Supplementary Information for

Ruthenium Catalyzed Stereo- and Chemoselective Oxidative Coupling of Vinyl Ketones: An Efficient Access to (*E*,*E*)-1,6-dioxo-2,4-dienes

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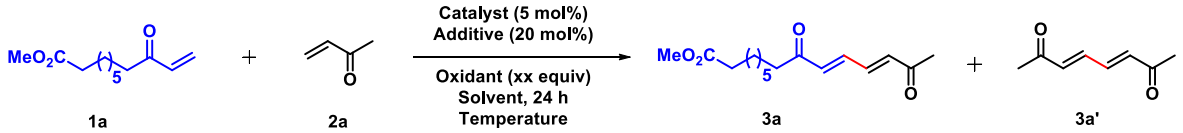
1. General Information

General Aspects: Experiments involving moisture andair sensitive components were performed in oven-dried glassware. Commercial solvents and reagents were used without further purification unless otherwise noted. Yields refer to chromatographically pure compounds, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plates (60F-254) using UV light as a visualizing agent and an p-anisaldehyde or ninhydrin stain, and heat as developing agents. Merck silica gel (particle size 100-200 and 230-400 mesh) was used for flash column chromatography. Neat compounds were used for record IR spectra. NMR spectra were recorded on either a BrukerAvance 400 (^{1}H, 400 MHz; ^{13}C, 100 MHz), BrukerAvance 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz), or JEOL DELTA (ECX) 500 (^{1}H, 500 MHz; ^{13}C, 125 MHz). Mass spectrometric data were obtained using WATERS-Q-Tof-Premier-HAB213 and WATERS-QTof-Premier-APCI-MS instruments and IR data recorded from PerkinElmer, FT-IR spectrometer. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, mspt= septet, dd = doublet of doublet, ddd = doublet of a doublet of a doublet, dt = doublet of a triplet, td = triplet of a doublet, m = multiplet, br = broad.

2. Table S1: Optimization of Reaction Conditions[a]

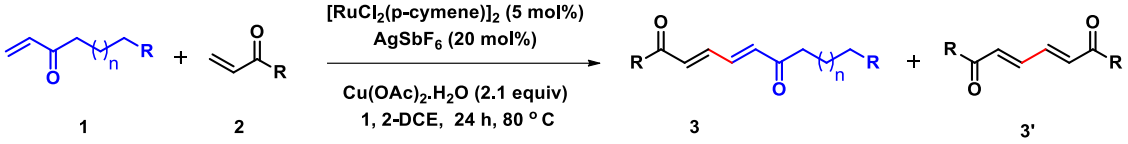


Entry	Catalyst (5 mol%)	Additive (20 mol%)	Oxidant 1.0 equiv.	Solvent	[c]Yield 3aa/ 3aa', (%)
1	$Cp^*Co(CO)I_2$ (**C1**)	$AgSbF_6$	$Cu(OAc)_2$	DCE	0
2	$[RuCl_2(p\text{-cymene})]_2$ **(C2)**	$AgSbF_6$	$Cu(OAc)_2$	DCE	40/20
3	$[Cp^*RuCl_2]_2$ **(C3)**	$AgSbF_6$	$Cu(OAc)_2$	DCE	35/20
4	$[RuCl_2(PPh_3)_3]$ **(C4)**	$AgSbF_6$	$Cu(OAc)_2$	DCE	0
5	$[CpRu(CH_3CN)_3]PF_6$ (**C5**)	-	-	DCE	0
6	$[Cp^*RhCl_2]_2$ **(C6)**	$AgSbF_6$	$Cu(OAc)_2$	DCE	30/30
7[b]	$[RuCl_2(p\text{-cymene})]_2$ **(C2)**	$AgSbF_6$	$Cu(OAc)_2$	MeOH	-
8[b]	$[RuCl_2(p\text{-cymene})]_2$ **(C2)**	$AgSbF_6$	$Cu(OAc)_2$	dioxane	40/20
9[b]	$[RuCl_2(p\text{-cymene})]_2$ **(C2)**	$AgSbF_6$	$Cu(OAc)_2$	TFE	Trace
10[b]	$[RuCl_2(p\text{-cymene})]_2$ **(C2)**	$AgSbF_6$	$Cu(OAc)_2$	HFIP	Trace
11[b]	$[RuCl_2(p\text{-cymene})]_2$ **(C2)**	$AgSbF_6$	$Cu(OAc)_2$	toluene	Trace
12[b]	$[RuCl_2(p\text{-cymene})]_2$ **(C2)**	$AgSbF_6$	$Cu(OAc)_2$	CH_2Cl_2	30/20
13[b]	$[RuCl_2(p\text{-cymene})]_2$ **(C2)**	$AgSbF_6$	$Cu(OAc)_2$	MeCN	Trace
14[b]	$[RuCl_2(p\text{-cymene})]_2$ **(C2)**	$AgSbF_6$	$Cu(OAc)_2$	^{t}AmOH	Trace

Reaction conditions: [a]**1a** (0.4 mmol), **2a** (0.3 mmol), $[Ru(p\text{-cymene})Cl_2]_2$ (5 mol %), additive (20 mol %) and oxidant (1.0 equiv.) in a specific solvent (3.0 mL) at 100 °C for 24 h. [b]Reaction carried out using 2.1 equiv of $Cu(OAc)_2.H_2O$ at 80 °C. [c]Isolated yields are of pure product **3aa** and **3aa'** w. r. t acrylate **2a.** TFE = Trifluoroethanol, HFIP = Hexafluoro-isopropanol, DCM = dichloromethane, ^{t}AmOH = t-amyl alcohol

3. Experimental Procedures

3.1. General procedure for the oxidative coupling reaction of vinyl ketones



A 8 mL screw-cap vial was charged with $[RuCl_2(p\text{-cymene})]_2$ (9.0 mg, 0.01 mmol, 5.0 mol%), $Cu(OAc)_2 \cdot H_2O$ (125 mg, 0.63 mmol, 2.1 equiv), $AgSbF_6$ (21 mg, 0.06 mmol, 20 mol%) and 1,2-dichloroethane (2.0 mL). The vial was sealed under nitrogen and allowed to stir at room temperature under nitrogen atmosphere for 10 minutes. To this vinyl ketone **1** (0.40 mmol, 1.33 equiv) and vinyl ketone **2** (0.25 equiv) were added using a syringe and the reaction mixture was stirred at 80 °C (using an oil bath). To this reaction mixture, vinyl ketone **2** (0.30 mmol, 0.75 equiv) in 1,2-DCE (2.0 ml) was added slowly using syringe pump over 12 hrs., at 80 °C. Then the reaction mixture was stirred at same temperature for next 12 hrs. After cooling down, the mixture was diluted with ethyl acetate, filtrated and concentrated to give the crude compound which was directly purified by silica gel column chromatography.

{Note: 0.2 mmol scale reactions were carried out for the synthesis of carbohydrate derivatives, **3qi-3rl**. During the synthesis of natural product **4**, we isolated homodimer of decyl vinyl ketone as a minor product but we didn't get pure ^{1}H NMR spectrum due to less compound. So we repeated same reaction in 3-batches (0.3 mmol × 3) to get pure spectra and for details, please see page 10).

3.1a. Examples with data

Compound 3aa Following general procedure, **3aa** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a colourless solid (65 mg, 0.23 mmol, 78%). **IR** (neat): ν_{max}/cm^{-1} 2933, 2852, 1735, 1681, 1585, 1465, 1438, 1402, 1361, 1310, 1230, 1175, 1113, 1072, 977, 882, 763. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 - 7.09 (m, 2H), 6.49 - 6.43 (m, 2H), 3.65 (s, 3H), 2.58 (t, *J* = 7.4 Hz, 2H), 2.31 (s, 3H), 2.28 (t, *J* = 7.6 Hz, 2H), 1.63 – 1.57 (m, 4H), 1.31 – 1.27 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.01, 197.84, 174.34, 139.88, 138.79, 136.78, 136.17, 51.57, 41.30, 34.11, 29.10, 29.04, 28.74, 27.97, 24.92, 23.95. **HRMS**(ESI-TOF) m/z calcd. for $C_{16}H_{25}O_4$ $[M+H]^+$ 281.1753; found 281.1751.

Following general procedure, **3aa'** was obtained as a white solid (7.5:2.5:hexane:EtOAc) (5 mg, 0.036 mmol, 12%); **IR** (neat): ν_{max}/cm^{-1} 3362, 3041, 2982, 2948, 2877, 1712, 1679, 1582, 1457, 1411, 1369, 1255, 991, 852, 735; **^{1}H NMR** (400 MHz,$CDCl_3$) δ 7.19 – 7.09 (m, 2H), 6.52 – 6.38 (m, 2H), 2.33 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.80 (2C), 139.76 (2C), 136.89 (2C), 27.94 (2C); **HRMS** m/z calcd for $C_8H_{11}O_2$ $[M+H]^+$ 139.0759; found 139.0762.

Compound 3ab/3ab' Following general procedure, **3ab** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a yellowish solid (65 mg, 0.22 mmol, 75%). **IR** (neat): ν_{max}/cm^{-1} 2930, 2853, 1735, 1682, 1585, 1464, 1435, 1406, 1376, 1308, 1225, 1169, 1073, 977, 881, 846, 762. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 – 7.12 (m, 2H), 6.52 – 6.42 (m, 2H), 3.65 (s, 3H), 2.60 (dt, *J* = 22.7, 7.3 Hz, 4H), 2.28 (t, *J* = 7.5 Hz, 2H), 1.61 – 1.57 (m, 4H), 1.30 (m, 6H), 1.12 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.44, 200.09, 174.35, 138.88, 138.81, 135.94, 135.87, 51.57, 41.32, 34.60, 34.11, 29.81, 29.79, 28.75, 24.92, 23.96, 7.97. **HRMS**(ESI-TOF) m/z calcd. for $C_{17}H_{27}O_4$ $[M+H]^+$ 295.1909; found 295.1906.

Following general procedure, **3ab'** was obtained as a colourless solid (7.5:2.5:hexane:EtOAc) (6 mg, 0.039 mmol, 13%); **IR** (neat): ν_{max}/cm^{-1} 3360, 3040, 2979, 2938, 2887, 1713, 1681, 1585, 1458, 1410, 1370, 1258, 999, 853, 738; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 – 7.09 (m, 2H), 6.51 – 6.41 (m, 2H), 2.62 (q, J = 7.3 Hz, 4H), 1.11 (t, J = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.46 (2C), 138.83 (2C), 135.82 (2C), 34.58 (2C), 7.96 (2C); **HRMS** m/z calcd for $C_{10}H_{15}O_2$ $[M+H]^+$ 167.1072; found 167.1076.

Compound 3ad Following general procedure, **3ad** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a colourless solid (76 mg, 0.23 mmol, 79%). **IR** (neat): ν_{max}/cm^{-1} 3357, 2932, 2856, 1736, 1681, 1585, 1466, 1436, 1402, 1368, 1305, 1224, 1169, 1071, 1027, 882, 724. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 – 7.08 (m, 2H), 6.56 – 6.38 (m, 2H), 3.65 (s, 3H), 2.58 (td, *J* = 7.4, 5.5 Hz, 4H), 2.30 (d, *J* = 7.5 Hz, 2H), 1.61 (dd, *J* = 8.5, 6.3 Hz, 6H), 1.34 – 1.30 (m, 8H),

0.92 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.09, 199.05, 174.31, 138.89, 138.85, 136.08, 136.01, 51.53, 41.32, 41.13, 34.10, 29.11, 29.08, 28.99, 26.20, 24.92, 23.97, 22.41, 13.92. **HRMS**(ESI-TOF) m/z calcd. for $C_{19}H_{31}O_4$ $[M+H]^+$ 323.2222; found 323.2231.

Following general procedure, **3ad'** was obtained as a white solid (7.5:2.5:hexane:EtOAc) (6 mg, 0.027 mmol, 9%); **IR** (neat): ν_{max}/cm^{-1} 3356, 3029, 2960, 2933, 2898, 1675, 1565, 1242, 1132, 1085, 1025, 870, 835, 720; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 – 7.12 (m, 2H), 6.52 – 6.43 (m, 2H), 2.61 (t, *J* = 6.9 Hz 4H), 1.64 – 1.59 (m, 4H), 1.36– 1.32 (m, 4H), 0.91 (t, *J* = 7.2Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.18 (2C), 138.90 (2C), 136.05 (2C), 41.11 (2C), 26.20 (2C), 22.40 (2C), 13.91 (2C); **HRMS** m/z calcd for $C_{14}H_{23}O_2$ $[M+H]^+$ 223.1698; found 223.1696.

Compound 3ae Following general procedure, **3ae** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a yellowish solid (77 mg, 0.24 mmol, 80%). **IR** (neat): ν_{max}/cm^{-1} 3353, 3047, 2934, 2858, 1733, 1668, 1581, 1460, 1430, 1399, 1362, 1220, 1172, 1062, 1027, 882, 724. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 - 7.17 (br d, 2H), 6.46 - 6.48 (br d, 2H), 3.65 (s, 3H), 2.57 (t, *J* = 7.4 Hz, 2H), 2.46 (d, *J* = 6.2 Hz, 2H), 2.28 (t, *J* = 7.3 Hz, 2H), 2.16 – 2.14 (m, 1H), 1.61 – 1.58 (m, 4H), 1.31 (m, 6H), 0.94 (d, *J* = 5.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.91, 199.36, 174.30, 138.89 (2C), 136.37, 136.06, 51.51, 50.35, 41.32, 34.10, 29.75, 29.02, 28.98, 25.35, 25.12, 25.01, 23.98, 22.68. **HRMS**(ESI-TOF) m/z calcd. for $C_{19}H_{31}O_4$ $[M+H]^+$ 323.2222; found 323.2229.

Following general procedure, **3ae'** was obtained as a white solid (7.5:2.5:hexane:EtOAc) (7 mg, 0.03 mmol, 10%); **IR** (neat): ν_{max}/cm^{-1} 3353, 3025, 2959, 2926, 2895, 1670, 1575, 1238, 1129, 1088, 1022, 868, 842, 719; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 - 7.12 (m, 2H), 6.50 – 6.44 (m, 2H), 2.46 (d, *J* = 6.9 Hz, 4H), 2.23 – 2.13 (m, 2H), 0.94 (d, *J* = 6.5 Hz, 12H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.80 (2C), 138.91 (2C), 136.39 (2C), 50.35 (2C), 25.10 (2C), 22.69 (2C); **HRMS** m/z calcd for $C_{14}H_{23}O_2$ $[M+H]^+$ 223.1698; found 223.1695.

Compound 3af Following general procedure, **3af** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a colourless solid (72 mg, 0.21 mmol, 70%). **IR** (neat): ν_{max}/cm^{-1} 3353, 29329, 2867, 1738, 1683, 1580, 1468, 1422, 1404, 1301, 1242, 1168, 1109, 1017, 885, 720. **^{1}H NMR** (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.02 (m, 2H), 6.62 – 6.28 (m, 2H), 3.65 (s, 3H), 2.57 (td, *J* = 7.4, 1.6 Hz, 4H), 2.29 (d, *J* = 7.4 Hz, 2H), 1.63 – 1.59 (m, 6H), 1.29 (dd, *J* = 5.7, 2.9 Hz, 12H), 0.87 (dd, *J* = 7.8, 5.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.24, 200.10, 174.35, 138.97, 138.88, 136.10, 136.02, 51.56, 41.43, 41.32, 34.14, 31.66, 29.09, 29.05, 28.99, 28.96, 24.92, 24.07, 23.97, 22.56, 14.10. **HRMS**(ESI-TOF) m/z calcd. for $C_{21}H_{35}O_4$ $[M+H]^+$ 351.2535; found 351.2542.

Following general procedure, **3af'** was obtained as a white solid (7.5:2.5:hexane:EtOAc) (8.0 mg, 0.03 mmol, 10%); **IR** (neat): ν_{max}/cm^{-1} 3355, 3044, 2956, 2927, 2885, 2854, 1680, 1575, 1464, 1402, 1368, 1340, 1236, 1214, 1129, 1078, 1012, 888, 832, 739, 722; **^{1}H NMR** (400 MHz,$CDCl_3$) δ 7.22 – 7.10 (m, 2H), 6.55 – 6.40 (m, 2H), 2.66 (t, *J* = 7.2 Hz, 4H), 1.65 – 1.59 (m, 4H), 1.34 – 1.26 (m, 12H), 0.87 (t, J = 6.7 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.21 (2C), 138.90 (2C), 136.06 (2C), 41.43 (2C), 31.66 (2C), 28.96 (2C), 24.08 (2C), 22.56 (2C), 14.10 (2C); **HRMS** m/z calcd for $C_{18}H_{31}O_2$ $[M+H]^+$ 279.2324; found 279.2327.

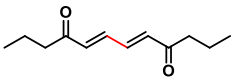
Compound 3ba Following general procedure, **3ba** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a colourless solid (71 mg, 0.24 mmol, 80%). **IR** (neat): ν_{max}/cm^{-1} 2927, 2851, 1735, 1680, 1584, 1437, 1359, 1229, 1016, 722. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24 – 7.04 (m, 2H), 6.56 – 6.38 (m, 2H), 3.65 (s, 3H), 2.58 (t, *J* = 7.4 Hz, 2H), 2.32 (s, 3H), 2.29 (t, *J* = 7.5 Hz, 2H), 1.61 (d, *J* = 7.2 Hz, 4H), 1.29 (s, 8H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.97, 197.74, 174.29, 139.80, 138.67, 136.67, 136.09, 51.46, 41.24, 34.05, 29.16, 29.09, 29.03 (2C), 27.87, 24.87, 23.92. **HRMS**(ESI-TOF) m/z calcd. for $C_{17}H_{26}O_4Na$ $[M+Na]^+$ 317.1729; found 317.1727.

Homodimer of methyl vinyl ketone was obtained as a minor product (4 mg, 0.03 mmol, 10%). For data please see **3aa'**.

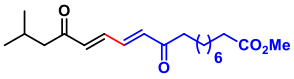
Compound 3bc Following general procedure, **3bc** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a colourless solid (72 mg, 0.22 mmol, 75%). **IR** (neat): ν_{max}/cm^{-1} 2927, 2853, 1730, 1681, 1585, 1438, 1369, 1224, 1030, 725. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 – 7.10 (m, 2H), 6.53 – 6.40 (m, 2H), 3.65 (s, 3H), 2.57 (td, *J* = 7.3, 2.5 Hz, 4H), 2.27

(d, *J* = 7.6 Hz, 2H), 1.67 – 1.59 (m, 6H), 1.28 (s, 8H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.02, 199.95, 174.27, 138.80 (2C), 135.99, 135.94, 51.43, 43.15, 41.25, 34.04, 29.15, 29.09, 29.02 (2C), 24.87, 23.94, 17.45, 13.71. **HRMS**(ESI-TOF) m/z calcd. for $C_{19}H_{31}O_4$ $[M+H]^+$ 323.2222; found 323.2228.

Following general procedure, **3bc'** was obtained as a colourless solid (7.5:2.5:hexane:EtOAc) (5 mg, 0.036 mmol, 12%); **IR** (neat): ν_{max}/cm^{-1} 2968, 2924, 2869, 1745, 1725, 1696, 1564, 1468, 1409, 1379, 1248, 1065, 880, 723; **^{1}H NMR** (400 MHz,$CDCl_3$) δ 7.21 – 7.11 (m, 2H), 6.52 – 6.40 (m, 2H), 2.56 (t, *J* = 7.3 Hz, 4H), 1.70– 1.61 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.95 (2C), 138.86 (2C), 136.05 (2C), 43.23 (2C), 17.54 (2C), 13.77 (2C); **HRMS** m/z calcd for $C_{12}H_{19}O_2$ $[M+H]^+$ 195.1385; found 195.1389.

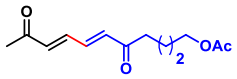


Compound 3be Following general procedure, **3be** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a colourless solid (78 mg, 0.23 mmol, 78%). **IR** (neat): ν_{max}/cm^{-1} 2928, 2852, 1736, 1680, 1581, 1468, 1365, 1222, 1029, 723. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23 – 7.06 (m, 2H), 6.55 – 6.40 (m, 2H), 3.65 (s, 3H), 2.57 (t, *J* = 7.4 Hz, 2H), 2.46 (d, *J* = 7.0 Hz, 2H), 2.28 (t, *J* = 7.5 Hz, 2H), 2.21 – 2.12 (m, 1H), 1.60 (d, *J* = 8.4 Hz, 4H), 1.29 (s, 8H), 0.94 (d, *J* = 6.7 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.04, 199.78, 174.29, 138.84(2C), 136.27, 135.99, 51.45, 50.24, 41.27, 34.04, 29.16, 29.10, 29.03 (2C), 25.00, 24.87, 23.94, 22.60 (2C). **HRMS**(ESI-TOF) m/z calcd. for $C_{20}H_{32}O_4Na$ $[M+Na]^+$ 359.2198; found 359.2197.



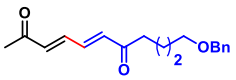
Homodimer of isobutyl vinyl ketone was obtained as a minor product (6 mg, 0.027 mmol, 9%). For data please see **3ae'**.

Compound 3ca Following general procedure, **3ca** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a white solid (50 mg, 0.21 mmol, 70%). **IR** (neat): ν_{max}/cm^{-1} 3473, 2952, 2948, 2832, 1723, 1645, 1476, 1379, 1223, 1216, 1102, 1023, 852, 742. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 - 7.10 (m, 2H), 6.49 - 6.49 (m, 2H), 4.08 (t, *J* = 6.9 Hz, 2H), 2.64 (t, *J* = 7.0 Hz, 2H), 2.32 (s, 3H), 2.04 (s, 3H), 1.71 – 1.66 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.23, 199.26, 171.23, 139.68, 138.97, 136.90, 135.96, 64.04, 40.61, 28.05, 27.98, 21.04, 20.34. **HRMS**(ESI-TOF) m/z calcd. for $C_{13}H_{19}O_4$ $[M+H]^+$ 239.1283; found 239.1285.



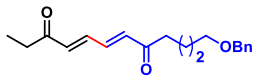
Homodimer of methyl vinyl ketone was obtained as a minor product (3.0 mg, 0.024 mmol, 8%). For data please see **3aa'**.

Compound 3da Following general procedure, **3da** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a colourless solid (65 mg, 0.22 mmol, 76%). **IR** (neat): ν_{max}/cm^{-1} 3403, 3023, 2925, 2941, 2865, 1714, 1648, 1445, 1389, 1228, 1204, 1118, 1056, 856, 737; **^{1}H NMR** (400 MHz,$CDCl_3$) δ 7.36 – 7.22 (m, 5H), 7.19 - 7.07 (m, 2H), 6.47 - 6.47 (m, 2H), 4.48 (s, 2H), 3.48 (t, *J* = 6.2 Hz, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.80 – 1.69 (m, 2H), 1.65 – 1.61 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.78, 197.83, 139.87, 138.83, 138.54, 136.77, 136.16, 128.47 (2C), 127.69, 127.69 (2C), 73.02, 70.02, 40.95, 29.21, 27.96, 20.90. **HRMS**(ESI-TOF) m/z calcd. for $C_{18}H_{23}O_3$ $[M+H]^+$ 287.1647; found 287.1645.



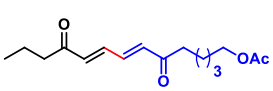
Homodimer of methyl vinyl ketone was obtained as a minor product (5.0 mg, 0.036 mmol, 12%). For data please see **3aa'**.

Compound 3db Following general procedure, **3db** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a colourless solid (65 mg, 0.21 mmol, 72%). **IR** (neat): ν_{max}/cm^{-1} 3355, 3042, 2937, 2852, 2798, 1713, 1679, 1487, 1375, 1244, 1214, 1126, 1071, 841, 725. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 5H), 7.19 – 7.10 (m, 2H), 6.50 – 6.40 (m, 2H), 4.48 (s, 2H), 3.48 (t, *J* = 6.2 Hz, 2H), 2.65 – 2.58 (m, 4H), 1.76 – 1.70 (m, 2H), 1.66 – 1.62 (m, 2H), 1.12 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.33, 199.76, 138.89, 138.79, 138.45, 135.91, 135.77, 128.36 (2C), 127.69, 127.59 (2C), 72.92, 69.92, 40.87, 34.49, 29.12, 20.81, 7.87. **HRMS**(ESI-TOF) m/z calcd. for $C_{19}H_{25}O_3$ $[M+H]^+$ 301.1804; found 301.1802.



Homodimer of ethyl vinyl ketone was obtained as a minor product (6.0 mg, 0.036 mmol, 12%). For data please see **3ab'**.

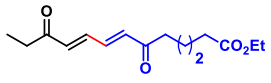
Compound 3cc Following general procedure, **3cc** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a colourless solid (63 mg, 0.22 mmol, 75%). **IR** (neat): ν_{max}/cm^{-1} 3463, 2971, 2910, 2812, 1754, 1739, 1608, 1423, 1335, 1246, 1202, 1158, 1087, 856, 703. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 - 7.12 (m, 2H), 6.41 - 6.49 (m, 2H), 4.02 (t, *J* = 6.6 Hz, 2H), 2.56 (dt, *J* = 17.7, 7.3 Hz, 4H), 2.00 (s, 3H), 1.65 – 1.60 (m, 6H), 1.35 (m, 2H), 0.91 (t, *J* =



7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.96, 199.61, 171.20, 139.03, 138.77, 136.71, 135.90, 64.28, 43.21, 41.05, 28.49, 25.60, 23.56, 21.02, 17.51, 13.77. **HRMS**(ESI-TOF) m/z calcd. for $C_{16}H_{25}O_4$ $[M+H]^+$ 281.1753; found 281.1756.

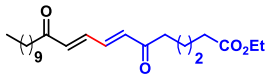
Homodimer of propyl vinyl ketone was obtained as a minor product (8.0 mg, 0.039 mmol, 13%). For data please see **3bc'**.

Compound 3gb Following general procedure, **3gb** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a colourless solid (55 mg, 0.20 mmol, 69%). **IR** (neat): ν_{max}/cm^{-1} 3360, 3043, 2918, 2873, 2850, 1731, 1714, 1681, 1583, 1463, 1311, 1217, 1174, 910, 793. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 7.13 (m, 2H), 6.53 – 6.42 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.63 (m, 4H), 2.31 (t, *J* = 7.0 Hz, 2H), 1.66 – 1.62 (m, 2H), 1.26 – 1.22 (m, 2H), 1.24 (t, *J* = 7.3 Hz, 3H), 1.12 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.35, 199.40, 173.39, 139.02, 138.63, 135.92, 135.81, 60.33, 40.77, 34.50, 34.03, 24.40, 23.28, 14.21, 7.85. **HRMS**(ESI-TOF) m/z calcd. for $C_{15}H_{23}O_4$ $[M+H]^+$ 267.1596; found 267.1594.

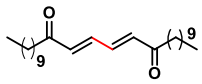


Homodimer of ethyl vinyl ketone was obtained as a minor product (6.0 mg, 0.036 mmol, 12%). For data please see **3ab'**.

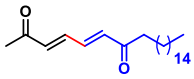
Compound 3gg Following general procedure, **3gg** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a white solid (70 mg, 0.18 mmol, 62%). **IR** (neat): ν_{max}/cm^{-1} 3354, 2953, 2919, 2850, 1727, 1676, 1585, 1469, 1406, 1374, 1253, 1217, 1186, 908, 862, 718. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.20 - 7.11 (m, 2H), 6.50 - 6.42 (m, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.63 – 2.54 (m, 4H), 2.30 – 2.24 (m, 2H), 1.68 – 1.58 (m, 10H), 1.10 – 1.21 (m, 10H), 1.23 (s, 3H), 0.84 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.22, 199.47, 173.47, 139.13, 138.78, 136.20, 135.87, 60.42, 41.44, 40.87, 34.12, 31.95, 30.11, 29.53, 29.43, 29.37, 29.04, 24.50, 24.11, 23.39, 22.74, 14.25, 14.18. **HRMS**(ESI-TOF) m/z calcd. for $C_{23}H_{39}O_4$ $[M+H]^+$ 379.2848; found 379.2842.



Following general procedure, **3gg'** was obtained as a colourless solid (7.5:2.5:hexane:EtOAc) (16 mg, 0.04 mmol, 14%); **IR** (neat): ν_{max}/cm^{-1} 2953, 2918, 2850, 1677, 1586, 1470, 1405, 1371, 1313, 1244, 1218, 1131, 1100, 906, 853, 750; **^{1}H NMR** (400 MHz,$CDCl_3$) δ 7.21 – 7.11 (m, 2H), 6.53 – 6.41 (m, 2H), 2.60 (t, *J* = 6.8 Hz, 4H), 1.65– 1.58 (m, 4H), 1.27– 6.4 (m, 28H), 0.86 (t, *J* = 6.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.24 (2C), 138.91 (2C), 136.06 (2C), 41.43 (2C), 31.96 (2C), 29.63 (2C), 29.54 (2C), 29.48 (2C), 29.38 (2C), 29.30 (2C), 24.12 (2C), 22.75 (2C), 14.19 (2C); **HRMS** m/z calcd for $C_{26}H_{47}O_2$ $[M+H]^+$ 391.3576; found 391.3572.

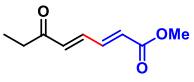


Compound 3ha Following general procedure, **3ha** was purified by silica column chromatography (pet ether/EtOAc at a 8.5:1.5 ratio), obtained as a colourless solid (78 mg, 0.22 mmol, 75%). **IR** (neat): ν_{max}/cm^{-1} 2915, 2849, 1674, 1594, 1467, 1359, 1235, 1082, 719. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 – 7.07 (m, 2H), 6.58 – 6.34 (m, 2H), 2.58 (t, *J* = 7.4 Hz, 2H), 2.32 (s, 3H), 1.61 (m, 2H), 1.30 – 1.23 (m, 26H), 0.87 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.04, 197.70, 139.80 , 138.63, 136.64, 136.12, 41.33, 31.92, 29.93 – 28.97 (11C), 27.86, 24.03, 22.68, 14.11. **HRMS**(ESI-TOF) m/z calcd. for $C_{23}H_{41}O_2$ $[M+H]^+$ 349.3107; found 349.3108.

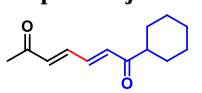


Homodimer of methyl vinyl ketone was obtained as a minor product (4.0 mg, 0.03 mmol, 10%). For data please see **3aa'**.

Compound 3ib Following general procedure, **3ib** was purified by silica column chromatography (pet ether/EtOAc at a 8.5:1.5 ratio), obtained as a colourless solid (34 mg, 0.20 mmol, 68%). **IR** (neat): ν_{max}/cm^{-1} 2923, 2852, 1708, 1690, 1594, 1436, 1329, 1248, 1149, 1033, 725. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 15.2, 11.4 Hz, 1H), 7.16 (dd, *J* = 15.4, 11.3 Hz, 1H), 6.44 (d, *J* = 15.4 Hz, 1H), 6.22 (d, *J* = 15.2 Hz, 1H), 3.77 (s, 3H), 2.62 (q, *J* = 7.3 Hz, 2H), 1.11 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.41, 166.29, 141.65, 138.00, 135.32, 128.34, 51.93, 34.47, 7.84. **HRMS**(ESI-TOF) m/z calcd. for $C_9H_{13}O_3$ $[M+H]^+$ 169.0865; found 169.0869.

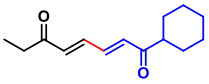


Compound 3ja Following general procedure, **3ja** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a colourless solid (34 mg, 0.16 mmol, 55%). **IR** (neat): ν_{max}/cm^{-1} 2920, 2853, 1713, 1675, 1584, 1445, 1409, 1372, 1330, 1279, 1263, 1140, 1109, 1091, 884, 794. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 - 7.10 (m, 2H), 6.58 - 6.43 (m, 2H), 2.60 – 2.50 (m, 1H), 2.31 (s, 3H), 1.86 – 1.77 (m, 4H), 1.42 – 1.24 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.65, 197.90, 139.94, 138.76, 136.66, 134.93, 49.64, 28.48 (2C), 28.00, 25.86, 25.69 (2C). **HRMS**(ESI-TOF)m/z calcd. for $C_{13}H_{19}O_2$ $[M+H]^+$ 207.1385; found 207.1388.



Homodimer of methyl vinyl ketone was obtained as a minor product (5.0 mg, 0.036 mmol, 12%). For data please see **3aa'**.

Compound 3jb Following general procedure, **3jb** was purified by silica column chromatography (pet ether/EtOAc at a 8:2



ratio), obtained as a colourless solid (37 mg, 0.17 mmol, 57%). **IR** (neat): ν_{max}/cm^{-1} 2923, 2850, 1678, 1582, 1449, 1408, 1369, 1331, 1264, 1238, 1142, 1118, 1066, 849, 702. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 – 7.12 (m, 2H), 6.62 – 6.41 (m, 2H), 2.61 (q, *J* = 7.2 Hz, 2H), 2.58 – 2.51 (m, 1H), 1.84 – 1.77 (m, 4H), 1.32 (m, 6H), 1.11 (t, *J* = 8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.71, 200.48, 138.91, 138.87, 135.74, 134.78, 49.64, 34.64, 28.48 (2C), 25.87, 25.69 (2C), 7.97. **HRMS**(ESI-TOF) m/z calcd. for $C_{14}H_{21}O_2$ $[M+H]^+$ 221.1542; found 221.1545.

Homodimer of ethyl vinyl ketone was obtained as a minor product (5.0 mg, 0.03 mmol, 10%). For data please see **3ab'**.

Compound 3kc Following general procedure, **3kc** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a colourless solid (68 mg, 0.20 mmol, 69%). $[\alpha]_D^{28}$ = +34.0 (*c* = 0.2, $CHCl_3$). **IR** (neat): ν_{max}/cm^{-1} 3444, 3028, 2937, 2964, 2877, 1795, 1630, 1464, 1387, 1239, 1197, 1071, 953, 864, 723. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2, 2H), 7.57 - 7.53 (t, *J* = 8.5 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.17 - 7.09 (m, 2H), 6.46 - 6.40 (m, 2H), 5.19 (m, 1H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.55 (t, *J* = 7.3 Hz, 2H), 2.05 (dd, *J* = 14.2, 7.0 Hz, 2H), 1.65 (dd, *J* = 14.7, 7.3 Hz, 2H), 1.37 (d, *J* = 6.3 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.94, 198.82, 166.19, 139.26, 138.63, 136.26, 135.77, 133.03, 129.62 (3C), 128.44 (2C), 70.98, 43.25, 37.27, 30.20, 20.36, 17.53, 13.80. **HRMS**(ESI-TOF) m/z calcd. for $C_{20}H_{25}O_4$ $[M+H]^+$ 329.1753; found 329.1750.

Homodimer of propyl vinyl ketone was obtained as a minor product (8.0 mg, 0.042 mmol, 14%). For data please see **3bc'**.

Compound 3lc Following general procedure, **3lc** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a brownish solid (50 mg, 0.19 mmol, 65%). **IR** (neat): ν_{max}/cm^{-1} 3404, 3027, 2960, 2925, 2852, 1711, 1677, 1585, 1496, 1453, 1366, 1218, 1185, 1068, 820, 747. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.20 (m, 3H), 7.12 - 7.19 (m, 2H), 6.48 - 6.44 (m, 2H), 2.95 (dt, J = 6.3, 5.5 Hz, 4H), 2.56 (t, J = 7.2 Hz, 2H), 1.64 – 1.60 (m, 2H), 0.95 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.96, 198.86, 140.89, 139.26, 138.72, 136.24, 135.86, 128.62 (2C), 128.41 (2C), 126.31, 43.27, 42.90, 29.94, 17.54, 13.79. **HRMS**(ESI-TOF) m/z calcd. for $C_{17}H_{21}O_2$ $[M+H]^+$ 257.1542; found 257.1546.

Homodimer of propyl vinyl ketone was obtained as a minor product (9.0 mg, 0.045 mmol, 15%). For data please see **3bc'**.

Compound 3le Following general procedure, **3le** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a brownish solid (56 mg, 0.21 mmol, 70%). **IR** (neat): ν_{max}/cm^{-1} 3408, 3025, 2961, 2940, 2828, 1721, 1652, 1586, 1423, 1405, 1360, 1208, 1126, 1087, 746, 699. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.25 (m, 2H), 7.19 (m, 3H), 7.18 - 7.12 (m, 2H), 6.48 - 6.42 (m, 2H), 2.99 – 2.89 (m, 4H), 2.45 (d, *J* = 7.1 Hz, 2H), 2.19 – 2.13 (m, 1H), 0.93 (d, J = 6.7 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 199.84, 198.90, 139.29, 138.79, 136.52, 135.92, 128.63 (2C), 128.43 (2C), 126.32, 50.35, 42.93, 29.92, 29.83, 25.08, 22.69 (2C). **HRMS**(ESI-TOF) m/z calcd. for $C_{18}H_{23}O_2$ $[M+H]^+$ 271.1698; found 271.1695.

Homodimer of isobutyl vinyl ketone was obtained as a minor product (12.0 mg, 0.054 mmol, 18%). For data please see **3ae'**.

Compound 3ma Following general procedure, **3ma** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a colourless solid (38 mg, 0.19 mmol, 65%). **IR** (neat): ν_{max}/cm^{-1} 2969, 2934, 2880, 1746, 1680, 1589, 1472, 1410, 1382, 1362, 1232, 1209, 1145, 1136, 1074, 889, 728. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (dd, *J* = 15.5, 11.3 Hz, 1H), 7.03 (d, *J* = 11.3 Hz, 1H), 6.42 (d, *J* = 15.5 Hz, 1H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.33 (s, 3H), 2.02 (s, 3H), 1.60 – 1.58 (m, 2H), 1.34 – 1.32 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.81, 198.04, 143.83, 137.46, 135.14, 134.16, 37.67, 28.10, 26.73, 22.50, 14.00, 12.64. **HRMS**(ESI-TOF) m/z calcd. for $C_{12}H_{19}O_2$ $[M+H]^+$ 195.1385; found 195.1383.

Compound 3mc Following general procedure, **3mc** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a colourless solid (45 mg, 0.20 mmol, 67%). **IR** (neat): ν_{max}/cm^{-1} 2960, 2932, 2874, 1711, 1690, 1614, 1463, 1409, 1367, 1259, 1210, 1176, 1126, 1094, 906, 732. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 15.3, 11.4 Hz, 1H), 7.02 (d, *J* = 11.4 Hz, 1H), 6.45 (d, *J* = 15.4 Hz, 1H), 2.72 (t, *J* = 7.3 Hz, 2H), 2.58 (t, *J* = 7.3 Hz, 2H), 2.01 (s, 3H), 1.70 – 1.65 (m, 2H), 1.60 – 1.56 (m, 2H), 1.36 – 1.31 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.87, 200.26, 143.70, 136.50, 134.44, 134.32, 43.40, 37.66, 26.75, 22.51, 17.64, 13.99, 13.82, 12.61. **HRMS**(ESI-TOF) m/z calcd. for $C_{14}H_{23}O_2$ $[M+H]^+$ 223.1698; found 223.1695.

Compound 3me Following general procedure, **3me** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a colourless solid (45 mg, 0.19 mmol, 64%). **IR** (neat): ν_{max}/cm^{-1} 2956,

2941, 2869, 1721, 1695, 1611, 1436, 1421, 1376, 1262, 1205, 1167, 1160, 1001, 896, 726. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 15.3, 11.4 Hz, 1H), 7.02 (d, *J* = 11.4 Hz, 1H), 6.45 (d, *J* = 15.3 Hz, 1H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.47 (d, *J* = 6.9 Hz, 2H), 2.19 – 2.16 (m, 1H), 2.02 (s, 3H), 1.63 – 1.59 (m, 2H), 1.37 – 1.33 (m, 2H), 0.96 (d, *J* = 6.6 Hz, 6H), 0.92 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.86, 200.06, 143.78, 136.55, 134.70, 134.31, 50.53, 37.66, 32.00, 26.75, 25.18, 22.62, 22.52, 13.99, 12.63. **HRMS**(ESI-TOF) m/z calcd. for $C_{15}H_{25}O_2$ $[M+H]^+$ 237.1855; found 237.1859.

Compound 3mf Following general procedure, **3mf** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a colourless solid (41 mg, 0.15 mmol, 52%). **IR** (neat): ν_{max}/cm^{-1} 2958, 2932, 2870, 1723, 1636, 1610, 1447, 1423, 1373, 1260, 1208, 1170, 1165, 1009, 816, 723. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 15.4, 11.4 Hz, 1H), 7.03 (d, *J* = 11.4 Hz, 1H), 6.45 (d, *J* = 15.3 Hz, 1H), 2.72 (t, *J* = 7.4 Hz, 2H), 2.59 (t, *J* = 7.4 Hz, 2H), 2.01 (s, 3H), 1.62 (dq, *J* = 22.8, 7.5 Hz, 6H), 1.35 – 1.29 (m, 6H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 201.83 (s), 200.36, 143.70, 136.47, 134.42, 134.30, 41.58, 37.66, 31.67, 29.00, 26.76, 24.19, 22.56, 22.51, 14.09, 13.98, 12.61. **HRMS**(ESI-TOF) m/z calcd. for $C_{17}H_{29}O_2$ $[M+H]^+$ 265.2168; found 265.2169.

Compound 3ni Following general procedure, **3ni** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a viscous liquid (90 mg, 0.12 mmol, 61%). R_f = 0.45 (EtOAc-Hexane 2:8). **IR** (neat): V_{max}/cm^{-1}: 3088, 3064, 3031, 2924, 2858, 1952, 1722, 1659, 1496, 1454, 1364, 1270, 1204, 1093, 1028. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32-7.20 (m, 25H), 6.82 (dt, *J* = 15.5, 6.5 Hz, 1H), 5.71 (dt, *J* = 15.5, 1.5 Hz, 1H), 4.69 (d, *J* = 3.0 Hz, 1H), 4.67 (d, *J* = 4.0 Hz, 1H), 4.63-4.58 (m, 2H), 4.56-4.54 (m, 2H), 4.48 (d, *J* = 3.0 Hz, 2H), 4.30 (d, *J* = 2.0 Hz, 2H), 4.09-4.07 (m, 1H), 4.05 (d, *J* = 4.5 Hz, 1H), 3.97 (t, *J* = 4.5 Hz, 1H), 3.89 (dd, *J* = 9.5, 4.5 Hz, 1H), 3.85 (dd, *J* = 10.0, 4.5 Hz, 1H), 3.69-3.66 (m, 4H), 2.65 (dt, *J* = 12.5, 7.0 Hz, 2H), 2.26 (dd, *J* = 14.5, 7.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.2, 166.8, 147.9, 138.6, 138.1, 137.2, 128.4, 128.3, 128.2, 127.8, 127.7, 127.7, 127.6, 127.5, 127.4, 121.3, 84.5, 80.7, 79.3, 78.4, 74.7, 74.6, 73.3, 72.2, 71.7, 69.3, 51.3, 38.4, 25.4. **HRMS**(ESI-TOF) m/z calcd. for $C_{47}H_{50}O_8Na$ $[M+Na]^+$: 765.3403; found 765.3409.

Compound 3oi Following general procedure, **3oi** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a viscous liquid (93 mg, 0.12 mmol, 63%). R_f = 0.45 (EtOAc-Hexane 2:8). **IR** (neat): V_{max}/cm^{-1}: 3088, 3064, 3031, 2923, 2853, 1721, 1665, 1453, 1360, 1261, 1210, 1098. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32-7.23 (m, 23H), 7.16-7.15 (m, 2H), 6.73 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.63 (dt, *J* = 15.5, 1.0 Hz, 1H), 4.68-4.66 (m, 2H), 4.61 (d, *J* = 12.5 Hz, 3H), 4.49 (s, 2H), 4.46 (d, *J* = 3.0 Hz, 1H), 4.43 (d, *J* = 3.5 Hz, 1H), 4.37 (d, *J* = 12.0 Hz, 1H), 4.02 (s, 3H), 3.86 (dd, *J* = 10.5, 4.0 Hz, 1H), 3.74-3.64 (m, 5H), 2.40-2.31 (m, 2H), 2.16-2.04 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 208.6, 166.8, 147.9, 138.1, 137.2, 128.4, 128.3, 128.3, 128.1, 127.8, 127.7, 127.5, 127.5, 127.4, 121.2, 83.7, 80.6, 79.1, 78.2, 74.6, 74.2, 73.3, 71.9, 69.2, 51.3, 37.8, 25.4. **HRMS**(ESI-TOF) m/z calcd. for $C_{47}H_{50}O_8Na$ $[M+Na]^+$: 765.3403; found 765.3408.

Compound 3oj Following general procedure, **3oj** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a viscous liquid (102 mg, 0.13 mmol, 65%). R_f = 0.45 (EtOAc-Hexane 2:8). **IR** (neat): V_{max}/cm^{-1}: 3087, 3061, 3028, 2924, 1718, 1663, 1453, 1275, 1260, 1098. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.18 (m, 23H), 7.15-7.14 (m, 2H), 6.71 (dt, *J* = 15.6, 6.8 Hz, 1H), 5.62 (dt, *J* = 15.6, 1.6 Hz, 1H), 4.68 – 4.65 (m, 2H), 4.61 (d, *J* = 11.6 Hz, 3H), 4.49 (s, 2H), 4.45 (d, *J* = 2.8 Hz, 1H), 4.42 (d, *J* = 2.8 Hz, 1H), 4.36 (d, *J* = 12.0 Hz, 1H), 4.10 (t, *J* = 6.8 Hz, 2H), 4.01 (d, *J* = 1.6 Hz, 3H), 3.85 (dd, *J* = 10.4, 4.0 Hz, 1H), 3.74-3.71 (m, 1H), 3.65 (dd, *J* = 10.0, 4.8 Hz, 1H), 2.40-2.34 (m, 2H), 2.140 – 2.03 (m, 2H), 1.66-1.59 (m, 2H), 1.41-1.36 (m, 2H), 0.93 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 208.6, 166.5, 153.5, 147.5, 138.8, 138.4, 138.1, 137.9, 137.2, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.6, 127.5, 127.4, 121.6, 83.8, 80.6, 79.2, 78.3, 74.6, 74.2, 73.4, 71.9, 69.3, 64.0, 37.9, 30.7, 25.4, 19.1, 13.7. **HRMS**(ESI-TOF) m/z calcd. for $C_{50}H_{56}O_8Na$ $[M+Na]^+$: 807.3873; found 807.3869.

Compound 3ok Following general procedure, 3**ok** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a viscous liquid (94 mg, 0.12 mmol, 60%). R_f = 0.45 (EtOAc-Hexane 2:8). **IR** (neat): V_{max}/cm^{-1}: 3444, 3089, 3064, 2959, 2925, 2872, 1722, 1652, 1496, 1454, 1315, 1266, 1207, 1095, 1027. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31-7.25 (m, 23H), 7.17-7.16 (m, 2H), 6.73 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.64 (dd, *J* = 15.5, 1.0 Hz, 1H), 4.69 (s, 2H), 4.67 (m, 1H), 4.61 (s, 1H), 4.50 (s, 2H), 4.50 (s, 2H), 4.46 (d, *J* = 2.0 Hz, 1H), 4.44 (d, *J* = 2.5 Hz, 1H), 4.37 (d, *J* = 12.0 Hz, 1H), 4.03 – 4.02 (m, 3H), 3.91 (d, *J* = 1.0 Hz, 1H), 3.90 (d, *J* = 1.0 Hz, 1H), 3.87 (dd, *J* = 10.0, 4.0 Hz, 1H), 3.75-3.74 (m, 1H), 3.67 (dd, *J* = 10.0, 5.0 Hz, 1H), 2.42-2.36 (m, 2H), 2.17-2.04 (m, 2H), 1.96 (dt, *J* = 13.5, 6.5 Hz, 1H), 0.96 (dd, *J* = 7.0, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 208.6, 166.5, 147.5, 138.5, 138.4, 138.1, 137.9, 137.2, 128.5, 128.4, 128.3, 128.1, 127.9, 127.8, 127.7, 127.5, 127.5, 127.3, 126.9, 121.6, 83.8, 80.6, 79.2, 78.3, 74.6, 74.2, 73.3, 71.9, 70.3, 69.2, 65.3, 37.8, 27.7, 25.4, 19.1. **HRMS**(ESI-TOF) m/z calcd. for $C_{50}H_{56}O_8Na$ $[M+Na]^+$: 807.3873; found 807.3870.

Compound 3ol Following general procedure, **3ol** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a viscous liquid (89 mg, 0.11 mmol, 55%). R_f = 0.45 (EtOAc-Hexane 2:8). **IR** (neat): V_{max}/cm^{-1}: 3421, 3031, 3063, 2923, 2853, 1715, 1653, 1496, 1453, 1362, 1262, 1177, 1094, 1026; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35-7.28 (m, 23H), 7.16 (dd, *J* = 7.0, 2.0 Hz, 2H), 6.71 (dt, *J* = 15.5, 7.0 Hz, 1H), 5.61 (d, *J* = 15.5 Hz, 1H), 4.81-4.77 (m, 1H), 4.68 (d, *J* = 2.0 Hz, 1H), 4.66 (d, *J* = 2.5 Hz, 1H), 4.61 (dd, *J* = 12.0, 3.0 Hz, 3H), 4.49 (s, 2H), 4.46 (d, *J* = 5.0 Hz, 1H), 4.44 (d, *J* = 5.0 Hz, 1H), 4.36 (d, *J* = 12.0 Hz, 1H), 4.02 (d, *J* = 3.5 Hz, 3H), 3.86 (dd, *J* = 10.0, 4.0 Hz, 1H), 3.78-3.72 (m, 1H), 3.66 (dd, *J* = 10.0, 5.0 Hz, 1H), 2.41-2.35 (m, 2H), 2.14-2.07 (m, 2H), 1.87-1.85 (m, 2H), 1.74-1.2 (m, 2H), 1.59-1.54 (d, 2H), 1.44-1.34 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 208.6, 165.9, 147.1, 128.4, 128.3, 128.1, 127.9, 127.9, 127.7, 127.5, 127.5, 127.4, 122.2, 83.8, 80.5, 79.2, 78.3, 74.6, 74.2, 73.3, 72.3, 71.9, 69.2, 37.8, 31.6, 25.3, 23.7. **HRMS**(ESI-TOF) m/z calcd. for $C_{52}H_{58}O_8Na$ $[M+Na]^+$: 833.4029; found 833.4039.

4. Synthesis of bioactive natural products 4, 5, 6 and 7

Compound 4 Following general procedure, **4** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a white solid (48 mg, 0.14 mmol, 48%). **IR** (neat): ν_{max}/cm^{-1} 2954, 2918, 2850, 1706, 1678, 1586, 1469, 1406, 1373, 1245, 1216, 1077, 718. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 – 7.11 (m, 2H), 6.53 – 6.39 (m, 2H), 2.57 (t, *J* = 7.4 Hz, 4H), 1.66 – 1.59 (m, 6H), 1.32 – 1.25 (m, 16H), 0.88 (t, *J* = 7.3 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.24 (2C), 138.91 (2C), 136.06 (2C), 41.43, 41.38, 31.96, 31.46, 29.63, 29.54, 29.48, 29.38(2C), 29.30, 24.12, 23.80, 22.77, 22.64, 14.09, 13.99. **HRMS**(ESI-TOF) m/z calcd. for $C_{22}H_{39}O_2$ $[M+H]^+$ 335.2950; found 335.2958.

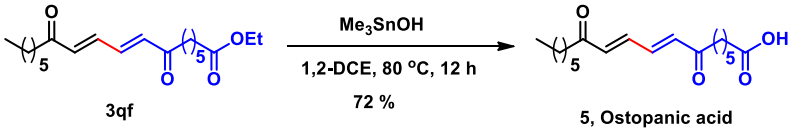
Following general procedure, **3gn'** was obtained as a yellowish solid (7.5:2.5:hexane:EtOAc) (7 mg, 0.03 mmol, 10%); **IR** (neat): ν_{max}/cm^{-1} 2955, 2926, 2854, 1742, 1714, 1677, 1588, 1466, 1406, 1374, 1240, 1130, 1078, 1009, 721; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 – 7.11 (m, 2H), 6.55 – 6.38 (m, 2H), 2.59 (t, *J* = 7.3 Hz, 4H), 1.63 (m, 4H), 1.31 – 1.27 (m, 8H), 0.89 (t, *J* = 6.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.24 (2C), 138.91 (2C), 136.06 (2C), 41.43 (2C), 31.96 (2C), 24.12 (2C), 22.75 (2C), 14.19 (2C); **HRMS** m/z calcd for $C_{16}H_{27}O_2$ $[M+H]^+$ 251.2011; found 251.2010.

Note: When reaction was carried out in 0.3 mmol scale, we didn't get pure ^{1}H NMR spectrum of homodimer of decyl vinyl ketone. So we repeated same reaction in 3 batches (0.3 mmol × 3), combined and purified to get pure spectra. homodimer of decyl vinyl ketone was obtained as a colourless solid, please see **3gg'** for data (7.5:2.5:hexane:EtOAc). Yield was calculated w.r.t. one batch (7 mg, 0.018 mmol, 6%). Overall yield from three batches (0.3 * 3) = 21 mg, 0.054 mmol, 6%. **IR** (neat): ν_{max}/cm^{-1} 2953, 2918, 2850, 1677, 1586, 1470, 1405, 1371, 1313, 1244, 1218, 1131, 1100, 906, 853, 750; **^{1}H NMR** (400 MHz,$CDCl_3$) δ 7.21 – 7.11 (m, 2H), 6.53 – 6.41 (m, 2H), 2.60 (t, *J* = 6.8 Hz, 4H), 1.65– 1.58 (m, 4H), 1.27– 6.4 (m, 28H), 0.86 (t, *J* = 6.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.24 (2C), 138.91 (2C), 136.06 (2C), 41.43 (2C), 31.96 (2C), 29.63 (2C), 29.54 (2C), 29.48 (2C), 29.38 (2C), 29.30 (2C), 24.12 (2C), 22.75 (2C), 14.19 (2C); **HRMS** m/z calcd for $C_{26}H_{47}O_2$ $[M+H]^+$ 391.3576; found 391.3572.

Compound 3qf Following general procedure, **3qf** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a brownish solid (52 mg, 0.15 mmol, 52%). **IR** (neat): ν_{max}/cm^{-1} 3354, 3047, 2928, 2866, 1729, 1680, 1579, 1467, 1421, 1366, 1344, 1241, 1215, 1173, 1107, 1078, 848, 723. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 – 7.11 (m, 2H), 6.53 – 6.41 (m, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.58 (m, 4H), 2.29 (t, *J* = 7.4 Hz, 2H), 1.65 – 1.60 (m, 6H), 1.37 – 1.25 (m, 11H), 0.87 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 200.19, 199.78, 173.72, 139.02, 138.81, 136.15, 135.95, 60.34, 41.44, 41.05, 34.18, 31.65, 28.96, 28.70, 24.75, 24.07, 23.61, 22.56, 14.32, 14.10. **HRMS**(ESI-TOF) m/z calcd. for $C_{20}H_{33}O_4$ $[M+H]^+$ 337.2379; found 337.2377.

Homodimer of hexyl vinyl ketone was obtained as a minor product (12 mg, 0.042 mmol, 14%). For data please see **3af'**.

Synthesis of Ostopanic Acid, 5

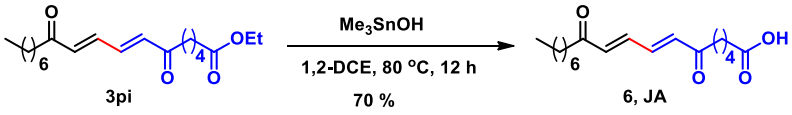


To a magnetically stirred solution of ester **3qf** (40 mg, 0.12 mmol) in 1,2-dichloroethane (3 mL) was added Me_3SnOH (216 mg, 1.2 mmol) and the reaction mixture was stirred at 80 °C for 12 h. The solvent was removed by rotary evaporation and the mixture was diluted with EtOAc. Water (5 mL) was poured into mixture and the phases were separated and extracted with EtOAc (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, evaporation of the solvent and purification of the residue on silica gel column chromatography using 40% EtOAc-hexane as an eluent furnished **ostopanic acid** (**5**) (27 mg, 72%) as a white solid. R_f = 0.60 (EtOAc-hexane 3:7). **IR** (neat): ν_{max}/cm^{-1} 2925, 2854, 1708, 1679, 1465, 1404, 1367, 1254, 1128, 1107, 1078, 957, 722. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.21 – 7.11 (m, 2H), 6.52 – 6.42 (m, 2H), 2.59 (t, *J* = 7.1 Hz, 2H), 2.57 (t, *J* = 7.3 Hz, 2H),2.34 (t, *J* = 7.5 Hz, 2H), 1.67 – 1.59 (m, 6H), 1.39 – 1.28 (m, 8H), 0.86 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 200.21, 199.73, 177.83, 139.07, 138.80, 136.17, 135.92, 41.44, 40.99, 33.52, 31.65, 28.96, 28.54, 24.49, 24.07, 23.56, 22.56, 14.09. **HRMS**(ESI-TOF) m/z calcd. for $C_{18}H_{28}O_4Na$ $[M+Na]^+$: 331.1885; found 331.1889.

Compound 3gm Following general procedure, **3gm** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a yellowish solid (50 mg, 0.15 mmol, 50%). **IR** (neat): ν_{max}/cm^{-1} 3358, 2953, 2928, 2855, 1732, 1677, 1586, 1466, 1406, 1374, 1271, 1251, 1129, 1105, 1087, 862, 838. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.22 – 7.10 (m, 2H), 6.55 – 6.36 (m, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 2.64 – 2.54 (m, 4H), 2.31 (t, *J* = 5.7 Hz, 2H), 1.67 – 1.61 (m, 6H), 1.65 – 1.21 (m, 11H), 0.85 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.24, 199.50, 173.49, 139.14, 138.80, 136.20, 135.87, 60.43, 41.43, 40.87, 34.12, 31.73, 29.19, 24.50, 24.10, 23.96, 23.54, 23.03, 14.22, 14.13. **HRMS**(ESI-TOF) m/z calcd. for $C_{20}H_{33}O_4$ $[M+H]^+$ 337.2379; found 337.2376.

Following general procedure, **3gm'** was obtained as a colourless solid (7.5:2.5:hexane:EtOAc) (11 mg, 0.036 mmol, 12%); **IR** (neat): ν_{max}/cm^{-1} 3355, 3047, 2953, 2954, 2887, 2855, 1714, 1677, 1585, 1469, 1405, 1372, 1323, 1265, 1229, 1130, 1088, 1058, 801, 738. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 – 7.10 (m, 2H), 6.53 – 6.39 (m, 2H), 2.62 (t, *J* = 6.8 Hz, 4H), 1.63 – 7.10 (m, 4H), 1.30 – 1.24 (m, 16H), 0.86 (t, *J* = 6.9 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.23 (2C), 138.90 (2C), 136.05 (2C), 41.42 (2C), 31.73 (2C), 29.19 (2C), 29.19 (2C), 24.12 (2C), 22.67 (2C), 14.14 (2C); **HRMS** m/z calcd. for $C_{20}H_{35}O_2$ $[M+H]^+$ 307.2637; found 307.2628.

Synthesis of JA, 6



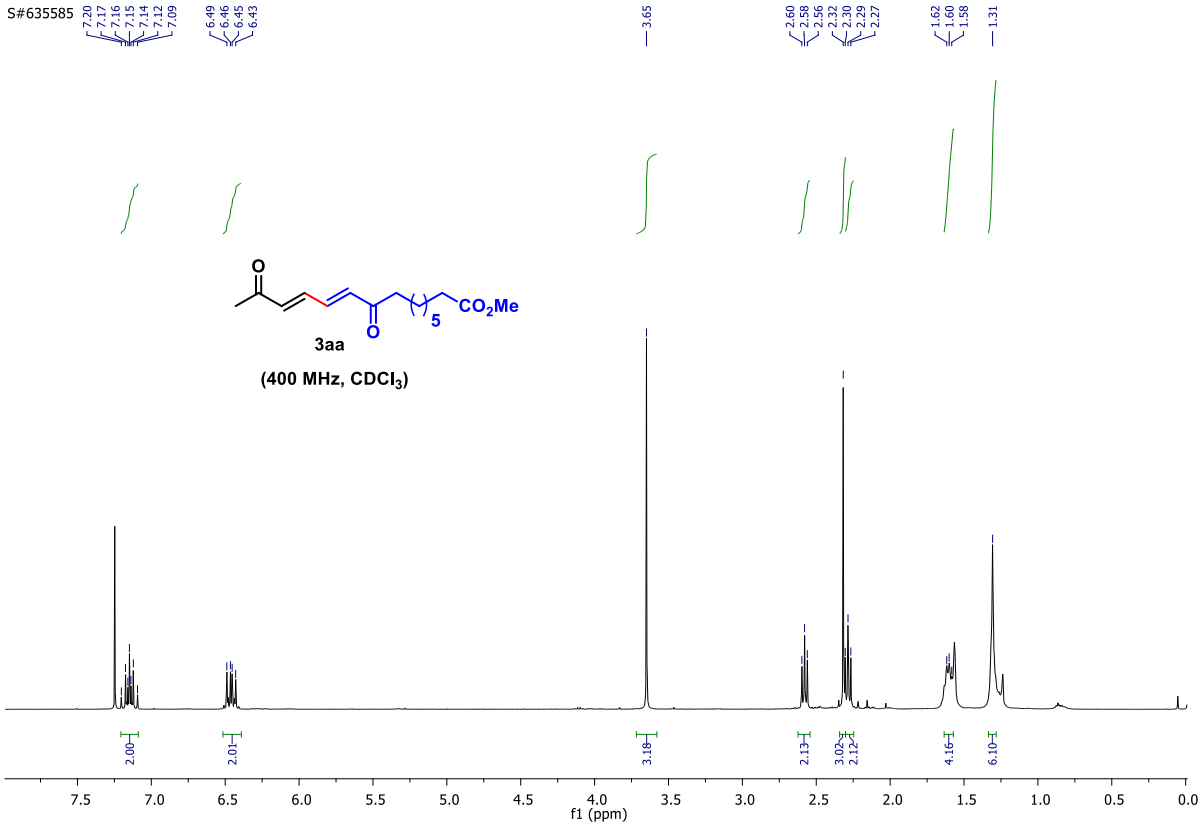
To a magnetically stirred solution of ester **3gm** (40 mg, 0.11 mmol) in 1,2-dichloroethane (3 mL) was added Me_3SnOH (207 mg, 1.18 mmol) and the reaction mixture was stirred at 80 °C for 12 h. The solvent was removed by rotary evaporation and the mixture was diluted with EtOAc. Water (5 mL) was poured into mixture and the phases were separated and extracted with EtOAc (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, evaporation of the solvent and purification of the residue on silica gel column chromatography using 40% EtOAc-hexane as eluent furnished **JA** (**6**) (24 mg, 70%) as a white solid. R_f = 0.60 (EtOAc-hexane 3:7). **IR** (neat): ν_{max}/cm^{-1} 3046, 2925, 2854, 1708, 1680, 1580, 1464, 1404, 1376, 1313, 1266, 1128, 1104, 1083, 953, 723. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.21 – 7.11 (m, 2H), 6.54 – 6.41 (m, 2H), 2.60 (m, 4H), 2.37 (t, *J* = 6.9 Hz, 2H), 1.68 – 1.60 (m, 6H), 1.29 – 1.25 (m, 8H), 0.86 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 200.28, 199.41, 178.41, 139.22, 138.78, 136.25, 135.83, 41.45, 40.81, 33.65, 31.74, 29.20, 29.14, 24.26, 24.16, 23.26, 22.68, 14.15. **HRMS**(ESI-TOF) m/z calcd. for $C_{18}H_{28}O_4Na$ $[M+Na]^+$: 331.1885; found: 331.1883.

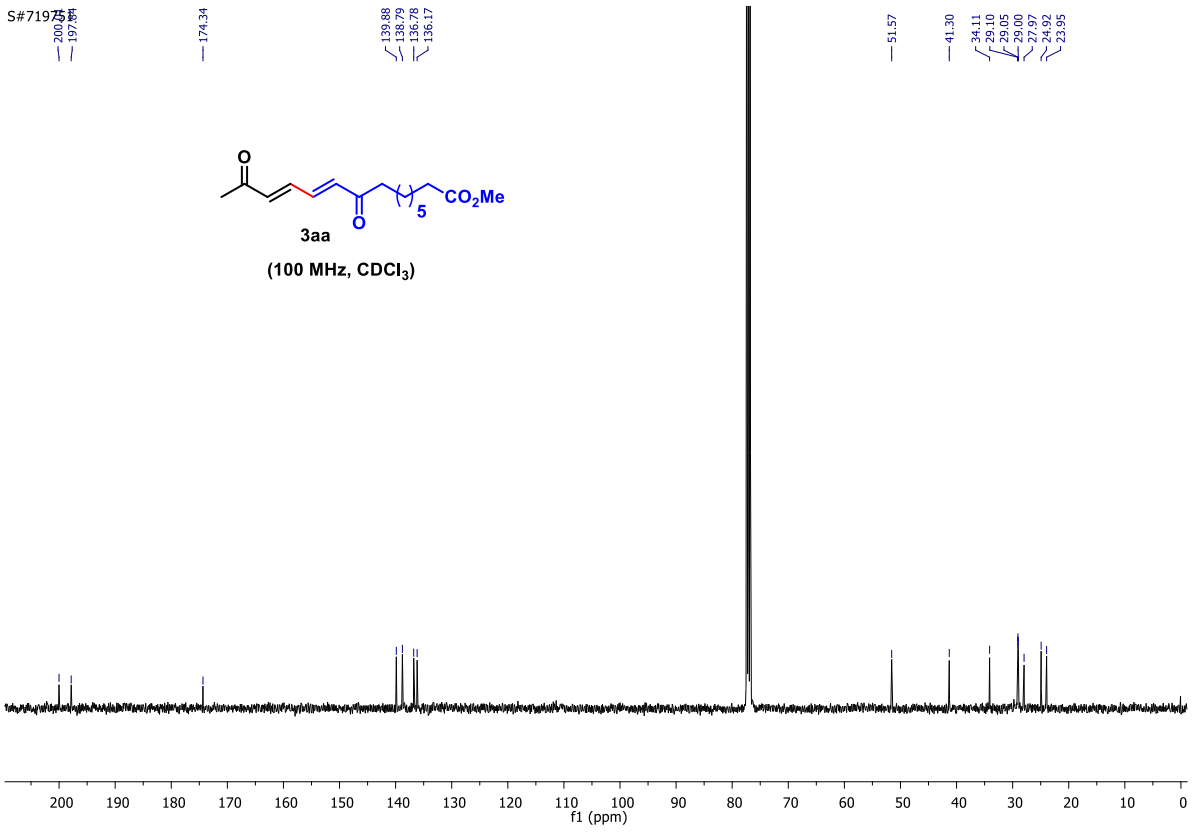
Synthesis of southern part (C1-C13) of macrolactin-T, 7

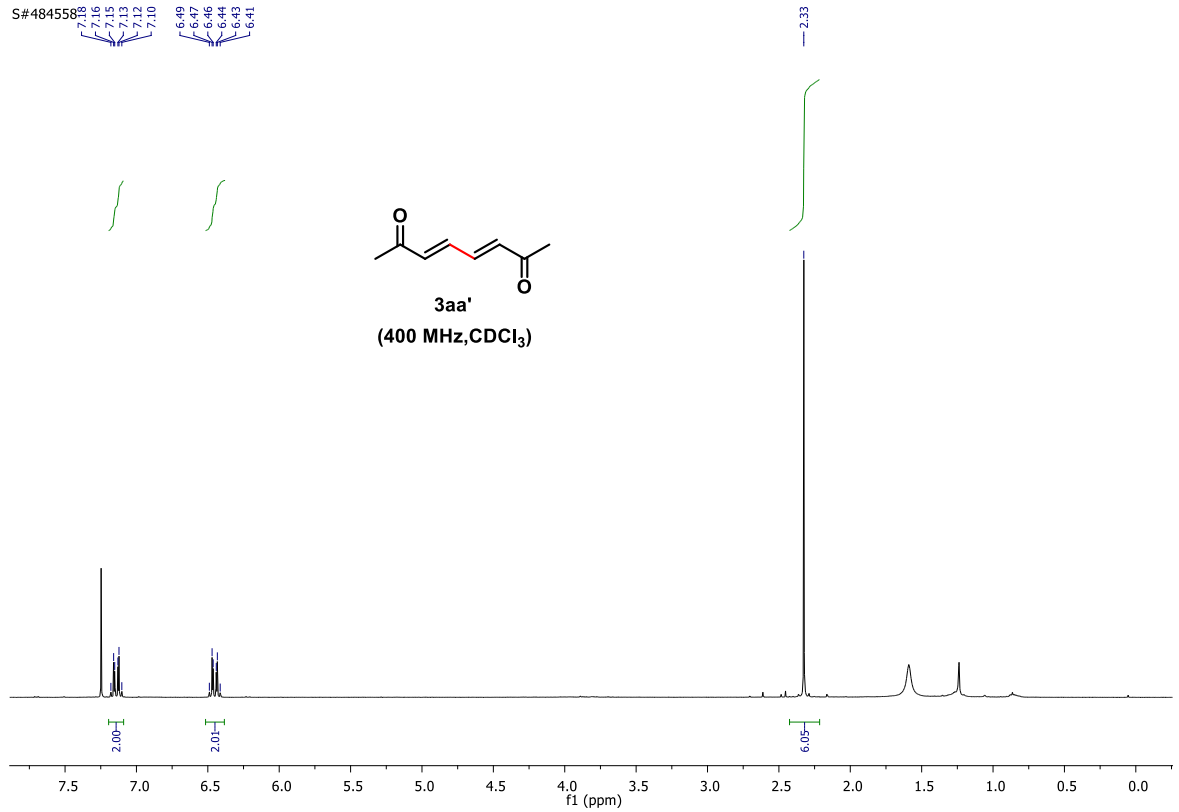
Following general procedure, **7** was purified by silica column chromatography (pet ether/EtOAc at a 8:2 ratio), obtained as a colourless solid (61 mg, 0.20 mmol, 68%). $[\alpha]_D^{28}$ = +10.0 (*c* = 0.3, $CHCl_3$). **IR** (neat): ν_{max}/cm^{-1} 3442, 3024, 2927, 2914, 2887, 1765, 1637, 1498, 1341, 1289, 1158, 1071, 954, 827, 741. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.53 (t, *J* = 8.5 Hz, *J* = 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.14 - 7.07 (m, 2H), 6.46 - 6.37 (m, 2H), 5.19 (m, 1H), 2.75 (t, *J* =6.2 Hz, 2H), 2.29 (s, 3H), 2.07 – 2.02 (m, 2H), 1.37 (d, *J* = 6.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 198.78, 197.73, 166.14, 139.62, 139.09, 136.91, 135.90, 133.04, 129.62 (3C), 128.44 (2C), 70.97, 37.26, 30.19, 27.92, 20.36. **HRMS**(ESI-TOF) m/z calcd. for $C_{18}H_{21}O_4$ $[M+H]^+$ 301.1440; found 301.1443.

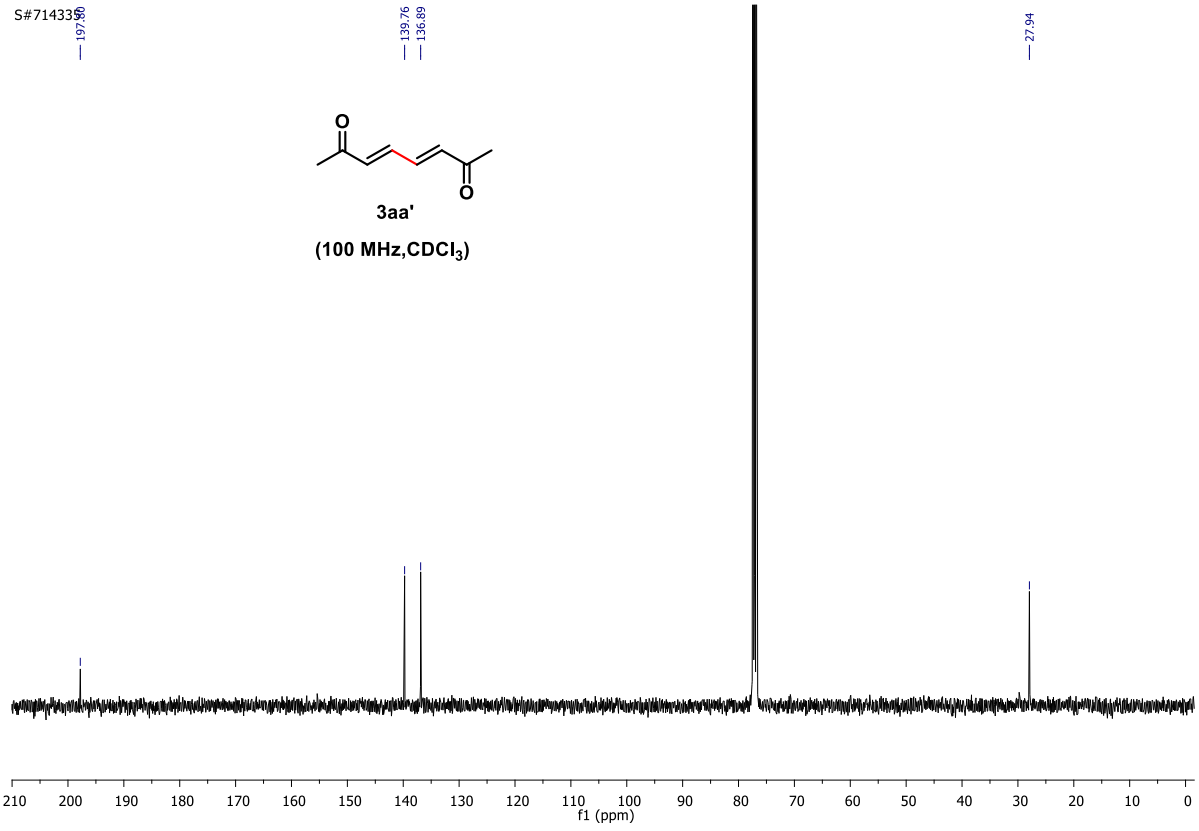
Homodimer of methyl vinyl ketone was obtained as a minor product (5.0 mg, 0.039 mmol, 13%). For data please see **3aa'**.

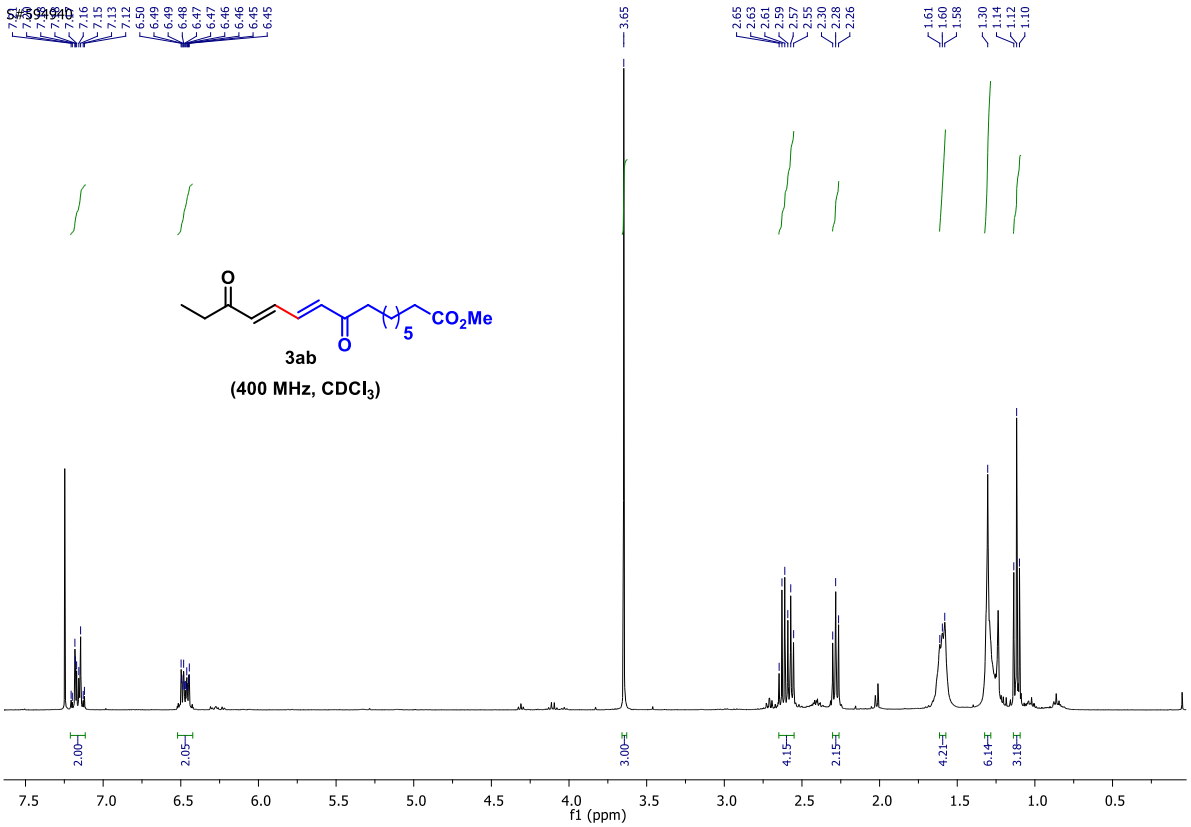
5. ^{1}H and ^{13}C NMR Spectra of Compounds 3

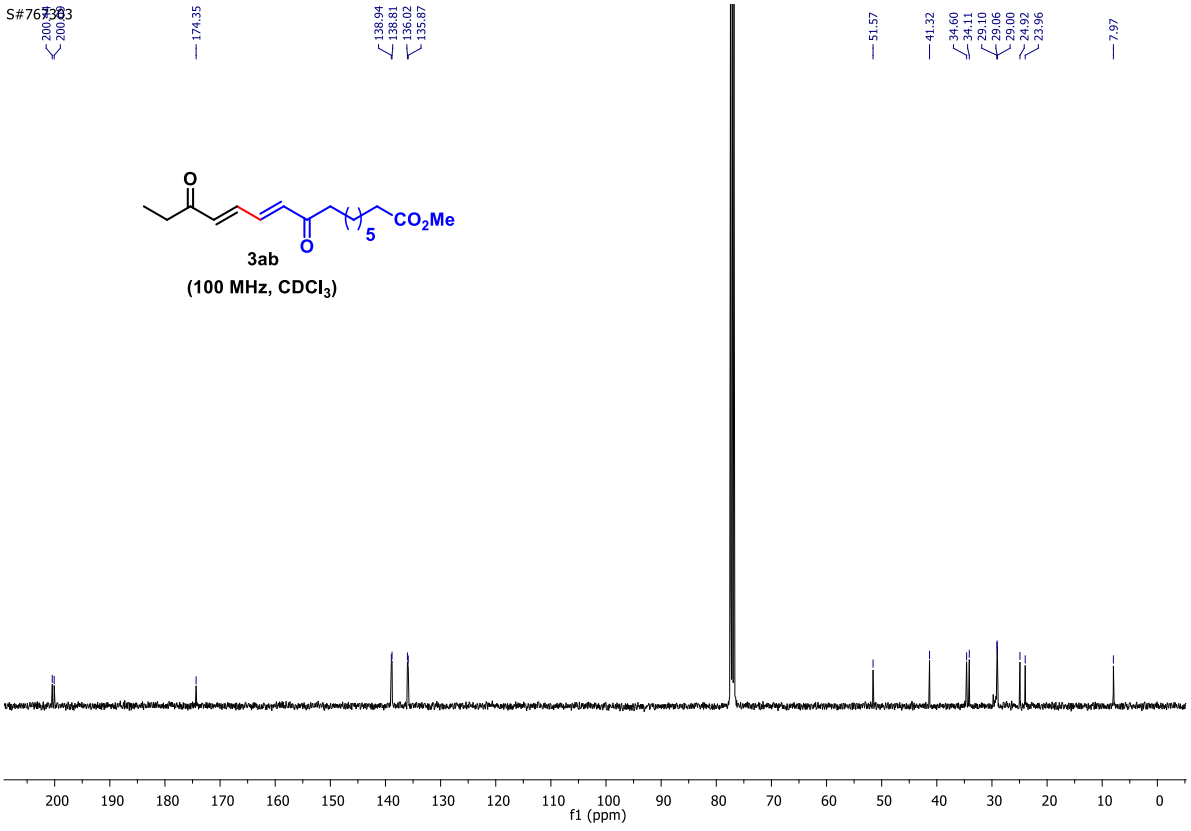




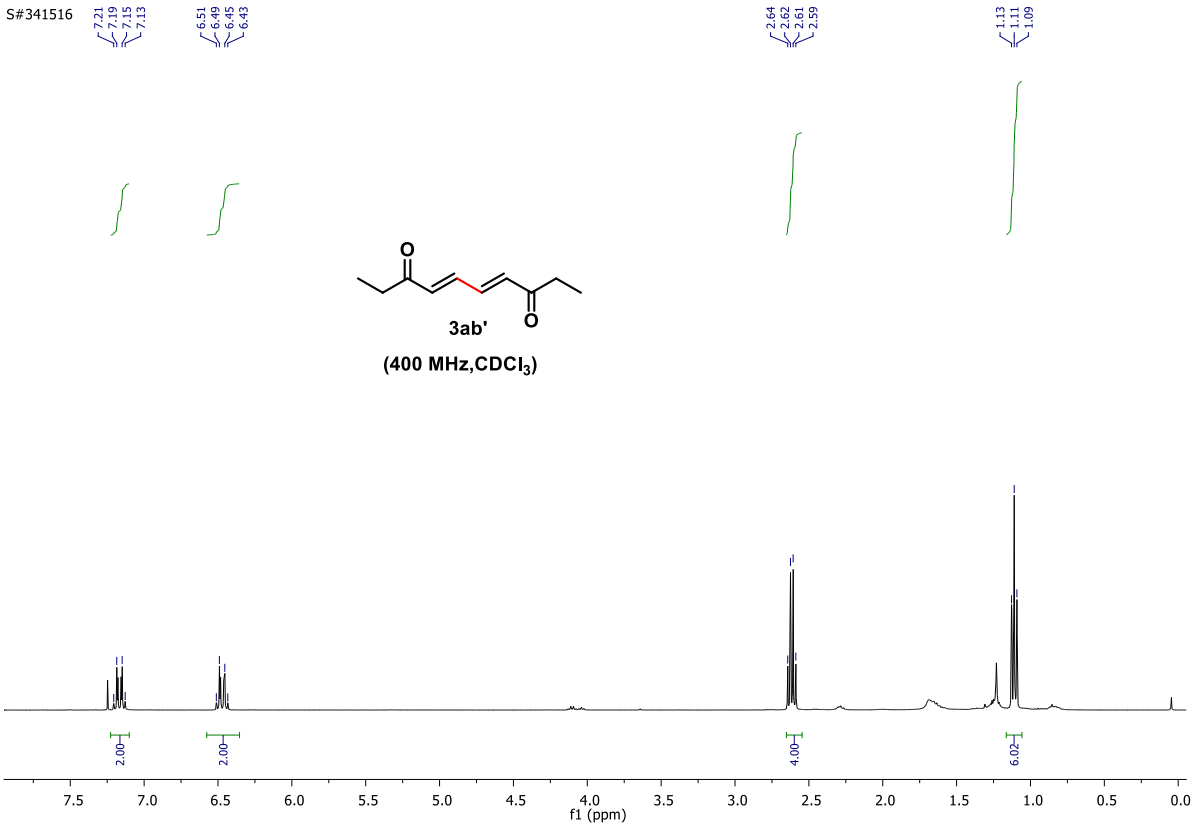

S#484558
7.18
7.16
7.15
7.13
7.12
7.10
6.49
6.47
6.46
6.44
6.43
6.41
2.33
3aa'
(400 MHz,CDCl3)
2.00
2.01
6.05
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


S#714335
197.90
139.76
136.89
27.94
3aa'
(100 MHz,CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


S#594940
3.65
2.65
2.63
2.61
2.59
2.57
2.55
2.30
2.28
2.26
1.61
1.60
1.58
1.30
1.14
1.12
1.10
O
O
5
CO2Me
3ab
(400 MHz, CDCl3)
2.00
2.05
3.00
4.15
2.15
4.21
6.14
3.18
f1 (ppm)


S#767363
200.36
200.13
174.35
138.94
138.81
136.02
135.87
51.57
41.32
34.60
34.11
29.10
29.06
29.00
24.92
23.96
7.97
O
O
5
CO2Me
3ab
(100 MHz, CDCl3)
f1 (ppm)

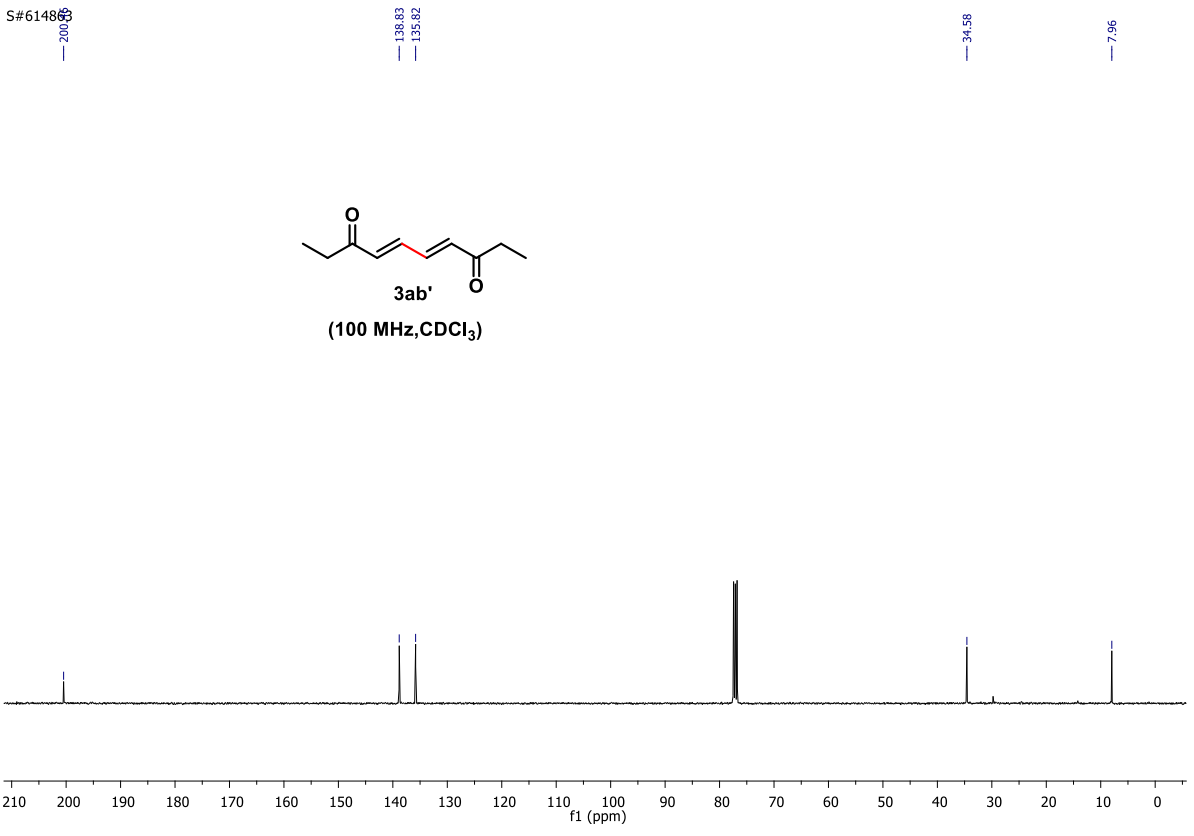
S#341516



3ab'

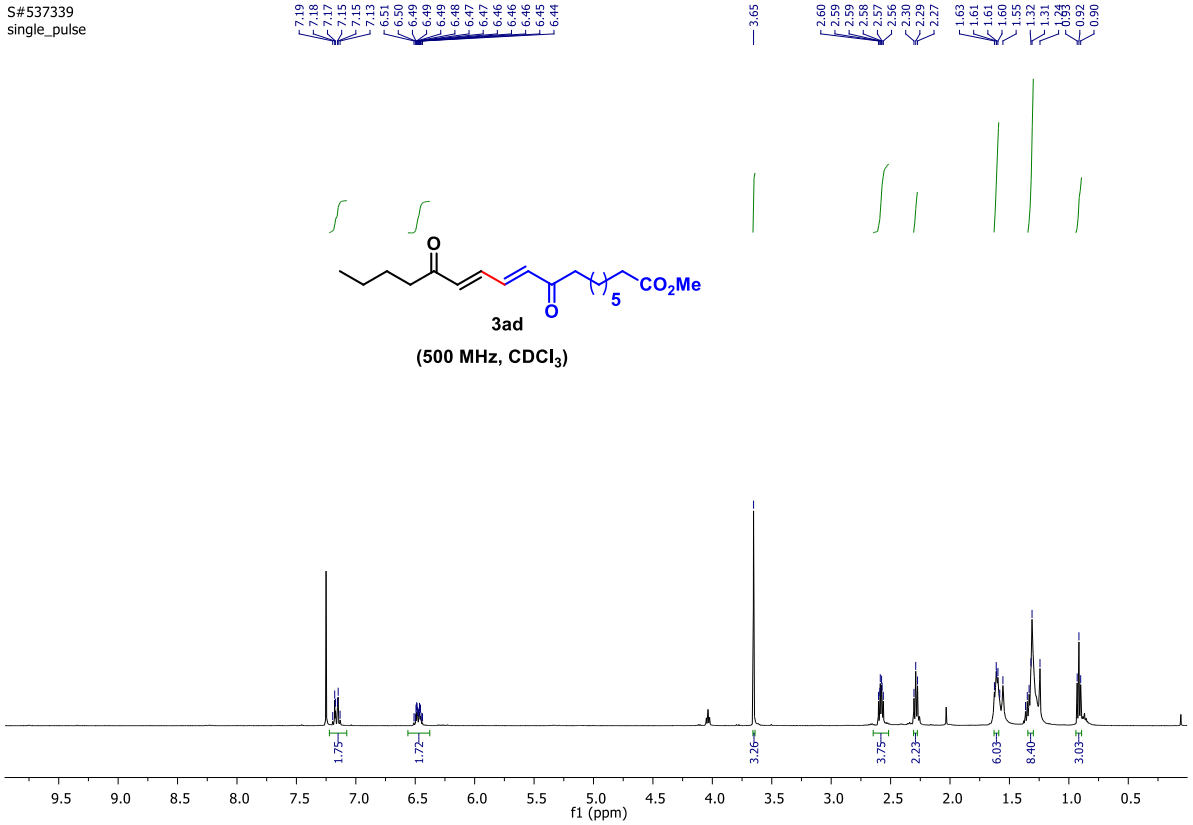
(400 MHz,$CDCl_3$)

S#614863



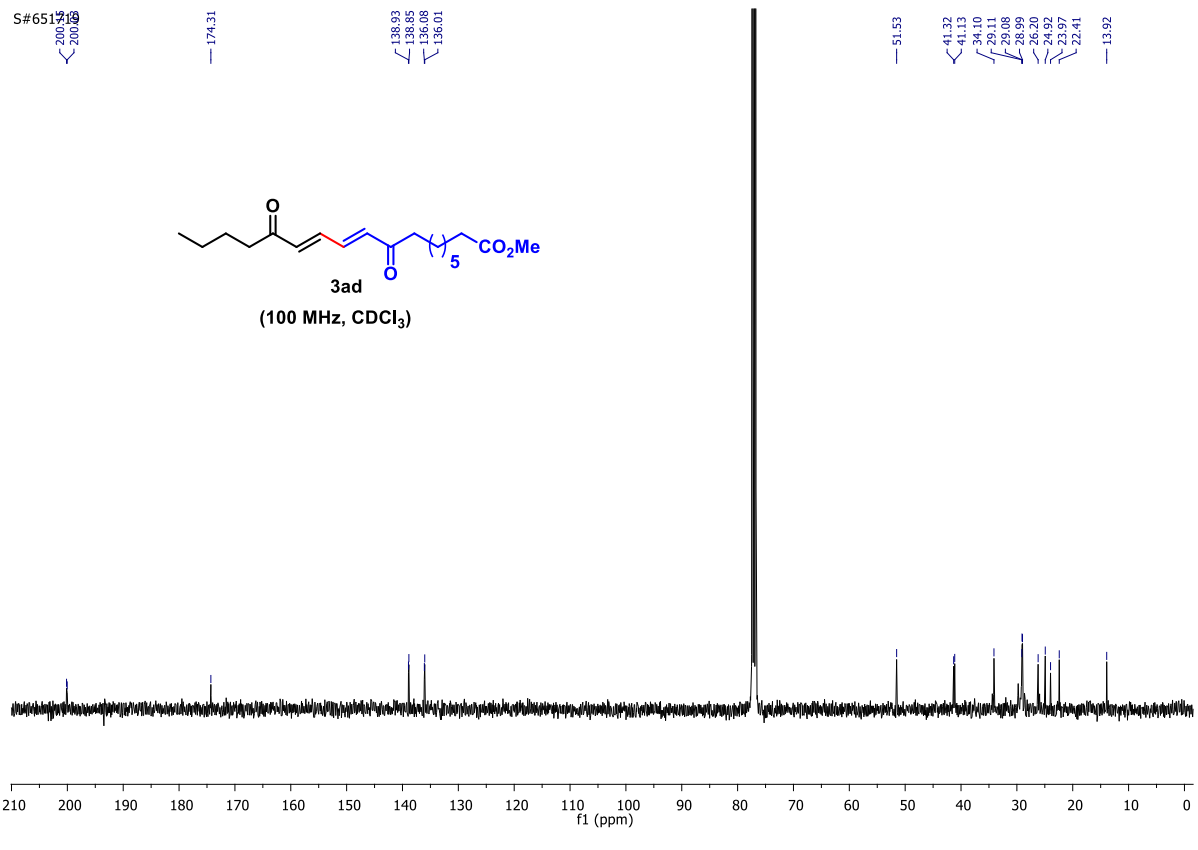
3ab'

(100 MHz,$CDCl_3$)



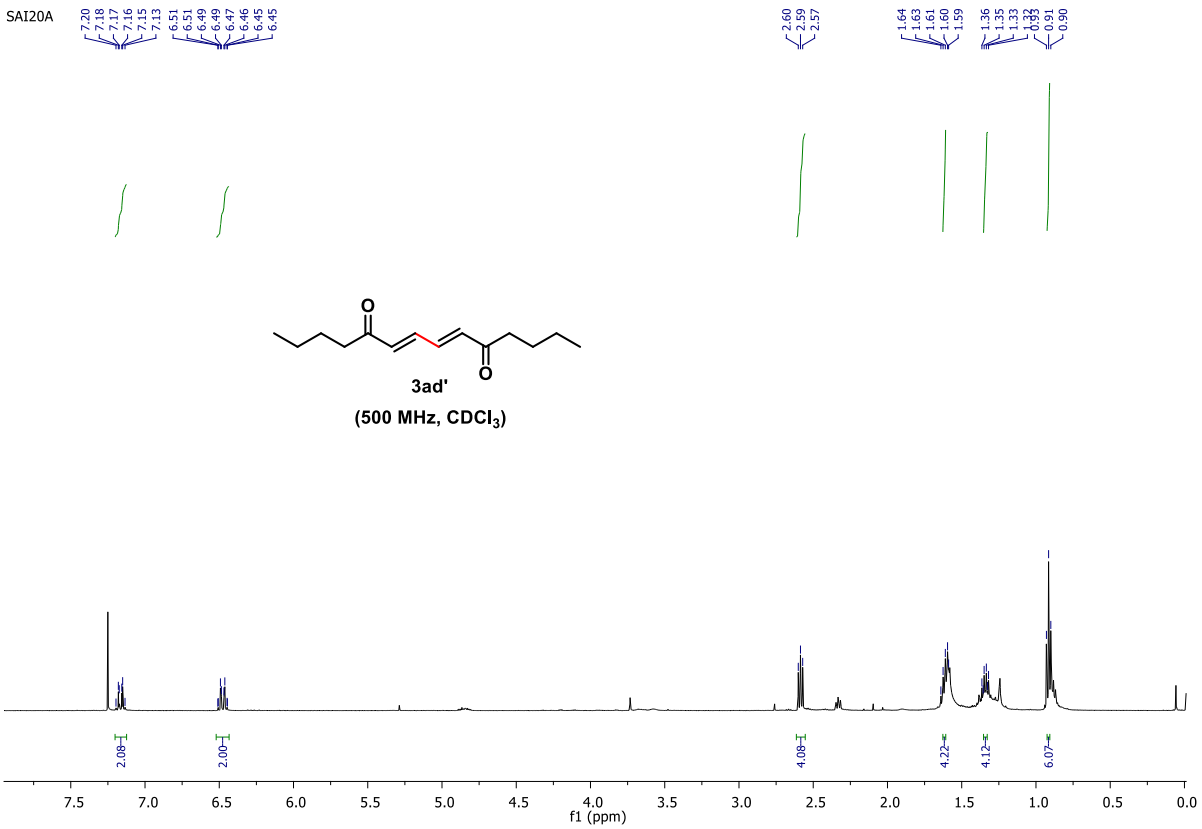
3ad

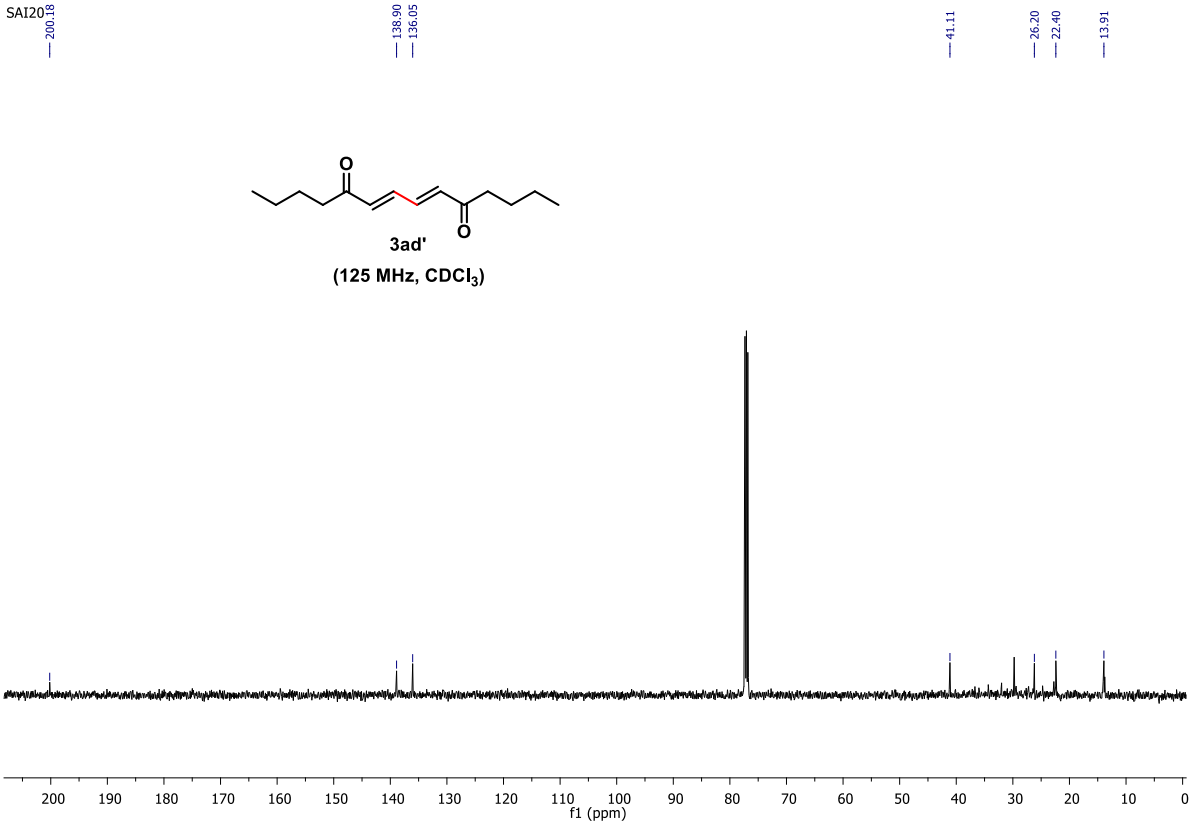
(500 MHz, $CDCl_3$)

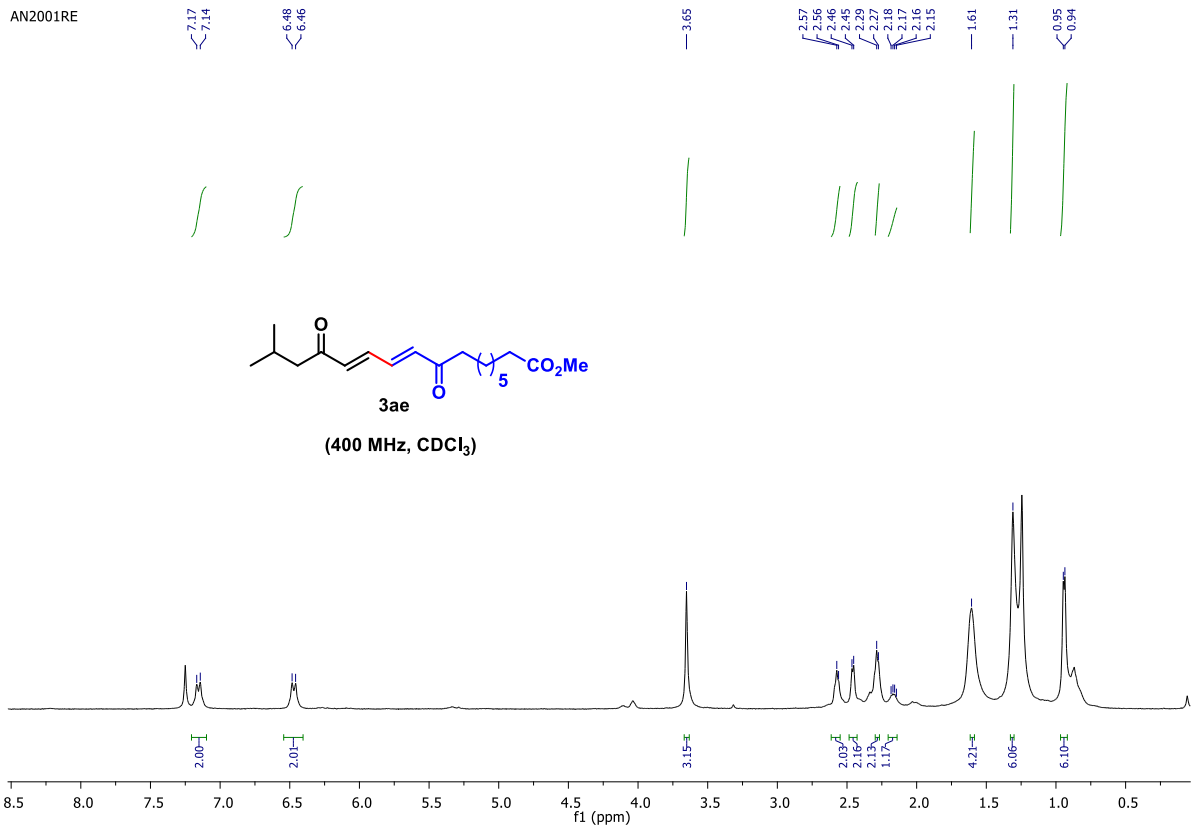


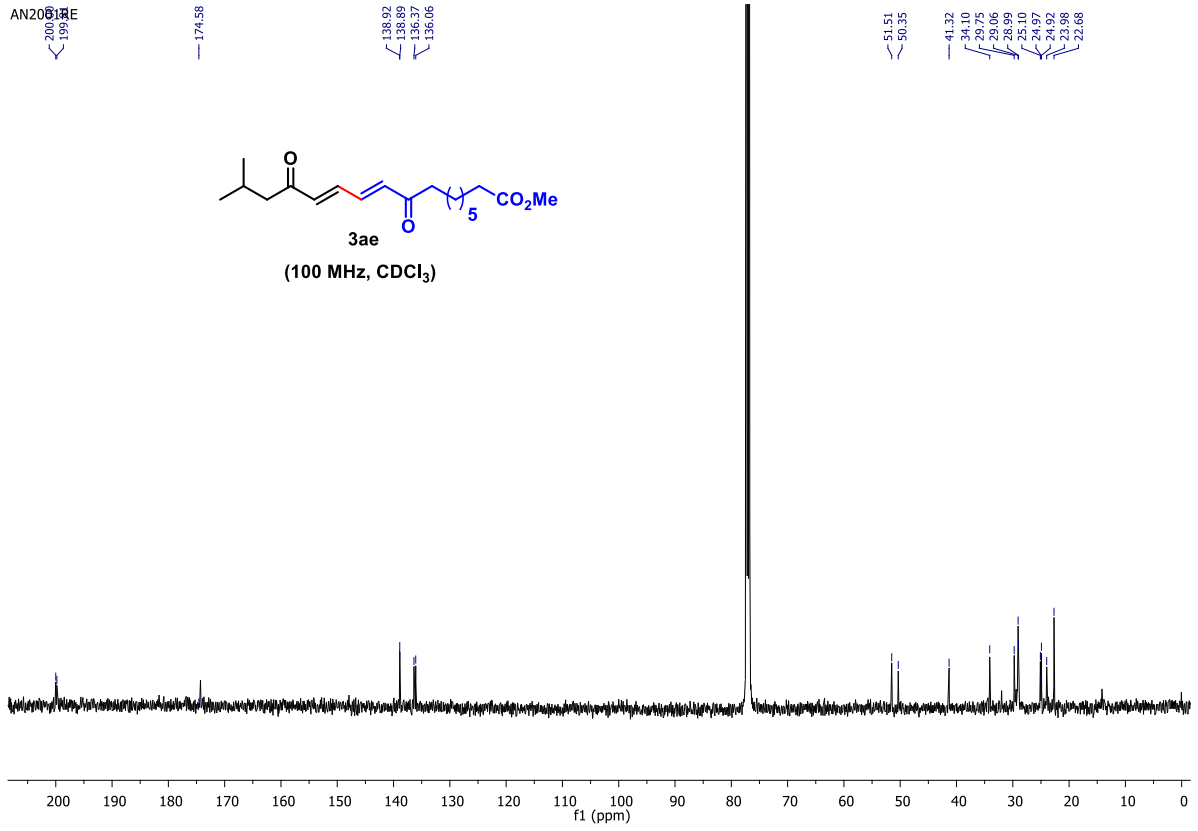
3ad

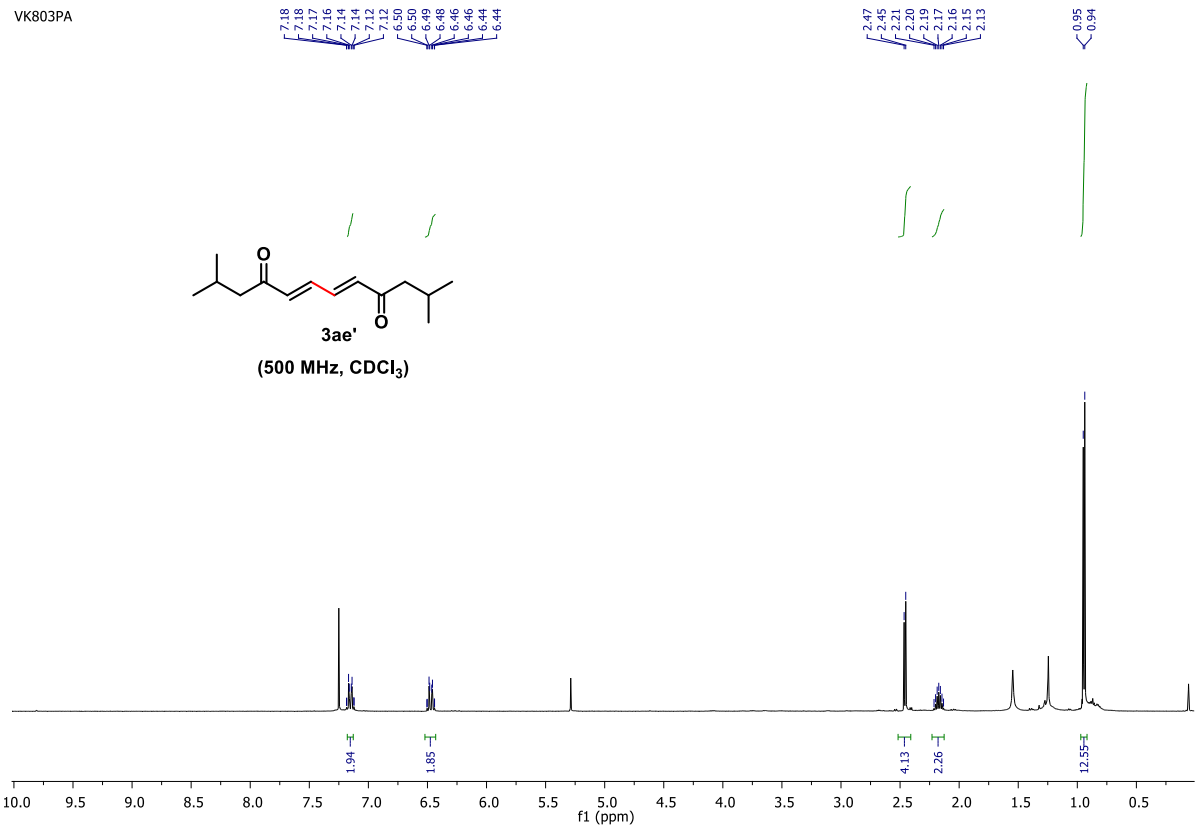
(100 MHz, $CDCl_3$)

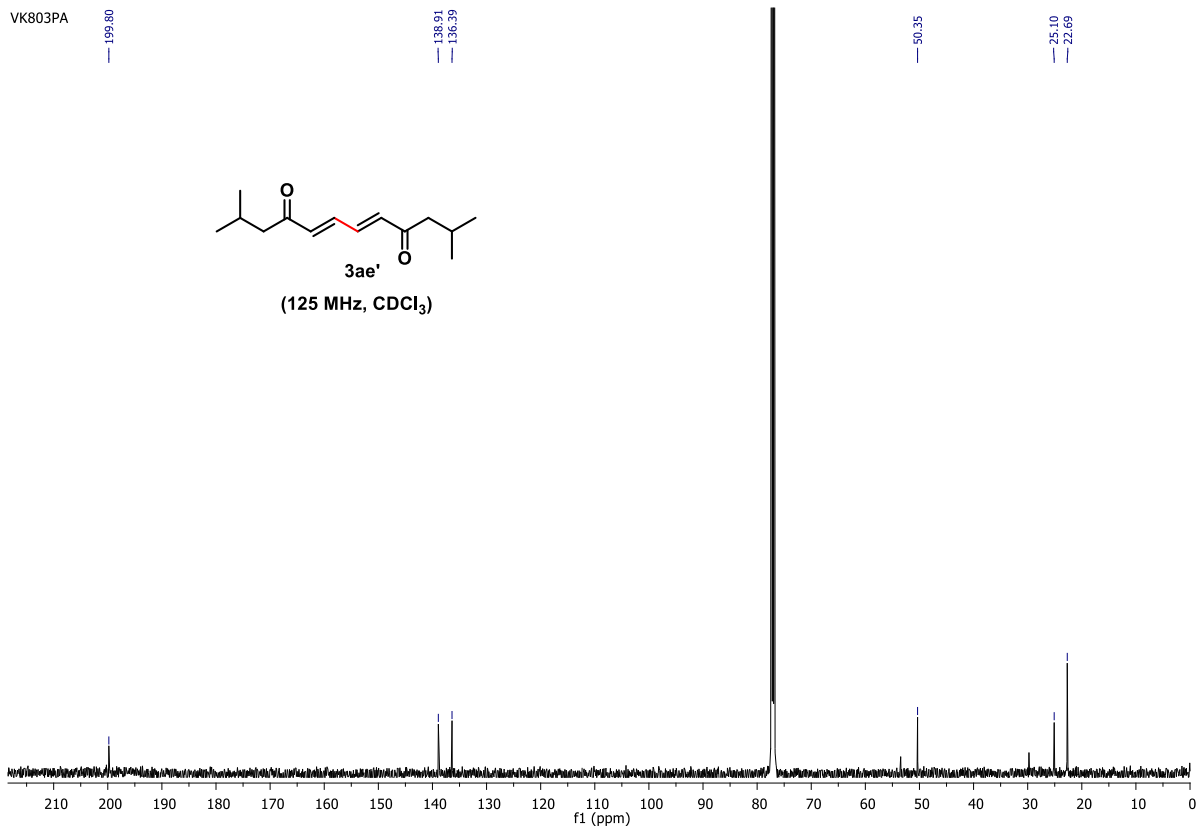

SAI20A
7.20
7.18
7.17
7.16
7.15
7.13
6.51
6.51
6.49
6.49
6.47
6.46
6.45
6.45
2.60
2.59
2.57
1.64
1.63
1.61
1.60
1.59
1.36
1.35
1.33
1.32
0.93
0.91
0.90
O
O
3ad'
(500 MHz, CDCl3)
2.08
2.00
4.08
4.22
4.12
6.07
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


SAI20
200.18
138.90
136.05
41.11
26.20
22.40
13.91
O
O
3ad'
(125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

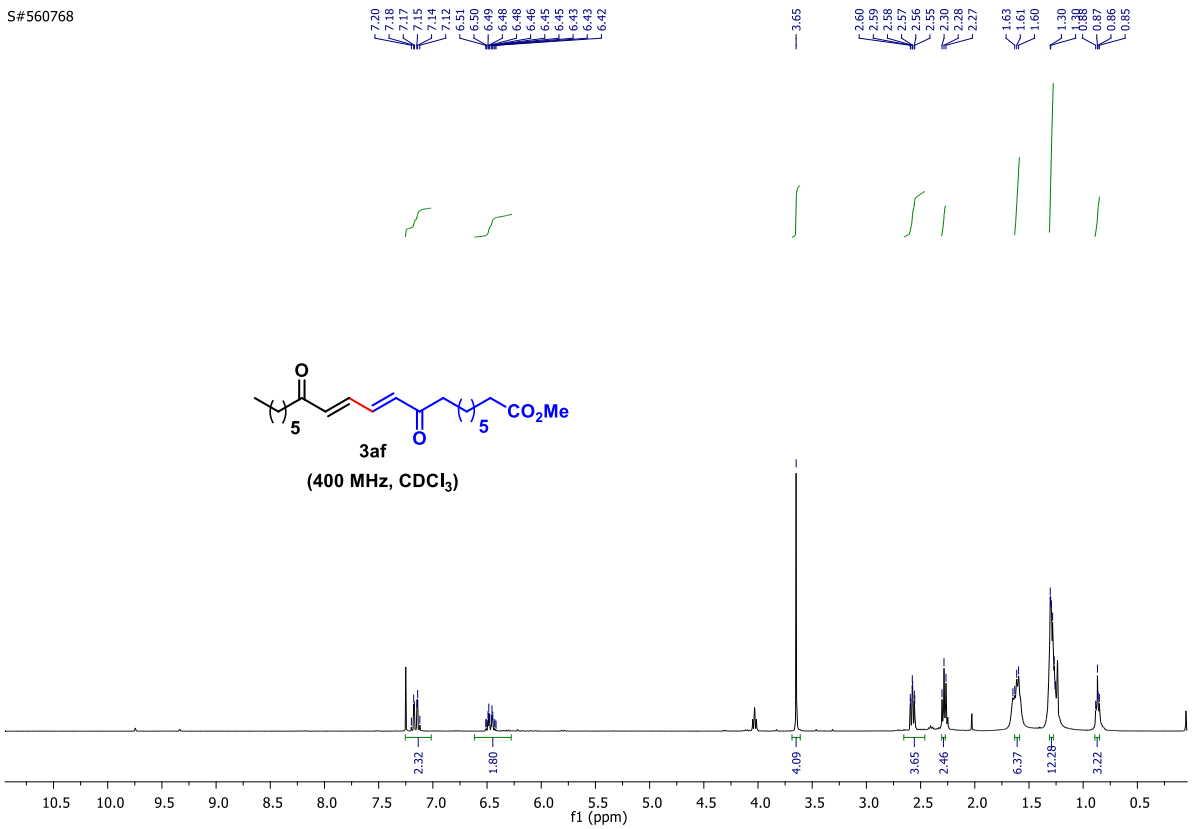

AN2001RE
7.17
7.14
6.48
6.46
3.65
2.57
2.56
2.46
2.45
2.29
2.27
2.18
2.17
2.16
2.15
1.61
1.31
0.95
0.94
O
O
5
CO2Me
3ae
(400 MHz, CDCl3)
2.00
2.01
3.15
2.03
2.16
2.13
1.17
4.21
6.06
6.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


AN2001RE
200.01
199.94
174.58
138.92
138.89
136.37
136.06
51.51
50.35
41.32
34.10
29.75
29.06
28.99
25.10
24.97
24.92
23.98
22.68
O
O
5
CO2Me
3ae
(100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


VK803PA
7.18
7.18
7.17
7.16
7.14
7.14
7.12
7.12
6.50
6.50
6.49
6.48
6.46
6.46
6.44
6.44
2.47
2.45
2.21
2.20
2.19
2.17
2.16
2.15
2.13
0.95
0.94
O
O
3ae'
(500 MHz, CDCl3)
1.94
1.85
4.13
2.26
12.55
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


VK803PA
199.80
138.91
136.39
50.35
25.10
22.69
O
O
3ae'
(125 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

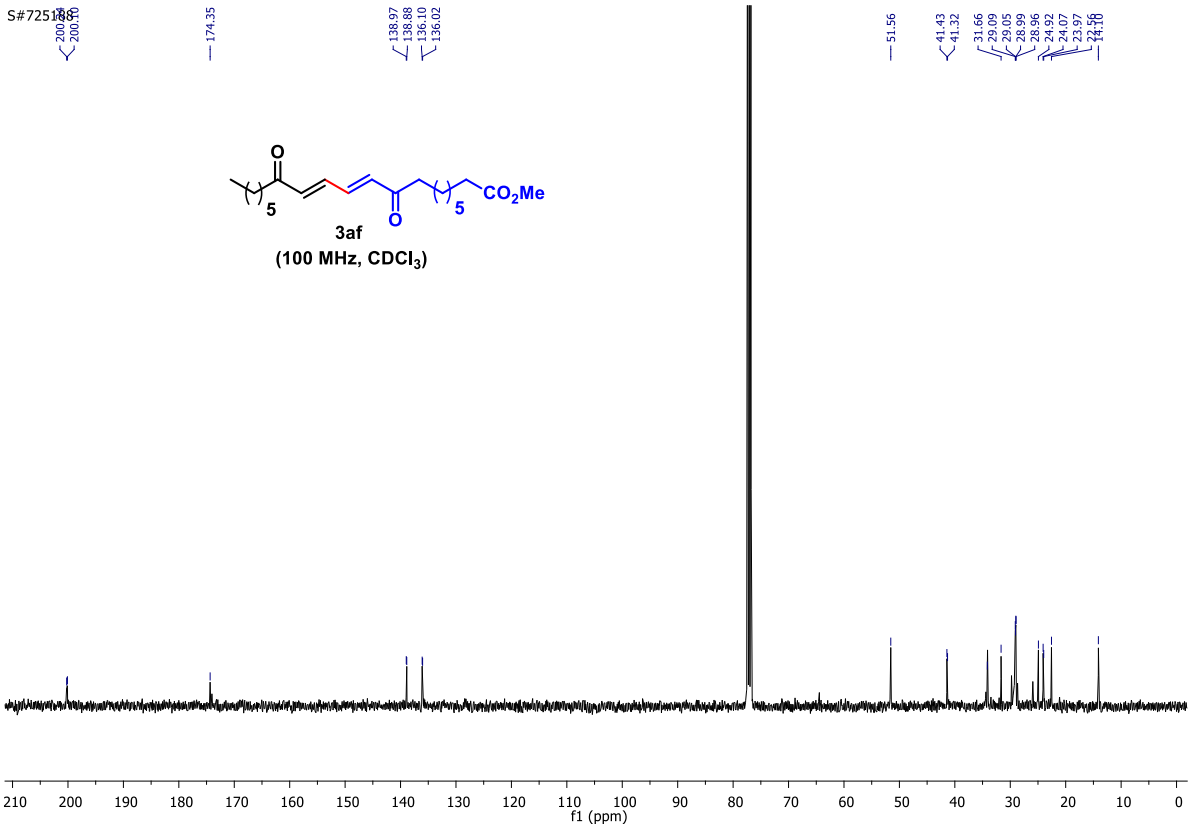
S#560768



3af

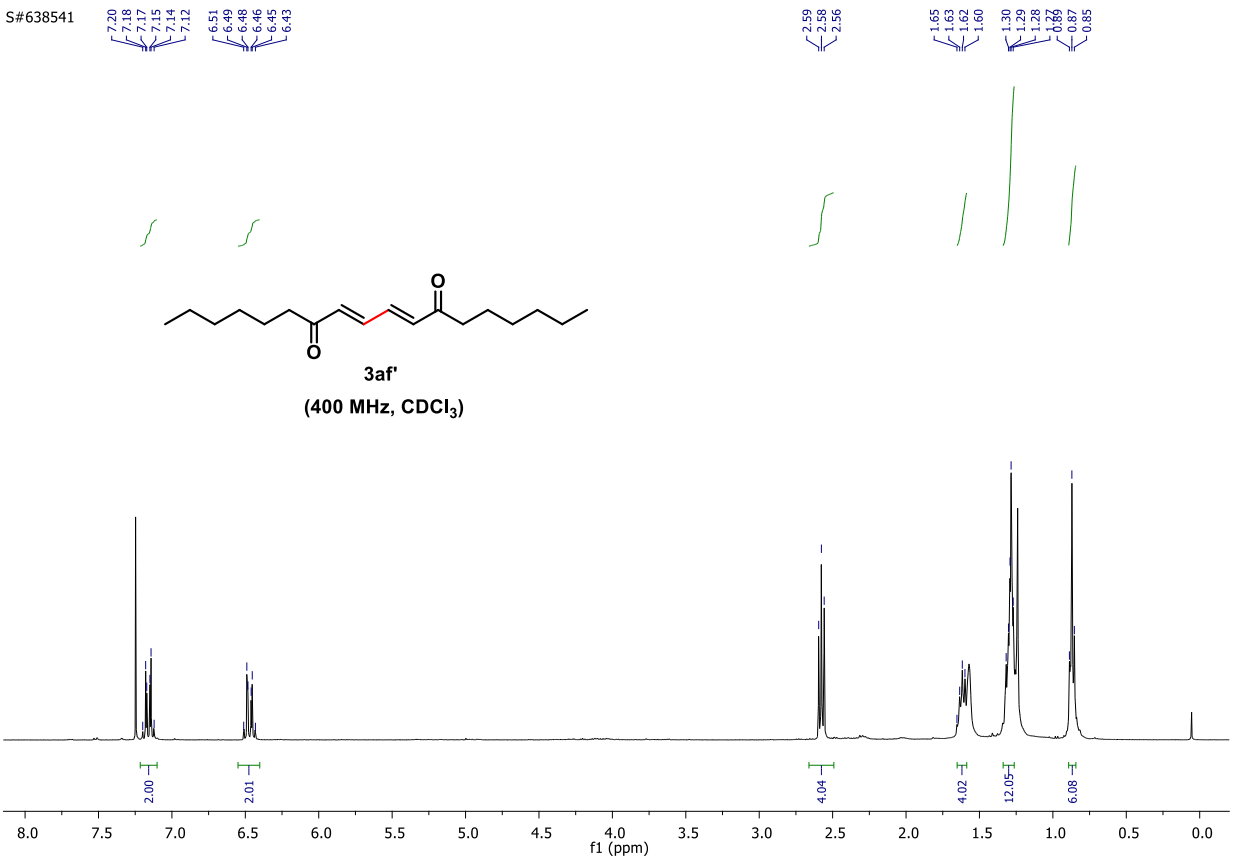
(400 MHz, $CDCl_3$)

S#725183



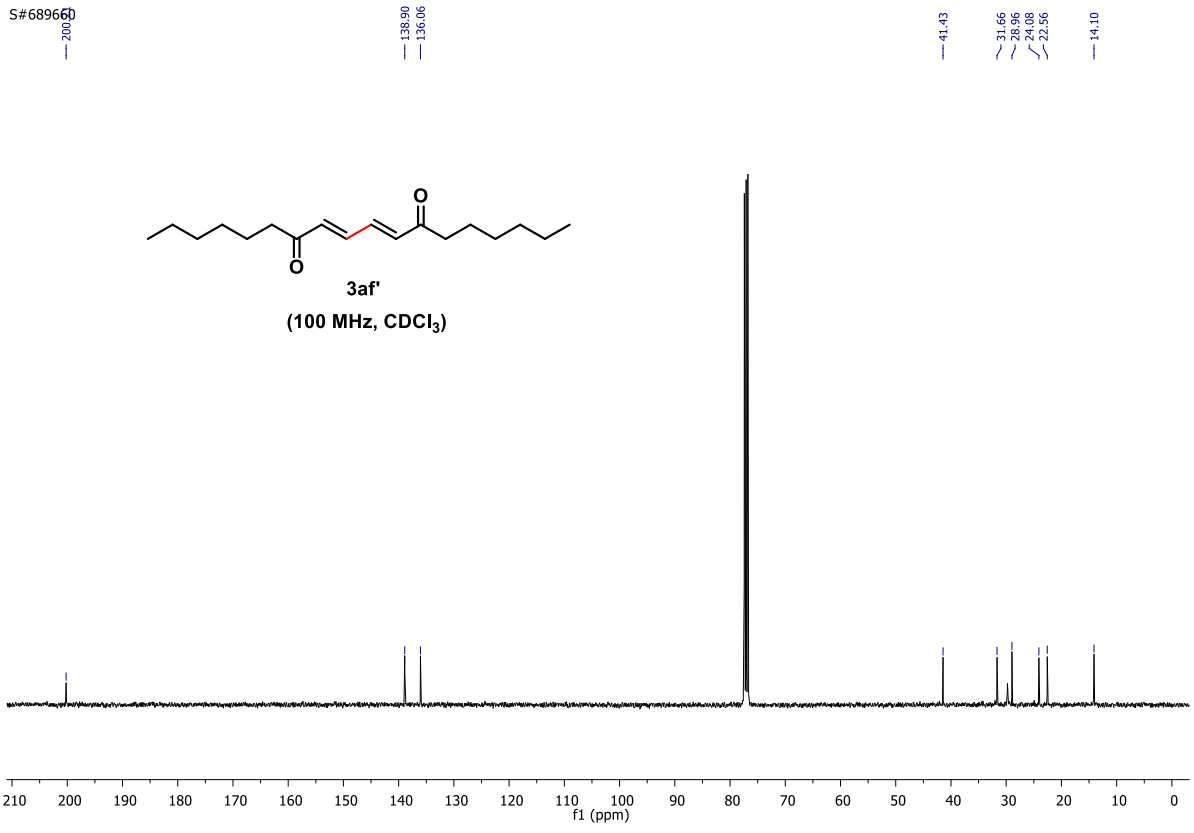
3af

(100 MHz, $CDCl_3$)



3af'

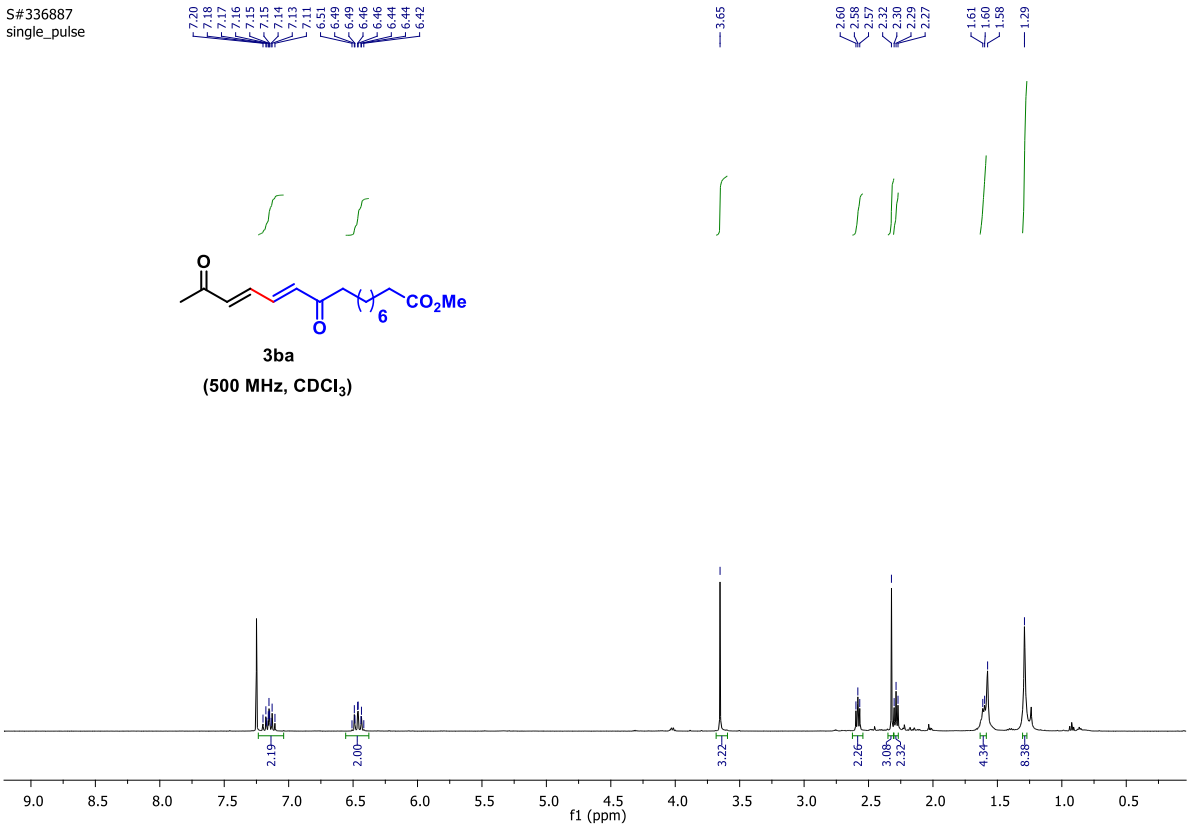
(400 MHz, $CDCl_3$)



3af'

(100 MHz, $CDCl_3$)

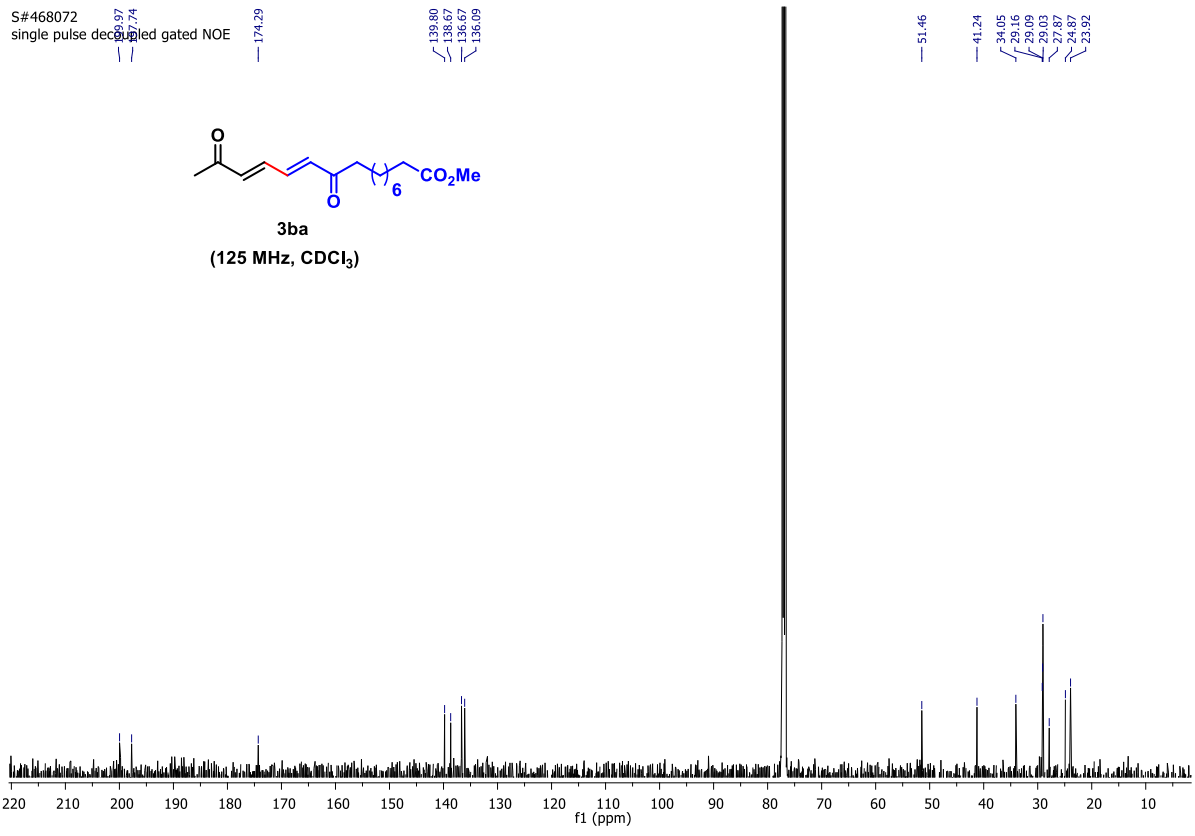
S#336887
single_pulse



3ba

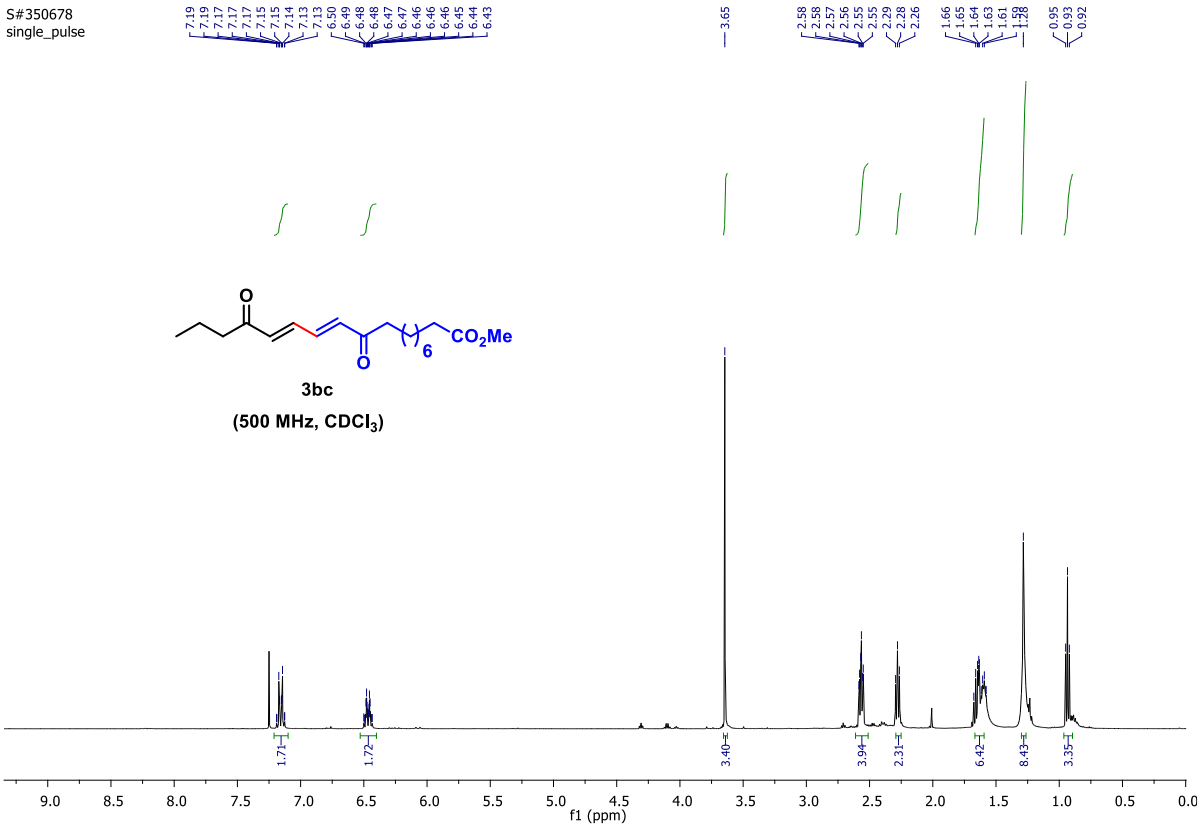
(500 MHz, $CDCl_3$)

S#468072
single pulse decoupled gated NOE



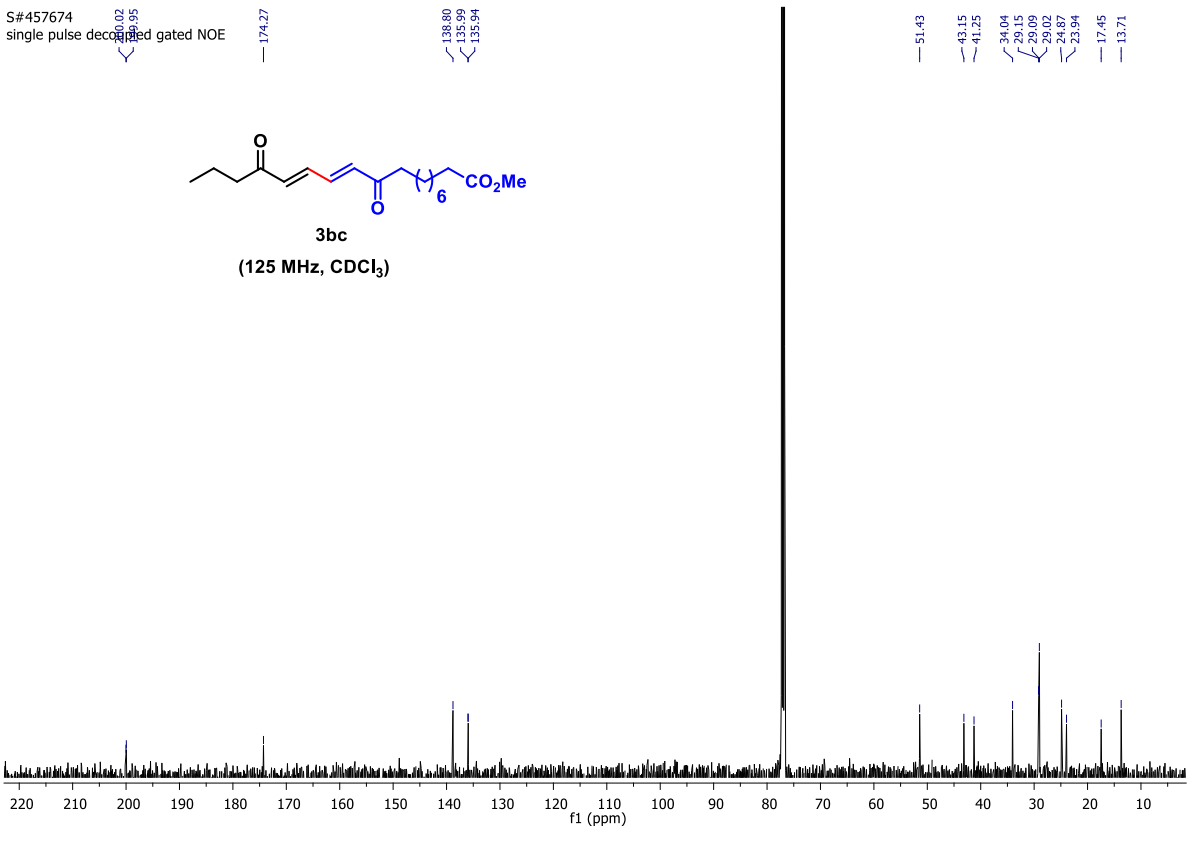
3ba

(125 MHz, $CDCl_3$)



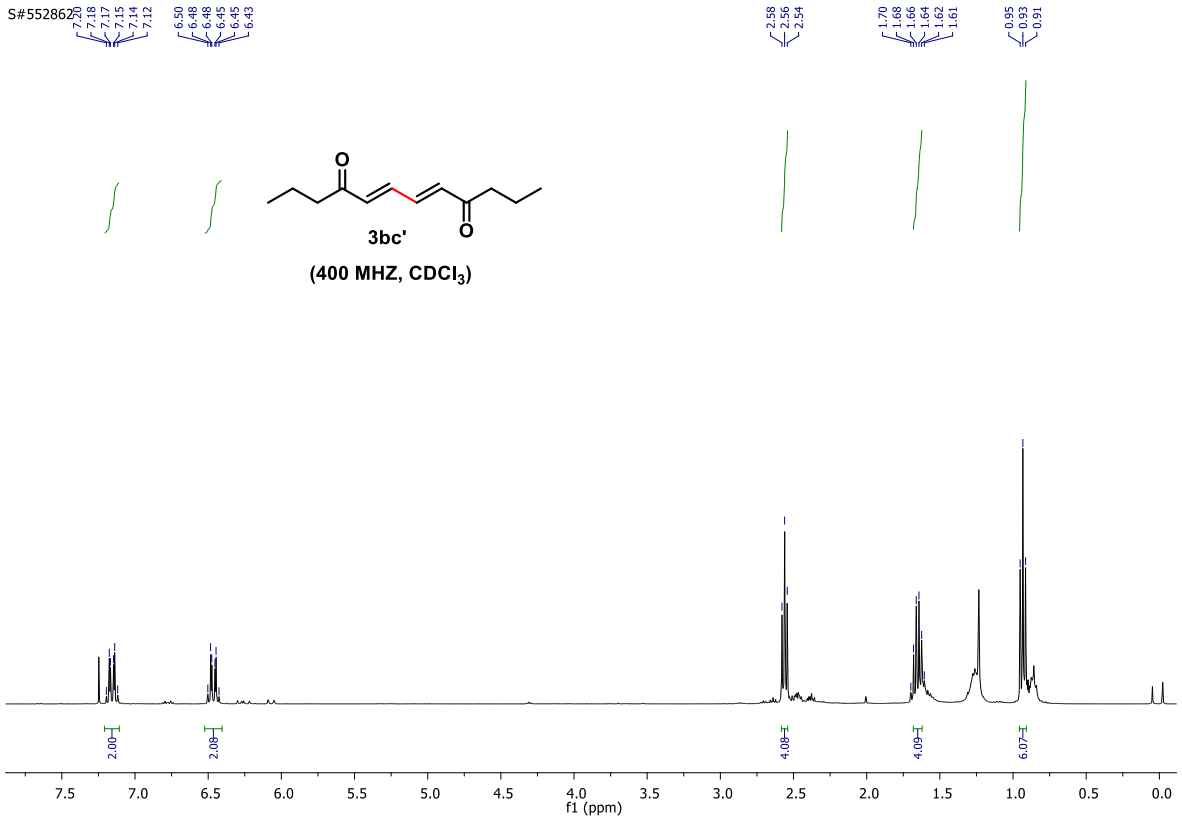
3bc

(500 MHz, $CDCl_3$)



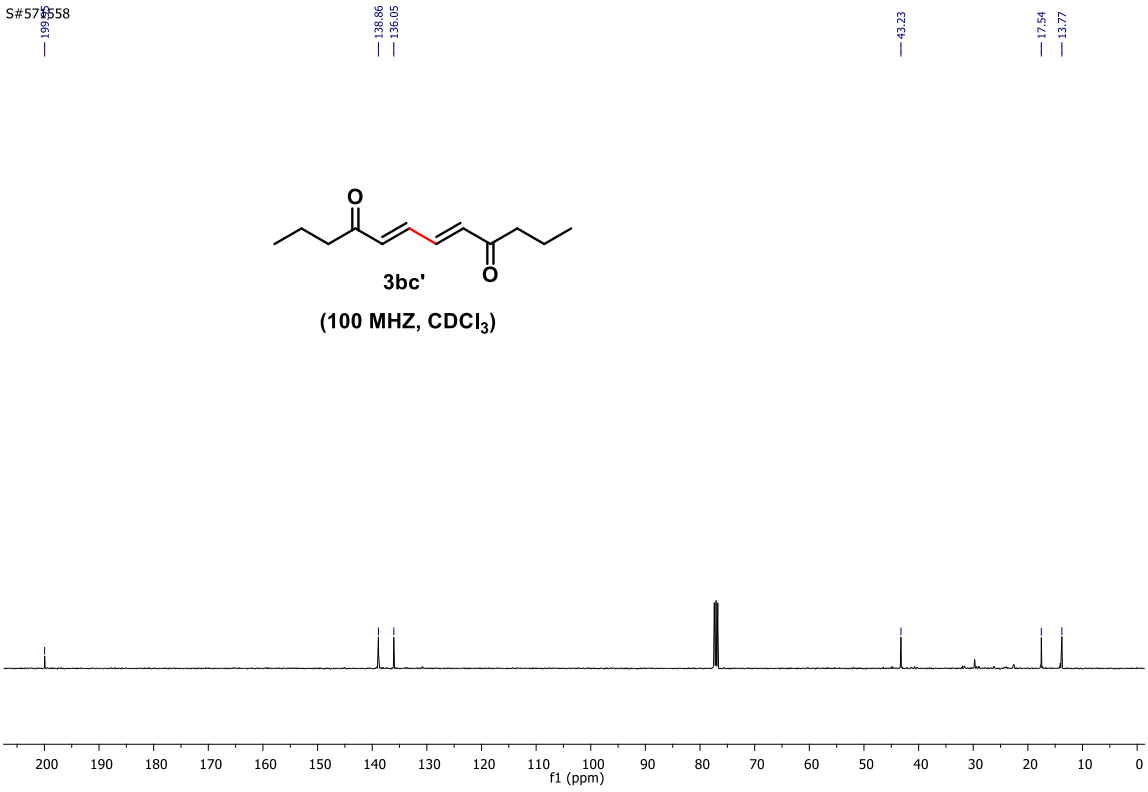
3bc

(125 MHz, $CDCl_3$)



3bc'

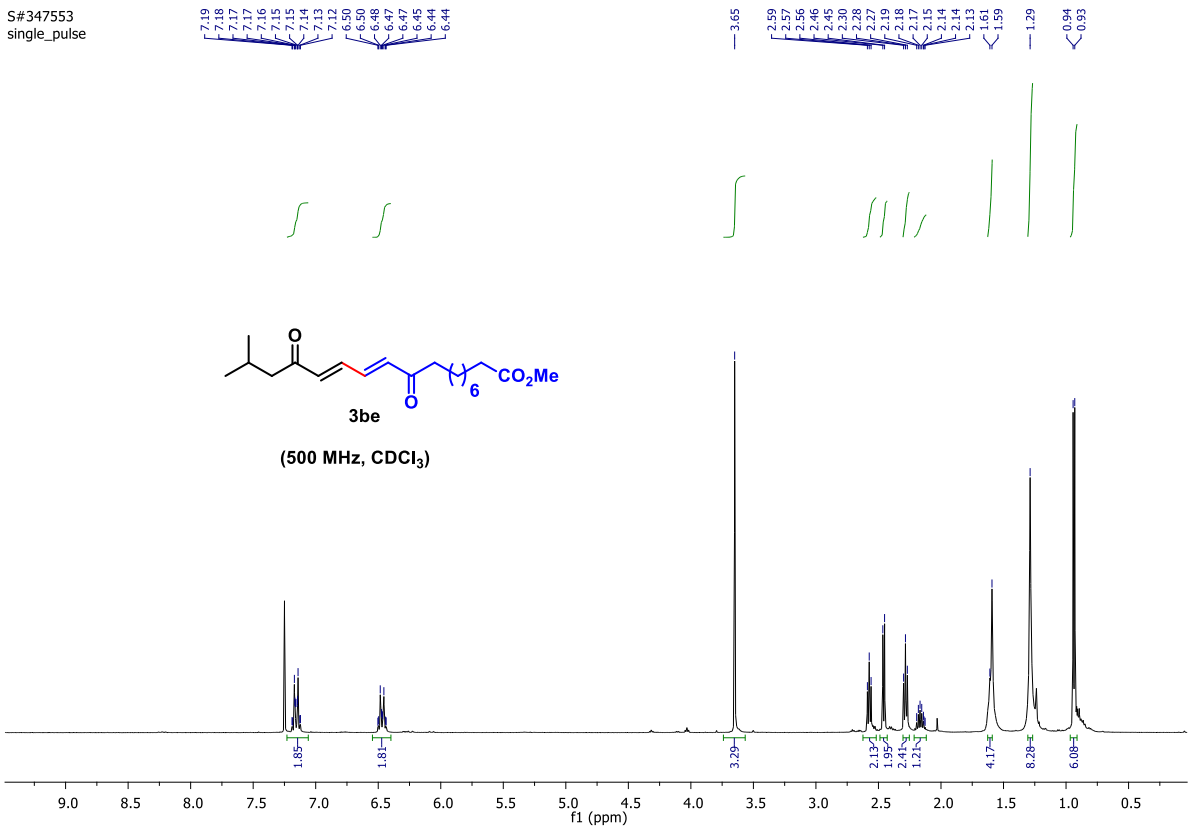
(400 MHZ, $CDCl_3$)



3bc'

(100 MHZ, $CDCl_3$)

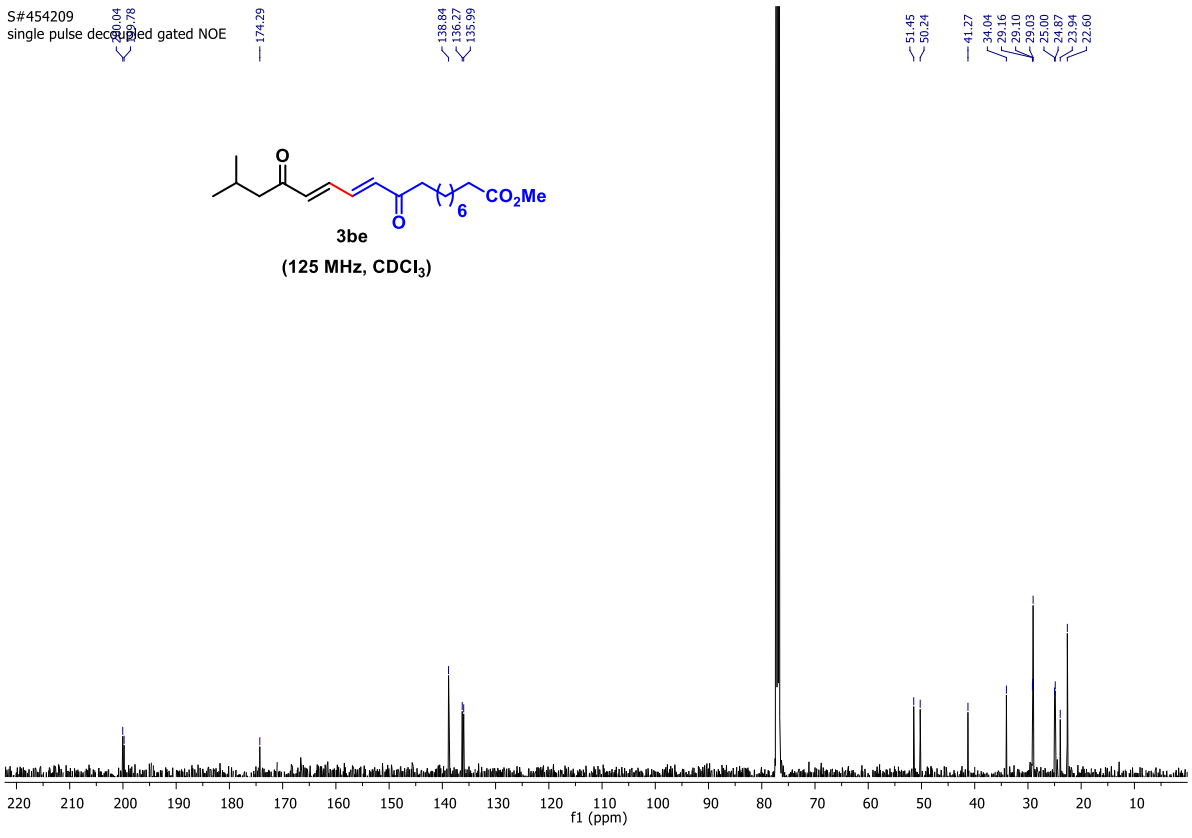
S#347553
single_pulse



3be

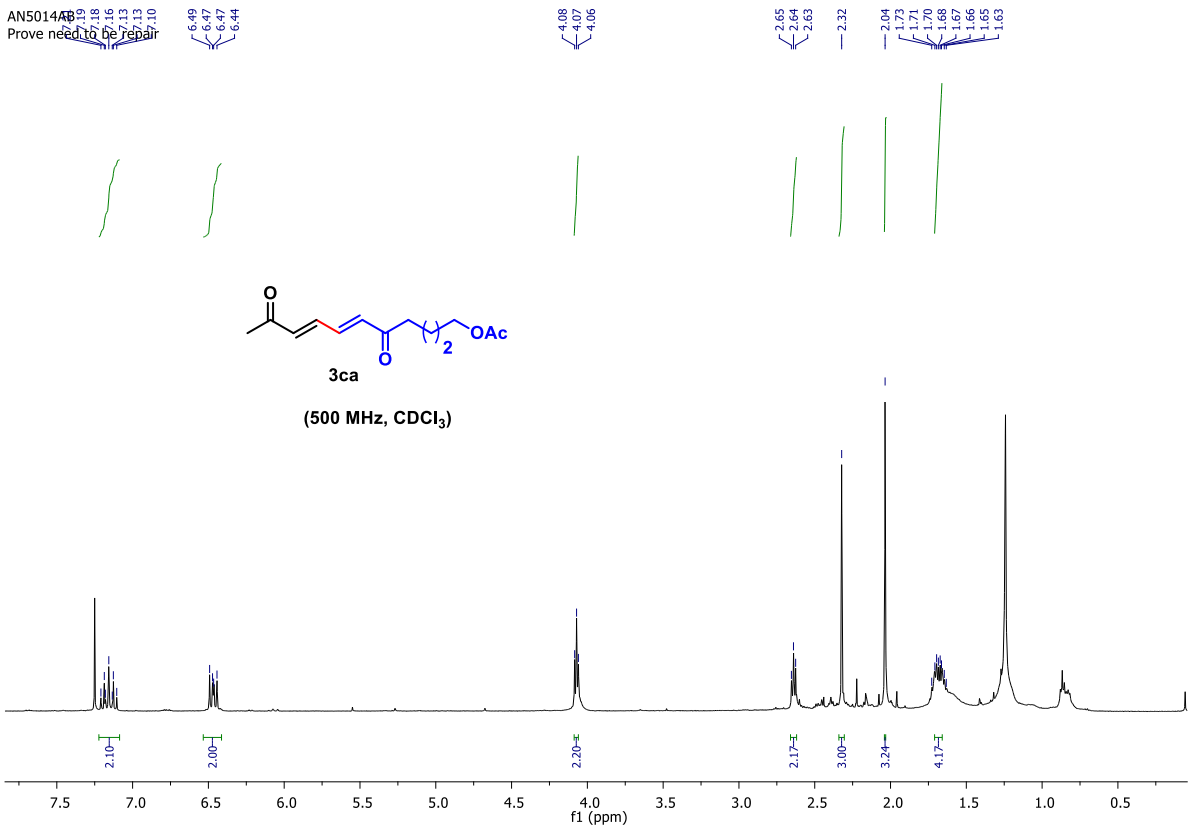
(500 MHz, $CDCl_3$)

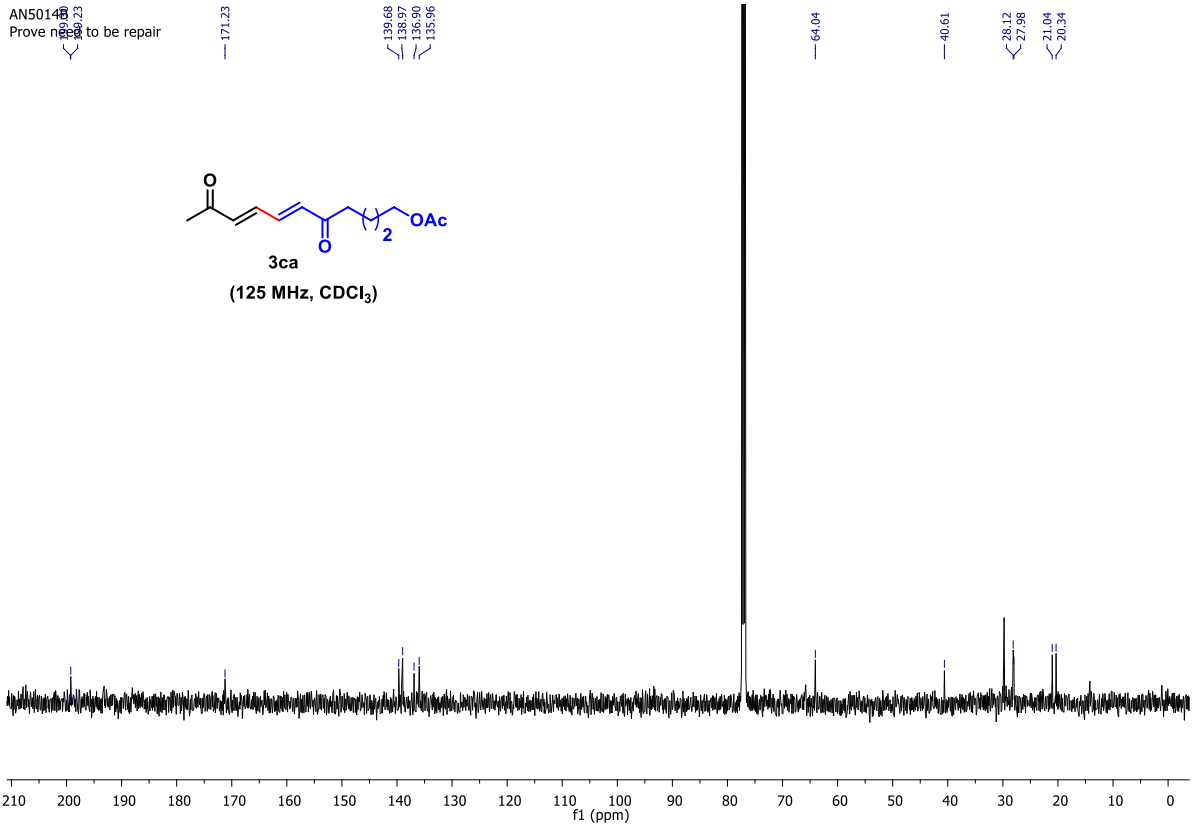
S#454209
single pulse decoupled gated NOE

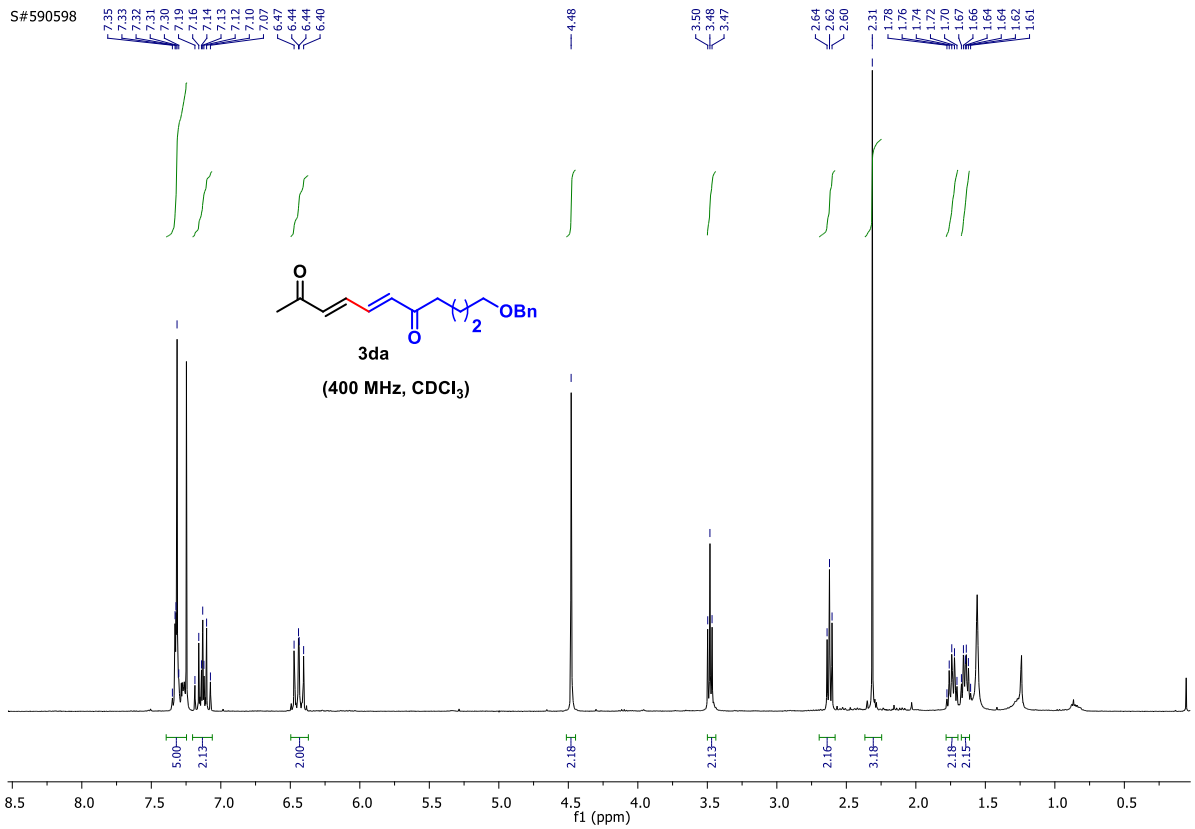


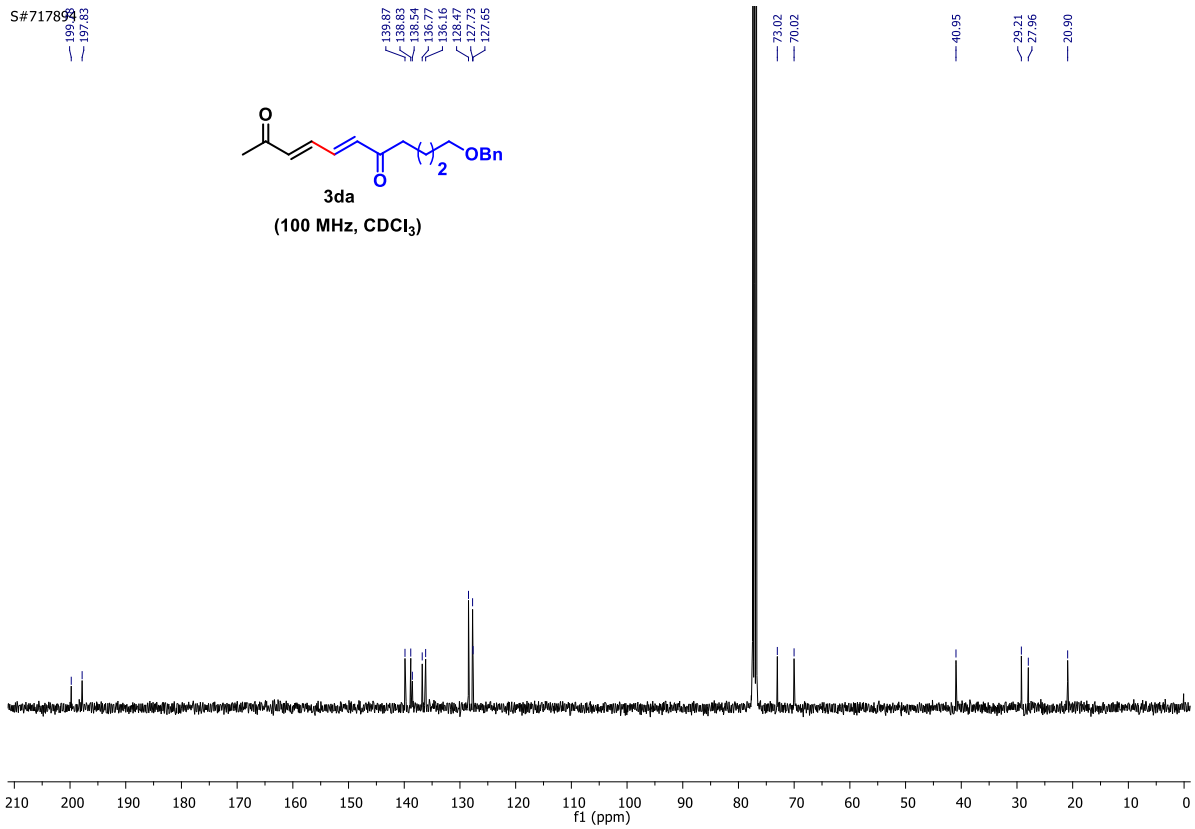
3be

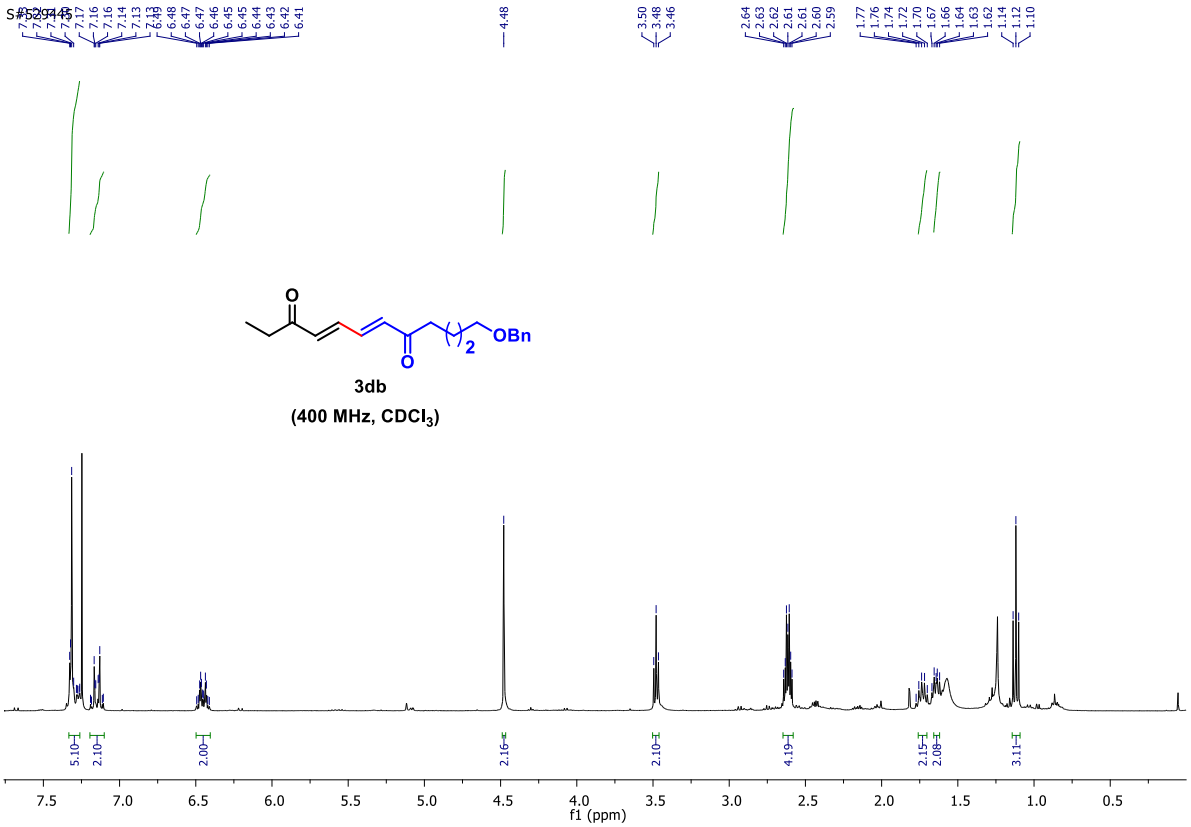
(125 MHz, $CDCl_3$)

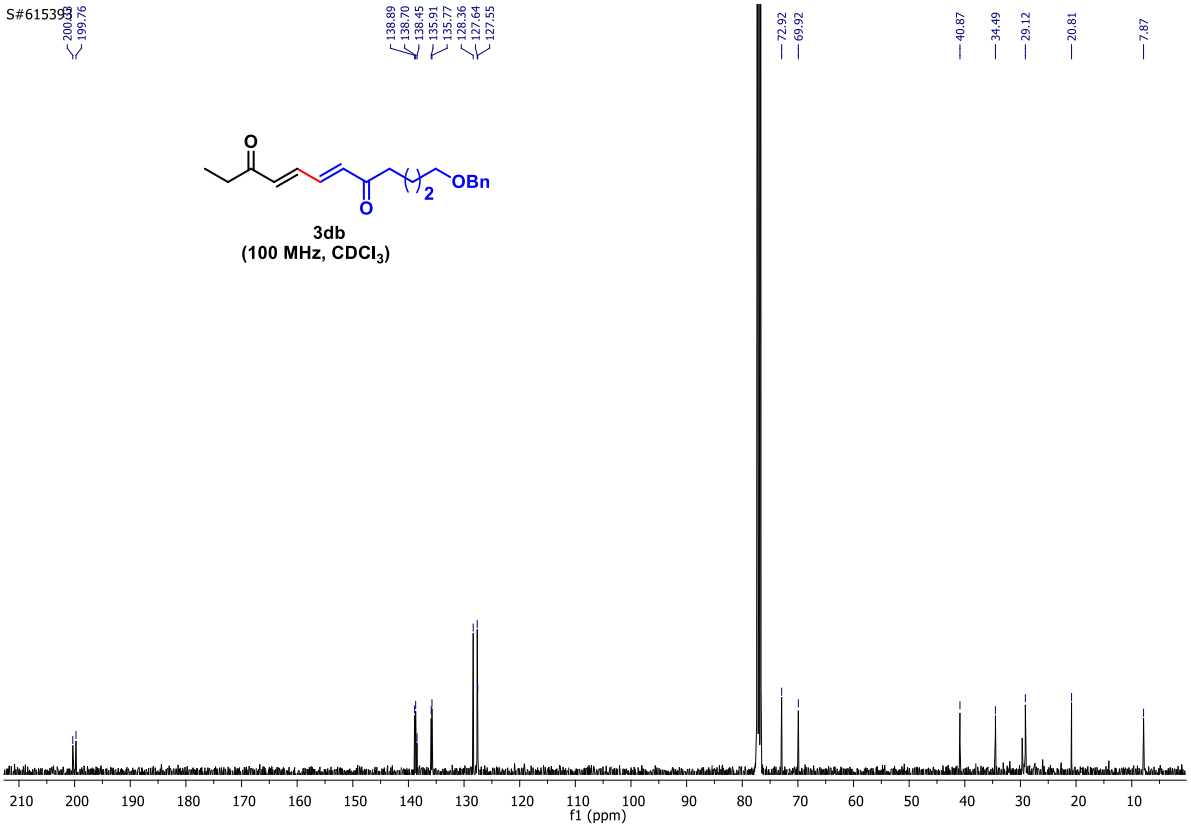

AN5014AB
Prove need to be repair
7.18
7.16
7.13
7.10
6.49
6.47
6.47
6.44
4.08
4.07
4.06
2.65
2.64
2.63
2.32
2.04
1.73
1.71
1.70
1.68
1.67
1.66
1.65
1.63
O
O
2
OAc
3ca
(500 MHz, CDCl3)
2.10
2.00
2.20
2.17
3.00
3.24
4.17
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

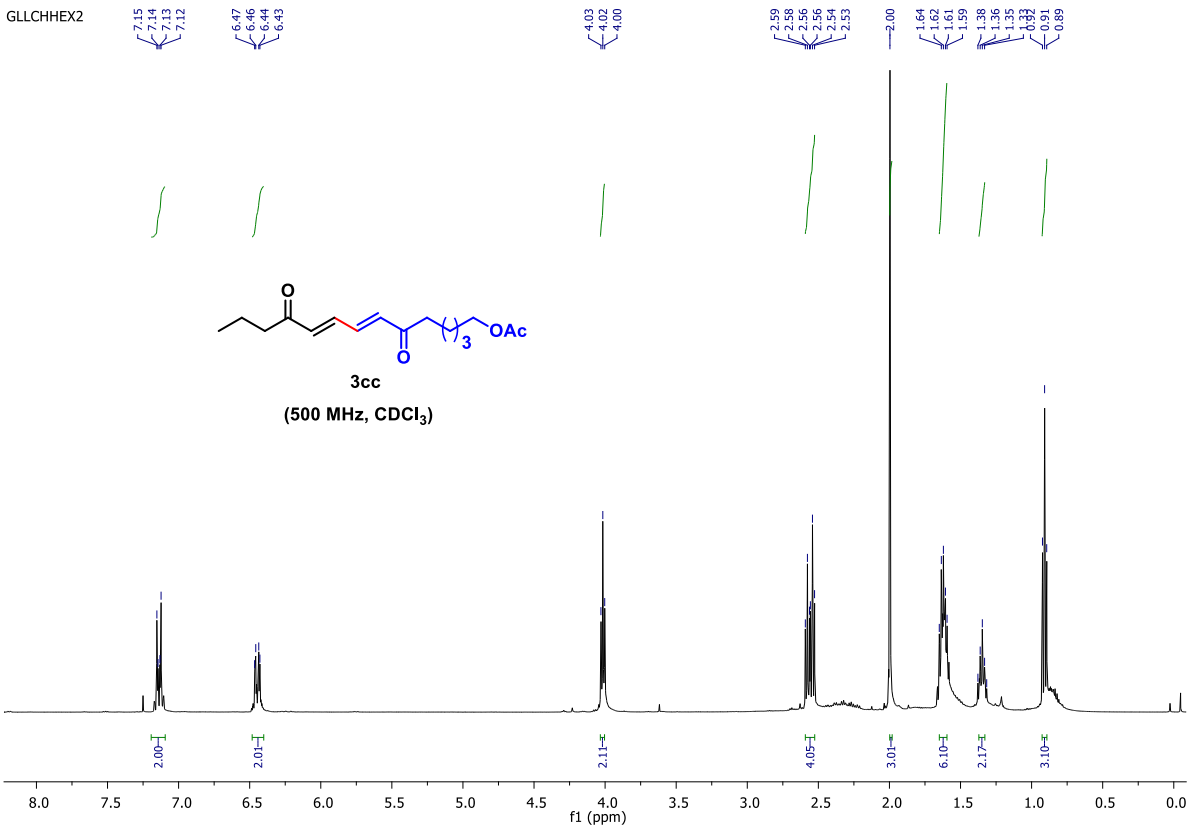

AN5014B
Prove need to be repair
171.23
139.68
138.97
136.90
135.96
64.04
40.61
28.12
27.98
21.04
20.34
O
O
2
OAc
3ca
(125 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


S#590598
7.35
7.33
7.32
7.31
7.30
7.19
7.16
7.14
7.13
7.12
7.10
7.07
6.47
6.44
6.44
6.40
4.48
3.50
3.48
3.47
2.64
2.62
2.60
2.31
1.78
1.76
1.74
1.72
1.70
1.67
1.66
1.64
1.64
1.62
1.61
O
O
2
OBn
3da
(400 MHz, CDCl3)
5.00
2.13
2.00
2.18
2.13
2.16
3.18
2.18
2.15
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


S#717894
199.43
197.83
139.87
138.83
138.54
136.77
136.16
128.47
127.73
127.65
73.02
70.02
40.95
29.21
27.96
20.90
O
O
2
OBn
3da
(100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

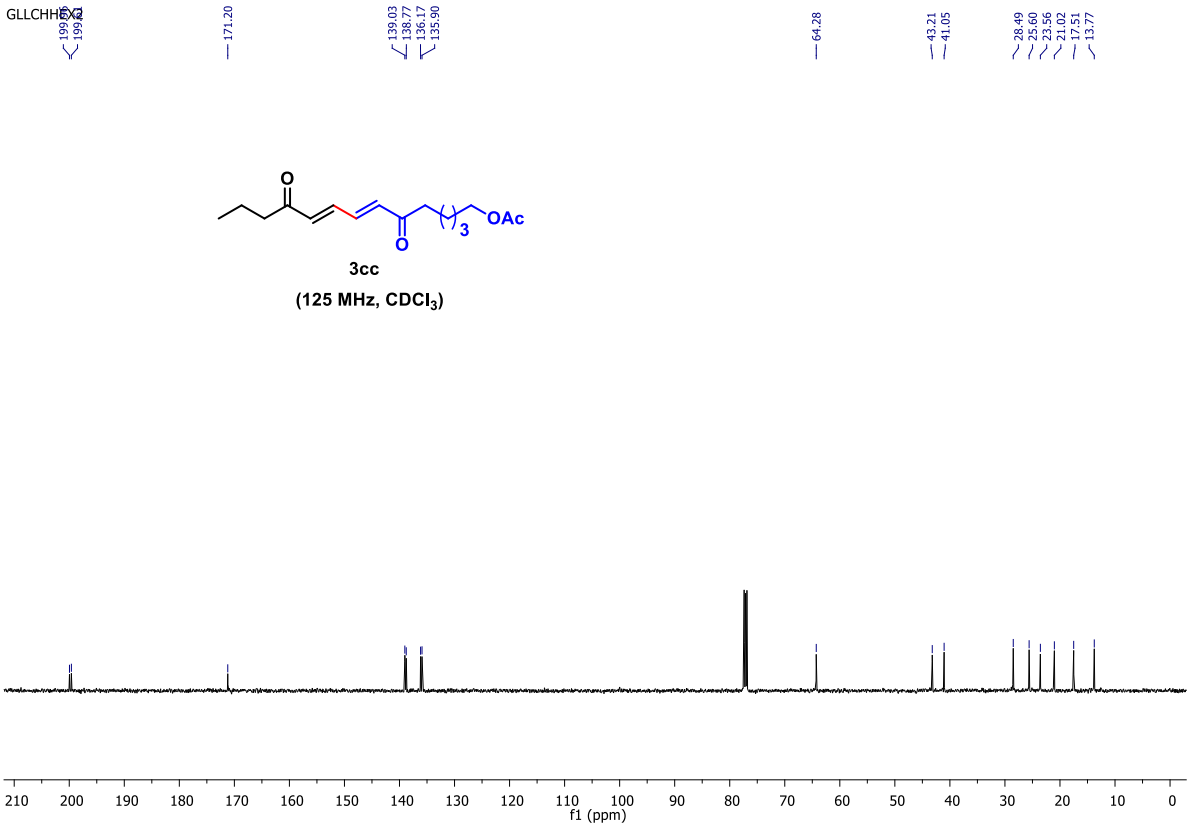

S#529445
7.17
7.16
7.14
7.13
6.48
6.47
6.46
6.45
6.44
6.43
6.42
6.41
4.48
3.50
3.48
3.46
2.64
2.63
2.62
2.61
2.60
2.59
1.77
1.76
1.74
1.72
1.70
1.67
1.66
1.64
1.63
1.62
1.14
1.12
1.10
O
O
2
OBn
3db
(400 MHz, CDCl3)
5.10
2.10
2.00
2.16
2.10
4.19
2.15
2.08
3.11
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


S#615393
200.03
199.76
138.89
138.70
138.45
135.91
135.77
128.36
127.64
127.55
72.92
69.92
40.87
34.49
29.12
20.81
7.87
O
O
2
OBn
3db
(100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)



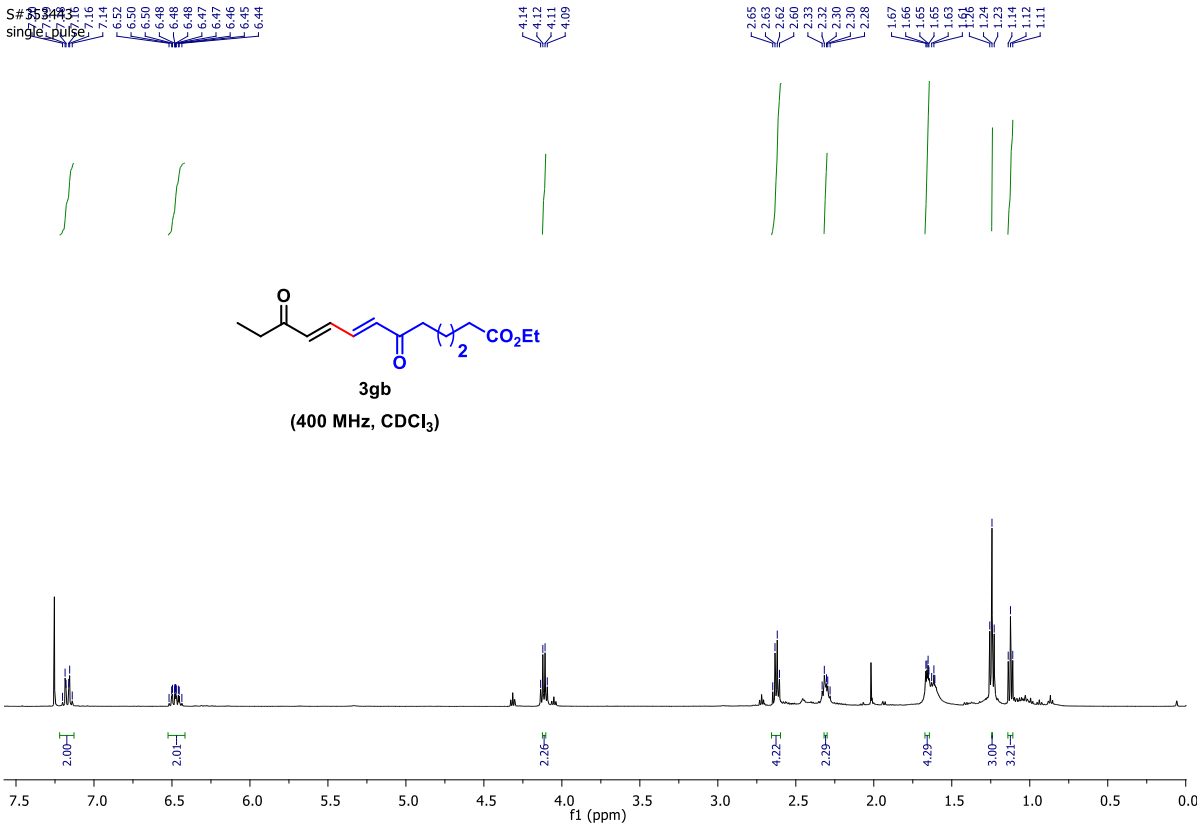
3cc

(500 MHz, $CDCl_3$)



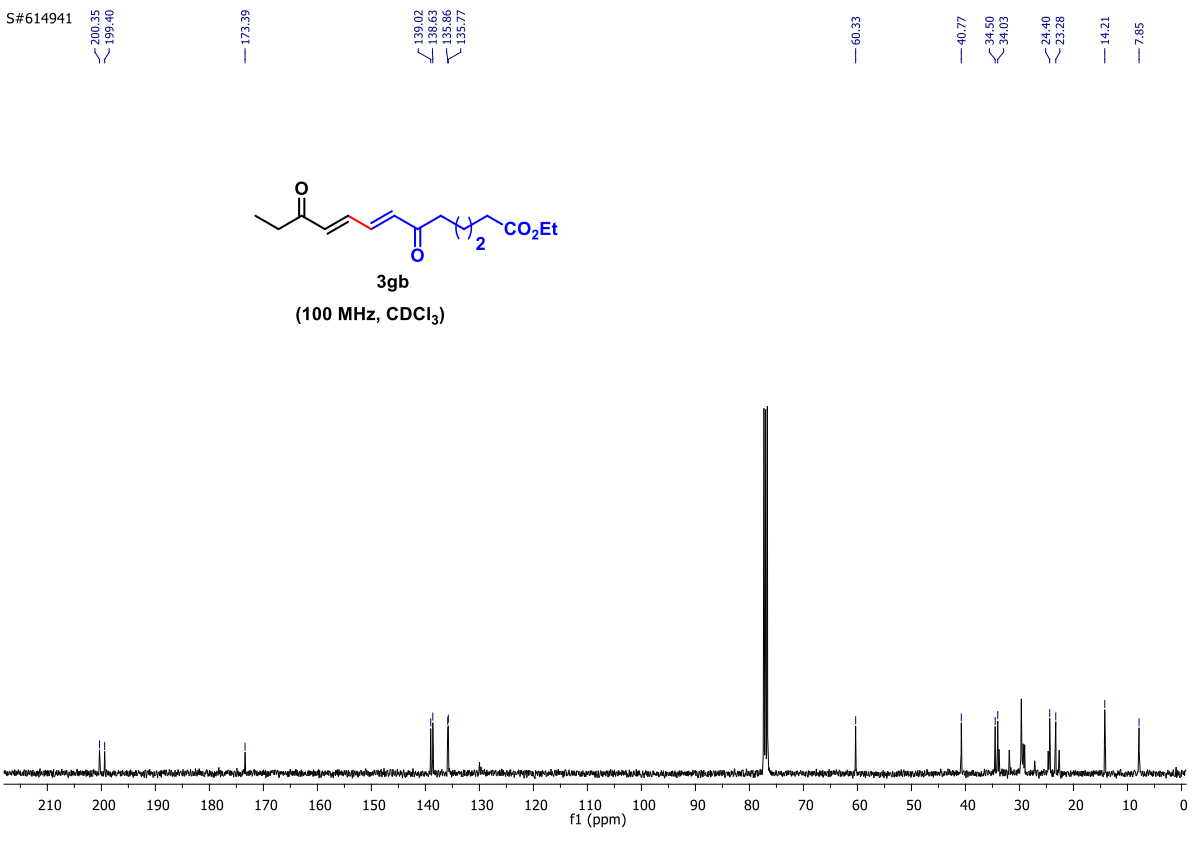
3cc

(125 MHz, $CDCl_3$)



3gb

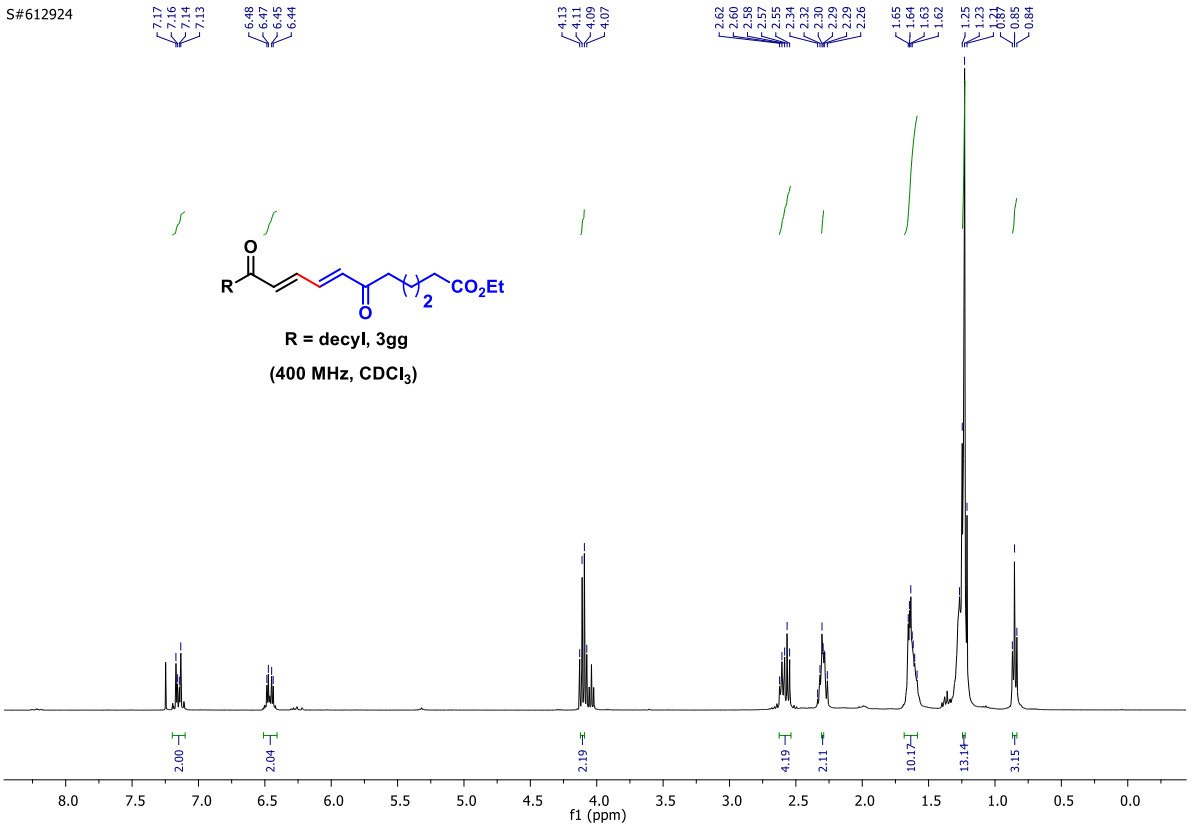
(400 MHz, $CDCl_3$)



3gb

(100 MHz, $CDCl_3$)

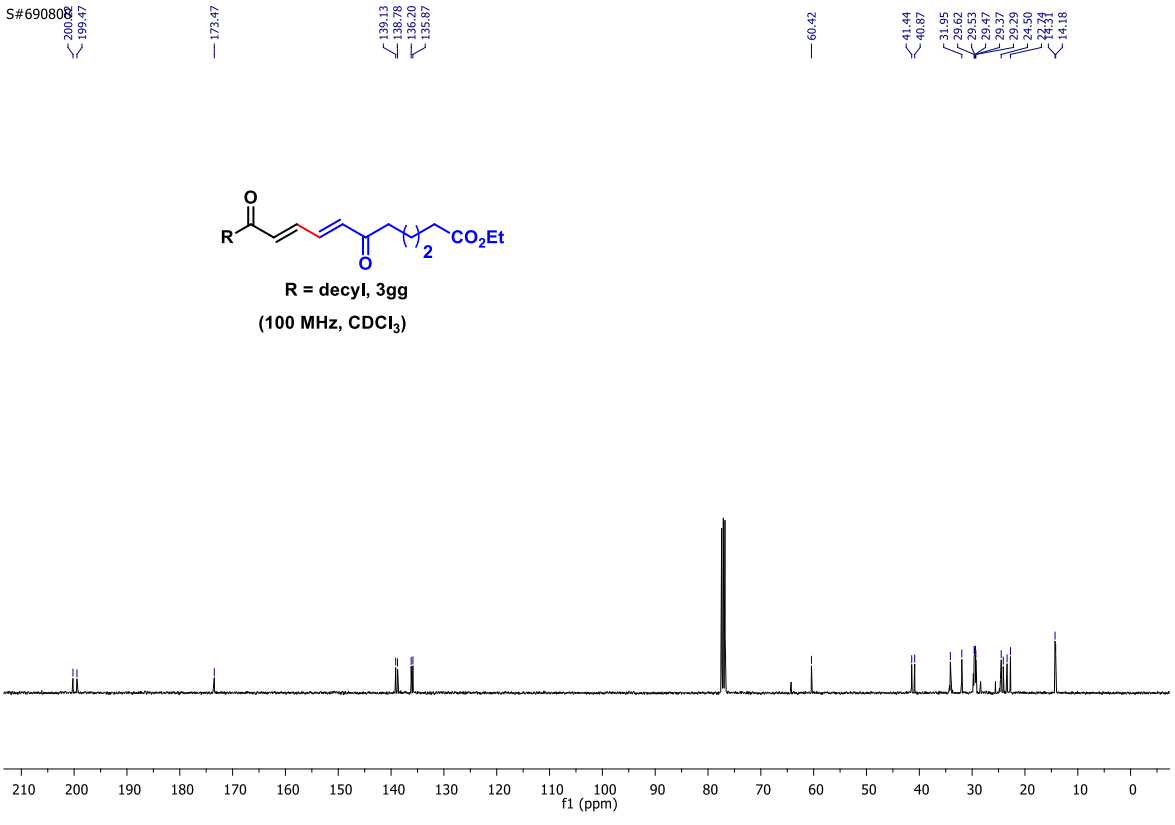
S#612924



R = decyl, 3gg

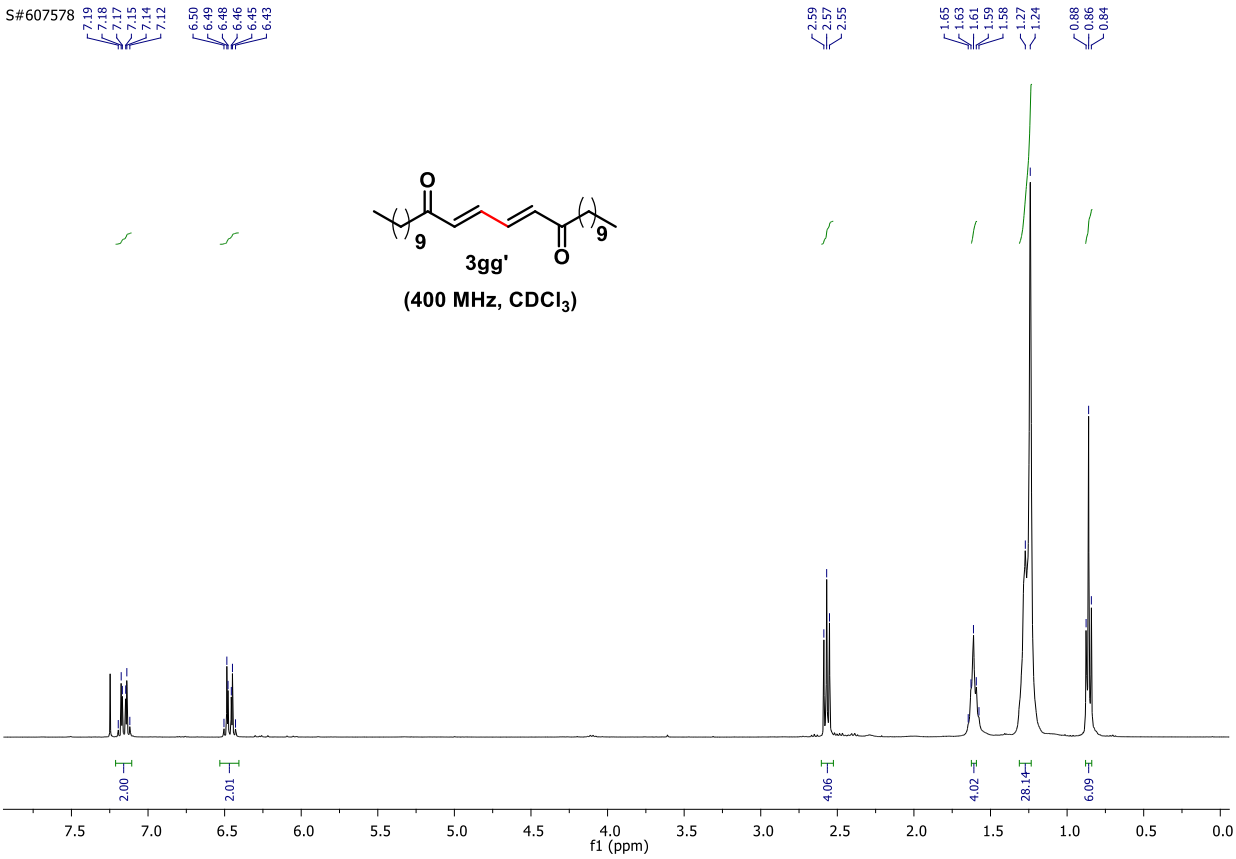
(400 MHz, $CDCl_3$)

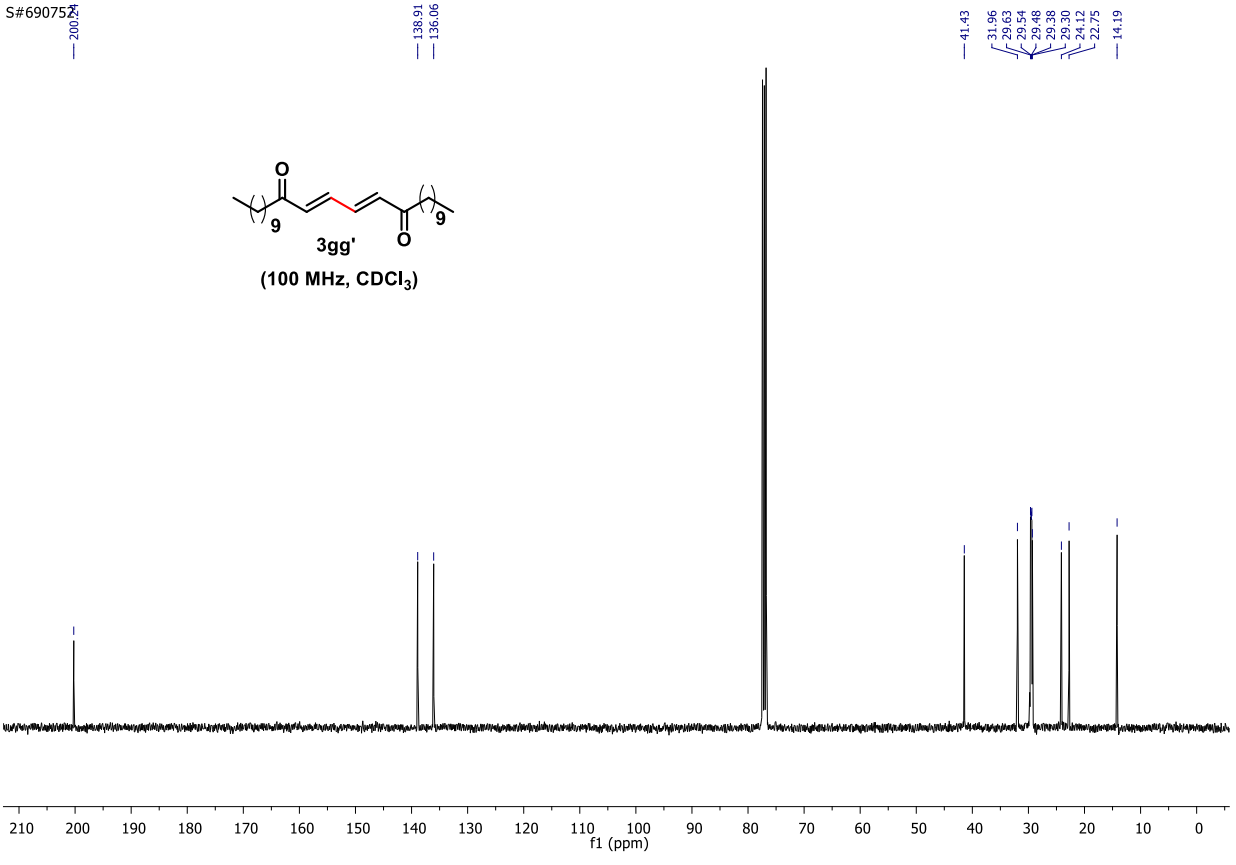
S#690808

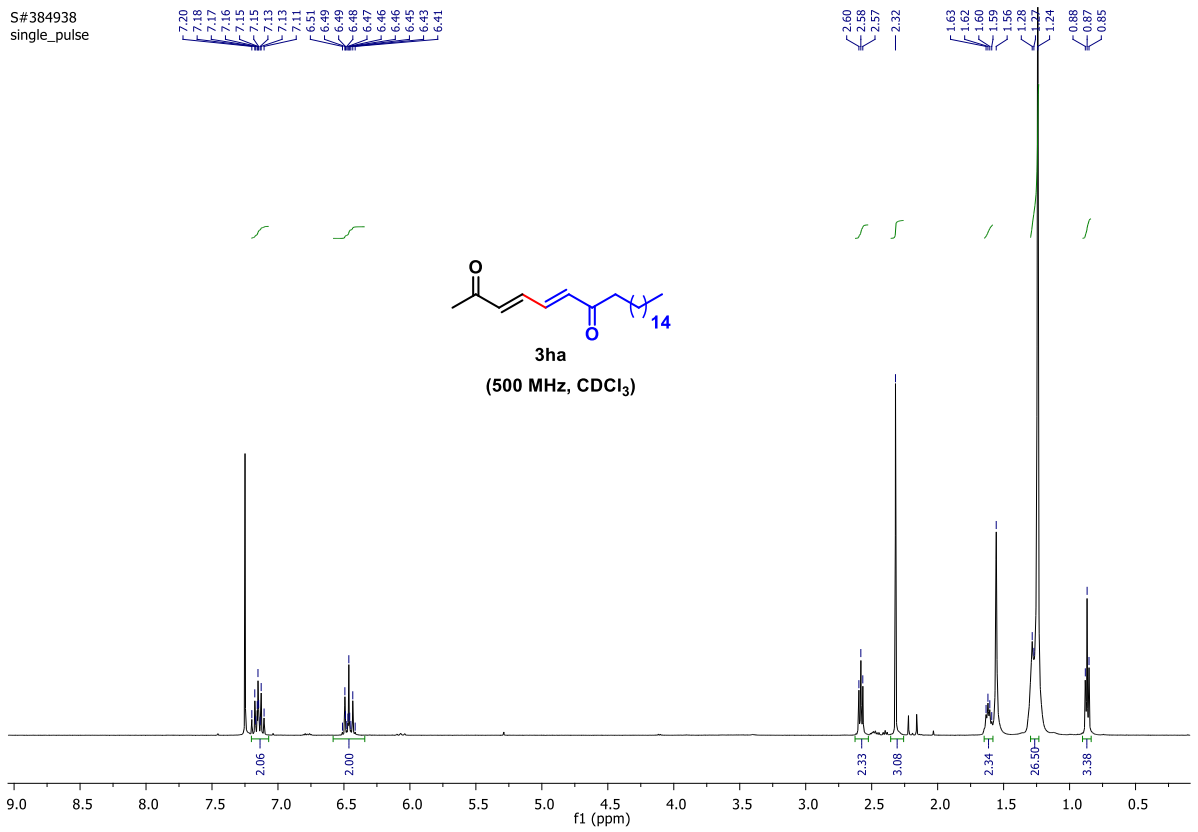


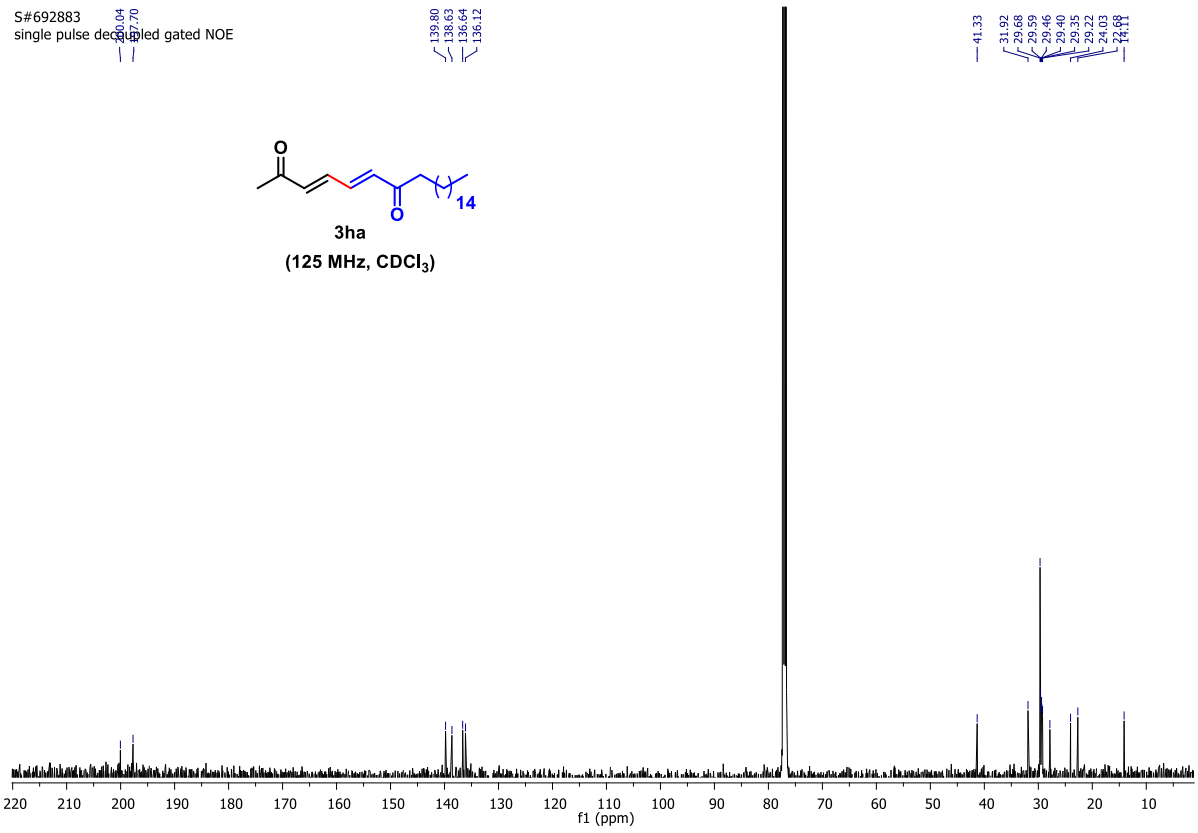
R = decyl, 3gg

(100 MHz, $CDCl_3$)

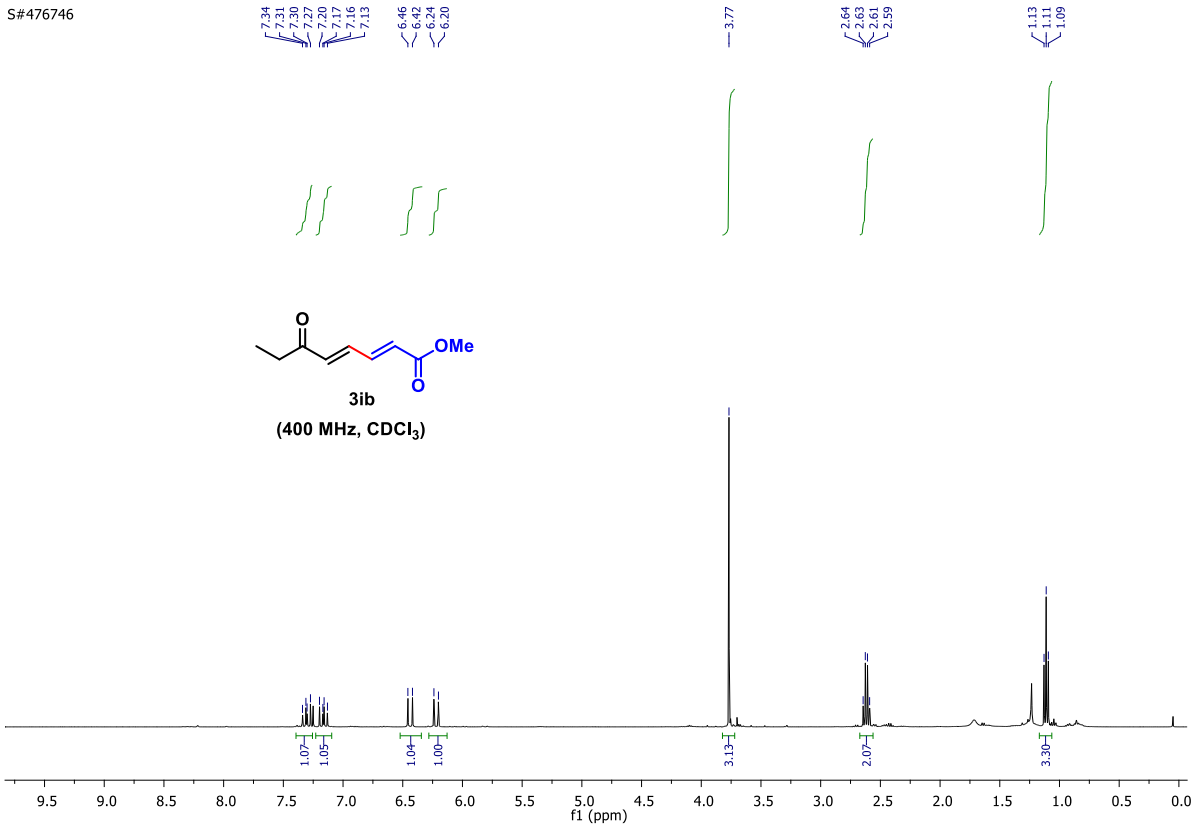

S#607578
7.19
7.18
7.17
7.15
7.14
7.12
6.50
6.49
6.48
6.46
6.45
6.43
2.59
2.57
2.55
1.65
1.63
1.61
1.59
1.58
1.27
1.24
0.88
0.86
0.84
O
9
9
O
3gg'
(400 MHz, CDCl3)
2.00
2.01
4.06
4.02
28.14
6.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


S#690752
200.74
138.91
136.06
41.43
31.96
29.63
29.54
29.48
29.38
29.30
24.12
22.75
14.19
O
9
9
O
3gg'
(100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


S#384938
single_pulse
7.20
7.18
7.17
7.16
7.15
7.15
7.13
7.13
7.11
6.51
6.49
6.49
6.48
6.47
6.46
6.46
6.45
6.43
6.41
2.60
2.58
2.57
2.32
1.63
1.62
1.60
1.59
1.56
1.28
1.22
1.24
0.88
0.87
0.85
O
O
14
3ha
(500 MHz, CDCl3)
2.06
2.00
2.33
3.08
2.34
26.50
3.38
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


S#692883
single pulse decoupled gated NOE
200.04
197.70
139.80
138.63
136.64
136.12
41.33
31.92
29.68
29.59
29.46
29.40
29.35
29.22
24.03
22.68
14.11
O
O
14
3ha
(125 MHz, CDCl3)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

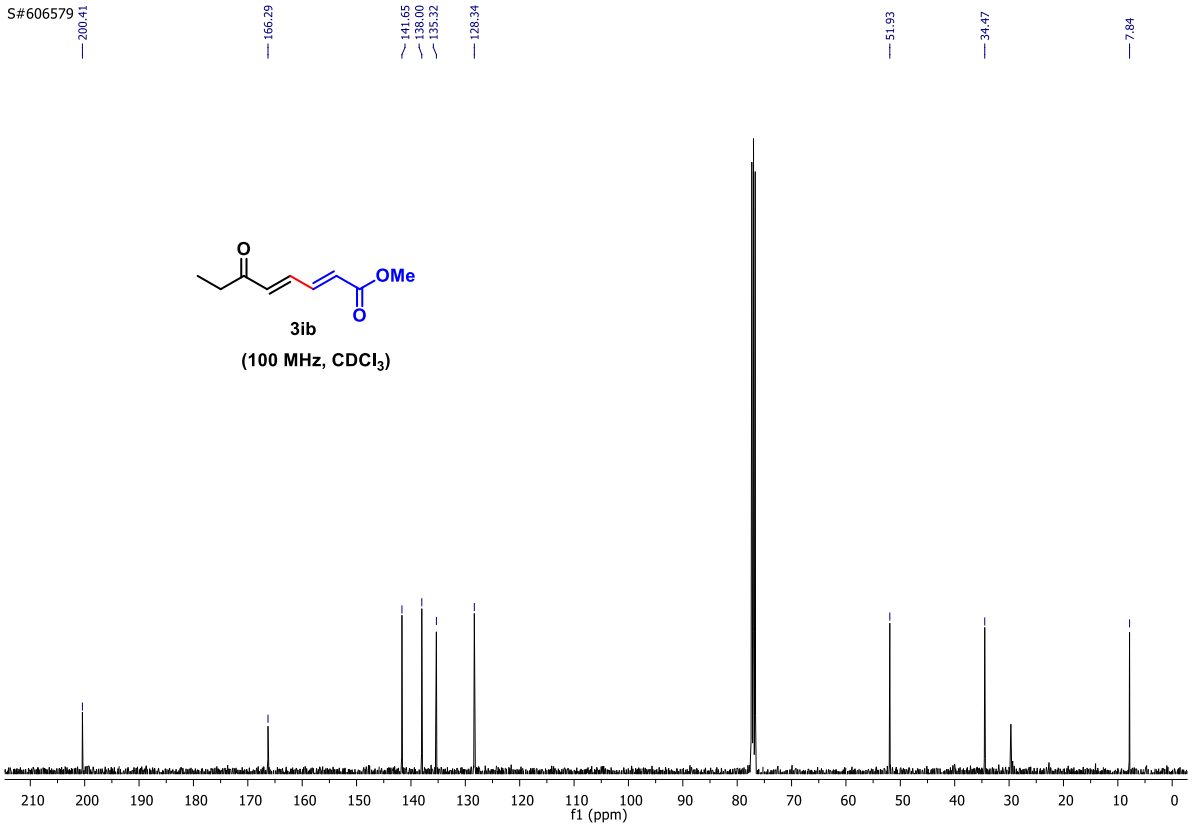
S#476746



3ib

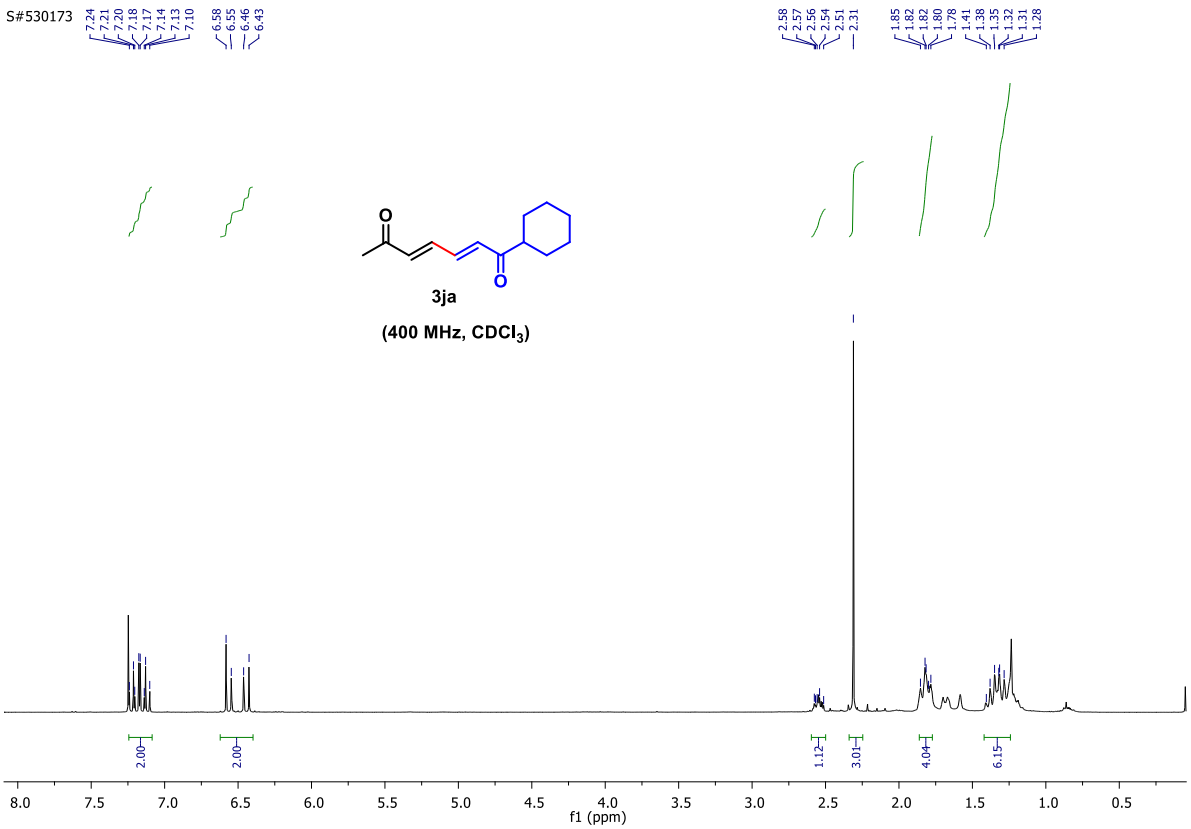
(400 MHz, $CDCl_3$)

S#606579



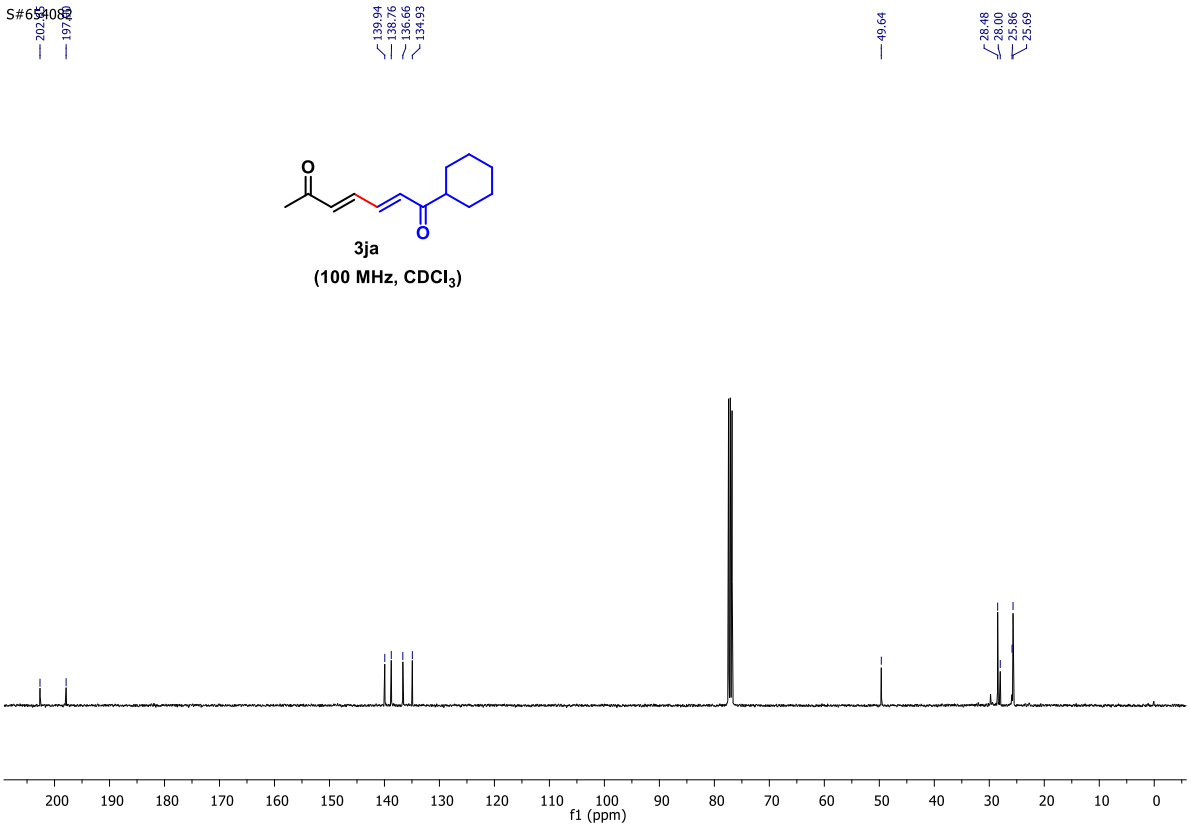
3ib

(100 MHz, $CDCl_3$)



3ja

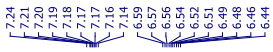
(400 MHz, $CDCl_3$)

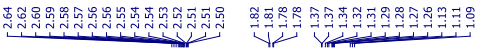


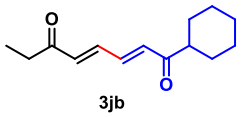
3ja

(100 MHz, $CDCl_3$)

S#332104

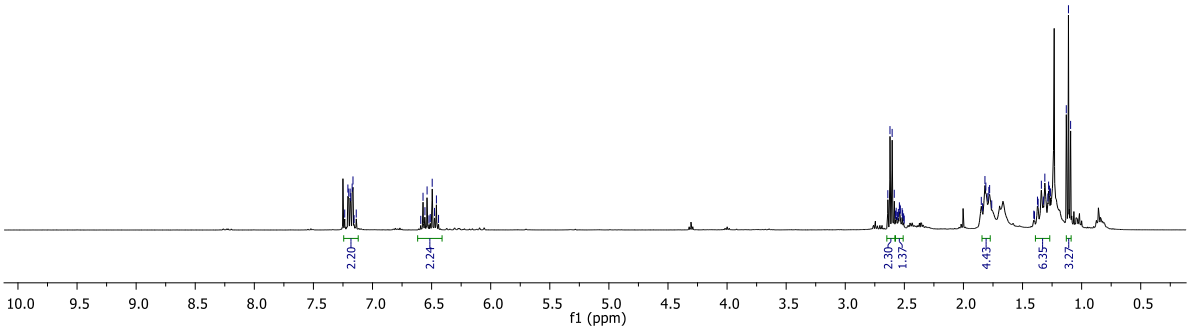




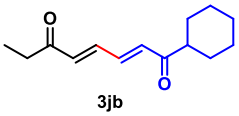


3jb

(400 MHz, $CDCl_3$)

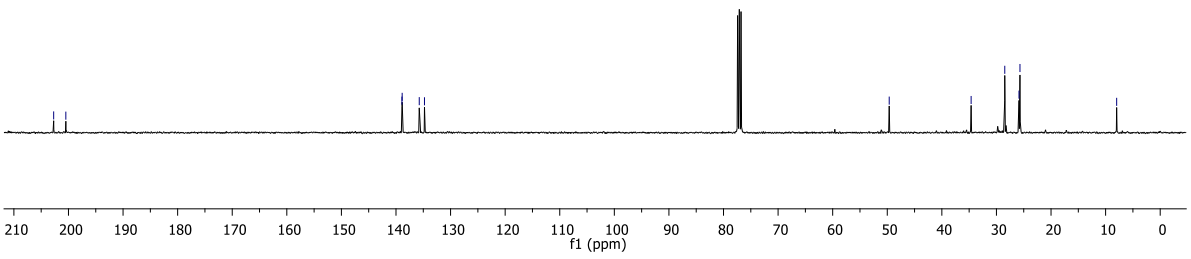


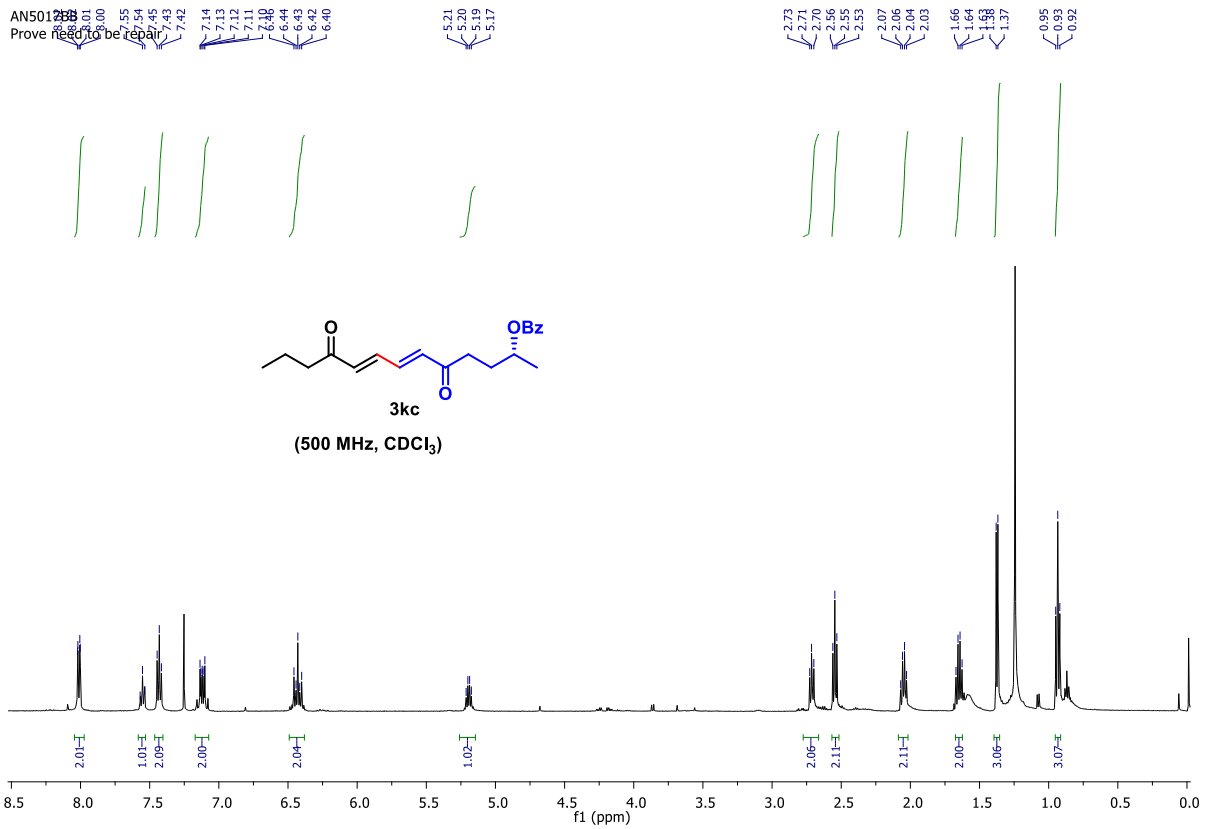
S#712256

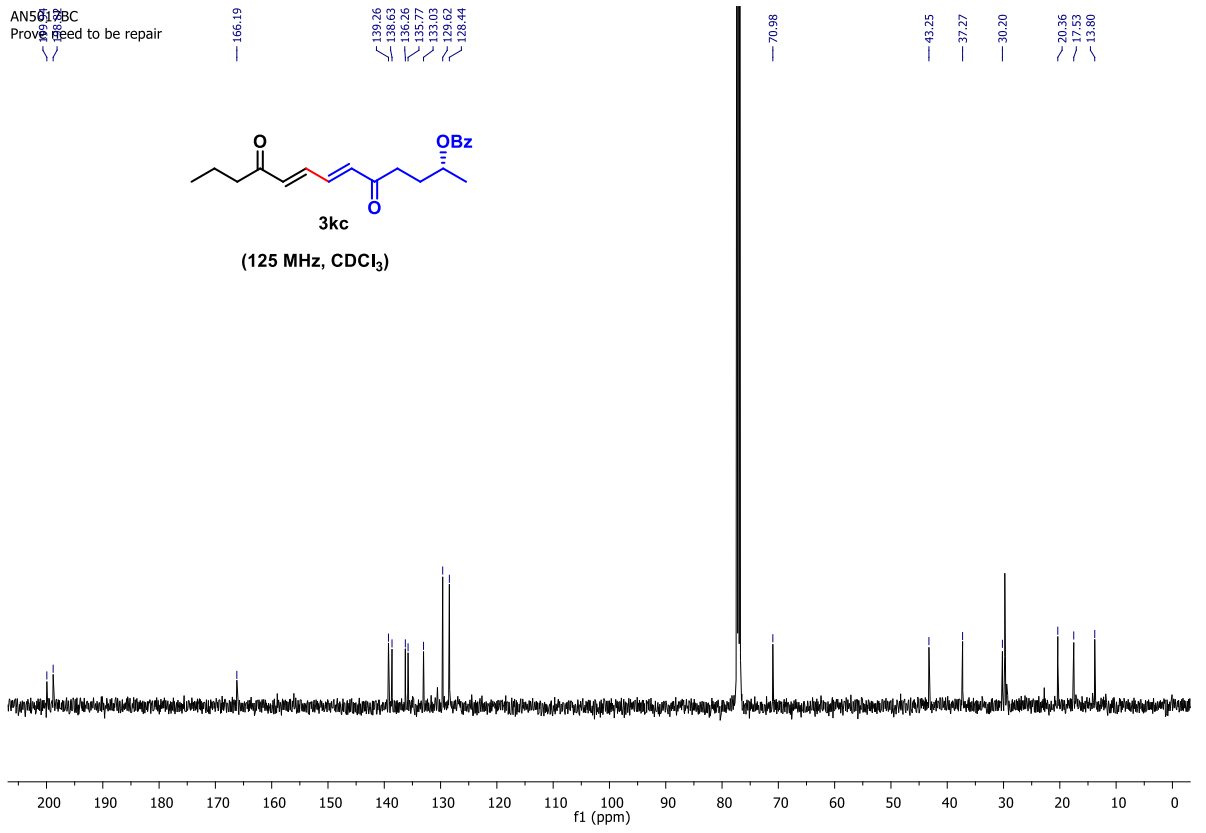


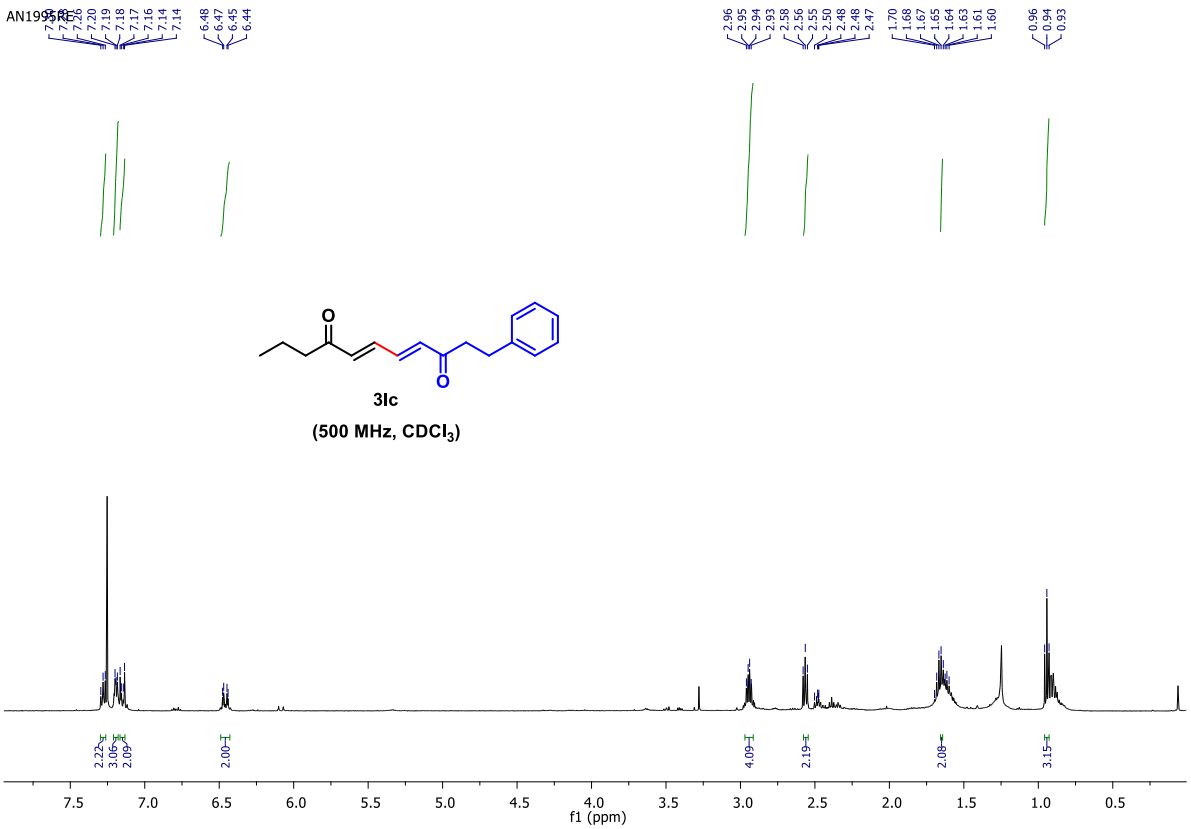
3jb

(100 MHz, $CDCl_3$)



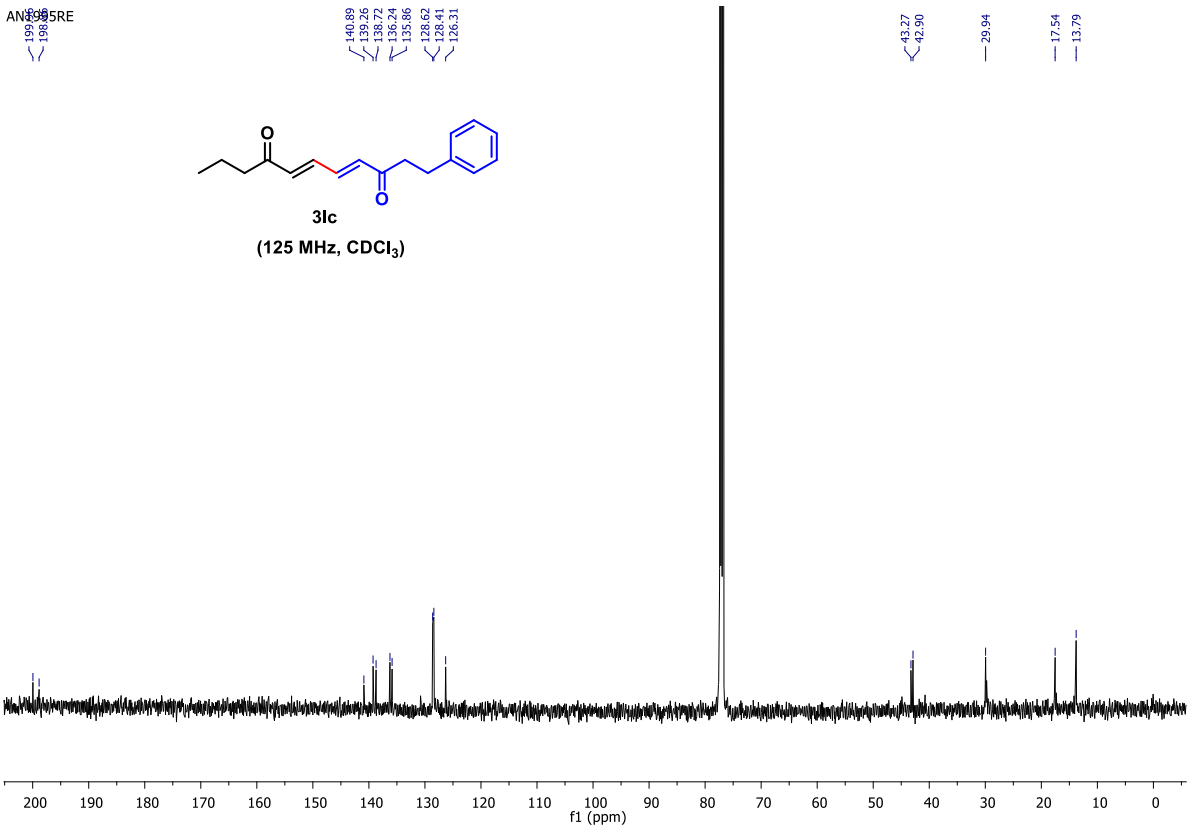

AN5012BB
Prove need to be repair
8.01
8.00
7.55
7.54
7.45
7.43
7.42
7.14
7.13
7.12
7.11
7.10
6.44
6.43
6.42
6.40
5.21
5.20
5.19
5.17
2.73
2.71
2.70
2.56
2.55
2.53
2.07
2.06
2.04
2.03
1.66
1.64
1.58
1.37
0.95
0.93
0.92
O
OBz
O
3kc
(500 MHz, CDCl3)
2.01
1.01
2.09
2.00
2.04
1.02
2.06
2.11
2.11
2.00
3.06
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


AN5012BC
Prove need to be repair
166.19
139.26
138.63
136.26
135.77
133.03
129.62
128.44
70.98
43.25
37.27
30.20
20.36
17.53
13.80
O
OBz
O
3kc
(125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



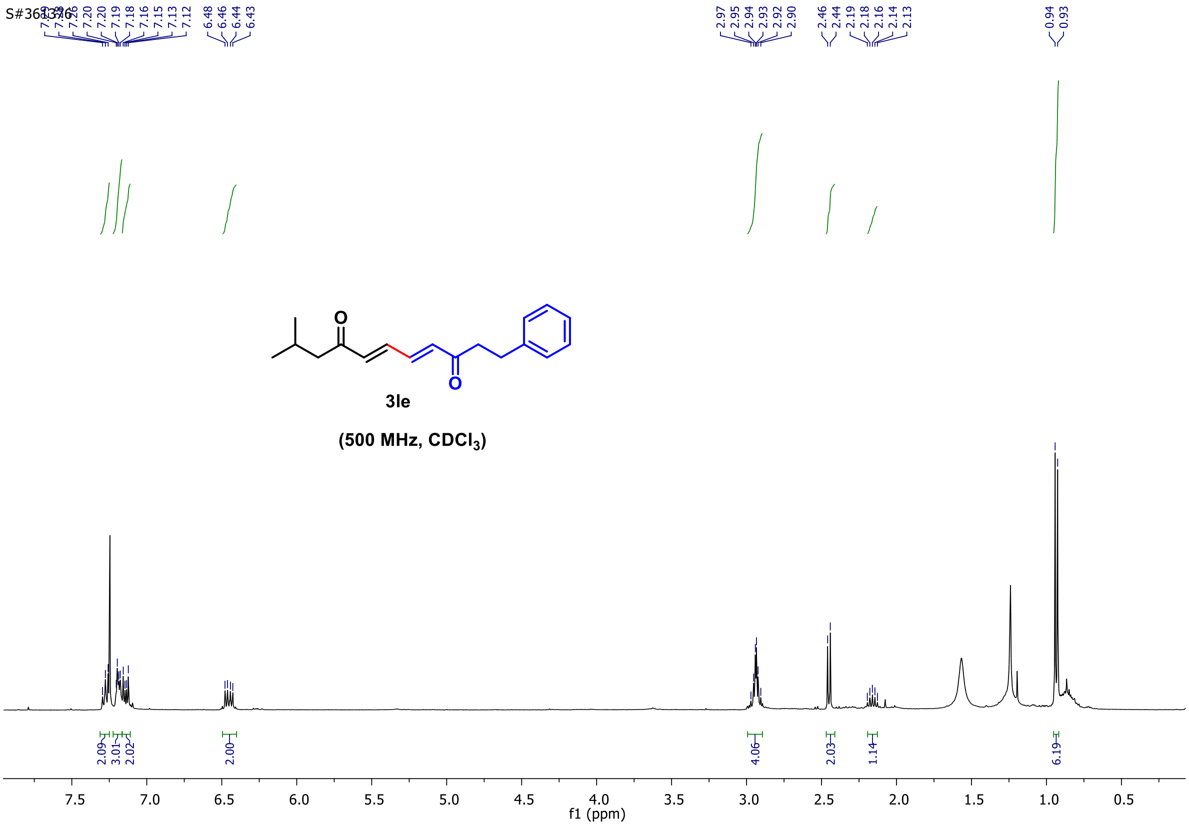
3Ic

(500 MHz, $CDCl_3$)

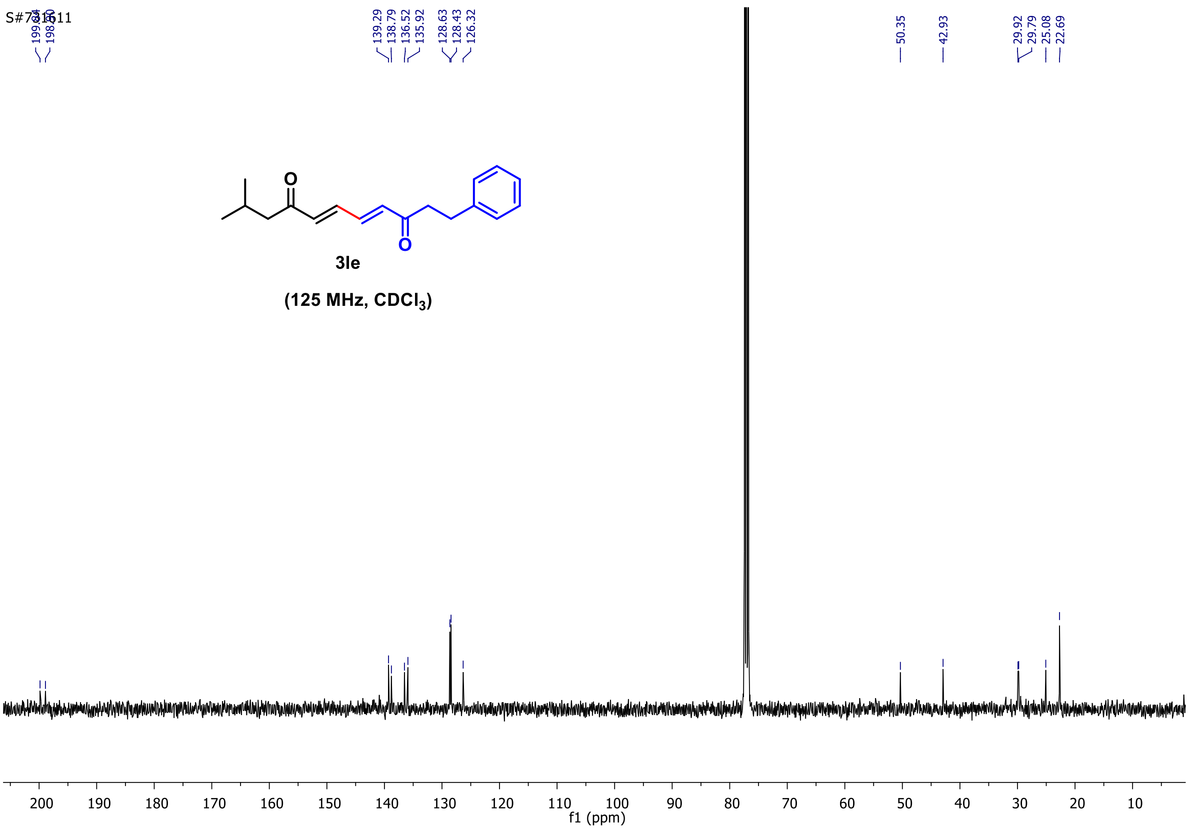


3Ic

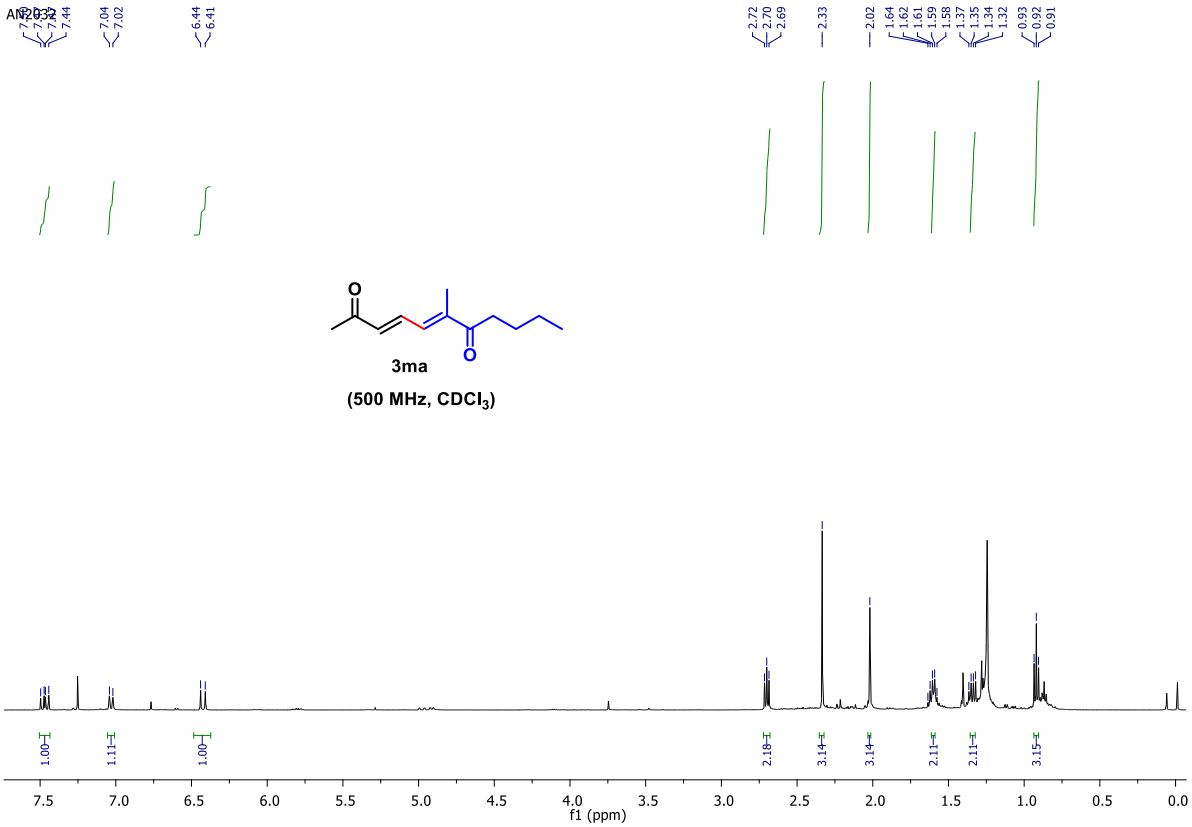
(125 MHz, $CDCl_3$)



3le
(500 MHz, CDCl3)
2.09 3.01 2.02 2.00 4.06 2.03 1.14 6.19
6.48 6.46 6.44 6.43
2.97 2.95 2.94 2.93 2.92 2.90
2.46 2.44 2.19 2.18 2.16 2.14 2.13
0.94 0.93
f1 (ppm)

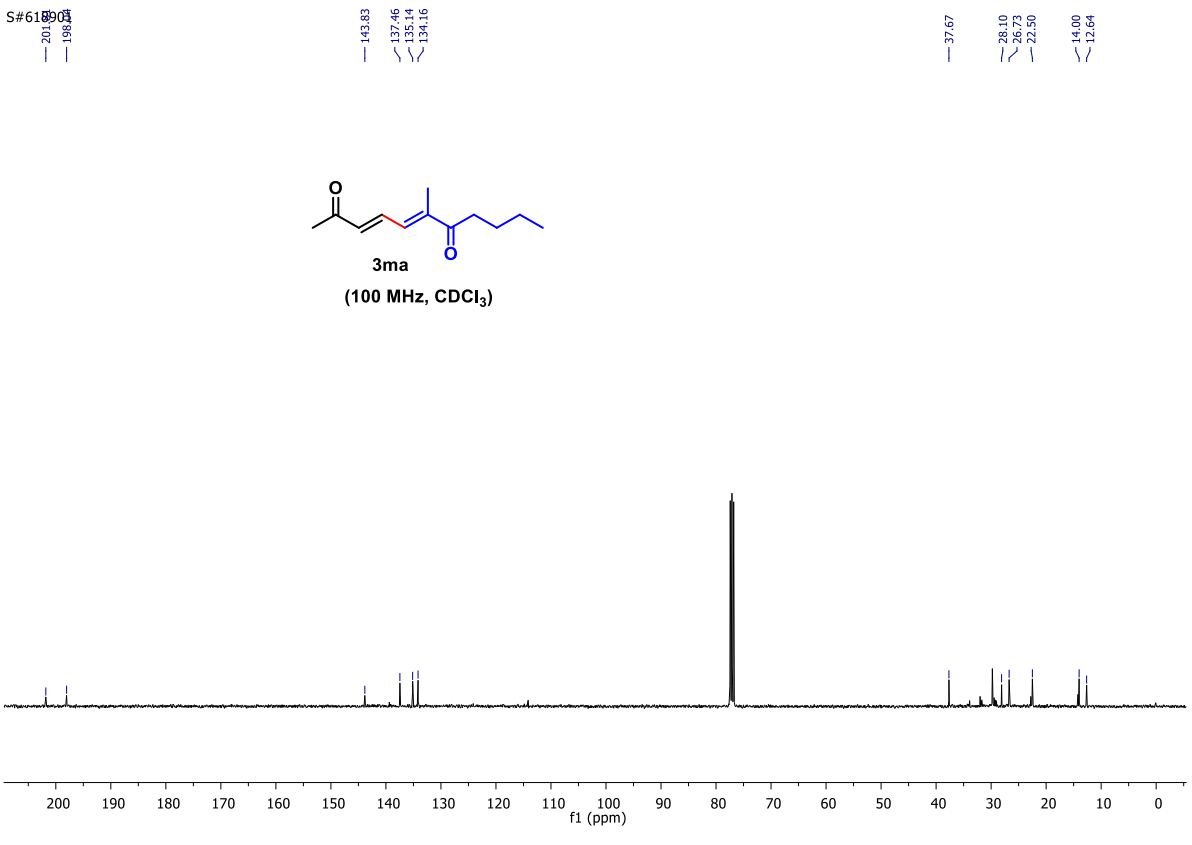


3le
(125 MHz, CDCl3)
139.29 138.79 136.52 135.92 128.63 128.43 126.32
50.35
42.93
29.92 29.79 25.08 22.69
f1 (ppm)



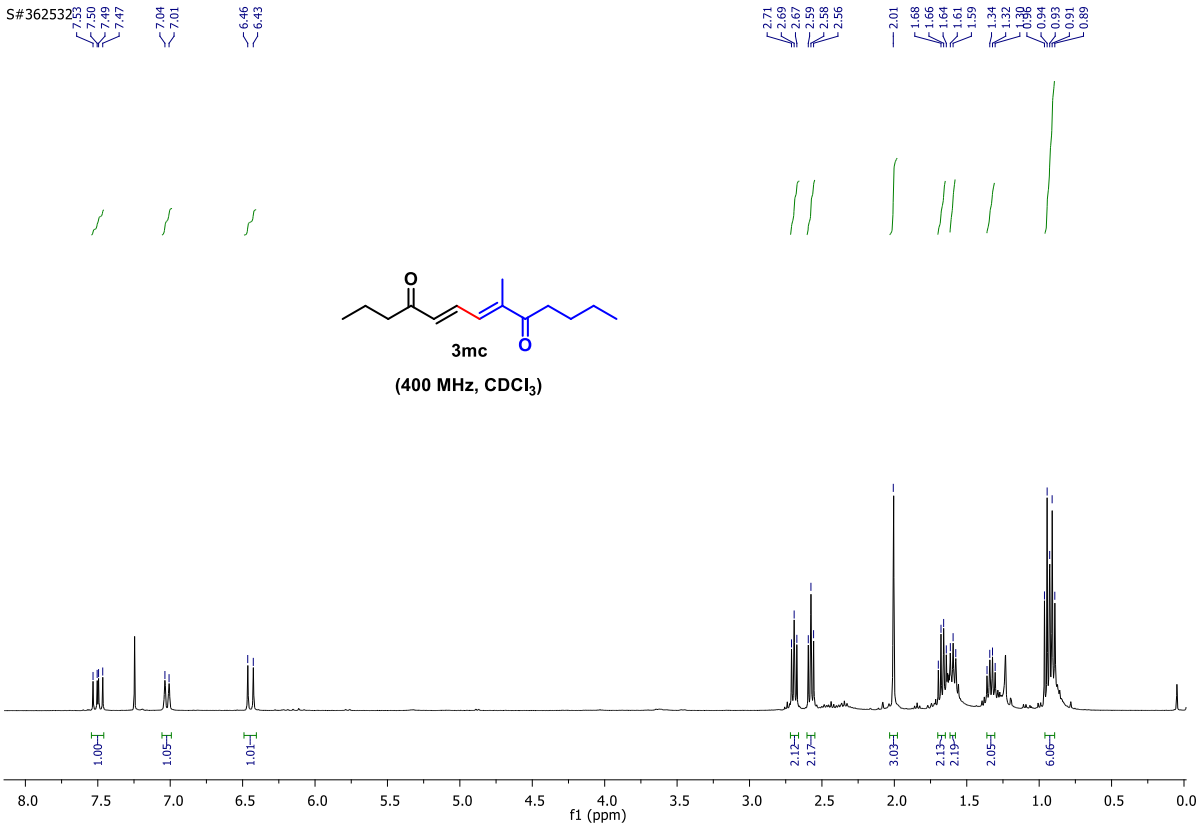
3ma

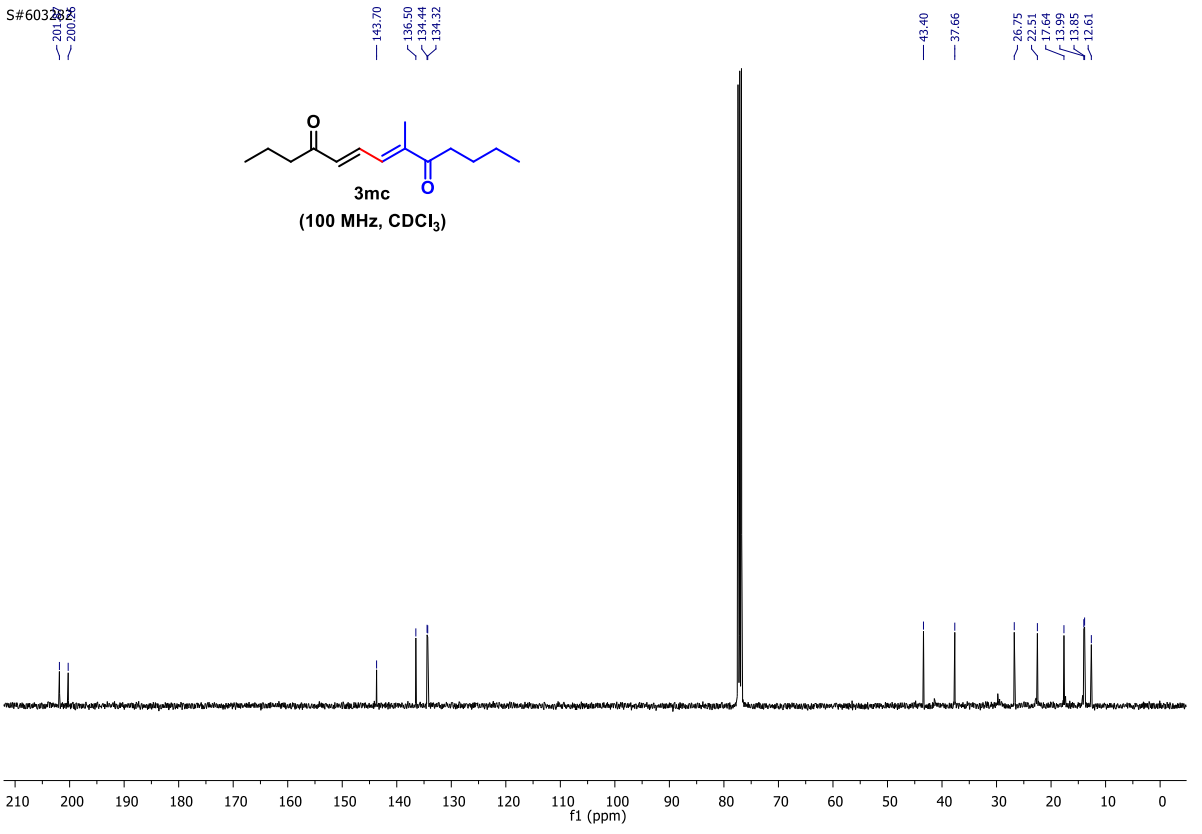
(500 MHz, $CDCl_3$)

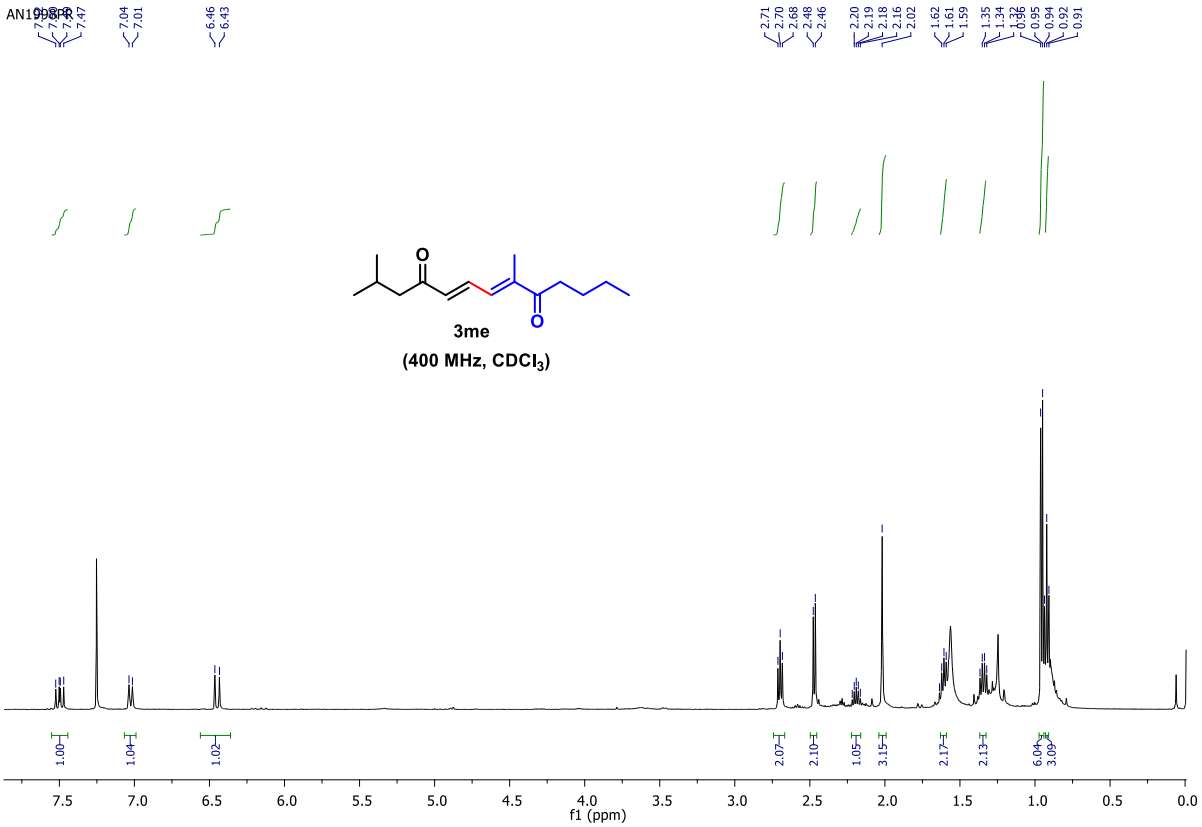


3ma

(100 MHz, $CDCl_3$)

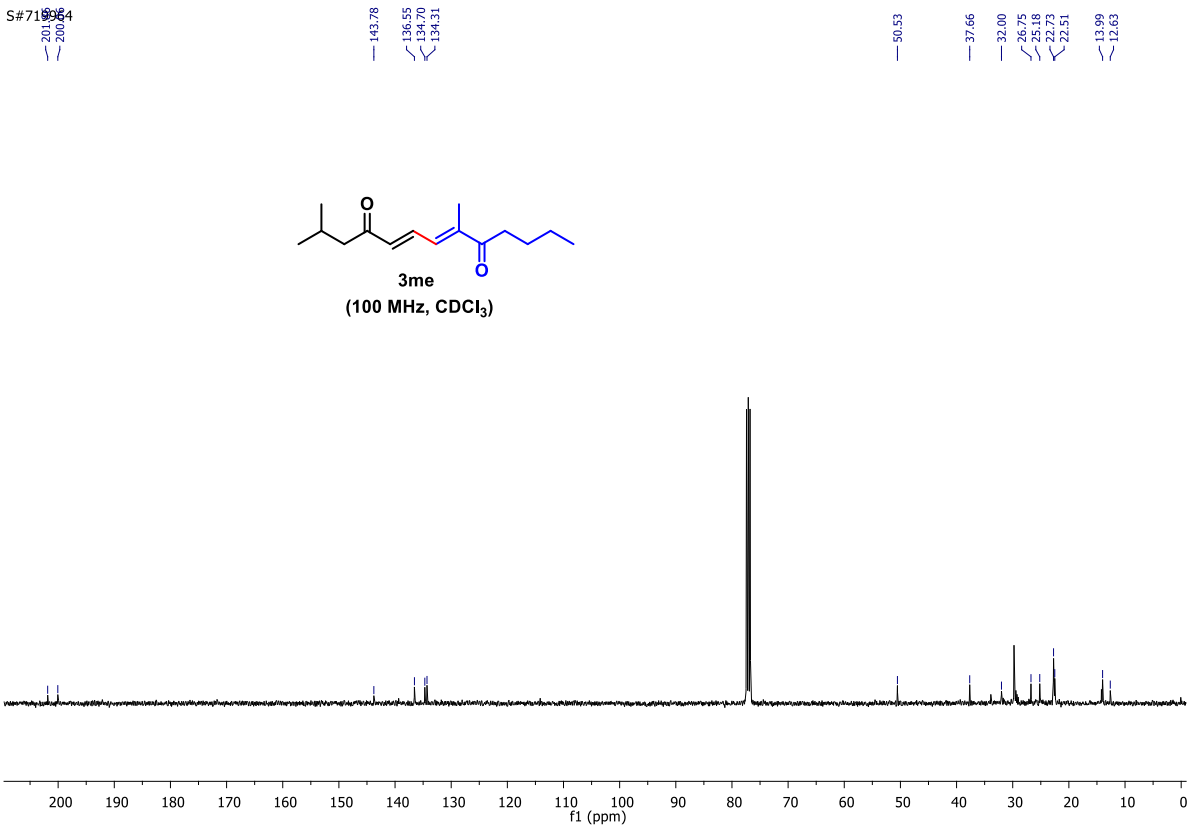

S#362532
7.53
7.50
7.49
7.47
7.04
7.01
6.46
6.43
2.71
2.69
2.67
2.59
2.58
2.56
2.01
1.68
1.66
1.64
1.61
1.59
1.34
1.32
1.30
0.94
0.93
0.91
0.89
O
O
3mc
(400 MHz, CDCl3)
1.00
1.05
1.01
2.12
2.17
3.03
2.13
2.19
2.05
6.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


S#603286
201.22
200.96
143.70
136.50
134.44
134.32
43.40
37.66
26.75
22.51
17.64
13.99
13.85
12.61
O
O
3mc
(100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



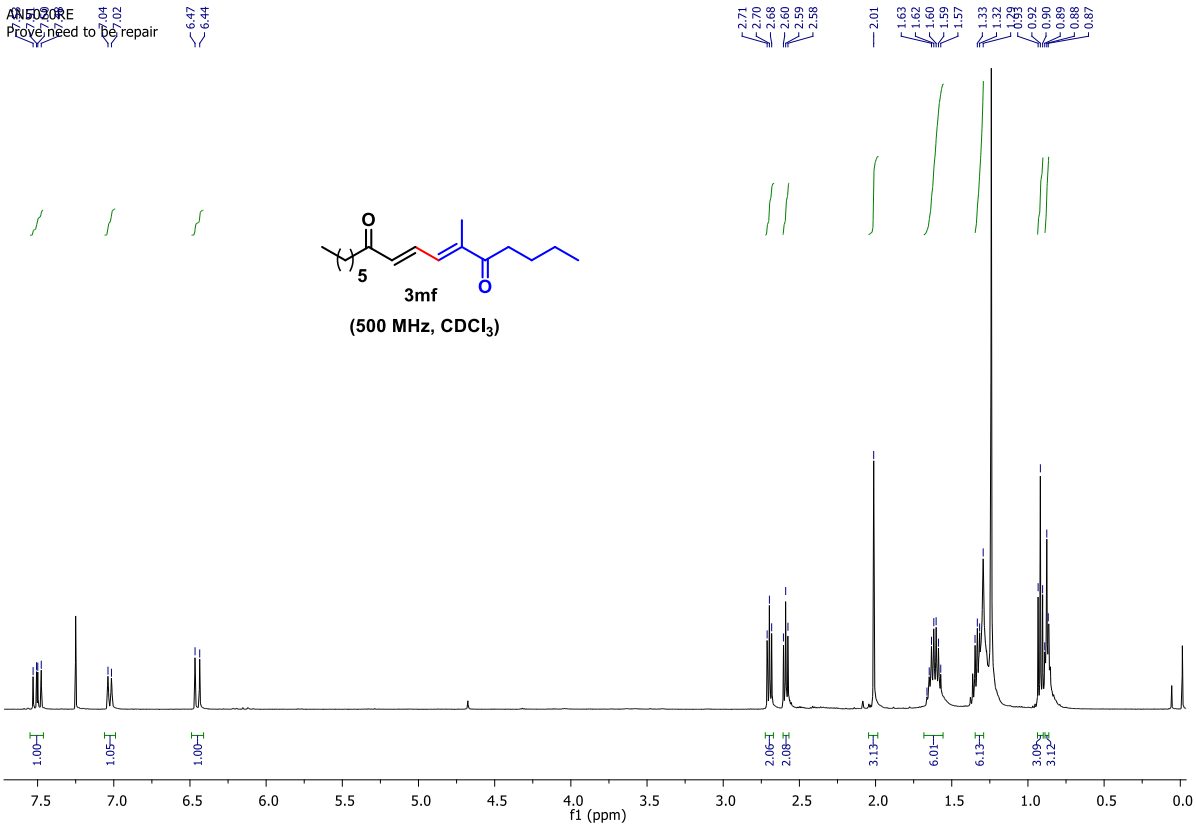
3me

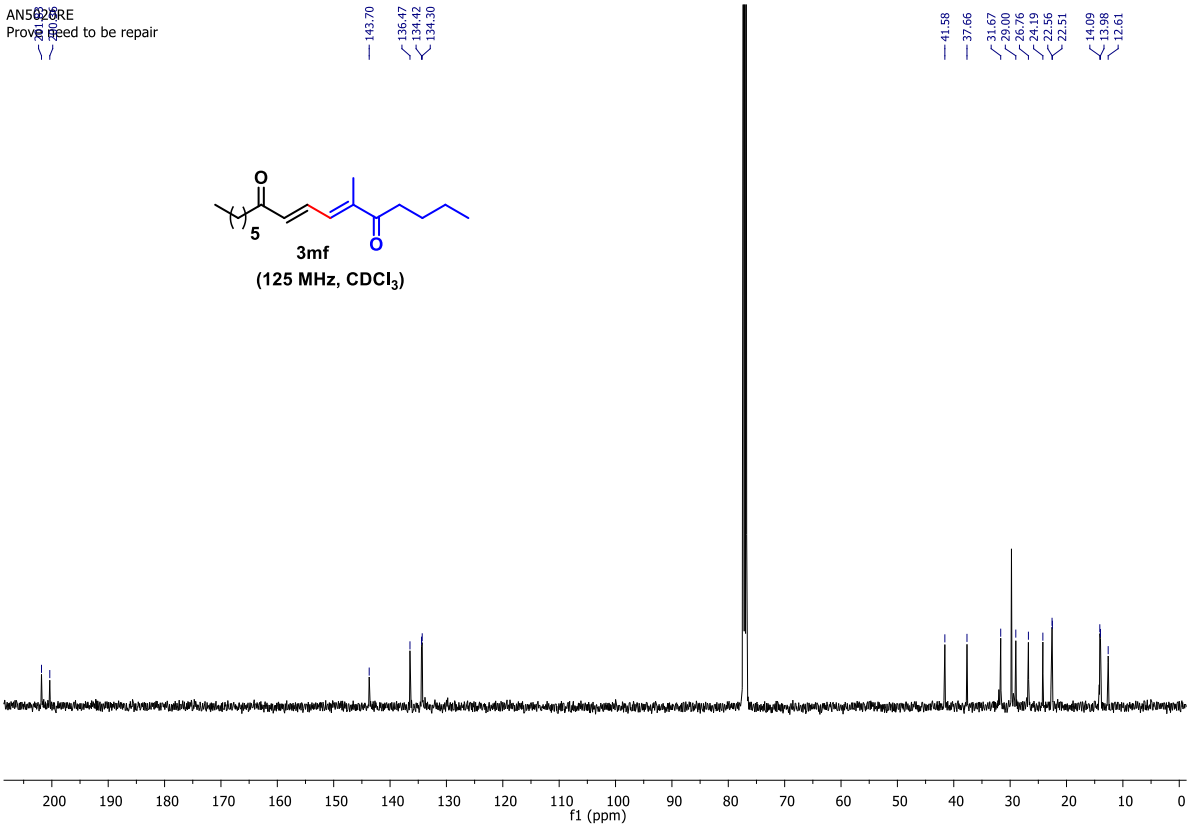
(400 MHz, $CDCl_3$)

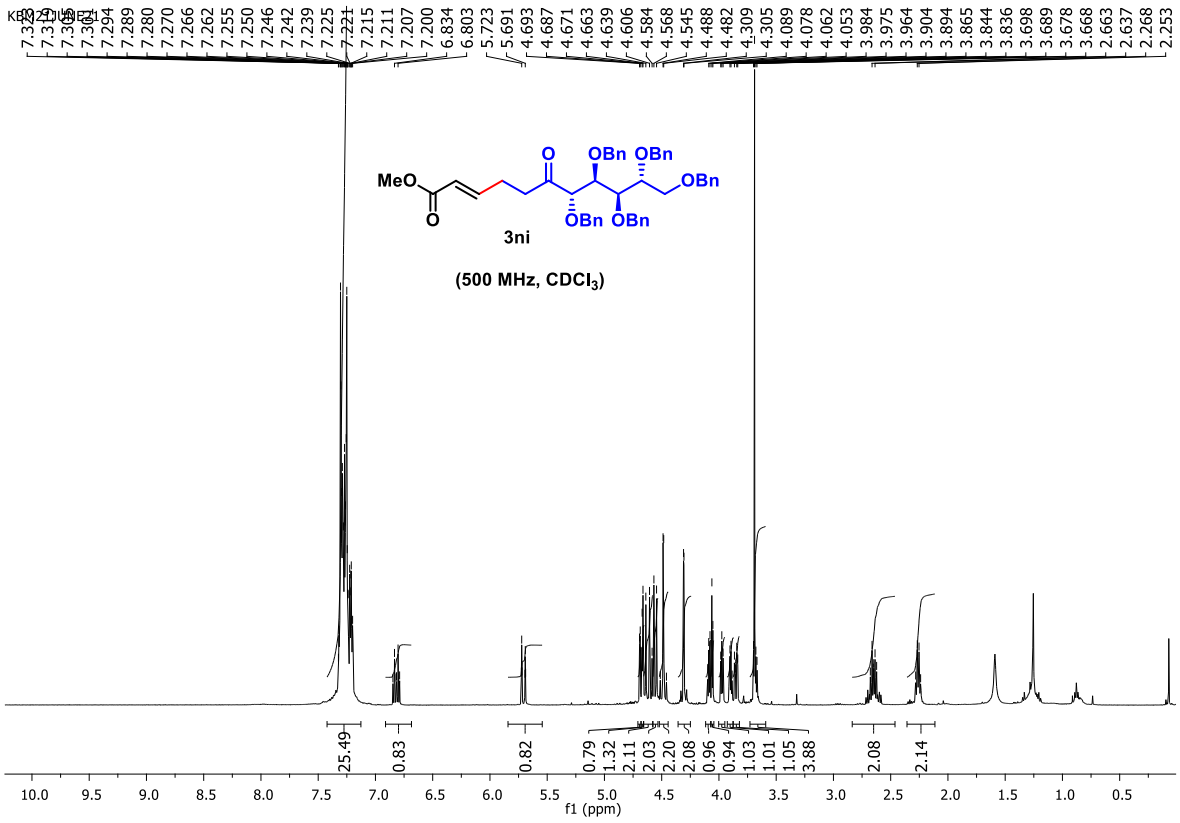


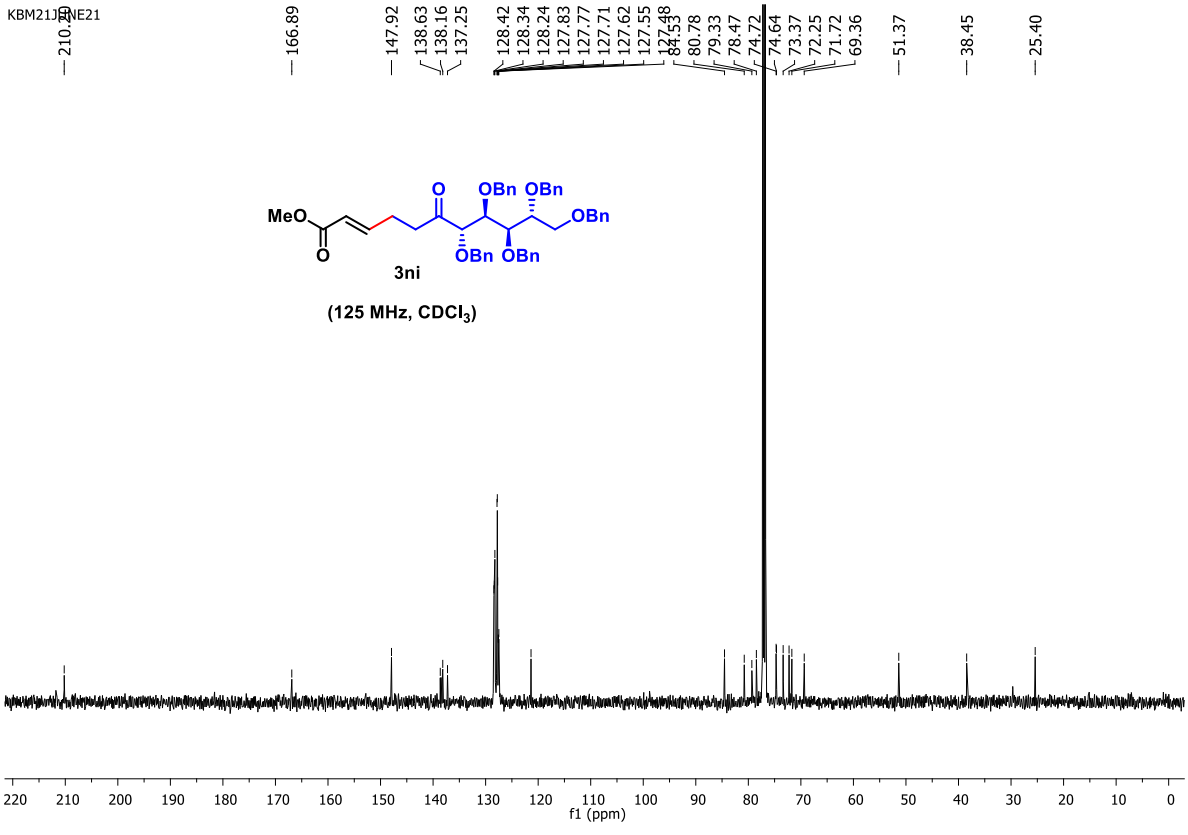
3me

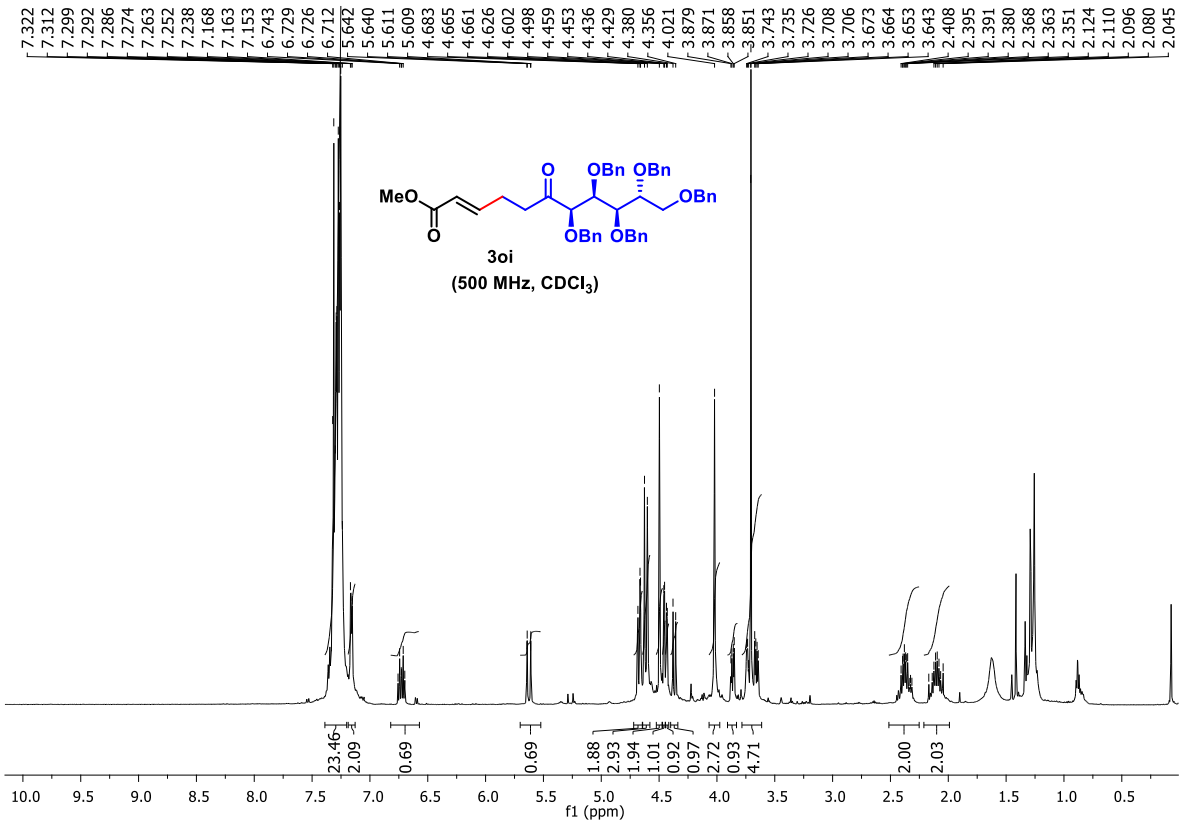
(100 MHz, $CDCl_3$)

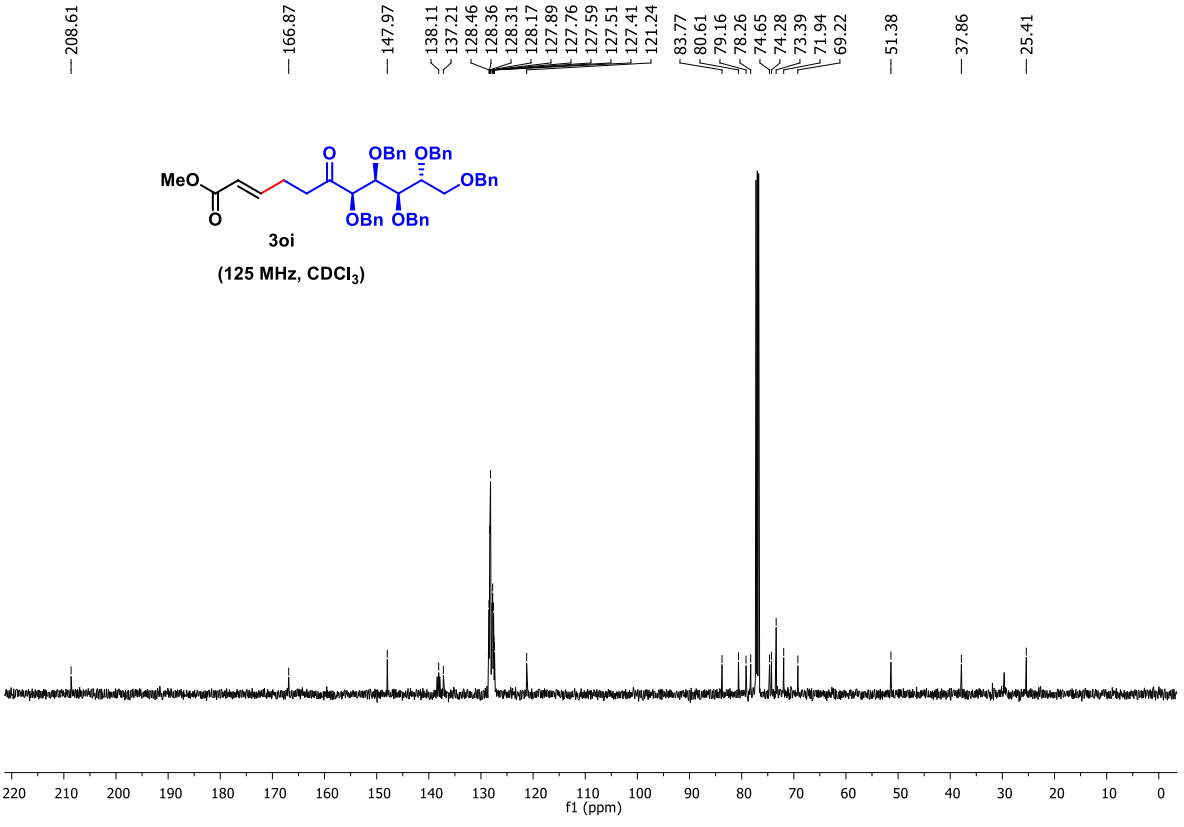

AN502OR
Prove need to be repair
3mf
(500 MHz, CDCl3)
f1 (ppm)

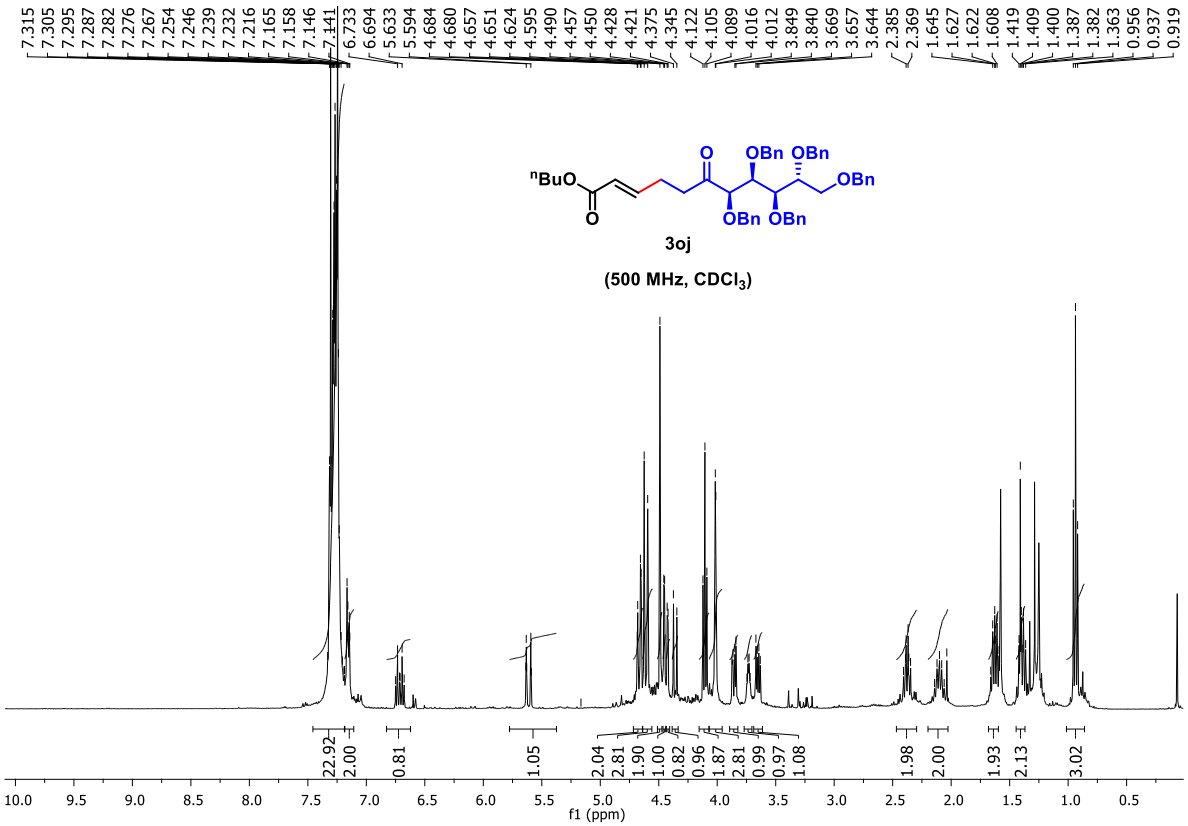

AN502OR
Prove need to be repair
3mf
(125 MHz, CDCl3)
f1 (ppm)

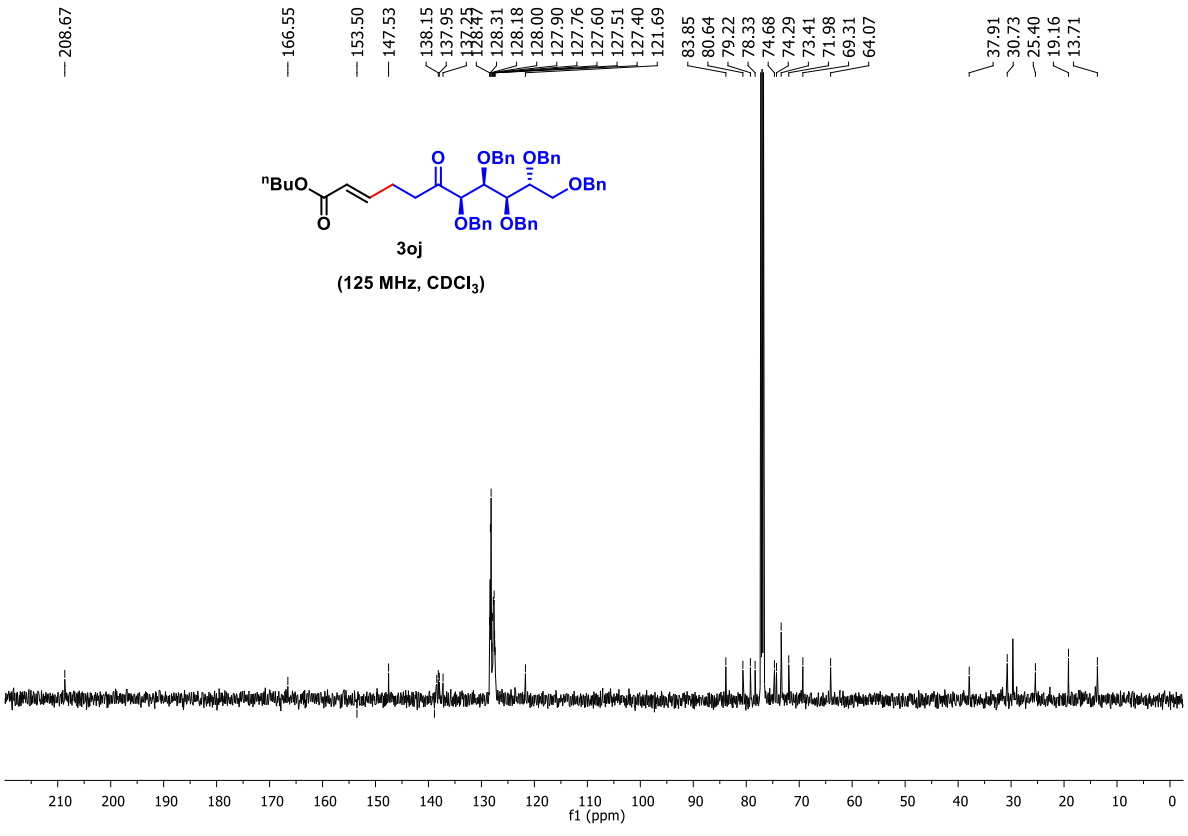

MeO
O
O
OBn OBn
OBn
OBn OBn
3ni
(500 MHz, CDCl3)
25.49
0.83
0.82
0.79
1.32
2.11
2.03
2.20
2.08
0.96
0.94
1.03
1.01
1.05
3.88
2.08
2.14
f1 (ppm)

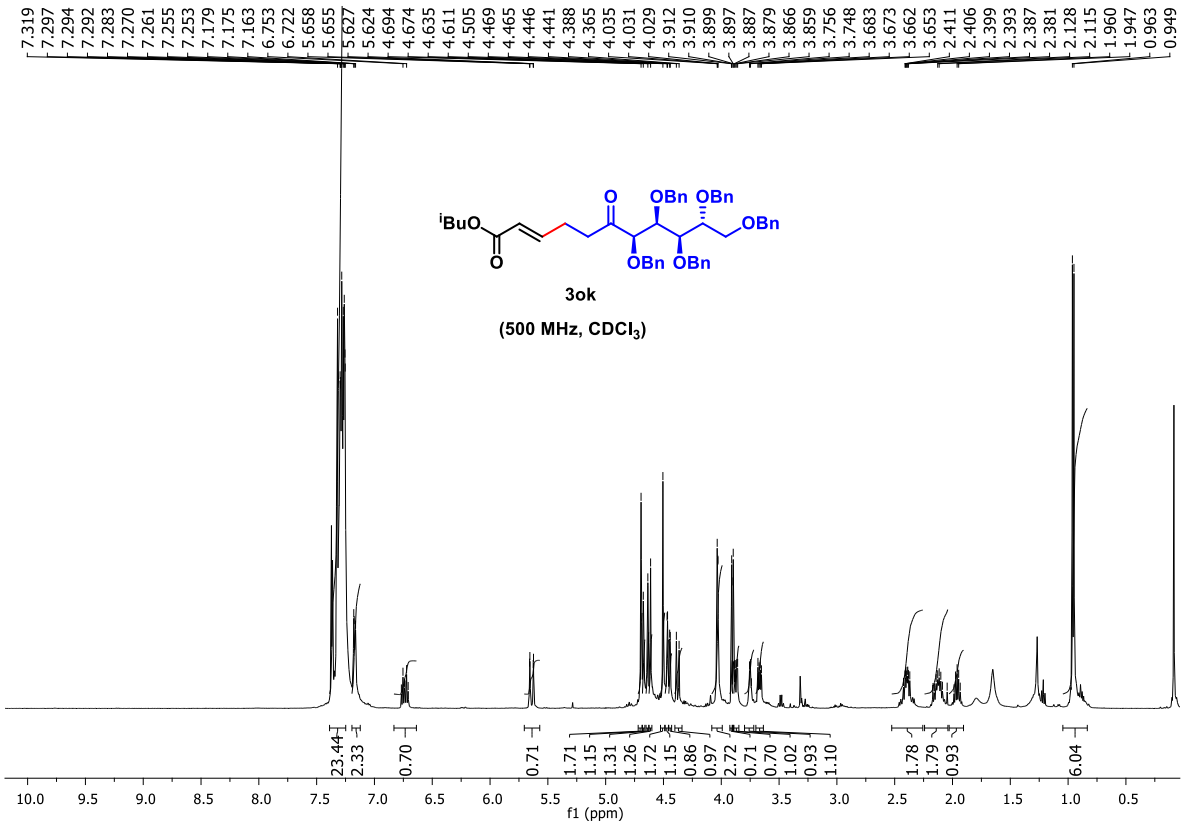

210.29
166.89
147.92
138.63
138.16
137.25
128.42
128.34
128.24
127.83
127.77
127.71
127.62
127.55
127.48
84.53
80.78
79.33
78.47
74.72
74.64
73.37
72.25
71.72
69.36
51.37
38.45
25.40
MeO
O
O
OBn OBn
OBn
OBn OBn
3ni
(125 MHz, CDCl3)
f1 (ppm)


7.322 7.312 7.299 7.292 7.286 7.274 7.263 7.252 7.238 7.168 7.163 7.153 6.743 6.729 6.726 6.712 5.642 5.640 5.611 5.609 4.683 4.665 4.661 4.626 4.602 4.498 4.459 4.453 4.436 4.429 4.380 4.356 4.021 3.879 3.871 3.858 3.851 3.743 3.735 3.726 3.708 3.706 3.673 3.664 3.653 3.643 2.408 2.395 2.391 2.380 2.368 2.363 2.351 2.124 2.110 2.096 2.080 2.045
MeO
O
O
OBn OBn
OBn
OBn OBn
3oi
(500 MHz, CDCl3)
23.46 2.09 0.69 0.69 1.88 2.93 1.94 1.01 0.92 0.97 2.72 0.93 4.71 2.00 2.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


208.61 166.87 147.97 138.11 137.21 128.46 128.36 128.31 128.17 127.89 127.76 127.59 127.51 127.41 121.24 83.77 80.61 79.16 78.26 74.65 74.28 73.39 71.94 69.22 51.38 37.86 25.41
MeO
O
O
OBn OBn
OBn
OBn OBn
3oi
(125 MHz, CDCl3)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

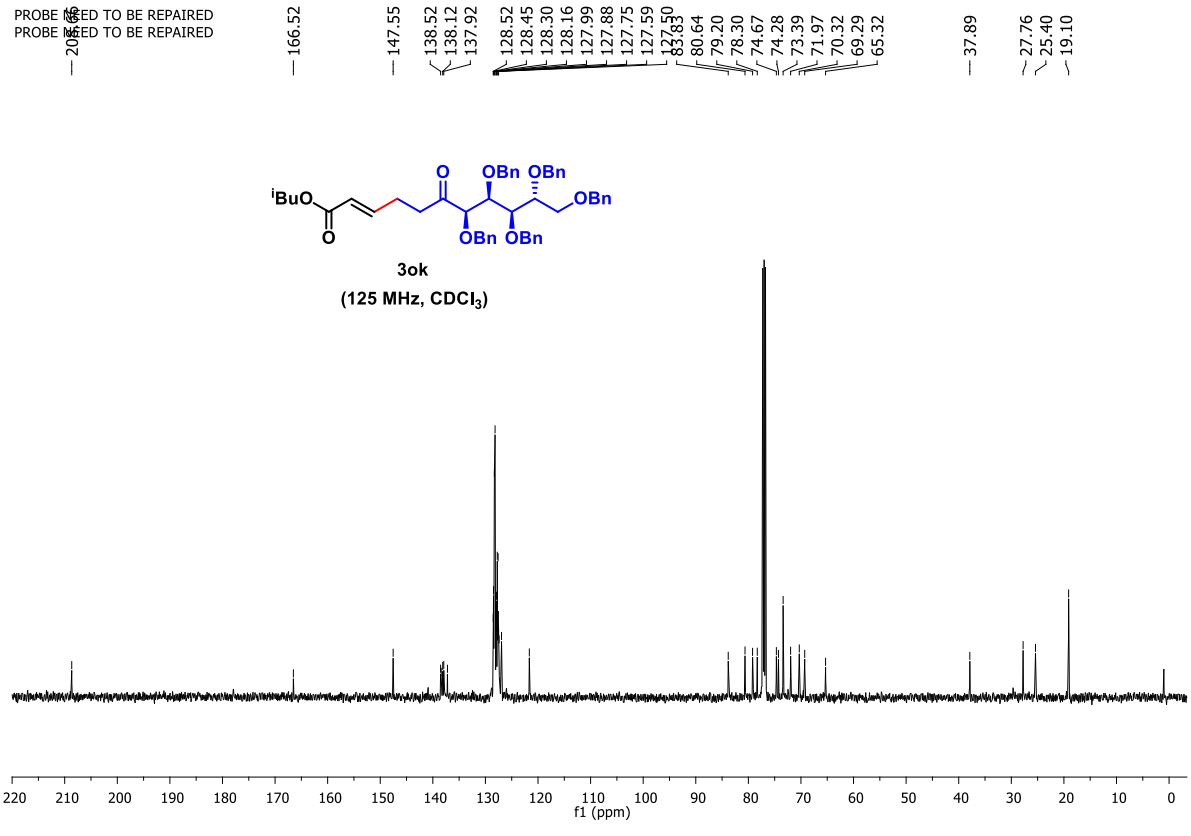

7.315 7.305 7.295 7.287 7.282 7.276 7.267 7.254 7.246 7.239 7.232 7.216 7.165 7.158 7.146 7.141 6.733 6.694 5.633 5.594 4.684 4.680 4.657 4.651 4.624 4.595 4.490 4.457 4.450 4.428 4.421 4.375 4.345 4.122 4.105 4.089 4.016 4.012 3.849 3.840 3.669 3.657 3.644 2.385 2.369 1.645 1.627 1.622 1.608 1.419 1.409 1.400 1.387 1.382 1.363 0.956 0.937 0.919
nBuO
O
O
OBn OBn
OBn
OBn OBn
3oj
(500 MHz, CDCl3)
22.92 2.00 0.81 1.05 2.04 2.81 1.90 1.00 0.82 0.96 1.87 2.81 0.99 0.97 1.08 1.98 2.00 1.93 2.13 3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


208.67 166.55 153.50 147.53 138.15 137.95 137.25 128.47 128.31 128.18 128.00 127.90 127.76 127.60 127.51 127.40 121.69 83.85 80.64 79.22 78.33 74.68 74.29 73.41 71.98 69.31 64.07 37.91 30.73 25.40 19.16 13.71
nBuO
O
O
OBn OBn
OBn
OBn OBn
3oj
(125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



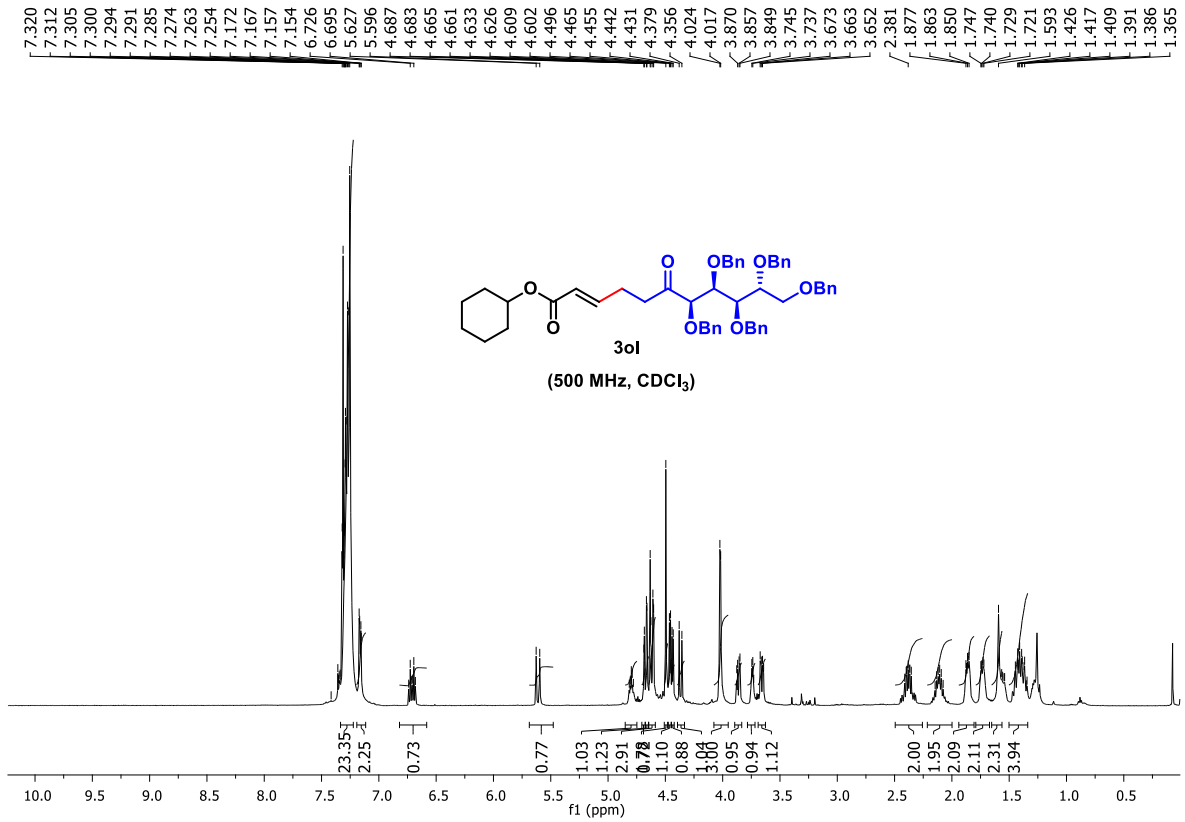
3ok

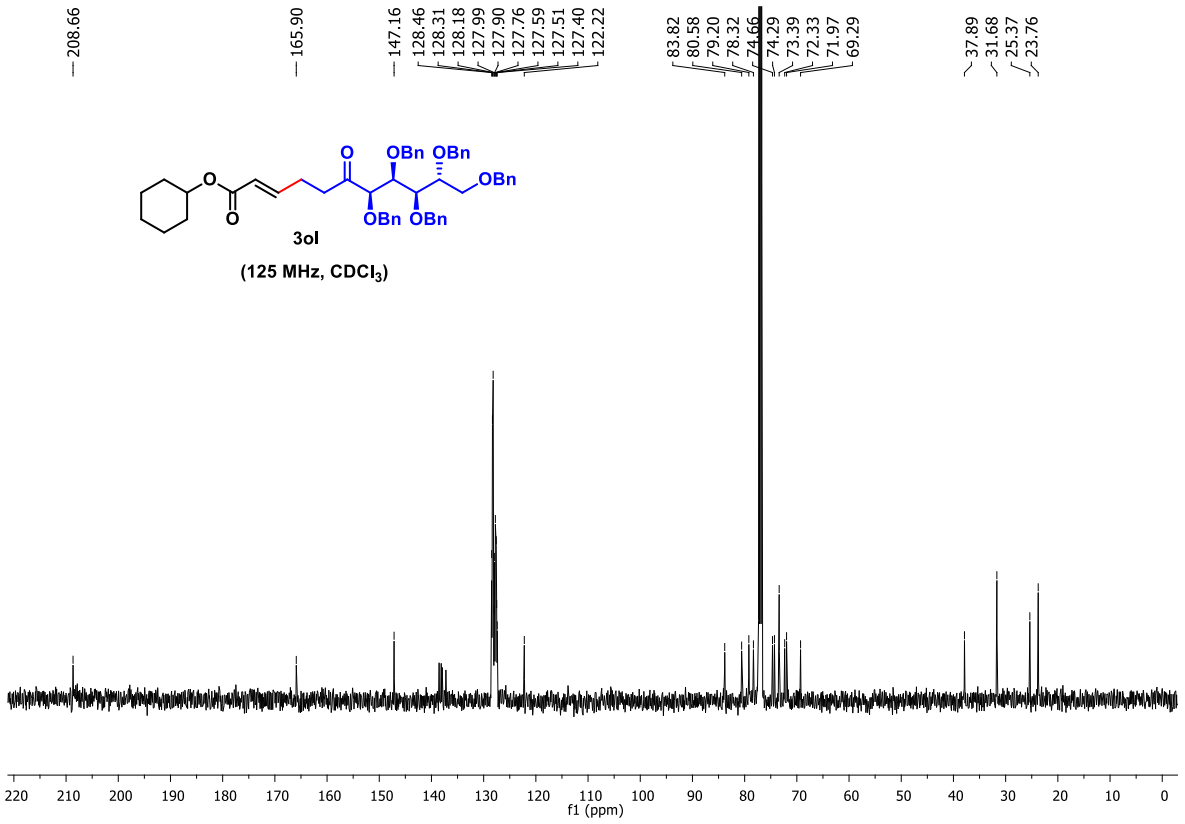
(500 MHz, $CDCl_3$)



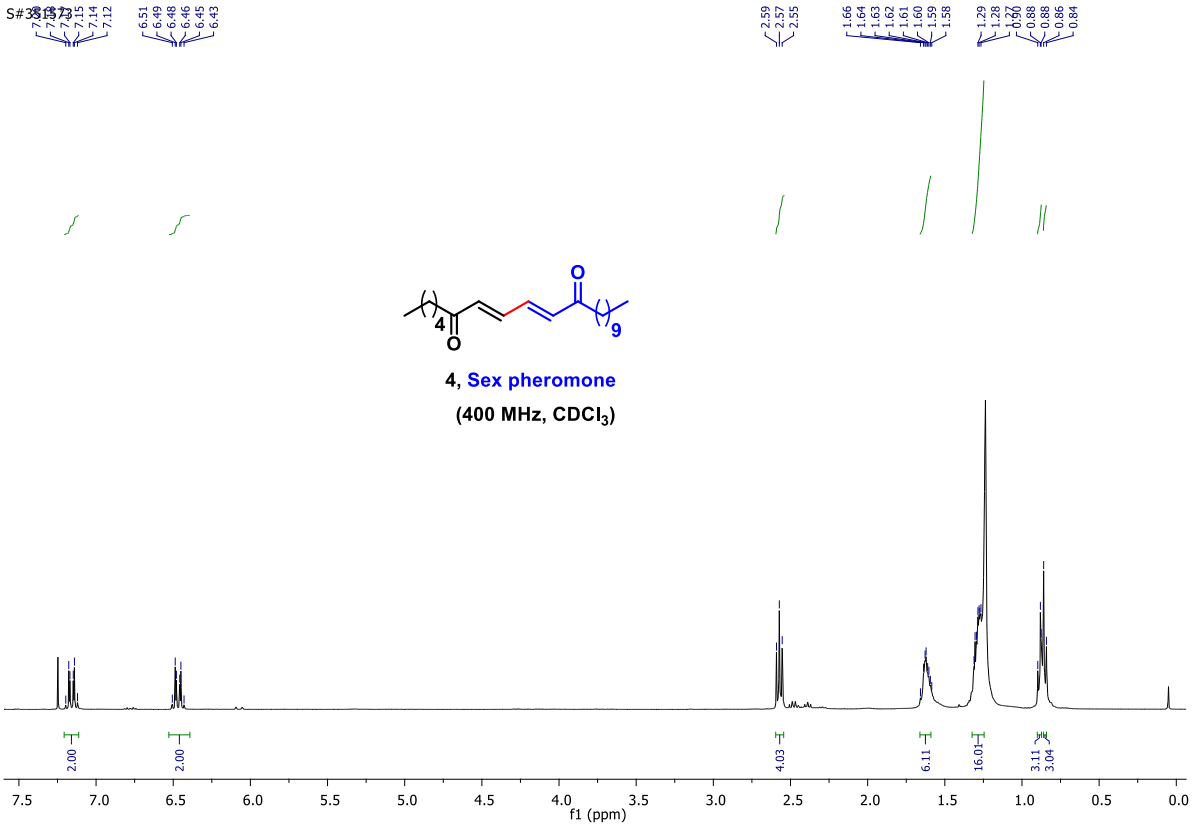
3ok

(125 MHz, $CDCl_3$)


7.320
7.312
7.305
7.300
7.294
7.291
7.285
7.274
7.263
7.254
7.172
7.167
7.157
7.154
6.726
6.695
5.627
5.596
4.687
4.683
4.665
4.661
4.633
4.626
4.609
4.602
4.496
4.465
4.455
4.442
4.431
4.379
4.356
4.024
4.017
3.870
3.857
3.849
3.745
3.737
3.673
3.663
3.652
2.381
1.877
1.863
1.850
1.747
1.740
1.729
1.721
1.593
1.426
1.417
1.409
1.391
1.386
1.365
O
OBn OBn
OBn
O
O
OBn OBn
3ol
(500 MHz, CDCl3)
23.35
2.25
0.73
0.77
1.03
1.23
2.91
1.10
0.88
1.04
3.00
0.95
0.94
1.12
2.00
1.95
2.09
2.11
2.31
3.94
f1 (ppm)

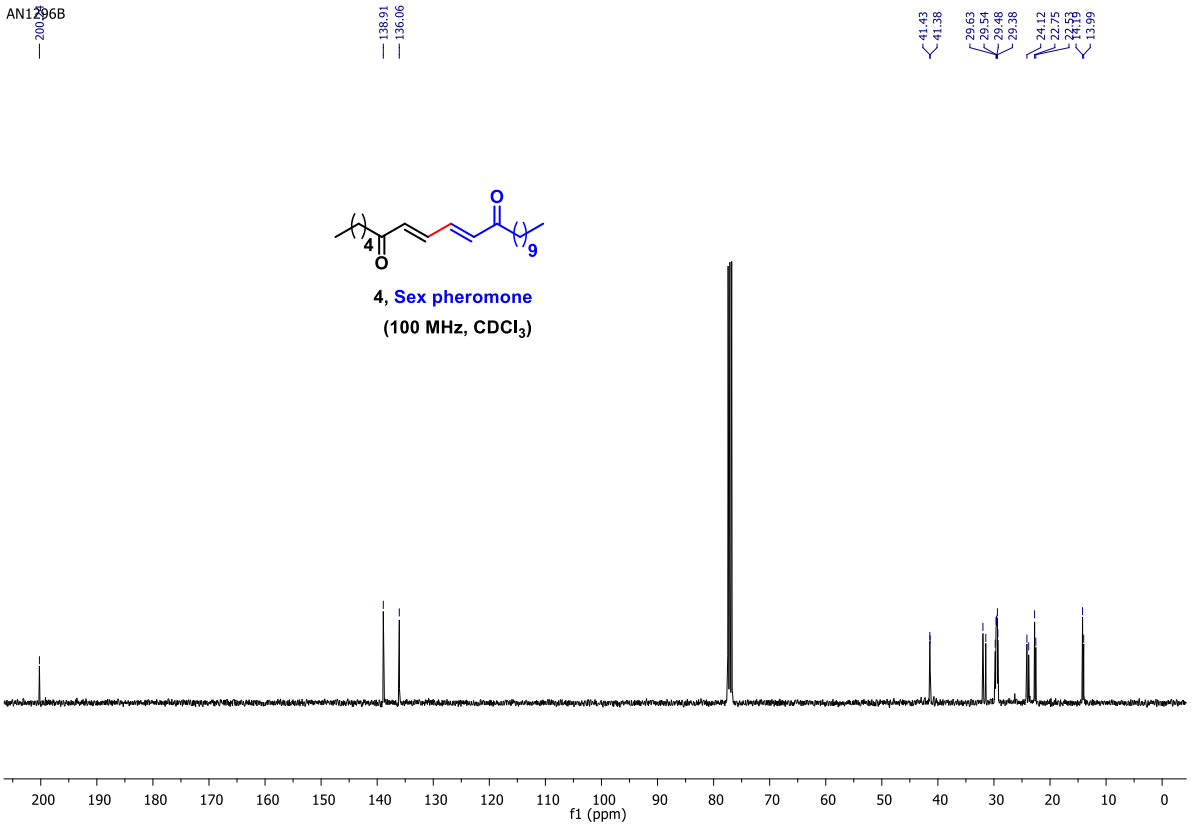

208.66
165.90
147.16
128.46
128.31
128.18
127.99
127.90
127.76
127.59
127.51
127.40
122.22
83.82
80.58
79.20
78.32
74.66
74.29
73.39
72.33
71.97
69.29
37.89
31.68
25.37
23.76
O
OBn OBn
OBn
O
O
OBn OBn
3ol
(125 MHz, CDCl3)
f1 (ppm)

6. ^{1}H and ^{13}C NMR Spectra for the bioactive natural products 4, 5, 6 and 7



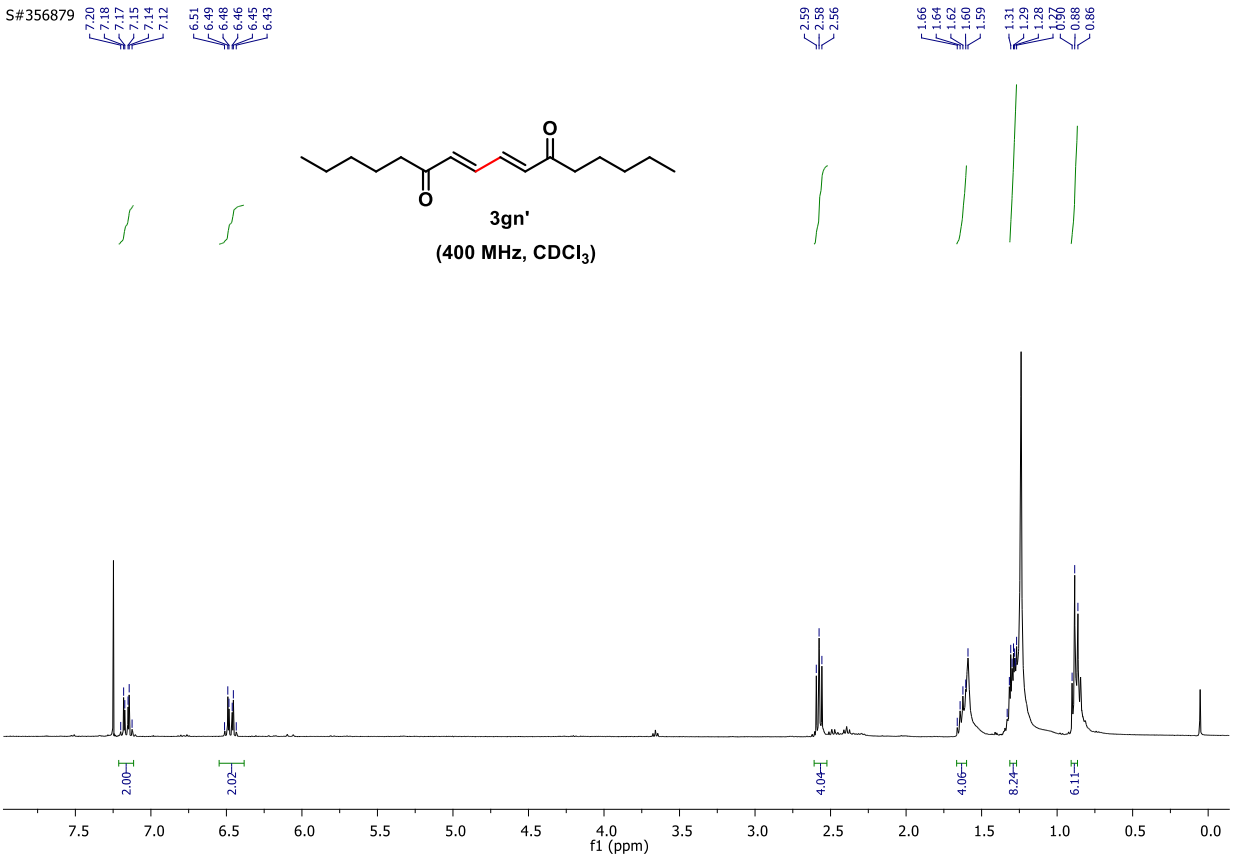
4, Sex pheromone

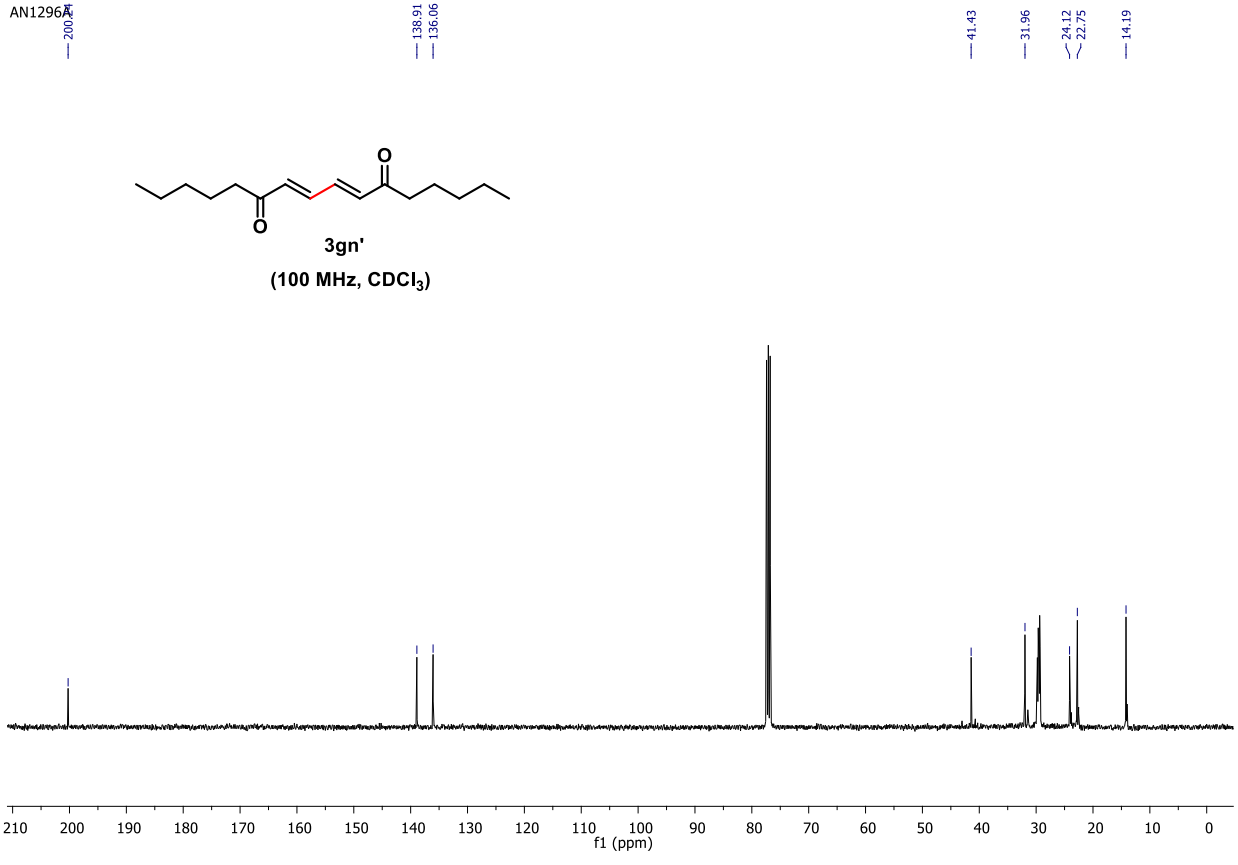
(400 MHz, $CDCl_3$)

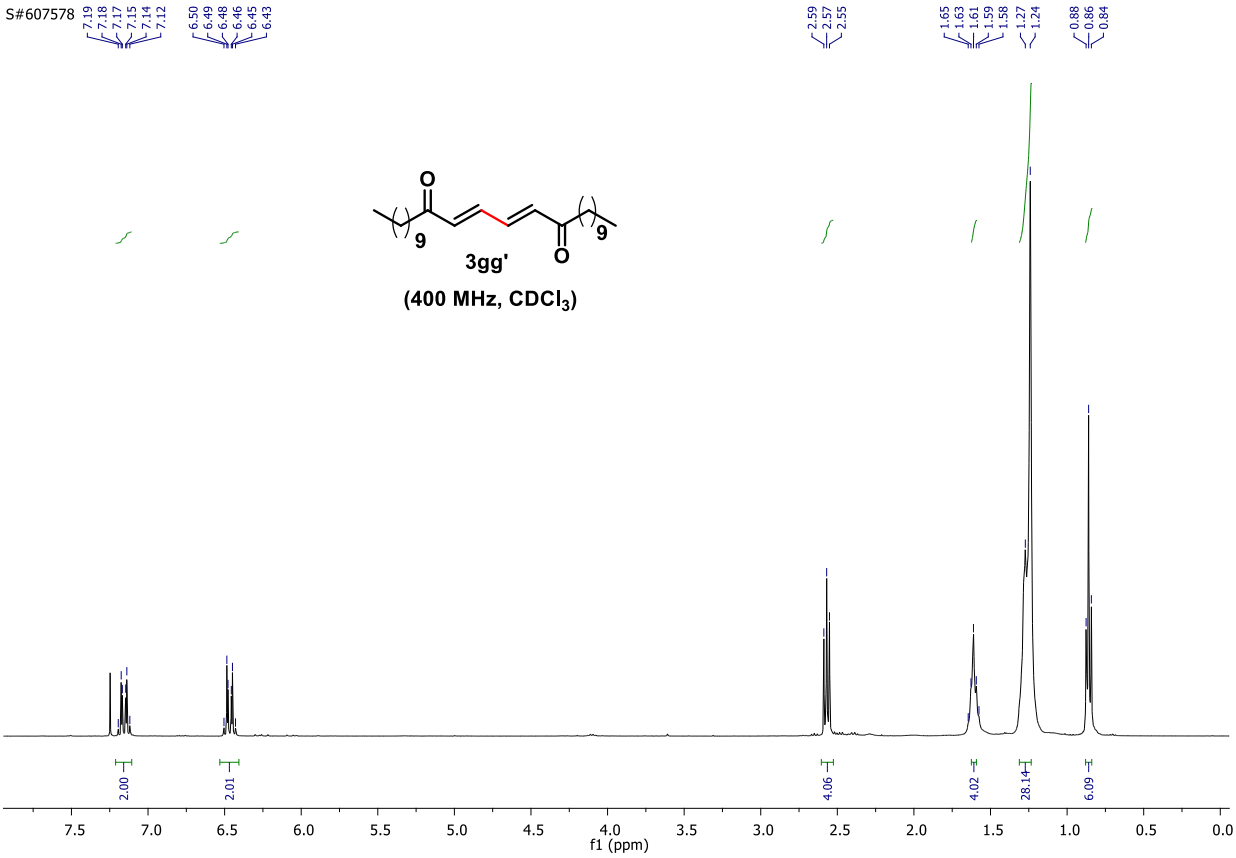


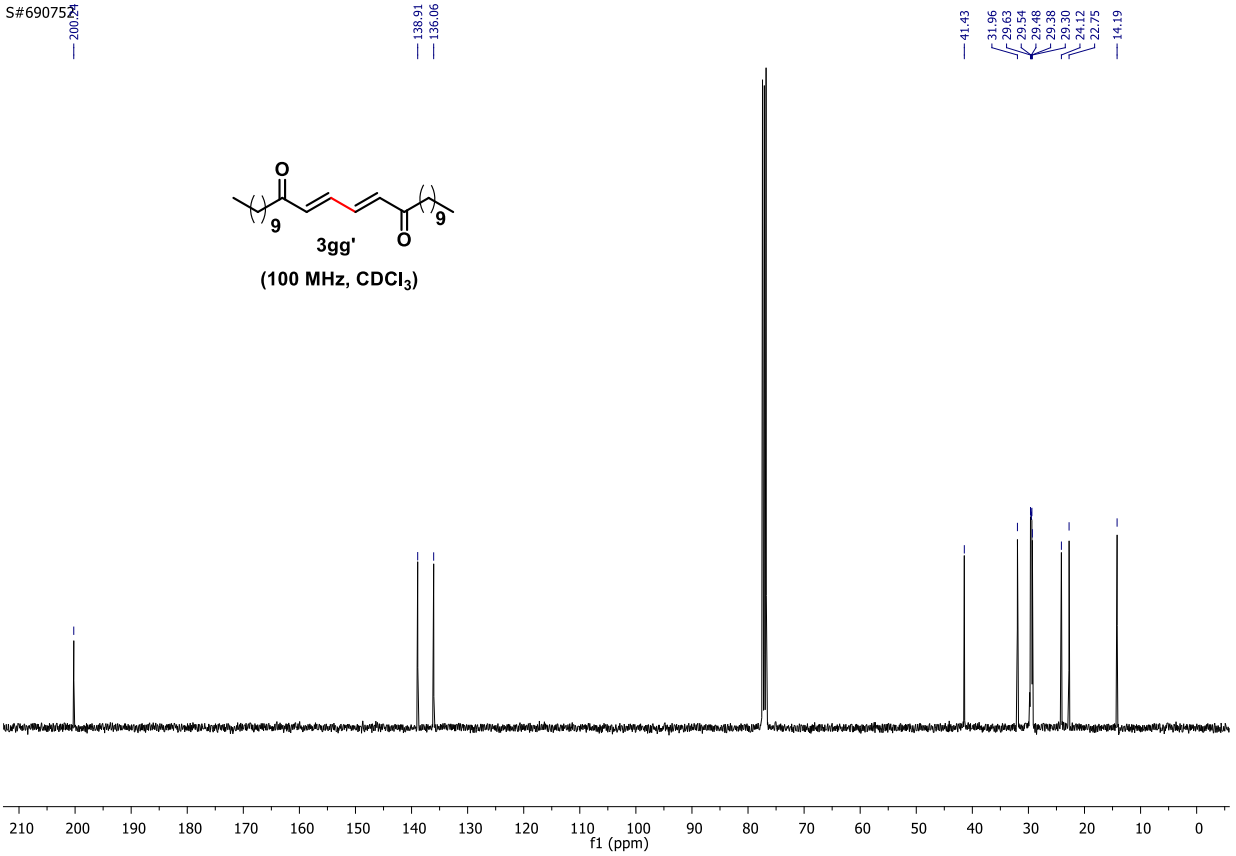
4, Sex pheromone

(100 MHz, $CDCl_3$)

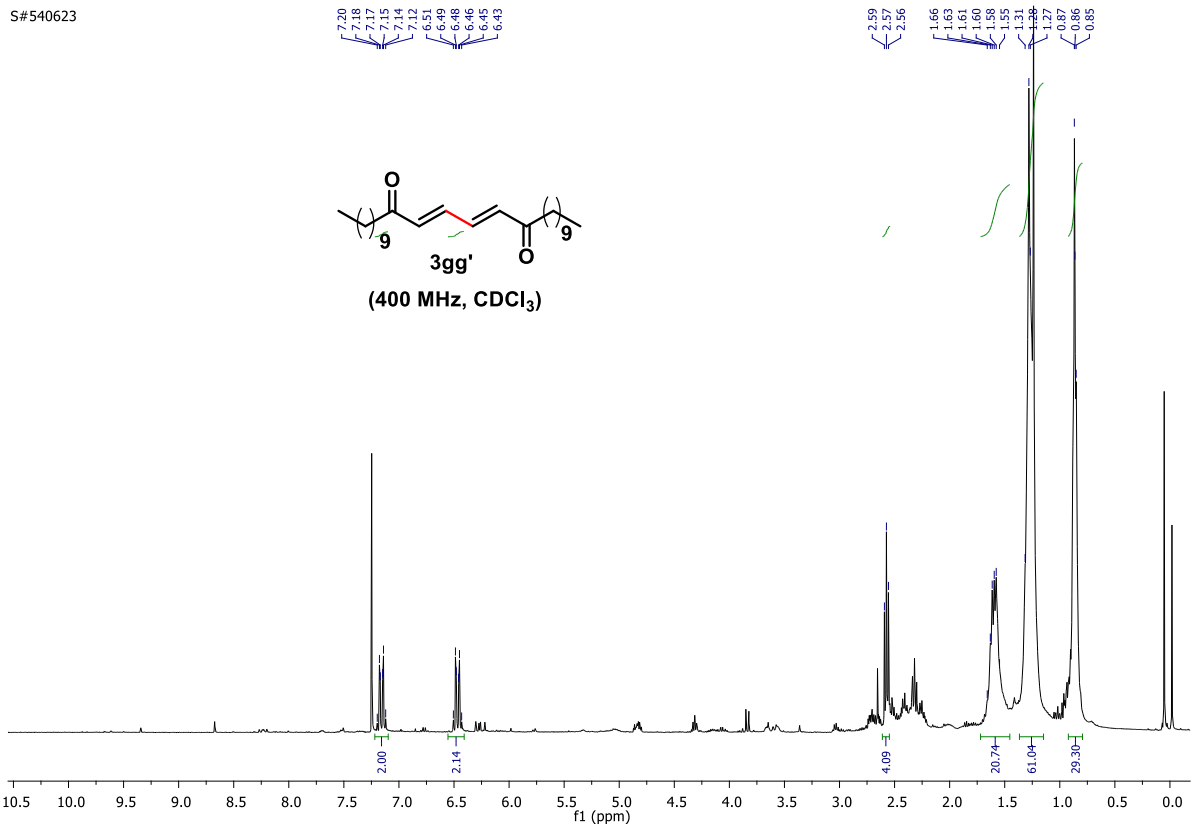

S#356879
7.20
7.18
7.17
7.15
7.14
7.12
6.51
6.49
6.48
6.46
6.45
6.43
2.59
2.58
2.56
1.66
1.64
1.62
1.60
1.59
1.31
1.29
1.28
1.27
0.90
0.88
0.86
O
O
3gn'
(400 MHz, CDCl3)
2.00
2.02
4.04
4.06
8.24
6.11
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

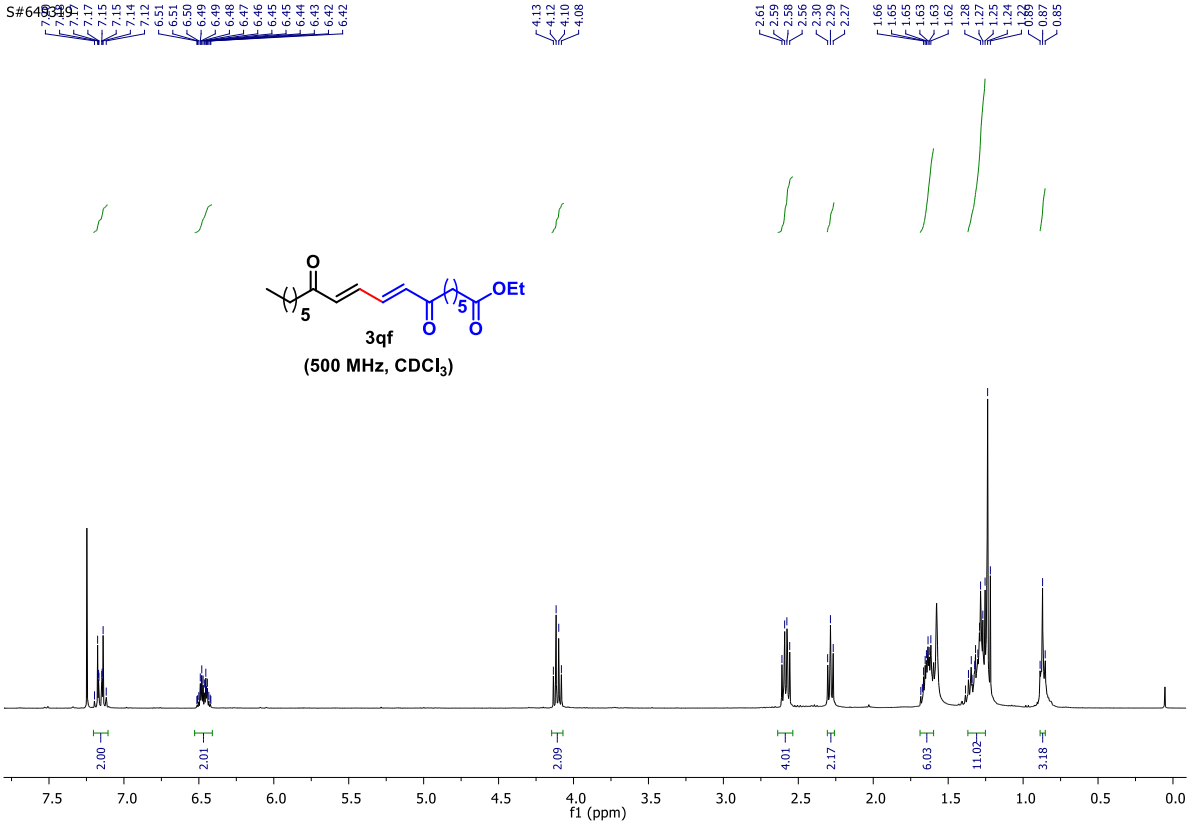

AN1296A
200.2
138.91
136.06
41.43
31.96
24.12
22.75
14.19
O
O
3gn'
(100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

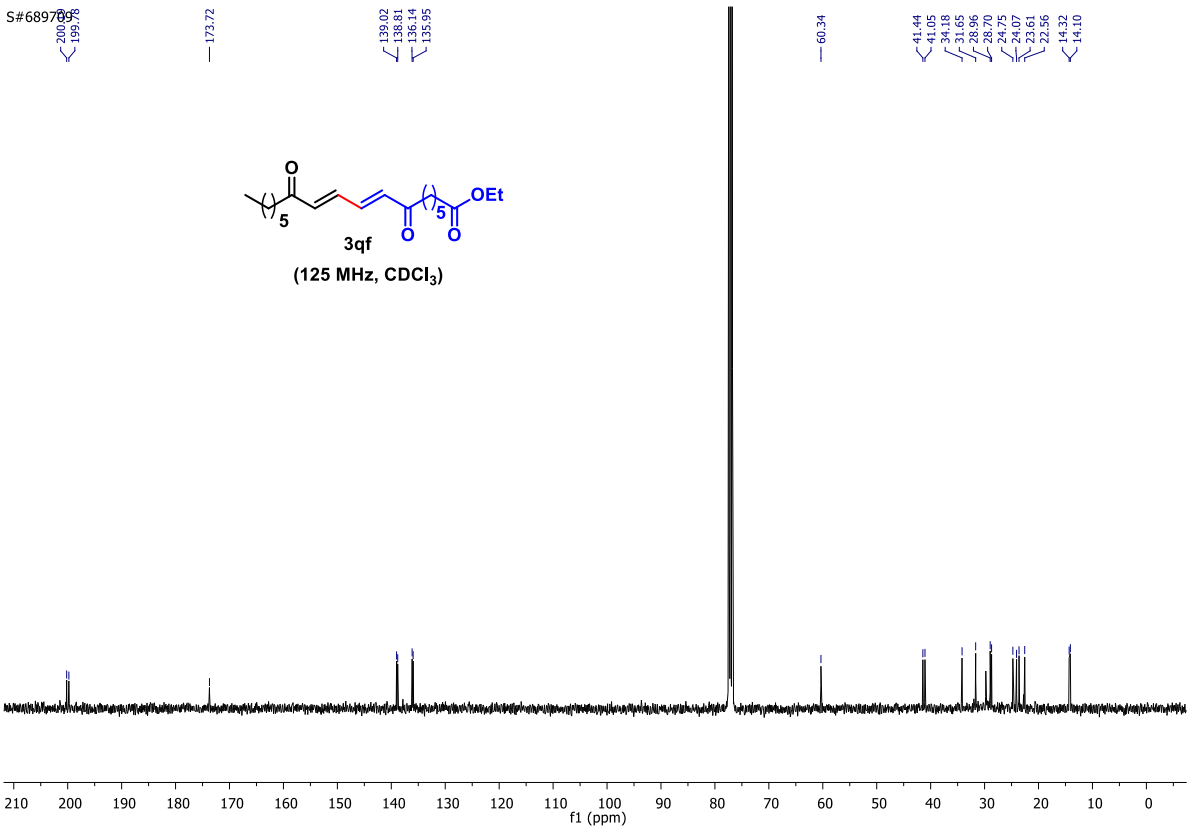

S#607578
7.19
7.18
7.17
7.15
7.14
7.12
6.50
6.49
6.48
6.46
6.45
6.43
2.59
2.57
2.55
1.65
1.63
1.61
1.59
1.58
1.27
1.24
0.88
0.86
0.84
O
9
O
9
3gg'
(400 MHz, CDCl3)
2.00
2.01
4.06
4.02
28.14
6.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

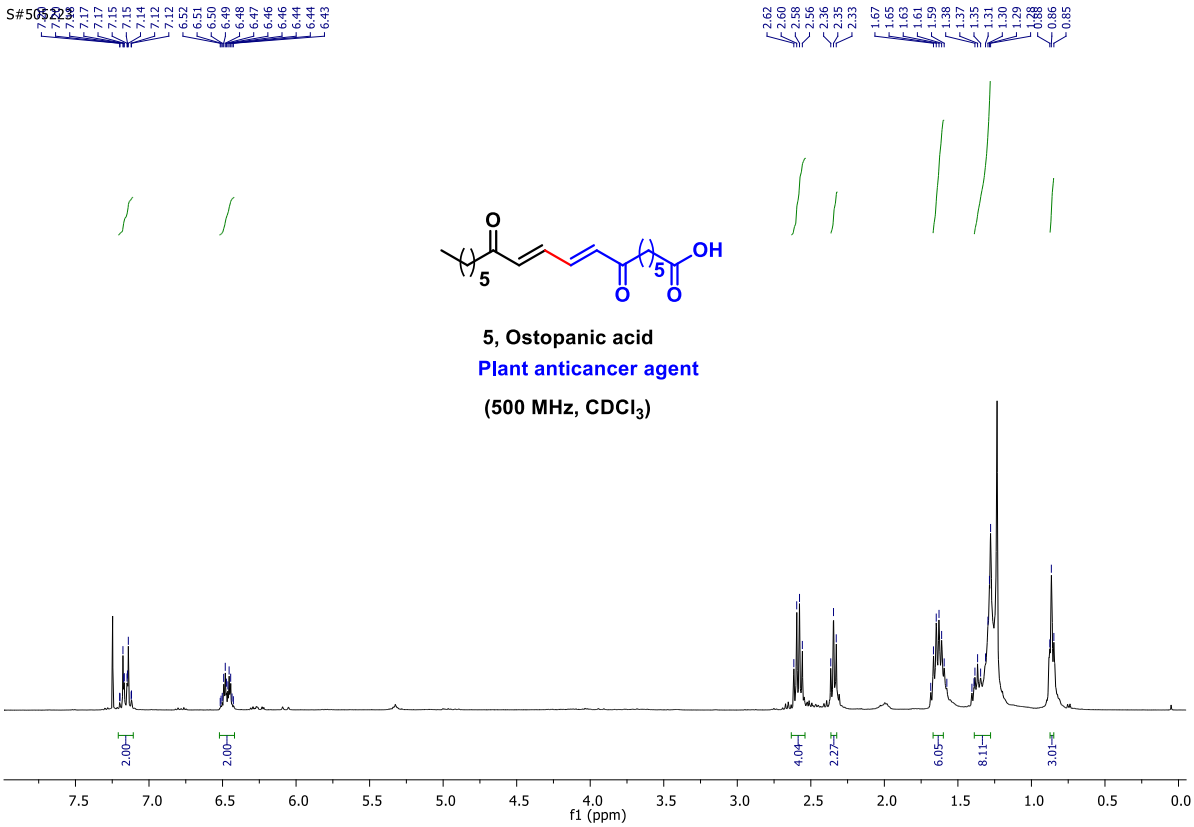

S#690752
200.27
138.91
136.06
41.43
31.96
29.63
29.54
29.48
29.38
29.30
24.12
22.75
14.19
O
9
O
9
3gg'
(100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR spectrum of homodimer of decyl vinyl ketone obtained from 0.3 mmol scale. (6% yield)




S#649310
7.18
7.17
7.15
7.14
7.12
6.51
6.50
6.49
6.48
6.47
6.46
6.45
6.44
6.43
6.42
4.13
4.12
4.10
4.08
2.61
2.59
2.58
2.56
2.30
2.29
2.27
1.66
1.65
1.63
1.62
1.28
1.27
1.25
1.24
0.89
0.87
0.85
OEt
3qf
(500 MHz, CDCl3)
2.00
2.01
2.09
4.01
2.17
6.03
11.02
3.18
f1 (ppm)

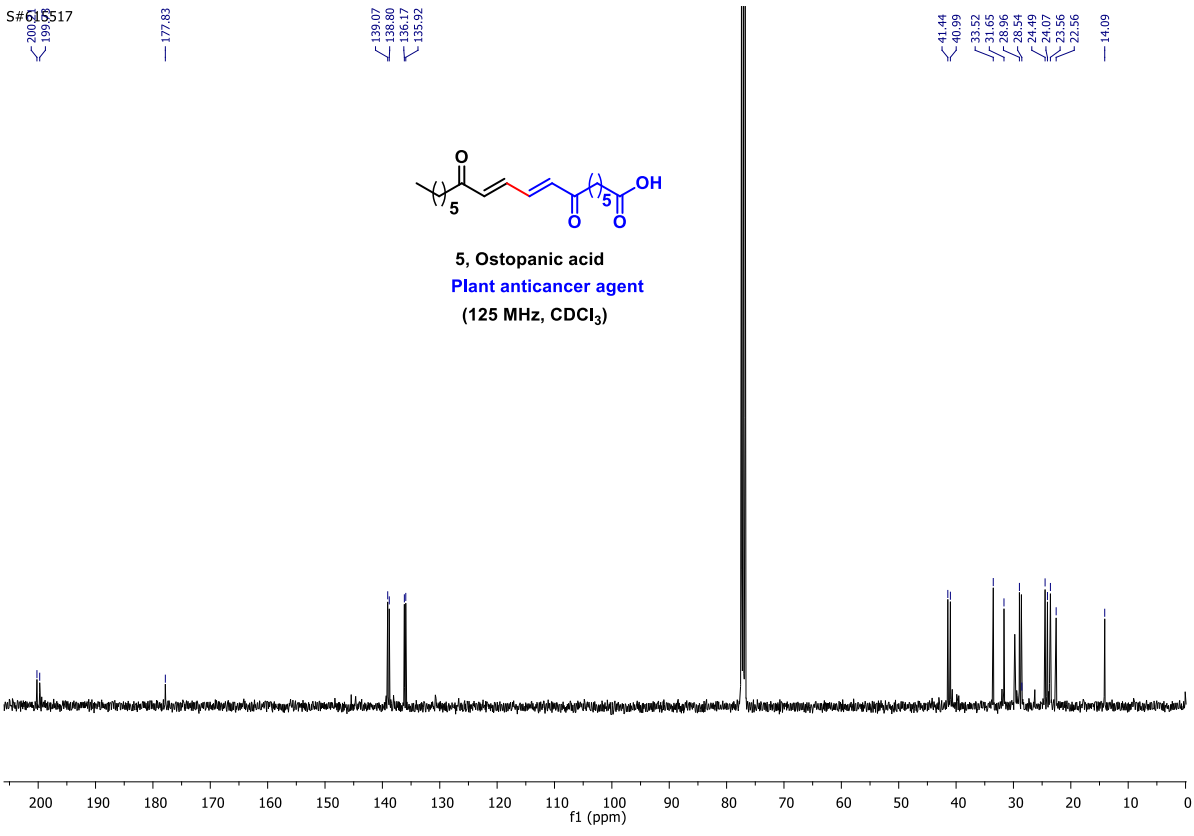

S#689709
200.08
199.78
173.72
139.02
138.81
136.14
135.95
60.34
41.44
41.05
34.18
31.65
28.96
28.70
24.75
24.07
23.61
22.56
14.32
14.10
OEt
3qf
(125 MHz, CDCl3)
f1 (ppm)



5, Ostopanic acid

Plant anticancer agent

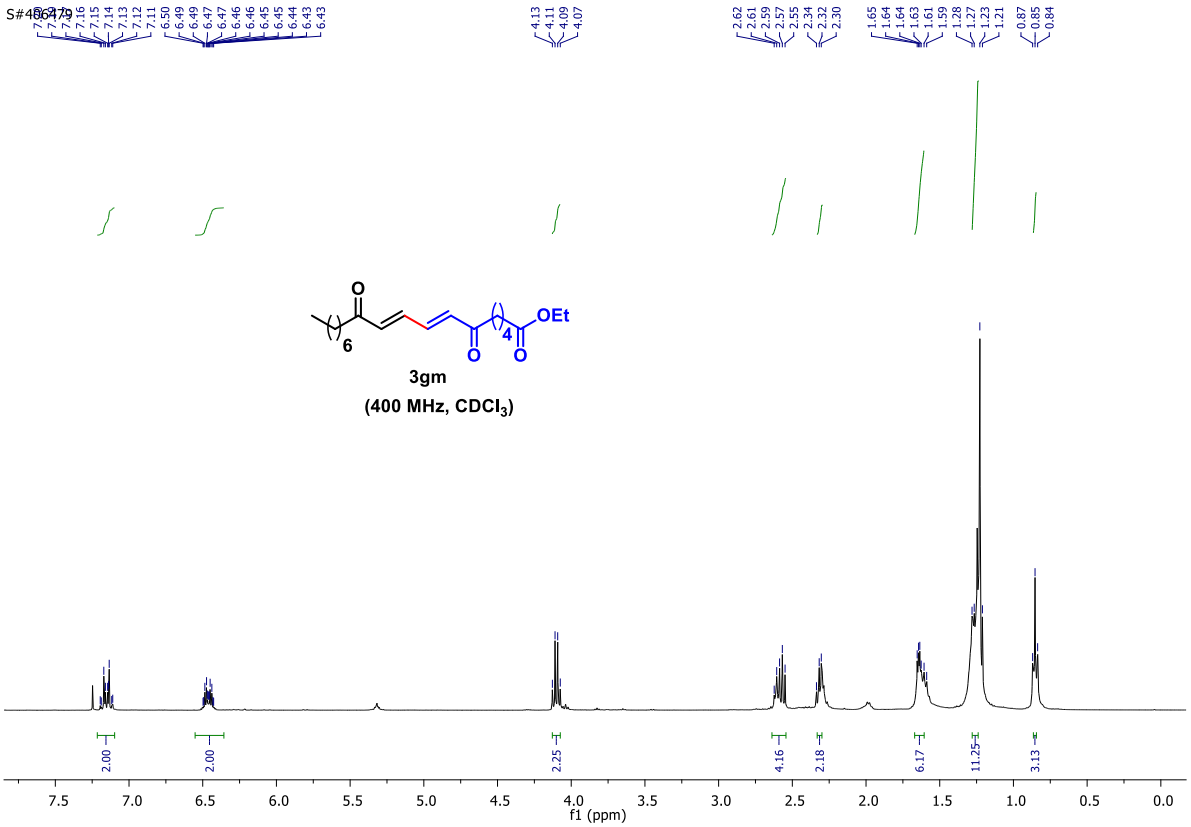
(500 MHz, $CDCl_3$)



5, Ostopanic acid

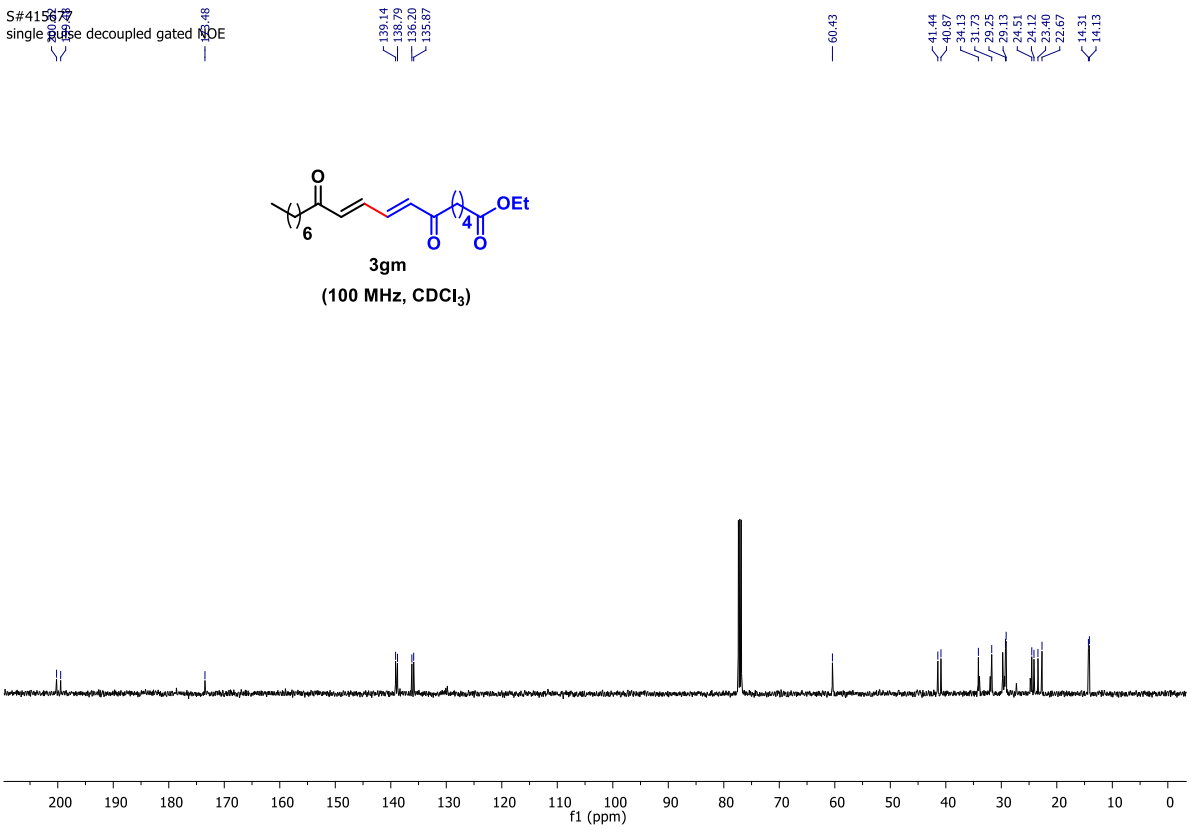
Plant anticancer agent

(125 MHz, $CDCl_3$)



3gm

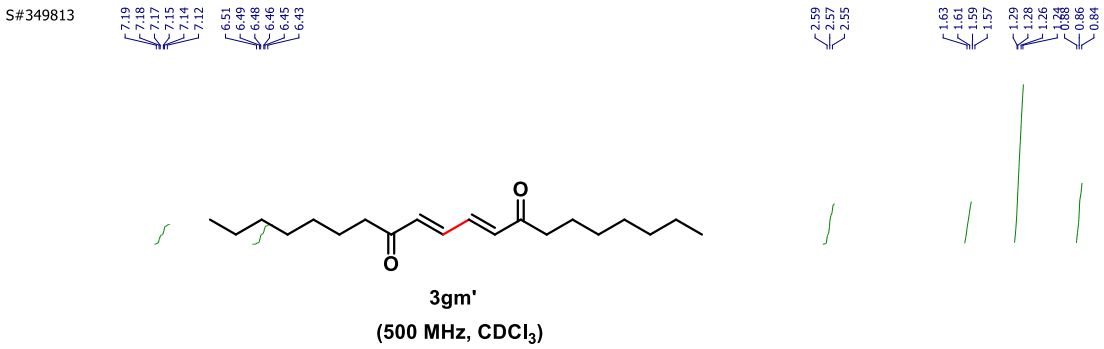
(400 MHz, $CDCl_3$)



3gm

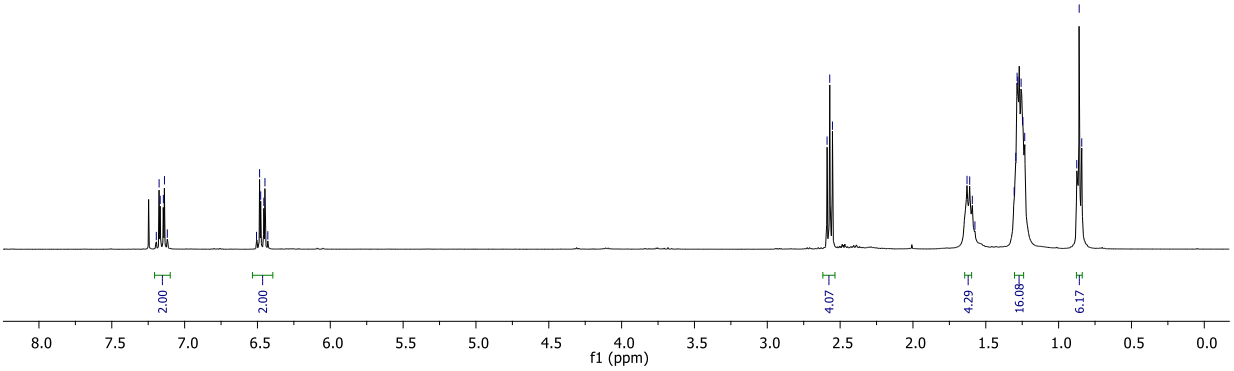
(100 MHz, $CDCl_3$)

S#349813

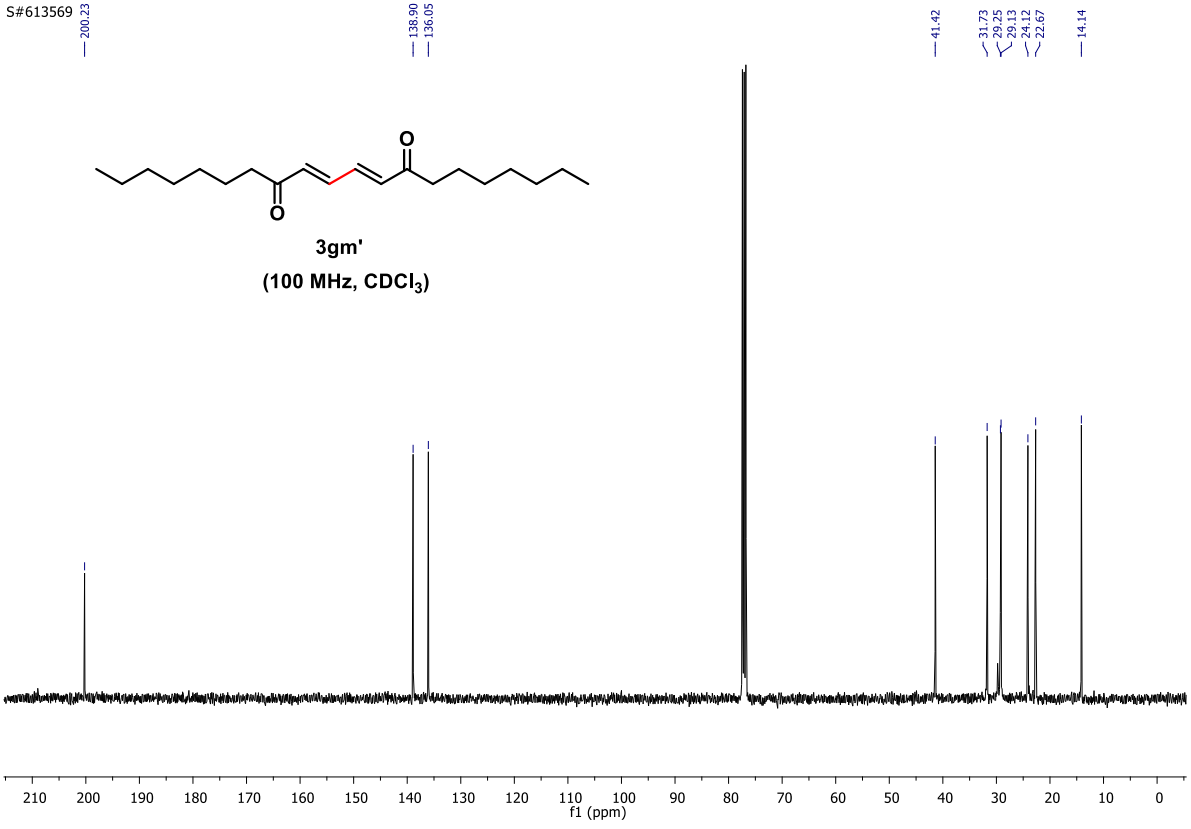


3gm'

(500 MHz, $CDCl_3$)

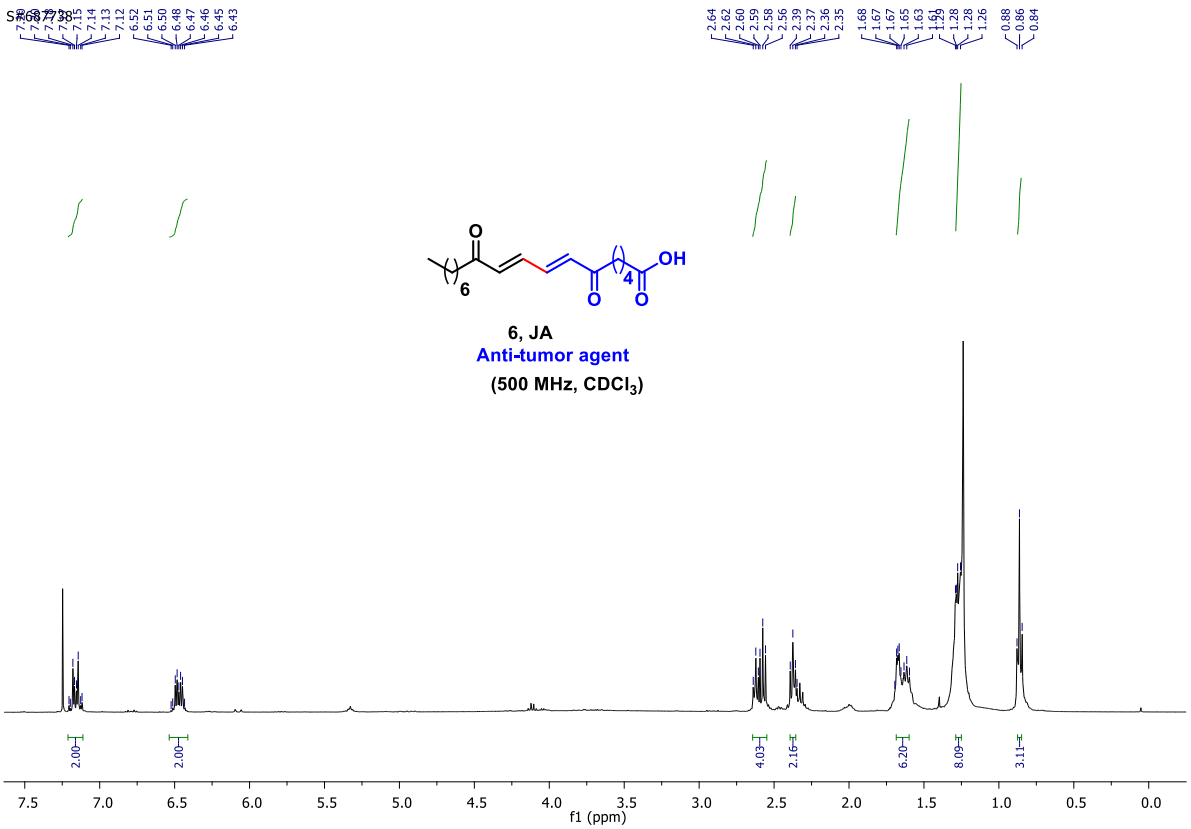


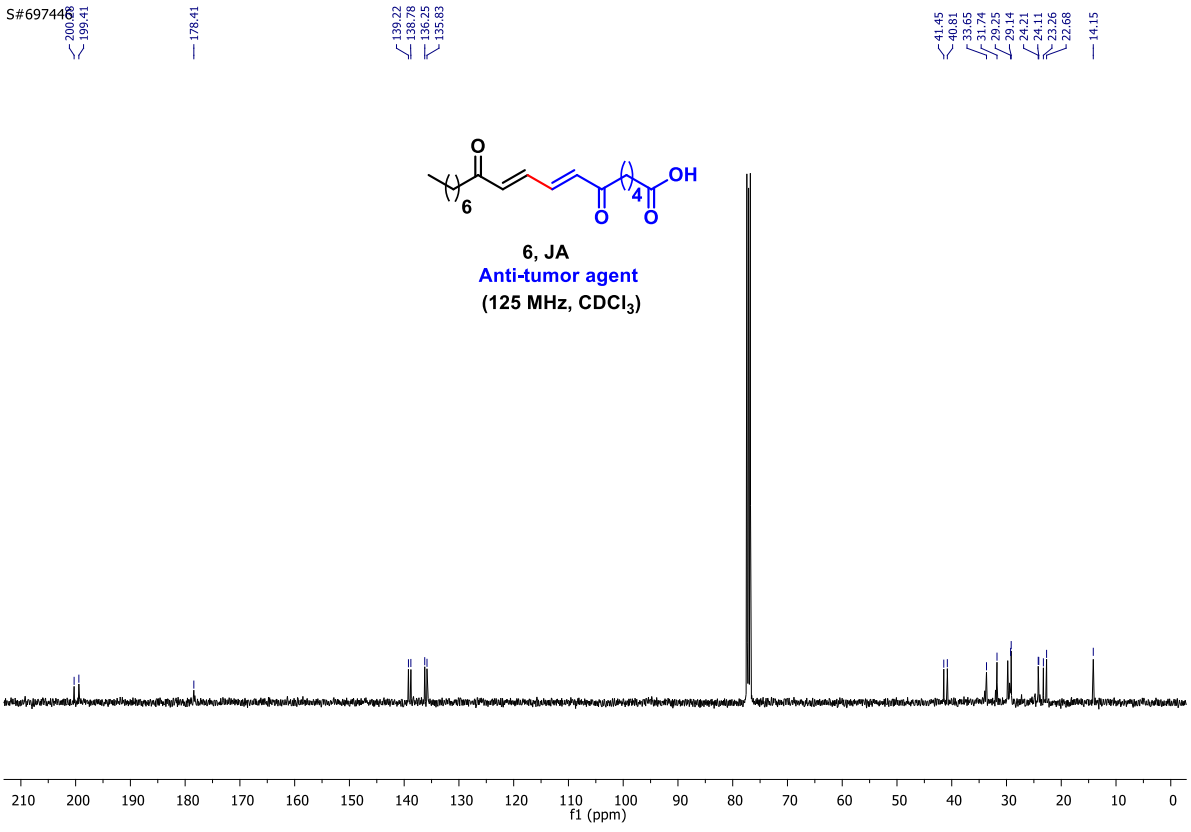
S#613569

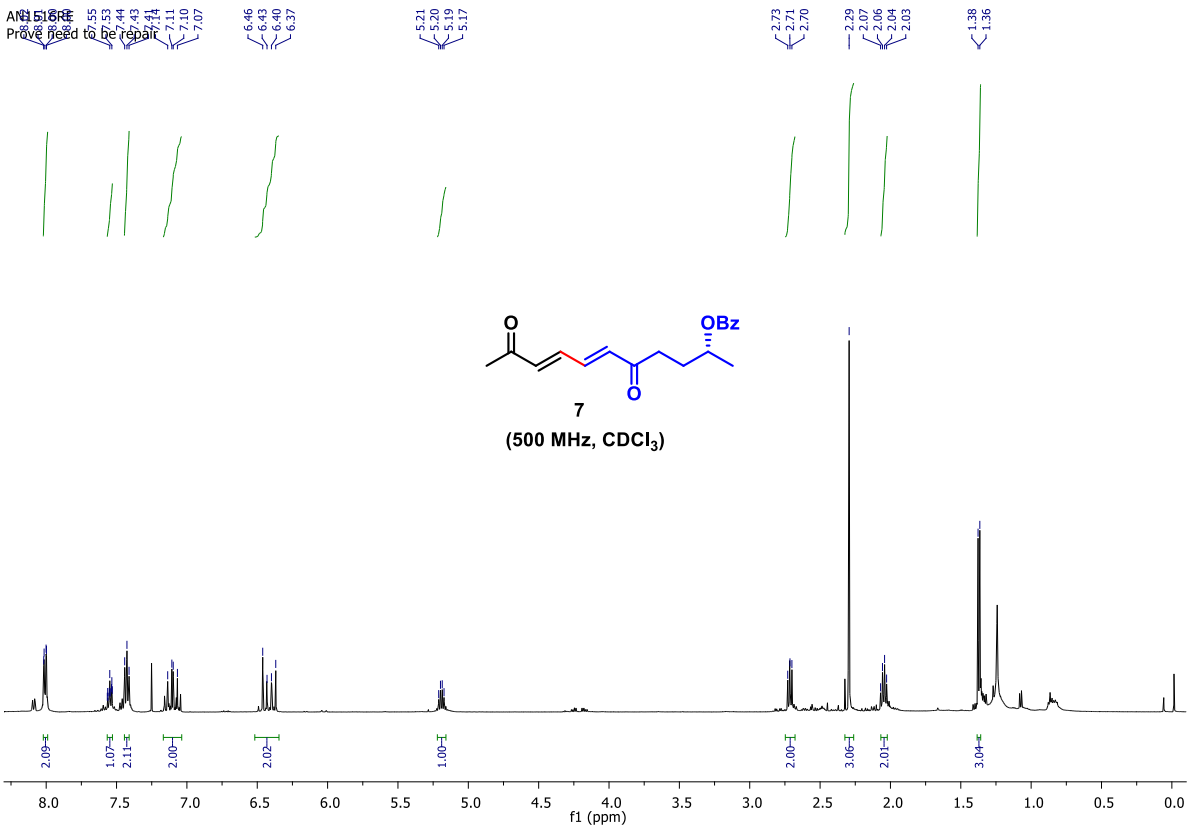


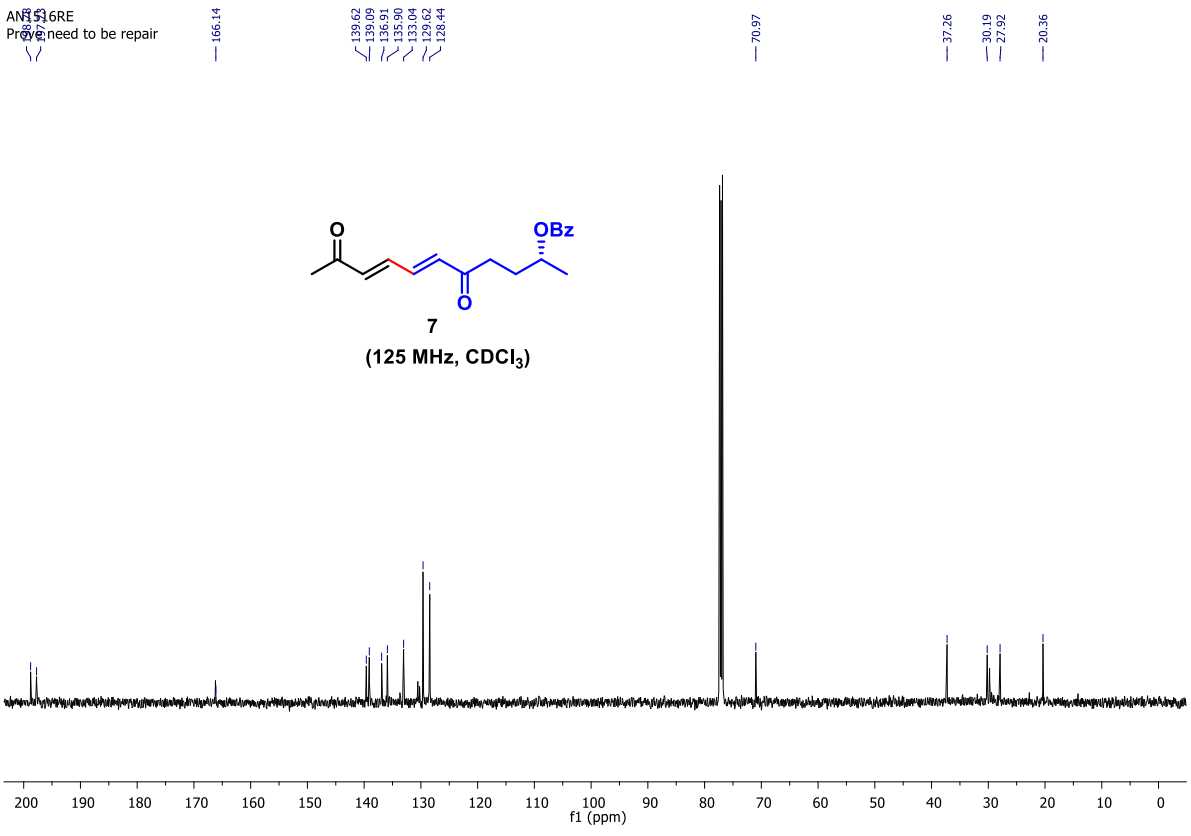
3gm'

(100 MHz, $CDCl_3$)


S#687735
7.69 7.68 7.67 7.66 7.65 7.64 7.63 7.62 7.61 7.60 7.59 7.58 7.57 7.56 7.55 7.54 7.53 7.52 7.51 7.50 7.49 7.48 7.47 7.46 7.45 7.44 7.43 7.42 7.41 7.40 7.39 7.38 7.37 7.36 7.35 7.34 7.33 7.32 7.31 7.30 7.29 7.28 7.27 7.26 7.25 7.24 7.23 7.22 7.21 7.20 7.19 7.18 7.17 7.16 7.15 7.14 7.13 7.12 6.52 6.51 6.50 6.48 6.47 6.46 6.45 6.43
2.64 2.62 2.60 2.59 2.58 2.56 2.39 2.37 2.36 2.35 1.68 1.67 1.67 1.65 1.63 1.61 1.29 1.28 1.28 1.26 0.88 0.86 0.84
O
OH
6
4
O
O
6, JA
Anti-tumor agent
(500 MHz, CDCl3)
2.00 2.00 4.03 2.16 6.20 8.09 3.11
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


S#697446
200.08 199.41 178.41 139.22 138.78 136.25 135.83 41.45 40.81 33.65 31.74 29.25 29.14 24.21 24.11 23.26 22.68 14.15
O
OH
6
4
O
O
6, JA
Anti-tumor agent
(125 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


AN1516RE
Prove need to be repair
7.58
7.56
7.55
7.53
7.44
7.43
7.41
7.41
7.11
7.10
7.07
6.46
6.43
6.40
6.37
5.21
5.20
5.19
5.17
2.73
2.71
2.70
2.29
2.07
2.06
2.04
2.03
1.38
1.36
O
OBz
O
7
(500 MHz, CDCl3)
2.09
1.07
2.11
2.00
2.02
1.00
2.00
3.06
2.01
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


AN1516RE
Prove need to be repair
166.14
139.62
139.09
136.91
135.90
133.04
129.62
128.44
70.97
37.26
30.19
27.92
20.36
O
OBz
O
7
(125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Comparison table

^{1}H and ^{13}C NMR comparison between natural and synthetic (*7E,9E*)-henicosa-7,9-diene-6,11-dione (4)

^{1}H-NMR in $CDCl_3$		^{13}C-NMR in $CDCl_3$	
Natural 400 MHz	**Synthetic 500 MHz**	**Natural 100 MHz**	**Synthetic 125 MHz**
0.92 - 0.86 (m)	0.88 - 0.85 (m)	200.11	200.24
1.36 - 1.28 (m)	1.32 – 1.25 (m)	200.10	200.24
1.67 - 1.59 (m)	1.66 – 1.59 (m)	138.80	138.91
2.60 (t, *J* = 7.5 Hz)	2.57 (t, *J* = 7.4 Hz)	138.79	138.91
6.49 (dd, *J* = 11.5, 2.8 Hz)	6.53 – 6.39 (m)	135.97	136.06
7.18 (dd, *J* = 11.5, 2.8 Hz)	7.21 – 7.11 (m)	135.96	136.06
		41.35	41.43
		41.31	41.38
		31.88	31.96
		31.38	31.46
		29.55	29.63
		29.46	29.54
		29.40	29.48
		29.30	29.38
		29.22	29.30
		24.04	24.12
		23.72	23.80
		22.67	22.77
		22.45	22.64
		14.11	14.09
		13.91	13.99

^{1}H and ^{13}C NMR comparison between natural and synthetic Ostopanic acid (5)

^{1}H-NMR in $CDCl_3$		^{13}C-NMR in $CDCl_3$	
Natural 400 MHz	**Synthetic 500 MHz**	**Natural 100 MHz**	**Synthetic 125 MHz**
0.87 (t, *J* = 6.7 Hz)	0.87 (t, *J* = 6.8 Hz)	200.2	200.21
1.30 (m)	1.39 – 1.28 (m)	199.7	199.73
1.64 (m)	1.67 – 1.59 (m)	178.3	177.83
2.36 (t, *J* = 7.4 Hz)	2.34 (t, *J* = 7.5 Hz)	139.0	139.07
2.57 (t, *J* = 7.4 Hz)	2.57 (t, *J* = 7.3 Hz)	138.7	138.80
2.59 (t, *J* = 7.0 Hz)	2.59 (t, *J* = 7.1 Hz)	136.1	136.17
6.50 - 6.43 (m)	6.52 – 6.42 (m)	135.8	135.92
7.19 - 7.13 (m)	7.21 – 7.11 (m)	41.6	41.44
		40.7	40.99
		33.7	33.52
		31.5	31.65
		28.8	28.96
		28.5	28.54
		24.4	24.49
		24.0	24.07
		23.5	23.56
		22.4	22.56
		14.0	14.09