Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Transposition of Acrylate Moiety in TMSOTf-Mediated Reaction of Alkynyl Vinylogous Carbonates Gives Heterocyclic Dienes

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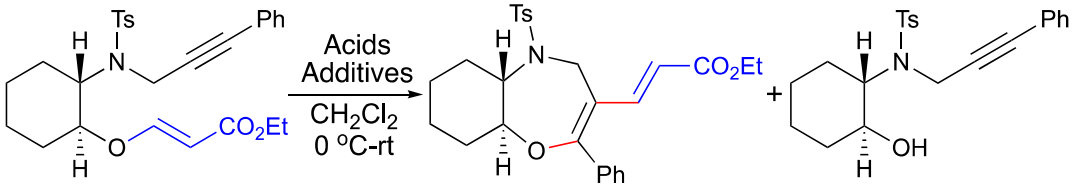
General experimental:

Melting points are recorded using dbk programmable melting point apparatus in capillary tubes and are uncorrected. IR spectra were recorded on Nicolet 6700 spectrophotometer. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on Bruker Avance 400 spectrometer. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on Bruker Avance 500 spectrometer. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion with reference to either internal tetramethylsilane or residual $CHCl_3$ (7.26 ppm for ^{1}H) or the central line (77.16 ppm) of $CDCl_3$ (for ^{13}C). In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was determined by recording the DEPT-135 experiment and is given in parentheses.

High resolution mass measurements were carried out using Maxis impact (brucker) instrument using direct inlet mode. X-ray diffraction studies were carried out using Bruker Single Crystal Kappa Apex II. Analytical thin-layer chromatographies (TLC) were performed on glass plates (7.5 × 2.5 and 9 × 5.0 cm) coated with Merck or Acme's silica gel G containing 13% calcium sulfate as binder or on pre-coated 0.2 mm thick Merck 60 F_{245} silica plates and various combinations of ethyl acetate and Petroleum ether were used as eluent. Visualization of spots was accomplished by either exposure to iodine vapour or $KMnO_4$ stain or vanillin strain. All small-scale dry reactions were carried out using standard syringe septum technique. Dry dichloromethane was prepared by refluxing over anhydrous P_2O_5 and distillation on to calcium hydride. Dry DMF was prepared by stirring on CaH and distillation on to molecular sevies. $BF_3{\cdot}OEt_2$, $Cu(OTf)_2$, TMSOTf, TfOH, AgOTf, CuI, Et_3SiH and BBr_3 (1M heptane) were obtained from Aldrich. All other Lewis/Bronsted acids, Iodobenzene, NaH (60% dispersion in mineral oil), benzyl bromide, cyclohexene oxide, cyclopentene oxide, propargyl bromide (80% in toluene), Mg turning, DMP, $[Pd(PPh_3)_2]Cl_2$, $Pd(OAc)_2$, PPh_3, aryl iodides are commercial reagents and were used as such without further purification. All other internal alkynyl vinylogous carbonate were prepared using literature established protocol.

Table S1. Optimization table for synthesis of 1,4-oxazepines



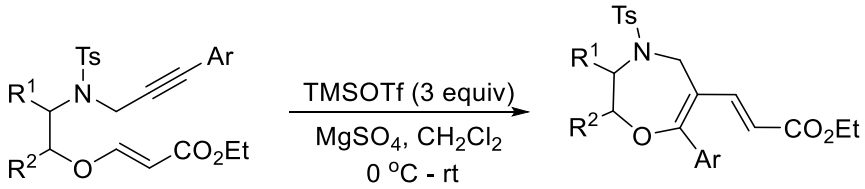
1a **3a** **4a**

Entry	Acids[a] (equiv)	Additives	Time (h)	Yield (%)[b,d] (**3a**)	Yield (%)[b] (**4a**)
1	TMSOTf (1.0)	-	0.5	35	31
2	TMSOTf (1.0)	4Å MS	0.5	40	27
3	TMSOTf (1.0)	$MgSO_4$	0.5	45	26
4	$In(OTf)_3$ (0.2)	$MgSO_4$	2	-	86
5	$Sc(OTf)_3$ (0.2)	$MgSO_4$	2	-	88
6	Ag(OTf) (1)	$MgSO_4$	12	-	82
7	$BF_3{\cdot}OEt_2$ (1)	$MgSO_4$	2	Trace	77
8	TfOH (1)	$MgSO_4$	0.5	-	86
9	TMSOTf (2)	$MgSO_4$	0.5	54 (50)[c]	20 (14)[c]
10	TMSOTf (3)	$MgSO_4$	0.5	68 (65)[c]	11 (6)[c]
11	TMSOTf (4)	$MgSO_4$	0.5	65	9
12	TMSOTf (5)	$MgSO_4$	0.5	60	31
13	TMSOTf (5)	Na_2SO_4	0.5	65	14
14	TMSOTf (3)	$Ca(SO_4)_2$	0.5	42	17
15	TMSOTf (3)	CaH_2	0.5	23	-
16	TMSOTf (3)	$CaCl_2$	0.5	31	11
17	$TiCl_4$[e] (1)	1	0.5	-	76

[a]all reactions were carried out using **1** (0.15 mmol), with slow addition of acids at 0 °C in dry solvent (3 ml) for 0.5-12h. [b]NMR yield using 1,3,5-trimethoxybenzene as an internal standard. [c]Yield of isolated product after purification by silica gel column chromatography. [d]*E*/*Z* selectivity was measured by ^{1}H NMR on crude reaction mixture and was found to be $\geq$19:1. [e]without $MgSO_4$.

Experimental Procedure

Representative experimental procedure for synthesis of substituted 1,4-oxazepine and dihydropyran derivatives:

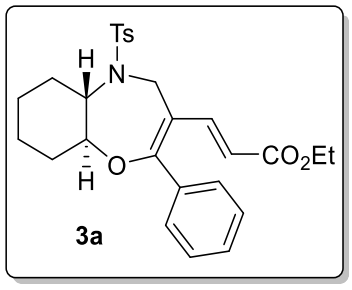


To a magnetically stirred suspension of activated magnesium sulfate (40 equiv) and vinylogous carbonate in dry CH_2Cl_2 (5 mL), TMSOTf was added dropwise at 0 ^oC. Reaction was monitored by TLC, quenched with saturated aq. solution of $NaHCO_3$ upon completion, extracted with CH_2Cl_2 (3 × 5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using EtOAc-petroleum ether as eluent furnished 1,4-oxazepines.

7.4 General procedure for synthesis of 1,4-oxazepines:

ethyl(E)-3-((5aS*,9aS*)-2-phenyl-5-tosyl-4,5,5a,6,7,8,9,9a octahydrobenzo[b][1,4]oxazepin-3-yl)acrylate **3a:**

To a magnetically stirred suspension of activated magnesium sulfate (0.730 gm, 6.04 mmol) and vinylogous carbonate **1a** (73.0 mg, 0.151 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (83 µL, 0.456 mmol) was added dropwise at 0 ^oC. Reaction was monitored by TLC, quenched with saturated aq. solution of $NaHCO_3$ upon completion, extracted with CH_2Cl_2 (3 × 5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using EtOAc-petroleum ether as eluent furnished 1,4-oxazepines **3a** (46.4 mg, 65%).



Physical appearance: Yellow solid.

M.P: 128-130 ^oC.

R_f: 0.5 (3:7, EtOAc: Petroleum ether).

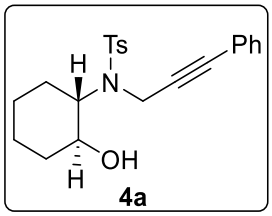
IR (neat): 2933, 2860, 1708, 1600, 1586, 1447, 1306, 1267, 1093, 814, 756, 577 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.23 (t, *J* =7.2 Hz, 2H), 7.16 (d, *J* = 16.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 7.5 Hz, 2H), 5.77 (d, *J* = 16.0 Hz, 1H), 4.73 (d, *J* = 18.8 Hz, 1H), 4.15-4.10 (m, 4H), 3.95 (td, *J* = 10.8, 4.0 Hz, 1H), 2.23-2.18 (m, 4H), 1.86 (d, *J* = 13.2 Hz, 1H), 1.80 (d, *J* = 12.8 Hz, 1H), 1.68-1.63 (m, 4H), 1.24 (t, *J* = 7.2 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.6 (C), 164.4 (C), 144.0 (CH), 143.1 (C), 137.9 (C), 134.2 (C), 130.3 (2 × CH), 130.2 (CH), 129.6 (2 × CH), 127.8 (2 × CH), 127.0 (2 × CH), 113.0 (CH), 109.1 (C), 83.3 (CH), 62.8 (CH), 60.2 (CH_2), 41.0 (CH_2), 32.8 (CH_2), 32.7 (CH_2), 24.4 (CH_2), 24.3 (CH_2), 21.4 (CH_3), 14.4 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. For $C_{27}H_{31}NNaO_5S$ 504.1815, found 504.1814.

***N-((1S*,2S*)-2-hydroxycyclohexyl)-4-methyl-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide* 4a:**



4a

Physical appearance: Brown solid.

M.P: 86-88 ^oC.

R_f: 0.5 (2:8, EtOAc: Petroleum ether).

IR (neat): 3548, 2936, 2862, 2126, 1334, 1163, 1091, 1073, 1042, 885, 768 cm^{-1}.

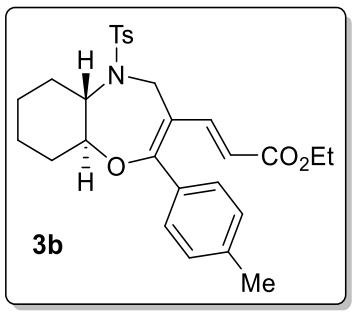
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.32-7.25 (m, 3H), 7.23-7.18 (m, 4H), 4.45 (d, *J* = 18.8 Hz, 1H), 4.28 (d, *J* = 18.8 Hz, 1H), 3.66-3.64 (m, 2H), 2.47 (s, 1H), 2.35 (s, 3H), 2.12 (d, *J* = 12 Hz, 1H), 1.73-1.67 (m, 3H), 1.58-1.48 (m, 1H), 1.35-1.18 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 143.6 (C), 137.8 (C), 131.6 (2 × CH), 129.6 (2 × CH), 128.8 (CH), 128.4 (2 × CH), 127.7 (2 × CH), 122.0 (C), 84.9 (C), 84.8 (C), 70.1 (CH), 64.4 (CH), 33.9 (CH_2), 33.1 (CH_2), 29.5 (CH_2), 25.4 (CH_2), 24.2 (CH_2), 21.6 (CH_3).

HRMS (ESI, M+Na$^+$): m/z calcd. For $C_{22}H_{25}NNaO_3S$ 406.1447 found 406.1449.

***ethyl(E)-3-((5aS*,9aS*)-2-(p-tolyl)-5-tosyl-4,5,5a,6,7,8,9,9a-octahydrobenzo[b][1,4]oxazepin-3-yl)acrylate* 3b:**

To a magnetically stirred suspension of activated magnesium sulfate (0.651 gm, 5.408 mmol) and vinylogous carbonate **1b** (67.0 mg, 0.135 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (74 µL, 0.405 mmol) was added dropwise at 0 ^oC as described for the 1,4-oxazepine **3a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the 1,4-oxazepine **3b** (49.0 mg, 73%).



3b

Physical appearance: White solid.

M.P: 244-246 ^oC.

R_f: 0.5 (3:7, EtOAc: Petroleum ether).

IR (neat): 2940, 1704, 1604, 1585, 1267, 1157, 1038, 760 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 16.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 5.74 (d, *J*

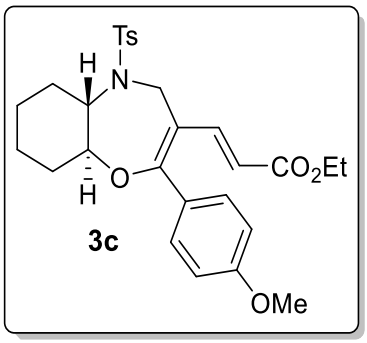
= 16.0 Hz, 1H), 4.71 (d, *J* = 18.4 Hz, 1H), 4.17-4.08 (m, 4H), 3.95 (td, *J* = 10.8, 3.6 Hz, 1H), 2.32 (s, 3H), 2.22-2.17 (m, 4H), 1.86 (d, *J* = 12.8 Hz, 1H), 1.80 (d, *J* = 13.2 Hz, 1H), 1.67-1.31 (m, 4H), 1.25 (t, *J* = 7.2 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.7 (C), 164.7 (C), 144.4 (CH), 143.1 (C), 140.4 (C), 137.9 (C), 131.4 (C), 130.2 (2 × CH), 129.6 (2 × CH), 128.5 (2 × CH), 127.0 (2 × CH), 112.4 (CH), 108.6 (C), 83.1 (CH), 62.8 (CH), 60.1 (CH_2), 41.0 (CH_2), 32.8 (CH_2), 32.7 (CH_2), 24.4 (CH_2), 24.3 (CH_2), 21.5 (CH_3), 21.4 (CH_3), 14.4 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{28}H_{34}NO_5S$ 496.2152, found 496.2152.

***ethyl(E)-3-((5aS*,9aS*)-2-(4-methoxyphenyl)-5-tosyl-4,5,5a,6,7,8,9,9a-octahydrobenzo[b][1,4]oxazepin-3-yl)acrylate* 3c:**

To a magnetically stirred suspension of activated magnesium sulfate (0.707 gm, 5.87 mmol) and vinylogous carbonate **1c** (75.0 mg, 0.146 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (80 µL, 0.439 mmol) was added dropwise at 0 ^oC as described for the 1,4-oxazepine **3a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the 1,4-oxazepine **3c** (25.0 mg, 34%).



3c

Physical appearance: White solid.

M.P: 210-212 ^oC.

R_f: 0.5 (3:7, EtOAc: Petroleum ether).

IR (neat): 2925, 2852, 1708, 1599, 1462, 1306, 1253, 1170, 755 cm^{-1}.

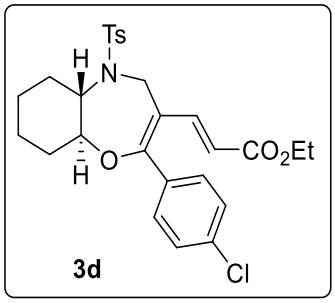
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* =15.6 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.82-6.74 (m, 4H), 5.74 (d, *J* = 16.0 Hz, 1H), 4.71 (d, *J* = 18.8 Hz, 1H), 4.17-4.07 (m, 4H), 3.95 (td, *J* =11.2, 4.4 Hz, 1H), 3.80 (s, 3H), 2.22 (s, 3H), 1.87 (d, *J* =12.8 Hz, 1H), 1.81 (d, *J* =13.2 Hz, 1H), 1.68-1.41 (m, 6H), 1.26 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.8 (C), 164.5 (C), 161.2 (C), 144.5 (CH), 143.0 (C), 138.0 (C), 131.9 (2 ×CH), 129.6 (2 × CH), 127.0 (2 × CH), 126.6 (C), 113.3 (2 × CH), 112.2 (CH), 108.1 (C), 83.0 (CH), 62.8 (CH), 60.2 (CH_2), 55.5 (CH_3), 41.1 (CH_2), 32.8 (CH_2), 32.7 (CH_2), 24.4 (2 × CH_2), 21.5 (CH_3), 14.5 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{28}H_{34}NO_6S$ 512.2115, found 512.2115.

***ethyl(E)-3-((5aS*,9aS*)-2-(4-chlorophenyl)-5-tosyl-4,5,5a,6,7,8,9,9a-octahydrobenzo[b][1,4]oxazepin-3-yl)acrylate* 3d:**

To a magnetically stirred suspension of activated magnesium sulfate (0.792 gm, 6.583 mmol) and vinylogous carbonate **1d** (85.0 mg, 0.164 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (89 µL, 0.494 mmol) was added dropwise at 0 ^oC as described for the 1,4-oxazepine **3a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the 1,4-oxazepine **3d** (45.0 mg, 53%).



3d

Physical appearance: Brown solid.

M.P: 190-192 ^oC.

R_f: 0.5 (3:7, EtOAc: Petroleum ether).

IR (neat): 2939, 1706, 1598, 1584, 1304, 1265, 1176, 1038, 759 cm^{-1}.

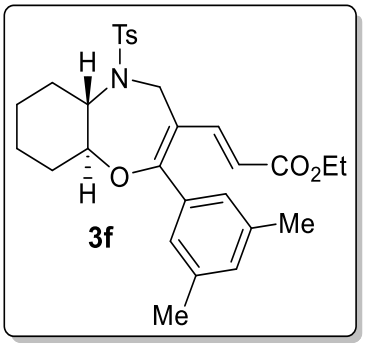
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.11-7.06 (m, 3H), 6.77 (d, *J* = 8.8 Hz, 2H), 5.78 (d, *J* = 15.6 Hz, 1H), 4.71 (d, *J* = 18.8 Hz, 1H), 4.16-4.08 (m, 4H), 3.95 (td, *J* = 10.8, 3.6 Hz, 1H), 2.22-2.16 (m, 5H), 1.86 (d, *J* = 13.6 Hz, 1H), 1.80 (d, *J* = 12.8 Hz, 1H), 1.63-1.41 (m, 3H), 1.34-1.20 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.4 (C), 162.9 (C), 143.3 (CH), 143.1 (C), 137.9 (C), 136.2 (C), 132.7 (C), 131.5 (2 × CH), 129.6 (2 × CH), 128.0 (2 × CH), 127.0 (2 × CH), 113.5 (CH), 109.5 (C), 83.4 (CH), 62.7 (CH), 60.3 (CH_2), 40.9 (CH_2), 32.7 (CH_2), 32.6 (CH_2), 24.3 (CH_2), 24.2 (CH_2), 21.4 (CH_3), 14.4 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{27}H_{31}ClNO_5S$ 516.1623, found 516.1622.

***ethyl(E)-3-((5aS*,9aS*)-2-phenyl-5-tosyl-4,5,5a,6,7,8,9,9a octahydrobenzo[b][1,4]oxazepin-3-yl)acrylate* 3f:**

To a magnetically stirred suspension of activated magnesium sulfate (0.737 gm, 6.12 mmol) and vinylogous carbonate **1f** (78.0 mg, 0.153 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (84 µL, 0.459 mmol) was added dropwise at 0 ^oC as described for the 1,4- oxazepine **3a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the 1,4-oxazepine **3f** (40.0 mg, 51%).



3f

Physical appearance: Sticky solid.

R_f: 0.5 (3:7, EtOAc: Petroleum ether).

IR (neat): 2936, 1708, 1604, 1585, 1250, 1170, 1044, 758 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.18-7.12 (m, 3H), 6.94 (s, 1H), 6.45 (s, 2H), 5.74 (d, *J* = 16.0 Hz, 1H), 4.74 (d, *J* = 18.4 Hz, 1H), 4.19-4.08 (m, 4H), 3.94 (td, *J* = 10.4, 3.6 Hz, 1H), 2.25 (s, 6H), 2.23 (s, 3H), 1.87 (d, *J* = 13.2 Hz, 1H), 1.81 (d, *J* = 13.2 Hz, 1H), 1.67-1.39 (m, 4H), 1.33-1.23 (m, 5H).

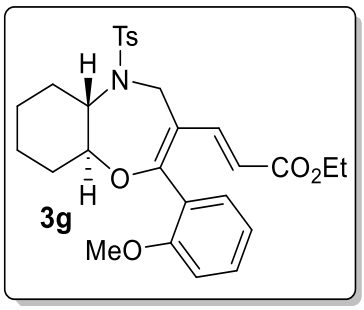
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.5 (C), 164.9 (C), 144.3 (CH), 142.9 (C), 138.0 (C), 137.3 (2 × C), 134.2 (C), 131.8 (CH), 129.6 (2 × CH), 128.0 (2 × CH), 127.0 (2 × CH), 112.6 (CH), 109.0 (C), 83.3 (CH), 62.8 (CH), 60.1 (CH_2), 41.0 (CH_2), 32.7 (2 × CH_2), 24.4 (CH_2), 24.3 (CH_2), 21.5 (CH_3), 21.3 (2 × CH_3), 14.4 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. For $C_{29}H_{36}NO_5S$ 510.2333, found 510.2332.

(Note: Compound 6g shows rotamers and data written for the major isomer.)

***ethyl(E)-3-((5aS*,9aS*)-2-(2-methoxyphenyl)-5-tosyl-4,5,5a,6,7,8,9,9a-octahydrobenzo[b][1,4]oxazepin-3-yl)acrylate* 3g:**

To a magnetically stirred suspension of activated magnesium sulfate (0.97 gm, 8.05 mmol) and vinylogous carbonate **1g** (103.0 mg, 0.201 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (111 µL, 0.604 mmol) was added dropwise at 0 ^{o}C as described for the 1,4-oxazepine **3a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the 1,4-oxazepine **3g** (57.0 mg, 55%).



Physical appearance: Yellow solid.

M.P: 156-158 ^{o}C.

R_f: 0.5 (3:7, EtOAc: Petroleum ether).

IR (neat): 2931, 2858, 1707, 1605, 1590, 1262, 1177, 1034, 756, 666 cm^{-1}.

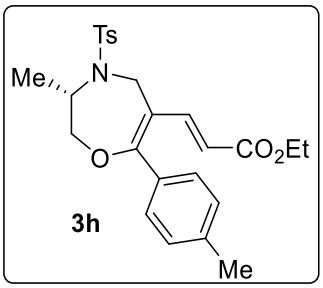
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.29-7.26 (m, 1H), 7.21 (d, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 16.0 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 6.73 (t, *J* = 6.8 Hz, 1H), 6.0 (s, 1H), 5.72 (d, *J* = 16.0 Hz, 1H), 4.72 (d, *J* = 18.4 Hz, 1H), 4.17-4.08 (m, 4H), 3.94 (s, 1H), 3.74 (s, 3H), 2.36 (s, 3H), 2.24 (d, *J* = 9.6 Hz, 1H), 2.15 (d, *J* = 8.4 Hz, 1H), 1.82 (t, *J* = 14 Hz, 2H), 1.64-1.28 (m, 4H), 1.23 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.5 (C), 163.6 (C), 158.0 (C), 143.9 (C), 143.2 (CH), 138.3 (C), 131.8 (CH), 131.4 (CH), 129.7 (2 × CH), 127.2 (2 × CH), 123.5 (C), 119.8 (CH), 112.6 (CH), 111.4 (CH), 111.1 (C), 83.5 (CH), 63.2 (CH), 60.2 (CH_2), 55.4 (CH_3), 40.9 (CH_2), 32.6 (CH_2), 32.5 (CH_2), 24.5 (CH_2), 24.4 (CH_2), 21.5 (CH_3), 14.4 (CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. For $C_{28}H_{34}NO_6S$ 512.2135, found 512.2134.

***ethyl(S,E)-3-(3-methyl-7-(p-tolyl)-4-tosyl-2,3,4,5-tetrahydro-1,4-oxazepin-6-yl)acrylate* 3h:**

To a magnetically stirred suspension of activated magnesium sulfate (1.056 gm, 8.78 mmol) and vinylogous carbonate **1h** (100.0 mg, 0.219 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (119 µL, 0.658 mmol) was added dropwise at 0 ^oC as described for the 1,4-oxazepine **3a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the 1,4-oxazepine **3h** (42.0 mg, 42%).



3h

Physical appearance: Pale yellow solid.

M.P: 73-75 ^oC.

R_f: 0.5 (3:7, EtOAc: Petroleum ether).

$[\alpha]_D^{25}$: -501.805 (c 0.345, $CHCl_3$).

IR (neat): 3019, 2996, 1701, 1608, 1364, 1216, 1130, 759, 669 cm^{-1}.

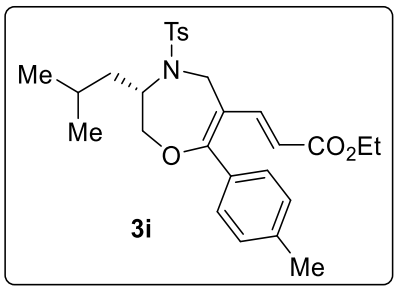
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 16.0 Hz, 1H), 7.05 (dd, *J* = 8.0, 3.2 Hz, 4H), 6.78 (d, *J* = 8.0 Hz, 2H), 5.78 (d, *J* = 16.0 Hz, 1H), 4.70 (d, *J* = 18.8 Hz, 1H), 4.59-4.53 (m,1H), 4.26 (dd, *J* = 12.8, 5.6 Hz, 1H), 4.16-4.04 (m, 4H), 2.32 (s, 3H), 2.20 (s, 3H), 1.28-1.23 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.6 (C), 165.1 (C), 144.0 (CH), 143.1 (C), 140.5 (C), 137.8 (C), 131.2 (C), 130.2 (2 × CH), 129.5 (2 × CH), 128.5 (2 × CH), 127.0 (2 × CH), 113.0 (CH), 108.9 (C), 74.9 (CH_2), 60.2 (CH_2), 53.9 (CH), 39.6 (CH_2), 21.4 (2 ×CH_3), 16.6 (CH_3), 14.4 (CH_3).

HRMS (ESI, M+H^+): m/z calcd. For $C_{25}H_{30}NO_5S$ 456.1862, found 456.1861.

***ethyl(S,E)-3-(3-isobutyl-7-(p-tolyl)-4-tosyl-2,3,4,5-tetrahydro-1,4-oxazepin-6-yl)acrylate* 3i:**

To a magnetically stirred suspension of activated magnesium sulfate (1.639 gm, 13.66 mmol) and vinylogous carbonate **1i** (170.0 mg, 0.341 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (185 µL, 1.025 mmol) was added dropwise at 0 ^oC as described for the 1,4-oxazepine **3a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the 1,4-oxazepine **3i** (80.0 mg, 43 %).



3i

Physical appearance: Pale yellow solid.

M.P: 80-82 ^oC.

R_f: 0.5 (3:7, EtOAc: Petroleum ether).

$[\alpha]_D^{25}$: -507.720 (c 0.605, $CHCl_3$).

IR (neat): 2955, 1708, 1601, 1466, 1311, 1261, 1174, 1095, 1037, 824, 670 cm^{-1}.

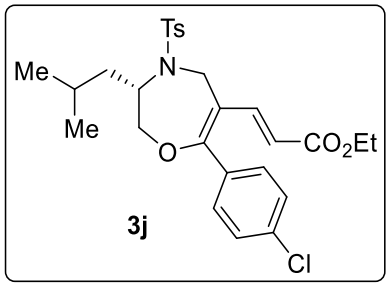
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 16.0 Hz, 1H), 7.05-7.00 (m, 4H), 6.73 (d, *J* = 6.8 Hz, 2H), 5.77 (d, *J* = 16.0 Hz, 1H), 4.67 (d, *J* = 18.8 Hz, 1H), 4.56-4.48 (m,1H), 4.33 (dd, *J* = 12.4, 5.6 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 4.04 (d, *J* = 18.8 Hz, 1H), 3.99 (t, *J* = 12.0 Hz, 1H), 2.32 (s, 3H), 2.16 (s, 3H), 1.89-1.79 (m, 1H), 1.56-1.49 (m, 1H), 1.25 (t, *J* = 7.2 Hz, 4H), 1.01 (d, *J* = 6.4 Hz, 3H), 1.00 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.5 (C), 165.2 (C), 143.9 (CH), 143.0 (C), 140.4 (C), 137.7 (C), 131.1 (C), 130.1 (2 × CH), 129.4 (2 × CH), 128.4 (2 × CH), 127.2 (2 × CH), 113.1 (CH), 109.0 (C), 74.7 (CH_2), 60.1 (CH_2), 56.2 (CH), 40.1 (2 × CH_2), 24.7 (CH), 23.0 (CH_3), 22.6 (CH_3), 21.4 (CH_3), 21.3 (CH_3), 14.4 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{28}H_{36}NO_5S$ 498.2342, found 498.2341.

***ethyl(S,E)-3-(7-(4-chlorophenyl)-3-isobutyl-4-tosyl-2,3,4,5-tetrahydro-1,4-oxazepin-6-yl)acrylate* 3j:**

To a magnetically stirred suspension of activated magnesium sulfate (1.85 gm, 15.44 mmol) and vinylogous carbonate **1j** (200.0 mg, 0.386 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (209 µL, 1.158 mmol) was added dropwise at 0 ^oC as described for the 1,4-oxazepine **3a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the 1,4-oxazepine **3j** (85.0 mg, 43%).



3j

Physical appearance: Pale yellow solid.

M.P: 78-80 ^oC.

R_f: 0.5 (3:7, EtOAc: Petroleum ether).

$[\alpha]_D$ ^{25}: -478.035 (c 0.525, $CHCl_3$).

IR (neat): 2956, 1702, 1601, 1489, 1339, 1259, 1155, 1095, 758, 671 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.27-7.20 (m, 2H), 7.11 (d, *J* = 16 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.80-6.76 (m, 2H), 5.82 (d, *J* = 16.0Hz, 1H), 4.69 (d, *J* = 18.8 Hz, 1H), 4.58-4.51 (m,1H), 4.35 (dd, *J* = 12.8, 6.0 Hz, 1H), 4.16 (q, *J* = 6.8 Hz, 2H), 4.10 (d, *J* = 18.4 Hz, 1H), 4.00 (t, *J* = 12.0 Hz, 1H), 2.19 (s, 3H), 1.90-1.80 (m, 1H), 1.58-1.50 (m, 1H), 1.28-1.22 (m, 4H), 1.02 (d, *J* = 6.4 Hz, 3H), 1.01 (d, *J* = 6.4 Hz, 3H).

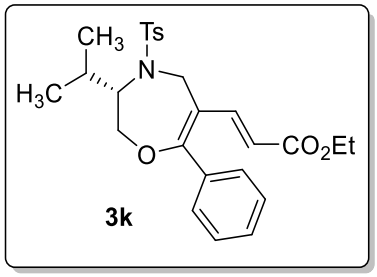
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.3 (C), 163.4 (C), 143.1 (C), 142.9 (CH),137.8 (C), 136.2 (C), 132.4 (C), 131.4 (2 × CH), 129.4 (2 × CH), 127.9 (2 ×

CH), 127.2 (2 × CH), 114.2 (CH), 110.0 (C), 74.9 (CH_2), 60.3 (CH_2), 56.2 (CH), 40.1 (CH_2), 40.0 (CH_2), 24.7 (CH), 23.0 (CH_3), 22.6 (CH_3), 21.3 (CH_3), 14.4 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{27}H_{33}ClNO_5S$ 518.1772, found 518.1771.

ethyl(S,E)-3-(3-isopropyl-7-phenyl-4-tosyl-2,3,4,5-tetrahydro-1,4-oxazepin-6-yl)acrylate **3k:**

To a magnetically stirred suspension of activated magnesium sulfate (0.697 gm, 5.79 mmol) and vinylogous carbonate **1k** (68.0 mg, 0.145 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (79 µL, 0.434 mmol) was added dropwise at 0 ^oC as described for the 1,4-oxazepine **3a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the 1,4-oxazepine **3k** (31.0 mg, 46%).



3k

Physical appearance: Sticky solid.

$[\alpha]_D$ ^{25}: -76.407 (c 0.155, $CHCl_3$).

R_f: 0.5 (3:7, EtOAc: Petroleum ether).

IR (neat): 2966, 1708, 1601, 1466, 1336, 1262, 1156, 1095, 1037, 904, 758 cm^{-1}.

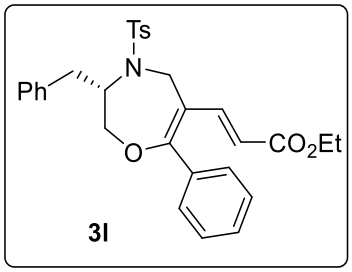
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 16.0 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 7.0 Hz, 2H), 5.79 (d, *J* = 16.0 Hz, 1H), 4.73 (d, *J* = 18.5 Hz, 1H), 4.54 (dd, *J* = 12.0, 5.0 Hz, 1H), 4.24-4.08 (m, 4H), 4.04 (d, *J* = 18.5 Hz, 1H), 2.15 (s, 3H), 1.93-1.84 (m, 1H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.15 (d, *J* = 7.0 Hz, 3H), 1.02 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 167.5 (C), 164.9 (C), 143.6 (CH), 143.1 (C), 137.8 (C), 134.0 (C), 130.2 (2 × CH), 130.1 (CH), 129.4 (2 × CH), 127.7 (2 × CH), 127.3 (2 × CH), 113.7 (CH), 109.4 (C), 74.1 (CH_2), 63.4 (CH), 60.2 (CH_2), 41.1 (CH_2), 30.5 (CH), 21.3 (CH_3), 20.5 (CH_3), 19.3 (CH_3), 14.4 (CH_3).

HRMS (ESI, M+Na^+): m/z calcd. For $C_{26}H_{31}NNaO_5S$ 492.1815, found 492.1819.

ethyl(S,E)-3-(3-benzyl-7-phenyl-4-tosyl-2,3,4,5-tetrahydro-1,4-oxazepin-6-yl)acrylate **3l:**

To a magnetically stirred suspension of activated magnesium sulfate (0.633 gm, 5.25 mmol) and vinylogous carbonate **1l** (68.0 mg, 0.131 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (72 µL, 0.394 mmol) was added dropwise at 0 ^oC as described for the 1,4-oxazepine **3a** followed by purification on a silica gel



3l

column using ethyl acetate-petroleum ether as eluent furnished the 1,4-oxazepine **3l** (36.0 mg, 53%).

Physical appearance: Sticky solid.

R_f: 0.5 (3:7, EtOAc: Petroleum ether).

$[\alpha]_D^{25}$: -295.752 (c 0.455, $CHCl_3$).

IR (neat): 2922, 1701, 1601, 1587, 1366, 1262, 1156, 1044, 848, 756 cm^{-1}.

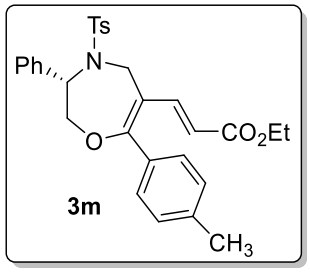
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.5 Hz, 2H), 7.36-7.26 (m, 6H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.15 (d, *J* = 16.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 7.5 Hz, 2H), 5.76 (d, *J* = 16.0 Hz, 1H), 4.71-4.65 (m, 2H), 4.26-4.18 (m, 2H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.87 (d, *J* = 18.5 Hz, 1H), 3.15 (dd, *J* = 13.5, 3.5 Hz, 1H), 2.97 (dd, *J* = 13.5, 8.5 Hz, 1H), 2.20 (s, 3H), 1.26 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 167.5 (C), 164.6 (C), 143.7 (CH), 143.3 (C), 137.7 (C), 136.5 (C), 134.1 (C), 130.2 (3 × CH), 129.6 (2 × CH), 129.5 (2 × CH), 128.9 (2 × CH), 127.8 (2 × CH), 127.2 (CH), 127.1 (2 × CH), 113.5 (CH), 109.2 (C), 73.3 (CH_2), 60.3 (CH_2), 58.9 (CH), 40.7 (CH_2), 39.2 (CH_2), 21.4 (CH_3), 14.4 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{30}H_{32}NO_5S$ 518.2000, found 518.2000.

***ethyl(S,E)-3-(3-phenyl-7-(p-tolyl)-4-tosyl-2,3,4,5-tetrahydro-1,4-oxazepin-6-yl)acrylate* 3m:**

To a magnetically stirred suspension of activated magnesium sulfate (0.484 gm, 4.016 mmol) and vinylogous carbonate **1m** (52.0 mg, 0.100 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (55 µL, 0.301 mmol) was added dropwise at 0 ^oC as described for the 1,4-oxazepine **3a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the 1,4-oxazepine **3m** (29.0 mg, 56%).



3m

Physical appearance: white solid.

M.P: 104-106 ^oC.

R_f: 0.5 (3:7, EtOAc: Petroleum ether).

$[\alpha]_D^{25}$: -305.288 (c 0.355, $CHCl_3$).

IR (neat): 2979, 2919, 1705, 1601, 1588, 1364, 1261, 1166, 1137, 1038, 759 cm^{-1}.

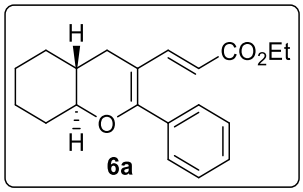
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.43-7.39 (m, 4H), 7.35-7.32 (m, 1H), 7.21 (d, *J* = 16.0 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 4H), 6.80 (d, *J* = 8.0 Hz, 2H), 5.80 (d, *J* = 16.0 Hz, 1H), 5.65 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.90 (d, *J* = 19.0 Hz, 1H), 4.71 (dd, *J* = 12.5, 6.0 Hz, 1H), 4.41 (t, *J* = 12.5 Hz, 1H), 4.23 (d, *J* = 18.5 Hz, 1H), 4.15 (q, *J* = 7.5 Hz, 2H), 2.35 (s, 3H), 2.23 (s, 3H), 1.26 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 167.5 (C), 165.0 (C), 143.8 (CH), 143.4 (C), 140.6 (C), 137.6 (C), 136.8 (C), 131.1 (C), 130.2 (2 × CH), 129.6 (2 × CH), 129.2 (2 × CH), 128.6 (2 × CH), 128.3 (CH), 127.2 (2 × CH), 126.1 (2 × CH), 113.3 (CH), 108.9 (C), 74.0 (CH_2), 60.8 (CH), 60.2 (CH_2), 41.5 (CH_2), 21.5 (CH_3), 21.4 (CH_3), 14.4 (CH_3).

HRMS (ESI, M+Na^+): m/z calcd. For $C_{30}H_{31}NaNO_5S$ 540.1815, found 540.1818.

***ethyl(E)-3-((4aR*,8aS*)-2-phenyl-4a,5,6,7,8,8a-hexahydro-4H-chromen-3-yl)acrylate* 6a:**

To a magnetically stirred suspension of activated magnesium sulfate (0.709 gm, 5.88 mmol) and vinylogous carbonate **5a** (46.0 mg, 0.147 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (81 µL, 0.442 mmol) was added dropwise at 0 ^oC. Reaction was monitored by TLC, quenched with saturated aq. solution of $NaHCO_3$ upon completion, extracted with CH_2Cl_2 (3 × 5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using EtOAc-petroleum ether as eluent furnished the dihydropyran **6a** (37.0 mg, 80%).



6a

Physical appearance: White solid.

M.P: 82-84 ^oC.

R_f: 0.6 (1:9, EtOAc: Petroleum ether).

IR (neat): 2931, 2858, 1710, 1605, 1592, 1364, 1242, 1151, 1017, 699 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (d, *J* = 15.5 Hz, 1H), 7.42-7.38 (m, 5H), 5.68 (d, *J* = 15.0 Hz, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.65 (td, *J* = 10.0, 4.0 Hz, 1H), 2.41 (dd, *J* = 16.5, 5.5 Hz, 1H), 2.18 (dd, *J* = 9.5, 5.5 Hz, 1H), 2.01 (d, *J* = 13.0 Hz, 1H), 1.90-1.85 (m, 2H) 1.75 (d, *J* = 13.0 Hz, 1H), 1.71-1.62 (m, 1H), 1.47-1.28 (m, 3H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.14-1.05 (m, 1H).

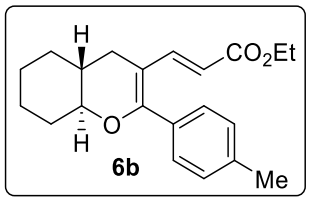
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 168.1 (C), 160.6 (C), 145.2 (CH), 134.9 (C), 130.0 (2 × CH), 129.5 (CH), 128.3 (2 × CH), 111.8 (CH), 108.7 (C), 80.2 (CH), 59.9 (CH_2), 36.9 (CH), 31.9 (CH_2), 31.8 (CH_2), 29.1 (CH_2), 25.5 (CH_2), 24.7 (CH_2), 14.5 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{20}H_{25}O_3$ 313.1829, found 313.1829.

***ethyl(E)-3-((4aR*,8aS*)-2-(p-tolyl)-4a,5,6,7,8,8a-hexahydro-4H-chromen-3-yl)acrylate* 6b:**

To a magnetically stirred suspension of activated magnesium sulfate (1.27 gm, 10.538 mmol) and vinylogous carbonate **5b** (86.0 mg, 0.263 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (143.0 µL, 0.790 mmol) was added dropwise at 0 ^oC as described for the

dihydropyran **6a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the dihydropyran **6b** (60.0 mg, 70%).



Physical appearance: sticky solid.

R_f: 0.6 (1:9, EtOAc: Petroleum ether).

IR (neat): 2930, 1738, 1594, 1243, 1152, 1040, 760 cm^{-1}.

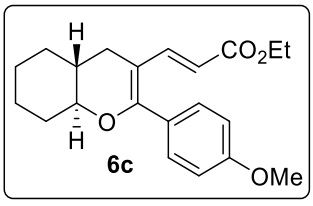
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 15.6 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 5.70 (d, *J* = 15.2 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.65-3.59 (m, 1H), 2.42-2.37 (m, 4H), 2.19-2.17 (m, 1H), 1.99 (d, *J* = 13.2 Hz, 1H), 1.89-1.82 (m, 2H), 1.74-1.59 (m, 2H), 1.49-1.28 (m, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.12-1.02 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 168.0 (C), 160.7 (C), 145.4 (CH), 139.5 (C), 131.9 (C), 129.8 (2 × CH), 128.9 (2 × CH), 111.3 (CH), 108.2 (C), 79.9 (CH), 59.7 (CH_2), 36.8 (CH), 31.8 (CH_2), 31.7 (CH_2), 29.0 (CH_2), 25.4 (CH_2), 24.6 (CH_2), 21.4 (CH_3), 14.4 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{21}H_{27}O_3$ 327.1965, found 327.1964.

***ethyl(E)-3-((4aR*,8aS*)-2-(4-methoxyphenyl)-4a,5,6,7,8,8a-hexahydro-4H-chromen-3-yl)acrylate* 6c:**

To a magnetically stirred suspension of activated magnesium sulfate (1.4 gm, 11.213 mmol) and vinylogous carbonate **5c** (96.0 mg, 0.280 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (152 µL, 0.841 mmol) was added dropwise at 0 ^oC as described for the dihydropyran **6a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the dihydropyran **6c** (36.0 mg, 38%).



Physical appearance: Yellow liquid.

R_f: 0.6 (1:9, EtOAc: Petroleum ether).

IR (neat): 2932, 1706, 1605, 1282, 1252, 1151, 1038, 835 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 15.5 Hz, 1H), 7.34 (d, *J* = 9.0 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 5.65 (d, *J* = 15.5 Hz, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.82 (s, 3H), 3.64-3.59 (m, 1H), 2.39 (dd, *J* = 16.0, 5.5 Hz, 1H), 2.17 (d, *J* = 10.0 Hz, 1H), 1.99 (d, *J* = 12.5 Hz, 1H), 1.87-1.81 (m, 2H), 1.73 (d, *J* = 12.5 Hz, 1H), 1.66-1.62 (m, 1H), 1.48-1.30 (m, 3H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.11-1.04 (m, 1H).

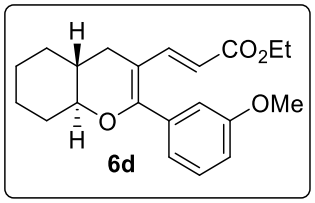
^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 168.2 (C), 160.6 (C), 160.5 (C), 145.6 (CH), 131.4 (2 × CH), 127.3 (C), 113.7 (2 × CH), 111.2 (CH), 108.0 (C), 80.0 (CH), 59.8

(CH_2), 55.4 (CH_3), 36.9 (CH), 31.9 (CH_2), 31.8 (CH_2), 29.2 (CH_2), 25.4 (CH_2), 24.7 (CH_2), 14.5 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{21}H_{27}O_4$ 343.1929, found 343.1929.

***ethyl(E)-3-((4aR*,8aS*)-2-(3-methoxyphenyl)-4a,5,6,7,8,8a-hexahydro-4H-chromen-3-yl)acrylate* 6d:**

To a magnetically stirred suspension of activated magnesium sulfate (913 mg, 7.592 mmol) and vinylogous carbonate **5d** (65.0 mg, 0.189 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (103 µL, 0.569 mmol) was added dropwise at 0 ^oC as described for the dihydropyran **6a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the dihydropyran **6d** (29.0 mg, 45%).



Physical appearance: Pale yellow liquid.

R_f: 0.6 (1:9, EtOAc: Petroleum ether).

IR (neat): 2937, 1706, 1605, 1591, 1288, 1152, 1044, 759 cm^{-1}.

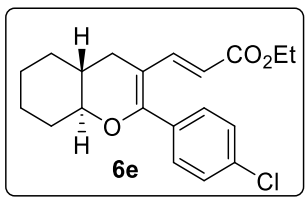
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 15.5 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 9.0 Hz, 2H), 5.67 (d, *J* = 15.5 Hz, 1H), 4.14 (q, *J* = 7.0 Hz, 2H), 3.81 (s, 3H), 3.66-3.61 (m, 1H), 2.40 (dd, *J* = 16.0, 5.5 Hz, 1H), 2.18 (d, *J* = 10.0 Hz, 1H), 2.00 (d, *J* = 13.0 Hz, 1H), 1.89-1.84 (m, 2H), 1.74 (d, *J* = 13.0 Hz, 1H), 1.70-1.62 (m, 1H), 1.49-1.29 (m, 3H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.12-1.05 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 168.0 (C), 160.2 (C), 159.4 (C), 145.1 (CH), 136.1 (C), 129.2 (CH), 122.6 (CH), 115.5 (CH), 115.1 (CH), 111.9 (CH), 108.7 (C), 80.2 (CH), 59.9 (CH_2), 55.4 (CH_3), 36.8 (CH), 31.9 (CH_2), 31.8 (CH_2), 29.1 (CH_2), 25.4 (CH_2), 24.7 (CH_2), 14.5 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{21}H_{27}O_4$ 343.1931, found 343.1930.

***ethyl(E)-3-((4aR*,8aS*)-2-(4-chlorophenyl)-4a,5,6,7,8,8a-hexahydro-4H-chromen-3-yl)acrylate* 6e:**

To a magnetically stirred suspension of activated magnesium sulfate (0.869 gm, 7.150 mmol) and vinylogous carbonate **5e** (62.0 mg, 0.178 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (97 µL, 0.536 mmol) was added dropwise at 0 ^oC as described for the dihydropyran **6a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the dihydropyran **6e** (42.0 mg, 69%).



Physical appearance: White solid.

M.P: 83-85 ^{o}C.

R_f: 0.6 (1:9, EtOAc: Petroleum ether).

IR (neat): 2933, 1707, 1606, 1242, 1153, 1044, 834, 759 cm^{-1}.

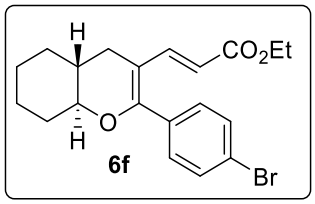
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 15.2 Hz, 1H), 7.37-7.33 (m, 4H), 5.69 (d, *J* = 15.6 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.65-3.59 (m, 1H), 2.39 (dd, *J* = 16.4, 5.6 Hz, 1H), 2.18-2.16 (m, 1H), 2.00 (d, *J* = 12.8 Hz, 1H), 1.89-1.82 (m, 2H), 1.75-1.59 (m, 2H), 1.48-1.28 (m, 3H), 1.24 (t, *J* = 6.8 Hz, 3H), 1.13-1.03 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.9 (C), 159.1 (C), 144.5 (CH), 135.5 (C), 133.3 (C), 131.2 (2 × CH), 128.5 (2 × CH), 112.4 (CH), 109.1 (C), 80.2 (CH), 60.0 (CH_2), 36.8 (CH), 31.8 (CH_2), 31.7 (CH_2), 29.0 (CH_2), 25.4 (CH_2), 24.6 (CH_2), 14.5 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{20}H_{24}ClO_3$ 347.1445, found 347.1445.

***ethyl(E)-3-((4aR*,8aS*)-2-(4-bromophenyl)-4a,5,6,7,8,8a-hexahydro-4H-chromen-3-yl)acrylate* 6f:**

To a magnetically stirred suspension of activated magnesium sulfate (0.678 gm, 5.622 mmol) and vinylogous carbonate **5f** (55.0 mg, 0.140 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (77 µL, 0.421 mmol) was added dropwise at 0 ^{o}C as described for the dihydropyran **6a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the dihydropyran **6f** (40.0 mg, 73%).



6f

Physical appearance: Yellow Solid.

M.P: 97-100 ^{o}C.

R_f: 0.6 (1:9, EtOAc: Petroleum ether).

IR (neat): 2931, 1708, 1603, 1243, 1176, 1153, 706 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.47 (m, 3H), 7.29-7.27 (m, 2H), 5.69 (d, *J* = 15.6 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.65-3.59 (m, 1H), 2.39 (dd, *J* = 16.4, 5.6 Hz, 1H), 2.18-2.16 (m, 1H), 2.01-1.98 (m, 1H), 1.88-1.81 (m, 2H), 1.75-1.60 (m, 2H), 1.45-1.28 (m, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.13-1.03 (m, 1H).

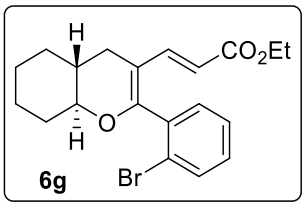
^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.9 (C), 159.1 (C), 144.4 (CH), 133.7 (C), 131.5 (4 × CH), 123.8 (C), 112.5 (CH), 109.1 (C), 80.2 (CH), 60.0 (CH_2), 36.8 (CH), 31.8 (CH_2), 31.7 (CH_2), 29.0 (CH_2), 25.4 (CH_2), 24.6 (CH_2), 14.5 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{20}H_{24}BrO_3$ 391.0929, found 391.0928.

(Note: Compound 6g shows rotamers and data written for the major isomer.)

***ethyl(E)-3-((4aR*,8aS*)-2-(2-bromophenyl)-4a,5,6,7,8,8a-hexahydro-4H-chromen-3-yl)acrylate* 6g:**

To a magnetically stirred suspension of activated magnesium sulfate (1.0gm, 8.791 mmol) and vinylogous carbonate **5g** (86.0 mg, 0.219 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (120.0 µL, 0.659 mmol) was added dropwise at 0 ^oC as described for the dihydropyran **6a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the dihydropyran **6g** (38.0 mg, 44%)**.**



Physical appearance: Yellow liquid.

R_f: 0.5 (1.5:8.5, EtOAc: Petroleum ether).

IR (neat): 2930, 1713, 1601, 1466, 1230, 1113, 1001, 773 cm^{-1}.

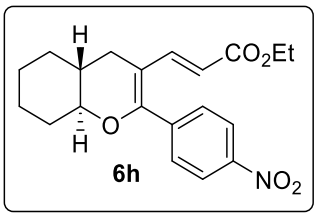
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (t, *J* = 7.6 Hz, 1H), 7.34-7.22 (m, 3H), 7.13 (d, *J* = 15.2 Hz, 1H), 5.67 (d, *J* = 15.6 Hz, 1H), 4.10 (q, *J* = 6.8 Hz, 2H) 3.70 (dt, *J* = 10.4, 4.4 Hz, 1H), 2.37 (dd, *J* = 16.4, 5.2 Hz, 1H), 2.15-2.12 (m, 1H), 2.02-1.86 (m, 3H), 1.76-1.68 (m, 2H), 1.43-1.25 (m, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.16-1.07 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.8 (C), 159.6 (C), 143.9 (CH), 135.7 (C), 133.3 (CH), 132.1 (CH), 130.7 (CH), 127.2 (CH), 124.1 (C), 112.4 (CH), 110.6 (C), 80.1 (CH), 60.0 (CH_2), 36.7 (CH), 32.0 (CH_2), 31.6 (CH_2), 28.5 (CH_2), 25.5 (CH_2), 24.8 (CH_2), 14.4 (CH_3).

HRMS (ESI, M+H^+): m/z calcd. For $C_{20}H_{24}BrO_3$ 391.0925, found 391.0924.

***ethyl(E)-3-((4aR*,8aS*)-2-(4-nitrophenyl)-4a,5,6,7,8,8a-hexahydro-4H-chromen-3-yl)acrylate* 6h:**

To a magnetically stirred suspension of activated magnesium sulfate (1.6 gm, 13.215 mmol) and vinylogous carbonate **5h** (118.0 mg, 0.330 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (180 µL, 0.991 mmol) was added dropwise at 0 ^oC as described for the dihydropyran **6a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the dihydropyran **6h** (71.0 mg, 60%).



Physical appearance: Yellow solid.

M.P: 118-120 ^oC.

R_f: 0.6 (1:9, EtOAc: Petroleum ether).

IR (neat): 2936, 1706, 1607, 1522, 1347, 1244, 1154, 1039, 759 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 15.6 Hz, 1H), 5.75 (d, *J* = 15.2 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 3.67-

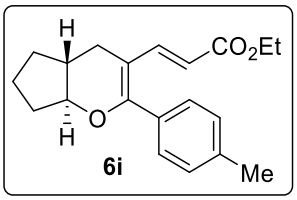
3.62 (m, 1H), 2.42 (dd, *J* = 16.4, 5.2 Hz, 1H), 2.17 (d, *J* = 8.0 Hz, 1H), 2.00 (d, *J* = 12.8 Hz, 1H), 1.92-1.85 (m, 2H), 1.73 (d, *J* = 12.8 Hz, 1H), 1.67-1.64 (m, 1H), 1.44-1.29 (m, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.13-1.04 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.5 (C), 157.3 (C), 148.0 (C), 143.2 (CH), 141.0 (C), 130.8 (2 × CH), 123.4 (2 × CH), 113.9 (CH), 110.8 (C), 80.4 (CH), 60.1 (CH_2), 36.7 (CH), 31.7 (CH_2), 31.6 (CH_2), 29.0 (CH_2), 25.3 (CH_2), 24.6 (CH_2), 14.4 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{20}H_{24}NO_5$ 358.1658, found 358.1657.

ethyl(E)-3-((4aR*,7aS*)-2-(p-tolyl)-4,4a,5,6,7,7a-hexahydrocyclopenta[b]pyran-3-yl)acrylate **6i:**

To a magnetically stirred suspension of activated magnesium sulfate (1.20 gm, 9.730 mmol) and vinylogous carbonate **5i** (76.0 mg, 0.243 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (133 µL, 0.729 mmol) was added dropwise at 0 ^oC as described for the dihydropyran **6a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the dihydropyran **6i** (40.0 mg, 53%).



6i

Physical appearance: Yellow sticky solid.

R_f: 0.6 (1:9, EtOAc: Petroleum ether).

IR (neat): 2950, 1711, 1605, 1582, 1310, 1244, 1176, 1037, 829, 756 cm-1.

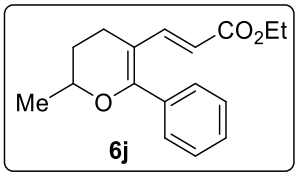
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, *J* = 15.5 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.71 (d, *J* = 15.5 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 3.82-3.76 (m, 1H), 2.59 (dd, *J* = 15.5, 5.5 Hz, 1H), 2.37 (s, 3H), 2.32-2.27 (m, 1H), 2.18-2.12 (m, 1H), 2.08-2.00 (m, 2H), 1.92-1.79 (m, 2H), 1.75-1.67 (m, 2H), 1.25 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 168.0 (C), 162.0 (C), 145.8 (CH), 139.6 (C), 132.1 (C), 130.0 (2 × CH), 128.9 (2 × CH), 111.7 (CH), 109.2 (C), 82.6 (CH), 59.8 (CH_2), 39.6 (CH), 29.2 (CH_2), 28.4 (CH_2), 27.6 (CH_2), 21.4 (CH_3), 20.0 (CH_2), 14.5 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{20}H_{25}O_3$ 313.1828, found 313.1827.

***ethyl(E)-3-(2-methyl-6-phenyl-3,4-dihydro-2H-pyran-5-yl)acrylate* 6j:**

To a magnetically stirred suspension of activated magnesium sulfate (1.44 gm, 12.04 mmol) and vinylogous carbonate **5j** (82.0 mg, 0.301 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (165 µL, 0.903 mmol) was added dropwise at 0 ^oC as described for the dihydropyran **6a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the dihydropyran **6j** (42.0 mg, 51%).



6j

Physical appearance: White solid.

M.P: 65-67 ^oC.

R_f: 0.5 (1.5:8.5, EtOAc: Petroleum ether).

IR (neat): 2931, 1708, 1605, 1592, 1265, 1247, 1039, 768, 699 cm^{-1}.

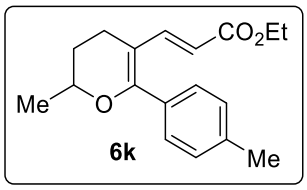
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, *J* = 15.2 Hz, 1H), 7.43-7.38 (m, 5H), 5.69 (d, *J* = 15.6 Hz, 1H), 4.24-4.10 (m, 3H), 2.42-2.25 (m, 2H), 2.08-2.02 (m,1H), 1.78-1.67 (m,1H), 1.40 (d, *J* = 6.0 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 168.0 (C), 160.7 (C), 145.2 (CH), 135.0 (C), 129.9 (2 × CH), 129.5 (CH) 128.2 (2 × CH), 111.8 (CH), 108.3 (C), 73.4 (CH), 59.9 (CH_2), 28.9 (CH_2), 21.5 (CH_2), 20.8 (CH_3), 14.5 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{17}H_{21}O_3$ 273.1502, found 287. 273.1501.

***ethyl (E)-3-(2-methyl-6-(p-tolyl)-3,4-dihydro-2H-pyran-5-yl)acrylate* 6k:**

To a magnetically stirred suspension of activated magnesium sulfate (1.7gm, 13.967 mmol) and vinylogous carbonate **5k** (100.0 mg, 0.349 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (190 µL, 1.047 mmol) was added dropwise at 0 ^oC as described for the dihydropyran **6a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the dihydropyran **6k** (60.0 mg, 60%).



6k

Physical appearance: Yellow liquid.

R_f: 0.6 (1:9, EtOAc: Petroleum ether).

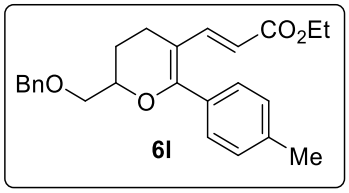
IR (neat): 2955, 1707, 1596, 1268, 1177, 758 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 15.5 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 2H), 5.67 (d, *J* = 15.5 Hz, 1H), 4.17-4.13 (m, 3H), 2.39-2.35 (m, 4H), 2.31-2.24 (m,1H), 2.05-2.01 (m, 1H), 1.74-1.66 (m,1H), 1.39 (d, *J* = 6.5 Hz, 3H), 1.25 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 168.0 (C), 160.8 (C), 145.4 (CH), 139.5 (C), 132.0 (C), 129.8 (2 × CH), 128.8 (2 × CH), 111.3 (CH), 107.9 (C), 73.3 (CH), 59.8 (CH_2), 28.8 (CH_2), 21.5 (CH_2), 21.4 (CH_3), 20.8 (CH_3), 14.4 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{18}H_{23}O_3$ 287.1669, found 287.1669.

***ethyl(E)-3-(2-((benzyloxy)methyl)-6-(p-tolyl)-3,4-dihydro-2H-pyran-5-yl)acrylate* 6l:** To a magnetically stirred suspension of activated magnesium sulfate (980 mg, 8.153 mmol) and vinylogous carbonate **5l** (80.0 mg, 0.203 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (110 µL, 0.611 mmol) was added dropwise at 0 ^oC as described for the dihydropyran **6a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the dihydropyran **6l** (51.0 mg, 64%).



6l

Physical appearance: sticky solid.

R_f: 0.6 (1:9, EtOAc: Petroleum ether).

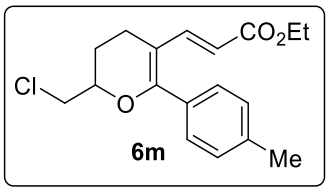
IR (neat): 2919, 2741, 1725, 1713, 1601, 1268, 1124, 717 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, *J* = 15.5 Hz, 1H), 7.36-7.28 (m, 7H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.70 (d, *J* = 15.5 Hz, 1H), 4.61 (d, *J* = 2.0 Hz, 2H), 4.27-4.21 (m, 1H), 4.16 (q, *J* = 7.0 Hz, 2H), 3.74 (dd, *J* = 10.0, 5.5 Hz, 1H), 3.66 (dd, *J* = 10.0, 5.0 Hz, 1H), 2.43-2.27 (m, 5H), 2.13-2.10 (m, 1H), 1.88-1.80 (m, 1H), 1.26 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$, DEPT): δ 168.0 (C), 160.4 (C), 145.2 (CH), 139.6 (C), 138.1 (C), 131.8 (C), 129.9 (2 × CH), 128.9 (2 × CH), 128.5 (2 × CH), 127.8 (CH), 127.7 (2 × CH), 111.8 (CH), 108.3 (C), 76.0 (CH), 73.6 (CH_2), 72.0 (CH_2), 59.9 (CH_2), 24.2 (CH_2), 21.4 (CH_3), 21.1 (CH_2), 14.5 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{25}H_{29}O_4$ 393.2064, found 393.2064.

***ethyl(E)-3-(2-(chloromethyl)-6-(p-tolyl)-3,4-dihydro-2H-pyran-5-yl)acrylate* 6m:** To a magnetically stirred suspension of activated magnesium sulfate (1.0 gm, 8.727 mmol) and vinylogous carbonate **5m** (70.0 mg, 0.218 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (119 µL, 0.654 mmol) was added dropwise at 0 ^oC as described for the dihydropyran **6a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the dihydropyran **6m** (40.0 mg, 57%).



6m

Physical appearance: sticky solid.

R_f: 0.6 (1:9, EtOAc: Petroleum ether).

IR (neat): 2939, 1705, 1605, 1313, 1268, 1177, 1045, 821, 758 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 15.6 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.70 (d, *J* = 15.6 Hz, 1H), 4.24-4.20 (m, 1H), 4.15 (q, *J* = 6.8

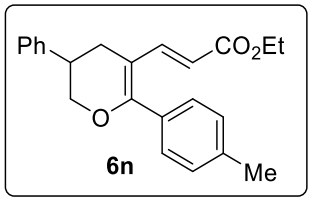
Hz, 2H), 3.74 (dd, *J* = 12.8, 6.0 Hz, 1H), 3.65 (dd, *J* = 11.2, 5.2 Hz, 1H), 2.46-2.27 (m, 5H), 2.20-2.15 (m, 1H), 1.91-1.81 (m,1H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.8 (C), 159.7 (C), 144.7 (CH), 139.9 (C), 131.4 (C), 129.9 (2 × CH), 129.0 (2 × CH), 112.4 (CH), 108.3 (C), 76.1 (CH), 60.0 (CH_2), 45.6 (CH_2), 24.8 (CH_2), 21.5 (CH_3), 20.9 (CH_2), 14.4 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{18}H_{22}ClO_3$ 321.1254, found 321.1254.

***ethyl(E)-3-(3-phenyl-6-(p-tolyl)-3,4-dihydro-2H-pyran-5-yl)acrylate* 6n:**

To a magnetically stirred suspension of activated magnesium sulfate (1.3 gm, 10.905 mmol) and vinylogous carbonate **5n** (95.0 mg, 0.272 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (148 µL, 0.817 mmol) was added dropwise at 0 ^oC as described for the dihydropyran **6a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the dihydropyran **6n** (58.0 mg, 61%).



6n

Physical appearance: Pale yellow solid.

M.P: 80-82 ^oC.

R_f: 0.6 (1:9, EtOAc: Petroleum ether).

IR (neat): 2966, 1706, 1606, 1598, 1253, 1175, 826, 678 cm^{-1}.

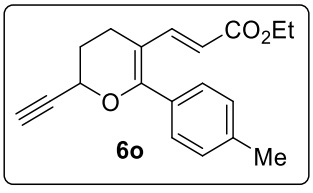
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 15.6 Hz, 1H), 7.40-7.22 (m, 9H), 5.72 (d, *J* = 15.6 Hz, 1H), 4.44-4.40 (m, 1H), 4.16 (q, *J* = 7.2 Hz, 2H), 4.08 (t, *J* = 10.4 Hz, 1H), 3.29-3.22 (m, 1H), 2.71 (dd, *J* = 16.4, 4.4 Hz, 1H), 2.50 (dd, *J* = 16.8, 10.8 Hz, 1H), 2.40 (s, 3H), 1.25 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 168.0 (C), 160.5 (C), 145.0 (CH), 141.2 (C), 139.8 (C), 131.6 (C), 129.8 (2 × CH), 129.0 (2 × CH), 128.9 (2 × CH), 127.5 (2 × CH), 127.3 (CH), 112.1 (CH), 108.5 (C), 71.4 (CH_2), 59.9 (CH_2), 38.6 (CH), 29.3 (CH_2), 21.5 (CH_3), 14.5 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{23}H_{25}O_3$ 349.1801, found 349.1801.

***ethyl(E)-3-(2-ethynyl-6-(p-tolyl)-3,4-dihydro-2H-pyran-5-yl)acrylate* 6o:**

To a magnetically stirred suspension of activated magnesium sulfate (910 mg, 7.55 mmol) and vinylogous carbonate **5o** (56.0 mg, 0.188 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (102 µL, 0.566 mmol) was added dropwise at 0 ^oC as described for the dihydropyran **6a** followed by purification on a silica gel



6o

column using ethyl acetate-petroleum ether as eluent furnished the dihydropyran **6o** (25.0 mg, 47%).

Physical appearance: Yellow liquid.

R_f: 0.6 (1:9, EtOAc: Petroleum ether).

IR (neat): 3021, 3003, 2344, 1685, 1606, 1251, 1216, 1044, 759, 669 cm^{-1}.

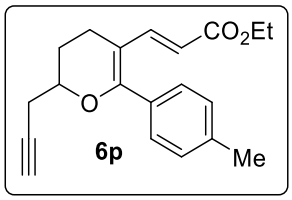
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 15.6 Hz, 1H), 7.30 (dd, *J* = 6.4, 1.6 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.72 (d, *J* = 15.6 Hz, 1H), 4.96-4.93 (m, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.52-2.44 (m, 2H), 2.40-2.31 (m, 4H), 2.25-2.19 (m, 1H), 2.18-2.10 (m, 1H), 1.25 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.9 (C), 158.9 (C), 144.8 (CH), 139.8 (C), 131.5 (C), 129.9 (2 × CH), 129.0 (2 × CH), 112.7 (CH), 108.6 (C), 81.1(C), 74.0 (CH), 65.9 (CH), 60.0 (CH_2), 27.4 (CH_2), 21.5 (CH_3), 19.6 (CH_2), 14.5 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{19}H_{21}O_3$ 297.1487, found 297.1486.

***ethyl(E)-3-(2-(prop-2-yn-1-yl)-6-(p-tolyl)-3,4-dihydro-2H-pyran-5-yl)acrylate* 6p:**

To a magnetically stirred suspension of activated magnesium sulfate (1.56 gm, 13.01 mmol) and vinylogous carbonate **5p** (101.0 mg, 0.325 mmol) in dry CH_2Cl_2 (5 mL), TMSOTf (176 µL, 0.976 mmol) was added dropwise at 0 ^oC as described for the dihydropyran **6a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the dihydropyran **6p** (38.0 mg, 38%).



Physical appearance: sticky solid.

R_f: 0.6 (1:9, EtOAc: Petroleum ether).

IR (neat): 3278, 2932, 2344, 1705, 1605, 1312, 1177, 759 cm^{-1}.

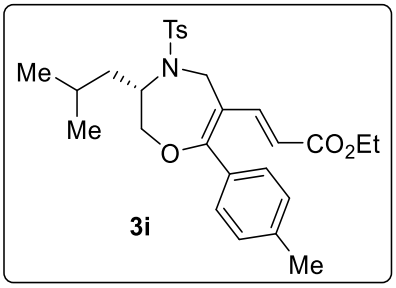
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 15.6 Hz, 1H), 7.31 (d, *J* = 8.4, Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.70 (d, *J* = 15.2 Hz, 1H), 4.21-4.12 (m, 3H), 2.70 (abxm, *J* = 16.8, 5.6, 2.8 Hz, 1H), 2.53 (abxm, *J* = 16.8, 7.2, 2.4 Hz, 1H), 2.45-2.21 (m, 6H), 2.06 (t, *J* = 2.8 Hz, 1H), 1.89-1.80 (m, 1H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.9 (C), 160.1 (C), 145.0 (CH), 139.7 (C), 131.7 (C), 129.9 (2 × CH), 128.9 (2 × CH), 112.1 (CH), 108.3 (C), 79.8 (C), 74.8 (CH), 70.8 (CH), 59.9 (CH_2), 26.1 (CH_2), 24.7 (CH_2), 21.5 (CH_3), 21.1 (CH_2), 14.5 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{20}H_{23}O_3$ 311.1664, found 311.1663.

***ethyl(S,E)-3-(3-isobutyl-7-(p-tolyl)-4-tosyl-2,3,4,5-tetrahydro-1,4-oxazepin-6-yl)acrylate* 3i (gram scale synthesis):**

To a magnetically stirred suspension of activated magnesium sulfate (9.771 gm, 81.181 mmol) and vinylogous carbonate **1i** (1.01 gm, 0.341 mmol) in dry CH_2Cl_2 (30 mL), TMSOTf (1.10 mL, 6.088 mmol) was added dropwise at 0 ^oC as described for the 1,4-oxazepine **3a** followed by purification on a silica gel column using ethyl acetate-petroleum ether as eluent furnished the 1,4-oxazepine **3i** (430.0 mg, 43%).



3i

Physical appearance: Pale yellow solid.

M.P: 80-82 ^oC.

R_f: 0.5 (3:7, EtOAc: Petroleum ether).

$[\alpha]_D^{25}$: -507.720 (c 0.605, $CHCl_3$).

IR (neat): 2955, 1708, 1601, 1466, 1311, 1261, 1174, 1095, 1037, 824, 670 cm^{-1}.

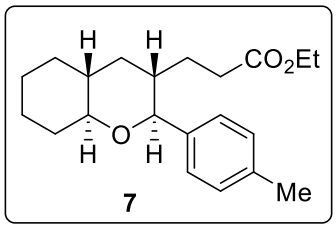
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 16.0 Hz, 1H), 7.05-7.00 (m, 4H), 6.73 (d, *J* = 6.8 Hz, 2H), 5.77 (d, *J* = 16.0 Hz, 1H), 4.67 (d, *J* = 18.8 Hz, 1H), 4.56-4.48 (m,1H), 4.33 (dd, *J* = 12.4, 5.6 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 4.04 (d, *J* = 18.8 Hz, 1H), 3.99 (t, *J* = 12.0 Hz, 1H), 2.32 (s, 3H), 2.16 (s, 3H), 1.89-1.79 (m, 1H), 1.56-1.49 (m, 1H), 1.25 (t, *J* = 7.2 Hz, 4H), 1.01 (d, *J* = 6.4 Hz, 3H), 1.00 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 167.5 (C), 165.2 (C), 143.9 (CH), 143.0 (C), 140.4 (C), 137.7 (C), 131.1 (C), 130.1 (2 × CH), 129.4 (2 × CH), 128.4 (2 × CH), 127.2 (2 × CH), 113.1 (CH), 109.0 (C), 74.7 (CH_2), 60.1 (CH_2), 56.2 (CH), 40.1 (CH_2), 40.0 (CH_2), 24.7 (CH), 23.0 (CH_3), 22.7 (CH_3), 21.4 (CH_3), 21.3 (CH_3), 14.4 (CH_3).

HRMS (ESI, M+ H^+): m/z calcd. For $C_{28}H_{36}NO_5S$ 498.2342, found 498.2341.

***ethyl3-((2S*,3S*,4aR*,8aS*)-2-(p-tolyl)octahydro-2H-chromen-3-yl)propanoate* 7:**

To a magnetically stirred solution of dihydropyran **6b** (50.0 mg, 0.153 mmol) and Et_3SiH (74.0 µL, 0.459 mmol) in dry CH_2Cl_2 (3 mL), TMSOTf (28 µL, 0.153 mmol) was added dropwise at 0 ^oC. Reaction was monitored by TLC, quenched with saturated aq. solution of $NaHCO_3$ extracted with CH_2Cl_2 (3 × 5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate petroleum ether as eluent furnished dihydropyran derivative **7** (47.0 mg, 93%).



7

Physical appearance: Yellow liquid.

R_f: 0.6 (1:9, EtOAc: Petroleum ether).

IR (neat): 2927, 1735, 1449, 1336, 1241, 1164, 1091, 1060, 967, 778 cm^{-1}.

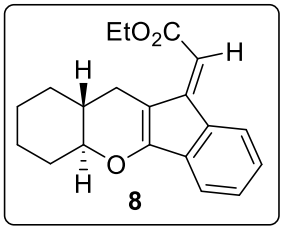
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.63 (d, *J* = 1.2 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.10 (td, *J* = 10.0, 3.6 Hz, 1H), 2.32 (s, 3H), 2.16-2.19 (m, 1H), 1.98-1.23 (m, 14H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.05-0.95 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 173.9 (C), 138.7 (C), 136.0 (C), 128.8 (2 × CH), 125.4 (2 × CH), 83.4 (CH), 81.6 (CH), 60.2 (CH_2), 39.2 (CH), 36.2 (CH), 34.8 (CH_2), 32.8 (CH_2), 32.5 (CH_2), 31.8 (CH_2), 26.0 (CH_2), 25.2 (CH_2), 21.3 (CH_2), 21.2 (CH_3), 14.3 (CH_3).

HRMS (ESI, M+Na^+): m/z calcd. For $C_{21}H_{30}NaO_3$ 353.2087, found 353.2093.

***ethyl(Z)-2-((5aS*,9aR*)-6,7,8,9,9a,10-hexahydroindeno[1,2-b]chromen-11(5aH)-ylidene)acetate* 8:**

To a well evacuated, magnetically stirred mixture of dihydropyran derivative **6g** (36.0 mg, 0.0897 mmol) was added $Pd(OAc)_2$ (4.0 mg, 0.016 mmol), PPh_3 (9.4 mg, 0.035 mmol) followed by dry acetonitrile (5 mL) and trimethylamine (50.0 µL, 0.358 mmol L) at room temperature. The colour of the solution turns yellow. This mixture was heated at 80 ^oC and the solution turns brownish black in half an hour. After *ca*.14 hr (TLC control), the reaction mixture was concentrated under reduced pressure. Purification of the residue over a silica gel column using EtOAc-petroleum ether as eluent furnished tetracyclic hydroindeno chromene derivative **8** (26.0 mg, 90%).



8

Physical appearance: Yellow liquid.

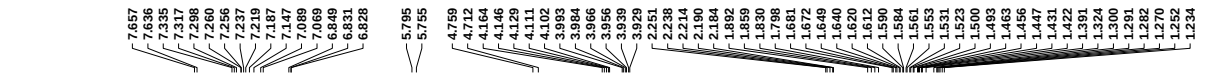
R_f: 0.6 (1:9, EtOAc: Petroleum ether).

IR (neat): 2929, 1716, 1595, 1573, 1446, 1169, 1154, 1002, 759 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 8.4 Hz, 1H), 7.20-7.14 (m, 2H), 6.32 (s, 1H), 4.24 (q, *J* = 6.8 Hz, 2H), 3.78 (td, *J* = 10.8, 4.4 Hz, 1H), 2.81 (dd, *J* = 17.2, 4.8 Hz, 1H), 2.38 (dd, *J* = 17.2, 10.8 Hz, 1H), 2.28 (dd, *J* = 7.2, 3.2 Hz, 1H), 2.01 (d, *J* = 13.2 Hz, 1H), 1.90 (d, *J* = 12.4 Hz, 1H), 1.74 (d, *J* = 12.8 Hz, 1H), 1.60-1.39 (m, 4H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.20-1.10 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 166.8 (C), 163.0 (C), 148.9 (C), 137.4 (C), 136.1 (C), 129.0 (CH), 126.8 (CH), 119.1 (CH), 117.2 (CH), 109.3 (CH), 108.7 (C), 81.3 (CH), 60.4 (CH_2), 38.0 (CH), 32.2 (2 × CH_2), 29.6 (CH_2), 25.8 (CH_2), 24.9 (CH_2), 14.5 (CH_3).

HRMS (ESI, M+Na^+): m/z calcd. For $C_{20}H_{22}NaO_3$ 333.1461, found 333.1458.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7.187
7.147
7.089
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6.828
5.795
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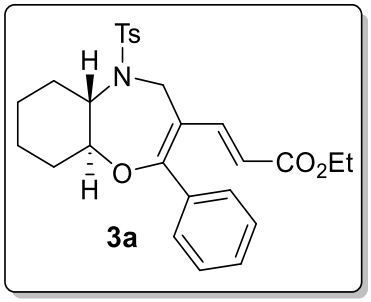
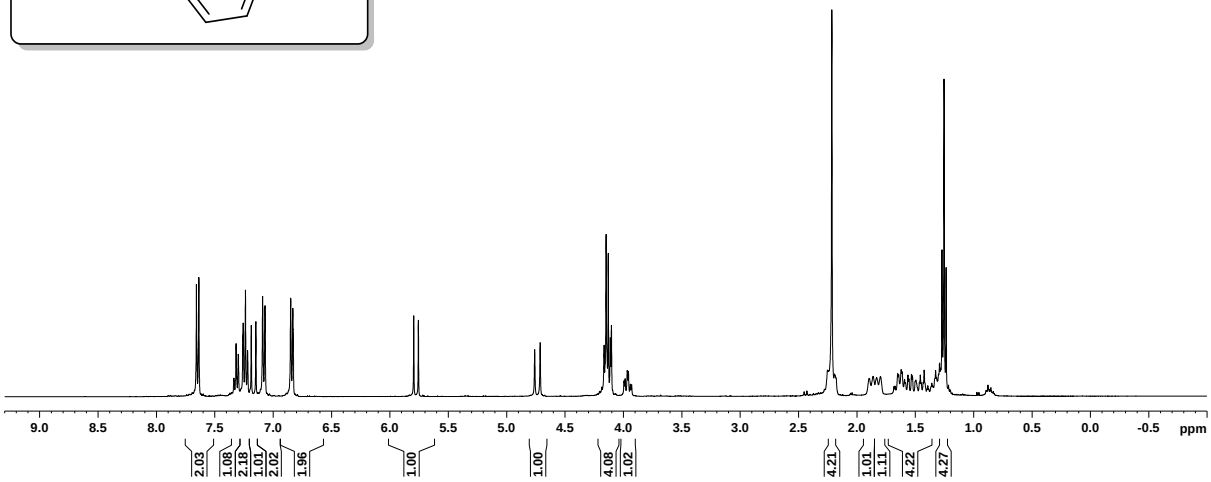

Ts
H
N
O
H
CO2Et
3a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1.0
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ppm
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2.18
1.01
2.02
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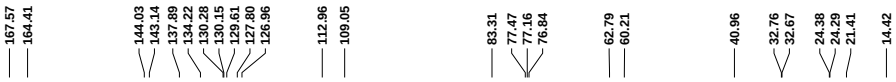
1.00
1.00
4.08
1.02
4.21
1.01
1.11
4.22
4.27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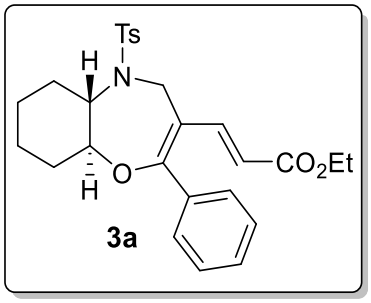
Ts
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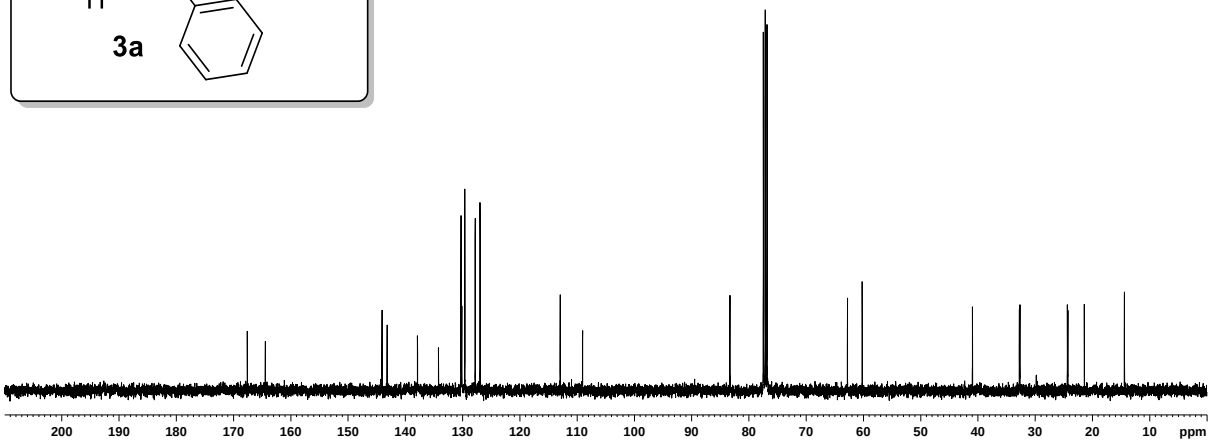
N
O
H
CO2Et
3a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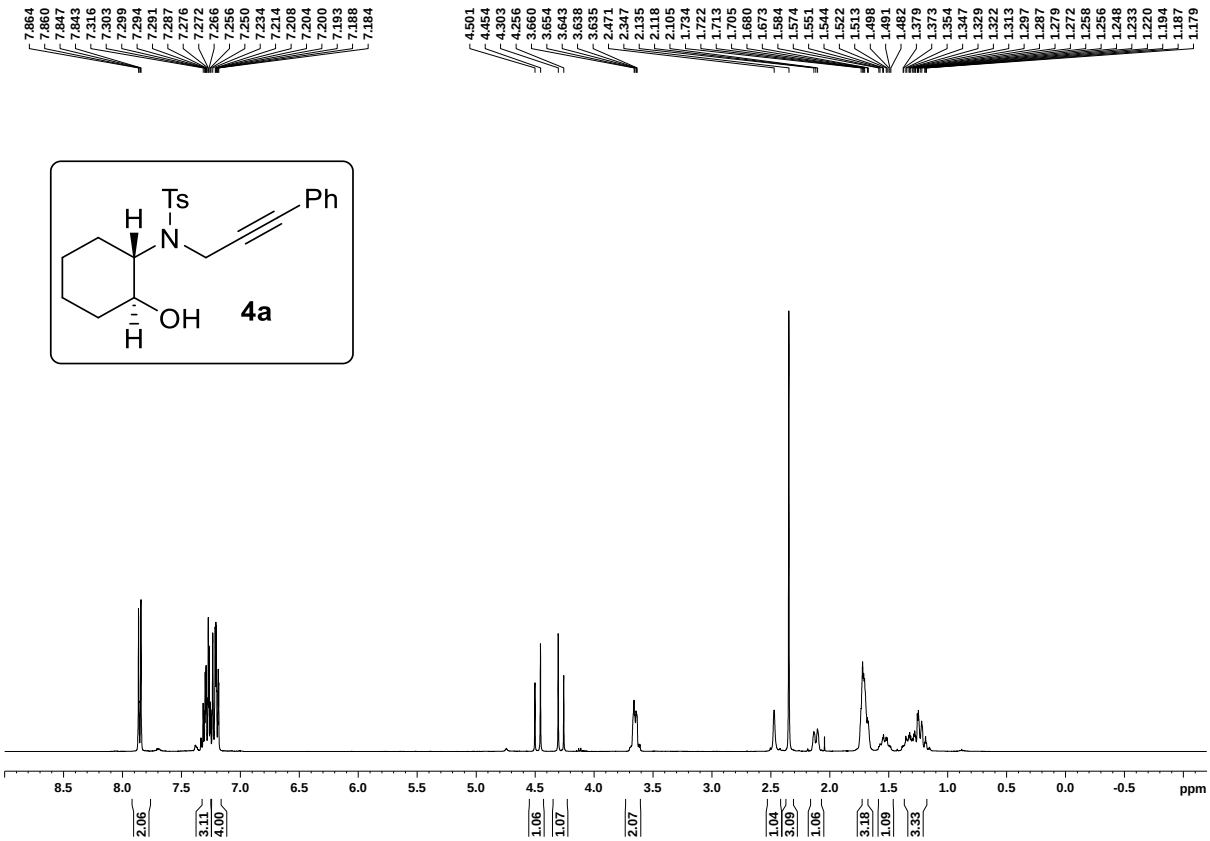
10
ppm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7.256
7.250
7.234
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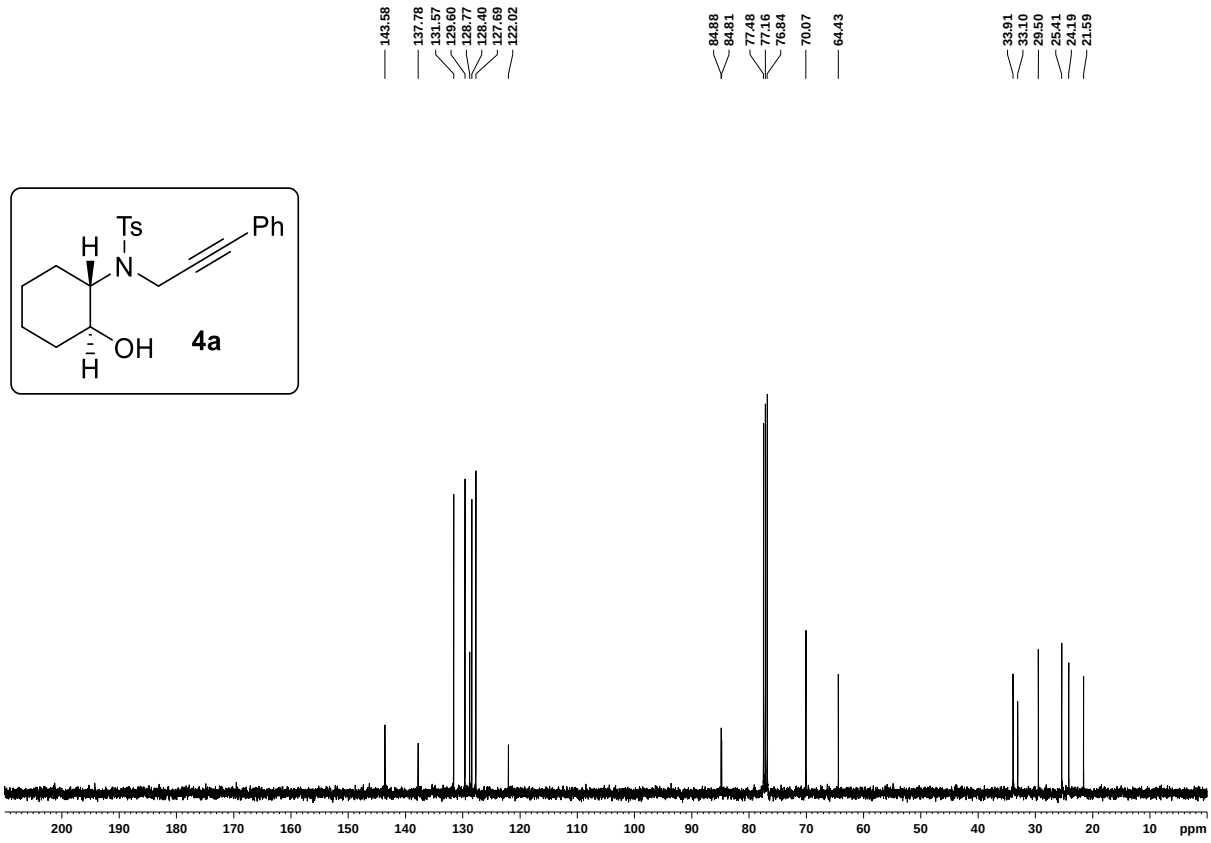
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70.07
64.43
33.91
33.10
29.50
25.41
24.19
21.59
Ts
Ph
H
N
OH
H
4a
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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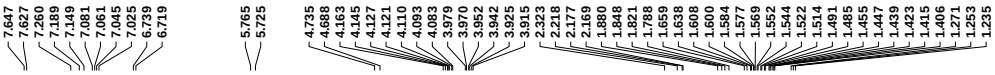
ppm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5.725
4.735
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4.163
4.145
4.127
4.121
4.110
4.093
4.083
3.979
3.970
3.952
3.942
3.925
3.915
2.323
2.218
2.177
2.169
1.880
1.848
1.821
1.788
1.659
1.638
1.608
1.600
1.584
1.577
1.569
1.552
1.544
1.522
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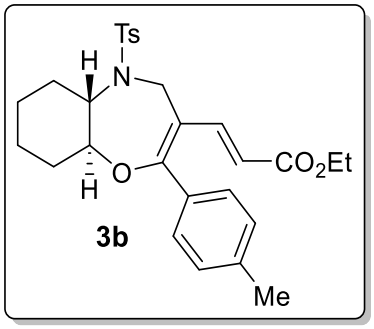
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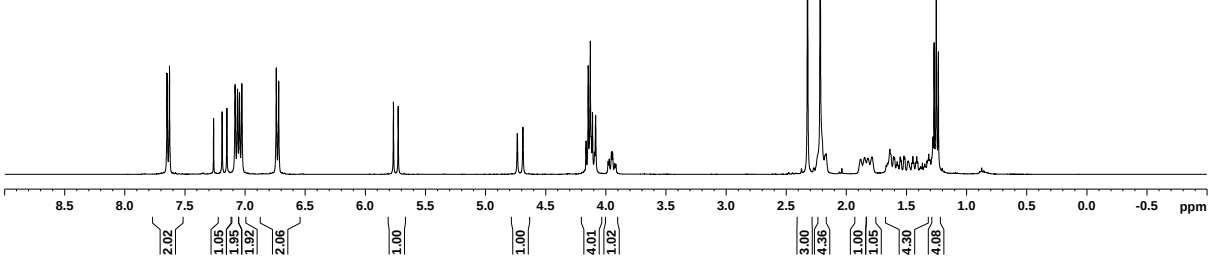
O
H
CO2Et
3b
Me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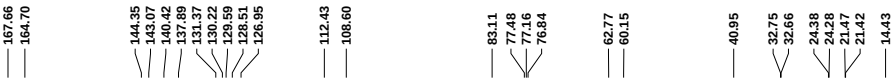
4.08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77.48
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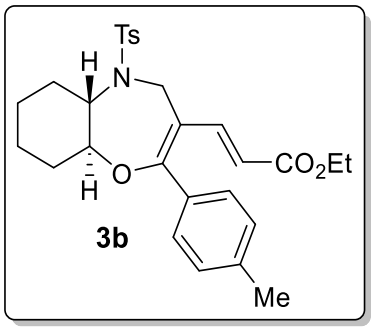
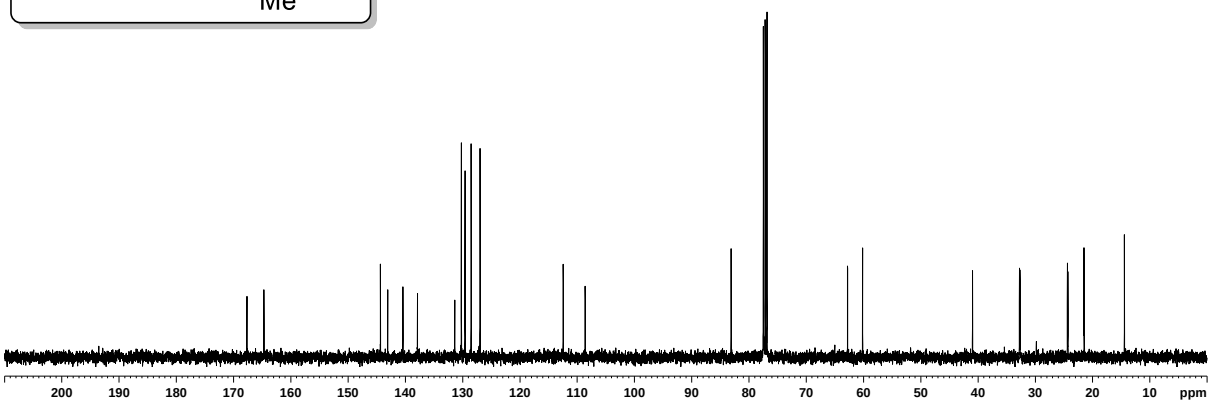
21.42
14.43


Ts
H
N
O
H
CO2Et
3b
Me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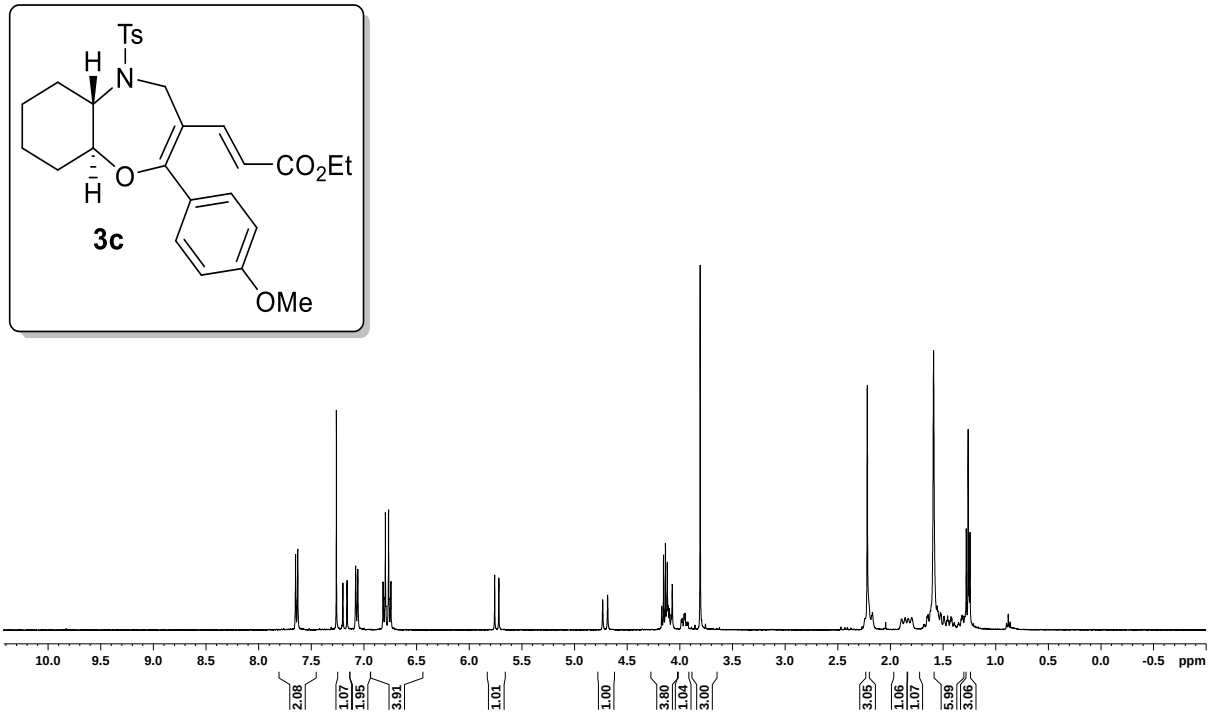
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6.765
6.759
6.747
6.742
5.757
5.717
4.731
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4.170
4.153
4.135
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4.108
4.097
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4.070
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3.971
3.957
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3.804
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2.170
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1.640
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1.588
1.554
1.546
1.524
1.516
1.493
1.487
1.462
1.455
1.446
1.431
1.422
1.414
1.277
1.260
1.242
Ts
H
N
O
H
CO2Et
3c
OMe
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9.5
9.0
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8.0
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7.0
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4.0
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ppm
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1.07
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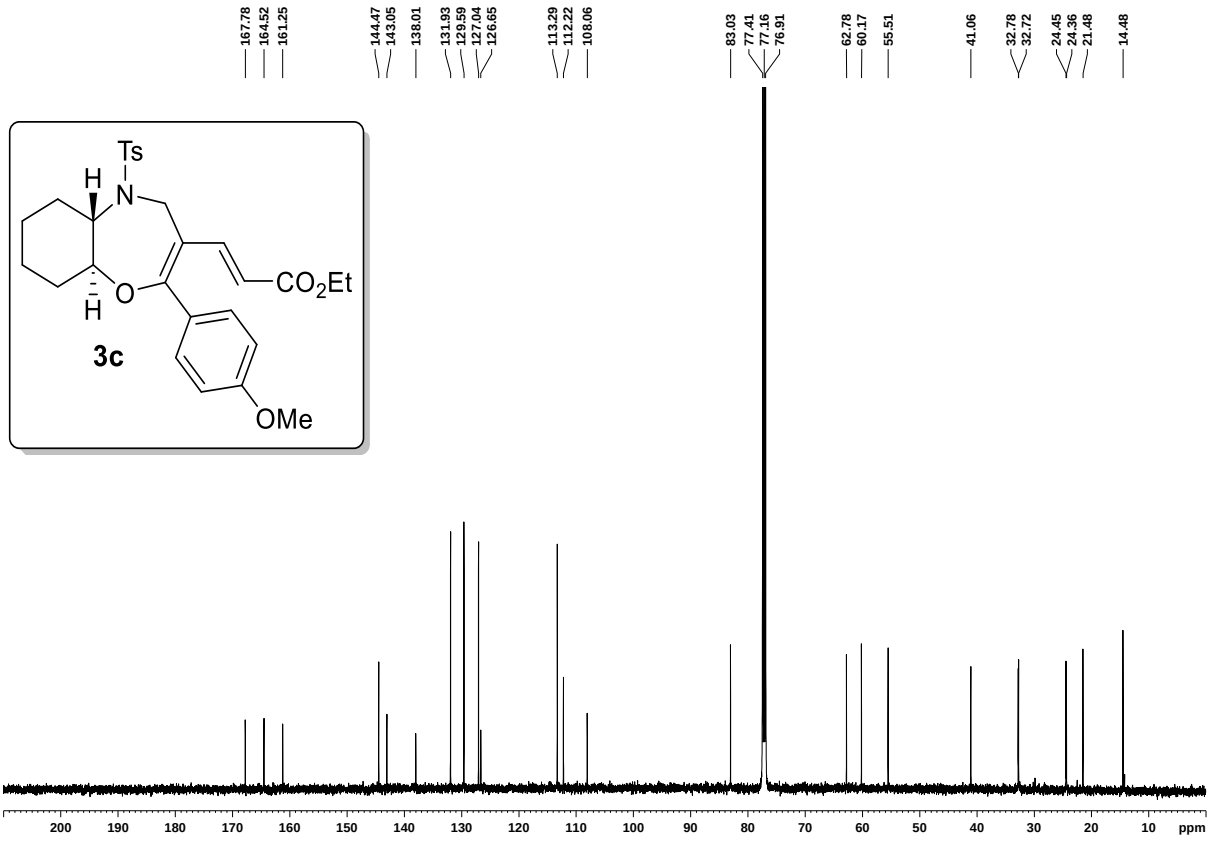
3.06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77.16
76.91
62.78
60.17
55.51
41.06
32.78
32.72
24.45
24.36
21.48
14.48
Ts
H
N
O
H
CO2Et
3c
OMe
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150
140
130
120
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100
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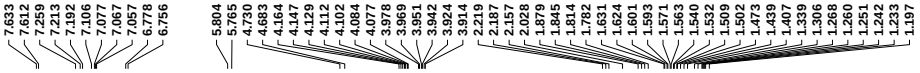
30
20
10
ppm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4.683
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4.147
4.129
4.112
4.102
4.084
4.077
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3.924
3.914
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2.157
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1.845
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1.782
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1.624
1.601
1.593
1.571
1.563
1.540
1.532
1.509
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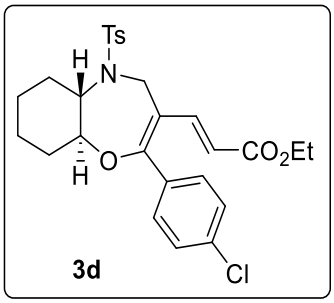
1.233
1.197


Ts
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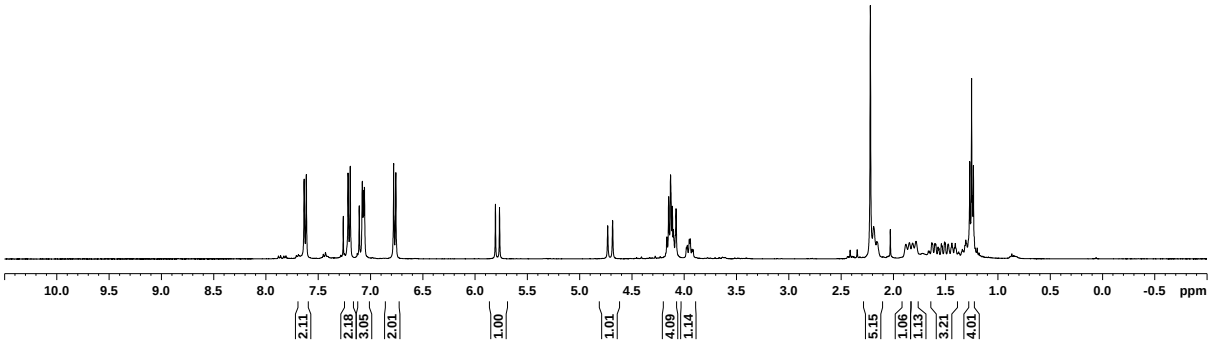
N
O
H
CO2Et
Cl
3d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1.5
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0.0
-0.5
ppm
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1.01
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1.06
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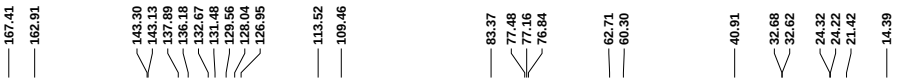
4.01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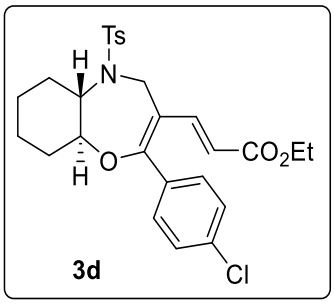
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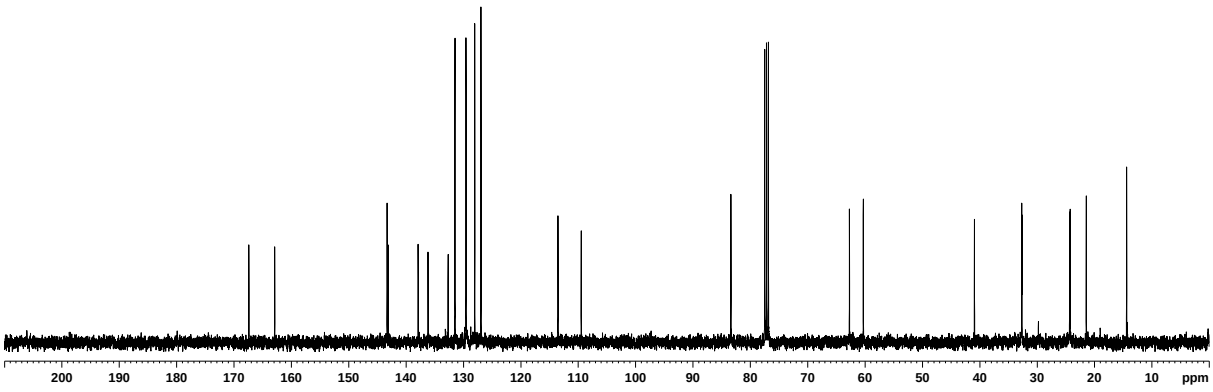
N
O
H
CO2Et
Cl
3d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150
140
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30
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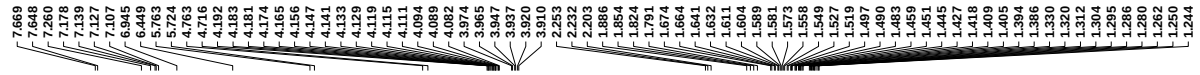
10
ppm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4.156
4.147
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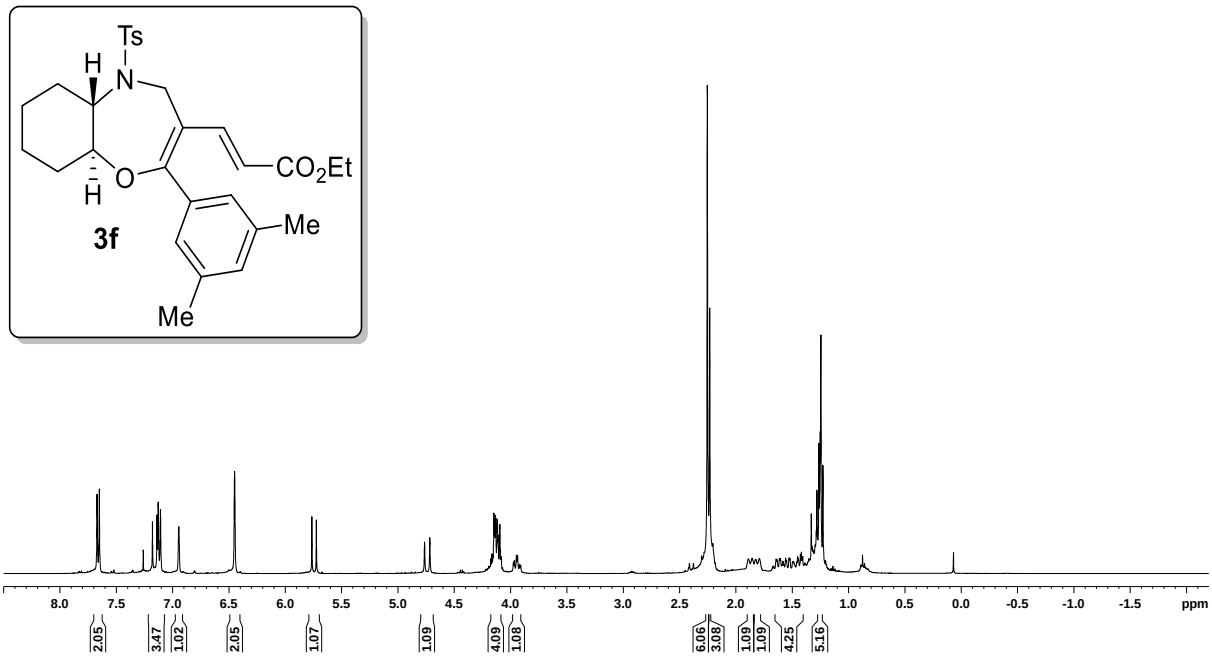
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N
O
H
CO2Et
Me
Me
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1.09
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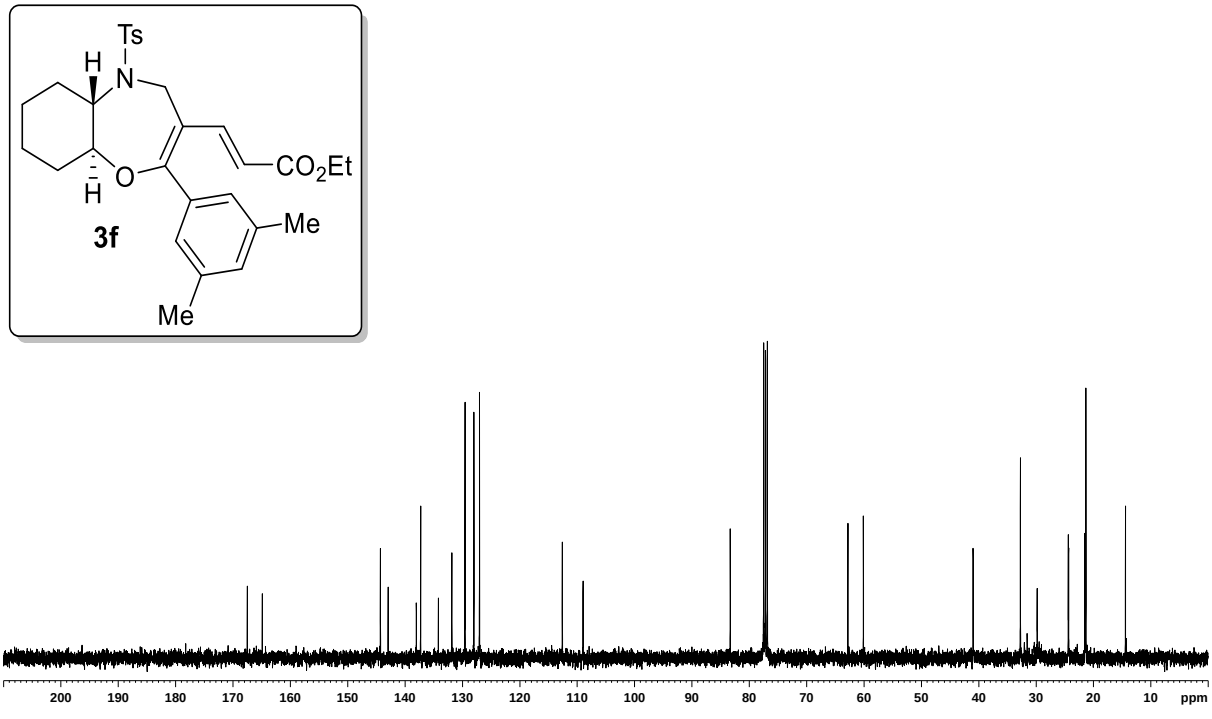
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O
H
CO2Et
Me
Me
3f
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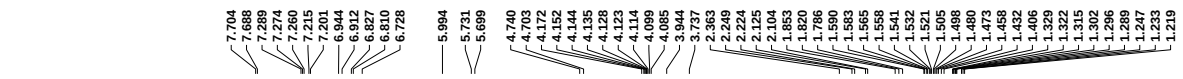
10
ppm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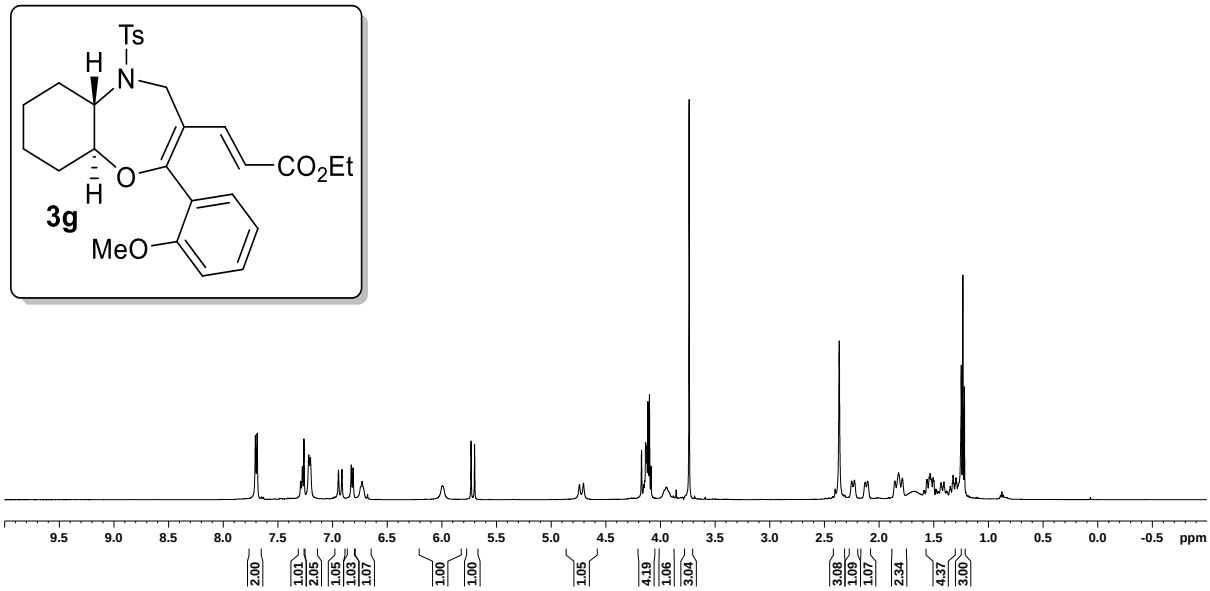
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O
H
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MeO
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2.0
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0.5
0.0
-0.5
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1.07
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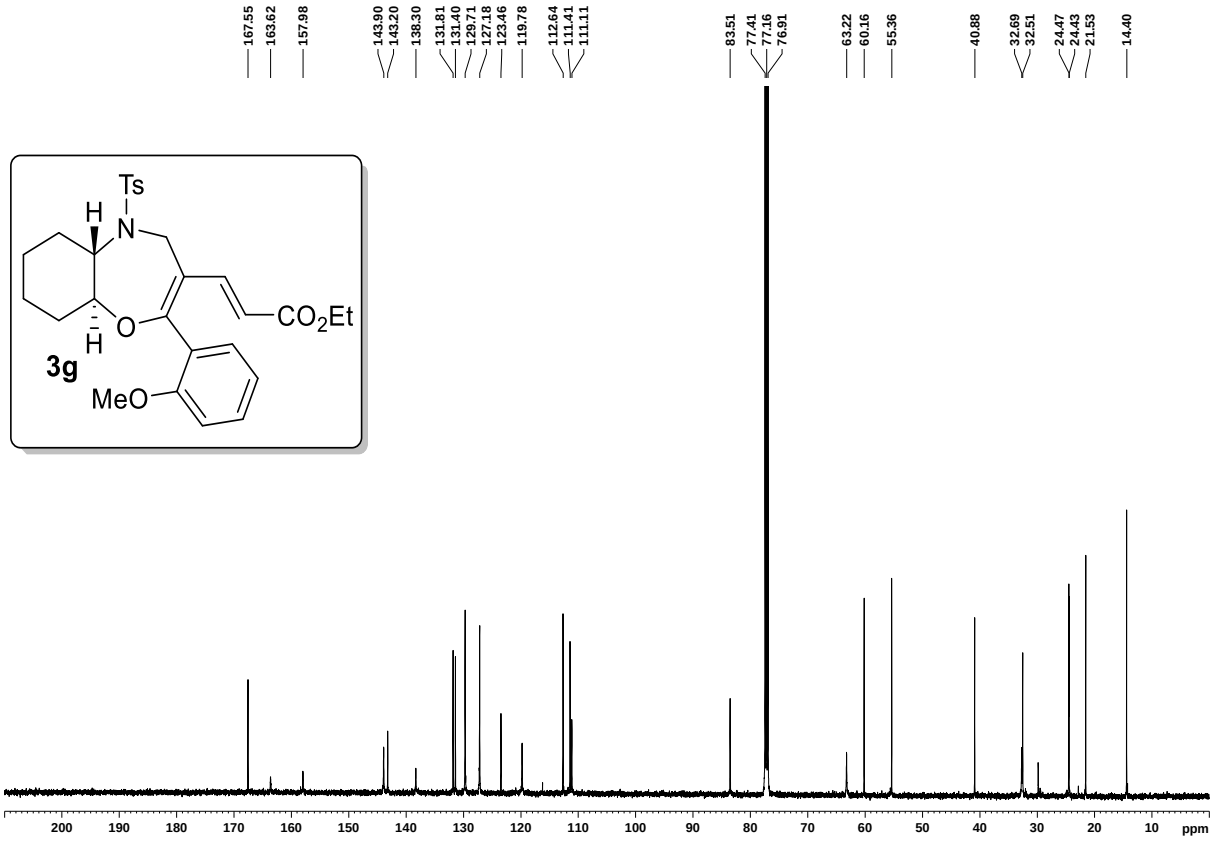
3.00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77.16
76.91
63.22
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32.51
24.47
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21.53
14.40
Ts
H
N
O
H
CO2Et
3g
MeO
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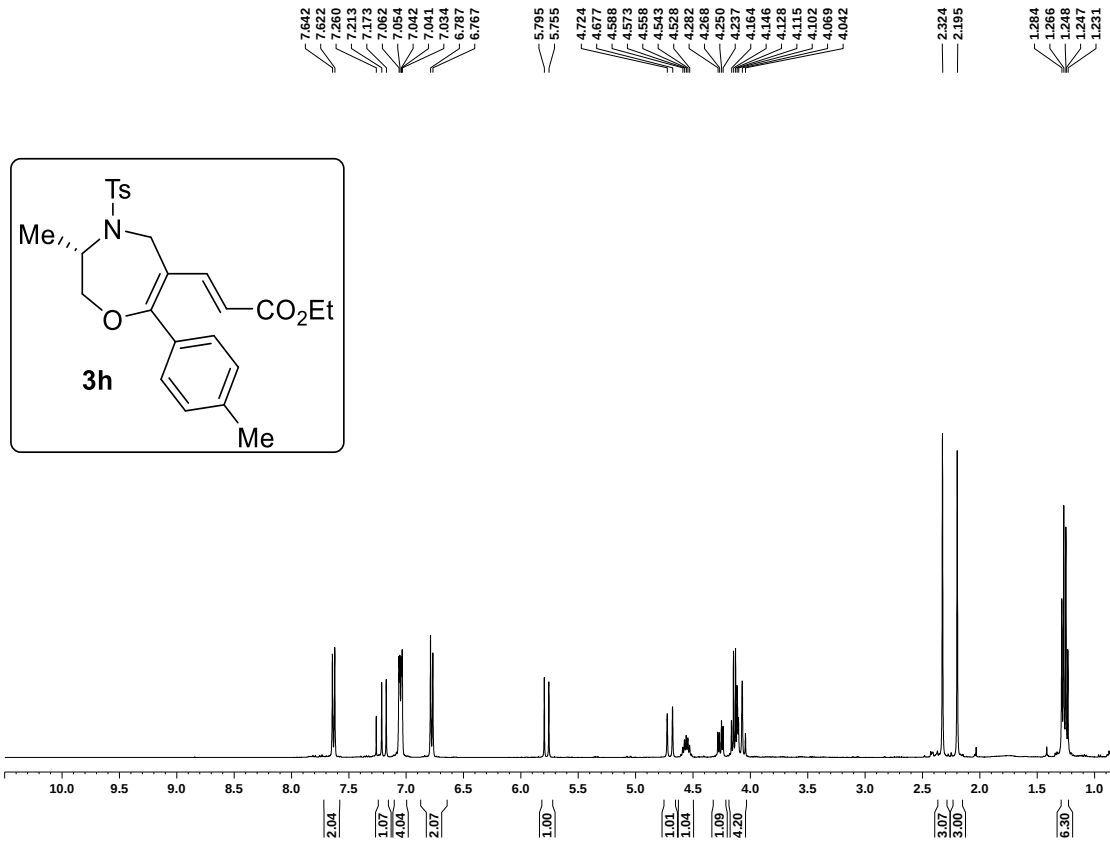
10
ppm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N
Me
O
CO2Et
3h
Me
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7.5
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6.5
6.0
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5.0
4.5
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1.04
1.09
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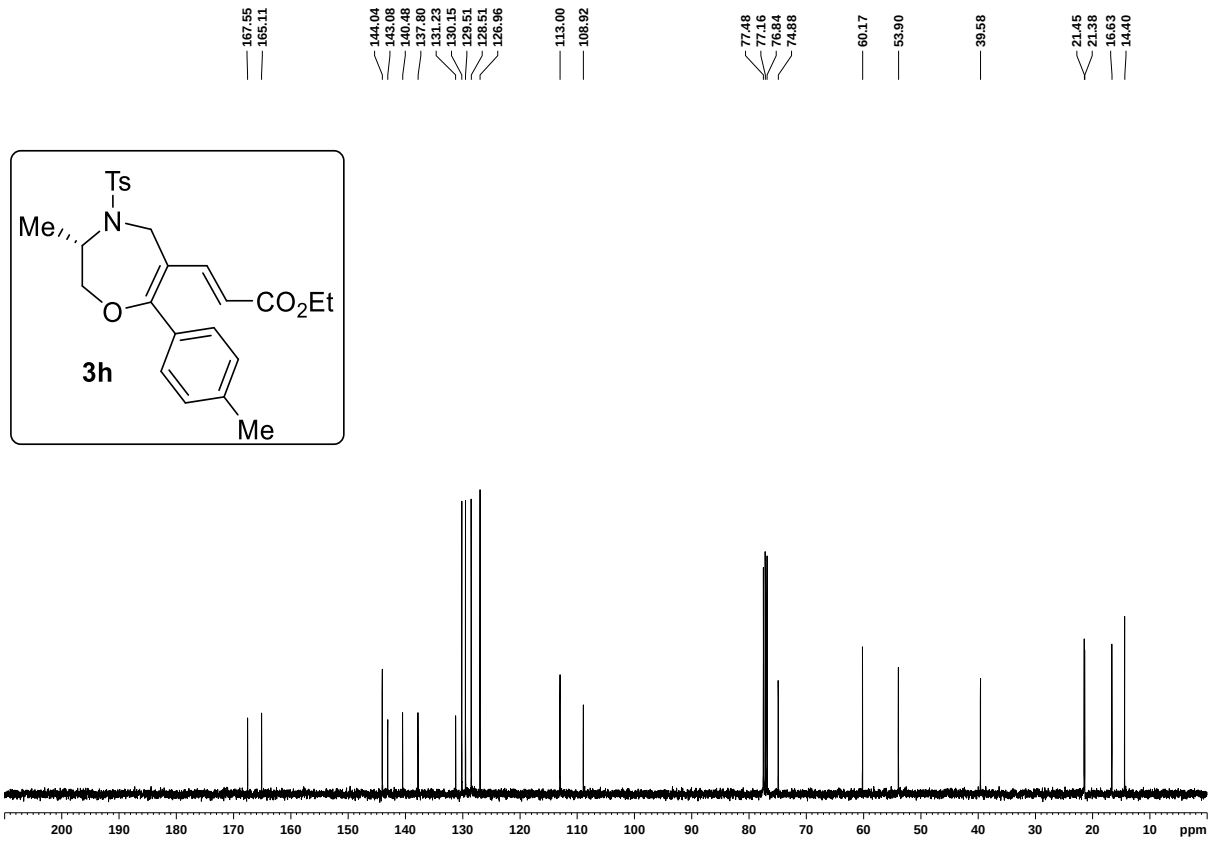
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39.58
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16.63
14.40
Ts
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Me
O
CO2Et
3h
Me
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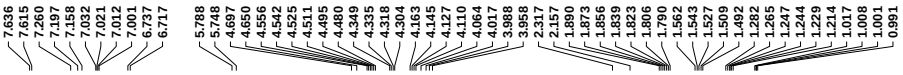
10
ppm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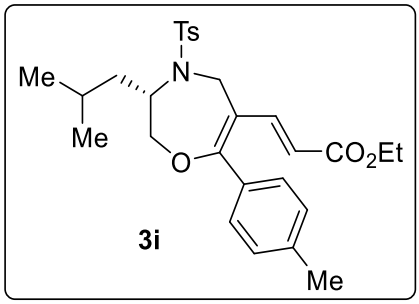
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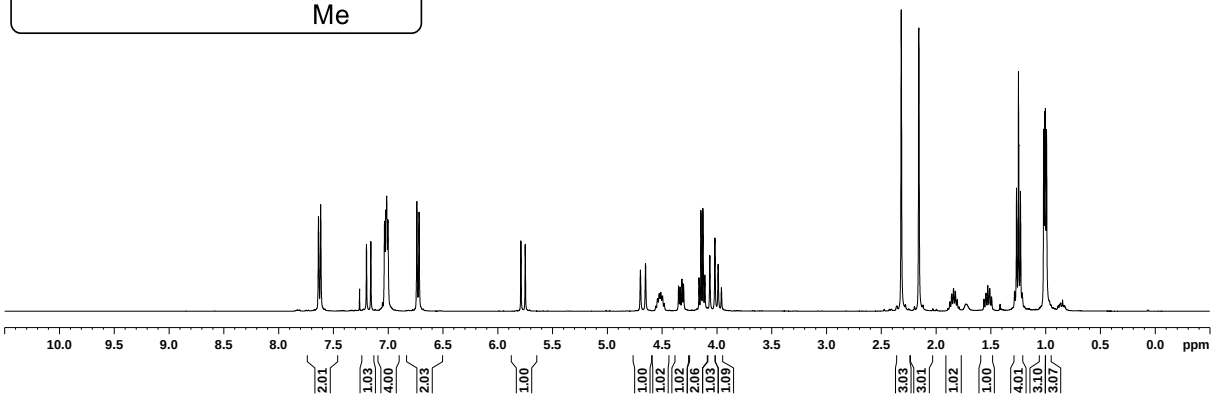
Me
O
CO2Et
Me

3i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1.00
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1.02
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1.09
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3.01
1.02
1.00
4.01
3.10
3.07


167.53
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140.41
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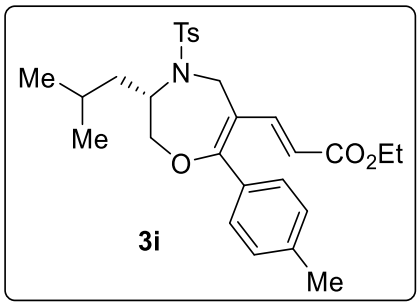
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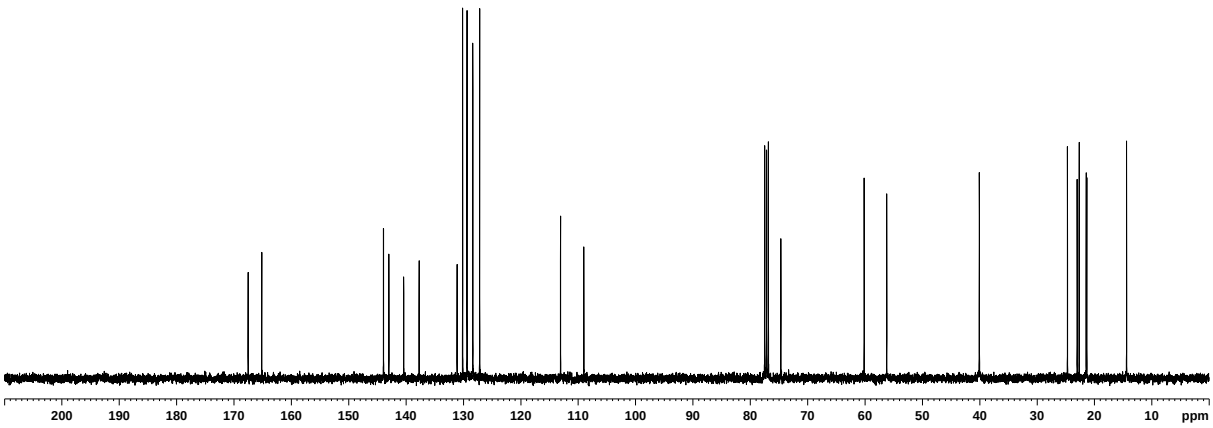
Me
Me
O
CO2Et
Me

3i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6.775
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4.582
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4.362
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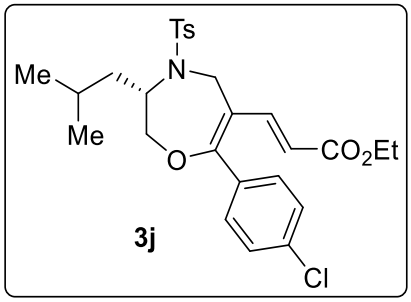
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Me
Me
O
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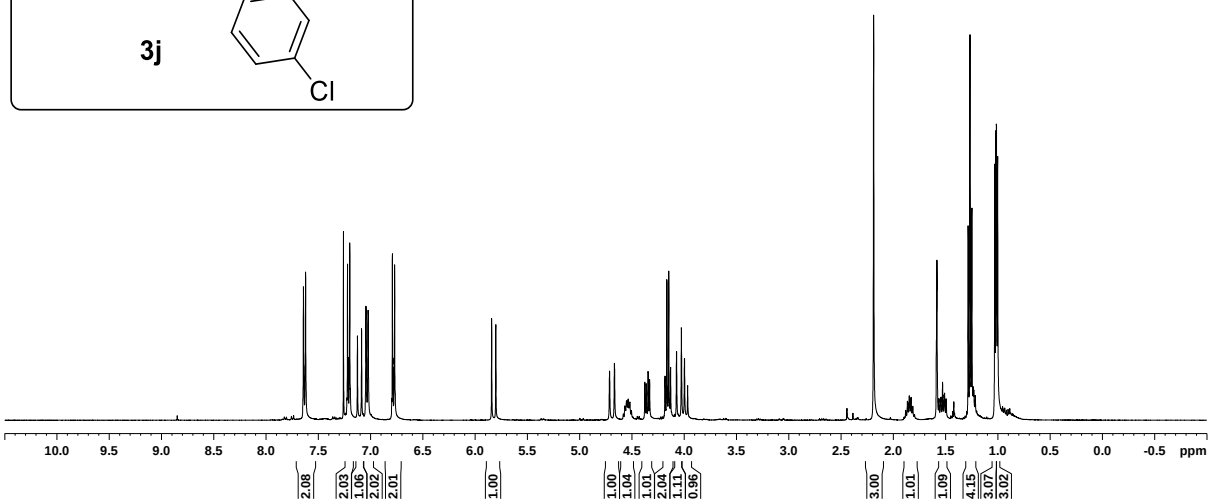
3j
Cl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ppm
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2.02
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2.04
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3.00
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1.09
4.15
3.07
3.02


167.30
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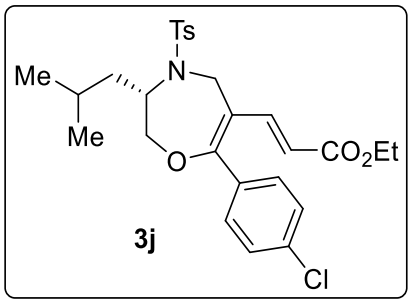
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Me
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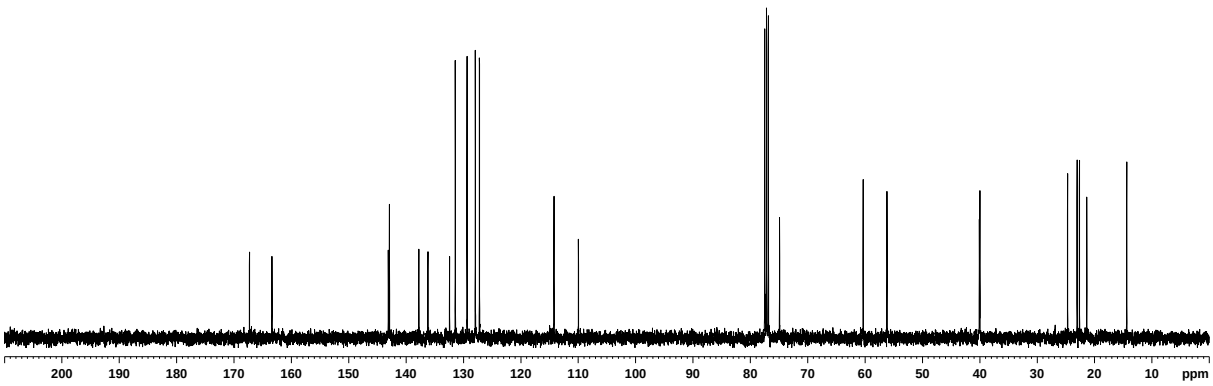
3j
Cl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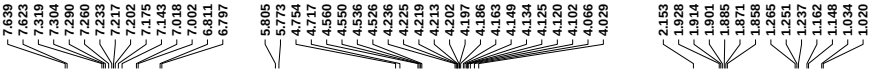
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7.018
7.002
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6.797
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4.717
4.560
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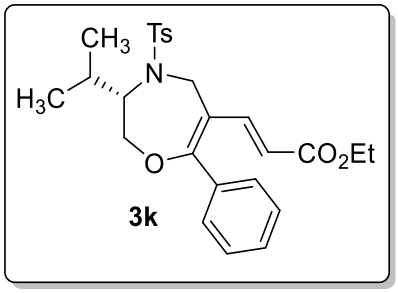
1.020


CH3
Ts
N
H3C
O
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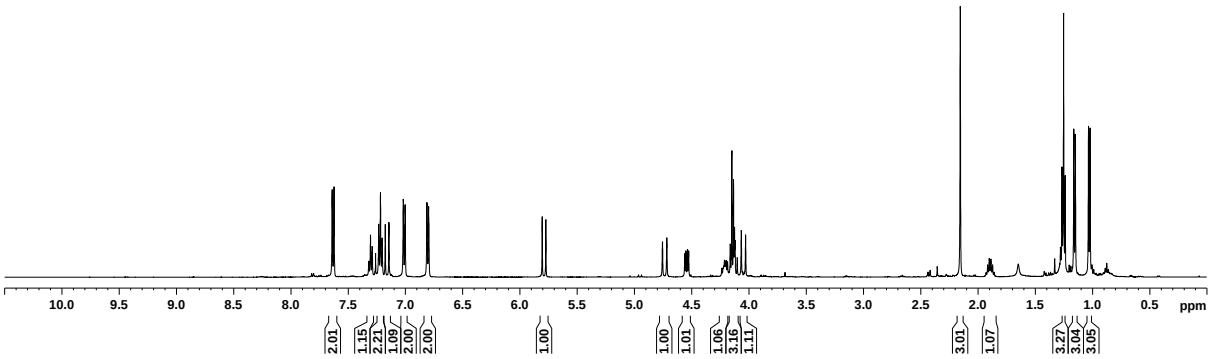
3k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2.21
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2.00
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1.00
1.00
1.01
1.06
3.16
1.11
3.01
1.07
3.27
3.04
3.05


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143.11
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129.41
127.66
127.33
113.66
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20.51
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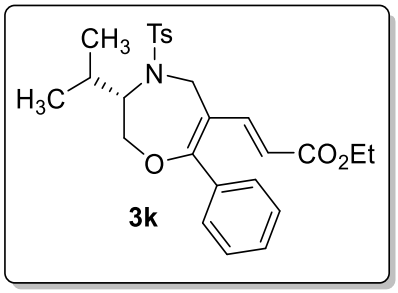
14.41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Ts
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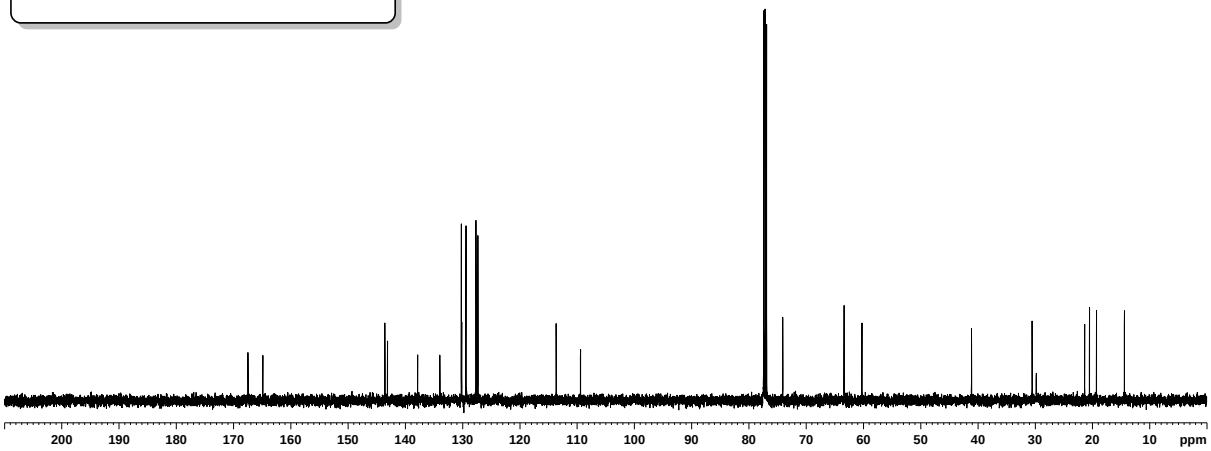
H3C
O
CO2Et
3k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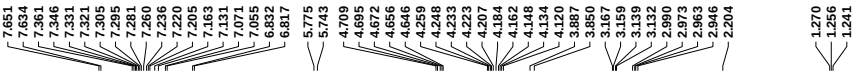
ppm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7.163
7.131
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7.055
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5.775
5.743
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4.695
4.672
4.656
4.646
4.259
4.248
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4.207
4.184
4.162
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4.120
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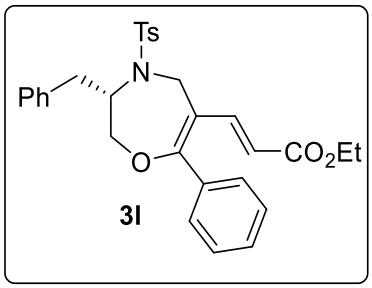
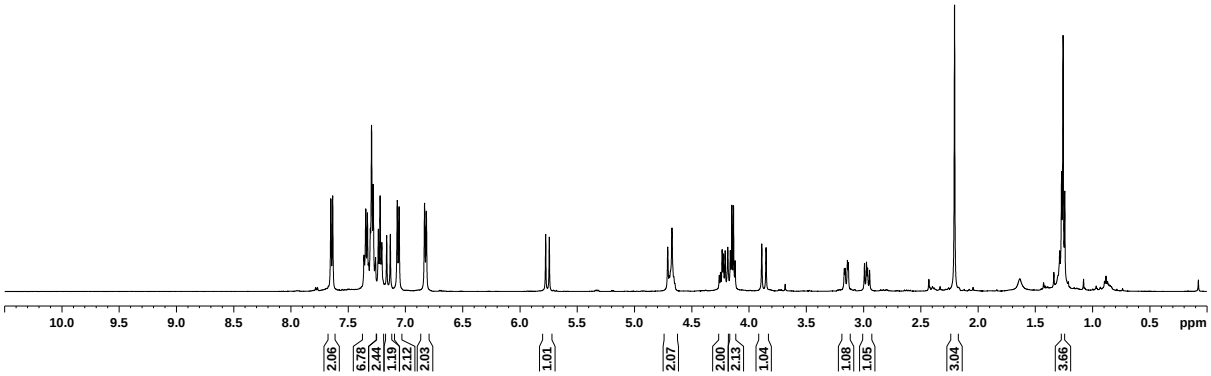

Ts
N
Ph
O
CO2Et
3l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1.0
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ppm
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2.03
1.01
2.07
2.00
2.13
1.04
1.08
1.05
3.04
3.66


167.46
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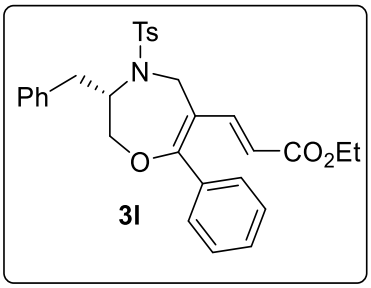
Ts
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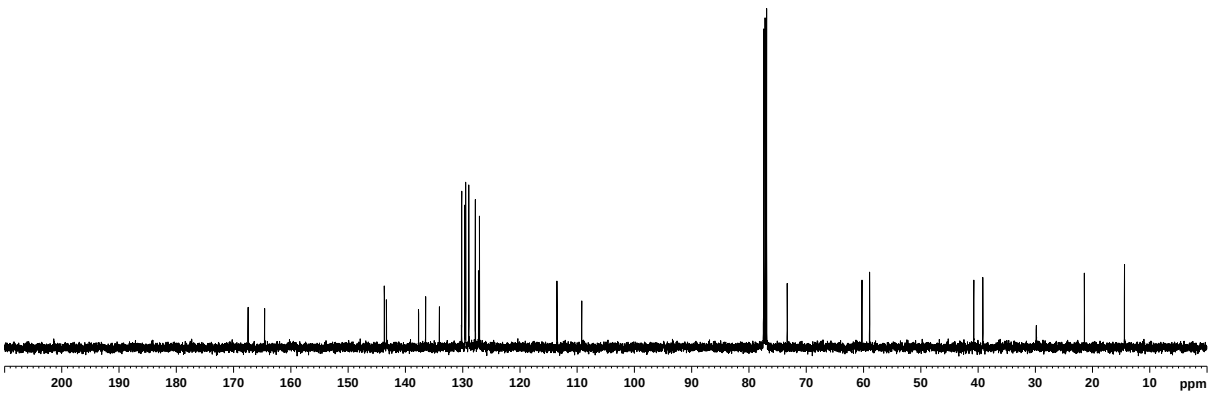
Ph
O
CO2Et
3l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100
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80
70
60
50
40
30
20
10
ppm


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7.408
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7.348
7.336
7.324
7.260
7.224
7.192
7.092
7.077
7.062
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6.793
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5.782
5.667
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5.644
5.632
4.913
4.876
4.724
4.712
4.699
4.687
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4.406
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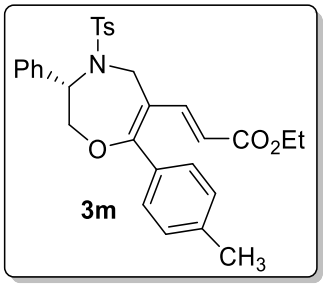
1.246


Ts
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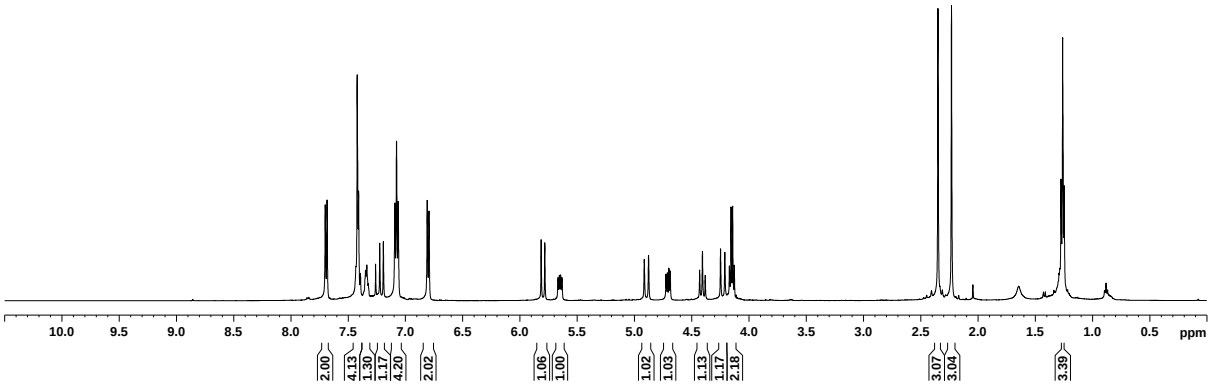
Ph
O
CO2Et
3m
CH3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4.0
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1.0
0.5
ppm
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1.00
1.02
1.03
1.13
1.17
2.18
3.07
3.04
3.39


167.54
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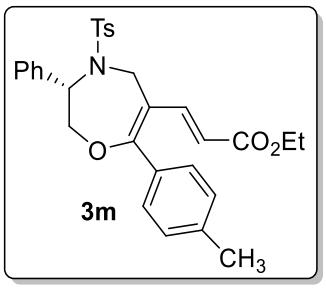
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Ph
O
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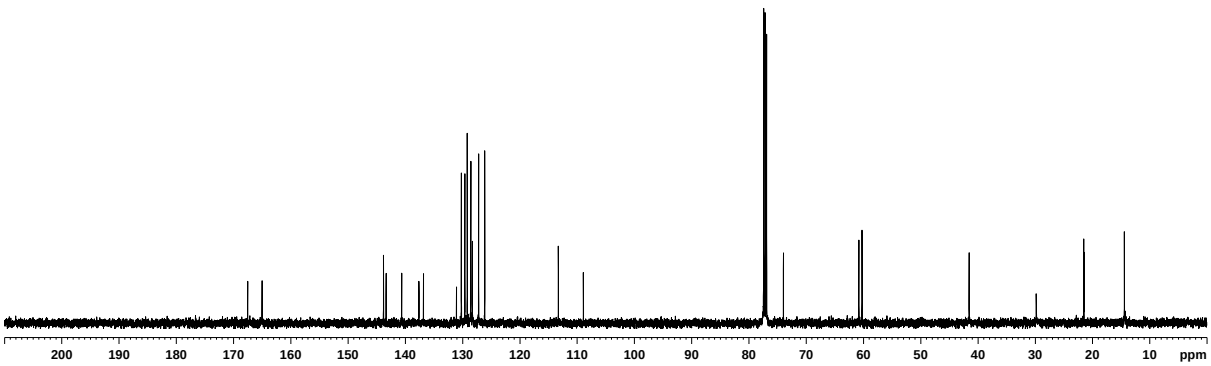
3m
CH3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80
70
60
50
40
30
20
10
ppm


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5.665
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4.130
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3.668
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2.180
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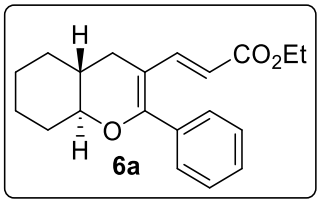
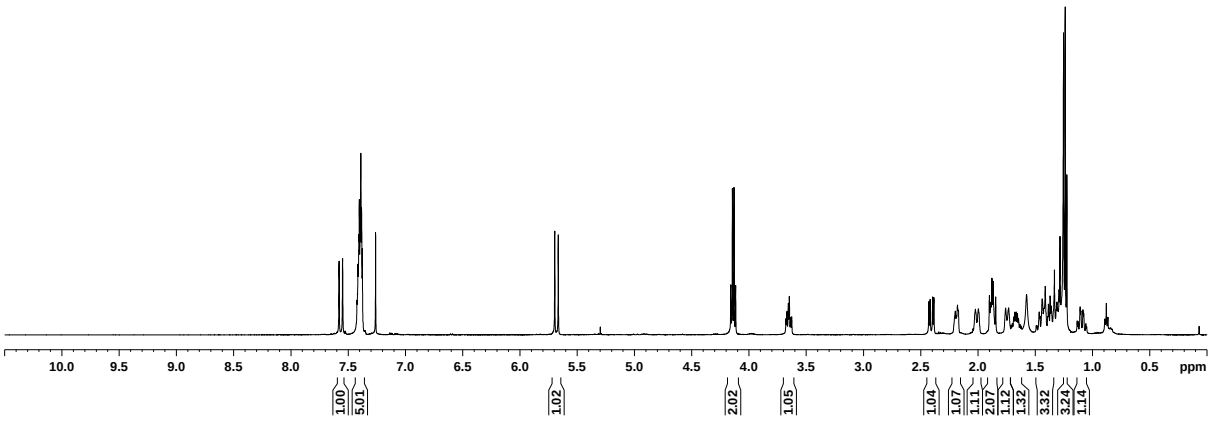

H
CO2Et
O
H
6a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ppm
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1.02
2.02
1.05
1.04
1.07
1.11
2.07
1.12
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3.32
3.24
1.14


168.09
160.58
145.25
134.87
129.97
129.52
128.28
111.83
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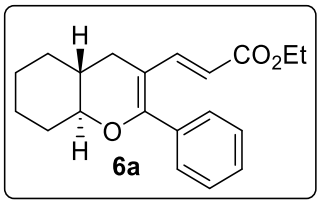
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CO2Et
O
H
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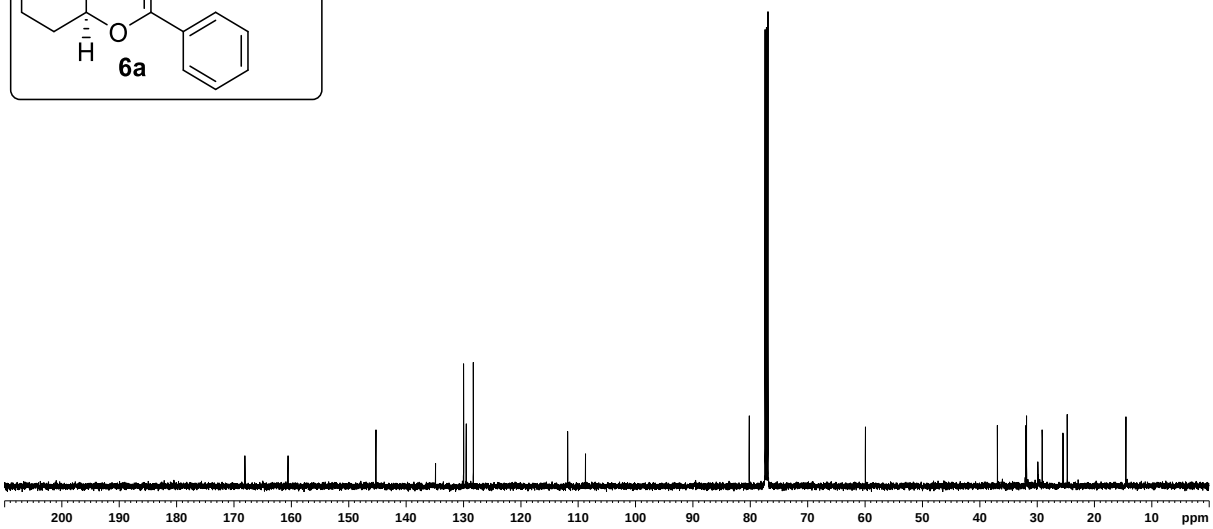
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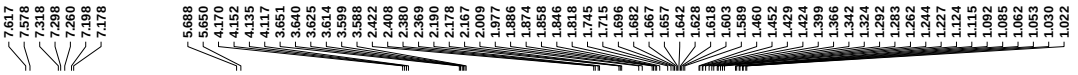
10
ppm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2.190
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2.009
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1.886
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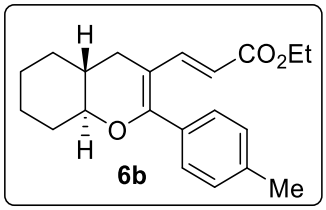
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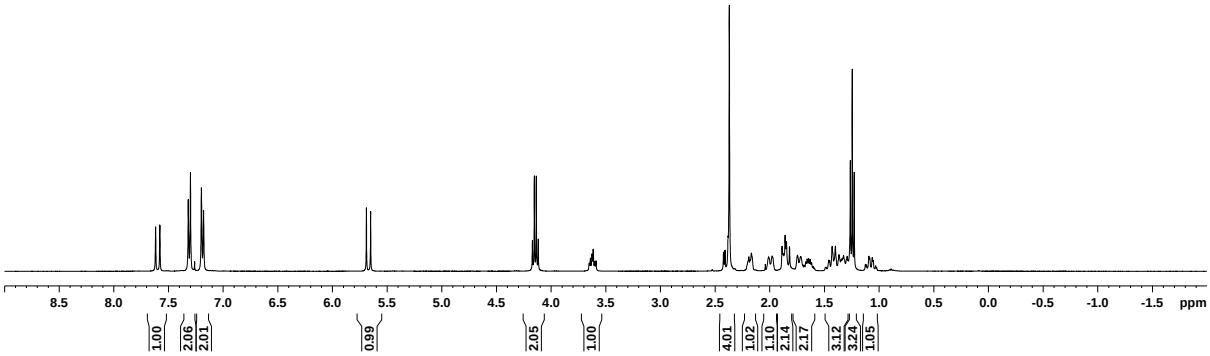
CO2Et
O
H
6b
Me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0.0
-0.5
-1.0
-1.5
ppm
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2.06
2.01
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2.05
1.00
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1.02
1.10
2.14
2.17
3.12
3.24
1.05


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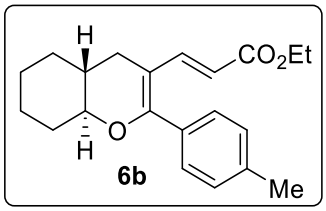
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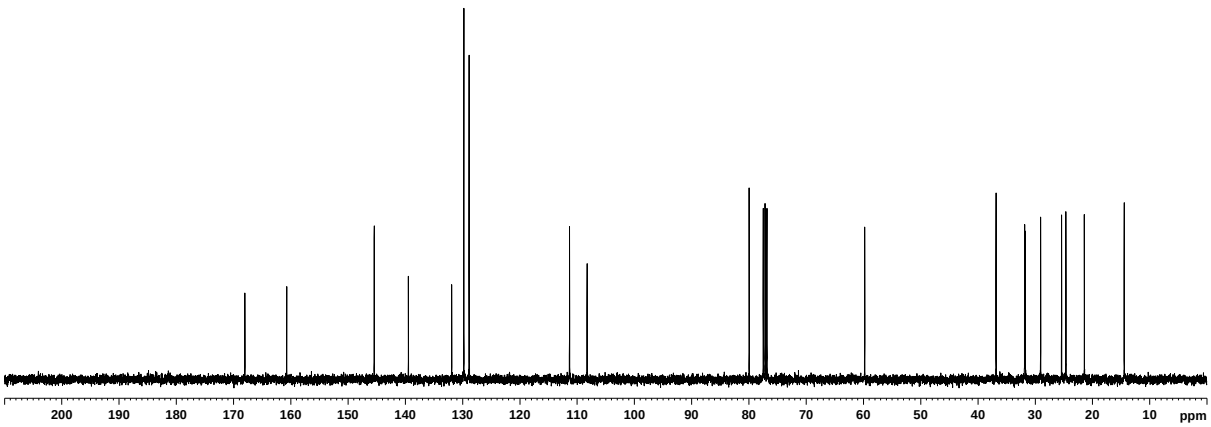
CO2Et
O
H
6b
Me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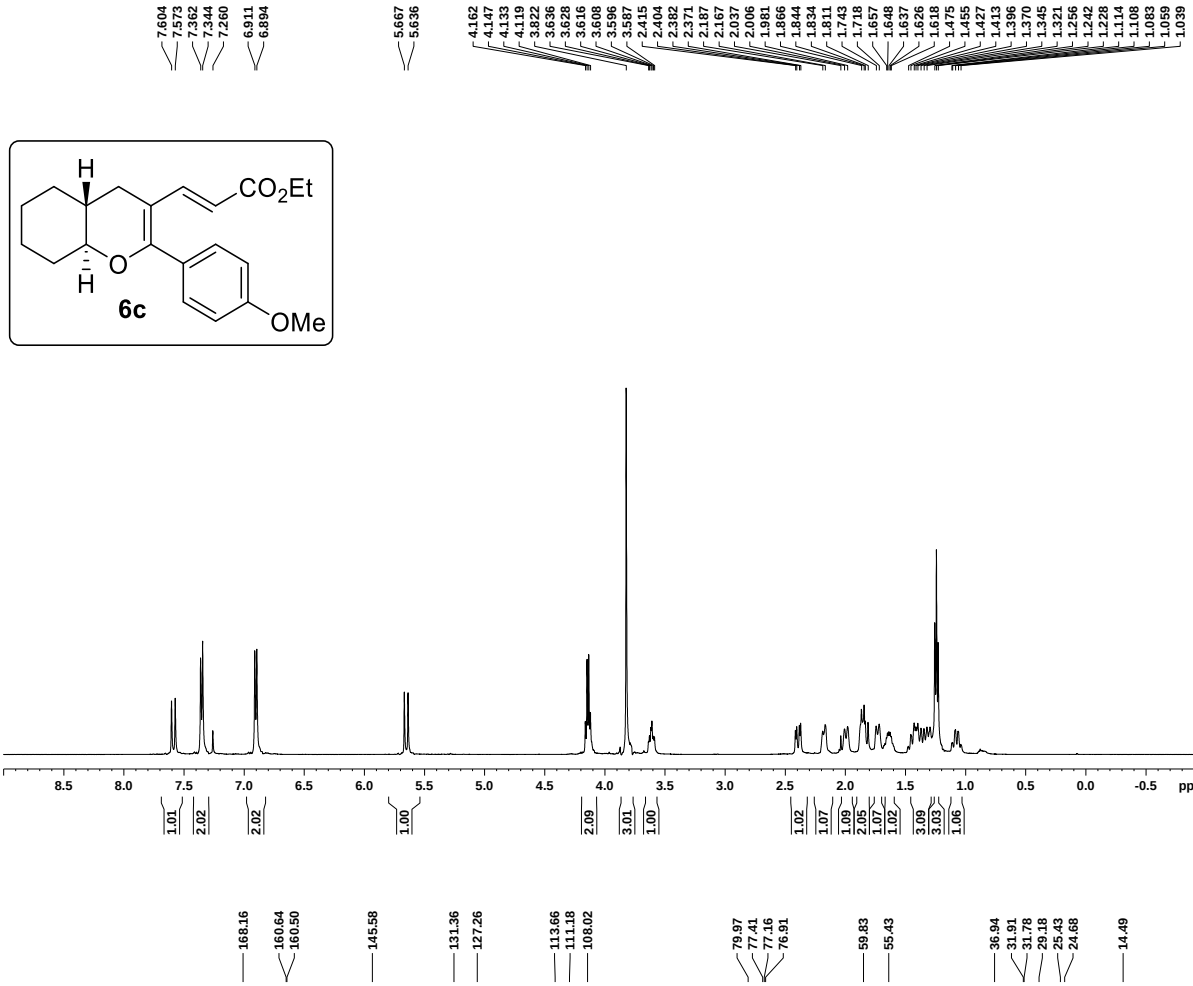
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1.370
1.345
1.321
1.256
1.242
1.228
1.114
1.108
1.083
1.059
1.039
H
CO2Et
O
H
6c
OMe
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7.5
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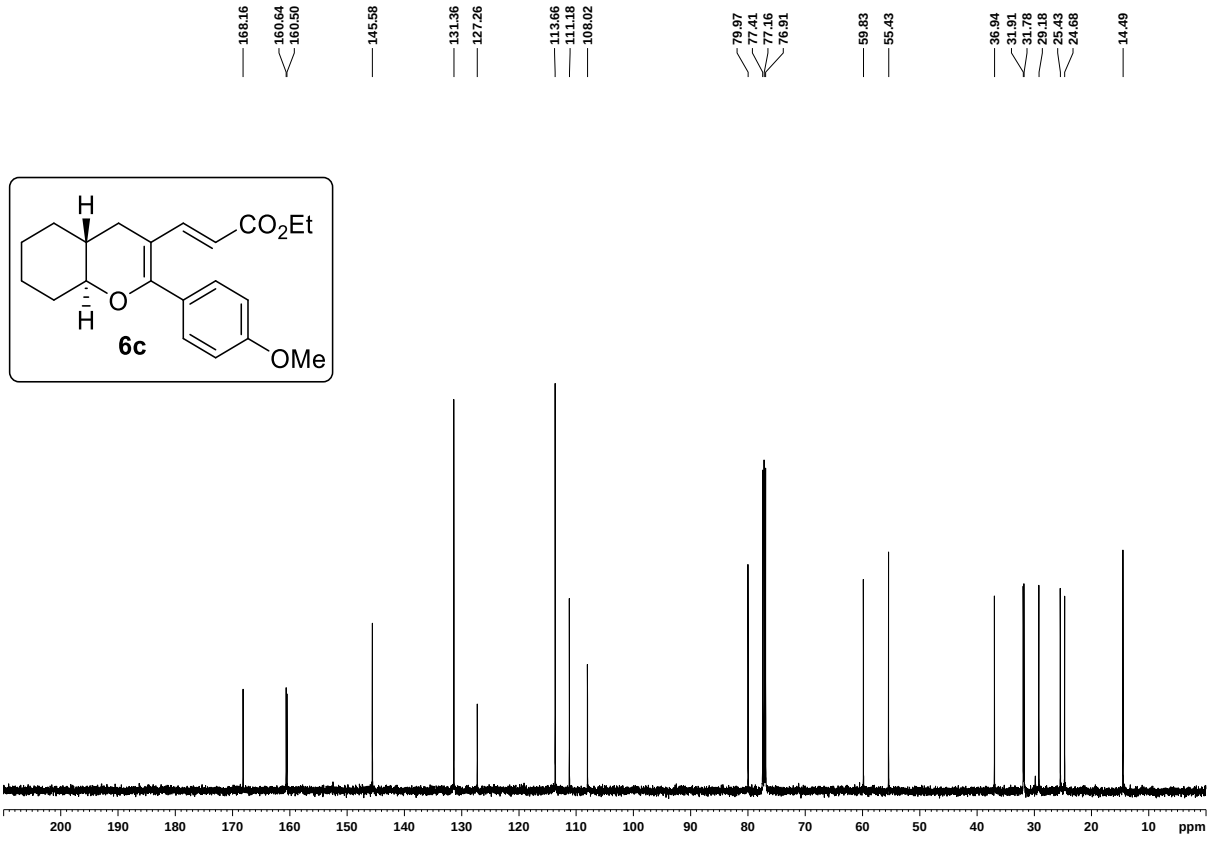
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29.18
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14.49
H
CO2Et
O
H
6c
OMe
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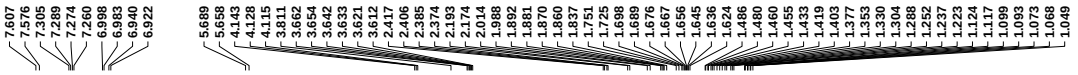
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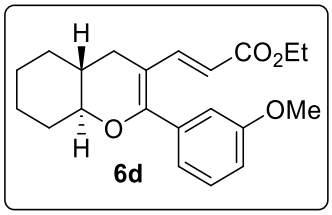
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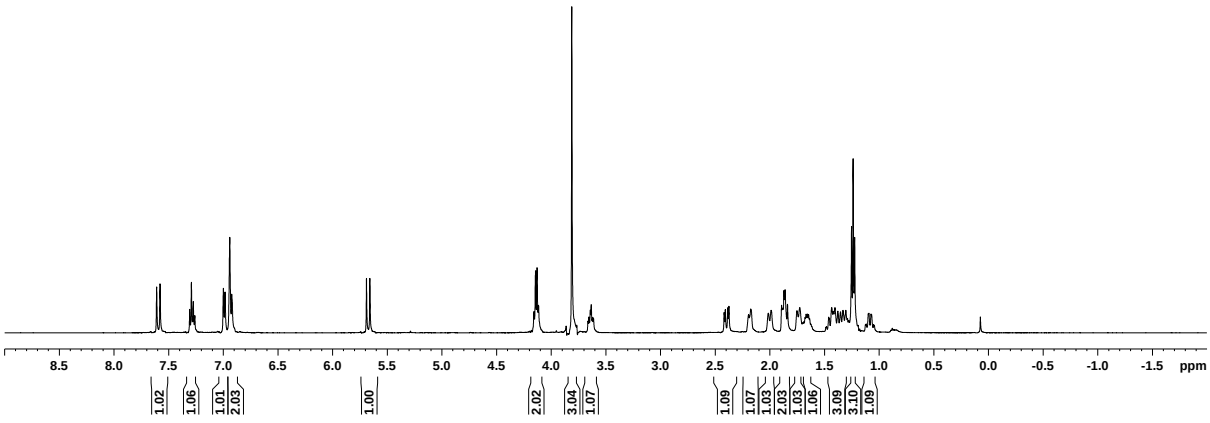
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-1.5
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2.03
1.00
2.02
3.04
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1.09
1.07
1.03
2.03
1.03
1.06
3.09
3.10
1.09


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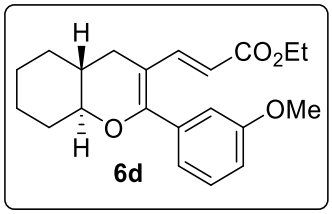
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OMe
H
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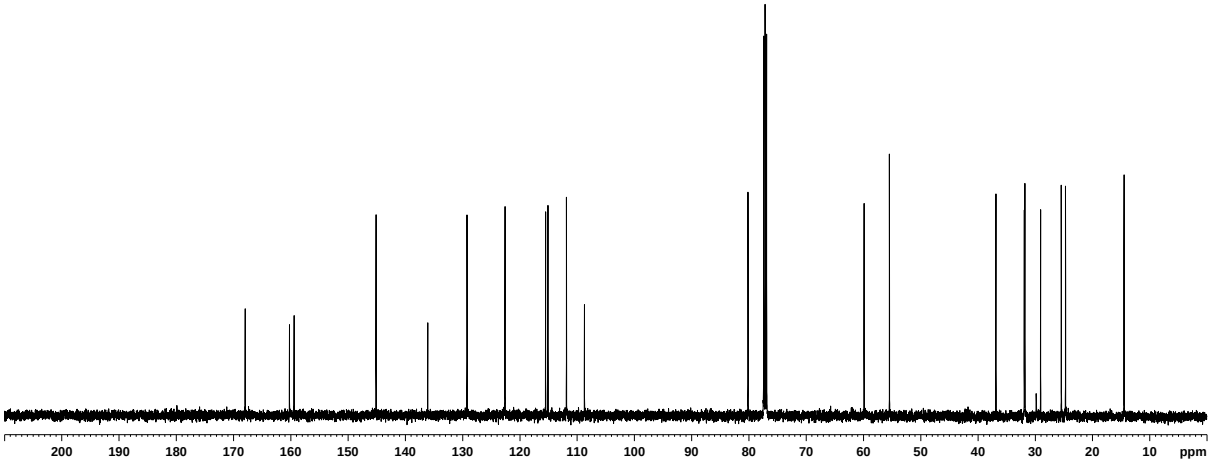
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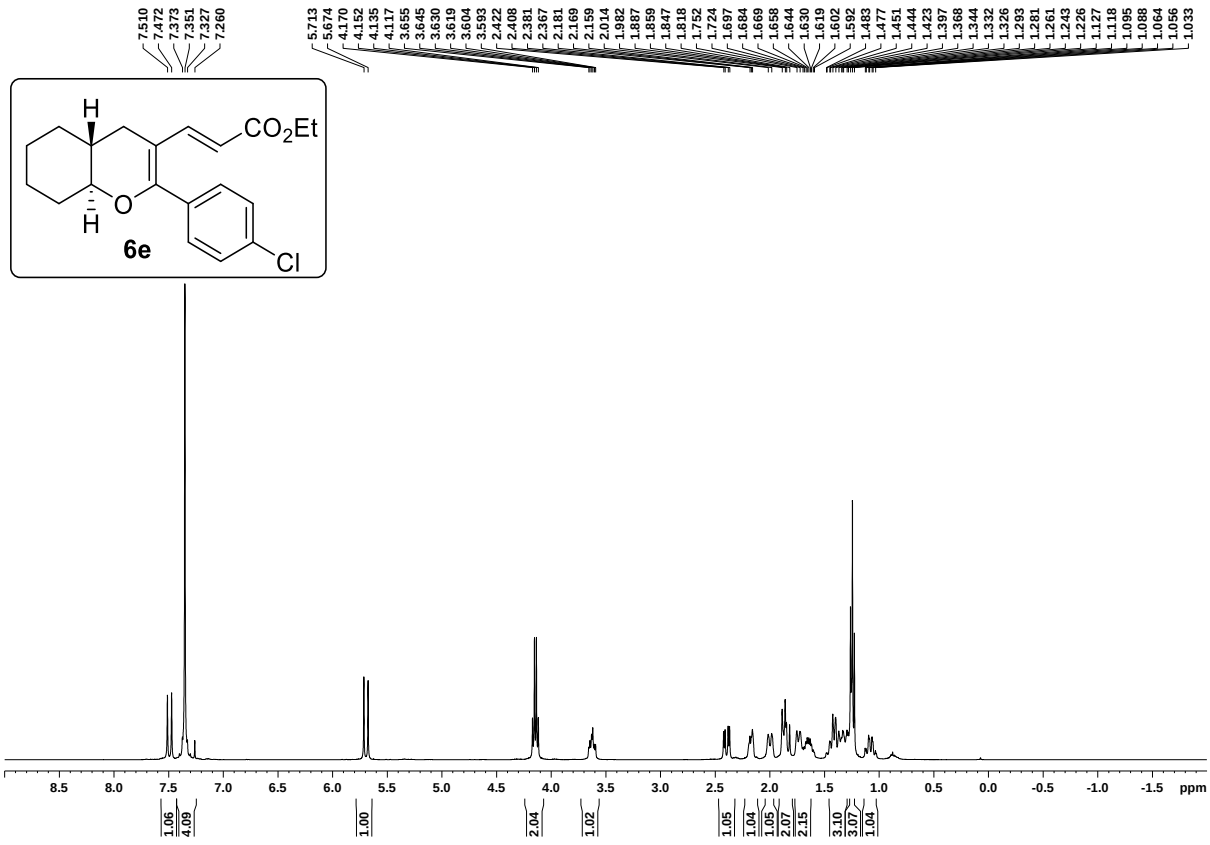
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1.630
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1.477
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1.243
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1.118
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1.088
1.064
1.056
1.033
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CO2Et
O
H
6e
Cl
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4.0
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-1.5
ppm
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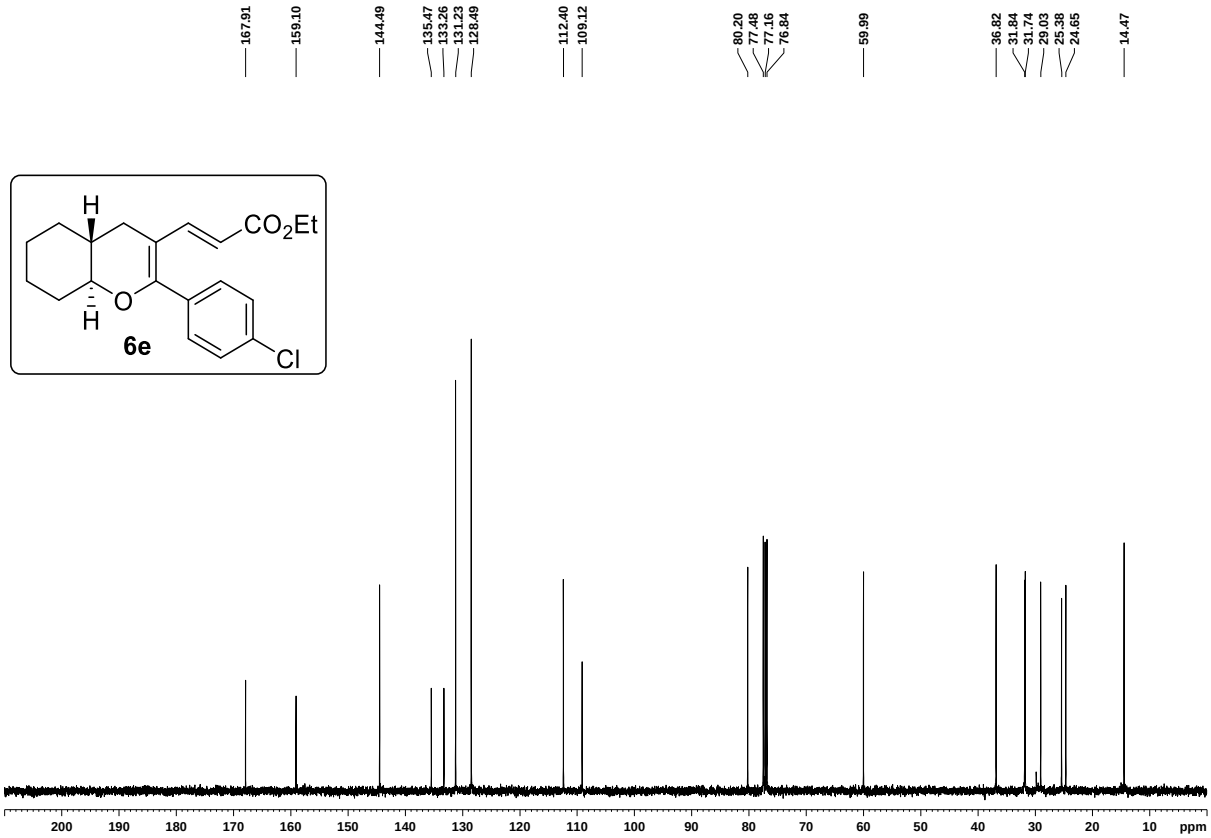
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59.99
36.82
31.84
31.74
29.03
25.38
24.65
14.47
H
CO2Et
O
H
6e
Cl
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150
140
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120
110
100
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70
60
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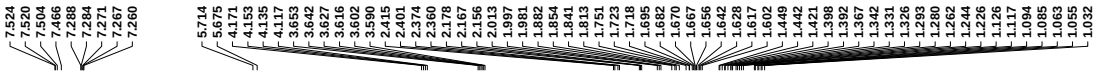
30
20
10
ppm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4.135
4.117
3.653
3.642
3.627
3.616
3.602
3.590
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2.167
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2.013
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1.718
1.695
1.682
1.670
1.667
1.656
1.642
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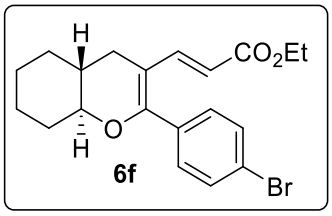
1.032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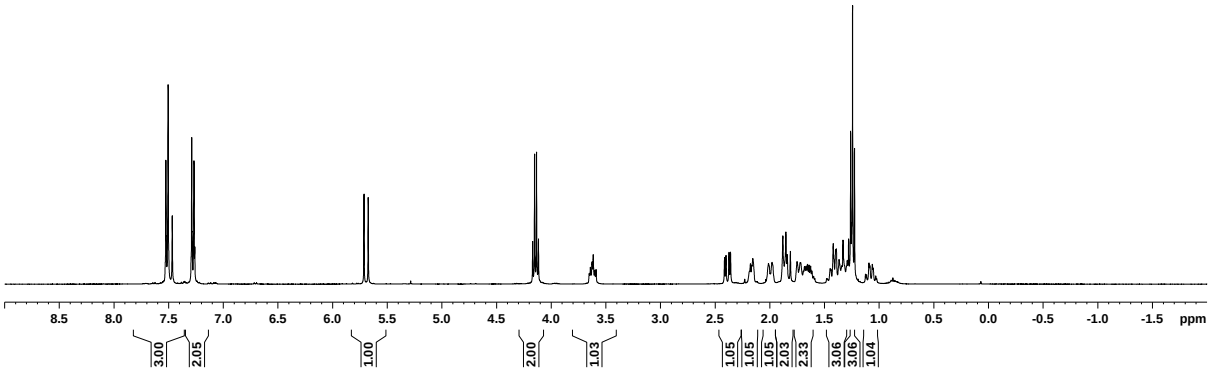
CO2Et
O
H
6f
Br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0.0
-0.5
-1.0
-1.5
ppm
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1.00
2.00
1.03
1.05
1.05
1.05
2.03
2.33
3.06
3.06
1.04


167.90
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131.46
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112.46
109.14
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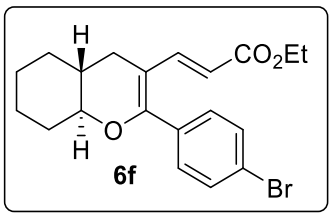
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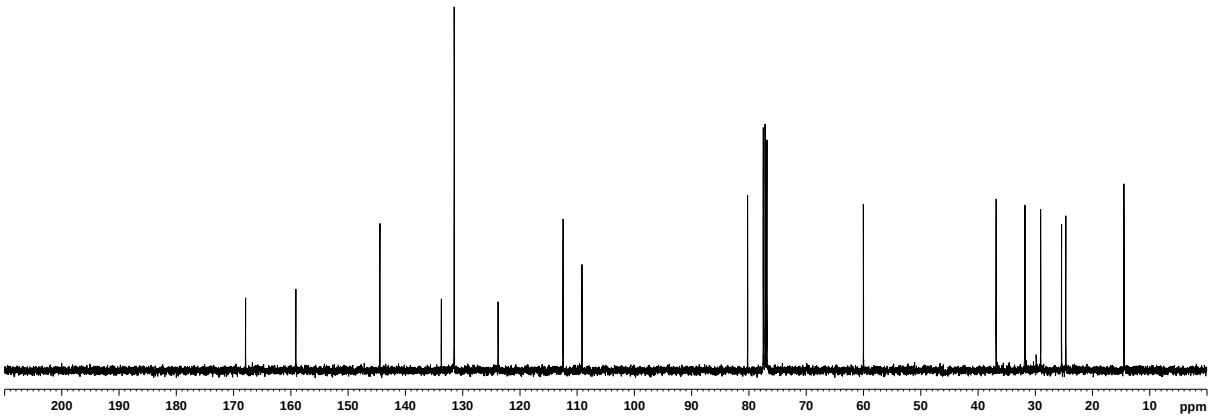
CO2Et
O
H
6f
Br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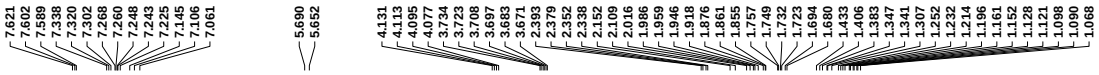
ppm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5.652
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4.095
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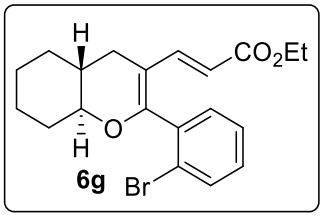
1.090
1.068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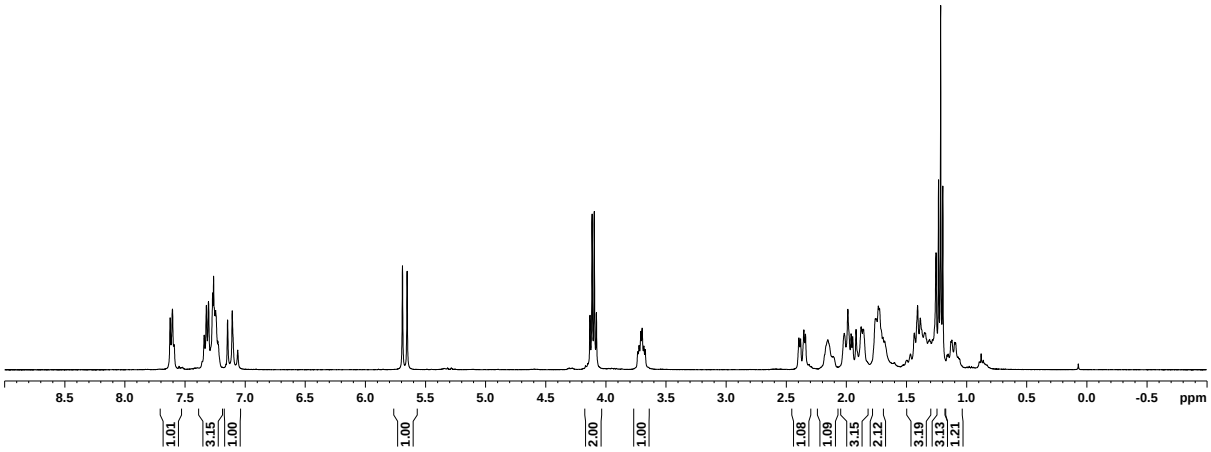
H
6g
Br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0.0
-0.5
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1.00
1.00
2.00
1.00
1.08
1.09
3.15
2.12
3.19
3.13
1.21


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159.56
143.90
135.68
133.33
132.12
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127.22
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112.44
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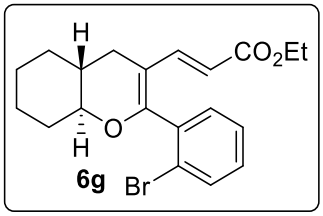
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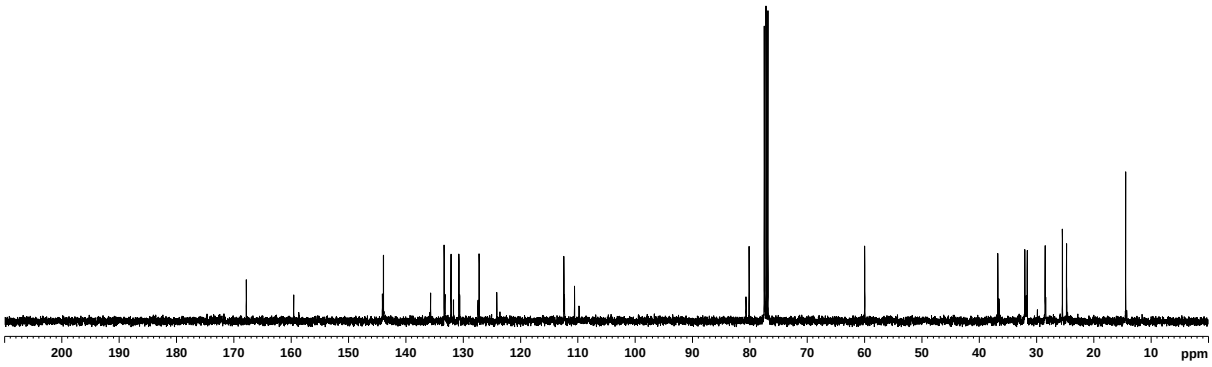
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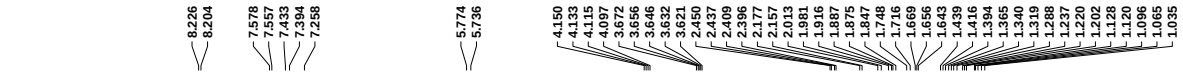
ppm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2.157
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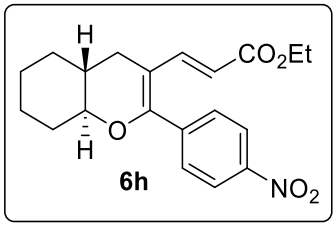
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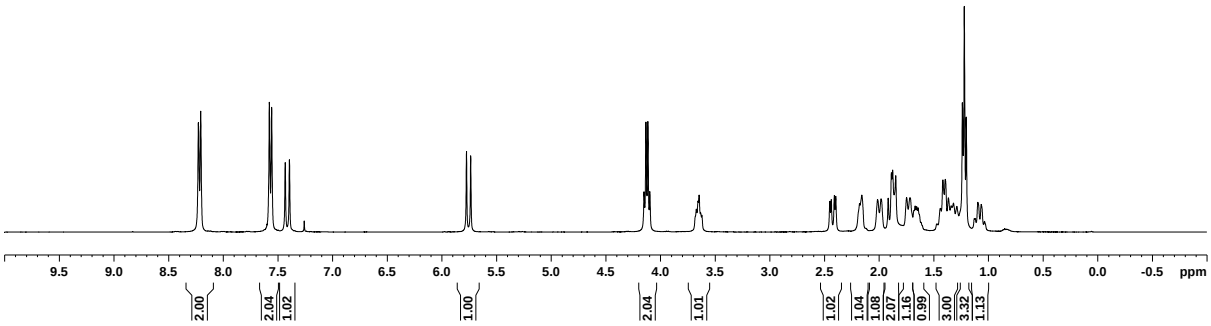
H
6h
NO2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2.0
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1.0
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ppm
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1.02
1.00
2.04
1.01
1.02
1.04
1.08
2.07
1.16
0.99
3.00
3.32
1.13


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141.04
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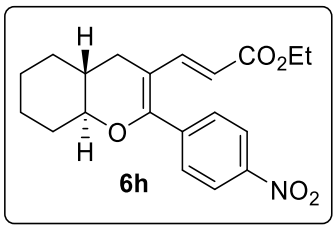
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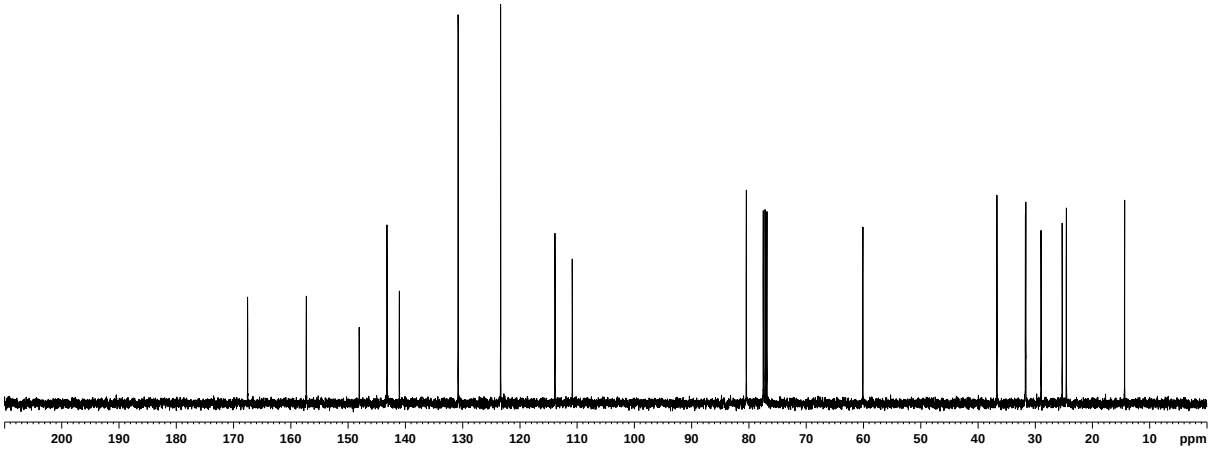
O
H
6h
NO2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80
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50
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30
20
10
ppm


7.619
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7.314
7.298
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4.152
4.138
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2.152
2.144
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2.083
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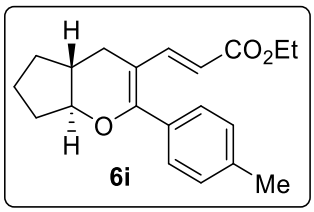
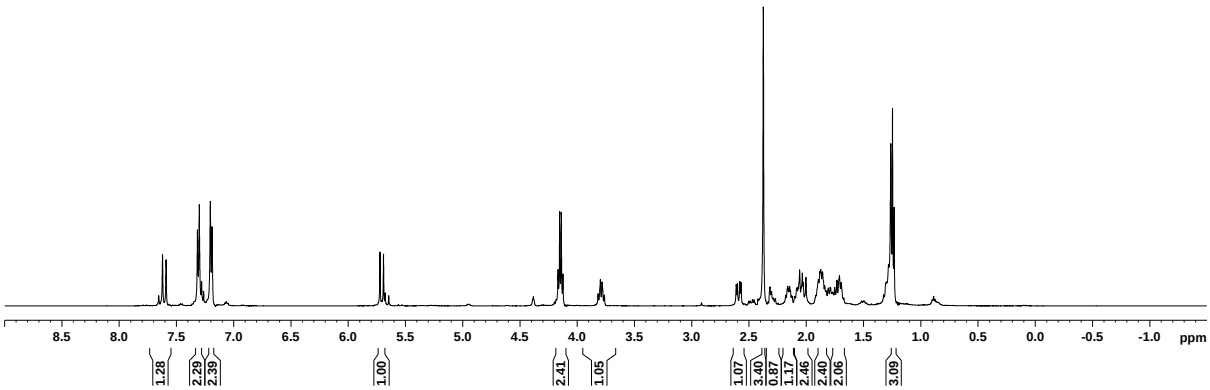
1.231


H
CO2Et
O
H
6i
Me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1.07
3.40
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2.46
2.40
2.06
3.09


168.05
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139.61
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129.95
128.93
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109.24
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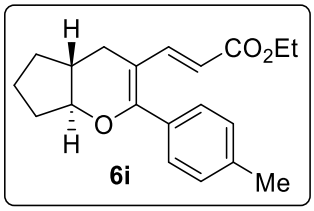
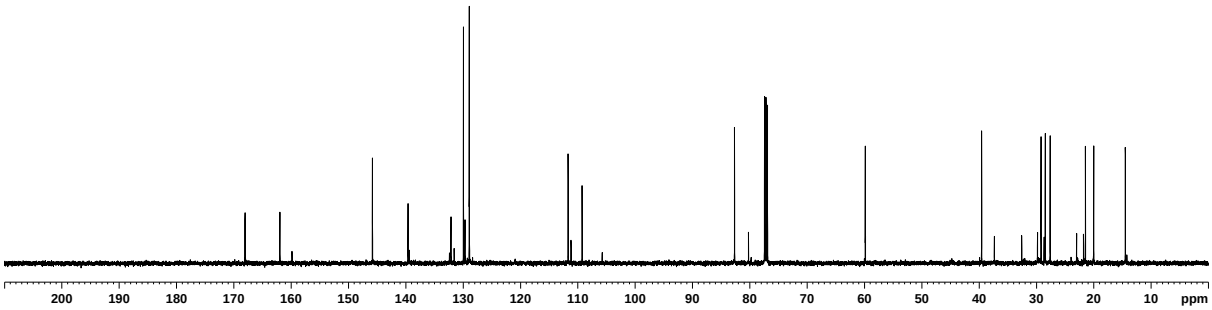

H
CO2Et
O
H
6i
Me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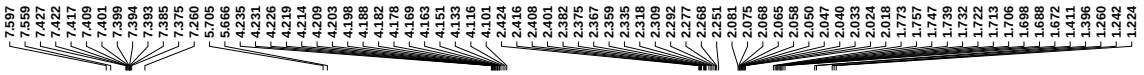
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7.260
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5.666
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4.226
4.219
4.214
4.209
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4.198
4.188
4.182
4.178
4.169
4.163
4.151
4.133
4.116
4.101
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2.408
2.401
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2.375
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2.309
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2.251
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2.058
2.050
2.047
2.040
2.033
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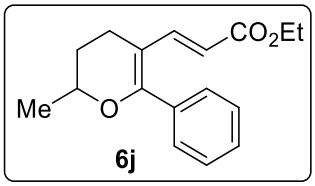
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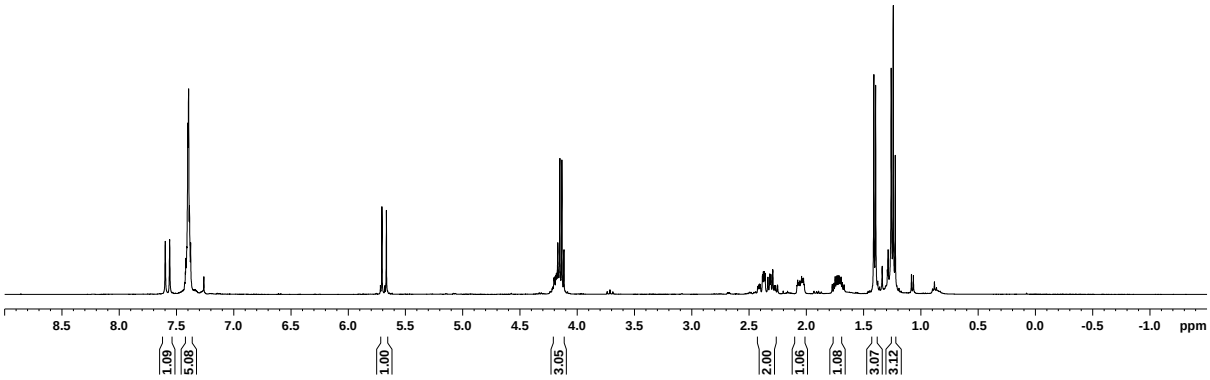
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ppm
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5.08
1.00
3.05
2.00
1.06
1.08
3.07
3.12


168.04
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129.91
129.50
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20.82
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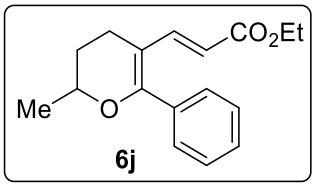
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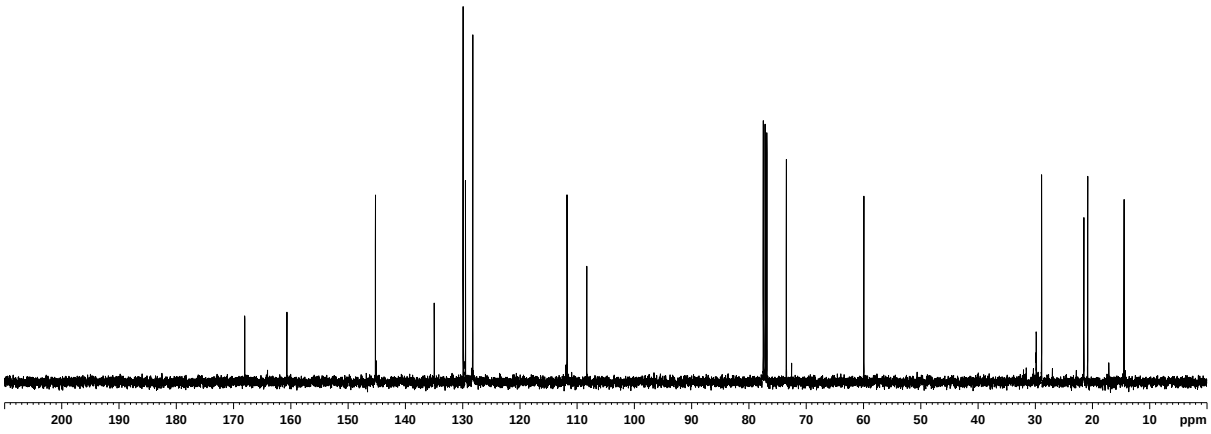
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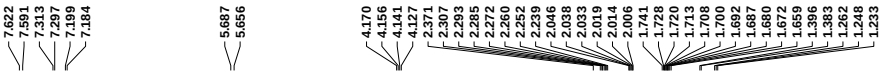
10
ppm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4.141
4.127
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2.293
2.285
2.272
2.260
2.252
2.239
2.046
2.038
2.033
2.019
2.014
2.006
1.741
1.728
1.720
1.713
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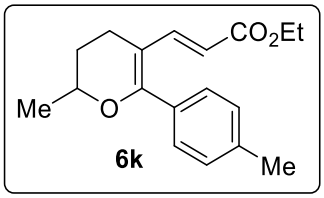
1.248
1.233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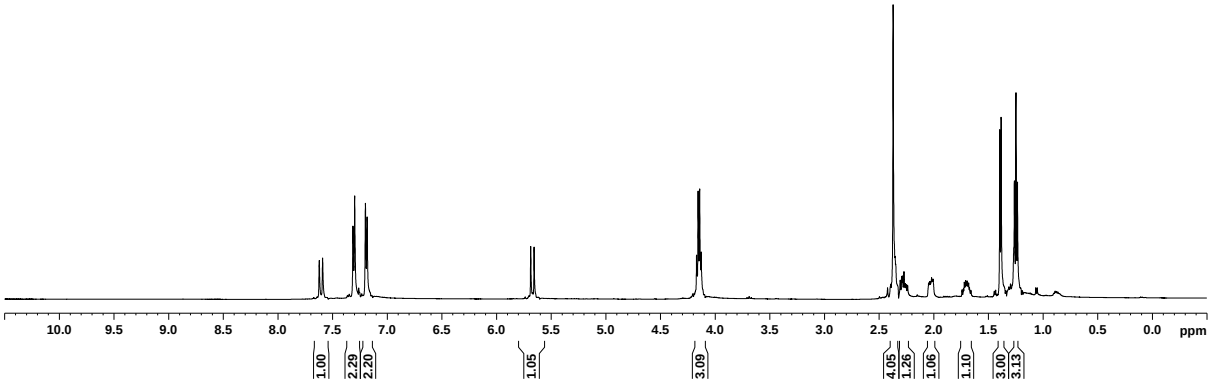
Me
O
Me
6k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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.00
2.29
2.20
1.05
3.09
4.05
1.26
1.06
1.10
3.00
3.13


168.00
160.84
145.41
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132.03
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20.75
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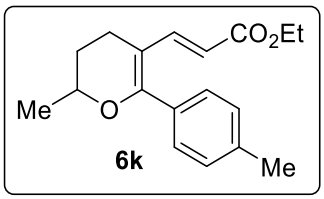
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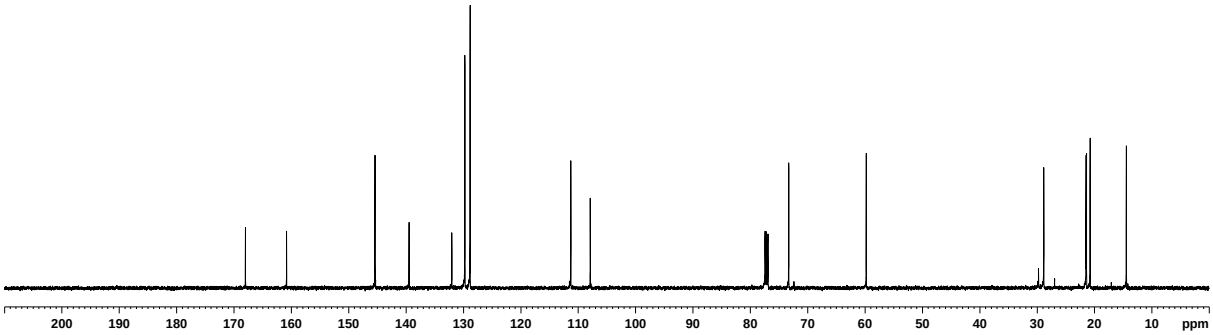
Me
O
Me
6k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90
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50
40
30
20
10
ppm


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7.300
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7.285
7.260
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4.249
4.243
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4.232
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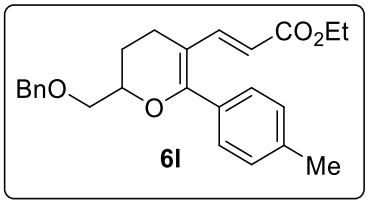
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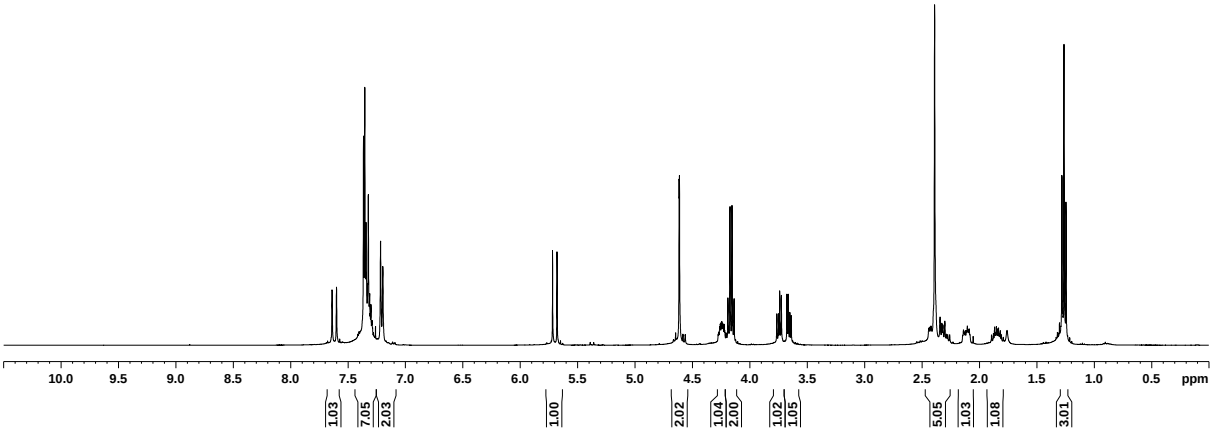
BnO
O
Me

6l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4.0
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3.0
2.5
2.0
1.5
1.0
0.5
ppm
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7.05
2.03
1.00
2.02
1.04
2.00
1.02
1.05
5.05
1.03
1.08
3.01


167.99
160.39
145.20
139.63
138.14
131.80
129.88
128.87
128.50
127.79
127.74
111.77
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77.16
76.84
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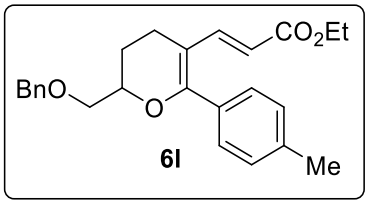
21.09
14.46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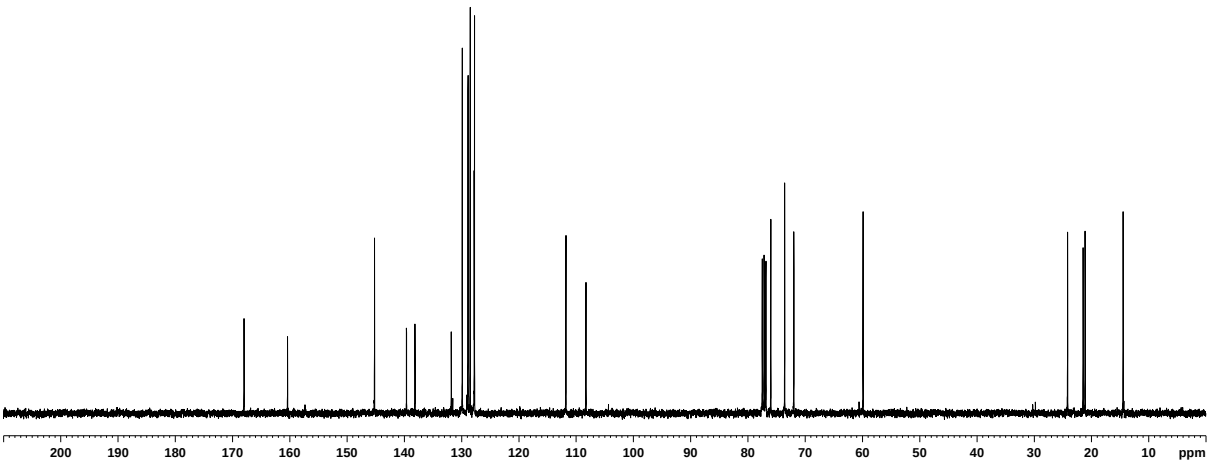
BnO
O
Me

6l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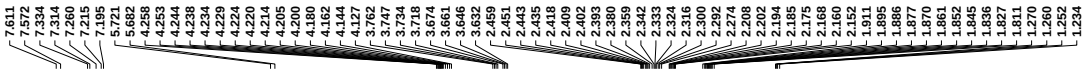
10
ppm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4.238
4.234
4.229
4.224
4.220
4.214
4.205
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2.202
2.194
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2.175
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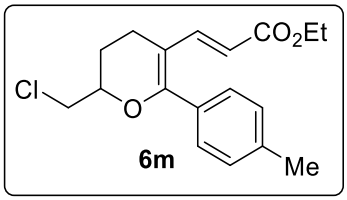
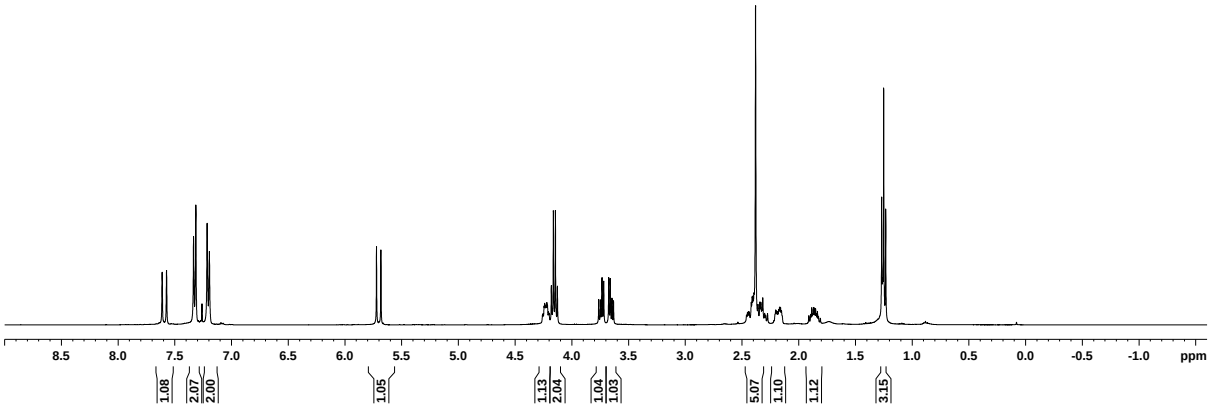

CO2Et
Cl
O
6m
Me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0.0
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-1.0
ppm
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1.05
1.13
2.04
1.04
1.03
5.07
1.10
1.12
3.15


167.85
159.70
144.72
139.89
131.39
129.86
128.97
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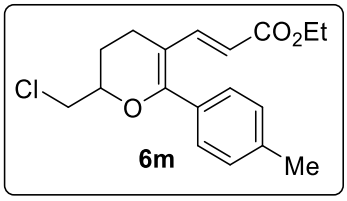
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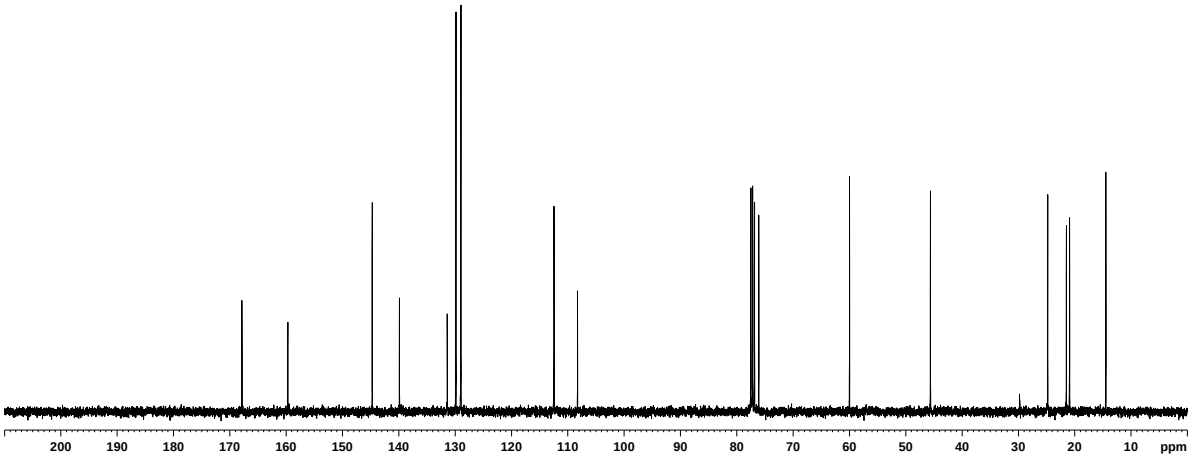
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80
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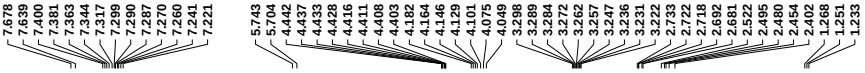
30
20
10
ppm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7.260
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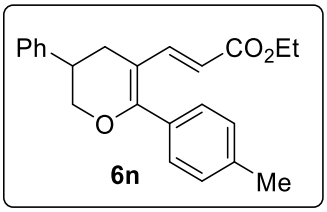
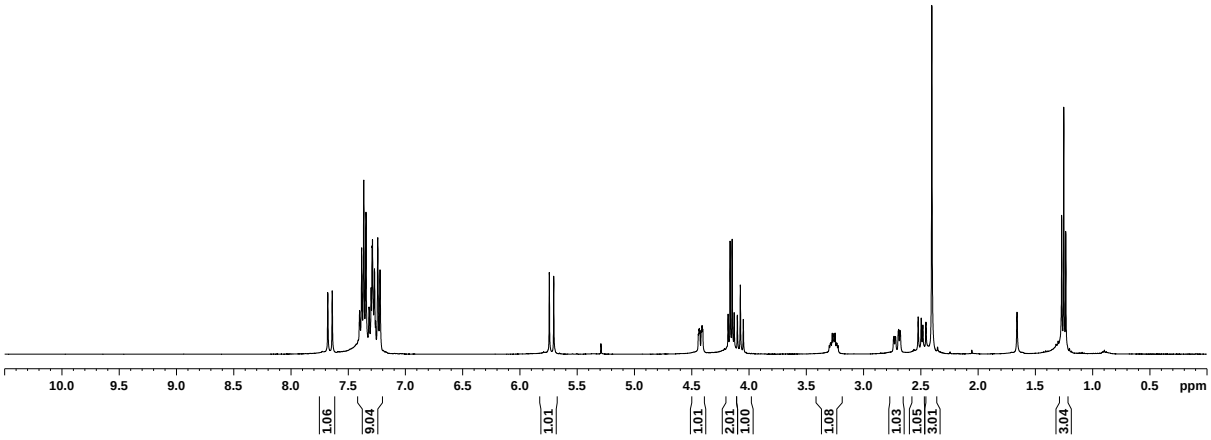

Ph
CO2Et
O
Me
6n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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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9.04
1.01
1.01
2.01
1.00
1.08
1.03
1.05
3.01
3.04


167.97
160.54
144.97
141.20
139.85
131.57
129.84
129.03
128.98
127.46
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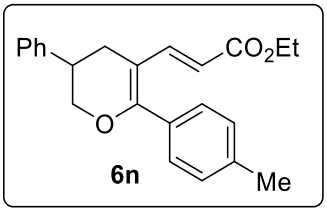
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CO2Et
O
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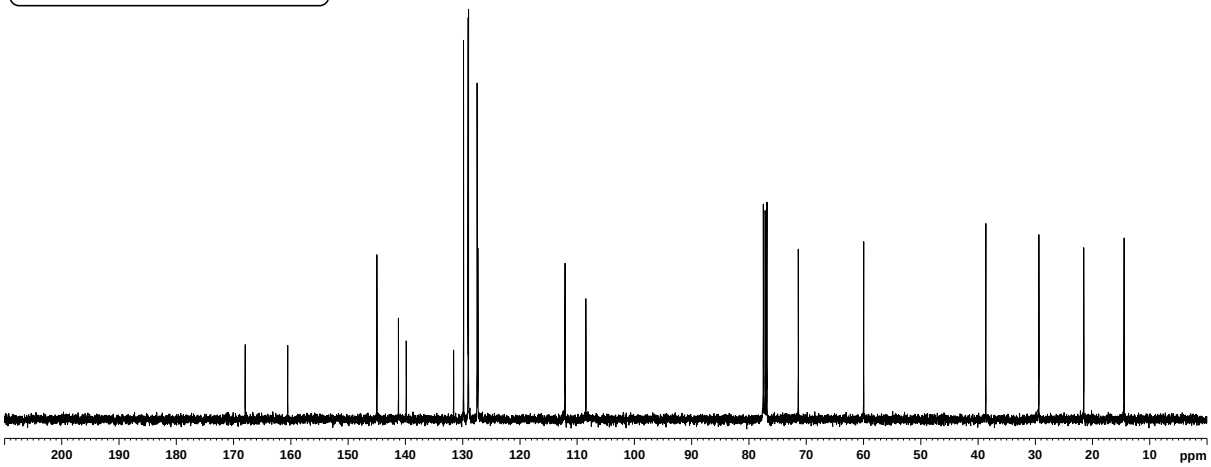
6n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120
110
100
90
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50
40
30
20
10
ppm


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7.314
7.310
7.298
7.294
7.260
7.205
7.185
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5.699
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4.952
4.945
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4.936
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4.141
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2.194
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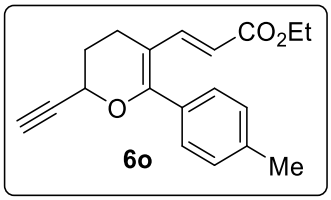
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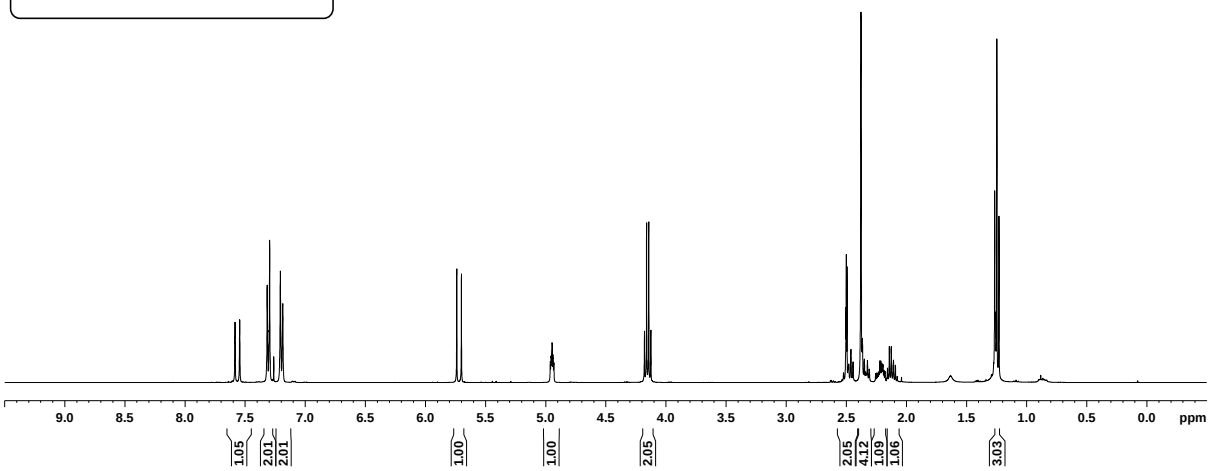
O
6o
Me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2.0
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0.0
ppm
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2.01
1.00
1.00
2.05
2.05
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1.09
1.06
3.03


167.86
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144.81
139.82
131.53
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112.65
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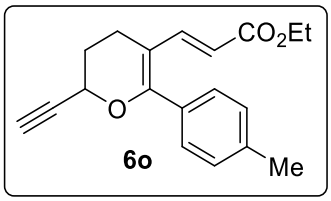
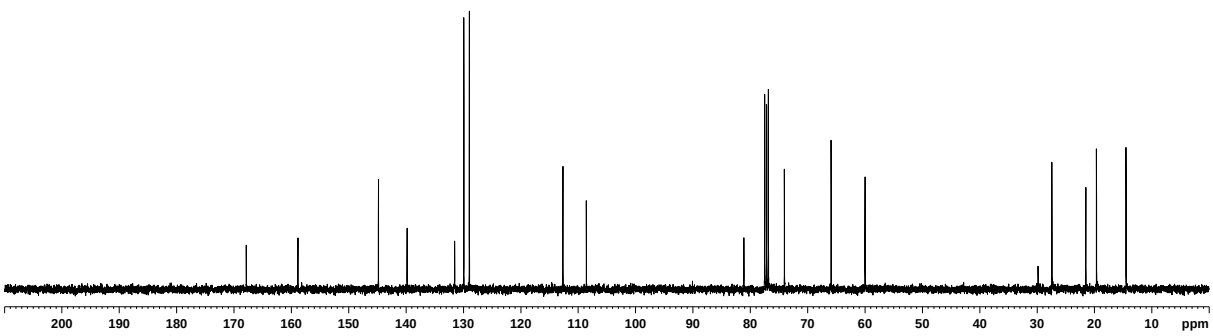
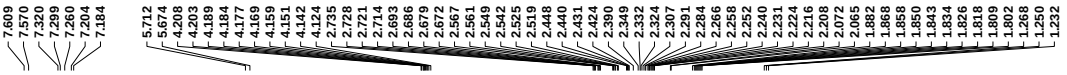
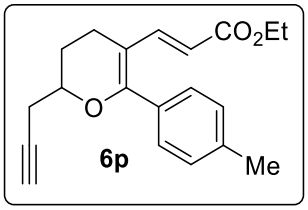
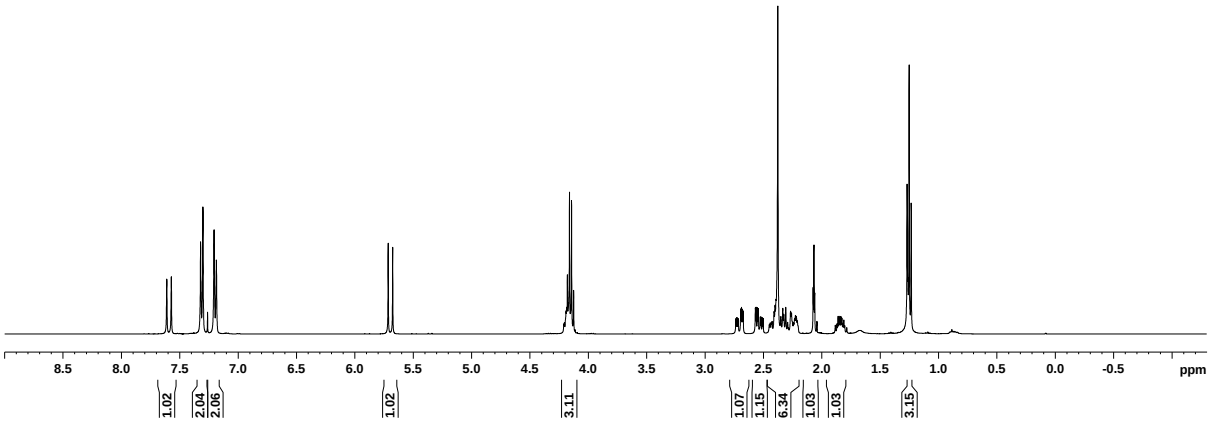
77.16
76.84
74.04
65.90
59.99
27.41
21.49
19.64
14.49


CO2Et
O
6o
Me

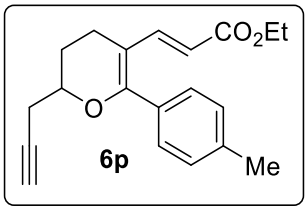

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

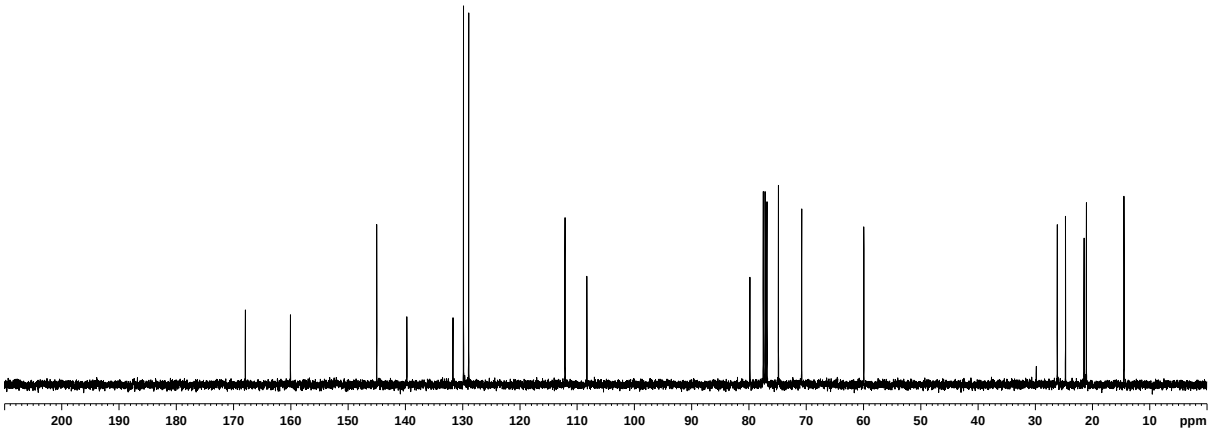

7.609
7.570
7.320
7.299
7.260
7.204
7.184
5.712
5.674
4.208
4.203
4.189
4.184
4.177
4.169
4.159
4.151
4.142
4.124
2.735
2.728
2.721
2.714
2.693
2.686
2.679
2.672
2.567
2.561
2.549
2.542
2.525
2.519
2.448
2.440
2.431
2.424
2.390
2.349
2.332
2.324
2.307
2.291
2.284
2.266
2.258
2.252
2.240
2.231
2.224
2.216
2.208
2.072
2.065
1.882
1.868
1.858
1.850
1.843
1.834
1.826
1.818
1.809
1.802
1.268
1.250
1.232


CO2Et
O
6p
Me

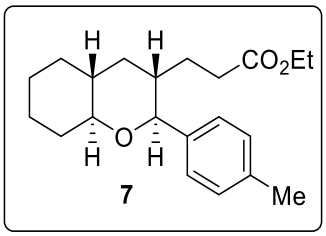

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
1.02
2.04
2.06
1.02
3.11
1.07
1.15
6.34
1.03
1.03
3.15

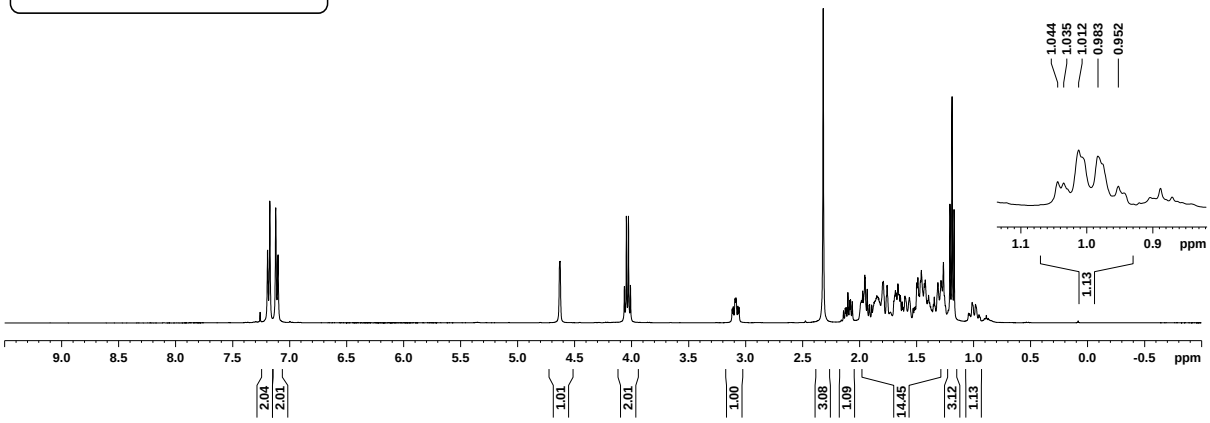

167.94
160.06
145.00
139.74
131.68
129.85
128.94
112.12
108.29
79.82
77.48
77.16
76.84
74.83
70.77
59.93
26.13
24.70
21.46
21.05
14.48


CO2Et
O
6p
Me

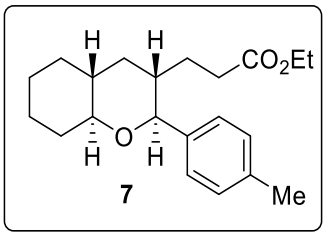

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

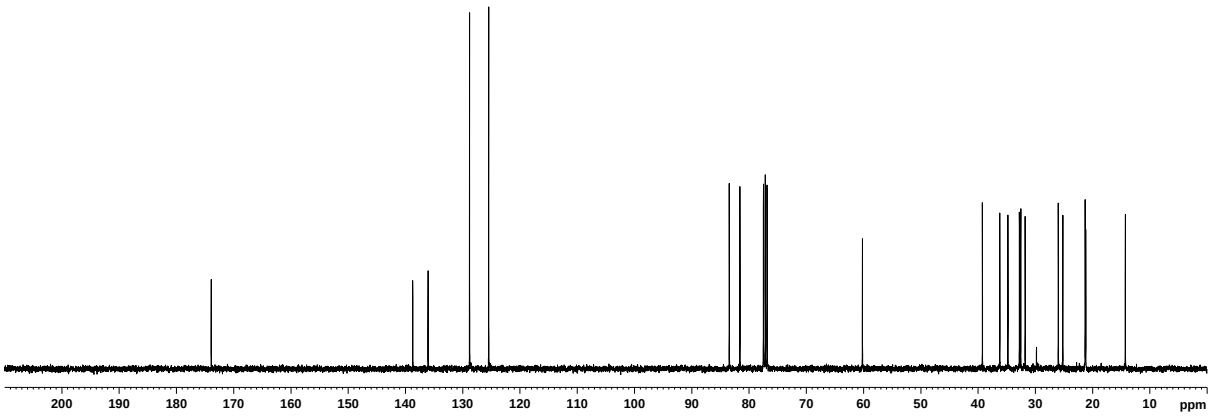

7.193
7.173
7.121
7.102
4.631
4.627
4.063
4.045
4.027
4.010
3.117
3.108
3.092
3.084
3.068
3.058
2.319
2.140
2.125
2.117
2.102
2.087
2.079
2.064
1.983
1.972
1.954
1.951
1.933
1.915
1.911
1.893
1.872
1.866
1.854
1.848
1.843
1.838
1.831
1.791
1.758
1.685
1.677
1.663
1.653
1.641
1.626
1.618
1.602
1.597
1.564
1.530
1.519
1.511
1.499
1.489
1.477
1.466
1.458
1.432
1.424
1.402
1.394
1.386
1.377
1.364
1.353
1.345
1.313
1.286
1.265
1.207
1.189
1.171
1.044
1.012
0.983


H
H
CO2Et
O
H
H
7
Me

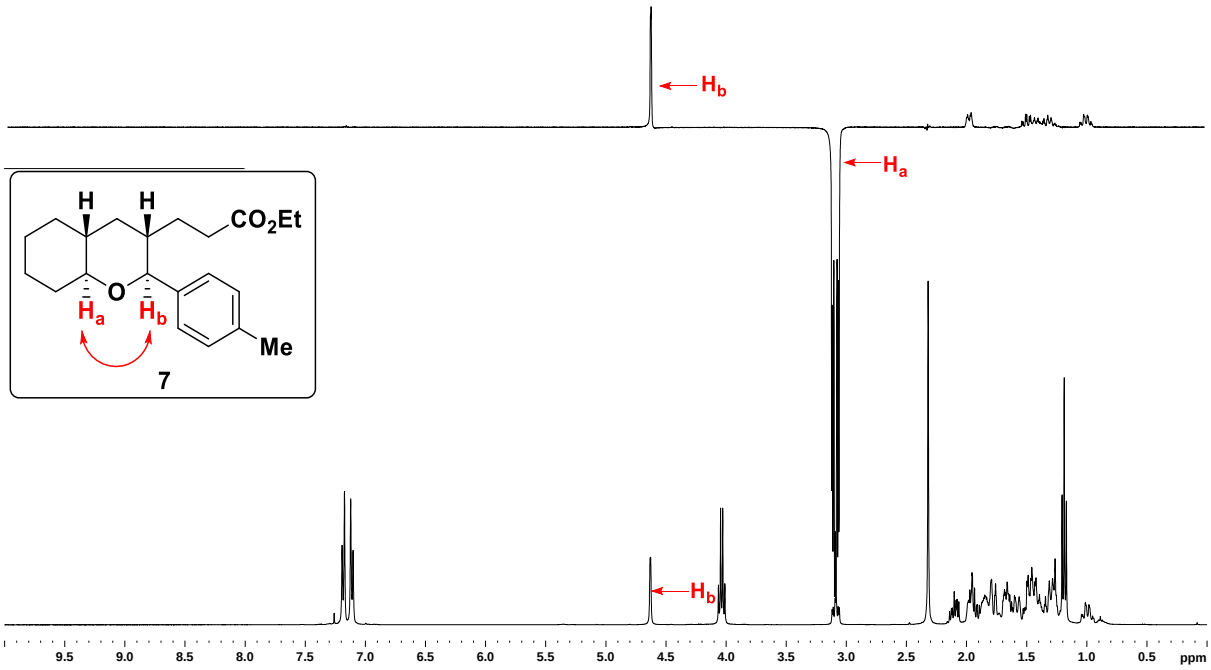

1.044
1.035
1.012
0.983
0.952
1.1
1.0
0.9
ppm
1.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
2.04
2.01
1.01
2.01
1.00
3.08
1.09
14.45
3.12
1.13

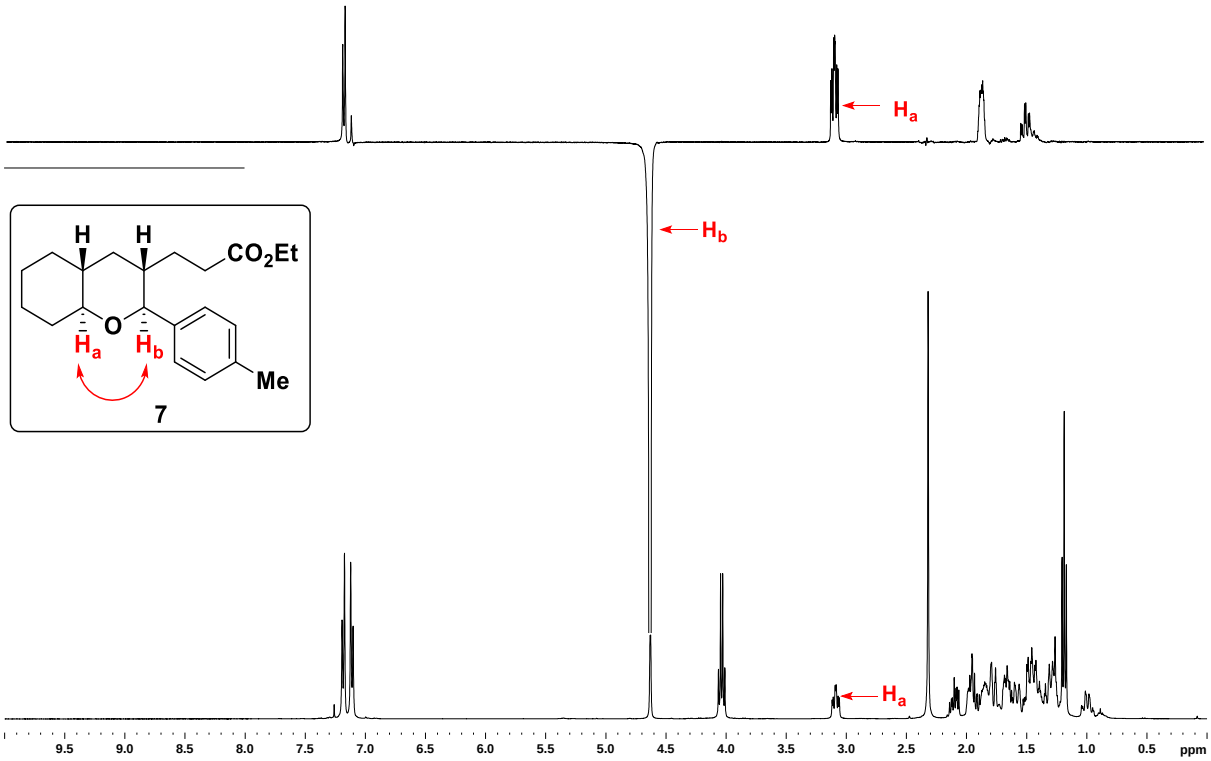

173.87
138.69
136.01
128.76
125.42
83.44
81.58
77.48
77.16
76.84
60.18
39.23
36.19
34.77
32.77
32.53
31.76
25.98
25.18
21.28
21.17
14.27

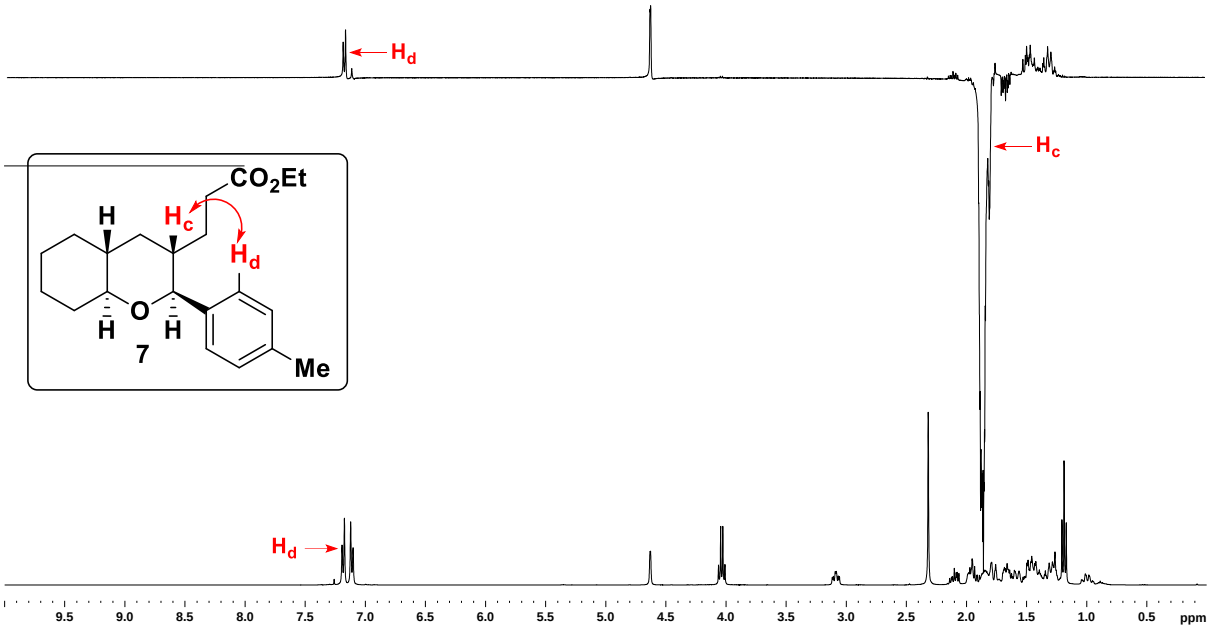

H
H
CO2Et
O
H
H
7
Me

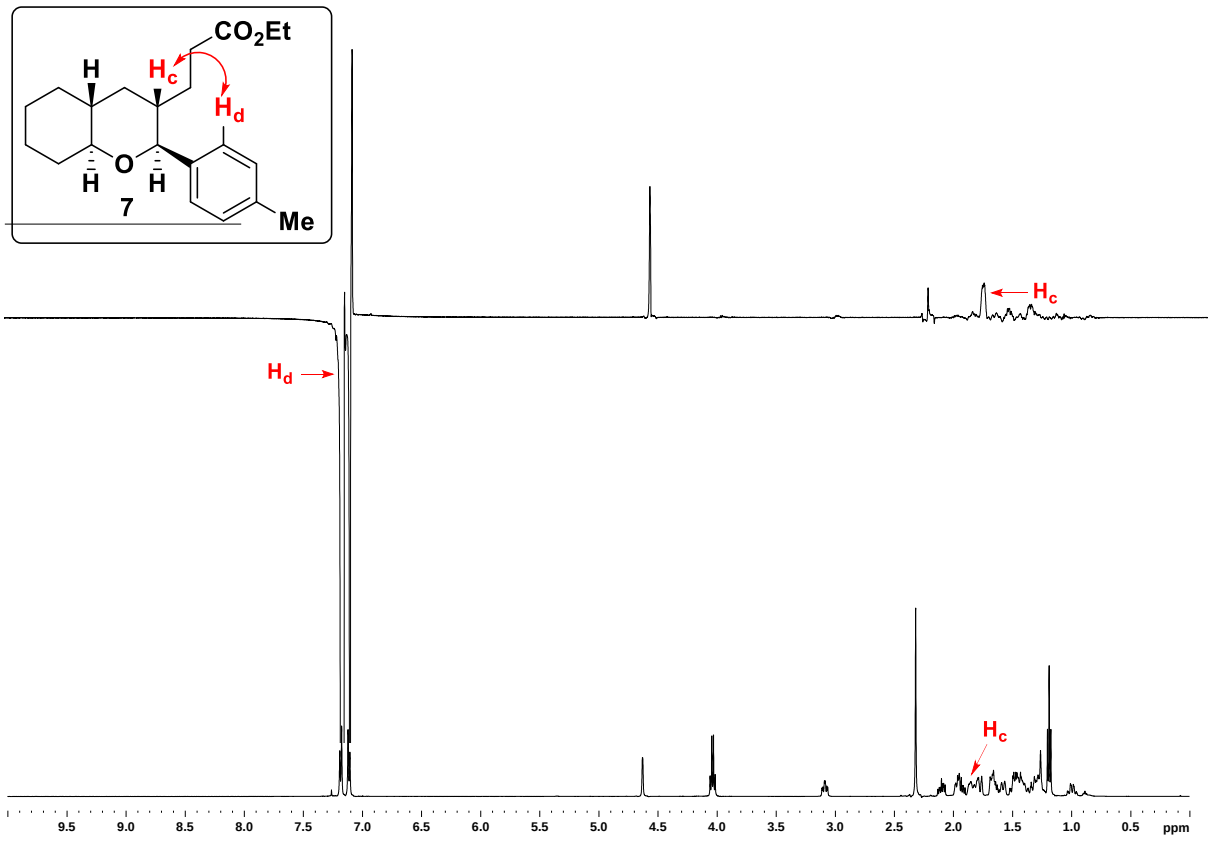

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

NOE, $CDCl_3$, 400 MHz

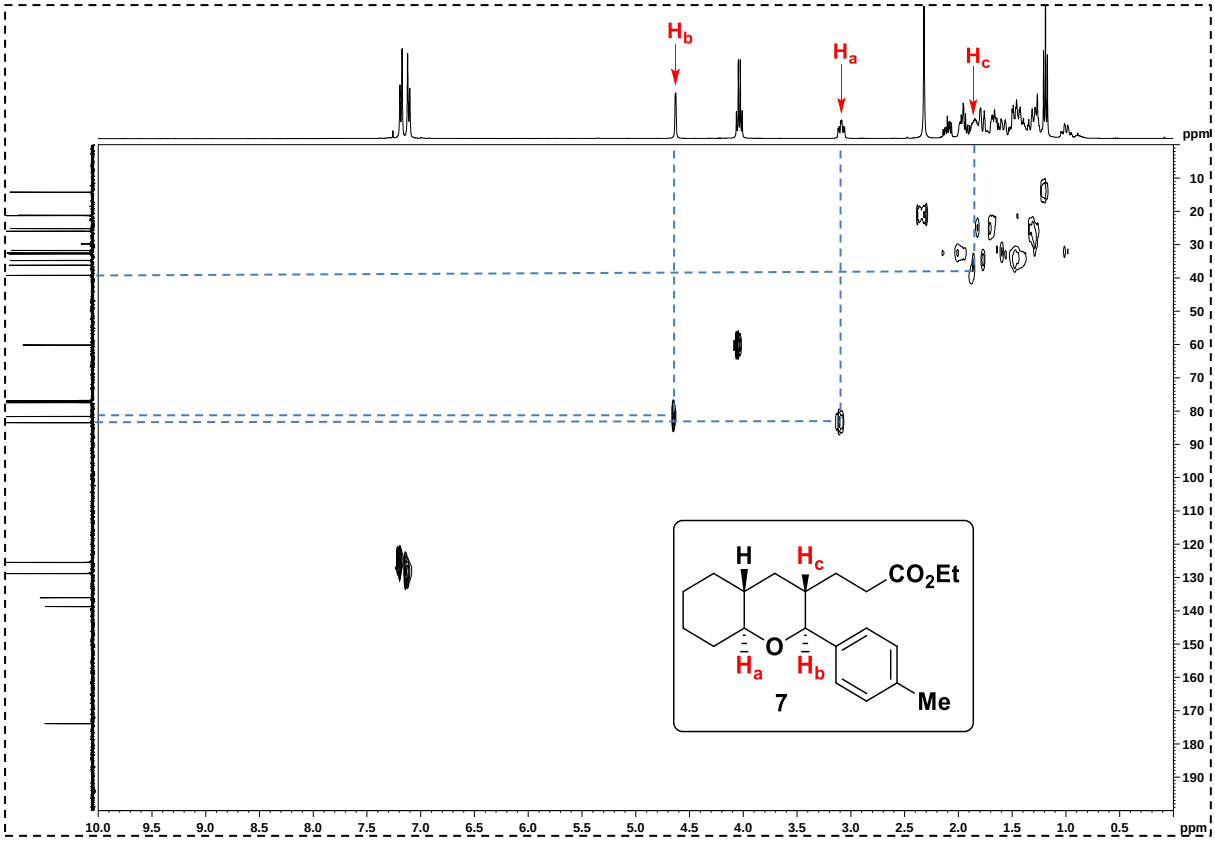


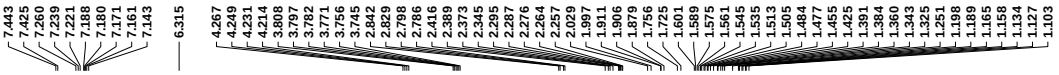


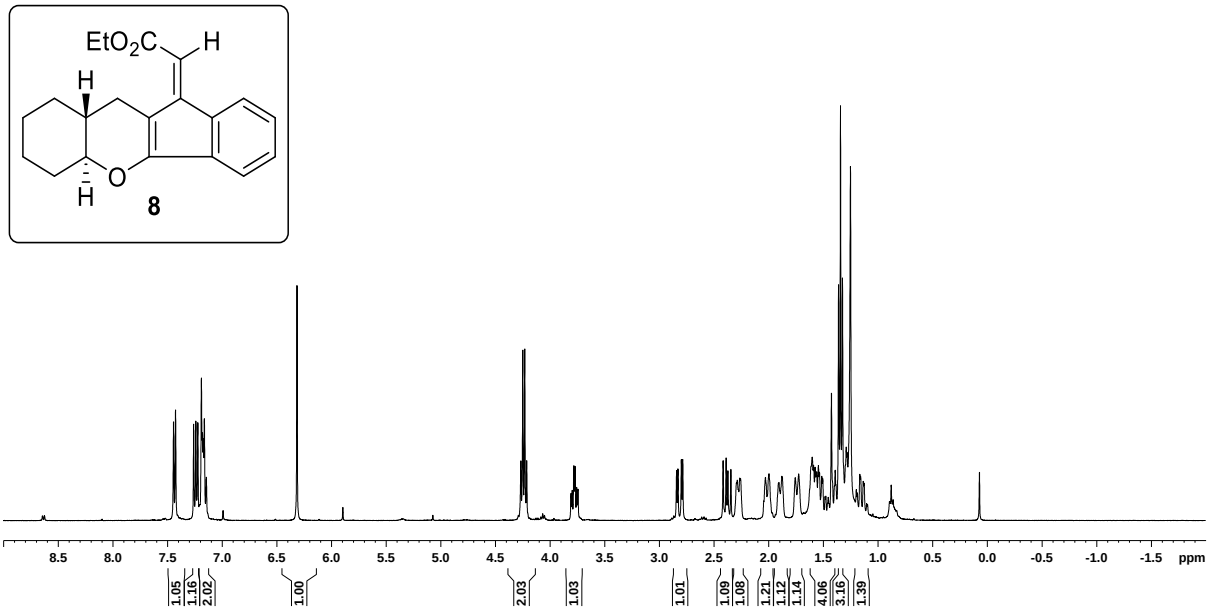

H_d
H_c
CO_2Et
H
H_c
H_d
O
H
H
7
Me
H_d
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


CO_2Et
H
H_c
H_d
O
H
H
7
Me
H_c
H_d
H_c
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 ppm

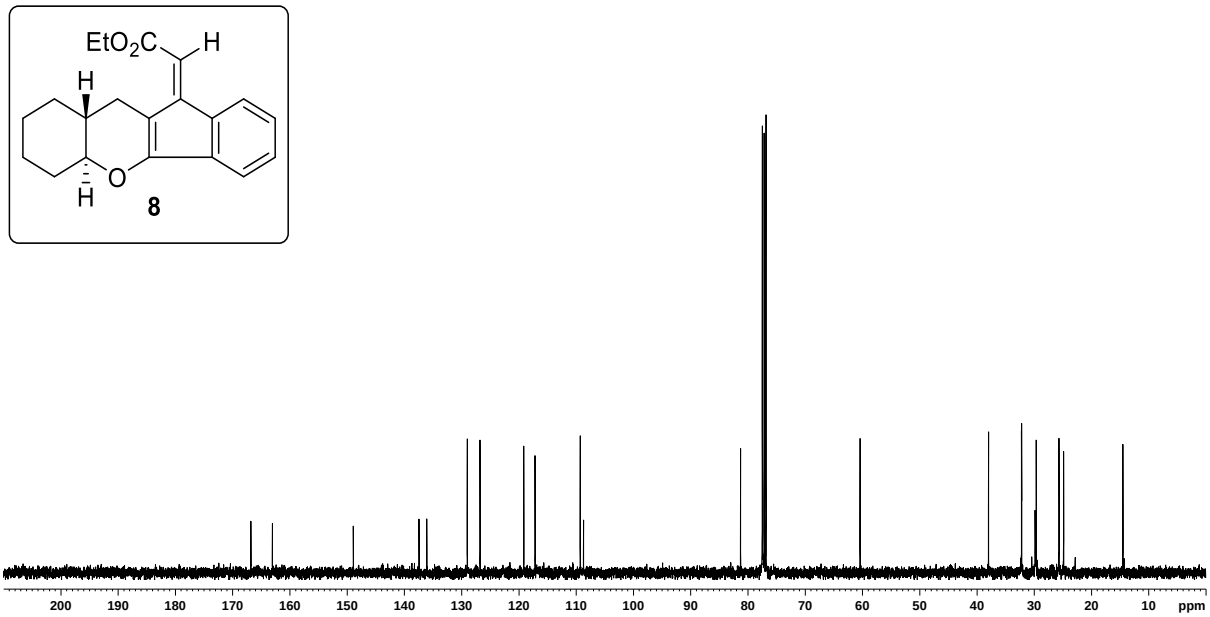
HSQC, $CDCl_3$, 400 MHz



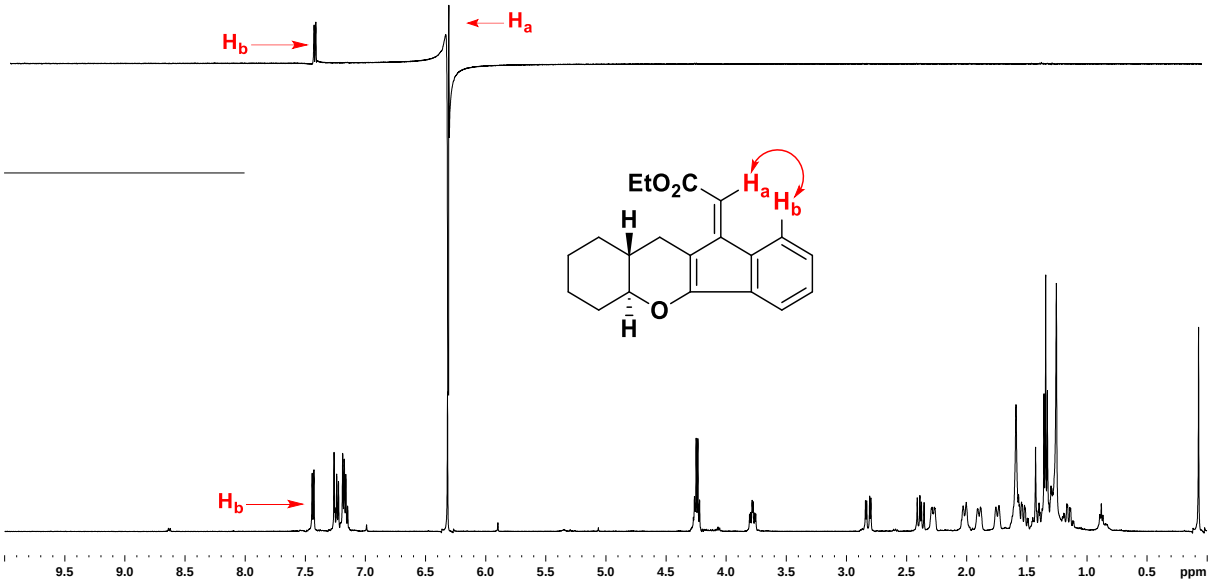

7.443
7.425
7.260
7.239
7.221
7.188
7.180
7.171
7.161
7.143
6.315
4.267
4.249
4.231
4.214
3.808
3.797
3.782
3.771
3.756
3.745
2.842
2.829
2.798
2.786
2.416
2.389
2.373
2.345
2.295
2.287
2.276
2.264
2.257
2.029
1.997
1.911
1.906
1.879
1.756
1.725
1.601
1.589
1.575
1.561
1.545
1.535
1.513
1.505
1.484
1.477
1.455
1.425
1.391
1.384
1.360
1.343
1.325
1.251
1.198
1.189
1.165
1.158
1.134
1.127
1.103

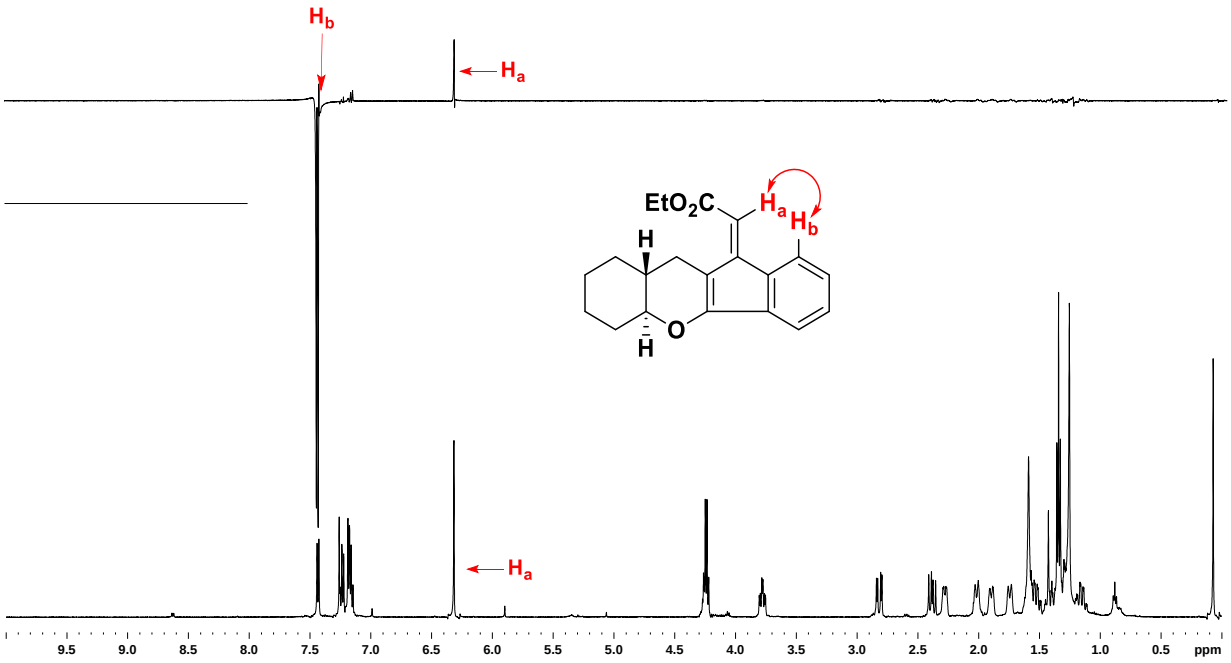

EtO2C
H
H
O
H
8
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
ppm
1.05
1.16
2.02
1.00
2.03
1.03
1.01
1.09
1.08
1.21
1.12
1.14
4.06
3.16
1.39


166.77
163.02
148.88
137.41
136.05
129.01
126.79
119.14
117.18
109.28
108.71
81.28
77.48
77.16
76.84
60.40
37.98
32.21
32.18
29.64
25.67
24.85
14.50

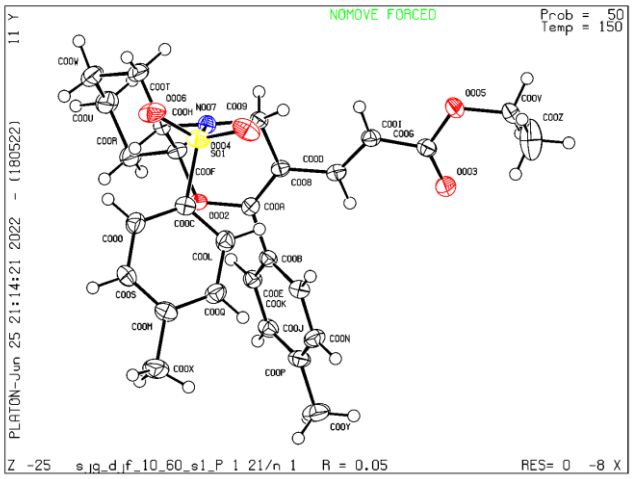

EtO2C
H
H
O
H
8
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

NOE, $CDCl_3$, 400 MHz





X-Ray crystallographic analysis:
Crystal data and structure refinement for 3b:



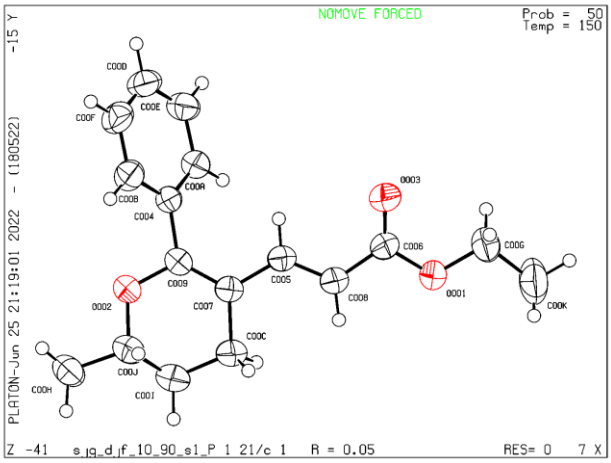
Identification code		3b	
Solvent		CH_2Cl_2	
CCDC	2181886		
Bond precision:	C-C = 0.0031 A	Wavelength=0.71073	
Cell:	a=11.7622 (4)	b=14.0804 (3)	c=16.2304 (5)
	alpha=90	beta=105.570 (3)	gamma=90
Temperature:	150 K		
	Calculated	Reported	
Volume	2589.38 (14)	2589.38 (14)	
Space group	P 21/n	P 1 21/n 1	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C28 H33 N O5 S [+ solvent]	C28 H33 N O5 S	
Sum formula	C28 H33 N O5 S [+ solvent]	C28 H33 N O5 S	
Mr	495.61	495.61	
Dx,g cm-3	1.271	1.271	
Z	4	4	
Mu (mm-1)	0.163	0.163	
F000	1056.0	1056.0	
F000’	1056.97		
h,k,lmax	13,16,19	13,16,19	
Nref	4565	4561	
Tmin,Tmax	0.991,0.996	0.902,1.000	
Tmin’	0.931		

Correction method= # Reported T Limits: Tmin=0.902 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 0.999 Theta(max)= 24.999

R(reflections)= 0.0463(3604) wR2(reflections)= 0.1255(4561)

S = 1.064 Npar= 320

Crystal data and structure refinement for 6j:



Identification code			**6j**
Solvent			CH_2Cl_2
CCDC	2181887		
Bond precision:	C-C = 0.0031 A		Wavelength=0.71073
Cell:	a=8.8310(4)	b=10.8732(4)	c=16.2743(9)
	alpha=90	beta=103.292(5)	gamma=90
Temperature:	150 K		

	Calculated	Reported
Volume	1520.82(13)	1520.82(13)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C17 H20 O3	C17 H20 O3
Sum formula	C17 H20 O3	C17 H20 O3
Mr	272.33	272.33
Dx,g cm-3	1.189	1.189
Z	4	4
Mu (mm-1)	0.080	0.080
F000	584.0	584.0
F000’	584.29	
h,k,lmax	10,12,19	10,12,19
Nref	2682	2668
Tmin,Tmax	0.997,0.998	0.385,1.000
Tmin’	0.994	

Correction method= # Reported T Limits: Tmin=0.385 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 0.995 Theta(max)= 25.000

R(reflections)= 0.0521(2181) wR2(reflections)= 0.1420(2668)

S = 1.061 Npar= 184