Supporting Information

Lewis Base Mediated Halogenation/Semipinacol Rearrangement of Diazo Compounds: A New Access to α-Halo-Quaternary Ketones

Haibin Mao,[†] Zhongkai Tang,[†] Hongwen Hu,[†] Yixiang Cheng,[†] Wen-Hua Zheng,[†]

and Chengjian Zhu*[,†,‡]

[†] School of Chemistry and Chemical Engineering, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, 210093 P. R. China

[‡]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai, 200032, P. R. China

Fax: (+86)25-83594886, E-mail: cjzhu@nju.edu.cn

Contents

General information

All reagents and all solvents were obtained from commercial suppliers and used without further purification except as indicated below. Reactions were monitored by TLC on silica gel plates (GF254). ^{1}H ,^{13}C and ^{19}F-NMR spectra were recorded on a Bruker Avance instrument (400 MHz, 100 MHz and 376 MHz, respectively) and internally referenced to tetramethylsilane signal or residual protio solvent signals. ^{1}H-NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) with the solvent signal as the internal standard ($CDCl_3$ at 7.26 ppm). ^{13}C-NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.00 ppm). Data are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (double of doublet), br (broad) or m (multiplets), coupling constants (Hz) and integration. HPLC analysis were performed on a chiral column (Daicel Chiralpak OD-H, AD-H, IA-H, IB-H, IC-H column, Chromatography Interface 600 Series Link and Series 200 pump), with Series 200 UV/VIS detection at 254 nm. Optical rotations were measured on Rudolph Research Analytical Autopol III Automatic Polarimeter with a 50 mm cell. HRESIMS were recorded on an Agilent 6210 TOF LC/MS equipped with an electrospray ionization (ESI) probe operating in positive or negative ion mode.

Experimental section

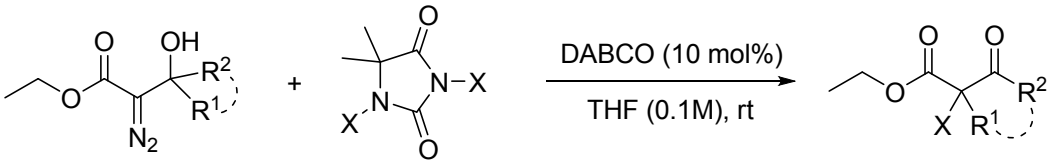
Materials

α-diazo alcohols **2** were prepared according to the literature.[1]

Electrophilic halogen source were purchased from TCI.

Cinchona alkaloids catalysts were purchased from Sigma-Aldrich.

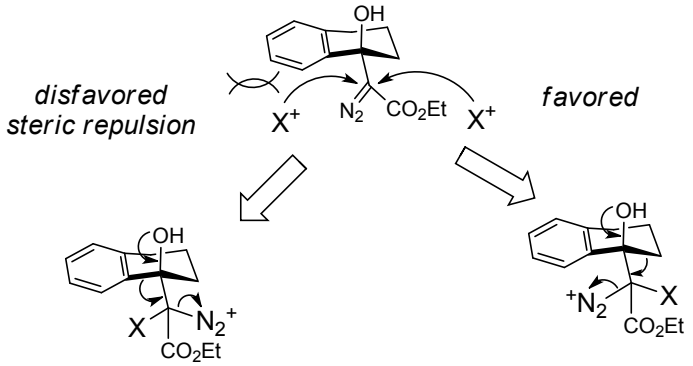
General procedure for the halogenation/semipinacol rearrangement catalyzed by DABCO



2 **3a**: X = Cl **3b**: X = Br **4**

Electrophilic halogen source **3a**/**3b** (0.25 mmol) was added to a stirring solution of DABCO (0.02 mmol), α-diazo alcohols **2** (0.2 mmol) in THF (2.0 mL) at room temperature. The reaction was monitored by thin layer chromatography. After the reaction was considered complete, the crude reaction mixture was filtered, and the solution was concentrated under vacuum. The residue was then purified by flash chromatography on silica gel (PE/Et_2O = 15:1) to give the corresponding product **4**.

Possible reasons for the results that alkyl migration occurred dominantly, in the case of the diazo compound derived from α-tetralone.

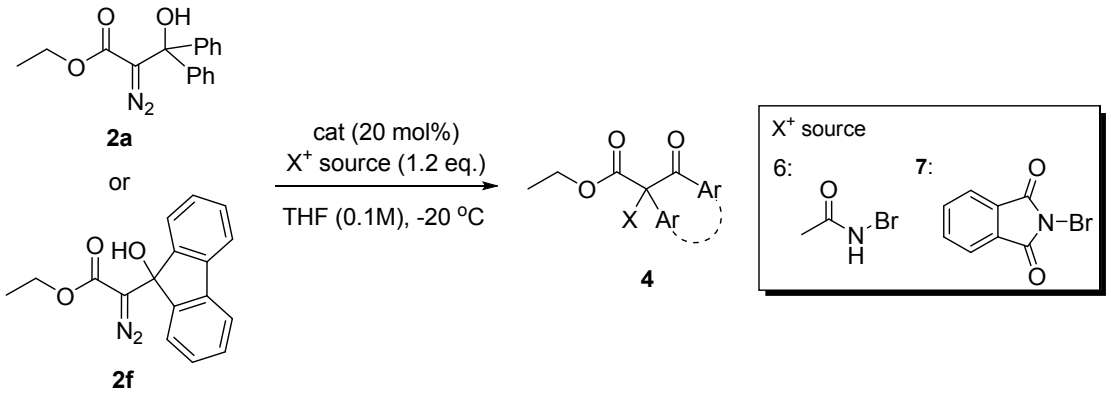


we envisioned that there are two major factors, which resulting in the chemoselectivity of migration. I) The steric repulsion induced alkyl-face selective

electrophilic halogen addition of diazo carbon. II) The rule of trans-migration in the semipinacol rearrangement.

Efforts to the catalytic asymmetric version of this halogenation/semipinacol rearrangement

Table S1 Screening for the Optimal Catalyst.[a]



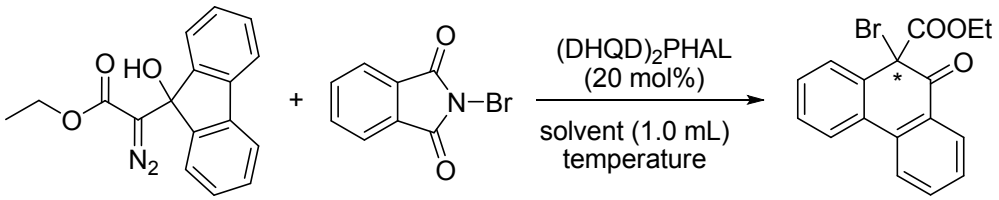
entry	cat	X^+ source	substrate	*t* (h)	yield (%)[b]	*ee* (%)[c]
1	$(DHQD)_2PHAL$	**3b**	**2a**	36	71	6
2	$(DHQD)_2AQN$	**3b**	**2a**	36	70	3
3	$(DHQD)_2PYR$	**3b**	**2a**	36	71	2
4	$(DHQ)_2PHAL$	**3b**	**2a**	36	72	-5[d]
5	$(DHQ)_2AQN$	**3b**	**2a**	36	75	-2[d]
6	$(DHQD)_2PHAL$	**6**	**2a**	60	48	9
7	$(DHQD)_2AQN$	**6**	**2a**	60	51	-8[d]
8	$(DHQD)_2PYR$	**6**	**2a**	60	43	4
9	$(DHQ)_2PHAL$	**6**	**2a**	60	46	-7[d]
10	$(DHQ)_2AQN$	**6**	**2a**	60	55	8
11	$(DHQD)_2PHAL$	NBS	**2a**	36	76	7
12	$(DHQD)_2PHAL$	**7**	**2a**	60	47	12
13	$(DHQD)_2PHAL$	**3a**	**2a**	48	72	2
14[e]	$(DHQD)_2PHAL$	NCS	**2a**	48	41	0

15	**$(DHQD)_2PHAL$**	**7**	**2f**	**1**	**73**	**13**

[a] The reaction was carried out with 0.10 mmol of **2a**/**2f**, 0.12 mmol of X^+ source, 20 mol % of cat (0.02 mmol) in THF (1.0 mL) at -20℃. [b] Yield of isolated product. [c] *ee* values were determined by chiral HPLC analysis. [d] The opposite configuration. [e] The reaction was performed at room temperature.

Initially, we examined a number of cinchona alkaloid derivatives for enantioinduction of the reaction (Table S1, entries 1-10). This led to identification of hydroquinidine 1,4-phthalazinediyl diether ($(DHQD)_2PHAL$) as the optimal catalyst, which provided the desired product in 48% yield with 9% ee when employing N-bromoacetamide **6** as the bromine source (Table S1, entry 6). To further increase the reaction enantioselectivity, various electrophilic halogen source was screened with $(DHQD)_2PHAL$ (Table S1, entries 1, 6, 11-14). The experimental results revealed that highly active (**3b**) or low active (NCS) halogen source blocked the stereocontrol of the reaction (Table S1, entries 1, 14). N-Bromophthalimide **7** gave the highest enantioselectivity (Table S1, entry 12). When highly active substrate **2f** was used instead of **2a**, the yield could be effectively improved.

Table S2 Further optimization of the asymmetric reaction conditions.[a]



2f (0.1 mmol) **7** (0.02 mmol X 6) **4o**

entry	solvent	T(℃)	yield (%)[b]	*ee*(%)[c]
1	toluene	rt	52	19
2	CCl_4	rt	49	19

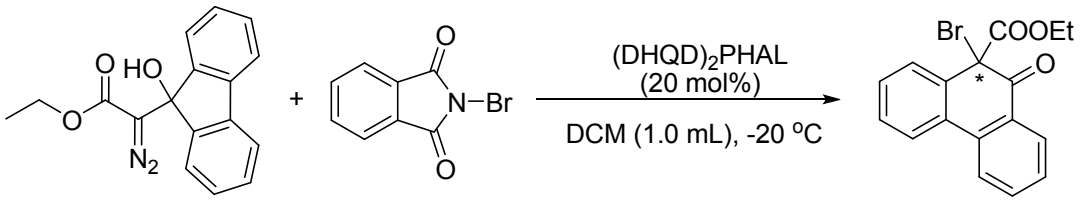
3	$CHCl_3$	rt	81	45
4	DCM	rt	84	63
5	THF	rt	73	16
6	1,4-dioxane	rt	72	16
7	MeCN	rt	75	35
8	DCM	35	83	59
9	DCM	0	85	68
10	DCM	-20	86	70
11	DCM	-40	86	41
12	DCM	-78	86	20
13[d]	**DCM**	**-20**	**86**	**72**

[a] 0.12 mmol **7** was added to a solution (0.10 M) of 0.10 mmol **2f** and 20 mol % $(DHQD)_2PHAL$ (0.02 mmol) in six portions (0.02 mmol every 1 h, reaction time of 6 h). [b] Yield of isolated product. [c] *ee* values were determined by chiral HPLC analysis. [d] 0.12 mmol **7** was added in twelve portions (0.01 mmol every 15 min, reaction time of 3 h).

During the optimization of the reaction conditions, the enantioselectivity was not satisfactory. We envisioned that the low enantioselectivity result from the background reaction. To minimize the background reaction as much as possible, 1.2 equiv. **7** was added to the reaction in six portions (0.2 equiv. every 1 h), which effectively increased the ee. After screening some solvents (Table S2, entries 1-7), it was found that the reaction conducted in DCM gave the highest enantioselectivity (63% ee). Lowering the reaction temperature from 25 to -20℃ could further increased the

enantioselectivity to 70% ee (Table S2, entries 8-12). The enantioselectivity could be somewhat improved by reducing the amount of each feeding (Table S2, entry 13).

General procedure for the asymmetric bromination/semipinacol rearrangement of 2f catalyzed by $(DHQD)_2PHAL$

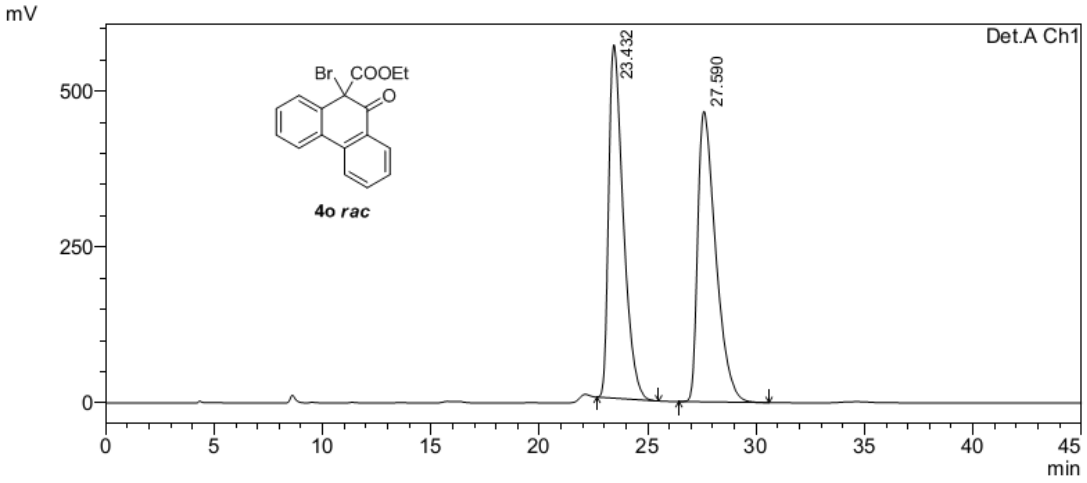


2f (0.1 mmol) + **7** (0.01 mmol X 12) → **4o** 86% yield 72% ee

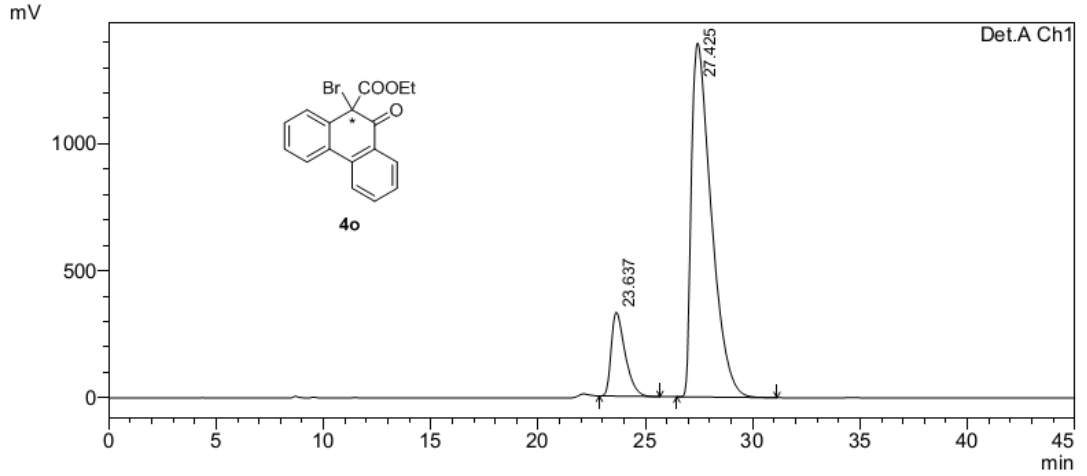
To a round-bottom flask were added **2f** (29.4 mg, 0.1 mmol), catalyst $(DHQD)_2PHAL$ (15.5 mg, 0.02 mmol) and DCM (1.0 mL). The mixture was stirred for 10 minutes at -20℃. And then 0.12 mmol **7** was added in twelve portions (0.01 mmol every 15 min, reaction time of 3 h). After the reaction was considered complete, the crude reaction mixture was filtered, and the solution was concentrated under vacuum. The residue was then purified by flash chromatography on silica gel (PE/Et_2O = 10:1) to give the corresponding product **4o** (29.7 mg, 86% yield, 72% ee).

HPLC Analysis:

HPLC (Chiralpak OD-H, hexane/*i*-PrOH = 97:3, flow rate 0.75 mL/min, λ = 254 nm), retention time: 27.43 min (major), 23.64 min (minor). $[\alpha]_D^{25.0}$ = 9.57 (c = 0.38, EA, 72% ee).



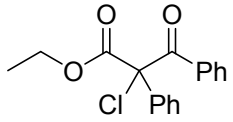
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.432	26449437	566838	49.646	54.893
2	27.590	26826209	465776	50.354	45.107
Total		53275645	1032614	100.000	100.000



Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.637	14842881	330498	14.180	19.175
2	27.425	89828719	1393104	85.820	80.825
Total		104671599	1723602	100.000	100.000

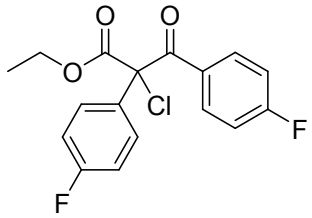
Characterization of compounds 4



Ethyl 2-chloro-3-oxo-2,3-diphenylpropanoate (4a)

oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.85-7.83 (m, 2H), 7.60-7.58 (m, 2H), 7.50-7.46 (m, 1H), 7.39-7.31 (m, 5H), 4.29-4.23 (m, 2H), 1.18 (t, J = 7.2Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 190.3, 167.2, 135.3, 133.3, 133.1, 130.4, 129.1, 128.4, 128.2, 128.0, 75.8, 63.4, 13.8.

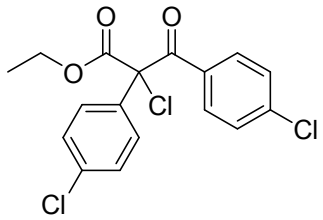
HRMS: exact mass calculated: 325.0607 $[M+Na]^+$, found 325.0604.



Ethyl 2-chloro-2,3-bis(4-fluorophenyl)-3-oxopropanoate (4b)

oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.90-7.87 (m, 2H), 7.58-7.54 (m, 2H), 7.11-7.02 (m, 4H), 4.32-4.24 (m, 2H), 1.21 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 188.6, 166.9, 164.4, 163.0 (d, J = 248.4 Hz), 133.2 (d, J = 10.3 Hz), 131.0 (d, J = 3.7 Hz), 130.0 (d, J = 7.5 Hz), 129.1 (d, J = 8.4 Hz), 115.6 (d, J = 6.4 Hz), 115.4 (d, J = 5.9 Hz), 74.9, 63.6, 13.8. ^{19}F-NMR (376 MHz, $CDCl_3$): δ (ppm) -103.47, -112.01 .

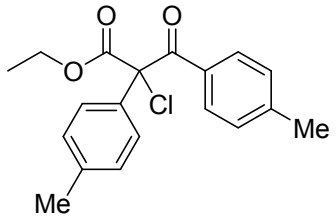
HRMS: exact mass calculated: 361.0419 $[M+Na]^+$, found 361.0415.



Ethyl 2-chloro-2,3-bis(4-chlorophenyl)-3-oxopropanoate (4c)

oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79-7.77 (m, 2H), 7.52-7.49 (m, 2H), 7.38-7.36 (m, 2H), 7.35-7.33 (m, 2H), 4.32-4.24 (m, 2H), 1.22 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 188.8, 166.6, 140.1, 135.5, 133.5, 131.8, 131.1, 130.0, 129.4, 128.7, 74.9, 63.8, 13.8.

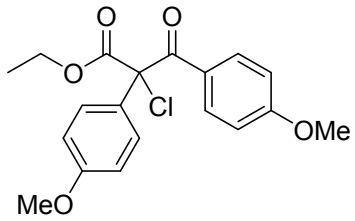
HRMS: exact mass calculated: 392.9828 $[M+Na]^+$, found 392.9820.



Ethyl 2-chloro-3-oxo-2,3-dip-tolylpropanoate (4d)

oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 4.30-4.22 (m, 2H), 2.35 (s, 6H), 1.20 (t, J = 6.8 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 190.1, 167.4, 144.3, 139.0, 132.6, 130.7, 130.5, 129.0, 128.9, 127.9, 75.8, 63.8, 21.7, 21.2, 13.8.

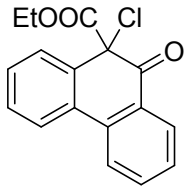
HRMS: exact mass calculated: 353.0920 $[M+Na]^+$, found 353.0917.



Ethyl 2-chloro-2,3-bis(4-methoxyphenyl)-3-oxopropanoate (4e)

oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.85-7.83 (m, 2H), 7.50-7.48 (m, 2H), 6.90-6.87 (m, 2H), 6.82-6.80 (m, 2H), 4.30-4.22 (m, 2H), 3.81 (s, 3H), 3.80 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 189.2, 167.6, 163.5, 159.9, 133.0, 129.4, 127.7, 125.6, 113.7, 113.4, 75.7, 63.2, 55.5, 55.3, 13.8.

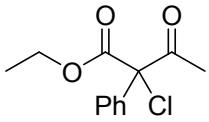
HRMS: exact mass calculated: 385.0819 $[M+Na]^+$, found 385.0817.



Ethyl 9-chloro-10-oxo-9,10-dihydrophenanthrene-9-carboxylate (4f)

light yellow crystals (from $CHCl_3$/PE), mp: 107.5-109.1℃. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 8.14 (dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, 1H), 8.01 (t, J = 7.6 Hz, 2H), 7.76-7.71 (m, 1H), 7.53-7.46 (m, 3H), 7.41 (td, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 1H), 4.32-4.22 (m, 2H), 1.18 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 189.0, 166.7, 136.4, 135.6, 134.5, 130.3, 129.7, 129.5, 129.3, 129.1, 129.0, 127.4, 124.2, 123.5, 69.4, 63.6, 13.8.

HRMS: exact mass calculated: 323.0451 $[M+Na]^+$, found 323.0449.

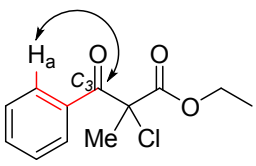


Ethyl 2-chloro-3-oxo-2-phenylbutanoate (4g)

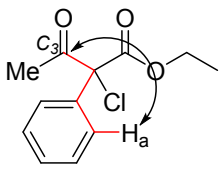
oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.52-7.49 (m, 2H), 7.41-7.39 (m, 3H), 4.35-4.29 (m, 2H), 2.33 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 197.5, 167.0, 133.9, 129.1, 128.4, 127.7, 77.3, 63.3, 25.8, 13.9.

HRMS: exact mass calculated: 263.0451 $[M+Na]^+$, found 263.0443.

The selectivity of migration was determined by the analysis of HMBC (Heteronuclear Multiple Bond Correlation) experiment:

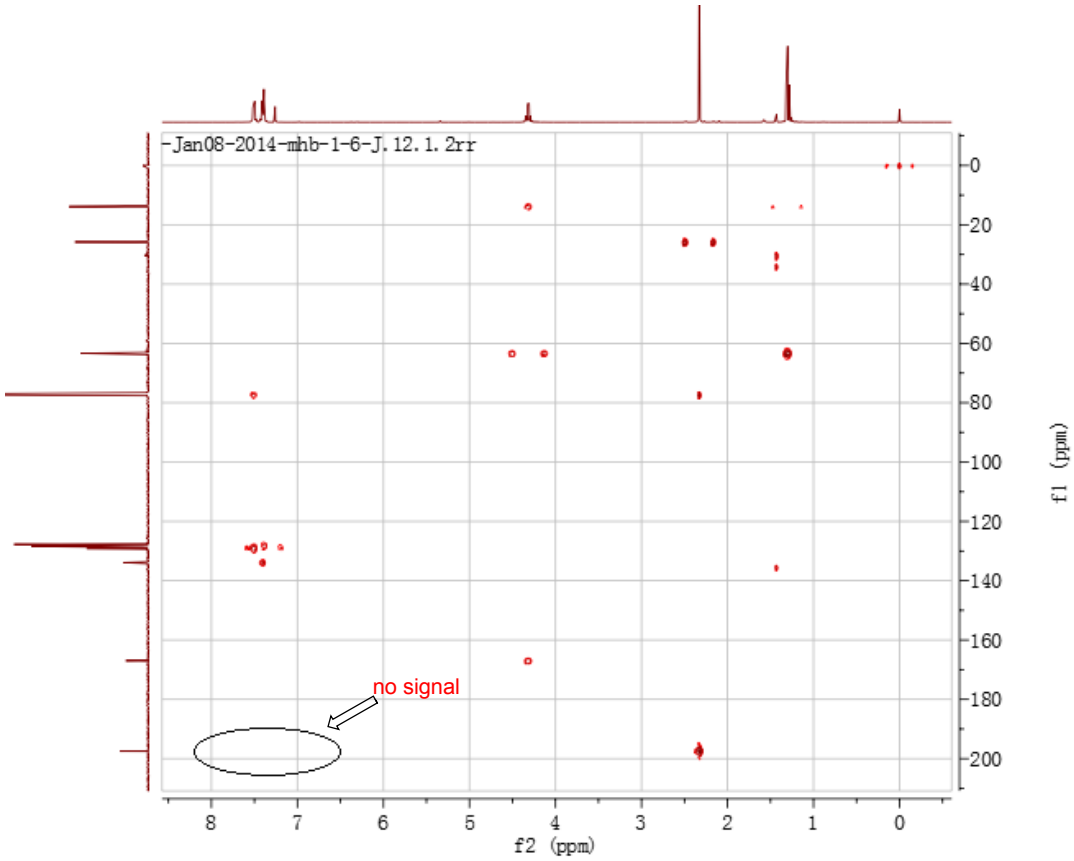


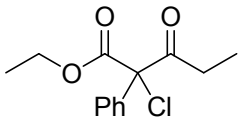
For the product derived from alkyl migration H_a and C_3 would show HMBC signal



For the product derived from phenyl ring migration H_a and C_3 would not show HMBC signal

The actual spectra: (H_a and C_3 did not show HMBC signal)

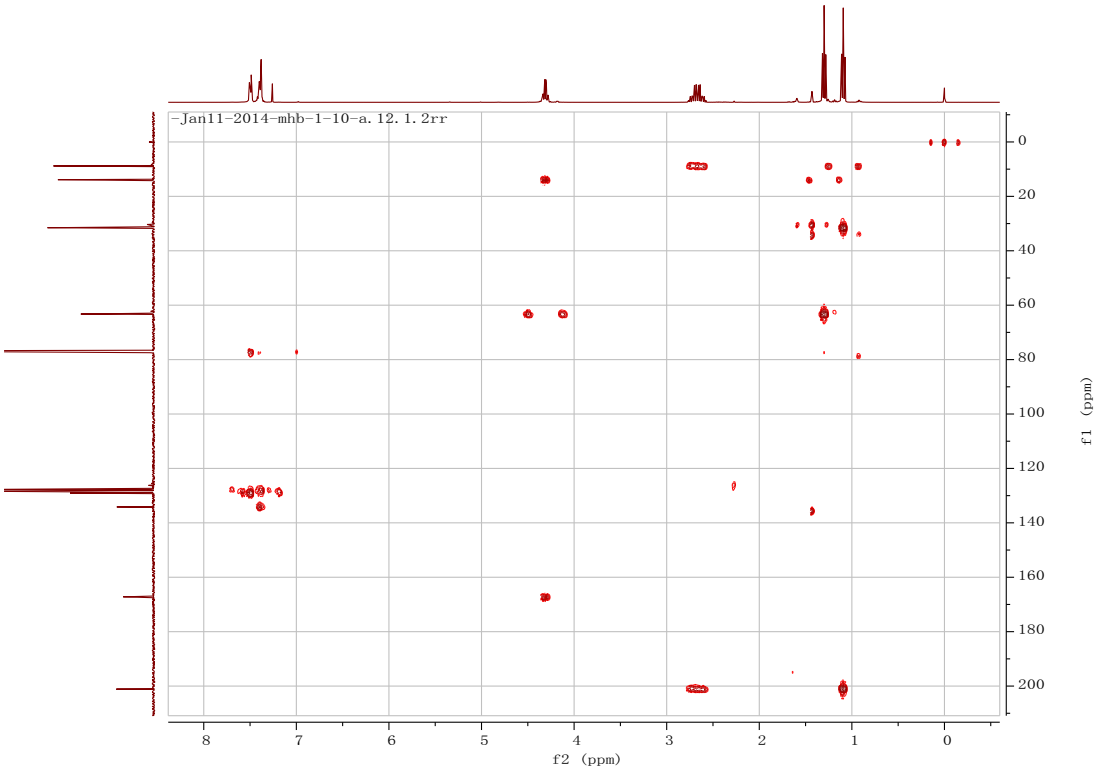


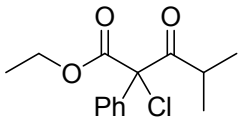


Ethyl 2-chloro-3-oxo-2-phenylpentanoate (4h)

oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.51-7.48 (m, 2H), 7.42-7.37 (m, 3H), 4.34-4.28 (m, 2H), 2.74-2.59 (m, 2H), 1.30 (t, J = 7.2 Hz, 3H), 1.09 (t, J = 7.6 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 201.1, 167.2, 134.2, 129.1, 128.4, 127.8, 77.4, 63.4, 31.5, 13.9, 8.8.

HRMS: exact mass calculated: 277.0607 $[M+Na]^+$, found 277.0603.

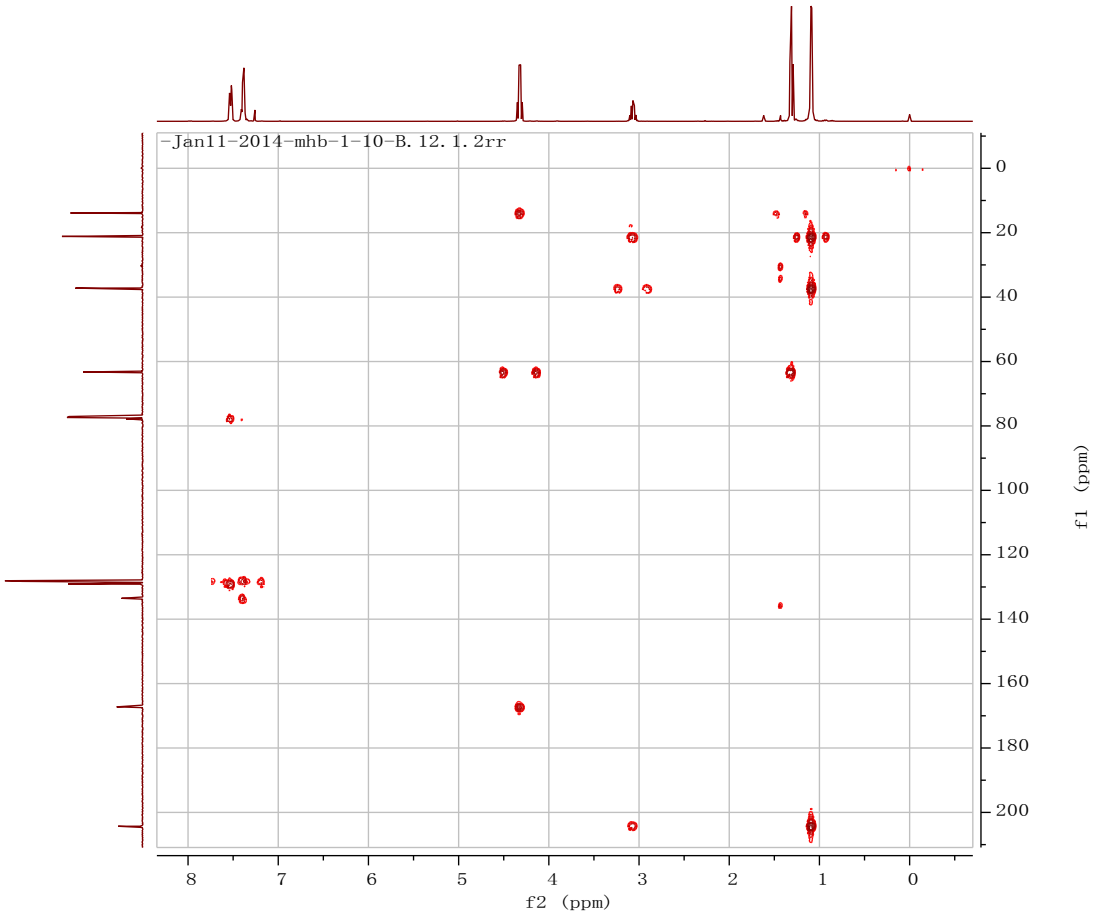


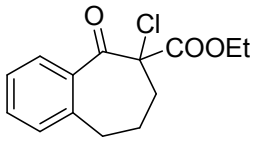


Ethyl 2-chloro-4-methyl-3-oxo-2-phenylpentanoate (4i)

oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.54-7.52 (m, 2H), 7.40-7.37 (m, 3H), 4.32 (q, J = 7.2 Hz, 2H), 3.07 (m, 1H), 1.31 (t, J = 7.2 Hz, 3H), 1.10 (d, J = 3.6 Hz, 3H), 1.08 (d, J = 3.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 204.3, 167.2, 133.5, 129.1, 128.3, 128.1, 77.8, 63.2, 37.2, 21.2, 21.1, 13.9.

HRMS: exact mass calculated: 291.0764 $[M+Na]^+$, found 291.0759.



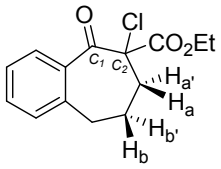


Ethyl 6-chloro-5-oxo-6,7,8,9-tetrahydro-5H-benzo[7]annulene-6-carboxylate (4j)

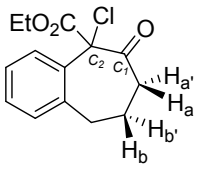
oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.49-7.47 (m, 1H), 7.44-7.40 (m, 1H), 7.32-7.28 (m, 1H), 7.18-7.16 (m, 1H), 4.24-4.19 (m, 2H), 3.02-2.95 (m, 1H), 2.90-2.83 (m, 1H), 2.72-2.65 (m, 1H), 2.31-2.25 (m, 1H), 2.19-2.09 (m, 1H), 2.03-1.93 (m, 1H), 1.21 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 198.8, 167.9, 138.1, 138.0, 132.0, 129.3, 129.1, 126.8, 74.5, 62.9, 36.0, 32.6, 22.9, 13.8.

HRMS: exact mass calculated: 289.0607 $[M+Na]^+$, found 289.0604.

The selectivity of migration was determined by the analysis of HMBC (Heteronuclear Multiple Bond Correlation) experiment:

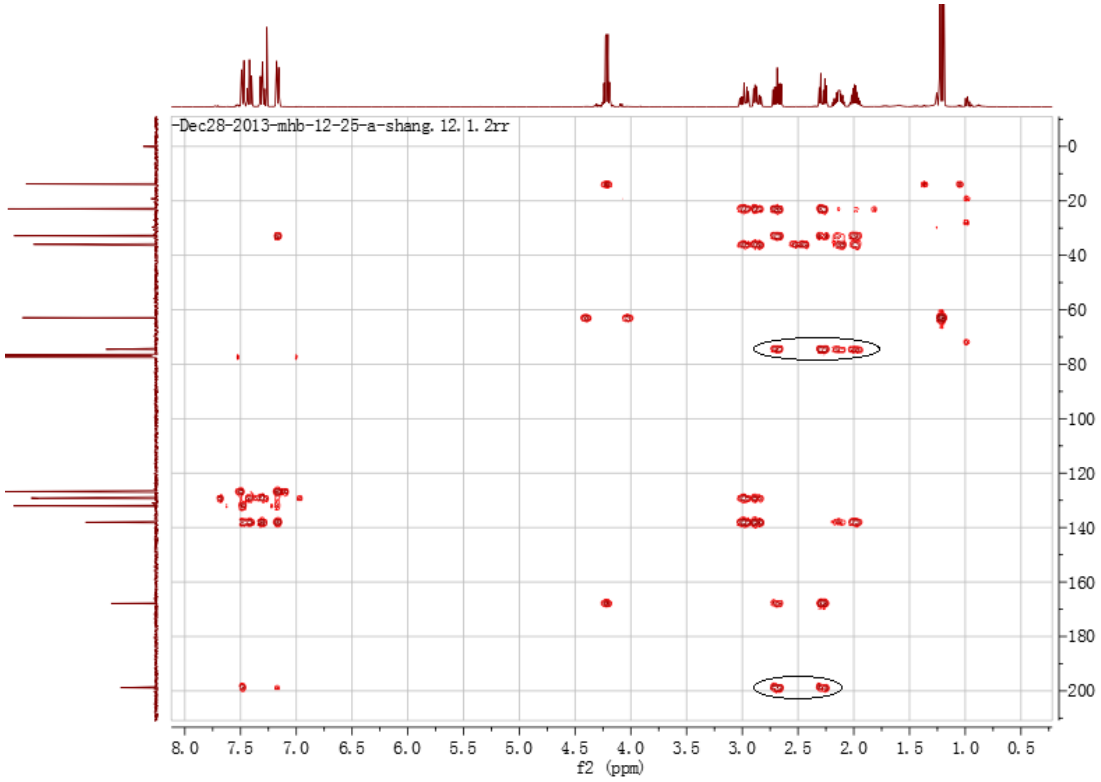


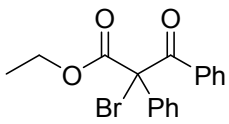
For the product derived from alkyl migration
C_1 and H_a, $H_{a'}$ would show HMBC signal
C_1 and H_b, $H_{b'}$ would not show HMBC signal
C_2 and H_a, $H_{a'}$, H_b, $H_{b'}$ would show HMBC signal



For the product derived from phenyl ring migration
C_1 and H_a, $H_{a'}$, H_b, $H_{b'}$ would show HMBC signal
C_2 and H_a, $H_{a'}$ would show HMBC signal
C_2 and H_b, $H_{b'}$ would not show HMBC signal

The actual spectra: (C_1 and H_a, $H_{a'}$ showed HMBC signal. C_1 and H_b, $H_{b'}$ did not show HMBC signal. C_2 and H_a, $H_{a'}$, H_b, $H_{b'}$ showed HMBC signal)

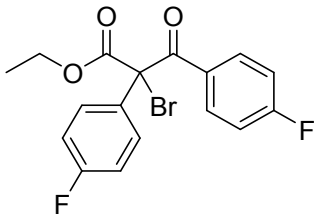




Ethyl 2-bromo-3-oxo-2,3-diphenylpropanoate (4k)

oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.83-7.81 (m, 2H), 7.65-7.63 (m, 2H), 7.49-7.46 (m, 1H), 7.36-7.31 (m, 5H), 4.26-4.20 (m, 2H), 1.11 (t, J = 7.2Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 189.6, 167.4, 136.0, 133.4, 133.2, 130.3, 129.1, 129.0, 128.4, 128.2, 69.3, 63.3, 13.6.

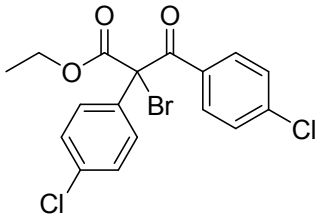
HRMS: exact mass calculated: 369.0102 $[M+Na]^+$, found 369.0099.



Ethyl 2-bromo-2,3-bis(4-fluorophenyl)-3-oxopropanoate (4l)

oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.88-7.85 (m, 2H), 7.63-7.59 (m, 2H), 7.08-7.01 (m, 4H), 4.28-4.22 (m, 2H), 1.15 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 187.9, 167.1, 165.5 (d, J = 255.7 Hz), 162.8 (d, J = 249.2 Hz), 133.1 (d, J = 9.6 Hz), 131.7 (d, J = 3.6 Hz), 131.0 (d, J = 8.7 Hz), 129.4 (d, J = 3.4 Hz), 115.7, 115.5, 68.1, 63.6, 13.6. ^{19}F-NMR (376 MHz, $CDCl_3$): δ (ppm) -103.57, -111.66.

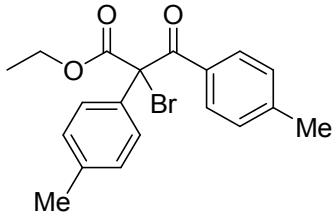
HRMS: exact mass calculated: 404.9914 $[M+Na]^+$, found 404.9910.



Ethyl 2-chloro-2,3-bis(4-chlorophenyl)-3-oxopropanoate (4m)

oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.78-7.76 (m, 2H), 7.56-7.54 (m, 2H), 7.35-7.32 (m, 4H), 4.28-4.22 (m, 2H), 1.16 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 188.1, 166.9, 140.0, 135.4, 134.2, 131.7, 131.3, 130.3, 128.8, 128.7, 68.0, 63.7, 13.7.

HRMS: exact mass calculated: 436.9323 $[M+Na]^+$, found 436.9321.

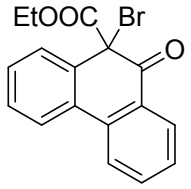


Ethyl 2-bromo-3-oxo-2,3-dip-tolylpropanoate (4n)

oil. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73 (d, J = 8.4 Hz, 2H), 7.52-7.50 (m, 2H), 7.16-7.11 (m, 4H), 4.26-4.19 (m, 2H), 2.35 (s, 3H), 2.34 (s, 3H), 1.13 (t, J = 7.2 Hz,

3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 189.2, 167.6, 144.1, 139.1, 133.3, 130.8, 130.5, 129.1, 128.9, 128.8, 69.5, 63.2, 21.7, 21.2, 13.6.

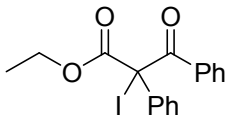
HRMS: exact mass calculated: 397.0415 $[M+Na]^+$, found 397.0412.



Ethyl 9-bromo-10-oxo-9,10-dihydrophenanthrene-9-carboxylate (4o)

yellow block crystals (from $CHCl_3$/PE), mp:117.5-118.4℃. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 8.17 (dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, 1H), 8.03 (t, J = 8.4 Hz, 2H), 7.76-7.72 (m, 1H), 7.53-7.46 (m, 2H), 7.44-7.39 (m, 2H), 4.40-4.30 (m, 2H), 1.24 (t, J = 7.2 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 189.0, 166.5, 136.1, 135.4, 135.1, 130.2, 129.8, 129.4, 129.11, 129.08, 129.0, 127.3, 124.5, 123.5, 63.9, 62.3, 14.0.

HRMS: exact mass calculated: 366.9946 $[M+Na]^+$, found 366.9942.

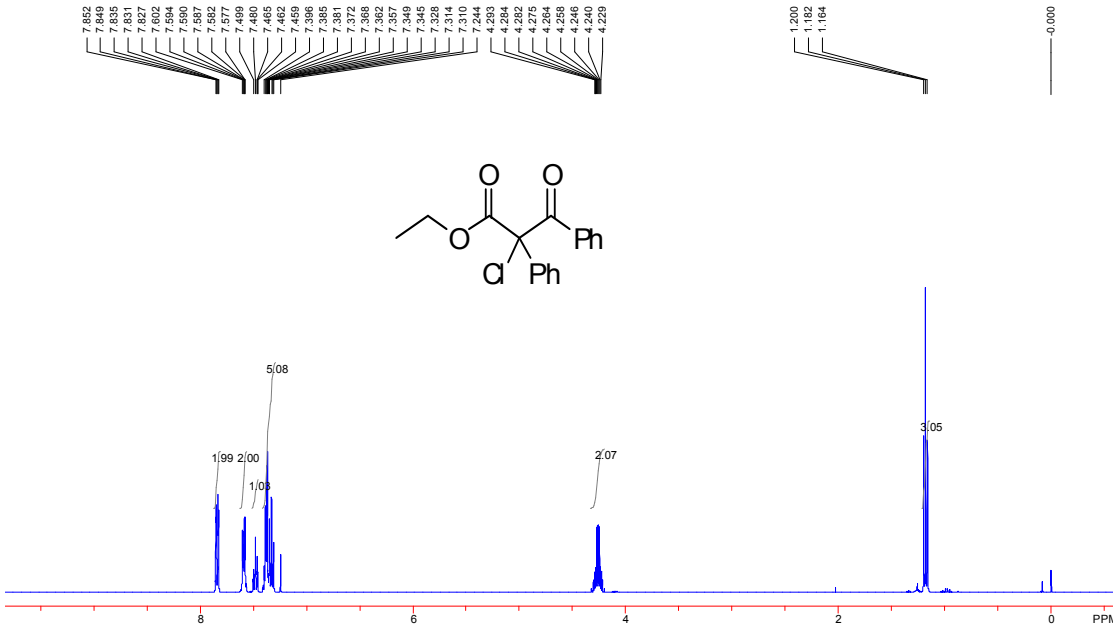


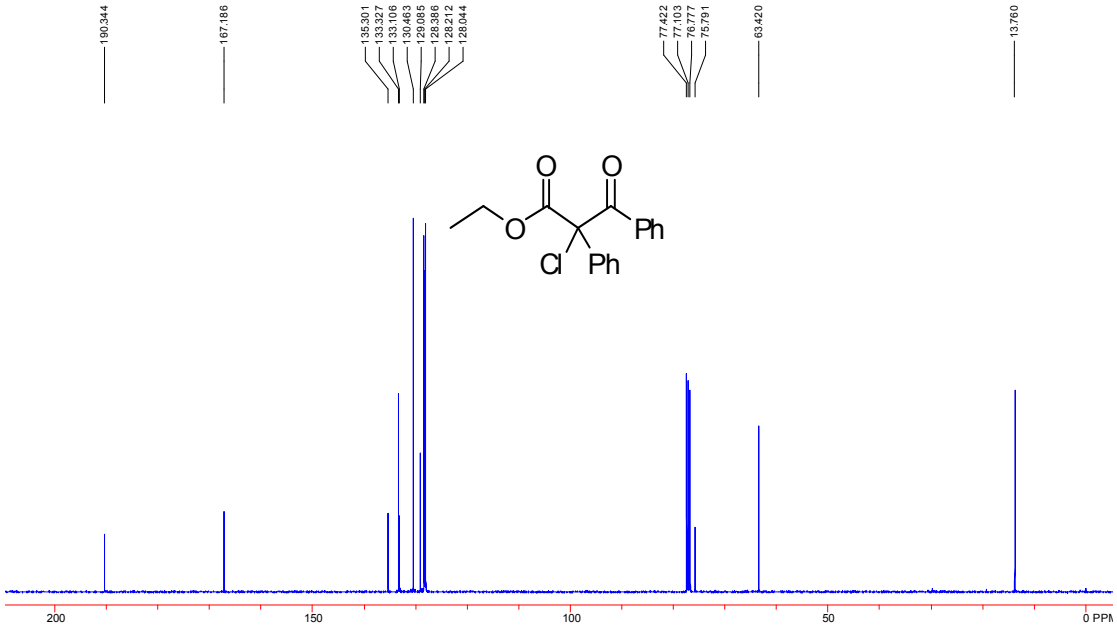
Ethyl 2-iodo-3-oxo-2,3-diphenylpropanoate (4p)

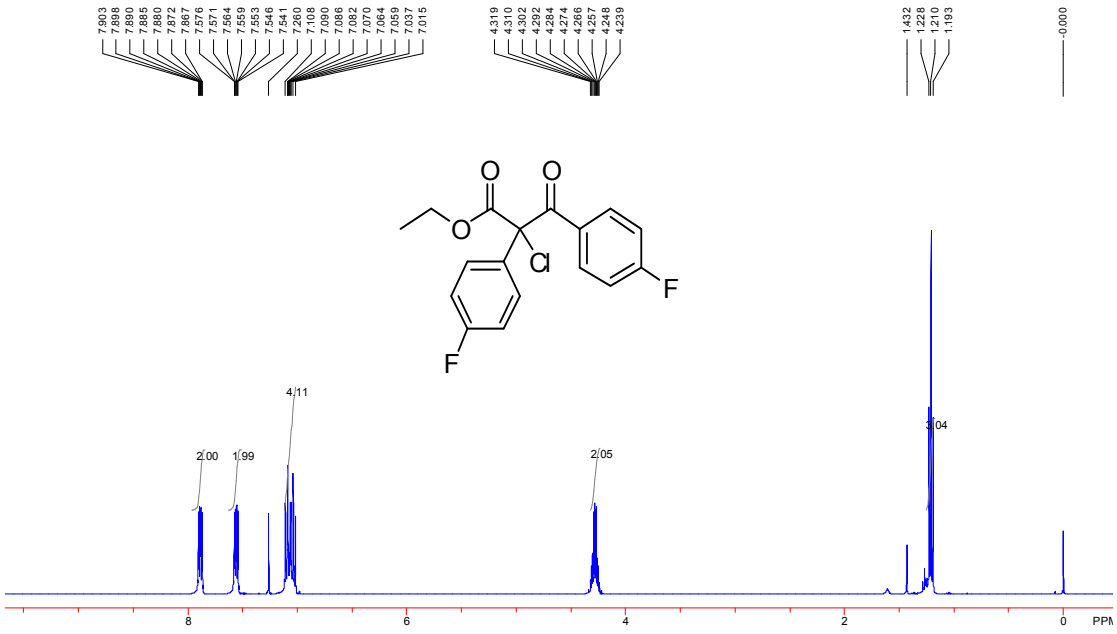
white solid. This compound should be stored in the refrigerator (-20℃) under argon atmosphere. ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) 7.76-7.72 (m, 4H), 7.47-7.43 (m, 1H), 7.32-7.24 (m, 5H), 4.19-4.13 (m, 2H), 0.99 (t, J = 7.2Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) 189.5, 169.3, 138.6, 133.0, 132.2, 130.1, 128.8, 128.69, 128.65, 128.4, 62.8, 55.4, 13.2.

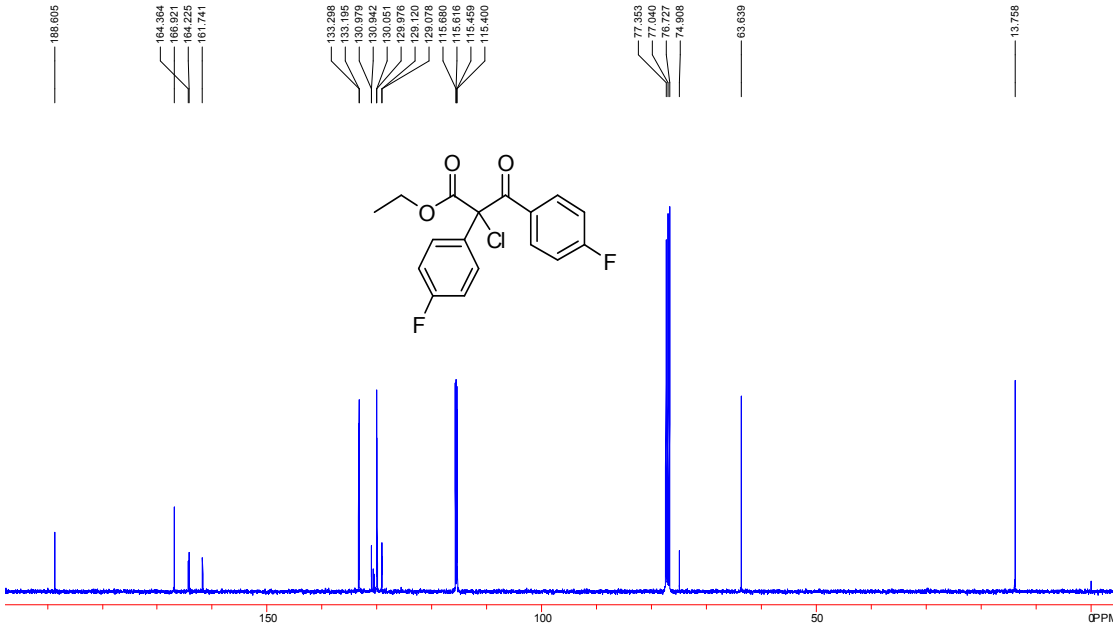
HRMS: exact mass calculated: 416.9964 $[M+Na]^+$, found 416.9960.

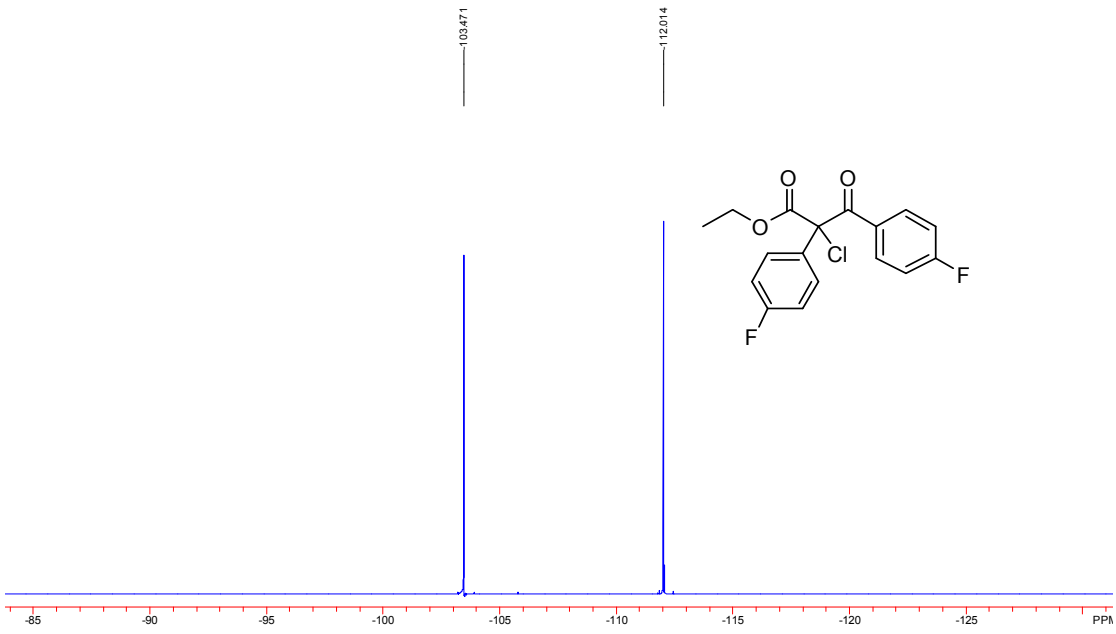
NMR Spectra

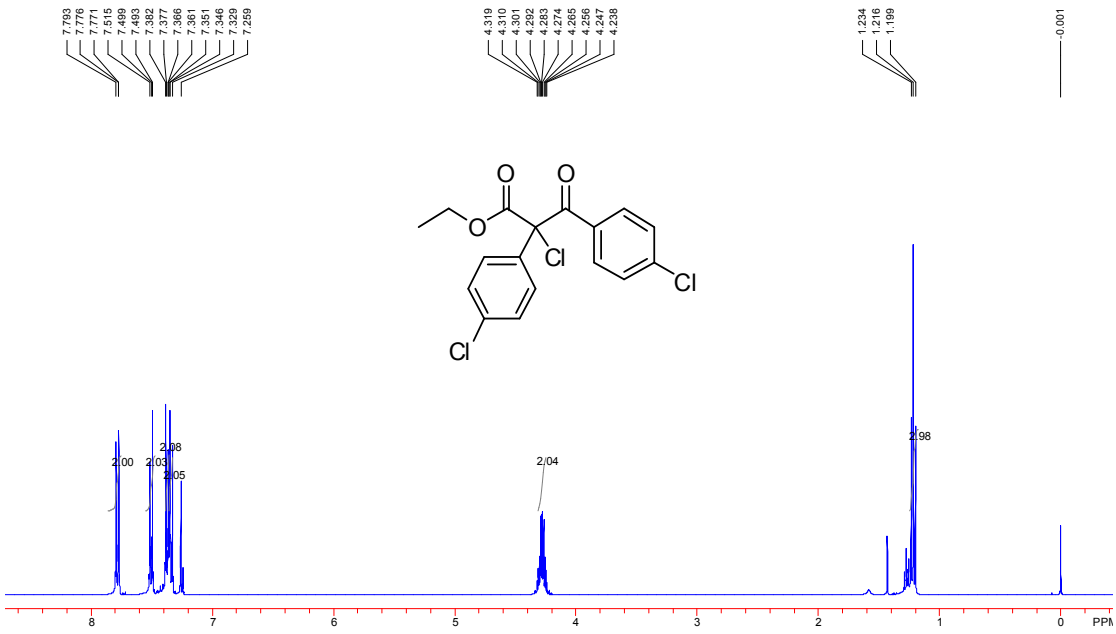

7.852
7.849
7.835
7.831
7.827
7.602
7.594
7.590
7.587
7.582
7.577
7.499
7.480
7.465
7.462
7.459
7.396
7.385
7.381
7.372
7.368
7.362
7.357
7.349
7.345
7.328
7.314
7.310
7.244
4.293
4.284
4.282
4.275
4.264
4.258
4.246
4.240
4.229
1.200
1.182
1.164
0.000
O
O
O
Ph
Cl
Ph
5.08
1.99
2.00
1.03
2.07
3.05
8
6
4
2
0
PPM

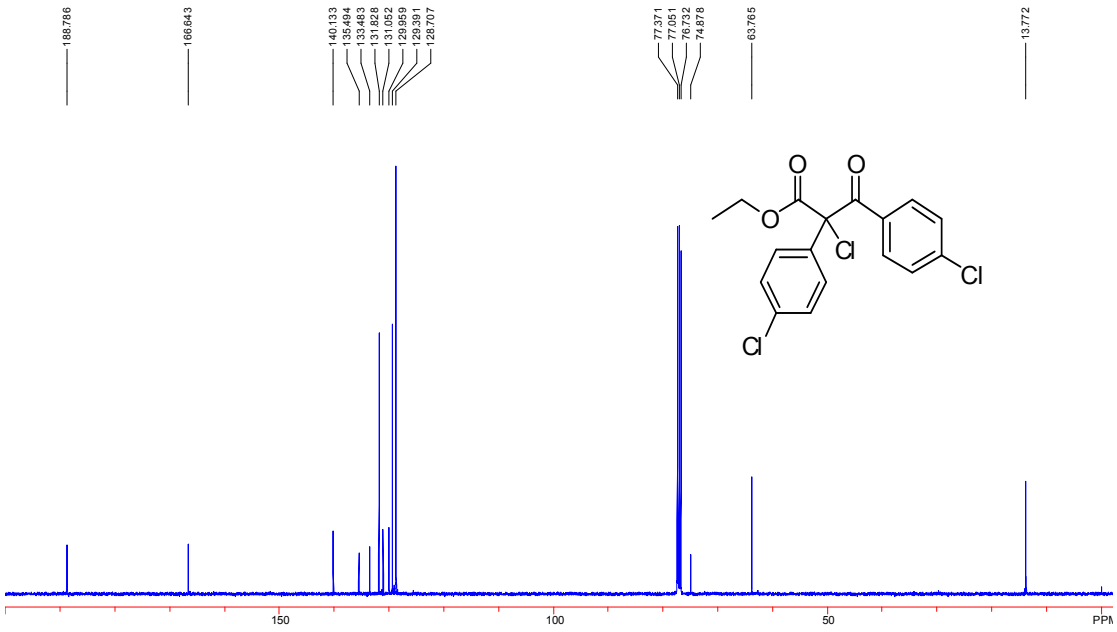

190.344
167.186
135.301
133.327
133.106
130.463
129.085
128.386
128.212
128.044
77.422
77.103
76.777
75.791
63.420
13.760
O
O
O
Ph
Cl
Ph
200
150
100
50
0 PPM

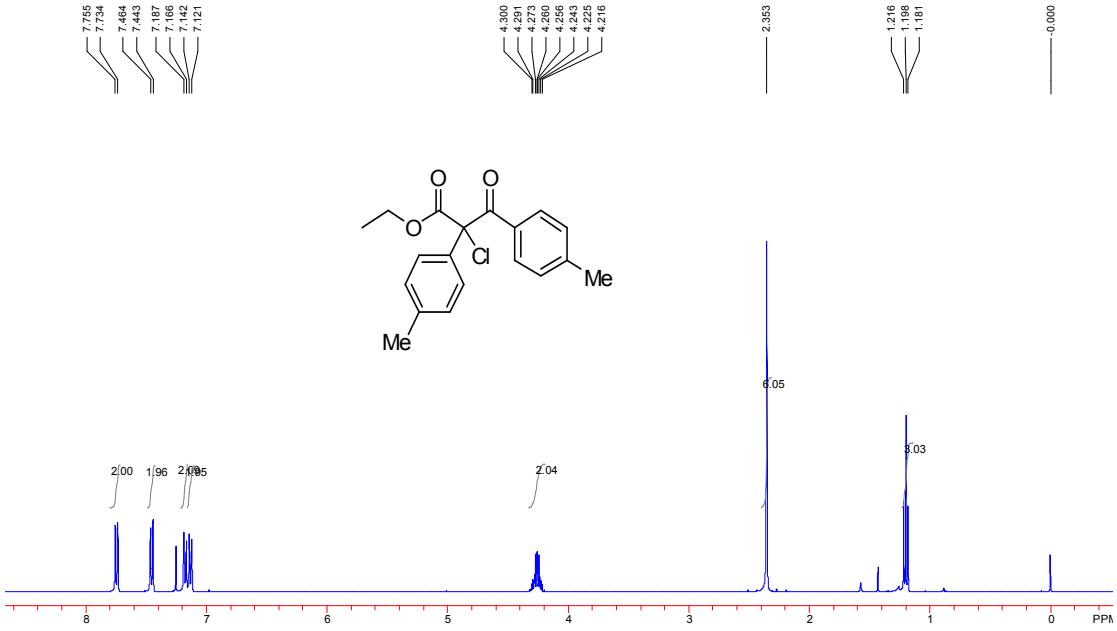

7.903
7.898
7.890
7.885
7.880
7.872
7.867
7.576
7.571
7.564
7.559
7.553
7.546
7.541
7.260
7.108
7.090
7.086
7.082
7.070
7.064
7.059
7.037
7.015
4.319
4.310
4.302
4.292
4.284
4.274
4.266
4.257
4.248
4.239
1.432
1.228
1.210
1.193
0.000
O
O
O
Cl
F
F
4.11
2.00
1.99
2.05
3.04
8
6
4
2
0
PPM

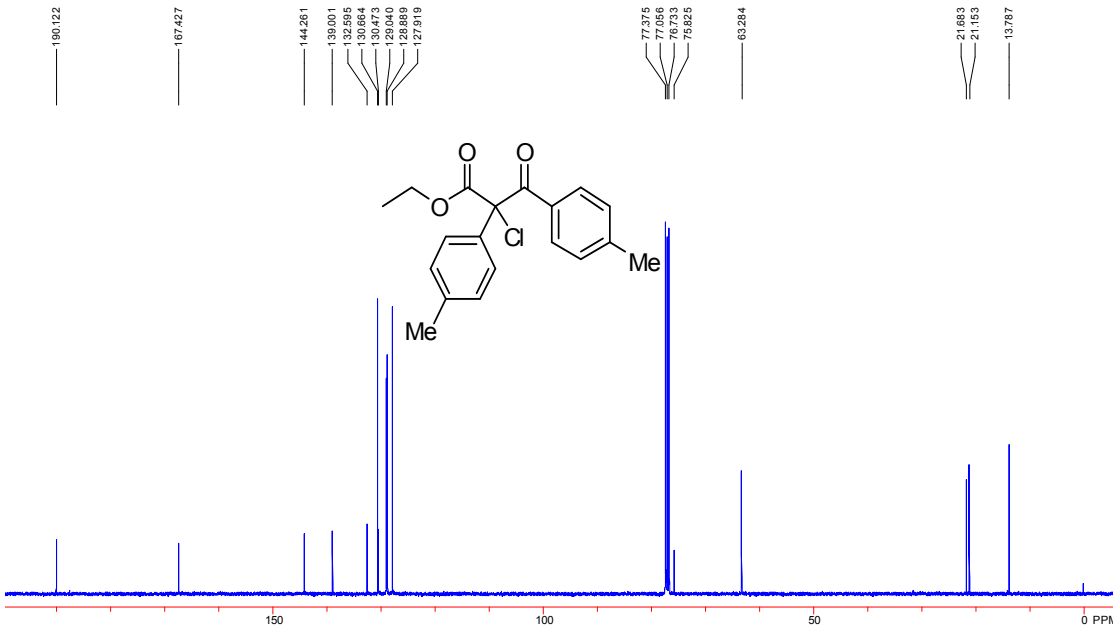

188.605
164.364
164.225
161.741
133.298
133.195
130.979
130.942
130.051
129.976
129.120
129.078
115.680
115.616
115.459
115.400
77.353
77.040
76.727
74.908
63.639
13.758
O
O
O
Cl
F
F
150
100
50
0
PPM

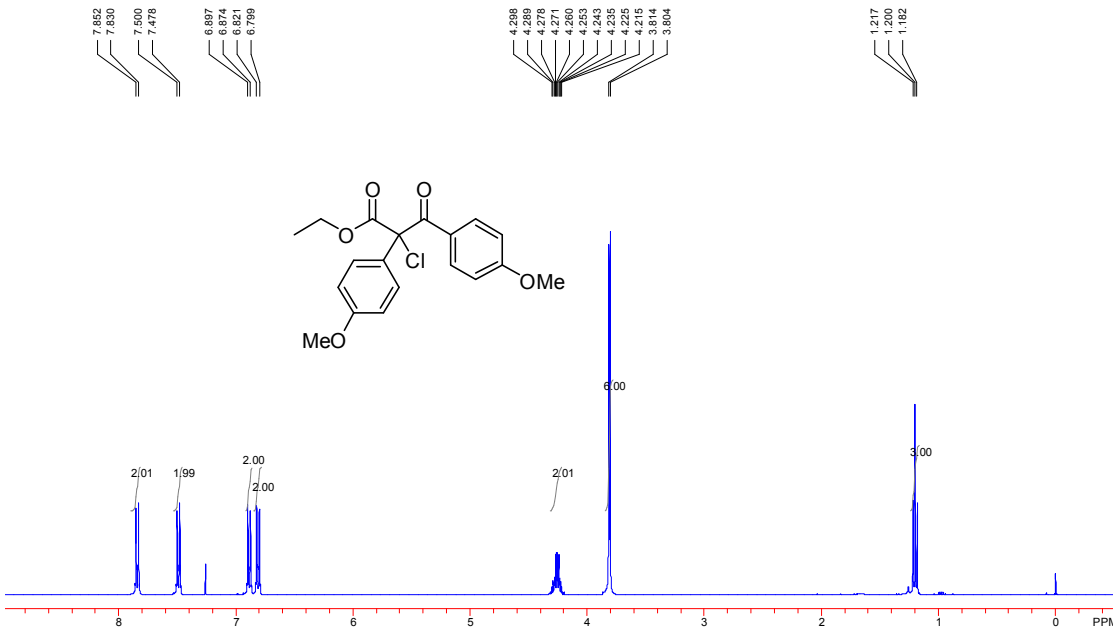

103.471
112.014
O
O
O
Cl
F
F
-85
-90
-95
-100
-105
-110
-115
-120
-125
PPM

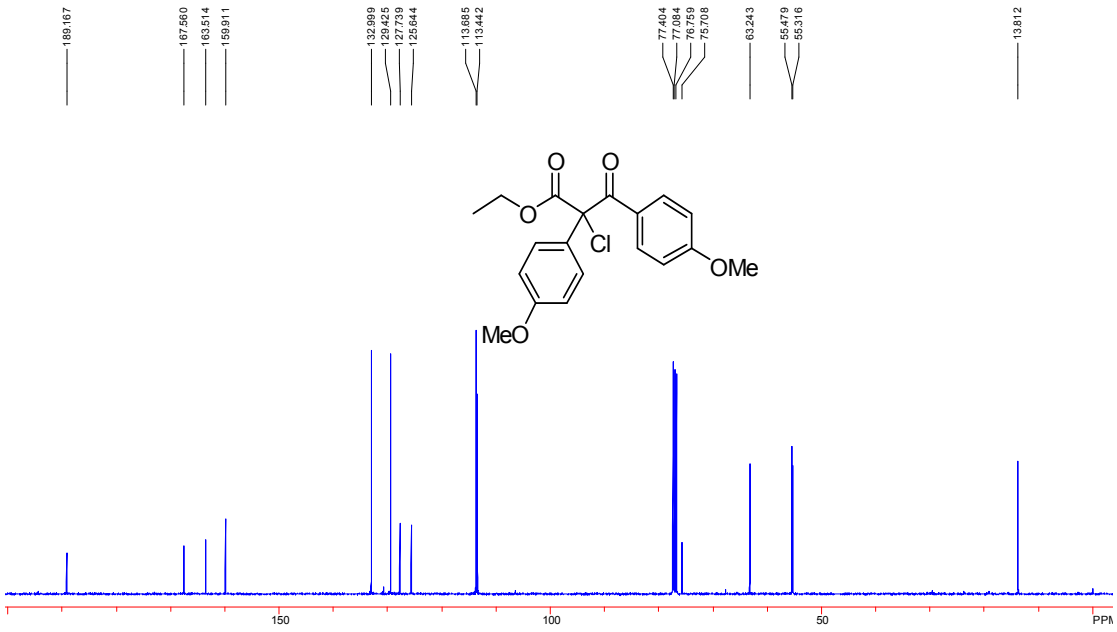

7.793
7.776
7.771
7.515
7.499
7.493
7.382
7.377
7.366
7.361
7.351
7.346
7.329
7.259
4.319
4.310
4.301
4.292
4.283
4.274
4.265
4.256
4.247
4.238
1.234
1.216
1.199
0.001
O
O
O
Cl
Cl
Cl
2.00
2.03
2.08
2.05
2.04
2.98
8
7
6
5
4
3
2
1
0
PPM

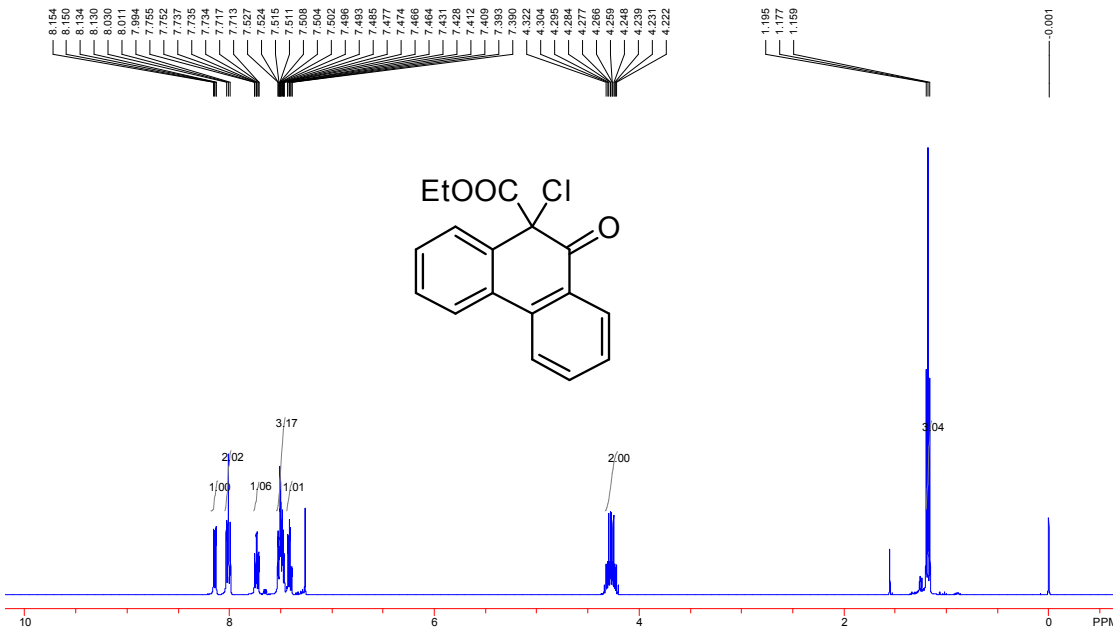

188.786
166.643
140.133
135.494
133.483
131.828
131.052
129.959
129.391
128.707
77.371
77.051
76.732
74.878
63.765
13.772
O
O
O
Cl
Cl
Cl
150
100
50
PPM

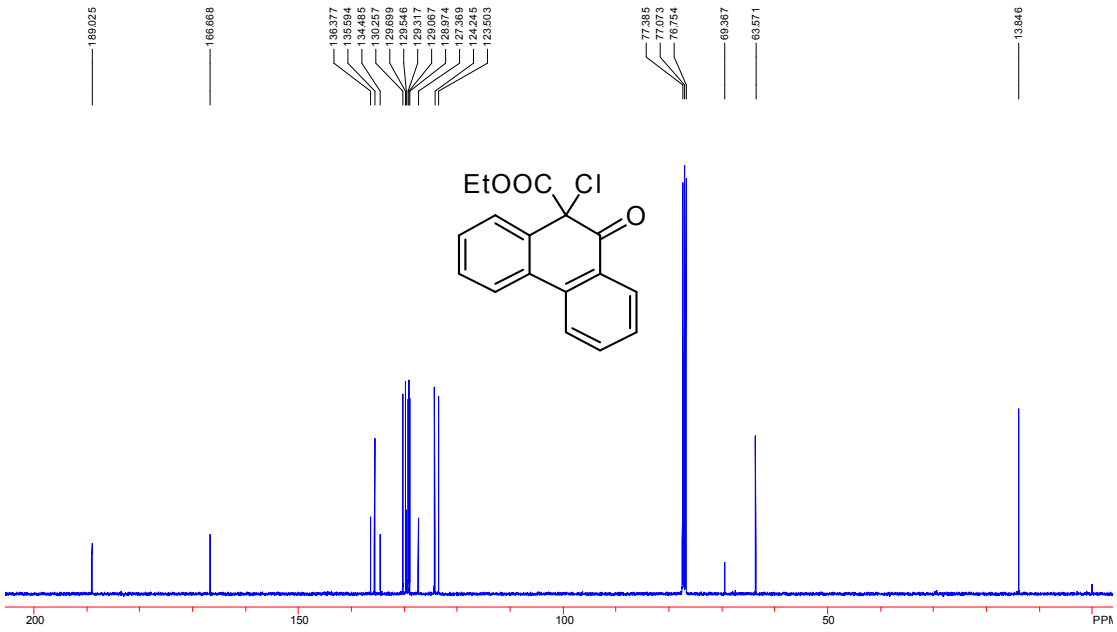

7.755
7.734
7.464
7.443
7.187
7.166
7.142
7.121
4.300
4.291
4.273
4.260
4.256
4.243
4.225
4.216
2.353
1.216
1.198
1.181
0.000
O
O
O
Cl
Me
Me
6.05
3.03
2.00
1.96
2.04
8
7
6
5
4
3
2
1
0
PPM

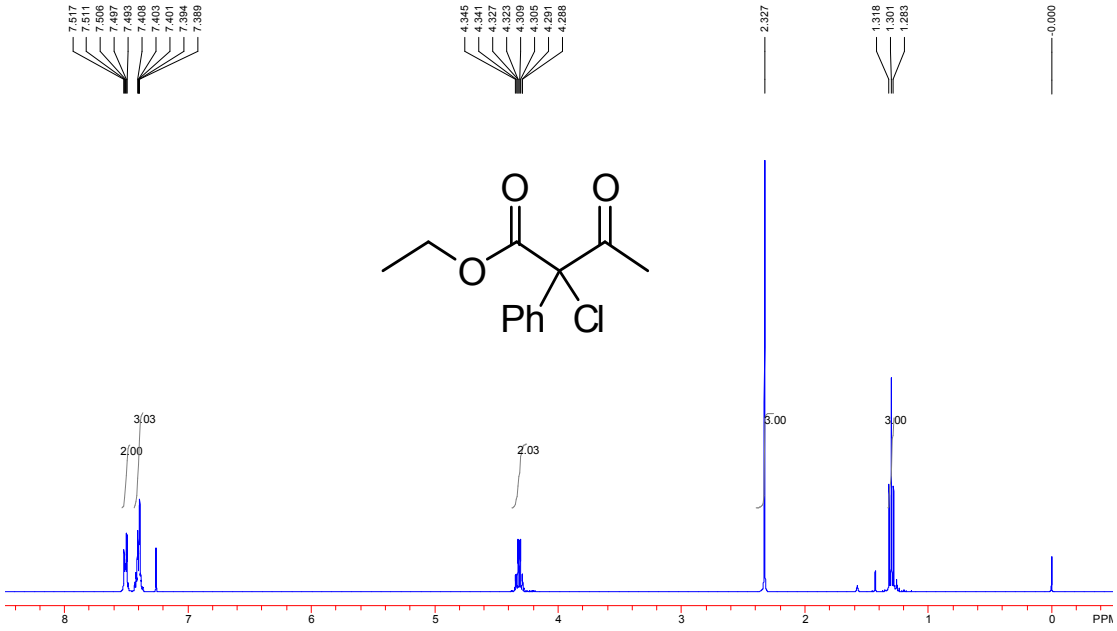

190.122
167.427
144.261
139.001
132.595
130.664
130.473
129.040
128.889
127.919
77.375
77.056
76.733
75.825
63.284
21.683
21.153
13.787
O
O
O
Cl
Me
Me
150
100
50
0 PPM


7.852
7.830
7.500
7.478
6.897
6.874
6.821
6.799
4.298
4.289
4.278
4.271
4.260
4.253
4.243
4.235
4.225
4.215
3.814
3.804
1.217
1.200
1.182
O
O
O
Cl
OMe
MeO
2.01
1.99
2.00
2.00
2.01
6.00
3.00
8
7
6
5
4
3
2
1
0
PPM

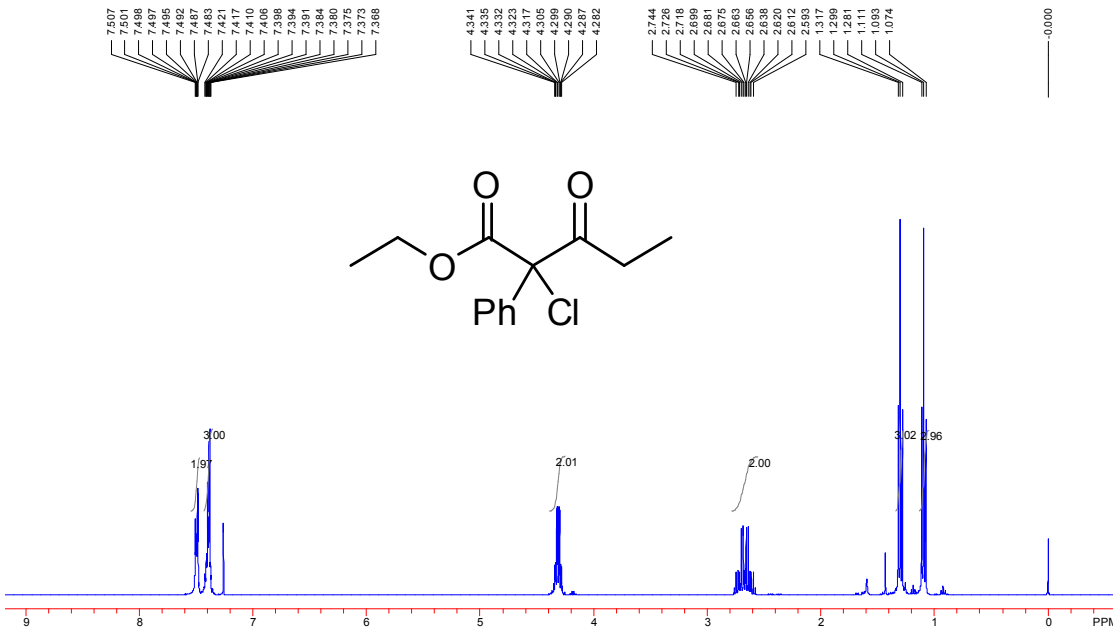

189.167
167.560
163.514
159.911
132.999
129.425
127.739
125.644
113.685
113.442
77.404
77.084
76.759
75.708
63.243
55.479
55.316
13.812
O
O
O
Cl
OMe
MeO
150
100
50
PPM

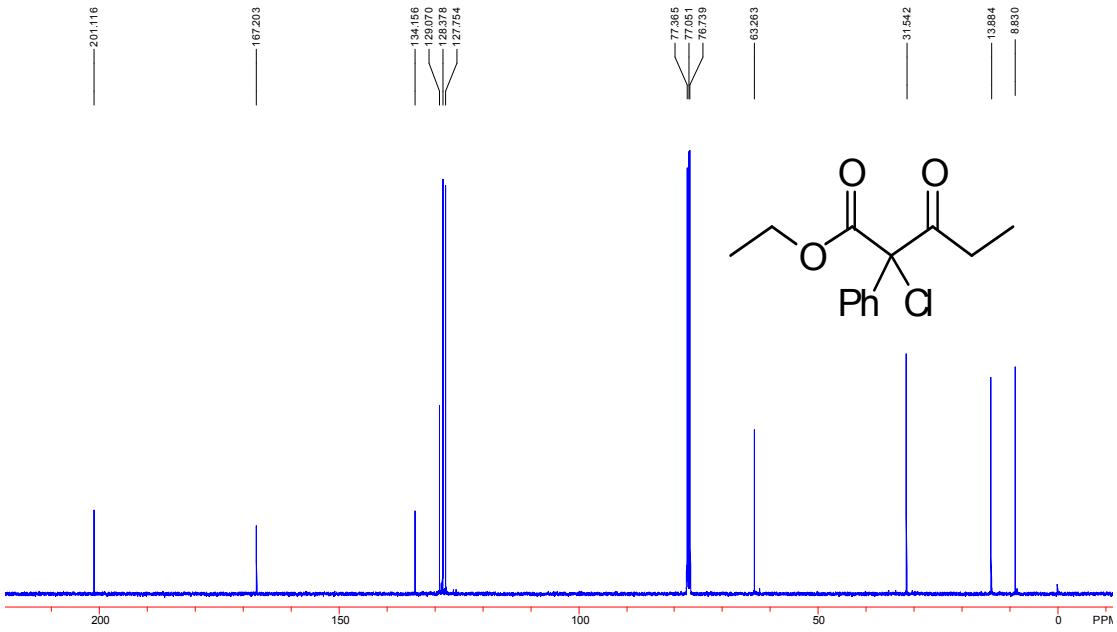

8.154
8.150
8.134
8.130
8.030
8.011
7.994
7.755
7.752
7.737
7.735
7.734
7.717
7.713
7.527
7.524
7.515
7.511
7.508
7.504
7.502
7.496
7.493
7.485
7.477
7.474
7.466
7.464
7.431
7.428
7.412
7.409
7.393
7.390
4.322
4.304
4.295
4.284
4.277
4.266
4.259
4.248
4.239
4.231
4.222
1.195
1.177
1.159
0.001
EtOOC
Cl
O
3.17
2.02
1.00
1.06
1.01
2.00
3.04
10
8
6
4
2
0
PPM

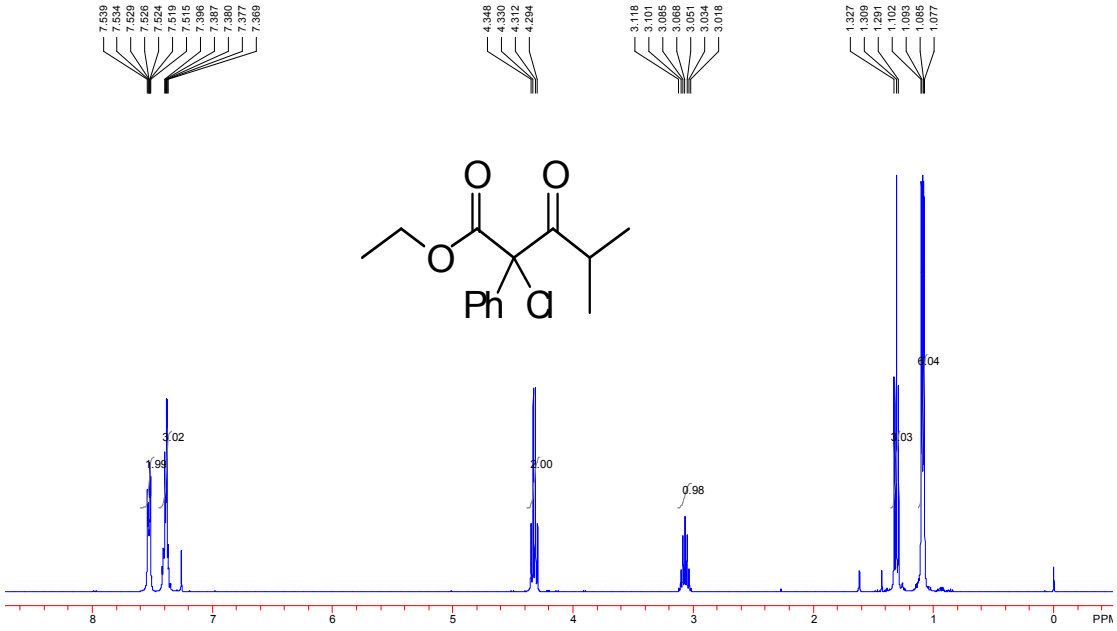

189.025
166.668
136.377
135.594
134.485
130.257
129.699
129.546
129.317
129.067
128.974
127.369
124.245
123.503
77.385
77.073
76.754
69.367
63.571
13.846
EtOOC
Cl
O
200
150
100
50
PPM


7.517
7.511
7.506
7.497
7.493
7.408
7.403
7.401
7.394
7.389
4.345
4.341
4.327
4.323
4.309
4.305
4.291
4.288
2.327
1.318
1.301
1.283
0.000
O
O
O
Ph
Cl
3.03
2.00
2.03
3.00
3.00
8
7
6
5
4
3
2
1
0
PPM

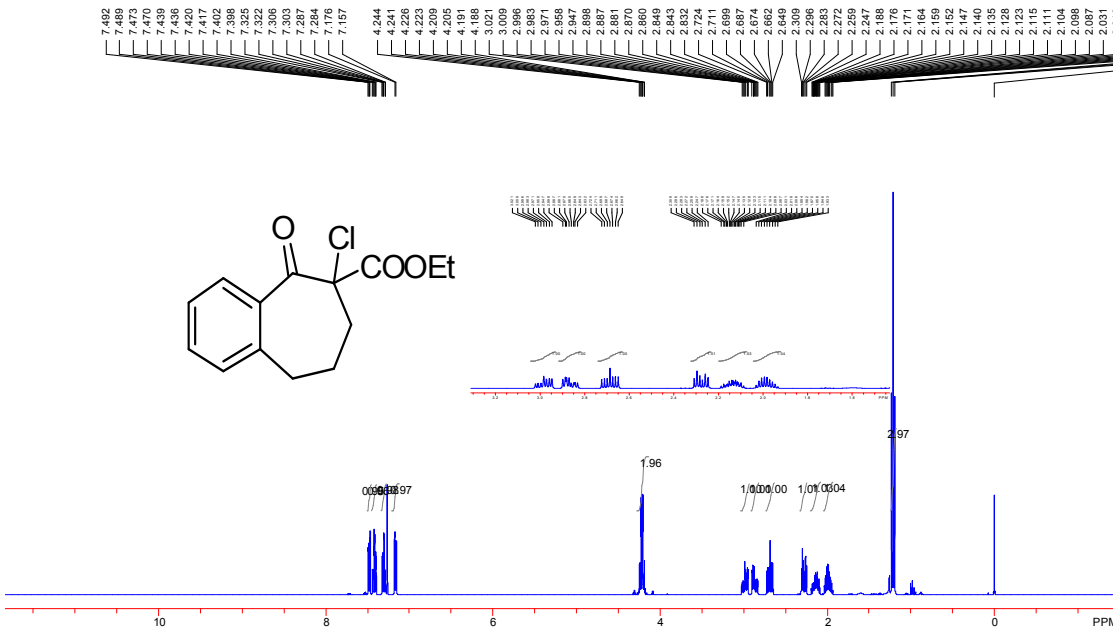

197.510
166.997
133.896
129.145
128.423
127.722
77.366
77.048
76.729
63.326
25.815
13.871
O
O
O
Ph
Cl
200
150
100
50
PPM

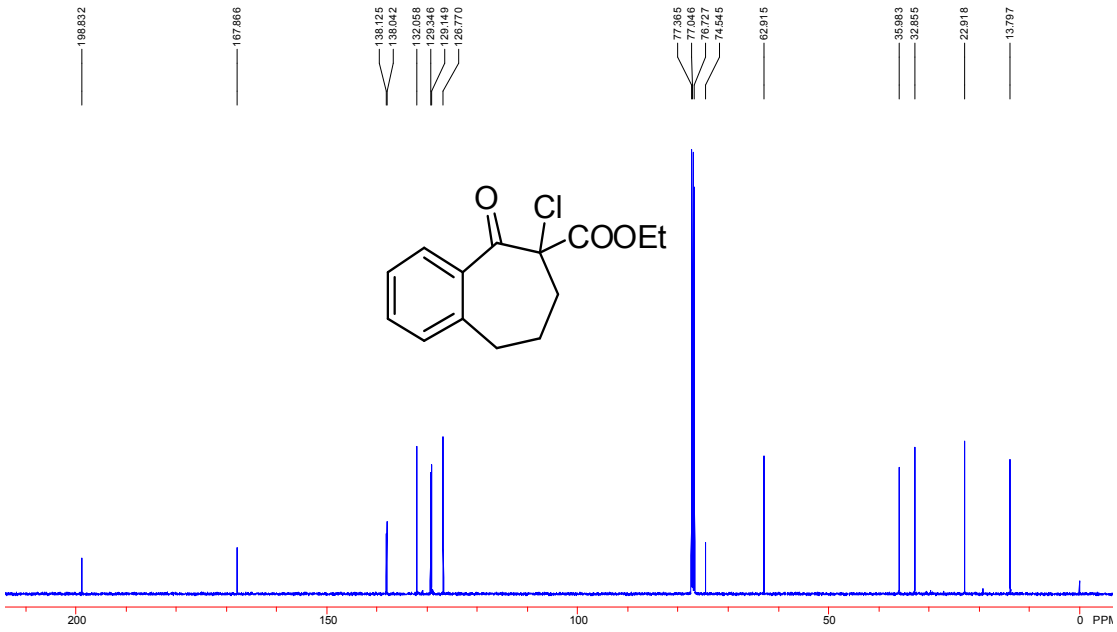

7.507
7.501
7.498
7.497
7.495
7.492
7.487
7.483
7.421
7.417
7.410
7.406
7.398
7.394
7.391
7.384
7.380
7.375
7.373
7.368
4.341
4.335
4.332
4.323
4.317
4.305
4.299
4.290
4.287
4.282
2.744
2.726
2.718
2.699
2.681
2.675
2.663
2.656
2.638
2.620
2.612
2.593
1.317
1.299
1.281
1.111
1.093
1.074
0.000
O
O
O
Ph
Cl
3.00
1.97
2.01
2.00
3.02
2.96
9
8
7
6
5
4
3
2
1
0
PPM

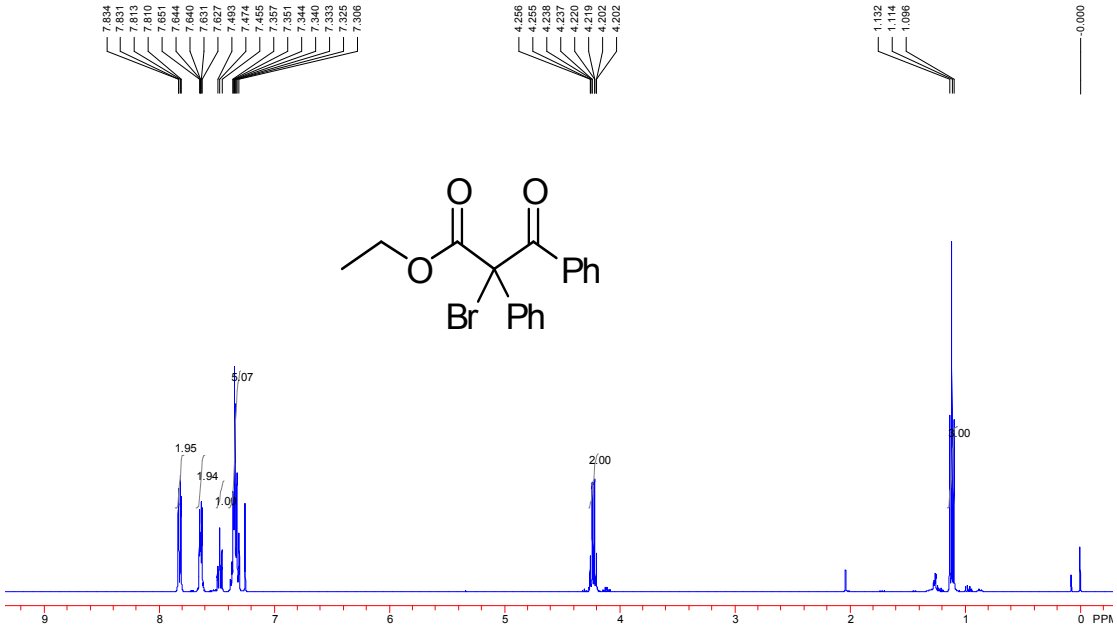

201.116
167.203
134.156
129.070
128.378
127.754
77.365
77.051
76.739
63.263
31.542
13.884
8.830
O
O
O
Ph
Cl
200
150
100
50
0
PPM

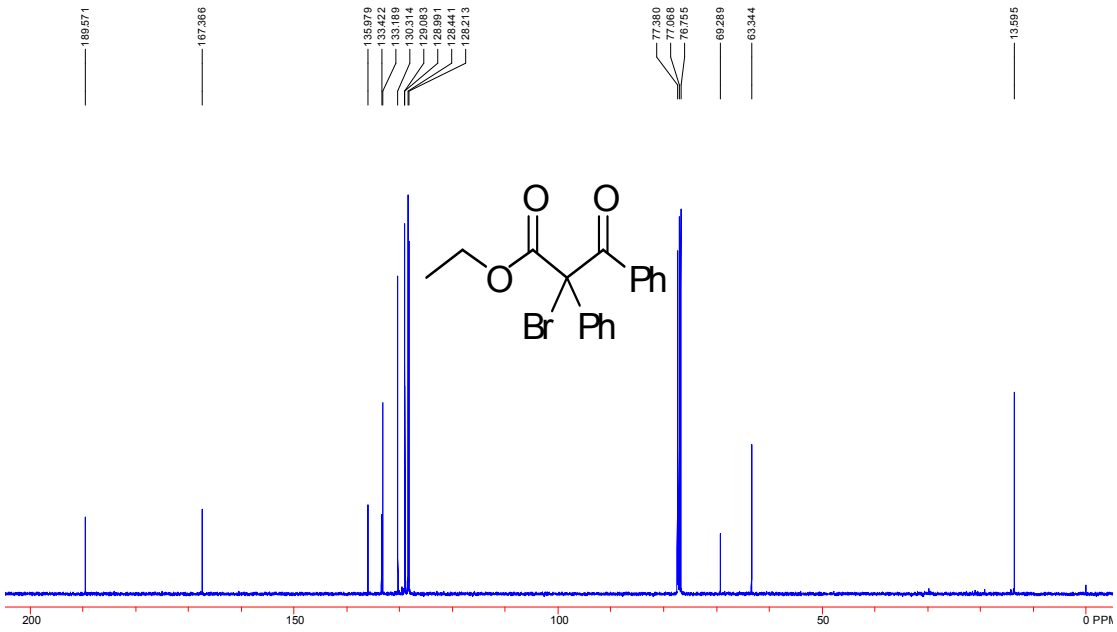

7.539
7.534
7.529
7.526
7.524
7.519
7.515
7.396
7.387
7.380
7.377
7.369
4.348
4.330
4.312
4.294
3.118
3.101
3.085
3.068
3.051
3.034
3.018
1.327
1.309
1.291
1.102
1.093
1.085
1.077
O
O
O
Ph
Cl
3.02
1.99
2.00
0.98
6.04
3.03
8
7
6
5
4
3
2
1
0
PPM

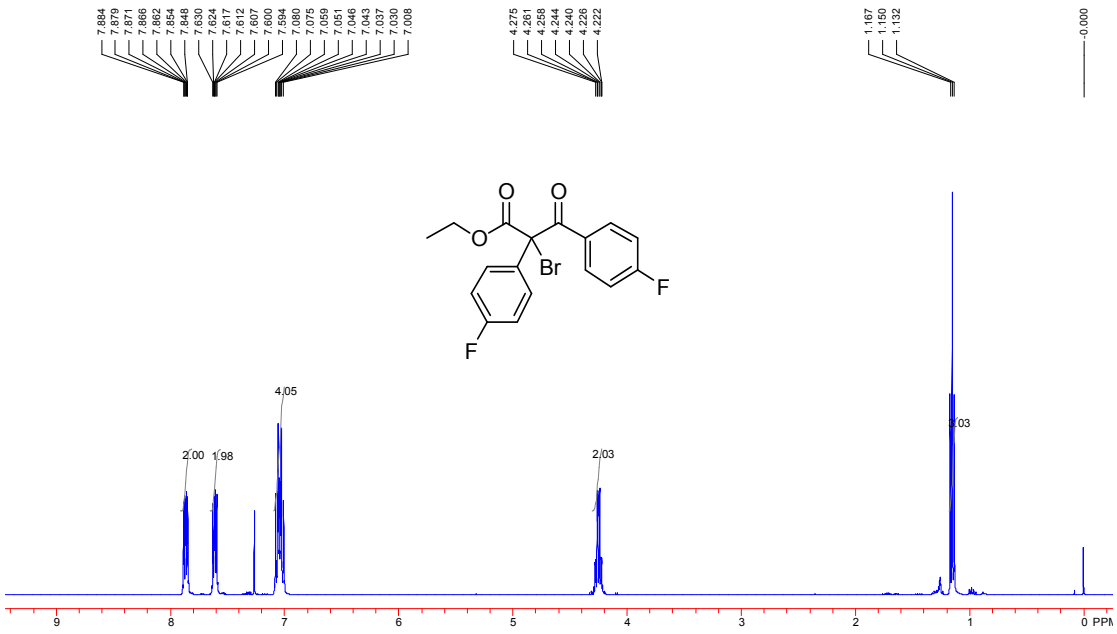

204.299
167.232
133.518
129.103
128.267
128.063
77.808
77.395
77.076
76.750
63.248
37.216
21.170
21.139
13.895
O
O
O
Ph
Cl
200
150
100
50
0
PPM

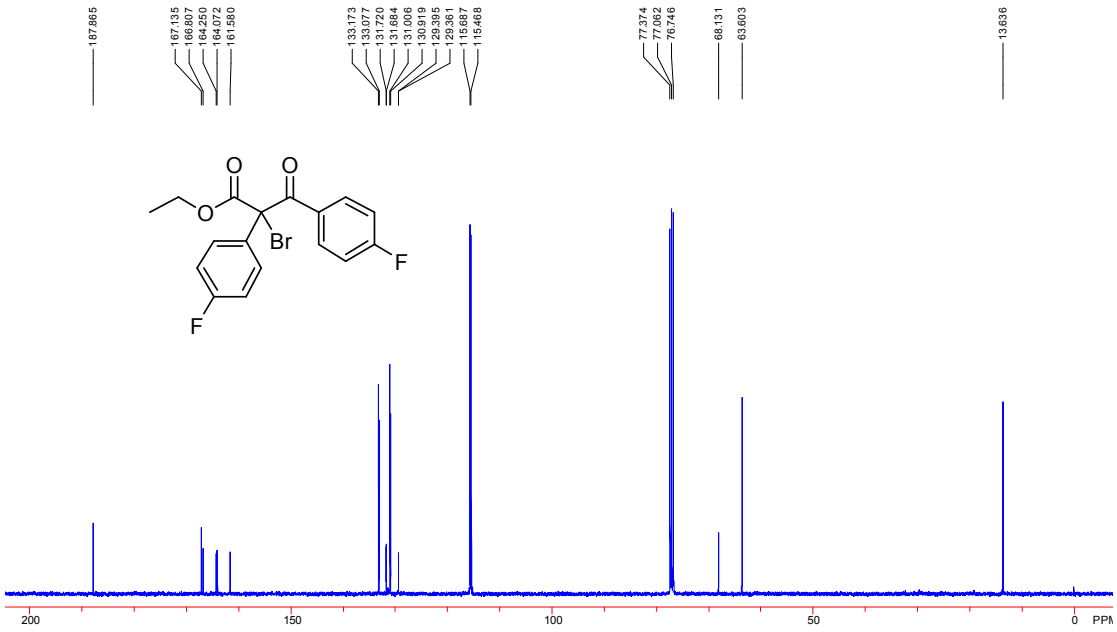

O
Cl
COOEt
2.97
1.96
10
8
6
4
2
0
PPM


198.832
167.866
138.125
138.042
132.058
129.346
129.149
126.770
77.365
77.046
76.727
74.545
62.915
35.983
32.855
22.918
13.797
O
Cl
COOEt
200
150
100
50
0 PPM

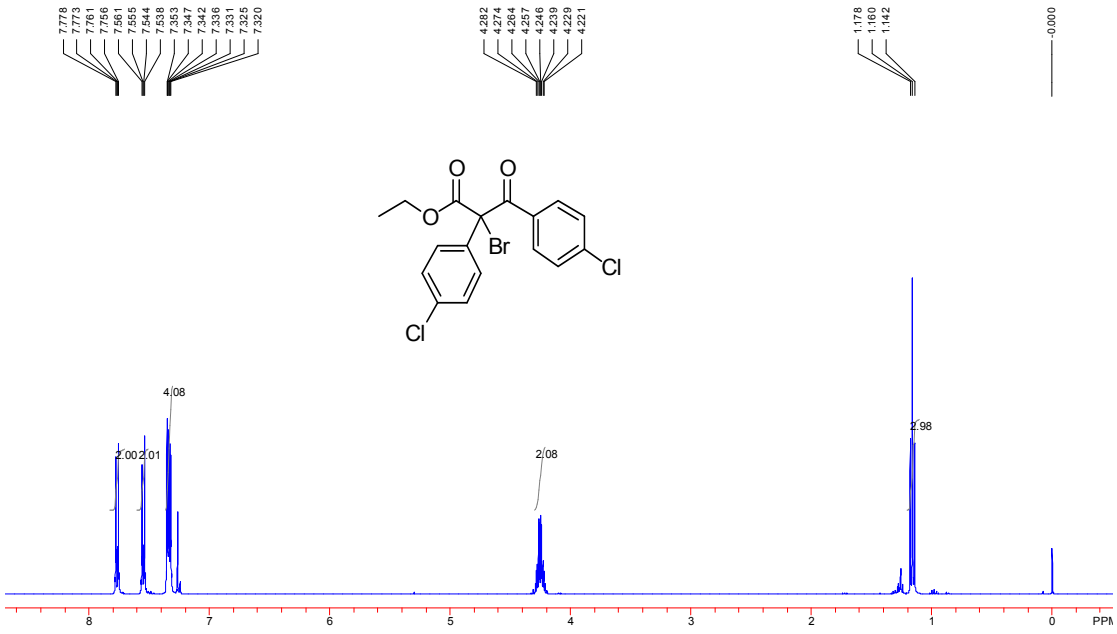

7.834
7.831
7.813
7.810
7.651
7.644
7.640
7.631
7.627
7.493
7.474
7.455
7.357
7.351
7.344
7.340
7.333
7.325
7.306
4.256
4.255
4.238
4.237
4.220
4.219
4.202
4.202
1.132
1.114
1.096
0.000
O
O
O
Ph
Br
Ph
5.07
1.95
1.94
1.00
2.00
3.00
9
8
7
6
5
4
3
2
1
0 PPM

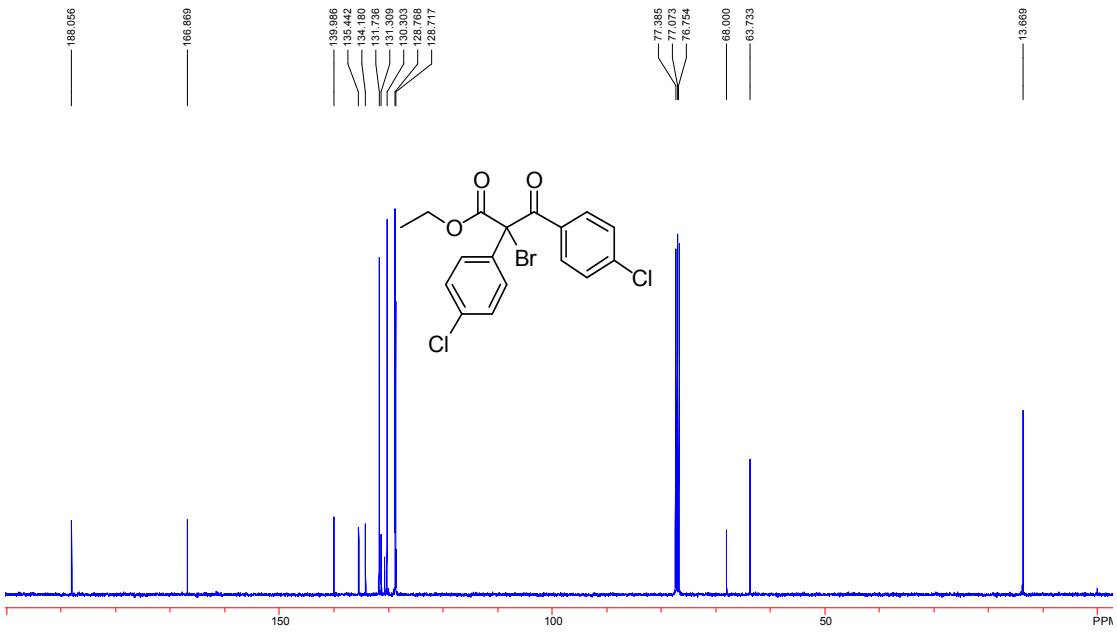

189.571
167.366
135.979
133.422
133.189
130.314
129.083
128.991
128.441
128.213
77.380
77.068
76.755
69.289
63.344
13.595
O
O
O
Ph
Br
Ph
200
150
100
50
0 PPM

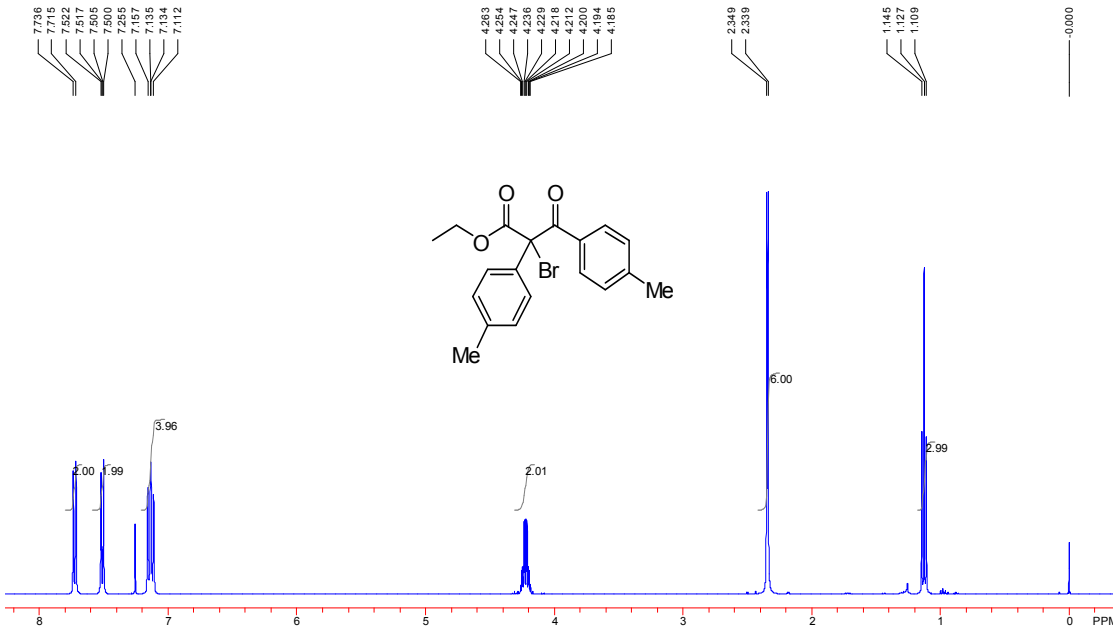

7.884
7.879
7.871
7.866
7.862
7.854
7.848
7.630
7.624
7.617
7.612
7.607
7.600
7.594
7.080
7.075
7.059
7.051
7.046
7.043
7.037
7.030
7.008
4.275
4.261
4.258
4.244
4.240
4.226
4.222
1.167
1.150
1.132
0.000
O
O
O
Br
F
F
4.05
2.00
1.98
2.03
3.03
9
8
7
6
5
4
3
2
1
0 PPM

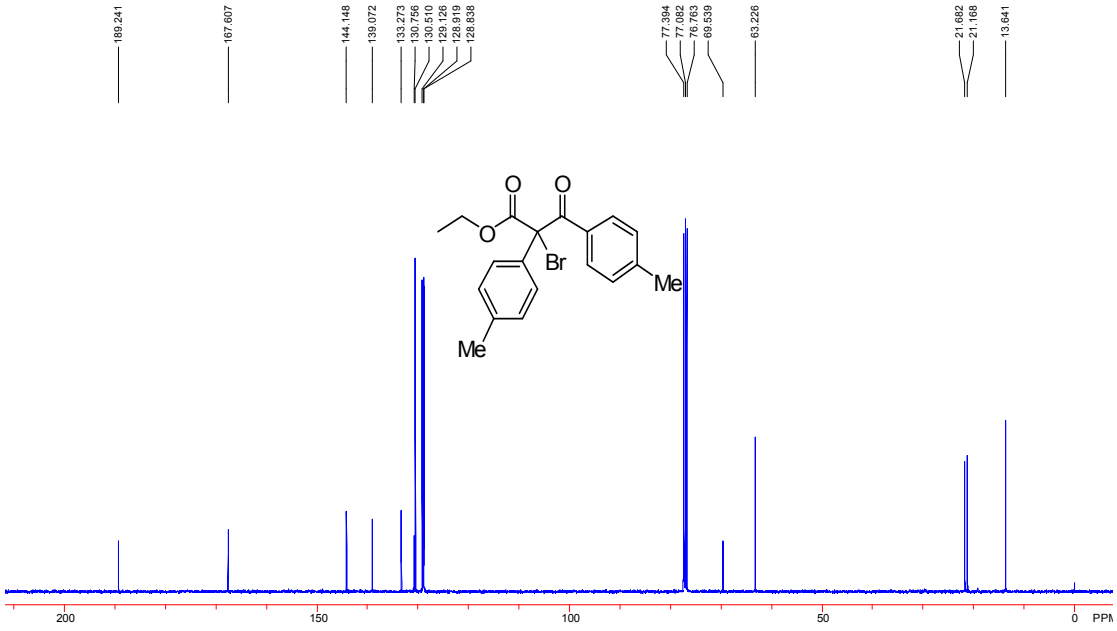

187.865
167.135
166.807
164.250
164.072
161.580
133.173
133.077
131.720
131.684
131.006
130.919
129.395
129.361
115.687
115.468
77.374
77.062
76.746
68.131
63.603
13.636
O
O
O
Br
F
F
200
150
100
50
0
PPM

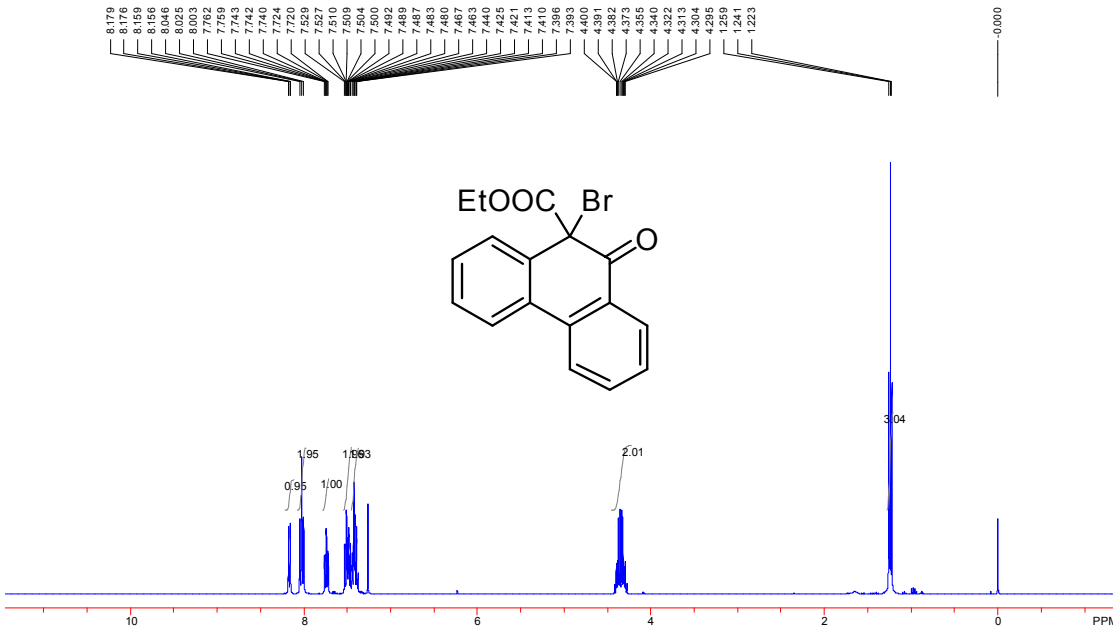

103.569
111.660
O
O
O
Br
F
F
-80
-90
-100
-110
-120
-130
PPM

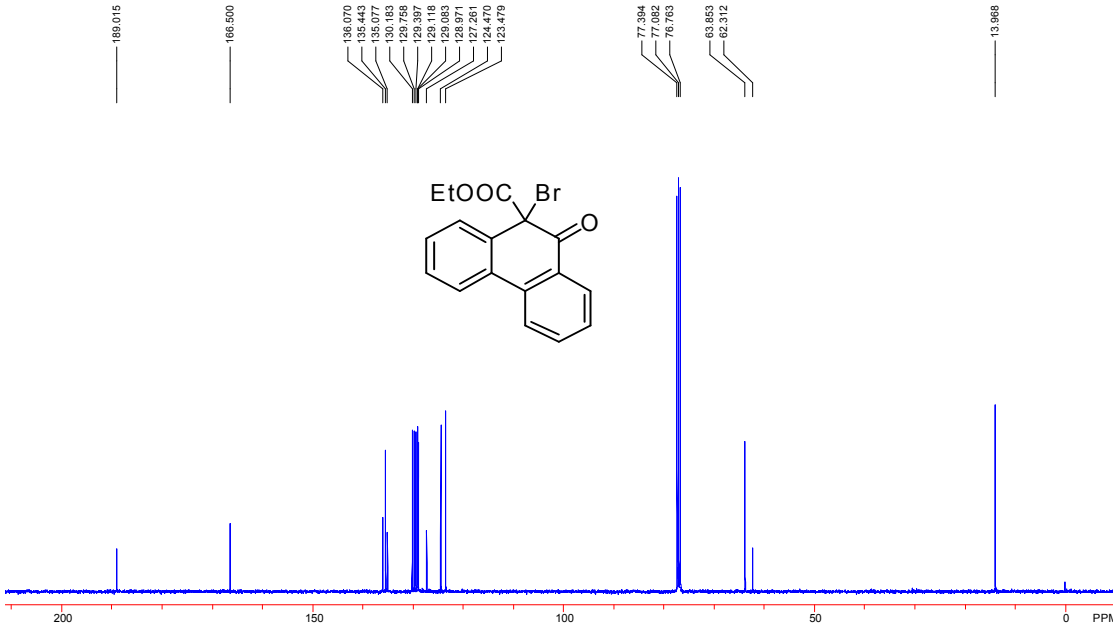

7.778
7.773
7.761
7.756
7.561
7.555
7.544
7.538
7.353
7.347
7.342
7.336
7.331
7.325
7.320
4.282
4.274
4.264
4.257
4.246
4.239
4.229
4.221
1.178
1.160
1.142
0.000
O
O
O
Br
Cl
Cl
4.08
2.00
2.01
2.08
2.98
8
7
6
5
4
3
2
1
0
PPM

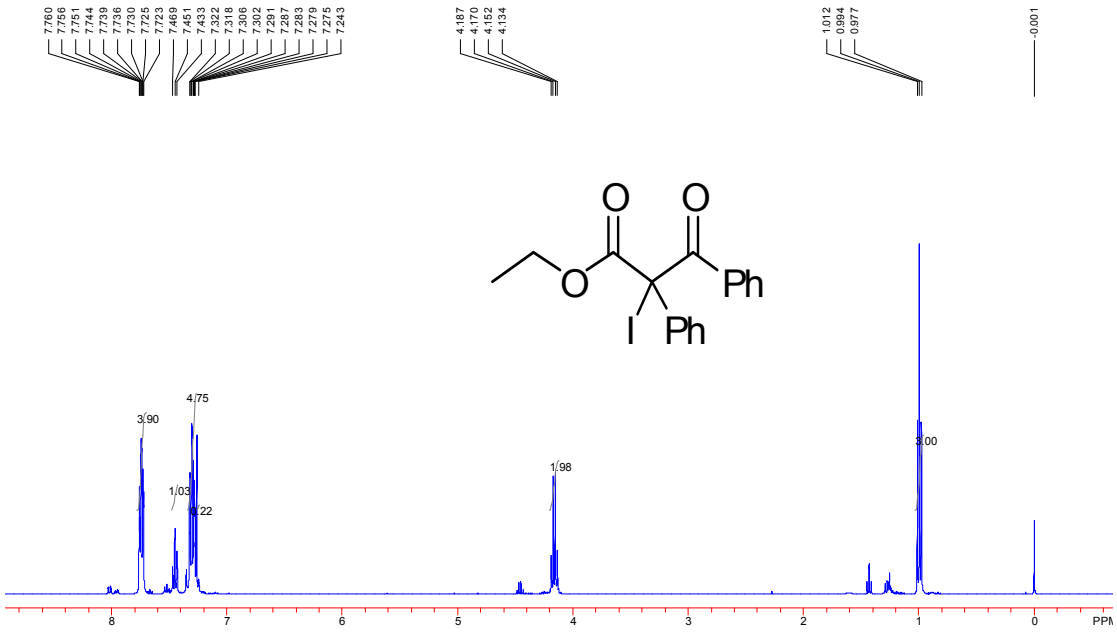

188.056
166.869
139.986
135.442
134.180
131.736
131.309
130.303
128.768
128.717
77.385
77.073
76.754
68.000
63.733
13.669
O
O
O
Br
Cl
Cl
150
100
50
PPM

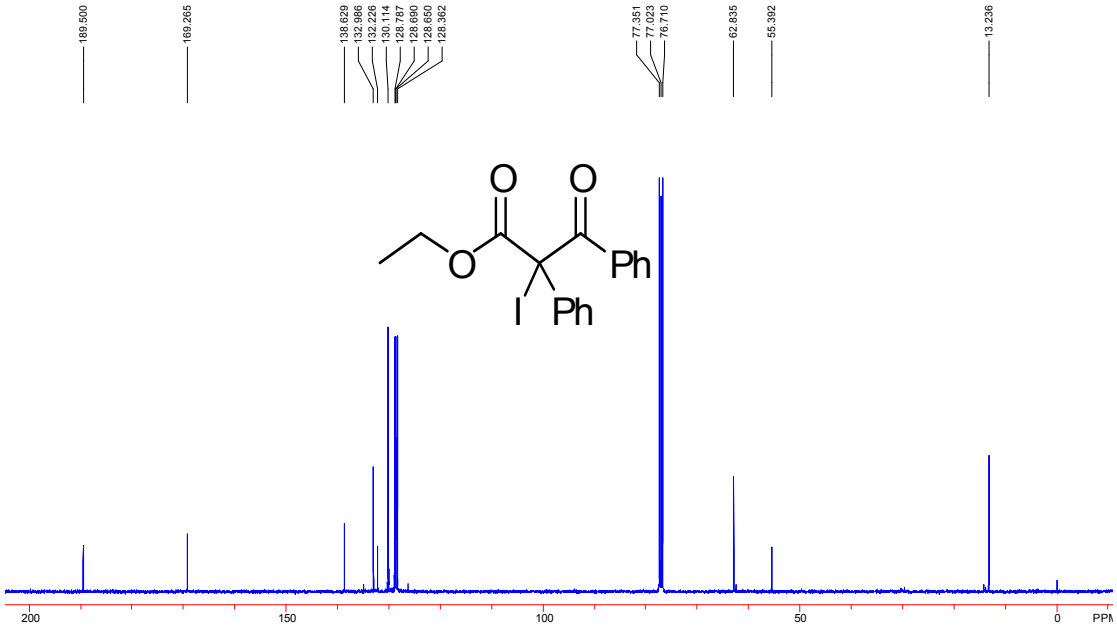

7.736
7.715
7.522
7.517
7.505
7.500
7.255
7.157
7.135
7.134
7.112
4.263
4.254
4.247
4.236
4.229
4.218
4.212
4.200
4.194
4.185
2.349
2.339
1.145
1.127
1.109
-0.000
O
O
O
Br
Me
Me
6.00
3.96
2.00
1.99
2.01
2.99
8
7
6
5
4
3
2
1
0
PPM


189.241
167.607
144.148
139.072
133.273
130.756
130.510
129.126
128.819
128.838
77.394
77.082
76.763
69.539
63.226
21.682
21.168
13.641
O
O
O
Br
Me
Me
200
150
100
50
0
PPM


8.179
8.176
8.159
8.156
8.046
8.025
8.003
7.762
7.759
7.743
7.742
7.740
7.724
7.720
7.529
7.527
7.510
7.509
7.504
7.500
7.492
7.489
7.487
7.483
7.480
7.467
7.463
7.440
7.425
7.421
7.413
7.410
7.396
7.393
4.400
4.391
4.382
4.373
4.355
4.340
4.322
4.313
4.304
4.295
1.259
1.241
1.223
-0.000
EtOOC
Br
O
3.04
2.01
1.95
1.00
0.95
10
8
6
4
2
0
PPM


189.015
166.500
136.070
135.443
135.077
130.183
129.758
129.397
129.118
129.083
128.971
127.261
124.470
123.479
77.394
77.082
76.763
63.853
62.312
13.968
EtOOC
Br
O
200
150
100
50
0
PPM





Reference

[1] A. Gioiello, F. Venturoni, B. Natalini, R. Pellicciari, *J. Org. Chem.* **2009**, *74*, 3520-3523.