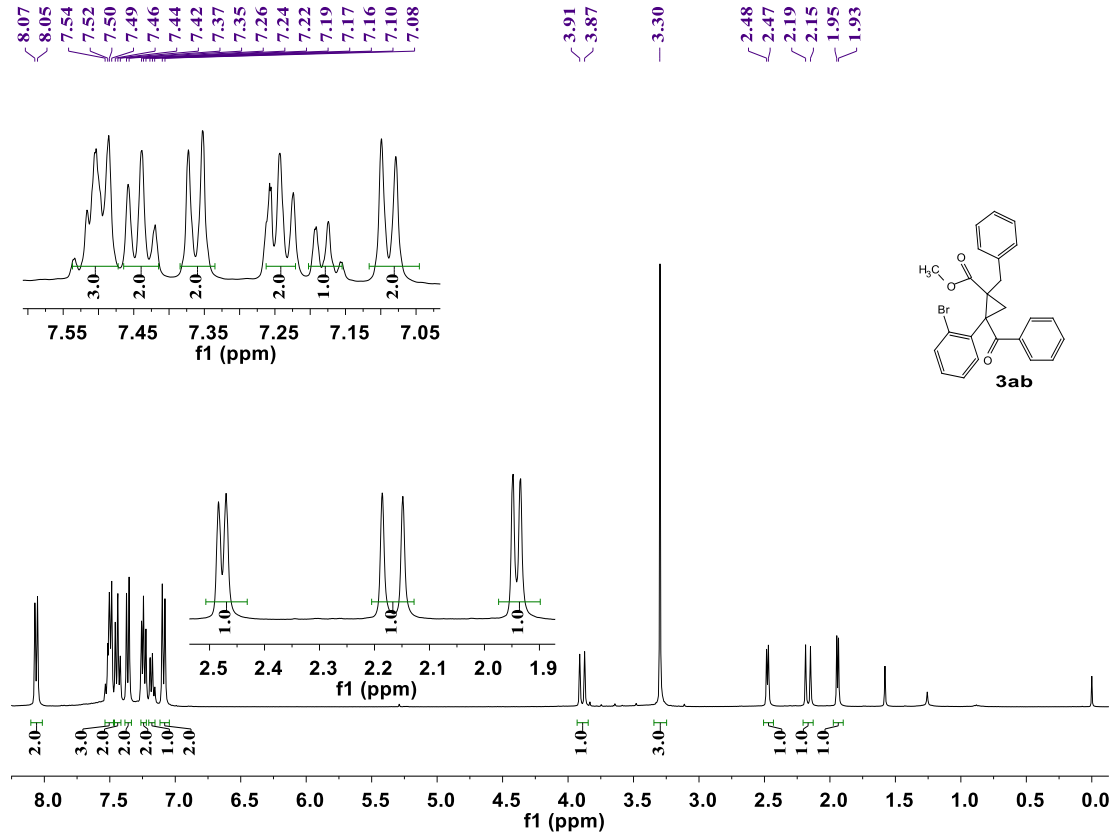

196.6 173.7 143.1 139.7 137.7 135.3 132.5 129.9 129.3 128.4 128.3 127.9 52.1 52.1 45.4 34.8 20.3 13.7
4la
f1 (ppm)


8.03 8.02 8.01 8.00 8.00 7.48 7.46 7.46 7.46 7.45 7.45 7.45 7.44 7.44 7.43 7.42 7.41 7.41 7.40 7.39 7.38 7.23 7.21 7.21 7.20 7.19 7.16 7.16 7.14 3.42 2.30 2.29 2.29 2.28 2.28 2.28 1.70 1.70 1.69 1.68 1.35 1.33 1.31 1.29 1.27 1.25 0.86 0.84 0.83 0.82
5.0 2.0 1.0
7.50 7.40 7.30 7.20 7.10
f1 (ppm)
4.0 4.0
1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5
f1 (ppm)
2.0 5.0 2.0 1.0 3.0 1.0 1.0 1.0 4.0 4.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
H3C O O CH3 O
3ma


196.3 171.4 136.1 136.0 132.9 130.0 129.5 128.4 128.3 127.5 51.8 46.0 37.2 32.7 30.1 22.6 21.2 14.0
137 135 133 131 129 127
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
H3C O O CH3 O
3ma


7.85 7.83 7.82 7.55 7.54 7.52 7.46 7.44 7.42 7.40 7.38 7.35 7.35 7.33 7.30 7.30 7.28 7.26 6.37 6.35
3.72 3.41 3.40 3.39 3.38 3.37 3.35
1.83 1.81 1.80 1.78 1.77 1.74 1.59 1.57 1.55 1.22 1.20 1.19 1.17 0.85 0.83 0.81
4ma
f1 (ppm)


196.6 173.7 143.1 139.8 137.7 135.3 132.5 129.9 129.3 128.4 128.3 127.9 100.0 52.1 45.6 32.4 29.1 22.3 13.8
4ma
f1 (ppm)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8.05
7.54
7.52
7.50
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7.46
7.44
7.42
7.37
7.35
7.26
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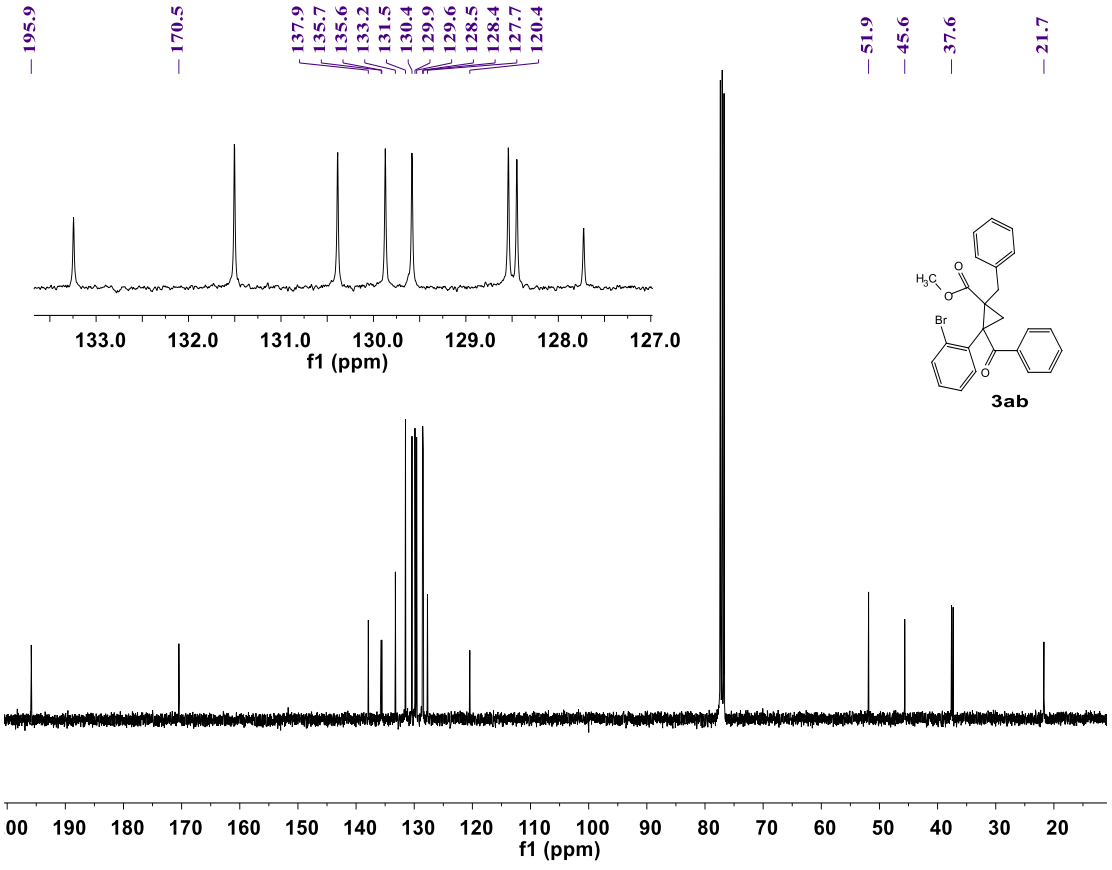
7.22
7.19
7.17
7.16
7.10
7.08
3.91
3.87
3.30
2.48
2.47
2.19
2.15
1.95
1.93
3.0
2.0
2.0
2.0
1.0
2.0
7.55 7.45 7.35 7.25 7.15 7.05
f1 (ppm)
1.0
1.0
1.0
2.5 2.4 2.3 2.2 2.1 2.0 1.9
f1 (ppm)
2.0
3.0
2.0
2.0
2.0
1.0
2.0
1.0
3.0
1.0
1.0
1.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
H3C
O
O
Br
O
3ab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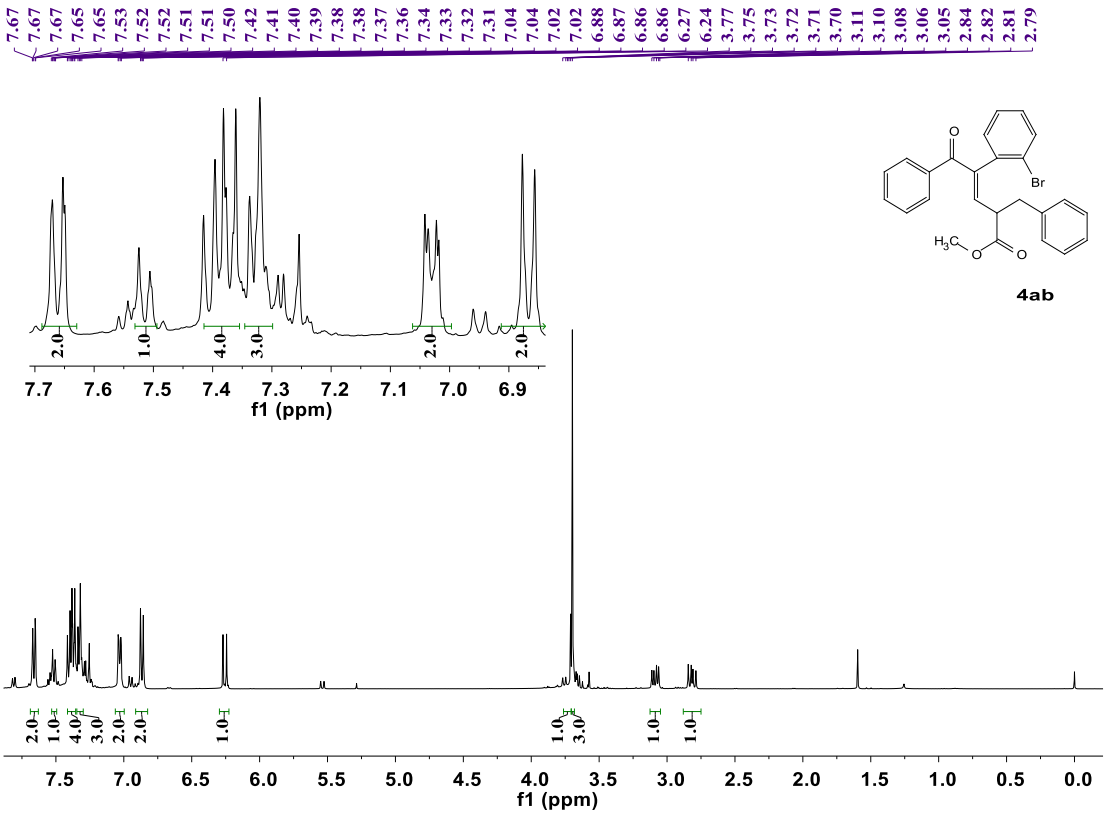
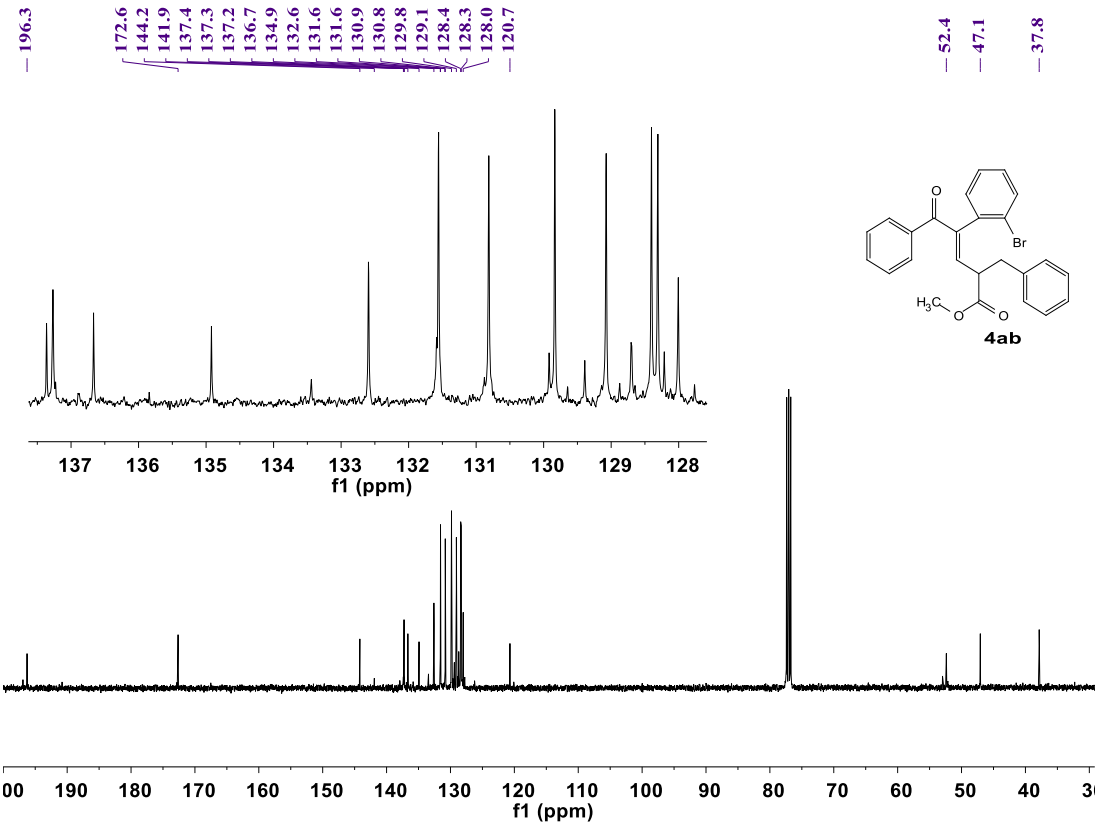
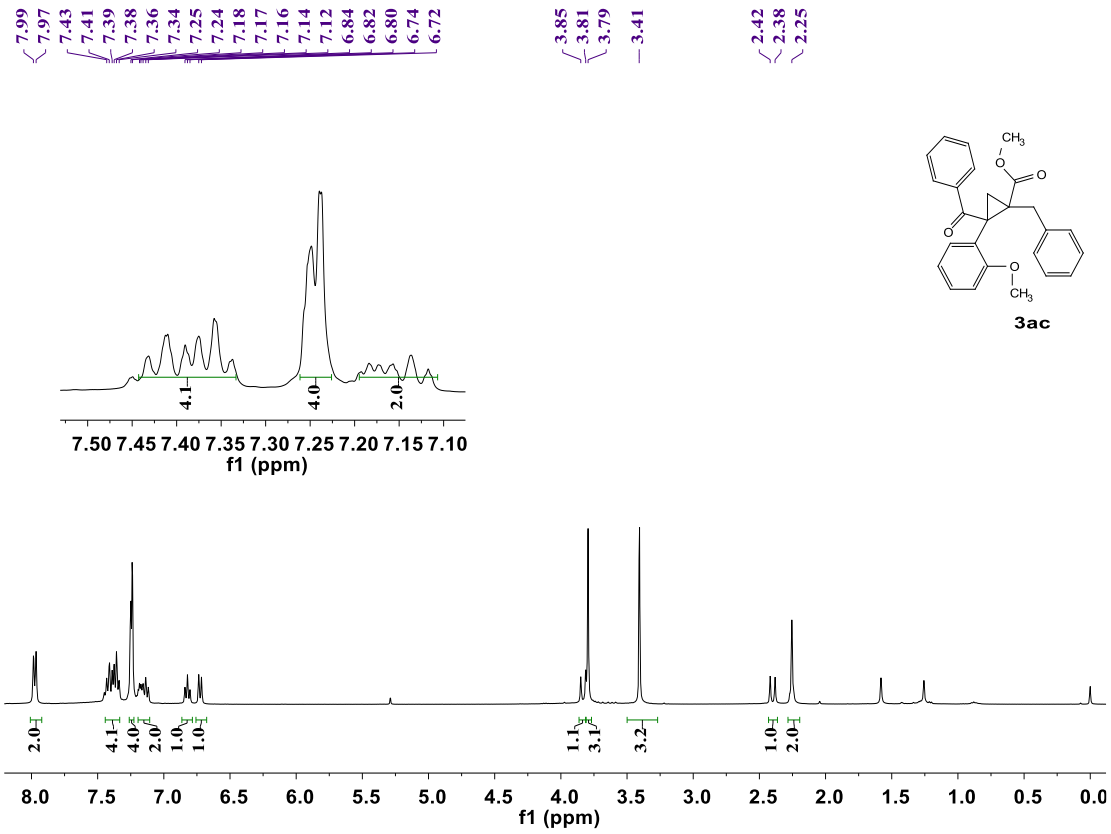
170.5
137.9
135.7
135.6
133.2
131.5
130.4
129.9
129.6
128.5
128.4
127.7
120.4
51.9
45.6
37.6
21.7
133.0 132.0 131.0 130.0 129.0 128.0 127.0
f1 (ppm)
H3C
O
O
Br
O
3ab
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


7.67 7.67 7.67 7.65 7.65 7.53 7.52 7.52 7.51 7.51 7.50 7.42 7.41 7.40 7.39 7.38 7.38 7.37 7.36 7.34 7.33 7.32 7.31 7.04 7.04 7.02 7.02 6.88 6.87 6.86 6.86 6.27 6.24 3.77 3.75 3.73 3.72 3.71 3.70 3.11 3.10 3.08 3.06 3.05 2.84 2.82 2.81 2.79
2.0 1.0 4.0 3.0 2.0 2.0
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
O
Br
H3C
O
O
4ab
2.0 1.0 4.0 3.0 2.0 1.0 1.0 3.0 1.0 1.0
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


196.3
172.6 144.2 141.9 137.4 137.3 137.2 136.7 134.9 132.6 131.6 131.6 130.9 130.8 129.8 129.1 128.4 128.3 128.0
120.7
52.4 47.1 37.8
137 136 135 134 133 132 131 130 129 128
f1 (ppm)
O
Br
H3C
O
O
4ab
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40
f1 (ppm)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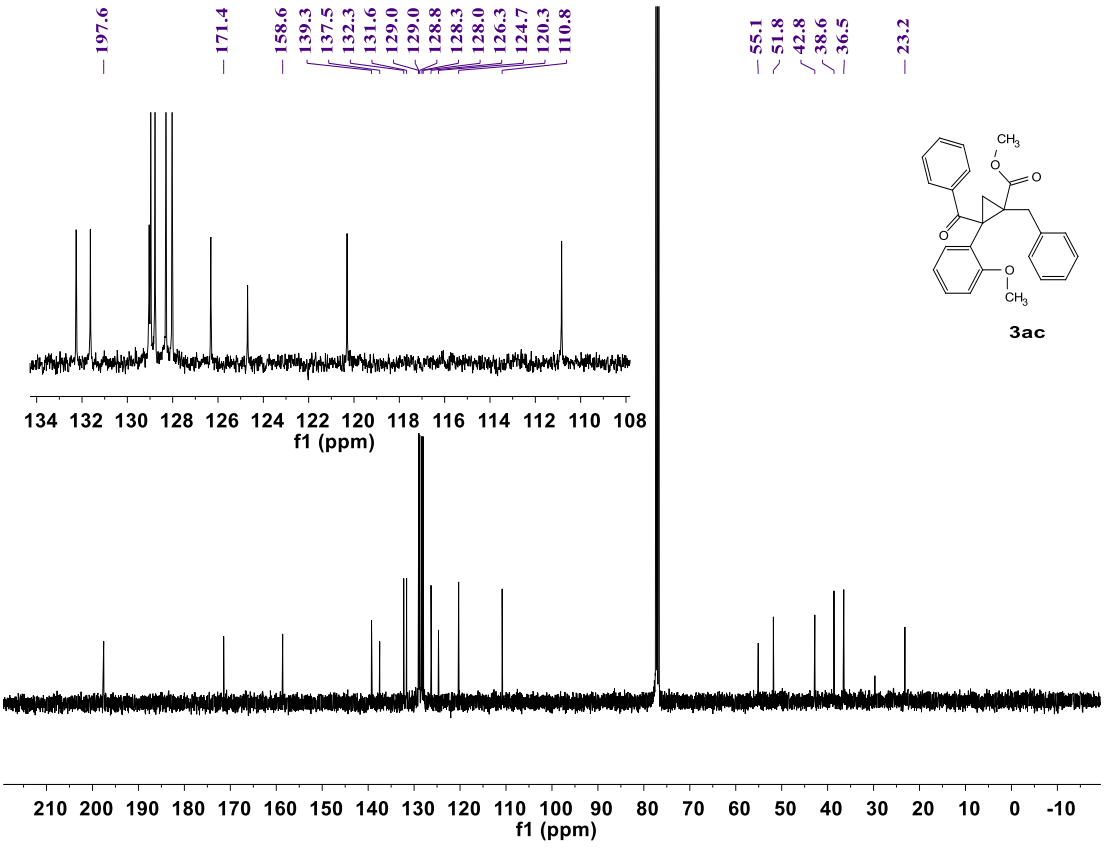
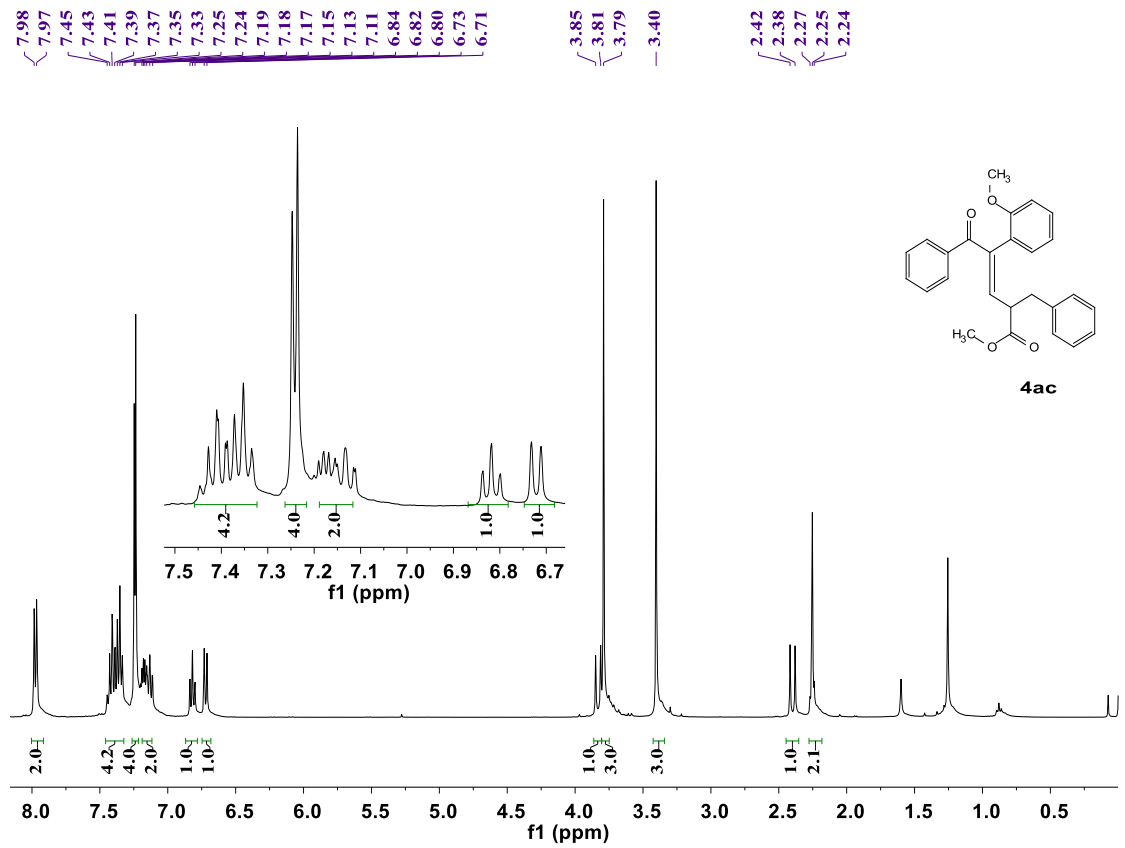
7.43
7.41
7.39
7.38
7.36
7.34
7.25
7.24
7.18
7.17
7.16
7.14
7.12
6.84
6.82
6.80
6.74
6.72
3.85
3.81
3.79
3.41
2.42
2.38
2.25
4.1
4.0
2.0
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)
3ac
2.0
4.1
4.0
2.0
1.0
1.0
1.1
3.1
3.2
1.0
2.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


197.6
171.4
158.6
139.3
137.5
132.3
131.6
129.0
129.0
128.8
128.3
128.0
126.3
124.7
120.3
110.8
55.1
51.8
42.8
38.6
36.5
23.2
134 132 130 128 126 124 122 120 118 116 114 112 110 108
f1 (ppm)
3ac
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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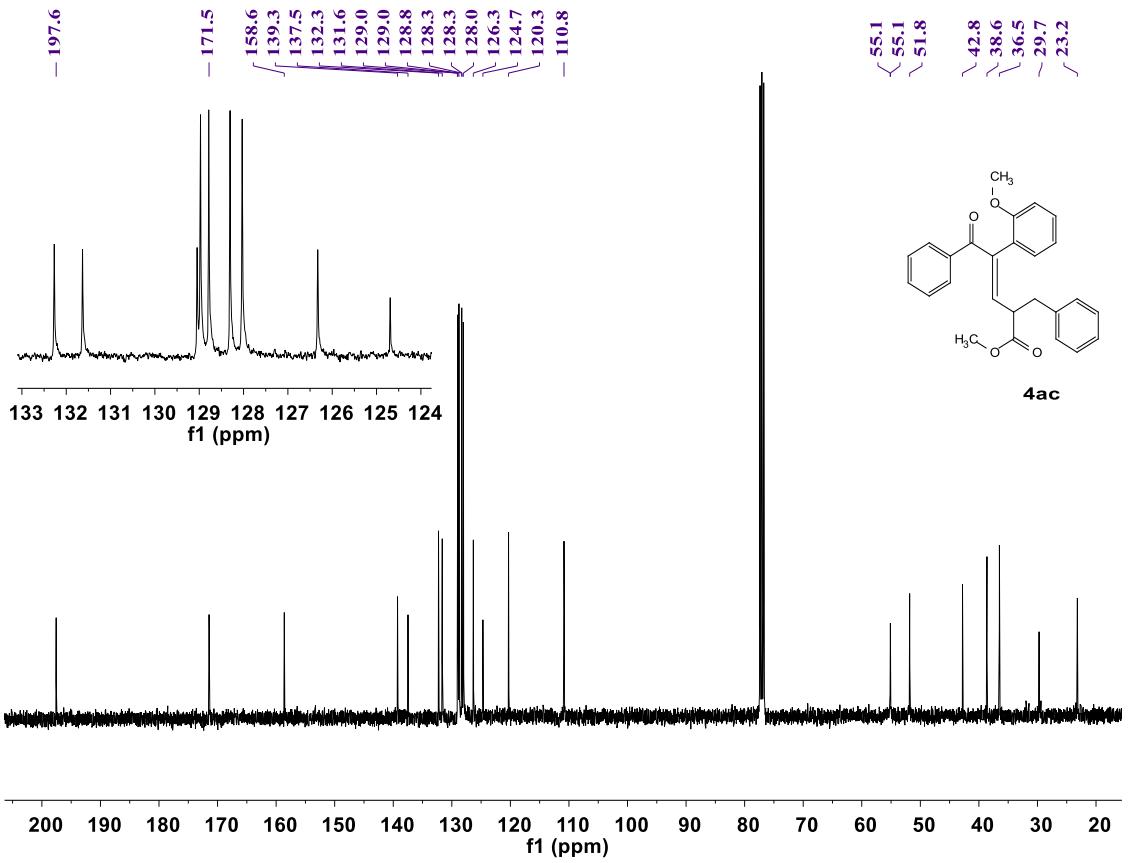
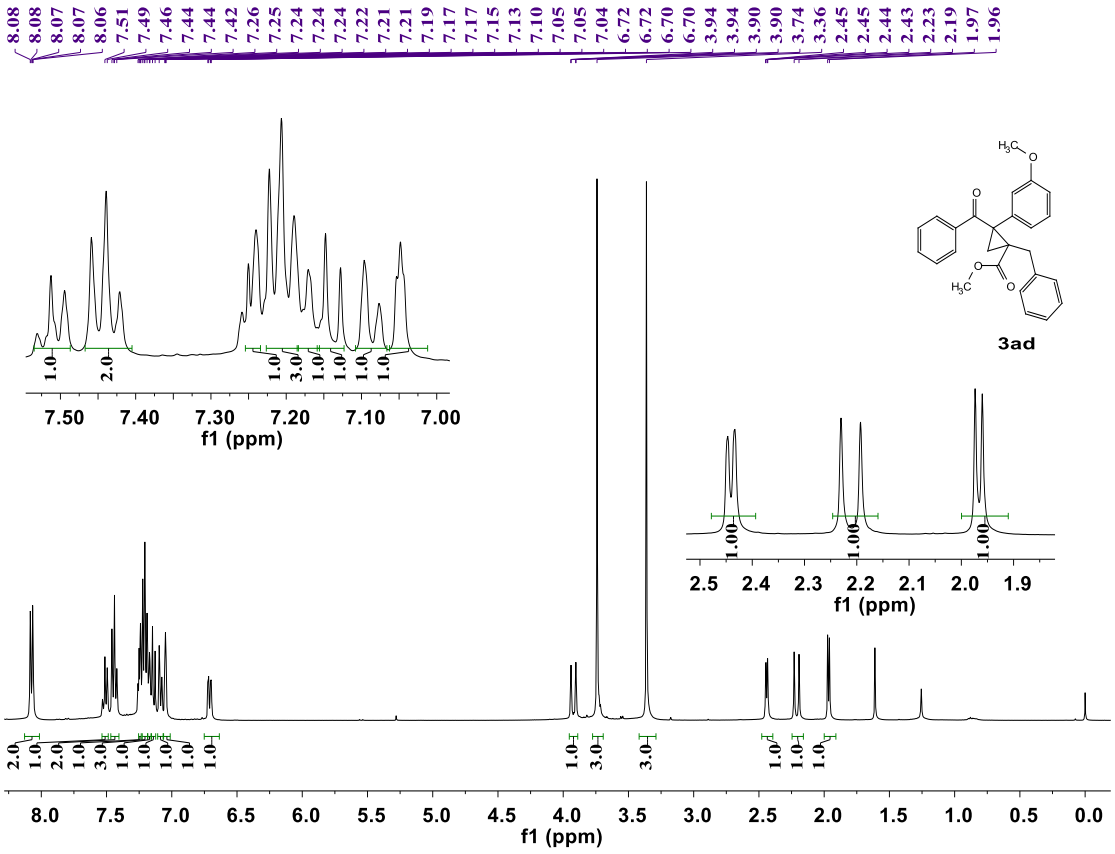
7.97
7.45
7.43
7.41
7.39
7.37
7.35
7.33
7.25
7.24
7.19
7.18
7.17
7.15
7.13
7.11
6.84
6.82
6.80
6.73
6.71
3.85
3.81
3.79
3.40
2.42
2.38
2.27
2.25
2.24
4.2
4.0
2.0
1.0
1.0
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
CH3
O
O
H3C
O
O
4ac
2.0
4.2
4.0
2.0
1.0
1.0
1.0
3.0
3.0
1.0
2.1
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


197.6
171.5
158.6
139.3
137.5
132.3
131.6
129.0
129.0
128.8
128.3
128.3
128.0
126.3
124.7
120.3
110.8
55.1
55.1
51.8
42.8
38.6
36.5
29.7
23.2
133 132 131 130 129 128 127 126 125 124
f1 (ppm)
CH3
O
O
H3C
O
O
4ac
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)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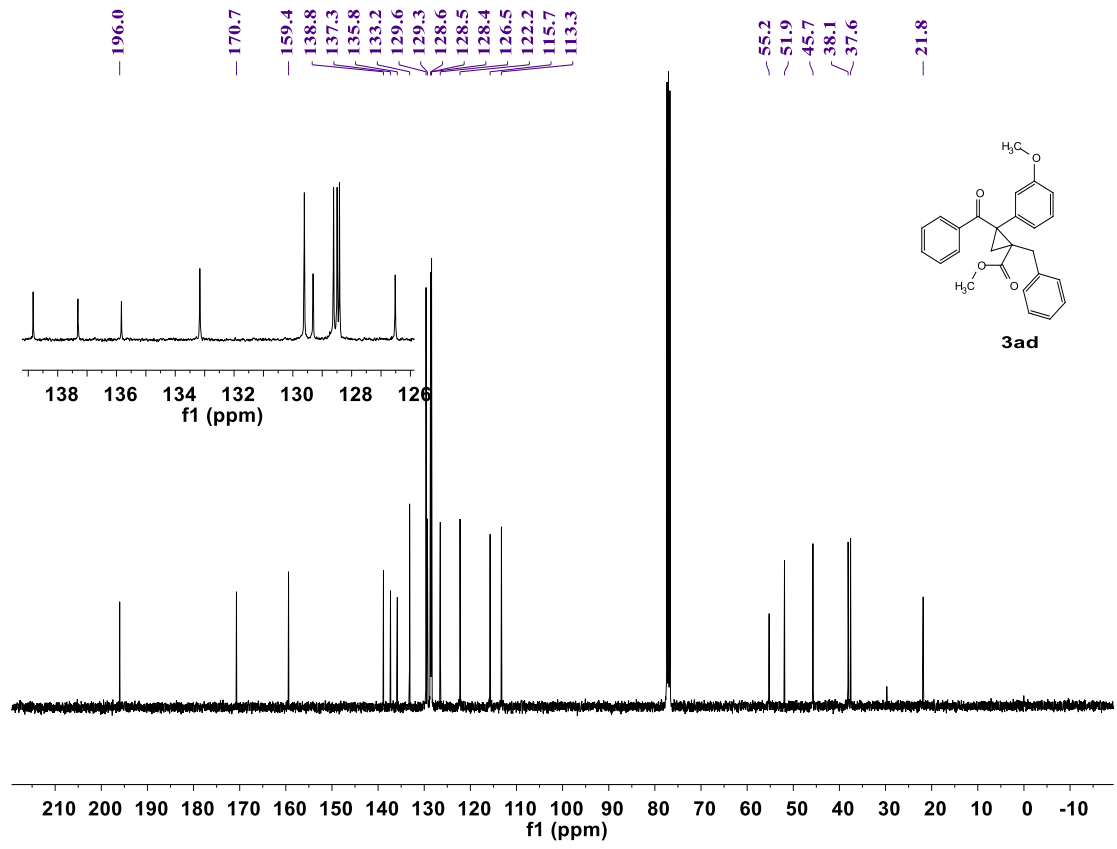
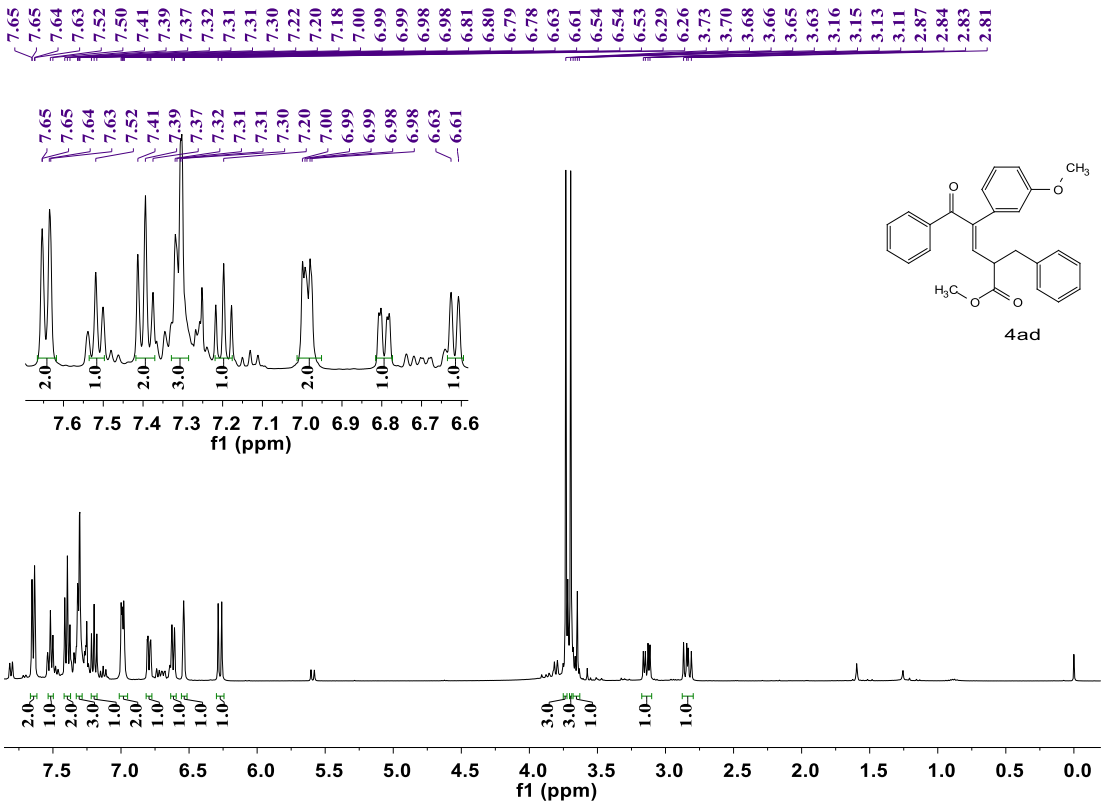
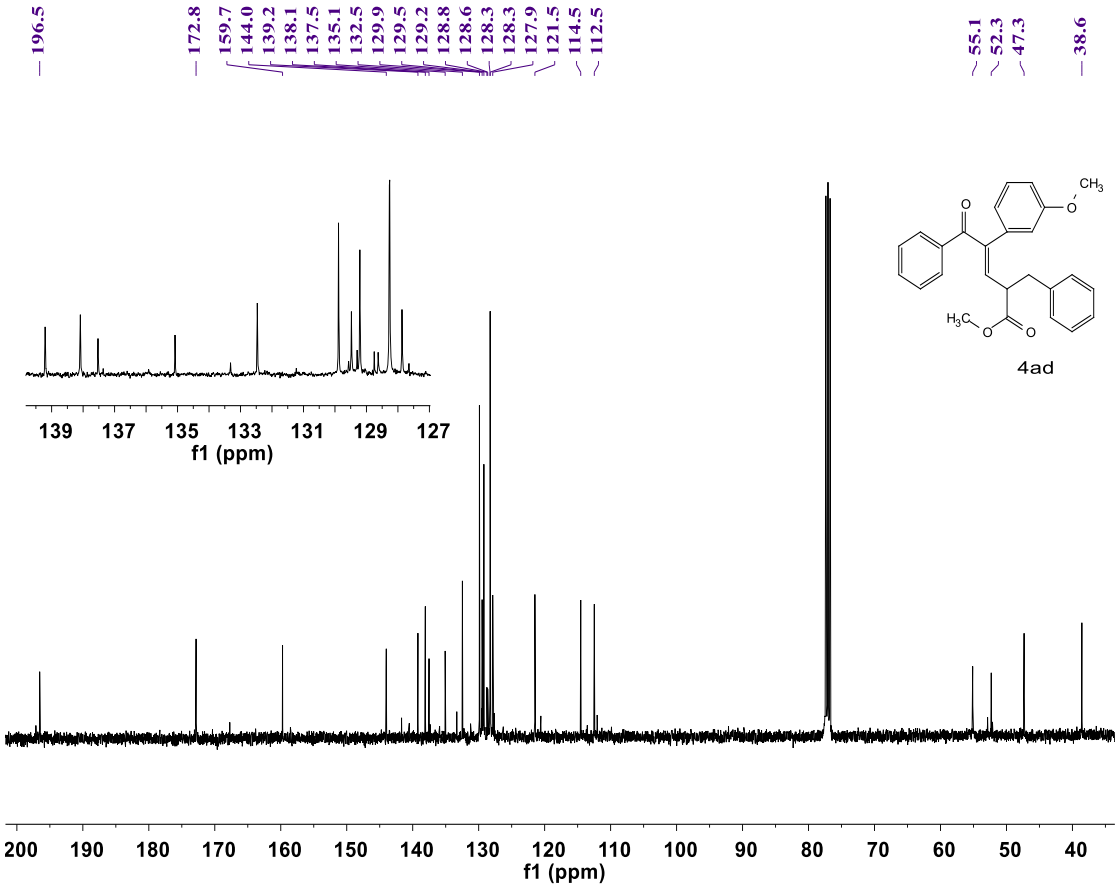
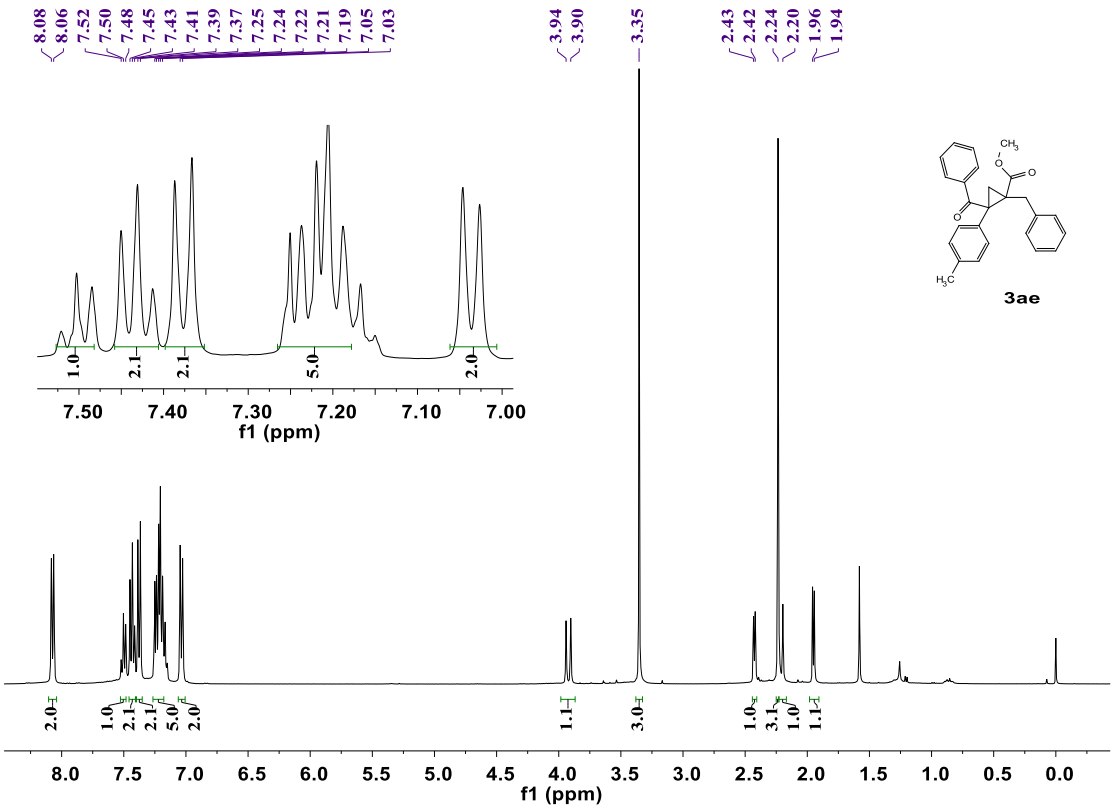
3ad
f1 (ppm)


196.0 170.7 159.4 138.8 137.3 135.8 133.2 129.6 129.3 128.6 128.5 128.4 126.5 122.2 115.7 113.3 55.2 51.9 45.7 38.1 37.6 21.8
3ad
f1 (ppm)


7.65 7.65 7.64 7.63 7.52 7.50 7.41 7.39 7.37 7.32 7.31 7.31 7.30 7.22 7.20 7.18 7.00 6.99 6.99 6.98 6.98 6.81 6.80 6.79 6.78 6.63 6.61 6.54 6.54 6.53 6.29 6.26 3.73 3.70 3.68 3.66 3.65 3.63 3.16 3.15 3.13 3.11 2.87 2.84 2.83 2.81
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6
f1 (ppm)
4ad
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


196.5
172.8
159.7 144.0 139.2 138.1 137.5 135.1 132.5 129.9 129.5 129.2 128.8 128.6 128.3 128.3 127.9 121.5 114.5 112.5
55.1 52.3 47.3 38.6
139 137 135 133 131 129 127
f1 (ppm)
4ad
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40
f1 (ppm)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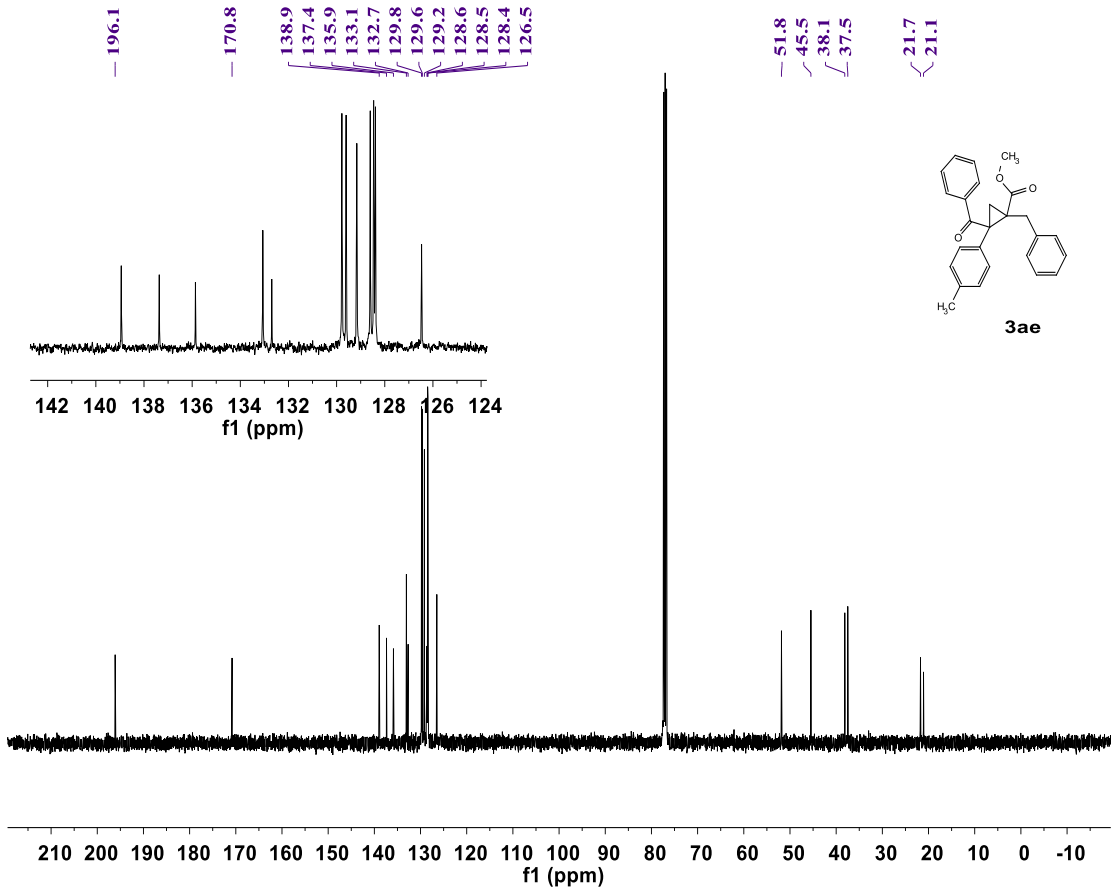
7.50
7.48
7.45
7.43
7.41
7.39
7.37
7.25
7.24
7.22
7.21
7.19
7.05
7.03
3.94
3.90
3.35
2.43
2.42
2.24
2.20
1.96
1.94
1.0
2.1
2.1
5.0
2.0
7.50 7.40 7.30 7.20 7.10 7.00
f1 (ppm)
2.0
1.0
2.1
2.1
5.0
2.0
1.1
3.0
1.0
3.1
1.0
1.1
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
3ae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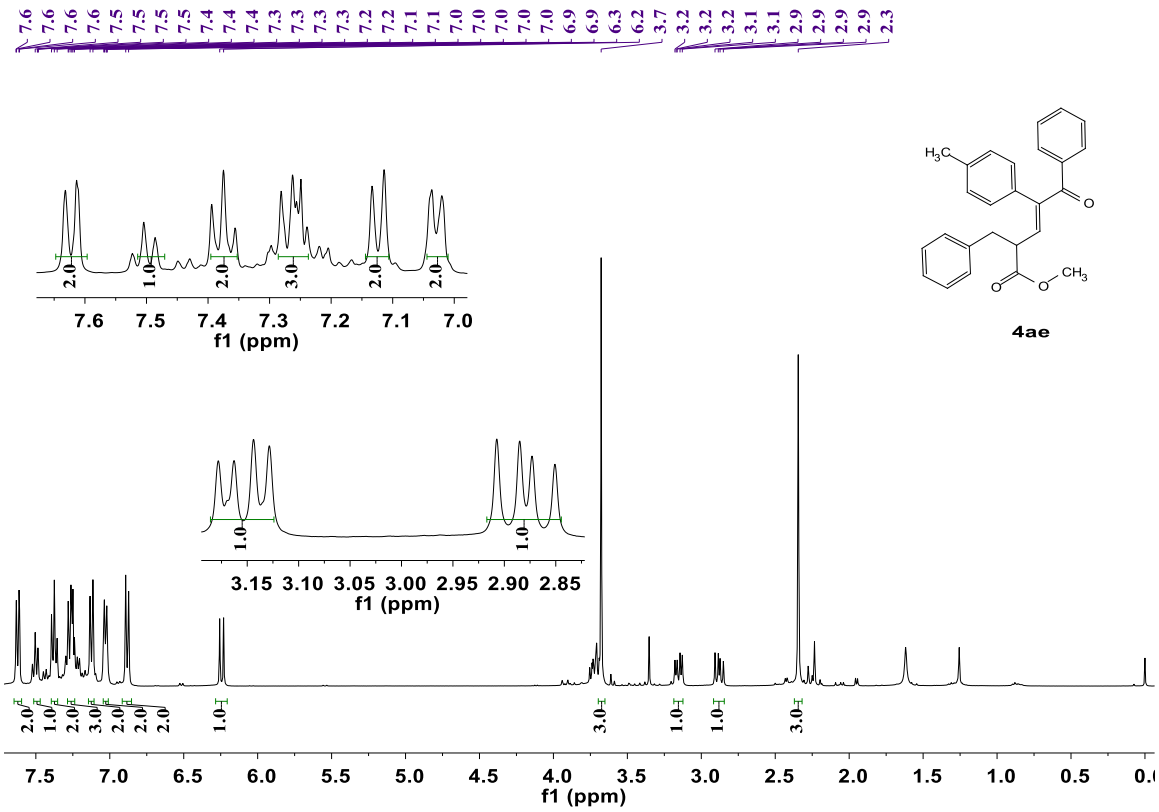
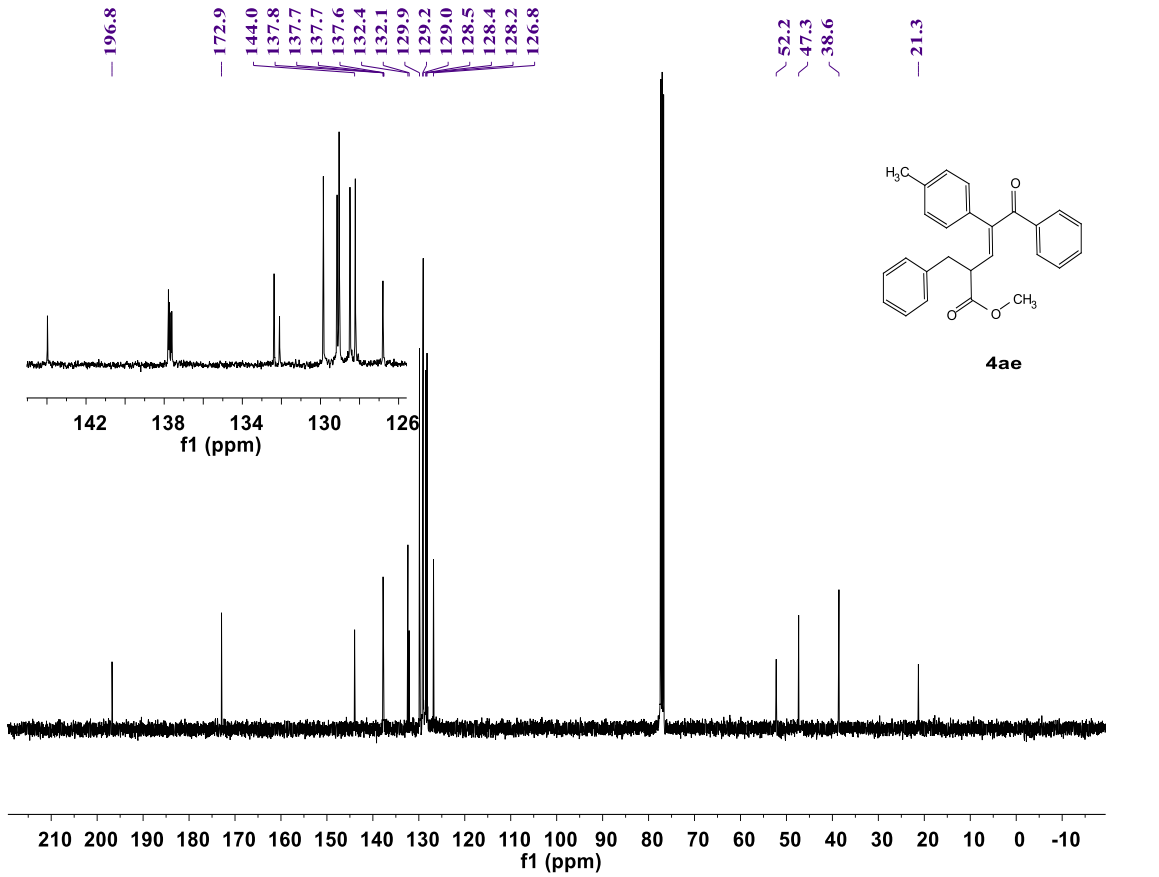
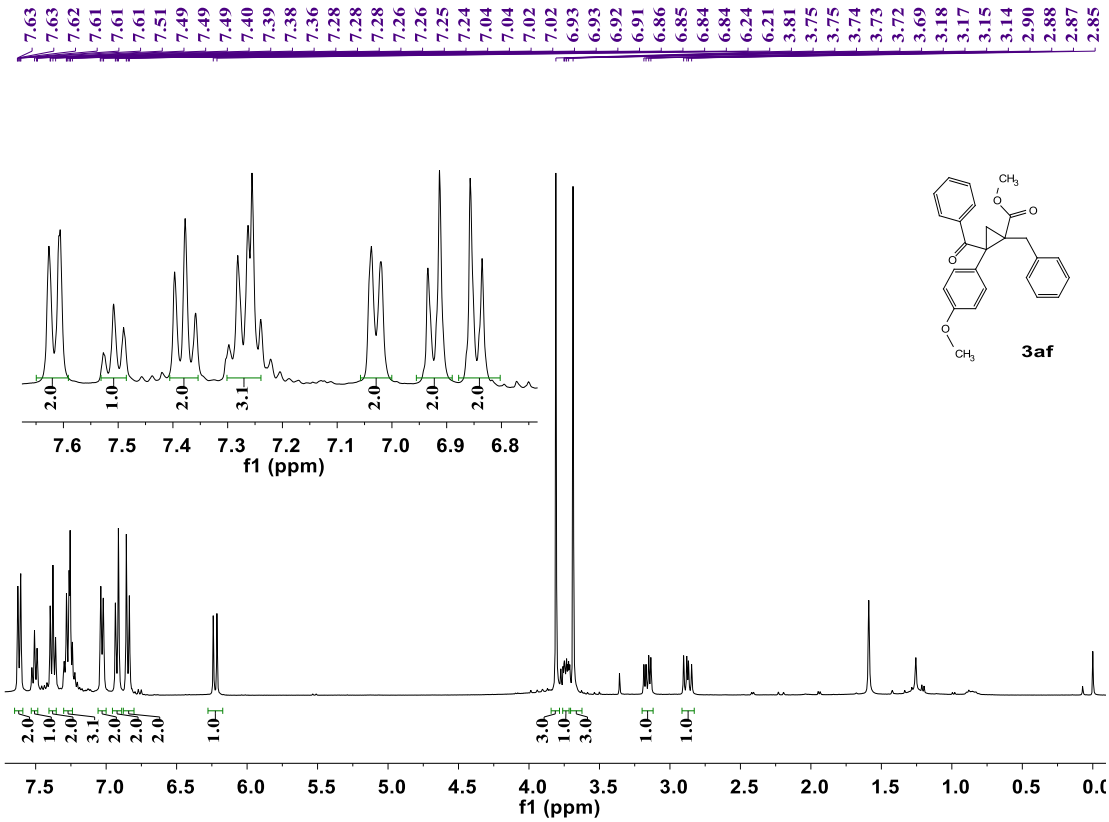
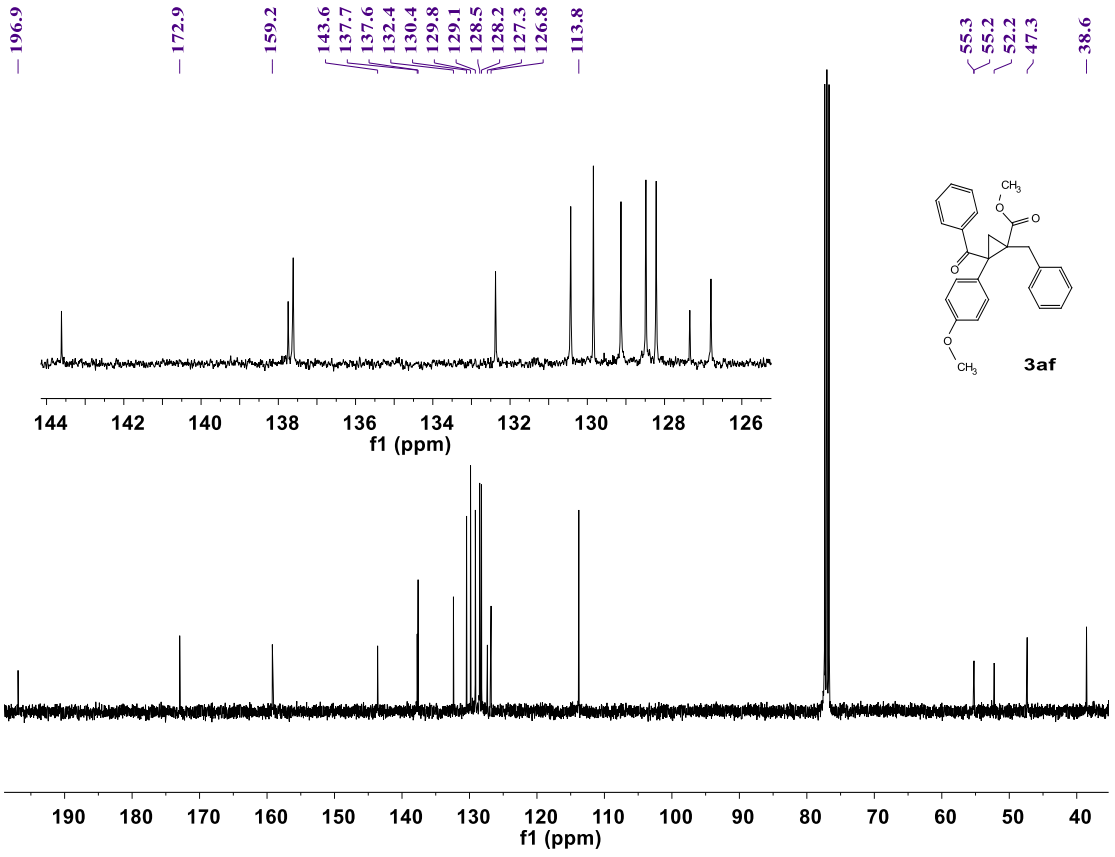
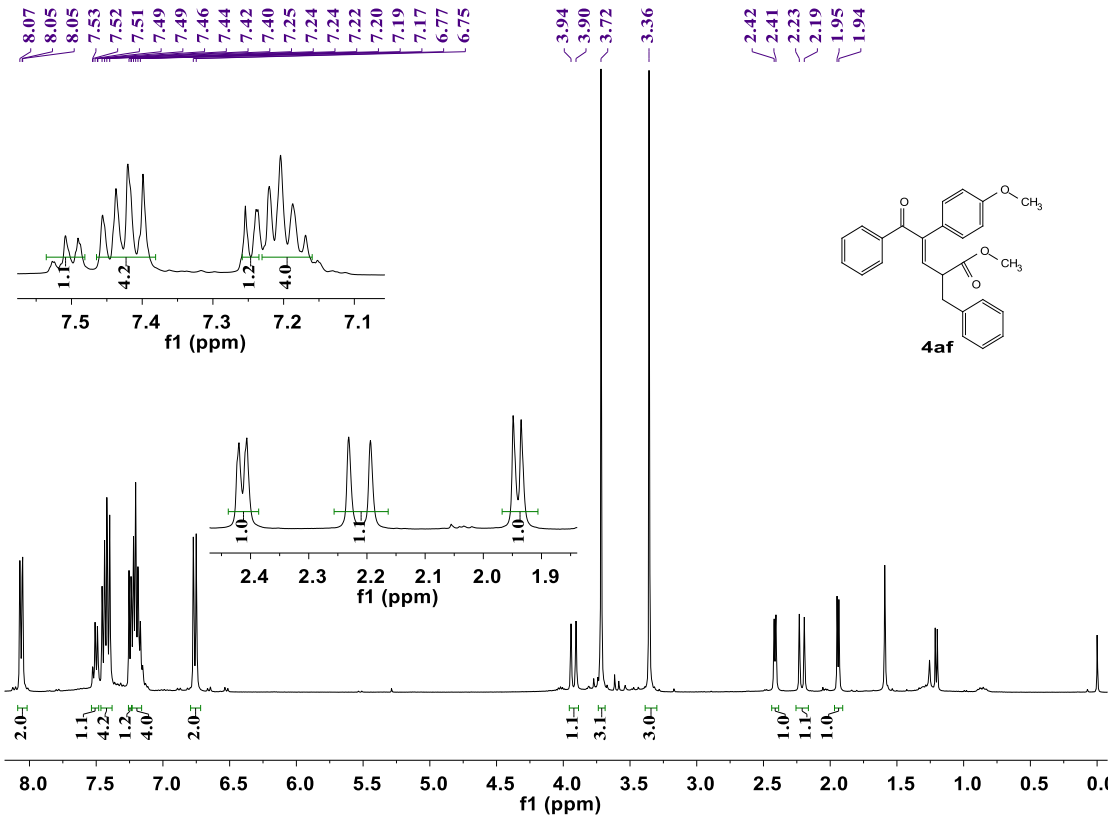
138.9
137.4
135.9
133.1
132.7
129.8
129.6
129.2
128.6
128.5
128.4
126.5
51.8
45.5
38.1
37.5
21.7
21.1
142 140 138 136 134 132 130 128 126 124
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
3ae


7.6 7.6 7.6 7.6 7.5 7.5 7.5 7.5 7.4 7.4 7.4 7.3 7.3 7.3 7.3 7.2 7.2 7.1 7.1 7.0 7.0 7.0 7.0 7.0 6.9 6.9 6.3 6.2 3.7 3.2 3.2 3.2 3.1 3.1 2.9 2.9 2.9 2.9 2.3
2.0 1.0 2.0 3.0 2.0 2.0
7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
1.0 1.0
3.15 3.10 3.05 3.00 2.95 2.90 2.85
f1 (ppm)
2.0 1.0 2.0 3.0 2.0 2.0 2.0 1.0 3.0 1.0 1.0 3.0
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
H3C
O
O
O
CH3
4ae


196.8 172.9 144.0 137.8 137.7 137.7 137.6 132.4 132.1 129.9 129.2 129.0 128.5 128.4 128.2 126.8 52.2 47.3 38.6 21.3
142 138 134 130 126
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
H3C
O
O
O
CH3
4ae


7.63 7.63 7.62 7.61 7.61 7.61 7.51 7.49 7.49 7.49 7.40 7.39 7.38 7.36 7.28 7.28 7.28 7.26 7.26 7.25 7.24 7.04 7.04 7.02 7.02 6.93 6.93 6.92 6.91 6.86 6.85 6.84 6.84 6.24 6.21 3.81 3.75 3.75 3.74 3.73 3.72 3.69 3.18 3.17 3.15 3.14 2.90 2.88 2.87 2.85
3af
f1 (ppm)
f1 (ppm)


196.9 172.9 159.2 143.6 137.7 137.6 132.4 130.4 129.8 129.1 128.5 128.2 127.3 126.8 113.8 55.3 55.2 52.2 47.3 38.6
3af
f1 (ppm)
f1 (ppm)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8.05
8.05
7.53
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7.49
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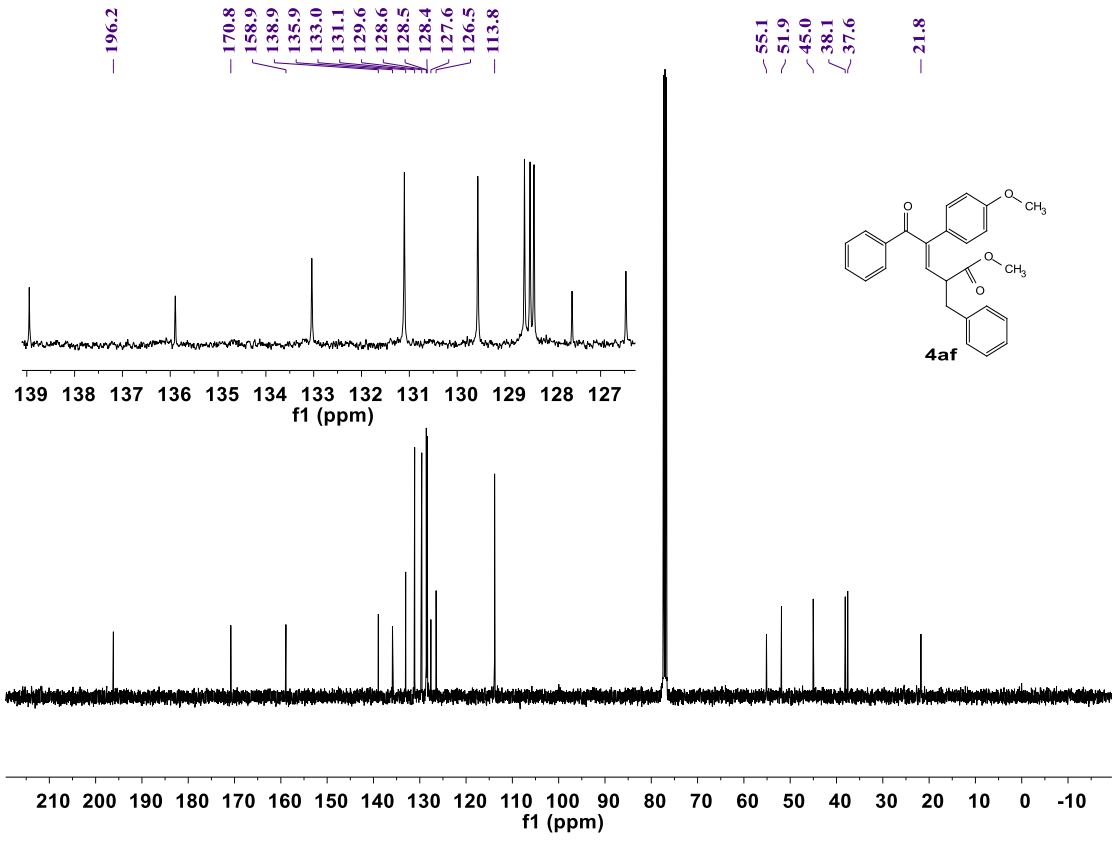
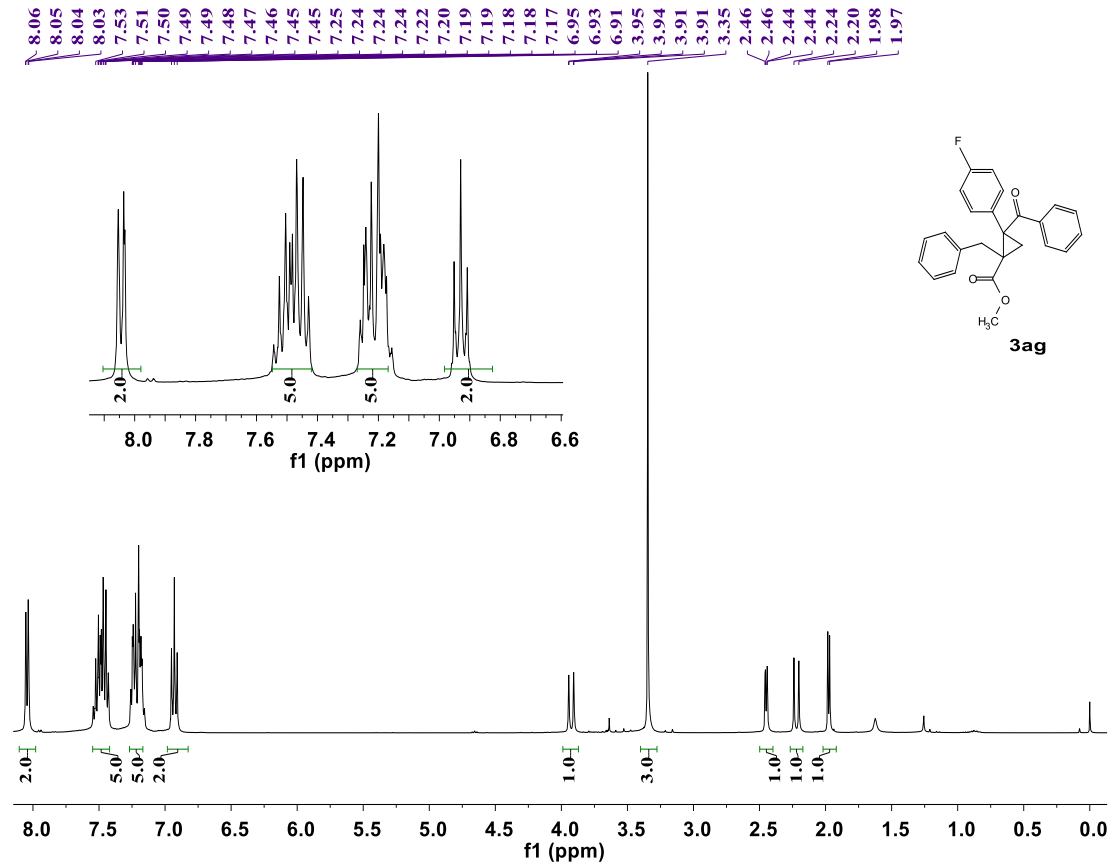
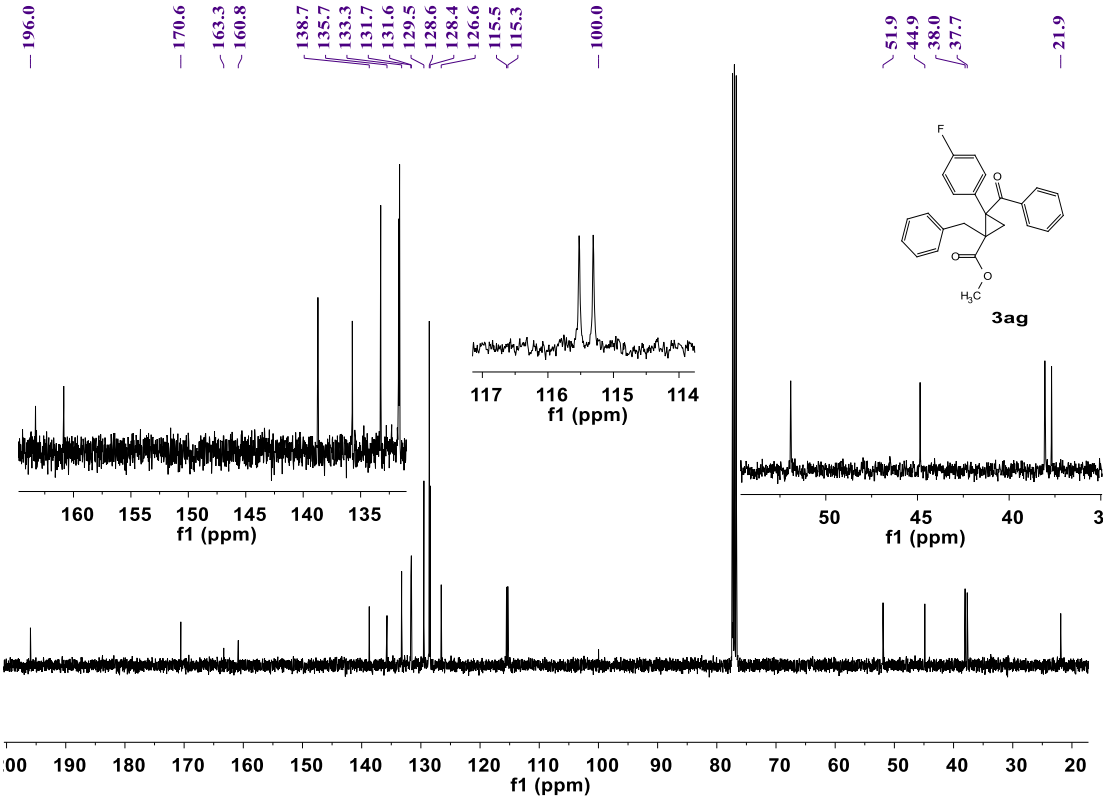
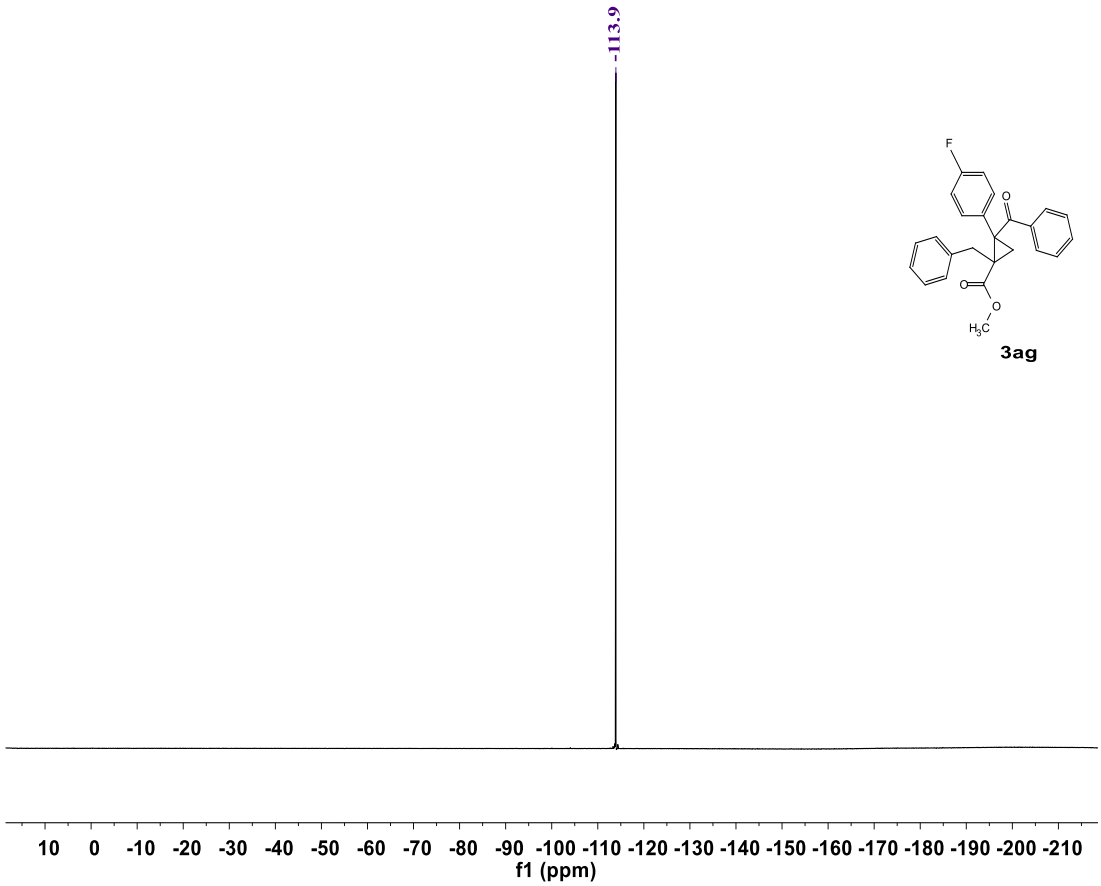
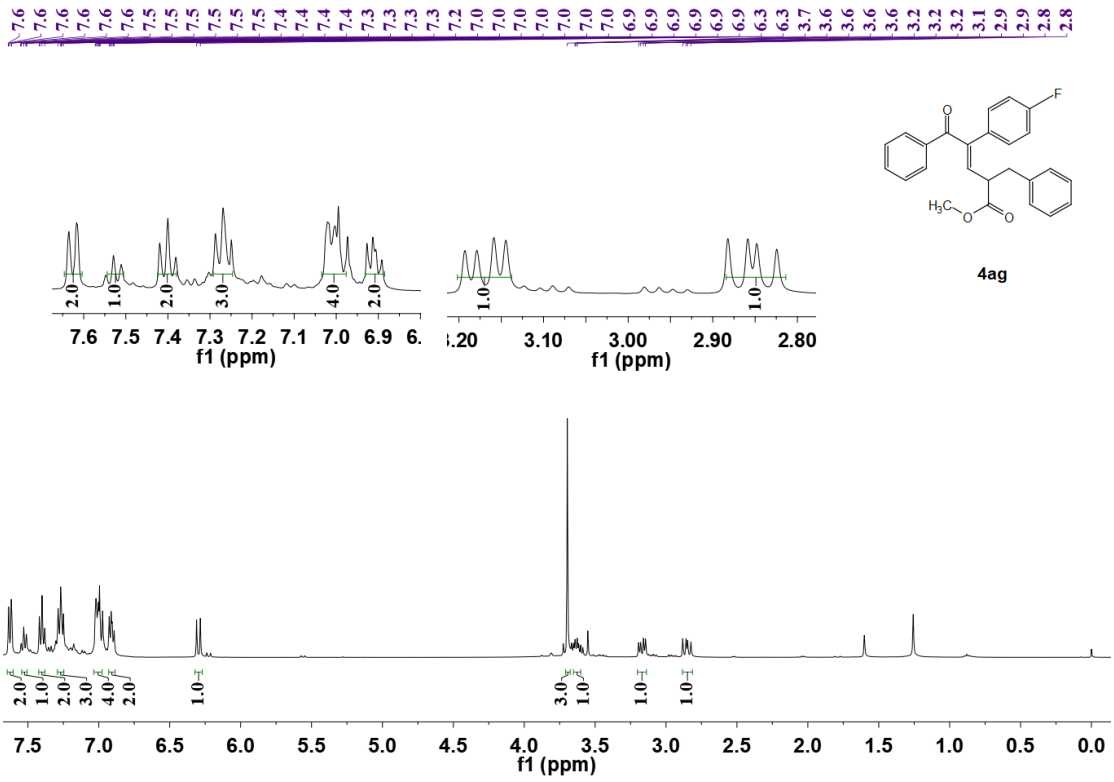
7.40
7.25
7.24
7.24
7.22
7.20
7.19
7.17
6.77
6.75
3.94
3.90
3.72
3.36
2.42
2.41
2.23
2.19
1.95
1.94
1.1
4.2
1.2
4.0
7.5 7.4 7.3 7.2 7.1
f1 (ppm)
1.0
1.1
1.0
2.4 2.3 2.2 2.1 2.0 1.9
f1 (ppm)
4af
2.0
1.1
4.2
1.2
4.0
2.0
1.1
3.1
3.0
1.0
1.1
1.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

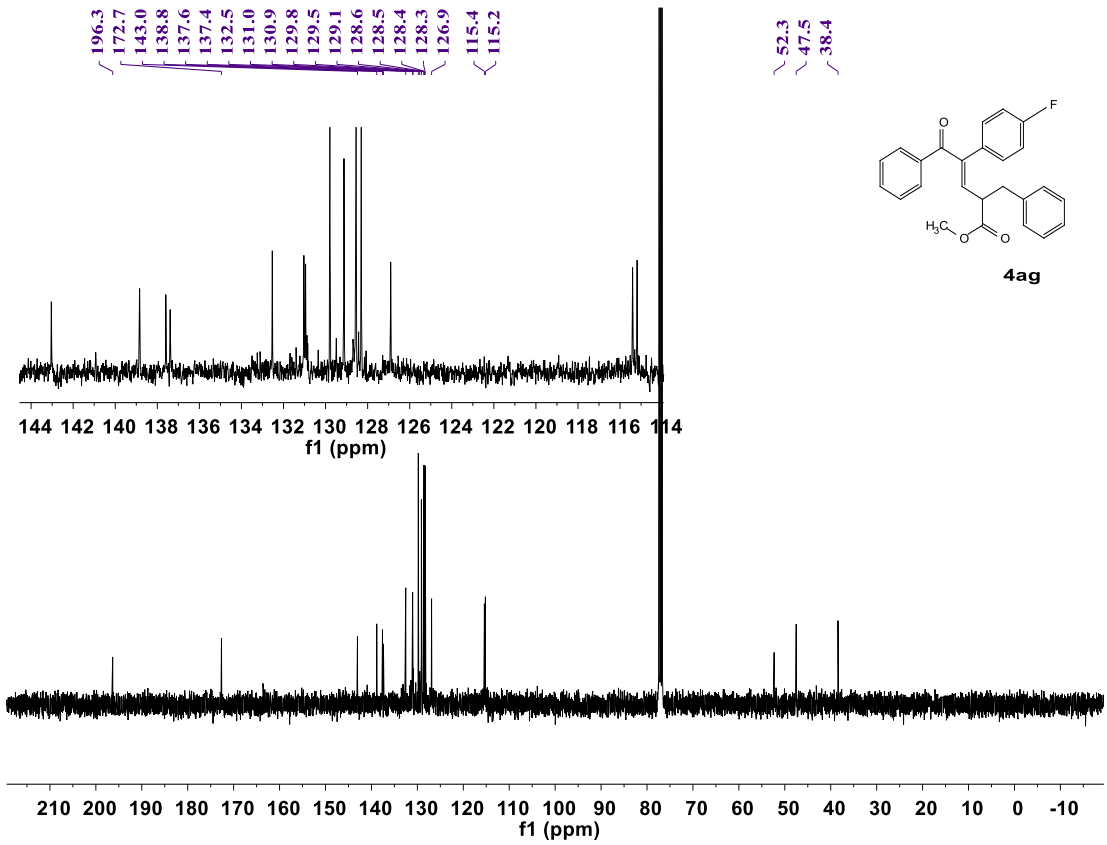

196.2
170.8
158.9
138.9
135.9
133.0
131.1
129.6
128.6
128.5
128.4
127.6
126.5
113.8
55.1
51.9
45.0
38.1
37.6
21.8
139 138 137 136 135 134 133 132 131 130 129 128 127
f1 (ppm)
4af
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.06 8.05 8.04 8.03 7.53 7.51 7.50 7.49 7.49 7.48 7.47 7.46 7.45 7.45 7.25 7.24 7.24 7.24 7.22 7.20 7.19 7.19 7.18 7.18 7.17 6.95 6.93 6.91 3.95 3.94 3.91 3.91 3.35 2.46 2.46 2.44 2.44 2.24 2.20 1.98 1.97
F
O
O
O
H3C
3ag
2.0 5.0 5.0 2.0
8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6
f1 (ppm)
2.0 5.0 5.0 2.0 1.0 3.0 1.0 1.0 1.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

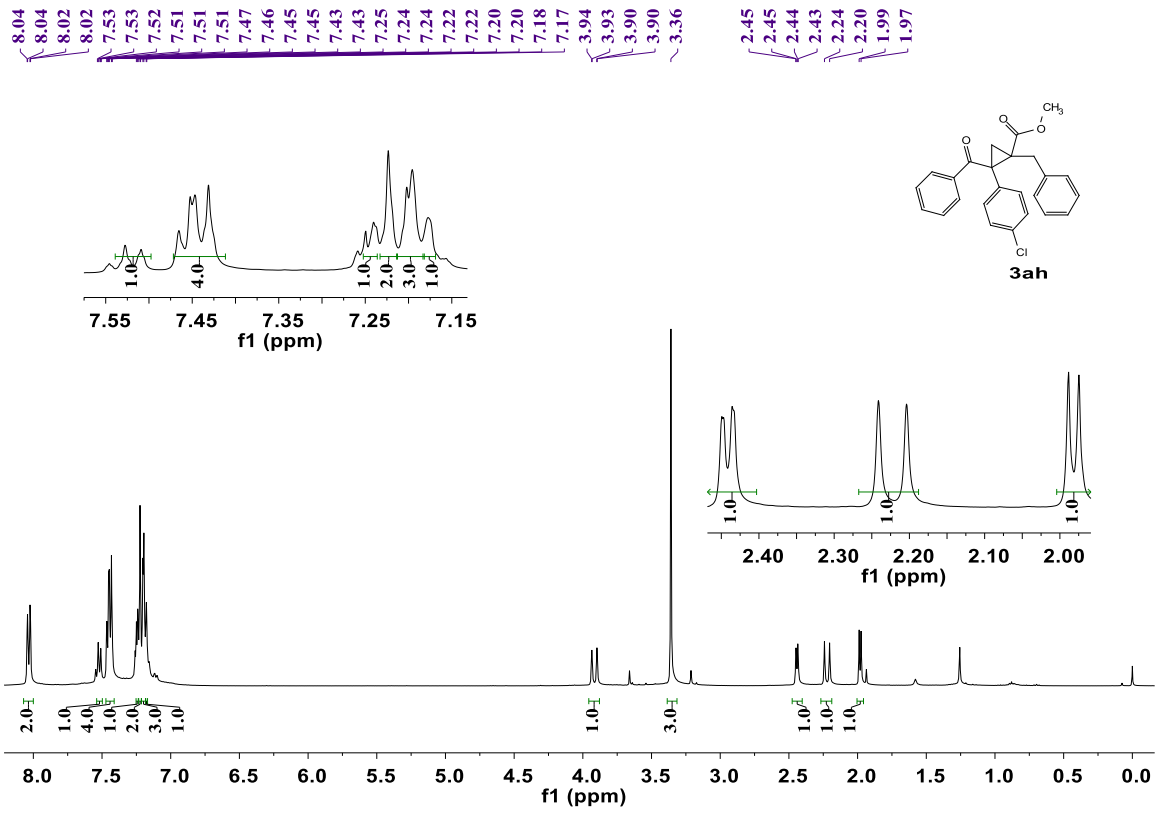

196.0 170.6 163.3 160.8 138.7 135.7 133.3 131.7 131.6 129.5 128.6 128.4 126.6 115.5 115.3 100.0 51.9 44.9 38.0 37.7 21.9
F
O
O
O
H3C
3ag
117 116 115 114
f1 (ppm)
160 155 150 145 140 135
f1 (ppm)
50 45 40
f1 (ppm)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

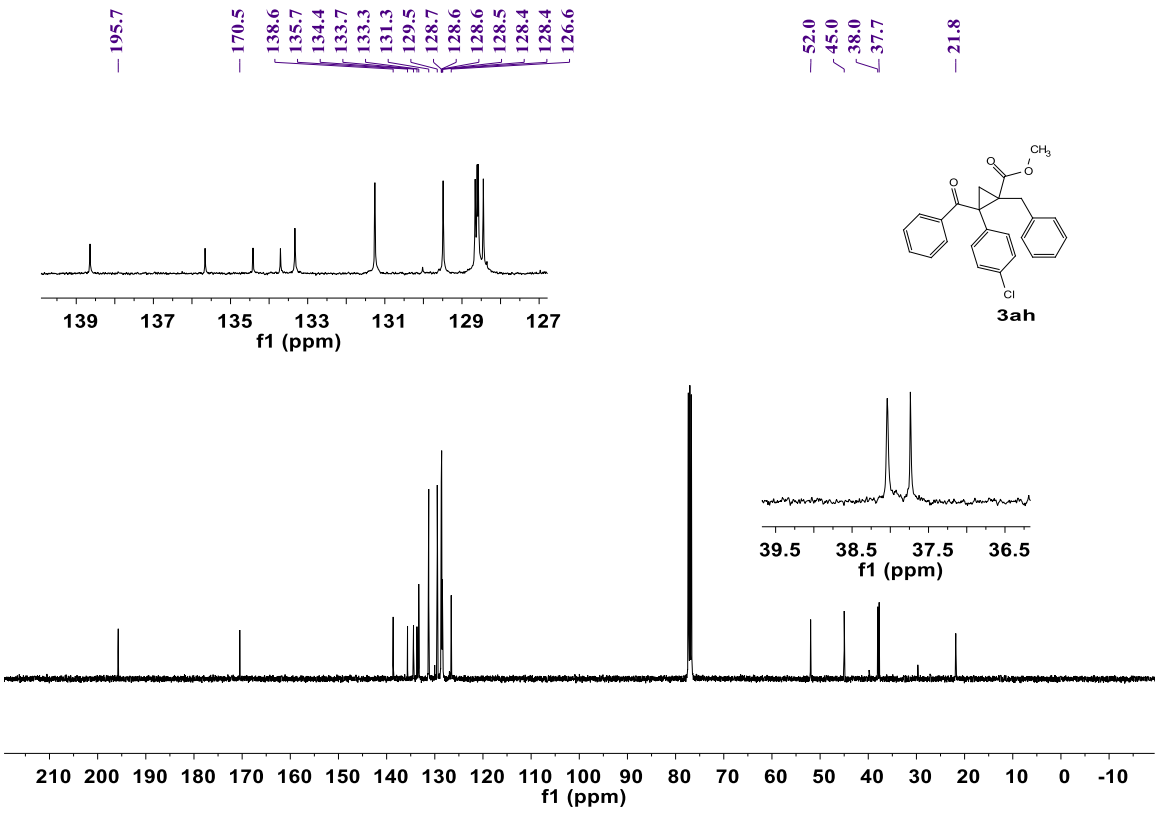

-113.9
F
O
O
O
H3C
3ag
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

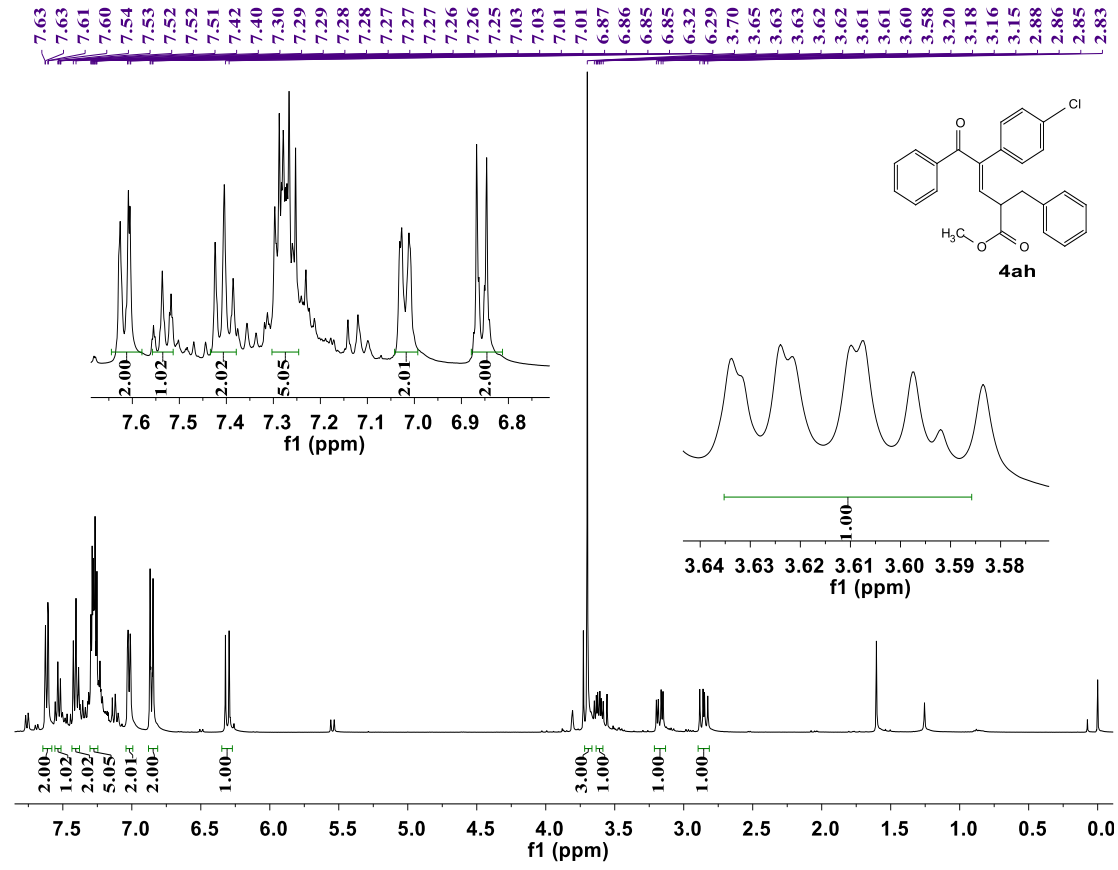

7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
3.20 3.10 3.00 2.90 2.80
f1 (ppm)
F
O
H3C
O
O
4ag
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

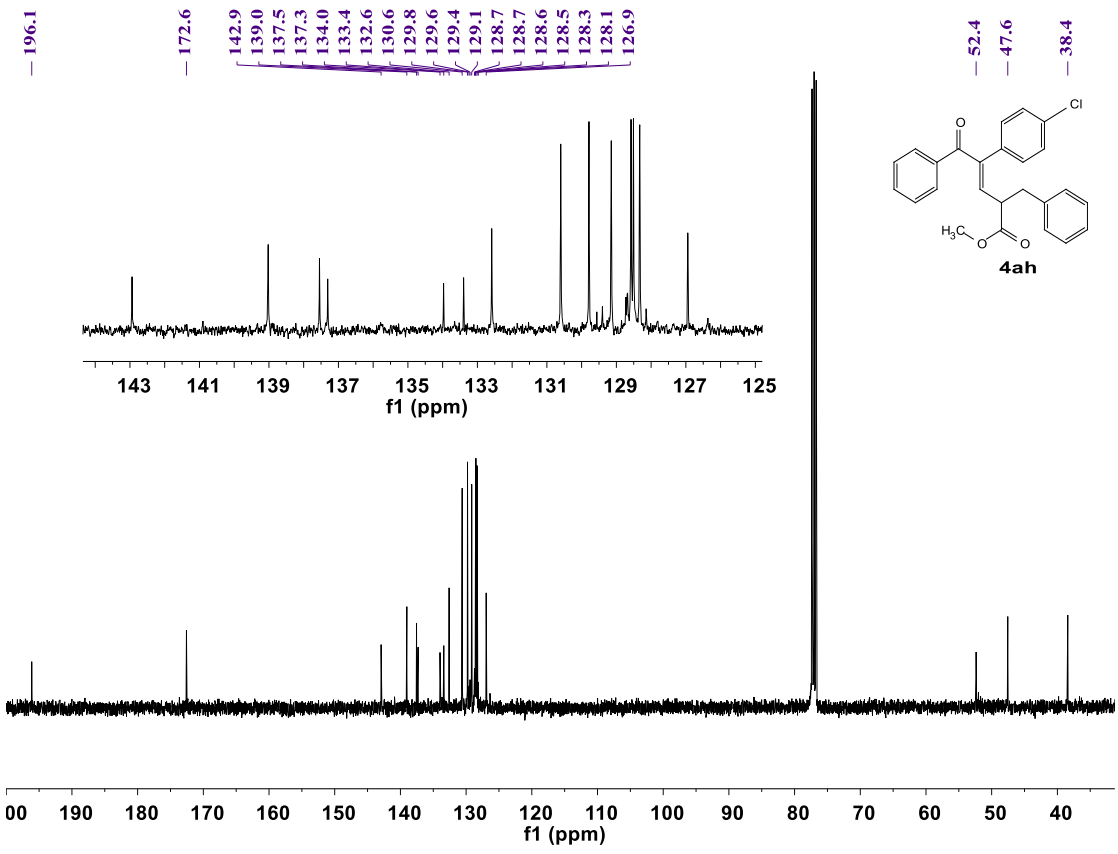

196.3
172.7
143.0
138.8
137.6
137.4
132.5
131.0
130.9
129.8
129.5
129.1
128.6
128.5
128.4
128.3
126.9
115.4
115.2
52.3
47.5
38.4
F
O
H3C
O
O
4ag
144 142 140 138 136 134 132 130 128 126 124 122 120 118 116 114
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

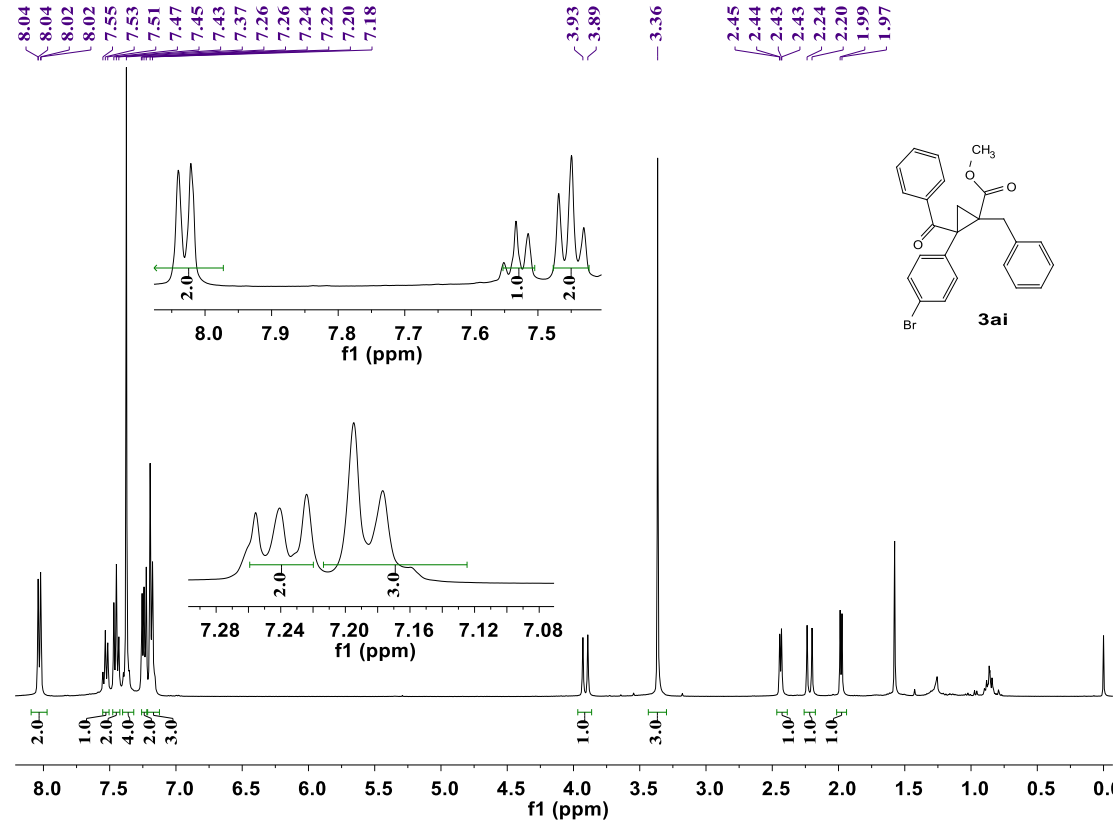

-113.9
F
O
H3C
O
O
4ag
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

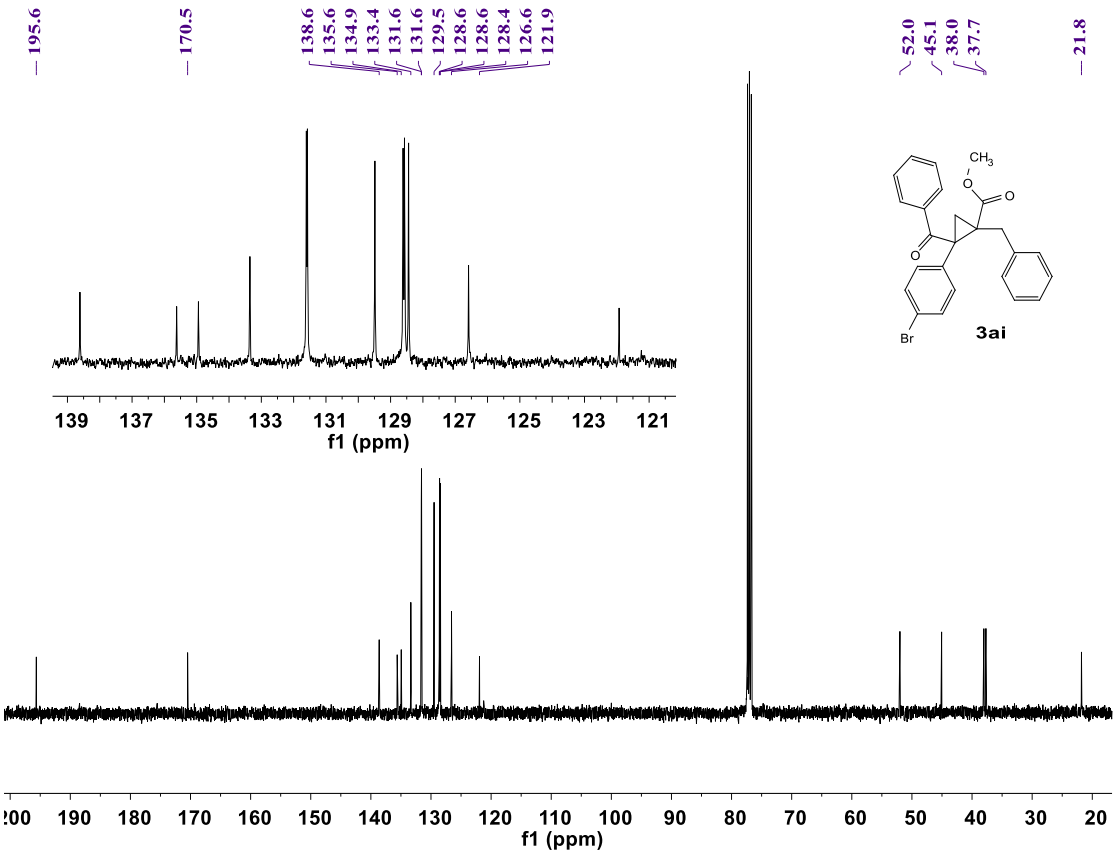

8.04 8.04 8.02 8.02 7.53 7.53 7.52 7.51 7.51 7.51 7.47 7.46 7.45 7.45 7.43 7.43 7.25 7.24 7.24 7.22 7.22 7.20 7.20 7.18 7.17 3.94 3.93 3.90 3.90 3.36 2.45 2.45 2.44 2.43 2.24 2.20 1.99 1.97
3ah
f1 (ppm)

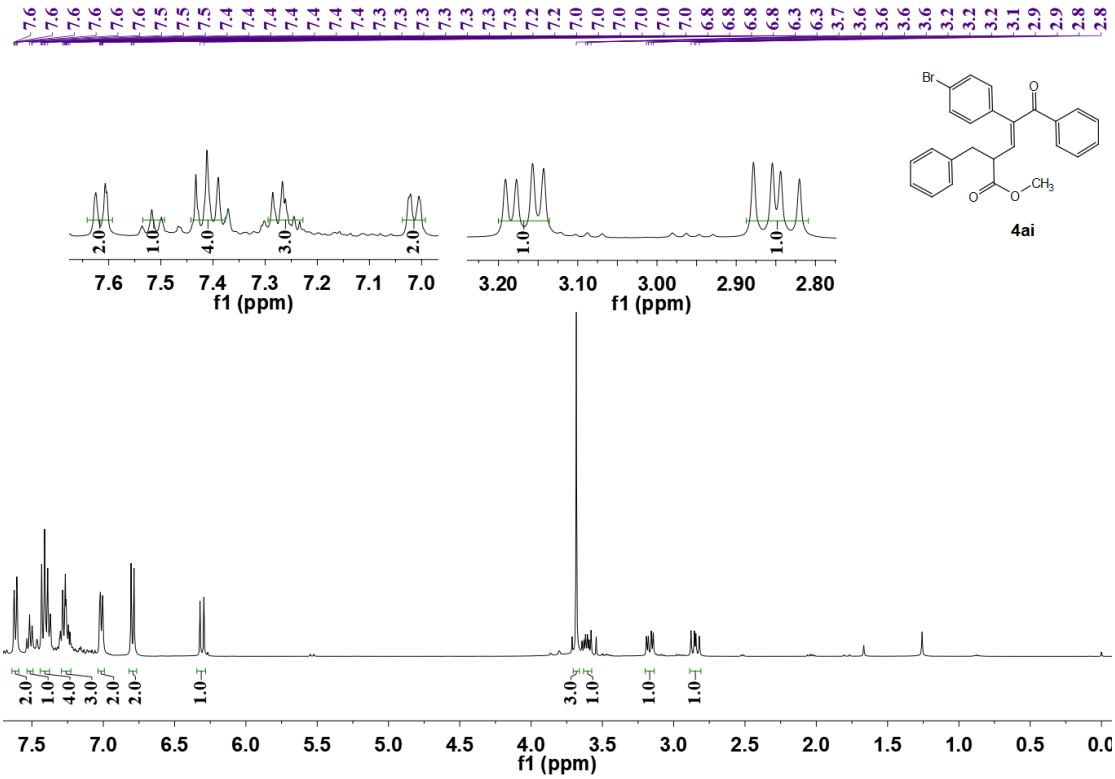

195.7 170.5 138.6 135.7 134.4 133.7 133.3 131.3 129.5 128.7 128.6 128.6 128.5 128.4 128.4 126.6 52.0 45.0 38.0 37.7 21.8
3ah
f1 (ppm)

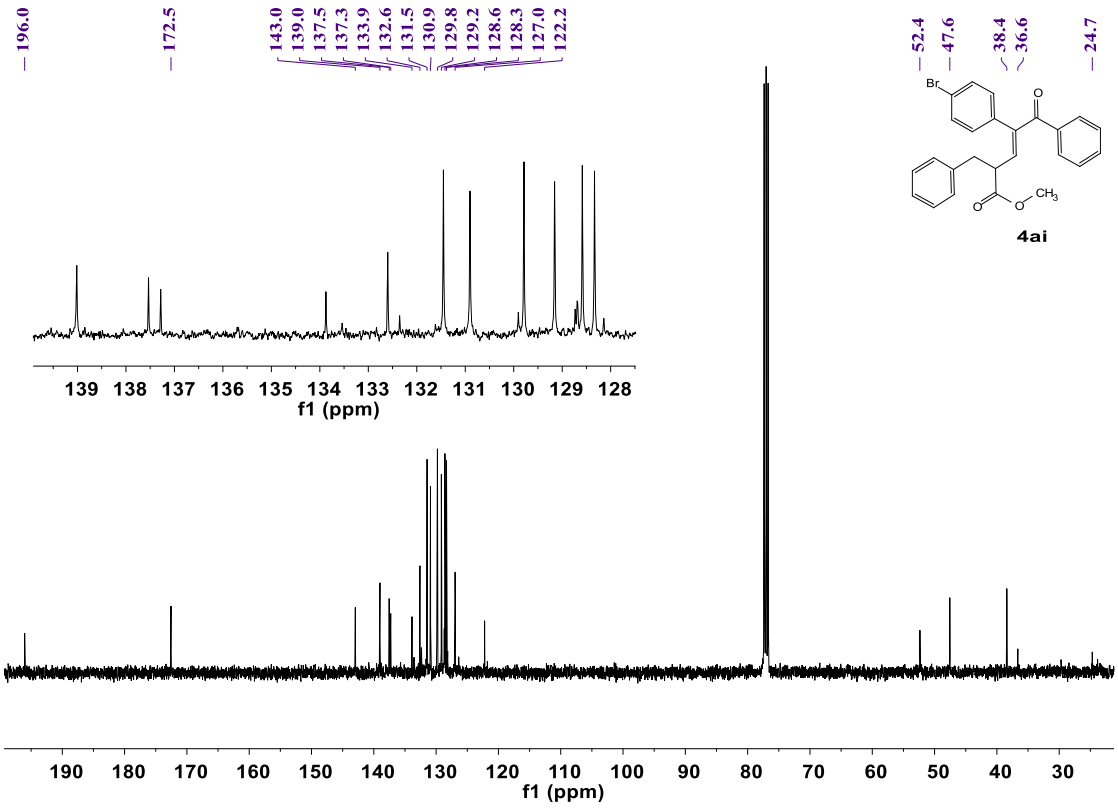

7.63 7.63 7.61 7.60 7.54 7.53 7.52 7.52 7.51 7.42 7.40 7.30 7.29 7.29 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.25 7.03 7.03 7.01 7.01 6.87 6.86 6.85 6.85 6.32 6.29 3.70 3.65 3.63 3.63 3.62 3.62 3.61 3.61 3.60 3.58 3.20 3.18 3.16 3.15 2.88 2.86 2.85 2.83
Cl
O
H3C
O
O
4ah
2.00 1.02 2.02 5.05 2.01 2.00
7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
1.00
3.64 3.63 3.62 3.61 3.60 3.59 3.58
f1 (ppm)
2.00 1.02 2.02 5.05 2.01 2.00 1.00 3.00 1.00 1.00 1.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

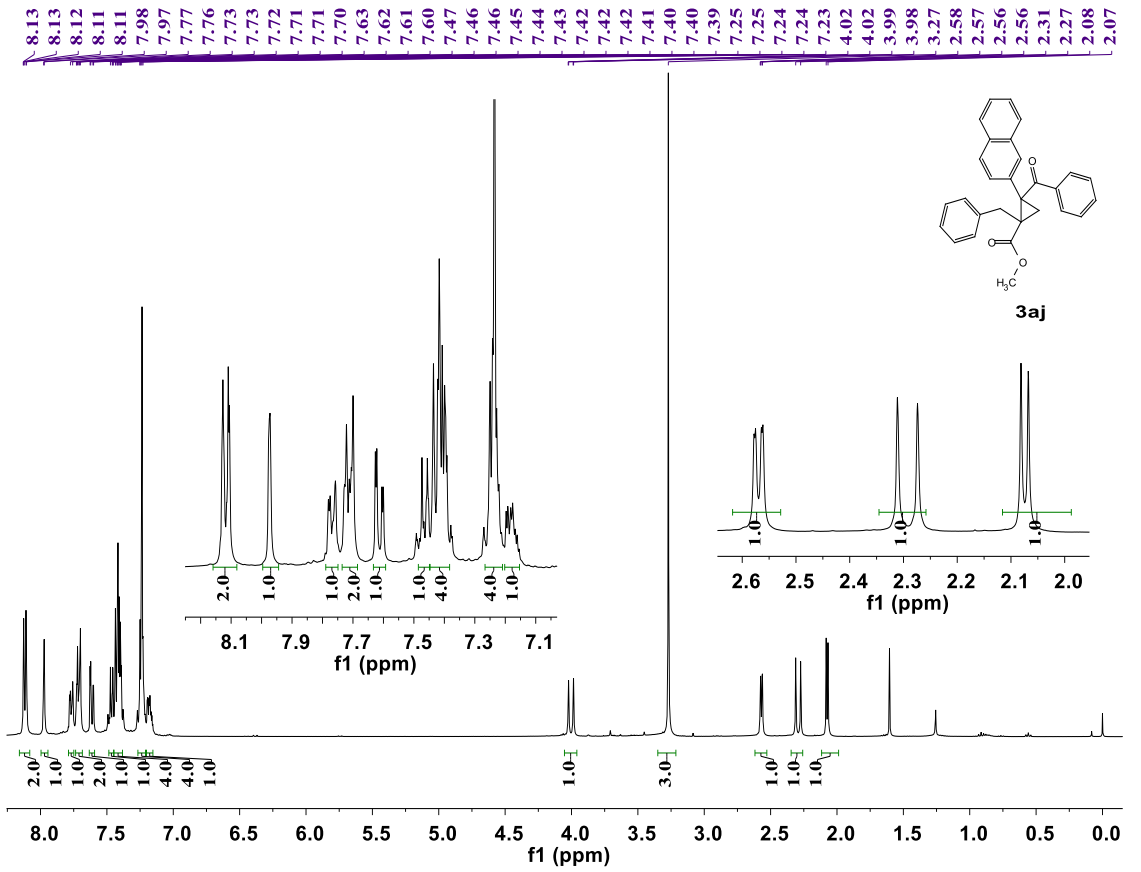

196.1
172.6
142.9 139.0 137.5 137.3 134.0 133.4 132.6 130.6 129.8 129.6 129.4 129.1 128.7 128.7 128.6 128.5 128.3 128.1 126.9
52.4
47.6
38.4
Cl
O
H3C
O
O
4ah
143 141 139 137 135 133 131 129 127 125
f1 (ppm)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40
f1 (ppm)

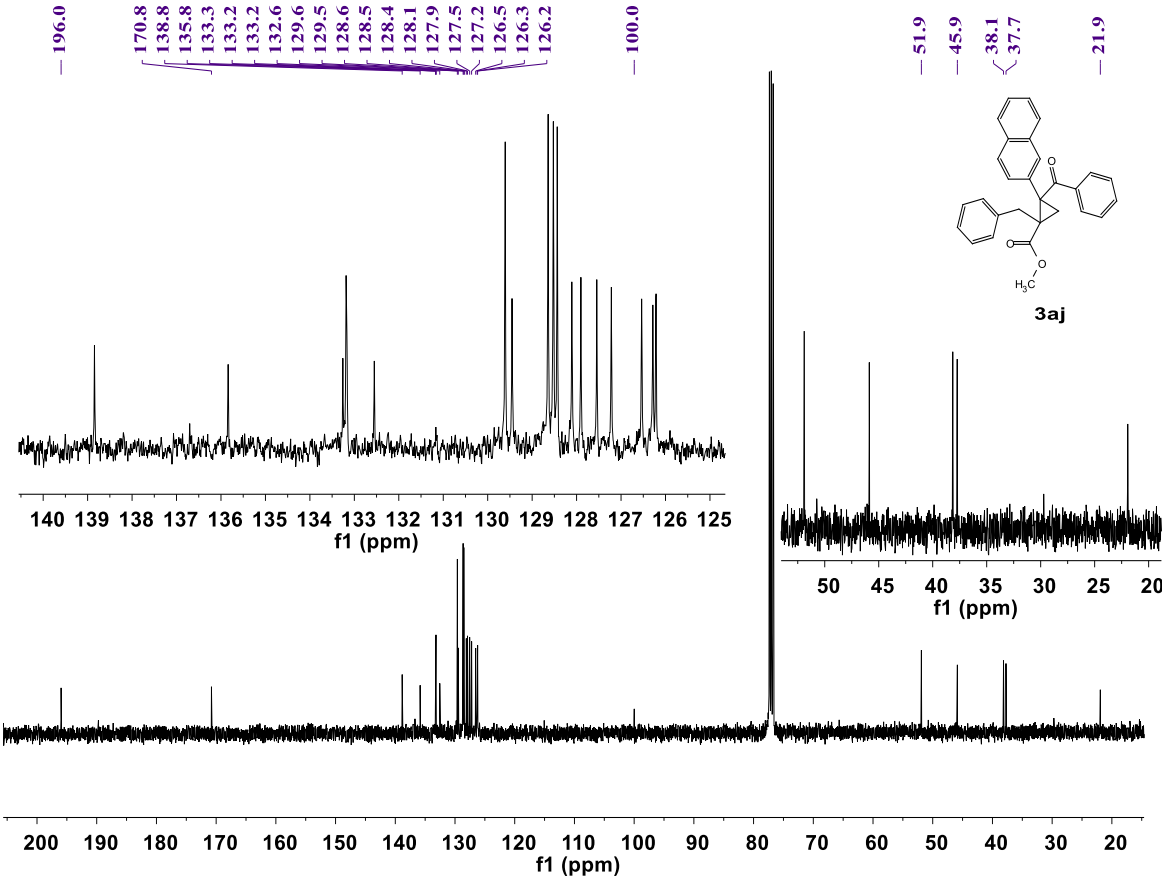

8.04
8.04
8.02
8.02
7.55
7.53
7.51
7.47
7.45
7.43
7.37
7.26
7.26
7.24
7.22
7.20
7.18
3.93
3.89
3.36
2.45
2.44
2.43
2.43
2.24
2.20
1.99
1.97
2.0
1.0
2.0
4.0
2.0
3.0
1.0
3.0
1.0
1.0
1.0
f1 (ppm)
3ai

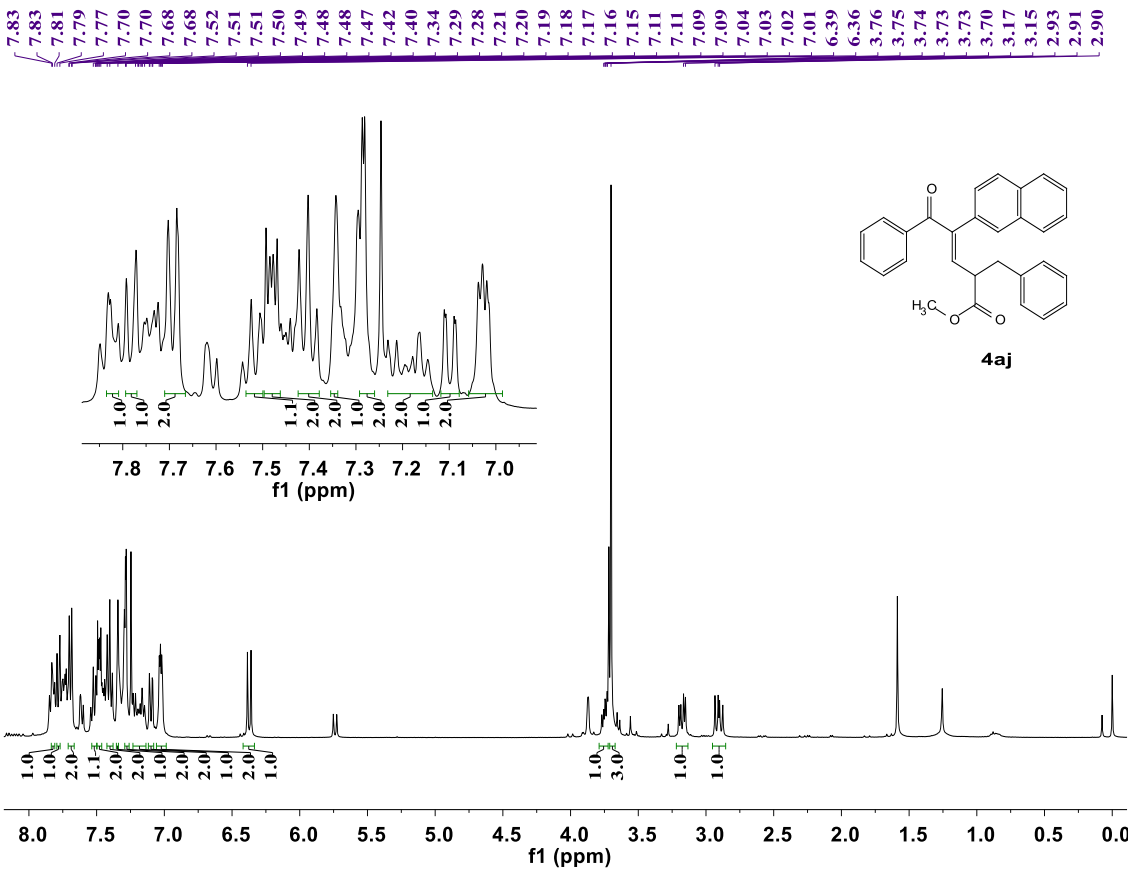

195.6
170.5
138.6
135.6
134.9
133.4
131.6
131.6
129.5
128.6
128.6
128.4
126.6
121.9
52.0
45.1
38.0
37.7
21.8
f1 (ppm)
3ai

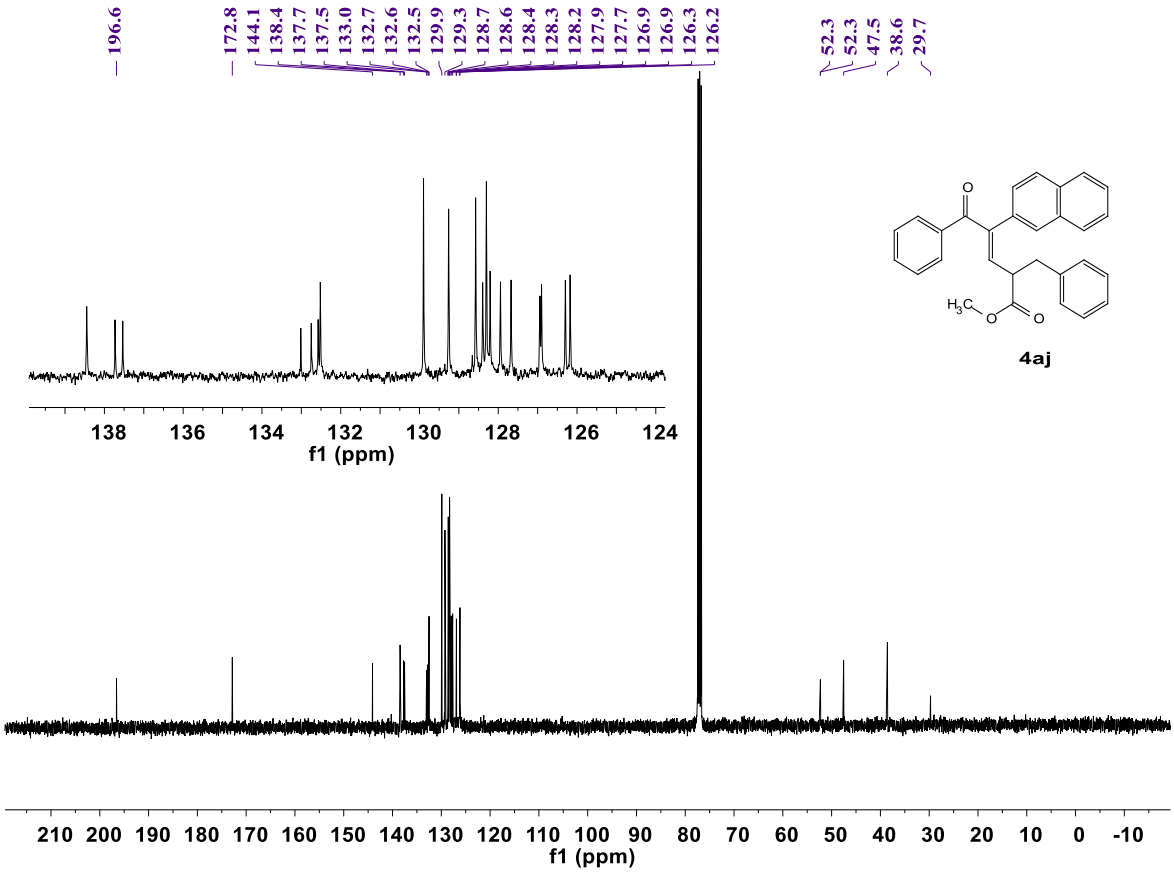

7.6 7.6 7.6 7.6 7.6 7.6 7.5 7.5 7.5 7.4 7.4 7.4 7.4 7.4 7.4 7.3 7.3 7.3 7.3 7.3 7.3 7.3 7.2 7.2 7.0 7.0 7.0 7.0 7.0 7.0 6.8 6.8 6.8 6.8 6.3 6.3 3.7 3.6 3.6 3.6 3.6 3.2 3.2 3.2 3.1 2.9 2.9 2.8 2.8
Br
O
O
O
CH3
4ai
2.0 1.0 4.0 3.0 2.0
7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
1.0 1.0
3.20 3.10 3.00 2.90 2.80
f1 (ppm)
2.0 1.0 4.0 3.0 2.0 2.0 1.0 3.0 1.0 1.0 1.0
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

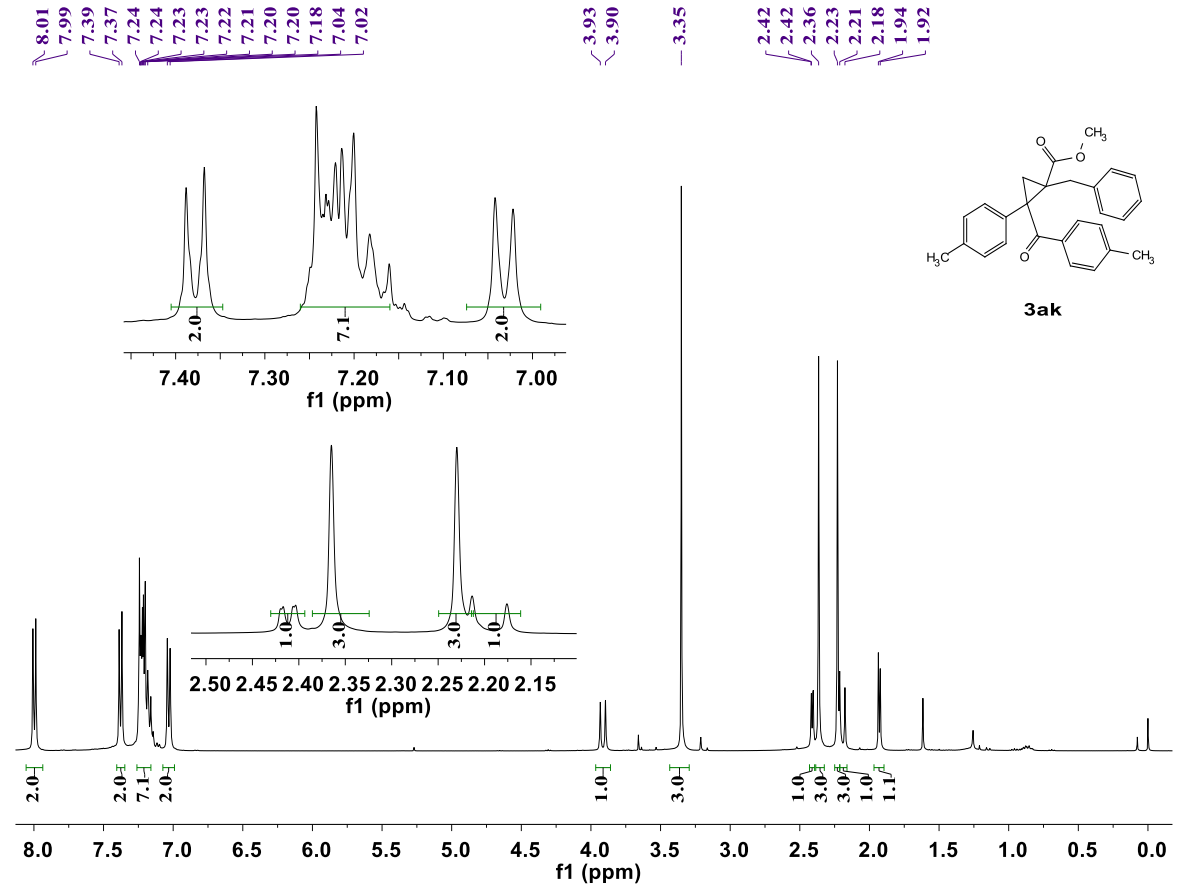

196.0
172.5
143.0 139.0 137.5 137.3 133.9 132.6 131.5 130.9 129.8 129.2 128.6 128.3 127.0 122.2
52.4 47.6 38.4 36.6 24.7
Br
O
O
O
CH3
4ai
139 138 137 136 135 134 133 132 131 130 129 128
f1 (ppm)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
f1 (ppm)

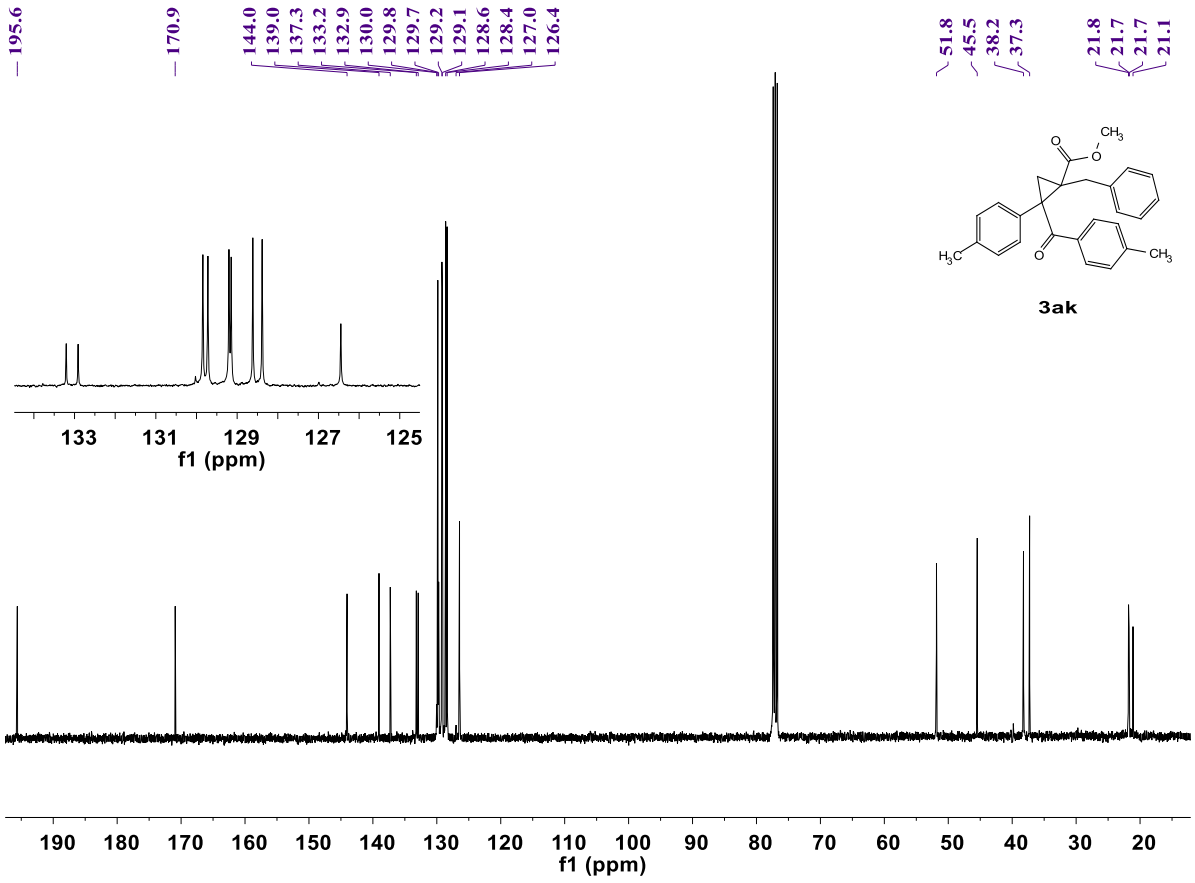

8.13 8.13 8.12 8.11 8.11 7.98 7.97 7.77 7.76 7.73 7.73 7.72 7.71 7.71 7.70 7.63 7.62 7.61 7.60 7.47 7.46 7.46 7.45 7.44 7.43 7.42 7.42 7.42 7.41 7.40 7.40 7.39 7.25 7.25 7.24 7.24 7.23 4.02 4.02 3.99 3.98 3.27 2.58 2.57 2.56 2.56 2.31 2.27 2.08 2.07
3aj
f1 (ppm)

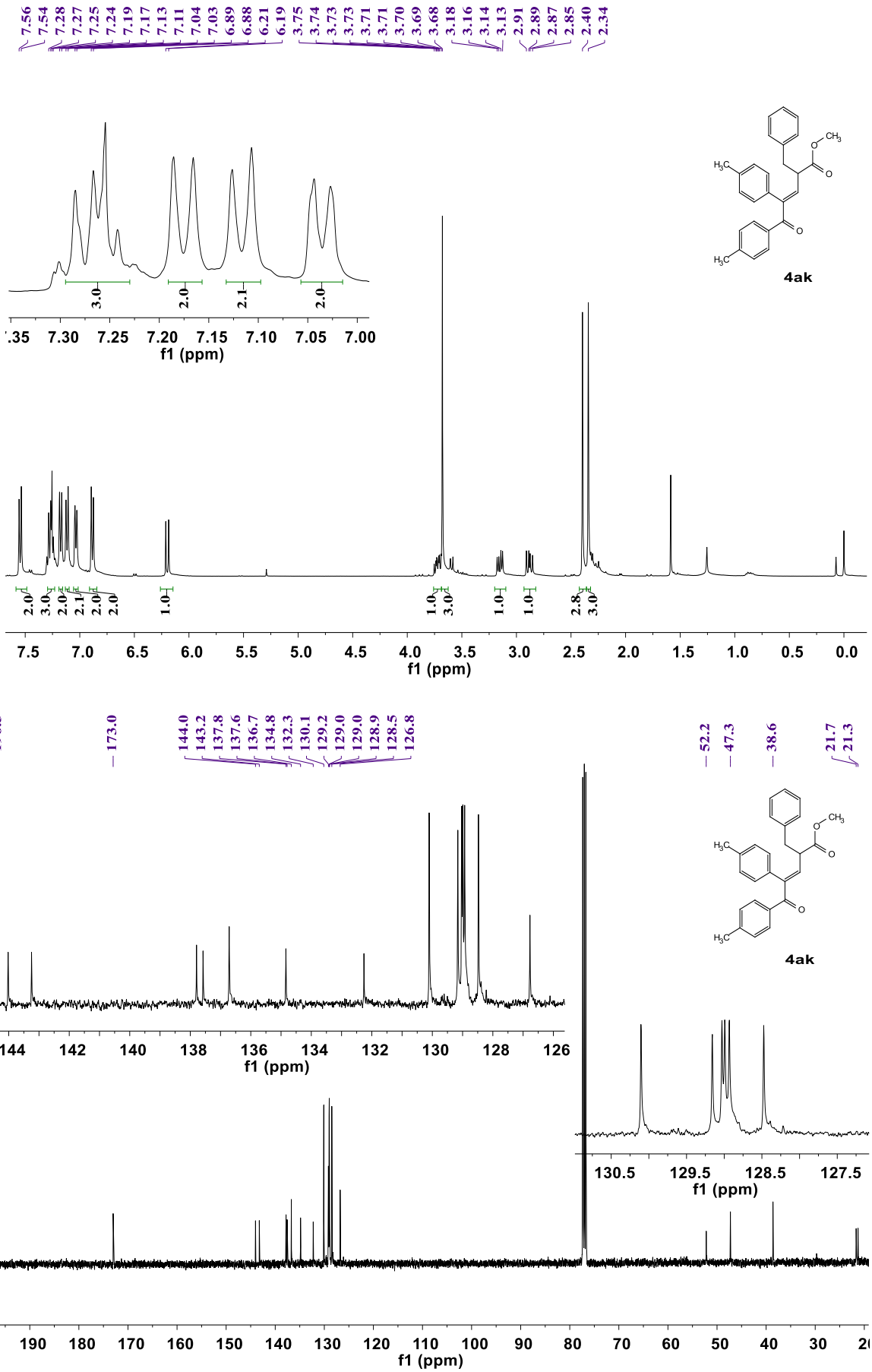

196.0 170.8 138.8 135.8 133.3 133.2 133.2 132.6 129.6 129.5 128.6 128.5 128.4 128.1 127.9 127.5 127.2 126.5 126.3 126.2 100.0 51.9 45.9 38.1 37.7 21.9
3aj
f1 (ppm)

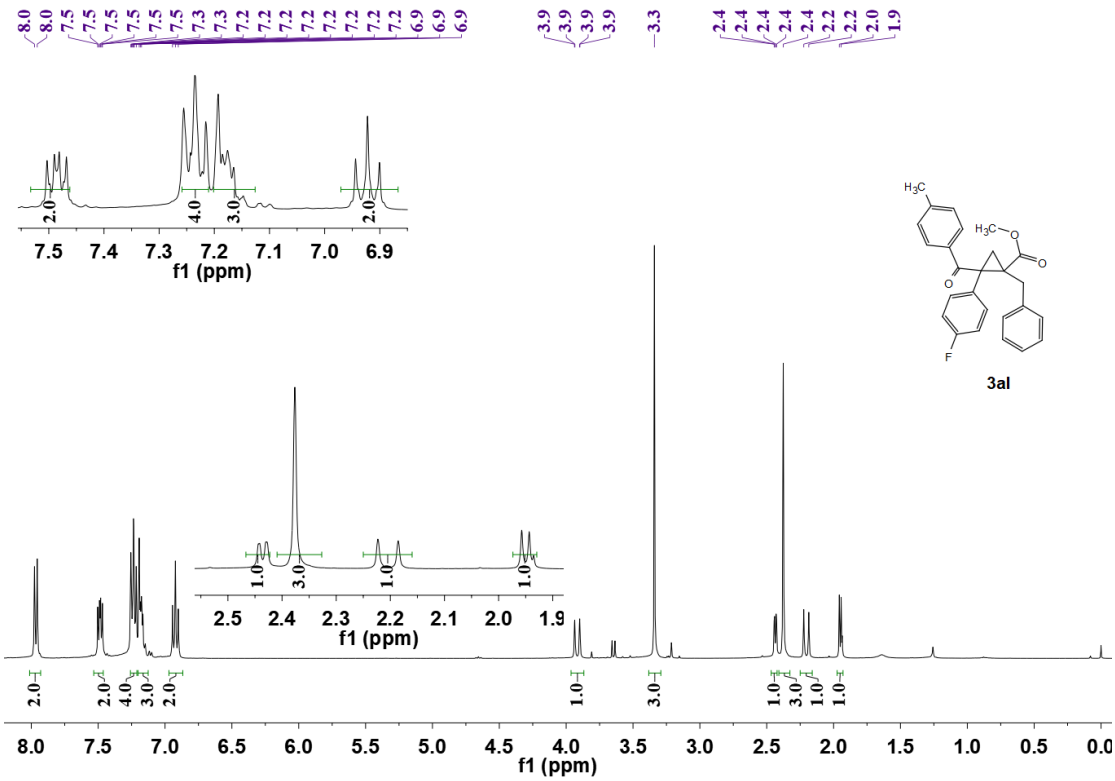

7.83 7.83 7.81 7.79 7.77 7.70 7.70 7.68 7.68 7.52 7.51 7.51 7.50 7.49 7.48 7.48 7.47 7.42 7.40 7.34 7.29 7.28 7.21 7.20 7.19 7.18 7.17 7.16 7.15 7.11 7.11 7.09 7.09 7.04 7.03 7.02 7.01 6.39 6.36 3.76 3.75 3.74 3.73 3.73 3.70 3.17 3.15 2.93 2.91 2.90
1.0 1.0 2.0 1.1 2.0 2.0 1.0 2.0 2.0 1.0 2.0
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
O
H3C
O
O
4aj
1.0 1.0 2.0 1.1 2.0 2.0 1.0 2.0 2.0 1.0 2.0 1.0 3.0 1.0 1.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

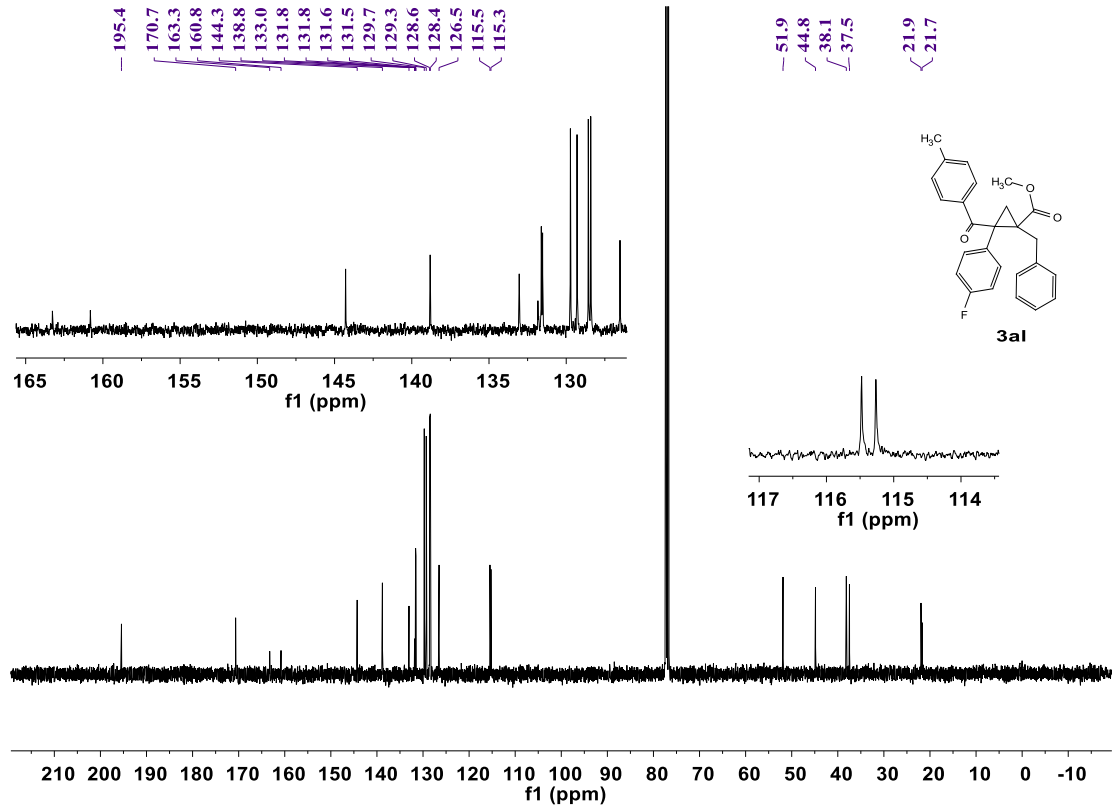

196.6
172.8 144.1 138.4 137.7 137.5 133.0 132.7 132.6 132.5 129.9 129.3 128.7 128.6 128.4 128.3 128.2 127.9 127.7 126.9 126.9 126.3 126.2
52.3 52.3 47.5 38.6 29.7
138 136 134 132 130 128 126 124
f1 (ppm)
O
H3C
O
O
4aj
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

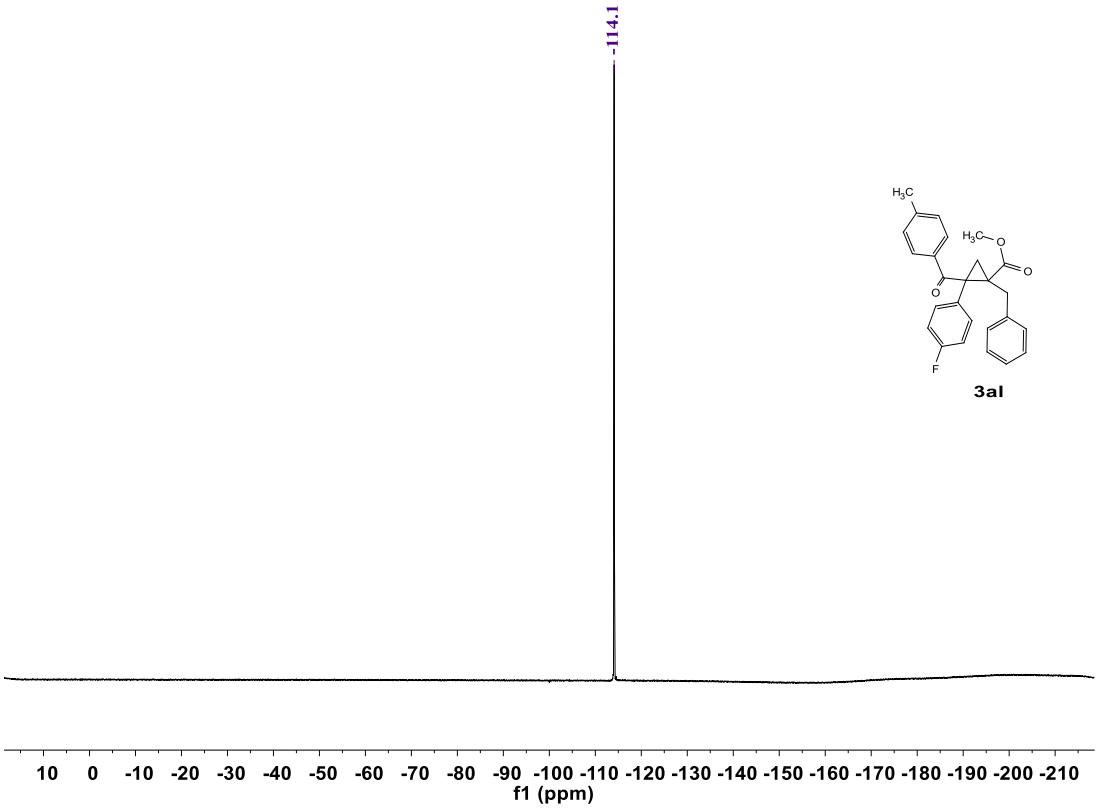

8.01
7.99
7.39
7.37
7.24
7.24
7.23
7.23
7.22
7.21
7.20
7.20
7.18
7.04
7.02
3.93
3.90
3.35
2.42
2.42
2.36
2.23
2.21
2.18
1.94
1.92
3ak
f1 (ppm)
2.0
7.1
2.0
1.0
3.0
3.0
1.0
2.0
2.0
7.1
2.0
1.0
3.0
1.0
3.0
1.0
1.1


195.6
170.9
144.0
139.0
137.3
133.2
132.9
130.0
129.8
129.7
129.2
129.1
128.6
128.4
127.0
126.4
51.8
45.5
38.2
37.3
21.8
21.7
21.7
21.1
3ak
f1 (ppm)

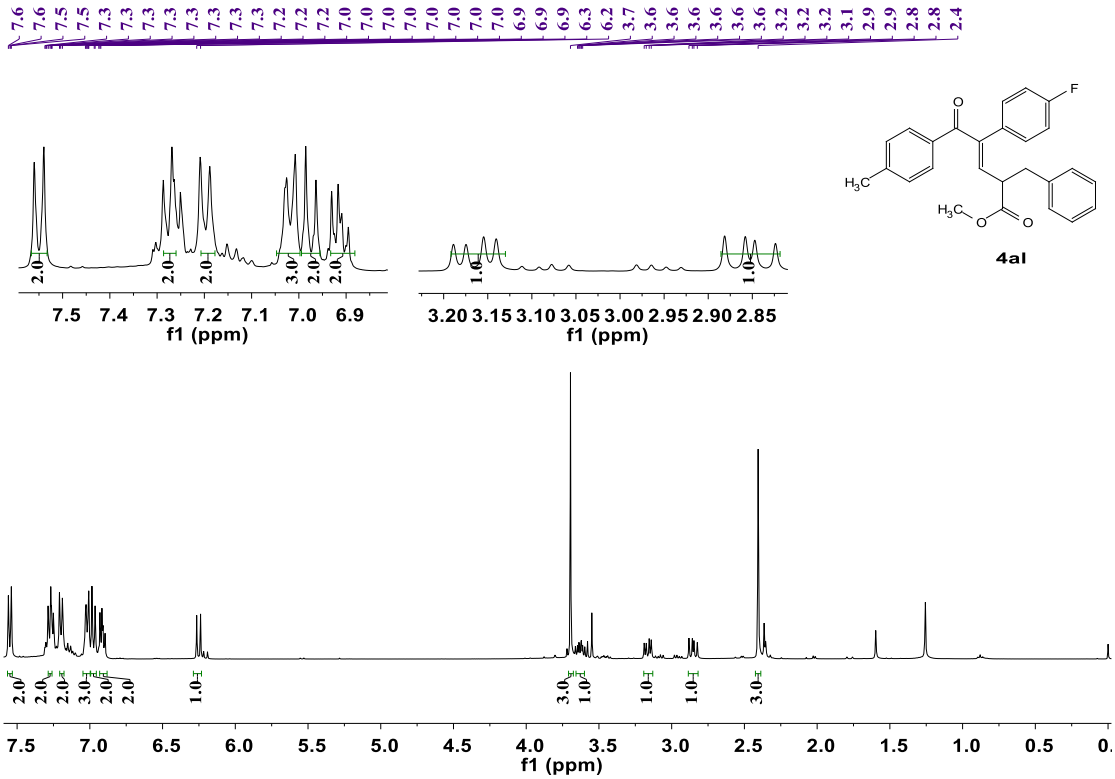

7.56 7.54 7.28 7.27 7.25 7.24 7.19 7.17 7.13 7.11 7.04 7.03 6.89 6.88 6.21 6.19 3.75 3.74 3.73 3.73 3.71 3.71 3.70 3.69 3.68 3.18 3.16 3.14 3.13 2.91 2.89 2.87 2.85 2.40 2.34
4ak
f1 (ppm)
196.5 173.0 144.0 143.2 137.8 137.6 136.7 134.8 132.3 130.1 129.2 129.0 129.0 128.9 128.5 126.8 52.2 47.3 38.6 21.7 21.3
4ak
f1 (ppm)


8.0 8.0 7.5 7.5 7.5 7.5 7.5 7.3 7.3 7.2 7.2 7.2 7.2 7.2 7.2 7.2 6.9 6.9
3.9 3.9 3.9 3.9
3.3
2.4 2.4 2.4 2.4 2.4 2.2 2.2 2.0 1.9
2.0 4.0 3.0 2.0
7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.0 3.0 1.0 1.0
2.5 2.4 2.3 2.2 2.1 2.0 1.9
f1 (ppm)
2.0 2.0 4.0 3.0 2.0 1.0 3.0 1.0 3.0 1.0 1.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
3al

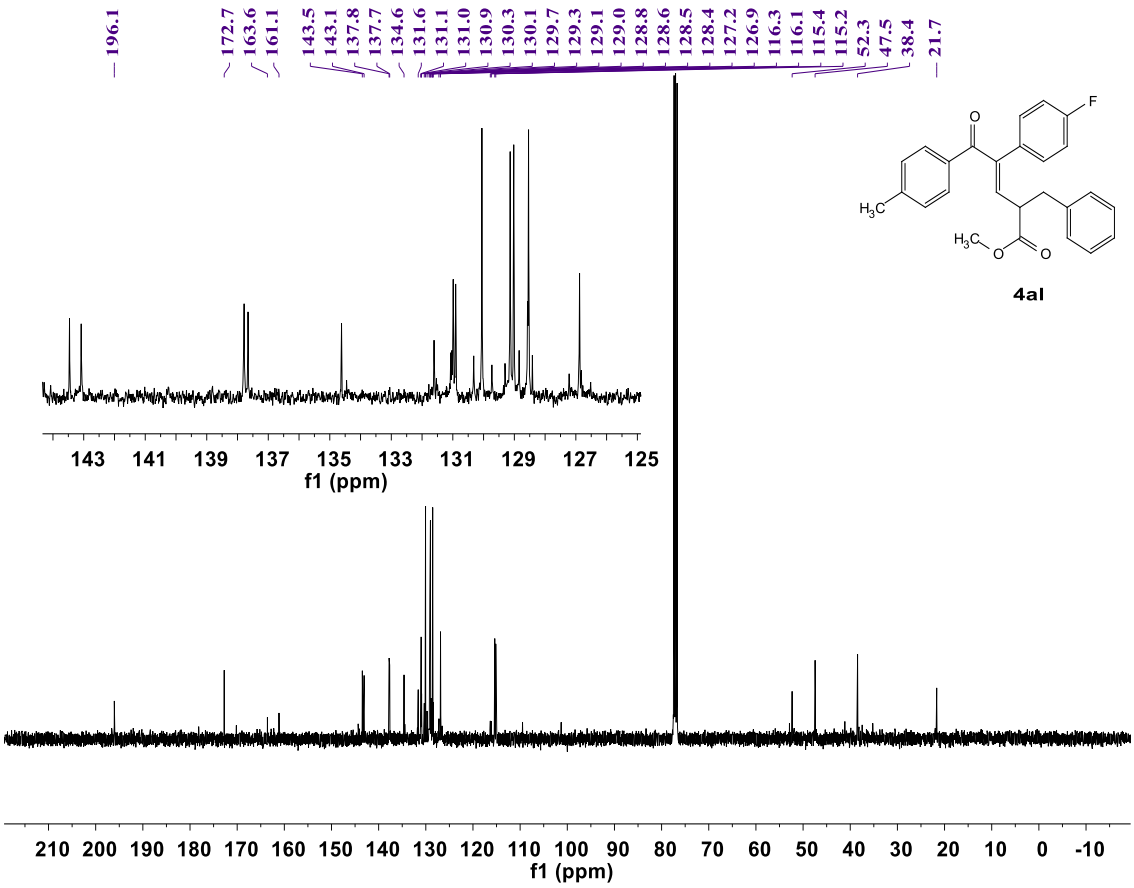

195.4 170.7 163.3 160.8 144.3 138.8 133.0 131.8 131.8 131.6 131.5 129.7 129.3 128.6 128.4 126.5 115.5 115.3
51.9 44.8 38.1 37.5
21.9 21.7
165 160 155 150 145 140 135 130
f1 (ppm)
117 116 115 114
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
3al

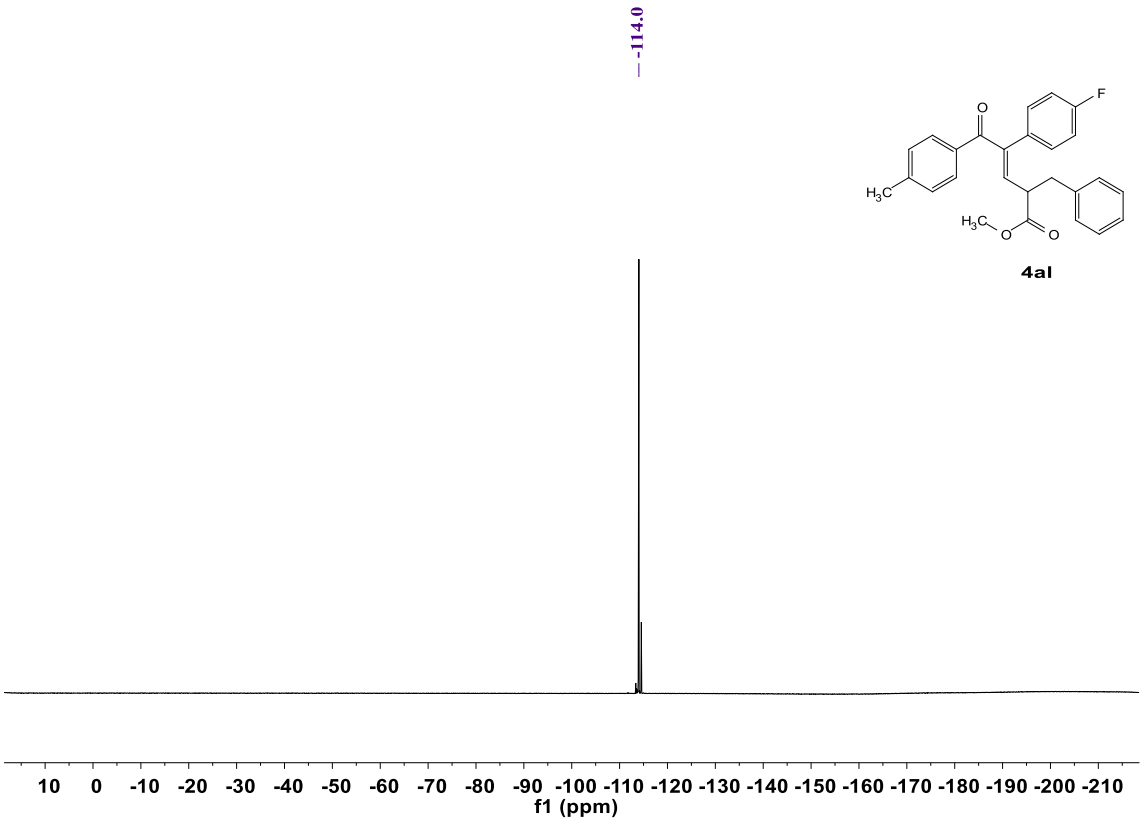

-114.1
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

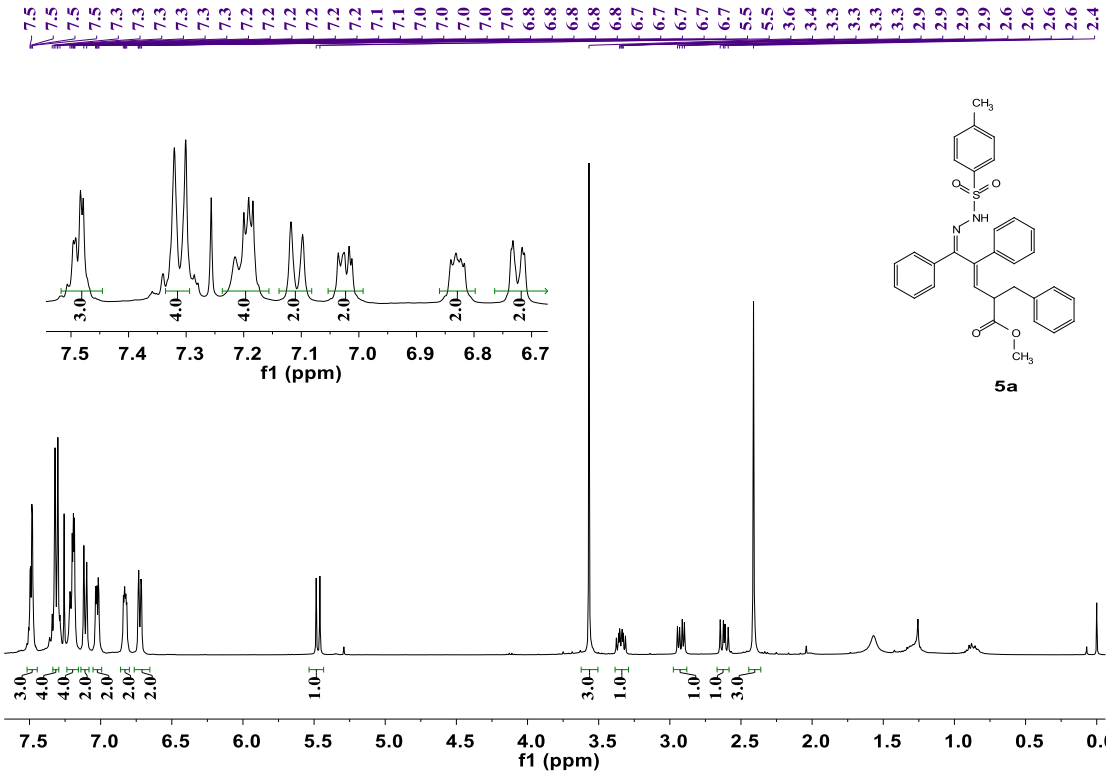
3al

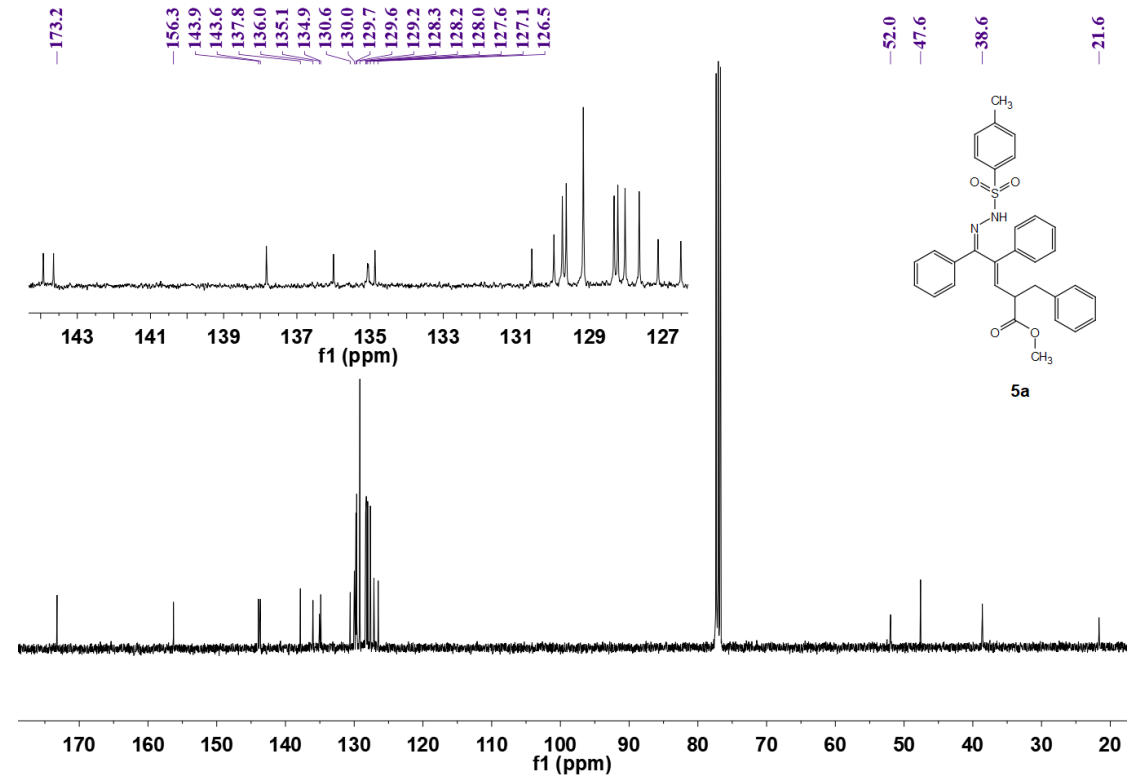

7.6 7.6 7.5 7.5 7.3 7.3 7.3 7.3 7.3 7.3 7.3 7.2 7.2 7.2 7.0 7.0 7.0 7.0 7.0 7.0 7.0 6.9 6.9 6.9 6.3 6.2 3.7 3.6 3.6 3.6 3.6 3.6 3.2 3.2 3.2 3.1 2.9 2.9 2.8 2.8 2.4
2.0 2.0 2.0 3.0 2.0 2.0
7.5 7.4 7.3 7.2 7.1 7.0 6.9
f1 (ppm)
1.0 1.0
3.20 3.15 3.10 3.05 3.00 2.95 2.90 2.85
f1 (ppm)
2.0 2.0 2.0 3.0 2.0 2.0 1.0 3.0 1.0 1.0 1.0 3.0
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

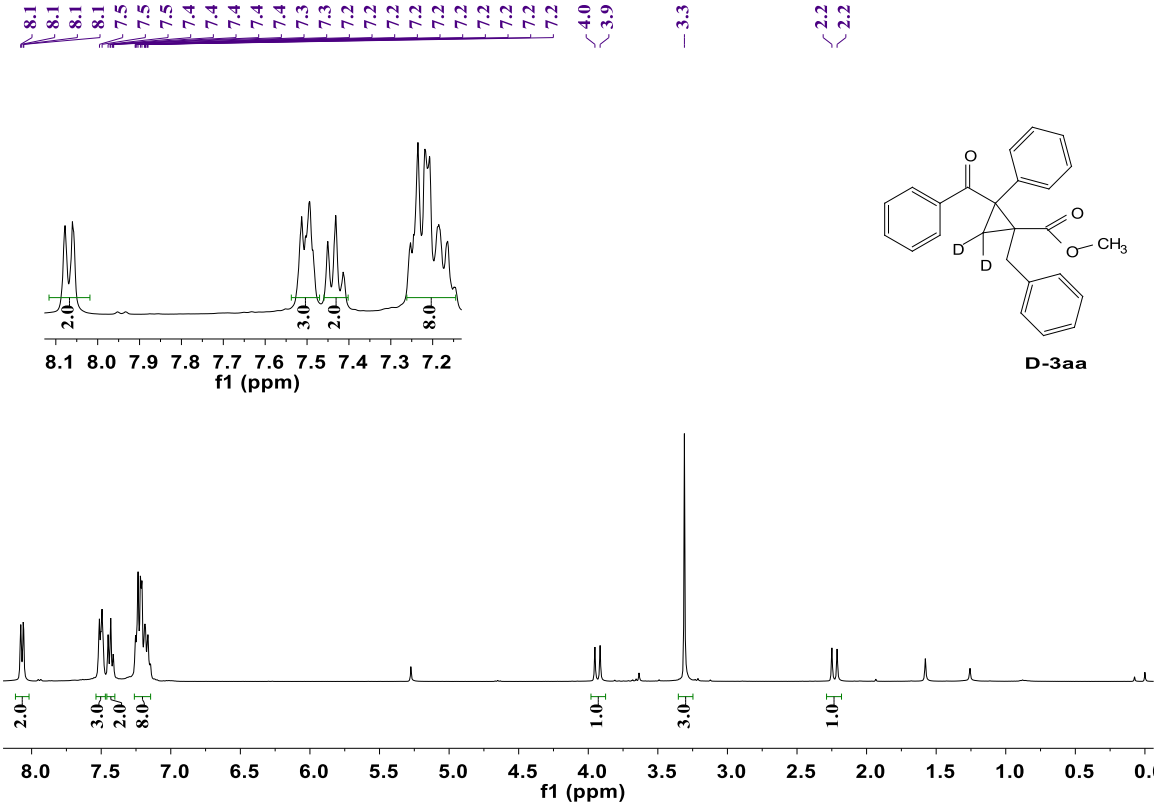
4al

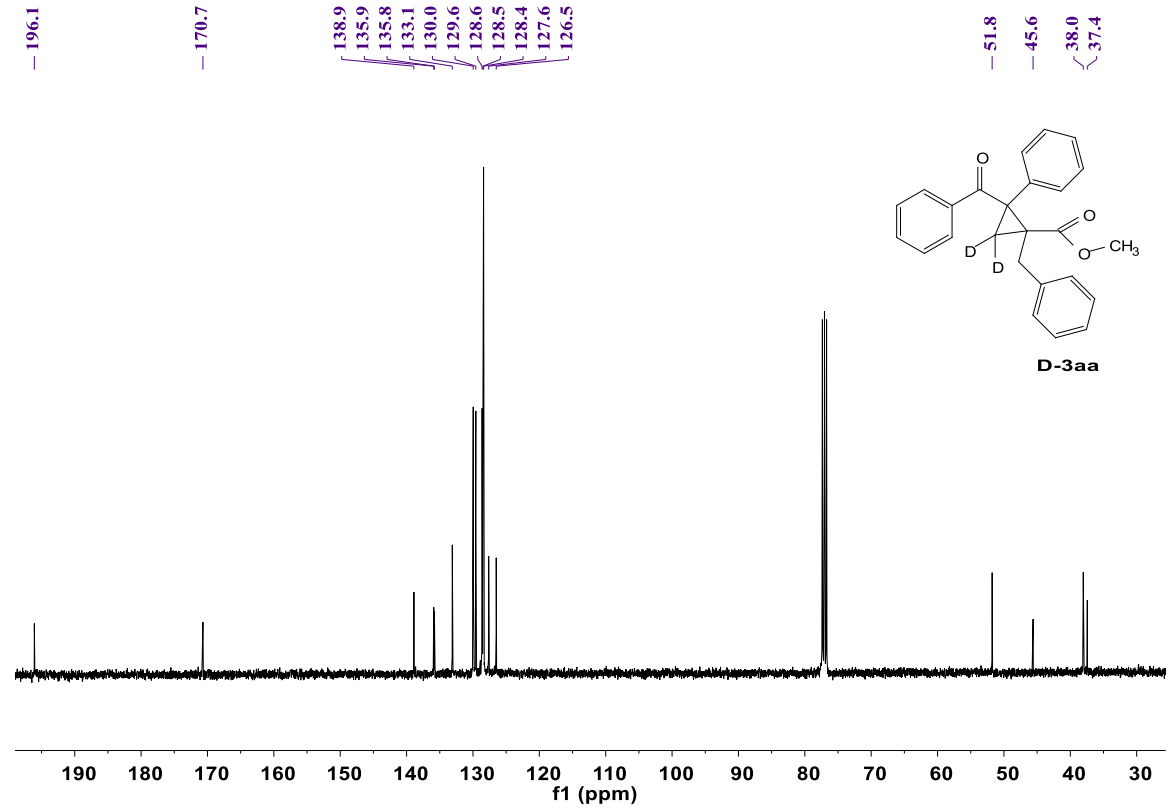

196.1
172.7
163.6
161.1
143.5
143.1
137.8
137.7
134.6
131.6
131.1
131.0
130.9
130.3
130.1
129.7
129.3
129.1
129.0
128.8
128.6
128.5
128.4
127.2
126.9
116.3
116.1
115.4
115.2
52.3
47.5
38.4
21.7
F
O
H3C
H3C
O
O
4al
143 141 139 137 135 133 131 129 127 125
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

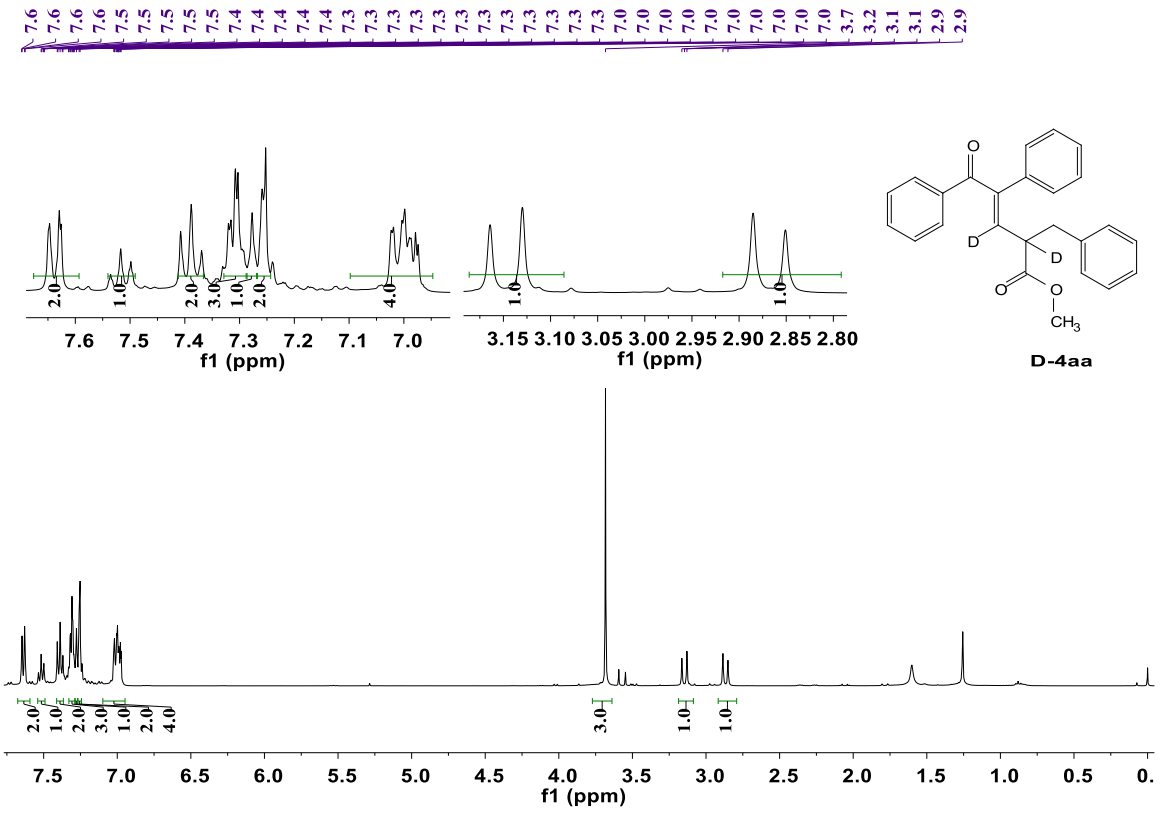

-114.0
F
O
H3C
H3C
O
O
4al
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

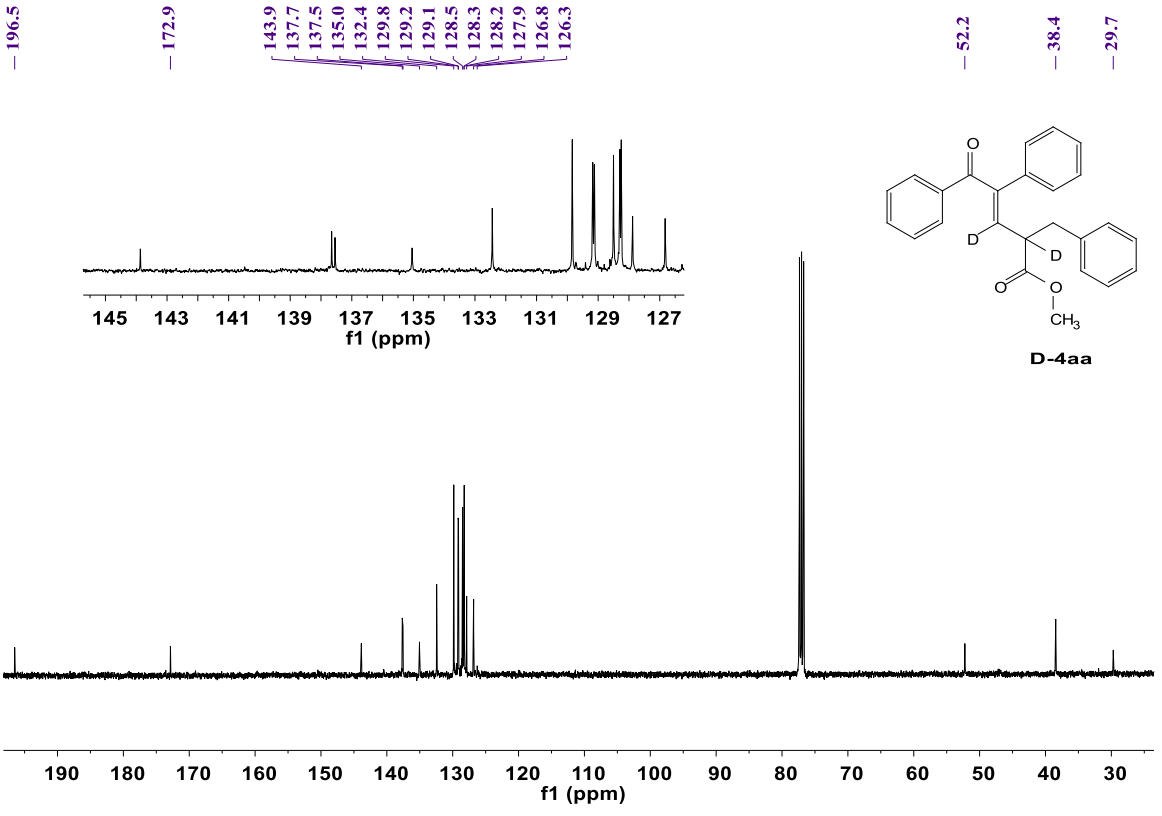

7.5 7.5 7.5 7.5 7.3 7.3 7.3 7.3 7.3 7.3 7.2 7.2 7.2 7.2 7.2 7.1 7.1 7.0 7.0 7.0 7.0 7.0 6.8 6.8 6.8 6.8 6.7 6.7 6.7 6.7 5.5 5.5 3.6 3.4 3.3 3.3 3.3 3.3 2.9 2.9 2.9 2.9 2.6 2.6 2.6 2.6 2.4
3.0 4.0 4.0 2.0 2.0 2.0 2.0
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
CH3
S
O
O
NH
N
O
O
CH3
5a
3.0 4.0 4.0 2.0 2.0 2.0 2.0 1.0 3.0 1.0 1.0 1.0 3.0
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

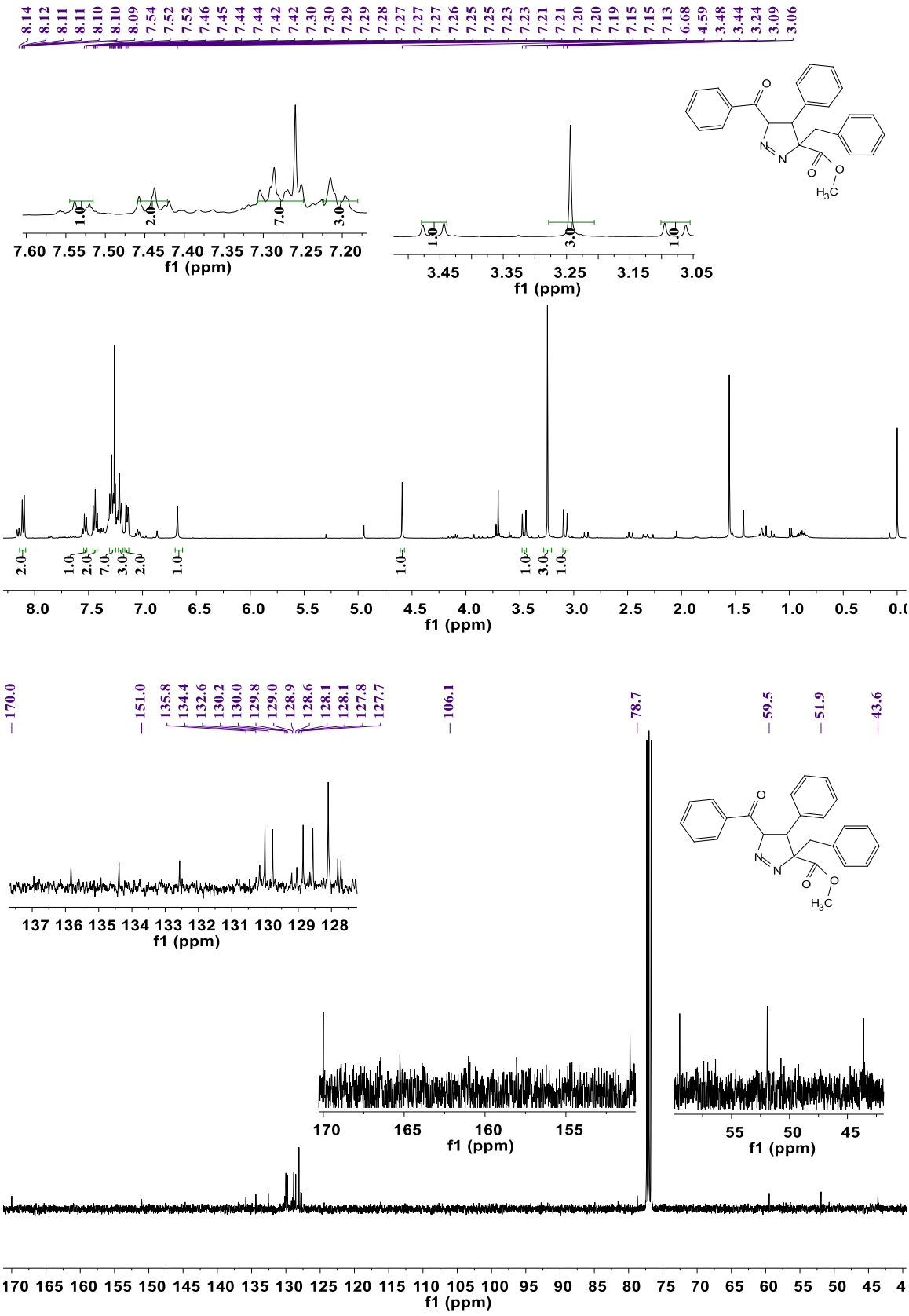

173.2
156.3 143.9 143.6 137.8 136.0 135.1 134.9 130.6 130.0 129.7 129.6 129.2 128.3 128.2 128.0 127.6 127.1 126.5
52.0 47.6 38.6 21.6
143 141 139 137 135 133 131 129 127
f1 (ppm)
CH3
S
O
O
NH
N
O
O
CH3
5a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)


8.1 8.1 8.1 8.1 7.5 7.5 7.5 7.4 7.4 7.4 7.4 7.4 7.3 7.3 7.2 7.2 7.2 7.2 7.2 7.2 7.2 7.2 7.2 4.0 3.9 3.3 2.2 2.2
2.0 3.0 2.0 8.0
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)
O
O
O
CH3
D
D
D-3aa
2.0 3.0 2.0 8.0 1.0 3.0 1.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


196.1 170.7 138.9 135.9 135.8 133.1 130.0 129.6 128.6 128.5 128.4 127.6 126.5 51.8 45.6 38.0 37.4
O
O
O
CH3
D
D
D-3aa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
f1 (ppm)


7.6 7.6 7.6 7.6 7.5 7.5 7.5 7.5 7.5 7.4 7.4 7.4 7.4 7.4 7.3 7.3 7.3 7.3 7.3 7.3 7.3 7.3 7.3 7.3 7.3 7.0 7.0 7.0 7.0 7.0 7.0 7.0 7.0 7.0 7.0 3.7 3.2 3.1 3.1 2.9 2.9
2.0 1.0 2.0 3.0 1.0 2.0 4.0
7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
1.0 1.0
3.15 3.10 3.05 3.00 2.95 2.90 2.85 2.80
f1 (ppm)
O
D
D
O
O
CH3
D-4aa
2.0 1.0 2.0 3.0 1.0 2.0 4.0
3.0 1.0 1.0
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


196.5
172.9
143.9 137.7 137.5 135.0 132.4 129.8 129.2 129.1 128.5 128.3 128.2 127.9 126.8 126.3
52.2
38.4
29.7
145 143 141 139 137 135 133 131 129 127
f1 (ppm)
O
D
D
O
O
CH3
D-4aa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30
f1 (ppm)


8.14 8.12 8.11 8.11 8.10 8.10 8.09 7.54 7.52 7.52 7.46 7.45 7.44 7.44 7.42 7.42 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.27 7.26 7.25 7.25 7.23 7.23 7.21 7.21 7.20 7.20 7.19 7.15 7.15 7.13 6.68 4.59 3.48 3.44 3.24 3.09 3.06
1.0 2.0 7.0 3.0
7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25 7.20
f1 (ppm)
1.0 3.0 1.0
3.45 3.35 3.25 3.15 3.05
f1 (ppm)
O
N
N
O
O
H3C
2.0 1.0 2.0 7.0 3.0 2.0 1.0 1.0 1.0 3.0 1.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
170.0 151.0 135.8 134.4 132.6 130.2 130.0 129.8 129.0 128.9 128.6 128.1 128.1 127.8 127.7 106.1 78.7 59.5 51.9 43.6
137 136 135 134 133 132 131 130 129 128
f1 (ppm)
170 165 160 155
f1 (ppm)
55 50 45
f1 (ppm)
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45
f1 (ppm)