Gold-Catalyzed Intermolecular Reactions between Propiolic Acids with Alkenes: [4+2] Annulation and Enyne Cross Metathesis

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Supporting Information

Table of Contents

I. General Remarks

All commercially available reagents were used without further purification (**3a**, **3d-f**, **3h-i**, **3k-n**, **3p-r** and (*R*)-DM-SEGPHOS ligand). Anhydrous chloroform (reagent grade) was purified by washing with water followed by drying ($CaCl_2$) before distillation over $CaCl_2$. TLC analysis was carried out on Merck silica gel 60 F254 TLC plate and was visualized by UV lamp and potassium permanganate solution. Flash column chromatography was performed on Kieselgel 60 (230-400 mesh). Chiral HPLC assay was conducted on Younglin ACME 9000 system attached with UV detector. ^{1}H and ^{13}C NMR spectra were recorded on a Varian (400 MHz) spectrometer with TMS as an internal standard. High resolution mass spectra (HRMS) were conducted at Korea Basic Science Institute (KBSI) at Taegu, Korea.

II. Alkene Synthesis

The alkenes **3b**,[1] (*E*)-**3j**,[2,3] **3r**,[1] (*Z*-major)-**3n**[1] and (*Z*-major)-**3u**[1,4] were synthesized via Wittig olefination ($RPPh_3Br$/*n*BuLi)[1] or Horner-Emmons reaction ($RP(O)(OMe)_2$/*n*BuLi)[2] of the corresponding aldehydes. The allene **3o** was synthesized according to S. Ma's protocol.[5] Compound **3t** was synthesized by olefin metathesis using Grubbs (I) catalyst.[6]

[References]

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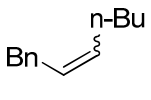
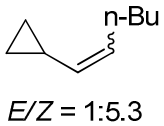


Compound **3s** (colorless oil); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.13 (m, *E&Z* isomer, 5H), 5.64-5.44 (m, *E&Z* isomer, 2H), 3.40 (d, *J* = 6.2 Hz, *Z* isomer, 2H), 3.33 (d, *J* = 5.9 Hz, *E* isomer, 2H), 2.16 (q, *J* = 6.3 Hz, *Z* isomer, 2H), 2.01 (q, *J* = 6.2 Hz, *E* isomer, 2H), 1.50-1.30 (m, *E&Z* isomer, 4H), 0.92 (t, *J* = 7.0 Hz, *Z* isomer, 3H), 0.90 (t, *J* = 6.6 Hz, E isomer, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 132.8, 131.7, 129.4, 129.1, 129.1, 129.0, 128.6, 126.5, 126.4, 39.8, 34.2, 32.9, 32.6, 32.4, 27.6, 23.1, 22.9, 14.7, 14.6.

Compound **3u** (colorless oil); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.30 (dt, *J* = 15.2, 6.6 Hz, *E* isomer, H), 5.31 (dt, *J* = 11.0, 7.4 Hz, *Z* isomer, H), 4.95 (dd, *J* = 15.2, 8.6 Hz, *E* isomer, H), 4.73 (t, *J* = 10.2 Hz, *Z* isomer, H), 2.16 (q, *J* = 7.0 Hz, *Z* isomer, 2H), 1.97 (q, *J* = 6.7 Hz, *E* isomer, 2H), 1.64-1.48 (m, *Z* isomer, H), 1.46-1.24 (m, *E* isomer 5H & *Z* isomer 4H), 0.89 (t, J = 7.0 Hz, *Z* isomer 3H), 0.88 (t, J = 7.0 Hz, *E* isomer 3H), 0.78-0.68 (m, *Z* isomer 2H), 0.68-0.60 (m, *E* isomer 2H), 0.38-0.24 (m, *E&Z* isomer 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.4, 134.3, 129.0, 32.9, 32.7, 32.6, 28.0, 23.0, 22.9, 14.7, 14.6, 14.2, 10.2, 7.5, 7.0.



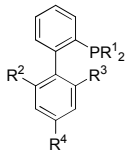
III. Optimization Conditions for [4+2] Annulation and Enyne Metathesis

1. Conditions screened for [4+2] Annulation: Optimal conditions for [4+2] annulation were probed with styrene (**3a**) as a prototypical substrate with propiolic acid (**4a**) (Table S1-S4).

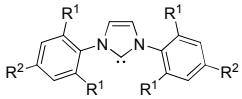
Table S1. The effect of ligand[a]

entry	ligand	condition	product[b]
1	PPh_3	rt (4h)	50 %
2	JohnPhos (**L$_1$**)	rt (4h)	76 %
3	Cy-JohnPhos	rt (4h)	61 %
4	*t*-Bu-Xphos	rt (4h)	47 %
5	IPr	rt (4h)	38 %
6	IMes	rt (4h)	13 %

[a] Au(I)-complex were generated *in-situ*. [b] Crude yield (^{1}H NMR, 1,3,5-trimethoxy-benzene as an internal standard).

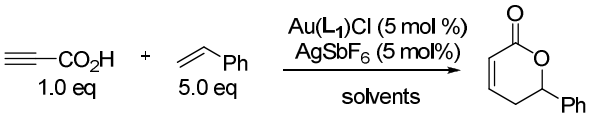


JohnPhos: R^1 = *t*Bu, $R^2/R^3/R^4$ = H
Cy-JohnPhos: R^1 = *c*-C_6H_{11}, $R^2/R^3/R^4$ = H
***t*Bu-XPhos**: R^1 = *t*Bu, $R^2/R^3/R^4$ = *i*Pr
SPhos: R^1 = *c*-C_6H_{11}, R^2/R^3 = OMe, R^4 = H
***t*Bu-DavePhos**: R^1 = *t*Bu, R^2 = NMe_2, R^3/R^4 = H



IPr: R^1 = *i*Pr, R^2 = H
IMes: R^1, R^2 = Me

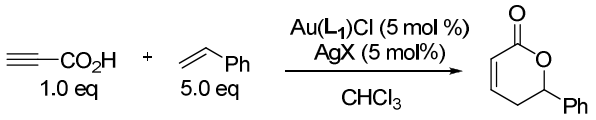
Table S2. The effect of solvents[a]



entry	solvent	condition	product[b]
1	CH_2Cl_2	rt (4 h)	54 %
2	CH_2Cl_2	rt (12 h)	66 %
3	1,2-dichloroethane[c]	rt (12 h)	66 %
4	1,2-dichloroethane	rt (12 h)	68 %
5	C_6H_6	rt (12 h)	56 %
6	CH_3NO_2	rt (12 h)	54 %
7	$CHCl_3$[c]	rt (4 h)	59 %
8	$CHCl_3$	rt (4 h)	78 %

[a] Au(I)-complex were generated *in-situ*. [b] Crude yield (^{1}H NMR, 1,3,5-trimethoxy-benzene as an internal standard). [c] Cy-JohnPhos was used.

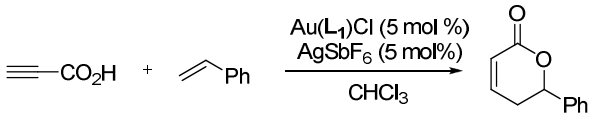
Table S3. The effect of counter-anion (AgX)[a]



entry	AgX	condition	product[b]
1	$AgNTf_2$	rt (4 h)	40 %
2	AgOTf	rt (4 h)	47 %
3	$AgSbF_6$	rt (4 h)	80 %
4	$AgBF_4$	rt (4 h)	27 %
5	$AgClO_4$	rt (4 h)	NR[c]

[a] Au(I)-complex were generated *in-situ*. [b] Crude yield (^{1}H NMR, 1,3,5-trimethoxy-benzene as an internal standard). [c] No reaction; starting materials remained intact.

Table S4. The effect of ratio of alkenes and propiolic acid[a]

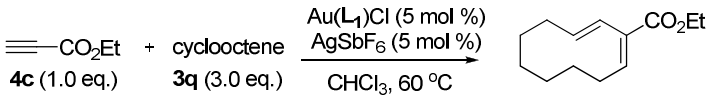


entry	propiolic acid	alkene	condition	product (%)[b]
1	1 eq.	2 eq.	40 ^oC (15 h)	36
2	2 eq.	1 eq.	40 ^oC (15 h)	38
3	5 eq.	1 eq.	rt (24 h)	80 (79)
4	5 eq.	1 eq.	40 ^oC (2 h)	(75)
5	5 eq.	1 eq.	rt (4 h)	(72)
6	1 eq.	5 eq.	rt (4 h)	(75)
7	1 eq.	3 eq.	rt (4 h)	79
8	1 eq.	1.5 eq.	rt (24 h)	58

[a] Au(I)-complex were generated *in-situ*. [b] Crude yield by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard; Isolated yield after chromatography in parenthesis.

2. Conditions screened for enyne metathesis: The conditions for metathesis were probed with *cis*-cyclooctene (**3q**) with ethyl propiolate (**4c**) (Table S5).

Table S5. Deviation from optimal conditions[a]

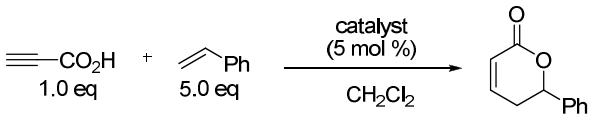


entry	deviation from optimal condition	condition	product (%)[b]
1	None	60 °C (1.5 h)	75
2	ligand (Cy-JohnPhos)	60 °C (1.5 h)	50
3	ligand (*t*Bu-Xphos)	60 °C (1.5 h)	14
4	ligand (SPhos)	60 °C (1.5 h)	50
5	ligand (*t*-Bu-DavePhos)	60 °C (1.5 h)	NR
6	ligand (PPh_3)	60 °C (1.5 h)	50
7	ligand (IPr)	60 °C (1.5 h)	37
8	AgX (AgOTf)	60 °C (1.5 h)	63
9	AgX ($AgBF_4$)	60 °C (1.5 h)	57
10	AgX ($AgClO_4$)	60 °C (1.5 h)	NR
11	AgX ($AgNTf_2$)	60 °C (1.5 h)	62
12	solvent (CH_2Cl_2)	60 °C (2.5 h)	70
13	solvent (1,4-dioxane)	60 °C (2.5 h)	46
14	solvent (CH_3NO_2)	60 °C (2.5 h)	45
15	solvent (toluene)	60 °C (2.5 h)	44
16	solvent (CH_3CN)	60 °C (2.5 h)	NR
17	ratio (1 eq. of **4a** + 1 eq. of **3q**)	60 °C (1.5 h)	47
18	ratio (1 eq. of **4a** + 1.5 eq. of **3q**)	60 °C (1.5 h)	75
19	ratio (1 eq. of **4a** + 3.0 eq. of **3q**)	60 °C (1.5 h)	75

[a] Au(I)-complex were generated *in-situ*. [b] Crude yield by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard.

3. Other catalytic systems examined: Additionally, the following conditions were also examined (Tables S6-S7).

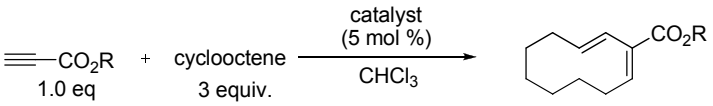
Table S6. Other conditions examined for [4+2] annulation[a]



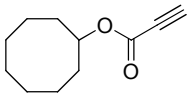
entry	catalyst	condition	product[b]
1	None	40 °C (2 h)	NR
2	$AuCl_3$	70 °C (2 h)	NR
3	$AgSbF_6$	40 °C (15 h)	NR
4	$[Cu(OTf)]_2 \cdot C_6H_6$	rt (12 h)	NR
5	$Cu(OTf)_2$	rt (12 h)	NR
6	TfOH (20 %)	100 °C (2 h)	NR
7	TfOH (1 eq.)	rt (12 h)	NR
8	$BF_3 \cdot OEt_2$ (1 eq.)	100 °C (2 h)	NR

[a] Au(I)-complex were generated *in-situ*. [b] Crude yield (^{1}H NMR, 1,3,5-trimethoxy-benzene as an internal standard).

Table S7. Other conditions examined for enyne metathesis[a]



entry	R	catalyst	condition	product[b]
1	H	None	100 °C (2 h)	**S1** (trace)
2	Et	AgOTf	60 °C (2 h)	43 %
3	Et	TfOH (20 %)	100 °C (2 h)	NR
4	H	TfOH (20 %)	rt (1.5 h)	**S1** (36 %)
5	H	$BF_3 \cdot OEt_2$ (1 equiv.)	rt (1.5 h)	**S1** (38 %)



S1

[a] Au(I)-complex were generated *in-situ*. [b] Crude yield (^{1}H NMR, 1,3,5-trimethoxy-benzene as an internal standard).

IV. General Procedure for [4+2] Annulation and Enyne Cross Metathesis

Method A (Table 1, footnote c)*:* To a solution of an alkene (1.5 mmol, 5.0 equiv.) in $CHCl_3$ (1.5 mL) was added [Au(JohnPhos)]Cl (0.015 mmol, 5 mol%) and $AgSbF_6$ (0.015 mmol, 5 mol%). The reaction mixture was stirred for 5 min at RT, before the addition of propiolic acid (0.3 mmol, 1.0 equiv.). After stirring the mixture at RT for indicated time (see Table 1-3), the solvent was removed and the residue was purified by chromatography (EtOAc/n-Hex).

Method B (Table 1, footnote d)*:* Similar protocol to *Method A* was followed except that *tert*-butyl propiolate (1 equiv.) was used in place of propiolic acid.

Method C (enyne metathesis in Table 2)*:* Similar protocol to *Method A* was followed except that 1.5 equiv. of alkene and 1.0 equiv. of propiolic acid was used.

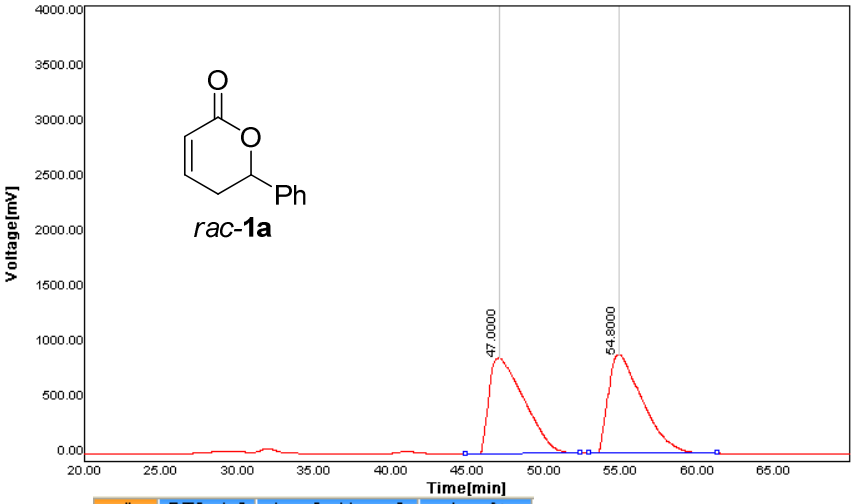
V. Asymmetric [4+2] Annulation (eq 5)

Representative Procedure (Reaction of 3k with 4b in 1,2-dichloroethane): To a solution of (*R*)-DM-SEGPHOS$(AuCl)_2$ (0.0075 mmol, 2.5 mol %) and $AgSbF_6$ (0.015 mmol, 5 mol %) in 1,2-dichloroethane (3.0 mL) was added 2-methyl-2-butene **3k** (105.2 mg, 1.5 mmol, 5 equiv.) and *tert*-butyl propiolate **4b** (37.8 mg, 0.30 mmol, 1 equiv.). The mixture was stirred 24 h at room temperature, while the progress of the reaction was monitored by TLC. After 24 h at RT, the reaction was quenched with triethylamine (3 drops) and was concentrated in vacuo. The residue was purified by silica gel chromatography (EA/nHex = 1:5) to give 27.7 mg (66 % yield) of product **1k** as a colorless oil.

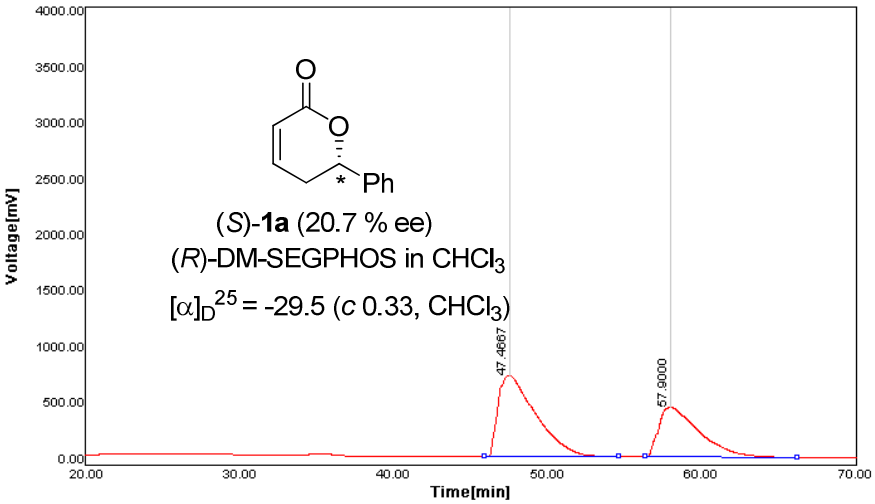
***(S)*-1a:** The enantioselectivity was determined on Chiralcel OD-H column (0.46 cm, I.D. x 25 cm) with *n*Hexane:*i*PrOH (50:1) as eluent (λ = 220 nm).

1k: Identical assay conditions except the eluent (*n*Hexane:*i*PrOH = 130:1).

* Absolute stereochemistry of **1k** was not determined.

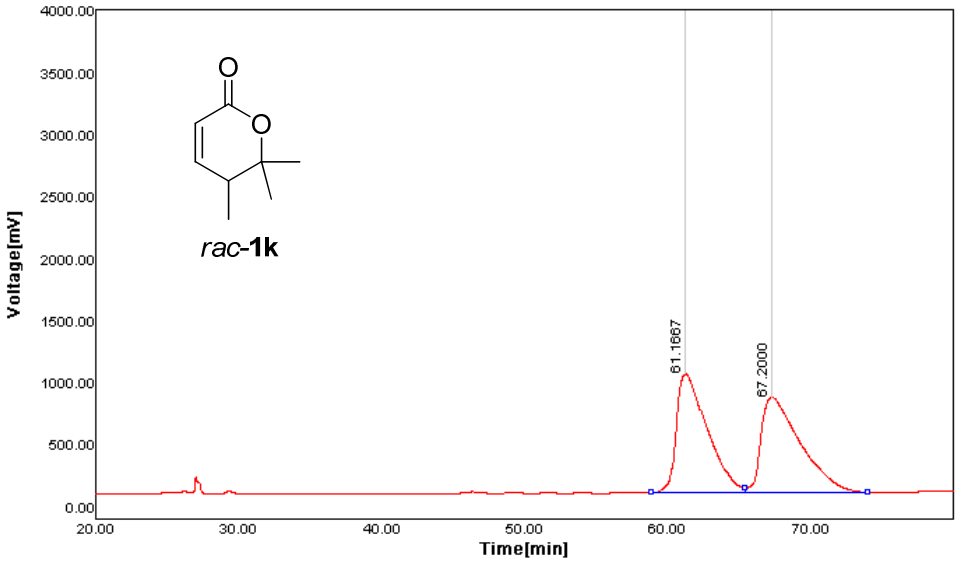


#	RT[min]	Area[mV*sec]	Area%
1	47,0000	137160,5625	49,68
2	54,8000	138910,8594	50,32

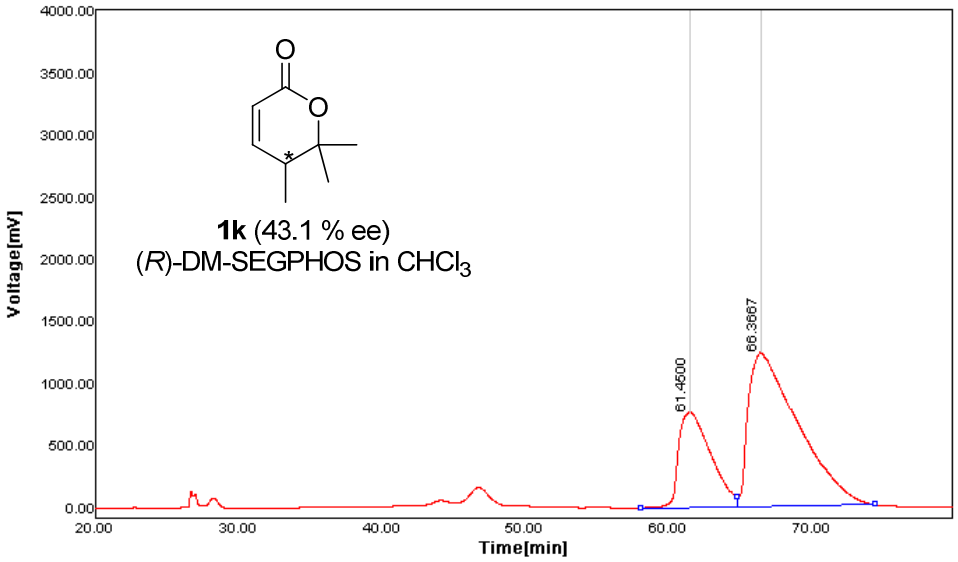


#	RT[min]	Area[mV*sec]	Area%
1	47,4667	123500,3438	60,31
2	57,9000	81288,7344	39,69

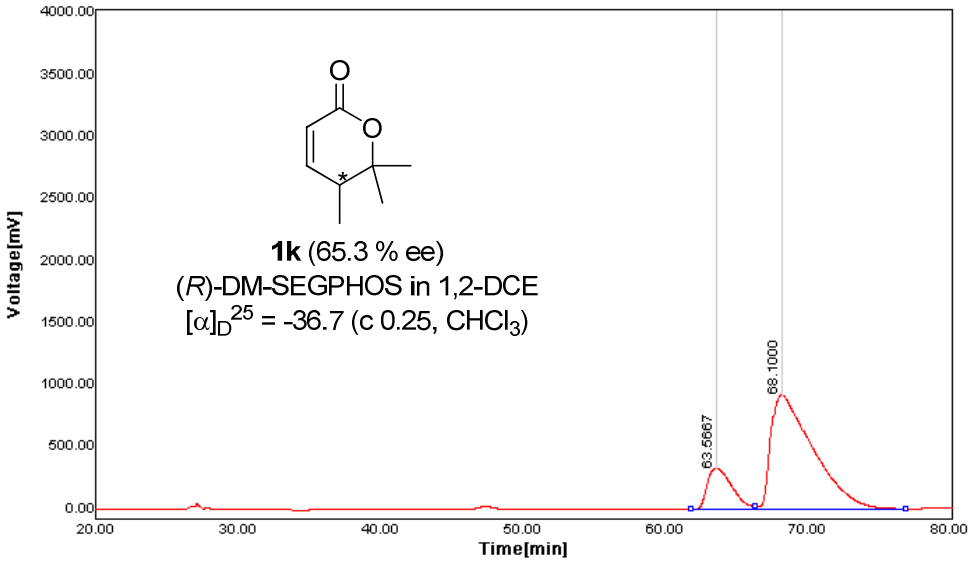
lit. $[\alpha]_D^{20}$ = -188 (*c* 1.5, $CHCl_3$) (Bazan-Tejeda, B.; Bluet, G.; Broustal, G.; Cmapagne, J. -M. *Chem. Eur. J.* **2006**, *12*, 8358)



#	RT[min]	Area[mV*sec]	Area%
1	61,1667	144199,5000	49,51
2	67,2000	147063,8125	50,49

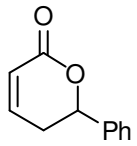


#	RT[min]	Area[mV*sec]	Area%
1	61,4500	118297,9453	28,46
2	66,3667	297392,5625	71,54

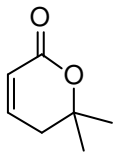


#	RT[min]	Area[mV*sec]	Area%
1	63,5667	39867,9922	17,35
2	68,1000	189971,6094	82,65

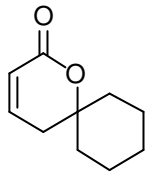
VI. Characterization Data of All Products



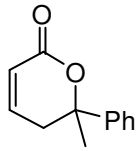
Compound **1a** (white solid, m.p. 56-58 ^{o}C); IR (thin film): 3057, 2923, 2853, 1716, 1685, 1495, 1457, 1411, 1251, 767, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98 (ddd, *J* = 8.4, 5.5, 2.9 Hz, H), 6.15 (dd, *J* = 9.9, 1.5 Hz, H), 5.46 (dd, *J* = 11.0, 4,7 Hz, H), 2.67 (ddt, *J* = 18.3, 11.0, 2.6 Hz, H), 2.61 (dt, *J* = 18.7, 4.8 Hz, H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 145.5, 139.1, 129.4, 129.3, 126.7, 122.4, 79.9, 32.3; HRMS(EI+) Calcd for $C_{11}H_{10}O_2$ [M+] 174.0681, found 174.0682. Spectral data gave a satisfactory match to previous reports.[7a]



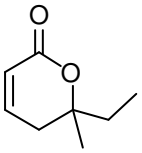
Compound **1c** (colorless oil); IR (thin film): 2979, 2934, 1716, 1653, 1385, 1288, 1216, 1098, 994, 950, 810, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.77 (dt, *J* = 9.9, 4.1 Hz, H), 6.04 (d, *J* = 9.6 Hz, H), 2.50-2.36 (m, 2H), 1.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 144.1, 121.6, 80.8, 36.2, 28.4; HRMS(EI+) Calcd for $C_7H_{10}O_2$ [M+] 126.0681, found 126.0680. Spectral data gave a satisfactory match to previous reports.[7b]



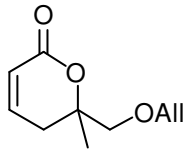
Compound **1d** (colorless oil); IR (thin film): 2935, 2860, 1715, 1653, 1238, 838, 816 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.74 (dt, *J* = 9.6, 4.4 Hz, H), 6.01 (dt, *J* = 9.9, 1.9 Hz, H), 2.41 (dd, *J* = 4.4, 2.2 Hz, H), 2.10-1.88 (m, 2H), 1.88-1.69 (m, 2H), 1.69-1.42 (m, 5H), 1.42-1.25 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 143.8, 121.6, 81.8, 36.9, 35.1, 25.9, 22.1; HRMS(EI+) Calcd for $C_{10}H_{14}O_2$ [M+] 166.0994, found 166.0993.



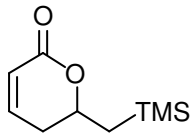
Compound **1e** (white solid, m.p. 47-48 ^{o}C); IR (thin film): 3060, 3030, 2981, 2932, 2893, 1713, 1626, 1496, 1446, 1380, 1262, 1091, 997, 965, 815, 760, 701; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.26 (m ,5H), 6.75 (ddd, *J* = 9.6, 5.2, 3.7 Hz, H), 6.01 (dt, *J* = 9.5, 1.8 Hz, H), 2.96 (ddd, *J* = 18.4, 5.2, 1.1 Hz, H), 2.80 (ddd, *J* = 18.3, 3.3, 2.5 Hz, H), 1.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 144.5, 144.1, 129.2, 128.2, 125.1, 122.5, 83.8, 36.0, 30.8; HRMS(EI+) Calcd for $C_{12}H_{12}O_2$ [M+] 188.0837, found 188.0838. Spectral data gave a satisfactory match to previous reports.[7c]



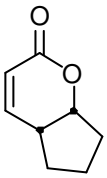
Compound **1f** (colorless oil); IR (thin film): 3054, 2977, 2939, 2884, 1715, 1630, 1463, 1384, 1265, 1106, 1092, 995, 957, 813 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.79 (dt, *J* = 9.9, 4.0 Hz, H), 6.03 (d, *J* = 9.9, 1.9 Hz, H), 2.50 (ddd, *J* = 18.7, 3.3, 2.6 Hz, H), 2.32 (ddd, *J* = 18.3, 4.8, 1.5 Hz, H), 1.84-1.64 (m, 2H), 1.40 (s, 3H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 144.1, 121.6, 83.2, 34.1, 340. 25.3, 8.7; HRMS(EI+) Calcd for $C_8H_{12}O_2$ [M+] 140.0837, found 140.0839. This sample was obtained as an inseparable mixture with product **1m** (0.15 equiv.). Spectral data gave a satisfactory match to previous reports.[7b]



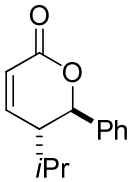
Compound **1g** (colorless oil); IR (thin film): 3080, 2979, 2927, 2857, 1716, 1646, 1455, 1381, 1289, 1249, 1134, 1079, 996, 913, 810, 743 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (dt, *J* = 9.8, 4.3 Hz, H), 6.02 (dt, *J* = 9.8, 1.9 Hz, H), 5.87 (ddt, *J* = 16.9, 10.5, 5.5 Hz, H), 5.26 (dd, *J* = 17.1, 1.5 Hz, H), 5.19 (dd, *J* = 9.5, 1.1 Hz, H), 4.04 (dd, *J* = 5.5, 1.6 Hz, H), 3.57 (d of ABq, *J* = 9.8 Hz, H), 3.39 (d of ABq, *J* = 9.7 Hz, H), 2.78 (ddd, *J* = 18.8, 3.9, 2.4 Hz, H), 2.29 (ddd, *J* = 18.8, 4.7, 2.0 Hz, H), 1.4 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.0, 144.2, 134.9, 121.3, 118.0, 82.0, 75.3, 73.2, 31.6, 24.5; HRMS(EI+) Calcd for $C_{10}H_{14}O_3$ [M+] 182.0943, found 182.0941.



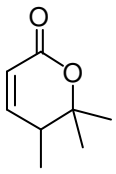
Compound **1h** (colorless oil); IR (thin film): 2953, 2897, 1721, 1384, 1251, 1136, 1052, 1018, 840, 818 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (ddd, *J* = 9.2, 5.5, 2.6 Hz, H), 6.01 (dd, *J* = 9.5, 1.5 Hz, H), 4.56 (dtd, *J* = 11.7, 7.3, 4.4 Hz, H), 2.87 (dt, *J* = 18.7, 4.4 Hz, H), 2.27 (ddt, *J* = 18.3, 11.0, 2.5 Hz, H), 1.25 (dd, *J* = 14.7, 7.3 Hz, H), 1.02 (dd, *J* = 14.3, 7.3 Hz, H), 0.12 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6, 145.6, 122.2, 77.6, 33.1, 24.9, -0.19; HRMS(EI+) Calcd for $C_9H_{16}O_2Si$ [M+] 184.0920, found 184.0916.



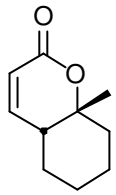
Compound **1i** (cis-isomer, pale yellow oil); IR (thin film): 2952, 2874, 1719, 1388, 1240, 1130, 1100, 1042, 987, 822 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.90 (dd, *J* = 9.5, 5.5 Hz, H), 5.93 (d, *J* = 9.9 Hz, H), 4.92 (td, *J* = 8.5, 2.6 Hz, H), 2.57 (tt, *J* = 9.2, 5.9 Hz, H), 2.20-1.84 (m, 4H), 1.80-1.66 (m, H), 1.66-1.48 (m, H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.1, 148.5, 119.9, 84.0, 39.0, 34.1, 31.7, 24.1; HRMS(EI+) Calcd for $C_8H_{10}O_2$ [M+] 138.0681, found 138.0683. The *cis*-stereochemistry was determined by 1D-NOE experiments.



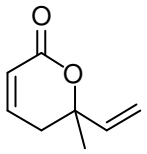
Compound **1j** (colorless oil); IR (thin film): 3034, 2913, 2930, 2874, 1727, 1455, 1386, 1248, 1226, 1057, 1002, 812, 762, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.30 (m, 5H), 6.85 (dd, *J* = 9.7, 3.1 H), 6.15 (dd, *J* = 10.2, 2.3 Hz, H), 5.32 (d, *J* = 9.0 Hz, H), 2.66 (tt, *J* = 5.5, 3.5 Hz, H), 1.75 (dsextet, *J* = 7.0, 4.3 Hz, H), 1.03 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.7, 146.7, 138.0, 128.7, 128.6, 127.0, 121.8, 82.5, 45.8, 27.7, 20.8, 17.6; HRMS(EI+) Calcd for $C_{14}H_{16}O_2$ [M+] 216.1150, found 216.1151. The *trans*-stereochemistry was determined by 1D-NOE experiments.



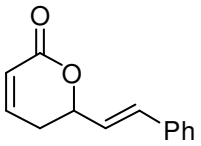
Compound **1k** (colorless oil); IR (thin film): 2981, 2936, 1716, 1653, 1272, 1133, 1088, 979, 823, 750, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.66 (dd, *J* = 9.5, 3.6 Hz, H), 5.98 (dd, *J* = 9.9, 1.8 Hz, H), 2.67-2.45 (m, 1H), 1.45 (s, 3H), 1.34 (s, 3H), 1.12 (d, *J* = 7.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 150.6, 120.5, 83.9, 38.6, 28.3, 23.2, 15.6; HRMS(FAB+) Calcd for $C_8H_{13}O_2$ [M+H] 141.0916, found 141.0914.



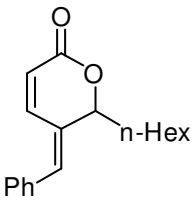
Compound **1l** (cis-isomer, colorless oil); IR (thin film): 2977, 2935, 2860, 1714, 1446, 1381, 1242, 1102, 993, 970, 819 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (dd, *J* = 9.5, 5.1 Hz, H), 5.98 (d, *J* = 9.1 Hz, H), 2.32-2.20 (m, H), 2.18-2.10 (m, H), 1.91-1.72 (m ,H), 1.72-1.52 (m, 3H), 1.52-1.38 (m, H), 1.38 (s, 3H), 1.32-1.18 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 149.7, 120.3, 80.9, 40.2, 36.5, 29.5, 26.4, 21.6; HRMS(FAB+) Calcd for $C_{10}H_{15}O_2$ [M+H] 167.1072, found 167.1075. The *cis-/trans*-isomers (ratio = 7.7:1) could not be separated. The *cis*-stereochemistry was determined by 1D-NOE experiments.



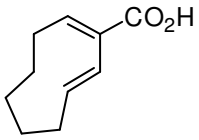
Compound **1m** (colorless oil); IR (thin film): 2981, 2933, 1714, 1653, 1381, 1279, 1252, 1104, 997, 950, 823, 809 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.73 (dt, *J* = 9.5, 4.4 Hz, H), 6.02 (dt, *J* = 9.9, 1.8 Hz, H), 5.86 (dd, *J* = 17.2, 11.0 Hz, H), 5.27 (d, *J* = 17.3 Hz, H), 5.16 (d, *J* = 11.0 Hz, H) 2.62-2.44 (m, 2H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 143.6, 140.9, 122.0, 115.4, 82.0, 34.9, 27.9; HRMS(FAB+) Calcd for $C_8H_{11}O_2$ [M+H] 139.0759, found 139.0757.



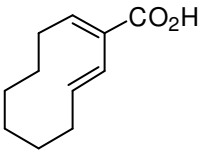
Compound **1n** (white solid); IR (thin film): 3056, 2916, 2848, 1722, 1494, 1449, 1382, 1265, 1245, 1057, 1021, 967, 814, 737, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 7.4 Hz, 2H),7.34 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, H), 6.93 (dt, *J* = 9.9, 4.0 Hz, H), 6.73 (d, *J* = 15.7 Hz, H), 6.28 (dd, *J* = 16.1, 6.2 Hz, H), 6.09 (d, *J* = 9.5 Hz, H), 5.11 (q, *J* = 7.0 Hz, H), 2.64-2.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 145.2, 136.4, 133.8, 129.4, 129.0, 127.4, 126.3, 122.4, 78.6, 30.4; HRMS(EI+) Calcd for $C_{13}H_{12}O_2$ [M+] 200.0837, found 200.0836. Spectral data gave a satisfactory match to previous reports.[7e]



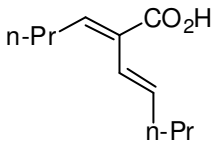
Compound **1o** (colorless oil); IR (thin film): 2953, 2928, 2857, 1719, 1653, 1233, 1117, 1032, 925, 828, 746, 698 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (m, 3H), 7.26 (d, *J* = 7.7 Hz, 2H), 7.36 (d, *J* = 9.6 Hz, H), 6.73 (s, H), 5.99 (dd, *J* = 9.9, 1.5 Hz, H), 5.05 (t, *J* = 6.6 Hz, H), 2.05-1.93 (m, H), 1.93-1.81 (m H), 1.60-1.50 (m, H), 1.50-1.40 (m, H), 1.40-1.18 (m, 6H), 0.88(t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.5, 139.8, 135.5, 133.3, 131.5, 130.0, 129.3, 120.3, 82.9, 36.4, 32.3, 29.6, 25.8, 23.2, 14.7; HRMS(EI+) Calcd for $C_{18}H_{22}O_2$ [M+] 270.1620, found 270.1623. The regiochemistry was determined from the COSY NMR spectra (δ 5.05 (t) peak correlated with aliphatic protons). The stereochemistry of the double bond was determined from the NOE contact of the vinyl proton (PhC*H*) with methine proton (C*H*O).



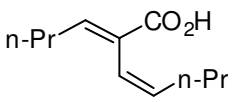
Compound **2pa** (white solid, m.p. 95-97 ^{o}C); IR (thin film): 3200(br), 2930, 2852, 2672, 2529, 1669, 1609, 1430, 1288, 976, 748, 704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, *J* = 6.8 Hz, H), 5.85 (d, *J* = 16.4 Hz, H), 5.69 (ddd, *J* = 16.0, 10.6, 5.5 Hz, H), 2.60-2.08 (m, 4H), 1.78-1.60 (m, 3H), 1.60-1.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 149.8, 138.0, 133.9, 123.0, 32.2, 30.5, 29.0, 28.6, 28.1; HRMS(EI+) Calcd for $C_{10}H_{14}O_2$ [M+] 166.0994, found 166.0994. The *trans*-geometry of unconjugated double bond was supported by the large coupling constant (*J* = 16.2 Hz). The *trans*-geometry of conjugated double bond was taken from the analogy to the products (*E,E*)-**2ra** and (*E,Z*)-**2ra**.



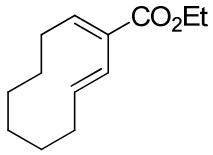
Compound **2qa** (white solid, m.p 109-111 ^{o}C); IR (thin film): 3100(br), 3005, 2957, 2926, 2849, 2622, 2550, 1682, 1653, 1600, 1457, 1424, 1297, 1273, 1207, 973, 916, 747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.03 (t, *J* = 8.0 Hz, H), 6.00 (d, *J* = 16.2 Hz, H), 5.58 (dt, *J* = 16.5, 7.7 Hz, H), 2.25 (q, *J* = 7.7 Hz, H), 2.19 (q, *J* = 7.7 Hz, 2H), 1.62-1.50 (m, 2H), 1.48-1.31 (m, 4H), 1.30-1.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 147.1, 139.1, 134.0, 124.0, 35.1, 28.0, 27.8, 27.0, 25.7, 23.7; HRMS(EI+) Calcd for $C_{11}H_{16}O_2$ [M+] 180.1150, found 180.1148. The *trans*-geometry of unconjugated double bond was supported by the large coupling constant (*J* = 16.3 Hz). The *trans*-geometry of conjugated double bond was taken from the analogy to the products (*E,E*)-**2ra** and (*E,Z*)-**2ra**.



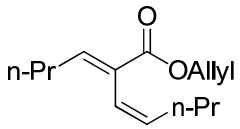
Compound *(E,E)*-**2ra** (colorless oil); IR (thin film): 3180(br), 2960, 2931, 2872, 2650, 2523, 1685, 1653, 1457, 1418, 1277, 967, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.5 (br s, H), 6.81 (t, *J* = 7.7 Hz, H), 6.11 (d, *J* = 16.2, Hz, H), 6.05 (dt, *J* = 15.7, 6.2 Hz, H) ,2,29 (q, *J* = 7.3 Hz, 2H), 2,14 (q, *J* = 7.0 Hz, 2H), 1.50 (sextet, *J* = 7.3 Hz, 2H), 1.46 (sextet, *J* = 7.3 Hz, 2H), 0.95 (t, *J* = 7.7 Hz, 3H), 0.93 (t, *J* = 7.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 145.0, 137.0, 129.7, 121.9, 35.9, 31.2, 22.6, 22.4, 14.1, 13.9; HRMS(EI+) Calcd for $C_{11}H_{18}O_2$ [M+] 182.1307, found 182.1308. The *trans*-geometry of unconjugated double bond was supported by the large coupling constant (*J* = 16.0 Hz). The *trans*-geometry of conjugated double bond was determined by NOE experiments after reduction of the acid into the alcohol (see Section **VII** below).



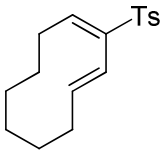
Compound *(E,Z)*-**2ra** (colorless oil); IR (thin film): 3170(br), 2960, 2932, 2872, 2648, 2533, 1686, 1653, 1418, 1281, 920, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): 6.96 (t, *J* = 7.3 Hz, H), 5.92 (d, *J* = 11.0 Hz, H), 5.71 (dt, *J* = 11.3, 7.4 Hz, H), 2.11 (q, *J* = 7.3 Hz, 2H), 1.87 (q, *J* = 7.0 Hz, 2H), 1.47 (sextet, *J* = 7.3 Hz, 2H), 1.38 (sextet, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.3 Hz, 3H), 0.87 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.3, 147.7, 136.3, 129.3, 122.3, 32.5, 31.9, 22.9, 22.3, 14.6, 14.5; HRMS(EI+) Calcd for $C_{11}H_{18}O_2$ [M+] 182.1307, found 182.1309. The *cis*-geometry of unconjugated double bond was supported by the small coupling constant (*J* = 11.2 Hz). The *trans*-geometry of conjugated double bond was determined by NOE experiments after reduction of the acid into the alcohol (see Section **VII** below).



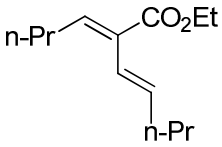
Compound **2qc** (colorless oil); IR (thin film): 2927, 2852, 1713, 1655, 1607, 1458, 1257, 1200, 1126, 1084, 1078, 1044, 1000, 973, 746 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (td, *J* =8.2, 0.8 Hz, H), 6.03 (d, *J* = 16.4 Hz, H), 5.55 (dt, *J* = 16.4, 7.8 Hz, H), 4.22 (q, *J* = 7.0 Hz, 2H), 2.23 (q, *J* = 7.8 Hz, 2H), 2.18 (q, *J* = 7.6 Hz, 2H), 1.53 (m ,2H), 1.48-1.12 (m, 6H), 1.30 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.6, 144.1, 138.4, 134.9, 124.7, 61.3, 35.1, 28.1, 27.8, 27.1, 25.4, 23.7, 15.0; HRMS(EI+) Calcd for $C_{13}H_{20}O_2$ [M+] 208.1463, found 208,1461.



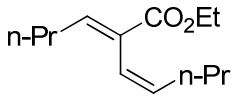
Compound (*E,Z*)-**2rd** (colorless oil); IR (thin film): 2959, 2931, 2873, 1718, 1647, 1457, 1379, 1243, 1217, 1143, 1088, 1049, 968, 928, 753, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84 (t, *J* = 7.4 Hz, H), 5.95 (d, *J* = 11.3 Hz, H), 6.04-5.88 (m, H), 5.67 (dt, *J* = 11.0 , 7.4 Hz, H), 5.33 (dd, *J* = 17.2, 1.6 Hz, H), 5.22 (dd, *J* = 10.1, 1.2 Hz, H), 4.64 (d, *J* = 7.0 Hz, 2H), 2.09 (q, *J* = 7.4 Hz, 2H), 1.86 (qd, *J* = 7.4, 1.6 Hz, 2H), 1.46 (sextet, *J* = 7.4 Hz, 2H), 1.37 (sextet, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 145.3, 135.7, 133.1, 129.8, 122.8, 118.5, 65.9, 32.3, 31.9, 22.9, 22.4, 14.6, 14.5; HRMS(EI+) Calcd for $C_{14}H_{22}O_2$ [M+] 222.3233, found 222.3234.



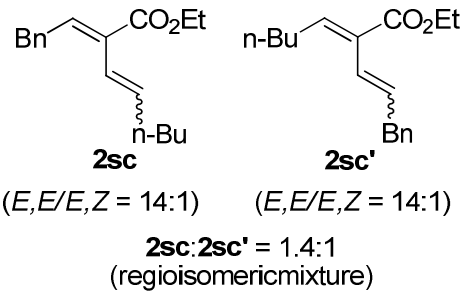
Compound **2qe** (white solid, m.p. 88-90 °C); IR (thin film): 2927, 2854, 1597, 1459, 1311, 1300, 1149, 1090, 982, 813, 730, 718, 667, 661 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 6.91 (t, *J* = 7.8 Hz, H), 5.76 (d, *J* = 16.0 Hz, H), 5.68 (dt, *J* = 16.0, 7.4 Hz, H), 2.42 (s, 3H), 2.22 (q, *J* = 7.4 Hz, 2H), 2.11 (q, *J* = 7.8 Hz, 2H), 1.58-1.48 (m, 2H), 1.48-1.36 (m, 2H), 1.36-1.18 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 144.2, 143.0, 141.6, 137.8, 130.2, 129.0, 119.9, 35.2, 27.6, 27.4, 26.9, 25.8, 24.0, 22.3; HRMS(EI+) Calcd for $C_{17}H_{22}O_2S$ [M+] 290.1342, found 290.1344.



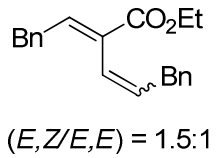
Compound (*E,E*)-**2rc** (colorless oil); IR (thin film): 2970, 2935, 2863, 1719, 1642, 1453, 1364, 1283, 1253, 1232, 1061, 776 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.58 (t, *J* = 7.4 Hz, H), 6.12 (d, *J* = 16.1 Hz, H), 6.01 (dt, *J* = 15.8, 6.9 Hz, H), 4.20 (q, *J* = 7.0 Hz, 2H), 2.26 (q, *J* = 7.3 Hz, 2H), 2.13 (q, *J* = 7.0 Hz, 2H), 1.53-1.40 (m, 4H), 1.30 (t, *J* = 7.0 Hz, 3H), 0.94 (t, *J* = 6.9 Hz, 3H), 0.93 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 141.7, 136.3, 130.8, 122.4, 60.7, 35.9, 30.9, 22.6, 22.5, 14.5, 14.2, 13.9; HRMS(EI+) Calcd for $C_{13}H_{22}O_2$ [M+] 210.1620, found 210.1621.



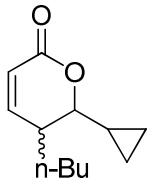
Compound (*E,Z*)-**2rc** (colorless oil); IR (thin film): 2960, 2932, 2873, 1717, 1632, 1463, 1360, 1270, 1248, 1222, 1061, 776, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.80 (t, *J* = 7.4 Hz, H), 5.93 (d, *J* = 11.3 Hz, H), 5.66 (dt, *J* = 11.3, 7.0 Hz, H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.08 (q, *J* = 7.4 Hz, 2H), 1.86 (qd, *J* = 7.4, 1.6 Hz, 2H), 1.46 (sextet, *J* = 7.4 Hz, 2H), 1.37 (sextet, *J* = 7.4 Hz, 2H), 1.29 (t, *J* = 7.0 Hz, 3H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 144.7, 135.5, 130.1, 123.0, 61.2, 32.3, 31.9, 22.9, 22.4, 14.9, 14.6, 14.4; HRMS(EI+) Calcd for $C_{13}H_{22}O_2$ [M+] 210.1620, found 210.1622.



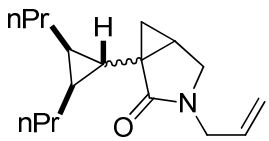
Compound **2sc/2sc'** (colorless oil, inseparable mixture of 1.4:1); IR (thin film): 3065, 2919, 1729, 1380, 1243, 1062, 1020, 814, 756, 666 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.19 (m, **2sc/2sc'**, 5H), 6.73 (t, *J* = 7.8 Hz, **2sc'**, H), 6.64 (t, *J* = 7.8 Hz, **2sc**, H), 6.28-6.17 (m, **2sc/2sc'**, 3H), 6.08 (dt, *J* = 15.6, 7.1 Hz, **2sc'**, H), 4.20 (q, *J* = 7.1 Hz, **2sc/2sc'**, 2H), 3.63 (d, *J* = 7.8 Hz, **2sc'**, 2H), 3.50 (d, *J* = 4.7 Hz, **2sc**, 2H), 2.27 (q, *J* = 7.5 Hz, **2sc**, 2H), 2.19 (q, *J* = 7.0 Hz, **2sc'**, 2H), 1.57-1.18 (m, **2sc/2sc'**, 4H), 1.30 (t, *J* = 7.0 Hz, **2sc**, 3H), 1.29 (t, *J* = 7.1 Hz, **2sc'**, 3H), 0.91 (t, *J* = 7.8 Hz, **2sc'**, 3H), 0.89 (t, *J* = 7.0 Hz, **2sc**, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.2, 143.3, 140.8, 140.0, 139.6, 138.0, 134.9, 131.8, 130.7, 129.3, 129.3, 129.2, 129.1, 127.1, 126.8, 124.2, 122.5, 61.3, 40.6, 35.5, 34.0, 32.0, 31.8, 29.1, 23.1,23.0, 14.9, 14.6, 14.5; HRMS(EI+) Calcd for $C_{18}H_{24}O_2$ [M+] 272.1776, found 272.1775.



Compound **2tc** (colorless oil, inseparable mixture); IR (thin film): 3084, 3062, 3027, 2957, 2927, 2871, 2858, 1716, 1649, 1602, 1494, 1453, 1377, 1237, 1196, 1140, 1030, 969, 739, 697, 635 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.09 (m, *E&Z* isomer, 10H), 7.04 (t, *J* =7.8 Hz, *Z* isomer, H), 6.78 (t, *J* = 7.4 Hz, *E* isomer, H), 6.32 (d, *J* = 15.6 Hz, *E* isomer, H), 6.26 (dt, *J* = 16.0, 6.3 Hz, *E* isomer, H), 6.18 (dd, *J* = 11.4, 1.2 Hz, *Z* isomer, H), 5.96 (dt, *J* = 11.3, 7.4 Hz, *Z* isomer, H), 4.21 (q, *J* = 7.1 Hz, *Z* isomer, 2H), 4.20 (q, *J* = 7.4 Hz, *E* isomer, 2H), 3.61 (d, *J* = 7.8 Hz, *E* isomer, 2H), 3.53 (d, *J* = 7.7 Hz, *E* isomer, 2H), 3.51 (d, *J* = 7.8 Hz, *Z* isomer, 2H), 3.32 (d, *J* = 7.0 Hz, *Z* isomer, 2H), 1.28 (t, *J* = 7.1 Hz, *Z* isomer, 3H), 1.27 (t, *J*= 7.6 Hz, *E* isomer, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 167.0, 142.5, 140.0, 139.9, 139.8, 139.1, 138.7, 135.2, 133.9, 13.0,8 129.6, 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 126.5, 126.4, 126.2, 126.1, 123.2, 123.0, 60.8, 60.7, 39.9, 35.8, 35.3, 34.8, 14.3, 14.2; HRMS(EI+) Calcd for $C_{21}H_{22}O_2$ [M+] 306.1620, found 306.1622.

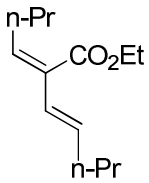


Compound **1u** (colorless oil, dr 3.8 :1); IR (thin film): 3007, 2956, 2931, 2861, 1722, 1465, 1380, 1251, 1029, 992, 822 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (dd, *J* = 9.8, 5.6 Hz, major, H), 6.82 (dd, *J* = 9.8, 3.6 Hz, minor, H), 5.99 (d, *J* = 9.8 Hz, major&minor, H), 3.63 (dd, *J* = 9.4, 5.5 Hz, major, H), 3.47 (dd, *J* = 8.9, 7.0 Hz, minor, H), 2.60-2.50 (m, minor, H), 2.50-2.40 (m, major, H), 1.88-1.28 (m, major&minor, 6H), 1.25-1.08 (m, major&minor, H), 0.98-0.86 (m, major&minor, 3H), 0.76-0.57 (m, major&minor, 2H), 0.57-0.44 (m, major&minor, H), 0.38-0.30 (m, minor, H), 0.30-0.20 (m, major, H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.4, 164.6, 151.3, 150.1, 121.2, 121.1, 87.3, 86.5, 40.2, 38.4, 31.3, 29.5, 29.2, 28.6, 23.6, 23.4, 15.1, 14.6, 12.2, 4.8, 4.5, 3.7, 2.7; HRMS(EI+) Calcd for $C_{12}H_{18}O_2$ [M+] 194.1307, found 194.1308.



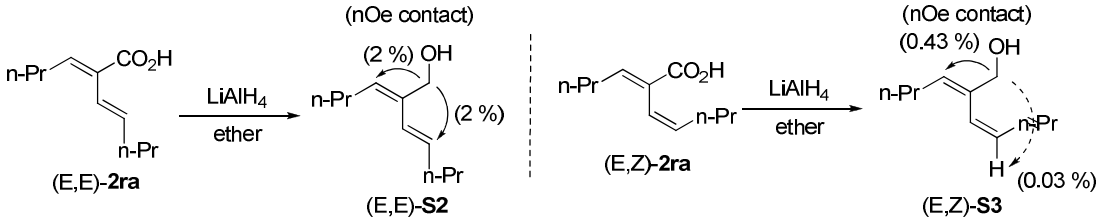
dr 1.8 : 1

Compound **6** (colorless oil); IR (thin film): 2956, 2927, 2871, 1691, 1643, 1487, 1456, 1414, 1287, 1207, 1132, 989, 923, 832, 762 cm^{-1}; (for major isomer) ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.65 (ddt, *J* = 16.8, 10.2, 6.7 Hz, H) 5.13 (d, *J* = 10.1 Hz, H), 5.10 (d, *J* = 15.6 Hz, H), 3.83 (dd, *J* = 15.2, 5.9 Hz, H), 3.74 (dd, *J* = 15.6, 6.3 Hz, H), 3.33 (dd, *J* = 10.2, 5.9 Hz, H), 3.10 (d, *J* = 10.1 Hz, H), 1.52-1.30 (m, 7H), 1.30-1.12 (m, 2H), 0.91 (t, *J* = 6.7 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.87-0.77 (m, 2H), 0.56 (t, *J* = 4.3 Hz, H), 0.54-0.45 (m, H), 0.45-0.34 (m, H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.5, 133.7, 118.1, 48.4, 45.5, 32.9, 31.0, 30.9, 23.8, 23.0, 22.5, 21.7, 18.0, 16.8, 14.9, 14.8; HRMS(EI+) Calcd for $C_{17}H_{27}NO$ [M+] 261.4024, found 261.4022.

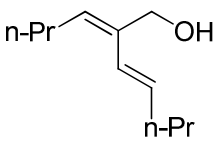


Compound (*Z,E*)-**2rc** (in Scheme 3) (colorless oil); IR (thin film): 2960, 2930, 2872, 1725, 1463, 1378, 1261, 1212, 1174, 1157, 1094, 1044, 961, 803 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.02 (d, *J* = 16.0 Hz, H), 5.75 (t, *J* = 7.8 Hz, H), 5.68 (dt, *J* = 16.1, 7.5 Hz, H), 4.28 (q, *J* = 7.4 Hz, 2H), 2.20 (q, *J* = 7.4 Hz, 2H), 2.06 (q, *J* = 7.0 Hz, 2H), 1.52- 1.37 (m ,4H), 1.33 (t, *J* = 7.4 Hz, 3H), 0.92 (t, *J* = 7.0 Hz, 3H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 136.6, 134.4, 132.3, 128.6, 61.2, 35.6, 32.3, 23.2, 23.0, 15.0, 14.5, 14.4; HRMS(EI+) Calcd for $C_{13}H_{22}O_2$ [M+] 210.3126, found 210.3125.

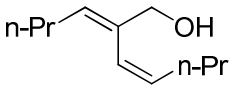
VII. Chemical Derivatization and Determination of Olefin Geometry



A solution of **2ra** in ether at 0 °C was treated with 2.05 equiv. of $LiAlH_4$ portionwise. After 1 h, the reaction was quenched with a saturated solution of Na_2SO_4. The white precipitate was filtered off and the residue was purified by chromatography (EtOAc/*n*Hex = 1:2) to give the respective alcohols. The stereochemistry of conjugated double bonds determined from the 1D-NOE experiments.

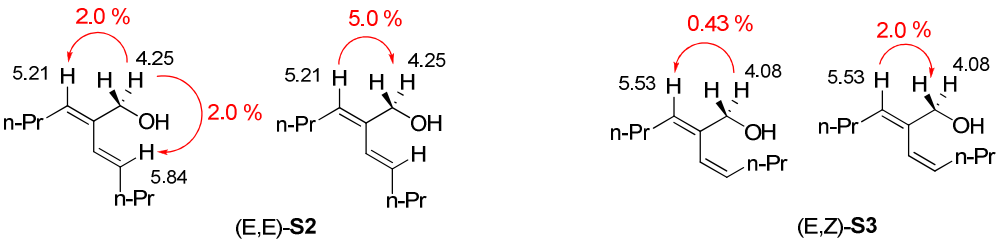


Compound (*E,E*)-**S2** (colorless oil); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.28 (d, *J* = 15.8 Hz, H), 5.84 (dt, *J* = 16.1, 7.0 Hz, H), 5.21 (t, *J* = 7.3 Hz, H), 4.25 (d, *J* = 5.9 Hz, 2H), 2.15 (q, *J* = 7.4 Hz, 2H), 2.12 (q, *J* = 7.0 Hz, 2H), 1.43 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.4, 131.9, 130.8, 125.3, 66.3, 36.2, 30.0, 24.5, 23.3, 14.5, 14.4.

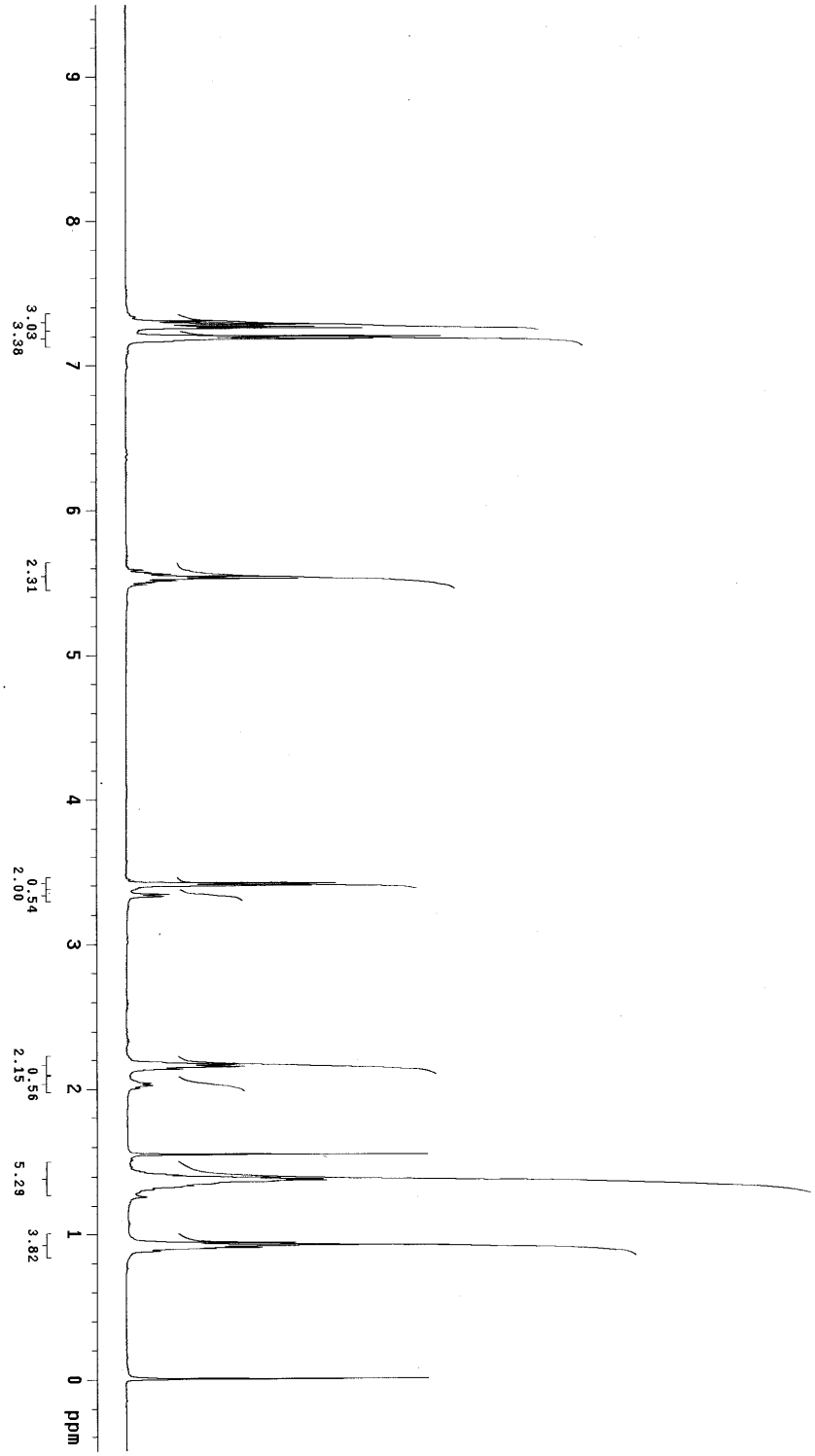


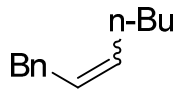
Compound (*E,Z*)-**S3** (colorless oil); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (d, *J* = 11.7 Hz, H), 5.59 (dt, *J* = 11.8, 7.0 Hz, H), 5.53 (t, *J* = 7.0 Hz, H), 4.08 (s, 2H), 1.98 (m, 4H), 1.38 (m, 4H), 0.90 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.0, 135.1, 129.6, 125.4, 67.9, 31.9, 31.5, 23.3, 23.2, 14.9, 14.6.

[Key NOE Contacts]



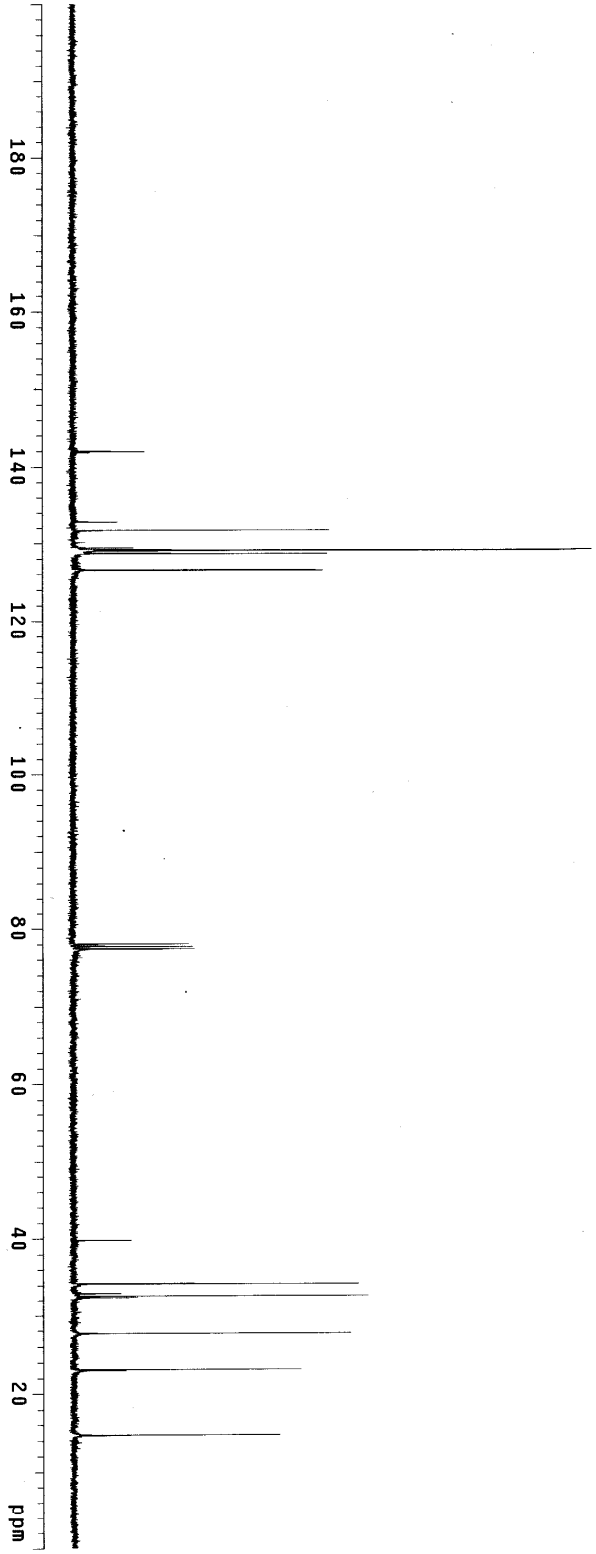
VIII. Copies of NMR Spectra

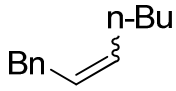




3s (*E*/*Z* = 1 : 3.8)

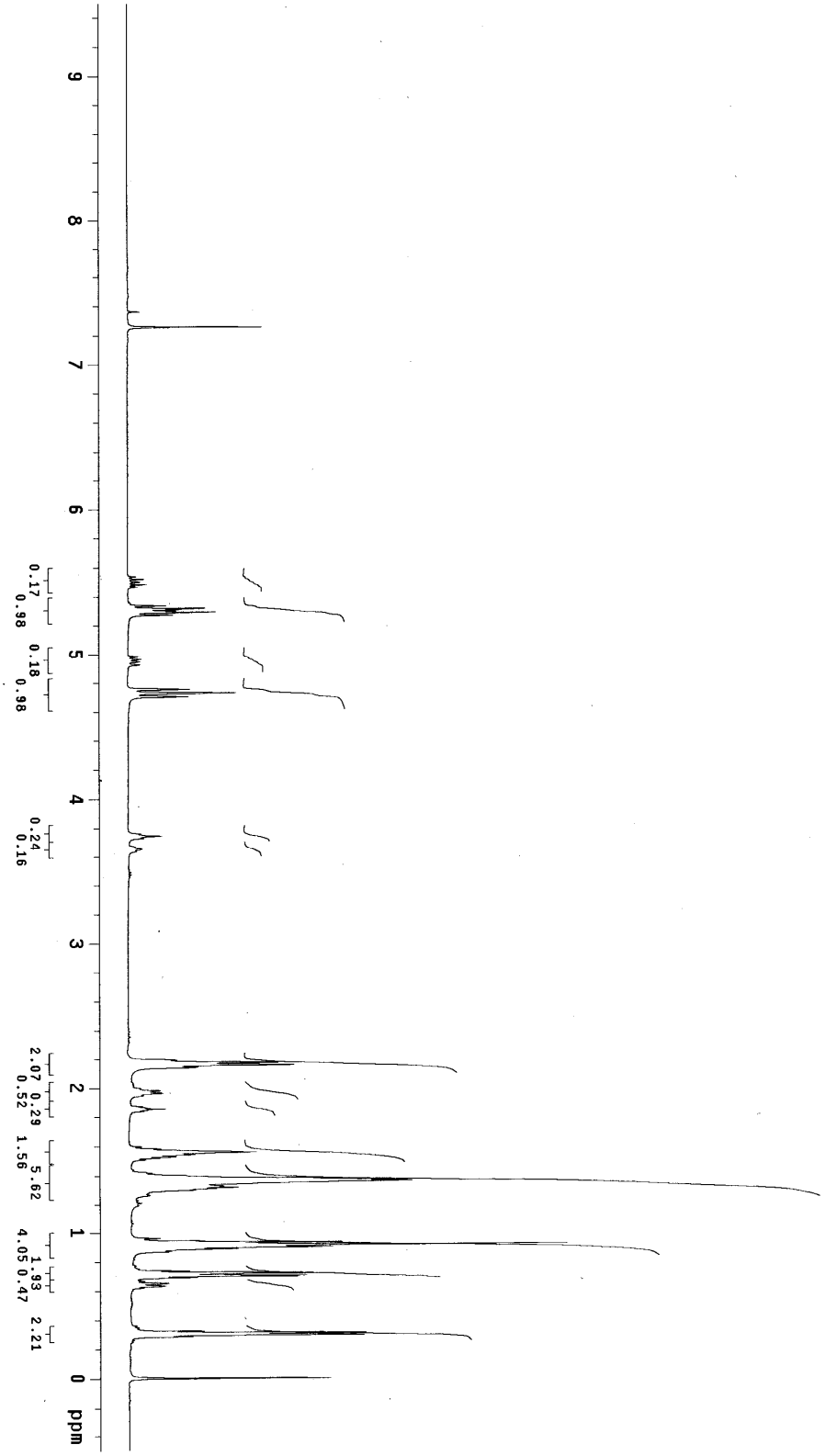
s2pu1

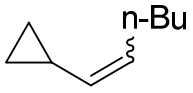




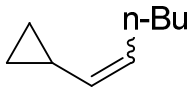
3s (*E*/*Z* = 1 : 3.8)

s2pul

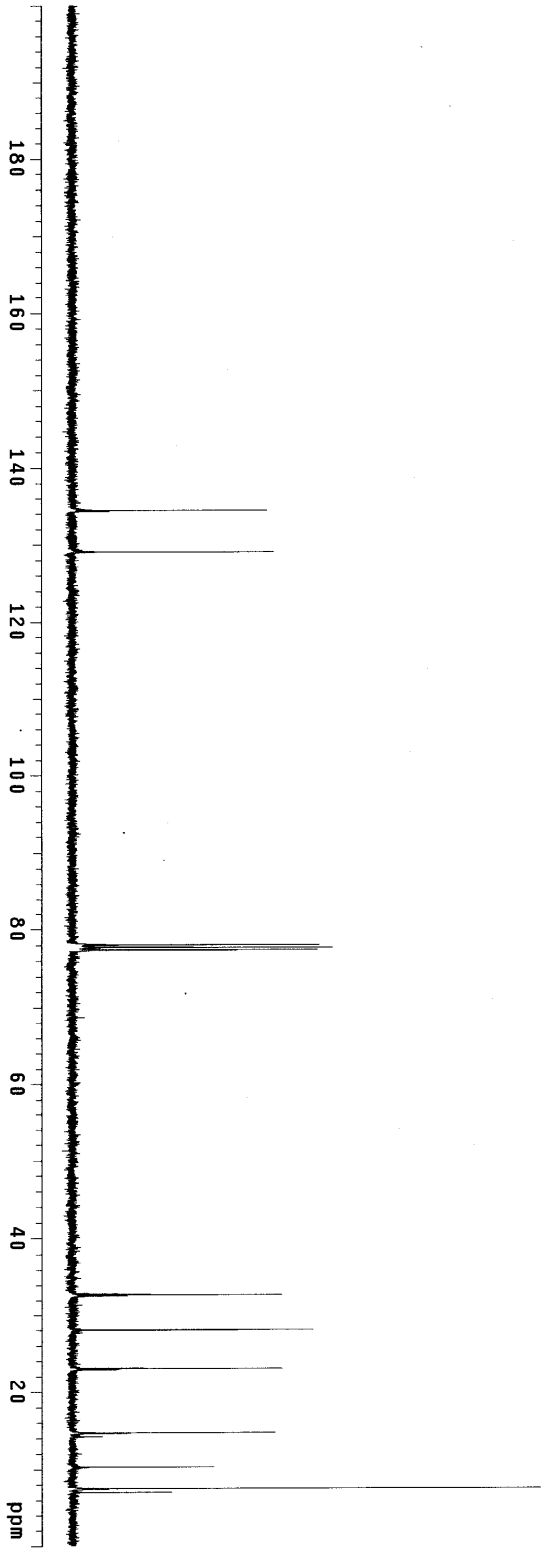

9
8
7
6
5
4
3
2
1
0
ppm
0.17
0.98
0.18
0.98
0.24
0.16
2.07
0.29
0.52
1.56
5.62
4.05
1.93
0.47
2.21

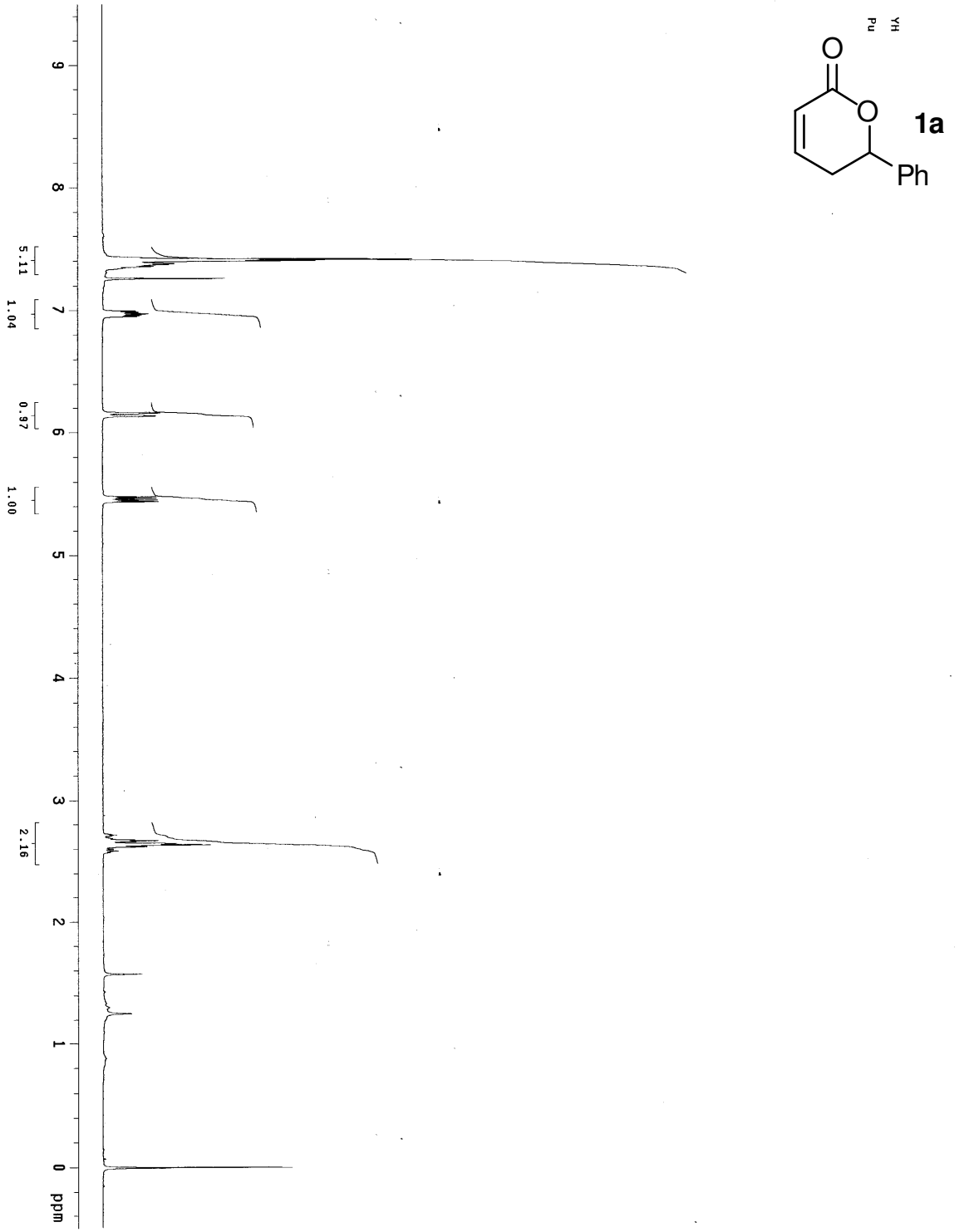

n-Bu

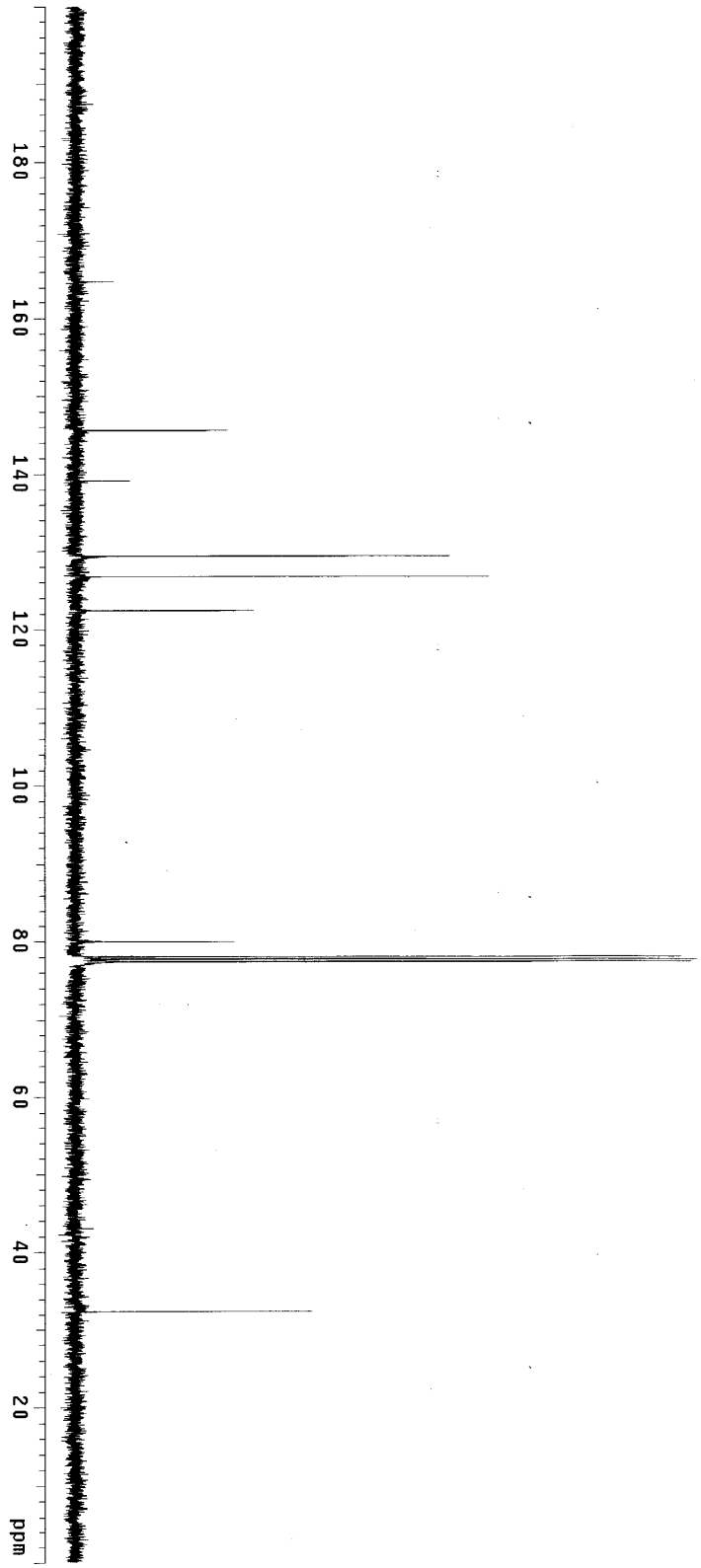
3u (*E*/*Z* = 1 : 5.3)

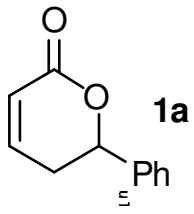


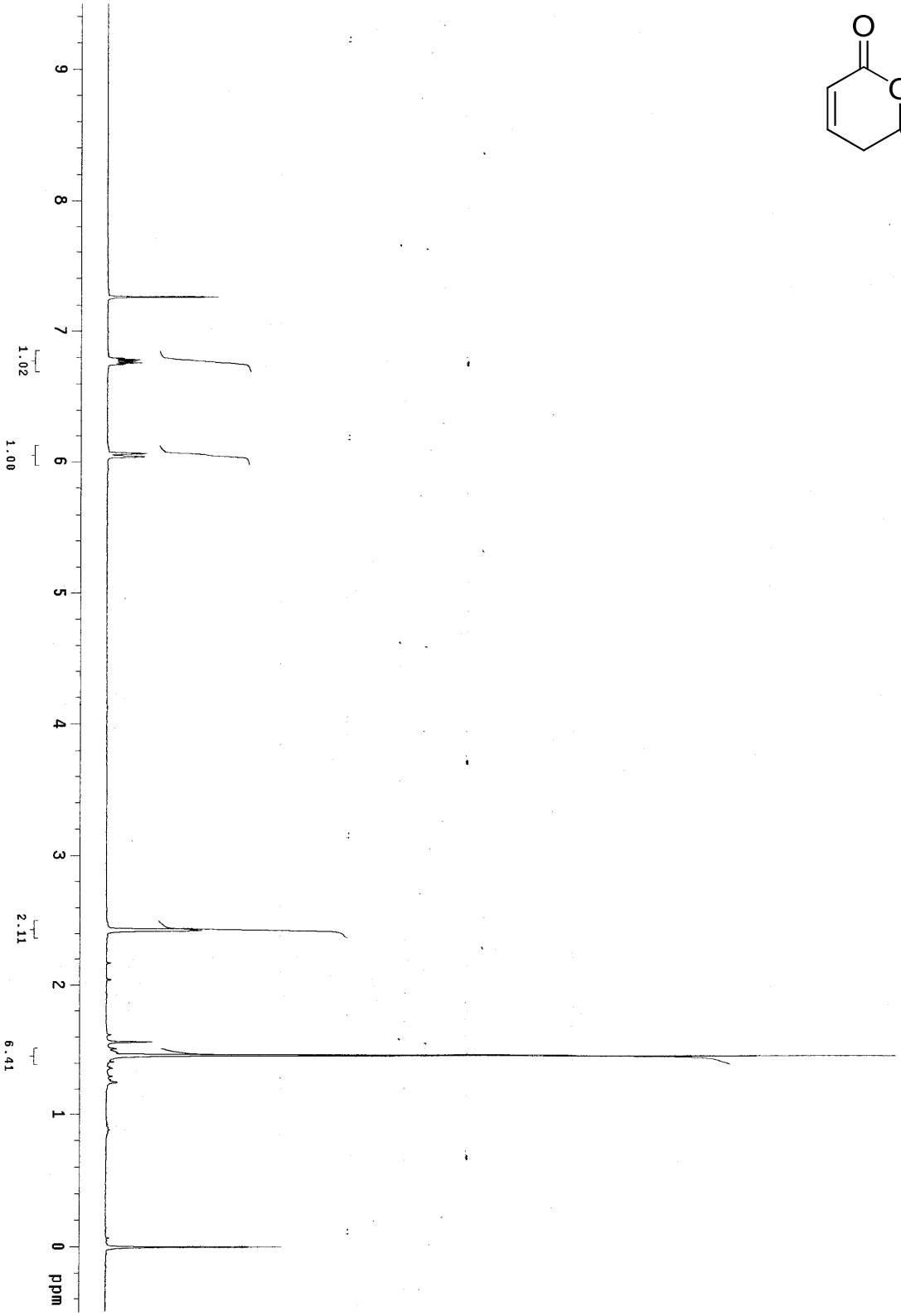
3u (*E*/*Z* = 1 : 5.3)

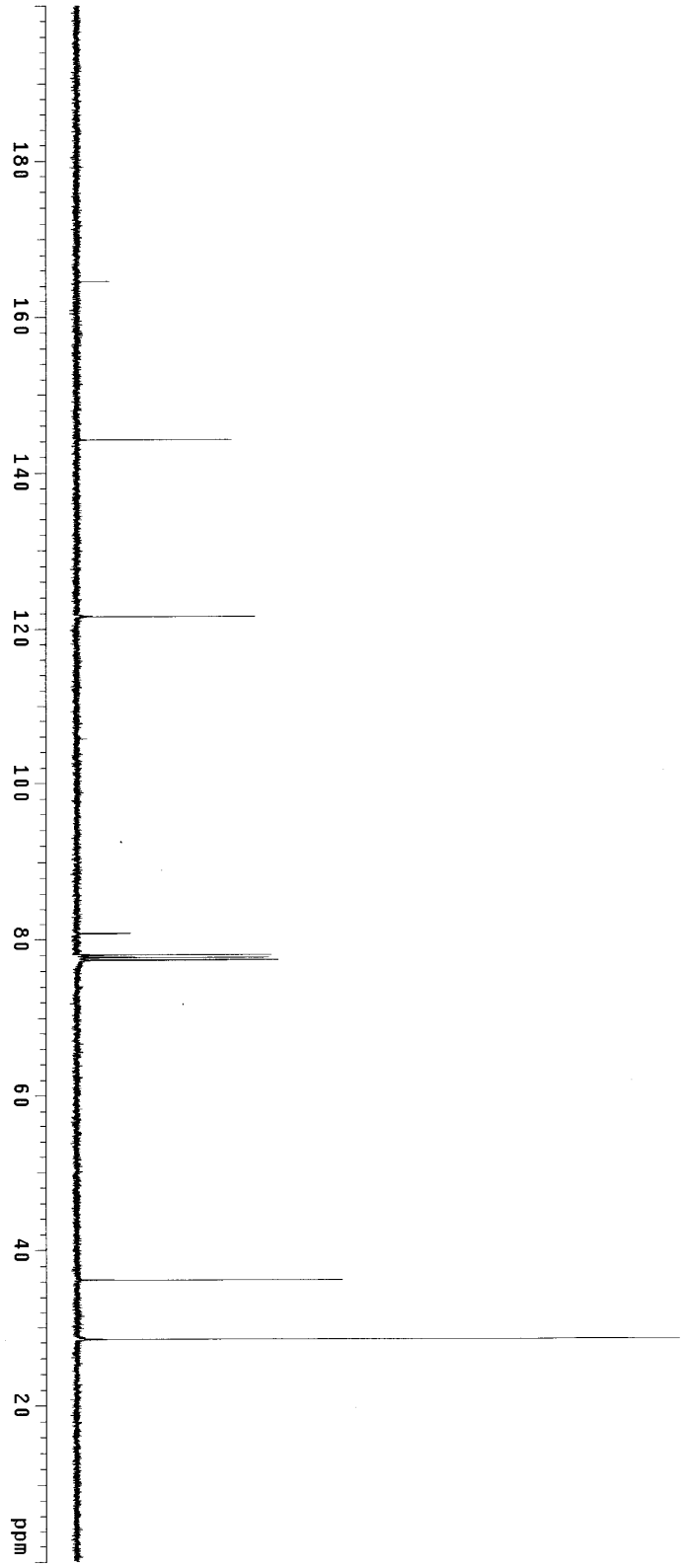


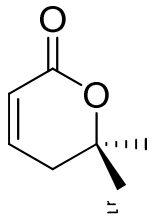

YH
Pu
O
O
1a
Ph
9
8
7
6
5
4
3
2
1
0
ppm
5.11
1.04
0.97
1.00
2.16


180
160
140
120
100
80
60
40
20
ppm

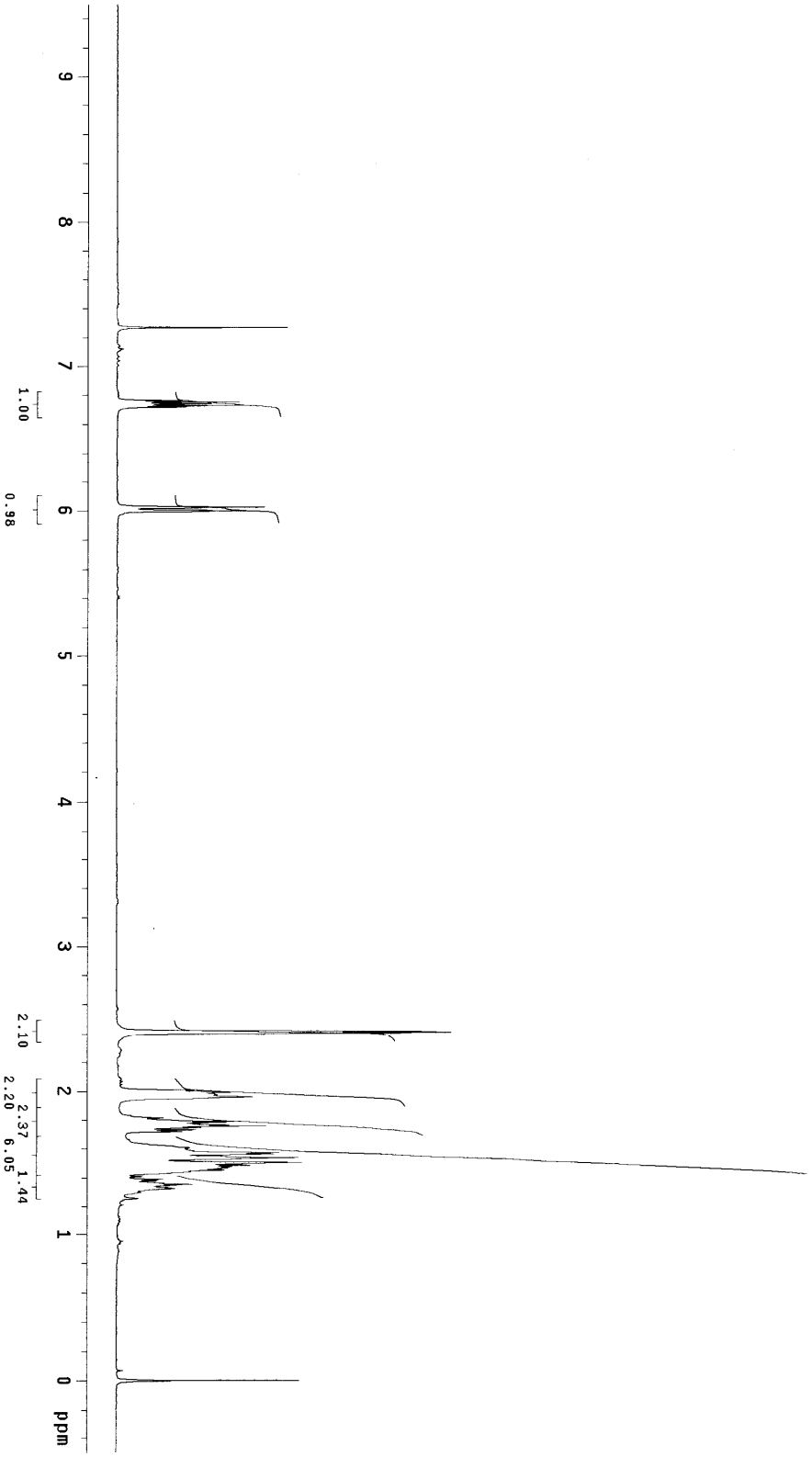

O
O
Ph
1a

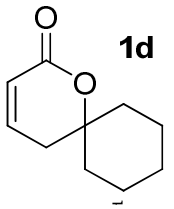

1c
6.41
2.11
1.00
1.02
ppm
0
1
2
3
4
5
6
7
8
9

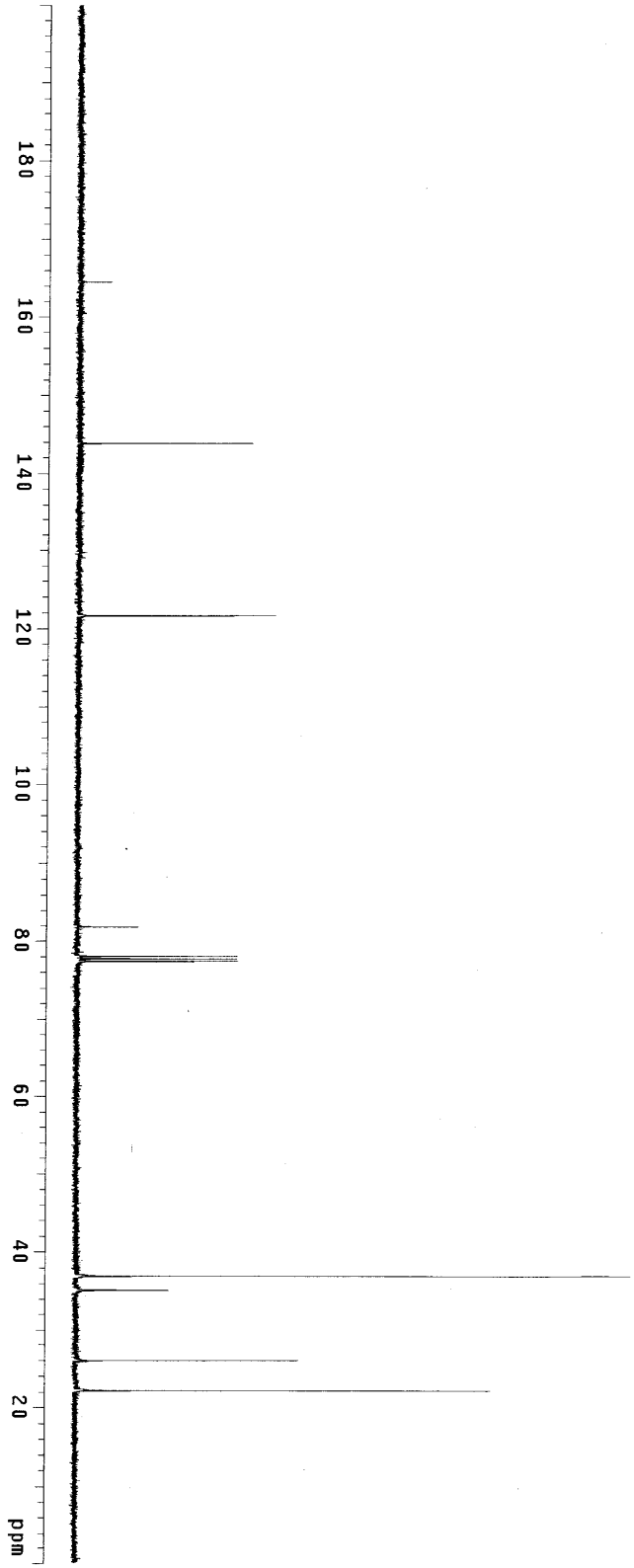


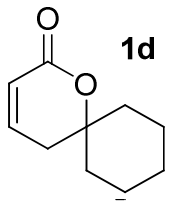


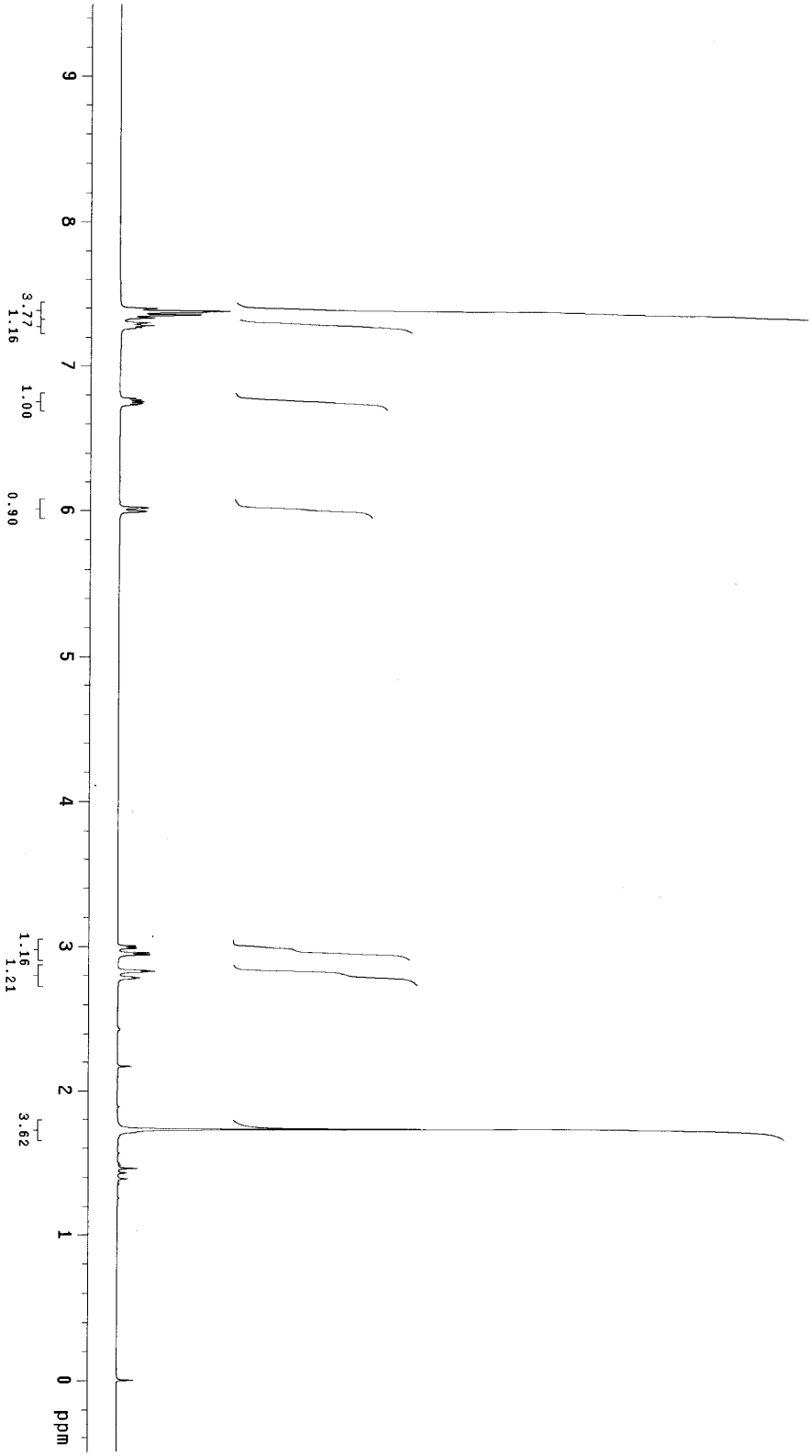
1c

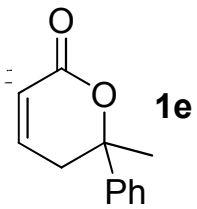

1.00
0.98
2.10
2.20
2.37
6.05
1.44
9
8
7
6
5
4
3
2
1
0
ppm


O
O
1d

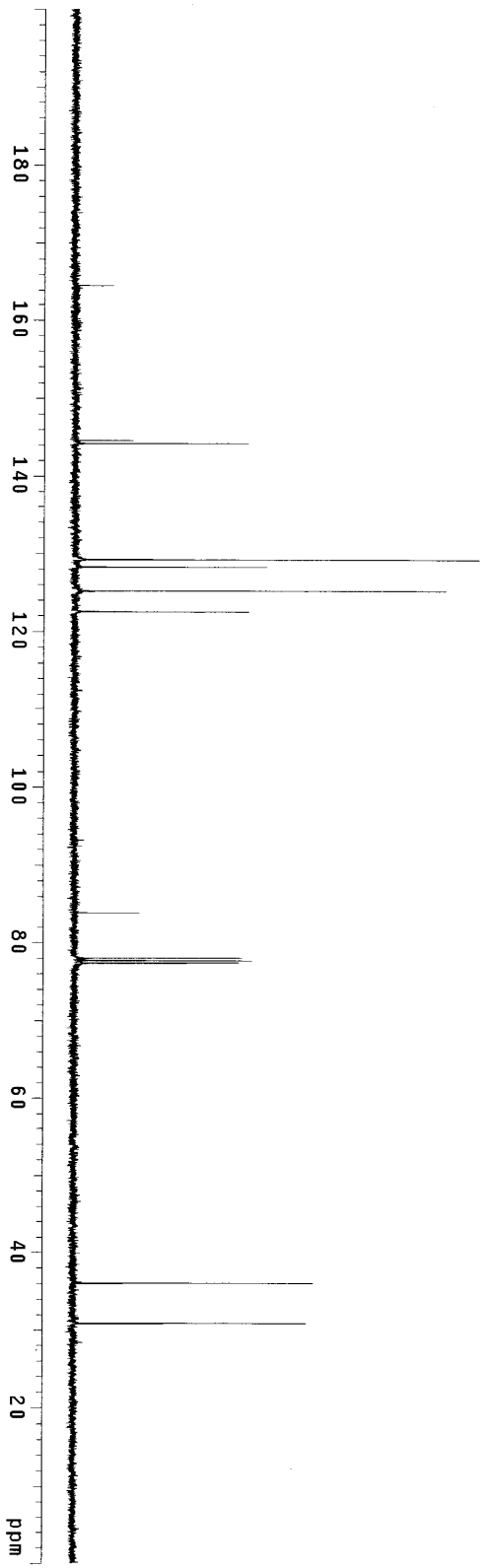

180
160
140
120
100
80
60
40
20
ppm

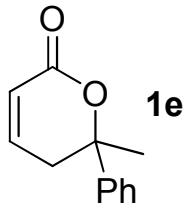

O
O
1d



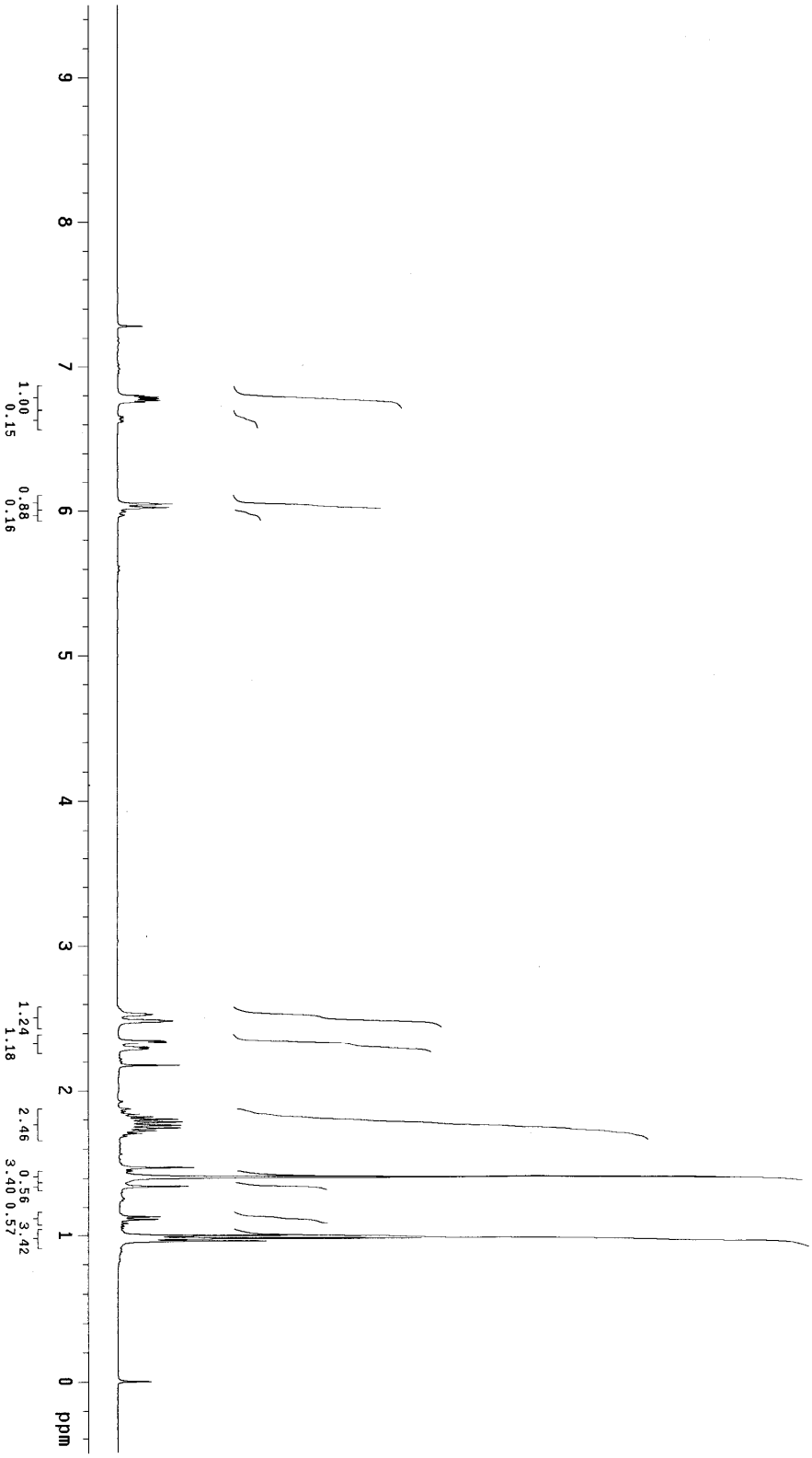


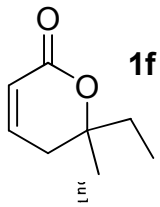
1e

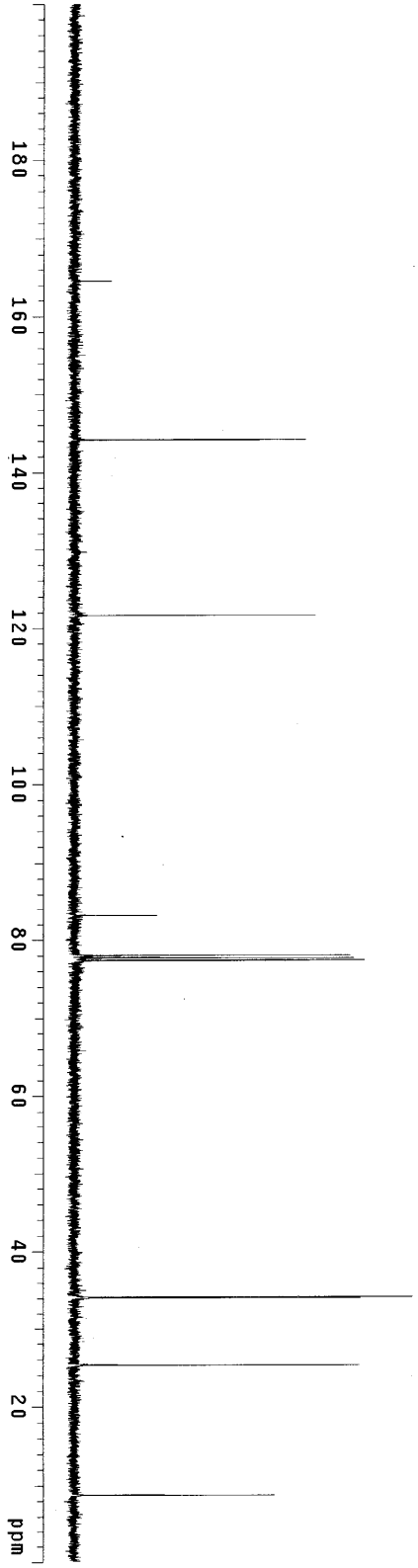


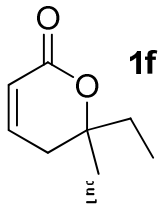


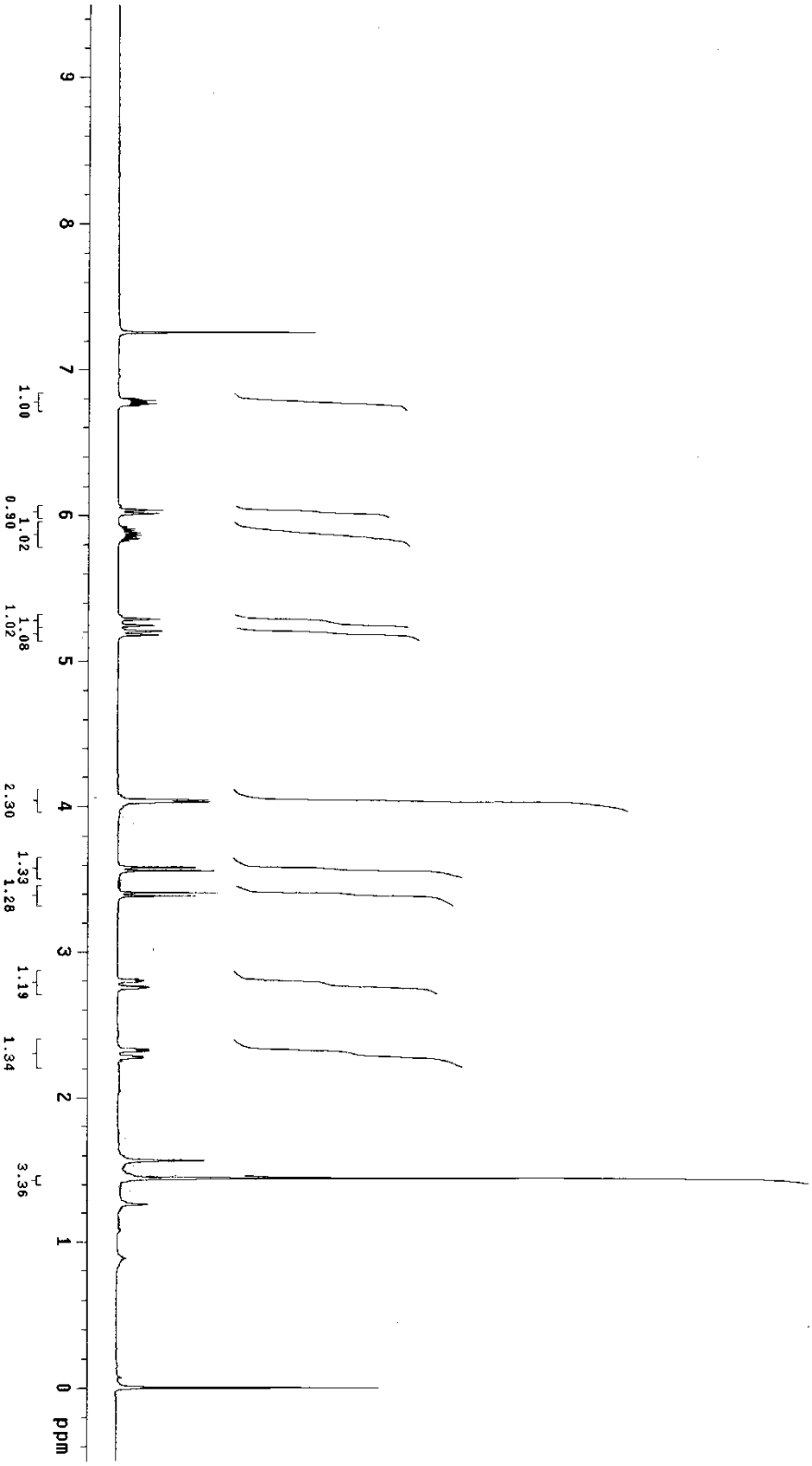
1e

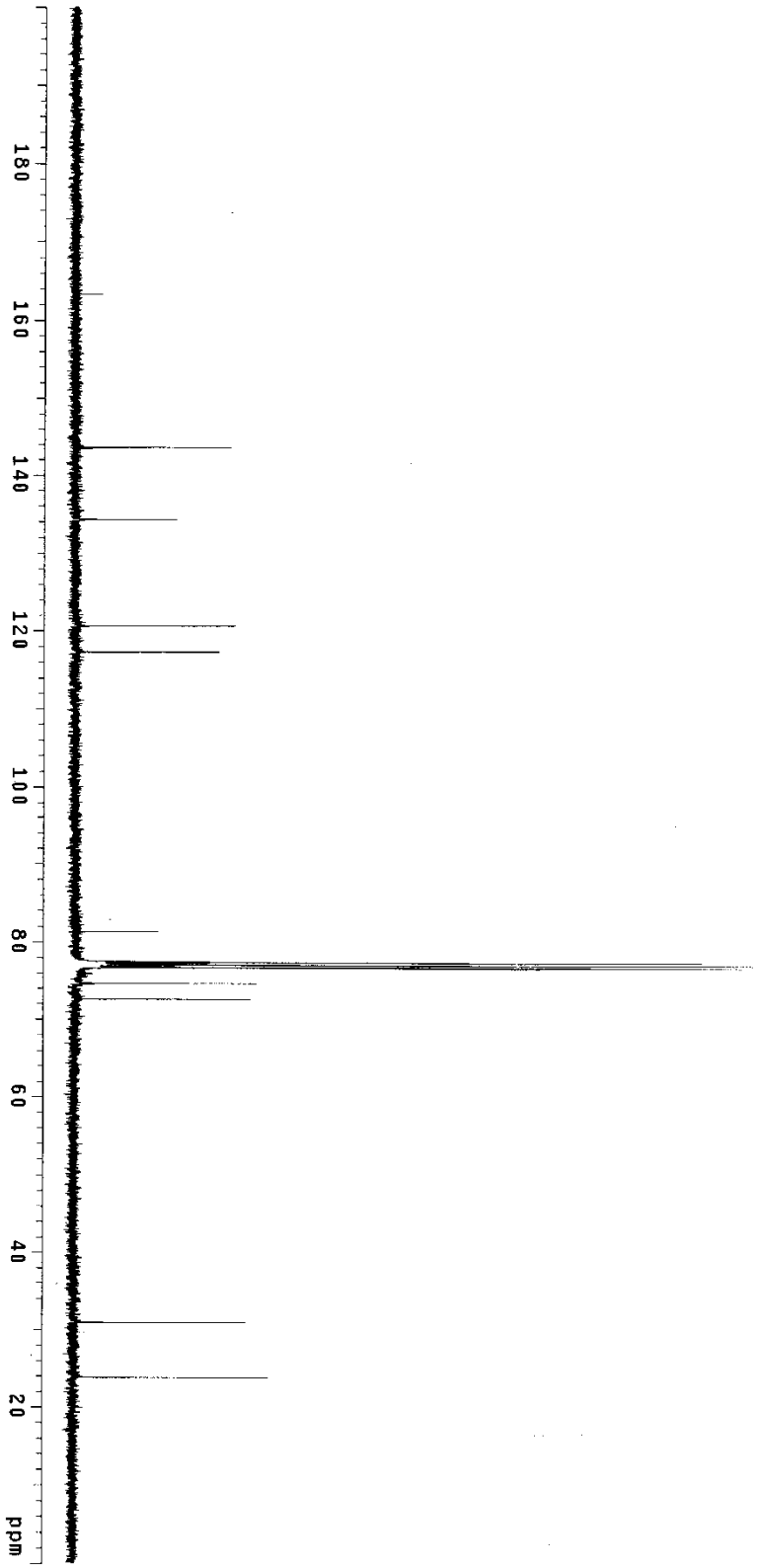

1.00
0.15
0.88
0.16
1.24
1.18
2.46
0.56
3.40
0.57
3.42
9
8
7
6
5
4
3
2
1
0
ppm

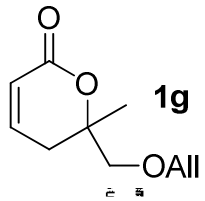

O
O
1f

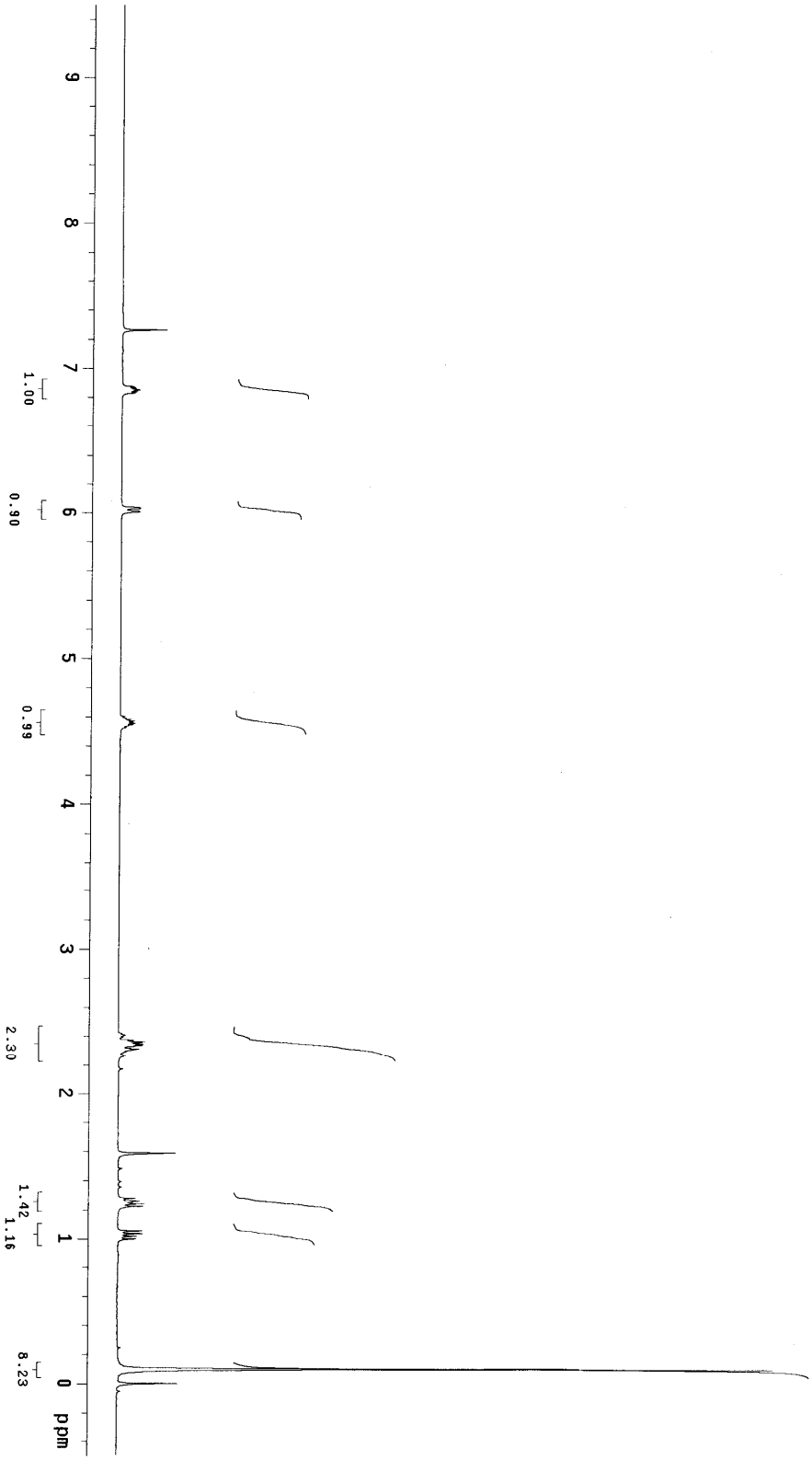

180
160
140
120
100
80
60
40
20
ppm

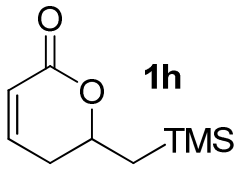

O
O
1f

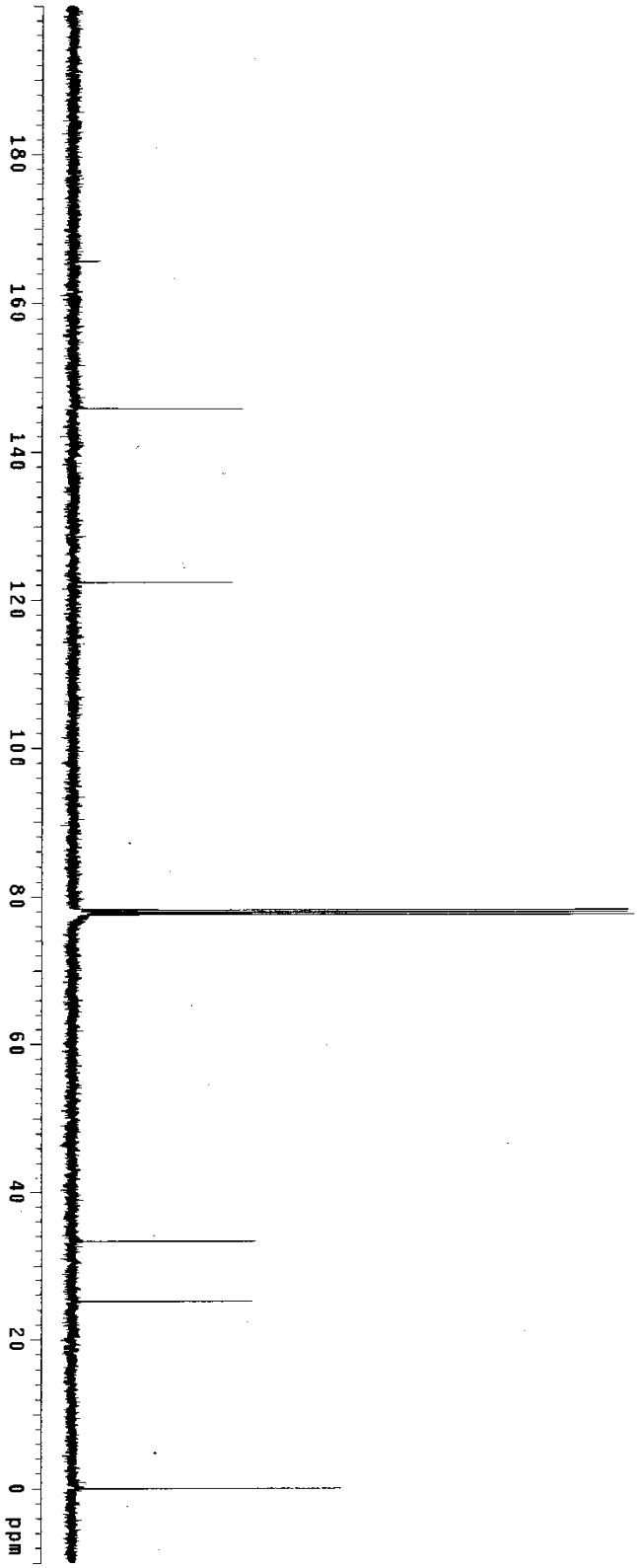

1g
OAll
1.00
1.02
0.90
1.08
1.02
2.30
1.33
1.28
1.19
1.34
3.36
ppm

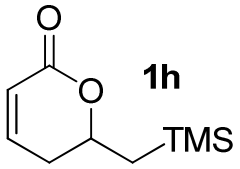

180
160
140
120
100
80
60
40
20
ppm


O
O
1g
OAll

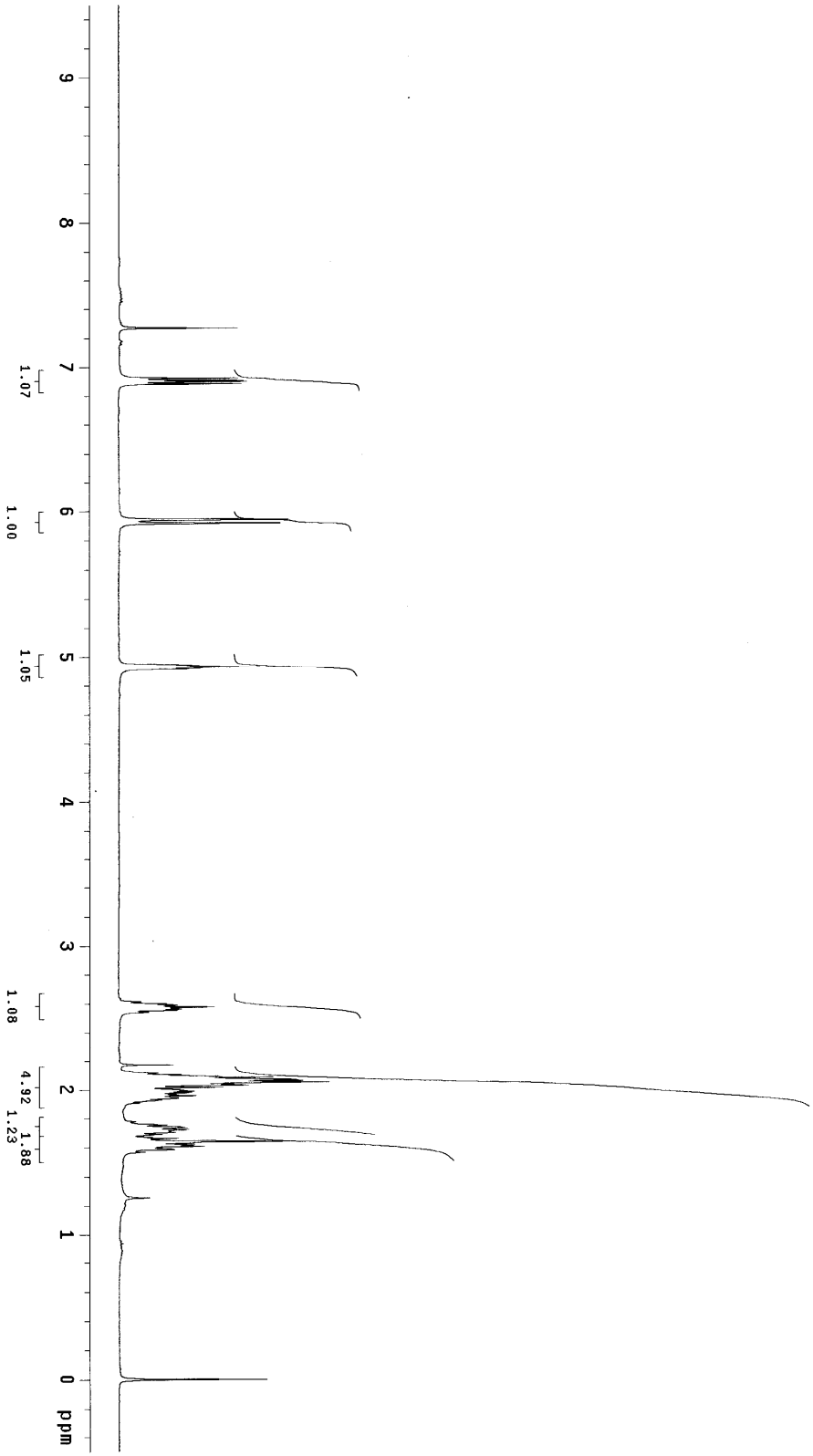

9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.90
0.99
2.30
1.42
1.16
8.23

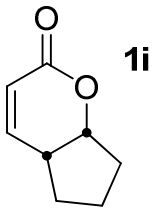

O
O
1h
TMS

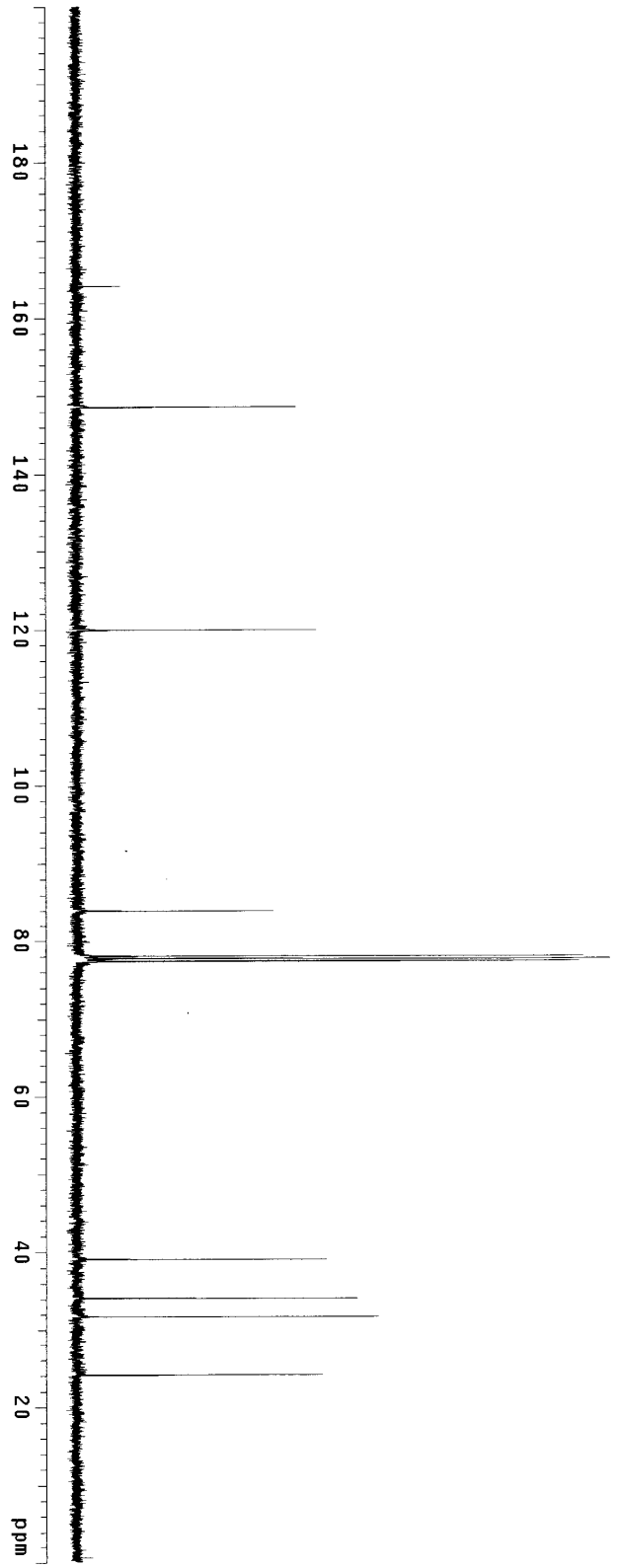


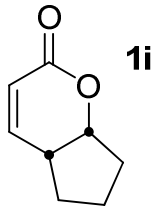


1h


9
8
7
6
5
4
3
2
1
0
ppm
1.07
1.00
1.05
1.08
4.92
1.88
1.23


O
O
1i

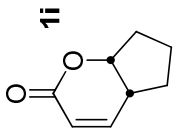

180
160
140
120
100
80
60
40
20
ppm


O
O
1i

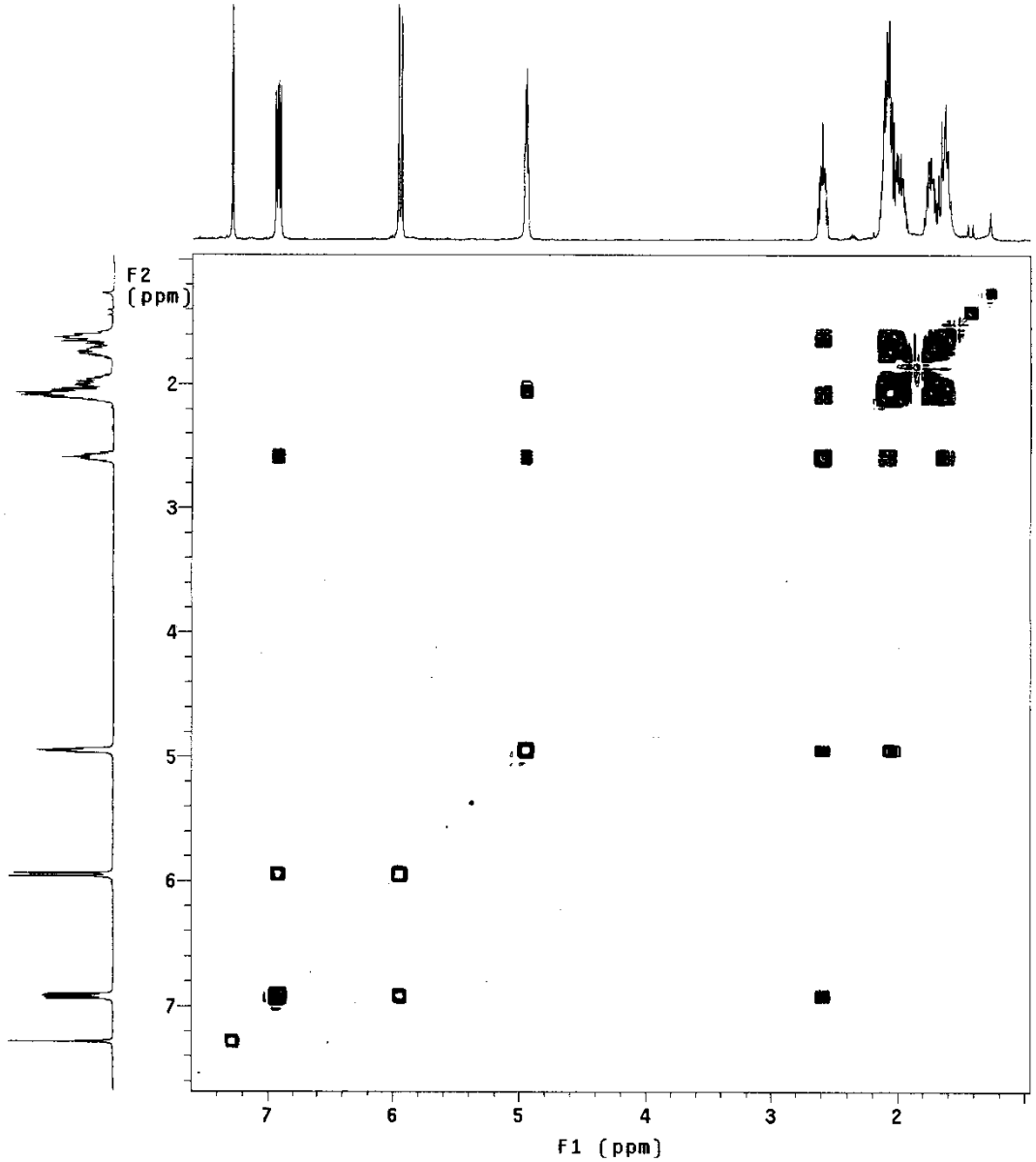
YHS-XV-107

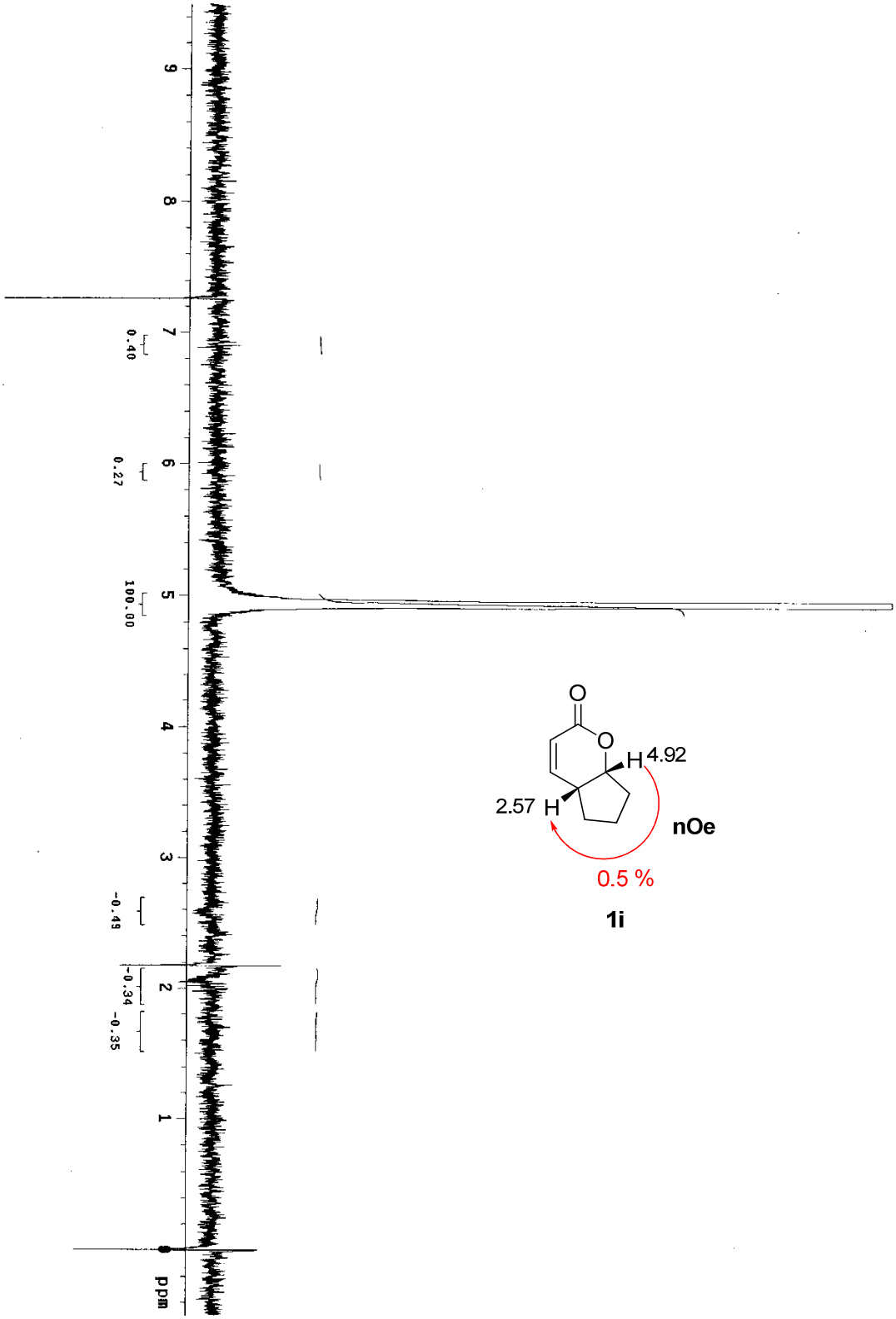
Pulse Sequence: COSY
Solvent: CDCl3
Ambient temperature
User: 1-12-87
Mercury-400BB "nmr400HY"

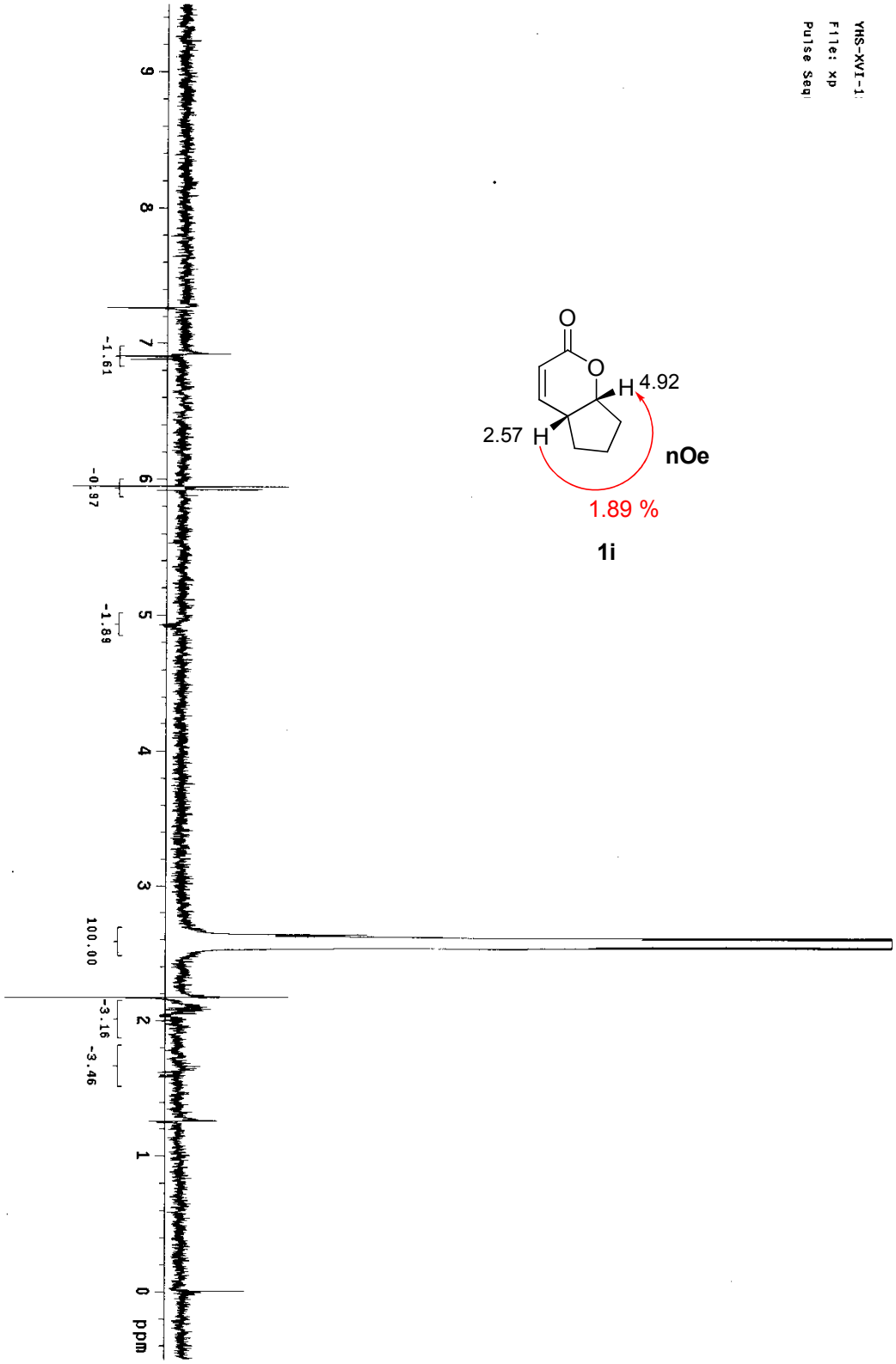
Relax. delay 1.000 sec
Acq. time 0.170 sec
Width 6009.6 Hz
2D Width 6009.6 Hz
2 repetitions
128 increments
OBSERVE H1, 399.8379254 MHz
DATA PROCESSING
Sq. sine bell 0.085 sec
F1 DATA PROCESSING
Sq. sine bell 0.021 sec
FT size 2048 x 2048
Total time 6 min, 46 sec

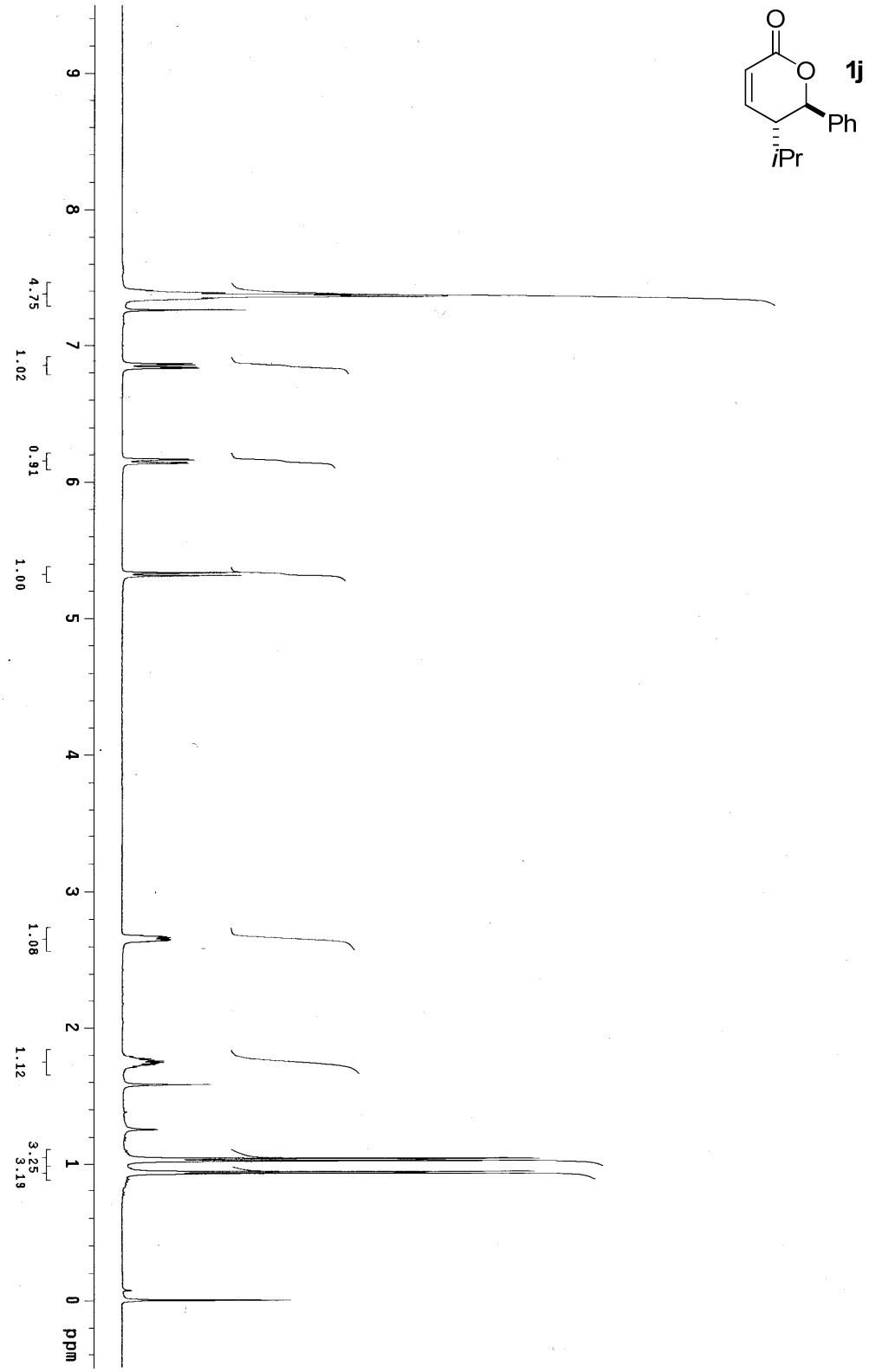


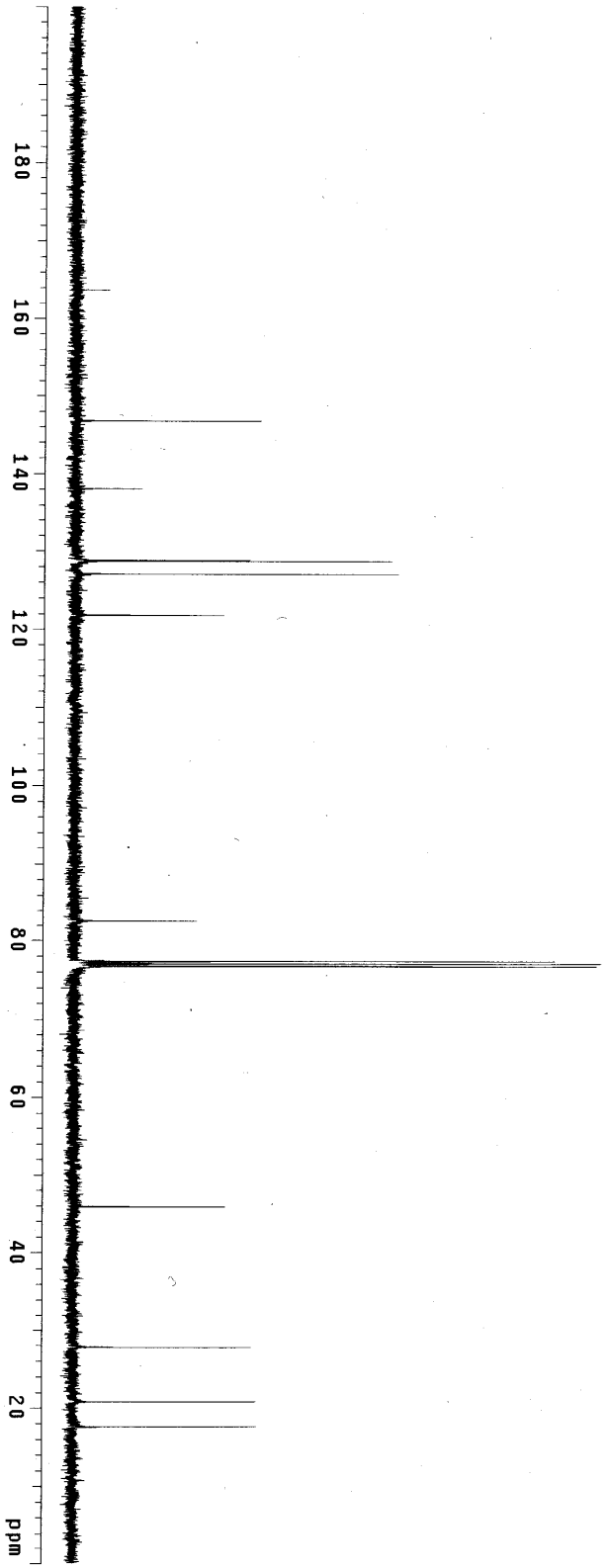
1i

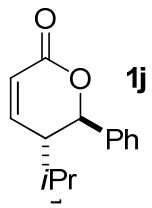


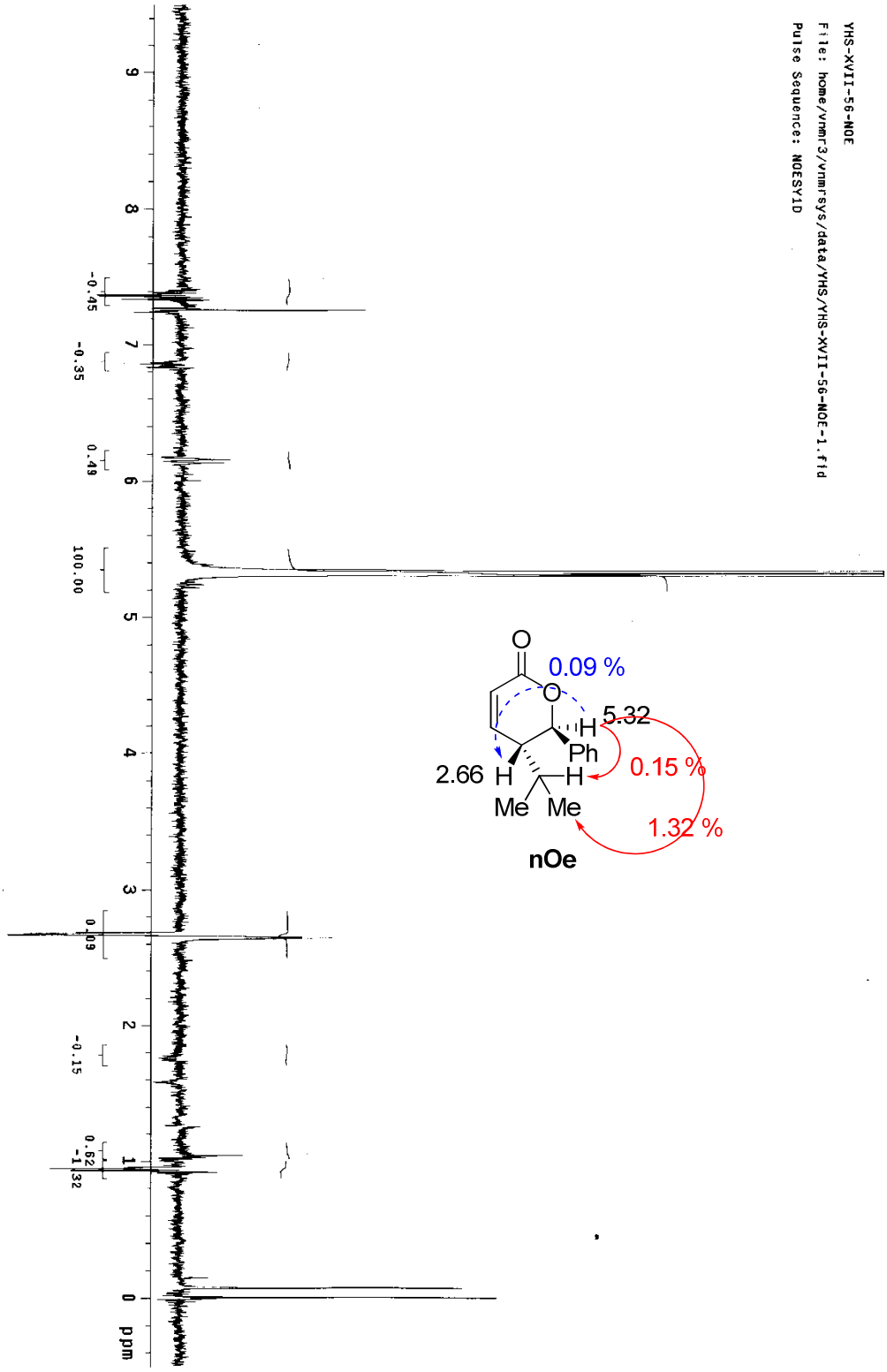

ppm
9
8
7
6
5
4
3
2
1
0.40
0.27
100.00
-0.49
-0.34
-0.35
O
O
H
4.92
2.57
H
nOe
0.5 %
1i

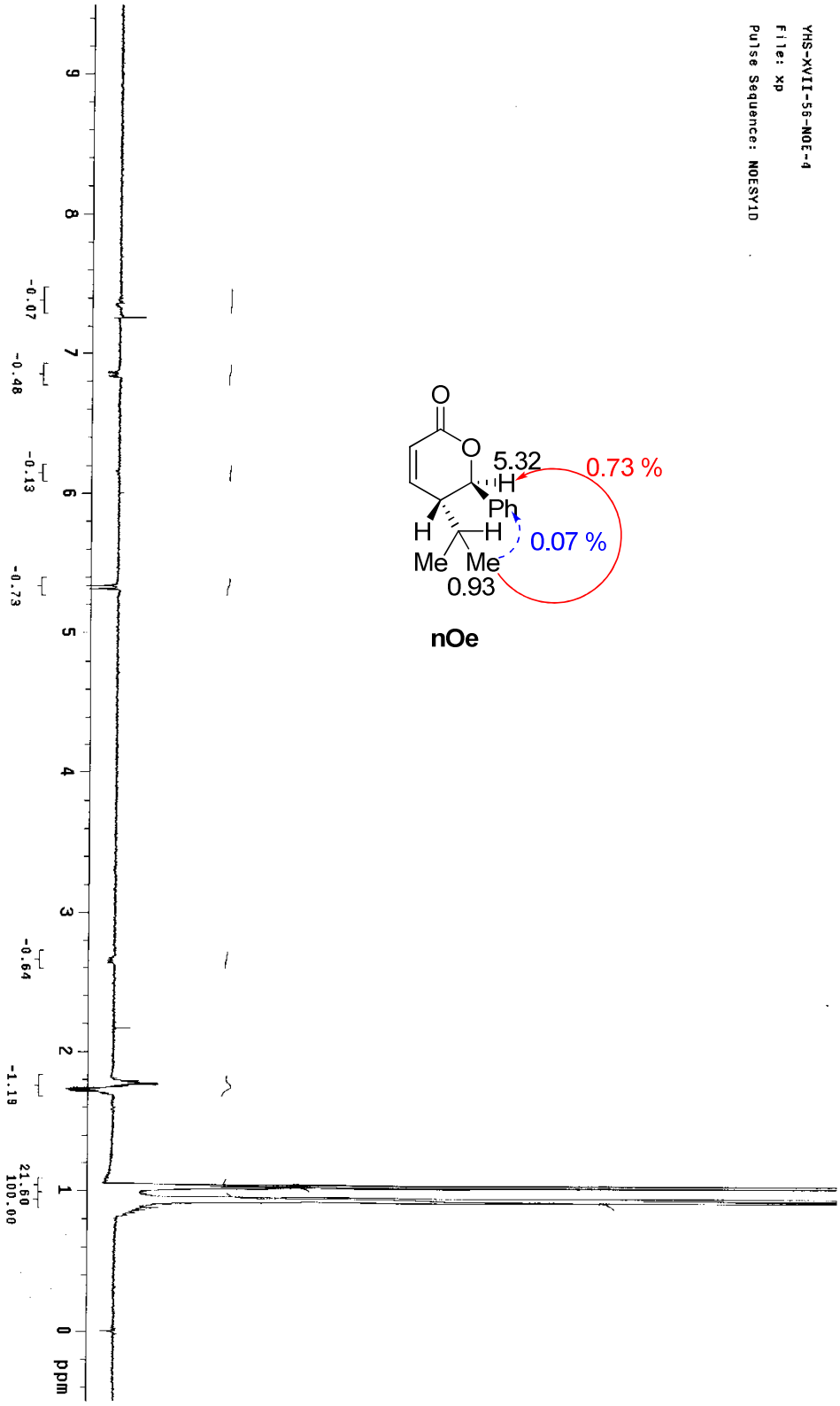

YHS-XVI-1
File: xp
Pulse Seq
O
O
H 4.92
2.57 H
nOe
1.89 %
1i
-1.61
-0.97
-1.89
100.00
-3.16
-3.46
ppm

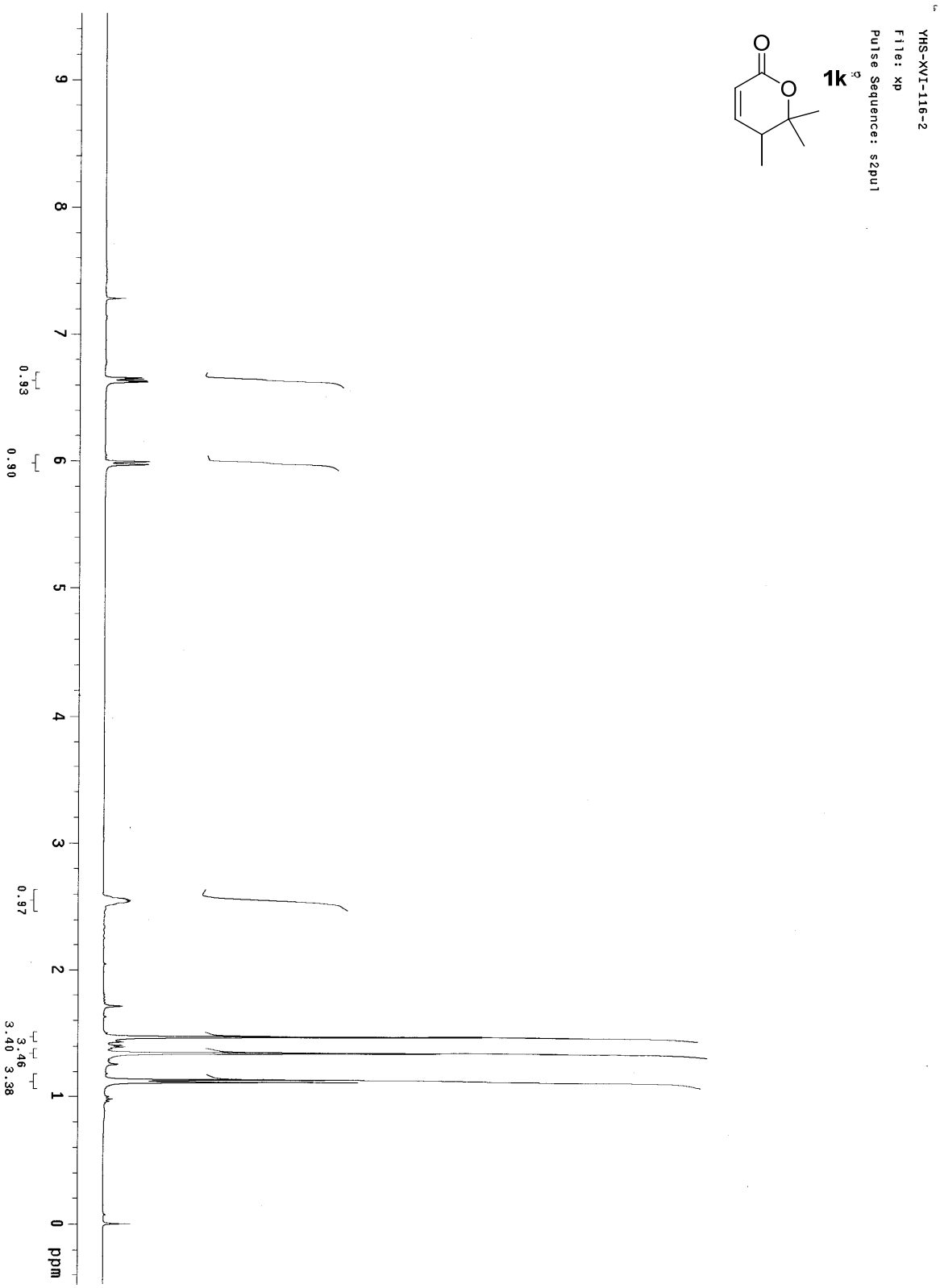

1j
Ph
iPr
9
8
7
6
5
4
3
2
1
0
ppm
4.75
1.02
0.91
1.00
1.08
1.12
3.25
3.19

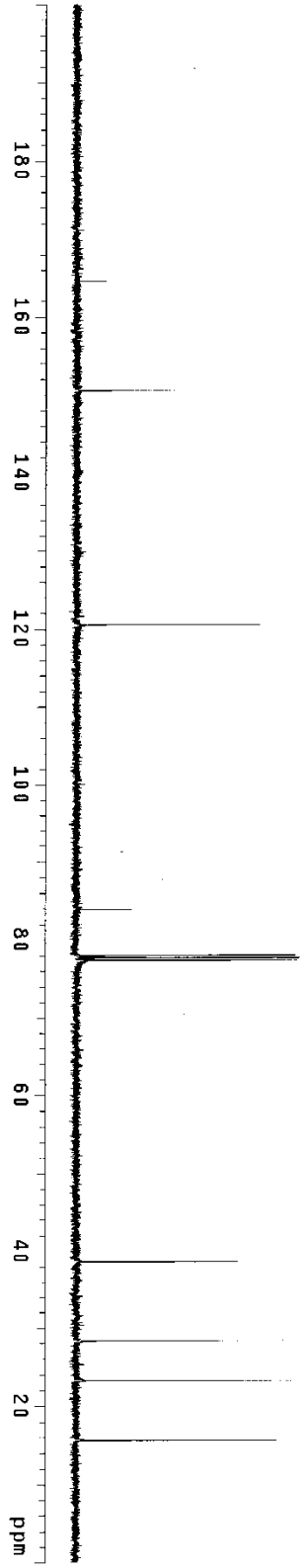

180
160
140
120
100
80
60
40
20
ppm

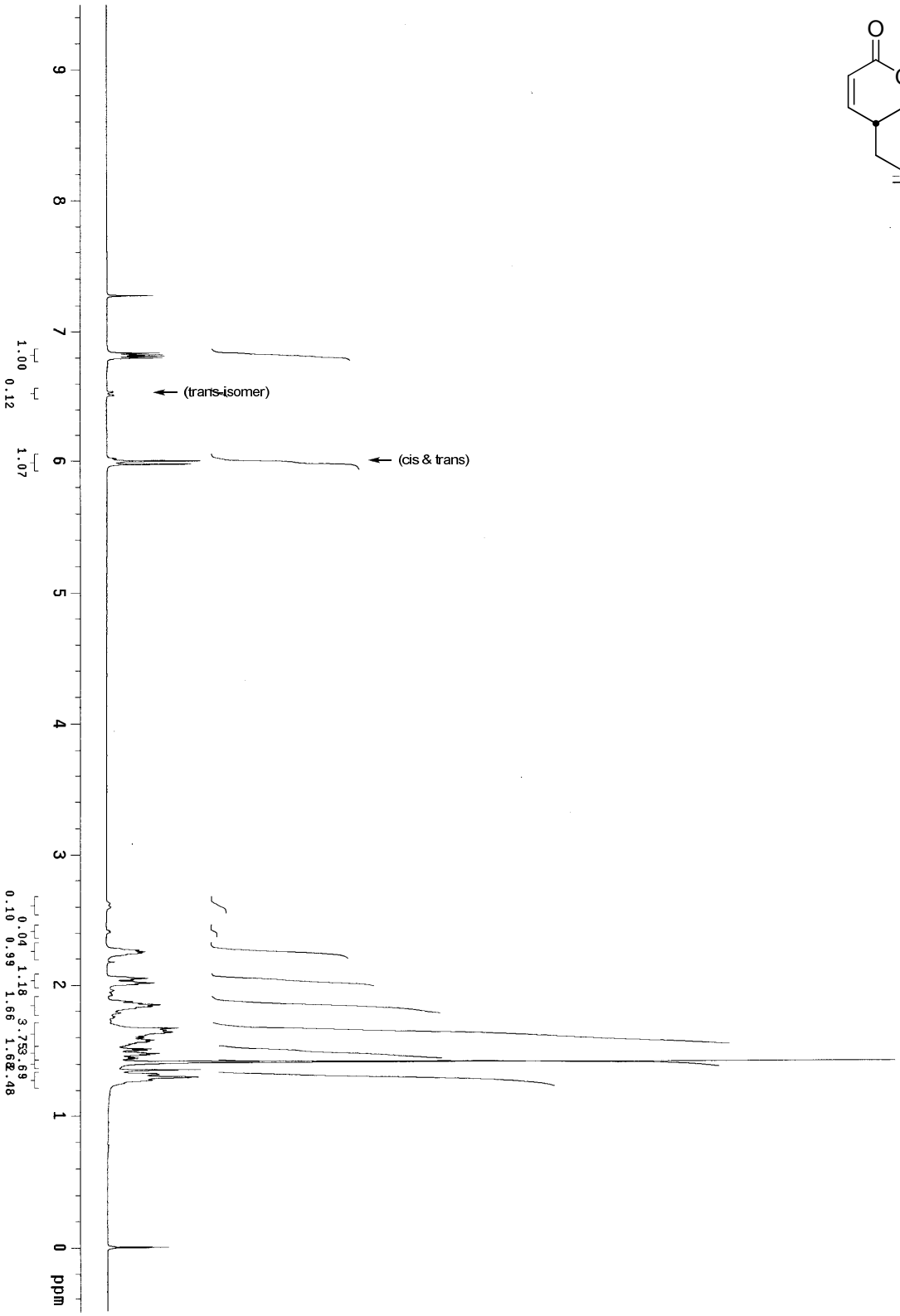

O
O
1j
Ph
iPr

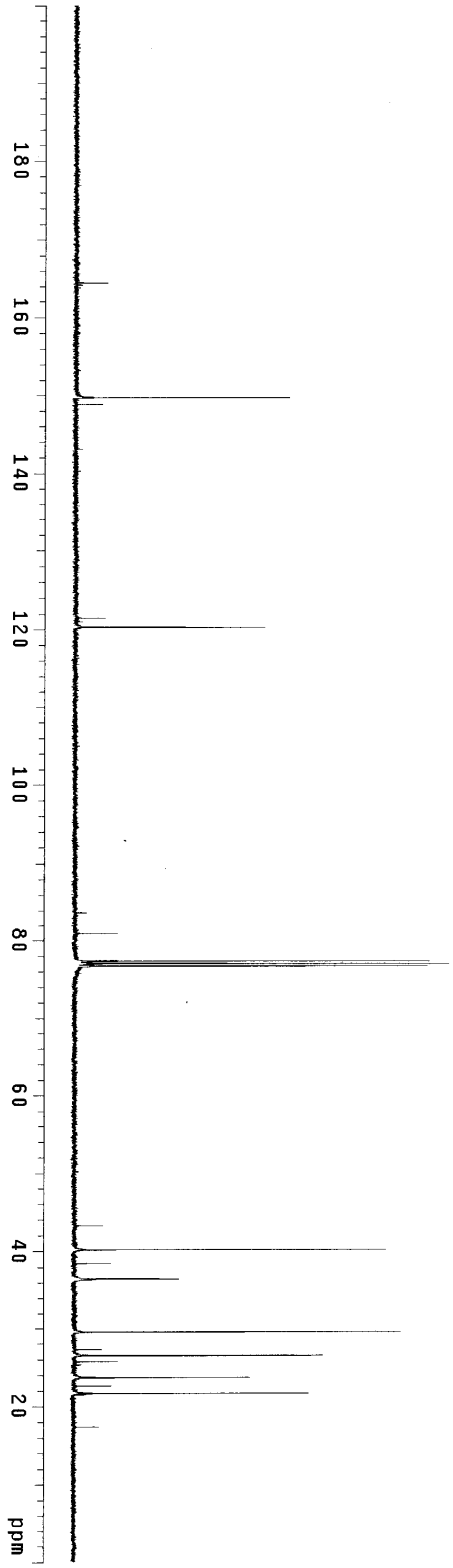

YHS-XVII-56-NOE
File: home/vnmr3/vnmrsys/data/YHS/YHS-XVII-56-NOE-1.fid
Pulse Sequence: NOESY1D
ppm
0.09 %
5.32
Ph
2.66
0.15 %
Me
Me
1.32 %
nOe

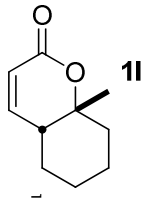

YHS-XVII-56-NOE-4
File: xp
Pulse Sequence: NOESY1D
O
O
5.32
H
Ph
H
H
Me
Me
0.93
0.73 %
0.07 %
nOe
9
8
7
6
5
4
3
2
1
0
ppm
-0.07
-0.48
-0.13
-0.73
-0.64
-1.19
21.60
100.00


YHS-XVI-116-2
File: xp
Pulse Sequence: s2pul
1k
0.93
0.90
0.97
3.46
3.40
3.38
9
8
7
6
5
4
3
2
1
0
ppm


YHS-XVI-116-2-C13
File: xp
Pulse Sequence: s2pul
1k
O
O
180
160
140
120
100
80
60
40
20
ppm


1l
(trans-isomer)
(cis & trans)
ppm
9
8
7
6
5
4
3
2
1
0
1.00
0.12
1.07
0.04
0.10
1.18
0.99
3.75
1.66
3.69
1.68
2.48

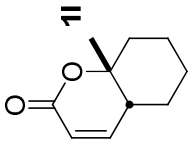

180
160
140
120
100
80
60
40
20
ppm

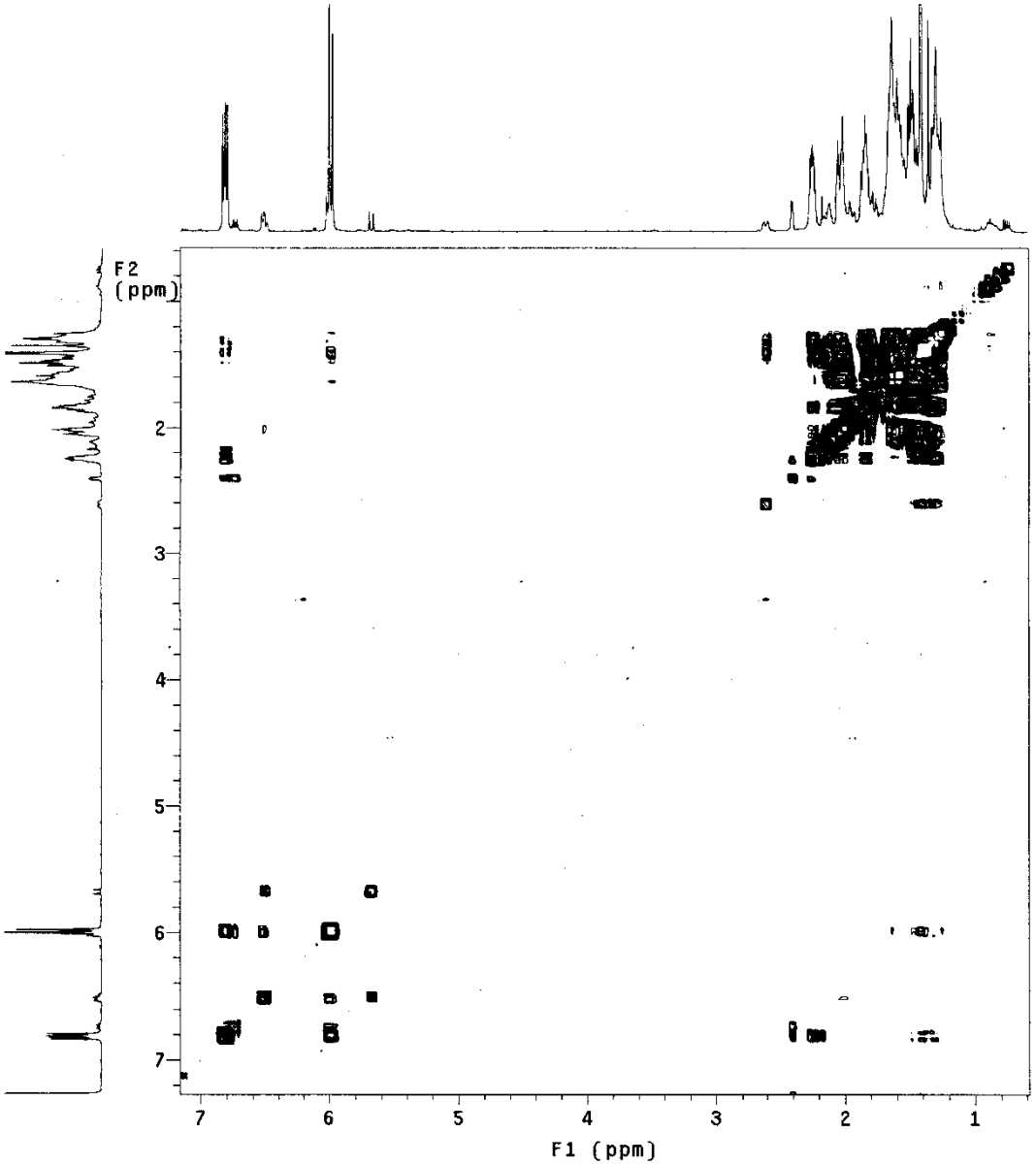

O
O
1l

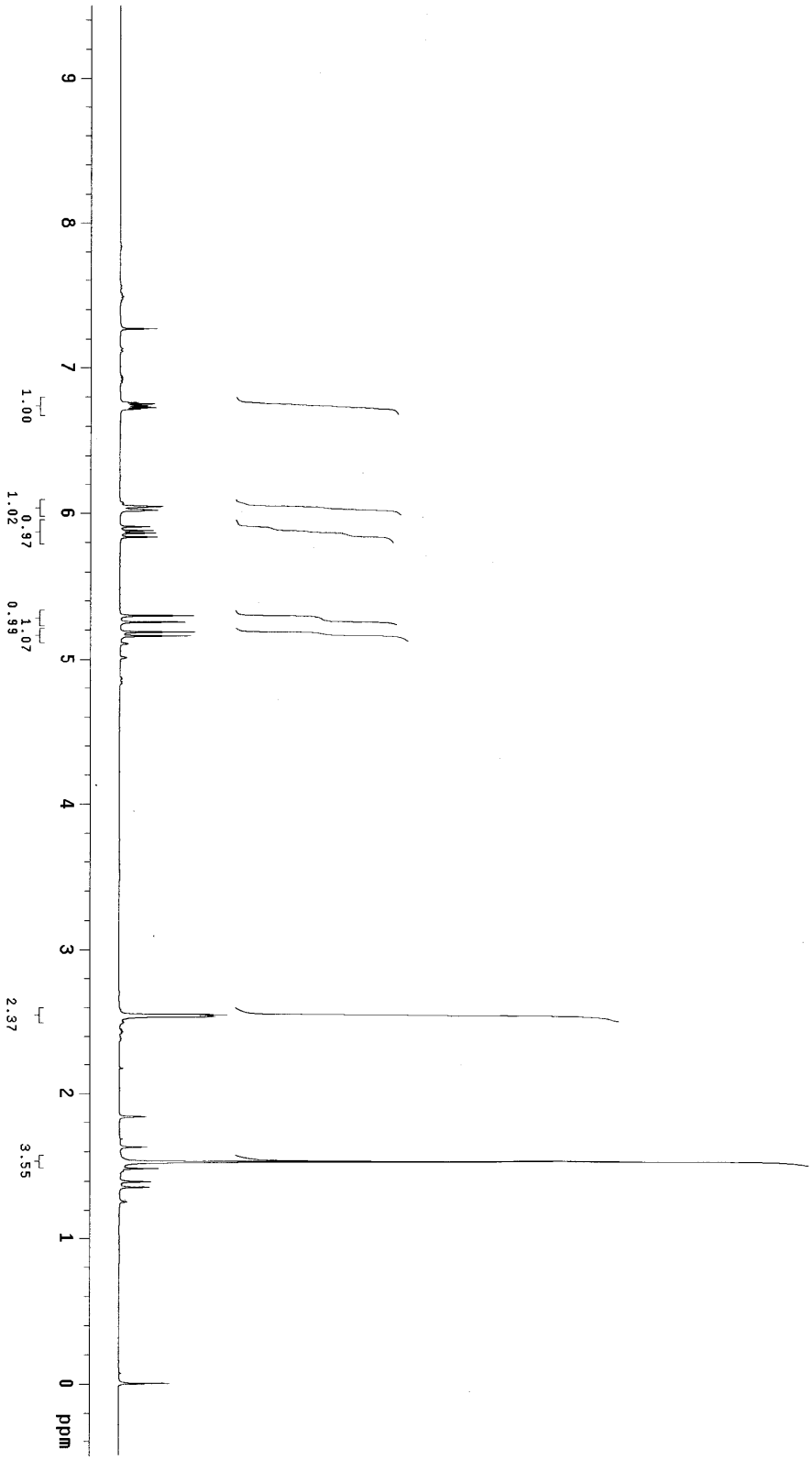
YHS-XVI-5

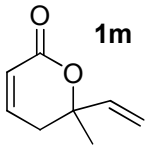
Pulse Sequence: COSY
Solvent: CDCl3
Ambient temperature
User: 1-12-87
Mercury-400BB "nmr400HY"

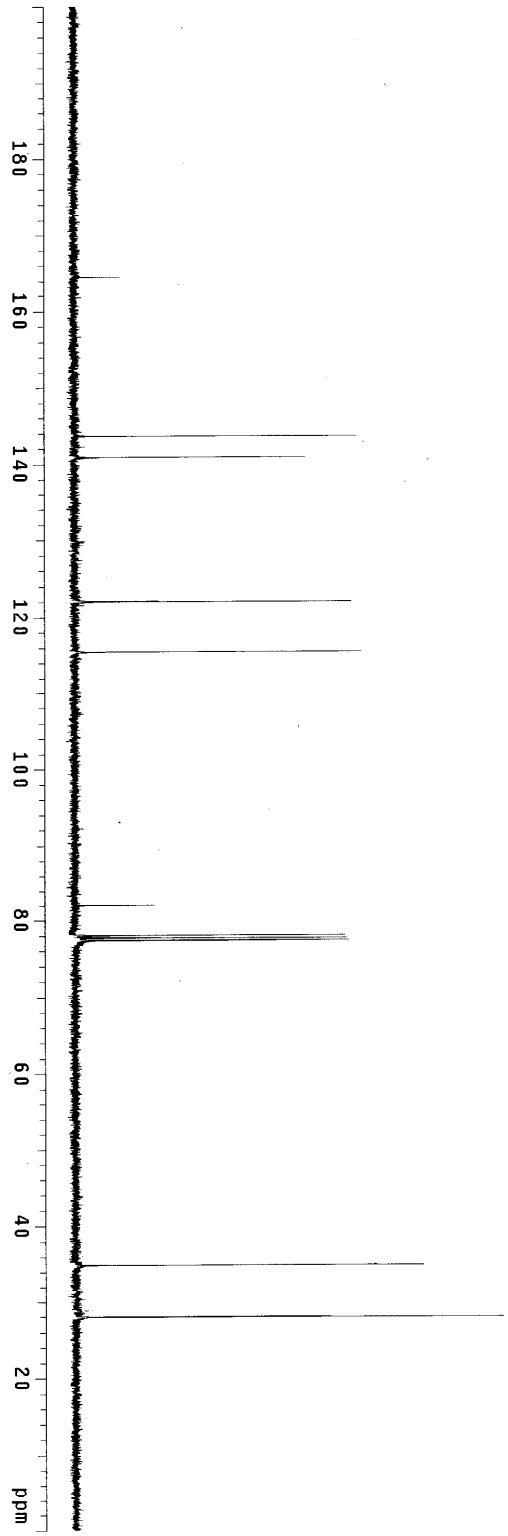
Relax. delay 1.000 sec
Acq. time 0.170 sec
Width 6009.6 Hz
2D Width 6009.6 Hz
2 repetitions
128 increments
OBSERVE H1, 399.8379320 MHz
DATA PROCESSING
Sq. sine bell 0.085 sec
F1 DATA PROCESSING
Sq. sine bell 0.021 sec
FT size 2048 x 2048
Total time 6 min, 46 sec

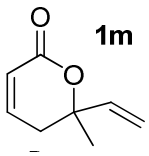


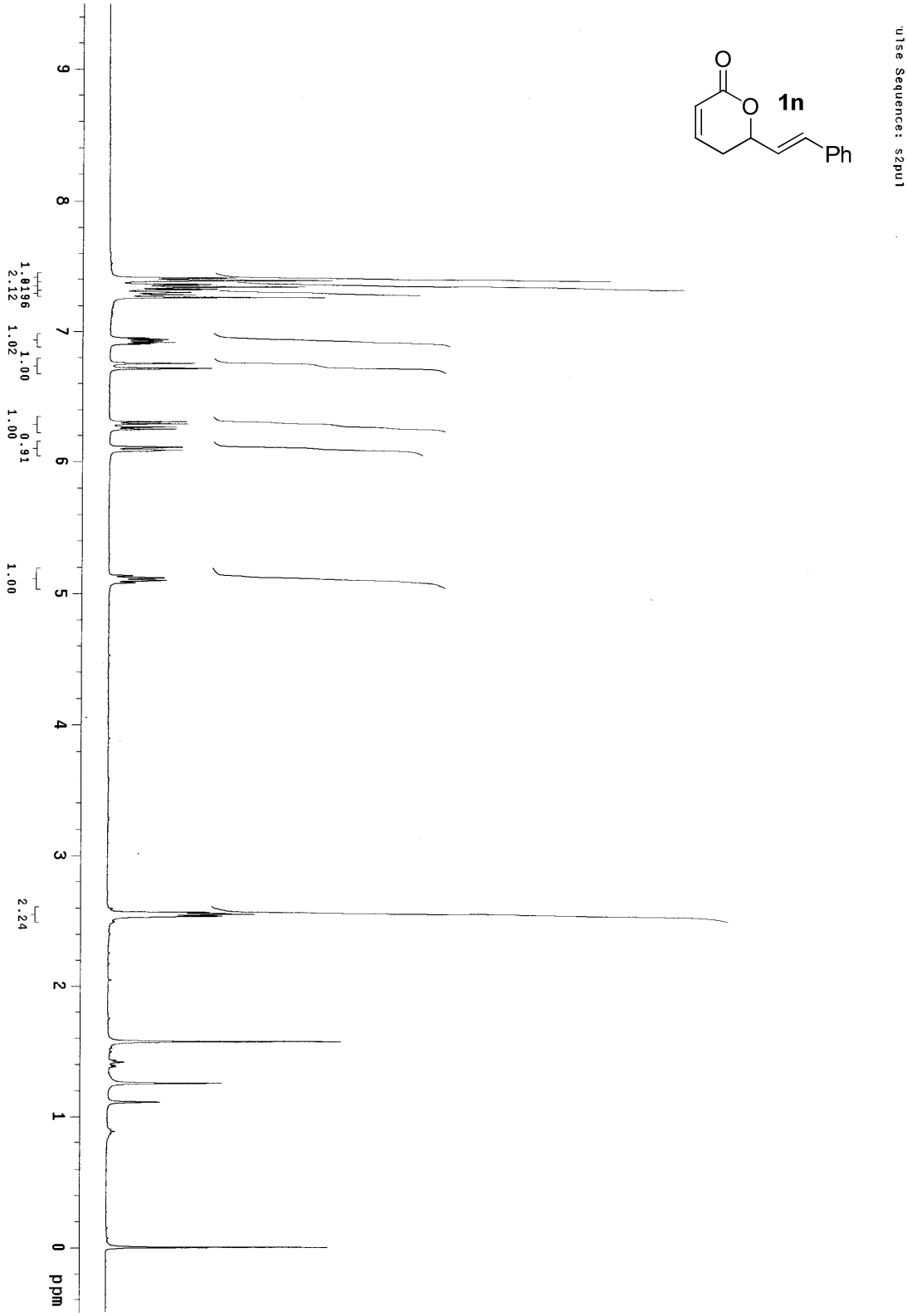


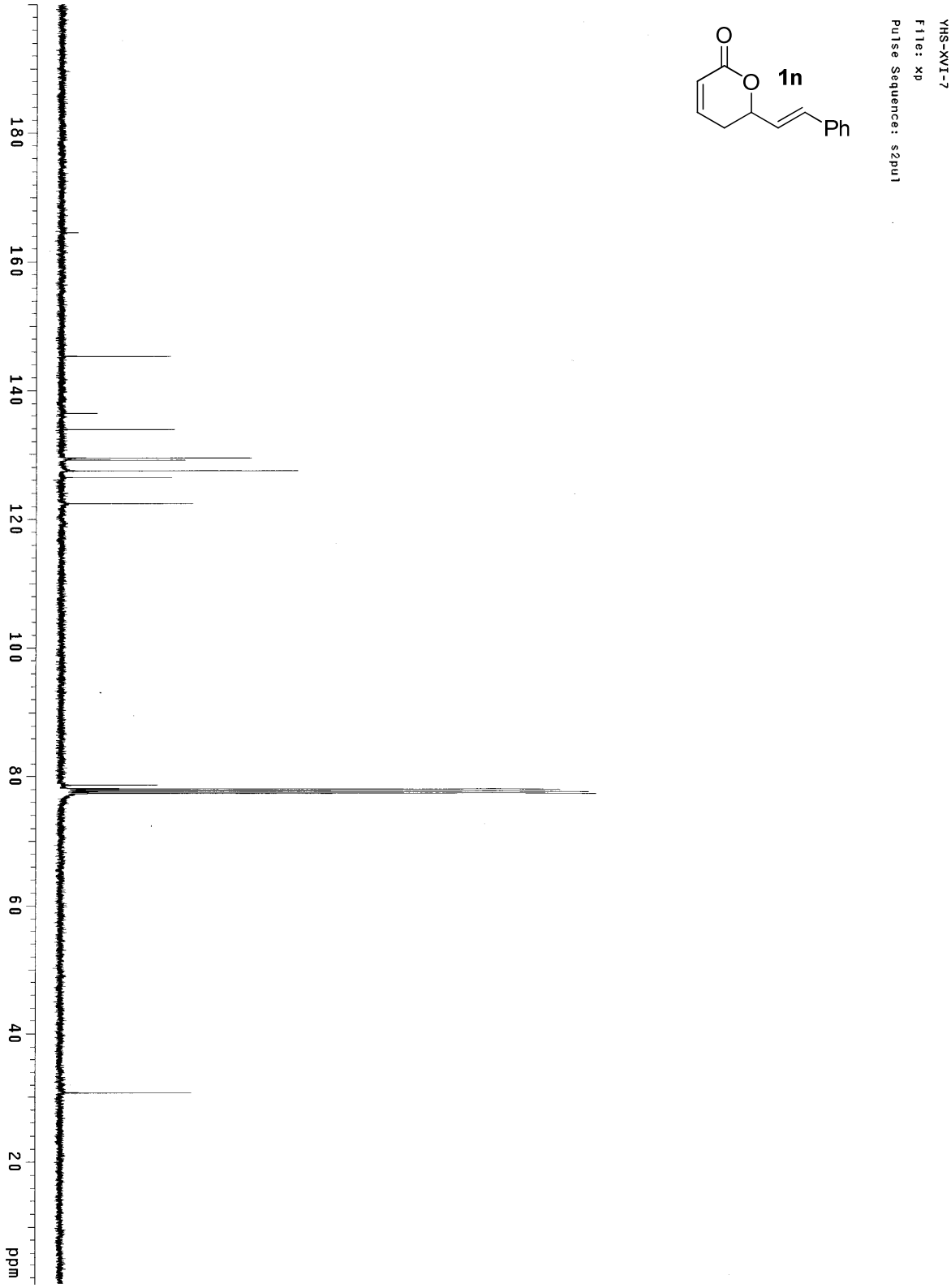

9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
0.97
0.99
1.07
2.37
3.55

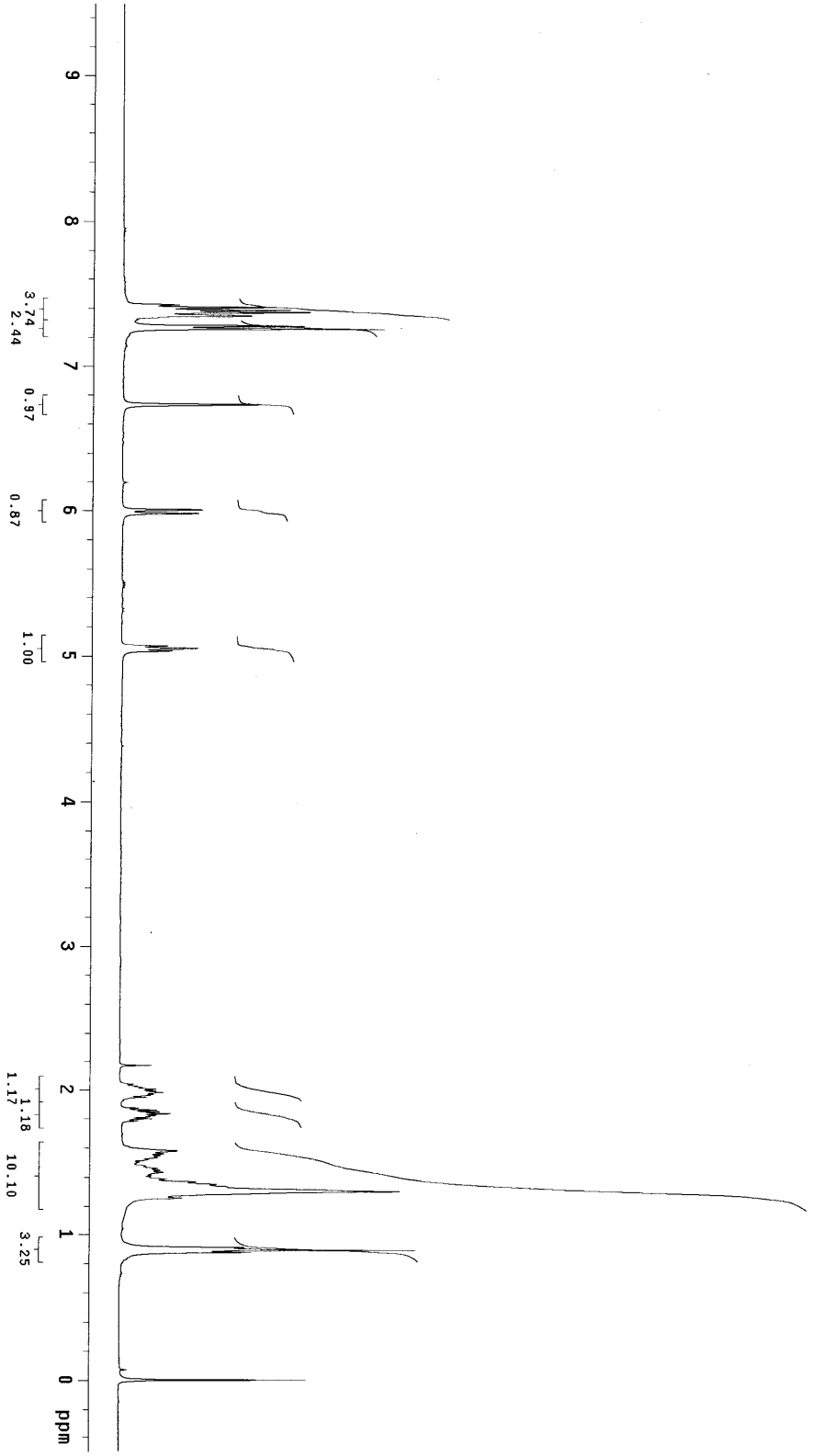

O
O
1m

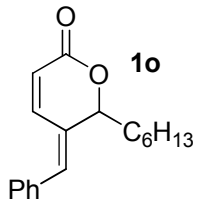

180
160
140
120
100
80
60
40
20
ppm

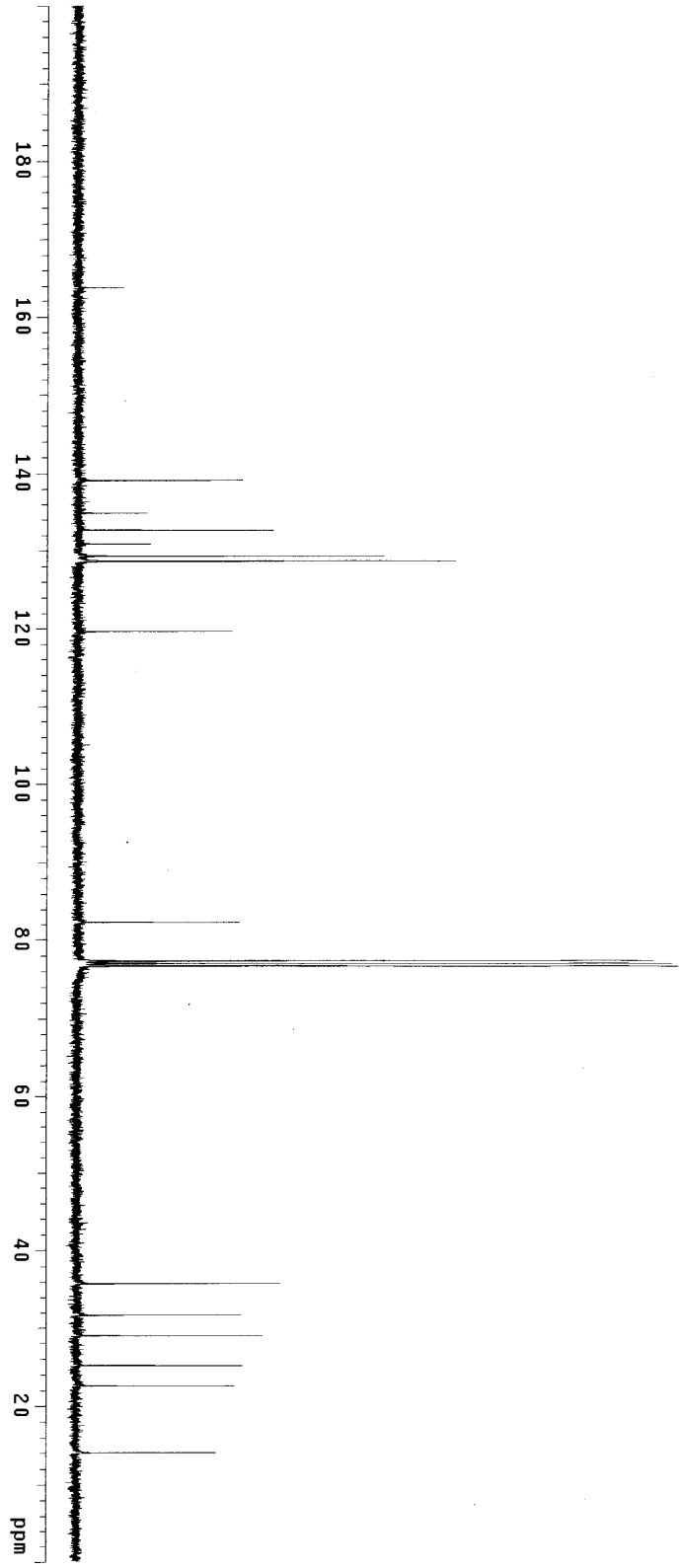

O
O
1m

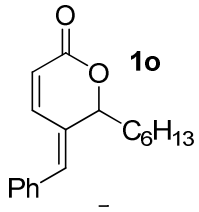

HS-XVI-7
ile: xp
ulse Sequence: s2pul
1n
Ph
O
O
9
8
7
6
5
4
3
2
1
0
ppm
1.0196
2.12
1.00
1.02
0.91
1.00
1.00
2.24


YHS-XVI-7
File: xp
Pulse Sequence: s2pul
1n
O
O
Ph
180
160
140
120
100
80
60
40
20
ppm


9
8
7
6
5
4
3
2
1
0
ppm
3.74
2.44
0.97
0.87
1.00
1.18
1.17
10.10
3.25


O
O
1o
C_6H_{13}
Ph

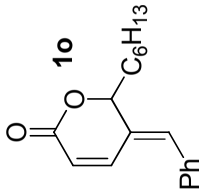

180
160
140
120
100
80
60
40
20
ppm

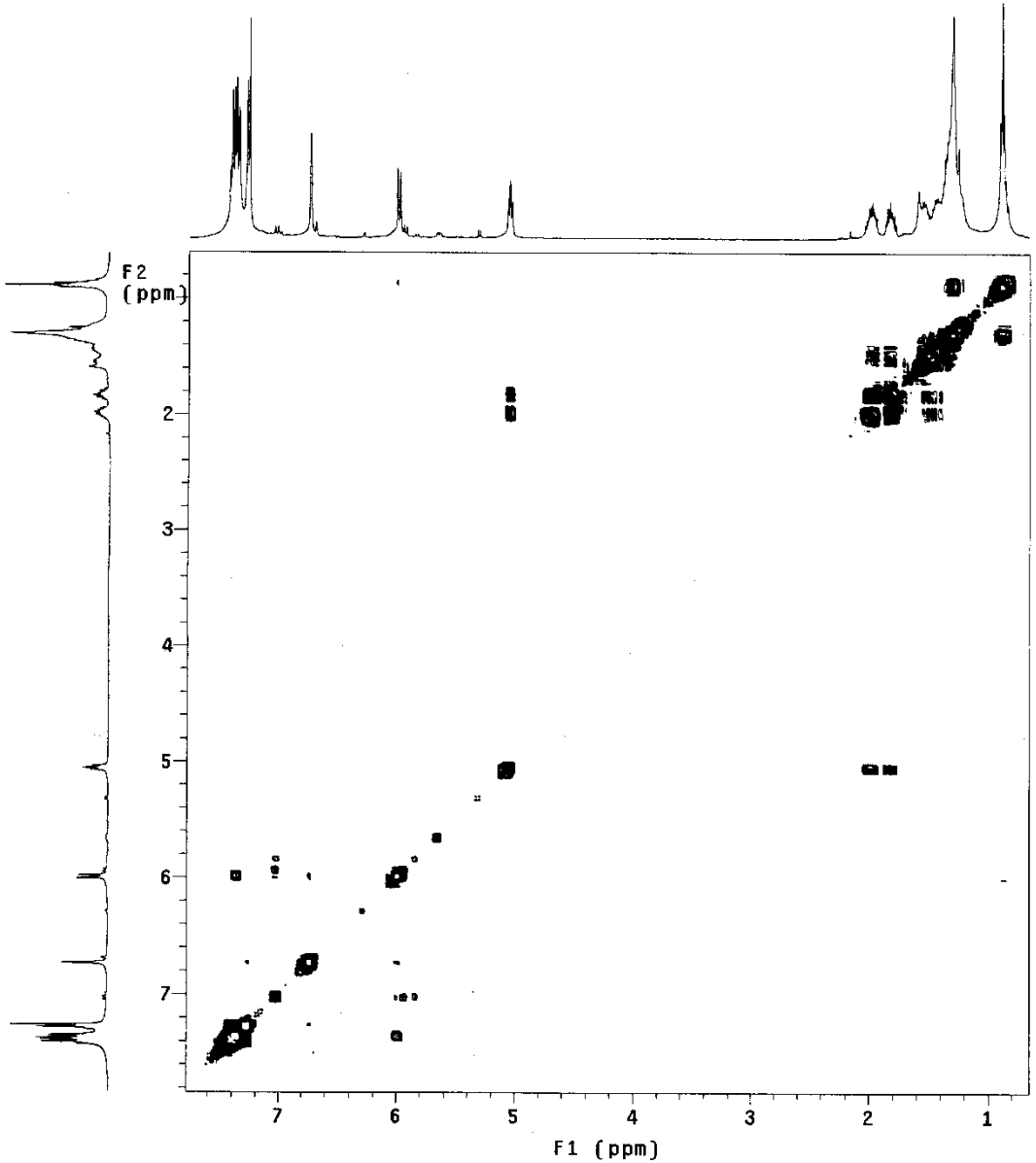

O
O
1o
C_6H_{13}
Ph

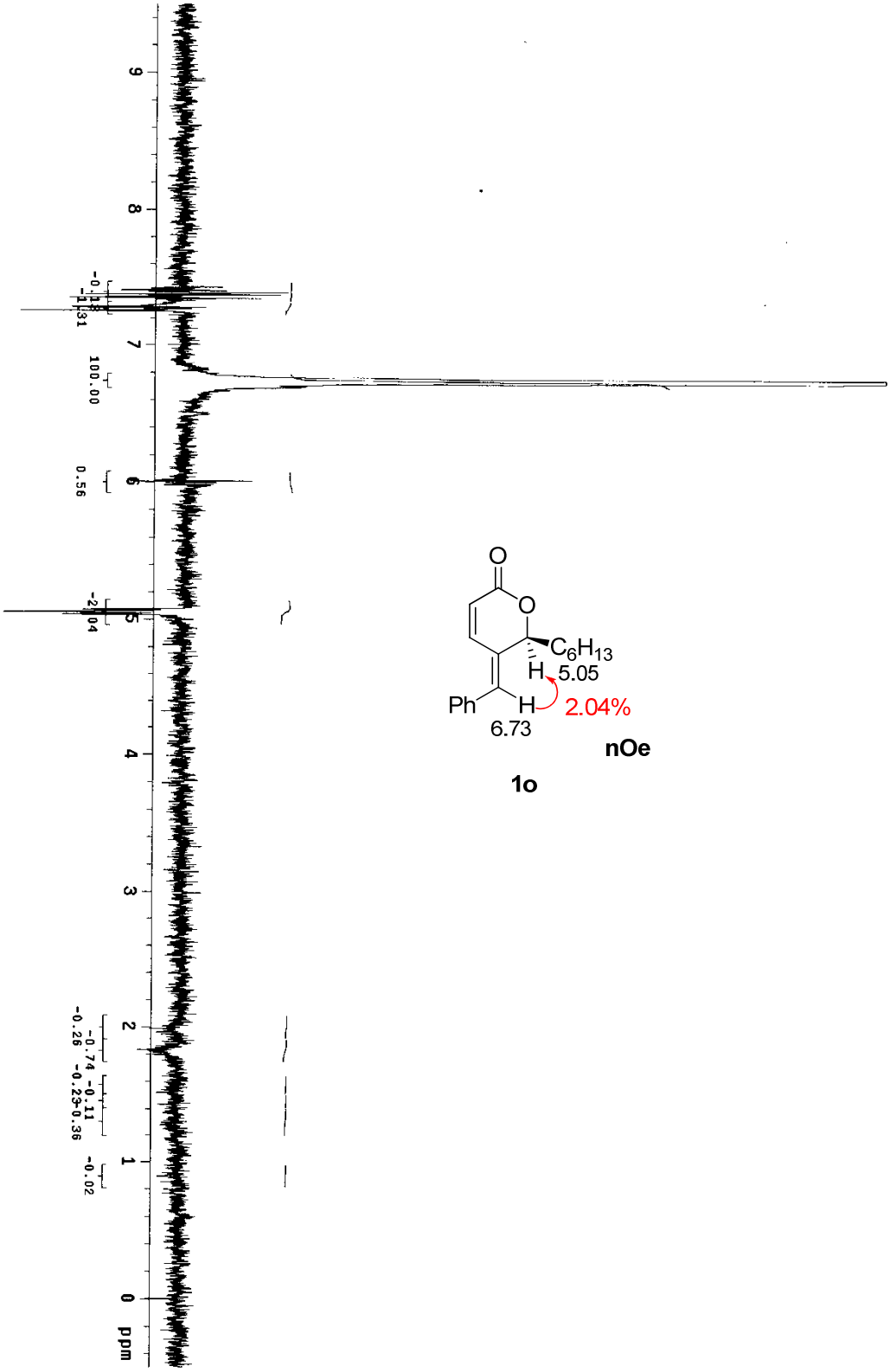
1H SENSITIVITY
0.1% ETHYLBENZENE

Pulse Sequence: COSY
Solvent: CDCl3
Ambient temperature
User: 1-12-87
Mercury-400BB "nmr400HY"

Relax. delay 1.000 sec
Acq. time 0.170 sec
Width 6009.6 Hz
2D Width 6009.6 Hz
2 repetitions
128 increments
OBSERVE H1, 399.8379331 MHz
DATA PROCESSING
Sq. sine bell 0.085 sec
F1 DATA PROCESSING
Sq. sine bell 0.021 sec
FT size 2048 x 2048
Total time 6 min, 46 sec

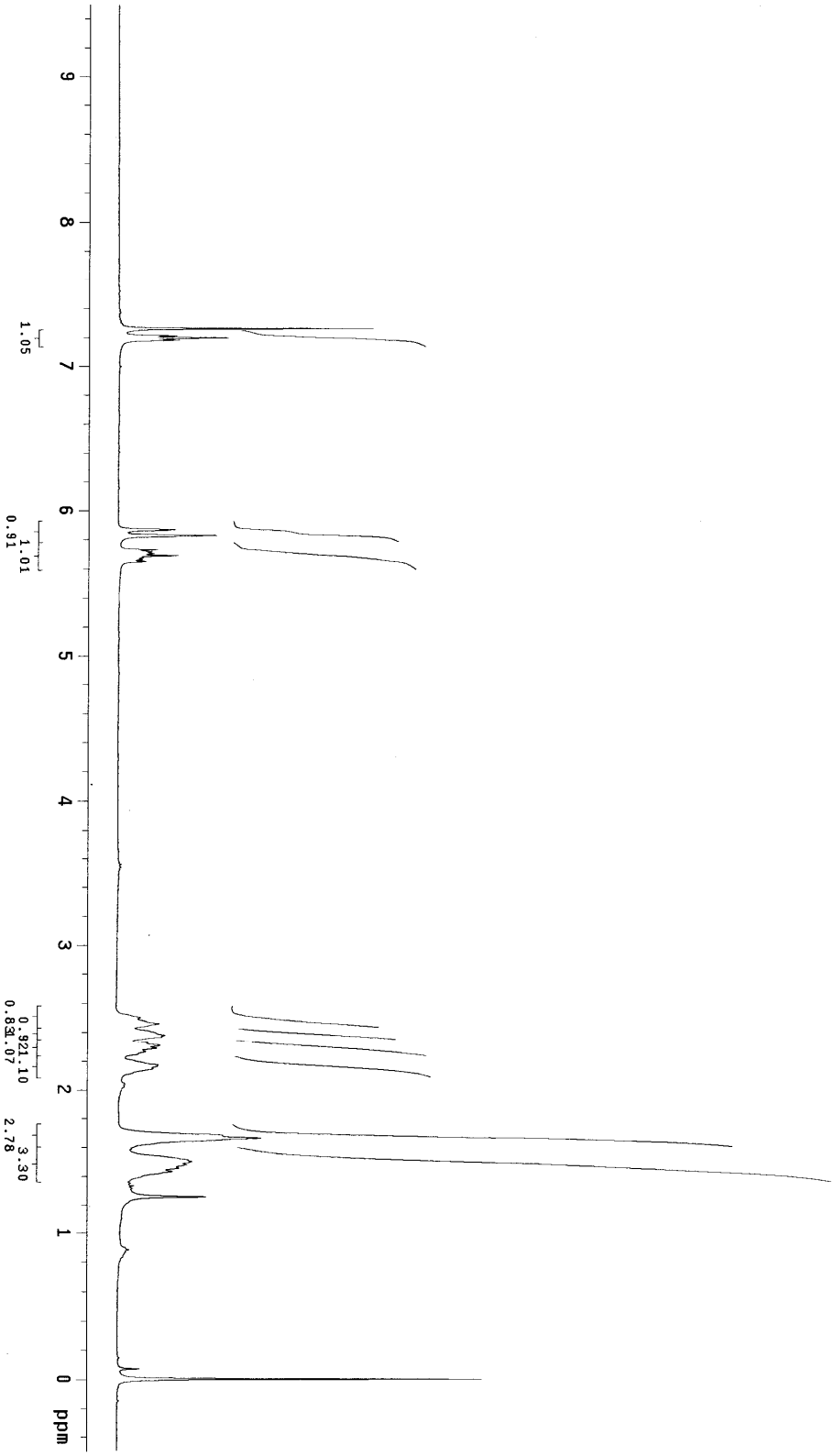


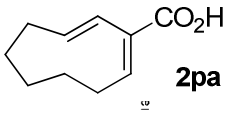



9
8
7
6
5
4
3
2
1
0
ppm
-0.13
-1.31
100.00
0.56
-2.04
-0.74
-0.11
-0.26
-0.25
-0.36
-0.02

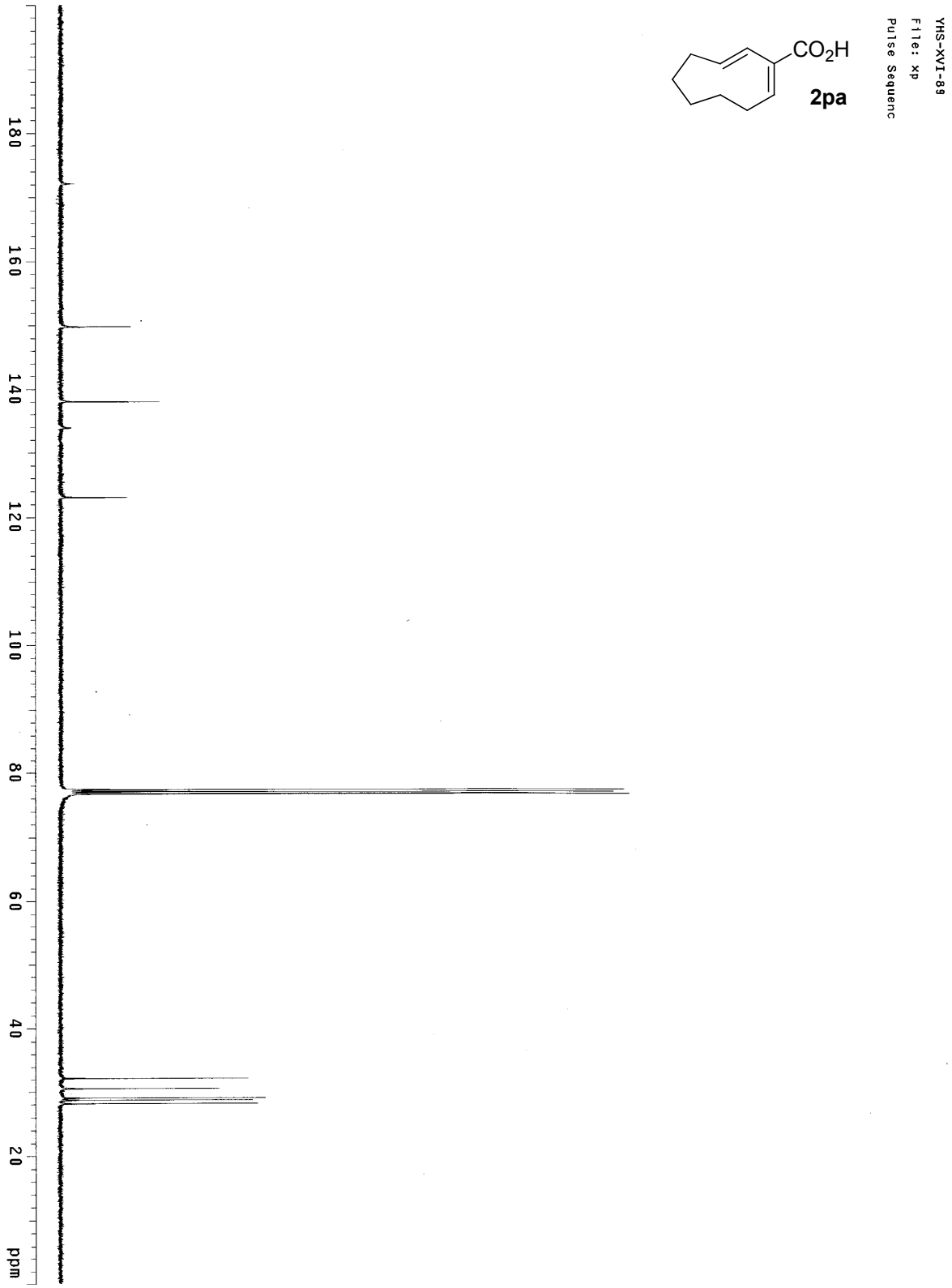
O
O
C_6H_{13}
H
5.05
Ph
H
6.73
2.04%
nOe

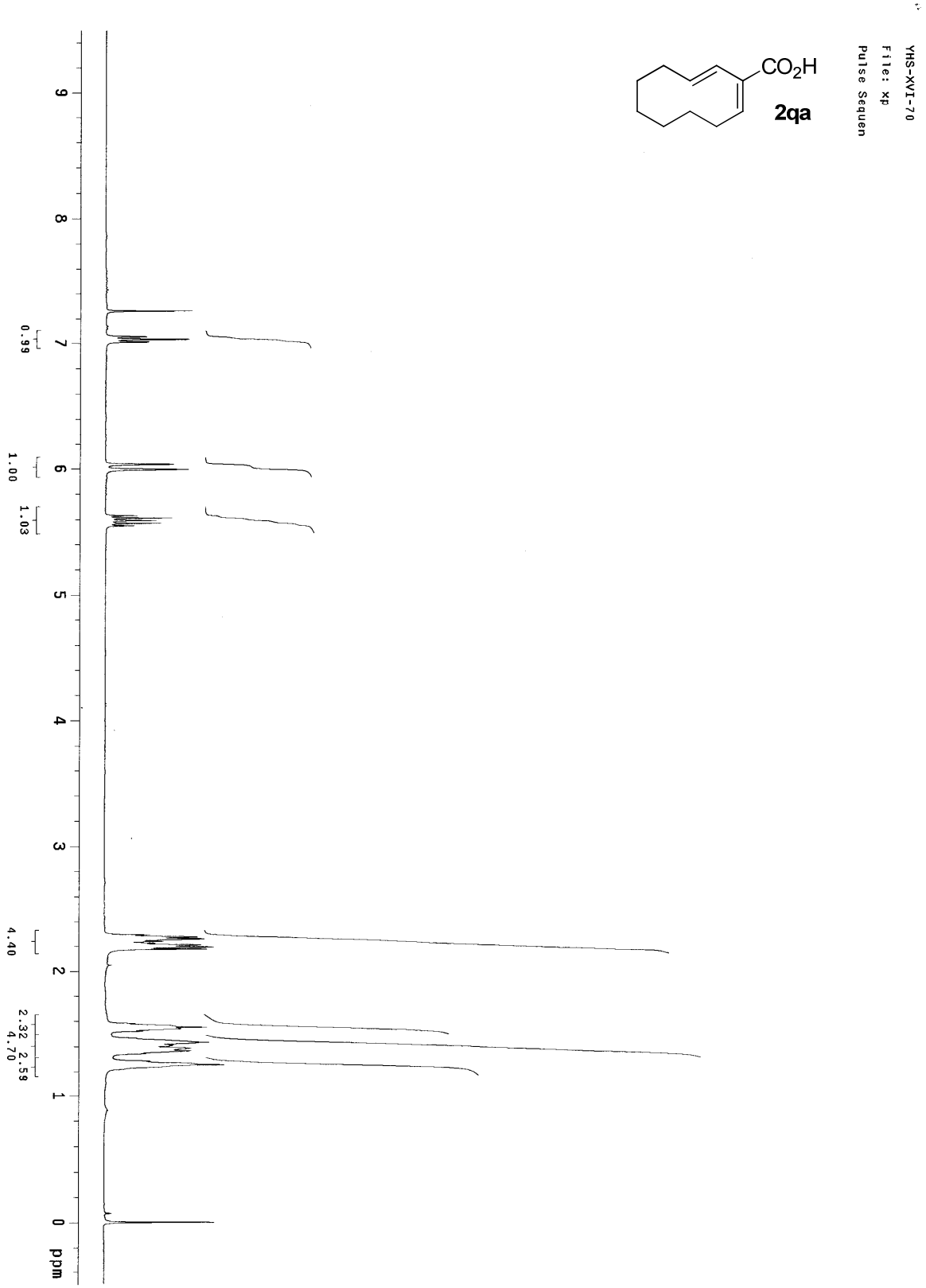
1o

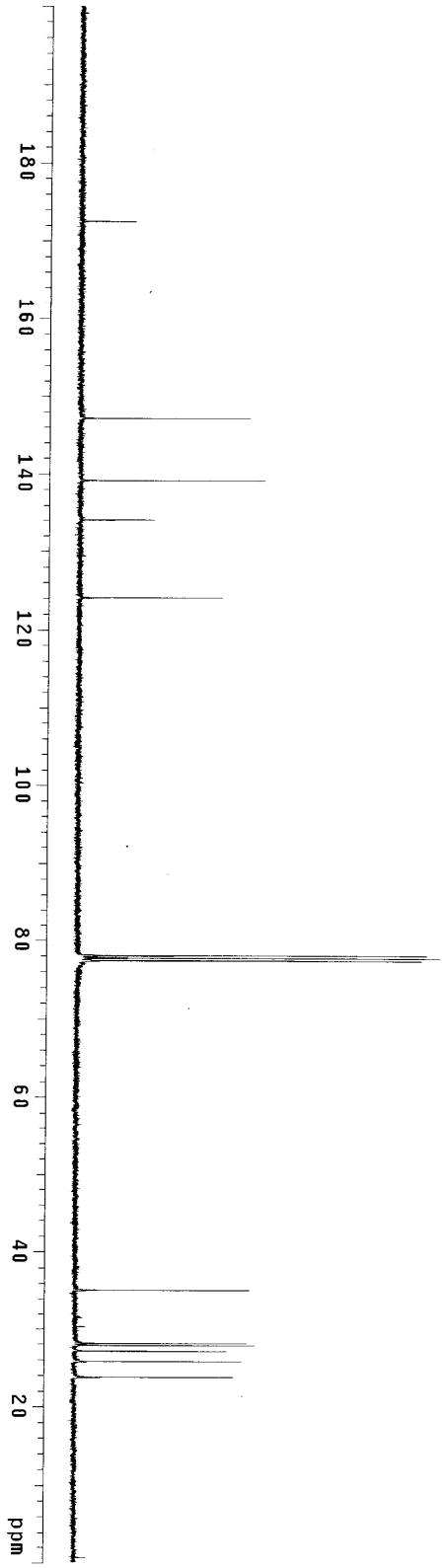


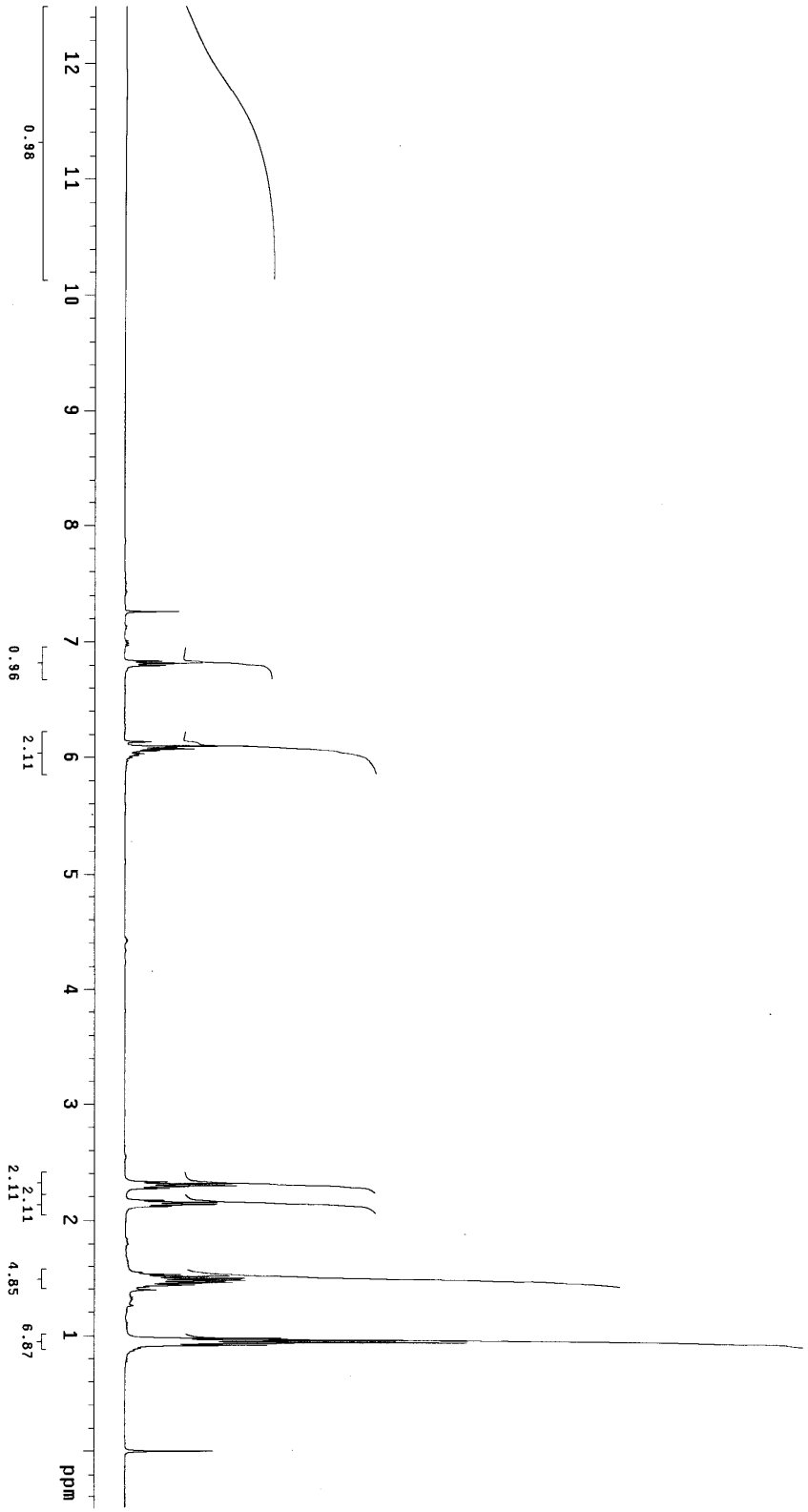


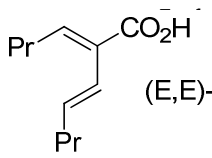
2pa


YHS-XVI-89
File: xp
Pulse Sequenc
CO2H
2pa
ppm
20
40
60
80
100
120
140
160
180

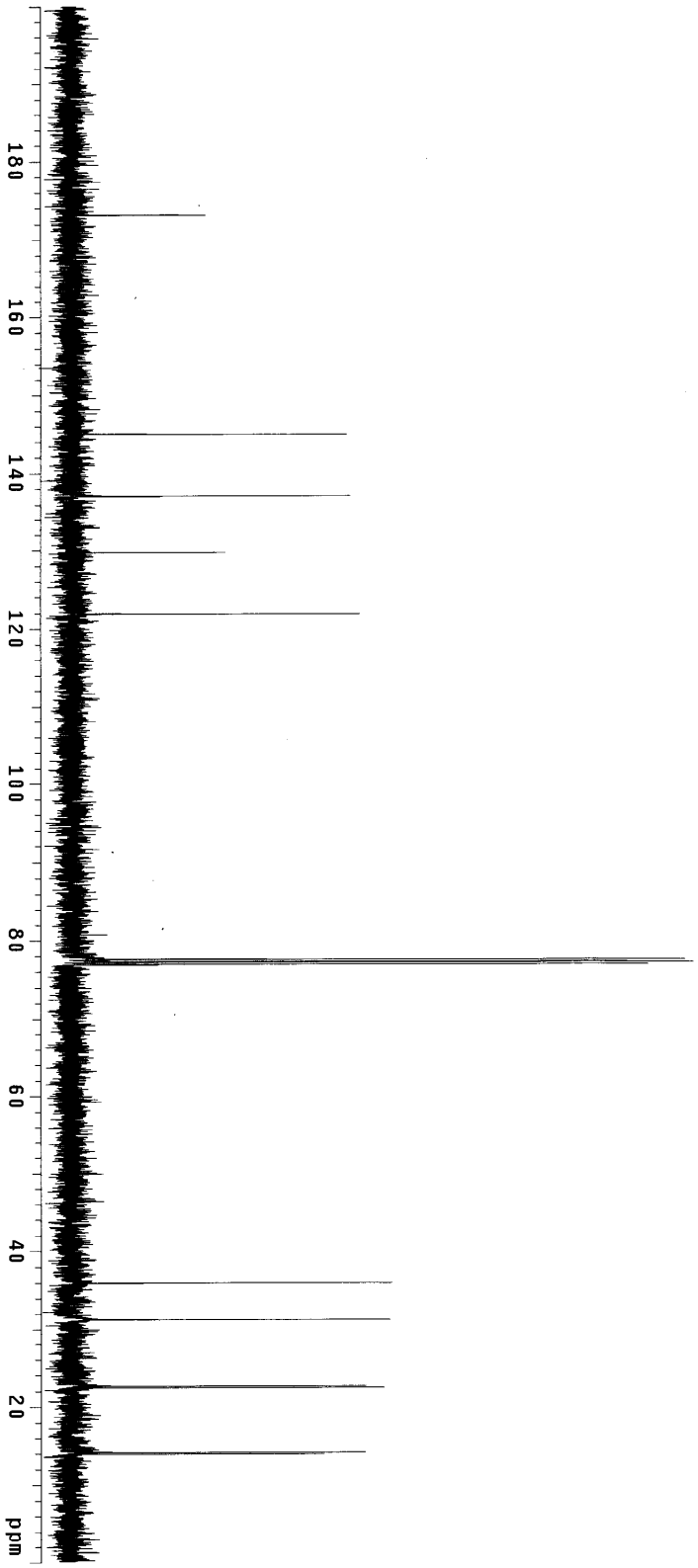

YHS-XVI-70
File: xp
Pulse Sequen
CO2H
2qa
9
8
7
6
5
4
3
2
1
0
ppm
0.99
1.00
1.03
4.40
2.32
2.59
4.70

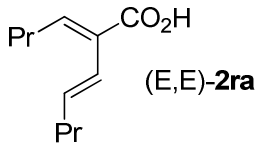

YHS-XVI-70
File: xp
Pulse Sequence: s2pul
CO2H
2qa
ppm
20
40
60
80
100
120
140
160
180





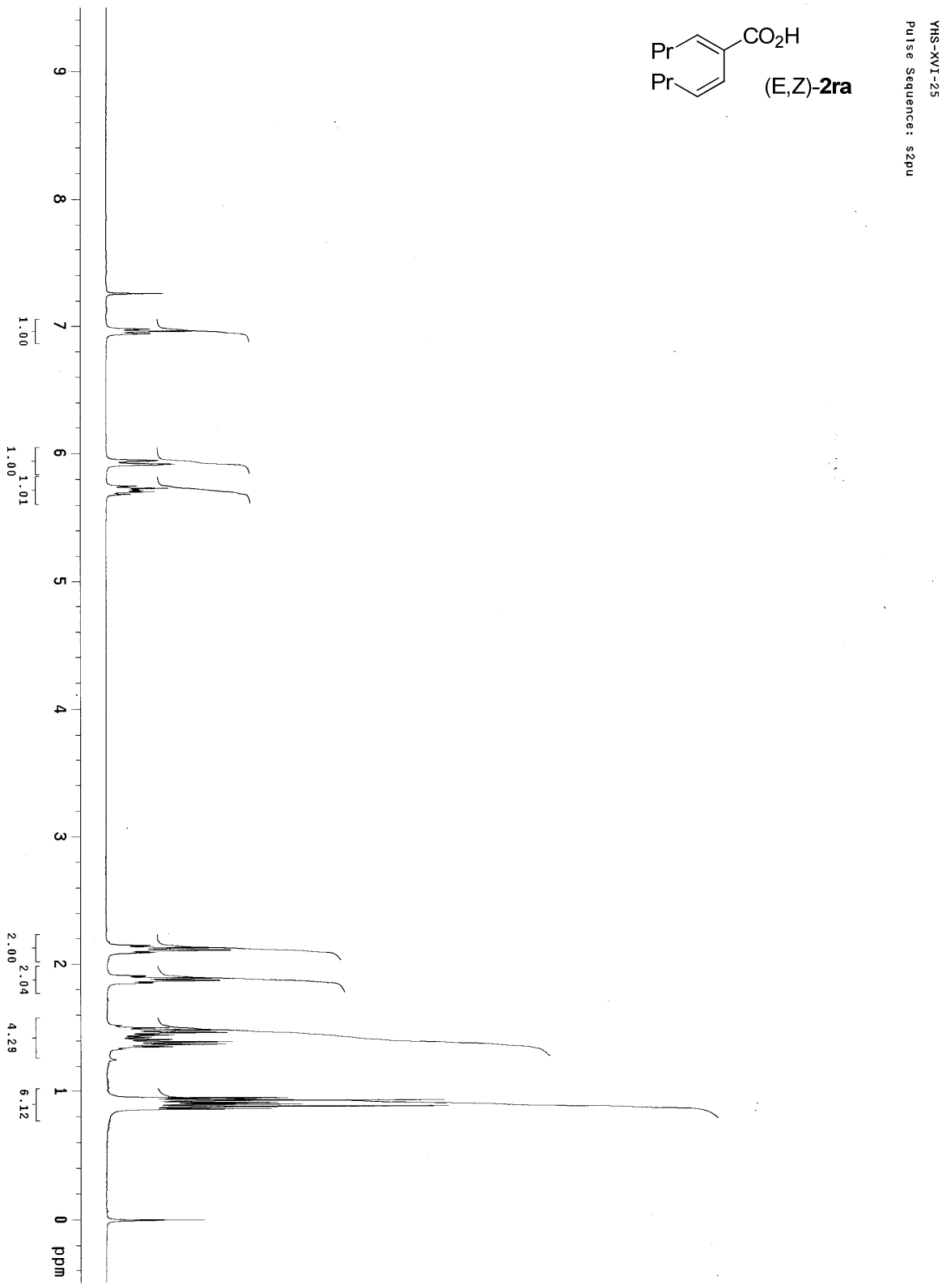
(E,E)-**2ra**

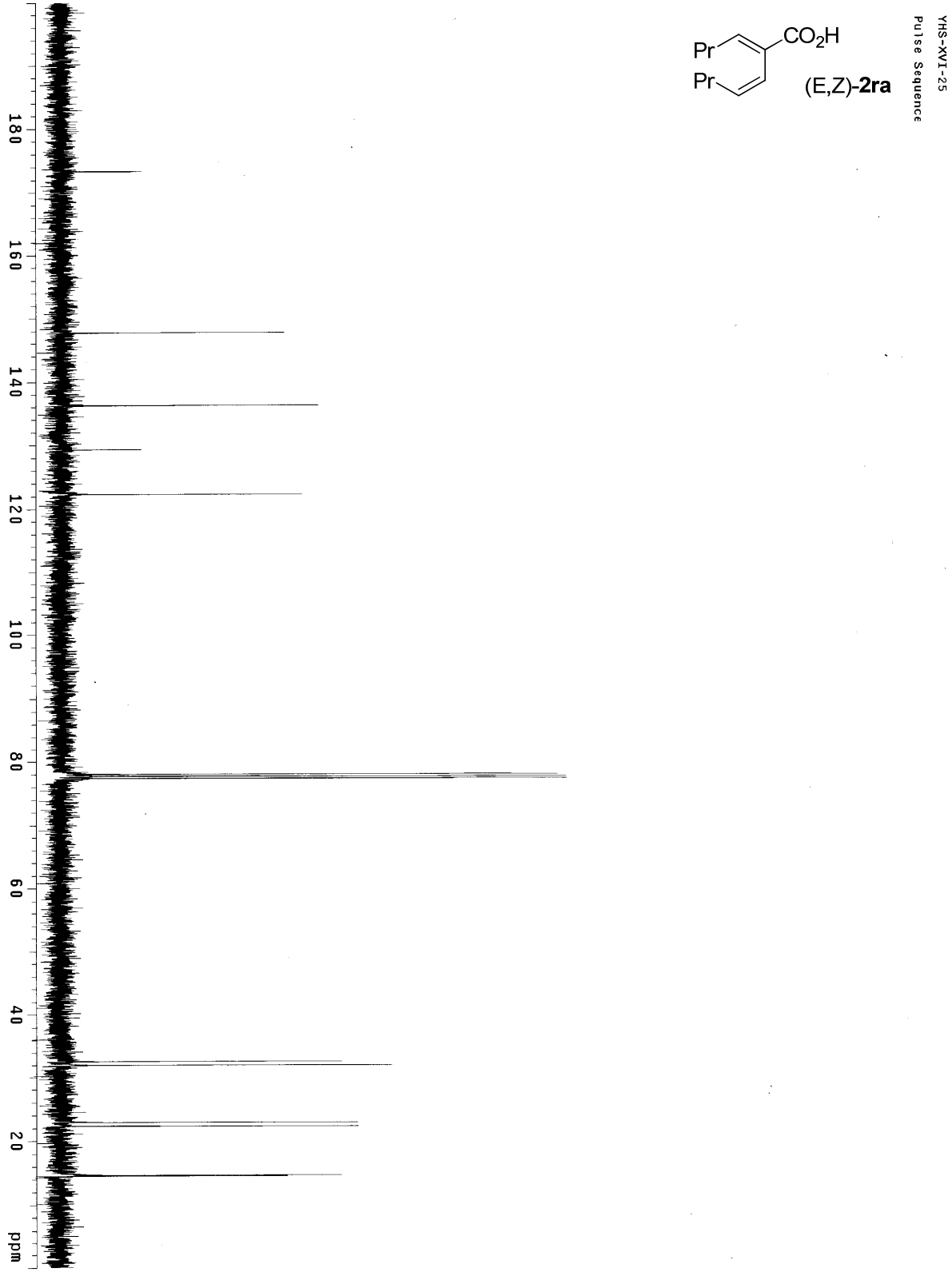


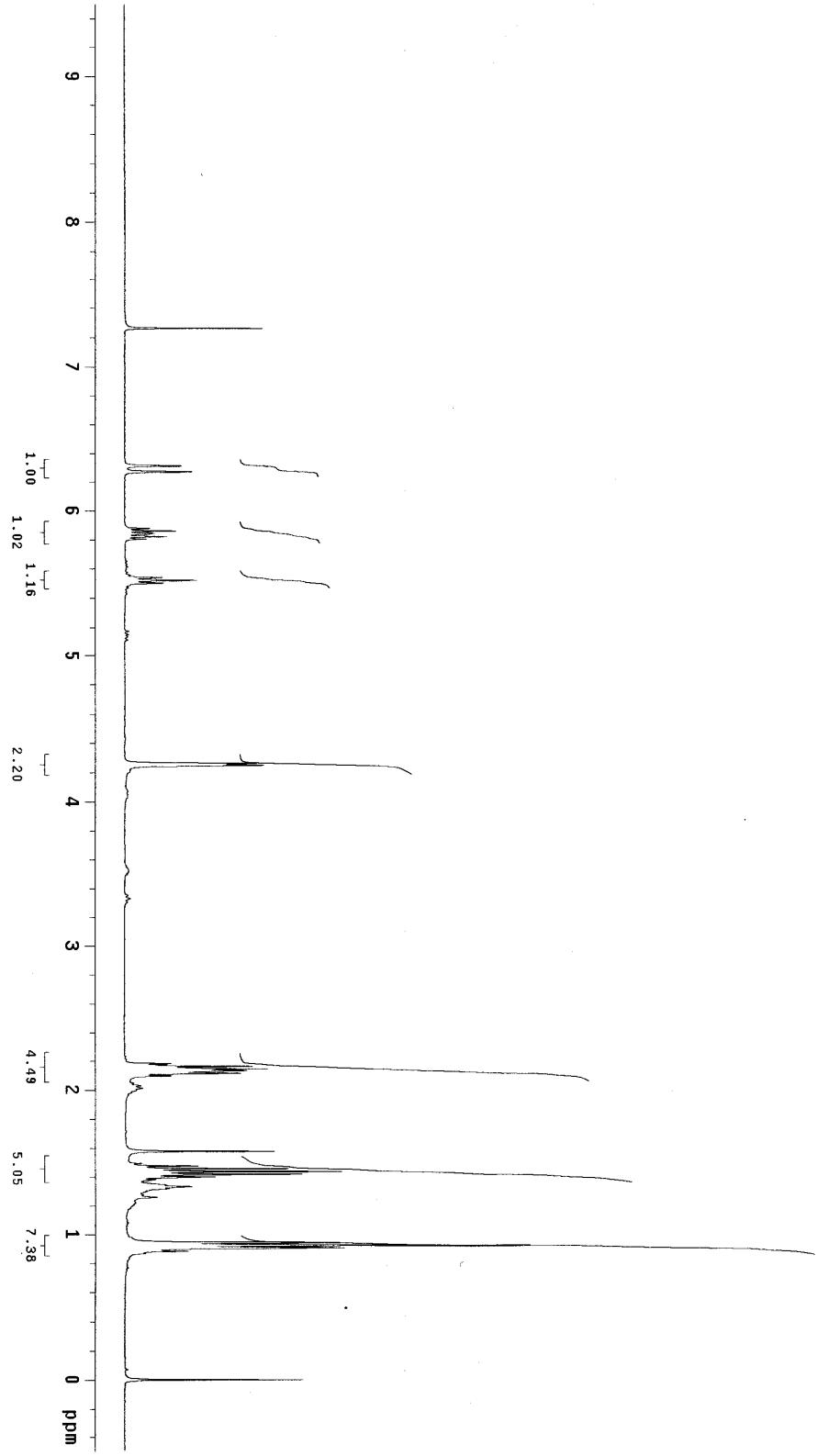


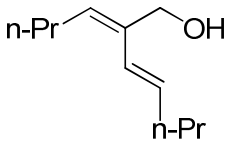
(E,E)-**2ra**

YHS-XVI-26
Pulse Sequence: s2pul

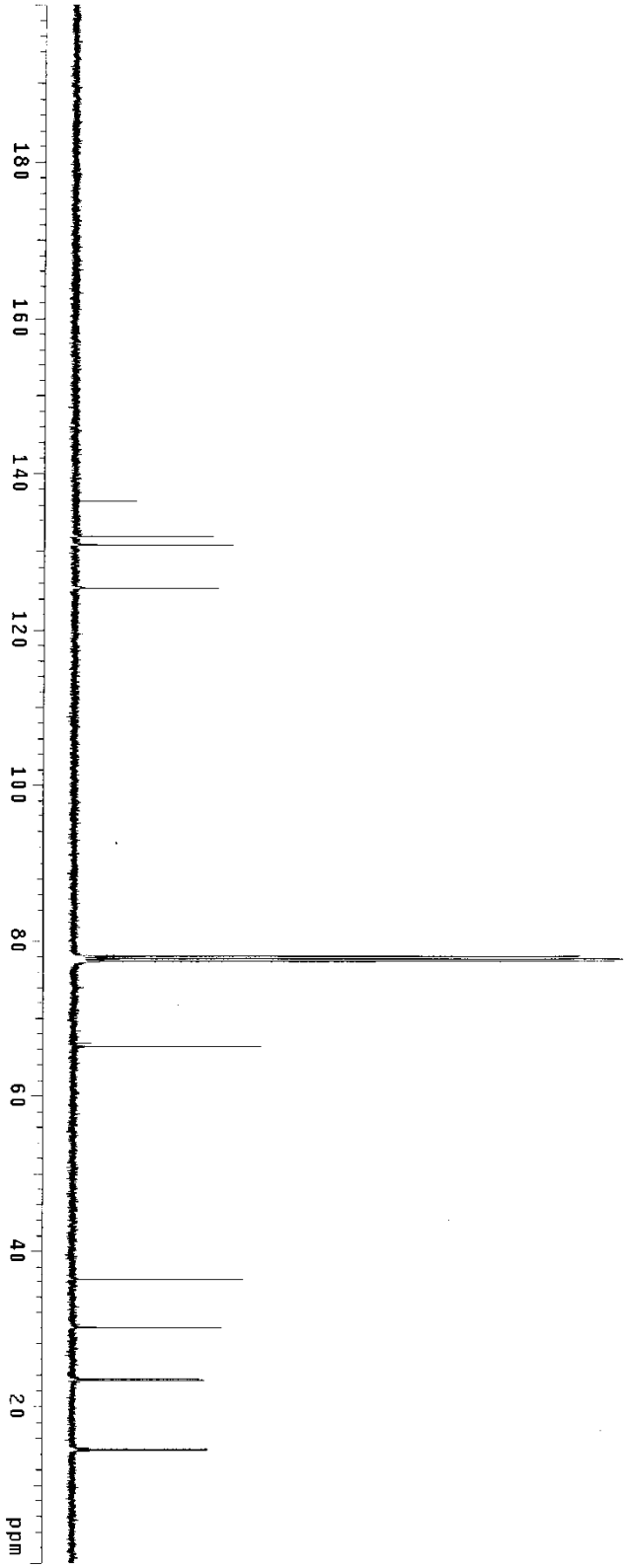

YHS-XVI-25
Pulse Sequence: s2pu
Pr
Pr
CO2H
(E,Z)-2ra
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.01
2.00
2.04
4.29
6.12

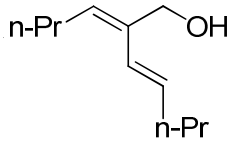

YHS-XVI-25
Pulse Sequence
Pr
Pr
CO2H
(E,Z)-2ra
180
160
140
120
100
80
60
40
20
ppm



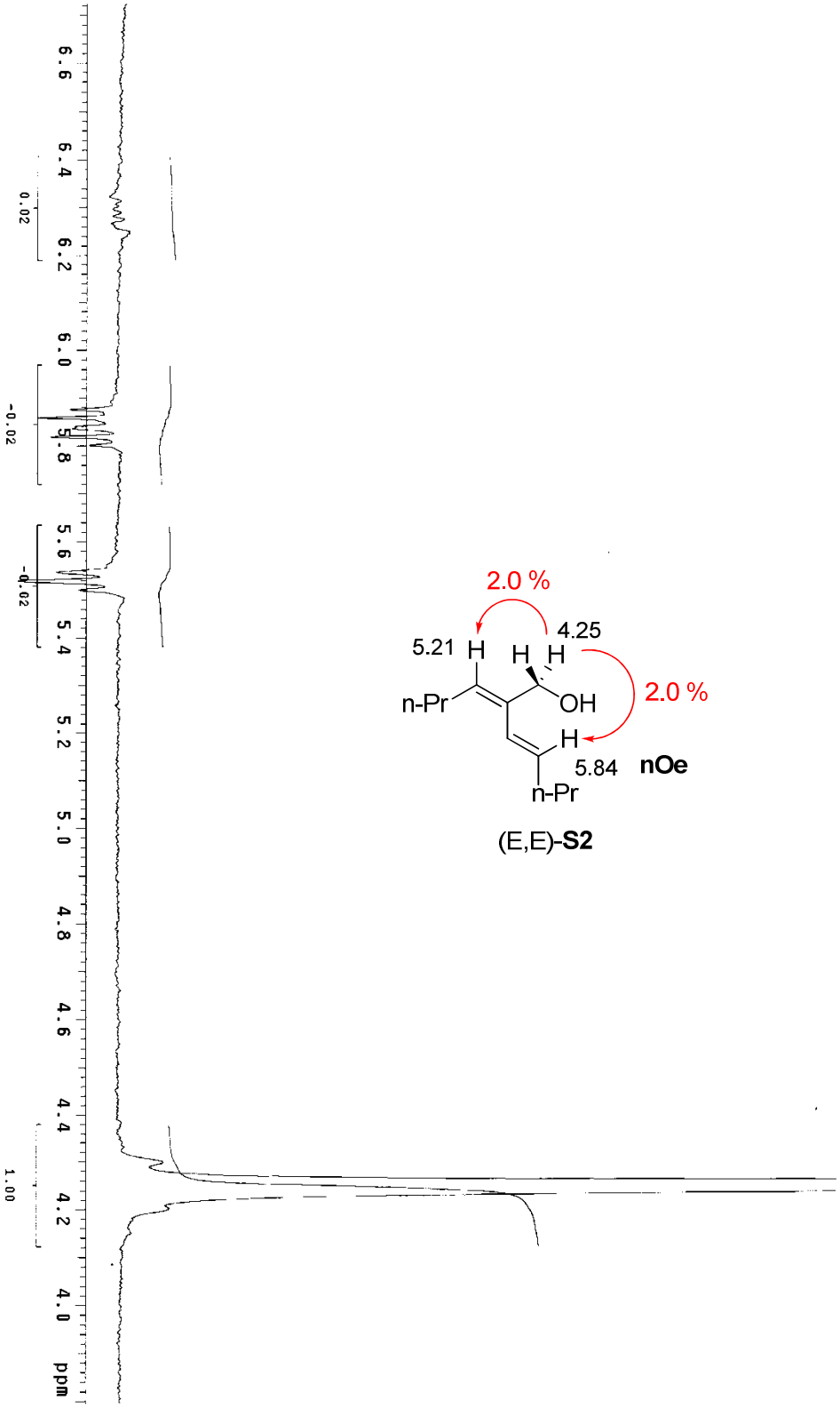


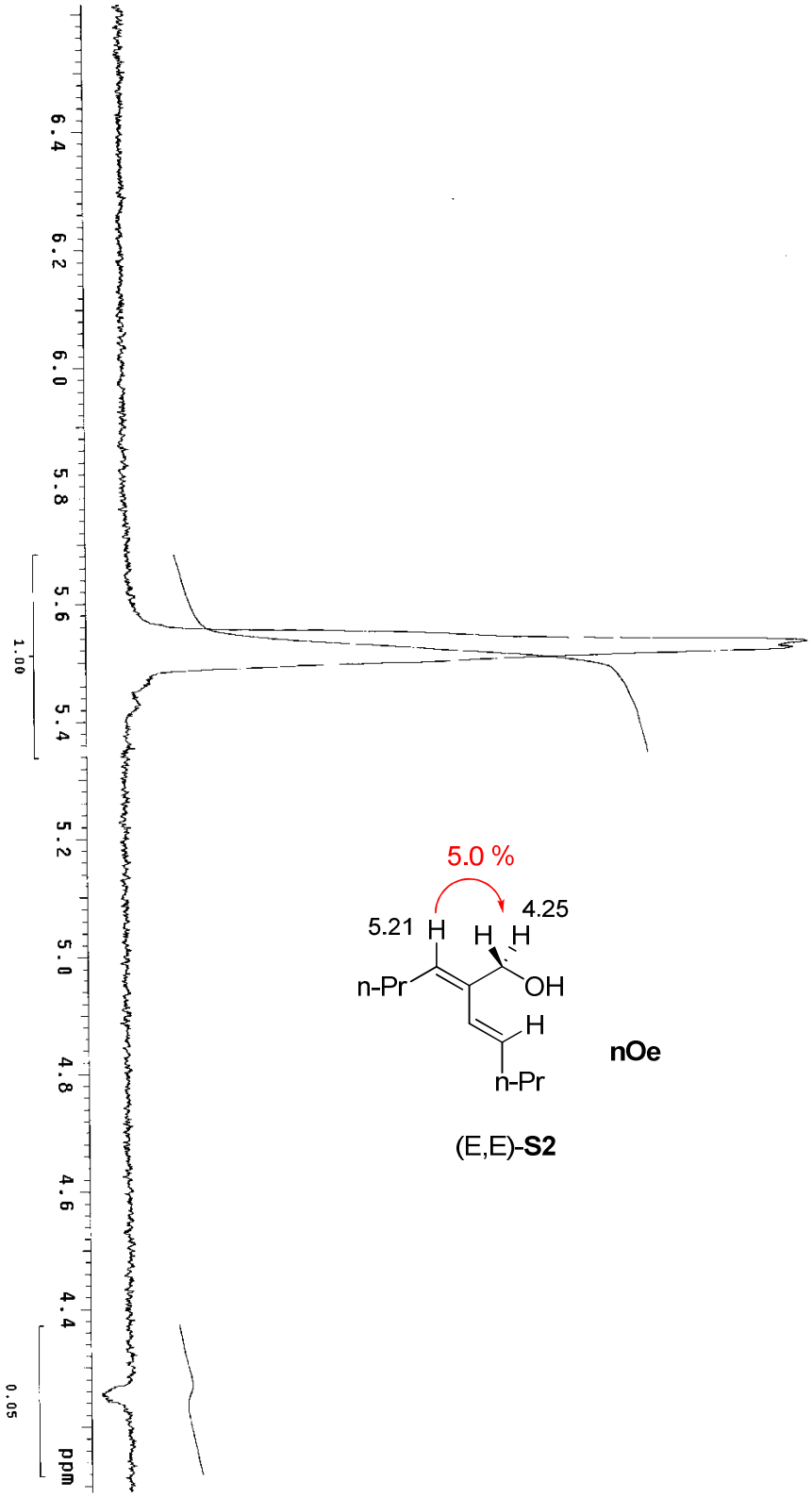
(E,E)-**S2**

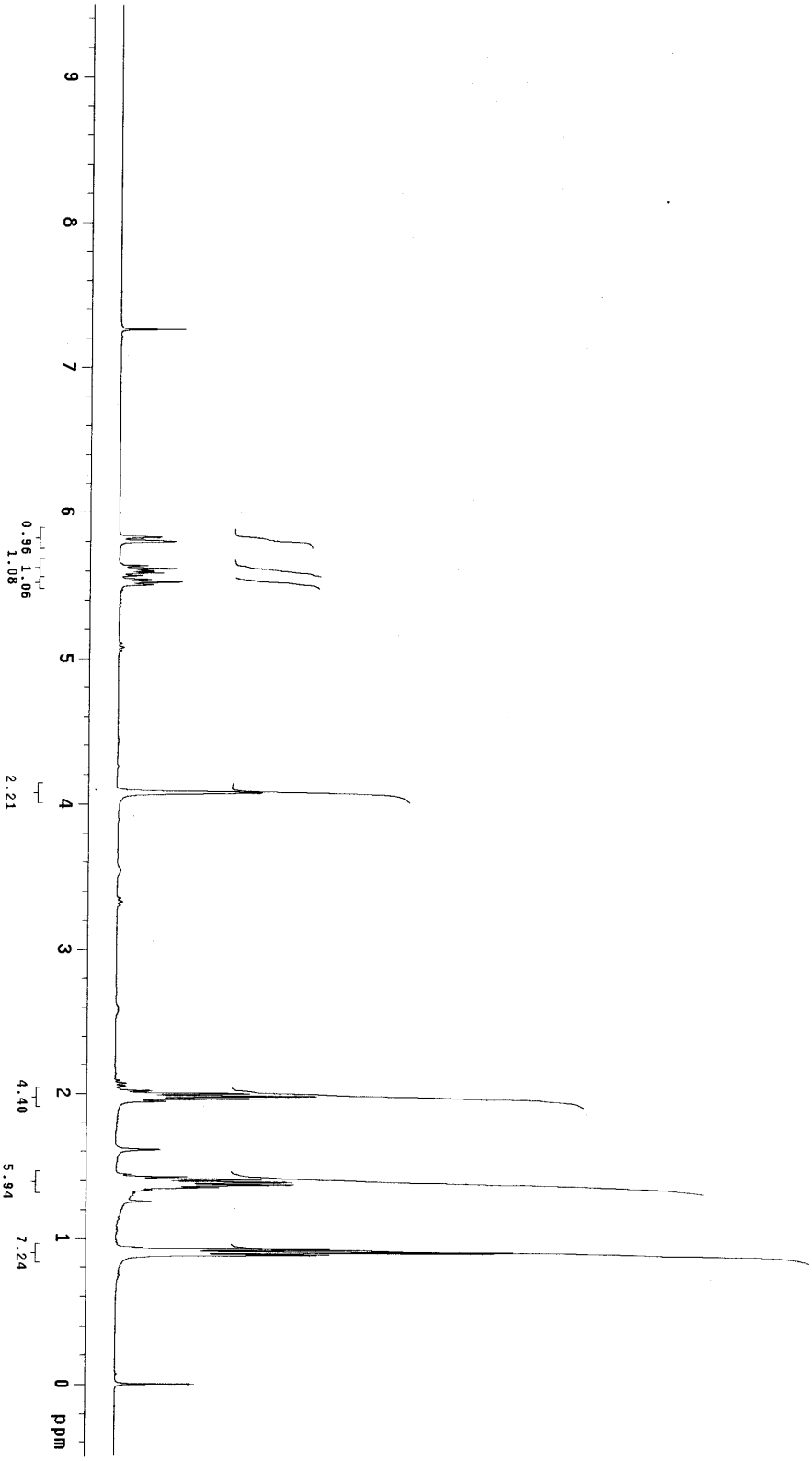


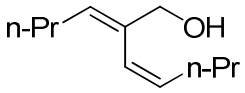


(E,E)-**S2**

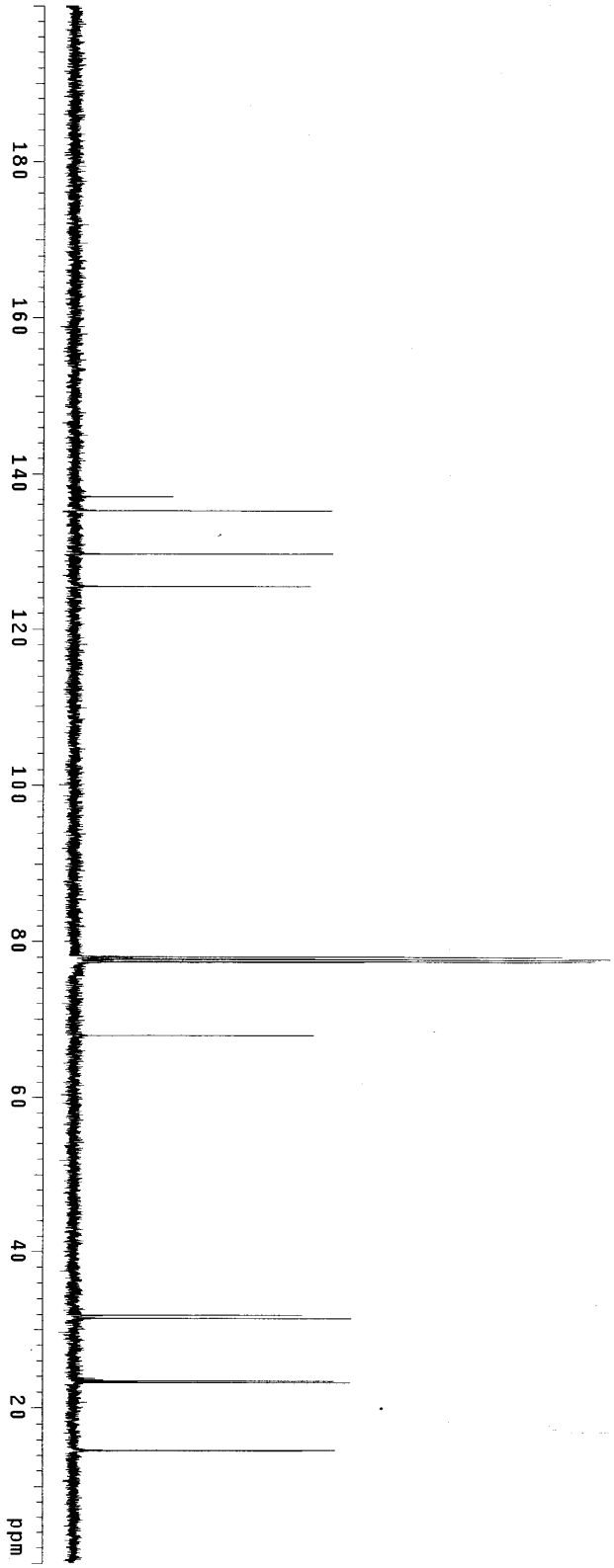

6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
ppm
0.02
-0.02
-0.02
1.00
2.0 %
5.21
4.25
H
H
H
n-Pr
OH
2.0 %
H
5.84
nOe
n-Pr
(E,E)-S2

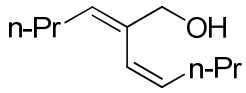

6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
ppm
1.00
0.05
5.0 %
5.21
4.25
H
H
H
n-Pr
OH
H
n-Pr
nOe
(E,E)-S2



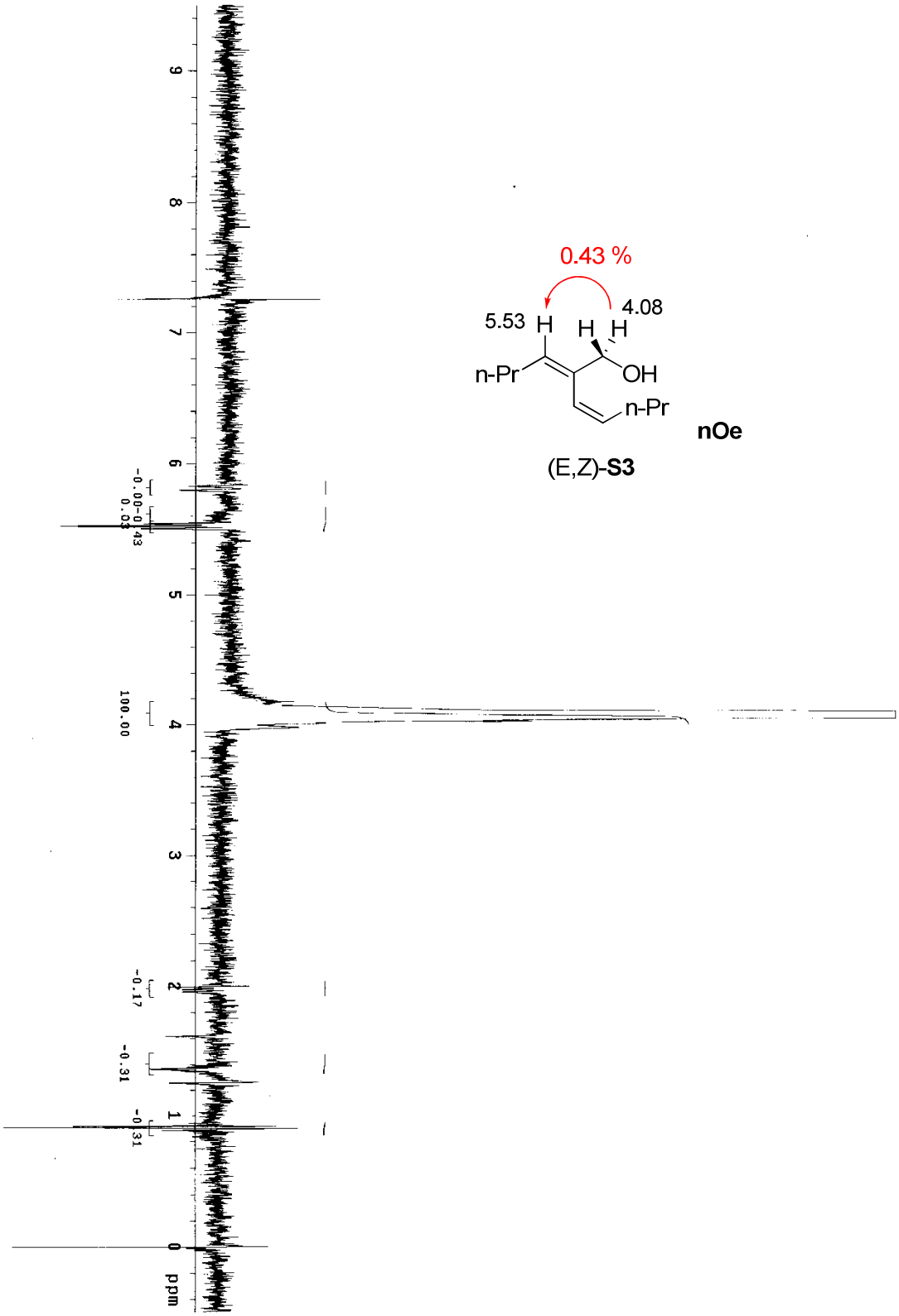


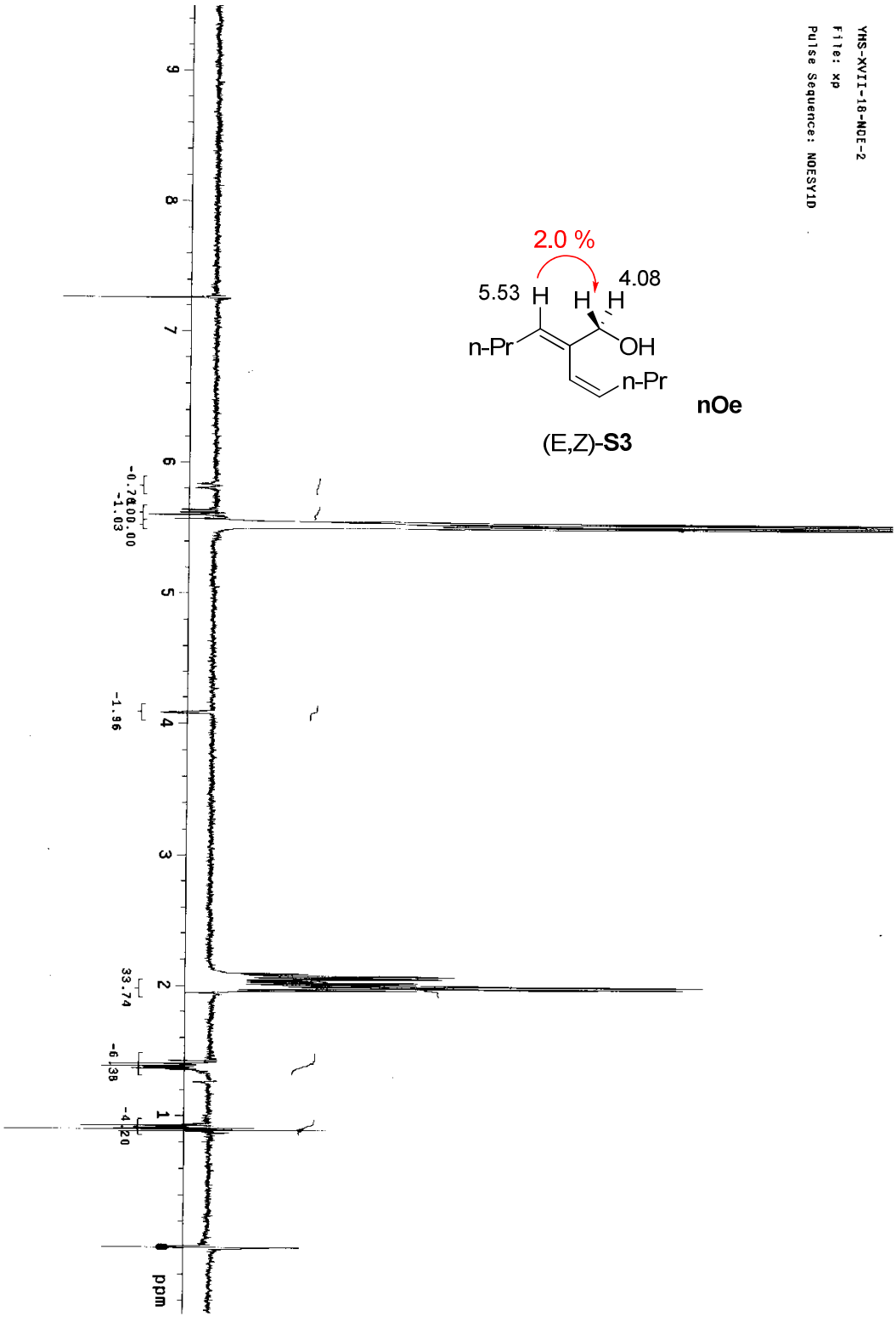
(E,Z)-**S3**

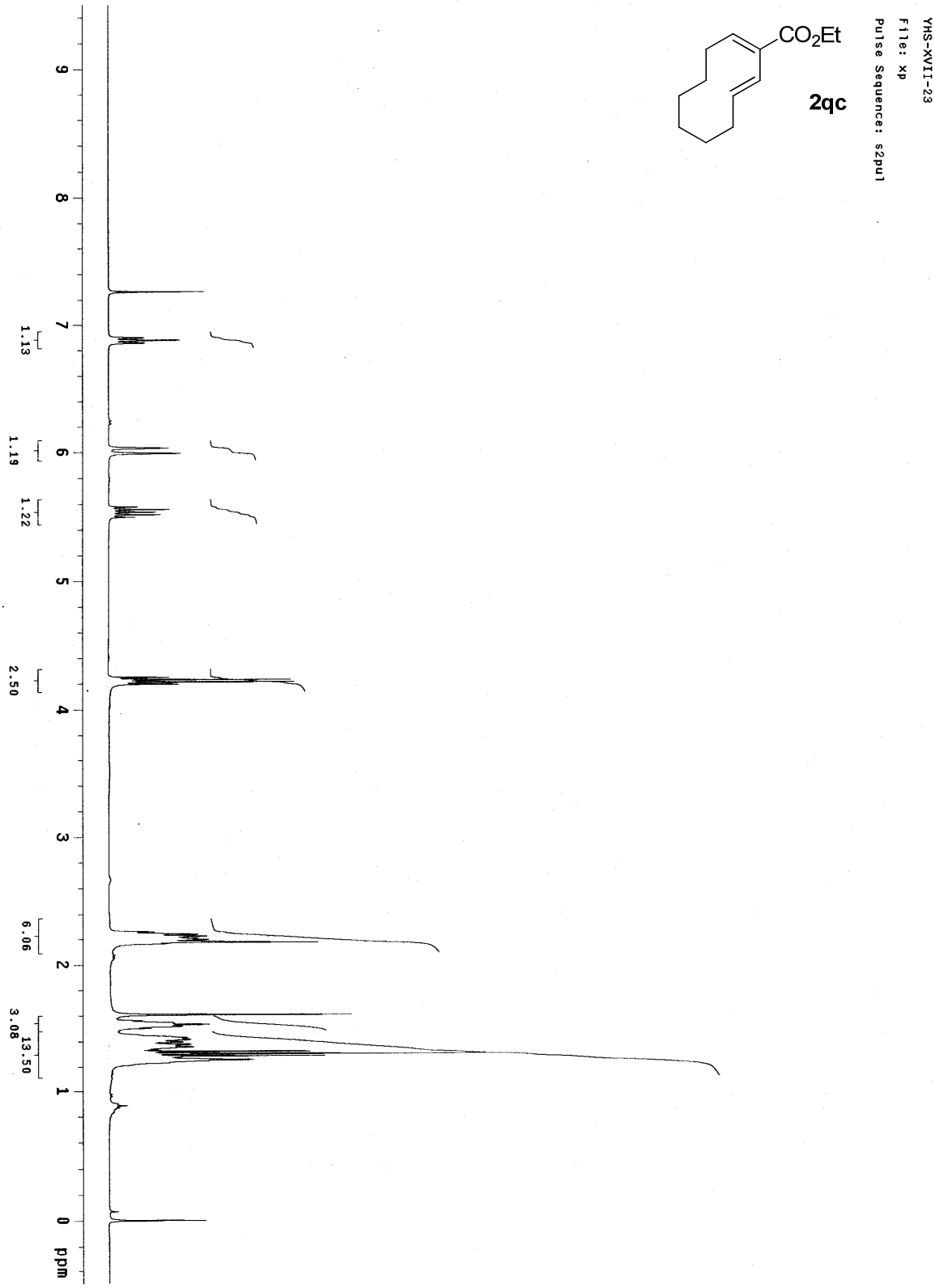


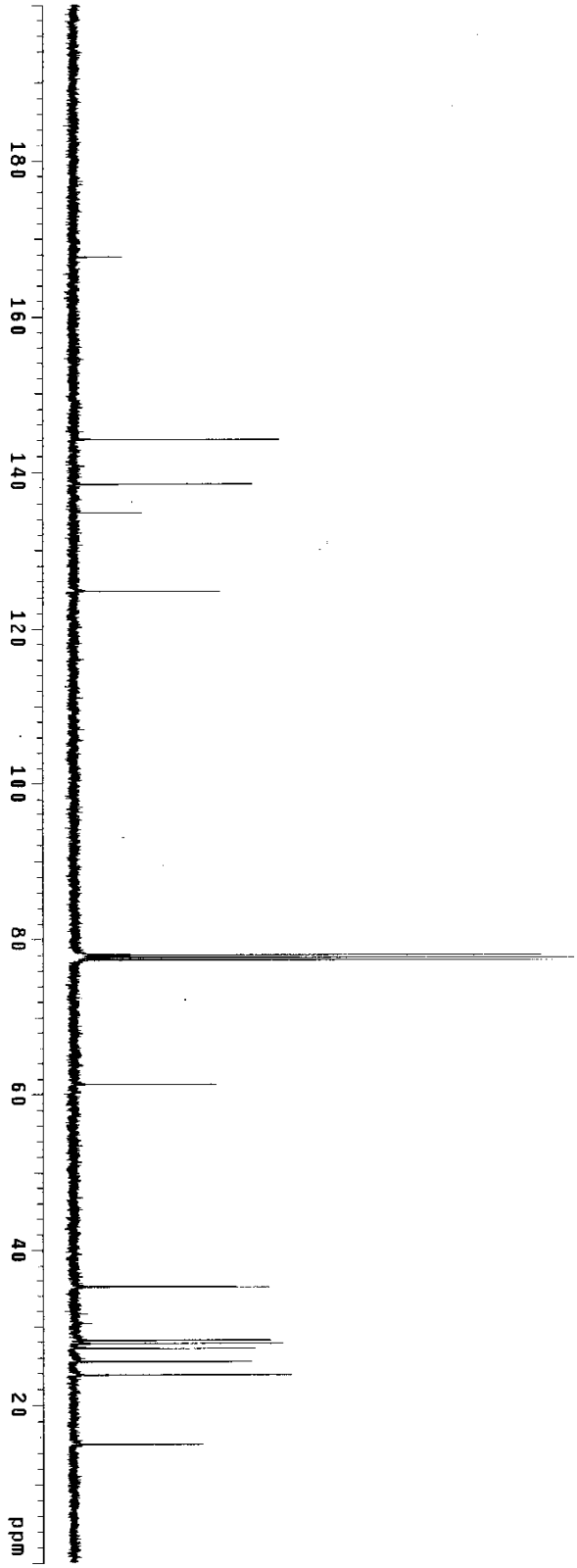


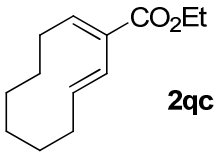
(E,Z)-**S3**


0.43 %
5.53
4.08
H
H
H
n-Pr
OH
n-Pr
nOe
(E,Z)-S3
ppm
0
1
2
3
4
5
6
7
8
9
-0.31
-0.31
-0.17
100.00
-0.00-0.43
0.03


YHS-XVII-18-NOE-2
File: xp
Pulse Sequence: NOESY1D
2.0 %
5.53
4.08
H
H
H
n-Pr
OH
n-Pr
nOe
(E,Z)-S3
ppm
9
8
7
6
5
4
3
2
1
0
-0.78
100.00
-1.03
-1.96
33.74
-6.38
-4.20

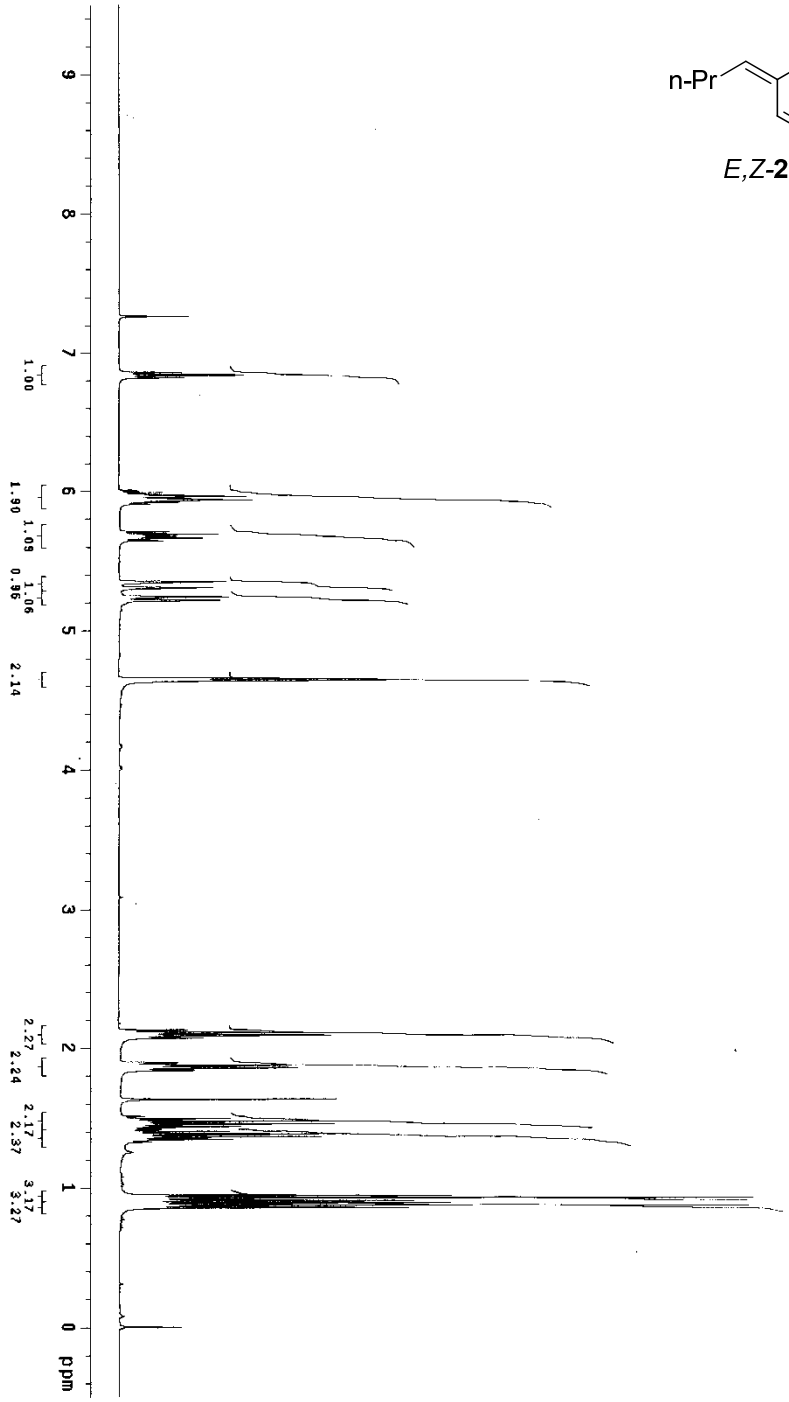

YHS-XVII-23
File: xp
Pulse Sequence: s2pul
CO2Et
2qc
ppm
0
1
2
3
4
5
6
7
8
9
13.50
3.08
6.06
2.50
1.22
1.19
1.13

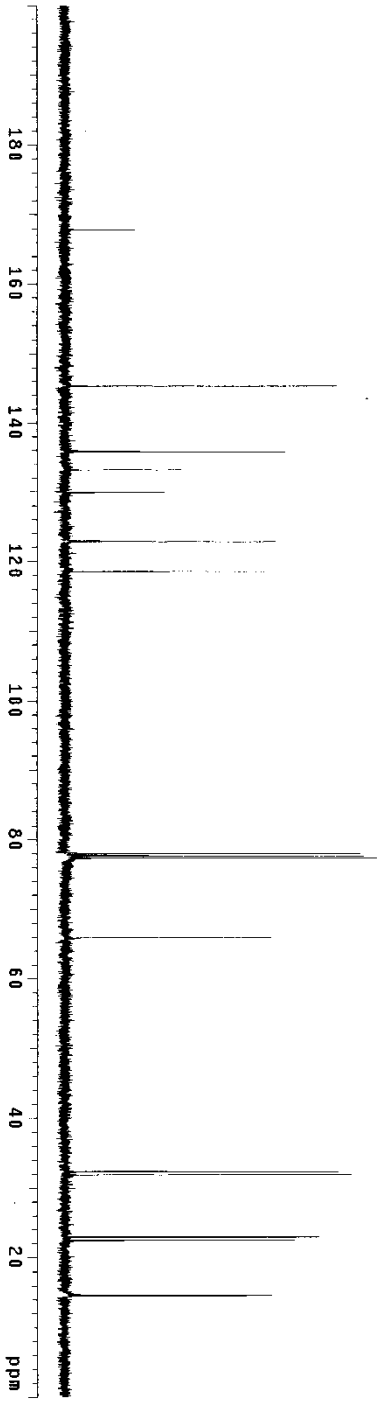


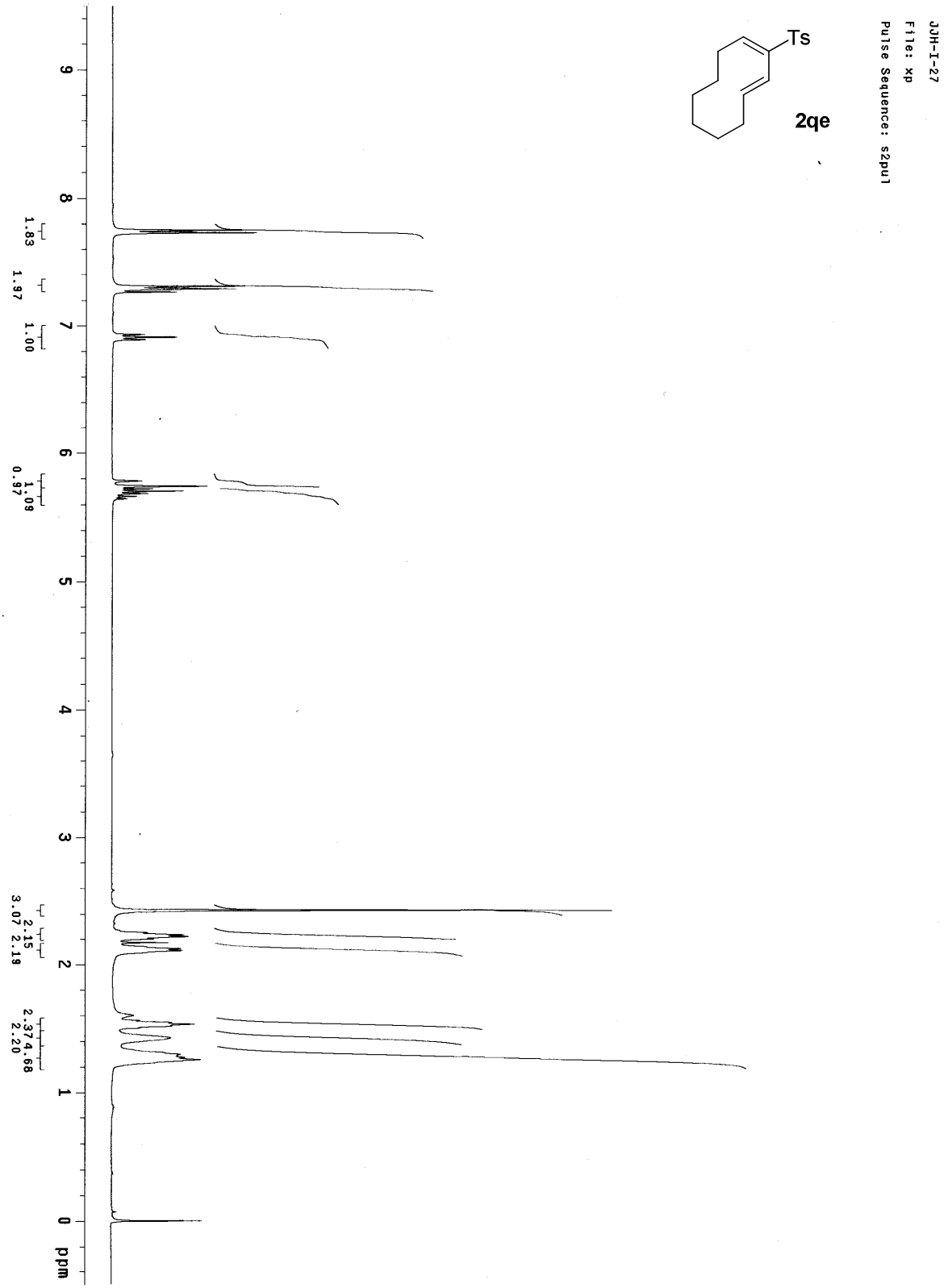


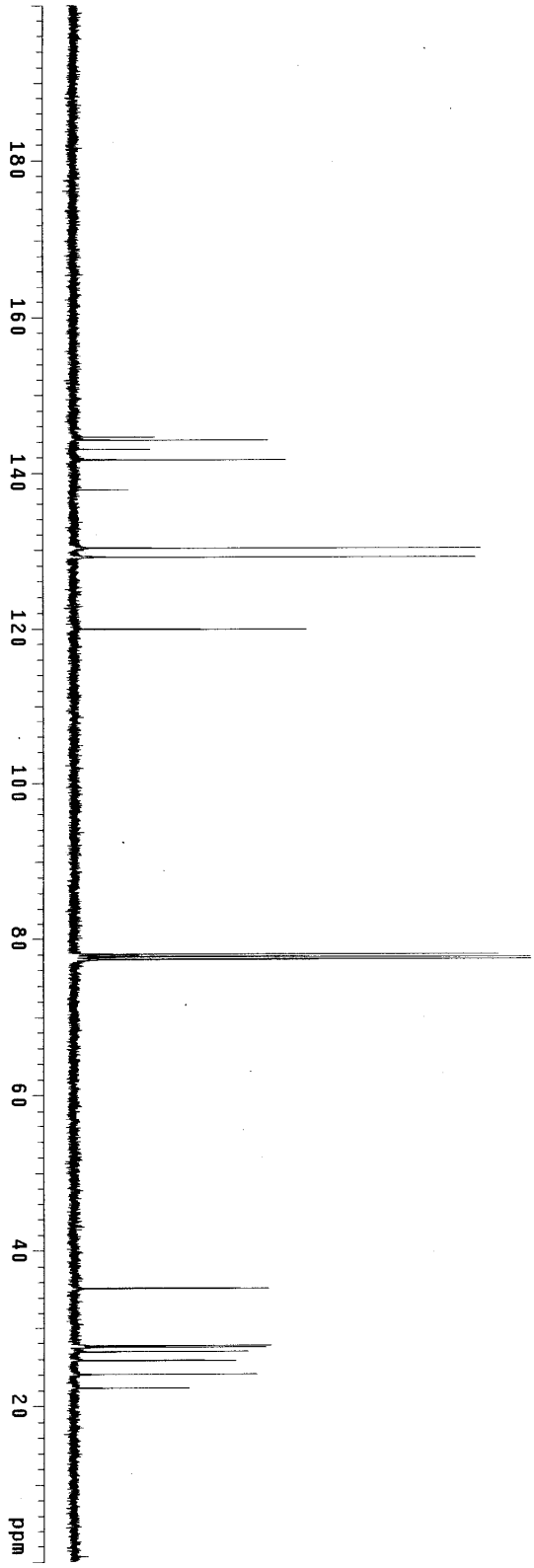
2qc

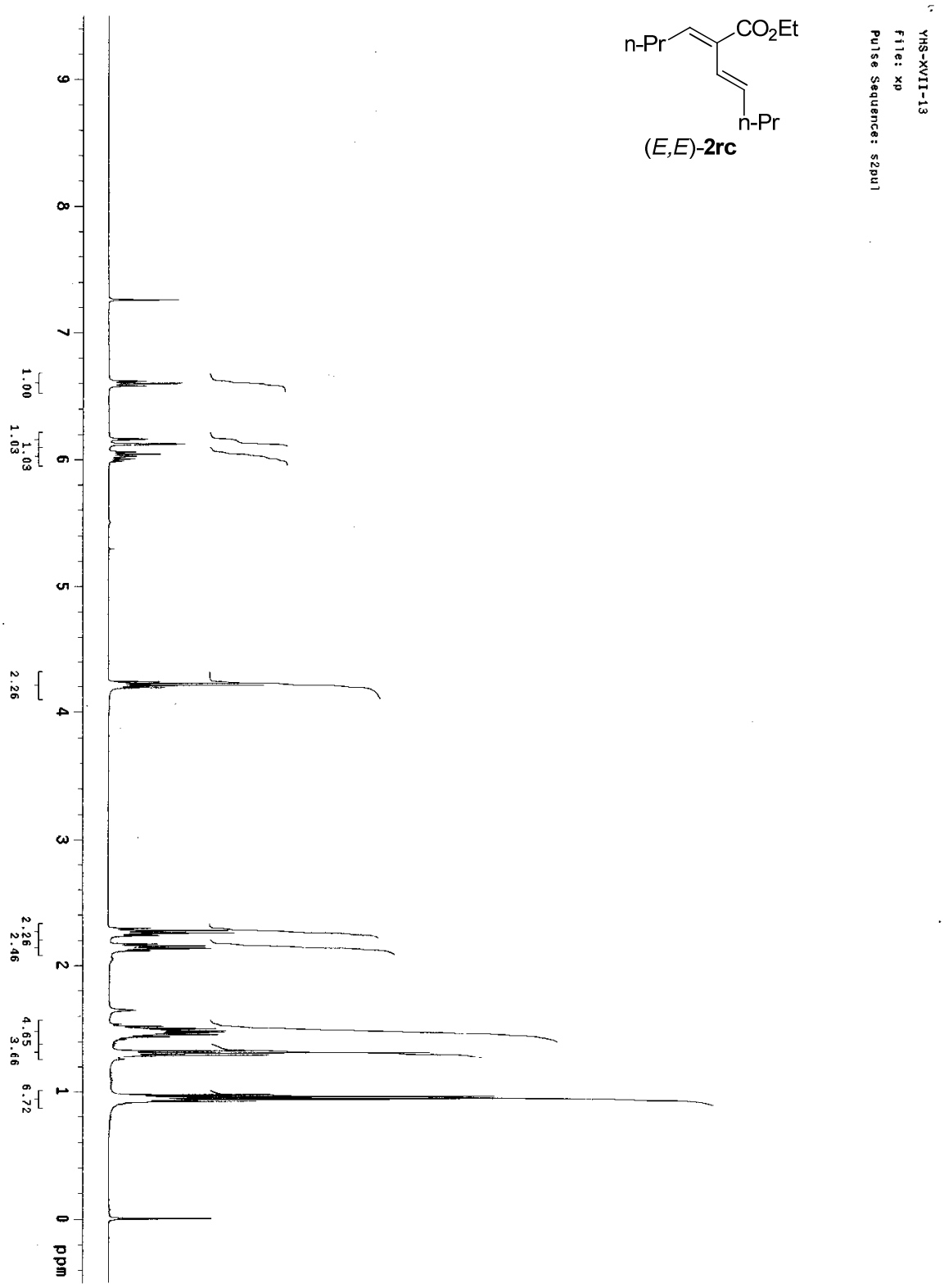
YHS-XVII-23
File: xp
Pulse Sequence: s2pul


YHS-XVII-137
File: xp
Pulse Sequence: s2pul
O
n-Pr
OAll
n-Pr
E,Z-2rd
ppm
0
1
2
3
4
5
6
7
8
9
3.17
3.27
2.17
2.37
2.27
2.24
2.14
1.06
0.96
1.09
1.90
1.00


YMS-XVII-137
File: xp
Pulse Sequence: s2pul
O
n-Pr
OAll
n-Pr
E,Z-2rd
ppm
20
40
60
80
100
120
140
160
180


JJH-I-27
File: xp
Pulse Sequence: s2pul
Ts
2qe
9
8
7
6
5
4
3
2
1
0
ppm
1.83
1.97
1.00
1.09
0.97
2.15
3.07
2.19
2.37
4.68
2.20


JJH-I-27
File: xp
Pulse Sequence: s2pul
Ts
2qe
180
160
140
120
100
80
60
40
20
ppm


YHS-XVII-13
File: xp
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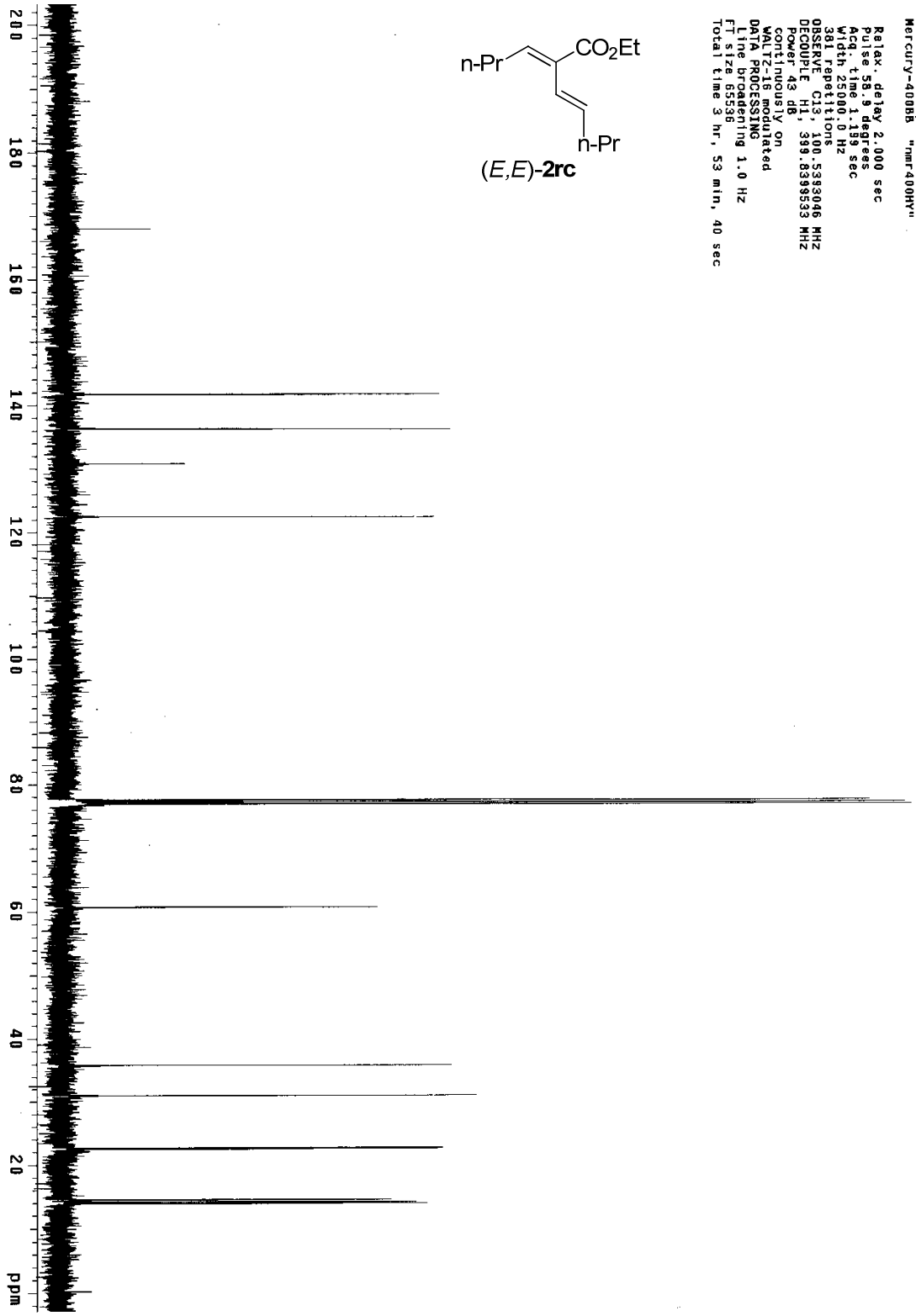
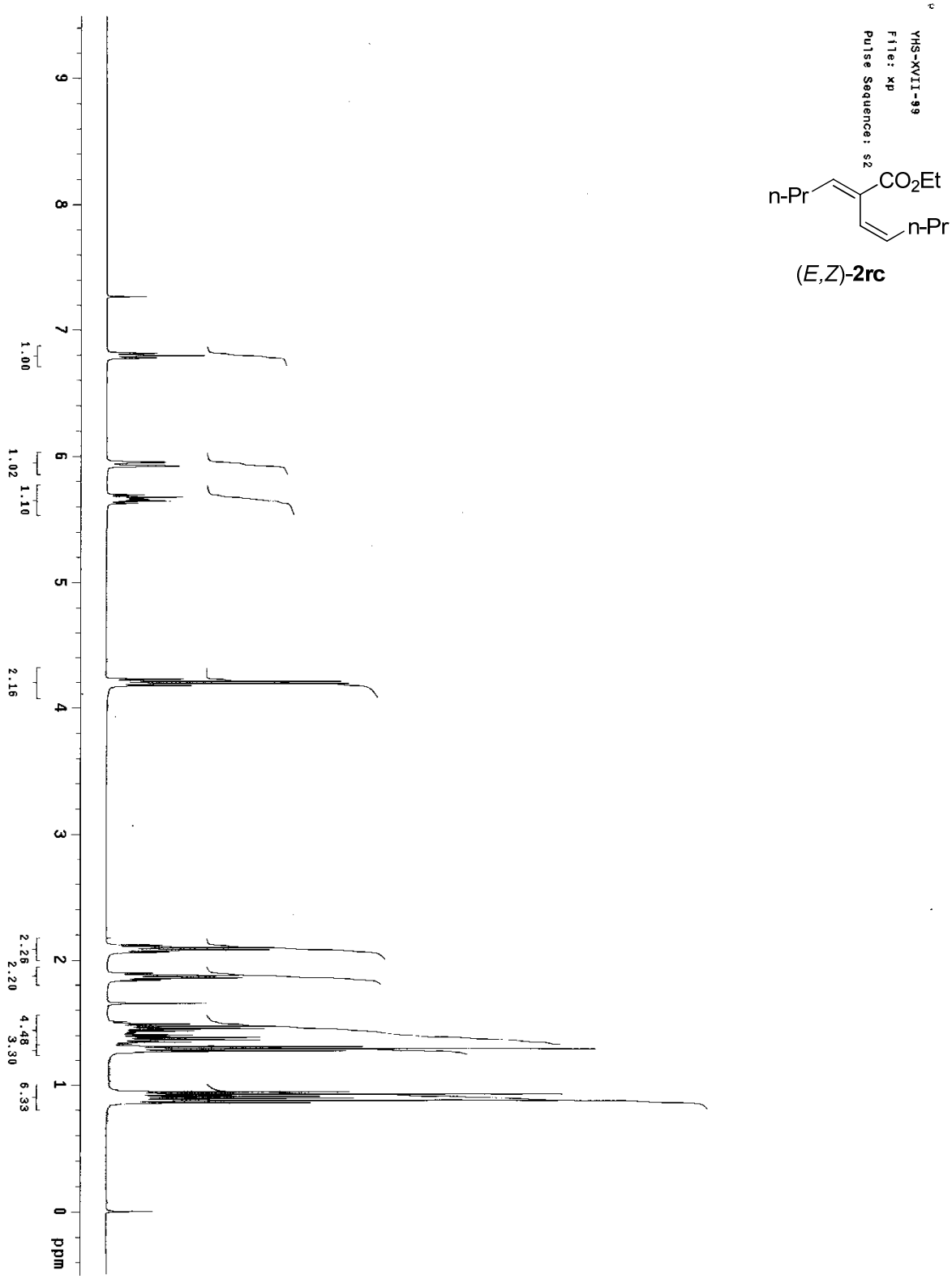
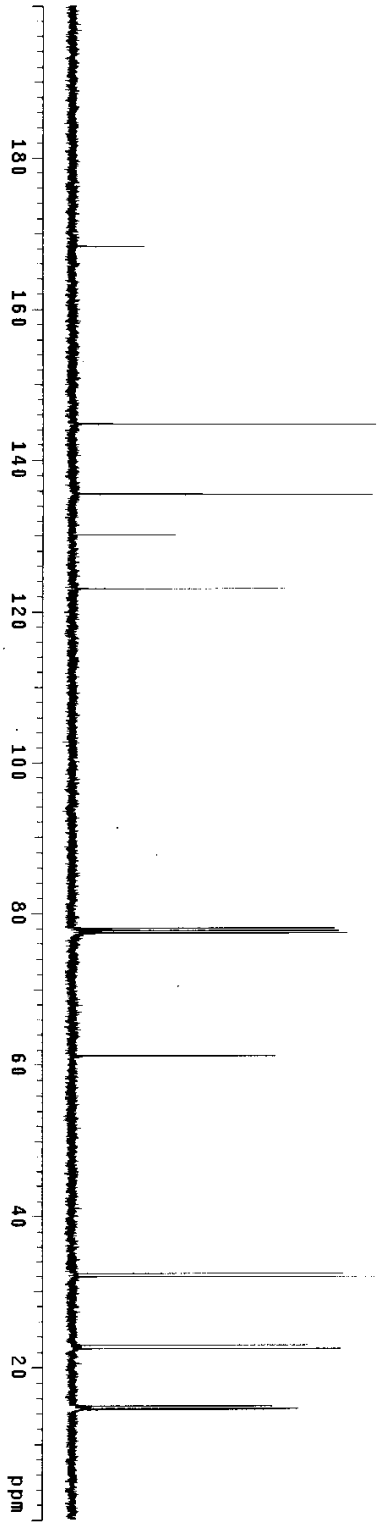
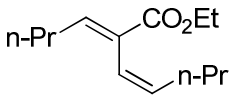
n-Pr
CO2Et
n-Pr
(E,E)-2rc
ppm
9
8
7
6
5
4
3
2
1
0
1.00
1.03
1.03
2.26
2.26
2.46
4.65
3.66
6.72

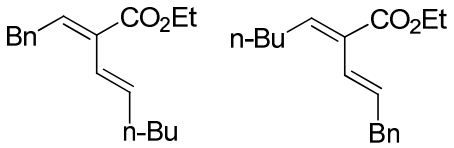

SS-XII-60A
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400BB "nmr400HY"
Relax. delay 2.000 sec
Pulse 58.9 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
381 repetitions
OBSERVE C13, 100.5393046 MHz
DECOUPLE H1, 399.8399533 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 3 hr, 53 min, 40 sec
n-Pr
CO2Et
n-Pr
(E,E)-2rc
200
180
160
140
120
100
80
60
40
20
ppm


YHS-XVII-99
File: xp
Pulse Sequence: s2
n-Pr
CO2Et
n-Pr
(E,Z)-2rc
ppm
0
1
2
3
4
5
6
7
8
9
6.33
3.30
4.48
2.20
2.26
2.16
1.10
1.02
1.00


YHS-XVII-99
File: xp
Pulse Sequence: s2pul
ppm
20
40
60
80
100
120
140
160
180

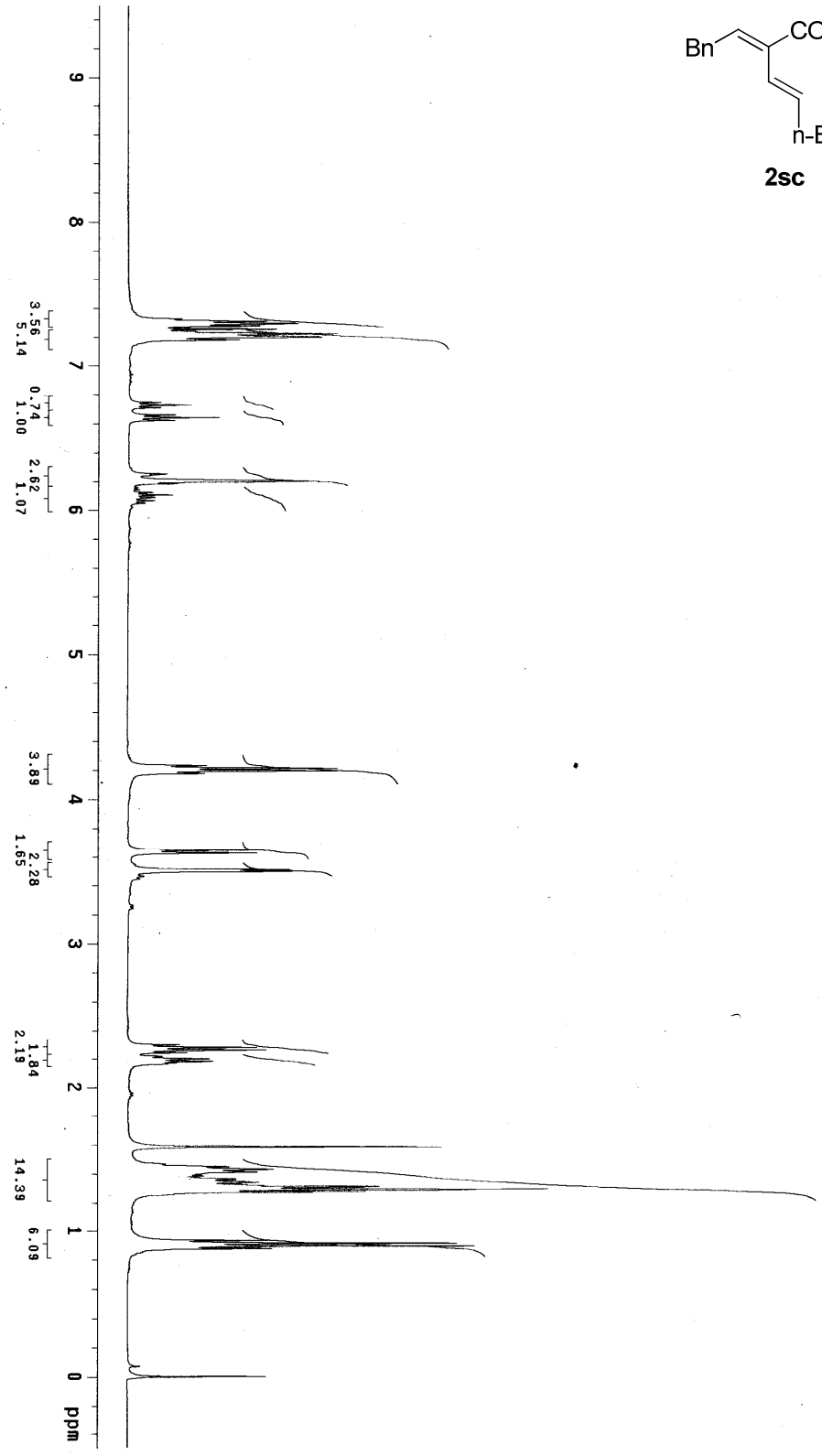

n-Pr
CO2Et
n-Pr

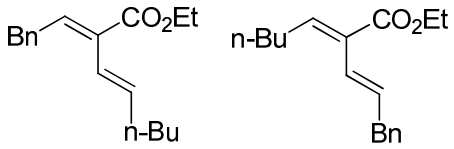
(*E,Z*)-**2rc**



2sc **2sc'**

2sc:2sc' = 1.4:1

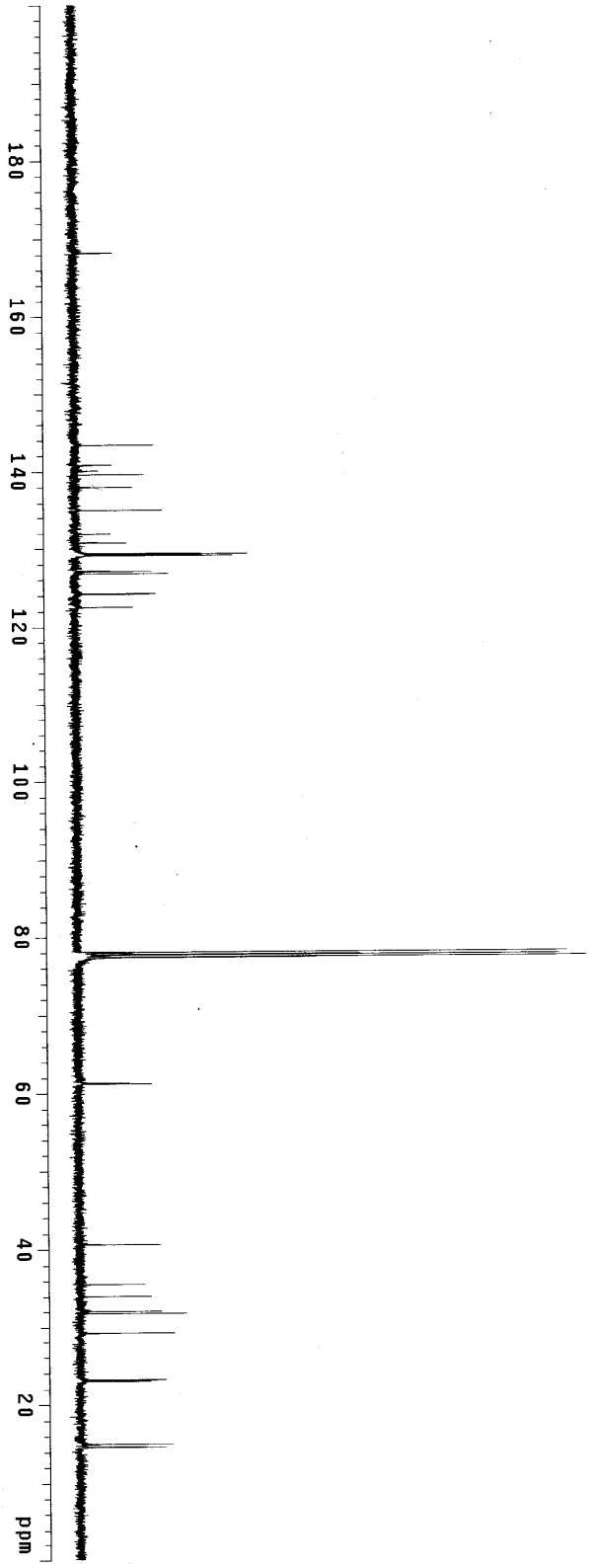


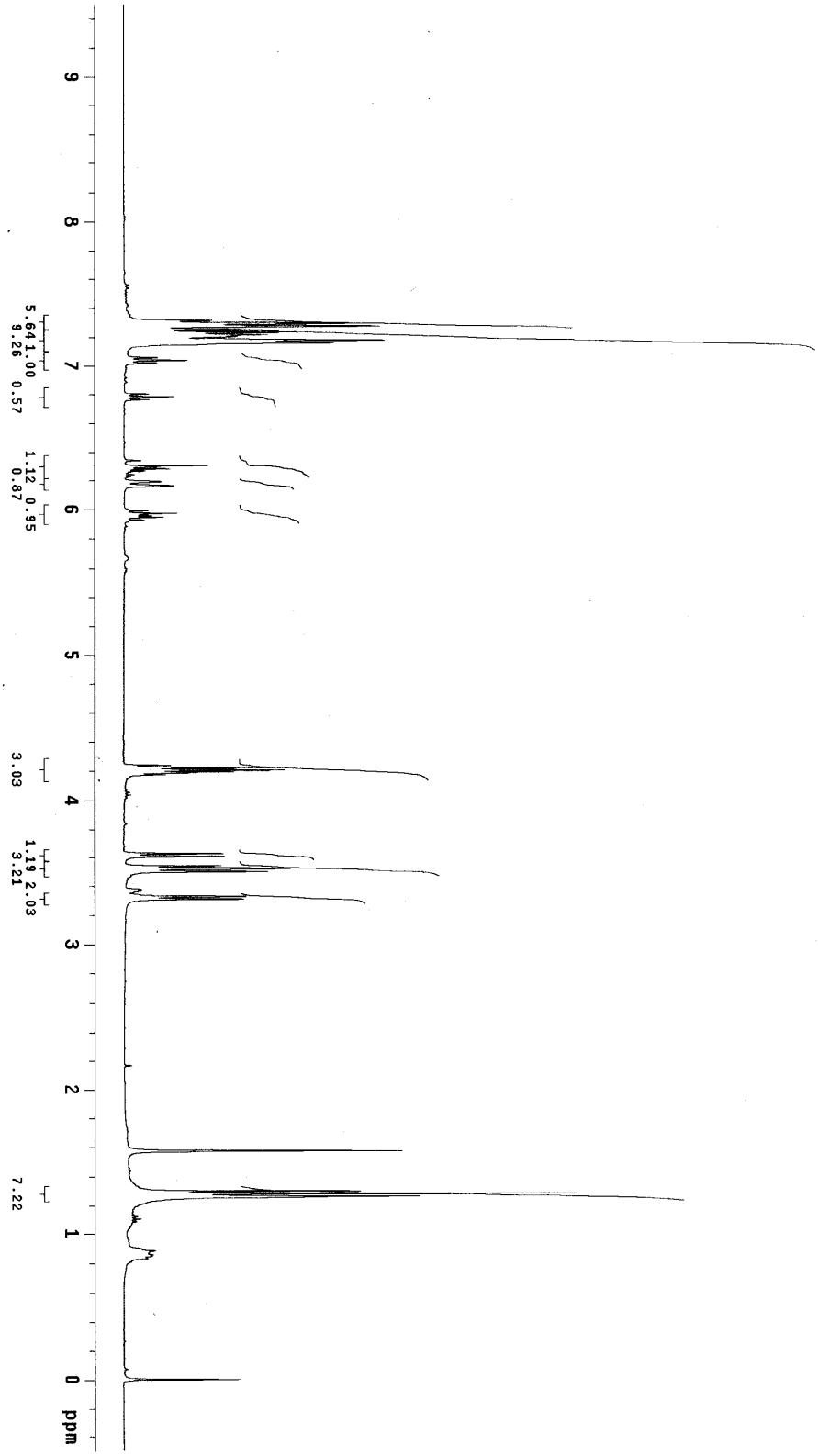


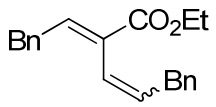
2sc **2sc'**

2sc:2sc' = 1.4:1

YHS-XVII-93
File: xp
Pulse Sequence: s2pul

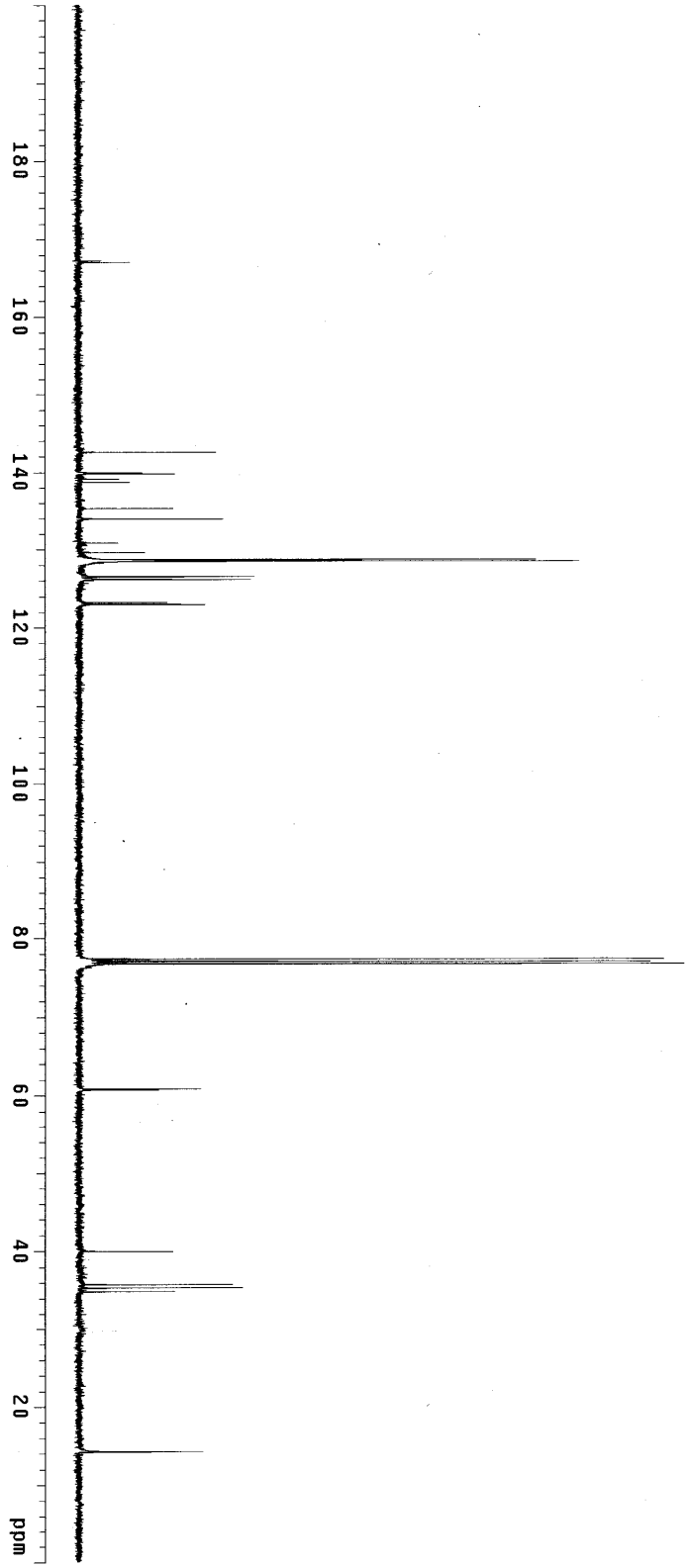


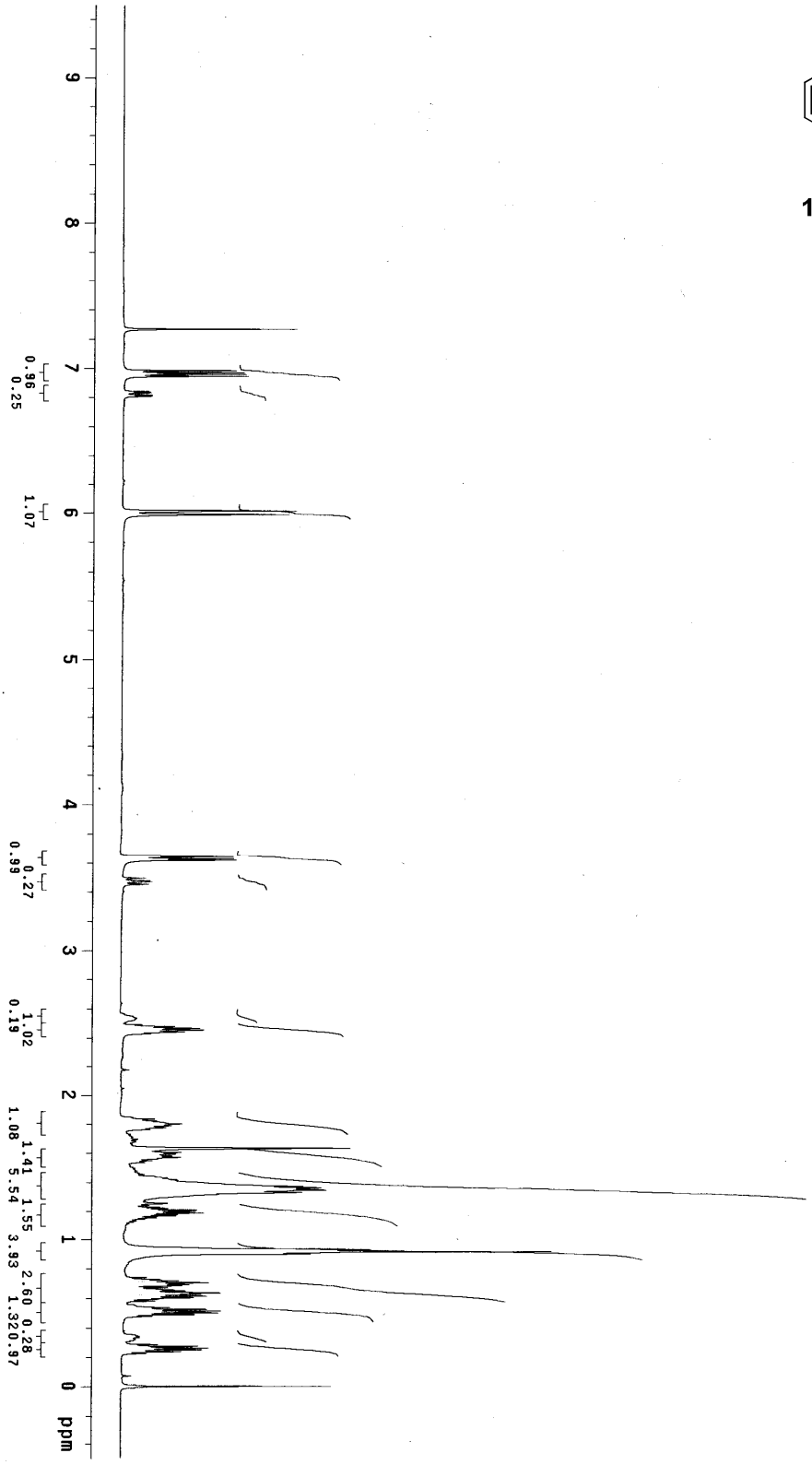


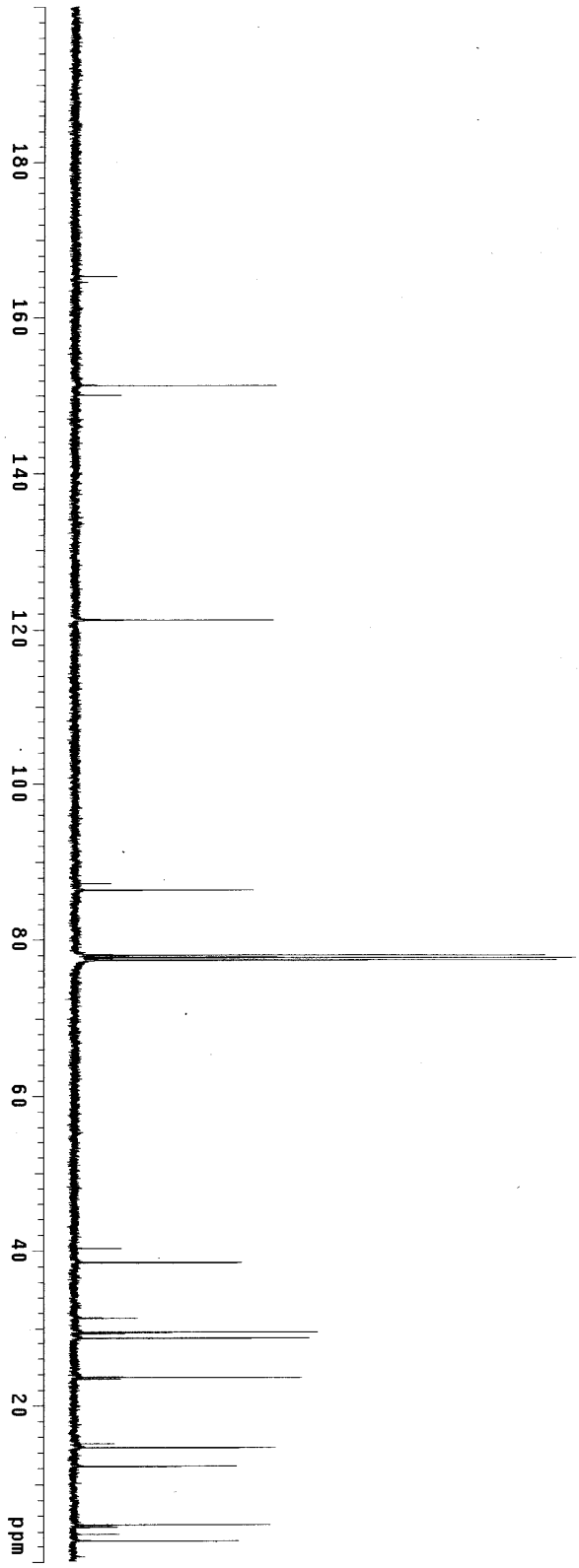


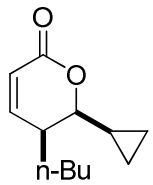
2tc (*E,Z/E,E*=1.5:1)

2pu1


YHS-XVII-84
File: xp
Pulse Sequence: s2pul
Bn
CO2Et
Bn
2tc (E,Z/E,E=1.5:1)
180
160
140
120
100
80
60
40
20
ppm

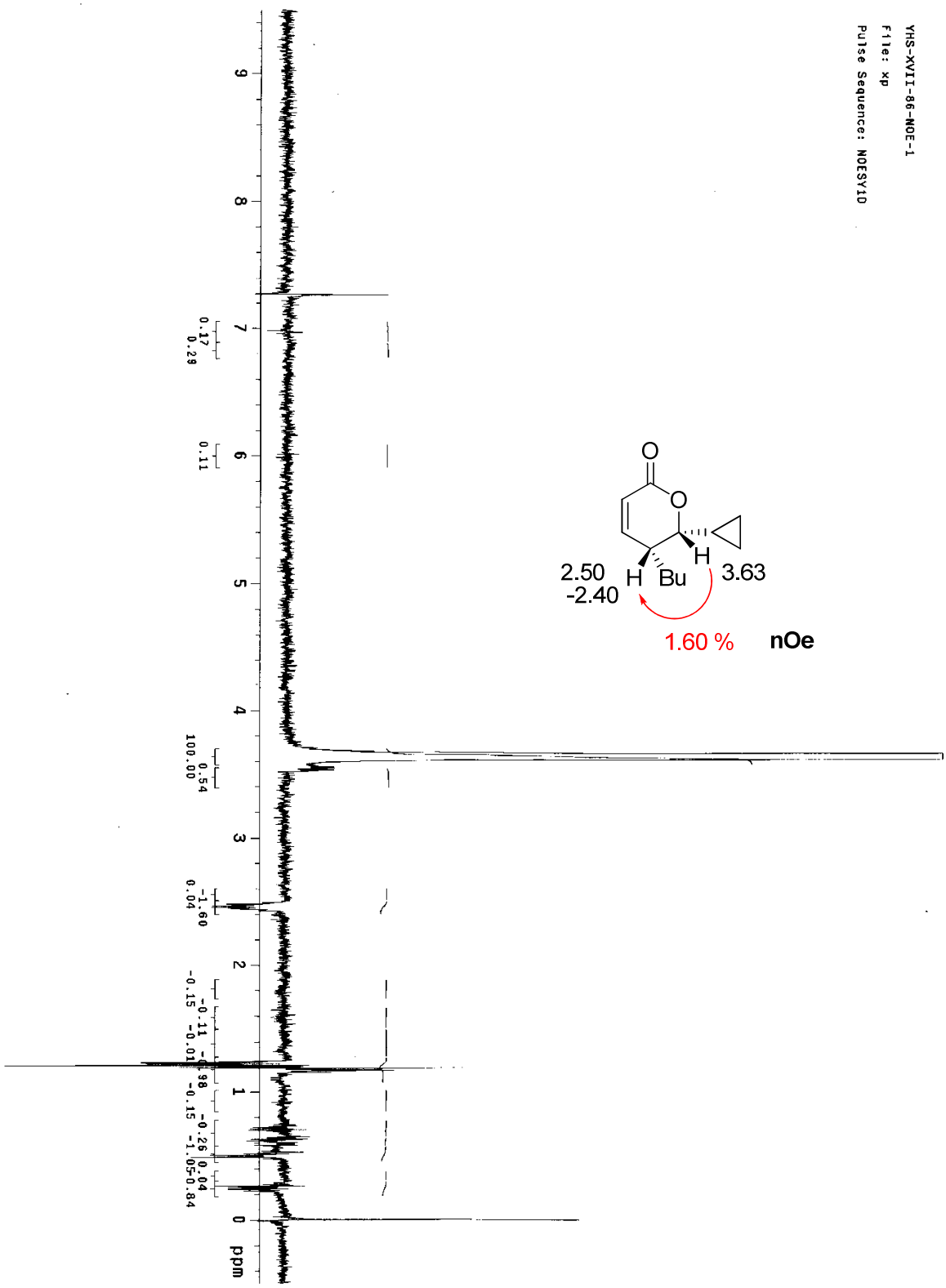

YHS-XVII-86
File: xp
Pulse Sequence: s2pul
n-Bu
1u (dr = 3.8:1)
9
8
7
6
5
4
3
2
1
0
ppm
0.96
0.25
1.07
0.27
0.99
1.02
0.19
1.41
1.08
1.55
5.54
2.60
3.93
0.28
1.32
0.97

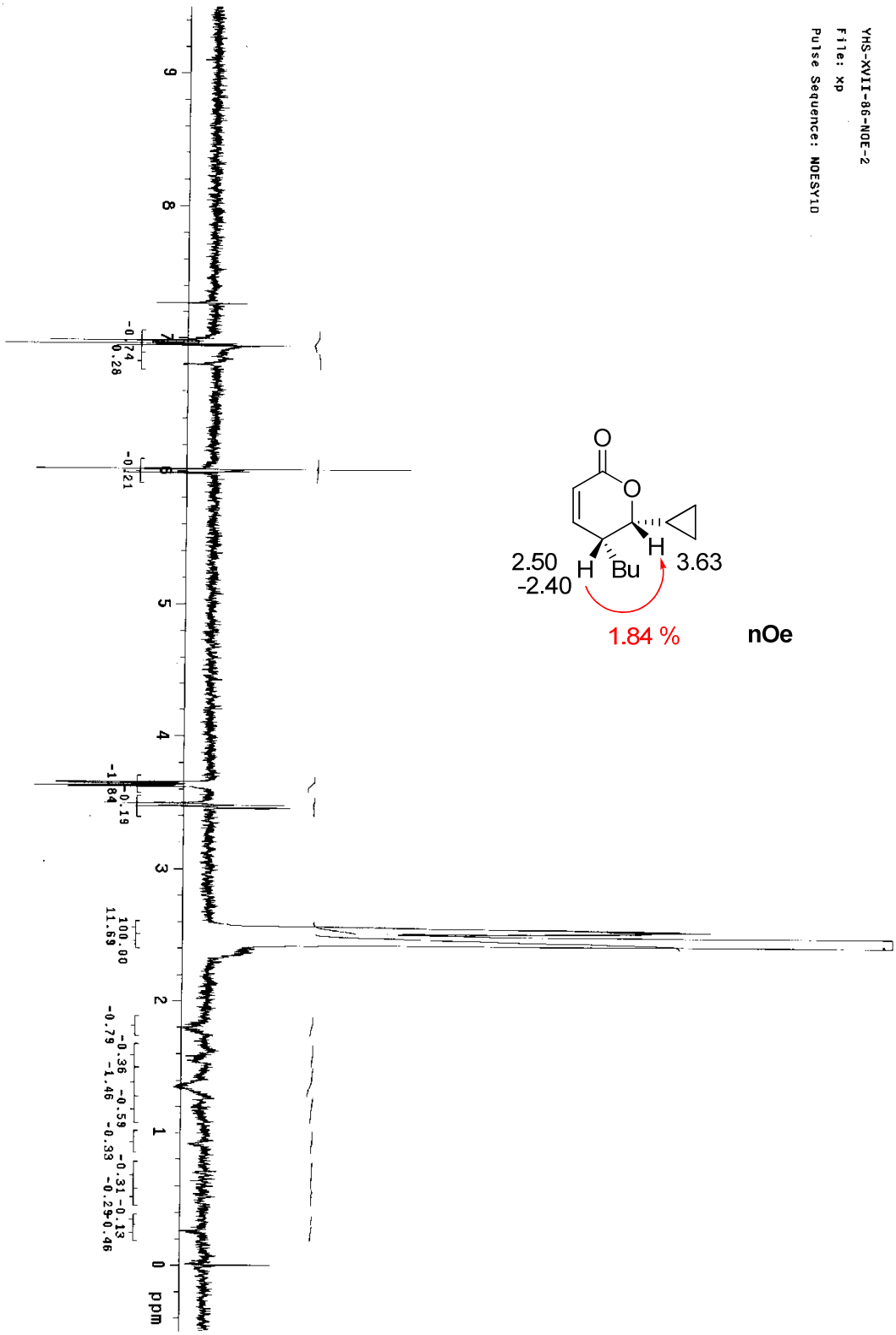


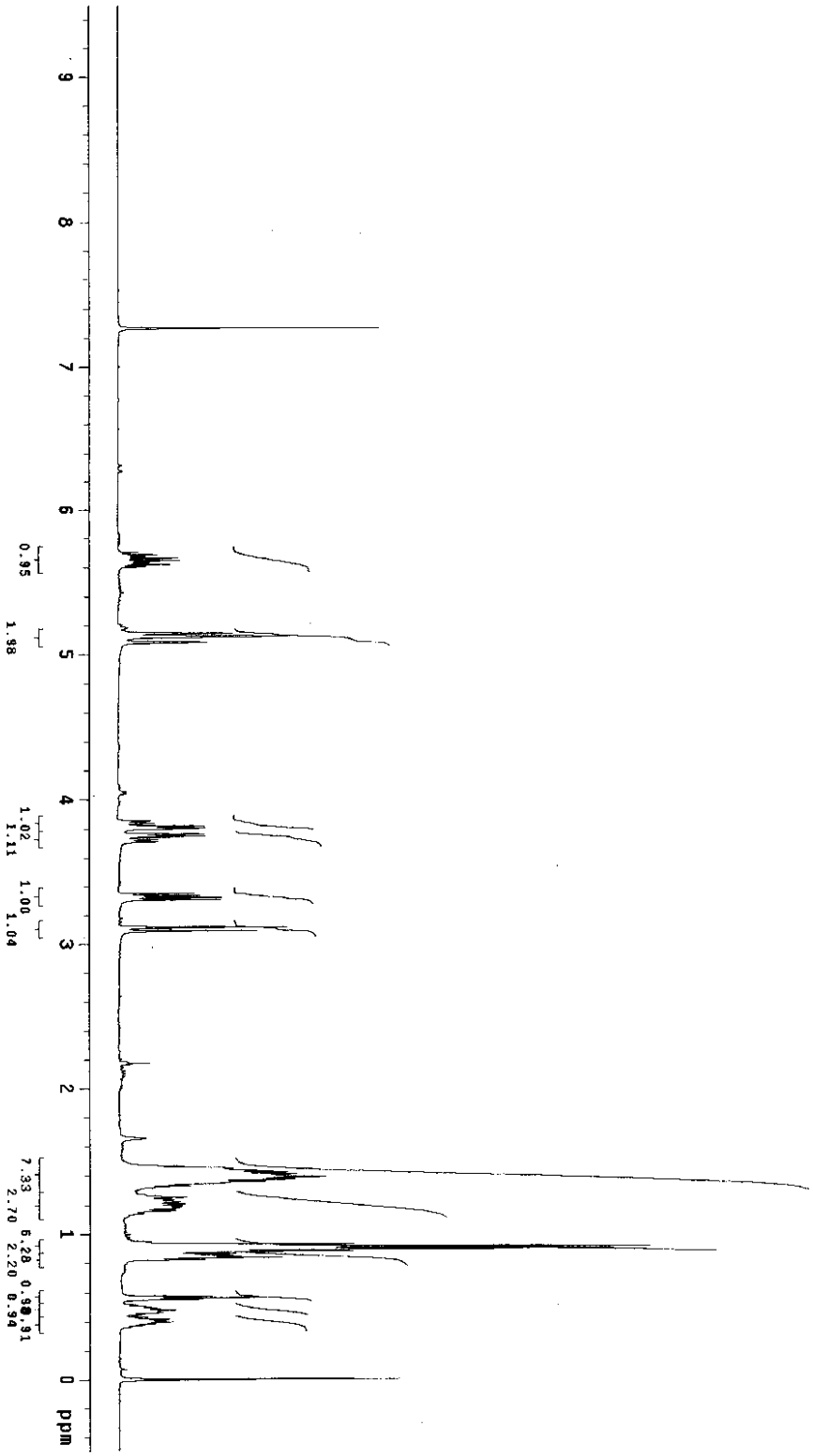


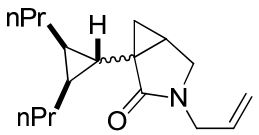
1u (dr = 3.8:1)

YHS-XVII-86
File: xp
Pulse Sequence: s2pul

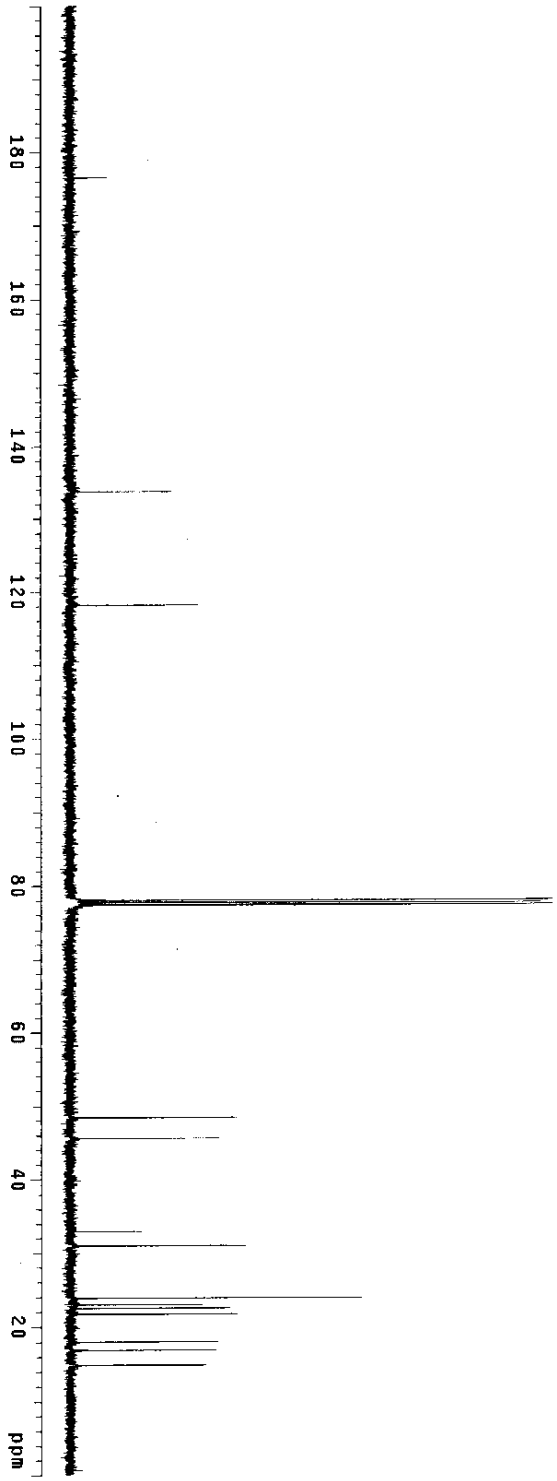

YHS-XVII-86-NOE-1
File: xp
Pulse Sequence: NOESY1D
O
O
H
H
Bu
2.50
-2.40
3.63
1.60 %
nOe
ppm

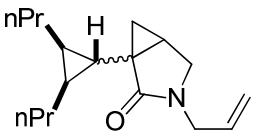

YHS-XVII-86-NOE-2
File: xp
Pulse Sequence: NOESY1D
O
O
H
H
Bu
2.50
-2.40
3.63
1.84 %
nOe
ppm



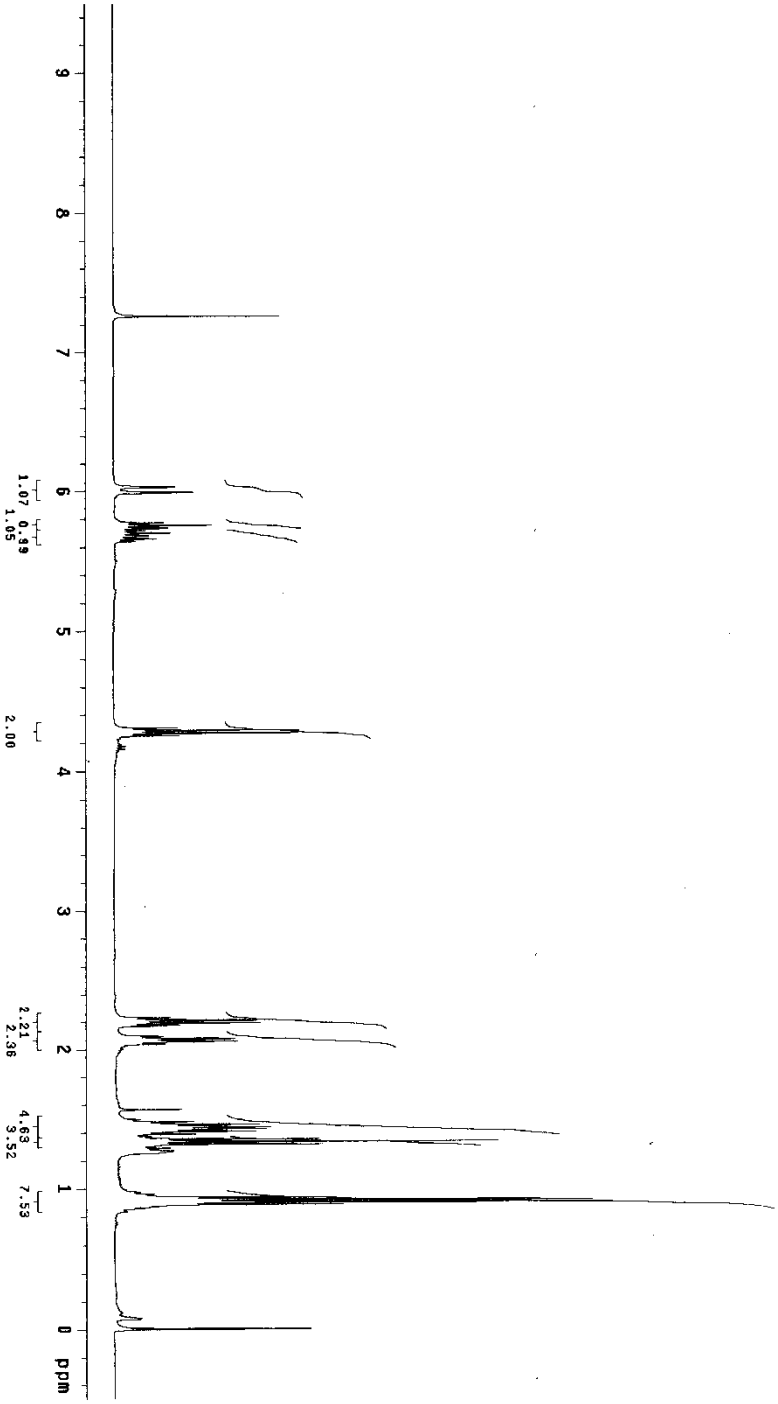


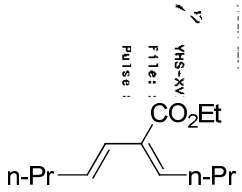
6 (major diastereomer)



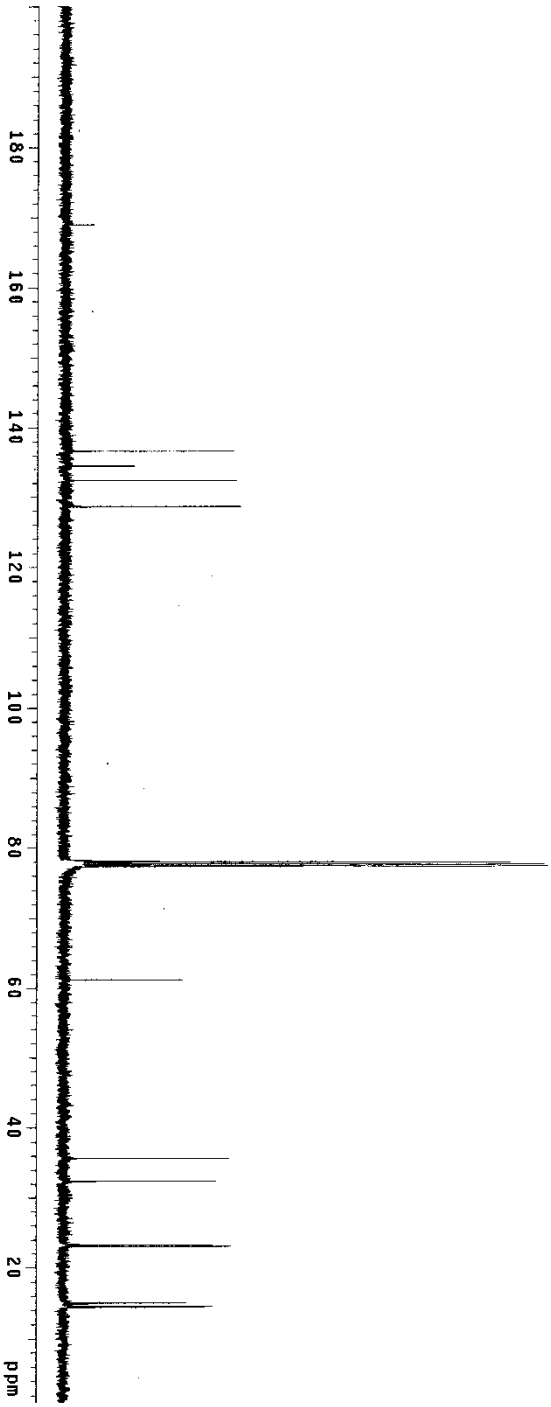


6 (major diastereomer)


9
8
7
6
5
4
3
2
1
0
ppm
1.07
0.99
1.05
2.00
2.21
2.36
4.63
3.52
7.53


CO2Et
n-Pr
n-Pr

Z,E-**2rc**


YHS-XVIII-55
File: xp
Pulse Sequence: s2pul
CO2Et
n-Pr
n-Pr
Z,E-2rc
ppm
20
40
60
80
100
120
140
160
180

IX. DFT Studies

1. Computational details

All DFT calculations were performed with the Gaussian 09 software package.[8] Geometry optimization of all the minima and transition states involved was carried out at the B3LYP level of theory.[9] The SDD basis set[10] was used for gold and the 6-31G(d) basis set[11] for the other atoms. The keyword "5D" was used to specify that five (instead of six) d-type orbitals were used for all elements in the calculations. The vibrational frequencies were computed at the same level to check whether each optimized structure was an energy minimum or a transition state and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298 K. To improve the calculation accuracy with the consideration of dispersion energies, single-point energies and solvent effects were computed at the M06/6-311+G(d,p)-SDD level (the SDD basis set for gold and the 6-311+G(d,p) basis set for the other atoms),[12] based on the gas-phase optimized structures. Solvation energies in chloroform ($CHCl_3$) were evaluated by a self-consistent reaction field (SCRF) using the CPCM model,[13] where UFF radii were used. In the paper and the Supporting Information, all discussed energies are Gibbs free energies in chloroform (ΔG_{sol}) at 298 K unless specified. The Gibbs free energies in gas phase (ΔG_{gas}) and the enthalpies in gas phase (ΔH_{gas}) are also given for reference.

[References]

8. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, revision A. 02; Gaussian, Inc.: Wallingford CT, 2009.
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12. Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.
13. (a) Barone, V.; Cossi, M. *J. Phys. Chem. A* **1998**, *102*, 1995. (b) Cossi, M.; Rega, N.; Scalmani, G.; Barone, V. *J. Comput. Chem.* **2003**, *24*, 669. (c) Takano, Y.; Houk, K. N. *J. Chem. Theory Comput.* **2005**, *1*, 70.

The DFT-calculated structures of transition states **TS1-c**, **TS1-t**, **TS3-in**, and **TS3-out** shown in Figure 1 of the paper are provided in Figure S1. As mentioned in the paper, there is obvious steric repulsion between the migrating methyl group and the carboxylic acid in **TS1-c**. This conclusion is supported by the disfavored eclipsed conformation along the developing C1−C4 bond in **TS1-c**, as evidenced by the C5-C1-C4-C6 dihedral angle of 28.8° (Figure S1).

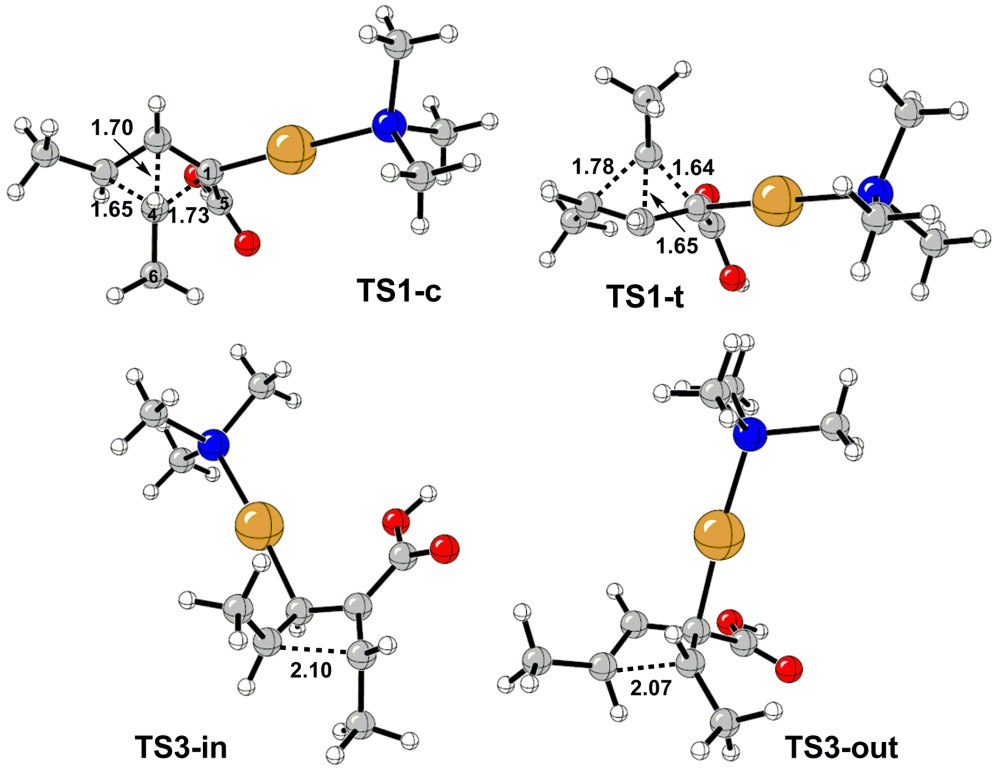

Figure S1. DFT-calculated structures of transition states **TS1-c**, **TS1-t**, **TS3-in**, and **TS3-out** (C gray; H white; O red; P blue; Au gold; distances are given in Å).

As mentioned in the paper, from cyclopropyl Au-carbenoid **A-trans**, the enyne metathesis pathway via transition state **TS1-t** is the most favored one, which requires an overall activation free energy of only 8.0 kcal/mol in $CHCl_3$ (Figure 1). As depicted in Figure S2, the cyclobutene formation pathway and the [4+2] annulation pathway from **A-trans** require overall activation free energies of 16.7 and 14.6 kcal/mol in $CHCl_3$, respectively. These two pathways are higher by 7-9 kcal/mol in energy than the enyne metathesis pathway via **TS1-t**, suggesting that neither cyclobutene **B-trans** nor [4+2] product **G** will be generated. This is in accord with the experimental results.

The formation of **A-trans** and other issues will be discussed in a full paper in the due course.

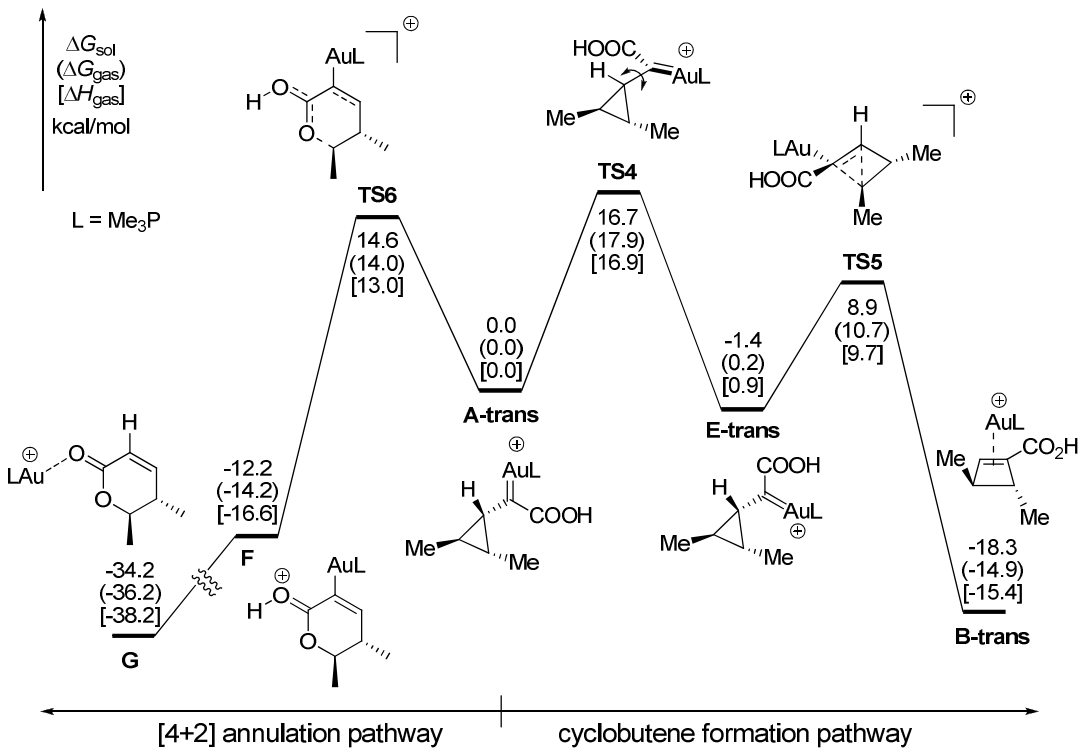

Figure S2. DFT-calculated free energy surfaces for cyclobutene formation and [4+2] annulation pathways.

In Figure S3, three different cyclobutene ring-opening pathways **a**, **b**, and **c** were compared. Calculations indicated that, in the presence of Au(I)-catalyst, pathways **a** (from gold-alkene complex **B-trans**) and **b** (from gold-carbonyl complex **B'-trans**) are much more favored than pathway **c** (from free cyclobutene **B''-trans**, Figure S3). However, in all cases, outward conrotation transition states are lower by 12-15 kcal/mol in energy than the corresponding inward conrotation transition states, showing that the *Z,E*-diene will be generated exclusively. This selectivity is contrary to the experimental result in the corresponding gold-catalyzed enyne metathesis reaction, where the *E,Z*-diene is the sole product. Therefore, the involvement of cyclobutene intermediates in the gold-catalyzed enyne metathesis reaction can be excluded.

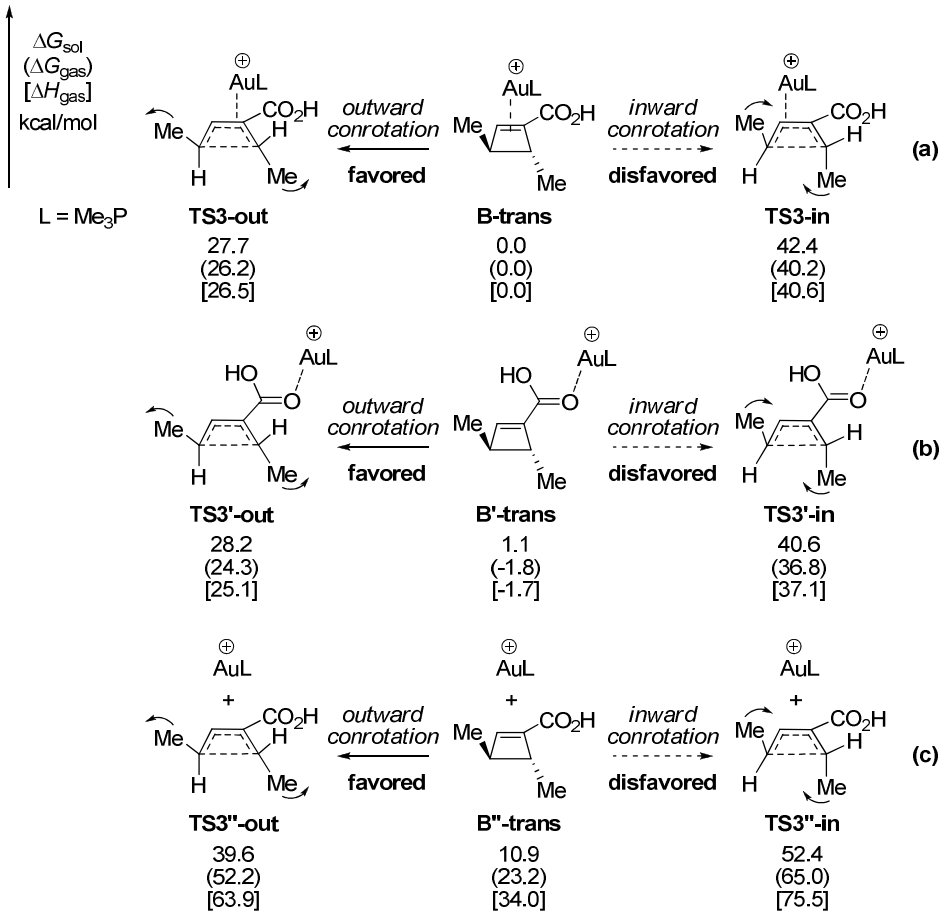

Figure S3. DFT-calculated energies for three different cyclobutene ring-opening pathways.

2. Coordinates of all stationary points

A-trans

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.261831	-0.809811	-0.474171
2	6	0	-1.419498	0.189655	-0.022725
3	6	0	-3.800371	-0.636712	-0.940429
4	15	0	2.993888	-0.197627	-0.046294
5	79	0	0.637469	0.008066	-0.026492
6	6	0	-3.657559	-1.123613	0.406899
7	1	0	-3.755583	-0.394417	1.207670
8	6	0	-1.929908	1.448381	0.588817
9	8	0	-2.440133	1.481180	1.690559
10	8	0	-1.683915	2.524937	-0.173447
11	1	0	-1.992434	3.313694	0.317245
12	1	0	-1.818755	-1.727700	-0.843901
13	6	0	3.871055	1.413787	-0.160346
14	1	0	3.602191	2.044817	0.691854
15	1	0	4.955302	1.259433	-0.164086
16	1	0	3.579735	1.930896	-1.079285
17	6	0	3.666296	-1.007493	1.461495
18	1	0	3.251487	-2.015075	1.558589
19	1	0	4.758114	-1.073391	1.405804
20	1	0	3.386990	-0.431423	2.348514
21	6	0	3.633427	-1.193749	-1.453094
22	1	0	4.726160	-1.254819	-1.413917
23	1	0	3.217435	-2.204730	-1.412067
24	1	0	3.334778	-0.734693	-2.400144
25	6	0	-4.369537	0.720741	-1.287735
26	1	0	-4.299138	1.433603	-0.463533
27	1	0	-3.887327	1.144255	-2.173031
28	1	0	-5.434454	0.590039	-1.512737
29	1	0	-3.966996	-1.400639	-1.700589
30	6	0	-3.793978	-2.568260	0.803878
31	1	0	-3.620775	-3.249418	-0.034693
32	1	0	-3.119293	-2.824912	1.625758
33	1	0	-4.821990	-2.724783	1.157423

TS1-t

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	2.864529	-0.056342	-0.007662
2	79	0	0.515506	0.002151	-0.069877
3	6	0	-2.361233	-0.659819	-1.067064
4	6	0	-1.596843	0.108106	-0.106211
5	6	0	-3.727087	-0.958120	-0.786649
6	6	0	-2.526217	-1.089101	0.514291
7	6	0	-1.991491	-2.426869	0.974140
8	1	0	-3.103382	-0.509041	1.235397
9	1	0	-1.267282	-2.847695	0.271541
10	1	0	-2.804041	-3.146267	1.116471
11	1	0	-1.490330	-2.294338	1.938174
12	6	0	3.633347	1.612203	-0.084516
13	1	0	3.289413	2.219304	0.758040
14	1	0	4.725118	1.533297	-0.047166
15	1	0	3.341704	2.112710	-1.012515
16	6	0	3.549019	-0.822567	1.517820
17	1	0	4.643968	-0.805232	1.497799
18	1	0	3.198626	-0.274380	2.397311
19	1	0	3.209396	-1.859368	1.598782
20	6	0	3.630706	-0.993213	-1.392584
21	1	0	3.337371	-0.549051	-2.348356
22	1	0	4.722712	-0.975468	-1.310037
23	1	0	3.288692	-2.032235	-1.374260
24	1	0	-1.825298	-1.422022	-1.628373
25	6	0	-2.087595	1.441222	0.406273
26	8	0	-2.694379	1.622507	1.442449
27	8	0	-1.713093	2.434750	-0.420887
28	1	0	-2.009802	3.274537	-0.017456
29	1	0	-4.034451	-1.927977	-1.179144
30	6	0	-4.873532	-0.024507	-0.493685
31	1	0	-5.609298	-0.517104	0.149236
32	1	0	-4.571850	0.912747	-0.027453
33	1	0	-5.368893	0.200696	-1.446194

C-t

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	2.829045	-0.093081	0.144766
2	79	0	0.490569	0.061285	-0.021144
3	6	0	-2.396291	0.872700	0.947473
4	6	0	-1.616349	0.120052	-0.269101
5	6	0	-3.583296	0.438532	1.483202
6	6	0	-2.361049	1.265585	-0.687570
7	6	0	-1.783758	2.635587	-0.928344
8	1	0	-3.326369	1.087235	-1.162545
9	1	0	-0.848887	2.789837	-0.381885
10	1	0	-2.496345	3.426592	-0.676524
11	1	0	-1.562286	2.711456	-2.001275
12	6	0	3.576314	-1.125178	-1.180674
13	1	0	3.340678	-0.700209	-2.160766
14	1	0	4.664083	-1.172849	-1.061935
15	1	0	3.166784	-2.138627	-1.137032
16	6	0	3.700925	1.522348	0.036729
17	1	0	4.784150	1.378294	0.110029
18	1	0	3.468941	2.006191	-0.916613
19	1	0	3.372668	2.178838	0.847954
20	6	0	3.412700	-0.845695	1.718099
21	1	0	2.996456	-1.851887	1.823378
22	1	0	4.506209	-0.906863	1.732116
23	1	0	3.077070	-0.242431	2.566735
24	1	0	-1.766602	1.509424	1.556425
25	6	0	-2.136885	-1.226672	-0.689439
26	8	0	-2.541041	-1.468018	-1.806310
27	8	0	-2.028308	-2.162749	0.281525
28	1	0	-2.302016	-3.012743	-0.116335
29	6	0	-4.657372	-0.385319	0.880579
30	1	0	-4.538927	-0.593364	-0.182998
31	1	0	-4.709711	-1.340393	1.425293
32	1	0	-5.625051	0.105447	1.049724
33	1	0	-3.766335	0.735251	2.517684

TS2-t

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	2.816257	-0.094941	0.138286
2	79	0	0.485322	0.079040	-0.010922
3	6	0	-2.358403	0.676730	1.122205
4	6	0	-1.680719	0.142380	-0.160790
5	6	0	-3.636992	0.418571	1.493336
6	6	0	-2.242368	1.218325	-0.902528
7	6	0	-1.832277	2.641202	-0.876134
8	6	0	3.547770	-1.134461	-1.189020
9	6	0	3.698492	1.514119	0.030729
10	6	0	3.385348	-0.853571	1.712821
11	6	0	-2.086965	-1.210688	-0.686110
12	8	0	-2.410323	-1.412326	-1.838824
13	8	0	-1.993875	-2.183520	0.244067
14	6	0	-4.699641	-0.383420	0.815346
15	1	0	-1.758075	1.319286	1.756932
16	1	0	-3.916662	0.803892	2.474704
17	1	0	-3.043202	0.972299	-1.607621
18	1	0	-1.067099	2.866270	-0.130866
19	1	0	-2.694465	3.309007	-0.766546
20	1	0	-1.416608	2.852168	-1.876098
21	1	0	3.316422	-0.706059	-2.168583
22	1	0	4.635044	-1.194346	-1.070666
23	1	0	3.126764	-2.143122	-1.145045
24	1	0	4.780396	1.360829	0.105773
25	1	0	3.472092	1.999144	-0.923273
26	1	0	3.374195	2.172697	0.841755
27	1	0	2.956686	-1.854536	1.817585
28	1	0	4.478052	-0.927823	1.728412
29	1	0	3.055348	-0.245543	2.560200
30	1	0	-2.218627	-3.023876	-0.201648
31	1	0	-4.476360	-0.647892	-0.219863
32	1	0	-4.873577	-1.310306	1.379202
33	1	0	-5.646508	0.169479	0.833149

***E*,*Z*-D**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-2.576574	-0.445158	-0.037939
2	79	0	-0.381133	0.325942	0.032558
3	6	0	-3.244523	-0.816637	1.631016
4	6	0	-3.741792	0.761341	-0.784660
5	6	0	-2.775079	-1.992200	-1.007880
6	1	0	-3.233101	0.087334	2.246744
7	1	0	-4.272989	-1.185209	1.551784
8	1	0	-2.625758	-1.575055	2.119181
9	1	0	-4.758253	0.353048	-0.782883
10	1	0	-3.729608	1.693376	-0.212323
11	1	0	-3.444728	0.980178	-1.814304
12	1	0	-2.163543	-2.786709	-0.570658
13	1	0	-3.824794	-2.305361	-1.004039
14	1	0	-2.452437	-1.830392	-2.040335
15	6	0	2.583736	0.052769	-1.328719
16	6	0	2.052179	0.488685	-0.031228
17	6	0	2.877279	-1.205275	-1.718511
18	6	0	1.484628	1.744191	0.179297
19	6	0	1.363872	2.843785	-0.842923
20	6	0	2.379897	-0.263067	1.247548
21	8	0	1.585249	-0.463406	2.144217
22	8	0	3.670791	-0.614081	1.295762
23	6	0	2.682264	-2.499596	-0.993656
24	1	0	2.767368	0.851259	-2.042046
25	1	0	3.314361	-1.302037	-2.711647
26	1	0	1.361088	2.051644	1.217850
27	1	0	1.231830	2.477693	-1.863288
28	1	0	2.276762	3.456448	-0.816756
29	1	0	0.528917	3.507343	-0.599782
30	1	0	3.826877	-1.039957	2.162638
31	1	0	2.055185	-2.420071	-0.102308
32	1	0	2.224246	-3.233918	-1.667342
33	1	0	3.653633	-2.915735	-0.695044

TS1-c

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-2.897073	-0.210264	0.057566
2	79	0	-0.557594	-0.039084	-0.095241
3	6	0	2.371231	-0.808897	-0.834395
4	6	0	1.534361	0.175602	-0.223370
5	6	0	3.713601	-0.879353	-0.316882
6	6	0	2.564057	-0.707110	0.850586
7	6	0	-3.759644	1.367748	-0.327001
8	6	0	-3.502298	-0.683907	1.728228
9	6	0	-3.638343	-1.447069	-1.083795
10	6	0	1.923407	1.633203	-0.210123
11	8	0	1.599556	2.422114	0.648544
12	8	0	2.617127	1.977853	-1.319986
13	1	0	1.916782	-1.754605	-1.134164
14	1	0	4.279413	0.050504	-0.303378
15	1	0	-3.424740	2.150361	0.360152
16	1	0	-4.843877	1.245238	-0.231144
17	1	0	-3.523520	1.681141	-1.348163
18	1	0	-4.596518	-0.729295	1.740561
19	1	0	-3.166762	0.050648	2.466203
20	1	0	-3.100804	-1.662751	2.006487
21	1	0	-3.381267	-1.198726	-2.117730
22	1	0	-4.728537	-1.460429	-0.979793
23	1	0	-3.245833	-2.443262	-0.859225
24	1	0	2.742264	2.947806	-1.288662
25	6	0	3.070850	0.170595	2.010514
26	1	0	3.593582	1.065563	1.677299
27	1	0	2.227175	0.471968	2.634112
28	1	0	3.757020	-0.446162	2.599346
29	1	0	2.126692	-1.634352	1.210668
30	6	0	4.534931	-2.140291	-0.429486
31	1	0	5.124311	-2.120301	-1.352455
32	1	0	5.236569	-2.216996	0.407023
33	1	0	3.907690	-3.037604	-0.440701

C-c

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-2.879725	0.202452	0.027727
2	79	0	-0.545712	-0.000026	-0.089688
3	6	0	2.393784	1.062949	-0.313369
4	6	0	1.566869	-0.285165	-0.194437
5	6	0	3.624350	1.210847	0.260705
6	6	0	2.263757	-0.276577	-1.444604
7	6	0	-3.632324	1.016346	-1.439574
8	6	0	-3.467713	1.180666	1.469202
9	6	0	-3.737215	-1.417624	0.166283
10	6	0	1.966950	-1.301521	0.836883
11	8	0	2.018323	-2.490801	0.607287
12	8	0	2.168504	-0.774382	2.067881
13	1	0	1.852312	1.942034	-0.645907
14	1	0	4.173115	0.320861	0.563360
15	1	0	-3.235549	2.030079	-1.547511
16	1	0	-4.721148	1.067962	-1.332252
17	1	0	-3.389080	0.450570	-2.343693
18	1	0	-4.561691	1.232802	1.476693
19	1	0	-3.061142	2.195087	1.420581
20	1	0	-3.124988	0.715290	2.398000
21	1	0	-3.497682	-2.040608	-0.700435
22	1	0	-4.821839	-1.273493	0.216178
23	1	0	-3.402777	-1.938807	1.068018
24	1	0	2.314894	-1.528659	2.672322
25	6	0	3.422339	-1.145224	-1.845582
26	1	0	3.968569	-1.566334	-1.000702
27	1	0	2.996164	-1.992823	-2.399281
28	1	0	4.106200	-0.620406	-2.518535
29	1	0	1.778554	0.233916	-2.275793
30	6	0	4.273365	2.512430	0.550579
31	1	0	4.413960	2.613912	1.636984
32	1	0	5.282640	2.536404	0.117073
33	1	0	3.696991	3.366211	0.186518

TS2-c

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-2.865134	0.212629	0.015877
2	79	0	-0.533425	0.013531	-0.091446
3	6	0	2.392918	1.116734	-0.177011
4	6	0	1.618616	-0.218631	-0.137924
5	6	0	3.696027	1.207164	0.188007
6	6	0	2.179661	-0.435247	-1.432933
7	6	0	-3.609303	1.057647	-1.437393
8	6	0	-3.446317	1.166394	1.475602
9	6	0	-3.726478	-1.407363	0.124085
10	6	0	1.937773	-1.227218	0.930554
11	8	0	1.998851	-2.423724	0.733331
12	8	0	2.067980	-0.671568	2.155327
13	1	0	1.861606	2.002630	-0.513712
14	1	0	4.224264	0.300687	0.483059
15	1	0	-3.204720	2.070061	-1.526820
16	1	0	-4.697723	1.115647	-1.328965
17	1	0	-3.370240	0.506074	-2.351292
18	1	0	-4.540002	1.224615	1.483619
19	1	0	-3.033746	2.179109	1.446508
20	1	0	-3.106601	0.681232	2.395319
21	1	0	-3.489724	-2.014878	-0.754263
22	1	0	-4.810581	-1.260234	0.177198
23	1	0	-3.393517	-1.945994	1.016036
24	1	0	2.187707	-1.409408	2.785055
25	6	0	3.162949	-1.462843	-1.863719
26	1	0	3.664244	-1.965723	-1.037735
27	1	0	2.578477	-2.231185	-2.396908
28	1	0	3.875969	-1.055291	-2.586865
29	1	0	1.813905	0.211621	-2.229511
30	6	0	4.459437	2.482607	0.297618
31	1	0	4.757431	2.654101	1.341033
32	1	0	5.391441	2.419899	-0.279632
33	1	0	3.883019	3.345564	-0.046636

***Z,E*-D**

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	-2.612111	0.439936	0.265314
2	79	0	-0.433205	-0.182280	-0.270313
3	6	0	2.449957	0.996007	-0.701406
4	6	0	2.000271	-0.343884	-0.319216
5	6	0	3.093587	1.865875	0.101785
6	6	0	1.428606	-1.220066	-1.237151
7	6	0	-3.686487	0.681295	-1.203898
8	6	0	-2.700562	2.012024	1.210733
9	6	0	-3.460656	-0.811910	1.305668
10	6	0	2.306175	-0.863236	1.074175
11	8	0	1.454662	-1.145108	1.891155
12	8	0	3.622499	-0.989834	1.279226
13	1	0	2.252597	1.272553	-1.736642
14	1	0	3.306024	1.588338	1.133145
15	1	0	-3.279207	1.474968	-1.836811
16	1	0	-4.699328	0.956041	-0.890106
17	1	0	-3.731119	-0.241845	-1.788860
18	1	0	-3.742749	2.248291	1.451656
19	1	0	-2.275065	2.827785	0.619345
20	1	0	-2.130017	1.919010	2.139258
21	1	0	-3.520661	-1.763281	0.769215
22	1	0	-4.473072	-0.474478	1.552779
23	1	0	-2.897103	-0.969286	2.229815
24	1	0	3.751509	-1.346890	2.181636
25	6	0	1.294720	-2.714706	-1.081076
26	1	0	1.256969	-3.033076	-0.036857
27	1	0	0.402045	-3.086629	-1.592555
28	1	0	2.159902	-3.196614	-1.557999
29	1	0	1.351873	-0.846015	-2.259409
30	6	0	3.587097	3.208301	-0.330300
31	1	0	3.164851	3.997657	0.305348
32	1	0	4.677232	3.270035	-0.214249
33	1	0	3.336623	3.425838	-1.372626

B-trans

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.768404	-0.529554	-1.179725
2	6	0	2.398076	-1.710990	-0.449245
3	6	0	1.984733	0.343919	-0.127693
4	6	0	2.626457	-0.726282	0.766760
5	6	0	2.068152	1.833002	-0.028644
6	8	0	2.514339	2.405139	0.937759
7	8	0	1.606804	2.447931	-1.140434
8	6	0	1.618831	-3.004630	-0.244906
9	6	0	4.075716	-0.459860	1.175045
10	1	0	1.520344	-0.363721	-2.226646
11	1	0	3.363070	-1.929625	-0.928304
12	1	0	2.028416	-0.985239	1.647912
13	1	0	2.192903	-3.700658	0.375628
14	1	0	0.660189	-2.817849	0.255924
15	1	0	4.129490	0.366339	1.888822
16	1	0	4.694972	-0.201687	0.307973
17	1	0	1.725882	3.410167	-1.012500
18	79	0	-0.343533	-0.040809	-0.157442
19	15	0	-2.645738	0.010275	0.248186
20	6	0	-3.151509	-1.010556	1.687045
21	1	0	-4.235503	-0.945252	1.830507
22	1	0	-2.875532	-2.055760	1.520013
23	1	0	-2.648683	-0.656914	2.591775
24	6	0	-3.626312	-0.605103	-1.176493
25	1	0	-3.354174	-1.640868	-1.399108
26	1	0	-4.695550	-0.557960	-0.943156
27	1	0	-3.425001	0.006881	-2.060415
28	6	0	-3.260538	1.705687	0.589551
29	1	0	-3.045730	2.358013	-0.261732
30	1	0	-4.342046	1.684624	0.762105
31	1	0	-2.764145	2.112404	1.475368
32	1	0	4.502379	-1.353099	1.643180
33	1	0	1.412710	-3.498399	-1.201003

TS3-in

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.626107	-0.548884	-0.730954
2	6	0	2.181908	-1.662370	0.054296
3	6	0	2.547618	0.443963	-0.196350
4	6	0	3.704613	-0.233656	0.233333
5	6	0	2.306236	1.854164	0.226659
6	8	0	3.032796	2.447381	0.992878
7	8	0	1.226945	2.405719	-0.371255
8	79	0	-0.492390	-0.192515	-0.225542
9	15	0	-2.787480	0.053246	0.137527
10	6	0	-3.414400	-0.891506	1.584175
11	6	0	-3.799084	-0.517342	-1.286711
12	6	0	-3.310620	1.790078	0.433773
13	6	0	4.657977	-0.994826	-0.679389
14	6	0	1.842239	-1.957872	1.492978
15	1	0	1.481559	-0.655095	-1.810500
16	1	0	2.566865	-2.537857	-0.476615
17	1	0	4.195883	0.138164	1.137147
18	1	0	1.195302	3.342698	-0.094451
19	1	0	-4.494098	-0.743954	1.694930
20	1	0	-3.211937	-1.957899	1.448879
21	1	0	-2.912314	-0.554909	2.495885
22	1	0	-3.601169	-1.574828	-1.484405
23	1	0	-4.865392	-0.385654	-1.073116
24	1	0	-3.539238	0.056838	-2.180798
25	1	0	-3.038450	2.411672	-0.424145
26	1	0	-4.394719	1.839908	0.582313
27	1	0	-2.809352	2.183855	1.322724
28	1	0	4.209798	-1.273662	-1.635451
29	1	0	5.068171	-1.885549	-0.193651
30	1	0	5.502412	-0.321864	-0.878531
31	1	0	2.690448	-2.406029	2.020490
32	1	0	1.036226	-2.705839	1.502134
33	1	0	1.497535	-1.075322	2.038228

TS3-out

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.192026	0.696337	-1.085056
2	6	0	-3.142039	1.479240	-0.400348
3	6	0	-1.820192	-0.323564	-0.148299
4	6	0	-2.315712	0.313655	1.092128
5	6	0	-1.872797	-1.799792	-0.393263
6	8	0	-2.052409	-2.627028	0.472898
7	8	0	-1.695725	-2.098547	-1.699757
8	1	0	-1.717597	0.942792	-2.032755
9	1	0	-1.739927	-3.071571	-1.780440
10	79	0	0.405574	0.016042	-0.031737
11	15	0	2.723120	0.207553	0.101999
12	6	0	3.551306	0.117334	-1.534478
13	1	0	4.636738	0.201538	-1.413733
14	1	0	3.317361	-0.835725	-2.017554
15	1	0	3.198172	0.928846	-2.177257
16	6	0	3.484694	-1.120651	1.115814
17	1	0	3.251439	-2.098772	0.685307
18	1	0	4.572082	-0.993160	1.150059
19	1	0	3.087450	-1.086637	2.134372
20	6	0	3.285283	1.785690	0.855205
21	1	0	2.884106	1.878173	1.868612
22	1	0	4.379430	1.814123	0.899483
23	1	0	2.929184	2.631650	0.260229
24	6	0	-3.180771	-0.342246	2.125937
25	1	0	-2.545636	-0.922528	2.808866
26	1	0	-3.704253	0.409783	2.724712
27	1	0	-3.898736	-1.042042	1.691857
28	6	0	-3.374758	2.956257	-0.562810
29	1	0	-4.206803	3.137925	-1.256117
30	1	0	-3.659615	3.409634	0.393330
31	1	0	-2.488530	3.474932	-0.939024
32	1	0	-1.729394	1.156911	1.446914
33	1	0	-4.005459	0.914516	-0.043732

TS4

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.476362	-0.441775	-0.634395
2	6	0	1.461316	0.491599	-0.158761
3	6	0	3.795276	-0.764498	0.033787
4	6	0	2.722661	-1.848982	-0.132213
5	15	0	-2.886905	-0.246526	-0.039961
6	79	0	-0.538518	0.136578	-0.070091
7	6	0	1.958044	1.780521	0.354411
8	8	0	2.243037	1.754573	1.537022
9	8	0	2.022675	2.810010	-0.475695
10	6	0	-3.383094	-1.863638	-0.758259
11	6	0	-3.833344	1.017074	-0.980896
12	6	0	-3.596028	-0.224305	1.655795
13	1	0	2.512962	-0.316314	-1.729341
14	1	0	2.346592	3.595708	0.012814
15	1	0	-3.053873	-1.925195	-1.799721
16	1	0	-4.471343	-1.980335	-0.720357
17	1	0	-2.916929	-2.679375	-0.197833
18	1	0	-4.906168	0.802651	-0.930825
19	1	0	-3.517062	1.017522	-2.028137
20	1	0	-3.646781	2.010059	-0.561552
21	1	0	-4.677022	-0.395484	1.616399
22	1	0	-3.403560	0.743951	2.126999
23	1	0	-3.132039	-1.005007	2.265634
24	6	0	5.084318	-0.810221	-0.755463
25	1	0	5.527950	0.187845	-0.847826
26	1	0	5.816201	-1.454609	-0.256413
27	1	0	4.923348	-1.201498	-1.766706
28	1	0	3.890501	-0.392131	1.053329
29	1	0	2.938071	-2.578924	-0.911389
30	6	0	1.993242	-2.400559	1.070849
31	1	0	1.821885	-1.627278	1.829990
32	1	0	1.018639	-2.817193	0.789320
33	1	0	2.576871	-3.204146	1.532439

E-trans

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.772915	-0.112330	-0.228205
2	6	0	1.608148	0.639503	-0.167628
3	6	0	2.874661	-1.620858	-0.755151
4	6	0	2.814958	-1.504777	0.680992
5	15	0	-2.709326	-0.294133	0.149984
6	79	0	-0.388547	0.129059	-0.038206
7	6	0	4.005107	-1.599814	1.598851
8	1	0	1.845013	-1.679067	1.140627
9	1	0	4.068465	-2.629700	1.973983
10	1	0	4.943049	-1.372527	1.083808
11	1	0	3.899392	-0.934974	2.461225
12	6	0	-3.383942	-1.405941	-1.149920
13	1	0	-4.462585	-1.539040	-1.014792
14	1	0	-3.198403	-0.977811	-2.139408
15	1	0	-2.894936	-2.383152	-1.097108
16	6	0	-3.717178	1.239299	0.040546
17	1	0	-3.546534	1.727647	-0.923415
18	1	0	-4.782547	1.005859	0.140418
19	1	0	-3.426177	1.932095	0.835651
20	6	0	-3.189150	-1.073041	1.744724
21	1	0	-4.272532	-1.228861	1.781759
22	1	0	-2.685751	-2.038020	1.855287
23	1	0	-2.892077	-0.428987	2.577613
24	1	0	3.734477	0.396277	-0.231793
25	6	0	1.821705	2.109903	-0.020528
26	8	0	1.913543	2.611231	1.078222
27	8	0	1.866481	2.761475	-1.189191
28	1	0	1.976972	3.715816	-0.999403
29	6	0	1.785400	-2.235488	-1.602792
30	1	0	0.797850	-2.138167	-1.144212
31	1	0	1.757606	-1.782075	-2.598172
32	1	0	2.000837	-3.304064	-1.720323
33	1	0	3.877015	-1.725273	-1.170819

TS5

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.601201	0.477107	-1.027689
2	6	0	-1.727179	-0.285619	-0.248886
3	6	0	-2.753813	1.832905	-0.451195
4	6	0	-2.604402	0.898324	0.788315
5	15	0	2.719402	0.059100	0.117990
6	79	0	0.386838	-0.040252	-0.039316
7	6	0	-2.030898	-1.751836	-0.140351
8	8	0	-2.194890	-2.324291	0.913715
9	8	0	-2.084145	-2.345957	-1.350433
10	6	0	3.399559	-1.059564	1.407285
11	6	0	3.564973	-0.424351	-1.440254
12	6	0	3.376831	1.725617	0.528295
13	6	0	-3.830571	0.385814	1.515926
14	6	0	-1.700013	2.922230	-0.603721
15	1	0	-3.437062	0.011872	-1.560214
16	1	0	-3.763930	2.216916	-0.609704
17	1	0	-1.805583	1.229182	1.446595
18	1	0	-2.259499	-3.296948	-1.203117
19	1	0	4.492737	-0.994601	1.429415
20	1	0	3.105775	-2.091976	1.196696
21	1	0	3.003437	-0.781155	2.388203
22	1	0	4.651949	-0.377981	-1.313716
23	1	0	3.269129	0.249383	-2.249665
24	1	0	3.279902	-1.443613	-1.716618
25	1	0	3.076532	2.444958	-0.239211
26	1	0	4.470327	1.699413	0.584887
27	1	0	2.977634	2.056549	1.491502
28	1	0	-4.173326	1.165205	2.206537
29	1	0	-3.589429	-0.507941	2.096482
30	1	0	-4.656215	0.147338	0.839145
31	1	0	-1.774949	3.388356	-1.591067
32	1	0	-0.688735	2.519056	-0.485496
33	1	0	-1.857379	3.697606	0.152853

TS6

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.164774	-0.844072	0.535199
2	6	0	1.382135	0.132219	0.050461
3	6	0	4.266939	-0.730991	-0.406955
4	15	0	-3.042347	-0.197400	-0.005510
5	79	0	-0.693601	-0.033898	0.029492
6	6	0	3.712705	-0.766425	0.928350
7	6	0	1.983590	1.373551	-0.497553
8	8	0	2.966207	1.385294	-1.229655
9	8	0	1.324426	2.492858	-0.163400
10	6	0	-3.735278	-0.622227	-1.655903
11	6	0	-3.728503	-1.471052	1.131079
12	6	0	-3.891343	1.363079	0.472639
13	1	0	1.760969	-1.830859	0.738906
14	1	0	1.774748	3.242724	-0.600122
15	1	0	-3.342113	-1.588524	-1.985183
16	1	0	-4.828385	-0.675570	-1.613027
17	1	0	-3.441890	0.136465	-2.387390
18	1	0	-3.423708	-1.253742	2.159022
19	1	0	-4.822382	-1.486203	1.077426
20	1	0	-3.343440	-2.458062	0.858203
21	1	0	-4.978778	1.236726	0.438856
22	1	0	-3.595264	1.650398	1.485811
23	1	0	-3.602134	2.166415	-0.211297
24	1	0	4.684405	0.202421	-0.770180
25	1	0	3.897180	-1.744877	1.385969
26	6	0	4.093269	0.372684	1.876016
27	1	0	5.148929	0.293842	2.155791
28	1	0	3.936395	1.352386	1.417351
29	1	0	3.493255	0.318217	2.788105
30	6	0	4.343849	-1.882798	-1.318332
31	1	0	3.845151	-2.781751	-0.951029
32	1	0	3.971653	-1.611019	-2.314525
33	1	0	5.417170	-2.099098	-1.465450

F

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.129878	-1.169422	0.271934
2	6	0	-1.352348	-0.092354	-0.031282
3	6	0	-4.218273	0.198179	0.352952
4	15	0	3.080141	-0.059991	0.075912
5	79	0	0.728333	-0.054878	0.014543
6	6	0	-3.632528	-1.202184	0.145147
7	1	0	-4.031288	-1.832036	0.950856
8	6	0	-2.112383	1.040062	-0.486927
9	8	0	-3.399582	1.200046	-0.399404
10	8	0	-1.492606	2.032874	-1.074885
11	1	0	-2.132567	2.727445	-1.334426
12	1	0	-1.655160	-2.102131	0.569600
13	6	0	3.838669	1.565174	-0.336079
14	1	0	3.497725	2.323939	0.374495
15	1	0	4.931521	1.503579	-0.297596
16	1	0	3.533166	1.871671	-1.340845
17	6	0	3.789701	-0.503988	1.714511
18	1	0	3.453405	-1.503763	2.004672
19	1	0	4.884265	-0.491085	1.678679
20	1	0	3.447630	0.207615	2.471758
21	6	0	3.853370	-1.244669	-1.100903
22	1	0	4.945575	-1.199575	-1.033642
23	1	0	3.522729	-2.262393	-0.873222
24	1	0	3.547411	-1.004187	-2.123371
25	6	0	-4.042346	-1.841373	-1.202604
26	1	0	-3.597801	-2.835072	-1.313496
27	1	0	-5.130749	-1.950803	-1.255475
28	1	0	-3.711955	-1.228774	-2.048180
29	6	0	-4.308358	0.669410	1.795914
30	1	0	-4.663140	1.702821	1.842526
31	1	0	-5.027239	0.040995	2.331992
32	1	0	-3.343218	0.599881	2.307819
33	1	0	-5.186981	0.290710	-0.141383

G

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.477778	-0.942492	-0.069944
2	6	0	3.302120	-1.508647	-0.389372
3	6	0	3.391536	1.300305	-0.167959
4	15	0	-3.059460	0.439785	0.157821
5	79	0	-0.949471	-0.395344	-0.071678
6	6	0	4.566420	0.484471	0.395942
7	1	0	5.484419	0.927655	-0.010936
8	6	0	2.071132	-0.737120	-0.252693
9	8	0	2.113204	0.561638	-0.018935
10	8	0	0.959158	-1.306730	-0.311701
11	1	0	5.389353	-1.535553	-0.088447
12	6	0	-3.101577	2.267167	0.325182
13	1	0	-2.656574	2.731493	-0.559499
14	1	0	-4.135217	2.613535	0.431392
15	1	0	-2.528445	2.573604	1.204914
16	6	0	-4.140657	0.047167	-1.272558
17	1	0	-4.216609	-1.037218	-1.393889
18	1	0	-5.141990	0.462174	-1.115013
19	1	0	-3.716127	0.470105	-2.187566
20	6	0	-3.933717	-0.213469	1.633474
21	1	0	-4.939443	0.215808	1.696705
22	1	0	-4.011421	-1.302464	1.567294
23	1	0	-3.376646	0.040659	2.539738
24	6	0	4.657441	0.536043	1.938566
25	1	0	5.493564	-0.068709	2.303005
26	1	0	4.816008	1.566546	2.273128
27	1	0	3.739407	0.157217	2.399848
28	6	0	3.538046	1.711592	-1.627271
29	1	0	2.639908	2.234952	-1.967829
30	1	0	4.388118	2.394076	-1.731055
31	1	0	3.710664	0.848524	-2.278130
32	1	0	3.218703	2.181265	0.453362
33	1	0	3.192429	-2.547641	-0.676835

B'-trans

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.424715	-1.153641	-0.367097
2	6	0	5.395724	-0.023781	-0.096353
3	6	0	3.331739	-0.387353	-0.150639
4	6	0	4.120907	0.875662	0.178463
5	6	0	1.919509	-0.677929	-0.212371
6	8	0	1.059893	0.201522	0.044605
7	8	0	1.597527	-1.920402	-0.553829
8	6	0	6.400155	-0.214375	1.041622
9	6	0	3.917459	2.101131	-0.707862
10	1	0	4.562026	-2.200518	-0.625302
11	1	0	5.918357	0.288763	-1.010913
12	1	0	4.046990	1.151760	1.237496
13	1	0	6.931886	0.722411	1.239198
14	1	0	5.900922	-0.525107	1.966176
15	1	0	2.930918	2.547299	-0.540925
16	1	0	3.999198	1.842757	-1.770240
17	1	0	0.625209	-2.021112	-0.565417
18	79	0	-1.062385	0.070838	0.036471
19	15	0	-3.349984	0.034274	0.061182
20	6	0	-4.072768	1.656303	-0.398975
21	1	0	-5.166363	1.600935	-0.371231
22	1	0	-3.734596	2.427111	0.299519
23	1	0	-3.752983	1.934725	-1.407200
24	6	0	-4.032999	-0.376229	1.713432
25	1	0	-3.694981	0.358890	2.449457
26	1	0	-5.127760	-0.372697	1.678436
27	1	0	-3.687250	-1.365887	2.025230
28	6	0	-4.070701	-1.187540	-1.101962
29	1	0	-3.741105	-2.196443	-0.837578
30	1	0	-5.164318	-1.145651	-1.056774
31	1	0	-3.745818	-0.968812	-2.123193
32	1	0	4.671366	2.864399	-0.485939
33	1	0	7.144668	-0.975588	0.784538

TS3'-in

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.438280	-0.965469	-0.687485
2	6	0	5.460313	-0.563794	0.203890
3	6	0	3.332853	-0.159921	-0.388771
4	6	0	3.914563	1.032398	0.173000
5	6	0	1.936047	-0.457127	-0.464977
6	8	0	1.058018	0.346965	-0.038776
7	8	0	1.620130	-1.625055	-1.024023
8	6	0	5.416733	-0.714958	1.715780
9	6	0	4.672951	2.056445	-0.634564
10	1	0	4.585014	-1.605031	-1.557347
11	1	0	6.489456	-0.555222	-0.173051
12	1	0	3.477895	1.448803	1.087738
13	1	0	4.398616	-0.801849	2.102434
14	1	0	5.963195	-1.631417	1.980215
15	1	0	5.072557	1.645890	-1.564493
16	1	0	5.490481	2.507490	-0.061669
17	1	0	0.648997	-1.704719	-1.091509
18	79	0	-1.043095	0.115770	0.018127
19	15	0	-3.323557	-0.034395	0.109542
20	6	0	-3.926175	-1.716331	0.526780
21	1	0	-5.020640	-1.722490	0.568896
22	1	0	-3.594003	-2.432575	-0.230214
23	1	0	-3.527978	-2.024427	1.497751
24	6	0	-4.131972	0.411406	-1.476250
25	1	0	-3.795900	-0.262167	-2.269756
26	1	0	-5.220226	0.335832	-1.377730
27	1	0	-3.867233	1.435720	-1.753848
28	6	0	-4.046382	1.083578	1.372449
29	1	0	-3.772603	2.119917	1.154634
30	1	0	-5.138005	0.993193	1.372680
31	1	0	-3.664237	0.823188	2.363704
32	1	0	3.980783	2.875739	-0.885032
33	1	0	5.923223	0.111617	2.224711

TS3'-out

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.417864	-1.107596	0.004162
2	6	0	-5.466825	-0.244958	0.406419
3	6	0	-3.323555	-0.262936	-0.184532
4	6	0	-3.942693	1.029199	-0.385083
5	6	0	-1.928603	-0.568409	-0.099698
6	8	0	-1.031082	0.318107	-0.186266
7	8	0	-1.634508	-1.859267	0.059209
8	6	0	-6.922366	-0.432960	0.076019
9	6	0	-3.477095	2.330702	0.200039
10	1	0	-4.526502	-2.150183	-0.290048
11	1	0	-5.268485	0.360151	1.288731
12	1	0	-4.548279	1.114402	-1.282182
13	1	0	-7.411249	0.535071	-0.083017
14	1	0	-7.069300	-1.041414	-0.820761
15	1	0	-3.029717	2.211225	1.191093
16	1	0	-4.304243	3.045226	0.267274
17	1	0	-0.665272	-1.979097	0.047506
18	79	0	1.065634	0.090227	-0.050332
19	15	0	3.345519	-0.051734	0.073622
20	6	0	3.954359	-0.446955	1.758627
21	1	0	5.048709	-0.492186	1.761489
22	1	0	3.625126	0.321641	2.463772
23	1	0	3.554742	-1.411749	2.083757
24	6	0	4.165797	1.519754	-0.401225
25	1	0	3.842060	2.325621	0.263736
26	1	0	5.253530	1.411459	-0.331369
27	1	0	3.897102	1.785600	-1.427621
28	6	0	4.050262	-1.336984	-1.030053
29	1	0	3.767706	-1.134241	-2.067046
30	1	0	5.142624	-1.342270	-0.949917
31	1	0	3.666617	-2.322276	-0.750005
32	1	0	-2.719821	2.781192	-0.458546
33	1	0	-7.447038	-0.913979	0.913433

B''-trans

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.491217	-1.168490	-0.536504
2	6	0	1.748018	-0.336610	-0.338526
3	6	0	-0.329973	-0.221744	-0.048395
4	6	0	0.783122	0.772219	0.249100
5	6	0	-1.780602	-0.112475	0.144196
6	8	0	-2.344190	0.865974	0.597646
7	8	0	-2.450921	-1.230068	-0.241063
8	6	0	2.827591	-0.896591	0.587123
9	6	0	0.731362	2.121557	-0.462758
10	1	0	0.324905	-2.169992	-0.924710
11	1	0	2.198053	-0.017961	-1.289406
12	1	0	0.943255	0.920120	1.325276
13	1	0	3.600193	-0.144224	0.785374
14	1	0	2.400214	-1.206209	1.548110
15	1	0	0.612749	1.991689	-1.545482
16	1	0	1.649412	2.695222	-0.287301
17	1	0	-3.393604	-1.044285	-0.070844
18	1	0	-0.117027	2.711155	-0.099867
19	1	0	3.318330	-1.769956	0.140784

TS3''-in

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.471064	-0.861565	-0.938928
2	6	0	1.774094	-0.792566	-0.373357
3	6	0	-0.299573	0.039734	-0.219201
4	6	0	0.626338	0.993314	0.316979
5	6	0	-1.724123	0.005635	0.135473
6	8	0	-2.262891	0.747566	0.937447
7	8	0	-2.409354	-0.961346	-0.534102
8	6	0	2.129819	-1.259744	1.027605
9	6	0	1.367435	2.014080	-0.517248
10	1	0	0.202185	-1.407638	-1.842913
11	1	0	2.634268	-0.879576	-1.051734
12	1	0	0.460217	1.341110	1.344239
13	1	0	1.265372	-1.256166	1.695953
14	1	0	2.515914	-2.290041	0.974457
15	1	0	1.474998	1.697685	-1.557795
16	1	0	2.361628	2.235886	-0.110731
17	1	0	-3.335783	-0.874481	-0.241345
18	1	0	2.923927	-0.651284	1.476378
19	1	0	0.804912	2.961412	-0.501203

TS3''-out

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.765396	-1.093114	-0.017999
2	6	0	-1.888492	-0.297576	0.346427
3	6	0	0.269519	-0.188125	-0.175604
4	6	0	-0.394834	1.071309	-0.384810
5	6	0	1.716008	-0.375676	-0.025431
6	8	0	2.549000	0.514084	0.001511
7	8	0	2.062256	-1.689005	0.079263
8	6	0	-3.313841	-0.586648	-0.054012
9	6	0	0.067362	2.396350	0.157747
10	1	0	-0.781030	-2.155423	-0.256929
11	1	0	-1.784311	0.290891	1.253856
12	1	0	-1.009828	1.132570	-1.277173
13	1	0	-3.372714	-1.163464	-0.982557
14	1	0	-3.838461	-1.149562	0.732655
15	1	0	0.456707	2.315626	1.176992
16	1	0	-0.745246	3.131379	0.142611
17	1	0	3.035025	-1.694889	0.150161
18	1	0	0.883497	2.788991	-0.465086
19	1	0	-3.875649	0.344130	-0.198639

Me_3PAu^+

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	79	0	-0.951163	0.000127	0.000150
2	15	0	1.338889	0.000121	-0.000161
3	6	0	1.994788	-0.037175	1.706552
4	1	0	3.090450	-0.040365	1.667294
5	1	0	1.656533	0.843292	2.259811
6	1	0	1.650027	-0.936984	2.223454
7	6	0	1.993860	1.496695	-0.821957
8	1	0	1.650706	2.394071	-0.299809
9	1	0	3.089544	1.463900	-0.802046
10	1	0	1.653420	1.536262	-1.860345
11	6	0	1.991746	-1.460688	-0.885644
12	1	0	1.643367	-1.460363	-1.922136
13	1	0	3.087468	-1.425821	-0.872808
14	1	0	1.654658	-2.378794	-0.396582

3. Computed energies of all stationary points

Table S8. Sum of electronic and thermal enthalpies (*H*, in Hartree), sum of electronic and thermal free energies (*G*, in Hartree), thermal correction to Enthalpy (*TCH*, in Hartree), thermal correction to Gibbs free energy (*TCGFE*, in Hartree), electronic energy (*E*, in Hartree), and total free energy in solution (E_S, in Hartree, solvent = $CHCl_3$)

Structure	H^a	G^a	TCH^a	$TCGFE^a$	E^b	$E_S{}^b$
A-trans	-1019.585183	-1019.657408	0.295543	0.223318	-1019.621256	-1019.673387
TS1-t	-1019.564351	-1019.635002	0.29455	0.2239	-1019.607586	-1019.661258
C-t	-1019.58042	-1019.652815	0.294665	0.22227	-1019.620482	-1019.674643
TS2-t	-1019.576221	-1019.64705	0.293391	0.222561	-1019.612696	-1019.666971
***E,Z*-D**	-1019.622158	-1019.695669	0.29578	0.222269	-1019.659554	-1019.713672
TS1-c	-1019.557012	-1019.62761	0.294773	0.224174	-1019.598522	-1019.652484
C-c	-1019.581406	-1019.654564	0.294674	0.221516	-1019.619121	-1019.672994
TS2-c	-1019.581754	-1019.654065	0.293401	0.22109	-1019.615845	-1019.669564
***Z,E*-D**	-1019.628023	-1019.700852	0.295624	0.222794	-1019.663014	-1019.716119
B-trans	-1019.605896	-1019.677294	0.295987	0.224589	-1019.646219	-1019.703826
TS3-in	-1019.54486	-1019.616794	0.293147	0.221213	-1019.578726	-1019.632878
TS3-out	-1019.567443	-1019.639307	0.293309	0.221444	-1019.601314	-1019.656598
TS4	-1019.557342	-1019.627939	0.292951	0.222353	-1019.591758	-1019.645853
E-trans	-1019.583063	-1019.65639	0.295426	0.222099	-1019.619648	-1019.674458
TS5	-1019.564721	-1019.635405	0.294043	0.223359	-1019.604274	-1019.659245
TS6	-1019.567984	-1019.638551	0.293502	0.222935	-1019.598514	-1019.649807
F	-1019.619262	-1019.687652	0.297837	0.229447	-1019.64996	-1019.698984
G	-1019.661126	-1019.730238	0.298021	0.228908	-1019.684566	-1019.733454
B'-trans	-1019.620407	-1019.692036	0.296421	0.224792	-1019.6493	-1019.702336
TS3'-in	-1019.561909	-1019.633746	0.293576	0.221739	-1019.58476	-1019.636325
TS3'-out	-1019.581314	-1019.653894	0.293431	0.220851	-1019.603733	-1019.655122
B''-trans	-423.004448	-423.049279	0.169164	0.124334	-423.0214816	-423.0273867
TS3''-in	-422.940895	-422.985215	0.166304	0.121985	-422.9525329	-422.9589364
TS3''-out	-422.95978	-423.006117	0.166193	0.119856	-422.9708559	-422.9771677
Me_3Pau^+	-596.549318	-596.593056	0.125103	0.081365	-596.5688437	-596.640182

[a] Computed at the B3LYP/6-31G(d)-SDD level.
[b] Computed at the M06/6-311+G(d,p)-SDD level.