

Organocatalytic Asymmetric Michael-type Reaction Between β , γ -Unsaturated α -Keto Ester and α -Nitro Ketone

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A: General Information and Starting Materials

General. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ were recorded on a Bruke Ultrashield TM 400 Plus (400 MHz) instrument. (s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, m = multiplet). Chromatography was carried out with silica gel (200-300 mesh) using mixtures of hexane and ethyl acetate as eluent. High resolution mass spectrometry was carried out using Electrospray Ionization-Quadrupole-Time of Flight (ESI-Q-TOF) mass spectrometer. Optical rotations were measured on perkin elmer polarimeter 341; concentrations (c) are reported in g per 100 mL. Enantiomeric excess was determined by chiral HPLC using Agilent 1100 Series with Chiralpak OD-H (0.46cm x 25 cm), Chiralpak AD-H (0.46cm x 25 cm), Chiralpak AS-H (0.46cm x 25 cm).

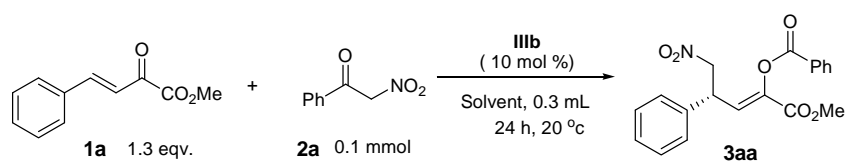
Materials. All solvent and inorganic reagents were of p.a. quality and used without purification. All the β , γ -unsaturated- α -keto esters were prepared following the literature procedures.⁽¹⁾ Unless otherwise noted, materials were obtained from commercial sources and used without purification.

B: General Procedure for Michael-type Reaction

Unless noted, the reaction was carried out as following: to a solution of Et_2O (0.5 mL) was added β , γ -unsaturated- α -keto ester **1** (0.13 mmol), α -nitro ketone **2** (0.1 mmol) and **IIIb** (15 mol %). The reaction mixture was stirred at given temperature for the time indicated and then the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel to yield the desired products **3**.

C: Optimization of Michael-type Reaction

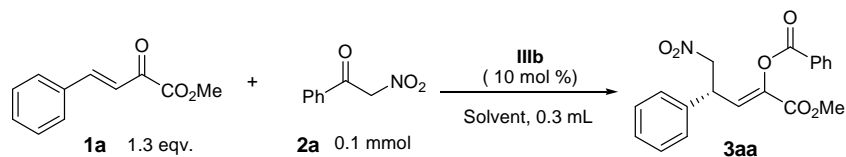
Table 1 The screening of solvent



Entry	solvent	yield %	ee %	Entry	solvent	yield %	ee %
1	CH_2Cl_2	69	77	11	t-BuOMe	44	93
2	CHCl_3	69	74	12	DMSO	45	40
3	THF	71	82	13	EtOH	26	69
4	EtOAc	70	79	14	Xylenes	61	80
5	Toluene	62	85	15	Petroleum ether (30-60 °C)	47	80
6	Et_2O	48	93	16	PhOMe	58	82
7	MeCN	78	62	17	PhOPh	76	84
8	MeOH	42	40	18	(n-Bu) $_2$ O	55	86
9	1,4-dioxane	79	80	19	hexane	53	80
10	DMF	44	8				

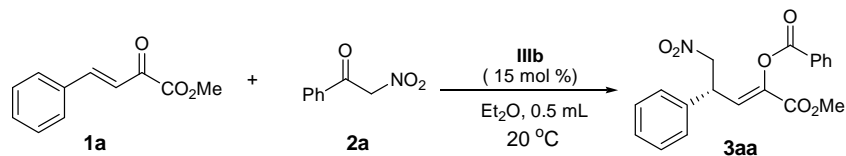
(1) Wu, Y.-C.; Liu, L.; Li, H.-J.; Wang, D.; Chen, Y.-J. *J. Org. Chem.* **2006**, *71*, 6592.

Table 2 The screening of temperature and mixture solvents



Entry	solvent	Tempt.	Time	yield	ee %	Entry	solvent	Tempt.	Time	yield	ee %
1		-10 °C	36 h	26	92	13	Et ₂ O 0.5 mL;	20 °C	24 h	48	94
2	THF	10 °C	24 h	66	82	14	IIIb (15 mol%)	5 °C	24 h	49	91
3		20 °C	24 h	71	82	15	Et ₂ O 0.3 mL;	5 °C	24 h	51	83
4		-10 °C	36 h	31	88	16	THF 0.1 mL;	10 °C	24 h	40	92
5	Toluene	10 °C	24 h	61	84	17	IIIb (15 mol%)	20 °C	66 h	48	93
6		20 °C	24 h	62	85	18	Et ₂ O 0.3 mL;	0 °C	36 h	52	92
7	t-BuOMe	20 °C	24 h	44	93	19	THF 0.2 mL;	5 °C	24 h	50	88
8		30 °C	24 h	42	90	20	IIIb (15 mol%)	10 °C	36 h	52	74
9		-10 °C	36 h	29	88	21		20 °C	66 h	56	89
10	Et ₂ O	20 °C	24 h	48	95	22	t-BuOMe 0.3 mL THF 0.1 mL	20 °C	66 h	41	93
11		30 °C	24 h	88	81	23	t-BuOMe 0.3 mL THF 0.2 mL	20 °C	66 h	45	90

Table 3 The screening of substrate ratio

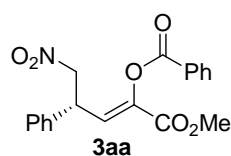


Entry	1a	2a	Time	yield	ee %	Entry	1a	2a	Time	yield	ee %
1	1.5	1.0	24 h	54	94	8	1.3	1.0	6 h	59	89
2	2.0	1.0	24 h	52	94	9	1.3	1.0	12 h	56	92
3	1.0	1.3	24 h	61	78	10	1.3	1.0	18 h	56	92
4	1.0	1.5	24 h	61	78	11 ^a	1.3	1.0	12 h	41	68
5	1.0	2.0	24 h	53	81	12 ^b	1.3	1.0	12 h	43	82
6	1.0	1.0	24 h	42	84	13 ^c	1.3	1.0	17.5 h	61	90
7	1.2	1.0	24 h	44	88	14 ^d	1.3	1.0	17.5 h	60	86

^a PhCO₂Li (15 mol %) was added. ^b PhCO₂H (15 mol %) was added. ^c II was added in 3 portions. ^d II was added in 5 portions.

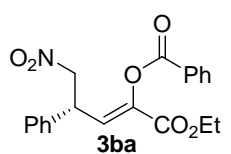
D: Characterization Data of Michael-type Products

(R,Z)-1-(methoxycarbonyl)-4-nitro-3-phenylbut-1-enyl benzoate (3aa)



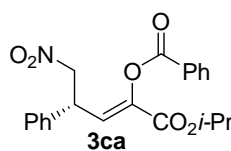
The product was obtained in 56% yield. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 8.13-8.10 (m, 2H), 7.69-7.64 (m, 1H), 7.54-7.50 (m, 2H), 7.36-7.29 (m, 3H), 7.24-7.21 (m, 2H), 6.78 (d, *J* = 9.6 Hz, 1H), 4.73 (d, *J* = 7.6 Hz, 2H), 4.62-4.56 (m, 1H), 3.78 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) 164.3, 161.8, 140.3, 136.6, 134.3, 130.6, 129.5, 128.9, 128.5, 128.2, 127.8, 127.6, 78.6, 52.9, 41.3 [α]_D²⁰ = -113.8 (c = 1.06 in CHCl₃, 94% ee). IR ν max: 3062, 3024, 2955, 1732, 1555, 1258, 1086, 707 cm⁻¹. HRMS: exact mass calculated for [M+Na]⁺ (C₁₉H₁₇NO₆Na) requires *m/z* 378.0954, found *m/z* 378.0971. The enantiomeric excess was determined by HPLC. [AD-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 14.337 min (minor), 16.904 min (major).

(R,Z)-1-(ethoxycarbonyl)-4-nitro-3-phenylbut-1-enyl benzoate (3ba)



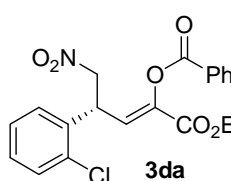
The product was obtained in 50% yield. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 8.13-8.11 (m, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.36-7.29 (m, 3H), 7.25-7.23 (m, 2H), 6.76 (d, *J* = 9.6 Hz, 1H), 4.74 (d, *J* = 7.6 Hz, 2H), 4.60 (dd, *J* = 8.0, 16.8 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.0 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) 164.3, 161.3, 140.5, 136.7, 134.2, 130.5, 129.5, 128.8, 128.4, 128.3, 127.6, 127.3, 78.6, 62.2, 41.3, 14.2. [α]_D²⁰ = -85.6 (c = 1.32 in CHCl₃, 84% ee). IR ν max: 2981, 1727, 1553, 1257, 1085, 705 cm⁻¹. HRMS: exact mass calculated for [M+Na]⁺ (C₂₀H₁₉NO₆Na) requires *m/z* 392.1110, found *m/z* 392.1127. The enantiomeric excess was determined by HPLC. [AD-H, 230 nm, hexane : IPA = 90 : 10, 1.0 mL/min]: 22.261 min (minor), 23.594 min (major).

(R,Z)-1-(isopropoxycarbonyl)-4-nitro-3-phenylbut-1-enyl benzoate (3ca)



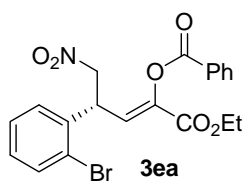
The product was obtained in 61% yield. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 8.13-8.10 (m, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.36-7.29 (m, 3H), 7.25-7.23 (m, 2H), 6.72 (d, *J* = 9.2 Hz, 1H), 5.13-5.05 (m, 1H), 4.74 (d, *J* = 8.0 Hz, 2H), 4.63-4.57 (m, 1H), 1.25-1.23 (m, 6H). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) 164.4, 160.9, 140.9, 136.8, 134.2, 130.5, 129.5, 128.8, 128.4, 127.6, 126.9, 78.6, 70.2, 41.3, 21.8. [α]_D²⁰ = -59.8 (c = 1.67 in CHCl₃, 72% ee). IR ν max: 3066, 3031, 2983, 2927, 1726, 1556, 1259, 1087, 706 cm⁻¹. HRMS: exact mass calculated for [M+Na]⁺ (C₂₁H₂₁NO₆Na) requires *m/z* 406.1267, found *m/z* 406.1277. The enantiomeric excess was determined by HPLC. [AD-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 13.466 min (major), 21.662 min (minor).

(R,Z)-1-(ethoxycarbonyl)-3-(2-chlorophenyl)-4-nitrobut-1-enyl benzoate (3da)



The product was obtained in 50% yield. ¹H-NMR (400 MHz, CDCl₃): δ (ppm) 8.06 (d, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 7.0 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.34 (d, *J* = 6.8 Hz, 1H), 7.27-7.19 (m, 3H), 6.83 (d, *J* = 8.8 Hz, 1H), 5.14-5.09 (m, 1H), 4.78-4.75 (m, 2H), 4.25 (q, *J* = 6.9 Hz, 2H), 1.27 (t, *J* = 6.8 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃): δ (ppm) 164.1, 161.3, 141.2, 134.4, 134.1, 133.7, 130.6, 130.5, 129.6, 129.1, 128.7, 128.3, 127.8, 126.1, 77.2, 62.2, 38.3, 14.2. IR ν max: 3066, 2984, 2914, 1730, 1556, 1258, 1086, 708 cm⁻¹. HRMS: exact mass calculated for [M+Na]⁺ (C₂₀H₁₈ClNO₆Na) requires *m/z* 426.0720, found *m/z* 426.0722. The enantiomeric excess was determined by HPLC. [AD-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 16.135 min (major), 21.987 min (minor).

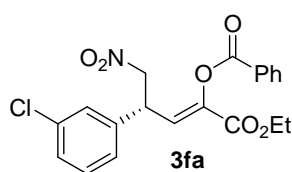
(R,Z)-1-(ethoxycarbonyl)-3-(2-bromophenyl)-4-nitrobut-1-enyl benzoate (3ea)



The product was obtained in 71% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.06 (d, $J = 8.0$ Hz, 2H), 7.63 (t, $J = 7.4$ Hz, 1H), 7.53-7.46 (m, 3H), 7.29-7.28 (m, 2H), 7.14-7.10 (m, 1H), 6.82 (d, $J = 8.8$ Hz, 1H), 5.15 (dd, $J = 8.2, 5.0$, 1H), 4.78-4.67 (m, 2H), 4.25 (q, $J = 7.1$ Hz, 2H), 1.27 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 164.1, 161.3, 141.2, 136.1, 134.1, 133.9, 130.5, 129.8, 129.0, 128.7, 128.4, 128.2, 126.2, 124.2, 77.4, 62.2, 40.5, 14.2. IR ν max: 3066, 2983, 2917, 1729, 1556, 1257, 1085, 707 cm^{-1} .

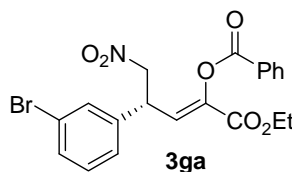
HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{20}\text{H}_{18}\text{BrNO}_6\text{Na}$) requires m/z 470.0215, found m/z 470.0219. The enantiomeric excess was determined by HPLC. [AD-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 17.776 min (major), 24.726 min (minor).

(R,Z)-1-(ethoxycarbonyl)-3-(3-chlorophenyl)-4-nitrobut-1-enyl benzoate (3fa)



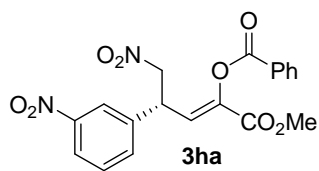
The product was obtained in 62% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.11 (d, $J = 8.0$ Hz, 2H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 2H), 7.27-7.23 (m, 3H), 7.14-7.11 (m, 1H), 6.71 (d, $J = 9.2$ Hz, 1H), 4.72 (d, $J = 8.0$ Hz, 2H), 4.57 (dd, $J = 7.8, 16.6$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 1.27 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 164.3, 161.2, 141.0, 138.7, 135.3, 134.3, 130.7, 130.5, 128.9, 128.7, 128.1, 127.9, 126.4, 125.8, 78.2, 62.3, 40.9, 14.2. $[\alpha]_D^{20} = -51.6$ ($c = 1.65$ in CHCl_3 , 84% ee). IR ν max: 3063, 2983, 2917, 1729, 1556, 1257, 1085, 708 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{20}\text{H}_{18}\text{ClNO}_6\text{Na}$) requires m/z 426.0720, found m/z 426.0736. The enantiomeric excess was determined by HPLC. [AD-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 11.985 min (minor), 13.443 min (major).

(R,Z)-1-(ethoxycarbonyl)-3-(3-bromophenyl)-4-nitrobut-1-enyl benzoate (3ga)



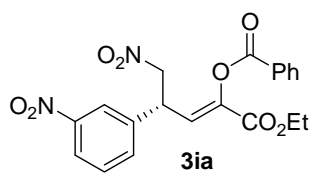
The product was obtained in 58% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.10 (d, $J = 8.0$ Hz, 2H), 7.67 (t, $J = 6.8$ Hz, 1H), 7.52 (t, $J = 7.2$ Hz, 2H), 7.41 (t, $J = 7.8$ Hz, 2H), 7.21-7.16 (m, 2H), 6.71 (d, $J = 9.6$ Hz, 1H), 4.72 (d, $J = 7.6$ Hz, 2H), 4.56 (dd, $J = 8.2, 16.2$ Hz, 1H), 4.25 (q, $J = 6.8$ Hz, 2H), 1.27 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 164.2, 161.2, 141.0, 139.0, 134.3, 131.6, 131.0, 130.8, 130.5, 128.9, 128.1, 126.4, 126.3, 123.4, 78.2, 62.3, 40.8, 14.2. $[\alpha]_D^{20} = -77.5$ ($c = 1.86$ in CHCl_3 , 91% ee). IR ν max: 3060, 2982, 2911, 1729, 1556, 1258, 1094, 708 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{20}\text{H}_{18}\text{BrNO}_6\text{Na}$) requires m/z 470.0215, found m/z 470.0229. The enantiomeric excess was determined by HPLC. [AD-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 12.063 min (minor), 13.926 min (major).

(R,Z)-1-(methoxycarbonyl)-4-nitro-3-(3-nitrophenyl)but-1-enyl benzoate (3ha)



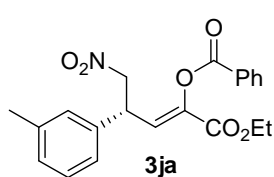
The product was obtained in 56% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.14 (d, $J = 7.2$ Hz, 2H), 8.08 (d, $J = 8.0$ Hz, 2H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.58 (d, $J = 7.6$ Hz, 1H), 7.54-7.50 (m, 3H), 6.78 (d, $J = 9.2$ Hz, 1H), 4.80 (d, $J = 8.0$ Hz, 2H), 4.70 (dd, $J = 8.2, 15.8$ Hz, 1H), 3.79 (s, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 164.1, 161.5, 148.9, 141.1, 138.8, 134.5, 133.9, 130.5, 128.9, 127.8, 126.1, 123.5, 122.7, 77.8, 53.1, 40.7. $[\alpha]_D^{20} = -66.8$ ($c = 1.66$ in CHCl_3 , 86% ee). IR ν max: 3066, 2956, 2914, 1732, 1556, 1531, 1281, 1258, 1087, 708 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{19}\text{H}_{16}\text{N}_2\text{O}_8\text{Na}$) requires m/z 423.0804, found m/z 423.0819. The enantiomeric excess was determined by HPLC. [AD-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 24.179 min (minor), 29.218 min (major).

(R,Z)-1-(ethoxycarbonyl)-4-nitro-3-(3-nitrophenyl)but-1-enyl benzoate (3ia)



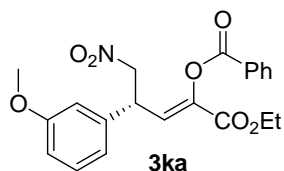
The product was obtained in 49% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.15-8.13 (m, 2H), 8.09-8.07 (m, 2H), 7.67 (t, $J = 7.5$ Hz, 1H), 7.59 (d, $J = 8.0$ Hz, 1H), 7.54-7.50 (m, 3H), 6.75 (d, $J = 9.0$ Hz, 1H), 4.80 (d, $J = 8.0$ Hz, 2H), 4.71 (dd, $J = 7.5, 16.5$ Hz, 1H), 4.24 (qd, $J = 1.1, 7.2$ Hz, 2H), 1.27 (t, $J = 7.8$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 164.2, 161.0, 148.7, 141.5, 138.9, 134.5, 133.9, 130.5, 128.9, 127.8, 125.6, 123.5, 122.7, 77.8, 62.4, 40.7, 14.1. $[\alpha]_{\text{D}}^{20} = -76.7$ ($c = 1.28$ in CHCl_3 , 90% ee). IR ν max: 3075, 2986, 2914, 1729, 1556, 1531, 1352, 1258, 1088, 708 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_8\text{Na}$) requires m/z 437.0961, found m/z 437.0963. The enantiomeric excess was determined by HPLC. [AD-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 22.833 min (minor), 28.893 min (major).

(R,Z)-1-(ethoxycarbonyl)-4-nitro-3-m-tolylbut-1-enyl benzoate (3ja)



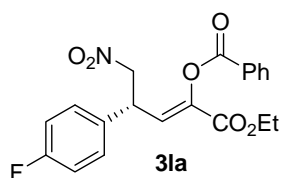
The product was obtained in 50% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.12 (d, $J = 7.5$ Hz, 2H), 7.66 (t, $J = 7.5$ Hz, 1H), 7.52 (t, $J = 7.8$ Hz, 2H), 7.22 (t, $J = 8.0$ Hz, 1H), 7.09 (d, $J = 7.5$ Hz, 1H), 7.03 (d, $J = 6.5$ Hz, 2H), 6.75 (d, $J = 9.5$ Hz, 1H), 4.73 (d, $J = 8.0$ Hz, 2H), 4.56 (dd, $J = 7.8, 17.3$ Hz, 1H), 4.24 (q, $J = 7.2$ Hz, 2H), 2.30 (s, 3H), 1.27 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 164.3, 161.4, 140.5, 139.3, 136.6, 134.2, 130.5, 129.4, 129.2, 128.8, 128.4, 127.5, 124.5, 78.6, 62.1, 41.3, 21.5, 14.2. $[\alpha]_{\text{D}}^{20} = -79.0$ ($c = 1.34$ in CHCl_3 , 82% ee). IR ν max: 3063, 2982, 2911, 1729, 1555, 1259, 1093, 705 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{21}\text{H}_{21}\text{NO}_6\text{Na}$) requires m/z 406.1267, found m/z 406.1286. The enantiomeric excess was determined by HPLC. [AD-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 10.135 min (minor), 11.03 min (major).

(R,Z)-1-(ethoxycarbonyl)-3-(3-methoxyphenyl)-4-nitrobut-1-enyl benzoate (3ka)



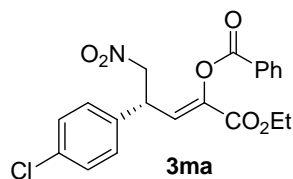
The product was obtained in 47% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.15 (d, $J = 8.0$ Hz, 2H), 7.67 (t, $J = 8.2$ Hz, 1H), 7.54 (t, $J = 7.6$ Hz, 2H), 7.30-7.28 (m, 1H), 6.84 (d, $J = 7.2$ Hz, 2H), 6.77 (d, $J = 14.4$ Hz, 2H), 4.75 (d, $J = 8.0$ Hz, 2H), 4.63-4.57 (m, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 3.78 (s, 3H), 1.29 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 164.3, 161.3, 160.3, 140.6, 138.1, 134.2, 130.5, 128.8, 128.3, 127.2, 119.6, 113.7, 113.6, 78.5, 62.1, 55.4, 41.2, 14.2. $[\alpha]_{\text{D}}^{20} = -89.8$ ($c = 1.34$ in CHCl_3 , 86% ee). IR ν max: 3060, 2981, 2933, 2838, 1729, 1601, 1555, 1260, 1090, 707 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{21}\text{H}_{21}\text{NO}_7\text{Na}$) requires m/z 422.1216, found m/z 422.1220. The enantiomeric excess was determined by HPLC. [AD-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 14.702 min (minor), 17.455 min (major).

(R,Z)-1-(ethoxycarbonyl)-3-(4-fluorophenyl)-4-nitrobut-1-enyl benzoate (3la)



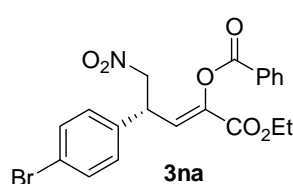
The product was obtained in 56% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.10 (d, $J = 7.6$ Hz, 2H), 7.67 (t, $J = 7.4$ Hz, 1H), 7.52 (t, $J = 7.8$ Hz, 2H), 7.23-7.19 (m, 2H), 7.02 (t, $J = 8.6$ Hz, 2H), 6.72 (d, $J = 9.6$ Hz, 1H), 4.71 (d, $J = 8.0$ Hz, 2H), 4.58 (dd, $J = 8.2, 16.2$ Hz, 1H), 4.25 (q, $J = 7.2$ Hz, 2H), 1.26 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 164.3, 161.3, 140.7, 134.3, 132.5 (d, $J_{\text{C-F}} = 3.4$ Hz), 130.5, 129.3 (d, $J_{\text{C-F}} = 8.4$ Hz), 128.9, 128.2, 127.0, 116.5 (d, $J_{\text{C-F}} = 21.7$ Hz), 78.5, 62.2, 40.6, 14.2. $[\alpha]_{\text{D}}^{20} = -73.4$ ($c = 1.55$ in CHCl_3 , 88% ee). IR ν max: 3066, 2983, 2911, 1728, 1556, 1258, 1098, 707 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{20}\text{H}_{18}\text{FNO}_6\text{Na}$) requires m/z 410.1016, found m/z 410.1007. The enantiomeric excess was determined by HPLC. [AD-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 18.542 min (major), 21.56 min (minor).

(R,Z)-1-(ethoxycarbonyl)-3-(4-chlorophenyl)-4-nitrobut-1-enyl benzoate (3ma)



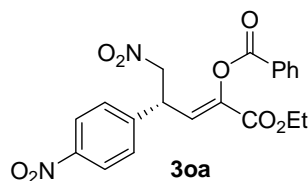
The product was obtained in 47% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.09 (d, $J = 7.2$ Hz, 2H), 7.66 (t, $J = 7.4$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 2H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.17 (d, $J = 8.4$ Hz, 2H), 6.70 (d, $J = 9.6$ Hz, 1H), 4.71 (d, $J = 8.0$ Hz, 2H), 4.57 (dd, $J = 8.0, 16.8$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 1.27 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 164.3, 161.2, 140.9, 135.2, 134.4, 134.3, 130.5, 129.7, 129.0, 128.9, 128.1, 126.6, 78.3, 62.3, 40.7, 14.2. $[\alpha]_{\text{D}}^{20} = -95.3$ ($c = 0.97$ in CHCl_3 , 87% ee). IR ν max: 3069, 2987, 2921, 2851, 1729, 1556, 1258, 1094, 707 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{20}\text{H}_{18}\text{ClNO}_6\text{Na}$) requires m/z 426.0720, found m/z 426.0737. The enantiomeric excess was determined by HPLC. [OD-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 24.455 min (major), 31.277 min (minor).

(R,Z)-1-(ethoxycarbonyl)-3-(4-bromophenyl)-4-nitrobut-1-enyl benzoate (3na)



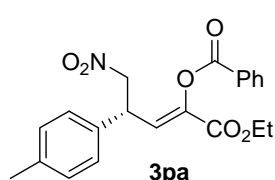
The product was obtained in 70% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.09 (d, $J = 7.0$ Hz, 2H), 7.66 (t, $J = 7.3$ Hz, 1H), 7.52 (t, $J = 7.8$ Hz, 2H), 7.45 (d, $J = 8.5$ Hz, 2H), 7.11 (d, $J = 8.5$ Hz, 2H), 6.70 (d, $J = 9.5$ Hz, 1H), 4.71 (d, $J = 8.5$ Hz, 2H), 4.55 (dd, $J = 7.5, 17.0$ Hz, 1H), 4.24 (q, $J = 7.2$ Hz, 2H), 1.26 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 164.3, 161.2, 140.8, 135.7, 134.3, 132.6, 130.5, 129.3, 128.9, 128.1, 126.6, 122.5, 78.2, 62.2, 40.7, 14.2. $[\alpha]_{\text{D}}^{20} = -67.5$ ($c = 2.61$ in CHCl_3 , 92% ee). IR ν max: 3066, 2982, 2930, 1729, 1556, 1259, 1104, 708 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{20}\text{H}_{18}\text{BrNO}_6\text{Na}$) requires m/z 470.0215, found m/z 470.0233. The enantiomeric excess was determined by HPLC. [OD-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 27.869 min (major), 43.752 min (minor).

(R,Z)-1-(ethoxycarbonyl)-4-nitro-3-(4-nitrophenyl)but-1-enyl benzoate (3oa)



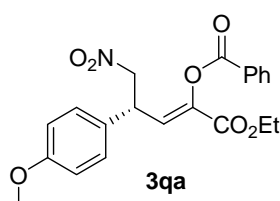
The product was obtained in 58% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.19 (d, $J = 9.0$ Hz, 2H), 8.07 (d, $J = 9.5$ Hz, 2H), 7.68 (t, $J = 7.5$ Hz, 1H), 7.52 (t, $J = 8.0$ Hz, 2H), 7.43 (d, $J = 9.0$ Hz, 2H), 6.72 (d, $J = 9.5$ Hz, 1H), 4.80-4.78 (m, 2H), 4.70 (dd, $J = 7.5, 16.0$ Hz, 1H), 4.26 (q, $J = 7.0$ Hz, 2H), 1.27 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 164.2, 161.0, 147.9, 143.9, 141.6, 134.5, 130.5, 129.0, 128.7, 127.9, 125.4, 124.7, 77.8, 62.5, 40.9, 14.2. $[\alpha]_{\text{D}}^{20} = -76.3$ ($c = 1.13$ in CHCl_3 , 84% ee). IR ν max: 3113, 3079, 2984, 2923, 1731, 1557, 1523, 1349, 1259, 1109, 709 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{20}\text{H}_{18}\text{N}_2\text{O}_8\text{Na}$) requires m/z 437.0961, found m/z 437.0975. The enantiomeric excess was determined by HPLC. [AD-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 39.567 min (major), 49.294 min (minor).

(R,Z)-1-(ethoxycarbonyl)-4-nitro-3-p-tolylbut-1-enyl benzoate (3pa)



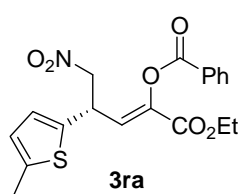
The product was obtained in 56% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.12 (d, $J = 7.2$ Hz, 2H), 7.66 (t, $J = 7.4$ Hz, 1H), 7.52 (t, $J = 7.8$ Hz, 2H), 7.15-7.10 (m, 4H), 6.74 (d, $J = 9.6$ Hz, 1H), 4.71 (d, $J = 8.0$ Hz, 2H), 4.56 (dd, $J = 7.6, 17.2$ Hz, 1H), 4.24 (q, $J = 7.2$ Hz, 2H), 2.31 (s, 3H), 1.26 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 164.3, 161.4, 140.3, 138.2, 134.2, 133.6, 130.5, 130.1, 128.8, 128.3, 127.5, 127.4, 78.6, 62.1, 40.9, 21.2, 14.2. $[\alpha]_{\text{D}}^{20} = -90.9$ ($c = 1.53$ in CHCl_3 , 82% ee). IR ν max: 3059, 2982, 2914, 1728, 1555, 1258, 1109, 708 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{21}\text{H}_{21}\text{NO}_6\text{Na}$) requires m/z 406.1267, found m/z 406.1283. The enantiomeric excess was determined by HPLC. [AD-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 13.374 min (minor), 15.741 min (major).

(R,Z)-1-(ethoxycarbonyl)-3-(4-methoxyphenyl)-4-nitrobut-1-enyl benzoate (3qa)



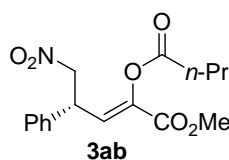
The product was obtained in 63% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.12 (d, $J = 8.0$ Hz, 2H), 7.66 (t, $J = 7.4$ Hz, 1H), 7.52 (t, $J = 7.2$ Hz, 2H), 7.15 (d, $J = 7.6$ Hz, 2H), 6.85 (d, $J = 7.2$ Hz, 2H), 6.73 (d, $J = 9.6$ Hz, 2H), 4.70 (d, $J = 8.0$ Hz, 2H), 4.54 (dd, $J = 7.8, 16.2$ Hz, 1H), 4.24 (q, $J = 7.1$ Hz, 2H), 3.77 (s, 3H), 1.26 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 164.3, 161.4, 159.6, 140.3, 134.2, 130.5, 128.8, 128.7, 128.6, 128.4, 127.6, 114.9, 78.8, 62.1, 55.4, 40.6, 14.2. $[\alpha]_{\text{D}}^{20} = -86.8$ ($c = 1.27$ in CHCl_3 , 73% ee). IR ν max: 2983, 2933, 2835, 1729, 1555, 1514, 1253, 1108, 709 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{21}\text{H}_{21}\text{NO}_7\text{Na}$) requires m/z 422.1216, found m/z 422.1217. The enantiomeric excess was determined by HPLC. [AD-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 18.496 min (minor), 22.41 min (major).

(S,Z)-1-(ethoxycarbonyl)-3-(5-methylthiophen-2-yl)-4-nitrobut-1-enyl benzoate (3ra)



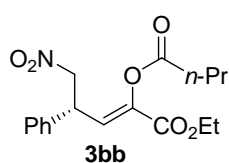
The product was obtained in 94% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 8.14 (d, $J = 7.6$ Hz, 2H), 7.66 (t, $J = 7.2$ Hz, 1H), 7.52 (t, $J = 7.2$ Hz, 2H), 6.71-6.67 (m, 2H), 6.59 (s, 1H), 4.81 (dd, $J = 8.0, 15.2$ Hz, 1H), 4.75-4.64 (m, 2H), 4.32-4.23 (m, 2H), 2.43 (s, 3H), 1.27 (t, $J = 6.6$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 164.3, 161.3, 140.6, 140.3, 136.2, 134.2, 130.6, 128.9, 128.3, 126.7, 125.7, 125.5, 78.8, 62.2, 36.7, 29.8, 15.4, 14.2. $[\alpha]_{\text{D}}^{20} = -59.5$ ($c = 1.13$ in CHCl_3 , 68% ee). IR ν max: 3066, 2984, 2958, 2922, 2854, 1731, 1556, 1261, 1083, 708 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{19}\text{H}_{19}\text{NSO}_6\text{Na}$) requires m/z 412.0831, found m/z 412.0842. The enantiomeric excess was determined by HPLC. [AD-H, 230 nm, hexane : IPA = 90 : 10, 1.0 mL/min]: 14.654 min (minor), 22.33 min (major).

(R,Z)-methyl 2-(butyryloxy)-5-nitro-4-phenylpent-2-enoate (3ab)



The product was obtained in 51% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.32-7.30 (m, 3H), 7.22 (d, $J = 6.8$ Hz, 2H), 6.64 (d, $J = 9.2$ Hz, 1H), 4.73-4.63 (m, 2H), 4.55-4.48 (m, 1H), 3.77 (s, 3H), 2.52-2.48 (m, 2H), 1.77-1.72 (m, 2H), 1.03 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 171.2, 161.9, 140.1, 136.7, 129.5, 128.5, 127.5, 127.3, 78.6, 52.8, 41.2, 35.6, 18.4, 13.7. $[\alpha]_{\text{D}}^{20} = -65.2$ ($c = 0.86$ in CHCl_3 , 96% ee). IR ν max: 2963, 2929, 2872, 1764, 1734, 1555 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{16}\text{H}_{19}\text{NO}_6\text{Na}$) requires m/z 344.1110, found m/z 344.1103. The enantiomeric excess was determined by HPLC. [AS-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 10.725 min (minor), 12.784 min (major).

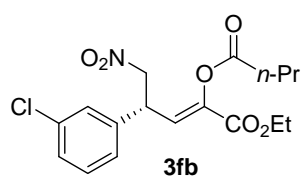
(R,Z)-ethyl 2-(butyryloxy)-5-nitro-4-phenylpent-2-enoate (3bb)



The product was obtained in 50% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.38-7.34 (m, 2H), 7.32-7.30 (m, 1H), 7.24-7.22 (m, 2H), 6.62 (d, $J = 9.6$ Hz, 1H), 4.73-4.63 (m, 2H), 4.55-4.49 (m, 1H), 4.22 (q, $J = 7.2$ Hz, 2H), 2.52-2.48 (m, 2H), 1.79-1.70 (m, 2H), 1.28 (t, $J = 7.2$ Hz, 3H), 1.03 (t, $J = 7.6$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 171.3, 161.4, 140.4, 136.8, 129.5, 128.4, 127.5, 126.9, 78.5, 62.1, 41.2, 35.6, 18.4, 14.2, 13.7. $[\alpha]_{\text{D}}^{20} = -57.5$ ($c = 0.89$ in CHCl_3 , 83% ee). IR ν max: 2966, 2914, 2870, 1763, 1728, 1555 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{17}\text{H}_{21}\text{NO}_6\text{Na}$) requires m/z 358.1267, found m/z 358.1259. [AS-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 9.026 min (minor), 10.001 min (major).

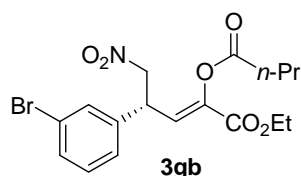
(R,Z)-ethyl 2-(butyryloxy)-4-(3-chlorophenyl)-5-nitropent-2-enoate (3fb)

The product was obtained in 45% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.30-7.29 (m, 2H), 7.23 (s, 1H), 7.15-7.22 (m, 1H), 6.57 (d, $J = 9.2$ Hz, 1H), 4.72-4.62 (m, 2H), 4.52-4.46 (m, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 2.52-2.48 (m, 2H), 1.79-1.70 (m, 2H), 1.29 (t, $J = 7.0$ Hz, 3H), 1.03 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz,



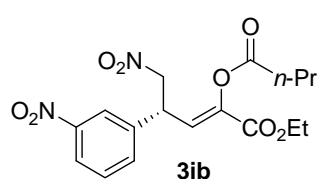
CDCl₃): δ (ppm) 171.2, 161.2, 140.8, 138.8, 135.3, 130.8, 128.7, 127.8, 126.0, 125.7, 78.2, 62.2, 40.8, 35.6, 18.4, 14.2, 13.7. $[\alpha]_D^{20} = -52.7$ ($c = 0.83$ in CHCl₃, 89% ee). IR ν max: 2966, 2914, 2872, 1762, 1725, 1553 cm⁻¹. HRMS: exact mass calculated for $[M+Na]^+$ (C₁₇H₂₀NO₆ClNa) requires m/z 392.0877, found m/z 392.0876. [AS-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 9.831 min (minor), 10.993 min (major).

(R,Z)-ethyl 4-(3-bromophenyl)-2-(butyryloxy)-5-nitropent-2-enoate (3gb)



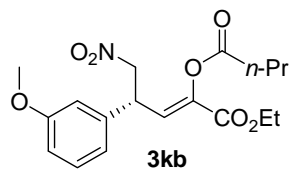
The product was obtained in 43% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.46-7.43 (m, 1H), 7.38 (t, $J = 1.8$ Hz, 1H), 7.23 (t, $J = 7.8$ Hz, 1H), 7.16 (d, $J = 7.8$ Hz, 1H), 6.56 (d, $J = 9.6$ Hz, 1H), 4.71-4.61 (m, 2H), 4.51-4.45 (m, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 2.52-2.48 (m, 2H), 1.79-1.70 (m, 2H), 1.29 (t, $J = 7.2$ Hz, 3H), 1.03 (t, $J = 7.4$ Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 171.2, 161.2, 140.8, 139.1, 131.7, 131.0, 130.7, 126.2, 126.0, 123.4, 78.2, 62.2, 40.7, 35.6, 18.4, 14.2, 13.7. $[\alpha]_D^{20} = -50.0$ ($c = 0.89$ in CHCl₃, 90% ee). IR ν max: 2965, 2926, 2866, 1763, 1728, 1555 cm⁻¹. HRMS: exact mass calculated for $[M+Na]^+$ (C₁₇H₂₀NO₆BrNa) requires m/z 436.0372, found m/z 436.0367. [AS-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 10.724 min (minor), 11.888 min (major).

(R,Z)-ethyl 2-(butyryloxy)-5-nitro-4-(3-nitrophenyl)pent-2-enoate (3ib)



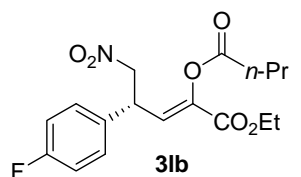
The product was obtained in 61% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.20-8.17 (m, 1H), 8.14-8.13 (m, 1H), 7.60-7.54 (m, 2H), 6.60 (d, $J = 9.2$ Hz, 1H), 4.80-4.70 (m, 2H), 4.66-4.60 (m, 1H), 4.24 (q, $J = 7.2$ Hz, 2H), 2.54-2.50 (m, 2H), 1.78-1.72 (m, 2H), 1.29 (t, $J = 7.2$ Hz, 3H), 1.03 (t, $J = 7.4$ Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 171.2, 161.0, 141.3, 139.0, 133.8, 130.6, 125.1, 123.5, 122.6, 77.8, 62.3, 40.7, 35.6, 18.4, 14.2, 13.7. $[\alpha]_D^{20} = -43.1$ ($c = 1.16$ in CHCl₃, 82% ee). IR ν max: 2967, 2929, 2876, 1763, 1729, 1556, 1531, 1351 cm⁻¹. HRMS: exact mass calculated for $[M+Na]^+$ (C₁₇H₂₀N₂O₈Na) requires m/z 403.1117, found m/z 403.1130. [AS-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 26.827 min (minor), 30.03 min (major).

(R,Z)-ethyl 2-(butyryloxy)-4-(3-methoxyphenyl)-5-nitropent-2-enoate (3kb)



The product was obtained in 63% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.27 (t, $J = 7.8$ Hz, 1H), 6.84-6.80 (m, 2H), 6.75 (t, $J = 2.0$ Hz, 1H), 6.60 (d, $J = 9.6$ Hz, 1H), 4.72-4.61 (m, 2H), 4.52-4.45 (m, 1H), 4.22 (q, $J = 7.2$ Hz, 2H), 3.79 (s, 3H), 2.52-2.48 (m, 2H), 1.79-1.71 (m, 2H), 1.28 (t, $J = 7.0$ Hz, 3H), 1.03 (t, $J = 7.4$ Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 171.3, 161.4, 160.3, 140.4, 138.3, 130.5, 126.8, 119.6, 113.7, 113.5, 78.4, 62.1, 55.4, 41.1, 35.6, 18.4, 14.2, 13.7. $[\alpha]_D^{20} = -47.9$ ($c = 1.15$ in CHCl₃, 73% ee). IR ν max: 2966, 2936, 2872, 1763, 1728, 1554 cm⁻¹. HRMS: exact mass calculated for $[M+H]^+$ (C₁₈H₂₄NO₇) requires m/z 366.1553, found m/z 366.1549. [AD-H, 230 nm, hexane : IPA = 90 : 10, 1.0 mL/min]: 12.418 min (major), 12.784 min (minor).

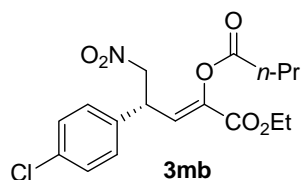
(R,Z)-ethyl 2-(butyryloxy)-4-(4-fluorophenyl)-5-nitropent-2-enoate (3lb)



The product was obtained in 69% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.23-7.19 (m, 2H), 7.07-7.02 (m, 2H), 6.58 (d, $J = 9.6$ Hz, 1H), 4.70-4.61 (m, 2H), 4.53-4.47 (m, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 2.54-2.45 (m, 2H), 1.79-1.70 (m, 2H), 1.28 (t, $J = 7.0$ Hz, 3H), 1.03 (t, $J = 7.4$ Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 171.2, 163.8, 161.3, 140.5, 132.6 (d, $J_{C-F} = 3.3$ Hz), 129.2 (d, $J_{C-F} = 8.1$ Hz), 126.5, 116.5 (d, $J_{C-F} = 21.5$ Hz), 78.5, 62.2, 40.5, 35.6, 18.4, 14.2, 13.7. $[\alpha]_D^{20} = -33.7$ ($c = 1.18$ in CHCl₃, 84%

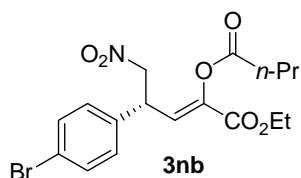
ee). IR ν max: 2966, 2920, 2866, 1761, 1719, 1553 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{H}]^+$ ($\text{C}_{17}\text{H}_{21}\text{NO}_6\text{F}$) requires m/z 354.1353, found m/z 354.1346. [AS-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 10.008 min (minor), 11.632 min (major).

(R,Z)-ethyl 2-(butyryloxy)-4-(4-chlorophenyl)-5-nitropent-2-enoate (3mb)



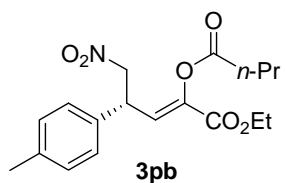
The product was obtained in 55% yield. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.34-7.32 (m, 2H), 7.18-7.16 (m, 2H), 6.56 (d, $J = 9.6$ Hz, 1H), 4.70-4.60 (m, 2H), 4.52-4.46 (m, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 2.54-2.45 (m, 2H), 1.79-1.70 (m, 2H), 1.28 (t, $J = 7.0$ Hz, 3H), 1.03 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 171.2, 161.2, 140.6, 135.3, 134.5, 129.7, 128.9, 126.2, 78.3, 62.2, 40.6, 35.6, 18.4, 14.2, 13.7. $[\alpha]_D^{20} = -69.5$ ($c = 1.03$ in CHCl_3 , 88% ee). IR ν max: 2967, 2933, 2876, 1763, 1728, 1555 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{17}\text{H}_{20}\text{NO}_6\text{ClNa}$) requires m/z 392.0877, found m/z 392.0881. [AS-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 10.533 min (minor), 12.037 min (major).

(R,Z)-ethyl 4-(4-bromophenyl)-2-(butyryloxy)-5-nitropent-2-enoate (3nb)



The product was obtained in 50% yield. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.48 (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 8.4$ Hz, 2H), 6.56 (d, $J = 9.2$ Hz, 1H), 4.70-4.61 (m, 2H), 4.50-4.44 (m, 1H), 4.22 (q, $J = 7.2$ Hz, 2H), 2.51-2.47 (m, 2H), 1.79-1.69 (m, 2H), 1.28 (t, $J = 7.2$ Hz, 3H), 1.02 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 171.2, 161.2, 140.7, 135.8, 132.6, 129.2, 126.1, 122.5, 78.2, 62.2, 40.6, 35.6, 18.4, 14.2, 13.7. $[\alpha]_D^{20} = -52.1$ ($c = 1.03$ in CHCl_3 , 94% ee). IR ν max: 2967, 2933, 2872, 1763, 1728, 1555 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{17}\text{H}_{20}\text{NO}_6\text{BrNa}$) requires m/z 436.0372, found m/z 436.0381. [AS-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 11.29 min (minor), 12.877 min (major).

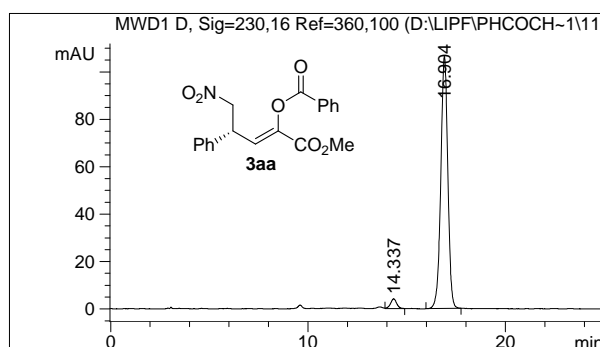
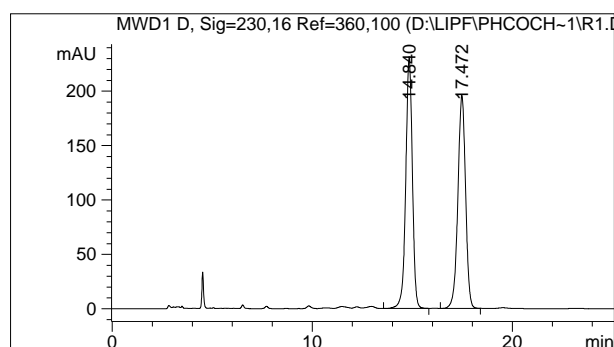
(R,Z)-ethyl 2-(butyryloxy)-5-nitro-4-p-tolylpent-2-enoate (3pb)



The product was obtained in 54% yield. ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.16 (d, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 8.0$ Hz, 2H), 6.60 (d, $J = 9.6$ Hz, 1H), 4.71-4.61 (m, 2H), 4.51-4.44 (m, 1H), 4.22 (q, $J = 7.2$ Hz, 2H), 2.52-2.48 (m, 2H), 2.32 (s, 3H), 1.80-1.70 (m, 2H), 1.28 (t, $J = 7.2$ Hz, 3H), 1.03 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 171.3, 161.4, 140.2, 138.3, 133.7, 130.1, 127.4, 127.2, 78.6, 62.0, 40.9, 35.6, 21.2, 18.4, 14.2, 13.7. $[\alpha]_D^{20} = -58.7$ ($c = 0.94$ in CHCl_3 , 78% ee). IR ν max: 2966, 2929, 2872, 1764, 1728, 1555 cm^{-1} . HRMS: exact mass calculated for $[\text{M}+\text{Na}]^+$ ($\text{C}_{18}\text{H}_{23}\text{NO}_6\text{Na}$) requires m/z 372.1423, found m/z 372.1422. [AS-H, 230 nm, hexane : IPA = 85 : 15, 1.0 mL/min]: 8.204 min (minor), 9.236 min (major).

E: CSP-HPLC Analysis of Michael-type Products

(*R,Z*)-1-(methoxycarbonyl)-4-nitro-3-phenylbut-1-enyl benzoate (**3aa**)

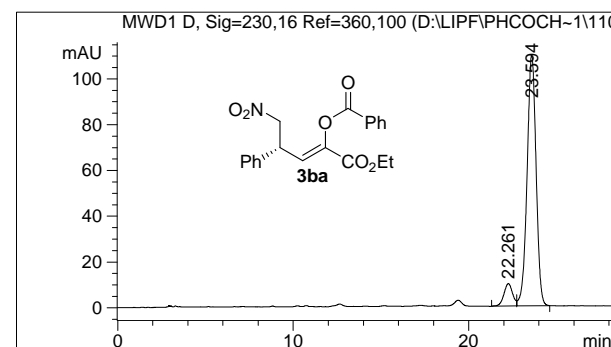
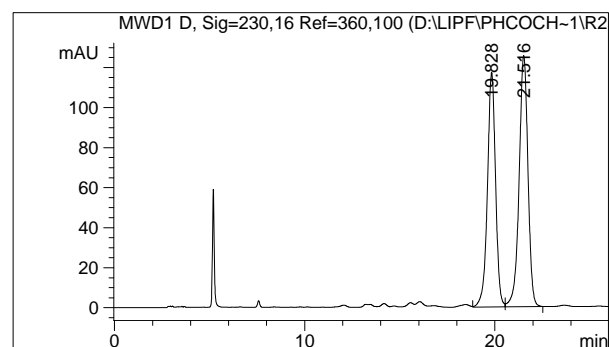


Racemic adduct

Chiral adduct

#	time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	14.84	5326.2	231.6	0.3523	50.282	1.049	1	14.337	89.9	4.1	0.3212	3.297	1.004
2	17.472	5266.6	196.4	0.4148	49.718	1.041	2	16.904	2636.9	106.4	0.3791	96.703	1.018

(*R,Z*)-1-(ethoxycarbonyl)-4-nitro-3-phenylbut-1-enyl benzoate (**3ba**)

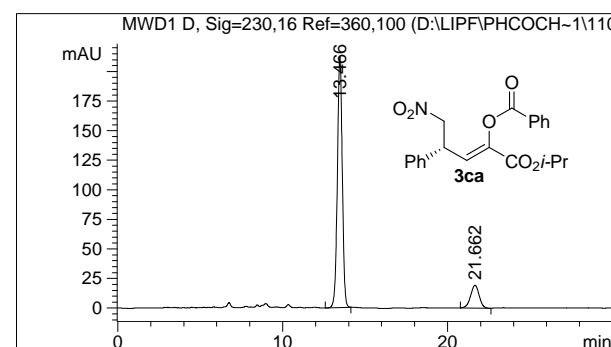
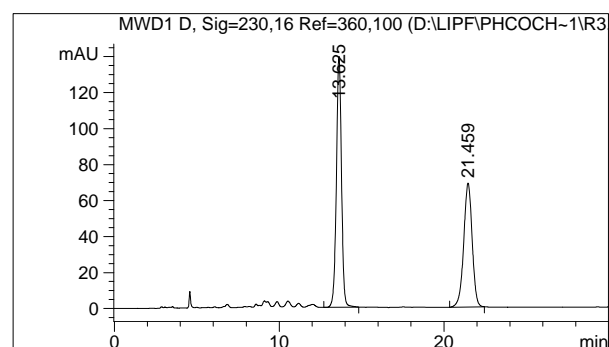


Racemic adduct

Chiral adduct

#	time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	19.828	3490	117.3	0.4571	46.244	1.039	1	22.261	341	9.9	0.5217	8.005	1.035
2	21.516	4056.9	125.5	0.495	53.756	1.072	2	23.594	3919	109.6	0.5531	91.995	1.041

(*R,Z*)-1-(isopropoxycarbonyl)-4-nitro-3-phenylbut-1-enyl benzoate (**3ca**)

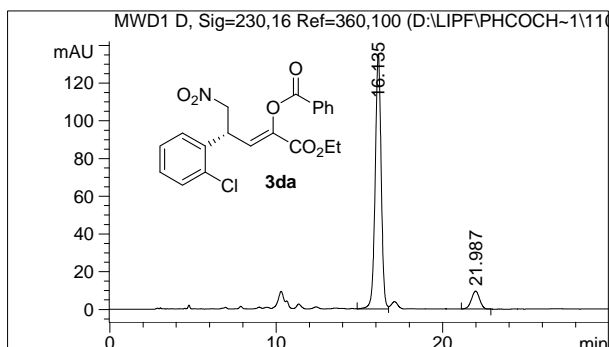
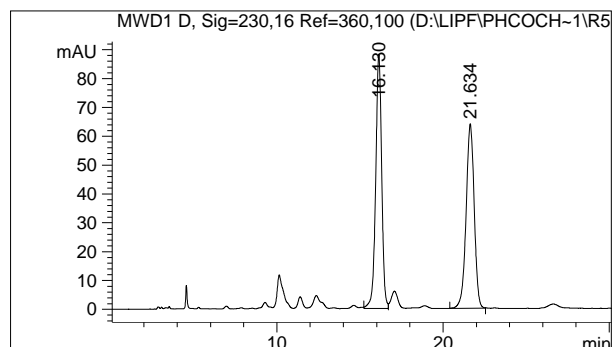


Racemic adduct

Chiral adduct

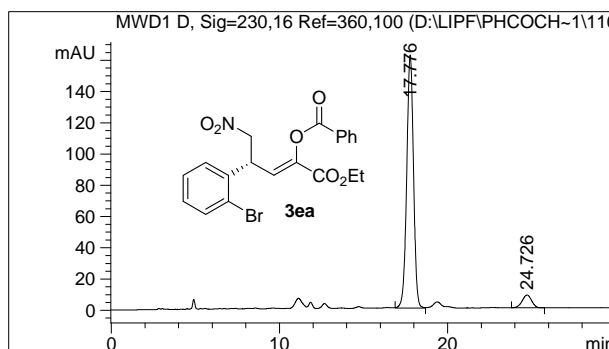
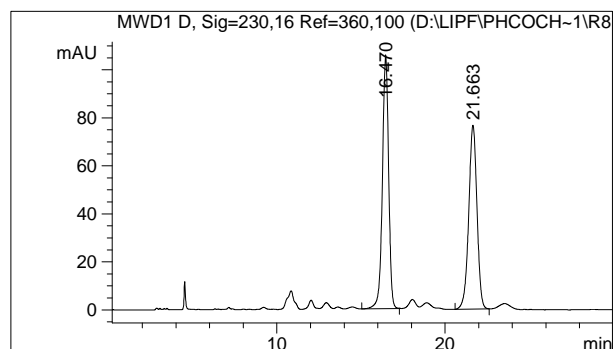
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	13.625	2994.9	139.4	0.3286	54.888	0.992	1	13.466	4392.5	212.3	0.3213	86.232	1.001
2	21.459	2461.5	69	0.5501	45.112	1.049	2	21.662	701.3	19.4	0.5557	13.768	1.049

(R,Z)-1-(ethoxycarbonyl)-3-(2-chlorophenyl)-4-nitrobut-1-enyl benzoate (3da)



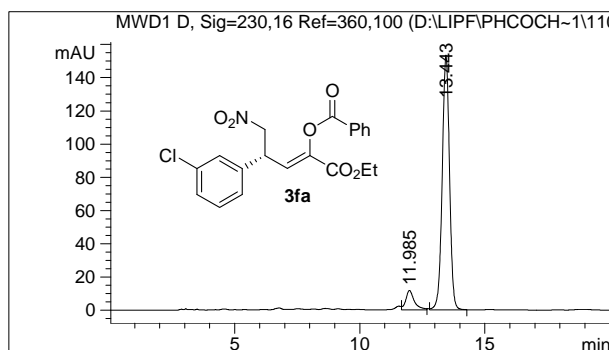
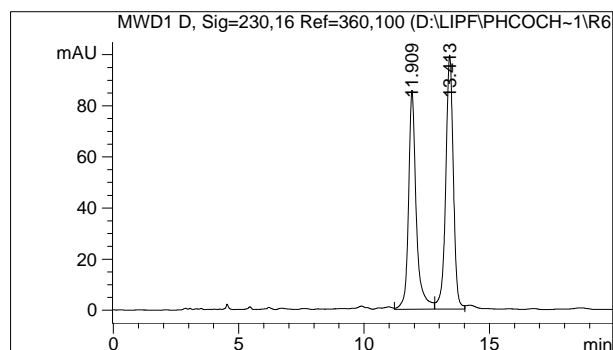
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	16.13	2209.6	88.1	0.3846	50.521	1.061	1	16.135	3360.4	135	0.3843	91.122	1.036
2	21.634	2164	64	0.5188	49.479	1.054	2	21.987	327.4	9.5	0.5086	8.878	1.025

(R,Z)-1-(ethoxycarbonyl)-3-(2-bromophenyl)-4-nitrobut-1-enyl benzoate (3ea)



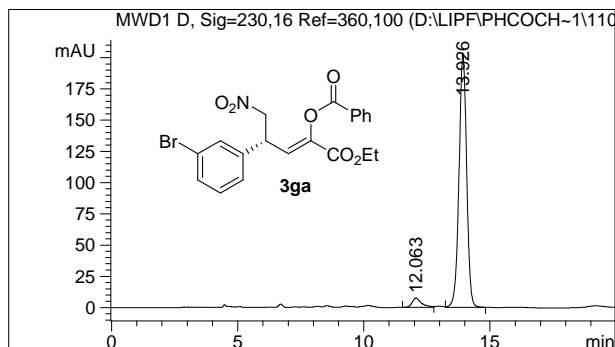
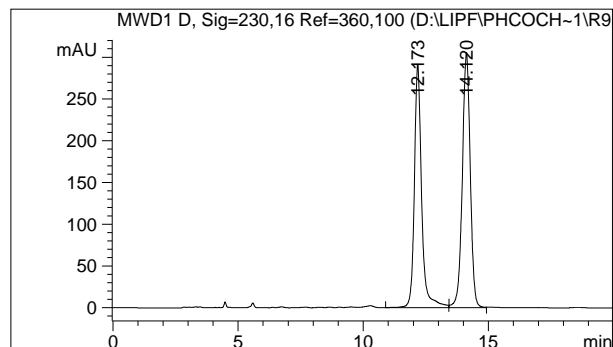
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	16.47	2722.6	105.8	0.3963	51.059	1.074	1	17.776	4527.9	162	0.432	93.386	1.028
2	21.663	2609.7	76.6	0.5256	48.941	1.035	2	24.726	320.7	8.2	0.5451	6.614	1.054

(R,Z)-1-(ethoxycarbonyl)-3-(3-chlorophenyl)-4-nitrobut-1-enyl benzoate (3fa)



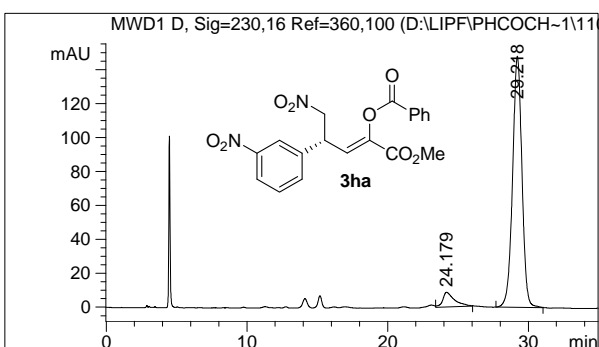
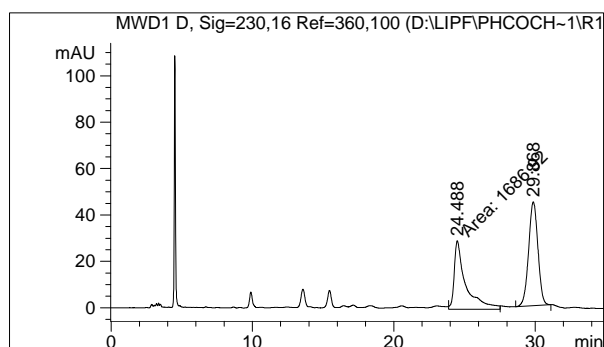
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	11.909	1827.8	85.7	0.3128	46.636	0.748	1	11.985	281.1	11.7	0.3455	8.280	0.689
2	13.413	2091.5	99.4	0.3214	53.364	1.044	2	13.443	3114	153.5	0.3127	91.720	1.005

(R,Z)-1-(ethoxycarbonyl)-3-(3-bromophenyl)-4-nitrobut-1-enyl benzoate (3ga)



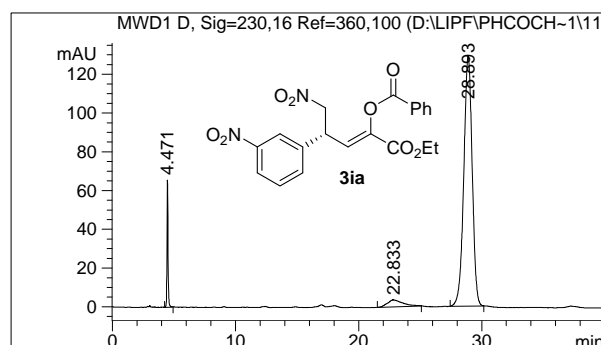
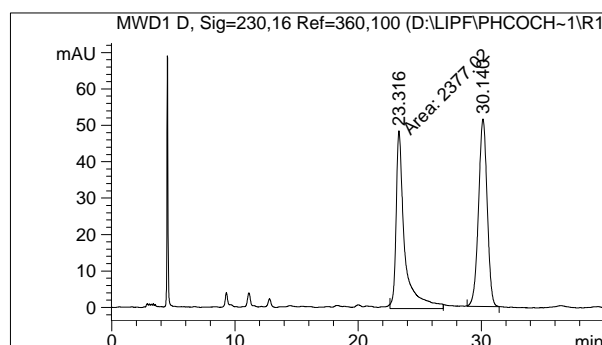
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	12.173	5907.5	291.4	0.3025	46.654	0.767	1	12.063	200.6	7.5	0.3881	4.467	0.613
2	14.12	6754.9	305.5	0.34	53.346	1.026	2	13.926	4289.7	203.8	0.3235	95.533	1.017

(R,Z)-1-(methoxycarbonyl)-4-nitro-3-(3-nitrophenyl)but-1-enyl benzoate (3ha)



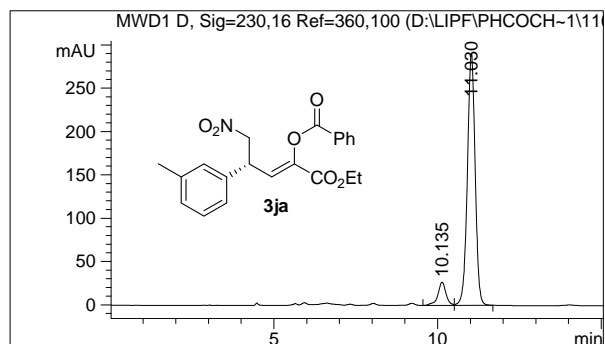
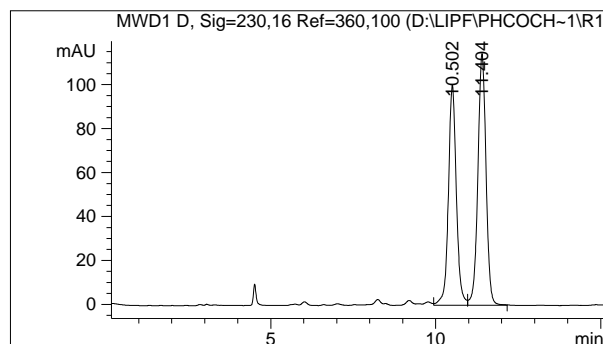
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	24.488	1686.9	29.5	0.9522	45.209	0.342	1	24.179	502.7	8.7	0.7569	6.831	0.464
2	29.868	2044.4	44.8	0.7085	54.791	0.988	2	29.218	6857.2	148	0.7126	93.169	1.016

(R,Z)-1-(ethoxycarbonyl)-4-nitro-3-(3-nitrophenyl)but-1-enyl benzoate (3ia)



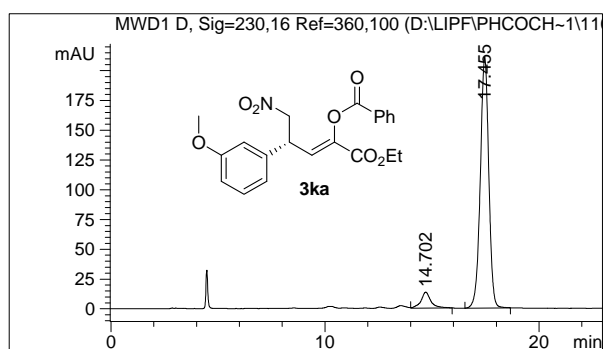
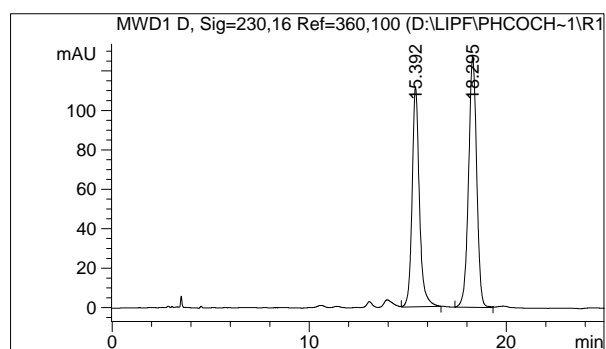
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	23.316	2377	48.9	0.8107	48.599	0.472	1	22.833	324.9	3.7	1.0488	5.037	0.62
2	30.14	2514.1	51.5	0.7377	51.401	1.038	2	28.893	6125.5	129.2	0.7351	94.963	1.05

(R,Z)-1-(ethoxycarbonyl)-4-nitro-3-m-tolylbut-1-enyl benzoate (3ja)



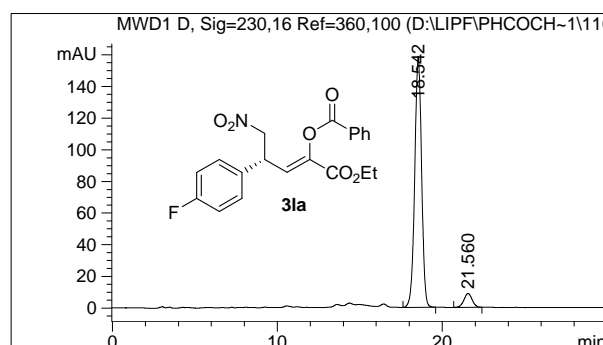
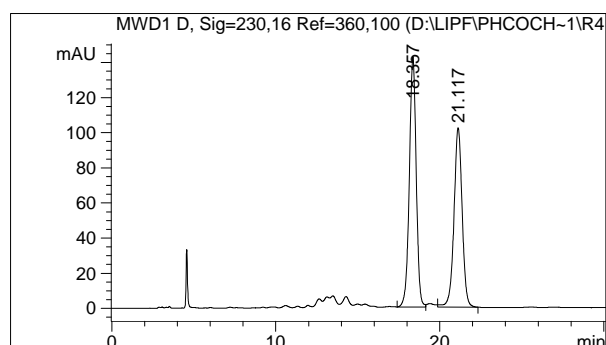
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	10.502	1681.6	100.5	0.2533	46.060	0.938	1	10.135	468.1	26.9	0.2611	8.876	1.068
2	11.404	1969.3	114.5	0.2647	53.940	0.998	2	11.03	4805.3	290.6	0.2549	91.124	1.017

(R,Z)-1-(ethoxycarbonyl)-3-(3-methoxyphenyl)-4-nitrobut-1-enyl benzoate (3ka)



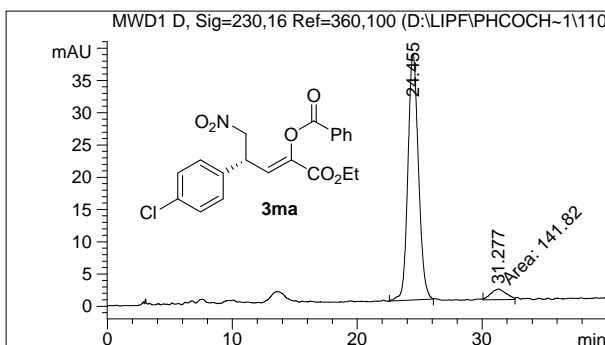
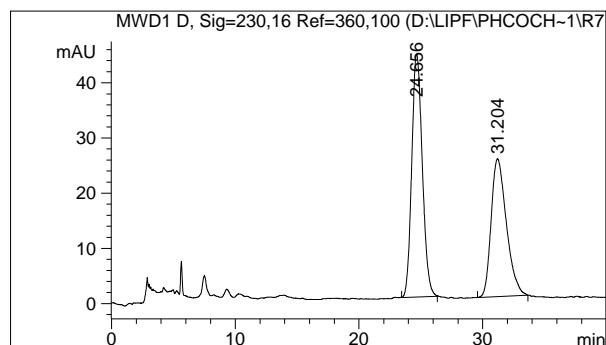
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	15.392	2863.6	111.3	0.3861	43.969	0.823	1	14.702	439	13.5	0.4679	7.057	0.87
2	18.295	3649.2	127.2	0.4428	56.031	1.024	2	17.455	5782.2	211.1	0.4195	92.943	1.024

(R,Z)-1-(ethoxycarbonyl)-3-(4-fluorophenyl)-4-nitrobut-1-enyl benzoate (3la)



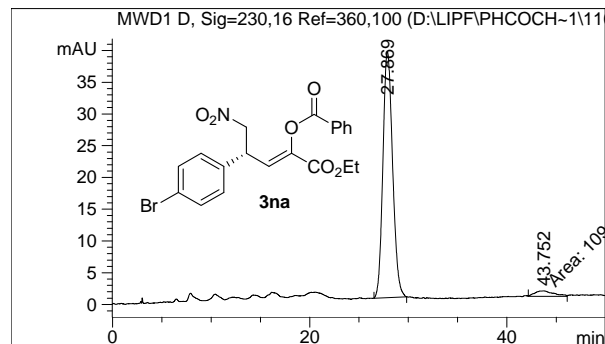
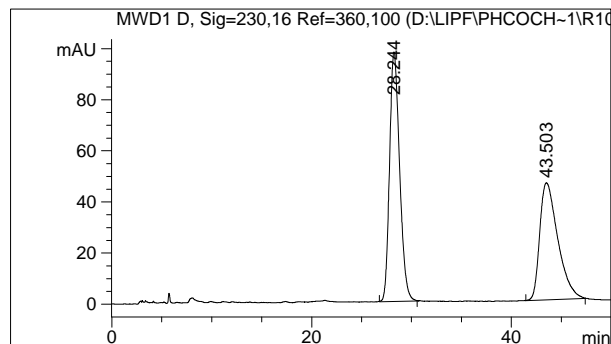
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	18.357	4149.9	142.7	0.4473	53.823	1.03	1	18.542	4588	158.6	0.4474	93.759	1.018
2	21.117	3560.4	102.2	0.5303	46.177	1.022	2	21.56	305.4	8.7	0.5224	6.241	0.991

(R,Z)-1-(ethoxycarbonyl)-3-(4-chlorophenyl)-4-nitrobut-1-enyl benzoate (3ma)



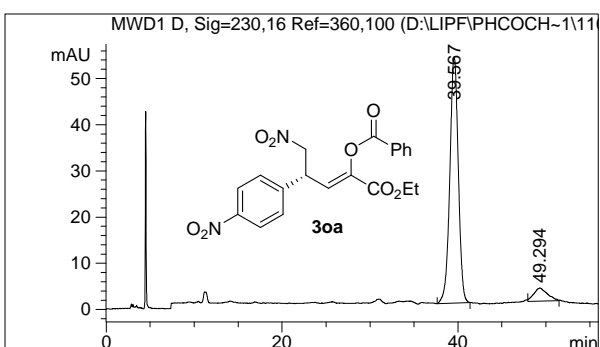
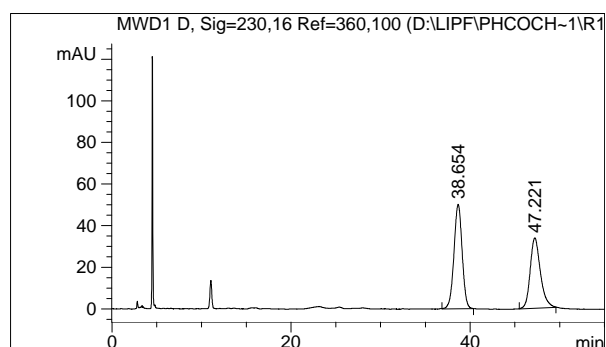
Racemic adduct						Chiral adduct							
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	24.656	2602.5	44	0.8955	54.924	0.81	1	24.455	2234.2	38.1	0.8636	94.031	0.885
2	31.204	2135.8	25	1.1443	45.076	0.685	2	31.277	141.8	1.7	1.4298	5.969	0.892

(R,Z)-1-(ethoxycarbonyl)-3-(4-bromophenyl)-4-nitrobut-1-enyl benzoate (3na)



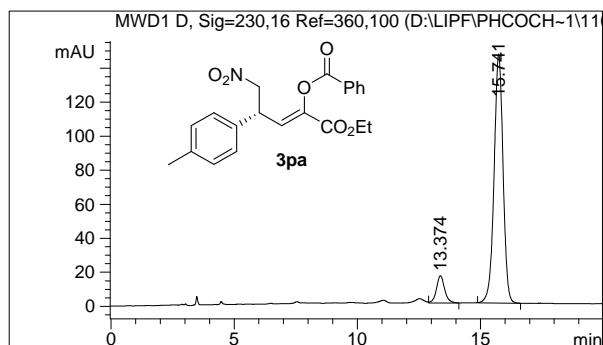
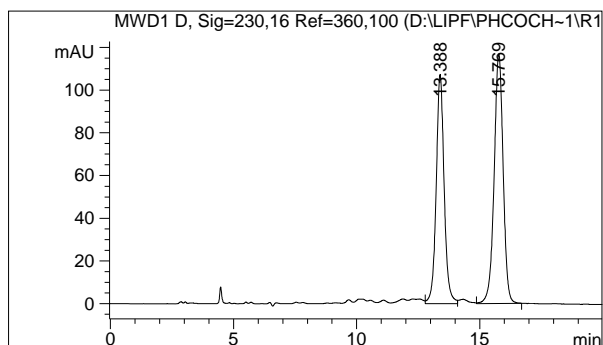
Racemic adduct						Chiral adduct							
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	28.244	6812.8	97.6	1.0484	54.295	0.75	1	27.869	2646	38.8	1.0261	96.014	0.806
2	43.503	5734.9	45.8	1.4763	45.705	0.562	2	43.752	109.8	8.5E-1	2.1473	3.986	0.883

(R,Z)-1-(ethoxycarbonyl)-4-nitro-3-(4-nitrophenyl)but-1-enyl benzoate (3oa)



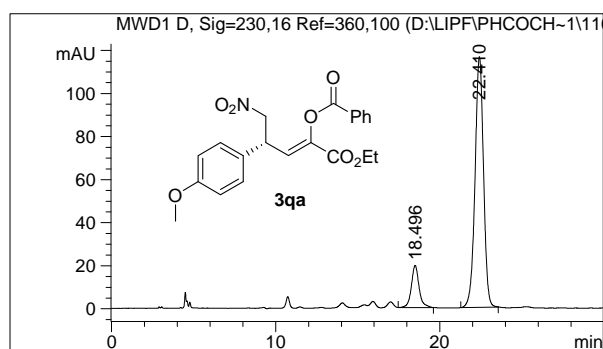
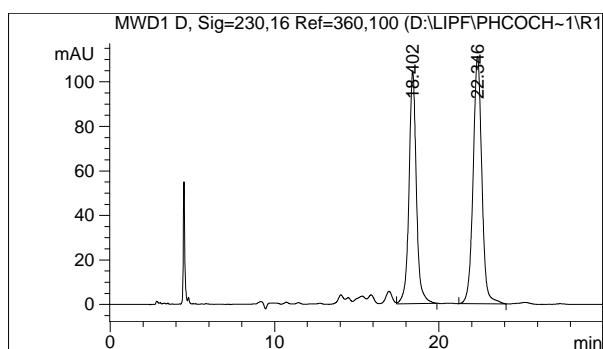
Racemic adduct						Chiral adduct							
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	38.654	3201.2	50.3	0.9751	54.461	1.027	1	39.567	3565.4	53.3	0.9823	92.119	1.027
2	47.221	2676.7	33.8	1.1105	45.539	0.8	2	49.294	305	2.8	1.2698	7.881	0.757

(R,Z)-1-(ethoxycarbonyl)-4-nitro-3-p-tolylbut-1-enyl benzoate (3pa)



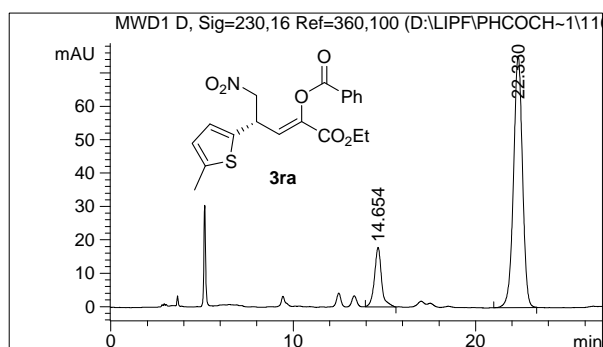
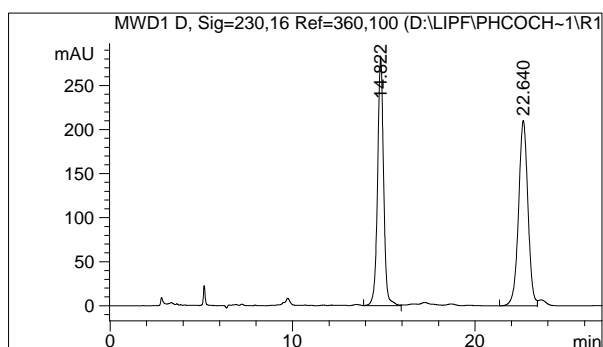
Racemic adduct						Chiral adduct							
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	13.388	2410.3	107.4	0.3399	44.702	0.923	1	13.374	372.2	16.1	0.3445	9.128	0.899
2	15.769	2981.6	116.9	0.3916	55.298	1.032	2	15.741	3705.3	146.5	0.3912	90.872	1.036

(R,Z)-1-(ethoxycarbonyl)-3-(4-methoxyphenyl)-4-nitrobut-1-enyl benzoate (3qa)



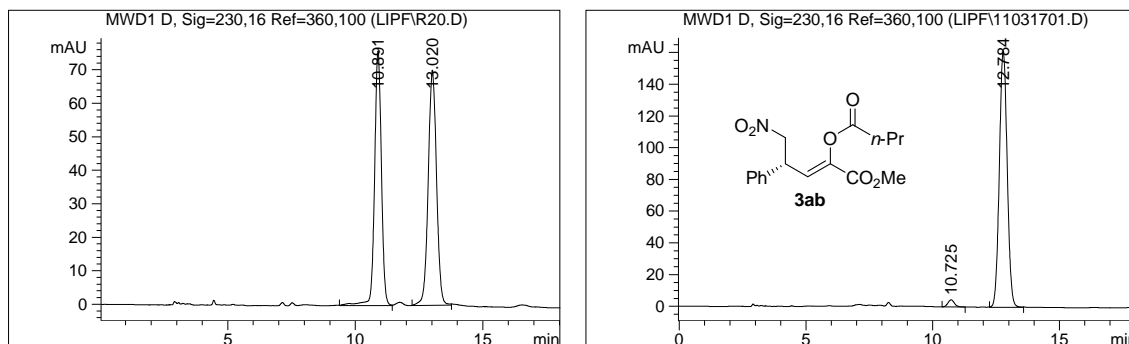
Racemic adduct						Chiral adduct							
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	18.402	3252.8	104.5	0.4712	44.251	0.939	1	18.496	646.7	19.7	0.4875	13.402	0.924
2	22.346	4098.1	111.2	0.5621	55.749	0.963	2	22.41	4178.8	116.5	0.5525	86.598	1.036

(S,Z)-1-(ethoxycarbonyl)-3-(5-methylthiophen-2-yl)-4-nitrobut-1-enyl benzoate (3ra)



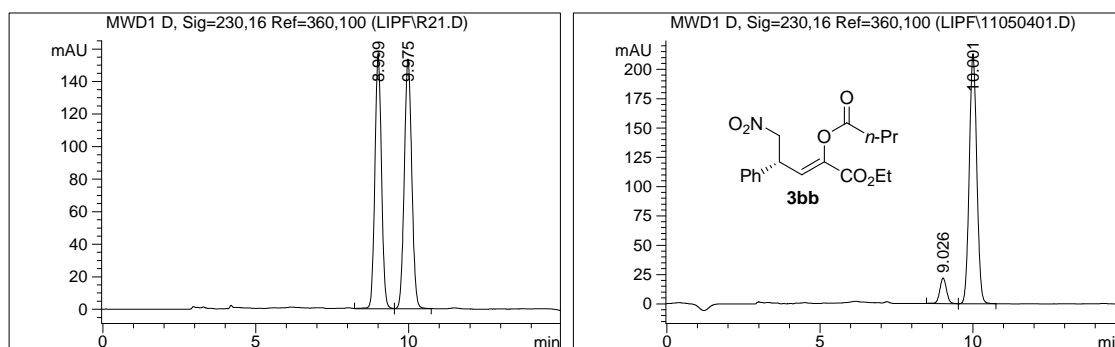
Racemic adduct						Chiral adduct							
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	14.822	6475.1	283.3	0.3486	46.341	0.963	1	14.654	482.7	17.9	0.4034	15.773	0.992
2	22.64	7497.5	210.1	0.5482	53.659	0.993	2	22.33	2577.6	75.4	0.5288	84.227	1.035

(R,Z)-methyl 2-(butyryloxy)-5-nitro-4-phenylpent-2-enoate (3ab)



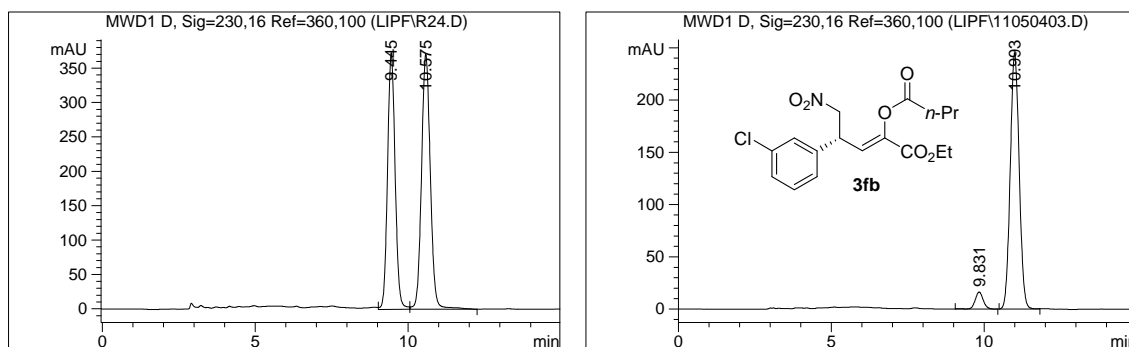
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	10.891	1420.1	76	0.2879	47.136	1.034	1	10.725	78.4	4.5	0.2752	2.207	0.89
2	13.02	1592.6	70.2	0.3528	52.864	0.979	2	12.784	3474.4	161.6	0.3348	97.793	0.936

(R,Z)-ethyl 2-(butyryloxy)-5-nitro-4-phenylpent-2-enoate (3bb)



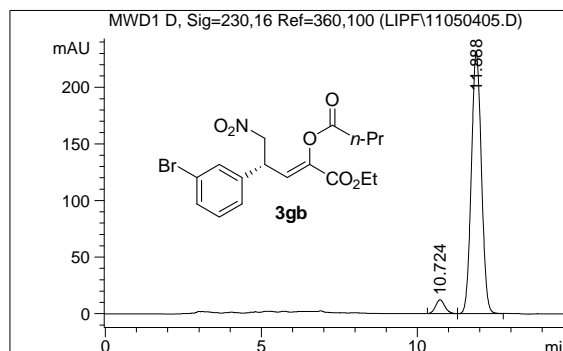
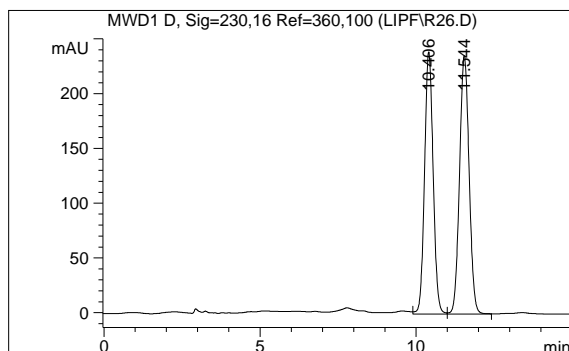
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	8.999	2351.9	156.8	0.233	47.448	0.946	1	9.026	332.1	21.8	0.2355	8.364	0.979
2	9.975	2604.9	153.5	0.266	52.552	0.939	2	10.001	3637.9	213.2	0.267	91.636	0.932

(R,Z)-ethyl 2-(butyryloxy)-4-(3-chlorophenyl)-5-nitropent-2-enoate (3fb)



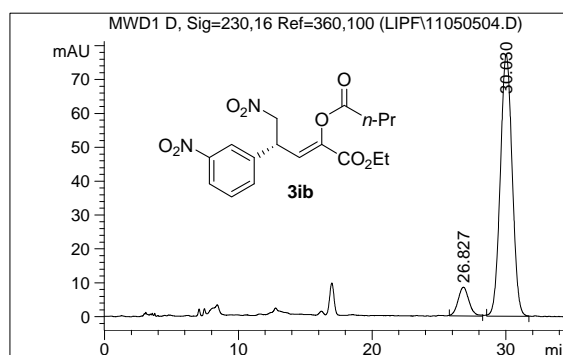
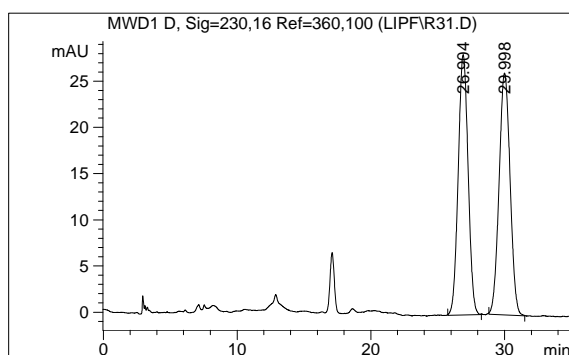
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	9.445	6463.4	373.4	0.2679	46.325	0.888	1	9.831	297.4	16.3	0.2812	5.641	0.947
2	10.575	7488.8	371	0.3115	53.675	0.885	2	10.993	4975	245.3	0.3166	94.359	0.934

(R,Z)-ethyl 4-(3-bromophenyl)-2-(butyryloxy)-5-nitro-2-enoate (3gb)



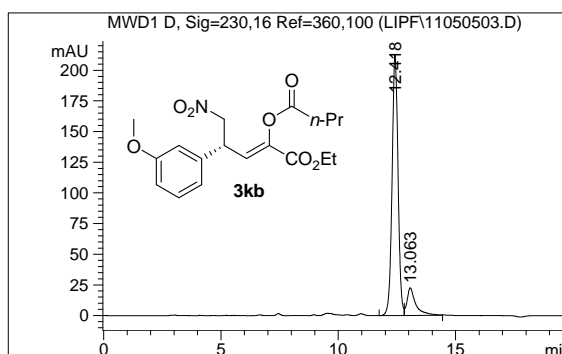
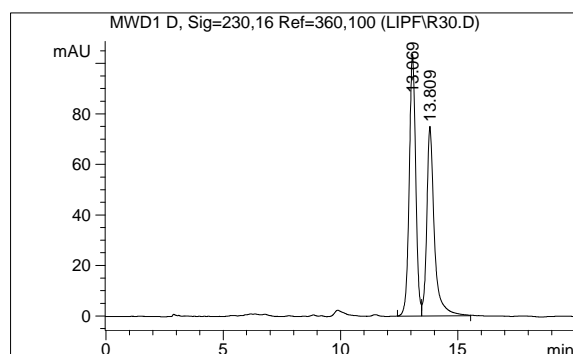
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	10.406	4578.1	239.5	0.297	47.606	0.924	1	10.724	253.5	12.2	0.3215	4.676	0.877
2	11.544	5038.5	236	0.3331	52.394	0.943	2	11.888	5166.8	231.3	0.3487	95.324	0.935

(R,Z)-ethyl 2-(butyryloxy)-5-nitro-4-(3-nitrophenyl)pent-2-enoate (3ib)



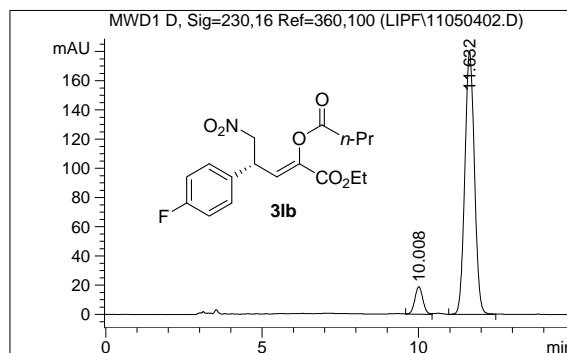
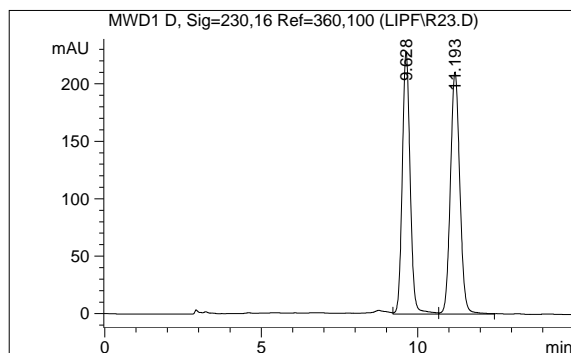
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	26.904	1446.3	28.2	0.8004	49.187	0.963	1	26.827	477.4	8.5	0.829	9.150	0.915
2	29.998	1494.1	26.2	0.8537	50.813	0.956	2	30.03	4739.6	77.2	0.9498	90.850	0.965

(R,Z)-ethyl 2-(butyryloxy)-4-(3-methoxyphenyl)-5-nitropent-2-enoate (3kb)



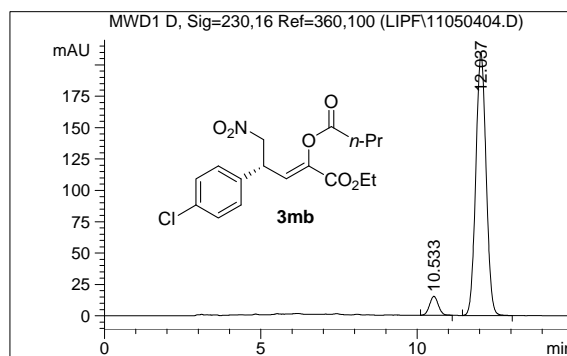
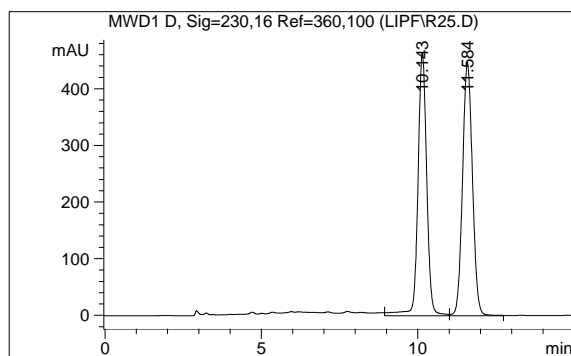
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	13.069	1988.3	103.6	0.2959	54.089	0.996	1	12.418	3765.5	213	0.2723	86.549	0.975
2	13.809	1687.7	75.1	0.3303	45.911	0.636	2	13.063	585.2	22.6	0.3666	13.451	0.497

(R,Z)-ethyl 2-(butyryloxy)-4-(4-fluorophenyl)-5-nitropent-2-enoate (3lb)



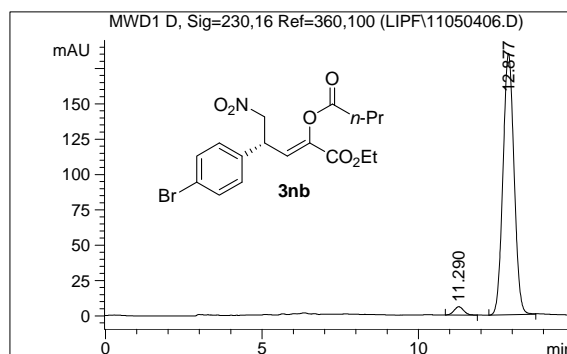
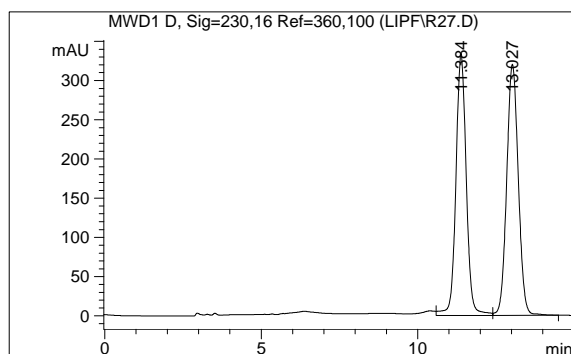
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	9.628	3999.6	228.1	0.2706	47.604	0.868	1	10.008	332.9	18.8	0.2767	7.991	0.954
2	11.193	4402.1	210.6	0.3258	52.396	0.902	2	11.632	3833.1	179.7	0.3329	92.009	0.94

(R,Z)-ethyl 2-(butyryloxy)-4-(4-chlorophenyl)-5-nitropent-2-enoate (3mb)



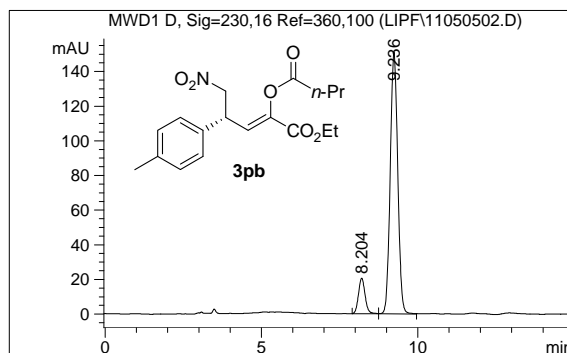
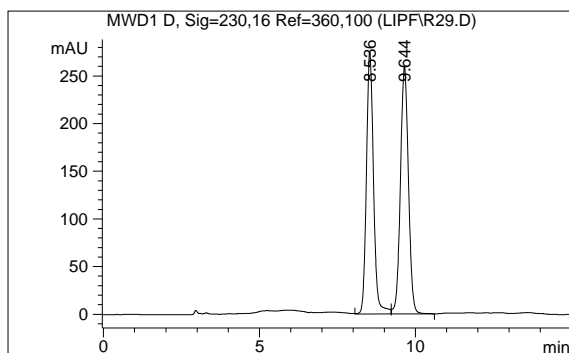
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	10.143	9092.7	463.7	0.3028	48.024	0.983	1	10.533	295.7	15.1	0.3043	5.834	0.928
2	11.584	9841	447.3	0.3447	51.976	0.915	2	12.037	4773.9	209.1	0.3563	94.166	0.942

(R,Z)-ethyl 4-(4-bromophenyl)-2-(butyryloxy)-5-nitropent-2-enoate (3nb)



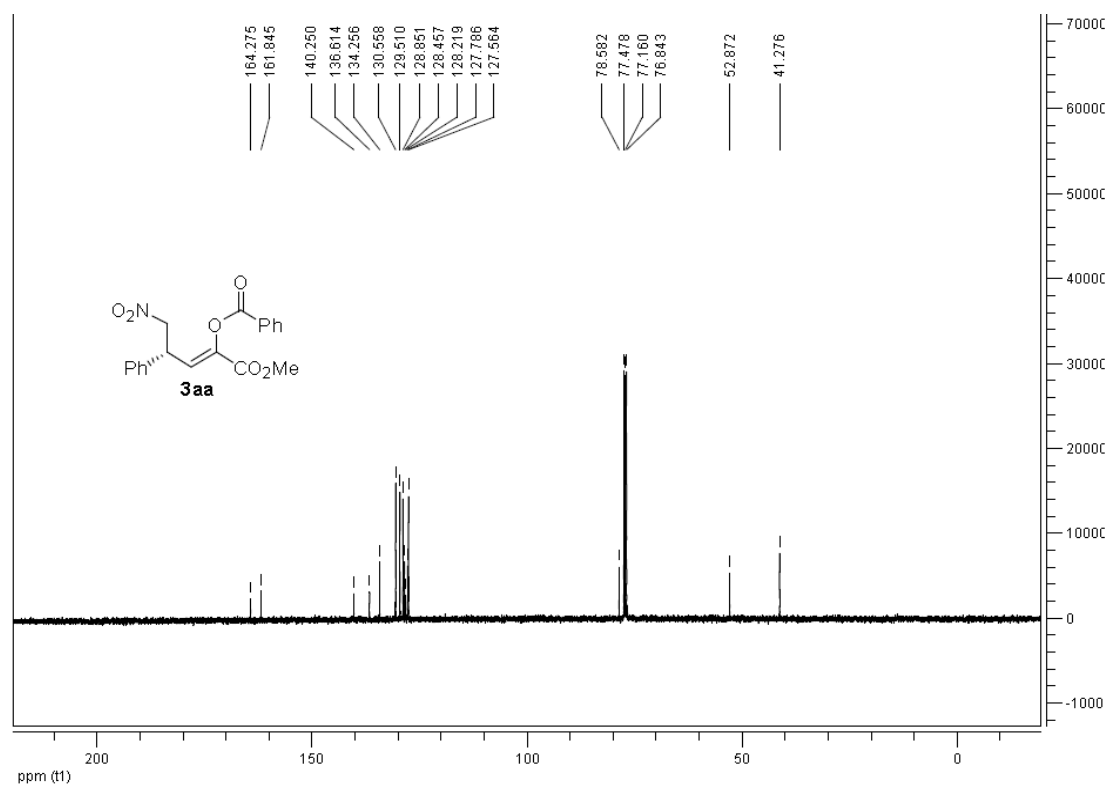
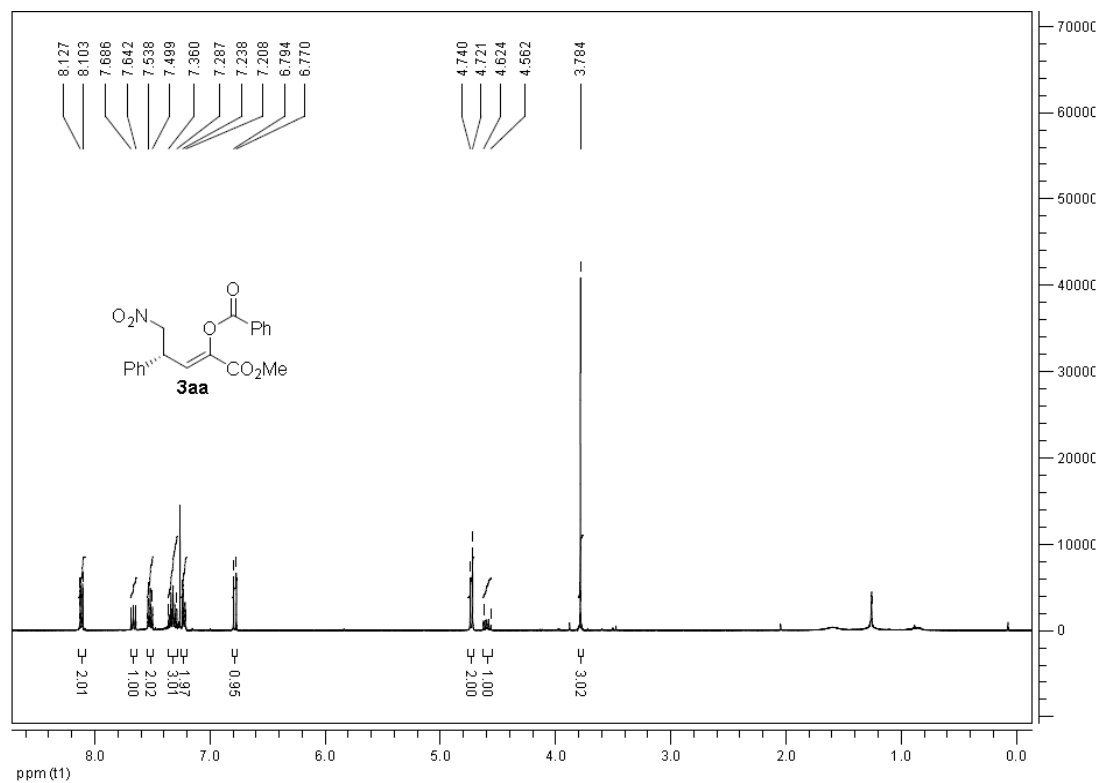
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	11.384	7736.5	334.3	0.358	48.381	0.936	1	11.29	126.3	5.8	0.3363	2.694	0.903
2	13.027	8254.4	320.3	0.4027	51.619	0.926	2	12.877	4561.9	184.9	0.3839	97.306	0.936

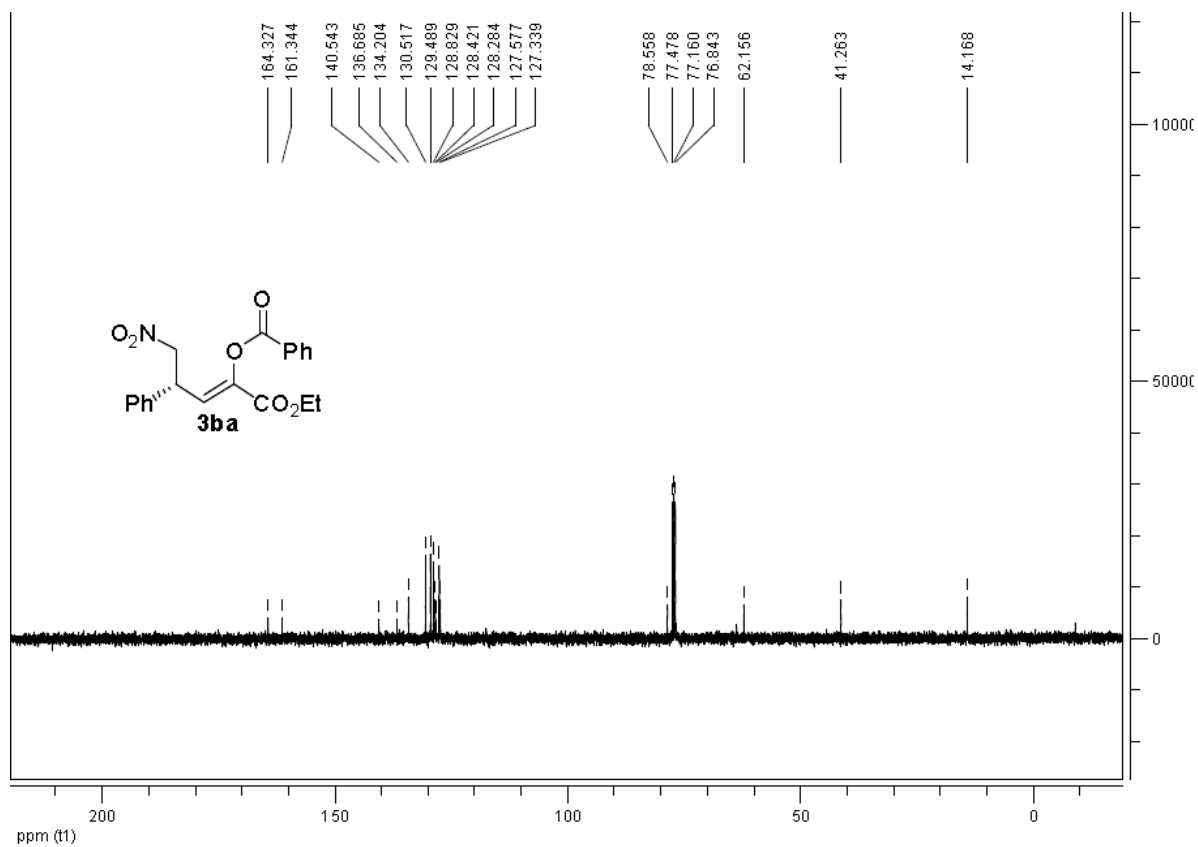
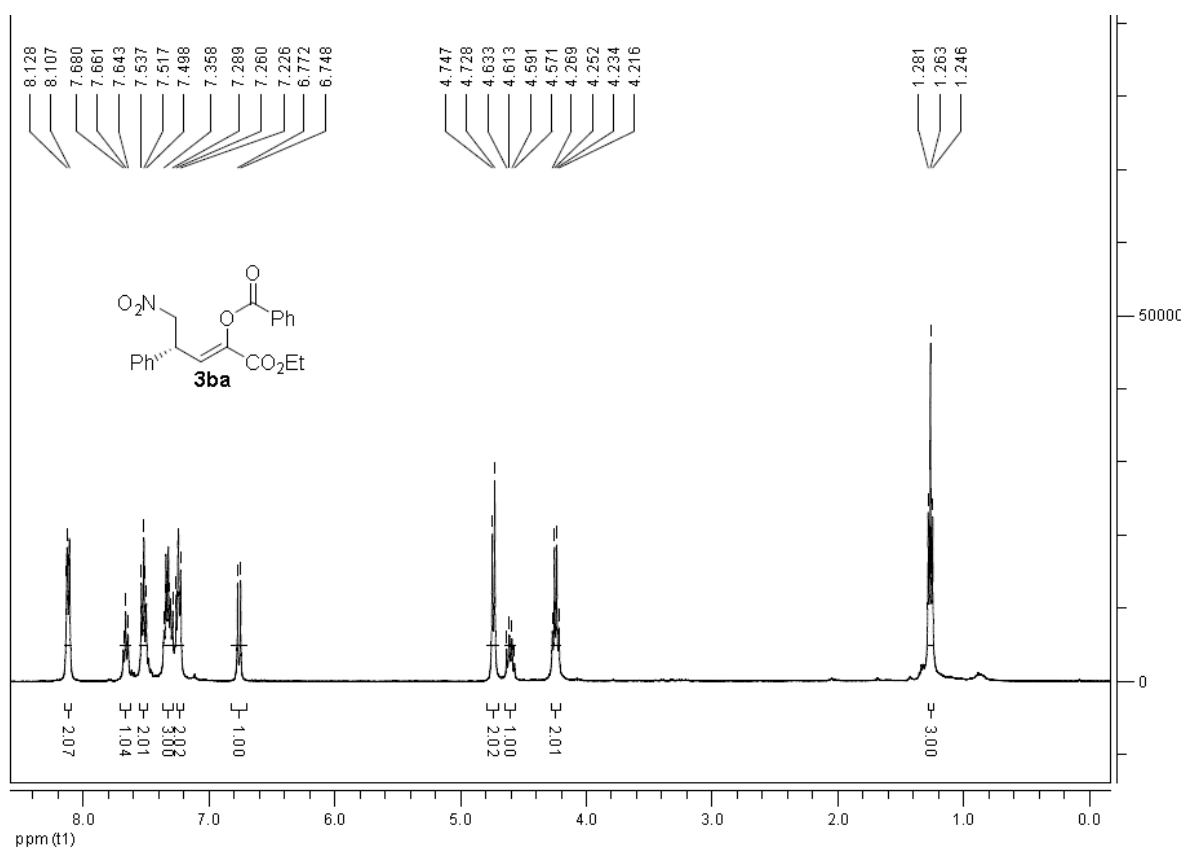
(R,Z)-ethyl 2-(butyryloxy)-5-nitro-4-p-tolylpent-2-enoate (3pb)

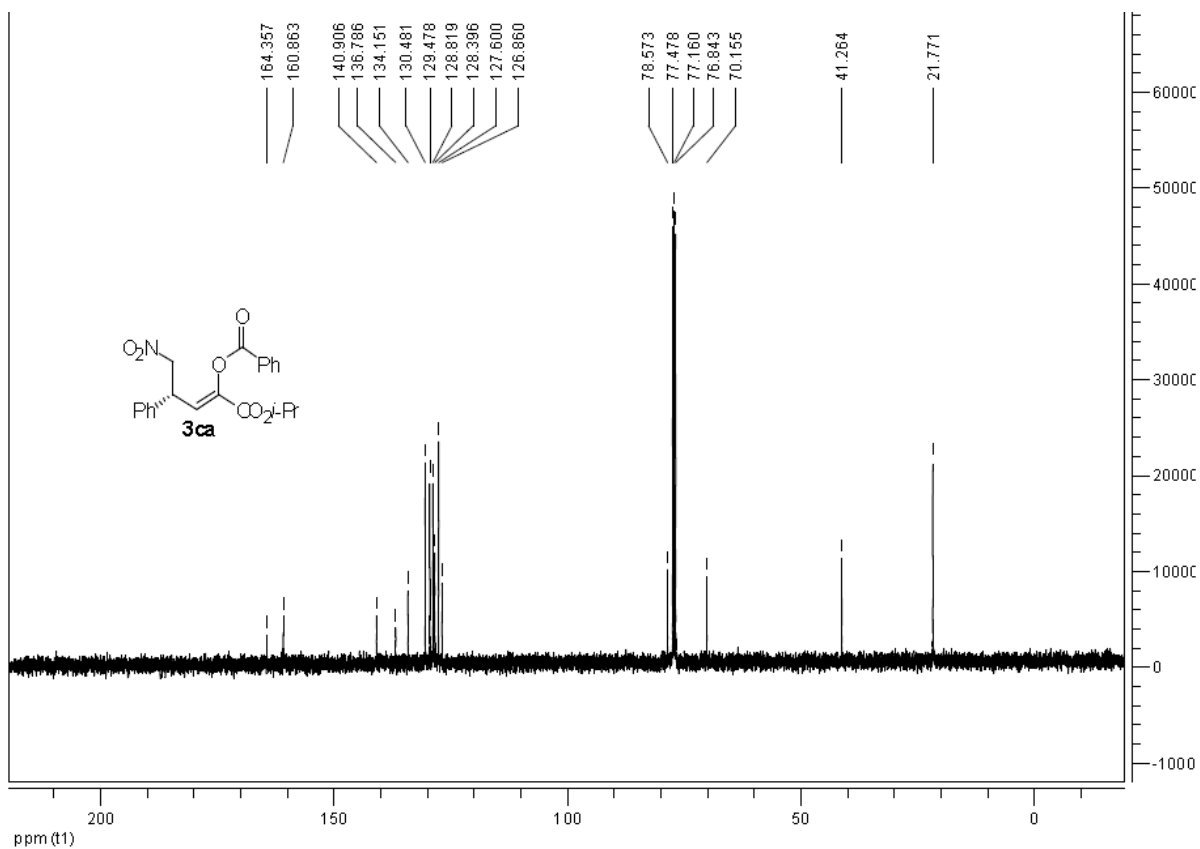
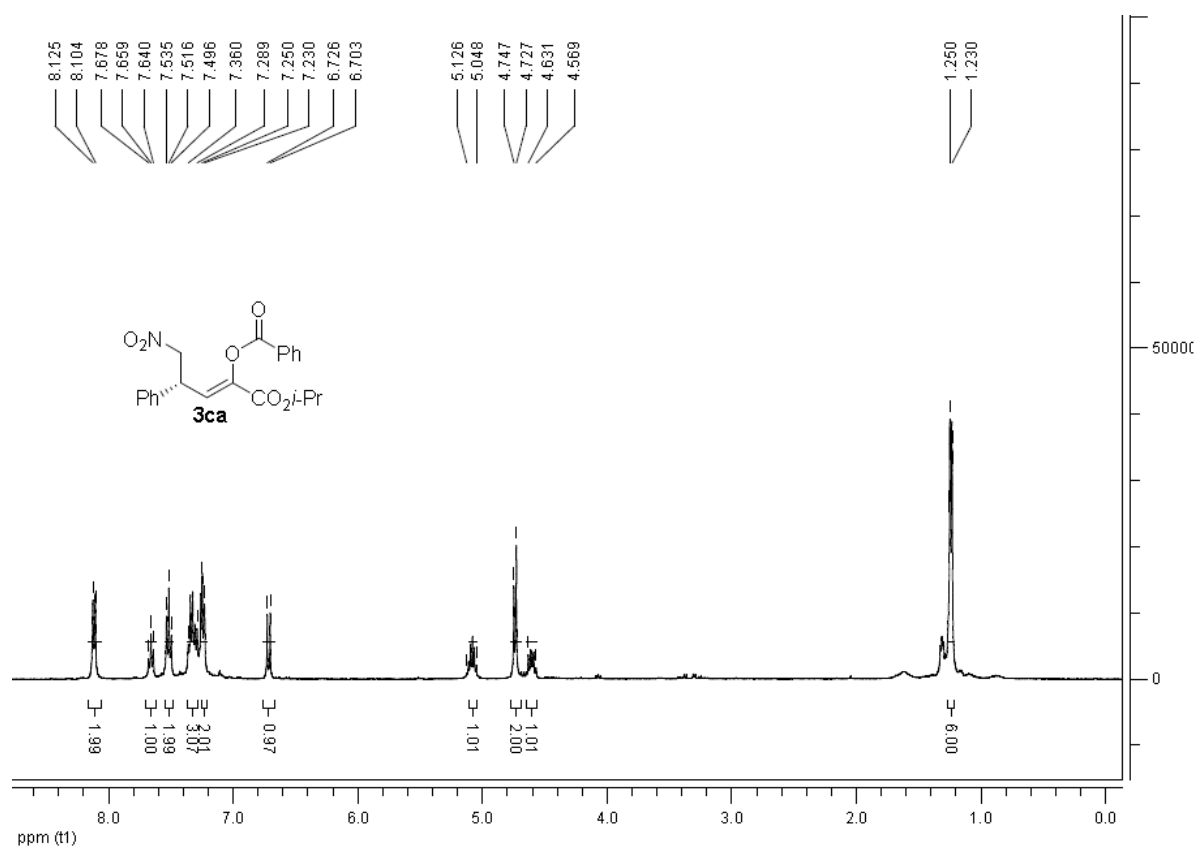


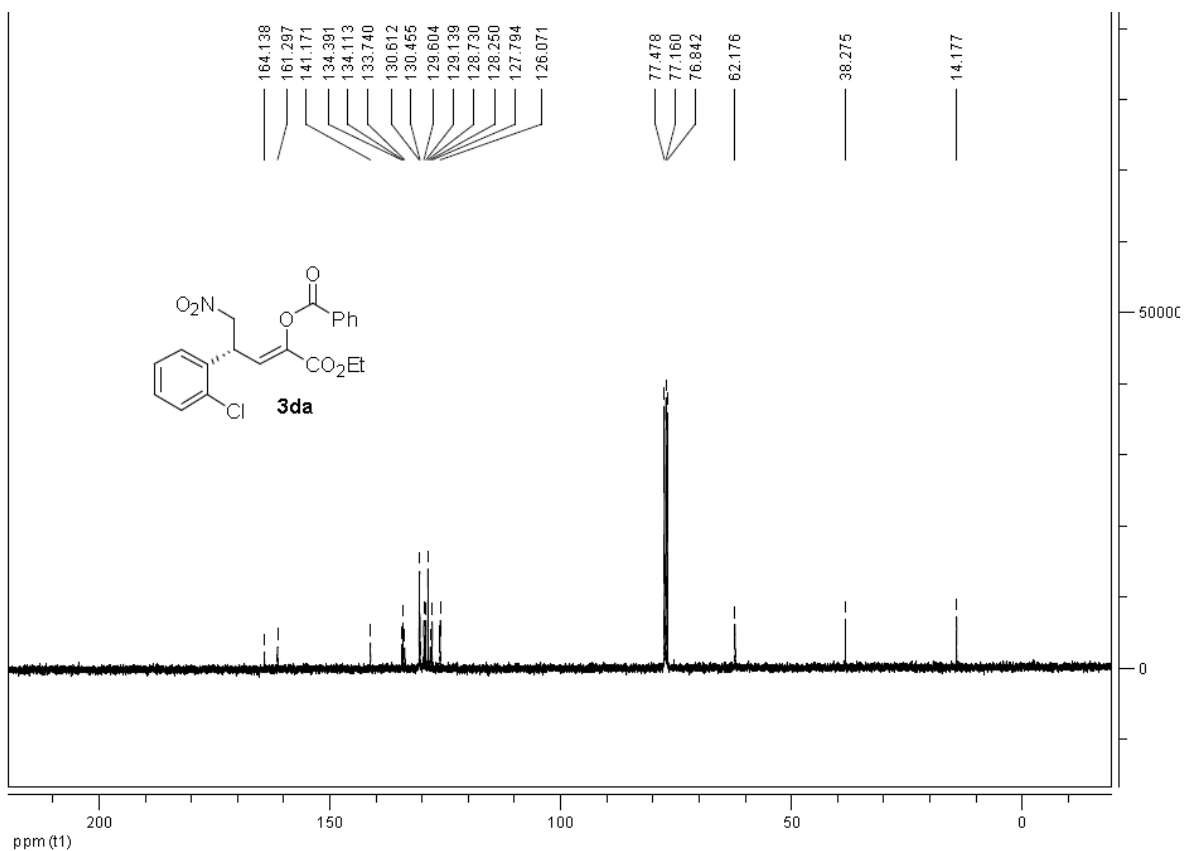
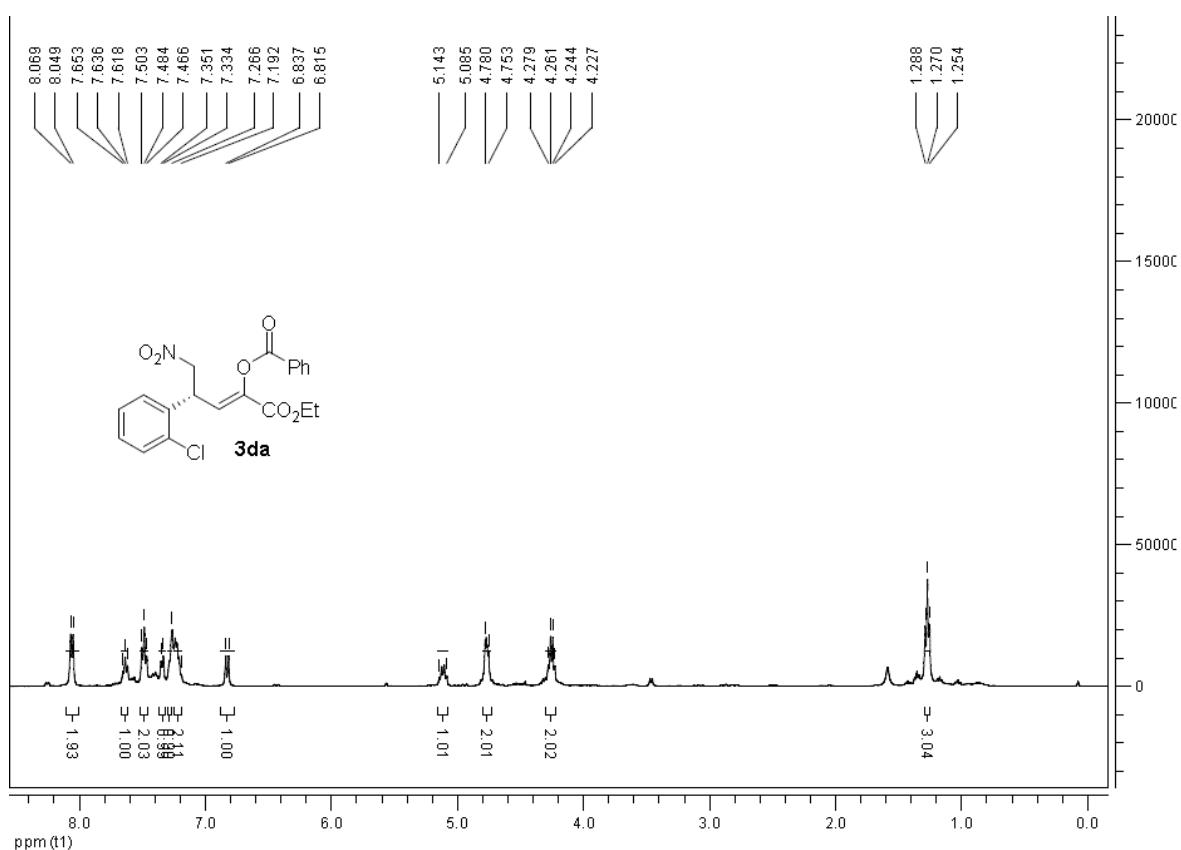
Racemic adduct							Chiral adduct						
#	Time	Area	Height	Width	Area%	Symmetry	#	Time	Area	Height	Width	Area%	Symmetry
1	8.536	4369.9	274.5	0.2457	48.486	0.841	1	8.204	304.1	20.6	0.228	10.731	0.877
2	9.644	4642.8	259.2	0.277	51.514	0.943	2	9.236	2529.3	151.3	0.261	89.269	0.935

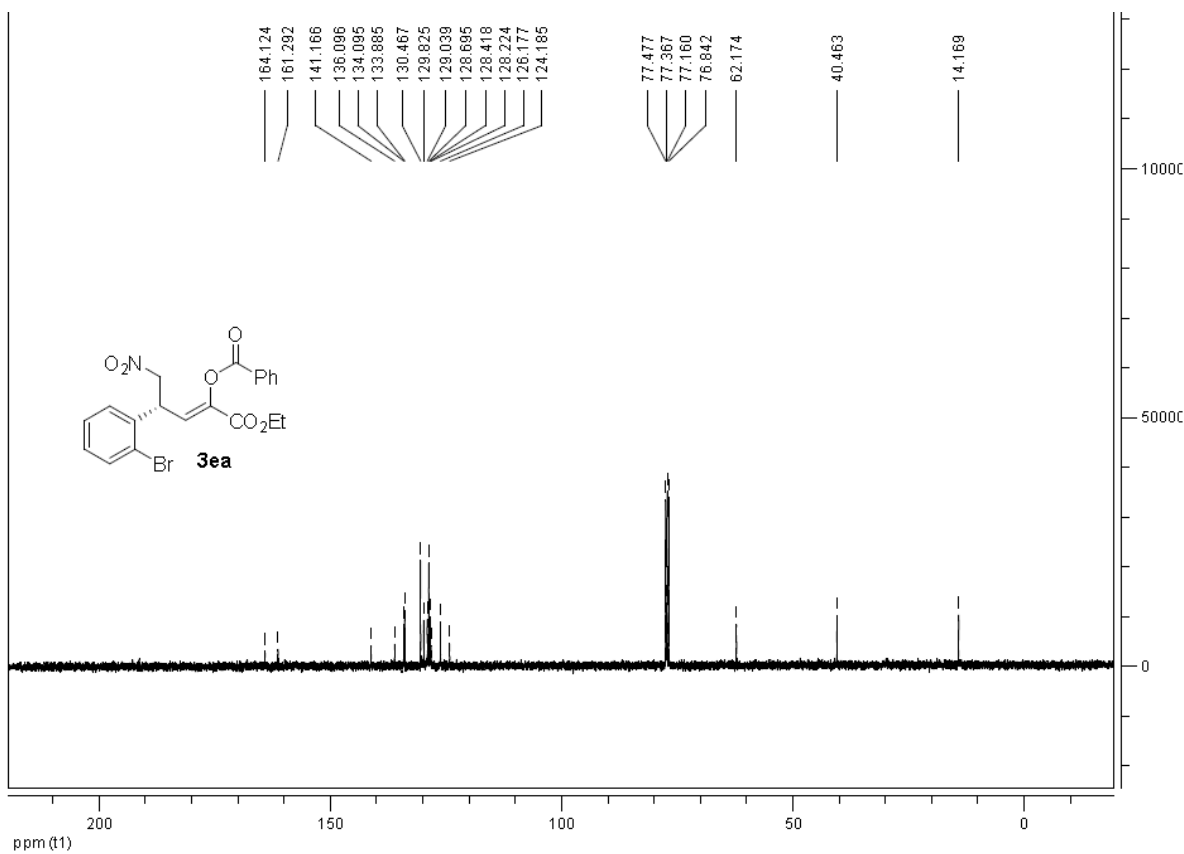
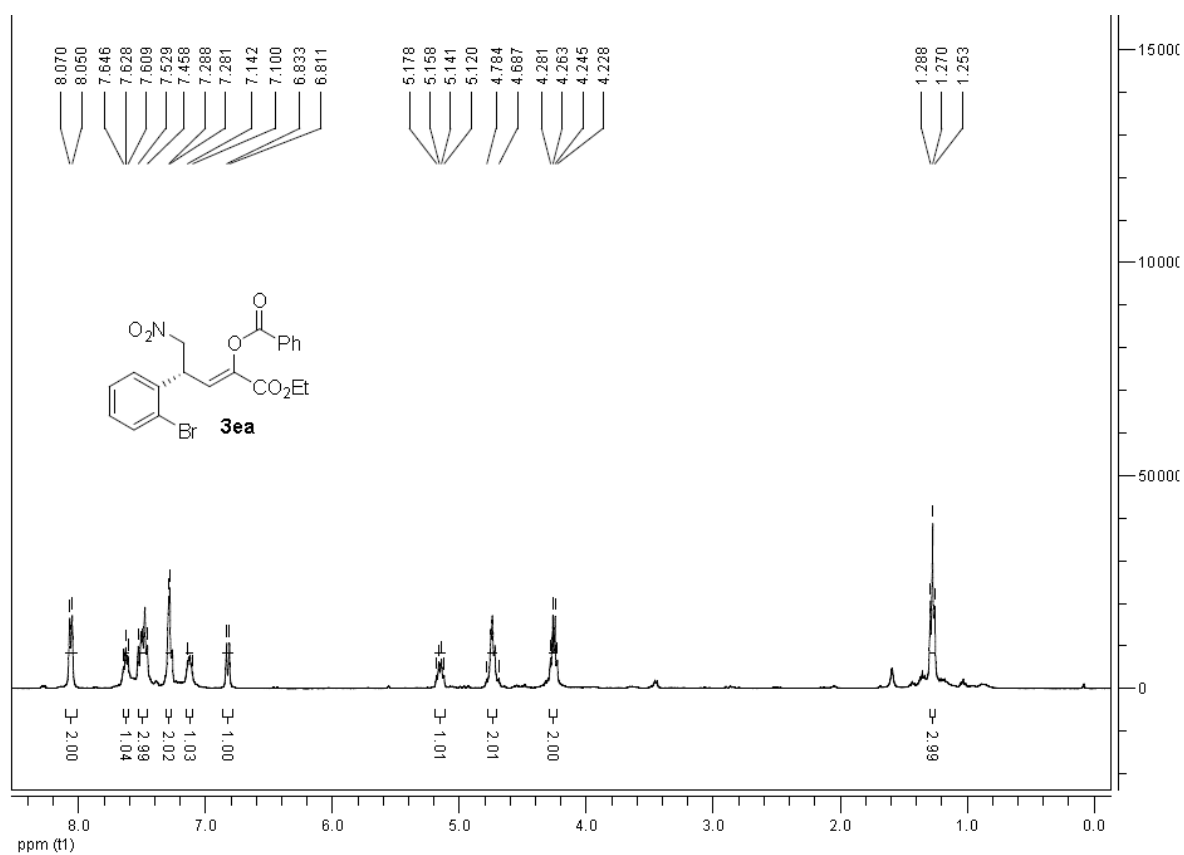
F: Copies of ^1H , and ^{13}C NMR spectra of Adducts

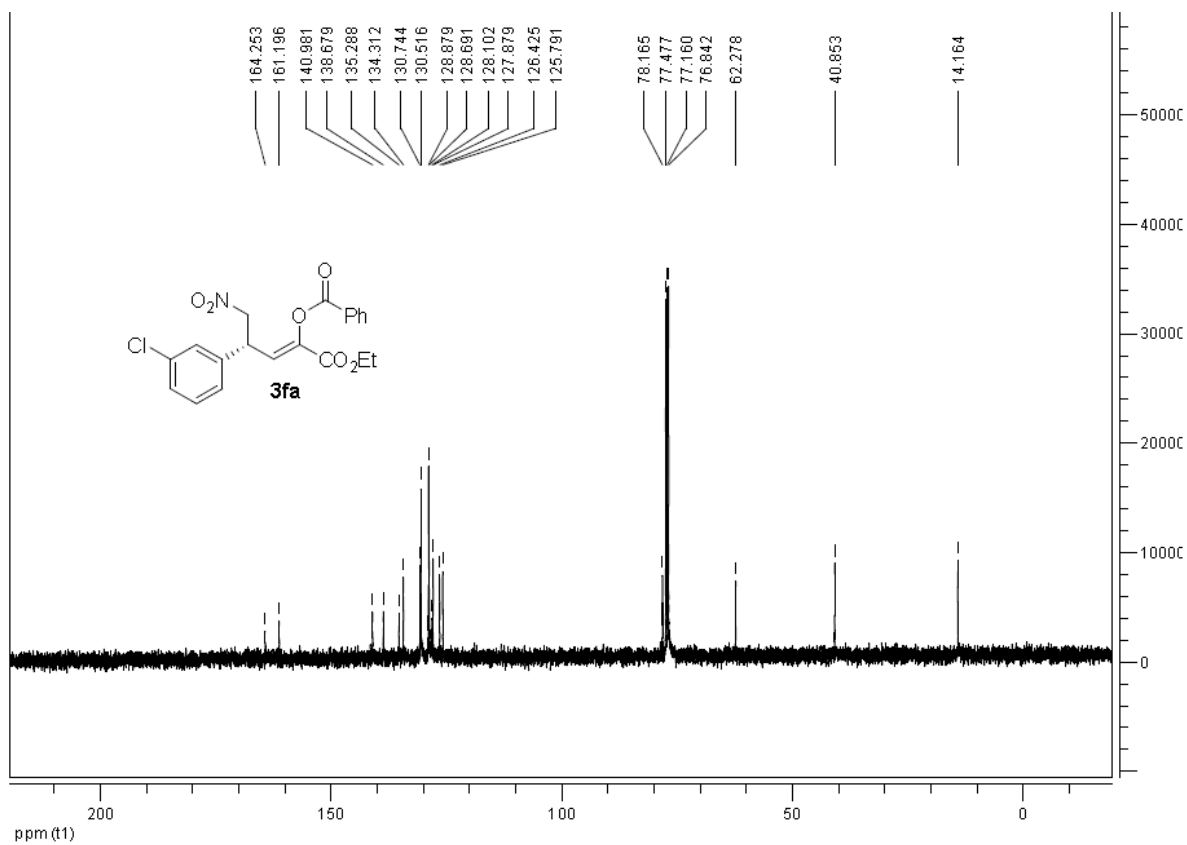
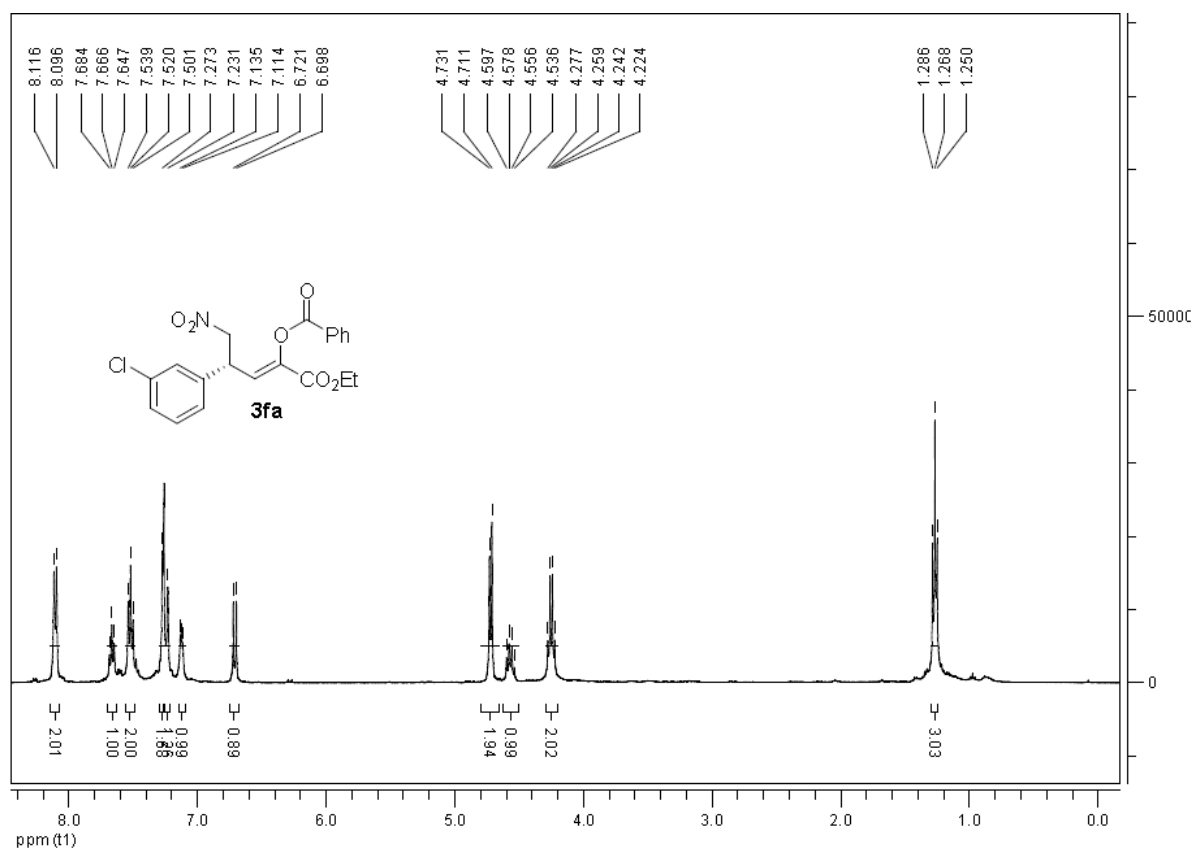


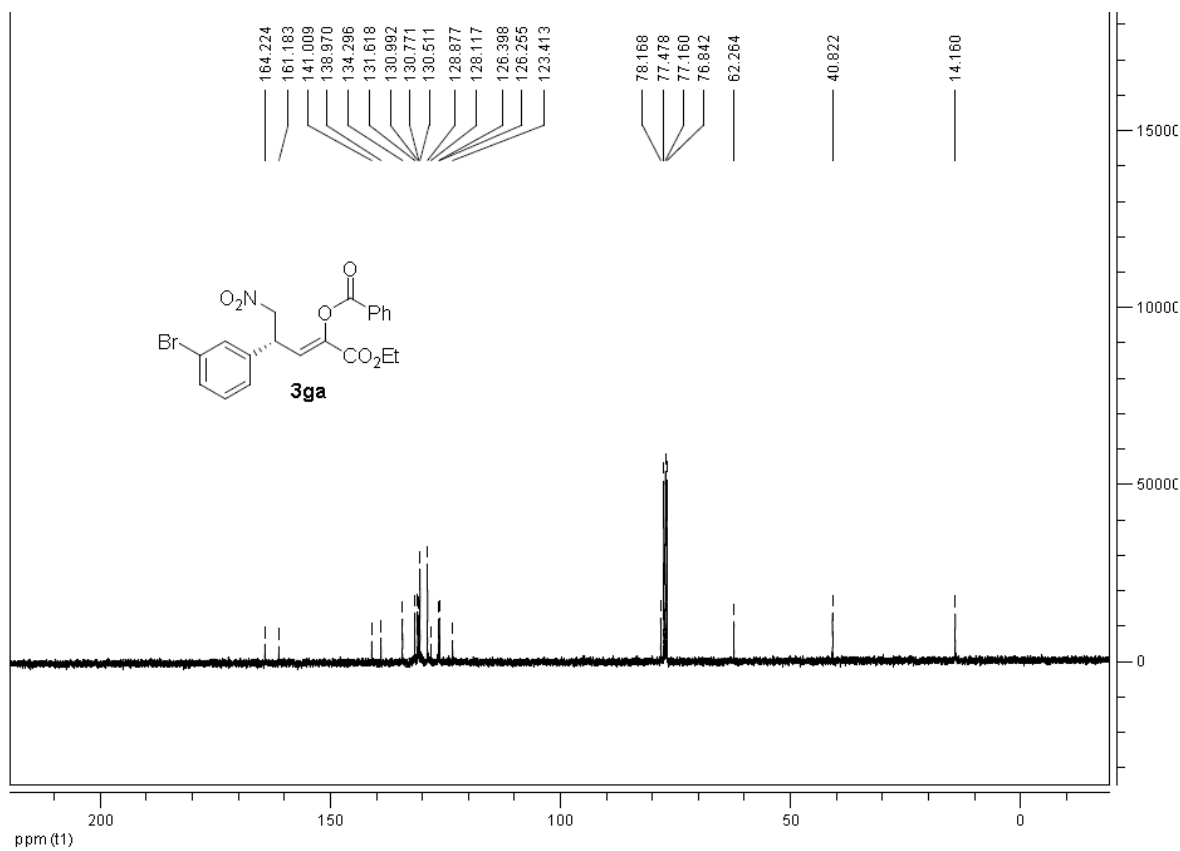
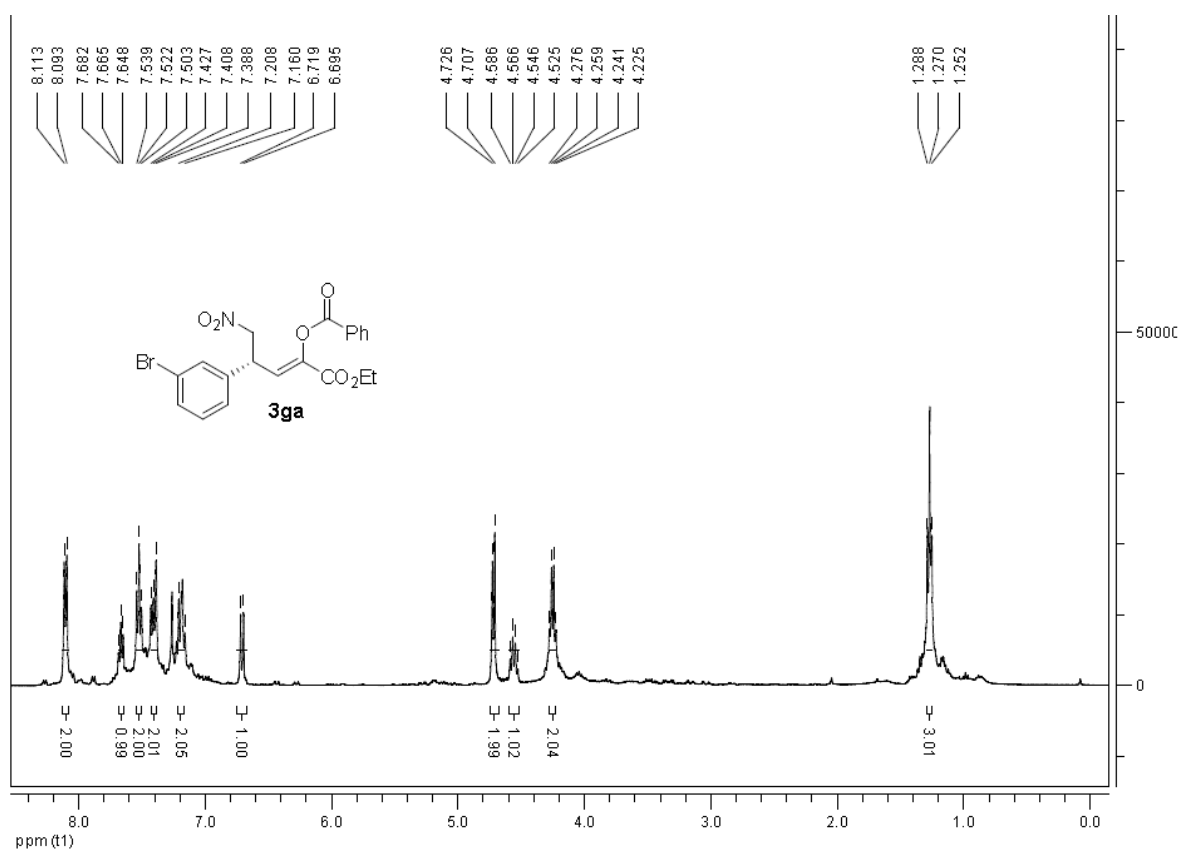


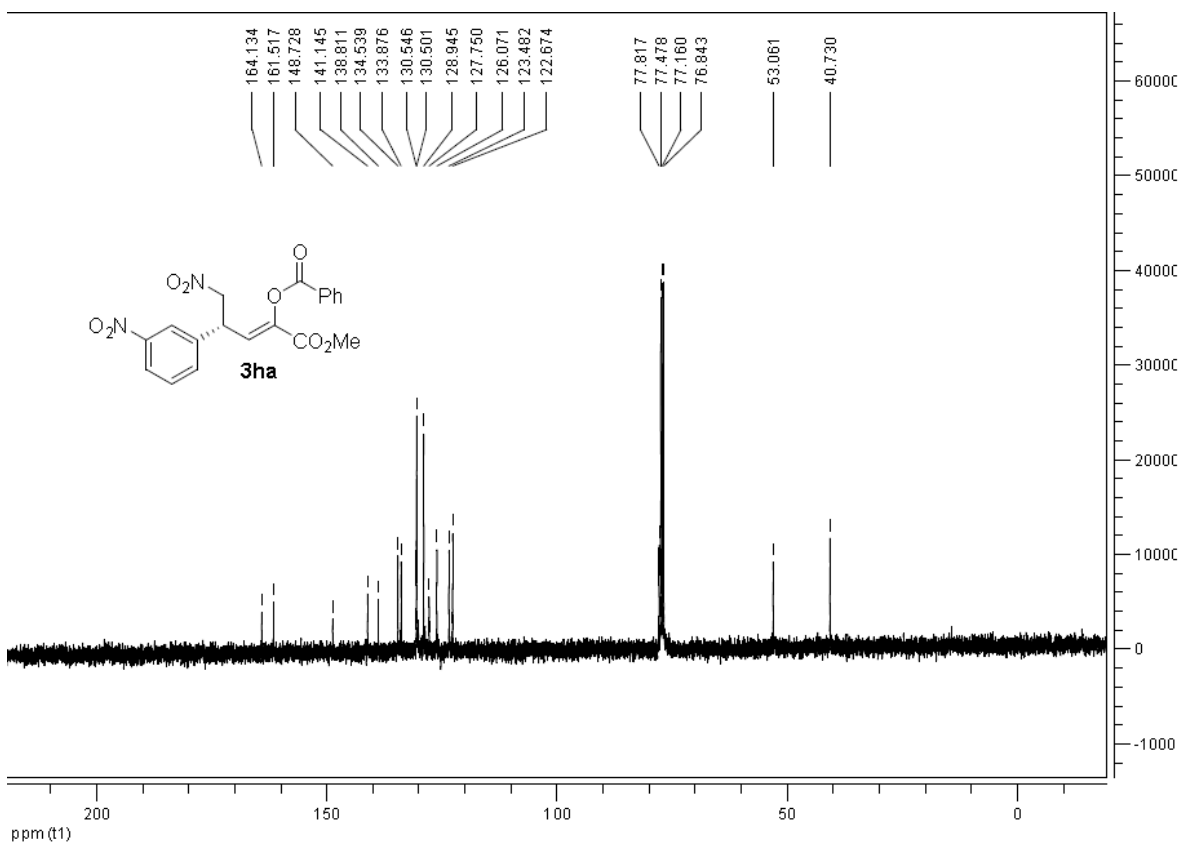
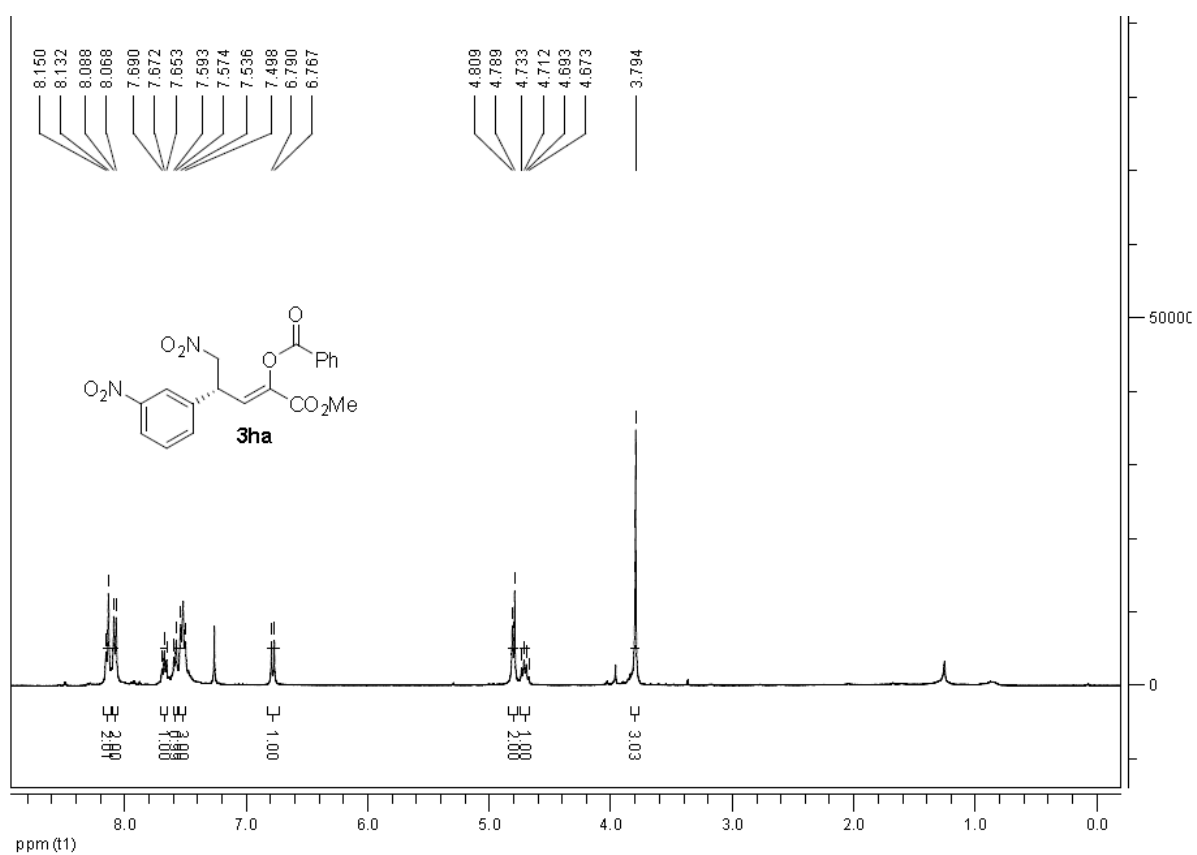


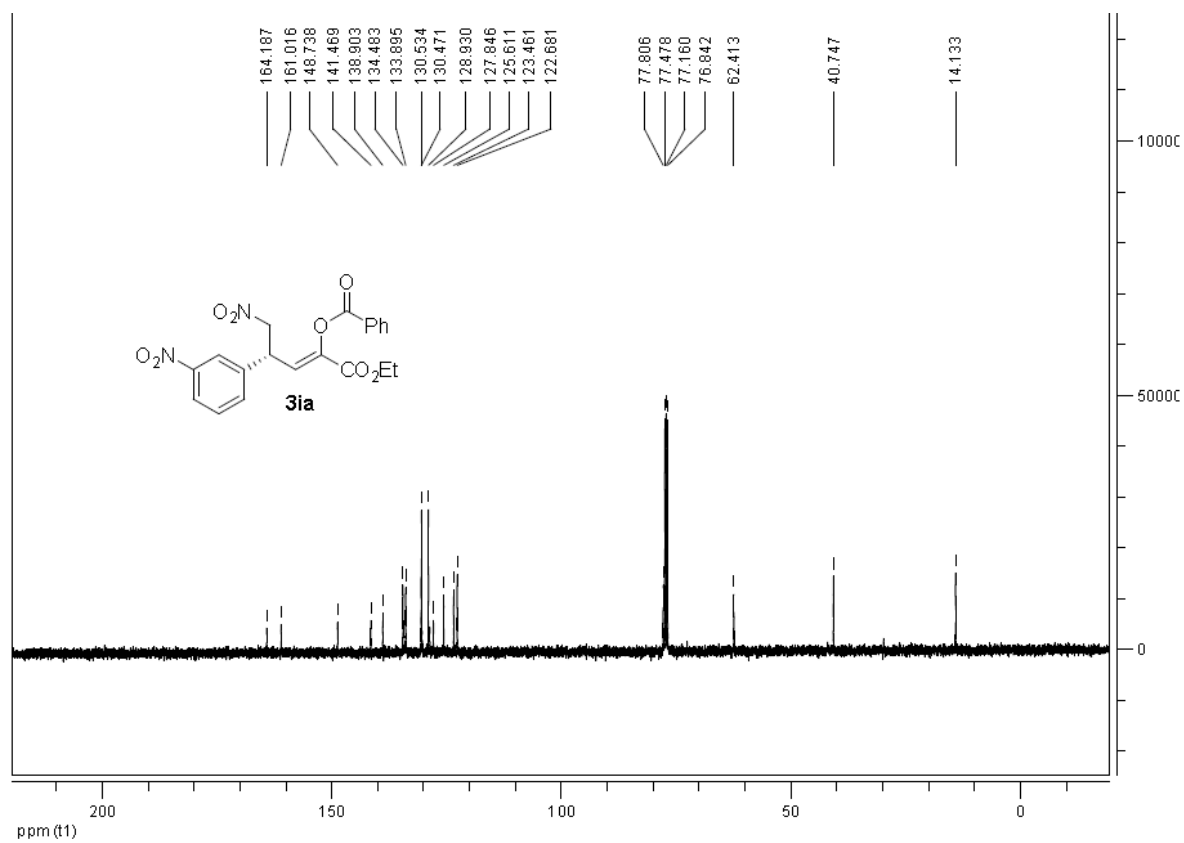
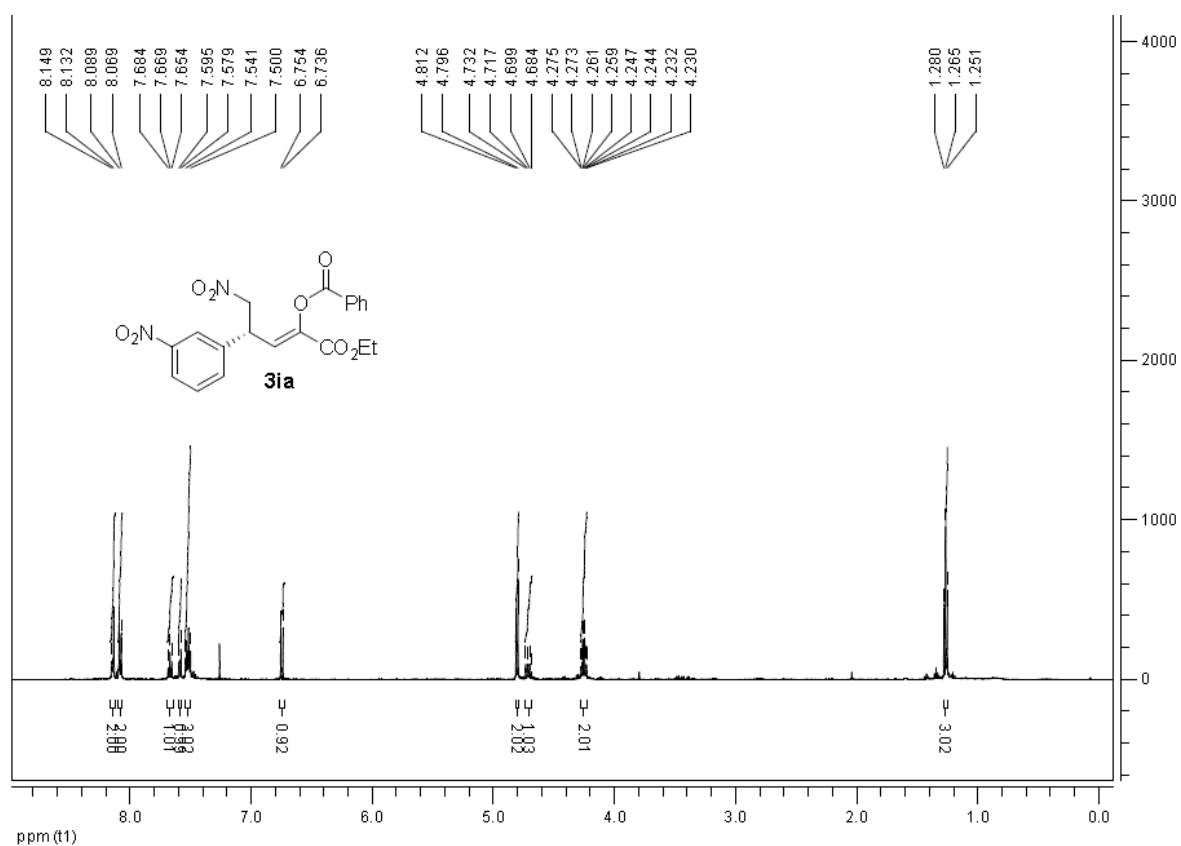


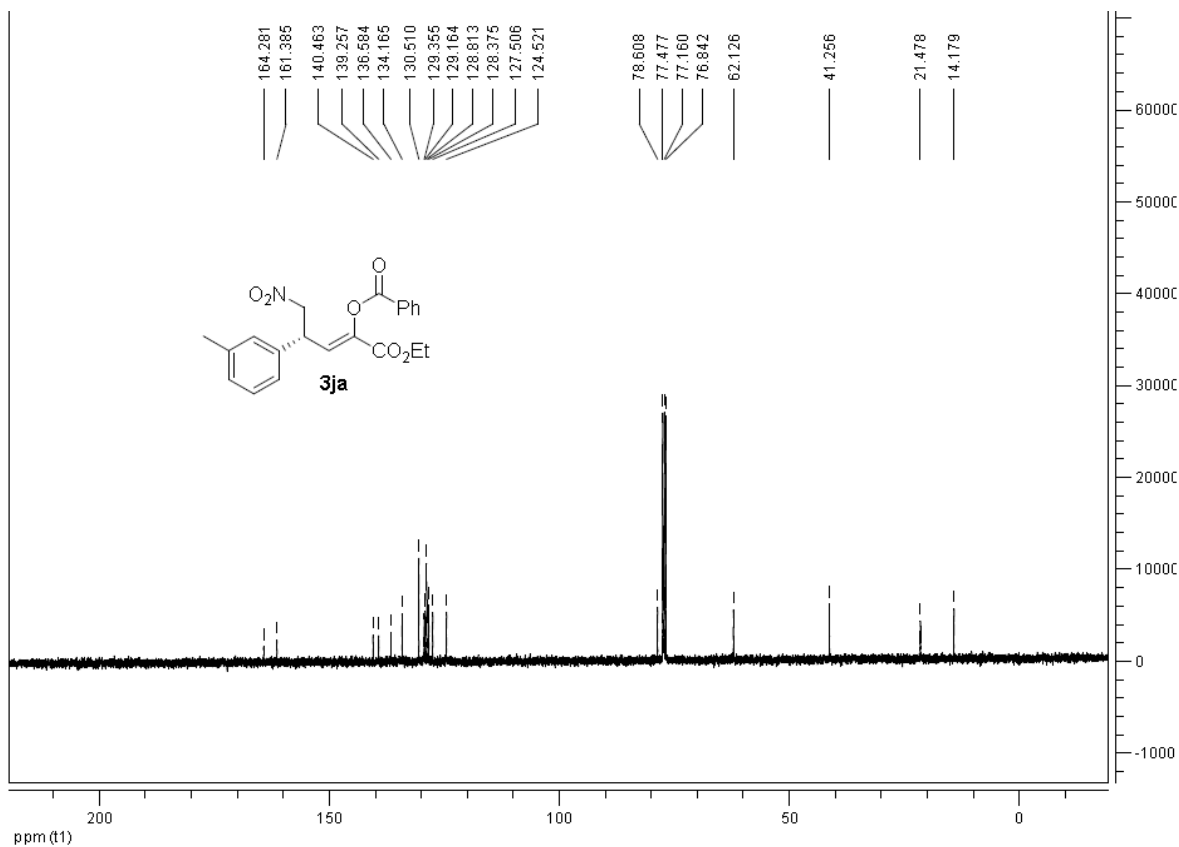
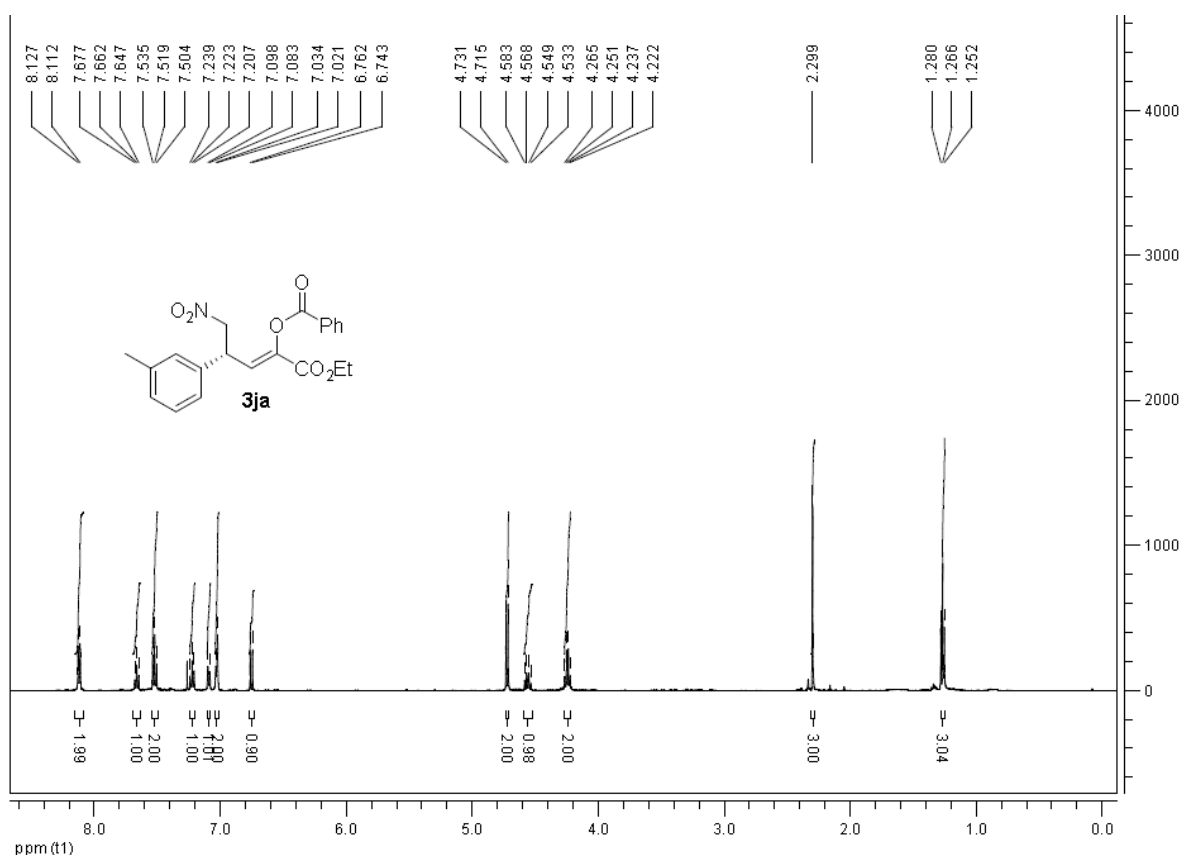


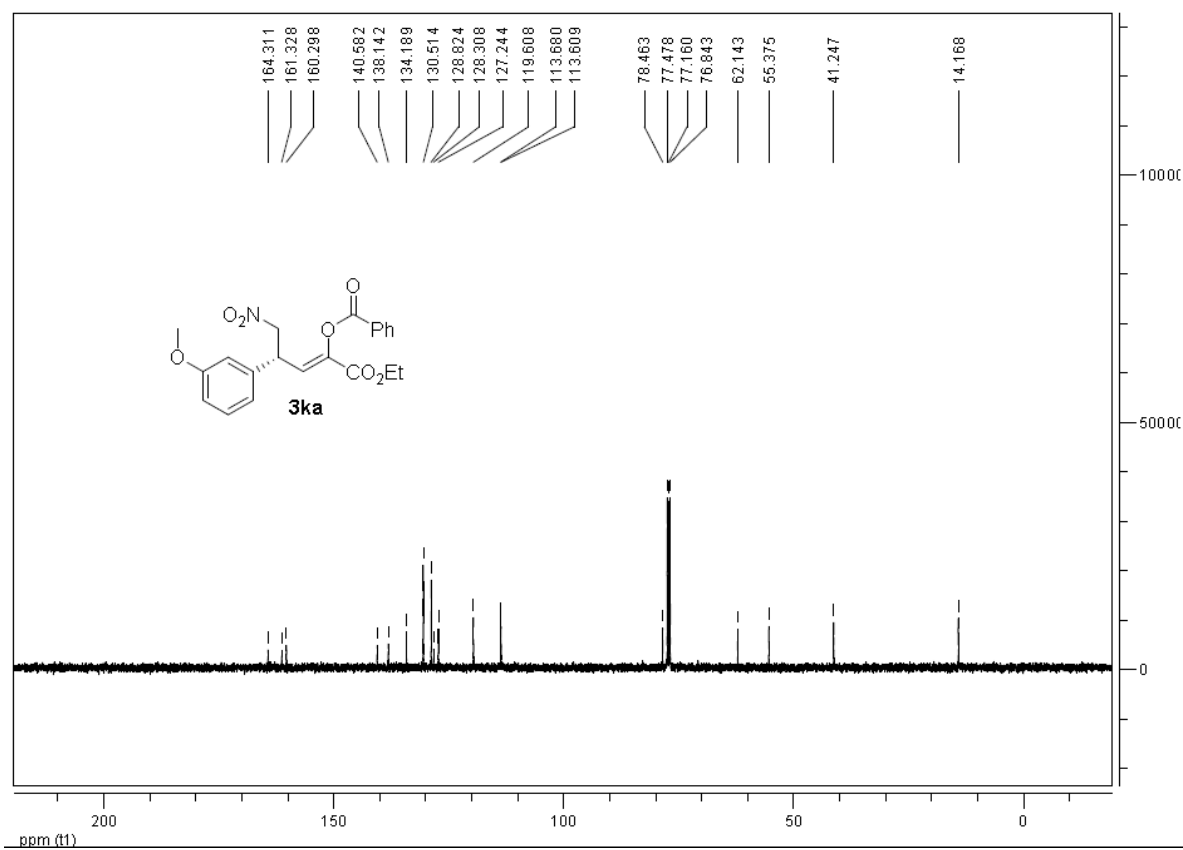
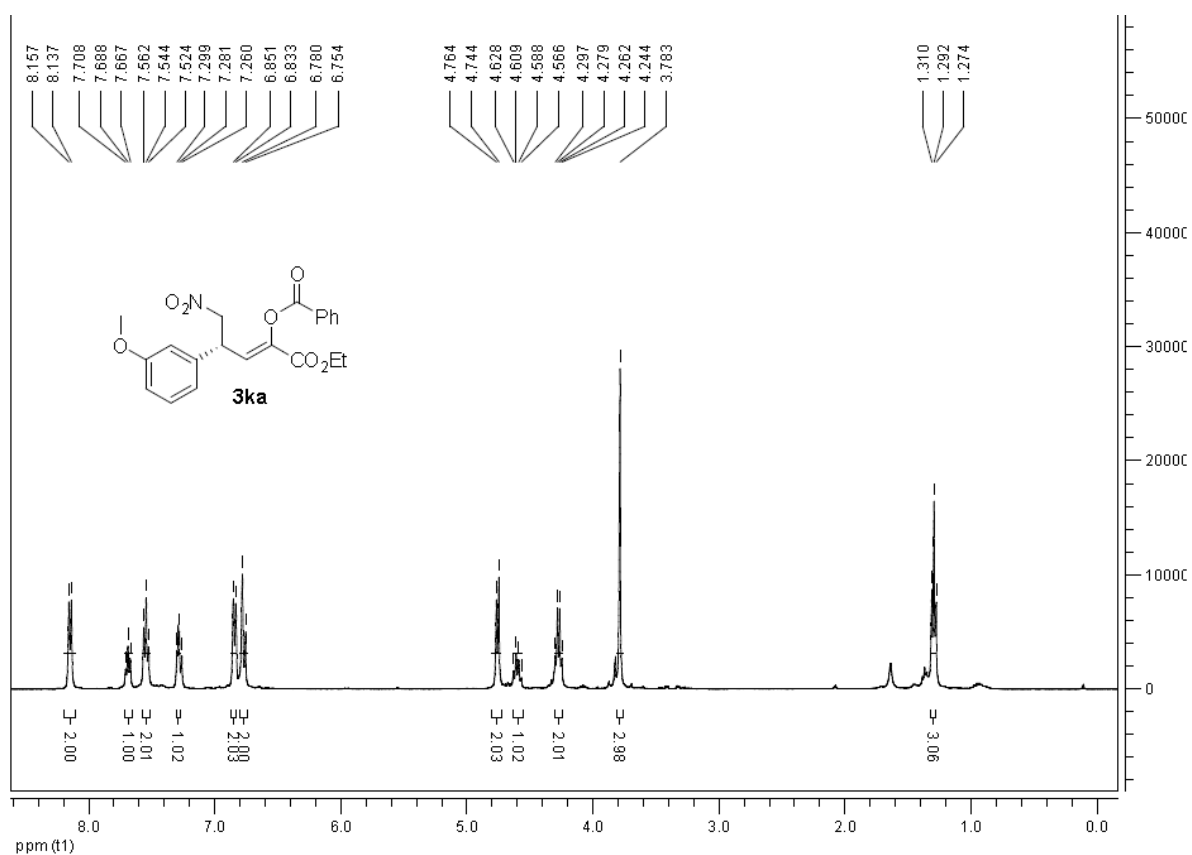


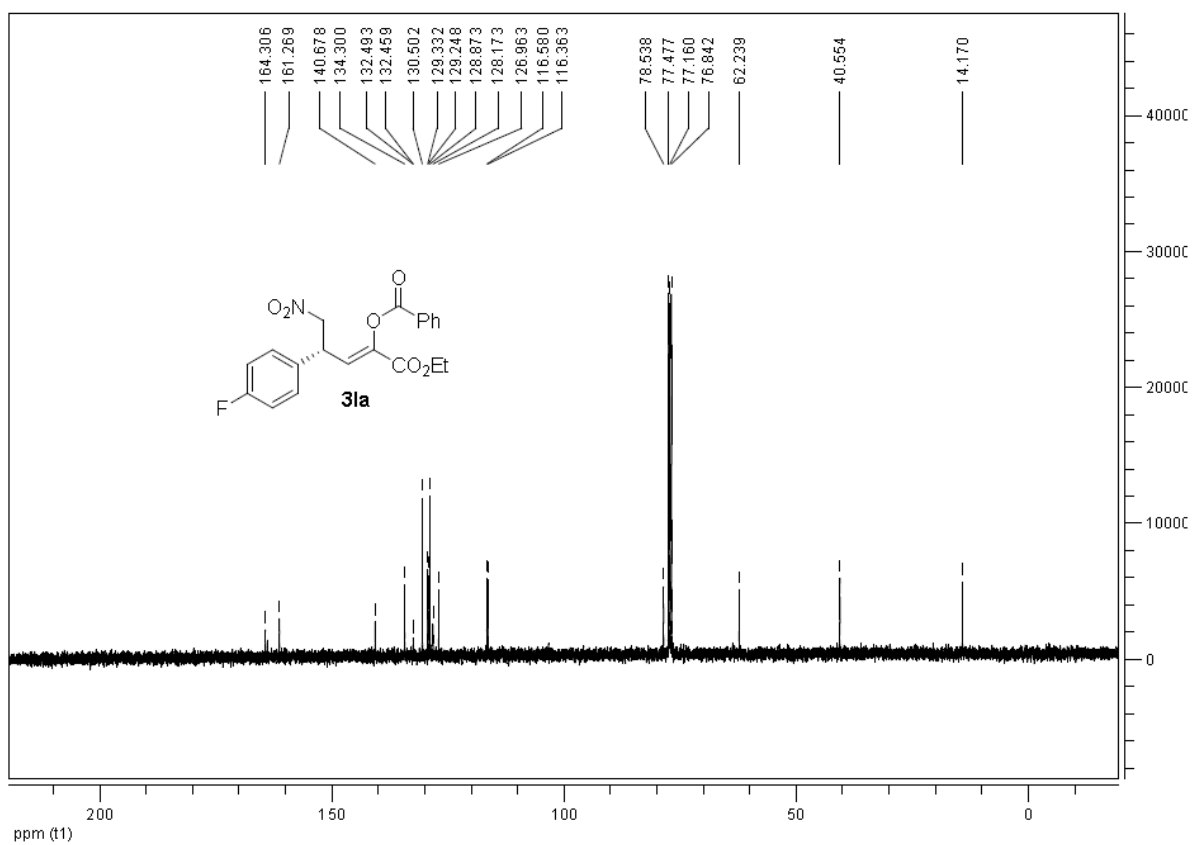
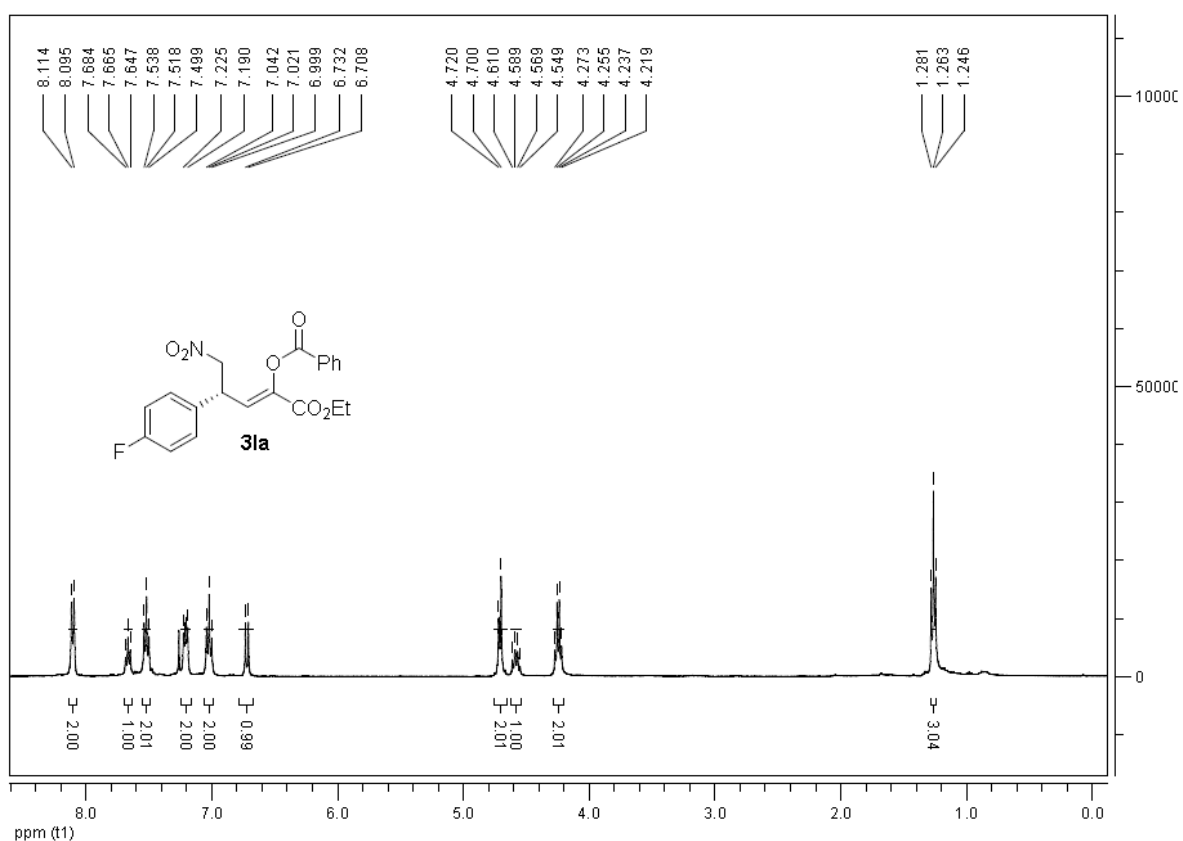


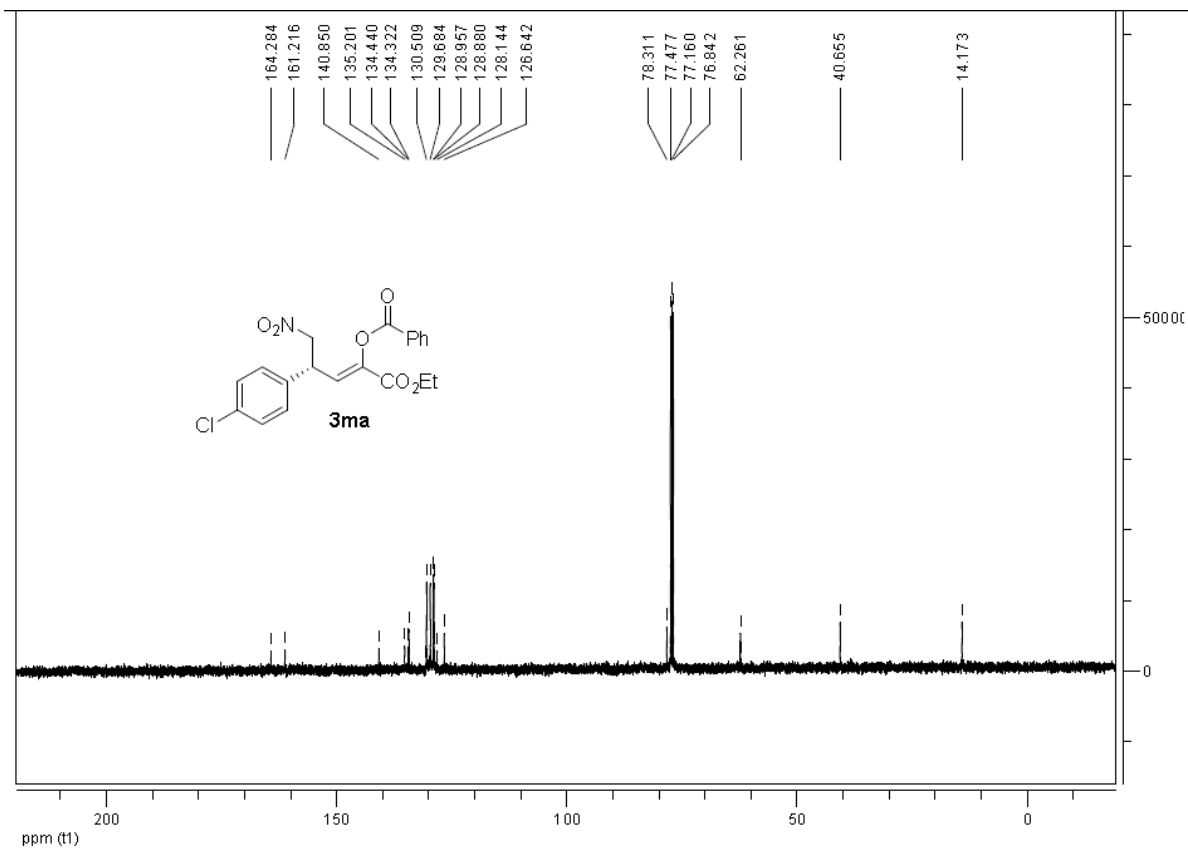
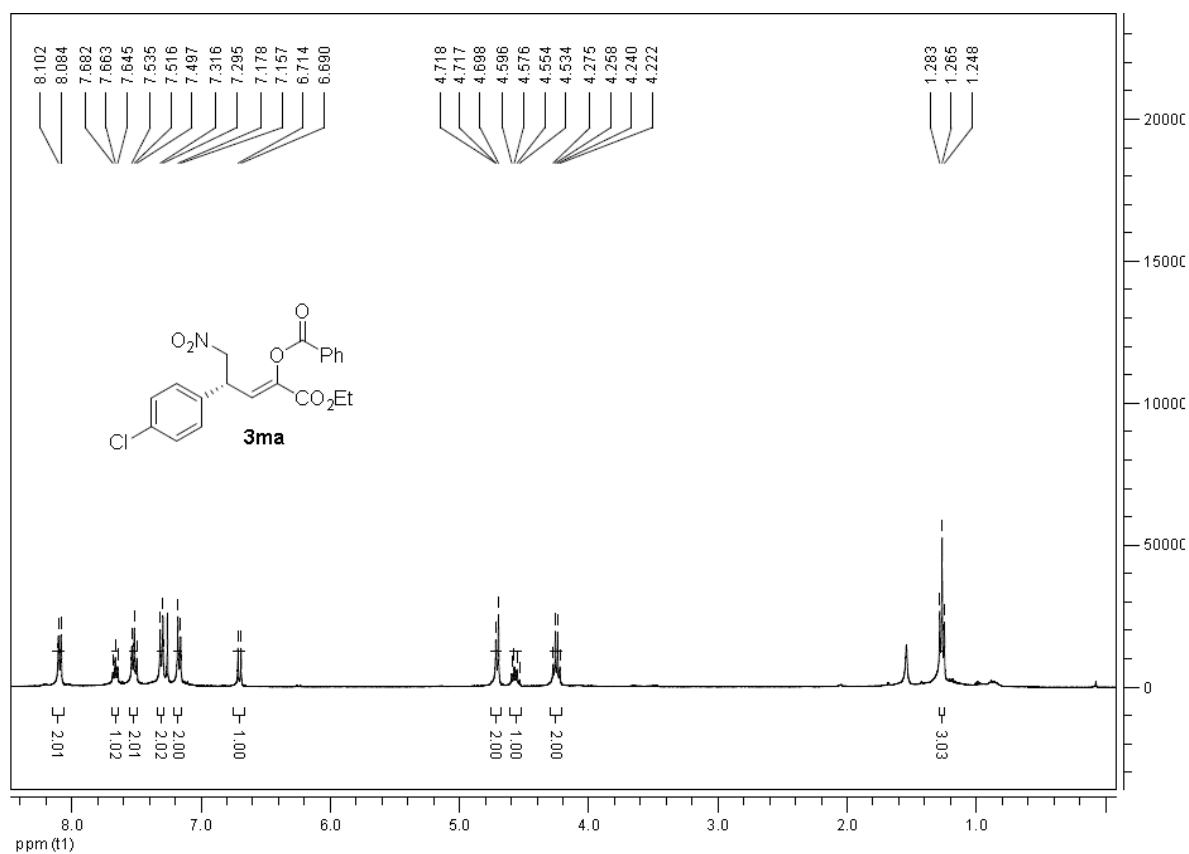


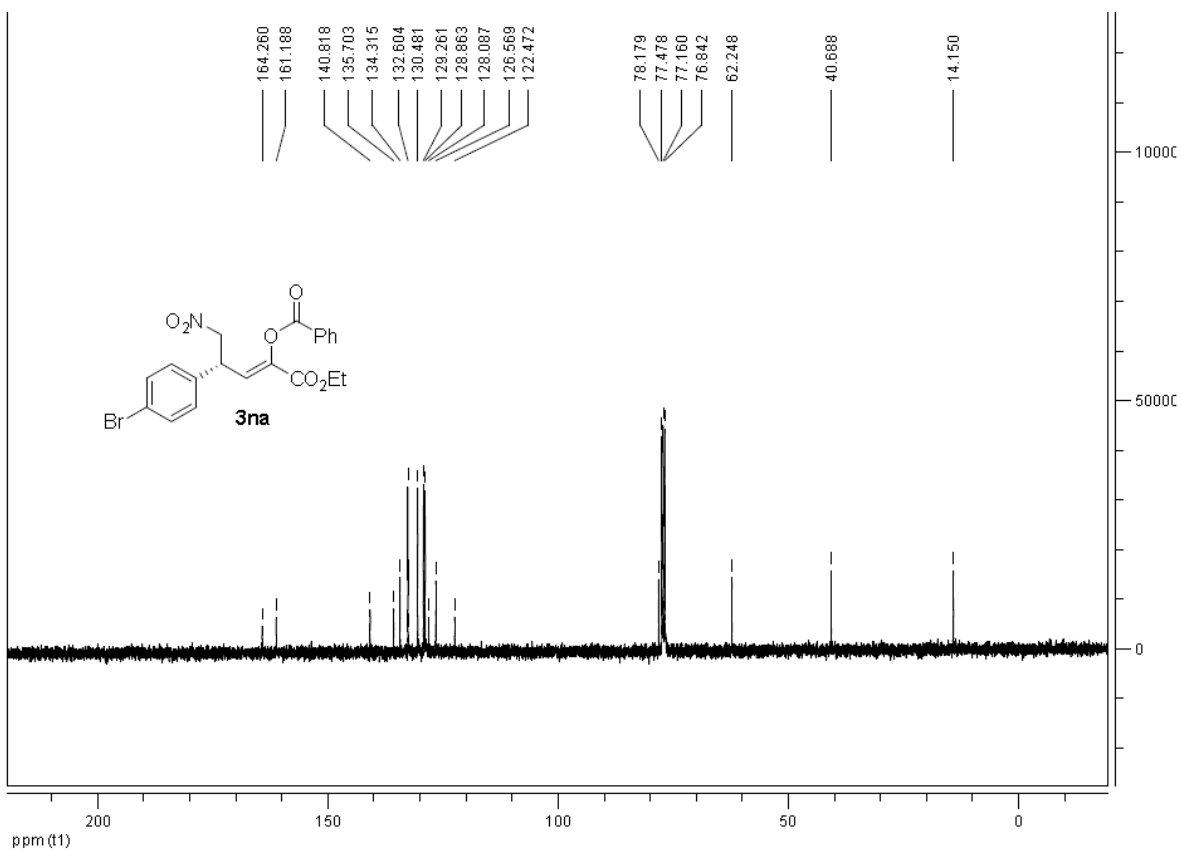
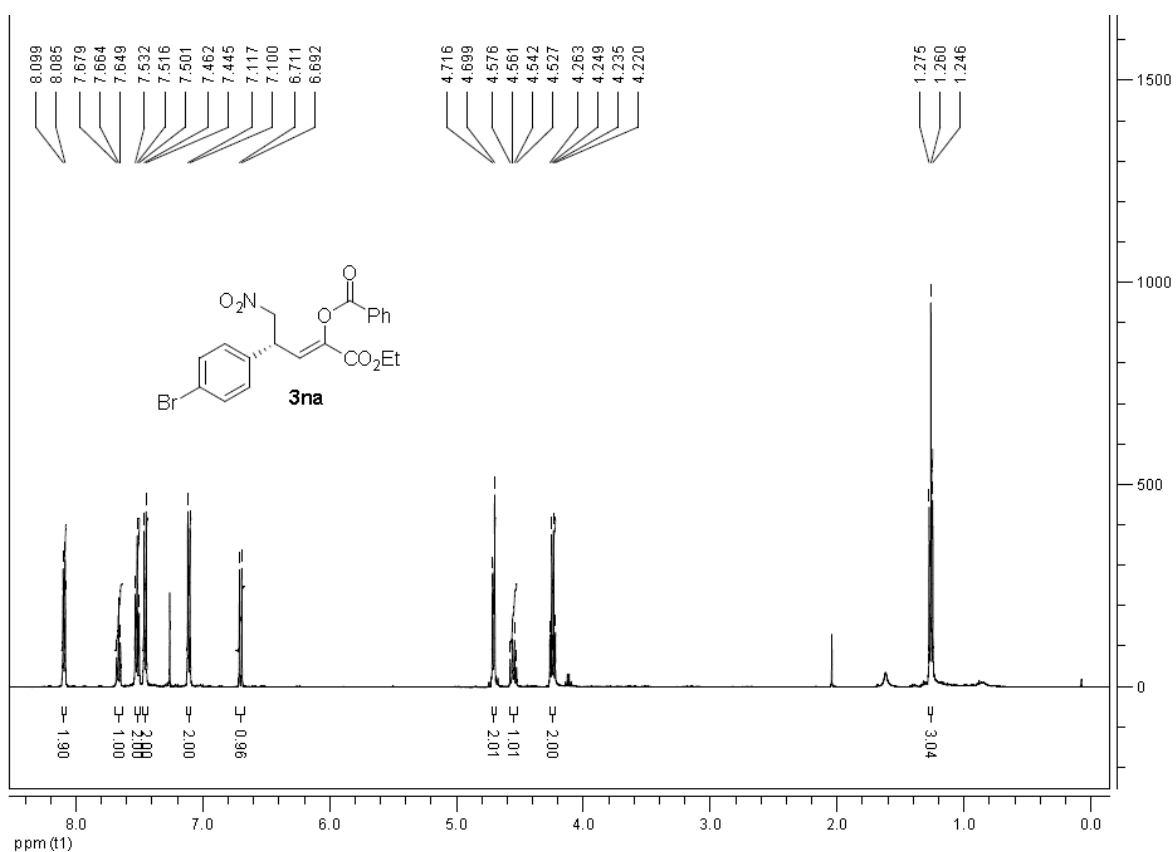


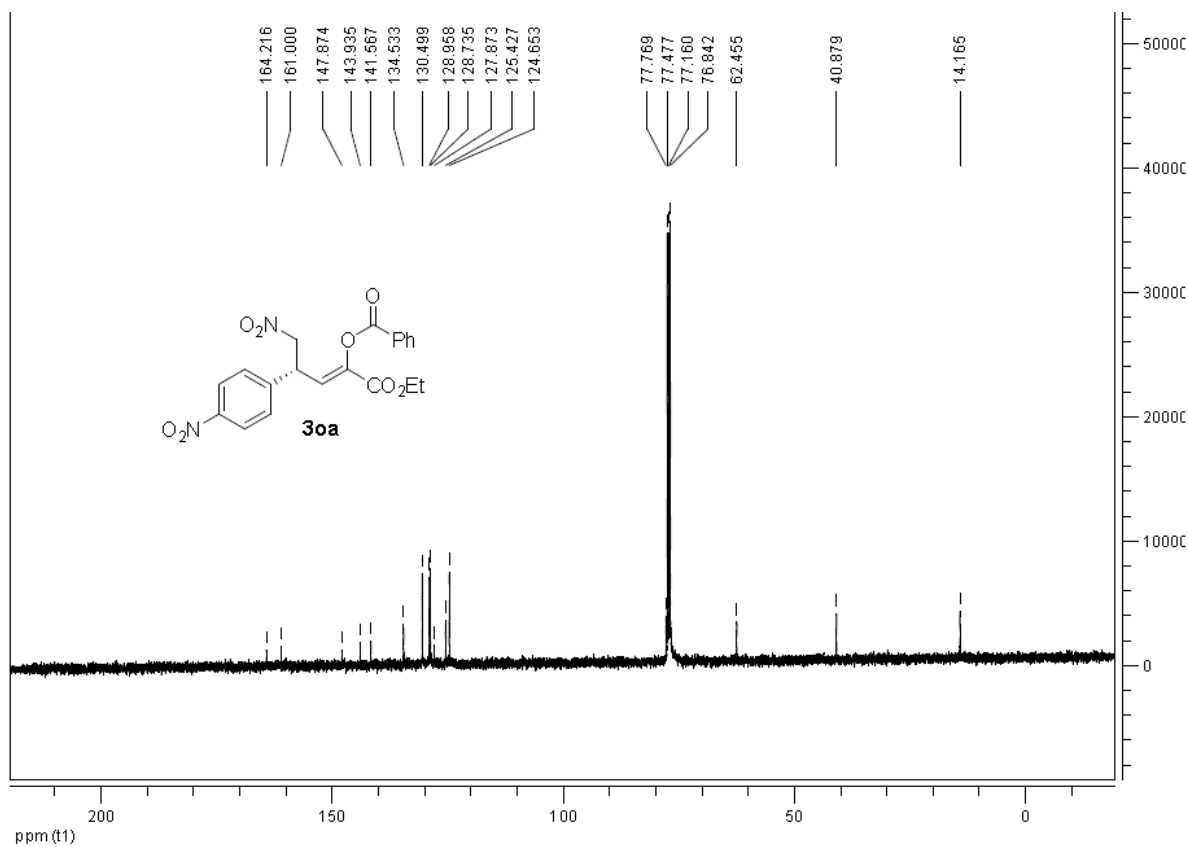
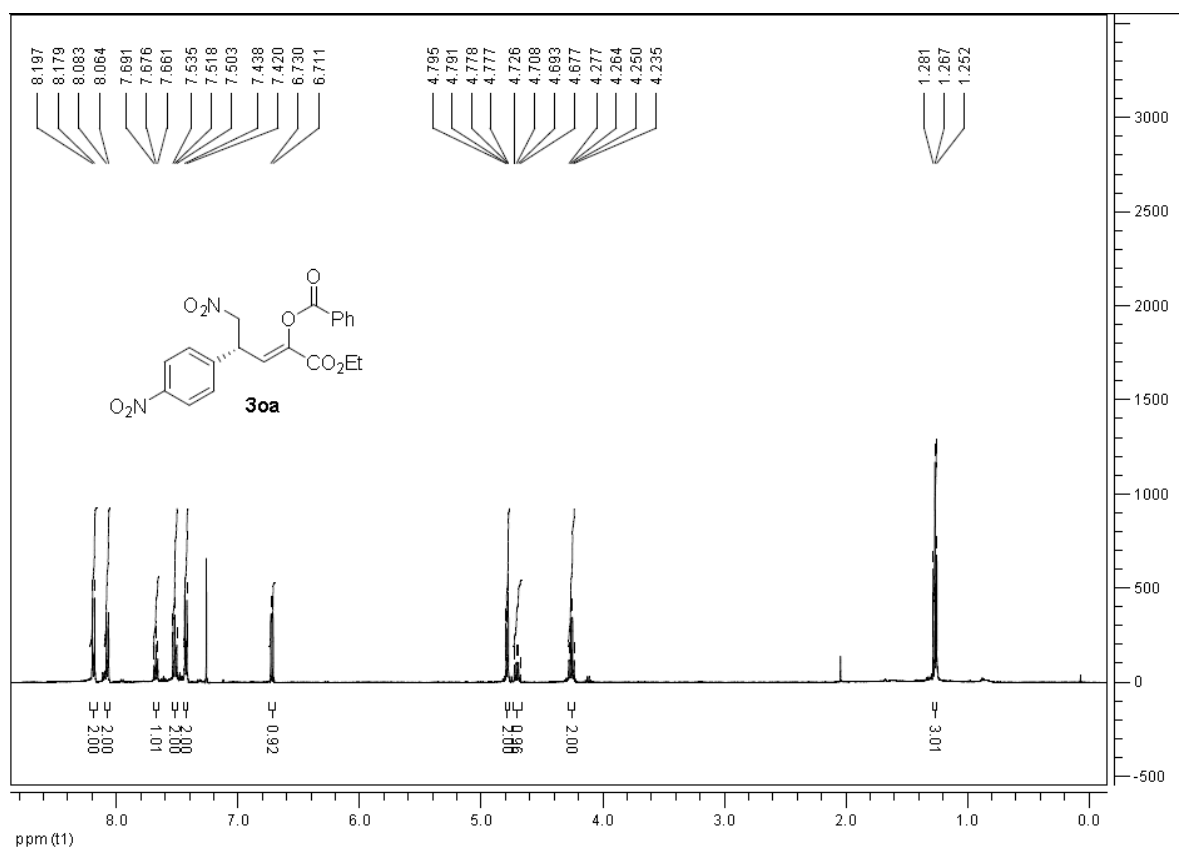


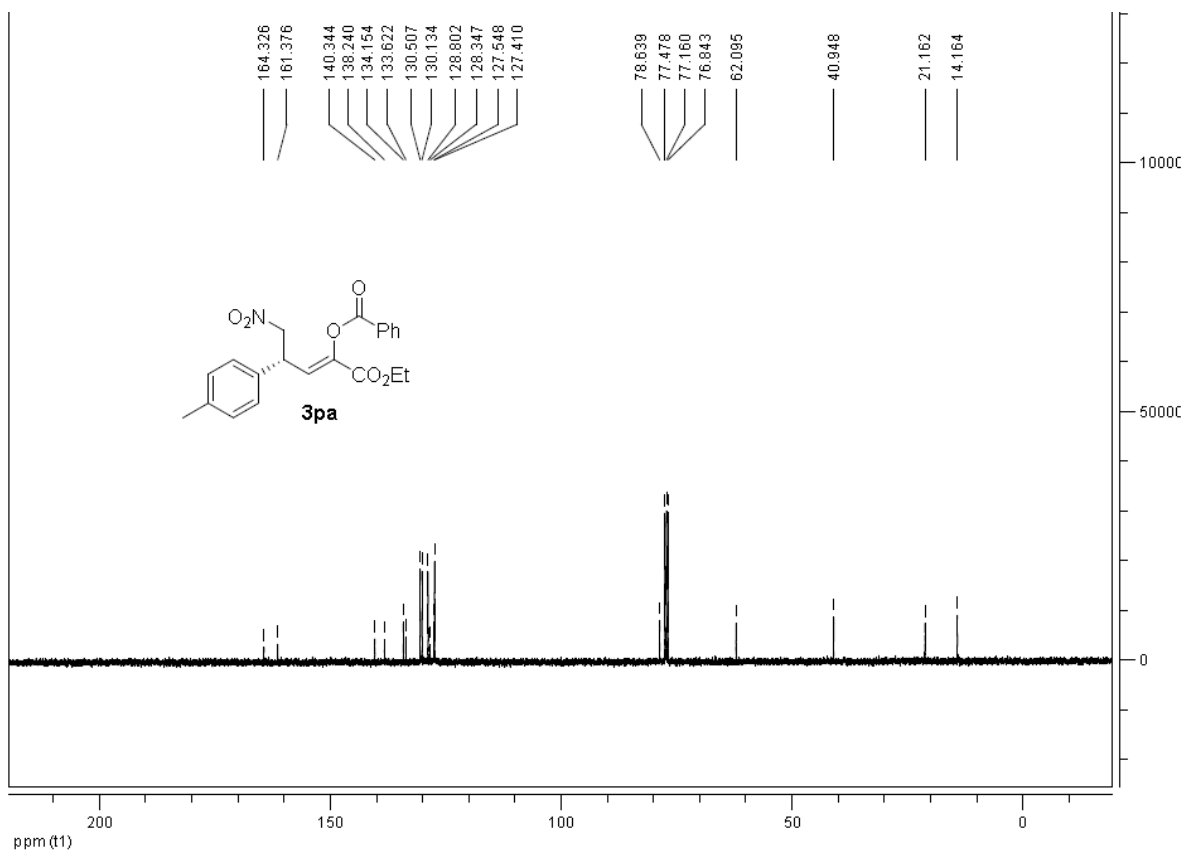
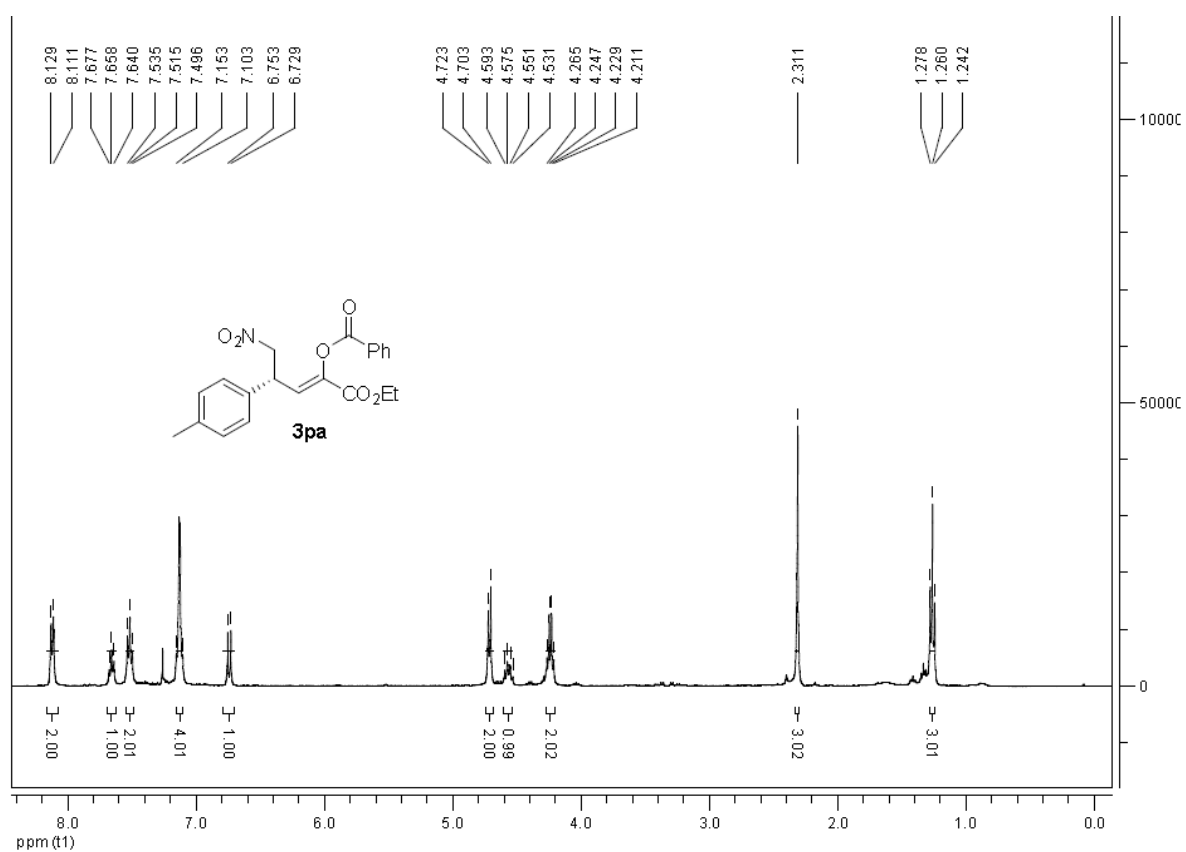


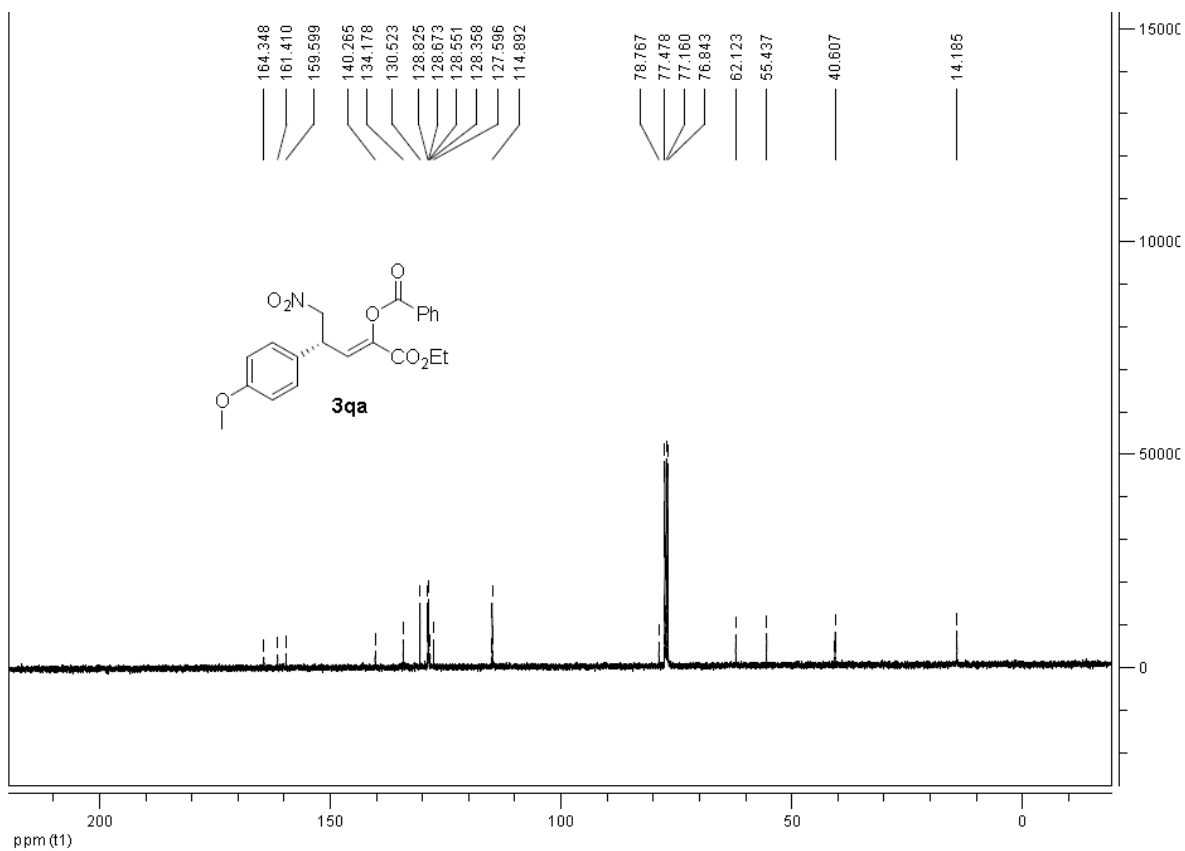
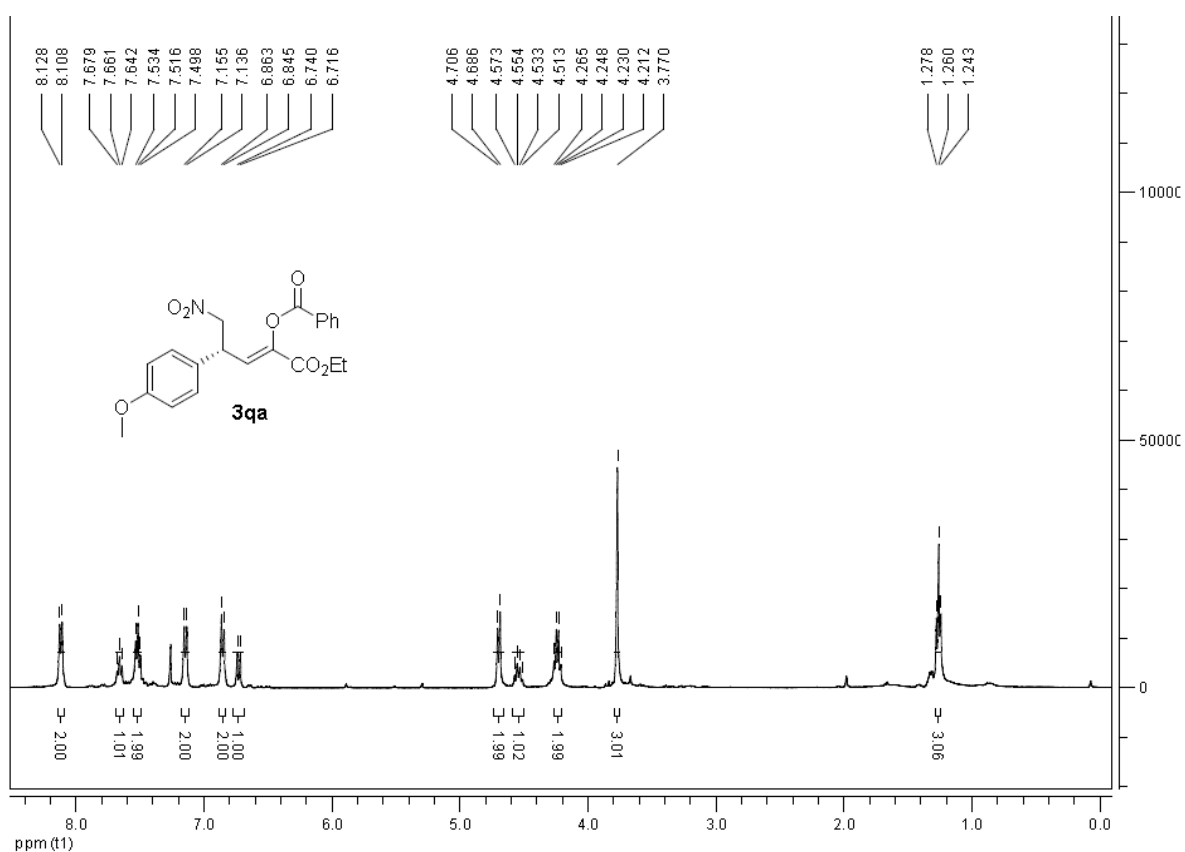


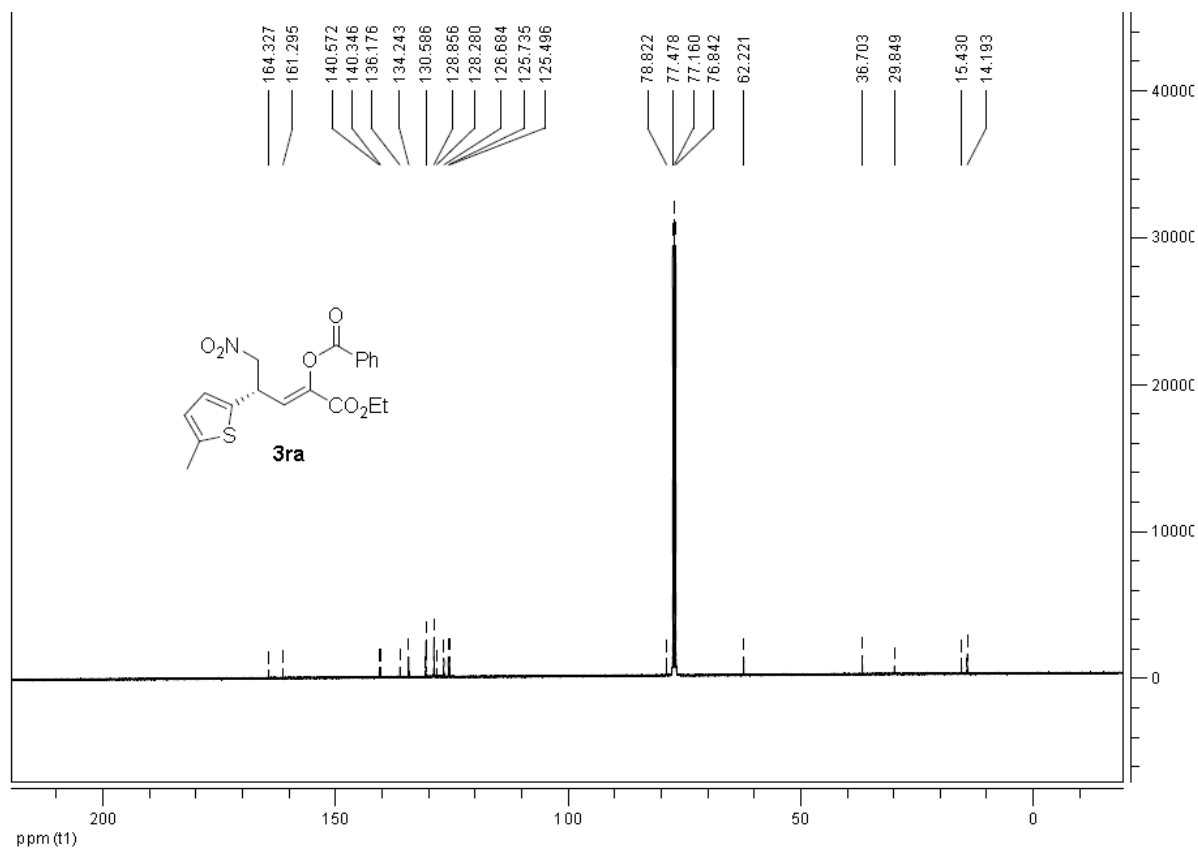
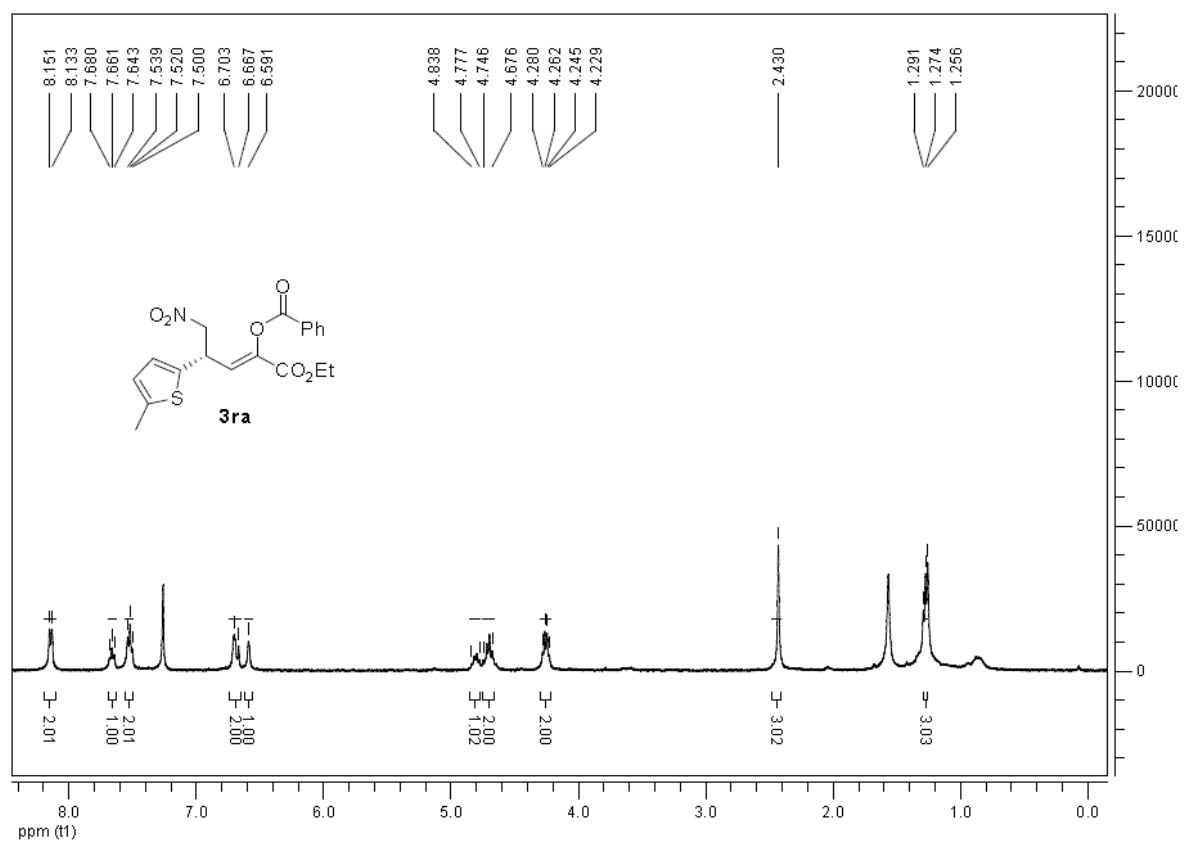


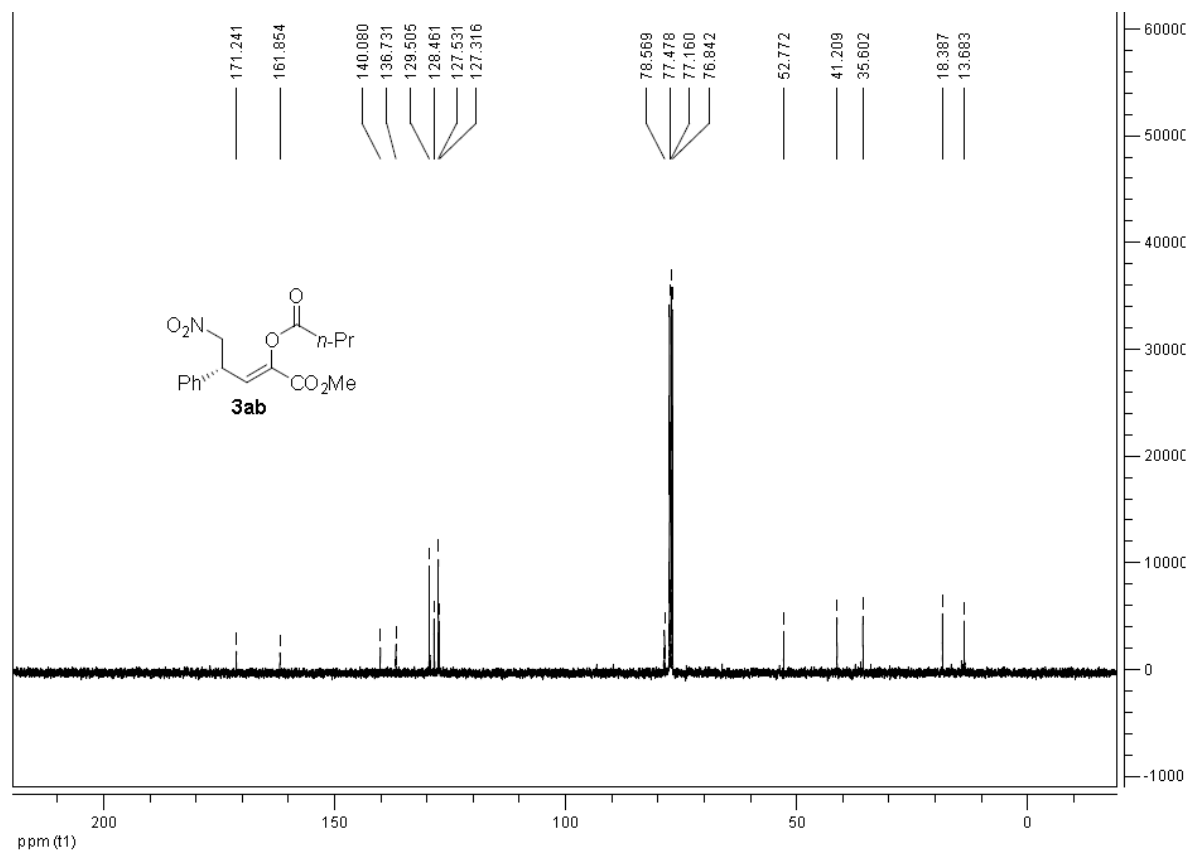
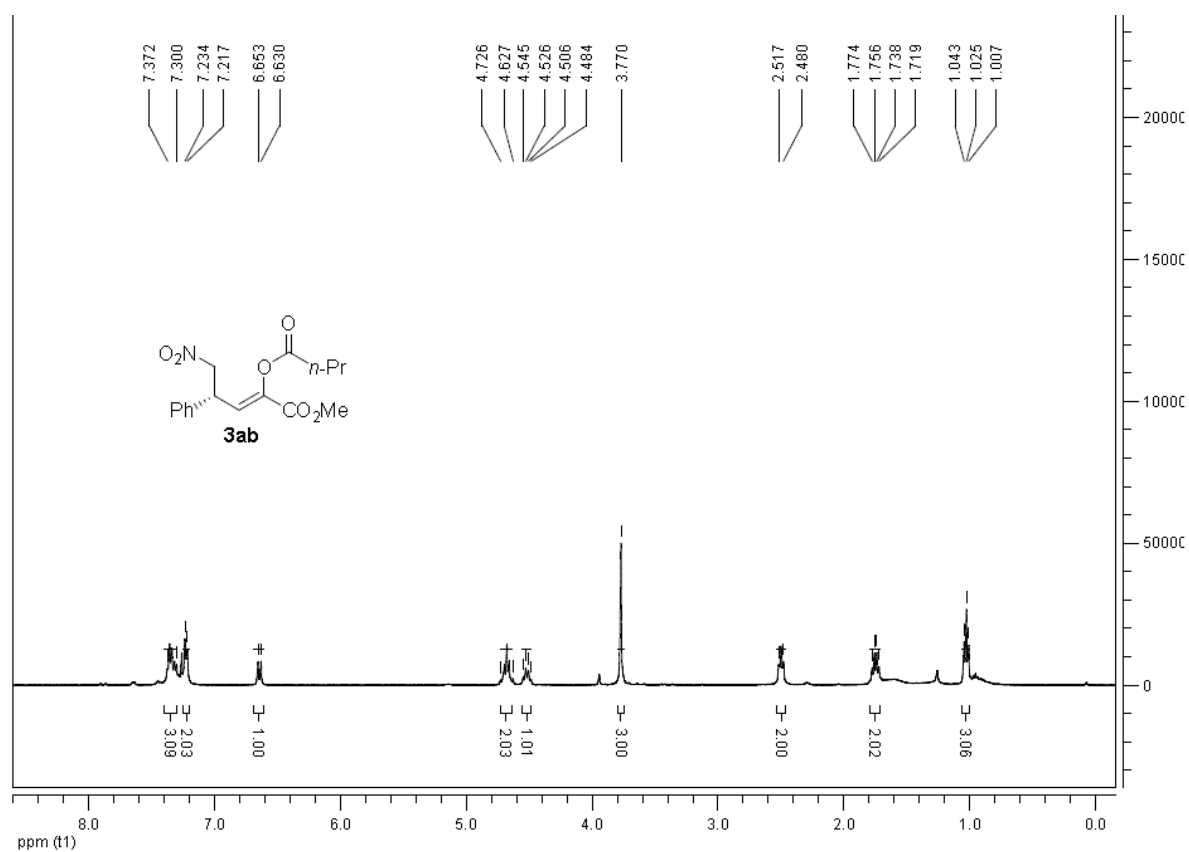


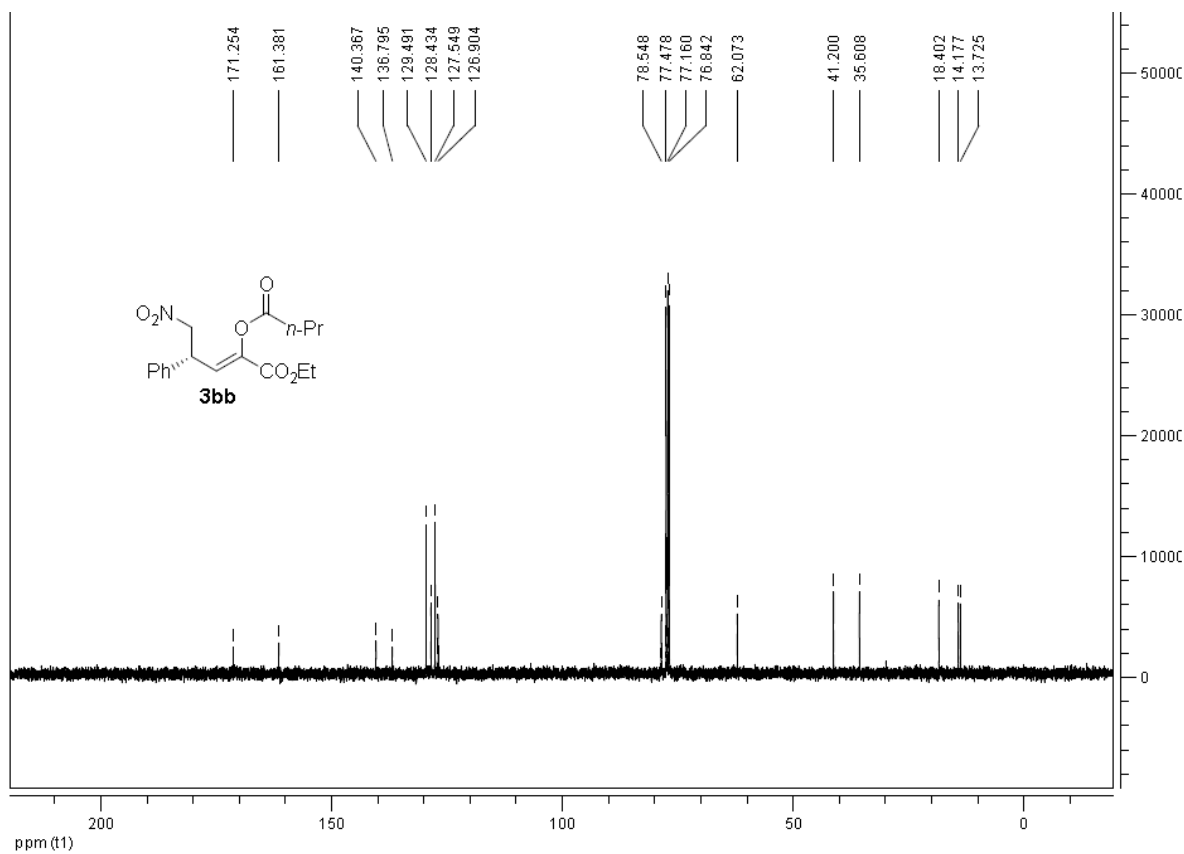
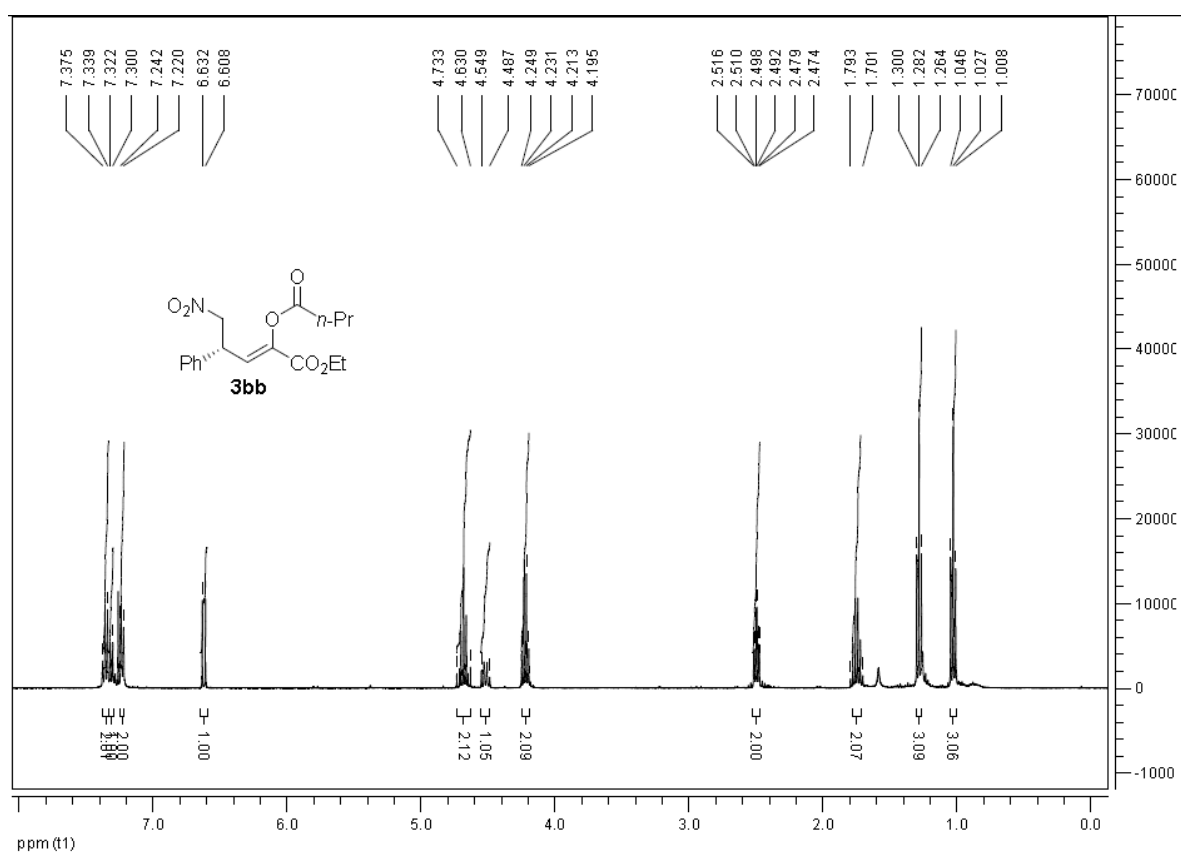


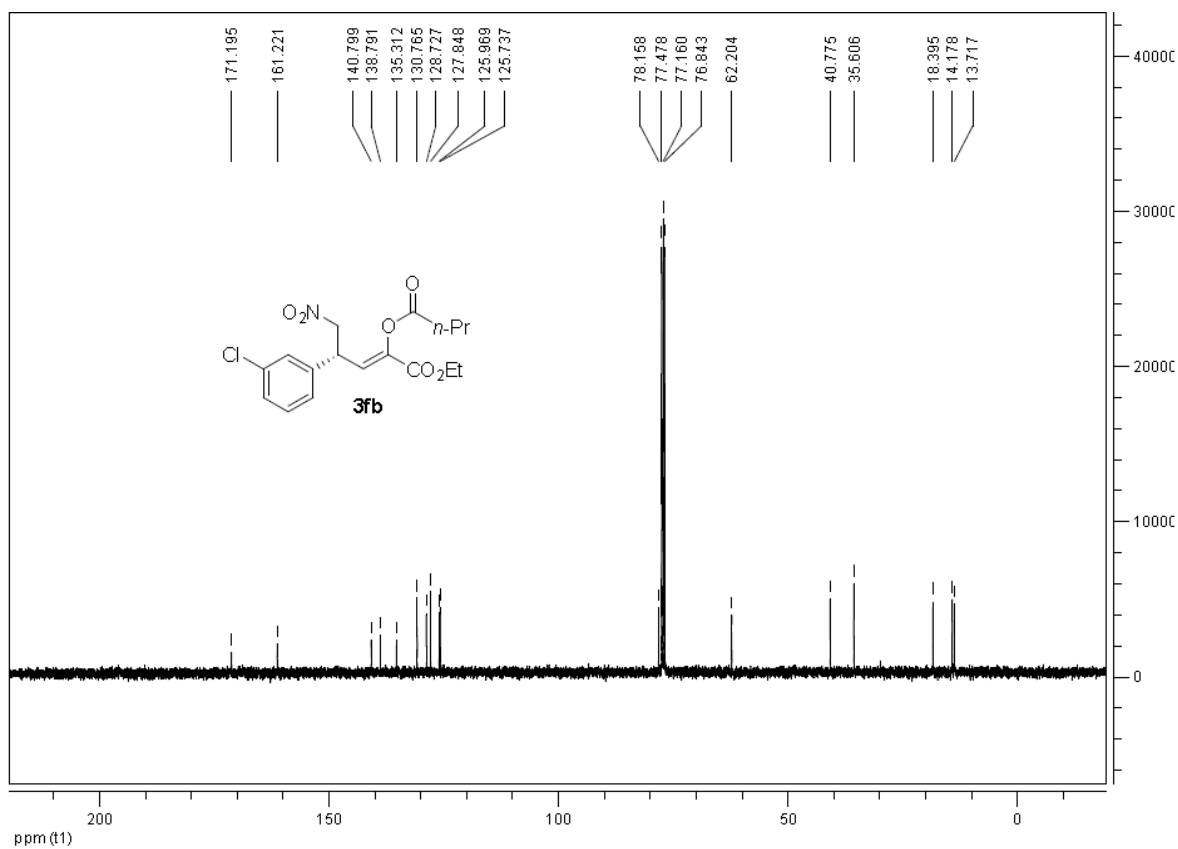
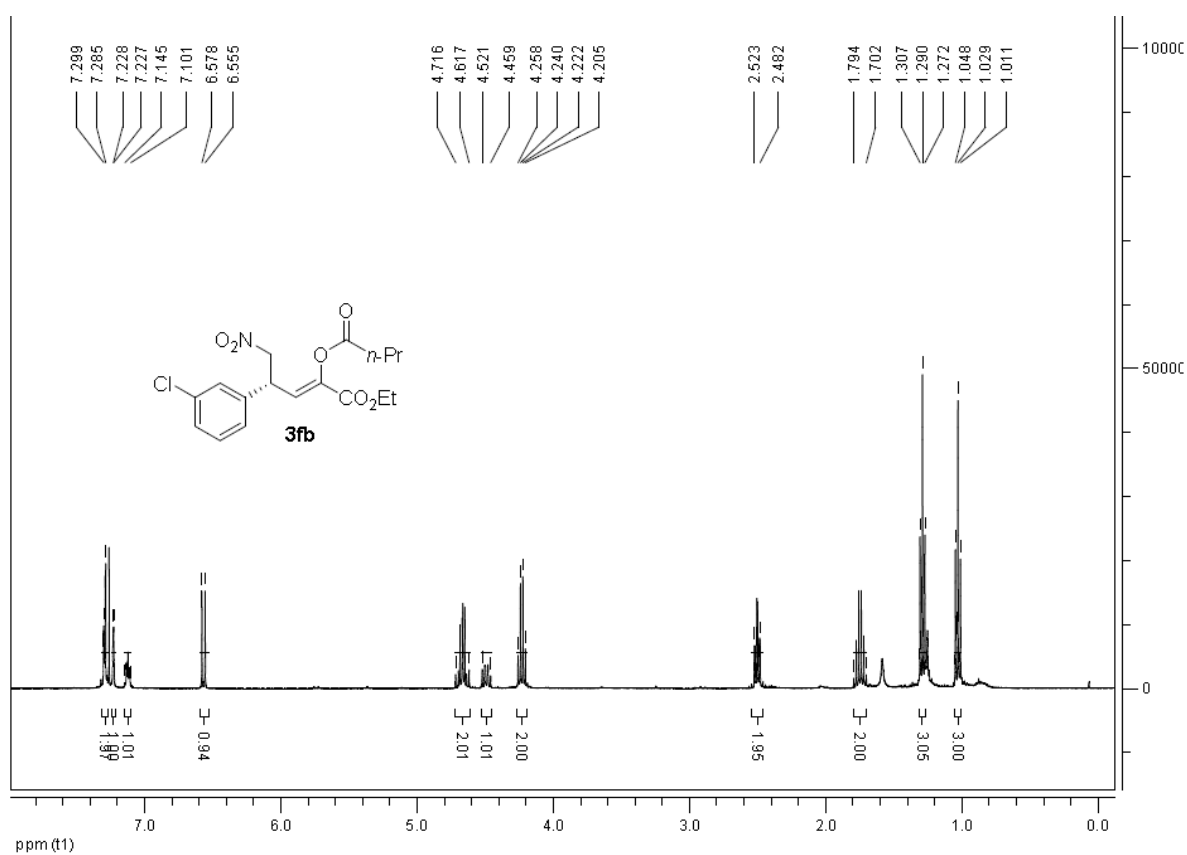


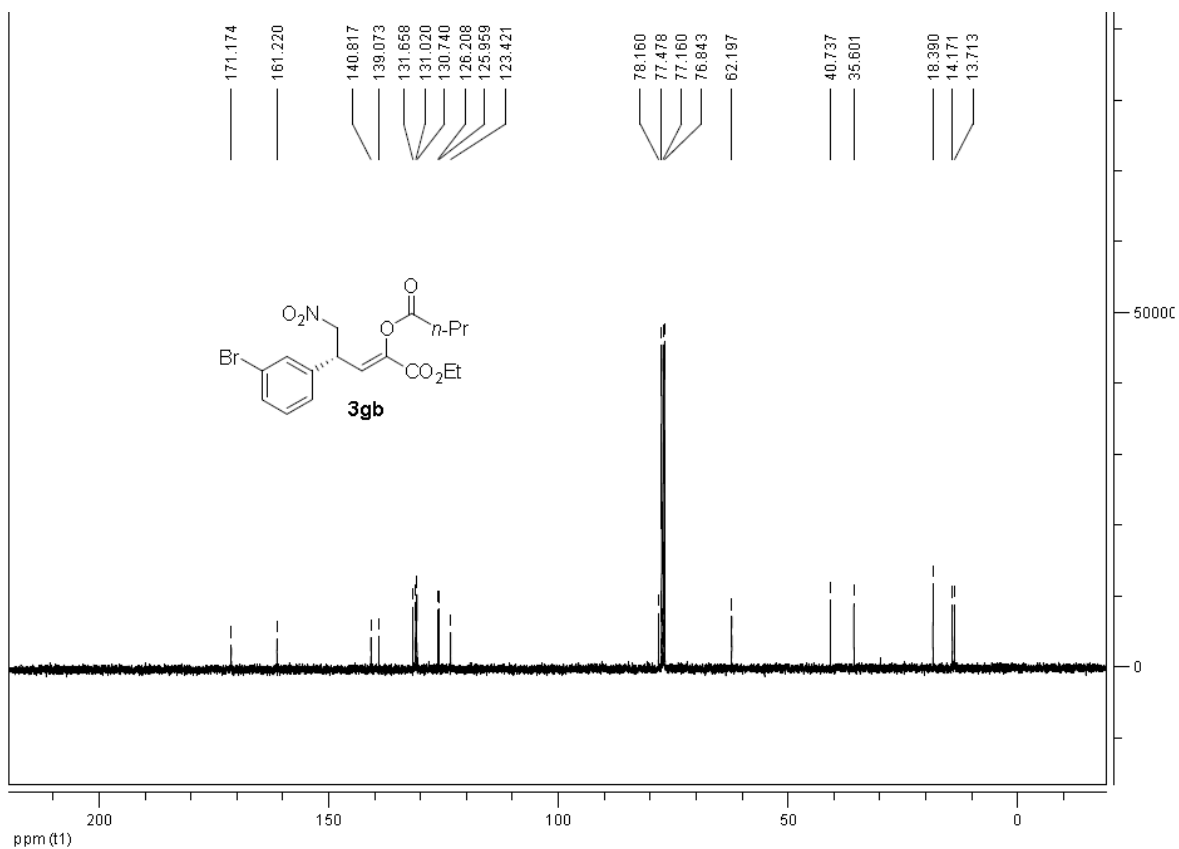
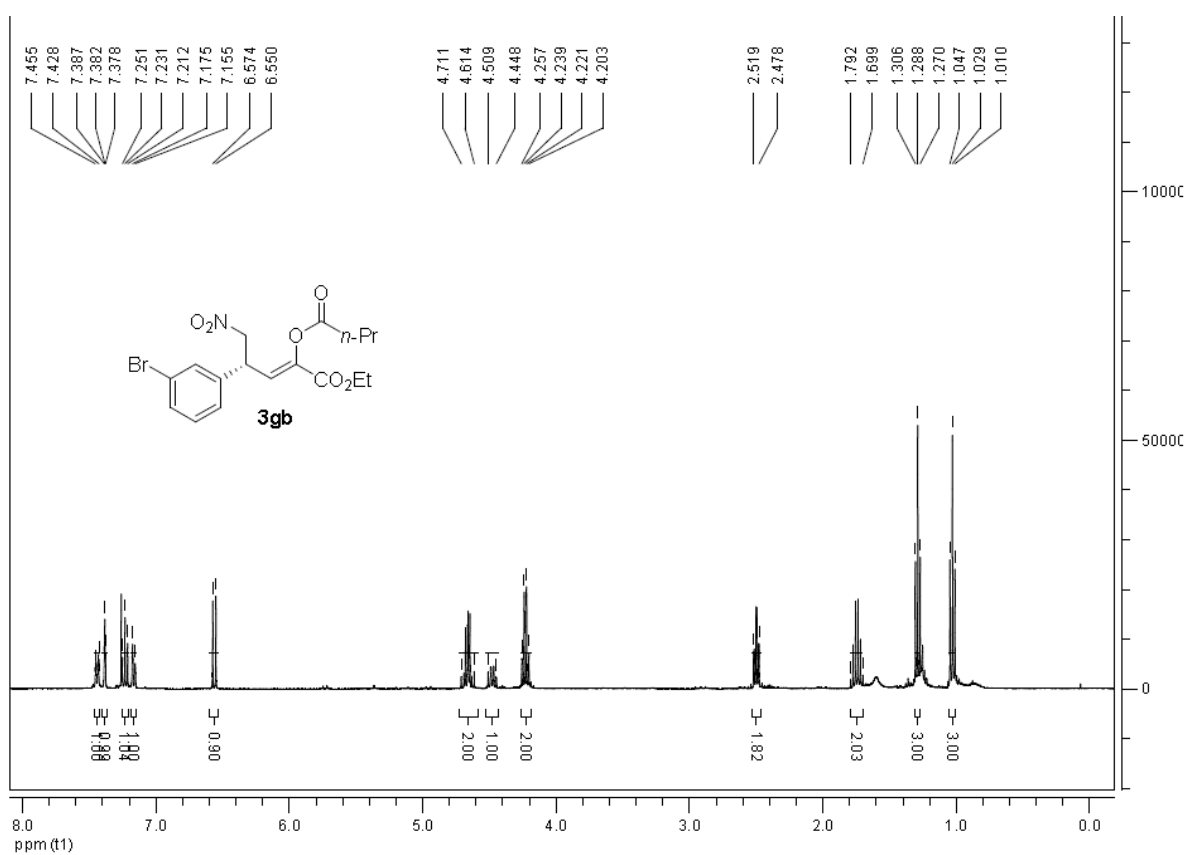


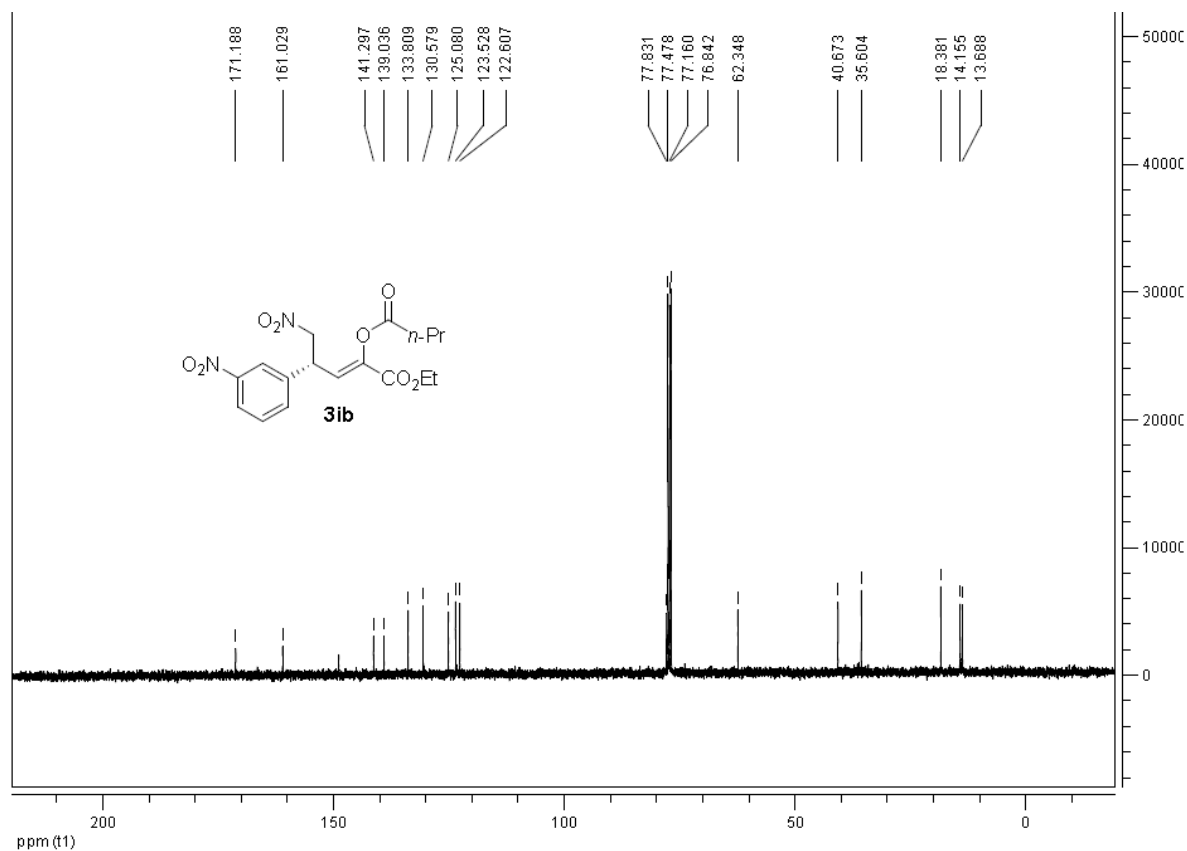
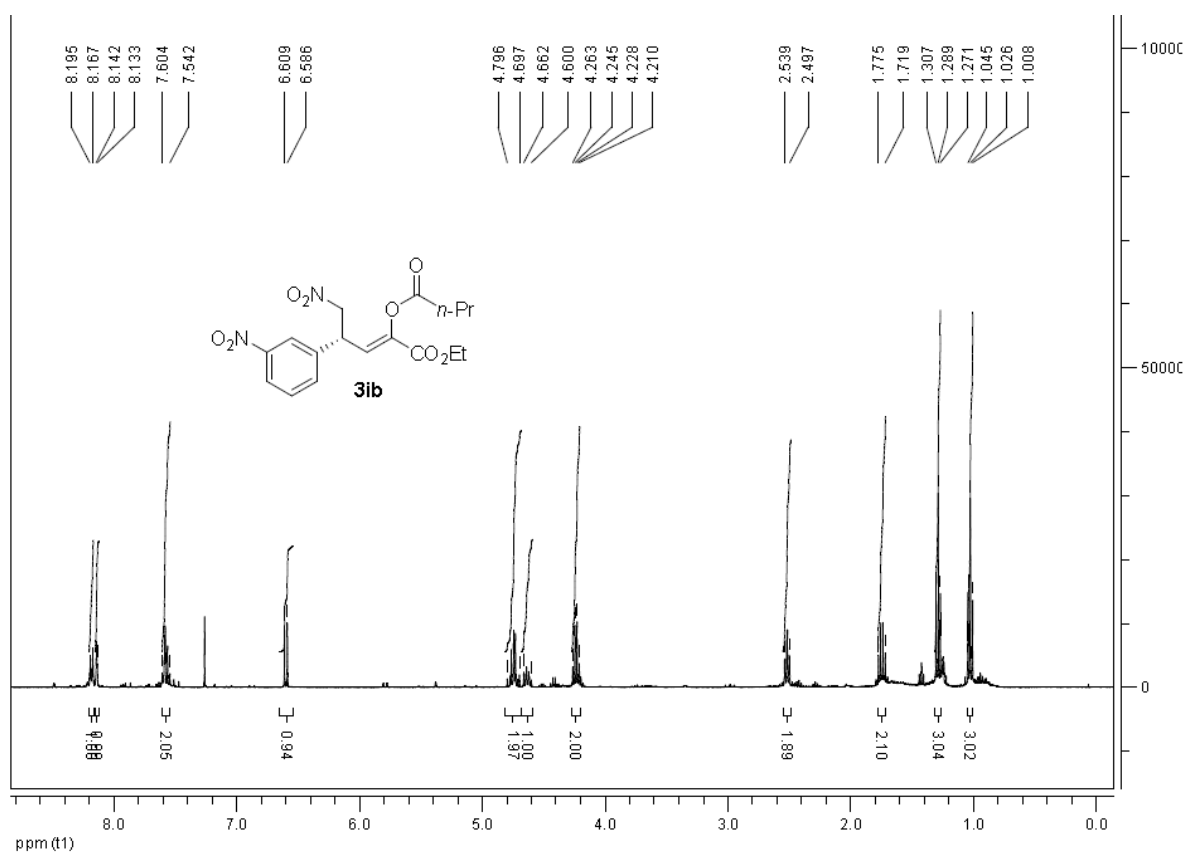


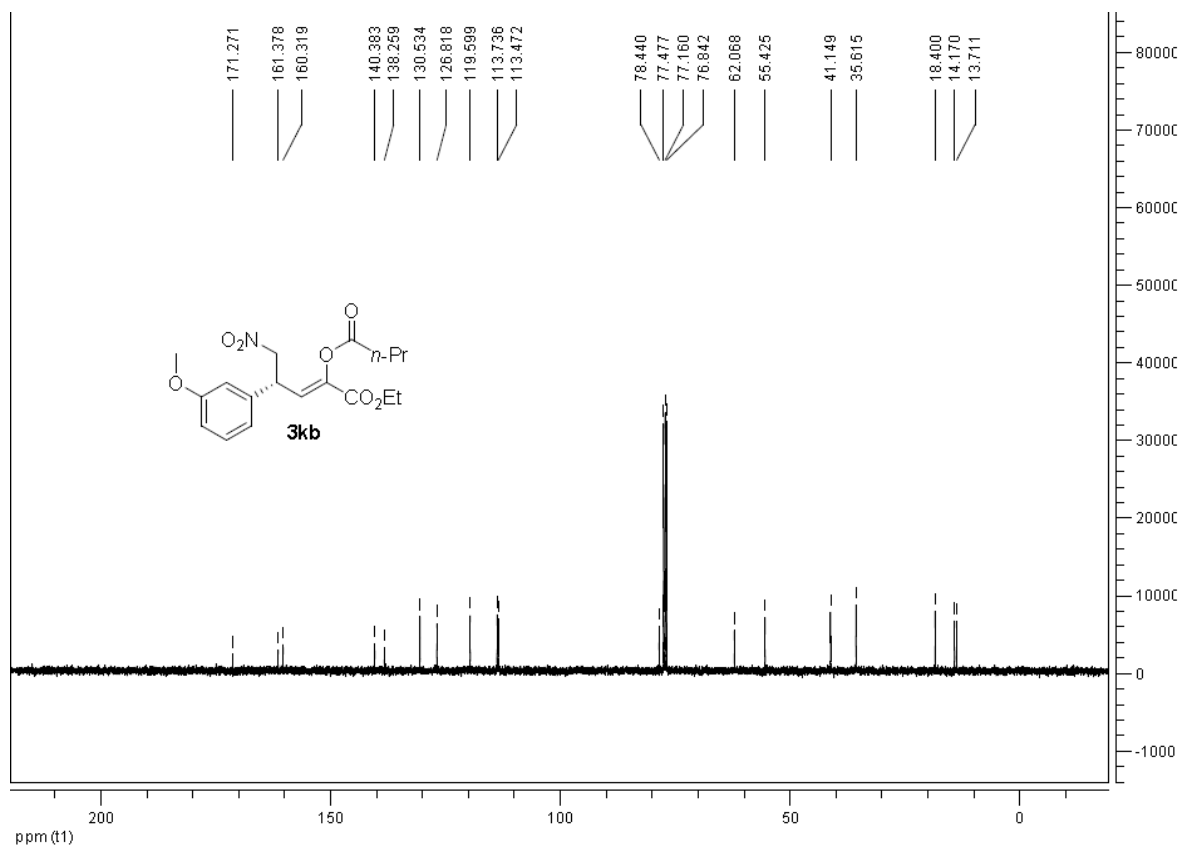
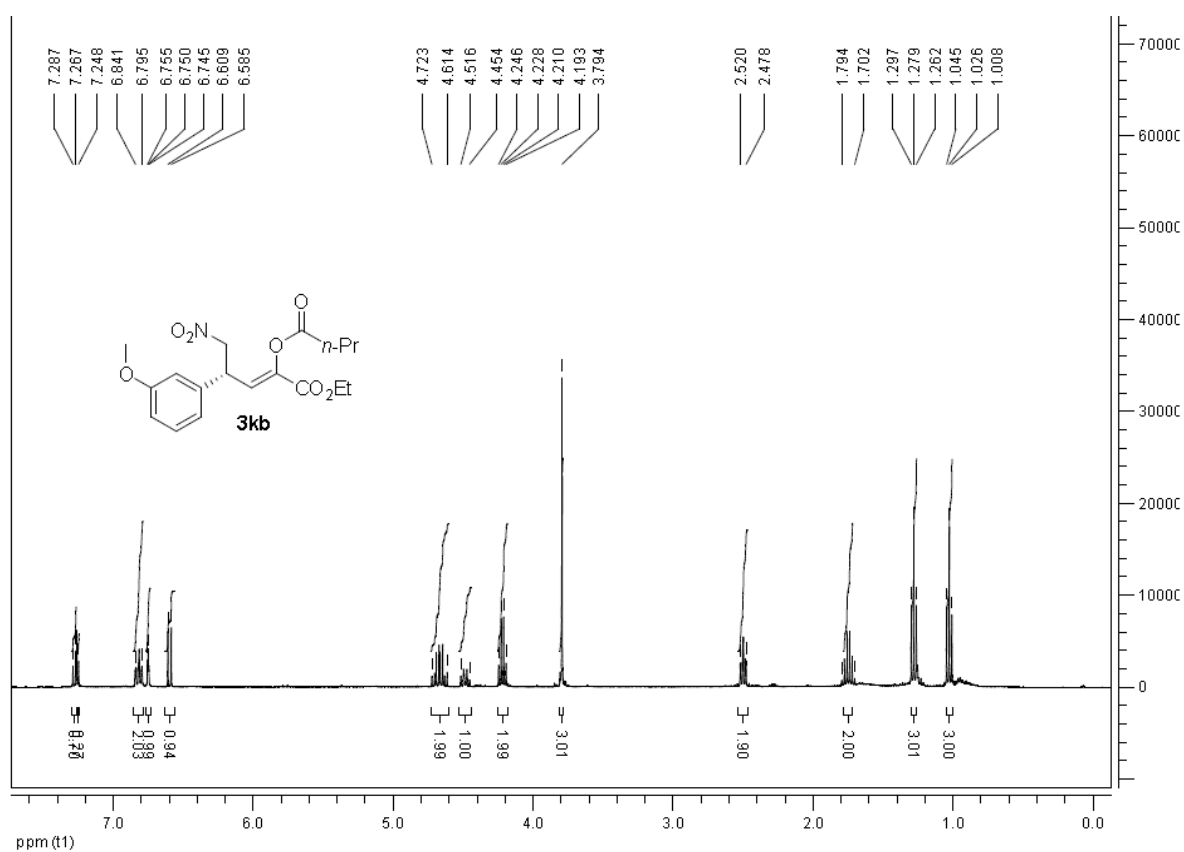


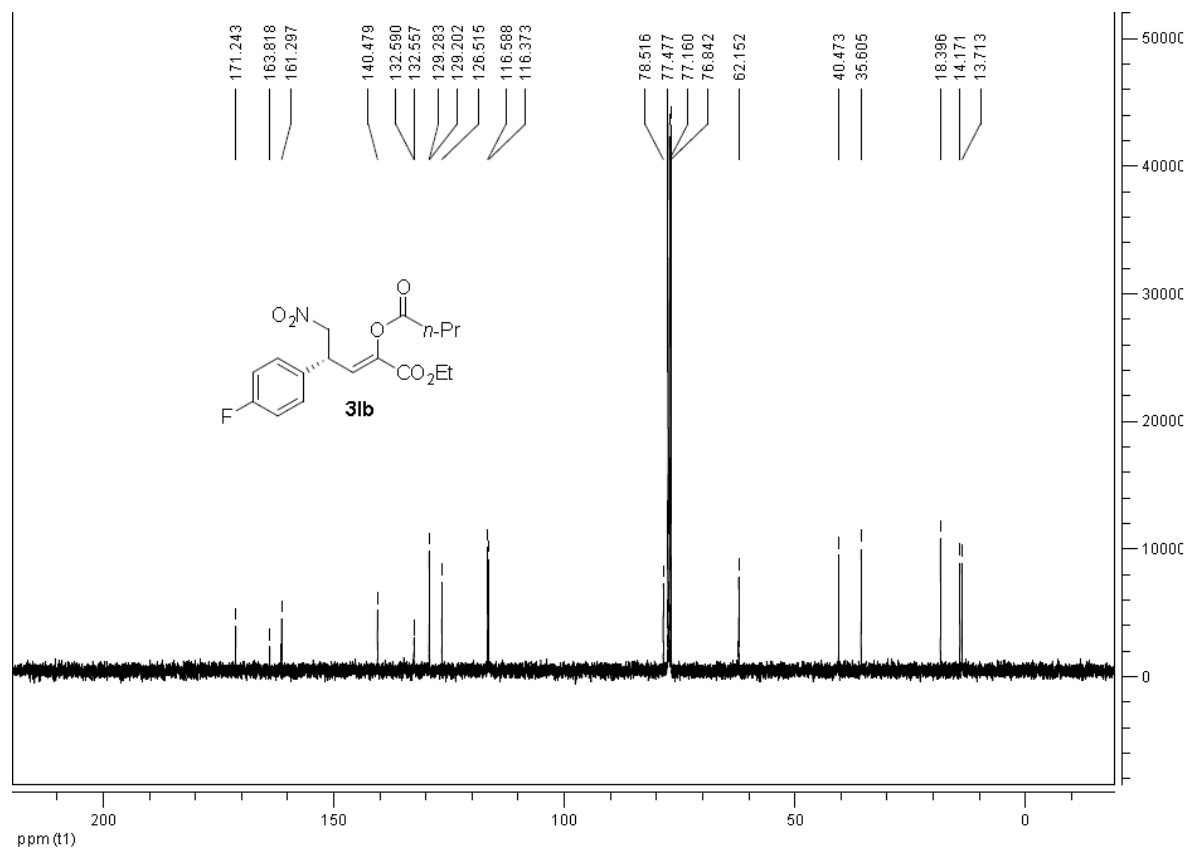
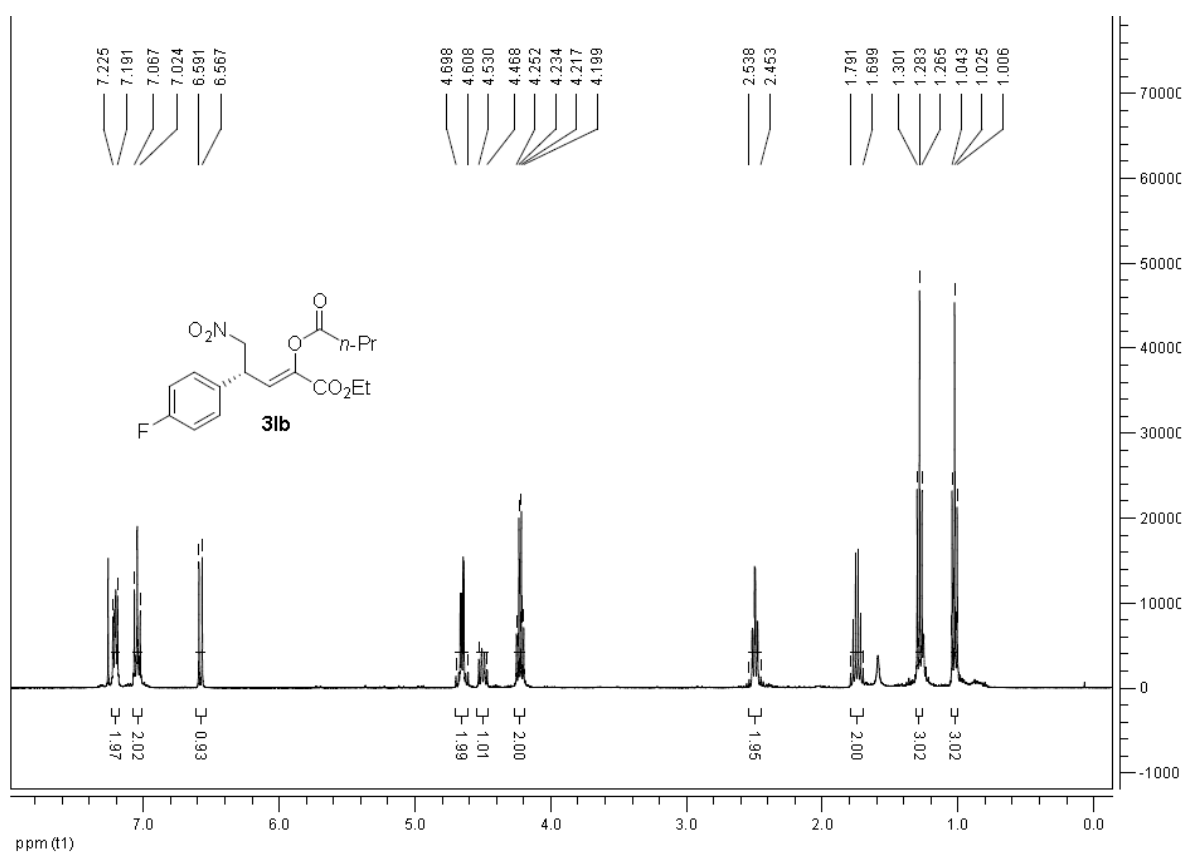


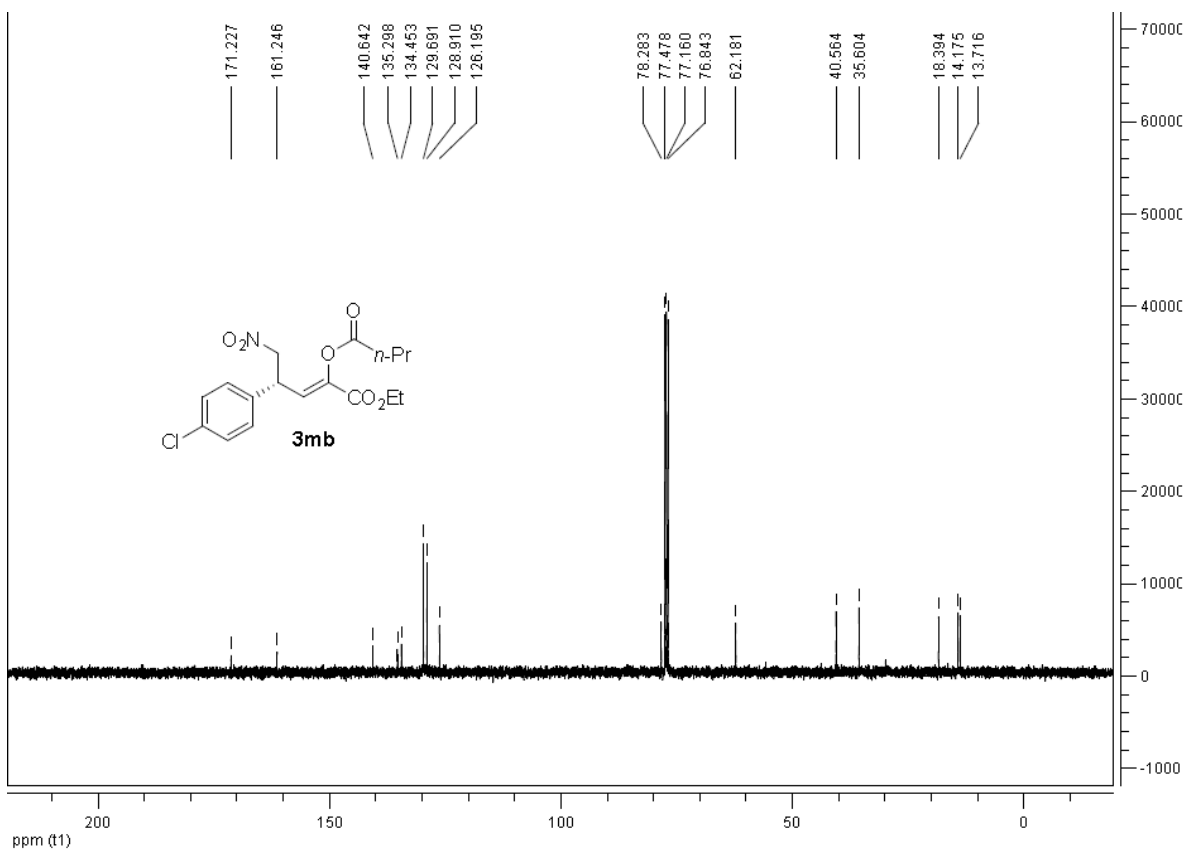
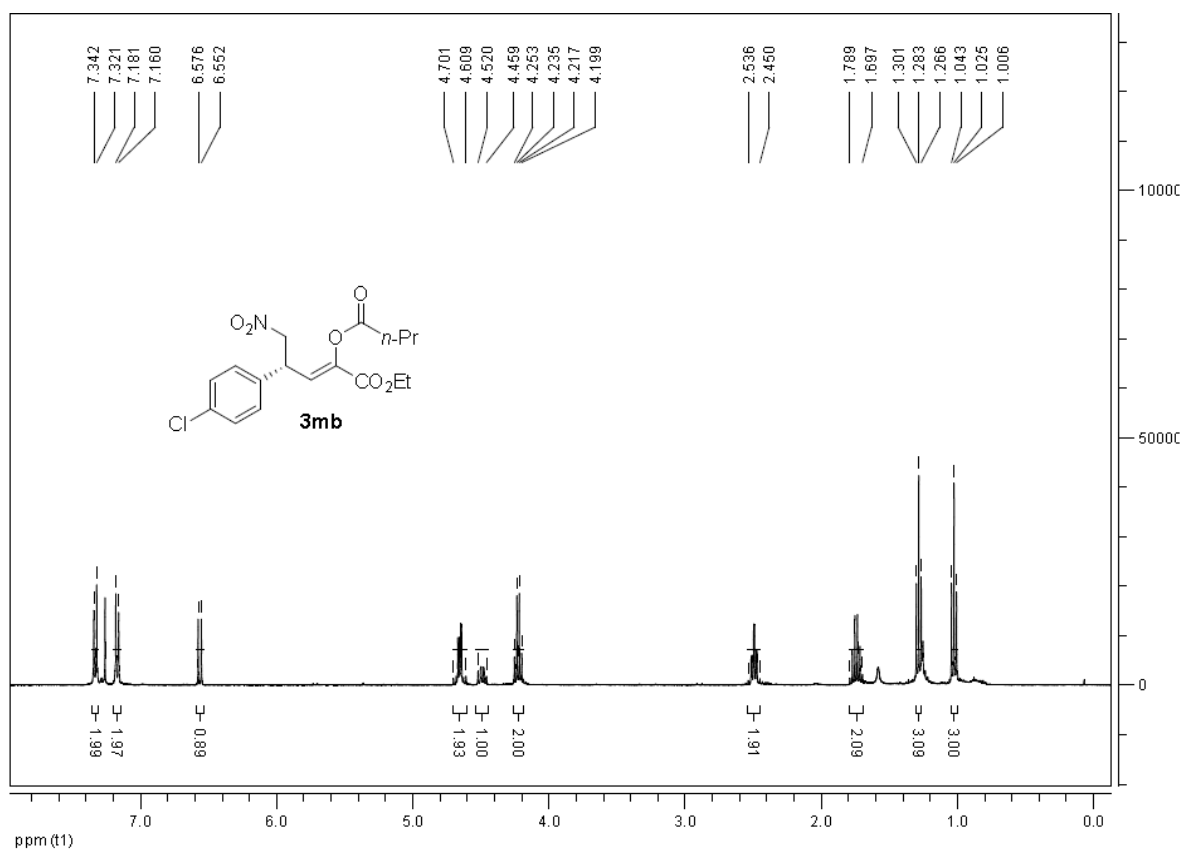


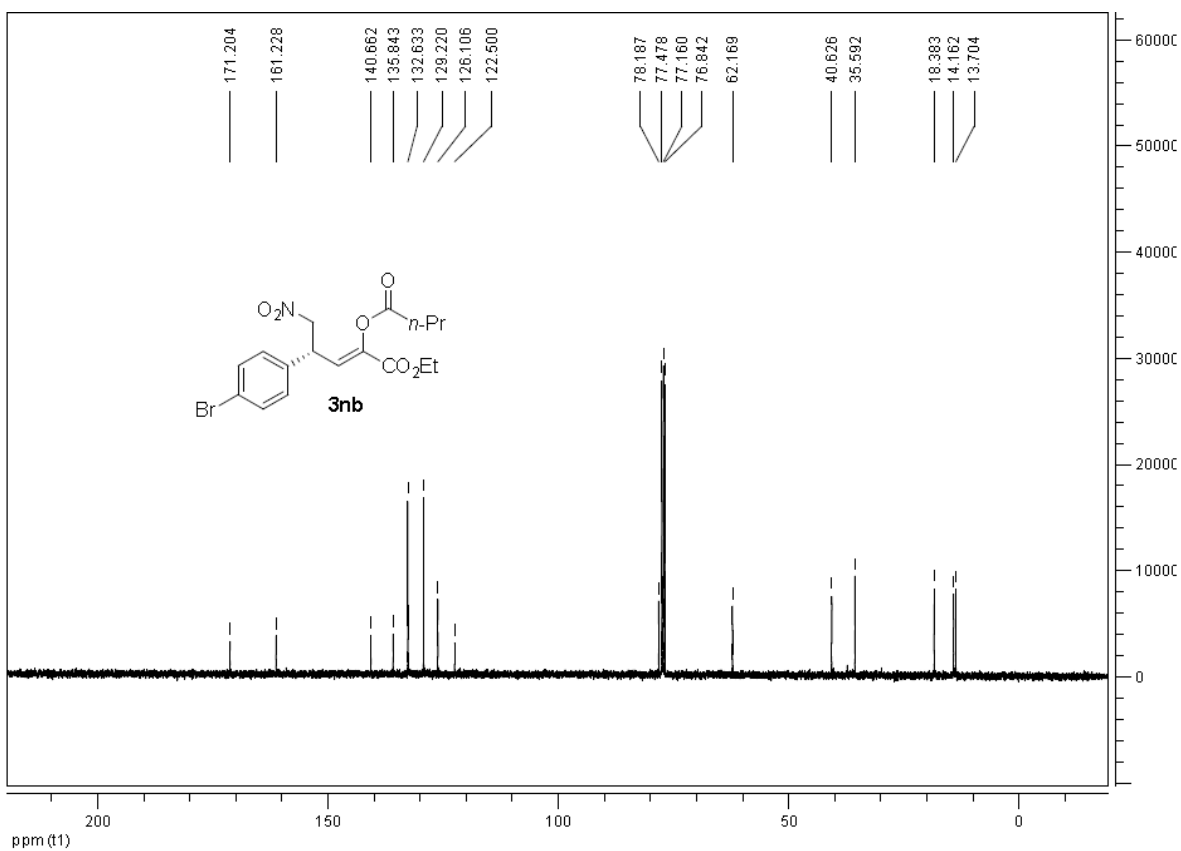
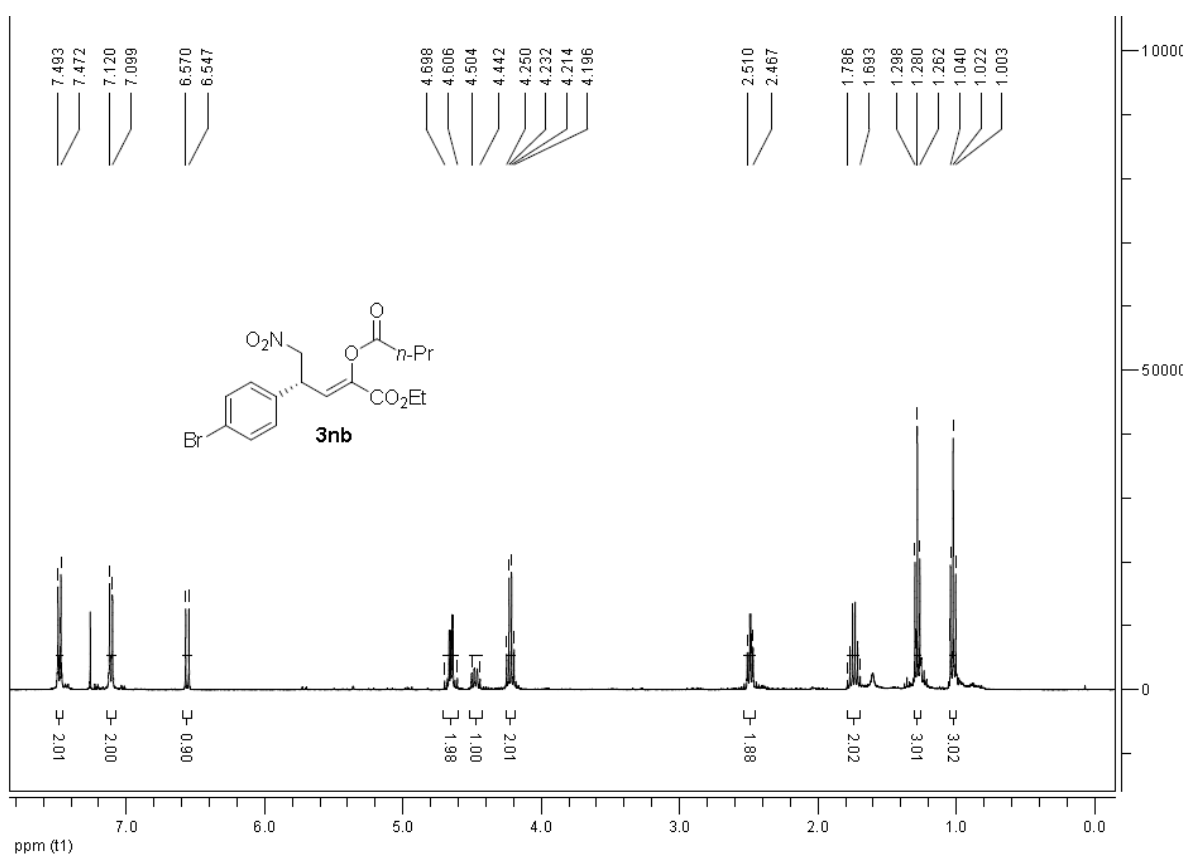


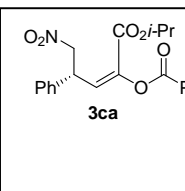












Supporting information

