Gold(I)-Catalyzed Coupling Reactions for the Synthesis of Diverse Small Molecules Using the Build/Couple/Pair Strategy

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Supporting Information

Contents:

I. Material and Methods:

Dry solvents were dispensed from a solvent purification system that passes solvents through packed columns (THF and CH_2Cl_2: dry neutral alumina; toluene: dry neutral alumina and Q5 reactant). Unless otherwise stated, all reagents were obtained from commercial sources and used without further purification. Infrared spectra were recorded on a Nicolet Avatar 370 DTGS FTIR. ^{1}H NMR spectra were recorded on Varian Unity/Inova 500 (500MHz), or Bruker Ultrashield 300(300MHz) spectrometers. ^{1}H data are reported as follows: chemical shift in parts per million relative to $CHCl_3$ (7.27 ppm) multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broadened), coupling constant (Hz), and integration. ^{13}C magnetic resonance spectra were recorded on Varian Unity/Inova 500(125MHz) or Bruker Ultrashield 300(75MHz) spectrometers. ^{13}C chemical shifts are reported in parts per million relative to solvent. All ^{13}C spectra were determined with broadband decoupling. High-resolution mass spectra were obtained through the Harvard University mass spectrometry facility. All reactions were magnetically stirred and monitored by thin-layer chromatography (TLC) using E. Merck silica gel 60 F254 precoated plates (0.25 mm). Flash chromatography was performed either on EM Science silica gel 60 (230–400 mesh) or using a CombiFlash companion system(Teledyne ISCO, Inc.) with pre-packed FLASH silica gel columns (Biotage, Inc.). SFC/MS chromatography was performed with a Berger analytic SFC using CO2 and MeOH as the mobile phase and using a Chiralcel OJ column, a Chiralcel OD column, or a Chiralpak® IC column purchased from Chiral Technology Inc.

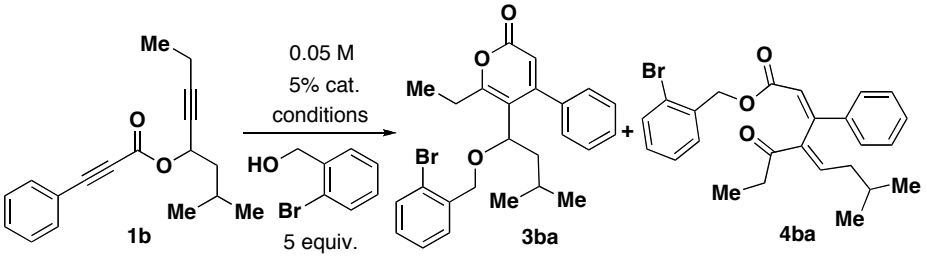
Ref. 8: Thomas, G. L.; Spandl, R. J.; Glansdorp, F. G.; Welch, M.; Bender, A.; Cockfield, J.; Lindsay, J. A.; Bryant, C.; Brown, D. F. J.; Loiseleur, O.; Rudyk, H.; Ladlow, M.; Spring, D. R. *Angew. Chem. Int. Ed.* **2008**, *47*, 2808-2812.

Ref. 24(c): Spicer, J. A.; Rewcastle, G. W.; Kaufman, M. D.; Black, S. L.; Plummer, M. S.; Denny, W. A.; Quin, J.; Shahripour, A. B.; Barrett, S. D.; Whitehead, C. E.; Milbank, J. B. J.; Ohren, J. F.; Gowan, R. C.; Omer, C.; Camp, H. S.; Esmaeil, N.; Moore, K.; Sebolt-Leopold, J. S.; Pryzbranowski, S.; Merriman, R. L.; Ortwine, D. F.; Warmus, J. S.; Flamme, C. M.; Pavlovsky, A. G.; Tecle, H. *J. Med. Chem.* **2007**, *50*, 5090-5102.

Ref. 24(d): Kim, K. S.; Zhang, L.; Schmidt, R.; Cai, Z.-W.; Wei, D.; Williams, D. K.; Lombardo, L. J.; Trainor, G. L.; Xie, D.; Zhang, Y.; An, Y.; Sack, J. S.; Tokarski, J. S.; Darienzo, C.; Kamath, A.; Marathe, P.; Zhang, Y.; Lippy, J.; Jeyaseelan, R.; Wautlet, B.; Henley, B.; Gullo-Brown, J.; Manne, V.; Hunt, J. T.; Fargnoli, J.; Borzilleri, R. M. *J. Med. Chem.* **2008**, *51*, 5330-5341.

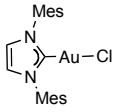
II. Supplementary tables

Table S1. Optimization of reaction conditions for the alcohol nucleophile



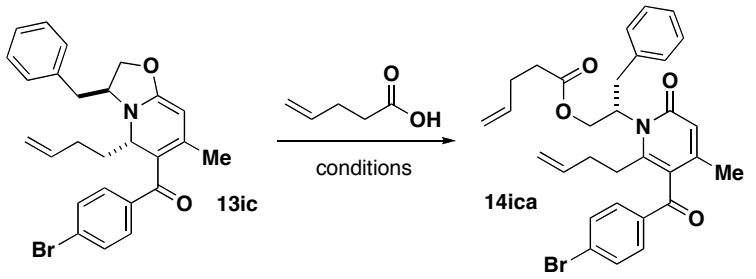
entry	cat.	conditions	yield[a] 3ba	yield[a] 4ba	ratio (3ba/4ba)
1	Ph_3PAuCl / $AgSbF_6$	CH_2Cl_2, rt, 4 h	30%	53%	1 : 1.8
2	Et_3PAuCl / $AgSbF_6$	CH_2Cl_2, rt, 1.5 h	13%	82%	1 : 6.3
3	$(p\text{-}CF_3\text{-}C_6H_4)_3PAuCl$ / $AgSbF_6$	CH_2Cl_2, rt, 6 h	44%	37%	1.2 : 1
4	(IMes)AuCl / $AgSbF_6$	CH_2Cl_2, rt, 1 h	10%	87%	1 : 8.7
5[b]	(IMes)AuCl / $AgSbF_6$	CH_2Cl_2, rt, 1.5 h	7%	86%	1 : 12
6[b]	$(^tBu)_3PAuCl$ / $AgSbF_6$	CH_2Cl_2, rt, 2 h	3%	89%	1 : 30
7	Ph_3PAuCl / $AgSbF_6$	toluene, rt, 2 h	56%	23%	2.4 : 1
8	Ph_3PAuCl / $AgSbF_6$	DCE, rt, 2 h	26%	53%	1 : 2
9	Ph_3PAuCl / $AgSbF_6$	Et_2O, rt, 4 h	38%	26%	1.5 : 1
10	Ph_3PAuCl / $AgSbF_6$	$CHCl_3$, rt, 2 h	53%	32%	1.6 : 1
11	Ph_3PAuCl / $AgSbF_6$	CH_2Cl_2, 0°C, 8 h	56%	36%	1.6 : 1
12[b]	$(p\text{-}CF_3\text{-}C_6H_4)_3PAuCl$ / $AgSbF_6$	toluene, 0°C, 8 h	61%	20%	3 : 1

[a] Isolated yield after column chromatography.
[b] 2 equiv. alcohol was used.



(IMes)AuCl

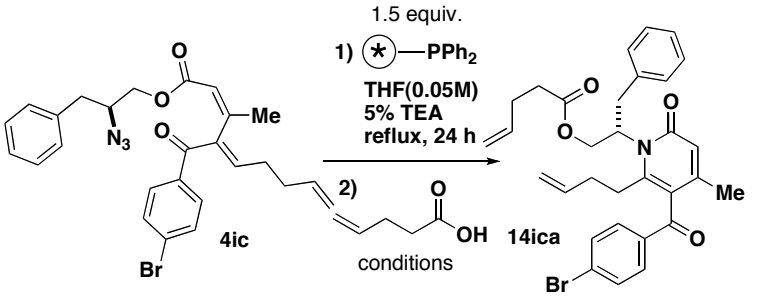
Table S2. Optimization of the ring-opening reaction of **13ic**



entry	conditions	amount of acid	yield[a]
1	THF(0.033 M), 50 °C, 13h	1.2 equiv.	NR
2	dioxane(0.033 M), reflux, 12h	4 equiv.	33%
3	dioxane(0.05 M), reflux, 4.5h	4 equiv.	29%
4	toluene(0.1 M), 80 °C, 5min	10 equiv.	59%
5	toluene(0.2 M), 60 °C, 15min	2 equiv.	48%
6	toluene(0.1 M), 50 °C, 6h:	1.2 equiv.	37%
7	toluene(0.05 M), 80 °C, 15min	2 equiv.	46%
8	toluene(0.1 M), O_2, 4 Å MS, 80 °C, 15min	3 equiv.	51%
9	toluene(0.1 M), O_2, 4 Å MS, 60 °C, 45min	3 equiv.	51%

[a] Isolated yield after column chromatography.

Table S3. Optimization of the two-step protocol for converting **4ic** to **14ica**



entry	conditions	amount of acid	yield[a]
1	toluene(0.1 M), O_2, 80 °C, 10min	10 equiv.	53%
2	toluene(0.1 M), O_2, 4 Å MS, 60 °C, 4h	3 equiv.	20%
3	toluene(0.1 M), O_2, 4 Å MS, 80 °C, 10min	10 equiv.	50%
4	toluene(0.1 M), O_2, 4 Å MS, 60 °C, 30min	10 equiv.	65%
5	toluene(0.025 M), O_2, 4 Å MS, 60 °C, 20min	10 equiv.	52%

[a] Isolated yield after 2 steps.

III. General experimental procedure

General procedure of synthesizing propargyl propiolates:
To a solution of propiolic acid (1.5 equiv.), propargyl alcohol (1 equiv.) and *N*,*N*-dimethylaminopyridine (DMAP, 0.1 equiv.) in dry CH_2Cl_2 was added *N*-(3-Dimethylaminopropyl)-*N*'-ethylcarbodiimide hydrochloride (EDCI, 1.2 equiv.) at 0 ^oC with stirring. The reaction mixture was stirred at room temperature overnight. The mixture was quenched with water, and extracted with EtOAc. The organic layers were then washed with saturated aqueous $NaHCO_3$, brine, dried over sodium sulfate, filtered, and evaporated under reduced pressure. The resulting residue was further purified by silica gel chromatography.

General procedure of the gold-catalyzed cascade reactions of propargyl propiolates in the presence of nucleophiles:
The propargyl propiolate and the nucleophile were dissolved in dry CH_2Cl_2 (0.05 M propargyl propiolate). 5 mol % gold(I) catalyst and 5 mol % $AgSbF_6$ were added respectively. The resulting reaction mixture was stirred at room temperature for 2 to 12 h. The solvent was evaporated to dryness and the residue was purified by flash chromatography on silica gel to furnish the final product.

General procedure of RCM:
A: The substrate was dissolved in dry CH_2Cl_2 (0.005 M substrate) in a round-bottom flask equipped with condenser. The vessel was degassed with argon, and then 10 mol % Grubbs 2nd generation catalyst was added. The resulting solution was stirred under room temperature for 4 hours. The mixture was concentrated into 2 mL under reduced pressure. $Pb(OAc)_4$ (5 equiv. to Grubbs 2nd generation catalyst) was added and the mixture was stirred at room temperature overnight. After removal of the solvent, the residue was purified by flash chromatography on silica gel.

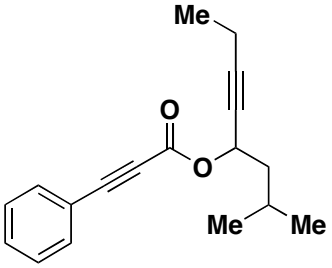
B: The substrate was dissolved in dry CH_2Cl_2 (0.005 M substrate) in a round-bottom flask equipped with condenser. The vessel was degassed with argon, and then 10 mol % Grubbs 1st generation catalyst was added. The resulting solution was stirred under reflux for 24 hours. The mixture was cooled to room temperature, and concentrated into 2 mL under reduced pressure. $Pb(OAc)_4$ (5 equiv. to Grubbs 1st generation catalyst) was added and the mixture was stirred at room temperature overnight. After removal of the solvent, the residue was purified by flash chromatography on silica gel.

C: The substrate was dissolved in dry CH_2Cl_2 (0.005 M substrate) in a round-bottom flask equipped with condenser. The vessel was degassed with argon, and then 10 mol % Hoveyda-Grubbs 2nd generation catalyst was added. The resulting solution was stirred under reflux for 6 - 24 hours. The mixture was cooled to room temperature and 1 mL ethyl vinyl ether was added. The volatiles were removed under reduced pressure. The resulting residue was purified by flash chromatography on silica gel.
D: The substrate was dissolved in dry CH_2Cl_2 (0.005 M substrate) in a round-bottom flask equipped with condenser. The vessel was degassed with argon, and then 10 mol % Hoveyda-Grubbs 1st generation catalyst was added. The resulting solution was stirred under reflux for 24 hours. The mixture was cooled to room temperature, and 1 mL ethyl vinyl ether was added. The volatiles were removed under reduced pressure. The resulting residue was purified by flash chromatography on silica gel.

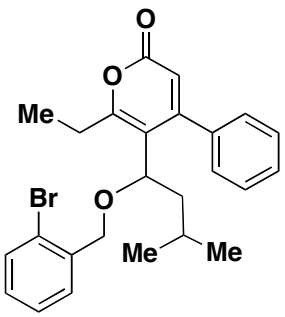
E: The substrate was dissolved in dry $PhCH_3$ (0.005 M substrate) in a round-bottom flask equipped with condenser. The vessel was degassed with argon, and then 10 mol % Hoveyda-Grubbs 2nd generation catalyst was added. The resulting solution was stirred under 60 °C for 11 hours. The mixture was cooled to room temperature and 1 mL ethyl vinyl ether was added. The volatiles were removed under reduced pressure. The resulting residue was purified by flash chromatography on silica gel.

General procedure for converting the coupling products with azido alcohols to 2-pyridones:
In a 4ml capped vial was coupling product in THF (0.05 M). Diphenylphosphinopolystyrene (1.5 equiv., 1.20 mmol/g, purchased from Novabiochem) was added and the mixture was stirred under room temperature for 12 h. 5% TEA was added and the solution was heated under reflux for 12 h. The reaction was cooled to room temperature and filtrated. The polymer was washed with ethyl acetate. The organic phase was collected and the volatiles were removed under reduced pressure. In a 10 mL round-bottomed flask was last step residue in $PhCH_3$ (0.1 M) to give a yellow solution. A spatula tip of 4 Å MS was added. The resulting solution was degassed with oxygen. The acid (10 equiv.) was added. The resulting solution was heated under 60 °C for 0.5 h. The reaction was cooled to room temperature and organic solvent was removed under vacuo. The crude product was purified by flash chromatography on silica gel.

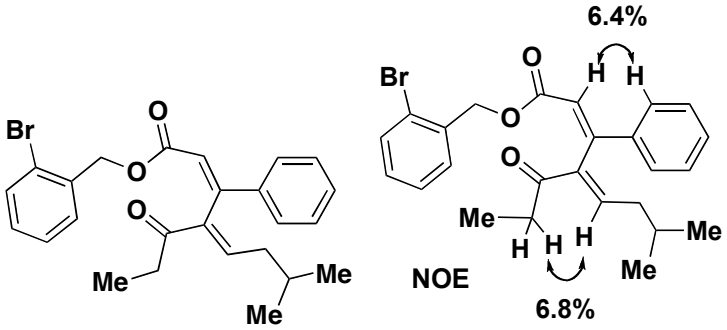
IV. ^{1}H, ^{13}C NMR and NOE data



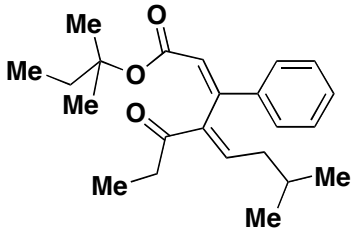
2-methyloct-5-yn-4-yl 3-phenylpropiolate (1b). Yield: 61%. IR (neat, cm^{-1}): 2958, 2872, 2359, 2215, 1709, 1282, 1185, 1161, 925, 758, 689; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.96 (d, *J*=6.4 Hz, 3 H), 0.95 (d, *J*=6.4 Hz, 3 H), 1.13 (t, *J*=7.6 Hz, 3 H), 1.64-1.70 (m, 1 H), 1.73-1.86 (m, 2 H), 2.19 - 2.25 (m, 2 H), 5.50-5.53 (m, 1 H), 7.36 (m, 2 H), 7.42-7.45 (m, 1 H), 7.57 ppm (d, *J*=6.8 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 12.30, 13.47, 22.20, 22.34, 24.64, 43.78, 65.06, 76.29, 80.49, 86.49, 88.24, 119.53, 128.45, 130.53, 132.85, 153.02 ppm; HRMS (EI) calcd. for $[C_{18}H_{21}O_2]$ $(M+H)^+$ 269.1541, found 269.1529.



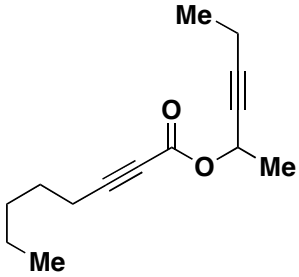
5-(1-(2-bromobenzyloxy)-3-methylbutyl)-6-ethyl-4-phenyl-2H-pyran-2-one (3ba). IR (neat, cm^{-1}): 2954, 2867, 1724, 1569, 1367, 1118, 749, 701; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.58 (d, J=6.4 Hz, 3 H), 0.84 (d, J=6.8 Hz, 3 H), 1.31 (t, J=7.6 Hz, 3 H), 1.30 - 1.35 (m, 1 H), 1.79 (br. s., 1 H), 1.90 (br. s., 1 H), 2.95 (m, 2 H), 4.31 (d, J=12.7 Hz, 1 H), 4.34 (m, 1 H), 4.56 (d, J=12.7 Hz, 1 H), 6.09 (s, 1 H), 7.17 (dd, J=7.3, 7.8 Hz, 1 H), 7.22 (br. s., 2 H), 7.29 (dd, J=7.3, 7.8 Hz, 1 H), 7.37 (d, J=7.8 Hz, 1 H), 7.44 (br. s., 3 H), 7.55 ppm (d, J=7.8 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 11.92, 21.01, 23.25, 24.60, 24.95, 45.40, 70.10, 74.17, 112.35, 115.21, 122.47, 127.19, 127.34, 128.38, 128.62, 128.75, 128.84, 132.33, 136.91, 137.08, 159.76, 161.85, 166.20 ppm; HRMS (EI) calcd. for $[C_{25}H_{28}BrO_3]$ $(M+H)^+$ 455.1222, found 455.1227.



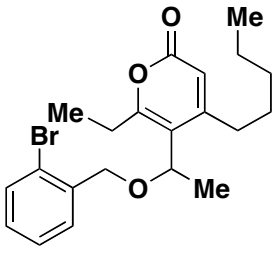
(2*Z*,4*E*)-2-bromobenzyl 7-methyl-3-phenyl-4-propionylocta-2,4-dienoate (4ba). IR (neat, cm^{-1}): 2958, 2361, 1717, 1673, 1447, 1264, 1155, 1030, 732, 702; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.57 (d, *J* = 7.8 Hz, 1 H), 7.42 - 7.48 (m, 2 H), 7.40 (dd, *J* =1.5, 7.8 Hz, 1 H), 7.33 - 7.37 (m, 3 H), 7.29 - 7.33 (m, 1 H), 7.19 (dt, *J* = 1.5, 7.6 Hz, 1 H), 6.87 (t, *J* = 7.3 Hz, 1 H), 6.56 (s, 1 H), 5.21 (br. s., 2 H), 2.77 (br. s., 1 H), 2.61 (dd, *J* = 7.1, 14.4 Hz, 1 H), 1.85 (br. s., 2 H), 1.65 (dt, *J* = 6.8, 13.3 Hz, 1 H), 1.07 (t, *J* = 7.1 Hz, 3 H), 0.79 (d, *J* = 5.9 Hz, 6 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 199.6, 165.1, 153.2, 141.2, 140.6, 138.2, 135.3, 132.8, 129.9, 129.8, 129.6, 128.7, 127.5, 126.9, 123.4, 118.1, 65.6, 38.7, 31.6, 28.1, 22.5, 8.1; HRMS (EI) calcd. for $[C_{25}H_{28}BrO_3]$ $(M+H)^+$ 455.1222, found 455.1231.



(2*Z*,4*E*)-*tert*-pentyl 7-methyl-3-phenyl-4-propionylocta-2,4-dienoate (4bb). Yield: 48%. IR (neat, cm^{-1}): 2957, 2360, 1707, 1606, 1447, 1384, 1274, 1190, 1144, 735, 696; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.43 (dd, *J* = 2.9, 6.8 Hz, 2 H), 7.30 - 7.38 (m, 3 H), 6.91 (t, *J* = 7.6 Hz, 1 H), 6.42 (s, 1 H), 2.65 - 2.85 (m, 1 H), 2.47 - 2.65 (m, 1 H), 1.81 - 1.93 (m, 2 H), 1.77 (q, *J* = 7.3 Hz, 2 H), 1.63 - 1.73 (m, 1 H), 1.34 - 1.43 (m, 7 H), 1.06 (t, *J* = 7.3 Hz, 3 H), 0.86 (t, *J* = 7.6 Hz, 3 H), 0.83 (br. s., 6 H); ^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 199.4, 164.9, 150.3, 140.7, 140.4, 138.6, 129.4, 128.7, 126.8, 121.2, 83.1, 38.6, 33.3, 32.0, 28.2, 25.5, 22.6, 8.2, 8.1; HRMS (EI) calcd. for $[C_{23}H_{36}NO_3]$ $(M+NH_4)^+$ 374.26897, found 374.27007.

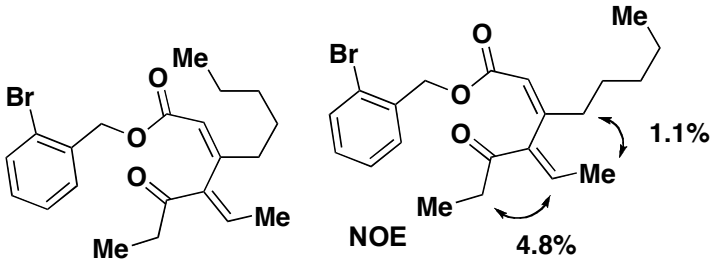


hex-3-yn-2-yl oct-2-ynoate (1c). Yield: 38%. IR (neat, cm^{-1}): 2937, 2873, 2232, 1710, 1456, 1241, 1050, 854, 752; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.91 (t, *J*=7.3 Hz, 3 H), 1.13 (t, *J*=7.6 Hz, 3 H), 1.29 - 1.42 (m, 4 H), 1.50 (d, *J*=6.4 Hz, 3 H), 1.55-1.63 (m, 2 H), 2.21 (dq, *J*=7.3, 2.0 Hz, 2 H), 2.33 (t, *J*=7.3 Hz, 2 H), 5.46-5.50 ppm (m, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 12.32, 13.49, 13.80, 18.65, 21.61, 22.04, 27.13, 30.93, 62.31, 72.88, 77.09, 87.55, 90.14, 152.77 ppm.

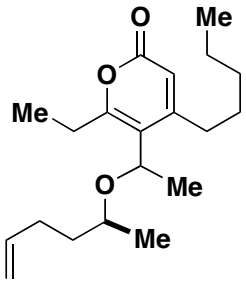


5-(1-(2-bromobenzyloxy)ethyl)-6-ethyl-4-pentyl-2*H*-pyran-2-one (3ca). IR (neat, cm^{-1}): 2930, 2870, 1716, 1539, 1456, 1439, 1375, 1043, 1026, 894, 856, 750, 734; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.53 (d, *J* = 8.3 Hz, 1 H), 7.44 (d, *J* = 7.8 Hz, 1 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.13 - 7.18 (m, 1 H), 6.03 (s, 1 H), 4.65 (q, *J* = 6.8 Hz, 1 H), 4.48 (s, 2 H), 2.68 - 2.81 (m, 2 H), 2.41 - 2.59 (m, 2 H), 1.48 - 1.58 (m, 6 H), 1.26 - 1.36 (m, 4 H), 1.22 (t, *J*

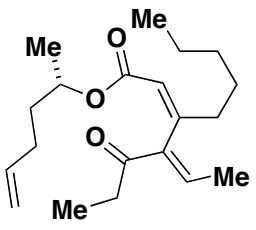
= 7.6 Hz, 3 H), 0.84 - 0.91 (m, 3 H); ^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 164.3, 162.4, 160.3, 137.0, 132.5, 129.0, 128.7, 127.3, 122.6, 115.7, 111.4, 71.5, 70.1, 32.5, 31.4, 28.5, 24.8, 22.2, 21.9, 13.8, 12.1; HRMS (EI) calcd. for [$C_{21}H_{28}BrO_3$] $(M+H)^+$ 407.1122, found 407.1207.



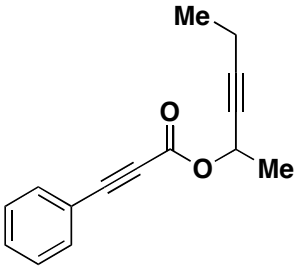
(*Z*)-2-bromobenzyl 3-((*E*)-4-oxohex-2-en-3-yl)oct-2-enoate (4ca). IR (neat, cm^{-1}): 2931, 2859, 1719, 1671, 1441, 1265, 1175, 1132, 1012, 750, 660; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.56 (d, *J* = 8.3 Hz, 1 H), 7.33 - 7.38 (m, 1 H), 7.27 - 7.33 (m, 1 H), 7.15 - 7.21 (m, 1 H), 6.67 (q, *J* = 6.8 Hz, 1 H), 6.01 (s, 1 H), 5.14 (s, 2 H), 2.58 - 2.72 (m, 2 H), 2.53 (t, *J* = 7.3 Hz, 1 H), 2.17 - 2.28 (m, 2 H), 1.73 (d, *J* = 7.3 Hz, 3 H), 1.42 - 1.50 (m, 2 H), 1.24 - 1.35 (m, 6 H), 1.05 (t, *J* = 7.3 Hz, 3 H), 0.85 - 0.92 (m, 4 H); ^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 219.1, 219.0, 218.9, 218.9, 218.8, 218.8, 218.6, 218.5, 218.5, 218.4, 218.4, 199.5, 165.0, 157.6, 143.1, 135.5, 135.3, 132.7, 129.8, 129.5, 127.4, 123.4, 118.1, 65.3, 38.7, 31.5, 31.0, 26.5, 22.4, 15.3, 13.9, 8.2; HRMS (EI) calcd. for [$C_{21}H_{28}BrO_3$] $(M+H)^+$ 407.11218, found 407.1239.



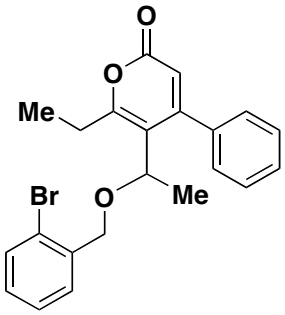
6-ethyl-5-(1-((*S*)-hex-5-en-2-yloxy)ethyl)-4-pentyl-2*H*-pyran-2-one (3cb). Yield: 7%. Diastereomer mixture (1.3:1) IR (neat, cm^{-1}): 2930, 2872, 2359, 2341, 1720, 1540, 1456, 1375, 1062, 909, 857, 735; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = *6.02 (s, 1 H), 6.02 (s, 1 H), *5.78 - 5.86 (m, 1H), 5.68 - 5.76 (m, 1 H), 4.87 - 5.08 (m, 2 H), 4.55 - 4.62 (m, 1 H), *3.42 (q, *J* = 5.9 Hz,, 1H), 3.34 (q, *J* = 6.0 Hz, 1 H), 2.63 - 2.86 (m, 2 H), 2.44 - 2.63 (m, 2 H), 2.08 - 2.19 (m, 1 H), 1.93 - 2.06 (m, 1 H), 1.50 - 1.68 (m, 4 H), 1.39 - 1.47 (m, 4 H), 1.32 - 1.39 (m, 4 H), 1.23 - 1.26 (m, 3 H), 1.16 (d, *J* = 5.9 Hz, 3 H), *1.06 (d, *J* = 6.3 Hz, 3 H), 0.83 - 0.97 (m, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 162.8, *162.8, 160.5, 138.3, 138.1, 117.6, 114.8, 114.7, 111.4, 111.4, 111.3, 111.2, 73.2, 72.6, 69.2, 69.2, 68.4, 38.0, 36.2, 35.6, 32.7, 32.6, 32.5, 31.6, 31.5, 31.2, 29.6, 28.6, 28.5, 25.1, 25.0, 22.6, 22.4, 22.3, 22.1, 20.4, 19.4, 13.9, 12.4, 12.3, 12.3 (* represents signals of minor isomer); HRMS (EI) calcd. for [$C_{20}H_{33}O_3$] $(M+H)^+$ 321.24242, found 321.25520.



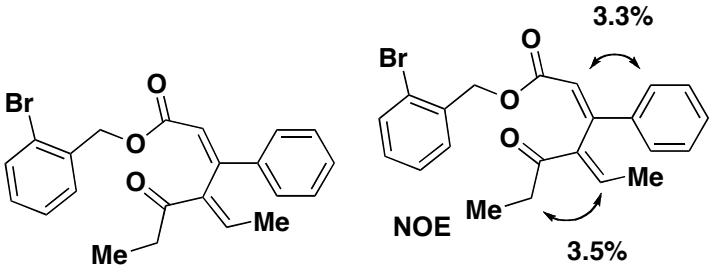
(*Z*)-((*S*)-hex-5-en-2-yl) 3-((*E*)-4-oxohex-2-en-3-yl)oct-2-enoate (4cb). Yield: 75%. IR (neat, cm^{-1}): 2933, 2860, 1713, 1673, 1459, 1376, 1271, 1190, 1124, 1091, 994, 911, 735; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 6.70 (q, *J* = 6.8 Hz, 1 H), 5.91 (s, 1 H), 5.77 (dd, *J* = 10.3, 17.1 Hz, 1 H), 4.91 - 5.06 (m, 2 H), 4.81 - 4.91 (m, 1 H), 2.69 (br. s., 2 H), 2.20 (br. s., 2 H), 1.97 - 2.10 (m, 2 H), 1.73 (d, *J* = 7.3 Hz, 3 H), 1.62 - 1.69 (m, 1 H), 1.50 - 1.57 (m, 1 H), 1.39 - 1.50 (m, 2 H), 1.23 - 1.37 (m, 5 H), 1.16 (d, *J* = 6.3 Hz, 3 H), 1.10 (t, *J* = 7.1 Hz, 3 H), 0.89 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (75MHz, CHLOROFORM-d) δ = 199.5, 165.1, 155.9, 143.2, 137.8, 134.9, 119.2, 114.9, 69.8, 38.6, 35.1, 31.6, 31.1, 29.6, 26.5, 22.5, 19.9, 15.2, 14.0, 8.2; HRMS (EI) calcd. for [$C_{20}H_{33}O_3$] $(M+H)^+$ 321.24242, found 321.25350.



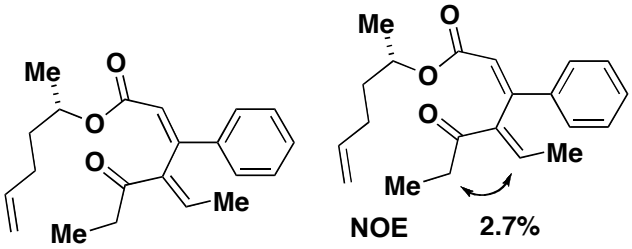
hex-3-yn-2-yl 3-phenylpropiolate (1d). Yield: 81%. IR (neat, cm^{-1}): 2980, 2938, 2215, 1706, 1276, 1185, 1161, 1048, 1001, 850, 756, 687; ^{1}H NMR (500 MHz, CHLOROFORM-*d*) δ ppm 1.13 (t, *J*=7.6 Hz, 3 H), 1.54 (d, *J*=6.8 Hz, 3 H), 2.17 - 2.27 (m, 2 H), 5.55 (d, *J*=6.8 Hz, 1 H), 7.36 (t, *J*=7.8 Hz, 2 H), 7.41 - 7.47 (m, 1 H), 7.57 (d, *J*=8.3 Hz, 2 H); ^{13}C NMR (126 MHz, CHLOROFORM-*d*) δ ppm 12.32, 13.48, 21.64, 62.67, 80.46, 86.57, 87.79, 94.71, 119.50, 128.50, 130.61, 132.93, 152.95; HRMS (EI) calcd. for $[C_{15}H_{15}O_2]$ $(M+H)^+$ 227.10666, found 227.10553.



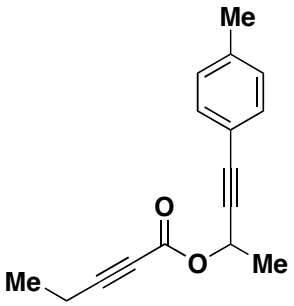
5-(1-(2-bromobenzyloxy)ethyl)-6-ethyl-4-phenyl-2*H*-pyran-2-one (3da). IR (neat, cm^{-1}): 2976, 2935, 1718, 1621, 1531, 1442, 1374, 1202, 1061, 1026, 892, 857, 750, 733, 700; ^{1}H NMR (500 MHz, CHLOROFORM-*d*) δ ppm 1.30 (t, *J*=7.3 Hz, 3 H), 1.45 (d, *J*=6.8 Hz, 3 H), 2.84 - 3.01 (m, 2 H), 4.32 (d, *J*=12.7 Hz, 1 H), 4.37 (q, *J*=6.5 Hz, 1 H), 4.42 (d, *J*=13.2 Hz, 1 H), 6.05 (s, 1 H), 7.10 - 7.21 (m, 3 H), 7.25 - 7.31 (m, 1 H), 7.31 - 7.37 (m, 1 H), 7.37 - 7.43 (m, 3 H), 7.52 (dd, *J*=7.8, 1.0 Hz, 1 H); ^{13}C NMR (75 MHz, CHLOROFORM-*d*) δ ppm 12.07, 21.84, 25.19, 69.97, 71.92, 112.45, 115.99, 122.45, 127.20, 127.34, 128.55, 128.70, 128.89, 132.45, 137.06, 137.11, 159.66, 162.03, 166.45; HRMS (EI) calcd. for $[C_{22}H_{22}BrO_3]$ $(M+H)^+$ 413.07468, found 413.07515.



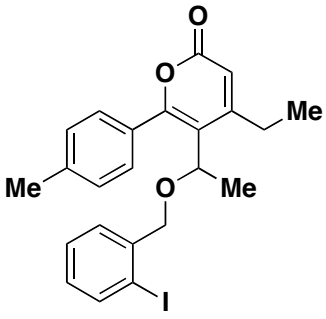
(2*Z*,4*E*)-2-bromobenzyl 4-ethylidene-5-oxo-3-phenylhept-2-enoate (4da). IR (neat, cm^{-1}): 3057, 2934, 1716, 1673, 1608, 1447, 1264, 1153, 1028, 909, 731, 701; ^{1}H NMR (500 MHz, CHLOROFORM-*d*) δ ppm 1.05 (t, *J*=7.3 Hz, 3 H), 1.65 (d, *J*=7.3 Hz, 3 H), 2.61- 2.71 (m, 2 H), 5.22 (s, 2 H), 6.59 (s, 1 H), 6.96 (q, *J*=7.3 Hz, 1 H), 7.15 - 7.23 (m, 1 H), 7.32 (t, *J*=8.1 Hz, 1 H), 7.34 - 7.38 (m, 3 H), 7.40 (d, *J*=7.8 Hz, 1 H), 7.42 - 7.48 (m, 2 H), 7.57 (d, *J*=7.8 Hz, 1 H); ^{13}C NMR (126 MHz, CHLOROFORM-*d*) δ ppm 7.99, 15.41, 31.47, 65.59, 118.25, 123.39, 126.79, 127.45, 128.76, 129.63, 129.78, 129.84, 132.72, 135.20, 137.11, 137.94, 141.26, 152.85, 165.04, 199.37; HRMS (EI) calcd. for $[C_{22}H_{22}BrO_3]$ $(M+H)^+$ 413.07468, found 413.07325.



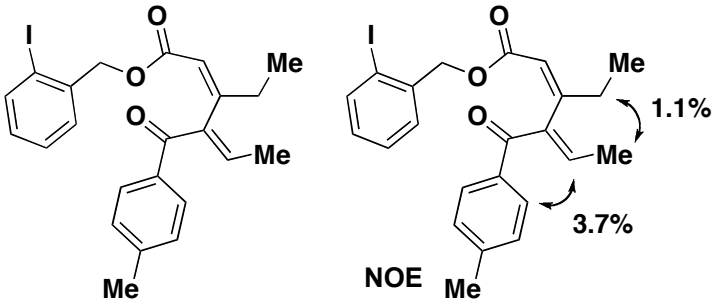
(2*Z*,4*E*)-((*S*)-hex-5-en-2-yl) 4-ethylidene-5-oxo-3-phenylhept-2-enoate (4db). Yield: 80%. IR (neat, cm^{-1}): 2978, 2929, 1708, 1675, 1609, 1447, 1265, 1172, 1026, 914, 733, 700; ^{1}H NMR (500 MHz, CHLOROFORM-*d*) δ ppm 0.79 - 0.91 (m, 1 H), 1.02 - 1.11 (t, *J*=7.3 Hz, 3 H), 1.21 (d, *J*=6.2 Hz, 3 H), 1.51 - 1.62 (m, 1 H), 1.62 - 1.76 (m, 5 H), 1.99 - 2.13 (m, 2 H), 2.52 - 2.84 (m, 2 H), 4.89 - 5.06 (m, 3 H), 5.74 - 5.84 (m, *J*=17.1, 10.3, 6.6, 6.6 Hz, 1 H), 6.49 (s, 1 H), 6.98 (q, *J*=7.0 Hz, 1 H), 7.31 - 7.39 (m, 3 H), 7.40 - 7.48 (m, 2 H); 13C NMR (75 MHz, CHLOROFORM-*d*) δ ppm 7.99, 15.29, 19.88, 29.62, 31.76, 35.07, 70.33, 114.92, 119.59, 126.76, 128.78, 129.60, 136.63, 137.69, 138.07, 141.27, 151.31, 165.19, 199.28; HRMS (EI) calcd. for $[C_{21}H_{27}O_3]$ $(M+H)^+$ 327.19547, found 327.19496.



4-p-tolylbut-3-yn-2-yl pent-2-ynoate (1e). Yield: 52%. IR (neat, cm^{-1}): 2986, 2938, 2234, 1709, 1233, 1077, 1048, 1025, 815, 749; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.21 (t, *J*=7.6 Hz, 3 H), 1.61 (d, *J*=6.8 Hz, 3 H), 2.32 - 2.38 (m, 5 H), 5.72 (q, *J*=6.7 Hz, 1 H), 7.10 (d, *J*=8.3 Hz, 2 H), 7.32 ppm (d, *J*=8.3 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 12.39, 21.38, 62.37, 72.26, 85.40, 85.86, 91.28, 119.01, 128.94, 131.72, 138.78, 152.67 ppm; HRMS (EI) calcd. for $[C_{16}H_{17}O_2]$ $(M+H)^+$ 241.1228, found 241.1229.

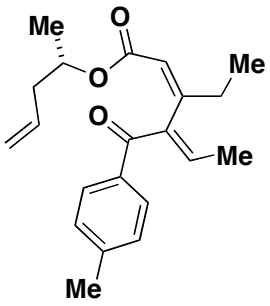


4-ethyl-5-(1-(2-iodobenzyloxy)ethyl)-6-*p*-tolyl-2*H*-pyran-2-one (3ea). Yield: 47%. IR (neat, cm^{-1}): 2973, 1720, 1622, 1541, 1504, 1265, 1075, 1013, 895, 865, 819, 732; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.76 (d, *J* = 7.8 Hz, 1 H), 7.27 - 7.32 (m, 2 H), 7.19 - 7.27 (m, 4 H), 6.93 (t, *J* = 7.3 Hz, 1 H), 6.24 (s, 1 H), 4.63 (q, *J* = 6.8 Hz, 1 H), 4.28 (d, *J* = 12.2 Hz, 1 H), 4.16 (d, *J* = 12.7 Hz, 1 H), 2.97 - 3.04 (m, 1 H), 2.78 - 2.86 (m, 1 H), 2.40 (s, 3 H), 1.61 (d, *J* = 6.8 Hz, 3 H), 1.23 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 162.6, 162.1, 159.5, 140.2, 139.9, 139.1, 129.7, 129.1, 129.1, 128.9, 128.5, 128.1, 116.5, 112.9, 97.9, 74.6, 73.3, 25.0, 21.6, 21.4, 13.0; HRMS (EI) calcd. for $[C_{23}H_{24}IO_3]$ $(M+H)^+$ 475.07646, found 475.07574.

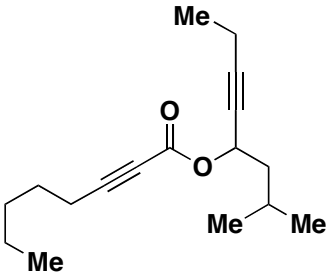


(2*Z*,4*E*)-2-iodobenzyl 3-ethyl-4-(4-methylbenzoyl)hexa-2,4-dienoate (4ea). IR (neat, cm^{-1}): 3054, 2972, 1717, 1643, 1266, 1183, 1151, 870, 733, 702; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.82 (d, *J* = 7.8 Hz, 1 H), 7.67 - 7.72 (m, *J* = 7.8 Hz, 2 H), 7.28 - 7.37 (m, 2 H), 7.19 - 7.24 (m, *J* = 7.8 Hz, 2 H), 6.99 (t, *J* = 7.3 Hz, 1 H), 6.42 (q, *J* = 7.3 Hz, 1 H), 6.07 (s, 1 H), 5.11 (s, 2 H), 2.38 - 2.47 (m, 5 H), 1.78 (d, *J* = 6.8 Hz, 3 H), 1.15 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 195.6, 164.9, 159.0, 142.2, 141.9, 140.1, 139.3, 138.6, 136.0, 129.7, 129.6, 129.2, 128.6, 128.3, 117.3, 98.0, 69.5, 31.7, 21.5, 15.5, 11.3; HRMS (EI) calcd. for $[C_{23}H_{24}IO_3]$

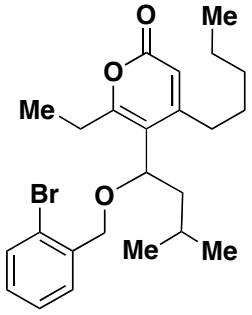
$(M+H)^+$ 475.0770, found 475.0749.



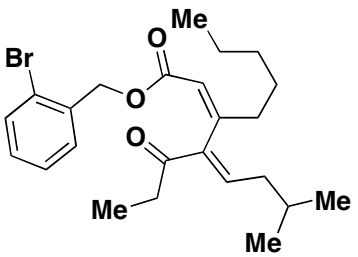
(2*Z*,4*E*)-((*S*)-pent-4-en-2-yl) 3-ethyl-4-(4-methylbenzoyl)hexa-2,4-dienoate (4eb). Yield: 77%. IR (neat, cm^{-1}): 2975, 2935, 2360, 1712, 1644, 1606, 1272, 1198, 1066, 916, 871, 733; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.68 - 7.77 (m, *J* = 7.8 Hz, 2 H), 7.20 - 7.26 (m, 2 H), 6.42 (q, *J* = 7.0 Hz, 1 H), 5.95 (s, 1 H), 5.67 - 5.79 (m, 1 H), 4.99 - 5.10 (m, 2 H), 4.89 - 4.99 (m, 1 H), 2.36 - 2.49 (m, 6 H), 2.21 - 2.36 (m, 2 H), 1.78 (d, *J* = 6.3 Hz, 3 H), 1.16 - 1.24 (m, 3 H), 1.09 - 1.16 (m, 3 H); ^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 195.6, 165.0, 157.3, 142.4, 141.8, 139.9, 136.1, 133.8, 129.7, 128.6, 118.3, 117.5, 69.3, 40.3, 31.5, 21.5, 19.4, 15.4, 11.3; HRMS (EI) calcd. for $[C_{21}H_{27}O_3]$ $(M+H)^+$ 327.1960, found 327.1967.

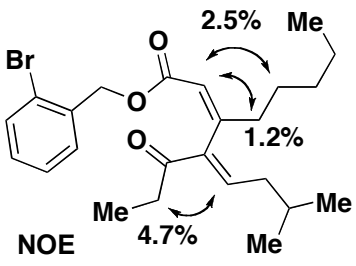


2-methyloct-5-yn-4-yl oct-2-ynoate (1f). Yield: 93%. IR (neat, cm^{-1}): 2957, 2935, 2872, 2232, 1710, 1239, 1057, 929, 750; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 5.44 (t, *J* = 7.3 Hz, 1 H), 2.32 (t, *J* = 7.3 Hz, 2 H), 2.17 - 2.25 (m, 2 H), 1.80 (dt, *J* = 6.7, 13.6 Hz, 1 H), 1.67 - 1.74 (m, 1 H), 1.54 - 1.67 (m, 4 H), 1.28 - 1.43 (m, 4 H), 1.13 (t, *J* = 7.6 Hz, 3 H), 0.94 (d, *J* = 2.9 Hz, 3 H), 0.93 (d, *J* = 2.9 Hz, 3 H), 0.91 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 152.9, 90.1, 88.1, 76.4, 72.9, 64.8, 43.8, 30.9, 27.2, 24.7, 22.4, 22.2, 22.0, 18.7, 13.8, 13.5, 12.4; HRMS (EI) calcd. for $[C_{17}H_{27}O_2]$ $(M+H)^+$ 263.20056, found 263.20018.

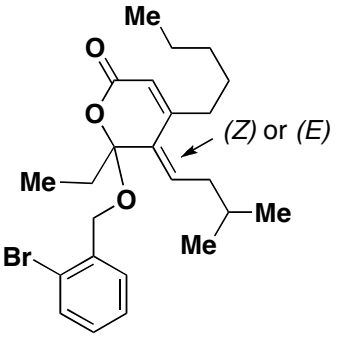


5-(1-(2-bromobenzyloxy)-3-methylbutyl)-6-ethyl-4-pentyl-2*H*-pyran-2-one (3fa). Yield: 43%. (Atropisomer with 3:2 ratio) IR (neat, cm^{-1}): 2956, 2926, 2856, 1717, 1539, 1466, 1265, 1074, 1026, 734, 703; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = $^{\#}$7.53 (d, *J* = 7.8 Hz, 1 H), $^{\#}$7.43 (d, *J* = 7.8 Hz, 1 H), $^{\#}$7.31 (t, *J* = 7.3 Hz, 1 H), $^{\#}$7.12 - 7.21 (m, 1 H), *6.09 (br. s., 1 H), 6.00 (br. s., 1 H), $^{\#}$4.35 - 4.60 (m, 3 H), $^{\#}$2.85 (br. s., 2 H), $^{\#}$2.50 - 2.70 (m, 1 H), $^{\#}$2.33 (br. s., 1 H), $^{\#}$1.83 - 2.07 (m, 2 H), $^{\#}$1.54 (br. s., 3 H), $^{\#}$1.13 - 1.33 (m, 6 H), $^{\#}$0.96 (d, *J* = 6.8 Hz, 3 H), $^{\#}$0.78 - 0.94 (m, 6 H); (* represents signal of the minor isomer; $^{\#}$ represents overlapping signals) ^{13}C NMR (126MHz, DMSO-d_6) δ = 165.3, 162.4, 162.0, 160.9, 137.7, 133.2, 133.1, 130.5, 130.4, 130.4, 130.3, 130.3, 128.5, 128.4, 123.3, 115.9, 114.9, 112.7, 110.8, 75.3, 72.9, 70.3, 45.9, 45.3, 32.9, 32.0, 31.9, 31.8, 31.7, 31.7, 29.6, 28.5, 25.5, 25.2, 24.9, 24.8, 24.2, 23.9, 22.5, 22.5, 21.7, 14.5, 12.9, 12.5; HRMS (EI) calcd. for $[C_{24}H_{34}BrO_3]$ $(M+H)^+$ 449.16858, found 449.16835.

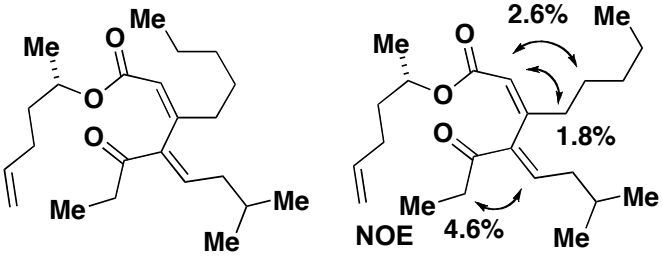




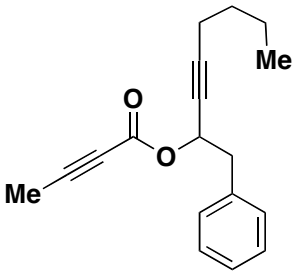
(2*Z*,4*E*)-2-bromobenzyl 7-methyl-3-pentyl-4-propionylocta-2,4-dienoate (4fa). IR (neat, cm^{-1}): 2955, 2929, 2870, 1721, 1672, 1463, 1269, 1176, 1129, 1097, 1013, 909, 750, 730; ^1H NMR (500MHz ,CHLOROFORM-d) δ = 7.55 (d, *J* = 7.8 Hz, 1 H), 7.35 (d, *J* = 7.8 Hz, 1 H), 7.29 (t, *J* = 7.8 Hz, 1 H), 7.13 - 7.20 (m, 1 H), 6.57 (t, *J* = 7.6 Hz, 1 H), 5.98 (s, 1 H), 5.13 (d, *J* = 12.2 Hz, 2 H), 2.70 (br. s., 1 H), 2.62 (br. s., 1 H), 2.12 - 2.31 (m, 2 H), 1.90 - 2.01 (m, 2 H), 1.67 - 1.75 (m, 1 H), 1.43 - 1.54 (m, 2 H), 1.31 - 1.32 (m, 4 H), 1.07 (t, *J* = 7.1 Hz, 3 H), 0.86 - 0.92 (m, 10 H); ^{13}C NMR (126MHz ,DMSO-d_6) δ = 199.7, 165.0, 158.0, 142.5, 139.3, 135.3, 132.7, 129.8, 129.5, 127.4, 123.3, 117.8, 65.2, 38.9, 38.6, 31.5, 31.0, 28.2, 26.4, 22.6, 22.4, 14.0, 8.2; HRMS (EI) calcd. for $[C_{24}H_{34}BrO_3]$ $(M+H)^+$ 449.16858, found 449.16642.



6-(2-bromobenzyloxy)-6-ethyl-5-(3-methylbutylidene)-4-pentyl-5,6-dihydro-2*H*-pyran-2-one. Yield: 33%. IR (neat, cm^{-1}): 2927, 2855, 1709, 1465, 1264, 997, 733, 703; ^1H NMR (500MHz ,CHLOROFORM-d) δ = 7.59 (d, *J* = 7.8 Hz, 1 H), 7.50 (d, *J* = 7.8 Hz, 1 H), 7.29 - 7.37 (m, 1 H), 7.10 - 7.17 (m, 1 H), 6.30 (t, *J* = 7.6 Hz, 1 H), 5.81 (s, 1 H), 4.63 (d, *J* = 13.2 Hz, 1 H), 4.51 (d, *J* = 13.2 Hz, 1 H), 2.32 - 2.54 (m, 4 H), 1.93 - 2.15 (m, 2 H), 1.67 - 1.77 (m, 1 H), 1.55 - 1.64 (m, 2 H), 1.34 - 1.44 (m, 4 H), 0.95 - 1.02 (m, 3 H), 0.79 - 0.95 (m, 10 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 163.4, 155.6, 138.5, 137.0, 132.2, 129.7, 128.7, 128.7, 127.4, 121.9, 113.7, 108.2, 64.6, 37.8, 34.9, 32.6, 31.9, 31.6, 29.4, 29.0, 28.1, 26.7, 22.7, 22.5, 22.4, 14.1, 14.0, 7.4; HRMS (EI) calcd. for $[C_{24}H_{34}BrO_3]$ $(M+H)^+$ 449.16858, found 449.16796.

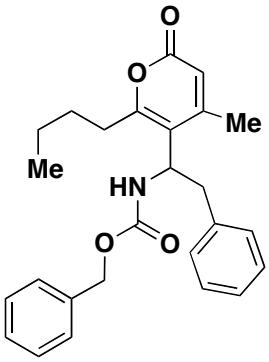


(2*Z*,4*E*)-((*S*)-hex-5-en-2-yl) 7-methyl-3-pentyl-4-propionylocta-2,4-dienoate (4fb). Yield: 73%. IR (neat, cm^{-1}): 2955, 2931, 2871, 1714, 1677, 1461, 1273, 1188, 1124, 1098, 993, 910, 872; ^1H NMR (500MHz ,CHLOROFORM-d) δ = 6.59 (t, *J* = 7.3 Hz, 1 H), 5.87 (s, 1 H), 5.73 - 5.81 (m, 1 H), 4.91 - 5.03 (m, 2 H), 4.78 - 4.89 (m, 1 H), 2.61 - 2.81 (m, 2 H), 2.12 - 2.28 (m, 2 H), 1.99 - 2.10 (m, 2 H), 1.95 (br. s., 2 H), 1.70 - 1.77 (m, 1 H), 1.59 - 1.69 (m, 1 H), 1.44 - 1.57 (m, 3 H), 1.31 (br. s., 4 H), 1.16 (d, *J* = 6.3 Hz, 3 H), 1.10 (t, *J* = 7.3 Hz, 3 H), 0.83 - 0.97 (m, 10 H); ^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 199.6, 165.1, 156.4, 142.7, 138.7, 137.8, 118.9, 114.8, 77.4, 76.6, 69.8, 38.8, 38.5, 35.1, 31.6, 31.2, 29.6, 28.3, 26.4, 22.6, 22.4, 19.9, 13.9, 8.2; HRMS (EI) calcd. for $[C_{23}H_{39}O_3]$ $(M+H)^+$ 363.28937, found 363.28999.

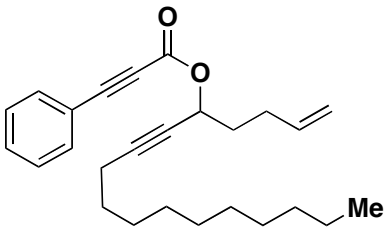


(2-(2-methylenepent-3-ynyl)oct-3-ynyl)benzene (1g). Yield: 38%. IR (neat, cm^{-1}): 2957, 2932, 2871, 2239, 1709, 1240, 1059, 972, 943, 747, 698, 531; ^1H NMR (500 MHz, $CDCl_3$) δ = 0.89 (t, *J*=7.3 Hz, 3 H), 1.31 - 1.39 (m, 2 H), 1.41 - 1.48 (m, 2 H), 1.96 (s, 3 H), 2.15 - 2.21 (m, 2 H), 3.02 - 3.13 (m, 2 H), 5.57 – 5.60 (m, 1 H), 7.22 - 7.33 ppm (m, 5 H); ^{13}C

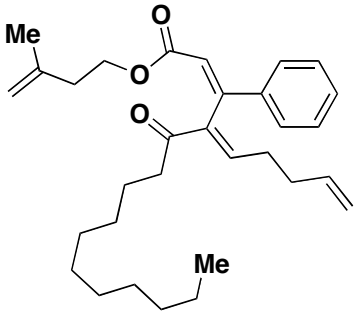
NMR (126 MHz, $CDCl_3$) δ = 3.61, 13.39, 18.17, 21.65, 30.19, 41.19, 66.39, 72.04, 76.21, 86.06, 87.85, 126.75, 128.11, 129.51, 135.67, 152.39 ppm; HRMS (EI) calcd. for $[C_{18}H_{25}NO_2]$ $(M+NH_4)^+$ 286.1807, found 286.1803.



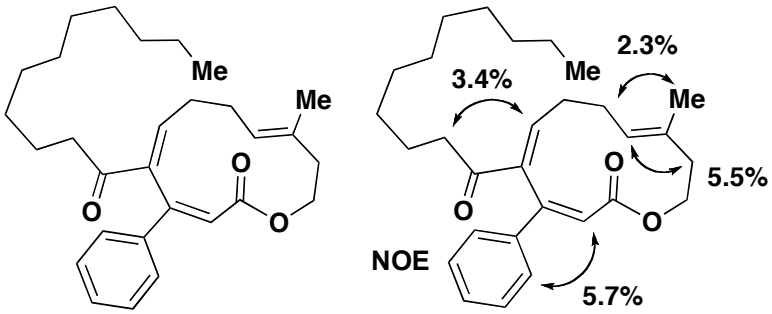
benzyl 1-(6-butyl-4-methyl-2-oxo-2*H*-pyran-5-yl)-2-phenylethylcarbamate (3g). Yield: 65%. IR (neat, cm^{-1}): 3315, 2960, 2359, 1698, 1538, 1497, 1264, 1028, 731, 698; ^1H NMR (500MHz ,DMSO-d_6) δ = 8.10 (br. s., 1 H), 7.24 - 7.39 (m, 7 H), 7.17 - 7.24 (m, 3 H), 5.93 (br. s., 1 H), 4.97 (s, 2 H), 4.70 (d, *J* = 6.8 Hz, 1 H), 3.09 (dd, *J* = 7.6, 12.9 Hz, 1 H), 2.90 (dd, *J* = 8.1, 12.9 Hz, 1 H), 1.97 - 2.21 (m, 2 H), 1.39 - 1.54 (m, 1 H), 1.26 - 1.37 (m, 2 H), 1.23 (br. s., 1 H), 0.84 (br. s., 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 162.0, 155.4, 136.4, 129.1, 128.8, 128.6, 128.6, 128.5, 128.4, 128.2, 128.1, 127.2, 66.9, 41.1, 31.7, 29.4, 22.6, 21.1, 21.0, 13.7; HRMS (EI) calcd. for $[C_{26}H_{30}NO_4]$ $(M+H)^+$ 420.21693, found 420.21822.



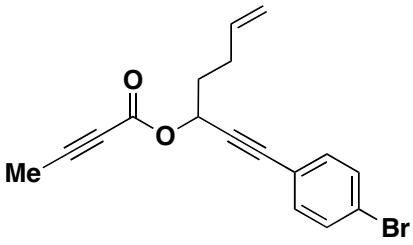
heptadec-1-en-6-yn-5-yl 3-phenylpropiolate (1h). Yield: 64%. IR (neat, cm^{-1}): 2924, 2853, 2212, 1711, 1277, 1168, 914, 756, 688; ^1H NMR (500 MHz, $CDCl_3$) δ = 0.87 (t, *J*=7.1 Hz, 3 H), 1.26 – 1,30 (m, 13 H), 1.34 - 1.38 (m, 2 H), 1.48 - 1.54 (m, 2 H), 1.88 - 1.99 (m, 2 H), 2.20 - 2.28 (m, 4 H), 5.02 (dd, *J*=10.3, 1.5 Hz, 1 H), 5.08 (dd, *J*=17.1, 1.5 Hz, 1 H), 5.48 – 5.50 (m, 1H), 5.79 – 5.87 (m, 1H), 7.37 (t, *J*=7.6 Hz, 2 H), 7.45 (t, *J*=7.3 Hz, 1 H), 7.59 ppm (d, *J*=6.8 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 14.08, 18.70, 22.65, 28.38, 28.80, 29.06, 29.20, 29.29, 29.49, 29.54, 31.87, 34.13, 65.89, 76.51, 80.47, 86.71, 87.62, 115.56, 119.58, 128.52, 130.64, 132.99, 136.88, 153.07 ppm; HRMS (EI) calcd. for $[C_{26}H_{38}NO_2]$ $(M+NH_4)^+$ 396.2903, found 396.2889.



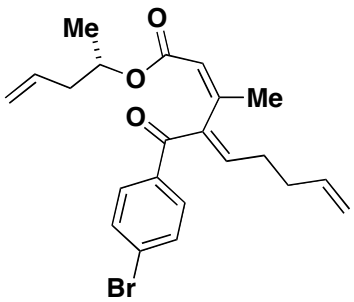
(2*Z*,4*E*)-3-methylbut-3-enyl 5-oxo-4-(pent-4-enylidene)-3-phenylpentadec-2-enoate (**4h**). Yield: 67%. IR (neat, cm^{-1}): 2923, 2853, 1714, 1676, 1447, 1262, 1162, 909, 771, 730; ^1H NMR (500MHz ,CHLOROFORM-d) δ = 7.43 (dd, *J* = 2.4, 7.3 Hz, 2 H), 7.32 - 7.38 (m, 3 H), 6.84 (t, *J* = 6.8 Hz, 1 H), 6.47 (s, 1 H), 5.65 (ddd, *J* = 4.1, 6.3, 16.8 Hz, 1 H), 4.94 (d, *J* = 8.3 Hz, 1 H), 4.91 (s, 1 H), 4.80 (s, 1 H), 4.73 (s, 1 H), 4.20 (t, *J* = 7.1 Hz, 2 H), 2.67 - 2.78 (m, 1 H), 2.61 (br. s., 1 H), 2.34 (t, *J* = 6.8 Hz, 2 H), 2.06 (br. s., 4 H), 1.75 (s, 3 H), 1.57 - 1.66 (m, 2 H), 1.27 - 1.33 (m, 4 H), 1.25 (br. s., 12 H), 0.88 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 199.2, 165.4, 152.2, 141.6, 140.9, 140.7, 138.3, 137.2, 129.7, 128.7, 126.9, 118.7, 115.4, 112.1, 62.5, 38.4, 36.6, 32.2, 31.9, 29.6, 29.5, 29.5, 29.3, 29.3, 29.1, 24.1, 22.6, 22.5, 14.1; HRMS (EI) calcd. for $[C_{31}H_{45}O_3]$ $(M+H)^+$ 465.3368, found 465.3365.



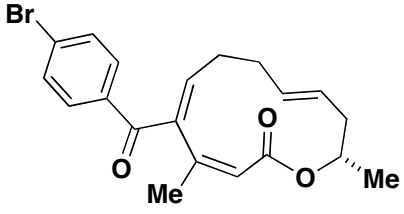
(3*Z*,5*E*,9*Z*)-10-methyl-4-phenyl-5-undecanoyloxacyclododeca-3,5,9-trien-2-one (5h). RCM condition A. Yield: 99%. IR (neat, cm^{-1}): 2922, 2852, 2360, 1717, 1695, 1602, 1147, 1263, 1162, 1015, 772, 734, 700; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.42 - 7.47 (m, 2 H), 7.34 - 7.38 (m, 3 H), 6.74 (dd, *J* = 4.1, 12.4 Hz, 1 H), 6.52 (s, 1 H), 4.93 (dd, *J* = 4.9, 10.7 Hz, 1 H), 4.47 - 4.54 (m, 1 H), 4.03 (ddd, *J* = 2.0, 5.2, 10.9 Hz, 1 H), 2.69 - 2.77 (m, 1 H), 2.36 - 2.46 (m, 2 H), 2.28 - 2.36 (m, 1 H), 2.20 - 2.27 (m, 1 H), 2.04 - 2.17 (m, 2 H), 1.93 - 2.03 (m, 1 H), 1.62 (s, 3 H), 1.53 - 1.60 (m, 3 H), 1.19 - 1.30 (m, 16 H), 0.87 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 199.0, 165.7, 150.3, 140.5, 140.1, 137.6, 131.8, 129.6, 128.8, 127.4, 126.7, 119.6, 60.5, 39.8, 38.7, 31.9, 30.1, 29.6, 29.5, 29.3, 29.2, 26.8, 23.8, 22.7, 15.4, 14.1; HRMS (EI) calcd. for $[C_{29}H_{41}O_3]$ $(M+H)^+$ 437.3055, found 437.3042.



1-(4-bromophenyl)hept-6-en-1-yn-3-yl but-2-ynoate (1i). Yield: 95%. IR (neat, cm^{-1}): 2925, 2239, 1709, 1486, 1239, 1059, 1010, 823, 736; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.40 - 7.49 (m, *J* = 8.3 Hz, 2 H), 7.25 - 7.33 (m, 2 H), 5.77 - 5.88 (m, *J* = 6.6, 6.6, 10.3, 17.0 Hz, 1 H), 5.62 (t, *J* = 6.6 Hz, 1 H), 4.99 - 5.13 (m, 2 H), 2.28 (q, *J* = 7.3 Hz, 2 H), 1.93 - 2.05 (m, 6 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 152.5, 136.5, 133.2, 131.5, 123.0, 120.9, 115.8, 86.6, 86.5, 85.0, 72.0, 65.2, 33.6, 29.1; HRMS (EI) calcd. for $[C_{17}H_{15}BrO_2Na]$ $(M+Na)^+$ 353.01476, found 353.01515.

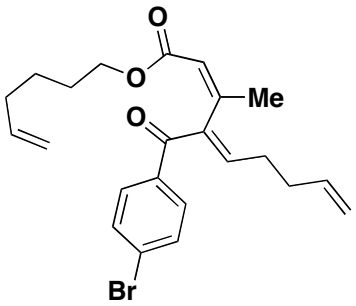


(2*Z*,4*E*)-((*S*)-pent-4-en-2-yl) 4-(4-bromobenzoyl)-3-methylnona-2,4,8-trienoate (4ia). Yield: 72%. IR (neat, cm^{-1}): 2978, 2360, 1708, 1648, 1267, 1108, 1123, 1011, 916, 735; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.69 - 7.78 (m, *J* = 8.8 Hz, 2 H), 7.54 - 7.61 (m, *J* = 8.8 Hz, 2 H), 6.18 (t, *J* = 7.6 Hz, 1 H), 5.96 (s, 1 H), 5.66 - 5.82 (m, 2 H), 4.98 - 5.10 (m, 4 H), 4.86 - 4.96 (m, 1 H), 2.21 - 2.36 (m, 5 H), 2.14 - 2.21 (m, 3 H), 2.11 (s, 3 H), 1.17 (d, *J* = 5.9 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 194.9, 164.7, 152.6, 143.5, 142.0, 137.3, 137.1, 133.7, 131.4, 131.2, 126.4, 120.0, 117.6, 115.7, 69.4, 40.2, 32.6, 29.1, 25.9, 19.5; HRMS (EI) calcd. for $[C_{22}H_{26}BrO_3]$ $(M+H)^+$ 417.10598, found 417.10656.

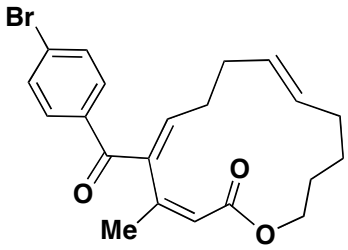


(*S*,3*Z*,5*E*,9*E*)-5-(4-bromobenzoyl)-4,12-dimethyloxacyclododeca-3,5,9-trien-2-one (5ia). RCM condition A. Yield: 70%. IR (neat, cm^{-1}): 2930, 1707, 1647, 1585, 1264, 1204, 1091, 868, 734; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.71 (d, *J* = 8.3 Hz, 2 H), 7.59 (d, *J* = 8.3 Hz, 2 H), *7.51 – 7.53 (d, *J* = 8.3 Hz, 2 H), *6.31

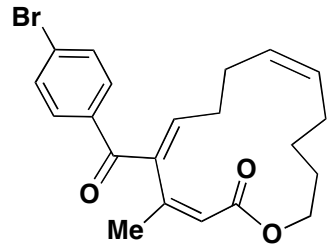
(dd, *J* = 3.9, 12.2 Hz, 1 H), 6.03 (dd, *J* = 4.9, 11.7 Hz, 1 H), 5.97 (s, 1 H), *5.94 (s, 1 H), 5.37 (ddd, *J* = 4.9, 9.9, 15.0 Hz, 1 H), 5.27 (ddd, *J* = 4.9, 10.4, 15.0 Hz, 1 H), 5.11 - 5.21 (m, 1 H), *4.85 - 4.88 (m, 1 H), *2.68 - 2.74 (m, 1 H), 2.36 - 2.45 (m, 1 H), 2.21 - 2.31 (m, 2 H), 2.11 (s, 3 H), 1.86 - 2.10 (m, 4 H), 1.25 (d, *J* = 6.4 Hz, 3 H), *1.16 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 195.3, 166.3, 150.4, 143.0, 142.1, 137.3, 132.9, 131.3, 131.2, 130.3, 127.6, 126.0, 120.7, 68.2, 41.3, 31.1, 29.1, 25.4, 20.2 (* represents signals of minor isomer); HRMS (EI) calcd. for $[C_{20}H_{21}BrO_3Na]$ $(M+Na)^+$ 411.05663, found 411.05725.



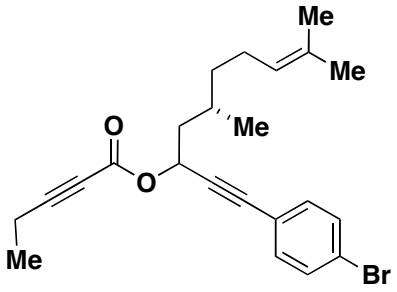
(2*Z*,4*E*)-hex-5-enyl 4-(4-bromobenzoyl)-3-methylnona-2,4,8-trienoate (4ib). Yield: 75%. IR (neat, cm^{-1}): 2936, 2359, 1711, 1648, 1206, 1145, 907, 728; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.69 - 7.77 (m, *J* = 8.3 Hz, 2 H), 7.53 - 7.62 (m, *J* = 7.8 Hz, 2 H), 6.18 (t, *J* = 7.6 Hz, 1 H), 5.98 (s, 1 H), 5.71 - 5.83 (m, 2 H), 4.92 - 5.09 (m, 4 H), 4.02 (t, *J* = 6.8 Hz, 2 H), 2.25 (q, *J* = 7.3 Hz, 2 H), 2.14 - 2.21 (m, 2 H), 2.12 (s, 3 H), 2.05 (q, *J* = 7.2 Hz, 2 H), 1.56 - 1.66 (m, 2 H), 1.39 - 1.45 (m, 2 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 194.9, 165.3, 152.9, 143.5, 141.9, 138.3, 137.2, 137.1, 131.4, 131.2, 126.4, 119.6, 115.7, 114.8, 63.8, 33.2, 32.6, 29.2, 28.0, 25.9, 25.1; HRMS (EI) calcd. for $[C_{23}H_{28}BrO_3]$ $(M+H)^+$ 431.12163, found 431.12256.



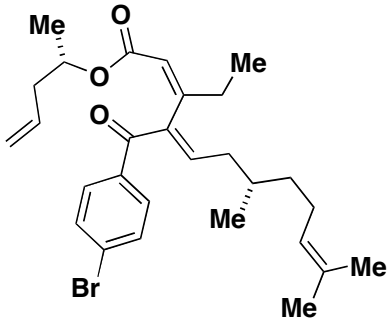
(3*Z*,5*E*,9*E*)-5-(4-bromobenzoyl)-4-methyloxacyclotetradeca-3,5,9-trien-2-one (5ib-E). RCM condition B. Yield: 29%. (RCM condition D. Yield: 37%.) IR (neat, cm^{-1}): 2927, 1709, 1649, 1585, 1441, 1394, 1265, 1208, 1189, 1069, 1042, 733, 702; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.71 (d, *J* = 8.3 Hz, 2 H), 7.59 (d, *J* = 7.8 Hz, 2 H), 6.11 (dd, *J* = 3.2, 11.5 Hz, 1 H), 5.97 (s, 1 H), 5.41 - 5.50 (m, 1 H), 5.29 - 5.39 (m, 1 H), 4.57 (ddd, *J* = 4.4, 7.0, 11.1 Hz, 1 H), 3.82 (ddd, *J* = 4.1, 6.6, 11.2 Hz, 1 H), 2.28 - 2.39 (m, 2 H), 2.14 - 2.25 (m, 2 H), 2.12 (s, 3 H), 2.03 - 2.09 (m, 3 H), 1.90 - 2.00 (m, 1 H), 1.57 - 1.76 (m, 4 H), 1.32 - 1.42 (m, 2 H), 1.19 - 1.31 (m, 3 H), 0.80 - 0.94 (m, 1 H); ^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 194.5, 165.6, 152.1, 143.6, 142.9, 137.1, 131.3, 131.2, 131.0, 129.3, 126.3, 120.0, 62.4, 30.9, 30.3, 28.9, 26.8, 26.1, 23.8; HRMS (EI) calcd. for $[C_{21}H_{24}BrO_3]$ $(M+H)^+$ 403.09033, found 403.09206.



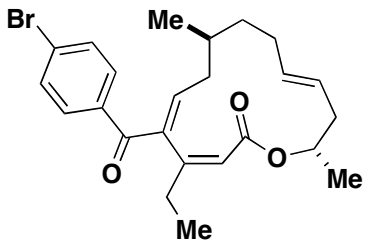
(3*Z*,5*E*,9*Z*)-5-(4-bromobenzoyl)-4-methyloxacyclotetradeca-3,5,9-trien-2-one (5ib-Z). RCM condition B. Yield: 21%. (RCM condition D. Yield: 16%.) IR (neat, cm^{-1}): 2929, 2360, 1713, 1647, 1584, 1265, 1202, 1011, 875, 853, 733, 702; ^1H NMR (500MHz ,CHLOROFORM-d) δ = 7.69 - 7.76 (m, 2 H), 7.56 - 7.63 (m, *J* = 8.3 Hz, 2 H), 6.27 (dd, *J* = 3.7, 11.5 Hz, 1 H), 6.00 (s, 1 H), 5.53 (td, *J* = 6.1, 10.1 Hz, 1 H), 5.36 - 5.45 (m, 1 H), 4.95 (td, *J* = 2.7, 11.6 Hz, 1 H), 3.78 (dt, *J* = 3.9, 11.2 Hz, 1 H), 2.24 - 2.37 (m, 2 H), 2.14 - 2.24 (m, 2 H), 2.07 - 2.11 (m, 3 H), 1.84 - 2.05 (m, 4 H), 1.65 - 1.76 (m, 1 H), 1.44 - 1.60 (m, 4 H), 1.12 - 1.24 (m, 1 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 194.9, 165.5, 152.1, 144.1, 141.0, 137.6, 131.4, 131.0, 130.9, 127.9, 126.4, 119.7, 60.4, 30.8, 27.5, 26.2, 26.0, 25.5, 24.7; HRMS (EI) calcd. for $[C_{21}H_{24}BrO_3]$ $(M+H)^+$ 403.09033, found 403.08902.



(5*S*)-1-(4-bromophenyl)-5,9-dimethyldec-8-en-1-yn-3-yl pent-2-ynoate (1j). Yield: 86%. IR (neat, cm^{-1}): 2915, 2235, 1710, 1486, 1235, 1178, 1050, 1011, 908, 823, 730; ^1H NMR (500MHz ,CHLOROFORM-d) δ = 7.39 - 7.48 (m, *J* = 8.3 Hz, 2 H), 7.25 - 7.32 (m, 2 H), 5.62 - 5.72 (m, 1 H), 5.09 (t, *J* = 7.1 Hz, 1 H), 2.36 (q, *J* = 7.3 Hz, 2 H), 1.94 - 2.08 (m, 3 H), 1.69 - 1.79 (m, 2 H), 1.64 - 1.69 (m, 4 H), 1.60 (d, *J* = 3.9 Hz, 3 H), 1.35 - 1.45 (m, 1 H), 1.17 - 1.30 (m, 5 H), 0.98 (dd, *J* = 4.1, 6.1 Hz, 3 H); ^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 152.8, 152.7, 133.3, 131.5, 131.5, 124.3, 122.9, 121.2, 91.6, 91.5, 87.4, 87.1, 84.9, 84.7, 72.2, 64.8, 64.4, 41.8, 41.5, 36.9, 36.7, 29.7, 29.2, 29.0, 25.7, 25.2, 19.5, 19.4, 17.6, 12.5, 12.4; HRMS (EI) calcd. for $[C_{23}H_{27}BrO_2Na]$ $(M+Na)^+$ 437.10866, found 437.10880.

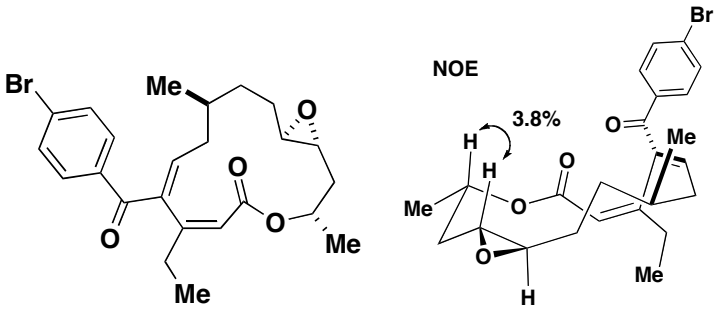


(*S*,2*Z*,4*E*)-((*S*)-pent-4-en-2-yl) 4-(4-bromobenzoyl)-3-ethyl-7,11-dimethyldodeca-2,4,10-trienoate (4ja). Yield: 83%. IR (neat, cm^{-1}): 2968, 2928, 1710, 1648, 1200, 1070,909, 730; ^1H NMR (500MHz ,CHLOROFORM-d) δ = 7.68 - 7.78 (m, *J* = 8.3 Hz, 2 H), 7.53 - 7.62 (m, *J* = 8.3 Hz, 2 H), 6.23 (t, *J* = 7.3 Hz, 1 H), 5.91 (s, 1 H), 5.67 - 5.78 (m, 1 H), 4.99 - 5.11 (m, 3 H), 4.91 (q, *J* = 6.3 Hz, 1 H), 2.39 (br. s., 2 H), 2.31 (dt, *J* = 6.7, 13.9 Hz, 1 H), 2.23 (dt, *J* = 6.9, 14.0 Hz, 1 H), 2.14 (dt, *J* = 6.5, 14.8 Hz, 1 H), 1.88 - 2.03 (m, 3 H), 1.68 (s, 3 H), 1.53 - 1.62 (m, 4 H), 1.27 - 1.38 (m, 1 H), 1.09 - 1.22 (m, 7 H), 0.88 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 195.1, 164.9, 157.9, 144.2, 142.3, 137.7, 133.7, 131.5, 131.3, 131.2, 126.1, 124.2, 117.9, 117.6, 69.4, 40.2, 37.2, 32.6, 31.8, 25.7, 25.5, 19.8, 19.5, 17.6, 11.2; HRMS (EI) calcd. for $[C_{28}H_{38}BrO_3]$ $(M+H)^+$ 501.19988, found 501.20165.

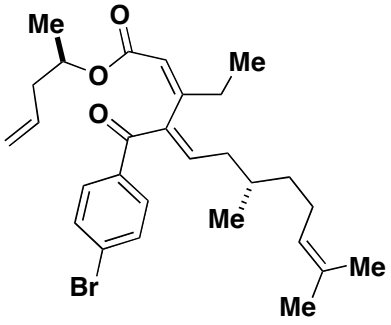


(3*Z*,5*E*,8*S*,11*E*,14*S*)-5-(4-bromobenzoyl)-4-ethyl-8,14-dimethyloxacyclotetradeca-3,5,11-trien-2-one (5ja). RCM condition C. Yield: 74%. IR (neat, cm^{-1}): 2930, 2359, 1706, 1647, 1264, 1205, 1069, 1055, 733, 702; ^1H NMR (500MHz ,CHLOROFORM-d) δ = 7.70 - 7.79 (m, 2 H), 7.59 (d, *J* = 7.3 Hz, 2 H), 6.29 (t, *J* = 8.1 Hz, 1 H), 5.89 (s, 1 H), 5.44 - 5.54 (m, 1 H), 5.35 - 5.44 (m, 1 H), 5.23 (dd, *J* = 6.3, 11.2 Hz, 1 H), 2.47 - 2.61 (m, 1 H), 2.26 - 2.42 (m, 2 H), 2.01 - 2.21 (m, 4 H), 1.89 - 1.99 (m, 1 H), 1.77 -

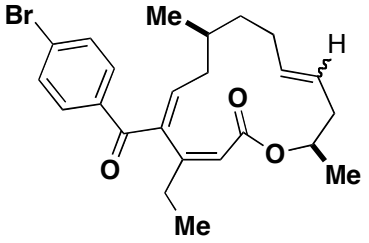
1.86 (m, 1 H), 1.69 - 1.77 (m, 1 H), 1.49 - 1.60 (m, 1 H), 1.12 - 1.24 (m, 8 H), 0.83 - 0.92 (m, 3 H); ^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 195.5, 165.3, 158.1, 144.6, 141.7, 137.6, 131.6, 131.2, 127.2, 126.0, 118.3, 68.0, 40.3, 36.3, 34.7, 31.5, 31.0, 28.3, 20.9, 19.7, 11.3; HRMS (EI) calcd. for $[C_{24}H_{30}BrO_3]$ $(M+H)^+$ 445.13728, found 445.13704.



(1*R*,3*S*,6*Z*,8*E*,11*S*,14*R*)-8-(4-bromobenzoyl)-7-ethyl-3,11-dimethyl-4,15-dioxabicyclo[12.1.0]pentadeca-6,8-dien-5-one (10). In a 4mL capped vial was compound **5ja** (16.6 mg, 0.037 mmol) in DCM (745 μL) to give a colorless solution. *m*CPBA (8.77 mg, 0.039 mmol) was added. The resulting solution was stirred under room temperature for 3 h. The reaction was quenched with 5% Na_2SO_3(aq), washed with $NaHCO_3$, brine and dried over Na_2SO_4. The crude product was added to a silica gel column and was eluted with 0-20% EA in hexane to give **10** (12.6 mg, 73% yield, diastereoselectivity 6.3:1). IR (neat, cm^{-1}): 2935, 2361, 1704, 1648, 1264, 1205, 1070, 731, 702; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.68 - 7.77 (m, 2 H), 7.55 - 7.63 (m, 2 H), 6.20 - 6.29 (m, 1 H), 5.93 (s, 1 H), 5.33 - 5.44 (m, 1 H), *5.16 - 5.20 (m, 1 H), 2.78 - 2.85 (m, 1 H), 2.67 - 2.73 (m, 1 H), 2.51 - 2.60 (m, 1 H), 2.32 - 2.44 (m, 1 H), 2.20 - 2.31 (m, 2 H), 2.07 - 2.16 (m, 1 H), 1.78 - 1.92 (m, 2 H), 1.55 - 1.64 (m, 1 H), 1.11 - 1.35 (m, 11 H), *0.97 (d, *J* = 6.8 Hz, 3 H), 0.92 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 195.3, 165.6, 160.2, 144.8, 140.2, 137.3, 131.4, 131.2, 126.3, 117.9, 66.5, 60.0, 54.7, 40.4, 35.6, 32.8, 32.4, 30.1, 29.0, 21.2, 18.5, 11.2 (* represents signals of minor isomer); HRMS (EI) calcd. for $[C_{24}H_{30}BrO_4]$ $(M+H)^+$ 461.13220, found 461.13234.

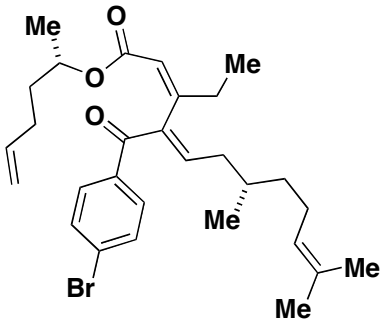


(*S*,2*Z*,4*E*)-((*R*)-pent-4-en-2-yl) 4-(4-bromobenzoyl)-3-ethyl-7,11-dimethyldodeca-2,4,10-trienoate (4jb). Yield: 77%. IR (neat, cm^{-1}): 2968, 2927, 1711, 1648, 1201, 1070, 907, 729; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.69 - 7.78 (m, *J* = 8.8 Hz, 2 H), 7.54 - 7.61 (m, *J* = 8.3 Hz, 2 H), 6.23 (t, *J* = 7.3 Hz, 1 H), 5.91 (s, 1 H), 5.72 (dd, *J* = 10.0, 17.3 Hz, 1 H), 5.00 - 5.11 (m, 3 H), 4.85 - 4.97 (m, 1 H), 2.39 (br. s., 2 H), 2.27 - 2.35 (m, 1 H), 2.19 - 2.27 (m, 1 H), 2.09 - 2.18 (m, 1 H), 1.89 - 2.01 (m, 3 H), 1.68 (s, 3 H), 1.52 - 1.63 (m, 4 H), 1.28 - 1.37 (m, 1 H), 1.12 - 1.22 (m, 8 H), 0.88 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 195.1, 164.9, 157.9, 144.2, 142.3, 142.3, 137.7, 133.7, 131.5, 131.3, 131.2, 126.1, 124.2, 117.9, 117.6, 69.4, 40.2, 37.2, 37.1, 36.9, 32.6, 32.6, 31.7, 25.7, 25.5, 19.8, 19.4, 17.6, 11.2; HRMS (EI) calcd. for $[C_{28}H_{38}BrO_3]$ $(M+H)^+$ 501.19988, found 501.19742.

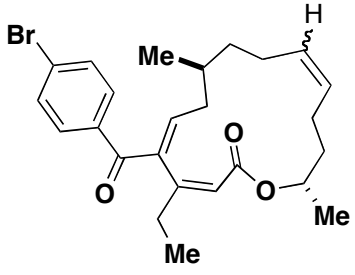


(3*Z*,5*E*,8*S*,14*R*)-5-(4-bromobenzoyl)-4-ethyl-8,14-dimethyloxacyclotetradeca-3,5,11-trien-2-one (5jb). RCM condition C. Yield: 77%. (*E*/*Z* = 3.3:1) IR (neat, cm^{-1}): 2963, 2930, 2360, 1709, 1647, 1201,

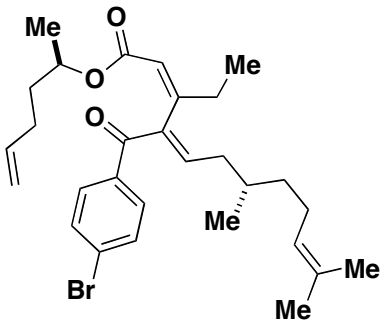
1068, 1051, 869, 734, 702; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.70 - 7.78 (m, 2 H), 7.56 - 7.62 (m, 2 H), 6.39 (dd, *J* = 5.6, 11.0 Hz, 1 H), *6.29 (dd, *J* = 7.3, 9.3 Hz, 1 H), 5.90 (s, 1 H), *5.89 (s, 1 H), *5.39 - 5.52 (m, 2 H), 5.27 - 5.36 (m, 2 H), *5.19 - 5.24 (m, 1 H), 5.08 - 5.15 (m, 1 H), 2.49 - 2.64 (m, 1 H), 2.25 - 2.39 (m, 1 H), 2.17 - 2.25 (m, 1 H), 2.07 - 2.17 (m, 2 H), 1.97 - 2.07 (m, 1 H), 1.86 - 1.97 (m, 1 H), *1.79 - 1.83 (m, 1 H), 1.66 - 1.76 (m, 1 H), 1.51 - 1.60 (m, 1 H), 1.41 - 1.51 (m, 1 H), 1.27 - 1.34 (m, 1 H), 1.22 - 1.27 (m, 1 H), 1.18 - 1.22 (m, 4 H), 1.11 - 1.18 (m, 3 H), *0.89 (d, *J* = 6.3 Hz, 3 H), 0.86 (d, *J* = 6.3 Hz, 3 H); ^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 195.5, 165.3, 157.9, 144.6, 144.2, 142.2, 138.0, 133.0, 131.6, 131.2, 131.2, 127.6, 126.1, 118.3, 68.4, *68.0, 40.4, 40.3, 38.3, 36.6, 36.3, 34.7, 31.9, 31.5, 31.5, 31.0, 28.9, 28.3, 21.1, 20.9, 19.7, 18.3, 11.3, 11.3 (* represents signals of minor isomer); HRMS (EI) calcd. for [$C_{24}H_{30}BrO_3$] $(M+H)^+$ 445.13728, found 445.13762.



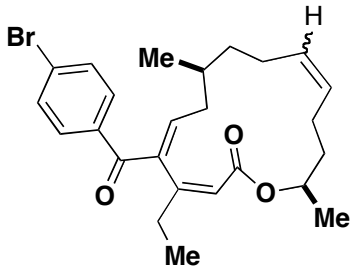
(*S*,2*Z*,4*E*)-((*S*)-hex-5-en-2-yl) 4-(4-bromobenzoyl)-3-ethyl-7,11-dimethyldodeca-2,4,10-trienoate (4jc). Yield: 84%. IR (neat, cm^{-1}): 2969, 2926, 2362, 1710, 1650, 1200, 1069, 911, 737; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.68 - 7.77 (m, *J* = 8.3 Hz, 2 H), 7.54 - 7.62 (m, *J* = 8.8 Hz, 2 H), 6.23 (t, *J* = 7.3 Hz, 1 H), 5.92 (s, 1 H), 5.71 - 5.83 (m, 1 H), 5.05 (t, *J* = 7.1 Hz, 1 H), 4.90 - 5.02 (m, 2 H), 4.83 - 4.90 (m, 1 H), 2.39 (br. s., 2 H), 2.09 - 2.18 (m, 1 H), 2.05 (td, *J* = 6.6, 14.5 Hz, 2 H), 1.88 - 2.00 (m, 3 H), 1.62 - 1.72 (m, 4 H), 1.50 - 1.62 (m, 5 H), 1.28 - 1.38 (m, 2 H), 1.10 - 1.22 (m, 8 H), 0.89 (d, *J* = 6.4 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 195.1, 165.0, 157.7, 144.2, 142.3, 137.8, 137.7, 131.5, 131.3, 131.2, 126.1, 124.3, 118.0, 114.8, 69.7, 37.2, 35.1, 32.6, 31.7, 29.6, 25.7, 25.5, 20.0, 19.8, 17.6, 11.2; HRMS (EI) calcd. for [$C_{29}H_{39}BrO_3Na$] $(M+Na)^+$ 537.19748, found 537.19729.



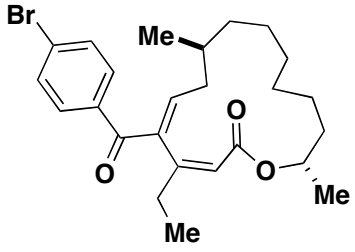
(3*Z*,5*E*,8*S*,15*S*)-5-(4-bromobenzoyl)-4-ethyl-8,15-dimethyloxacyclopentadeca-3,5,11-trien-2-one (5jc). RCM condition C. Yield: 86%. (*E*/*Z* = 1:2.1) IR (neat, cm^{-1}): 2929, 2360, 1707, 1648, 1206, 1067, 870, 734, 702; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = *7.77 (d, *J* = 8.3 Hz, 2 H), 7.74 (d, *J* = 8.3 Hz, 2 H), 7.59 (d, *J* = 8.3 Hz, 2 H), 6.19 - 6.27 (m, 1 H), 5.94 (s, 1 H), *5.88 (s, 1 H), 5.27 - 5.40 (m, 1 H), *5.17 - 5.22 (m, 1 H), 4.85 - 4.91 (m, 1 H), *4.74 – 4.79 (m, 1 H), 2.39 - 2.56 (m, 2 H), 2.25 - 2.39 (m, 2 H), 1.94 - 2.13 (m, 2 H), 1.84 - 1.93 (m, 1 H), 1.61 - 1.84 (m, 3 H), 1.44 - 1.54 (m, 1 H), 1.22 - 1.35 (m, 3 H), 1.15 - 1.21 (m, 3 H), 1.13 (d, *J* = 6.3 Hz, 3 H), *1.10 (d, *J* = 6.3 Hz, 3 H), 0.92 - 0.98 (m, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = *195.5, 195.4, 165.1, *164.4, 158.7, *158.3, 144.2, 144.0, 141.0, 139.9, 137.7, 137.5, 131.6, 131.5, 131.5, 131.4, 131.2, 131.2, 130.8, 130.6, 128.7, 128.6, 126.1, 126.1, 117.9, 116.9, 109.7, *69.7, 67.5, 36.0, 35.6, 35.3, 34.7, 34.1, 33.6, 32.7, 32.2, 32.0, 31.6, 31.0, 30.5, 26.3, 23.2, 21.5, 20.8, 20.6, 20.2, *11.3, 11.0 (* represents signals of minor isomer); HRMS (EI) calcd. for [$C_{25}H_{32}BrO_3$] $(M+H)^+$ 459.15293, found 459.15628.



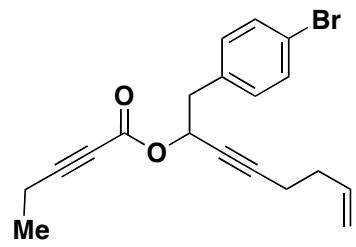
(*S*,2*Z*,4*E*)-((*R*)-hex-5-en-2-yl) 4-(4-bromobenzoyl)-3-ethyl-7,11-dimethyldodeca-2,4,10-trienoate (4jd). Yield: 75%. IR (neat, cm^{-1}): 2968, 2927, 2362, 1709, 1649, 1201, 1070, 873, 736; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.68 - 7.76 (m, *J* = 8.3 Hz, 2 H), 7.54 - 7.61 (m, *J* = 8.3 Hz, 2 H), 6.23 (t, *J* = 7.6 Hz, 1 H), 5.92 (s, 1 H), 5.71 - 5.82 (m, 1 H), 4.90 - 5.08 (m, 3 H), 4.82 - 4.90 (m, 1 H), 2.31 - 2.48 (m, 2 H), 2.09 - 2.19 (m, 1 H), 2.01 - 2.09 (m, 2 H), 1.87 - 2.01 (m, 4 H), 1.62 - 1.72 (m, 4 H), 1.52 - 1.60 (m, 6 H), 1.25 - 1.37 (m, 1 H), 1.11 - 1.22 (m, 7 H), 0.88 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 195.1, 165.0, 144.2, 142.3, 137.8, 137.7, 131.6, 131.3, 131.2, 126.1, 124.3, 118.0, 114.8, 69.7, 37.1, 37.0, 35.1, 32.6, 31.7, 29.6, 25.7, 25.5, 20.0, 19.8, 17.6, 11.2; HRMS (EI) calcd. for $[C_{29}H_{39}BrO_3Na]$ $(M+Na)^+$ 537.19748, found 537.19779.



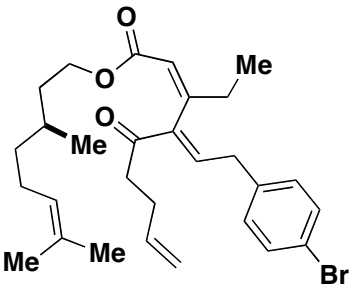
(3*Z*,5*E*,8*S*,15*R*)-5-(4-bromobenzoyl)-4-ethyl-8,15-dimethyloxacyclopentadeca-3,5,11-trien-2-one (5jd). RCM condition C. Yield: 97%. (*E*/*Z* = 1:1) IR (neat, cm^{-1}): 2928, 1708, 1647, 1264, 1205, 1069, 1012, 871, 734, 702; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = *7.76 (d, *J* = 8.3 Hz, 2 H), 7.73 (d, *J* = 8.3 Hz, 2 H), 7.58 (d, *J* = 8.3 Hz, 2 H), *6.30 (dd, *J* = 4.4, 11.2 Hz, 1 H), 6.12 (dd, *J* = 2.7, 11.0 Hz, 1 H), 5.94 (s, 1 H), *5.90 (s, 1 H), 5.16 - 5.33 (m, 2 H), 4.88 - 4.98 (m, 1 H), *4.75 - 4.80 (m, 1 H), 2.45 - 2.60 (m, 1 H), 2.24 - 2.37 (m, 2 H), 2.07 - 2.21 (m, 2 H), 1.94 - 2.03 (m, 1 H), 1.80 - 1.93 (m, 2 H), 1.63 - 1.80 (m, 3 H), 1.44 - 1.57 (m, 2 H), 1.35 - 1.42 (m, 1 H), 1.32 (q, *J* = 6.7 Hz, 1 H), 1.13 - 1.20 (m, 6 H), 0.95 (d, *J* = 6.8 Hz, 3 H), *0.89 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 195.6, 195.3, 165.1, 164.9, 158.4, 158.4, 143.9, 143.8, 142.6, 137.9, 137.6, 131.6, 131.4, 131.3, 131.2, 131.2, 129.7, 129.2, 126.0, 126.0, 117.7, 117.0, 69.7, 67.7, 36.7, 36.3, 35.5, 35.3, 34.8, 34.0, 32.2, 32.1, 31.6, 31.5, 29.7, 27.9, 23.2, 21.0, 21.0, 20.7, 20.3, 19.4, 11.2, 11.0 (* represents signals of minor isomer); HRMS (EI) calcd. for $[C_{25}H_{32}BrO_3]$ $(M+H)^+$ 459.15293, found 459.15213.



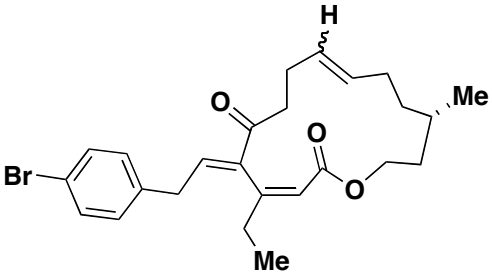
(3*Z*,5*E*,8*S*,15*S*)-5-(4-bromobenzoyl)-4-ethyl-8,15-dimethyloxacyclopentadeca-3,5-dien-2-one (11). In a 10 mL round-bottom flask was **5jd** (28.8 mg, 0.063 mmol) in EA (1.3 mL) to give a colorless solution. 10% Pd/C (3 mg) was added. The resulting solution was degassed with hydrogen and the stirring was continued for 8 h under room temperature. The volatiles were removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (0-10% EA in hexane) to give **11** (20.9 mg, 72% yield). IR (neat, cm^{-1}): 2930, 1705, 1648, 1264, 1207, 1070, 1012, 872, 733, 703; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.68 (d, *J* = 8.3 Hz, 2 H), 7.51 (d, *J* = 8.8 Hz, 2 H), 6.07 (dd, *J* = 3.4, 11.2 Hz, 1 H), 5.86 (s, 1 H), 4.95 - 5.06 (m, 1 H), 2.41 (ddd, *J* = 2.0, 7.3, 17.6 Hz, 1 H), 2.25 (dd, *J* = 7.6, 17.3 Hz, 1 H), 2.03 (ddd, *J* = 8.8, 11.1, 14.8 Hz, 1 H), 1.79 - 1.88 (m, 1 H), 1.66 - 1.75 (m, 1 H), 1.59 (dd, *J* = 6.8, 13.7 Hz, 1 H), 1.48 (s, 2 H), 1.24 - 1.41 (m, 7 H), 1.13 - 1.24 (m, 4 H), 1.02 - 1.13 (m, 8 H), 0.86 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 195.3, 165.3, 158.6, 143.7, 142.4, 137.5, 131.5, 131.2, 131.2, 131.2, 129.8, 127.9, 126.1, 117.1, 69.1, 36.5, 35.5, 34.0, 32.6, 31.7, 27.9, 27.0, 22.8, 22.2, 20.7, 20.6, 20.3, 11.1; HRMS (EI) calcd. for $[C_{25}H_{34}BrO_3]$ $(M+H)^+$ 461.16858, found 461.16757.



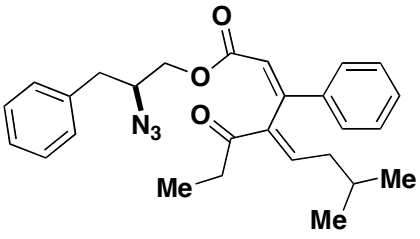
1-(4-bromophenyl)oct-7-en-3-yn-2-yl pent-2-ynoate (1k). Yield: 92%. IR (neat, cm^{-1}): 2982, 2940, 2235, 1736, 1712, 1235, 1078, 1046, 732; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.39 - 7.46 (m, *J* = 8.3 Hz, 2 H), 7.11 - 7.18 (m, *J* = 8.3 Hz, 2 H), 5.72 - 5.83 (m, 1 H), 5.54 (t, *J* = 6.6 Hz, 1 H), 4.99 - 5.09 (m, 2 H), 2.95 - 3.08 (m, 3 H), 2.35 (q, *J* = 7.3 Hz, 2 H), 2.23 - 2.29 (m, 2 H), 2.16 - 2.23 (m, 2 H), 1.21 (t, *J* = 7.6 Hz, 3 H); ^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 152.6, 136.5, 134.8, 131.4, 131.4, 121.0, 115.7, 91.6, 87.6, 72.1, 66.0, 40.6, 32.4, 18.5, 12.5, 12.4; HRMS (EI) calcd. for $[C_{19}H_{20}BrO_2]$ $(M+H)^+$ 359.06412, found 359.06380.



(2*Z*,4*E*)-((*S*)-3,7-dimethyloct-6-enyl) 4-(2-(4-bromophenyl)ethylidene)-3-ethyl-5-oxonona-2,8-dienoate (4k). Yield: 69%. IR (neat, cm^{-1}): 2964, 2925, 2359, 1713, 1675, 1458, 1266, 1193, 1072, 1011, 737; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.41 (d, *J* = 8.3 Hz, 2 H), 7.02 (d, *J* = 8.3 Hz, 2 H), 6.65 (t, *J* = 7.6 Hz, 1 H), 5.96 (s, 1 H), 5.78 - 5.88 (m, 1 H), 4.99 - 5.13 (m, 2 H), 4.96 (d, *J* = 10.3 Hz, 1 H), 3.97 - 4.09 (m, 2 H), 3.35 (br. s., 2 H), 2.71 - 2.87 (m, 2 H), 2.38 (q, *J* = 7.3 Hz, 2 H), 2.30 - 2.34 (m, 1 H), 2.19 - 2.30 (m, 1 H), 1.88 - 2.03 (m, 2 H), 1.68 (s, 3 H), 1.59 (s, 3 H), 1.45 - 1.52 (m, 1 H), 1.26 - 1.44 (m, 2 H), 1.06 - 1.21 (m, 5 H), 0.89 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 198.1, 165.5, 157.0, 143.1, 137.5, 137.5, 136.8, 131.8, 131.3, 130.2, 130.2, 124.5, 120.4, 118.5, 115.1, 62.7, 37.2, 37.0, 35.4, 35.1, 31.8, 29.5, 28.0, 25.7, 25.3, 19.3, 17.6, 11.3; HRMS (EI) calcd. for $[C_{29}H_{40}BrO_3]$ $(M+H)^+$ 515.21553, found 515.21416.

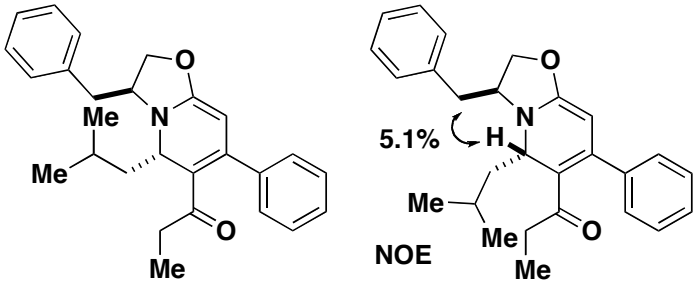


(*S*,3*Z*,5*E*)-5-(2-(4-bromophenyl)ethylidene)-4-ethyl-13-methyloxacyclopentadeca-3,9-diene-2,6-dione (5k). RCM condition C. Yield 69%. (*E*/*Z* = 1.3:1) IR (neat, cm^{-1}): 2967, 1712, 1265, 1195, 1072, 1012, 732, 703; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.39 - 7.45 (m, 2 H), 7.05 (d, *J* = 8.8 Hz, 2 H), 7.00 - 7.03 (m, 2 H), 6.65 - 6.75 (m, 1 H), *6.04 (s, 1 H), 5.98 (s, 1 H), 5.37 - 5.46 (m, 1 H), 5.25 - 5.36 (m, 1 H), 4.29 (ddd, *J* = 3.7, 7.2, 11.1 Hz, 1 H), 3.93 - 4.08 (m, 1 H), 3.25 - 3.48 (m, 3 H), 4.26 - 4.31 (m, 1 H), *4.11 - 4.15 (m, 1 H), 3.97 - 4.06 (m, 1 H), 3.32 – 3.43 (m, 2 H), 2.91 - 2.97 (m, 1 H), *2.76 - 2.82 (m, 1 H), 2.52 - 2.67 (m, 1 H), 2.38 - 2.45 (m, 1 H), 2.16 - 2.37 (m, 4 H), 2.00 - 2.08 (m, 2 H), 1.49 - 1.72 (m, 2 H), 1.28 - 1.46 (m, 2 H), 1.14 - 1.23 (m, 2 H), 1.05 - 1.14 (m, 4 H), 0.83 - 0.90 (m, 1 H), 0.81 (d, *J* = 6.3 Hz, 3 H), *0.67 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 197.1, 165.9, 155.4, 153.0, 142.9, 138.1, 137.6, 137.1, 131.9, 131.8, 131.8, 130.3, 130.3, 130.2, 129.6, 129.4, 120.8, 120.4, 119.3, *62.3, 61.3, 38.3, 37.0, 35.3, 35.2, 35.1, 35.0, 34.9, 31.6, 31.4, 28.9, 28.9, 25.6, 25.6, 25.3, 24.7, 19.6, 18.2, 11.6, 11.3 (* represents signals of minor isomer); HRMS (EI) calcd. for $[C_{25}H_{31}BrO_3Na]$ $(M+Na)^+$ 481.13488, found 481.13278.

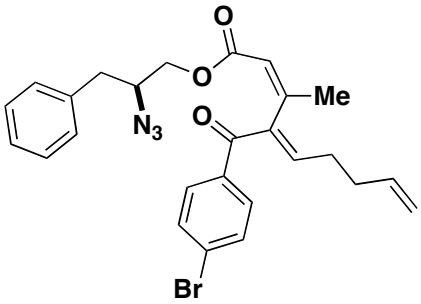


(2*Z*,4*E*)-((*S*)-2-azido-3-phenylpropyl) 7-methyl-3-phenyl-4-propionylocta-2,4-dienoate (4bc). Yield: 83%. IR (neat, cm^{-1}): 2956, 2360, 2213, 1717, 1673, 1605, 1265, 1153, 734, 699; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.45

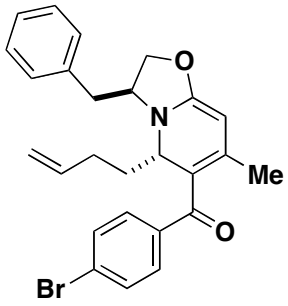
(d, *J* = 9.3 Hz, 2 H), 7.28 - 7.41 (m, 5 H), 7.18 - 7.28 (m, 3 H), 6.90 (t, *J* = 7.3 Hz, 1 H), 6.52 (s, 1 H), 4.21 (d, *J* = 10.7 Hz, 1 H), 4.00 - 4.10 (m, 1 H), 3.82 (br. s., 1 H), 2.74 - 2.92 (m, 3 H), 2.69 (br. s., 1 H), 1.85 (br. s., 2 H), 1.60 - 1.71 (m, 1 H), 1.11 (t, *J* = 7.3 Hz, 3 H), 0.80 (d, *J* = 5.9 Hz, 6 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 199.5, 164.9, 153.9, 141.3, 140.6, 138.1, 136.5, 129.9, 129.2, 128.7, 128.7, 127.0, 127.0, 117.6, 65.4, 61.7, 38.7, 37.3, 31.6, 28.1, 22.4, 8.1; HRMS (EI) calcd. for $[C_{27}H_{32}N_3O_3]$ $(M+H)^+$ 446.24382, found 446.24548.



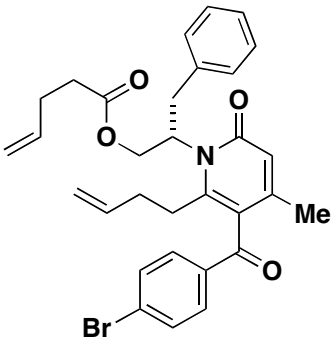
1-((3*S*,5*S*)-3-benzyl-5-isobutyl-7-phenyl-3,5-dihydro-2*H*-oxazolo[3,2-*a*]pyridin-6-yl)propan-1-one (13b). In a 4 mL capped vial, compound **4bc** (66.0 mg, 0.148 mmol) was dissolved in dry $PhCH_3$ (3.2 mL) and PPh_3 (58.0 mg, 1.5 equiv.) was added. The reaction mixture was heated under reflux for 24 h. The volatiles were removed under reduced pressure and purification of the crude product on silica gel (0-25% EA in hexane, 0.5% TEA) gave **13b** (58.9 mg, 99% yield) as a yellow viscous liquid. IR (neat, cm^{-1}): 2954, 2869, 1612, 1446, 1374,1132, 729, 698; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.34 - 7.39 (m, 3 H), 7.23 - 7.33 (m, 5 H), 7.16 (d, *J* = 6.3 Hz, 2 H), 5.12 - 5.20 (m, 1 H), 4.45 - 4.51 (m, 1 H), 4.44 (s, 1 H), 4.17 - 4.29 (m, 2 H), 3.11 (dd, *J* = 3.4, 13.7 Hz, 1 H), 2.83 (dd, *J* = 7.8, 13.7 Hz, 1 H), 1.59 - 1.82 (m, 4 H), 1.47 - 1.53 (m, 1 H), 1.04 (d, *J* = 6.3 Hz, 3 H), 1.00 (d, *J* = 5.9 Hz, 3 H), 0.83 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 197.7, 161.3, 154.9, 143.2, 135.5, 129.2, 128.8, 128.6, 128.5, 128.4, 128.3, 128.3, 127.2, 110.7, 77.4, 72.6, 58.9, 52.2, 40.2, 37.9, 33.9, 24.5, 23.6, 22.9, 10.1; HRMS (EI) calcd. for $[C_{27}H_{32}NO_2]$ $(M+H)^+$ 402.24276, found 402.24310.



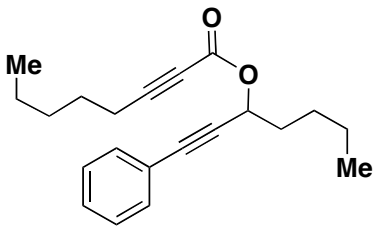
(2*Z*,4*E*)-((*S*)-2-azido-3-phenylpropyl) 4-(4-bromobenzoyl)-3-methylnona-2,4,8-trienoate (4ic). Yield: 83%. IR (neat, cm^{-1}): 2948, 2361, 2112, 1718, 1647, 1265, 1197, 1142, 910, 732, 700; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.73 (d, *J* = 8.3 Hz, 2 H), 7.58 (d, *J* = 8.3 Hz, 2 H), 7.27 - 7.34 (m, 2 H), 7.23 - 7.25 (m, 1 H), 7.19 (d, *J* = 6.8 Hz, 2 H), 6.20 (t, *J* = 7.3 Hz, 1 H), 6.05 (s, 1 H), 5.70 - 5.80 (m, 1 H), 4.96 - 5.08 (m, 2 H), 4.16 (dd, *J* = 3.7, 11.5 Hz, 1 H), 4.02 (dd, *J* = 7.3, 11.7 Hz, 1 H), 3.78 (dt, *J* = 3.7, 10.1 Hz, 1 H), 2.76 - 2.88 (m, 2 H), 2.23 - 2.30 (m, 2 H), 2.16 - 2.21 (m, 2 H), 2.15 (d, *J* = 1.5 Hz, 3 H); ^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 194.8, 164.6, 154.7, 143.7, 141.7, 137.2, 137.0, 136.5, 131.4, 131.3, 129.2, 128.7, 127.0, 126.5, 118.7, 115.8, 65.2, 61.8, 37.3, 32.6, 29.2, 26.1; HRMS (EI) calcd. for $[C_{26}H_{27}BrN_3O_3]$ $(M+H)^+$ 508.12303, found 508.12445.



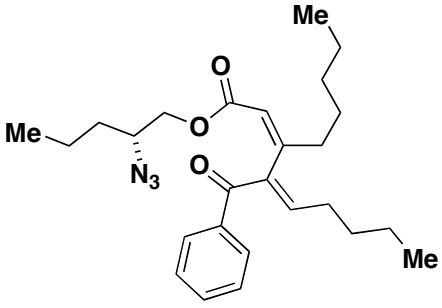
((3*S*,5*S*)-3-benzyl-5-(but-3-enyl)-7-methyl-3,5-dihydro-2*H*-oxazolo[3,2-*a*]pyridin-6-yl)(4-bromophenyl)methanone (13ic). In a 4 mL capped vial, compound **4ic** (61.0 mg, 0.120 mmol) was dissolved in dry THF (2.4 mL) and PPh_3 (47.2 mg, 1.5 equiv.) was added. 0.048 mL TEA was added. The reaction mixture was heated under reflux for 24 h. The volatiles were removed under reduced pressure and purification of the crude product on silica gel (0-20% EA in hexane, 1% TEA) gave **13ic** (39.1 mg, 70% yield) as a yellow viscous liquid. IR (neat, cm^{-1}): 2919, 2360, 1738, 1613, 1421, 1265, 1066, 1010, 910, 729, 700; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.52 (d, *J* = 6.8 Hz, 2 H), 7.40 (d, *J* = 6.8 Hz, 2 H), 7.25 - 7.35 (m, 3 H), 7.18 (d, *J* = 7.3 Hz, 2 H), 5.74 - 5.85 (m, 1 H), 4.91 - 5.08 (m, 3 H), 4.41 - 4.48 (m, 1 H), 4.36 (s, 1 H), 4.17 - 4.28 (m, 2 H), 3.15 (dd, *J* = 4.1, 13.9 Hz, 1 H), 2.79 (dd, *J* = 8.3, 13.7 Hz, 1 H), 2.07 - 2.16 (m, 2 H), 1.74 - 1.81 (m, 2 H), 1.67 (s, 3 H); ^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 191.6, 162.6, 154.0, 143.0, 138.3, 135.3, 131.4, 129.5, 129.1, 128.9, 127.2, 124.0, 114.6, 110.3, 78.2, 72.5, 58.3, 54.3, 37.4, 31.1, 29.1, 23.3; HRMS (EI) calcd. for $[C_{26}H_{27}BrNO_2]$ $(M+H)^+$ 464.12197, found 464.12233.



(*S*)-2-(5-(4-bromobenzoyl)-6-(but-3-enyl)-4-methyl-2-oxopyridin-1(2*H*)-yl)-3-phenylpropyl pent-4-enoate (14ica). Yield: 65%. IR (neat, cm^{-1}): 2923, 1736, 1656, 1582, 1465, 1151, 915, 732, 702; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.56 (d, *J* = 8.3 Hz, 2 H), 7.32 - 7.46 (m, 2 H), 7.23 - 7.32 (m, 4 H), 7.10 - 7.17 (m, 2 H), 6.35 (s, 1 H), 5.73 - 5.87 (m, 1 H), 5.48 - 5.61 (m, 1 H), 4.81 - 5.05 (m, 6 H), 4.28 - 4.38 (m, 1 H), 3.82 - 3.87 (m, 1 H), 3.17 (d, *J* = 9.8 Hz, 1 H), 2.30 - 2.45 (m, 4 H), 2.09 - 2.21 (m, 1 H), 1.89 - 2.04 (m, 3 H), 1.84 (s, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 195.2, 172.4, 163.4, 147.3, 146.3, 137.8, 136.4, 135.6, 135.5, 132.3, 130.7, 129.6, 129.4, 128.6, 126.8, 119.6, 119.3, 115.9, 115.7, 65.0, 60.4, 34.9, 33.4, 32.3, 30.5, 28.7, 19.5; HRMS (EI) calcd. for $[C_{31}H_{33}BrNO_4]$ $(M+H)^+$ 562.15930, found 562.13820.

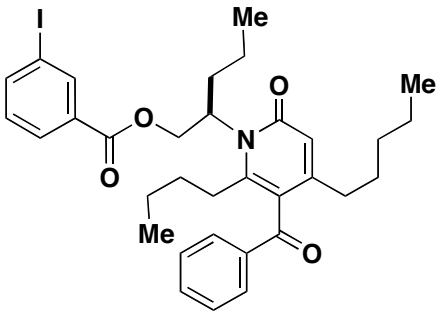


1-phenylhept-1-yn-3-yl oct-2-ynoate (1l). Yield: 39%. IR (neat, cm^{-1}): 2956, 2931, 2862, 2231, 1710, 1232, 957, 753, 690; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.90 (t, *J*=7.3 Hz, 3 H), 0.94 (t, *J*=7.3 Hz, 3 H), 1.29 - 1.43 (m, 6 H), 1.47 - 1.53 (m, 2 H), 1.56 - 1.62 (m, 2 H), 1.87 – 1.92 (m, 2 H), 2.33 (t, *J*=7.1 Hz, 2 H), 5.64 (t, *J*=6.8 Hz, 2 H), 7.26 - 7.33 (m, 3 H), 7.43 – 7.44 ppm (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 13.80, 13.88, 18.68, 22.04, 22.19, 27.12, 30.95, 34.46, 65.99, 72.81, 85.82, 90.51, 122.17, 128.18, 128.58, 131.84, 152.86 ppm; HRMS (EI) calcd. for $[C_{21}H_{30}NO_2]$ $(M+NH_4)^+$ 328.2277, found 328.2272.

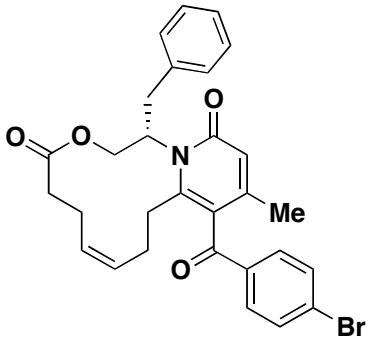


(2*Z*,4*E*)-((*R*)-2-azidopentyl) 4-benzoyl-3-pentylnona-2,4-dienoate (4l). Yield: 92%. IR (neat, cm^{-1}): 2958, 2931, 2872, 2109, 1721, 1647, 1270, 1187, 1155, 871, 735, 698; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.81 (d, *J* = 6.8 Hz, 2 H), 7.48 - 7.54 (m, 1 H), 7.40 - 7.47 (m, 2 H), 6.31 (t, *J* = 7.6 Hz, 1 H), 6.01 (s, 1 H), 4.10 - 4.22 (m, 1

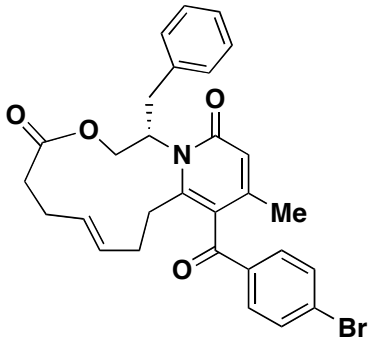
H), 4.00 (dd, *J* = 7.6, 11.5 Hz, 1 H), 3.50 - 3.59 (m, 1 H), 2.37 (br. s., 2 H), 2.14 (q, *J* = 7.6 Hz, 2 H), 1.55 - 1.62 (m 2 H), 1.42 - 1.52 (m, 3), 1.27 - 1.42 (m, 9H), 0.82 - 0.97 (m, 9 H); ^{13}C NMR (75MHz ,CHLOROFORM-d) δ = 195.9, 164.9, 158.5, 145.8, 141.2, 138.9, 131.3, 129.6, 128.0, 117.5, 65.8, 60.7, 39.1, 32.9, 31.5, 30.8, 29.8, 26.5, 22.5, 22.5, 19.1, 13.9, 13.8, 13.7; HRMS (EI) calcd. for $[C_{26}H_{38}N_3O_3]$ $(M+H)^+$ 440.29077, found 440.29103.



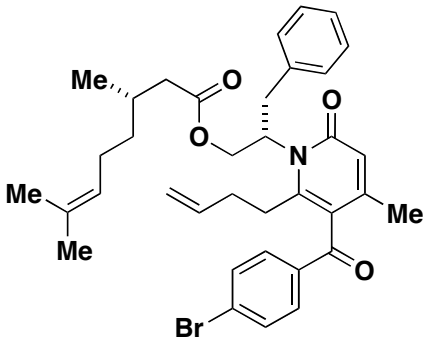
(*R*)-2-(5-benzoyl-6-butyl-2-oxo-4-pentylpyridin-1(2*H*)-yl)pentyl 3-iodobenzoate (14l). Yield: 45%. IR (neat, cm^{-1}): 2959, 2930, 2872, 2360, 2341, 1720, 1652, 1251, 733, 702; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 8.29 (s, 1 H), 7.89 (dd, *J* = 2.0, 7.8 Hz, 2 H), 7.77 (br. s., 2 H), 7.55 - 7.61 (m, 1 H), 7.41 (br. s., 2 H), 7.15 (t, *J* = 7.8 Hz, 1 H), 6.34 (s, 1 H), 5.19 (dd, *J* = 6.6, 9.0 Hz, 1 H), 4.79 - 4.91 (m, 1 H), 4.29 - 4.42 (m, 1 H), 2.40 - 2.51 (m, 1 H), 2.25 - 2.38 (m, 2 H), 2.07 - 2.23 (m, 3 H), 1.41 - 1.63 (m, 5 H), 1.27 - 1.41 (m, 2 H), 1.08 - 1.22 (m, 6 H), 0.99 (t, *J* = 7.3 Hz, 3 H), 0.78 (t, *J* = 6.8 Hz, 3 H), 0.73 (t, *J* = 7.3 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 196.6, 164.6, 163.6, 152.0, 146.9, 141.9, 138.4, 137.5, 134.1, 131.7, 130.1, 129.3, 129.0, 128.6, 119.9, 118.0, 93.9, 65.5, 58.6, 32.6, 32.2, 31.3, 31.2, 31.2, 28.2, 22.5, 22.2, 20.3, 14.1, 13.8, 13.3; HRMS (EI) calcd. for $[C_{33}H_{40}INO_4]$ $(M+H)^+$ 642.20748, found 642.20941.



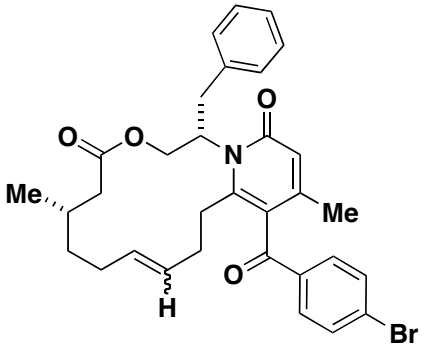
(*S*,*Z*)-1-benzyl-11-(4-bromobenzoyl)-12-methyl-1,2,5,6,9,10-hexahydropyrido[1,2-*d*][1,4]oxaazacyclododecine-4,14-dione (15ica-Z). In a 10 mL round-bottomed flask was **14ica** (11.2 mg, 0.020 mmol) in DCM (4 mL) to give a colorless solution. The solution was degassed with nitrogen. The Hoveyda-Grubbs 2nd catalyst (1.248 mg, 1.991 μmol) was added. The resulting solution was stirred under room temperature for 24h. 1 mL ethyl vinyl ether was added. The volatiles were removed under reduced pressure and the crude product was subjected to flash chromatography on silica gel (0-30% EA in hexand) to afford **15ica-Z** (5.3 mg, 50% yield) and **15ica-E** (2.9 mg, 27% yield). IR (neat, cm^{-1}): 3054, 2980, 2926, 2360, 2342, 1732, 1655, 1581, 1264, 1239, 1069, 1009, 920, 847, 732, 701; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.53 (d, *J* = 8.8 Hz, 2 H), 7.21 - 7.33 (m, 5 H), 7.11 - 7.18 (m, 2 H), 6.36 (s, 1 H), 5.27 - 5.45 (m, 2 H), 5.18 - 5.27 (m, 1 H), 4.58 (d, *J* = 12.7 Hz, 1 H), 4.24 - 4.33 (m, 1 H), 3.97 (t, *J* = 12.7 Hz, 1 H), 3.21 (dd, *J* = 3.4, 13.2 Hz, 1 H), 2.46 - 2.58 (m, 2 H), 2.30 - 2.42 (m, 3 H), 2.18 - 2.28 (m, 1 H), 1.95 - 2.03 (m, 1 H), 1.81 (s, 3 H), 1.76 (dt, *J* = 5.4, 10.1 Hz, 1 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 195.4, 172.8, 163.4, 147.0, 146.1, 137.9, 135.5, 132.3, 132.2, 130.8, 129.6, 129.4, 128.6, 128.6, 128.5, 128.1, 126.5, 119.9, 119.1, 65.3, 63.0, 35.4, 34.9, 30.0, 25.9, 23.2, 19.5; HRMS (EI) calcd. for $[C_{29}H_{29}BrNO_4]$ $(M+H)^+$ 534.12745, found 534.12690.



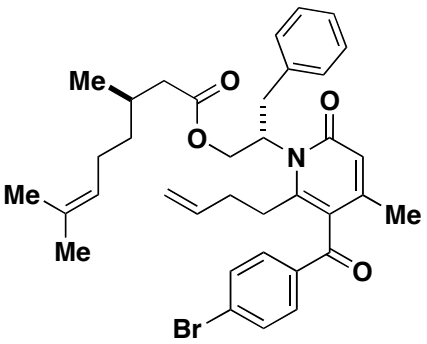
(*S*,*E*)-1-benzyl-11-(4-bromobenzoyl)-12-methyl-1,2,5,6,9,10-hexahydropyrido[1,2-*d*][1,4]oxaazacyclododecine-4,14-dione (15ica-E). IR (neat, cm^{-1}): 3056, 2925, 2856, 2361, 2341, 1730, 1653, 1581, 1265, 1243, 1069, 1009, 920, 846, 732, 701; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.48 - 7.58 (m, 2 H), 7.19 - 7.32 (m, 5 H), 7.09 - 7.14 (m, 2 H), 6.38 (s, 1 H), 5.30 - 5.47 (m, 3 H), 4.73 - 4.83 (m, 1 H), 4.47 (td, *J* = 3.7, 7.4 Hz, 1 H), 3.73 - 3.86 (m, 1 H), 3.11 (dd, *J* = 4.1, 13.4 Hz, 1 H), 2.35 - 2.46 (m, 2 H), 2.23 - 2.32 (m, 2 H), 1.90 - 2.04 (m, 3 H), 1.85 (s, 3 H); 1.79 – 1.88 (m, 1 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 195.2, 173.2, 163.8, 147.2, 137.4, 132.3, 132.2, 130.7, 130.6, 130.0, 129.6, 129.5, 129.2, 128.6, 128.5, 126.7, 120.1, 119.5, 68.0, 63.2, 61.7, 35.6, 33.3, 27.8, 25.6, 19.5, 19.5; HRMS (EI) calcd. for $[C_{29}H_{29}BrNO_4]$ $(M+H)^+$ 534.12745, found 534.12760.



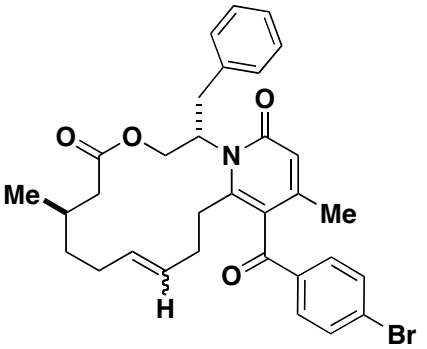
(*S*)-((*S*)-2-(5-(4-bromobenzoyl)-6-(but-3-enyl)-4-methyl-2-oxopyridin-1(2*H*)-yl)-3-phenylpropyl) 3,7-dimethyloct-6-enoate (14icb). Yield: 51%. IR (neat, cm^{-1}): 2962, 2918, 1734, 1656, 1582, 1529, 1266, 1149, 1068, 1009, 915, 847, 734, 702; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.56 (d, *J* = 8.8 Hz, 2 H), 7.32 - 7.45 (m, 1 H), 7.22 - 7.32 (m, 4 H), 7.08 - 7.18 (m, 2 H), 6.34 (s, 1 H), 5.54 (ddd, *J* = 6.3, 10.5, 16.8 Hz, 1 H), 5.07 (t, *J* = 7.1 Hz, 1 H), 4.79 - 4.98 (m, 4 H), 4.27 - 4.36 (m, 1 H), 3.86 (t, *J* = 11.7 Hz, 1 H), 3.16 (d, *J* = 12.2 Hz, 1 H), 2.30 (dd, *J* = 5.9, 14.6 Hz, 1 H), 2.06 - 2.21 (m, 2 H), 1.87 - 2.05 (m, 6 H), 1.83 (s, 3 H), 1.67 (s, 3 H), 1.59 (s, 3 H), 1.29 - 1.39 (m, 1 H), 1.15 - 1.27 (m, 1 H), 0.93 (d, *J* = 6.3 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 195.2, 172.7, 163.5, 147.3, 146.4, 137.9, 135.7, 135.5, 132.3, 131.6, 130.8, 129.6, 129.4, 128.6, 126.8, 124.1, 119.6, 119.3, 115.9, 64.9, 60.5, 41.6, 36.8, 34.9, 32.3, 30.5, 30.0, 25.7, 25.4, 19.6, 17.6; HRMS (EI) calcd. for $[C_{36}H_{43}BrNO_4]$ $(M+H)^+$ 632.23700, found 632.23621.



(1*S*,6*S*)-1-benzyl-13-(4-bromobenzoyl)-6,14-dimethyl-1,2,5,6,7,8,11,12-octahydropyrido[1,2-*d*][1,4]oxaazacyclotetradecine-4,16-dione (15icb). RCM condition E. Yield: 72% (*E*/*Z* = 1:6.6). IR (neat, cm^{-1}): 2960, 2928, 1731, 1655, 1582, 1265, 1009, 919, 731, 702; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.50 - 7.62 (m, 2 H), 7.22 - 7.42 (m, 5 H), *7.13 - 7.16 (m, 2 H), 7.05 - 7.11 (m, 2 H), 6.37 (s, 1 H), 5.39 - 5.44 (m, 1 H), *5.31 - 5.36 (m, 1 H), *5.14 - 5.18 (m, 1 H), 4.95 - 5.06 (m, 1 H), 4.85 - 4.95 (m, 2 H), *4.46 - 4.53 (m, 2 H),4.18 - 4.28 (m, 1 H), 3.91 (t, *J* = 12.4 Hz, 1 H), *3.77 - 3.83 (m, 1 H), 3.32 (dd, *J* = 3.2, 13.4 Hz, 1 H), *3.17 - 3.21 (m, 1 H), 2.38 - 2.50 (m, 1 H), 2.25 - 2.38 (m, 2 H), 1.99 - 2.20 (m, 3 H), 1.86 - 1.98 (m, 2 H), 1.75 - 1.86 (m, 4 H), 1.56 - 1.72 (m, 4 H), 1.31 - 1.41 (m, 2 H), 1.24 - 1.31 (m, 2 H), 1.03 (d, *J* = 7.3 Hz, 3 H), 0.80 - 0.93 (m, 1 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 195.2, 173.2, 163.1, 147.4, 146.2, 138.0, 135.4, 133.5, 132.3, 130.9, 130.8, 130.6, 129.6, 129.6, 129.5, 129.5, 129.4, 128.6, 128.6, 128.5, 127.6, 126.8, 126.7, 126.7, 119.4, 119.0, 119.0, 67.1, 62.2, 43.0, 40.2, 37.2, 36.0, 35.5, 31.5, 30.5, 29.7, 29.2, 28.6, 26.7, 23.4, 22.9, 21.0, 19.6, 14.1 (* represents signals of minor isomer); HRMS (EI) calcd. for $[C_{32}H_{35}BrNO_4]$ $(M+H)^+$ 576.17440, found 576.17479.



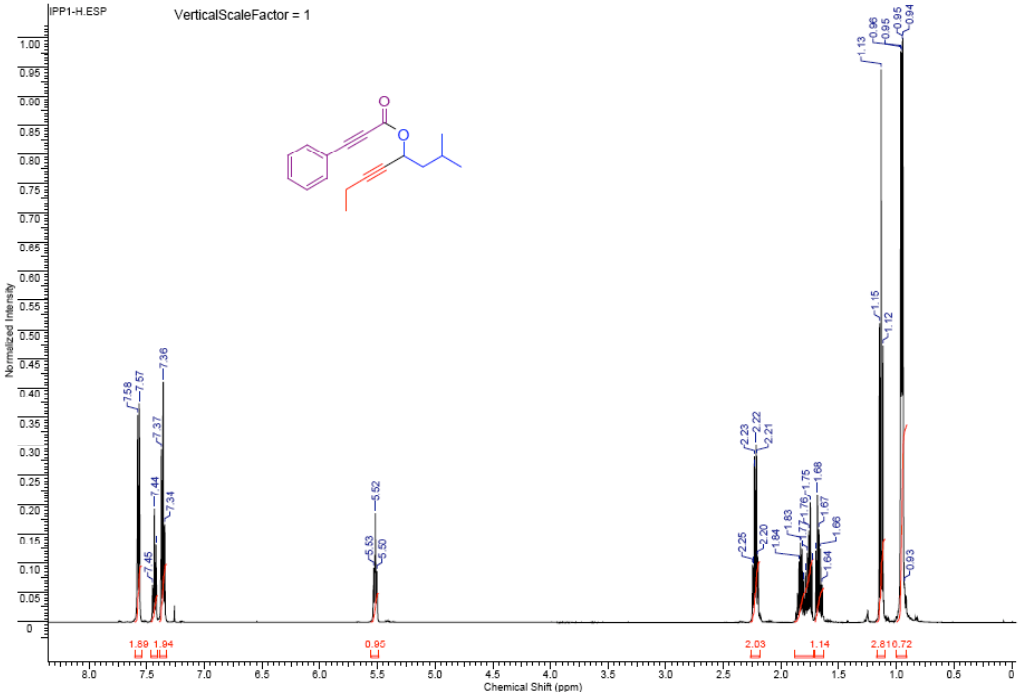
(*R*)-((*S*)-2-(5-(4-bromobenzoyl)-6-(but-3-enyl)-4-methyl-2-oxo pyridin-1(2*H*)-yl)-3-phenylpropyl) 3,7-dimethyloct-6-enoate (14icc). Yield: 51%. IR (neat, cm^{-1}): 2962, 2917, 1734, 1656, 1582, 1530, 1265, 1149, 1068, 1010, 916, 847, 734, 702; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.56 (d, *J* = 8.3 Hz, 2 H), 7.35 - 7.45 (m, 1 H), 7.24 - 7.35 (m, 4 H), 7.10 - 7.18 (m, 2 H), 6.34 (s, 1 H), 5.49 - 5.60 (m, 1 H), 5.07 (t, *J* = 6.6 Hz, 1 H), 4.90 - 4.96 (m, 2 H), 4.80 - 4.88 (m, 2 H), 4.26 - 4.38 (m, 1 H), 3.86 (t, *J* = 11.5 Hz, 1 H), 3.16 (d, *J* = 12.2 Hz, 1 H), 2.32 (dd, *J* = 5.9, 14.6 Hz, 1 H), 2.05 - 2.20 (m, 2 H), 1.87 - 2.05 (m, 6 H), 1.84 (s, 3 H), 1.67 (s, 3 H), 1.59 (s, 3 H), 1.28 - 1.39 (m, 1 H), 1.16 - 1.28 (m, 1 H), 0.93 (d, *J* = 6.3 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = 195.2, 172.6, 163.5, 147.3, 146.4, 137.9, 135.5, 132.3, 131.6, 130.8, 129.6, 129.4, 128.6, 126.8, 124.1, 119.6, 115.9, 64.9, 60.5, 41.6, 36.7, 34.9, 32.3, 30.5, 30.0, 25.7, 25.4, 19.6, 19.6, 17.7; HRMS (EI) calcd. for $[C_{36}H_{43}BrNO_4]$ $(M+H)^+$ 632.23700, found 632.23678.



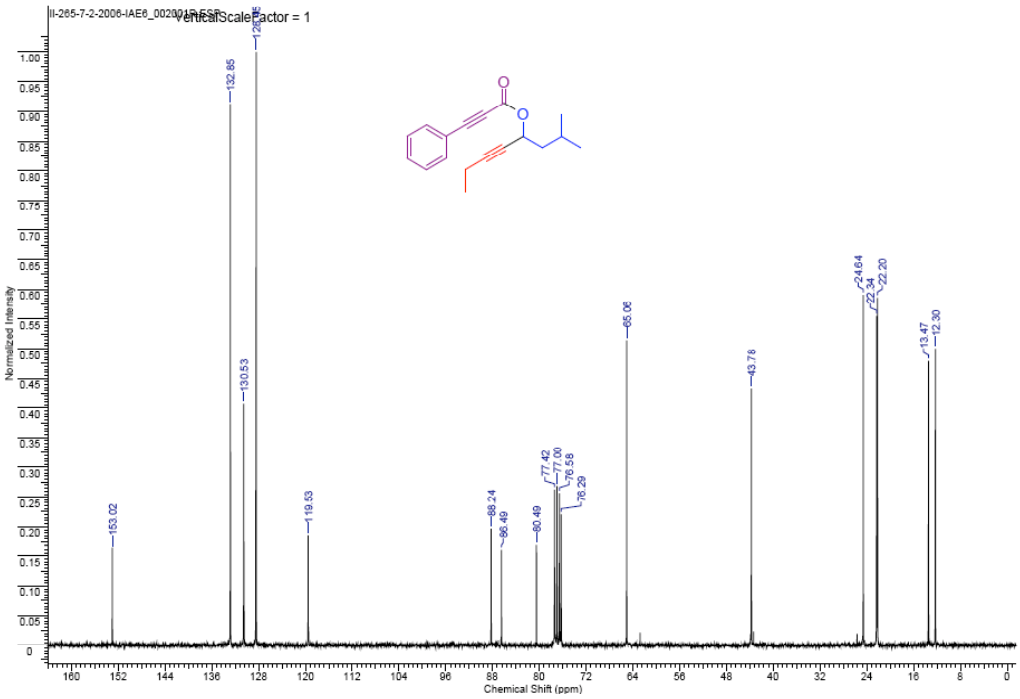
(1*S*,6*R*)-1-benzyl-13-(4-bromobenzoyl)-6,14-dimethyl-1,2,5,6,7 ,8,11,12-octahydropyrido[1,2-*d*][1,4]oxaazacyclotetradecine-4, 16-dione (15icc). RCM condition E. Yield: 81% (*E*/*Z* = 1:6.8). IR (neat, cm^{-1}): 2960, 2928, 1731, 1655, 1582, 1529, 1265, 1009, 919, 730, 701; ^{1}H NMR (500MHz ,CHLOROFORM-d) δ = 7.49 - 7.61 (m, 2 H), 7.21 - 7.43 (m, 5 H), 7.04 - 7.14 (m, 2 H), 6.37 (s, 1 H), *6.36 (s, 1 H), 5.40 - 5.48 (m, 1 H), *5.20 - 5.26 (m, 1 H), *5.13 (dd, *J* = 6.4, 11.7 Hz, 1 H), 5.07 (dd, *J* = 5.6, 12.4 Hz, 1 H), 4.96 - 5.04 (m, 1 H), 4.73 (dd, *J* = 1.5, 12.2 Hz, 1 H), *4.50 (dd, *J* = 2.9, 11.7 Hz, 1 H), *4.34 - 4.39 (m, 1 H), 4.14 - 4.24 (m, 1 H), 3.90 (t, *J* = 12.4 Hz, 1 H), *3.82 - 3.85 (m, 1 H), 3.31 (dd, *J* = 3.9, 13.2 Hz, 1 H), *3.21 - 3.25 (m, 1 H), 2.55 (dd, *J* = 4.1, 13.4 Hz, 1 H), 2.33 - 2.45 (m, 1 H), 2.20 - 2.33 (m, 2 H), 1.96 - 2.07 (m, 1 H), 1.74 - 1.95 (m, 7 H), 1.47 - 1.71 (m, 3 H), 1.14 - 1.33 (m, 2 H), 1.09 (d, *J* = 6.8 Hz, 3 H), *1.00 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (126MHz ,CHLOROFORM-d) δ = *195.3, 195.1, *172.8, 172.3, *163.4, 163.1, 147.6, *147.4, 146.0, 138.0, 135.5, 132.3, 132.2, 132.2, 130.8, 130.3, 129.6, 129.6, 129.5, 129.3, 129.0, 128.6, 128.6, 127.2, *127.1, 126.8, *126.7, 125.3, 119.3, 119.1, 118.9, 67.8, 62.0, 42.3, 39.9, 36.6, 36.3, 35.5, 31.7, 31.4, 29.8, 26.8, 25.1, 22.2, 21.7, 19.6; (* represents signals of minor isomer); HRMS (EI) calcd. for $[C_{32}H_{35}BrNO_4]$ $(M+H)^+$ 576.17440, found 576.17433.

V. ^{1}H and ^{13}C NMR spectra

Spectra. Spectral Data for **2-methyloct-5-yn-4-yl 3-phenylpropiolate** (**1b**)



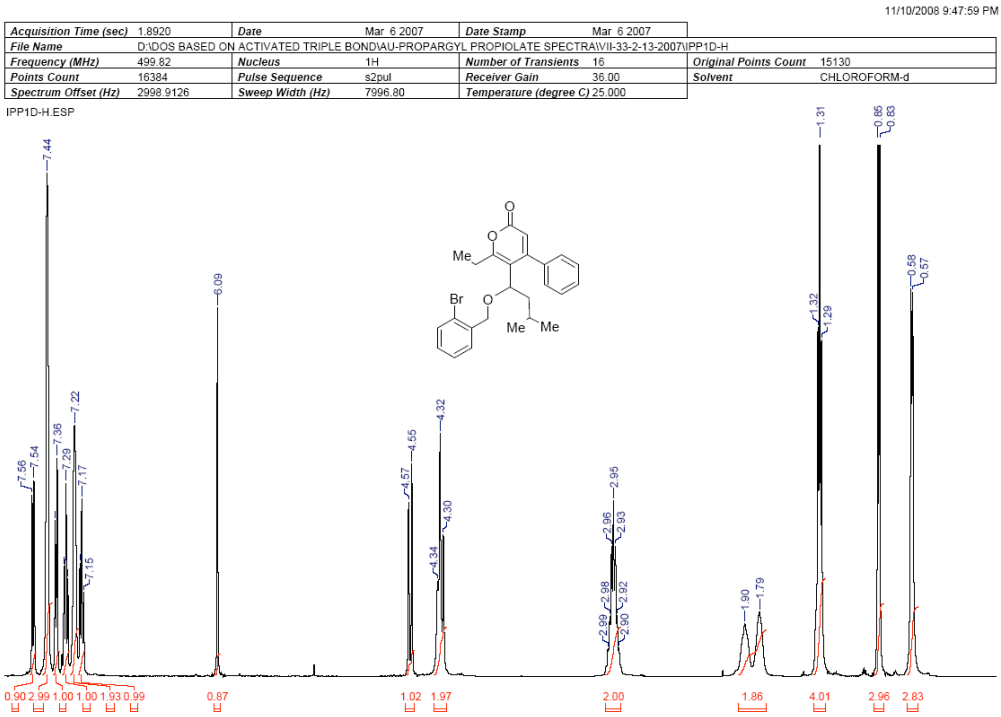
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1b**



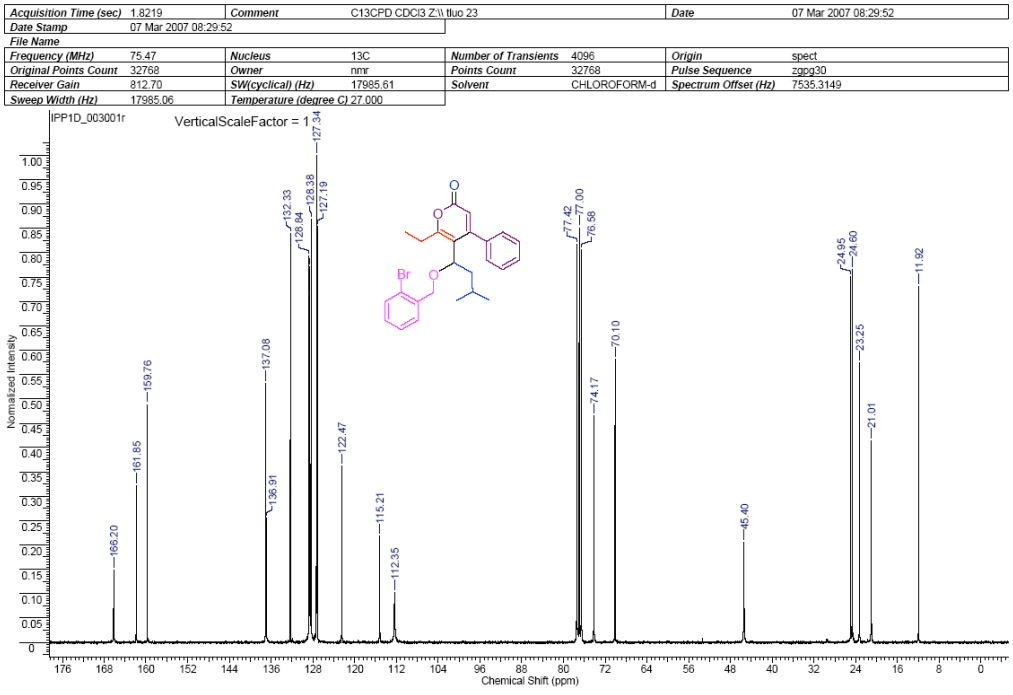
^{13}C NMR (75 MHz, $CDCl_3$) for compound **1b**

Spectra. Spectral Data for

5-(1-(2-bromobenzyloxy)-3-methylbutyl)-6-ethyl-4-phenyl-2H-pyran-2-one (3ba).



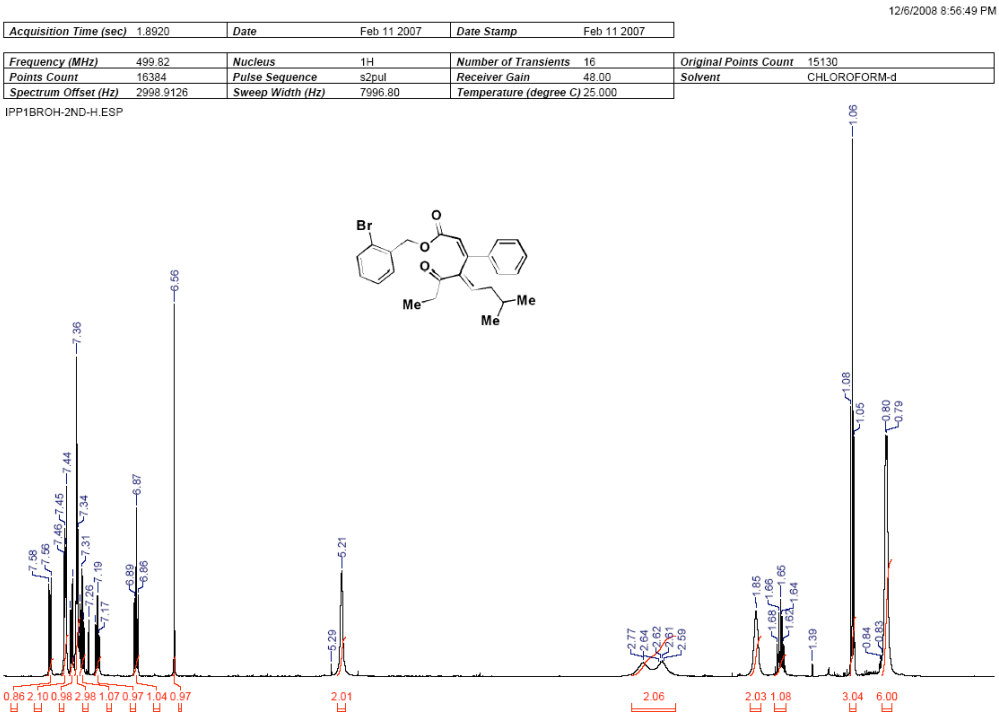
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ba**



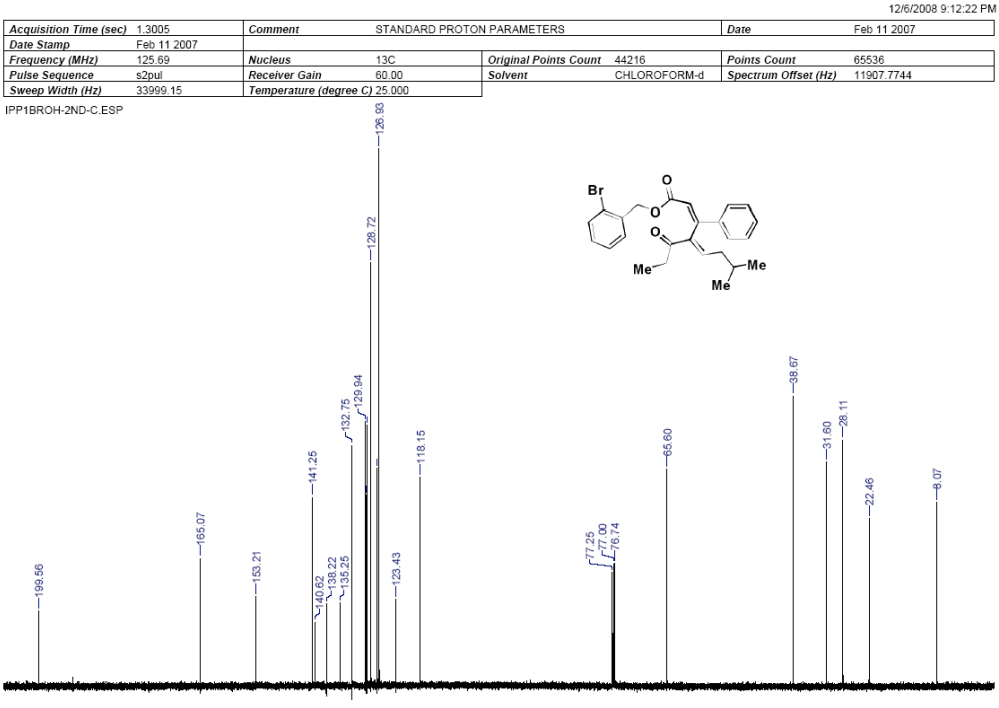
^{13}C NMR (75 MHz, $CDCl_3$) for compound **3ba**

Spectra. Spectral Data for

(2*Z*,4*E*)-2-bromobenzyl 7-methyl-3-phenyl-4-propionylocta-2,4-dienoate (4ba)



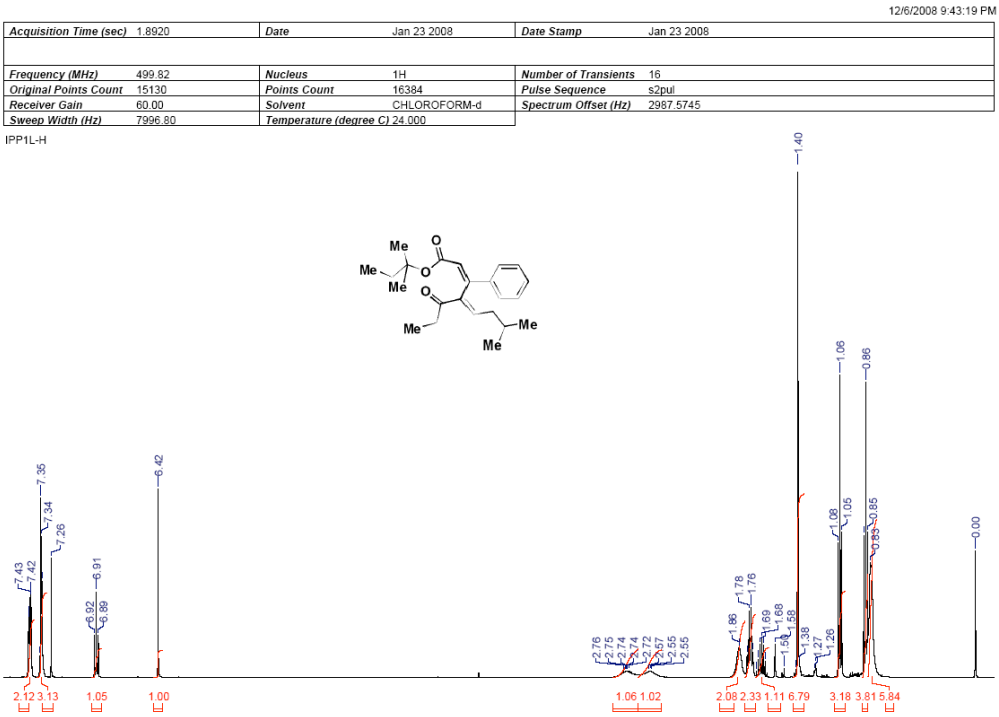
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4ba**



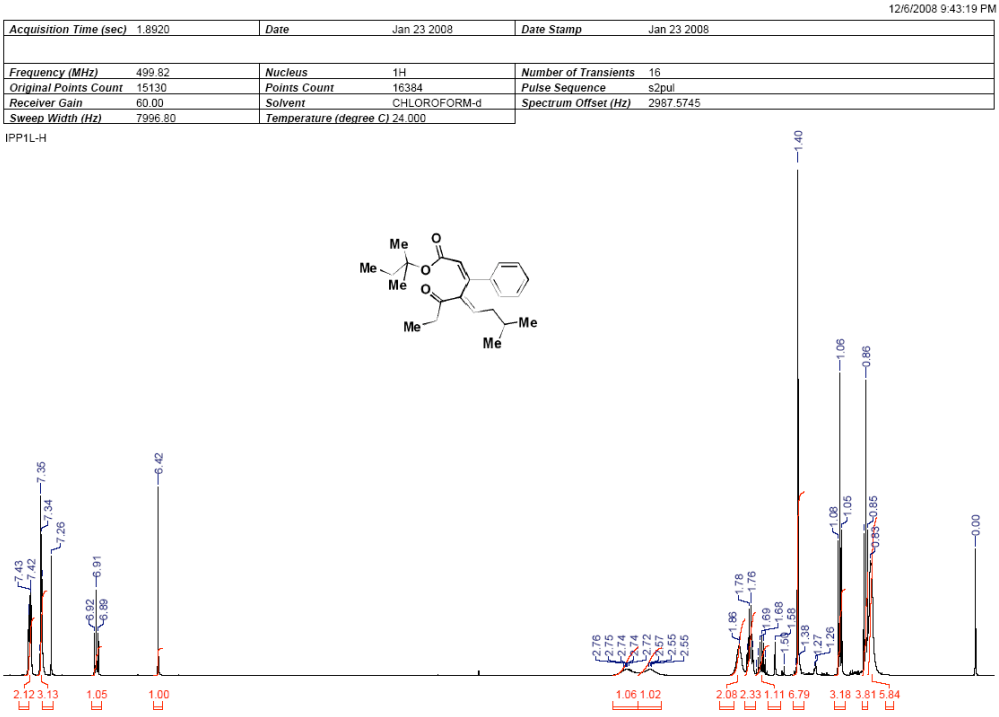
^{13}C NMR (126 MHz, $CDCl_3$) for compound **4ba**

Spectra. Spectral Data for

(2*Z*,4*E*)-*tert*-pentyl 7-methyl-3-phenyl-4-propionylocta-2,4-dienoate (4bb)

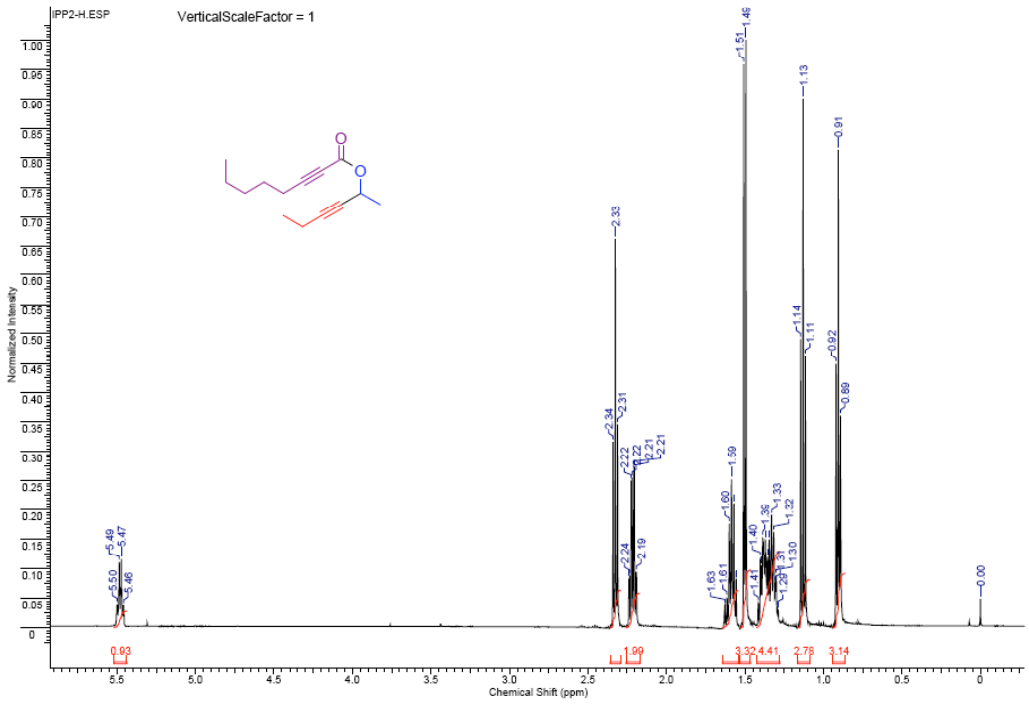


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4bb**

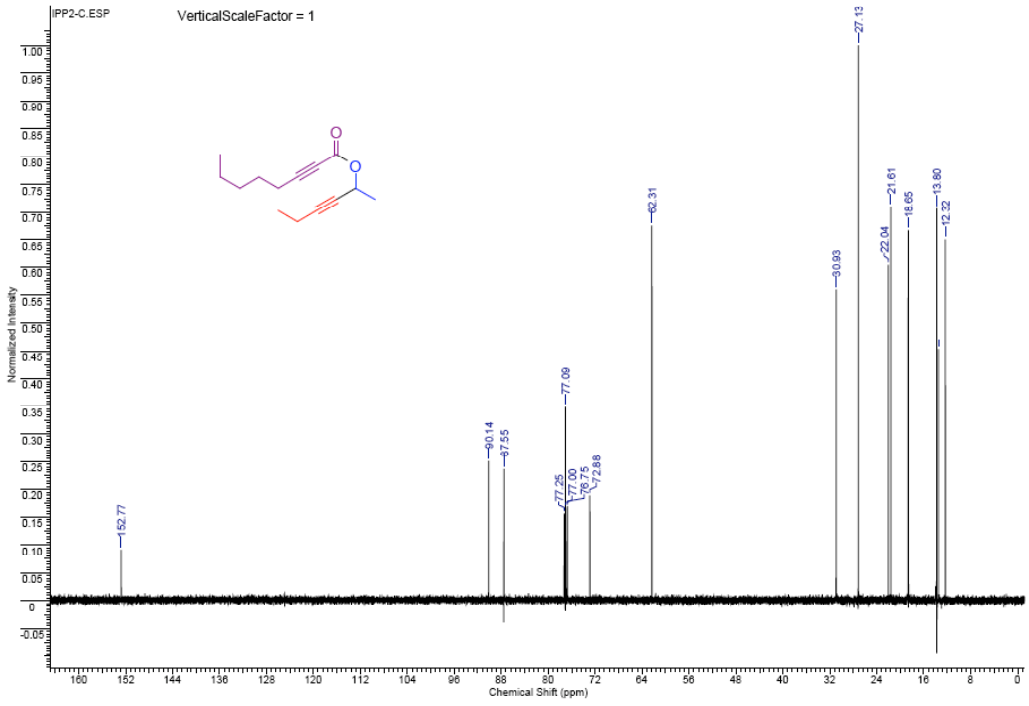


^{13}C NMR (75 MHz, $CDCl_3$) for compound **4bb**

Spectra. Spectral Data for **hex-3-yn-2-yl oct-2-ynoate (1c)**



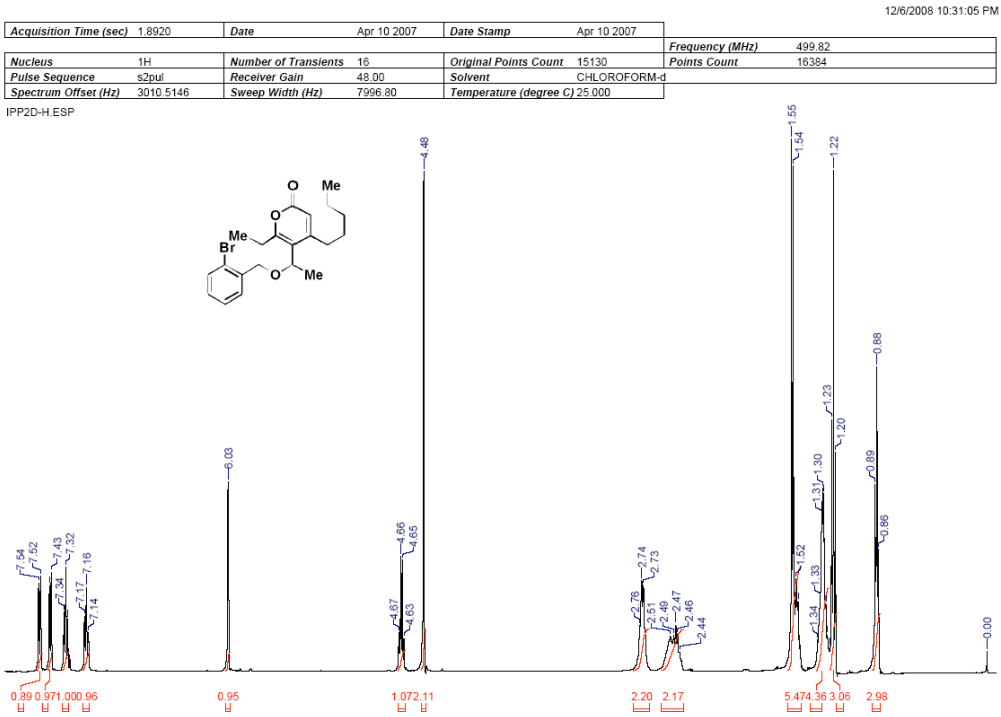
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1c**



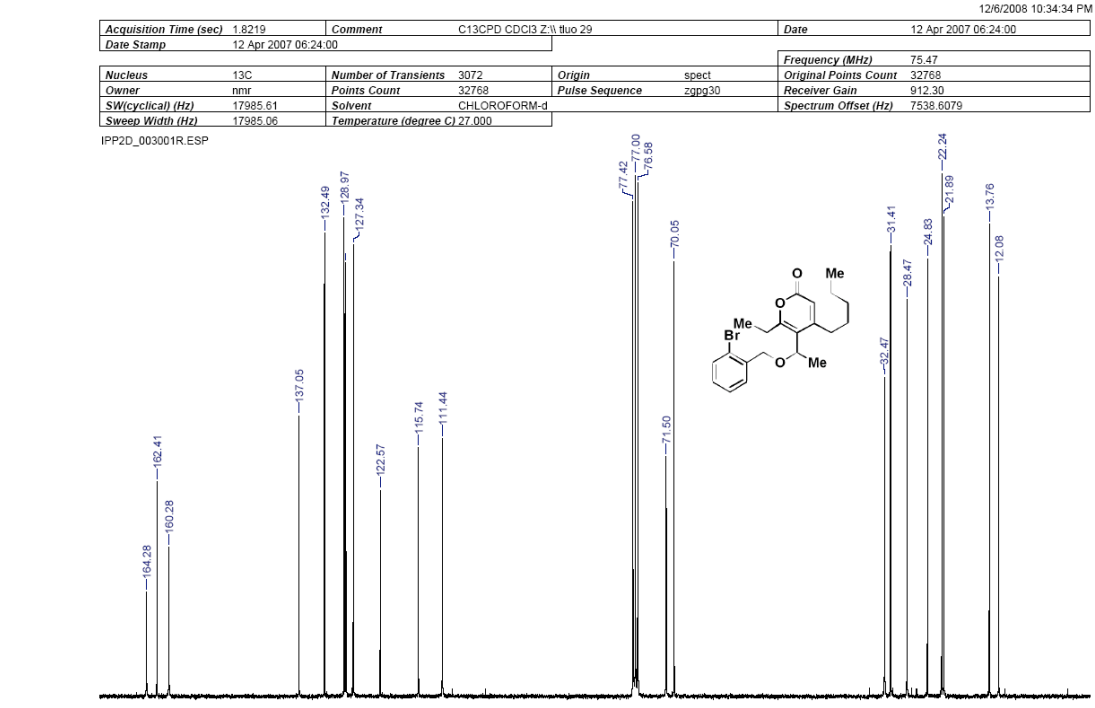
^{13}C NMR (126 MHz, $CDCl_3$) for compound **1c**

Spectra. Spectral Data for

5-(1-(2-bromobenzyloxy)ethyl)-6-ethyl-4-pentyl-2*H*-pyran-2-one (3ca)

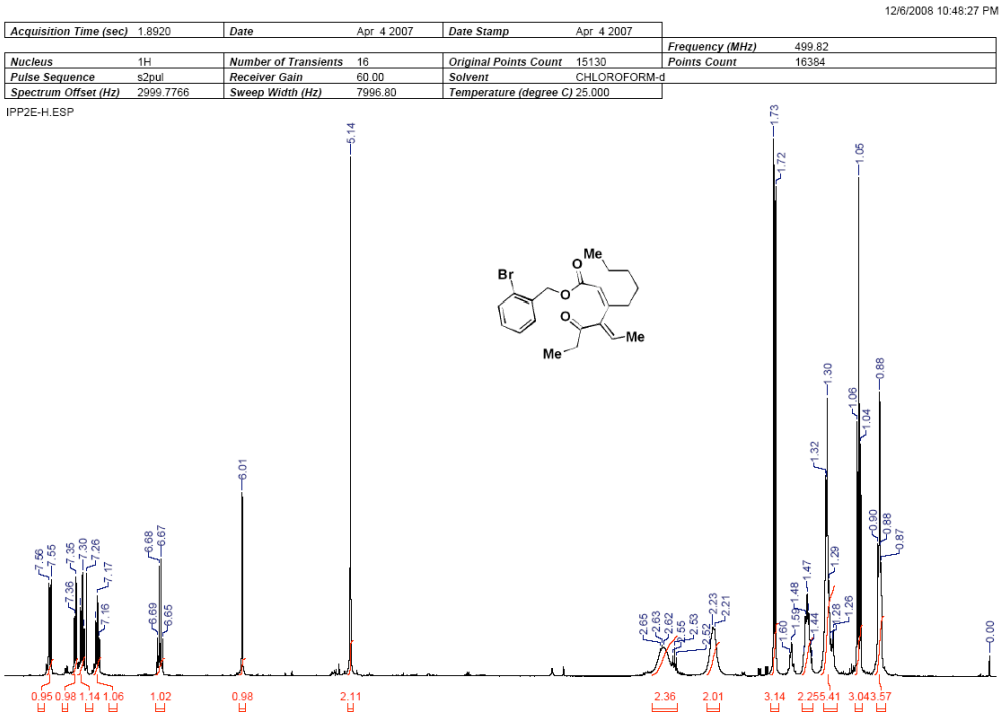


^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ca**

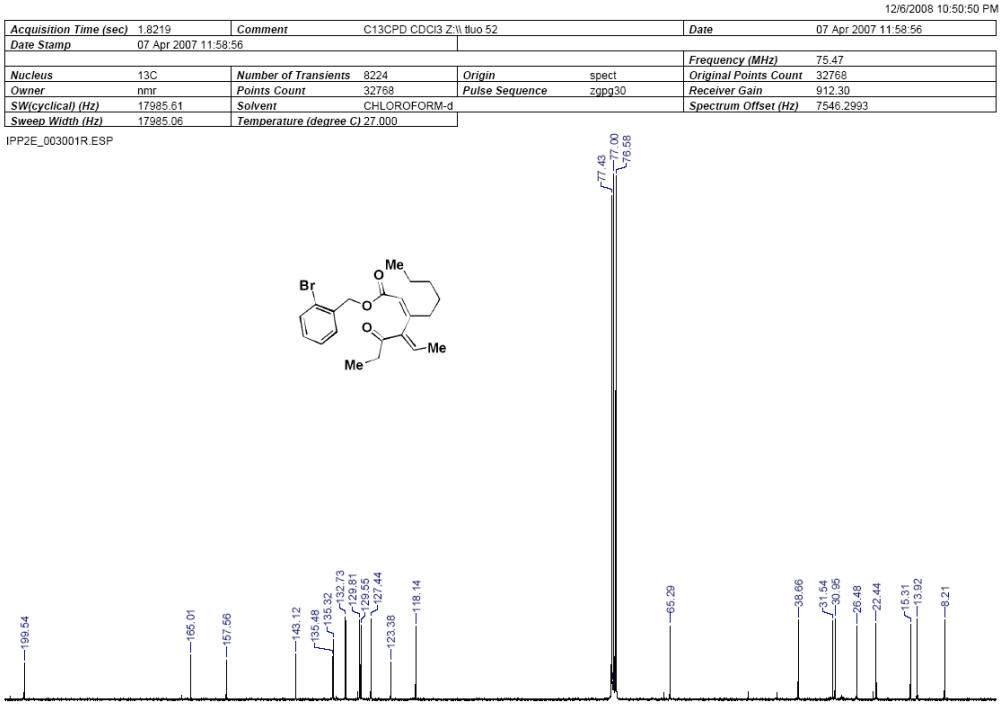


^{13}C NMR (75 MHz, $CDCl_3$) for compound **3ca**

Spectra. Spectral Data for ***(Z)*-2-bromobenzyl 3-((*E*)-4-oxohex-2-en-3-yl)oct-2-enoate (4ca)**

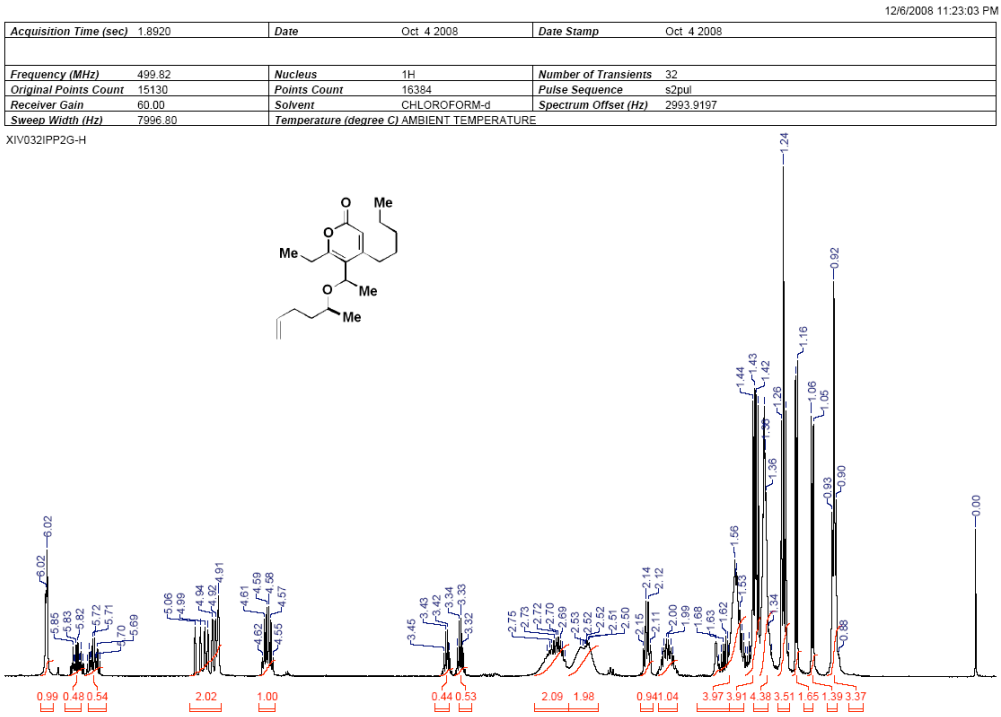


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4ca**

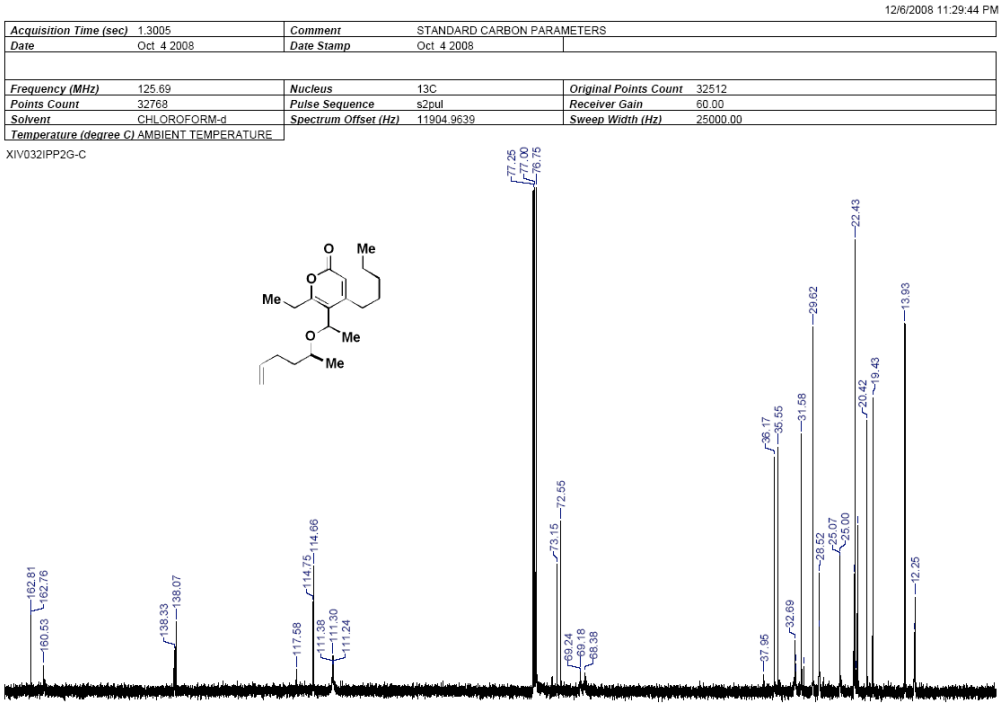


^{13}C NMR (75 MHz, $CDCl_3$) for compound **4ca**

Spectra. Spectral Data for **6-ethyl-5-(1-((*S*)-hex-5-en-2-yloxy)ethyl)-4-pentyl-2*H*-pyran-2-one (3cb)**



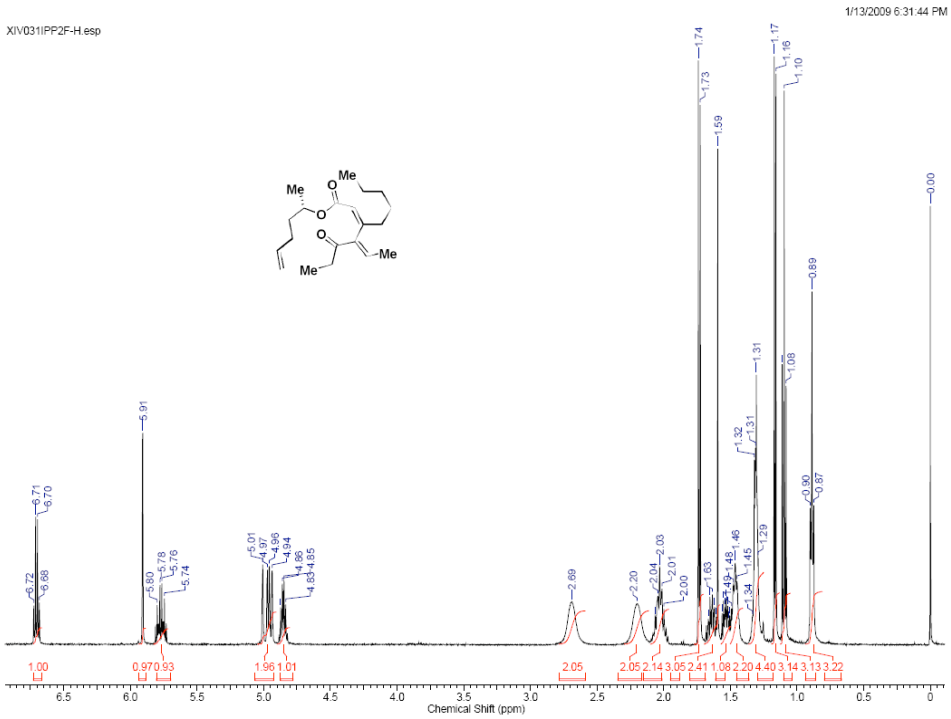
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3cb**



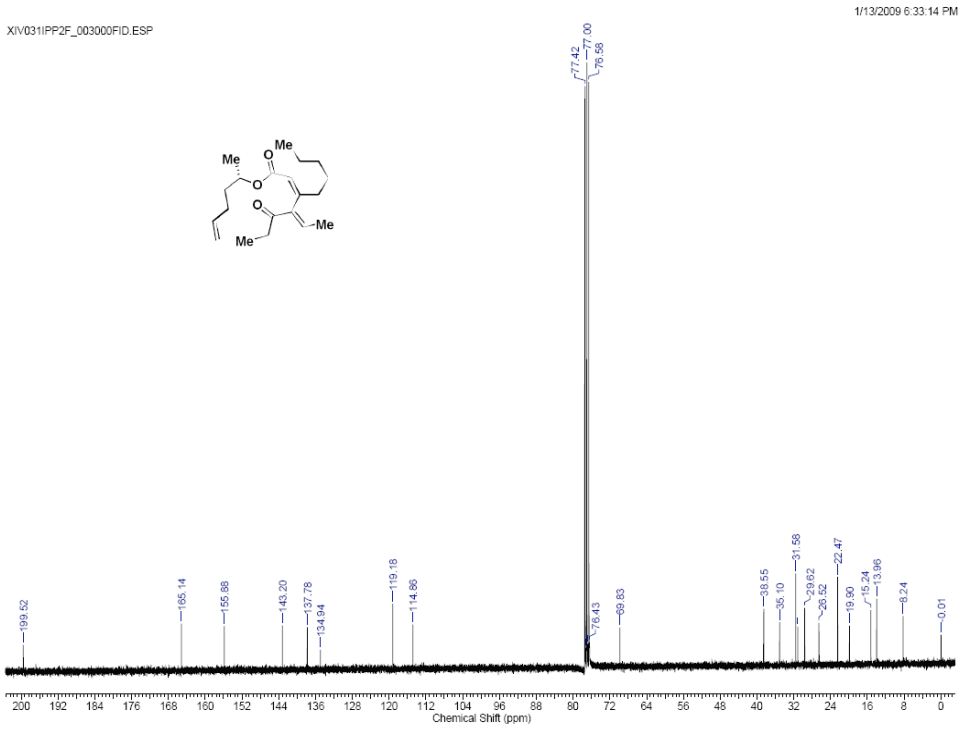
^{13}C NMR (126 MHz, $CDCl_3$) for compound **3cb**

Spectra. Spectral Data for

(2*Z*,4*E*)-((*S*)-hex-5-en-2-yl) 3-ethyl-4-ethylidene-5-oxohept-2-enoate (4cb).

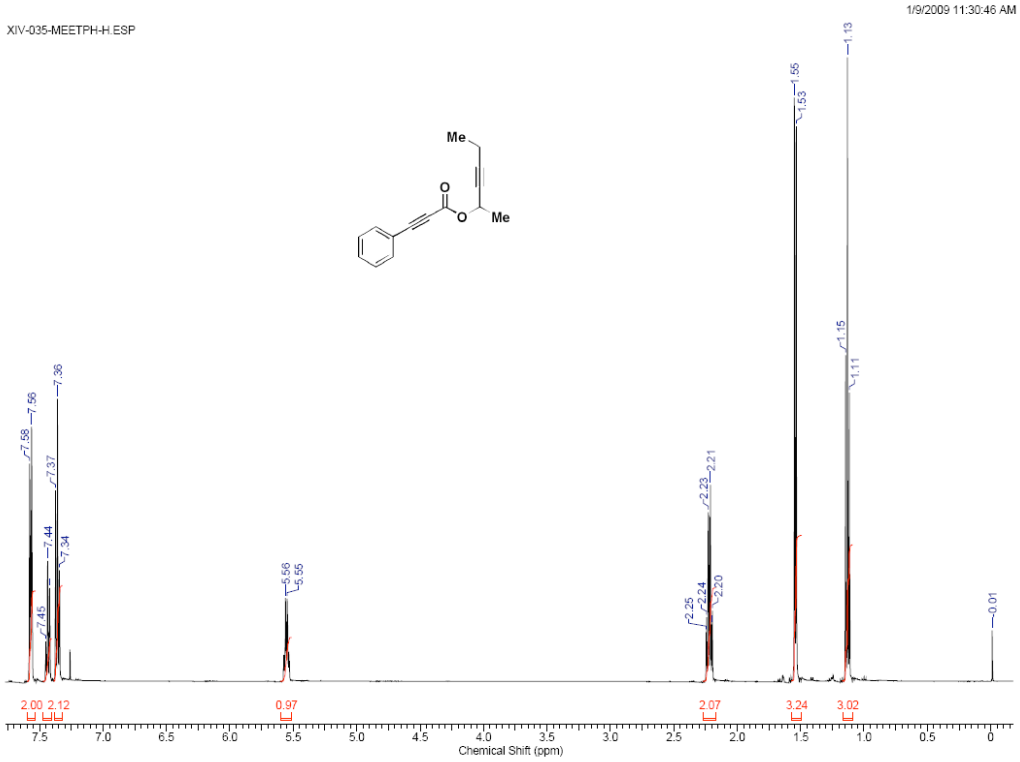


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4cb**

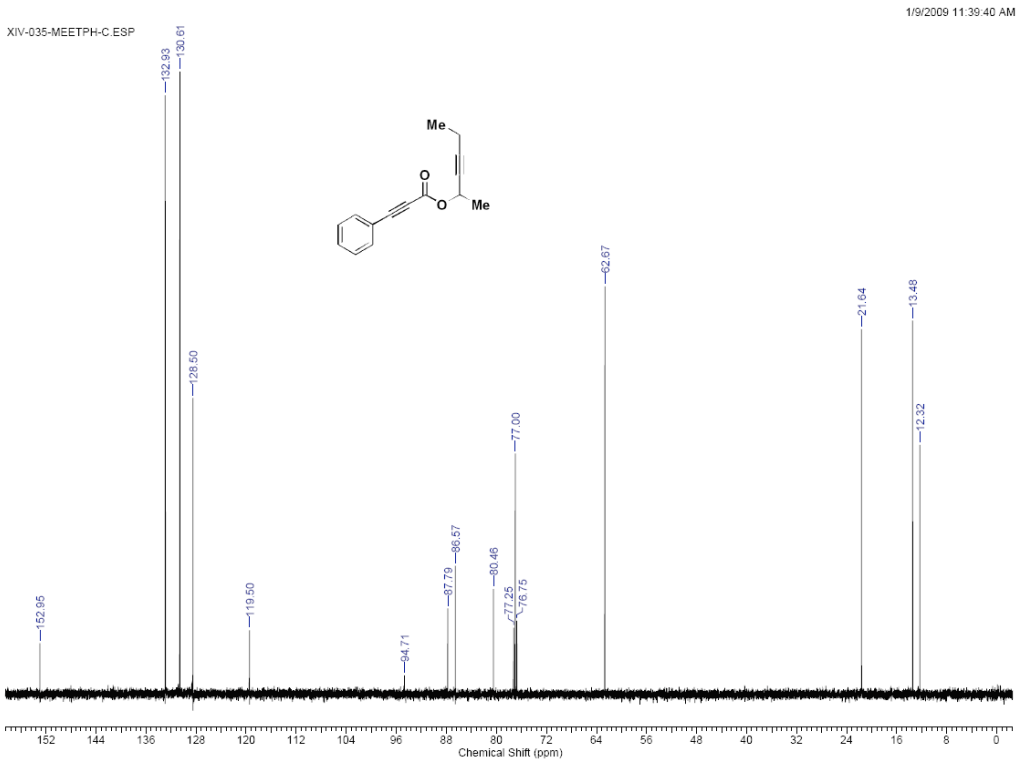


^{13}C NMR (75 MHz, $CDCl_3$) for compound **4cb**

Spectra. Spectral Data for **hex-3-yn-2-yl 3-phenylpropiolate** (**1d**).



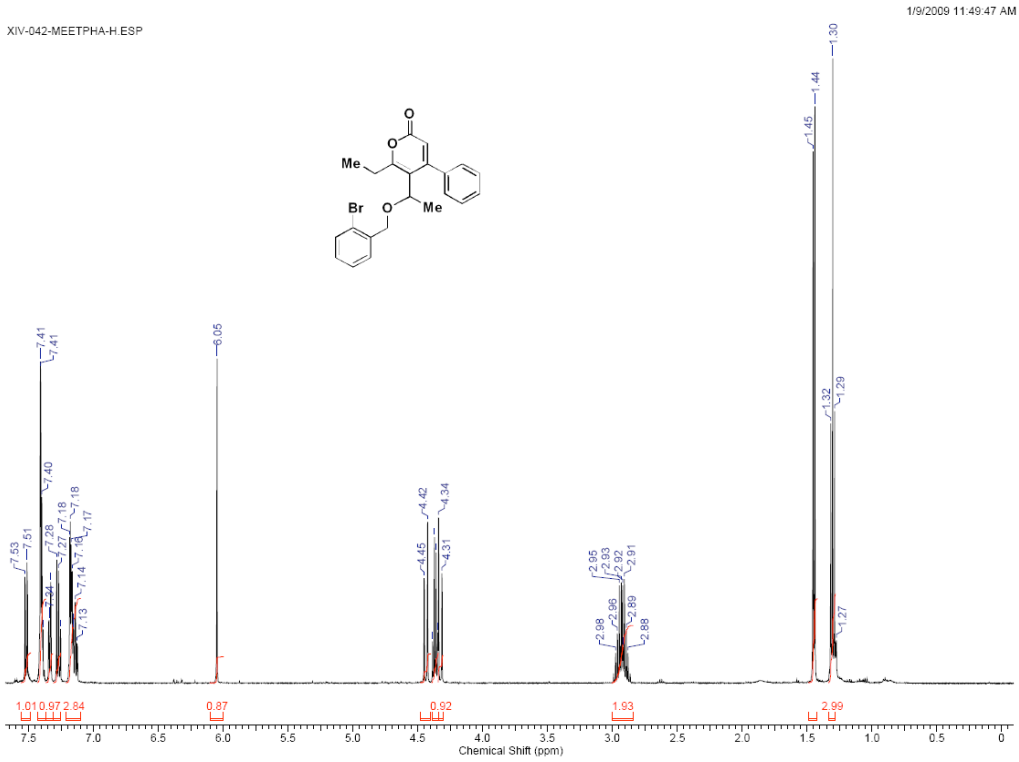
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1d**



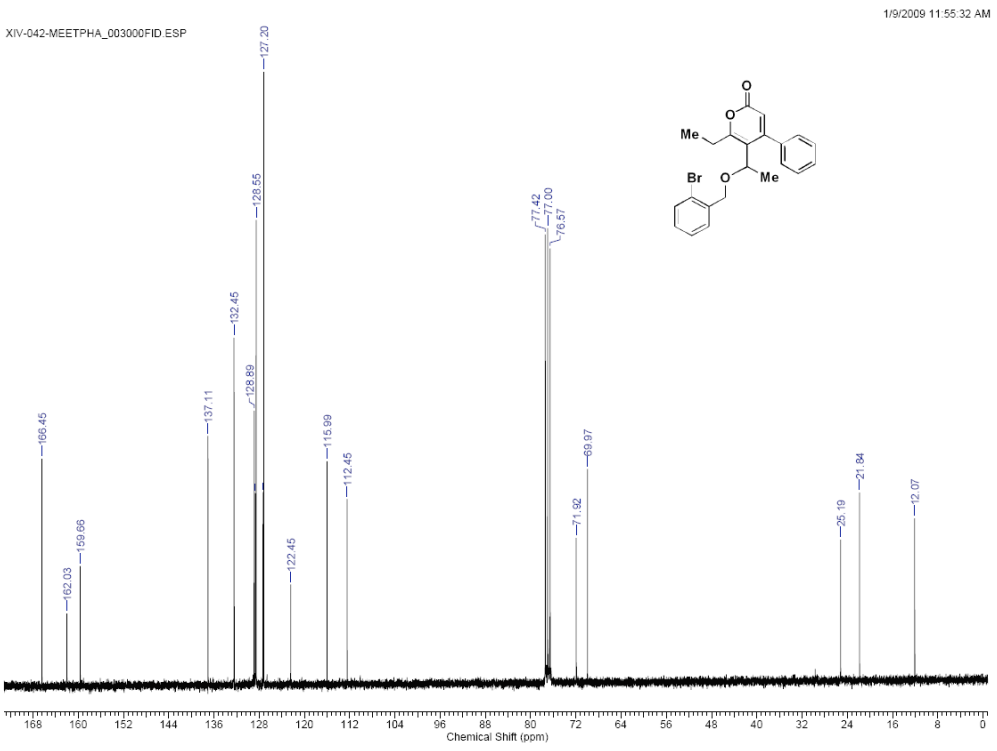
^{13}C NMR (126 MHz, $CDCl_3$) for compound **1d**

Spectra. Spectral Data for

5-(1-(2-bromobenzyloxy)ethyl)-6-ethyl-4-phenyl-2*H*-pyran-2-one (3da).

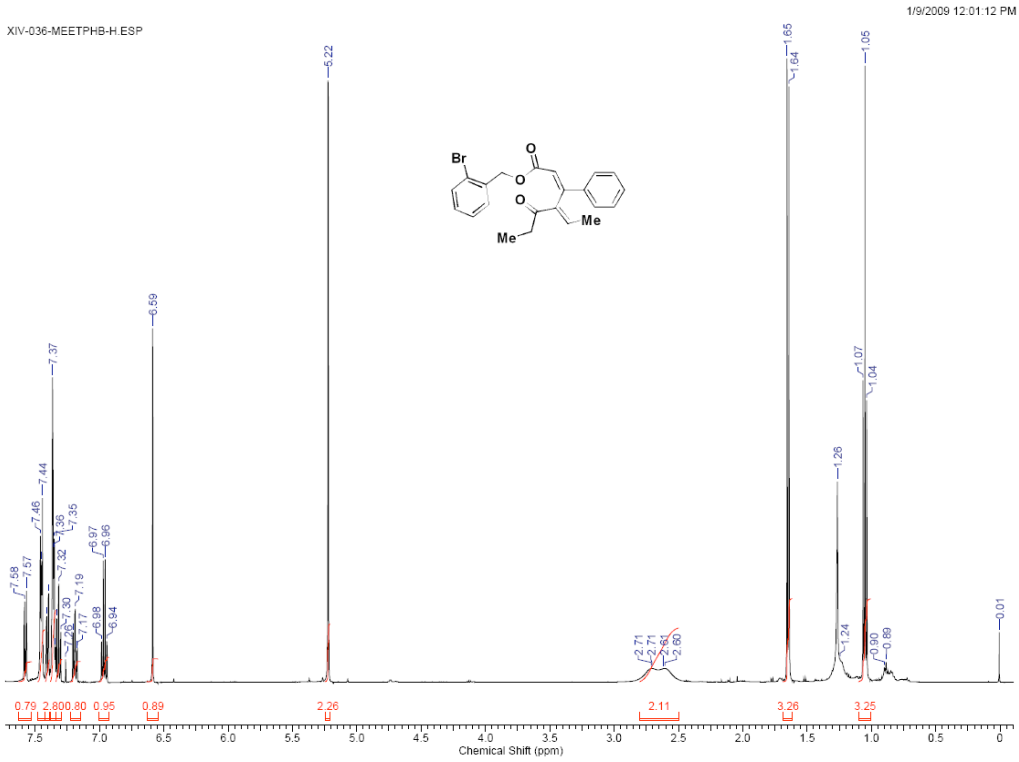


^{1}H NMR (500 MHz, $CDCl_3$) of compound **3da**

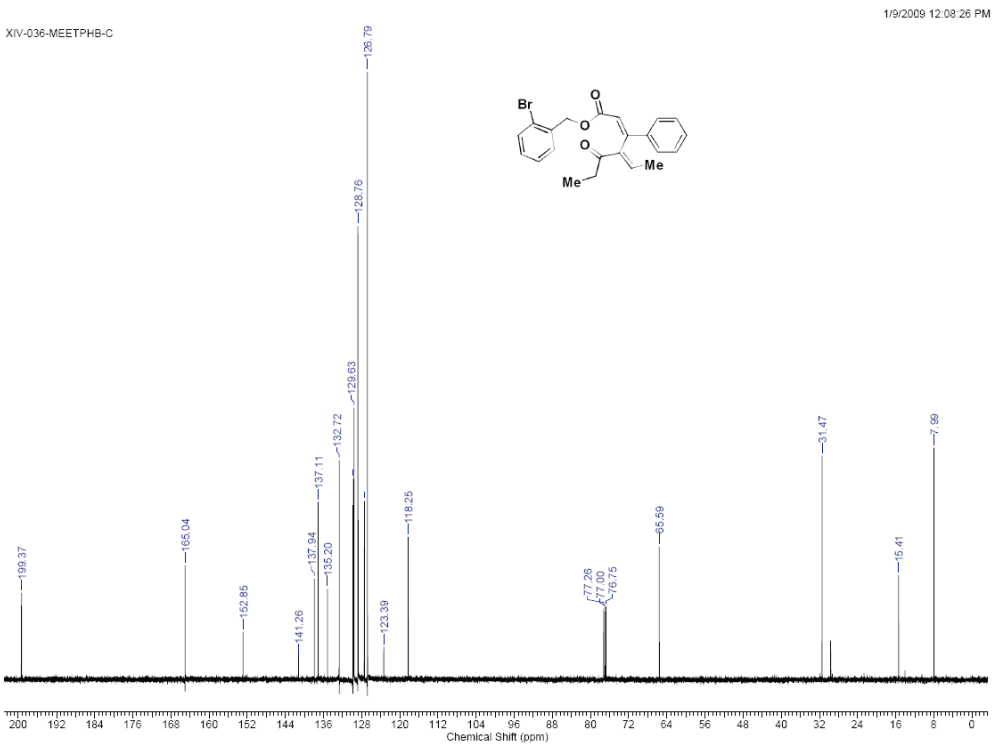


^{13}C NMR (75 MHz, $CDCl_3$) for compound **3da**

Spectra. Spectral Data for
(2*Z*,4*E*)-2-bromobenzyl 4-ethylidene-5-oxo-3-phenylhept-2-enoate (4da).

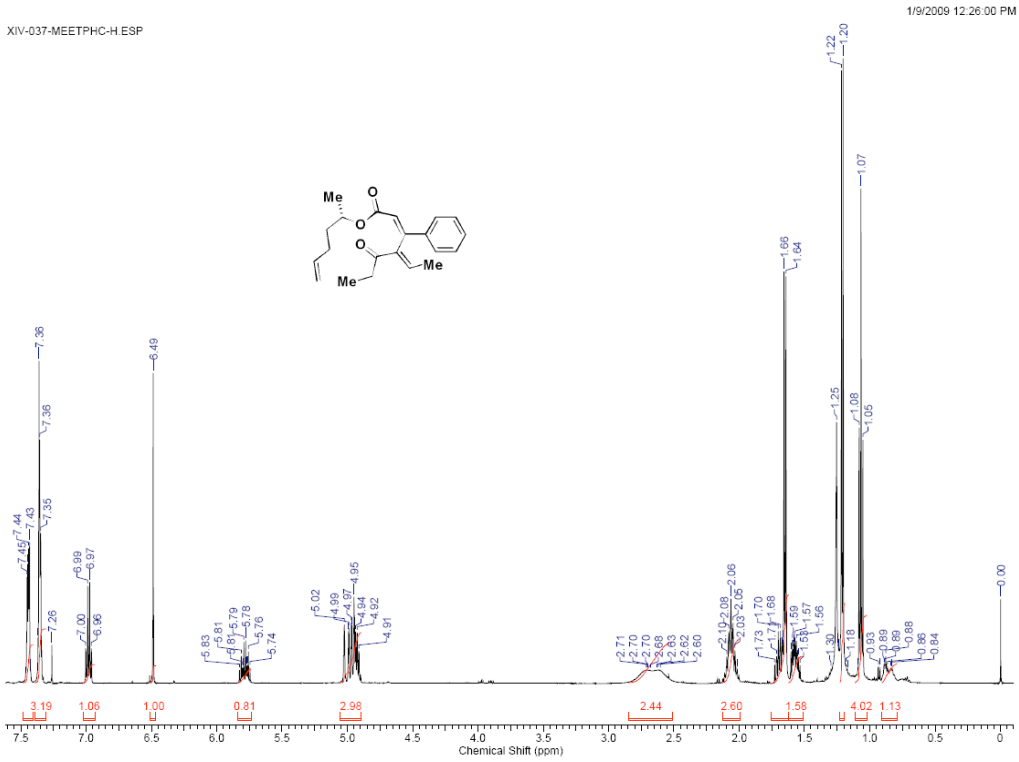


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4da**

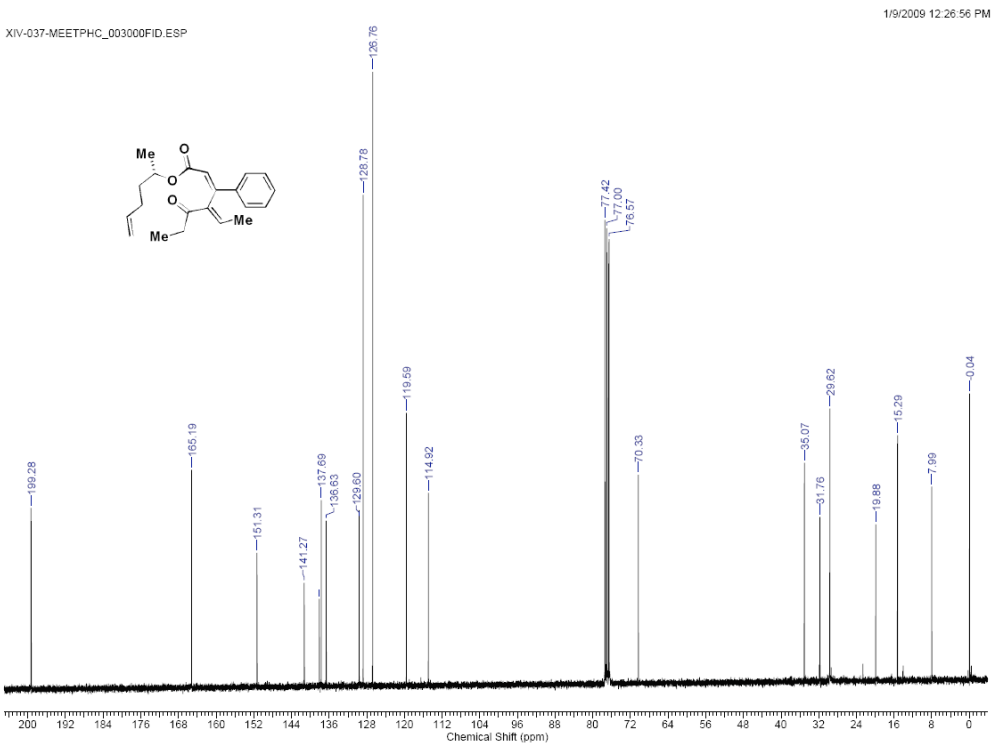


^{13}C NMR (126 MHz, $CDCl_3$) for compound **4da**

Spectra. Spectral Data for
(2*Z*,4*E*)-((*S*)-hex-5-en-2-yl) 4-ethylidene-5-oxo-3-phenylhept-2-enoate (4db).

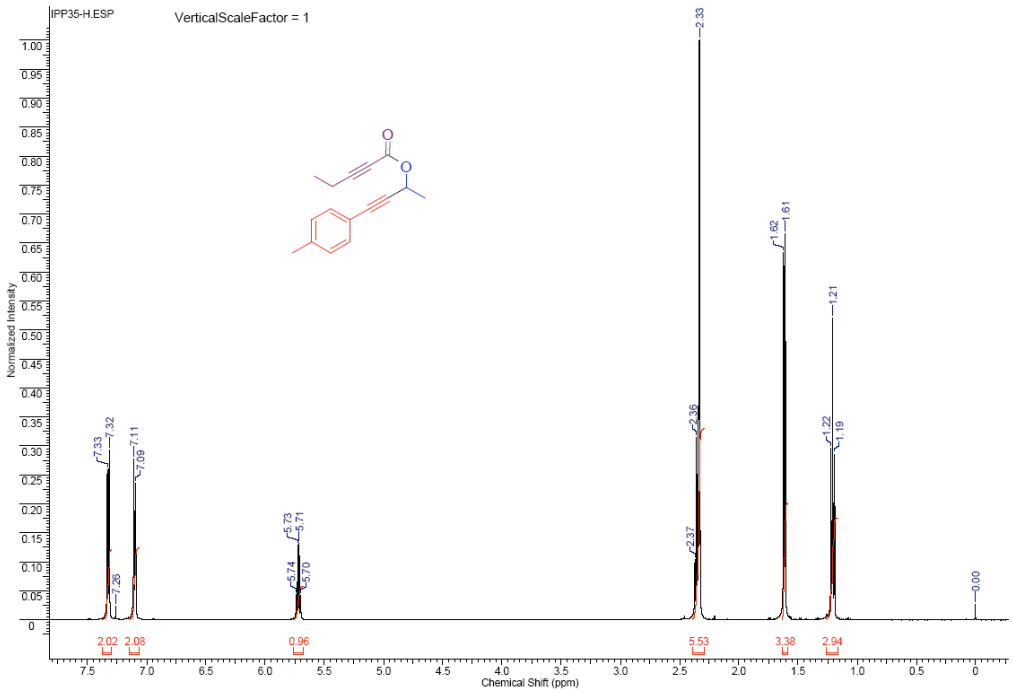


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4db**



^{13}C NMR (126 MHz, $CDCl_3$) for compound **4db**

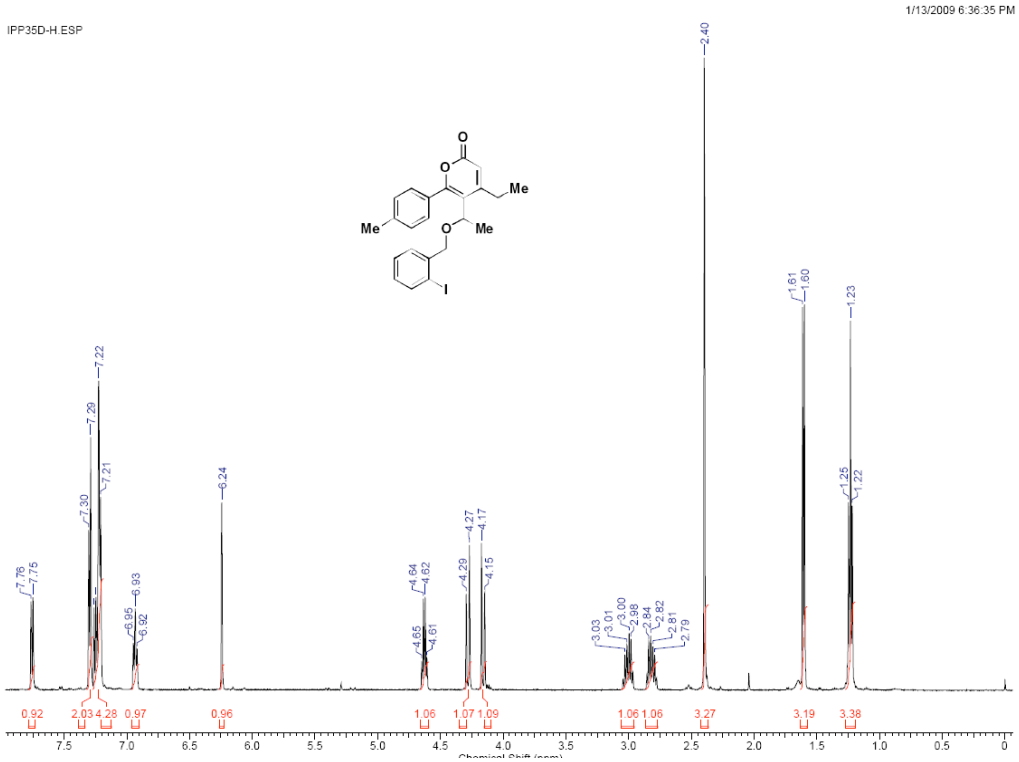
Spectra. Spectral Data for **4-p-tolylbut-3-yn-2-yl pent-2-ynoate** (**1e**).



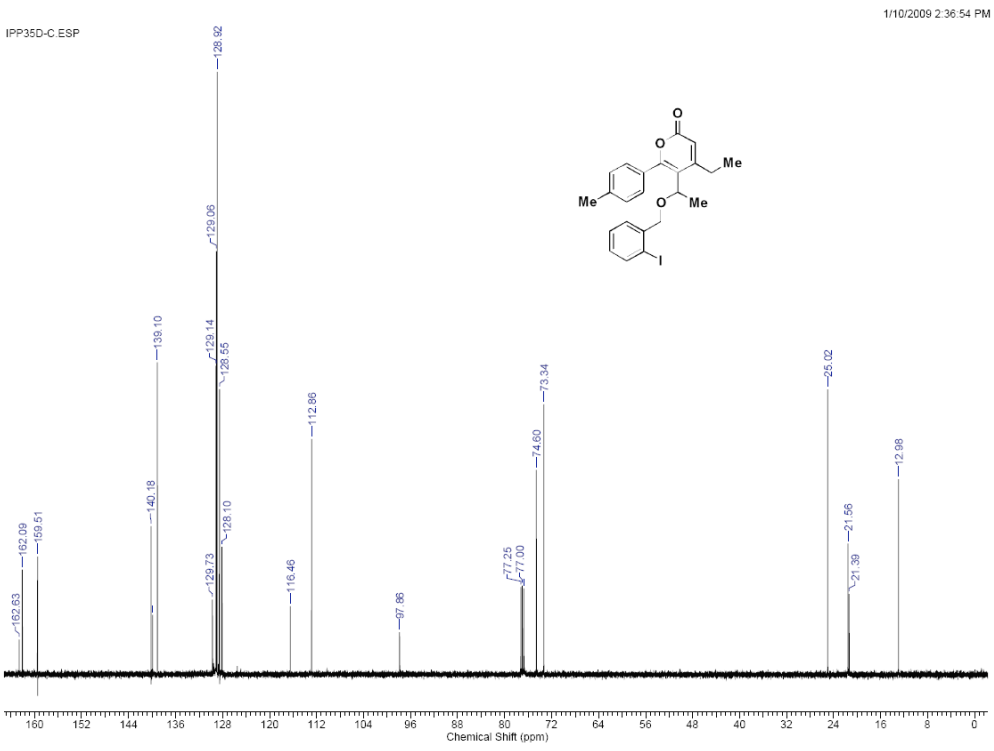
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1e**

^{13}C NMR (75 MHz, $CDCl_3$) for compound **1e**

Spectra. Spectral Data for
4-ethyl-5-(1-(2-iodobenzyloxy)ethyl)-6-*p*-tolyl-2*H*-pyran-2-one (3ea).

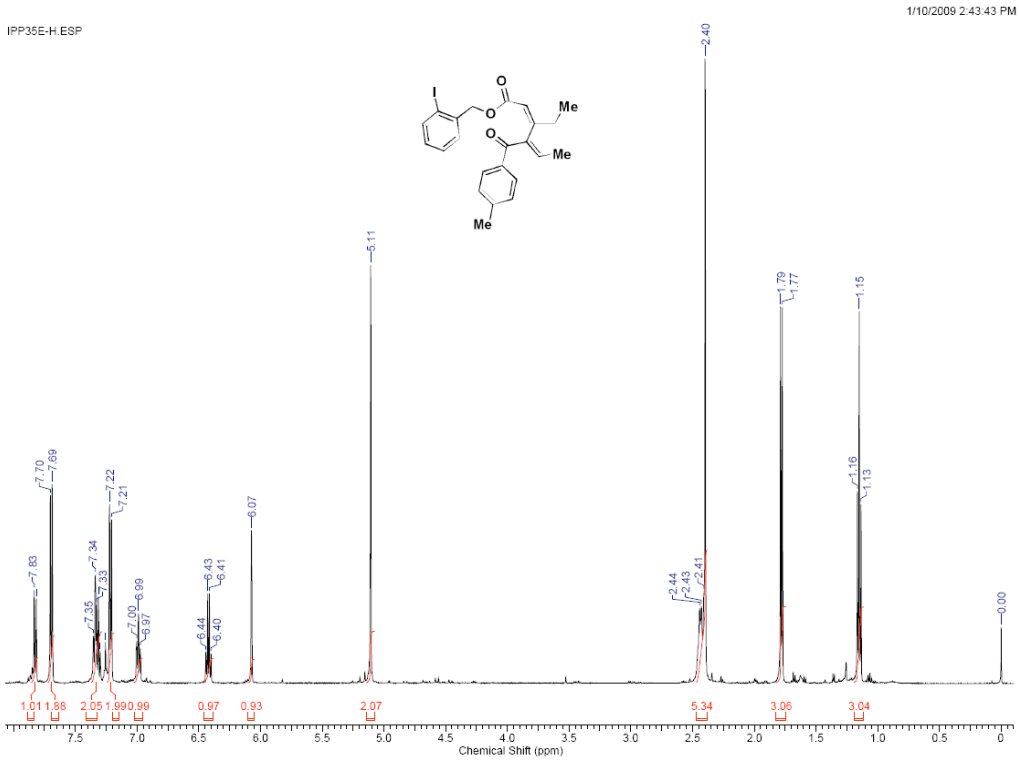


^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ea**

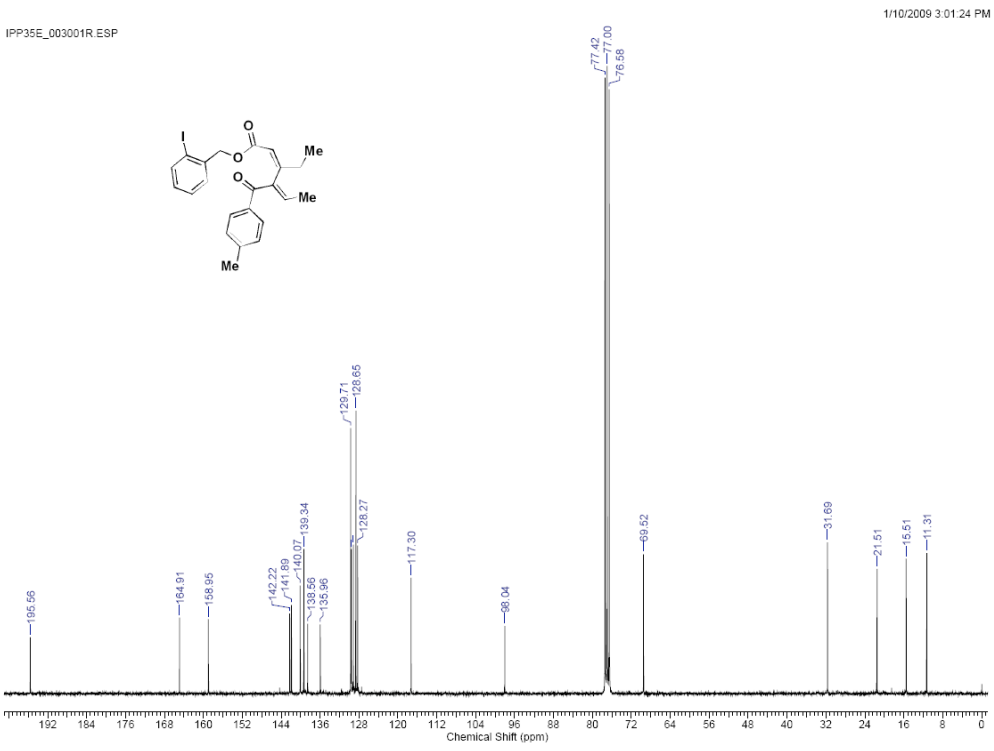


^{13}C NMR (126 MHz, $CDCl_3$) for compound **3ea**

Spectra. Spectral Data for
(2*Z*,4*E*)-2-iodobenzyl 3-ethyl-4-(4-methylbenzoyl)hexa-2,4-dienoate (4ea).

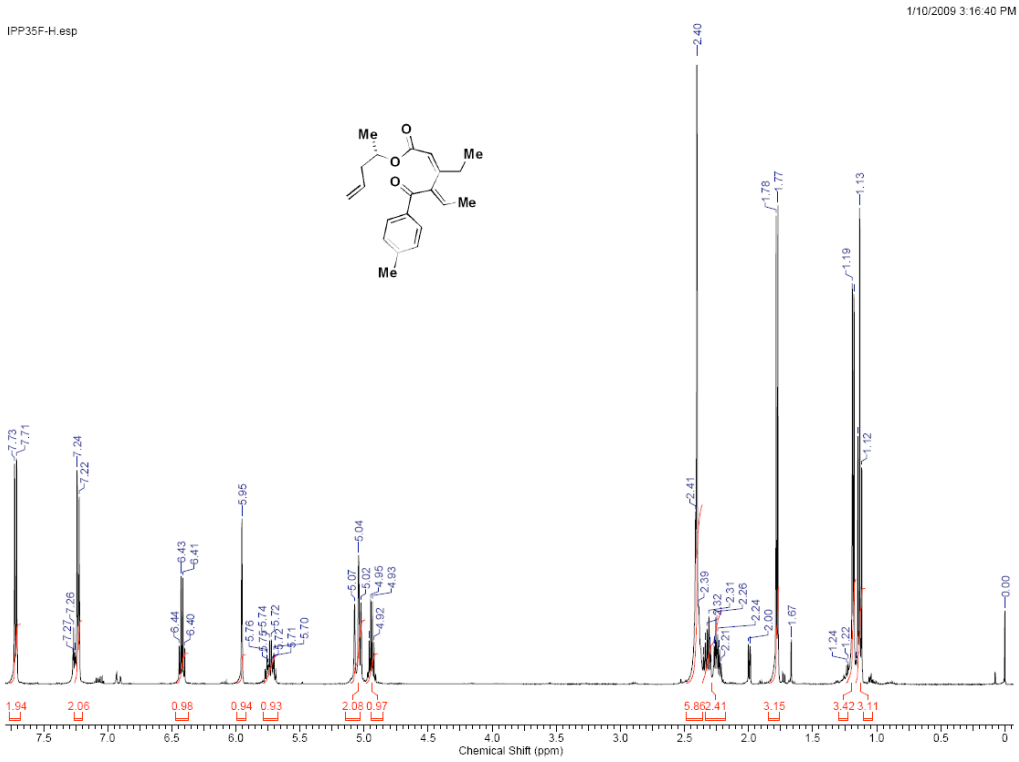


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4ea**

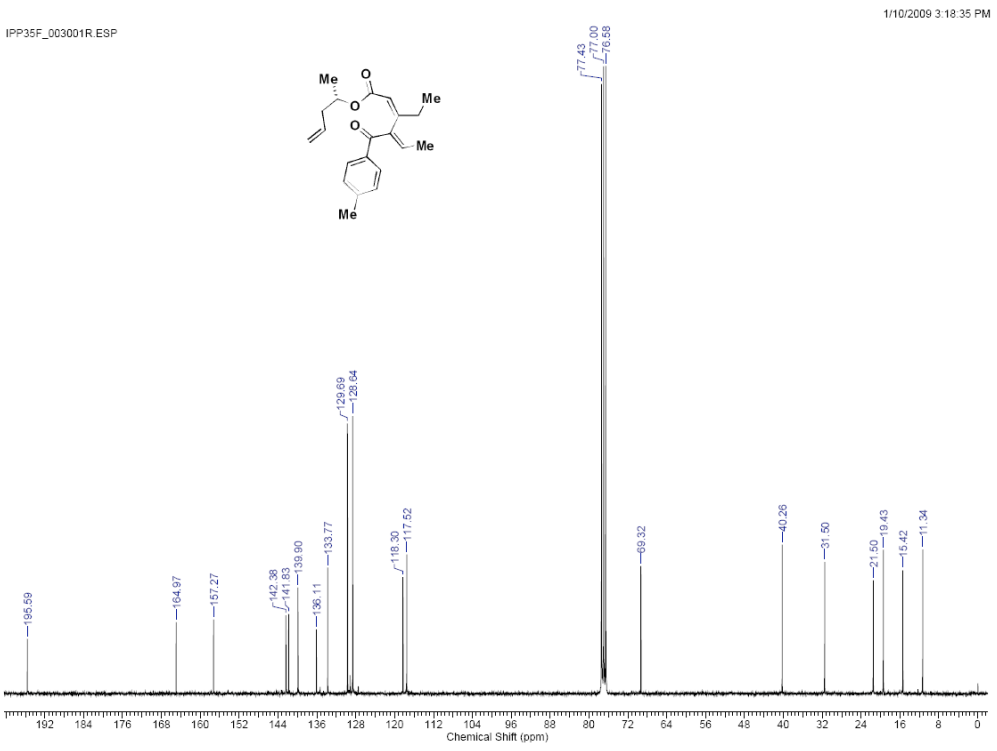


^{13}C NMR (75 MHz, $CDCl_3$) for compound **4ea**

Spectra. Spectral Data for
(2*Z*,4*E*)-((*S*)-pent-4-en-2-yl) 3-ethyl-4-(4-methylbenzoyl)hexa-2,4-dienoate (4eb).

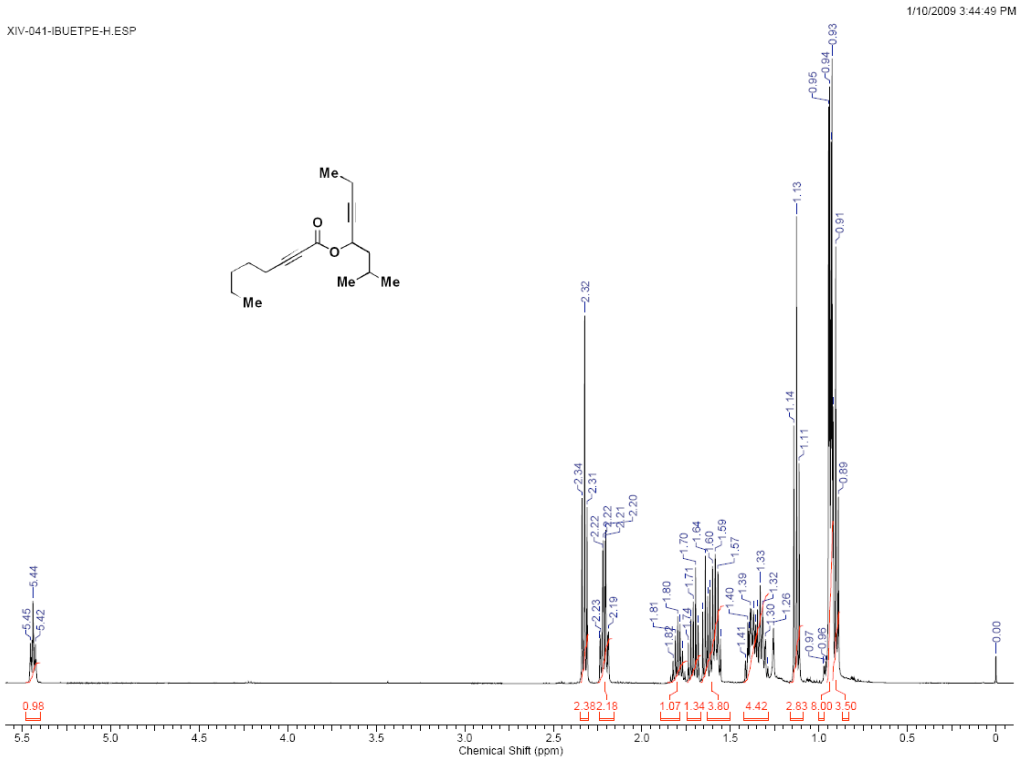


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4eb**

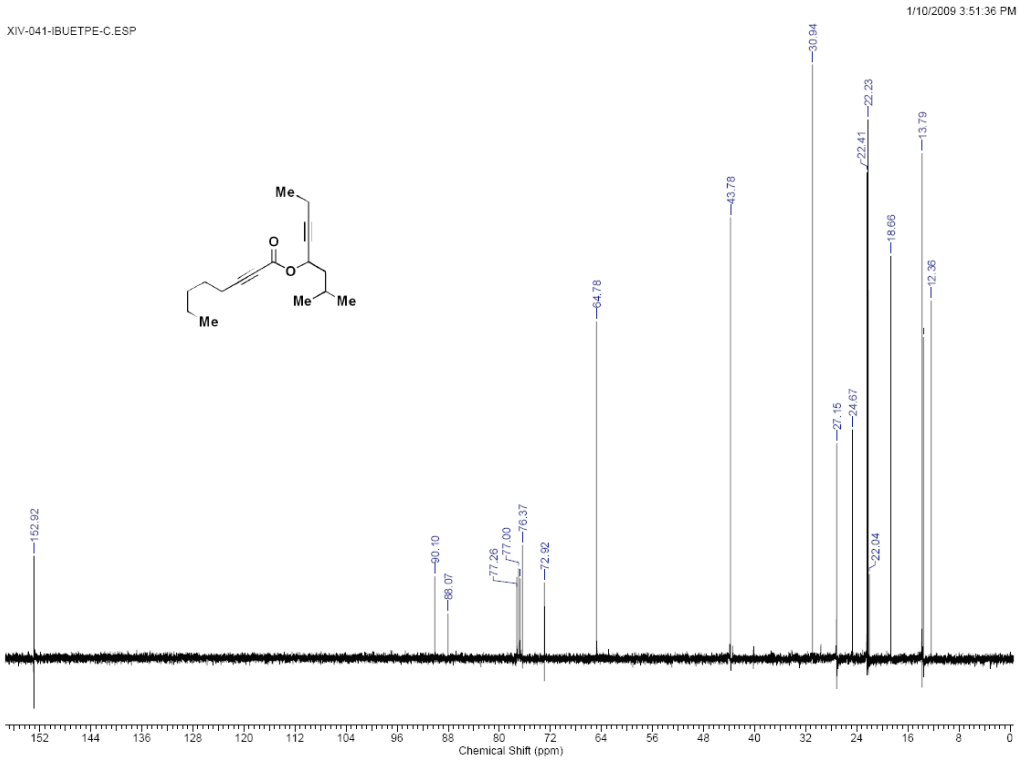


^{13}C NMR (126 MHz, $CDCl_3$) for compound **4eb**

Spectra. Spectral Data for **2-methyloct-5-yn-4-yl oct-2-ynoate (1f).**



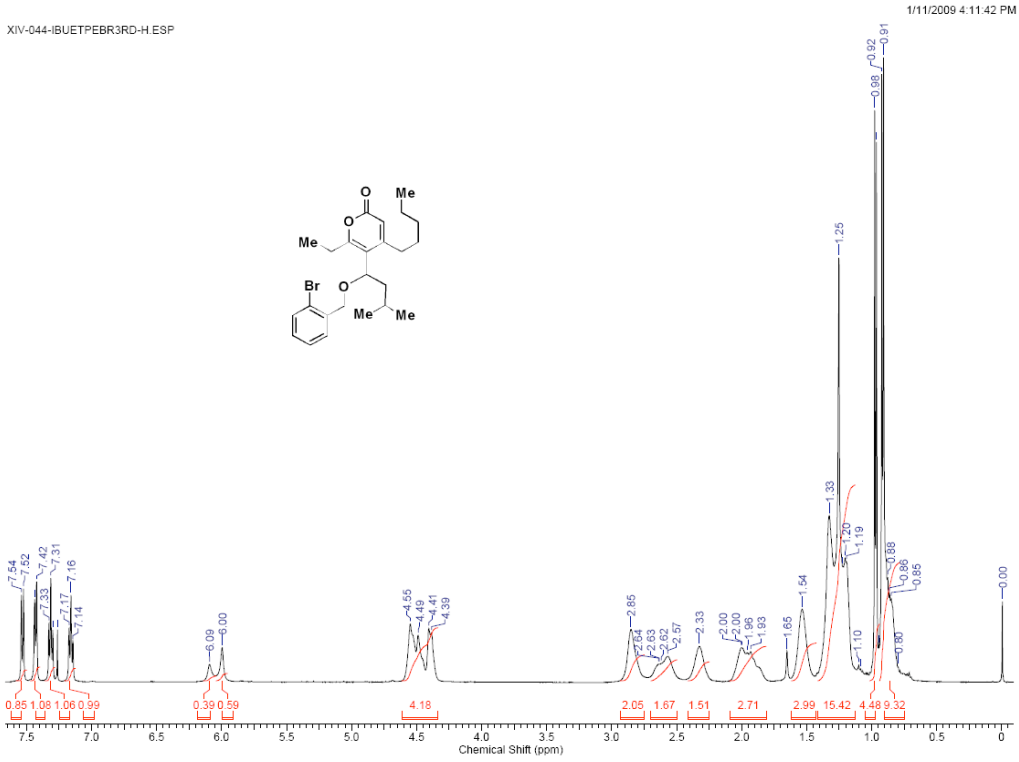
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1f**



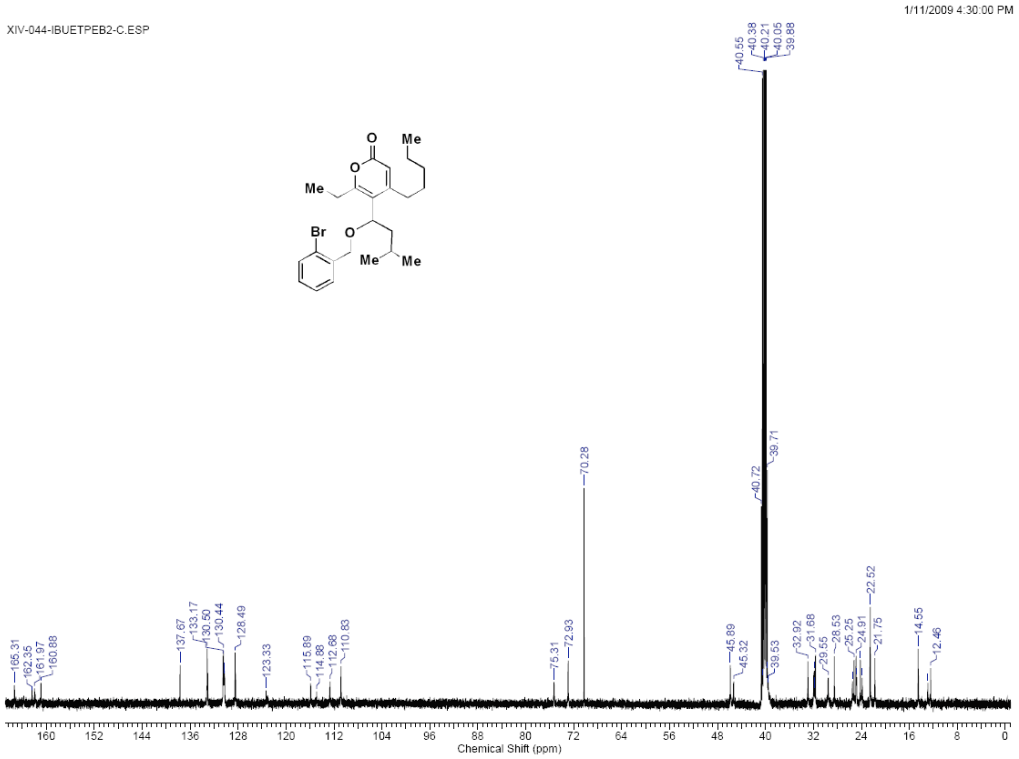
^{13}C NMR (126 MHz, $CDCl_3$) for compound **1f**

Spectra. Spectral Data for

5-(1-(2-bromobenzyloxy)-3-methylbutyl)-6-ethyl-4-pentyl-2*H*-pyran-2-one (3fa).



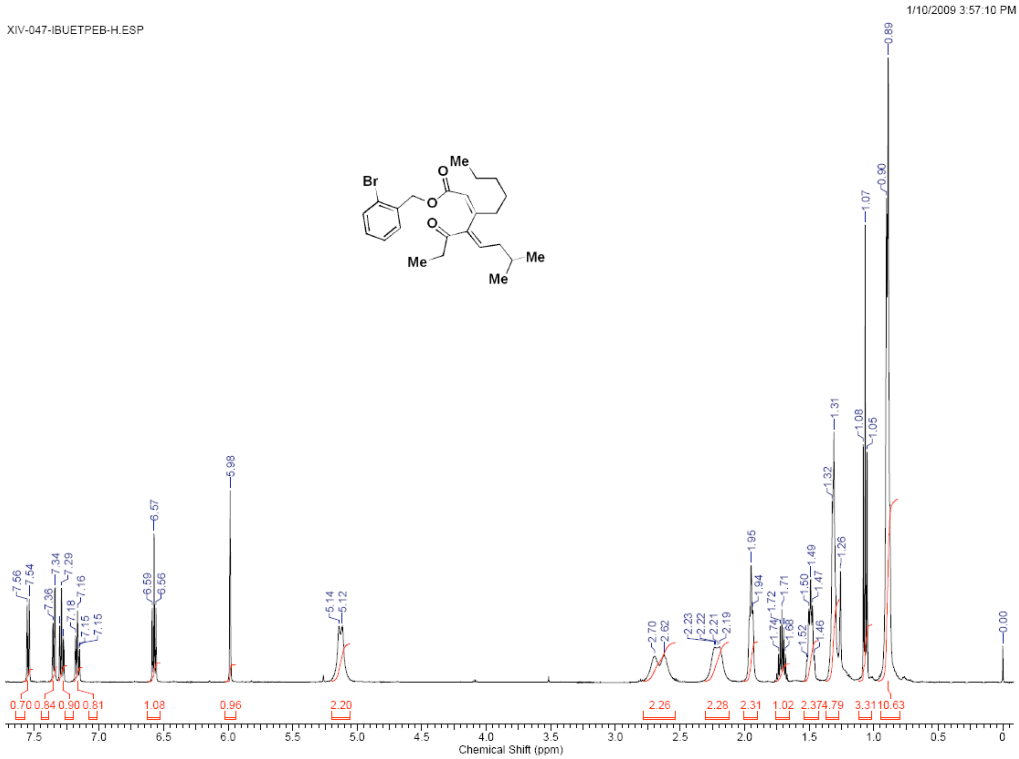
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3fa**



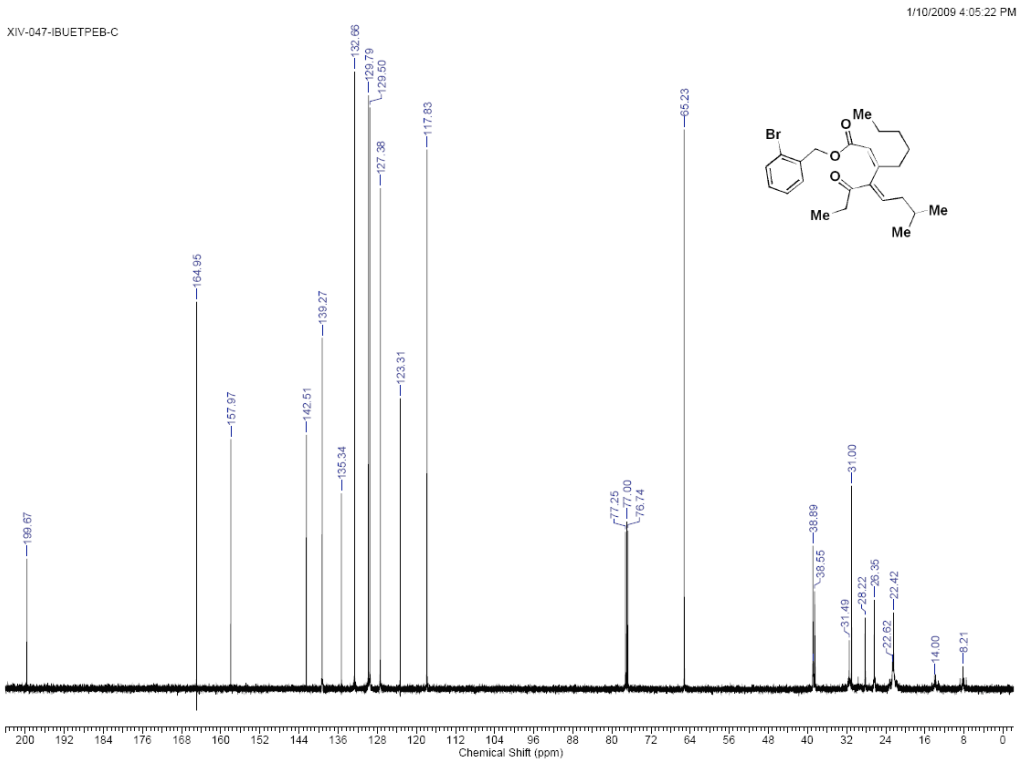
^{13}C NMR (126 MHz, DMSO-d_6) for compound **3fa**

Spectra. Spectral Data for

(2*Z*,4*E*)-2-bromobenzyl 7-methyl-3-pentyl-4-propionylocta-2,4-dienoate (4fa).



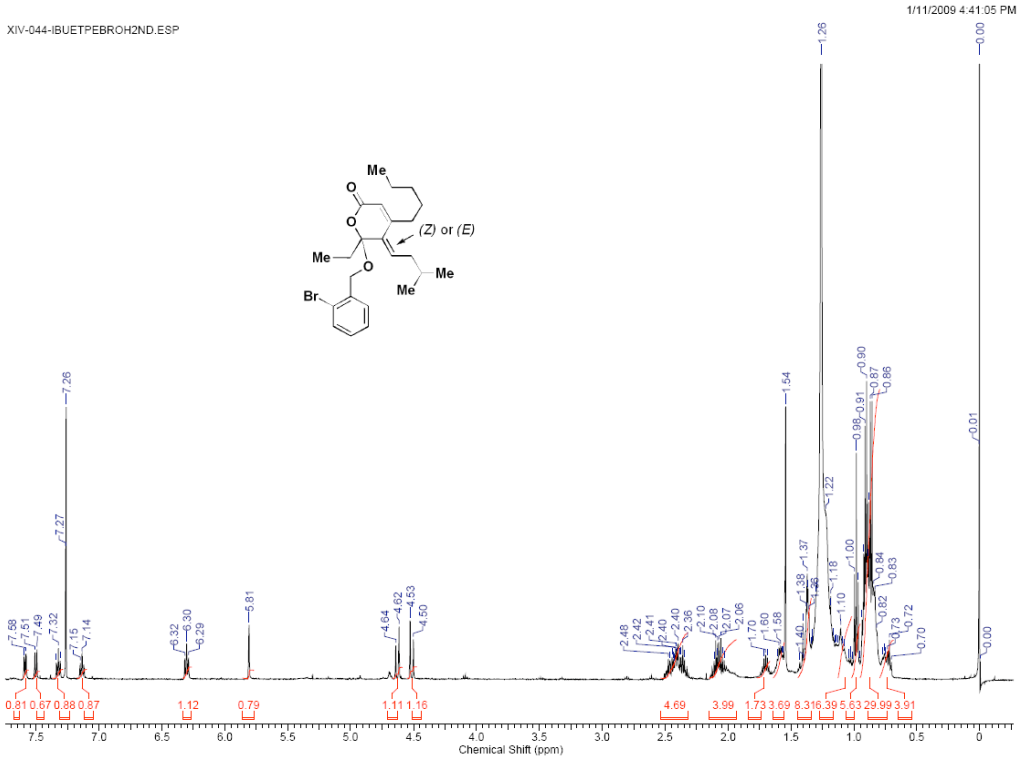
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4fa**



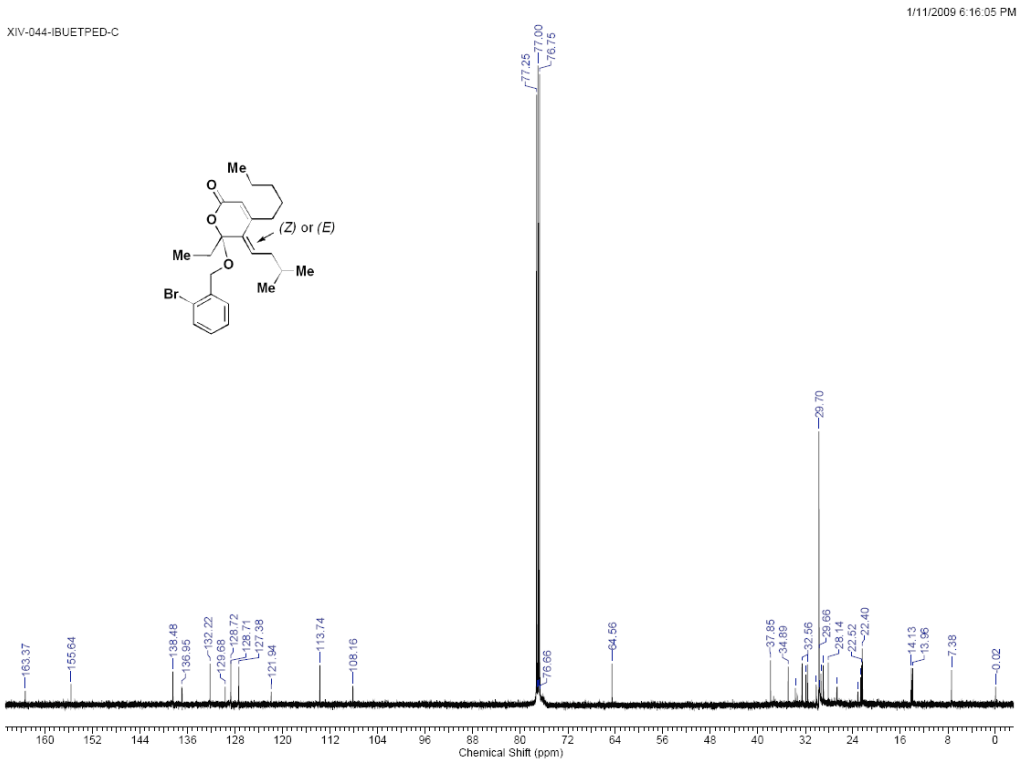
^{13}C NMR (126 MHz, $CDCl_3$) for compound **4fa**

Spectra. Spectral Data for

6-(2-bromobenzyloxy)-6-ethyl-5-(3-methylbutylidene)-4-pentyl-5,6-dihydro-2*H*-pyran-2-one.

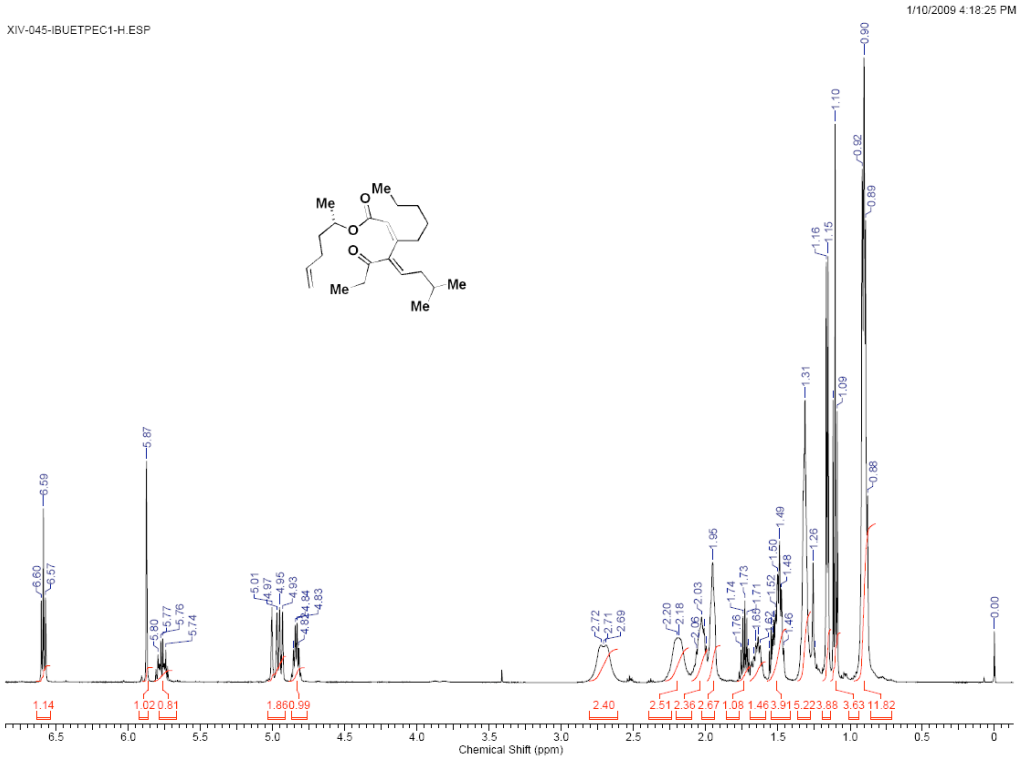


^{1}H NMR (500 MHz, $CDCl_3$)

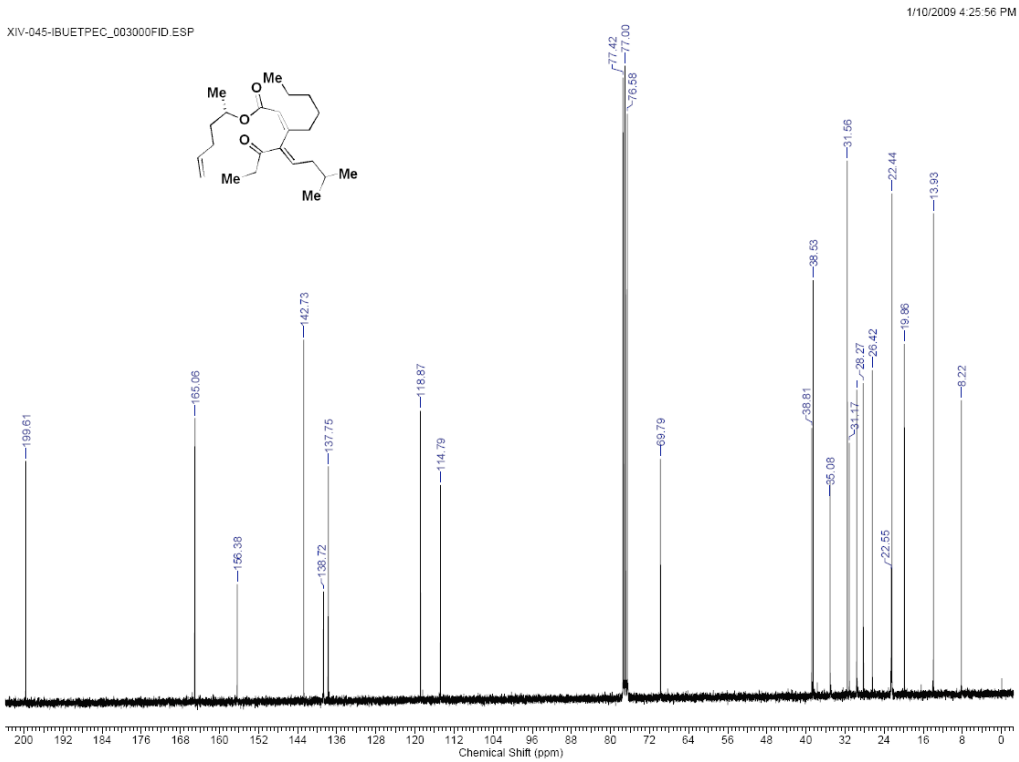


^{13}C NMR (126 MHz, $CDCl_3$)

Spectra. Spectral Data for
(2*Z*,4*E*)-((*S*)-hex-5-en-2-yl) 7-methyl-3-pentyl-4-propionylocta-2,4-dienoate (**4fb**).

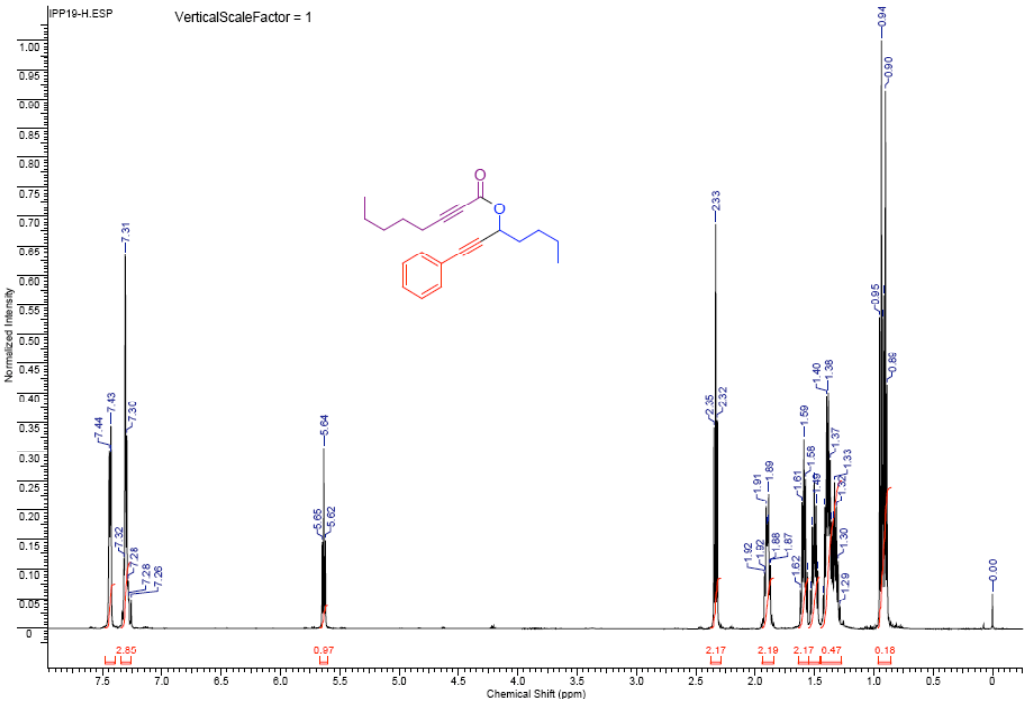


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4fb**

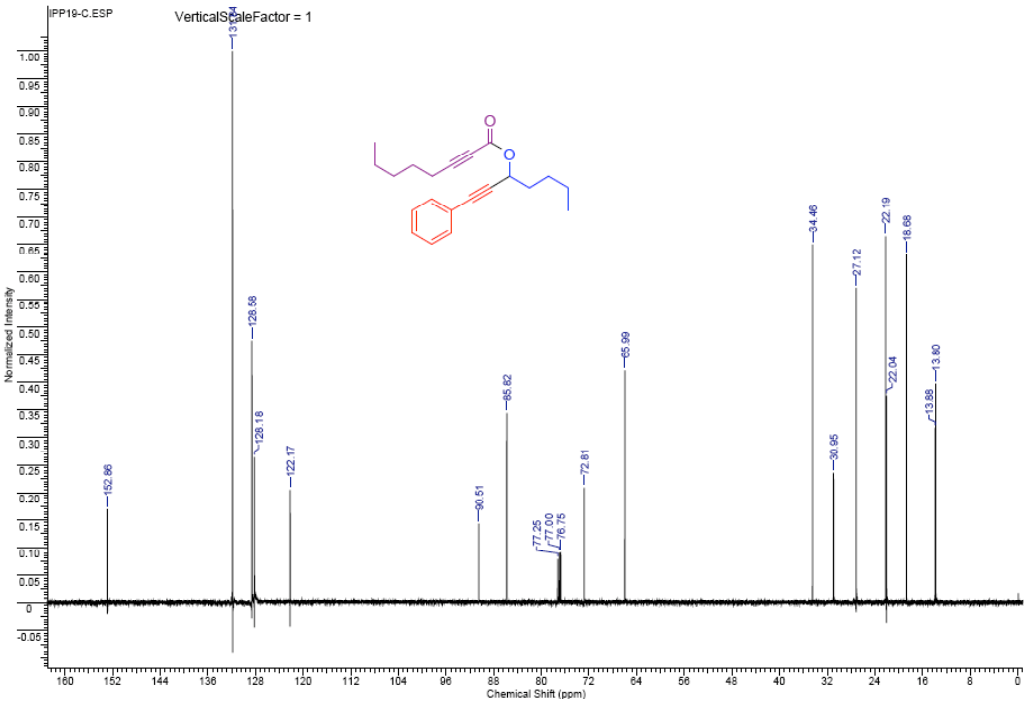


^{13}C NMR (75 MHz, $CDCl_3$) for compound **4fb**

Spectra. Spectral Data for **1-phenylhept-1-yn-3-yl oct-2-ynoate (1g)**



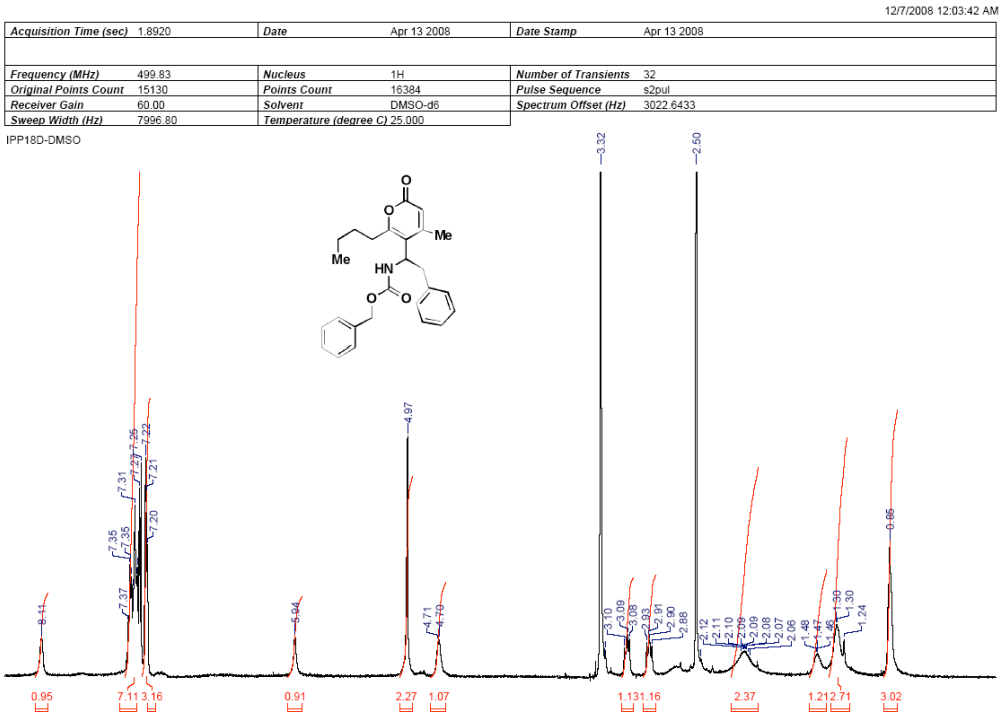
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1d**



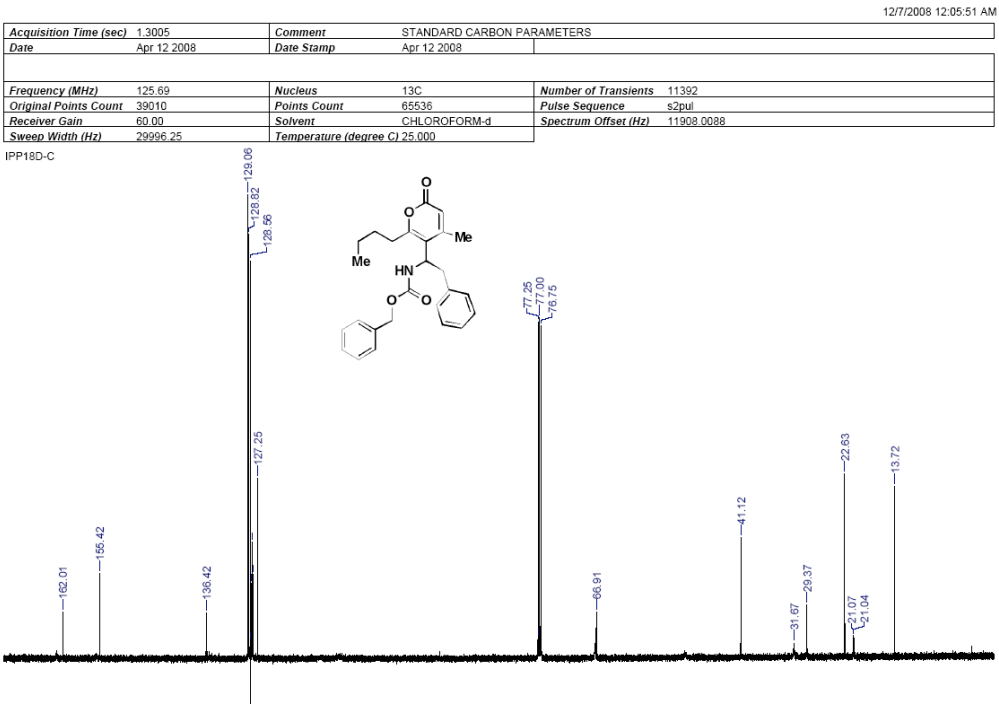
^{13}C NMR (126 MHz, $CDCl_3$) for compound **1d**

Spectra. Spectral Data for

benzyl 1-(6-butyl-4-methyl-2-oxo-2*H*-pyran-5-yl)-2-phenylethylcarbamate (3g)

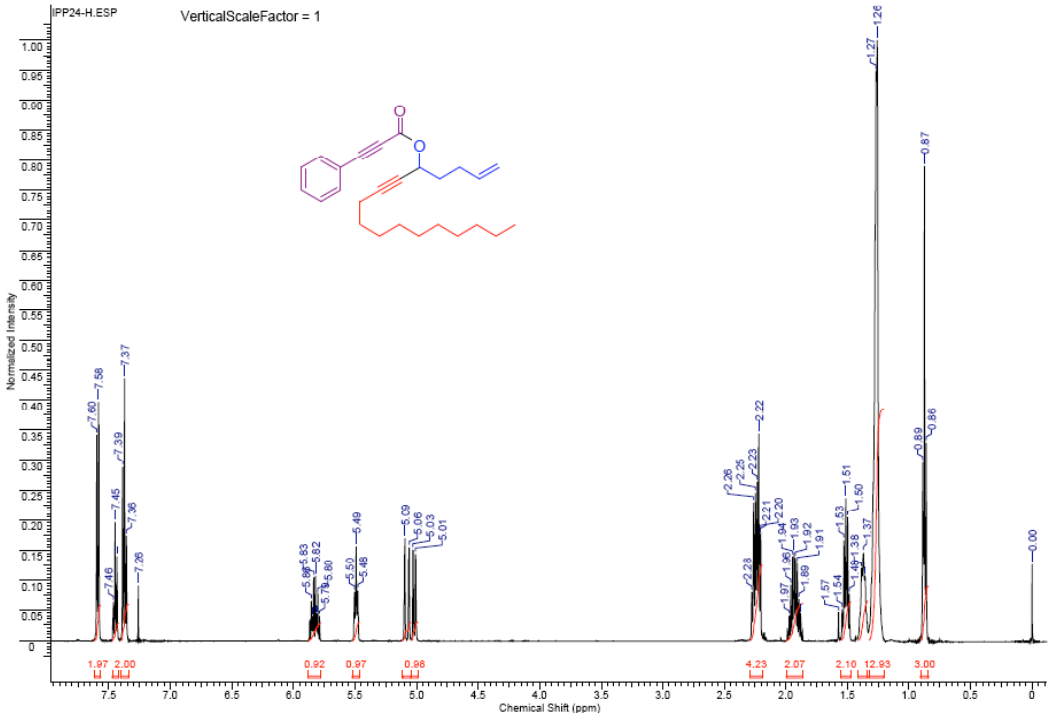


^{1}H NMR (500 MHz, DMSO- d_6) of compound **3g**

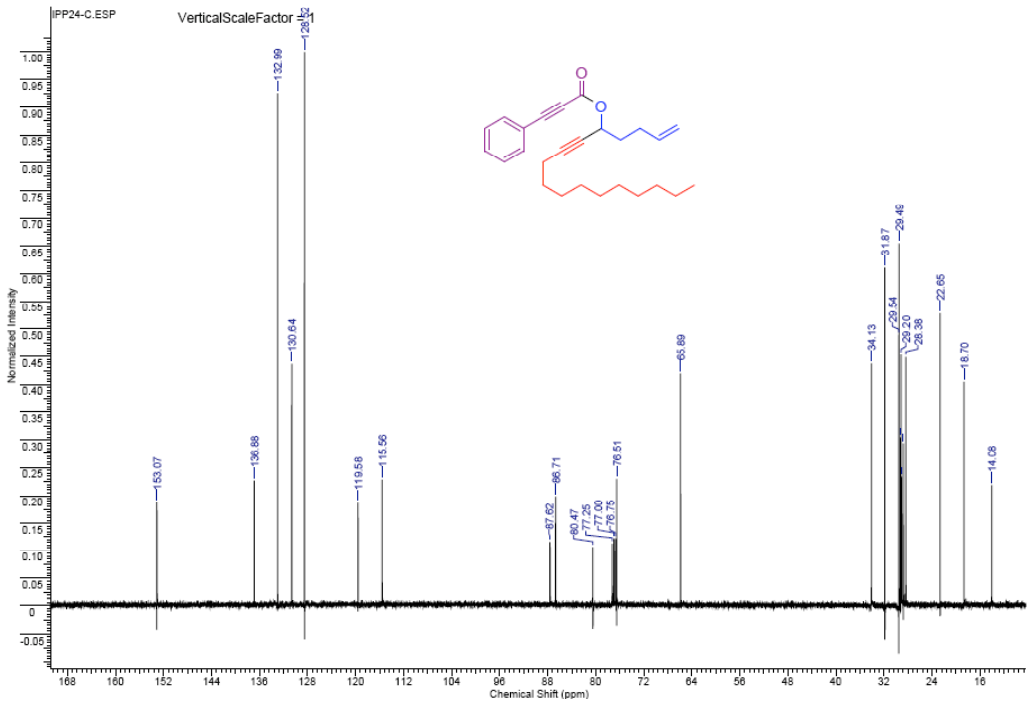


^{13}C NMR (126 MHz, $CDCl_3$) for compound **3g**

Spectra. Spectral Data for **heptadec-1-en-6-yn-5-yl 3-phenylpropiolate (1h)**

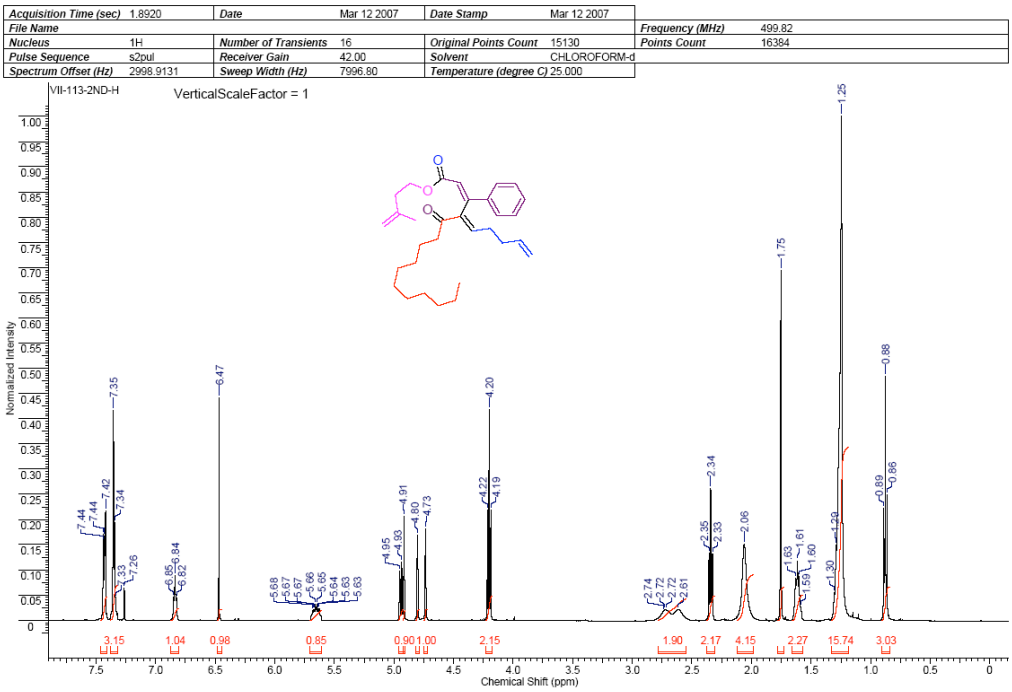


^{1}H NMR (500 MHz, $CDCl_3$) of compound **1h**

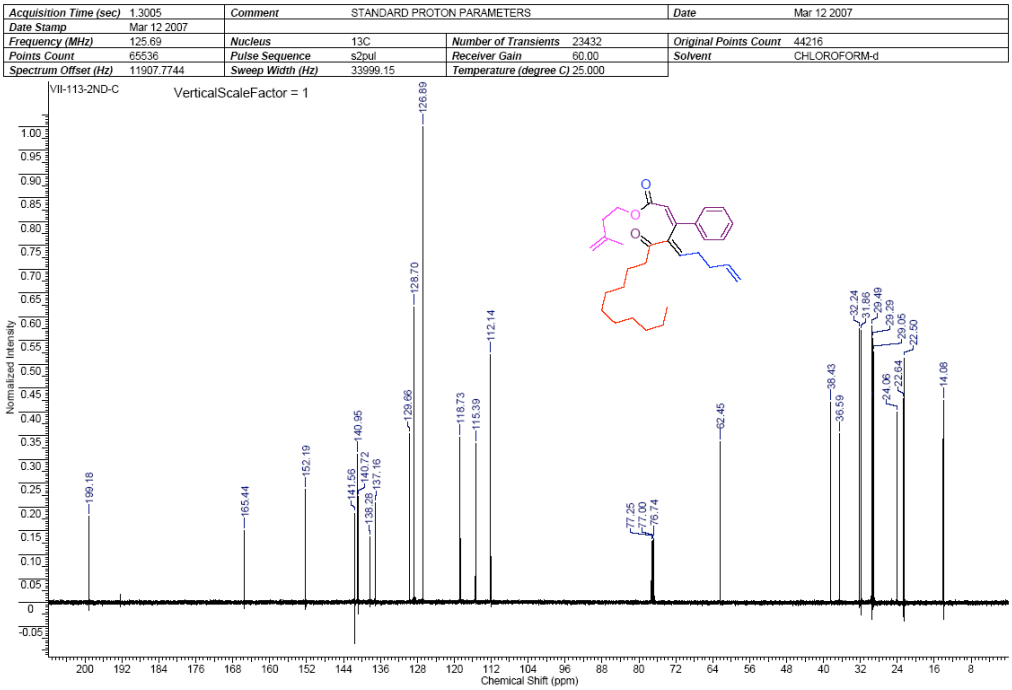


^{13}C NMR (126 MHz, $CDCl_3$) for compound **1h**

Spectra. Spectral Data for
(2*Z*,4*E*)-3-methylbut-3-enyl 5-oxo-4-(pent-4-enylidene)-3-phenylpentadec-2-enoate (4h).

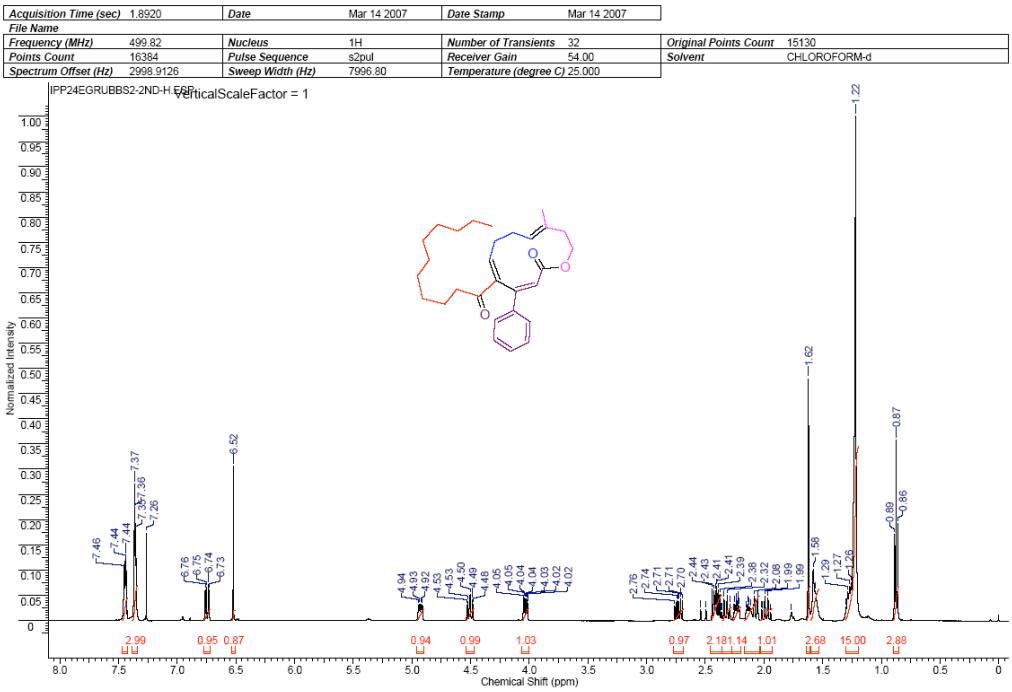


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4h**

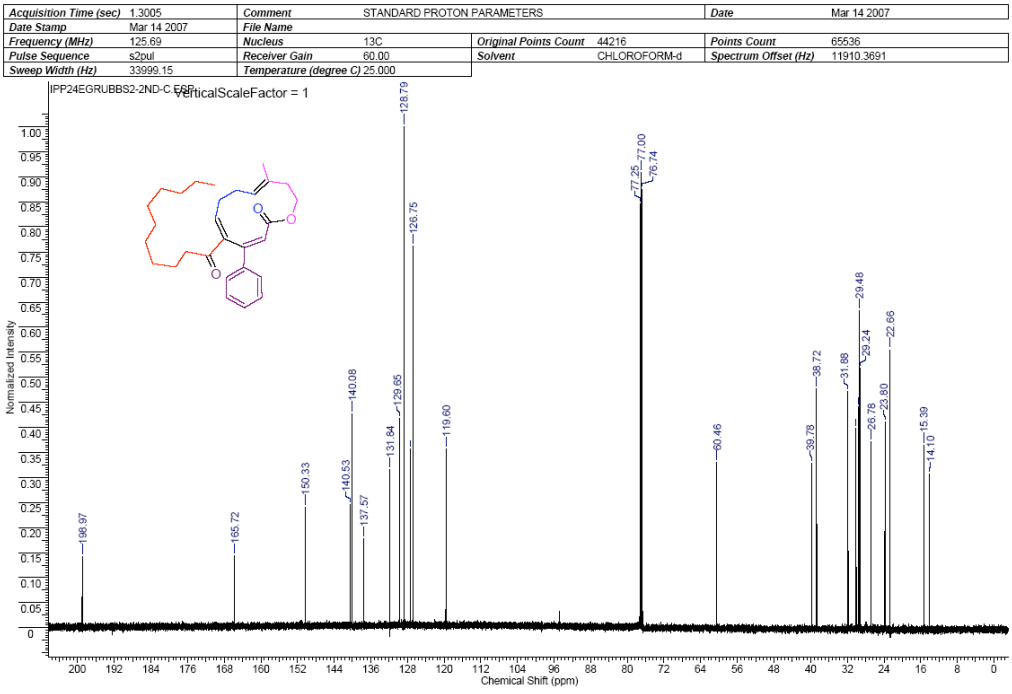


^{13}C NMR (126 MHz, $CDCl_3$) for compound **4h**

Spectra. Spectral Data for
(3*Z*,5*E*,9*Z*)-10-methyl-4-phenyl-5-undecanoyloxacyclododeca-3,5,9-trien-2-one (5h).



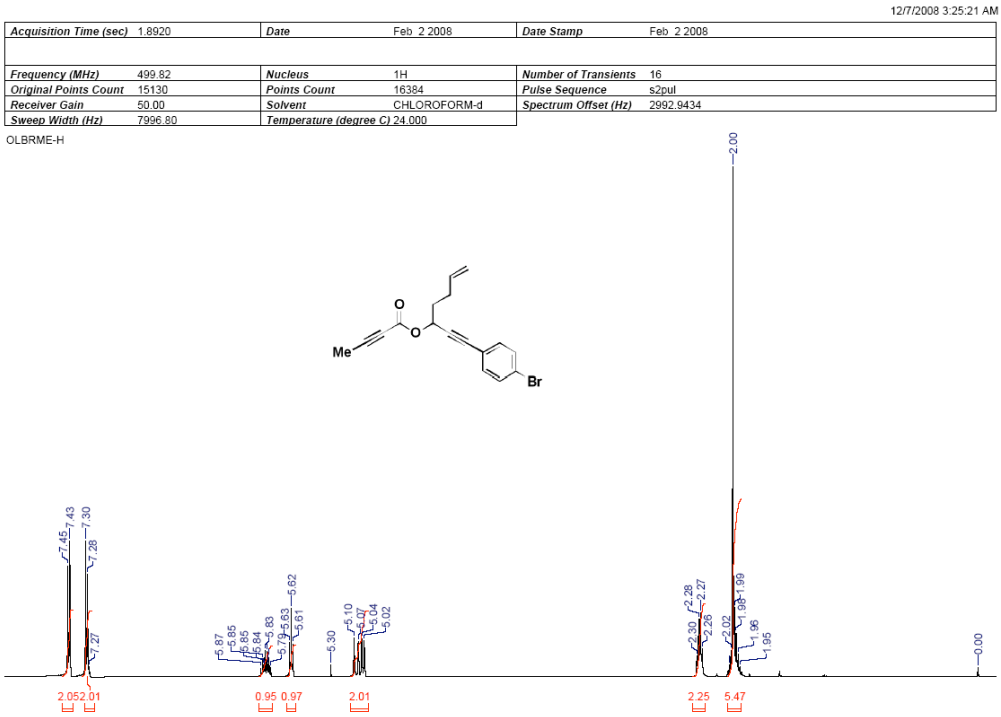
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5h**



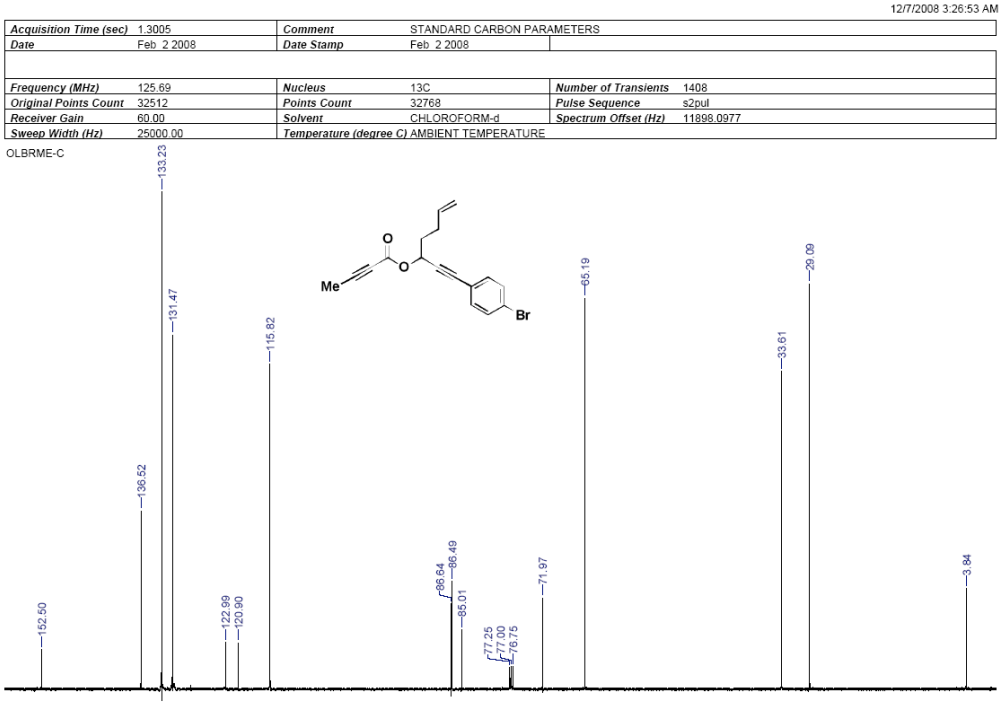
^{13}C NMR (126 MHz, $CDCl_3$) for compound **5h**

Spectra. Spectral Data for

1-(4-bromophenyl)hept-6-en-1-yn-3-yl but-2-ynoate (1i).



^{1}H NMR (500 MHz, $CDCl_3$) of compound **1i**



^{13}C NMR (126 MHz, $CDCl_3$) for compound **1i**

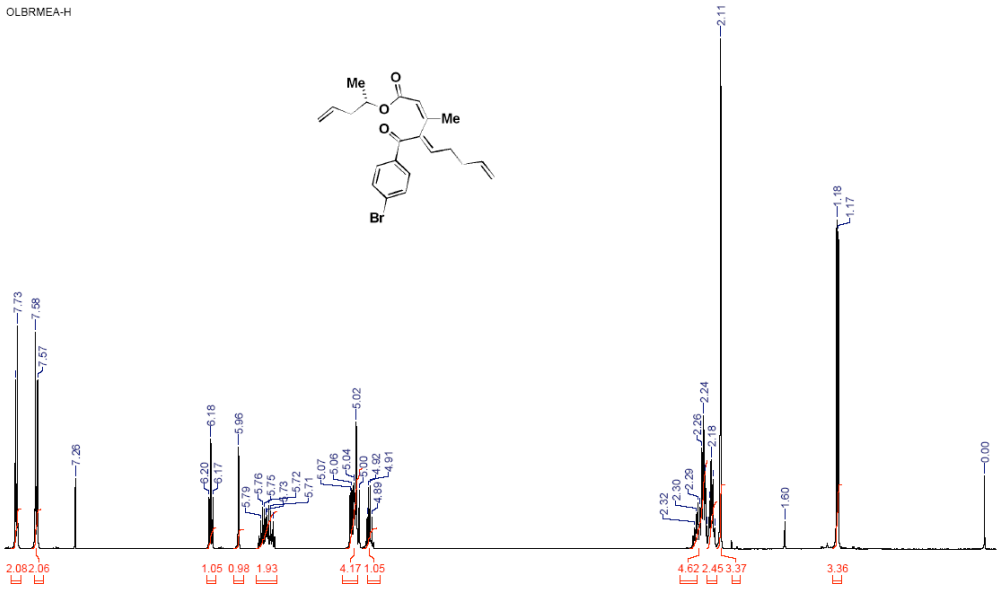
Spectra. Spectral Data for

(2*Z*,4*E*)-((*S*)-pent-4-en-2-yl) 4-(4-bromobenzoyl)-3-methylnona-2,4,8-trienoate (4ia).

12/7/2008 3:58:29 AM

Acquisition Time (sec)	1.8920	*Date*	Feb 4 2008	*Date Stamp*	Feb 4 2008
Frequency (MHz)	499.82	*Nucleus*	1H	*Number of Transients*	16
Original Points Count	15130	*Points Count*	16384	*Pulse Sequence*	s2pul
Receiver Gain	60.00	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	2989.0388
Sweep Width (Hz)	7996.80	*Temperature (degree C)*	24.000		

OLBRMEA-H

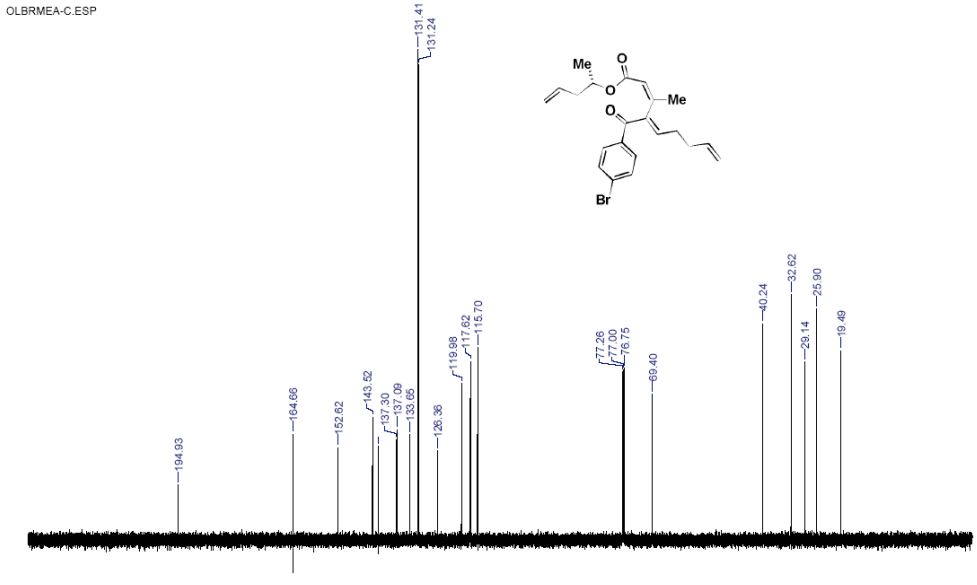


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4ia**

12/7/2008 4:06:49 AM

Acquisition Time (sec)	1.3005	*Date*	Feb 4 2008	*Date Stamp*	Feb 4 2008
Frequency (MHz)	125.69	*Nucleus*	13C	*Number of Transients*	128
Original Points Count	40863	*Points Count*	65536	*Pulse Sequence*	s2pul
Receiver Gain	60.00	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	13791.0264
Sweep Width (Hz)	31421.84	*Temperature (degree C)*	24.000		

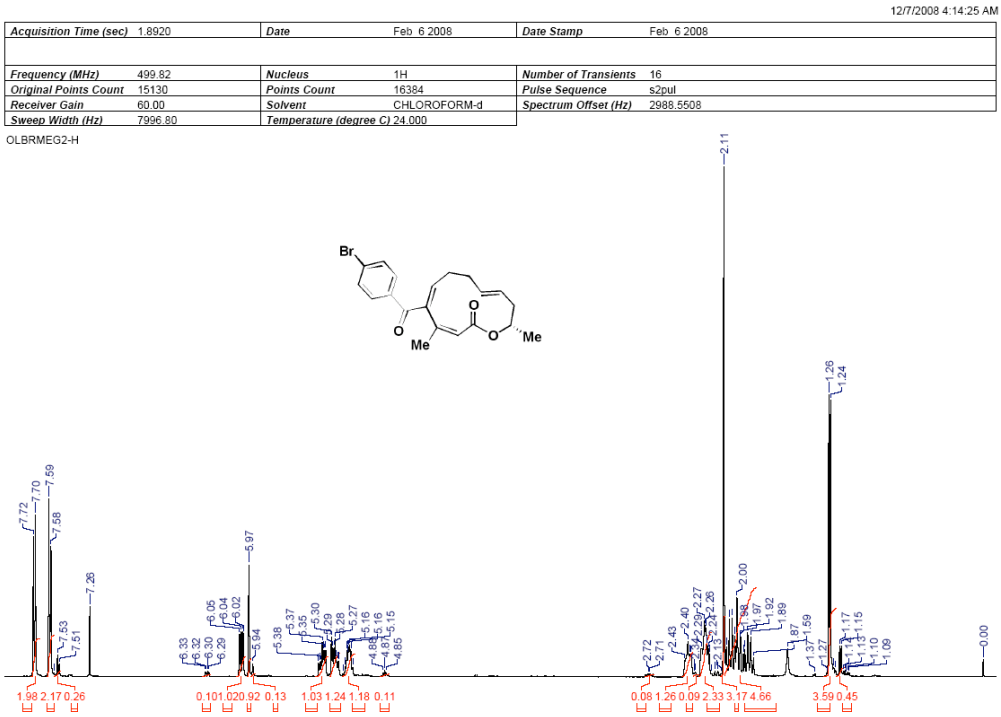
OLBRMEA-C.ESP



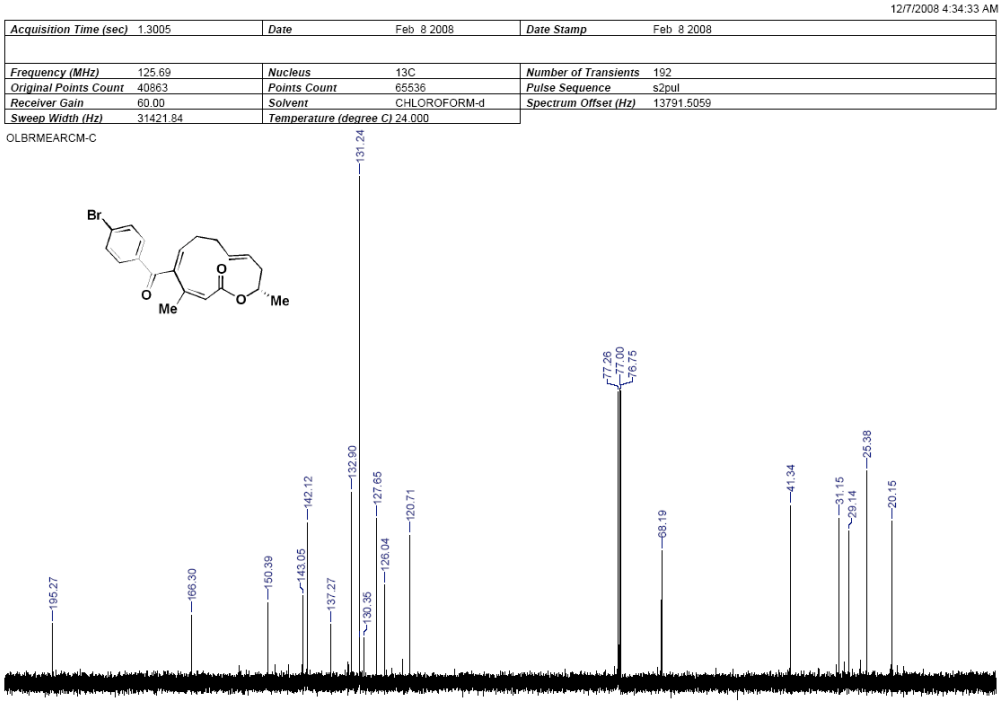
^{13}C NMR (126 MHz, $CDCl_3$) for compound **4ia**

Spectra. Spectral Data for

(*S*,3*Z*,5*E*,9*E*)-5-(4-bromobenzoyl)-4,12-dimethyloxacyclododeca-3,5,9-trien-2-one (5ia).



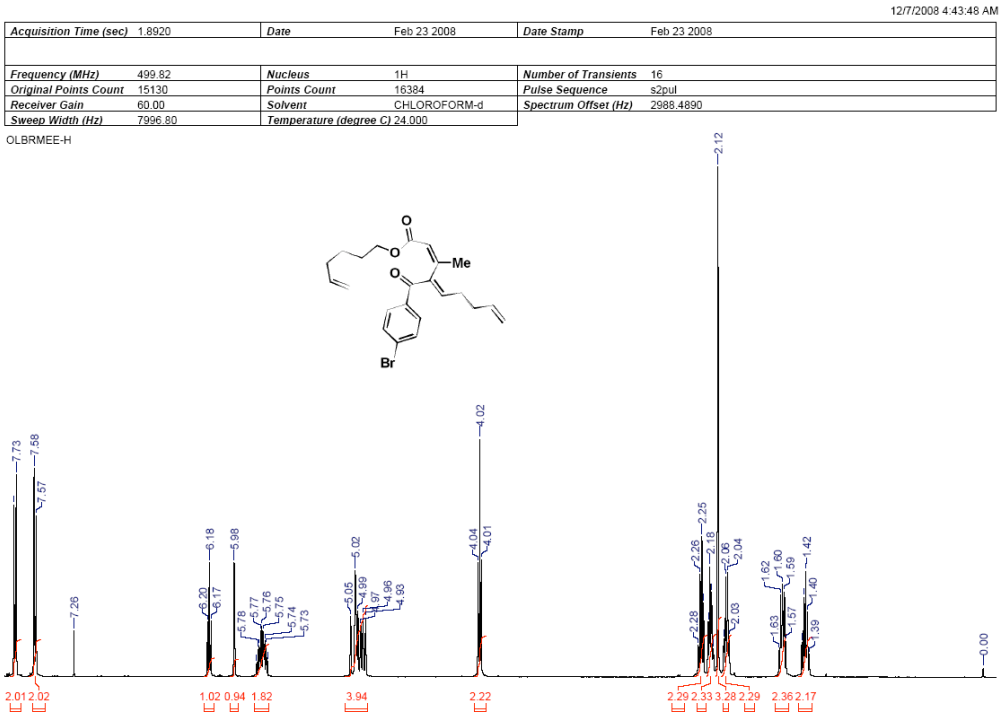
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5ia**



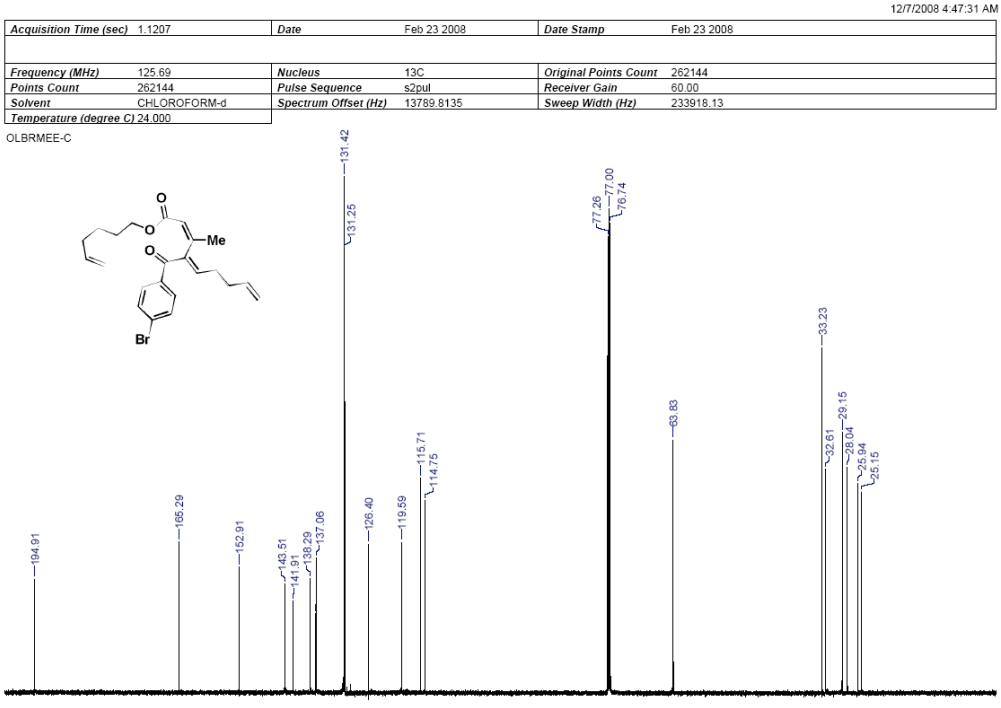
^{13}C NMR (126 MHz, $CDCl_3$) for compound **5ia**

Spectra. Spectral Data for

(2*Z*,4*E*)-hex-5-enyl 4-(4-bromobenzoyl)-3-methylnona-2,4,8-trienoate (4ib)



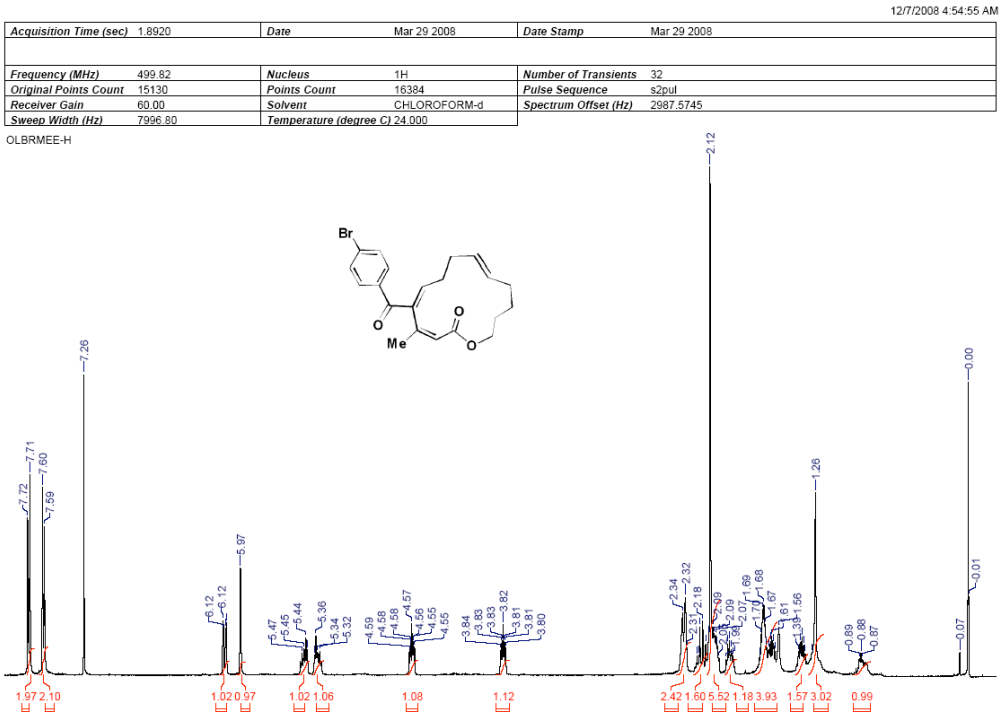
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4ib**



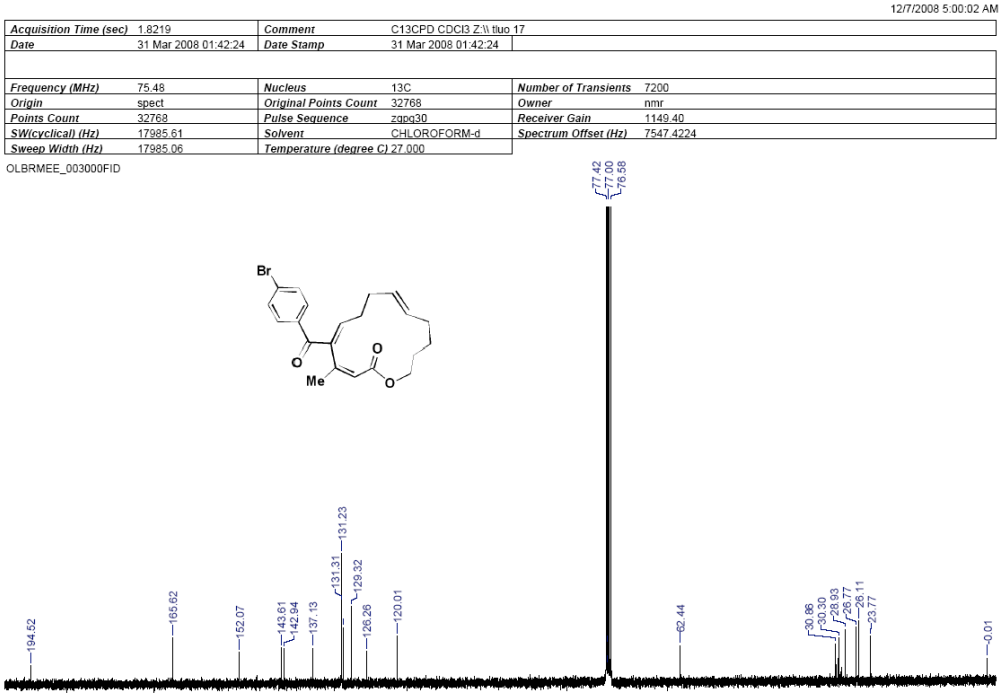
^{13}C NMR (126 MHz, $CDCl_3$) for compound **4ib**

Spectra. Spectral Data for

(3*Z*,5*E*,9*E*)-5-(4-bromobenzoyl)-4-methyloxacyclotetradeca-3,5,9-trien-2-one (5ib-E).



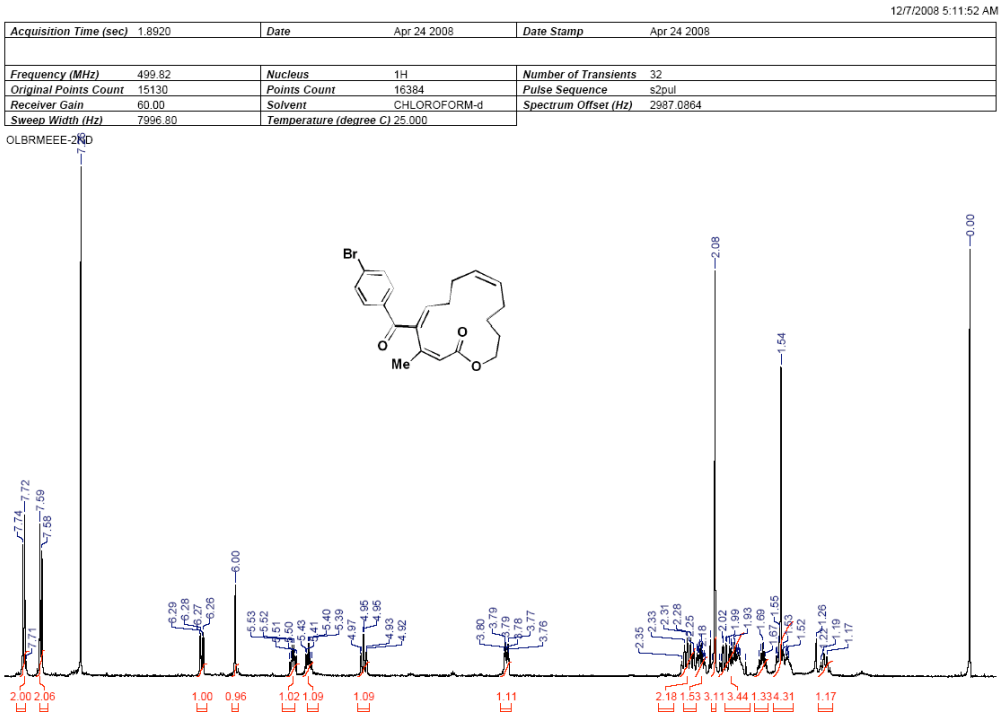
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5ib-E**



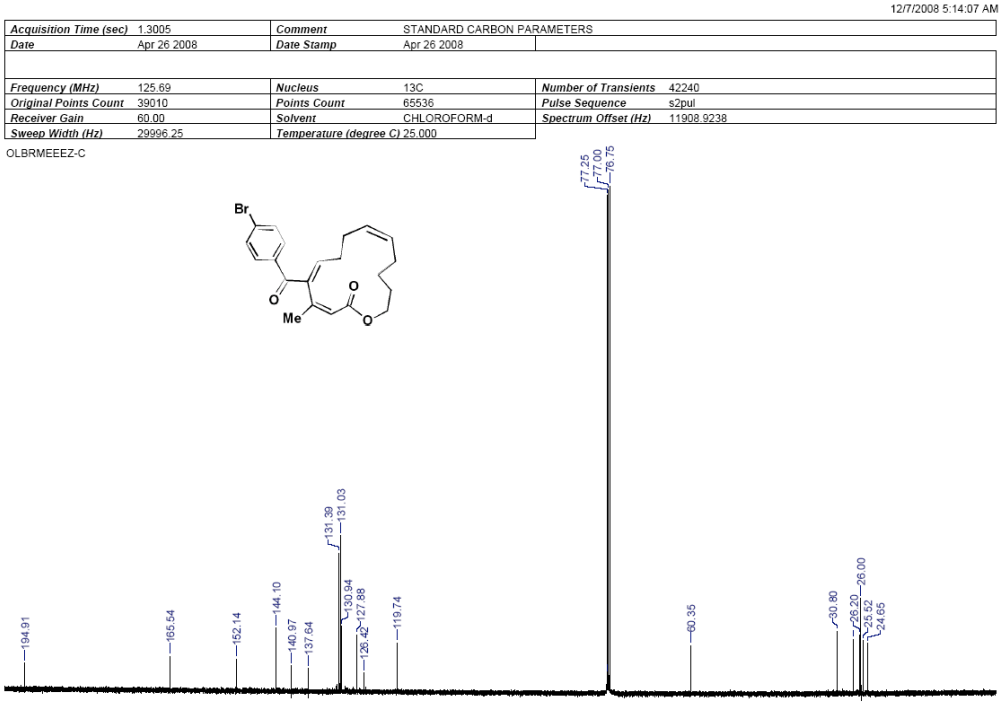
^{13}C NMR (126 MHz, $CDCl_3$) for compound **5ib-E**

Spectra. Spectral Data for

(3*Z*,5*E*,9*Z*)-5-(4-bromobenzoyl)-4-methyloxacyclotetradeca-3,5,9-trien-2-one (5ib-*Z*).



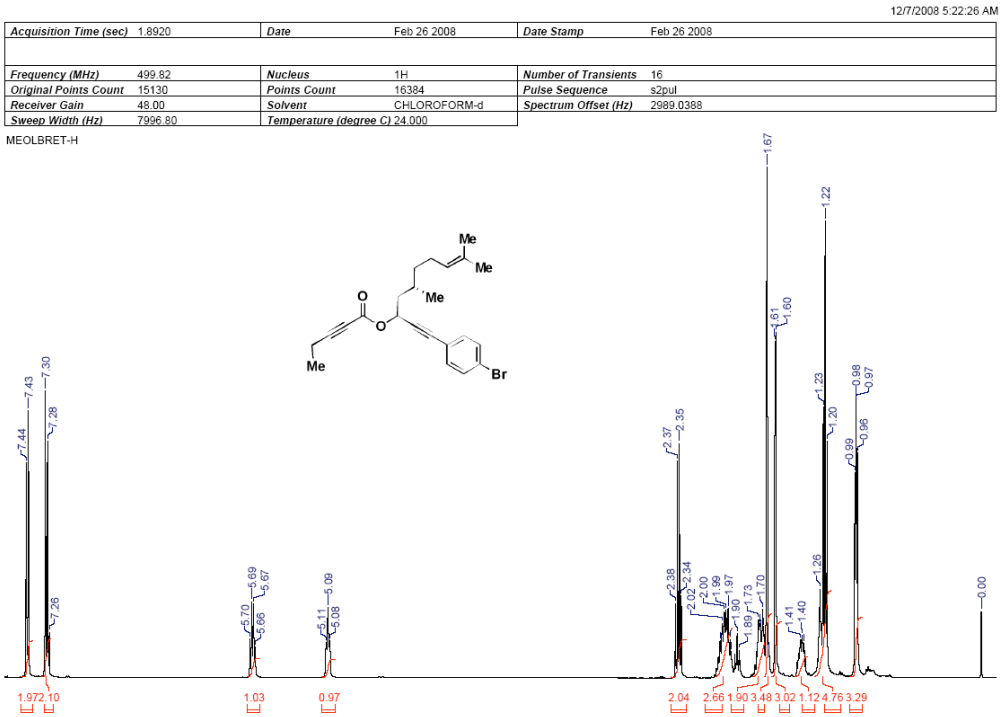
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5ib-Z**



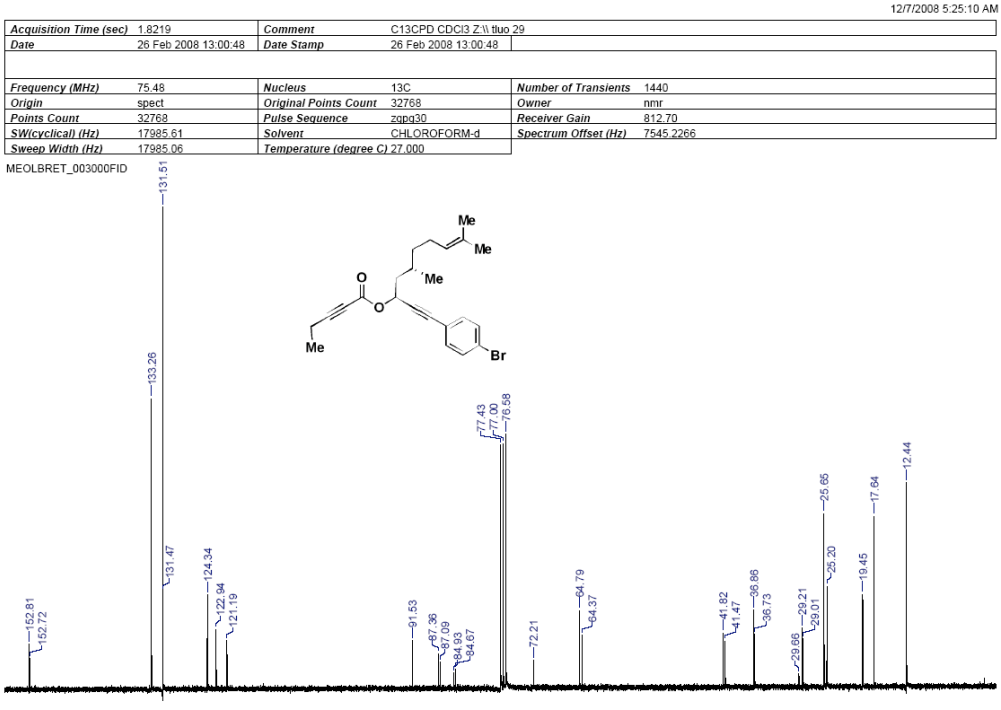
^{13}C NMR (126 MHz, $CDCl_3$) for compound **5ib-Z**

Spectra. Spectral Data for

(5*S*)-1-(4-bromophenyl)-5,9-dimethyldec-8-en-1-yn-3-yl pent-2-ynoate (1h).

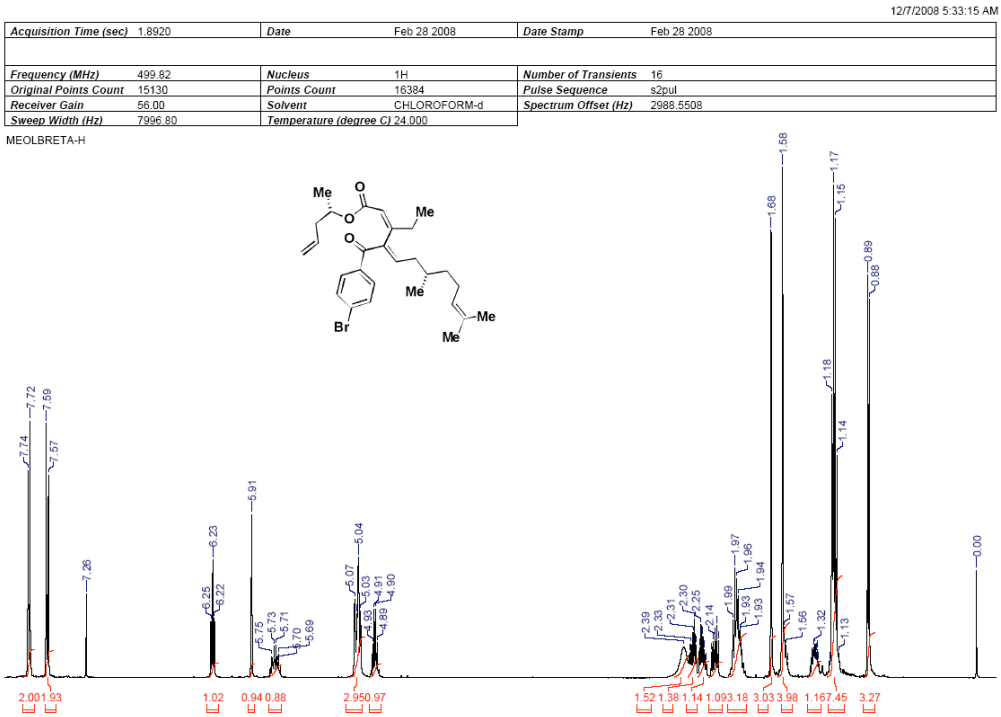


^{1}H NMR (500 MHz, $CDCl_3$) of compound **1j**

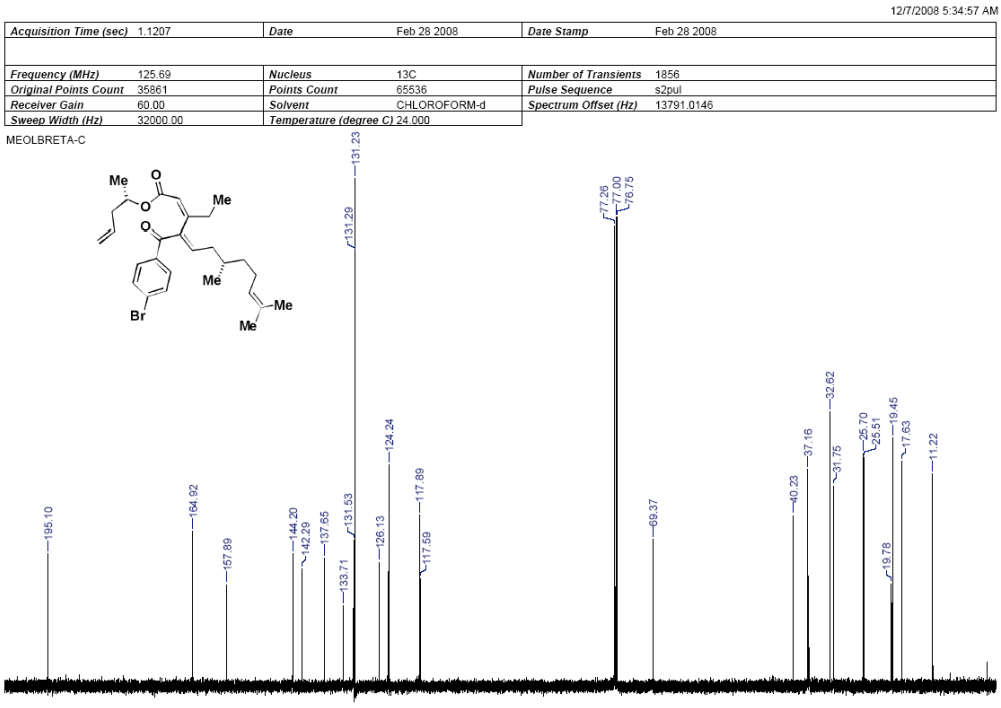


^{13}C NMR (75 MHz, $CDCl_3$) for compound **1j**

Spectra. Spectral Data for
(*S*,2*Z*,4*E*)-((*S*)-pent-4-en-2-yl) 4-(4-bromobenzoyl)-3-ethyl-7,11-dimethyldodeca-2,4,10-trienoate (4ja).

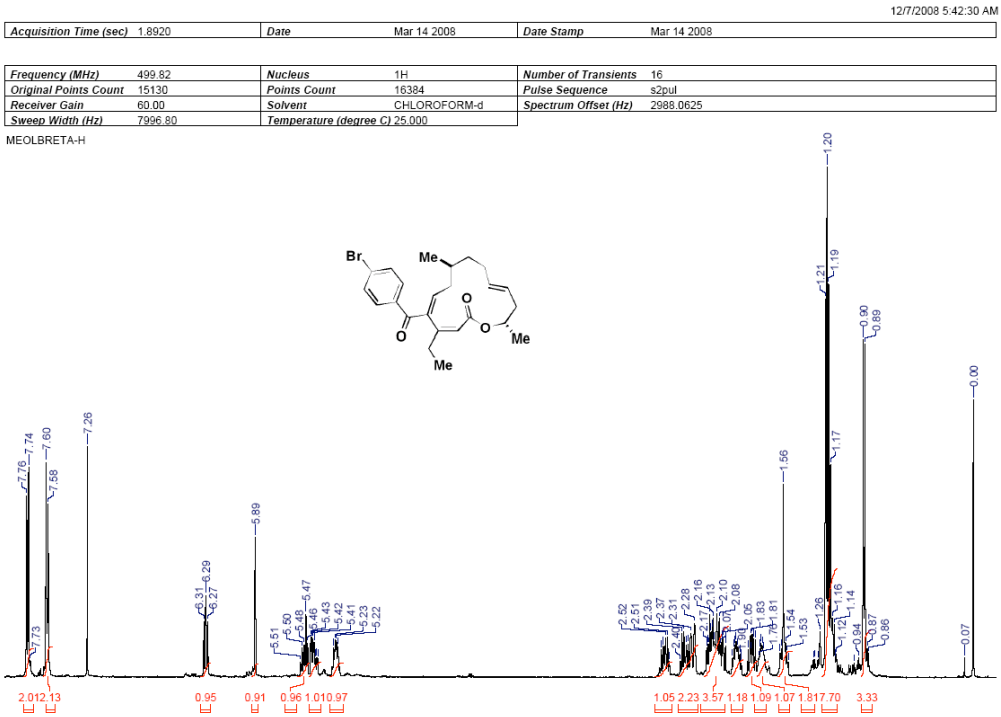


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4ja**

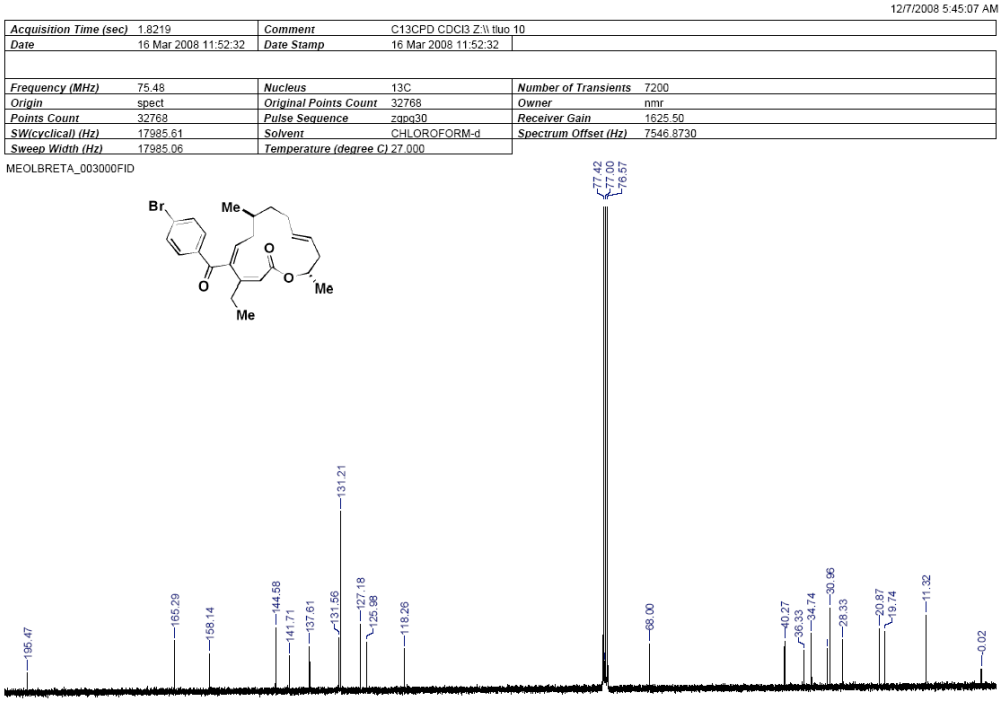


^{13}C NMR (126 MHz, $CDCl_3$) for compound **4ja**

Spectra. Spectral Data for
(3*Z*,5*E*,8*S*,11*E*,14*S*)-5-(4-bromobenzoyl)-4-ethyl-8,14-dimethyloxacyclotetradeca-3,5,11-trien-2-one (5ja).

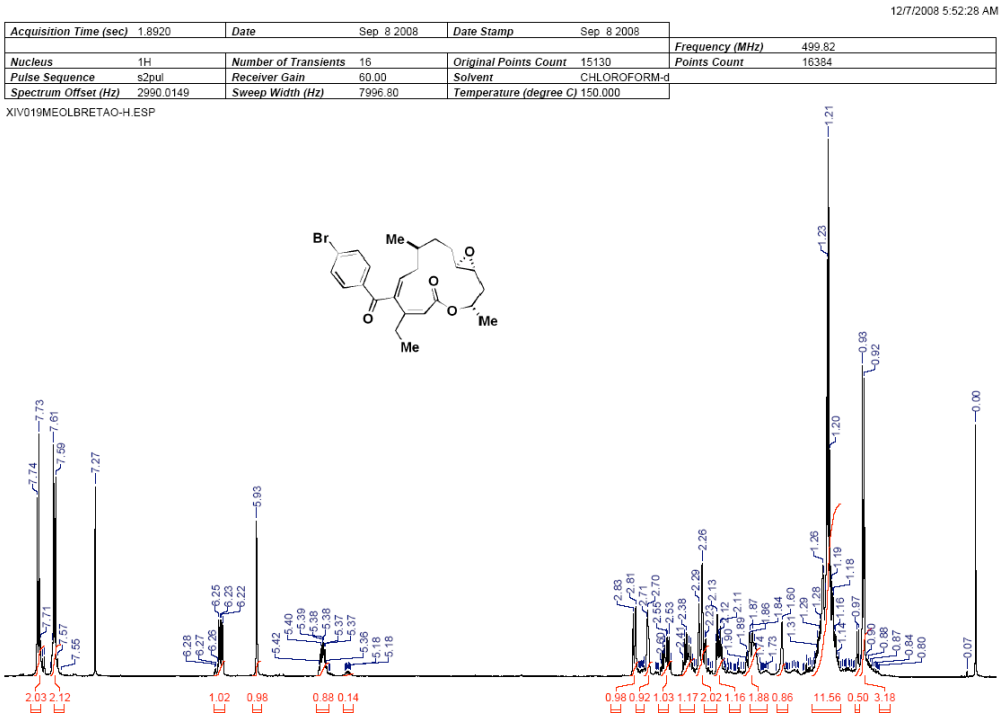


^{1}H NMR (500 MHz, $CDCl_3$) of compound **5ja**

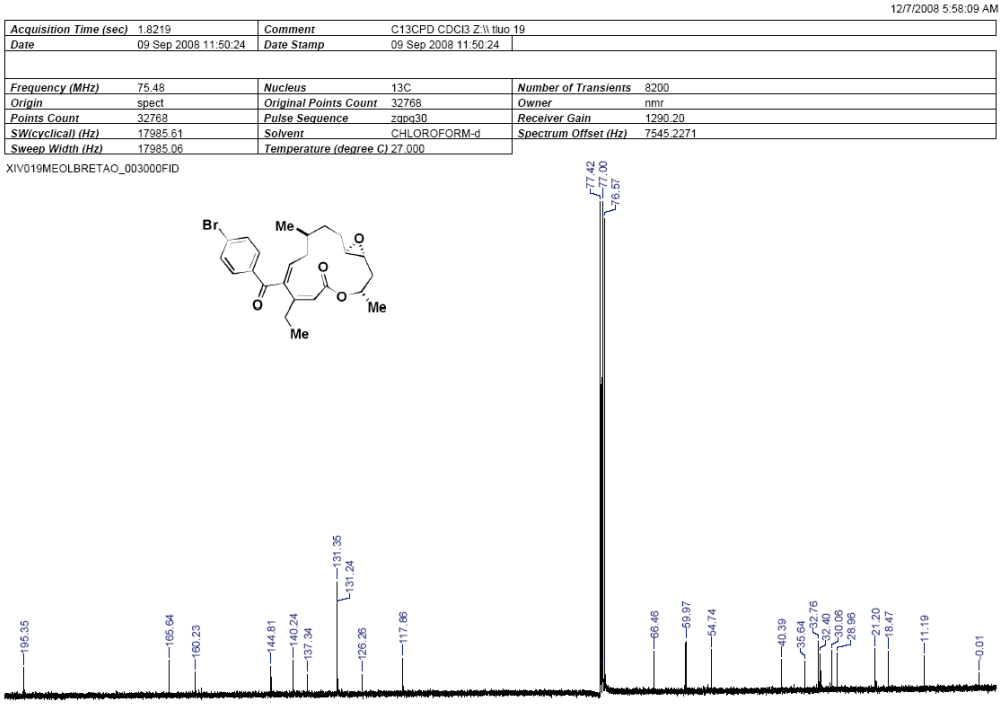


^{13}C NMR (75 MHz, $CDCl_3$) for compound **5ja**

Spectra. Spectral Data for **(1*R*,3*S*,6*Z*,8*E*,11*S*,14*R*)-8-(4-bromobenzoyl)-7-ethyl-3,11-dimethyl-4,15-dioxabicyclo[12.1.0]pentadeca-6,8-dien-5-one (10).**



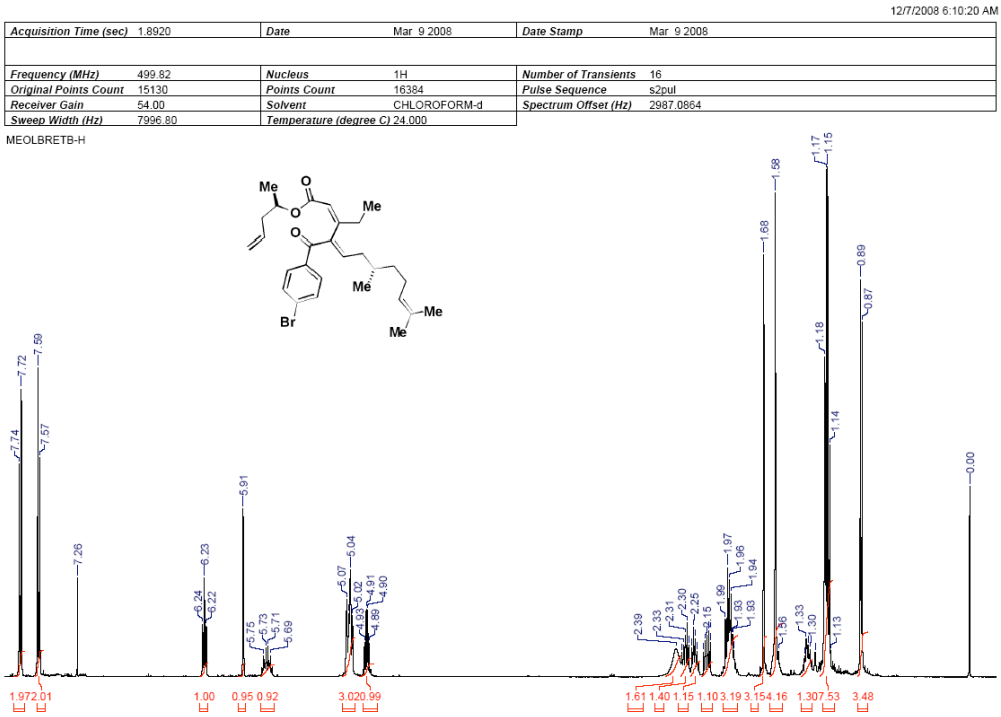
^{1}H NMR (500 MHz, $CDCl_3$) of compound **10**



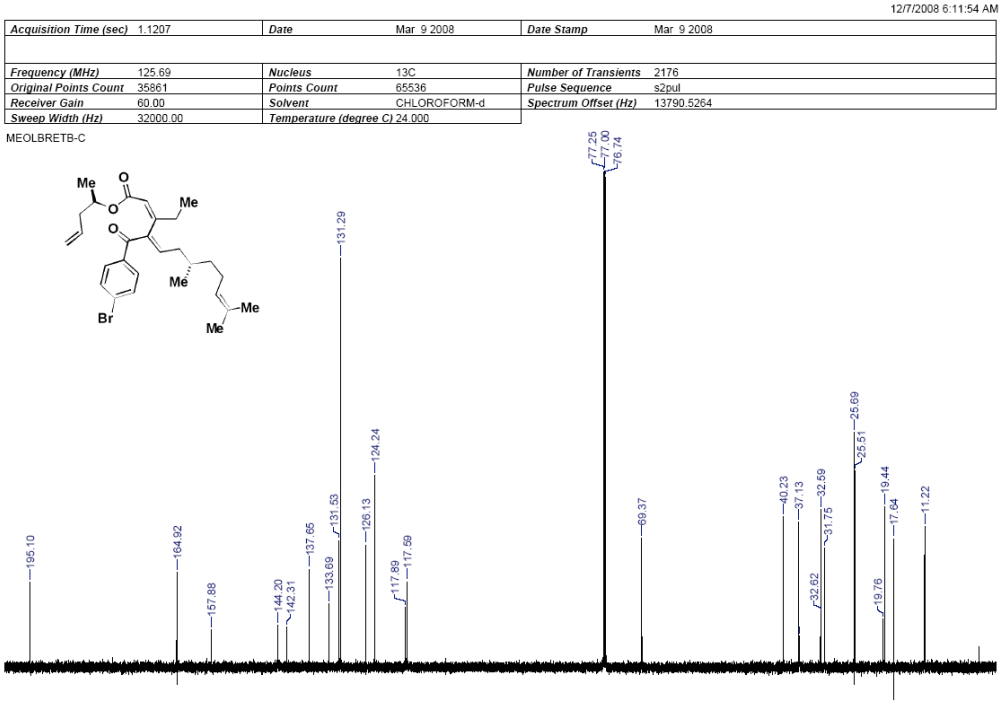
^{13}C NMR (75 MHz, $CDCl_3$) for compound **10**

Spectra. Spectral Data for

(*S*,2*Z*,4*E*)-((*R*)-pent-4-en-2-yl) 4-(4-bromobenzoyl)-3-ethyl-7,11-dimethyldodeca-2,4,10-trienoate (4jb).



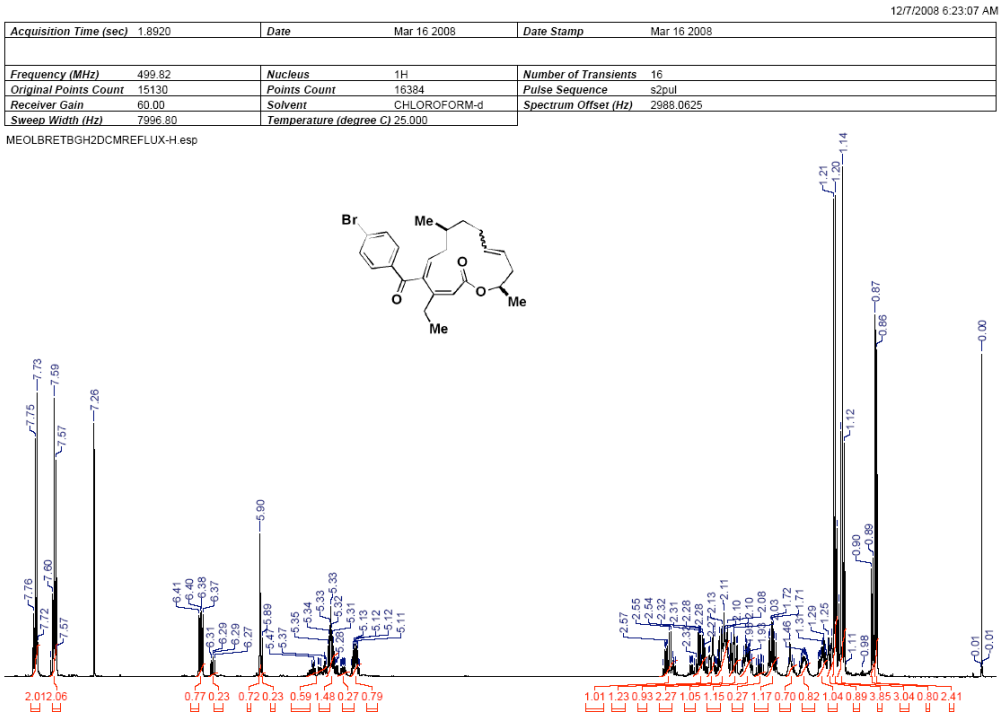
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4jb**



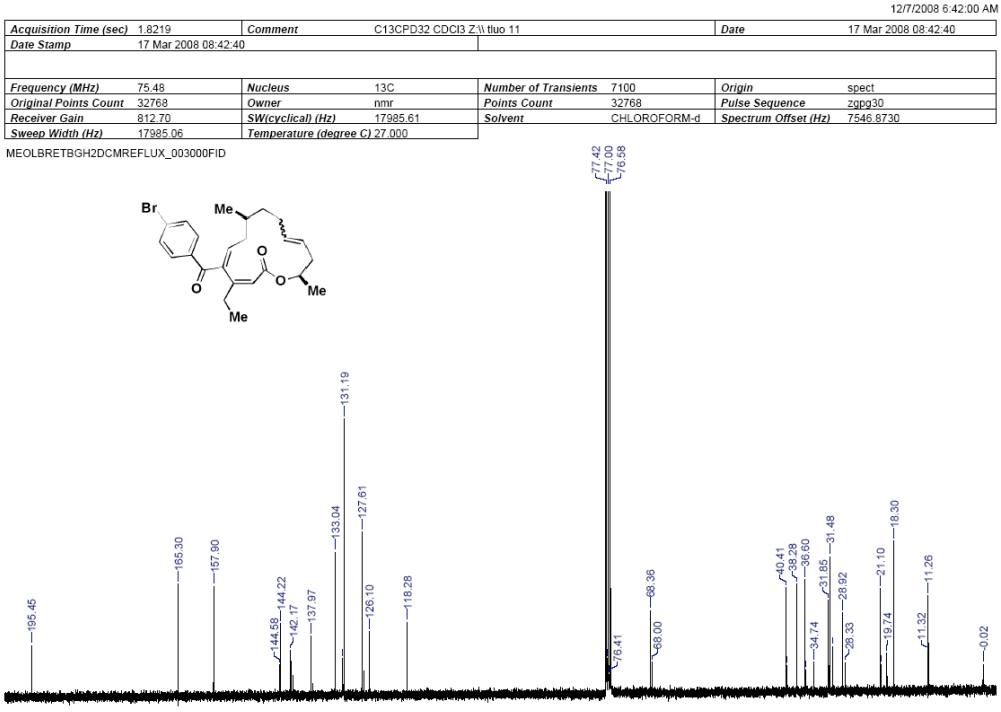
^{13}C NMR (126 MHz, $CDCl_3$) for compound **4jb**

Spectra. Spectral Data for

(3*Z*,5*E*,8*S*,14*R*)-5-(4-bromobenzoyl)-4-ethyl-8,14-dimethyloxacyclotetradeca-3,5,11-trien-2-one (5jb).



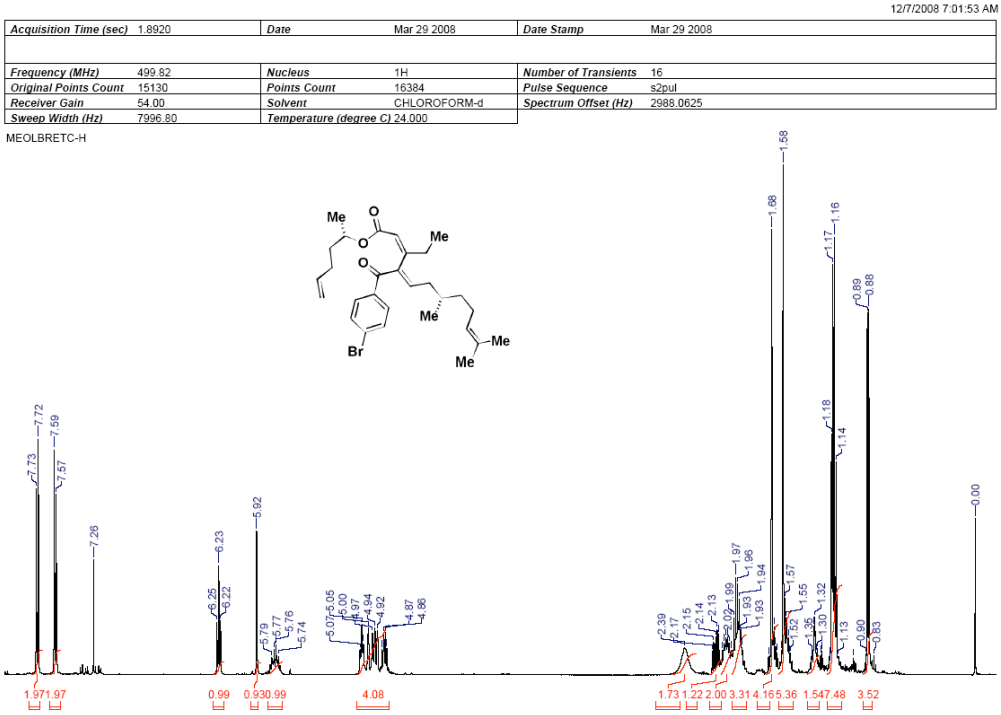
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5jb**



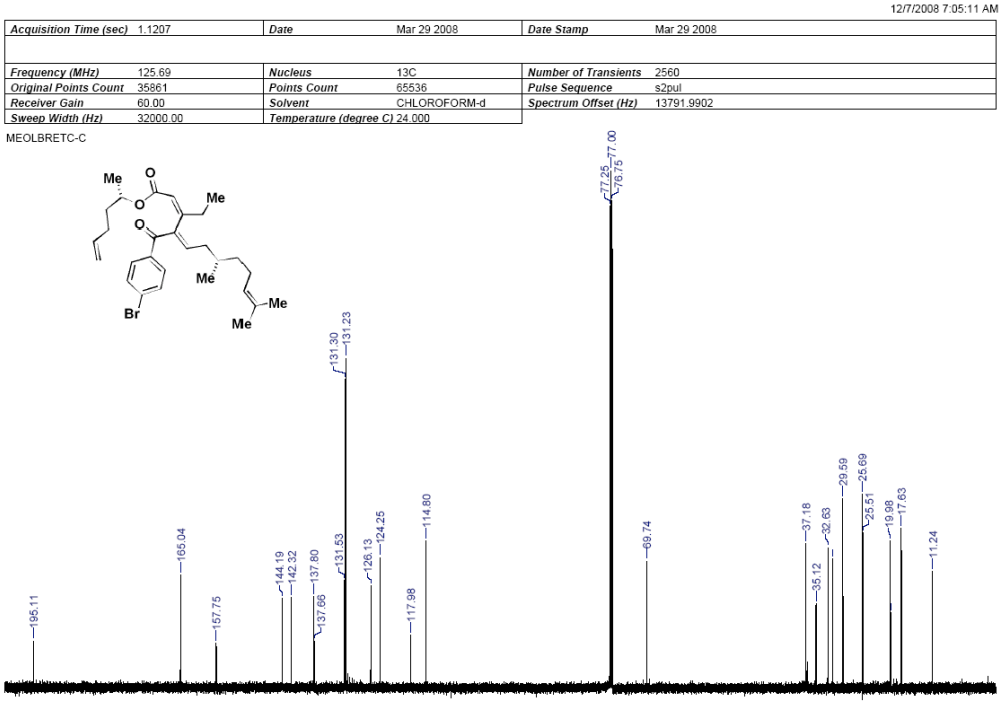
^{13}C NMR (126 MHz, $CDCl_3$) for compound **5jb**

Spectra. Spectral Data for

(*S*,2*Z*,4*E*)-((*S*)-hex-5-en-2-yl) 4-(4-bromobenzoyl)-3-ethyl-7,11-dimethyldodeca-2,4,10-trienoate (4jc).



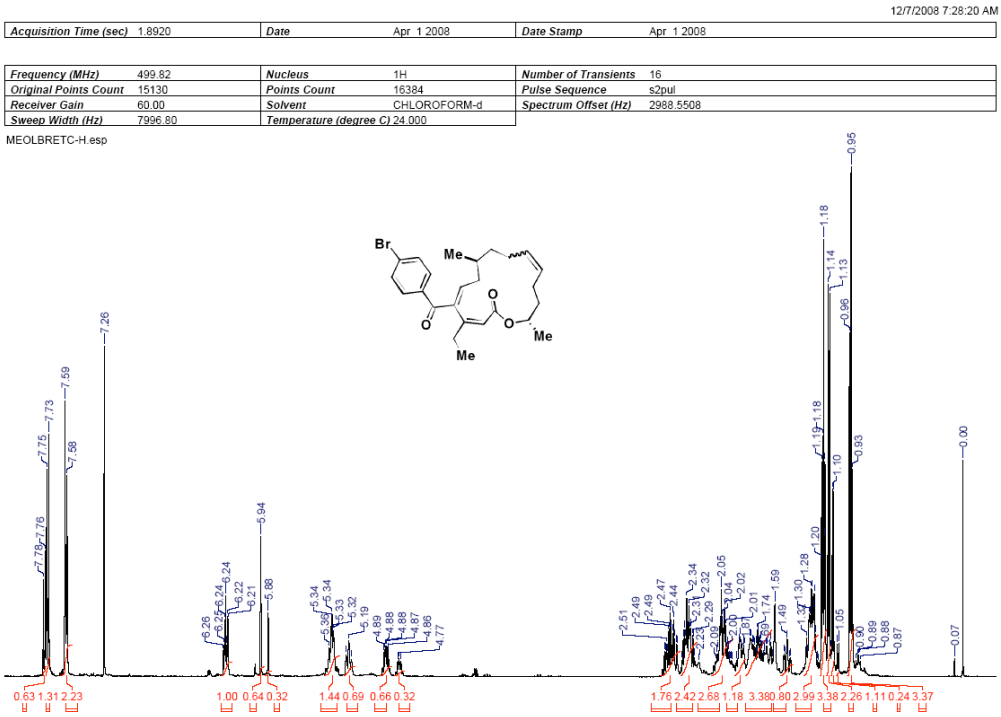
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4jc**



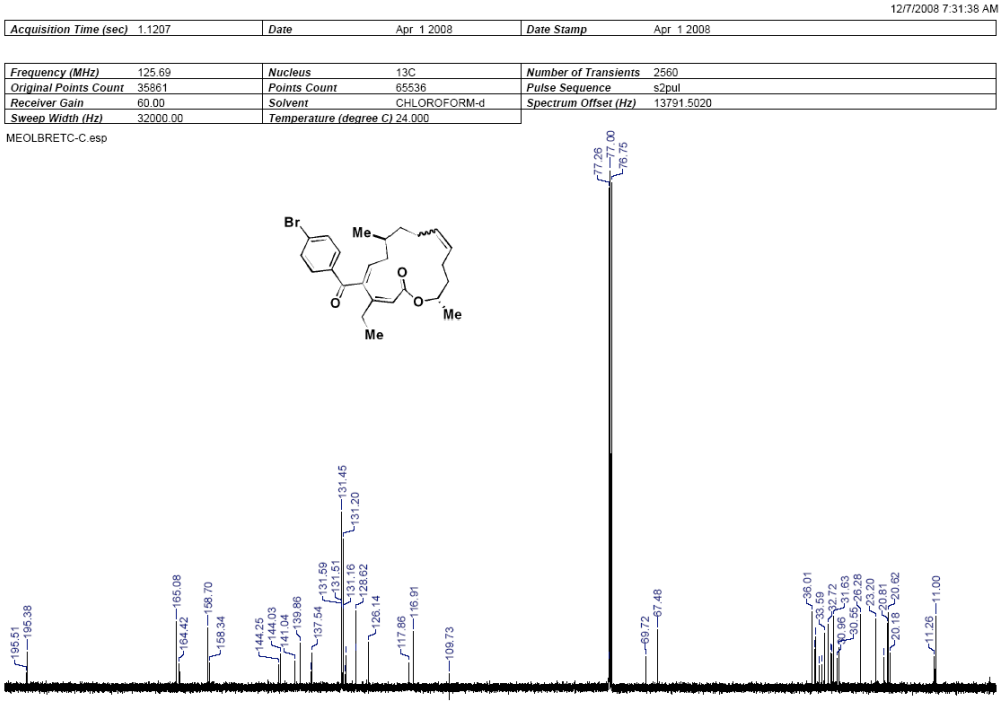
^{13}C NMR (126 MHz, $CDCl_3$) for compound **4jc**

Spectra. Spectral Data for

(3*Z*,5*E*,8*S*,15*S*)-5-(4-bromobenzoyl)-4-ethyl-8,15-dimethyloxacyclopentadeca-3,5,11-trien-2-one (5jc)

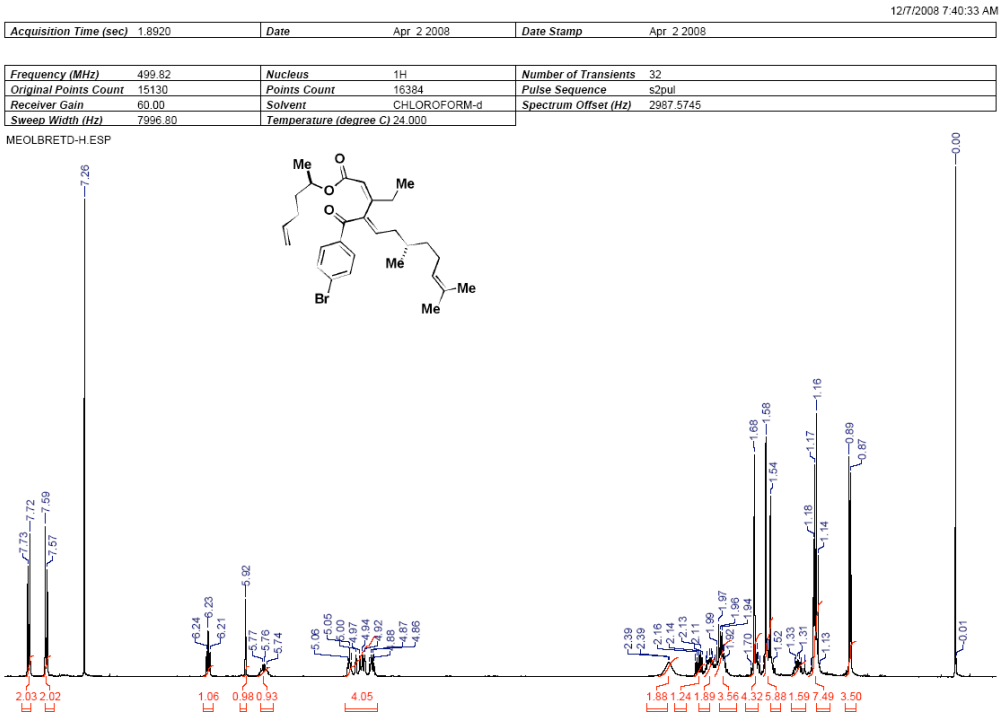


^{1}H NMR (500 MHz, $CDCl_3$) of compound **5jc**

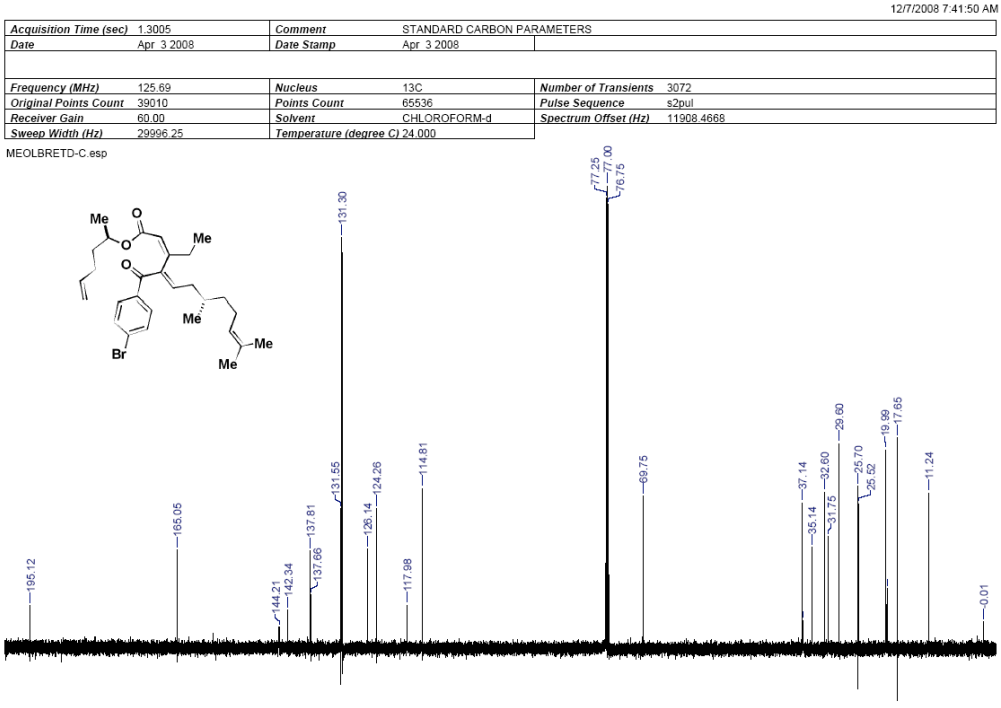


^{13}C NMR (126 MHz, $CDCl_3$) for compound **5jc**

Spectra. Spectral Data for **(*S*,2*Z*,4*E*)-((*R*)-hex-5-en-2-yl) 4-(4-bromobenzoyl)-3-ethyl-7,11-dimethyldodeca-2,4,10-trienoate (4jd).**



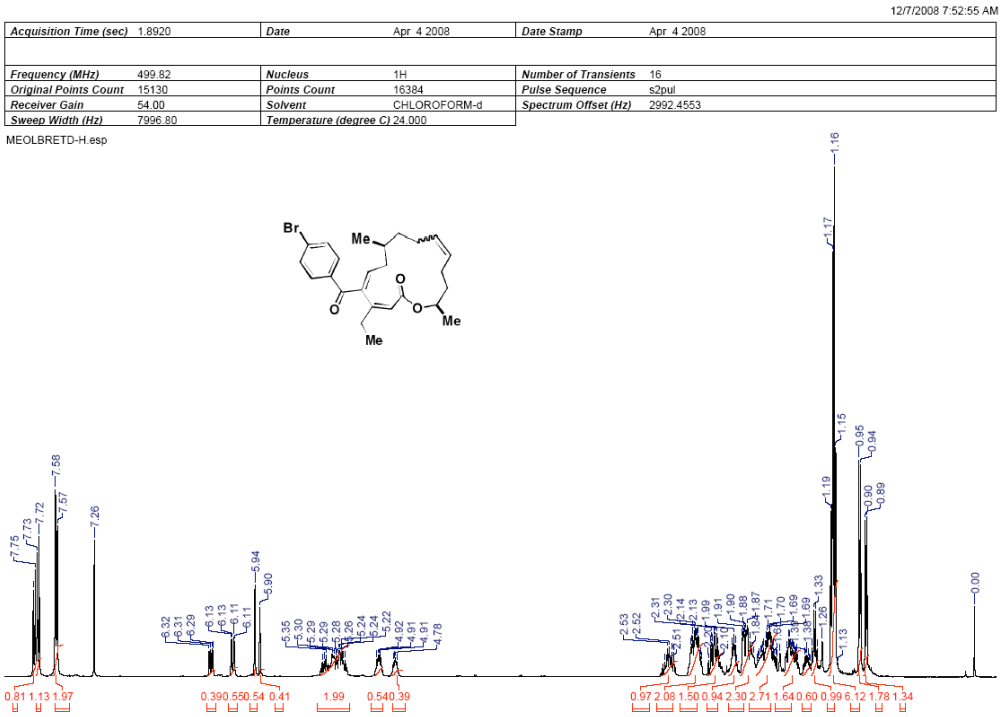
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4jd**



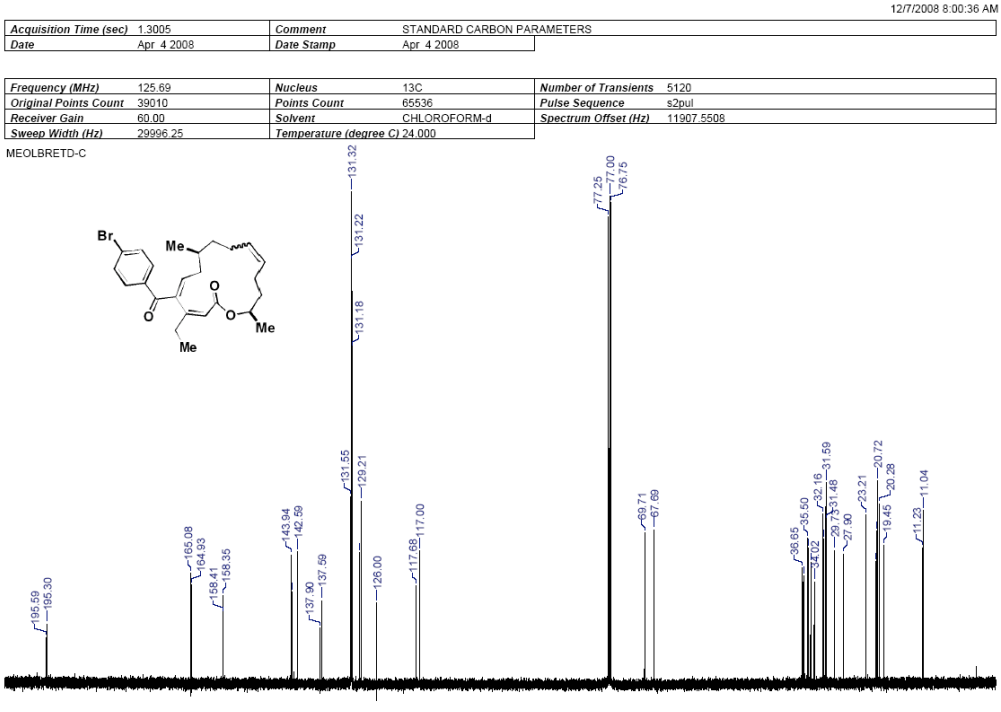
^{13}C NMR (126 MHz, $CDCl_3$) for compound **4jd**

Spectra. Spectral Data for

(3*Z*,5*E*,8*S*,15*R*)-5-(4-bromobenzoyl)-4-ethyl-8,15-dimethyloxacyclopentadeca-3,5,11-trien-2-one (5jd).



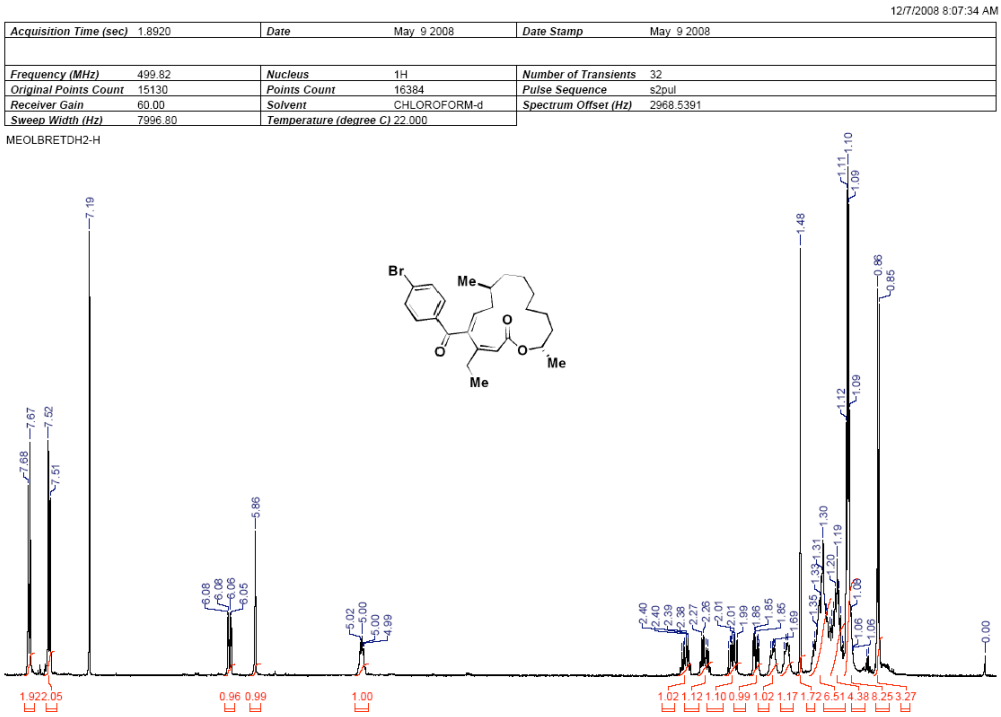
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5jd**



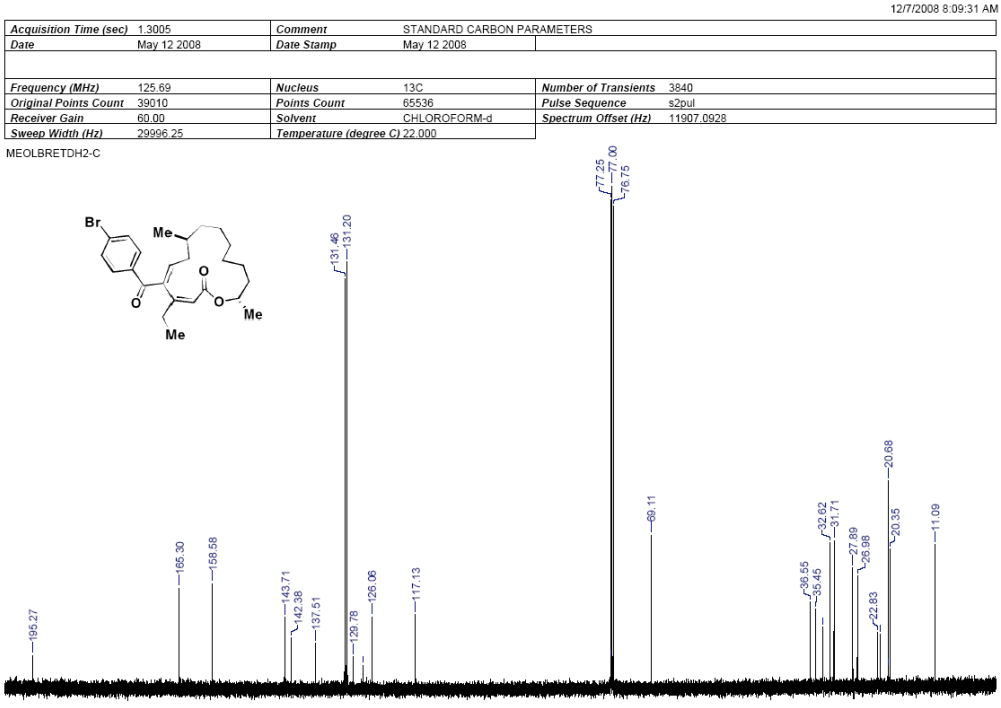
^{13}C NMR (126 MHz, $CDCl_3$) for compound **5jd**

Spectra. Spectral Data for

(3*Z*,5*E*,8*S*,15*S*)-5-(4-bromobenzoyl)-4-ethyl-8,15-dimethyloxacyclopentadeca-3,5-dien-2-one (11).

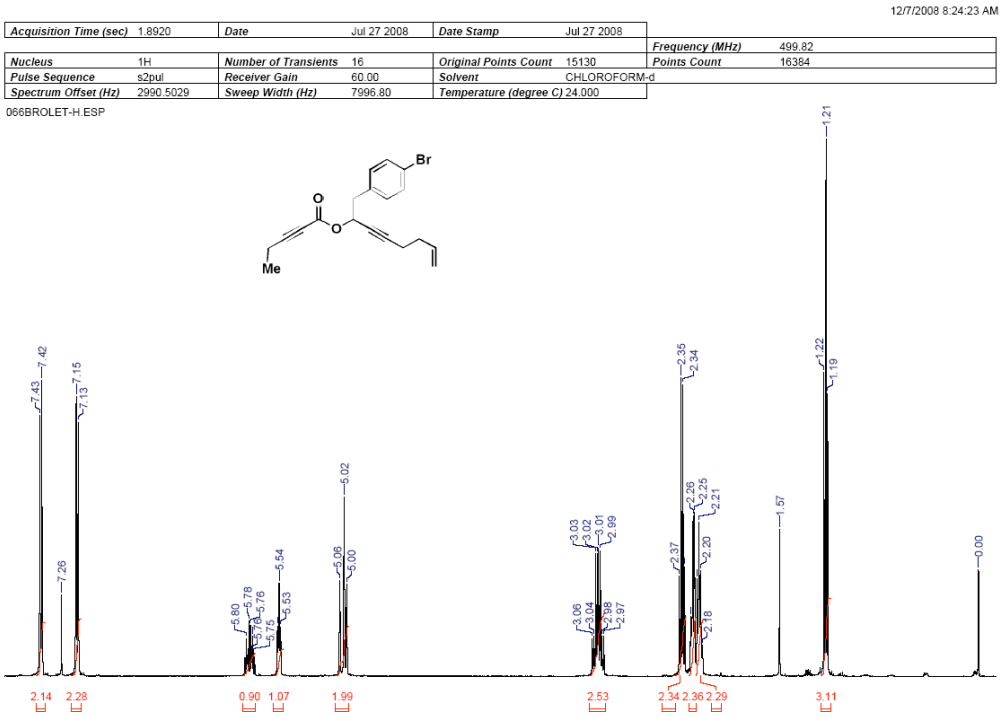


^{1}H NMR (500 MHz, $CDCl_3$) of compound **11**

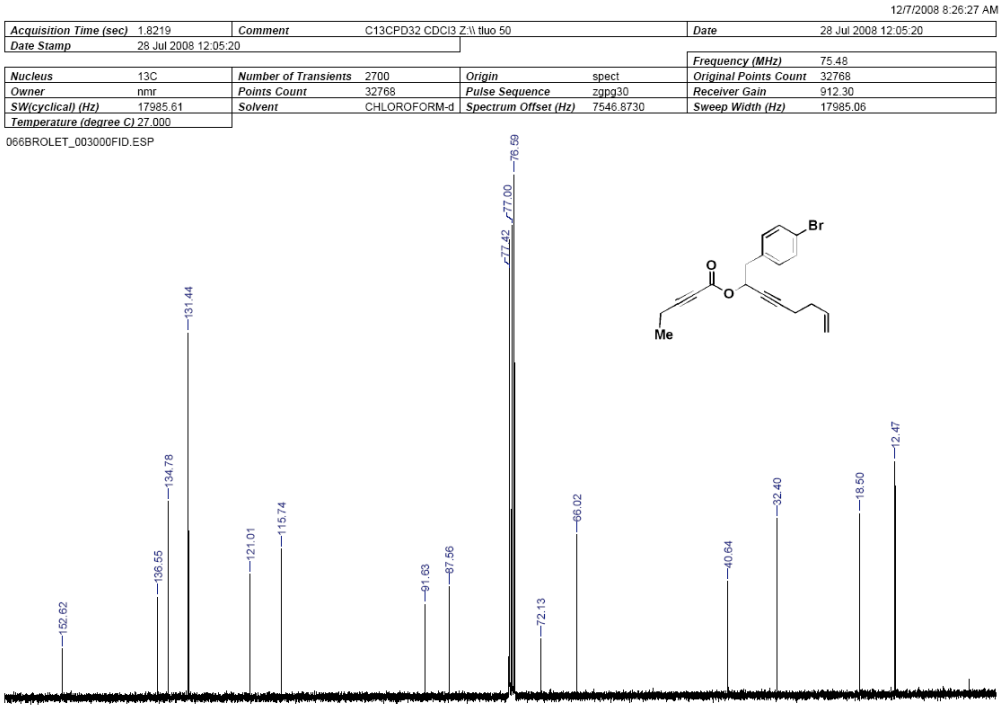


^{13}C NMR (126 MHz, $CDCl_3$) for compound **11**

Spectra. Spectral Data for **1-(4-bromophenyl)oct-7-en-3-yn-2-yl pent-2-ynoate (1k).**

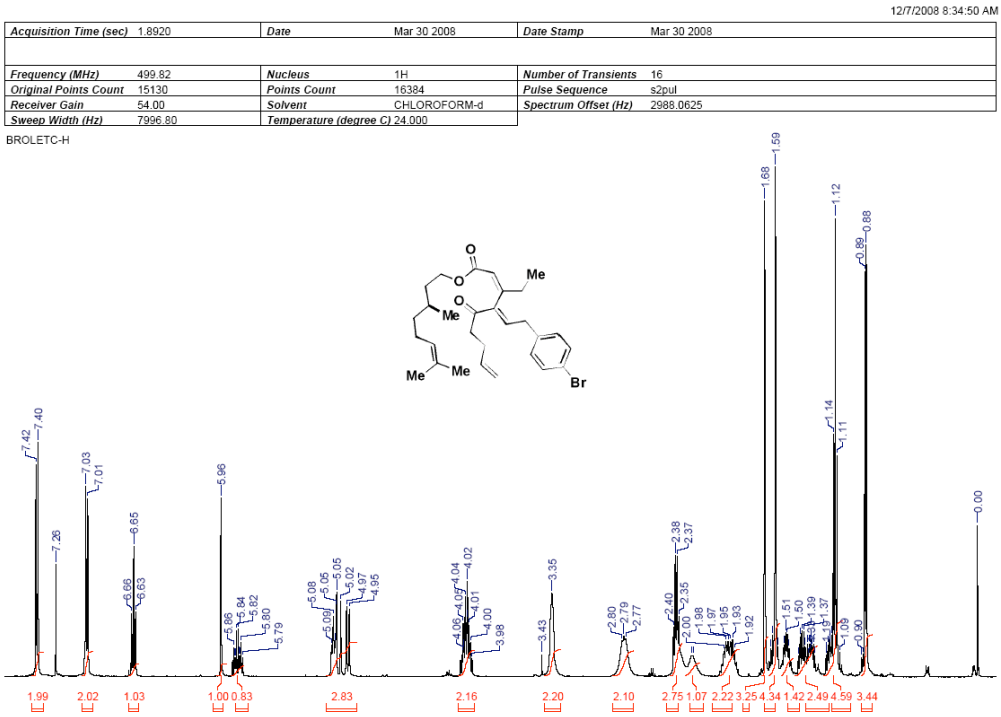


^{1}H NMR (500 MHz, $CDCl_3$) of compound **1k**

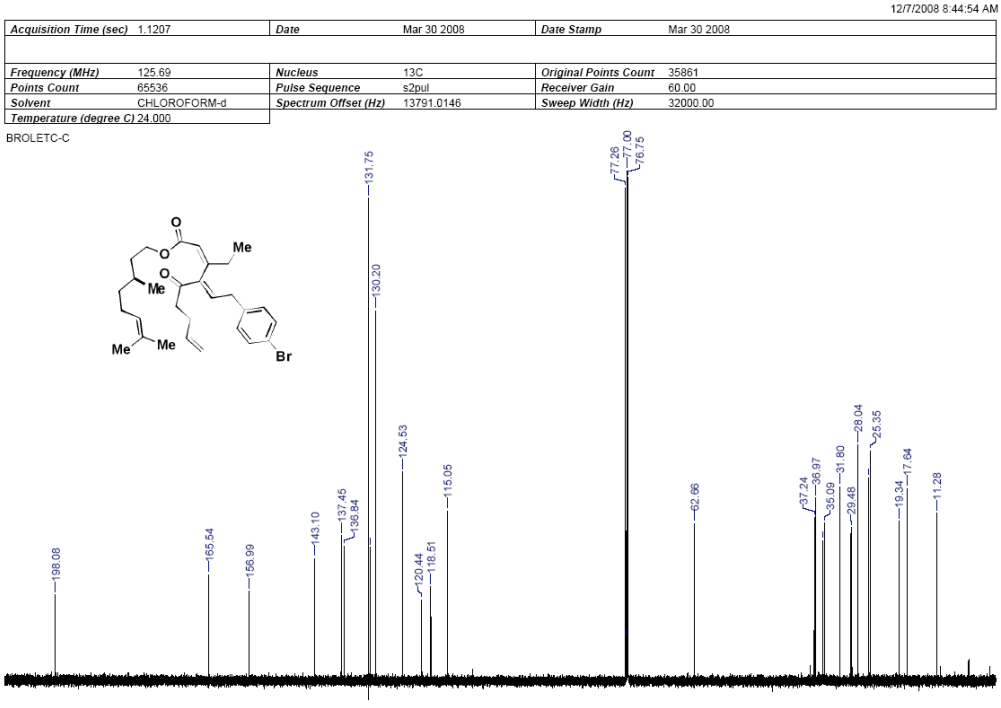


^{13}C NMR (126 MHz, $CDCl_3$) for compound **1k**

Spectra. Spectral Data for **(2*Z*,4*E*)-((*S*)-3,7-dimethyloct-6-enyl) 4-(2-(4-bromophenyl)ethylidene)-3-ethyl-5-oxonona-2,8-dienoate (4k).**



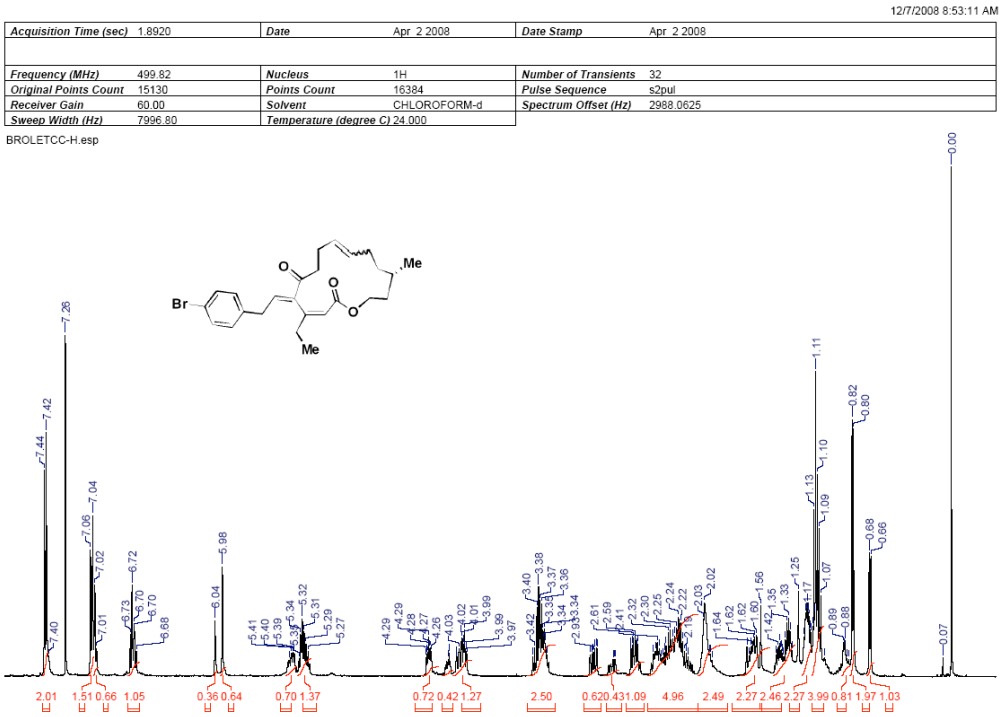
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4k**



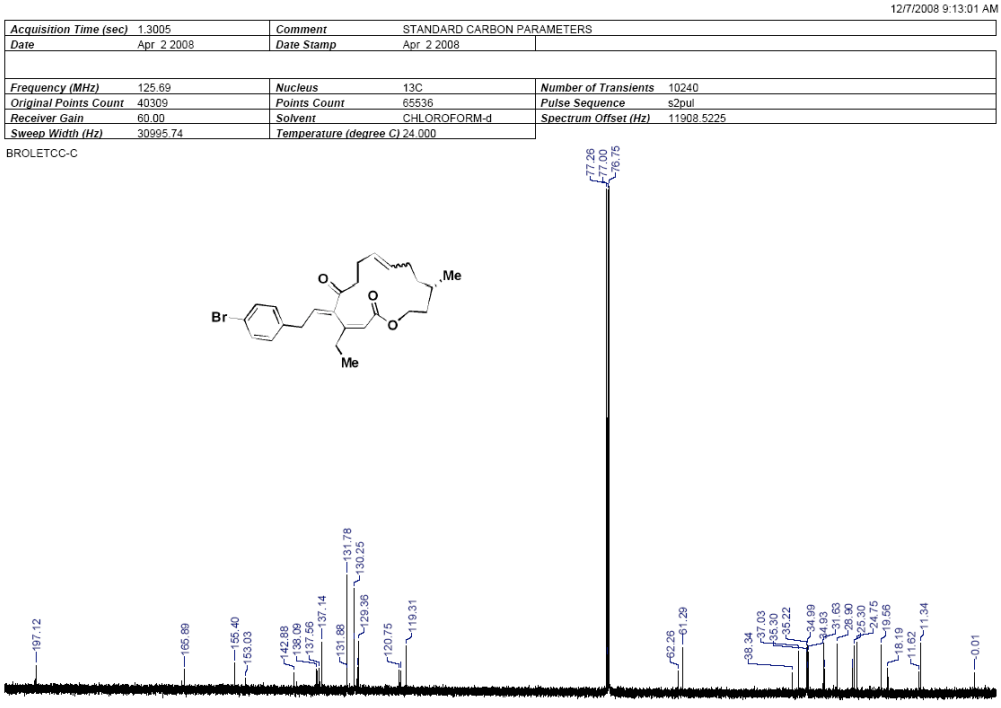
^{13}C NMR (126 MHz, $CDCl_3$) for compound **4k**

Spectra. Spectral Data for

(*S*,3*Z*,5*E*)-5-(2-(4-bromophenyl)ethylidene)-4-ethyl-13-methyloxacyclopentadeca-3,9-diene-2,6-dione (5k).



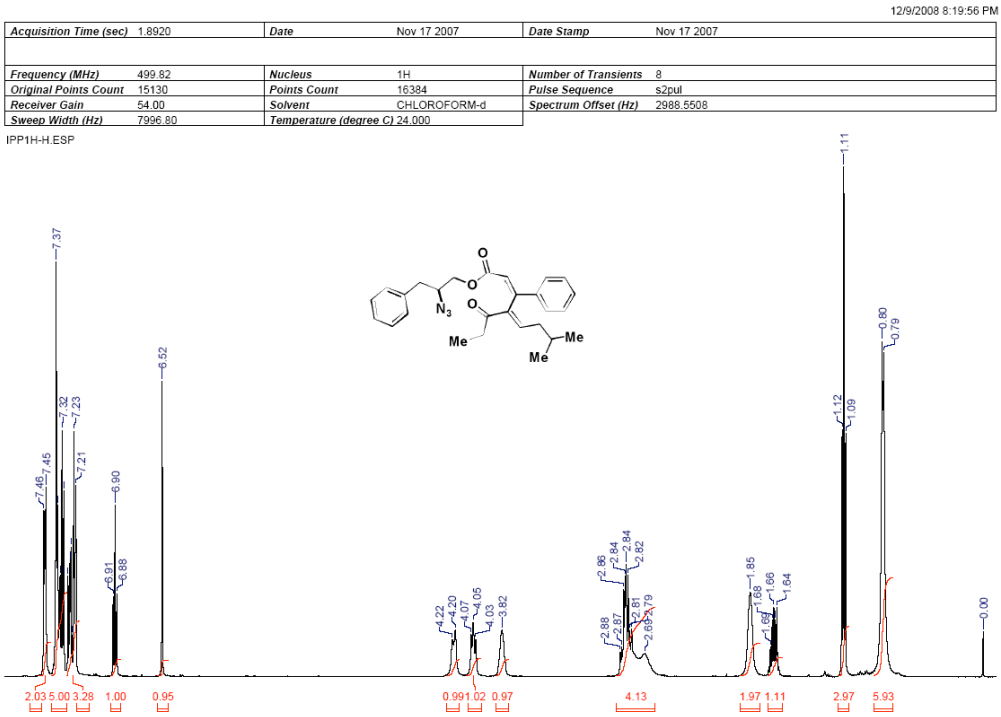
^{1}H NMR (500 MHz, $CDCl_3$) of compound **5k**



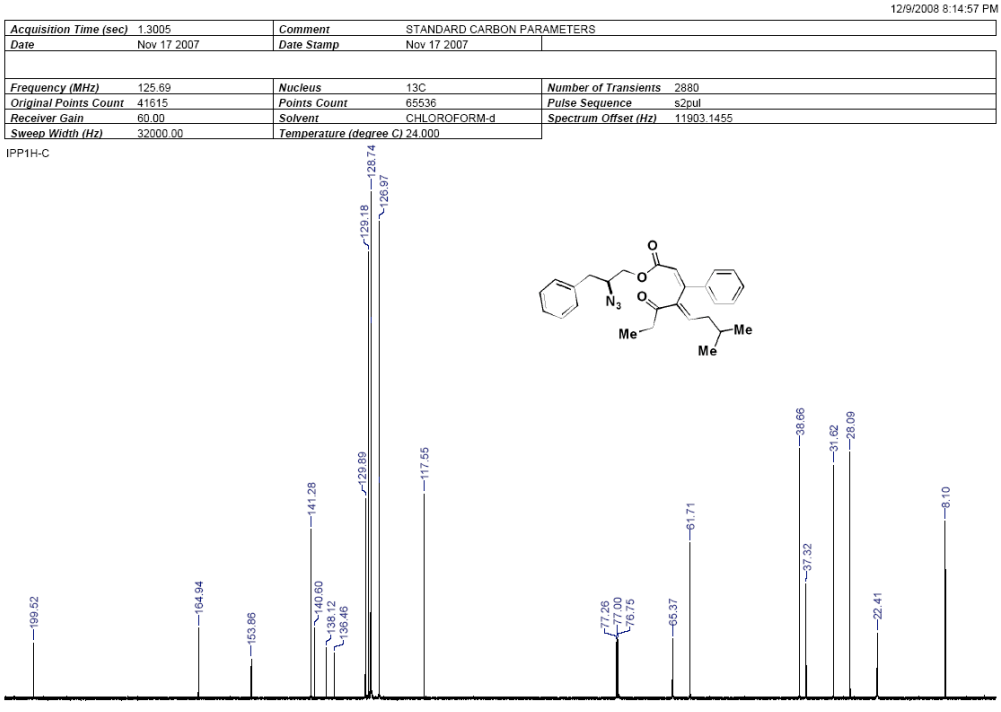
^{13}C NMR (126 MHz, $CDCl_3$) for compound **5k**

Spectra. Spectral Data for

(2*Z*,4*E*)-((*S*)-2-azido-3-phenylpropyl) 7-methyl-3-phenyl-4-propionylocta-2,4-dienoate (4bc).



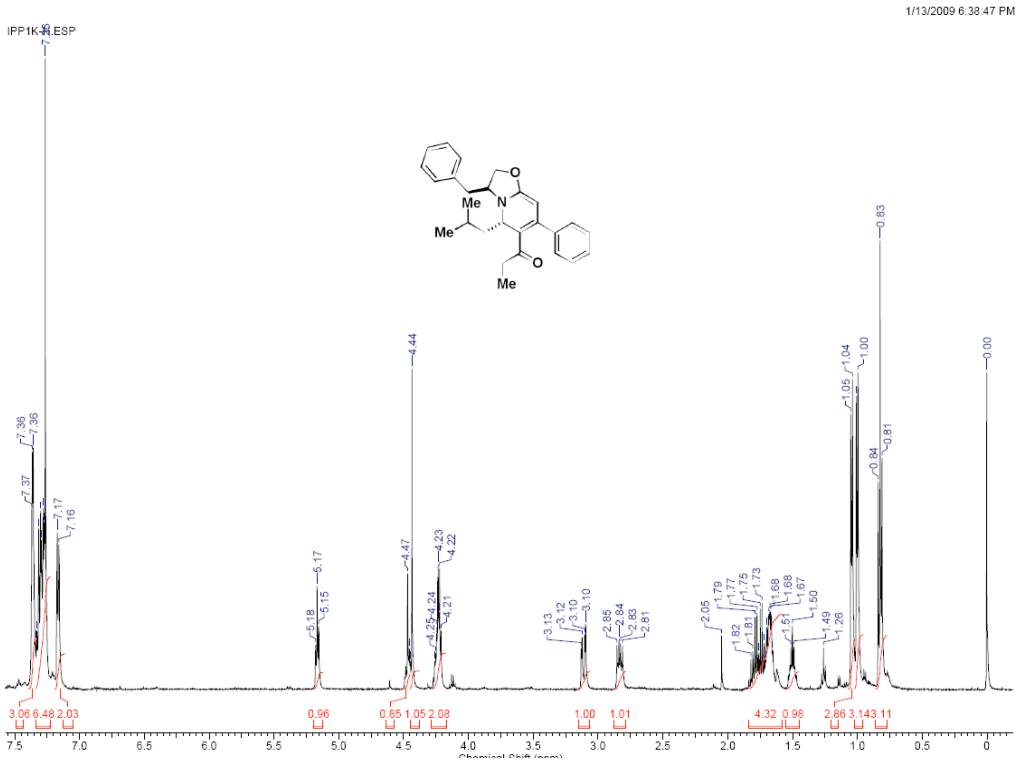
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4bc**



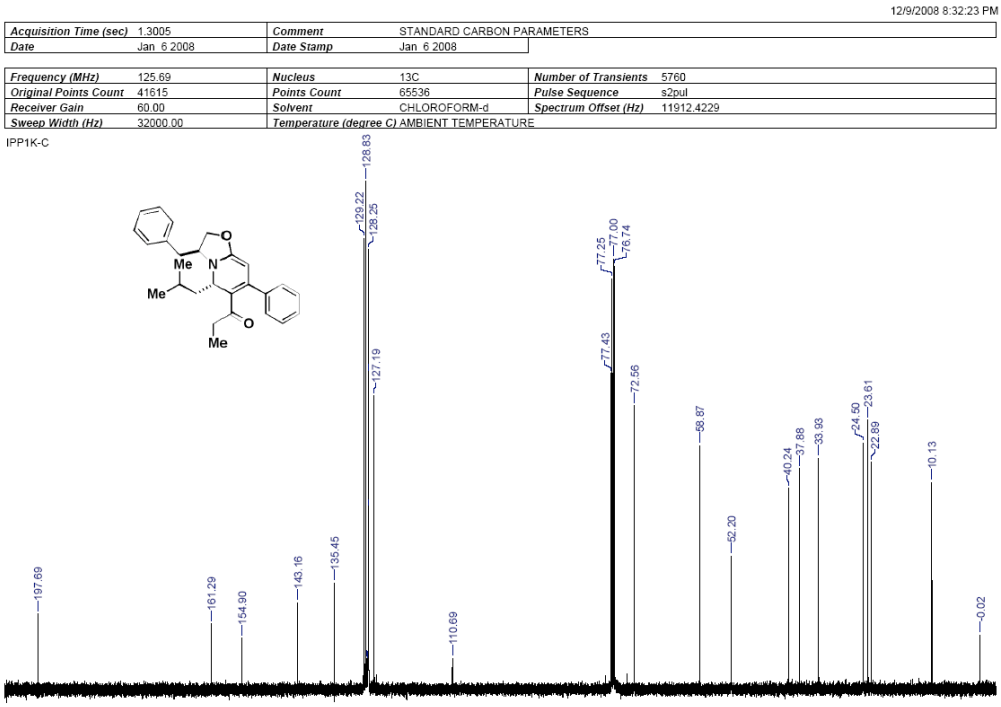
^{13}C NMR (126 MHz, $CDCl_3$) for compound **4bc**

Spectra. Spectral Data for

1-((3*S*,5*S*)-3-benzyl-5-isobutyl-7-phenyl-3,5-dihydro-2*H*-oxazolo[3,2-*a*]pyridin-6-yl)propan-1-one (13b).



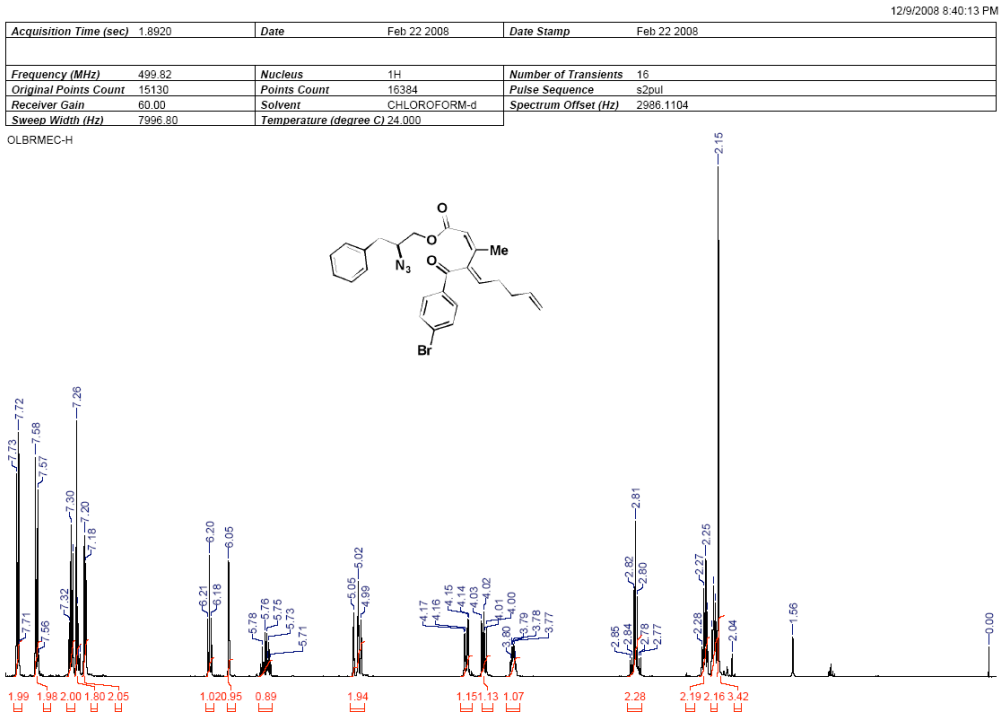
^{1}H NMR (500 MHz, $CDCl_3$) of compound **13b**



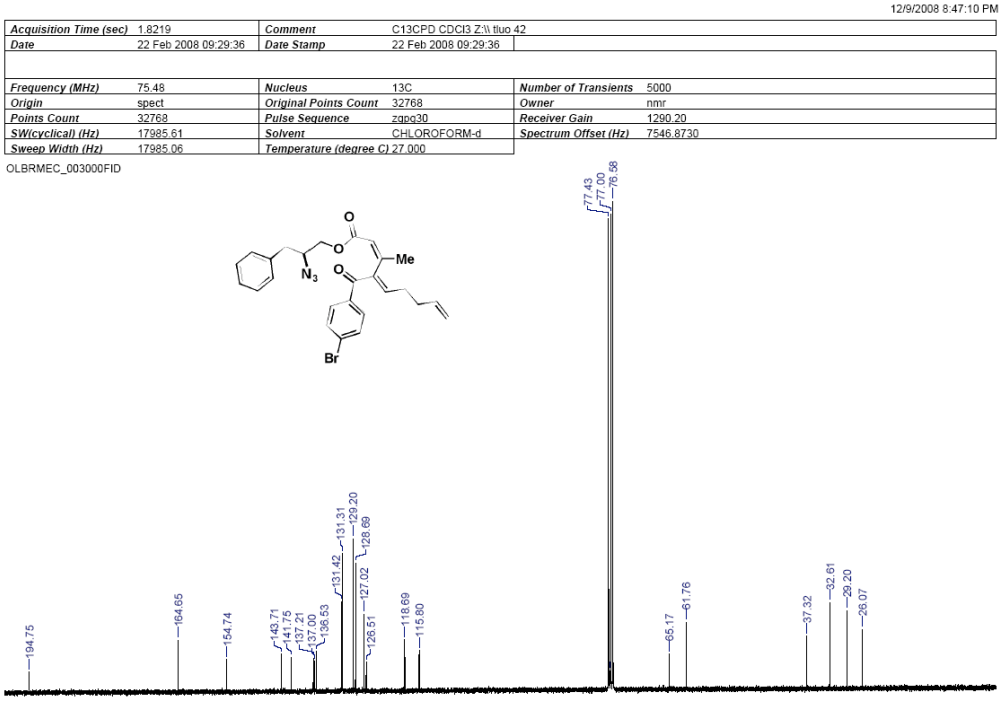
^{13}C NMR (126 MHz, $CDCl_3$) for compound **13b**

Spectra. Spectral Data for

(2*Z*,4*E*)-((*S*)-2-azido-3-phenylpropyl) 4-(4-bromobenzoyl)-3-methylnona-2,4,8-trienoate (4ic).

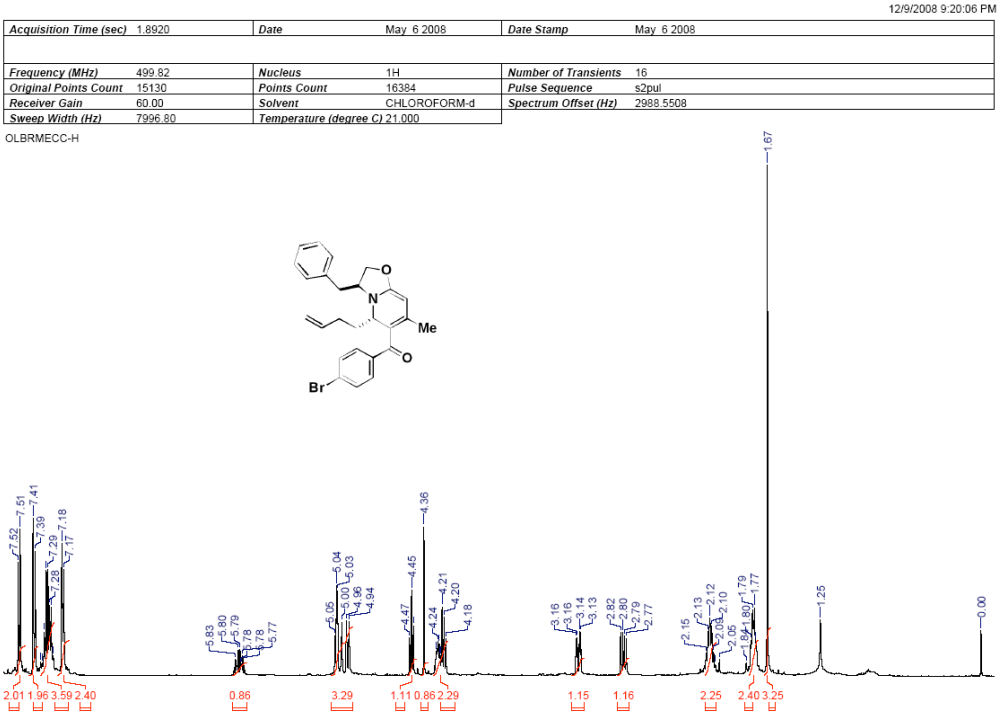


^{1}H NMR (500 MHz, $CDCl_3$) of compound **4ic**

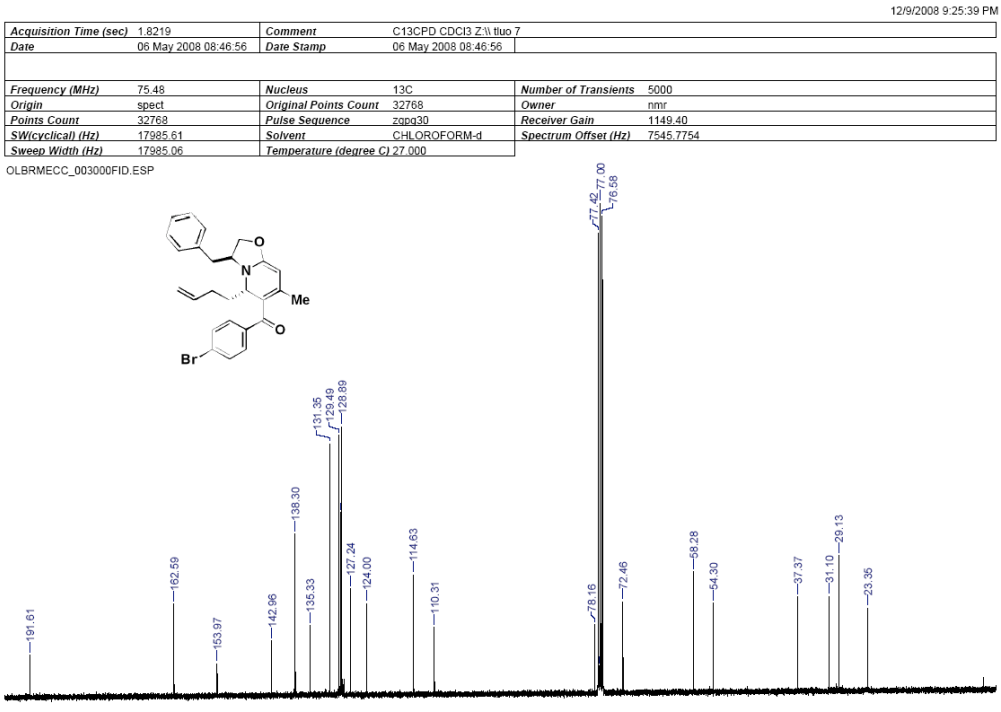


^{13}C NMR (75 MHz, $CDCl_3$) for compound **4ic**

Spectra. Spectral Data for **((3*S*,5*S*)-3-benzyl-5-(but-3-enyl)-7-methyl-3,5-dihydro-2*H*-oxazolo[3,2-*a*]pyridin-6-yl)(4-bromophenyl)methanone (13ic).**



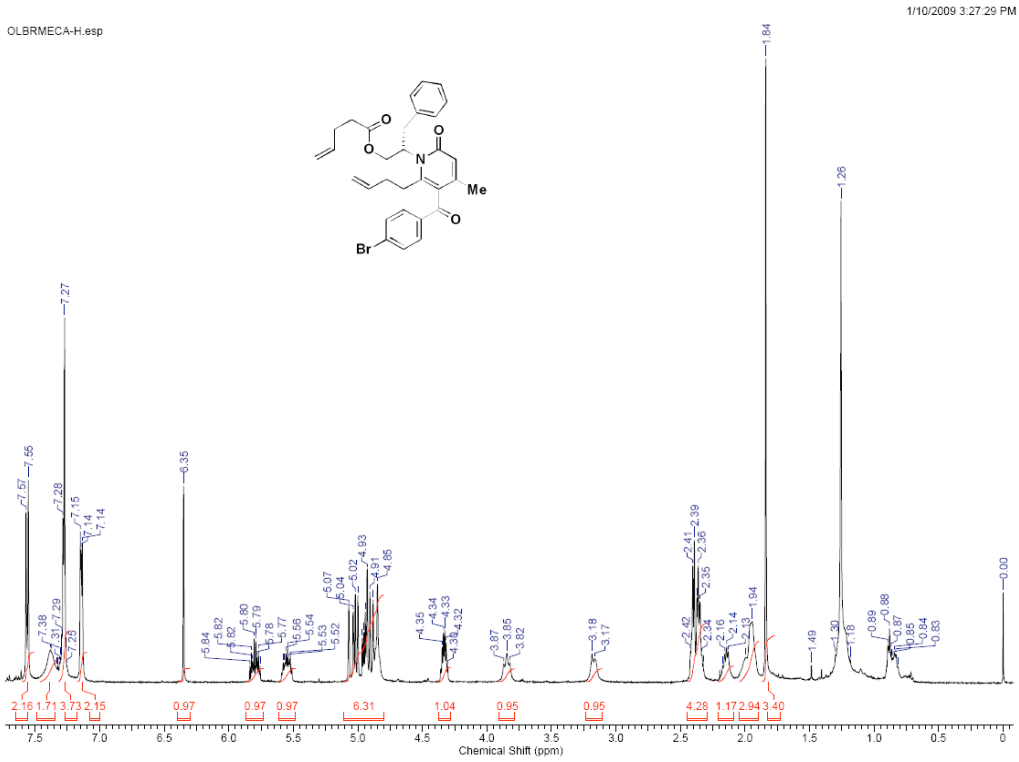
^{1}H NMR (500 MHz, $CDCl_3$) of compound **13ic**



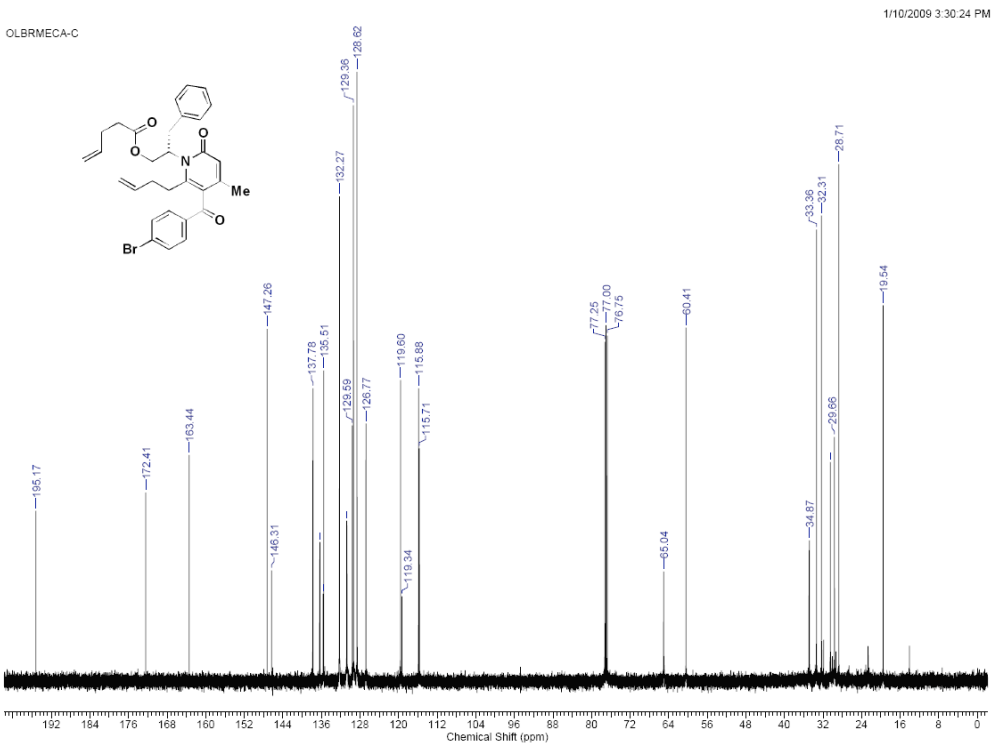
^{13}C NMR (126 MHz, $CDCl_3$) for compound **13ic**

Spectra. Spectral Data for

(*S*)-2-(5-(4-bromobenzoyl)-6-(but-3-enyl)-4-methyl-2-oxopyridin-1(2*H*)-yl)-3-phenylpropyl pent-4-enoate(14ica).

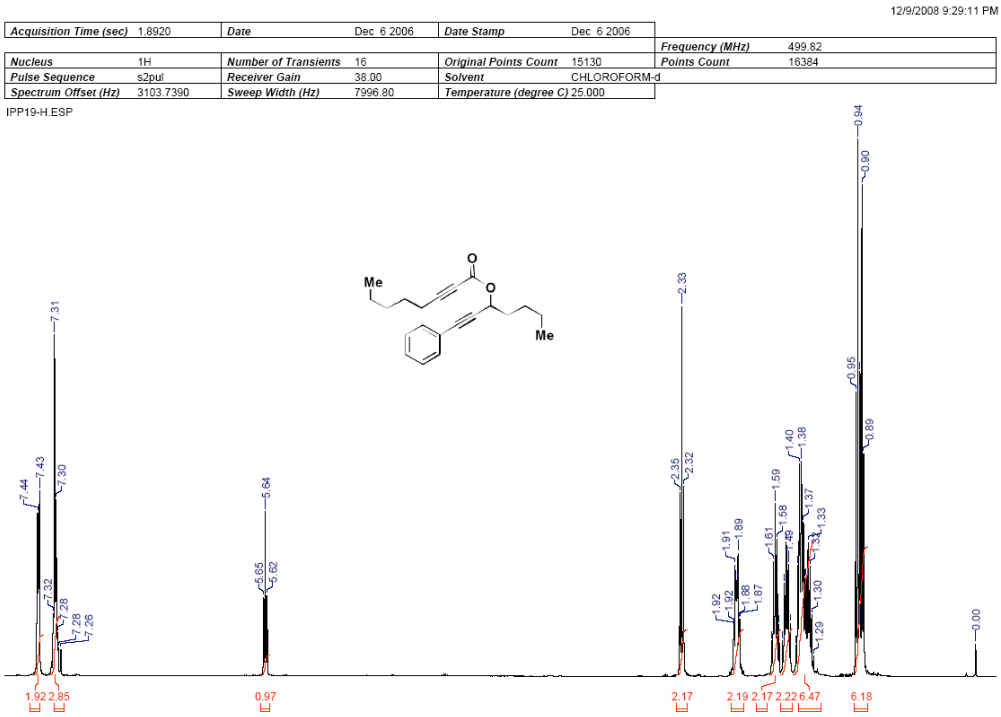


^{1}H NMR (500 MHz, $CDCl_3$) of compound **14ica**

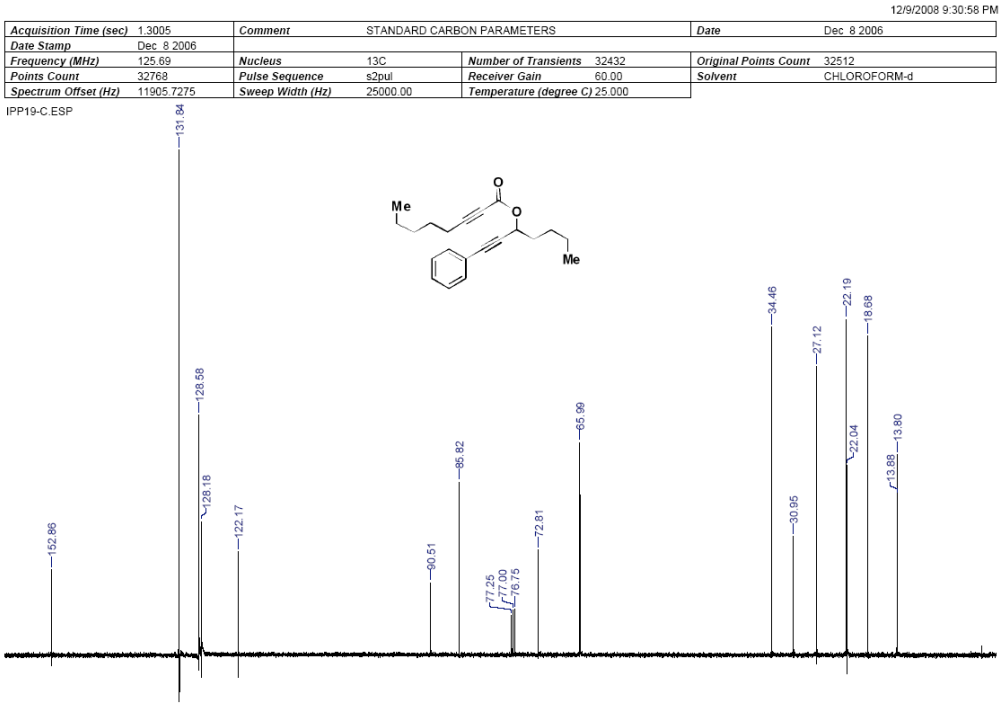


^{13}C NMR (126 MHz, $CDCl_3$) for compound **14ica**

Spectra. Spectral Data for **1-phenylhept-1-yn-3-yl oct-2-ynoate (1l)**.

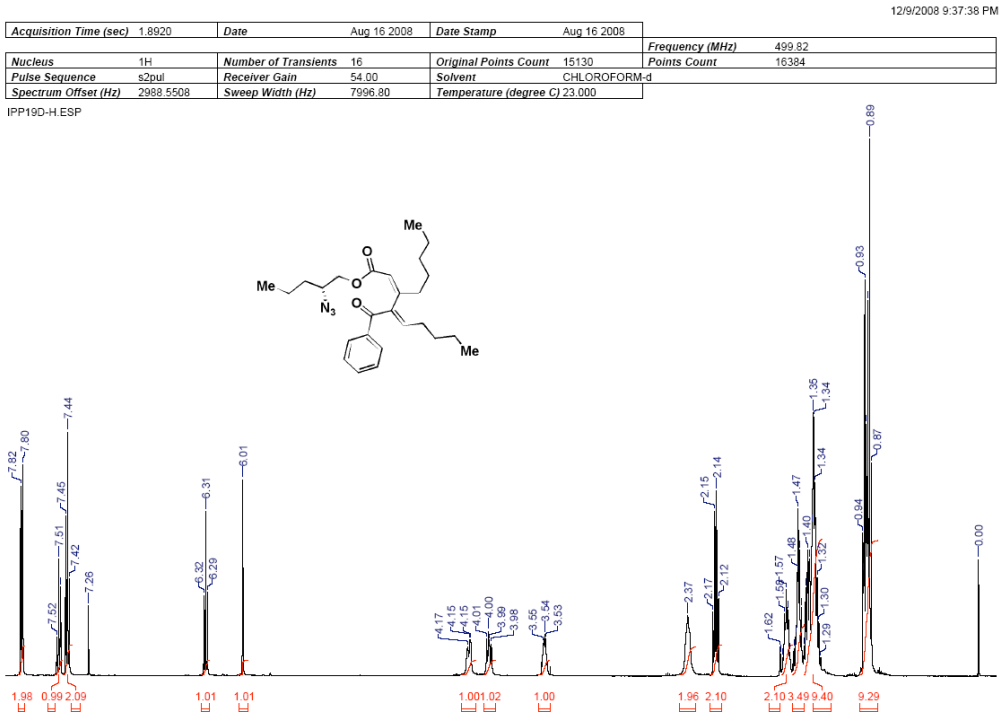


^{1}H NMR (500 MHz, $CDCl_3$) of compound **1l**

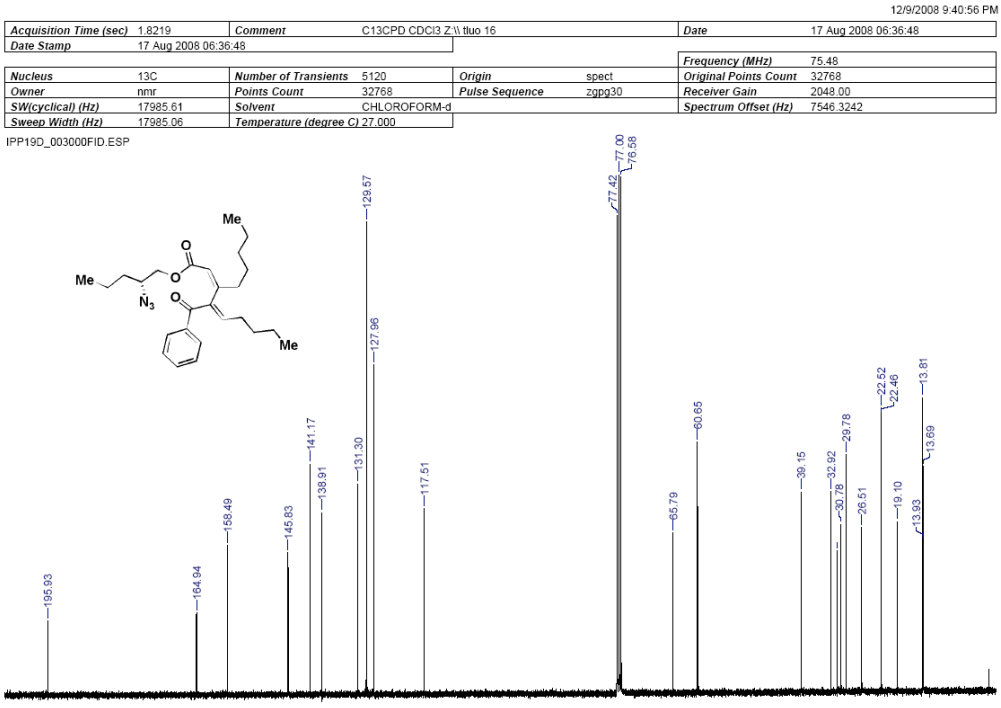


^{13}C NMR (75 MHz, $CDCl_3$) for compound **1l**

Spectra. Spectral Data for **(2*Z*,4*E*)-((*R*)-2-azidopentyl) 4-benzoyl-3-pentylnona-2,4-dienoate (4l)**.



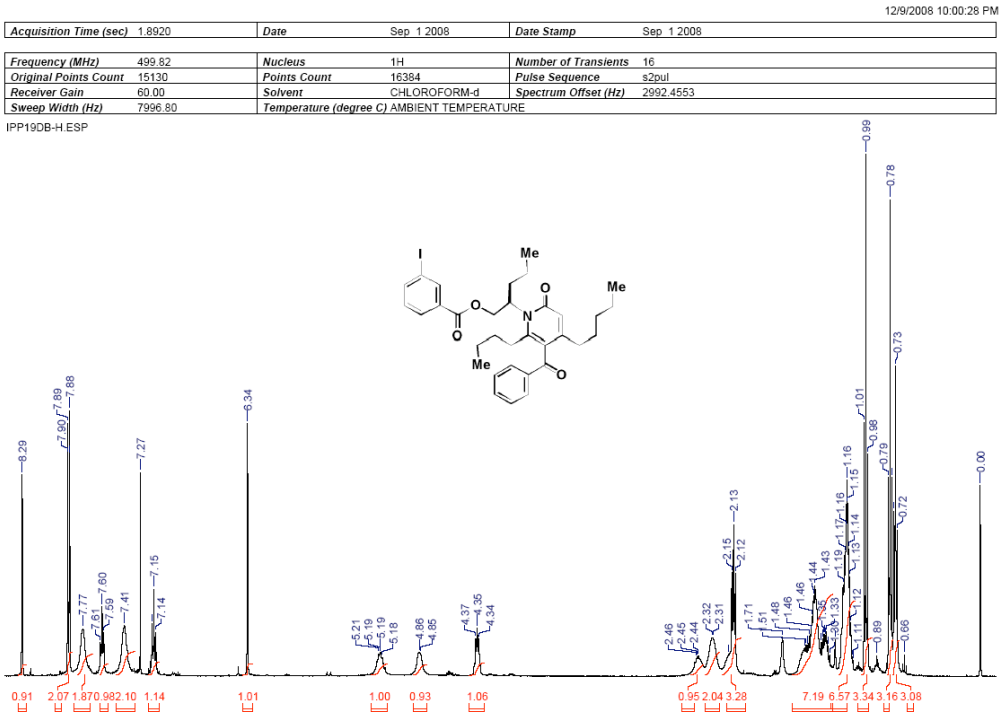
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4l**



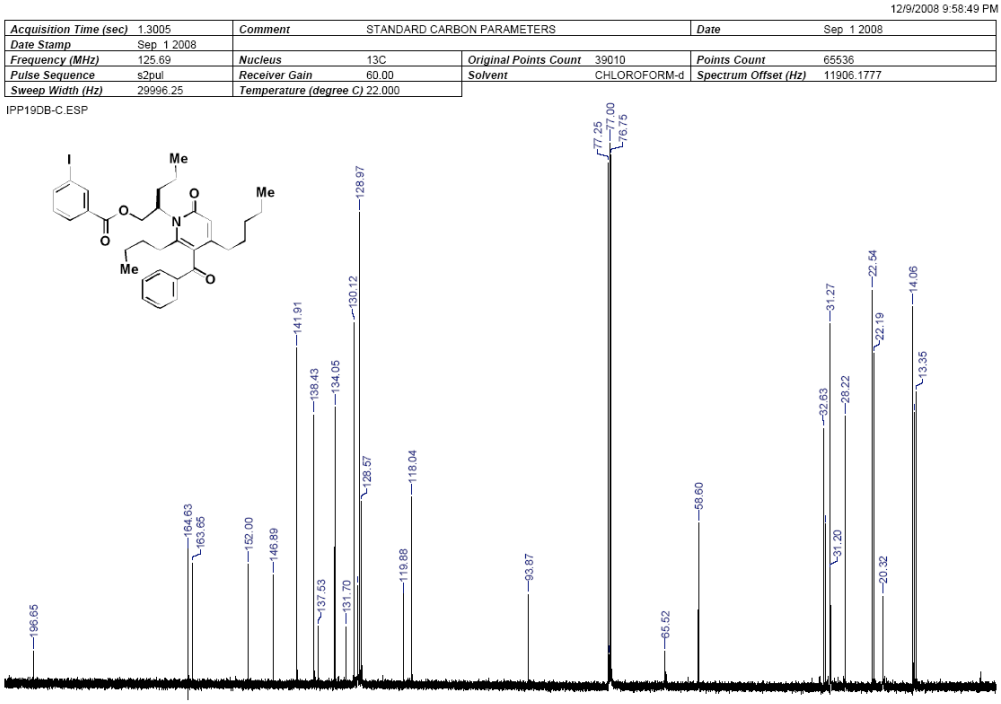
^{13}C NMR (75 MHz, $CDCl_3$) for compound **4l**

Spectra. Spectral Data for

(*R*)-2-(5-benzoyl-6-butyl-2-oxo-4-pentylpyridin-1(2*H*)-yl)pentyl 3-iodobenzoate (14l).



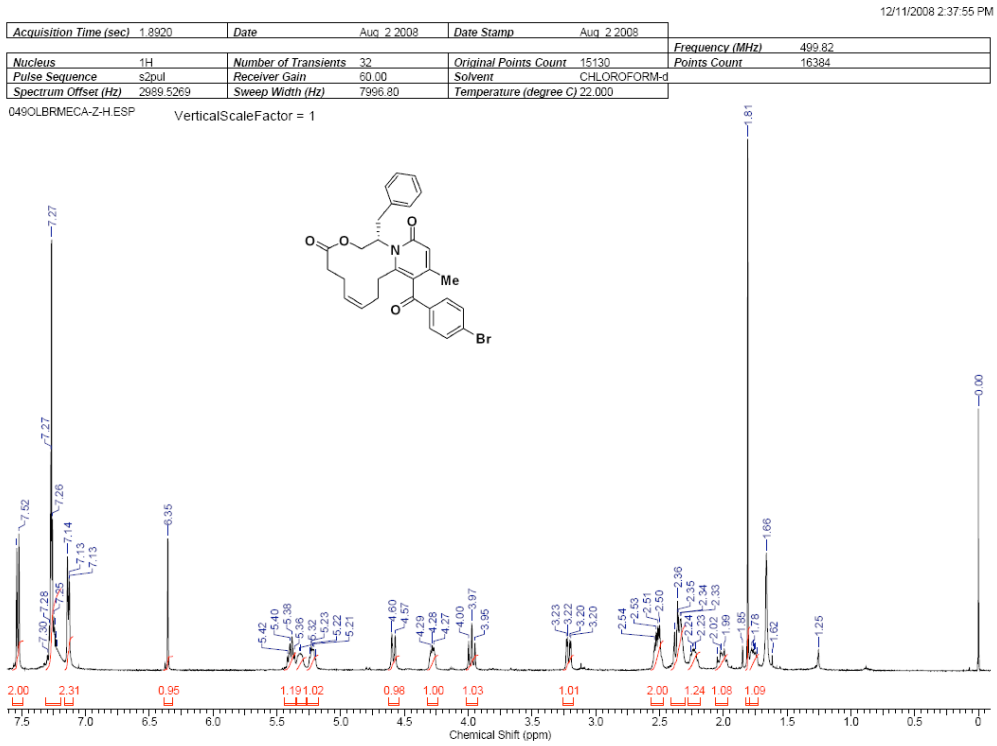
^{1}H NMR (500 MHz, $CDCl_3$) of compound **14l**



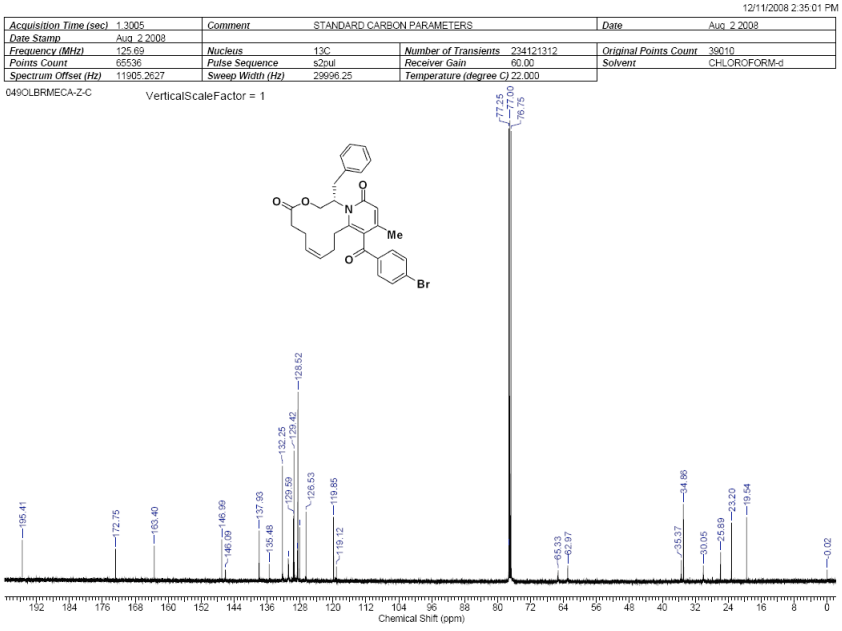
^{13}C NMR (126 MHz, $CDCl_3$) for compound **14l**

Spectra. Spectral Data for

(*S,Z*)-1-benzyl-11-(4-bromobenzoyl)-12-methyl-1,2,5,6,9,10-hexahydropyrido[1,2-*d*][1,4]oxaazacyclododecine-4,14-dione (15ica-Z).



^{1}H NMR (500 MHz, $CDCl_3$) of compound **15ica-Z**



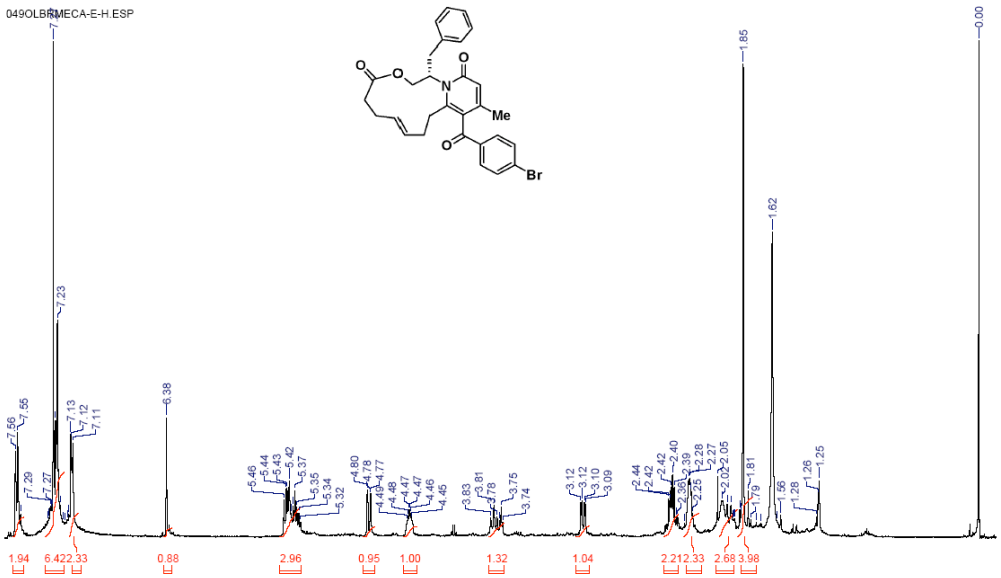
^{13}C NMR (126 MHz, $CDCl_3$) for compound **15ica-Z**

Spectra. Spectral Data for

(*S,E*)-1-benzyl-11-(4-bromobenzoyl)-12-methyl-1,2,5,6,9,10-hexahydropyrido[1,2-*d*][1,4]oxaazacyclododecine-4,14-dione (15ica-E)

12/11/2008 7:33:03 PM

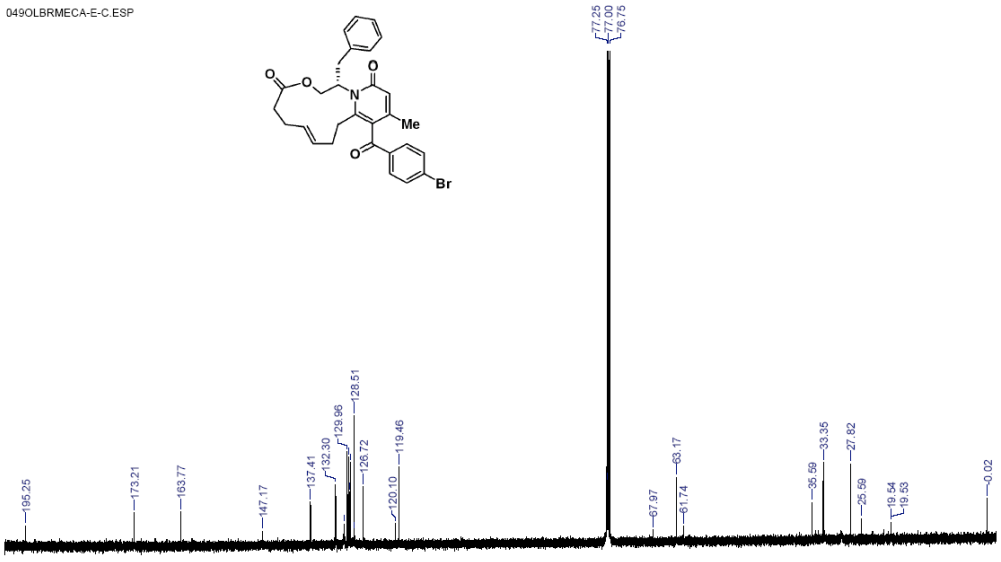
Acquisition Time (sec)	1.8920	*Date*	Jul 26 2008	*Date Stamp*	Jul 26 2008
Frequency (MHz)	499.82	*Nucleus*	1H	*Number of Transients*	32
Original Points Count	15130	*Points Count*	16384	*Pulse Sequence*	s2pul
Receiver Gain	60.00	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	2992.9434
Sweep Width (Hz)	7996.80	*Temperature (degree C)*	AMBIENT TEMPERATURE		



^{1}H NMR (500 MHz, $CDCl_3$) of compound **15ica-E**

12/11/2008 7:42:30 PM

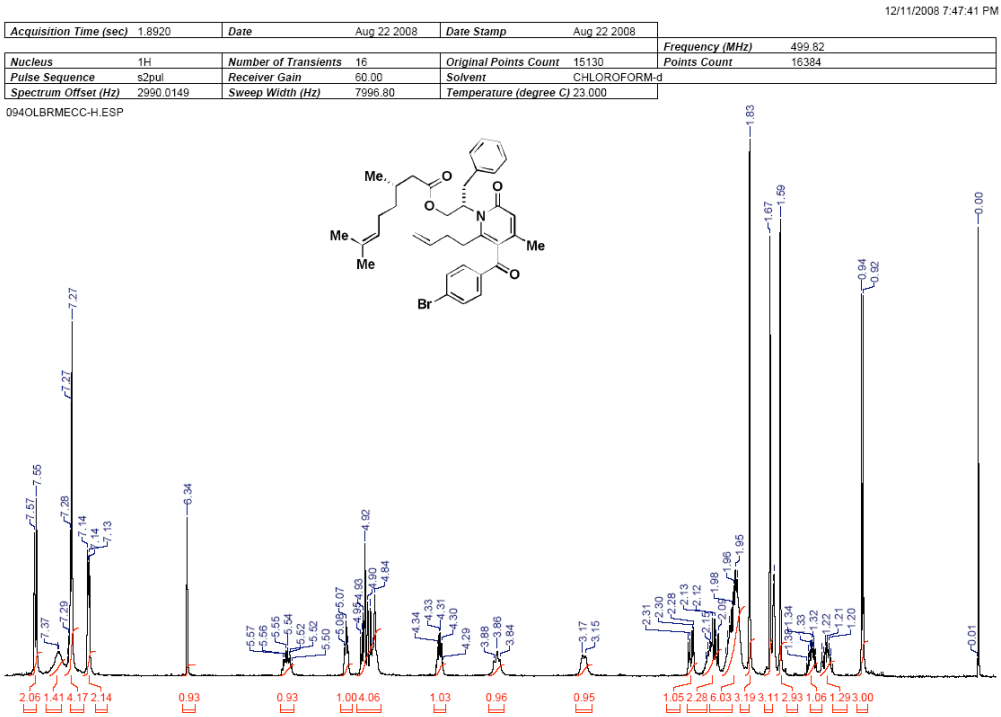
Acquisition Time (sec)	1.3005	*Comment*	STANDARD CARBON PARAMETERS		
Date	Jul 26 2008	*Date Stamp*	Jul 26 2008		
Frequency (MHz)	125.69	*Nucleus*	13C	*Original Points Count*	39010
Points Count	65536	*Pulse Sequence*	s2pul	*Receiver Gain*	60.00
Solvent	CHLOROFORM-d	*Spectrum Offset (Hz)*	11906.6357	*Sweep Width (Hz)*	29996.25
Temperature (degree C)	AMBIENT TEMPERATURE				



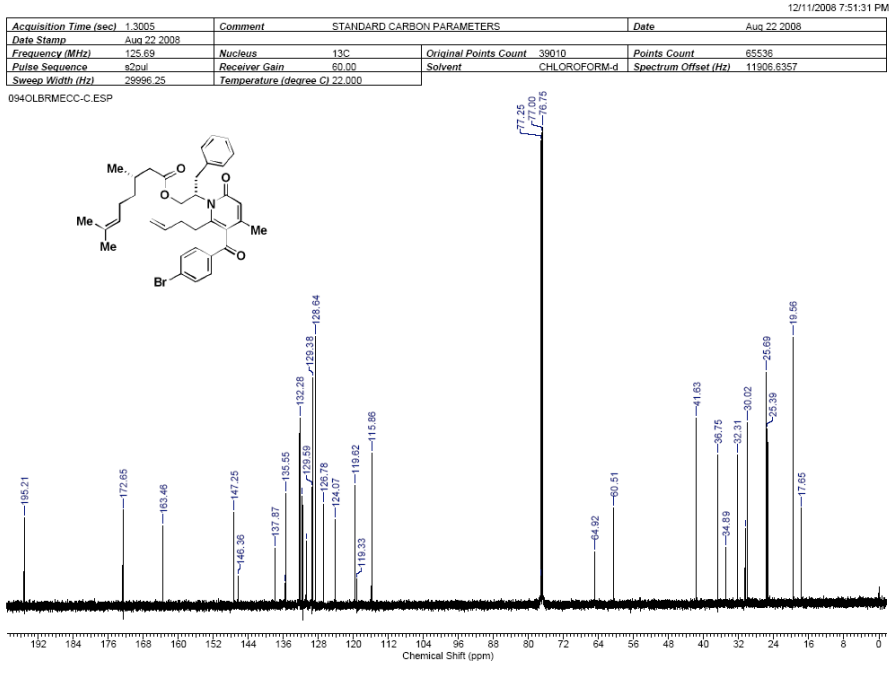
^{13}C NMR (126 MHz, $CDCl_3$) for compound **15ica-E**

Spectra. Spectral Data for

(*S*)-((*S*)-2-(5-(4-bromobenzoyl)-6-(but-3-enyl)-4-methyl-2-oxopyridin-1(2*H*)-yl)-3-phenylpropyl) 3,7-dimethyloct-6-enoate (14icb).



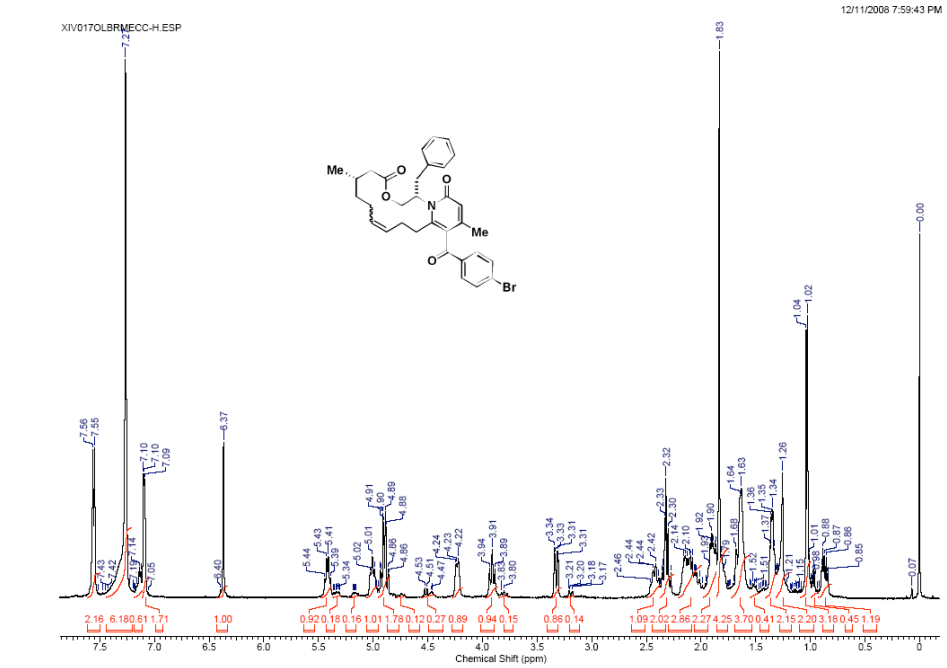
^{1}H NMR (500 MHz, $CDCl_3$) of compound **14icb**



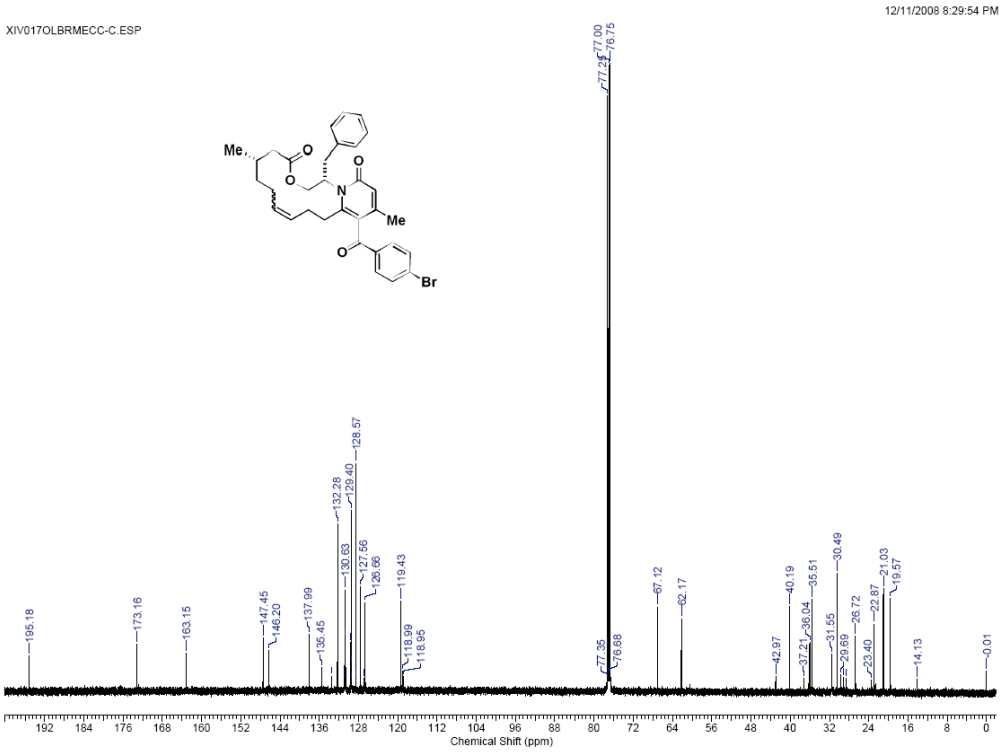
^{13}C NMR (126 MHz, $CDCl_3$) for compound **14icb**

Spectra. Spectral Data for

(1*S*,6*S*)-1-benzyl-13-(4-bromobenzoyl)-6,14-dimethyl-1,2,5,6,7,8,11,12-octahydropyrido[1,2-*d*][1,4]oxaazacyclotetradecine-4,16-dione (15icb).



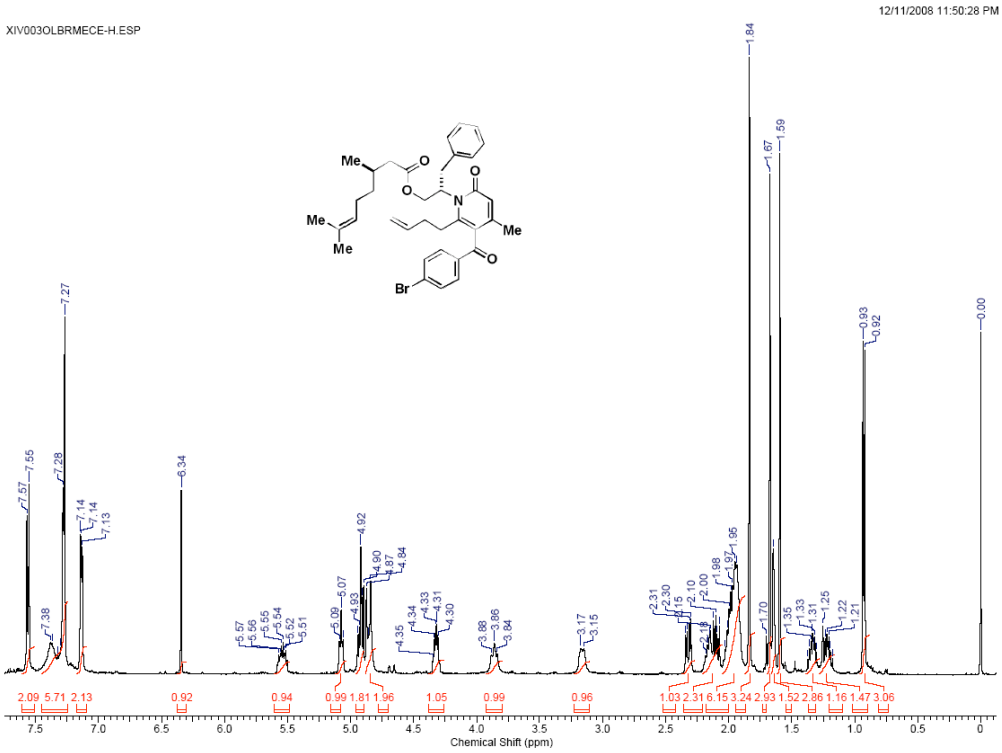
^{1}H NMR (500 MHz, $CDCl_3$) of compound **15icb**



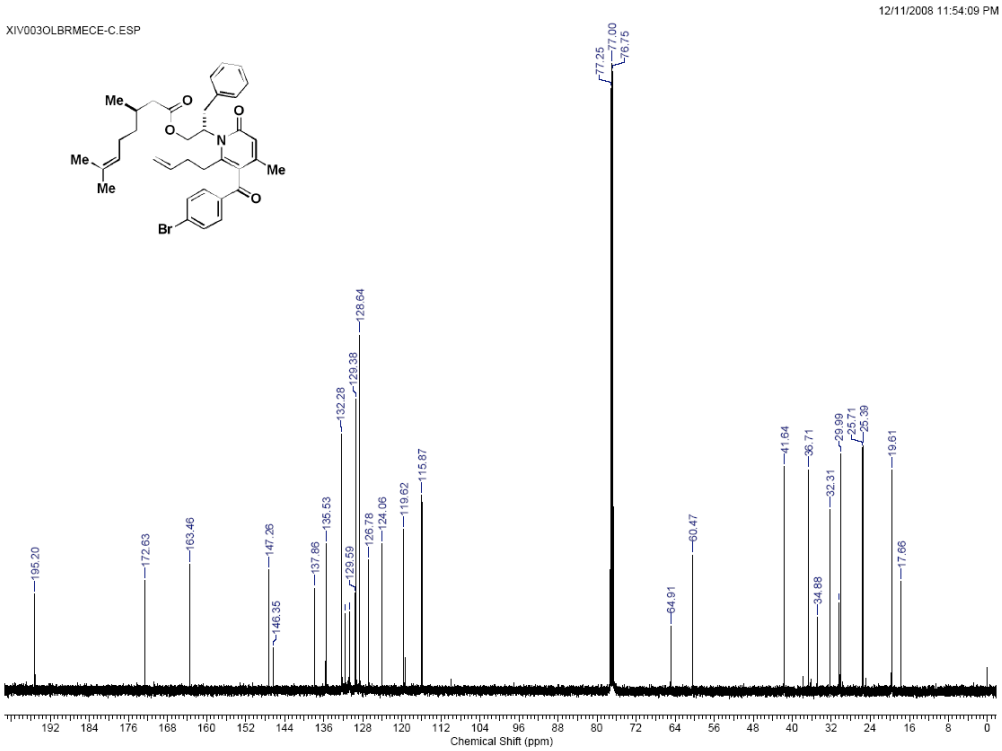
^{13}C NMR (126 MHz, $CDCl_3$) for compound **15icb**

Spectra. Spectral Data for

(*R*)-((*S*)-2-(5-(4-bromobenzoyl)-6-(but-3-enyl)-4-methyl-2-oxopyridin-1(2*H*)-yl)-3-phenylpropyl) 3,7-dimethyloct-6-enoate (14icc).

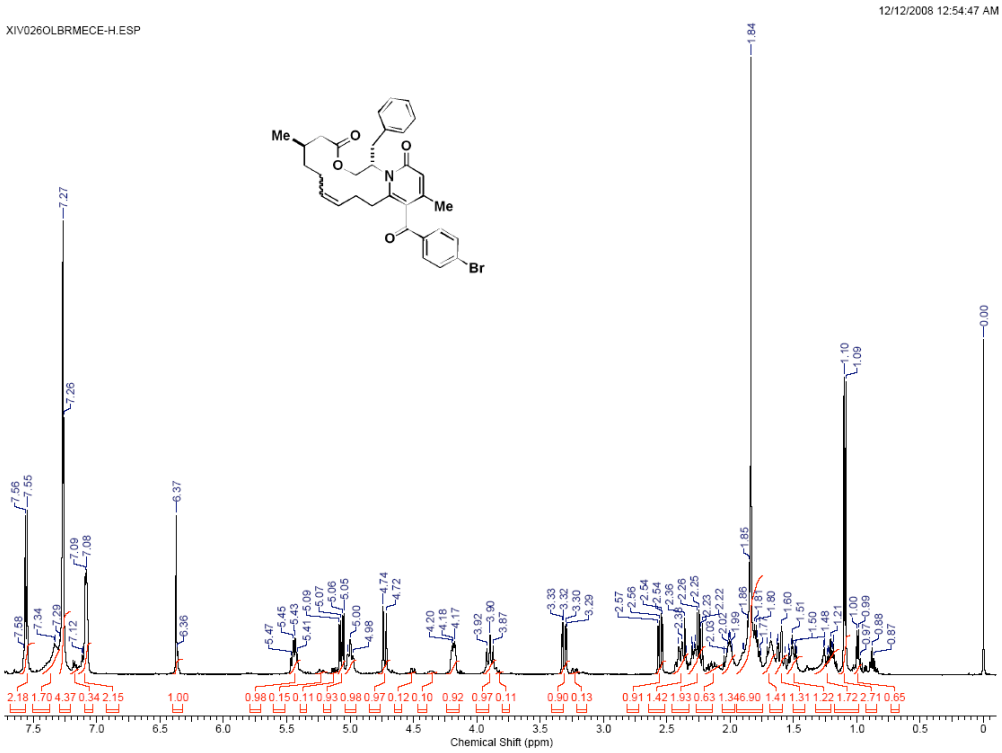


^{1}H NMR (500 MHz, $CDCl_3$) of compound **14icc**

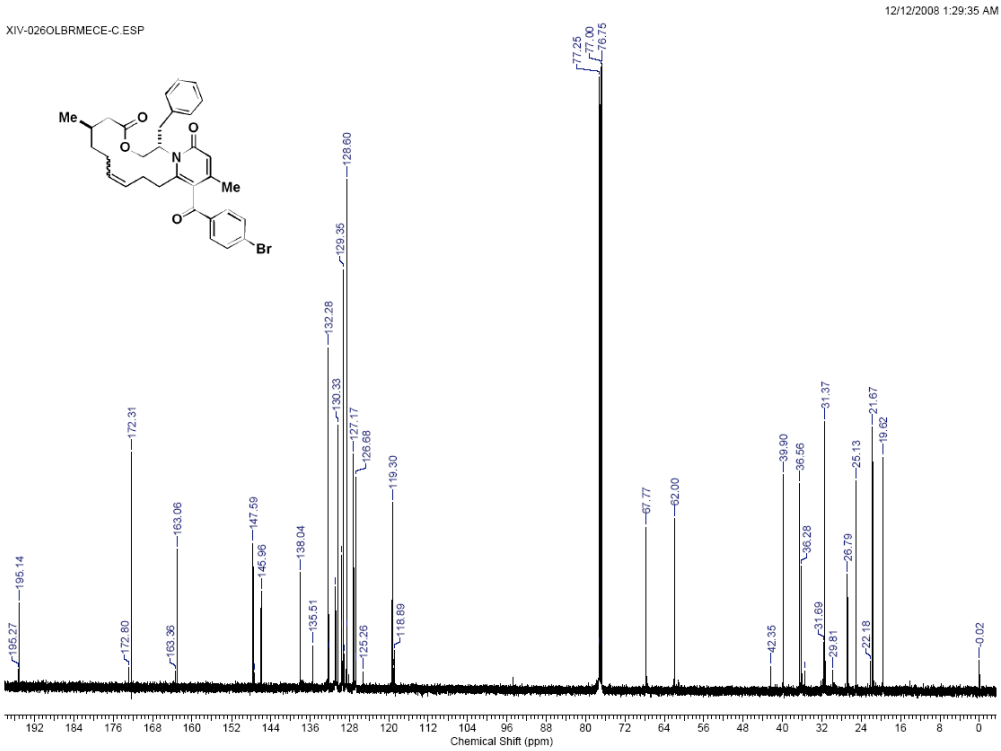


^{13}C NMR (126 MHz, $CDCl_3$) for compound **14icc**

Spectra. Spectral Data for **(1*S*,6*R*)-1-benzyl-13-(4-bromobenzoyl)-6,14-dimethyl-1,2,5,6,7,8,11,12-octahydropyrido[1,2-*d*][1,4]oxaazacyclotetradecine-4,16-dione (15icc).**



^{1}H NMR (500 MHz, $CDCl_3$) of compound **15icc**



^{13}C NMR (126 MHz, $CDCl_3$) for compound **15icc**