SUPPORTING INFORMATION

HIGHLY CONVERGENT, STEREOSPECIFIC SYNTHESIS OF 11-*CIS*-RETINOIDS BY METAL-CATALYZED CROSS-COUPLING REACTIONS OF *Z*-ALKENYLMETALS

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General Methods. Solvents were dried according to published methods and distilled before use.[1] All other reagents were commercial compounds of the highest purity available. Reactions were carried out under atmosphere of argon in flame-dried glassware with magnetic stirring. Visualization of analytical thin-layer chromatography (TLC) was accomplished with phosphomolybdic acid ethanolic solution (10%) stain followed by heating. Proton (^{1}H) and carbon (^{13}C) magnetic resonance spectra (NMR) were recorded using $CDCl_3$ as solvent. Chemical shifts (δ) are expressed in parts per million (ppm) relative to tetramethylsilane as internal reference. ^{13}C multiplicities were assigned with the aid of the DEPT pulse sequence.

Experimental Procedures.

All the solutions employed were degassed by argon bubbling during 15 min. Reactions and purification of the final products were carried out in the absence of light.

(7*E*,9*E*,11*Z*,13*E*)-9,13-Bis-demethyl-*tert*-butyldiphenylsilyl retinyl ether (**12**). *Suzuki reaction:* To a suspension of $Pd(PPh_3)_4$) (30 mg, 0.026 mmol) and pinacol dienylboronate **4a** (174 mg, 0.39 mmol) in THF (4 mL) was added, *via* cannula, a solution of trienyl iodide **2a** (50 mg, 0.16 mmol) in THF (2 mL). A solution of TlOH (10 % in water, 1.7 mL, 0.81 mmol) was added dropwise, and the stirring was continued for 5 h. The mixture was filtered through a short pad of neutral alumina and concentrated. Flash chromatography of the crude (Al_2O_3, hexane) yielded 58 mg (74%) of **12** as an unstable pale yellow oil. *Stille reaction:* To a solution trienyl iodide **2a** (50 mg, 0.17 mmol) and tributyldienylstannane **5a** (152 mg, 0.24 mmol) in DMF (4 mL) was added, in one portion, $PdCl_2(CH_3CN)_2$ (4 mg, 0.016 mmol). The reaction mixture was stirred for 8h, filtered through a short pad of neutral alumina (IV, hexane) and concentrated. Flash chromatography of the crude (Al_2O_3, hexane) afforded 54 mg (70% yield) of **12**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (s, 6H), 1.09 (s, 9H),

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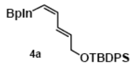
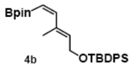
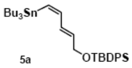
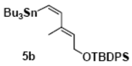
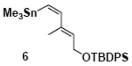
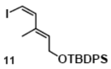
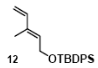
[1]Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4[th] Ed; Butterworth-Heinemann: Oxford, **1996**.

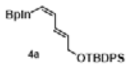
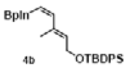
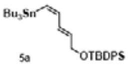
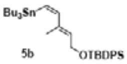
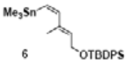
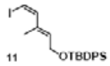
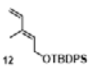
1.4-1.5 (m, 4H), 1.6-1.7 (m, 2H), 1.74 (s, 3H), 2.04 (t, *J* = 6.2 Hz, 2H), 4.31 (d, *J* = 5.1 Hz, 2H), 5.80 (dt, *J* = 15.0, 5.1 Hz, 1H), 5.98 (dd, *J* = 10.7, 11.3 Hz, 1H), 6.04 (dd, *J* = 10.7, 11.3 Hz, 1H), 6.15 (dd, *J* = 15.6, 10.0 Hz, 1H), 6.22 (d, *J* = 15.6 Hz, 1H), 6.32 (dd, *J* = 10.0, 14.6 Hz, 1H), 6.59 (dd, *J* = 14.6, 10.7 Hz, 1H), 6.78 (dd, *J* = 15.0, 10.7 Hz, 1H), 7.3-7.4 (m, 6H), 7.6-7.7 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2 (C), 19.3 (CH_2), 21.7 (CH_3), 26.8 (3xCH_3), 28.9 (2xCH_3), 33.2 (CH_2), 34.1 (C), 39.7 (CH_2), 64.3 (CH_2), 125.4 (CH), 126.3 (CH), 127.6 (4xCH), 128.2 (CH), 129.4 (CH), 129.6 (2xCH), 130.3 (C), 132.4 (CH), 132.9 (CH), 133.3 (CH), 133.6 (2xC), 134.7 (CH), 135.6 (4xCH), 137.4 (C) ppm. MS ESI-TOF *m/z* (%) 496 (2), 301 (28), 279 (100). HRMS (CI) calcd. for $C_{34}H_{44}OSi$, 496.3161; found, 496.3159.

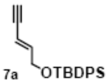
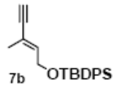
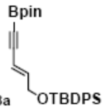
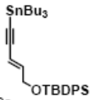
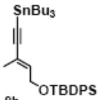
(7*E*,9*E*,11*Z*,13*E*)-9-Demethyl-*tert*-butyldiphenylsilyl retinyl ether (**13**). *Suzuki reaction:* Following the same procedure as described for compound **12**, reaction of trienyl iodide **2a** (56 mg, 0.18 mmol), dienyl boronate **4b** (179 mg, 0.4 mmol), $Pd(PPh_3)_4$ (21 mg, 0.018 mmol) and TlOH (10 % in water, 0.8 mL, 0.37 mmol), in THF (5 mL) for 5 h, afforded **13** (82 mg, 90% yield) as an unstable pale yellow oil. *Stille reaction:* Following the same procedure as described for compound **12**, reaction of trienyl iodide **2a** (50 mg, 0.16 mmol), tributyldienylstannane **5b** (156 mg, 0.25 mmol) and $PdCl_2(CH_3CN)_2$ (4.0 mg, 0.016 mmol) in DMF (4 mL), yielded 68 mg (83%) of **13**. ^{1}H NMR (750 MHz, $CDCl_3$) δ 1.03 (s, 6H), 1.05 (s, 9H), 1.4-1.5 (m, 2H), 1.5-1.6 (m, 2H), 1.67 (s, 3H), 1.72 (s, 3H), 2.02 (t, *J* = 6.3 Hz, 2H), 4.35 (d, *J* = 6.2 Hz, 2H), 5.69 (t, *J* = 6.2 Hz, 1H), 5.78 (d, *J* = 11.7 Hz, 1H), 6.00 (t, *J* = 11.7 Hz, 1H), 6.11 (dd, *J* = 15.6, 10.7 Hz, 1H), 6.18 (d, *J* = 15.6 Hz, 1H), 6.30 (dd, *J* = 14.4, 10.7 Hz, 1H), 6.69 (dd, *J* = 14.4, 11.7 Hz, 1H), 7.3-7.4 (m, 6H), 7.6-7.7 (m, 4H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 17.0 (CH_3), 18.8 (C), 19.2 (CH_2), 21.8 (CH_3), 26.8 (3xCH_3), 28.9 (2xCH_3), 33.3 (CH_2), 34.1 (C), 39.8 (CH_2), 61.1 (CH_2), 127.6 (4xCH), 127.9 (CH), 128.8 (CH), 129.6 (2xCH), 130.4 (C), 131.1 (CH), 132.1 (CH), 132.7 (CH), 133.4 (CH), 133.9 (2xC), 134.5 (C), 135.5 (CH), 135.6 (4xCH), 137.5 (C) ppm. MS (CI) *m/z* (%): 510 (58), 495 (2), 433 (5), 255 (75), 199 (100). HRMS (CI) calcd. for $C_{35}H_{46}OSi$, 510.3318; found, 510.3317.

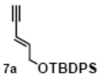
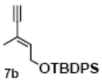
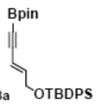
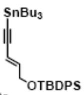
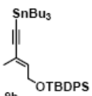
(7*E*,9*E*,11*Z*,13*E*)-13-Demethyl-*tert*-butyldiphenylsilyl retinyl ether (**14**). *Suzuki reaction with iodide:* Following the same procedure as described for compound **12**, reaction of trienyl iodide **2b** (113 mg, 0.36 mmol), pinacol dienylboronate **4a** (200 mg, 0.43 mmol), $Pd(PPh_3)_4$ (58 mg, 0.036 mmol) and TlOH (10 % in water, 2.9 mL, 1.30 mmol), in THF (8 mL) for 5 h, afforded 147 mg (80% yield) of **14** as an unstable pale yellow oil. *Suzuki reaction with triflate:* To a suspension of $Pd(PPh_3)_4$ (34 mg, 0.029 mmol), K_3PO_4 (123 mg, 0.58 mmol) and pinacol dienylboronate **4a** (199 mg, 0.44 mmol) in THF (4 mL) was added, *via* cannula, a solution of trienyl triflate **3** (100 mg, 0.29 mmol) in THF (2 mL), and the reaction mixture was stirred for 5h, filtered through a short pad of neutral alumina (IV, hexane), and concentrated. Flash chromatography of the crude (Al_2O_3, hexane) yielded 92 mg (63% yield) of **14**. *Stille reaction with iodide:* Following the same procedure as described for compound **12**, reaction of trienyl iodide **2b** (50 mg, 0.16 mmol), tributyldienylstannane **5a** (145.3 mg, 0.24 mmol) and $PdCl_2(CH_3CN)_2$ (4.0 mg, 0.016 mmol) in DMF (4 mL) afforded 47 mg (57%) of **14**. *Stille reaction with triflate:* To a solution of trienyl triflate **3** (113 mg, 0.334 mmol) and dienylstannane **5a** (225 mg, 0.367 mmol) in NMP (4 mL) were added, each in one portion, $Pd_2(dba)_3{\cdot}CHCl_3$ (8.0 mg, 0.008 mmol) and $AsPh_3$ (20 mg, 0.067 mmol) and the reaction mixture was stirred for 12 h, filtered through a short pad of neutral alumina, and concentrated. Flash chromatography of the crude (Al_2O_3, hexane) yielded 133 mg (78%) of **14**. ^{1}H NMR (750 MHz, $CDCl_3$) δ 1.04 (s, 6H), 1.09 (s, 9H), 1.4-1.5 (m, 4H), 1.6-1.7 (m, 4H), 1.73 (s, 3H), 1.94 (s, 3H), 2.03 (t, *J* = 6.2 Hz, 2H), 4.31 (d, *J* = 4.8 Hz, 2H), 5.82 (dt, *J* = 15.0, 4.8 Hz, 1H), 6.05 (t, *J* = 11.1 Hz, 1H), 6.12 (d, *J* = 16.1 Hz, 1H), 6.20 (d, *J* = 16.1 Hz, 1H), 6.33 (dd, *J* = 12.0, 11.1 Hz, 1H), 6.45 (d, *J* = 12.0 Hz, 1H), 6.83 (dd, *J* = 15.0, 11.1 Hz, 1H), 7.2-7.3 (m, 6H), 7.7-7.8 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.3 (CH_3), 19.2 (CH_2), 19.3 (C), 21.7 (CH_3), 26.8 (3xCH_3), 29.0 (2xCH_3), 33.1 (CH_2), 34.3 (C), 39.6 (CH_2), 64.3 (CH_2), 124.9 (CH), 125.2 (CH), 125.4 (CH), 127.1 (CH), 127.7 (4xCH), 128.3 (CH), 128.7 (CH), 129.6 (2xCH), 133.1 (CH), 133.7 (2xC), 135.6 (4xCH), 136.5 (C), 137.8 (C), 137.9 (CH) ppm. MS (CI) *m/z* (%) 510 (88), 433 (7), 255 (66), 199 (100). HRMS (CI) calcd. for $C_{35}H_{46}OSi$, 510.3318; found, 510.3312.

Tables of spectroscopic data.

^{1}H NMR 300 MHz, $CDCl_3$	H_1	H_2	H_3	H_4	H_5	Me-C_3	Si*t*Bu	SiPh	SnBu	SnMe	Bpin
 4a	5.36 d, 1H J_{cis} = 13.4	6.89 dd, 1H J_{cis} = 13.4 $J_{s\text{-}cis}$ = 11.2	7.27 dd, 1H $J_{s\text{-}cis}$ = 11.2 J_{trans} = 15.2	5.88 dt, 1H J_{trans} = 15.2 J = 4.2	4.29 d, 2H J = 4.2	---	1.08 s, 9H	7.3-7.5 m, 6H 7.6-7.8 m, 4H	---	---	1.25 s, 12 H
 4b	5.29 d, 1H J_{cis} = 14.8	6.69 d, 1H J_{cis} = 14.8	---	5.77 t, 1H J = 6.0	4.32 d, 2H J = 6.0	1.68 s, 3H	1.04 s, 9H	7.2-7.4 m, 6H 7.5-7.7 m, 4H	---	---	1.26 s, 12 H
 5a	6.06 d, 1H J_{cis} = 12.6 $^{2}J_{Sn\text{-}H}$ = 60.3	7.11 dd, 1H J_{cis} = 12.6 $J_{s\text{-}cis}$ = 10.6 $^{3}J_{Sn\text{-}Htrans}$ = 103.8	6.35 dd, 1H J_{trans} = 14.9 $J_{s\text{-}cis}$ = 10.6	5.81 dt J_{trans}= 14.9 J = 4.3	4.29 d, 2H J = 4.3	---	1.11 s, 9H	7.3-7.5 m, 6H 7.6-7.8 m, 4H	0.90, t, J = 7.2, 9H 0.9-1.0 m, 6H 1.2-1.4 m, 6H 1.4-1.6 m, 6H	---	---
 5b	5.83 d, 1H J_{cis} = 13.4 $^{2}J_{Sn\text{-}H}$ = 56.7	7.01 d, 1H J_{cis} = 13.4 $^{3}J_{Sn\text{-}H\ trans}$= 136.4	---	5.70 t, 1H J = 5.9	4.32 d, 2H J = 5.9	1.61 s, 3H	1.10 s, 9H	7.3-7.5 m, 6H 7.7-7.8 m, 4H	0.8-1.0 m, 15H 1.2-1.4 m, 6H 1.4-1.5 m, 6H	---	---
 6	5.83 d, 1H J_{cis} = 13.4 $^{2}J_{Sn\text{-}H}$ = 66.8	6.94 d, 1H J_{cis} = 13.4 $^{3}J_{Sn\text{-}H\ trans}$= 150.2	---	5.66 t, 1H J = 5.9	4.27 d, 2H J = 5.9	1.56 s, 3H	1.05 s, 9H	7.3-7.5 m, 6H 7.6-7.8 m, 4H	---	0.17 s, 9H $^{2}J_{Sn\text{-}H}$ = 54.2 Hz	---
 11	6.23 d, 1H J_{cis} = 8.5	6.77 d, 1H J_{cis}= 8.5	---	5.96 t, 1H J = 6.1	4.39 d, 2H J = 6.1	1.77 s, 3H	1.13 s, 9H	7.3-7.5 m, 6H 7.7-7.8 m, 4H	---	---	---
 12	5.05 d, 1H J_{cis} = 10.4 5.17 d, 1H J_{trans}= 17.4	6.44 dd, 1H J_{cis} = 10.4 J_{trans}= 17.4	---	5.74 t, 1H J = 5.9	4.43 d, 2H J = 5.9	1.64 s, 3H	1.13 s, 9H	7.3-7.5 m, 6H 7.6-7.8 m, 4H	---	---	---

^{13}C NMR 75 MHz, $CDCl_3$	C_1	C_2	C_3	C_4	C_5	Me-C_3	Si*t*Bu	SiPh	SnBu	SnMe	Bpin
 4a	118.4, CH	150.2, CH	129.2, CH	137.2, CH	63.6, CH_2	---	19.2, C 26.9, 3xCH_3	127.6, 4xCH 129.5, 2xCH 133.4, 2xC 135.5, 4xCH	---	---	24.8, 4xCH_3 83.0, 2xC
 4b	116.0, CH	150.3, CH	135.7, C	133.7, CH	61.3, CH_2	14.6, CH_3	19.1, C 26.8, 3xCH_3	127.6, 4xCH 129.5, 2xCH 133.6, 2xC 135.5, 4xCH	---	---	24.8, 4xCH_3 83.4, 2xC
 5a	134.0, CH	146.0, CH	131.5, CH	133.0, CH	63.9, CH_2	---	19.4, C 26.9, 3xCH_3	127.6, 4xCH 129.5, 2xCH 133.4, 2xC 135.5, 4xCH	10.5, 3xCH_2, $^{1}J_{Sn\text{-}C}$= 332.8 13.8, 3xCH_3 27.3, 3xCH_2 29.3, 3xCH_2	---	---
 5b	128.5, CH	150.6, CH	137.7, C	128.4, CH	61.4, CH_2	15.4, CH_3	19.3, C 26.9, 3xCH_3	127.5, 4xCH 129.5, 2xCH 133.6, 2xC 135.6, 4xCH	11.4, 3xCH_2, $^{1}J_{Sn\text{-}C}$= 336.2 13.8, 3xCH_3 27.4, 3xCH_2 29.3, 3xCH_2	---	---
 6	129.9, CH	150.7, CH	137.9, C	129.2, CH	61.1, CH_2	15.6, CH_3	19.6, C 26.8, 3xCH_3	127.6, 4xCH 129.6, 2xCH 133.7, 2xC 135.6, 4xCH	---	- 7.4, 3xCH_3	---
 11	76.2, CH	141.5, CH	133.3, C	133.1, CH	60.9, CH_2	15.8, CH_3	19.2, C 26.8, 3xCH_3	127.6, 4xCH 129.5, 2xCH 133.6, 2xC 135.5, 4xCH	---	---	---
 12	112.2, CH_2	140.8, CH	134.3, C	131.5, CH	61.2, CH_2	12.2, CH_3	19.3, C 27.0, 3xCH_3	127.6, 4xCH 129.5, 2xCH 133.6, 2xC 135.5, 4xCH	---	---	---

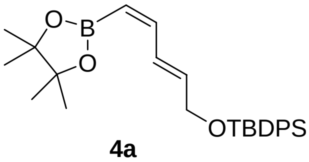
^{1}H NMR 300 MHz, $CDCl_3$	H_1	H_3	H_4	H_5	Me-C_3	Si*t*Bu	SiPh	SnBu	Bpin
 7a	2.91 d, 1H *J* = 2.3	5.94 dd, 1H J_{trans}= 15.8 *J* = 2.3	6.32 dt, 1H J_{trans} = 15.8 *J* = 3.8	4.25 d, 2H *J* = 3.8	---	1.10 s, 9H	7.3-7.5 m, 6H 7.6-7.8 m, 4H	---	---
 7b	2.83 s, 1H	---	6.15 tc, 1H *J* = 6.1 *J* = 1.1	4.30 d, 2H *J* = 6.1	1.67 d, 3H *J* = 1.1	1.10 s, 9H	7.3-7.4 m, 6H 7.6-7.8 m, 4H	---	---
 8a	---	5.99 dt, 1H J_{trans} = 15.8 *J* = 2.2	6.38 dt, 1H J_{rans} = 15.8 *J* = 3.8	4.25 dd, 2H *J* = 3.8 *J* = 2.2	---	1.04 s, 9H	7.2-7.4 m, 6H 7.5-7.7 m, 4H	---	1.29 s, 12H
 9a	---	5.99 dt, 1H J_{trans}= 15.7 *J* = 2.1	6.21 dt, 1H J_{trans}= 15.7 *J* = 4.0	4.25 dd, 2H *J* = 4.0 *J* = 2.1	---	1.10 s, 9H	7.2-7.4 m, 6H 7.5-7.7 m, 4H	0.95 t, *J* = 7.3, 9H 1.0-1.1 m, 6H 1.3-1.4 m, 6H 1.5-1.7 m, 6H	----
 9b	---	---	6.05 t, 1H *J* = 6.2	4.32 d, 2H *J* = 6.2	1.68 s, 3H	1.10 s, 9H	7.3-7.5 m, 6H 7.6-7.7 m, 4H	0.98 t, *J* = 7.3, 9H 1.0-1.1 m, 6H 1.3-1.4 m, 6H 1.6-1.7 m, 6H	----

^{13}C NMR 75 MHz, $CDCl_3$	C_1	C_2	C_3	C_4	C_5	Me-C_3	Si*t*Bu	SiPh	SnBu	Bpin
 7a	77.9, CH	81.8, C	107.5, CH	143.7, CH	63.4, CH_2	---	19.3, C 27.1, 3xCH_3	127.7, 4xCH 129.7, 2xCH 133.0, 2xC 135.3, 4xCH	---	--
 7b	86.1, CH	74.7, C	117.8, C	138.0, CH	60.7, CH_2	17.5, CH_3	19.3, C 26.9, 3xCH_3	127.7, 4xCH 129.6, 2xCH 133.4, 2xC 135.5, 4xCH	---	---
 8a	84.3, C	134.9, C	107.8, CH	145.8, CH	63.4, CH_2	---	19.3, C 26.7, 3xCH_3	127.7, 4xCH 129.8, 2xCH 133.1, 2xC 135.4, 4xCH	---	24.7, 4xCH_3 83.2, 2xC
 9a	93.6, C	108.3, C	109.4, CH	141.6, CH	63.6, CH_2	---	19.3, C 26.8, 3xCH_3	127.5, 4xCH 129.8, 2xCH 133.0, 2xC 135.3, 4xCH	11.2, 3xCH_2, $^1J_{Sn-C}$= 373.6 13.8, 3xCH_3 27.1, 3xCH_2 28.9, 3xCH_2	---
 9b	90.1, C	112.9, C	119.5, C	136.1, CH	60.8, CH_2	17.9, CH_3	19.1, C 26.7, 3xCH_3	127.6, 4xCH 129.7, 2xCH 133.6, 2xC 135.1, 4xCH	11.1, 3xCH_2, $^1J_{Sn-C}$= 374.0 13.7, 3xCH_3 26.9, 3xCH_2 28.9, 3xCH_2	---

^{1}H NMR $CDCl_3$	H_2	H_3	H_4	H_7	H_8	H_9	H_{10}	H_{11}	H_{12}	H_{13}	H_{14}	H_{15}	2Me-C_1	Me-C_5	Me-C_9	Me-C_{13}	Si*t*Bu	SiPh
(400 MHz) 9,13-bis-demethyl 11-*cis*-retinil ether **12**	1.4-1.5 m, 2H	1.6-1.7 m, 2H	2.04 t, 2H *J* = 6.2	6.22 d, 1H *J* = 15.6	6.15 dd, 1H *J* = 15.6 *J* = 10.0	6.32 dd, 1H *J* = 14.6 *J* = 10.0	6.59 dd, 1H *J* = 14.6 *J* = 10.7	6.04 dd, 1H *J* = 10.7 *J* = 11.3	5.98 dd, 1H *J* = 10.7 *J* = 11.3	6.78 dd, 1H *J* = 10.7 *J* = 15.0	5.80 dt, 1H *J* = 15.0 *J* = 5.1	4.31 d, 2H *J* = 5.1	1.04 s, 6H	1.74 s, 3H	---	---	1.09 s, 9H	7.3-7.4 m, 6H 7.6-7.7 m, 4H
(750 MHz) 9-demethyl 11-*cis*-retinil ether **13**	1.4-1.5 m, 2H	1.5-1.6 m, 2H	2.02 t, 2H *J* = 6.3	6.18 d, 1H *J* = 15.6	6.11 dd, 1H *J* = 15.6 *J* = 10.7	6.30 dd, 1H *J* = 14.4 *J* = 10.7	6.69 dd, 1H *J* = 14.4 *J* = 11.7	6.00 t, 1H *J* = 11.7	5.78 d, 1H *J* = 11.7	---	5.69 t, 1H *J* = 6.2	4.35 d, 2H *J* = 6.2	1.03 s, 6H	1.72 s, 3H	---	1.67 s, 3H	1.05 s, 9H	7.3-7.4 m, 6H 7.6-7.7 m, 4H
(750 MHz) 13-demethyl 11-*cis*-retinil ether **14**	1.4-1.5 m, 2H	1.6-1.7 m, 2H	2.03 t, 2H *J* = 6.2	6.20 d, 1H *J* = 16.1	6.12 d, 1H *J* = 16.1	---	6.45 d, 1H *J* = 12.0	6.33 dd, 1H *J* = 12.0 *J* = 11.1	6.05 t, 1H *J* = 11.1	6.83 dd, 1H *J* = 15.0 *J* = 11.1	5.82 dt, 1H *J* = 15.0 *J* = 4.8	4.31 d, 2H *J* = 4.8	1.04 s, 6H	1.73 s, 3H	1.94 s, 3H	---	1.09 s, 9H	7.2-7.3 m, 6H 7.7-7.8 m, 4H
(750 MHZ) 11-*cis*-retinil ether **15**	1.4-1.5 m, 2H	1.5-1.6 m, 2H	2.01 t, 2H *J* = 6.1	6.17 d, 1H *J* = 16.1	6.11 d, 1H *J* = 16.1	---	6.55 d, 1H *J* = 11.8	6.33 t, 1H *J* = 11.8	5.86 d, 1H *J* = 11.8	---	5.76 t, 1H *J* = 6.2	4.34 d, 2H *J* = 6.2	1.03 s, 6H	1.67 s, 3H	1.94 s, 3H	1.70 s, 3H	1.05 s, 9H	7.3-7.4 m, 6H 7.6-7.7 m, 4H
(400 MHz) 11-*cis*- retinol (**16**)	1.4-1.5 m, 2H	1.5-1.6 m, 2H	2.01 t, 2H *J* = 6.3	6.17 d, 1H *J* = 16.1	6.08 d, 1H *J* = 16.1	---	6.56 d, 1H *J* = 11.8	6.35 t, 1H *J* = 11.8	5.87 d, 1H *J* = 11.8	---	5.72 t, 1H *J* = 6.8	4.29 t, 2H *J* = 6.8	1.02 s, 6H	1.71 s, 3H	1.93 s, 3H	1.89 s, 3H	---	---
(400 MHz) 11-*cis*- retinal (**1**)	1.4-1.5 m, 2H	1.5-1.6 m, 2H	2.02 t, 2H *J* = 5.8	6.34 d, 1H *J* = 16.0	6.13 d, 1H *J* = 16.0	---	6.53 d, 1H *J* = 12.4	6.68 dd, 1H *J* = 12.4 *J* = 11.8	5.91 d, 1H *J* = 11.8	---	6.08 d, 1H *J* = 8.0	10.01 d, 1H *J* = 8.0	1.02 s, 6H	1.71 s, 3H	1.99 s, 3H	2.35 s, 3H	---	---

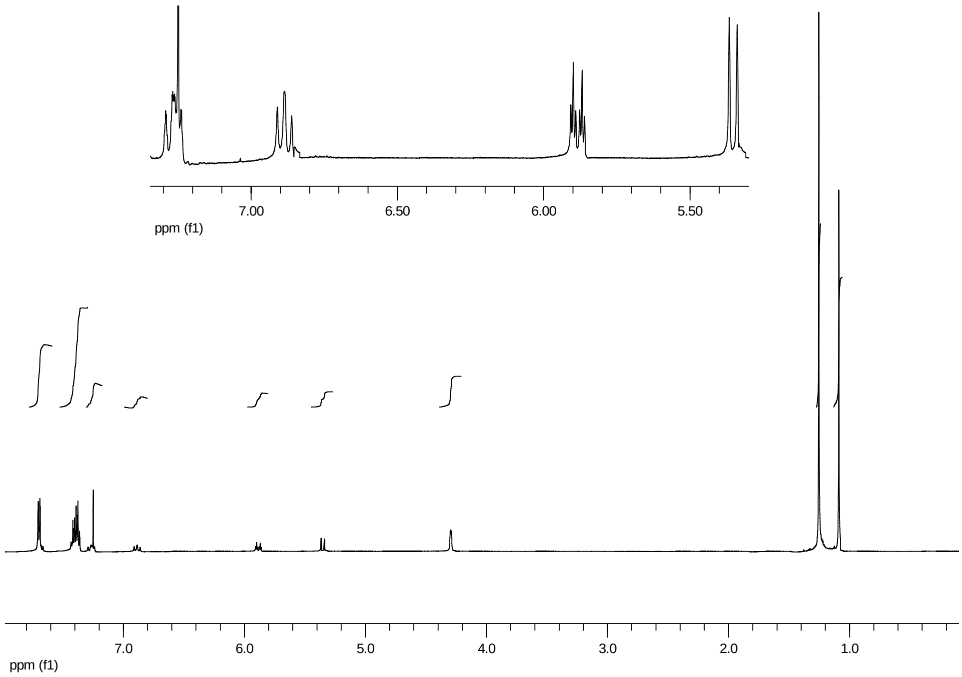
^{13}C NMR $CDCl_3$	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	2Me-C_1	Me-C_5	Me-C_9	Me-C_{13}	Si*t*Bu	SiPh
(100 MHz) 9,13-bis-demethyl 11-*cis*-retinil ether **12**	34.1 C	39.7 CH_2	19.3 CH_2	33.2 CH_2	130.3 C	137.4 C	132.4 CH	133.3 CH	134.7 CH	129.4 CH	126.3 CH	128.2 CH	125.4 CH	132.9 CH	64.3 CH_2	28.9 2xCH_3	21.7 CH_3	---	---	19.2, C 26.8 3xCH_3	127.6, 4xCH 129.6, 2xCH 133.6, 2xC 135.6, 4xCH
(75 MHz) 9-demethyl 11-*cis*-retinil ether **13**	34.1 C	39.8 CH_2	19.2 CH_2	33.3 CH_2	130.4 C	137.5 C	132.1 CH	133.4 CH	135.5 CH	127.9 CH	128.8 CH	132.7 CH	134.5 C	131.1 CH	61.1 CH_2	28.9 2xCH_3	21.8 CH_3	---	17.0 CH_3	18.8, C 26.8 3xCH_3	127.6, 4xCH 129.6, 2xCH 133.9, 2xC 135.6, 4xCH
(100 MHz) 13-demethyl 11-*cis*-retinil ether **14**	34.3 C	39.6 CH_2	19.2 CH_2	33.1 CH_2	128.7 C	136.5 C	127.1 CH	137.9 CH	137.8 C	124.9 CH	125.4 CH	128.3 CH	125.2 CH	133.1 CH	64.3 CH_2	29.0 2xCH_3	21.7 CH_3	12.3 CH_3	---	19.3, C 26.8 3xCH_3	127.7, 4xCH 129.6, 2xCH 133.7, 2xC 135.6, 4xCH
(75 MHZ) 11-*cis*-retinil ether **15**	34.3 C	39.6 CH_2	19.3 CH_2	33.0 CH_2	129.1 C	137.9 C	126.7 CH	138.2 CH	137.7 C	126.5 CH	124.7 CH	132.9 CH	136.8 C	131.1 CH	61.4 CH_2	28.9 2xCH_3	21.7 CH_3	12.2 CH_3	17.2 CH_3	18.8, C 26.8 3xCH_3	127.6, 4xCH 129.5, 2xCH 133.8, 2xC 135.5, 4xCH
(100 MHz) 11-*cis*- retinol (**16**)	34.2 C	39.6 CH_2	19.3 CH_2	33.0 CH_2	129.2 C	137.9 C	127.1 CH	138.0 CH	137.3 C	126.2 CH	125.3 CH	132.4 CH	136.5 C	130.1 CH	59.5 CH_2	28.9 2xCH_3	21.8 CH_3	12.2 CH_3	17.2 CH_3	---	---
(100 MHz) 11-*cis*- retinal (**1**)	34.3 C	39.5 CH_2	19.2 CH_2	33.0 CH_2	130.2 C	137.6 C	131.5 CH	137.4 CH	141.7 C	125.7 CH	129.7 CH	130.1 CH	155.9 C	129.7 CH	191.2 CH	29.0 2xCH_3	21.8 CH_3	12.4 CH_3	18.0 CH_3	---	---

NMR Spectra.

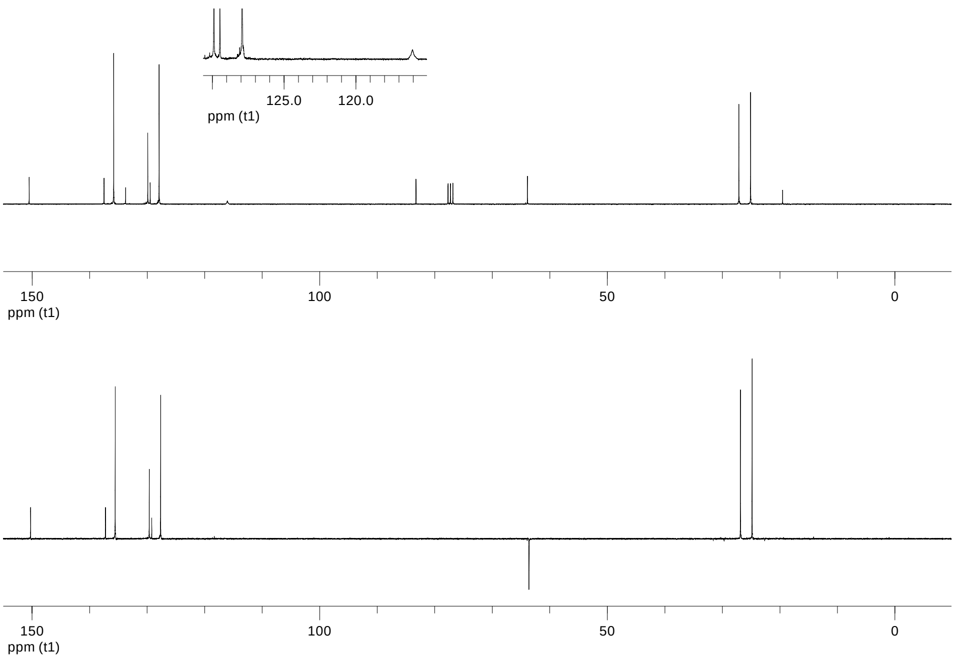


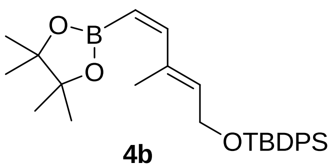
4a

^{1}H NMR (300 MHz, $CDCl_3$), Method A



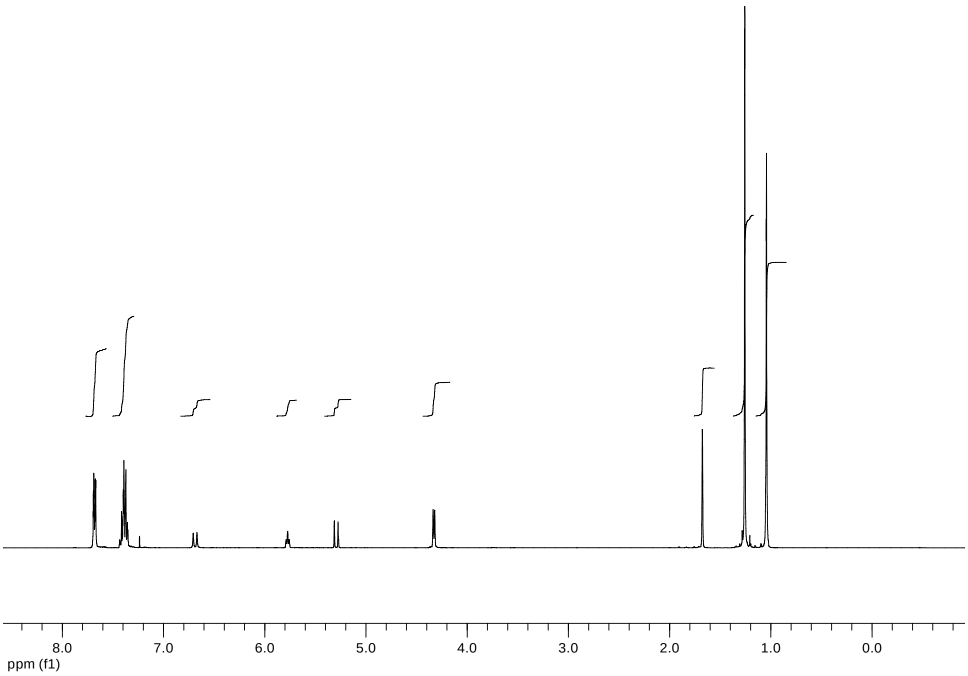
^{13}C NMR (75 MHz, $CDCl_3$), Method A



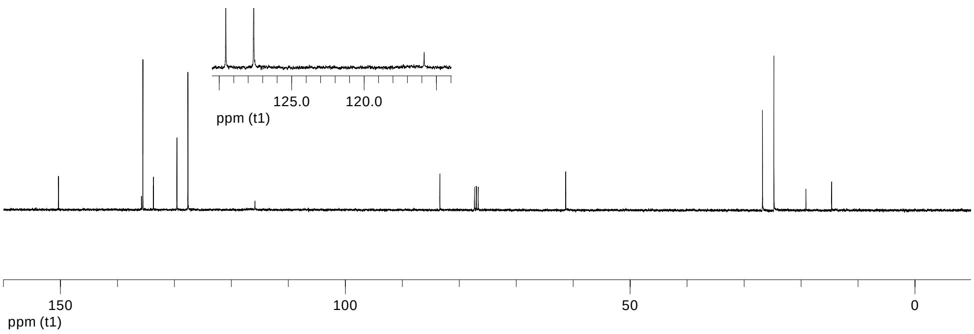


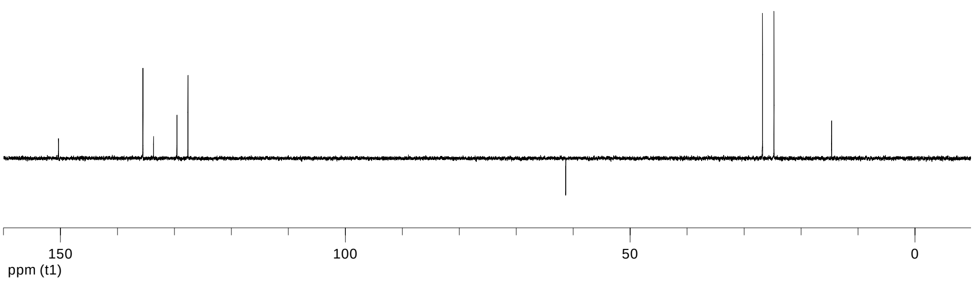
4b

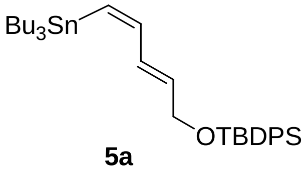
^{1}H NMR (300 MHz, $CDCl_3$), Method C



^{13}C NMR (75 MHz, $CDCl_3$), Method C

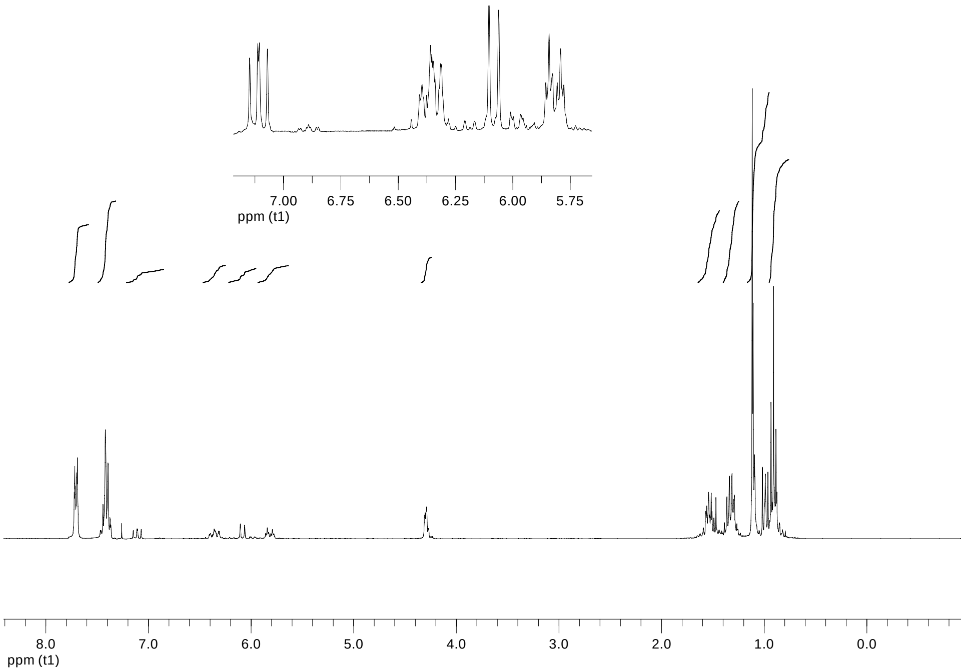




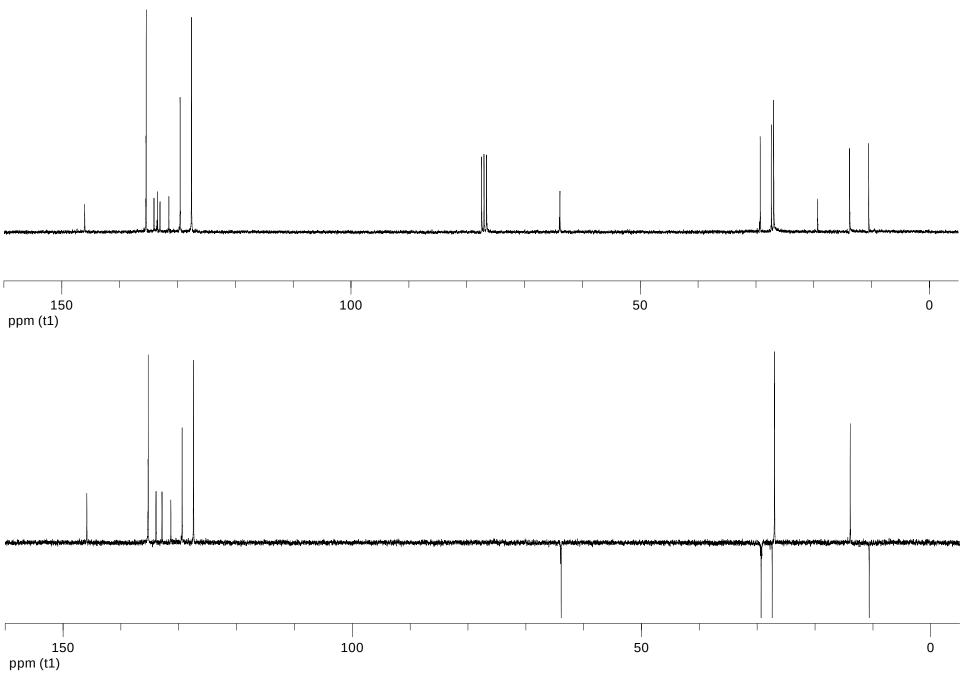


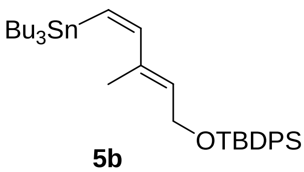
5a

^{1}H NMR (300 MHz, $CDCl_3$), Method B



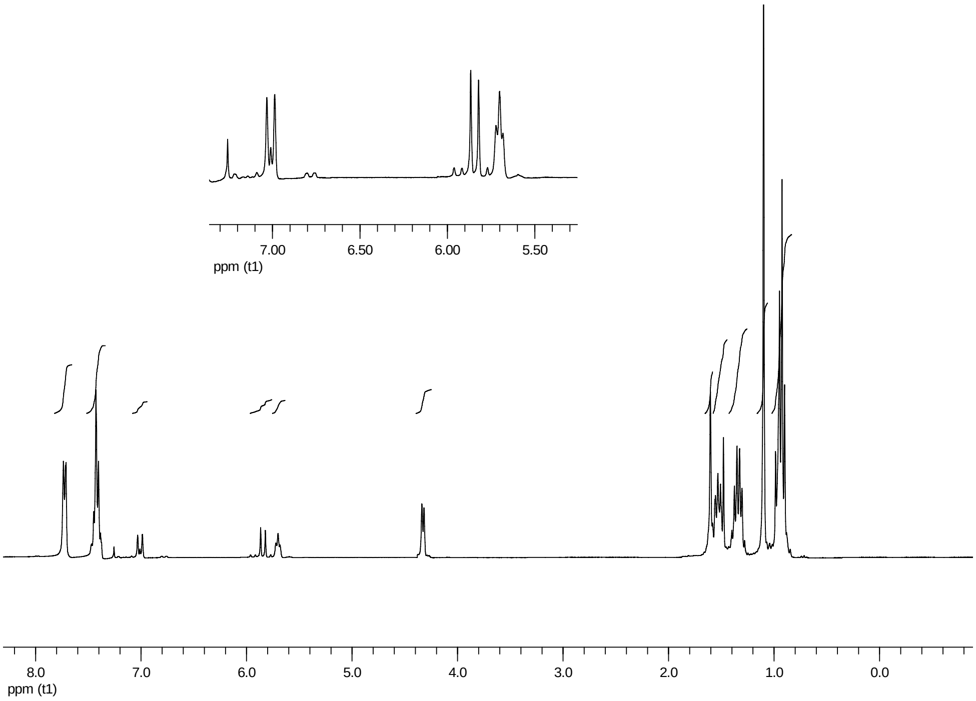
^{13}C NMR (75 MHz, $CDCl_3$), Method B



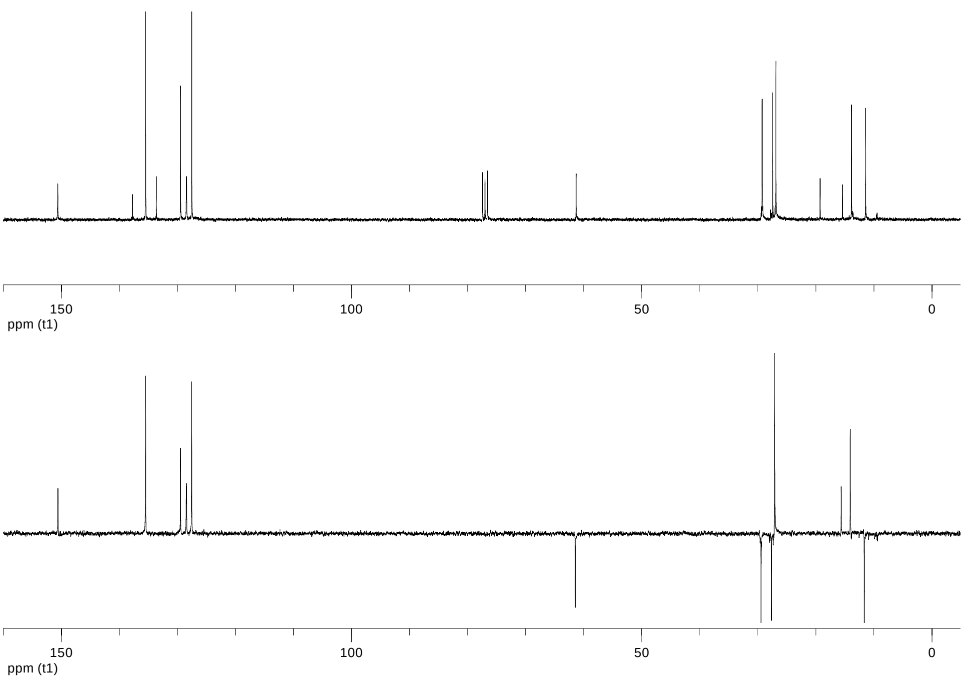


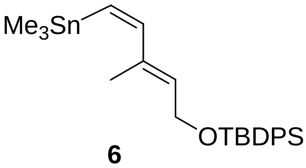
5b

^{1}H NMR (300 MHz, $CDCl_3$), Method B



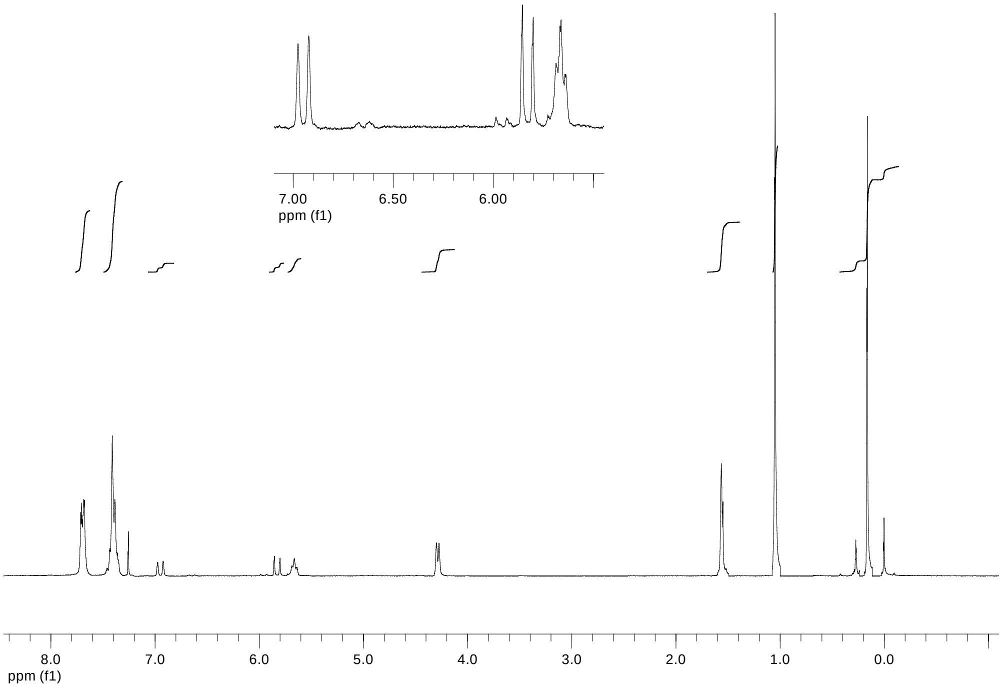
^{13}C NMR (75 MHz, $CDCl_3$), Method B



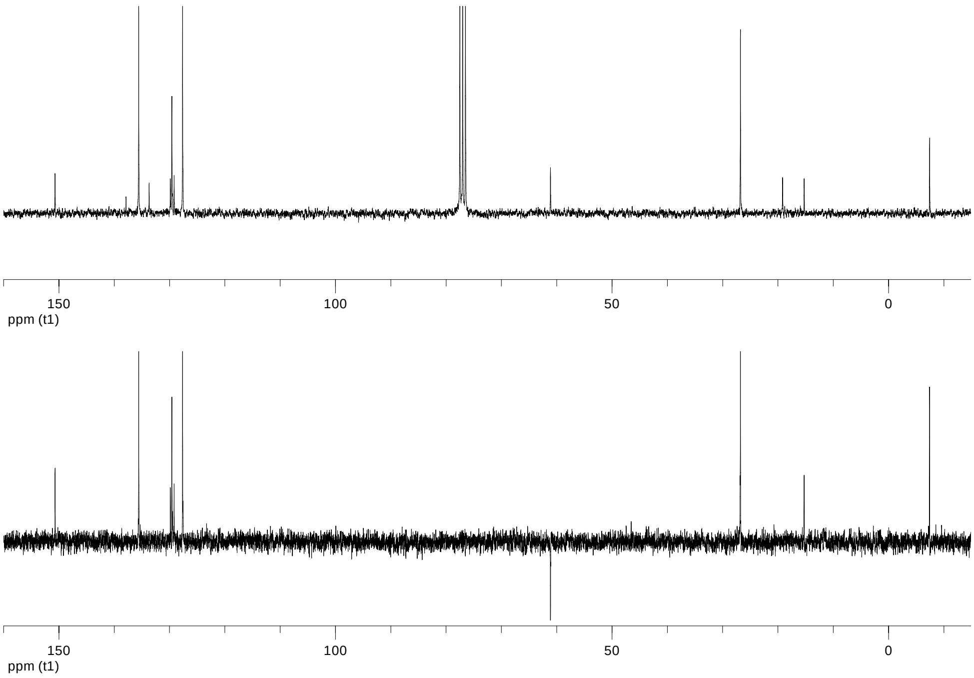


6

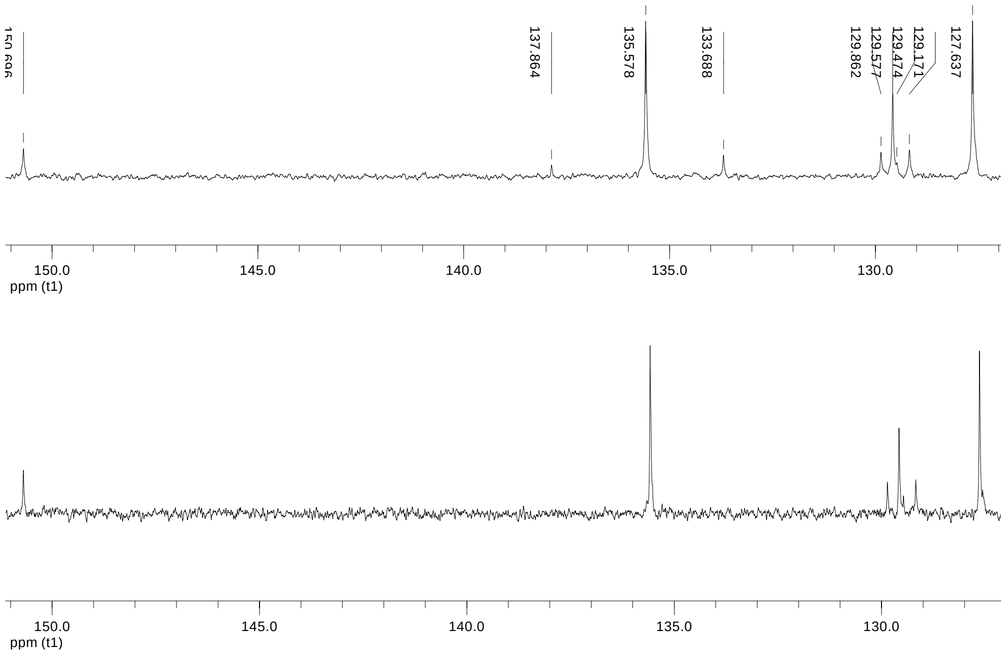
^{1}H NMR (300 MHz, $CDCl_3$), Method D

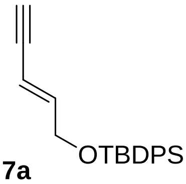


^{13}C NMR (75 MHz, $CDCl_3$), Method D



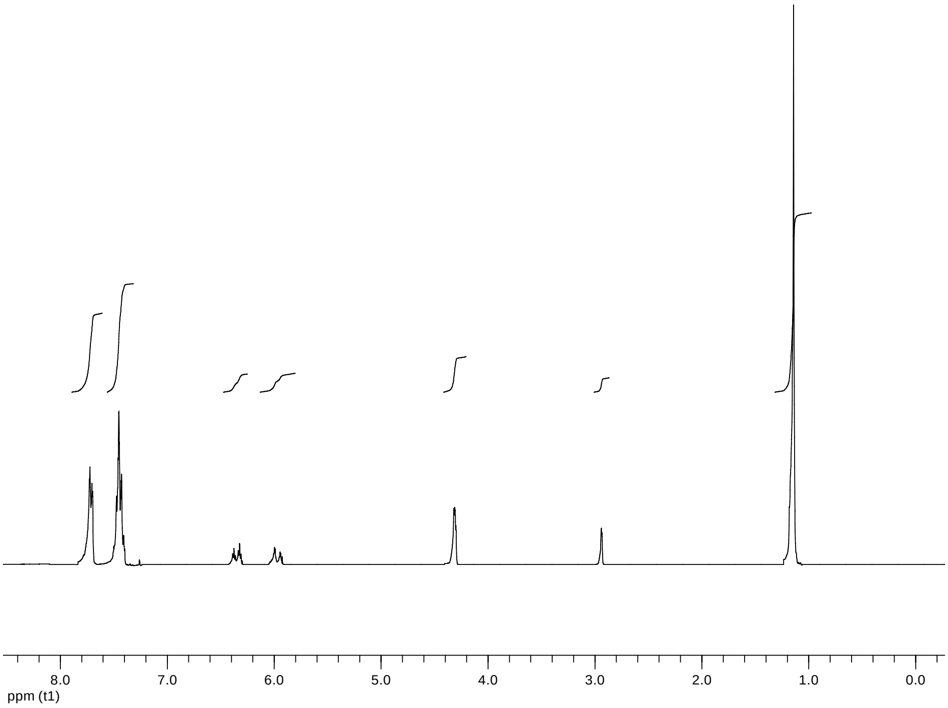
S13


150.696
137.864
135.578
133.688
129.862
129.577
129.474
129.171
127.637
150.0
145.0
140.0
135.0
130.0
ppm (t1)
150.0
145.0
140.0
135.0
130.0
ppm (t1)

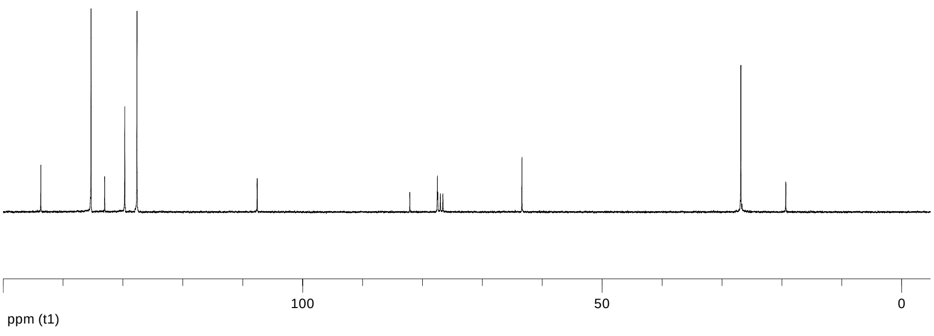


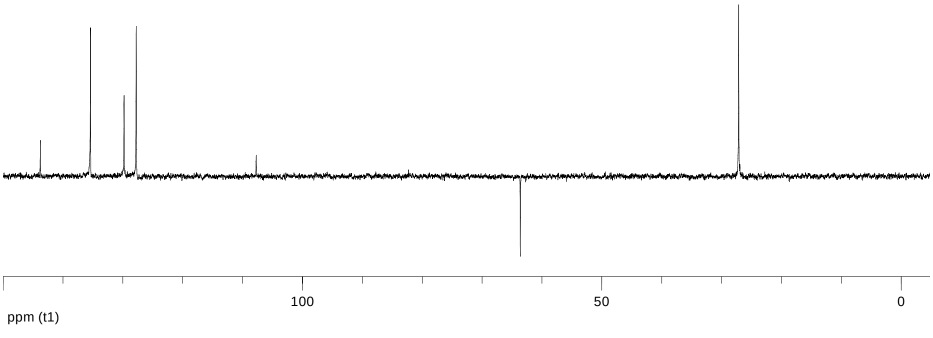
7a

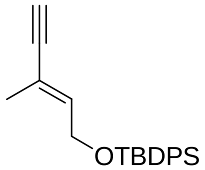
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

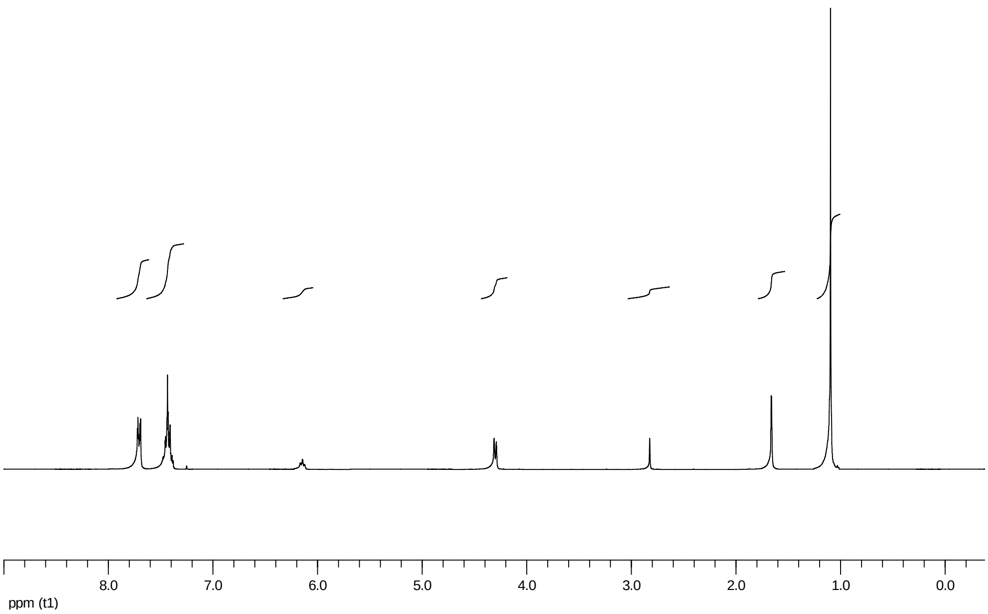




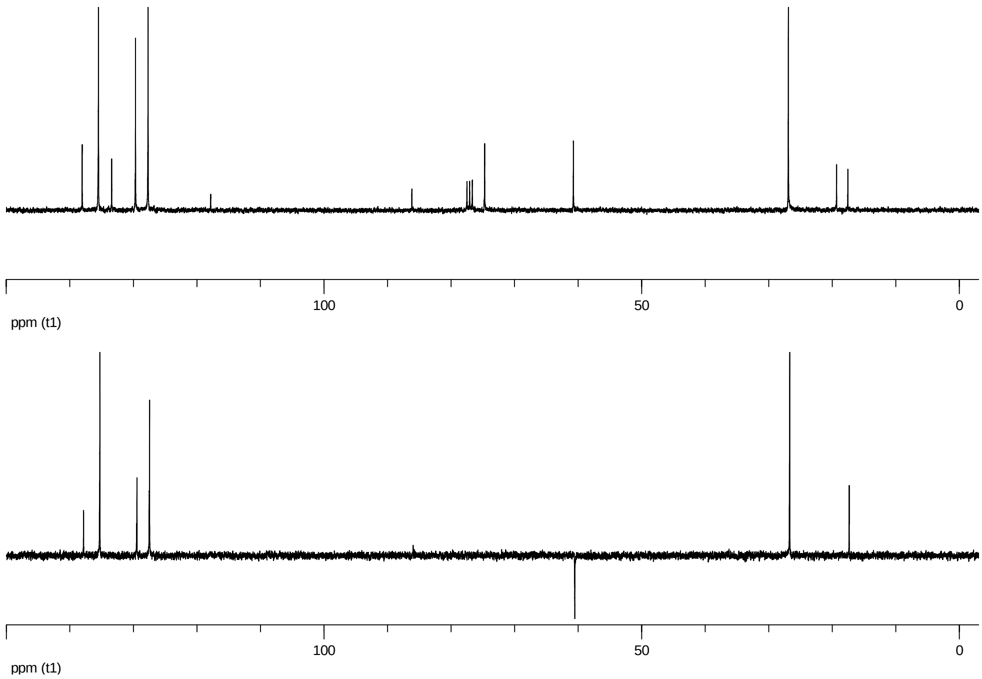


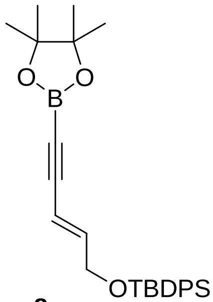
7b

^{1}H NMR (300 MHz, $CDCl_3$)



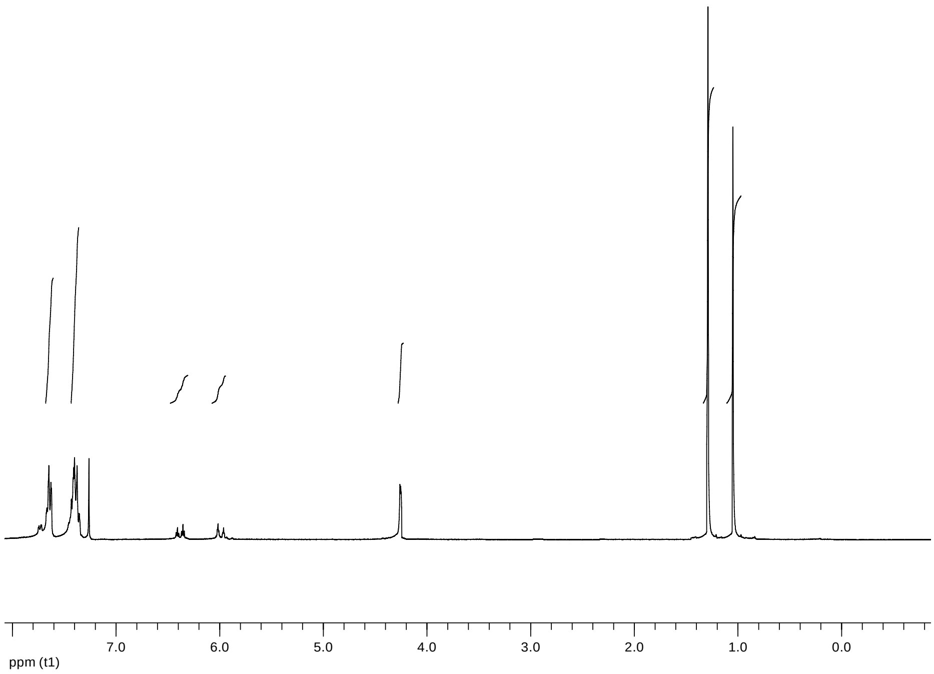
^{13}C NMR (75 MHz, $CDCl_3$)



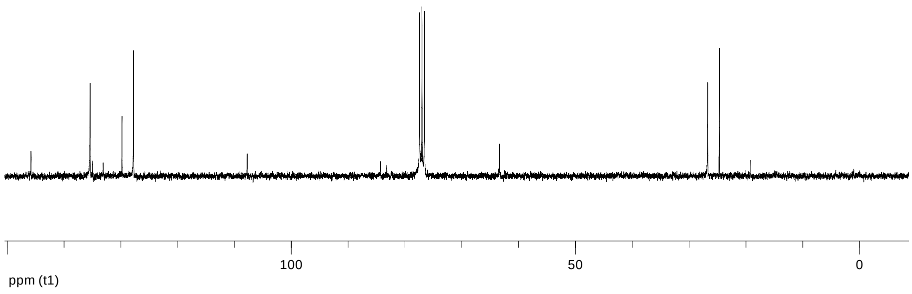


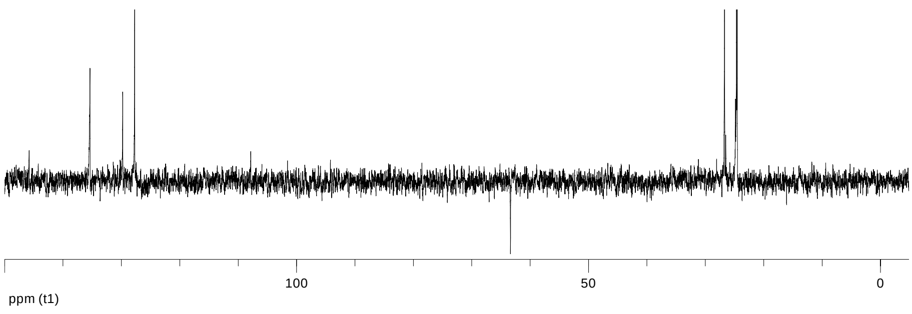
8a

^{1}H NMR (300 MHz, $CDCl_3$)

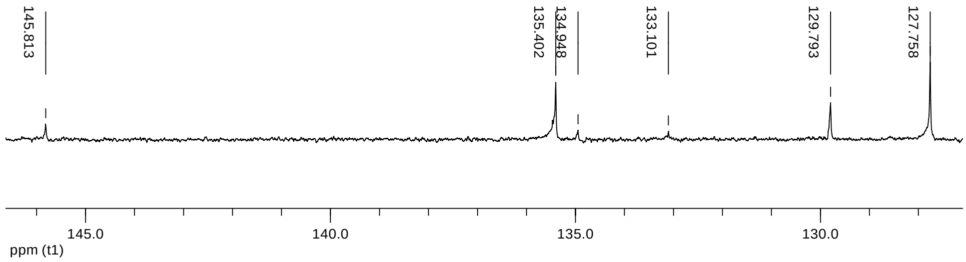


^{13}C NMR (75 MHz, $CDCl_3$)





S17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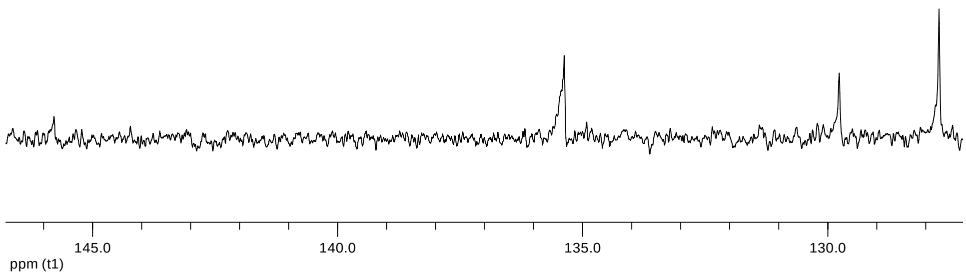
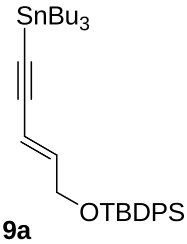
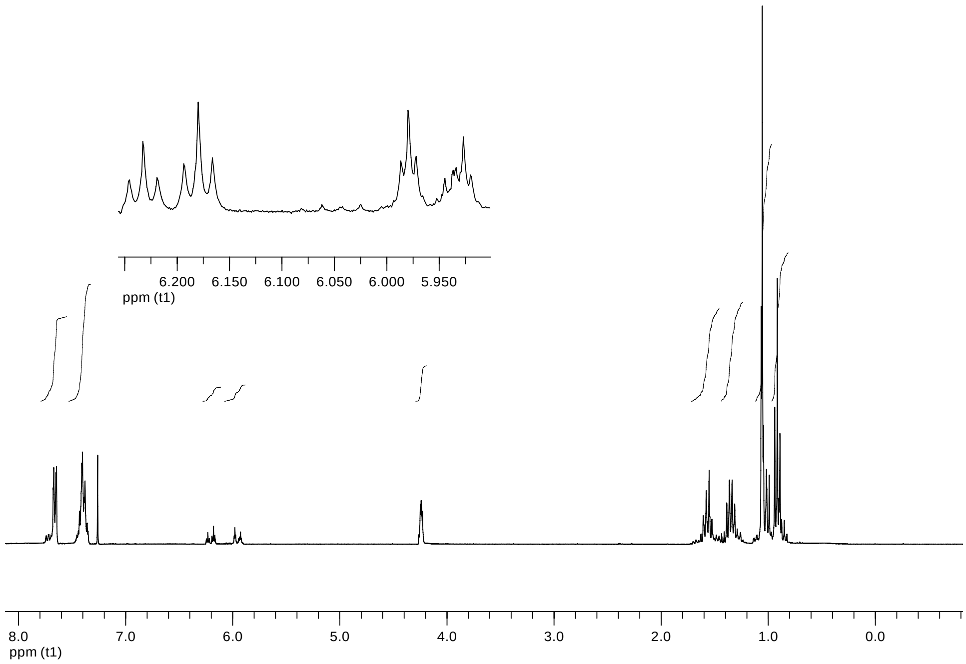
135.402
134.948
133.101
129.793
127.758
145.0
140.0
135.0
130.0
ppm (t1)


145.0
140.0
135.0
130.0
ppm (t1)

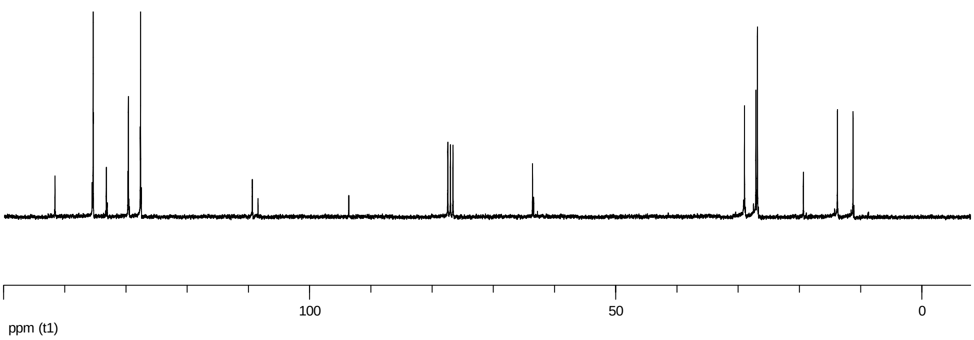


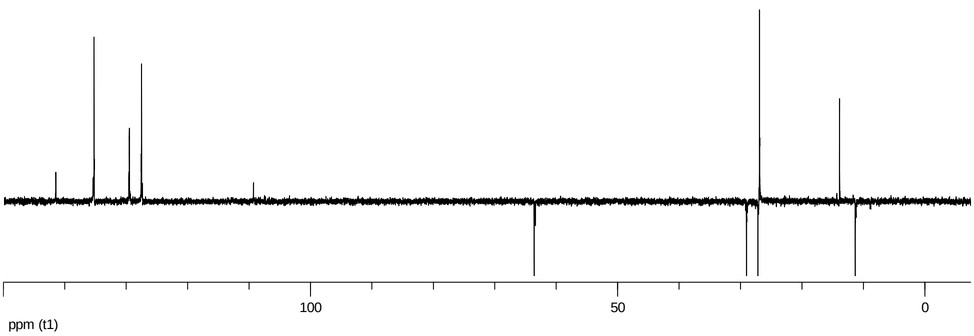
9a

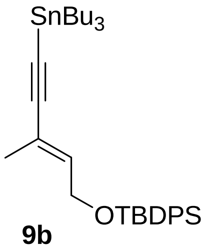
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

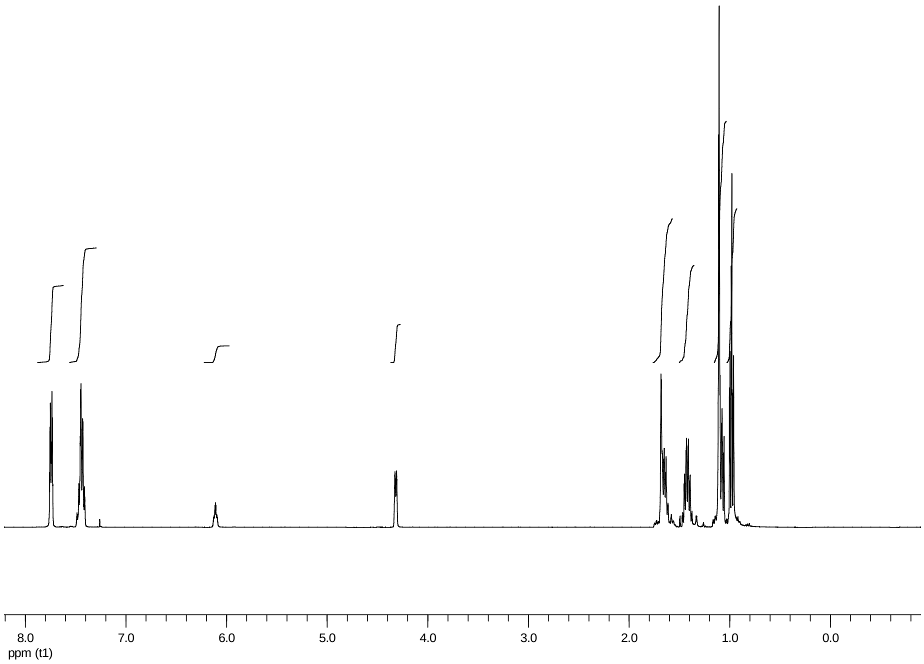




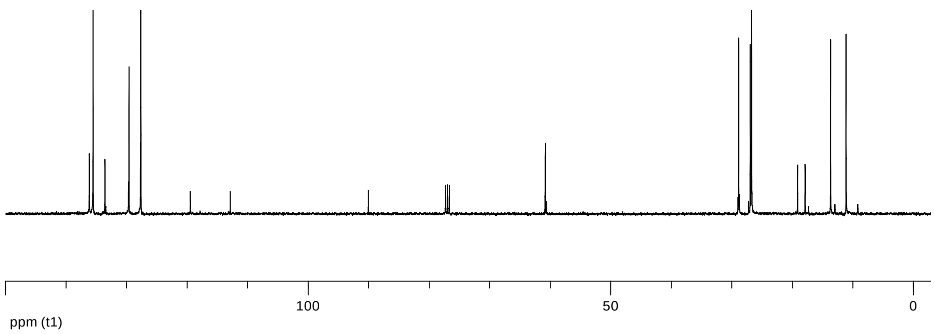


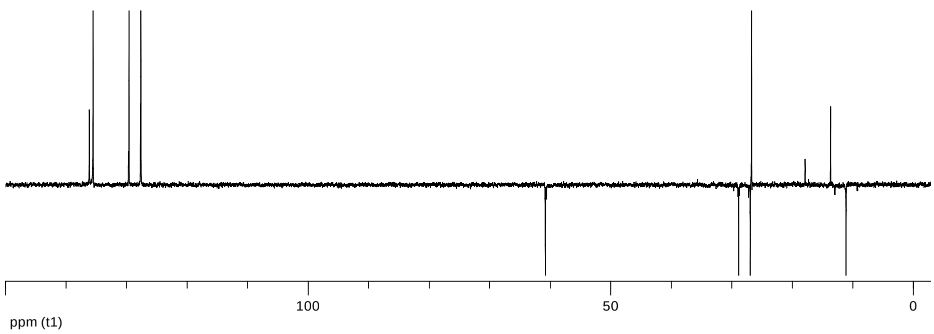
9b

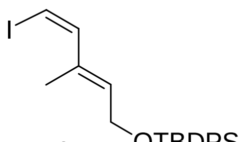
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

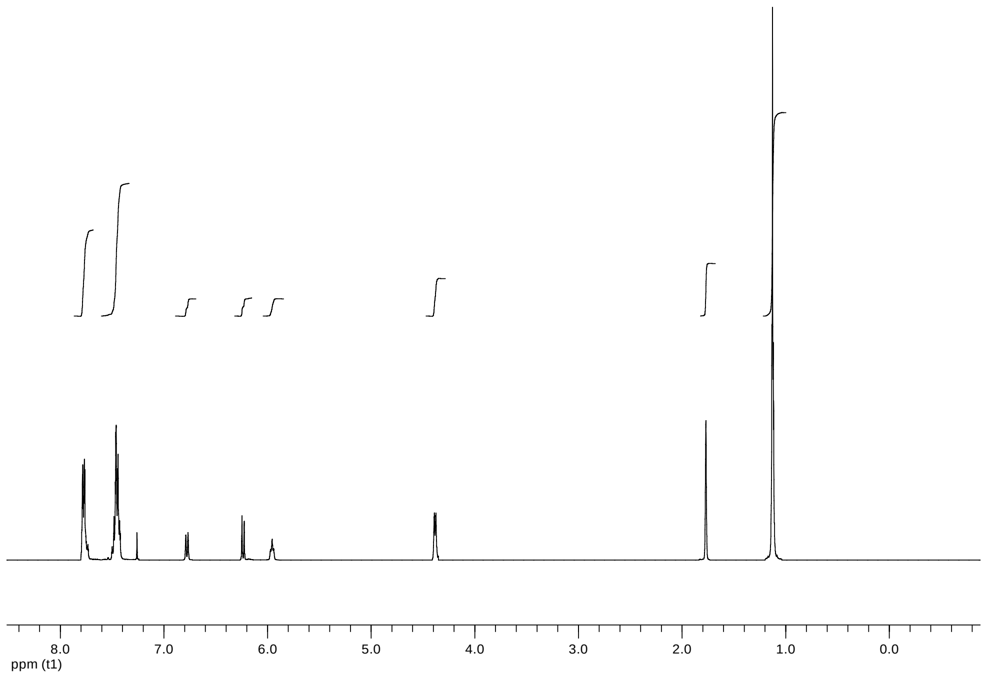




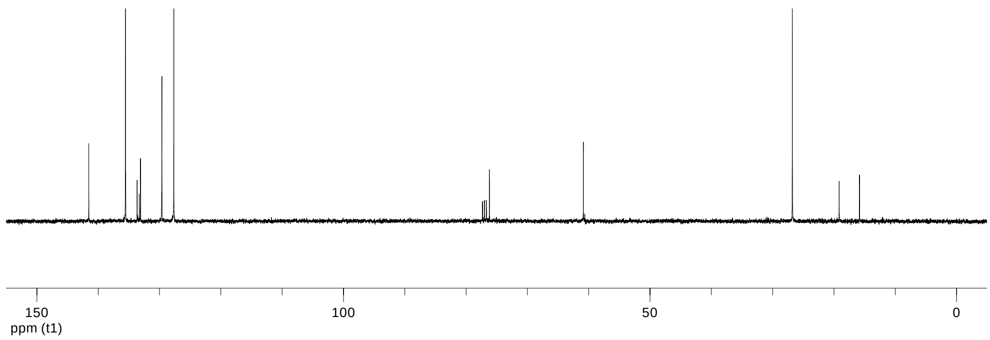


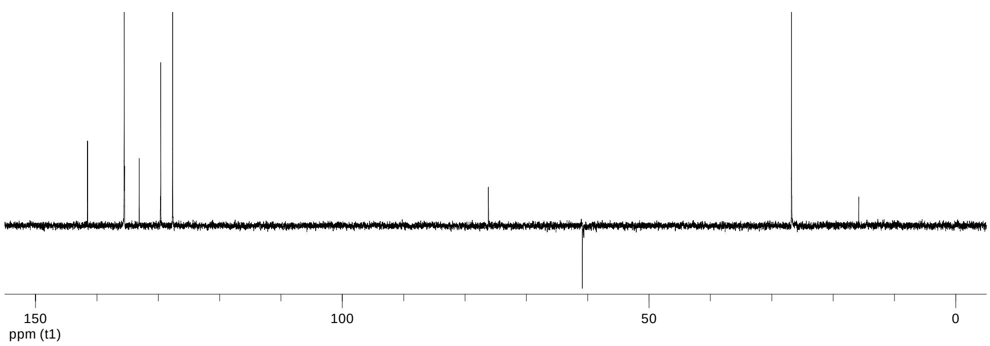
10

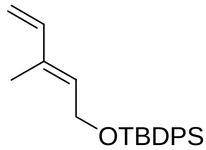
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)

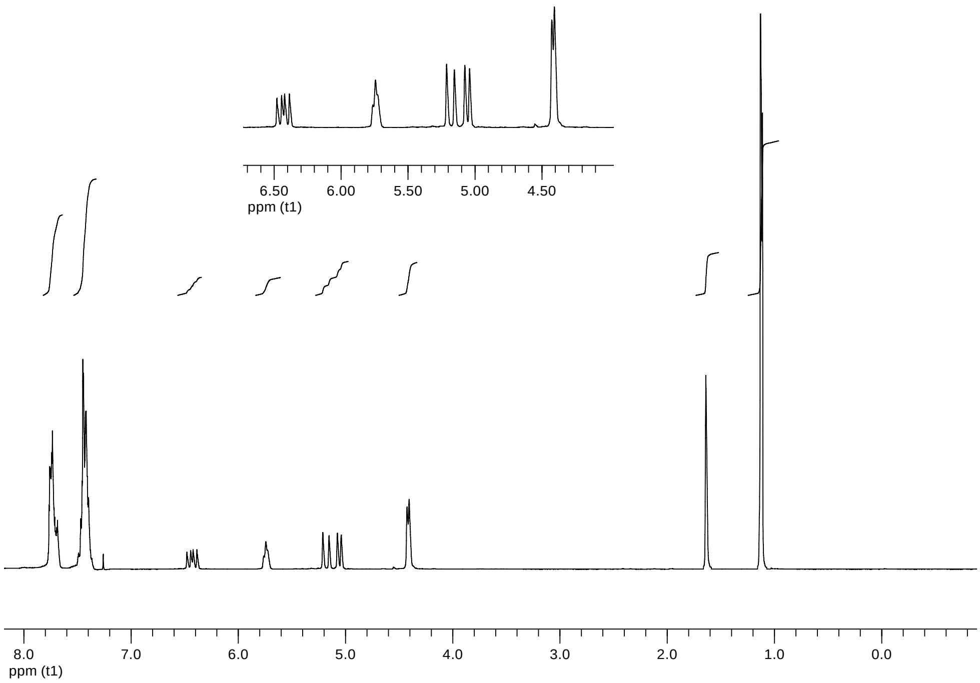




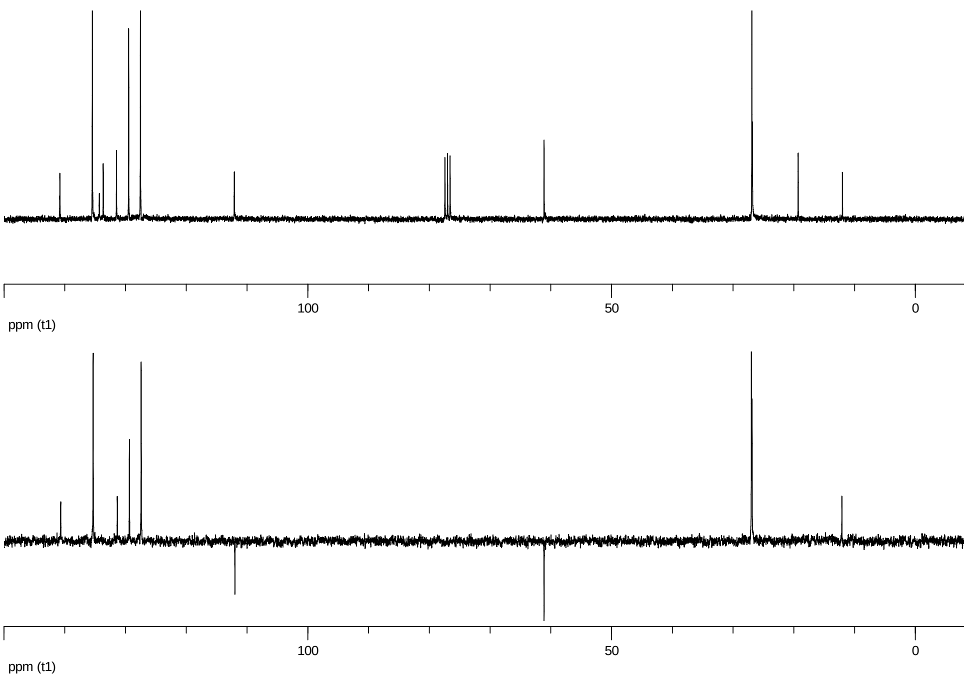


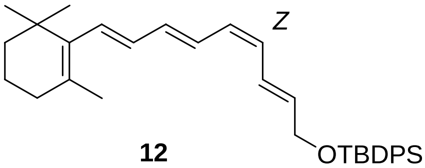
11

^{1}H NMR (300 MHz, $CDCl_3$)



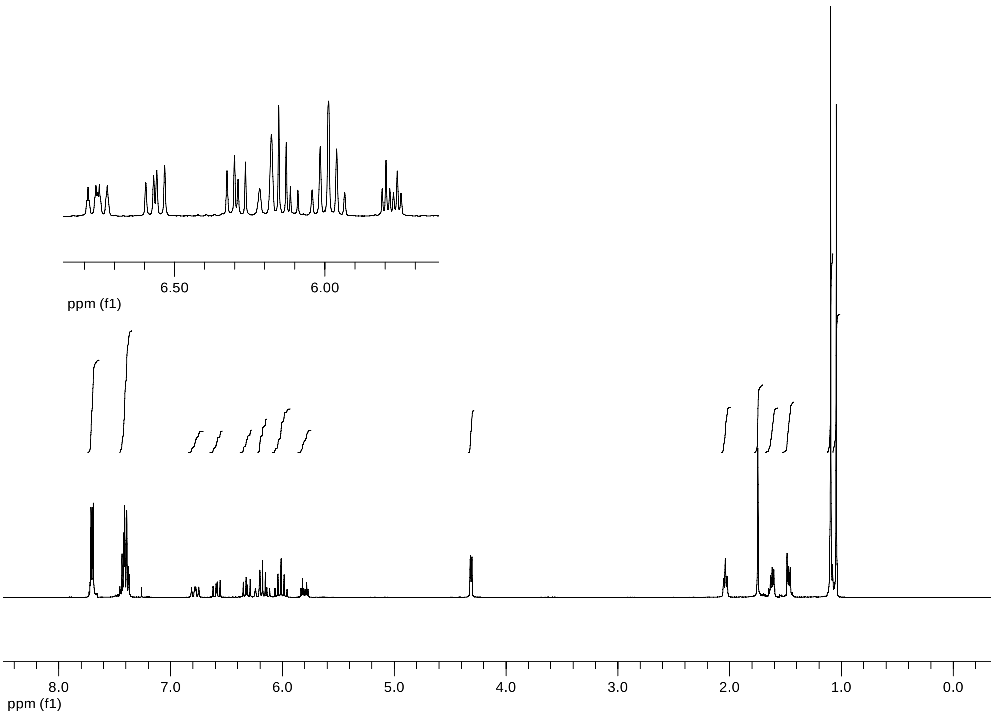
^{13}C NMR (75 MHz, $CDCl_3$)



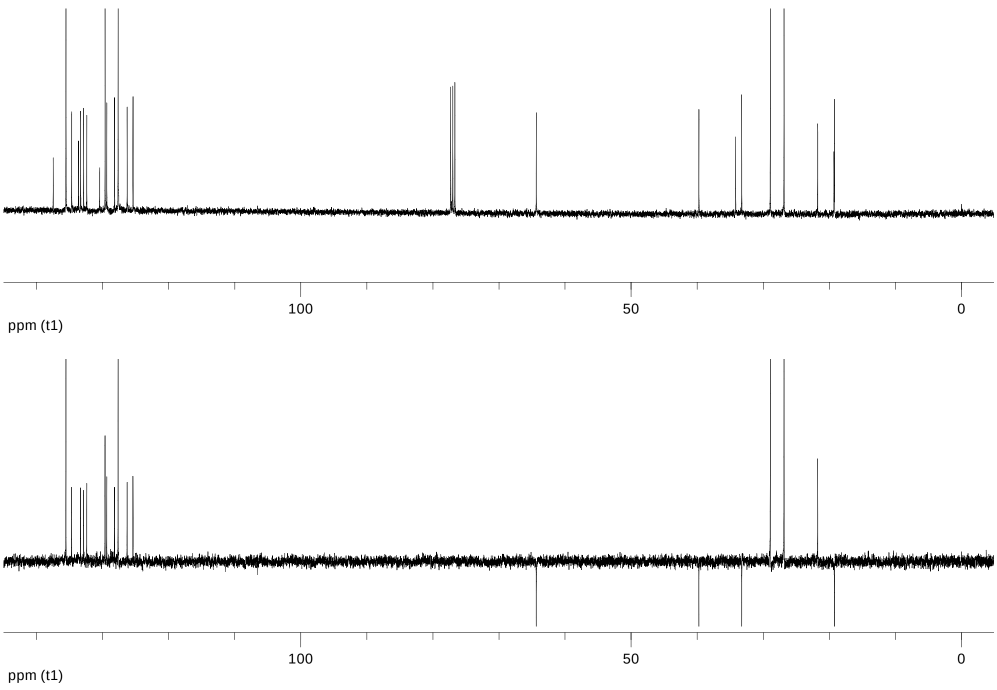


12

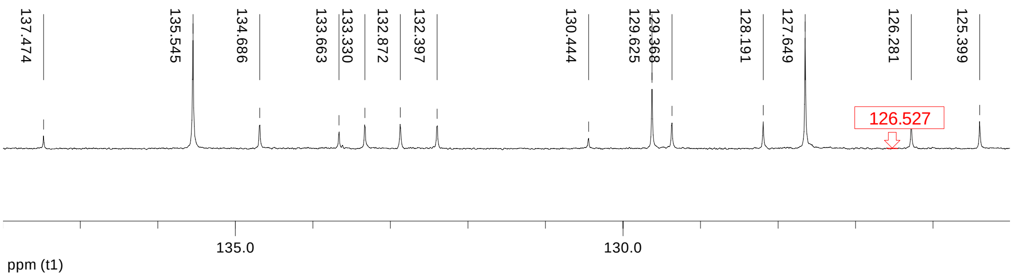
^{1}H NMR (400 MHz, $CDCl_3$), Suzuki reaction

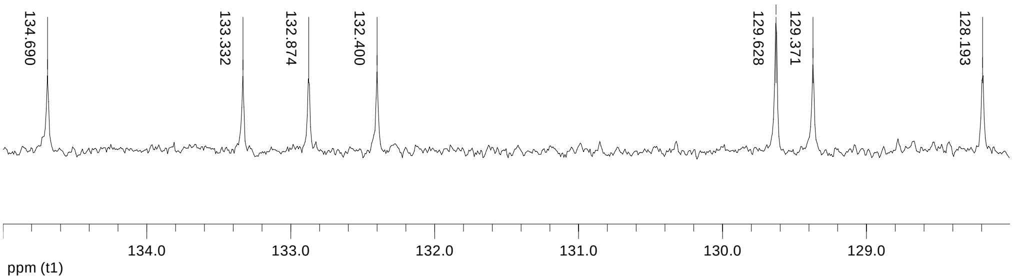


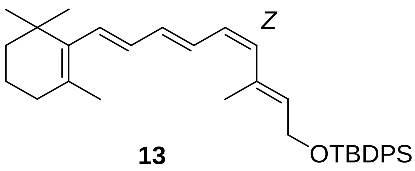
^{13}C NMR (100 MHz, $CDCl_3$), Suzuki reaction



S23

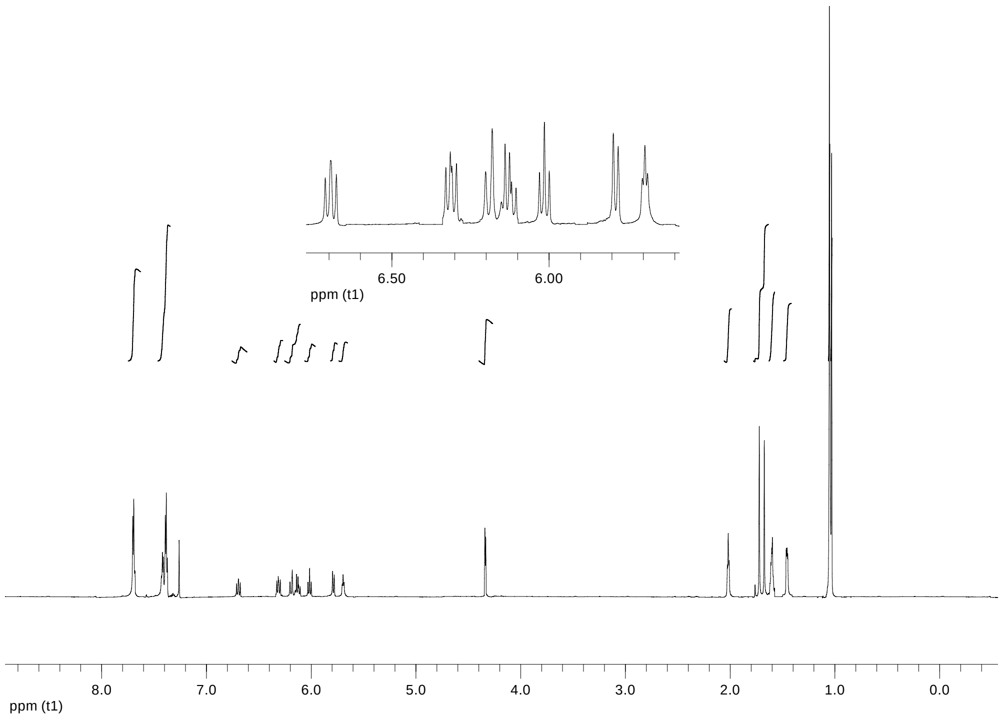

137.474
135.545
134.686
133.663
133.330
132.872
132.397
130.444
129.625
129.368
128.191
127.649
126.281
125.399
126.527
135.0
130.0
ppm (t1)


134.690
133.332
132.874
132.400
129.628
129.371
128.193
134.0
133.0
132.0
131.0
130.0
129.0
ppm (t1)

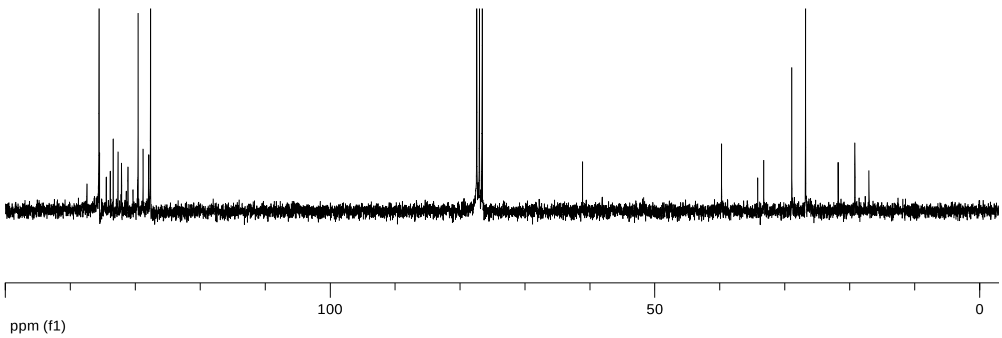


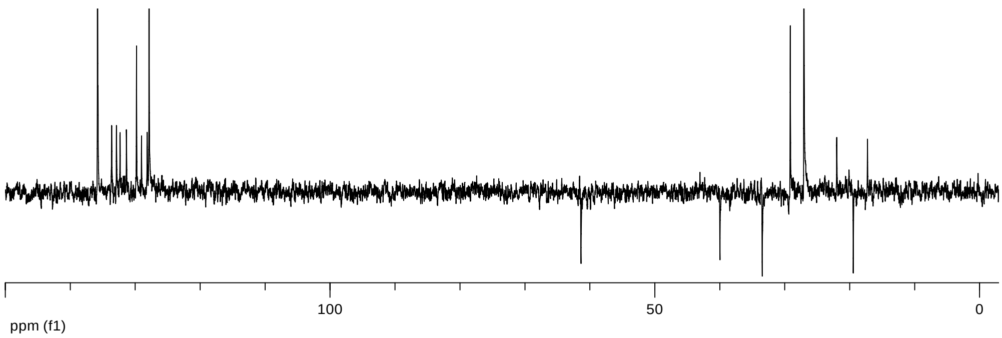
13

^{1}H NMR (750 MHz, $CDCl_3$), Suzuki reaction

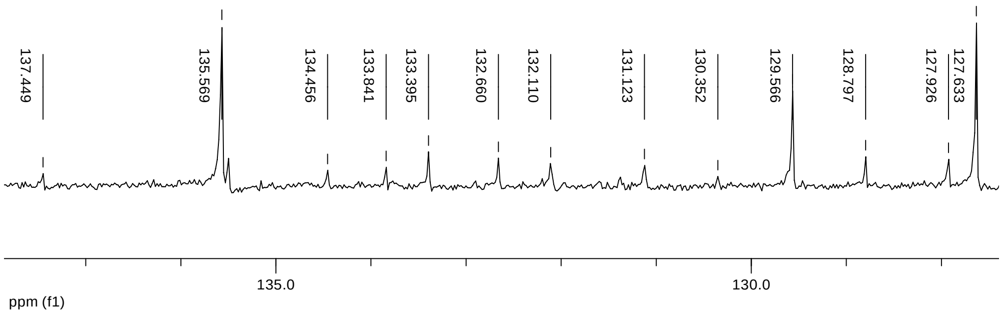


^{13}C NMR (75 MHz, $CDCl_3$), Suzuki reaction

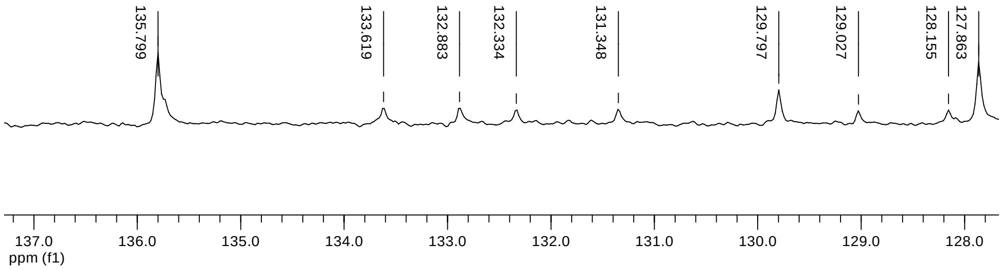




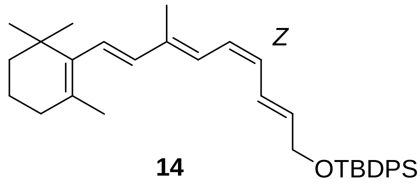
S25



137.449
135.569
134.456
133.841
133.395
132.660
132.110
131.123
130.352
129.566
128.797
127.926
127.633
135.0
130.0
ppm (f1)

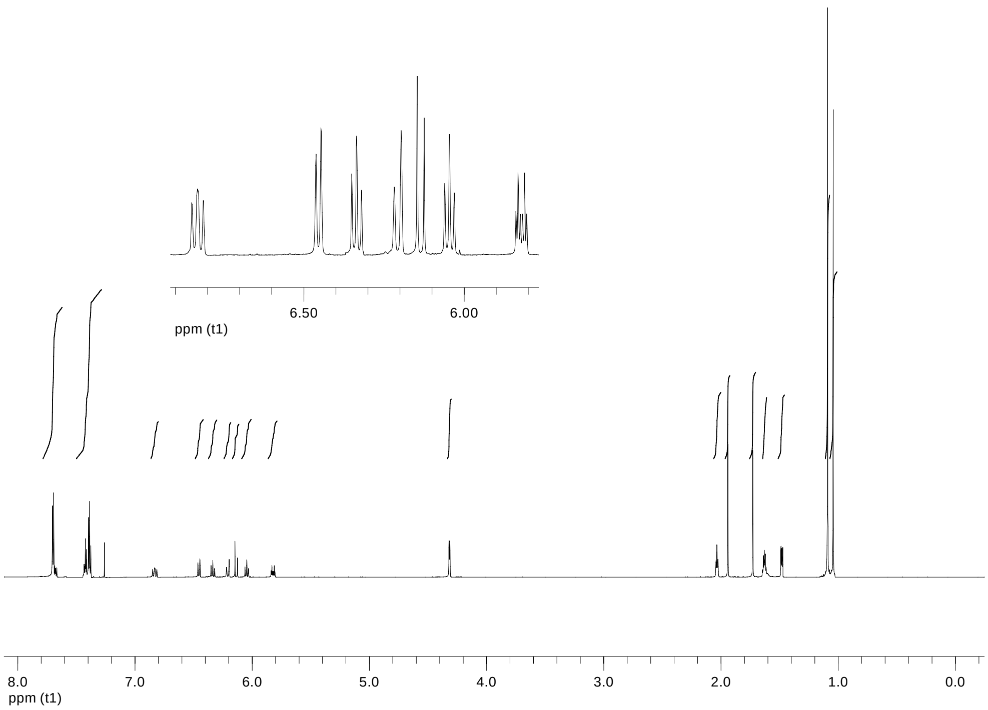


135.799
133.619
132.883
132.334
131.348
129.797
129.027
128.155
127.863
137.0
136.0
135.0
134.0
133.0
132.0
131.0
130.0
129.0
128.0
ppm (f1)

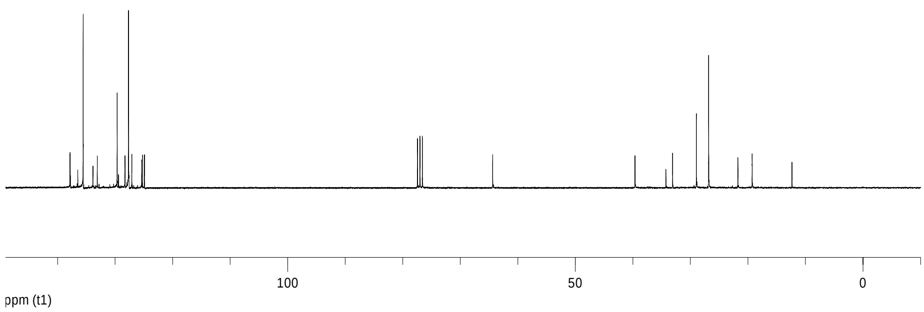


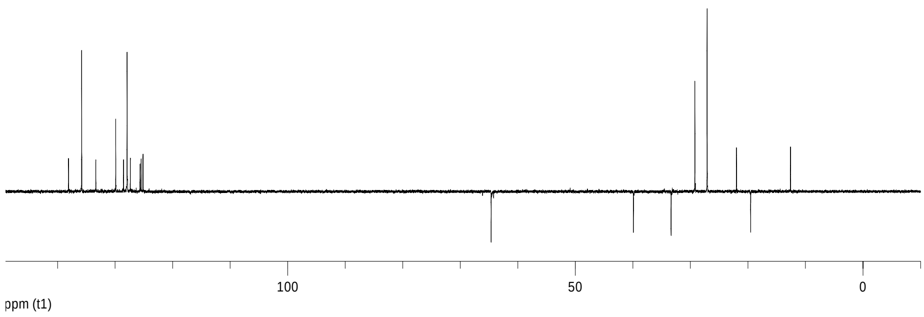
14

^{1}H NMR (750 MHz, $CDCl_3$), Suzuki reaction

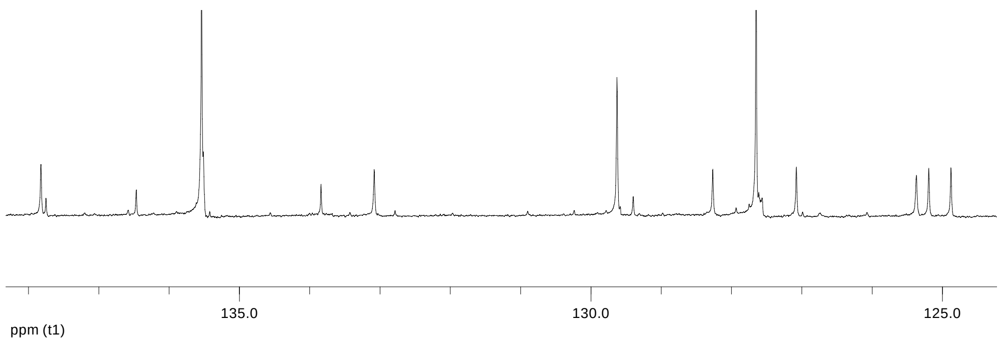


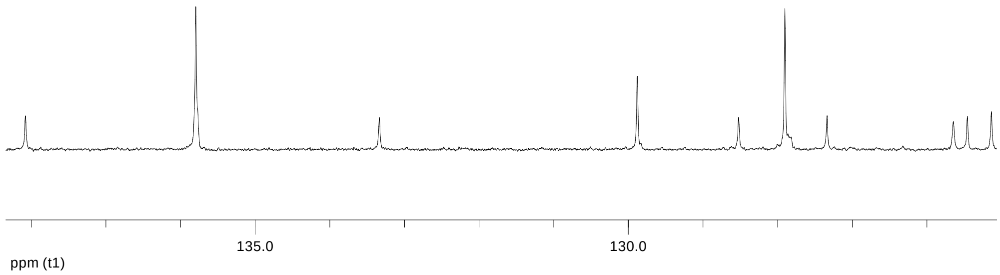
^{13}C NMR (100 MHz, $CDCl_3$), Suzuki reaction

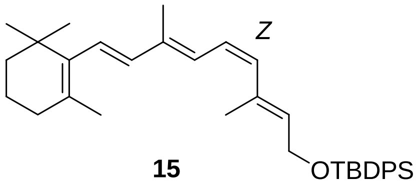




S27

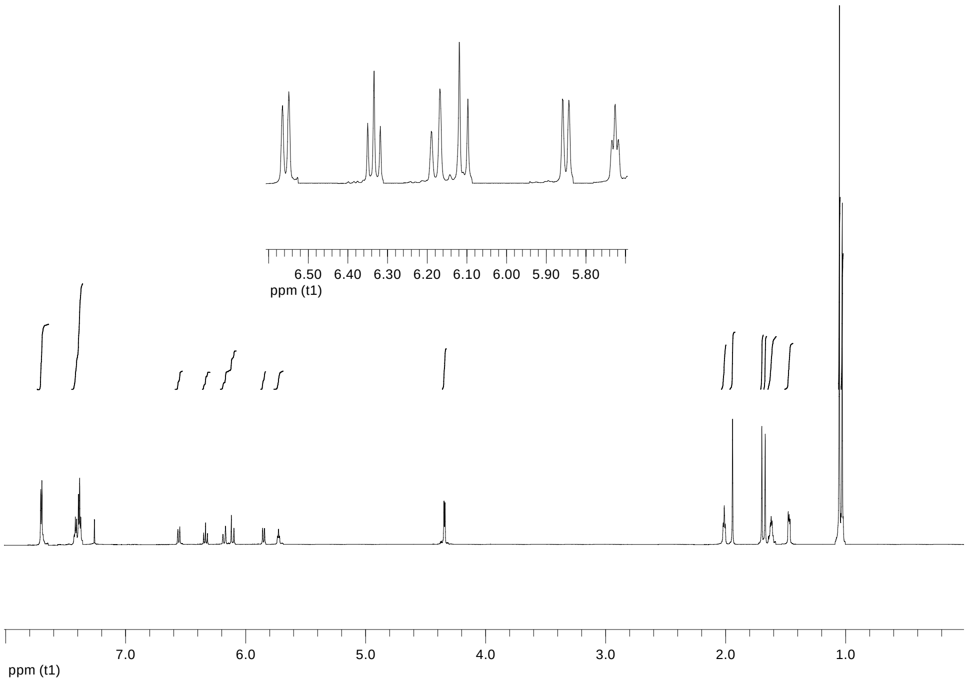




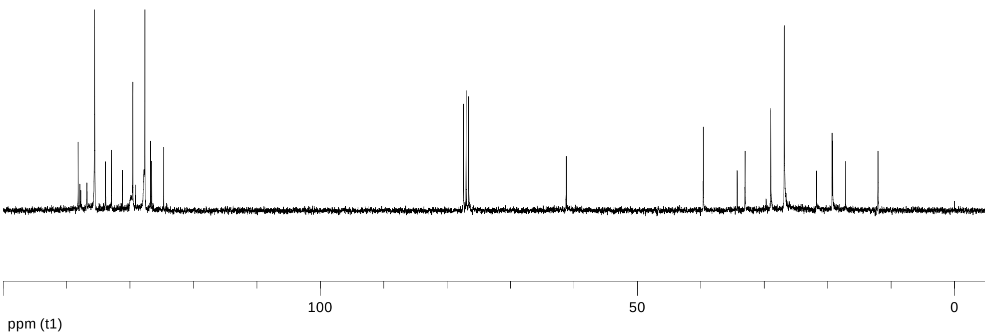


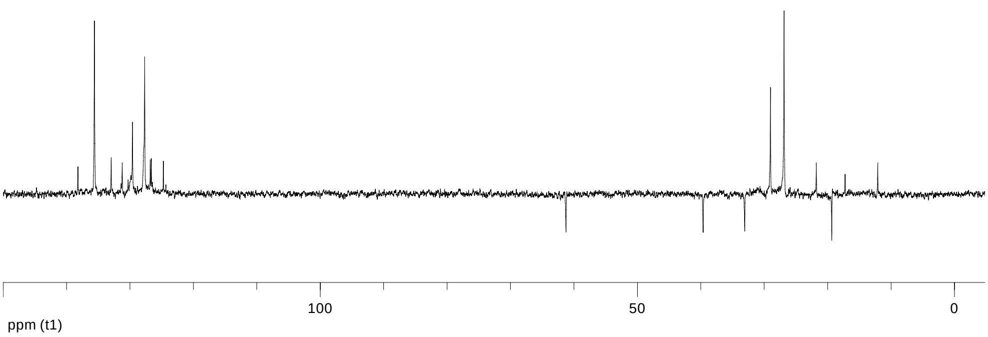
15

^{1}H NMR (750 MHz, $CDCl_3$), Suzuki reaction

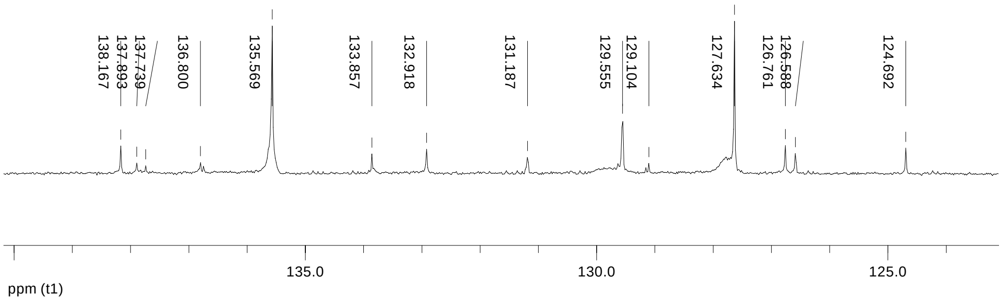


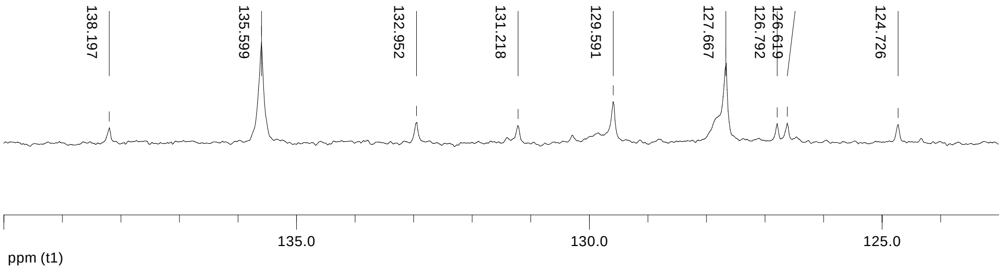
^{13}C NMR (75 MHz, $CDCl_3$), Suzuki reaction

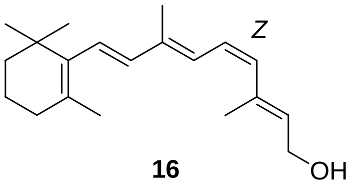




S29

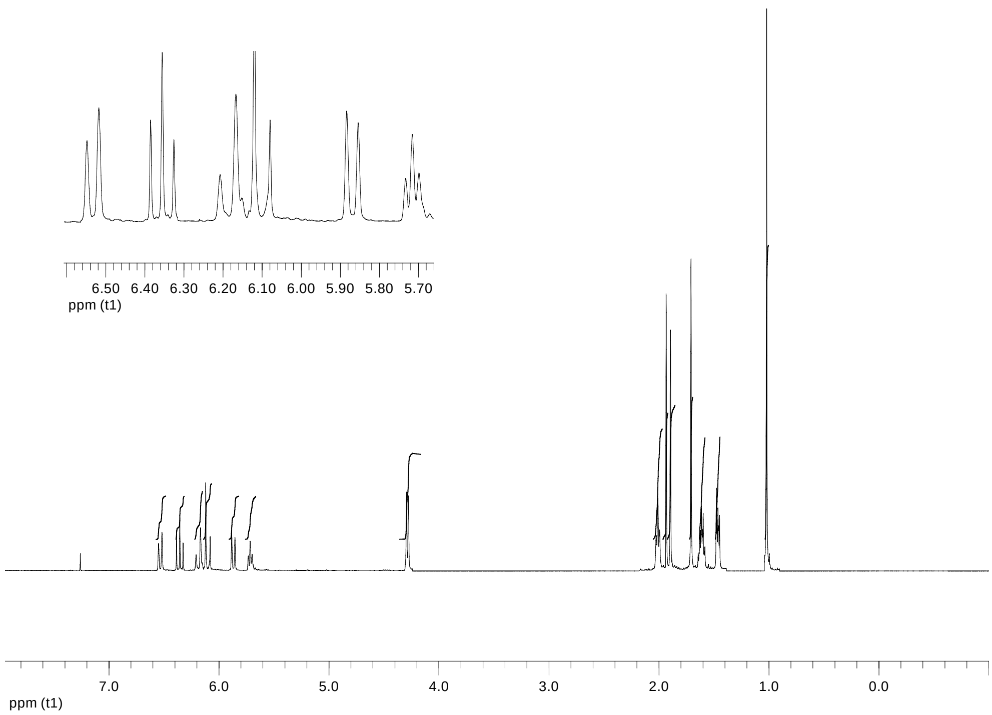

138.167
137.893
137.739
136.800
135.569
133.857
132.918
131.187
129.555
129.104
127.634
126.761
126.588
124.692
135.0
130.0
125.0
ppm (t1)


138.197
135.599
132.952
131.218
129.591
127.667
126.792
126.619
124.726
135.0
130.0
125.0
ppm (t1)

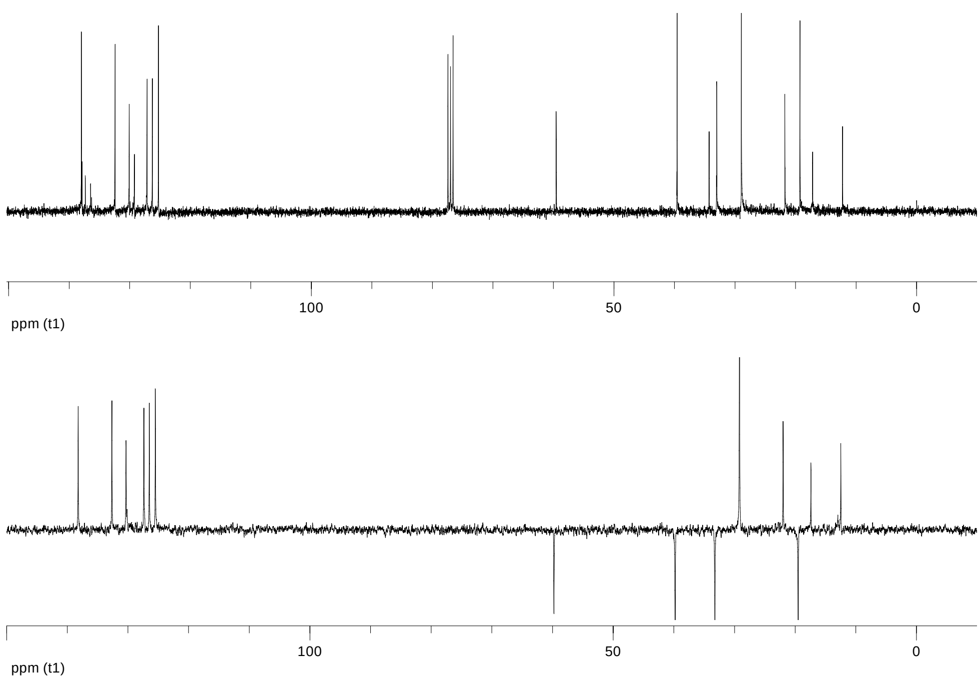


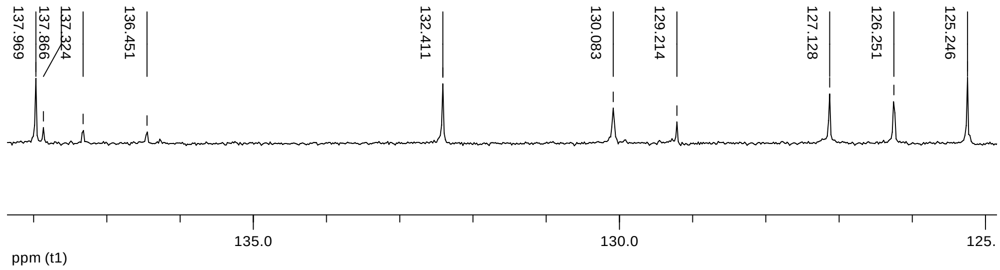
16

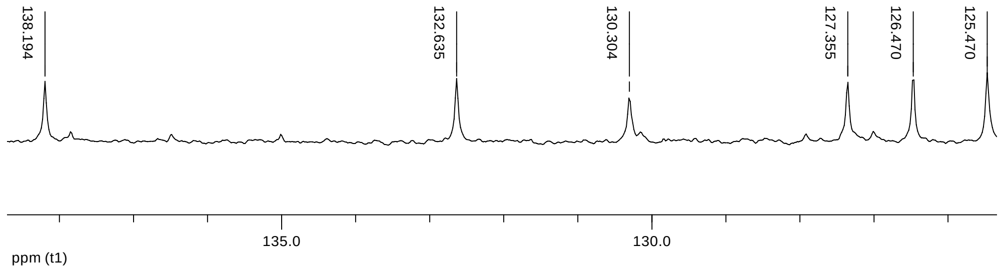
^{1}H NMR (400 MHz, $CDCl_3$)

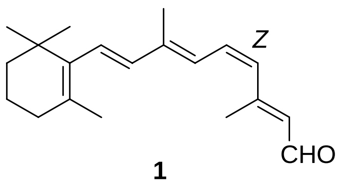


^{13}C NMR (100 MHz, $CDCl_3$)



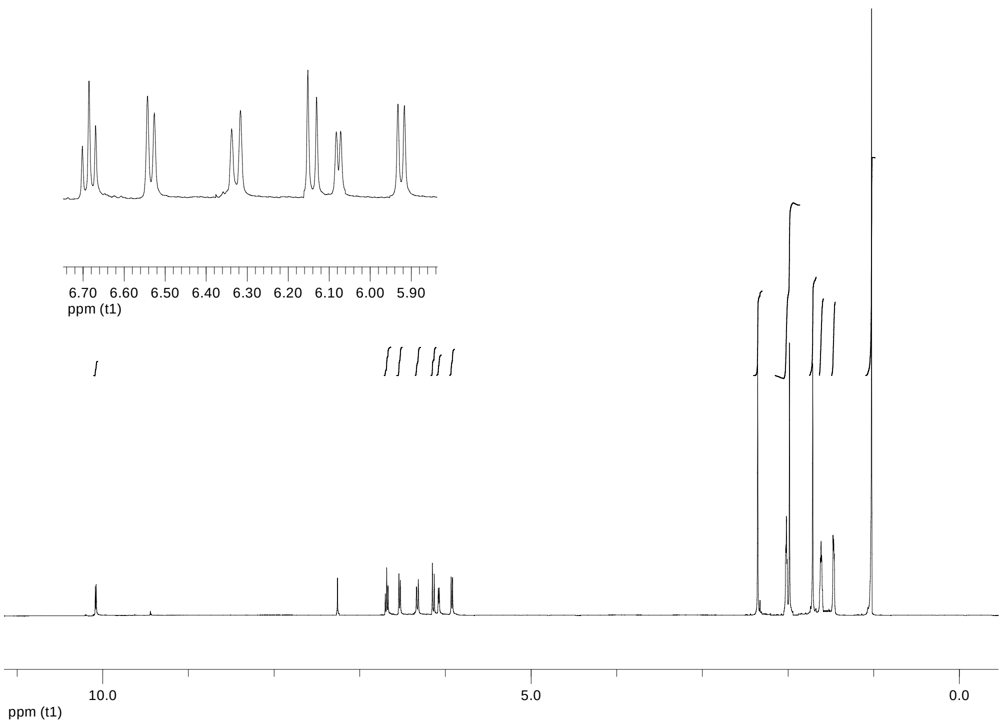

137.969
137.866
137.324
136.451
132.411
130.083
129.214
127.128
126.251
125.246
135.0
130.0
125.
ppm (t1)


138.194
132.635
130.304
127.355
126.470
125.470
135.0
130.0
ppm (t1)

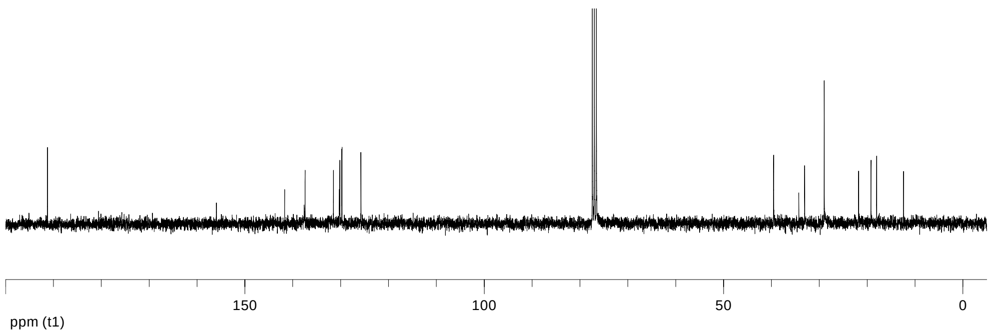


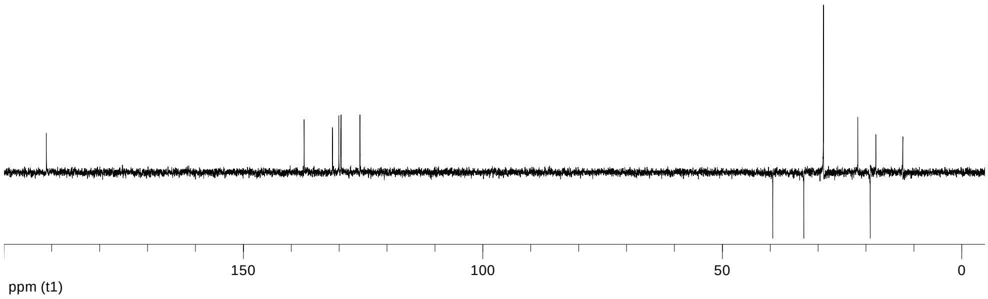
1

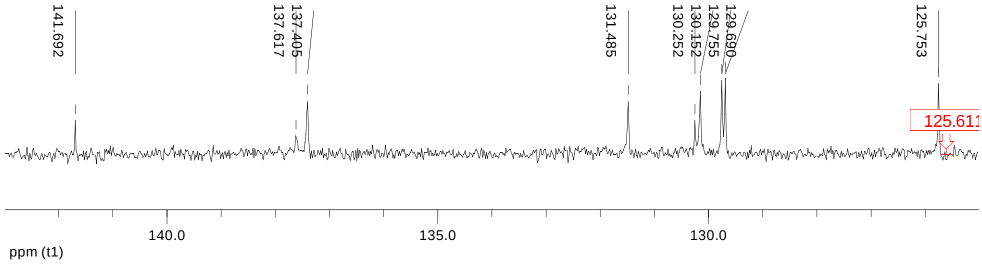
^{1}H NMR (400 MHz, $CDCl_3$)

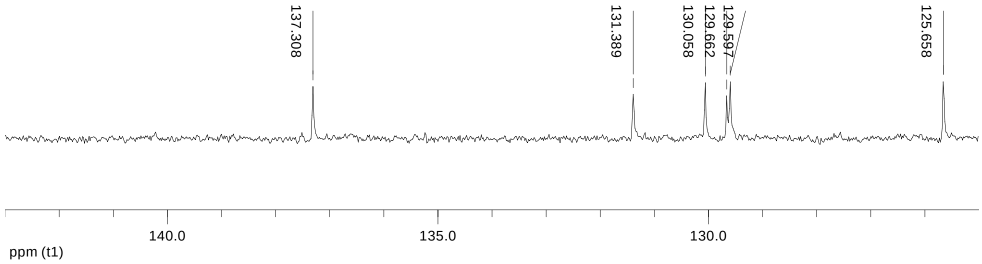


^{13}C NMR (100 MHz, $CDCl_3$)






141.692
137.617
137.405
131.485
130.252
130.152
129.755
129.690
125.753
125.611
140.0
135.0
130.0
ppm (t1)


137.308
131.389
130.058
129.662
129.597
125.658
140.0
135.0
130.0
ppm (t1)