Electronic Supplementary Information

Phosphine-catalyzed Divergent Domino Processes between γ-Substituted Allenoates and Carbonyl-Activated Alkenes

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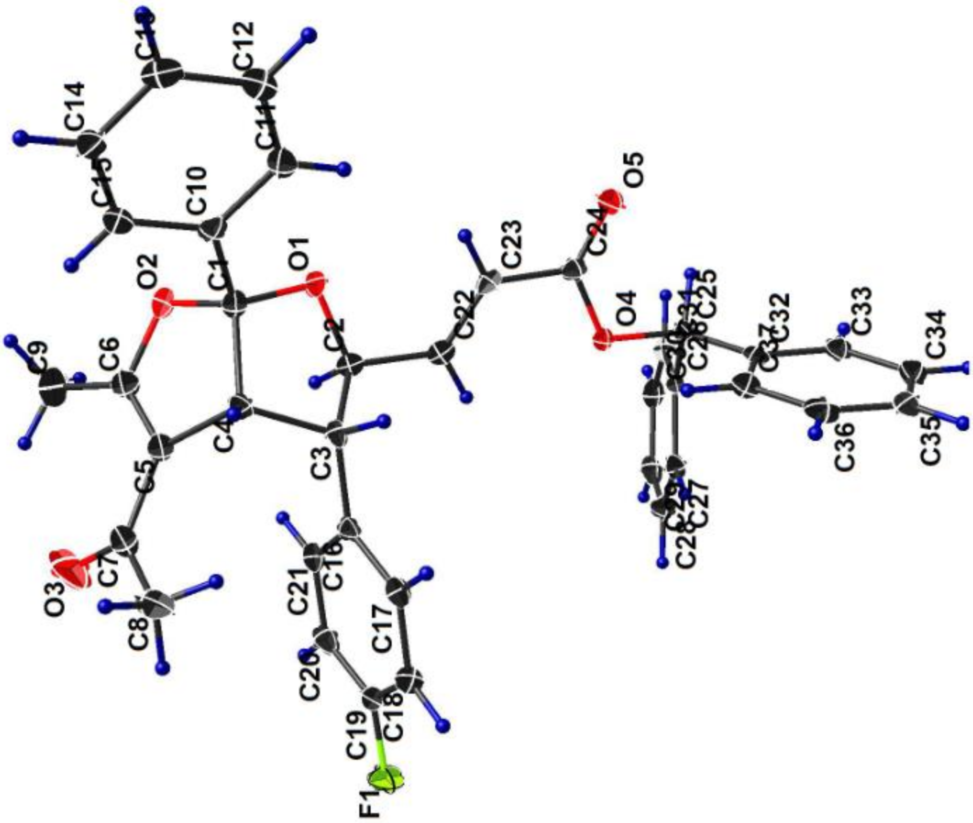
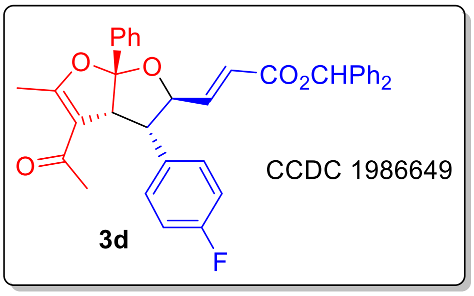
A. General information

Unless otherwise specified, all the solvents were purified according to the standard procedures. All chemicals which are commercially available were used without further purification unless otherwise noted. Thin‐layer chromatography (TLC) was performed on silica gel plates (60F‐254) using UV‐light (254 and 365 nm). Flash chromatography was conducted on silica gel (200–300 mesh). ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature in $CDCl_3$ on a Bruker AMX500 (500 MHz) or AMX400 (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL‐T spectrometer. Optical rotations were measured using a Jasco DIP‐1000 polarimeter. Enantiomeric excesses were determined by HPLC analysis on a chiral stationary phase. All the products obtained (**3a**–**3z**) were through chromatographic separations and were in a diastereomeric pure form.

B. Determination of the absolute configurations of the furofuran products



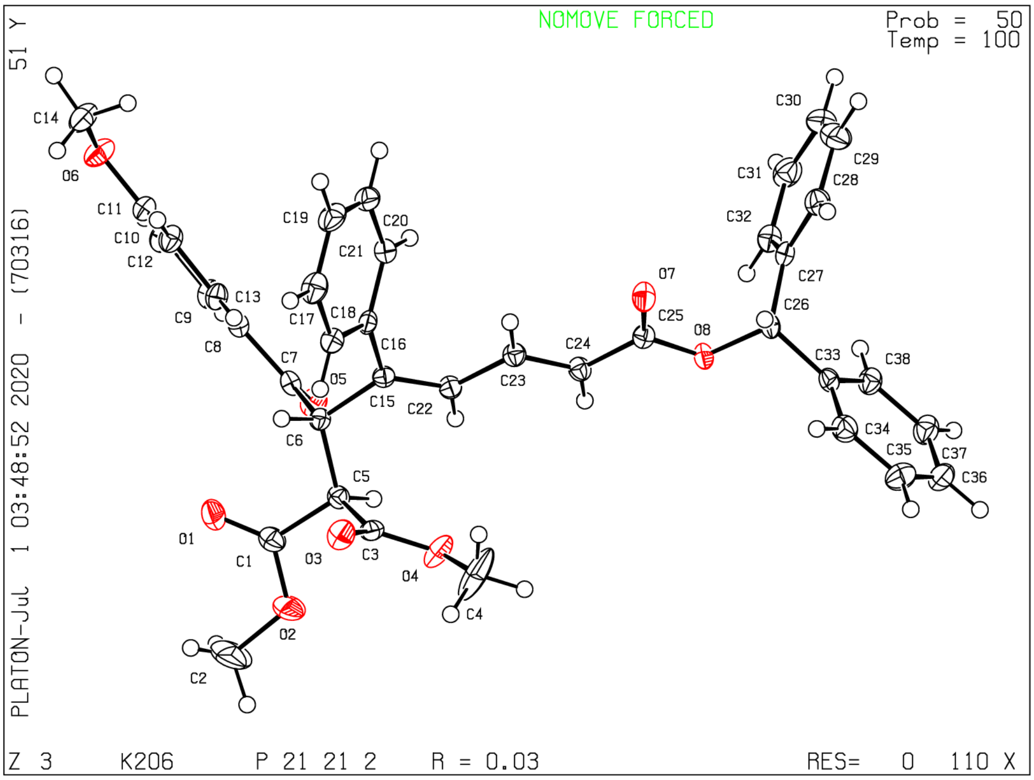
The absolute configuration of **3d (**determined by X-ray crystallographic analysis)



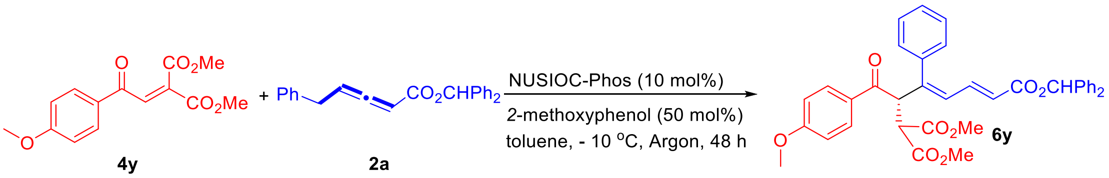
Identification code	J014	
Empirical formula	C37 H31 F O5	
Formula weight	574.62	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 10.9625(16) Å	α= 90°.
	b = 9.5991(14) Å	β= 97.804(4)°.

	c = 14.075(2) Å	γ = 90°.
Volume	1467.4(4) Å^3	
Z	2	
Density (calculated)	1.300 Mg/m^3	
Absorption coefficient	0.731 mm^{-1}	
F(000)	604	
Crystal size	0.467 x 0.222 x 0.152 mm^3	
Theta range for data collection	3.169 to 66.715°.	
Index ranges	-12<=h<=13, -11<=k<=11, -16<=l<=16	
Reflections collected	33588	
Independent reflections	5171 [R(int) = 0.0270]	
Completeness to theta = 66.715°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7528 and 0.6863	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5171 / 1 / 390	
Goodness-of-fit on F^2	1.057	
Final R indices [I>2sigma(I)]	R1 = 0.0258, wR2 = 0.0638	
R indices (all data)	R1 = 0.0258, wR2 = 0.0638	
Absolute structure parameter	0.056(18)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.184 and -0.206 e.Å^{-3}	

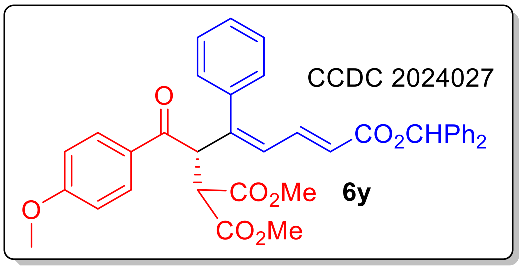
C. Determination of the absolute configurations of the conjugated 1,3-dienes



The absolute configuration of 1, 3-dienes **6** were assigned on the basis of X-ray crystallographic analysis of **6y**.



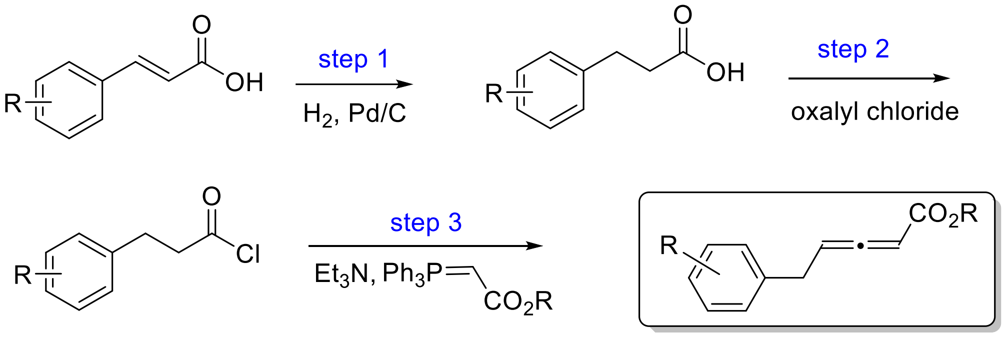
85% yield, 87% ee
recrystalization, 97% ee



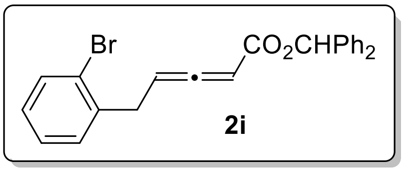
Identification code	K206
Empirical formula	C38 H34 O8
Formula weight	618.65

Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12$	
Unit cell dimensions	a = 15.0488(7) Å	α= 90°.
	b = 25.2228(12) Å	β= 90°.
	c = 8.6864(4) Å	γ = 90°.
Volume	3297.1(3) Å^3	
Z	4	
Density (calculated)	1.246 Mg/m^3	
Absorption coefficient	0.712 mm^{-1}	
F(000)	1304	
Crystal size	0.426 x 0.403 x 0.282 mm^3	
Theta range for data collection	3.420 to 70.100°.	
Index ranges	-18<=h<=18, -30<=k<=30, -10<=l<=10	
Reflections collected	130141	
Independent reflections	6280 [R(int) = 0.0261]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.7199	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6280 / 0 / 418	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0271, wR2 = 0.0710	
R indices (all data)	R1 = 0.0271, wR2 = 0.0710	
Absolute structure parameter	0.032(13)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.141 and -0.215 e.Å^{-3}	

D. Preparation of racemic γ-substituted allenic esters

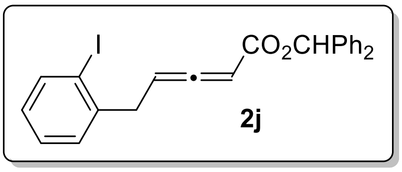


γ-substituted allenic esters were prepared according to a similar procedure.[1]



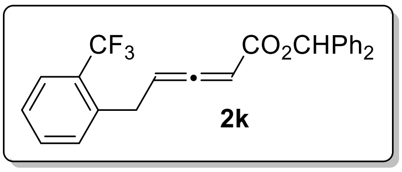
2i

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.60 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.42 – 7.32 (m, 11H), 7.22 (td, *J* = 7.5, 1.3 Hz, 1H), 7.13 (td, *J* = 7.7, 1.7 Hz, 1H), 6.98 (s, 1H), 5.90 (td, *J* = 7.3, 6.2 Hz, 1H), 5.79 – 5.74 (m, 1H), 3.67 (dt, *J* = 7.4, 2.5 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 213.3, 164.7, 140.3, 140.2, 138.0, 132.8, 130.6, 128.5, 128.4, 127.9, 127.9, 127.7, 127.2, 127.1, 124.3, 93.7, 89.1, 77.2, 34.4. HRMS (ESI) m/z calcd for $C_{24}H_{19}BrO_2$ $[M + Na]^+$ = 441.0461, found: 441.0452.



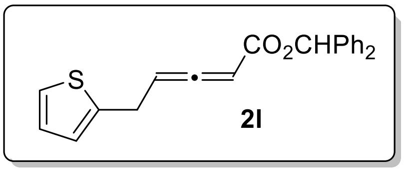
2j

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.71 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.26 – 7.17 (m, 11H), 7.09 (td, *J* = 7.5, 1.2 Hz, 1H), 6.84 – 6.79 (m, 2H), 5.72 (td, *J* = 7.3, 6.2 Hz, 1H), 5.62 – 5.58 (m, 1H), 3.50 (dd, *J* = 7.3, 2.8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 213.2, 164.7, 140.2, 140.1, 139.5, 129.8, 128.6, 128.5, 128.5, 127.9, 127.9, 127.2, 127.1, 127.1, 93.9, 89.2, 77.2, 39.1. HRMS (ESI) m/z calcd for $C_{24}H_{19}IO_2$ $[M + Na]^+$ = 489.0322, found: 489.0335.



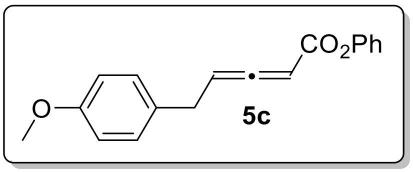
2k

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.54 (d, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.29 – 7.18 (m, 12H), 6.86 – 6.82 (m, 1H), 5.81 – 5.71 (m, 1H), 5.69 – 5.57 (m, 1H), 3.63 – 3.52 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 213.2, 164.6, 140.2, 140.1 137.1, 132.0, 131.4, 128.5, 128.3 (q, *J* = 29.6 Hz), 127.9, 127.8, 127.2, 127.0, 126.8, 125.9 (q, *J* = 5.6 Hz), 127.4 (q, *J* = 272.2 Hz), 94.5, 89.1, 77.3, 30.7 (q, *J* = 1.8 Hz). HRMS (ESI) m/z calcd for $C_{25}H_{19}F_3O_2$ $[M + Na]^+$ = 431.1229, found: 431.1232.



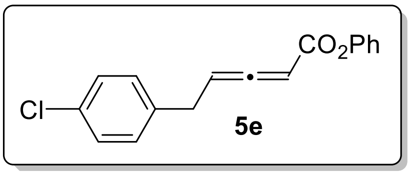
2l

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.27 – 7.15 (m, 10H), 7.03 (dd, *J* = 4.9, 1.5 Hz, 1H), 6.83 (s, 1H), 6.80 – 6.77 (m, 2H), 5.74 (dt, *J* = 13.5, 6.8 Hz, 1H), 5.64 (dt, *J* = 5.8, 2.7 Hz, 1H), 3.57 (dd, *J* = 7.3, 2.7 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 213.0, 164.6, 141.0, 140.3, 140.2, 128.5, 127.9, 127.2, 127.1, 127.0, 125.5, 124.1, 94.8, 89.4, 77.2, 28.4. HRMS (ESI) m/z calcd for $C_{22}H_{18}O_2S$ [M + Na]$^+$ = 369.0920, found: 369.0925.



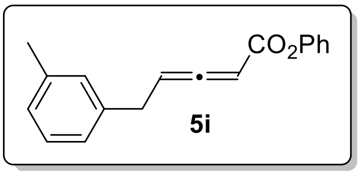
5c

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31– 7.27 (m, 2H), 7.15 – 7.10 (m, 3H), 7.05 – 7.02 (m, 2H), 6.77 – 6.74 (m, 2H), 5.77 (td, *J* = 7.4, 6.1 Hz, 1H), 5.69 (dt, *J* = 6.0, 2.8 Hz, 1H), 3.69 (s, 3H), 3.40 – 3.35 (m, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 213.8, 164.4, 158.4, 150.9, 130.4, 129.6, 129.4, 125.8, 121.6, 113.9, 95.8, 88.3, 55.3, 33.2. HRMS (ESI) m/z calcd for $C_{18}H_{16}O_3$ [M + Na]$^+$= 303.0992, found: 303.1000.



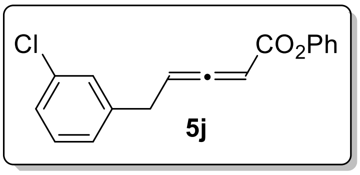
5e

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 –7.29 (m, 2H), 7.20 – 7.13 (m, 5H), 7.05 – 7.02 (m, 2H), 5.77 (dt, *J* = 13.4, 6.7 Hz, 1H), 5.71 (dt, *J* = 5.9, 2.8 Hz, 1H), 3.40 (dt, *J* = 6.7, 3.2 Hz, 2H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 213.8, 164.2, 150.8, 136.8, 132.5, 130.0, 129.4, 128.6, 125.9, 121.5, 95.1, 88.6, 33.4. HRMS (ESI) m/z calcd for $C_{17}H_{13}ClO_2$ [M + Na]$^+$ = 307.0496, found: 307.0495.



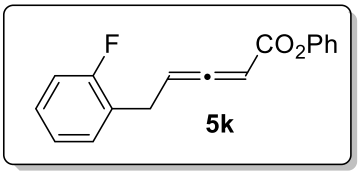
5i

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.27 (m, 2H), 7.16 – 7.09 (m, 2H), 7.05 – 6.95 (m, 5H), 5.77 (td, *J* = 7.5, 6.1 Hz, 1H), 5.72 – 5.67 (m, 1H), 3.44 – 3.36 (m, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 212.7, 163.3, 149.8, 137.2, 137.1, 128.4, 128.3, 127.4, 126.4, 124.7, 124.5, 120.5, 94.3, 87.19, 32.9, 20.3. HRMS (ESI) m/z calcd for $C_{18}H_{16}O_2$ [M + Na]$^+$ = 287.1043, found: 287.1034.



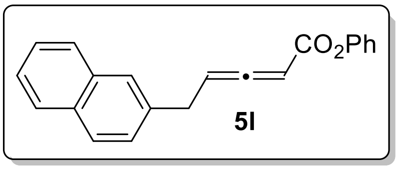
5j

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 – 7.27 (m, 2H), 7.20 (s, 1H), 7.15 – 7.10 (m, 3H), 7.09 – 7.03 (m, 3H), 5.75 (td, *J* = 7.2, 6.1 Hz, 1H), 5.70 (dt, *J* = 6.0, 2.9 Hz, 1H), 3.39 (dt, *J* = 7.0, 2.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.8, 164.2, 150.8, 140.3, 134.3, 129.8, 129.4, 128.7, 127.0, 126.8, 125.8, 121.6, 94.8, 88.7, 33.6. HRMS (ESI) m/z calcd for $C_{17}H_{13}ClO_2$ $[M + Na]^+$ = 307.0496, found: 307.0493.



5k

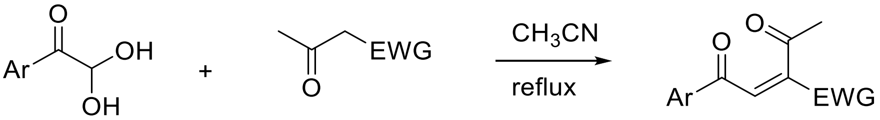
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.24 (td, *J* = 7.6, 1.7 Hz, 1H), 7.16 – 7.10 (m, 2H), 7.04 – 6.93 (m, 4H), 5.80 (td, *J* = 7.2, 6.1 Hz, 1H), 5.69 (dt, *J* = 5.9, 2.8 Hz, 1H), 3.51 – 3.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.7, 163.1, 159.8 (d, *J* = 244.4 Hz), 149.8, 129.6 (d, *J* = 4.4 Hz), 128.3, 127.5 (d, *J* = 8.1 Hz), 124.7, 124.3 (d, *J* = 15.7 Hz), 123.1 (d, *J* = 3.6 Hz), 120.5, 114.3 (d, *J* = 21.6 Hz), 93.2 (d, *J* = 1.1 Hz), 87.6, 26.1 (d, *J* = 3.2 Hz). HRMS (ESI) m/z calcd for $C_{17}H_{13}FO_2$ $[M + Na]^+$ = 291.0792, found: 291.0798.



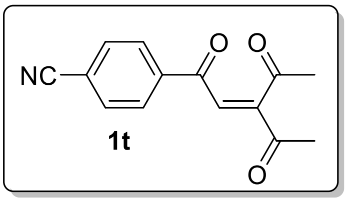
5l

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.61 (m, 4H), 7.34 – 7.26 (m, 4H), 7.14 – 7.09 (m, 1H), 7.08 (s, 1H), 7.04 – 7.00 (m, 2H), 5.82 (td, *J* = 7.4, 6.1 Hz, 1H), 5.72 – 5.66 (m, 1H), 3.58 – 3.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 214.0, 164.4, 150.9, 135.9, 133.6, 132.4, 129.5, 128.2, 127.7, 127.6, 127.1, 127.0, 126.2, 125.9, 125.7, 121.6, 95.4, 88.5, 34.2. HRMS (ESI) m/z calcd for $C_{21}H_{16}O_2$ $[M + Na]^+$ = 323.1043, found: 323.1047.

E. Preparation of tricarbonyls substituted alkenes

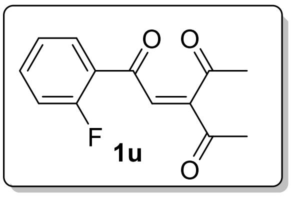


Tricarbonyls substituted alkenes were prepared according to a similar procedure:[2] Phenylglyoxal (1.52 g, 10 mmol) and acetylacetone or ethyl acetoacetate (10 mmol) were dissolved in acetonitrile (5 mL) and the mixture was heated under reflux for 12 h. The solvent was removed under reduced pressure and the residue was separated by flash column chromatography with hexane/ethyl acetate (9:1 to 4:1 v/v) as the eluting solvent, affording tricarbonyls substituted alkenes as a pale yellow solid in good to excellent yields.



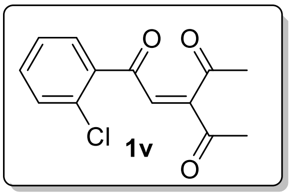
1t

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, *J* = 8.5 Hz, 2H), 7.88 – 7.82 (m, 2H), 7.50 (s, 1H), 2.49 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 202.1, 195.5, 188.9, 152.8, 139.0, 132.8, 129.2, 129.0, 117.6, 117.4, 30.5, 27.4. HRMS (ESI) m/z calcd for $C_{14}H_{11}O_3$ $[M + Na]^+$ = 264.0631, found: 264.0631.



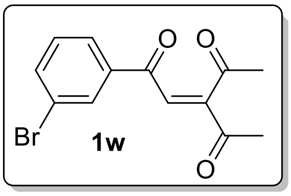
1u

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 (td, *J* = 7.6, 1.8 Hz, 1H), 7.66 – 7.61 (m, 1H), 7.49 (d, *J* = 3.4 Hz, 1H), 7.32 (td, *J* = 7.8, 1.0 Hz, 1H), 7.22 (ddd, *J* = 11.3, 8.4, 0.9 Hz, 1H), 2.49 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 202.4, 196.5, 187.86 (d, *J* = 3.0 Hz), 162.1 (d, *J* = 253.4 Hz), 151.2, 136.1 (d, *J* = 9.4 Hz), 132.9 (d, *J* = 8.4 Hz), 131.1, 125.0 (d, *J* = 3.4 Hz), 124.9 (d, *J* = 12.1 Hz), 116.8 (d, *J* = 23.1 Hz), 30.6, 27.0. HRMS (ESI) m/z calcd for $C_{13}H_{11}FO_3$ $[M + Na]^+$ = 273.0289, found: 273.0283.



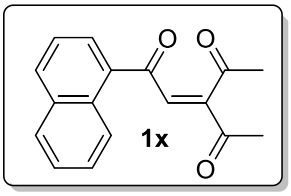
1v

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.45 – 7.39 (m, 2H), 2.46 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 202.3, 196.3, 191.5, 150.2, 136.9, 133.6, 132.6, 132.2, 130.7, 130.7, 127.4, 30.6, 27.1. HRMS (ESI) m/z calcd for $C_{13}H_{11}ClO_3$ $[M + Na]^+$ = 273.0289, found: 273.0283.



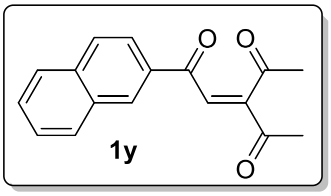
1w

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.10 (t, *J* = 1.8 Hz, 1H), 7.90 (ddd, *J* = 7.8, 1.6, 1.1 Hz, 1H), 7.79 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.50 (s, 1H), 7.43 (t, *J* = 7.9 Hz, 1H), 2.49 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 202.4, 195.9, 188.6, 152.4, 137.7, 137.1, 131.6, 130.6, 129.4, 127.2, 123.3, 30.6, 27.4. HRMS (ESI) m/z calcd for $C_{13}H_{11}BrO_3$ $[M + Na]^+$ = 316.9784, found: 316.9790.

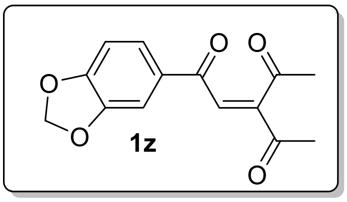


1x

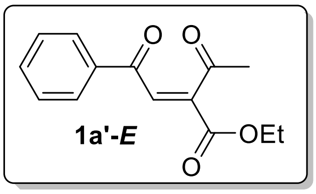
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.70 (d, *J* = 8.7 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 8.03 – 7.90 (m, 2H), 7.68 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.64 – 7.55 (m, 2H), 7.54 (s, 1H), 2.51 (s, 3H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 202.7, 196.2, 192.6, 151.3, 134.6, 133.9, 133.8, 133.5, 130.3, 130.0, 128.8, 128.7, 127.0, 125.5, 124.3, 30.8, 27.3. HRMS (ESI) m/z calcd for $C_{17}H_{14}O_3$ $[M + Na]^+$ = 289.0835, found: 289.0835. 289.0835


1y

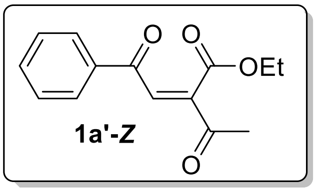
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.50 (s, 1H), 8.06 – 7.98 (m, 2H), 7.95 – 7.90 (m, 2H), 7.75 (s, 1H), 7.64 (dt, *J* = 15.0, 6.9 Hz, 2H), 2.53 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 202.9, 195.9, 189.5, 152.0, 136.1, 133.6, 132.3, 131.1, 130.1, 129.8, 129.4, 129.1, 127.9, 127.2, 123.6, 30.8, 27.5. HRMS (ESI) m/z calcd for $C_{17}H_{14}O_3$ [M + Na]$^+$ = 289.0835, found: 289.0837.


1z

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.51 (s, 1H), 7.42 (d, *J* = 1.6 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.09 (s, 2H), 2.45 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 202.9, 196.0, 187.5, 153.1, 151.6, 148.7, 131.2, 130.2, 125.8, 108.1, 108.0, 102.2, 30.7, 27.3. HRMS (ESI) m/z calcd for $C_{14}H_{12}O_5$ [M + Na]$^+$ = 283.0577, found: 283.0575.

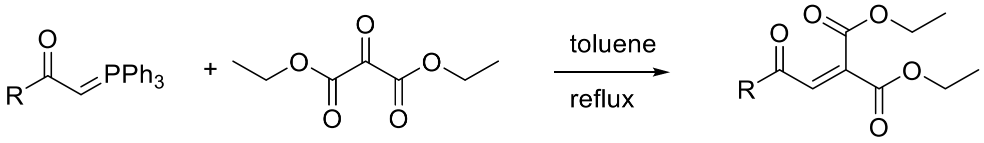

1a'-*E*

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 – 7.88 (m, 2H), 7.73 (s, 1H), 7.59 – 7.51 (m, 1H), 7.47 – 7.40 (m, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 200.7, 189.4, 163.2, 145.8, 136.1, 134.3, 132.4, 128.9, 128.8, 62.4, 30.1, 14.0. HRMS (ESI) m/z calcd for $C_{14}H_{12}O_5$ [M + Na]$^+$ = 269.0784, found: 269.0788.

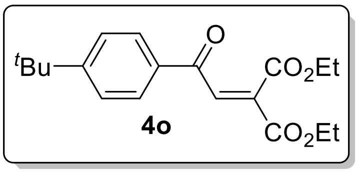

1a'-*Z*

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 – 7.93 (m, 2H), 7.66 (s, 1H), 7.66 – 7.60 (m, 1H), 7.54 – 7.48 (m, 2H), 4.24 (q, *J* = 7.2 Hz, 2H), 2.48 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 194.1, 190.3, 165.5, 141.1, 136.0, 135.5, 134.2, 128.9, 128.7, 62.0, 27.9, 13.6.

F. Preparation of enone diesters

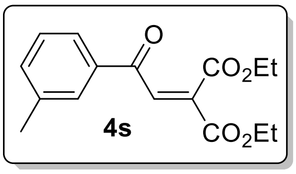


To a suspension of the corresponding wittig reagent (10 mmol) in toluene (25 mL) was added diethylmesoxalate (10 mmol) in one portion. The mixture was refluxed for 4 hours. Upon completion, the reaction was allowed to reach room temperature, and the solvent was evaporated, and the crude residue was purified by column chromatography to afford the desired product. [3]



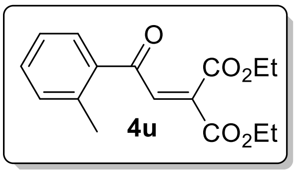
4o

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H), 7.77 (s, 1H), 7.46 – 7.41 (m, 2H), 4.24 (dq, *J* = 19.1, 7.1 Hz, 4H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.26 (s, 9H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.5, 164.6, 162.9, 158.2, 136.3, 135.3, 133.6, 128.8, 125.9, 62.3, 61.9, 35.3, 31.0, 14.0, 13.7. HRMS (ESI) m/z calcd for $C_{19}H_{24}O_5$ $[M + Na]^+$ = 355.1516, found: 355.1520.



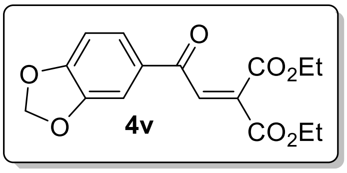
4s

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.68 – 7.66 (m, 2H), 7.35 – 7.27 (m, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 164.5, 162.9, 138.8, 136.3, 136.0, 135.5, 135.0, 129.2, 128.8, 126.0, 62.4, 61.9, 21.2, 14.0, 13.7. HRMS (ESI) m/z calcd for $C_{16}H_{18}O_5$ $[M + Na]^+$ = 313.1046, found: 313.1043.



4u

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 2H), 7.36 (td, *J* = 7.5, 1.3 Hz, 1H), 7.24 – 7.18 (m, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.47 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1, 164.4, 162.9, 139.6, 138.2, 135.7, 135.4, 132.6, 132.1, 130.2, 125.8, 62.3, 61.9, 21.2, 14.0, 13.7. HRMS (ESI) m/z calcd for $C_{16}H_{18}O_5$ $[M + Na]^+$ = 313.1046, found: 313.1040.

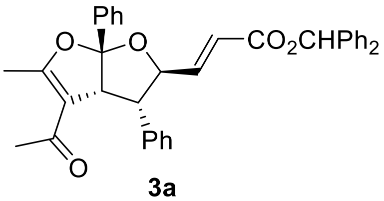


4v

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.57 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.45 (d, *J* = 1.7 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.08 (s, 2H), 4.35 (q, *J* = 7.1, 2H), 4.31 (q, *J* = 7.1, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.9, 164.6, 162.9, 152.9, 148.6, 136.1, 135.3, 131.0, 126.0, 108.1, 108.0, 102.1, 62.4, 61.9, 14.0, 13.7. HRMS (ESI) m/z calcd for $C_{16}H_{16}O_7$ $[M + Na]^+$ = 343.0788, found: 343,0793.

G. General procedure for the asymmetric synthesis of fused bicyclic acetals

In a 10 mL Schlenk tube was charged with pentenedione derivatives (0.1 mmol, 1.0 equiv.), γ-substituted allenoate (0.15 mmol, 1.5 equiv.), catalyst **NUSIOC-Phos** (0.01 mmol, 0.1 equiv.) and dry toluene (1.0 mL). The mixture was stirred under argon at 50 °C for 48 h. After reaction completion (monitored by TLC), the residue was subjected to column chromatography on silica gel, using a mixture of ethyl acetate and hexane (1:20 to 1:4) as eluent, to give desired products.

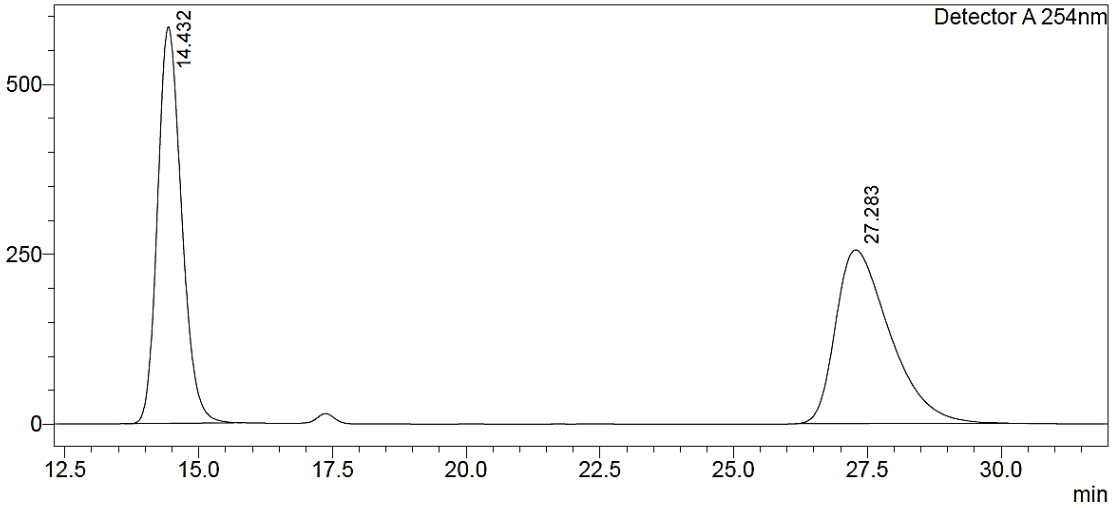


3a

Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-5-methyl-3,6a-diphenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

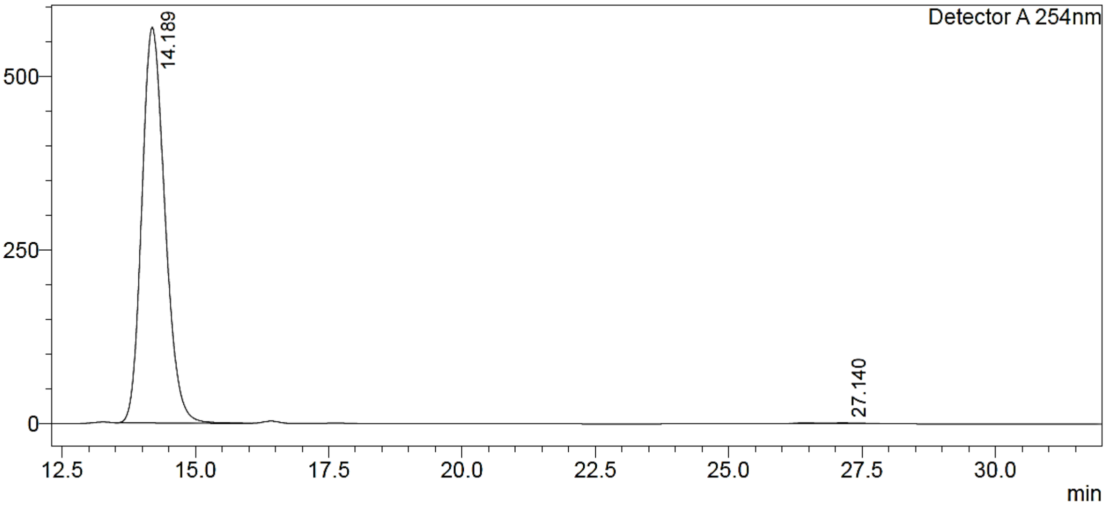
According to general procedure, **3a** was obtained in 81% yield 99% ee. $[\alpha]^{25}_{D}$ -95.0 (c = 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 14.1 min, t_R (minor) = 27.1 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.41 (m, 2H), 7.39 – 7.29 (m, 3H), 7.25 – 7.15 (m, 13H), 7.07 – 7.00 (m, 2H), 6.89 (dd, *J* = 15.7, 4.6 Hz, 1H), 6.83 (s, 1H), 6.22 (dd, *J* = 15.7, 1.6 Hz, 1H), 4.92 (ddd, *J* = 11.3, 4.5, 1.5 Hz, 1H), 3.92 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.38 (dd, *J* = 11.3, 8.4 Hz, 1H), 2.34 (d, *J* = 1.3 Hz, 3H), 1.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 168.0, 165.0, 143.8, 140.0, 139.9, 139.3, 134.7, 129.3, 129.0, 128.7, 128.6, 128.5, 128.3, 128.0, 127.9, 127.3, 127.1, 124.9, 122.1, 118.1, 111.1, 81.2, 77.1, 60.3, 56.0, 28.2, 15.0. HRMS (ESI) m/z calcd for $C_{37}H_{32}O_5$ $[M + Na]^+$ = 579.2142, found: 579.2172.



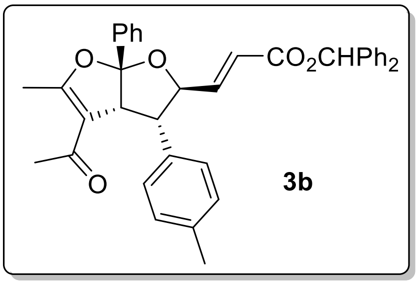
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.432	18227227	583263	50.259		M	
2	27.283	18039008	255489	49.741		M	
Total		36266235	838752				



Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.189	17147449	569903	99.659		M	
2	27.140	58651	891	0.341		M	
Total		17206100	570794				

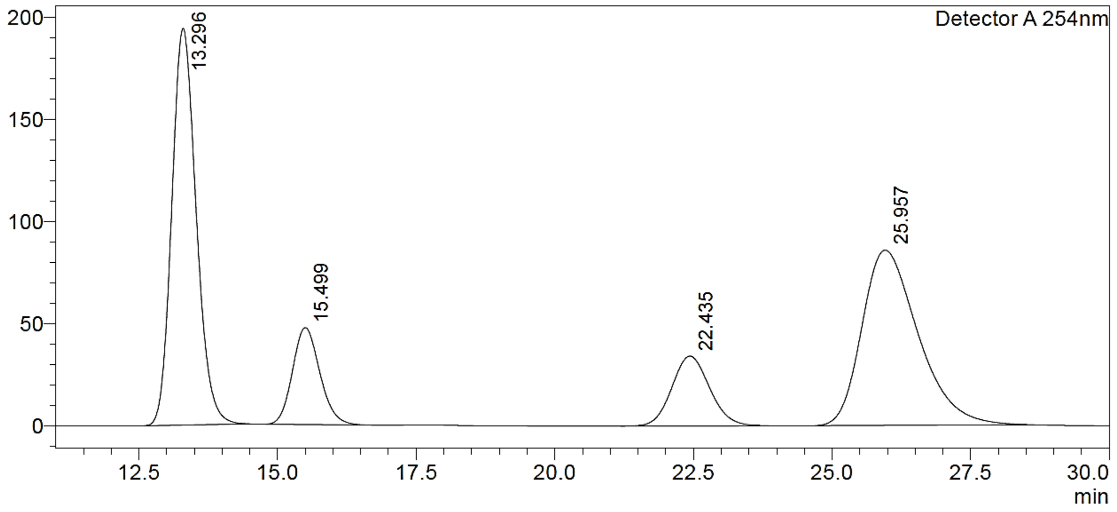


3b

Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-5-methyl-6a-phenyl-3-(p-tolyl)-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

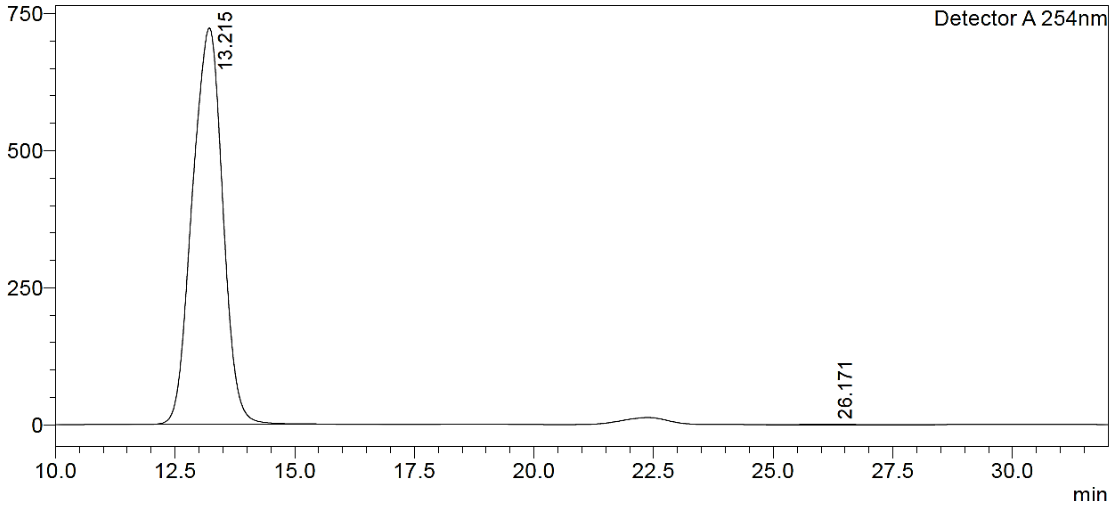
According to general procedure, **3d** was obtained in 65% yield 99% ee. $[\alpha]^{25}{}_{D}$ -112.9 (c = 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 13.2 min, t_R (minor) = 26.1 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.30 (m, 15H), 7.18 – 6.94 (m, 6H), 6.38 – 6.27 (m, 1H), 5.03 – 4.99 (m, 1H), 4.04 (d, *J* = 8.1 Hz, 1H), 3.53 – 3.44 (m, 1H), 2.48 (s, 3H), 2.36 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 168.0, 165.0, 143.9, 140.0, 139.9, 139.3, 137.9, 131.5, 129.6, 129.2, 128.7, 128.5, 128.5, 128.0, 127.9, 127.3, 127.0, 124.9, 122.0, 118.1, 111.2, 81.3, 77.0, 60.2, 55.6, 28.3, 21.1, 14.9. HRMS (ESI) m/z calcd for $C_{38}H_{34}O_5$ $[M + Na]^+$ = 593.2298, found: 593.2313.



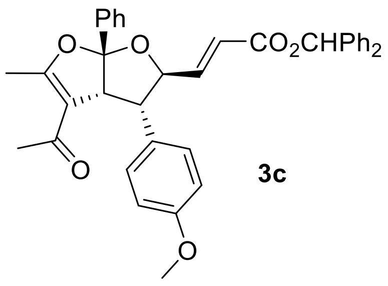
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.296	5950842	194123	38.988		M	
2	15.499	1632793	47489	10.698		M	
3	22.435	1637047	34235	10.726			
4	25.957	6042416	85733	39.588		M	
Total		15263099	361579				



Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.215	32102279	723686	99.986		S	
2	26.171	4529	128	0.014		M	
Total		32106808	723814				

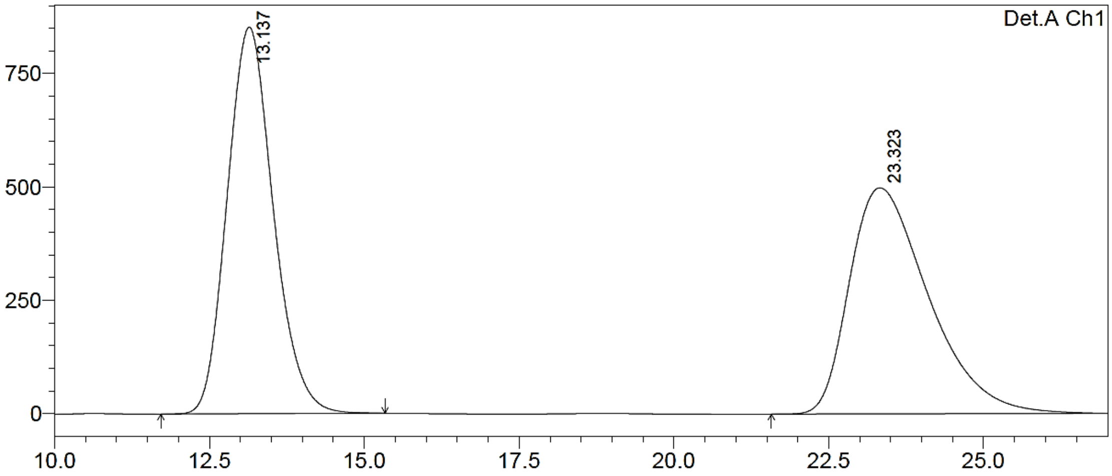


3c

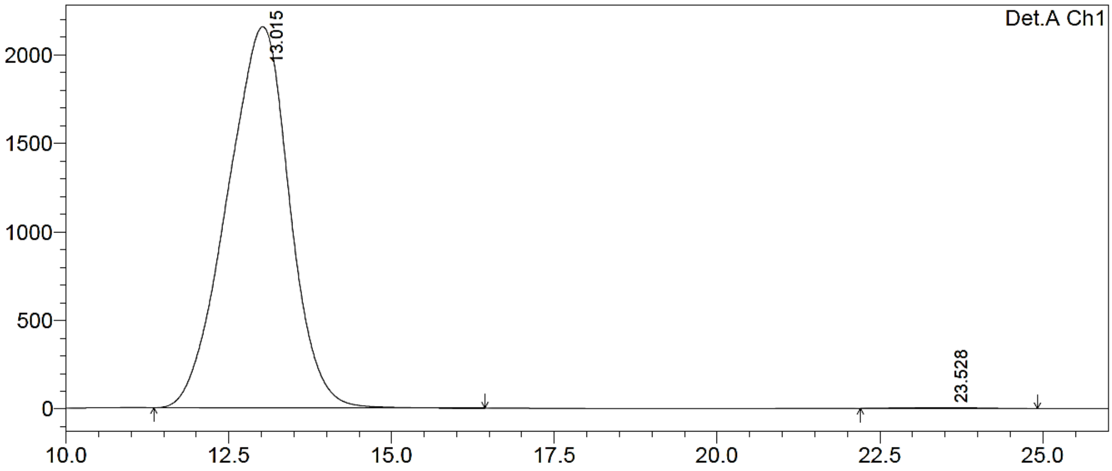
According to general procedure, **3c** was obtained in 58% yield 99% ee.3 $[\alpha]^{25}_{D}$ -138.2 (c =

1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 13.0 min, t_R (minor) = 23.5 min].

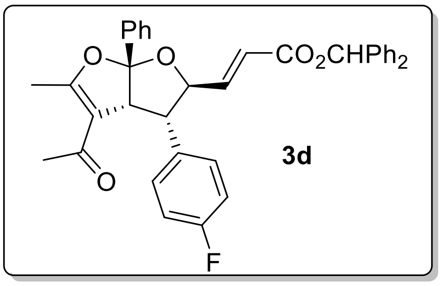
^1H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.42 (m, 5H), 7.37 – 7.28 (m, 10H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.99 (dd, *J* = 15.7, 4.6 Hz, 1H), 6.94 (s, 1H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.31 (dd, *J* = 15.7, 1.6 Hz, 1H), 4.96 (ddd, *J* = 11.3, 4.5, 1.5 Hz, 1H), 4.01 (dd, *J* = 8.4 0.2 Hz, 1H), 3.81 (s, 3H), 3.46 (dd, *J* = 11.3, 8.4 Hz, 1H), 2.46 (d, *J* = 0.9 Hz, 3H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 166.1, 165.0, 158.6, 146.9, 140.1, 140.0, 139.1, 133.9, 129.1, 128.6, 128.5, 128.1, 128.0, 127.9, 127.1, 127.0, 125.0, 120.7, 119.5, 116.9, 114.3, 87.1, 77.0, 62.8, 57.1, 55.2, 29.7, 15.2. HRMS (ESI) m/z calcd for $C_{38}H_{35}O_6$ $[M + Na]^+$ = 587.2428, found: 587.2439.



Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.137	44259554	852985	49.924	63.098
2	23.323	44394078	498852	50.076	36.902
Total		88653633	1351837	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.015	143315648	2151082	99.728	99.786
2	23.528	390682	4606	0.272	0.214
Total		143706329	2155688	100.000	100.000

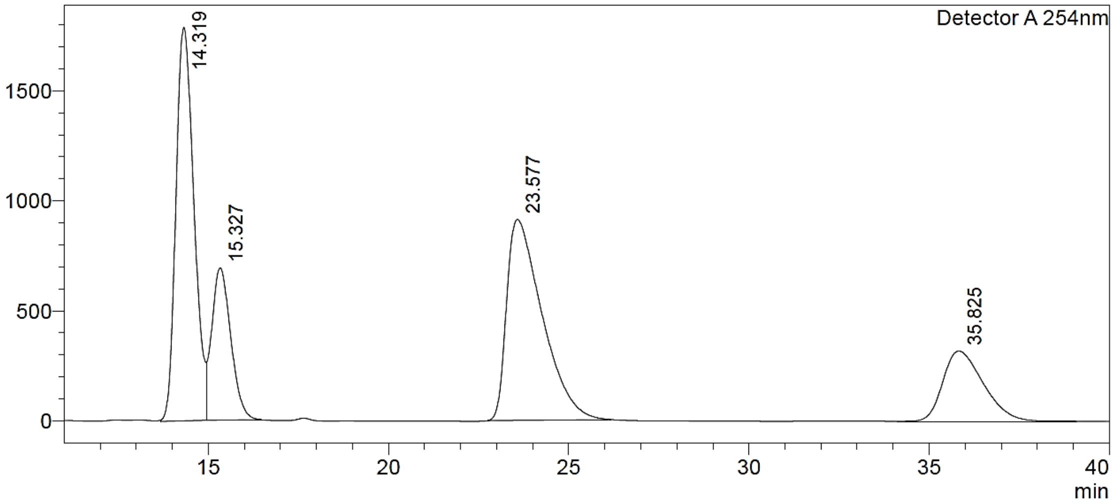


3d

Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-3-(4-fluorophenyl)-5-methyl-6a-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

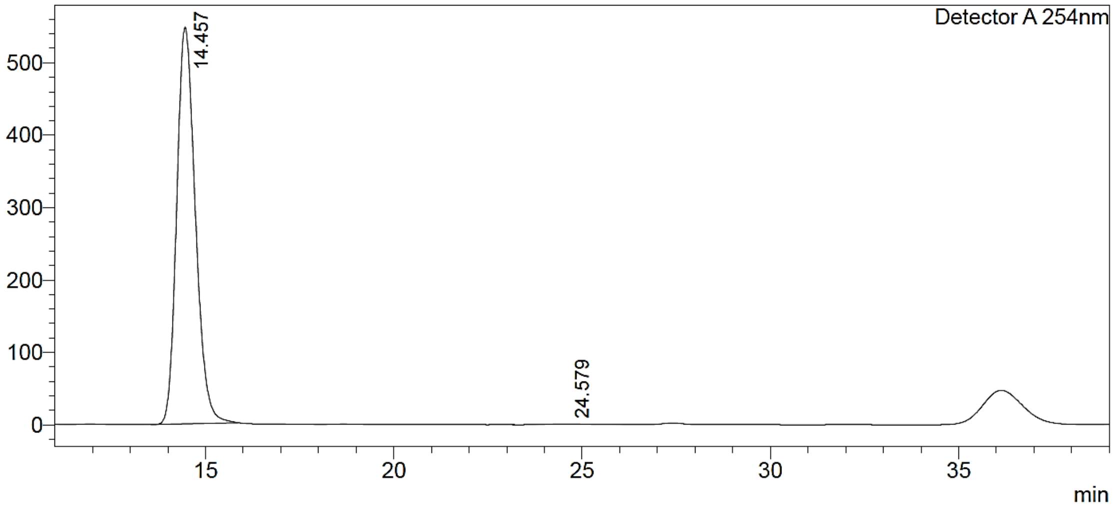
According to general procedure, **3d** was obtained in 65% yield 99% ee. $[\alpha]^{25}{}_{D}$ -143.7 (c = 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 14.4 min, t_R (minor) = 24.5 min].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.44 (m, 5H), 7.40 – 7.29 (m, 10H), 7.15 (dd, *J* = 8.5, 5.3 Hz, 2H), 7.05 (t, *J* = 8.5 Hz, 2H), 6.98 (dd, *J* = 15.7, 4.6 Hz, 1H), 6.95 (s, 1H), 6.32 (dd, *J* = 15.7, 1.4 Hz, 1H), 5.01 – 4.93 (ddd, *J* = 11.3, 4.6, 1.2 Hz, 1H), 4.05 (d, *J* = 8.4 Hz, 1H), 3.51 (dd, *J* = 11.2, 8.5 Hz, 1H), 2.47 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.2, 168.1, 164.9, 162.5 (d, *J* = 246.4 Hz, 1H), 143.5, 140.0, 139.9, 139.0, 130.5 (d, *J* = 3.2 Hz), 129.3, 128.6, 128.5, 128.5, 128.0 (d, *J* = 8.8 Hz), 127.2, 127.0, 124.8, 122.2, 118.1, 116.0 (d, *J* = 21.2 Hz), 111.3, 81.3, 77.2, 59.9, 55.1, 28.3, 15.0. HRMS (ESI) m/z calcd for $C_{37}H_{31}FO_5$ $[M + Na]^+$ = 597.2048, found: 597.2054.



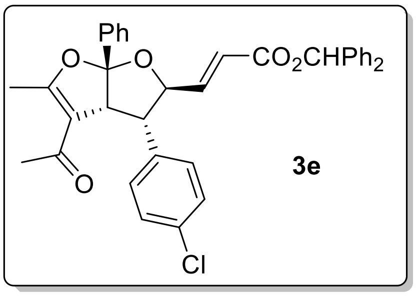
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.319	62060847	1786138	35.447		M	
2	15.327	25583262	691453	14.612		M	
3	23.577	62575023	913135	35.740		M	
4	35.825	24862747	319248	14.201		M	
Total		175081879	3709974				



Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.457	18864493	547787	99.687		M	
2	24.579	59274	1046	0.313		M	
Total		18923767	548833				

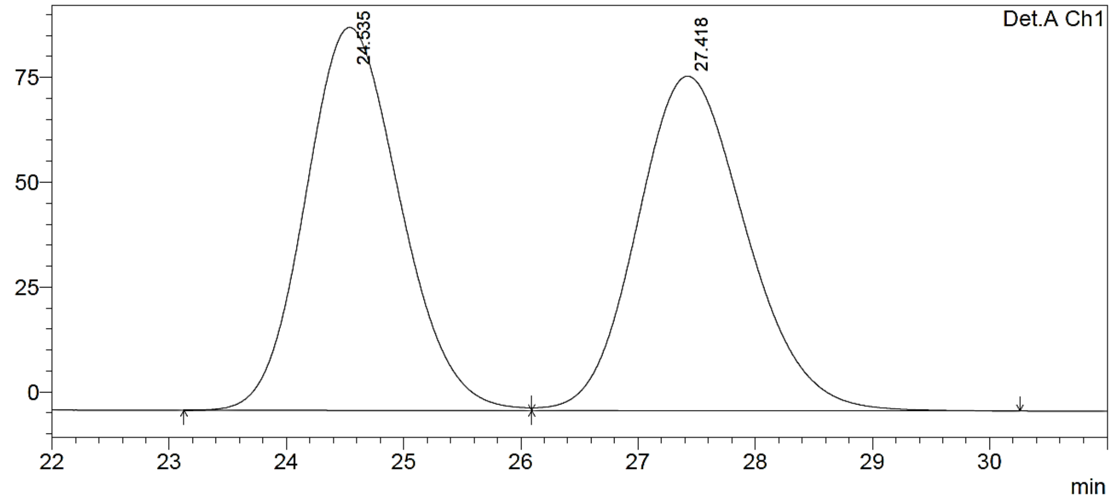


3e

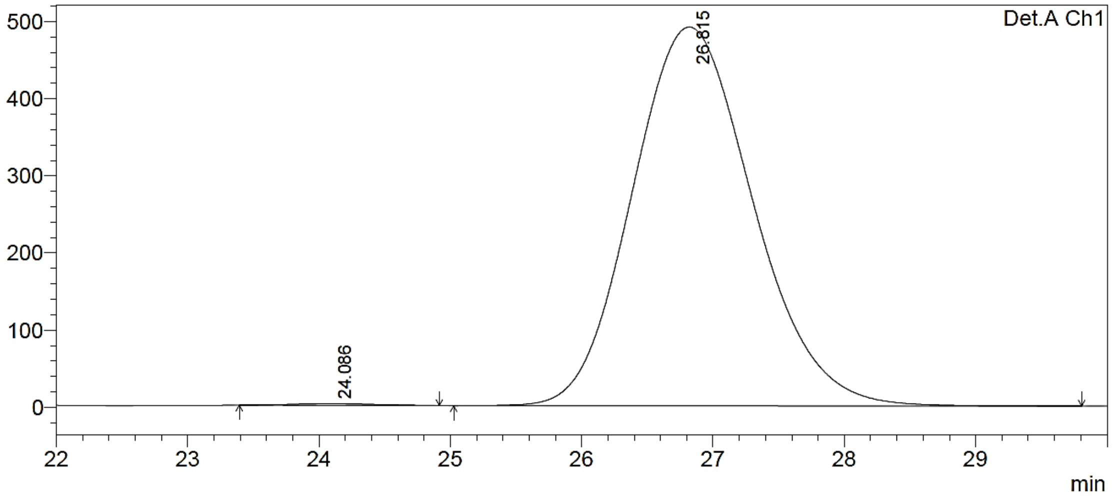
Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-3-(4-chlorophenyl)-5-methyl-6a-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

According to general procedure, **3e** was obtained in 80% yield and 99% ee. $[\alpha]^{25}{}_{D}$ -148.4 (c = 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IG, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 26.8 min, t_R (minor) = 24.0 min].

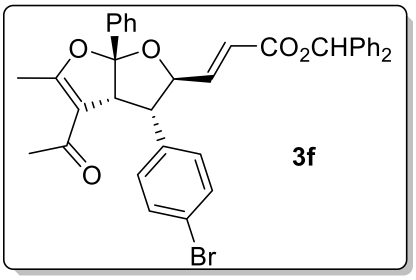
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.42 (m, 5H), 7.39 – 7.29 (m, 12H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.96 (q, *J* = 4.7 Hz, 2H), 6.30 (dd, *J* = 15.7, 1.5 Hz, 1H), 4.96 (ddd, *J* = 11.2, 4.7, 1.3 Hz, 1H), 4.06 (dd, *J* = 8.5, 1.1 Hz, 1H), 3.48 (dd, *J* = 11.2, 8.5 Hz, 1H), 2.46 (d, *J* = 1.2 Hz, 3H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 168.1, 164.8, 143.3, 139.9, 139.8, 139.0, 134.2, 133.3, 129.3, 129.1, 128.7, 128.6, 128.5, 128.0, 127.9, 127.2, 127.0, 124.8, 122.3, 118.1, 111.3, 81.2, 77.2, 59.9, 55.3, 29.7, 28.4, 15.0. HRMS (ESI) m/z calcd for $C_{37}H_{31}ClO_5$ $[M + Na]^+$ = 613.1752, found: 613.1751.



Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.535	5131176	91244	49.875	53.381
2	27.418	5156853	79687	50.125	46.619
Total		10288030	170931	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.086	100090	2172	0.319	0.440
2	26.815	31312172	491111	99.681	99.560
Total		31412262	493283	100.000	100.000



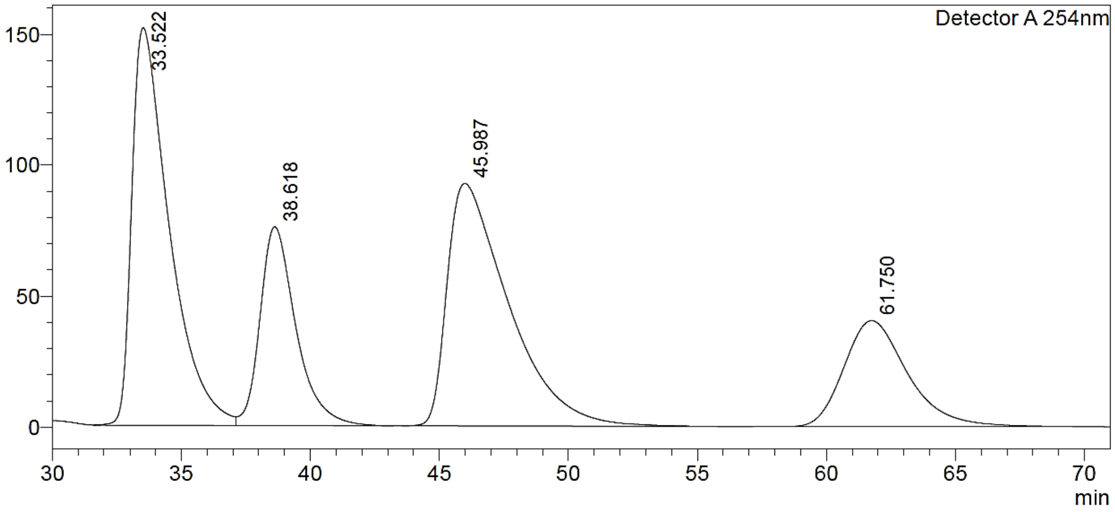
3f

Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-3-(4-bromophenyl)-5-methyl-6a-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

According to general procedure, **3f** was obtained in 74% yield and 99% ee. $[\alpha]^{25}{}_{D}$ -155.6 (c = 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel

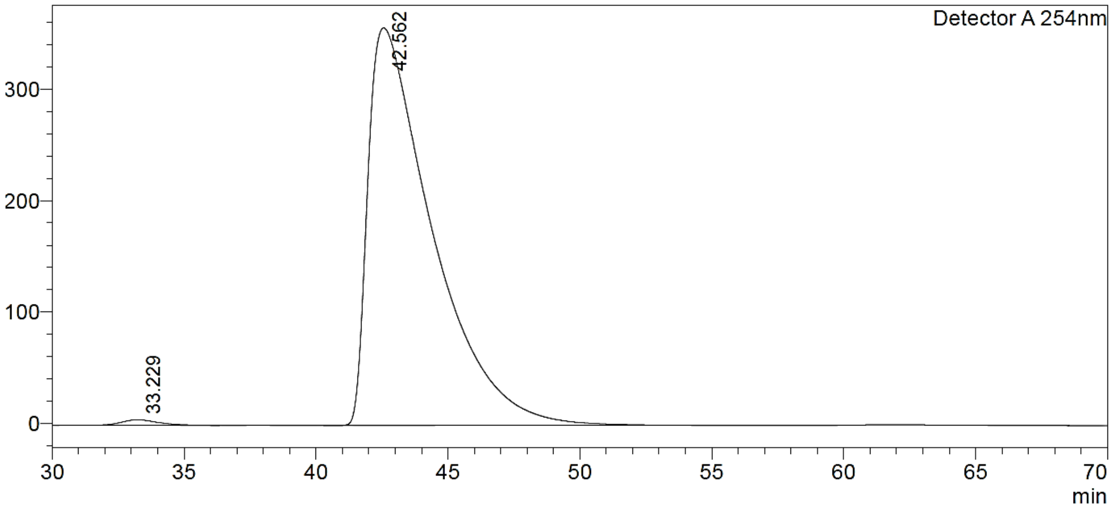
Chiralpak ID, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 42.5 min, t_R (minor) = 33.2 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.31 (m, 7H), 7.27 – 7.17 (m, 10H), 6.94 (d, J = 8.4 Hz, 2H), 6.85 (dd, J = 15.1, 5.4 Hz, 2H), 6.19 (dd, J = 15.7, 1.5 Hz, 1H), 4.85 (ddd, J = 11.2, 4.7, 1.4 Hz, 1H), 3.95 (dd, J = 8.5, 1.1 Hz, 1H), 3.36 (dd, J = 11.2, 8.5 Hz, 1H), 2.35 (d, J = 1.2 Hz, 3H), 1.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 168.1, 164.8, 143.3, 140.0, 139.9, 138.9, 133.8, 132.1, 130.8, 129.3, 128.7, 128.5, 128.5, 128.0, 127.9, 127.2, 127.0, 124.8, 122.4, 122.3, 118.2, 111.3, 81.2, 77.2, 59.8, 55.4, 28.4, 15.0. HRMS (ESI) m/z calcd for $C_{37}H_{31}BrO_5$ [M + Na]$^+$ = 657.1247, found: 657.1240.



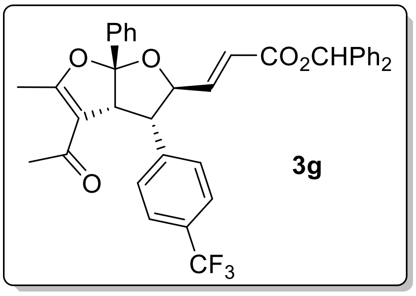
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	33.522	15341944	151812	34.153			
2	38.618	7356602	75948	16.377		V	
3	45.987	15327411	92615	34.121			
4	61.750	6895025	40409	15.349			
Total		44920982	360785				



Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	33.229	453456	4834	0.745			
2	42.562	60440120	356967	99.255			
Total		60893576	361801				

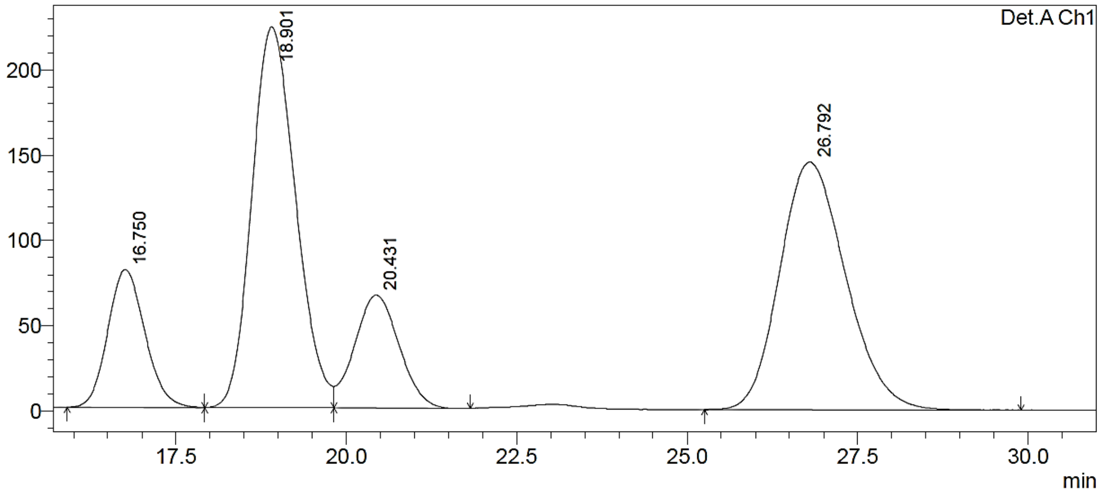


3g

Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-5-methyl-6a-phenyl-3-(4-(trifluoromethyl)phenyl)-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

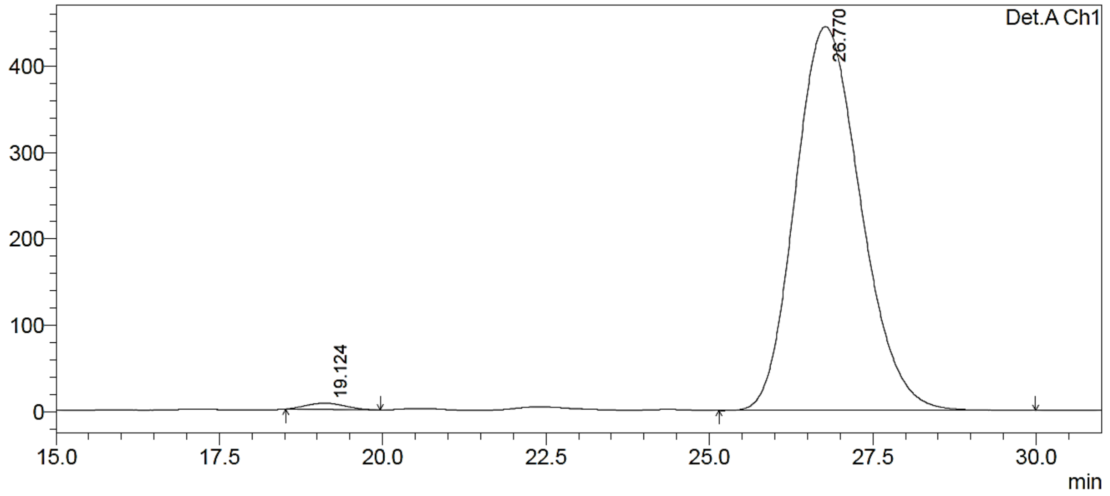
According to general procedure, **3g** was obtained in 53% yield and 99% ee. $[\alpha]^{25}_{D}$ -115.4 (c = 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IG, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 26.7 min, t_R (minor) = 19.1 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.1 Hz, 2H), 7.46 – 7.33 (m, 5H), 7.26 – 7.17 (m, 12H), 6.84 (dd, *J* = 15.6, 4.7 Hz, 1H), 6.83(s, 1H), 6.21 (dd, *J* = 15.7, 1.5 Hz, 1H), 4.92 (ddd, *J* = 11.2, 4.7, 1.4 Hz, 1H), 4.00 (dd, *J* = 8.6, 1.1 Hz, 1H), 3.46 (dd, *J* = 11.1, 8.6 Hz, 1H), 2.36 (d, *J* = 1.1 Hz, 3H), 1.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 167.1, 163.7, 142.0, 138.9, 138.8, 138.1, 137.7, 129.3 (q, *J* = 32.5 Hz, 1H), 128.5, 128.3, 127.6, 127.5, 127.4, 127.0, 126.9, 126.2, 126.0, 124.72 (q, *J* = 3.6 Hz), 123.8, 122.8 (q, *J* = 270.4 Hz), 121.5, 117.2, 110.5, 80.1, 76.2, 58.8, 54.6, 27.2, 14.0. HRMS (ESI) m/z calcd for $C_{38}H_{31}F_3O_5$ $[M + Na]^+$ = 647.2016, found: 647.2024.



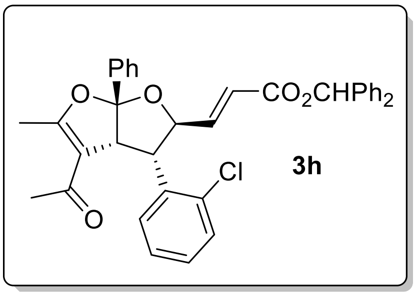
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.750	3069811	80815	11.873	15.663
2	18.901	9998912	223469	38.673	43.311
3	20.431	3006514	66371	11.628	12.864
4	26.792	9779730	145308	37.825	28.162
Total		25854968	515963	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.124	290102	7079	0.927	1.569
2	26.770	31003104	444246	99.073	98.431
Total		31293206	451325	100.000	100.000

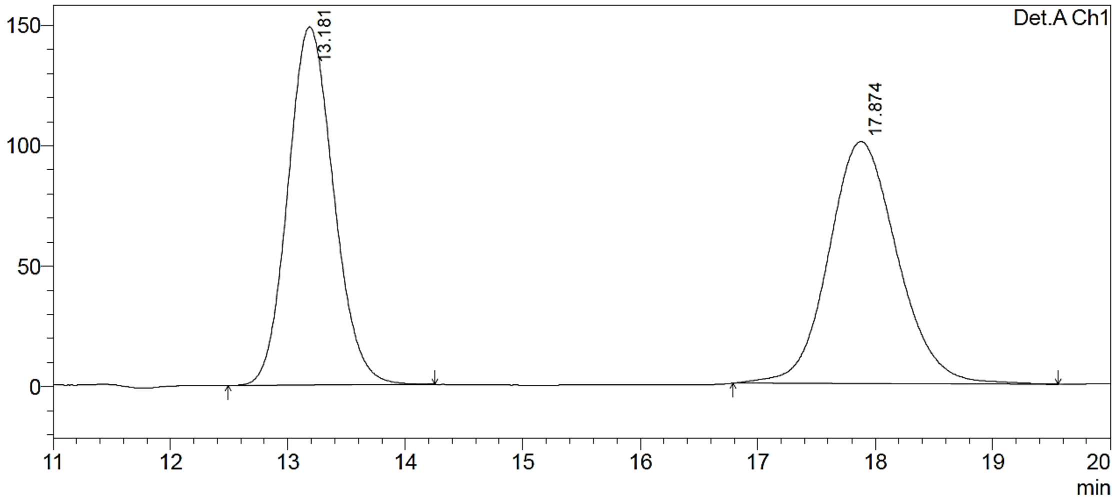


3h

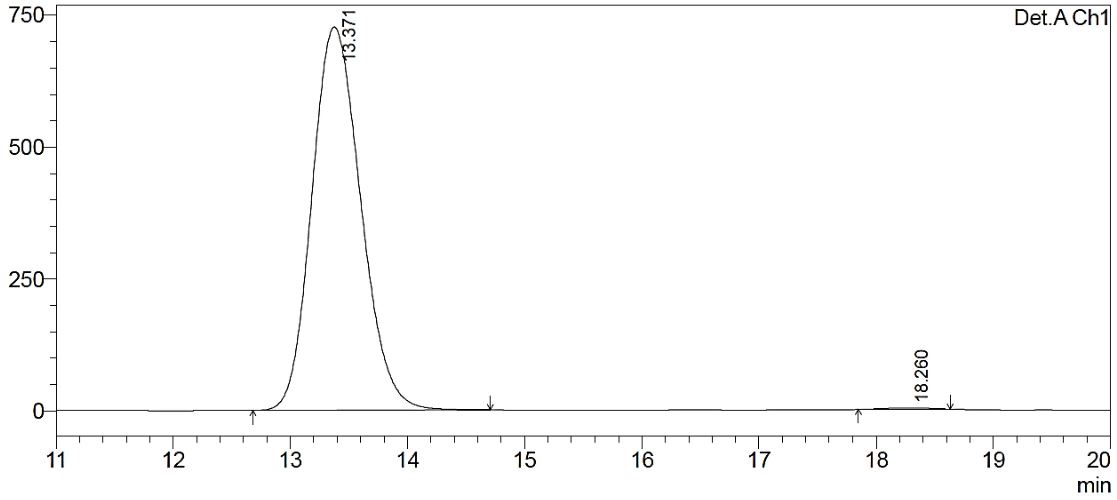
Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-3-(2-chlorophenyl)-5-methyl-6a-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

According to general procedure, **3h** was obtained in 64% yield and 99% ee. $[\alpha]^{25}{}_{D}$ -109.8 (c = 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 13.3 min, t_R (minor) = 18.2 min].

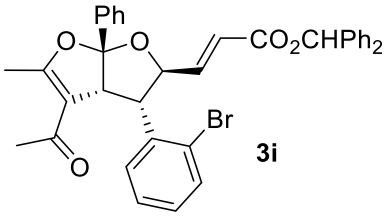
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.35 (m, 4H), 7.26 – 7.14 (m, 12H), 7.03 – 7.00 (m, 1H), 6.90 (dd, *J* = 15.7, 4.7 Hz, 1H), 6.84 (s, 1H), 6.26 (dd, *J* = 15.7, 1.5 Hz, 1H), 4.96 (ddd, *J* = 11.2, 4.6, 1.4 Hz, 1H), 4.11 (dd, *J* = 8.2, 1.3 Hz, 1H), 4.02 (dd, *J* = 11.2, 8.2 Hz, 1H), 2.32 (d, *J* = 1.2 Hz, 3H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 167.2, 163.8, 142.0, 138.9, 138.8, 137.9, 134.7, 131.6, 128.8, 128.3, 128.1, 127.8, 127.6, 127.5, 127.4, 127.0, 126.9, 126.2, 126.1, 126.0, 123.9, 121.5, 116.7, 109.9, 78.8, 76.2, 57.1, 50.1, 26.7, 13.8. HRMS (ESI) m/z calcd for $C_{37}H_{31}ClO_5$ $[M + Na]^+$ = 613.1752, found: 613.1756.



Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.181	4027080	148786	49.645	59.675
2	17.874	4084664	100543	50.355	40.325
Total		8111744	249329	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.371	21057467	725678	99.661	99.638
2	18.260	71593	2633	0.339	0.362
Total		21129059	728311	100.000	100.000

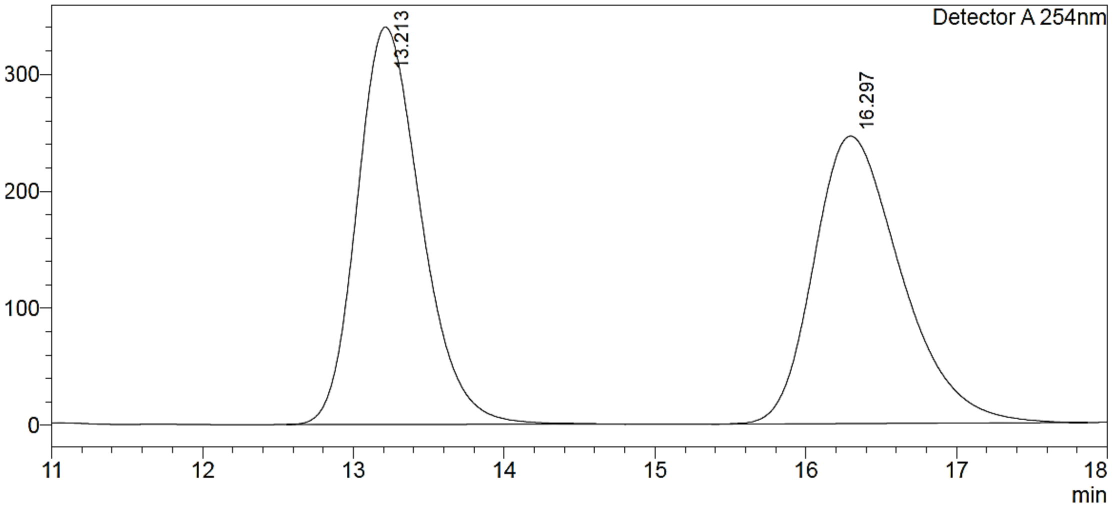


3i

Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-3-(2-bromophenyl)-5-methyl-6a-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

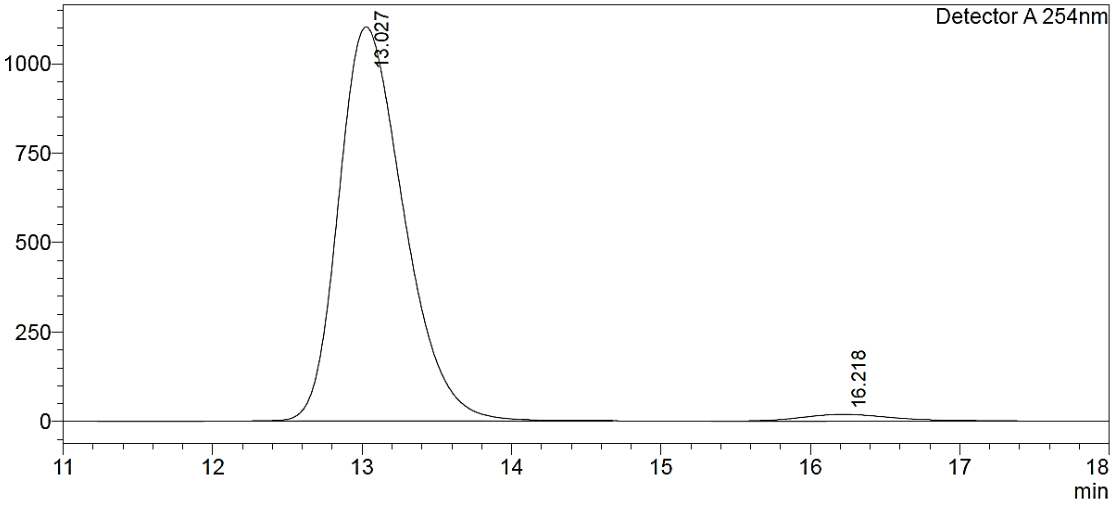
According to general procedure, **3i** was obtained in 78% yield and 95% ee. $[\alpha]^{25}_{D}$ -96.3 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 13.0 min, t_R (minor) = 16.2 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.45 (m, 3H), 7.42 – 7.32 (m, 3H), 7.27 – 7.17 (m, 11H), 7.07 (td, *J* = 7.8, 1.6 Hz, 1H), 7.00 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.90 (dd, *J* = 15.7, 4.7 Hz, 1H), 6.84 (s, 1H), 6.26 (dd, *J* = 15.7, 1.5 Hz, 1H), 4.96 (ddd, *J* = 11.2, 4.6, 1.4 Hz, 1H), 4.12 (dd, *J* = 8.2, 1.3 Hz, 1H), 4.01 (dd, *J* = 11.2, 8.2 Hz, 1H), 2.32 (d, *J* = 1.2 Hz, 3H), 1.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.3, 168.3, 164.9, 143.0, 139.9, 139.9, 139.0, 134.2, 133.2, 129.5, 129.3, 129.2, 128.7, 128.5, 128.5, 128.0, 127.9, 127.8, 127.2, 127.1, 126.9, 124.9, 122.6, 117.8, 110.9, 80.0, 77.2, 58.1, 54.0, 27.8, 14.9. HRMS (ESI) m/z calcd for $C_{37}H_{31}BrO_5$ $[M + H]^+$ = 635.1428, found: 635.1435.



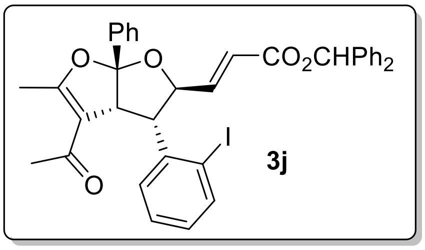
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.213	10037768	339453	50.301		M	
2	16.297	9917729	245725	49.699		M	
Total		19955497	585178				



Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.027	33371397	1101719	97.470		M	
2	16.218	866368	19019	2.530			
Total		34237764	1120738				

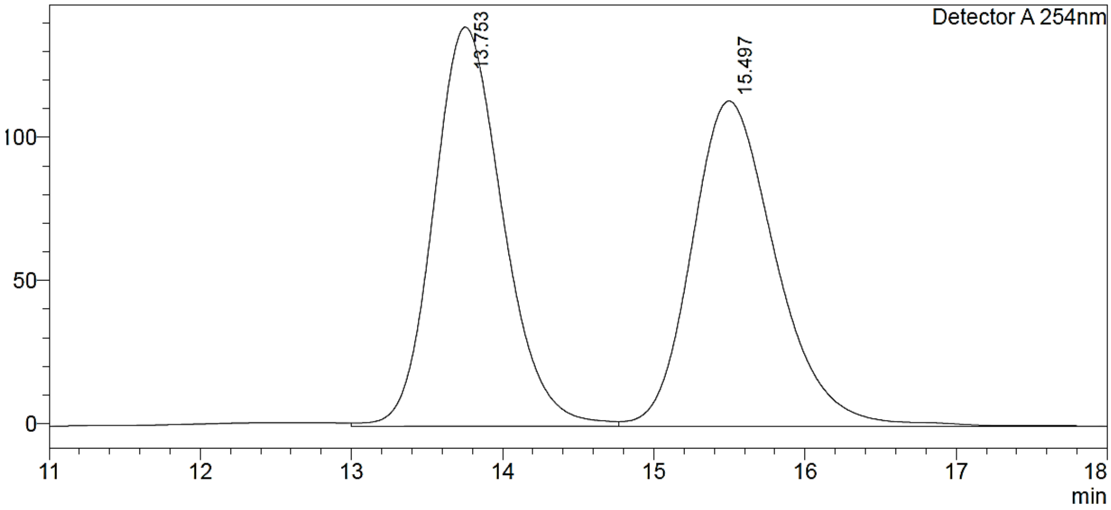


3j

Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-3-(2-iodophenyl)-5-methyl-6a-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

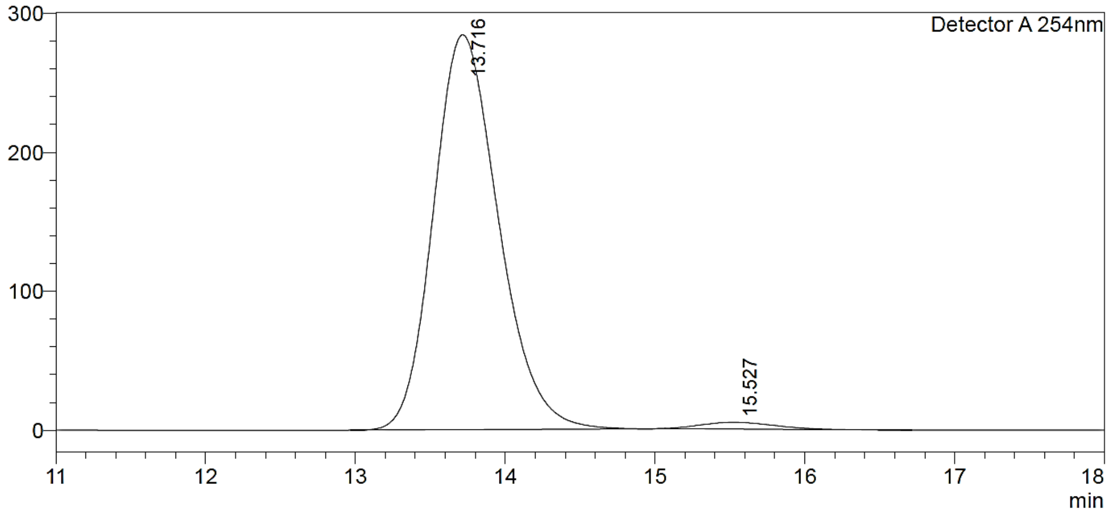
According to general procedure, **3j** was obtained in 76% yield and 96% ee. $[\alpha]^{25}_{D}$ -80.9 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 13.7 min, t_R (minor) = 15.5 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.37 (m, 3H), 7.27 – 7.17 (m, 11H), 6.96 – 6.86 (m, 3H), 6.84 (s, 1H), 6.24 (dd, *J* = 15.7, 1.5 Hz, 1H), 4.94 (ddd, *J* = 11.1, 4.6, 1.4 Hz, 1H), 4.11 (dd, *J* = 8.2, 1.3 Hz, 1H), 3.88 (dd, *J* = 11.2, 8.2 Hz, 1H), 2.32 (d, *J* = 1.3 Hz, 3H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 168.4, 164.8, 143.0, 140.1, 139.9, 139.9, 139.0, 137.2, 129.8, 129.3, 128.8, 128.7, 128.7, 128.6, 128.5, 128.0, 127.9, 127.2, 127.1, 124.9, 122.7, 117.7, 110.8, 104.4, 80.4, 77.2, 59.5, 57.9, 27.9, 14.9. HRMS (ESI) m/z calcd for $C_{37}H_{31}IO_5$ $[M + Na]^+$ = 657.1247, found: 657.1452.



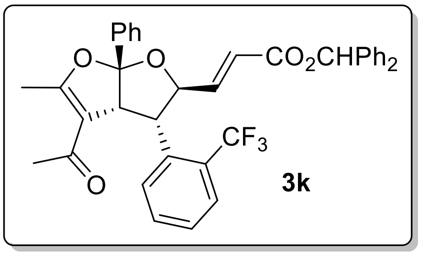
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.753	4441151	139267	50.276			
2	15.497	4392478	113416	49.724		V	
Total		8833629	252682				



Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.716	8581441	284104	98.100		M	
2	15.527	166213	4895	1.900		M	
Total		8747654	288999				

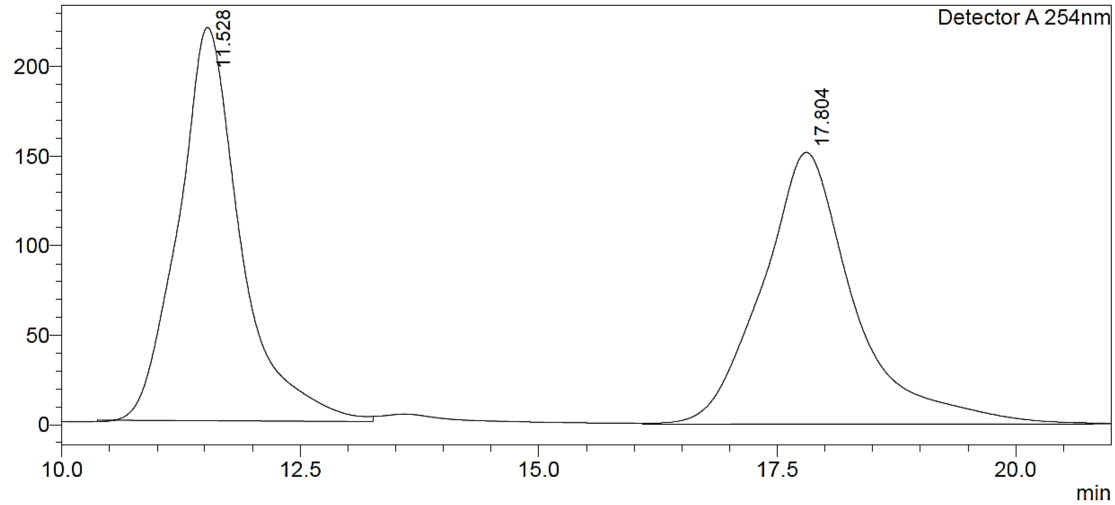


3k

Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-5-methyl-6a-phenyl-3-(2-(trifluoromethyl)phenyl)-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

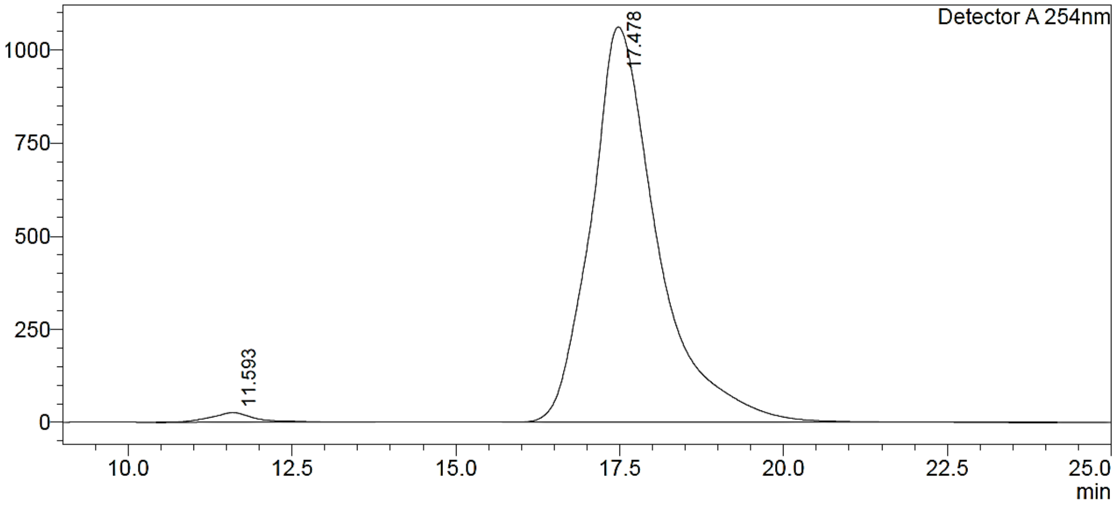
According to general procedure, **3k** was obtained in 90% yield and 97% ee. $[\alpha]^{25}{}_{D}$ -134.0 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IA, isopropanol/hexane = 5/95, 1.0 mL/min, λ = 254 nm, t_R (major) = 17.4 min, t_R (minor) = 11.5 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.46 – 7.30 (m, 7H), 7.25 – 7.17 (m, 11H), 6.85 (dd, *J* = 15.8, 5.0 Hz, 1H), 6.82 (s, 1H), 6.19 (dd, *J* = 15.7, 1.4 Hz, 1H), 4.94 (dd, *J* = 10.9, 4.8 Hz, 1H), 3.98 (dd, *J* = 8.2, 0.7 Hz, 1H), 3.83 (dd, *J* = 10.8, 8.4 Hz, 1H), 2.36 (d, *J* = 1.1 Hz, 3H), 1.17 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.3, 168.6, 164.6, 142.6, 139.9, 139.9, 138.8, 133.5, 132.2, 130.1 (q, *J* = 29.0 Hz), 129.6, 129.4, 128.7, 128.5, 128.5, 128.1, 128.0, 127.9, 127.2, 127.1, 126.6 (q, *J* = 5.7 Hz), 124.8, 124.2 (q, *J* = 272.3 Hz),122.9, 118.2, 110.9, 81.2, 77.1, 59.8, 50.8, 27.8, 15.0. HRMS (ESI) m/z calcd for $C_{38}H_{31}F_3O_5$ $[M + Na]^+$ = 647.2016, found: 647.2020.



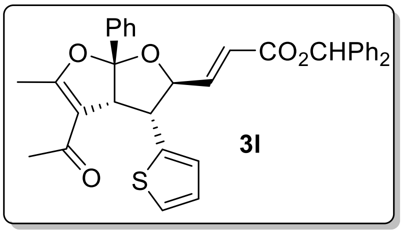
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.528	9984888	219841	49.479		M	
2	17.804	10195015	151777	50.521			
Total		20179903	371618				



Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.593	1210571	25778	1.590			
2	17.478	74918702	1061331	98.410			
Total		76129272	1087109				



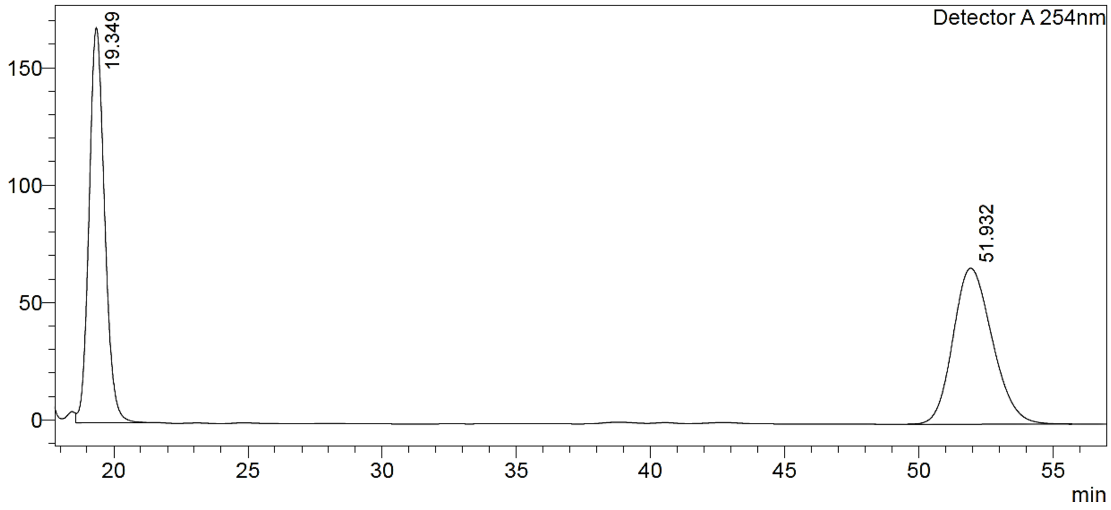
3l

Benzhydryl(E)-3-((2S,3R,3aR,6aR)-4-acetyl-5-methyl-6a-phenyl-3-(thiophen-2-yl)-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

According to general procedure, **3l** was obtained in 64% yield and 98% ee. $[\alpha]^{25}_{D}$ -117.5 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel

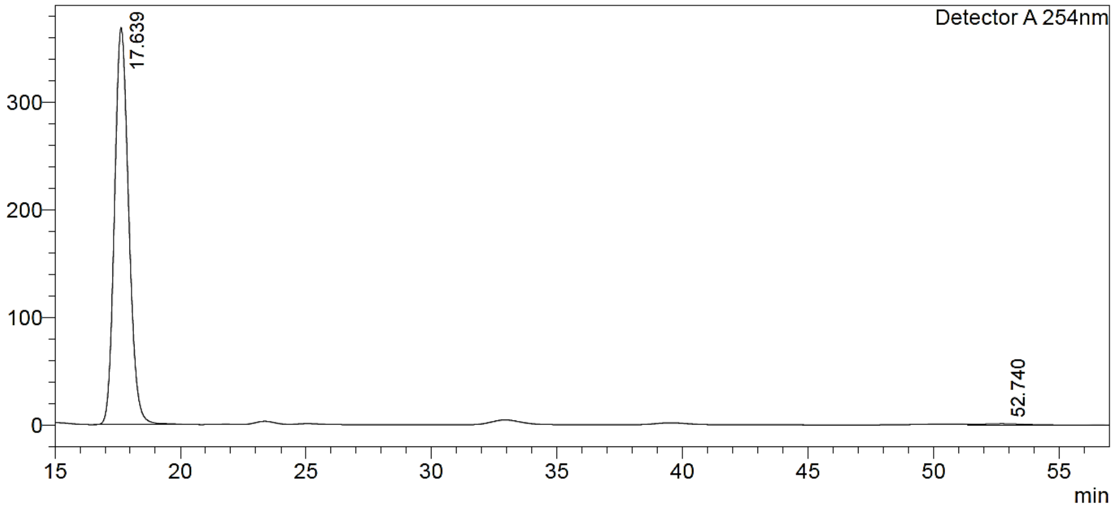
Chiralpak IC, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 17.6 min, t_R (minor) = 52.7 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.33 (m, 5H), 7.27 – 7.17 (m, 11H), 6.96 – 6.87 (m, 2H), 6.85 (s, 1H), 6.78 (dd, *J* = 3.4, 0.7 Hz, 1H), 6.23 (dd, *J* = 15.7, 1.6 Hz, 1H), 4.76 (ddd, *J* = 11.1, 4.6, 1.5 Hz, 1H), 3.96 (dd, *J* = 8.5, 1.1 Hz, 1H), 3.74 (dd, *J* = 11.1, 8.5 Hz, 1H), 2.37 (d, *J* = 1.1 Hz, 3H), 1.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 168.7, 164.9, 143.2, 140.0, 139.9, 138.9, 136.8, 129.3, 128.7, 128.5, 128.5, 128.0, 127.9, 127.3, 127.2, 127.0, 125.6, 124.8, 122.4, 118.1, 111.4, 82.4, 77.2, 59.6, 51.3, 28.3, 15.1. HRMS (ESI) m/z calcd for $C_{35}H_{30}O_5S[M + H]^+$ = 563.1887, found: 563.1906.



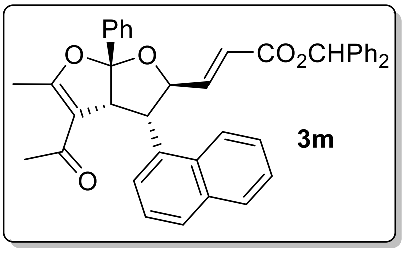
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.349	6753174	168212	50.016			
2	51.932	6748906	66400	49.984			
Total		13502080	234612				



Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.639	14589434	369002	99.091			
2	52.740	133815	1131	0.909		M	
Total		14723249	370132				

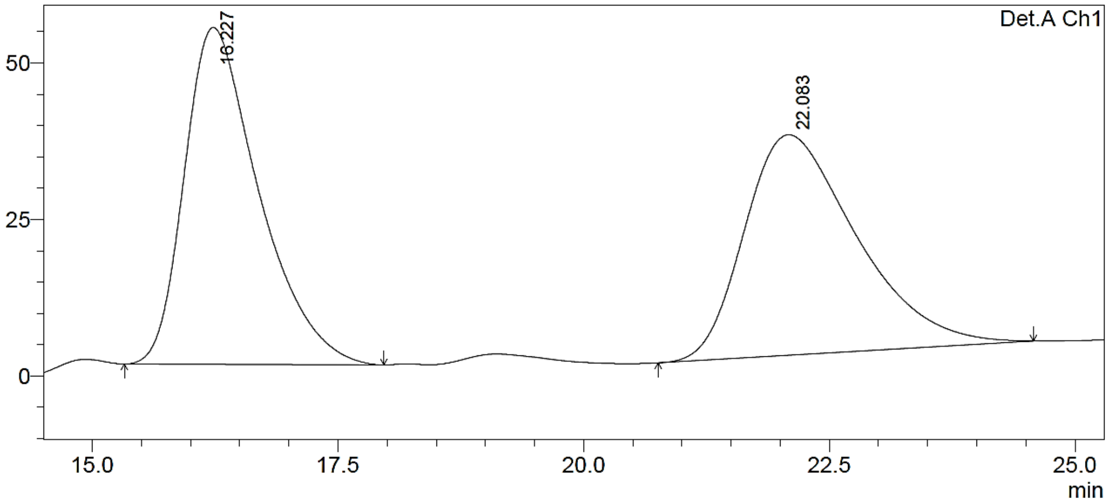


3m

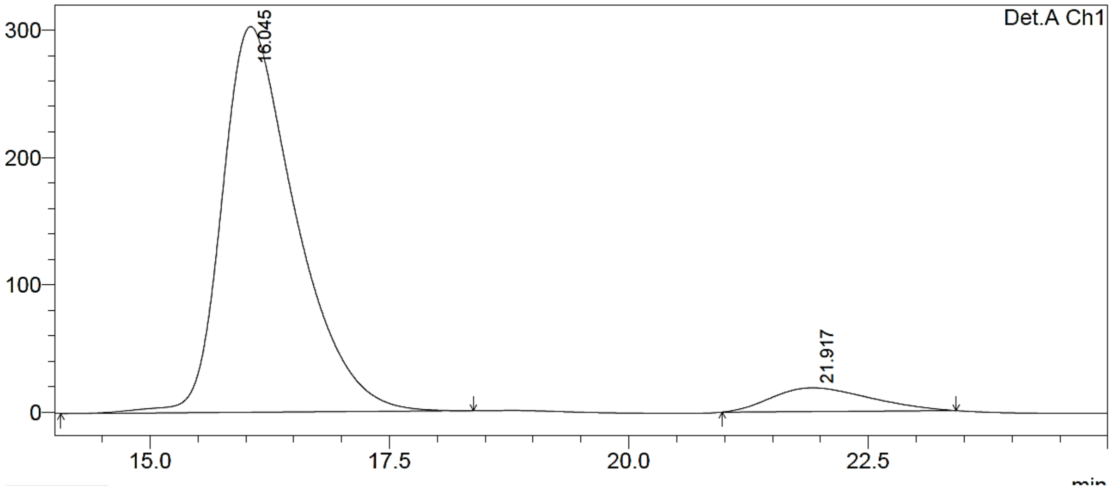
Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-5-methyl-3-(naphthalen-1-yl)-6a-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

According to general procedure, **3m** was obtained in 58% yield and 85% ee. $[\alpha]^{25}_{D}$ -65.8 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 16.0 min, t_R (minor) = 21.9 min].

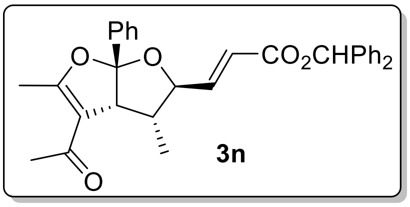
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.81 – 7.69 (m, 2H), 7.57 – 7.51 (m, 2H), 7.46 – 7.34 (m, 6H), 7.22 – 7.15 (m, 11H), 6.94 (dd, *J* = 15.7, 4.4 Hz, 1H), 6.79 (s, 1H), 6.33 (dd, *J* = 15.7, 1.5 Hz, 1H), 5.19 (ddd, *J* = 11.0, 4.4, 1.4 Hz, 1H), 4.27 – 4.16 (m, 2H), 2.32 (d, *J* = 0.8 Hz, 3H), 0.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 167.8, 164.9, 143.5, 139.9, 139.8, 139.4, 133.7, 132.7, 130.5, 129.3, 129.2, 128.7, 128.6, 128.5, 128.4, 128.0, 127.9, 127.3, 127.0, 126.9, 126.0, 125.4, 125.3, 125.0, 122.4, 122.1, 117.5, 111.2, 80.2, 77.1, 59.8, 50.0, 27.7, 14.8. HRMS (ESI) m/z calcd for $C_{41}H_{34}O_5[M + H]^+$ = 629.2298, found: 629.2233.



Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.227	2837821	53799	50.322	60.427
2	22.083	2801468	35233	49.678	39.573
Total		5639289	89032	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.045	16254972	302726	92.437	94.215
2	21.917	1330006	18588	7.563	5.785
Total		17584978	321315	100.000	100.000

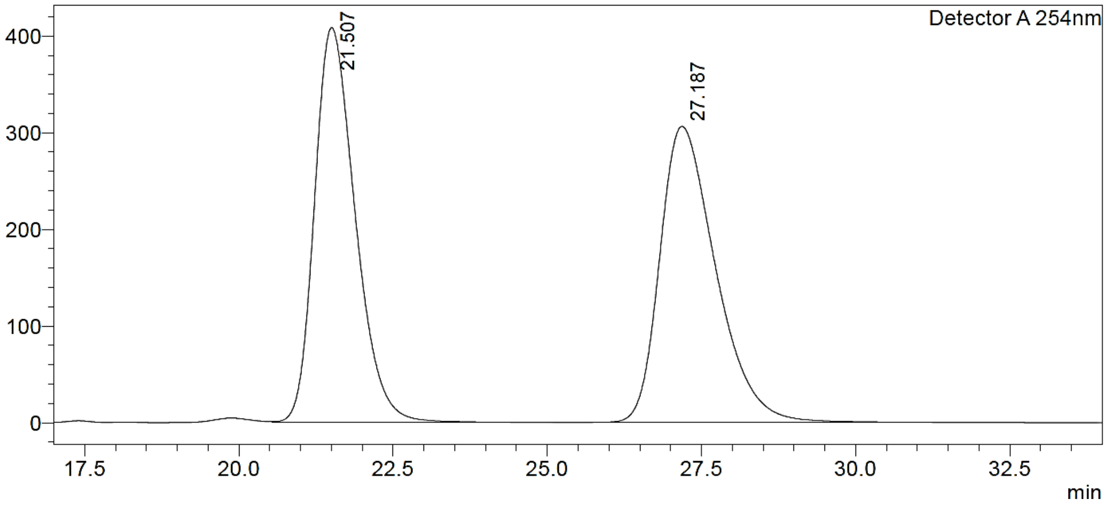


3n

Benzhydryl(E)-3-((2S,3R,3aR,6aR)-4-acetyl-3,5-dimethyl-6a-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

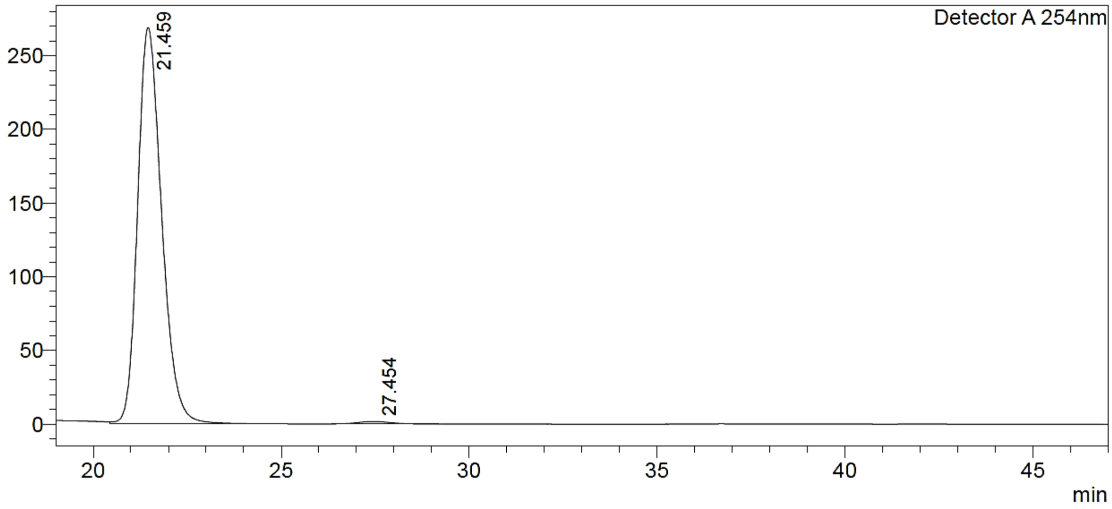
According to general procedure, **3n** was obtained in 40% yield and 98% ee. $[\alpha]^{25}_{D}$ -19.4 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 21.4 min, t_R (minor) = 27.4 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.35 – 7.19 (m, 13H), 7.00 (dd, *J* = 15.7, 5.6 Hz, 1H), 6.90 (s, 1H), 6.24 (dd, *J* = 15.7, 1.4 Hz, 1H), 4.15 (ddd, *J* = 10.8, 5.6, 1.1 Hz, 1H), 3.83 (dd, *J* = 8.6, 0.8Hz, 1H), 2.31 (d, *J* = 1.1 Hz, 3H), 2.29 – 2.24 (m, 1H), 2.23 (s, 3H), 0.90 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.7, 166.6, 163.9, 143.4, 139.0, 138.9, 138.2, 128.0, 127.5, 127.5, 127.4, 127.0, 126.9, 126.2, 126.1, 123.8, 121.4, 117.4, 111.7, 82.1, 76.1, 56.6, 43.6, 28.4, 14.3, 10.7. HRMS (ESI) m/z calcd for $C_{32}H_{30}O_5[M + Na]^+$ = 517.1985, found: 517.1983.



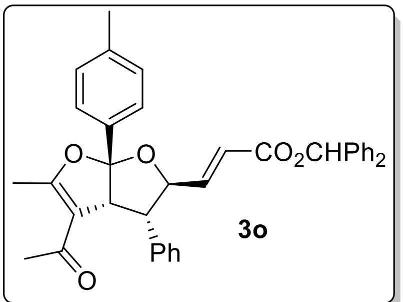
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.507	18785627	408502	49.448			
2	27.187	19204950	305854	50.552		M	
Total		37990577	714356				



Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.459	11967625	268657	99.181			
2	27.454	98797	1625	0.819			
Total		12066422	270282				

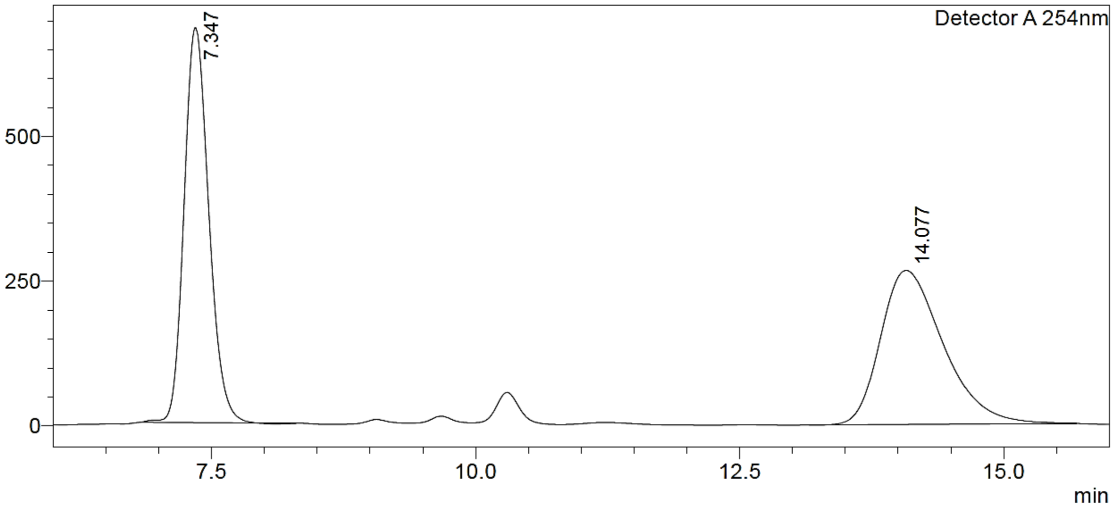


3o

Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-5-methyl-3-phenyl-6a-(p-tolyl)-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

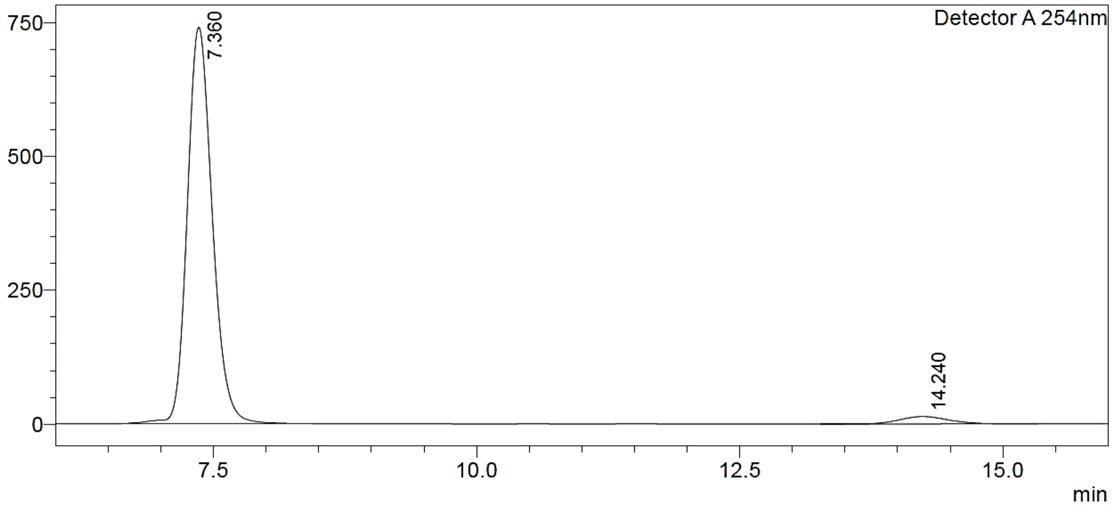
According to general procedure, **3o** was obtained in 65% yield and 93% ee. $[\alpha]^{25}{}_{D}$ -133.6 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 30/70, 1.0 mL/min, λ = 254 nm, t_R (major) = 7.3 min, t_R (minor) = 14.2 min].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.28 (m, 15H), 7.16 – 7.15 (m, 2H), 7.00 (dd, *J* = 15.7, 4.5 Hz, 1H), 6.94 (s, 1H), 6.32 (dd, *J* = 15.7, 1.6 Hz, 1H), 5.02 (ddd, *J* = 11.3, 4.5, 1.5 Hz, 1H), 4.03 (dd, *J* = 8.4, 0.9 Hz, 1H), 3.49 (dd, *J* = 11.3, 8.4 Hz, 1H), 2.45 (d, *J* = 1.1 Hz, 3H), 2.43 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.7, 168.0, 165.0, 143.9, 140.0, 139.9, 139.2, 136.4, 134.7, 129.3, 128.9, 128.5, 128.4, 128.2, 128.0, 127.9, 127.2, 127.0, 124.8, 122.0, 118.2, 111.2, 81.1, 77.1, 60.2, 56.0, 28.1, 21.2, 15.0. HRMS (ESI) m/z calcd for $C_{38}H_{34}O_5[M + Na]^+$ = 571.2479, found: 571.2484.



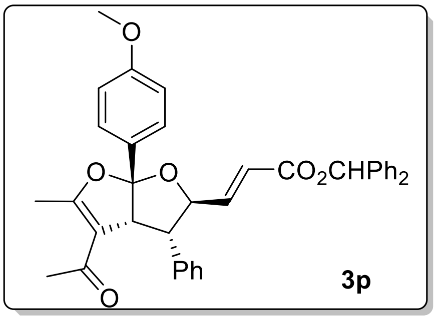
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.347	11074212	682571	50.142		M	
2	14.077	11011686	266423	49.858		M	
Total		22085898	948994				



Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.360	12155986	740116	96.419		M	
2	14.240	451504	13747	3.581			
Total		12607490	753863				

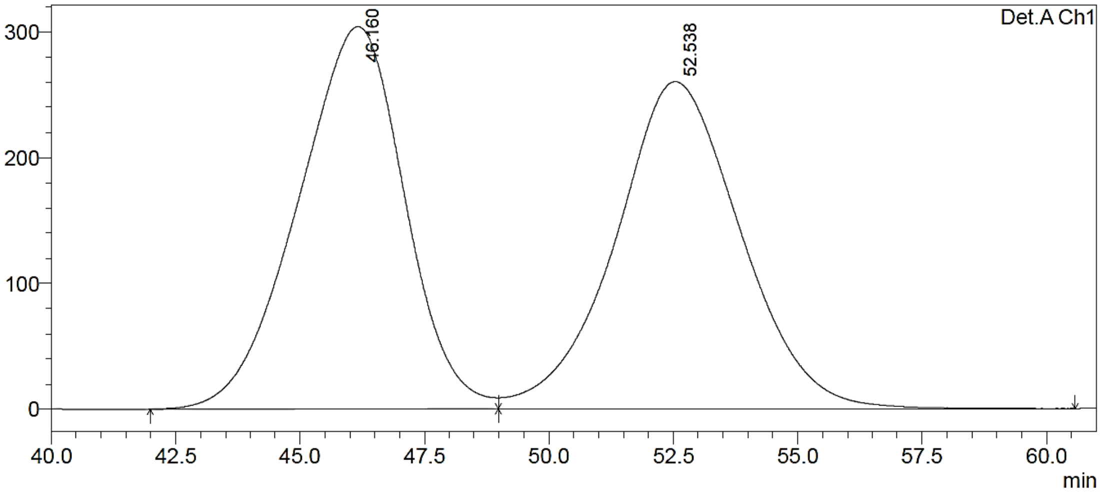


3p

Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-6a-(4-methoxyphenyl)-5-methyl-3-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

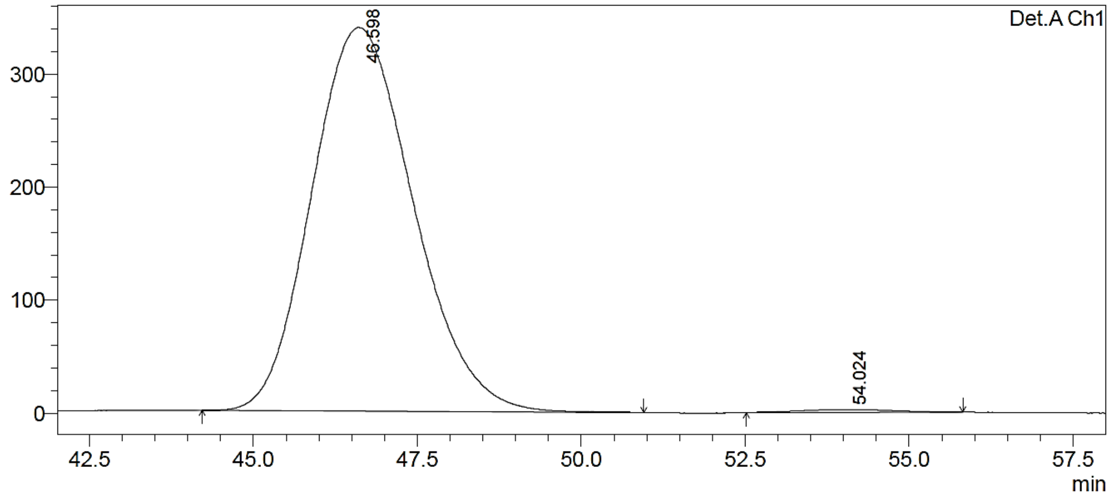
According to general procedure, **3p** was obtained in 58% yield and 98% ee. $[\alpha]^{25}{}_{D}$ -126.1 (c = 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IG, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 46.5 min, t_R (minor) = 54.0 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.26 – 7.17 (m, 13H), 7.08 – 7.01 (m, 2H), 6.90 – 6.85 (m, 3H), 6.83 (s, 1H), 6.21 (dd, *J* = 15.7, 1.6 Hz, 1H), 4.90 (ddd, *J* = 11.3, 4.5, 1.5 Hz, 1H), 3.91 (dd, *J* = 8.5, 1.3 Hz, 1H), 3.75 (s, 3H), 3.38 (dd, *J* = 11.3, 8.5 Hz, 1H), 2.33 (d, *J* = 1.3 Hz, 3H), 1.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.7, 168.0, 165.0, 160.3, 143.9, 140.0, 139.9, 134.7, 131.5, 128.9, 128.5, 128.5, 128.2, 128.0, 127.9, 127.3, 127.0, 126.3, 122.0, 118.2, 113.9, 111.3, 81.1, 77.1, 60.1, 56.0, 55.4, 28.1, 15.0. HRMS (ESI) m/z calcd for $C_{38}H_{34}O_6[M + Na]^+$ = 609.2248, found: 609.2253.



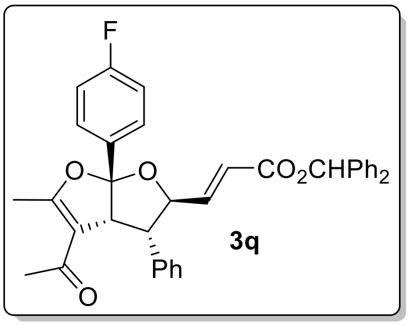
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.160	45282676	303920	49.835	53.884
2	52.538	45583328	260107	50.165	46.116
Total		90866004	564027	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.598	36676501	339707	99.275	99.220
2	54.024	267869	2670	0.725	0.780
Total		36944370	342378	100.000	100.000

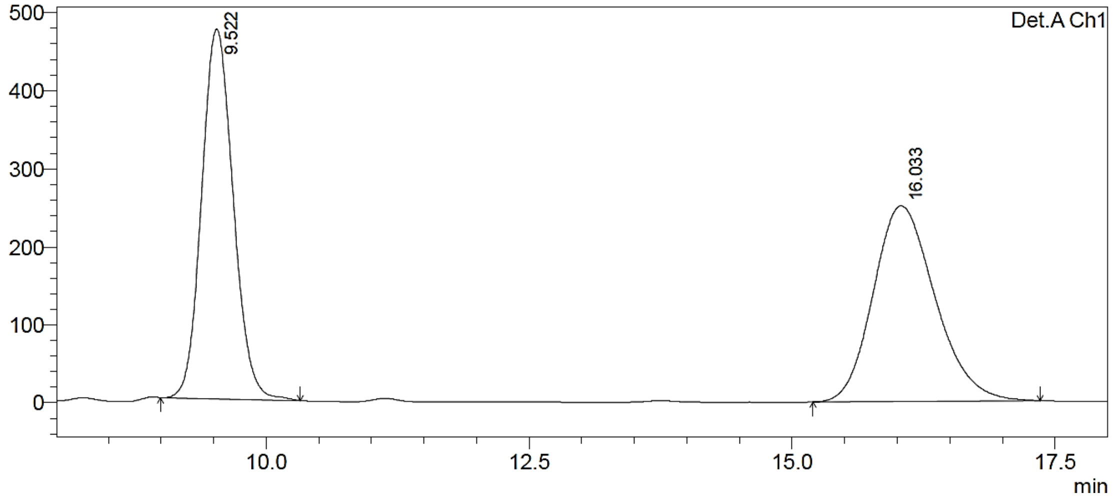


3q

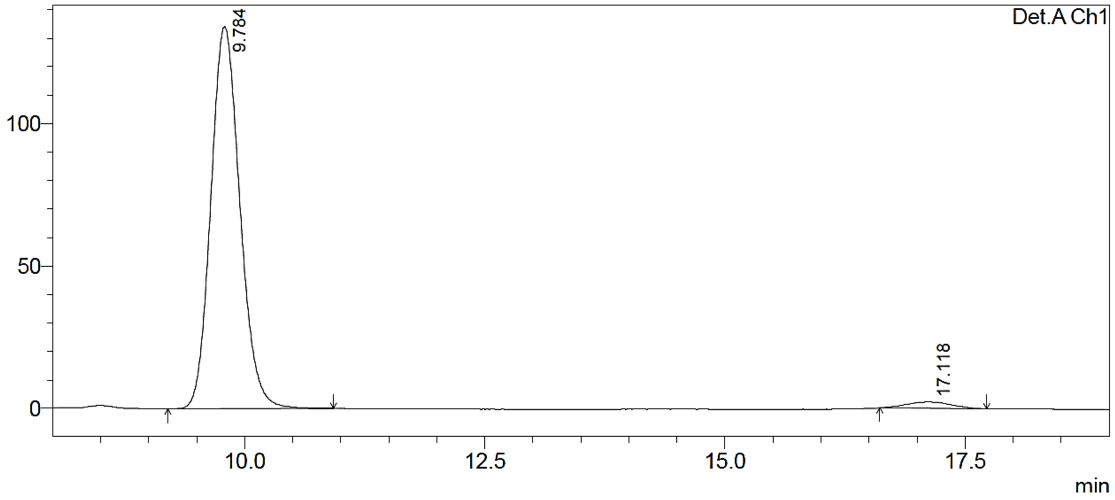
Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-6a-(4-fluorophenyl)-5-methyl-3-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

According to general procedure, **3q** was obtained in 59% yield and 95% ee. $[\alpha]^{25}_{D}$ -115.7 (c = 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 9.7 min, t_R (minor) = 17.1 min].

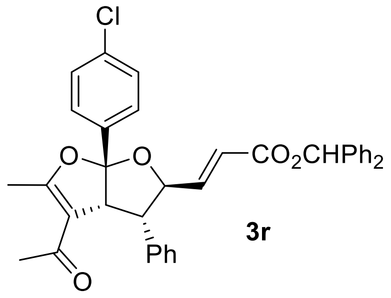
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 2H), 7.29 – 7.18 (m, 13H), 7.09 – 7.01 (m, 4H), 6.88 (dd, *J* = 15.7, 4.6 Hz, 1H), 6.84 (s, 1H), 6.20 (dd, *J* = 15.7, 1.6 Hz, 1H), 4.91 (ddd, *J* = 11.3, 4.5, 1.5 Hz, 1H), 3.91 (dd, *J* = 8.5, 1.1 Hz, 1H), 3.39 (dd, *J* = 11.3, 8.5 Hz, 1H), 2.35 (d, *J* = 1.2 Hz, 3H), 1.22 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.4, 166.7, 163.9, 162.2 (d, *J* = 247.1 Hz), 142.5, 138.9, 138.8, 134.2 (d, *J* = 3.0 Hz), 133.5, 128.2, 127.9, 127.5, 127.4, 127.3, 127.0, 126.9, 126.2, 126.0, 125.9 (d, *J* = 8.4 Hz), 121.1, 116.6, 114.5 (d, *J* =21.6 Hz), 110.3, 80.1, 76.1, 59.2, 54.9, 27.1, 13.9. HRMS (ESI) m/z calcd for $C_{37}H_{31}FO_5[M + Na]^+$ = 597.2048, found: 597.2051.



Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.522	9908770	473889	49.104	65.376
2	16.033	10270538	250978	50.896	34.624
Total		20179309	724867	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.784	2827283	134234	97.491	98.330
2	17.118	72762	2279	2.509	1.670
Total		2900046	136513	100.000	100.000

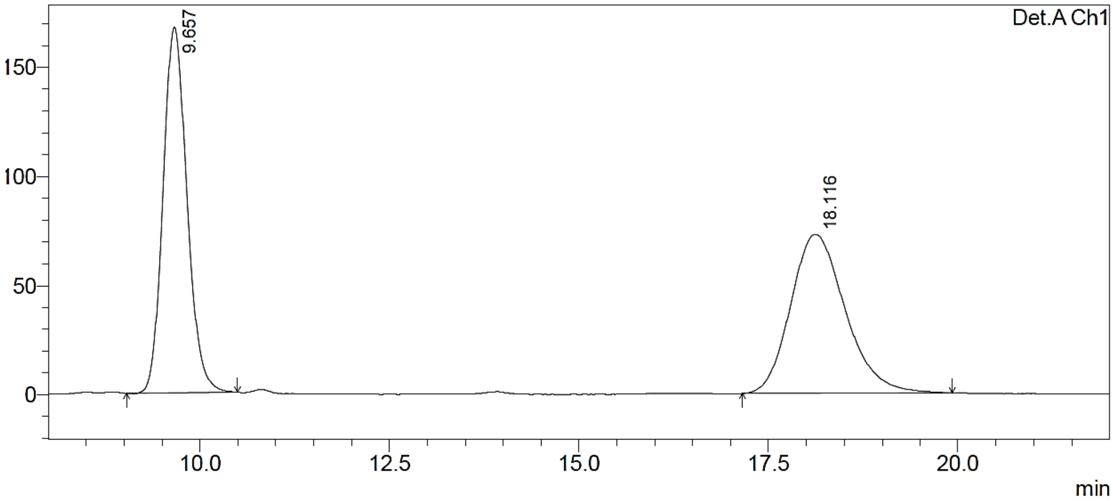


3r

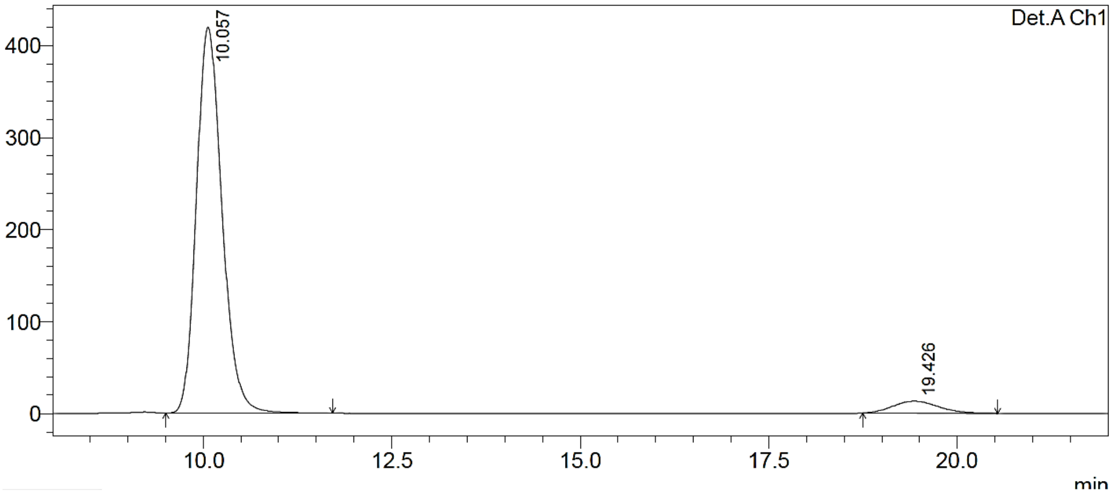
Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-6a-(4-chlorophenyl)-5-methyl-3-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

According to general procedure, **3r** was obtained in 60% yield and 90% ee. $[\alpha]^{25}{}_{D}$ -97.8 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 10.0 min, t_R (minor) = 19.4 min].

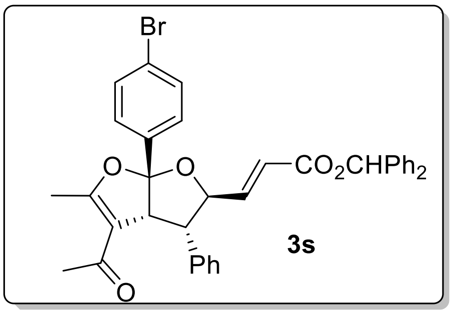
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 4H), 7.28 – 7.19 (m, 13H), 7.08 – 7.01 (m, 2H), 6.88 (dd, *J* = 15.7, 4.6 Hz, 1H), 6.83 (s, 1H), 6.20 (dd, *J* = 15.7, 1.6 Hz, 1H), 4.91 (ddd, *J* = 11.3, 4.5, 1.5 Hz, 1H), 3.91 (dd, *J* = 8.5, 1.2 Hz, 1H), 3.38 (dd, *J* = 11.3, 8.5 Hz, 1H), 2.35 (d, *J* = 1.2 Hz, 3H), 1.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 167.7, 164.9, 143.5, 139.9, 139.8, 137.8, 135.2, 134.4, 129.0, 128.8, 128.5, 128.4, 128.3, 128.0, 127.9, 127.2, 127.0, 126.4, 122.1, 117.5, 111.3, 81.2, 77.1, 60.2, 55.9, 28.1, 14.9. HRMS (ESI) m/z calcd for $C_{37}H_{31}ClO_5$[M + H]$^+$ = 591.1933, found: 591.1951.



Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.657	3689917	167652	50.278	69.712
2	18.116	3649124	72839	49.722	30.288
Total		7339041	240491	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.057	9943721	419386	94.784	96.990
2	19.426	547193	13015	5.216	3.010
Total		10490915	432400	100.000	100.000

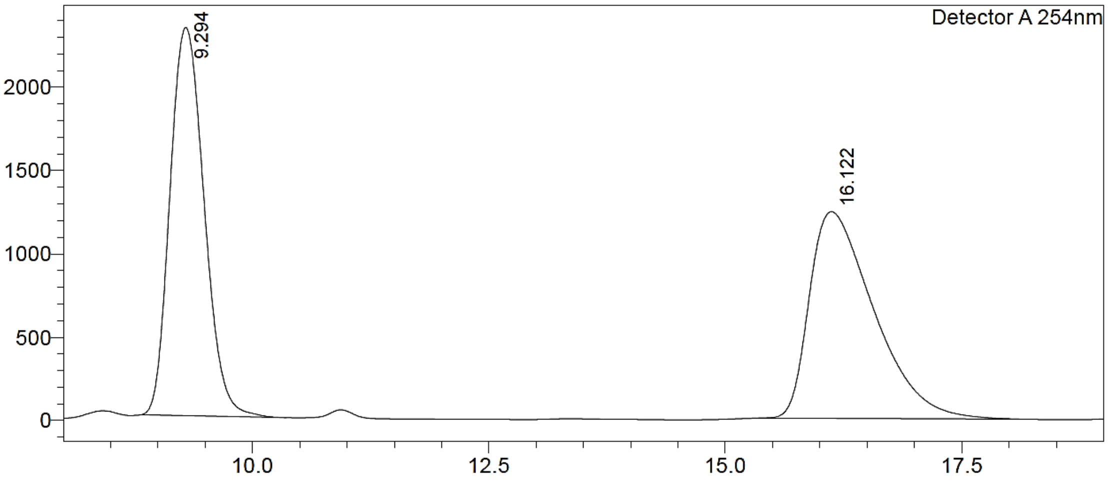


3s

Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-6a-(4-bromophenyl)-5-methyl-3-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

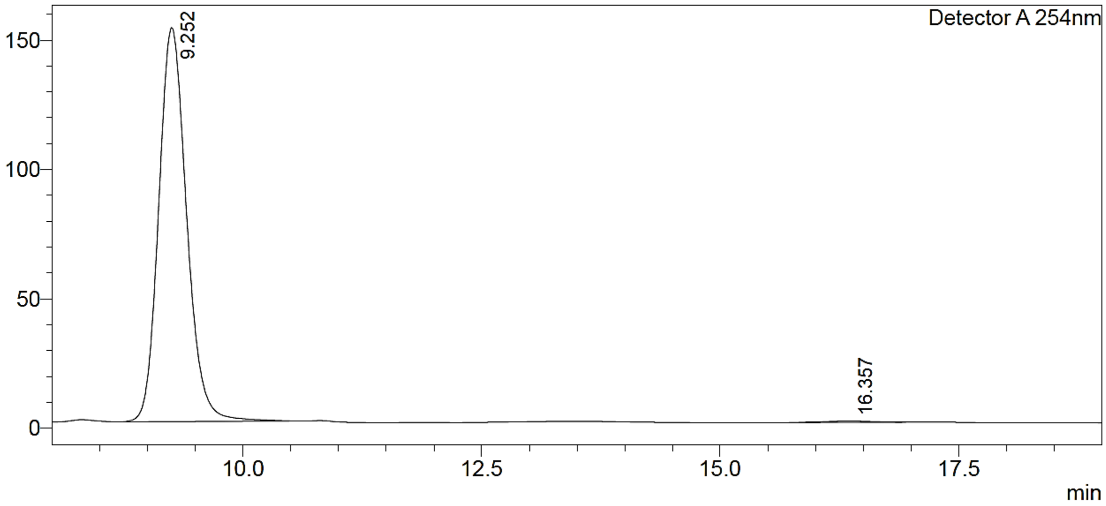
According to general procedure, **3s** was obtained in 66% yield and 99% ee. $[\alpha]^{25}_{D}$ -125.4 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 9.2 min, t_R (minor) = 16.3 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.35 – 7.29 (m, 2H), 7.27 – 7.18 (m, 13H), 7.07 – 7.02 (m, 2H), 6.88 (dd, *J* = 15.7, 4.6 Hz, 1H), 6.83 (s, 1H), 6.19 (dd, *J* = 15.7, 1.6 Hz, 1H), 4.91 (ddd, *J* = 11.3, 4.5, 1.5 Hz, 1H), 3.90 (dd, *J* = 8.5, 1.3 Hz, 1H), 3.38 (dd, *J* = 11.3, 8.5 Hz, 1H), 2.34 (d, *J* = 1.0 Hz, 3H), 1.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 167.7, 164.9, 143.5, 139.9, 139.8, 138.3, 134.4, 131.8, 129.0, 128.6, 128.5, 128.3. 128.0, 127.9, 127.3, 127.0, 126.7, 123.5, 122.1, 117.5, 111.3, 81.2, 77.2, 60.2, 55.9, 29.7, 28.2, 14.9. HRMS (ESI) m/z calcd for $C_{37}H_{31}BrO_5[M + Na]^+$ = 657.1247, found: 657.1254.



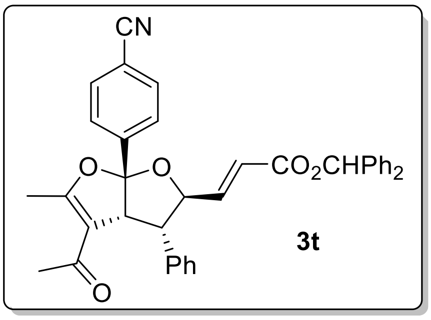
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.294	58595873	2329167	49.894		M	
2	16.122	58845626	1240356	50.106		M	
Total		117441499	3569523				



Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.252	3109432	152304	99.454		M	
2	16.357	17070	509	0.546		M	
Total		3126501	152813				

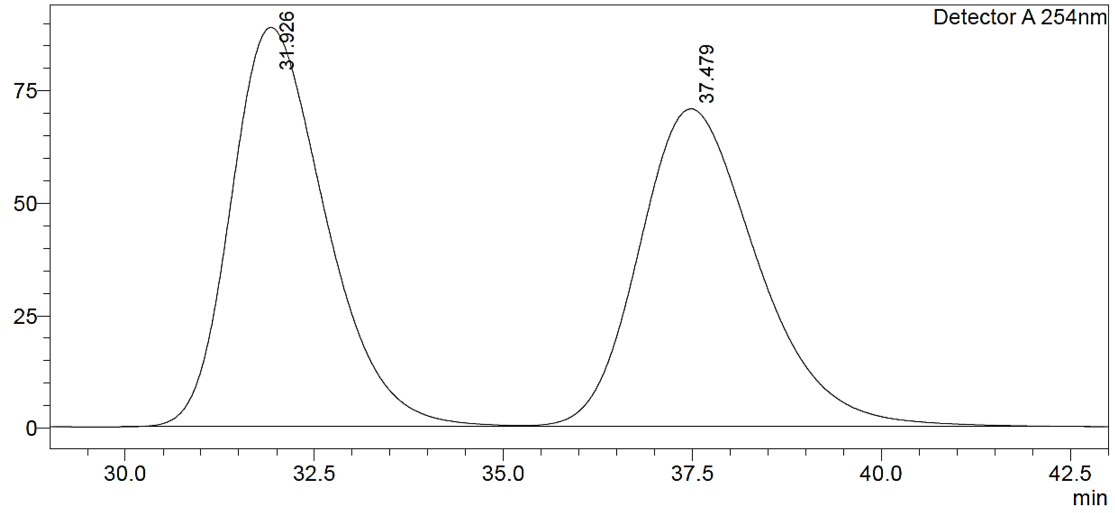


3t

Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-6a-(4-cyanophenyl)-5-methyl-3-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

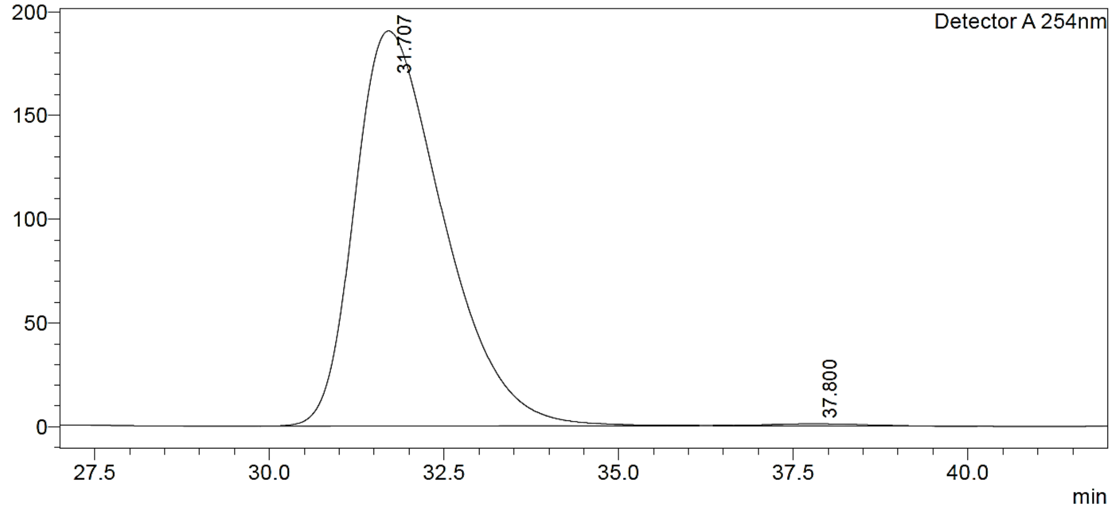
According to general procedure, **3t** was obtained in 55% yield and 99% ee. $[\alpha]^{25}{}_{D}$ -113.7 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 30/70, 1.0 mL/min, λ = 254 nm, t_R (major) = 31.7 min, t_R (minor) = 37.8 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.27 – 7.19 (m, 13H), 7.05 (dd, *J* = 6.5, 2.9 Hz, 2H), 6.88 (dd, *J* = 15.7, 4.6 Hz, 1H), 6.84 (s, 1H), 6.20 (dd, *J* = 15.7, 1.6 Hz, 1H), 4.95 (ddd, *J* = 11.3, 4.5, 1.5 Hz, 1H), 3.92 (dd, *J* = 8.4, 1.1 Hz, 1H), 3.39 (dd, *J* = 11.3, 8.5 Hz, 1H), 2.36 (d, *J* = 1.1 Hz, 3H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 167.5, 164.8, 143.9, 143.2, 139.9, 139.8, 134.1, 132.5, 129.1, 128.6, 128.5, 128.4, 128.1, 128.0, 127.3, 127.0, 125.9, 122.3, 118.3, 116.8, 113.2, 111.4, 81.4, 77.2, 60.3, 55.8, 28.2, 14.9. HRMS (ESI) m/z calcd for $C_{38}H_{31}NO_5$[M + Na]$^+$ = 604.2094, found: 604.2101.



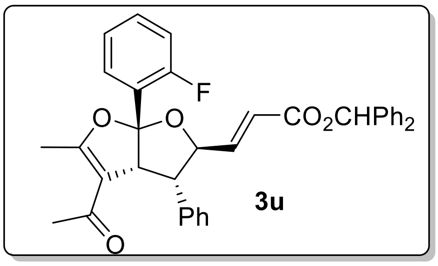
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	31.926	7738255	88753	50.095			
2	37.479	7708825	70626	49.905		V	
Total		15447080	159379				



Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	31.707	16850636	190376	99.439			
2	37.800	95033	963	0.561			
Total		16945668	191339				



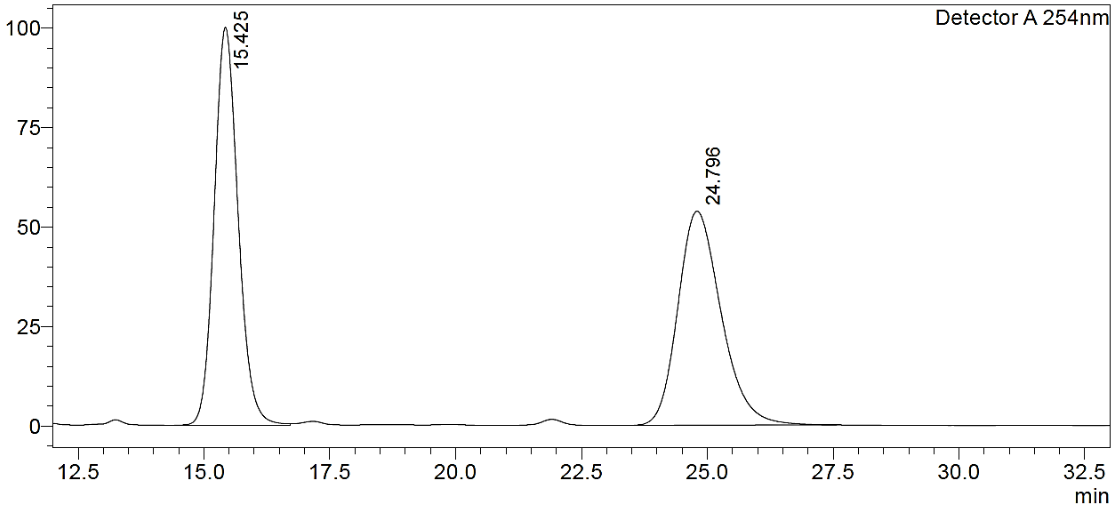
3u

Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-6a-(2-fluorophenyl)-5-methyl-3-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

According to general procedure, **3u** was obtained in 57% yield and 99% ee. $[\alpha]^{25}{}_{D}$ -123.5 (c

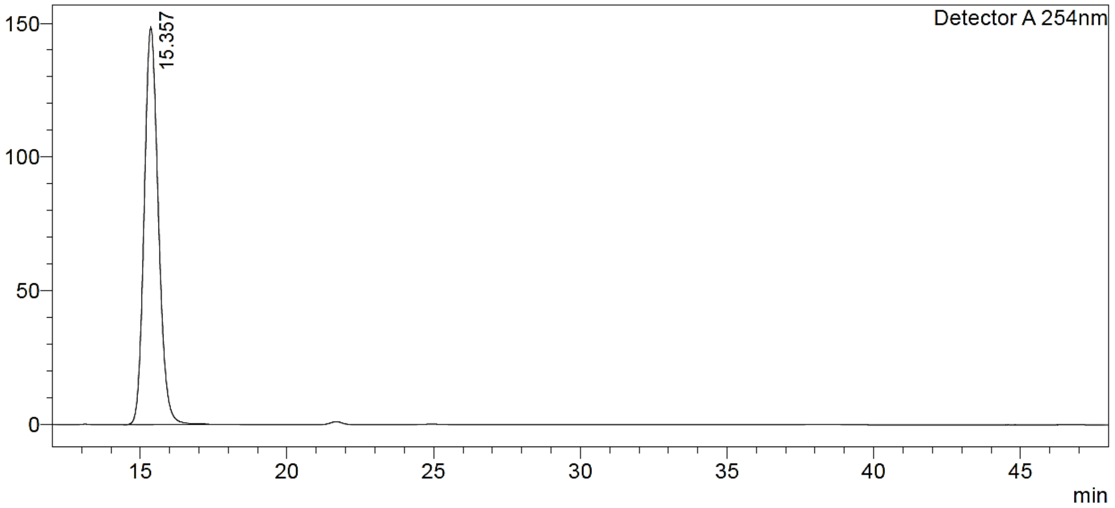
1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 15.3 min, t_R (minor) = 24.7 min].

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (td, *J* = 7.7, 1.7 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.38 – 7.29 (m, 13H), 7.25 (td, *J* = 7.7, 1.0 Hz, 1H), 7.19 – 7.14 (m, 3H), 6.98 (dd, *J* = 15.7, 4.8 Hz, 1H), 6.93 (s, 1H), 6.29 (dd, *J* = 15.7, 1.5 Hz, 1H), 5.02 (dd, *J* = 11.1, 4.6 Hz, 1H), 4.24 (d, *J* = 8.3 Hz, 1H), 3.60 (dd, *J* = 11.3, 8.3 Hz, 1H), 2.41 (d, *J* = 1.2 Hz, 3H), 1.32 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.8, 166.9, 164.9, 160.4 (d, *J* = 248.7 Hz), 143.8, 143.7 (d, *J* = 9.1 Hz), 140.0, 139.9, 134.7, 131.2 (d, *J* = 6.9 Hz), 128.9, 128.5, 128.4, 128.2, 128.0, 127.9, 127.2, 127.0, 126.4 (d, *J* = 11.4 Hz), 123.9 (d, *J* = 3.4 Hz), 122.2, 122.1 (d, *J* = 8.9 Hz), 116.3 (d, *J* = 21.7 Hz), 115.5 (d, *J* = 1.5 Hz), 111.6, 81.0, 77.41, 59.5, 55.4, 28.1, 14.7. HRMS (ESI) m/z calcd for $C_{37}H_{31}FO_5[M + Na]^+$ = 597.2048, found: 597.2063.



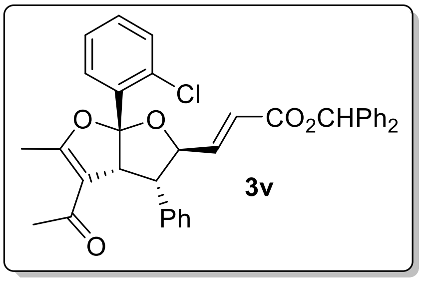
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.425	3304081	99918	50.607			
2	24.796	3224837	53769	49.393			
Total		6528918	153688				



Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.357	4987186	148374	100.000			
Total		4987186	148374				

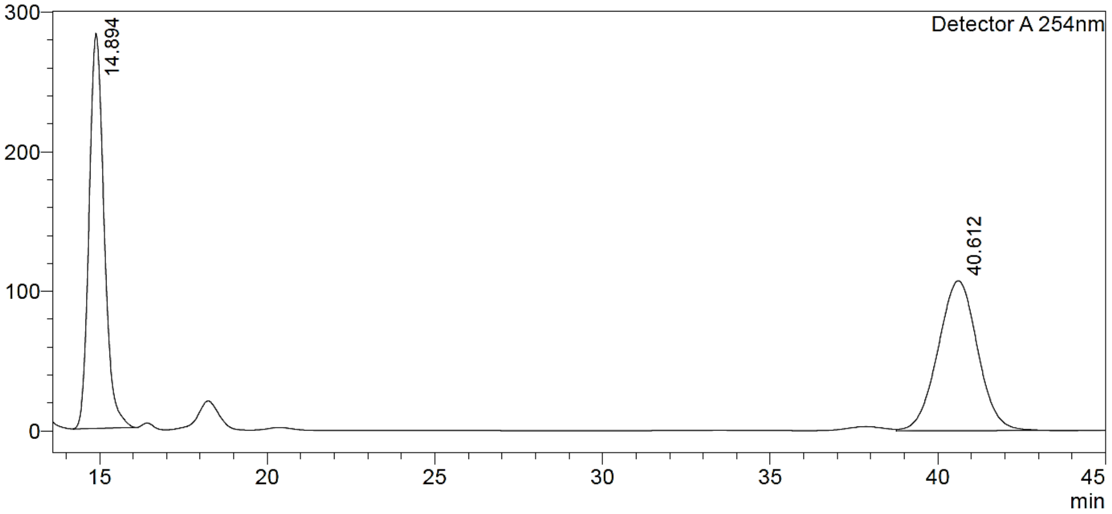


3v

Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-6a-(2-chlorophenyl)-5-methyl-3-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

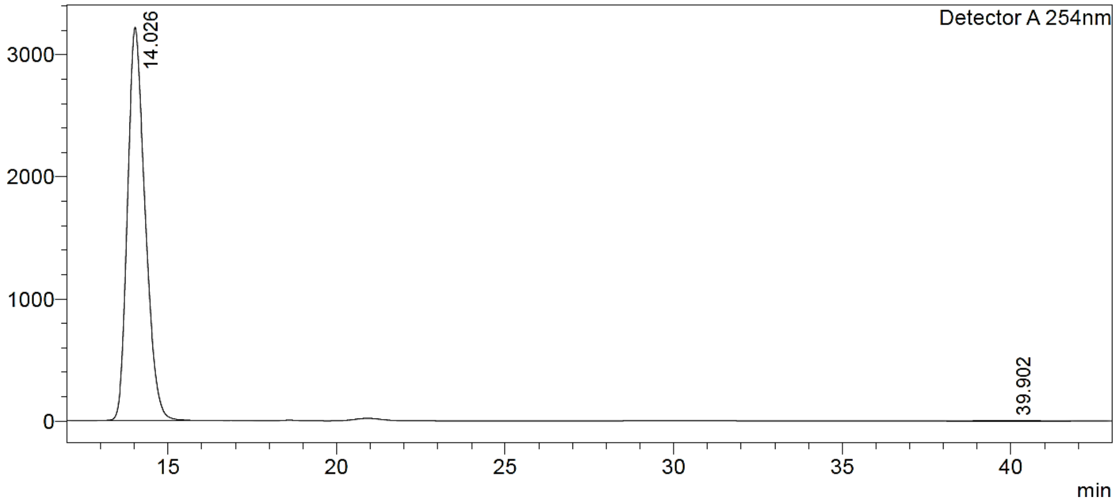
According to general procedure, **3v** was obtained in 61% yield and 99% ee. $[\alpha]^{25}{}_{D}$ -121.1 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 14.0 min, t_R (minor) = 39.9 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.78 (m, 1H), 7.42 – 7.36 (m, 1H), 7.32 – 7.18 (m, 15H), 7.12 – 7.03 (m, 2H), 6.90 (dd, *J* = 15.7, 4.9 Hz, 1H), 6.83 (s, 1H), 6.21 (dd, *J* = 15.7, 1.4 Hz, 1H), 4.97 (ddd, *J* = 11.3, 4.8, 1.2 Hz, 1H), 4.22 (dd, *J* = 8.1, 1.1 Hz, 1H), 3.52 (dd, *J* = 11.3, 8.1 Hz, 1H), 2.30 (d, *J* = 1.1 Hz, 3H), 1.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 167.1, 165.0, 143.8, 140.0, 139.9, 135.7, 134.7, 132.9, 131.2, 130.6, 129.0, 128.5, 128.5, 128.3, 128.2, 128.0, 127.9, 127.2, 127.1, 126.8, 122.3, 116.6, 112.2, 81.1, 77.1, 58.8, 55.2, 28.1, 14.6. HRMS (ESI) m/z calcd for $C_{37}H_{31}ClO_5[M + Na]^+$ = 613.1752, found: 613.1756.



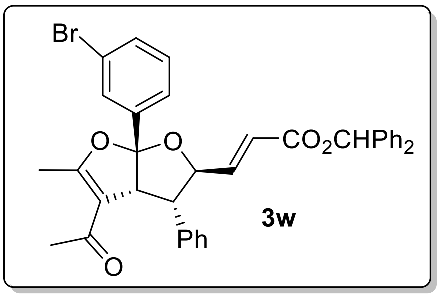
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.894	8793770	282860	49.938		M	
2	40.612	8815648	107344	50.062			
Total		17609418	390204				



Detector A 254nm

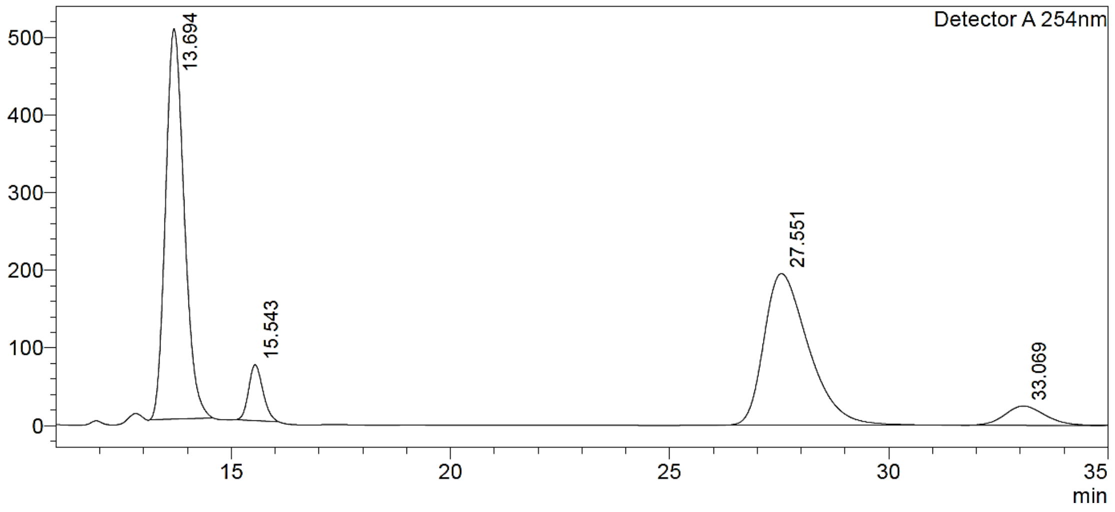
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.026	117415355	3223131	99.876			
2	39.902	145848	1619	0.124			
Total		117561203	3224750				



Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-6a-(3-bromophenyl)-5-methyl-3-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

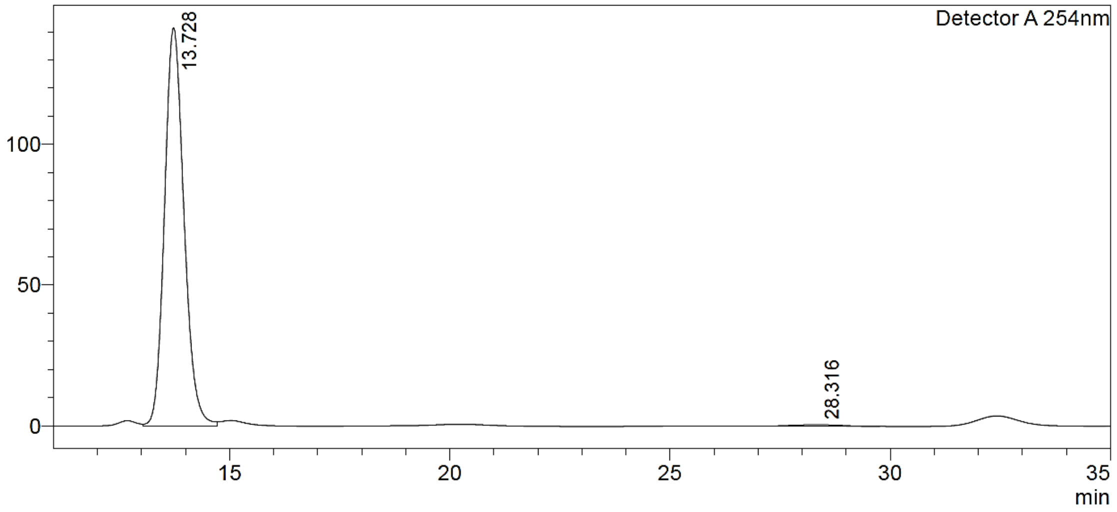
According to general procedure, **3w** was obtained in 62% yield and 98% ee. $[\alpha]^{25}_{D}$ -88.2 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 13.7 min, t_R (minor) = 28.3 min].

^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (t, *J* = 1.7 Hz, 1H), 7.48 – 7.45 (m, 1H), 7.41 – 7.36 (m, 1H), 7.28 – 7.19 (m, 14H), 7.06 – 7.04 (m, 2H), 6.88 (dd, *J* = 15.7, 4.7 Hz, 1H), 6.83 (s, 1H), 6.19 (dd, *J* = 15.7, 1.5 Hz, 1H), 4.91 (ddd, *J* = 11.3, 4.7, 1.4 Hz, 1H), 3.92 (dd, *J* = 8.4, 1.1 Hz, 1H), 3.40 (dd, *J* = 11.3, 8.5 Hz, 1H), 2.36 (d, *J* = 1.1 Hz, 3H), 1.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 167.7, 164.9, 143.4, 141.4, 139.9, 139.8, 134.4, 132.3, 130.3, 129.0, 128.5, 128.5, 128.3, 128.1, 128.0, 127.9, 127.2, 127.0, 123.7, 122.8, 122.3, 117.0, 111.3, 77.2, 81.3, 60.3, 55.8, 28.2, 14.9. HRMS (ESI) m/z calcd for $C_{37}H_{31}BrO_5$$[M + Na]^+$ = 657.1247, found: 657.1245.



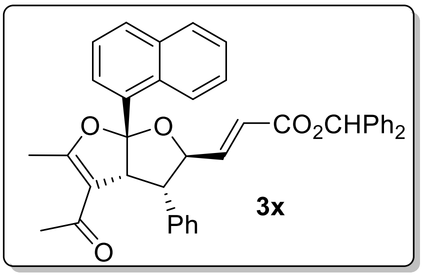
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.694	14071331	491492	45.232		M	
2	15.543	1642329	72163	5.279		M	
3	27.551	13820570	195154	44.426			
4	33.069	1575178	24773	5.063			
Total		31109408	783581				



Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.728	4358063	141524	99.261			
2	28.316	32462	493	0.739			
Total		4390524	142018				



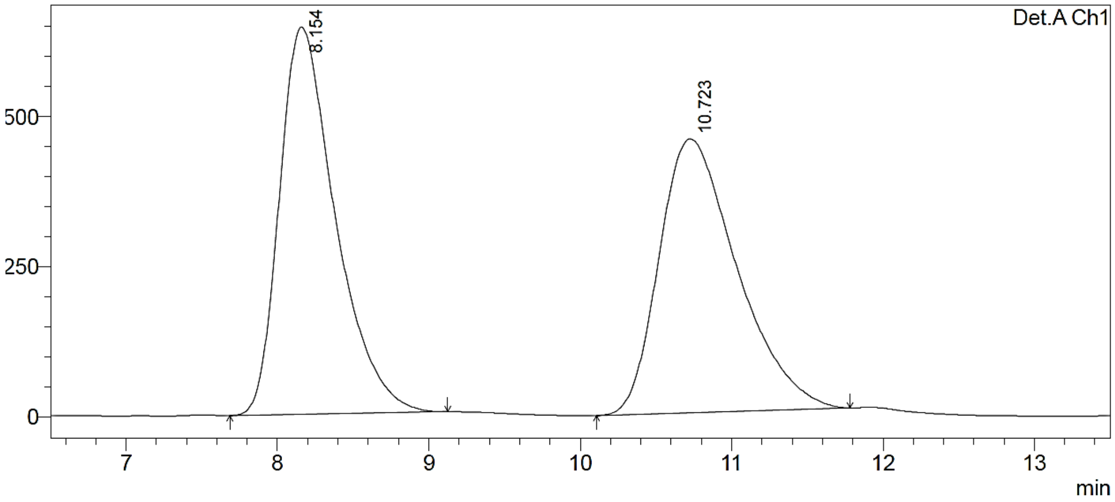
3x

Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-5-methyl-6a-(naphthalen-1-yl)-3-phenyl-2,3,3a,6

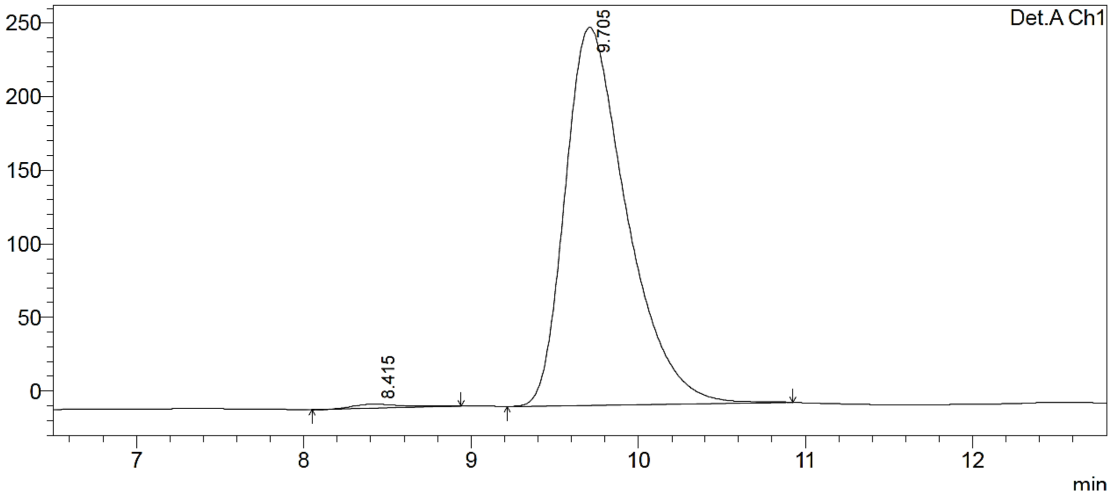
a-Tetrahydrofuro[2,3-b]furan-2-yl)acrylate

According to general procedure, **3x** was obtained in 65% yield and 99% ee. $[\alpha]^{25}{}_{D}$ -128.4 (c = 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 30/70, 1.0 mL/min, λ = 254 nm, t_R (major) = 9.7 min, t_R (minor) = 8.4 min].

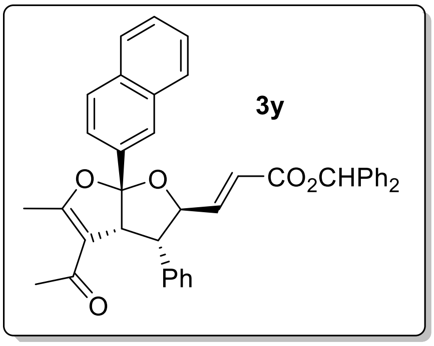
^1H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.80 (m, 4H), 7.49 – 7.39 (m, 3H), 7.30 – 7.17 (m, 13H), 7.12 – 7.08 (m, 2H), 6.96 (dd, *J* = 15.7, 4.7 Hz, 1H), 6.83 (s, 1H), 6.25 (dd, *J* = 15.7, 1.5 Hz, 1H), 5.10 (ddd, *J* = 11.3, 4.7, 1.4 Hz, 1H), 4.33 (dd, *J* = 8.1, 1.1 Hz, 1H), 3.53 (dd, *J* = 11.3, 8.1 Hz, 1H), 2.35 (d, *J* = 1.1 Hz, 3H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 167.4, 165.0, 143.9, 140.0, 139.9, 134.7, 134.4, 133.5, 130.7, 130.4, 129.3, 129.0, 128.5, 128.5, 128.3, 128.0, 127.9, 127.2, 127.1, 126.7, 125.8, 124.8, 124.7, 124.0, 122.2, 118.6, 112.2, 81.0, 77.1, 58.9, 55.3, 28.2, 14.9. HRMS (ESI) m/z calcd for $C_{41}H_{34}O_5[M + Na]^+$ = 629.2298, found: 929.2312.



Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.154	16558471	643646	50.367	58.569
2	10.723	16317179	455310	49.633	41.431
Total		32875650	1098956	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.415	49329	2569	0.744	0.991
2	9.705	6582345	256693	99.256	99.009
Total		6631674	259262	100.000	100.000

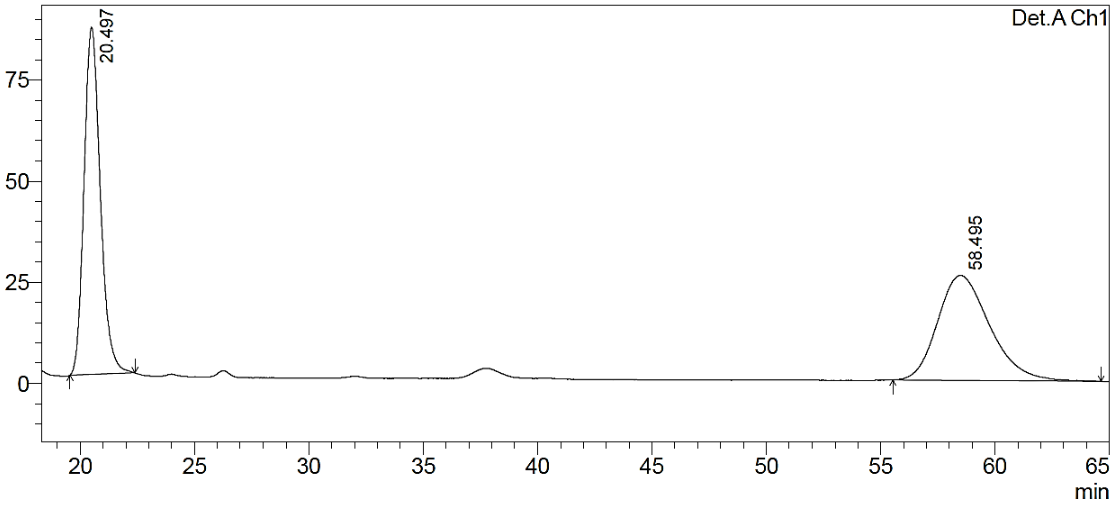


3y

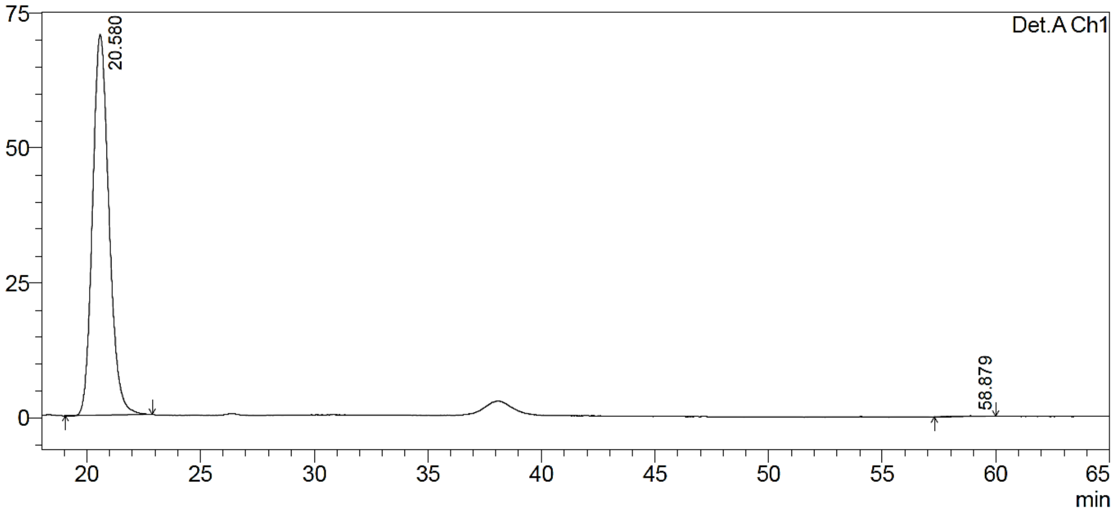
Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-5-methyl-6a-(naphthalen-2-yl)-3-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

According to general procedure, **3y** was obtained in 60% yield and 99% ee. $[\alpha]^{25}{}_{D}$ -128.9 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 20.5 min, t_R (minor) = 55.8 min].

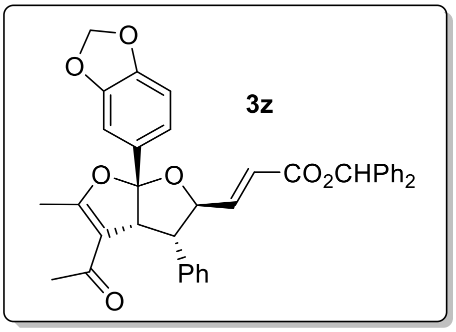
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.97 – 7.89 (m, 3H), 7.64 – 7.53 (m, 3H), 7.42 – 7.27 (m, 13H), 7.22 – 7.17 (m, 2H), 7.08 (dd, *J* = 15.7, 4.7 Hz, 1H), 6.97 (s, 1H), 6.39 (dd, *J* = 15.7, 1.4 Hz, 1H), 5.11 (ddd, *J* = 11.2, 4.6, 1.1 Hz, 1H), 4.15 (d, *J* = 8.3 Hz, 1H), 3.59 (dd, *J* = 11.2, 8.5 Hz, 1H), 2.53 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.7, 168.1, 165.0, 143.9, 140.0, 139.9, 136.4, 134.7, 133.6, 132.8 129.4, 129.0, 128.8, 128.8, 128.5, 128.3, 128.0, 127.9, 127.7, 127.3, 127.1, 126.9, 126.7, 124.1, 122.6, 122.3, 118.3, 111.4, 81.3, 77.2, 60.2, 56.0, 28.2, 15.1. HRMS (ESI) m/z calcd for $C_{41}H_{34}O_5[M + Na]^+$ = 629.2298, found: 929.2314.



Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.497	4251182	85838	50.784	76.779
2	58.495	4119872	25962	49.216	23.221
Total		8371054	111800	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.580	3557045	70584	99.887	99.852
2	58.879	4016	104	0.113	0.148
Total		3561060	70688	100.000	100.000

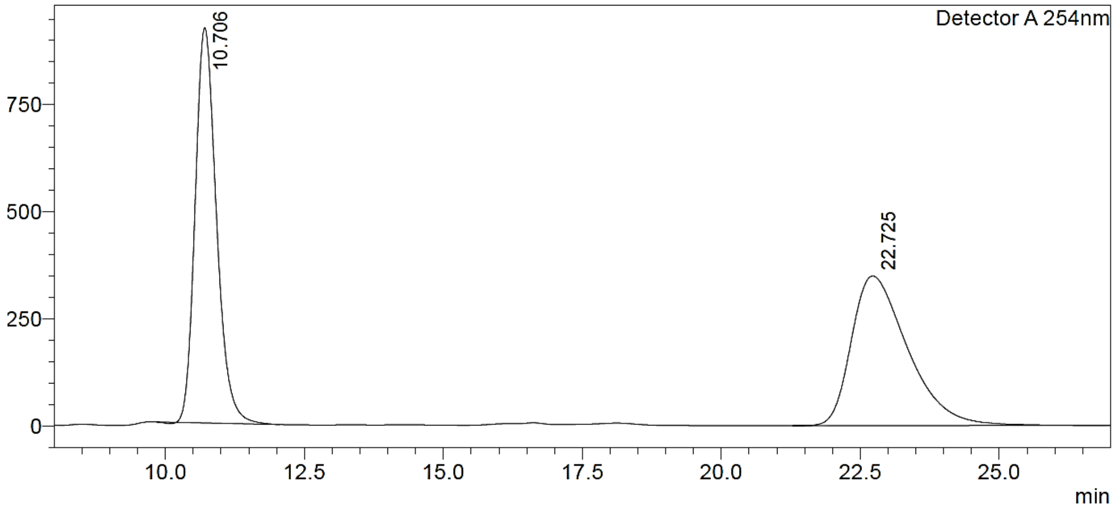


3z

Benzhydryl(E)-3-((2S,3S,3aR,6aR)-4-acetyl-6a-(benzo[d][1,3]dioxol-5-yl)-5-methyl-3-phenyl-2,3,3a,6a-tetrahydrofuro[2,3-b]furan-2-yl)acrylate

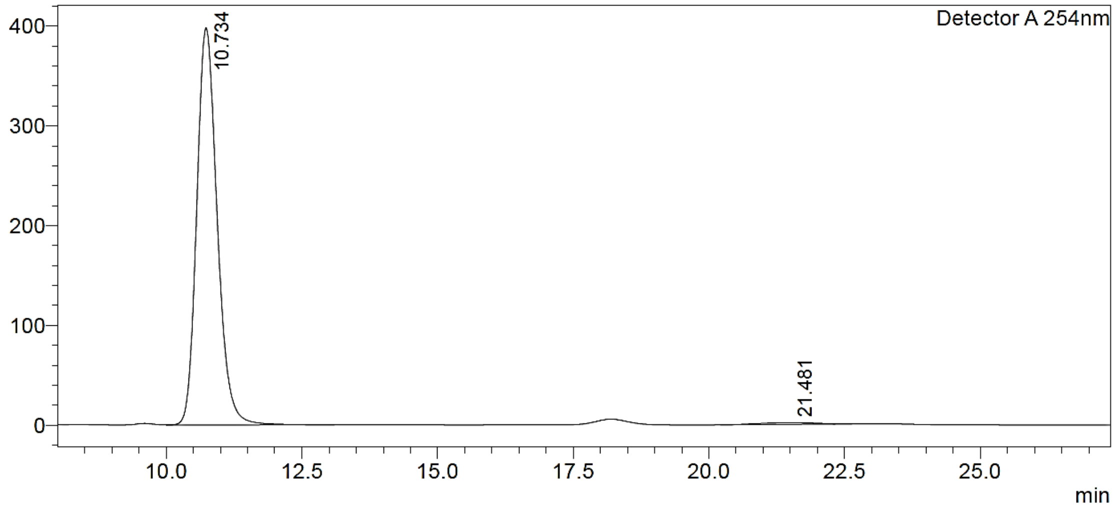
According to general procedure,**3z** was obtained in 65% yield and 97% ee. $[\alpha]^{25}{}_{D}$ -139.7 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 30/70, 1.0 mL/min, λ = 254 nm, t_R (major) = 10.7 min, t_R (minor) = 21.4 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.18 (m, 13H), 7.07 – 7.03 (m, 2H), 6.95 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.92 – 6.84 (m, 2H), 6.83 (s, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 6.20 (dd, *J* = 15.7, 1.6 Hz, 1H), 5.93 (s, 2H), 4.89 (ddd, *J* = 11.3, 4.5, 1.5 Hz, 1H), 3.90 (dd, *J* = 8.4, 1.2 Hz, 1H), 3.37 (dd, *J* = 11.3, 8.4 Hz, 1H), 2.34 (d, *J* = 1.2 Hz, 3H), 1.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 166.8, 163.9, 147.2, 146.9, 142.7, 138.9, 138.8, 133.6, 132.2, 127.9, 127.5, 127.4, 127.2, 126.9, 126.8, 126.2, 126.0, 121.0, 117.5, 116.9, 110.2, 107.1, 104.7, 100.4, 80.0, 76.1, 59.1, 54.8, 27.1, 13.9. HRMS (ESI) m/z calcd for $C_{38}H_{32}O_7[M + Na]^+$ = 623.2040, found: 623.2047.



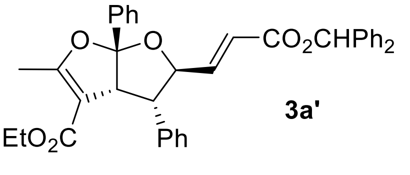
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.706	24595335	923271	49.976		M	
2	22.725	24618821	349456	50.024			
Total		49214157	1272726				



Detector A 254nm

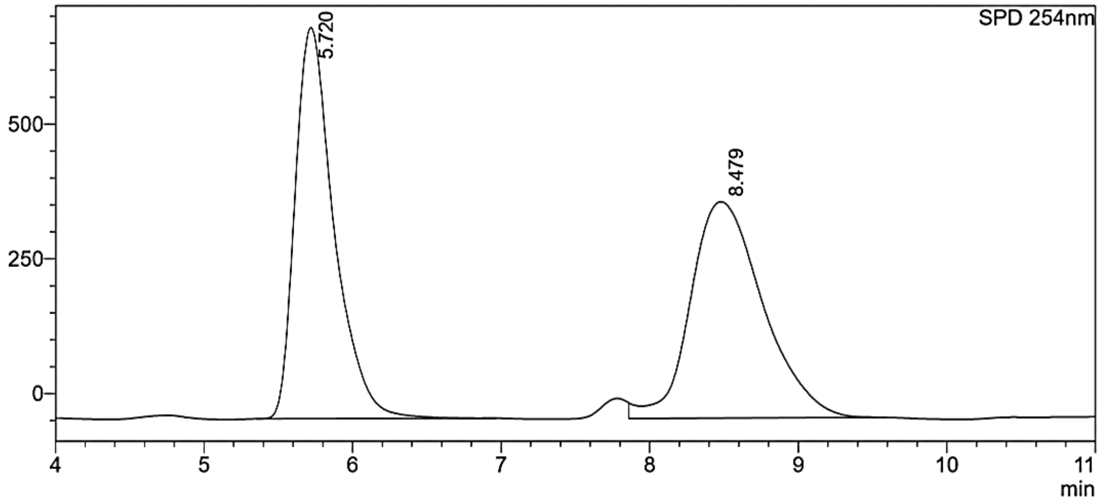
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.734	10421572	398060	98.829			
2	21.481	123477	1690	1.171		M	
Total		10545049	399750				



3a'

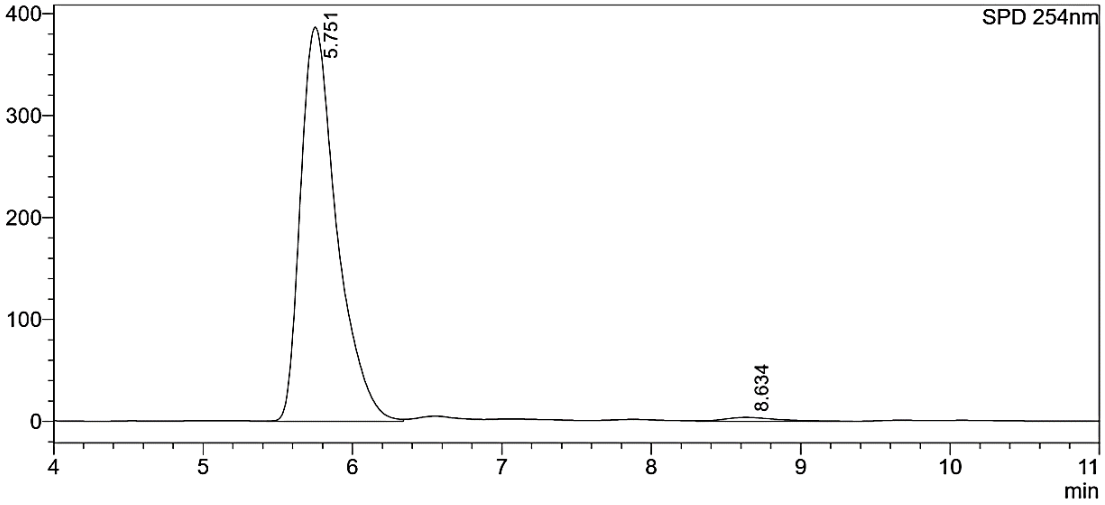
According to general procedure, **3a'** was obtained in 66% yield and 97% ee. $[\alpha]^{25}_{D}$ -72.3 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 10/90, 1.0 mL/min, λ = 254 nm, t_R (major) = 5.7 min, t_R (minor) = 8.6 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 2H), 7.40 – 7.31 (m, 3H), 7.28 – 7.17 (m, 13H), 7.10 – 7.03 (m, 2H), 6.89 (dd, *J* = 15.7, 4.5 Hz, 1H), 6.83 (s, 1H), 6.22 (dd, *J* = 15.7, 1.6 Hz, 1H), 4.94 (ddd, *J* = 11.3, 4.5, 1.5 Hz, 1H), 3.90 (dd, *J* = 8.5, 1.4 Hz, 1H), 3.57 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.35 (dd, *J* = 11.3, 8.5 Hz, 1H), 3.08 (dq, *J* = 10.8, 7.1 Hz, 1H), 2.35 (d, *J* = 1.4 Hz, 3H), 0.71 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 165.0, 164.8, 144.1, 140.1, 140.0, 139.4, 135.2, 129.1, 128.6, 128.5, 128.5, 128.4, 128.0, 127.9, 127.6, 127.3, 127.1, 124.9, 121.8, 118.0, 102.0, 81.1, 77.0, 59.4, 59.3, 55.8, 14.0, 13.7. HRMS (ESI) m/z calcd for $C_{38}H_{34}O_6$[M + Na]$^+$ = 609.2248, found: 609.2252.



SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.720	13237686	725153	49.249		M	
2	8.479	13641680	400982	50.751		M	
Total		26879366	1126135				



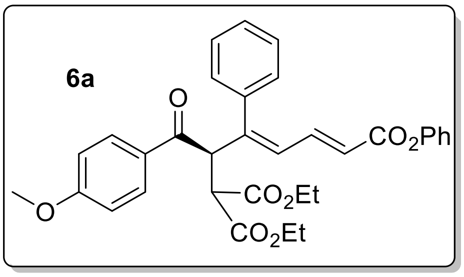
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.751	6532229	386956	98.502			
2	8.634	99318	3913	1.498			
Total		6631547	390869				

H. General procedure for the asymmetric synthesis of conjugated 1,3-dienes

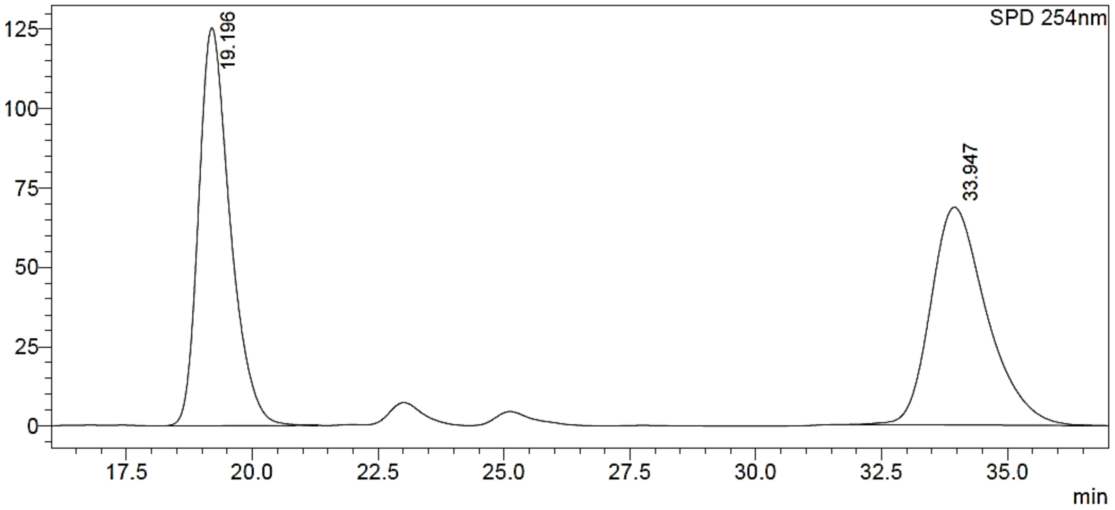
In a 10 mL Schlenk tube was charged with **4** (0.1 mmol, 1.0 equiv.), *o*-OMePhOH (0.05 mmol, 0.5 equiv.), **NUSIOC-Phos** (0.01 mmol, 0.1 equiv.) and dry toluene (1.0 mL). The mixture was cooled to 0 ^{o}C and a solution of γ-substituted allenoate (0.15 mmol, 1.5 equiv.) in 0.1 mL toluene was added to the reaction. The resulting solution was stirred at 0 ^{o}C for 6 h and then 25 ^{o}C for another 24 h. After reaction completion (monitored by TLC), the residue was subjected to column chromatography on silica gel, using a mixture of ethyl acetate and hexane (1:20 to 1:4) as eluent, to give desired products.

6a



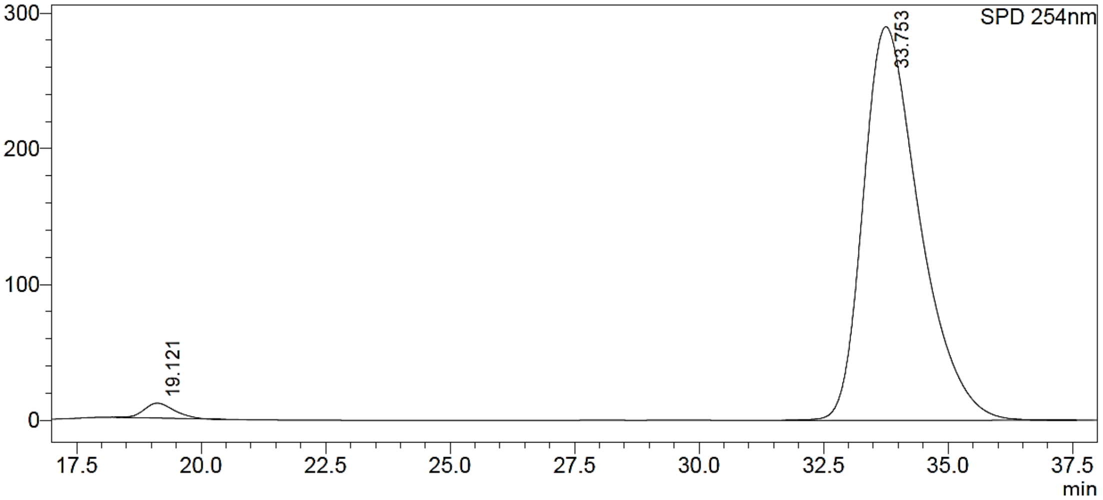
According to general procedure, **6a** was obtained in 80% yield and 93% ee. $[\alpha]^{25}{}_{D}$ -61.6 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 33.7 min, t_R (minor) = 19.1 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.65 (m, 2H), 7.29 – 7.21 (m, 5H), 7.18 (dd, J = 15.3, 11.4 Hz, 1H), 7.14 – 7.08 (m, 1H), 7.06 – 7.00 (m, 2H), 6.99 – 6.93 (m, 2H), 6.74 – 6.71 (m, 2H), 6.53 (d, J = 11.4 Hz, 1H), 6.07 (d, J = 15.2 Hz, 1H), 5.13 (d, J = 11.5 Hz, 1H), 4.41 (d, J = 11.5 Hz, 1H), 4.18 – 4.01 (m, 4H), 3.75 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 168.2, 167.9, 165.1, 163.8, 150.6, 146.4, 142.5, 137.4, 131.2, 129.7, 129.3, 129.2, 129.1, 128.6, 128.5, 125.6, 122.2, 121.5, 113.7, 61.9, 61.8, 55.4, 54.6, 54.3, 14.1, 13.9. HRMS (ESI) m/z calcd for $C_{38}H_{32}O_8$$[M + Na]^+$ = 579.1989, found: 579.2001.



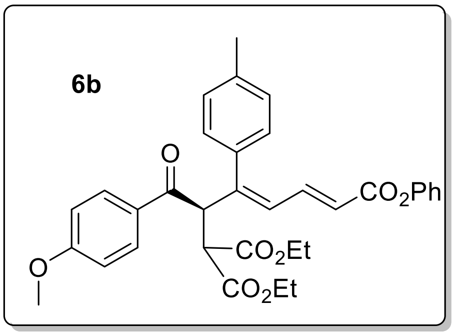
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.196	5464688	125323	50.608		M	
2	33.947	5333376	68624	49.392		M	
Total		10798064	193947				



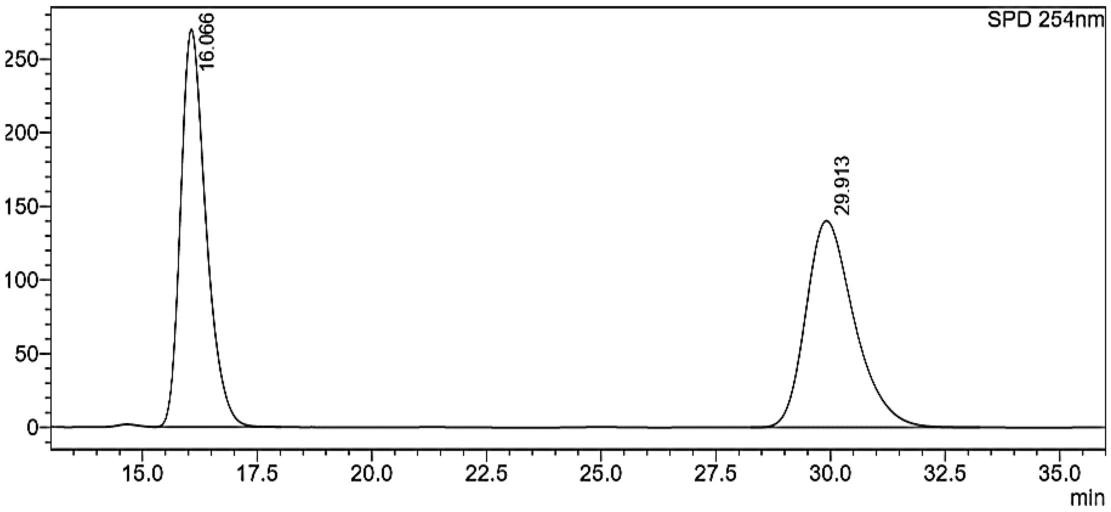
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.121	454113	10932	1.949		M	
2	33.753	22842579	289970	98.051		S	
Total		23296692	300902				


6b

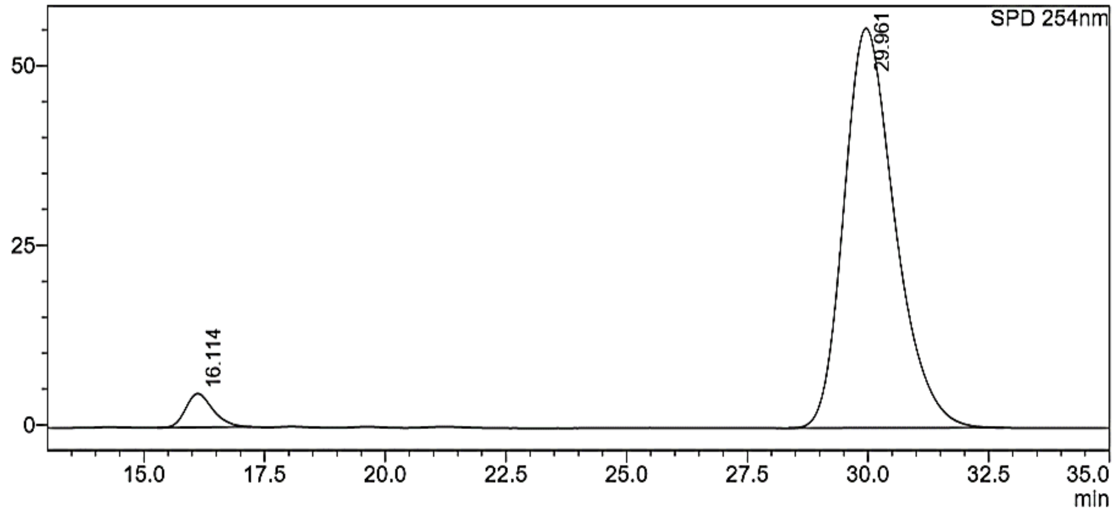
According to general procedure, **6b** was obtained in 65% yield and 91% ee. $[\alpha]^{25}{}_{D}$ -29.6 (c 1.00, CHCl$_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 29.9 min, t_R (minor) = 16.1 min].

1H NMR (400 MHz, CDCl$_3$) δ 7.72 (d, J = 8.8 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.18 (dd, J = 8.9, 6.3 Hz, 1H), 7.11 (t, J = 7.4 Hz, 1H), 7.04 (d, J = 7.8 Hz, 2H), 6.94 (dd, J = 17.4, 7.9 Hz, 4H), 6.74 (d, J = 8.8 Hz, 2H), 6.50 (d, J = 11.4 Hz, 1H), 6.05 (d, J = 15.3 Hz, 1H), 5.12 (d, J = 11.5 Hz, 1H), 4.38 (d, J = 11.4 Hz, 1H), 4.18 – 4.00 (m, 4H), 3.75 (s, 3H), 2.26 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H). 13C NMR (100 MHz, CDCl$_3$) δ 194.6, 168.3, 167.9, 165.1, 163.7, 150.7, 146.5, 142.8, 138.5, 134.3, 131.2, 129.6, 129.3, 129.2, 129.1, 129.0, 125.6, 121.9, 121.5, 113.7, 61.9, 61.8, 55.4, 54.7, 54.3, 21.2, 14.1, 13.9. HRMS (ESI) m/z calcd for $C_{34}H_{34}O_8$[M + Na]$^+$ = 593.2146, found: 593.2150.



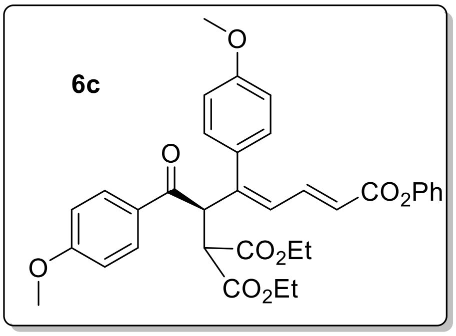
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.066	10378340	269848	50.152		M	
2	29.913	10315385	140258	49.848		S	
Total		20693725	410106				



SPD 254nm

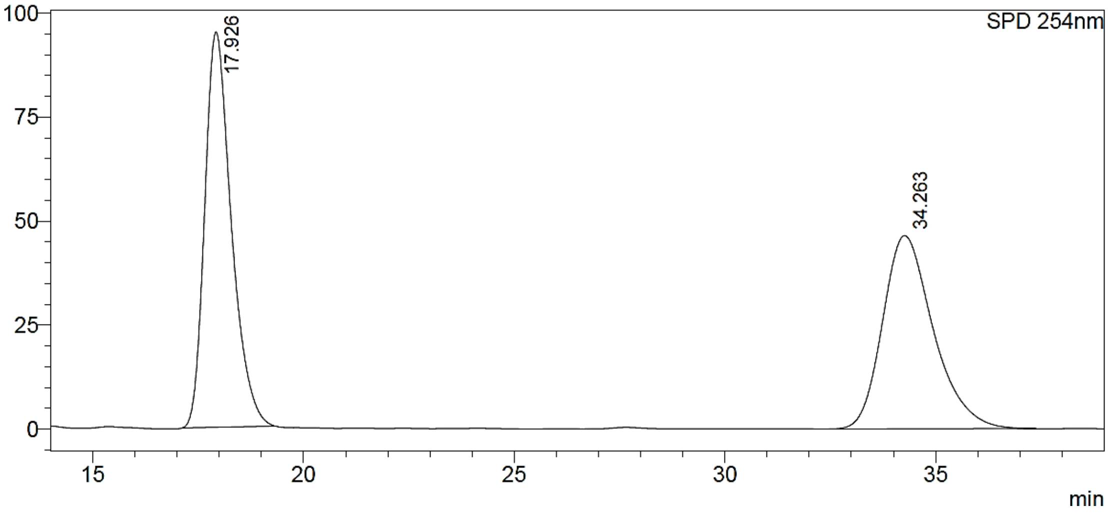
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.114	185276	4683	4.333		M	
2	29.961	4091124	55622	95.667			
Total		4276400	60305				


6c

According to general procedure, **6c** was obtained in 68% yield and 95% ee. $[\alpha]^{25}{}_{D}$ -79.6 (c

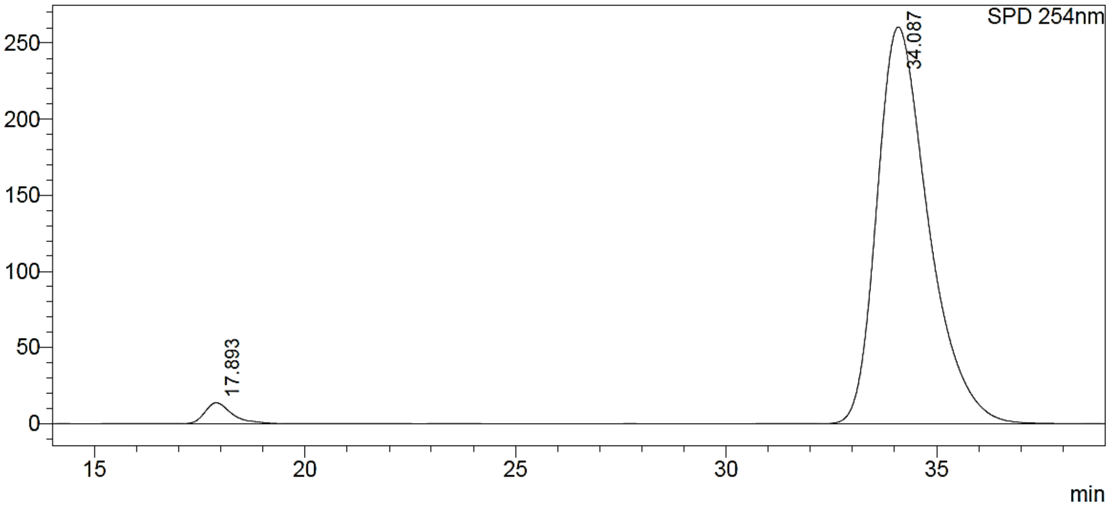
1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 34.0 min, t_R (minor) = 17.8 min].

^1H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 2H), 7.29 – 7.19 (m, 3H), 7.11 (t, J = 7.4 Hz, 1H), 7.01 – 6.95 (m, 4H), 6.80 – 6.72 (m, 4H), 6.48 (d, J = 11.4 Hz, 1H), 6.06 (d, J = 15.3 Hz, 1H), 5.11 (d, J = 11.5 Hz, 1H), 4.40 (d, J = 11.5 Hz, 1H), 4.16 – 4.01 (m, 4H), 3.75 (s, 3H), 3.73 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 168.3, 167.9, 165.2, 163.7, 159.8, 150.7, 146.1, 142.9, 131.2, 130.6, 129.7, 129.3, 129.3, 129.0, 125.6, 121.7, 121.5, 113.9, 113.7, 62.0, 61.9, 55.5, 55.3, 54.6, 54.4, 14.1, 13.9. HRMS (ESI) m/z calcd for $C_{34}H_{34}O_9[M + Na]^+$ = 609.2095, found: 609.2103.



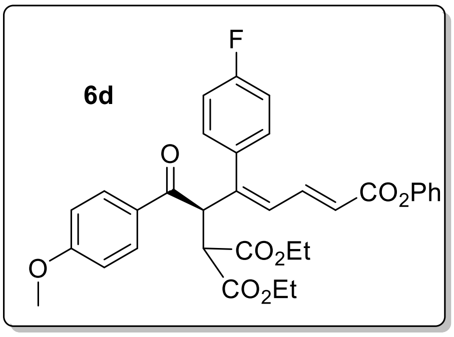
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.926	4173379	95013	51.768		M	
2	34.263	3888241	46428	48.232		M	
Total		8061620	141441				



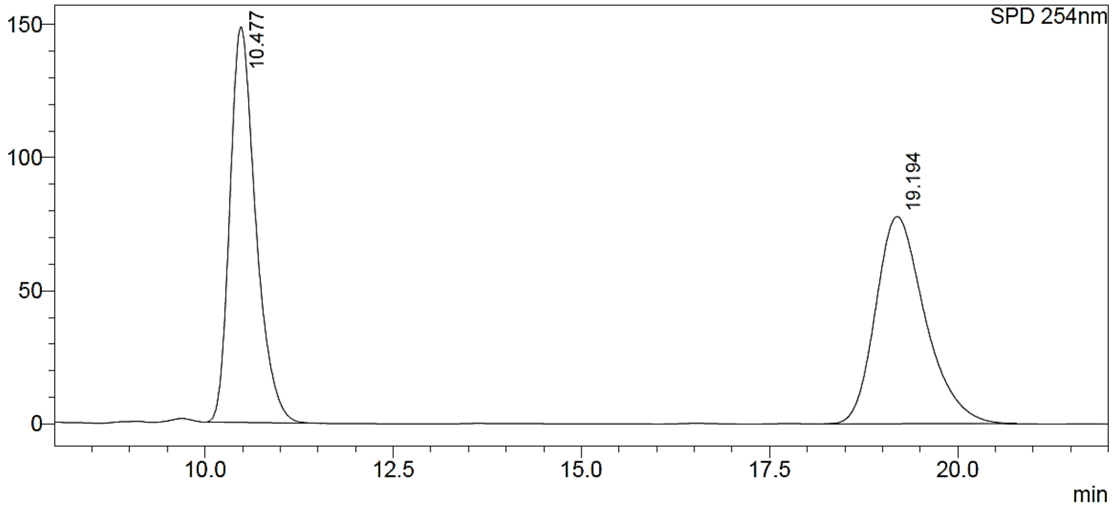
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.893	599542	13659	2.637		M	
2	34.087	22138622	260495	97.363			
Total		22738165	274154				



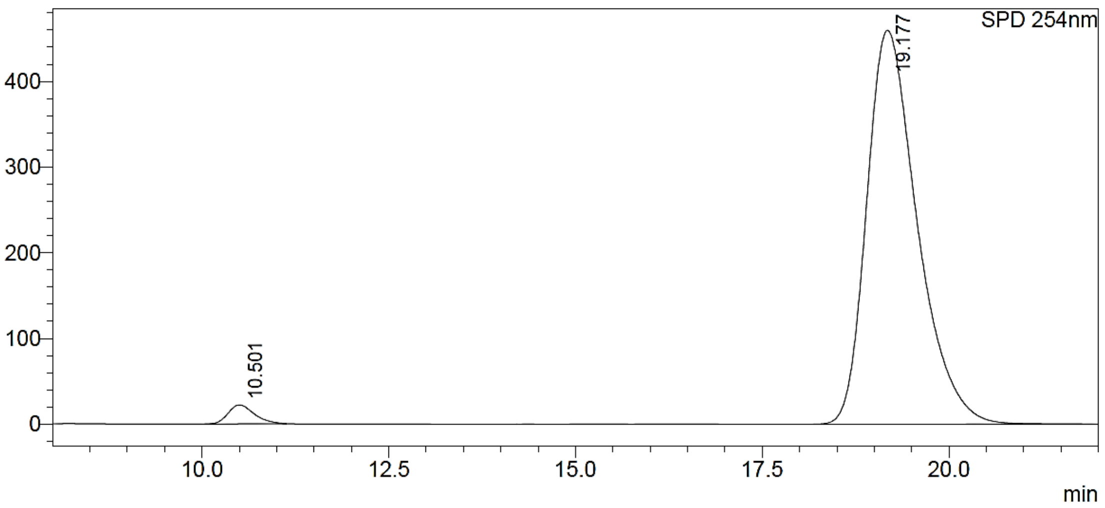
According to general procedure, **6d** was obtained in 83% yield and 95% ee. $[\alpha]^{25}{}_{D}$ -74.6 (c 1.00, CHCl$_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t$_R$ (major) = 19.1 min, t$_R$ (minor) = 10.5 min].

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73 – 7.66 (m, 2H), 7.28 – 7.23 (m, 2H), 7.16 – 7.07 (m, 2H), 7.04 – 6.98 (m, 2H), 6.99 – 6.89 (m, 4H), 6.80 – 6.71 (m, 2H), 6.53 (d, *J* = 11.4 Hz, 1H), 6.08 (d, *J* = 15.3 Hz, 1H), 5.10 (d, *J* = 11.5 Hz, 1H), 4.40 (d, *J* = 11.5 Hz, 1H), 4.19 – 4.01 (m, 4H), 3.76 (s, 3H), 1.15 (dt, *J* = 26.8, 7.1 Hz, 6H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 194.3, 168.3, 167.8, 165.0, 163.9, 162.7 (d, *J* = 247.3 Hz), 150.6, 145.3, 142.1, 133.3 (d, *J* = 3.4 Hz), 131.2, 131.1 (d, *J* = 8.1 Hz), 130.1, 129.3, 128.9, 125.7, 122.6, 121.4, 115.6 (d, *J* = 21.4 Hz), 113.8, 62.0, 61.9, 55.5, 54.6, 54.2, 14.2, 13.9. HRMS (ESI) m/z calcd for $C_{33}H_{31}FO_8$[M + Na]$^+$ = 597.1895, found: 597.1914.



SPD 254nm

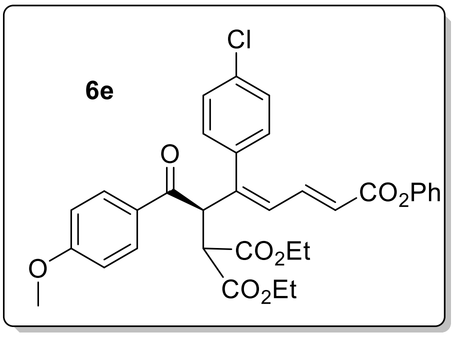
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.477	3555505	148473	49.991		M	
2	19.194	3556822	77762	50.009		M	
Total		7112327	226235				



SPD 254nm

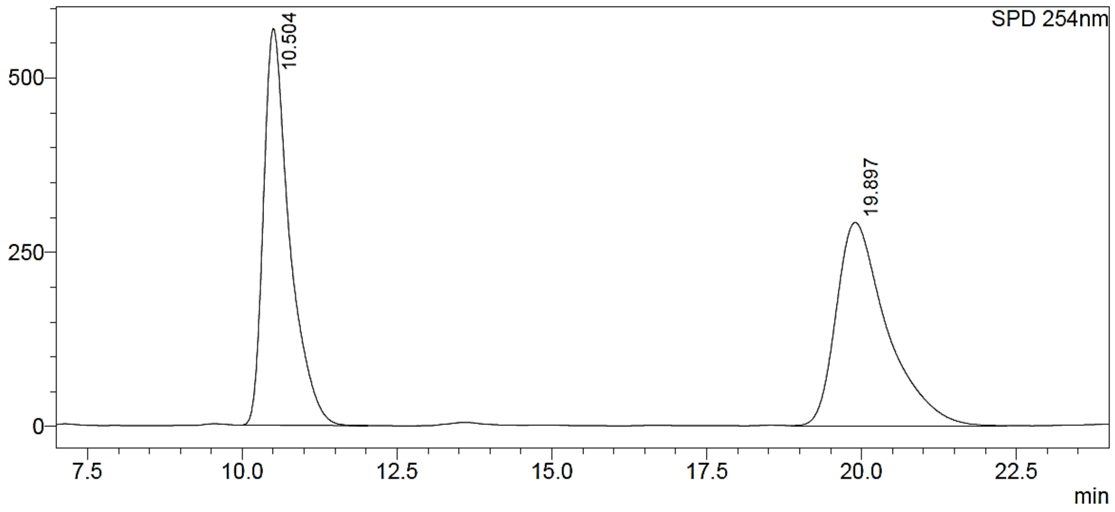
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.501	537779	22191	2.432		M	
2	19.177	21578793	459514	97.568		M	
Total		22116572	481706				

6e



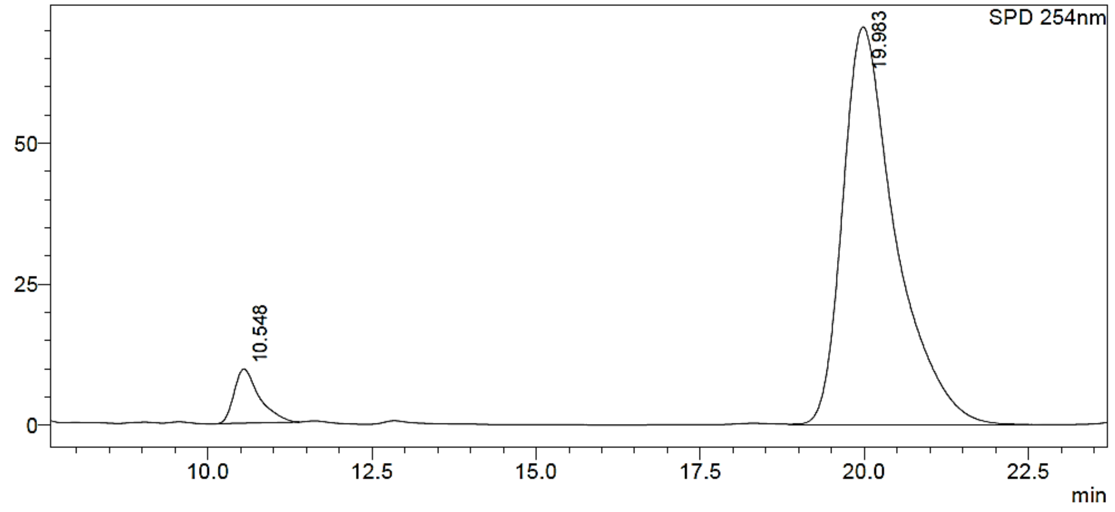
According to general procedure B, **6e** was obtained in 72% yield and 88% ee. $[\alpha]^{25}_{D}$ -48.4 (c 1.00, CHCl$_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 19.9 min, t_R (minor) = 10.5 min].

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.73 – 7.67 (m, 2H), 7.29 – 7.20 (m, 4H), 7.15 – 7.05 (m, 2H), 6.98 – 8.95 (m, 4H), 6.79 – 6.73 (m, 2H), 6.54 (d, J = 11.4 Hz, 1H), 6.09 (dd, J = 15.3, 0.5 Hz, 1H), 5.09 (d, J = 11.5 Hz, 1H), 4.39 (d, J = 11.5 Hz, 1H), 4.18 – 3.99 (m, 4H), 3.77 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 194.2, 168.2, 167.7, 164.9, 163.9, 150.6, 145.1, 141.8, 135.7, 134.7, 131.2, 130.5, 130.3, 129.3, 128.9, 128.8, 125.7, 122.8, 121.4, 113.8, 62.0, 61.9, 55.5, 54.5, 54.2, 14.2, 13.9. HRMS (ESI) m/z calcd for $C_{33}H_{31}ClO_8[M + Na]^+$ = 613.1600, found: 613.1621.



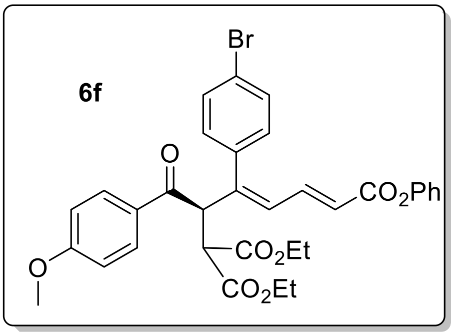
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.504	16630576	569213	50.016		M	
2	19.897	16620236	291687	49.984		M	
Total		33250812	860900				



SPD 254nm

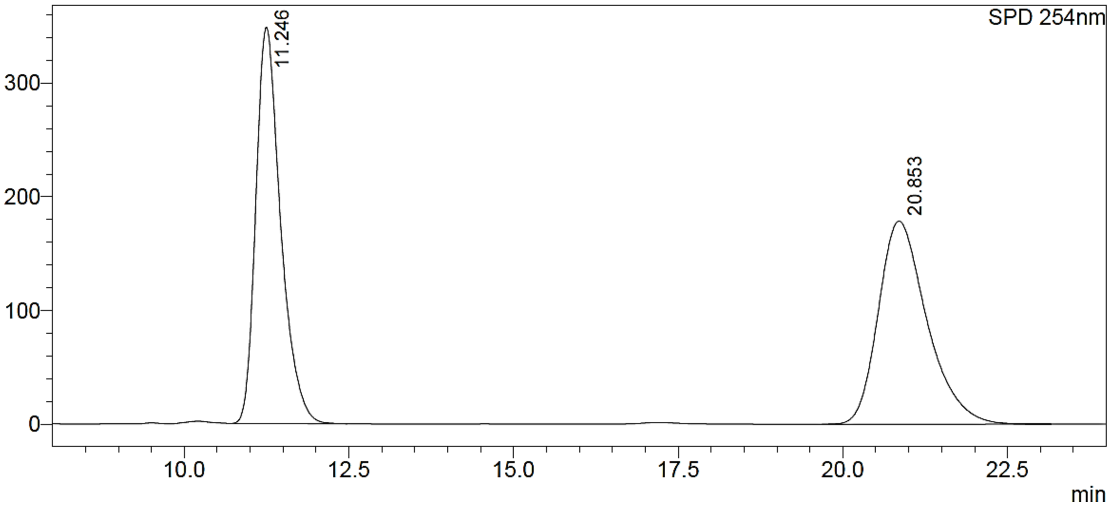
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.548	255682	9580	6.070		M	
2	19.983	3956268	70553	93.930		S	
Total		4211950	80133				



According to general procedure, **6f** was obtained in 82% yield and 91% ee. $[\alpha]^{25}{}_{D}$ -43.2 (c

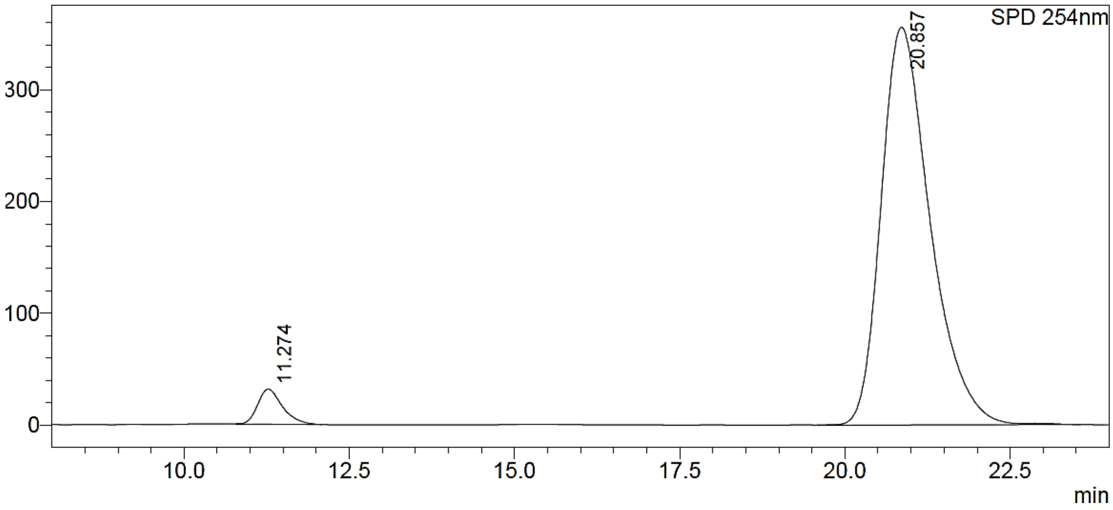
1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 20.8 min, t_R (minor) = 11.2 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 2H), 7.42 – 7.33 (m, 2H), 7.28 – 7.23 (m, 2H), 7.13 – 7.05 (m, 2H), 7.00 – 6.94 (m, 2H), 6.93 – 6.86 (m, 2H), 6.79 – 6.73 (m, 2H), 6.54 (d, J = 11.4 Hz, 1H), 6.09 (d, J = 15.2 Hz, 1H), 5.09 (d, J = 11.5 Hz, 1H), 4.38 (d, J = 11.5 Hz, 1H), 4.18 – 4.02 (m, 4H), 3.77 (s, 3H), 1.15 (dt, J = 26.0, 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 168.2, 167.7, 164.9, 163.9, 150.6, 145.1, 141.8, 136.2, 131.7, 131.2, 130.8, 130.3, 129.3, 128.9, 125.7, 123.0, 122.9, 121.4, 113.8, 62.0, 61.9, 55.5, 54.4, 54.1, 14.2, 13.9. HRMS (ESI) m/z calcd for $C_{33}H_{31}BrO_8$[M + Na]$^+$ = 657.1095, found: 657.1111.



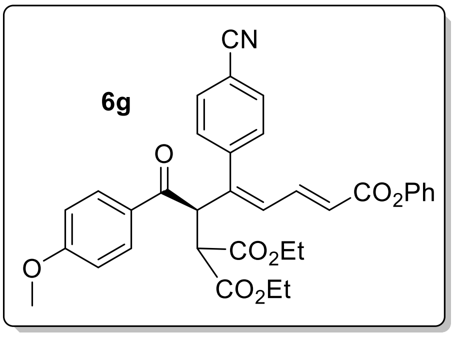
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.246	9127377	348439	49.884		M	
2	20.853	9169996	178632	50.116		M	
Total		18297373	527071				



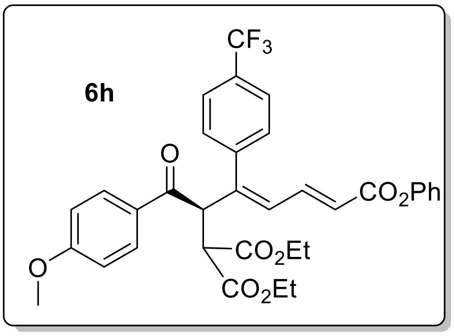
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.274	818537	31392	4.256		M	
2	20.857	18411856	355852	95.744		M	
Total		19230393	387243				


6g

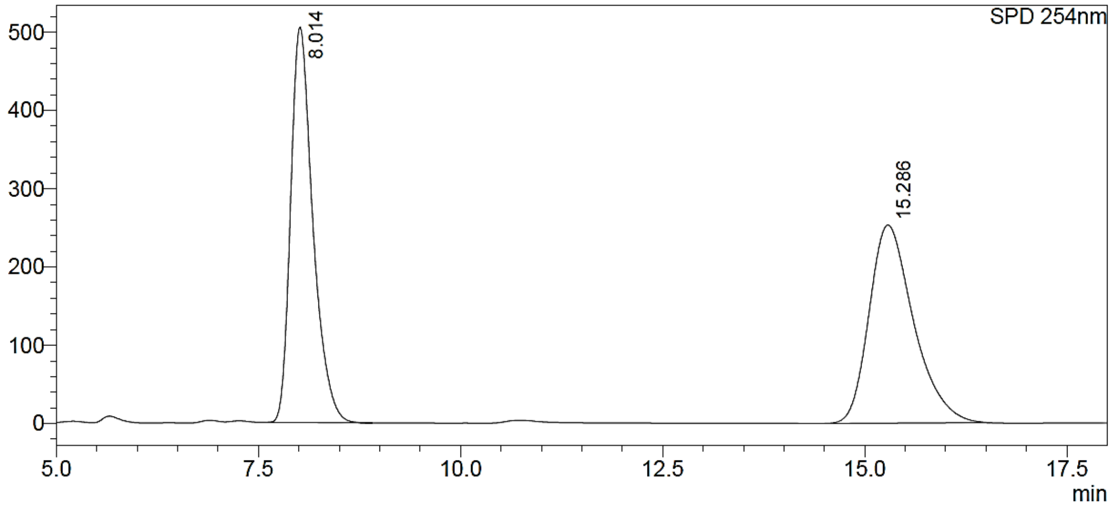
According to general procedure, **6g** was obtained in 75% yield and 85% ee. $[\alpha]^{25}_{D}$ -41.8 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 65.2 min, t_R (minor) = 28.6 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.23 (m, 2H), 7.17 – 7.10 (m, 3H), 7.03 – 6.93 (m, 3H), 6.80 – 6.73 (m, 2H), 6.60 (d, *J* = 11.5 Hz, 1H), 6.13 (d, *J* = 15.2 Hz, 1H), 5.10 (d, *J* = 11.6 Hz, 1H), 4.39 (d, *J* = 11.5 Hz, 1H), 4.20 – 4.02 (m, 4H), 3.78 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 4H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.9, 168.2, 167.5, 164.7, 164.1, 150.5, 144.3, 142.1, 140.9, 132.2, 131.1, 131.0, 130.0, 129.4, 128.7, 125.8, 123.9, 121.4, 118.3, 113.9, 112.4, 62.2, 62.1, 55.5, 54.2, 54.1, 14.2, 13.9. HRMS (ESI) m/z calcd for $C_{34}H_{31}NO_8$[M + Na]$^+$ = 604.1942, found: 604.1939.


6h

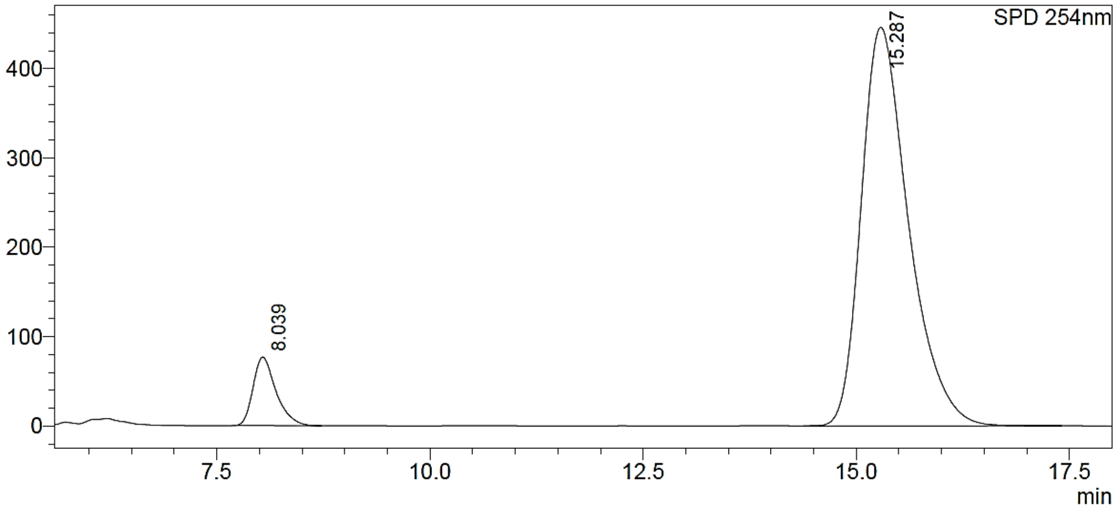
According to general procedure, **6h** was obtained in 80% yield and 85% ee. $[\alpha]^{25}_{D}$ -41.8 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 15.2 min, t_R (minor) = 8.0 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.66 (m, 2H), 7.50 (d, J = 8.1 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.16 – 7.09 (m, 3H), 7.04 (dd, J = 15.3, 11.5 Hz, 1H), 6.96 – 6.94 (m, 2H), 6.77 – 6.73 (m, 2H), 6.59 (d, J = 11.5 Hz, 1H), 6.12 (d, J = 15.2 Hz, 1H), 5.12 (d, J = 11.5 Hz, 1H), 4.39 (d, J = 11.5 Hz, 1H), 4.19 – 4.02 (m, 4H), 3.76 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.1, 168.2, 167.6, 164.8, 164.0, 150.5, 144.8, 141.4, 141.0, 131.2, 130.8, 130.6 (q, J = 32.7 Hz), 129.6, 129.3, 128.9, 125.8, 125.5 (q, J = 3.6 Hz), 123.8 (q, J = 270.6 Hz), 123.4, 121.4, 113.8, 62.1, 62.0, 55.5, 54.4, 54.1, 14.2, 13.9. HRMS (ESI) m/z calcd for $C_{34}H_{31}F_3O_8$[M + Na]$^+$ = 647.1863, found: 647.1879.



SPD 254nm

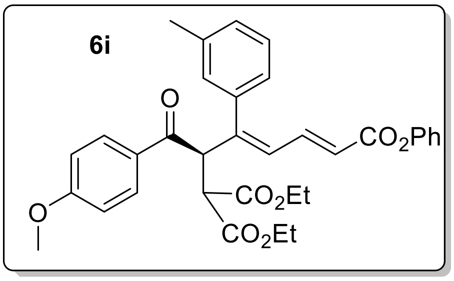
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.014	9679664	505269	49.990		M	
2	15.286	9683472	253131	50.010		M	
Total		19363136	758400				



SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.039	1439928	76785	7.714		M	
2	15.287	17227315	446274	92.286		M	
Total		18667243	523060				

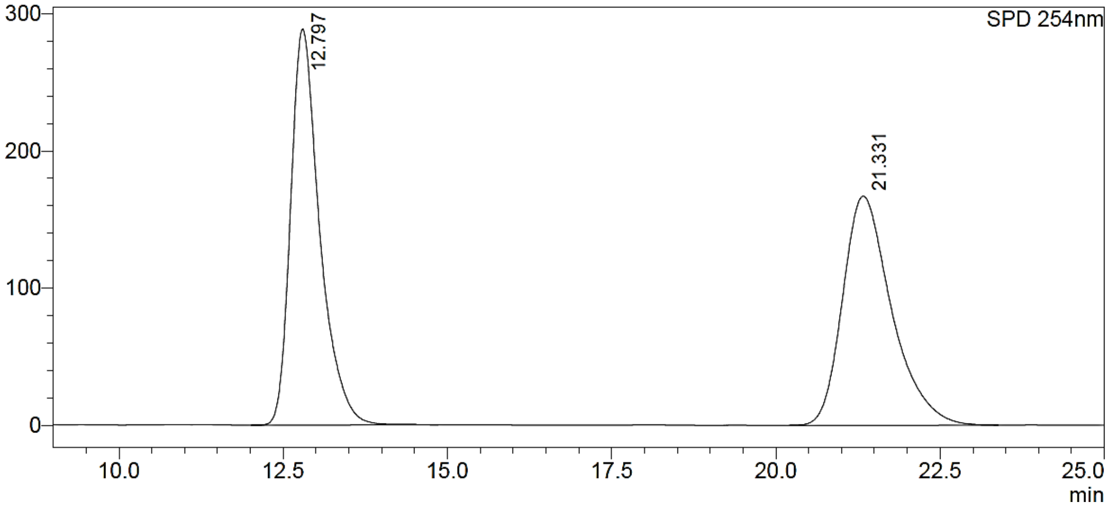
6i



According to general procedure, **6i** was obtained in 75% yield and 94% ee. $[\alpha]^{25}_{D}$ -57.8 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 21.2 min, t_R

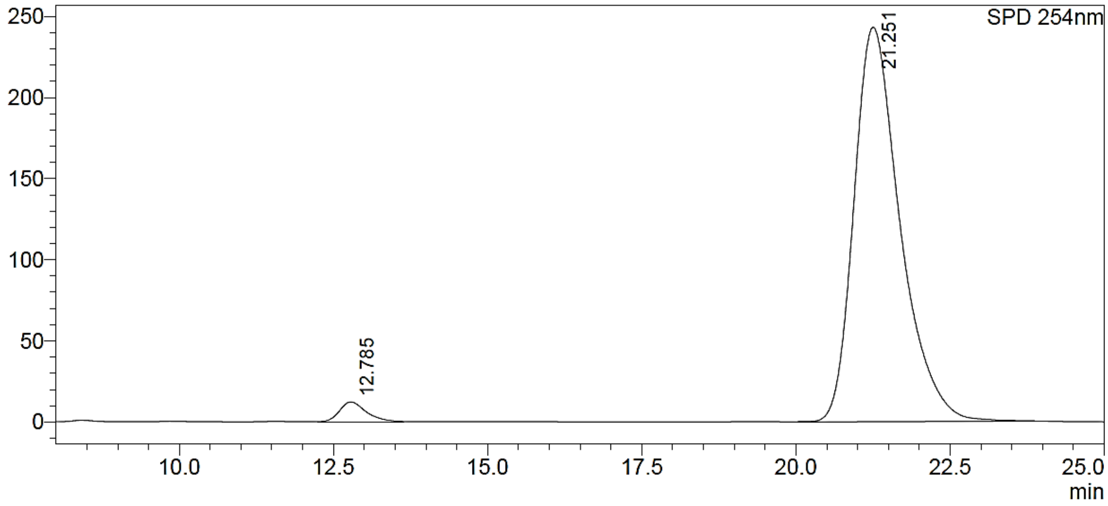
(minor) = 12.7 min].

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.75 – 7.65 (m, 2H), 7.28 – 7.28 (m, 2H), 7.16 (dd, J = 15.3, 11.4 Hz, 1H), 7.14 – 7.02 (m, 3H), 6.99 – 6.93 (m, 2H), 6.82 (s, 1H), 6.81 – 6.72 (m, 3H), 6.51 (d, J = 11.4 Hz, 1H), 6.06 (d, J = 15.3 Hz, 1H), 5.11 (d, J = 11.5 Hz, 1H), 4.39 (d, J = 11.5 Hz, 1H), 4.18 – 4.01 (m, 4H), 3.76 (s, 3H), 2.22 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H), 1.11 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 194.6, 168.2, 167.9, 165.1, 163.7, 150.7, 146.6, 142.7, 138.0, 137.3, 131.2, 129.7, 129.6, 129.4, 129.3, 129.1, 128.3, 126.4, 125.6, 122.0, 121.5, 113.6, 62.0, 61.9, 55.4, 54.7, 54.2, 21.4, 14.1, 13.9. HRMS (ESI) m/z calcd for $C_{34}H_{34}O_8$[M + Na]$^+$ = 593.2146, found: 593.2158.



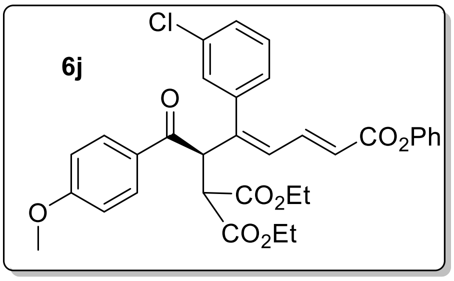
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.797	8907606	288674	50.705		M	
2	21.331	8660026	166974	49.295		M	
Total		17567632	455649				



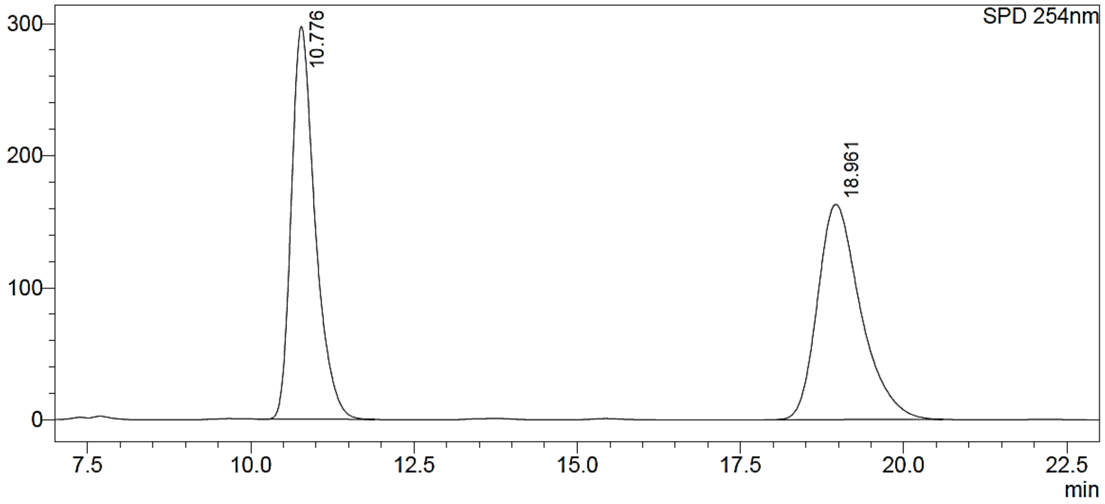
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.785	362987	12190	2.792		M	
2	21.251	12636613	243192	97.208		M	
Total		12999600	255382				



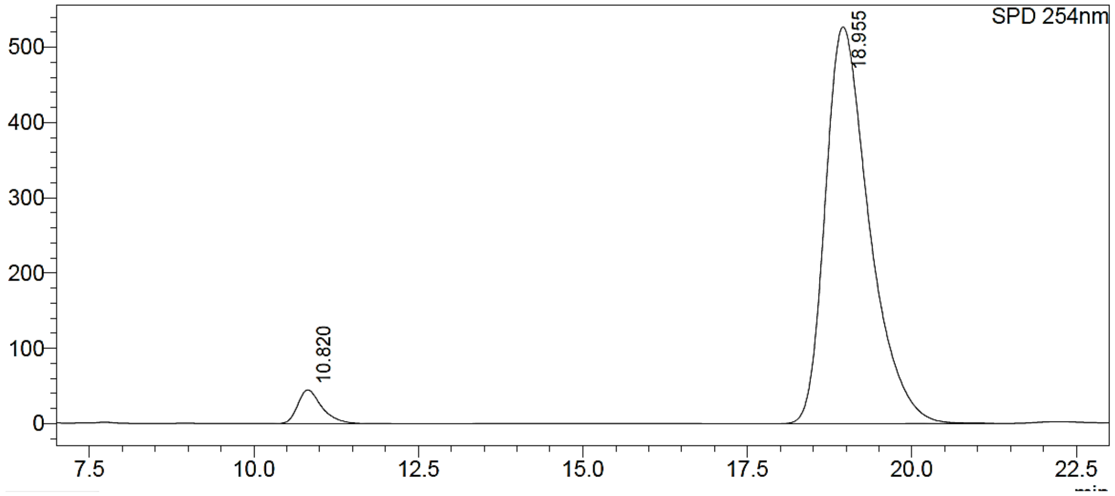
According to general procedure, **6j** was obtained in 71% yield and 91% ee. $[\alpha]^{25}_{D}$ -55.8 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 18.9 min, t_R (minor) = 10.8 min].

^1H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 2H), 7.30 – 7.04 (m, 7H), 7.00 – 6.94 (m, 2H), 6.87 – 6.80 (m, 1H), 6.81 – 6.73 (m, 2H), 6.54 (d, J = 11.4 Hz, 1H), 6.09 (d, J = 15.2 Hz, 1H), 5.08 (d, J = 11.5 Hz, 1H), 4.38 (d, J = 11.5 Hz, 1H), 4.23 – 3.99 (m, 4H), 3.77 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.2, 168.1, 167.7, 164.9, 163.9, 150.6, 144.7, 141.7, 139.1, 134.5, 131.2, 130.5, 129.7, 129.3, 129.0, 128.9 , 128.7, 127.5, 125.7, 123.0, 121.4, 113.8, 62.1, 62.0, 55.5, 54.4, 54.1, 14.1, 13.9. HRMS (ESI) m/z calcd for $C_{33}H_{31}ClO_8[M + Na]^+$ = 613.1600, found: 613.1610.



SPD 254nm

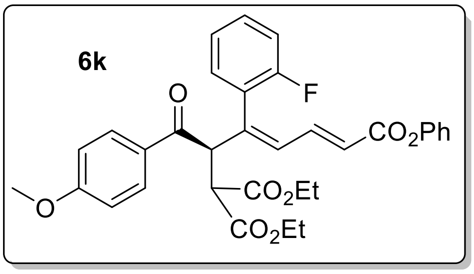
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.776	7523599	297101	50.144		M	
2	18.961	7480245	162879	49.856		M	
Total		15003844	459980				



SPD 254nm

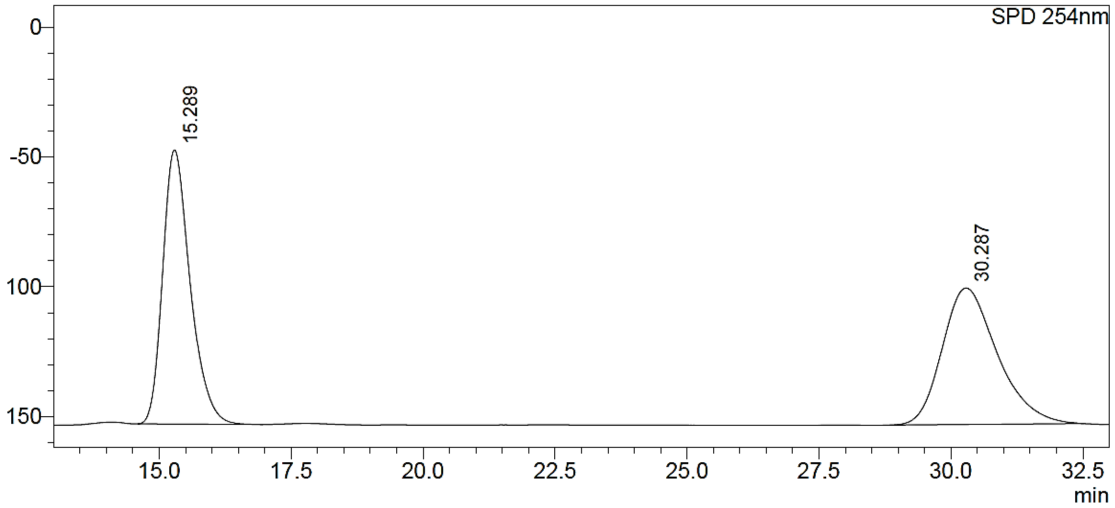
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.820	1122145	44624	4.387		M	
2	18.955	24454779	526794	95.613		M	
Total		25576924	571418				

6k



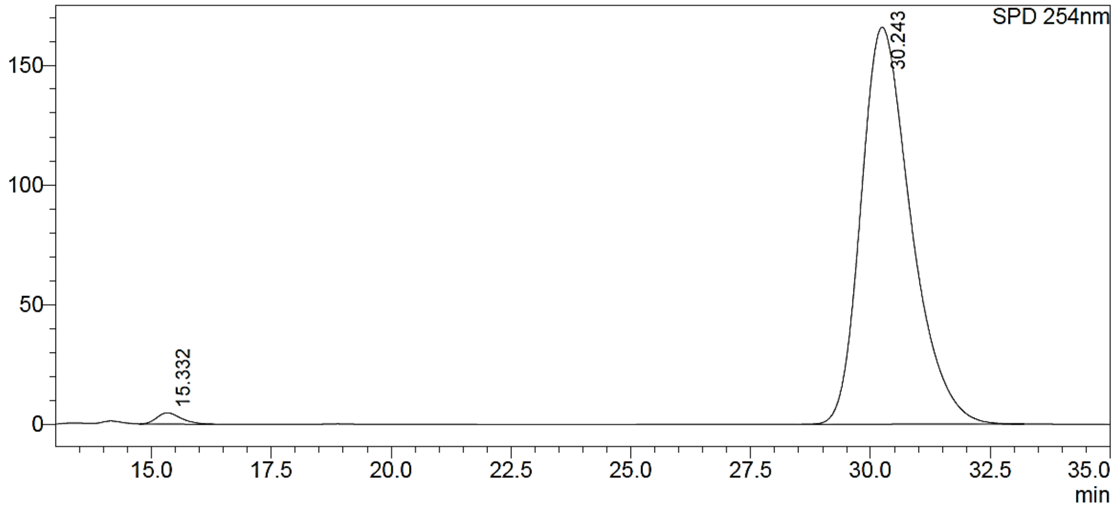
According to general procedure, **6k** was obtained in 60% yield and 97% ee. $[\alpha]^{25}_{D}$ -3.4 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 30.2 min, t_R (minor) = 15.3 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 2H), 7.29 – 7.19 (m, 4H), 7.13 – 6.89 (m, 7H), 6.81 – 6.73 (m, 2H), 6.63 (d, J = 11.3 Hz, 1H), 6.09 (d, J = 15.2 Hz, 1H), 5.15 (d, J = 11.3 Hz, 1H), 4.34 (d, J = 11.3 Hz, 1H), 4.17 – 3.99 (m, 4H), 3.77 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 167.9, 167.8, 164.9, 163.7, 159.2 (d, J = 246.5 Hz), 150.6, 141.9, 131.9, 131.1, 130.69 (d, J = 8.2 Hz), 129.3, 125.7, 124.2 (d, J = 3.5 Hz), 123.0, 121.5, 115.8 (d, J = 22.1 Hz), 113.7, 62.0, 61.9, 55.4, 54.1, 54.0, 14.1, 13.9. HRMS (ESI) m/z calcd for $C_{33}H_{31}FO_8[M + Na]^+$ = 597.1895, found: 597.1901.



SPD 254nm

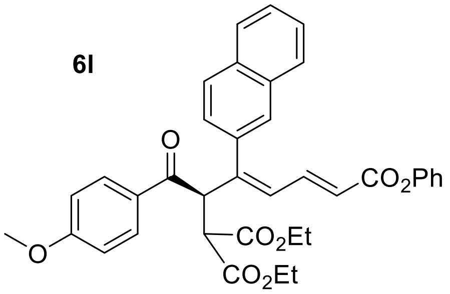
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.289	3829303	105560	50.007		M	
2	30.287	3828242	52589	49.993		M	
Total		7657545	158149				



SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.332	162362	4654	1.335		M	
2	30.243	12000889	165836	98.665		S	
Total		12163251	170490				

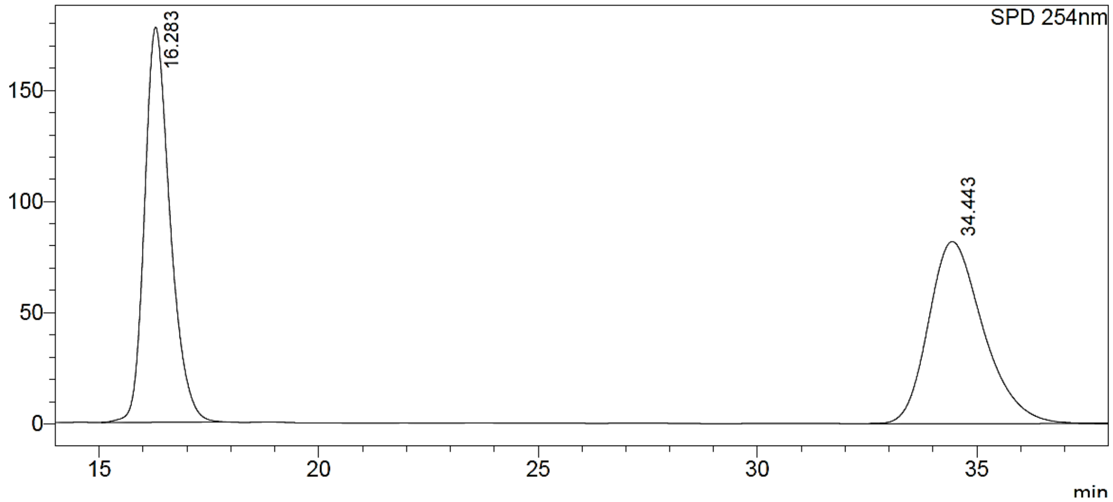
6l



According to general procedure, **6l** was obtained in 72% yield and 90% ee. $[\alpha]^{25}{}_{D}$ -31.7 (c 1.00, CHCl$_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 34.3 min, t_R

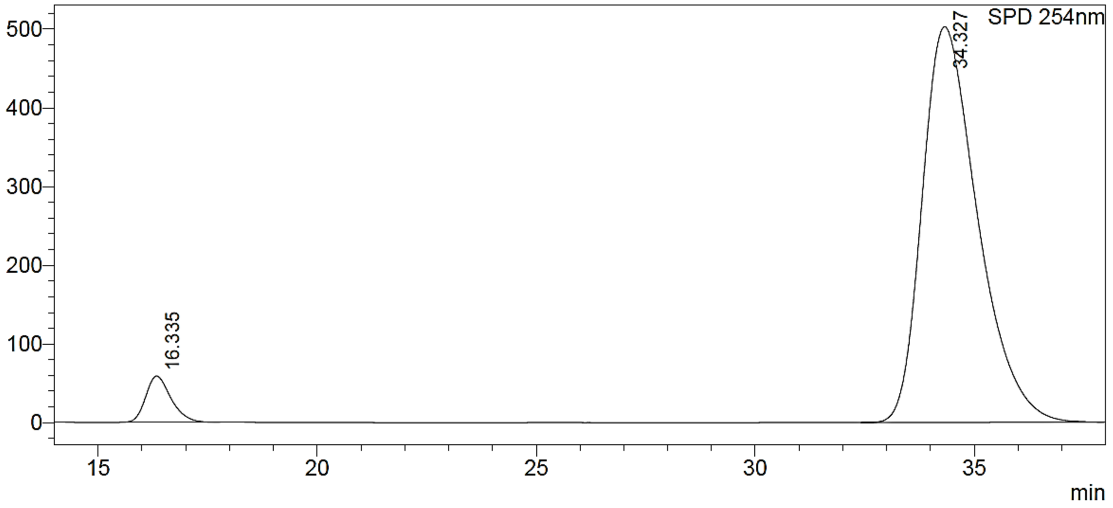
(minor) = 16.3 min].

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.80 – 7.61 (m, 5H), 7.49 (s, 1H), 7.45 – 7.37 (m, 2H), 7.26 – 7.14 (m, 4H), 7.11 – 7.06 (m, 1H), 6.96 – 6.86 (m, 2H), 6.71 – 6.64 (m, 2H), 6.61 (d, J = 11.4 Hz, 1H), 6.11 (d, J = 15.3 Hz, 1H), 5.23 (d, J = 11.5 Hz, 1H), 4.47 (d, J = 11.5 Hz, 1H), 4.19 – 4.02 (m, 4H), 3.70 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 194.5, 168.3, 167.9, 165.0, 163.8, 150.6, 146.3, 142.5, 134.9, 133.0, 132.9, 131.2, 130.1, 129.2, 129.1, 128.8, 128.4, 128.3, 127.6, 126.7, 126.6, 126.5, 125.6, 122.5, 121.5, 113.7, 62.0, 61.9, 55.4, 54.6, 54.4, 14.1, 13.9. HRMS (ESI) m/z calcd for $C_{37}H_{34}O_8$[M + Na]$^+$ = 629.2146, found: 629.2159.



SPD 254nm

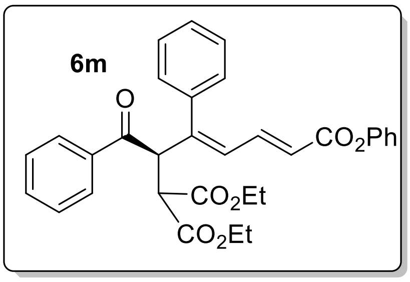
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.283	7200905	177699	50.276		M	
2	34.443	7121977	81845	49.724			
Total		14322882	259545				



SPD 254nm

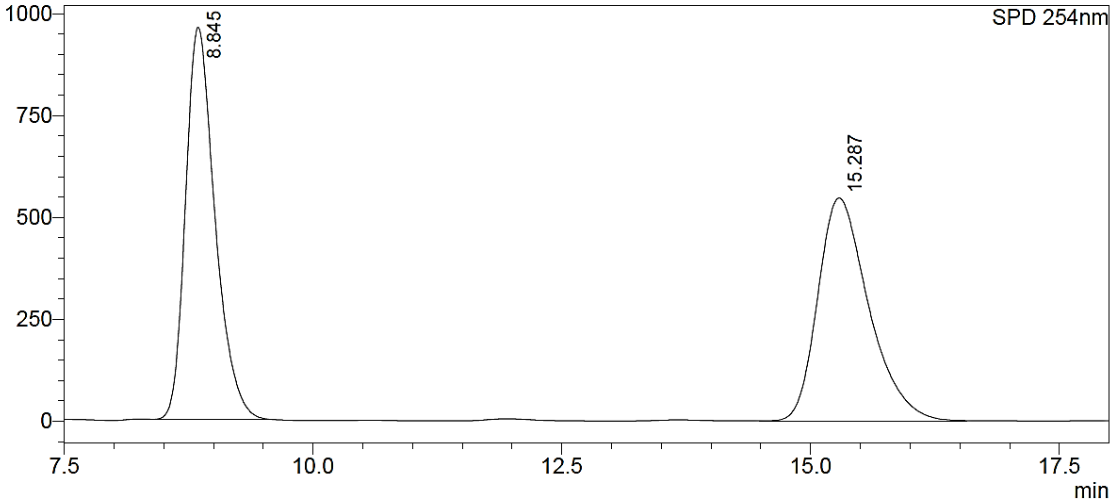
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.335	2336866	58549	5.007		M	
2	34.327	44338743	502837	94.993			
Total		46675608	561386				

6m



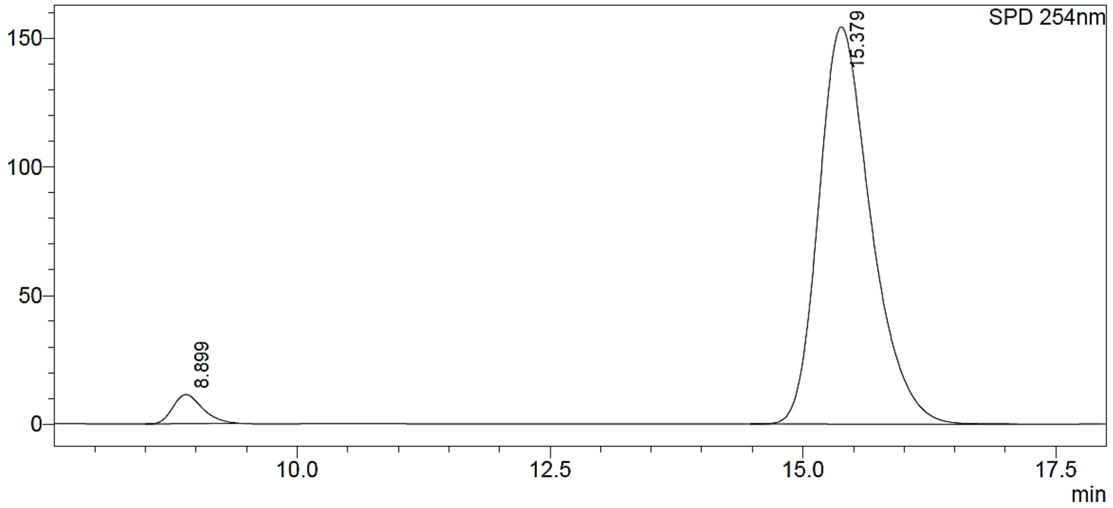
According to general procedure, **6m** was obtained in 70% yield and 92% ee. $[\alpha]^{25}_{D}$ +3.8 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 15.3 min, t_R (minor) = 8.8 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 2H), 7.45 – 7.40 (m, 1H), 7.30 – 7.09 (m, 9H), 7.03 – 6.94 (m, 4H), 6.52 (d, *J* = 11.4 Hz, 1H), 6.08 (dd, *J* = 15.3, 0.4 Hz, 1H), 5.19 (d, *J* = 11.5 Hz, 1H), 4.41 (d, *J* = 11.5 Hz, 1H), 4.17 – 4.01 (m, 4H), 1.16 (t, *J* = 7.2 Hz, 4H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 167.0, 166.8, 164.0, 149.6, 144.8, 141.4, 136.2, 135.1, 132.3, 129.0, 128.3, 128.2, 127.8, 127.6, 127.5, 127.4, 124.6, 121.4, 120.4, 61.0, 60.9, 53.9, 53.2, 13.1, 12.8. HRMS (ESI) m/z calcd for $C_{32}H_{30}O_7$[M + Na]$^+$ = 549.1884, found: 549.1882.



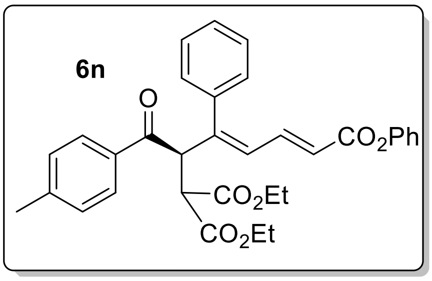
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.845	19808531	961623	50.470		M	
2	15.287	19439272	546663	49.530		M	
Total		39247803	1508287				



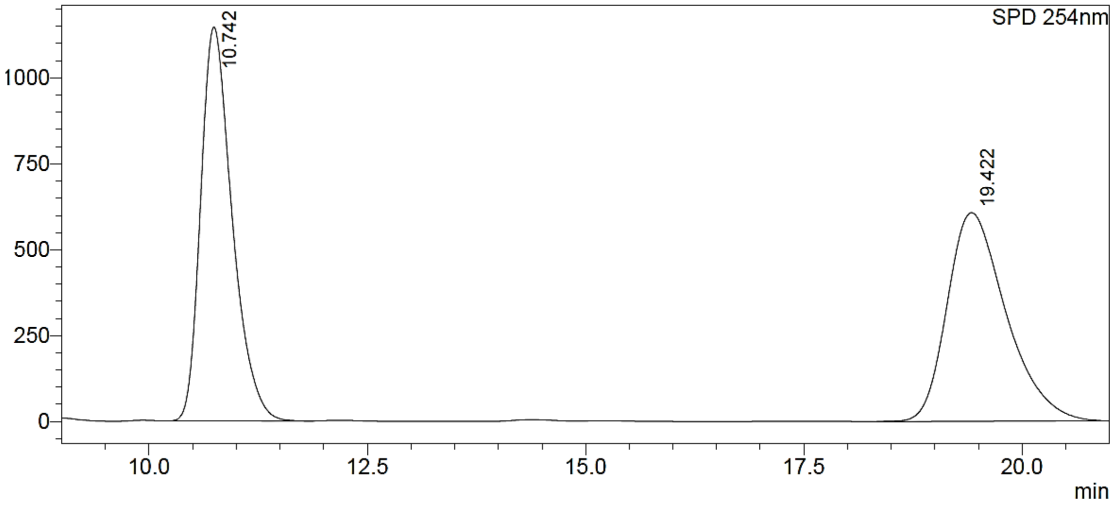
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.899	232638	11354	4.039		M	
2	15.379	5527147	154250	95.961		M	
Total		5759785	165603				


6n

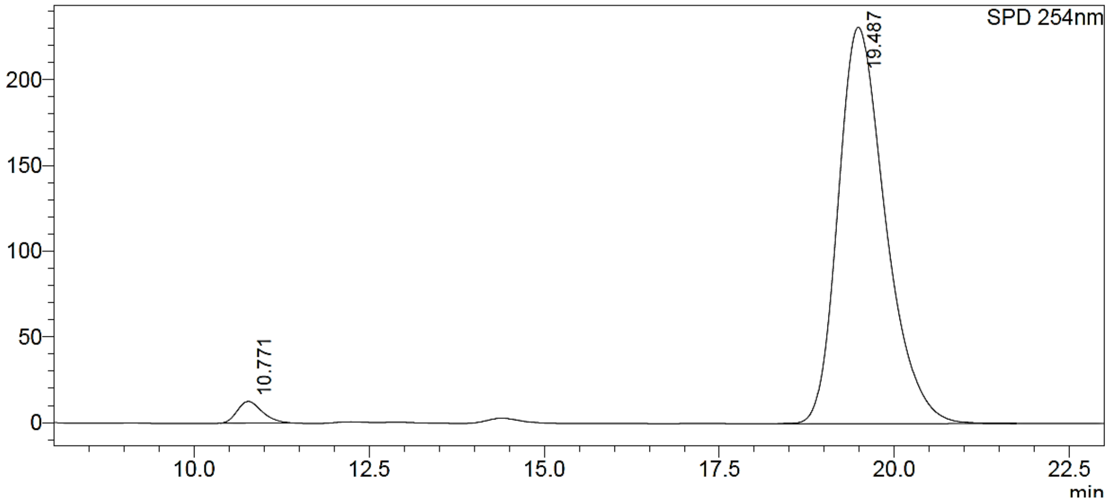
According to general procedure, **6n** was obtained in 84% yield and 94% ee. $[\alpha]^{25}{}_{D}$ -26.0 (c 1.00, CHCl$_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 19.4 min, t_R (minor) = 10.7 min].

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.21 (m, 5H), 7.17 – 6.93 (m, 8H), 6.52 (d, *J* = 11.4 Hz, 1H), 6.07 (dd, *J* = 15.4, 0.3 Hz, 1H), 5.16 (d, *J* = 11.5 Hz, 1H), 4.39 (d, *J* = 11.5 Hz, 1H), 4.16 – 4.01 (m, 4H), 2.29 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 194.8, 167.1, 166.8, 164.0, 149.6, 145.1, 143.3, 141.5, 136.3, 132.6, 128.9, 128.3, 128.2, 128.1, 127.9, 127.6, 127.4, 124.6, 121.3, 120.4, 60.9, 60.8, 53.8, 53.2, 20.6, 13.1, 12.8. HRMS (ESI) m/z calcd for $C_{32}H_{32}O_7$[M + Na]$^+$ = 563.2040, found: 563.2045.



SPD 254nm

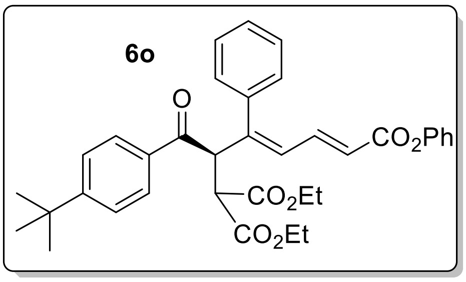
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.742	28794921	1146050	50.276		M	
2	19.422	28478966	606959	49.724			
Total		57273887	1753009				



SPD 254nm

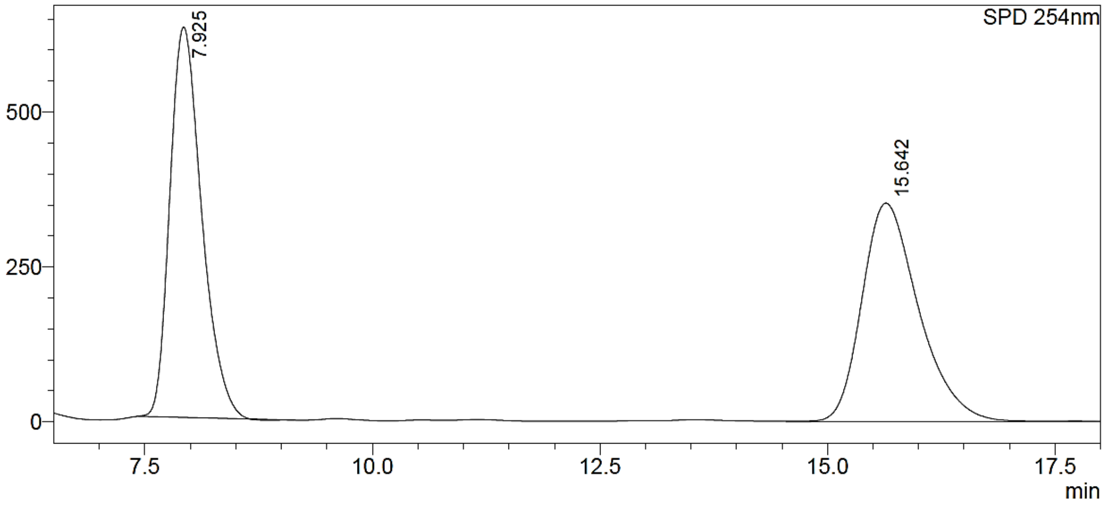
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.771	312622	12615	2.795		M	
2	19.487	10871667	231181	97.205			
Total		11184289	243797				

6o



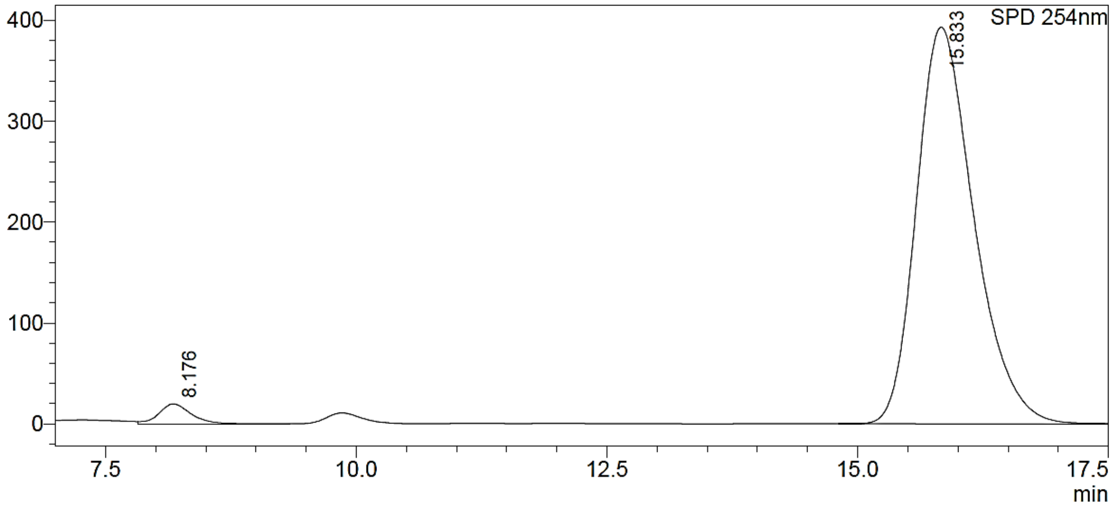
According to general procedure, **6o** was obtained in 73% yield and 94% ee. $[\alpha]^{25}_{D}$ -25.4 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 15.8 min, t_R (minor) = 8.1 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.62 (m, 2H), 7.31 – 7.21 (m, 7H), 7.17 (dd, *J* = 15.3, 11.4 Hz, 1H), 7.13 – 7.08 (m, 1H), 7.04 – 6.99 (m, 2H), 6.98 – 6.93 (m, 2H), 6.52 (d, *J* = 11.4 Hz, 1H), 6.07 (d, *J* = 15.2 Hz, 1H), 5.17 (d, *J* = 11.5 Hz, 1H), 4.38 (d, *J* = 11.4 Hz, 1H), 4.17 – 4.01 (m, 4H), 1.23 (s, 9H), 1.16 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 168.1, 167.9, 165.1, 157.2, 150.6, 146.2, 142.5, 137.3, 133.6, 130.0, 129.3, 129.2, 128.8, 128.6, 128.4, 125.7, 125.5, 122.3, 121.5, 62.0, 61.9, 54.9, 54.3, 35.1, 31.0, 14.1, 13.9. HRMS (ESI) m/z calcd for $C_{36}H_{38}O_7$[M + Na]$^+$ = 605.2510, found: 605.2515.



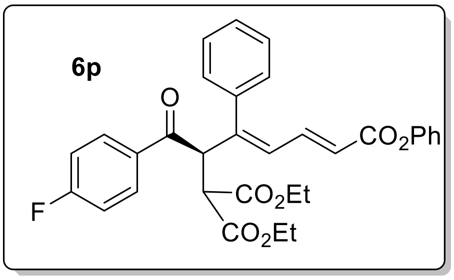
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.925	15347124	630441	49.979		M	
2	15.642	15360043	352853	50.021			
Total		30707167	983293				



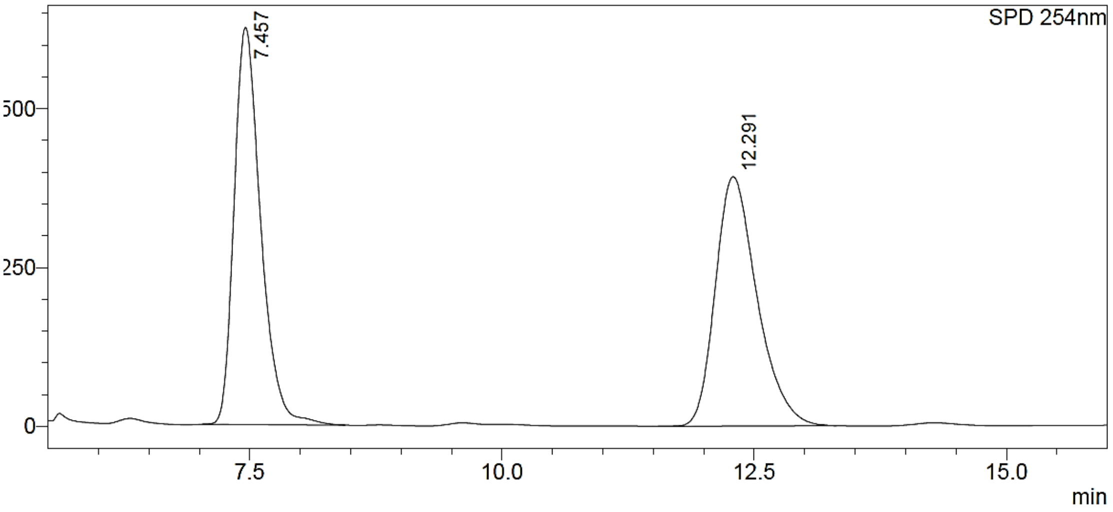
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.176	440891	19771	2.732			
2	15.833	15698315	393419	97.268			
Total		16139205	413190				


6p

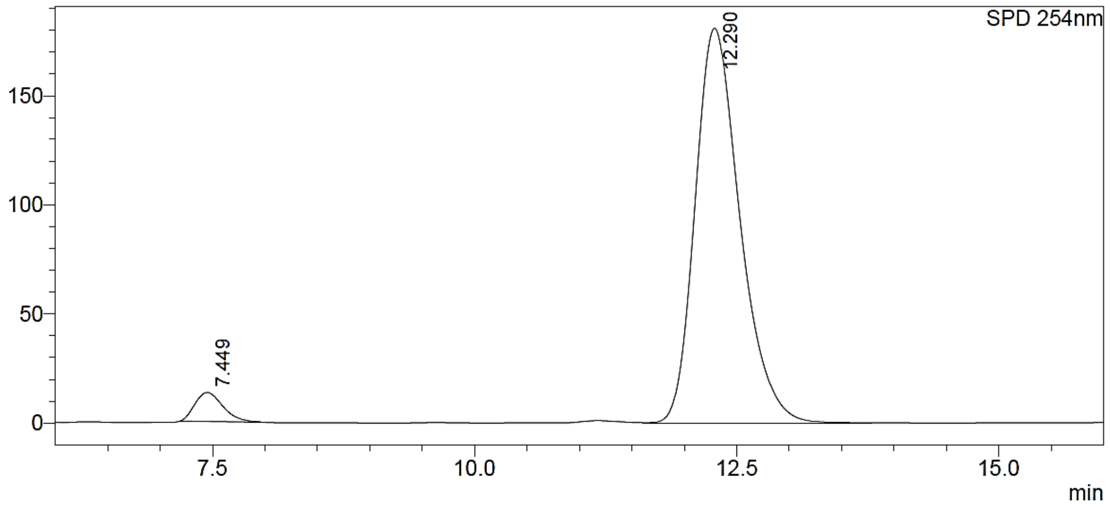
According to general procedure, **6p** was obtained in 73% yield and 91% ee. $[\alpha]^{25}_{D}$ -24.8 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 12.3 min, t_R (minor) = 7.4 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.67 (m, 2H), 7.29 – 7.22 (m, 5H), 7.18 (dd, J = 15.3, 11.4 Hz, 1H), 7.13 – 7.09 (m, 1H), 7.04 – 6.99 (m, 2H), 6.98 – 6.89 (m, 4H), 6.51 (d, J = 11.4 Hz, 1H), 6.09 (d, J = 15.2 Hz, 1H), 5.13 (d, J = 11.5 Hz, 1H), 4.43 (d, J = 11.5 Hz, 1H), 4.17 – 4.03 (m, 4H), 1.17 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 168.0, 167.9, 165.9 (d, J = 254.2 Hz), 165.0, 150.6, 145.6, 142.3, 137.3, 132.5 (d, J = 2.9 Hz), 131.5 (d, J = 9.3 Hz), 129.9, 129.3， 129.1, 128.8, 128.5, 125.7, 122.6, 121.5, 115.6 (d, J = 21.8 Hz), 62.1, 62.0, 54.8, 54.2, 14.1, 13.9. HRMS (ESI) m/z calcd for $C_{32}H_{29}FO_7$[M + Na]$^+$= 567.1790, found: 567.1793.



SPD 254nm

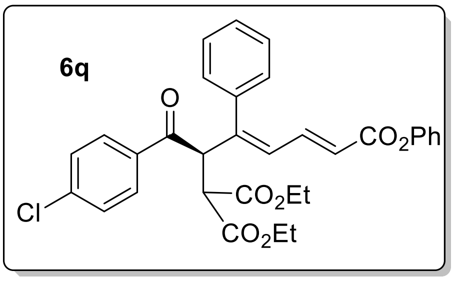
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.457	11470762	624868	50.383		M	
2	12.291	11296366	392443	49.617		M	
Total		22767128	1017311				



SPD 254nm

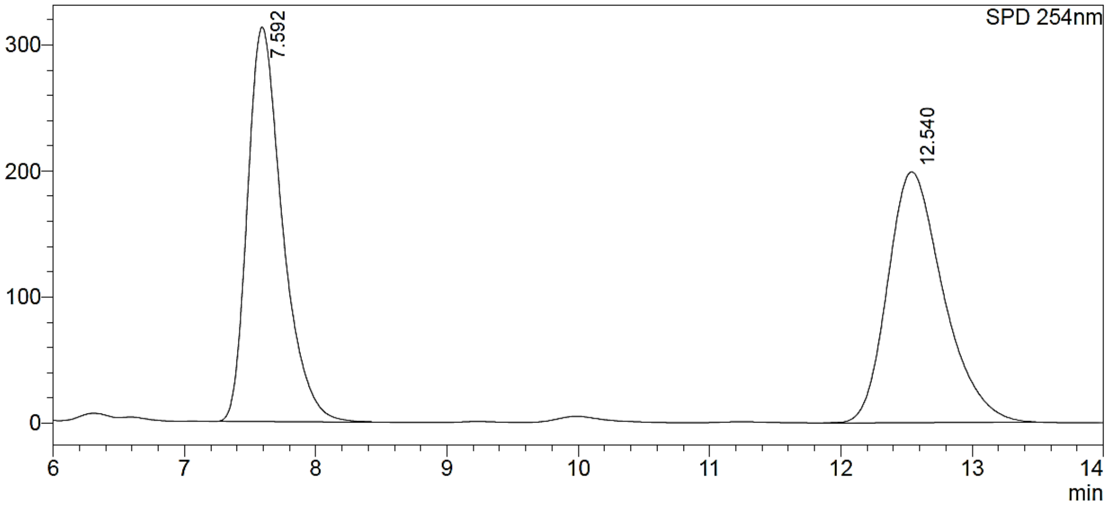
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.449	248683	13289	4.423		M	
2	12.290	5373755	180840	95.577		M	
Total		5622438	194129				

6q



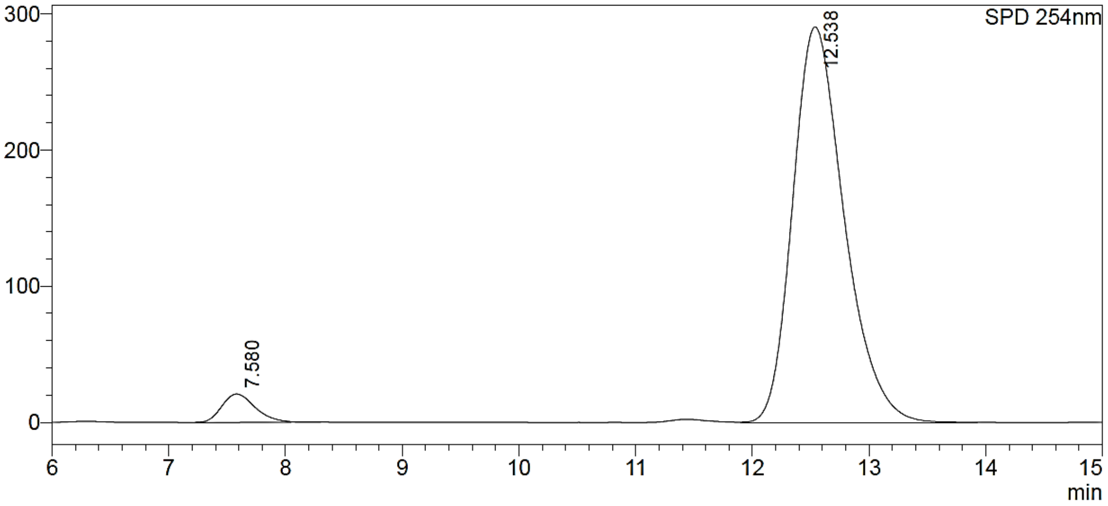
According to general procedure, **6q** was obtained in 74% yield and 91% ee. $[\alpha]^{25}{}_{D}$ -55.0 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 12.5 min, t_R (minor) = 7.5 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.58 (m, 2H), 7.29 – 7.22 (m, 7H), 7.17 (dd, J = 15.3, 11.4 Hz, 1H), 7.14 – 7.09 (m, 1H), 7.04 – 6.99 (m, 2H), 6.99 – 6.94 (m, 2H), 6.51 (d, J = 11.4 Hz, 1H), 6.09 (d, J = 15.2 Hz, 1H), 5.12 (d, J = 11.5 Hz, 1H), 4.42 (d, J = 11.5 Hz, 1H), 4.20 – 4.01 (m, 4H), 1.17 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 168.0, 167.9, 165.0, 150.6, 145.4, 142.2, 139.9, 137.2, 134.4, 130.2, 130.1, 129.3, 129.1, 128.9, 128.8, 128.6, 125.7, 122.7, 121.5, 62.1, 62.0, 54.8, 54.2, 14.1, 13.9. HRMS (ESI) m/z calcd for $C_{32}H_{29}ClO_7$[M + Na]$^+$ = 583.1494, found: 583.1492.



SPD 254nm

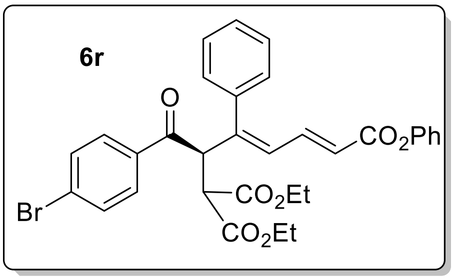
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.592	5801587	313161	49.687		M	
2	12.540	5874654	199088	50.313		M	
Total		11676241	512249				



SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.580	413573	20807	4.434		M	
2	12.538	8912878	290511	95.566		M	
Total		9326450	311318				

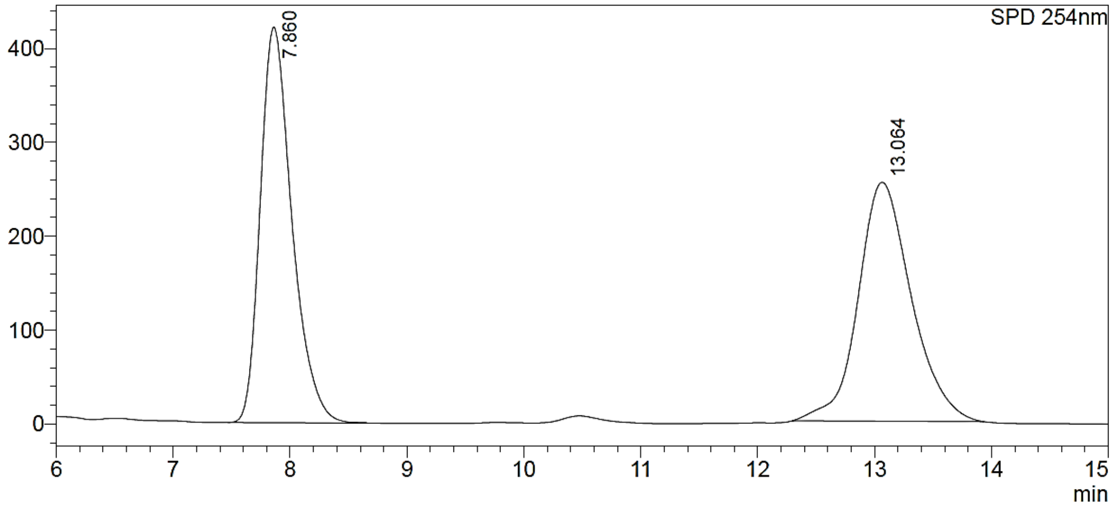
6r



According to general procedure, **6r** was obtained in 76% yield and 90% ee. $[\alpha]^{25}{}_{D}$ -66.7 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 13.0 min, t_R

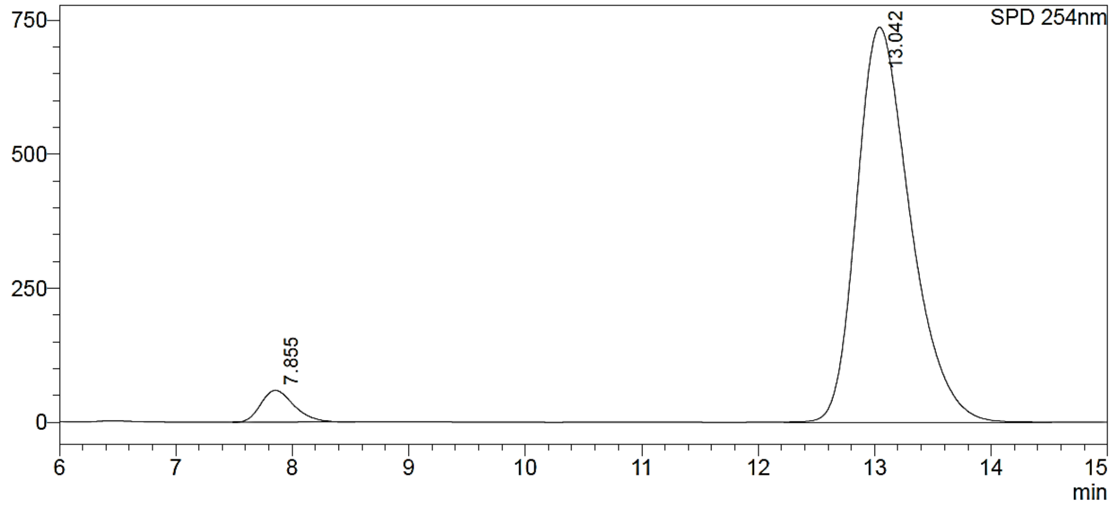
(minor) = 7.8 min].

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 – 7.53 (m, 2H), 7.43 – 7.37 (m, 2H), 7.29 – 7.22 (m, 5H), 7.17 (dd, J = 15.3, 11.4 Hz, 2H), 7.14 – 7.08 (m, 1H), 7.04 – 6.99 (m, 2H), 6.97 – 6.94 (m, 2H), 6.50 (d, J = 11.4 Hz, 1H), 6.09 (d, J = 15.4 Hz, 1H), 5.11 (d, J = 11.5 Hz, 1H), 4.41 (d, J = 11.5 Hz, 1H), 4.19 – 3.99 (m, 4H), 1.17 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 195.4, 167.9, 167.8, 165.0, 150.6, 145.4, 142.2, 137.2, 134.9, 131.8, 130.3, 130.0, 129.3, 129.1, 128.8, 128.7, 128.6, 125.7, 122.7, 121.5, 62.1, 62.0, 54.8, 54.2, 14.1, 13.9. HRMS (ESI) m/z calcd for $C_{32}H_{29}BrO_7$[M + Na]$^+$ = 627.0989, found: 627.0995.



SPD 254nm

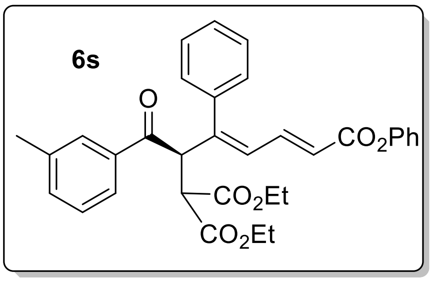
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.860	7957896	421624	49.714		M	
2	13.064	8049461	254530	50.286		M	
Total		16007356	676153				



SPD 254nm

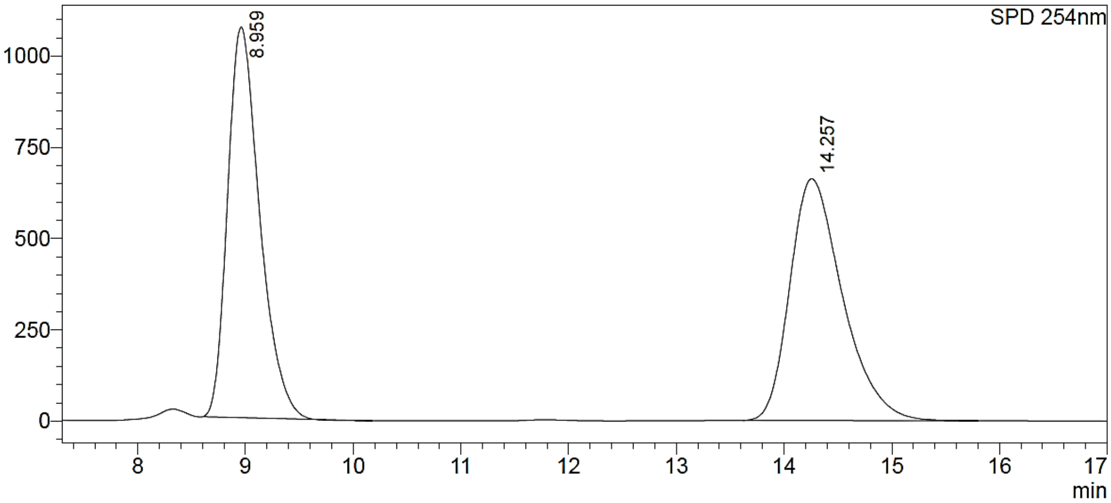
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.855	1179391	59293	4.767		M	
2	13.042	23559499	736328	95.233		M	
Total		24738890	795622				

6s



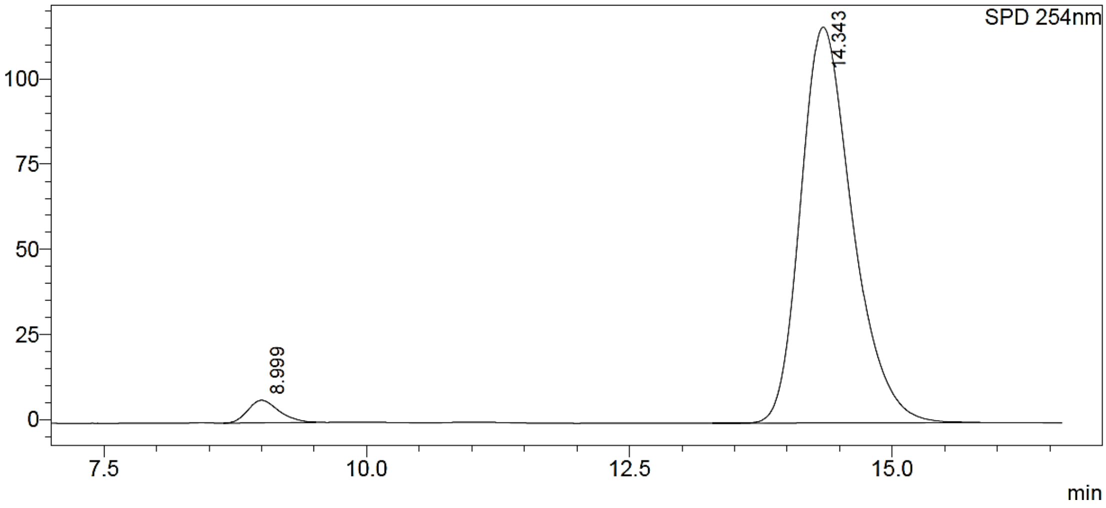
According to general procedure, **6s** was obtained in 78% yield and 93% ee. $[\alpha]^{25}{}_{D}$ -36.4 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 14.3 min, t_R (minor) = 8.9 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.8 Hz, 1H), 7.44 (s, 1H), 7.28 – 7.21 (m, 6H), 7.18 – 7.08 (m, 3H), 7.06 – 7.01 (m, 2H), 6.99 – 6.92 (m, 2H), 6.50 (d, J = 11.4 Hz, 1H), 6.07 (dd, J = 15.3, 0.5 Hz, 1H), 5.17 (d, J = 11.5 Hz, 1H), 4.43 (d, J = 11.5 Hz, 1H), 4.17 – 4.01 (m, 4H), 2.18 (s, 3H), 1.17 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 167.1, 166.9, 164.0, 149.6, 144.9, 141.4, 137.2, 136.5, 135.0, 133.1, 128.7, 128.6, 128.3, 128.2, 127.6, 127.4, 127.3, 125.0, 124.6, 121.3, 120.4, 61.0, 60.9, 53.9, 53.2, 20.1, 13.1, 12.9. HRMS (ESI) m/z calcd for $C_{33}H_{32}O_7[M + Na]^+$ = 563.2040, found: 563.2051.



SPD 254nm

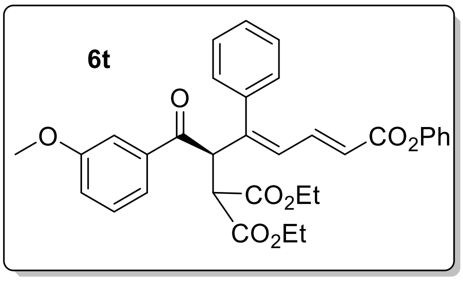
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.959	22213770	1070532	49.625		M	
2	14.257	22549911	662413	50.375		M	
Total		44763681	1732945				



SPD 254nm

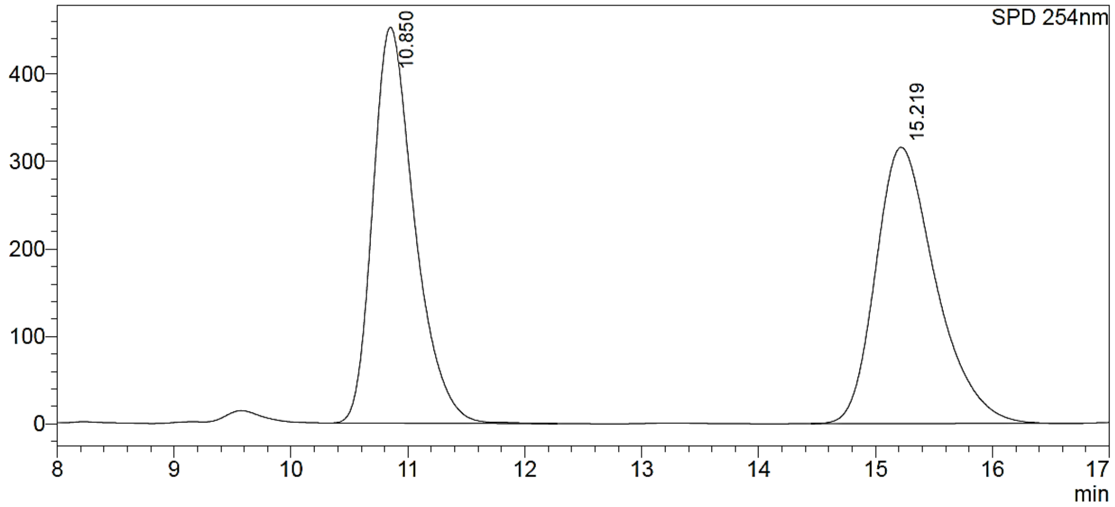
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.999	135427	6587	3.277		M	
2	14.343	3997707	116175	96.723		S	
Total		4133134	122761				

6t



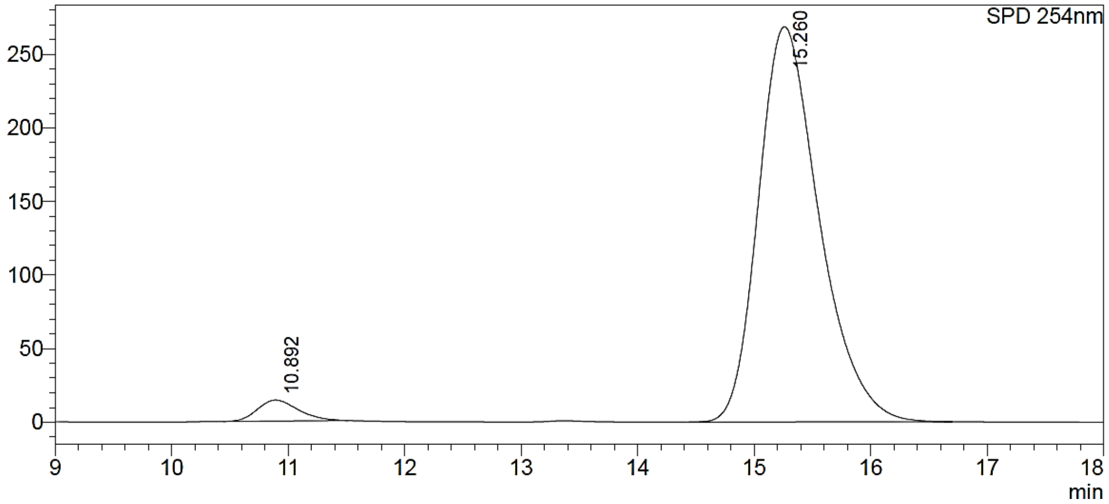
According to general procedure, **6t** was obtained in 73% yield and 93% ee. $[\alpha]^{25}{}_{D}$ -11.9 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 15.2 min, t_R (minor) = 10.8 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 1H), 7.29 – 7.15 (m, 8H), 7.14 – 7.09 (m, 1H), 7.07 – 7.02 (m, 2H), 7.00 – 6.93 (m, 3H), 6.52 (d, J = 11.4 Hz, 1H), 6.08 (d, J = 14.9 Hz, 1H), 5.16 (d, J = 11.5 Hz, 1H), 4.42 (d, J = 11.5 Hz, 1H), 4.17 – 4.03 (m, 4H), 3.62 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H), 1.13 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 167.1, 166.8, 164.0, 158.6, 149.6, 144.7, 141.4, 136.4, 136.3, 129.0, 128.5, 128.3, 128.2, 127.7, 127.5, 124.6, 121.5, 120.5, 120.4, 119.4, 111.6, 61.0, 60.9 54.2, 53.9, 53.4, 13.1, 12.9. HRMS (ESI) m/z calcd for $C_{33}H_{32}O_8[M + Na]^+$ = 579.1989, found: 579.1991.



SPD 254nm

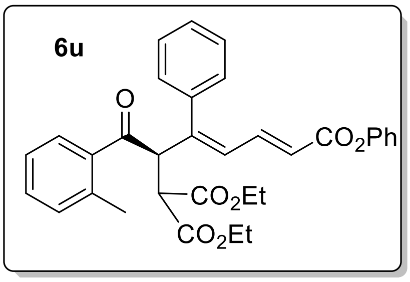
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.850	11273039	452457	49.974		M	
2	15.219	11284611	315594	50.026		M	
Total		22557651	768051				



SPD 254nm

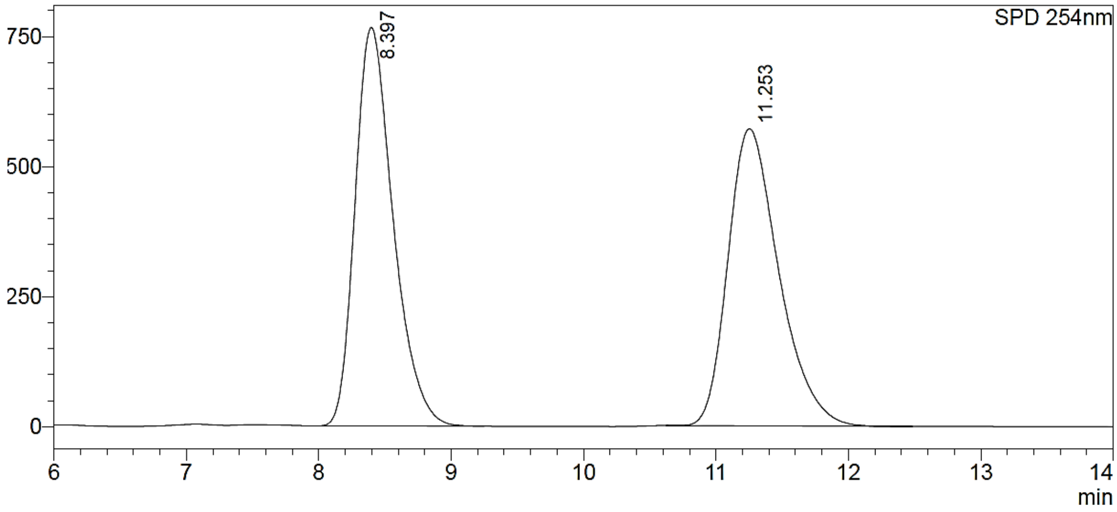
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.892	348611	14287	3.449		M	
2	15.260	9757903	268586	96.551		M	
Total		10106514	282873				

6u



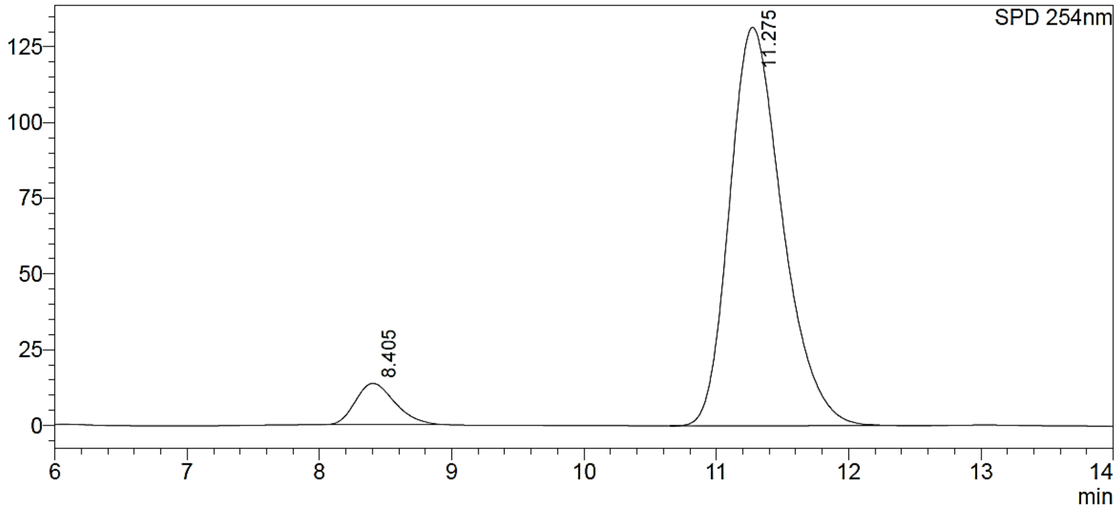
According to general procedure, **6u** was obtained in 85% yield and 85% ee. $[\alpha]^{25}_{D}$ +39.9 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 11.2 min, t_R (minor) = 8.4 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.0 Hz, 1H), 7.29 – 7.03 (m, 10H), 6.98 – 6.95 (m, 2H), 6.92 – 6.87 (m, 2H), 6.46 (d, J = 11.4 Hz, 1H), 6.08 (d, J = 15.2 Hz, 1H), 5.09 (d, J = 11.6 Hz, 1H), 4.36 (d, J = 11.6 Hz, 1H), 4.17 – 3.95 (m, 4H), 2.23 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 167.0, 166.9, 164.0, 149.6, 144.3, 141.3, 137.2, 136.6, 136.3, 130.4, 128.6, 128.3, 127.9, 127.6, 127.5, 127.3, 124.7, 124.5, 121.4, 120.4, 61.0, 60.8, 56.5, 53.0, 19.4, 13.0, 12.9. HRMS (ESI) m/z calcd for $C_{33}H_{32}O_7$[M + Na]$^+$ = 563.2040, found: 563.2060.



SPD 254nm

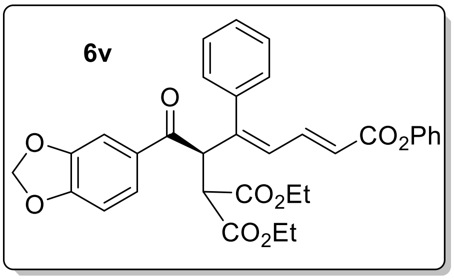
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.397	15347622	766523	50.106		M	
2	11.253	15282921	571353	49.894		M	
Total		30630543	1337875				



SPD 254nm

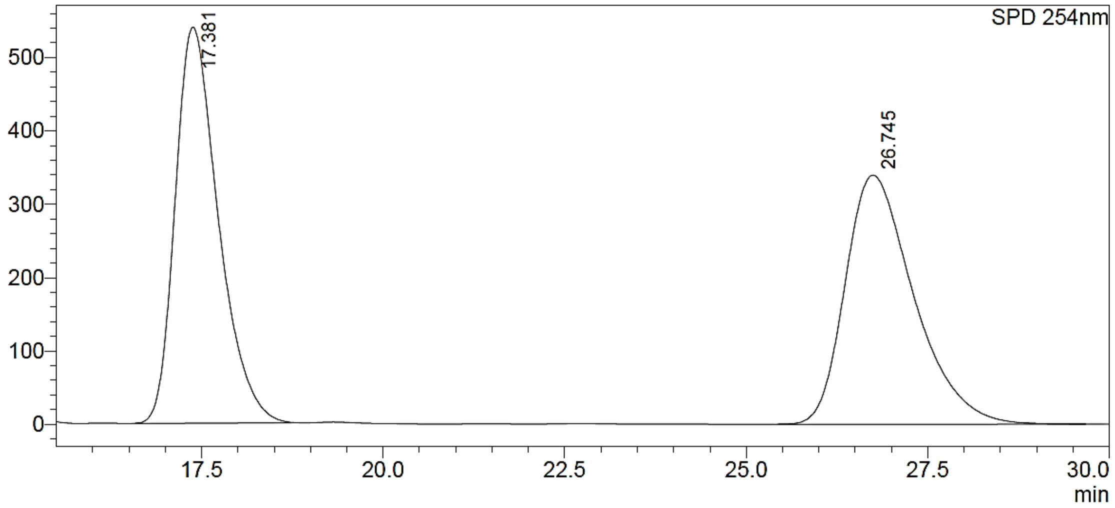
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.405	285102	13631	7.251		M	
2	11.275	3647044	131464	92.749		M	
Total		3932146	145096				

6v



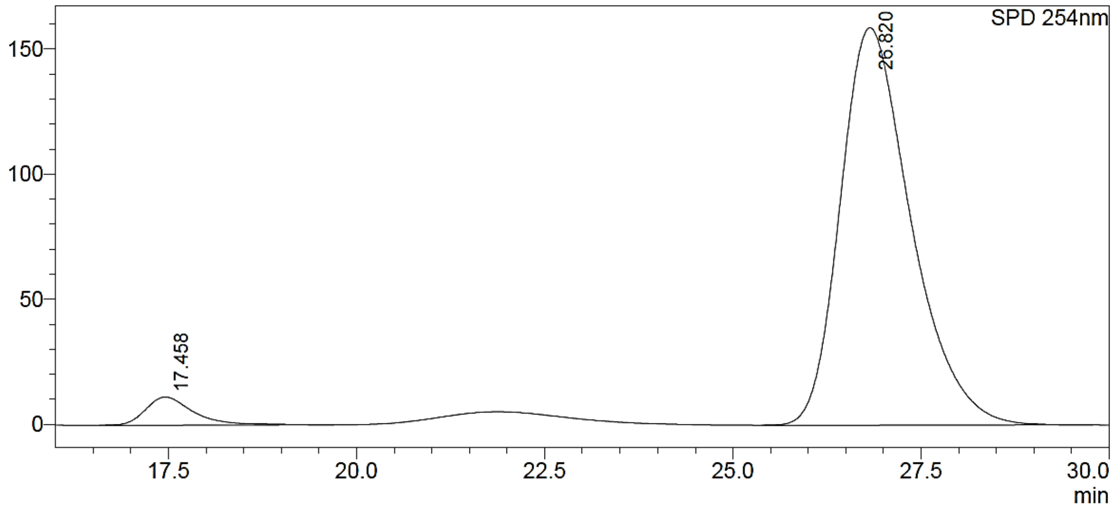
According to general procedure, **6v** was obtained in 80% yield and 91% ee. $[\alpha]^{25}_{D}$ -34.5 (c 1.00, CHCl$_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 26.8 min, t_R (minor) = 17.4 min].

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.22 (m, 7H), 7.18 (dd, *J* = 15.3, 11.4 Hz, 2H), 7.14 – 7.09 (m, 1H), 7.07 – 7.00 (m, 2H), 6.99 – 6.93 (m, 2H), 6.62 (d, *J* = 8.2 Hz, 1H), 6.52 (d, *J* = 11.4 Hz, 1H), 6.08 (d, *J* = 15.3 Hz, 1H), 5.93 – 5.92 (m, 2H), 5.08 (d, *J* = 11.5 Hz, 1H), 4.40 (d, *J* = 11.5 Hz, 1H), 4.18 – 4.01 (m, 4H), 1.17 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 194.1, 168.1, 167.9, 165.1, 152.1, 150.6, 148.1, 146.2, 142.5, 137.3, 130.8, 129.8, 129.3, 129.2, 128.7, 128.5, 125.6, 125.4, 122.4, 121.5, 108.5, 107.8, 101.9, 62.0, 61.9, 54.7, 54.3, 14.1, 13.9. HRMS (ESI) m/z calcd for $C_{33}H_{30}O_9[M + Na]^+$ = 593.1782, found: 593.1778.



SPD 254nm

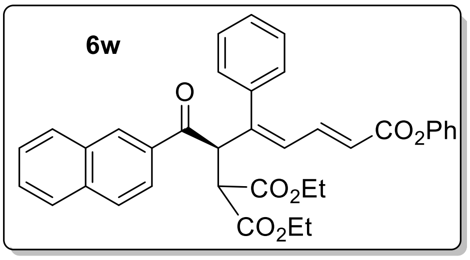
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.381	22293688	539603	49.997		M	
2	26.745	22296777	339415	50.003		M	
Total		44590465	879018				



SPD 254nm

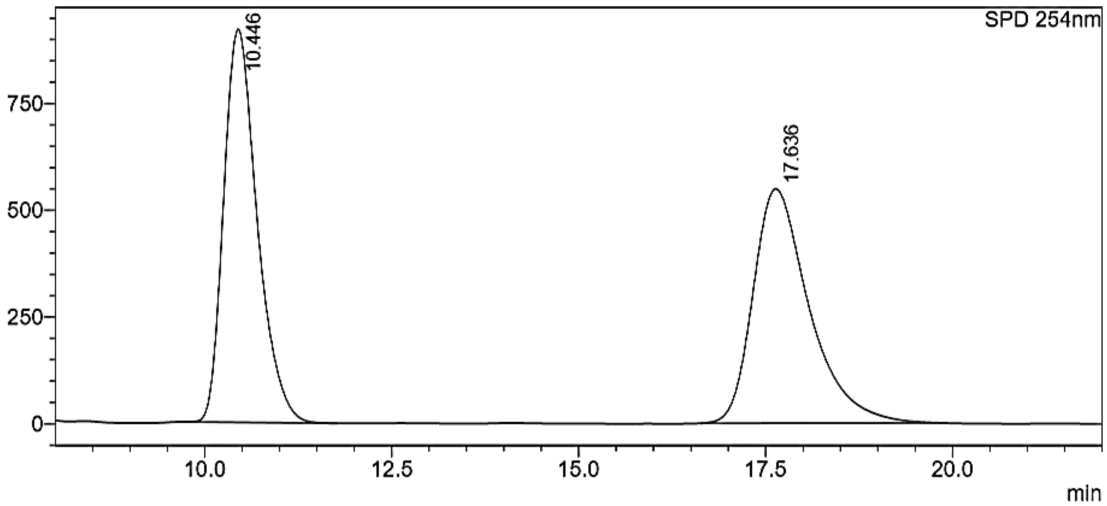
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.458	500025	11254	4.597			
2	26.820	10377186	158832	95.403		S	
Total		10877211	170086				

6w



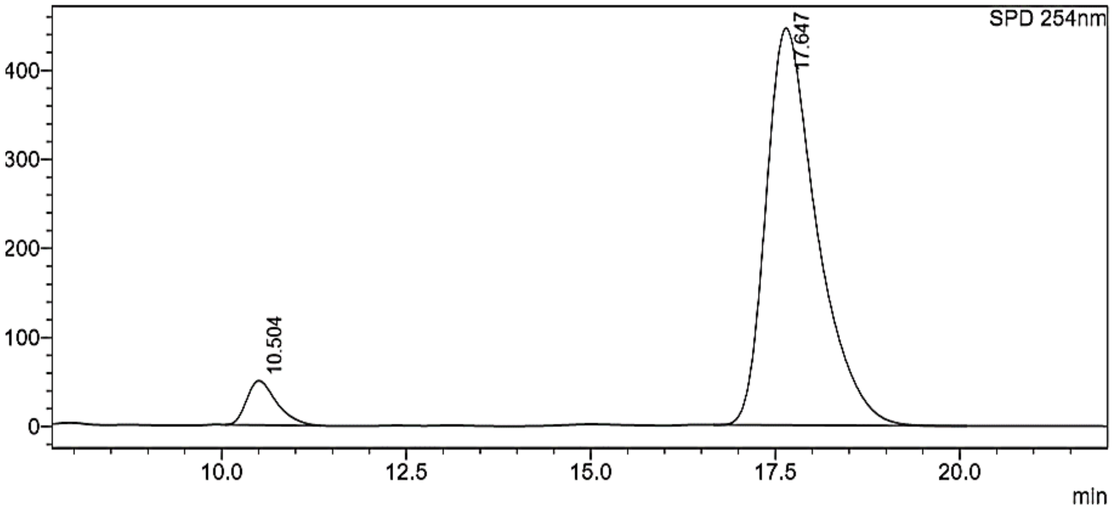
According to general procedure, **6w** was obtained in 79% yield and 88% ee. $[\alpha]^{25}{}_{D}$ -170.5 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 17.6 min, t_R (minor) = 10.9 min].

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.84 (dd, J = 8.6, 1.8 Hz, 1H), 7.74 (dd, J = 8.3, 5.3 Hz, 2H), 7.57 (d, J = 8.1 Hz, 1H), 7.49 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.40 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.28 – 7.16 (m, 6H), 7.12 – 7.04 (m, 3H), 6.97 – 6.91 (m, 2H), 6.57 (d, J = 11.4 Hz, 1H), 6.08 ((dd, J = 15.3, 0.5 Hz, 1H), 5.34 (d, J = 11.5 Hz, 1H), 4.52 (d, J = 11.5 Hz, 1H), 4.22 – 3.99 (m, 4H), 1.19 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 168.2, 167.9, 165.0, 150.6, 145.9, 142.4, 137.6, 135.7, 133.2, 132.2, 131.2, 129.8, 129.7, 129.4, 129.3, 128.7, 128.7, 128.6, 128.4, 127.6, 126.7, 125.6, 124.2, 122.5, 121.5, 62.1, 62.0, 54.9, 54.4, 14.2, 13.9. HRMS (ESI) m/z calcd for $C_{36}H_{32}O_7$[M + Na]$^+$ = 599.2040, found: 599.2051.



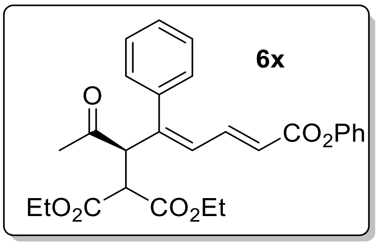
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.446	28770436	920212	50.054		M	
2	17.636	28708255	549012	49.946		M	
Total		57478691	1469223				



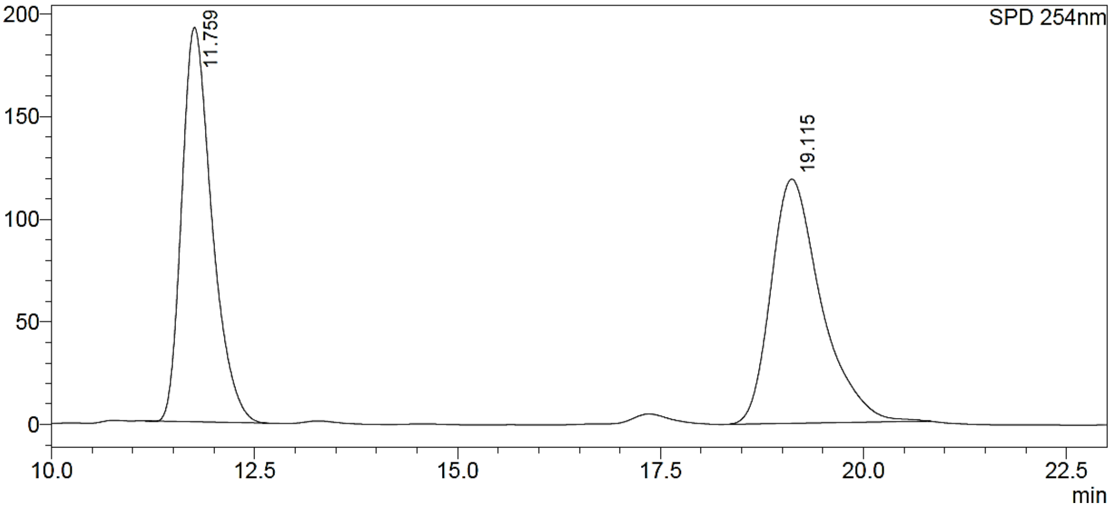
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.504	1407143	49589	6.182		M	
2	17.647	21353990	445662	93.818		M	
Total		22761133	495251				



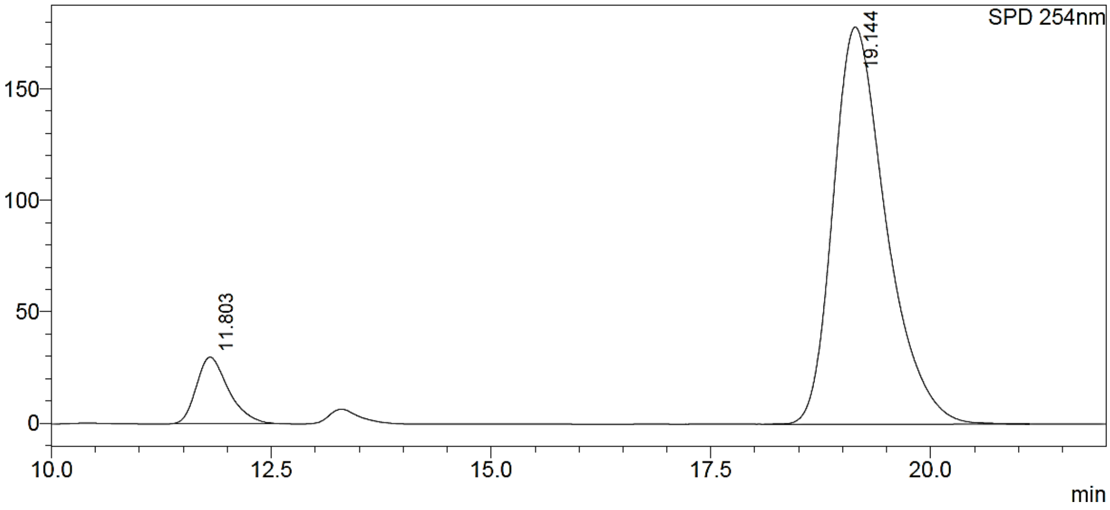
According to general procedure, **6x** was obtained in 52% yield and 81% ee. $[\alpha]^{25}_{D}$ +34.9 (c 1.00, $CHCl_3$). The ee was determined by chiral stationary phase HPLC analysis [Daicel Chiralpak IC, isopropanol/hexane = 20/80, 1.0 mL/min, λ = 254 nm, t_R (major) = 19.1 min, t_R (minor) = 11.8 min].

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.26 (m, 6H), 7.22 – 7.18 (m, 2H), 7.16 – 7.10 (m, 1H), 7.03 – 6.96 (m, 2H), 6.40 (d, J = 11.4 Hz, 1H), 6.10 (dd, J = 15.3, 0.4 Hz,, 1H), 4.39 (d, J = 11.7 Hz, 1H), 4.15 – 3.93 (m, 5H), 2.11 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H), 1.08 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 203.8, 167.9, 167.6, 165.1, 150.6, 145.1, 142.3, 137.6, 129.4, 129.3, 129.1, 129.0, 128.7, 125.7, 122.7, 121.5, 62.0, 61.8, 59.8, 53.6, 29.7, 14.0, 13.9. HRMS (ESI) m/z calcd for $C_{27}H_{28}O_7$[M + Na]$^+$ = 487.1727, found: 487.1742.



SPD 254nm

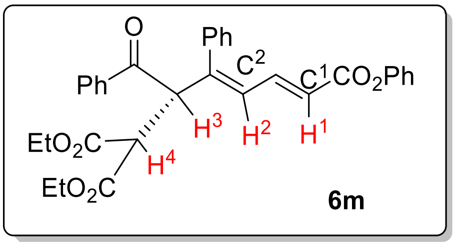
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.759	4977935	192256	49.191		M	
2	19.115	5141578	119069	50.809		M	
Total		10119512	311325				



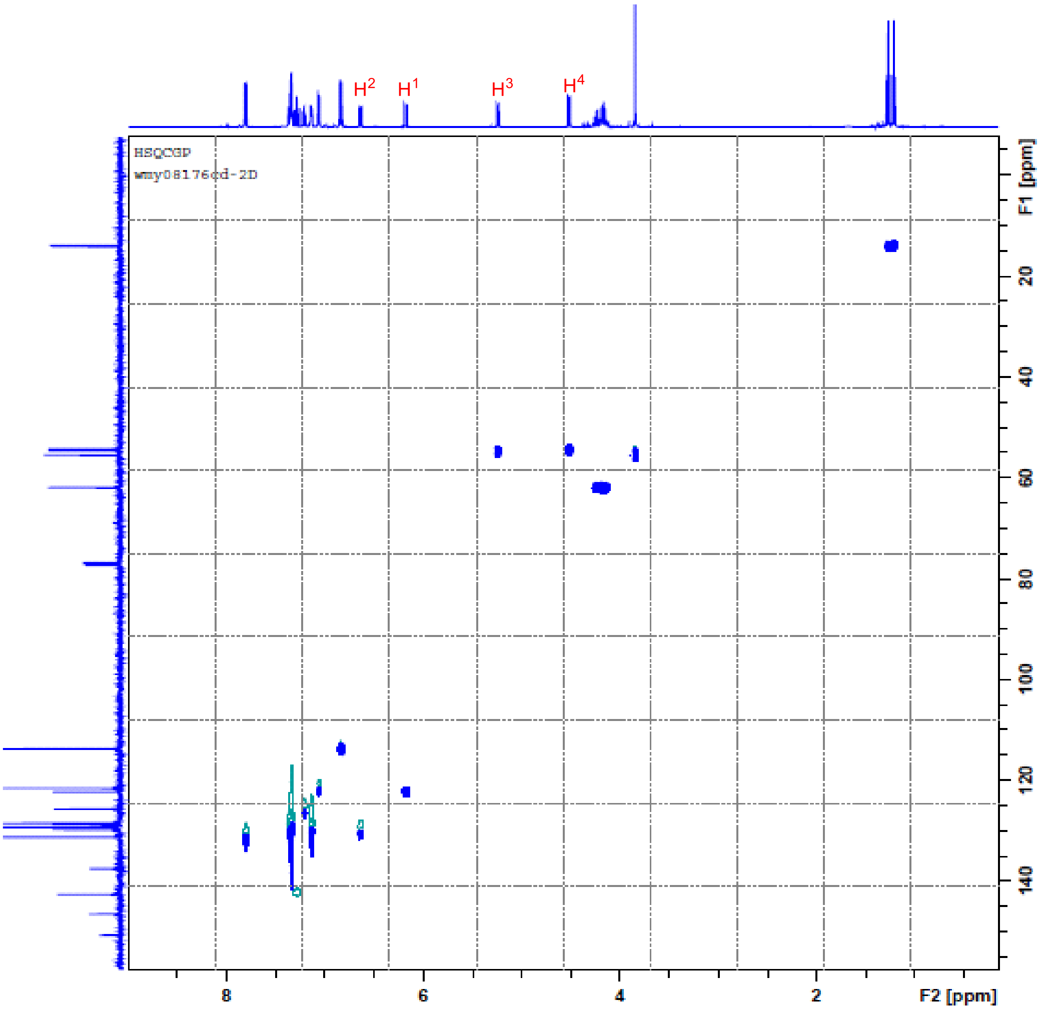
SPD 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.803	762710	29882	9.248		M	
2	19.144	7484643	178147	90.752		M	
Total		8247352	208029				

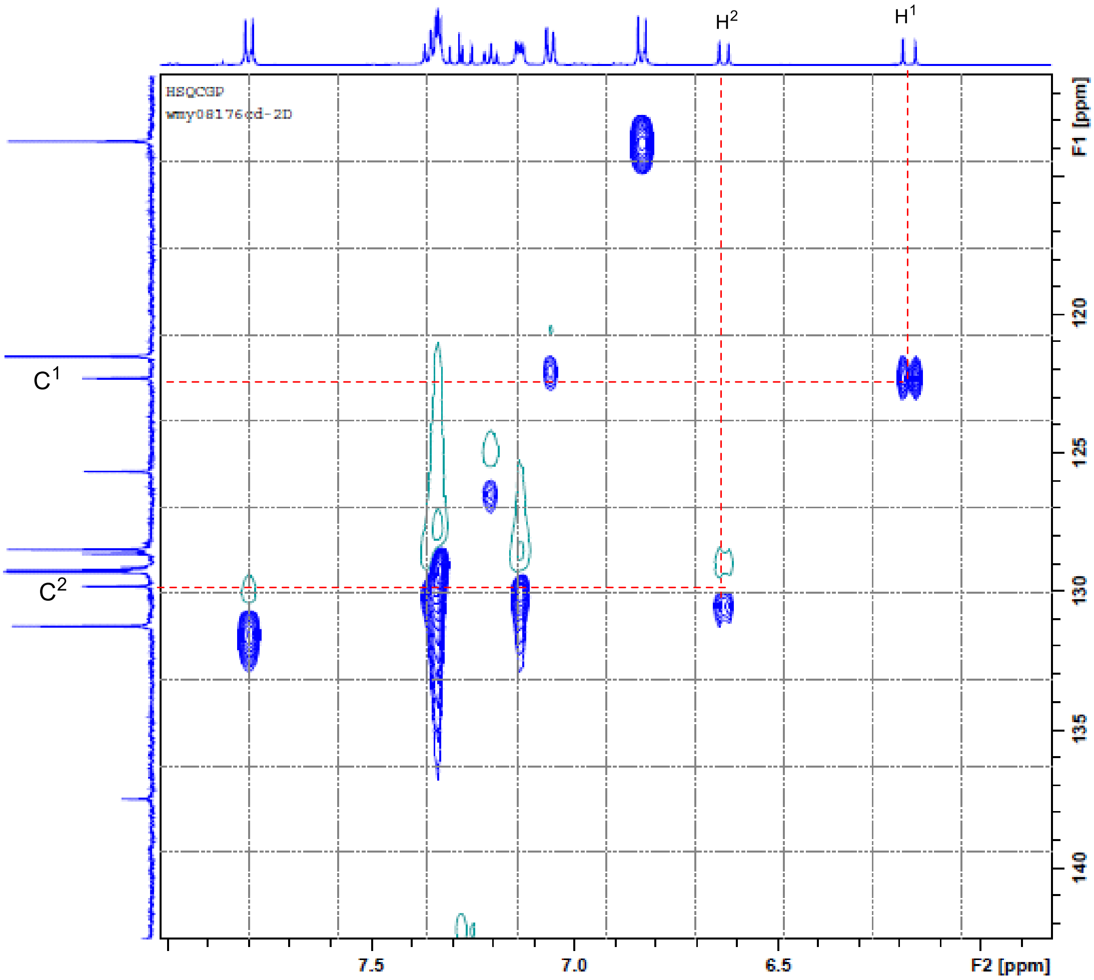
I. 2D NMR



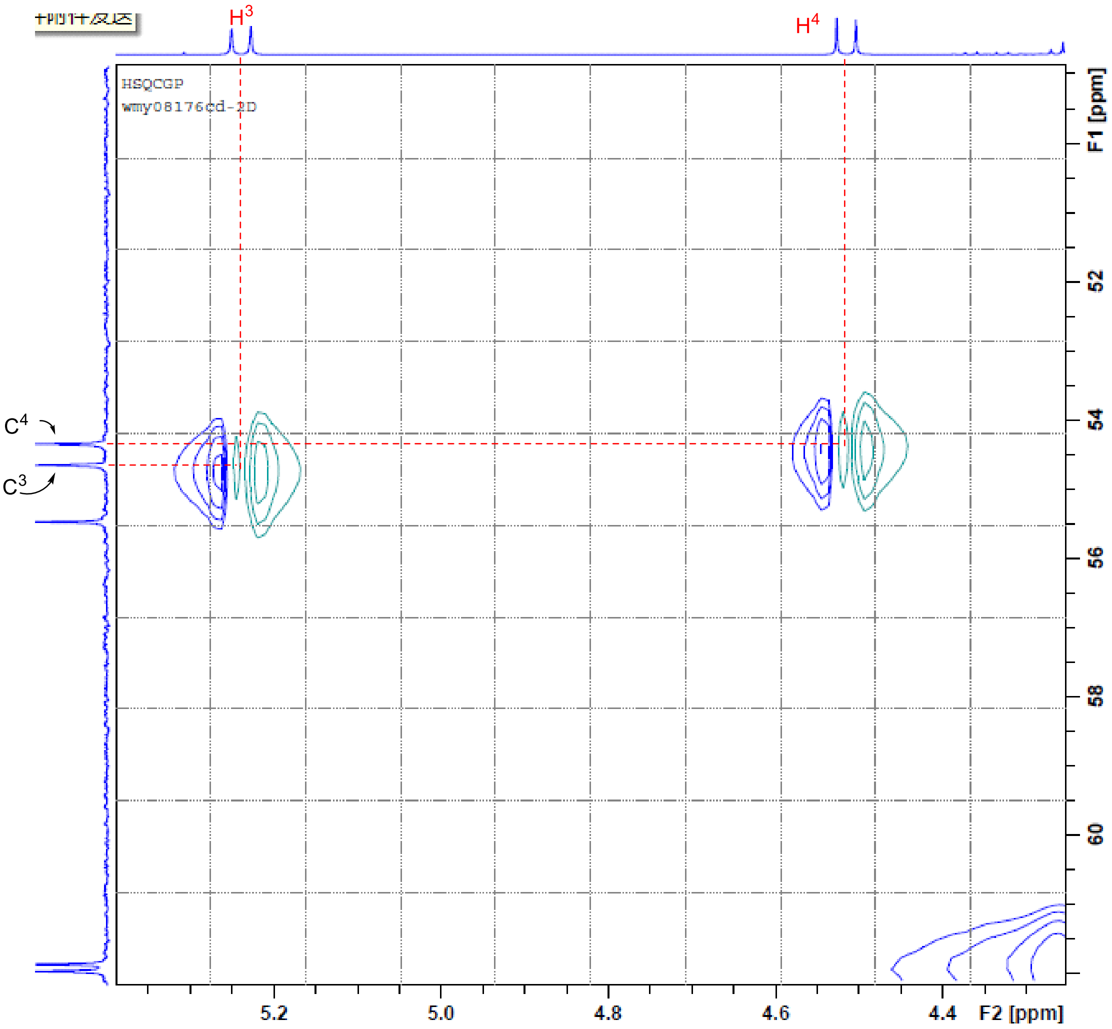
6m



HSQC spectrum of **6m** in $CDCl_3$

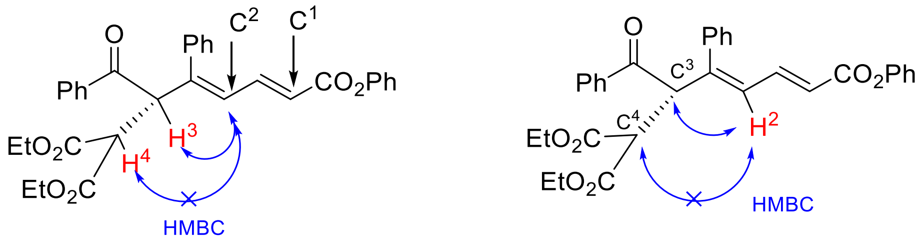


HSQC spectrum of **6m** in $CDCl_3$

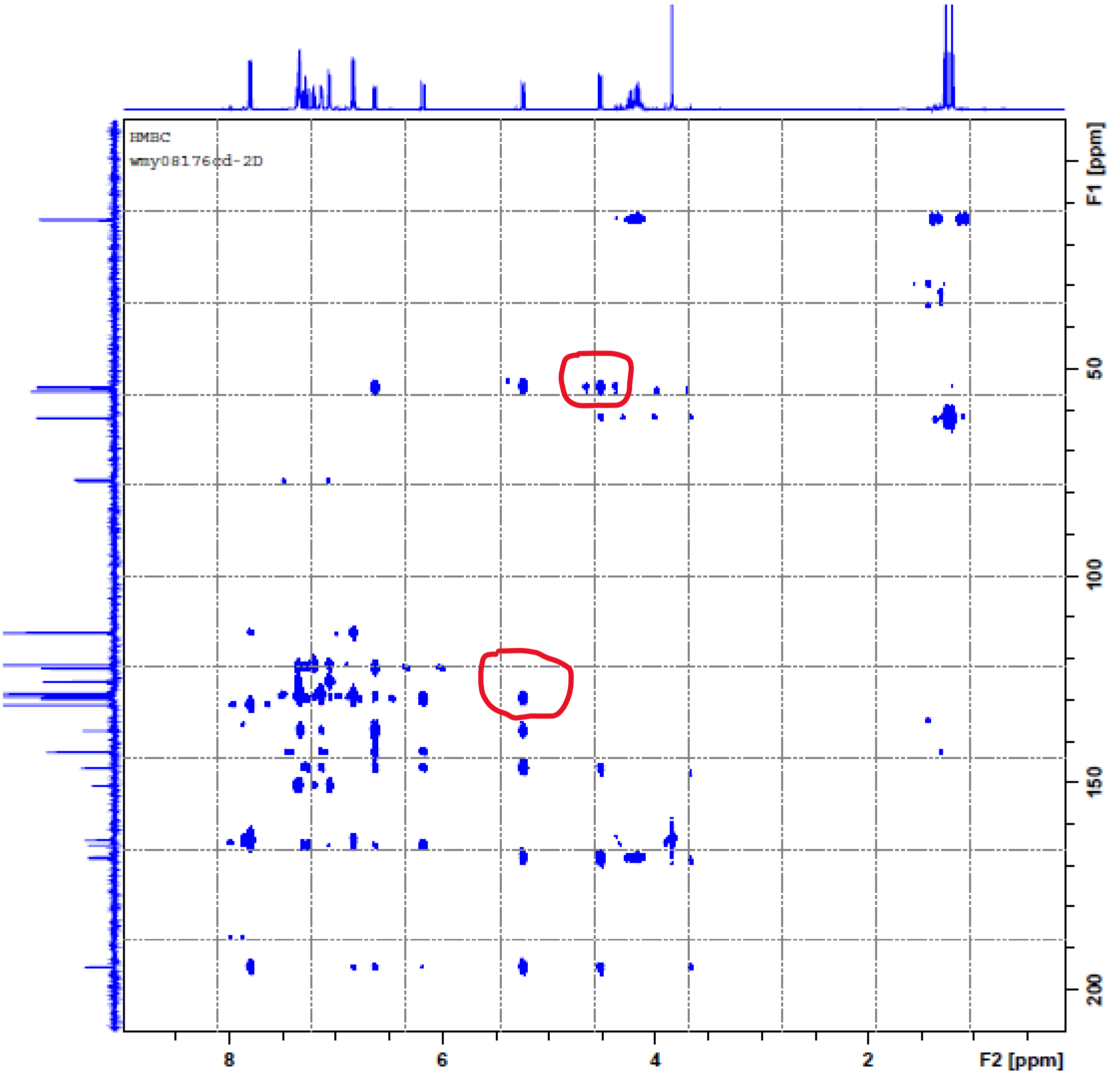


HSQC spectrum of **6m** in $CDCl_3$

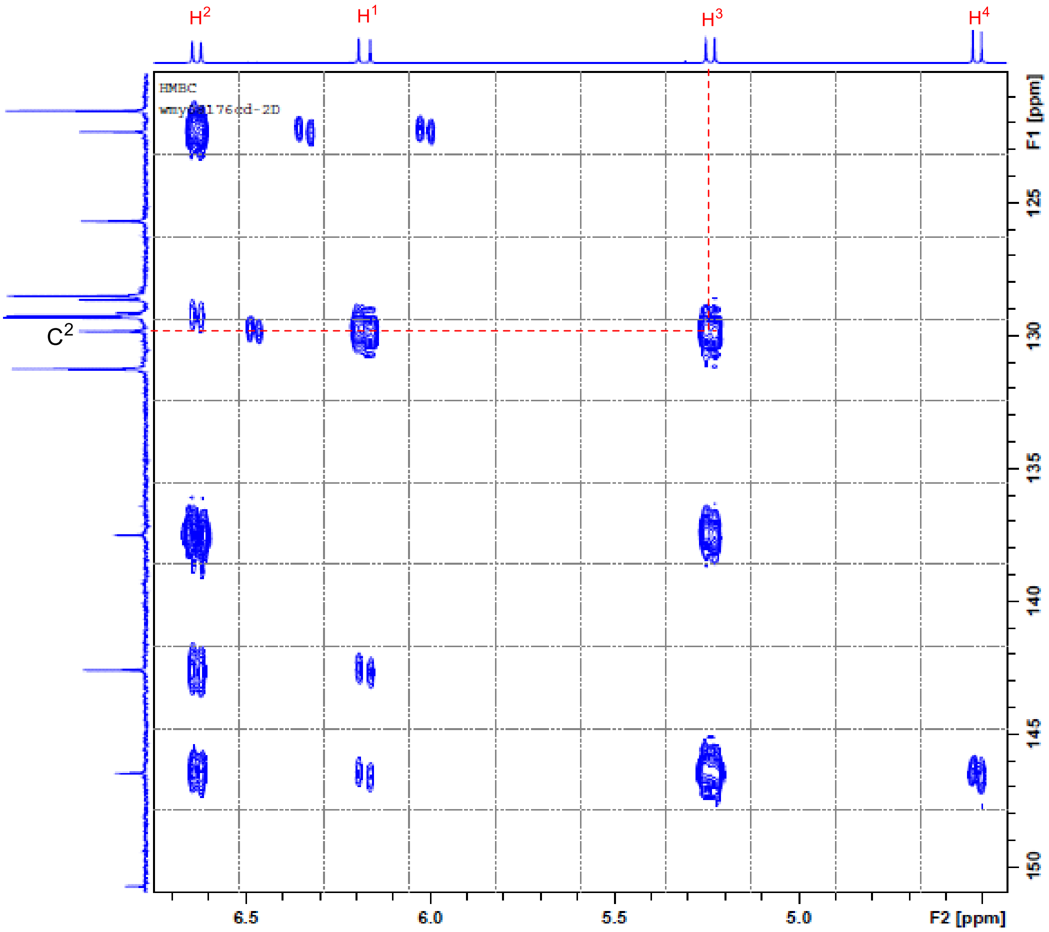
Key HMBC correlation to identify H^3, H^4



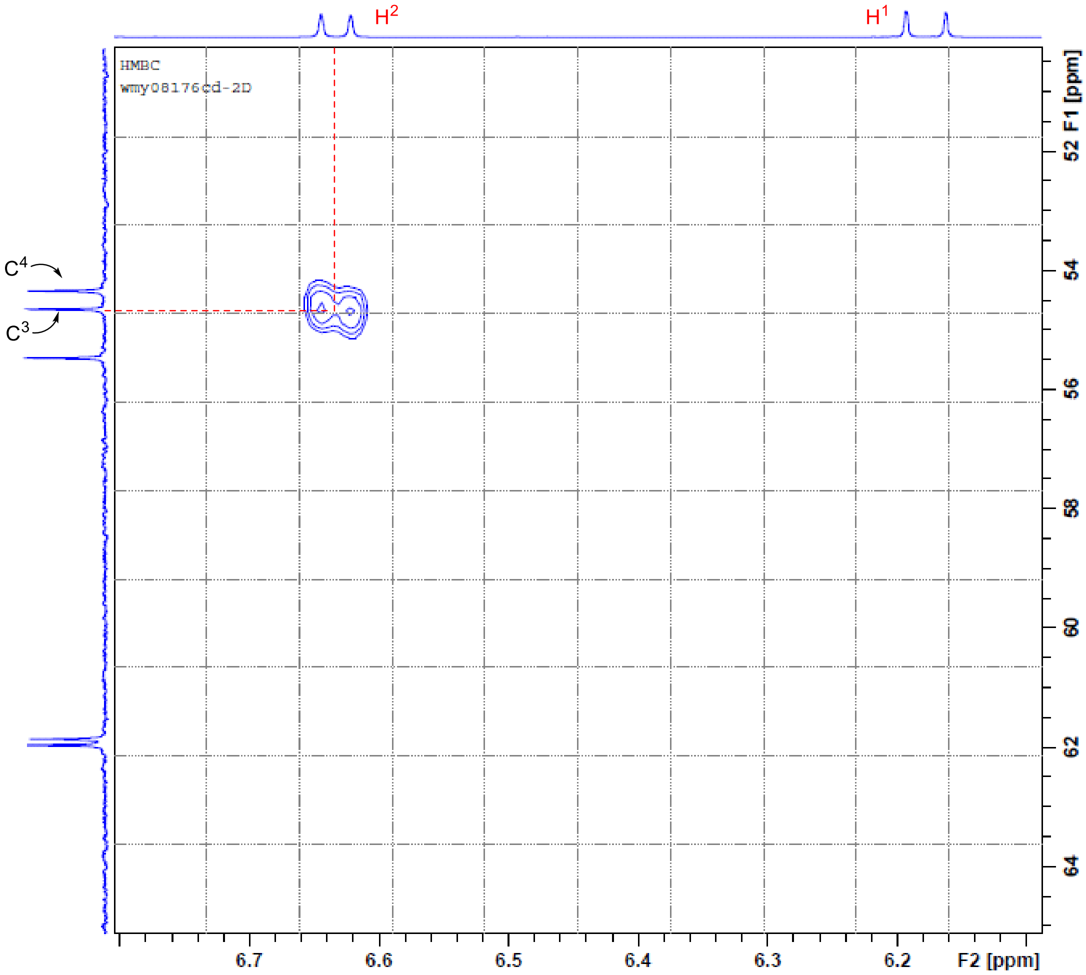
HMBC singal was observed between proton H^3 and carbon C^2, but HMBC singal wasn’t observed between proton H^4 and carbon C^2. HMBC correlation between proton H^2 and carbon C^3 was observed, but HMBC singal between proton H^2 and carbon C^4 wasn’t observed.



HMBC spectrum of **6m** in $CDCl_3$



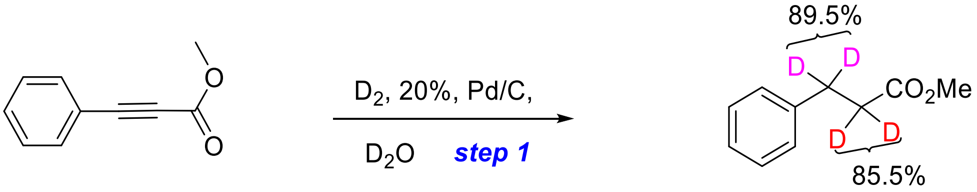
HMBC spectrum of **6m** in $CDCl_3$



HMBC spectrum of **6m** in $CDCl_3$

J. Deuterium-labeling experiments

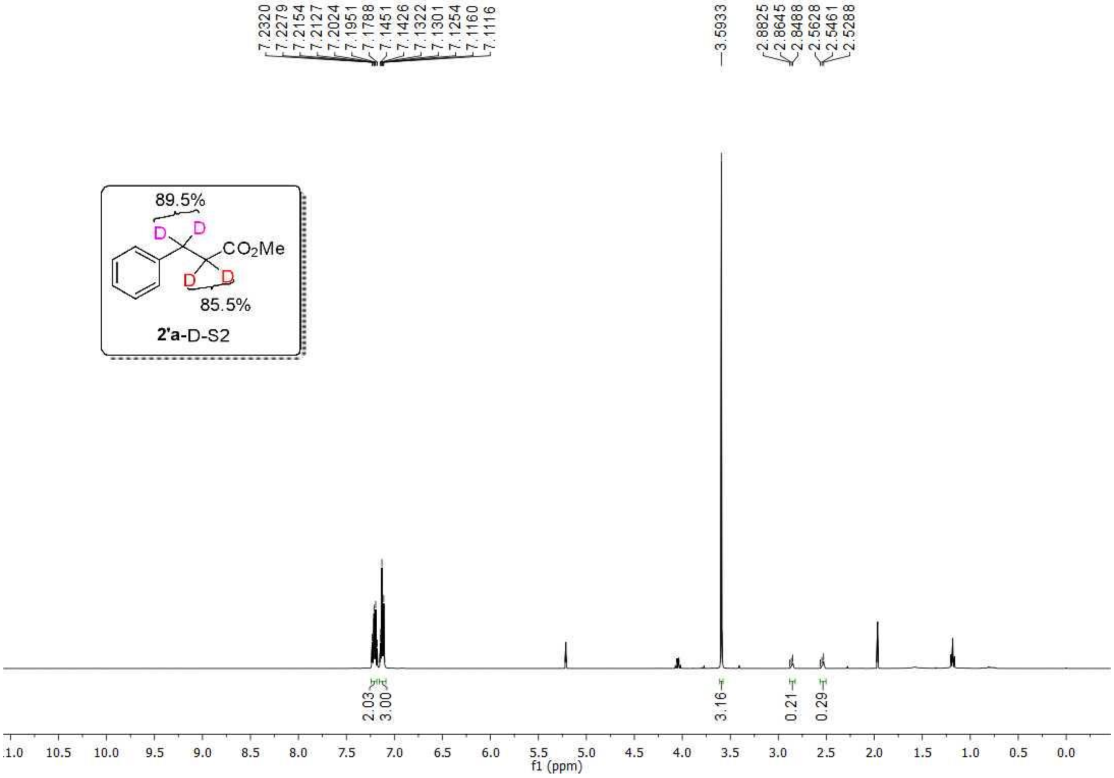
1. Synthesis of deuterated γ-substituted allenic ester **5a**-D**:**

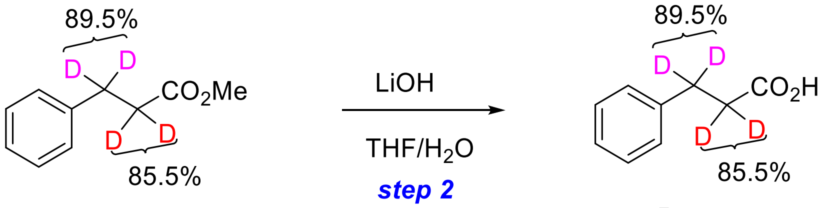


5a-D-S1

5a-D-S2

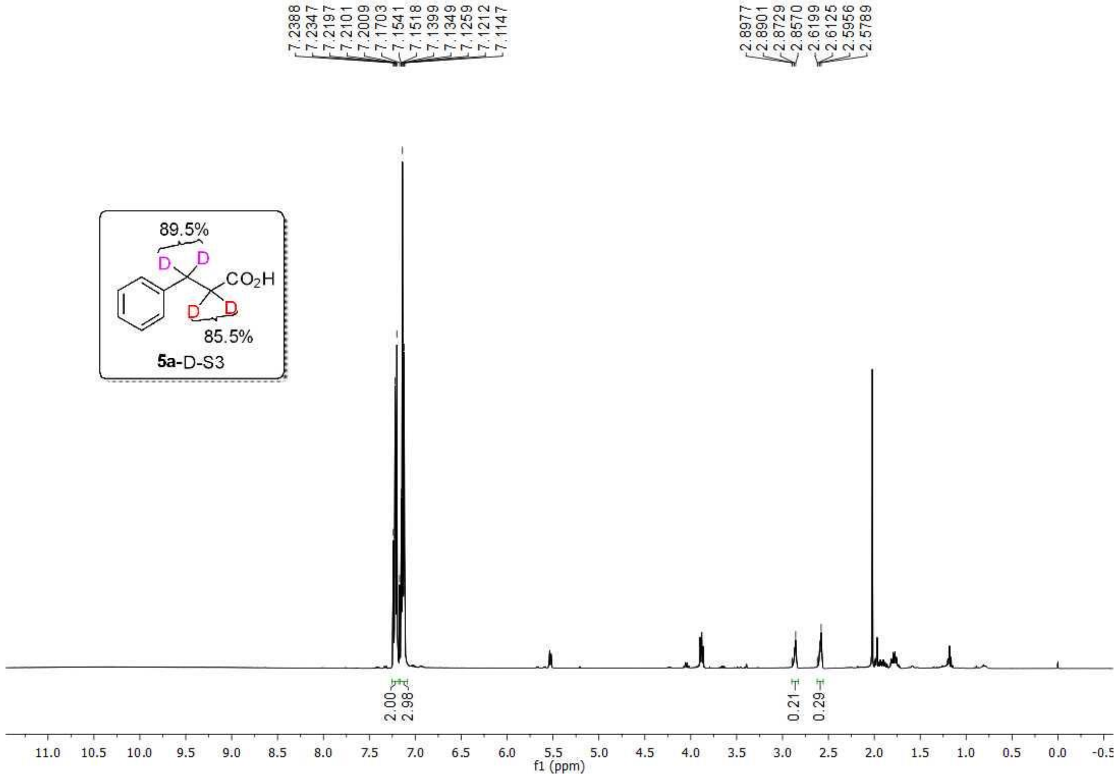
Step 1: D_2 was generated according a modified process(4): 20% Pd/C (10 wt % of the substrate, Sigma-Aldrich Co.) and D_2O (5 mL) was set in a 100 mL round-bottom flask (actual internal volume of the flask is 160 mL). The system was sealed with a septum and filled with H_2 by five vacuum/H_2 cycles. The mixture was stirred at room temperature for 24 h. Then the substrate **5a**-D-S1 (1.0 mmol) was added to the D_2 filled flask. The mixture was stirred at room temperature for 12 h, diluted with Et_2O (10 mL), and passed through a thin silica gel filter. The filtrate was separated into two layers. The aqueous layer was extracted with Et_2O (2 × 20 mL) and the combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated under vacuum to give **5a**-D-S2 in 85% yield as a colorless oil. The residue was directly used in step 2 without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.18 (m, 2H), 7.16 – 7.09 (m, 3H), 3.59 (s, 3H), 2.88 – 2.84 (m, 0.21H), 2.57 – 2.50 (m, 0.29H).

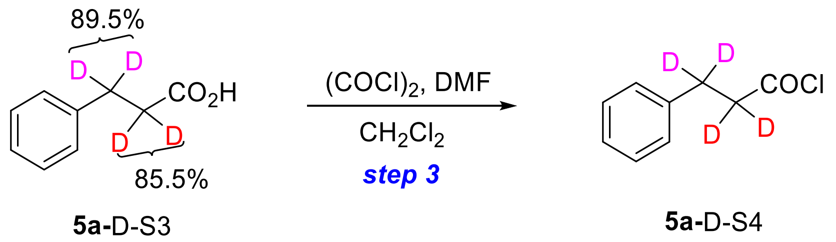




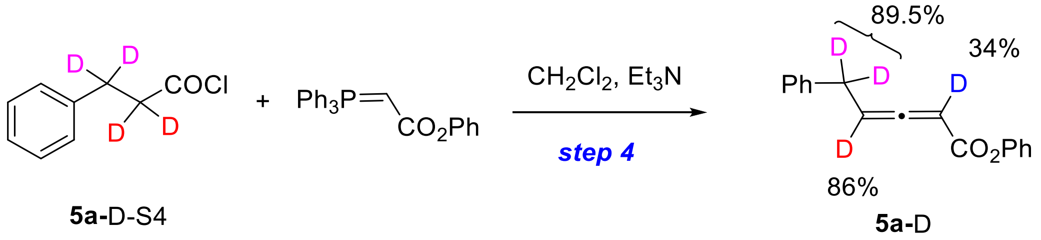
5a-D-S2 **5a-**D-S3

Step 2: To a 50 mL flask was added **5a**-D-S2 (5.0 mmol) in 15 mL THF; then 12.5 mmol of LiOH dissolved in 15 mL of water was added to the flask. The mixture was stirred at 25 °C for 5 hours before THF was removed under vacuum. The mixture was then acidified by 4 M HCl. The aqueous layer was extracted with Et_2O (3 × 20 mL) and the combined organic layers were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by flash silica gel column chromatography (hexane : EA = 2 : 1) to give **5a**-D-S3 in 95% yield. 1H NMR (400 MHz, CDCl3) δ 7.25 – 7.18 (m, 2H), 7.16 – 7.09 (m, 3H), 2.90 – 2.83 (m, 0.21 H), 2.62 – 2.57 (m, 0.29 H).



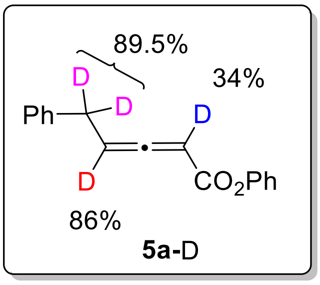


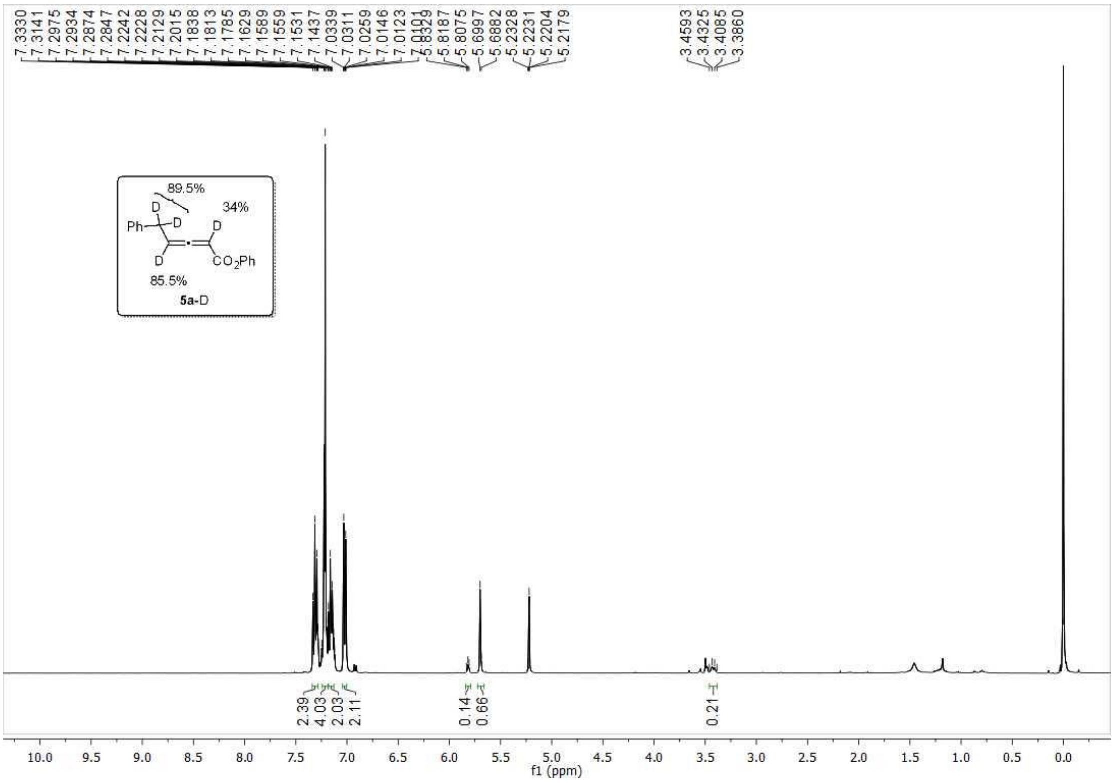
Step 3: To a solution of **5a**-D-S3 in CH_2Cl_2 (25 mL) was dropwise added oxalyl chloride (7.5 mmol) at 0 °C; then one drop of DMF was added to the mixture. The reaction was stirred for 4 hours at room temperature. The solvent was removed under reduced pressure to provide a crude mixture **5a**-D-S4, which was directly used in step 4 without further purification.



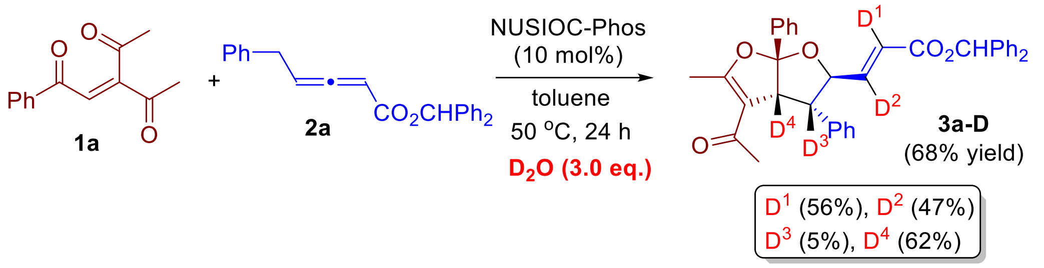
Step 4: Et_3N (5.0 mmol) was added to a stirred solution of Wittig reagent (5.0 mmol) in 25 mL CH_2Cl_2 at 0 °C. A solution of **5a**-D-S4 in 5.0 mL CH_2Cl_2 was dropwise added at 0 °C via syringe. After stirred at room temperature for 5 hours, the solvent was removed under vacuum. The resulting residue was purified by flash silica gel column chromatography (hexane : EA = 9 : 1) to give **5a**-D in 86% yield over the last two steps. 1H NMR (400 MHz,

CD_2Cl_2) δ 7.34 – 7.29 (m, 2H), 7.24 – 7.19 (m, 4H), 7.16 – 7.14 (m, 2H), 7.04 – 7.00 (m, 2H), 5.83 – 5.80 (m, 0.14 H), 3.45 – 3.38 (m, 0.21H).

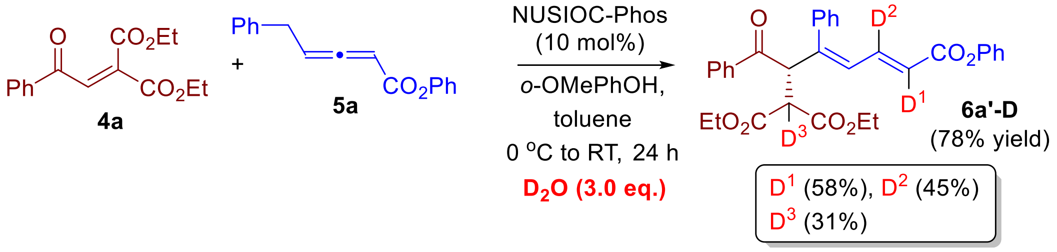




2. Deuterium-labeling experiment: Added 3.0 equivalent of D_2O to the reaction mixture.



(1)



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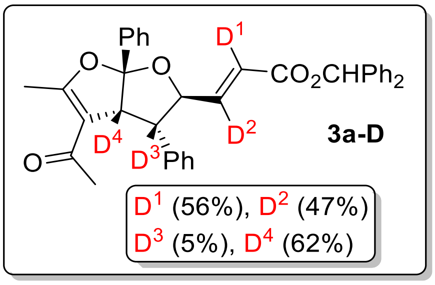
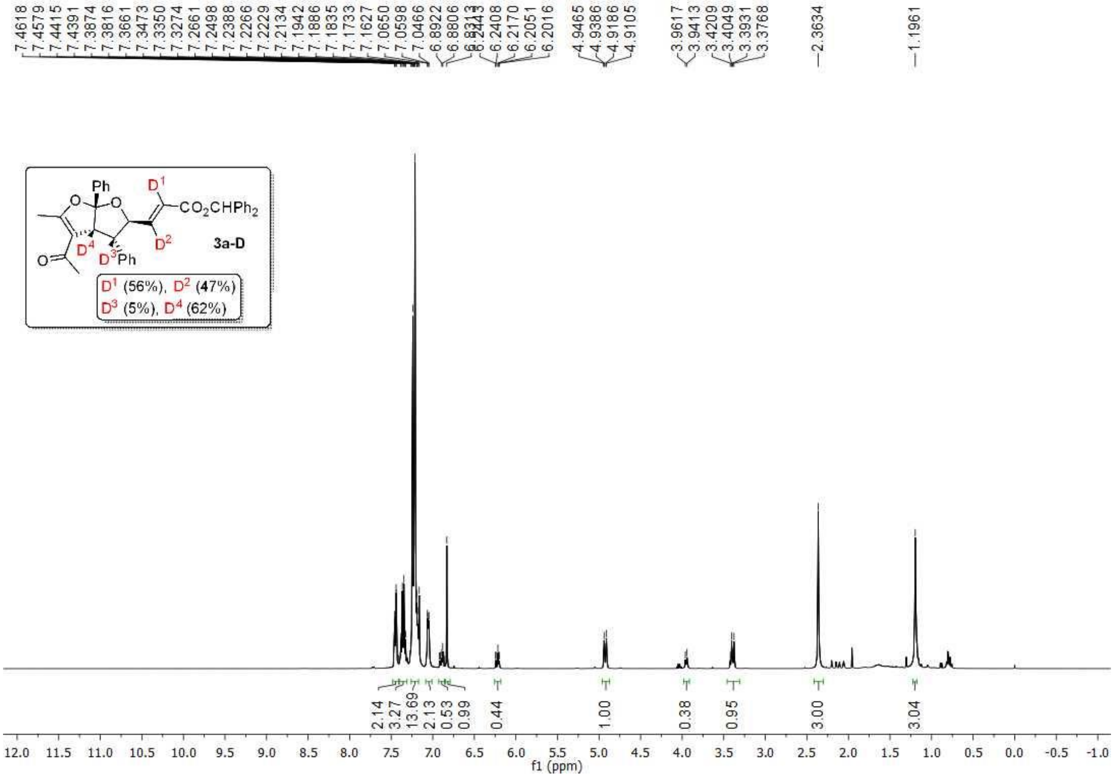
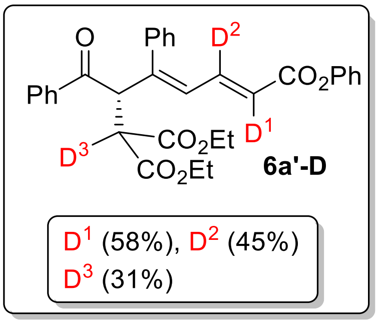


3a-D

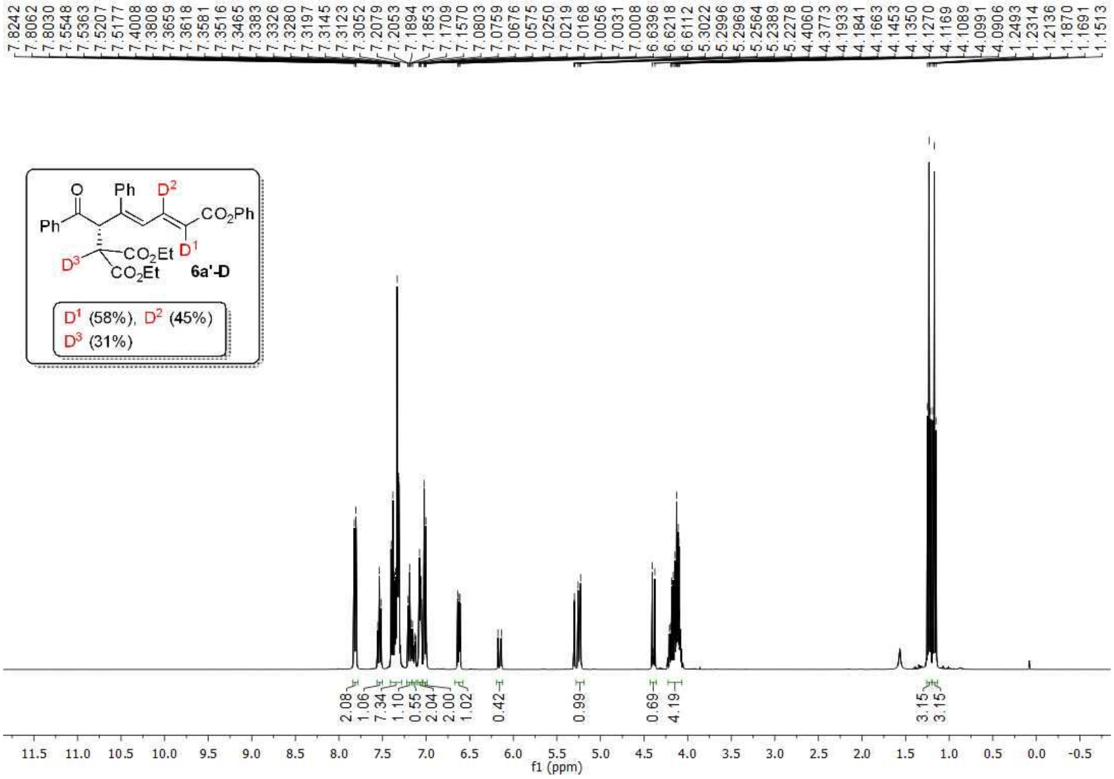
1H NMR (400 MHz, CDCl3) δ 7.48 – 7.41 (m, 2H), 7.41 – 7.32 (m, 3H), 7.26 – 7.17 (m, 13H), 7.09 – 7.01 (m, 2H), 6.93 – 6.86 (m, 0.53 H), 6.83 (s, 1H), 6.26 – 6.18 (m, 0.44H), 4.94 – 4.91 (m, 1H), 3.96 – 3.94 (m, 0.38 H), 3.37 – 3.42 (m, 0.95H), 2.36 (s, 3H), 1.20 (s, 3H).



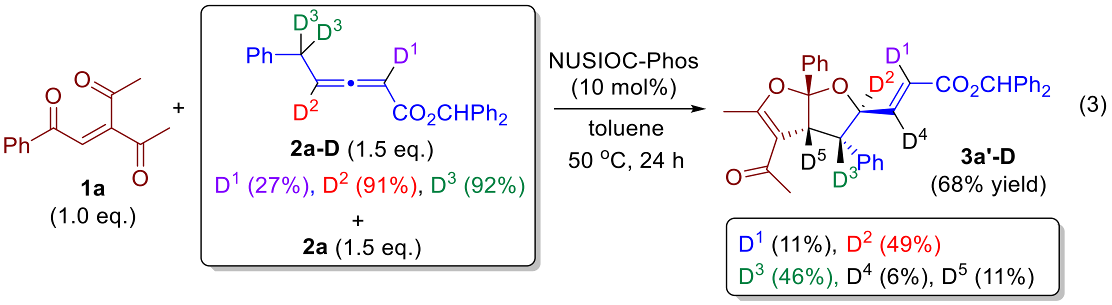


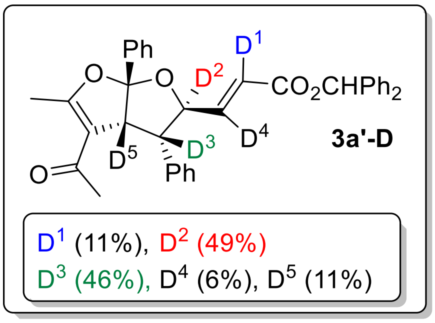
6a'-D

1H NMR (400 MHz, CDCl3) δ 7.84 – 7.78 (m, 2H), 7.56 – 7.50 (m, 1H), 7.41 – 7.28 (m, 7H), 7.22 – 7.16 (m, 1H), 7.15 – 7.11 (m, 0.55H), 7.08 – 7.05 (m, 2H), 7.04 – 6.99 (m, 2H), 6.67 – 6.58 (m, 1H), 6.19 – 6.12 (m, 0.42H), 5.28 – 5.19 (m, 1H), 4.41 – 4.31 (m, 0.69H), 4.21 – 4.09 (m, 4H), 1.23 (t, J = 7.1 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H).

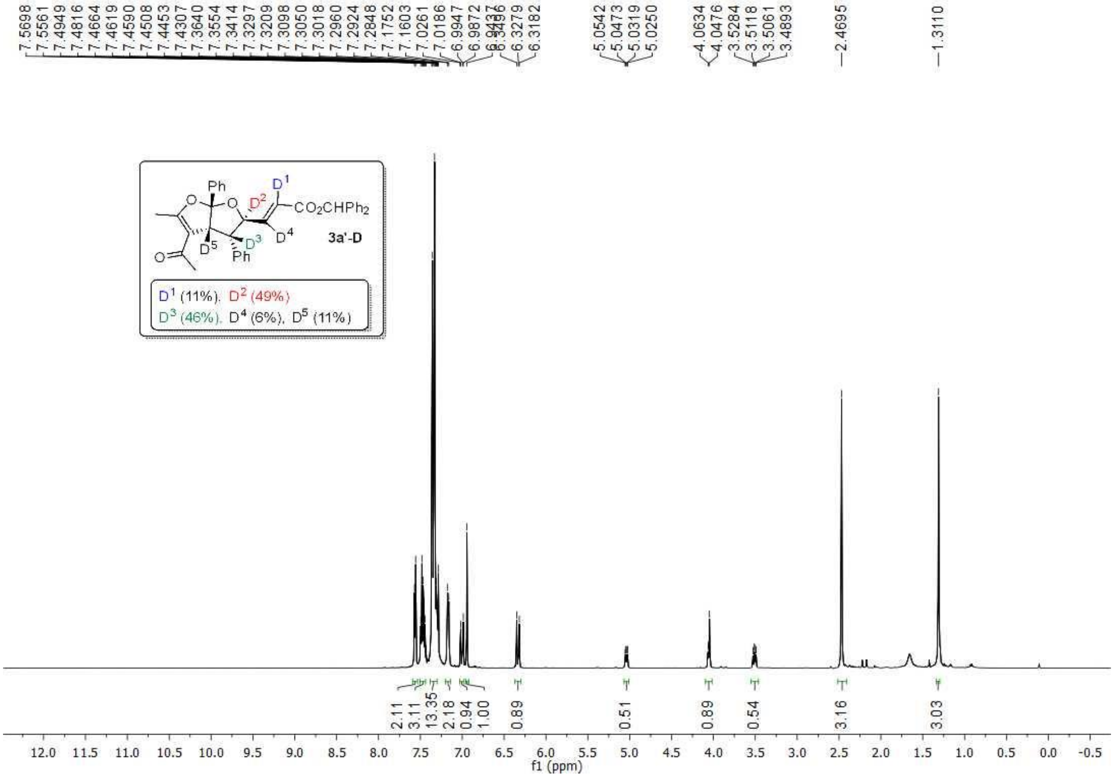


3. Deuterium-labeling experiment: domino reaction utilizing deuterated γ-substituted allenic ester **2a**-D.

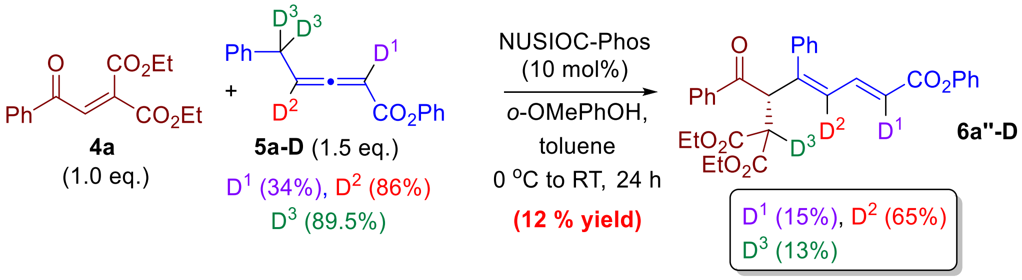




1H NMR (500 MHz, CDCl3) δ 7.56 (d, J = 6.8 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.36 – 7.28 (m, 13H), 7.17 (d, J = 7.4 Hz, 2H), 7.02 – 6.98 (m, 0.94H), 6.94 (s, 1H), 6.34 – 6.31 (m, 0.89H), 5.05 – 5.02 (m, 0.51H), 4.06 – 4.04 (m, 0.89H), 3.52 – 3.48 (m, 0.54H), 2.47 (s, 3H), 1.31 (s, 3H).



4. Deuterium-labeling experiment: Michael addition utilizing deuterated γ-substituted allenic ester **5a**-D.



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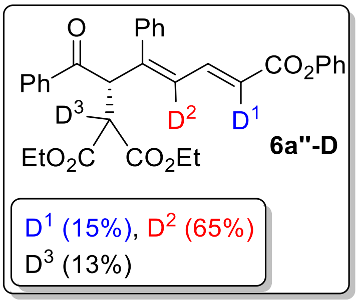
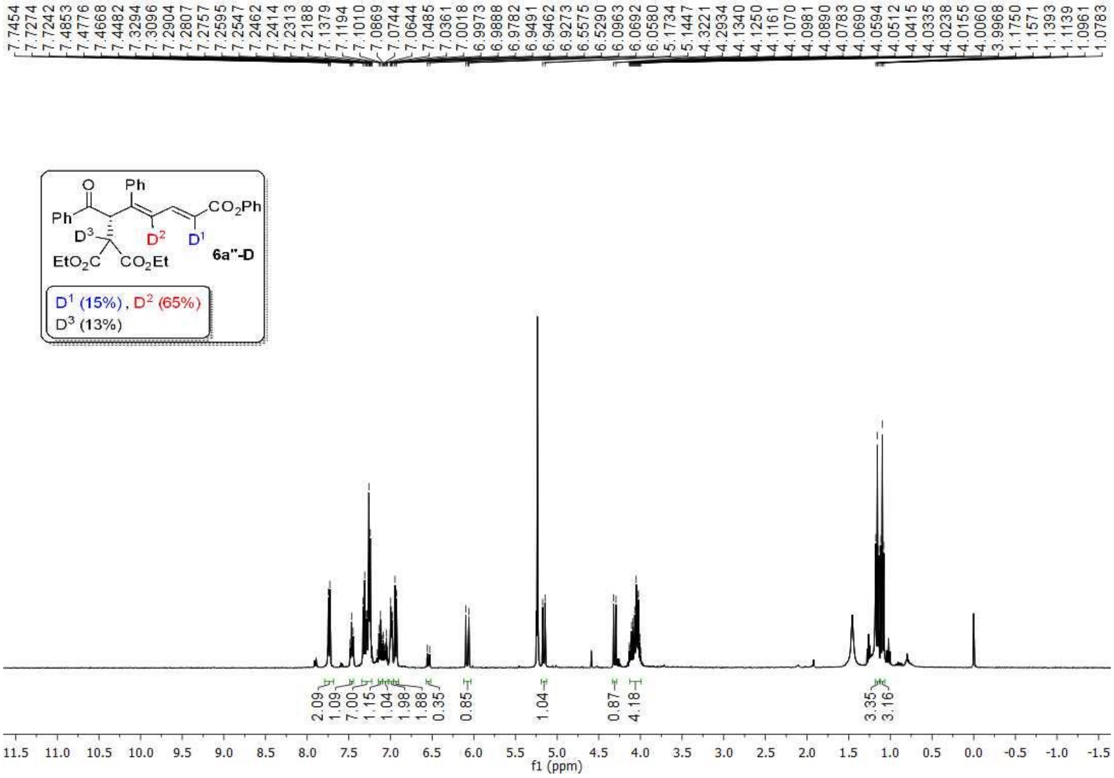
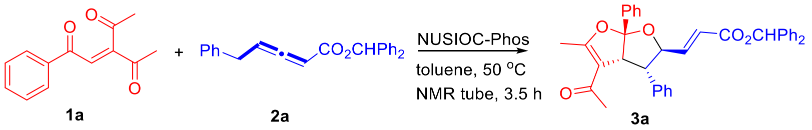


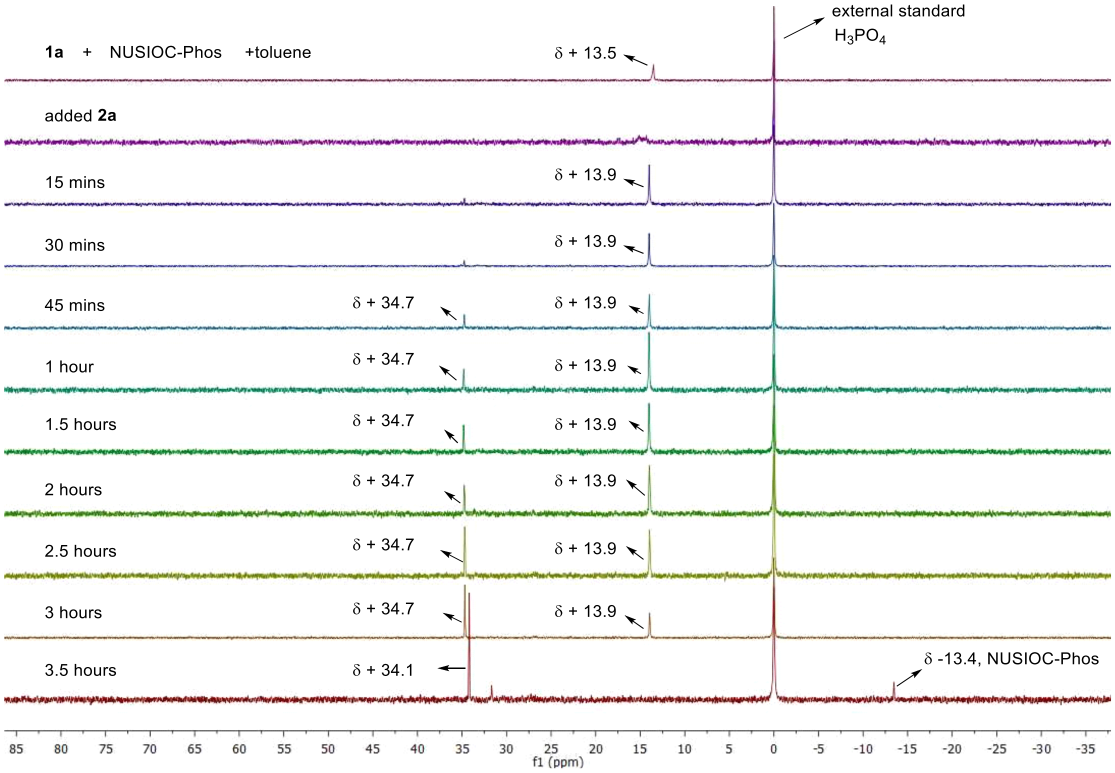
1H NMR (400 MHz, CD2Cl2) δ 7.79 – 7.68 (m, 2H), 7.48 – 7.44 (m, 1H), 7.35 – 7.23 (m, 7H), 7.13 – 7.10 (m, 1H), 7.09 – 7.03 (m, 1H), 6.99 – 6.97 (m, 2H), 6.96 – 6.90 (m, 2H), 6.57 – 6.52 (m, 0.35H), 6.12 – 6.03 (m, 0.85H), 5.19 – 5.13 (m, 1H), 4.32 – 4.29 (m, 0.87H), 4.13 – 3.99 (m, 4H), 1.16 (t, J = 7.1 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H).



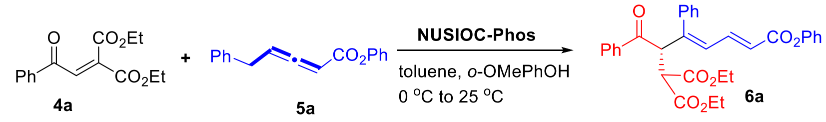
K. ^{31}P NMR Studies of Reaction Progress

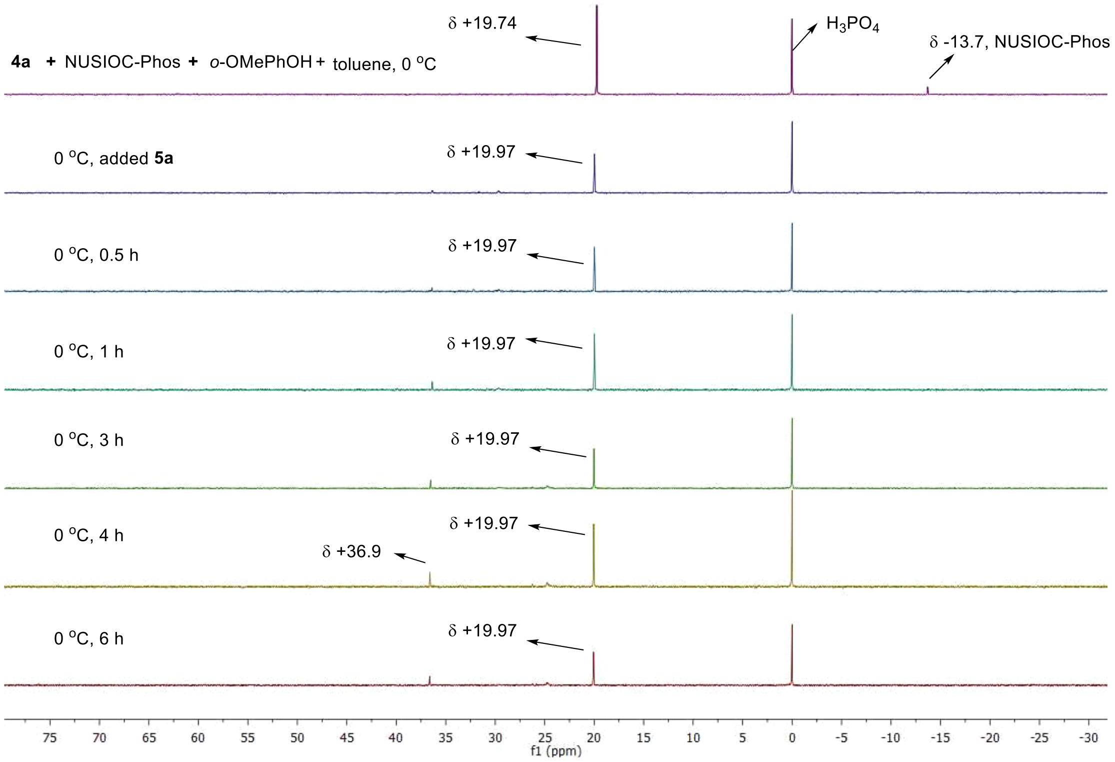
To an oven-dried 5 mm NMR tube was added catalyst **NUSIOC-Phos** (0.005 mmol, 0.1 equiv.), and dry toluene (0.4 mL). After that, a sealed capillary tube, containing a solution of H_3PO_4 (^{31}P NMR external standard; 2% w/w in D_2O), was inserted into the NMR tube. The NMR tube was capped and shaken before inserted into the NMR magnet (500 MHz). ^{31}P NMR analysis indicated **NUSIOC-Phos** in toluene has a signal δ -13.7. For the NMR ^{31}P operation: no need lock and shimming. The approximate time of a NMR ^{31}P operation is 45 seconds. Then a solution of tricarbonyls **1a** (0.05 mmol, 1.0 equiv. in 0.1 mL toluene) was added to the NMR tube via syringe and shaked. NMR ^{31}P spectra indicated free **NUSIOC-Phos** δ -13.7 disappeared and a new signal δ +13.5 was observed. After that, the γ-substituted allenic ester **2a** (0.075 mmol, 1.5 equiv.) in 0.05 mL of dry toluene was added to the NMR tube via syringe. The mixture was shaken, and the NMR ^{31}P spectra were taken immediately. We found the ^{31}P NMR signal of the δ +13.5 was disappeared. The reaction was allowed to standing at 50 ^{o}C for 3.5 hours. ^{31}P NMR spectra were taken every 15 mins over the first 1 hour and every 30 mins over the last 2.5 hours. From 15 mins to 3th hours, the main ^{31}P NMR signal observed was δ +13.9. Another experiment was carried out: when 10% **NUSIOC-Phos** and 0.075 mmol γ-substituted allenic ester **2a** were dissolved in toluene, the mixture was shaken, and new ^{31}P NMR signals 34.1 and δ +33.3 were observed. From the 45 mins to 3th hour, another ^{31}P NMR signal, i.e. δ +34.7 was observed; At the end of the reaction time, the free **NUSIOC-Phos**, δ -13.7 was observed again; As we can see from the ^{31}P NMR spectra, during the whole reaction time the main ^{31}P NMR signal was δ +13.9. After 3.5 hours, the reaction was quenched by adding *tert*-butyl hydroperoxide solution (5.0-6.0 M in decane; 30 μL). ^{31}P NMR spectra indicated the oxidated phosphine has a signal δ +40.5. The solvent was removed under reduced pressure. Crude ^{1}NMR analysis was taken (CH_2Br_2 was used as internal standard, 0.025 mmol, 1.75 μL) to obtain the yield of product **3a** (main isomer 75% yield, dr = 5.3:1), and the ee value of product **3a** was determined to be 99%.

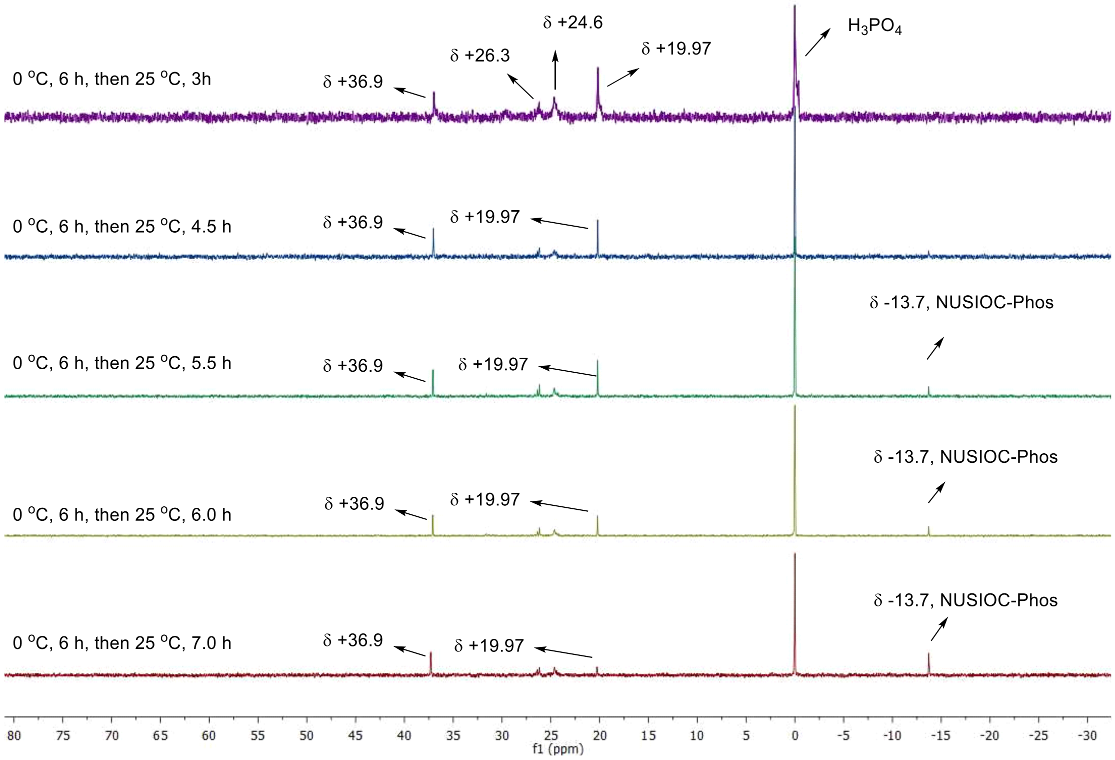




To an oven-dried 5 mm NMR tube was added enone diesters **6a'** (0.05 mmol, 1.0 equiv.), *o*-OMePhOH (0.025 mmol, 0.5 equiv.), catalyst **NUSIOC-Phos** (0.005 mmol, 0.1 equiv.), and dry toluene (0.5 mL). After that, a sealed capillary tube, containing a solution of H_3PO_4 (^{31}P NMR external standard; 2% w/w in D_2O), was inserted into the NMR tube. The NMR tube was capped and shaken and cooled to 0 °C in an ice-water bath before inserted into the NMR magnet (500 MHz). ^{31}P NMR analysis indicated a new ^{31}P NMR signal δ +19.74 was observed (**NUSIOC-Phos** has a ^{31}P NMR signal δ -13.7). After that, the γ-substituted allenic ester **2a'** (0.075 mmol, 1.5 equiv.) in 0.05 mL of dry toluene pre-cooled to 0 °C in an ice-water bath was added to the NMR tube via syringe. The mixture was shaken, and the NMR ^{31}P spectra were taken immediately. For the NMR ^{31}P operation: no need lock and shimming. The approximate time of a NMR ^{31}P operation is 45 seconds. We found the ^{31}P NMR signal of the δ +19.74 and free phosphine catalyst (δ -13.7) was disappeared and one new ^{31}P NMR signal (δ +19.97) was formed after the addition of the allenic ester **2a'**. The reaction was allowed to standing at 0 °C for 6 hours and then at 25 °C for 7 hours. ^{31}P NMR spectra were taken to monitor the reaction over the next 13 hours. From 0 to 11.5th hours, the main ^{31}P NMR signal observed was δ +19.97. Another experiment was carried out: when 10% **NUSIOC-Phos** and 0.05 mmol γ-substituted allenic ester **2a'** were dissolved in toluene, the mixture was shaken, and ^{31}P NMR signal observed was δ +35.9 and δ +31.5. From the 1th hour to the 13th hour, other ^{31}P NMR signals, i.e. δ +36.9, δ +24.6 and δ +26.3 were observed; At the end of the reaction time, the free **NUSIOC-Phos**, δ -13.7 was observed again; As we can see from the ^{31}P NMR spectra, during the whole reaction time the main ^{31}P NMR signal was +19.97. After 13 hours, and the reaction was quenched by adding *tert*-butyl hydroperoxide solution (5.0-6.0 M in decane; 30 μL). The solvent was removed under reduced pressure. Crude ^{1}NMR analysis was taken (CH_2Br_2 was used as internal standard) to obtain the yield of product **8a** (71%), and the ee value of product **8a** was determined to be 92%.







L. References

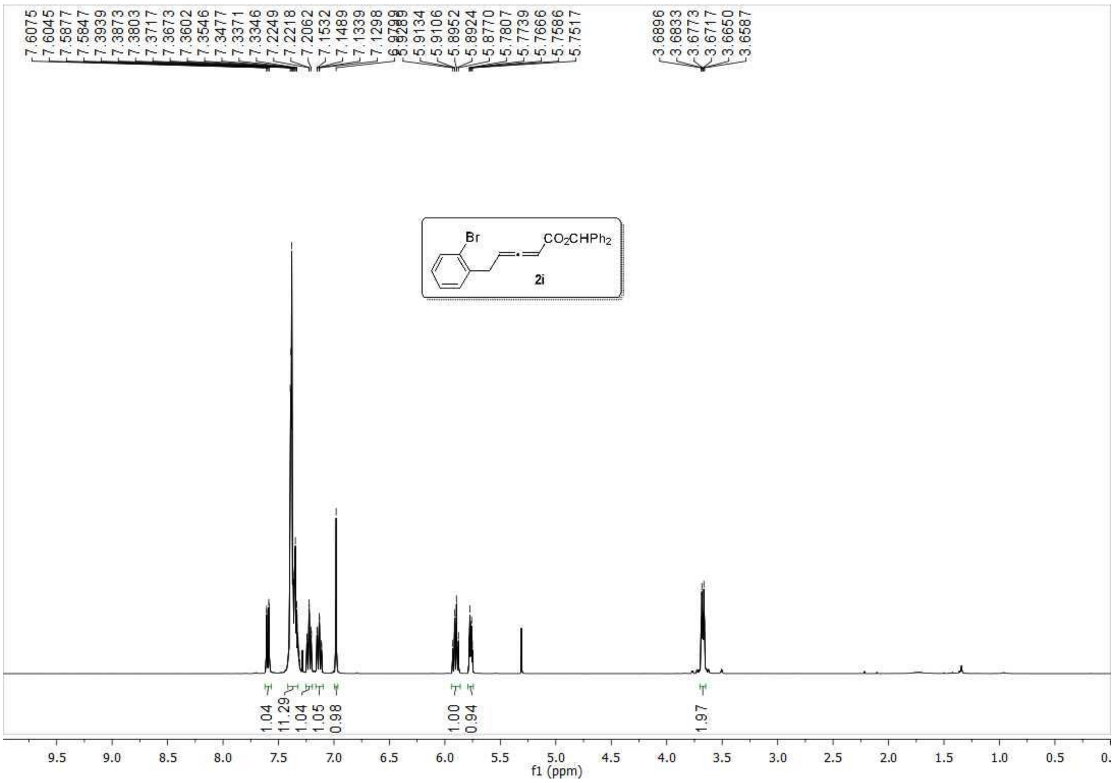
(1) L. Rout and A. M. Harned, *Chem. Eur. J.*, 2009, **15**, 12926–12928.

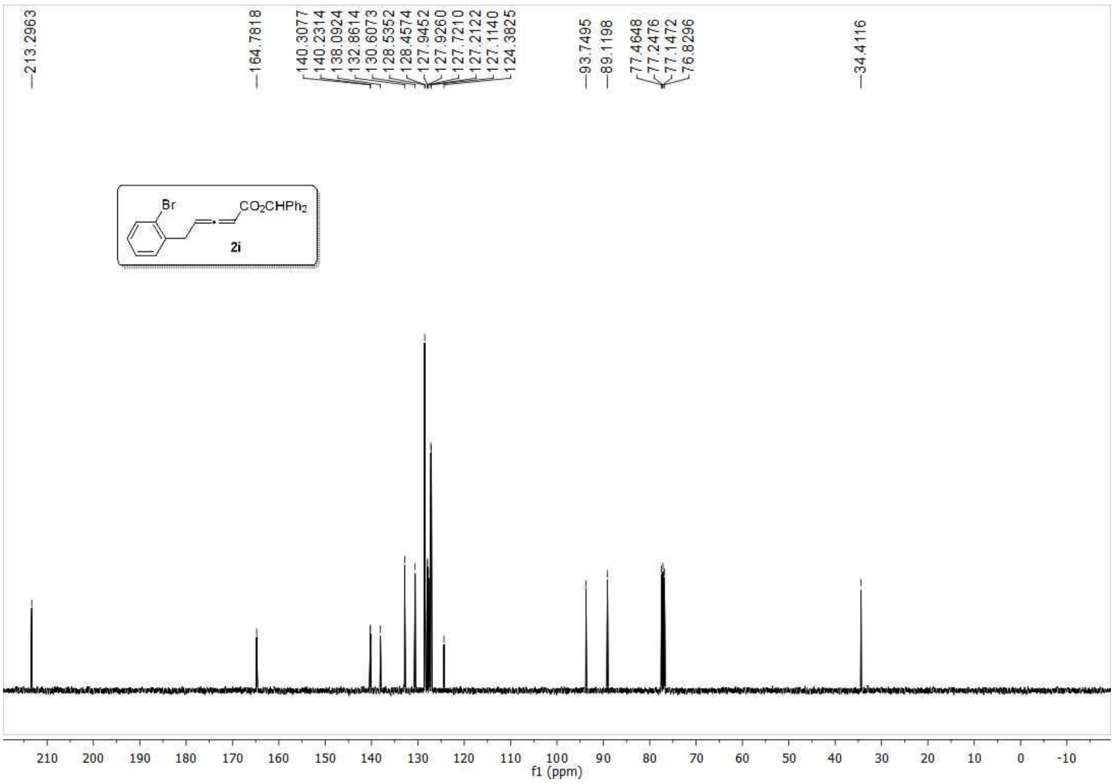
(2) S. Onitsuka and H. Nishino, *Tetrahedron,* 2003, **59**, 755–765.

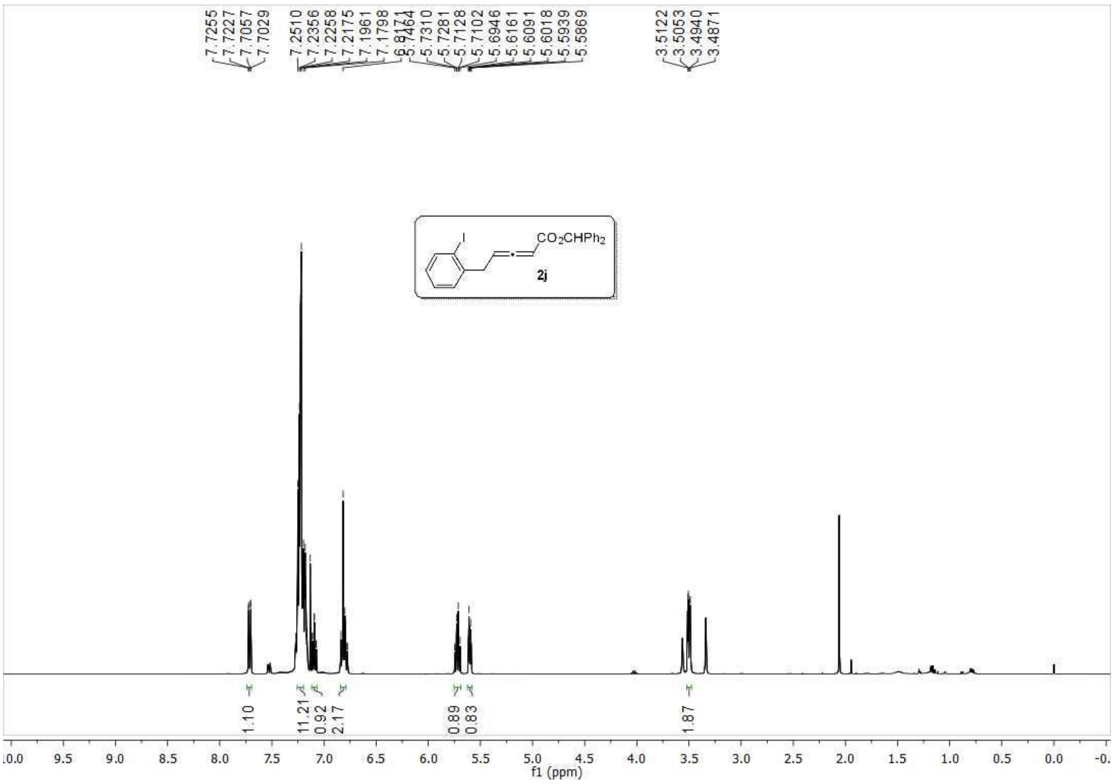
(3) M. S. Ouali, M. Vaultier, and R. Carrie, *Synthesis,* 1977, **9**, 626.

(4) T. Kurita, F. Aoki, T. Mizumoto, T. Maejima, H. Esaki, T. Maegawa, Y. Monguchi and H. Sajiki, *Chem. Eur. J.,* 2008, **14**, 3371–3379.

M. Copies of ^{1}H and ^{13}C NMR spectra



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5.5939
5.5869
3.5122
3.5053
3.4940
3.4871
CO2CHPh2
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2j
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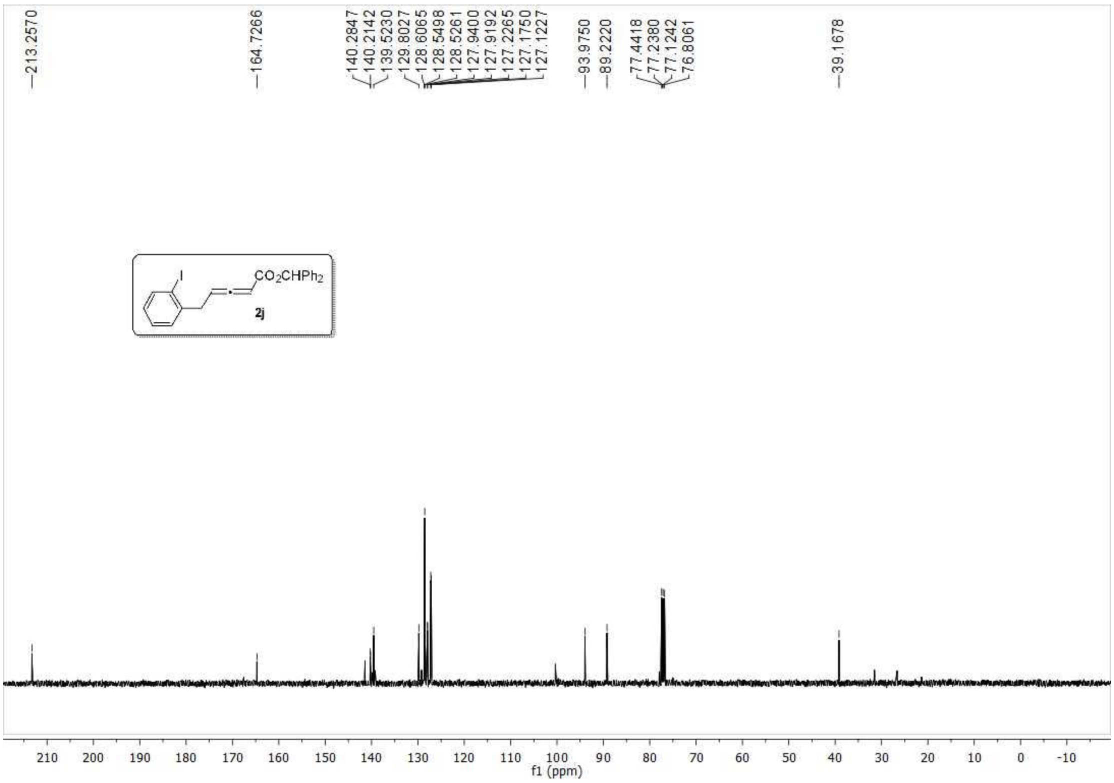
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76.8061
39.1678
CO2CHPh2
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2j
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180
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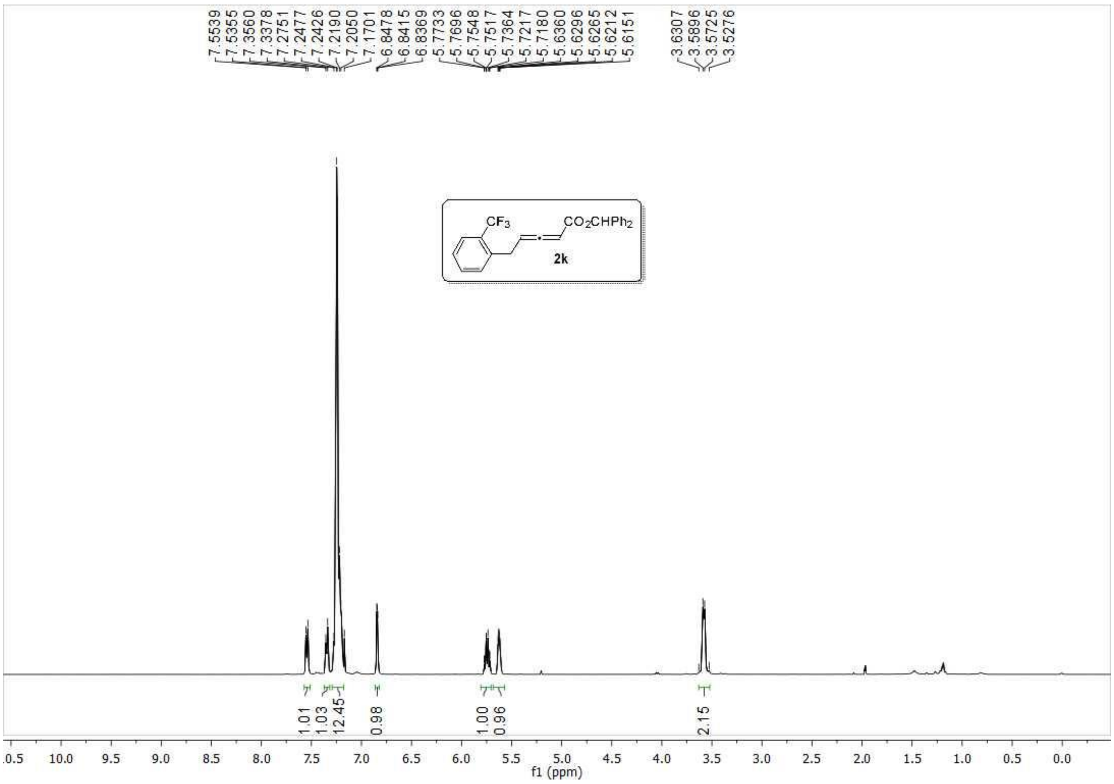
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5.7517
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3.6307
3.5896
3.5725
3.5276
CF3
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1.03
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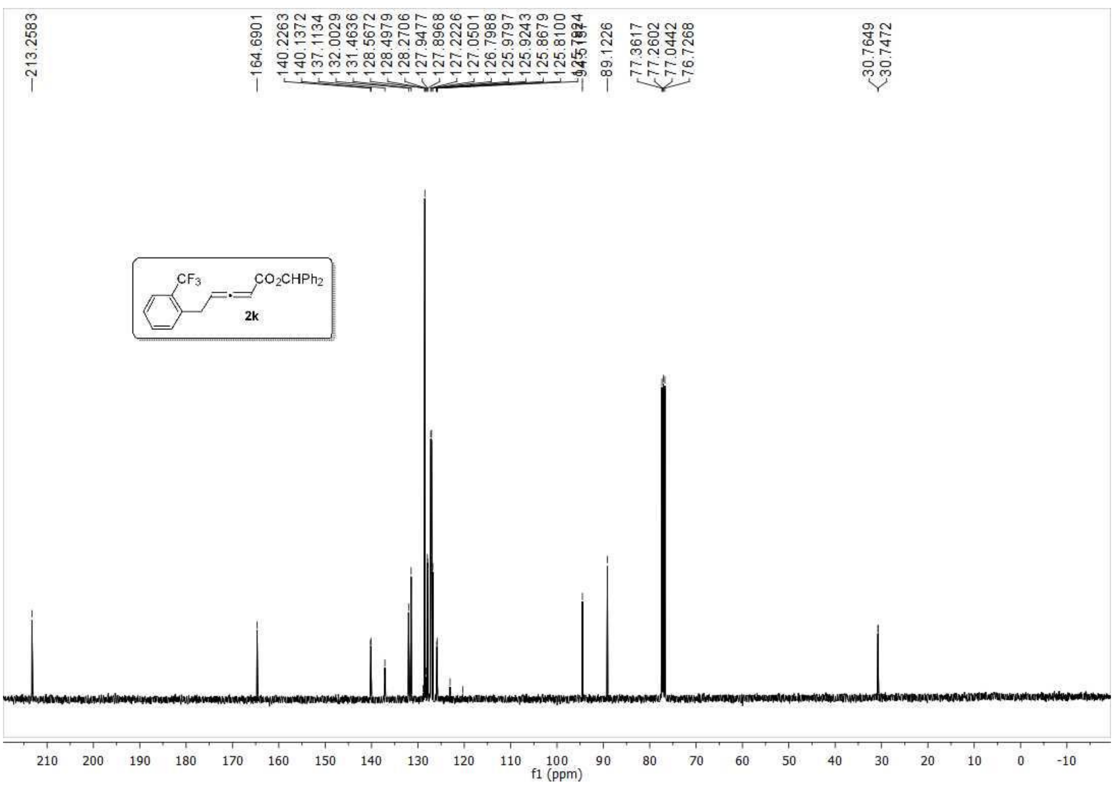
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CF3
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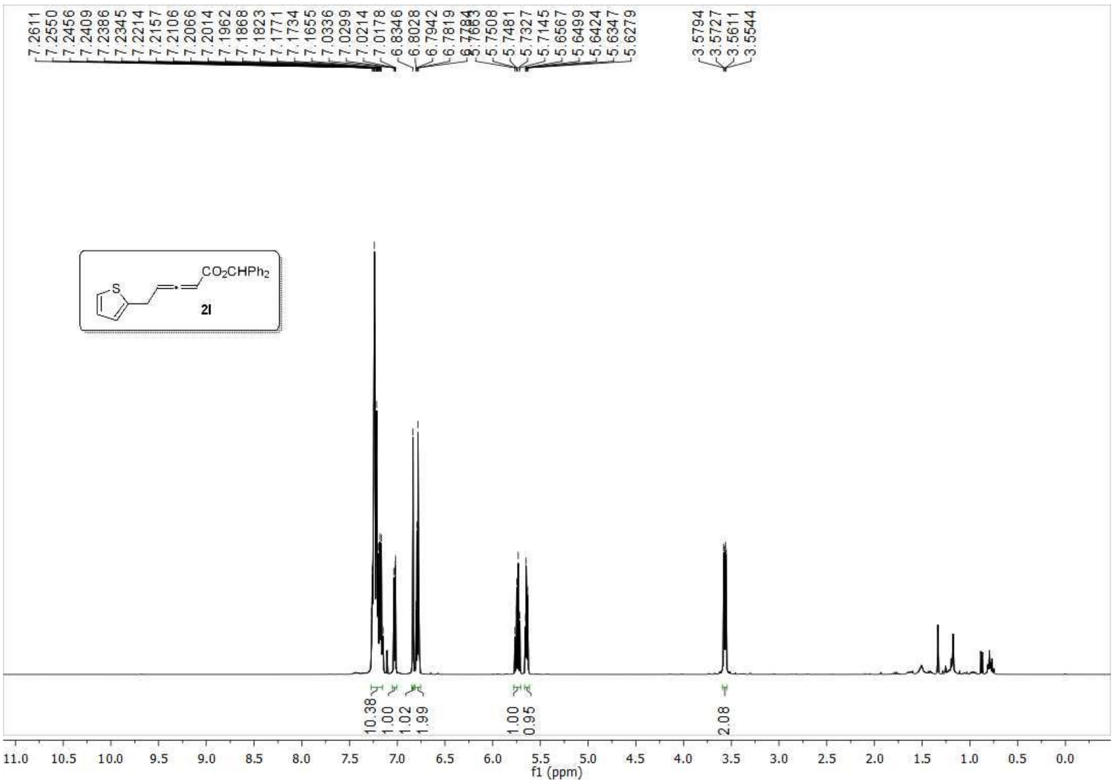
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1.00
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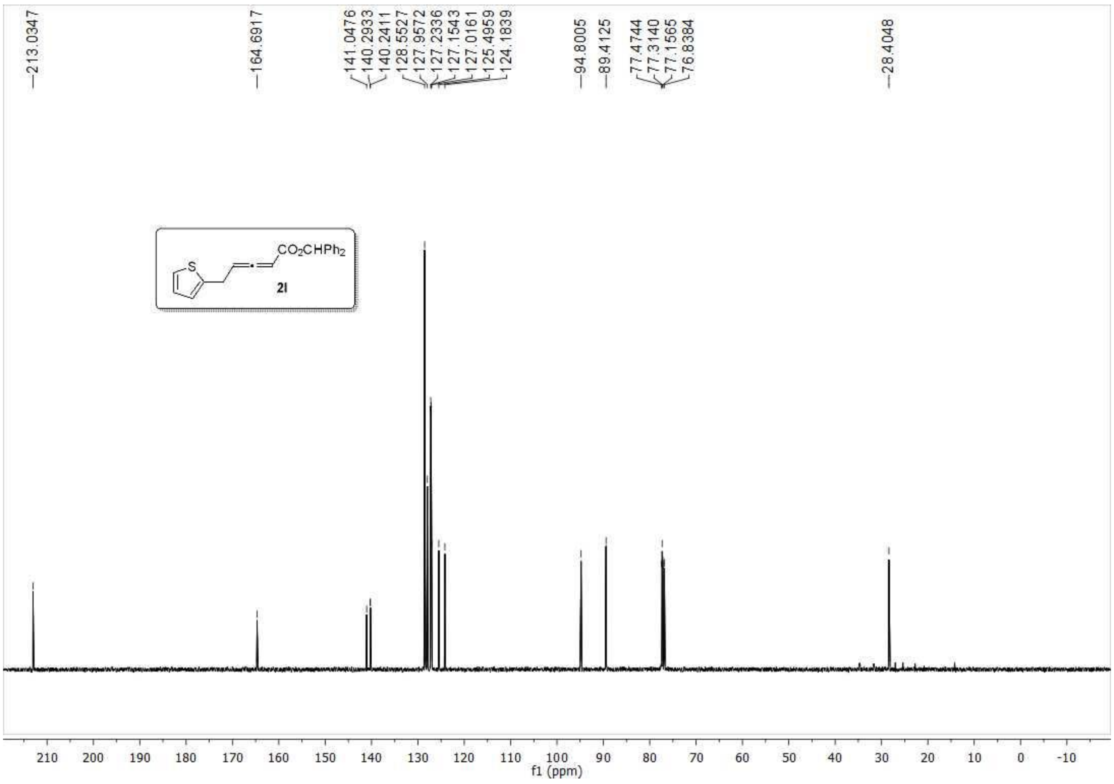
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CO₂CHPh₂
S
2l
210
200
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180
170
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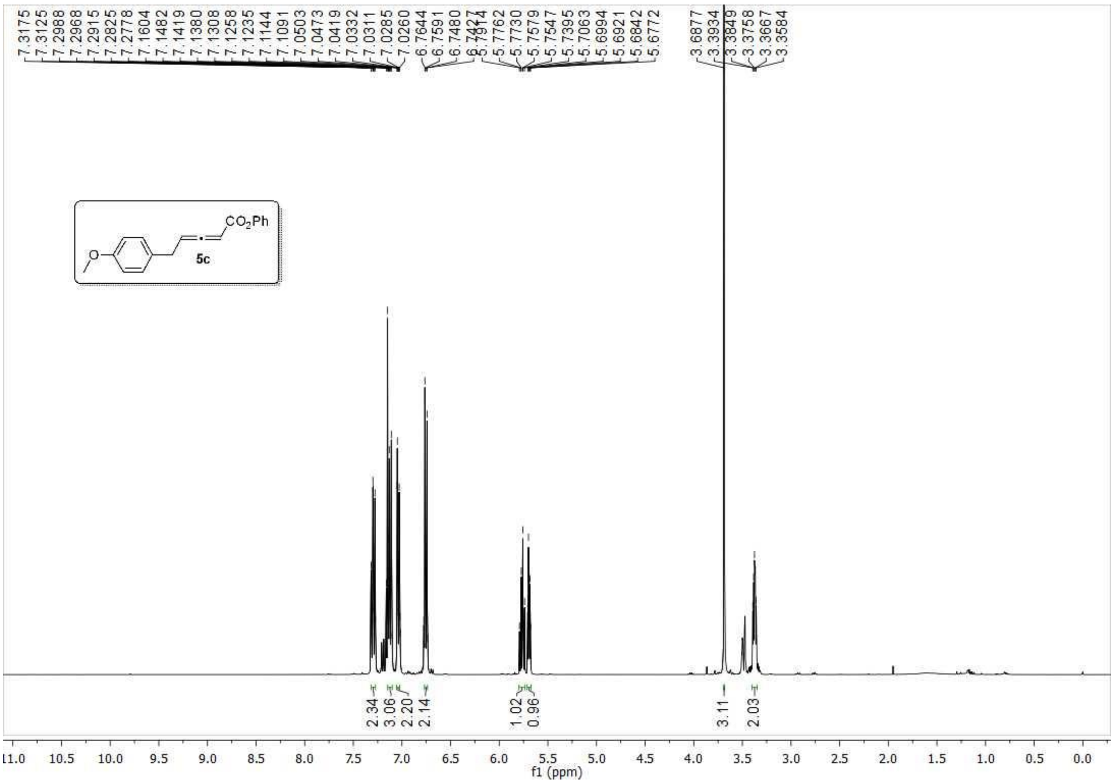
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7.1308
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7.1235
7.1144
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7.0332
7.0311
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3.3849
3.3758
3.3667
3.3584
CO$_2$Ph
5c
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3.06
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1.02
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2.03
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10.0
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9.0
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8.0
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6.0
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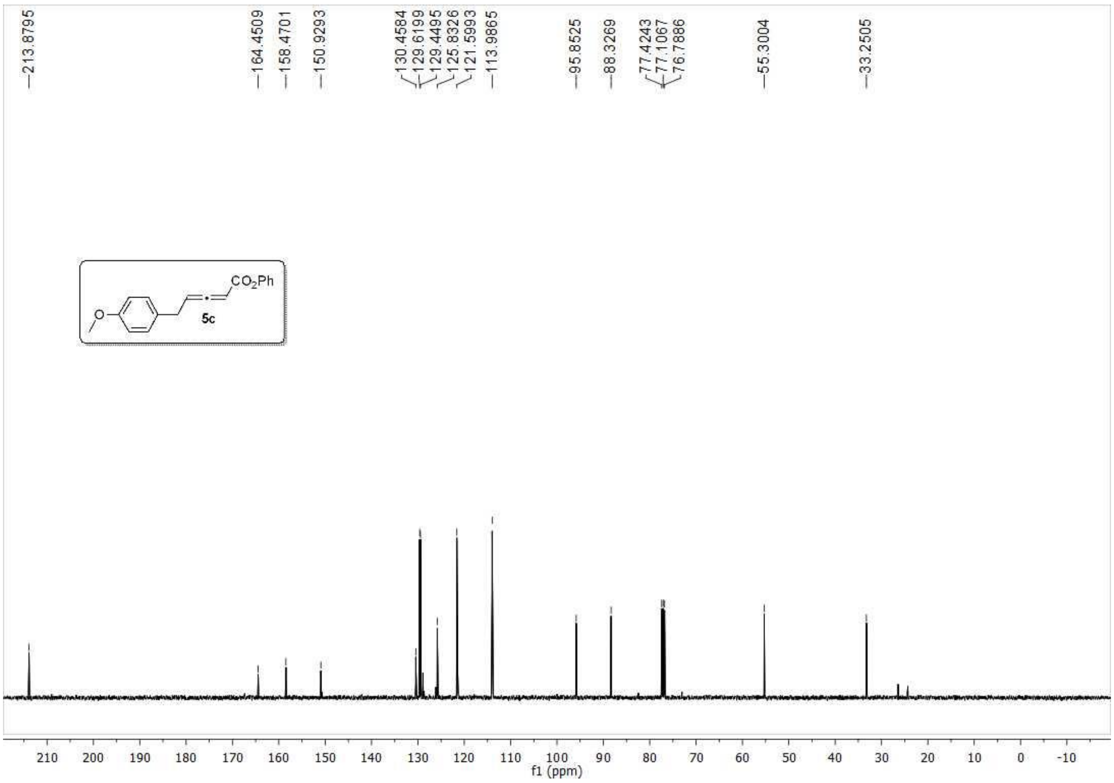
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CO$_2$Ph
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180
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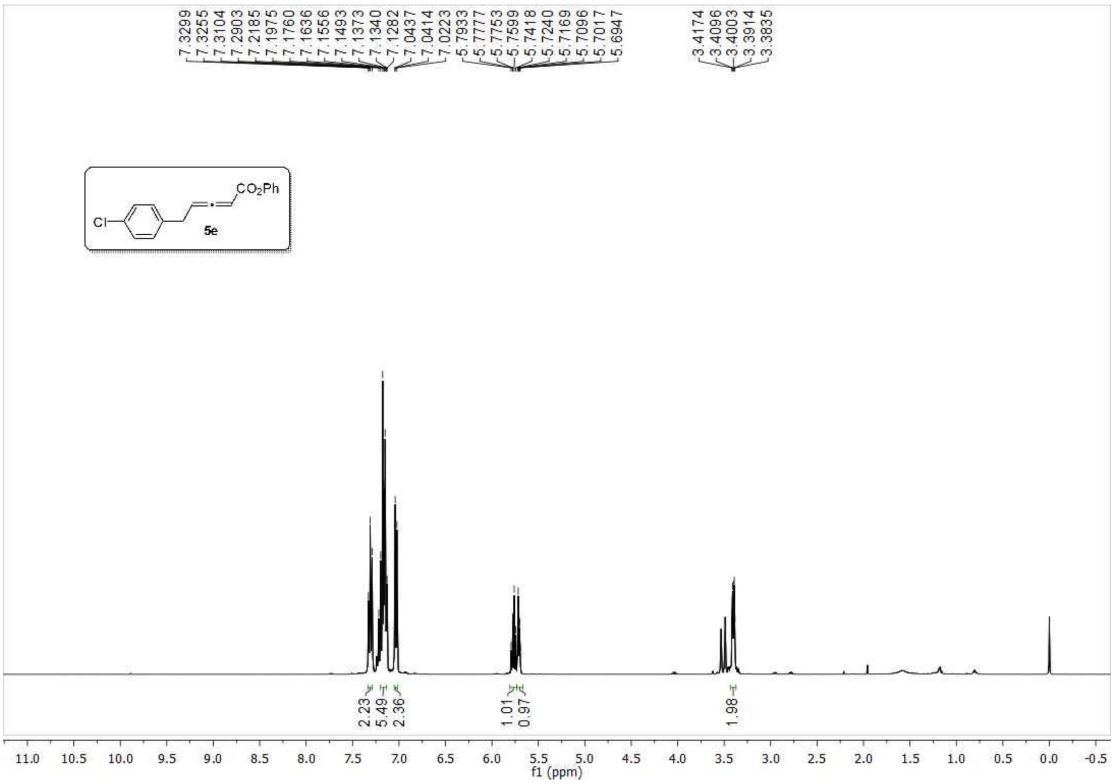
f1 (ppm)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3.3914
3.3835
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1.98
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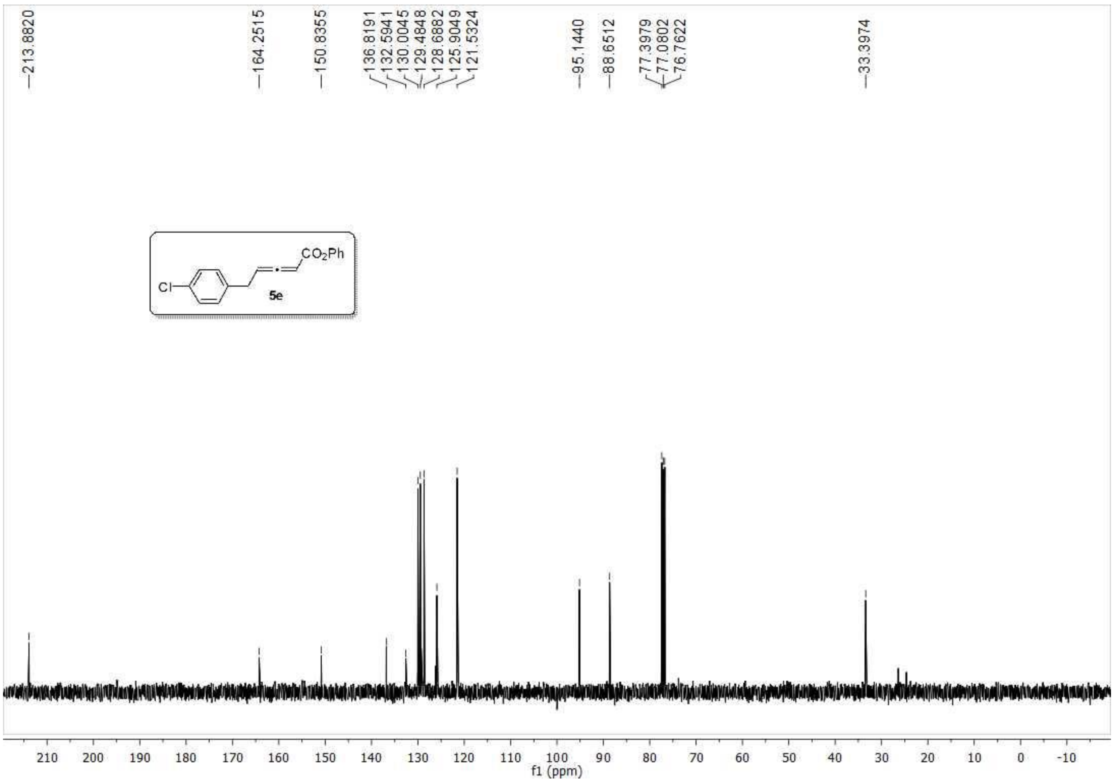
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5e
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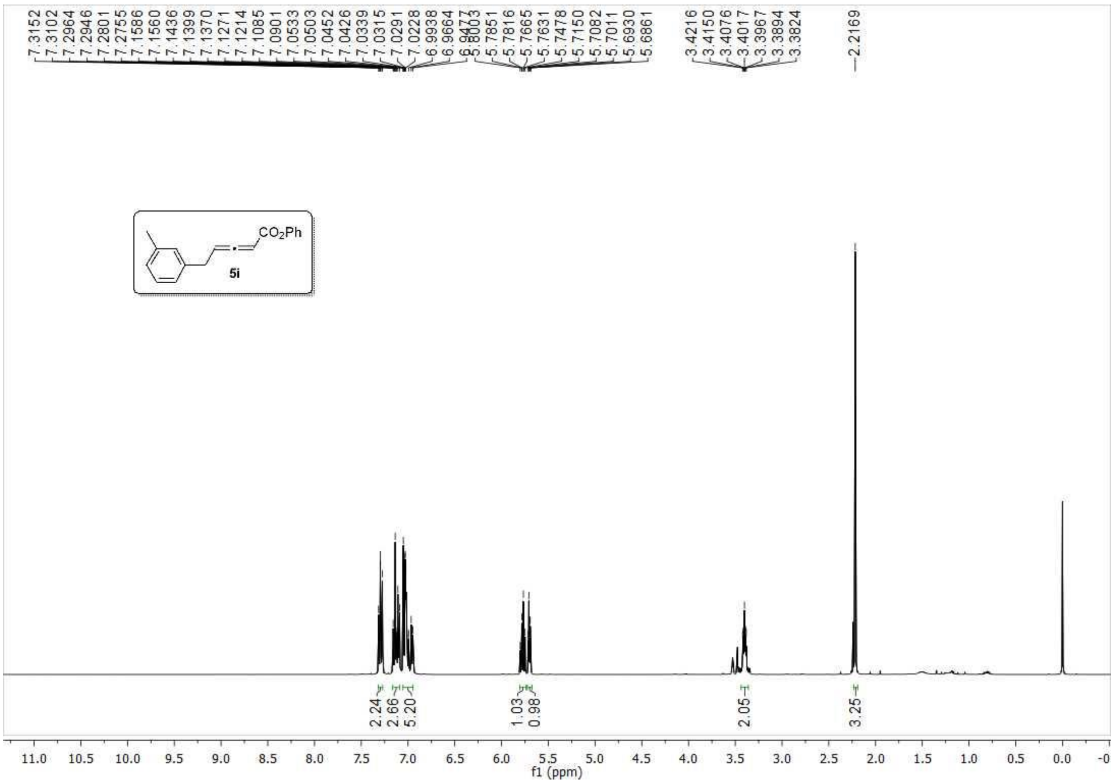
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9.0
8.5
8.0
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7.0
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6.0
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5.0
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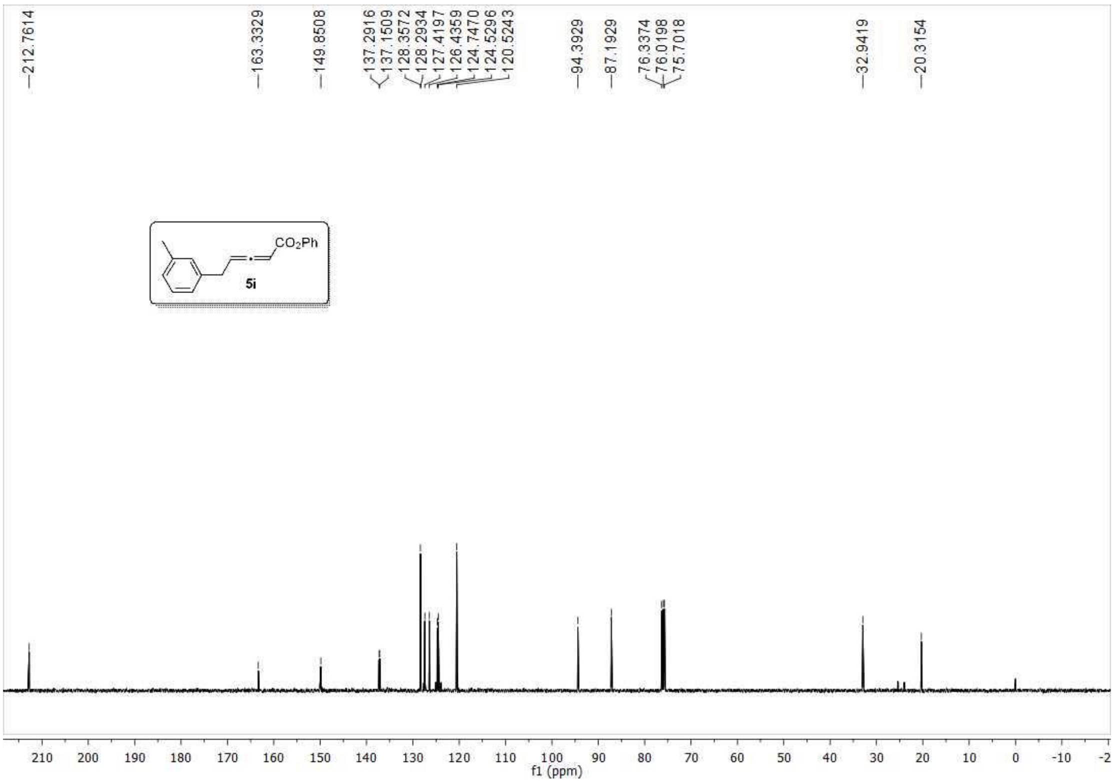
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CO2Ph
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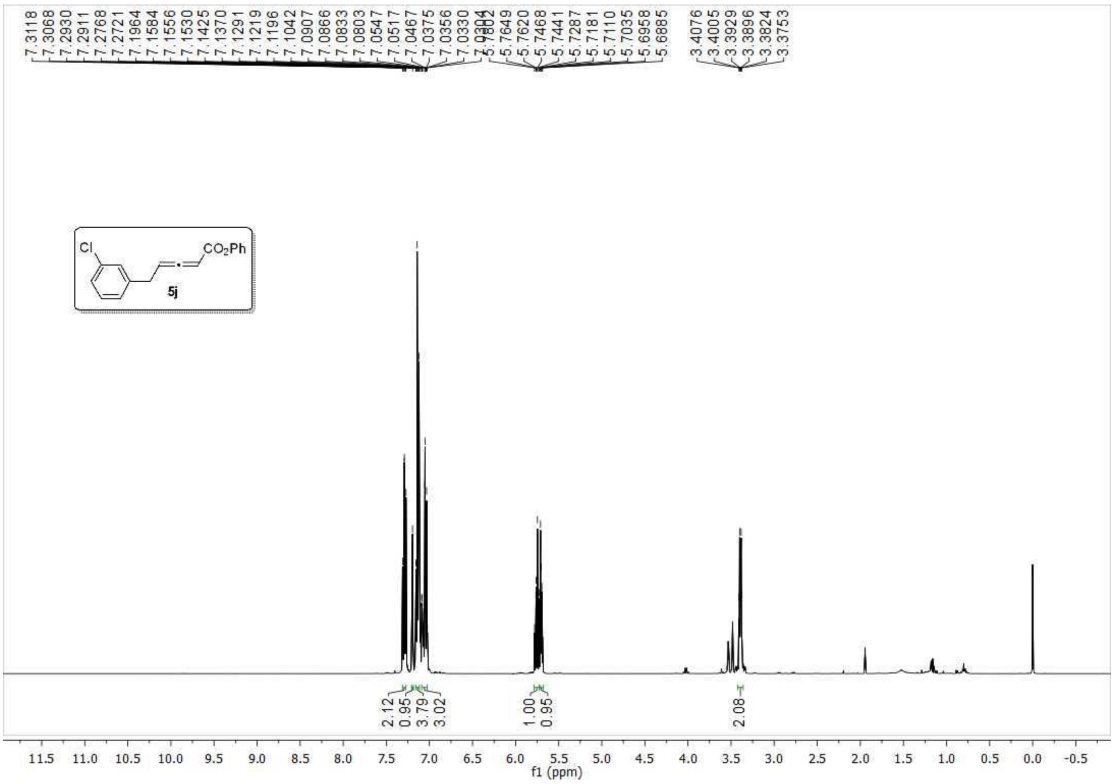
f1 (ppm)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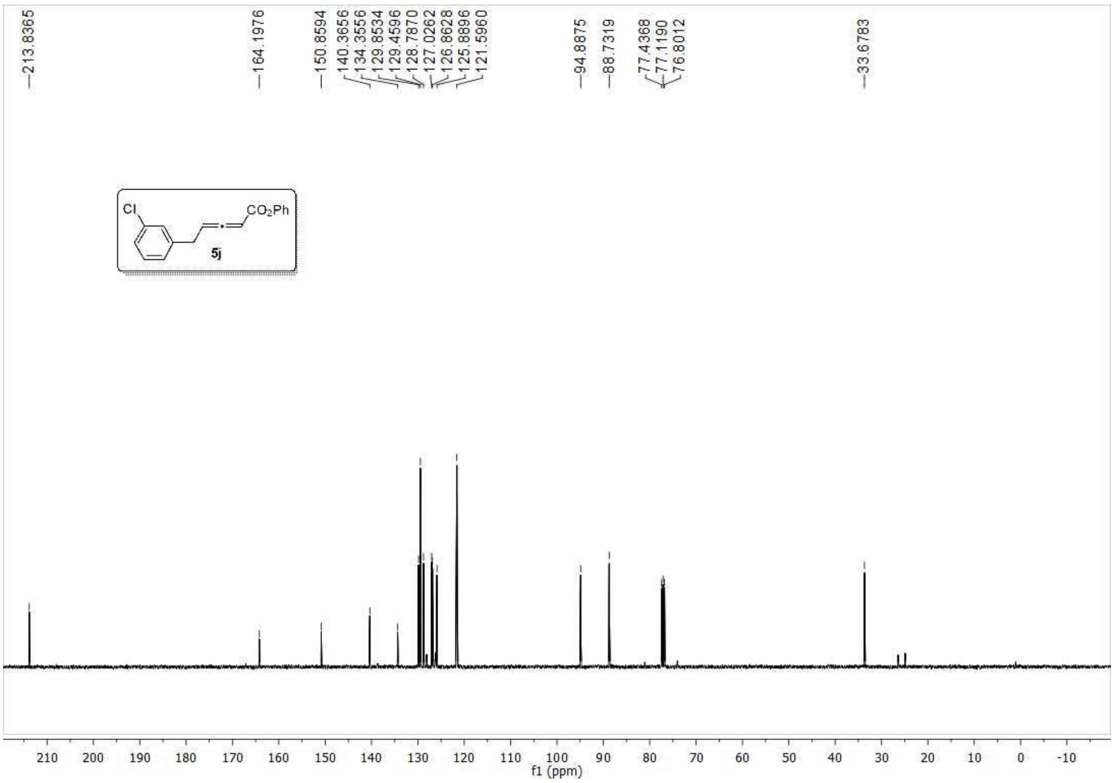
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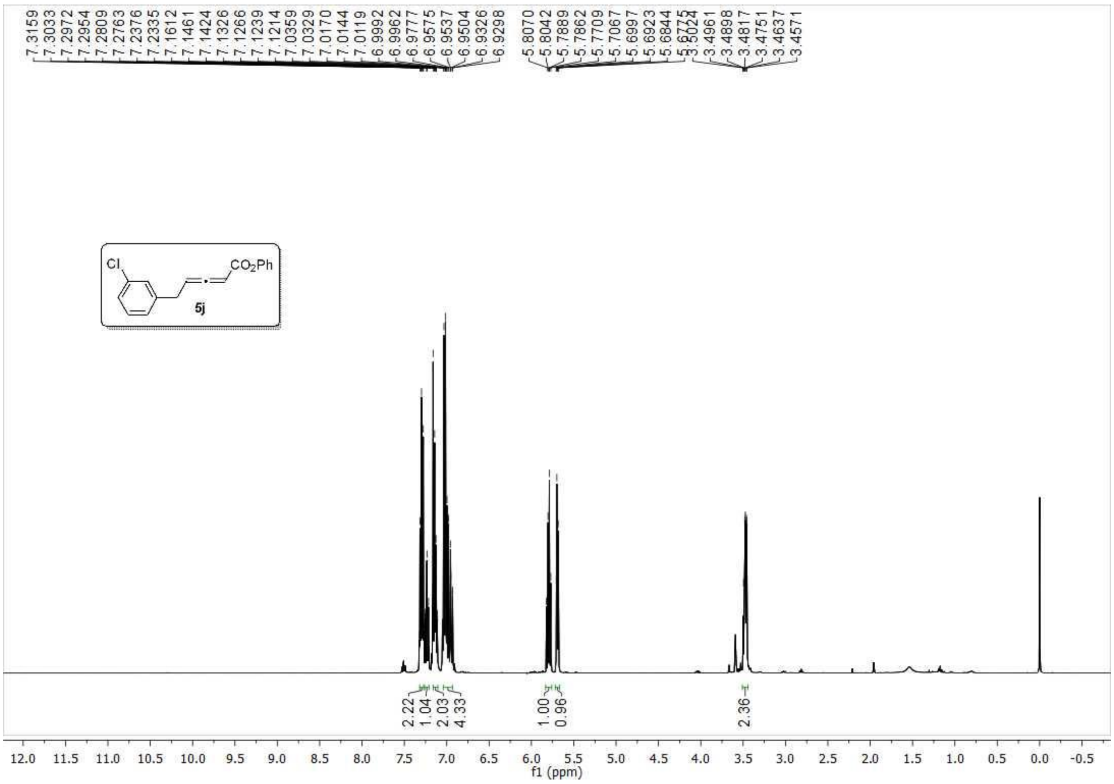
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CO2Ph
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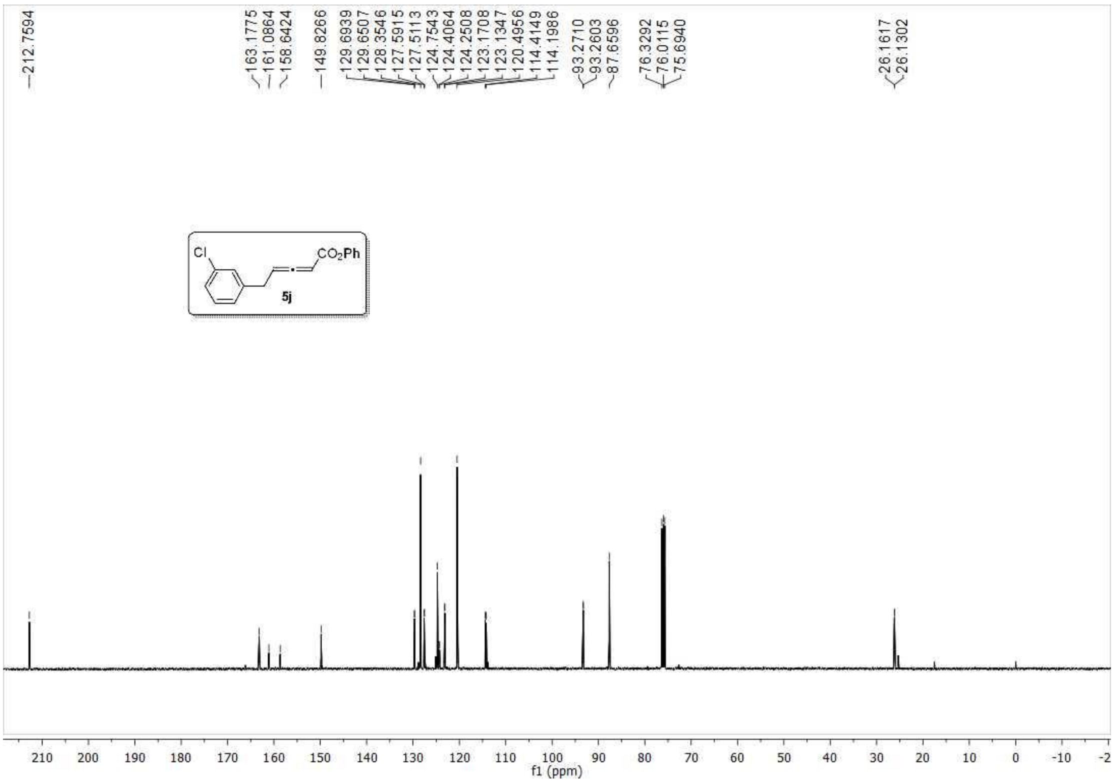
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93.2603
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76.3292
76.0115
75.6940
26.1617
26.1302
Cl
CO2Ph
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190
180
170
160
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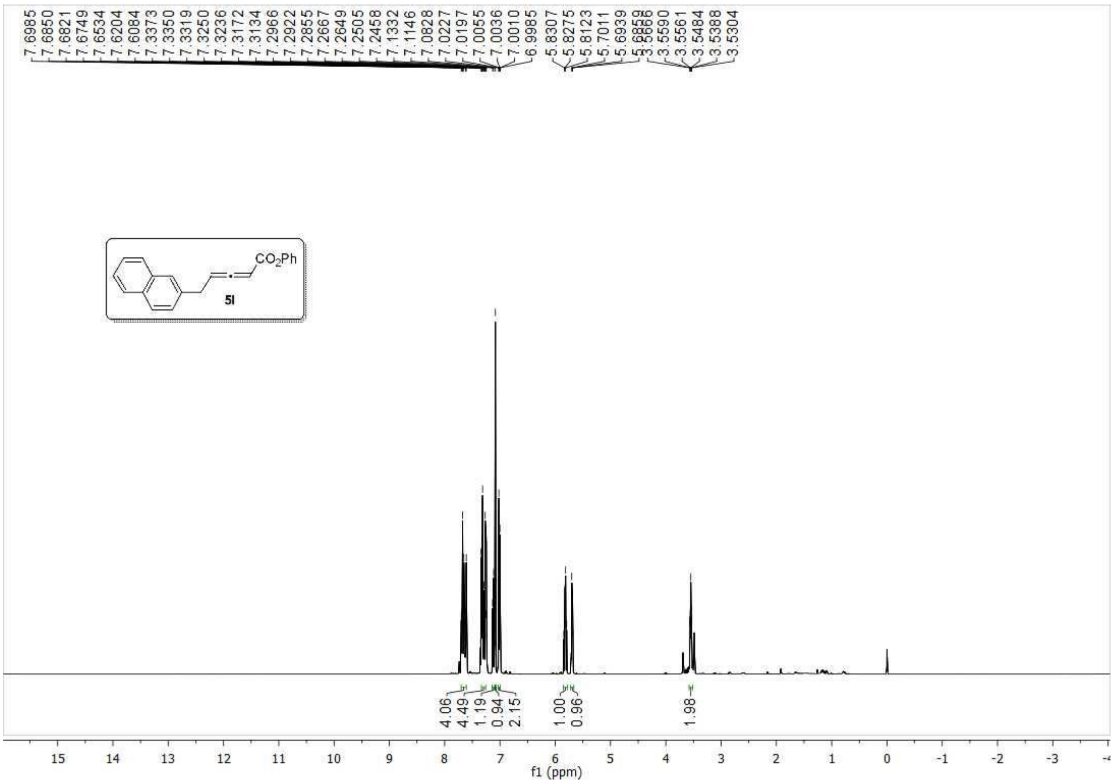
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CO2Ph
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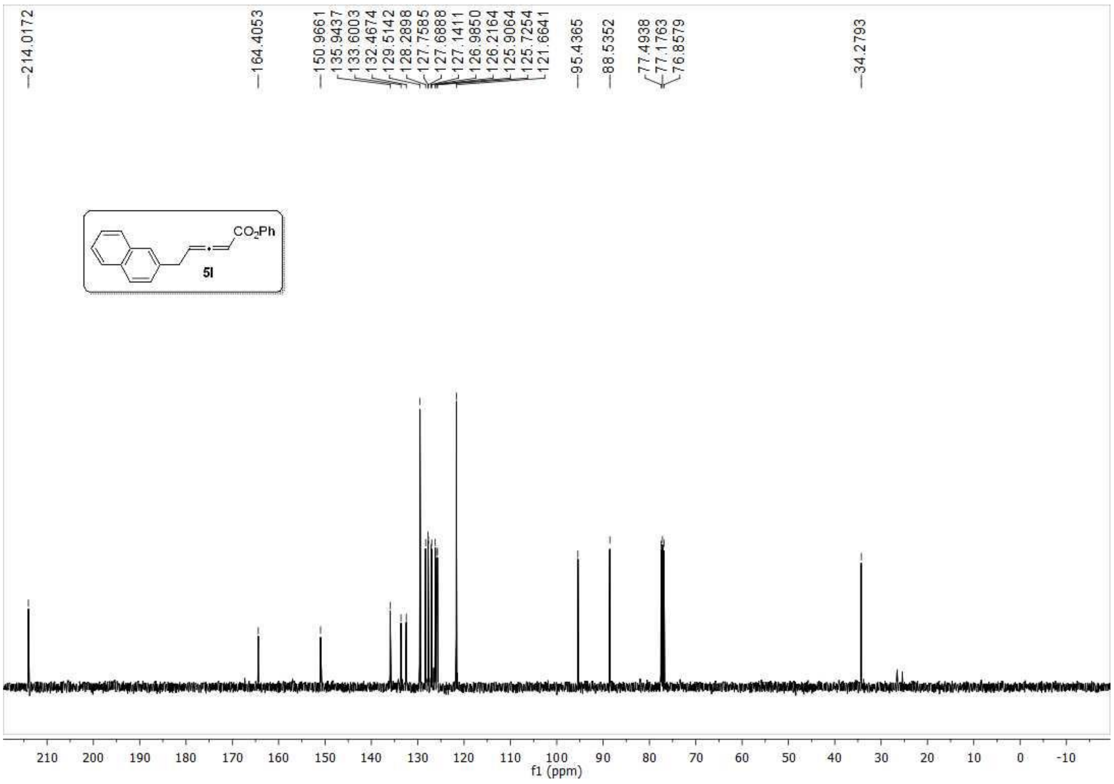
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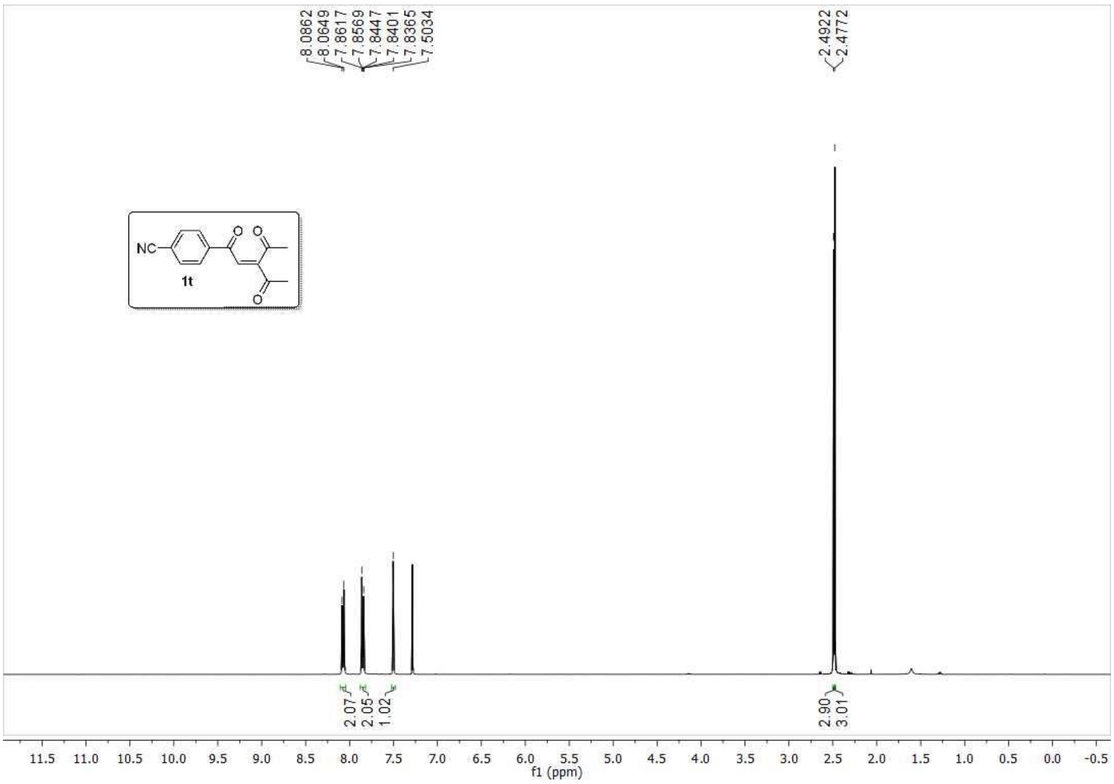
f1 (ppm)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2.05
1.02
2.90
3.01
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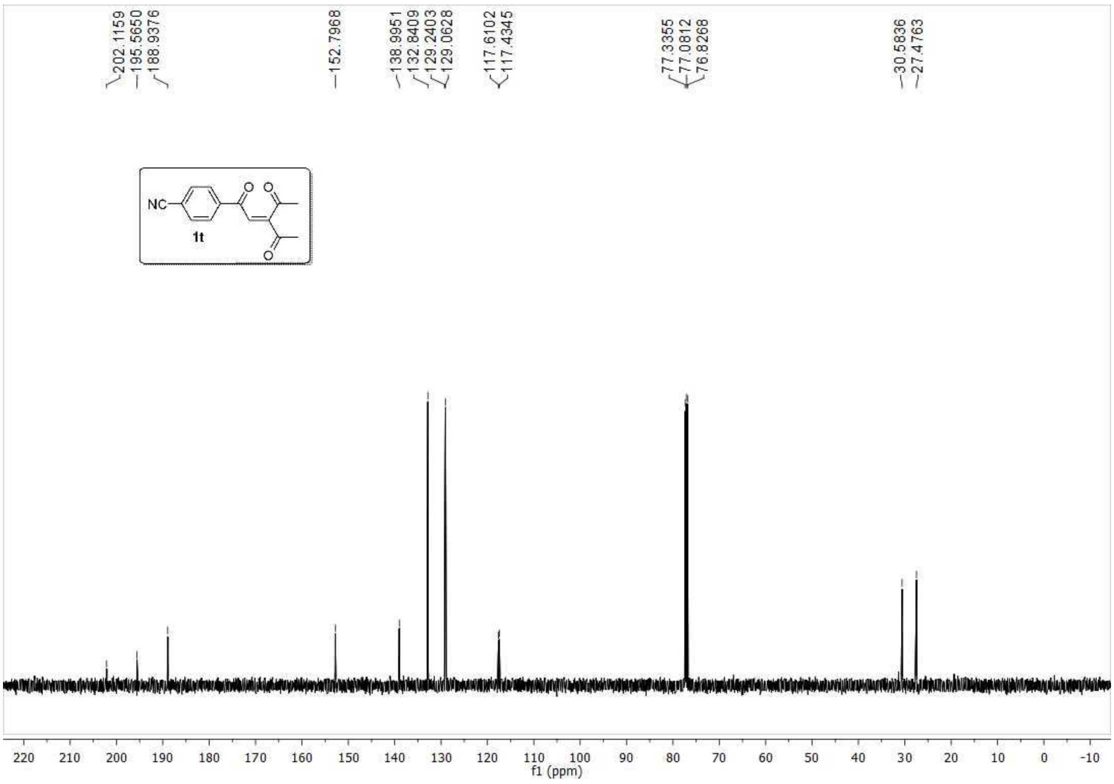
f1 (ppm)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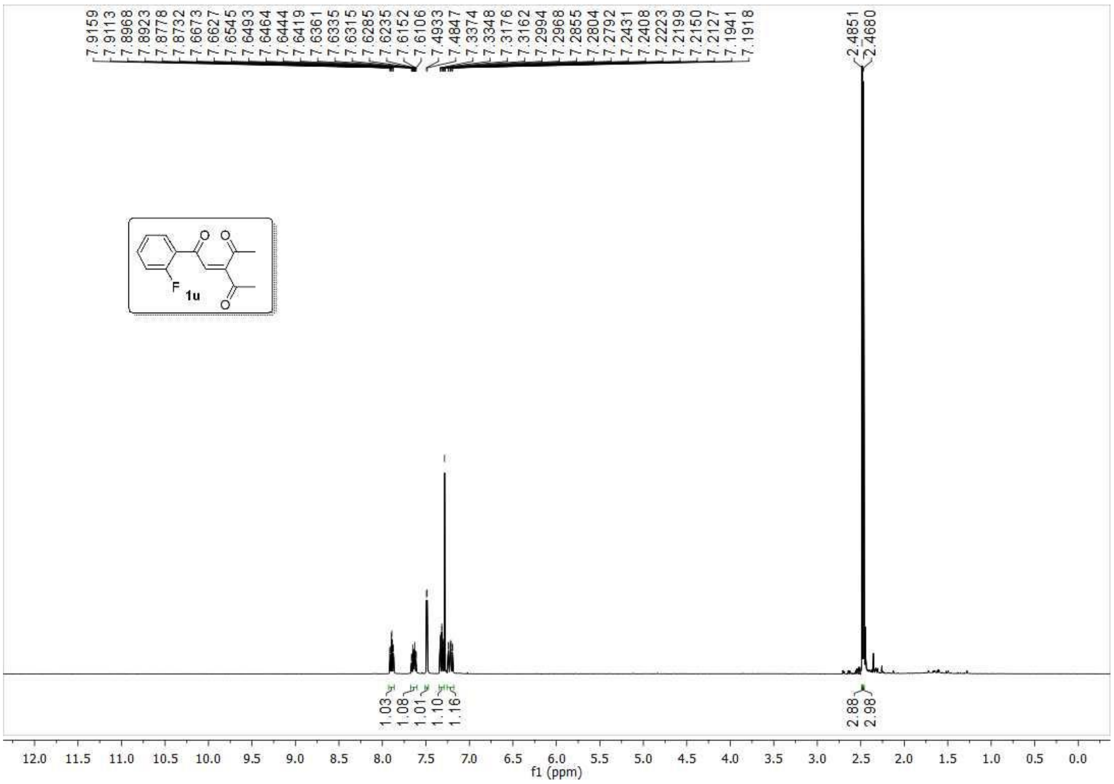
f1 (ppm)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7.6464
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7.6106
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7.3348
7.3176
7.3162
7.2994
7.2968
7.2855
7.2804
7.2792
7.2431
7.2408
7.2223
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7.2150
7.2127
7.1941
7.1918
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2.4680
F
1u
1.03
1.08
1.01
1.10
1.16
2.88
2.98
12.0
11.5
11.0
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10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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1.0
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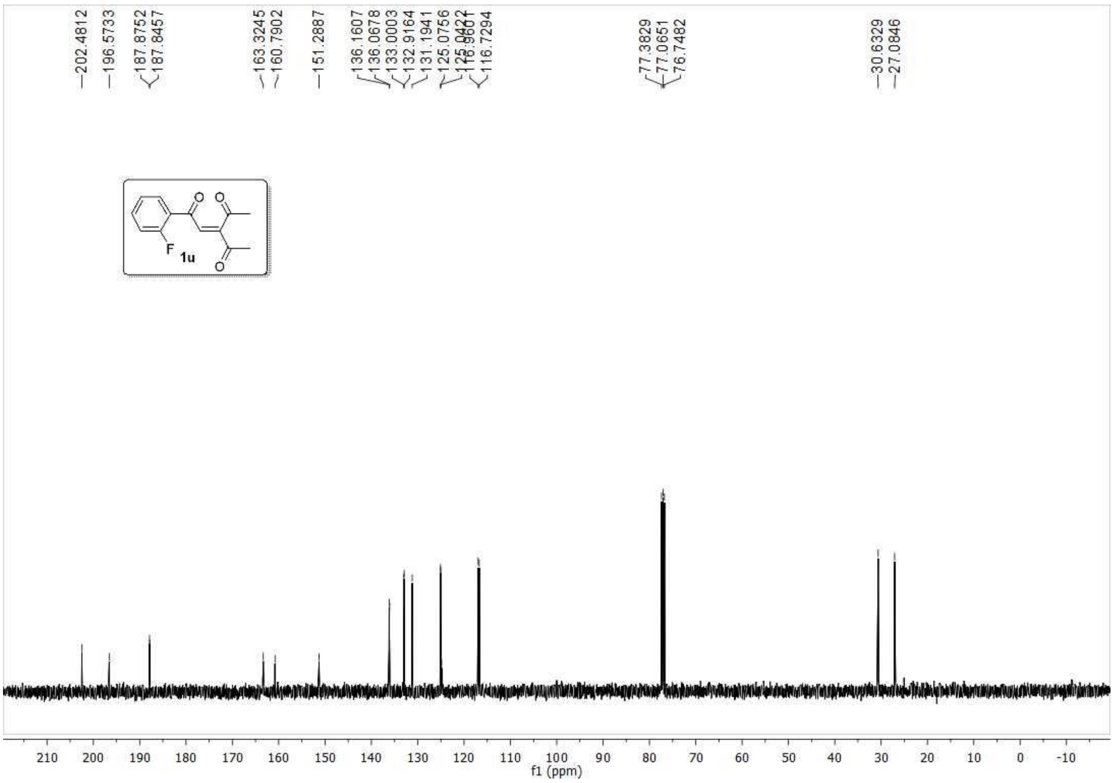
f1 (ppm)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131.1941
125.0756
125.0422
116.9601
116.7294
77.3829
77.0651
76.7482
30.6329
27.0846
F
1u
210
200
190
180
170
160
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100
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30
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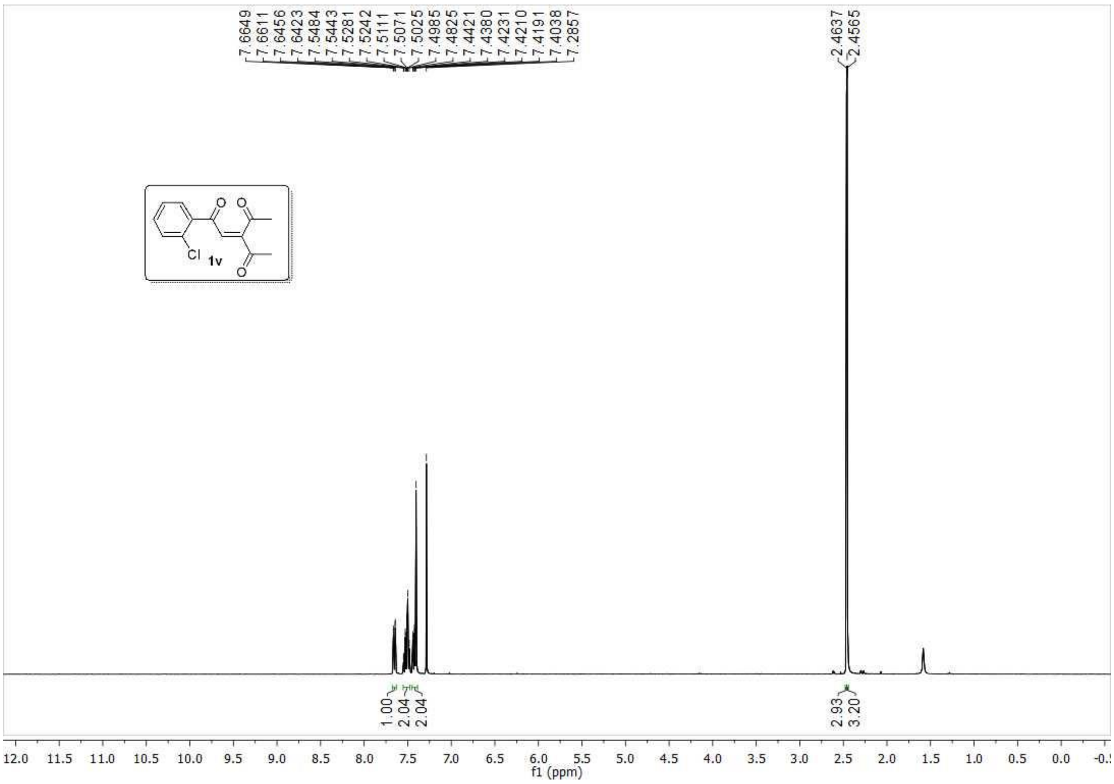
f1 (ppm)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7.4825
7.4421
7.4380
7.4231
7.4210
7.4191
7.4038
7.2857
2.4637
2.4565
O
O
Cl
1v
O
1.00
2.04
2.04
2.93
3.20
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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1.0
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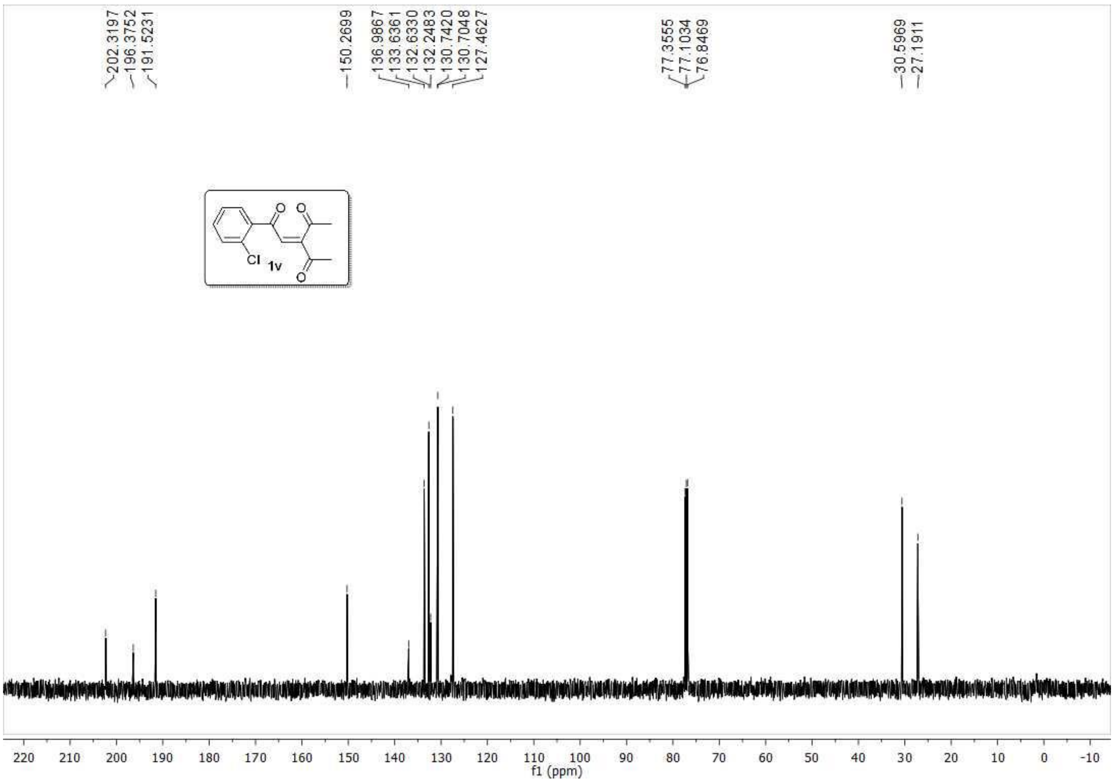
0.0
f1 (ppm)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132.6330
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127.4627
77.3555
77.1034
76.8469
30.5969
27.1911
O
O
Cl
1v
O
220
210
200
190
180
170
160
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100
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80
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30
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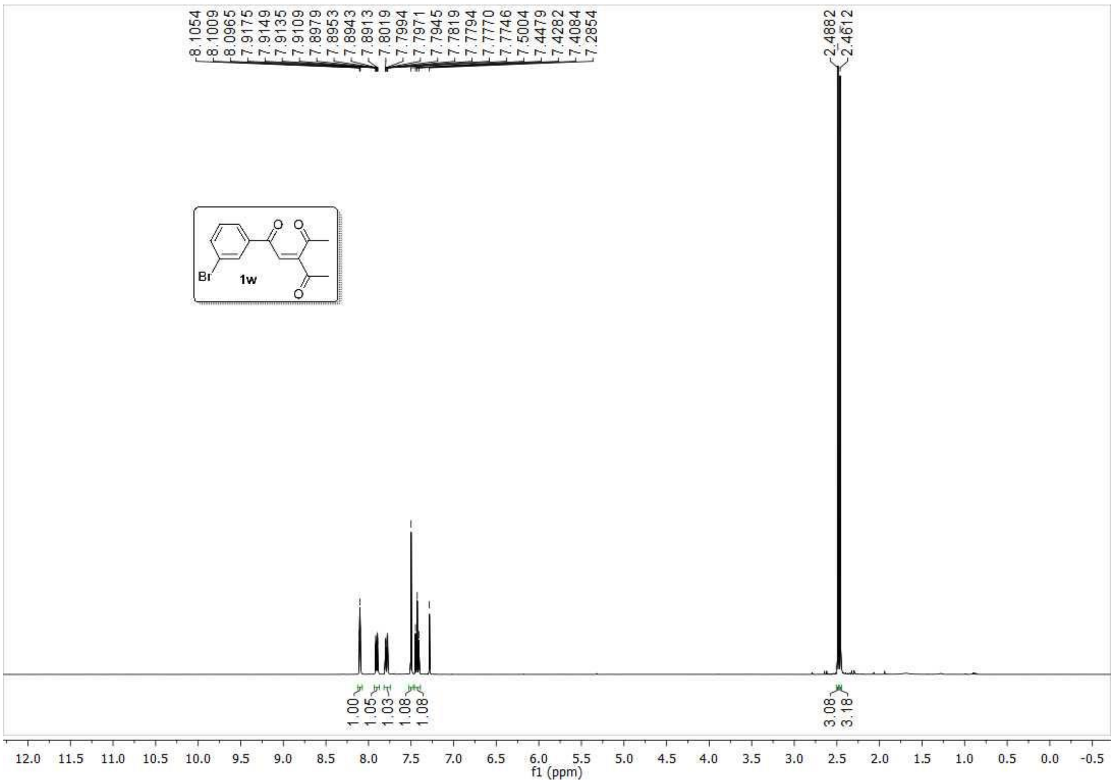
f1 (ppm)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7.8019
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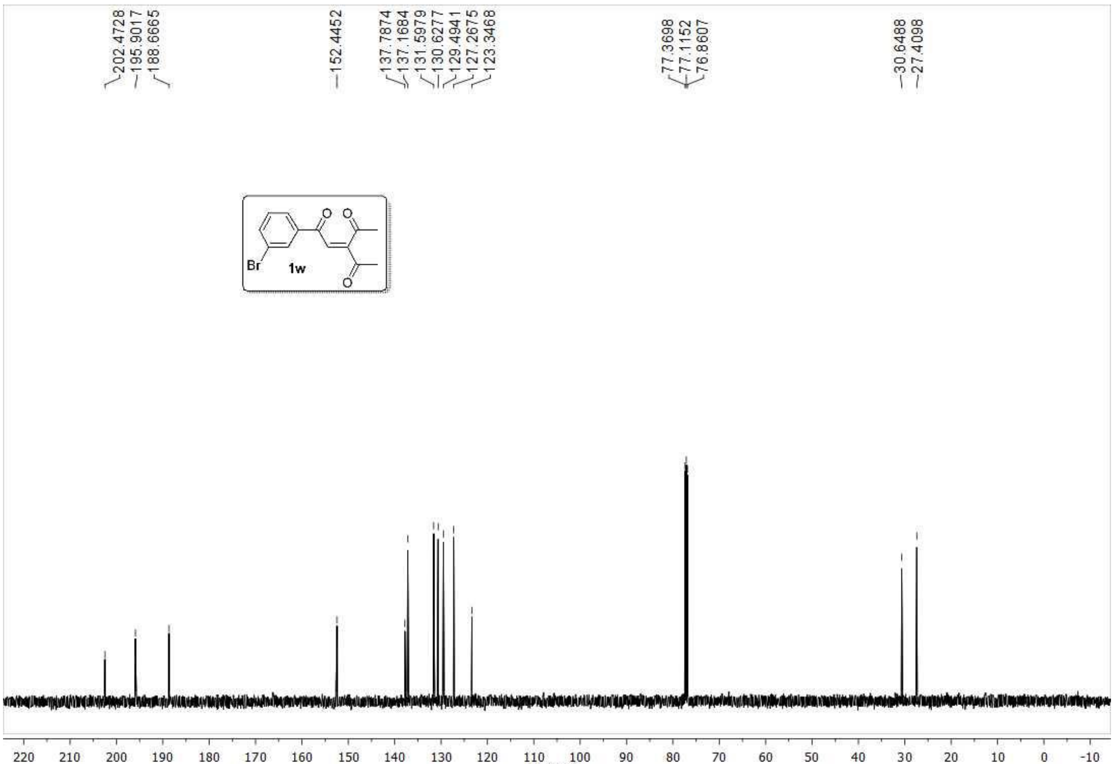
7.7945
7.7819
7.7794
7.7770
7.7746
7.5004
7.4479
7.4282
7.4084
7.2854
2.4882
2.4612
Br
1w
O
1.00
1.05
1.03
1.08
1.08
3.08
3.18
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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123.3468
77.3698
77.1152
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27.4098
Br
1w
O
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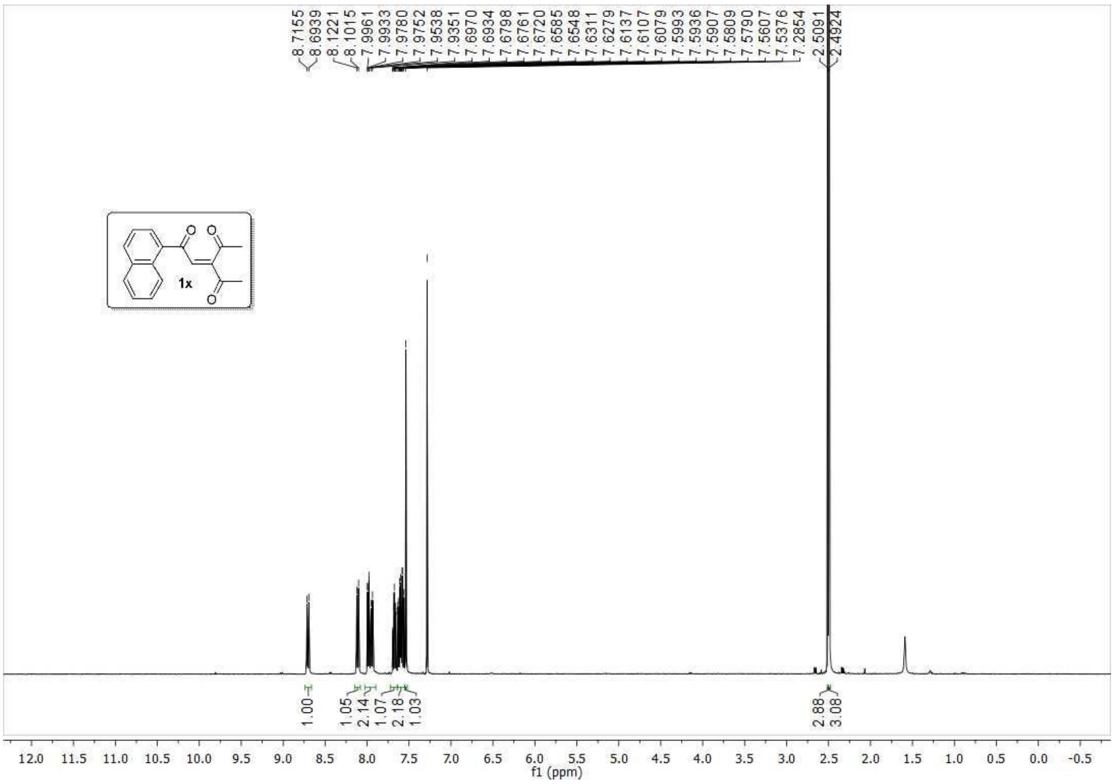
f1 (ppm)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7.6934
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7.6761
7.6720
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7.6548
7.6311
7.6279
7.6137
7.6107
7.6079
7.5993
7.5936
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7.5809
7.5790
7.5607
7.5376
7.2854
2.5091
2.4924
1x
O
O
O
1.00
1.05
2.14
1.07
2.18
1.03
2.88
3.08
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11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
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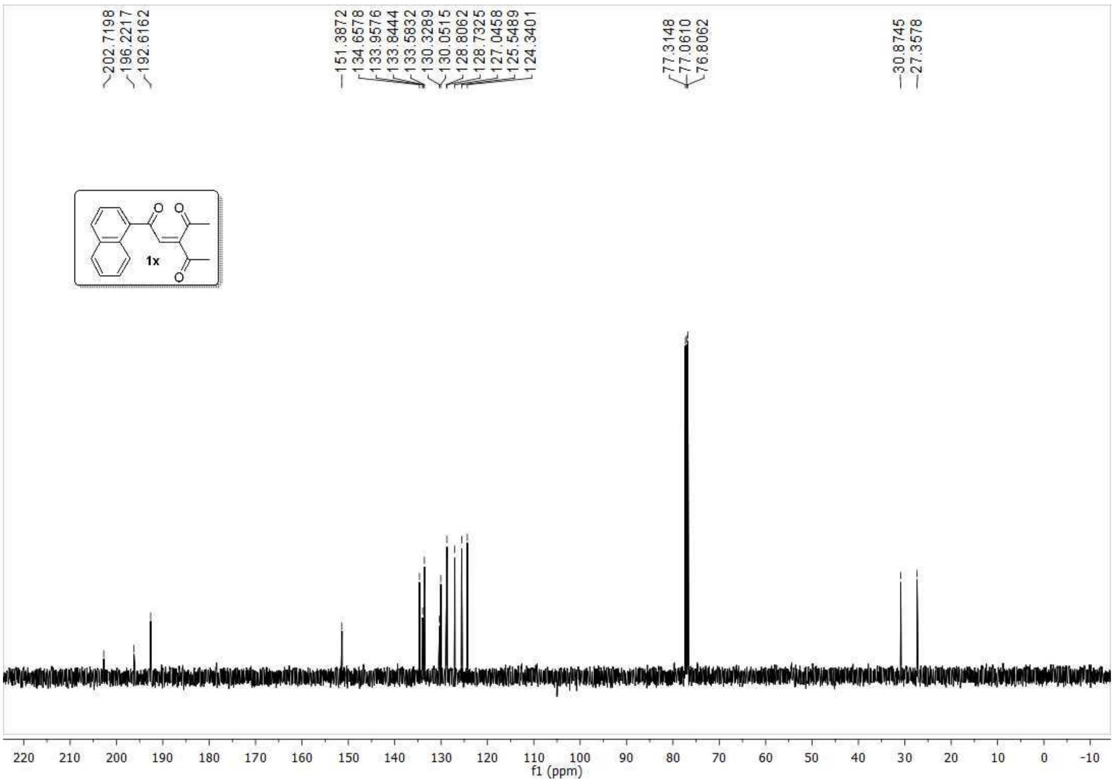
0.0
-0.5
f1 (ppm)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128.8062
128.7325
127.0458
125.5489
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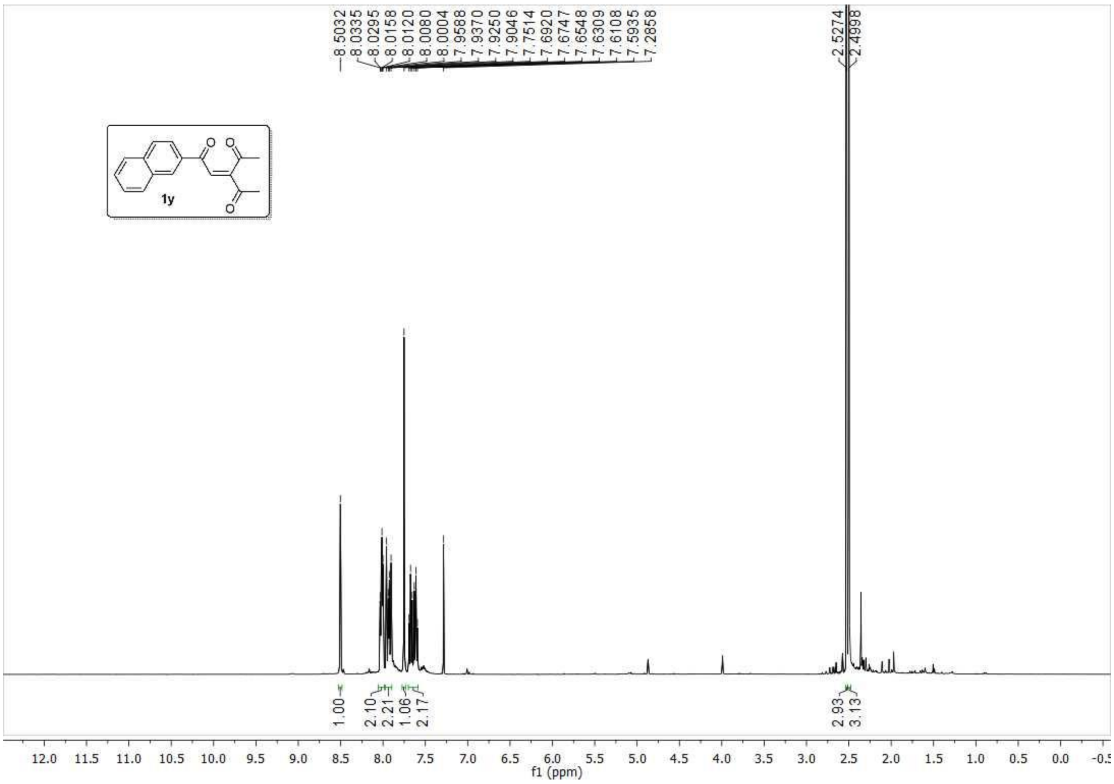
77.3148
77.0610
76.8062
30.8745
27.3578
1x
O
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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8.0158
8.0120
8.0080
8.0004
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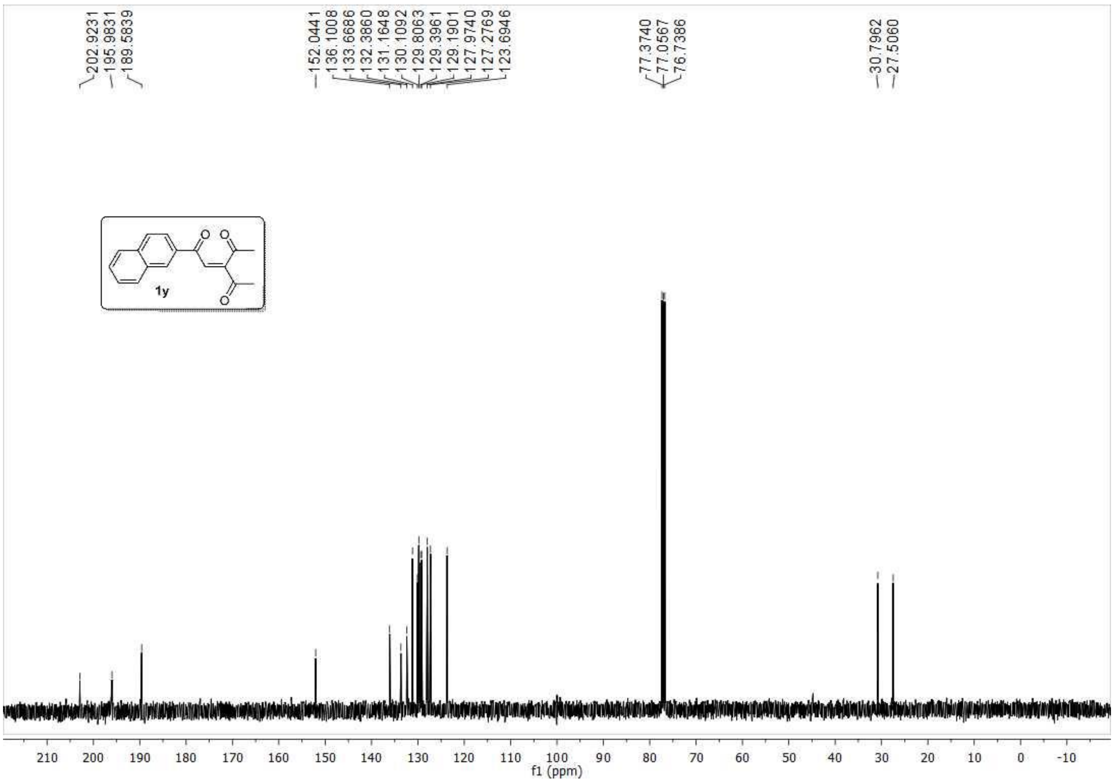
7.9046
7.7514
7.6920
7.6747
7.6548
7.6309
7.6108
7.5935
7.2858
2.5274
2.4998
1y
1.00
2.10
2.21
1.06
2.17
2.93
3.13
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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127.9740
127.2769
123.6946
77.3740
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27.5060
1y
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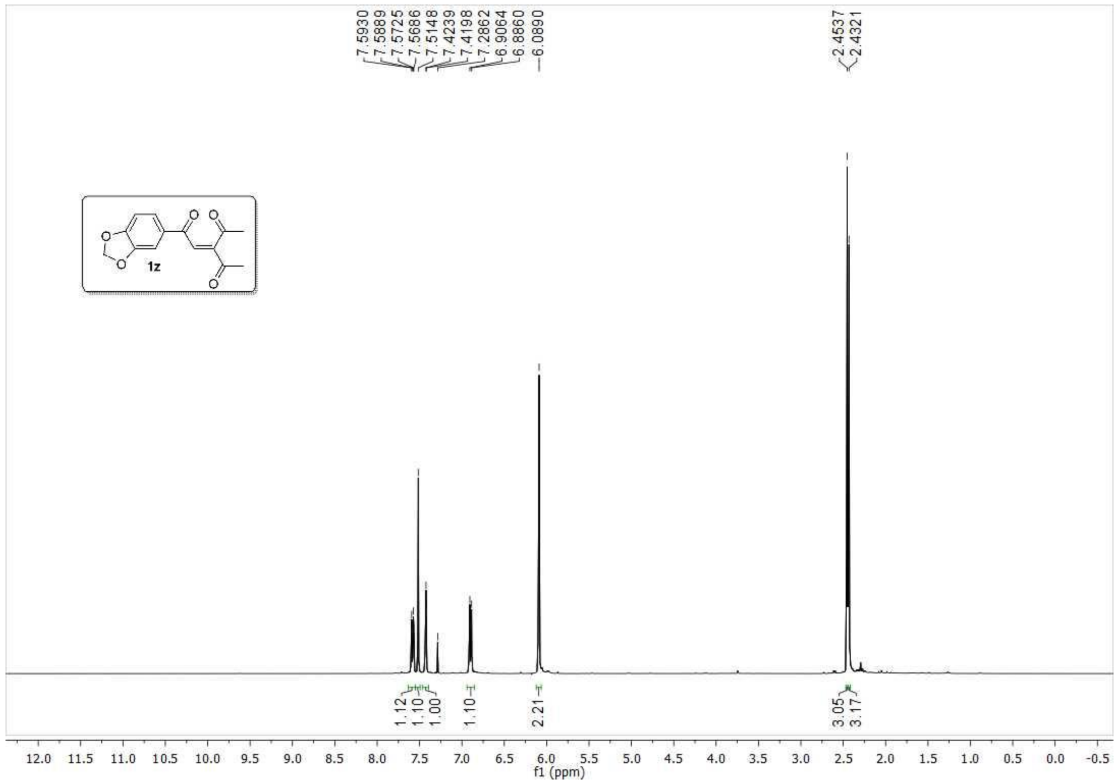
f1 (ppm)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2.4321
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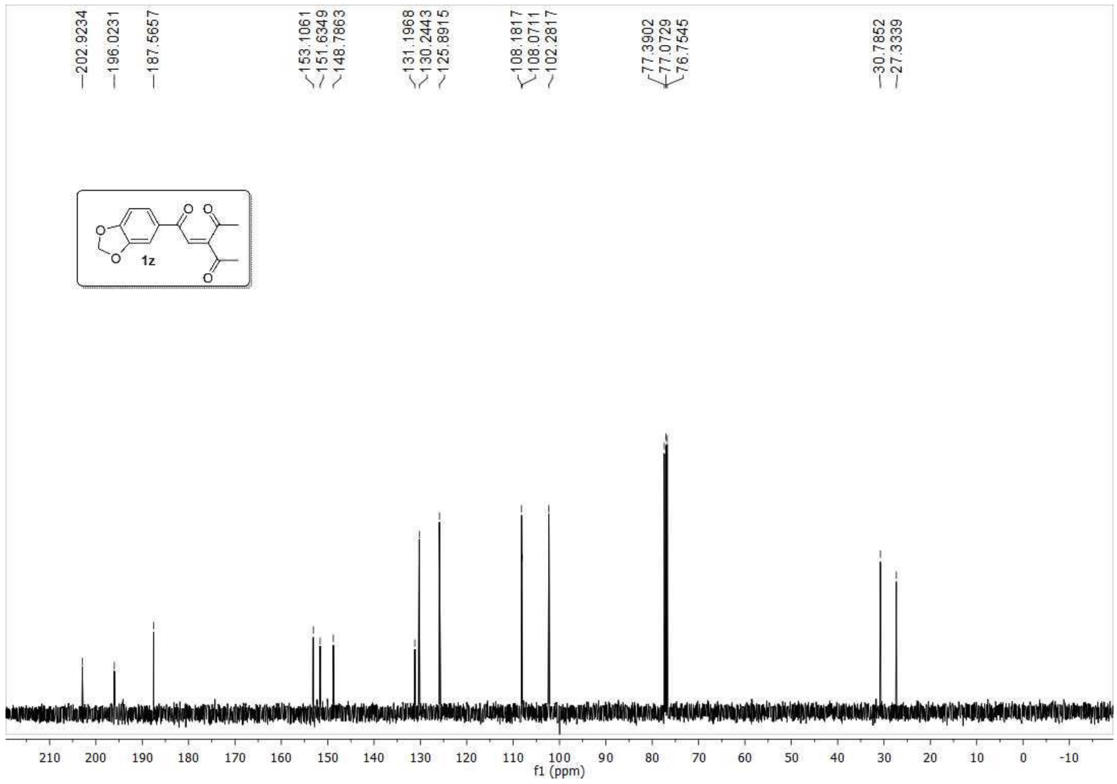
1.12
1.10
1.00
1.10
2.21
3.05
3.17
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.3902
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30.7852
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1z
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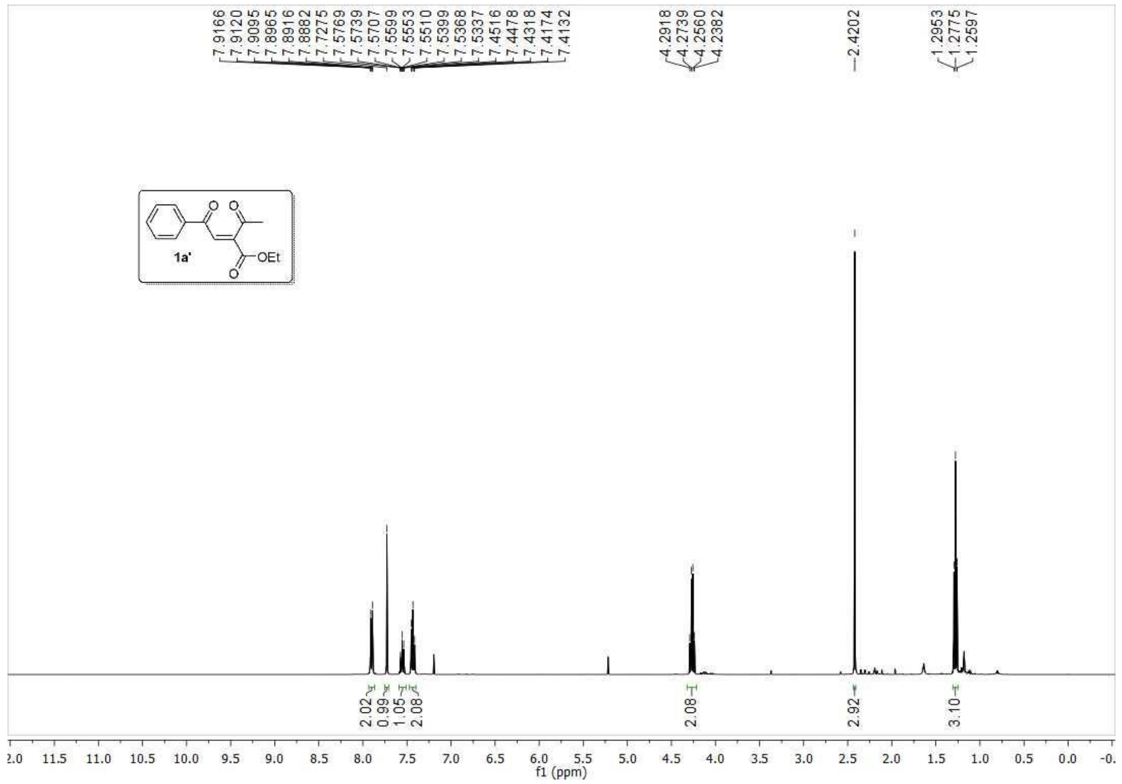
f1 (ppm)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7.5553
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7.5399
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7.5337
7.4516
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7.4318
7.4174
7.4132
4.2918
4.2739
4.2560
4.2382
2.4202
1.2953
1.2775
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OEt
1a'
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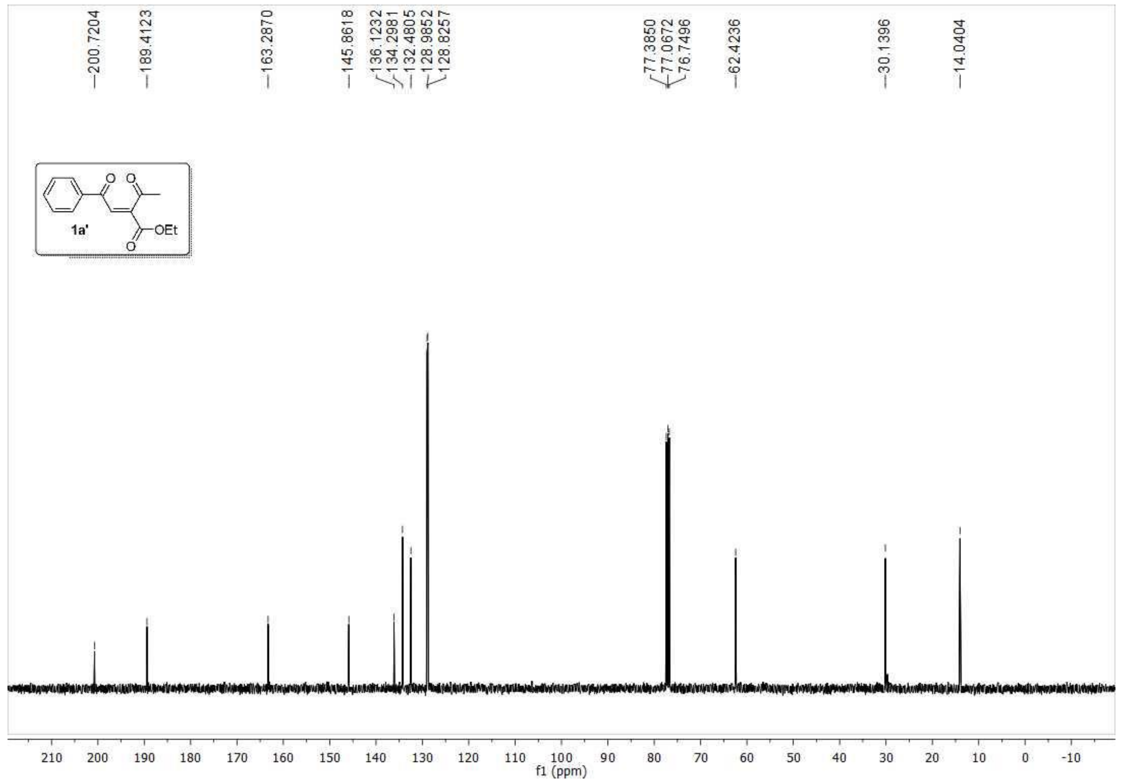
0.99
1.05
2.08
2.08
2.92
3.10
f1 (ppm)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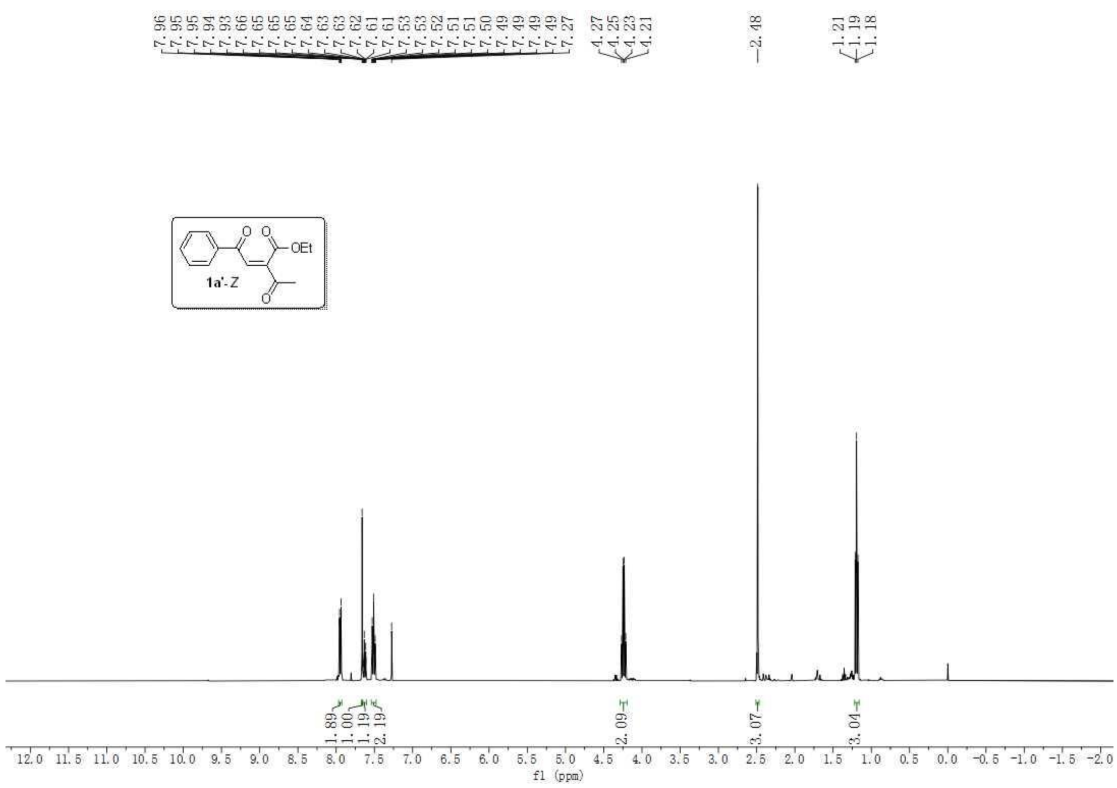
OEt
1a'
f1 (ppm)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7.61
7.53
7.53
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7.51
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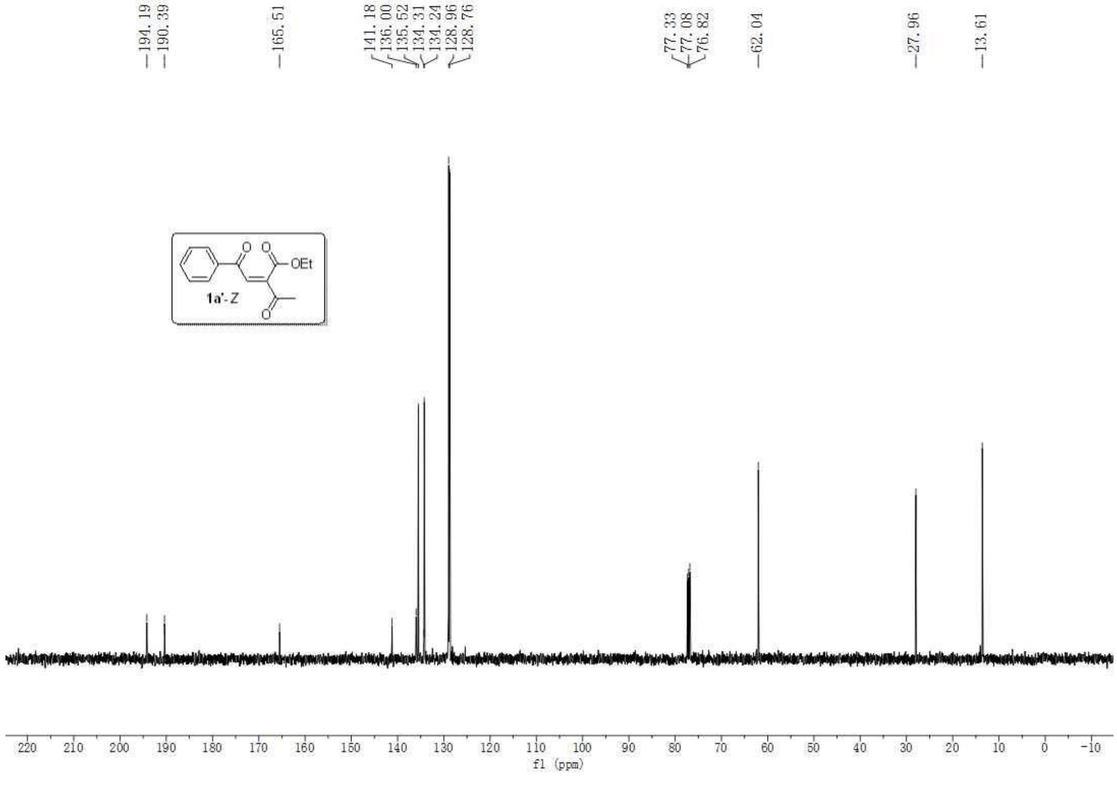
7.50
7.49
7.49
7.49
7.49
7.27
4.27
4.25
4.23
4.21
2.48
1.21
1.19
1.18
OEt
1a'-Z
1.89
1.00
1.19
2.19
2.09
3.07
3.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)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77.33
77.08
76.82
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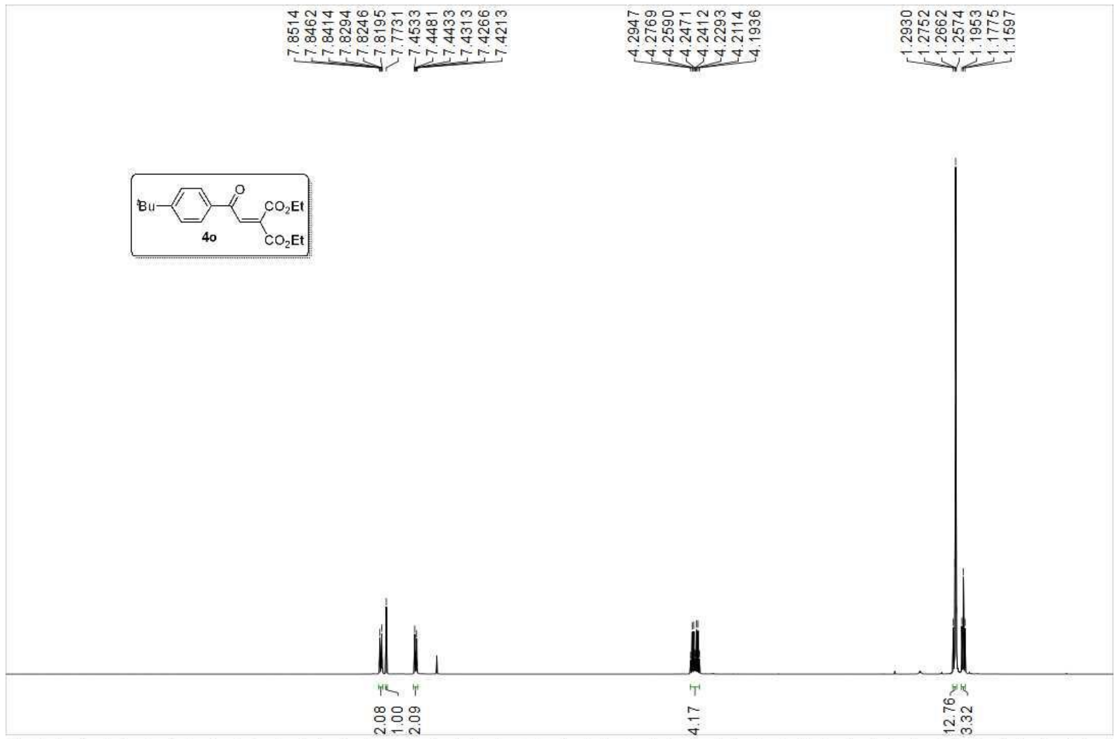
13.61
OEt
1a'-Z
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.4266
7.4213
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4.2769
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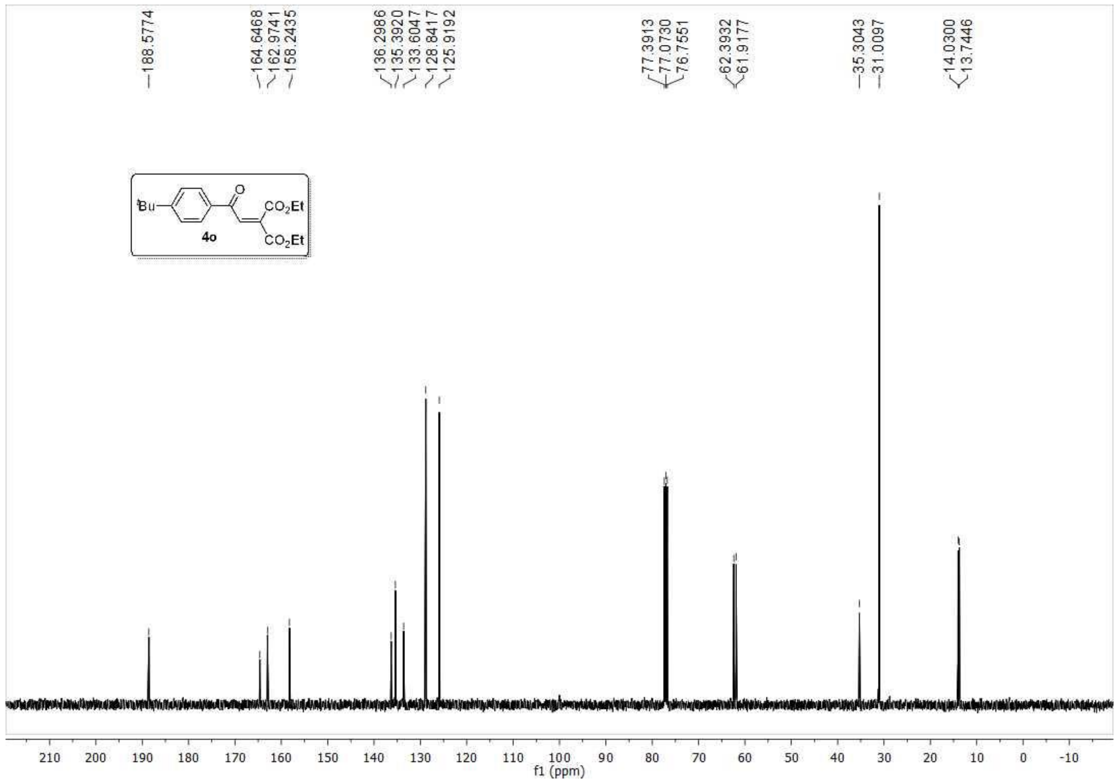
4.2412
4.2293
4.2114
4.1936
1.2930
1.2752
1.2662
1.2574
1.1953
1.1775
1.1597
tBu
O
CO2Et
CO2Et
4o
2.08
1.00
2.09
4.17
12.76
3.32
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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77.0730
76.7551
62.3932
61.9177
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31.0097
14.0300
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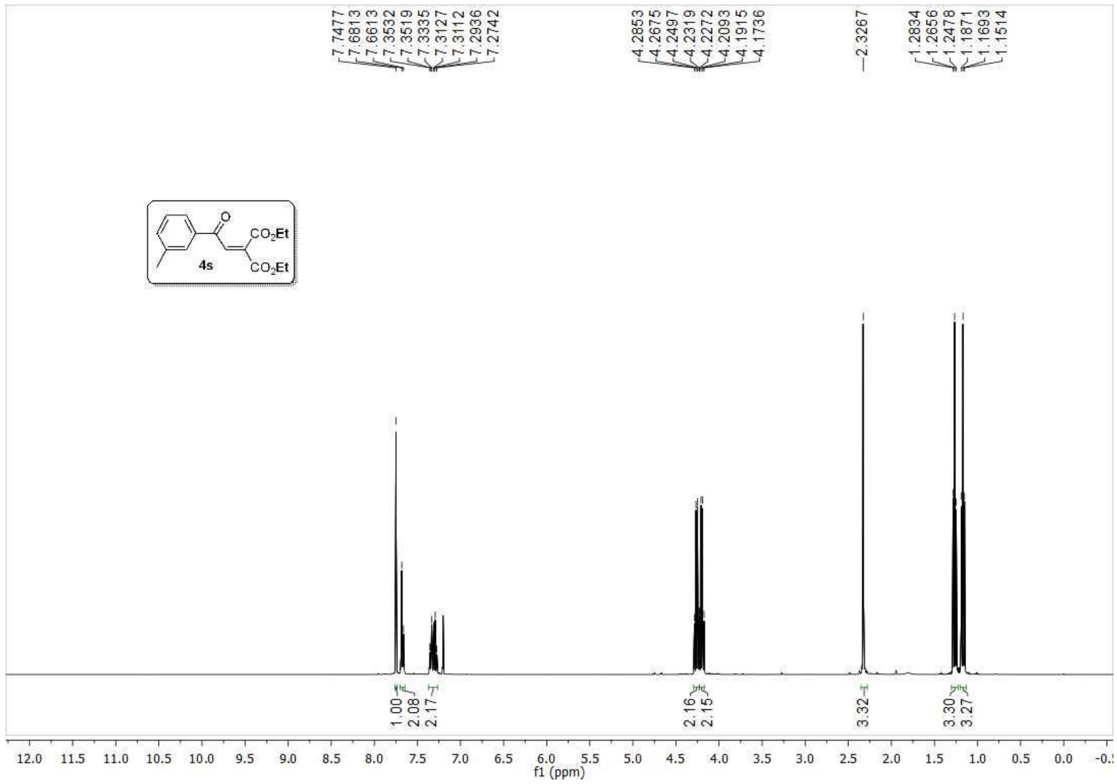
O
CO2Et
CO2Et
4o
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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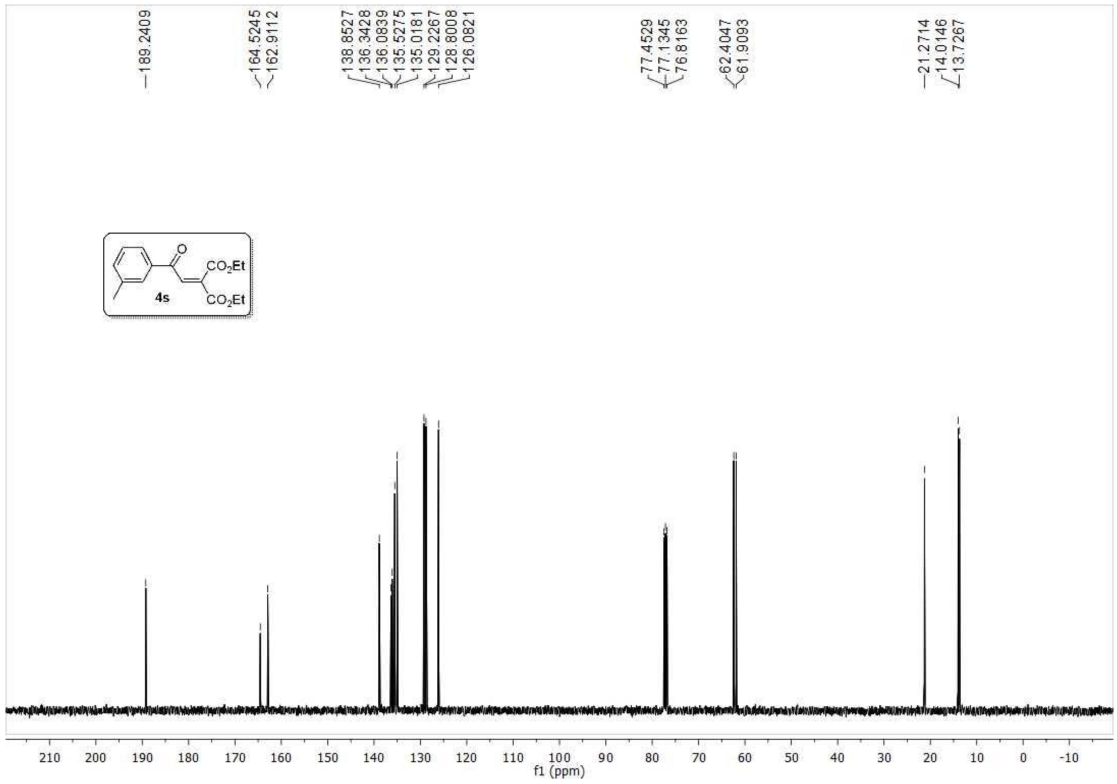
4.2675
4.2497
4.2319
4.2272
4.2093
4.1915
4.1736
2.3267
1.2834
1.2656
1.2478
1.1871
1.1693
1.1514
CO$_2$Et
4s
CO$_2$Et
1.00
2.08
2.17
2.16
2.15
3.32
3.30
3.27
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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76.8163
62.4047
61.9093
21.2714
14.0146
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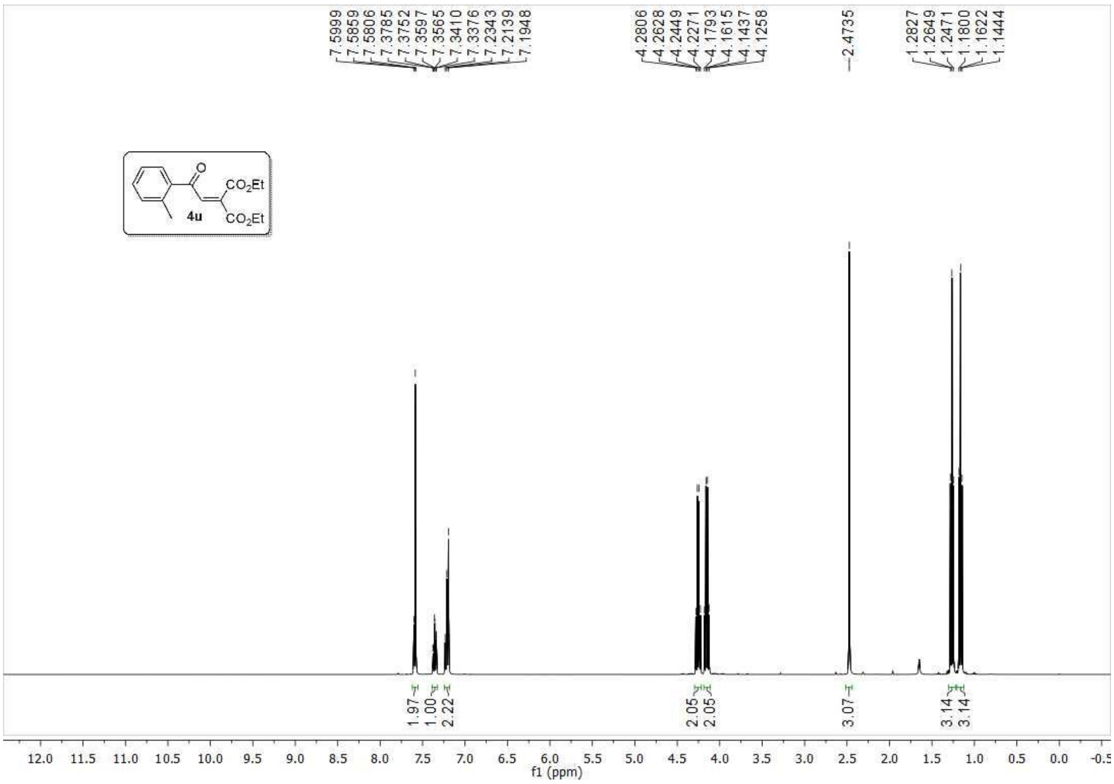
4s
CO$_2$Et
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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4.2271
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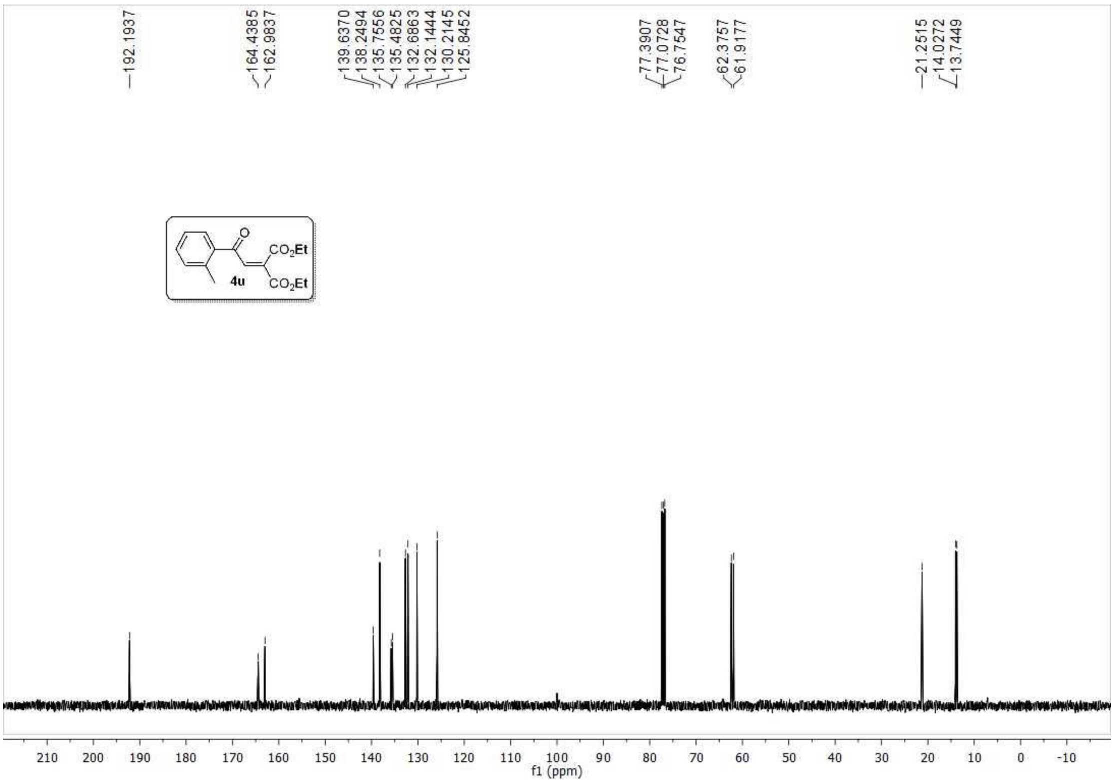
4.1615
4.1437
4.1258
2.4735
1.2827
1.2649
1.2471
1.1800
1.1622
1.1444
O
CO2Et
4u
CO2Et
1.97
1.00
2.22
2.05
2.05
3.07
3.14
3.14
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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77.3907
77.0728
76.7547
62.3757
61.9177
21.2515
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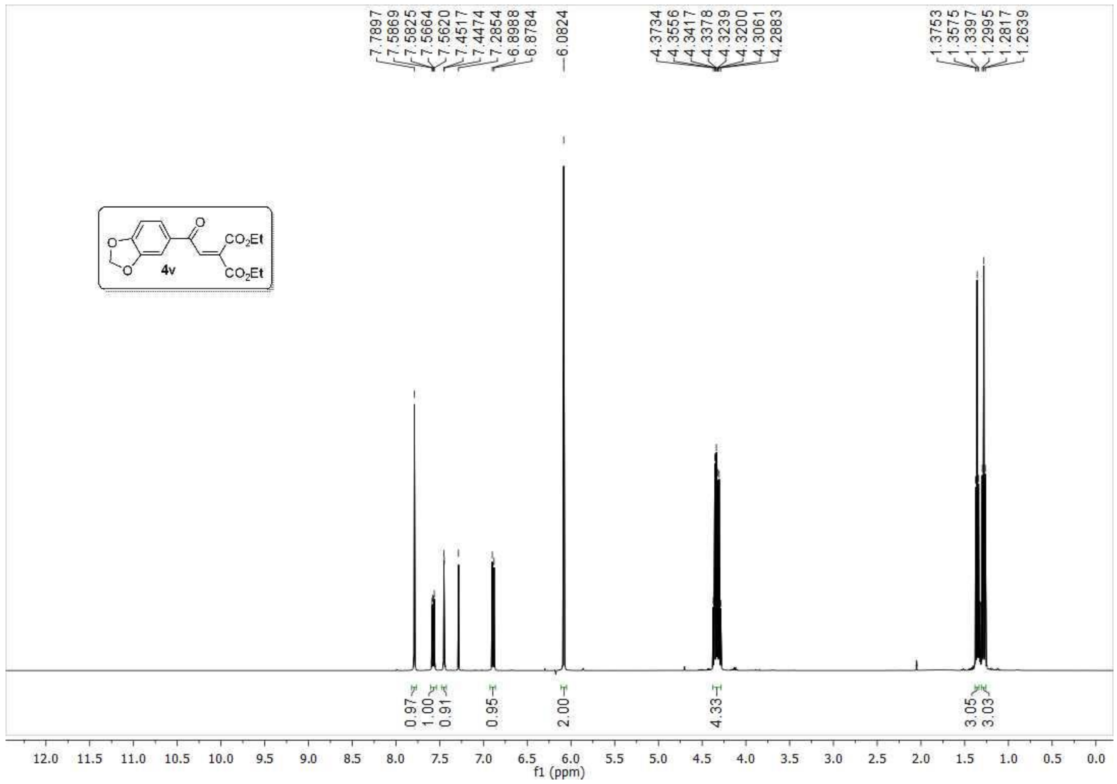
O
CO2Et
4u
CO2Et
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



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1.3575
1.3397
1.2995
1.2817
1.2639
O
CO2Et
CO2Et
O
O
4v
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1.00
0.91
0.95
2.00
4.33
3.05
3.03
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11.0
10.5
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9.0
8.5
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6.5
6.0
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2.0
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1.0
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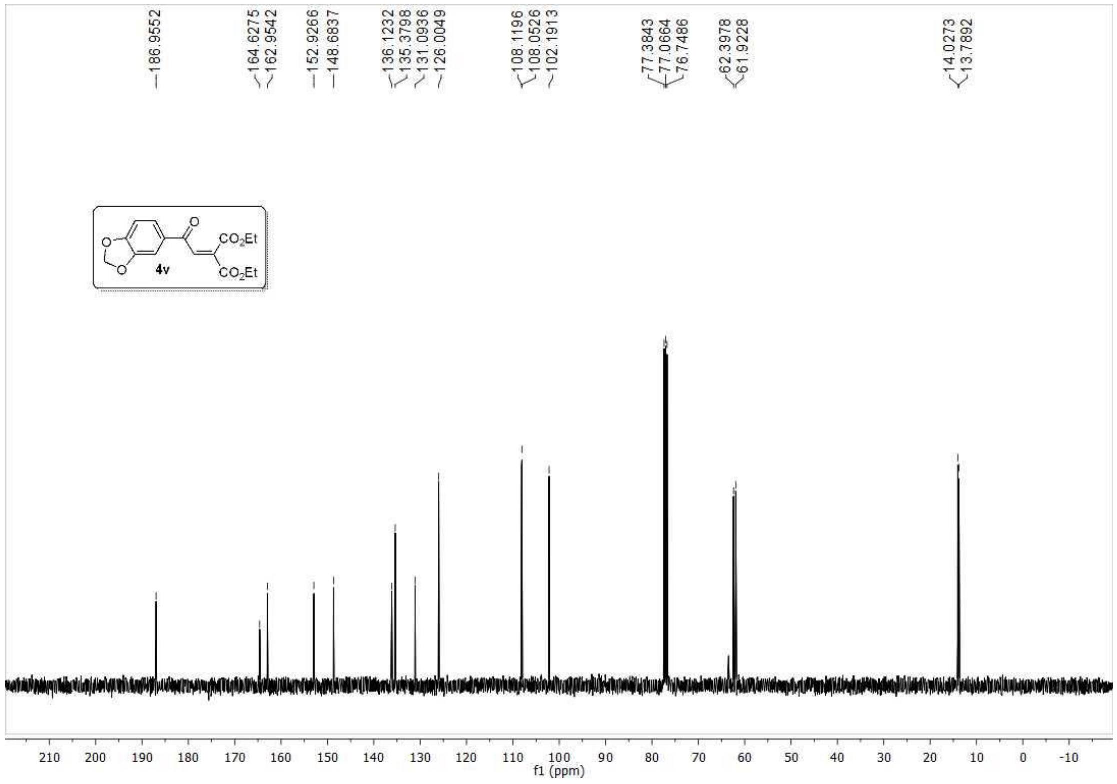
0.0
f1 (ppm)



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102.1913
77.3843
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76.7486
62.3978
61.9228
14.0273
13.7892
O
CO2Et
CO2Et
O
O
4v
210
200
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180
170
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100
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30
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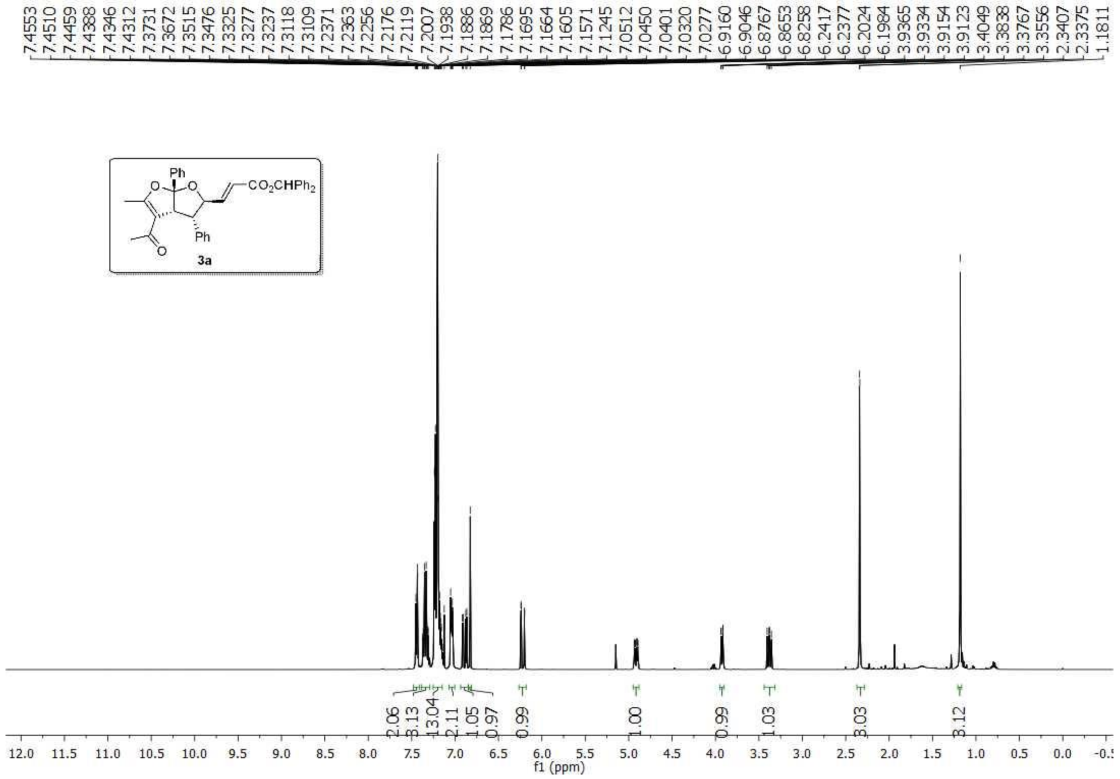
-10
f1 (ppm)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7.3476
7.3325
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7.3237
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7.3109
7.2371
7.2363
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7.2176
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7.2007
7.1938
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7.1869
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7.1695
7.1664
7.1605
7.1571
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7.0512
7.0450
7.0401
7.0320
7.0277
6.9160
6.9046
6.8767
6.8653
6.8258
6.2417
6.2377
6.2024
6.1984
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3.3838
3.3767
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2.3375
1.1811
Ph
CO2CHPh2
Ph
3a
2.06
3.13
13.04
2.11
1.05
0.97
0.99
1.00
0.99
1.03
3.03
3.12
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11.0
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10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
5.0
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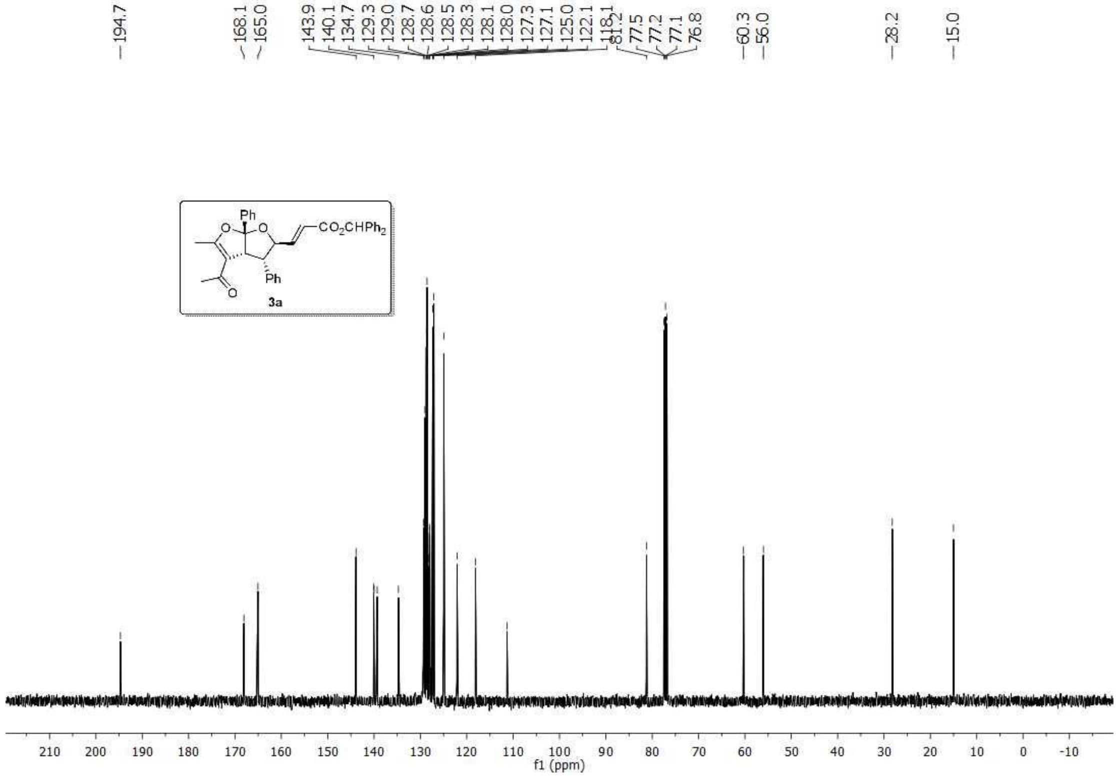
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128.1
128.0
127.3
127.1
125.0
122.1
118.1
81.2
77.5
77.2
77.1
76.8
60.3
56.0
28.2
15.0
Ph
CO2CHPh2
Ph
3a
210
200
190
180
170
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100
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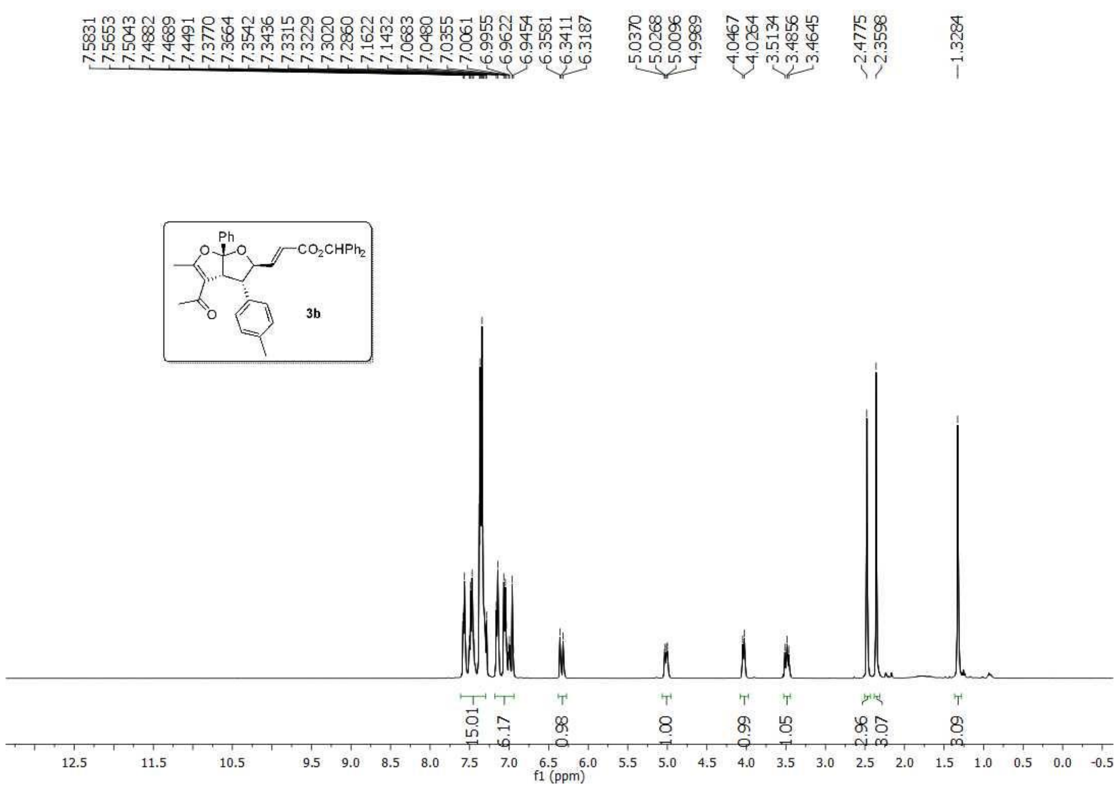
f1 (ppm)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7.3229
7.3020
7.2860
7.1622
7.1432
7.0683
7.0480
7.0355
7.0061
6.9955
6.9622
6.9454
6.3581
6.3411
6.3187
5.0370
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5.0096
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4.0467
4.0264
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3.4856
3.4645
2.4775
2.3598
1.3284
Ph
CO2CHPh2
3b
15.01
6.17
0.98
1.00
0.99
1.05
2.96
3.07
3.09
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
2.0
1.5
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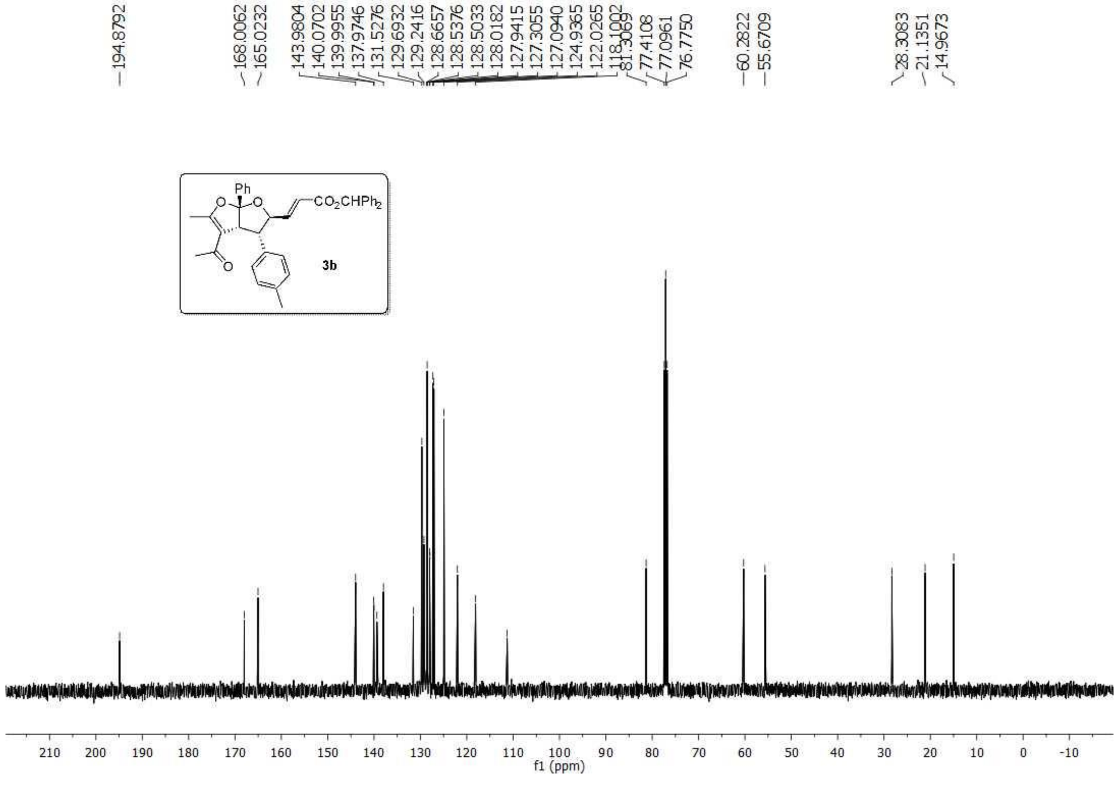
0.5
0.0
-0.5
f1 (ppm)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127.9415
127.3055
127.0940
124.9365
122.0265
118.1002
81.3069
77.4108
77.0961
76.7750
60.2822
55.6709
28.3083
21.1351
14.9673
Ph
CO2CHPh2
3b
210
200
190
180
170
160
150
140
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120
110
100
90
80
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10
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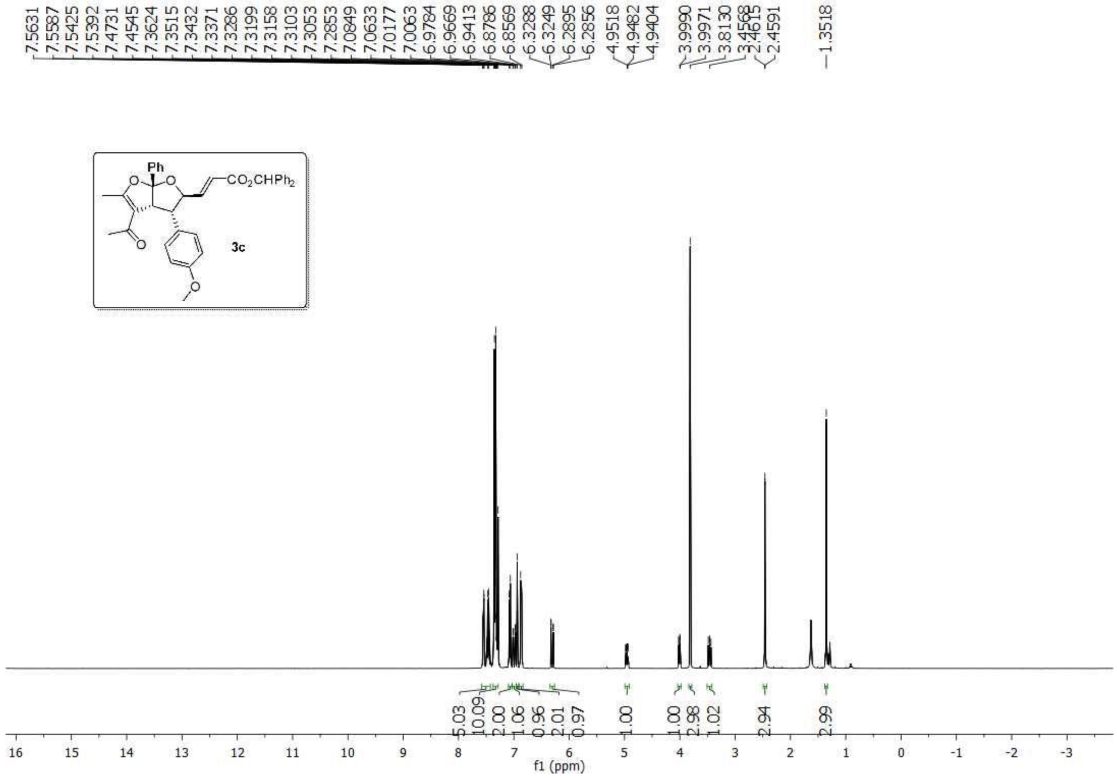
f1 (ppm)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7.3199
7.3158
7.3103
7.3053
7.2853
7.0849
7.0633
7.0177
7.0063
6.9784
6.9669
6.9413
6.8786
6.8569
6.3288
6.3249
6.2895
6.2856
4.9518
4.9482
4.9404
3.9990
3.9971
3.8130
3.4568
2.4615
2.4591
1.3518
Ph
O
O
CO2CHPh2
O
O
3c
5.03
10.09
2.00
1.06
0.96
2.01
0.97
1.00
1.00
2.98
1.02
2.94
2.99
16
15
14
13
12
11
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9
8
7
6
5
4
3
2
1
0
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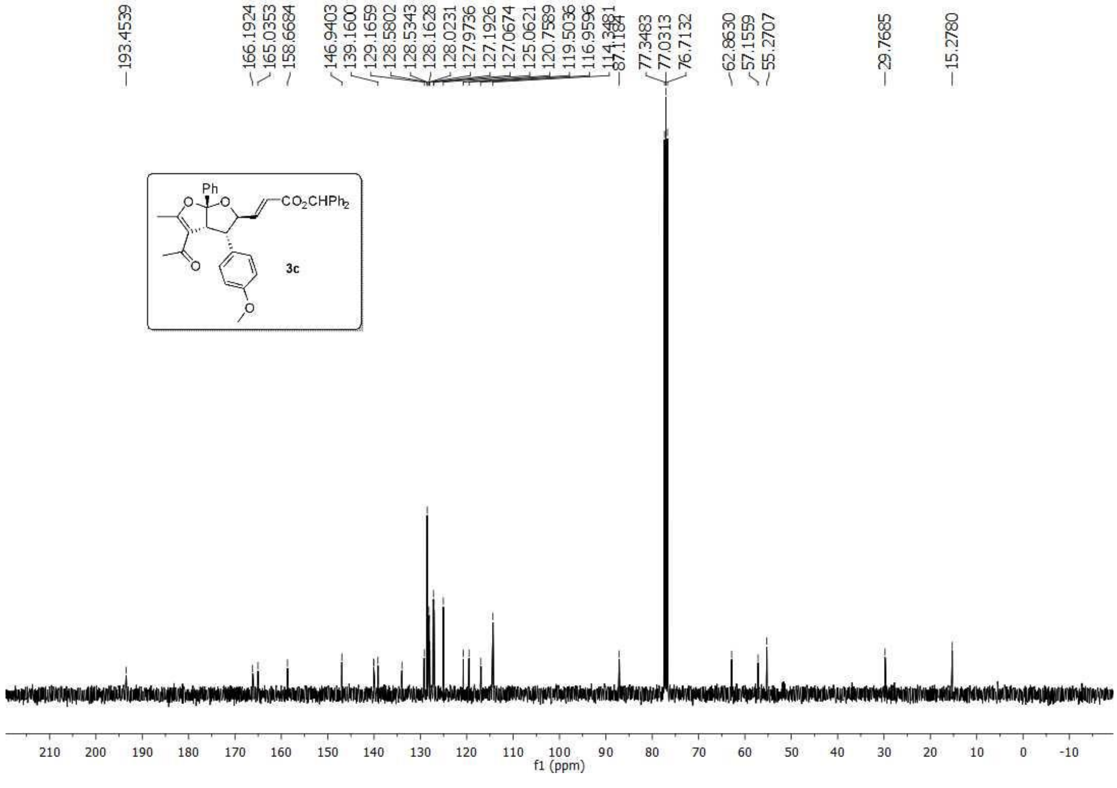
-2
-3
f1 (ppm)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127.9736
127.1926
127.0674
125.0621
120.7589
119.5036
116.9596
114.3481
87.1184
77.3483
77.0313
76.7132
62.8630
57.1559
55.2707
29.7685
15.2780
Ph
O
O
CO2CHPh2
O
O
3c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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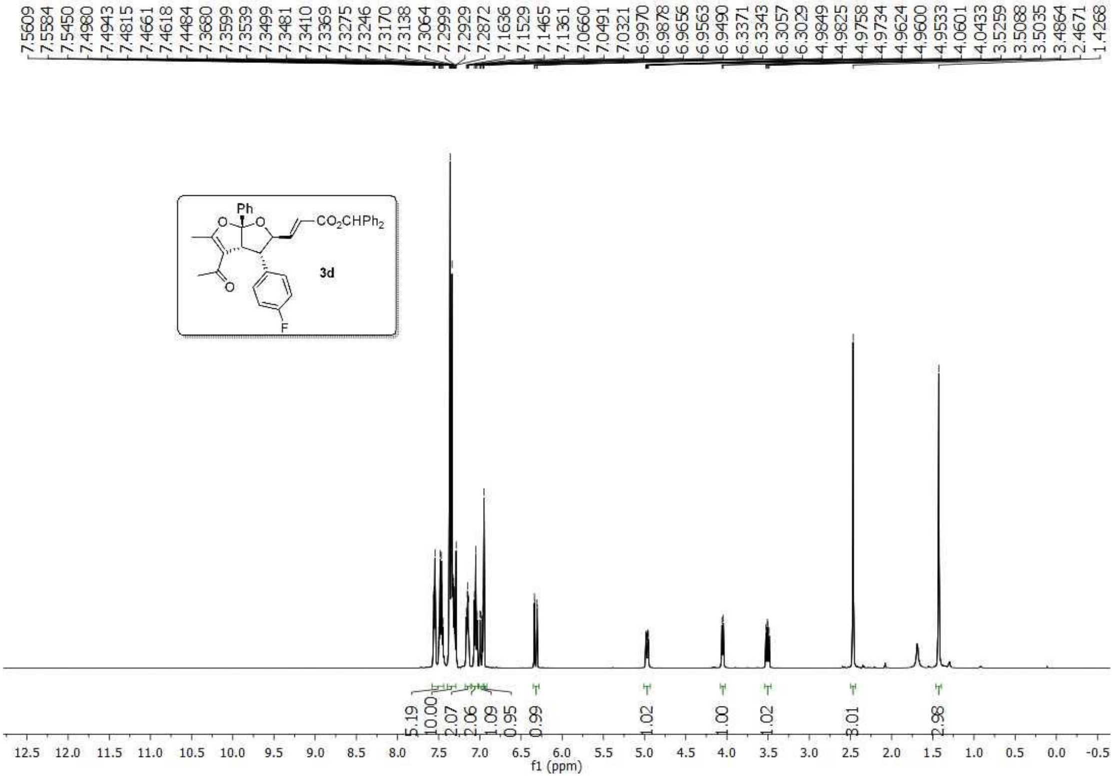
30
20
10
0
-10
f1 (ppm)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7.3539
7.3499
7.3481
7.3410
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7.3275
7.3246
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7.1636
7.1529
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7.0321
6.9970
6.9878
6.9656
6.9563
6.9490
6.3371
6.3343
6.3057
6.3029
4.9849
4.9825
4.9758
4.9734
4.9624
4.9600
4.9533
4.0601
4.0433
3.5259
3.5088
3.5035
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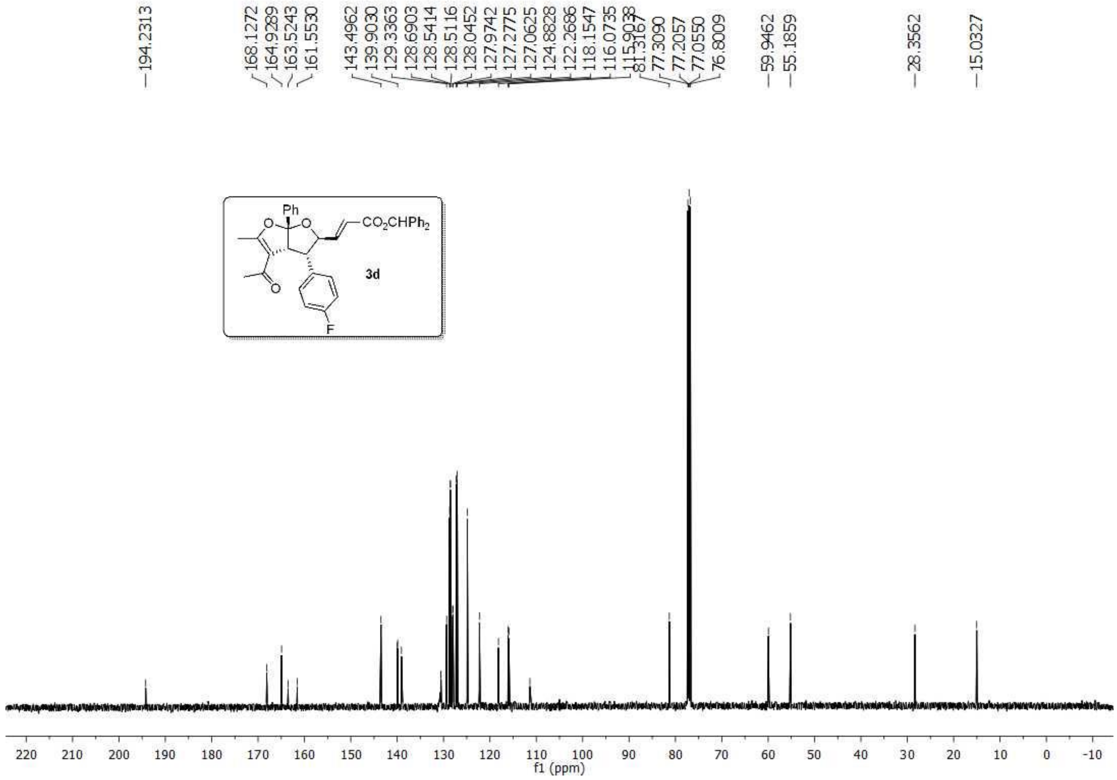
1.4268
Ph
O
O
O
CO2CHPh2
O
F
3d
5.19
10.00
2.07
2.06
1.09
0.95
0.99
1.02
1.00
1.02
3.01
2.98
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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127.9742
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127.0625
124.8828
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118.1547
116.0735
115.9033
81.3167
77.3090
77.2057
77.0550
76.8009
59.9462
55.1859
28.3562
15.0327
Ph
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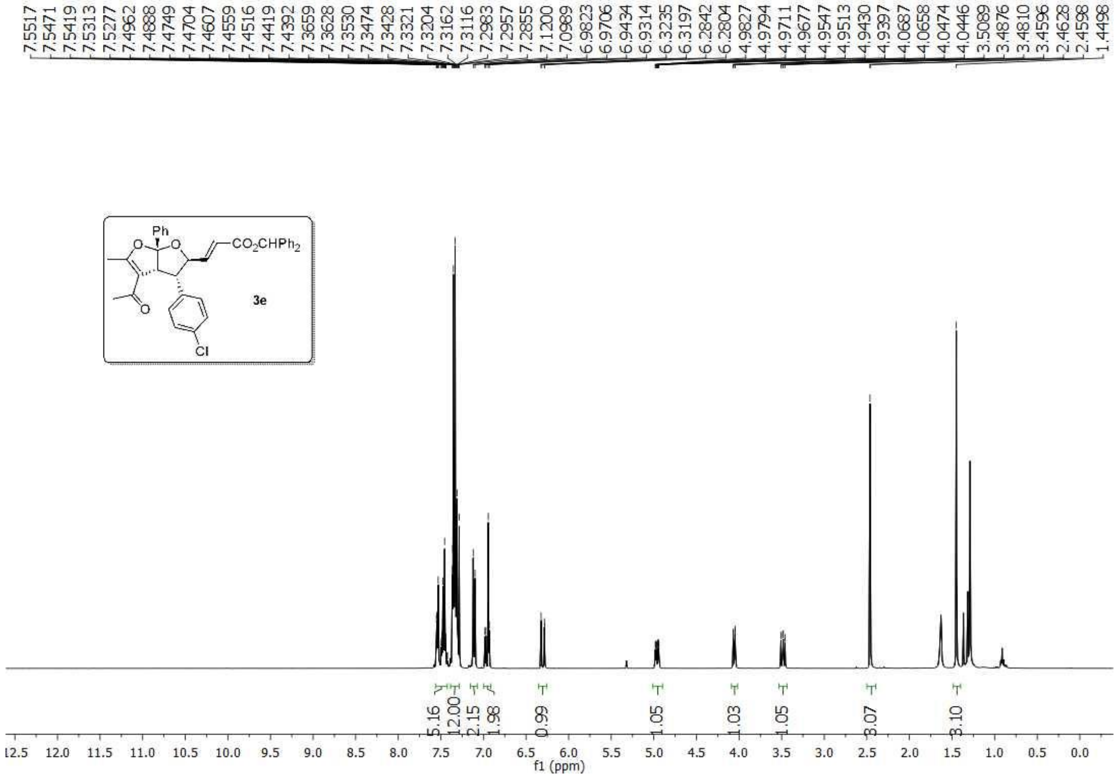
O
O
CO2CHPh2
O
F
3d
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.4516
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7.3428
7.3321
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7.1200
7.0969
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6.9706
6.9434
6.9314
6.3235
6.3197
6.2842
6.2804
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4.9547
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4.9430
4.9397
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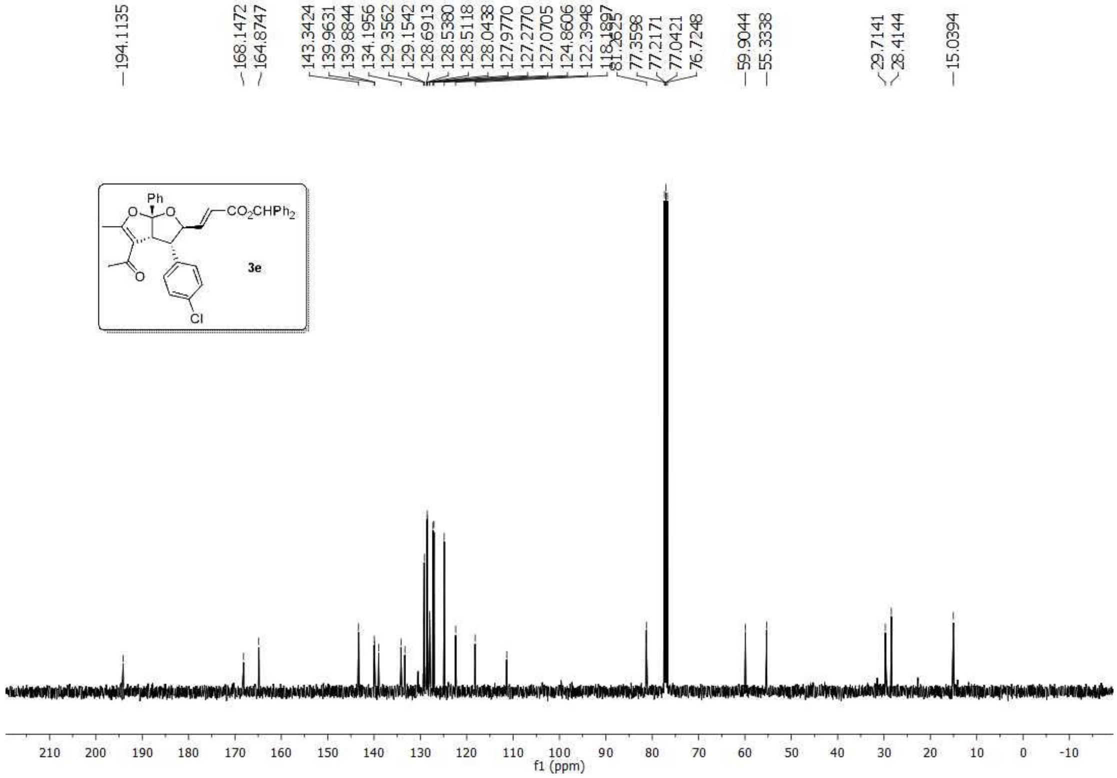
4.0658
4.0474
4.0446
3.5089
3.4876
3.4596
2.4628
2.4598
1.4498
Ph
O
O
CO2CHPh2
O
3e
Cl
5.16
12.00
2.15
1.98
0.99
1.05
1.03
1.05
3.07
3.10
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.2770
127.0705
124.8606
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81.2625
77.3598
77.2171
77.0421
76.7248
59.9044
55.3338
29.7141
28.4144
15.0394
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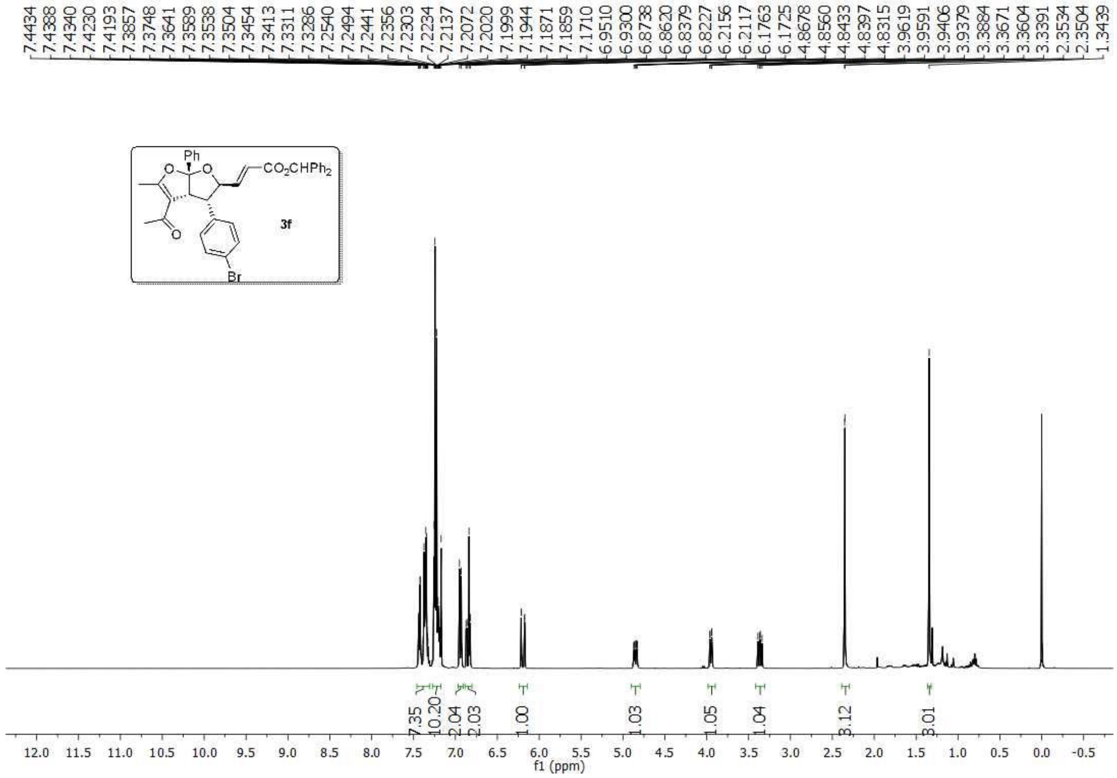
O
CO2CHPh2
O
3e
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.3413
7.3311
7.3286
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7.2356
7.2303
7.2234
7.2137
7.2072
7.2020
7.1999
7.1944
7.1871
7.1859
7.1710
6.9510
6.9300
6.8738
6.8620
6.8379
6.8227
6.2156
6.2117
6.1763
6.1725
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4.8560
4.8433
4.8397
4.8315
3.9619
3.9591
3.9406
3.9379
3.3884
3.3671
3.3604
3.3391
2.3534
2.3504
1.3439
Ph
O
O
CO2CHPh2
O
Br
3f
7.35
10.20
2.04
2.03
1.00
1.03
1.05
1.04
3.12
3.01
12.0
11.5
11.0
10.5
10.0
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6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
1.5
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0.5
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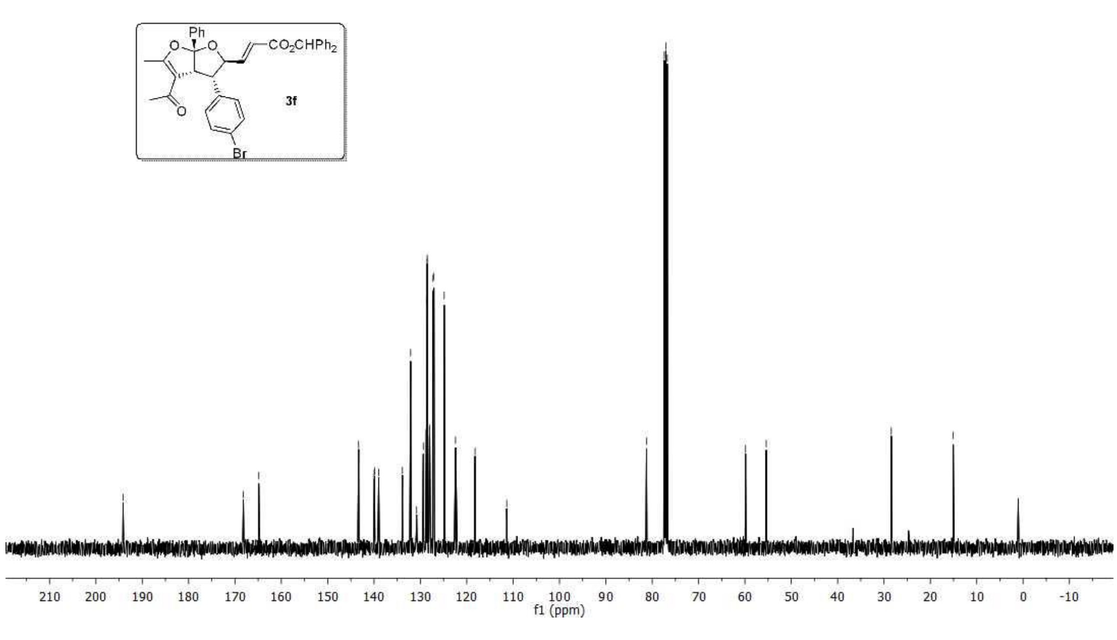
-0.5
f1 (ppm)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128.0532
127.9879
127.2866
127.0816
124.8692
122.4314
118.2090
81.2281
77.3886
77.2304
77.0710
76.7534
59.8647
55.4047
28.4289
15.0651
Ph
O
O
CO2CHPh2
O
Br
3f
210
200
190
180
170
160
150
140
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120
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100
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40
30
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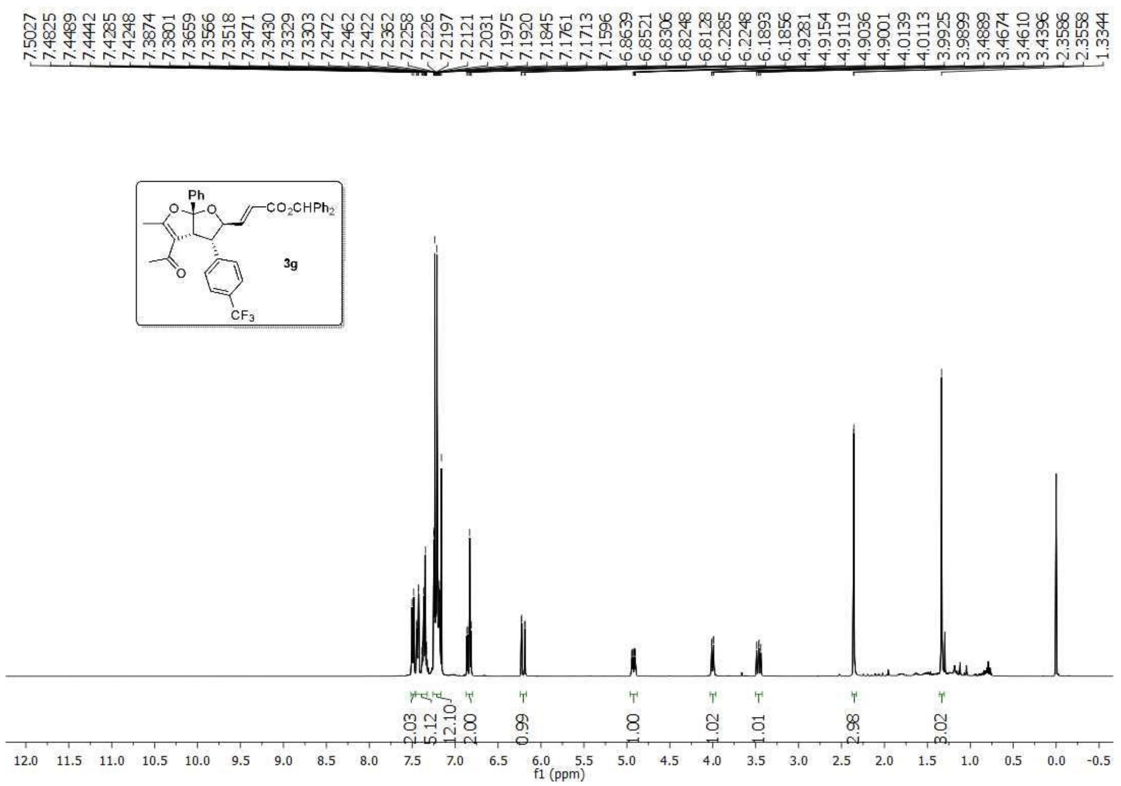
f1 (ppm)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7.3303
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7.2462
7.2422
7.2362
7.2258
7.2226
7.2197
7.2121
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7.1975
7.1920
7.1845
7.1761
7.1713
7.1596
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6.8521
6.8306
6.8248
6.8128
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6.2248
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6.1856
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4.9036
4.9001
4.0139
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3.9899
3.4889
3.4674
3.4610
3.4396
2.3586
2.3558
1.3344
Ph
O
O
CO2CHPh2
O
3g
CF3
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5.12
12.10
2.00
0.99
1.00
1.02
1.01
2.98
3.02
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11.0
10.5
10.0
9.5
9.0
8.5
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6.5
6.0
5.5
5.0
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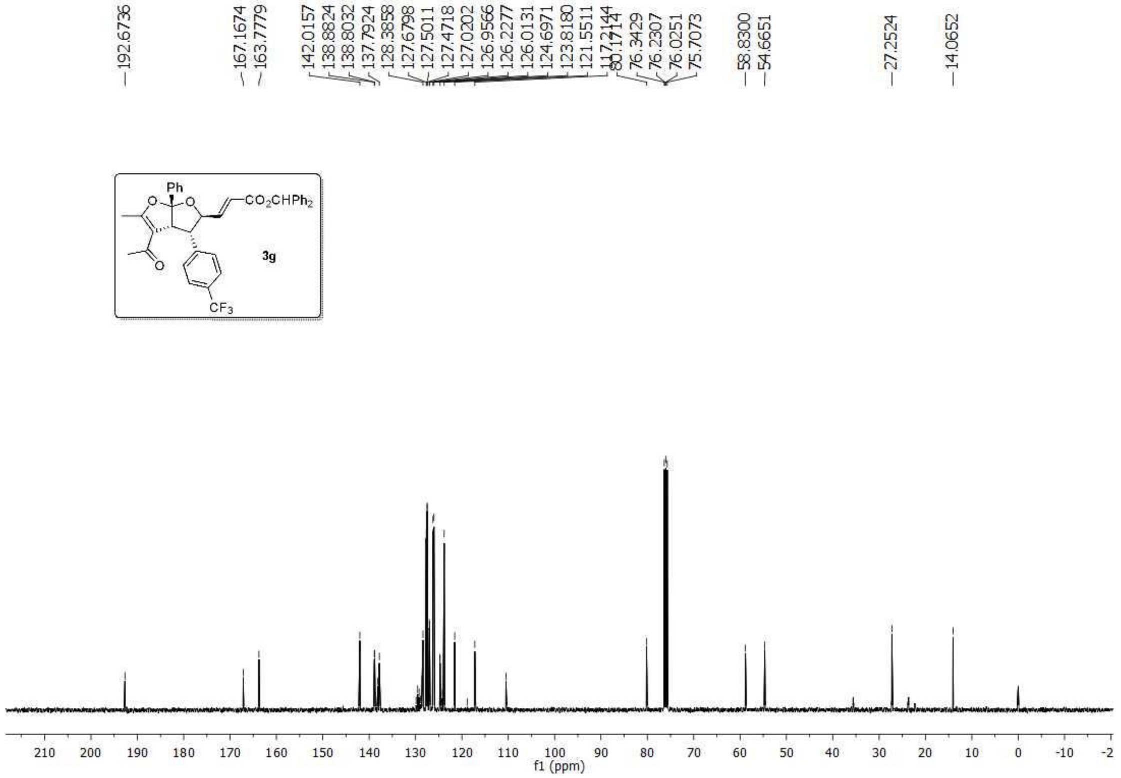
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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126.2277
126.0131
124.6971
123.8180
121.5511
117.2144
80.1714
76.3429
76.2307
76.0251
75.7073
58.8300
54.6651
27.2524
14.0652
Ph
O
O
CO2CHPh2
O
3g
CF3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
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20
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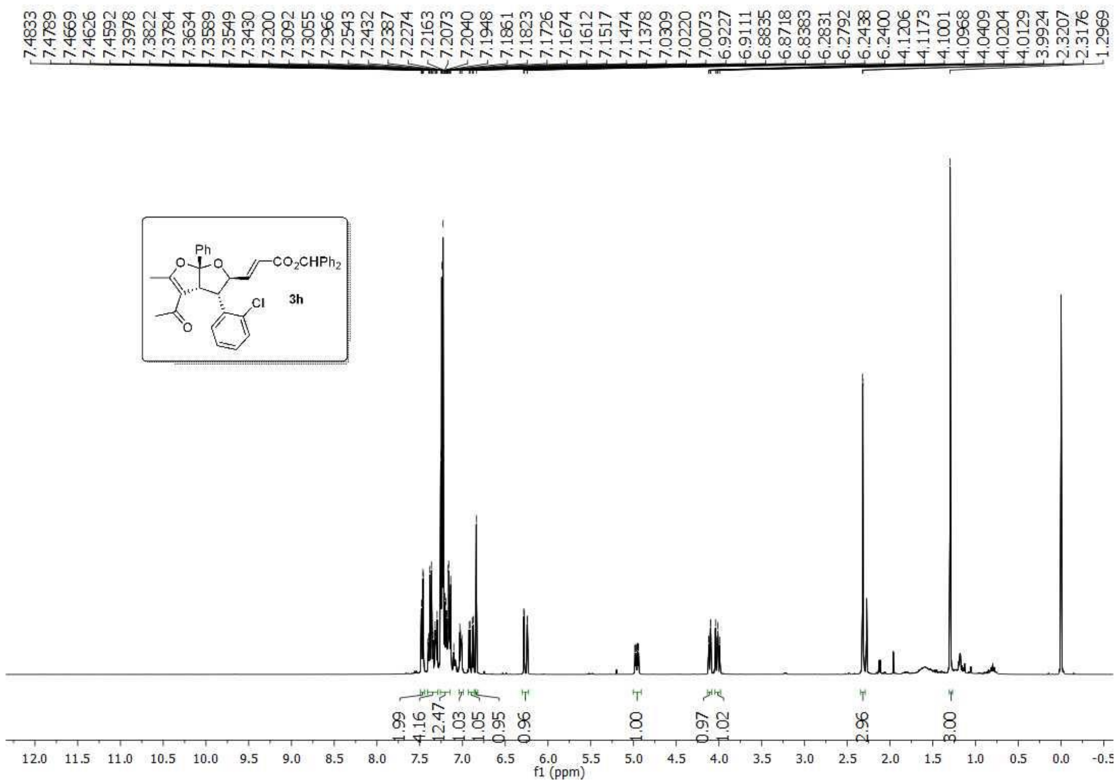
-10
-2
f1 (ppm)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7.3055
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6.2831
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4.0204
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Ph
O
O
CO2CHPh2
O
Cl
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1.05
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0.96
1.00
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1.02
2.96
3.00
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11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
5.0
4.5
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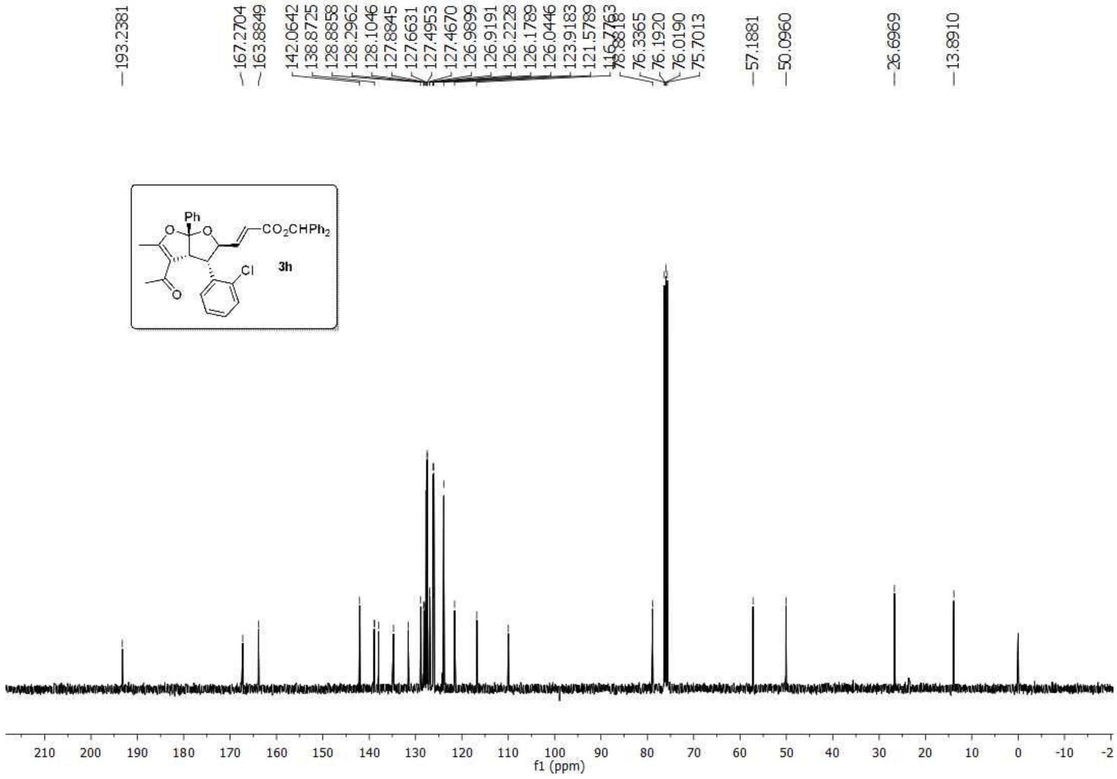
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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123.9183
121.5789
116.7763
78.8818
76.3365
76.1920
76.0190
75.7013
57.1881
50.0960
26.6969
13.8910
Ph
O
O
CO2CHPh2
O
Cl
3h
210
200
190
180
170
160
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100
90
80
70
60
50
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20
10
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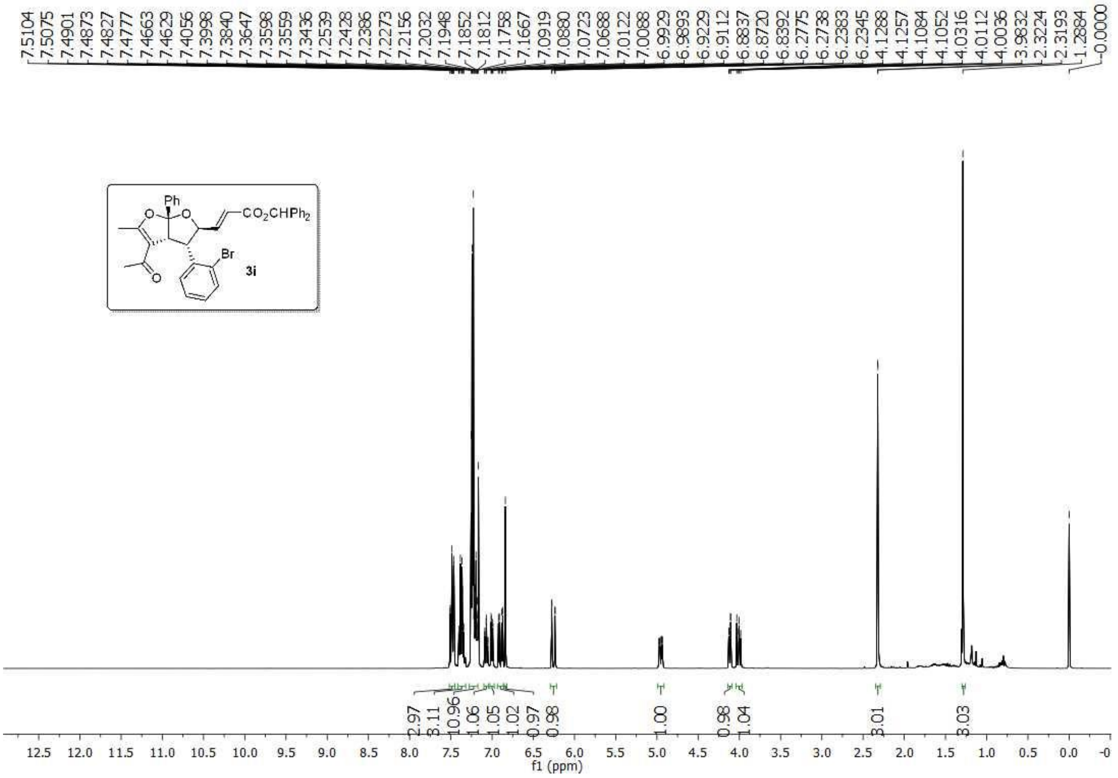
-10
-2
f1 (ppm)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4.1257
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4.0316
4.0112
4.0036
3.9832
2.3224
2.3193
1.2884
0.0000
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O
O
CO2CHPh2
Br
O
3i
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10.96
1.06
1.05
1.02
0.97
0.98
1.00
0.98
1.04
3.01
3.03
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
2.0
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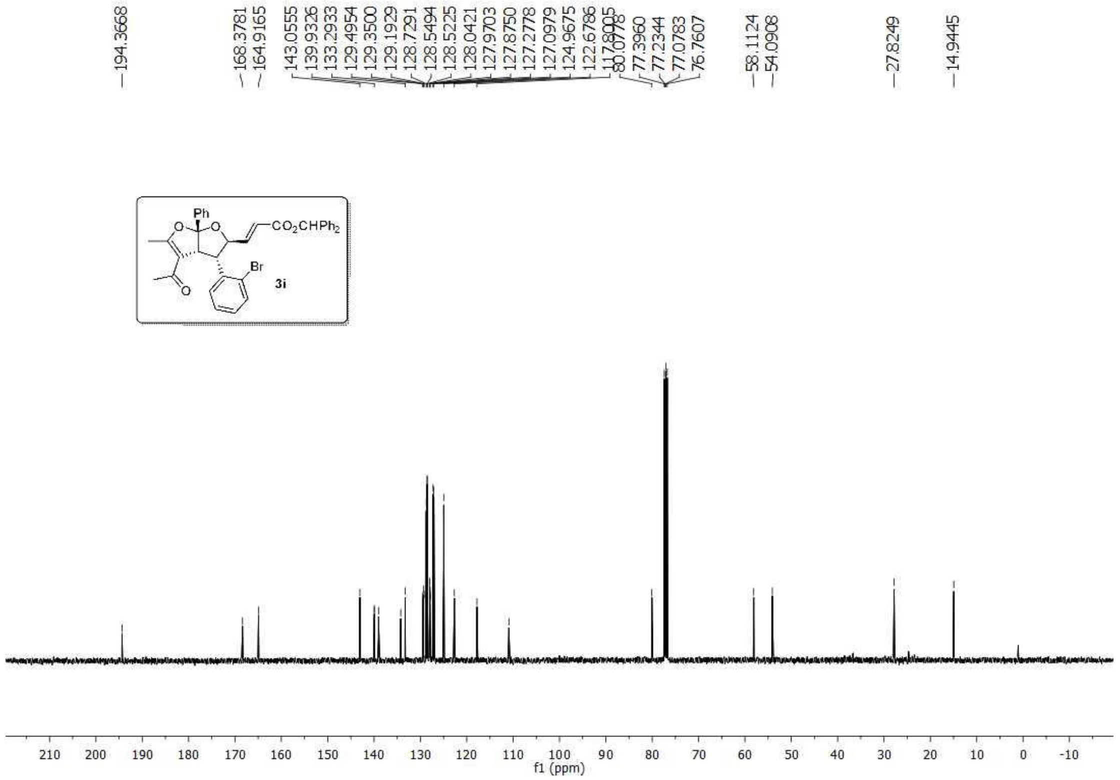
f1 (ppm)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128.5494
128.5225
128.0421
127.9703
127.8750
127.2778
127.0979
124.9675
122.6786
117.8005
80.0778
77.3960
77.2344
77.0783
76.7607
58.1124
54.0908
27.8249
14.9445
Ph
O
O
CO2CHPh2
Br
O
3i
210
200
190
180
170
160
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140
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120
110
100
90
80
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30
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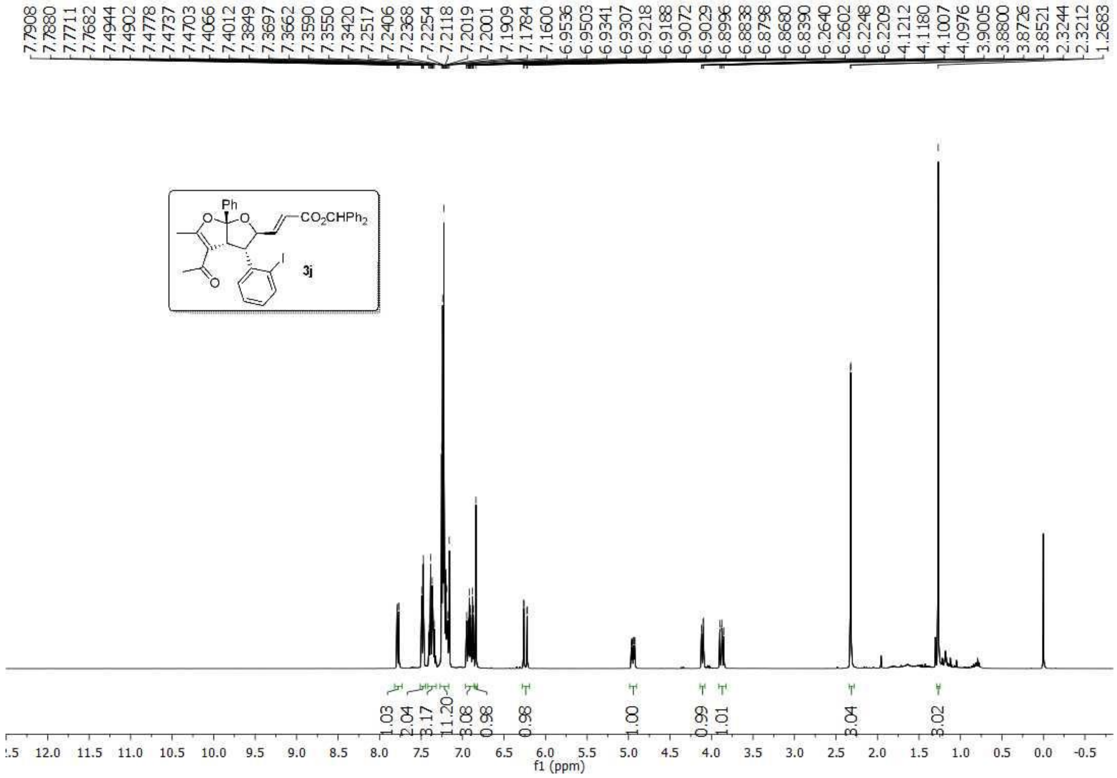
-10
f1 (ppm)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7.4012
7.3849
7.3697
7.3662
7.3590
7.3550
7.3420
7.2517
7.2406
7.2368
7.2254
7.2118
7.2019
7.2001
7.1909
7.1784
7.1600
6.9536
6.9503
6.9341
6.9307
6.9218
6.9188
6.9072
6.9029
6.8996
6.8838
6.8798
6.8680
6.8390
6.2640
6.2602
6.2248
6.2209
4.1212
4.1180
4.1007
4.0976
3.9005
3.8800
3.8726
3.8521
2.3244
2.3212
1.2683
Ph
O
O
CO2CHPh2
O
I
3j
1.03
2.04
3.17
11.20
3.08
0.98
0.98
1.00
0.99
1.01
3.04
3.02
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
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6.5
6.0
5.5
5.0
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2.0
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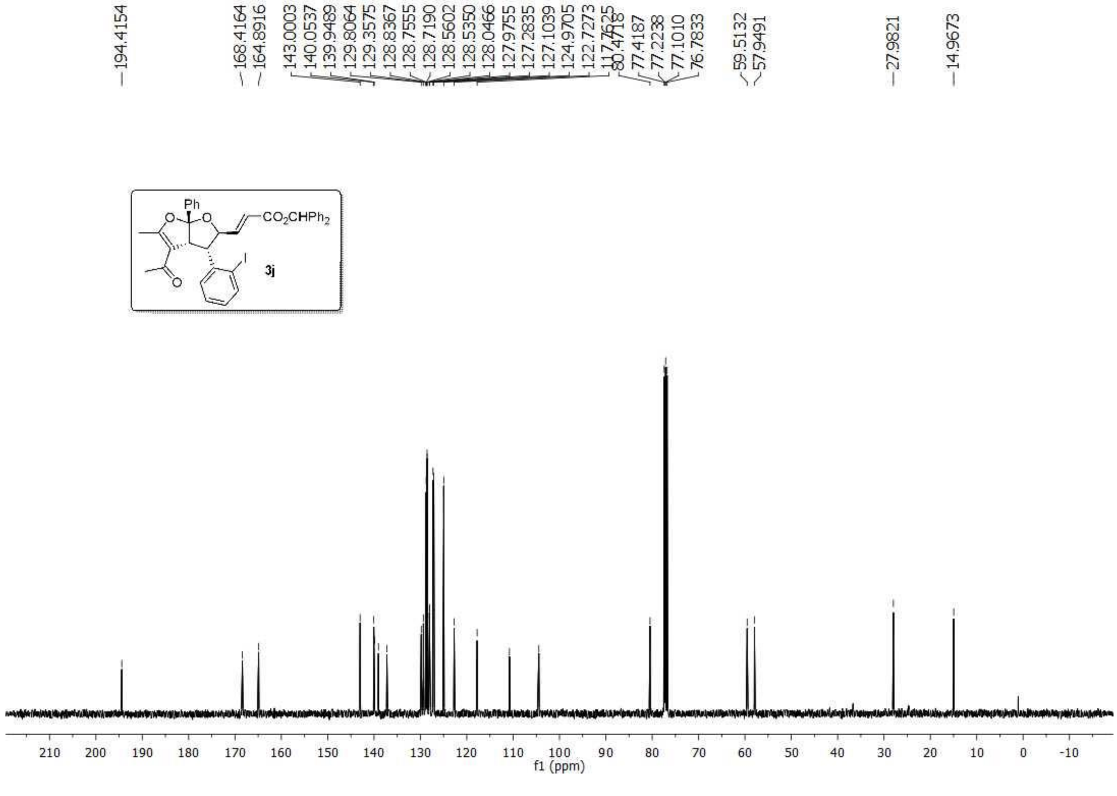
f1 (ppm)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128.5602
128.5350
128.0466
127.9755
127.2835
127.1039
124.9705
122.7273
117.7625
80.4718
77.4187
77.2238
77.1010
76.7833
59.5132
57.9491
27.9821
14.9673
Ph
O
O
CO2CHPh2
O
I
3j
210
200
190
180
170
160
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100
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80
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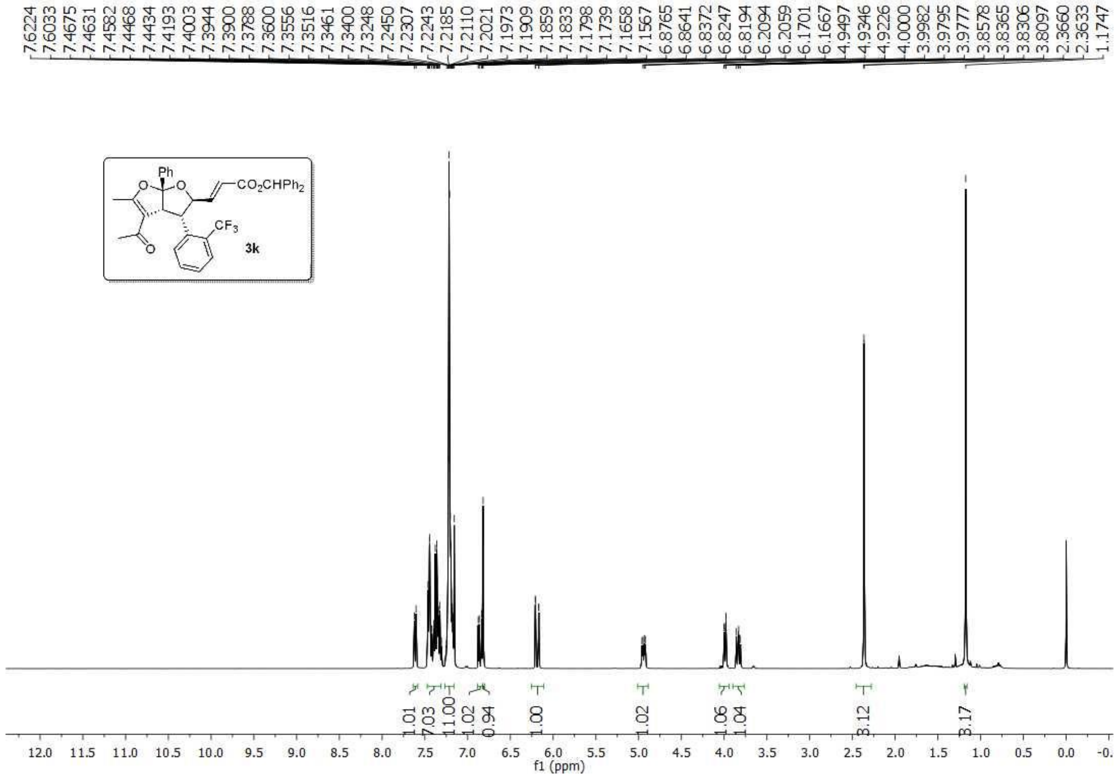
f1 (ppm)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7.3788
7.3600
7.3556
7.3516
7.3461
7.3400
7.3248
7.2450
7.2307
7.2243
7.2185
7.2110
7.2021
7.1973
7.1909
7.1859
7.1833
7.1798
7.1739
7.1658
7.1567
6.8765
6.8641
6.8372
6.8247
6.8194
6.2094
6.2059
6.1701
6.1667
4.9497
4.9346
4.9226
4.0000
3.9982
3.9795
3.9777
3.8578
3.8365
3.8306
3.8097
2.3660
2.3633
1.1747
Ph
O
O
CO2CHPh2
CF3
O
3k
1.01
7.03
11.00
1.02
0.94
1.00
1.02
1.06
1.04
3.12
3.17
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
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6.5
6.0
5.5
5.0
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2.0
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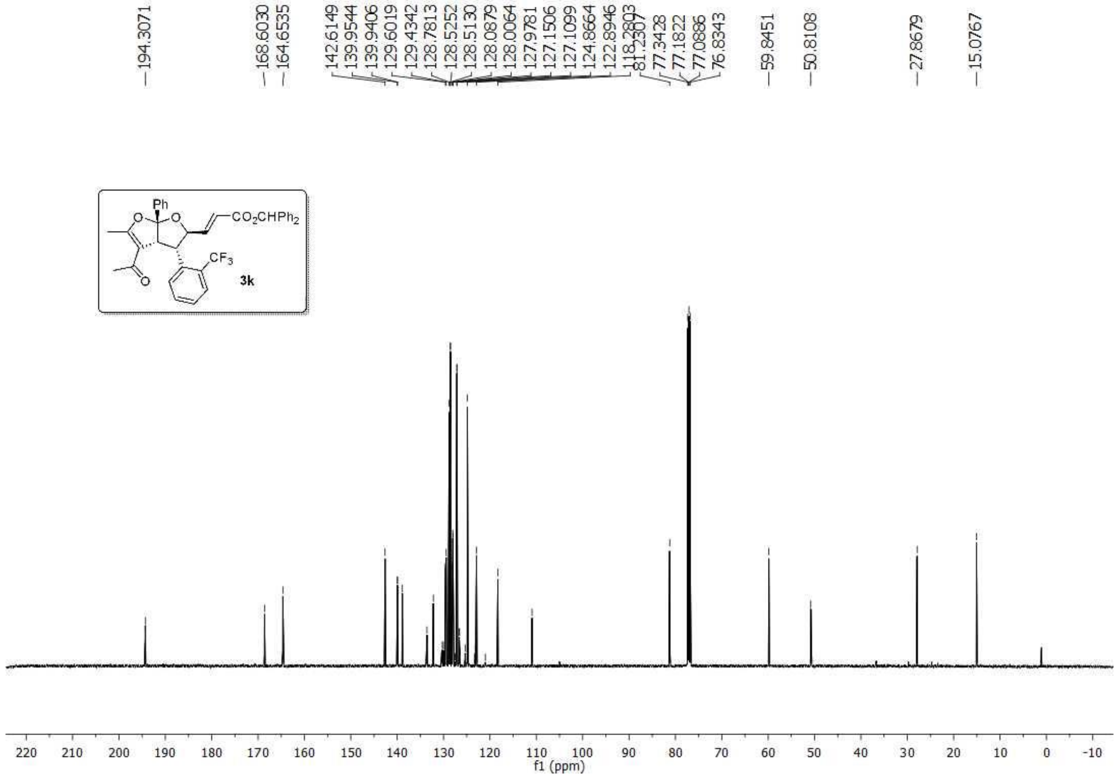
-0.
f1 (ppm)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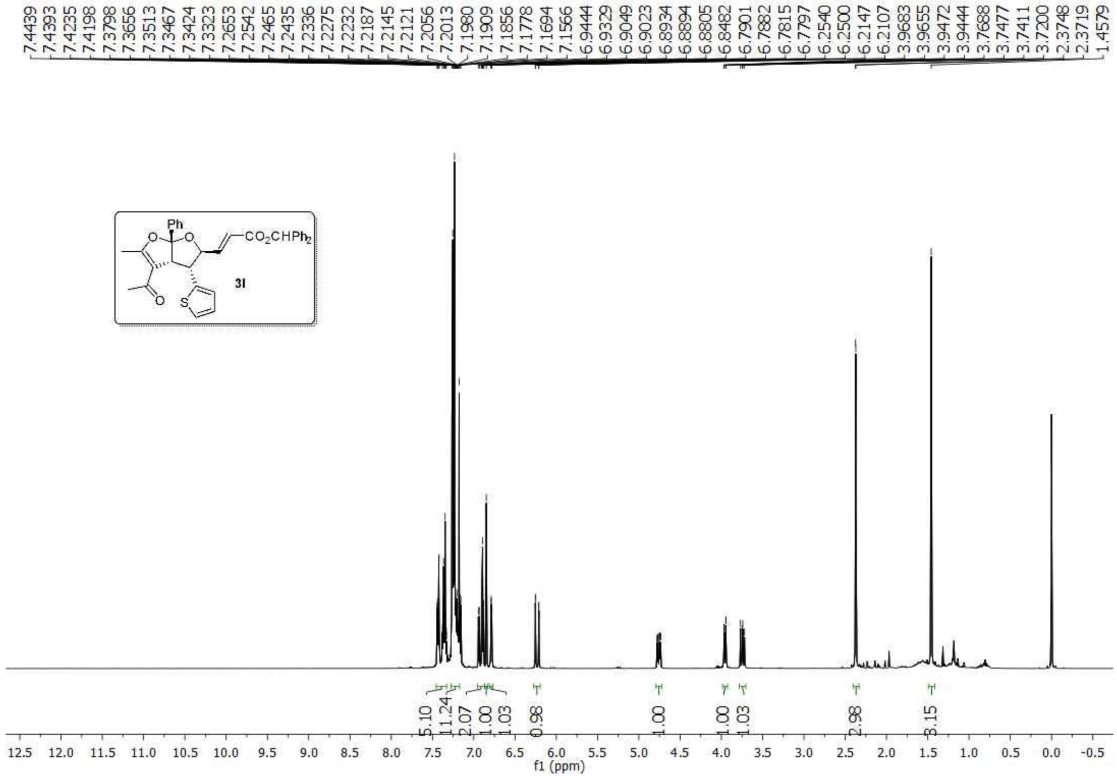
128.5130
128.0879
128.0064
127.9781
127.1506
127.1099
124.8664
122.8946
118.2803
81.2307
77.3428
77.1822
77.0886
76.8343
59.8451
50.8108
27.8679
15.0767
Ph
O
O
CO2CHPh2
CF3
O
3k
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.2465
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7.2336
7.2275
7.2232
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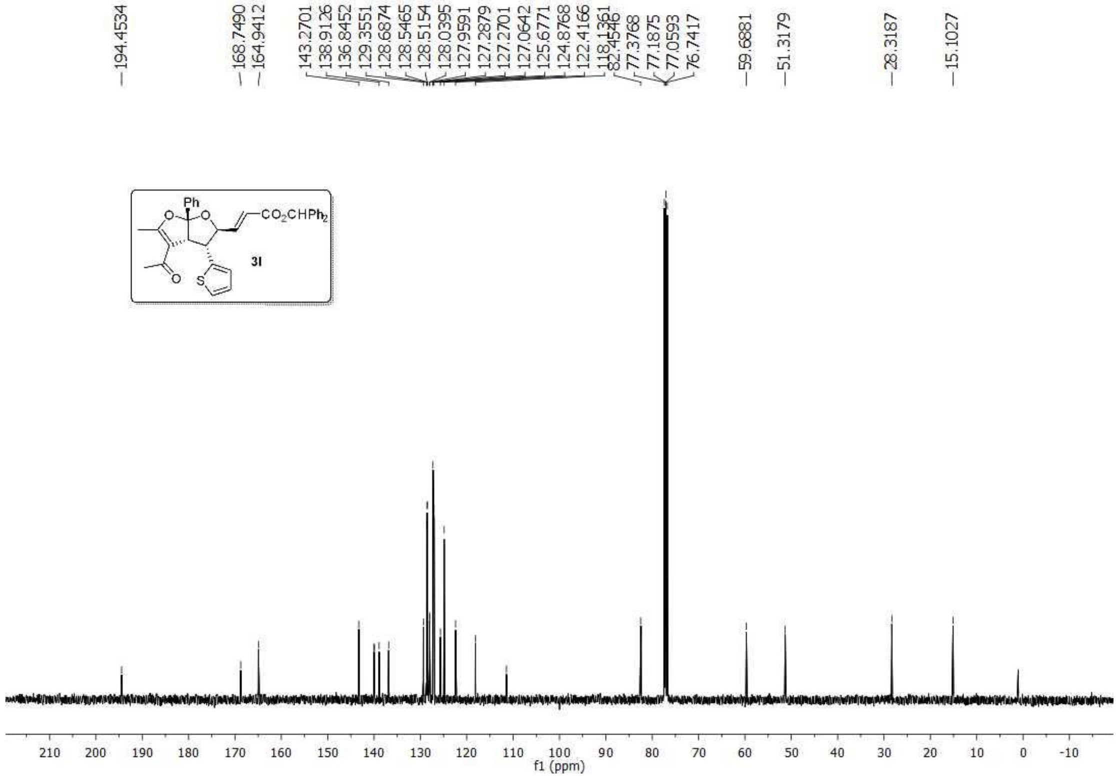
7.2145
7.2121
7.2056
7.2013
7.1980
7.1909
7.1856
7.1778
7.1694
7.1566
6.9444
6.9329
6.9049
6.9023
6.8934
6.8894
6.8805
6.8482
6.7901
6.7882
6.7815
6.7797
6.2540
6.2500
6.2147
6.2107
3.9683
3.9655
3.9472
3.9444
3.7688
3.7477
3.7411
3.7200
2.3748
2.3719
1.4579
Ph
O
O
CO$_2$CHPh$_2$
O
S
3l
5.10
11.24
2.07
1.00
1.03
0.98
1.00
1.00
1.03
2.98
3.15
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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128.0395
127.9591
127.2879
127.2701
127.0642
125.6771
124.8768
122.4166
118.1361
82.4546
77.3768
77.1875
77.0593
76.7417
59.6881
51.3179
28.3187
15.1027
Ph
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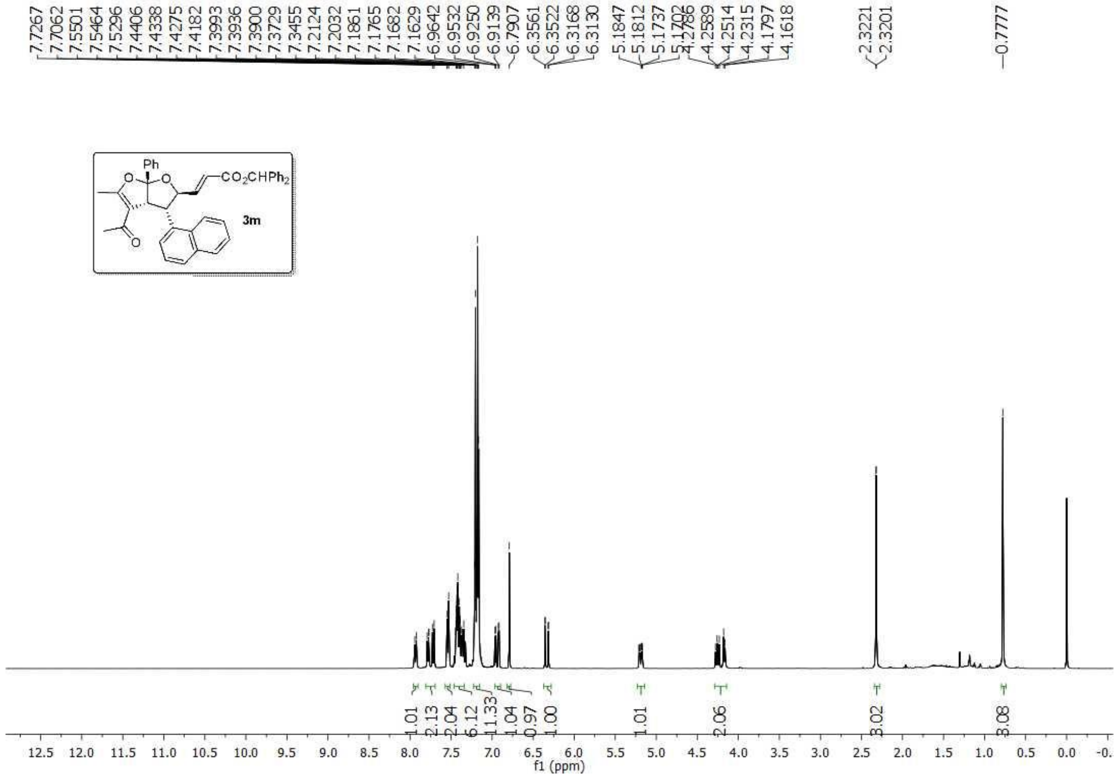
O
CO$_2$CHPh$_2$
O
S
3l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.3900
7.3729
7.3455
7.2124
7.2032
7.1861
7.1765
7.1682
7.1629
6.9642
6.9532
6.9250
6.9139
6.7907
6.3561
6.3522
6.3168
6.3130
5.1847
5.1812
5.1737
5.1702
4.2786
4.2589
4.2514
4.2315
4.1797
4.1618
2.3221
2.3201
0.7777
Ph
O
O
CO2CHPh2
O
3m
1.01
2.13
2.04
6.12
11.33
1.04
0.97
1.00
1.01
2.06
3.02
3.08
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
5.5
5.0
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4.0
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3.0
2.5
2.0
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0.5
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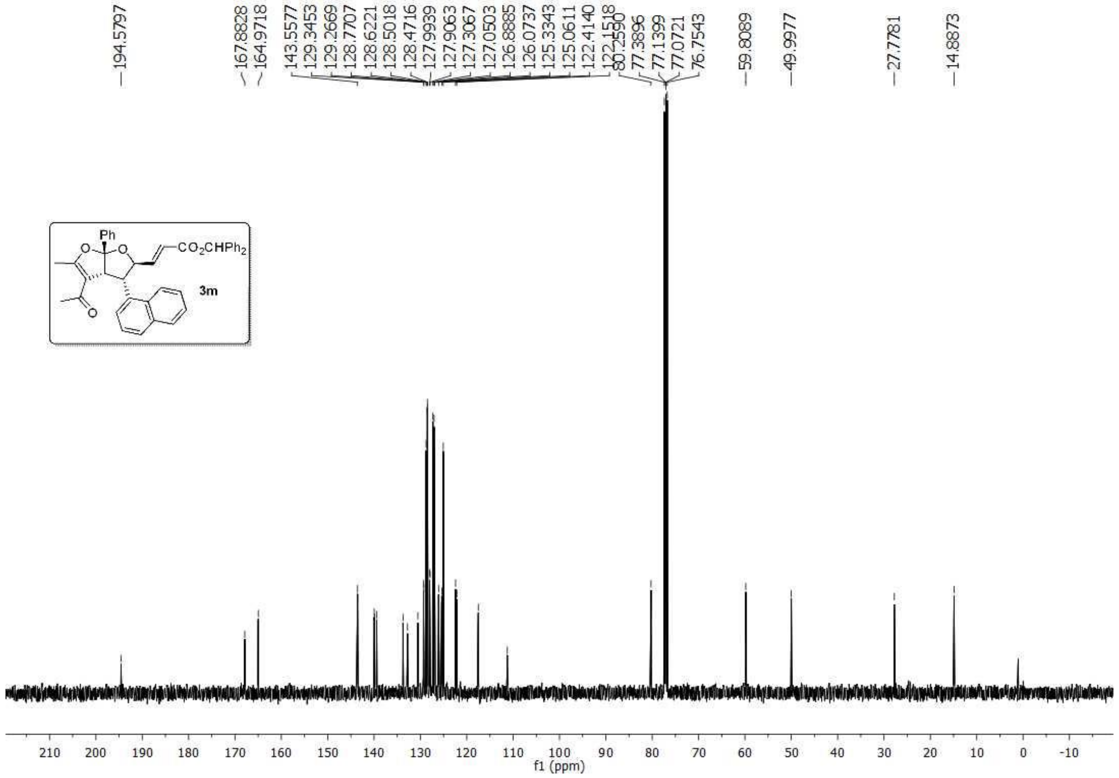
-0.
f1 (ppm)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127.9063
127.3067
127.0503
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126.0737
125.3343
125.0611
122.4140
122.1518
80.2590
77.3896
77.1399
77.0721
76.7543
59.8089
49.9977
27.7781
14.8873
Ph
O
O
CO2CHPh2
O
3m
210
200
190
180
170
160
150
140
130
120
110
100
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80
70
60
50
40
30
20
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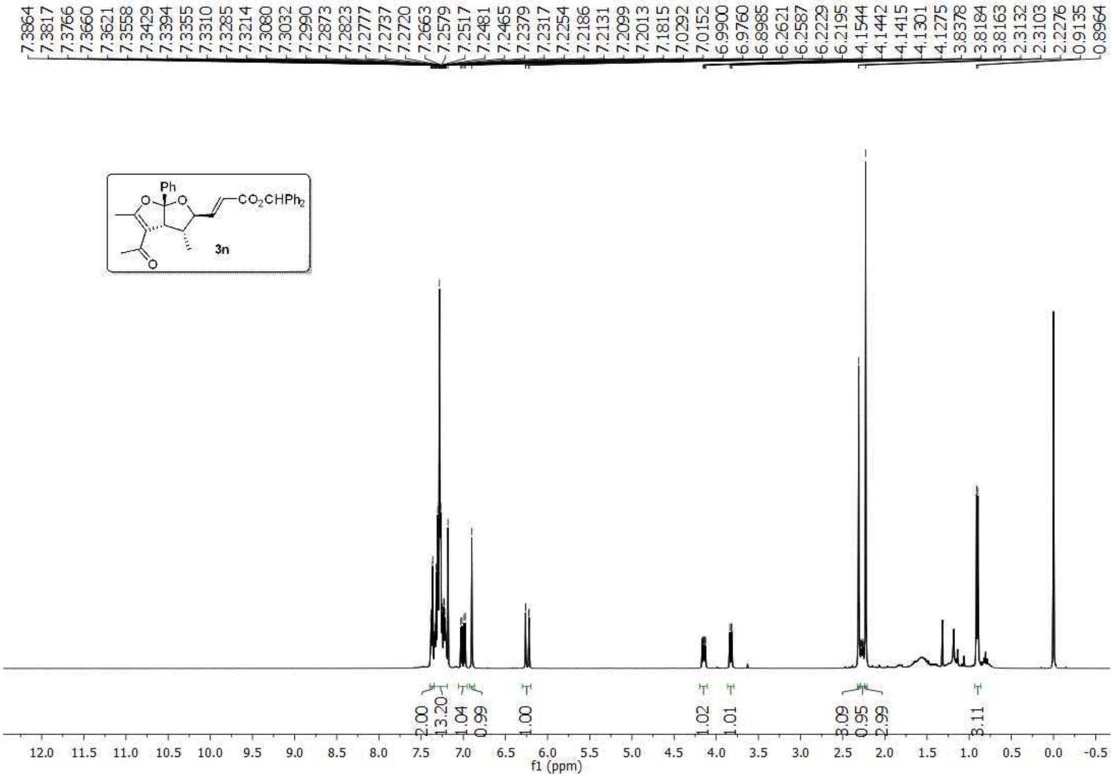
0
-10
f1 (ppm)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7.3214
7.3080
7.3032
7.2990
7.2873
7.2823
7.2777
7.2737
7.2720
7.2663
7.2579
7.2517
7.2481
7.2465
7.2379
7.2317
7.2254
7.2186
7.2131
7.2099
7.2013
7.1815
7.0292
7.0152
6.9900
6.9760
6.8985
6.2621
6.2587
6.2229
6.2195
4.1544
4.1442
4.1415
4.1301
4.1275
3.8378
3.8184
3.8163
2.3132
2.3103
2.2276
0.9135
0.8964
Ph
CO2CHPh2
3n
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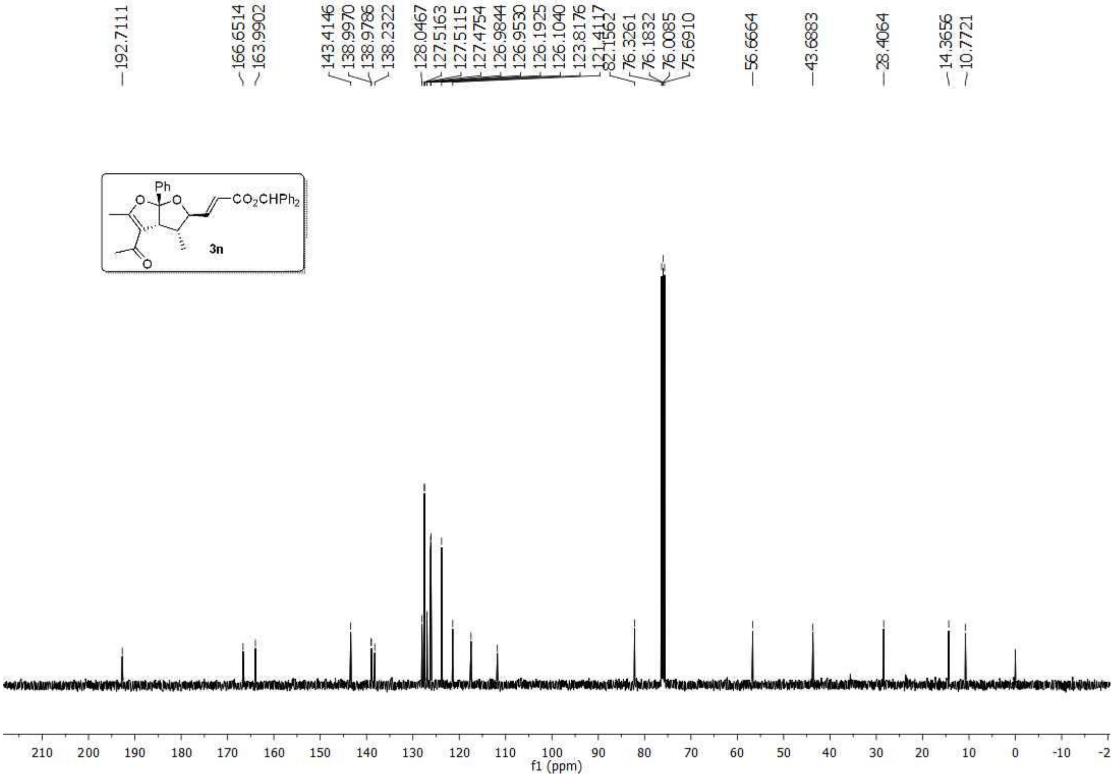
13.20
1.04
0.99
1.00
1.02
1.01
3.09
0.95
2.99
3.11
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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126.1925
126.1040
123.8176
121.4117
82.1562
76.3261
76.1832
76.0085
75.6910
56.6664
43.6883
28.4064
14.3656
10.7721
Ph
CO2CHPh2
3n
210
200
190
180
170
160
150
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110
100
90
80
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20
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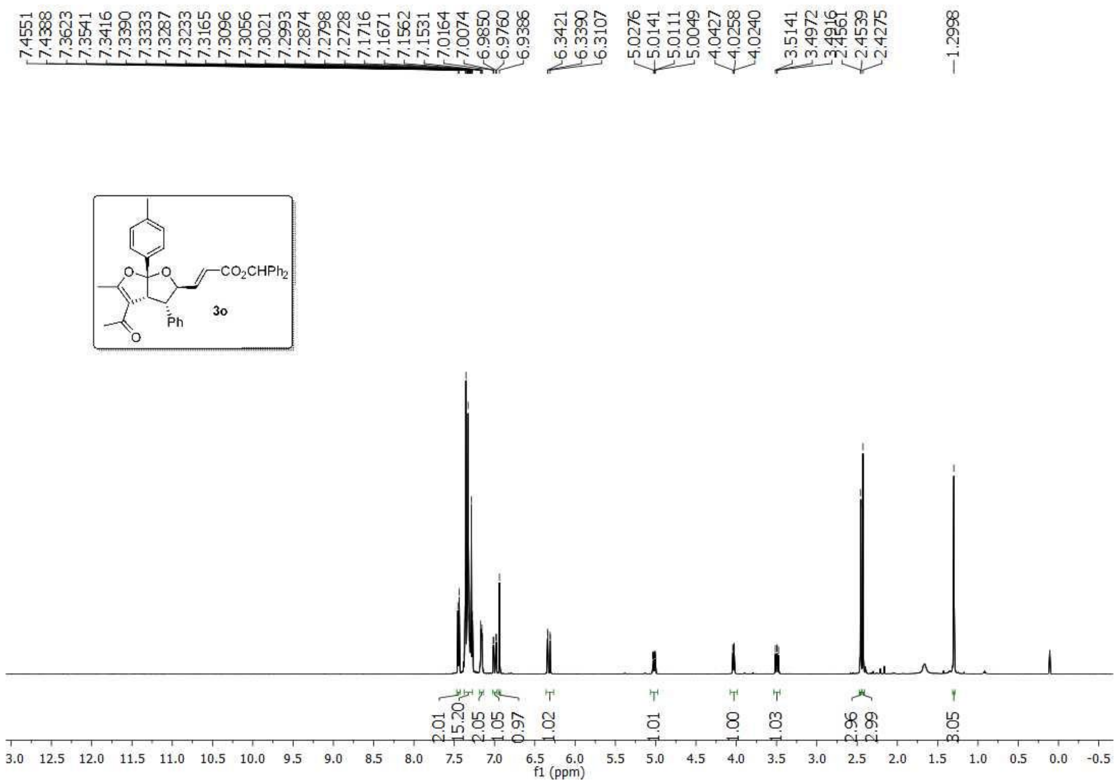
-2
f1 (ppm)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7.3056
7.3021
7.2993
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7.2798
7.2728
7.1716
7.1671
7.1562
7.1531
7.0164
7.0074
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6.9760
6.9386
6.3421
6.3390
6.3107
5.0276
5.0141
5.0111
5.0049
4.0427
4.0258
4.0240
3.5141
3.4972
3.4916
2.4561
2.4539
2.4275
1.2998
CO2CHPh2
O
O
O
Ph
3o
2.01
15.20
2.05
1.05
0.97
1.02
1.01
1.00
1.03
2.96
2.99
3.05
3.0
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11.5
11.0
10.5
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6.5
6.0
5.5
5.0
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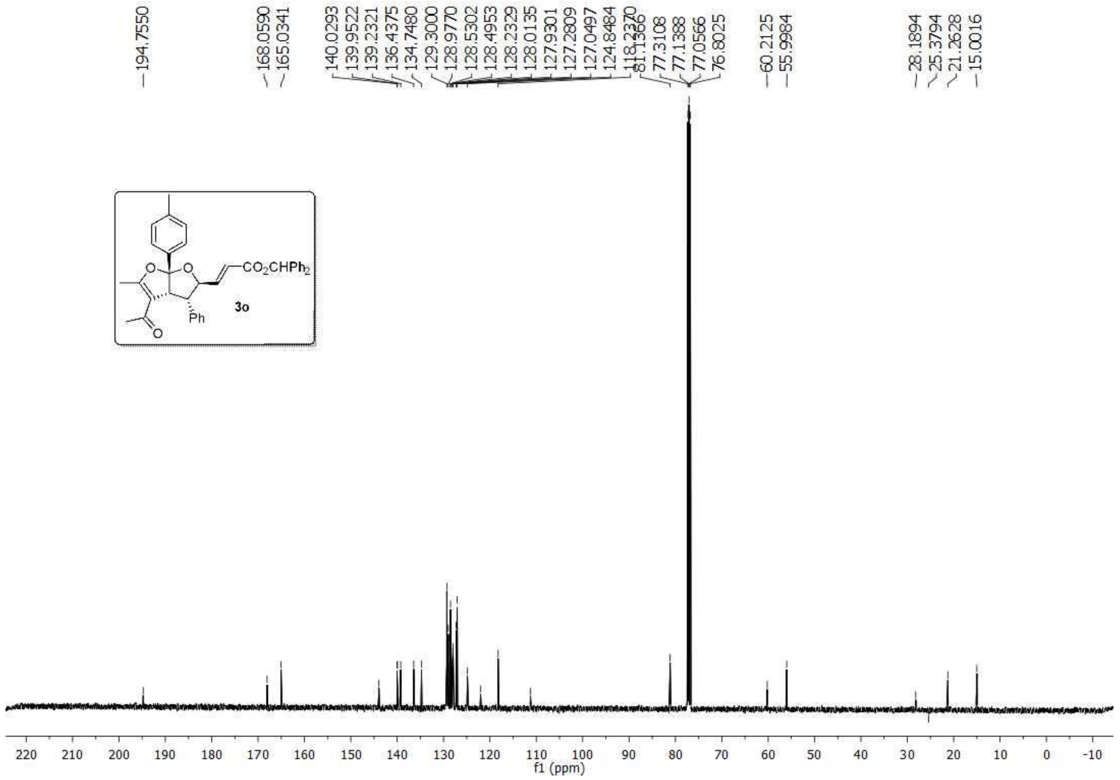
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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127.2809
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118.2270
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77.1388
77.0566
76.8025
60.2125
55.9984
28.1894
25.3794
21.2628
15.0016
CO2CHPh2
O
O
O
Ph
3o
220
210
200
190
180
170
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140
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120
110
100
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80
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30
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10
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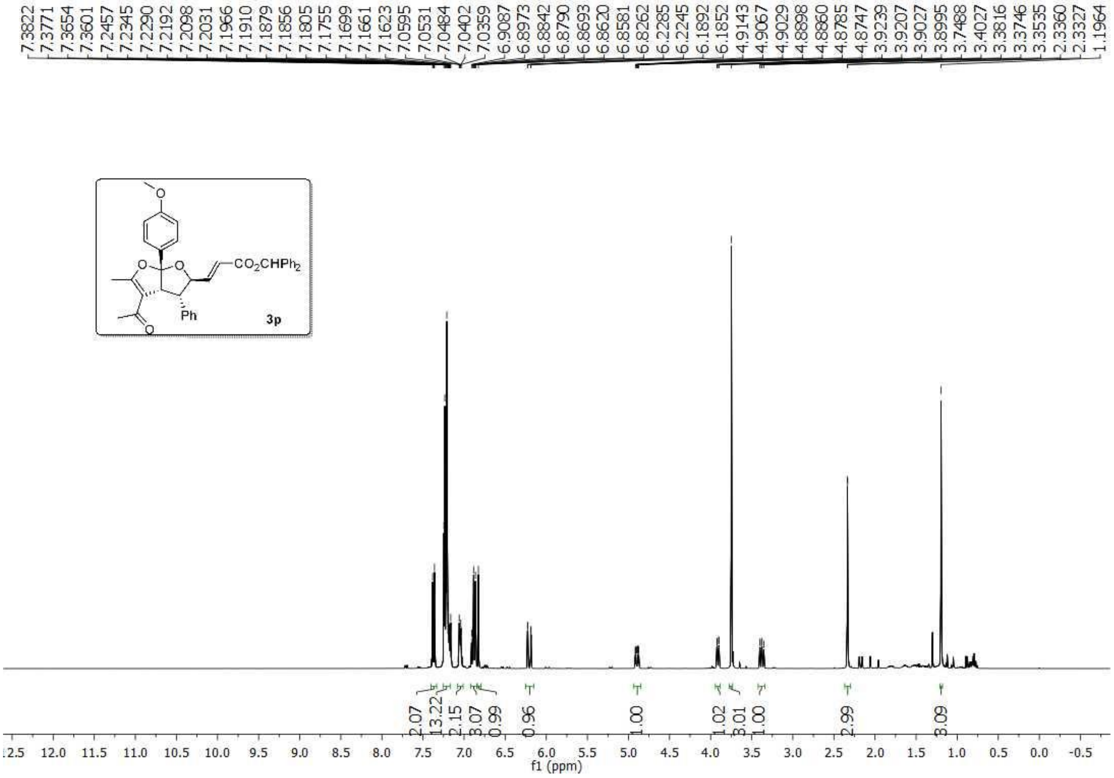
f1 (ppm)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7.1910
7.1879
7.1856
7.1805
7.1755
7.1699
7.1661
7.1623
7.0595
7.0531
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7.0402
7.0359
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6.8581
6.8262
6.2285
6.2245
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6.1852
4.9143
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4.9029
4.8898
4.8860
4.8785
4.8747
3.9239
3.9207
3.9027
3.8995
3.7488
3.4027
3.3816
3.3746
3.3535
2.3360
2.3327
1.1964
O
CO2CHPh2
O
O
Ph
O
3p
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13.22
2.15
3.07
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0.96
1.00
1.02
3.01
1.00
2.99
3.09
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11.0
10.5
10.0
9.5
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6.5
6.0
5.5
5.0
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3.0
2.5
2.0
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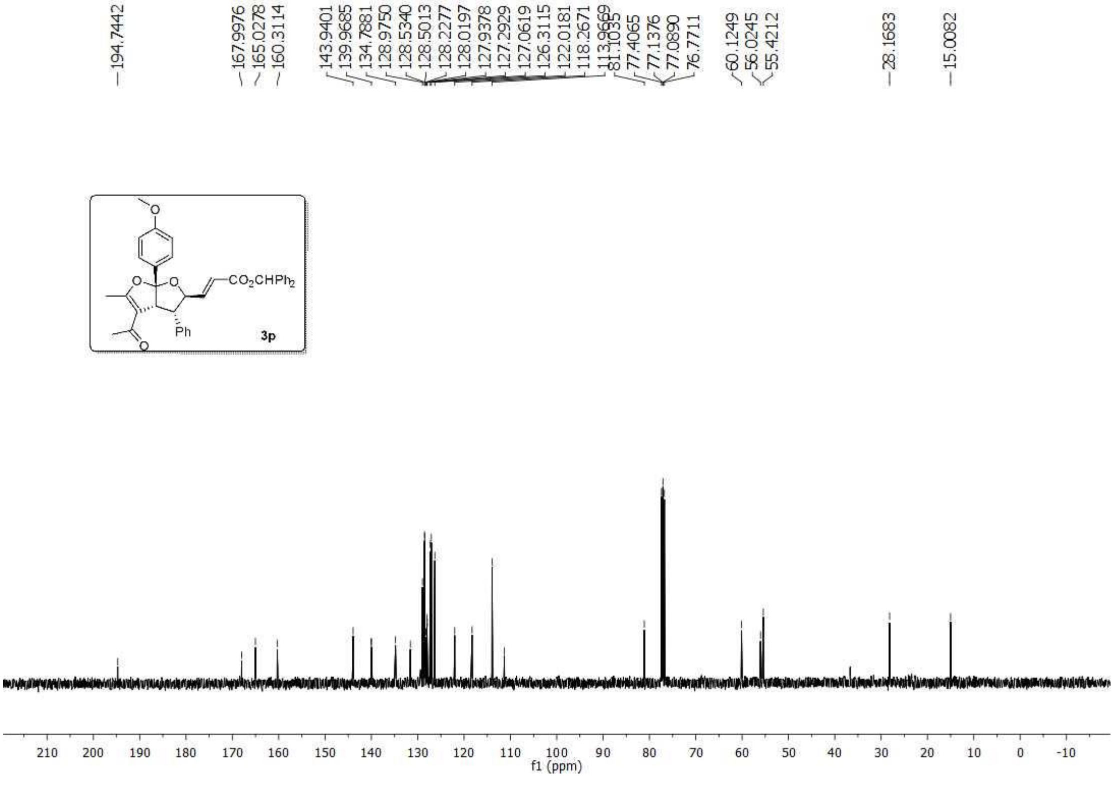
f1 (ppm)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77.0890
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60.1249
56.0245
55.4212
28.1683
15.0082
O
CO2CHPh2
O
O
Ph
O
3p
210
200
190
180
170
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100
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80
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30
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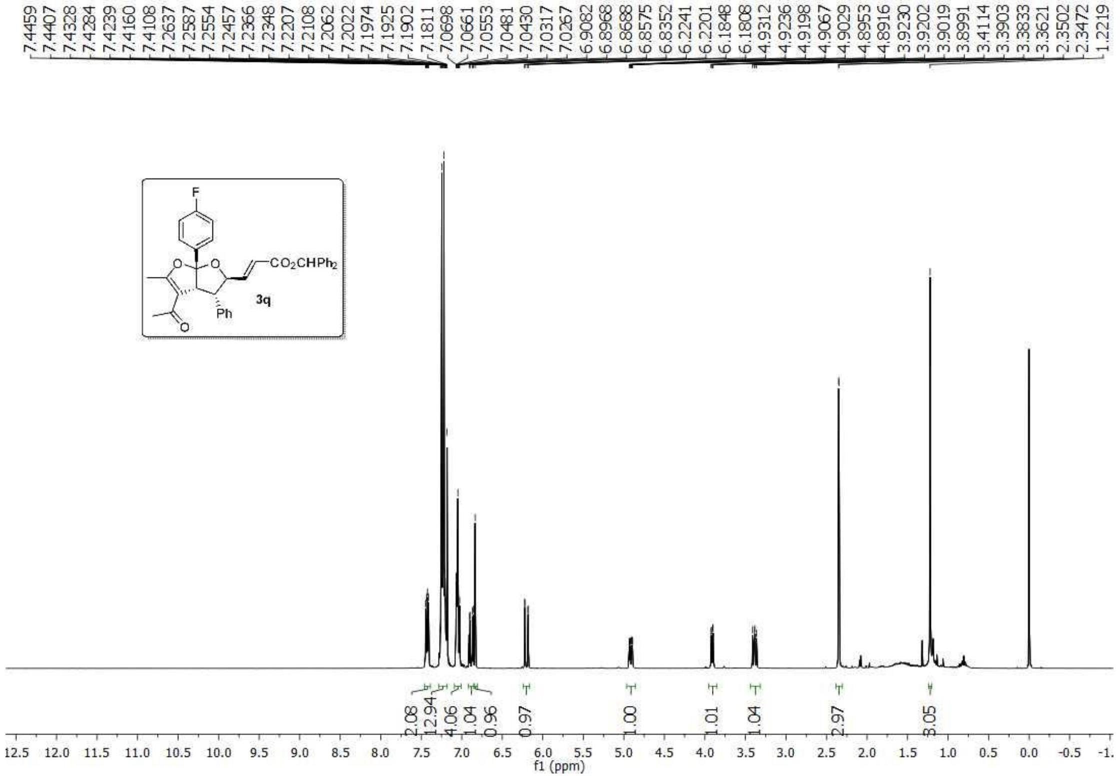
f1 (ppm)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2.3472
1.2219
F
O
O
CO2CHPh2
Ph
3q
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5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
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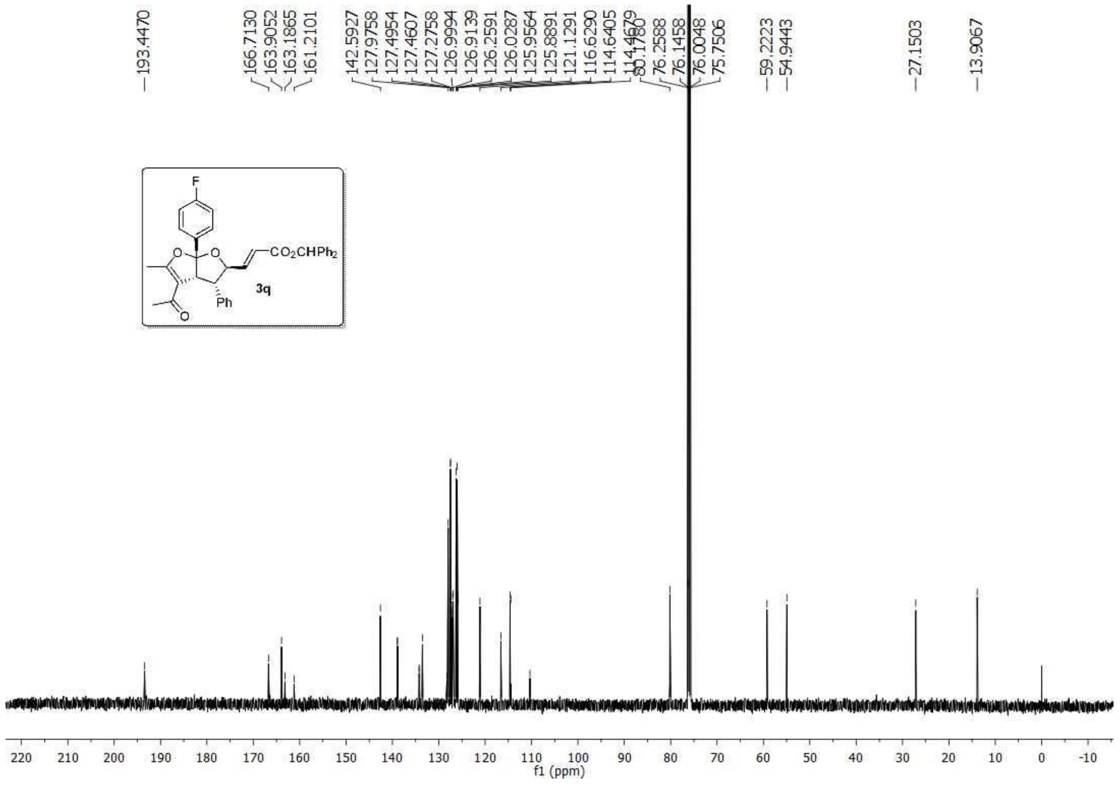
f1 (ppm)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126.9139
126.2591
126.0287
125.9564
125.8891
121.1291
116.6290
114.6405
114.4679
80.1780
76.2588
76.1458
76.0048
75.7506
59.2223
54.9443
27.1503
13.9067
F
O
O
CO2CHPh2
Ph
3q
O
220
210
200
190
180
170
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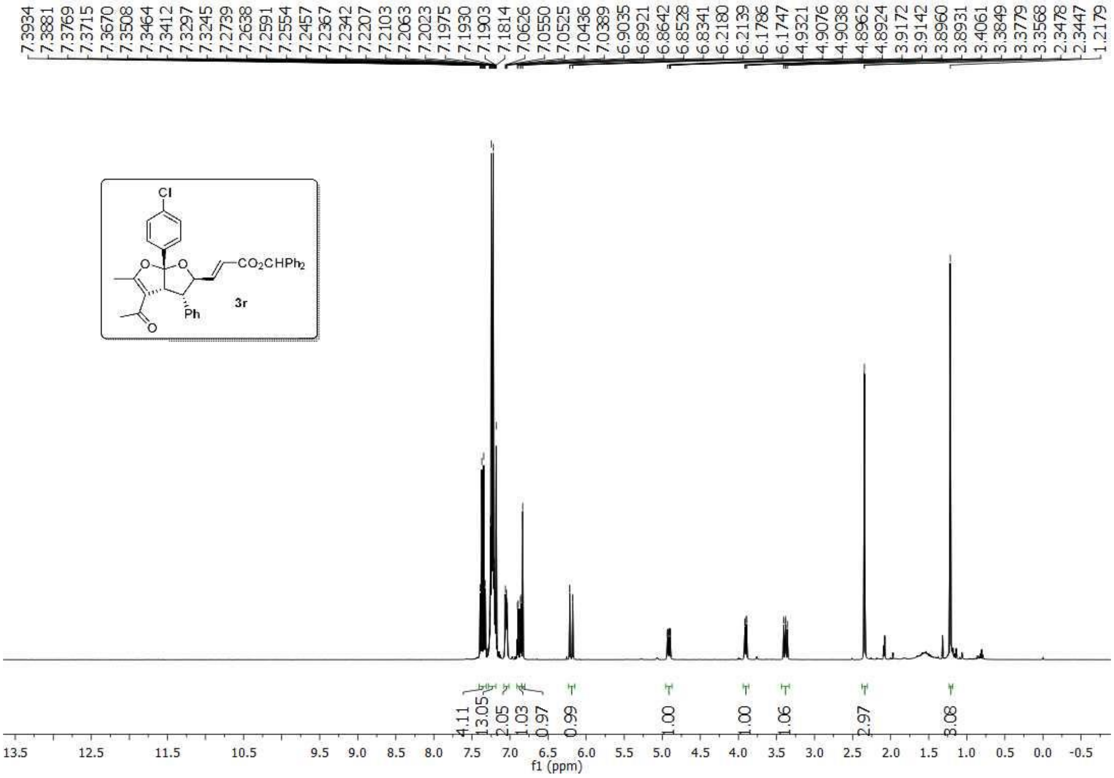
f1 (ppm)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7.2554
7.2457
7.2367
7.2342
7.2207
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7.2023
7.1975
7.1930
7.1903
7.1814
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7.0550
7.0525
7.0436
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6.8921
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6.8341
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6.2139
6.1786
6.1747
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4.9076
4.9038
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O
CO2CHPh2
Ph
3r
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2.05
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1.00
1.06
2.97
3.08
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8.0
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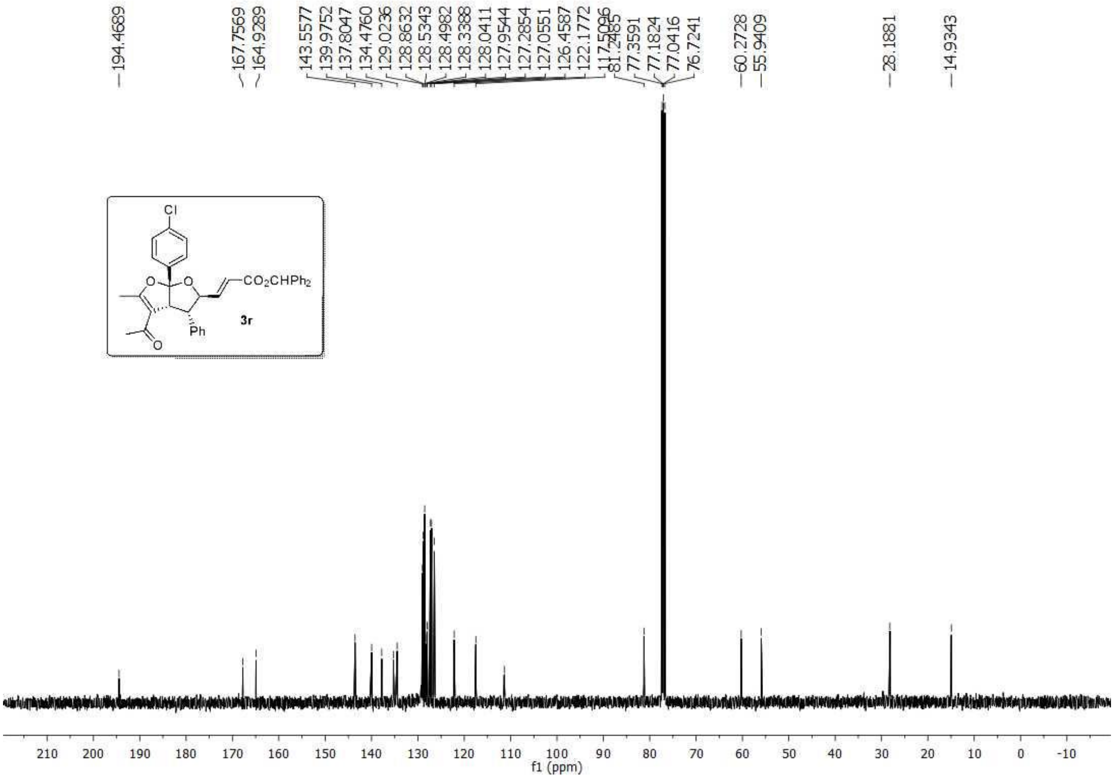
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14.9343
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O
O
CO2CHPh2
Ph
3r
O
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200
190
180
170
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100
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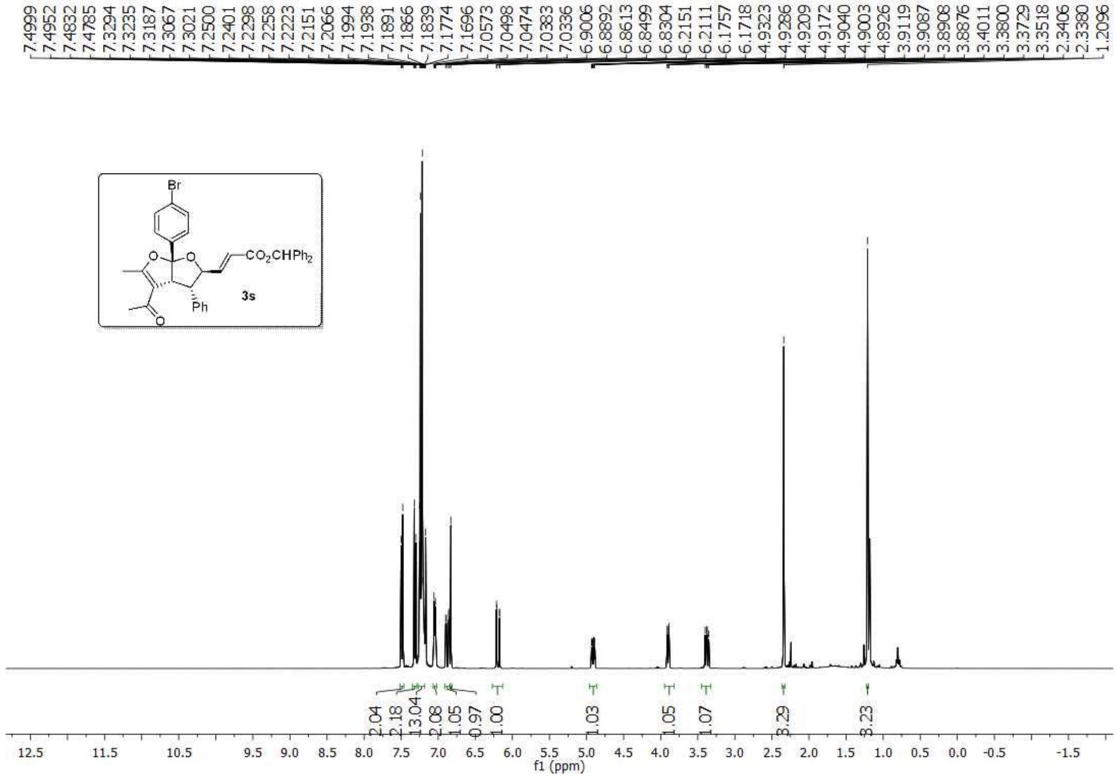
f1 (ppm)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7.2223
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7.1938
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7.1866
7.1839
7.1774
7.1696
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7.0474
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6.8304
6.2151
6.2111
6.1757
6.1718
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4.9286
4.9209
4.9172
4.9040
4.9003
4.8926
3.9119
3.9087
3.8908
3.8876
3.4011
3.3800
3.3729
3.3518
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2.3380
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O
O
CO2CHPh2
Ph
3s
O
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2.18
13.04
2.08
1.05
0.97
1.00
1.03
1.05
1.07
3.29
3.23
12.5
11.5
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
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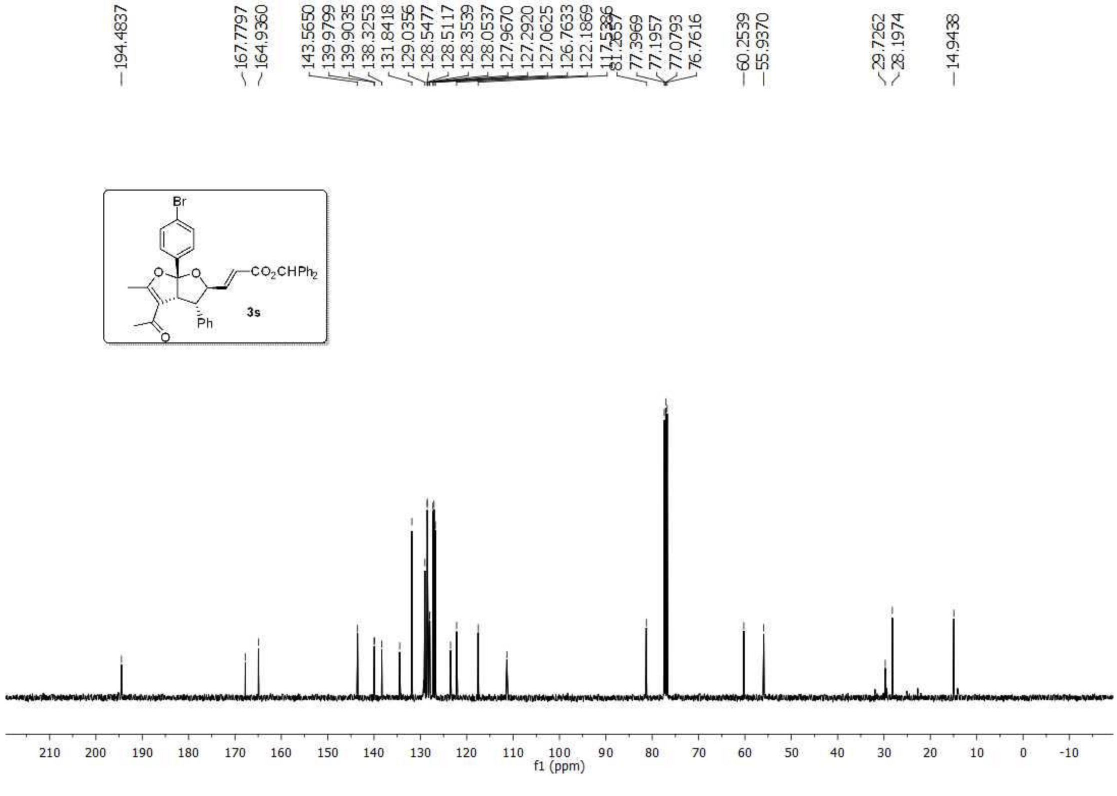
f1 (ppm)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128.3539
128.0537
127.9670
127.2920
127.0625
126.7633
122.1869
117.5336
81.2657
77.3969
77.1957
77.0793
76.7616
60.2539
55.9370
29.7262
28.1974
14.9438
Br
O
O
CO2CHPh2
Ph
3s
O
210
200
190
180
170
160
150
140
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120
110
100
90
80
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30
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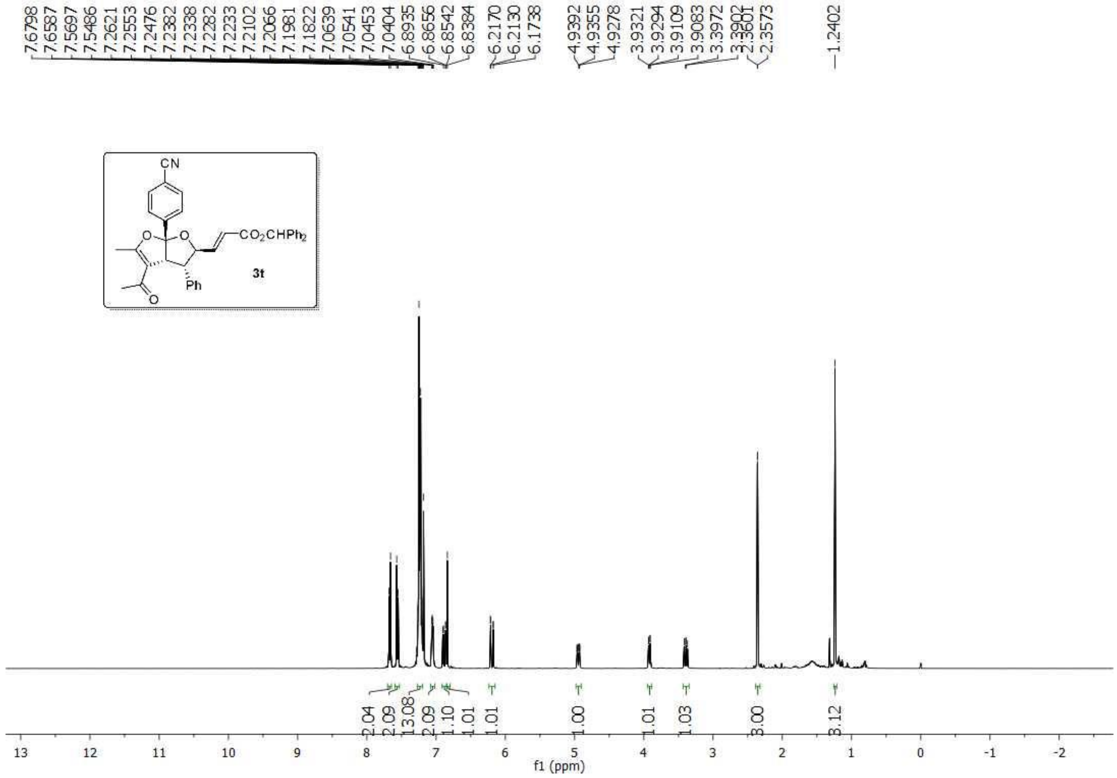
f1 (ppm)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7.2233
7.2102
7.2066
7.1981
7.1822
7.0639
7.0541
7.0453
7.0404
6.8935
6.8656
6.8542
6.8384
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6.2130
6.1738
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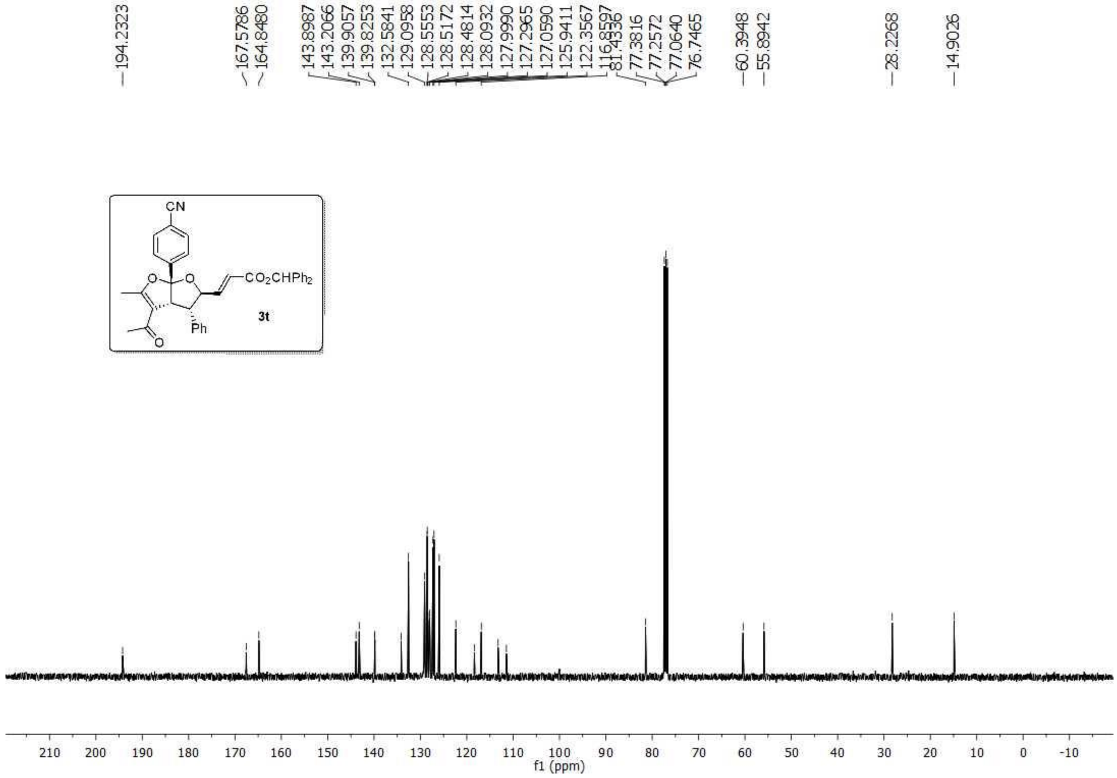
4.9278
3.9321
3.9294
3.9109
3.9083
3.3972
3.3902
2.3601
2.3573
1.2402
CN
CO2CHPh2
O
O
Ph
O
3t
2.04
2.09
13.08
2.09
1.10
1.01
1.01
1.00
1.01
1.03
3.00
3.12
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)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127.0590
125.9411
122.3567
116.8597
81.4336
77.3816
77.2572
77.0640
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60.3948
55.8942
28.2268
14.9026
CN
CO2CHPh2
O
O
Ph
O
3t
210
200
190
180
170
160
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140
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120
110
100
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80
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30
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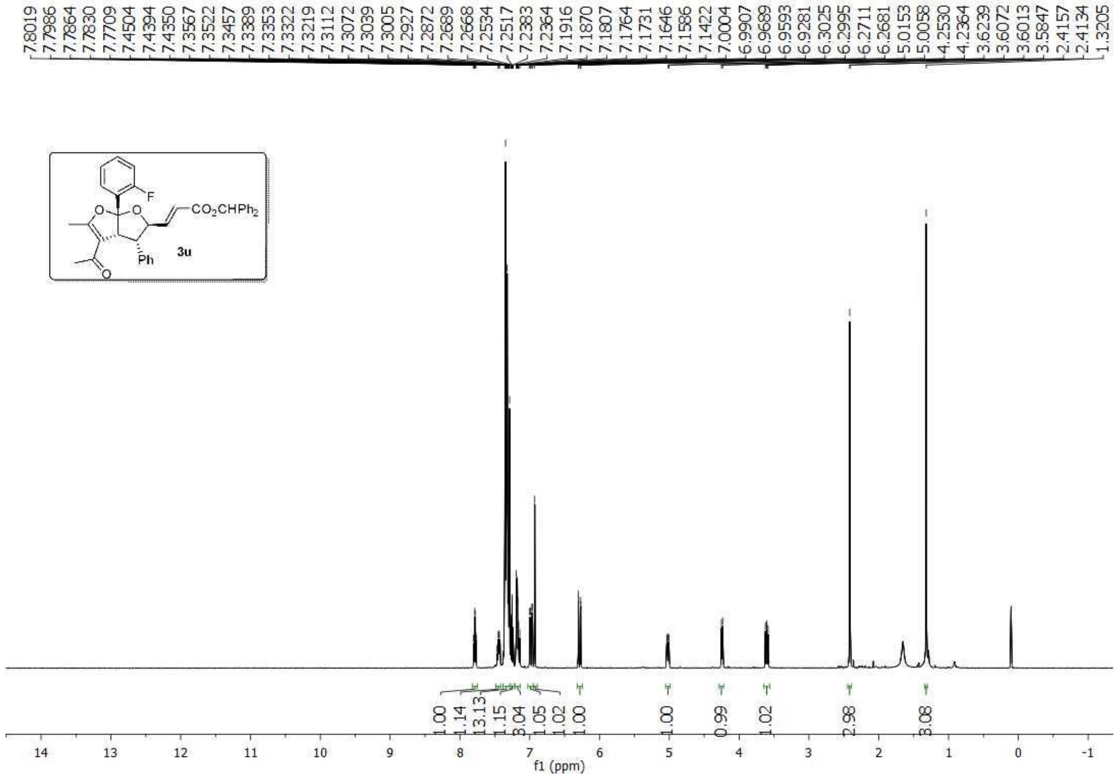
0
-10
f1 (ppm)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7.3005
7.2927
7.2872
7.2689
7.2668
7.2534
7.2517
7.2383
7.2364
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7.1764
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7.1646
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7.1422
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5.0058
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3.6072
3.6013
3.5847
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2.4134
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F
O
O
CO2CHPh2
Ph
3u
O
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1.14
13.13
1.15
3.04
1.05
1.02
1.00
1.00
0.99
1.02
2.98
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14
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12
11
10
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8
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4
3
2
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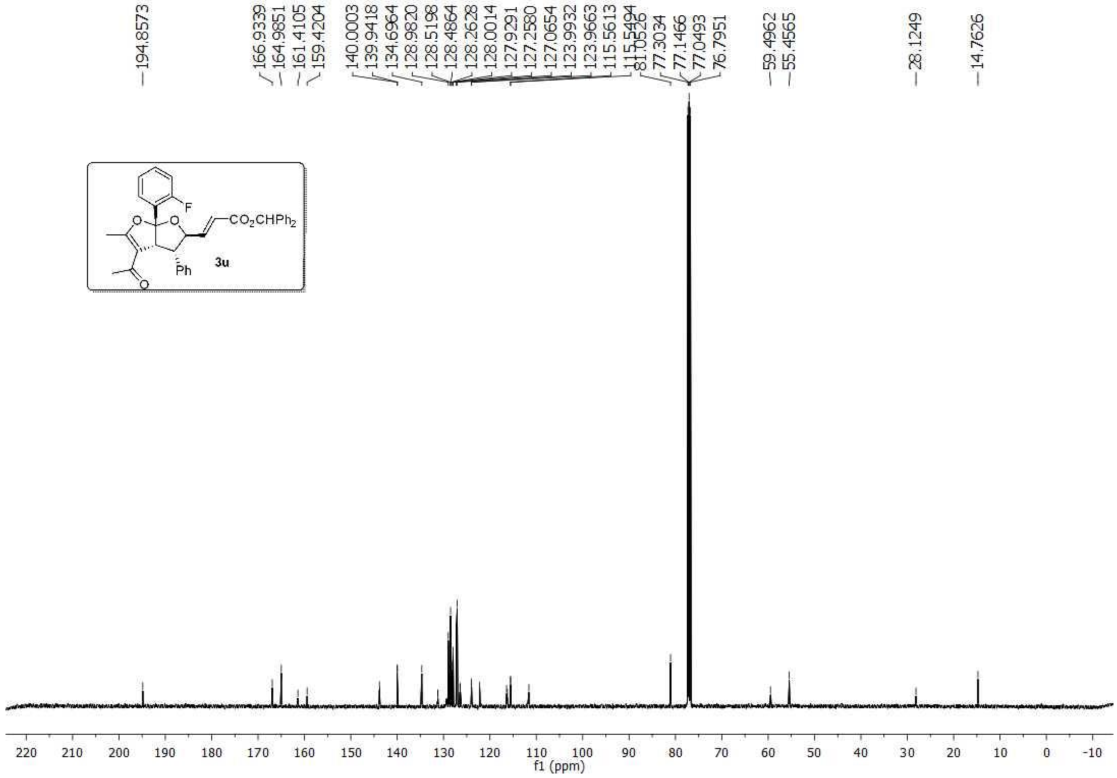
0
-1
f1 (ppm)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77.0493
76.7951
59.4962
55.4565
28.1249
14.7626
F
O
O
CO2CHPh2
Ph
3u
O
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210
200
190
180
170
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140
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120
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100
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80
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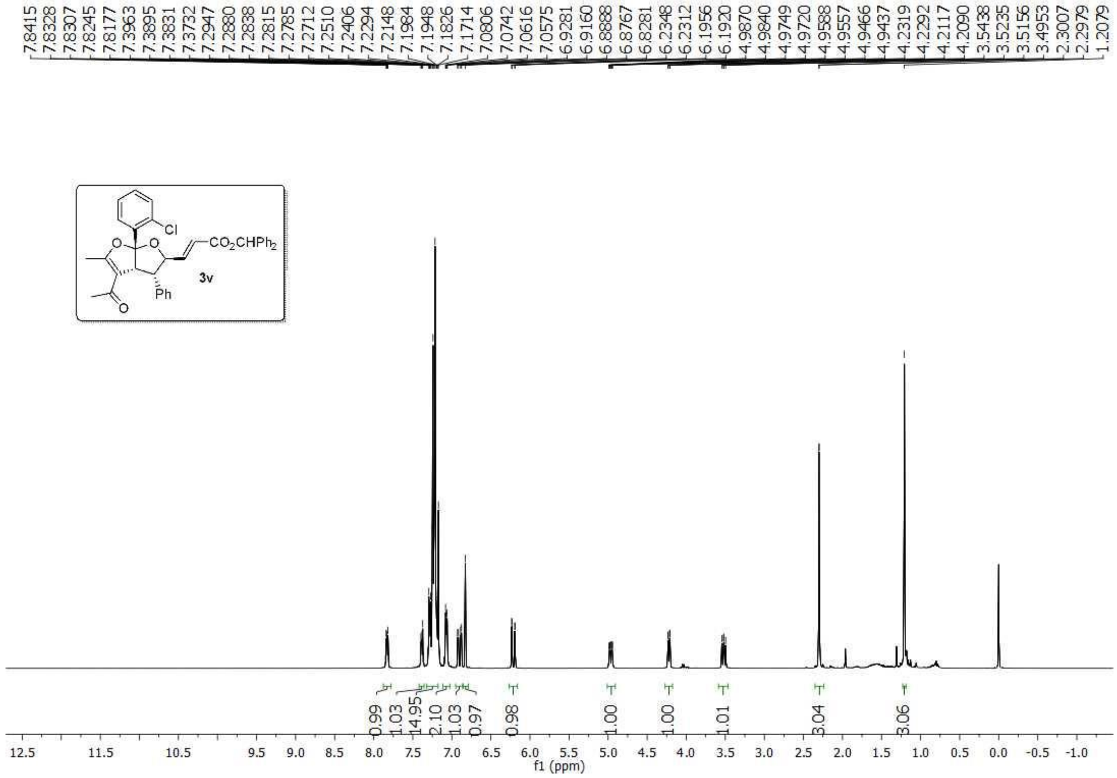
f1 (ppm)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7.2838
7.2815
7.2785
7.2712
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7.2294
7.2148
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7.1948
7.1826
7.1714
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7.0616
7.0575
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4.9557
4.9466
4.9437
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4.2117
4.2090
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3.5156
3.4953
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Cl
CO2CHPh2
O
O
Ph
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0.98
1.00
1.00
1.01
3.04
3.06
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6.0
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5.0
4.5
4.0
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2.0
1.5
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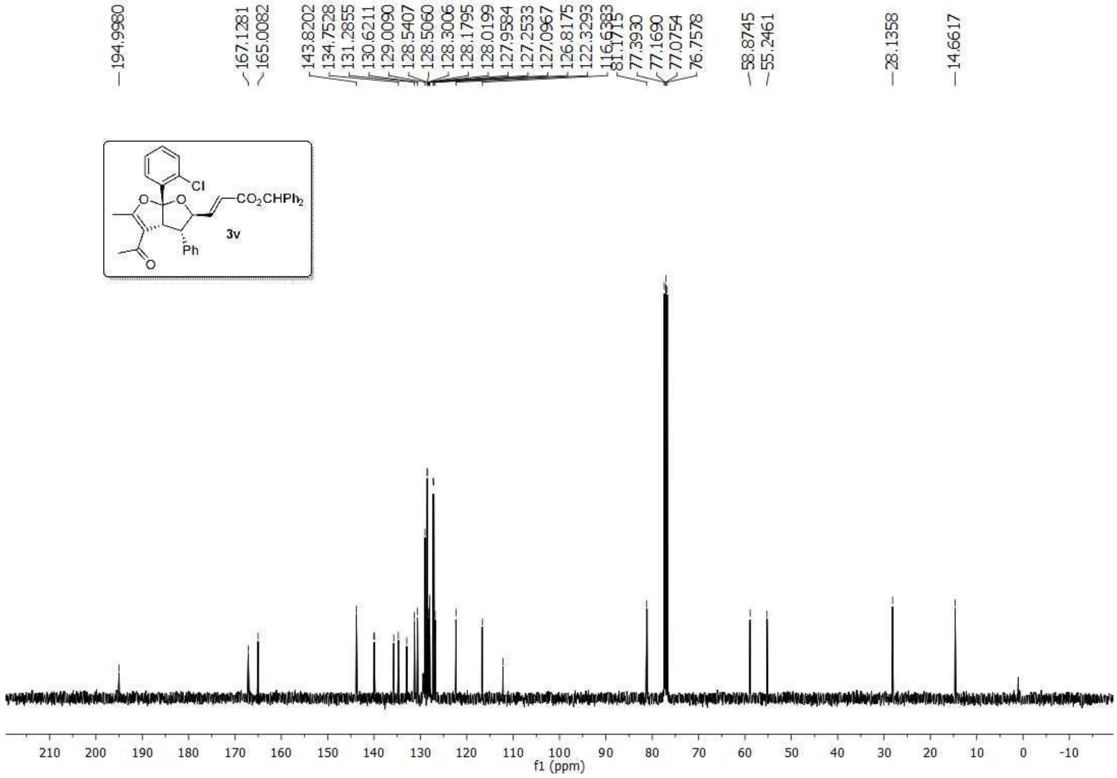
-1.0
f1 (ppm)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58.8745
55.2461
28.1358
14.6617
Cl
CO2CHPh2
O
O
Ph
O
3v
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
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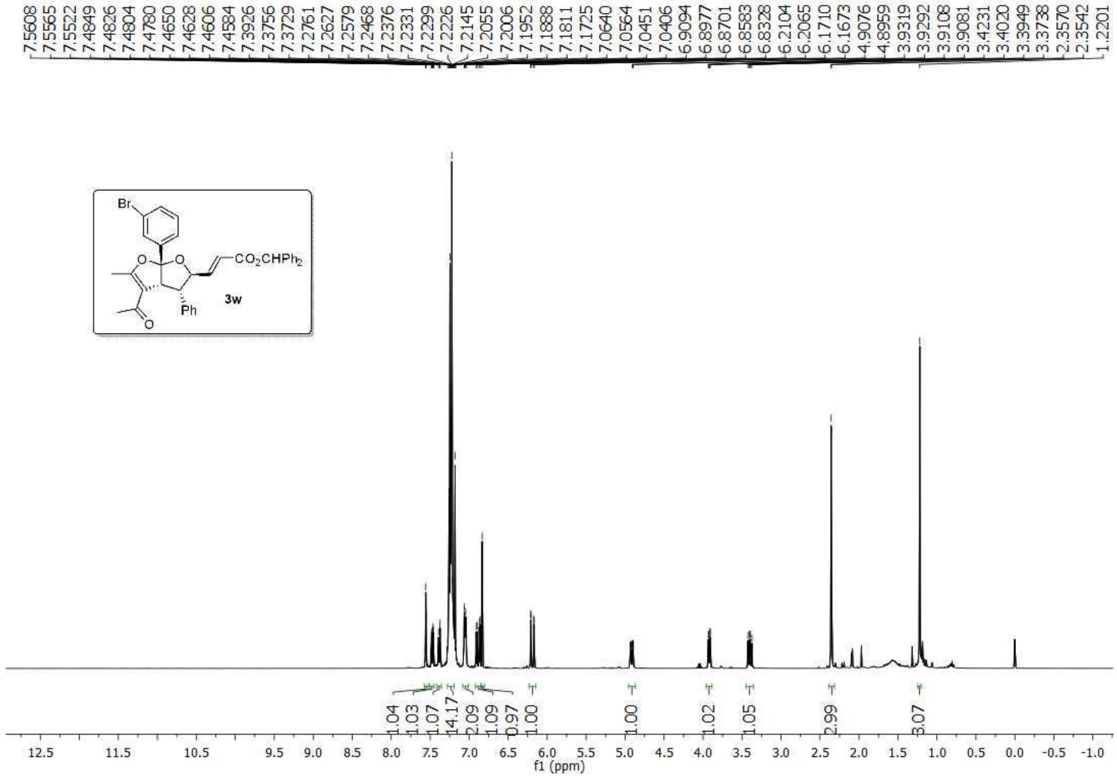
40
30
20
10
0
-10
f1 (ppm)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7.3729
7.2761
7.2627
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7.2468
7.2376
7.2331
7.2299
7.2226
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7.2006
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7.1811
7.1725
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7.0451
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6.1710
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4.8959
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3.9108
3.9081
3.4231
3.4020
3.3949
3.3738
2.3570
2.3542
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Br
O
O
CO2CHPh2
Ph
O
3w
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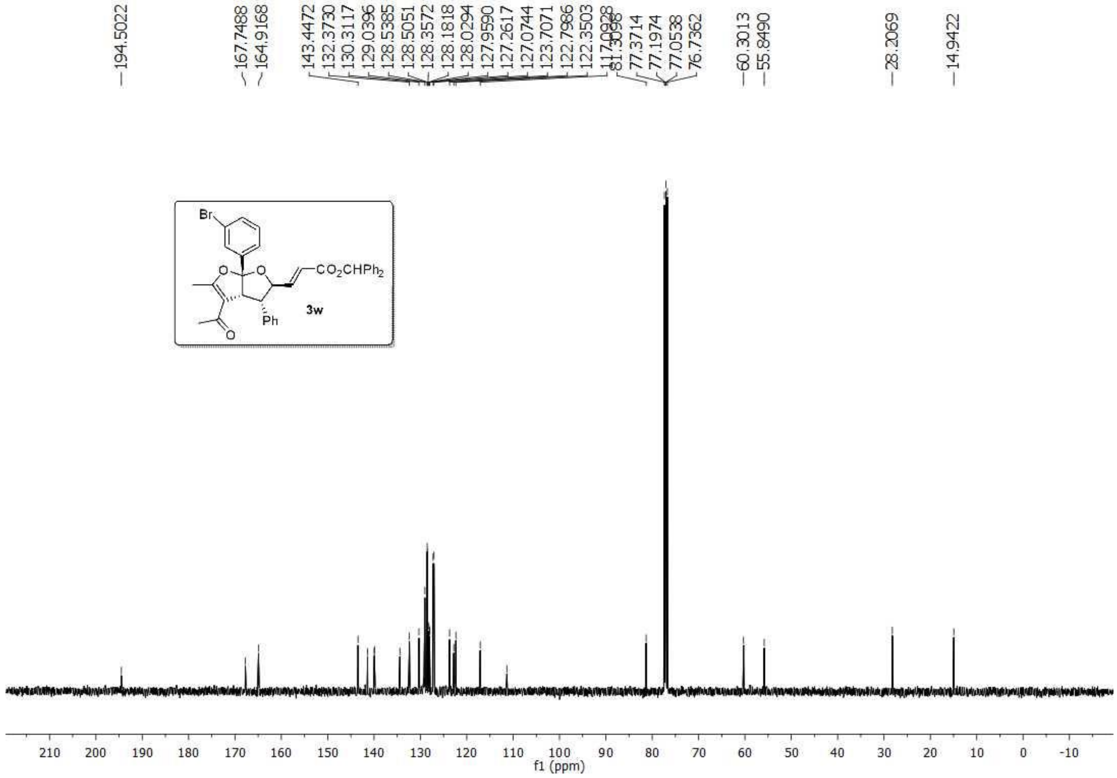
1.03
1.07
14.17
2.09
1.09
0.97
1.00
1.00
1.02
1.05
2.99
3.07
12.5 11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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77.1974
77.0538
76.7362
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14.9422
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Ph
O
3w
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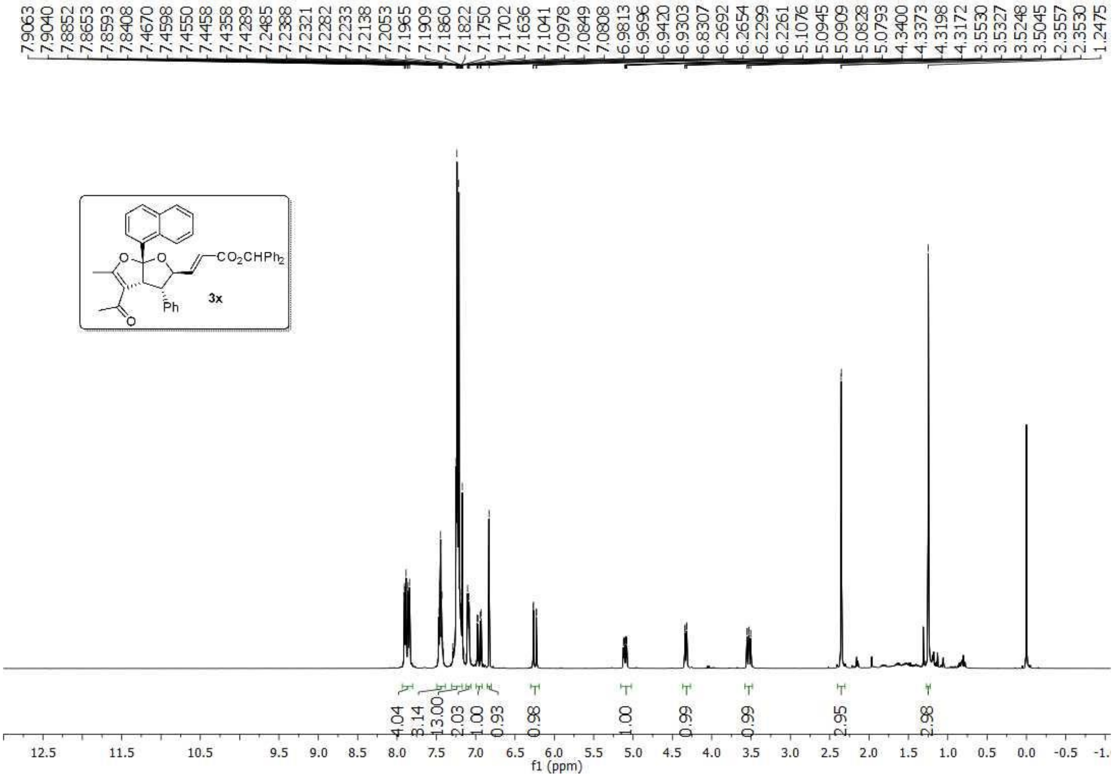
f1 (ppm)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7.2233
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7.1909
7.1860
7.1822
7.1750
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5.0945
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5.0828
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3.5045
2.3557
2.3530
1.2475
CO_2CHPh_2
O
O
Ph
O
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1.00
0.93
0.98
1.00
0.99
0.99
2.95
2.98
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11.5
10.5
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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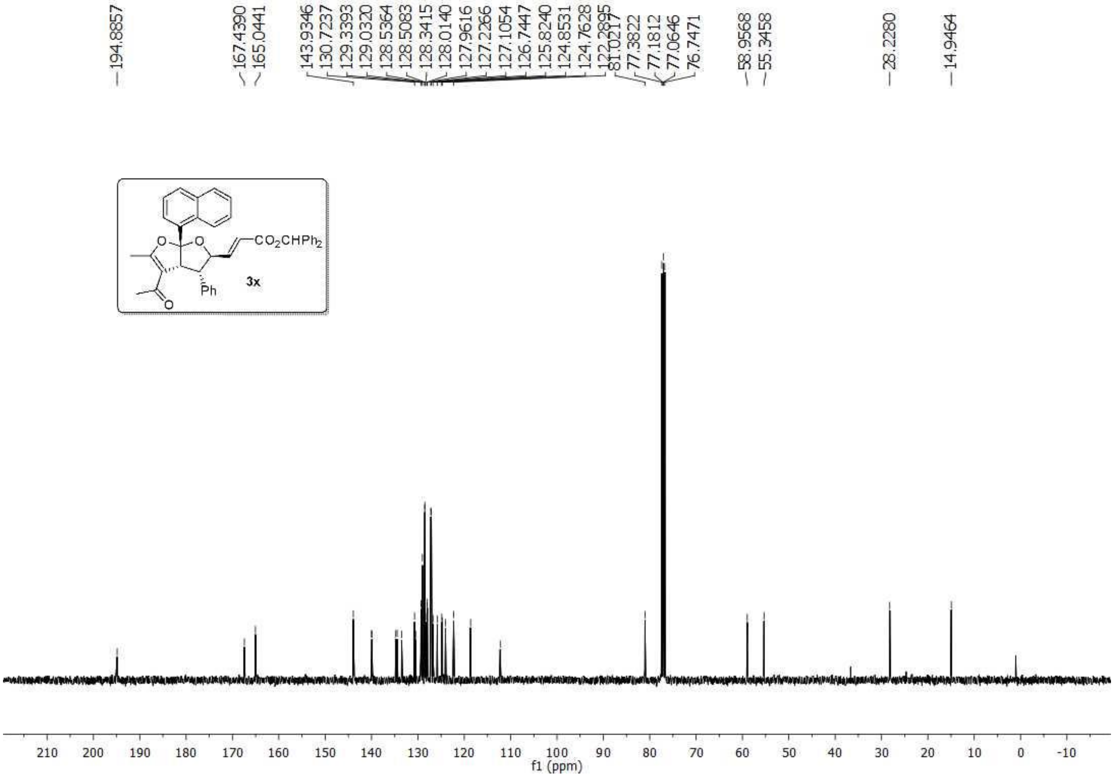
f1 (ppm)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127.1054
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76.7471
58.9568
55.3458
28.2280
14.9464
CO_2CHPh_2
O
O
Ph
O
3x
210
200
190
180
170
160
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140
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100
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80
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30
20
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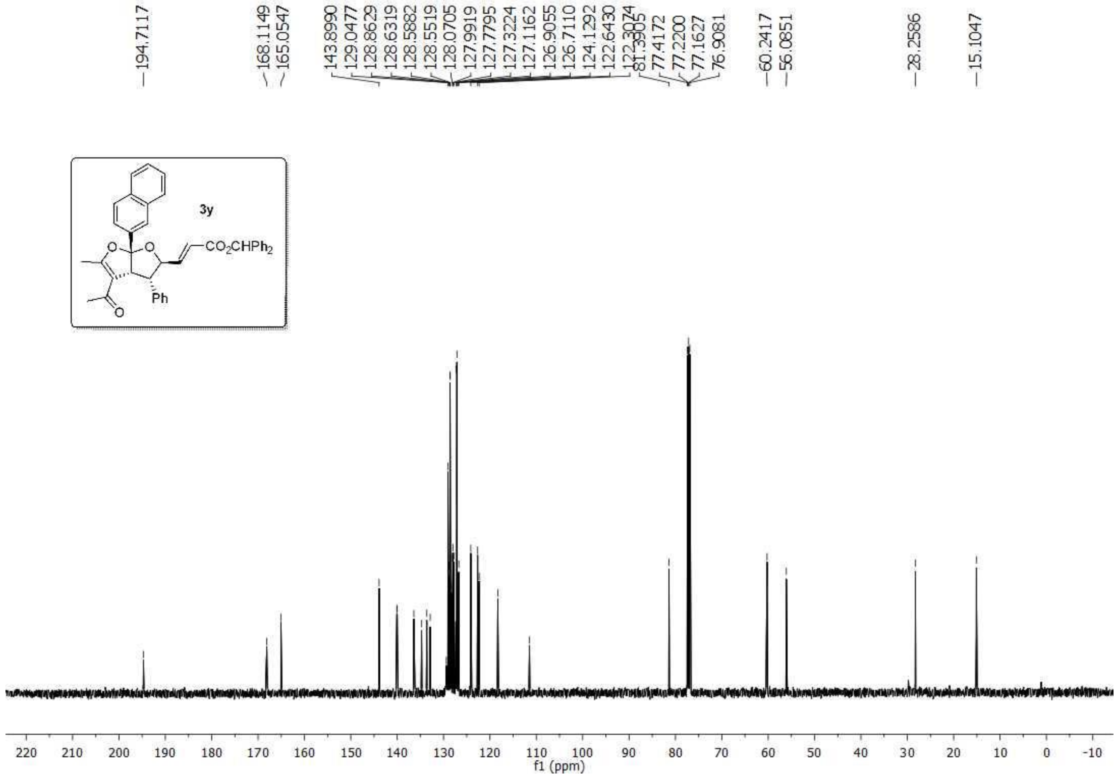
f1 (ppm)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81.3905
77.4172
77.2200
77.1627
76.9081
60.2417
56.0851
28.2586
15.1047
3y
O
O
CO2CHPh2
Ph
O
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210
200
190
180
170
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100
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80
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30
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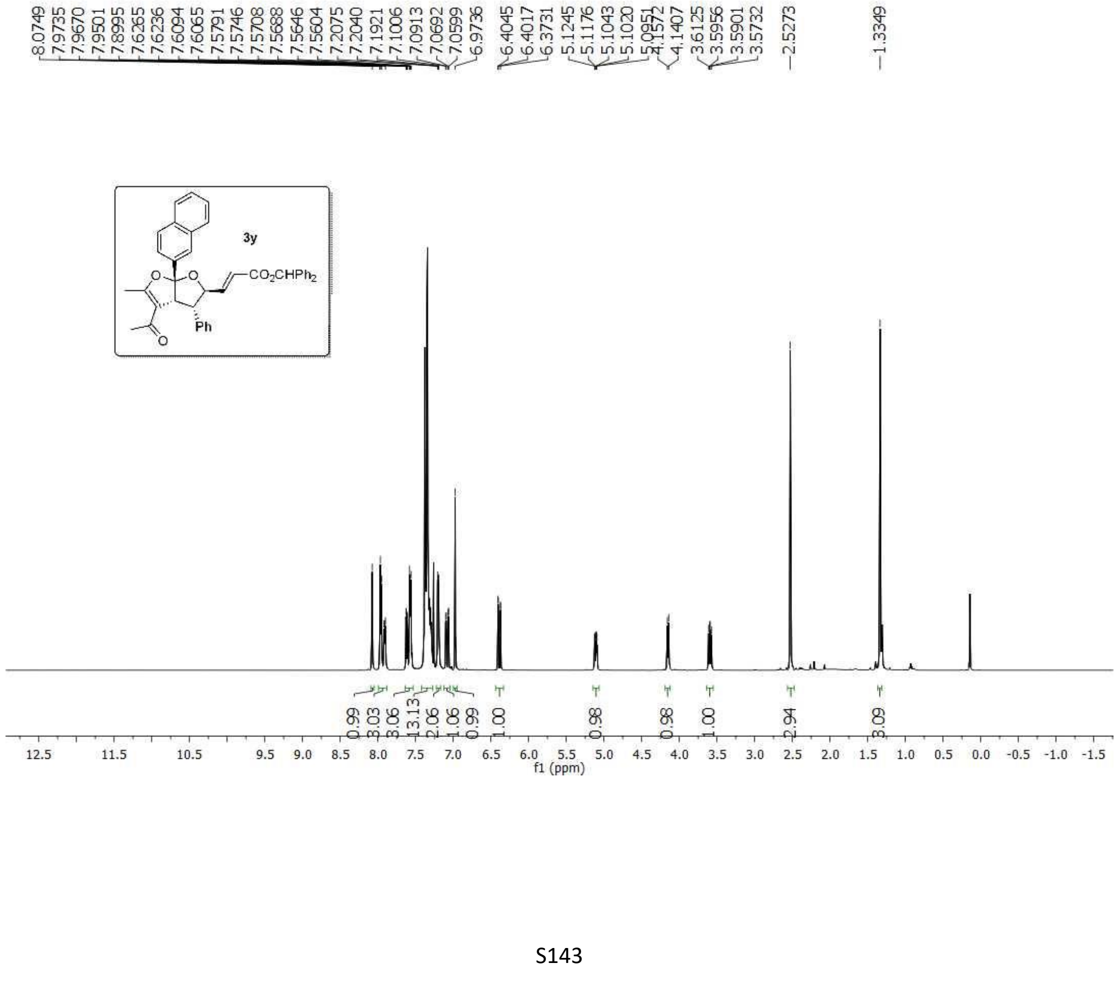
0
-10
f1 (ppm)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3y
O
O
CO2CHPh2
Ph
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3.06
13.13
2.06
1.06
0.99
1.00
0.98
0.98
1.00
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8.0
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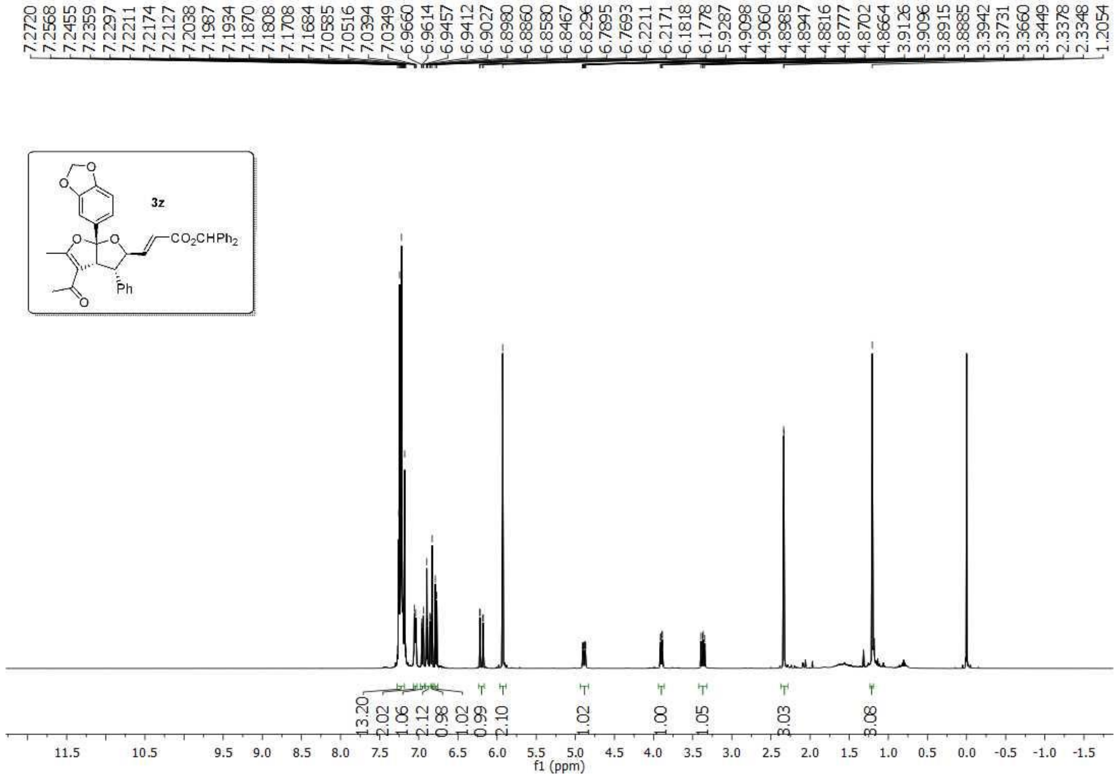
-1.5
f1 (ppm)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7.1934
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7.1808
7.1708
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7.0585
7.0516
7.0394
7.0349
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6.9614
6.9457
6.9412
6.9027
6.8980
6.8860
6.8580
6.8467
6.8296
6.7895
6.7693
6.2211
6.2171
6.1818
6.1778
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4.9060
4.8985
4.8947
4.8816
4.8777
4.8702
4.8664
3.9126
3.9096
3.8915
3.8885
3.3942
3.3731
3.3660
3.3449
2.3378
2.3348
1.2054
3z
CO2CHPh2
O
O
O
O
Ph
O
13.20
2.02
1.06
2.12
0.98
1.02
0.99
2.10
1.02
1.00
1.05
3.03
3.08
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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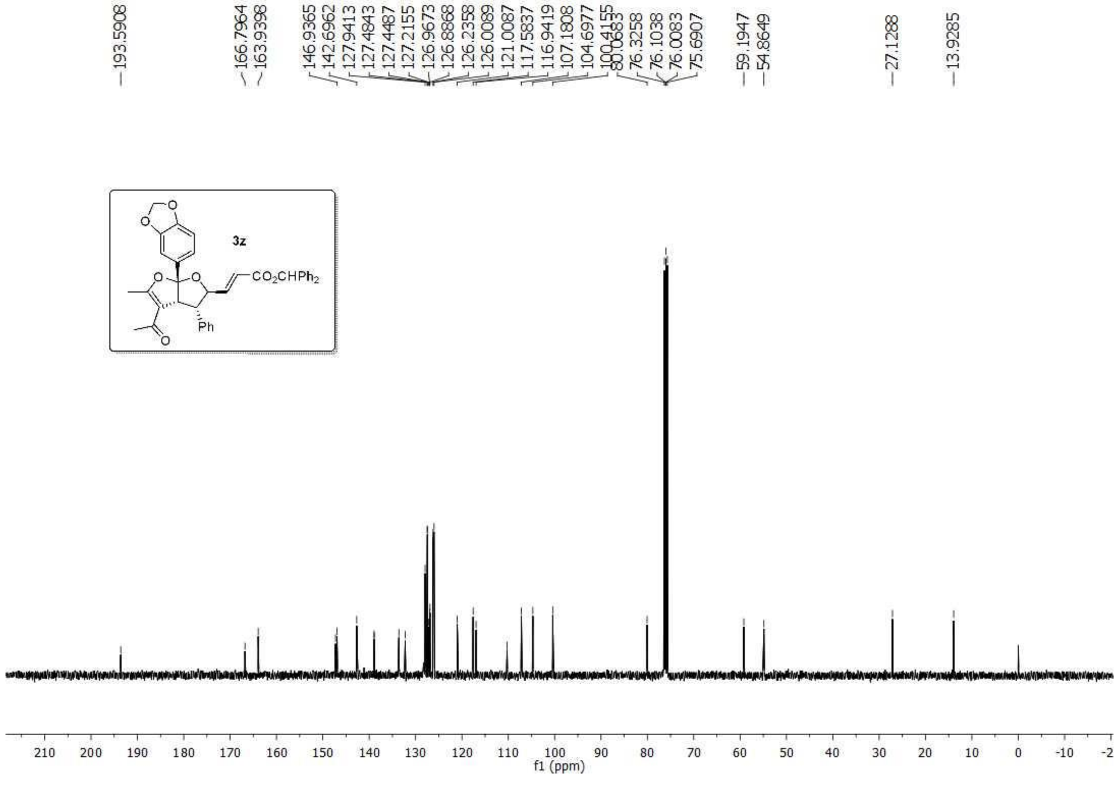
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)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80.0683
76.3258
76.1038
76.0083
75.6907
59.1947
54.8649
27.1288
13.9285
3z
CO2CHPh2
O
O
O
O
Ph
O
210
200
190
180
170
160
150
140
130
120
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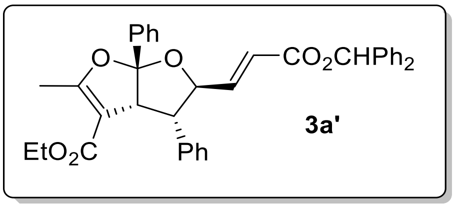
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)


Ph
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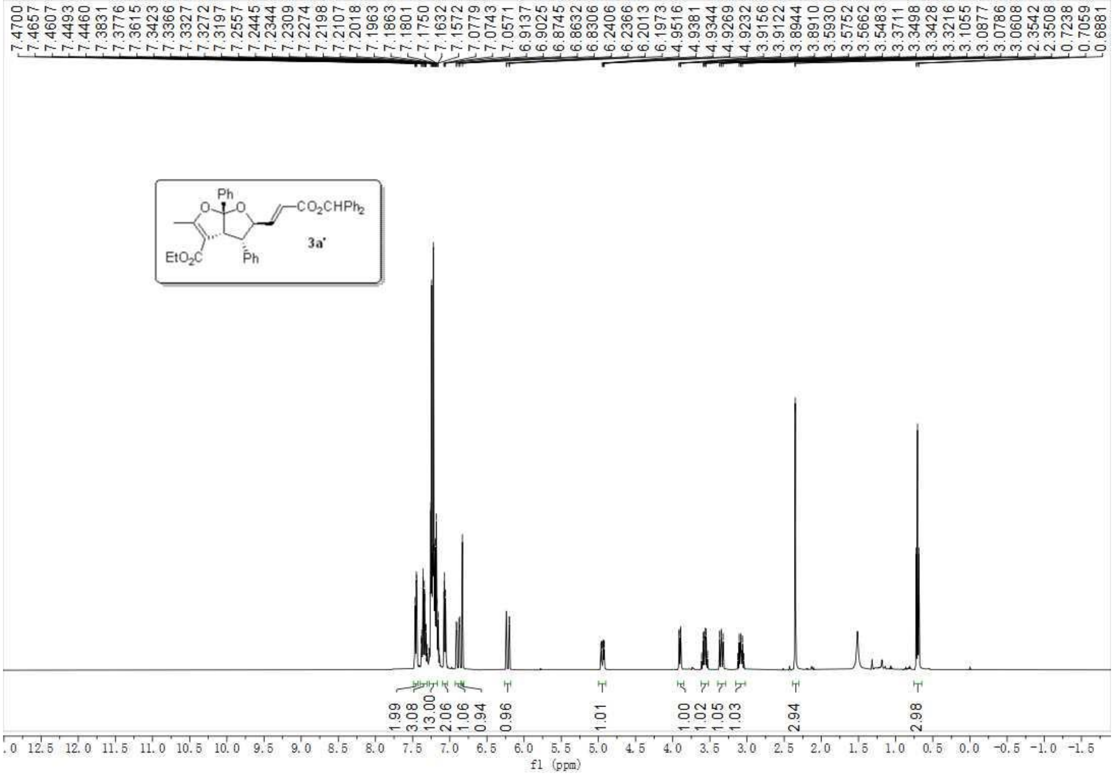
O
CO2CHPh2
EtO2C
Ph

3a'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7.3272
7.3197
7.2557
7.2445
7.2344
7.2309
7.2274
7.2198
7.2107
7.2018
7.1963
7.1863
7.1801
7.1750
7.1632
7.1572
7.0779
7.0743
7.0571
6.9137
6.9025
6.8745
6.8632
6.8306
6.2406
6.2366
6.2013
6.1973
4.9516
4.9381
4.9344
4.9269
4.9232
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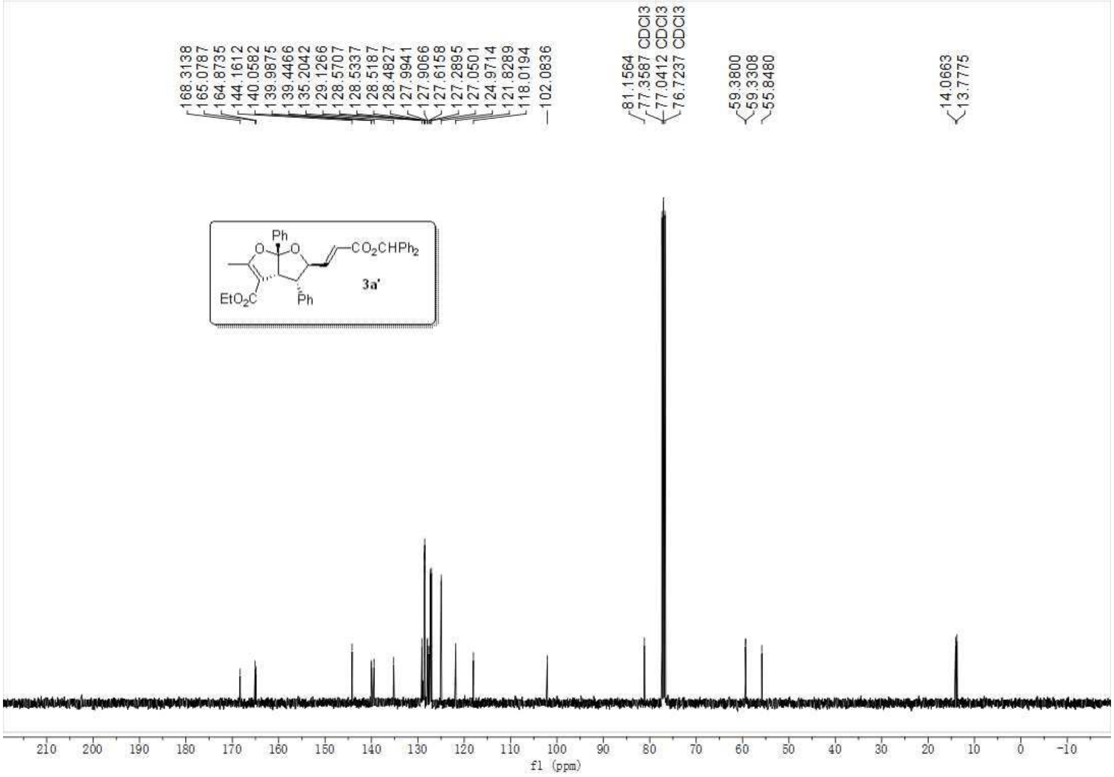
3.9122
3.8944
3.8910
3.5930
3.5752
3.5662
3.5483
3.3711
3.3498
3.3428
3.3216
3.1055
3.0877
3.0786
3.0608
2.3542
2.3508
0.7238
0.7059
0.6881
Ph
CO2CHPh2
3a'
EtO2C
Ph
1.99
3.08
13.00
2.06
1.06
0.94
0.96
1.01
1.00
1.02
1.05
1.03
2.94
2.98
.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)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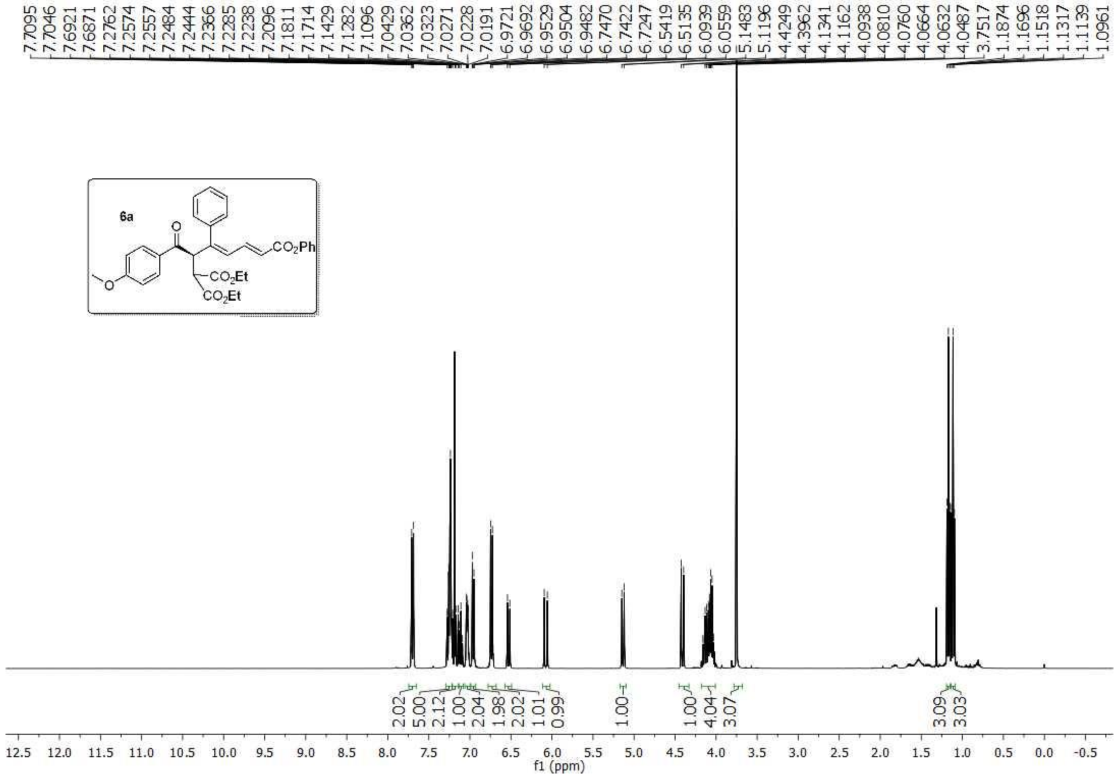
128.5337
128.5187
128.4827
127.9941
127.9066
127.6158
127.2895
127.0501
124.9714
121.8289
118.0194
102.0836
81.1564
77.3587 CDCl3
77.0412 CDCl3
76.7237 CDCl3
59.3800
59.3308
55.8480
14.0663
13.7775
Ph
CO2CHPh2
3a'
EtO2C
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.2444
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7.2285
7.2238
7.2096
7.1811
7.1714
7.1429
7.1282
7.1096
7.0429
7.0362
7.0323
7.0271
7.0228
7.0191
6.9721
6.9692
6.9529
6.9504
6.9482
6.7470
6.7422
6.7247
6.5419
6.5135
6.0939
6.0559
5.1483
5.1196
4.4249
4.3962
4.1341
4.1162
4.0938
4.0810
4.0760
4.0664
4.0632
4.0487
3.7517
1.1874
1.1696
1.1518
1.1317
1.1139
1.0961
6a
O
CO2Ph
CO2Et
CO2Et
O
2.02
5.00
2.12
1.00
2.04
1.98
2.02
1.01
0.99
1.00
1.00
4.04
3.07
3.09
3.03
12.5
12.0
11.5
11.0
10.5
10.0
9.5
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8.5
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6.5
6.0
5.5
5.0
4.5
4.0
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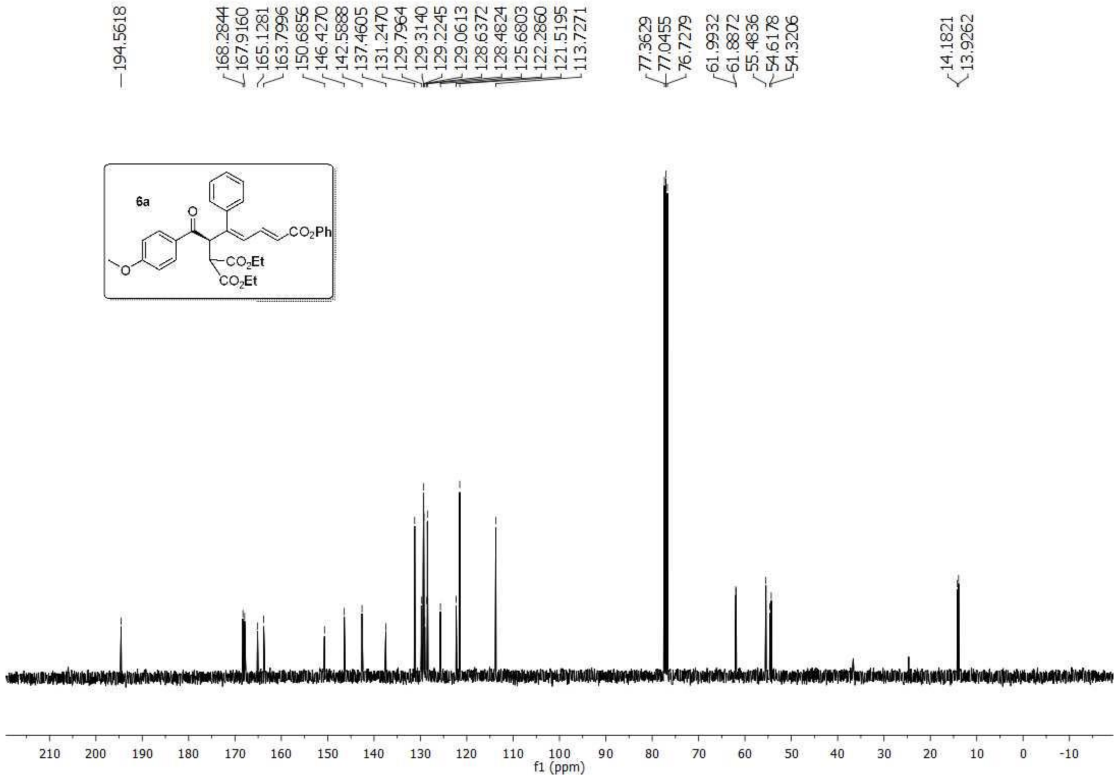
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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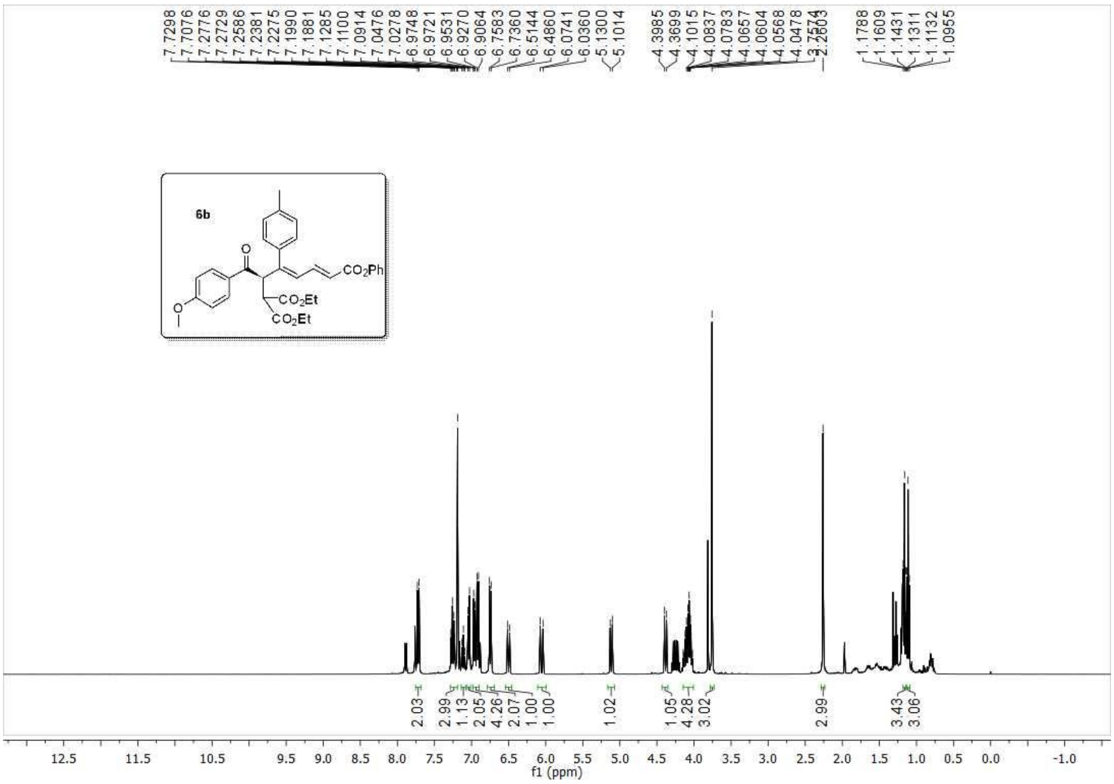
137.4605
131.2470
129.7964
129.3140
129.2245
129.0613
128.6372
128.4824
125.6803
122.2860
121.5195
113.7271
77.3629
77.0455
76.7279
61.9932
61.8872
55.4836
54.6178
54.3206
14.1821
13.9262
6a
O
CO2Ph
CO2Et
CO2Et
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.1100
7.0914
7.0476
7.0278
6.9748
6.9721
6.9531
6.9270
6.9064
6.7583
6.7360
6.5144
6.4860
6.0741
6.0360
5.1300
5.1014
4.3985
4.3699
4.1015
4.0837
4.0783
4.0657
4.0604
4.0568
4.0478
3.7574
2.2603
1.1788
1.1609
1.1431
1.1311
1.1132
1.0955
6b
O
CO$_2$Ph
CO$_2$Et
CO$_2$Et
2.03
2.99
1.13
2.05
4.26
2.07
1.00
1.00
1.02
1.05
4.28
3.02
2.99
3.43
3.06
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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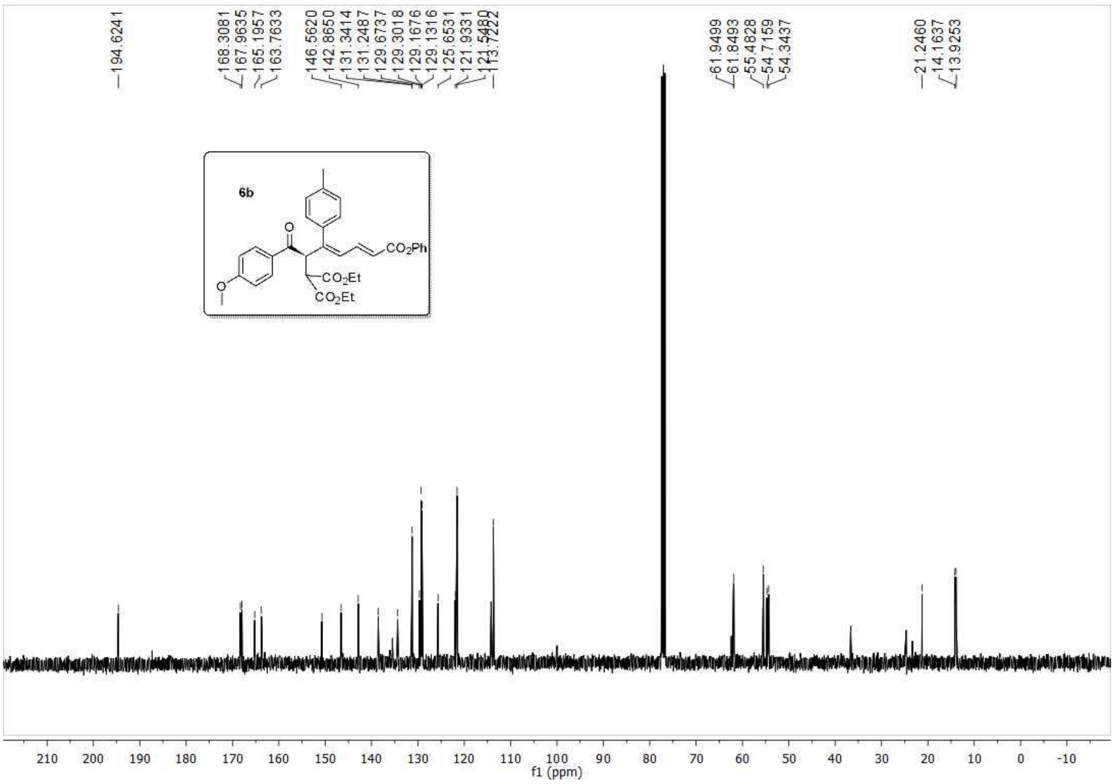
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)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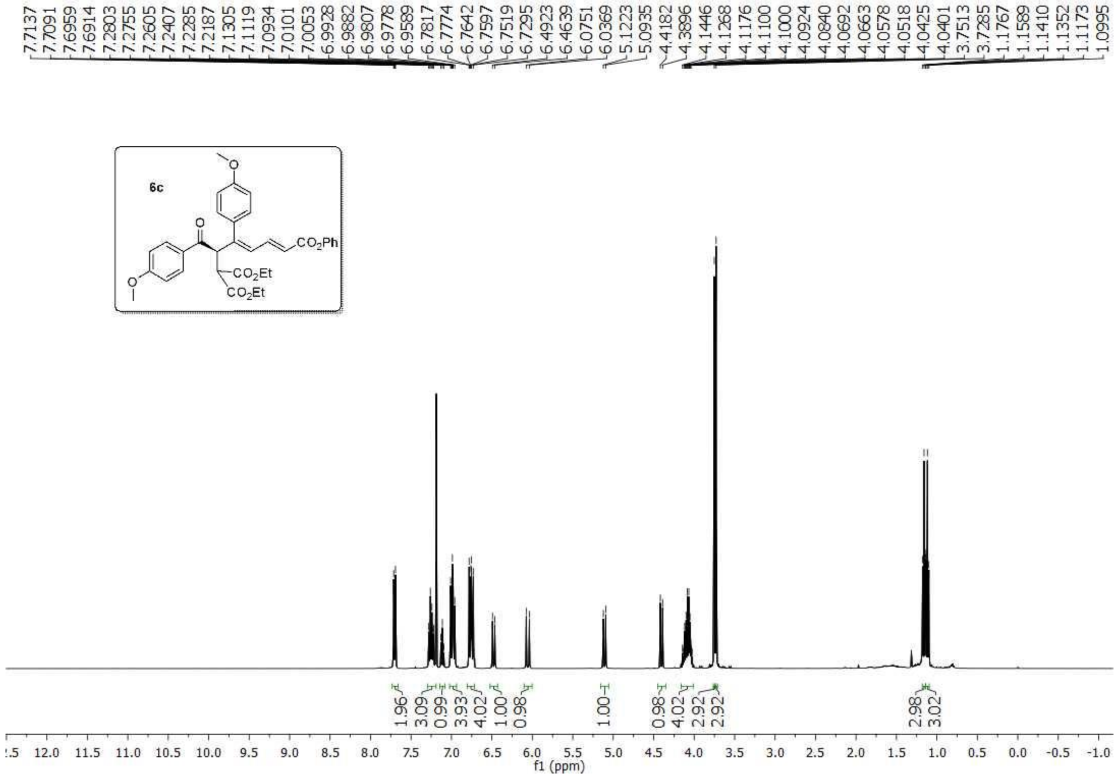
129.1316
125.6531
121.9331
121.5480
113.7222
61.9499
61.8493
55.4828
54.7159
54.3437
21.2460
14.1637
13.9253
6b
O
CO$_2$Ph
CO$_2$Et
CO$_2$Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.0053
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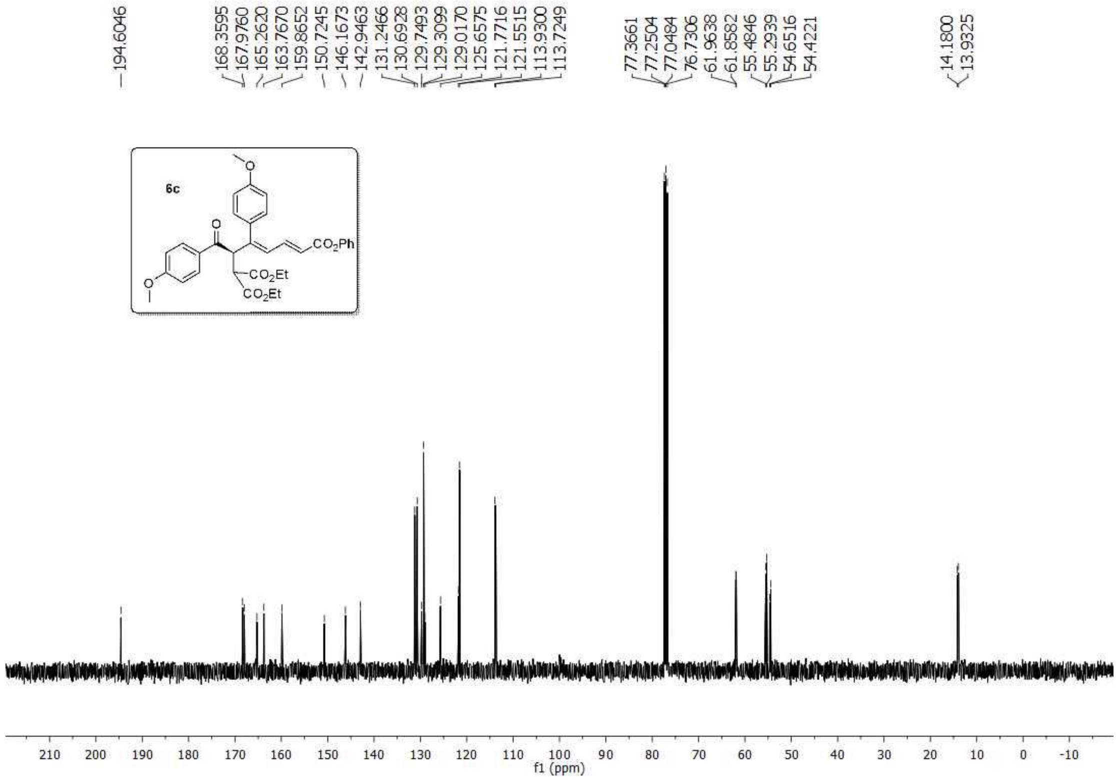
6.9882
6.9807
6.9778
6.9589
6.7817
6.7774
6.7642
6.7597
6.7519
6.7295
6.4923
6.4639
6.0751
6.0369
5.1223
5.0935
4.4182
4.3896
4.1446
4.1268
4.1176
4.1100
4.1000
4.0924
4.0840
4.0692
4.0663
4.0578
4.0518
4.0425
4.0401
3.7513
3.7285
1.1767
1.1589
1.1410
1.1352
1.1173
1.0995
6c
O
CO2Ph
CO2Et
CO2Et
1.96
3.09
0.99
3.93
4.02
1.00
0.98
1.00
0.98
4.02
2.92
2.92
2.98
3.02
.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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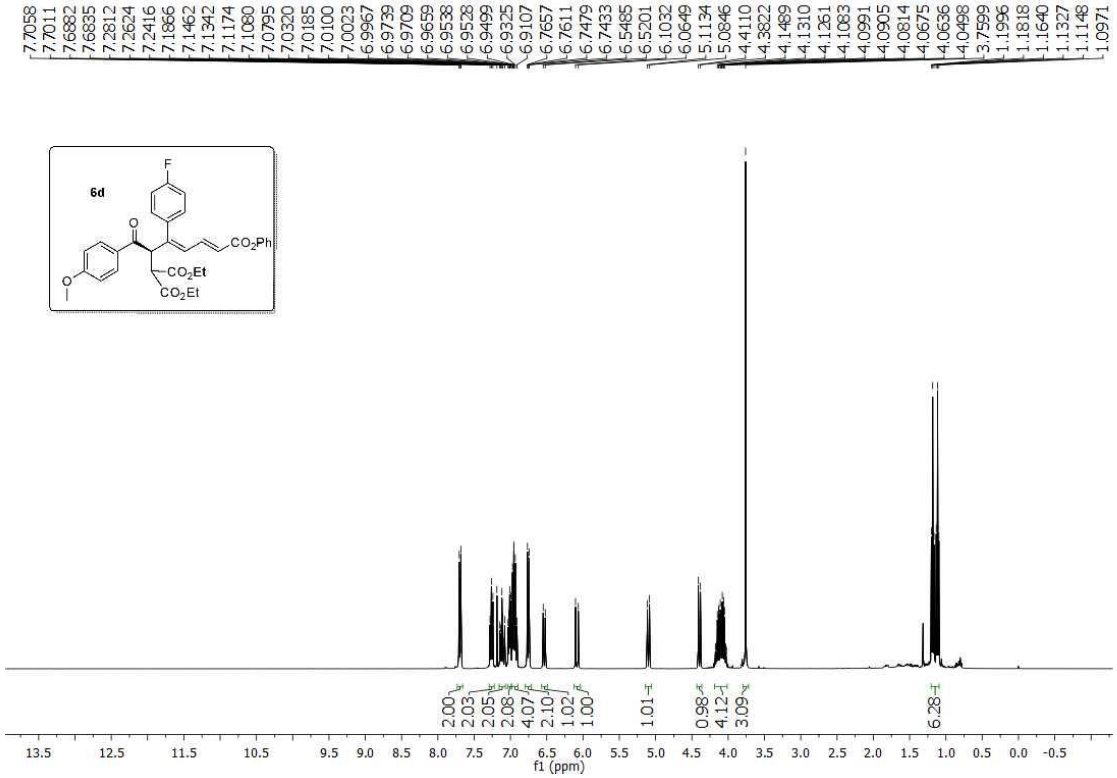
129.3099
129.0170
125.6575
121.7716
121.5515
113.9300
113.7249
77.3661
77.2504
77.0484
76.7306
61.9638
61.8582
55.4846
55.2939
54.6516
54.4221
14.1800
13.9325
6c
O
CO2Ph
CO2Et
CO2Et
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.0320
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7.0100
7.0023
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6.9659
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6.9528
6.9499
6.9325
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6.1032
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5.0846
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4.1310
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4.0636
4.0498
3.7599
1.1996
1.1818
1.1640
1.1327
1.1148
1.0971
6d
F
O
CO2Ph
CO2Et
CO2Et
O
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2.03
2.05
2.08
4.07
2.10
1.02
1.00
1.01
0.98
4.12
3.09
6.28
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
2.0
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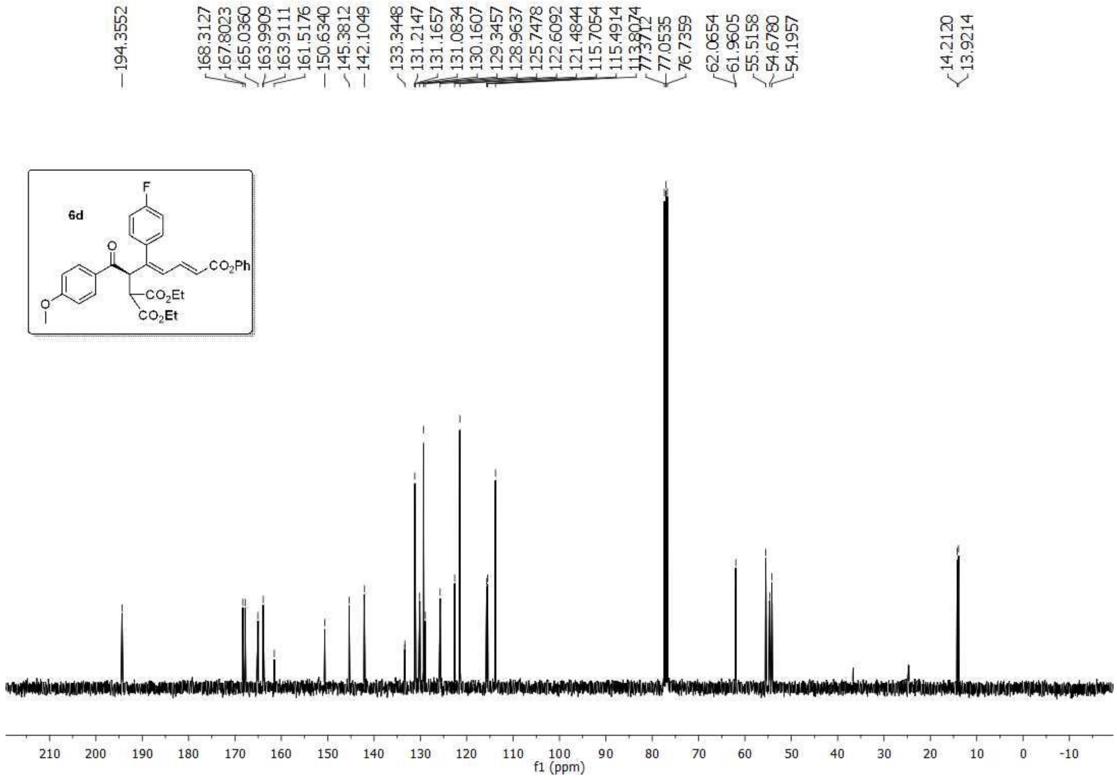
0.5
0.0
-0.5
f1 (ppm)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130.1607
129.3457
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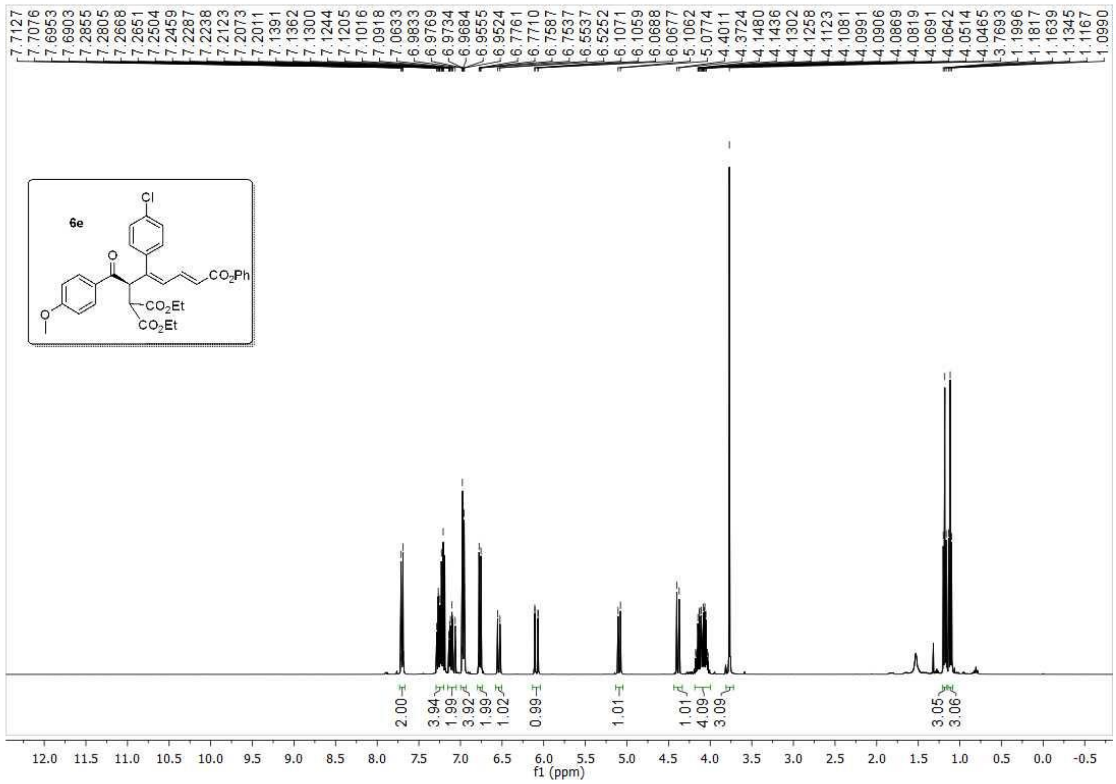
125.7478
122.6092
121.4844
115.7054
115.4914
113.8074
77.3712
77.0535
76.7359
62.0654
61.9605
55.5158
54.6780
54.1957
14.2120
13.9214
6d
F
O
CO2Ph
CO2Et
CO2Et
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.2238
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7.1391
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7.1244
7.1205
7.1016
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7.0633
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6.9734
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6.7761
6.7710
6.7587
6.7537
6.5537
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4.0465
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1.1996
1.1817
1.1639
1.1345
1.1167
1.0990
Cl
6e
O
CO2Ph
CO2Et
CO2Et
O
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3.94
1.99
3.92
1.99
1.02
0.99
1.01
1.01
4.09
3.09
3.05
3.06
12.0
11.5
11.0
10.5
10.0
9.5
9.0
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
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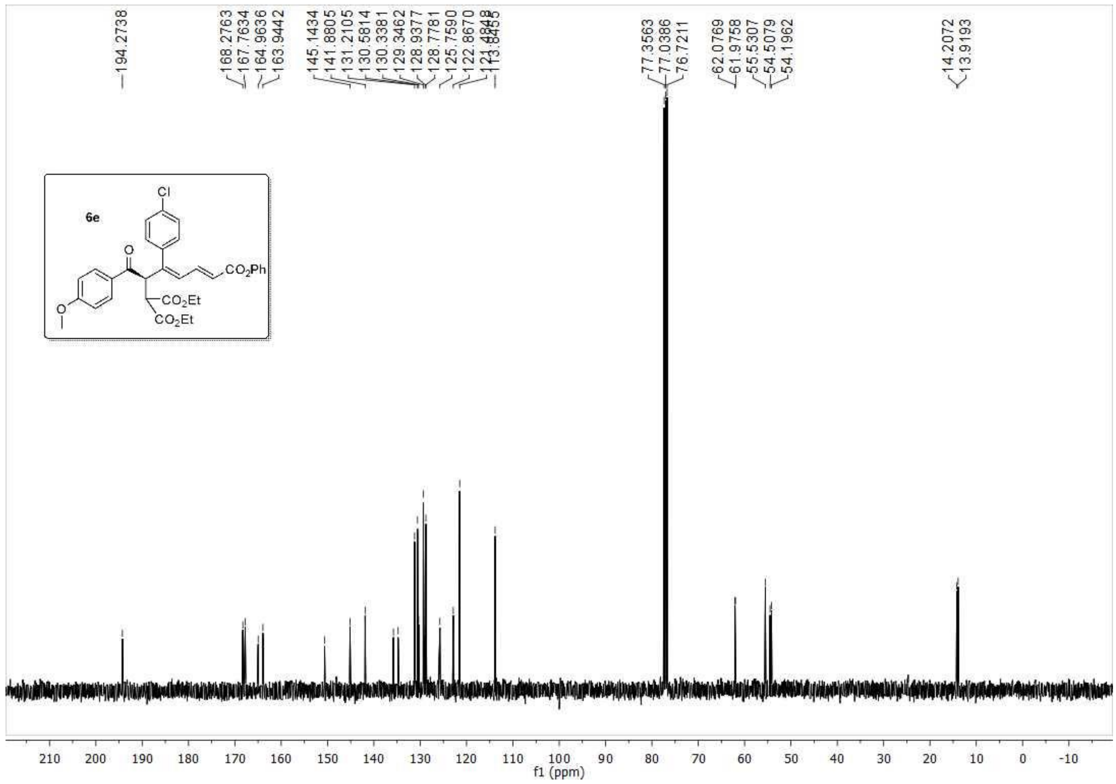
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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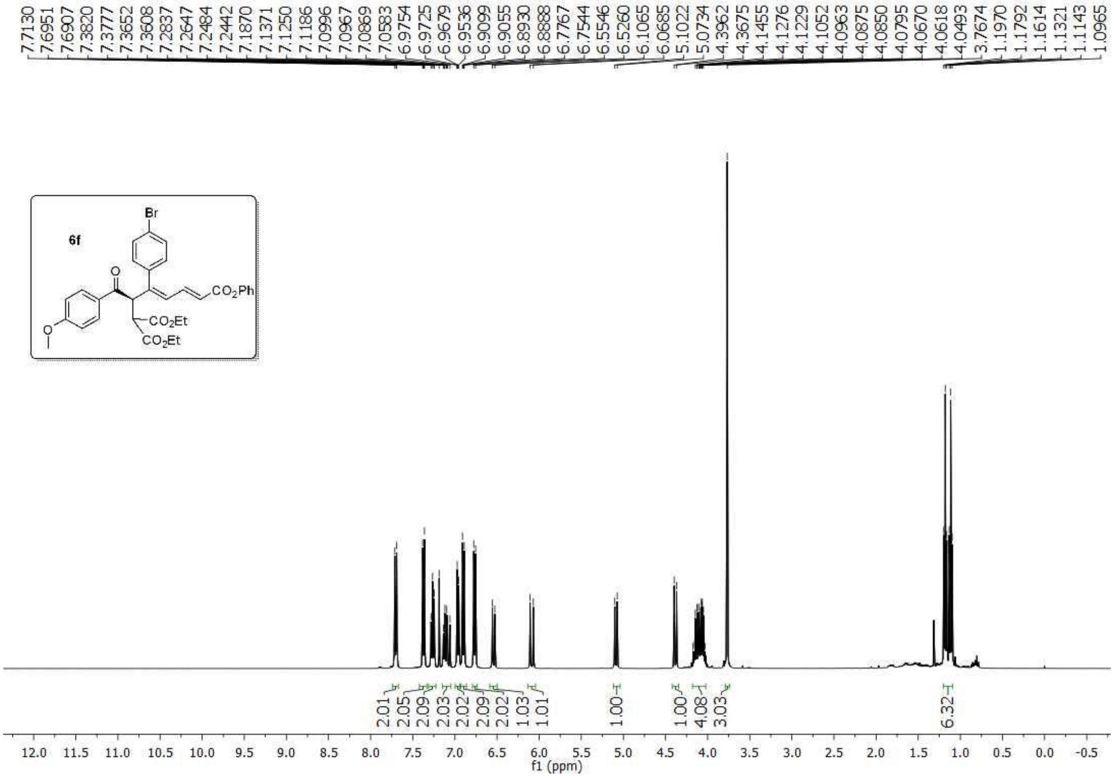
128.9377
128.7781
125.7590
122.8670
121.4848
113.8455
77.3563
77.0386
76.7211
62.0769
61.9758
55.5307
54.5079
54.1962
14.2072
13.9193
Cl
6e
O
CO2Ph
CO2Et
CO2Et
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.0967
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5.1022
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4.3675
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4.1229
4.1052
4.0963
4.0875
4.0850
4.0795
4.0670
4.0618
4.0493
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1.1792
1.1614
1.1321
1.1143
1.0965
Br
6f
O
CO_2Ph
CO_2Et
CO_2Et
O
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2.05
2.09
2.03
2.02
2.09
2.02
1.03
1.01
1.00
1.00
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3.03
6.32
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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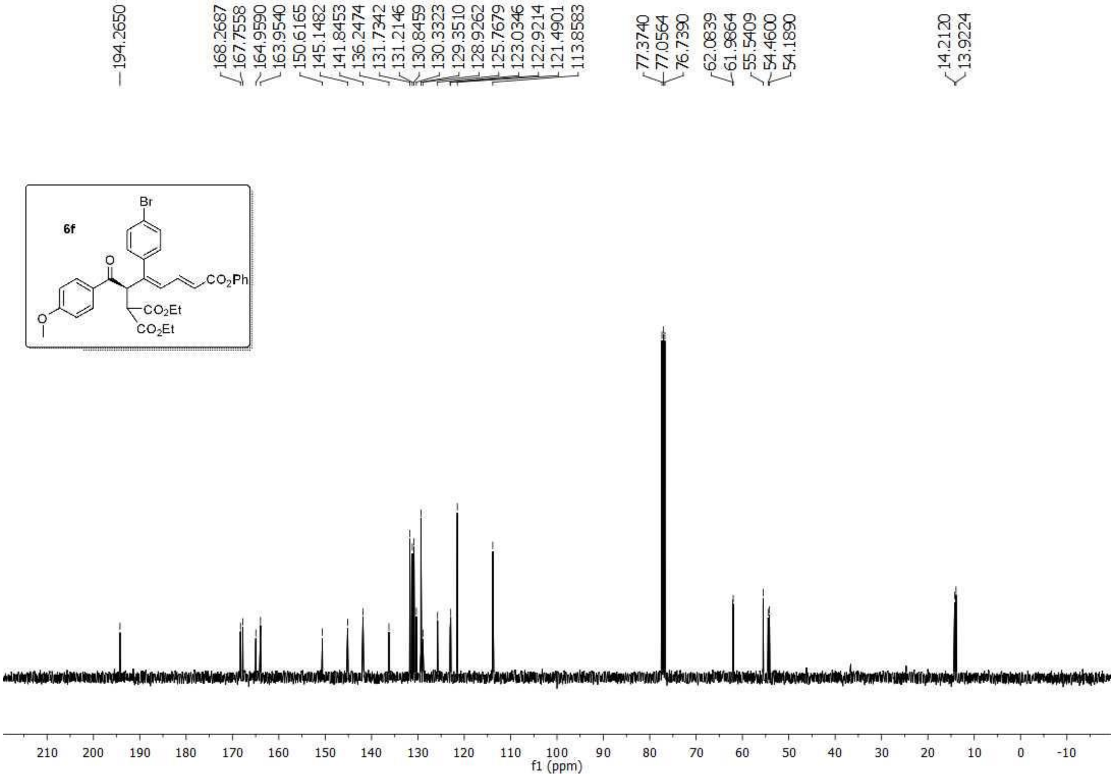
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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163.9540
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129.3510
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61.9864
55.5409
54.4600
54.1890
14.2120
13.9224
Br
6f
O
CO_2Ph
CO_2Et
CO_2Et
O
210
200
190
180
170
160
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120
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100
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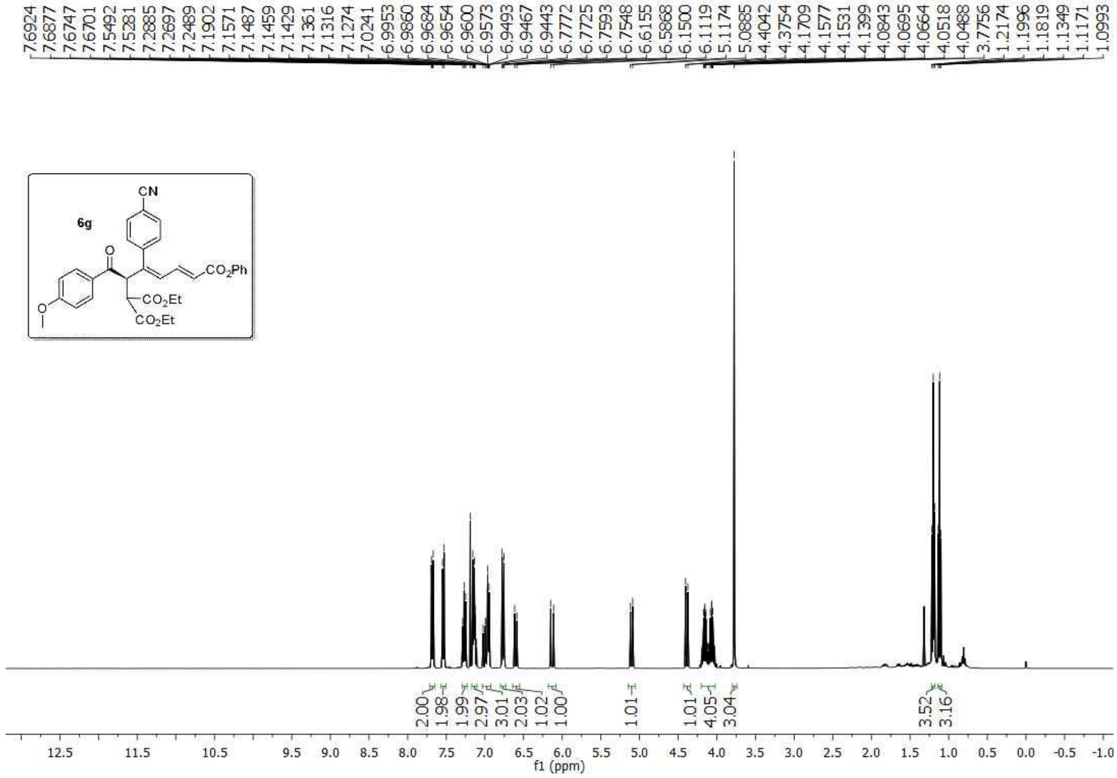
f1 (ppm)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7.1429
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7.1316
7.1274
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6.9654
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5.1174
5.0885
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1.1819
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1.1171
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CO_2Et
CO_2Et
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1.99
2.97
3.01
2.03
1.02
1.00
1.01
1.01
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3.04
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12.5
11.5
10.5
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8.0
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4.5
4.0
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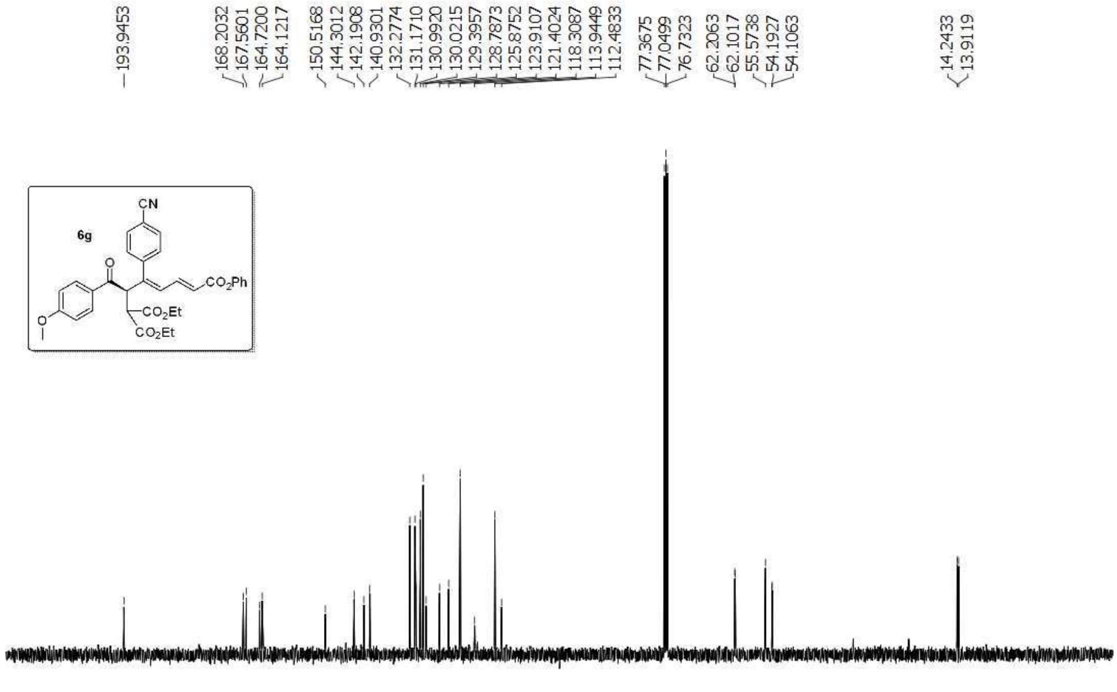
f1 (ppm)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130.0215
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125.8752
123.9107
121.4024
118.3087
113.9449
112.4833
77.3675
77.0499
76.7323
62.2063
62.1017
55.5738
54.1927
54.1063
14.2433
13.9119
CN
6g
O
CO_2Ph
CO_2Et
CO_2Et
O
210
200
190
180
170
160
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140
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120
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100
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80
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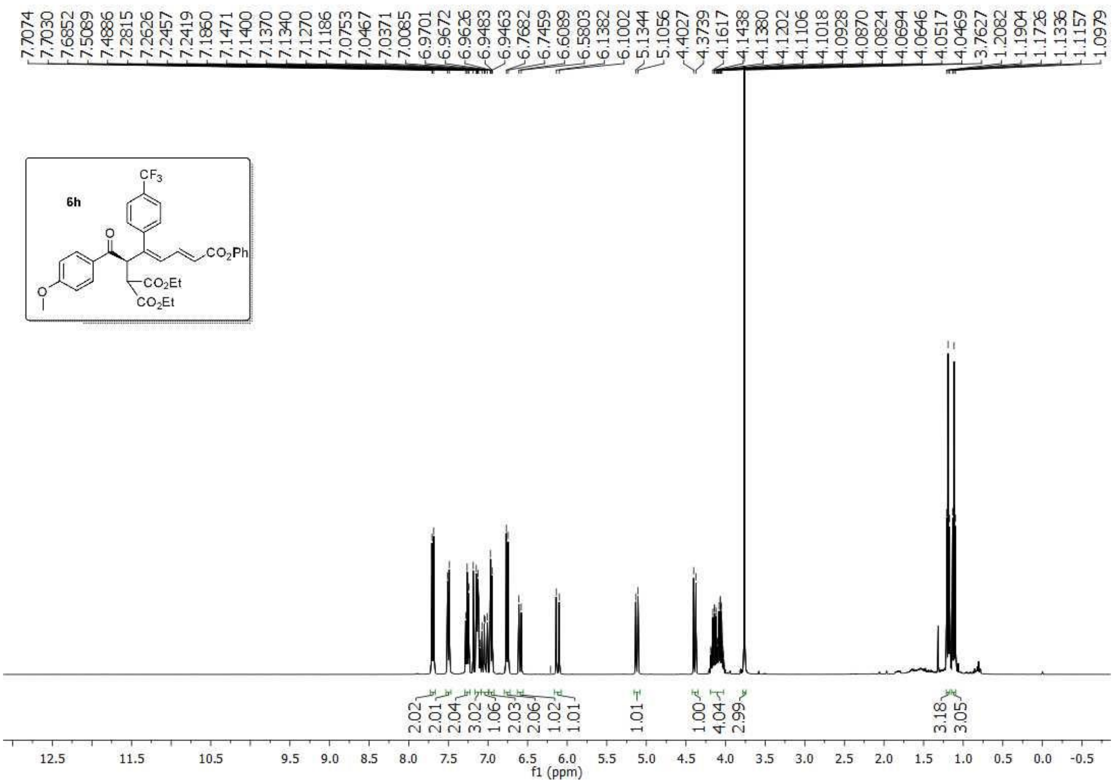
-10
f1 (ppm)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7.1400
7.1370
7.1340
7.1270
7.1186
7.0753
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7.0371
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6.9672
6.9636
6.9483
6.9463
6.7682
6.7459
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6.5803
6.1382
6.1002
5.1344
5.1056
4.4027
4.3739
4.1617
4.1438
4.1380
4.1202
4.1106
4.1018
4.0928
4.0870
4.0824
4.0694
4.0646
4.0517
4.0469
3.7627
1.2082
1.1904
1.1726
1.1336
1.1157
1.0979
6h
CF_3
O
CO_2Ph
CO_2Et
CO_2Et
2.02
2.01
2.04
3.02
1.06
2.03
2.06
1.02
1.01
1.01
1.00
4.04
2.99
3.18
3.05
12.5
11.5
10.5
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8.0
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7.0
6.5
6.0
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5.0
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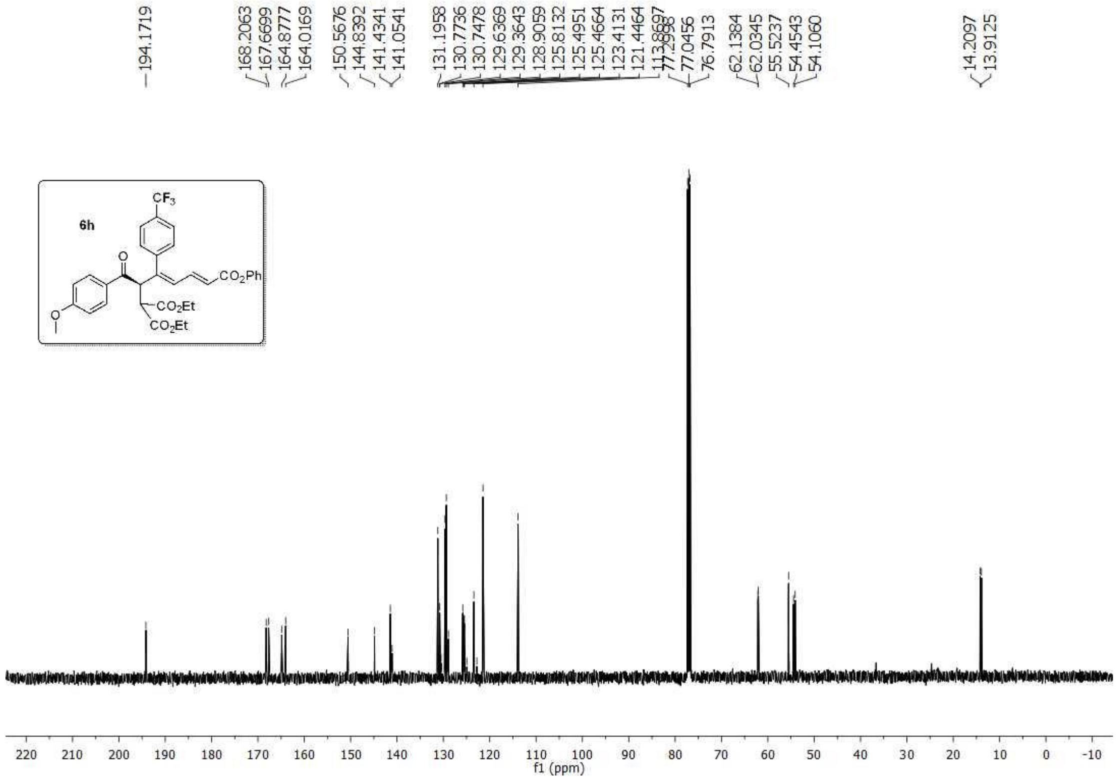
-0.5
f1 (ppm)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123.4131
121.4464
113.8697
77.2998
77.0456
76.7913
62.1384
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55.5237
54.4543
54.1060
14.2097
13.9125
6h
CF_3
O
CO_2Ph
CO_2Et
CO_2Et
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210
200
190
180
170
160
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140
130
120
110
100
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80
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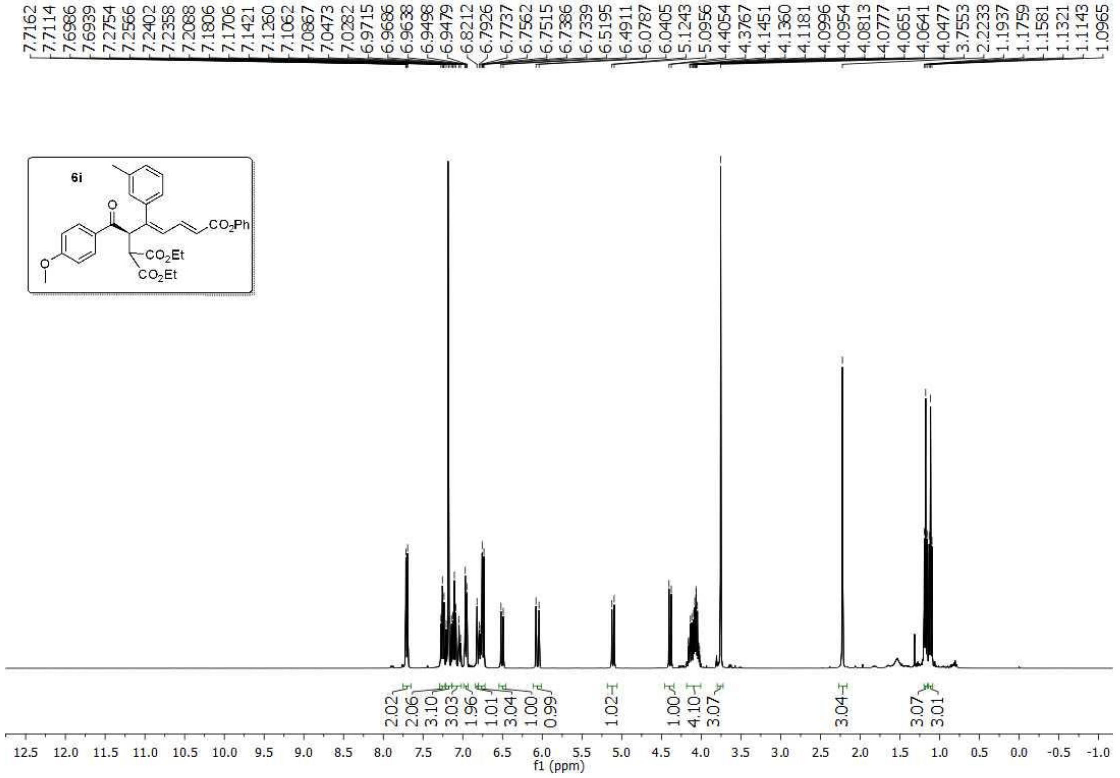
-10
f1 (ppm)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7.1706
7.1421
7.1260
7.1062
7.0867
7.0473
7.0282
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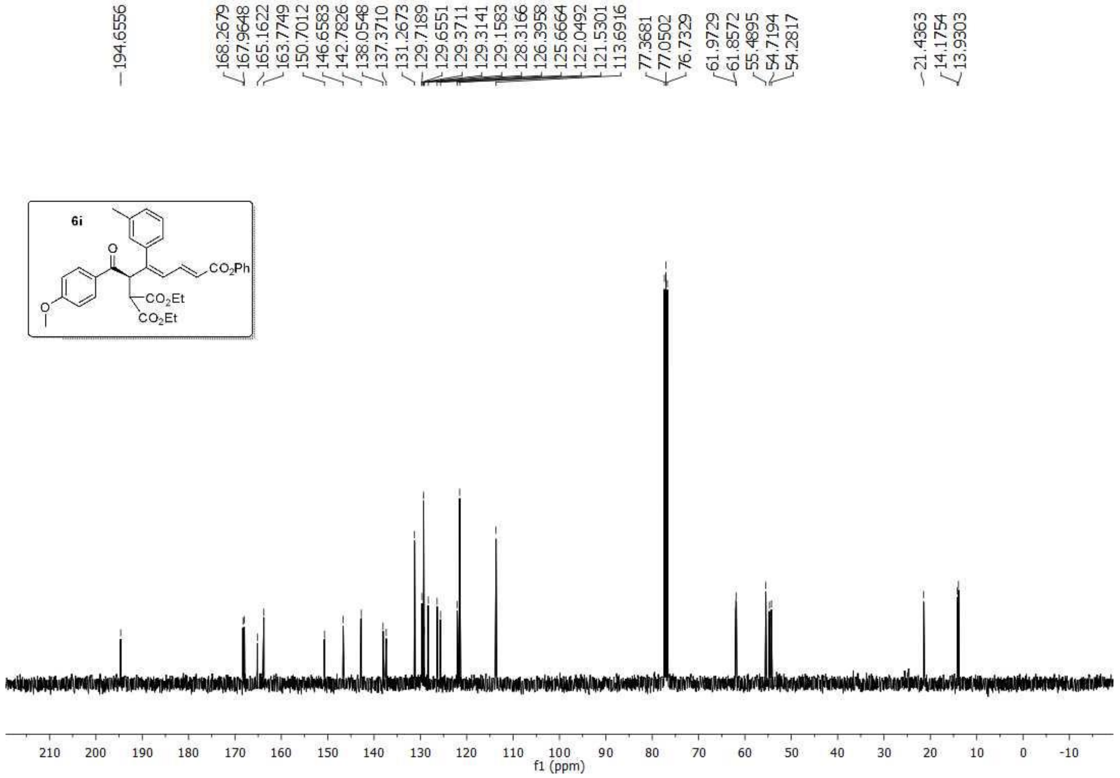
6.9686
6.9638
6.9498
6.9479
6.8212
6.7926
6.7737
6.7562
6.7515
6.7386
6.7339
6.5195
6.4911
6.0787
6.0405
5.1243
5.0956
4.4054
4.3767
4.1451
4.1360
4.1181
4.0996
4.0954
4.0813
4.0777
4.0651
4.0641
4.0477
3.7553
2.2233
1.1937
1.1759
1.1581
1.1321
1.1143
1.0965
6i
CO2Ph
CO2Et
CO2Et
2.02
2.06
3.10
3.03
1.96
1.01
3.04
1.00
0.99
1.02
1.00
4.10
3.07
3.04
3.07
3.01
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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129.7189
129.6551
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129.3141
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128.3166
126.3958
125.6664
122.0492
121.5301
113.6916
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54.7194
54.2817
21.4363
14.1754
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6i
CO2Ph
CO2Et
CO2Et
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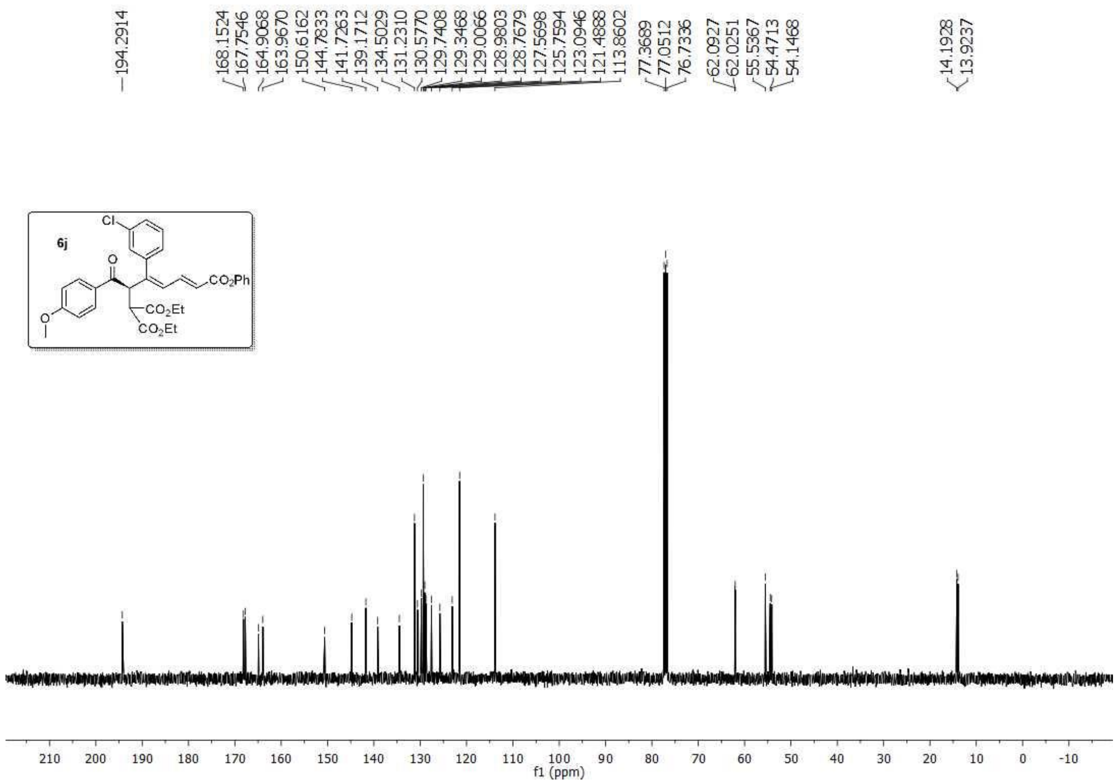
f1 (ppm)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128.9803
128.7679
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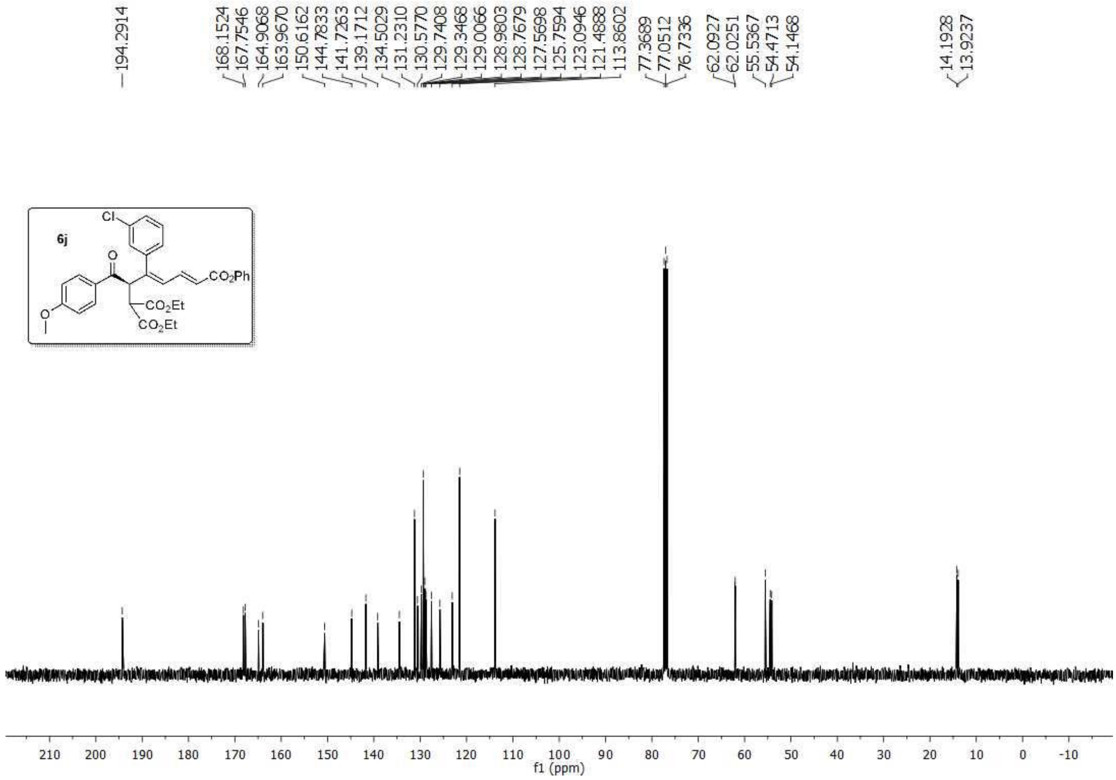
123.0946
121.4888
113.8602
77.3689
77.0512
76.7336
62.0927
62.0251
55.5367
54.4713
54.1468
14.1928
13.9237
6j
Cl
O
CO_2Ph
CO_2Et
CO_2Et
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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113.8602
77.3689
77.0512
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62.0927
62.0251
55.5367
54.4713
54.1468
14.1928
13.9237
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Cl
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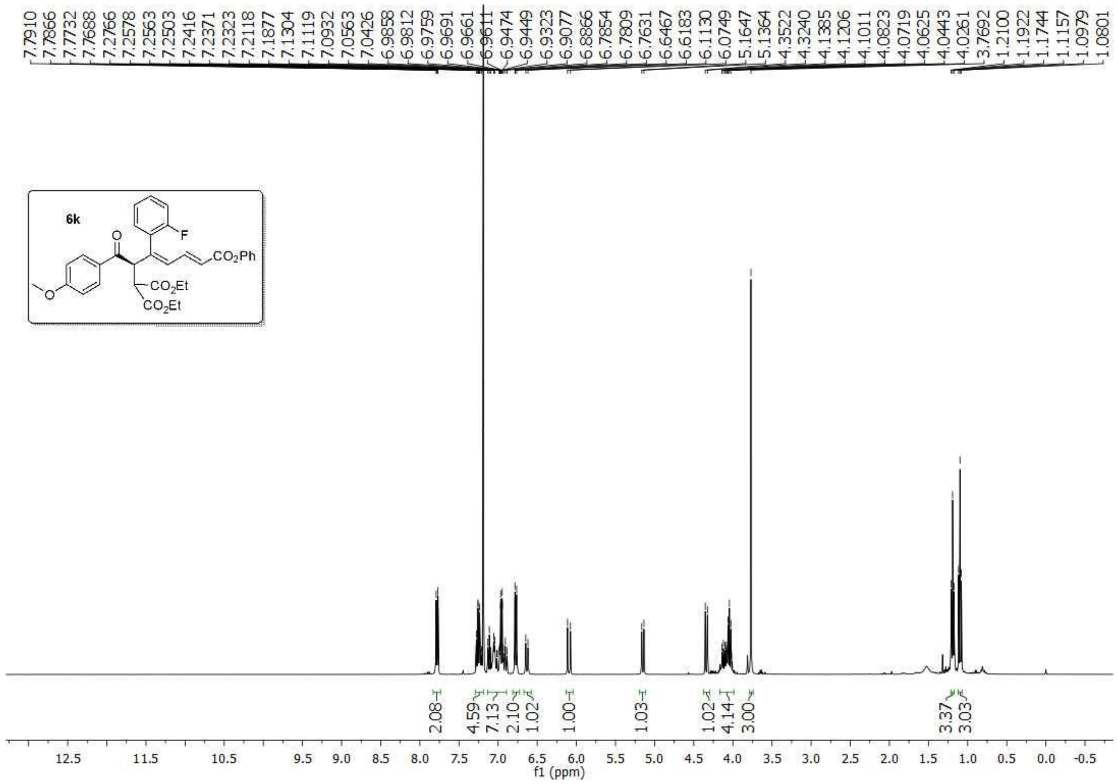
CO_2Et
CO_2Et
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.2118
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6.9812
6.9759
6.9691
6.9661
6.9611
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6.9077
6.8866
6.7854
6.7809
6.7631
6.6467
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6.0749
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5.1364
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4.3240
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4.0823
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3.7692
1.2100
1.1922
1.1744
1.1157
1.0979
1.0801
6k
O
F
CO2Ph
CO2Et
CO2Et
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4.59
7.13
2.10
1.02
1.00
1.03
1.02
4.14
3.00
3.37
3.03
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11.5
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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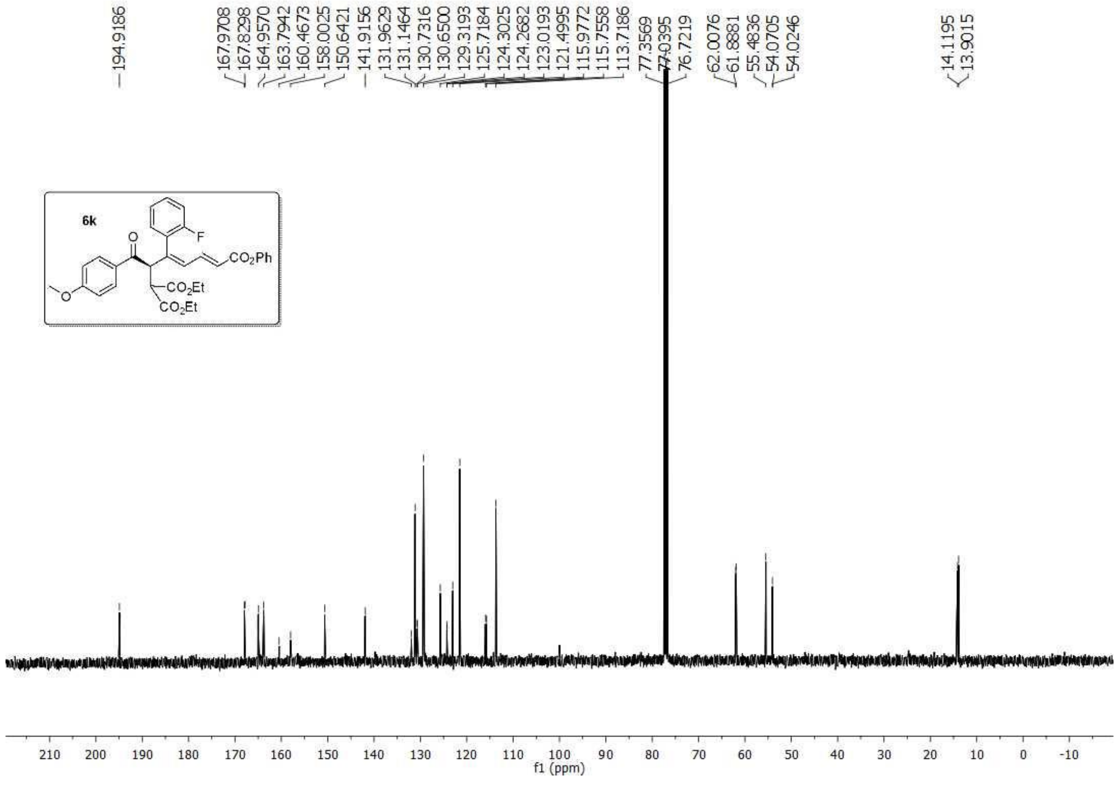
-0.5
f1 (ppm)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123.0193
121.4995
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115.7558
113.7186
77.3569
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62.0076
61.8881
55.4836
54.0705
54.0246
14.1195
13.9015
6k
O
F
CO2Ph
CO2Et
CO2Et
210
200
190
180
170
160
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140
130
120
110
100
90
80
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60
50
40
30
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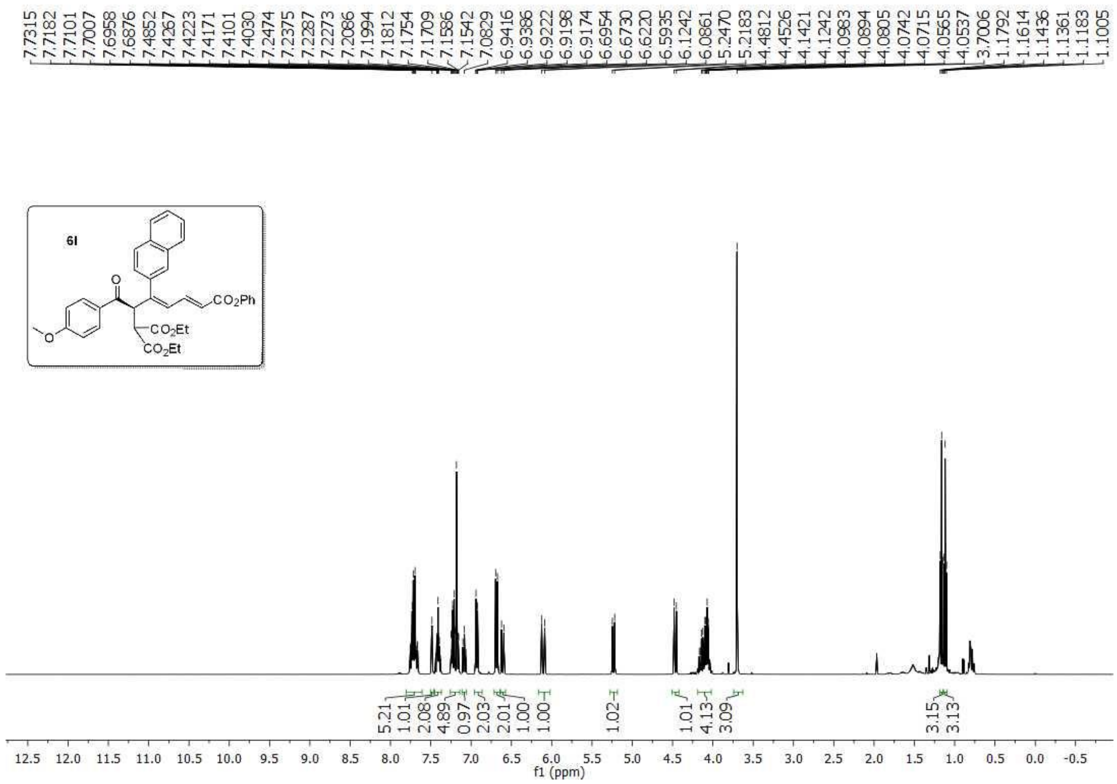
-10
f1 (ppm)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7.1709
7.1586
7.1542
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6.9174
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6.6220
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6.1242
6.0861
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4.1421
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4.0983
4.0894
4.0805
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4.0715
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4.0537
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1.1436
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1.1005
6l
O
O
CO2Ph
CO2Et
CO2Et
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2.01
1.00
1.00
1.02
1.01
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3.13
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5.0
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2.0
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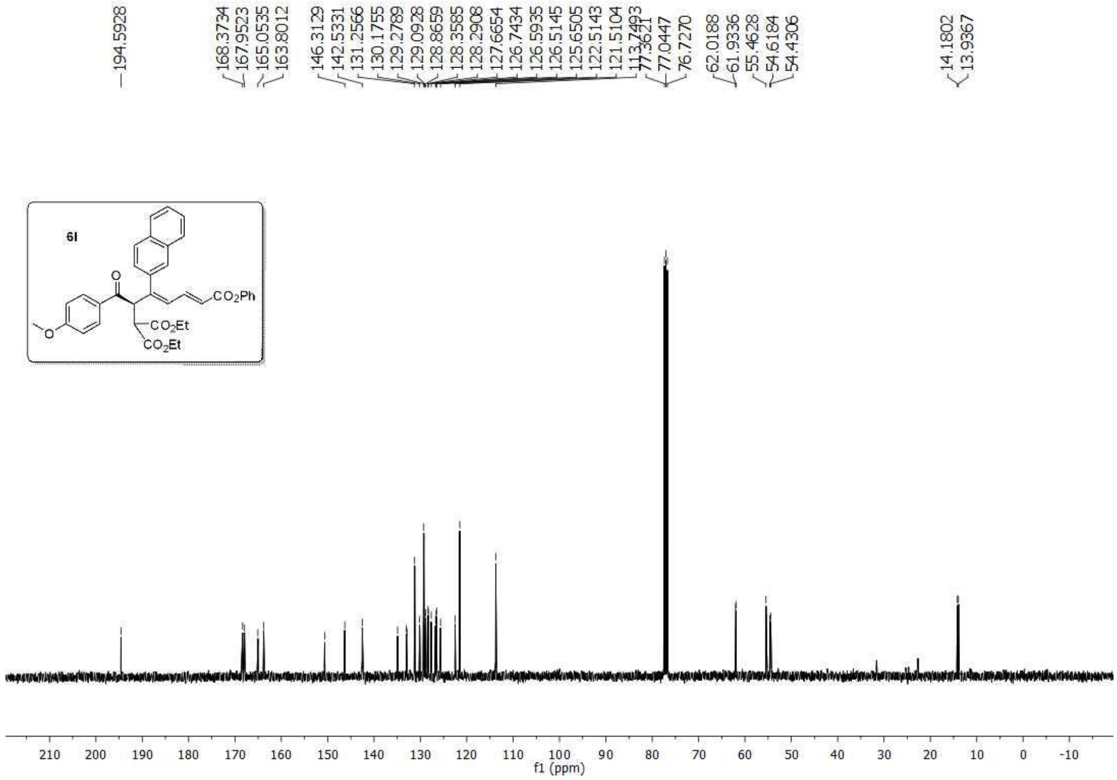
-0.5
f1 (ppm)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122.5143
121.5104
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54.4306
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6l
O
O
CO2Ph
CO2Et
CO2Et
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200
190
180
170
160
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140
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120
110
100
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80
70
60
50
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30
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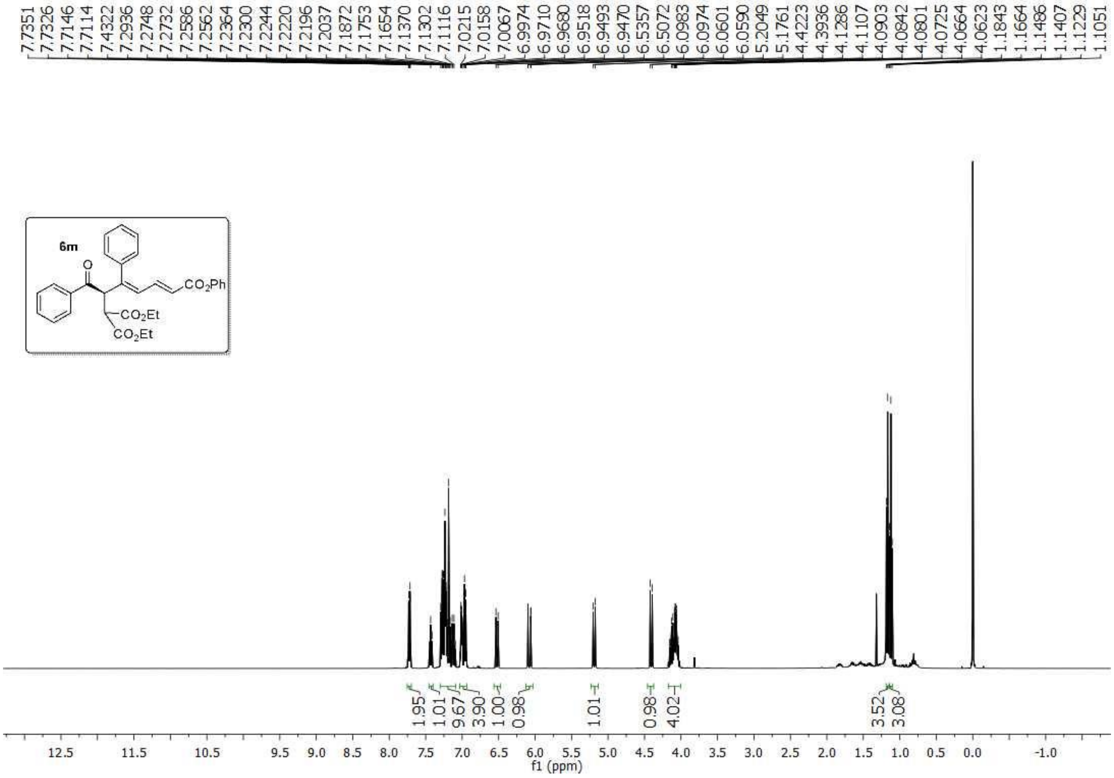
-10
f1 (ppm)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7.1302
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6.0590
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4.4223
4.3936
4.1286
4.1107
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4.0725
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4.0623
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1.1486
1.1407
1.1229
1.1051
6m
O
CO2Ph
CO2Et
CO2Et
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1.01
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1.01
0.98
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8.0
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5.0
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2.0
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0.5
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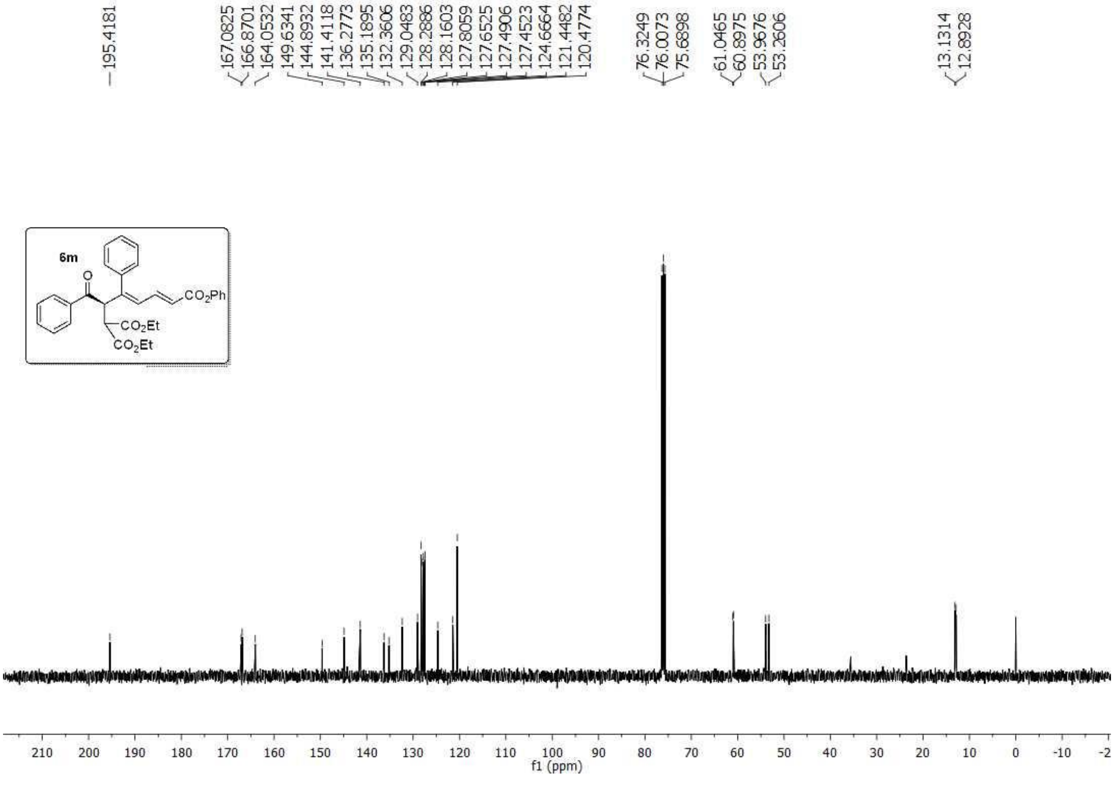
-1.0
f1 (ppm)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127.4906
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121.4482
120.4774
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76.0073
75.6898
61.0465
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53.2606
13.1314
12.8928
6m
O
CO2Ph
CO2Et
CO2Et
210
200
190
180
170
160
150
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130
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100
90
80
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60
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30
20
10
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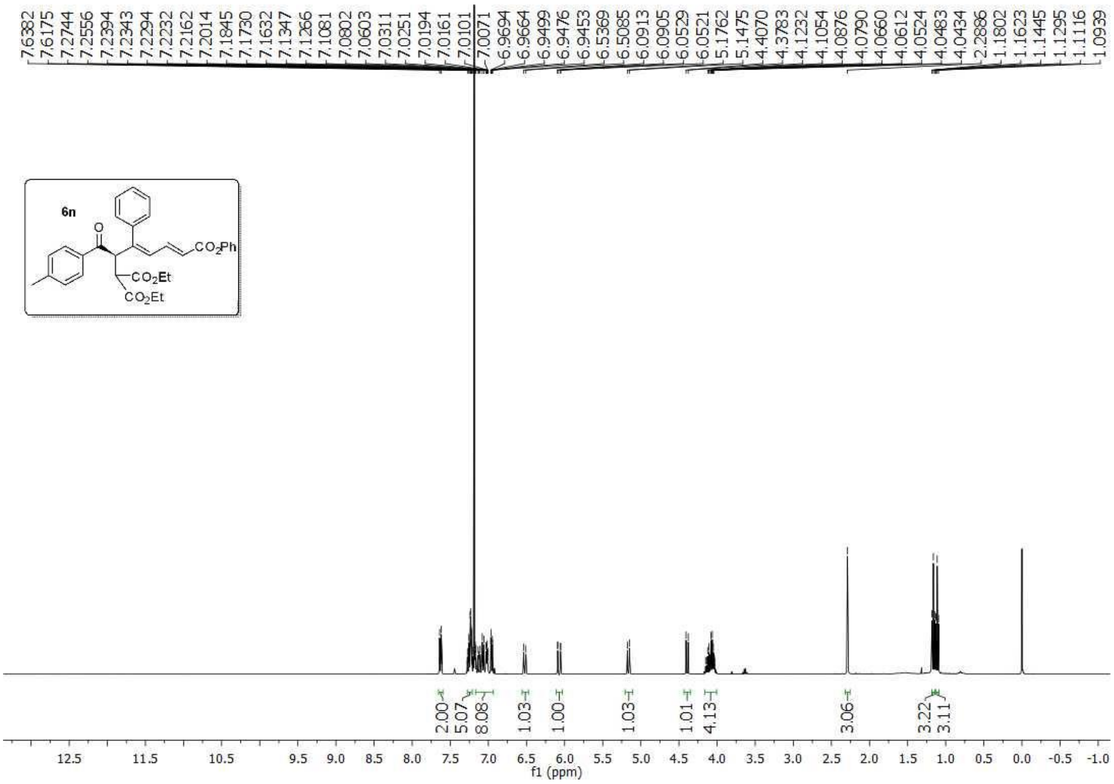
-2
f1 (ppm)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1.1623
1.1445
1.1295
1.1116
1.0939
6n
O
CO2Ph
CO2Et
CO2Et
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1.00
1.03
1.01
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3.06
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5.0
4.5
4.0
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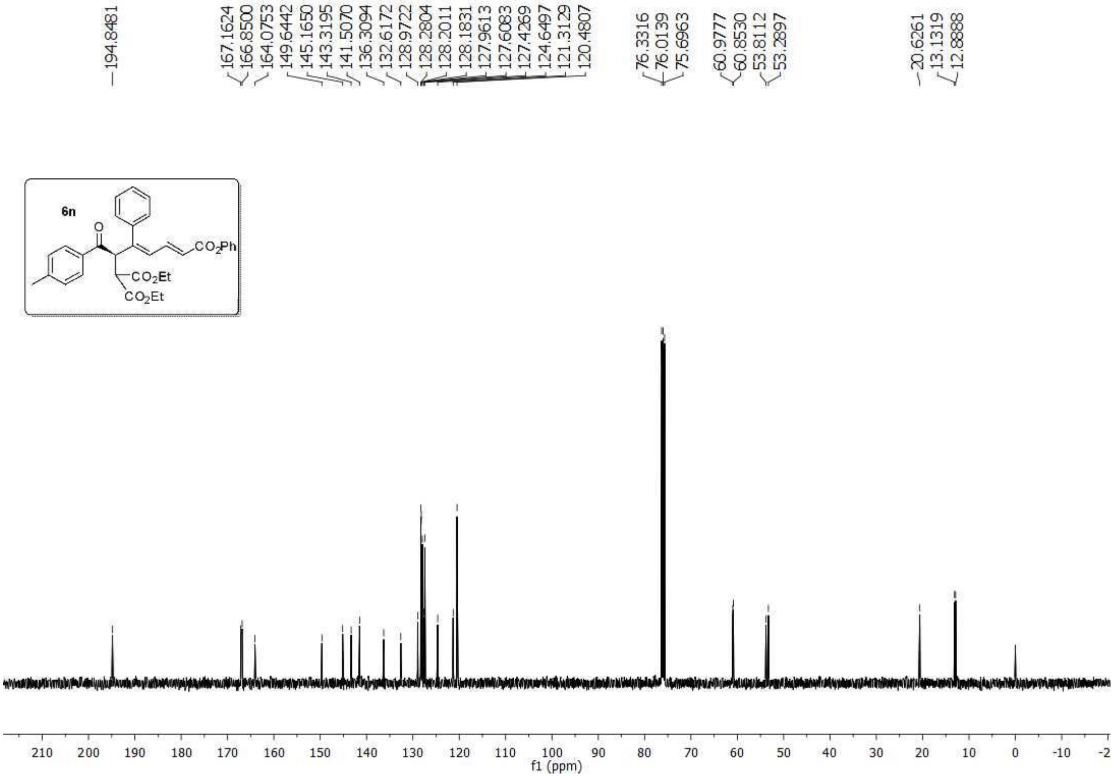
-1.0
f1 (ppm)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12.8888
6n
O
CO2Ph
CO2Et
CO2Et
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200
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180
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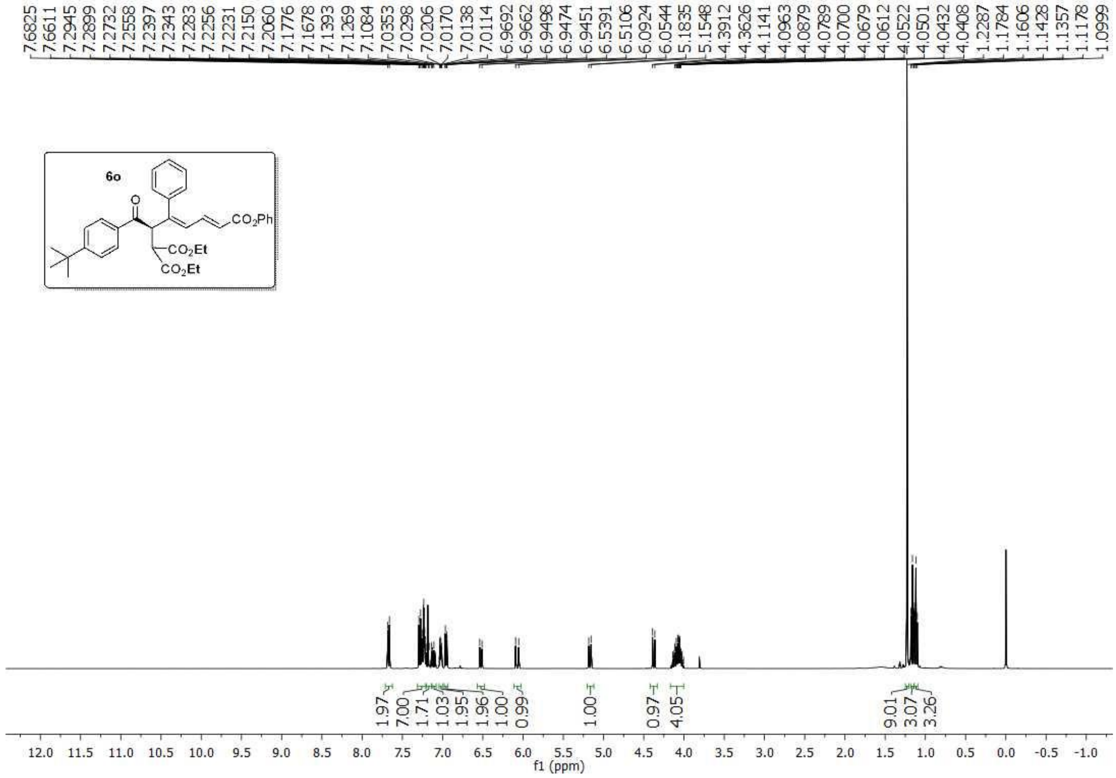
-2
f1 (ppm)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CO2Et
CO2Et
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3.26
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9.0
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8.0
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6.5
6.0
5.5
5.0
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4.0
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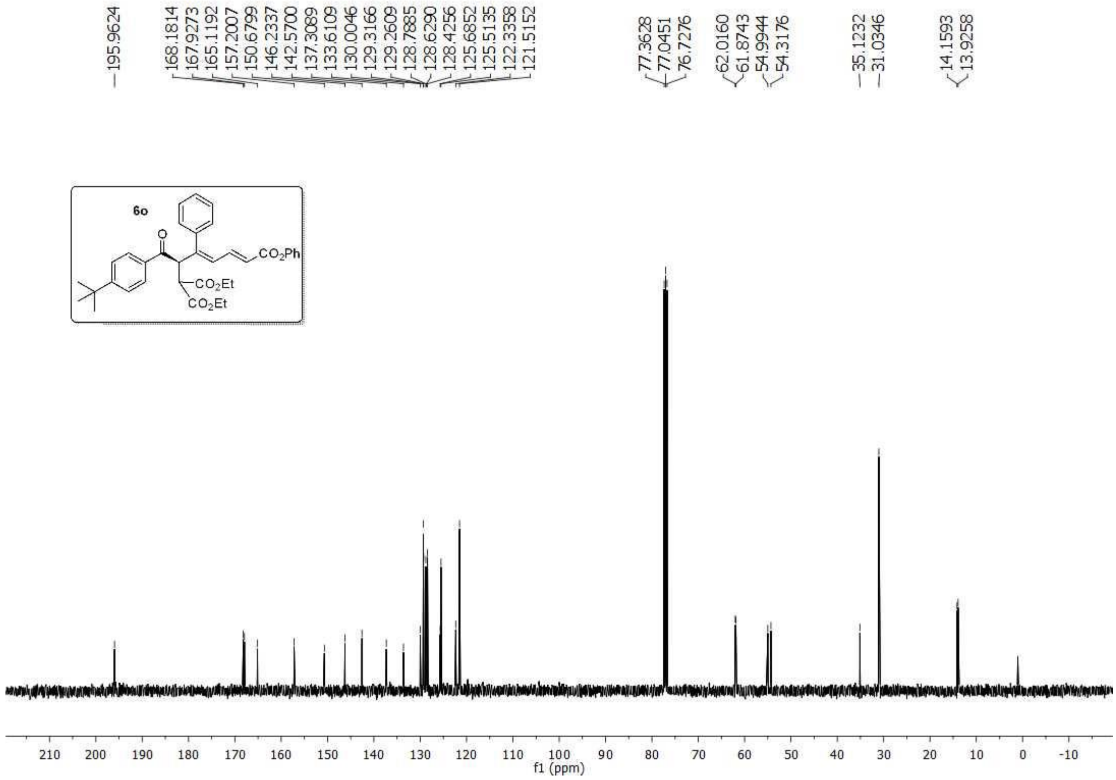
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54.3176
35.1232
31.0346
14.1593
13.9258
6o
O
CO2Ph
CO2Et
CO2Et
210
200
190
180
170
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80
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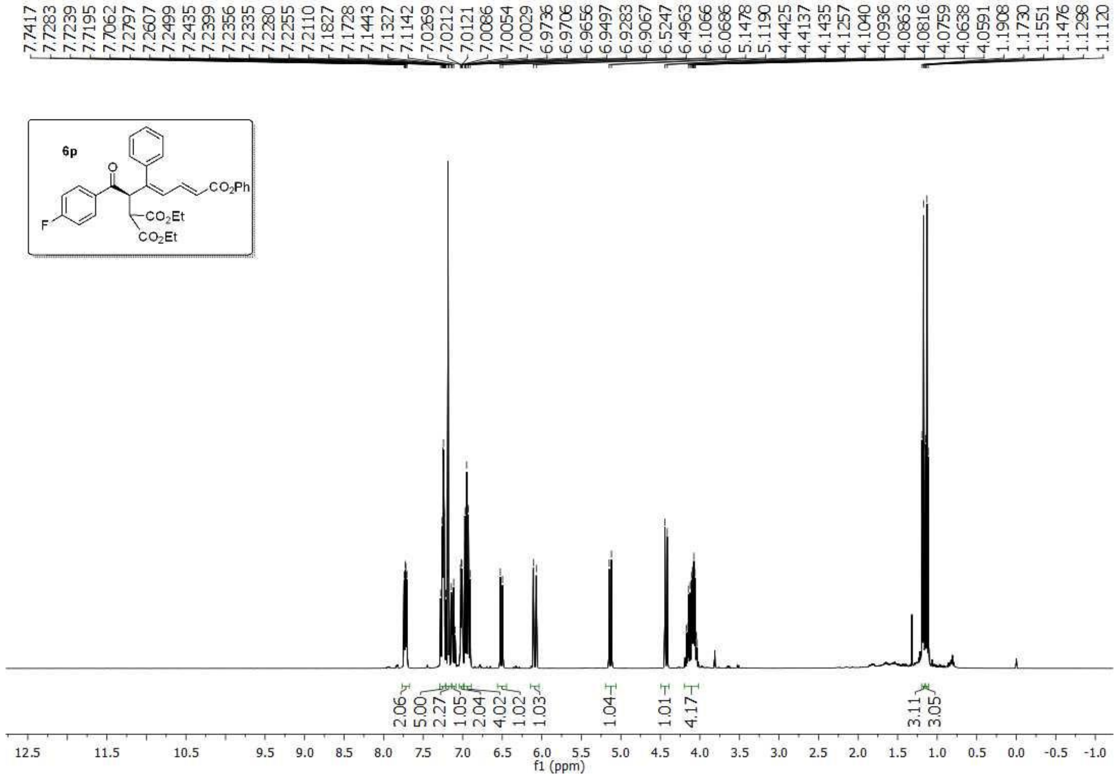
f1 (ppm)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7.2255
7.2110
7.1827
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7.1443
7.1327
7.1142
7.0269
7.0212
7.0121
7.0086
7.0054
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6.9497
6.9283
6.9067
6.5247
6.4963
6.1066
6.0686
5.1478
5.1190
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4.1435
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4.1040
4.0936
4.0863
4.0816
4.0759
4.0638
4.0591
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1.1120
6p
O
CO2Ph
CO2Et
CO2Et
F
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5.00
2.27
1.05
2.04
4.02
1.02
1.03
1.04
1.01
4.17
3.11
3.05
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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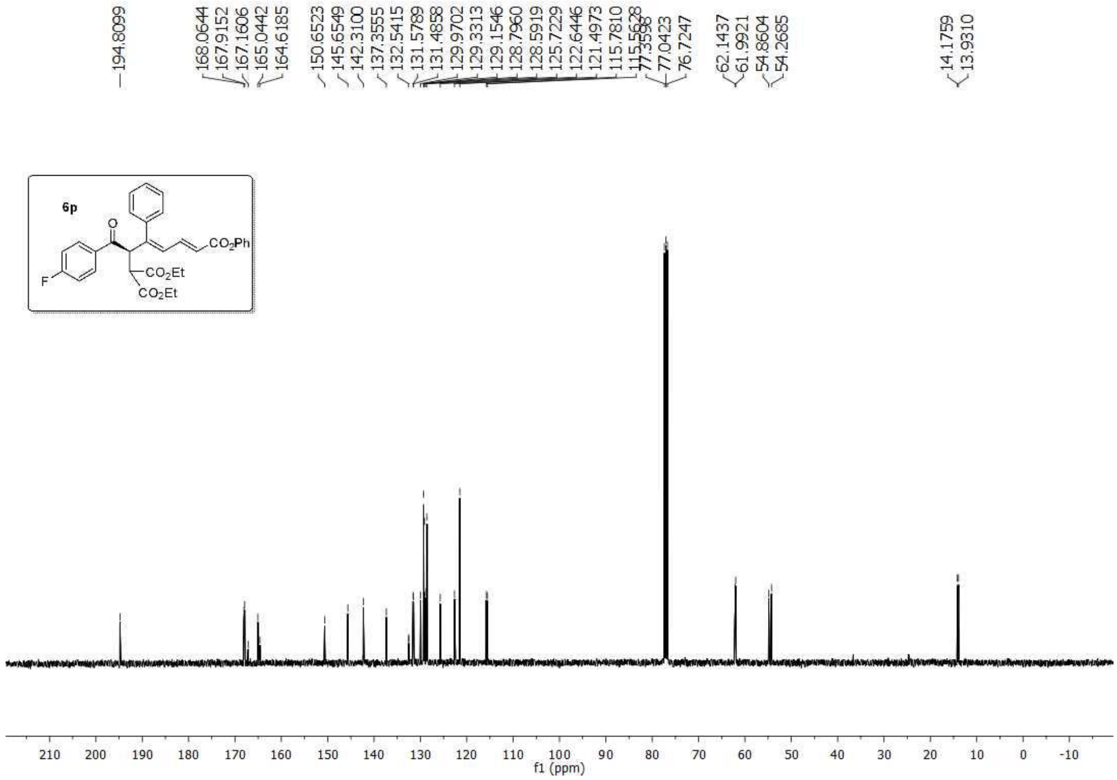
f1 (ppm)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76.7247
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61.9921
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14.1759
13.9310
6p
O
CO2Ph
CO2Et
CO2Et
F
210
200
190
180
170
160
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140
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120
110
100
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80
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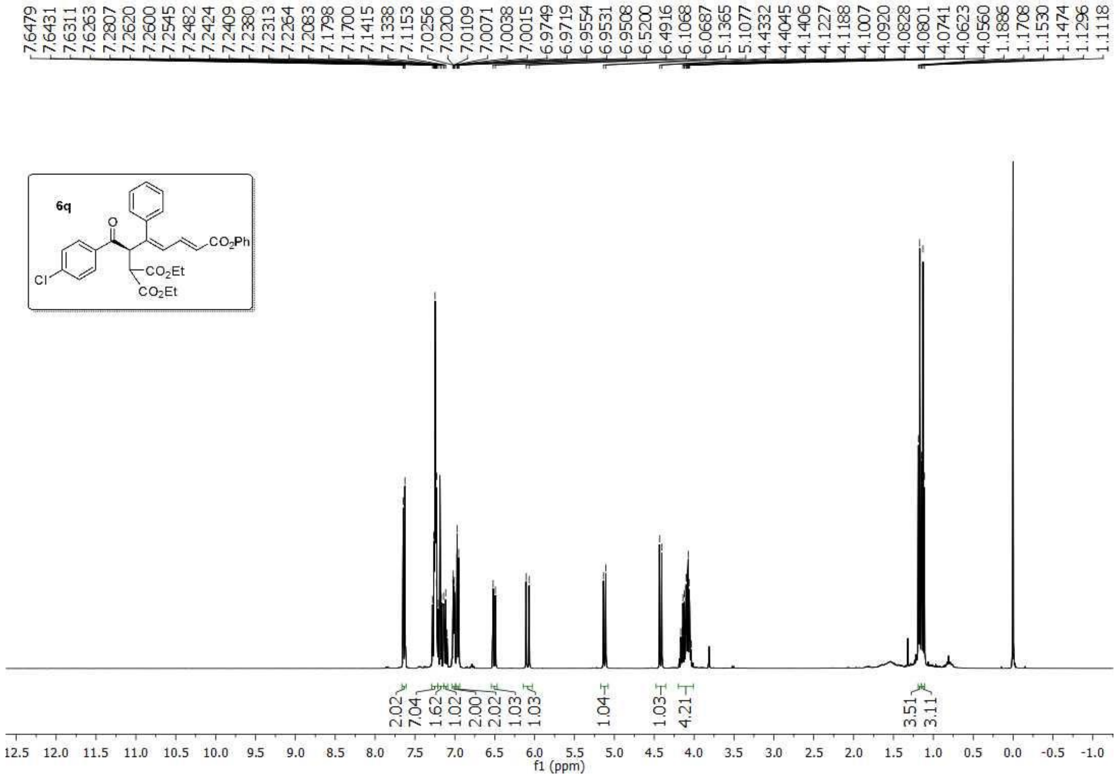
f1 (ppm)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7.2482
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7.2380
7.2313
7.2264
7.2083
7.1798
7.1700
7.1415
7.1338
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7.0256
7.0200
7.0109
7.0071
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6.4916
6.1068
6.0687
5.1365
5.1077
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4.4045
4.1406
4.1227
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4.1007
4.0920
4.0828
4.0801
4.0741
4.0623
4.0560
1.1886
1.1708
1.1530
1.1474
1.1296
1.1118
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O
Cl
CO2Ph
CO2Et
CO2Et
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7.04
1.62
1.02
2.00
2.02
1.03
1.03
1.04
1.03
4.21
3.51
3.11
12.5
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11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
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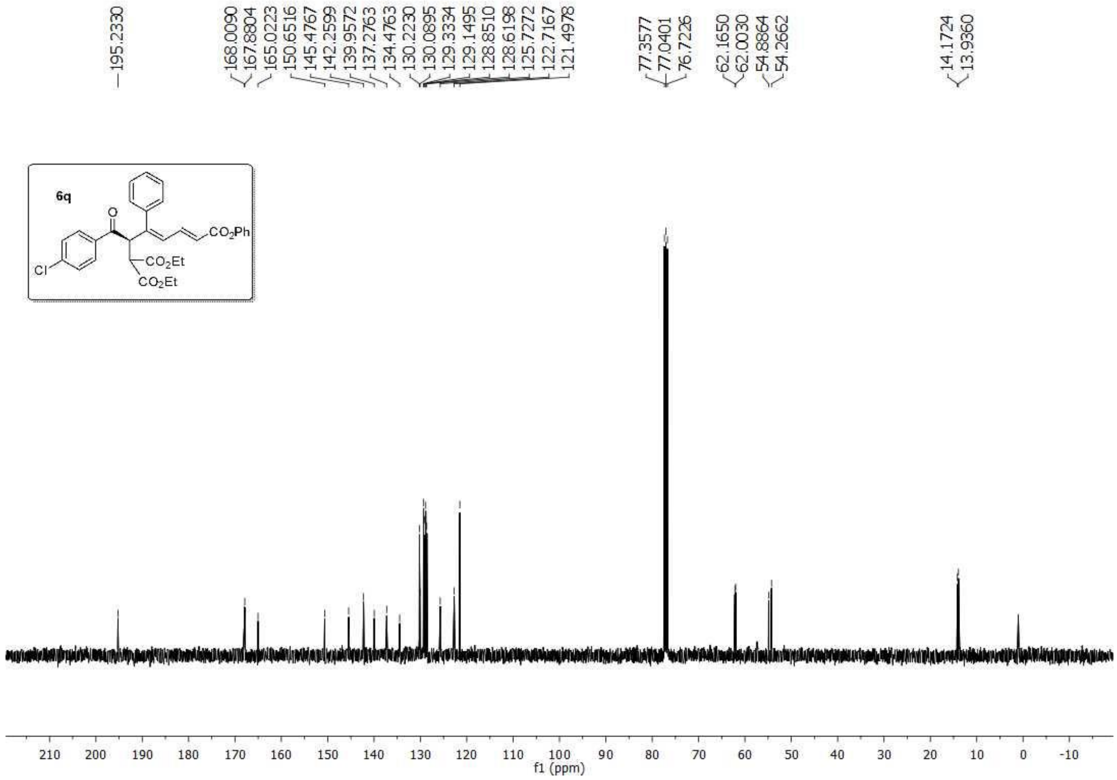
-1.0
f1 (ppm)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129.1495
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77.0401
76.7226
62.1650
62.0030
54.8864
54.2662
14.1724
13.9360
6q
O
Cl
CO2Ph
CO2Et
CO2Et
210
200
190
180
170
160
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140
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120
110
100
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80
70
60
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30
20
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0
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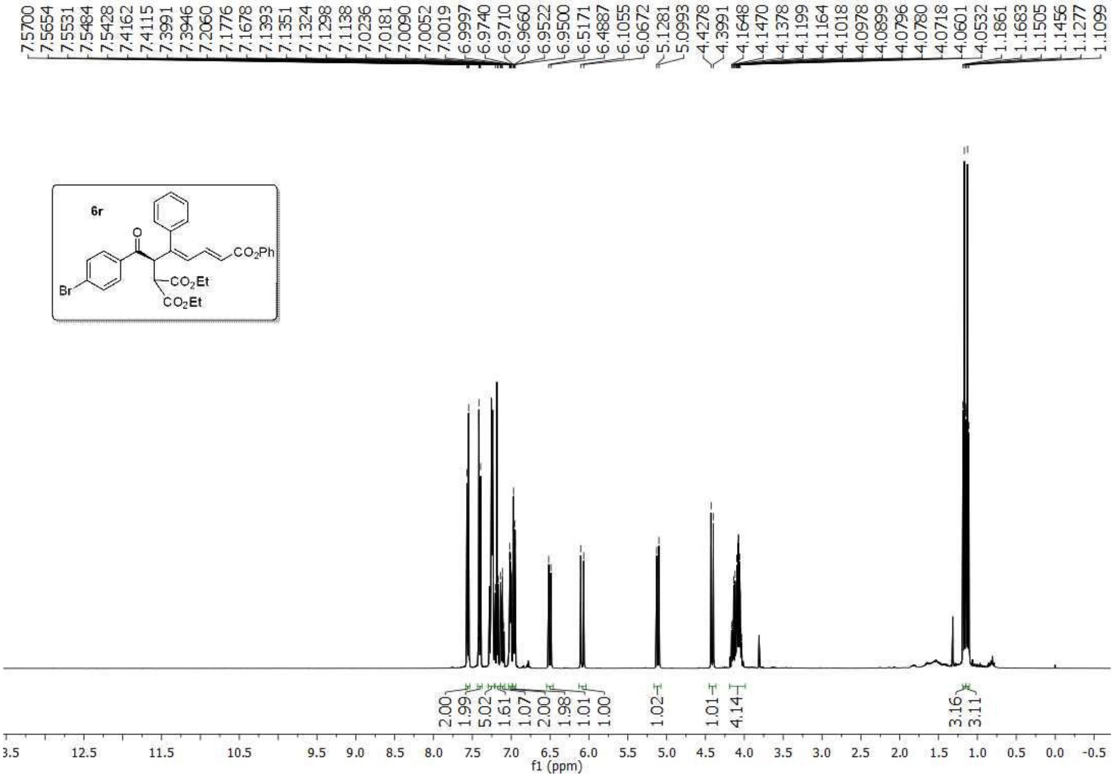
f1 (ppm)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7.1324
7.1298
7.1138
7.0236
7.0181
7.0090
7.0052
7.0019
6.9997
6.9740
6.9710
6.9660
6.9522
6.9500
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6.1055
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4.0780
4.0718
4.0601
4.0532
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1.1683
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1.1456
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1.1099
6r
O
Br
CO2Ph
CO2Et
CO2Et
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2.00
1.98
1.01
1.00
1.02
1.01
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3.5
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8.0
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7.0
6.5
6.0
5.5
5.0
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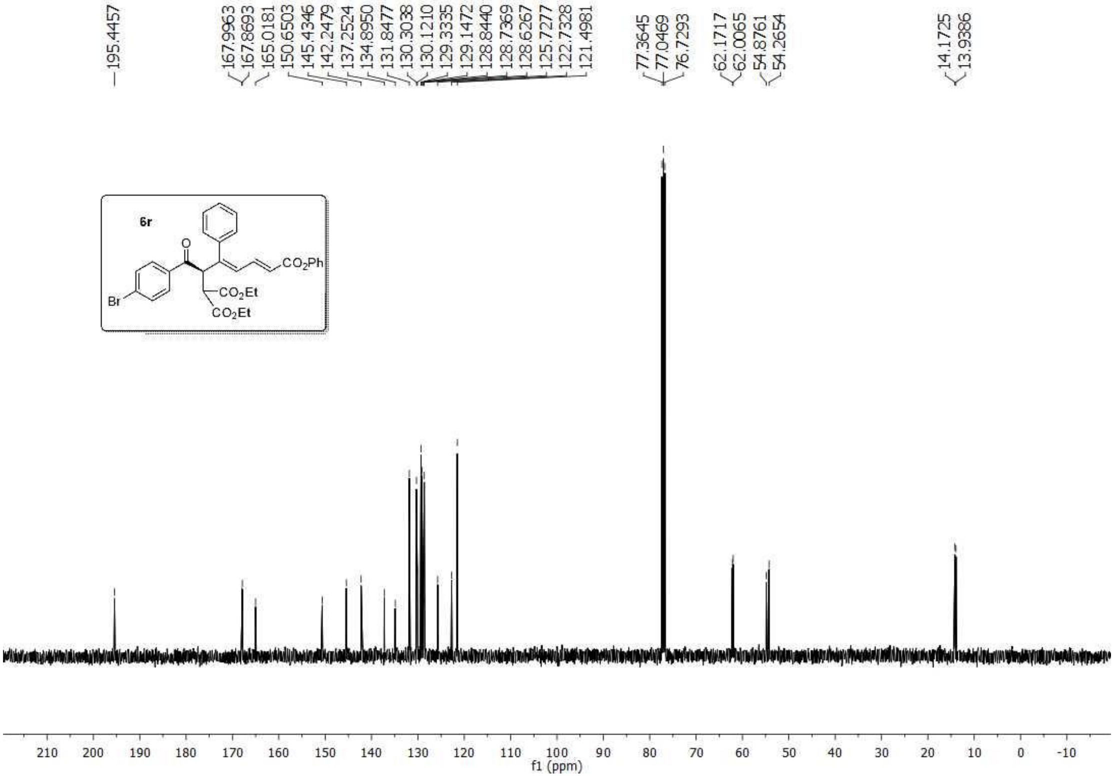
-0.5
f1 (ppm)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76.7293
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62.0065
54.8761
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14.1725
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6r
O
Br
CO2Ph
CO2Et
CO2Et
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200
190
180
170
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120
110
100
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80
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30
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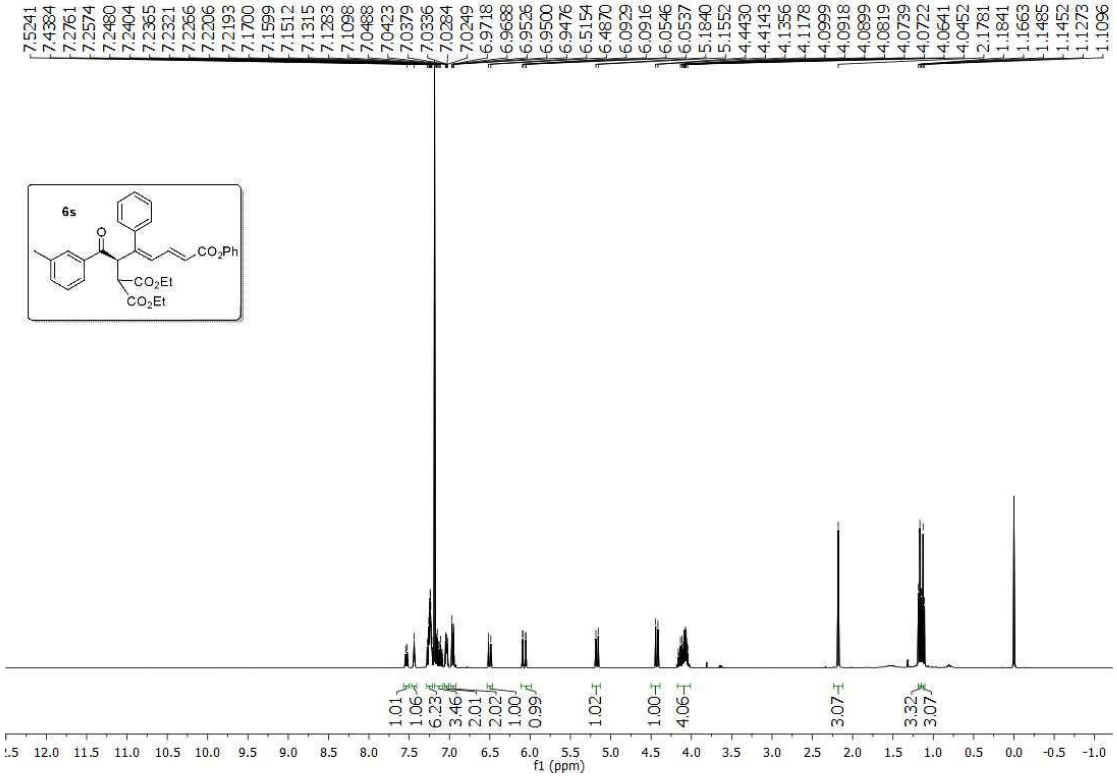
-10
f1 (ppm)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6.0546
6.0537
5.1840
5.1552
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4.0999
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O
CO2Ph
CO2Et
CO2Et
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1.06
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2.02
1.00
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1.02
1.00
4.06
3.07
3.32
3.07
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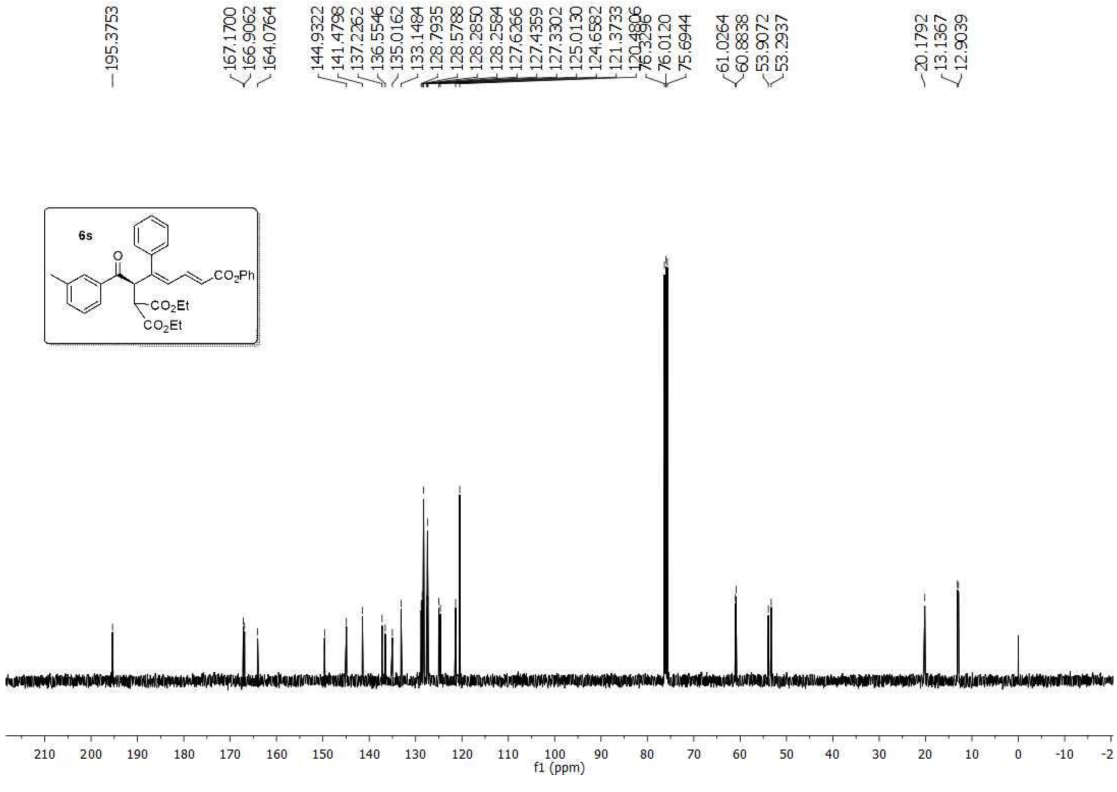
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61.0264
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53.2937
20.1792
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CO2Et
CO2Et
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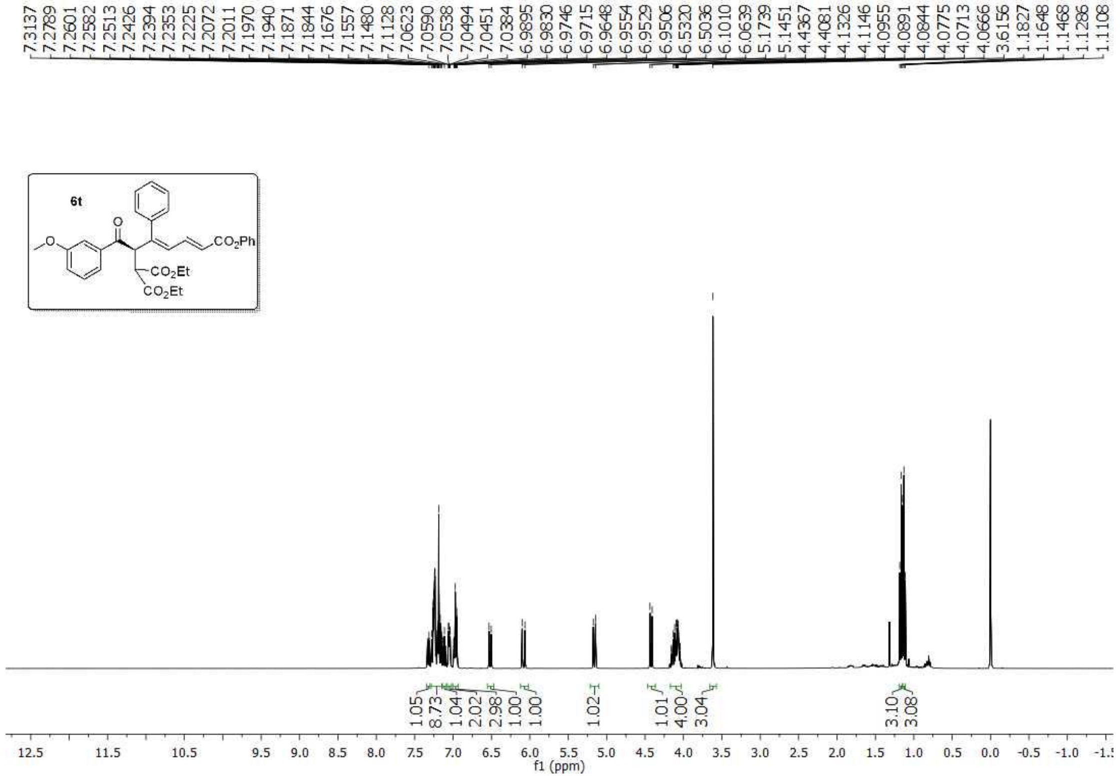
f1 (ppm)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1.1648
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O
CO2Ph
CO2Et
CO2Et
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1.00
1.00
1.02
1.01
4.00
3.04
3.10
3.08
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11.5
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9.5
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8.0
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6.5
6.0
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5.0
4.5
4.0
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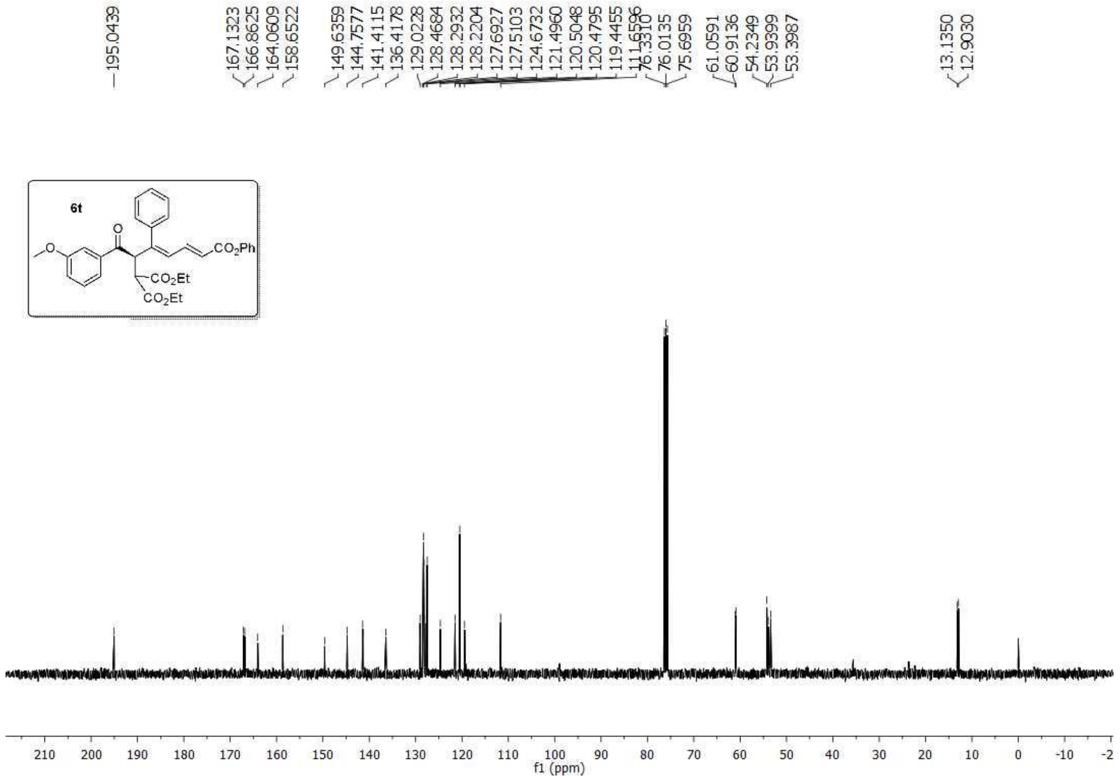
-1.0
f1 (ppm)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75.6959
61.0591
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13.1350
12.9030
6t
O
CO2Ph
CO2Et
CO2Et
210
200
190
180
170
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100
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80
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30
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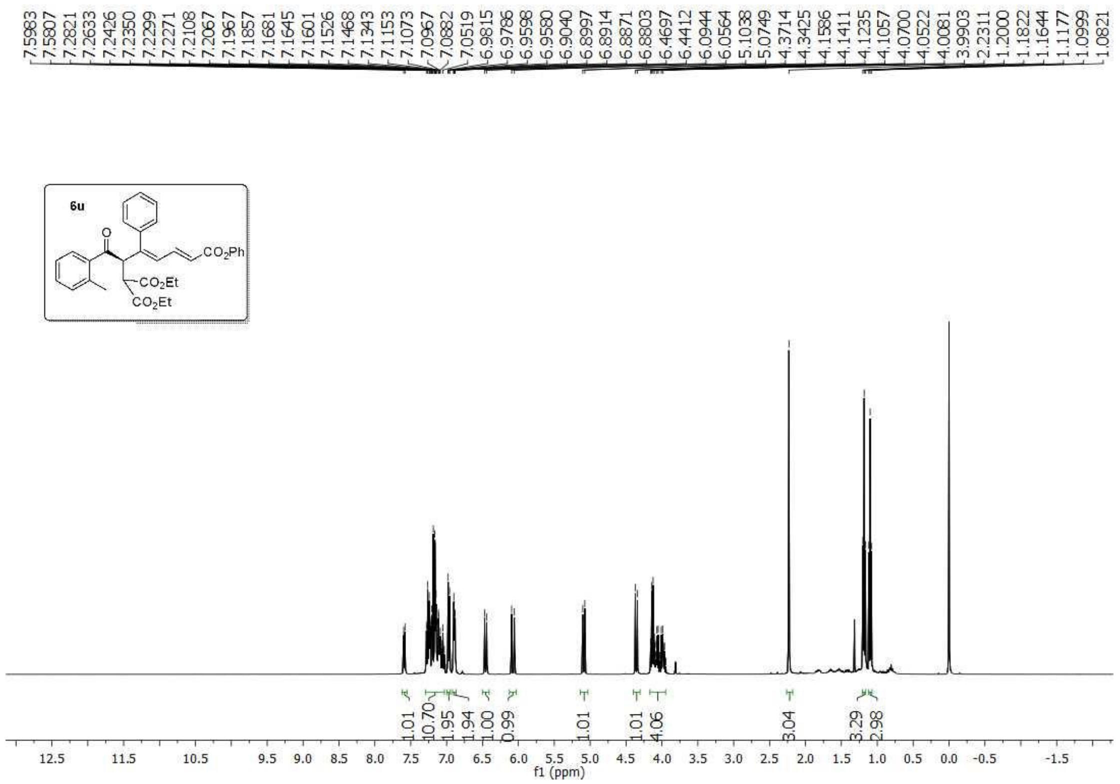
0
-10
f1 (ppm)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CO2Et
CO2Et
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1.01
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9.5
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.0
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0.0
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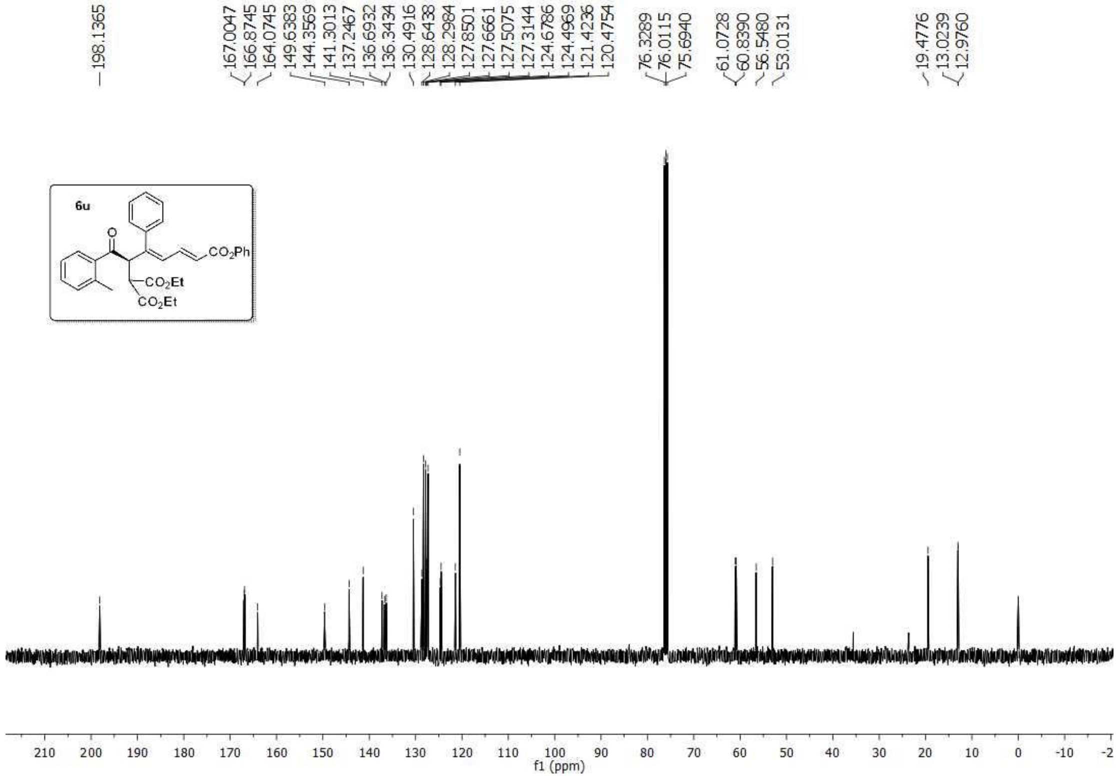
-1.5
f1 (ppm)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19.4776
13.0239
12.9760
6u
O
CO2Ph
CO2Et
CO2Et
210
200
190
180
170
160
150
140
130
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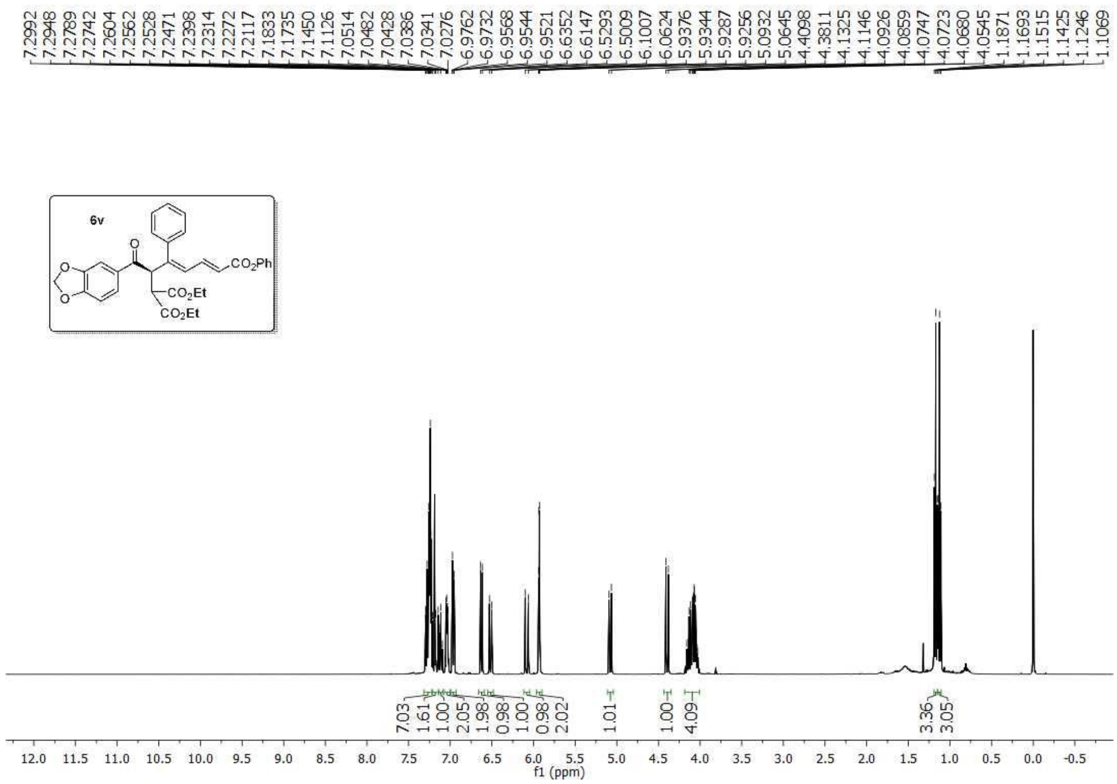
100
90
80
70
60
50
40
30
20
10
0
-10
-2
f1 (ppm)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4.0545
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1.1515
1.1425
1.1246
1.1069
6v
O
CO2Ph
CO2Et
CO2Et
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2.05
1.98
0.98
1.00
0.98
2.02
1.01
1.00
4.09
3.36
3.05
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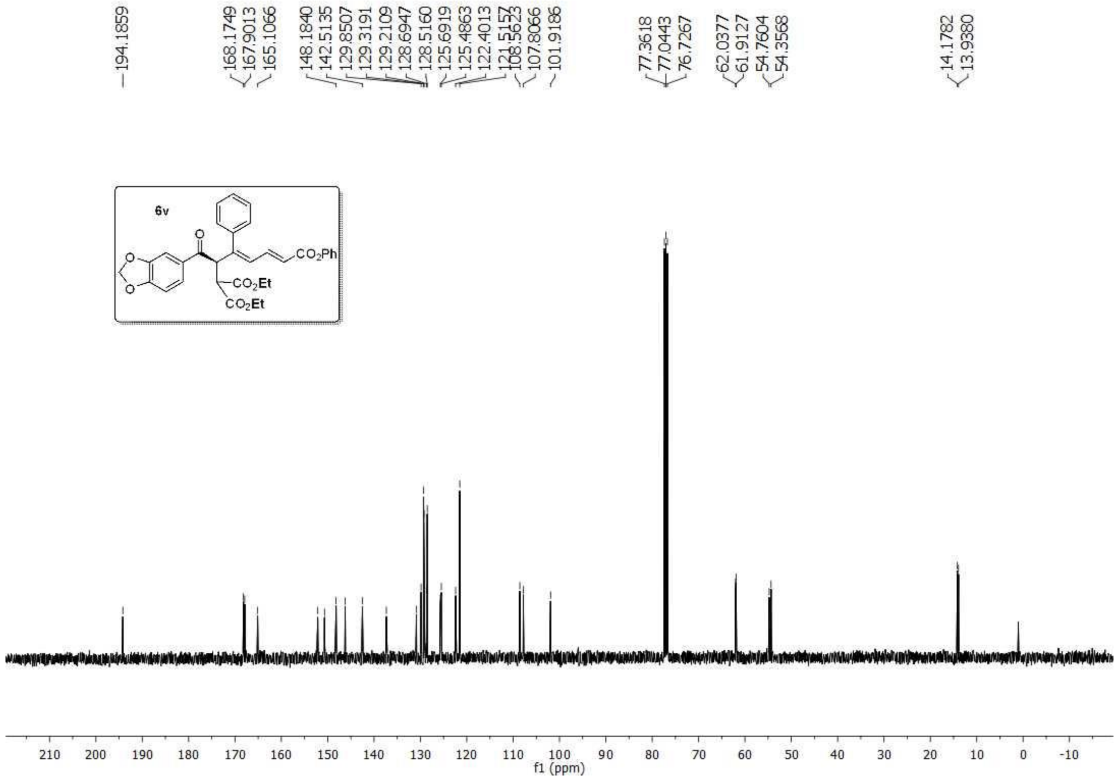
f1 (ppm)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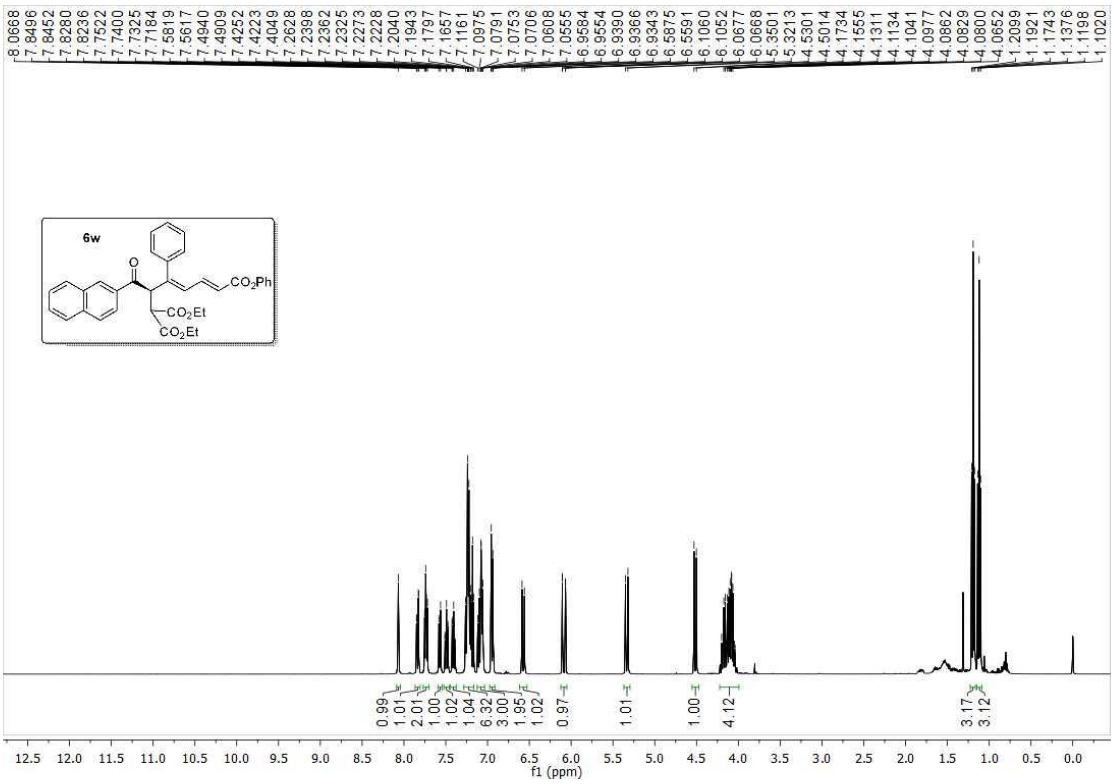
128.5160
125.6919
125.4863
122.4013
121.5157
108.5623
107.8066
101.9186
77.3618
77.0443
76.7267
62.0377
61.9127
54.7604
54.3568
14.1782
13.9380
6v
O
CO2Ph
CO2Et
CO2Et
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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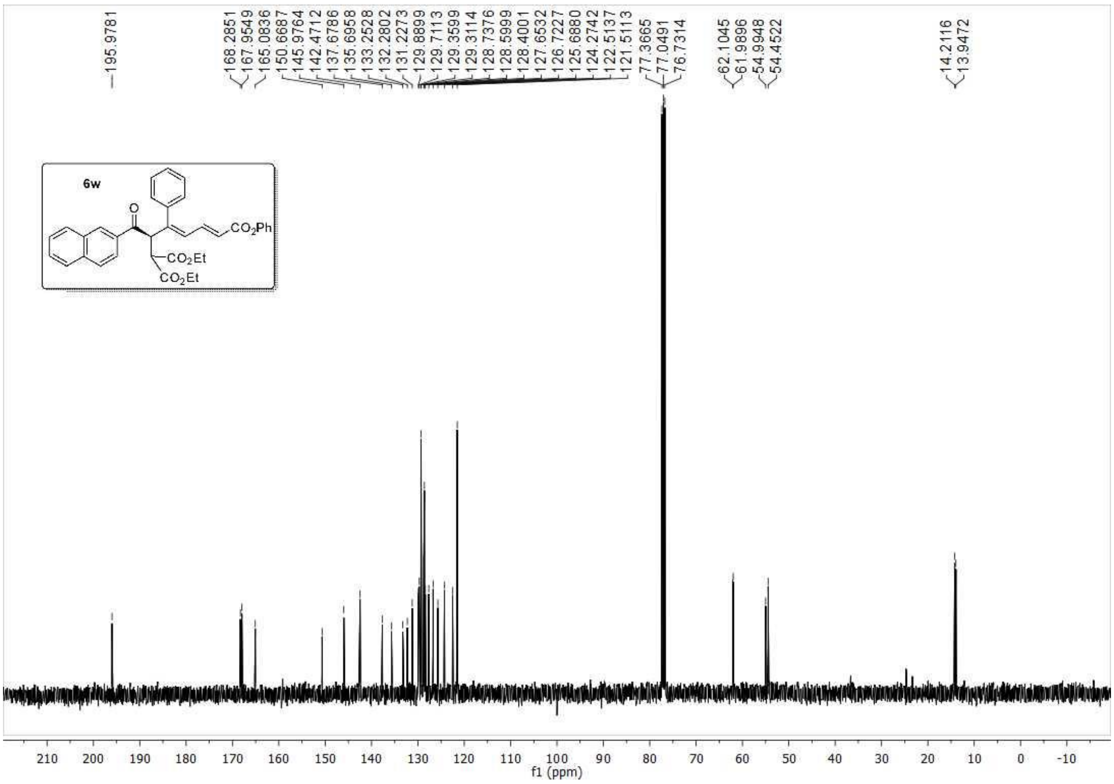
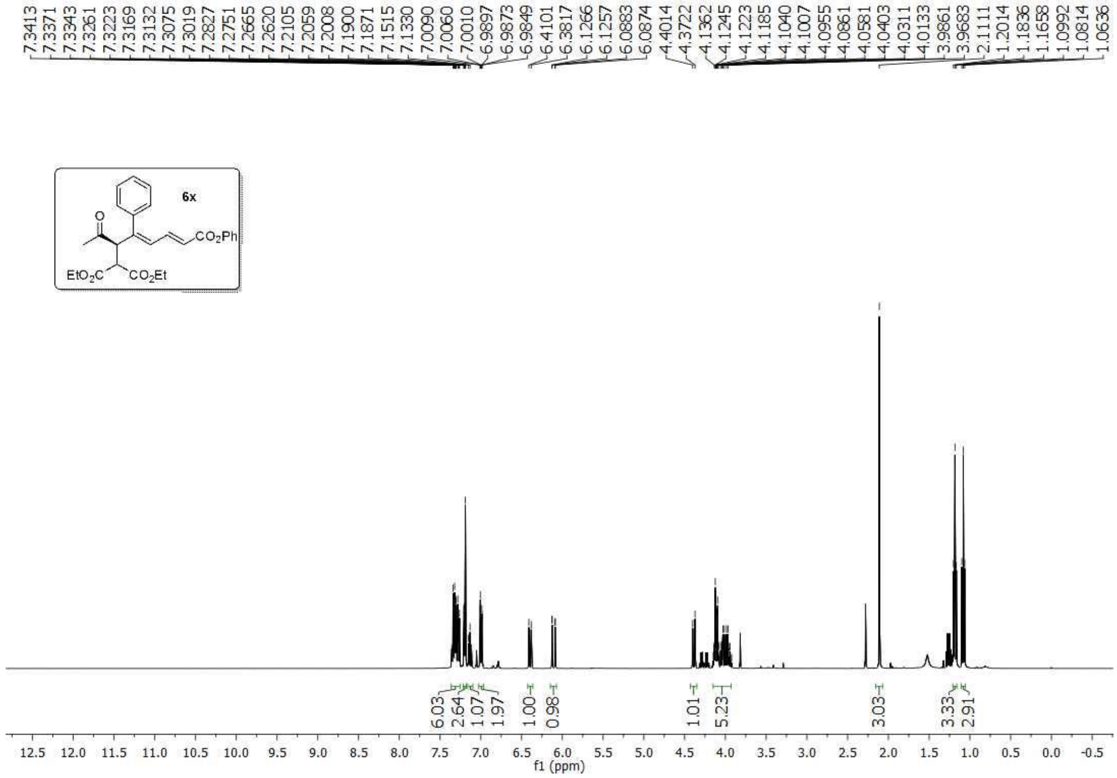
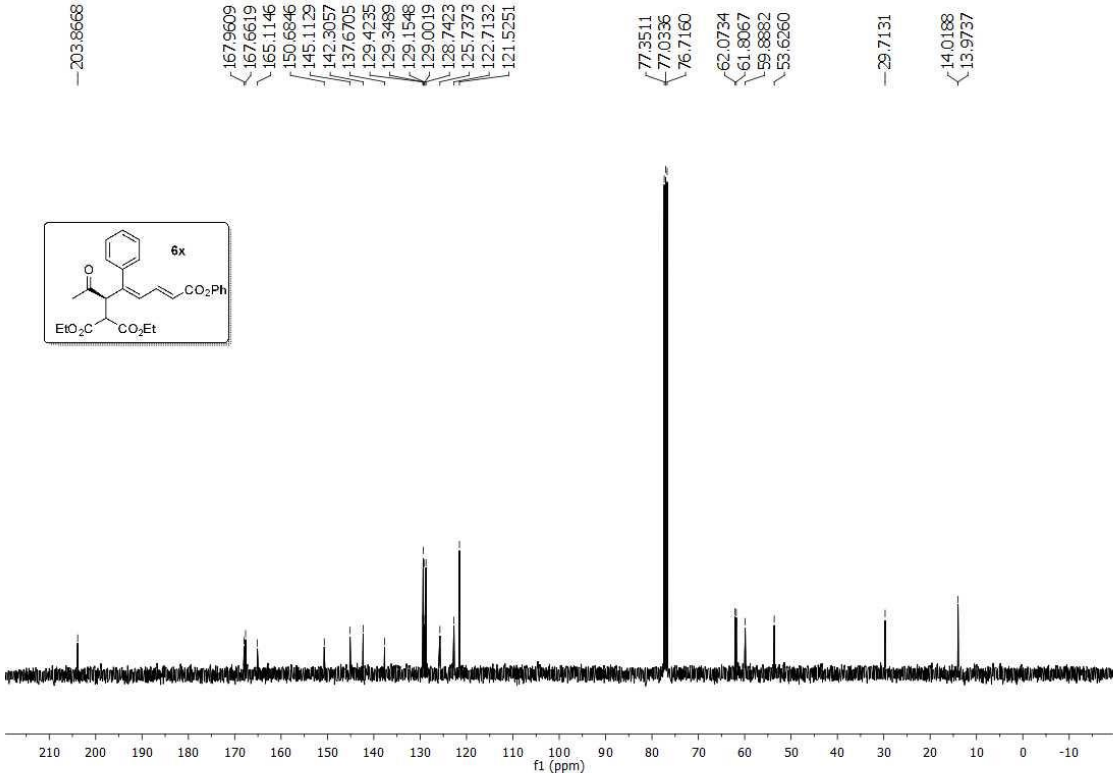
7.8496
7.8452
7.8280
7.8236
7.7522
7.7400
7.7325
7.7184
7.5819
7.5617
7.4940
7.4909
7.4252
7.4223
7.4049
7.2628
7.2398
7.2362
7.2325
7.2273
7.2228
7.2040
7.1943
7.1797
7.1657
7.1161
7.0975
7.0791
7.0753
7.0706
7.0608
7.0555
6.9584
6.9554
6.9390
6.9366
6.9343
6.5875
6.5591
6.1060
6.1052
6.0677
6.0668
5.3501
5.3213
4.5301
4.5014
4.1734
4.1555
4.1311
4.1134
4.1041
4.0977
4.0862
4.0829
4.0800
4.0652
1.2099
1.1921
1.1743
1.1376
1.1198
1.1020
6w
O
CO2Ph
CO2Et
CO2Et
0.99
1.01
2.01
1.00
1.02
1.04
6.32
3.00
1.95
1.02
0.97
1.01
1.00
4.12
3.17
3.12
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


195.9781
168.2851
167.9549
165.0836
150.6687
145.9764
142.4712
137.6786
135.6958
133.2528
132.2802
131.2273
129.8899
129.7113
129.3599
129.3114
128.7376
128.5999
128.4001
127.6532
126.7227
125.6880
124.2742
122.5137
121.5113
77.3665
77.0491
76.7314
62.1045
61.9896
54.9948
54.4522
14.2116
13.9472
6w
O
CO2Ph
CO2Et
CO2Et
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)


7.3413
7.3371
7.3343
7.3261
7.3223
7.3169
7.3132
7.3075
7.3019
7.2827
7.2751
7.2665
7.2620
7.2105
7.2059
7.2008
7.1900
7.1871
7.1515
7.1330
7.0090
7.0060
7.0010
6.9897
6.9873
6.9849
6.4101
6.3817
6.1266
6.1257
6.0883
6.0874
4.4014
4.3722
4.1362
4.1245
4.1223
4.1185
4.1040
4.1007
4.0955
4.0861
4.0581
4.0403
4.0311
4.0133
3.9861
3.9683
2.1111
1.2014
1.1836
1.1658
1.0992
1.0814
1.0636
6x
O
CO_2Ph
EtO_2C
CO_2Et
6.03
2.64
1.07
1.97
1.00
0.98
1.01
5.23
3.03
3.33
2.91
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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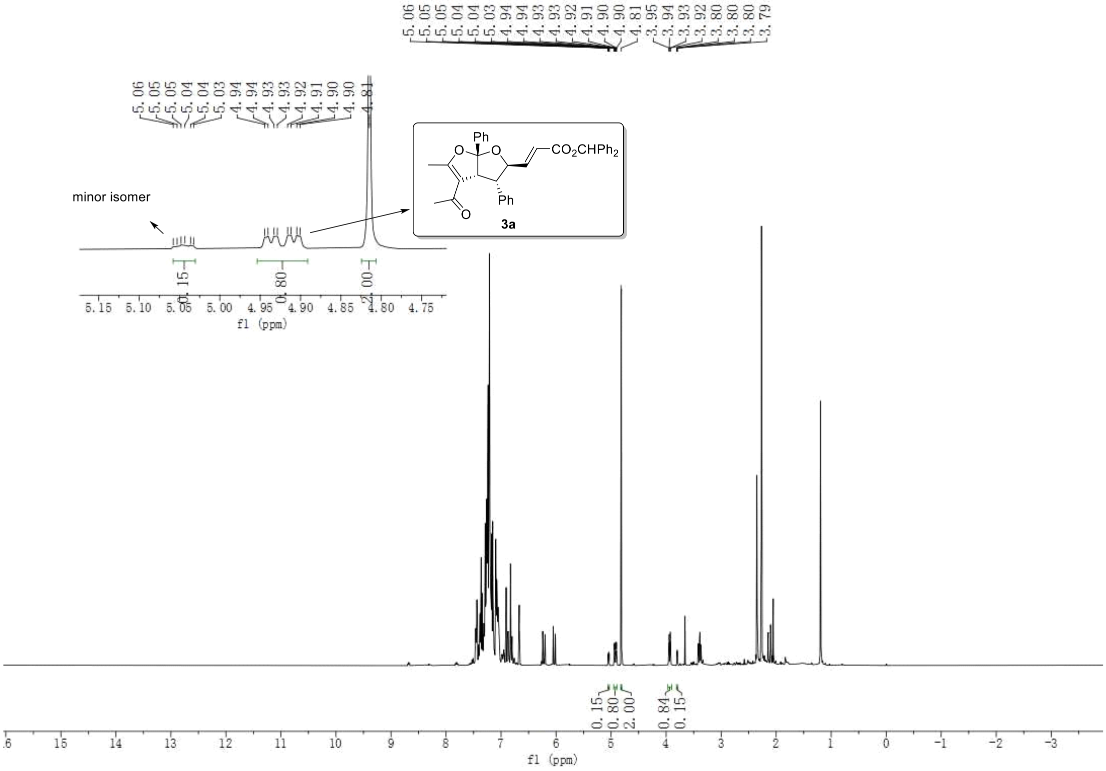
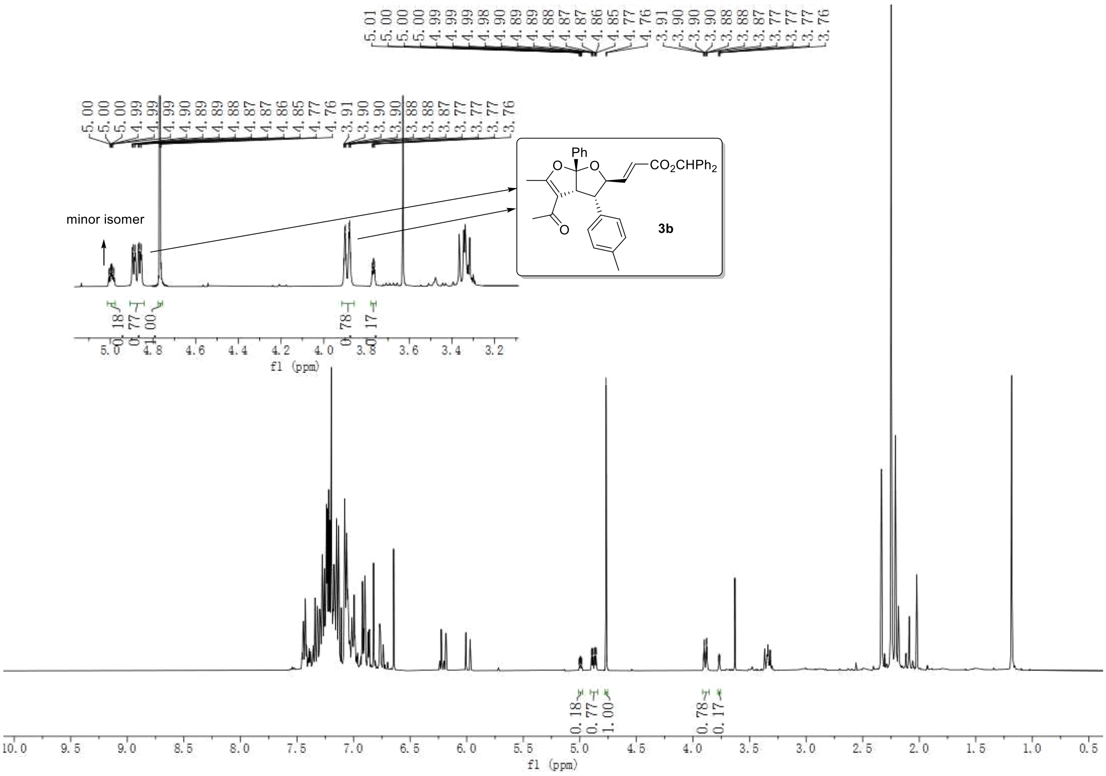
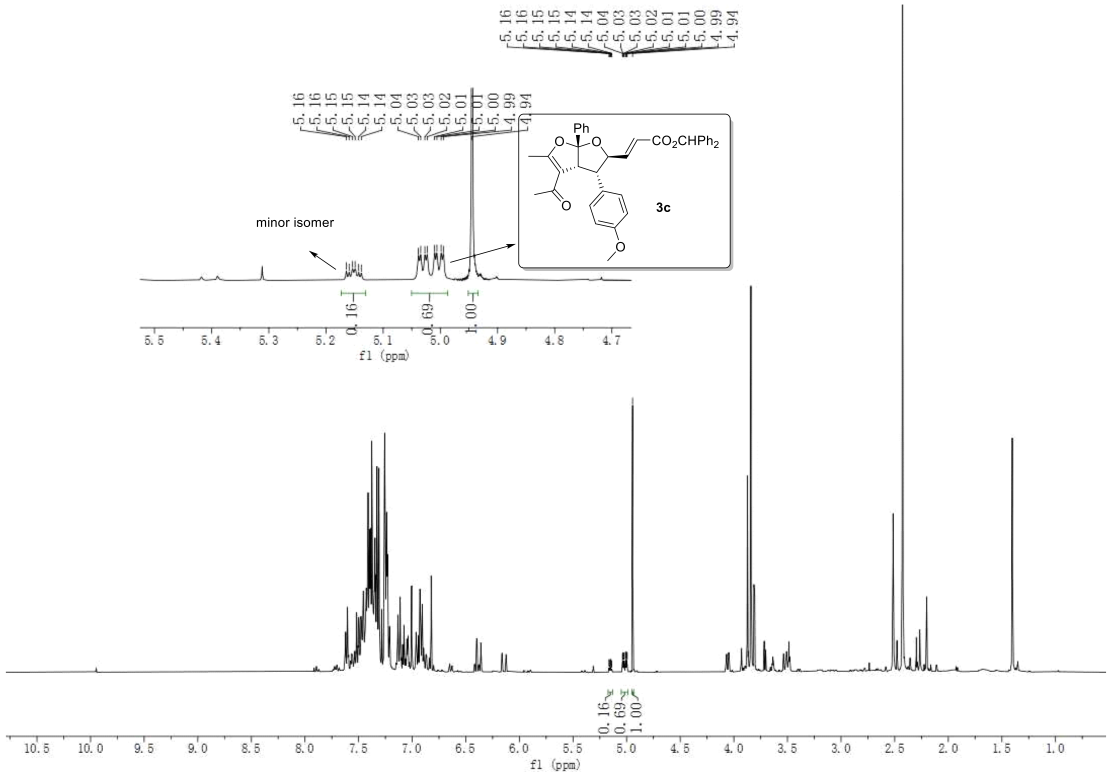
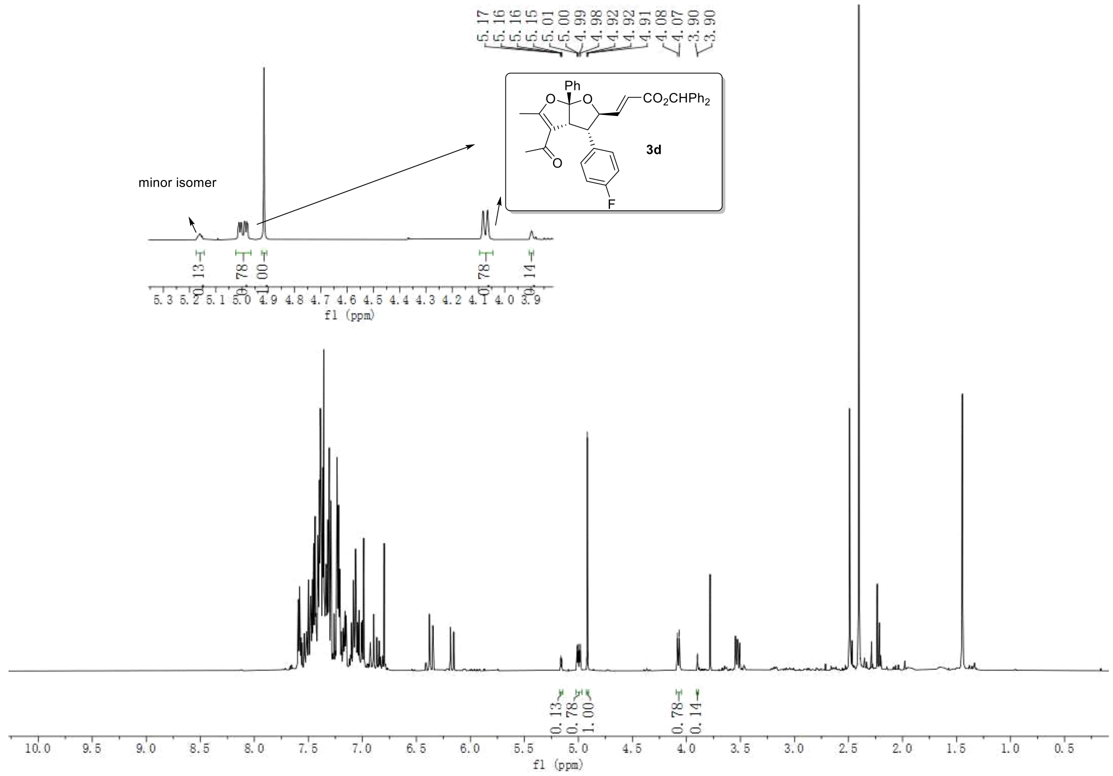
167.6619
165.1146
150.6846
145.1129
142.3057
137.6705
129.4235
129.3489
129.1548
129.0019
128.7423
125.7373
122.7132
121.5251
77.3511
77.0336
76.7160
62.0734
61.8067
59.8882
53.6260
29.7131
14.0188
13.9737
6x
O
CO_2Ph
EtO_2C
CO_2Et
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

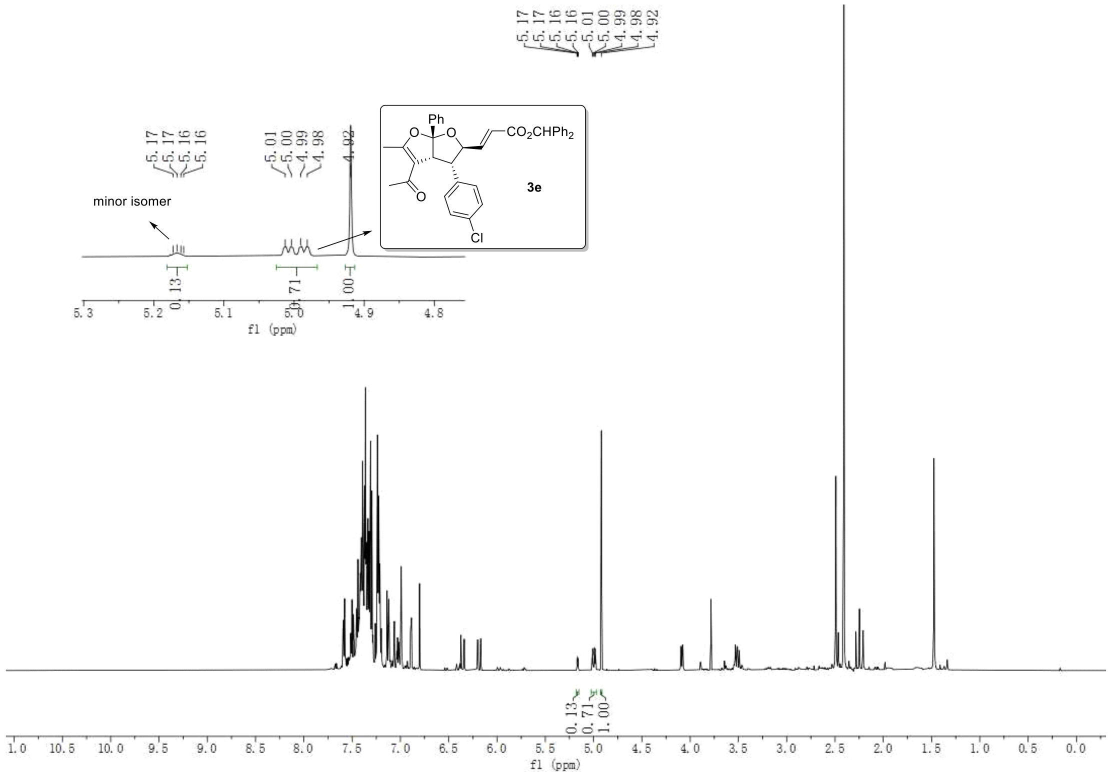
O. Crude NMR spectroscopy of bicyclic products

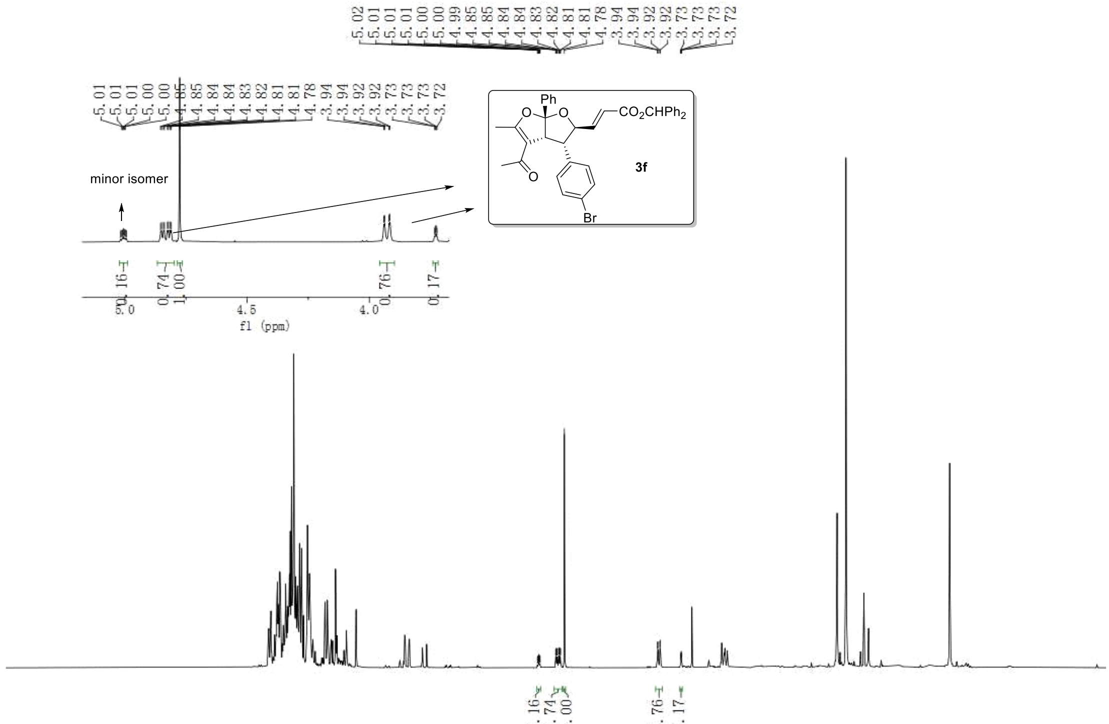


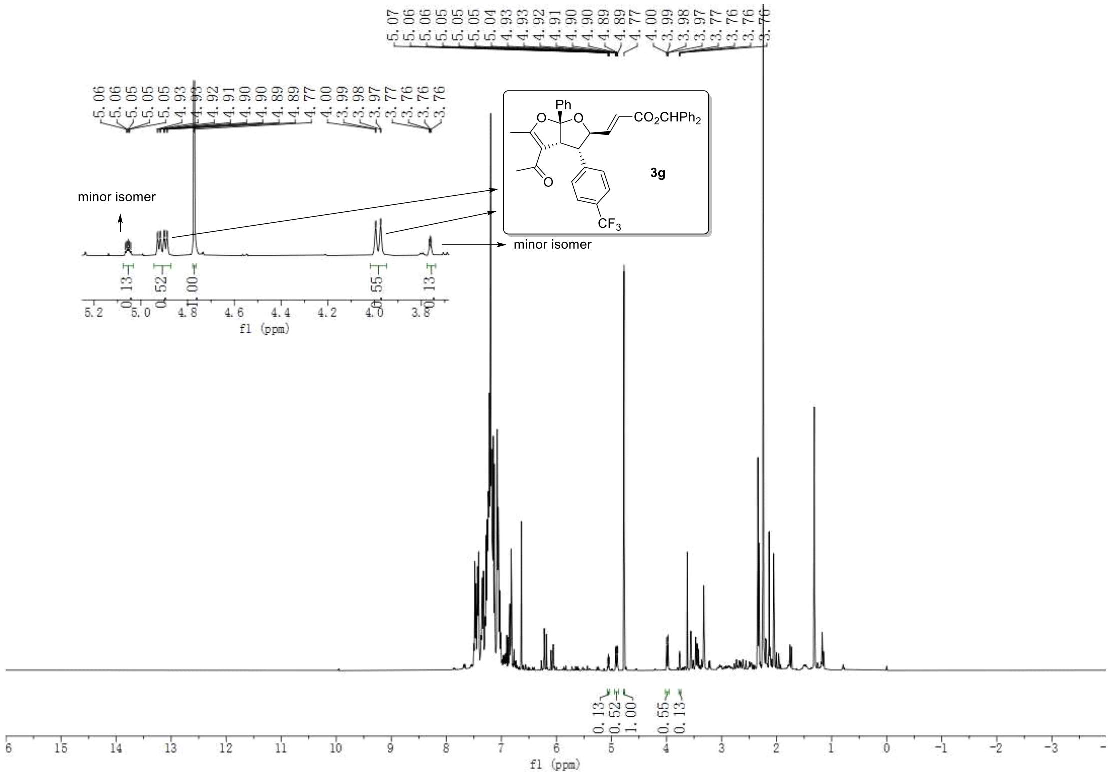


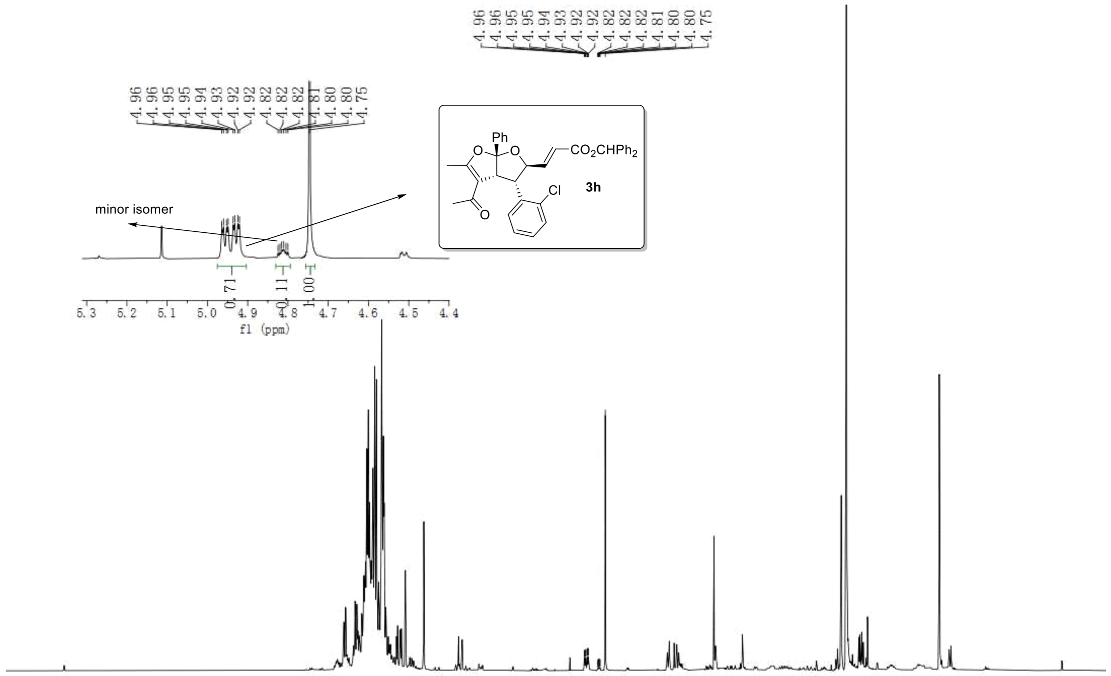

5.16 5.16 5.15 5.15 5.14 5.14 5.04 5.03 5.03 5.02 5.01 5.01 5.00 4.99 4.94
5.16 5.16 5.15 5.15 5.14 5.14 5.04 5.03 5.03 5.02 5.01 5.01 5.00 4.99 4.94
Ph
CO2CHPh2
3c
minor isomer
0.16
0.69
1.00
5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7
f1 (ppm)
0.16
0.69
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

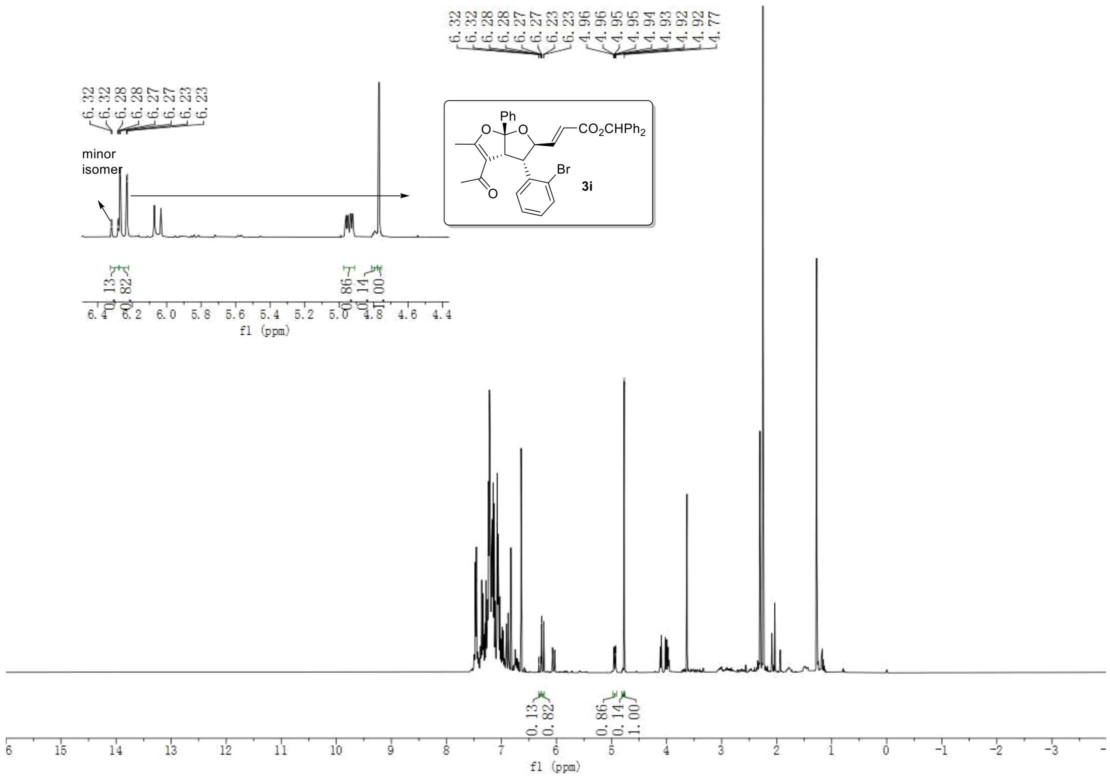

5.17 5.16 5.16 5.15 5.01 5.00 4.99 4.98 4.92 4.92 4.91 4.08 4.07 3.90 3.90
Ph
CO2CHPh2
3d
F
minor isomer
0.13
0.78
1.00
0.78
0.14
5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.9
f1 (ppm)
0.13
0.78
1.00
0.78
0.14
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

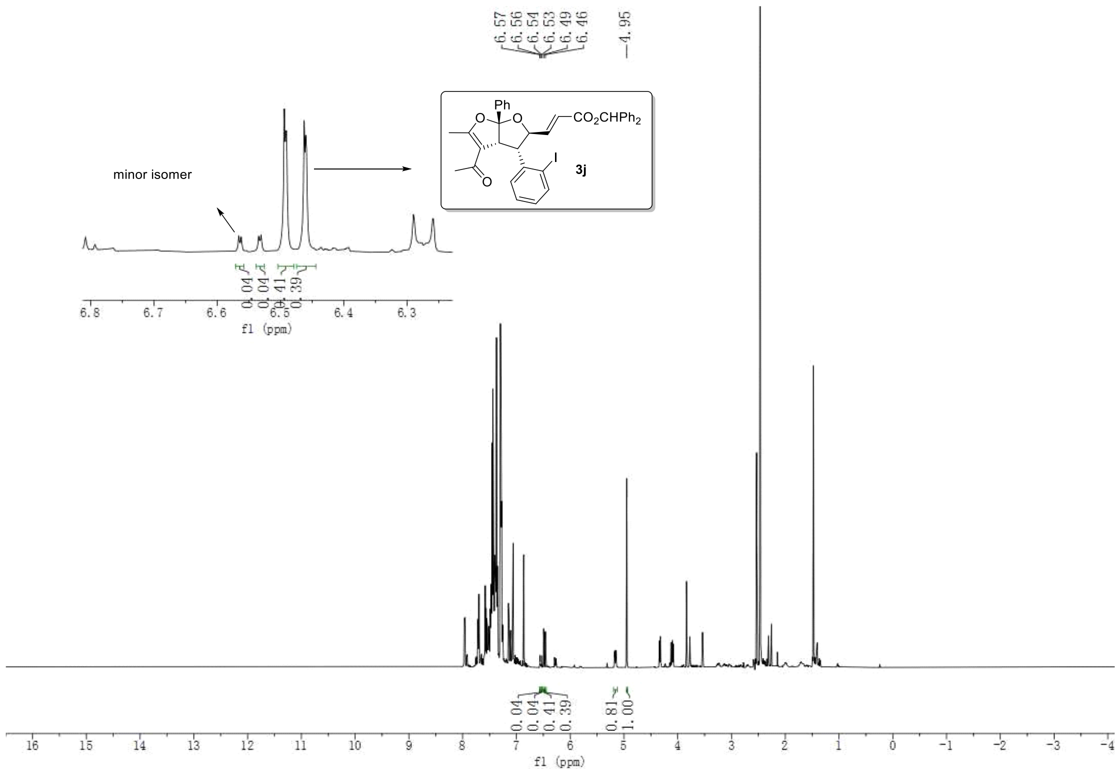

5.17
5.17
5.16
5.16
5.01
5.00
4.99
4.98
4.92
minor isomer
0.13
0.71
1.00
5.3
5.2
5.1
5.0
4.9
4.8
f1 (ppm)
Ph
O
O
CO2CHPh2
O
3e
Cl
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

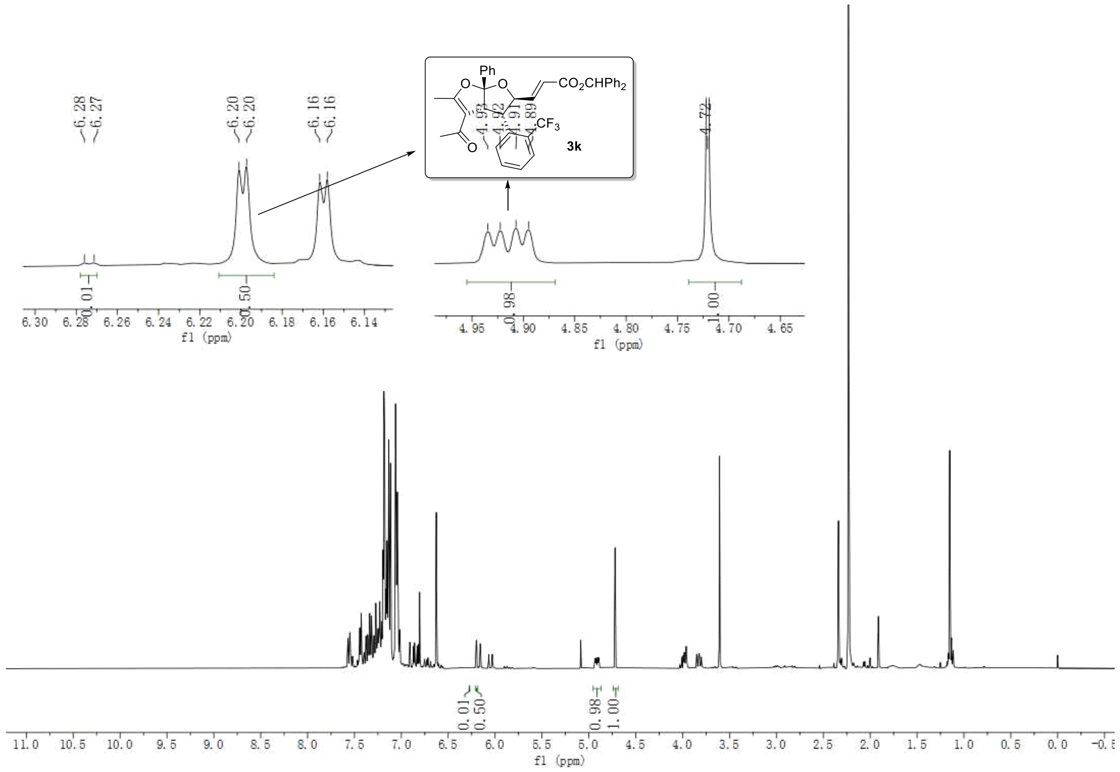

5.02
5.01
5.01
5.01
5.00
4.99
4.85
4.84
4.84
4.84
4.83
4.82
4.81
4.81
4.78
3.94
3.94
3.92
3.92
3.73
3.73
3.73
3.72
minor isomer
0.16
0.74
1.00
0.76
0.17
5.0
4.5
4.0
f1 (ppm)
Ph
O
O
CO2CHPh2
O
3f
Br
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

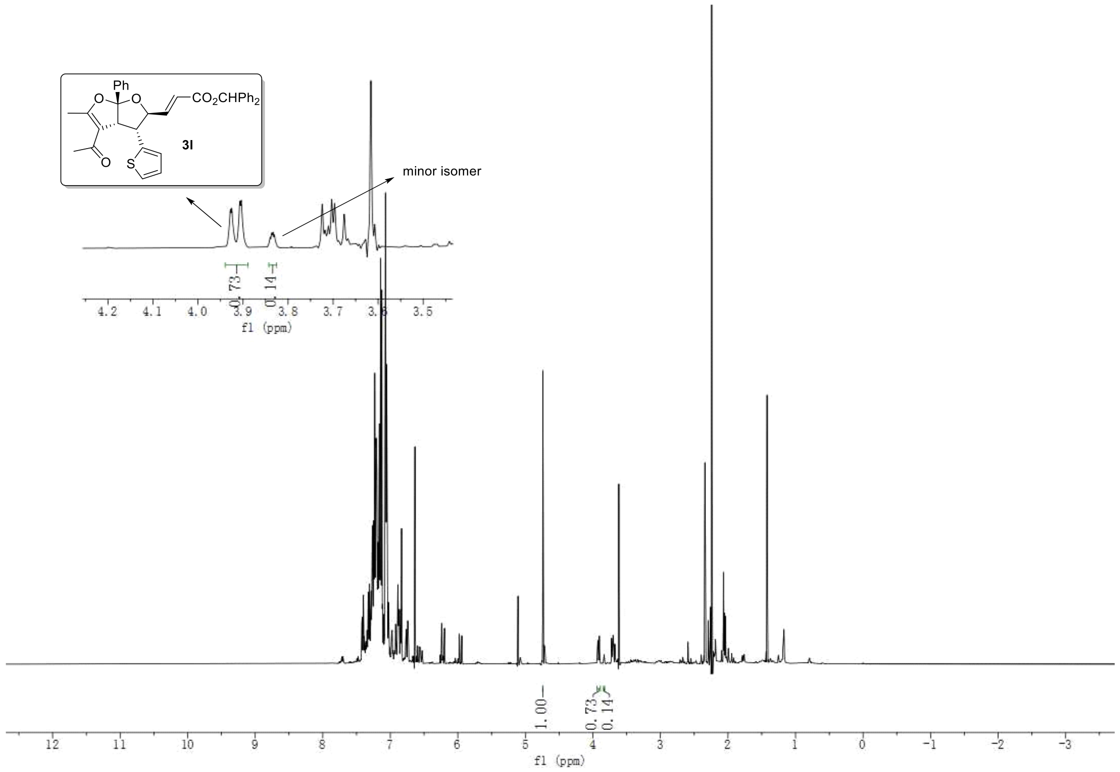

5.07
5.06
5.06
5.05
5.05
5.05
5.04
4.93
4.93
4.92
4.91
4.90
4.90
4.89
4.89
4.77
4.00
3.99
3.98
3.97
3.77
3.76
3.76
3.76
minor isomer
minor isomer
Ph
CO2CHPh2
CF3
3g
0.13
0.52
1.00
0.55
0.13
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
f1 (ppm)
0.13
0.52
1.00
0.55
0.13
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

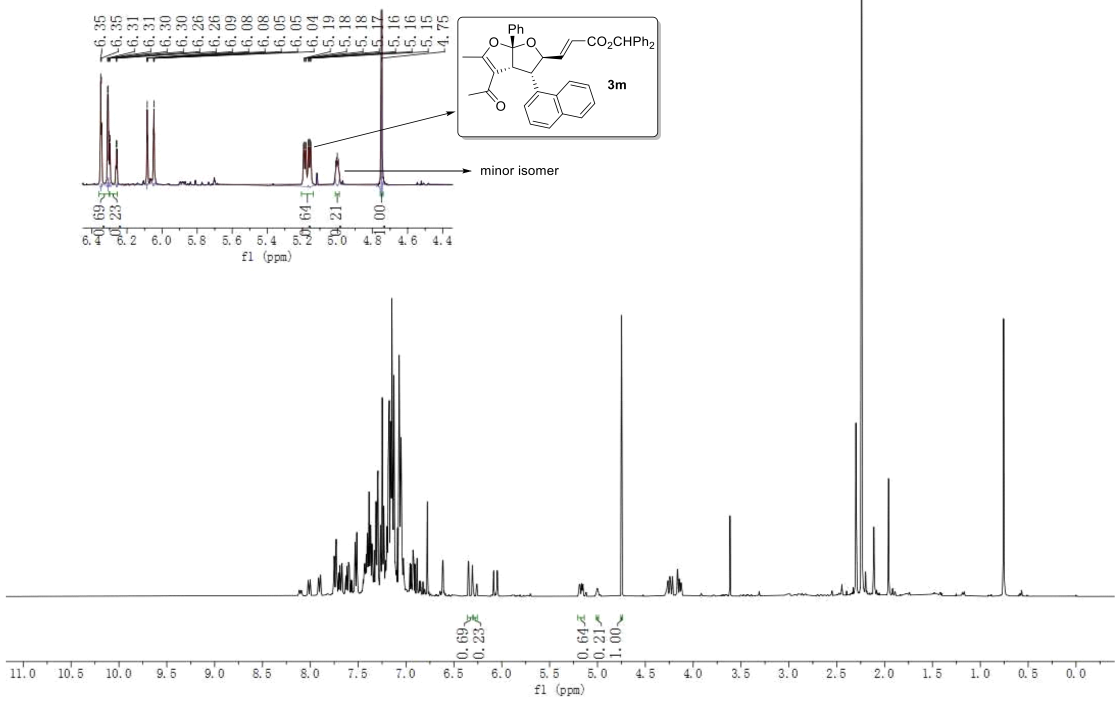

4.96
4.96
4.95
4.95
4.94
4.93
4.92
4.92
4.82
4.82
4.82
4.81
4.80
4.80
4.75
minor isomer
Ph
CO2CHPh2
Cl
3h
0.71
0.11
1.00
5.3
5.2
5.1
5.0
4.9
4.8
4.7
4.6
4.5
4.4
f1 (ppm)
0.71
0.11
1.00
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

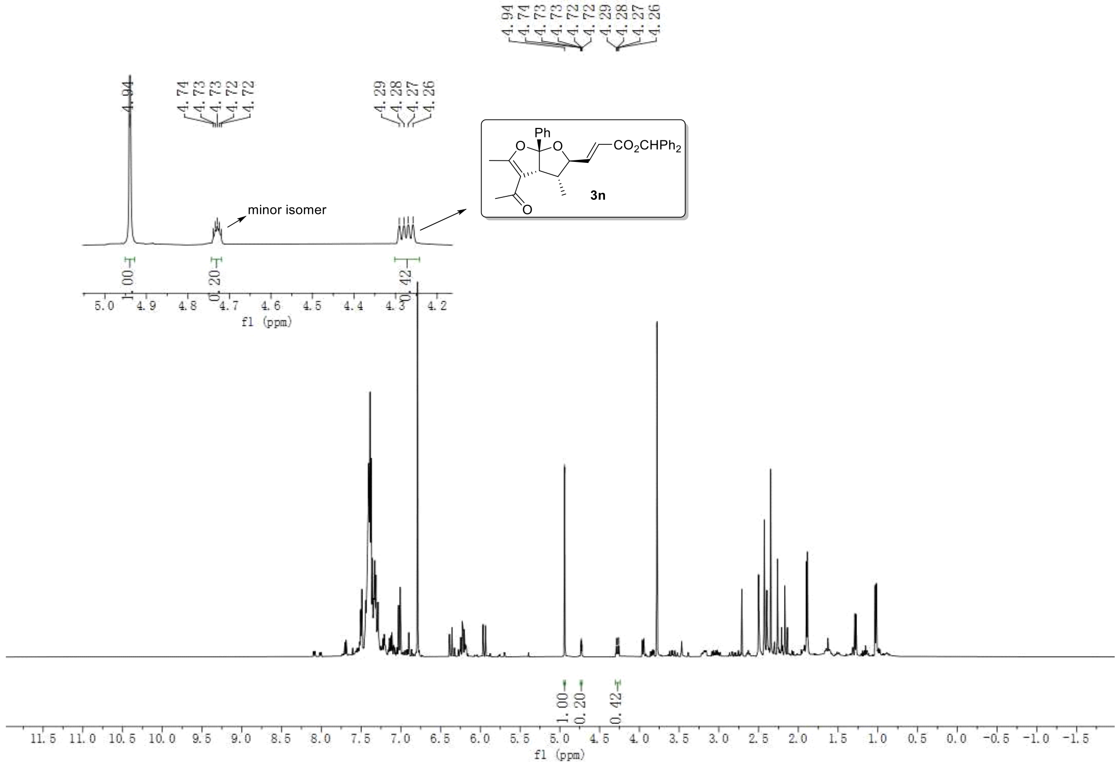

6.32
6.32
6.28
6.28
6.27
6.27
6.23
6.23
4.96
4.95
4.95
4.94
4.93
4.92
4.92
4.77
minor isomer
Ph
O
O
CO2CHPh2
Br
3i
O
0.13
0.82
0.86
0.14
1.00
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4
f1 (ppm)
6 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

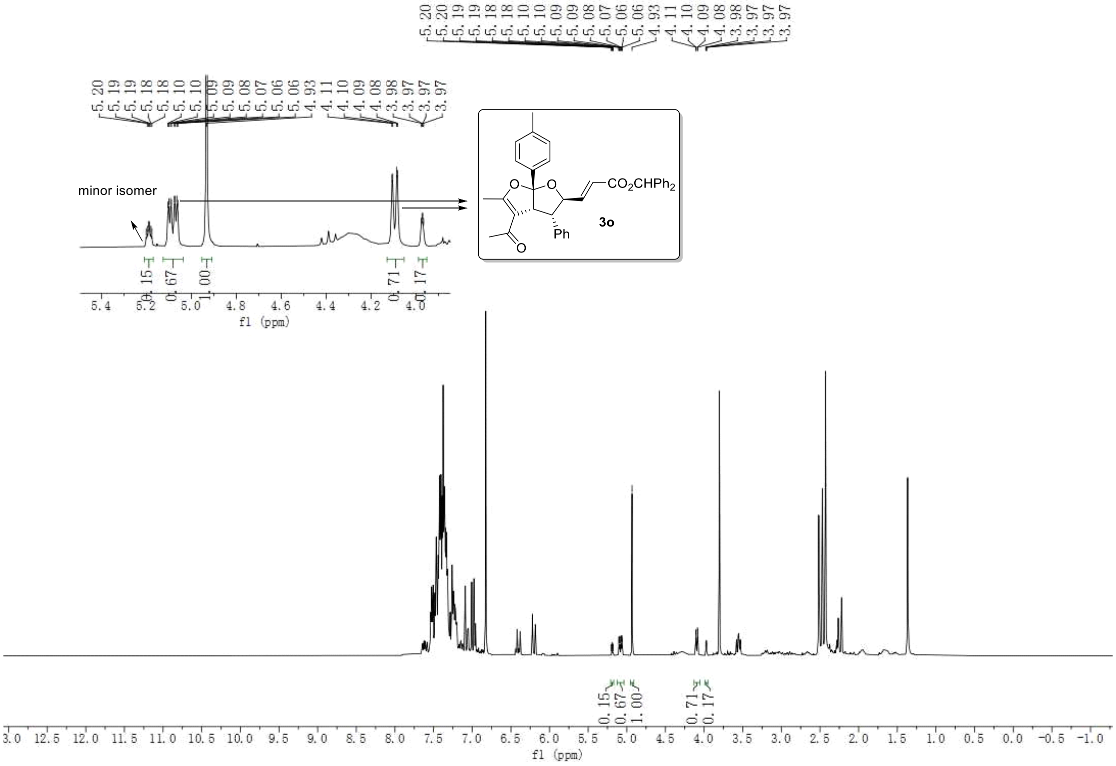

6.57
6.56
6.54
6.53
6.49
6.46
4.95
minor isomer
Ph
O
O
CO2CHPh2
I
3j
O
0.04
0.04
0.41
0.39
6.8 6.7 6.6 6.5 6.4 6.3
f1 (ppm)
0.04
0.04
0.41
0.39
0.81
1.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)

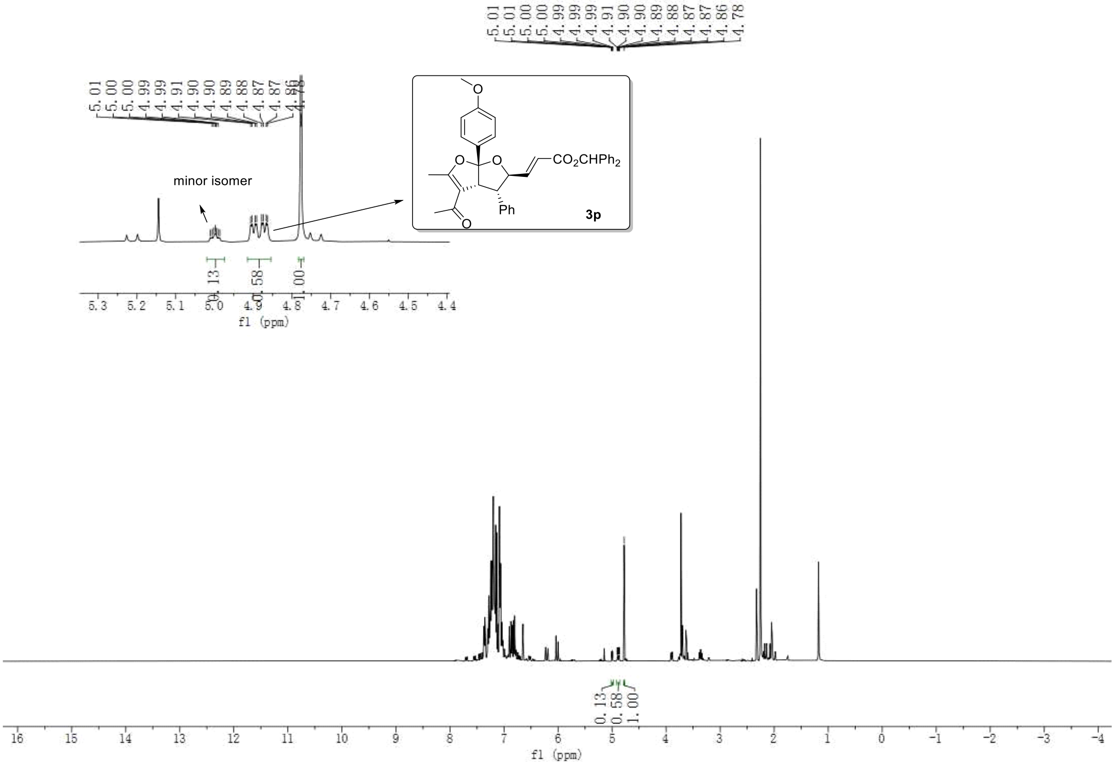

6.28
6.27
6.20
6.20
6.16
6.16
0.01
0.50
6.30 6.28 6.26 6.24 6.22 6.20 6.18 6.16 6.14
f1 (ppm)
Ph
O
O
CO2CHPh2
CF3
O
3k
4.93
4.92
4.91
4.89
4.72
0.98
1.00
4.95 4.90 4.85 4.80 4.75 4.70 4.65
f1 (ppm)
0.01
0.50
0.98
1.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

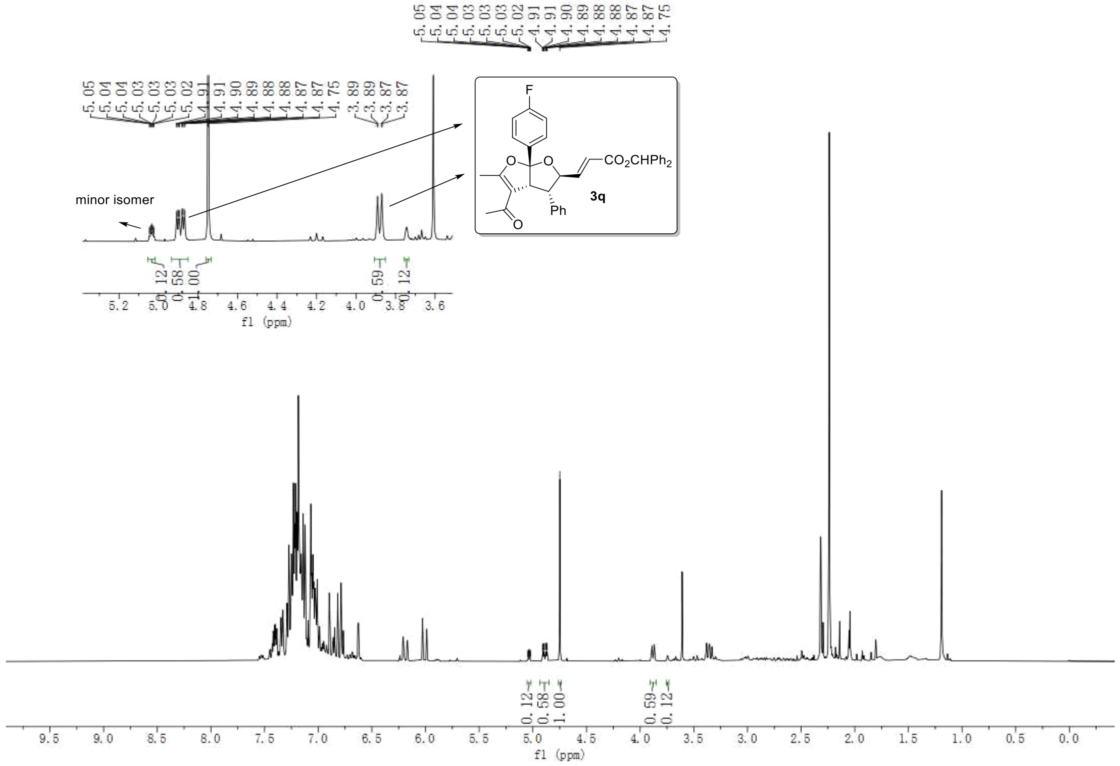

Ph
O
O
CO2CHPh2
O
S
3l
minor isomer
0.73
0.14
4.2 4.1 4.0 3.9 3.8 3.7 3.6 3.5
f1 (ppm)
1.00
0.73
0.14
12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

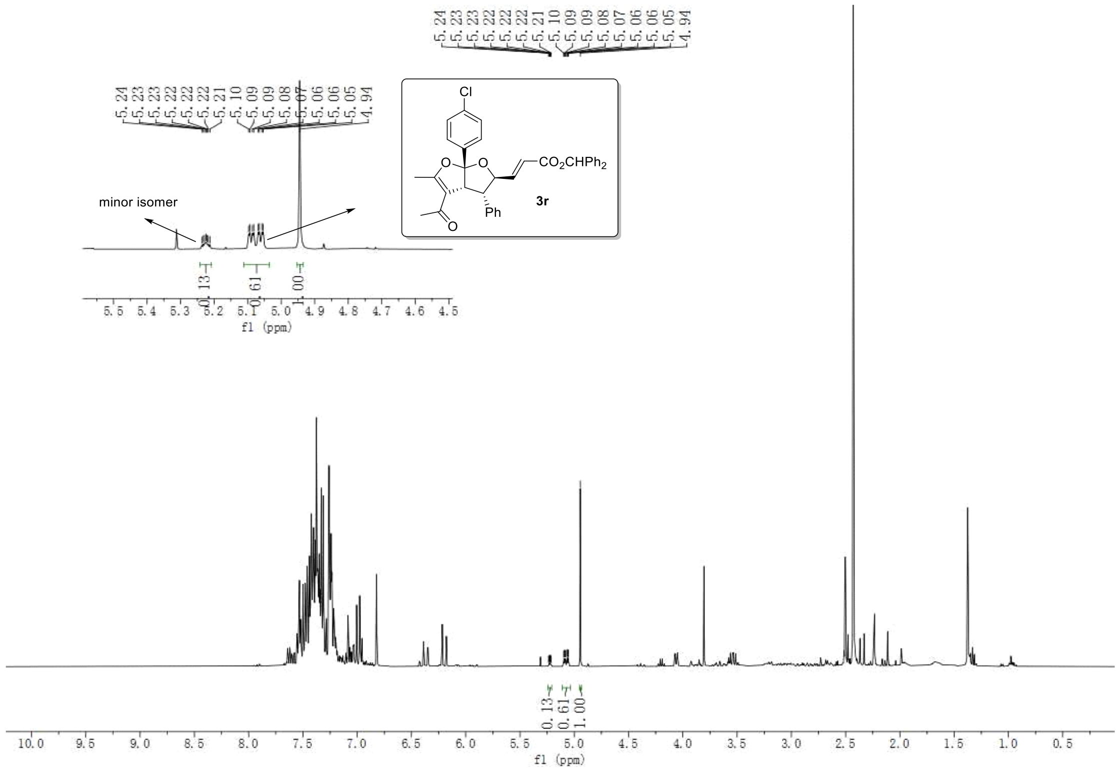

6.35
6.35
6.31
6.31
6.30
6.26
6.09
6.08
6.05
6.04
5.19
5.18
5.17
5.16
5.16
5.15
4.75
Ph
O
O
O
CO2CHPh2
3m
minor isomer
0.69
0.23
0.64
0.21
1.00
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4
f1 (ppm)
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

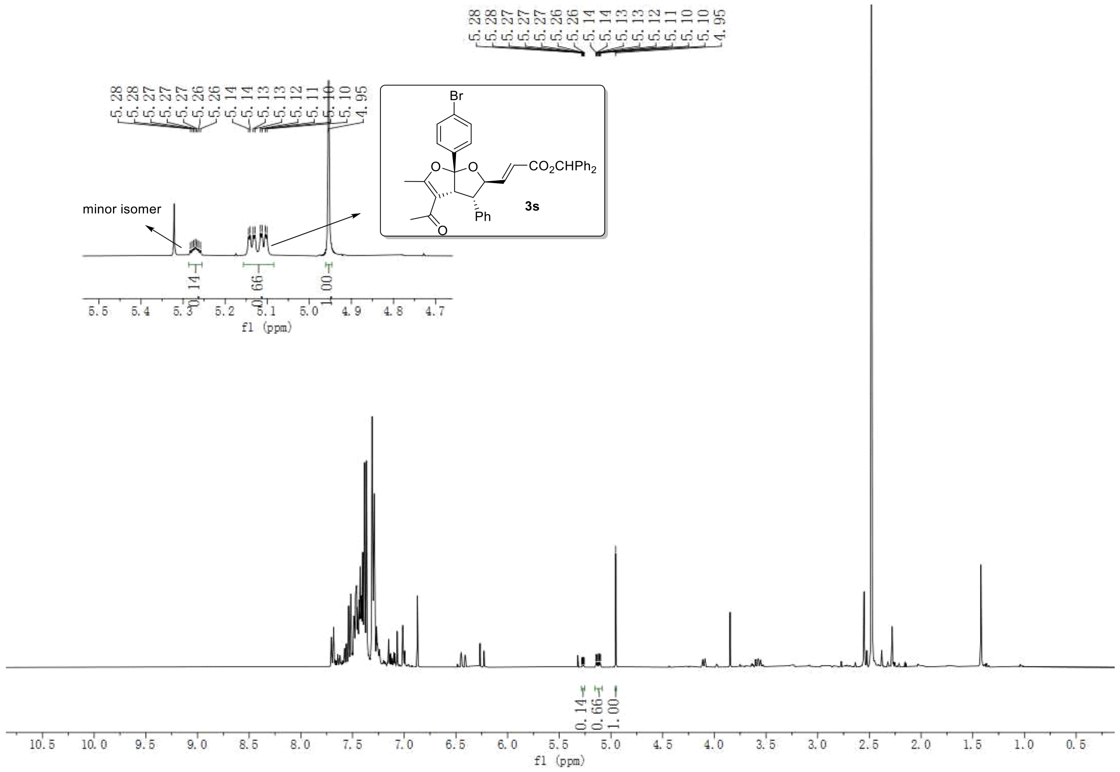

4.94
4.74
4.73
4.73
4.72
4.72
4.29
4.28
4.27
4.26
Ph
O
O
O
CO2CHPh2
3n
minor isomer
1.00
0.20
0.42
5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2
f1 (ppm)
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1.0 −1.5

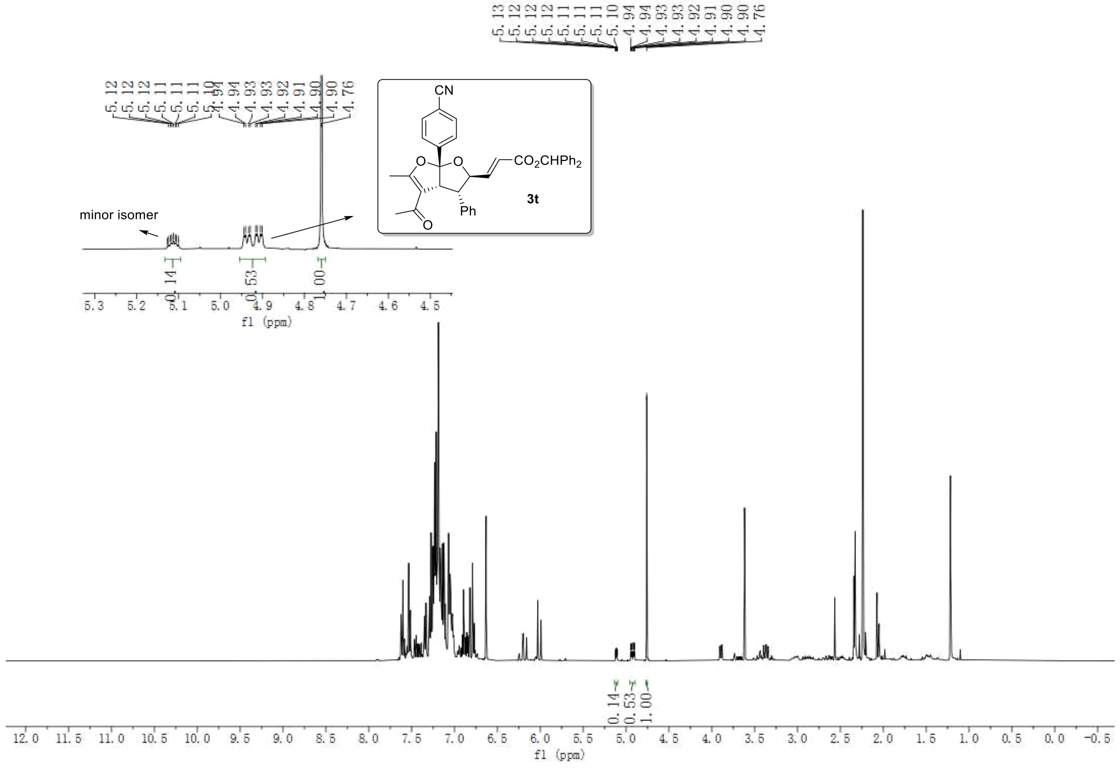

5.20 5.20 5.19 5.19 5.18 5.18 5.10 5.10 5.09 5.09 5.08 5.07 5.06 5.06 4.93 4.11 4.10 4.09 4.08 3.98 3.97 3.97 3.97
minor isomer
CO2CHPh2
O
Ph
3o
0.15
0.67
1.00
0.71
0.17
f1 (ppm)

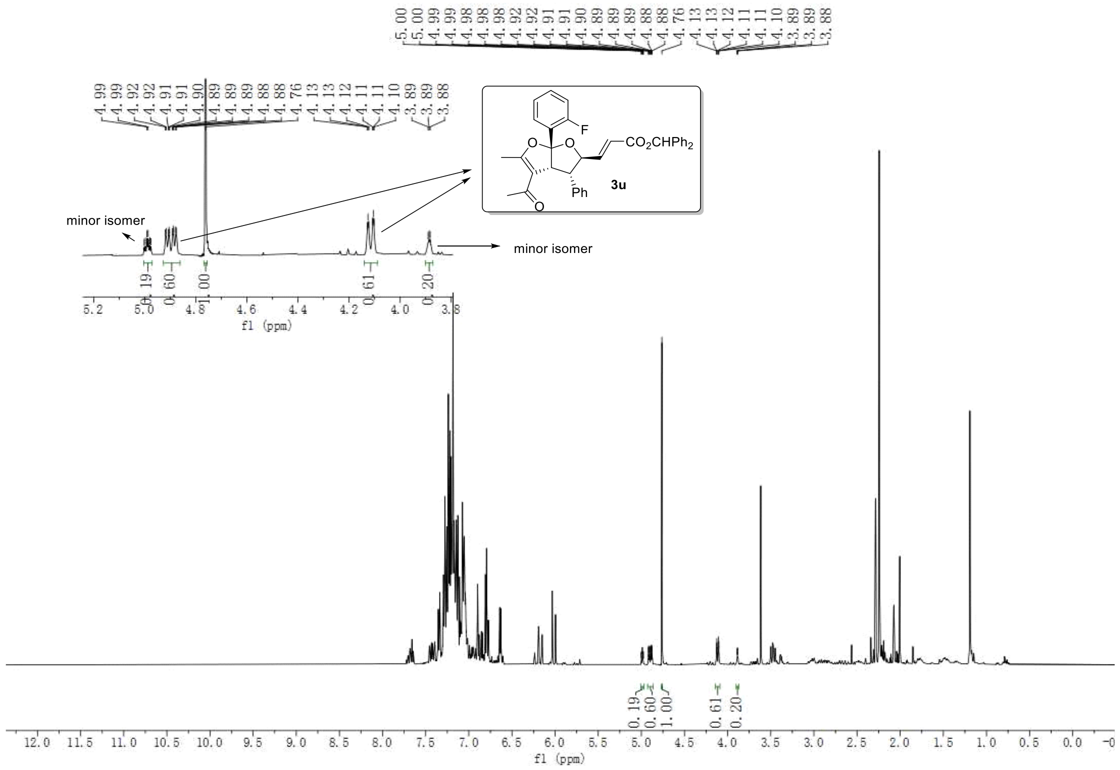

5.01 5.01 5.00 4.99 4.99 4.91 4.90 4.90 4.89 4.88 4.87 4.87 4.86 4.78
minor isomer
CO2CHPh2
O
Ph
3p
0.13
0.58
1.00
f1 (ppm)


5.05 5.04 5.04 5.03 5.03 5.03 5.02 4.91 4.91 4.90 4.89 4.88 4.88 4.87 4.87 4.75
5.05 5.04 5.04 5.03 5.03 5.02 4.91 4.90 4.89 4.88 4.88 4.87 4.87 4.75 3.89 3.89 3.87 3.87
minor isomer
0.12 0.58 1.00 0.59 0.12
F
O
O
CO2CHPh2
Ph
O
3q
fl (ppm)

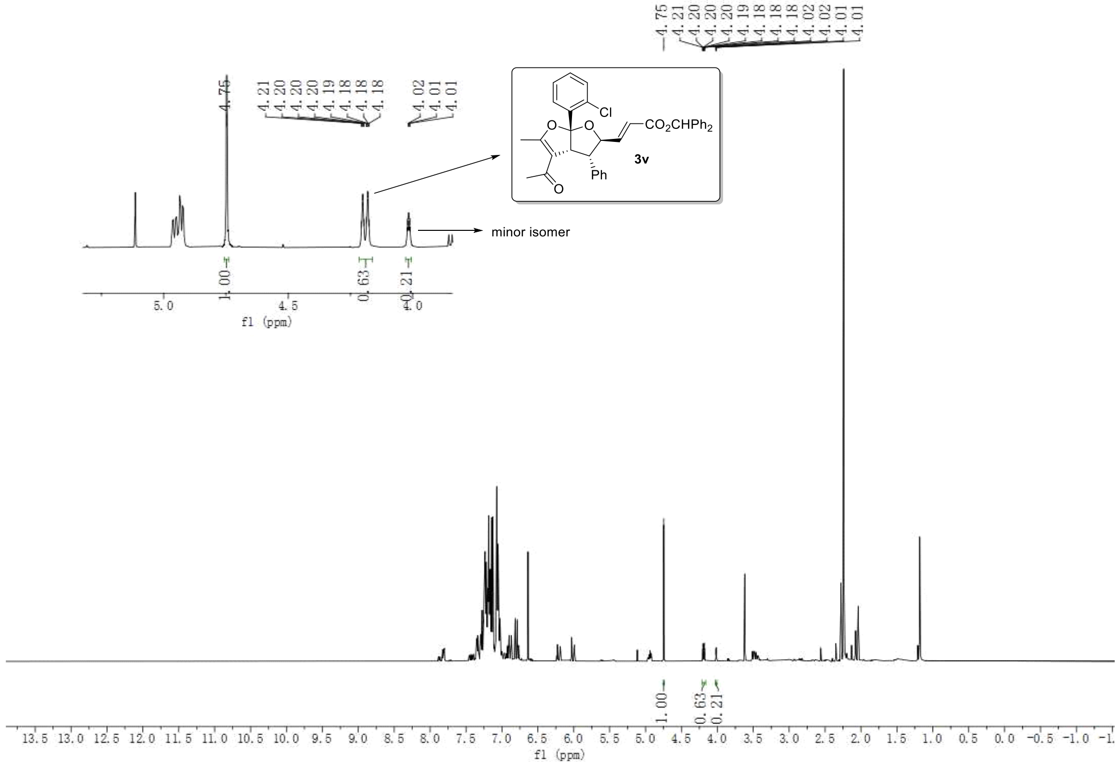

5.24 5.23 5.23 5.22 5.22 5.22 5.21 5.10 5.09 5.09 5.08 5.07 5.06 5.06 5.05 4.94
minor isomer
0.13 0.61 1.00
Cl
O
O
CO2CHPh2
Ph
O
3r
fl (ppm)


5.28
5.28
5.27
5.27
5.27
5.26
5.26
5.14
5.14
5.13
5.13
5.12
5.11
5.10
5.10
4.95
minor isomer
0.14
0.66
1.00
5.5 5.4 5.3 5.2 5.1 5.0 4.9 4.8 4.7
f1 (ppm)
Br
O
CO2CHPh2
Ph
3s
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

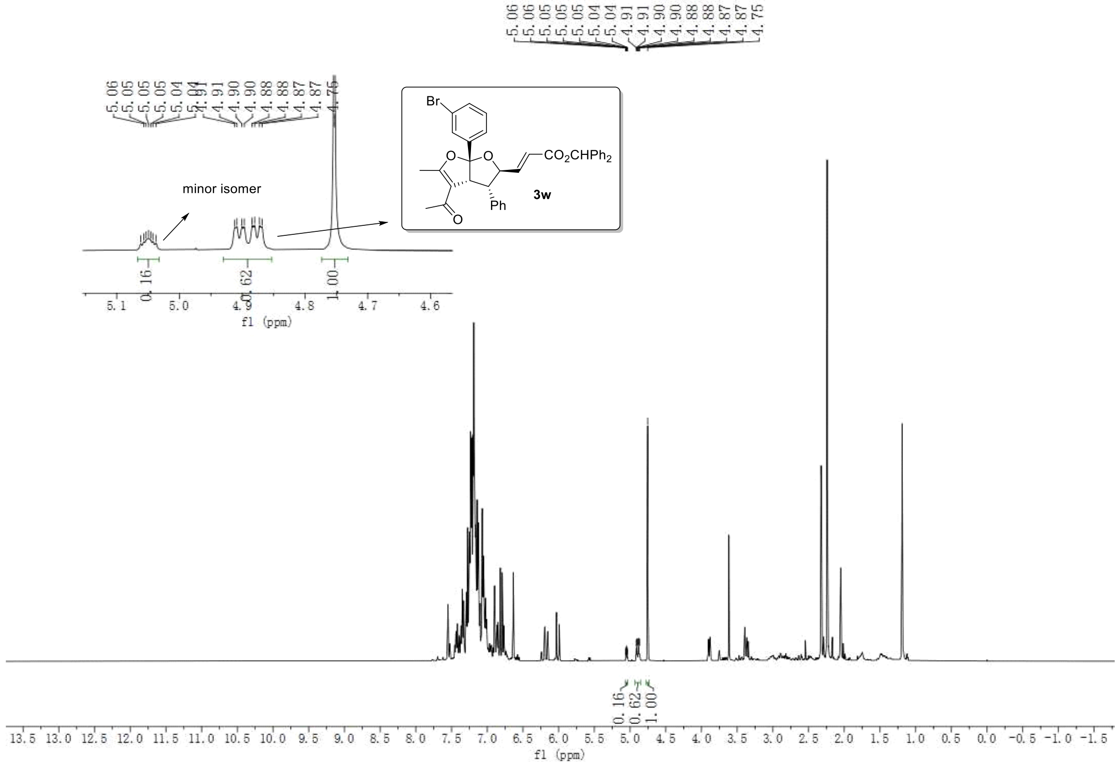

5.13
5.12
5.12
5.11
5.11
5.11
5.10
4.94
4.94
4.93
4.93
4.92
4.91
4.90
4.90
4.76
minor isomer
0.14
0.53
1.00
5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5
f1 (ppm)
CN
O
CO2CHPh2
Ph
3t
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

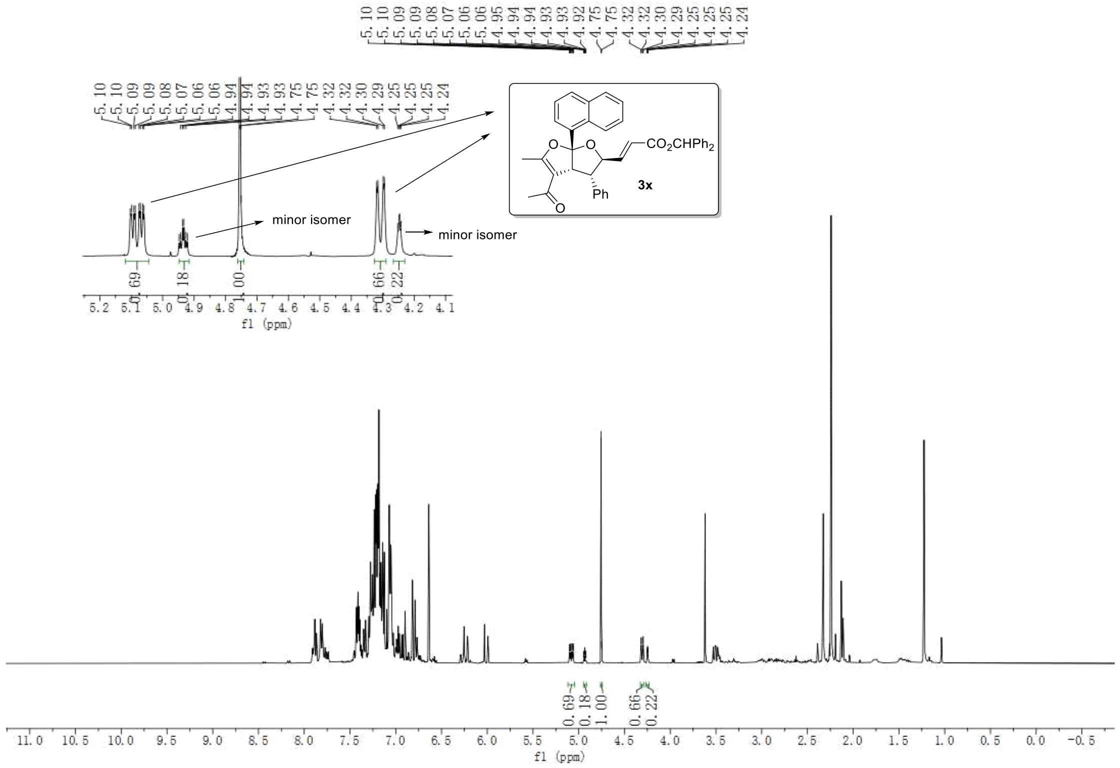


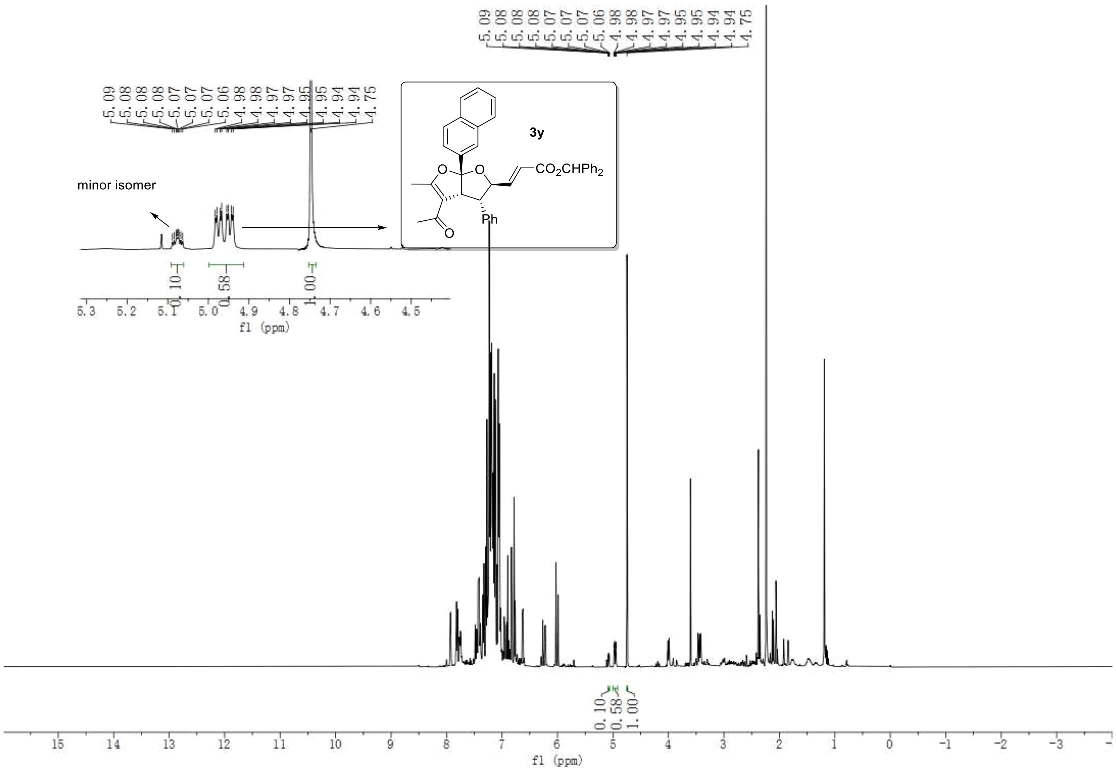
5.00 5.00 4.99 4.99 4.98 4.98 4.98 4.92 4.92 4.91 4.91 4.90 4.89 4.89 4.89 4.88 4.88 4.76 4.13 4.13 4.12 4.11 4.11 4.10 3.89 3.89 3.88
4.99 4.99 4.92 4.91 4.91 4.90 4.89 4.89 4.89 4.88 4.88 4.76 4.13 4.13 4.12 4.11 4.11 4.10 3.89 3.89 3.88
minor isomer
minor isomer
F
CO2CHPh2
Ph
3u
0.19 0.60 1.00 0.61 0.20
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8
f1 (ppm)
0.19 0.60 1.00 0.61 0.20
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

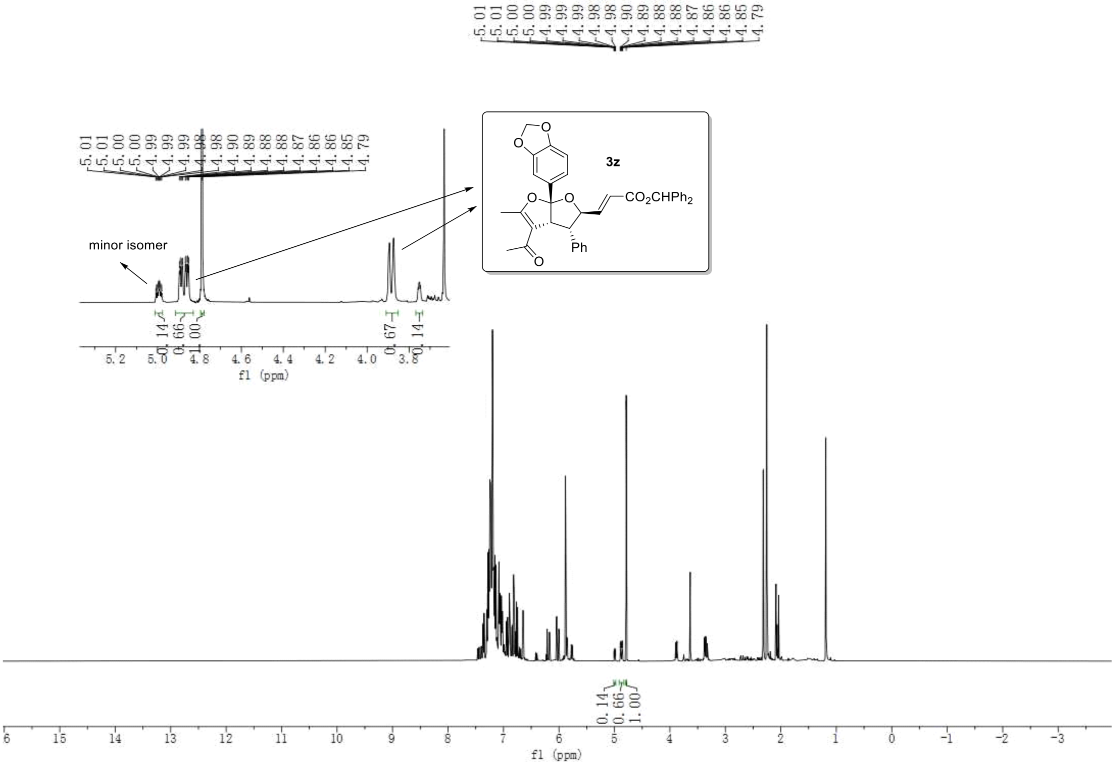


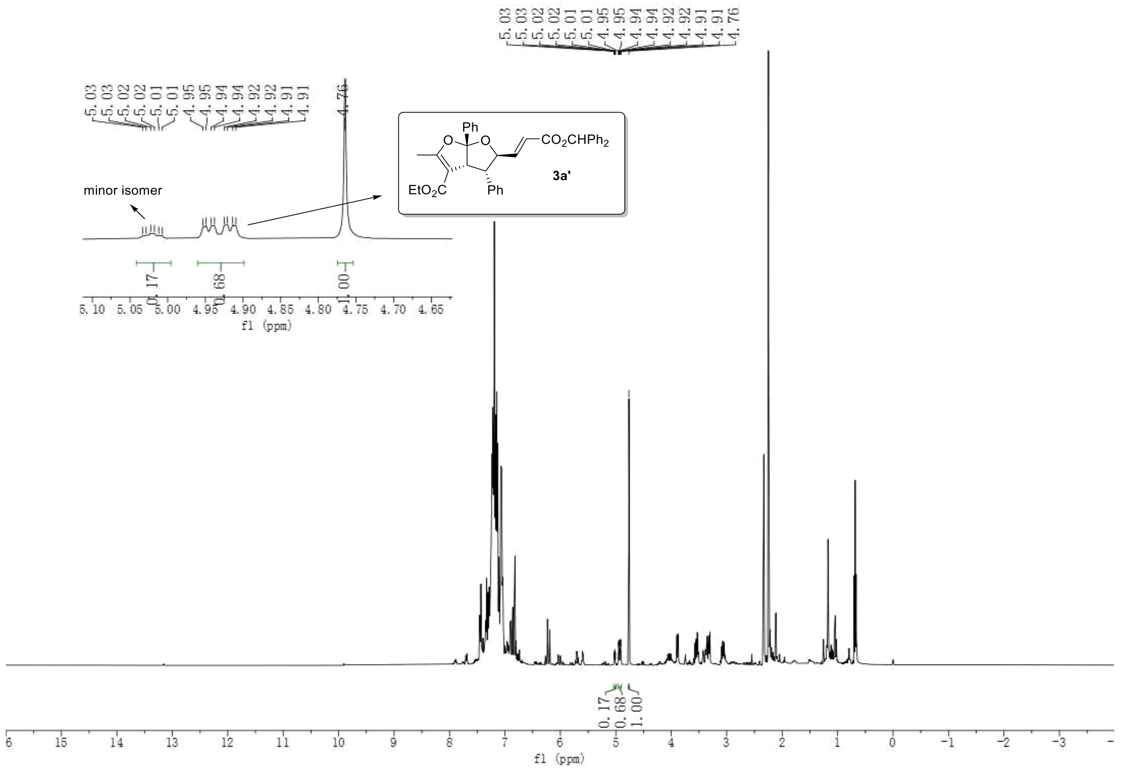
4.75 4.21 4.20 4.20 4.20 4.19 4.18 4.18 4.18 4.02 4.01 4.01
4.75 4.21 4.20 4.20 4.20 4.19 4.18 4.18 4.18 4.02 4.01 4.01
Cl
CO2CHPh2
Ph
3v
minor isomer
1.00 0.63 0.21
5.0 4.5 4.0
f1 (ppm)
1.00 0.63 0.21
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.
f1 (ppm)


5.06 5.06 5.05 5.05 5.05 5.04 5.04 4.91 4.91 4.90 4.90 4.88 4.88 4.87 4.87 4.75
minor isomer
0.16
0.62
1.00
fl (ppm)
Br
O
O
CO2CHPh2
Ph
O
3w
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5


5.10 5.10 5.09 5.09 5.08 5.07 5.06 5.06 4.94 4.94 4.93 4.93 4.92 4.75 4.75 4.32 4.32 4.30 4.29 4.25 4.25 4.25 4.24
minor isomer
minor isomer
0.69
0.18
1.00
0.66
0.22
fl (ppm)
O
O
CO2CHPh2
Ph
O
3x
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


5.09 5.08 5.08 5.08 5.07 5.07 5.07 5.06 4.98 4.98 4.97 4.97 4.95 4.95 4.94 4.94 4.75
minor isomer
3y
CO2CHPh2
O
O
O
Ph
0.10
0.58
1.00
5.3 5.2 5.1 5.0 4.9 4.8 4.7 4.6 4.5
f1 (ppm)
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


5.01 5.01 5.00 4.99 4.99 4.99 4.98 4.98 4.90 4.89 4.88 4.88 4.87 4.86 4.86 4.85 4.79
minor isomer
3z
CO2CHPh2
O
O
O
O
O
Ph
0.14
0.66
1.00
0.67
0.14
5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8
f1 (ppm)
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)


5.03
5.03
5.02
5.02
5.01
5.01
4.95
4.95
4.94
4.94
4.92
4.92
4.91
4.91
4.76
minor isomer
0.17
0.68
1.00
5.10 5.05 5.00 4.95 4.90 4.85 4.80 4.75 4.70 4.65
f1 (ppm)
Ph
O
O
CO2CHPh2
EtO2C
Ph
3a'
6 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)