Supplementary Materials for

# Ketyl Radical Reactivity via Atom Transfer Catalysis

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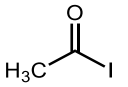
## Experimental section

**General Methods**. Unless noted, all commercial reagents were used as purchased without further purification, and all reactions were carried out under nitrogen. Silicycle F60 (230-400 mesh) silica gel or a CombiFlash® Automated Flash Chromatograph was used for flash column chromatography. Thin layer chromatography (TLC) analyses were performed using Merck silica gel 60 $F_{254}$ plates and visualized under UV or phosphomolybdic acid stain. $^{1}H$ and $^{13}C$ NMR spectra were recorded using a Bruker AVIII 400 or AVIII 600 MHz NMR spectrometer and are reported as chemical shifts (δ ppm), multiplicity (s = singlet, br = broad, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), relative integral. $^{1}H$ NMR spectra were referenced with respect to $CDCl_3$ (δ = 7.26 ppm) or DMSO-$d_6$ (δ = 2.54 ppm) as internal references and $^{13}C$ NMR spectra were referenced with respect to $CDCl_3$ (δ = 77.00 ppm) as an internal reference. High resolution mass spectra were obtained using Bruker MicrOTOF (ESI). IR spectra were recorded using a Thermo Fisher Nicolet iS10 FT-IR and are reported in terms of frequency of absorption ($cm^{-1}$).

### General procedure for the synthesis of acyl iodides:

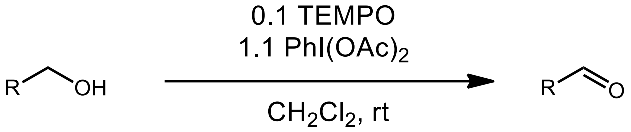
$$1.05\ \mathrm{NaI} + 1.0\ \mathrm{RCOCl} \xrightarrow[0\ ^{\circ}\mathrm{C}\text{-rt, 2 h}]{\text{neat}} \mathrm{RCOI}$$

To a round-bottom flask was added sodium iodide (1.05 equiv.) and the corresponding acyl chloride (1.0 equiv.) at 0 °C. Then the reaction was warmed up to room temperature and stirred further for 2 hours, after which the reaction mixture was filtered to remove sodium chloride. The crude product was purified by distillation and the pure product was stored in the freezer.

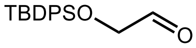


**Acetyl iodide.** Distillation at 140 °C under 1 atm afforded the title product in 51% yield as a yellow liquid. $^{1}H$ NMR ($CDCl_3$, 600 MHz): δ 2.97 (s, 3H); $^{13}C$ NMR ($CDCl_3$, 150 MHz): δ 47.24, 156.07. The spectroscopic data is in agreement with the National Institute of Advanced Industrial Science and Technology (AIST).

**General procedure for the synthesis of aldehydes 28-SM, 29-SM, 32-SM:** *(41)*

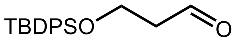


To a dry round-bottom flask, the respective alcohol (1.0 equiv.), $CH_2Cl_2$, and TEMPO (0.1 equiv.) were added and stirred until dissolution. To the stirring solution, iodobenzene diacetate (1.1 equiv.) was added and the reaction stirred at room temperature until the consumption of the starting alcohol (monitored by TLC). After completion, the reaction was diluted with $CH_2Cl_2$ and washed with saturated $Na_2S_2O_3$ solution, then saturated $NaHCO_3$ solution, and saturated brine solution. The combined organic extracts were dried over $Na_2SO_4$. Then the solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel.



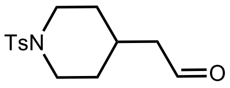
**28-SM**

**2-((*tert*-Butyldiphenylsilyl)oxy)acetaldehyde.** Column chromatography on silica gel (eluent: hexanes/ethyl actetate = 5.7:1) afforded the title product in 68% yield as a white solid. $^{1}H$ NMR ($CDCl_3$, 600 MHz): $\delta$ 1.12 (s, 9H), 4.23 (s, 2H), 7.39-7.42 (m, 4H), 7.44-7.47 (m, 2H), 7.67 (d, $J$ = 6.7 Hz, 4H), 9.73 (s, 1H); $^{13}C$ NMR ($CDCl_3$, 150 MHz): $\delta$ 19.40, 26.86, 70.15, 128.05, 130.19, 132.70, 135.65, 201.67. $R_f$ = 0.64 (25% ethyl acetate/75% hexanes). The spectroscopic data is in agreement with that previously reported. *(42)*



**29-SM**

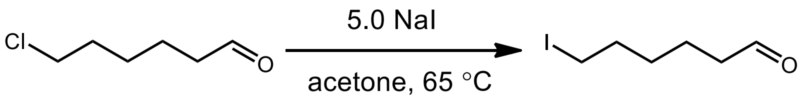
**3-((*tert*-Butyldiphenylsilyl)oxy)propanal.** Column chromatography on silica gel (eluent: hexanes/ethyl actetate = 5.7:1) afforded the title product in 40% yield as a white solid. $^{1}H$ NMR ($CDCl_3$, 600 MHz): $\delta$ 1.04 (s, 9H), 2.60 (td, $J$ = 9.0, 2.2 Hz, 2H), 4.02 (t, $J$ = 6.0 Hz, 2H), 7.38-7.41 (m, 4H), 7.43-7.45 (m, 2H), 7.66 (dm, $J$ = 6.5 Hz, 4H), 9.82 (t, $J$ = 2.2 Hz, 1H); $^{13}C$ NMR ($CDCl_3$, 150 MHz): $\delta$ 19.30, 26.92, 46.55, 58.48, 127.91, 129.95, 133.46, 135.70, 201.88. $R_f$ = 0.41 (10% ethyl acetate/90% hexanes). The spectroscopic data is in agreement with that previously reported. *(43)*



**32-SM**

**2-(1-Tosylpiperidin-4-yl)acetaldehyde.** Column chromatography on silica gel (eluent: hexanes/ethyl actetate = 1.5:1) afforded the title product in 84% yield as a white solid. $^1$H NMR (CDCl$_3$, 600 MHz): δ 1.36 (qd, *J* = 25.1, 12.2, 4.1 Hz, 2H), 1.75 (dm, *J* = 14.0 Hz, 2H), 1.78-1.85 (m, 1H), 2.25 (td, *J* = 18, 2.5 Hz, 2H), 2.37 (dd, *J* = 6.7, 1.4 Hz, 2H), 2.43 (s, 3H), 3.75 (d, *J* = 11.8 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 9.72 (t, *J* = 1.4 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ 21.63, 29.84, 31.42, 46.29, 49.99, 127.85, 129.74, 133.35, 143.63, 200.94. R$_f$ = 0.39 (50% ethyl acetate/50% hexanes). The spectroscopic data is in agreement with that previously reported. *(41)*

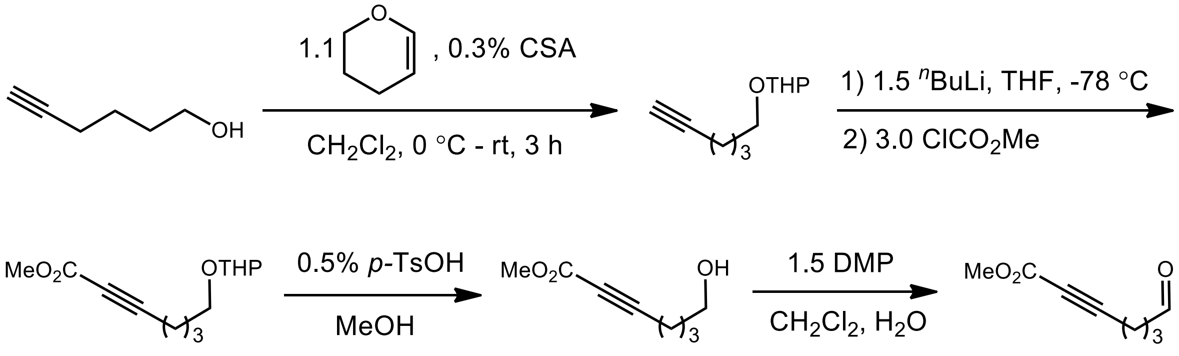
**Procedure for the synthesis of aldehyde 34-SM:**



**34-SM**

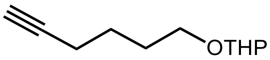
**6-Iodohexanal.** 6-Chlorohexanal (404 mg, 3 mmol) was added to a solution of NaI (2.25 g, 15 mmol) in acetone (10 mL) and the reaction was stirred at 50 °C for 10 h. Then the reaction mixture was diluted with Et$_2$O, washed with aqueous Na$_2$S$_2$O$_3$ solution and brine. The combined organic extracts were dried with Na$_2$SO$_4$ and concentrated to provide the pure iodide (532 mg, 78%) as a pale yellow oil. $^1$H NMR (CDCl$_3$, 400 MHz): δ 1.38-1.49 (m, 2H), 1.65 (m, 2H), 1.84 (m, 2H), 2.45 (dt, *J* = 1.56, 10.88 Hz, 2H), 3.19 (t, *J* = 6.90 Hz, 2H), 9.77 (t, *J* = 1.56 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ 6.52, 21.05, 30.06, 33.24, 43.73, 202.25. The spectroscopic data is in agreement with that previously reported. *(44)*

**Procedure for the synthesis of aldehyde 44:** *(45)*

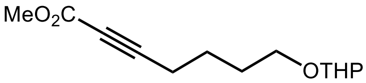


**44**

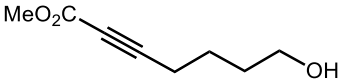
All the spectroscopic data are in agreement with that previously reported. *(45)*



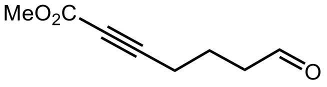
**1-Hex-5-ynyloxy-tetrahydro-pyran.** CSA (7 mg, 0.03 mmol) was added to a solution of hexynol (2.5 mL, 22.8 mmol) and 3,4-dihydro-2*H*-pyran (2.3 mL, 25 mmol) in DCM at 0 °C. The reaction was warmed to room temperature and stirred for 4 hours. Then the reaction was quenched with saturated aqueous $NaHCO_3$ and the aqueous layer was extracted with $CH_2Cl_2$. The combined organic extracts were dried over $Na_2SO_4$ and concentrated to provide the product as colorless oil quantitatively. $^1H$ NMR ($CDCl_3$, 400 MHz): δ 1.48-1.74 (m, 10H), 1.77-1.87 (m, 1H), 1.93 (t, $J$ = 2.56 Hz, 1 H), 2.21 (td, $J$ = 2.56, 6.91 Hz, 2H), 3.37-3.42 (m, 1H), 3.46-3.51 (m, 1H), 3.71-3.77 (m, 1H), 3.82 (m, 1 H), 4.56 (t, $J$ = 3.38 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 18.37, 19.73, 25.47, 25.61, 28.93, 30.85, 62.39, 67.01, 68.46, 84.49, 98.91.



**Methyl 7-((tetrahydro-2*H*-pyran-2-yl)oxy)hept-2-ynoate.** $^n$BuLi (24.4 mL, 34.2 mmol, 1.4 M in hexane) was added to a solution of alkyne (4.2 g, 22.8 mmol) in THF (20 mL) at 0 ºC over 30 min. After stirring 2 hours, the mixture was syringed into a solution of methyl chloroformate (5.29 mL, 68.4 mmol) in THF (5 mL) over 30 minutes, while maintaining a temperature between -25 and -35 ºC. The reaction was stirred for 30 minutes at -35 °C. The cooling bath was then removed and the reaction was stirred for an additional 1 h at room temperature. The reaction was careful quenched with aqueous $NH_4Cl$ and extracted with $Et_2O$. The combined organic extracts were dried over $Na_2SO_4$ and concentrated. The crude product was purified by column chromatography (eluent: hexanes/ethyl acetate = 95:5) to yield the pure product as a colorless oil (5.06 g, 92%). $^1H$ NMR ($CDCl_3$, 400 MHz): δ 1.53-1.63 (m, 5H), 1.69-1.77 (m, 5H), 1.80-1.87 (m, 1H), 2.39-2.44 (m, 2H), 3.40-3.46 (m, 1H), 3.50- 3.55 (m, 1H), 3.76-3.82 (m, 1H), 3.78 (s, 3H), 3.85-3.90 (m, 1H), 4.58-4.60 (m, 1H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 18.66, 19.76, 24.67, 25.60, 28.99, 30.85, 52.69, 62.49, 66.82, 73.17, 89.70, 99.02, 154.38.



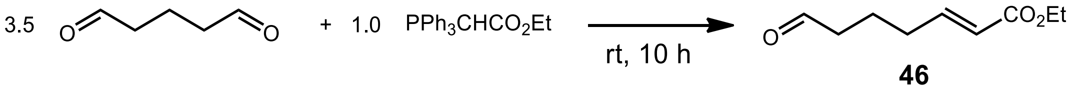
**Methyl 7-hydroxyhept-2-ynoate.** The THP-protected alkyne (5.06 g, 21.05 mmol) and *p*-TsOH (21mg, 0.11 mmol) were stirred in MeOH at room temperature for 15 hours. The reaction was quenched with saturated aqueous $NaHCO_3$ and methanol was removed under reduced pressure. The product was extracted with $Et_2O$ and $CH_2Cl_2$. The combined organic layers were washed with brine, dried over $Na_2SO_4$ and concentrated. The crude product was purified by column chromatography (eluent: hexanes/ethyl acetate = 70:30) to provide the desired alcohol (711 mg, 21%). $^1$H NMR ($CDCl_3$, 400 MHz): δ 1.39 (br, 1.39, 1H), 1.67-1.70 (m, 4H), 2.37-2.41 (m, 2H), 3.68 (br, 2H), 3.75 (s, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 18.59, 24.03, 31.76, 52.71, 62.26, 73.29, 89.50, 154.35.



**44**

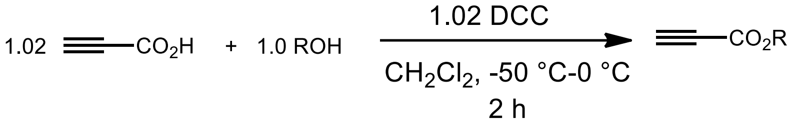
**Methyl 7-oxohept-2-ynoate**. DMP (2.05 g, 5 mmol) was added to a solution of alcohol (503 mg, 3.22 mmol) in $CH_2Cl_2$ (30 mL). The mixture of $CH_2Cl_2$ (30 mL) and $H_2O$ (0.13 mL) was added via addition funnel (~1 drop/sec). The reaction was stirred for 30 minutes. The reaction was then diluted with $Et_2O$ (50 mL) and concentrated. The obtained slurry was filtered, washed with $Et_2O$ (30 mL) and then concentrated. Column chromatography (eluent: hexanes/ethyl acetate = 95:5 to 90:10) afforded the title product (282 mg, 40%) as a pale yellow oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ 1.89 (m, 2H), 2.41 (t, $J$ = 6.90 Hz, 2H), 2.61 (t, $J$ = 6.90 Hz, 2H), 3.75 (s, 3H), 9.78 (s, 1H); $^{13}$C NMR ($CDCl_3$, 150 MHz): δ 18.05, 20.02, 42.43, 52.73, 73.80, 88.21, 154.12, 201.06.

**Procedure for the synthesis of aldehyde 46:** *(46)*

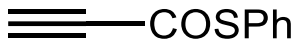


**(*E*)-Ethyl 7-oxohept-2-enoate.** According to the known procedure, to a solution of glutaraldehyde (3.5 g, 35 mmol) in $CH_2Cl_2$ (15 mL) was added a solution of (carbethoxymethylene)triphenylphosphorane (3.48 g, 10 mmol) in $CH_2Cl_2$ (20 mL) via syringe pump (2 mL/h) at room temperature. Then the solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate = 50:1 to 20:1 to 10:1) to afford the title product in 59% yield as a colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ 1.29 (t, $J$ = 7.2 Hz, 3H), 1.77-1.85 (m, 2 H), 2.25 (dq, $J$ = 7.2, 1.6 Hz, 2H), 2.48 (dt, $J$ = 7.2, 1.6 Hz, 2H), 4.19 (q, $J$ = 6.8 Hz, 2H), 5.84 (dt, $J$ = 15.6, 1.6 Hz, 1H), 6.91 (dt, $J$ = 15.6, 7.2 Hz, 1H), 9.78 (t, $J$ = 1.6 Hz, 1H). The spectroscopic data is in agreement with that previously reported. *(46)*

**General procedure for the synthesis of alkynes 17-SM, 19-SM, 21-SM, 22-SM, 38-SM, 41-SM, 42-SM, 43-SM:** *(47)*

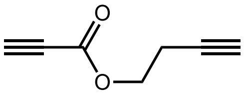


To the solution of alcohol (1.0 equiv.) in $CH_2Cl_2$ was added propiolic acid (1.02 equiv.) and DCC (1.02 equiv.) at -50 °C. The reaction was warmed up to 0 °C and stirred at 0 °C for 2 hours and then the reaction mixture was filtered. Then the solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel.



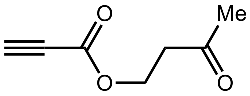
**17-SM**

**S-Phenyl prop-2-ynethioate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 50:1) afforded the title product in 86% yield as a pale yellow oil. $^1H$ NMR ($CDCl_3$, 400 MHz): δ 3.40 (s, 1H), 7.45-7.47 (m, 5H); $^{13}C$ NMR ($CDCl_3$, 150 MHz): δ 78.82, 81.09, 126.06, 129.45, 130.23, 134.54, 174.91. $R_f$ = 0.5 (10% ethyl acetate/90% hexanes). The spectroscopic data is in agreement with that previously reported. *(48)*



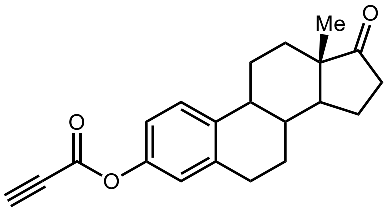
**19-SM**

**But-3-yn-1-yl propiolate.** Extra 5% DMAP was used as a catalyst. Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 50:1) afforded the title product in 34% yield as a pale yellow oil. $^1H$ NMR ($CDCl_3$, 400 MHz): δ 2.03 (t, $J$ = 2.8 Hz, 1H), 2.59 (dt, $J$ = 6.8, 2.8 Hz, 2H), 2.91 (s, 1H), 4.31 (t, $J$ = 6.8 Hz, 2H). $R_f$ = 0.5 (10% ethyl acetate/90% hexanes). The spectroscopic data is in agreement with that previously reported. *(49)*



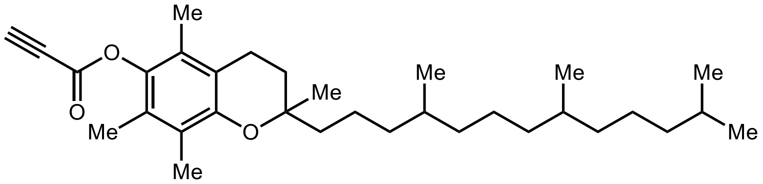
**21-SM**

**3-Oxobutyl propiolate**. Extra 10% DMAP was used as a catalyst. Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 7:1-4:1) afforded the title product in 54% yield as a pale yellow oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ 2.20 (s, 3H), 2.82 (t, *J* = 6.4 Hz, 2H), 2.88 (s, 1H), 4.45 (t, *J* = 6.4 Hz, 2H). $R_f$ = 0.4 (20% ethyl acetate/80% hexanes). The spectroscopic data is in agreement with that previously reported. *(50)*



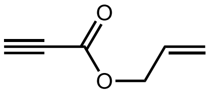
**22-SM**

**(*13S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl propiolate.** Extra 3% DMAP was used as a catalyst. Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 10:1-8:1) afforded the title product in 31% yield as a light yellow solid. $^1$H NMR ($CDCl_3$, 400 MHz): δ 0.91 (s, 3H), 1.40-1.68 (m, 6H), 1.95-2.19 (m, 4H), 2.26-2.32 (m, 1 H), 2.38-2.43 (m, 1H), 2.51 (dd, *J* = 18.4, 8.4 Hz, 1H), 2.92 (dd, *J* = 8.4, 4.0 Hz, 1H), 3.06 (s, 1H), 6.87 (d, *J* = 2.8 Hz, 1H), 6.91 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 13.78, 21.55, 25.69, 26.23, 29.34, 31.50, 35.80, 37.90, 44.11, 47.88, 50.39, 74.32, 76.59, 118.33, 121.16, 126.56, 138.22, 138.31, 147.65, 151.22, 220.64. IR (film): 3202, 2930, 2861, 2109, 1726, 1489, 1192, 1179, 908, 738 cm$^{-1}$; HRMS (ESI) for $C_{21}H_{22}O_3Na$ $[M+Na]^+$: calcd 345.1467, found 345.1451. $R_f$ = 0.42 (20% ethyl acetate/80% hexanes).



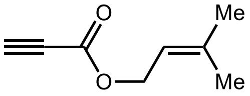
**38-SM**

**2,5,7,8-Tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl propiolate.** Extra 2% DMAP was used as a catalyst. Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 100:1-50:1) afforded the title product in 50% yield as a colorless oil. $^1$H NMR (CDCl$_3$, 600 MHz): δ 0.84-0.87 (m, 12H), 1.04-1.15 (m, 6H), 1.21-1.47 (m, 15H), 1.49-1.59 (m, 3H), 1.73-1.84 (m, 2H), 2.01 (s, 3H), 2.05 (s, 3H), 2.09 (s, 3H), 2.59 (t, $J$ = 6.6 Hz, 2H), 3.04 (s, 1H); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ 11.80, 12.06, 12.90, 19.59, 19.62, 19.65, 19.68, 19.74, 20.58, 21.02, 22.61, 22.69, 23.90 (br), 24.44, 24.80, 27.97, 31.00, 31.04, 32.69, 32.72, 32.78, 32.80, 37.31, 37.35, 37.37, 37.41, 37.42, 37.46, 37.47, 37.54, 37.57, 39.39, 40.12 (br), 74.48, 75.24, 76.06, 117.60, 123.33, 124.80, 126.51, 139.84, 149.95, 151.44. IR (film): 2925, 2867, 2123, 1730, 1460, 1194, 1108, 1066, 905 cm$^{-1}$; HRMS (ESI) for $C_{32}H_{50}O_3Na$ [M+Na]$^+$: calcd 505.3658, found 505.3638. R$_f$ = 0.7 (10% ethyl acetate/90% hexanes).



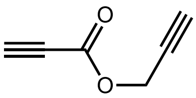
**41-SM**

**Allyl propiolate.** Extra 8% DMAP was used as a catalyst. Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 50:1) afforded the title product in 54% yield as a pale yellow oil. $^1$H NMR (CDCl$_3$, 400 MHz): δ 2.89 (s, 3H), 4.67-4.69 (m, 2H), 5.27-5.31 (m, 1H), 5.34-5.40 (m, 1H), 5.87-5.97 (m, 1H). R$_f$ = 0.5 (10% ethyl acetate/90% hexanes). The spectroscopic data is in agreement with that previously reported. *(51)*



**42-SM**

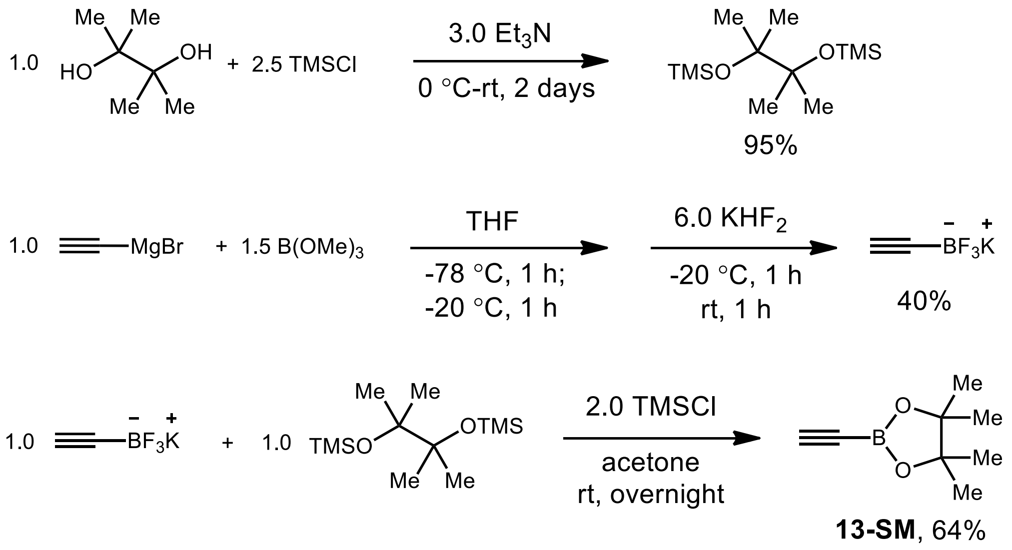
**3-Methylbut-2-en-1-yl propiolate.** Extra 10% DMAP was used as a catalyst. Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 50:1) afforded the title product in 58% yield as a pale yellow oil. $^1$H NMR (CDCl$_3$, 400 MHz): δ 1.72 (s, 3H), 1.77 (s, 3H), 2.85 (s, 3H), 4.69 (d, $J$ = 7.2 Hz, 2H), 5.34-5.40 (m, 1H). R$_f$ = 0.5 (10% ethyl acetate/90% hexanes).



**43-SM**

**Prop-2-yn-1-yl propiolate.** Extra 0.2% DMAP was used as a catalyst. Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 50:1) afforded the title product in 11% yield as a pale yellow oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ 2.54 (t, *J* = 6.4 Hz, 1H), 2.94 (s, 1H), 4.78 (d, *J* = 2.4 Hz, 2H). $R_f$ = 0.5 (10% ethyl acetate/90% hexanes). The spectroscopic data is in agreement with that previously reported. *(52)*

**Procedure for the synthesis of alkyne 13-SM:**

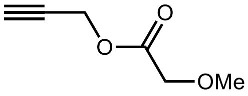


**2,2,4,4,5,5,7,7-Octamethyl-3,6-dioxa-2,7-disilaoctane.** According to the known procedure, TMSCl (6.35 mL, 50.0 mmol) was added dropwise to a stirred solution of pinacol (2.36 g, 20.0 mmol) and $Et_3N$ (8.36 mL, 60.0 mmol) in DCM (40 mL) at 0 °C and the resultant mixture was stirred at room temperature for 48 h. The mixture was then cooled to 0 ºC and water was added. The organic layer was separated, dried over $Na_2SO_4$. Then the solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel (eluent: hexanes) to afford the title product in 95% yield as a colorless oil. $^1$H NMR ($CDCl_3$, 600 MHz): δ 0.09 (s, 18H), 1.19 (s, 12H). The spectroscopic data is in agreement with that previously reported. *(53)*

**Potassium ethynyltrifluoroborate.** According to the known procedure, in a 200 mL of 2-neck flask, to the ethynyl Grignard reagent (40 mmol, 0.5 M in THF, 80 mL), was added $B(OMe)_3$ (6.68 mL, 60 mmol) at -78 °C. The mixture was stirred at -78 °C for 1 h and then stirred at -20 °C for 1 h. To the reaction mixture was added $KHF_2$ (19 g, 240 mmol) in distilled water (20 mL) at -20 °C. The aqueous mixture was stirred at this temperature for 1 h and then at room temperature for 1 h. The obtained reaction mixture was concentrated and dried under vacuum for 4 h. The crude product was dissolved in hot acetone and the residue was removed by filtration. The filtrate was concentrated to afford the title product (2.1 g, 40%) as an off-white solid. $^{1}$H NMR (DMSO-$d_6$, 600 MHz): δ 1.91 (s, 1H); $^{19}$F NMR (DMSO-$d_6$, 565 MHz): δ -132.34 (q). The spectroscopic data is in agreement with that previously reported. *(54)*

**2-Ethynyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.** According to the known procedure, to a solution of the potassium ethynyltrifluoroborate (2.3 g, 17.4 mmol) and 2,3-dimethyl-2,3- butanediol bis(trimethylsilyl) ether (4.57 mL, 17.4 mmol) in dry acetone (50 mL) was added TMSCl (4.42 mL, 34.8 mmol) at room temperature. The mixture was stirred overnight. The precipitates were removed by filtration. The filtrate was concentrated in vacuo. Then the crude oil was purified by distillation to afford the desired alkyne as a colorless oil (b.p. = 75 °C /20 mmHg, 1.7g, 64% yield). $^{1}$H NMR (CDCl$_3$, 400 MHz): 1.28 (s, 12H), 2.48 (s, 1H); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ 24.59, 57.23, 84.53, 90.13. The spectroscopic data is in agreement with that previously reported. *(55)*

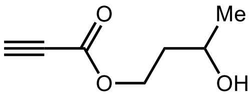
**Procedure for the synthesis of alkyne 18-SM:** *(56)*



**18-SM**

**Prop-2-yn-1-yl 2-methoxyacetate.** According to the known procedure, neutral Al$_2$O$_3$ (1.53 g, 15 mmol) was added to propargylic alcohol (0.58 mL, 10 mmol, stirring not required) and then mixed with methoxyacetyl chloride (1.83 mL, 20 mmol) in one portion. The resultant dispersion was stoppered tightly and kept aside unstirred at 25 °C for 4h. Then the dispersion was taken with EtOAc (3 mL) and filtered. The solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate = 30:1-20:1) to afford the title product in 70% yield as a colorless oil. $^{1}$H NMR (CDCl$_3$, 400 MHz): δ 2.49 (t, $J$ = 2.8 Hz, 1H), 3.44 (s, 3H), 4.07 (s, 2H), 4.75 (d, $J$ = 2.4 Hz, 2H ); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 52.12, 59.38, 69.55, 75.27, 77.07, 169.41. R$_f$ = 0.3 (10% ethyl acetate/90% hexanes). The spectroscopic data is in agreement with that previously reported. *(57)*

**Procedure for the synthesis of alkyne 20-SM:** *(58)*

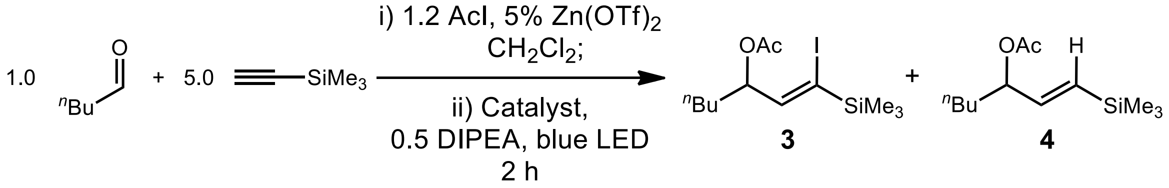


**20-SM**

**3-Hydroxybutyl propiolate.** According to the known procedure, to a suspended solution of sodium cyanoborohydride (628 mg, 10.0 mmol) and zinc chloride (680 mg, 5.0 mmol) in diethyl ether (30 mL) at 0 ºC was added 3-oxobutyl propiolate (1.4 g, 10.0 mmol). The reaction mixture was stirred at room temperature for 4 h, diluted with diethyl ether (3 mL), and quenched with water. The aqueous layer was extracted with diethyl ether and the combined ether extracts were dried over $Na_2SO_4$. Then the solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate = 7:1-4:1) to afford the title product in 60% yield as a colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ 1.22 (d, $J$ = 6.0 Hz, 3H), 1.70-1.87 (m, 2 H), 1.90 (br, 1H), 2.90 (s, 1H), 3.92 (br, 1H), 4.25-4.30 (m, 1H), 4.36-4.42 (m, 1H); $^{13}$C NMR ($CDCl_3$, 150 MHz): δ 23.62, 37.46, 63.54, 64.63, 74.54, 74.88, 152.83. IR (film): 3261, 2969, 2935, 2117, 1702, 1378, 1238, 1137, 1035, 754 cm$^{-1}$; HRMS (ESI) for $C_7H_{10}IO_3Na$ $[M+Na]^+$: calcd 165.0528, found 165.0493. $R_f$ = 0.38 (20% ethyl acetate/80% hexanes).

**Table S1:** Reaction optimization

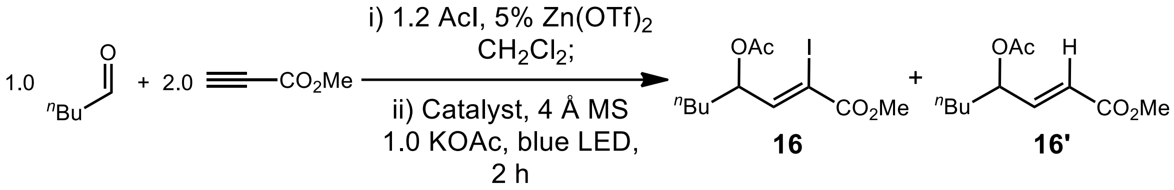
**(Procedure A)**



| entry | catalyst | Yield (3:4) | *Z*:*E* (3) |
|---|---|---|---|
| 1 | 10% $[CpFe(CO)_2]_2$ | 20%, >20:1 | 2:1 |
| 2* | 1% $Ru(bpy)_3Cl_2$ | 31%, >20:1 | 3:1 |
| 3* | 1% $Ir(ppy)_2(dttbbpy)PF_6$ | 60%, >20:1 | >20:1 |
| **4** | **10% $Mn_2(CO)_{10}$** | **78%, >20:1** | **>20:1** |

* 3.0 DIPEA was used, and the reaction was run for 24 h.

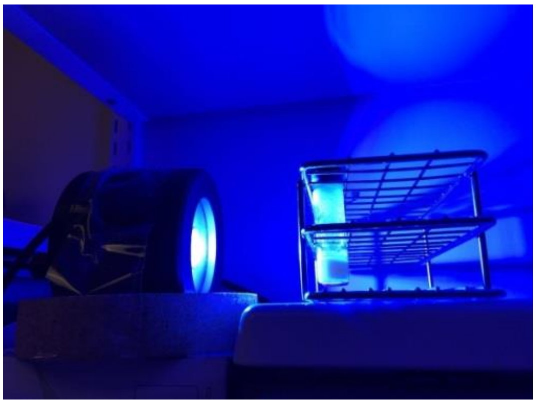
**(Procedure B)**



| entry | catalyst | Yield (16:16') | *Z*:*E* (16) |
|---|---|---|---|
| 1* | 1% $Ru(bpy)_3Cl_2$ | 28%, 6:1 | 1:1 |
| 2* | 1% $Ir(ppy)_3$ | 32%, 4:1 | 3:1 |
| 3 | 20% $[CpFe(CO)_2]_2$ | 60%, >20:1 | 1:1 |
| **4** | **20% $Mn_2(CO)_{10}$** | **65%, 14:1** | **14:1** |

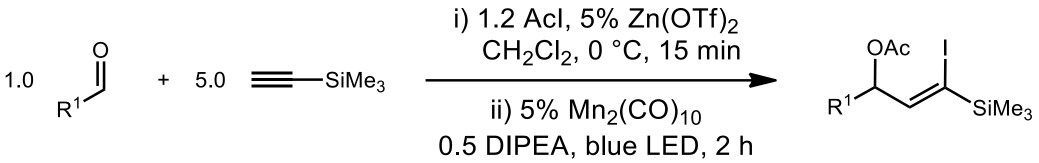
* 1.0 DIPEA was used, and the reaction was run for 24 h without 4Å MS.

**Fig. S1:** Light set-up



## General procedure for the synthesis of vinyl iodides.

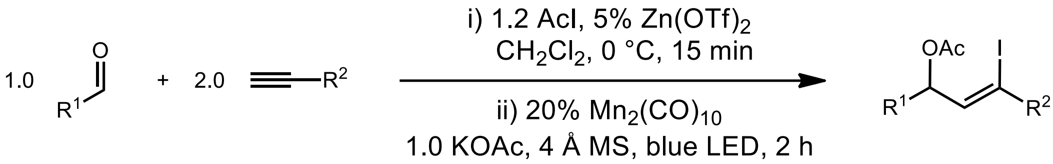
### Procedure A (When triethylsilyl acetylene or trimethylsilyl acetylene was used):



To an 8 mL vial was added DCM (0.5 mL), AcI (0.6 mmol), $Zn(OTf)_2$ (0.025 mmol) and aldehyde (0.5 mmol) consecutively at 0 ºC. The mixture was stirred at the same temperature for 15 min. To this mixture was added DIPEA (0.25 mmol) at 0 ºC, then the mixture was stirred for another 15 min. After that triethylsilyl acetylene (2.5 mmol) and $Mn_2(CO)_{10}$ (0.025 mmol) were added to the mixture. The reaction mixture was degassed by chill-pump-thaw for 20 min, then irradiated with one 90 W blue LED lamp (Kessil A360WE tuna blue) or two 45 W blue LED lamps (Kessil A160WE tuna blue) at approximately 5 cm away from the light source. The reaction temperature was around 40 ºC. After 2 h, the solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel. *Z:E* ratios were determined using purified products via $^1$H NMR.

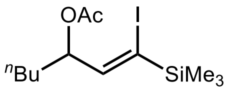
***Note**: 1) The quality of AcI is crucial for the reaction since HI generated from impure AcI would destroy $Mn_2(CO)_{10}$ to yield poor yield and selectivity. 2) $Zn(OTf)_2$ was used to eliminate side product (<10%) formation in α-acetoxy iodide generation. 3) The concentration of the reaction is crucial for the selectivity as lower concentration affords poor selectivity. 4) Peak absorbance of the light: 458 nm.

### Procedure B (When other alkynes were used):



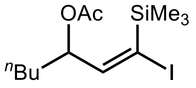
To an 8 mL vial was added DCM (1.0 mL), AcI (0.6 mmol), $Zn(OTf)_2$ (0.025 mmol) and aldehyde (0.5 mmol) consecutively at 0 ºC. The mixture was stirred at the same temperature for 15 min. To this mixture was added 4Å MS (25 mg) and KOAc (0.5 mmol) at 0 ºC, then the mixture was stirred for another 15 min. After that alkyne (1.0 mmol) and $Mn_2(CO)_{10}$ (0.1 mmol) were added to the mixture. The reaction mixture was degassed by chill-pump-thaw for 20 min, then irradiated with one 90 W blue LED lamp (Kessil A360WE tuna blue) or two 45 W blue LED lamps (Kessil A160WE tuna blue) at approximately 5 cm away from the light source. The reaction temperature was around 40 ºC. After 2 h, the solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel. *Z:E* ratios were determined using purified products via $^{1}$H NMR.

***Note**: 1) The quality of AcI is crucial for the reaction since HI generated from impure AcI would destroy $Mn_2(CO)_{10}$ to yield poor yield and selectivity. 2) $Zn(OTf)_2$ was used to eliminate side product (<10%) formation in α-acetoxy iodide generation. 3) The concentration of the reaction is crucial for the selectivity as lower concentration affords poor selectivity. 4) Peak absorbance of the light: 458 nm.



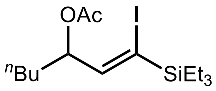
**(*Z*)-3**

**(*Z*)-1-Iodo-1-(trimethylsilyl)hept-1-en-3-yl acetate.** 10% $Mn_2(CO)_{10}$ catalyst was used. Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 100:1) afforded the title product in 78% yield as a colorless oil. *Z:E* ratio: >20:1. $^{1}$H NMR ($CDCl_3$, 600 MHz): δ 0.18 (s, 9H), 0.90 (t, *J* = 7.2 Hz, 3H), 1.31-1.37 (m, 4H), 1.60-1.69 (m, 2H), 2.06 (s, 3H), 5.46-5.50 (m, 1H), 6.16 (d, *J* = 7.2 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 150 MHz): δ -1.58, 13.92, 21.13, 22.50, 26.95, 32.88, 79.72, 113.52, 145.52, 170.05. IR (film): 2956, 2861, 1738, 1369, 1227, 1018, 839 cm$^{-1}$; HRMS (ESI) for $C_{12}H_{23}IO_2SiNa$ $[M+Na]^+$: calcd 377.0410, found 377.0393. $R_f$ = 0.35 (5% ethyl acetate/95% hexanes).



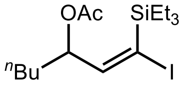
**(*E*)-3**

**(*E*)-1-Iodo-1-(trimethylsilyl)hept-1-en-3-yl acetate.** $^{1}$H NMR ($CDCl_3$, 600 MHz): δ 0.32 (s, 9H), 0.90 (t, *J* = 7.2 Hz, 3H), 1.23-1.36 (m, 4H), 1.46-1.52 (m, 1H), 1.62-1.68 (m, 1H), 2.04 (s, 3H), 5.32-5.35 (m, 1H), 7.01 (d, *J* = 9.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 150 MHz): δ 0.89, 13.89, 21.13, 22.48, 27.08, 34.09, 74.40, 113.46, 153.09, 170.10. IR (film): 2957, 2932, 2861, 1739, 1370, 1231, 1018, 843 cm$^{-1}$; HRMS (ESI) for $C_{12}H_{23}IO_2SiNa$ $[M+Na]^+$: calcd 377.0410, found 377.0394. $R_f$ = 0.38 (5% ethyl acetate/95% hexanes).



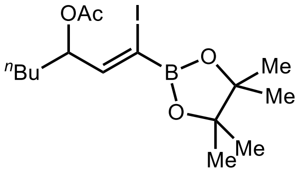
**(*Z*)-12**

**(*Z*)-1-Iodo-1-(triethylsilyl)hept-1-en-3-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 100:1) afforded the title product in 78% yield as a colorless oil. *Z:E* ratio: >20:1. $^{1}$H NMR ($CDCl_3$, 600 MHz): δ 0.69 (q, *J* = 8.4 Hz, 6H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.8 Hz, 9H), 1.30-1.37 (m, 4H), 1.59-1.71 (m, 2H), 2.04 (s, 3H), 5.46-5.50 (m, 1H), 6.16 (d, *J* = 6.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 150 MHz): δ 2.89, 6.99, 13.91, 21.08, 22.51, 26.91, 32.85, 79.90, 110.00, 147.24, 169.95. IR (film): 2954, 2873, 1740, 1368, 1227, 1004, 965, 824 cm$^{-1}$; HRMS (ESI) for $C_{15}H_{29}IO_2SiNa$ $[M+Na]^+$: calcd 419.0879, found 419.0857. $R_f$ = 0.35 (5% ethyl acetate/95% hexanes).



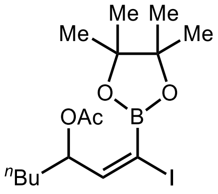
**(*E*)-12**

**(*E*)-1-Iodo-1-(triethylsilyl)hept-1-en-3-yl acetate.** $^{1}$H NMR ($CDCl_3$, 400 MHz): δ 0.76-0.93 (m, 9H), 0.98 (t, *J* = 8.0 Hz, 9H), 1.23-1.36 (m, 4H), 1.44-1.53 (m, 1H), 1.61-1.70 (m, 1H), 2.03 (s, 3H), 5.22-5.28 (m, 1H), 7.16 (d, *J* = 10.0 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 4.63, 7.29, 13.90, 21.11, 22.53, 27.13, 34.50, 74.70, 111.46, 155.16, 170.03. IR (film): 2955, 2933, 2874, 1740, 1369, 1230, 1017, 1002 cm$^{-1}$; HRMS (ESI) for $C_{15}H_{29}IO_2SiNa$ $[M+Na]^+$: calcd 419.0879, found 419.0865. $R_f$ = 0.38 (5% ethyl acetate/95% hexanes).



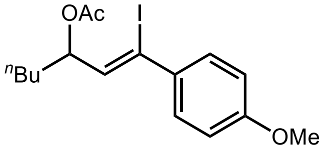
**(*Z*)-13**

**(*Z*)-1-Iodo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-1-en-3-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 30:1-20:1-8:1) afforded the title product and the isomer in 52% yield as a colorless oil. *Z:E* ratio: 6:1. $^{1}$H NMR ($CDCl_3$, 600 MHz): δ 0.90 (t, *J* = 6.6 Hz, 3H), 1.24-1.35 (m, 16H), 1.64-1.68 (m, 2H), 2.05 (s, 3H), 5.44-5.48 (m, 1H), 6.79 (d, *J* = 7.2 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 13.91, 21.04, 22.48, 24.72, 24.75, 26.97, 32.41, 78.92, 85.00, 152.39, 170.20. IR (film): 2955, 2928, 1738, 1371, 1326, 1230, 1141, 1019, 849 cm$^{-1}$; HRMS (ESI) for $C_{15}H_{26}IO_4BNa$ $[M+Na]^+$: calcd 431.0867, found 431.0675. $R_f$ = 0.1 (9% ethyl acetate/91% hexanes).



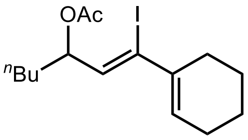
**(*E*)-13**

**(*E*)-1-Iodo-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-1-en-3-yl acetate.** $^1$H NMR ($CDCl_3$, 600 MHz): δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.22-1.35 (m, 16H), 1.51-1.68 (m, 2H), 2.02 (s, 3H), 5.61-5.65 (m, 1H), 6.96 (d, *J* = 9.0 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 150 MHz): δ 13.88, 21.13, 22.26, 24.58, 24.73, 26.91, 33.74, 74.82, 85.00, 155.37, 169.96. IR (film): 2931, 2858, 1738, 1371, 1323, 1230, 1141, 1017, 967, 847 cm$^{-1}$; HRMS (ESI) for $C_{15}H_{26}IO_4BNa$ $[M+Na]^+$: calcd 431.0867, found 431.0692. $R_f$ = 0.30 (9% ethyl acetate/91% hexanes).



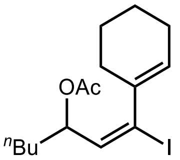
**(*Z*)-14**

**(*Z*)-1-Iodo-1-(4-methoxyphenyl)hept-1-en-3-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 30:1) afforded the title product and the isomer in 56% yield as a colorless oil. *Z:E* ratio: 7:1. $^1$H NMR ($CDCl_3$, 600 MHz): δ *Z* isomer (major): 0.92 (t, *J* = 7.2 Hz, 3H), 1.35-1.41 (m, 4H), 1.67-1.79 (m, 2H), 2.07 (s, 3H), 3.82 (s, 3H), 5.51-5.54 (m, 1H), 5.87 (d, *J* = 7.8 Hz, 1H), 6.81-6.84 (m, 2H), 7.40-7.42 (m, 2H); *E* isomer (minor): 0.84 (t, *J* = 7.2 Hz, 3H), 1.19-1.23 (m, 4H), 1.47-1.63 (m, 2H), 2.01 (s, 3H), 3.81 (s, 3H), 5.10-5.14 (m, 1H), 6.35 (d, *J* = 9.0 Hz, 1H), 6.84-6.85 (m, 2H), 7.26-7.27 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ *Z* isomer (major): 13.93, 21.11, 22.56, 27.03, 33.58, 55.37, 79.37, 106.01, 113.50, 129.79, 135.05, 135.33, 160.04, 170.09; *E* isomer (minor): 13.80, 21.05, 22.31, 26.90, 33.96, 55.26, 72.78, 100.45, 113.61, 129.58, 133.94, 140.77, 159.54, 169.85. IR (film): 2952, 2858, 1734, 1603, 1506, 1369, 1230, 1176, 1030, 961, 826 cm$^{-1}$; HRMS (ESI) for $C_{16}H_{21}IO_3Na$ $[M+Na]^+$: calcd 411.0433, found 411.0414. $R_f$ = 0.25 (9% ethyl acetate/91% hexanes).



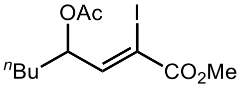
**(*Z*)-15**

**(*Z*)-1-(Cyclohex-1-en-1-yl)-1-iodohept-1-en-3-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 100:1) afforded the title product and the isomer in 50% yield as a colorless oil. *Z:E* ratio: 2.2:1. $^1$H NMR (CDCl$_3$, 600 MHz): δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.31-1.36 (m, 4H), 1.55-1.59 (m, 3H), 1.63-1.69 (m, 3H), 2.05 (s, 3H), 2.15-2.16 (m, 2H), 2.24-2.33 (m, 2H), 5.55-5.58 (m, 1H), 5.75 (d, *J* = 7.2 Hz, 1H), 6.18 (d, *J* = 4.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 13.95, 21.17, 22.15, 22.56, 22.84, 26.13, 27.02, 27.76, 33.66, 79.54, 112.75, 132.04, 134.07, 136.78, 170.15. IR (film): 2928, 2861, 1736, 1369, 1228, 1017, 957, 957, 799 cm$^{-1}$; HRMS (ESI) for $C_{15}H_{23}IO_2Na$ [M+Na]$^+$: calcd 385.0640, found 385.0645. R$_f$ = 0.35 (5% ethyl acetate/95% hexanes).



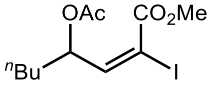
**(*E*)-15**

**(*E*)-1-(Cyclohex-1-en-1-yl)-1-iodohept-1-en-3-yl acetate.** $^1$H NMR (CDCl$_3$, 600 MHz): δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.23-1.34 (m, 4H), 1.46-1.52 (m, 1H), 1.56-1.64 (m, 3H), 1.65-1.73 (m, 2H), 2.00-2.04 (m, 2H), 2.01 (s, 3H), 2.14-2.18 (m, 2H), 5.36-5.40 (m, 1H), 5.73-5.75 (m, 1H), 6.03 (d, *J* = 9.6 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 13.85, 21.16, 21.74, 22.21, 22.36, 25.22, 27.11, 27.86, 34.13, 72.33, 107.77, 127.18, 138.59, 138.79, 169.90. IR (film): 2929, 2834, 1738, 1435, 1368, 1228, 1015, 957, 922, 725 cm$^{-1}$; HRMS (ESI) for $C_{15}H_{23}IO_2Na$ [M+Na]$^+$: calcd 385.0640, found 385.0618. R$_f$ = 0.40 (5% ethyl acetate/95% hexanes).



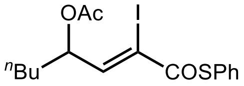
**(*Z*)-16**

**(*Z*)-Methyl 4-acetoxy-2-iodooct-2-enoate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 30:1) afforded the title product and the isomer in 65% yield as a colorless oil. *Z:E* ratio: 14:1. $^1$H NMR (CDCl$_3$, 600 MHz): δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.31-1.39 (m, 4H), 1.63-1.75 (m, 2H), 2.06 (s, 3H), 3.82 (s, 3H), 5.38-5.42 (m, 1H), 7.16 (d, $J$ = 7.2 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 13.84, 20.88, 22.41, 26.87, 32.27, 53.71, 77.64, 93.78, 150.48, 162.93, 170.19. IR (film): 2954, 2861, 1726, 1618, 1433, 1225, 1020, 893, 745 cm$^{-1}$; HRMS (ESI) for $C_{11}H_{17}IO_4Na$ $[M+Na]^+$: calcd 363.0069, found 363.0047. $R_f$ = 0.25 (9% ethyl acetate/91% hexanes).



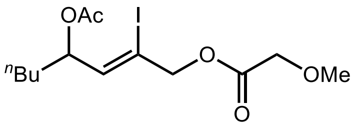
**(*E*)-16**

**(*E*)-Methyl 4-acetoxy-2-iodooct-2-enoate.** $^1$H NMR ($CDCl_3$, 400 MHz): δ 0.88 (t, $J$ = 7.6 Hz, 3H), 1.27-1.36 (m, 4H), 1.58-1.70 (m, 2 H), 2.02 (s, 3H), 3.80 (s, 3H), 5.78-5.84 (m, 1H), 6.72 (d, $J$ = 8.4 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 13.83, 20.91, 22.30, 26.96, 33.16, 53.28, 73.19, 86.41, 153.30, 163.54, 170.11. IR (film): 2954, 2860, 1716, 1608, 1433, 1221, 1143, 882, 783 cm$^{-1}$; HRMS (ESI) for $C_{11}H_{17}IO_4Na$ $[M+Na]^+$: calcd 363.0069, found 363.0032. $R_f$ = 0.3 (9% ethyl acetate/91% hexanes).



**17**

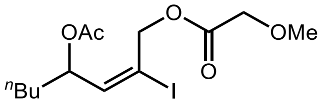
**(*Z*)-2-Iodo-1-oxo-1-(phenylthio)oct-2-en-4-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 50:1 to 30:1) afforded the title product in 57% yield as a colorless oil. *Z:E* ratio: >20:1. $^1$H NMR ($CDCl_3$, 600 MHz): δ 0.93 (t, $J$ = 7.2 Hz, 3H), 1.34-1.43 (m, 4H), 1.69-1.81 (m, 2H), 2.10 (s, 3H), 5.49-5.52 (m, 1H), 7.20 (d, $J$ = 7.2 Hz, 1H), 7.41-7.46 (m, 5H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 13.83, 20.87, 22.42, 26.92, 32.43, 77.58, 102.48, 127.81, 129.30, 129.82, 134.73, 147.87, 170.11, 186.22. IR (film): 2957, 2858, 1739, 1682, 1440, 1369, 1226, 1060, 1022, 745 cm$^{-1}$; HRMS (ESI) for $C_{16}H_{19}IO_3SNa$ $[M+Na]^+$: calcd 440.9997, found 440.9972. $R_f$ = 0.30 (9% ethyl acetate/91% hexanes).



**(*Z*)-18**

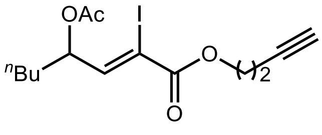
**(*Z*)-4-Acetoxy-2-iodooct-2-en-1-yl 2-methoxyacetate.** Column chromatography on silica gel (eluent:

hexanes/ethyl acetate = 10:1-7:1) afforded the title product and the isomer in 54% yield as a colorless oil. *Z:E* ratio: 3:1. $^1$H NMR (CDCl$_3$, 600 MHz): δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.27-1.36 (m, 4H), 1.57-1.69 (m, 2H), 2.04 (s, 3H), 3.46 (s, 3H), 4.09 (s, 2H), 4.81 (dd, *J* = 13.2, 1.2 Hz, 1H), 4.85 (d, *J* = 13.2, 1.2 Hz, 1H), 5.34-5.38 (m, 1H), 5.98 (dt, *J* = 7.8, 1.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ 13.83, 20.97, 22.42, 26.84, 31.14, 59.44, 69.67, 71.30, 77.47, 99.96, 137.59, 169.25, 169.99. IR (film): 2957, 2856, 1735, 1370, 1229, 1176, 1124, 1019, 961, 933 cm$^{-1}$; HRMS (ESI) for $C_{13}H_{21}IO_5Na$ [M+Na]$^+$: calcd 407.0331, found 407.0310. R$_f$ = 0.20 (9% ethyl acetate/91% hexanes).



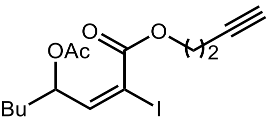
**(*E*)-18**

**(*E*)-4-Acetoxy-2-iodooct-2-en-1-yl 2-methoxyacetate.** $^1$H NMR (CDCl$_3$, 600 MHz): δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.22-1.36 (m, 4H), 1.52-1.69 (m, 2H), 2.04 (s, 3H), 3.47 (s, 3H), 4.11 (s, 2H), 4.78 (d, *J* = 13.2 Hz, 1H), 5.16 (d, *J* = 12.6 Hz, 1H), 5.44-5.48 (m, 1H), 6.31 (d, *J* = 9.6 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ13.85, 20.99, 22.36, 26.95, 33.68, 59.48, 66.37, 69.76, 71.45, 98.70, 143.95, 169.46, 170.15. IR (film): 2931, 2862, 1737, 1370, 1230, 1178, 1126, 1018, 968, 932 cm$^{-1}$; HRMS (ESI) for $C_{13}H_{21}IO_5Na$ [M+Na]$^+$: calcd 407.0331, found 407.0314. R$_f$ = 0.25 (9% ethyl acetate/91% hexanes).



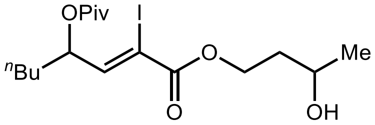
**(*Z*)-19**

**(*Z*)-But-3-yn-1-yl 4-acetoxy-2-iodooct-2-enoate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 30:1) afforded the title product and the isomer in 50% yield as a colorless oil. *Z:E* ratio: 8:1. $^1$H NMR (CDCl$_3$, 600 MHz): δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.31-1.40 (m, 4H), 1.63-1.76 (m, 2H), 2.02 (t, *J* = 3.0 Hz, 1H), 2.07 (s, 3H), 2.60 (dt, *J* = 7.2, 3.0 Hz, 2H), 4.28-4.34 (m, 2H), 5.39-5.43 (m, 1H), 7.19 (d, *J* = 7.8 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ 13.83, 18.88, 20.88, 22.42, 26.92, 32.31, 64.39, 70.22, 77.66, 79.45, 93.80, 150.76, 162.15, 170.16. IR (film): 3291, 2957, 2858, 1722, 1371, 1223, 1020, 745 cm$^{-1}$; HRMS (ESI) for $C_{14}H_{19}IO_4Na$ [M+Na]$^+$: calcd 401.0226, found 401.0203. R$_f$ = 0.25 (9% ethyl acetate/91% hexanes).



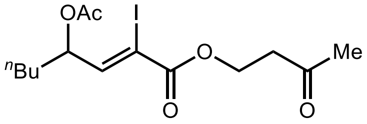
**(*E*)-19**

**(*E*)-But-3-yn-1-yl 4-acetoxy-2-iodooct-2-enoate.** $^1$H NMR (CDCl$_3$, 600 MHz): δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.29-1.36 (m, 4H), 1.61-1.70 (m, 2H), 2.02 (t, *J* = 2.4 Hz, 1H), 2.04 (s, 3H), 2.56-2.65 (m, 2H), 4.28-4.35 (m, 2H), 5.82-5.86 (m, 1H), 6.75 (d, *J* = 8.4 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 13.85, 18.79, 20.93, 22.41, 26.99, 33.28, 64.18, 70.31, 73.22, 79.46, 86.70, 153.18, 162.87, 170.04. IR (film): 2955, 2861, 1724, 1370, 1225, 1018, 647 cm$^{-1}$; HRMS (ESI) for $C_{14}H_{19}IO_4Na$ [M+Na]$^+$: calcd 401.0226, found 401.0200. R$_f$ = 0.30 (9% ethyl acetate/91% hexanes).



**20**

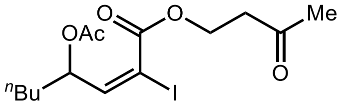
**(*Z*)-3-Hydroxybutyl 4-acetoxy-2-iodooct-2-enoate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 7:1 to 4:1) afforded the title product in 55% yield as a colorless oil. *Z:E* ratio: >20:1. $^1$H NMR (CDCl$_3$, 400 MHz): δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.21 (s, 9H), 1.25 (d, *J* = 6.0 Hz, 3H), 1.32-1.41 (m, 4H), 1.62-1.91 (m, 5H), 3.91-3.98 (m, 1H), 4.26-4.32 (m, 1H), 4.40-4.46 (m, 1H), 5.33-5.38 (m, 1H), 7.14 (dd, *J* = 7.6, 0.8 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 13.83, 22.32, 23.61, 26.92, 27.08, 32.12, 37.76, 38.80, 64.29, 64.96, 64.97, 77.50, 93.50, 93.51, 150.79, 162.60, 162.62, 177.80. IR (film): 3350, 2959, 2871, 1713, 1479, 1245, 1146, 1092, 1034, 968 cm$^{-1}$; HRMS (ESI) for $C_{17}H_{29}IO_5Na$ [M+Na]$^+$: calcd 463.0957, found 463.0932. R$_f$ = 0.40 (20% ethyl acetate/80% hexanes).



**(*Z*)-21**

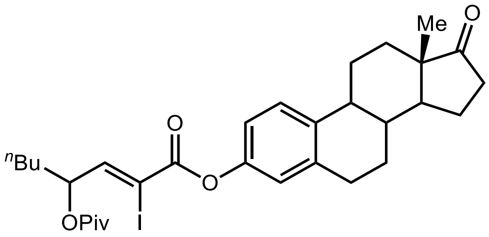
**(*Z*)-3-Oxobutyl 4-acetoxy-2-iodooct-2-enoate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 10:1 to 8:1) afforded the title product and the isomer in 64% yield as a colorless oil. *Z:E* ratio: 12:1. $^1$H NMR (CDCl$_3$, 400 MHz): δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.29-1.39 (m, 4H), 1.60-1.74 (m, 2H), 2.06 (s, 3H), 2.20 (s, 3H), 2.82 (t, *J* = 6.4 Hz, 2H), 4.45 (t, *J* = 6.4 Hz, 2H), 5.36-5.41

(m, 1H), 7.12 (d, *J* = 8.0 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 13.81, 20.86, 22.39, 26.90, 30.29, 32.28, 41.99, 61.74, 77.61, 93.70, 150.63, 162.25, 170.14, 205.03. IR (film): 2957, 2856, 1716, 1370, 1223, 1167, 1022, 746 cm$^{-1}$; HRMS (ESI) for $C_{14}H_{21}IO_5Na$ [M+Na]$^+$: calcd 419.0331, found 419.0322. R$_f$ = 0.40 (20% ethyl acetate/80% hexanes).



**(*E*)-21**

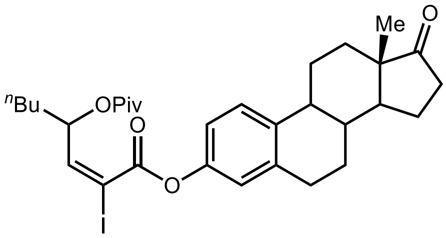
**(*E*)-3-Oxobutyl 4-acetoxy-2-iodooct-2-enoate.** $^1$H NMR (CDCl$_3$, 400 MHz): δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.26-1.36 (m, 4H), 1.57-1.69 (m, 2H), 2.03 (s, 3H), 2.21 (s, 3H), 2.84 (t, *J* = 6.6 Hz, 2H), 4.43-4.49 (m, 2H), 5.77-5.80 (m, 1H), 6.71 (d, *J* = 8.4 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 13.85, 20.93, 22.40, 26.96, 30.27, 33.22, 41.82, 61.39, 73.08, 86.85, 152.92, 162.97, 170.07, 205.03. IR (film): 2960, 2861, 1716, 1369, 1223, 1166, 1018, 971 cm$^{-1}$; HRMS (ESI) for $C_{14}H_{21}IO_5Na$ [M+Na]$^+$: calcd 419.0331, found 419.0312. R$_f$ = 0.45 (20% ethyl acetate/80% hexanes).



**(*Z*)-22**

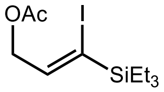
**(*Z*)-(13*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 2-iodo-4-(pivaloyloxy)oct-2-enoate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 30:1-15:1-10:1) afforded the title product and the isomer in 50% yield as a light yellow foam. *Z:E* ratio: 5:1. $^1$H NMR (CDCl$_3$, 400 MHz): δ 0.91 (s, 3H), 0.94 (t, *J* = 6.8 Hz, 3H), 1.23 (s, 9H), 1.35-1.80 (m, 12H), 1.95-2.19 (m, 4H), 2.26-2.32 (m, 1H), 2.39-2.44 (m, 1H), 2.51 (dd, *J* = 18.4, 8.8 Hz, 1H), 2.91 (dd, *J* = 8.4, 4.4 Hz, 1H), 5.39-5.44 (m, 1H), 6.87 (d, *J* = 2.8 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.8 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 13.78, 13.87, 21.54, 22.32, 25.72, 26.26, 26.96, 27.08, 29.33, 31.50, 32.04, 35.79, 37.94, 38.80, 44.10, 47.88, 50.39, 77.67, 93.11, 118.36, 121.20, 126.40, 137.75, 138.09, 148.88, 152.15, 161.20, 177.89, 220.65. IR (film): 2957, 2871, 1729, 1492, 1219, 1181, 1146, 1086, 910, 730 cm$^{-1}$; HRMS (ESI) for $C_{31}H_{41}IO_5Na$

[M+Na]$^+$: calcd 643.1896, found 643.1899. R$_f$ = 0.45 (20% ethyl acetate/80% hexanes).



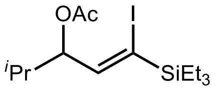
**(*E*)-22**

**(*E*)-(13*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl 2-iodo-4-(pivaloyloxy)oct-2-enoate.** $^1$H NMR (CDCl$_3$, 600 MHz): δ 0.87 (t, *J* = 7.2 Hz, 3H), 0.91 (s, 3H), 1.21 (s, 9H), 1.28-1.75 (m, 12H), 1.95-2.08 (m, 3H), 2.15 (tt, *J* = 18.0, 9.0 Hz, 1H), 2.29 (dt, *J* = 10.2, 3.6 Hz, 1H), 2.40-2.43 (m, 1H), 2.51 (dd, *J* = 18.6, 8.4 Hz, 1H), 2.92 (dd, *J* = 9.0, 4.2 Hz, 1H), 5.85-5.89 (m, 1H), 6.86 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.90 (d, *J* = 2.4 Hz, 1H), 6.94 (dt, *J* = 8.4, 2.4 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 13.86, 13.95, 21.62, 22.41, 25.79, 26.34, 27.14, 29.42, 31.58, 33.17, 35.89, 38.02, 38.81, 44.20, 47.98, 50.48, 73.35, 85.30, 85.34, 118.50, 121.29, 121.30, 126.53, 137.96, 138.22, 148.51, 155.61, 155.69, 161.93, 161.95, 177.73, 220.78. IR (film): 2957, 2871, 1732, 1492, 1222, 1179, 1150, 1083, 912, 731 cm$^{-1}$; HRMS (ESI) for $C_{31}H_{41}IO_5Na$ [M+Na]$^+$: calcd 643.1896, found 643.1882. R$_f$ = 0.50 (20% ethyl acetate/80% hexanes).



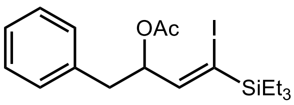
**23**

**(*Z*)-3-Iodo-3-(triethylsilyl)allyl acetate.** General Procedure A. 10% $Mn_2(CO)_{10}$ was used. Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 95:5) afforded the title product in 46% yield as a light yellow oil. *Z:E* ratio: >20:1. $^1$H NMR (CDCl$_3$, 400 MHz): δ 0.71 (q, *J* = 7.9 Hz, 6H), 0.96 (t, *J* = 7.9 Hz, 9H), 2.10 (s, 3H), 4.67 (d, J = 4.9 Hz, 1 H), 6.42 (t, J = 4.9 Hz, 1 H); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ 3.03, 7.18, 20.98, 71.12, 110.96, 143.48, 170.75. IR (film): 2953, 2874, 1742, 1373, 1220, 1034, 1003, 720, 692 cm$^{-1}$; HRMS (ESI) for $C_{11}H_{21}IO_2Na$ [M+Na]$^+$: calcd 363.0253, found 363.0225. R$_f$ = 0.35 (5% ethyl acetate/95% hexanes).



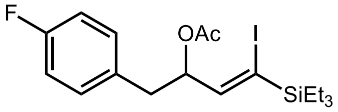
**24**

**(*Z*)-1-Iodo-4-methyl-1-(triethylsilyl)pent-1-en-3-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 98:2) afforded the title product in 70% yield as a light yellow oil. *Z:E* ratio: >20:1. $^1$H NMR (CDCl$_3$, 400 MHz): δ 0.71 (q, *J* = 7.83 Hz, 6H), 0.95 (t, *J* = 7.83 Hz, 9H), 0.96 (d, *J* = 6.64 Hz, 1H), 1.98-2.10 (m, 1H), 2.06 (s, 3H), 5.38 (dd, *J* = 5.64, 7.52 Hz, 1H), 6.13 (d, J = 7.52 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ 3.10, 7.20, 17.72, 18.46, 21.19, 31.98, 83.61, 111.88, 145.87, 170.15. IR (film): 2956, 2874, 1741, 1368, 1227, 1004, 977, 721, 692 cm$^{-1}$; HRMS (ESI) for $C_{14}H_{27}IO_2SiNa$ [M+Na]$^+$: calcd 405.0723, found 405.0698. R$_f$ = 0.35 (5% ethyl acetate/95% hexanes).



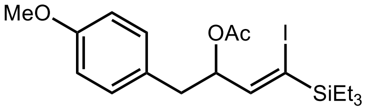
**25**

**(*Z*)-4-Iodo-1-phenyl-4-(triethylsilyl)but-3-en-2-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl actetate = 9:1) afforded the title product and the isomer in 68% yield as a colorless oil. *Z:E* ratio: 9:1. $^1$H NMR (CDCl$_3$, 600 MHz): δ *Z*-isomer (major): 0.95 (t, *J* = 8.0 Hz, 9H), 2.03 (s, 3H), 5.72 (qm, *J* = 6.4 Hz, 1H), 6.18 (dm, *J* = 6.9 Hz, 1H); *E*-isomer (minor): 0.78-0.82 (m, 3H), 0.91 (t, *J* = 7.9 Hz, 9H), 2.01 (s, 3H), 2.85 (dd, *J* = 13.7, 6.2 Hz, 1H), 5.45-5.49 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 2H); Overlap (major and minor): 0.68-0.72 (q), 2.94-3.04 (m), 7.23-7.26 (m), 7.28-7.33 (m); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ *Z*-isomer (major): 3.29, 7.13, 21.08, 39.37, 80.48, 111.10, 126.82, 128.39, 129.95, 136.60, 146.70, 169.79; *E*-isomer (minor): 4.94, 7.35, 41.35, 75.22, 112.62, 127.01, 128.59, 129.86, 136.17, 154.24. IR (film): 3028, 2953, 1741, 1369, 1227, 732, 698 cm$^{-1}$; HRMS (ESI) for $C_{18}H_{27}INaO_2Si$ [M+Na]$^+$: calcd 453.0723, found 453.0718. R$_f$ = 0.56 (major), 0.59 (minor) (10% ethyl acetate/90% hexanes).



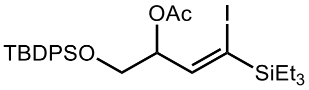
**26**

**(*Z*)-1-(4-Fluorophenyl)-4-iodo-4-(triethylsilyl)but-3-en-2-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl actetate = 5.7:1) afforded the title product and the isomer in 73% yield as a yellow oil. Z:E ratio: 11:1. $^{1}$H NMR (CDCl$_3$, 600 MHz): δ *Z*-isomer (major): 2.01 (s, 3H), 5.65-5.68 (m, 1H), 6.14 (d, *J* = 7.0 Hz, 1H), 7.17-7.20 (m, 2H); *E*-isomer (minor): 0.77-0.82 (m, 3H), 1.99 (s, 3H), 2.80 (dd, *J* = 13.8, 6.3 Hz, 1H), 5.39-5.43 (m, 1H), 7.12-7.14 (m, 2H); Overlap (major and minor): 0.66-0.70 (m), 0.88-0.94 (m), 2.89-2.98 (m), 6.94-6.98 (m); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ *Z*-isomer (major): 3.04, 7.12, 21.08, 38.39, 80.35, 111.28, 115.13 (d, *J* = 21.6 Hz,) 131.28 (d, *J* = 7.8 Hz), 132.14 (d, *J* = 3.23 Hz), 146.30, 161.97 (d, *J* = 244.5 Hz), 169.79; *E*-isomer (minor): 4.71, 7.31, 40.36, 74.98, 112.82, 115.37 (d, *J* = 21.6 Hz), 131.20 (overlap with major), 153.83, 169.73; $^{19}$F NMR (CDCl$_3$, 564 MHz): δ -116.05 (*E*-isomer), -116.36 (*Z*-isomer). IR (film): 2954, 2875, 1740, 1509, 1222, 1019, 732 cm$^{-1}$; HRMS (ESI) for $C_{18}H_{26}FINaO_2Si$ [M+Na]$^+$: calcd 471.0628, found 471.0617. $R_f$ = 0.50 (both isomers, 10% ethyl acetate/90% hexanes).



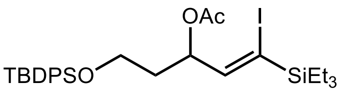
**27**

**(*Z*)-4-Iodo-1-(4-methoxyphenyl)-4-(triethylsilyl)but-3-en-2-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl actetate = 9:1) afforded the title product in 67% yield as a yellow oil. *Z:E* ratio: >20:1. $^{1}$H NMR (CDCl$_3$, 600 MHz): δ 0.68 (q, *J* = 7.9 Hz, 6H), 0.92 (t, *J* = 7.9 Hz, 9H), 2.01 (s, 3H), 2.88-2.95 (m, 2H), 3.78 (s, 3H), 5.63-5.66 (m, 1H), 6.15 (d, *J* = 6.9 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ 3.27, 7.11, 21.05, 38.45, 55.37, 80.62, 110.92, 113.95, 128.64, 130.84, 146.80, 158.76, 169.73. IR (film): 2953, 2874, 1739, 1512, 1228, 1020, 721 cm$^{-1}$; HRMS (ESI) for $C_{19}H_{29}INaO_3Si$ [M+Na]$^+$: calcd 483.0828, found 483.0827. $R_f$ = 0.46 (10% ethyl acetate/90% hexanes).



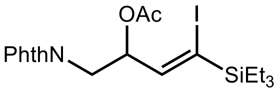
**28**

**(*Z*)-1-((*tert*-Butyldiphenylsilyl)oxy)-4-iodo-4-(triethylsilyl)but-3-en-2-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl actetate = 20:1) afforded the title product in 76% yield as a yellow oil. *Z:E* ratio: >20:1. $^{1}$H NMR (CDCl$_3$, 600 MHz): δ 0.70 (q, *J* = 8.0 Hz, 6H), 0.94 (t, *J* = 7.9 Hz, 9H), 1.04 (s, 9H), 2.05 (s, 3H), 3.79-3.85 (m, 2H), 5.64-5.66 (m, 1H), 6.33 (d, *J* = 7.0 Hz, 1H), 7.37-7.44 (m, 6H), 7.65-7.69 (m, 4H); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ 3.26, 7.12, 19.41, 21.00, 26.90, 64.23, 80.45, 112.16, 127.81, 129.80, 129.83, 133.53, 133.63, 135.69, 135.79, 144.56, 169.78. IR (film): 3071, 2954, 2873, 1742, 1229, 1111 cm$^{-1}$; HRMS (ESI) for $C_{28}H_{41}INaO_3Si_2$ [M+Na]$^+$: calcd 631.1537, found 631.1524. R$_f$ = 0.33 (5% ethyl acetate/95% hexanes).



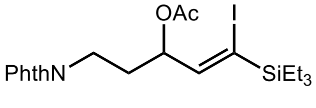
**29**

**(*Z*)-5-((*tert*-Butyldiphenylsilyl)oxy)-1-iodo-1-(triethylsilyl)pent-1-en-3-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl actetate = 5.7:1) afforded the title product and the isomer in 81% yield as a colorless oil. *Z:E* ratio: 4:1. $^1$H NMR (CDCl$_3$, 600 MHz): δ *Z*-isomer (major): 0.69 (q, *J* = 7.8 Hz, 6H), 1.87-1.93 (m, 1H), 3.71-3.75 (m, 2H), 5.65-5.68 (m, 1H), 6.18 (d, *J* = 6.9 Hz, 1H); *E*-isomer (minor): 0.80-0.85 (m, 3H), 1.81-1.84 (m, 2H), 3.64-3.67 (m, 2H), 5.51-5.55 (m, 1H), 7.16 (d, *J* = 9.99 Hz, 1H); Overlap (major and minor): 0.88-0.98 (m), 1.06 (s, minor), 1.07 (s, major), 1.98 (s, minor), 1.99 (s, major), 1.97-2.02 (m), 7.36-7.43 (m), 7.64-7.70 (m); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ *Z*-isomer (major): 3.05, 7.18, 19.33, 21.14, 27.00, 35.96, 59.74, 77.59, 109.90, 127.78, 129.71, 129.73, 133.83, 133.87, 135.75, 147.20, 169.92; *E*-isomer (minor): 4.65, 7.45, 19.23, 26.88, 37.59, 59.47, 71.88, 111.38, 127.82, 129.79, 129.81, 133.58, 133.61, 135.45, 135.69, 155.20. IR (film): 3070, 2953, 2874, 1742, 1427, 1228, 1110, 700 cm$^{-1}$; HRMS (ESI) for $C_{29}H_{43}INaO_3Si_2$ [M+Na]$^+$: calcd 645.1693, found 645.1687. R$_f$ = 0.36 (major), 0.44 (minor) (10% ethyl acetate/90% hexanes).



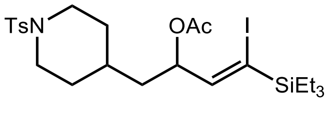
**30**

**(*Z*)-1-(1,3-Dioxoisoindolin-2-yl)-4-iodo-4-(triethylsilyl)but-3-en-2-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl actetate = 5.7:1) afforded the title product in 60% yield as a colorless oil. *Z:E* ratio: >20:1. $^1$H NMR (CDCl$_3$, 600 MHz): δ 0.67 (qm, *J* = 5.7 Hz, 6H), 0.90 (t, *J* = 7.8 Hz, 9H), 2.02 (s, 3H) 3.95 (d, *J* = 6.2 Hz, 2H), 5.82 (dt, *J* = 7.2, 6.2 Hz, 1H), 6.25 (d, *J* = 7.3 Hz, 1H), 7.69-7.74 (m, 2H), 7.81-7.86 (m, 2H); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 2.98, 7.12, 21.02, 39.31, 77.32, 114.21, 123.48, 132.09, 134.17, 143.59, 168.09, 169.86. IR (film): 2953, 2874, 1776, 1742, 1714, 1390, 1368, 1221, 1021, 720, 715 cm$^{-1}$; HRMS (ESI) for $C_{20}H_{26}INNaO_4Si$ [M+Na]$^+$: calcd 522.0573, found 522.0569. $R_f = 0.5$ (25% ethyl acetate/75% hexanes).



**31**

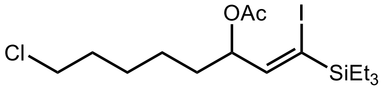
**(*Z*)-5-(1,3-Dioxoisoindolin-2-yl)-1-iodo-1-(triethylsilyl)pent-1-en-3-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl actetate = 5.7:1) afforded the title product and the isomer in 72% yield as a yellow oil. *Z:E* ratio: 6:1. $^1$H NMR ($CDCl_3$, 600 MHz): δ *Z*-isomer (major) 0.92 (t, *J* = 7.9 Hz, 9H), 2.00 (s, 3H), 2.12-2.17 (m, 1H), 3.74-3.79 (m, 1H), 5.43-5.47 (m, 1H), 6.23 (d, *J* = 6.7 Hz, 1H); *E*-isomer (minor): 0.74-0.78 (m, 3H), 0.85 (t, *J* = 7.7 Hz, 9H), 2.06 (s, 3H), 3.67-3.71 (m, 1H), 5.18-5.22 (m, 1H), 7.12 (d, *J* = 9.4 Hz, 1H); Overlap (major and minor) 0.65-0.69 (m), 2.03-2.09 (m), 3.82-3.88 (m), 7.69-7.72 (m), 7.83-7.85 (m); $^{13}$C NMR ($CDCl_3$, 150 MHz): δ *Z*-isomer (major): 2.95, 7.12, 21.00, 31.36, 34.11, 78.19, 110.67, 123.35, 132.24, 134.06, 146.39, 168.22, 169.93; *E*-isomer (minor): 4.48, 7.28, 21.07, 33.14, 33.92, 72.00, 111.76, 123.38, 132.12, 134.14, 154.17, 168.16, 170.15. IR (film): 2953, 2874, 1772, 1741, 1710, 1394, 1369, 1226, 1005, 718 cm$^{-1}$; HRMS (ESI) for $C_{21}H_{28}INNaO_4Si$ [M+Na]$^+$: calcd 536.0730, found 536.0724. $R_f$ = 0.42 (both isomers, 25% ethyl acetate/75% hexanes).



**32**

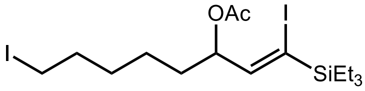
**(*Z*)-4-Iodo-1-(1-tosylpiperidin-4-yl)-4-(triethylsilyl)but-3-en-2-yl.** Column chromatography on silica gel (eluent: hexanes/ethyl actetate = 5.7:1) afforded the title product and the isomer in 66% yield as a colorless oil. *Z:E* ratio: 7:1. $^1$H NMR ($CDCl_3$, 600 MHz): δ *Z*-isomer (major): 0.67 (q, *J* = 7.9 Hz, 6H), 0.91 (t, *J* = 7.9 Hz, 9H), 1.83 (dd, *J* = 111.4, 2.9 Hz, 2H), 2.01 (s, 3H), 2.43 (s, 3H), 5.50-5.53 (m, 1H), 6.13 (d, *J* = 6.8 Hz, 1H); *E*-isomer (minor): 0.72-0.79 (m, 3H), 0.82-0.86 (m, 3H), 0.94 (t, *J* = 7.8 Hz, 9H), 1.65-1.69 (m, 2H), 1.85 (d, *J* = 12.6 Hz, 1H), 1.98 (s, 3H), 2.17 (s, 3H), 5.31-5.35 (m, 1H), 7.11 (d, *J* = 9.6 Hz, 1H); Overlap (major and minor): 1.25-1.30 (m), 1.35-1.42 (m), 1.45-1.49 (m), 1.59-1.63 (m), 2.18-2.25 (m), 3.74-3.77 (m), 7.32 (d, *J* = 8.1 Hz), 7.63 (d, *J* = 8.3 Hz); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ

*Z*-isomer (major): 2.96, 7.11, 21.18, 21.61, 31.06, 31.63, 32.24, 39.62, 46.34, 46.35, 77.94, 110.45, 127.82, 129.67, 133.34, 143.46, 147.09, 170.01; *E*-isomer (minor): 4.64, 7.40, 29.78, 30.99, 31.34, 41.40, 72.16, 111.61, 127.65, 129.89, 133.23, 143.54, 154.74. IR (film): 2952, 2874, 1737, 1229, 1163, 722, 548 cm$^{-1}$; HRMS (ESI) for $C_{24}H_{38}INNaO_4SSi$ $[M+Na]^+$: calcd 614.1233, found 614.1225. $R_f = 0.54$ (both isomers, 25% ethyl acetate/75% hexanes).



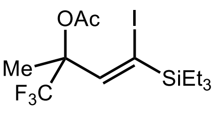
**33**

**(*Z*)-8-Chloro-1-iodo-1-(triethylsilyl)oct-1-en-3-yl acetate.** General Procedure A. 10% $Mn_2(CO)_{10}$ catalyst and 0.5 equiv. KOAc were used instead of DIPEA. Column chromatography on silica gel (eluent: hexanes/ethyl actetate = 99:1) afforded the title product in 67% yield as a brown oil. *Z:E* ratio: >20:1. $^1$H NMR ($CDCl_3$, 600 MHz): δ 0.70 (q, *J* = 7.9 Hz, 6H), 0.94 (t, *J* = 7.9 Hz, 9H), 1.37-1.43 (m, 2H), 1.46-1.51 (m, 2H), 1.62-1.73 (m, 2H), 1.76-1.81 (m, 2H), 2.06 (s, 3H), 3.53 (t, *J* = 6.7 Hz, 2H), 5.47-5.51 (m, 1H), 6.17 (d, *J* = 6.9 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 150 MHz): δ 3.05, 7.18, 21.25, 24.28, 26.84, 32.57, 33.13, 45.02, 79.87, 110.53, 147.14, 170.13. IR (film): 2952, 2874, 1740, 1457, 1370, 1231, 1018, 733 cm$^{-1}$; HRMS (ESI) for $C_{16}H_{30}ClINaO_2Si$ $[M+Na]^+$: calcd 467.0646 and 469.0616, found 467.0633 and 469.0616. $R_f = 0.57$ (10% ethyl acetate/90% hexanes).



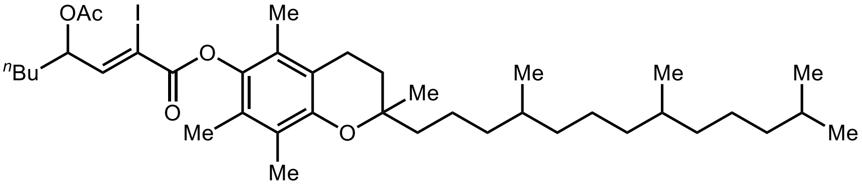
**34**

**(Z)-1,8-Diiodo-1-(triethylsilyl)oct-1-en-3-yl acetate.** General Procedure A. 10% $Mn_2(CO)_{10}$ catalyst and 0.5 equiv. KOAc were used instead of DIPEA. Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 98:2) provided the title product in 64% yield as a light yellow oil. *Z:E* ratio: >20:1. $^1$H NMR ($CDCl_3$, 400 MHz): δ 0.70 (q, *J* = 7.84 Hz, 6H), 0.94 (t, *J* = 7.84 Hz, 9H), 1.41 (m, 4 H), 1.66 (m, 2H), 1.83 (m, 2H), 2.06 (s, 3H), 3.18 (t, *J* = 7.09 Hz, 2H), 5.48 (m, 1 H), 6.17 (d, J = 7.03 Hz, 1 H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 3.05, 6.89, 7.21, 21.28, 23.93, 30.43, 33.09, 33.45, 79.86, 110.55, 147.12, 170.13. IR (film): 2952, 2873, 1738, 1369, 1228, 1004, 721, 692 cm$^{-1}$; HRMS (ESI) for $C_{16}H_{30}I_2O_2SiNa$ $[M+Na]^+$: calcd 559.0002, found 558.9973. $R_f = 0.33$ (5% ethyl acetate/95% hexanes).



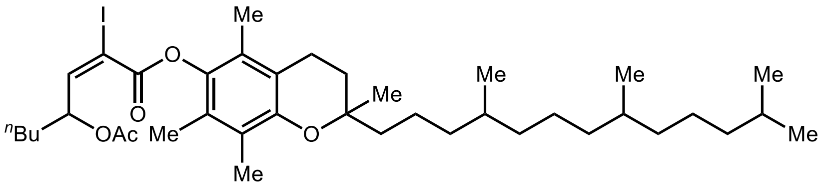
**35**

**(*Z*)-1,1,1-Trifluoro-4-iodo-2-methyl-4-(triethylsilyl)but-3-en-2-yl acetate.** To an 8 mL vial was added the premade α-acyloxy iodide (0.5 mmol), DCM (0.5 mL) and DIPEA (0.25 mmol) at 0 ºC, then the mixture was stirred for another 15 min. After that triethylsilyl acetylene (2.5 mmol) and $Mn_2(CO)_{10}$ (0.025 mmol) were added to the mixture. The reaction mixture was degassed by chill-pump-thaw for 20 min, then irradiated with 90 W blue LED lamp at approximately 5 cm away from the light source. The reaction temperature was around 40 ºC. After 2 h, the solvent was removed under vacuum and the crude product was purified by Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 100:1) to afford the title product in 78% yield as a colorless oil. *Z:E* ratio: >20:1. $^1$H NMR ($CDCl_3$, 600 MHz): δ 0.71 (q, *J* = 7.8 Hz, 6H), 0.94 (t, *J* = 7.8 Hz, 9H), 1.83 (d, *J* = 0.6 Hz, 3H), 2.19 (s, 3H), 6.56 (d, *J* = 0.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 150 MHz): δ 2.95, 6.82, 20.07, 21.34, 80.30 (q, *J* = 29.6 Hz), 109.94, 124.07 (q, *J* = 283.4 Hz), 139.55, 167.36. IR (film): 2952, 2873, 1758, 1367, 1226, 1159, 1104, 1004, 732 cm$^{-1}$; HRMS (ESI) for $C_{13}H_{22}F_3IO_2SiNa$ [M+Na]$^+$: calcd 445.0284, found 445.0285. $R_f$ = 0.35 (5% ethyl acetate/95% hexanes).



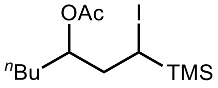
**(*Z*)-38**

**(*Z*)-2,5,7,8-Tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl 4-acetoxy-2-iodooct-2-enoate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 200:1-150:1-100:1) afforded the title product and the isomer in 63% yield as a colorless oil. *Z:E* ratio: 1.6:1. $^1$H NMR ($CDCl_3$, 600 MHz): δ 0.84-0.87 (m, 12H), 0.94 (t, *J* = 7.2 Hz, 3H), 1.04-1.16 (m, 6H), 1.20-1.45 (m, 19H), 1.50-1.57 (m, 3H), 1.72-1.84 (m, 4H), 1.97 (s, 3H), 2.01 (s, 3H), 2.09 (s, 3H), 2.11 (s, 3H), 2.59 (t, *J* = 6.0 Hz, 2H), 5.51-5.54 (m, 1H), 7.41 (d, *J* = 7.8 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 150 MHz): δ 11.78, 12.15, 12.99, 13.87, 19.59, 19.62, 19.64, 19.68, 19.74, 20.60, 20.93, 21.02, 22.44, 22.61, 22.69, 23.63 (br), 24.22 (br), 24.44, 24.79, 27.00, 27.97, 31.15 (br), 32.40, 32.69, 32.72, 32.78, 32.80, 37.30, 37.35, 37.40, 37.42, 37.46, 37.49, 37.54, 37.57, 39.38, 39.58 (br), 40.45 (br), 75.16, 77.60, 92.60, 117.54, 123.23, 124.78, 126.54, 141.03, 149.69, 151.41, 161.10, 170.17. IR (film): 2924, 2863, 1741, 1459, 1373, 1200, 1072, 1020, 738 cm$^{-1}$; HRMS (ESI) for $C_{39}H_{63}IO_5Na$ [M+Na]$^+$: calcd 761.3618, found 761.3636. $R_f$ = 0.35 (5% ethyl acetate/95% hexanes).



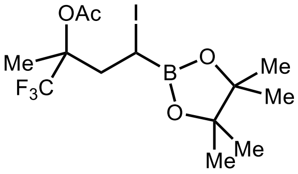
**(*E*)-38**

**(*E*)-2,5,7,8-Tetramethyl-2-(4,8,12-trimethyltridecyl)chroman-6-yl 4-acetoxy-2-iodooct-2-enoate.** $^1$H NMR (CDCl$_3$, 600 MHz): δ 0.84-0.88 (m, 15H), 1.06-1.16 (m, 6H), 1.21-1.44 (m, 19H), 1.49-1.60 (m, 3H), 1.66-1.84 (m, 4H), 2.04 (br, 3H), 2.07 (s, 3H), 2.08 (br, 3H), 2.10 (s, 3H), 2.60 (t, *J* = 6.6 Hz, 2H), 5.88-5.92 (m, 1H), 6.90 (d, *J* = 8.4 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 100 MHz): δ 11.80, 12.19, 13.04, 13.88, 19.57, 19,61, 19.63, 19.67, 19.73, 20.58, 20.97, 21.01, 22.44, 22.61, 22.70, 23.67 (br), 24.11 (br), 24.43, 24.79, 27.15, 27.96, 31.08, 32.69, 32.75, 33.25, 37.27, 37.38, 37.43, 37.51, 37.53, 39.36, 39.62 (br), 40.40 (br), 73.76, 75.11, 84.90, 117.52, 123.24, 124.86, 126.60, 140.63, 149.72, 155.55, 161.64, 170.15. IR (film): 2924, 2861, 1743, 1459, 1374, 1228, 1188, 1107, 1017, 972 cm$^{-1}$; HRMS (ESI) for $C_{39}H_{63}IO_5Na$ [M+Na]$^+$: calcd 761.3618, found 761.3591. $R_f$ = 0.40 (5% ethyl acetate/95% hexanes).



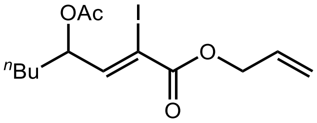
**36**

**1-Iodo-1-(trimethylsilyl)heptan-3-yl acetate.** General Procedure B. 5% $Mn_2(CO)_{10}$ was used. Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 100:1) afforded the title product of two isomers in 76% yield as a colorless oil. Ratio of the two isomers: 2:1. $^1$H NMR (CDCl$_3$, 600 MHz): δ 0.14 (s, minor), 0.15 (s, major), 0.87-0.91 (m, overlap), 1.26-1.32 (m, overlap), 1.43-1.66 (m, overlap), 1.75-1.88 (m, overlap), 2.04 (s, minor), 2.05 (s, major), 2.93 (dd, *J* = 12.0, 3.6 Hz, minor), 3.07 (dd, *J* = 12.0, 3.0 Hz, major), 5.06-5.12 (m, overlap); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ -2.29, -2.25, 13.89, 13.94, 14.93, 16.87, 21.13, 21.29, 22.55, 22.61, 26.82, 27.30, 31.86, 34.19, 37.50, 38.27, 74.81, 75.76, 170.42, 170.48. IR (film): 2954, 2858, 1736, 1372, 1232, 1020, 837 cm$^{-1}$; HRMS (ESI) for $C_{12}H_{15}IO_2SiNa$ [M+Na]$^+$: calcd 379.0566, found 379.0538. $R_f$ = 0.35 (5% ethyl acetate/95% hexanes).



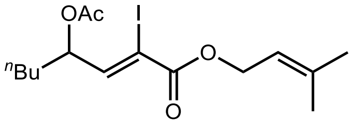
**37**

**1,1,1-Trifluoro-4-iodo-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl acetate.** To an 8 mL vial was added the premade α-acyloxy iodide (0.5 mmol), DCM (0.5 mL) and KOAc (0.25 mmol) at 0 ºC, then the mixture was stirred for another 15 min. After that alkenyl boronate ester (1.0 mmol) and $Mn_2(CO)_{10}$ (0.025 mmol) were added to the mixture. The reaction mixture was degassed by chill-pump-thaw for 20 min, then irradiated with 90 W blue LED lamp at approximately 5 cm away from the light source. The reaction temperature was around 40 ºC. After 2 h, the solvent was removed under vacuum and the crude product was purified by Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 30:1 to 20:1) afforded the title product of two isomers in 36% yield as a colorless oil. Ratio of the two isomers: 1.3:1. $^1$H NMR ($CDCl_3$, 400 MHz): δ 1.25 (s, minor), 1.26 (s, major), 1.65-1.66 (m, overlap), 2.07 (s, minor), 2.10 (s, major), 2.66 (dd, $J$ = 14.8, 4.0, minor), 2.77 (dd, $J$ = 15.6, 10.4, major), 2.85-2.92 (m, minor), 2.98-3.03 (m, major), 3.35 (dd, $J$ = 10.4, 3.6, major), 3.42-3.46 (m, minor); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 18.16, 18.83, 21.88, 22.07, 24.06, 24.23, 24.30, 24.34, 38.97, 39.55, 82.34 (q, $J$ = 19 Hz), 82.53 (q, $J$ = 19 Hz), 84.13, 84.16, 124.54 (q, $J$ = 188.2 Hz), 124.68 (q, $J$ = 188.1 Hz), 168.85. IR (film): 2980, 2933, 1752, 1382, 1372, 1158, 1142, 1097, 969, 865 cm$^{-1}$; HRMS (ESI) for $C_{13}H_{21}BF_3IO_4Na$ $[M+Na]^+$: calcd 459.0427, found 459.0410. $R_f$ = 0.25 (9% ethyl acetate/91% hexanes).



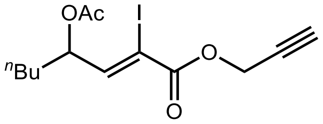
**41**

**(*Z*)-Allyl 4-acetoxy-2-iodooct-2-enoate.** General Procedure B. Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 30:1 to 20:1) afforded the title product and the isomer in 42% yield as a colorless oil. *Z*:*E* ratio: 11:1. $^1$H NMR ($CDCl_3$, 400 MHz): δ 0.91 (t, $J$ = 7.6 Hz, 3H), 1.31-1.40 (m, 4H), 1.63-1.76 (m, 2H), 2.07 (s, 3H), 2.56-2.65 (m, 2H), 4.69-4.71 (m, 2H), 5.27-5.30 (m, 1H), 5.36-5.45 (m, 2H), 5.90-6.00 (m, 1H), 7.19 (d, $J$ = 8.0 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 13.86, 20.92, 22.42, 26.91, 32.31, 67.41, 77.67, 94.10, 118.92, 131.41, 150.52, 162.08, 170.20. IR (film): 2957, 2930, 2861, 1718, 1370, 1220, 1020, 746 cm$^{-1}$; HRMS (ESI) for $C_{13}H_{19}IO_4Na$ [M+Na]$^+$: calcd 389.0226, found 389.0205. $R_f$ = 0.25 (9% ethyl acetate/91% hexanes).



**42**

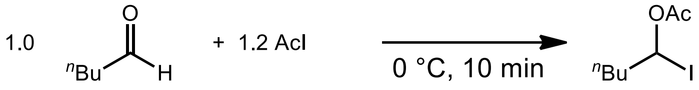
**(*Z*)-3-Methylbut-2-en-1-yl 4-acetoxy-2-iodooct-2-enoate.** General Procedure B. Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 30:1 to 20:1) afforded the title product and the isomer in 44% yield as a colorless oil. *Z:E* ratio: 7:1. $^1$H NMR ($CDCl_3$, 400 MHz): δ 0.91 (t, *J* = 7.2 Hz, 3H), 1.31-1.40 (m, 4H), 1.63-1.76 (m, 2H), 1.73 (d, *J* = 0.8 Hz, 3H), 1.77 (d, *J* = 0.8 Hz, 3H), 2.07 (s, 3H), 4.70 (d, *J* = 7.2 Hz, 2H), 5.36-5.45 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 13.87, 18.12, 20.93, 22.43, 25.78, 26.92, 32.35, 63.83, 77.74, 94.98, 118.00, 139.85, 149.99, 162.45, 170.20. IR (film): 2960, 2933, 2861, 1713, 1370, 1219, 1017, 733 cm$^{-1}$; HRMS (ESI) for $C_{15}H_{23}IO_4Na$ [M+Na]$^+$: calcd 417.0539, found 417.0521. $R_f$ = 0.25 (9% ethyl acetate/91% hexanes). (06-65)



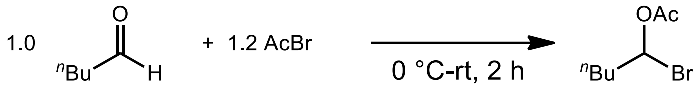
**43**

**(*Z*)-Prop-2-yn-1-yl 4-acetoxy-2-iodooct-2-enoate.** General Procedure B. Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 30:1 to 20:1) afforded the title product and the isomer in 42% yield as a colorless oil. *Z:E* ratio: 8:1. $^1$H NMR ($CDCl_3$, 400 MHz): δ 0.92 (t, *J* = 7.6 Hz, 3H), 1.30-1.42 (m, 4H), 1.62-1.79 (m, 2H), 2.08 (s, 3H), 2.53 (t, *J* = 2.4 Hz, 1H), 4.81 (dd, *J* = 2.4, 0.8 Hz, 2H), 5.39-5.44 (m, 1H), 7.23 (d, *J* = 7.6 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 13.86, 20.91, 22.42, 26.93, 32.25, 54.19, 75.62, 76.96, 77.70, 93.08, 151.53, 161.70, 170.23. IR (film): 2955, 2933, 2858, 1725, 1369, 1219, 1032, 744 cm$^{-1}$; HRMS (ESI) for $C_{13}H_{17}IO_4Na$ [M+Na]$^+$: calcd 387.0069, found 387.0047. $R_f$ = 0.25 (9% ethyl acetate/91% hexanes).

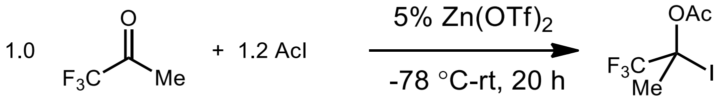
**Procedure for the synthesis of α-acetoxy halides.**



To an 8 mL vial was added acetyl iodide (98 µL, 1.2 mmol) and pentanal (106 µL, 1.0 mmol). The mixture was stirred at 0 °C for 10 minutes. The reaction mixture was quenched with $H_2O$, extracted with $CH_2Cl_2$, washed with $Na_2S_2O_3$ (10% aq.), sat. $NaHCO_3$ and dried over $Na_2SO_4$. Then the solvent was removed under vacuum to afford the product as a yellow liquid (210 mg, 82%). $^1$H NMR ($CDCl_3$, 600 MHz): δ 0.92 (t, *J* = 7.2 Hz, 3H), 1.33-1.45 (m, 4H), 2.07 (s, 3H), 2.13-2.16 (m, 2H), 6.78 (t, *J* = 6.0 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 150 MHz): δ 13.82, 21.16, 21.60, 29.52, 41.59, 55.72, 168.51.



α-Acetoxy bromide was made from pentanal and acetyl bromide following the same procedure. Yield: 59%. $^1$H NMR ($CDCl_3$, 600 MHz): δ 0.92 (t, *J* = 7.2 Hz, 3H), 1.32-1.48 (m, 4H), 2.10 (s, 3H), 2.06-2.14 (m, 2H), 6.59 (t, *J* = 6.0 Hz, 1H). $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 13.83, 20.96, 21.85, 27.90, 39.07, 76.40, 168.52. HRMS (ESI) for $C_7H_{13}BrO_2Na$ $[M+Na]^+$: calcd 230.9997, found 230.9992.



To an 8 mL vial was added acetyl iodide (0.82 mL, 12 mmol), $Zn(OTf)_2$ (364 mg, 1.0 mmol), and 1,1,1-trifluoraoacetone (0.90 mL, 10 mmol) at -78 °C. Then the mixture was stirred at room temperature for 20 h. The reaction mixture was quenched with $H_2O$, extracted with $CH_2Cl_2$, washed with $Na_2S_2O_3$ (10% aq.) and dried over $Na_2SO_4$. Then the solvent was removed under vacuum to afford the product as a light pink liquid (1.6 g, 57%). $^1$H NMR ($CDCl_3$, 400 MHz): δ 2.14 (s, 3H), 2.38 (q, *J* = 0.8 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 150 MHz): δ 22.07, 28.63, 60.93 (q, *J* = 32.8 Hz), 122.52 (q, *J* = 279 Hz), 167.28.

## Electrochemical Measurements

Cyclic voltammograms were recorded using a Gamry Reference 600 Potentiostat. A glassy carbon disk (3 mm diameter, CH Instrument, part # CHI104), Pt mesh, and nonaqueous Ag/Ag$^+$ electrode were used as the working, counter and reference electrode, respectively. The nonaqueous Ag/Ag$^+$ electrode was prepared in an electrode kit (CH instrument, part # CH112) in which a silver wire was immersed into an acetonitrile solution containing 0.01 M $AgNO_3$ and 0.1 M tetrabutylammonium perchlorate ($TBAClO_4$). The electrolyte solution was 1 mM substrate/0.1 M $LiClO_4$ in anhydrous acetonitrile, and was bubbled with argon for 20 minutes prior the measurement. A scan rate of 10 mV/s was used. The potential of the reference electrode (0.30 V vs SCE) was calibrated using the redox potential of ferrocene as the standard (E° (Fc$^+$/Fc) = 0. 40 V vs SCE).

**Fig. S2:** Cyclic voltammogram of α-acetoxy iodide

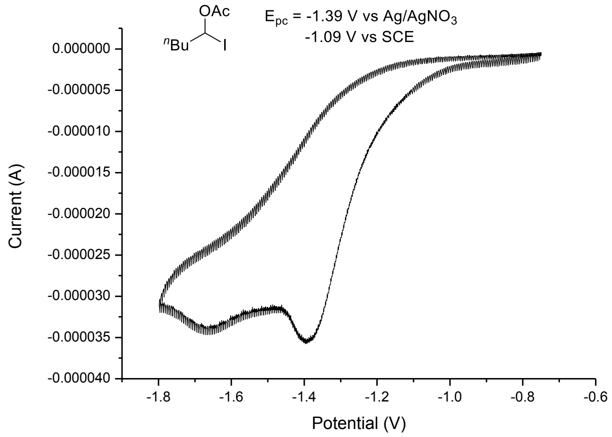
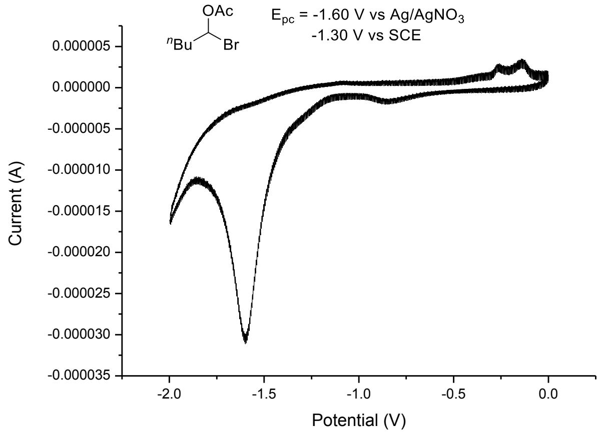


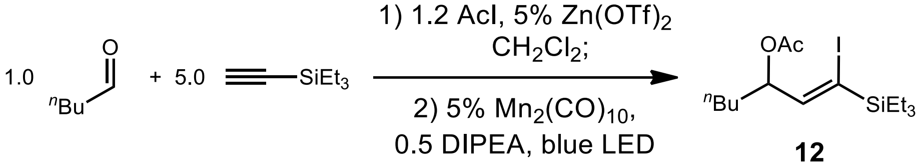
**Fig. S3:** Cyclic voltammogram of α-acetoxy bromide



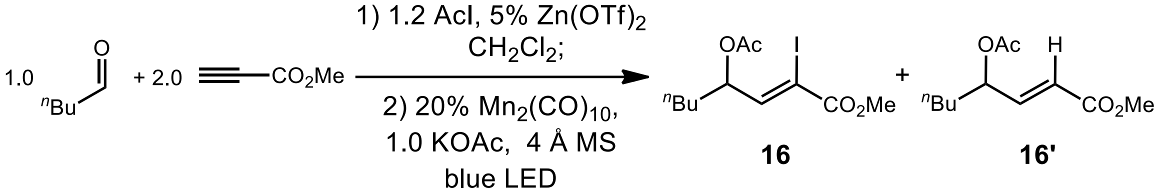
## Mechanistic investigations

### a. Origin of *Z*-selectivity: Time study and isomerization.

**Table S2: Time study** According to procedure A (When triethylsilyl acetylene was used) and the procedure B (When methyl propiolate was used), the reaction was stopped at different time points. Isolated yields were obtained by column chromatography on silica gel. *Z*:*E* ratios were determined using purified products via $^1$H NMR.

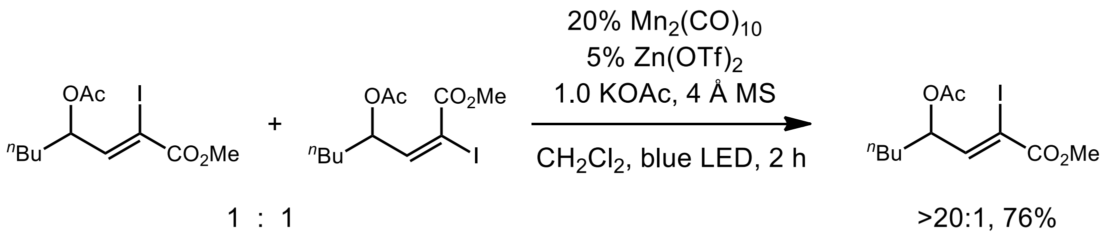


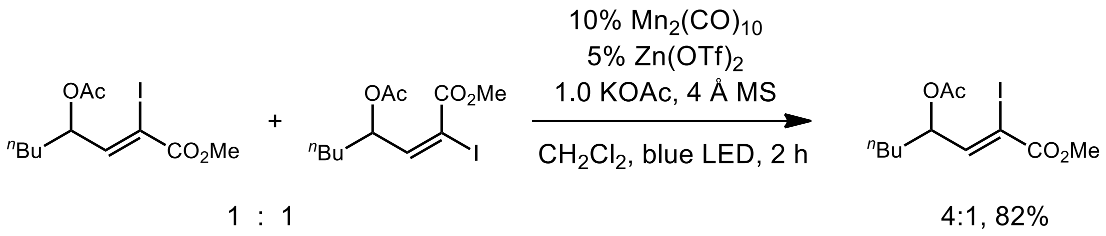
| entry | time | Yield | *Z:E* (12) |
|---|---|---|---|
| 1 | 5 min | 42% | 6:1 |
| 2 | 15 min | 71% | 7:1 |
| 3 | 30 min | 75% | 9:1 |
| **4** | **2 h** | **78%** | **>20:1** |



| entry | time | Yield (16:16') | *Z:E* (16) |
|---|---|---|---|
| 1 | 15 min | 70%, >20:1 | 1:1 |
| 2 | 30 min | 67%, >20:1 | 3:1 |
| 3 | 1 h | 63%, >20:1 | 6:1 |
| **4** | **2 h** | **65%, 14:1** | **14:1** |
| 5 | 5 h | 58%, 8:1 | 12:1 |

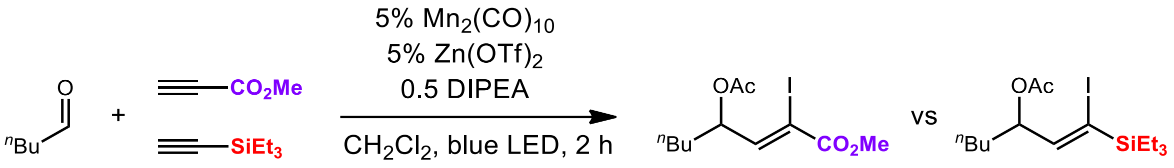
**Fig. S4: Isomerization** According to the procedure B, the 1:1 mixture of vinyl iodide **16** was resubjected to the standard condition for 2 h.





### b. Polarity of ketyl radical.

**Fig. S5:** Preferential reactivity with electron-deficient olefins



2 eq each

**16**, 63%, 2:1 **12**, not observed

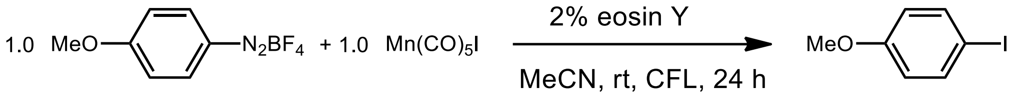
To an 8 mL vial was added DCM (0.5 mL), AcI (0.6 mmol), Zn(OTf)$_2$ (0.025 mmol) and aldehyde (0.5 mmol) consecutively at 0 ºC. The mixture was stirred at the same temperature for 15 min. To this mixture was added DIPEA (0.25 mmol) at 0 ºC, then the mixture was stirred for another 15 min. Triethylsilyl acetylene (1.0 mmol), methyl propiolate (1.0 mmol), and Mn$_2$(CO)$_{10}$ (0.025 mmol) were added to the mixture. The reaction mixture was degassed by chill-pump-thaw for 20 min at -78 °C, then irradiated with one 90 W Blue LED lamp at approximately 5 cm away from the light source. After 2 h, the solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate = 98:2) to provide solely **16** in 63% yield**.** *Z:E* ratio: 2:1.

### c. Catalyst turnover: stoichiometric atom transfer is a viable mechanism.

To an 8 mL vial was added MeCN (0.5 mL), 4-methoxybenzenediazonium tetrafluoroborate (22.2 mg, 0.1 mmol), Mn(CO)$_5$I (32.1 mg, 0.1 mmol) and eosin Y (1.2 mg, 0.001 mmol) consecutively at room temperature. The reaction mixture was degassed by chill-pump-thaw for 20 min, then irradiated with two

26 W CFL lamps (at approximately 5 cm away from the light source). After 20 h, the solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel. $^1$H NMR ($CDCl_3$, 600 MHz): δ 3.78 (s, 3H), 6.67-6.70 (m, 2H), 7.54-7.57 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 55.30, 82.66, 116.36, 138.18, 159.47.

**Table S3:** Stoichiometric atom transfer



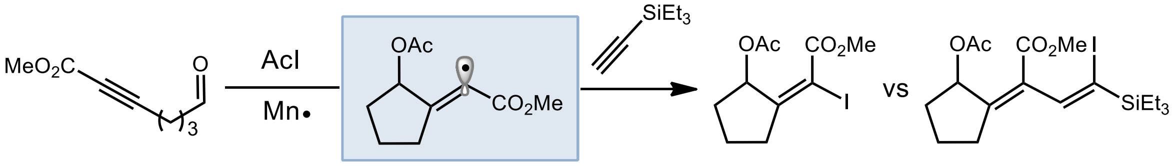
**40**, 70%

| entry | conditions | Yield |
|---|---|---|
| **1** | **No variation** | **70%** |
| 2 | No eosin Y, light | 43% |
| 3 | No eosin Y, no light, rt | 3% |
| 4 | No eosin Y, no light, 50 °C | 68% |

***Note:** The vial was covered by aluminum foil under no light condition.

### d. Cascade reactions:

**Fig. S6:** Two components

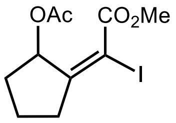


**45**, 63%, 2:1 *E*:*Z*

not observed

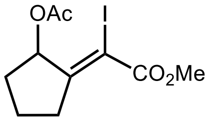
To an 8 mL vial was added DCM (0.5 mL), AcI (0.6 mmol), $Zn(OTf)_2$ (0.025 mmol) and aldehyde (0.5 mmol) consecutively at 0 °C. The mixture was stirred at the same temperature for 15 min. To this mixture was added DIPEA (0.25 mmol) at 0 °C, then the mixture was stirred for another 15 min. Triethylsilyl acetylene (2.5 mmol) and $Mn_2(CO)_{10}$ (0.025 mmol) was added to the mixture. The reaction was degassed by chill-pump-thaw for 20 min at -78 °C, then irradiated with one 90 W Blue LED lamp (at approximately 5 cm away from the light source). After 2 h, the crude product was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate = 95:5) to provide solely **45** in 63% yield as a light yellow oil. *E:Z* ratio: 2:1.

*Note: Same yield and selectivity were obtained without triethylsilyl acetylene.



**(*E*)-45**

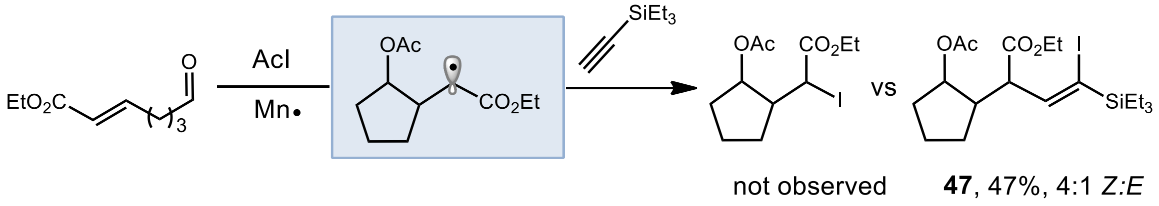
**(*E*)-methyl 2-(2-acetoxycyclopentylidene)-2-iodoacetate.** $^1$H NMR ($CDCl_3$, 400 MHz): δ 1.70-1.81 (m, 1H), 2.02 (s, 3H), 1.84-2.04 (m, 2 H), 2.08-2.18 (m, 1H), 2.37-2.48 (td, J = 7.82, 18.97 Hz, 1H), 2.61-2.72 (m, 1H), 3.76 (s, 3H), 5.99 (m, 1H); $^{13}$C NMR ($CDCl_3$, 150 MHz): δ 21.03, 21.85, 35.60, 42.00, 53.34, 74.43, 162.91, 164.01, 169.89. IR (film): 1705, 1226, 1021, 756 cm$^{-1}$; HRMS (ESI) for $C_{10}H_{13}IO_4Na$ $[M+Na]^+$: calcd 346.9756, found 346.9728. $R_f = 0.23$ (10% ethyl acetate/90% hexanes).



**(*Z*)-45**

**(*Z*)-Methyl 2-(2-acetoxycyclopentylidene)-2-iodoacetate.** $^1$H NMR ($CDCl_3$, 600 MHz): δ 1.83-2.04 (m, *J* = 4H), 2.10 (s, 3H), 2.73 (m, 1 H), 2.93-3.00 (m, 1H), 3.81 (s, 3H), 5.56 (m, 1H); $^{13}$C NMR ($CDCl_3$, 150 MHz): δ 21.09, 24.91, 33.19, 35.52, 53.35, 82.28, 85.83, 164.40, 164.46, 170.29. IR (film): 2952, 1736, 1709, 1220, 1030 cm$^{-1}$; HRMS (ESI) for $C_{10}H_{13}IO_4Na$ $[M+Na]^+$: 346.9756, found 346.9744. $R_f$ = 0.31 (10% ethyl acetate/90% hexanes)

**Fig. S7:** Three components



To an 8 mL vial was added DCM (0.5 mL), AcI (0.6 mmol), $Zn(OTf)_2$ (0.025 mmol) and aldehyde (0.5 mmol) consecutively at 0 ºC. The mixture was stirred at the same temperature for 15 min. To this mixture was added DIPEA (0.25 mmol) at 0 ºC, then the mixture was stirred for another 15 min. Triethylsilyl acetylene (2.5 mmol) and $Mn_2(CO)_{10}$ (0.025 mmol) was added to the mixture. The reaction was degassed by chill-pump-thaw for 20 min at -78 °C, then irradiated with one 90 W Blue LED lamp (at approximately 5 cm away from the light source). After 2 h, the crude product was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate = 95:5) to afford product **47** of several isomers in 47% yield as a colorless oil.

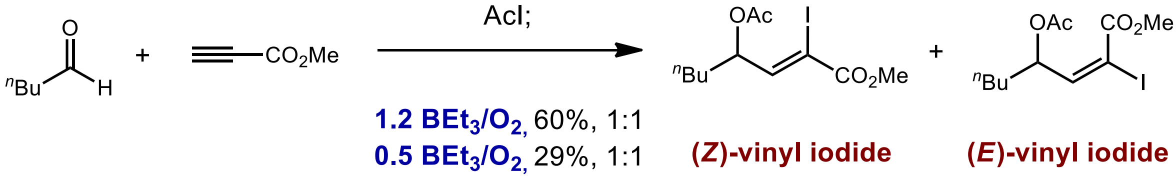
**(*Z*)-Ethyl 2-(2-acetoxycyclopentyl)-4-iodo-4-(triethylsilyl)but-3-enoate.**

First fraction (22% yield, containing two isomers): Rf = 0.30 (9% ethyl acetate/91% hexanes). Ratio of the two *Z* isomers: 3:1, *Z:E* ratio of the major isomers > 20:1. $^1$H NMR ($CDCl_3$, 400 MHz): δ 0.64-0.71 (q, overlap), 0.89-0.93 (t, overlap), 1.22-1.26 (t, overlap), 1.60-1.92 (m, overlap), 1.98 (s), 2.05 (s), 2.32-2.40 (m), 2.46-2.53 (m), 3.57 (t, *J* = 8.8 Hz), 3.72 (dd, *J* = 10.8, 8.8 Hz), 4.11-4.17 (q, overlap), 4.89-4.93 (m), 4.99 (t, *J* = 5.2 Hz), 6.08 (d, *J* = 8.8 Hz), 6.21 (d, *J* = 9.2 Hz); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 3.00, 3.01, 6.97, 7.02, 14.17, 14.19, 21.25, 21.83, 22.04, 22.84, 27.63, 28.29, 32.27, 32.57, 46.03, 47.15, 55.70, 57.67, 60.78, 60.81, 76.16, 78.38, 112.60, 113.67, 144.55, 144.98, 170.29, 170.34, 171.52, 171.85. IR (film): 2953, 2874, 1731, 1370, 1235, 1148, 1017, 732 cm$^{-1}$; HRMS (ESI) for $C_{19}H_{33}IO_4SiNa$ $[M+Na]^+$: calcd 503.1090, found 503.1067.

Second fraction (25% yield, containing three isomers): $R_f$ = 0.25 (9% ethyl acetate/91% hexanes). Ratio of the two *Z* isomers: 4:1, *Z:E* ratio of the major isomers 4:1. $^1$H NMR ($CDCl_3$, 400 MHz): δ 0.66-0.87 (q, overlap), 0.90-1.00 (t, overlap), 1.18-1.26 (t, overlap), 1.53-1.97 (m, overlap), 1.98 (s), 2.00 (s), 2.06 (s), 2.21-2.30 (m), 2.32-2.40 (m), 2.43-2.50 (m), 3.30 (t, *J* = 10.8 Hz), 3.61 (t, *J* = 8.8 Hz), 3.79 (dd, *J* = 10.4, 9.2 Hz), 4.05-4.16 (q, overlap), 4.90-4.94 (m), 5.10-5.13 (m), 5.15-5.18 (m), 6.04 (d, *J* = 9.2 Hz), 6.13 (d, *J* = 9.2 Hz), 7.13 (d, *J* = 11.2 Hz); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 3.00, 3.01, 4.78, 7.02, 7.27, 7.31, 14.04, 14.07, 14.10, 20.98, 21.15, 21.23, 21.90, 22.02, 22.56, 27.48, 27.55, 28.20, 32.03, 32.64, 32.74, 45.82, 47.05, 51.20, 55.29, 57.20, 60.79, 60.85, 60.92, 76.05, 76.12, 78.30, 109.82, 112.66, 113.48, 144.32, 145.13, 153.12, 170.04, 170.43, 171.27, 171.66, 172.02. IR (film): 2953, 2874, 1732, 1370, 1236, 1149, 1019, 723 cm$^{-1}$; HRMS (ESI) for $C_{19}H_{33}IO_4SiNa$ $[M+Na]^+$: calcd 503.1090, found 503.1080. (06-188, 204, 201)

## e. Unlikely propagation pathway

**Fig. S8:** Stoichiometric experiment

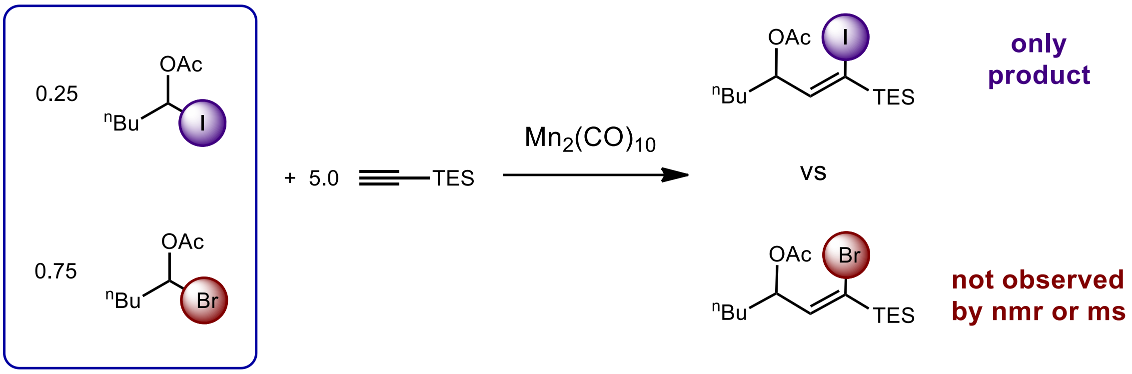


To an 8 mL vial was added aldehyde (53 μL, 0.5 mmol) and AcI (50 μL, 0.6 mmol). The mixture was stirred at 0℃ for 15 min. To this mixture was added $CH_2Cl_2$ (0.5 mL), methyl propiolate (89 µL, 1.0 mmol), iodoethane (201 µL, 2.5 mmol) and $BEt_3$ (0.6 mL, 0.6 mmol, 1.0 M in hexanes) at 0℃. Then $O_2$ (11.2 mL, 0.5 mmol) was bubbled through the solution via syringe pump (12 mL/h) at 0℃. After the addition was finished, the reaction was warmed up to room temperature and stirred for another 2 hours. Then the solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel. *Z*:*E* ratios were determined using purified products via $^1$H NMR.

**Hypothesis:** The yield should be lower when catalytic $BEt_3$ was used compared with the stoichiometric case to support a non-propagative mechanism.

**Result:** Stoichiometric $BEt_3$ (1.2 equiv.) yielded 60% of the desired product while substoichiometric $BEt_3$ (0.5 equiv.) provided only 29% of the desired product indicating propagation pathway is unlikely.

**Fig. S9:** Competition experiment

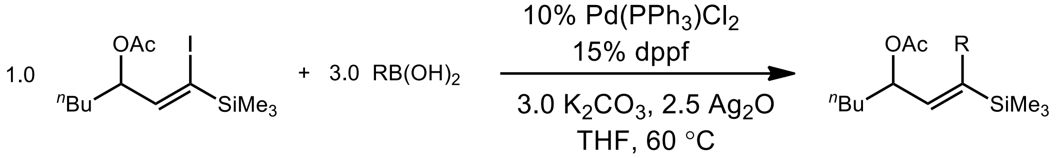


To an 8 mL vial was added DCM (0.5 mL), α-acetoxy bromide (0.125 mmol), α-acetoxy iodide (0.375 mmol) and DIPEA (0.25 mmol) consecutively at 0 ºC. The mixture was stirred for 15 min. Triethylsilyl acetylene (2.5 mmol) and $Mn_2(CO)_{10}$ (0.025 mmol) were added to the mixture. The reaction mixture was degassed by chill-pump-thaw for 20 min, then irradiated with one 90 W blue LED lamp (Kessil A360WE tuna blue) at approximately 5 cm away from the light source. The reaction temperature was approximately 40 ºC. After 2 h, the solvent was removed under vacuum and the crude product was detected by ESI-ms and purified by column chromatography on silica gel.

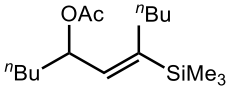
**Hypothesis:** The vinyl radical formed in the reaction is capable of abstracting a halogen atom from α-acetoxy iodide or α-acetoxy bromide. If a propagative mechanism is operative, both vinyl iodide and vinyl bromide should form.

**Result**: Only vinyl iodide was observed, which does not support an efficient propagation pathway.

**Synthetic manipulation of vinyl iodide:** *(59)*

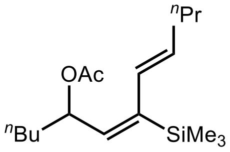


A suspension of boronic acid (3.0 equiv.), vinyl iodide (1.0 equiv.), $Pd(PPh_3)_2Cl_2$ (0.1 equiv.), dppf (0.15 equiv.), powdered $K_2CO_3$ (3 equiv.), and $Ag_2O$ (2.5 equiv.) in THF was stirred under nitrogen at 60°C for 12 h in a sealed tube. The reaction was filtered and washed with diethyl ether. The organic layer was combined and concentrated under vacuum. The residue was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate = 100:1) to afford the product.



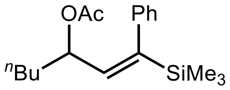
**48**

**(*E*)-7-(Trimethylsilyl)undec-6-en-5-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 100:1) afforded the title product in 77% yield as a colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ 0.08 (s, 9H), 0.89 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H), 1.20-1.38 (m, 8H), 1.44-1.52 (m, 1H), 1.61-1.70 (m, 1H), 2.03 (s, 3H), 2.10-2.19 (m, 1H), 2.22-2.29 (m, 1H), 5.56-5.64 (m, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ -1.22, 13.95, 21.39, 22.54, 23.11, 27.31, 30.12, 32.54, 34.65, 70.54, 137.13, 145.66, 170.31. IR (film): 2956, 2931, 2861, 1736, 1369, 1234, 1015, 833, 752 cm$^{-1}$; HRMS (ESI) for $C_{16}H_{32}O_2SiNa$ $[M+Na]^+$: calcd 307.2069, found 307.2066. $R_f$ = 0.4 (5% ethyl acetate/95% hexanes).



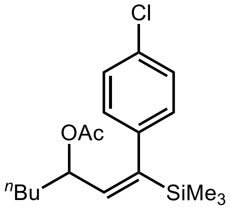
**49**

**(6*E*, 8*E*)-7-(Trimethylsilyl)dodeca-6,8-dien-5-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 100:1) afforded the title product in 73% yield as a yellow oil. $^1$H NMR (600 MHz, $CDCl_3$): δ 6.33 (d, *J* = 15.9 Hz, 1H), 5.72 (q, *J* = 7.2 Hz, 1H), 5.66-5.61 (m, 1H), 5.53 (d, *J* = 8.5 Hz, 1H), 2.08 (q, *J* = 7.2 Hz, 2H), 2.03 (s, 3H), 1.68-1.62 (m, 1H), 1.53-1.47 (m, 1H), 1.45-1.39 (m, 2H), 1.33-1.21 (m, 4H), 0.91 (t, *J* = 7.4 Hz, 3H), 0.88 (t, J = 7.1 Hz, 3H), 0.13 (s, 9H); $^{13}$C NMR (150 MHz, $CDCl_3$): δ 170.32, 142.51, 137.69, 134.46, 128.53, 71.40, 35.68, 34.67, 27.36, 22.79, 22.65, 21.41, 14.01, 13.70, -0.59. IR (film): 2958, 2862, 1738, 1370, 1235, 1018, 837 cm$^{-1}$; HRMS (ESI) for $C_{17}H_{32}NaO_2Si$ [M+Na]$^+$: calcd 319.2069, found 319.2051. Rf = 0.36 (3% ethyl acetate in hexanes).



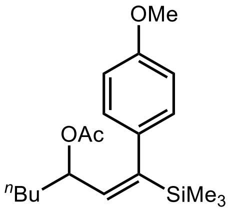
**50**

**(*E*)-1-Phenyl-1-(trimethylsilyl)hept-1-en-3-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 100:1) afforded the title product in 62% yield as a brown oil. $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.31-7.27 (m, 2H), 7.20-7.16 (m, 1H), 6.95-6.93 (m, 2H), 5.82 (d, *J* = 8.2 Hz, 1H), 5.15-5.10 (m, 1H), 1.98 (s, 3H), 1.60-1.52 (m, 1H), 1.47-1.38 (m, 1H), 1.21-1.13 (m, 4H), 0.83-0.80 (m, 3H), 0.06 (s, 9H); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ 170.01, 148.11, 141.48, 138.65, 128.16, 127.50, 125.87, 72.64, 34.53, 27.22, 22.49, 21.30, 13.91, -1.69. IR (film): 2957, 2861, 1739, 1370, 1246, 836 cm$^{-1}$; HRMS (ESI) for $C_{18}H_{28}O_2SiNa$ [M+Na]$^+$: calcd 327.1757, found 327.1740. R$_f$ = 0.47 (5% ethyl acetate/95% hexanes).



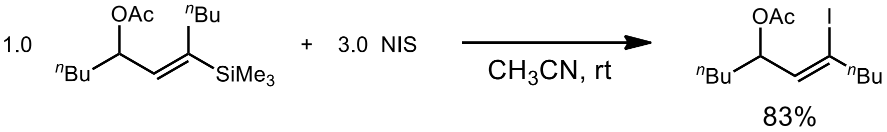
**51**

**(*E*)-1-(4-Chlorophenyl)-1-(trimethylsilyl)hept-1-en-3-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 100:1) afforded the title product in 72% yield as a brown oil. $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.27 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 2H), 5.81 (d, *J* = 8.3 Hz, 1H), 5.07 (q, *J* = 7.2 Hz, 1H), 1.98 (s, 3H), 1.61-1.52 (m, 1H), 1.45-1.38 (m, 1H), 1.21-1.14 (m, 4H), 0.84-0.81 (m, 3H), 0.05 (s, 9H); $^{13}$C NMR (CDCl$_3$, 150 MHz): δ 169.98, 146.95, 140.01, 139.38, 132.00, 128.92, 128.45, 72.57, 34.49, 27.25, 22.51, 21.22, 13.87, -1.72. IR (film): 2956, 2861, 1738, 1487, 1370, 1234, 1015, 838 cm$^{-1}$; HRMS (ESI) for $C_{18}H_{27}O_2ClSiNa$ [M+Na]$^+$: calcd 361.1367, found 361.1337. R$_f$ = 0.4 (5% ethyl acetate/95% hexanes).

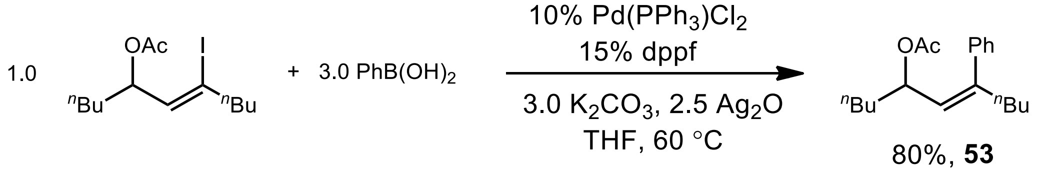


**52**

**(*E*)-1-(4-Methoxyphenyl)-1-(trimethylsilyl)hept-1-en-3-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 100:1) afforded the title product in 56% yield as a brown oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ 6.88-6.83 (m, 4H), 5.80 (d, *J* = 8.3 Hz, 1H), 5.18-5.13 (m, 1H), 3.80 (s, 3H), 1.99 (s, 3H), 1.61-1.52 (m, 1H), 1.46-1.38 (m, 1H), 1.20-1.13 (m, 4H), 0.84-0.80 (m, 3H), 0.05 (s, 9H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 170.06, 158.02, 147.68, 138.89, 133.60, 128.51, 113.78, 72.66, 55.31, 34.51, 27.22, 22.51, 21.35, 13.93, -1.67. IR (film): 2955, 2860, 1737, 1506, 1239, 1035, 837 cm$^{-1}$; HRMS (ESI) for $C_{19}H_{30}O_3ClSiNa$ [M+Na]$^+$: calcd 357.1862, found 357.184. $R_f$ = 0.46 (10% ethyl acetate in hexanes).



According to the known literature procedure *(60)*, the vinylsilane (42.7 mg, 0.15 mmol) was dissolved in acetonitrile (4 mL) at room temperature and treated with NIS (67.5 mg, 0.3 mmol). The reaction was stirred for 18 h and another portion of NIS (33.7 mg, 0.15 mmol) was added to fully consume the starting material. After 2 h the mixture was washed with saturated aqueous $Na_2SO_3$ and dried over $Na_2SO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (eluent: hexanes/ethyl acetate = 100:1) to afford product in 83% yield as a pale yellow oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ 0.90 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 1.25-1.39 (m, 6H), 1.47-1.54 (m, 2H), 1.57-1.72 (m, 2H), 2.04 (s, 3H), 2.46-2.50 (m, 2H), 5.34-5.39 (m, 1H), 5.56 (dt, *J* = 1.2, 8.0 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 13.79, 13.94, 21.14, 21.27, 22.53, 26.96, 31.30, 33.53, 45.09, 78.71, 111.18, 133.47, 170.10. IR (film): 2956, 2930, 2860, 1739, 1370, 1231, 1018 cm$^{-1}$; HRMS (ESI) for $C_{13}H_{23}IO_2Na$ [M+Na]$^+$: calcd 361.0640, found 361.0623. $R_f$ = 0.35 (5% ethyl acetate/95% hexanes).



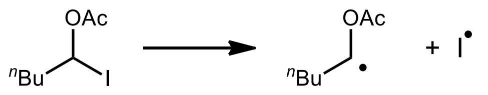
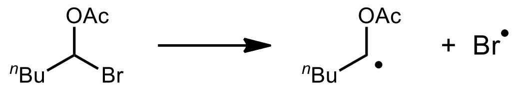
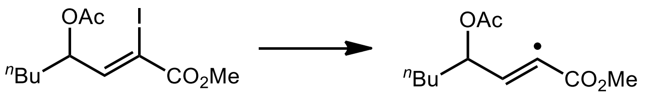
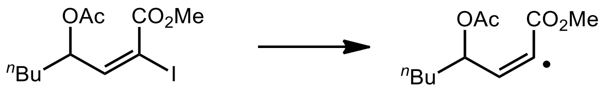
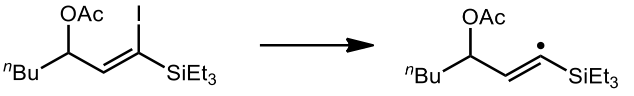
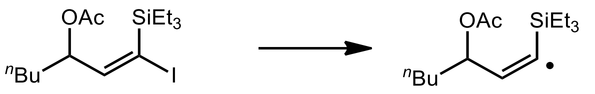
**(*Z*)-7-Phenylundec-6-en-5-yl acetate.** Column chromatography on silica gel (eluent: hexanes/ethyl acetate = 100:1) afforded the title product in 80% yield as a colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ 0.83 (t, *J* = 7.2 Hz, 3H), 0.86 (t, *J* = 6.8 Hz, 3H), 1.13-1.36 (m, 8H), 1.42-1.51 (m, 1H), 1.56-1.65 (m, 1H), 1.98 (s, 3H), 2.31-2.35 (m, 2H), 5.12-5.17 (m, 1H), 5.38 (dt, *J* = 1.2, 9.2 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 13.86, 13.88, 21.30, 22.22, 22.39, 27.12, 29.82, 34.76, 39.15, 72.52, 125.27, 126.88, 127.96, 128.04, 140.44, 145.46, 170.01. IR (film): 2956, 2930, 2860, 1734, 1466, 1368, 1236, 1016, 701 cm$^{-1}$; HRMS (ESI) for $C_{10}H_{28}O_2Na$ $[M+Na]^+$: calcd 311.1987, found 311.1964. $R_f$ = 0.33 (5% ethyl acetate/95% hexanes).

**Computational studies:**

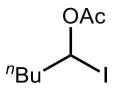
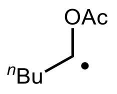
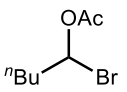
**Table S4:** Density functional theory (DFT) calculations

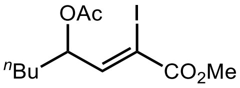
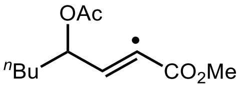
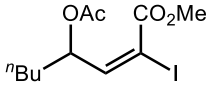
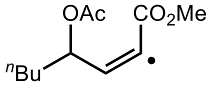
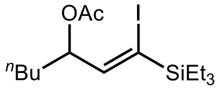
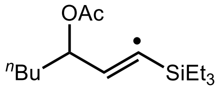
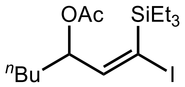
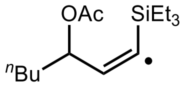
DFT calculations were performed using Spartan '16. All geometries were optimized using the ωB97X-D method with 6-31G* basis set to determinate homolytic bond dissociation enthalpies (BDE). All the optimizations were done using a CPCM implicit solvation model simulating THF.

**a. Bond Dissociation Enthalpy (BDE) Calculations**

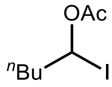
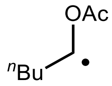
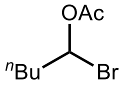
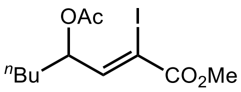
| Fragmentation Reaction | BDE (kcal/mol) |
|---|---|
|  | 57.72 |
|  | 71.15 |
|  | 68.45 |
|  | 64.91 |
|  | 62.25 |
|  | 61.14 |

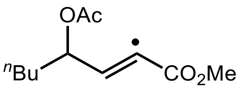
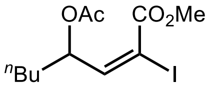
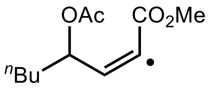
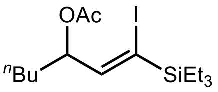
**b. Total energy**

| | Total Energy (hartrees) | Total Energy (kcal/mol) |
|---|---|---|
|  | -436.315478 | -273791.8893 |
|  | -424.852787 | -266598.9475 |
|  | -2998.8398 | -1881798.964 |

|  |  |  |
|---|---|---|
|  | -741.493982 | -465294.1472 |
|  | -730.01531 | -458090.4737 |
|  | -741.489455 | -465291.3064 |
|  | -730.01531 | -458091.1772 |
|  | -1040.220037 | -652747.4352 |
|  | -1028.75012 | -645549.9591 |
|  | -1040.213848 | -652743.5515 |
|  | -1028.745699 | -645547.1848 |
| $I^\bullet$ | -11.370712 | -7135.224116 |
| $Br^\bullet$ | -2573.873636 | -1615128.871 |

## c. Optimized Cartesian Coordinates

| | Cartesian Coordinates | | | | | |
|---|---|---|---|---|---|---|
|  | 1 | C | C1 | 1.5101045 | -0.3160772 | 0.4001013 |
| | 2 | H | H3 | 1.1501530 | -1.2159342 | 0.8965908 |
| | 3 | O | O1 | 1.6049600 | -0.4638942 | -0.9821028 |
| | 4 | C | C2 | 1.7763165 | -1.6732930 | -1.5954651 |
| | 5 | O | O2 | 1.8985647 | -1.6576480 | -2.7933824 |
| | 6 | C | C3 | 1.7739362 | -2.9189994 | -0.7537552 |
| | 7 | H | H1 | 2.5404205 | -2.8763738 | 0.0261353 |
| | 8 | H | H5 | 1.9706202 | -3.7670456 | -1.4085311 |
| | 9 | H | H6 | 0.8005966 | -3.0554573 | -0.2712727 |
| | 10 | I | I1 | 3.5446960 | -0.0548793 | 1.2576307 |
| | 11 | C | C4 | 0.6530543 | 0.8922460 | 0.7144158 |
| | 12 | H | H2 | 1.0929051 | 1.7811033 | 0.2493054 |
| | 13 | H | H4 | 0.6601502 | 1.0455801 | 1.7982992 |
| | 14 | C | C5 | -0.7850986 | 0.6910260 | 0.2231589 |
| | 15 | H | H7 | -0.7851145 | 0.5599299 | -0.8653458 |
| | 16 | H | H9 | -1.1942135 | -0.2327754 | 0.6551869 |
| | 17 | C | C6 | -1.6860288 | 1.8694335 | 0.5958551 |
| | 18 | H | H8 | -1.2627728 | 2.7925643 | 0.1788939 |
| | 19 | H | H10 | -1.6886433 | 1.9928380 | 1.6866815 |
| | 20 | C | C7 | -3.1177633 | 1.6885247 | 0.0944810 |
| | 21 | H | H11 | -3.1408690 | 1.5927170 | -0.9971957 |
| | 22 | H | H12 | -3.7457987 | 2.5416931 | 0.3713542 |
| | 23 | H | H13 | -3.5701753 | 0.7847214 | 0.5189607 |
|  | 1 | C | C1 | 0.9676760 | -0.6195099 | -0.4775438 |
| | 2 | H | H3 | 0.3697727 | -1.3233041 | -1.0519148 |
| | 3 | O | O1 | 2.3313569 | -0.6652322 | -0.6748104 |
| | 4 | C | C2 | 3.0026361 | -1.8375113 | -0.8125506 |
| | 5 | O | O2 | 4.1835848 | -1.7797571 | -1.0607021 |
| | 6 | C | C3 | 2.2265006 | -3.1132609 | -0.6377335 |
| | 7 | H | H1 | 1.6274981 | -3.0841943 | 0.2771836 |
| | 8 | H | H5 | 2.9297200 | -3.9449555 | -0.6035935 |
| | 9 | H | H6 | 1.5415089 | -3.2596061 | -1.4798940 |
| | 10 | C | C4 | 0.4519013 | 0.7227631 | -0.1041376 |
| | 11 | H | H2 | 0.6200914 | 1.4377879 | -0.9283651 |
| | 12 | H | H4 | 1.0285179 | 1.1064662 | 0.7489336 |
| | 13 | C | C5 | -1.0391038 | 0.6899972 | 0.2418995 |
| | 14 | H | H7 | -1.6049639 | 0.3083463 | -0.6189957 |
| | 15 | H | H9 | -1.2061434 | -0.0179588 | 1.0644134 |
| | 16 | C | C6 | -1.5813143 | 2.0641837 | 0.6349658 |
| | 17 | H | H8 | -1.4069639 | 2.7701476 | -0.1878392 |
| | 18 | H | H10 | -1.0123844 | 2.4430355 | 1.4941729 |
| | 19 | C | C7 | -3.0696880 | 2.0336656 | 0.9781875 |
| | 20 | H | H11 | -3.6620590 | 1.6889378 | 0.1225153 |
| | 21 | H | H12 | -3.4334069 | 3.0271034 | 1.2607824 |
| | 22 | H | H13 | -3.2647364 | 1.3528554 | 1.8150268 |
|  | 1 | C | C1 | 1.5029644 | -0.3313961 | 0.4036668 |
| | 2 | H | H3 | 1.1290354 | -1.2312990 | 0.8898279 |
| | 3 | O | O1 | 1.5981919 | -0.4721647 | -0.9807644 |
| | 4 | C | C2 | 1.7899652 | -1.6781306 | -1.5952456 |
| | 5 | O | O2 | 1.9109486 | -1.6601585 | -2.7931456 |
| | 6 | C | C3 | 1.8075124 | -2.9251348 | -0.7548319 |
| | 7 | H | H1 | 2.5645608 | -2.8680642 | 0.0327812 |
| | 8 | H | H5 | 2.0278209 | -3.7676649 | -1.4092592 |
| | 9 | H | H6 | 0.8320765 | -3.0830271 | -0.2830556 |
| | 10 | C | C4 | 0.6533558 | 0.8809550 | 0.7201411 |
| | 11 | H | H2 | 1.1037409 | 1.7655231 | 0.2565172 |
| | 12 | H | H4 | 0.6639812 | 1.0307856 | 1.8045196 |
| | 13 | C | C5 | -0.7861759 | 0.6953634 | 0.2301162 |
| | 14 | H | H7 | -0.7884148 | 0.5659236 | -0.8586379 |
| | 15 | H | H9 | -1.2042715 | -0.2251553 | 0.6605871 |
| | 16 | C | C6 | -1.6763731 | 1.8811501 | 0.6048577 |
| | 17 | H | H8 | -1.2449319 | 2.8012284 | 0.1895278 |
| | 18 | H | H10 | -1.6778444 | 2.0026802 | 1.6959031 |
| | 19 | C | C7 | -3.1096926 | 1.7139358 | 0.1033076 |
| | 20 | H | H11 | -3.1337821 | 1.6211983 | -0.9886180 |
| | 21 | H | H12 | -3.7305303 | 2.5716004 | 0.3825155 |
| | 22 | H | H13 | -3.5696518 | 0.8128443 | 0.5254488 |
| | 23 | Br | Br1 | 3.3375143 | -0.1009927 | 1.1638404 |
|  | 1 | H | H1 | 1.6103575 | 2.0810467 | -3.2794658 |
| | 2 | C | C1 | 1.3817234 | 2.4275922 | -2.2631190 |
| | 3 | H | H2 | 2.3456136 | 2.5431432 | -1.7502132 |
| | 4 | C | C2 | 0.6691010 | 3.7771793 | -2.3283314 |
| | 5 | H | H4 | 1.2774749 | 4.5236030 | -2.8495075 |
| | 6 | H | H5 | 0.4581883 | 4.1572282 | -1.3219430 |
| | 7 | H | H6 | -0.2861222 | 3.6902362 | -2.8591509 |
| | 8 | C | C3 | 0.5534534 | 1.3632125 | -1.5426979 |
| | 9 | H | H7 | -0.4091887 | 1.2419431 | -2.0575100 |
| | 10 | H | H8 | 0.3224952 | 1.7129787 | -0.5278329 |
| | 11 | C | C4 | 1.2716251 | 0.0162696 | -1.4796217 |
| | 12 | H | H3 | 2.2286523 | 0.1195199 | -0.9533526 |
| | 13 | H | H9 | 1.4955627 | -0.3354078 | -2.4934384 |
| | 14 | C | C5 | 0.4531494 | -1.0834228 | -0.7992643 |
| | 15 | H | H11 | -0.5039167 | -1.1946757 | -1.3159908 |
| | 16 | O | O1 | 1.2305907 | -2.2871679 | -0.9363719 |
| | 17 | C | C6 | 0.6814822 | -3.5182101 | -0.8484972 |
| | 18 | O | O2 | 1.4234766 | -4.4675946 | -0.9499759 |
| | 19 | C | C7 | -0.8072288 | -3.6402976 | -0.6496630 |
| | 20 | H | H10 | -1.1341335 | -3.1063101 | 0.2472871 |
| | 21 | H | H13 | -1.0521706 | -4.6973937 | -0.5526406 |
| | 22 | H | H14 | -1.3477551 | -3.2232449 | -1.5054299 |
| | 23 | C | C8 | 0.2622391 | -0.8037225 | 0.6614980 |
| | 24 | H | H15 | 1.1515177 | -0.9460982 | 1.2743756 |
| | 25 | C | C9 | -0.8300574 | -0.3795412 | 1.3011973 |
| | 26 | I | I1 | -2.6687435 | -0.0307558 | 0.3330980 |
| | 27 | C | C10 | -0.7399606 | -0.1413780 | 2.7797923 |
| | 28 | O | O3 | 0.2845207 | -0.3144743 | 3.4063389 |
| | 29 | O | O4 | -1.8804440 | 0.2693508 | 3.3169617 |
| | 30 | C | C11 | -1.8546423 | 0.5142352 | 4.7300321 |
| | 31 | H | H12 | -1.5943986 | -0.4007047 | 5.2660277 |
| | 32 | H | H16 | -2.8626607 | 0.8357026 | 4.9854598 |
| | 33 | H | H17 | -1.1298011 | 1.2971585 | 4.9619496 |

|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
|  | 1 | H | H1 | 1.2011926 | 2.0758811 | -3.3682301 |
|  | 2 | C | C1 | 1.2234577 | 2.4030248 | -2.3204366 |
|  | 3 | H | H2 | 2.2823209 | 2.4621758 | -2.0361796 |
|  | 4 | C | C2 | 0.5815022 | 3.7839583 | -2.1987697 |
|  | 5 | H | H4 | 1.0939104 | 4.5181327 | -2.8291605 |
|  | 6 | H | H5 | 0.6193414 | 4.1432362 | -1.1637681 |
|  | 7 | H | H6 | -0.4712090 | 3.7545600 | -2.5034395 |
|  | 8 | C | C3 | 0.5283652 | 1.3555735 | -1.4497091 |
|  | 9 | H | H7 | -0.5283571 | 1.2818604 | -1.7424707 |
|  | 10 | H | H8 | 0.5380908 | 1.6905958 | -0.4045622 |
|  | 11 | C | C4 | 1.1842564 | -0.0203153 | -1.5593434 |
|  | 12 | H | H3 | 2.2261543 | 0.0262772 | -1.2188035 |
|  | 13 | H | H9 | 1.1990792 | -0.3453122 | -2.6064510 |
|  | 14 | C | C5 | 0.4524802 | -1.0984805 | -0.7616964 |
|  | 15 | H | H11 | -0.5856667 | -1.1577093 | -1.0993852 |
|  | 16 | O | O1 | 1.1396078 | -2.3332599 | -1.0396002 |
|  | 17 | C | C6 | 0.5465718 | -3.5386506 | -0.9089435 |
|  | 18 | O | O2 | 1.2265778 | -4.5195267 | -1.1060219 |
|  | 19 | C | C7 | -0.9182475 | -3.5983055 | -0.5583617 |
|  | 20 | H | H10 | -1.1360204 | -3.0438241 | 0.3586261 |
|  | 21 | H | H13 | -1.1937392 | -4.6443834 | -0.4280675 |
|  | 22 | H | H14 | -1.5208167 | -3.1670806 | -1.3645509 |
|  | 23 | C | C8 | 0.5098995 | -0.8331446 | 0.7210121 |
|  | 24 | H | H15 | 1.5017405 | -0.9144394 | 1.1781213 |
|  | 25 | C | C9 | -0.5261389 | -0.4859438 | 1.4554877 |
|  | 26 | C | C10 | -0.6679891 | -0.1451041 | 2.8762613 |
|  | 27 | O | O3 | 0.2589015 | -0.1562581 | 3.6604410 |
|  | 28 | O | O4 | -1.9214113 | 0.1710802 | 3.1877305 |
|  | 29 | C | C11 | -2.1572481 | 0.5189058 | 4.5601041 |
|  | 30 | H | H12 | -1.9027916 | -0.3200451 | 5.2112269 |
|  | 31 | H | H16 | -3.2204428 | 0.7434962 | 4.6232020 |
|  | 32 | H | H17 | -1.5633718 | 1.3930252 | 4.8357384 |
|  | 1 | C | C1 | -0.1075981 | -0.2415801 | -0.7434049 |
|  | 2 | H | H3 | -1.0630557 | 0.1136256 | -1.1270605 |
|  | 3 | C | C2 | 0.6030822 | 0.9210031 | -0.0464761 |
|  | 4 | H | H5 | -0.0821208 | 1.3048097 | 0.7168253 |
|  | 5 | H | H6 | 0.7353509 | 1.7132466 | -0.7934097 |
|  | 6 | C | C3 | 1.9496375 | 0.5693672 | 0.5863307 |
|  | 7 | H | H4 | 1.8082614 | -0.1969520 | 1.3608824 |
|  | 8 | H | H8 | 2.6121070 | 0.1339662 | -0.1719277 |
|  | 9 | C | C4 | 2.6245030 | 1.7900076 | 1.2127664 |
|  | 10 | H | H9 | 1.9522674 | 2.2279989 | 1.9626303 |
|  | 11 | H | H10 | 2.7702498 | 2.5576368 | 0.4410408 |
|  | 12 | C | C5 | 3.9661453 | 1.4531058 | 1.8608102 |
|  | 13 | H | H7 | 3.8410080 | 0.7081945 | 2.6554228 |
|  | 14 | H | H11 | 4.4292284 | 2.3417959 | 2.3022164 |
|  | 15 | H | H12 | 4.6642498 | 1.0401146 | 1.1233239 |
|  | 16 | O | O1 | 0.7348245 | -0.6455925 | -1.8386510 |
|  | 17 | C | C6 | 0.2542187 | -1.3329414 | -2.8964163 |
|  | 18 | O | O2 | 1.0392089 | -1.6533544 | -3.7588516 |
|  | 19 | C | C7 | -1.2201195 | -1.6439009 | -2.9539283 |
|  | 20 | H | H1 | -1.5533545 | -2.1830926 | -2.0624910 |
|  | 21 | H | H13 | -1.4048206 | -2.2531964 | -3.8379749 |
|  | 22 | H | H14 | -1.8049300 | -0.7210941 | -3.0264015 |
|  | 23 | C | C8 | -0.2855593 | -1.4288356 | 0.1726218 |
|  | 24 | H | H15 | 0.5750142 | -2.0934612 | 0.1865152 |
|  | 25 | C | C9 | -1.3394890 | -1.7348943 | 0.9356581 |
|  | 26 | I | I1 | -1.2965257 | -3.4955033 | 2.0989127 |
|  | 27 | C | C10 | -2.6319246 | -0.9852886 | 1.0247695 |
|  | 28 | O | O3 | -3.6765061 | -1.4665875 | 1.3997712 |
|  | 29 | O | O4 | -2.4929034 | 0.2846837 | 0.6430080 |
|  | 30 | C | C11 | -3.6900115 | 1.0771354 | 0.6460746 |
|  | 31 | H | H2 | -4.4248509 | 0.6520822 | -0.0403435 |
|  | 32 | H | H16 | -3.3795328 | 2.0659078 | 0.3135146 |
|  | 33 | H | H17 | -4.1060543 | 1.1215933 | 1.6542424 |
|  | 1 | C | C1 | 0.0603401 | -0.2855638 | -0.7319777 |
|  | 2 | H | H3 | -0.7959895 | 0.1116896 | -1.2817228 |
|  | 3 | C | C2 | 0.9035816 | 0.8841214 | -0.2263777 |
|  | 4 | H | H5 | 0.2457137 | 1.5214088 | 0.3770932 |
|  | 5 | H | H6 | 1.2024531 | 1.4704501 | -1.1042918 |
|  | 6 | C | C3 | 2.1402549 | 0.4933951 | 0.5829139 |
|  | 7 | H | H4 | 1.8375483 | -0.0428954 | 1.4921217 |
|  | 8 | H | H8 | 2.7577636 | -0.1992144 | -0.0020727 |
|  | 9 | C | C4 | 2.9776569 | 1.7101927 | 0.9791483 |
|  | 10 | H | H9 | 2.3542195 | 2.4053323 | 1.5572341 |
|  | 11 | H | H10 | 3.2837900 | 2.2488143 | 0.0725951 |
|  | 12 | C | C5 | 4.2138297 | 1.3308953 | 1.7927602 |
|  | 13 | H | H7 | 3.9308807 | 0.8151995 | 2.7178767 |
|  | 14 | H | H11 | 4.7985207 | 2.2157419 | 2.0656364 |
|  | 15 | H | H12 | 4.8654122 | 0.6588881 | 1.2222077 |
|  | 16 | O | O1 | 0.8953951 | -1.0574631 | -1.6096387 |
|  | 17 | C | C6 | 0.3903927 | -1.8423899 | -2.5854715 |
|  | 18 | O | O2 | 1.1707055 | -2.5185937 | -3.2157957 |
|  | 19 | C | C7 | -1.0903599 | -1.8037915 | -2.8601831 |
|  | 20 | H | H1 | -1.6851073 | -1.9781012 | -1.9601215 |
|  | 21 | H | H13 | -1.3160321 | -2.5652016 | -3.6062167 |
|  | 22 | H | H14 | -1.3719720 | -0.8220467 | -3.2561781 |
|  | 23 | C | C8 | -0.4244438 | -1.1879020 | 0.3931041 |
|  | 24 | H | H15 | 0.3257319 | -1.8477161 | 0.8295784 |
|  | 25 | C | C9 | -1.6497170 | -1.1713932 | 0.8544154 |
|  | 26 | C | C10 | -2.9439190 | -0.5718993 | 0.5724538 |
|  | 27 | O | O3 | -3.4574197 | -0.5813495 | -0.5322841 |
|  | 28 | O | O4 | -3.5041429 | -0.0493025 | 1.6617359 |
|  | 29 | C | C11 | -4.7935960 | 0.5524270 | 1.4737172 |
|  | 30 | H | H2 | -4.7207030 | 1.3925970 | 0.7797529 |
|  | 31 | H | H16 | -5.0983772 | 0.8970765 | 2.4602198 |
|  | 32 | H | H17 | -5.5024109 | -0.1834051 | 1.0877672 |
|  | 1 | H | H1 | 1.5894546 | 2.3934859 | -4.3797290 |
|  | 2 | C | C1 | 1.5047202 | 2.5998007 | -3.3047210 |
|  | 3 | H | H2 | 2.5183236 | 2.5150621 | -2.8910451 |
|  | 4 | C | C2 | 0.9800022 | 4.0186758 | -3.0917641 |
|  | 5 | H | H4 | 1.6374809 | 4.7612952 | -3.5557324 |
|  | 6 | H | H5 | 0.9090806 | 4.2518311 | -2.0226910 |
|  | 7 | H | H6 | -0.0201160 | 4.1357357 | -3.5252690 |
|  | 8 | C | C3 | 0.6083490 | 1.5458528 | -2.6546892 |
|  | 9 | H | H7 | -0.4053353 | 1.6223965 | -3.0705023 |
|  | 10 | H | H8 | 0.5218580 | 1.7633347 | -1.5817447 |
|  | 11 | C | C4 | 1.1368090 | 0.1260516 | -2.8525459 |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
| 12 | H | H3 | 2.1566297 | 0.0445130 | -2.4552299 |
| 13 | H | H9 | 1.1861428 | -0.1106683 | -3.9219367 |
| 14 | C | C5 | 0.2703228 | -0.9434448 | -2.1851925 |
| 15 | H | H11 | -0.7475928 | -0.8903918 | -2.5814796 |
| 16 | O | O1 | 0.8709957 | -2.2038165 | -2.5475730 |
| 17 | C | C6 | 0.2157011 | -3.3765290 | -2.4321346 |
| 18 | O | O2 | 0.8248822 | -4.3869802 | -2.7023876 |
| 19 | C | C7 | -1.2270558 | -3.3661386 | -1.9972509 |
| 20 | H | H10 | -1.3386846 | -2.8933188 | -1.0170541 |
| 21 | H | H13 | -1.5767617 | -4.3968127 | -1.9479852 |
| 22 | H | H14 | -1.8435854 | -2.8085065 | -2.7093502 |
| 23 | C | C8 | 0.2874431 | -0.8047980 | -0.6892740 |
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| 31 | C | C11 | -0.3948948 | 2.7771532 | 1.7246955 |
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| 35 | C | C12 | -1.9103387 | -0.3329284 | 2.9815381 |
| 36 | H | H22 | -2.4160033 | -1.2430379 | 2.6333711 |
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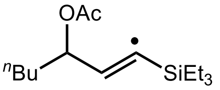

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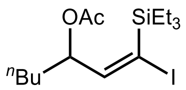

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| 21 | H | H13 | -0.7444965 | -1.7899937 | -4.4541036 |
| 22 | H | H14 | -1.0623415 | -0.2477997 | -3.6256416 |
| 23 | C | C8 | 0.6918241 | -1.0878597 | -0.5480875 |
| 24 | H | H15 | 1.5407253 | -1.7633365 | -0.6448116 |
| 25 | C | C9 | -0.3187216 | -1.3674013 | 0.2822906 |
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|  | 32 H | H16 | -2.6999325 | -2.2234639 | -1.6075947 |
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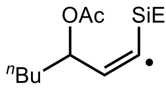
|  | 1 C | C1 | 0.8111619 | -0.3042043 | -1.6582618 |
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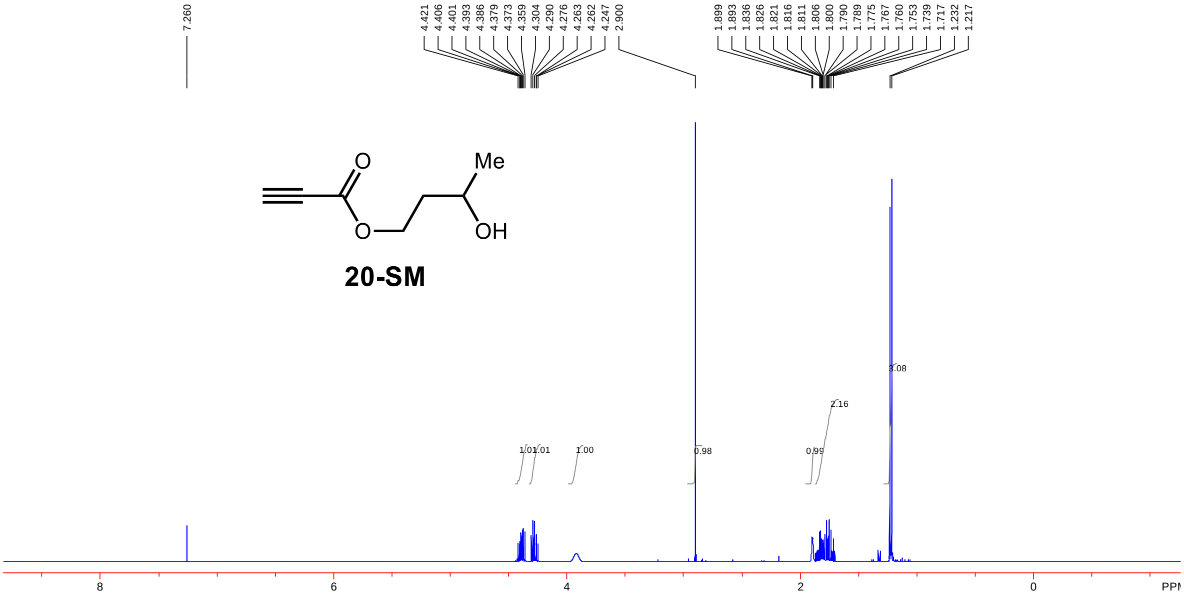
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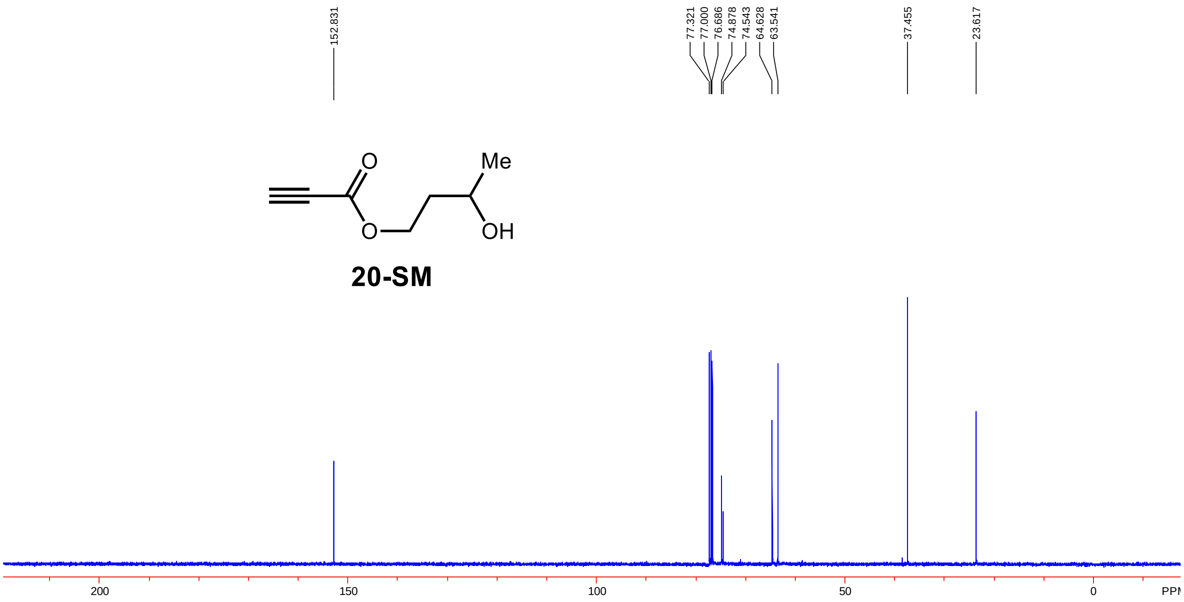
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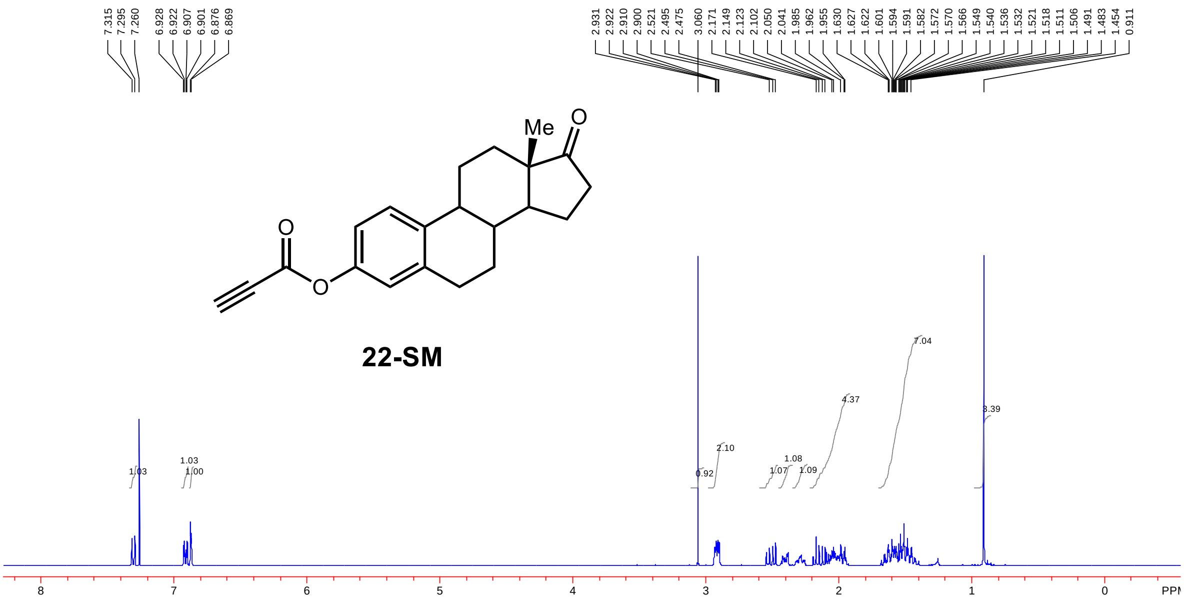
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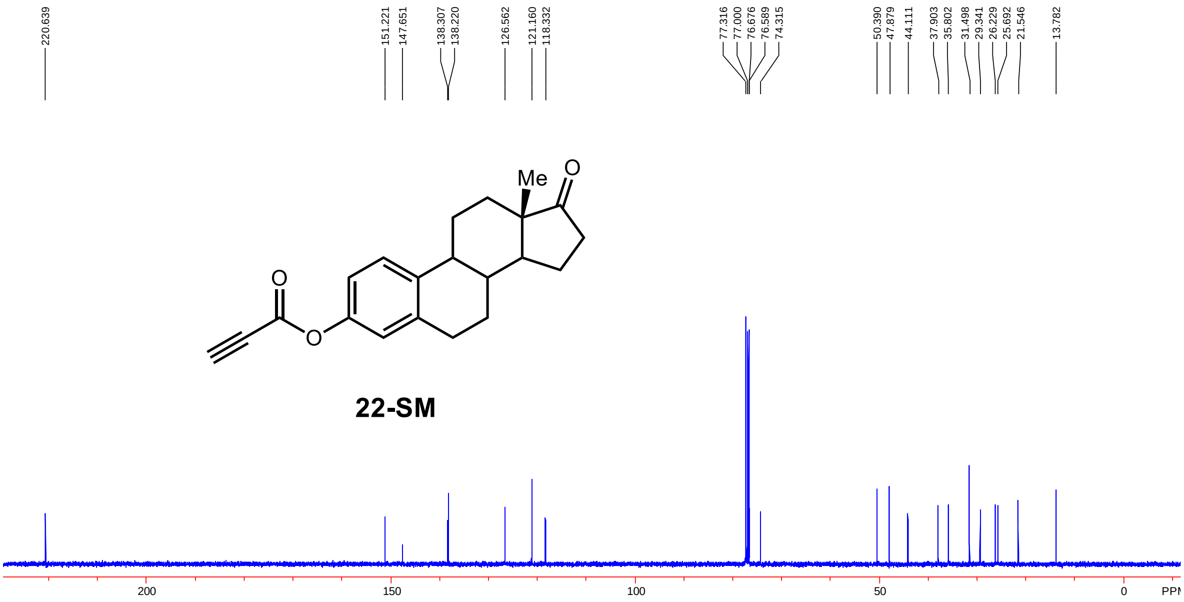
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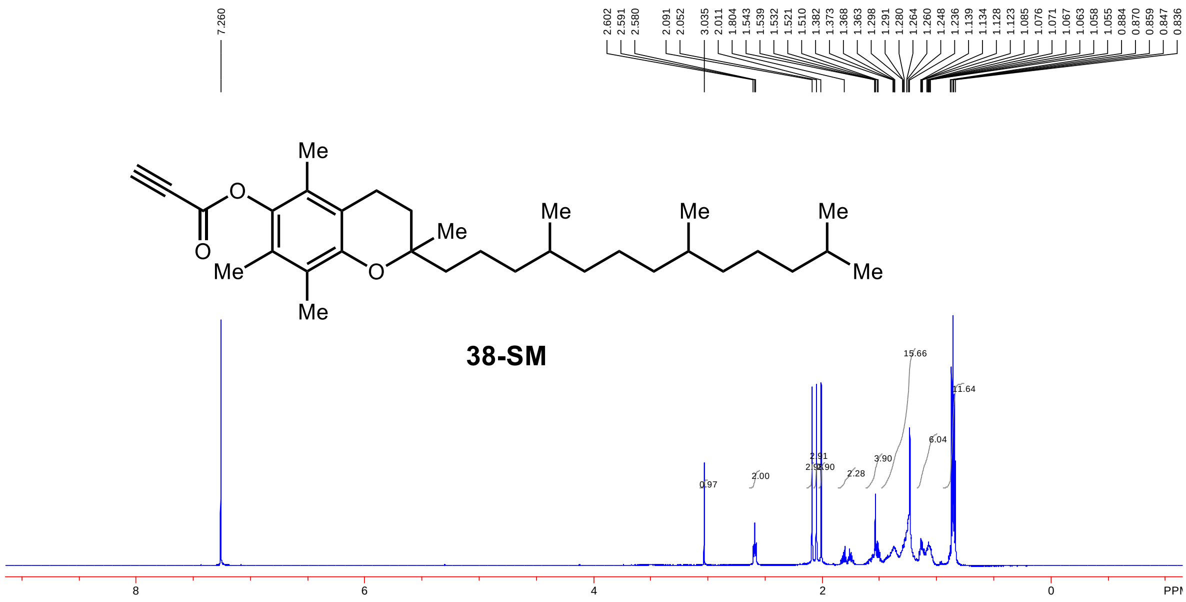
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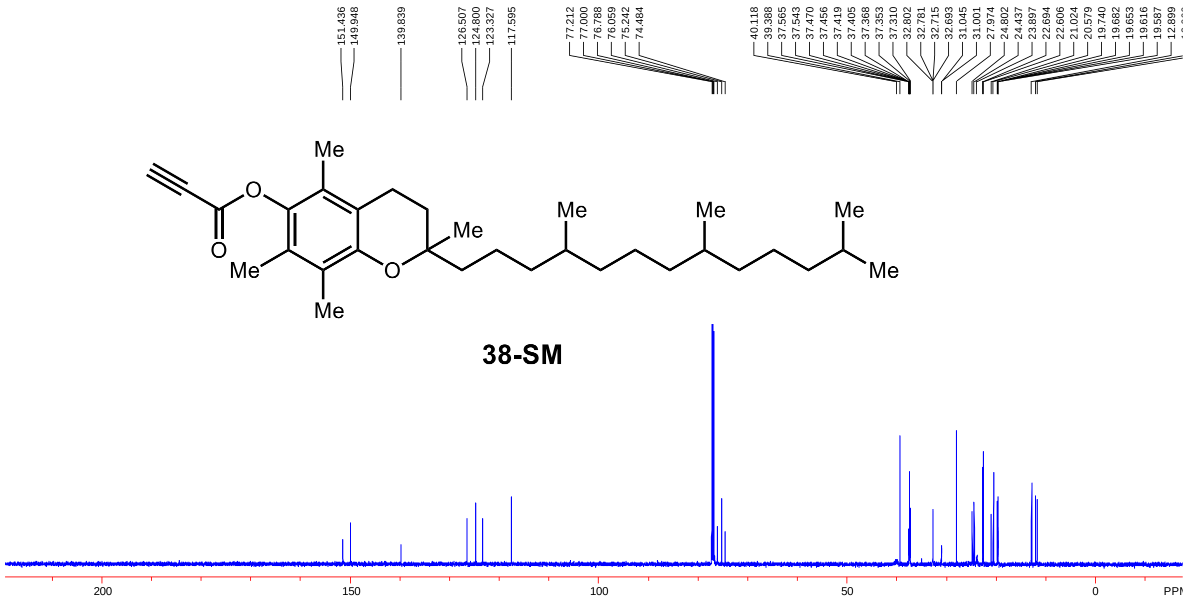
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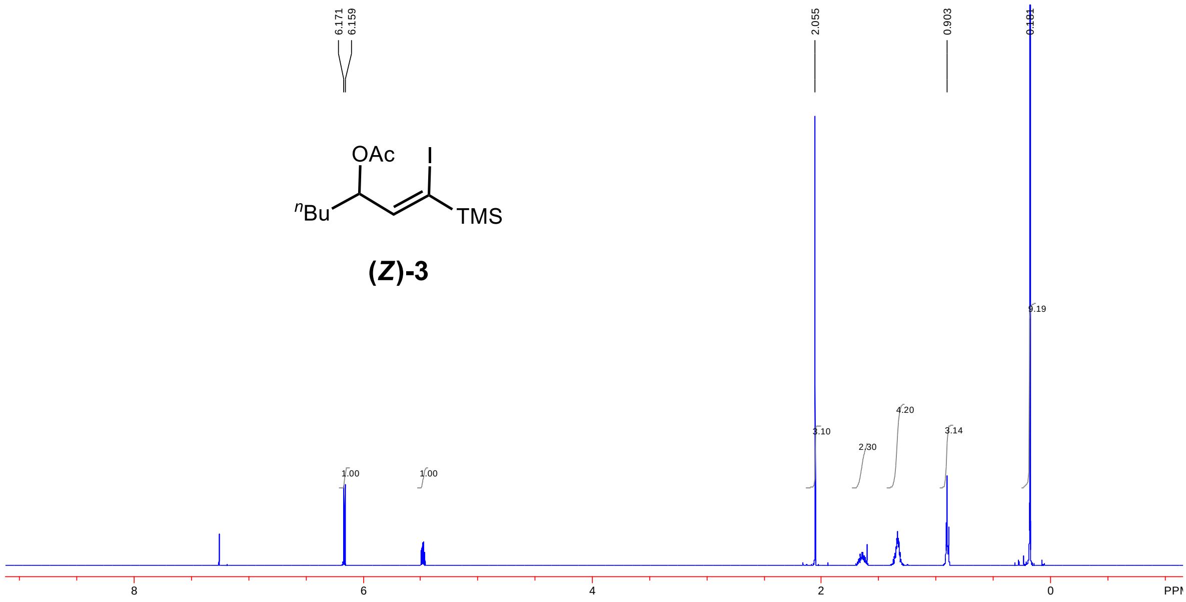
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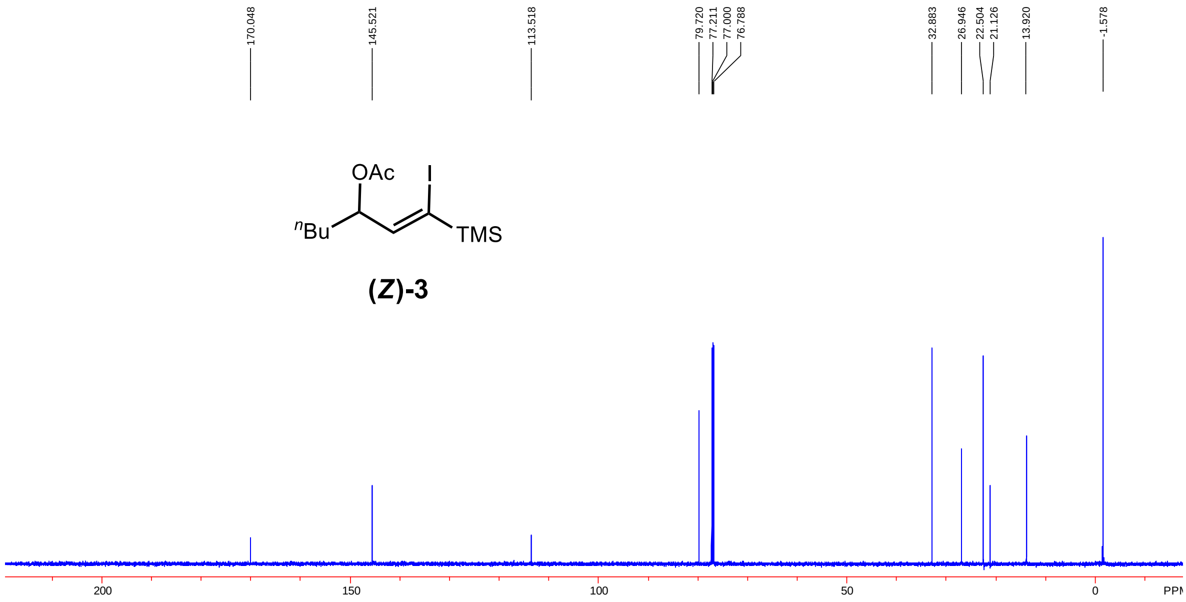
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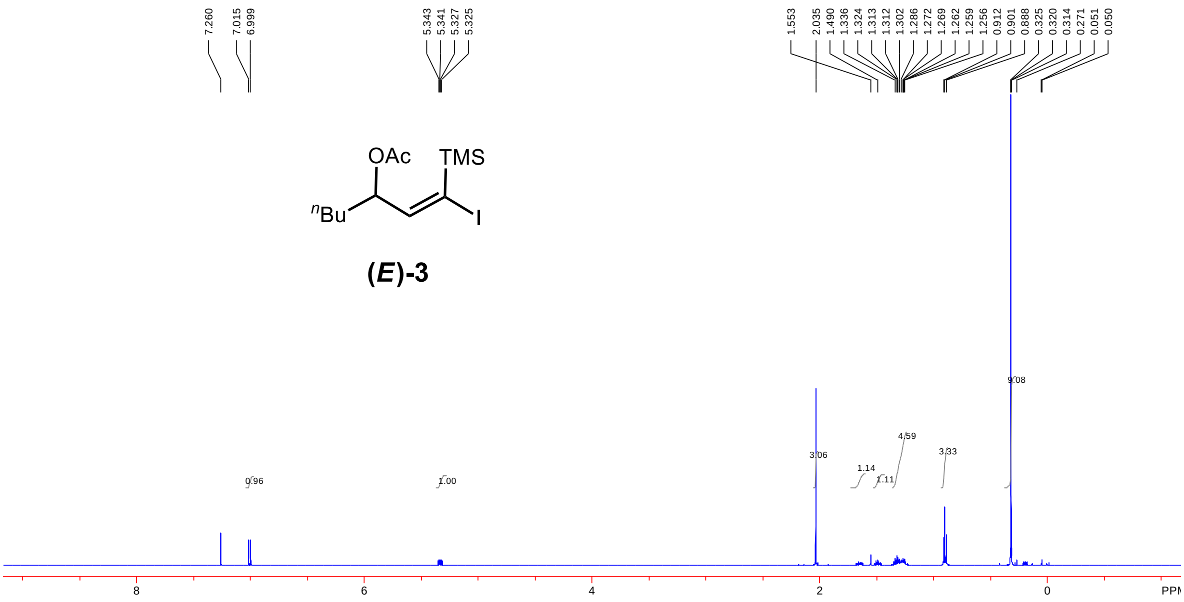
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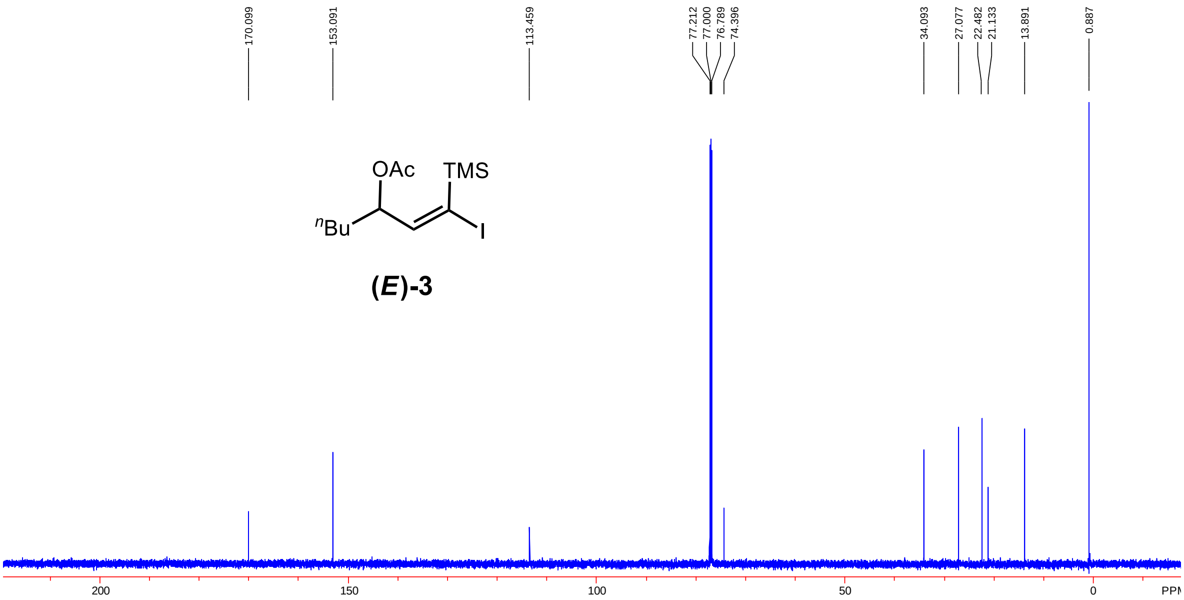
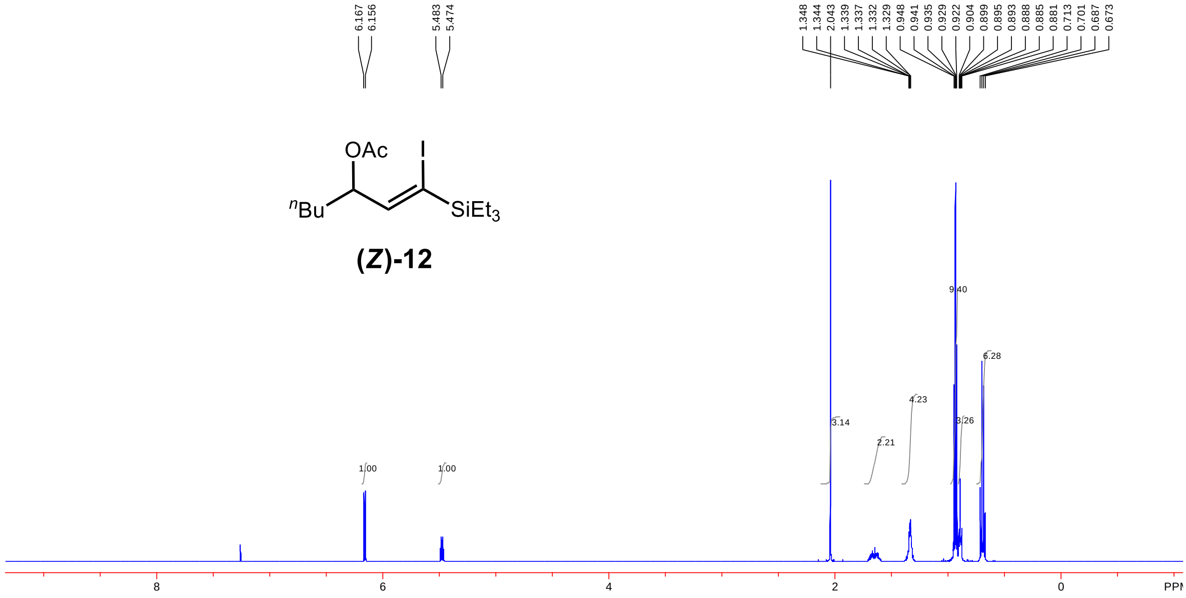
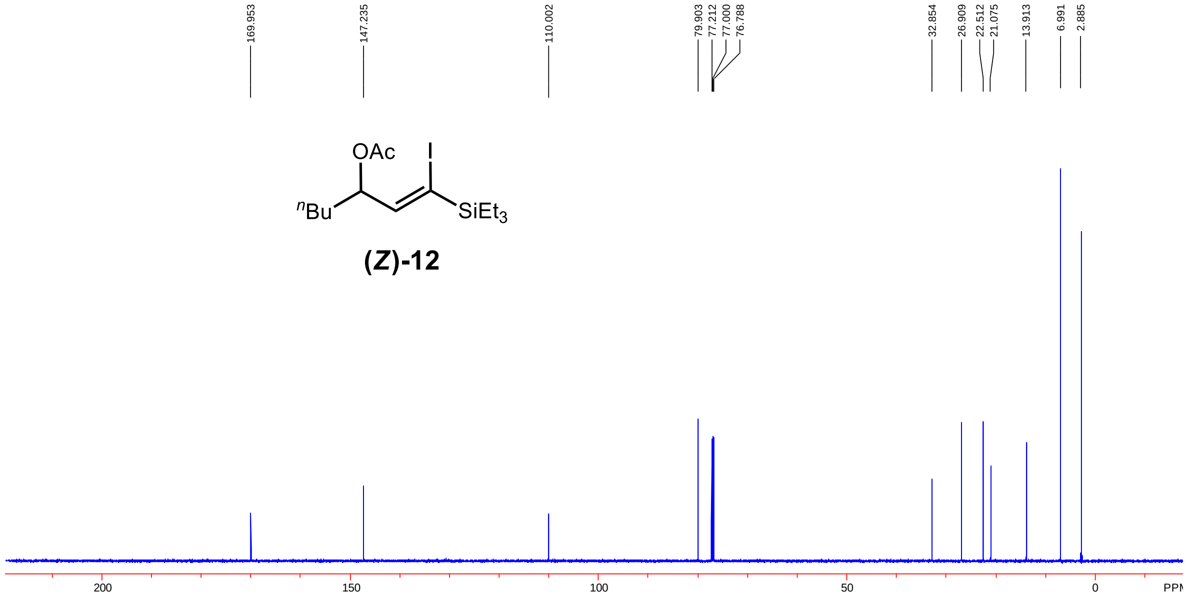
0.888
0.325
0.320
0.314
0.271
0.051
0.050
OAc
TMS
nBu
I
(E)-3
0.96
1.00
3.06
1.14
1.11
4.59
3.33
9.08
8
6
4
2
0
PPM

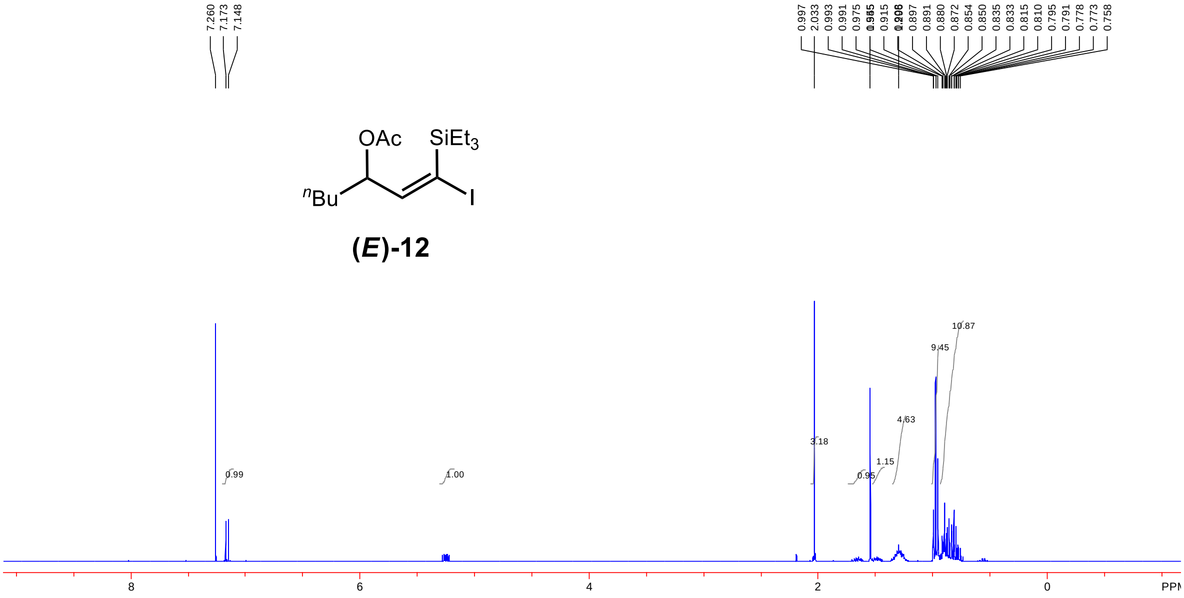

170.099
153.091
113.459
77.212
77.000
76.789
74.396
34.093
27.077
22.482
21.133
13.891
0.887
OAc
TMS
nBu
I
(E)-3
200
150
100
50
0
PPM

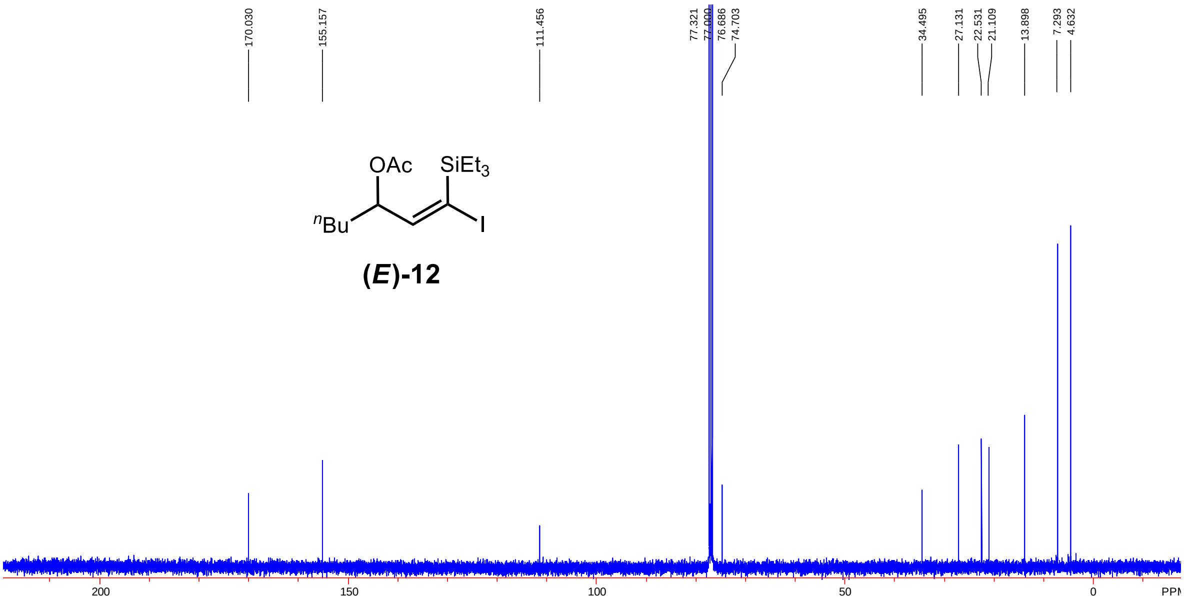

6.167
6.156
5.483
5.474
1.348
1.344
2.043
1.339
1.337
1.332
1.329
0.948
0.941
0.935
0.929
0.922
0.904
0.899
0.895
0.893
0.888
0.885
0.881
0.713
0.701
0.687
0.673
OAc
I
nBu
SiEt3
1.00
1.00
3.14
2.21
4.23
9.40
3.26
6.28
8
6
4
2
0
PPM

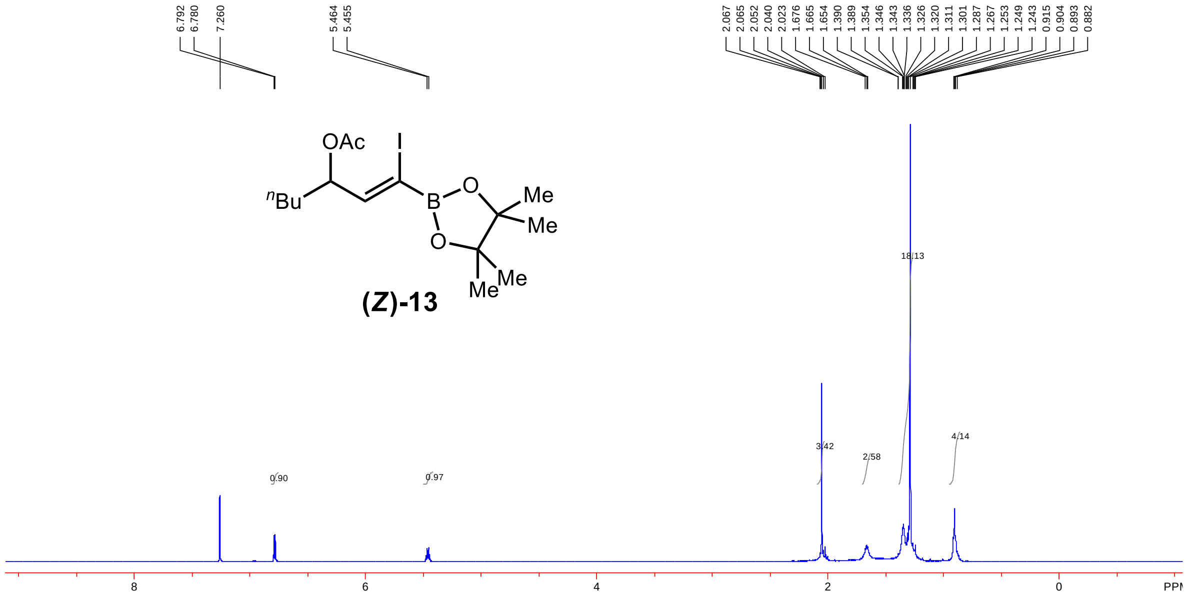
**(*Z*)-12**


169.953
147.235
110.002
79.903
77.212
77.000
76.788
32.854
26.909
22.512
21.075
13.913
6.991
2.885
OAc
I
nBu
SiEt3
200
150
100
50
0
PPM

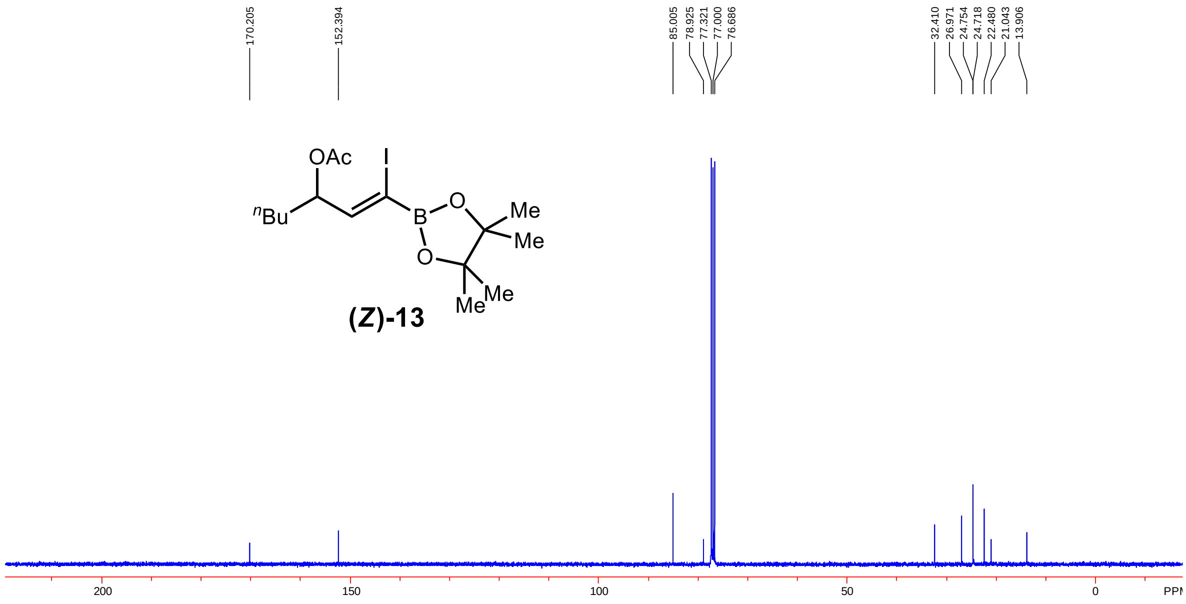
**(*Z*)-12**


7.260
7.173
7.148
0.997
2.033
0.993
0.991
0.975
0.915
0.897
0.891
0.880
0.872
0.854
0.850
0.835
0.833
0.815
0.810
0.795
0.791
0.778
0.773
0.758
OAc
SiEt3
nBu
I
(E)-12
10.87
9.45
4.63
3.18
1.15
0.95
0.99
1.00
8
6
4
2
0
PPM

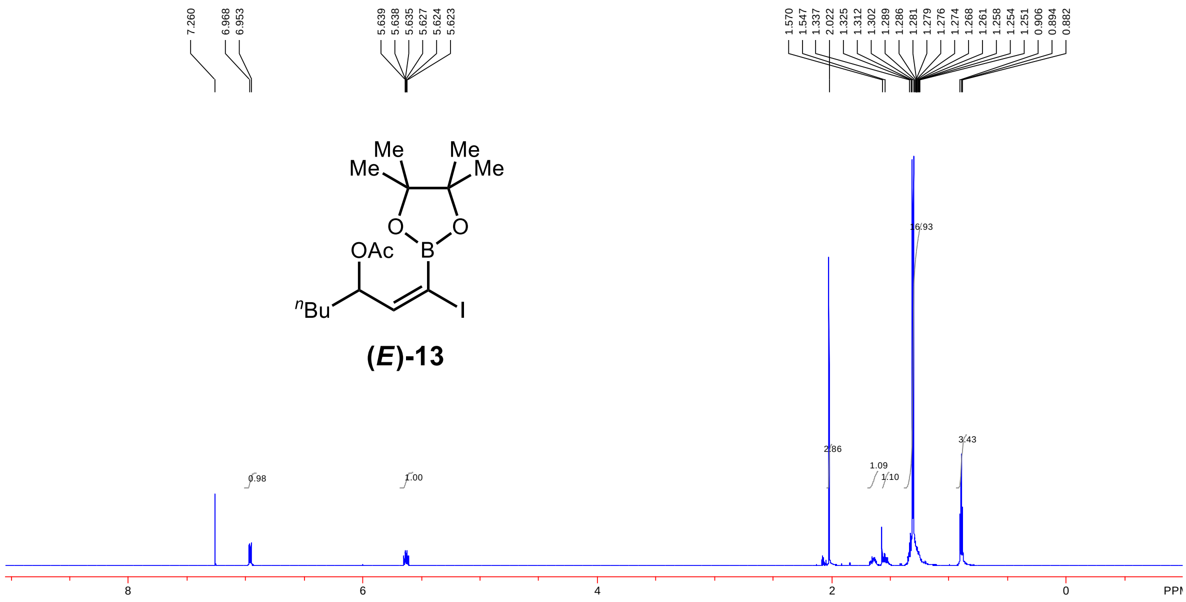

170.030
155.157
111.456
77.321
77.000
76.686
74.703
34.495
27.131
22.531
21.109
13.898
7.293
4.632
OAc
SiEt3
nBu
I
(E)-12
200
150
100
50
0
PPM

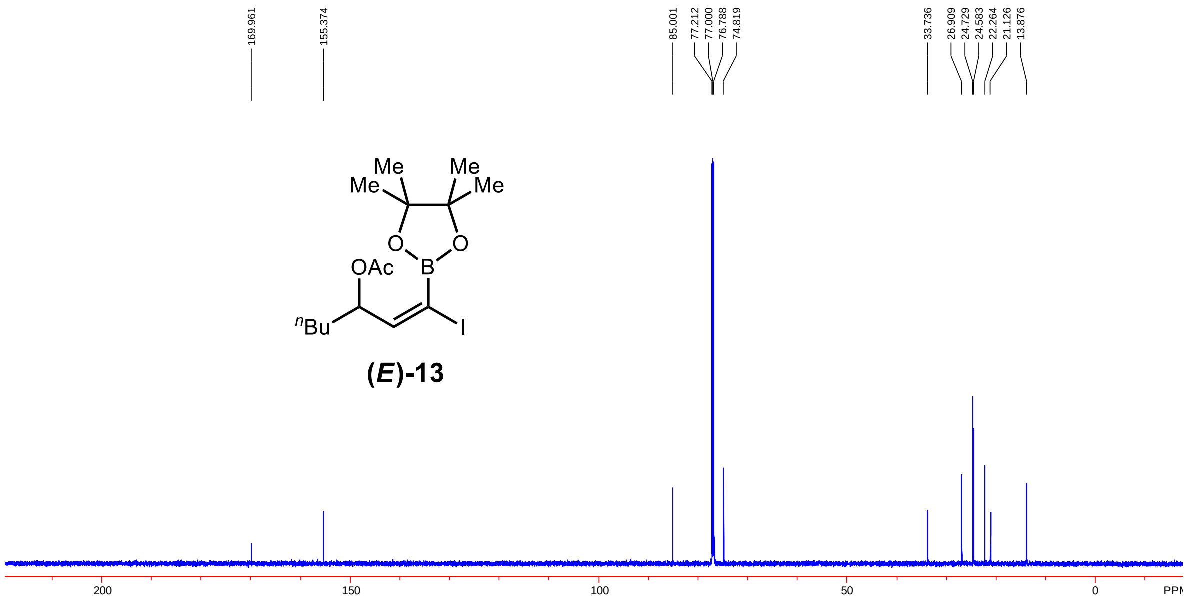

6.792
6.780
7.260
5.464
5.455
2.067
2.065
2.052
2.040
2.023
1.676
1.665
1.654
1.390
1.389
1.354
1.346
1.343
1.336
1.326
1.320
1.311
1.301
1.287
1.267
1.253
1.249
1.243
0.915
0.904
0.893
0.882
OAc
I
ⁿBu
B
O
O
Me
Me
Me
Me
0.90
0.97
3.42
2.58
18.13
4.14
8
6
4
2
0
PPM

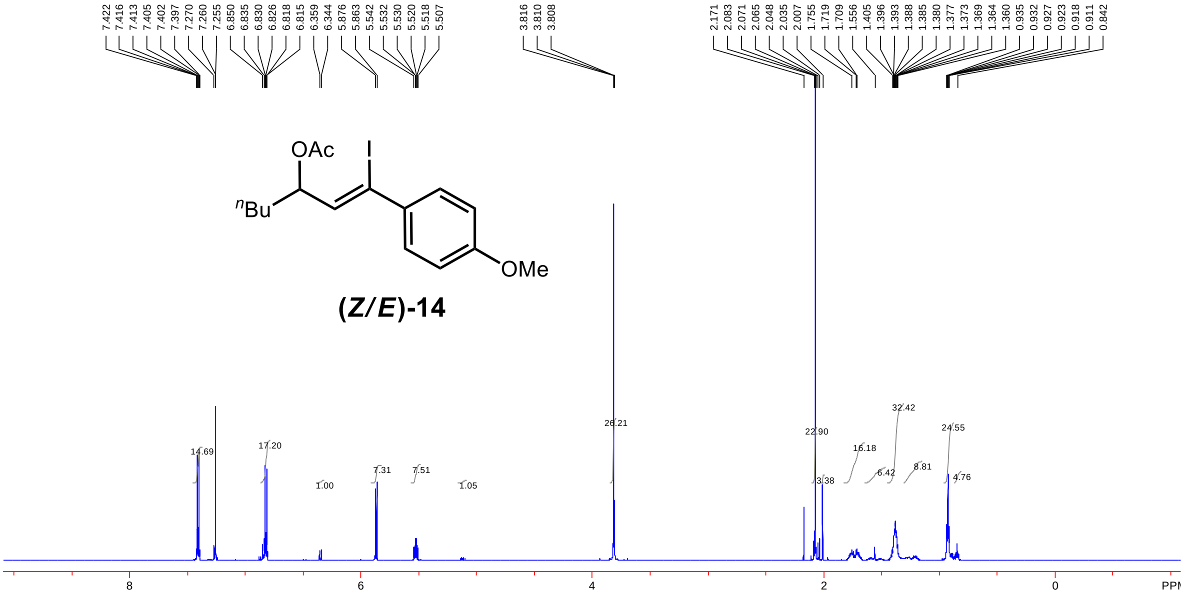
(Z)-13


170.205
152.394
85.005
78.925
77.321
77.000
76.686
32.410
26.971
24.754
24.718
22.480
21.043
13.906
OAc
I
ⁿBu
B
O
O
Me
Me
Me
Me
200
150
100
50
0
PPM

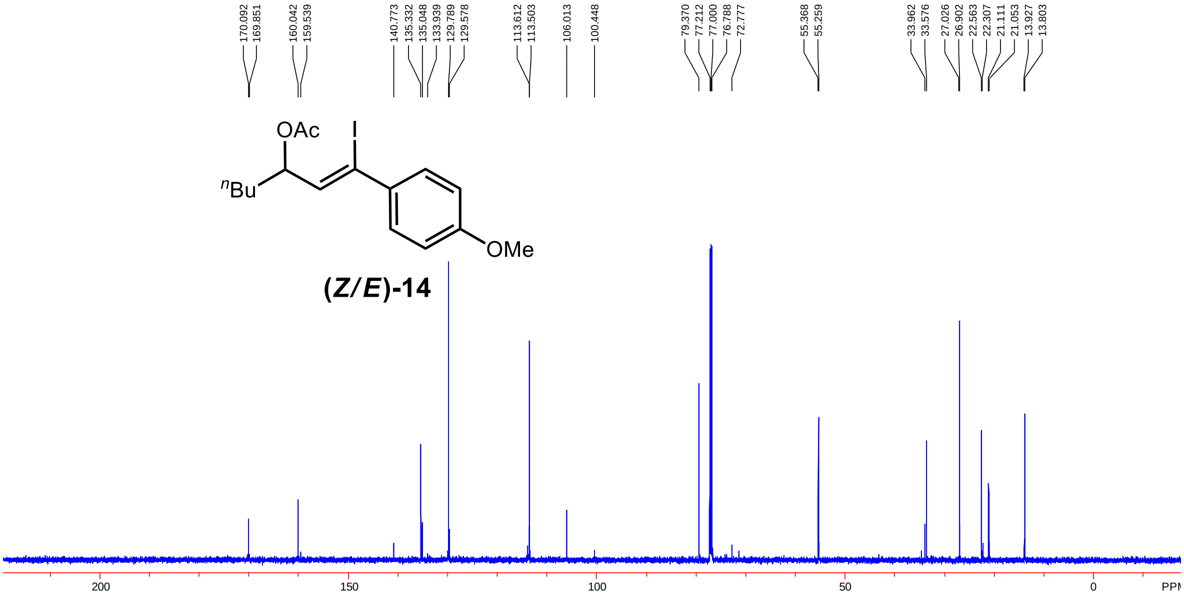
(Z)-13


7.260
6.968
6.953
5.639
5.638
5.635
5.627
5.624
5.623
1.570
1.547
1.337
2.022
1.325
1.312
1.302
1.289
1.286
1.281
1.279
1.276
1.274
1.268
1.261
1.258
1.254
1.251
0.906
0.894
0.882
Me
Me
Me
Me
O
O
B
OAc
nBu
I
(E)-13
16.93
2.86
1.09
1.10
3.43
0.98
1.00
8
6
4
2
0
PPM

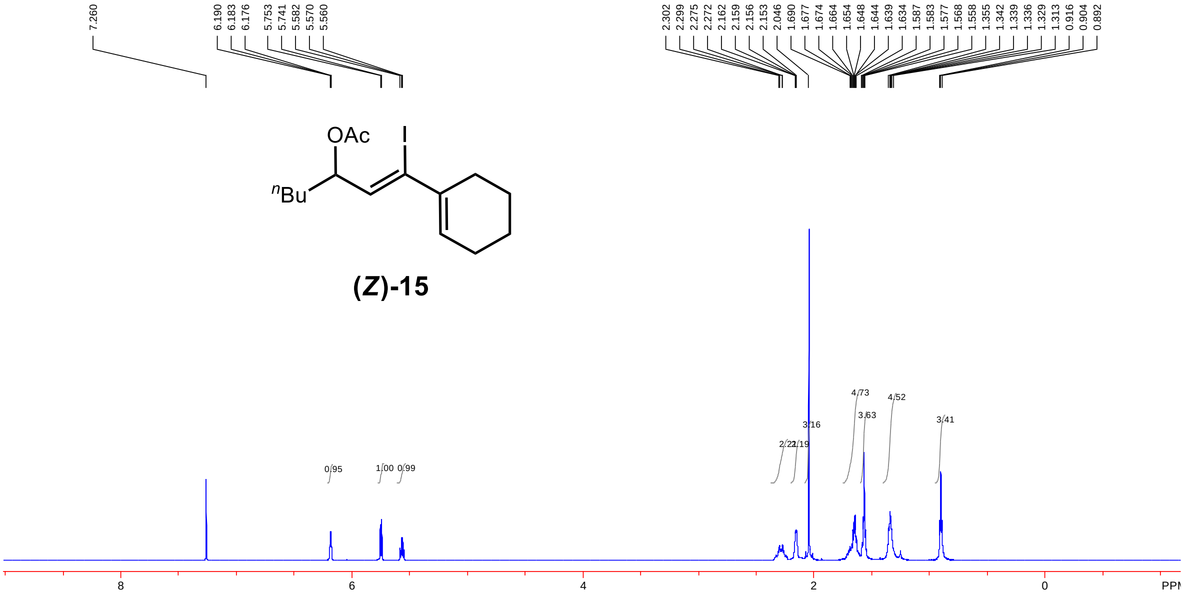

169.961
155.374
85.001
77.212
77.000
76.788
74.819
33.736
26.909
24.729
24.583
22.264
21.126
13.876
Me
Me
Me
Me
O
O
B
OAc
nBu
I
(E)-13
200
150
100
50
0
PPM


7.422
7.416
7.413
7.405
7.402
7.397
7.270
7.260
7.255
6.850
6.835
6.830
6.826
6.818
6.815
6.359
6.344
5.876
5.863
5.542
5.532
5.530
5.520
5.518
5.507
3.816
3.810
3.808
2.171
2.083
2.071
2.065
2.048
2.035
2.007
1.755
1.719
1.709
1.556
1.405
1.396
1.393
1.388
1.385
1.380
1.377
1.373
1.369
1.364
1.360
0.935
0.932
0.927
0.923
0.918
0.911
0.842
OAc
I
$^n$Bu
OMe
14.69
17.20
1.00
7.31
7.51
1.05
26.21
22.90
3.38
16.18
6.42
32.42
8.81
24.55
4.76
8
6
4
2
0
PPM

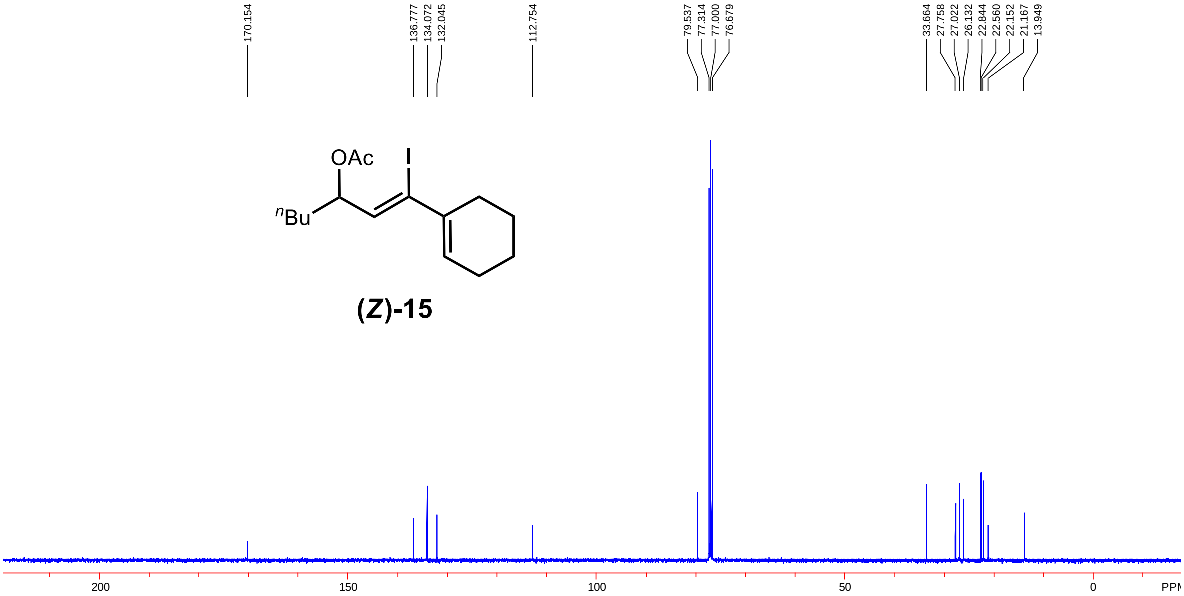
**(*Z*/*E*)-14**


170.092
169.851
160.042
159.539
140.773
135.332
135.048
133.939
129.789
129.578
113.612
113.503
106.013
100.448
79.370
77.212
77.000
76.788
72.777
55.368
55.259
33.962
33.576
27.026
26.902
22.563
22.307
21.111
21.053
13.927
13.803
OAc
I
$^n$Bu
OMe
200
150
100
50
0
PPM

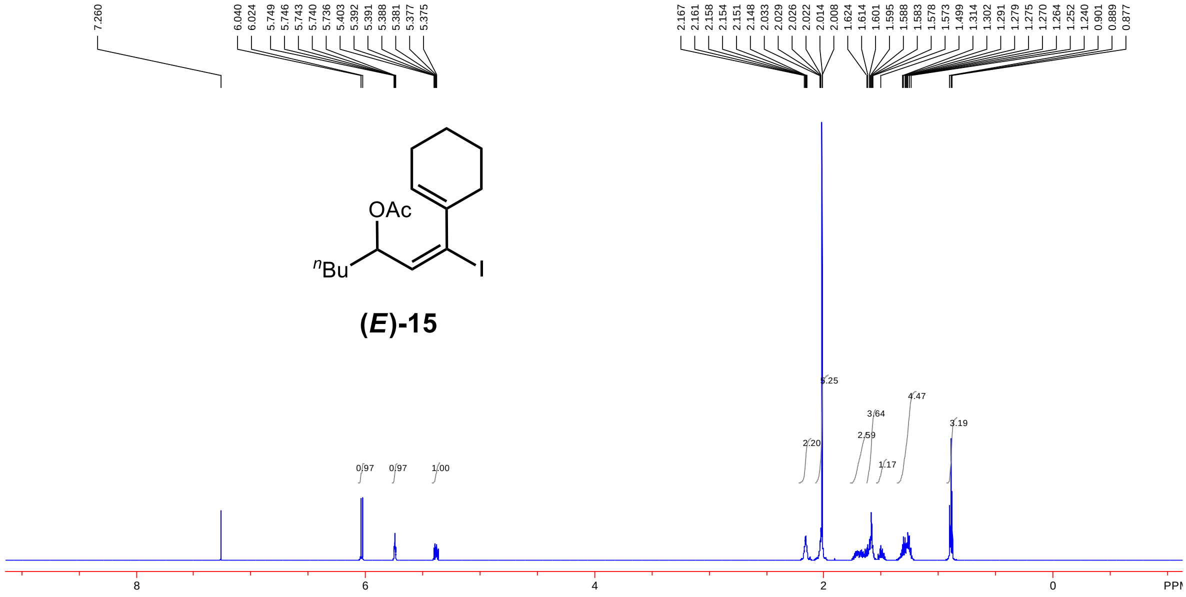
**(*Z*/*E*)-14**

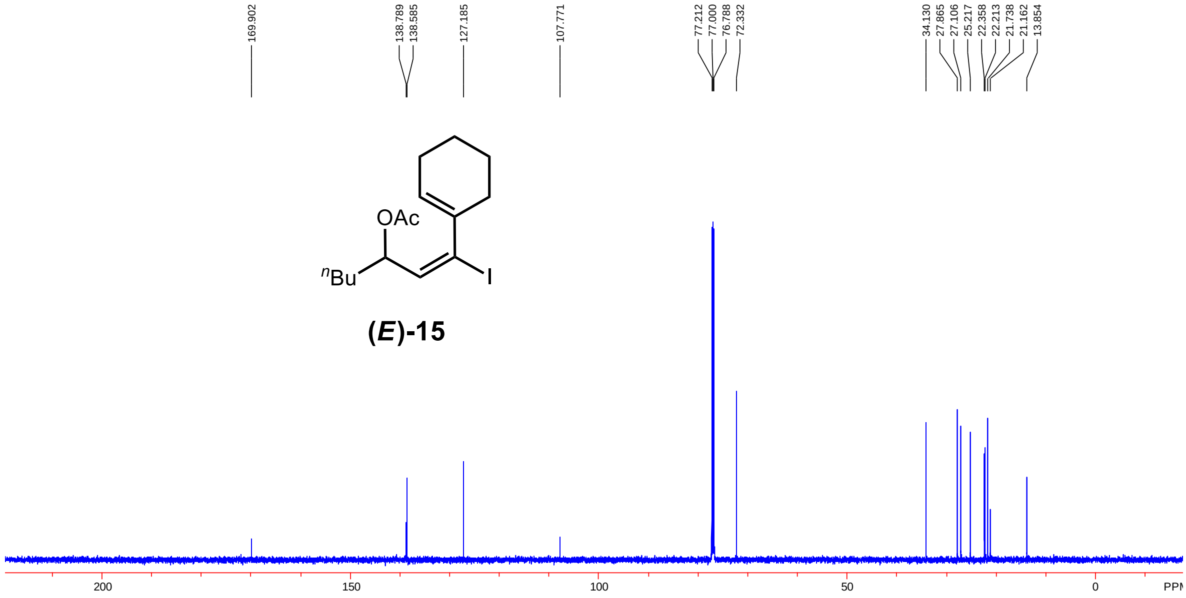

7.260
6.190
6.183
6.176
5.753
5.741
5.582
5.570
5.560
2.302
2.299
2.275
2.272
2.162
2.159
2.156
2.153
2.046
1.690
1.677
1.674
1.664
1.654
1.648
1.644
1.639
1.634
1.587
1.583
1.577
1.568
1.558
1.355
1.342
1.339
1.336
1.329
1.313
0.916
0.904
0.892
OAc
I
nBu
0.95
1.00
0.99
2.22
2.19
3.16
4.73
3.63
4.52
3.41
8
6
4
2
0
PPM

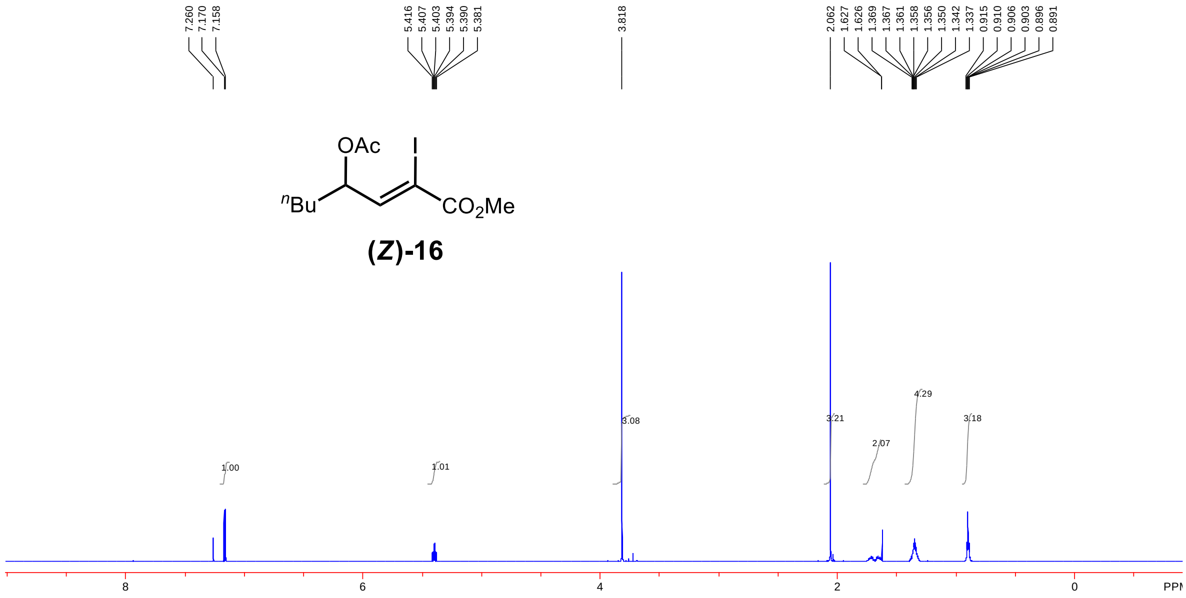
**(Z)-15**


170.154
136.777
134.072
132.045
112.754
79.537
77.314
77.000
76.679
33.664
27.758
27.022
26.132
22.844
22.560
22.152
21.167
13.949
OAc
I
nBu
200
150
100
50
0
PPM

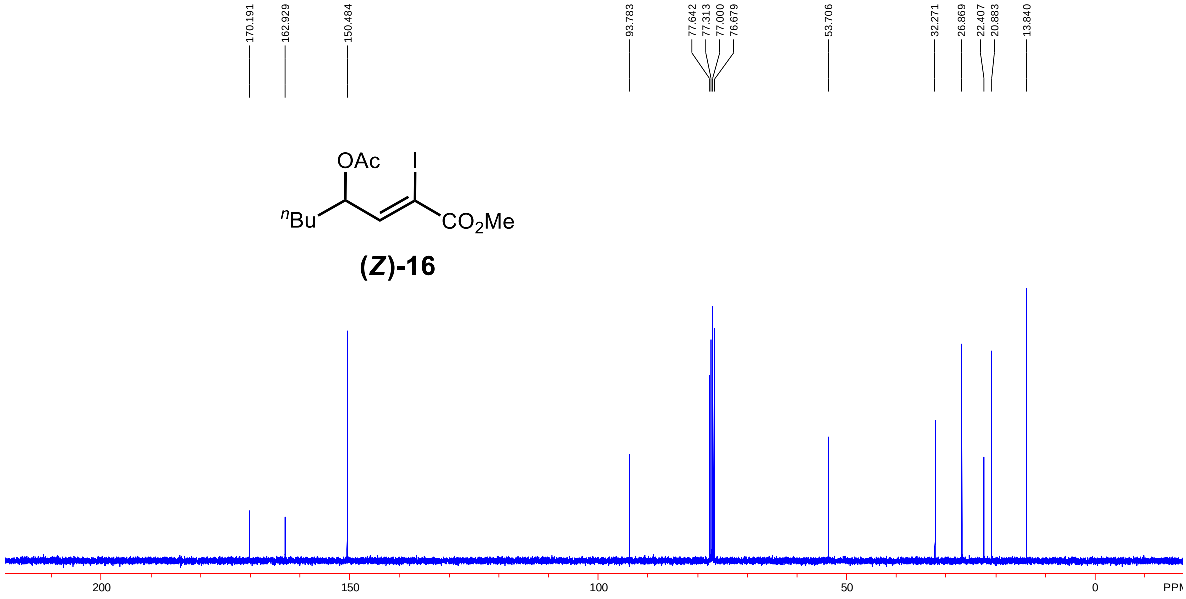
**(Z)-15**


7.260
6.040
6.024
5.749
5.746
5.743
5.740
5.736
5.403
5.392
5.391
5.388
5.381
5.377
5.375
2.167
2.161
2.158
2.154
2.151
2.148
2.033
2.029
2.026
2.022
2.014
2.008
1.624
1.614
1.601
1.595
1.588
1.583
1.578
1.573
1.499
1.314
1.302
1.291
1.279
1.275
1.270
1.264
1.252
1.240
0.901
0.889
0.877
OAc
$^n$Bu
I
(E)-15
0.97
0.97
1.00
2.20
5.25
2.59
3.64
1.17
4.47
3.19
8
6
4
2
0
PPI

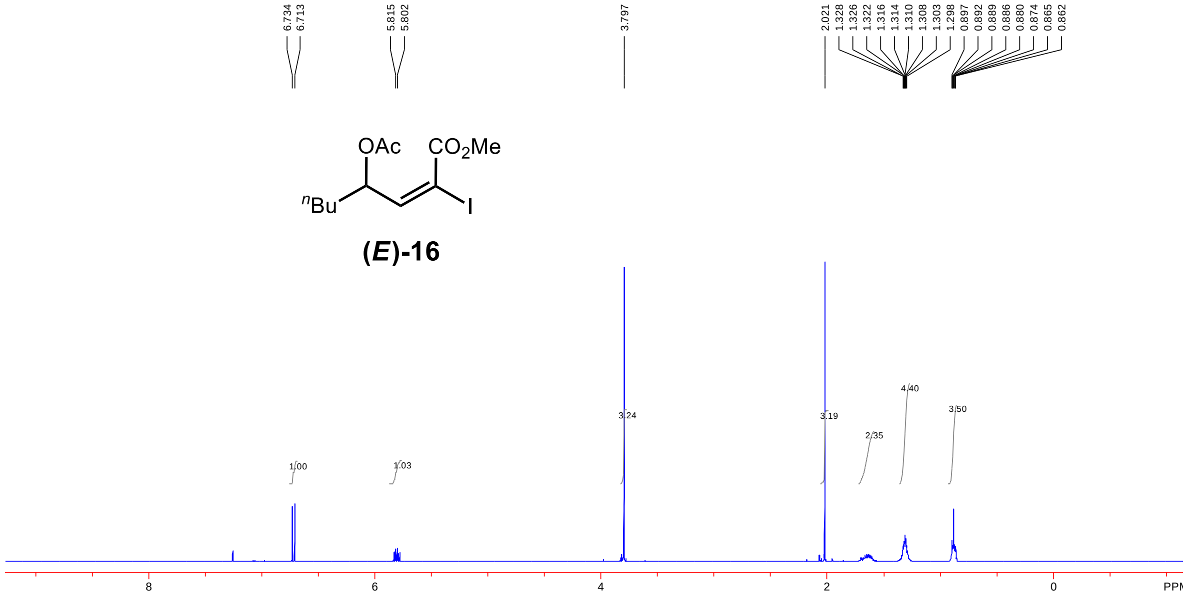

169.902
138.789
138.585
127.185
107.771
77.212
77.000
76.788
72.332
34.130
27.865
27.106
25.217
22.358
22.213
21.738
21.162
13.854
OAc
$^n$Bu
I
(E)-15
200
150
100
50
0
PPI


**(*Z*)-16**

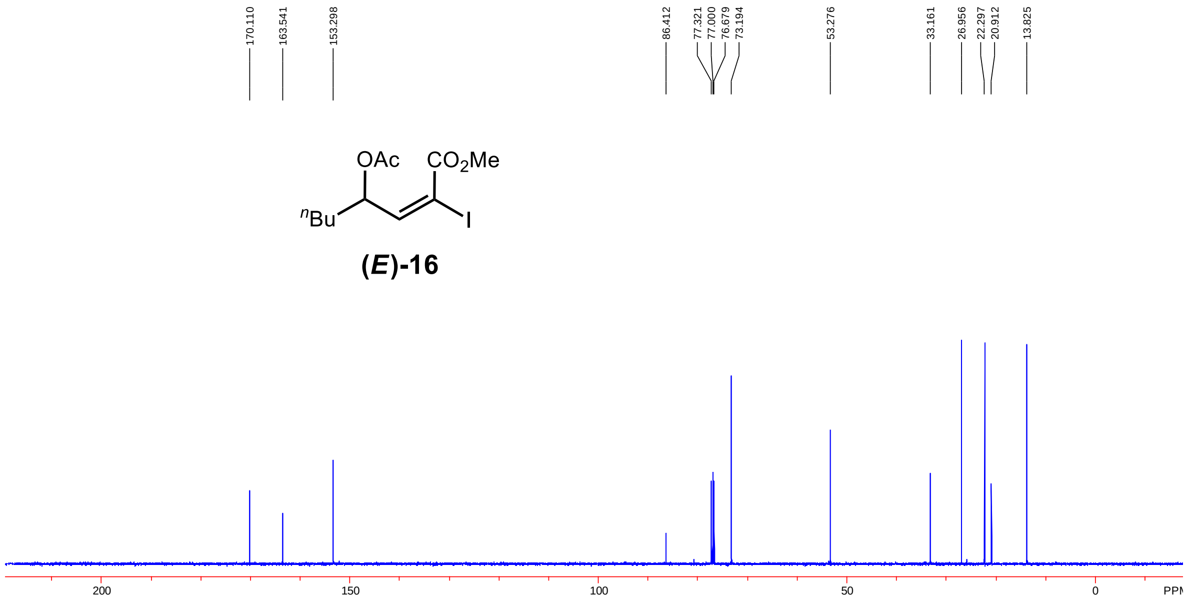
7.260
7.170
7.158
5.416
5.407
5.403
5.394
5.390
5.381
3.818
2.062
1.627
1.626
1.369
1.367
1.361
1.358
1.356
1.350
1.342
1.337
0.915
0.910
0.906
0.903
0.896
0.891
OAc
I
ⁿBu
CO2Me
1.00
1.01
3.08
3.21
2.07
4.29
3.18
8
6
4
2
0
PPM


**(*Z*)-16**

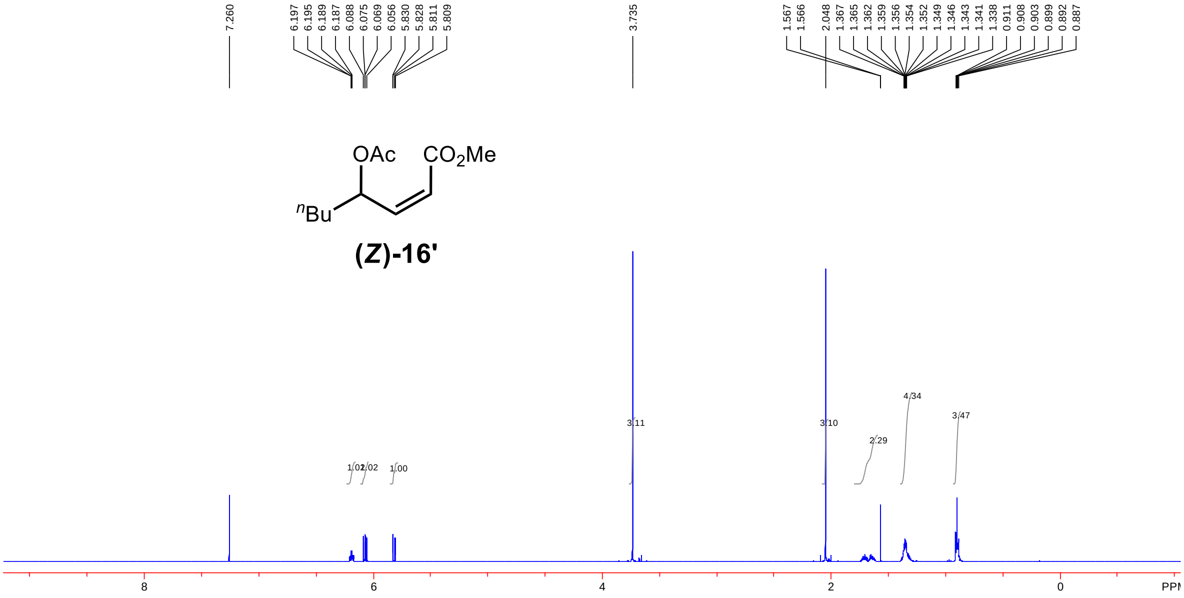
170.191
162.929
150.484
93.783
77.642
77.313
77.000
76.679
53.706
32.271
26.869
22.407
20.883
13.840
OAc
I
ⁿBu
CO2Me
200
150
100
50
0
PPM

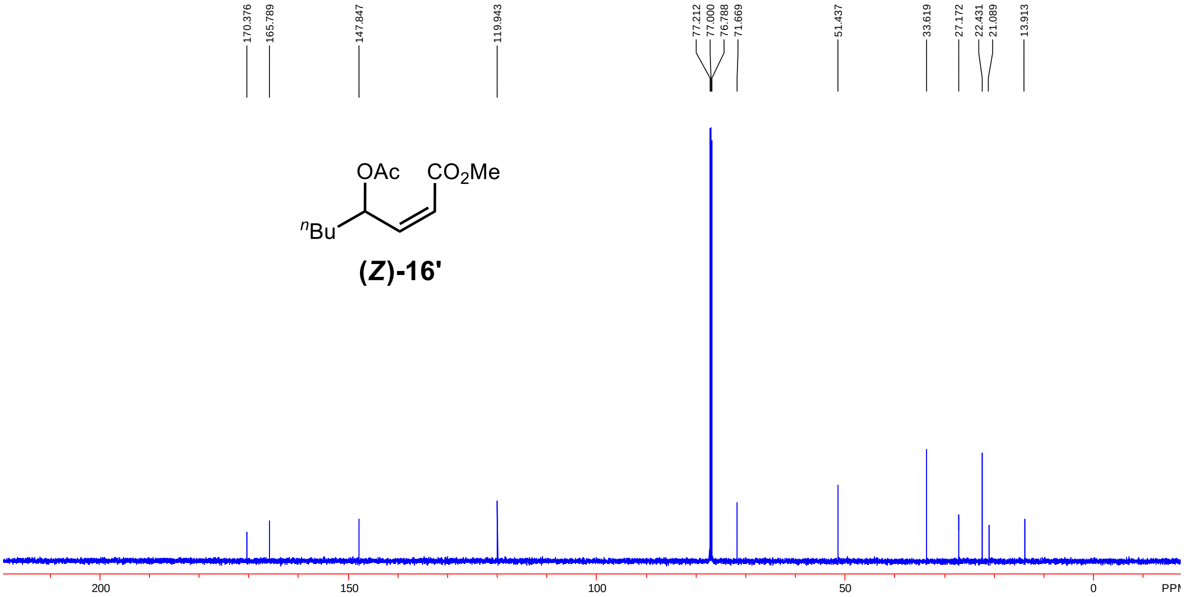

6.734
6.713
5.815
5.802
3.797
2.021
1.328
1.326
1.322
1.316
1.314
1.310
1.308
1.303
1.298
0.897
0.892
0.889
0.886
0.880
0.874
0.865
0.862
OAc
CO$_2$Me
$^n$Bu
I
1.00
1.03
3.24
3.19
2.35
4.40
3.50
8
6
4
2
0
PPM

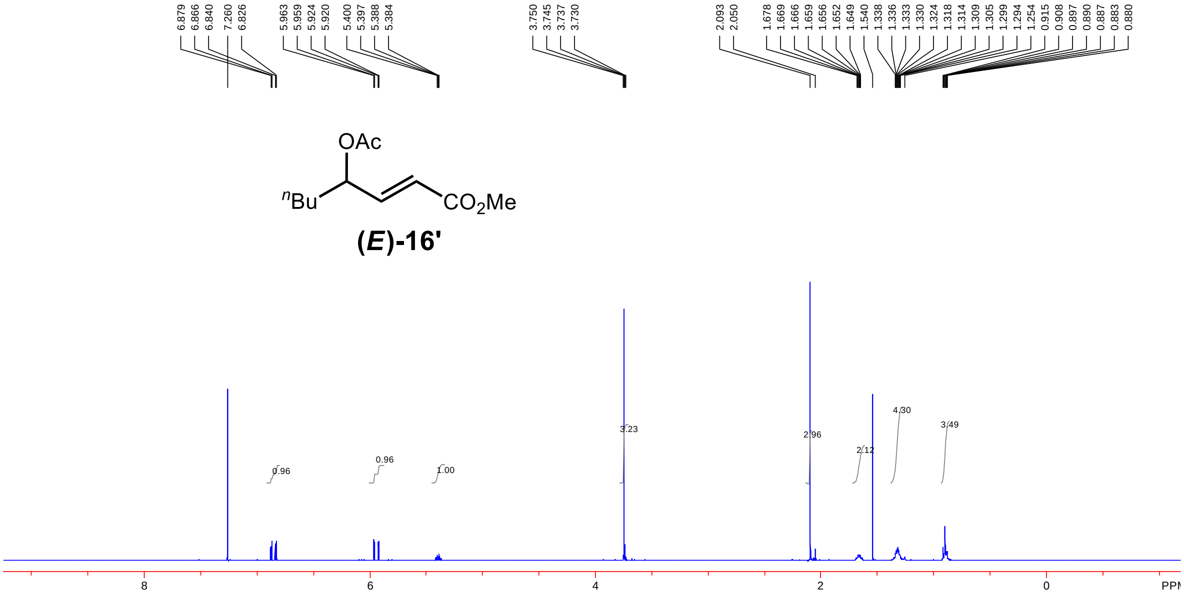
**(*E*)-16**


170.110
163.541
153.298
86.412
77.321
77.000
76.679
73.194
53.276
33.161
26.956
22.297
20.912
13.825
OAc
CO$_2$Me
$^n$Bu
I
200
150
100
50
0
PPM

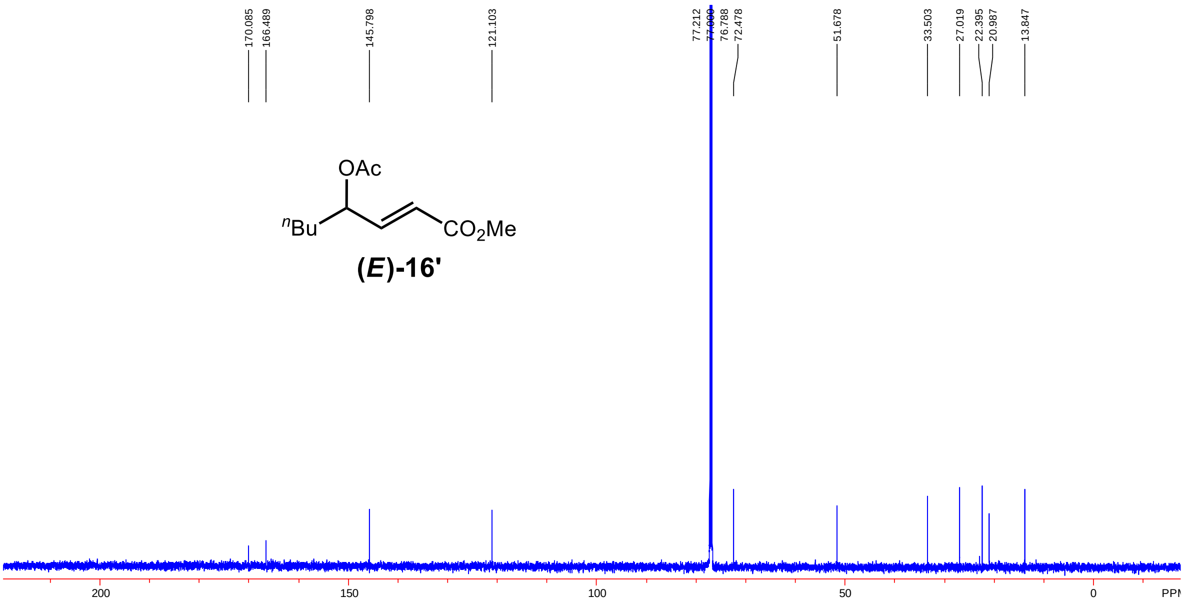
**(*E*)-16**


7.260
6.197
6.195
6.189
6.187
6.088
6.075
6.069
6.056
5.830
5.828
5.811
5.809
3.735
1.567
1.566
2.048
1.367
1.365
1.362
1.359
1.356
1.354
1.352
1.349
1.346
1.343
1.341
1.338
0.911
0.908
0.903
0.899
0.892
0.887
OAc
CO2Me
nBu
(Z)-16'
1.02
1.02
1.00
3.11
3.10
2.29
4.34
3.47
8
6
4
2
0
PPM

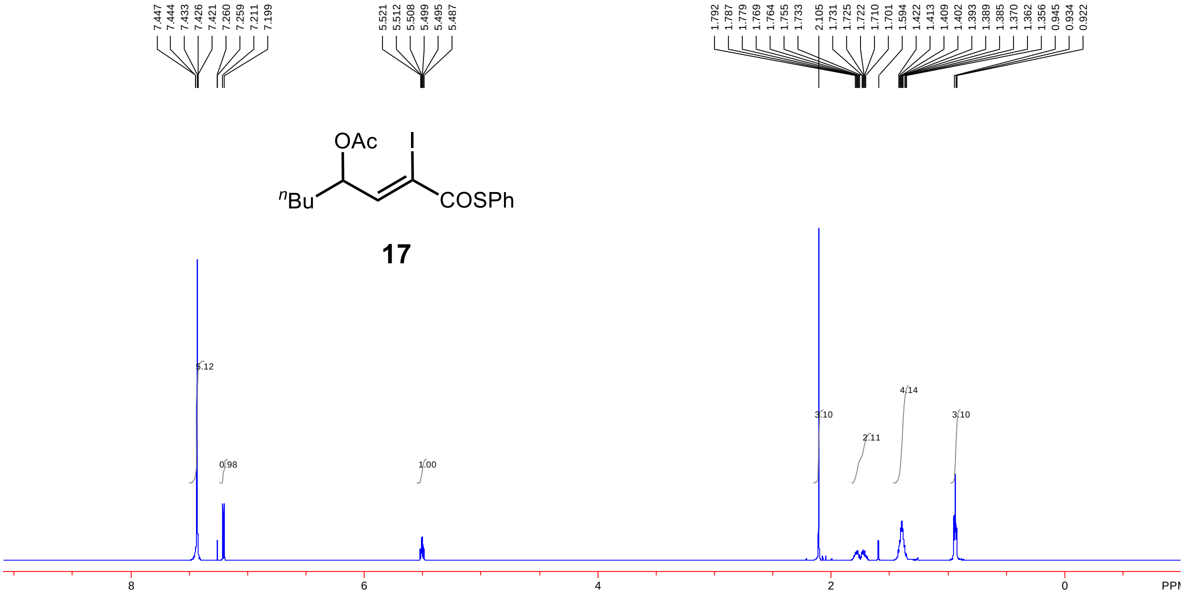

170.376
165.789
147.847
119.943
77.212
77.000
76.788
71.669
51.437
33.619
27.172
22.431
21.089
13.913
OAc
CO2Me
nBu
(Z)-16'
200
150
100
50
0
PPM


6.879
6.866
6.840
7.260
6.826
5.963
5.959
5.924
5.920
5.400
5.397
5.388
5.384
3.750
3.745
3.737
3.730
2.093
2.050
1.678
1.669
1.666
1.659
1.656
1.652
1.649
1.540
1.338
1.336
1.333
1.330
1.324
1.318
1.314
1.309
1.305
1.299
1.294
1.254
0.915
0.908
0.897
0.890
0.887
0.883
0.880
OAc
$^n$Bu
CO$_2$Me
0.96
0.96
1.00
3.23
2.96
2.12
4.30
3.49
8
6
4
2
0
PPM

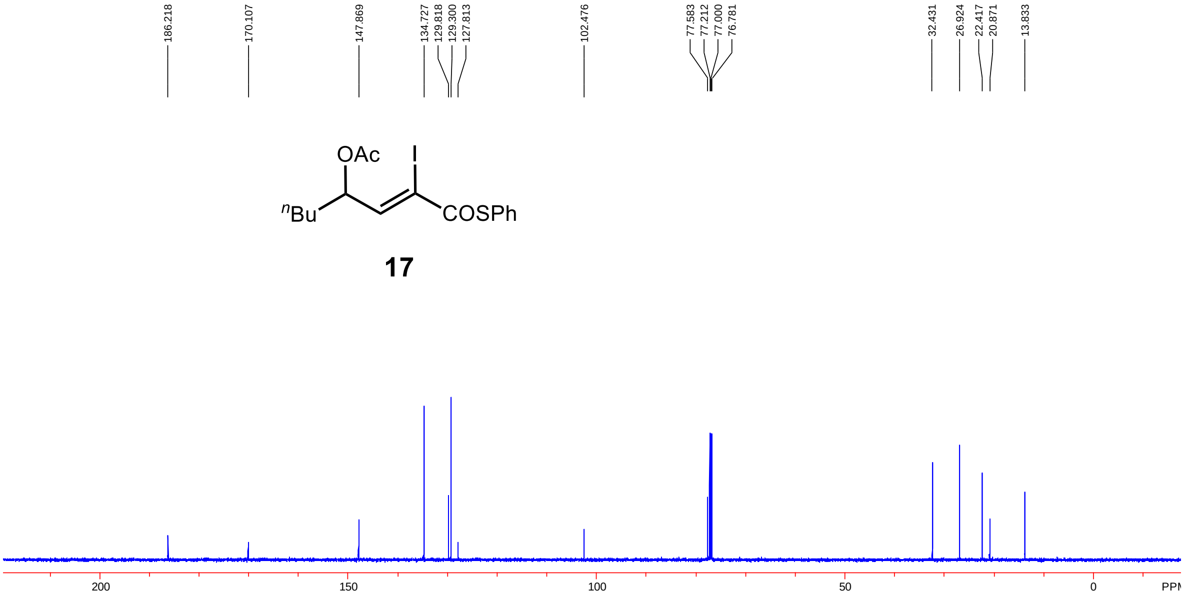
**(*E*)-16'**


170.085
166.489
145.798
121.103
77.212
77.000
76.788
72.478
51.678
33.503
27.019
22.395
20.987
13.847
OAc
$^n$Bu
CO$_2$Me
200
150
100
50
0
PPM

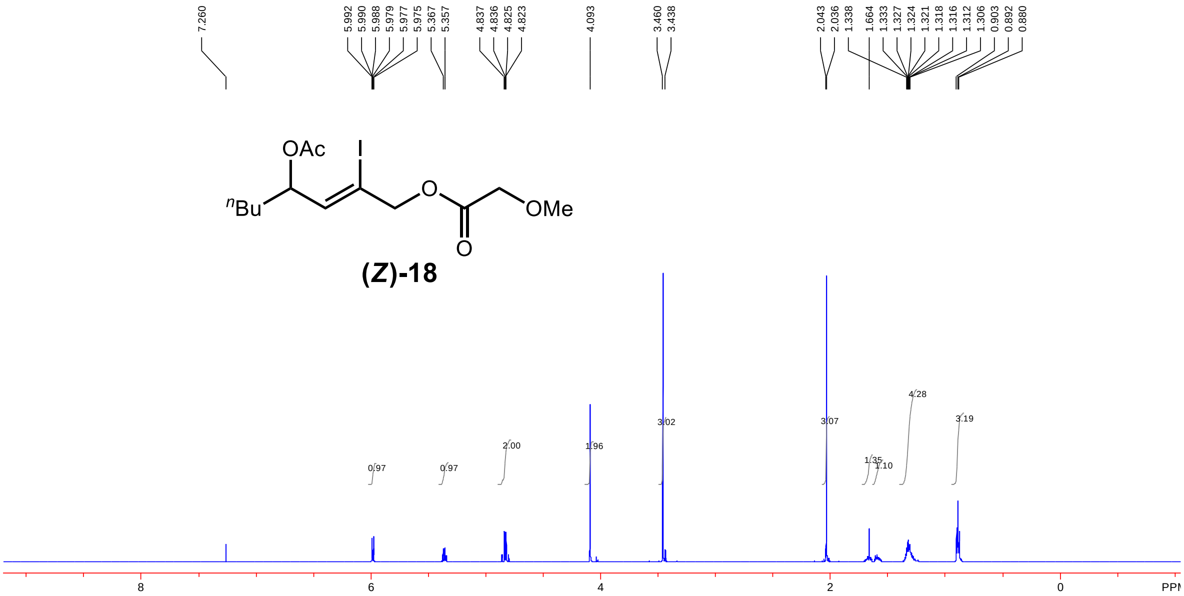
**(*E*)-16'**

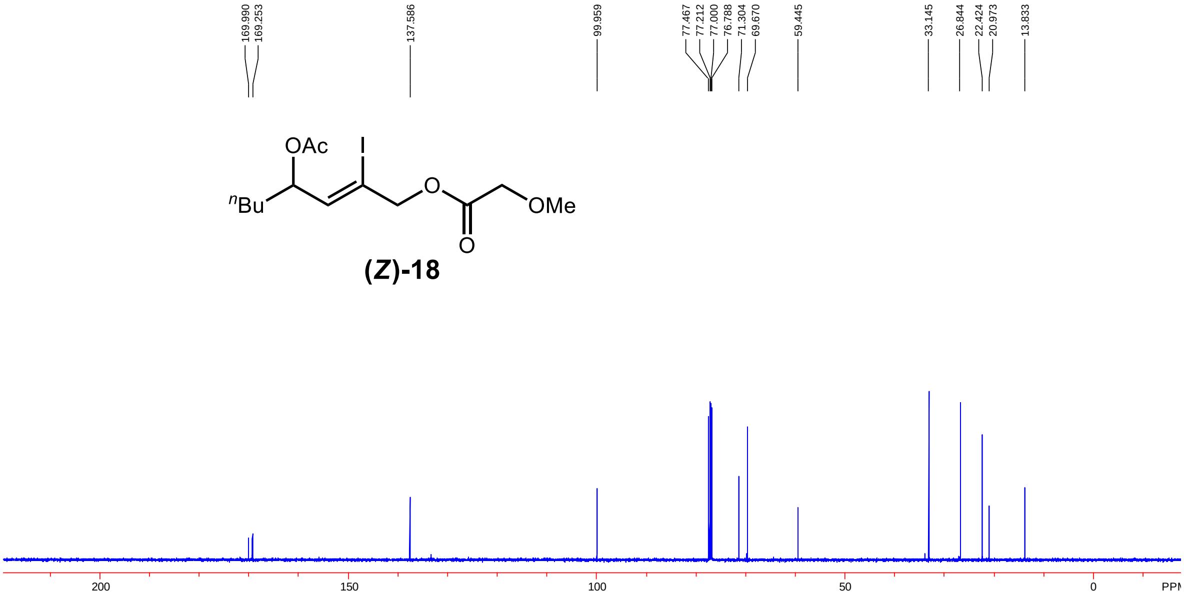

7.447
7.444
7.433
7.426
7.421
7.260
7.259
7.211
7.199
5.521
5.512
5.508
5.499
5.495
5.487
1.792
1.787
1.779
1.769
1.764
1.755
1.733
2.105
1.731
1.725
1.722
1.710
1.701
1.594
1.422
1.413
1.409
1.402
1.393
1.389
1.385
1.370
1.362
1.356
0.945
0.934
0.922
OAc
I
$^n$Bu
COSPh
5.12
0.98
1.00
3.10
2.11
4.14
3.10
8
6
4
2
0
PP

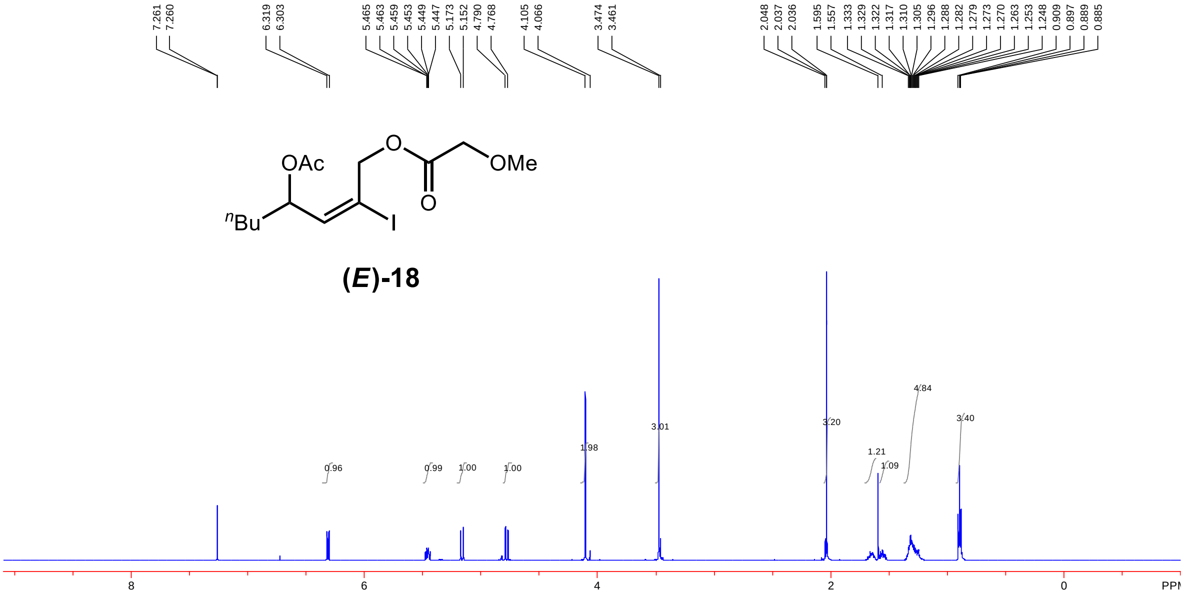
**17**


186.218
170.107
147.869
134.727
129.818
129.300
127.813
102.476
77.583
77.212
77.000
76.781
32.431
26.924
22.417
20.871
13.833
OAc
I
$^n$Bu
COSPh
200
150
100
50
0
PP

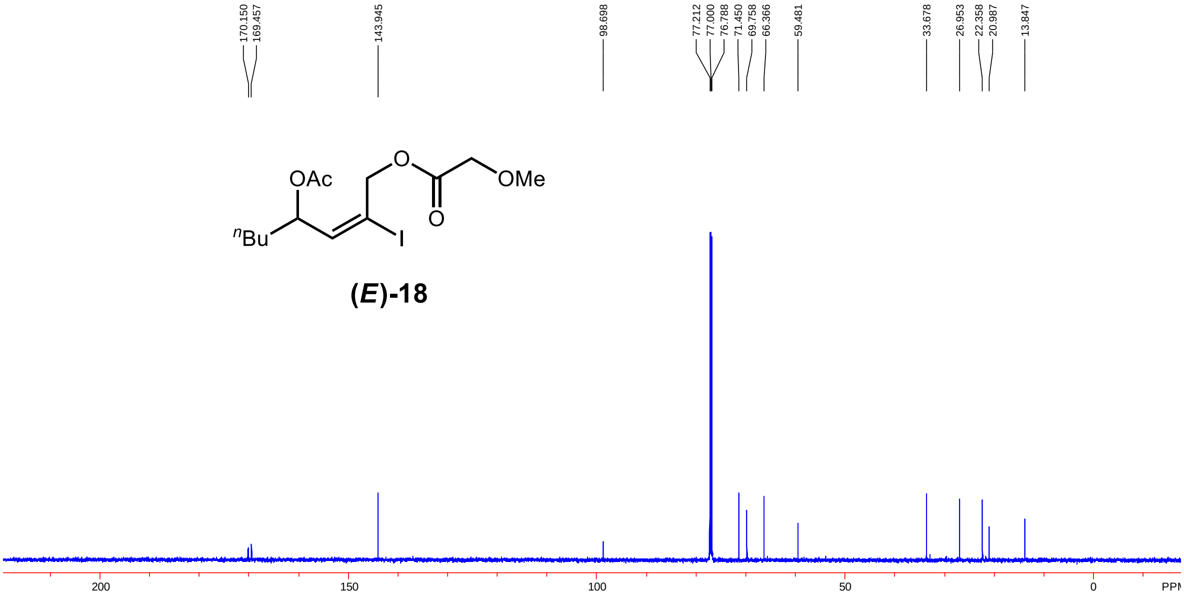
**17**


7.260
5.992
5.990
5.988
5.979
5.977
5.975
5.367
5.357
4.837
4.836
4.825
4.823
4.093
3.460
3.438
2.043
2.036
1.338
1.664
1.333
1.327
1.324
1.321
1.318
1.316
1.312
1.306
0.903
0.892
0.880
OAc
I
$^n$Bu
O
OMe
O
(Z)-18
0.97
0.97
2.00
1.96
3.02
3.07
1.35
1.10
4.28
3.19
8
6
4
2
0
PPM

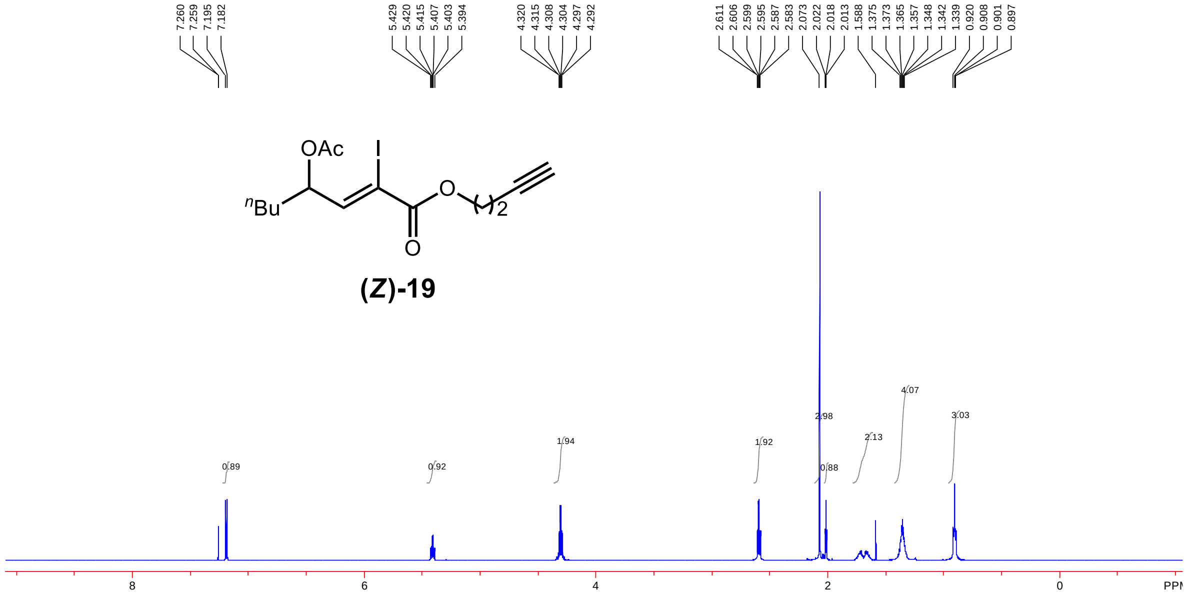

169.990
169.253
137.586
99.959
77.467
77.212
77.000
76.788
71.304
69.670
59.445
33.145
26.844
22.424
20.973
13.833
OAc
I
$^n$Bu
O
OMe
O
(Z)-18
200
150
100
50
0
PPM


7.261
7.260
6.319
6.303
5.465
5.463
5.459
5.453
5.449
5.447
5.173
5.152
4.790
4.768
4.105
4.066
3.474
3.461
2.048
2.037
2.036
1.595
1.557
1.333
1.329
1.322
1.317
1.310
1.305
1.296
1.288
1.282
1.279
1.273
1.270
1.263
1.253
1.248
0.909
0.897
0.889
0.885
OAc
O
OMe
O
ⁿBu
I
0.96
0.99
1.00
1.00
1.98
3.01
3.20
1.21
1.09
4.84
3.40
8
6
4
2
0
PPM

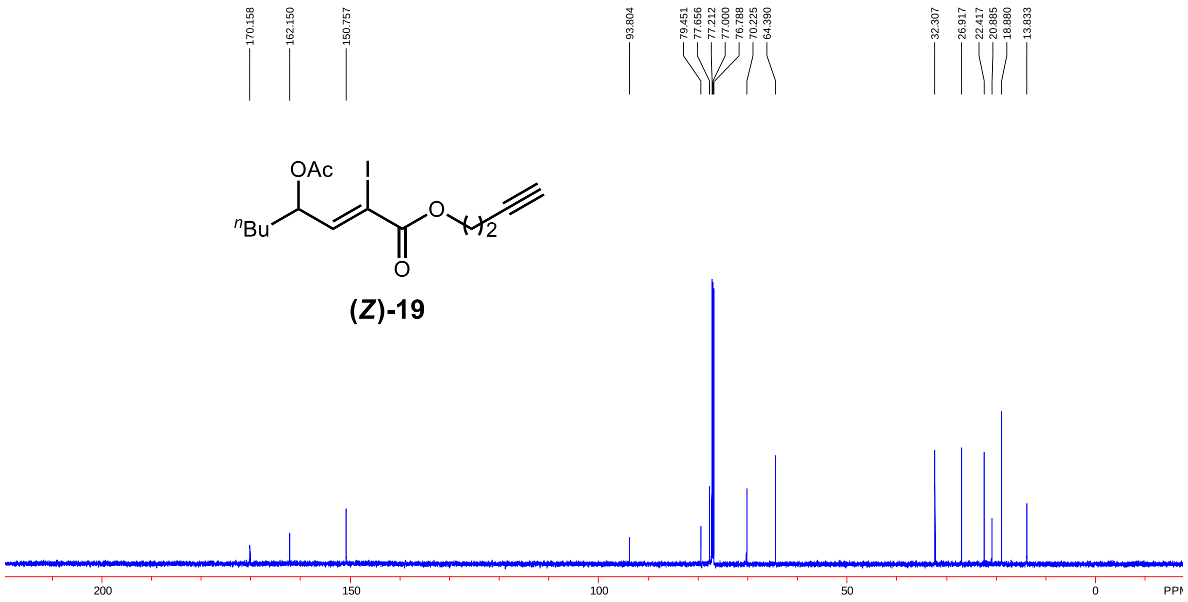
(*E*)-18


170.150
169.457
143.945
98.698
77.212
77.000
76.788
71.450
69.758
66.366
59.481
33.678
26.953
22.358
20.987
13.847
OAc
O
OMe
O
ⁿBu
I
200
150
100
50
0
PPM

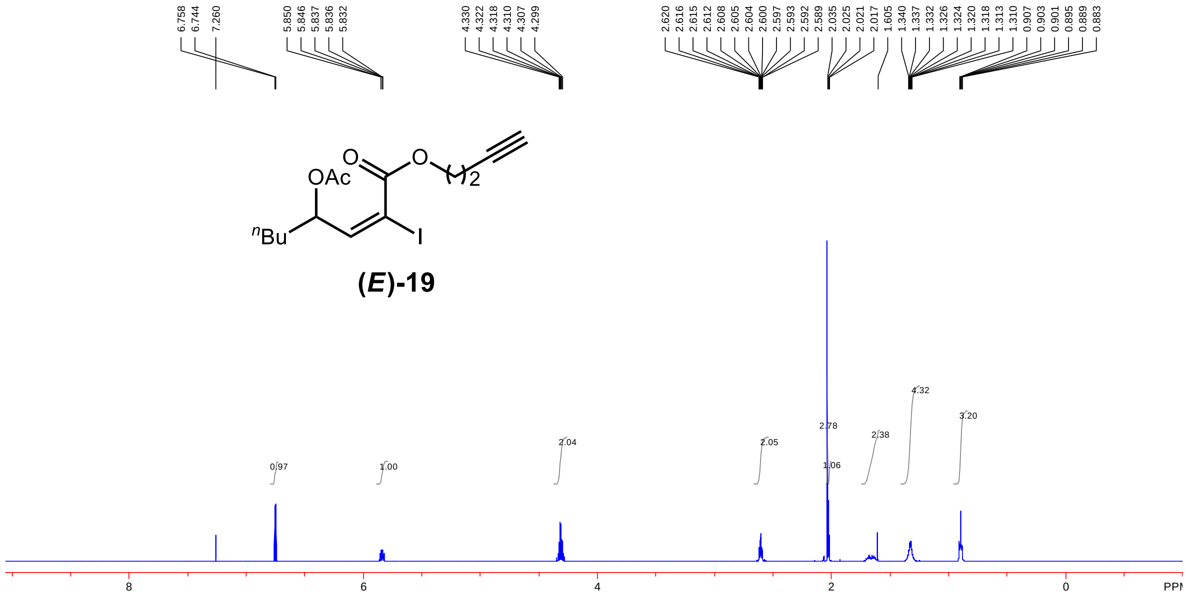
(*E*)-18


7.260
7.259
7.195
7.182
5.429
5.420
5.415
5.407
5.403
5.394
4.320
4.315
4.308
4.304
4.297
4.292
2.611
2.606
2.599
2.595
2.587
2.583
2.073
2.022
2.018
2.013
1.588
1.375
1.373
1.365
1.357
1.348
1.342
1.339
0.920
0.908
0.901
0.897
OAc
I
O
O
nBu
2
0.89
0.92
1.94
1.92
2.98
0.88
2.13
4.07
3.03
8
6
4
2
0
PPM

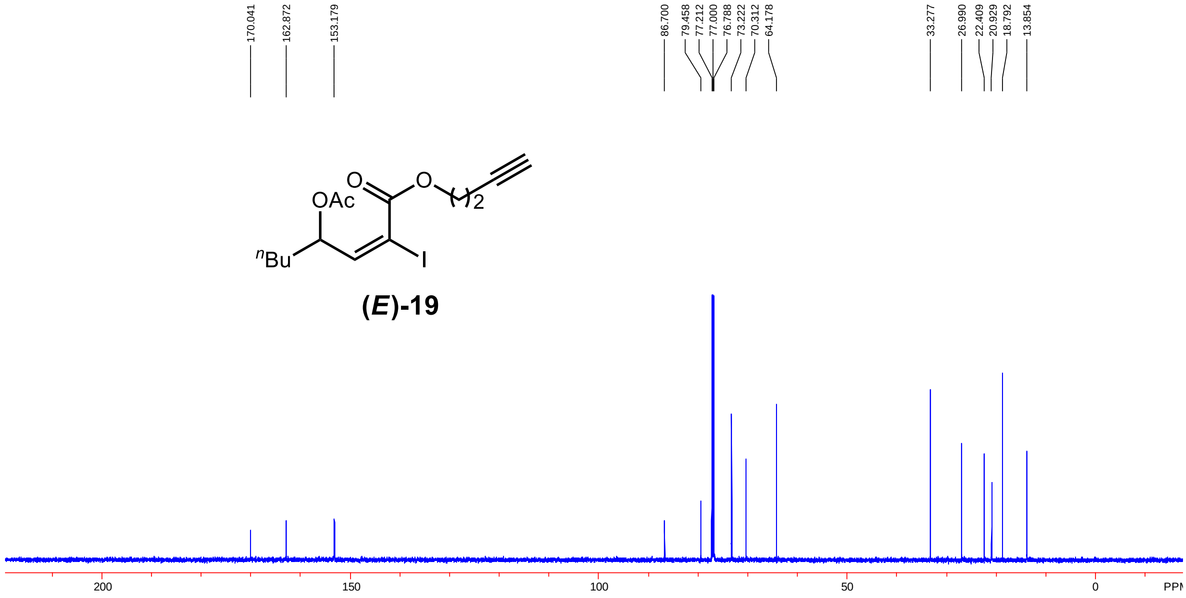
(*Z*)-19


170.158
162.150
150.757
93.804
79.451
77.656
77.212
77.000
76.788
70.225
64.390
32.307
26.917
22.417
20.885
18.880
13.833
OAc
I
O
O
nBu
2
200
150
100
50
0
PPM

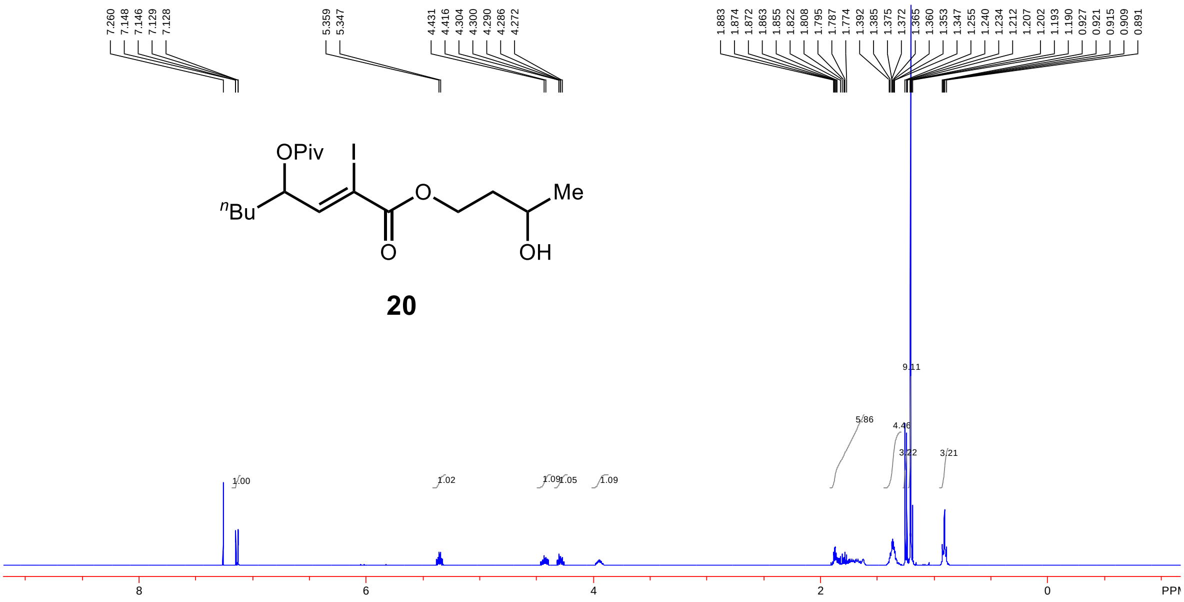
(*Z*)-19


6.758
6.744
7.260
5.850
5.846
5.837
5.836
5.832
4.330
4.322
4.318
4.310
4.307
4.299
2.620
2.616
2.615
2.612
2.608
2.605
2.604
2.600
2.597
2.593
2.592
2.589
2.035
2.025
2.021
2.017
1.605
1.340
1.337
1.332
1.326
1.324
1.320
1.318
1.313
1.310
0.907
0.903
0.901
0.895
0.889
0.883
O
O
OAc
2
nBu
I
0.97
1.00
2.04
2.05
2.78
1.06
2.38
4.32
3.20
8
6
4
2
0
PP

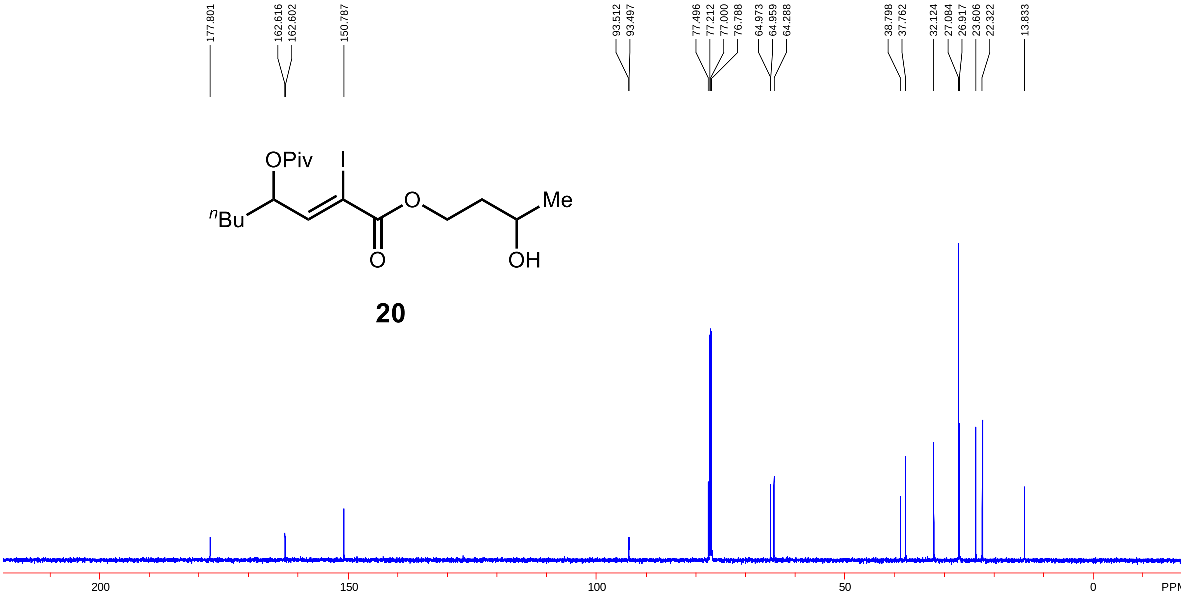
**(*E*)-19**


170.041
162.872
153.179
86.700
79.458
77.212
77.000
76.788
73.222
70.312
64.178
33.277
26.990
22.409
20.929
18.792
13.854
O
O
OAc
2
nBu
I
200
150
100
50
0
PP

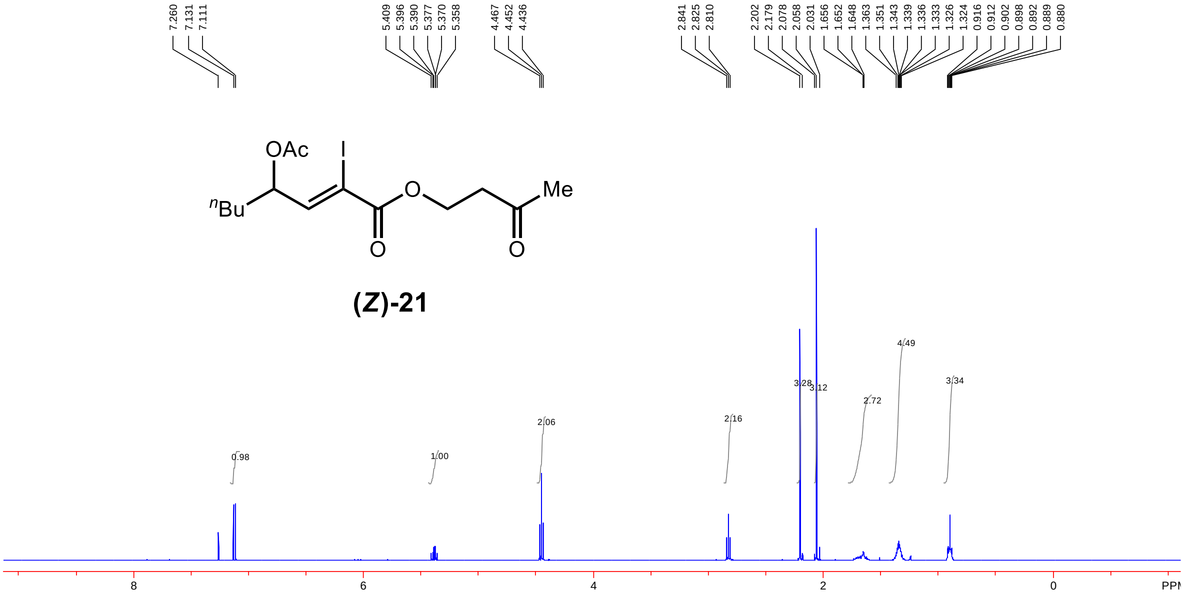
**(*E*)-19**


7.260
7.148
7.146
7.129
7.128
5.359
5.347
4.431
4.416
4.304
4.300
4.290
4.286
4.272
1.883
1.874
1.872
1.863
1.855
1.822
1.808
1.795
1.787
1.774
1.392
1.385
1.375
1.372
1.365
1.360
1.353
1.347
1.255
1.240
1.234
1.212
1.207
1.202
1.193
1.190
0.927
0.921
0.915
0.909
0.891
OPiv
I
$^n$Bu
O
O
Me
OH
9.11
5.86
4.46
3.22
3.21
1.00
1.02
1.09
1.05
1.09
8
6
4
2
0
PPM

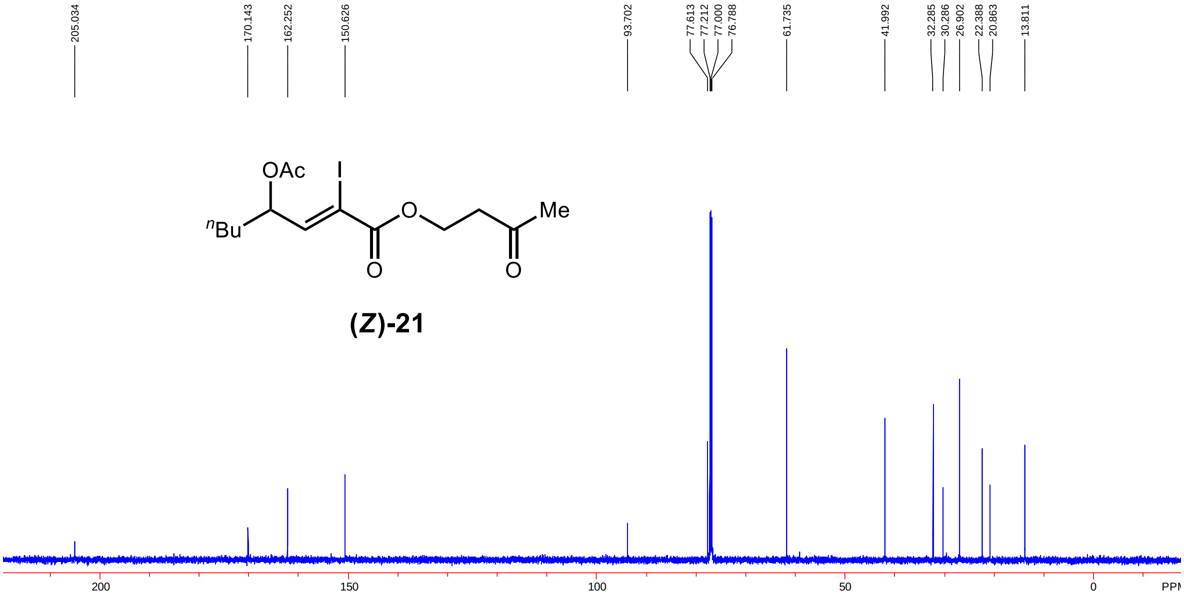
**20**


177.801
162.616
162.602
150.787
93.512
93.497
77.496
77.212
77.000
76.788
64.973
64.959
64.288
38.798
37.762
32.124
27.084
26.917
23.606
22.322
13.833
OPiv
I
$^n$Bu
O
O
Me
OH
200
150
100
50
0
PPM

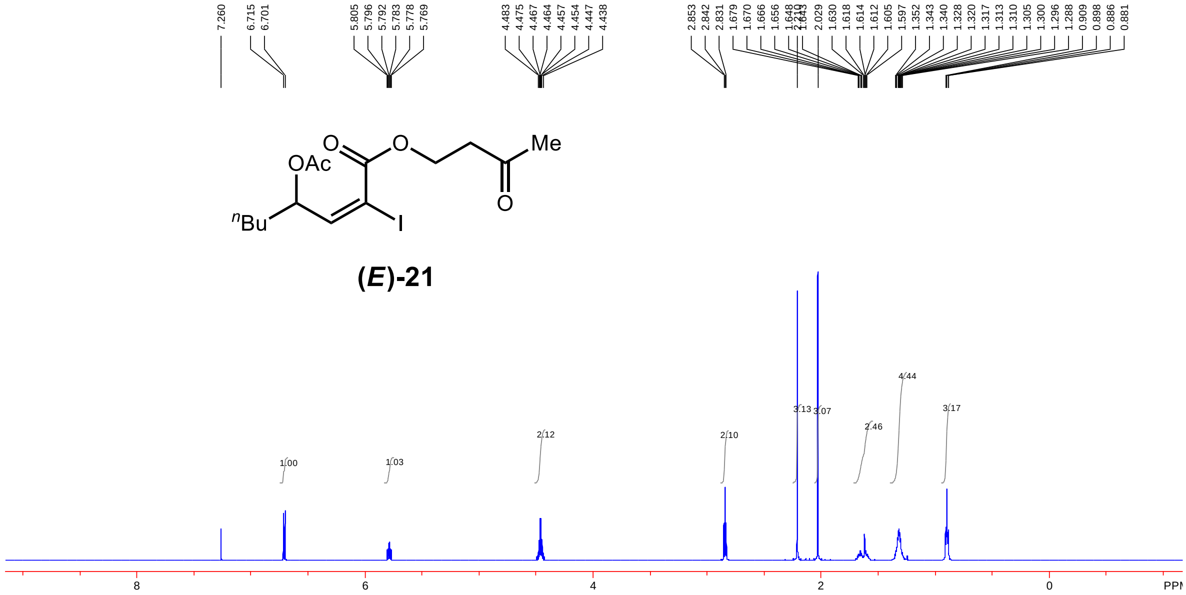
**20**


7.260
7.131
7.111
5.409
5.396
5.390
5.377
5.370
5.358
4.467
4.452
4.436
2.841
2.825
2.810
2.202
2.179
2.078
2.058
2.031
1.656
1.652
1.648
1.363
1.351
1.343
1.339
1.336
1.333
1.326
1.324
0.916
0.912
0.902
0.898
0.892
0.889
0.880
OAc
I
O
Me
$^n$Bu
O
O
0.98
1.00
2.06
2.16
3.28
3.12
2.72
4.49
3.34
8
6
4
2
0
PPM

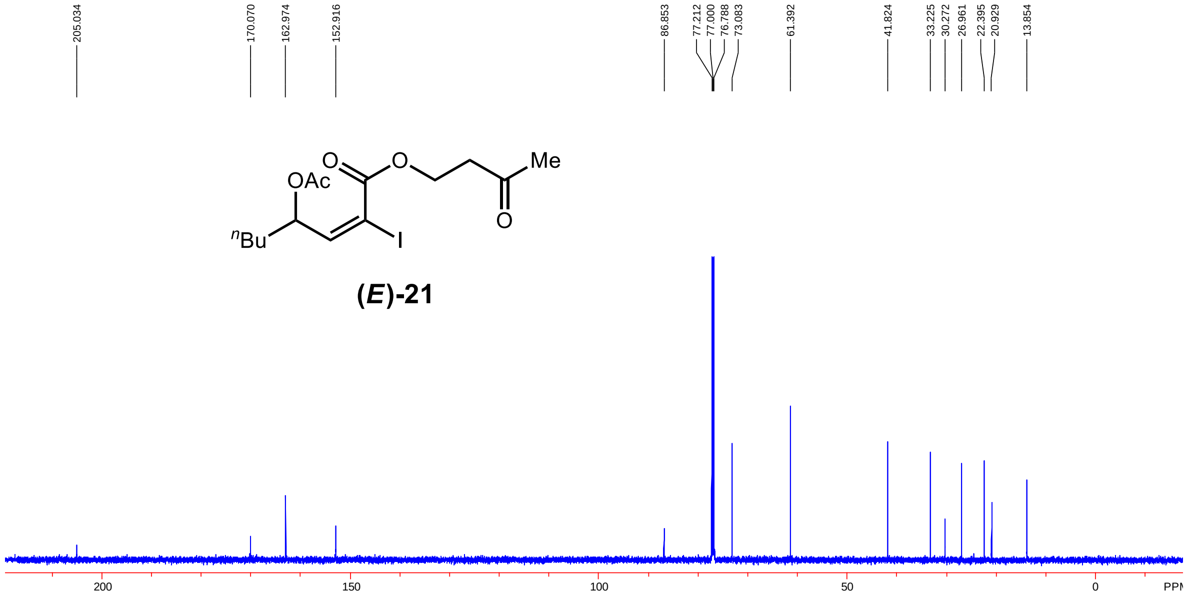
**(Z)-21**


205.034
170.143
162.252
150.626
93.702
77.613
77.212
77.000
76.788
61.735
41.992
32.285
30.286
26.902
22.388
20.863
13.811
OAc
I
O
Me
$^n$Bu
O
O
200
150
100
50
0
PPM

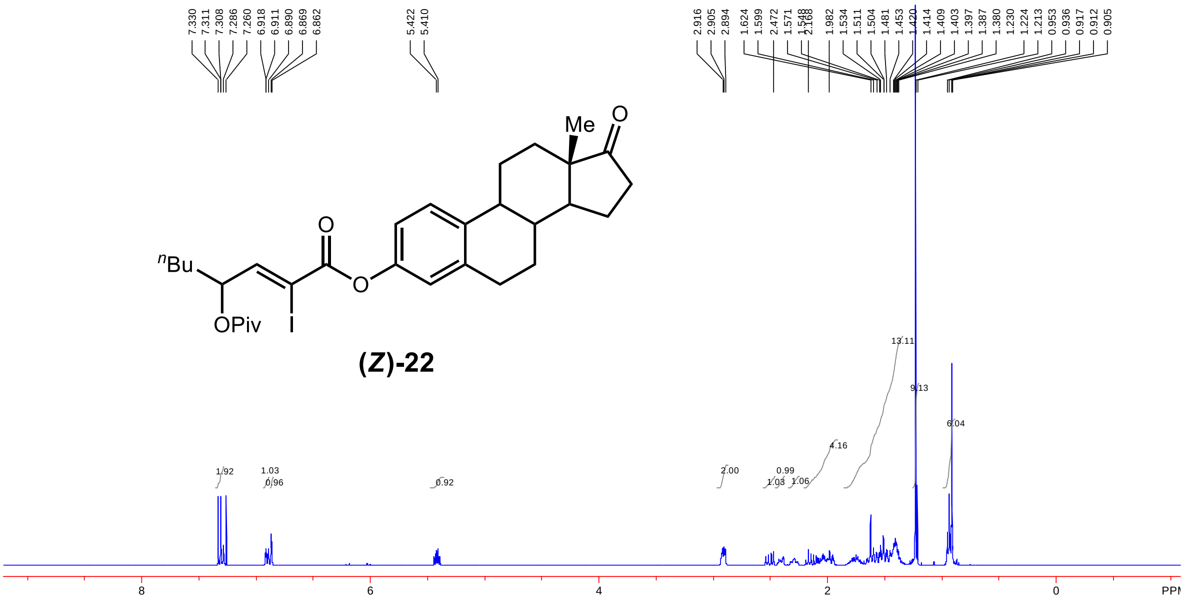
**(Z)-21**


7.260
6.715
6.701
5.805
5.796
5.792
5.783
5.778
5.769
4.483
4.475
4.467
4.464
4.457
4.454
4.447
4.438
2.853
2.842
2.831
1.679
1.670
1.666
1.656
1.648
2.210
1.643
2.029
1.630
1.618
1.614
1.612
1.605
1.597
1.352
1.343
1.340
1.328
1.320
1.317
1.313
1.310
1.305
1.300
1.296
1.288
0.909
0.898
0.886
0.881
OAc
O
O
Me
O
I
$^n$Bu
1.00
1.03
2.12
2.10
3.13
3.07
2.46
4.44
3.17
8
6
4
2
0
PPM

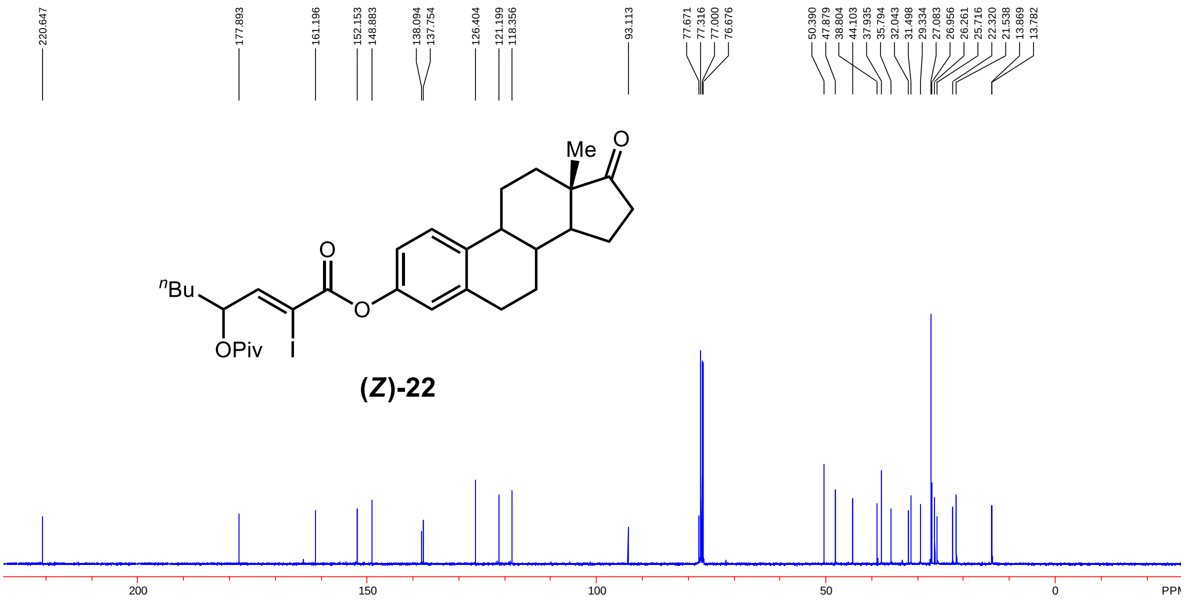
**(*E*)-21**


205.034
170.070
162.974
152.916
86.853
77.212
77.000
76.788
73.083
61.392
41.824
33.225
30.272
26.961
22.395
20.929
13.854
OAc
O
O
Me
O
I
$^n$Bu
200
150
100
50
0
PPM

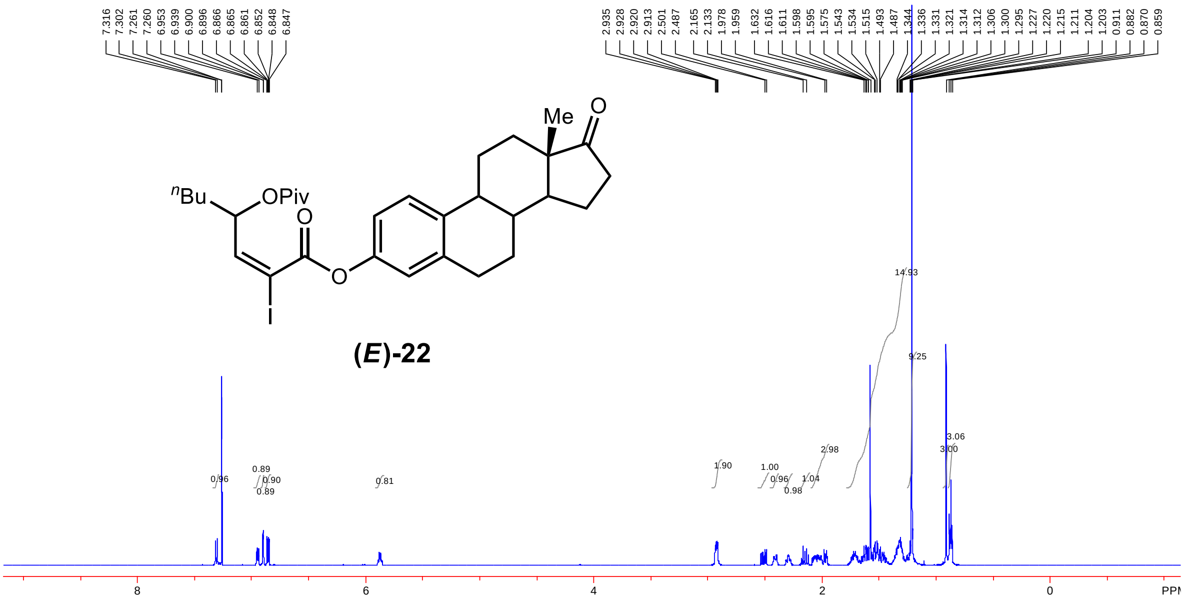
**(*E*)-21**


7.330
7.311
7.308
7.286
7.260
6.918
6.911
6.890
6.869
6.862
5.422
5.410
2.916
2.905
2.894
1.624
1.599
2.472
1.571
1.548
2.168
1.982
1.534
1.511
1.504
1.481
1.453
1.420
1.414
1.409
1.403
1.397
1.387
1.380
1.230
1.224
1.213
0.953
0.936
0.917
0.912
0.905
Me
O
O
O
ⁿBu
OPiv
I
13.11
9.13
6.04
4.16
1.92
1.03
0.96
0.92
2.00
0.99
1.03
1.06
8
6
4
2
0
PPM

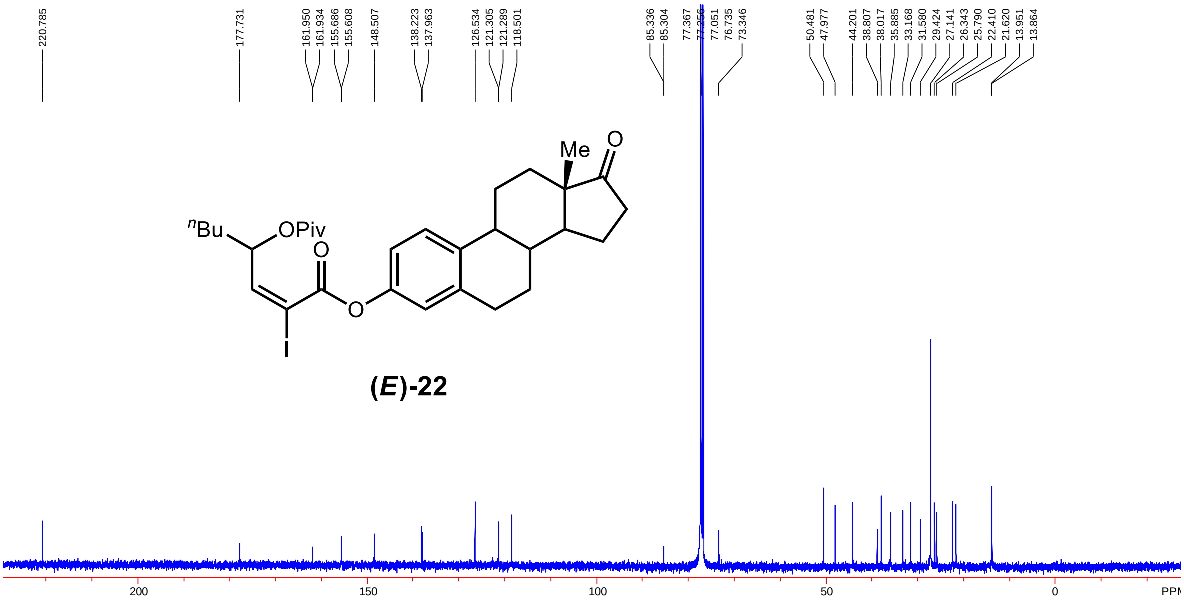
(Z)-22


220.647
177.893
161.196
152.153
148.883
138.094
137.754
126.404
121.199
118.356
93.113
77.671
77.316
77.000
76.676
50.390
47.879
38.804
44.103
37.935
35.794
32.043
31.498
29.334
27.083
26.956
26.261
25.716
22.320
21.538
13.869
13.782
Me
O
O
O
ⁿBu
OPiv
I
200
150
100
50
0
PPM

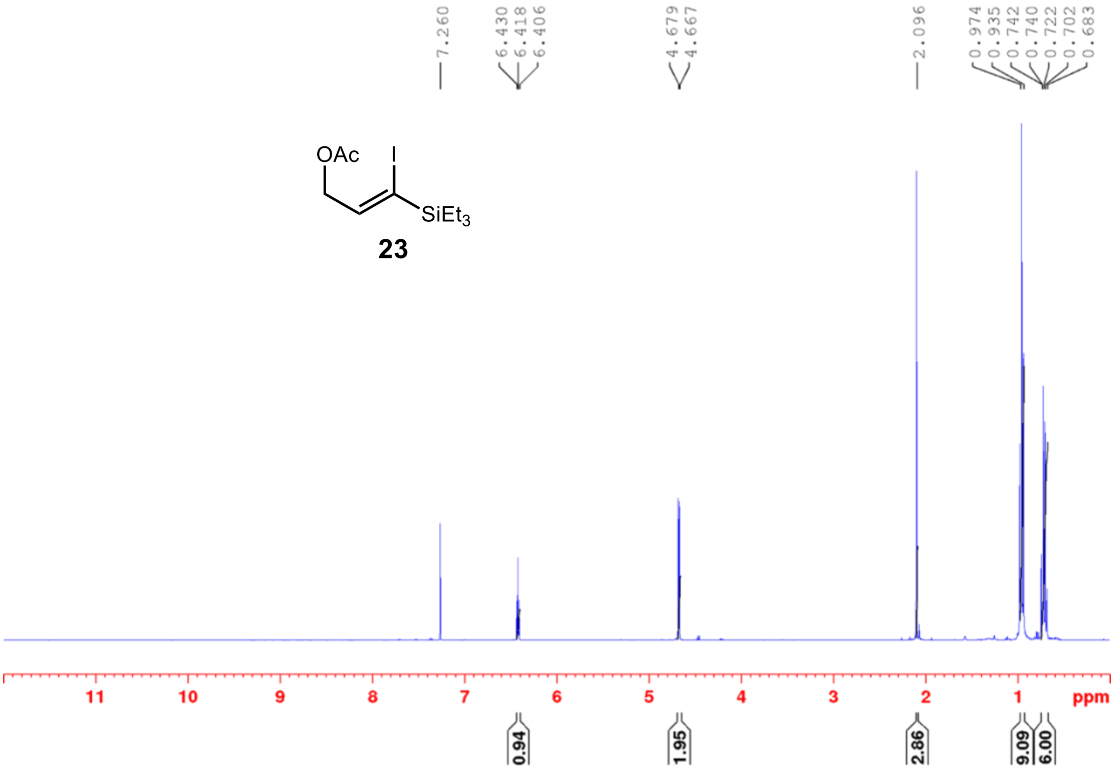
(Z)-22

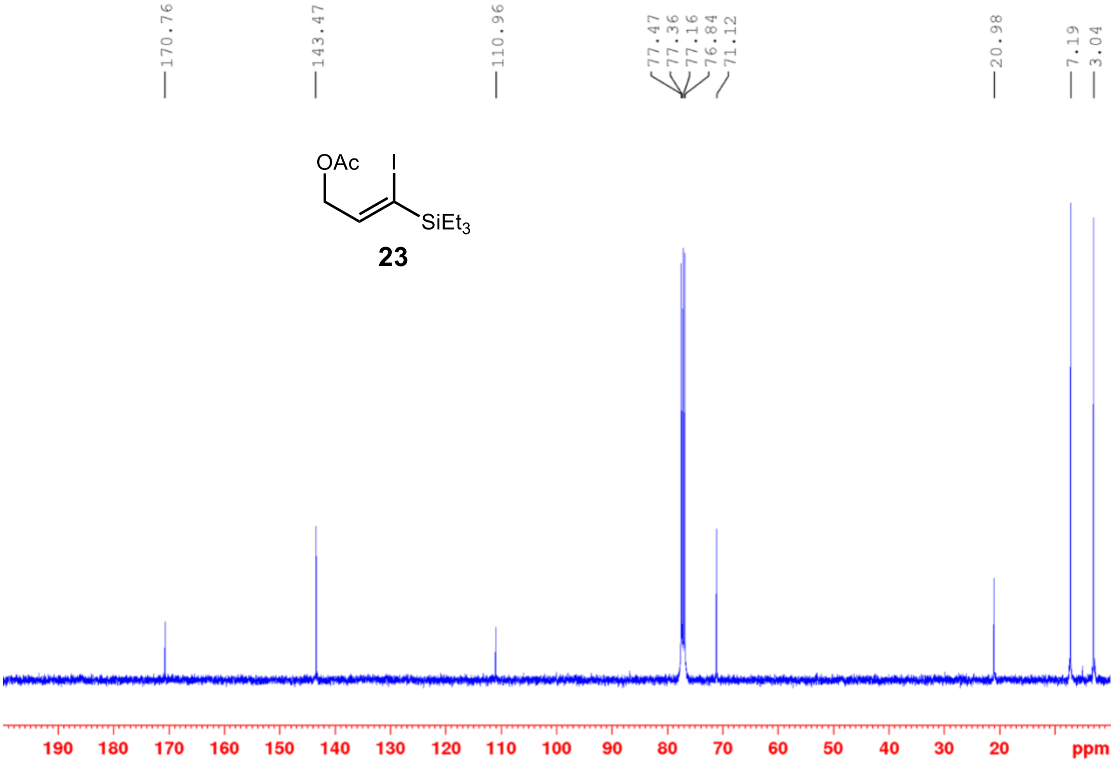

7.316
7.302
7.261
7.260
6.953
6.939
6.900
6.896
6.866
6.865
6.861
6.852
6.848
6.847
2.935
2.928
2.920
2.913
2.501
2.487
2.165
2.133
1.978
1.959
1.632
1.616
1.611
1.598
1.595
1.575
1.543
1.534
1.515
1.493
1.487
1.344
1.336
1.331
1.321
1.314
1.312
1.306
1.300
1.295
1.227
1.220
1.215
1.211
1.204
1.203
0.911
0.882
0.870
0.859
$^n$Bu
OPiv
O
O
I
Me
O
0.96
0.89
0.90
0.89
0.81
1.90
1.00
0.96
0.98
1.04
2.98
14.93
9.25
3.06
3.00
8
6
4
2
0
PPM

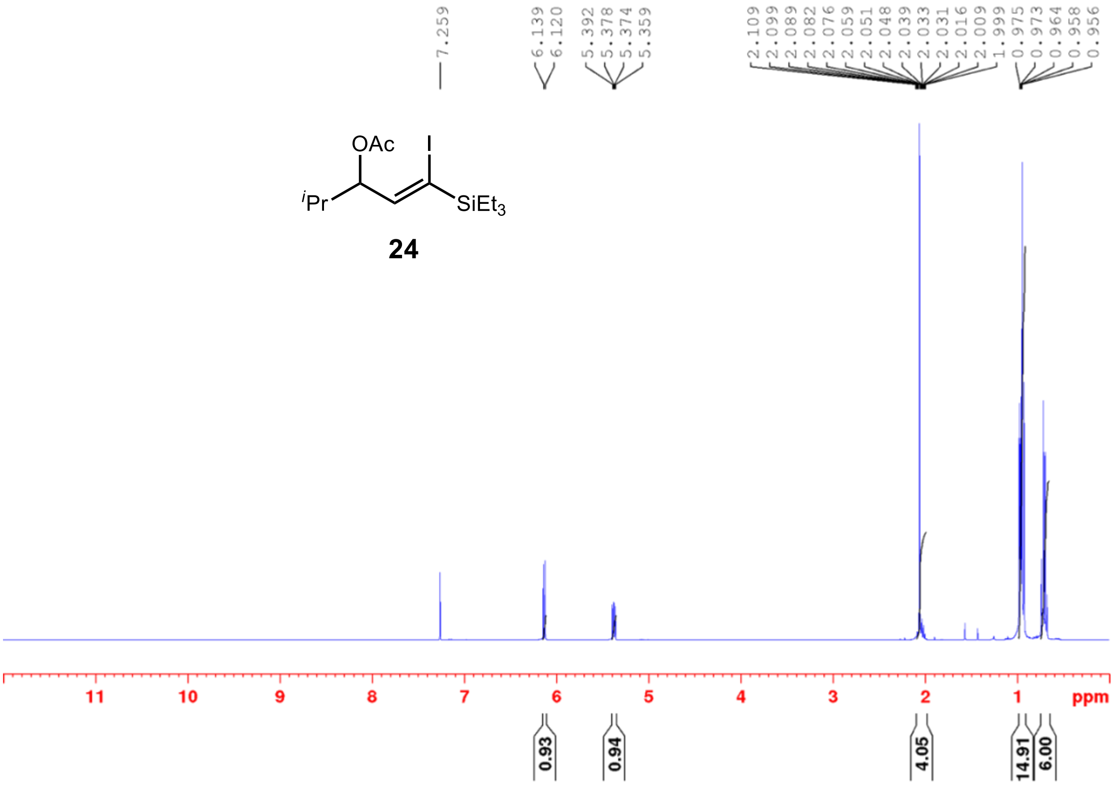
**(*E*)-22**

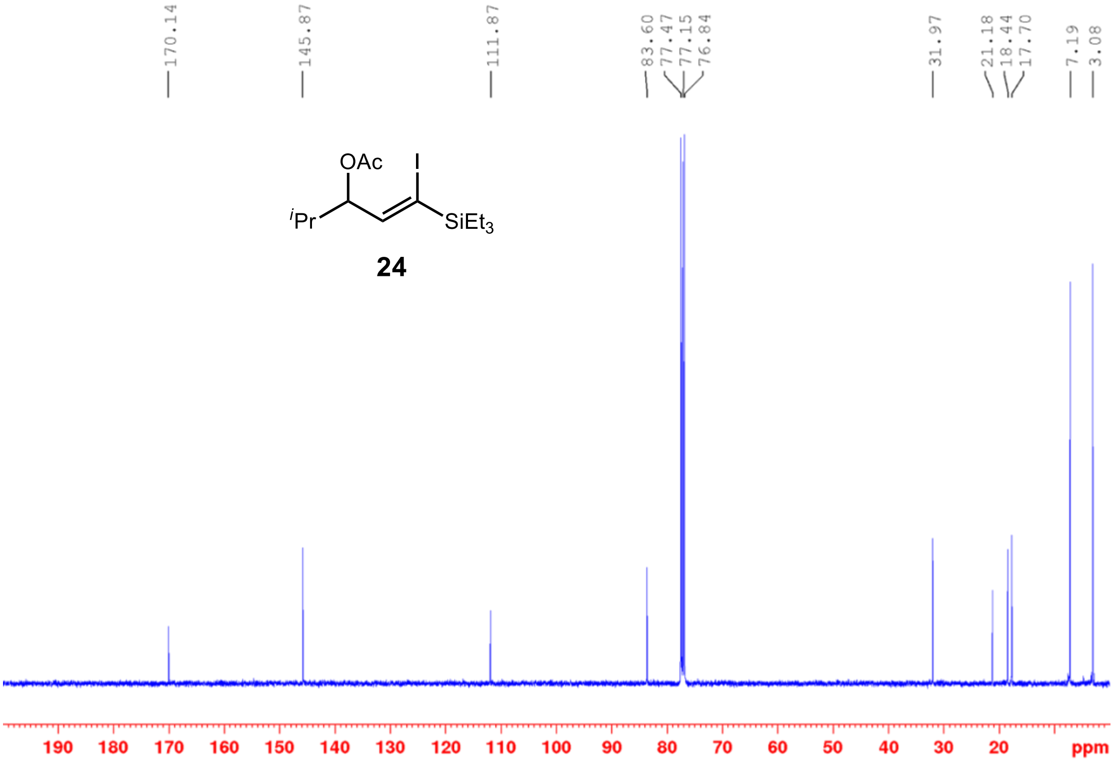

220.785
177.731
161.950
161.934
155.686
155.608
148.507
138.223
137.963
126.534
121.305
121.289
118.501
85.336
85.304
77.367
77.256
77.051
76.735
73.346
50.481
47.977
44.201
38.807
38.017
35.885
33.168
31.580
29.424
27.141
26.343
25.790
22.410
21.620
13.951
13.864
$^n$Bu
OPiv
O
O
I
Me
O
200
150
100
50
0
PPM

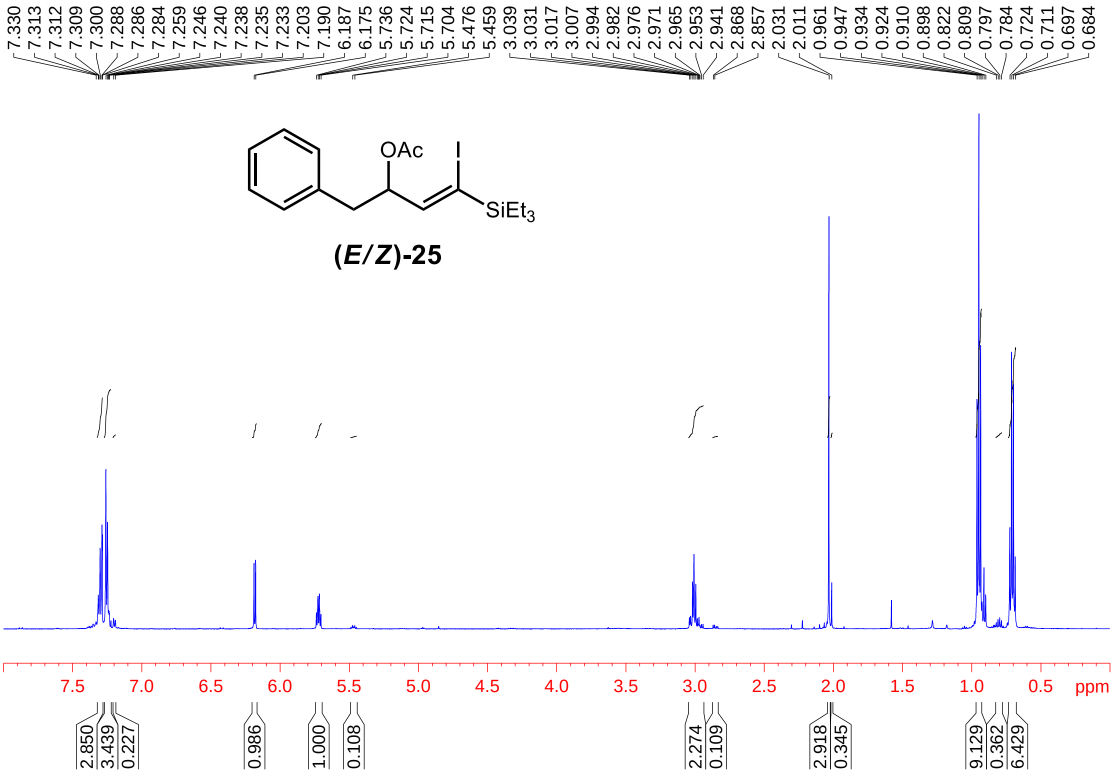
**(*E*)-22**


7.260
6.430
6.418
6.406
4.679
4.667
2.096
0.974
0.935
0.742
0.740
0.722
0.702
0.683
OAc
I
SiEt3
23
11
10
9
8
7
6
5
4
3
2
1
ppm
0.94
1.95
2.86
9.09
6.00

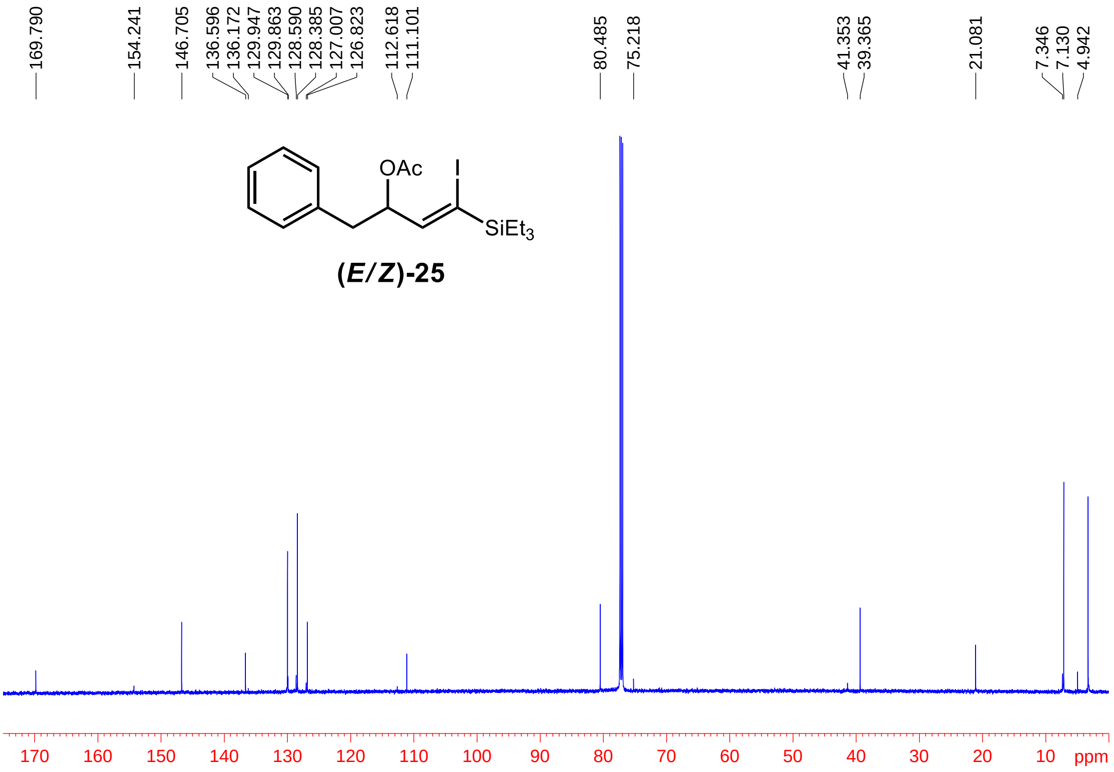

170.76
143.47
110.96
77.47
77.36
77.16
76.84
71.12
20.98
7.19
3.04
OAc
I
SiEt3
23
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.259
6.139
6.120
5.392
5.378
5.374
5.359
2.109
2.099
2.089
2.082
2.076
2.059
2.051
2.048
2.039
2.033
2.031
2.016
2.009
1.999
0.975
0.973
0.964
0.958
0.956
OAc
I
iPr
SiEt3
24
11
10
9
8
7
6
5
4
3
2
1
ppm
0.93
0.94
4.05
14.91
6.00

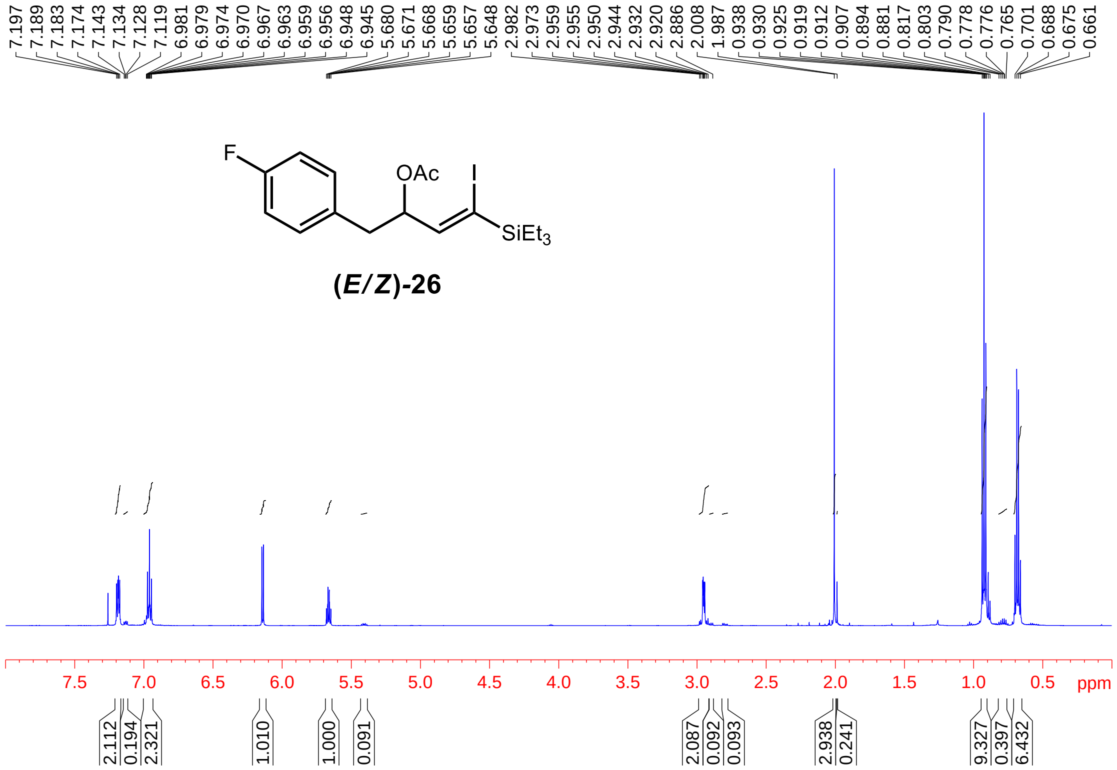

170.14
145.87
111.87
83.60
77.47
77.15
76.84
31.97
21.18
18.44
17.70
7.19
3.08
OAc
I
iPr
SiEt3
24
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

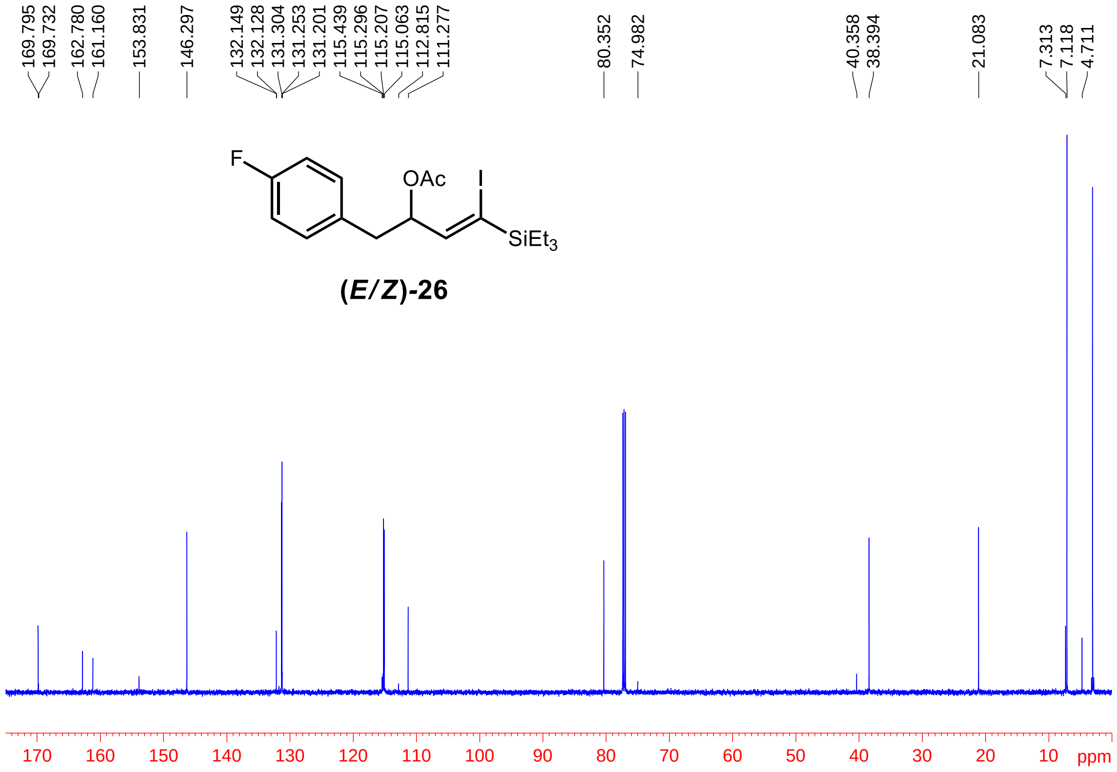

7.330
7.313
7.312
7.309
7.300
7.288
7.286
7.284
7.259
7.246
7.240
7.238
7.235
7.233
7.203
7.190
6.187
6.175
5.736
5.724
5.715
5.704
5.476
5.459
3.039
3.031
3.017
3.007
2.994
2.982
2.976
2.971
2.965
2.953
2.941
2.868
2.857
2.031
2.011
0.961
0.947
0.934
0.924
0.910
0.898
0.822
0.809
0.797
0.784
0.724
0.711
0.697
0.684
OAc
I
SiEt$_3$
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.850
3.439
0.227
0.986
1.000
0.108
2.274
0.109
2.918
0.345
9.129
0.362
6.429

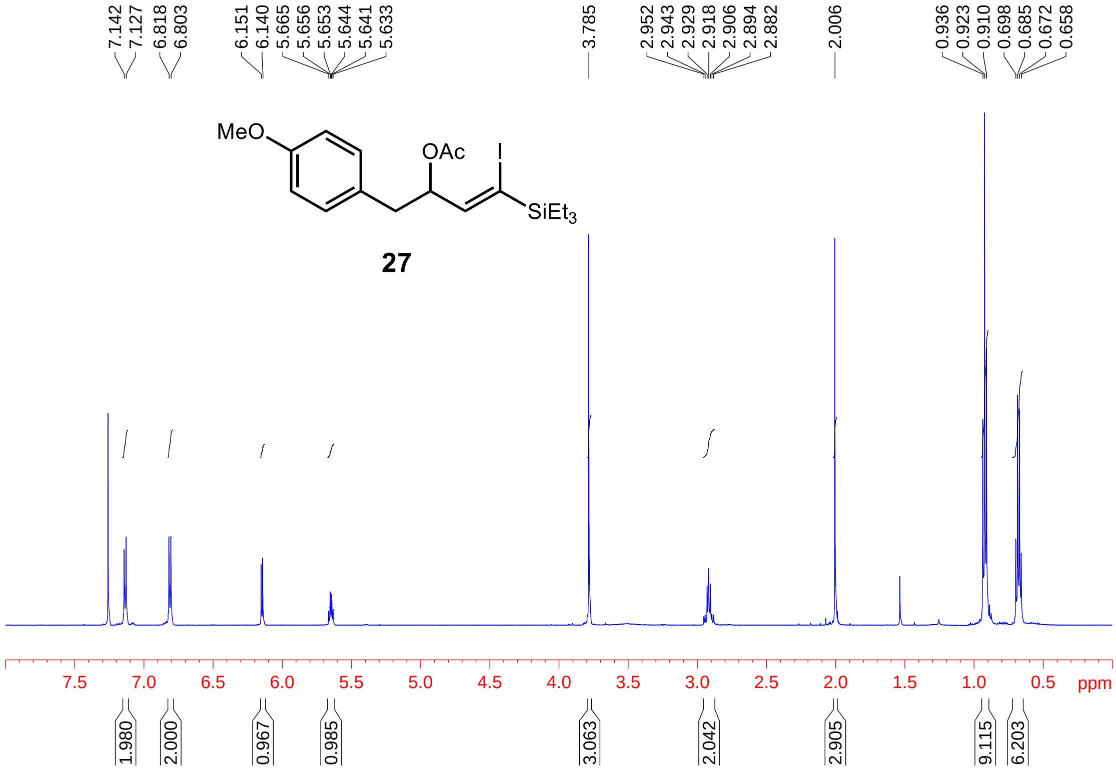
**(*E*/*Z*)-25**

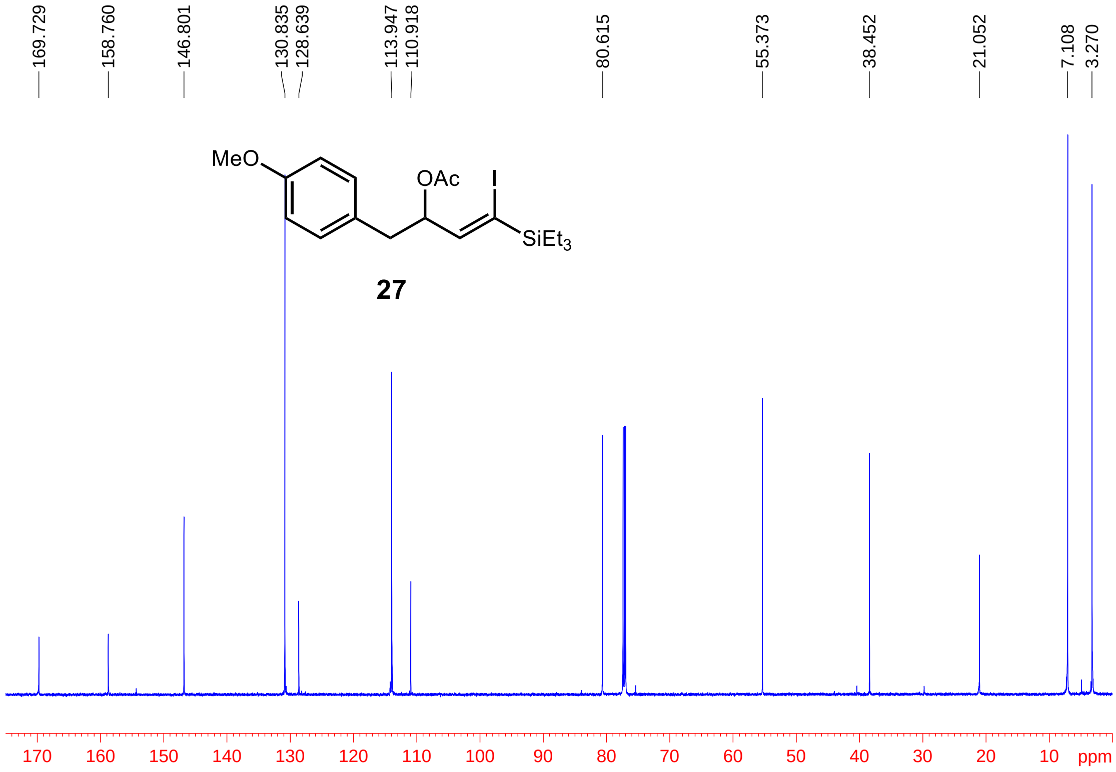

169.790
154.241
146.705
136.596
136.172
129.947
129.863
128.590
128.385
127.007
126.823
112.618
111.101
80.485
75.218
41.353
39.365
21.081
7.346
7.130
4.942
OAc
I
SiEt$_3$
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

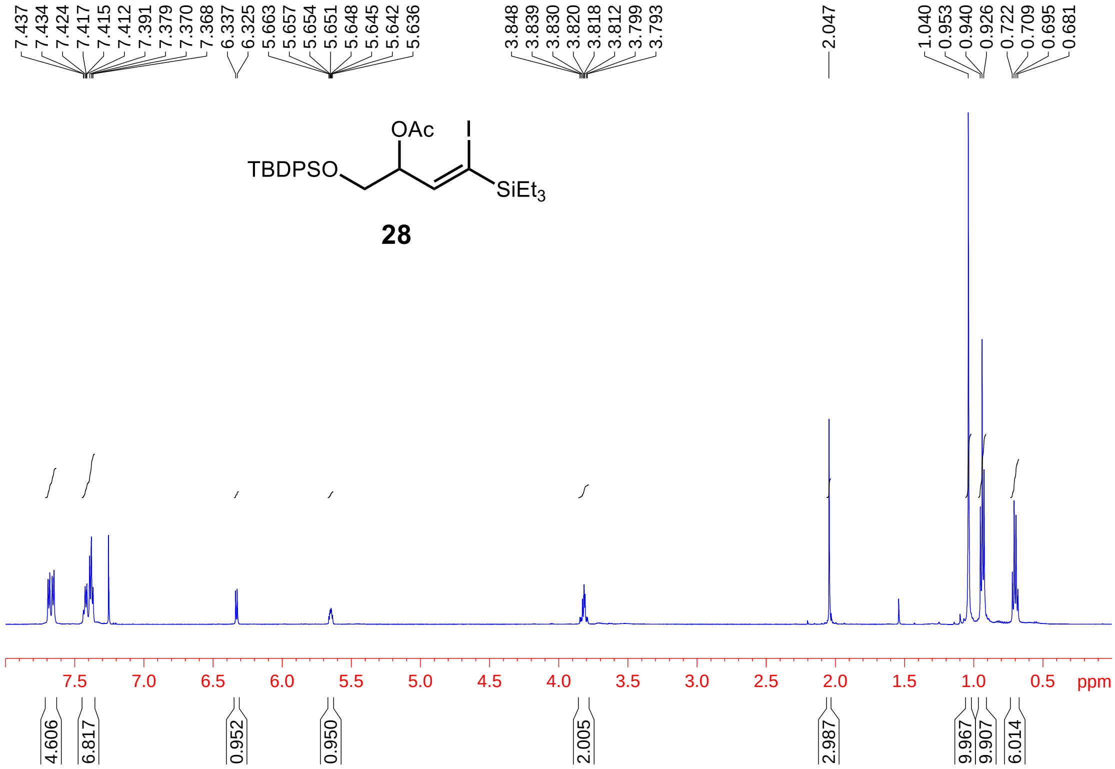
**(*E*/*Z*)-25**

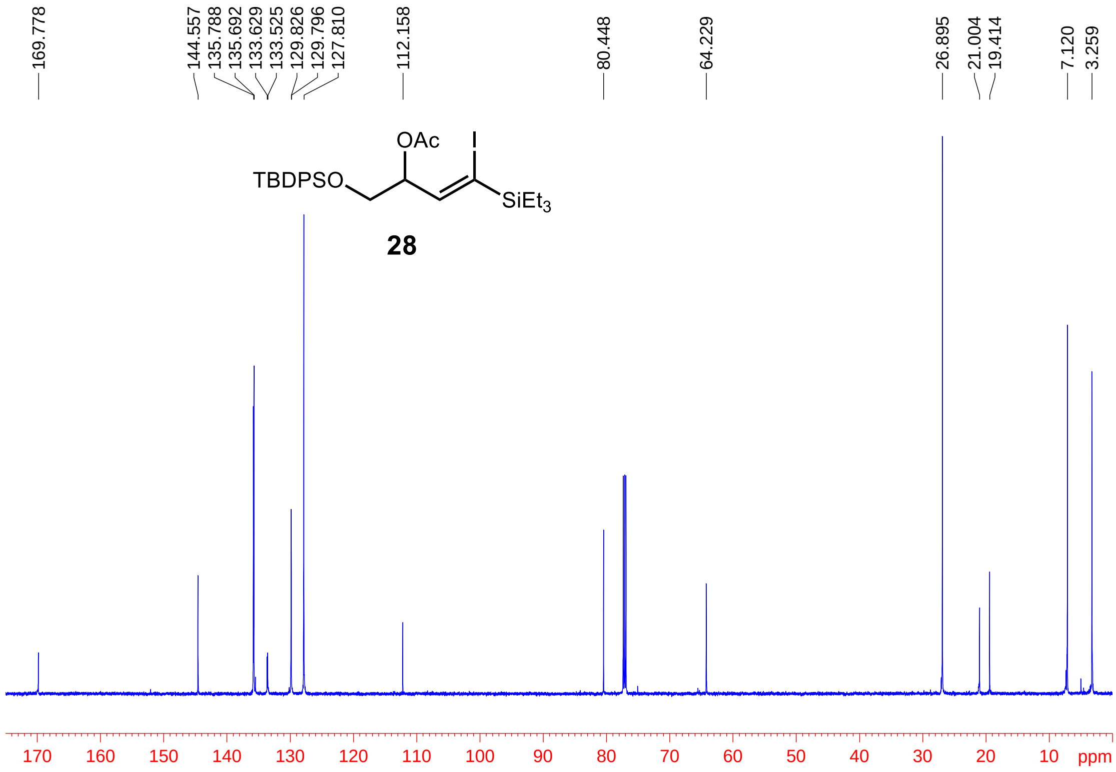

7.197
7.189
7.183
7.174
7.143
7.134
7.128
7.119
6.981
6.979
6.974
6.970
6.967
6.963
6.959
6.956
6.948
6.945
5.680
5.671
5.668
5.659
5.657
5.648
2.982
2.973
2.959
2.955
2.950
2.944
2.932
2.920
2.886
2.008
1.987
0.938
0.930
0.925
0.919
0.912
0.907
0.894
0.881
0.817
0.803
0.790
0.778
0.776
0.765
0.701
0.688
0.675
0.661
F
OAc
I
SiEt3
(E/Z)-26
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.112
0.194
2.321
1.010
1.000
0.091
2.087
0.092
0.093
2.938
0.241
9.327
0.397
6.432

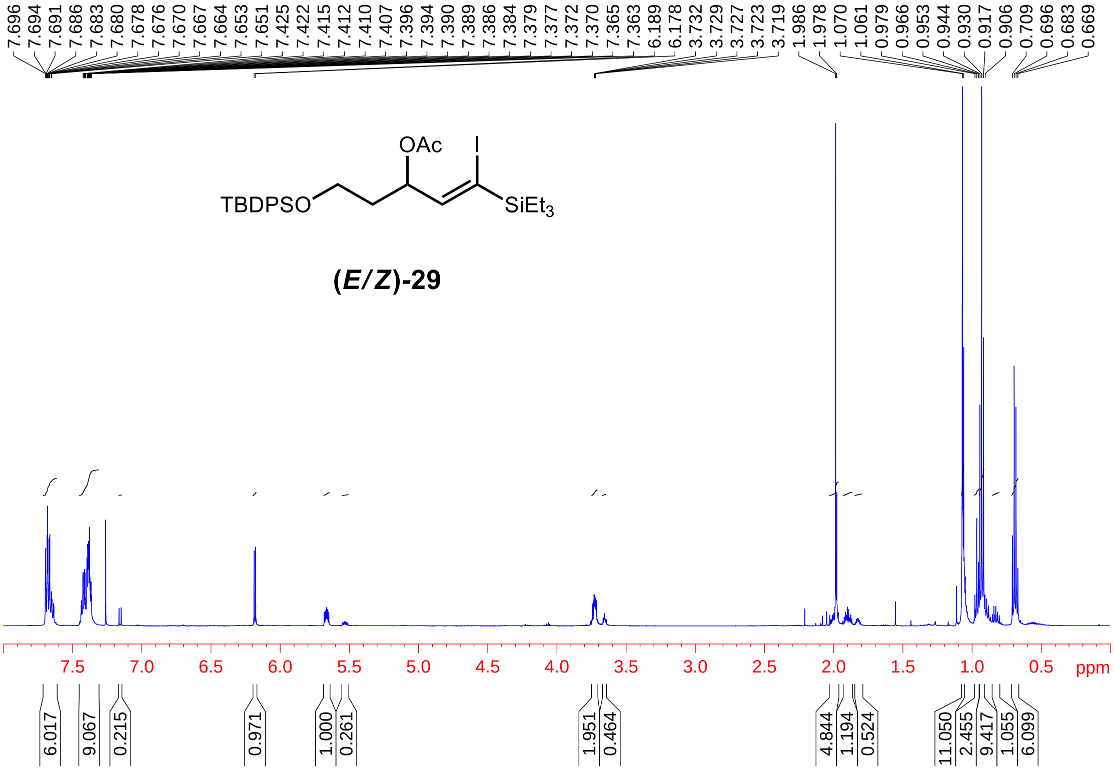

169.795
169.732
162.780
161.160
153.831
146.297
132.149
132.128
131.304
131.253
131.201
115.439
115.296
115.207
115.063
112.815
111.277
80.352
74.982
40.358
38.394
21.083
7.313
7.118
4.711
F
OAc
I
SiEt3
(E/Z)-26
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.142
7.127
6.818
6.803
6.151
6.140
5.665
5.656
5.653
5.644
5.641
5.633
3.785
2.952
2.943
2.929
2.918
2.906
2.894
2.882
2.006
0.936
0.923
0.910
0.698
0.685
0.672
0.658
MeO
OAc
I
SiEt3
27
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.980
2.000
0.967
0.985
3.063
2.042
2.905
9.115
6.203

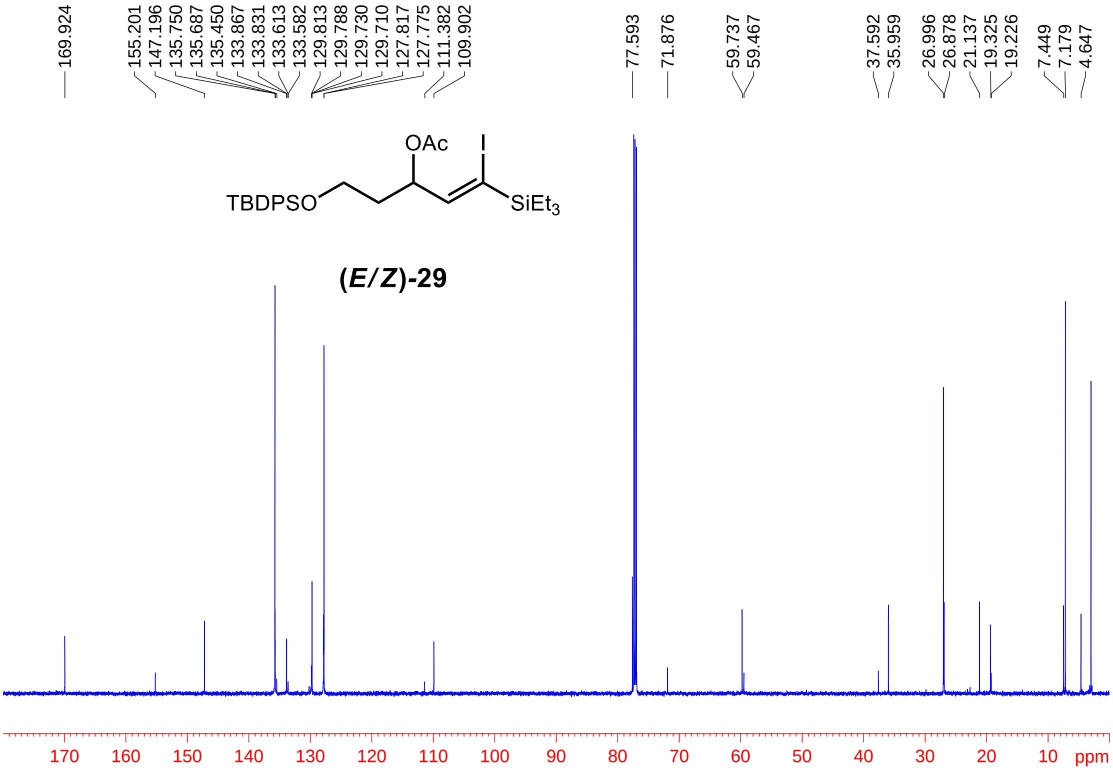

169.729
158.760
146.801
130.835
128.639
113.947
110.918
80.615
55.373
38.452
21.052
7.108
3.270
MeO
OAc
I
SiEt3
27
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.437 7.434 7.424 7.417 7.415 7.412 7.391 7.379 7.370 7.368 6.337 6.325 5.663 5.657 5.654 5.651 5.648 5.645 5.642 5.636
3.848 3.839 3.830 3.820 3.818 3.812 3.799 3.793
2.047
1.040 0.953 0.940 0.926 0.722 0.709 0.695 0.681
OAc
I
TBDPSO
SiEt3
28
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.606 6.817 0.952 0.950 2.005 2.987 9.967 9.907 6.014

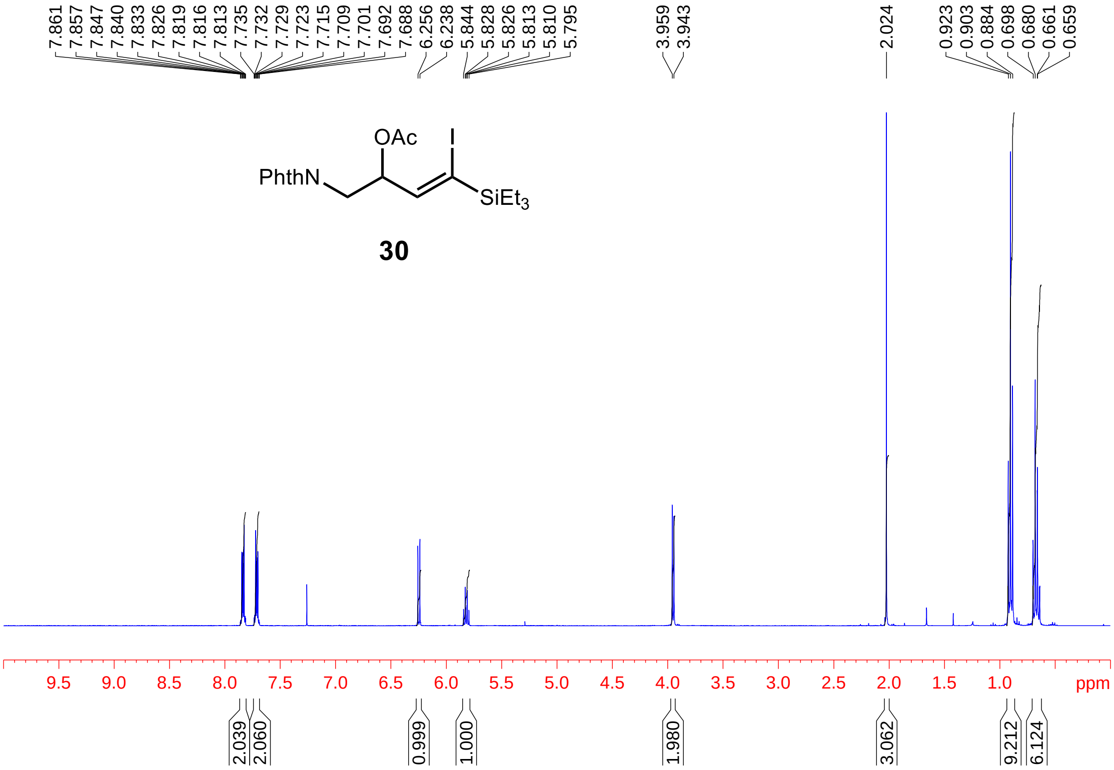

169.778
144.557 135.788 135.692 133.629 133.525 129.826 129.796 127.810
112.158
80.448
64.229
26.895 21.004 19.414
7.120 3.259
OAc
I
TBDPSO
SiEt3
28
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

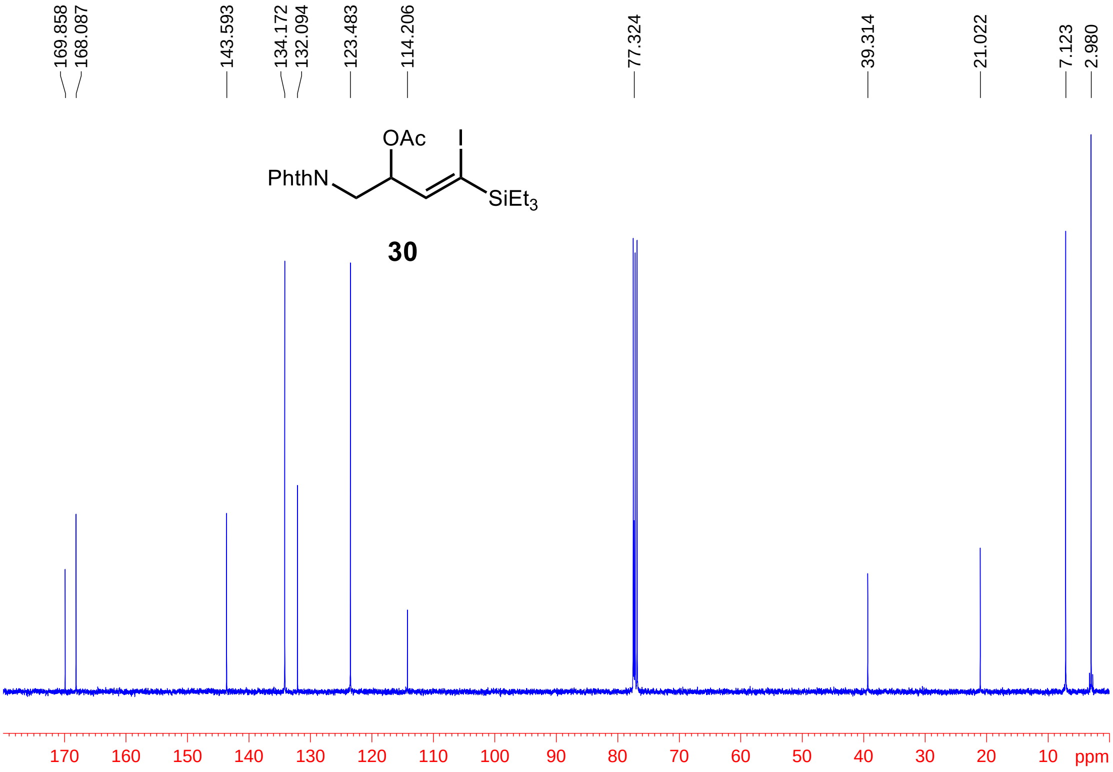

7.696
7.694
7.691
7.686
7.683
7.680
7.678
7.676
7.670
7.667
7.664
7.653
7.651
7.425
7.422
7.415
7.412
7.410
7.407
7.396
7.394
7.390
7.389
7.386
7.384
7.379
7.377
7.372
7.370
7.365
7.363
6.189
6.178
3.732
3.729
3.727
3.723
3.719
1.986
1.978
1.070
1.061
0.979
0.966
0.953
0.944
0.930
0.917
0.906
0.709
0.696
0.683
0.669
OAc
I
TBDPSO
SiEt3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
6.017
9.067
0.215
0.971
1.000
0.261
1.951
0.464
4.844
1.194
0.524
11.050
2.455
9.417
1.055
6.099

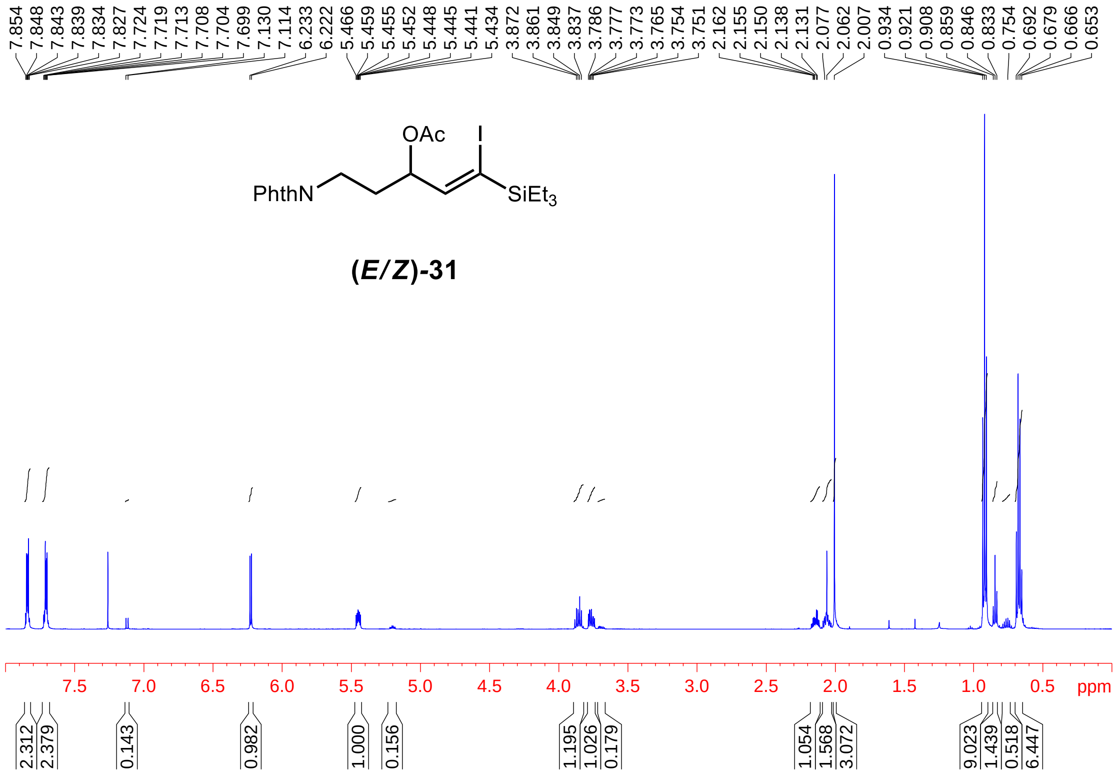
(*E*/*Z*)-29


169.924
155.201
147.196
135.750
135.687
135.450
133.867
133.831
133.613
133.582
129.813
129.788
129.730
129.710
127.817
127.775
111.382
109.902
77.593
71.876
59.737
59.467
37.592
35.959
26.996
26.878
21.137
19.325
19.226
7.449
7.179
4.647
OAc
I
TBDPSO
SiEt3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

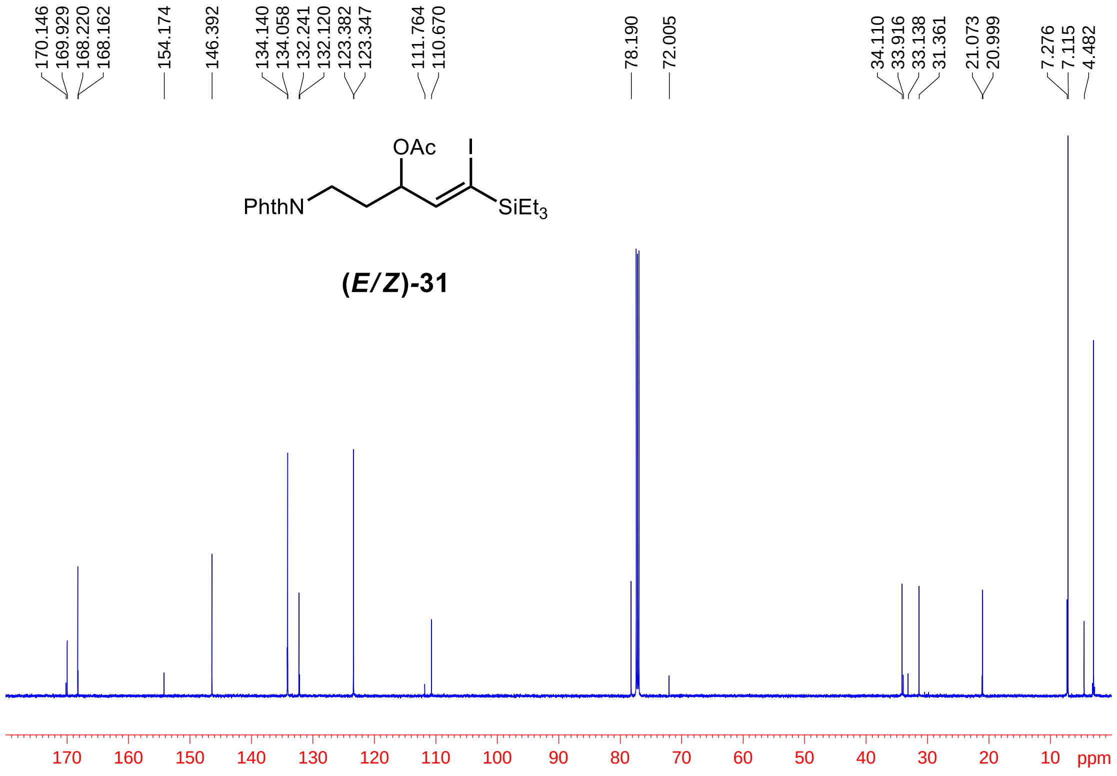
(*E*/*Z*)-29


7.861
7.857
7.847
7.840
7.833
7.826
7.819
7.816
7.813
7.735
7.732
7.729
7.723
7.715
7.709
7.701
7.692
7.688
6.256
6.238
5.844
5.828
5.826
5.813
5.810
5.795
3.959
3.943
2.024
0.923
0.903
0.884
0.698
0.680
0.661
0.659
OAc
I
PhthN
SiEt3
30
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.039
2.060
0.999
1.000
1.980
3.062
9.212
6.124

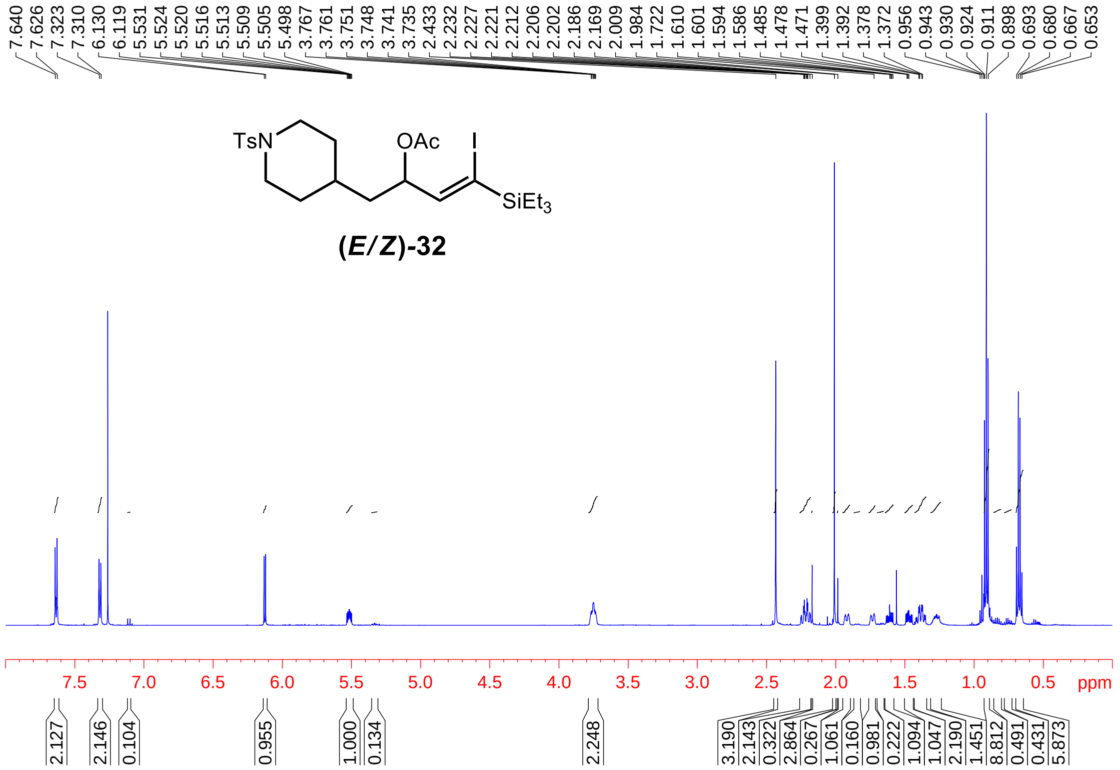

169.858
168.087
143.593
134.172
132.094
123.483
114.206
77.324
39.314
21.022
7.123
2.980
OAc
I
PhthN
SiEt3
30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.854
7.848
7.843
7.839
7.834
7.827
7.724
7.719
7.713
7.708
7.704
7.699
7.130
7.114
6.233
6.222
5.466
5.459
5.455
5.452
5.448
5.445
5.441
5.434
3.872
3.861
3.849
3.837
3.786
3.777
3.773
3.765
3.754
3.751
2.162
2.155
2.150
2.138
2.131
2.077
2.062
2.007
0.934
0.921
0.908
0.859
0.846
0.833
0.754
0.692
0.679
0.666
0.653
OAc
I
PhthN
SiEt3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.312
2.379
0.143
0.982
1.000
0.156
1.195
1.026
0.179
1.054
1.568
3.072
9.023
1.439
0.518
6.447

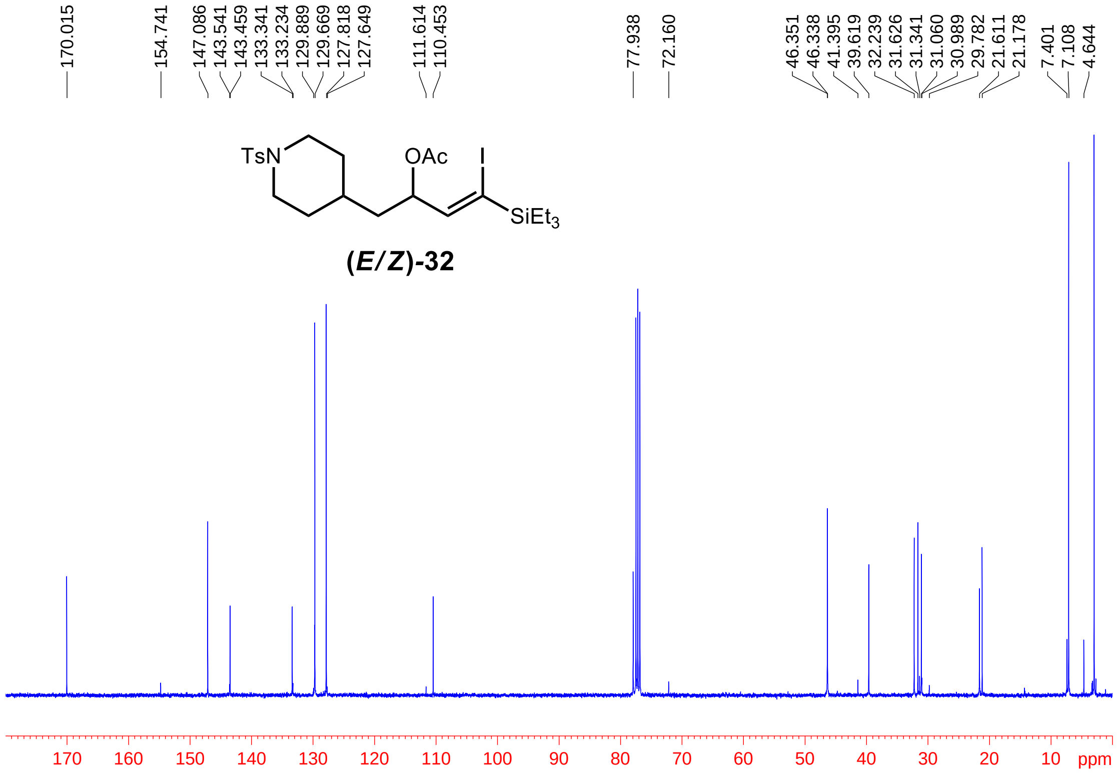
**(*E*/*Z*)-31**


170.146
169.929
168.220
168.162
154.174
146.392
134.140
134.058
132.241
132.120
123.382
123.347
111.764
110.670
78.190
72.005
34.110
33.916
33.138
31.361
21.073
20.999
7.276
7.115
4.482
OAc
I
PhthN
SiEt3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

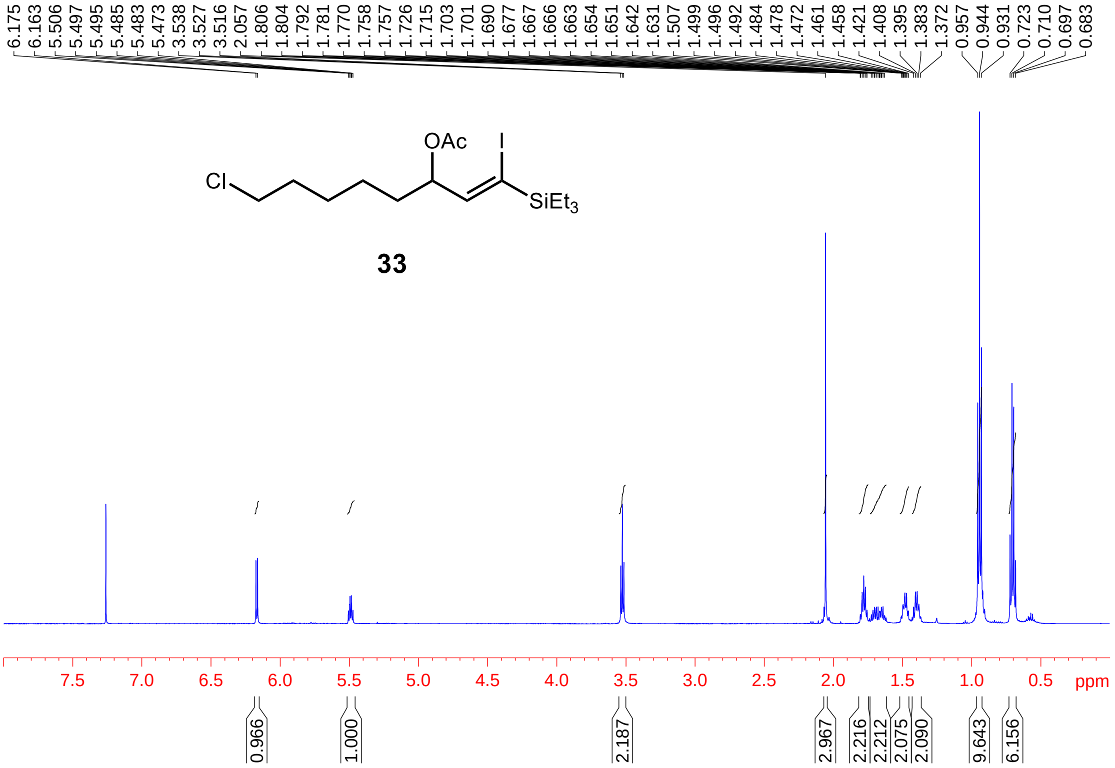
**(*E*/*Z*)-31**


7.640
7.626
7.323
7.310
6.130
6.119
5.531
5.524
5.520
5.516
5.513
5.509
5.505
5.498
3.767
3.761
3.751
3.748
3.741
3.735
2.433
2.232
2.227
2.221
2.212
2.206
2.202
2.186
2.169
2.009
1.984
1.722
1.610
1.601
1.594
1.586
1.485
1.478
1.471
1.399
1.392
1.378
1.372
0.956
0.943
0.930
0.924
0.911
0.898
0.693
0.680
0.667
0.653
TsN
OAc
I
SiEt3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.127
2.146
0.104
0.955
1.000
0.134
2.248
3.190
2.143
0.322
2.864
0.267
1.061
0.160
0.981
0.222
1.094
1.047
2.190
1.451
8.812
0.491
0.431
5.873

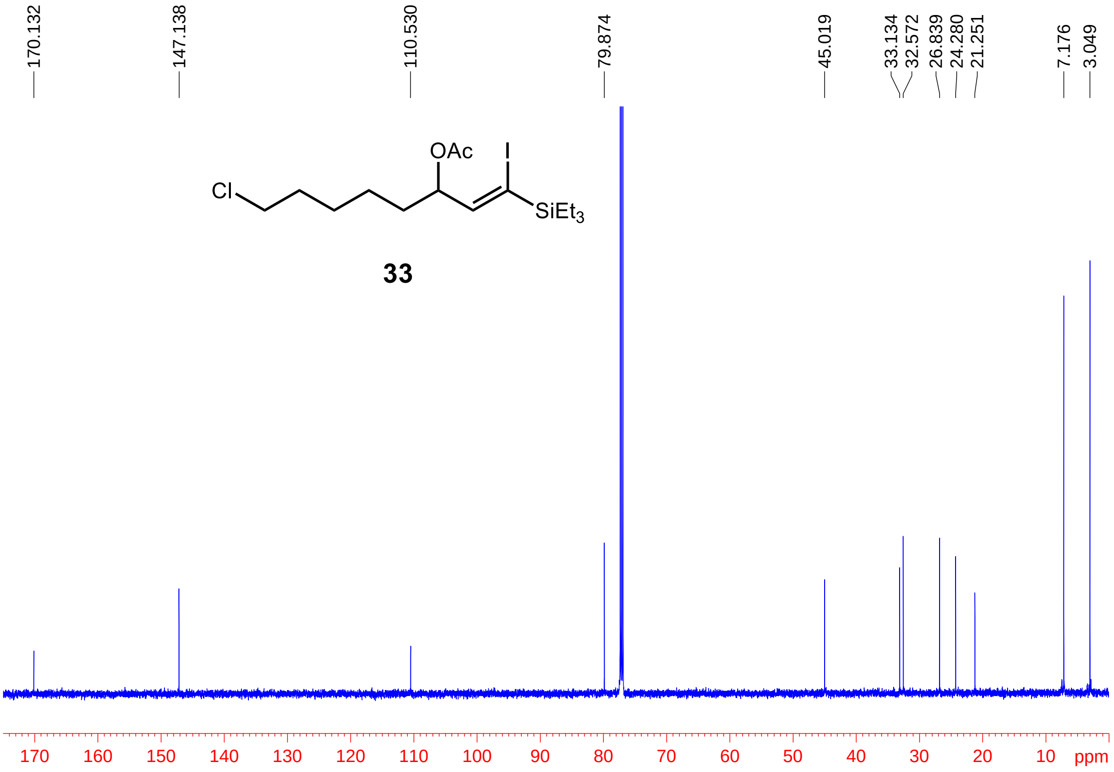
**(*E*/*Z*)-32**


170.015
154.741
147.086
143.541
143.459
133.341
133.234
129.889
129.669
127.818
127.649
111.614
110.453
77.938
72.160
46.351
46.338
41.395
39.619
32.239
31.626
31.341
31.060
30.989
29.782
21.611
21.178
7.401
7.108
4.644
TsN
OAc
I
SiEt3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

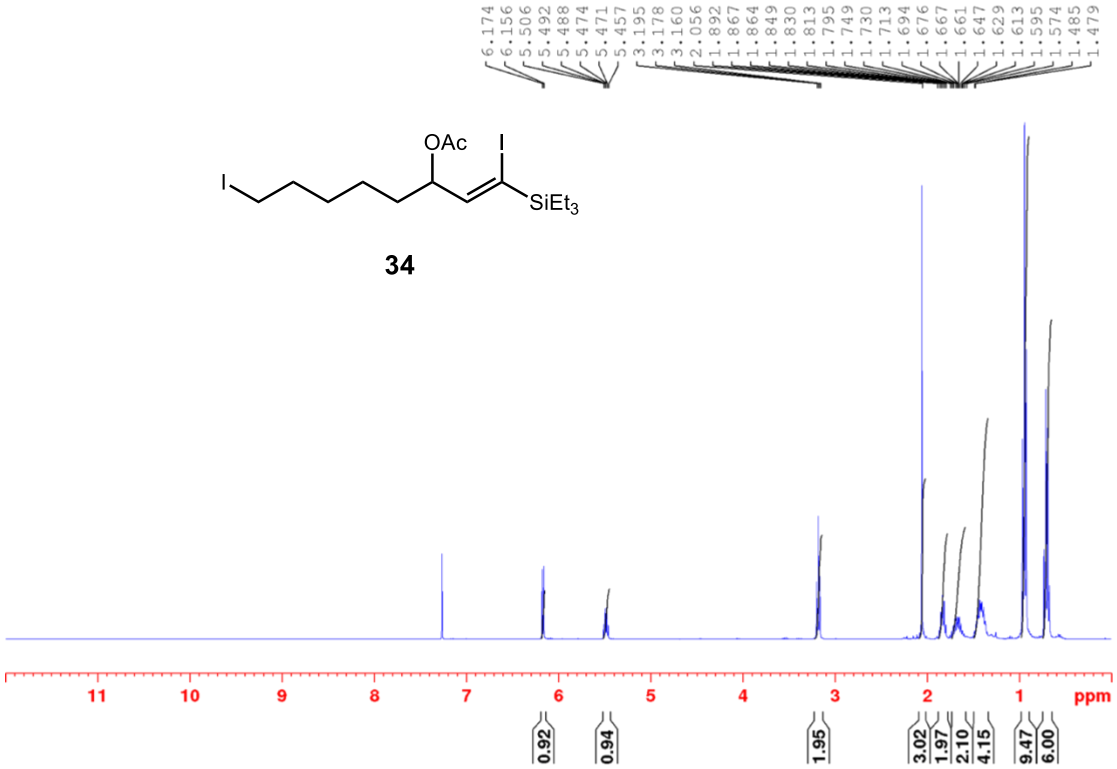
**(*E*/*Z*)-32**

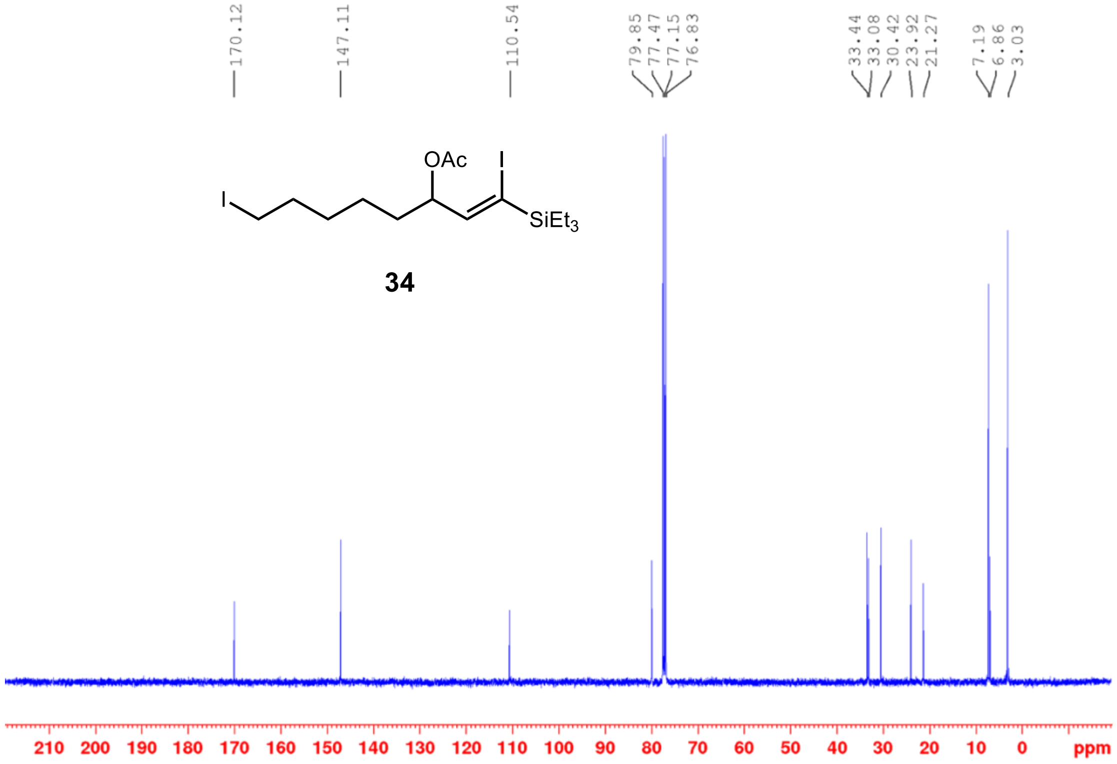

6.175
6.163
5.506
5.497
5.495
5.485
5.483
5.473
3.538
3.527
3.516
2.057
1.806
1.804
1.792
1.781
1.770
1.758
1.757
1.726
1.715
1.703
1.701
1.690
1.677
1.667
1.666
1.663
1.654
1.651
1.642
1.631
1.507
1.499
1.496
1.492
1.484
1.478
1.472
1.461
1.458
1.421
1.408
1.395
1.383
1.372
0.957
0.944
0.931
0.723
0.710
0.697
0.683
OAc
I
Cl
SiEt3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.966
1.000
2.187
2.967
2.216
2.212
2.075
2.090
9.643
6.156

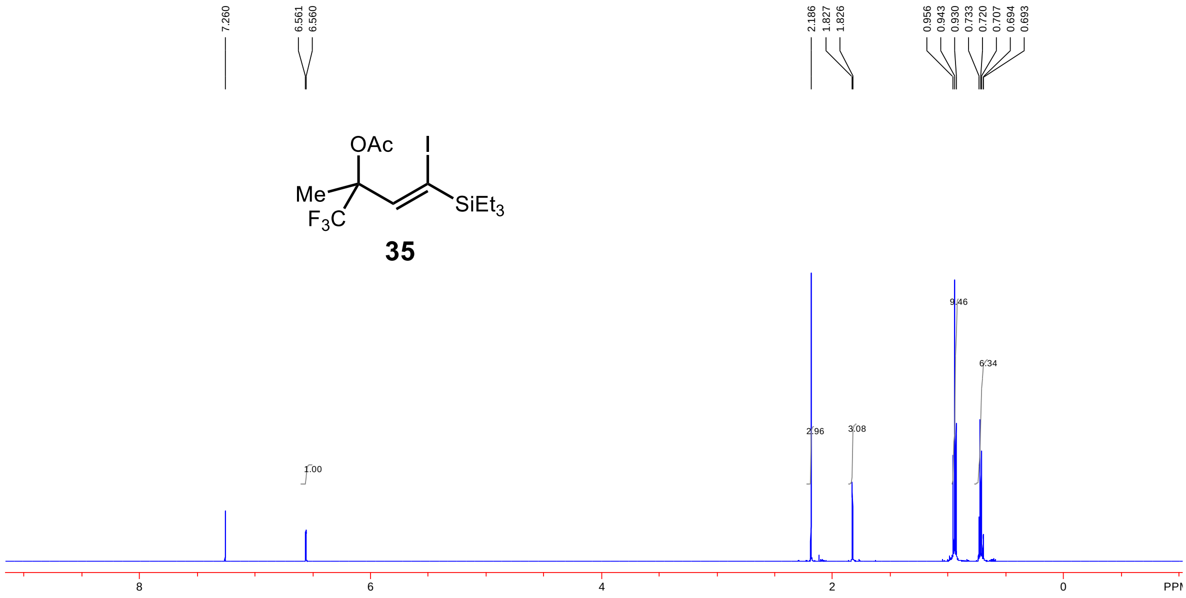
**33**

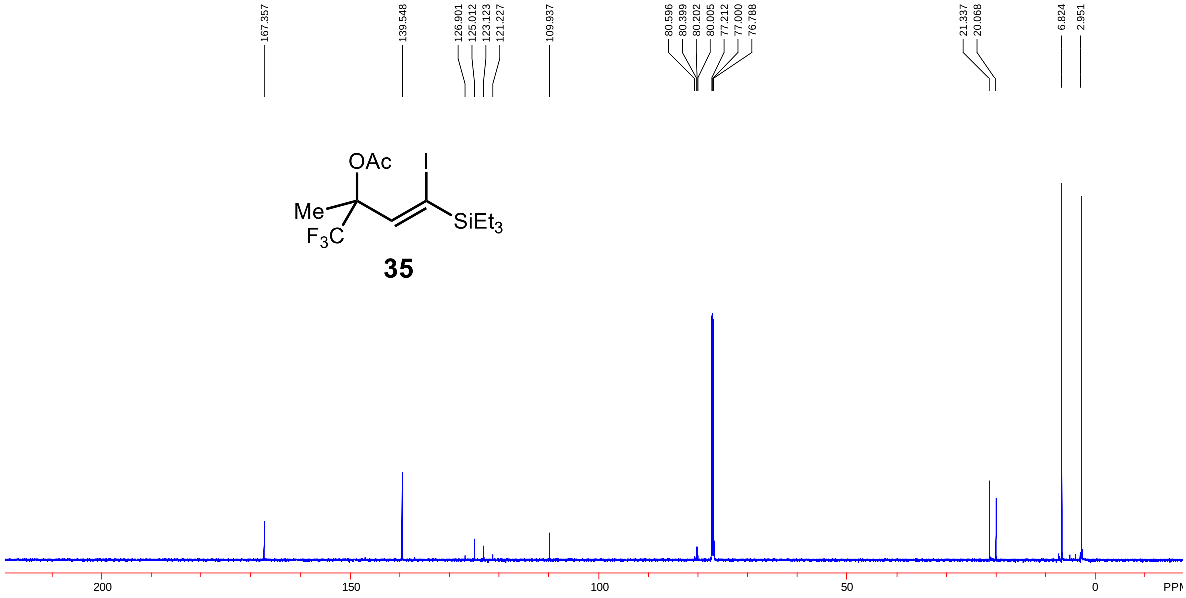

170.132
147.138
110.530
79.874
45.019
33.134
32.572
26.839
24.280
21.251
7.176
3.049
OAc
I
Cl
SiEt3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

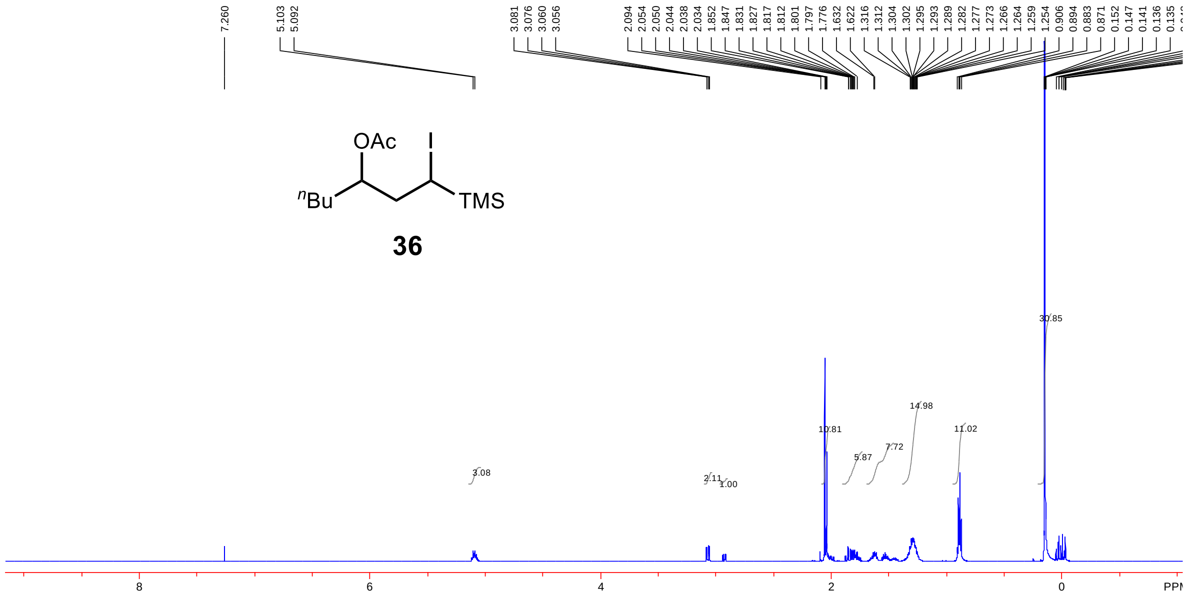
**33**

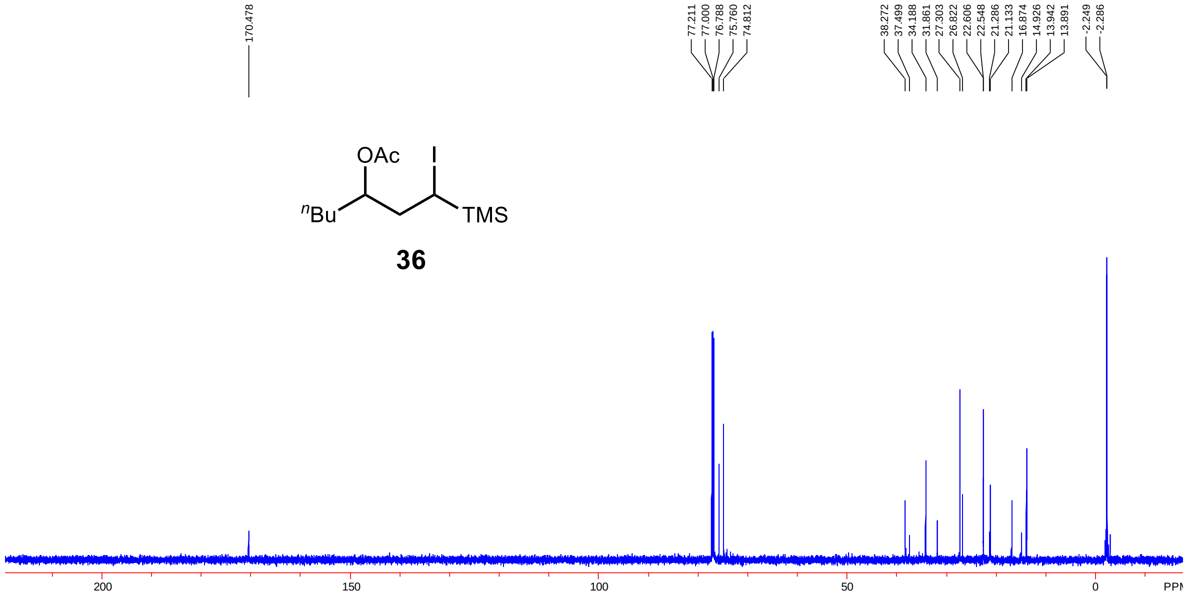

6.174
6.156
5.506
5.492
5.488
5.474
5.471
5.457
3.195
3.178
3.160
2.056
1.892
1.867
1.864
1.849
1.830
1.813
1.795
1.749
1.730
1.713
1.694
1.676
1.667
1.661
1.647
1.629
1.613
1.595
1.574
1.485
1.479
OAc
I
I
SiEt3
34
11
10
9
8
7
6
5
4
3
2
1
ppm
0.92
0.94
1.95
3.02
1.97
2.10
4.15
9.47
6.00

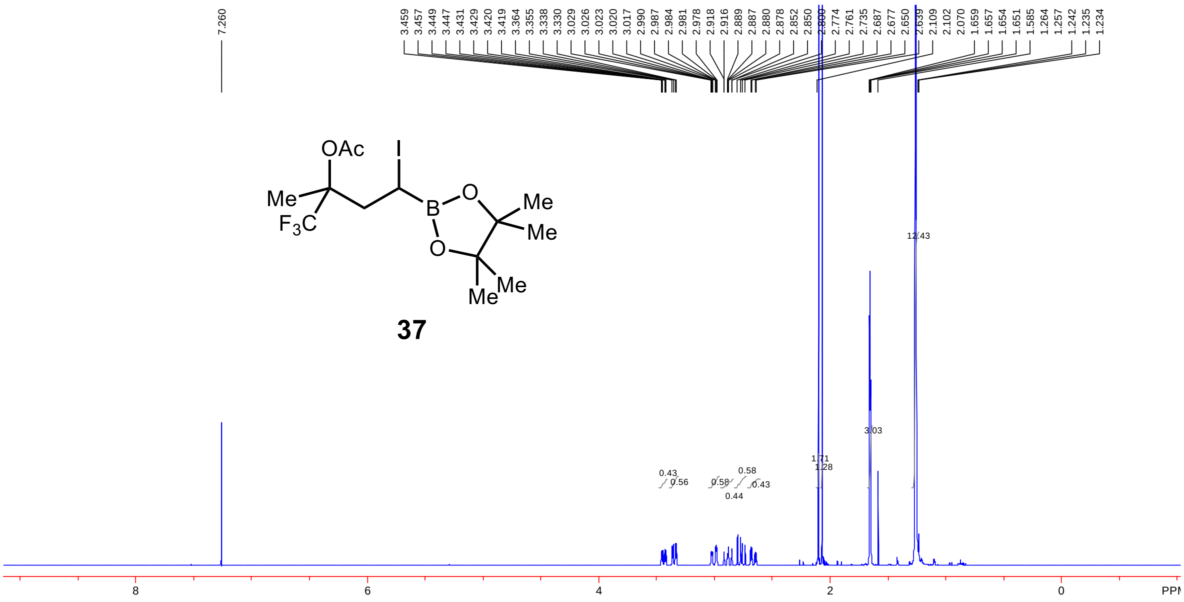

170.12
147.11
110.54
79.85
77.47
77.15
76.83
33.44
33.08
30.42
23.92
21.27
7.19
6.86
3.03
OAc
I
I
SiEt3
34
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

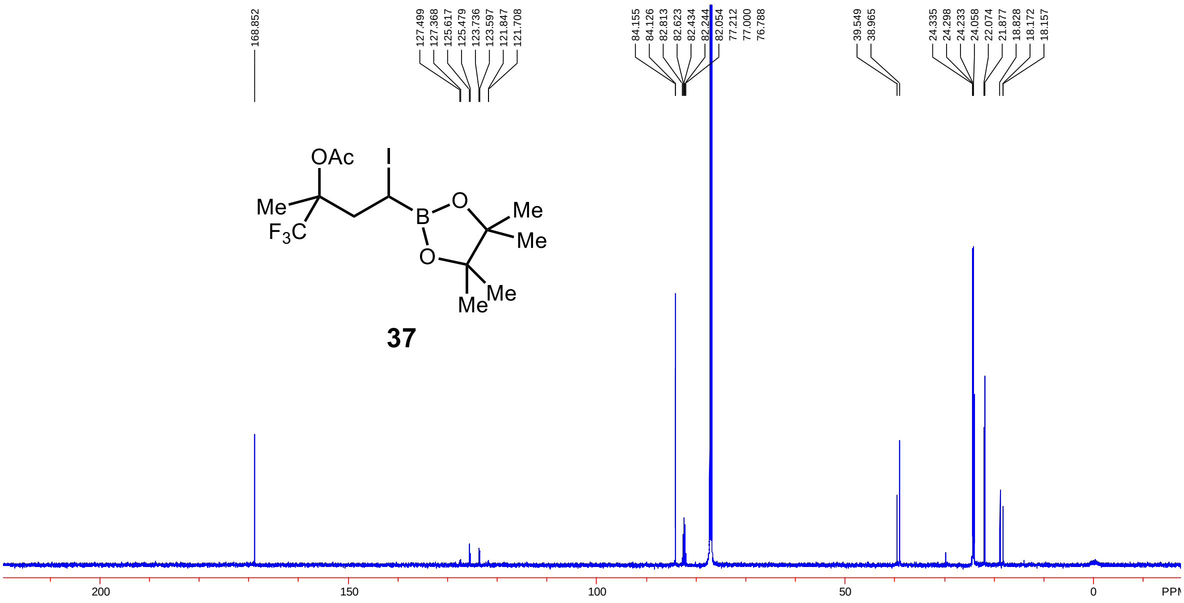

7.260
6.561
6.560
2.186
1.827
1.826
0.956
0.943
0.930
0.733
0.720
0.707
0.694
0.693
OAc
I
Me
$F_3C$
$SiEt_3$
35
9.46
6.34
2.96
3.08
1.00
8
6
4
2
0
PPM

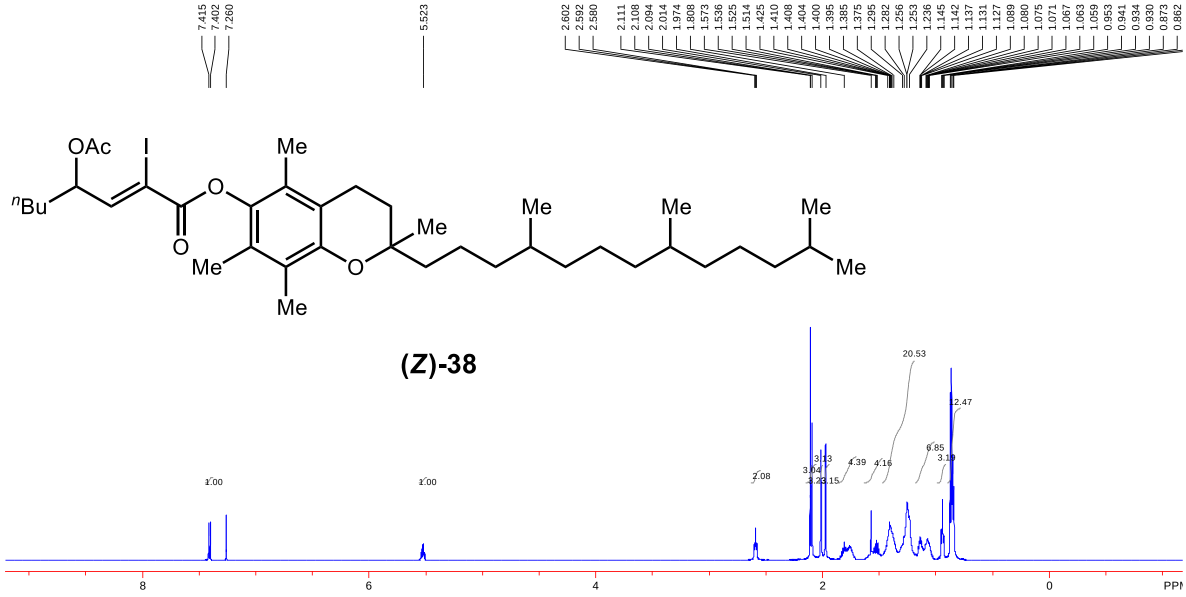

167.357
139.548
126.901
125.012
123.123
121.227
109.937
80.596
80.399
80.202
80.005
77.212
77.000
76.788
21.337
20.068
6.824
2.951
OAc
I
Me
$F_3C$
$SiEt_3$
35
200
150
100
50
0
PPM


7.260
5.103
5.092
3.081
3.076
3.060
3.056
2.094
2.054
2.050
2.044
2.038
2.034
1.852
1.847
1.831
1.827
1.817
1.812
1.801
1.797
1.776
1.632
1.622
1.316
1.312
1.304
1.302
1.295
1.293
1.289
1.282
1.277
1.273
1.266
1.264
1.259
1.254
0.906
0.894
0.883
0.871
0.152
0.147
0.141
0.136
0.135
OAc
I
nBu
TMS
36
30.85
14.98
10.81
11.02
5.87
7.72
3.08
2.11
1.00
8
6
4
2
0
PPM

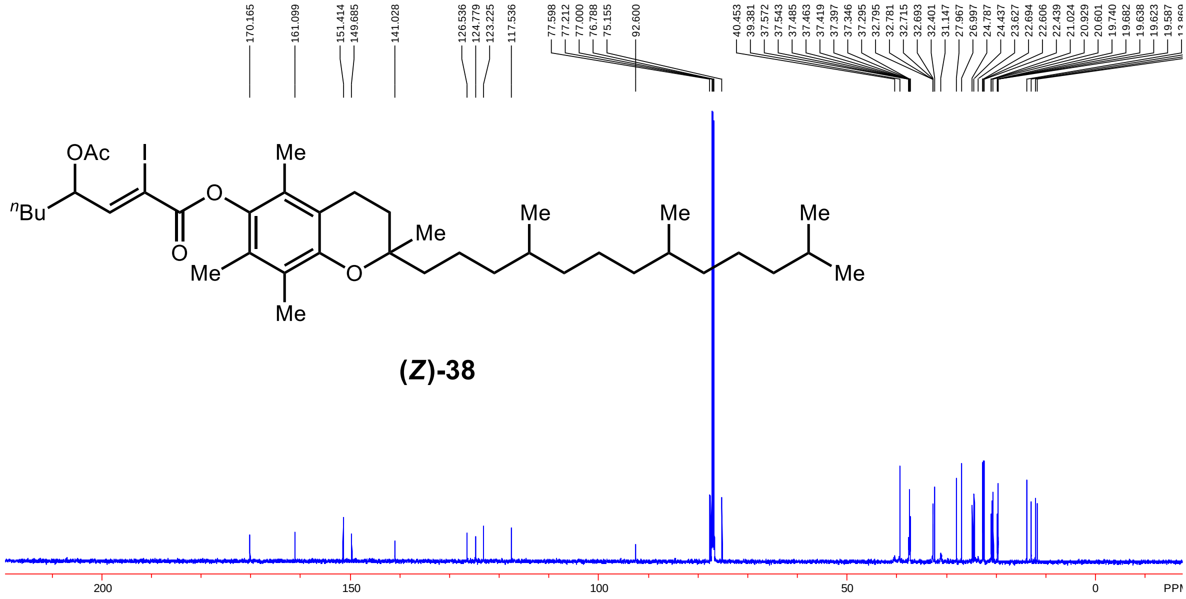

170.478
77.211
77.000
76.788
75.760
74.812
38.272
37.499
34.188
31.861
27.303
26.822
22.606
22.548
21.286
21.133
16.874
14.926
13.942
13.891
-2.249
-2.286
OAc
I
nBu
TMS
36
200
150
100
50
0
PPM


7.260
3.459
3.457
3.449
3.447
3.431
3.429
3.420
3.419
3.364
3.355
3.338
3.330
3.029
3.026
3.023
3.020
3.017
2.990
2.987
2.984
2.981
2.978
2.918
2.916
2.889
2.887
2.880
2.878
2.852
2.850
2.800
2.774
2.761
2.735
2.687
2.677
2.650
2.639
2.109
2.102
2.070
1.659
1.657
1.654
1.651
1.585
1.264
1.257
1.242
1.235
1.234
OAc
I
Me
F3C
B
O
O
Me
Me
Me
Me
37
12.43
3.03
1.71
1.28
0.43
0.56
0.58
0.58
0.44
0.43
8
6
4
2
0
PPM

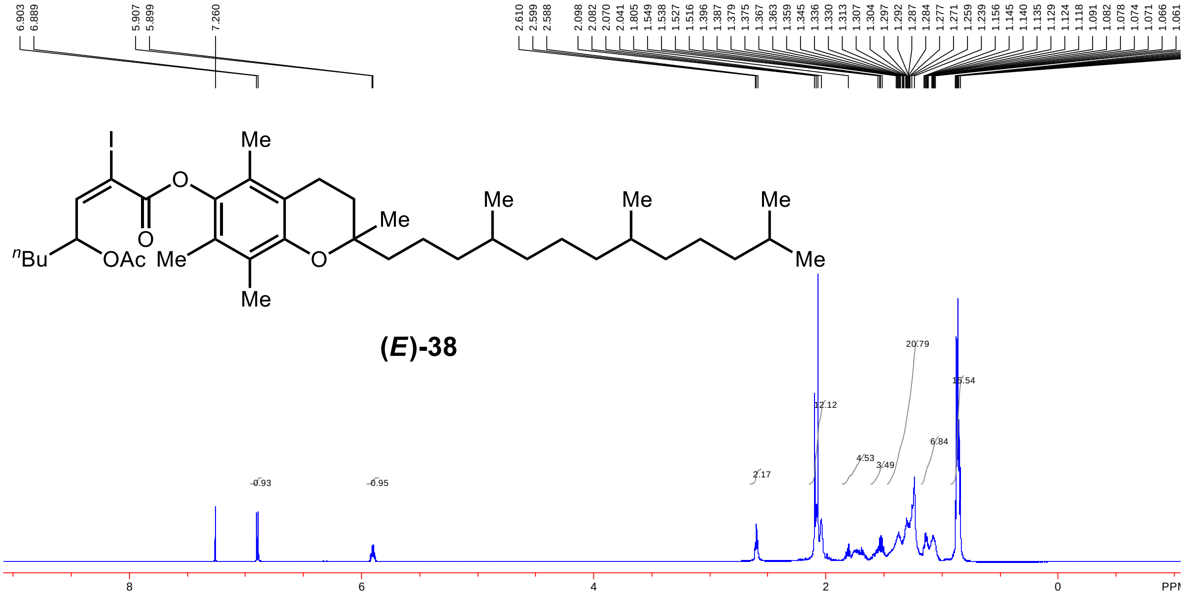

168.852
127.499
127.368
125.617
125.479
123.736
123.597
121.847
121.708
84.155
84.126
82.813
82.623
82.434
82.244
82.054
77.212
77.000
76.788
39.549
38.965
24.335
24.298
24.233
24.058
22.074
21.877
18.828
18.172
18.157
OAc
I
Me
F3C
B
O
O
Me
Me
Me
Me
37
200
150
100
50
0
PPM


7.415
7.402
7.260
5.523
2.602
2.592
2.580
2.111
2.108
2.094
2.014
1.974
1.808
1.573
1.536
1.525
1.514
1.425
1.410
1.408
1.404
1.400
1.395
1.385
1.375
1.295
1.282
1.256
1.253
1.236
1.145
1.142
1.137
1.131
1.127
1.089
1.080
1.075
1.071
1.067
1.063
1.059
0.953
0.941
0.934
0.930
0.873
0.862
OAc
I
O
$^n$Bu
O
Me
Me
Me
O
Me
Me
Me
Me
Me
1.00
1.00
2.08
3.04
3.13
3.23
3.15
4.39
4.16
20.53
12.47
6.85
3.19
8
6
4
2
0
PPM

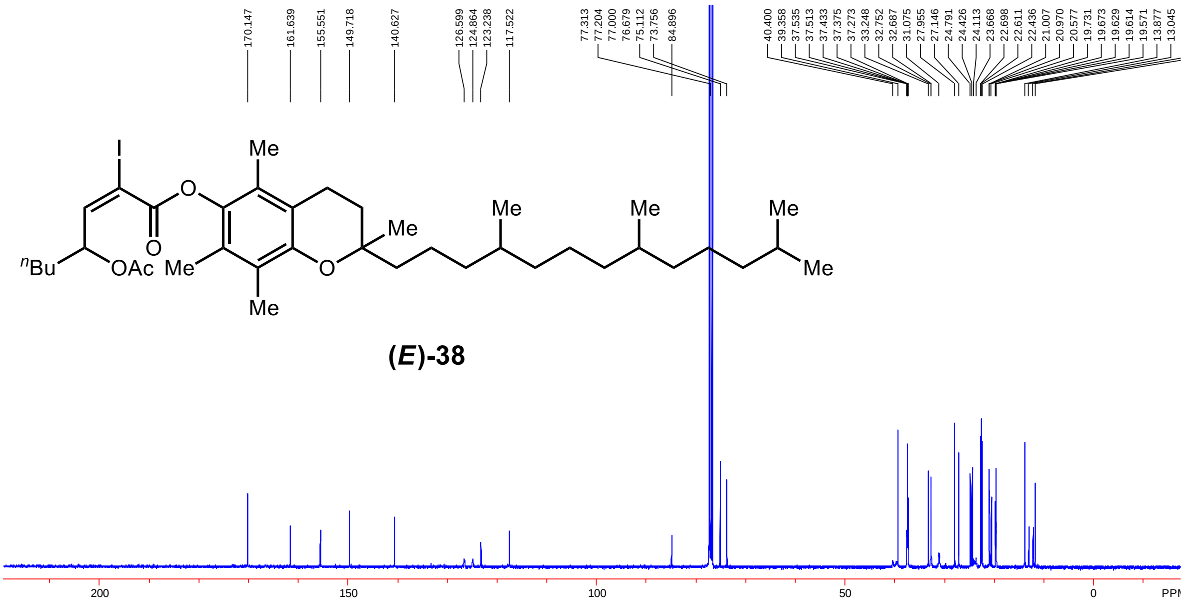
**(*Z*)-38**


170.165
161.099
151.414
149.685
141.028
126.536
124.779
123.225
117.536
77.598
77.212
77.000
76.788
75.155
92.600
40.453
39.381
37.572
37.543
37.485
37.463
37.419
37.397
37.346
37.295
32.795
32.781
32.715
32.693
32.401
31.147
27.967
26.997
24.787
24.437
23.627
22.694
22.606
22.439
21.024
20.929
20.601
19.740
19.682
19.638
19.623
19.587
OAc
I
O
$^n$Bu
O
Me
Me
Me
O
Me
Me
Me
Me
Me
200
150
100
50
0
PPM

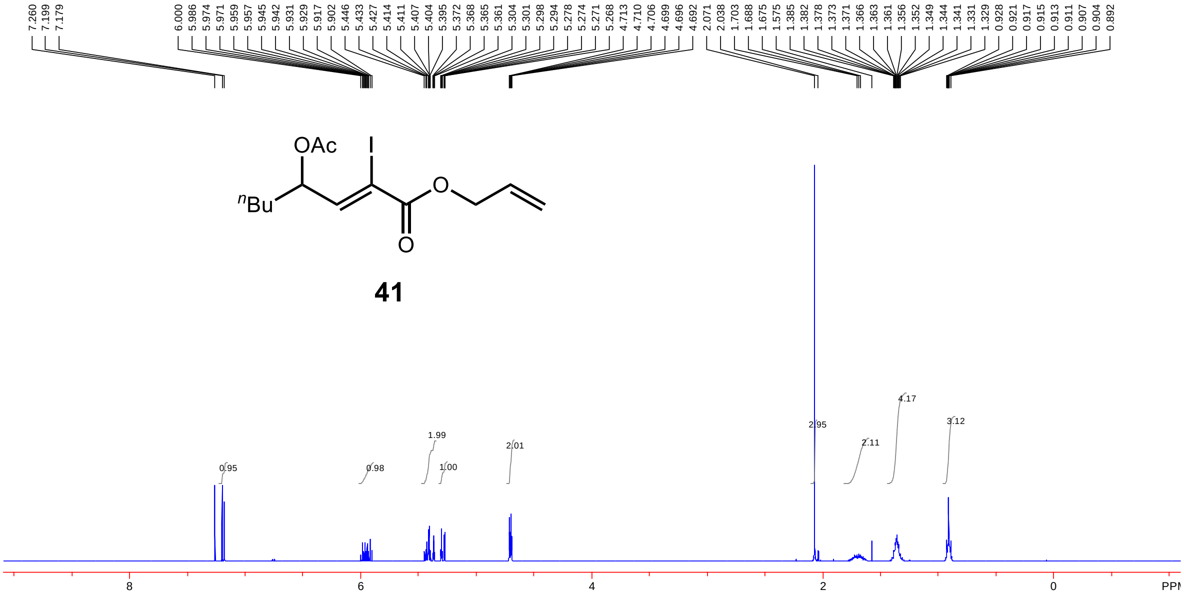
**(*Z*)-38**


6.903
6.889
5.907
5.899
7.260
2.610
2.599
2.588
2.098
2.082
2.070
2.041
1.805
1.549
1.538
1.527
1.516
1.396
1.387
1.379
1.375
1.367
1.363
1.359
1.345
1.336
1.330
1.313
1.307
1.304
1.297
1.292
1.287
1.284
1.277
1.271
1.259
1.239
1.156
1.145
1.140
1.135
1.129
1.124
1.118
1.091
1.082
1.078
1.074
1.071
1.066
1.061
I
O
Me
Me
Me
Me
Me
O
$^n$Bu
OAc
Me
O
Me
Me
0.93
0.95
2.17
12.12
4.53
3.49
20.79
6.84
15.54
8
6
4
2
0
PP

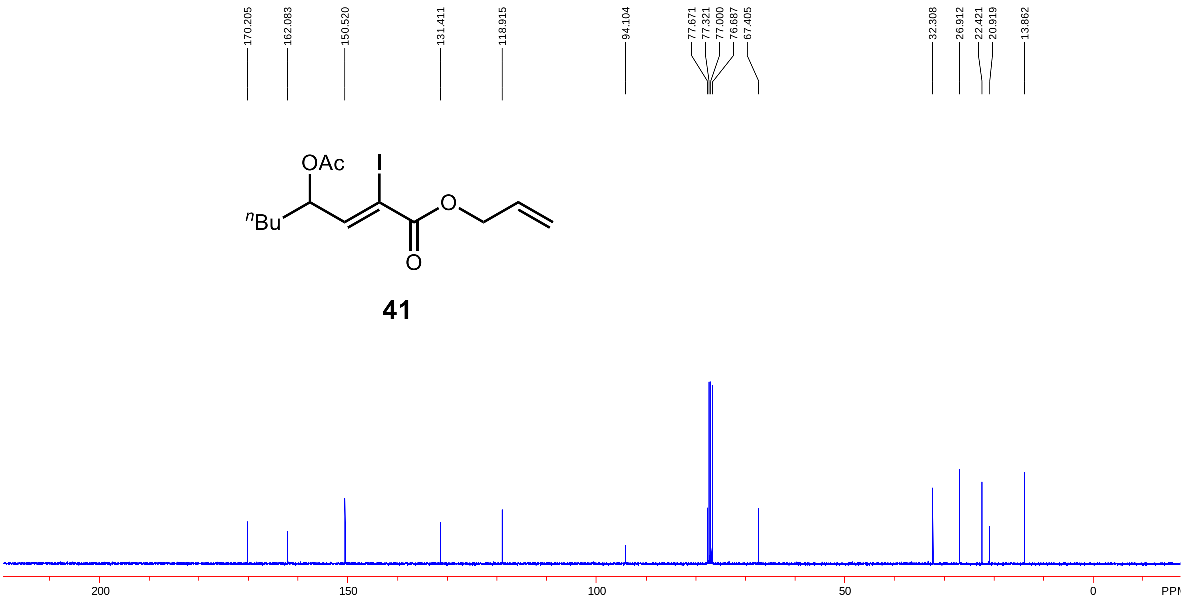
**(*E*)-38**


170.147
161.639
155.551
149.718
140.627
126.599
124.864
123.238
117.522
77.313
77.204
77.000
76.679
75.112
73.756
84.896
40.400
39.388
37.535
37.513
37.433
37.375
37.273
33.248
32.752
32.687
31.075
27.955
27.146
24.791
24.426
24.113
23.668
22.698
22.611
22.436
21.007
20.970
20.577
19.731
19.673
19.629
19.614
19.571
13.877
13.045
I
O
Me
Me
Me
Me
Me
O
$^n$Bu
OAc
Me
O
Me
Me
200
150
100
50
0
PP

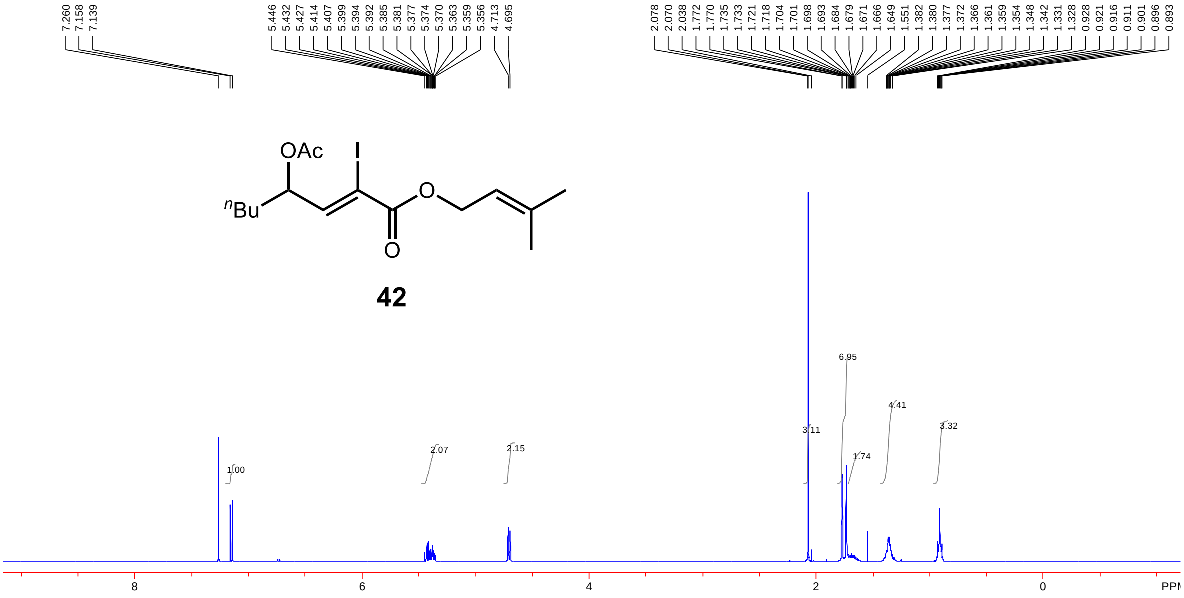
**(*E*)-38**


7.260
7.199
7.179
6.000
5.986
5.974
5.971
5.959
5.957
5.945
5.942
5.931
5.929
5.917
5.902
5.446
5.433
5.427
5.414
5.411
5.407
5.404
5.395
5.372
5.368
5.365
5.361
5.304
5.301
5.298
5.294
5.278
5.274
5.271
5.268
4.713
4.710
4.706
4.699
4.696
4.692
2.071
2.038
1.703
1.688
1.675
1.575
1.385
1.382
1.378
1.373
1.371
1.366
1.363
1.361
1.356
1.352
1.349
1.344
1.341
1.331
1.329
0.928
0.921
0.917
0.915
0.913
0.911
0.907
0.904
0.892
OAc
I
$^n$Bu
O
O
0.95
0.98
1.99
1.00
2.01
2.95
2.11
4.17
3.12
8
6
4
2
0
PPM

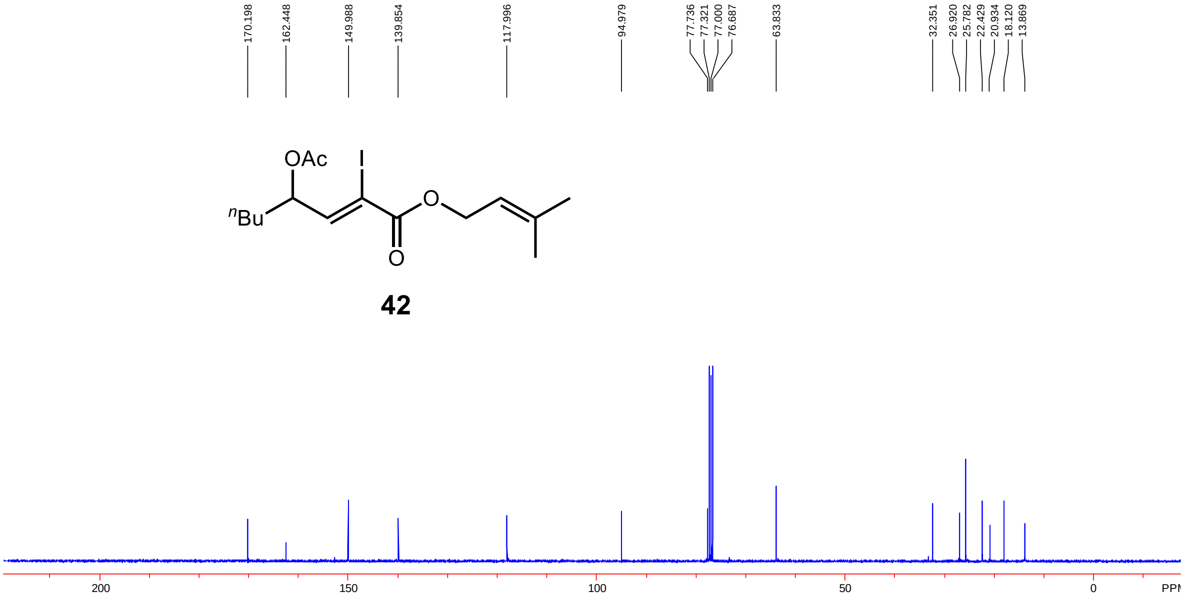
**41**


170.205
162.083
150.520
131.411
118.915
94.104
77.671
77.321
77.000
76.687
67.405
32.308
26.912
22.421
20.919
13.862
OAc
I
$^n$Bu
O
O
200
150
100
50
0
PPM

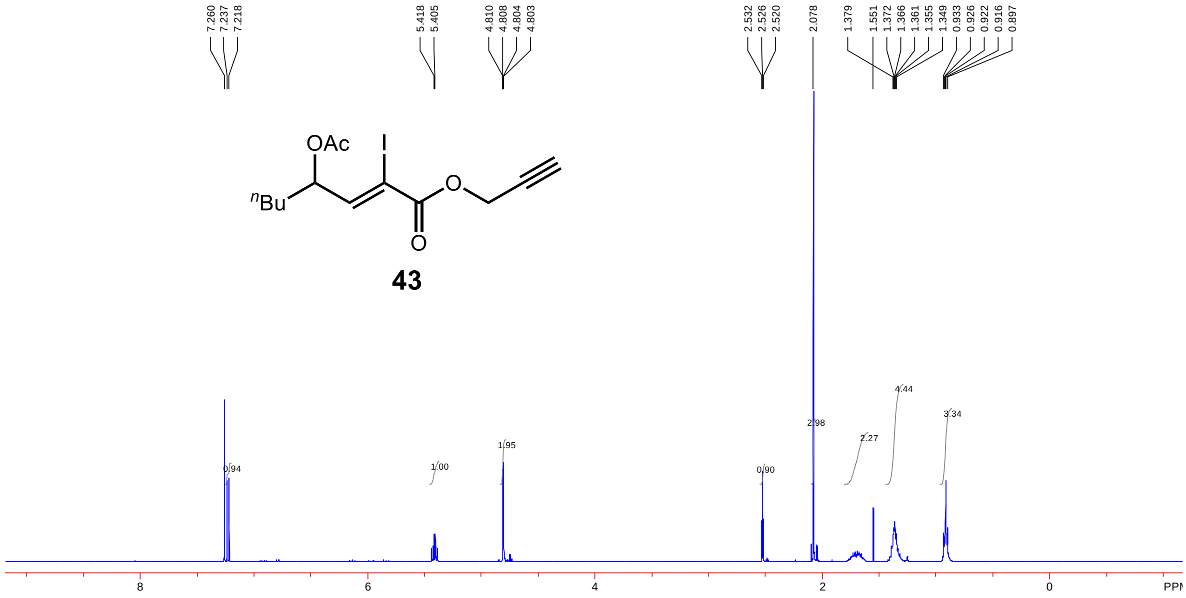
**41**


**42**

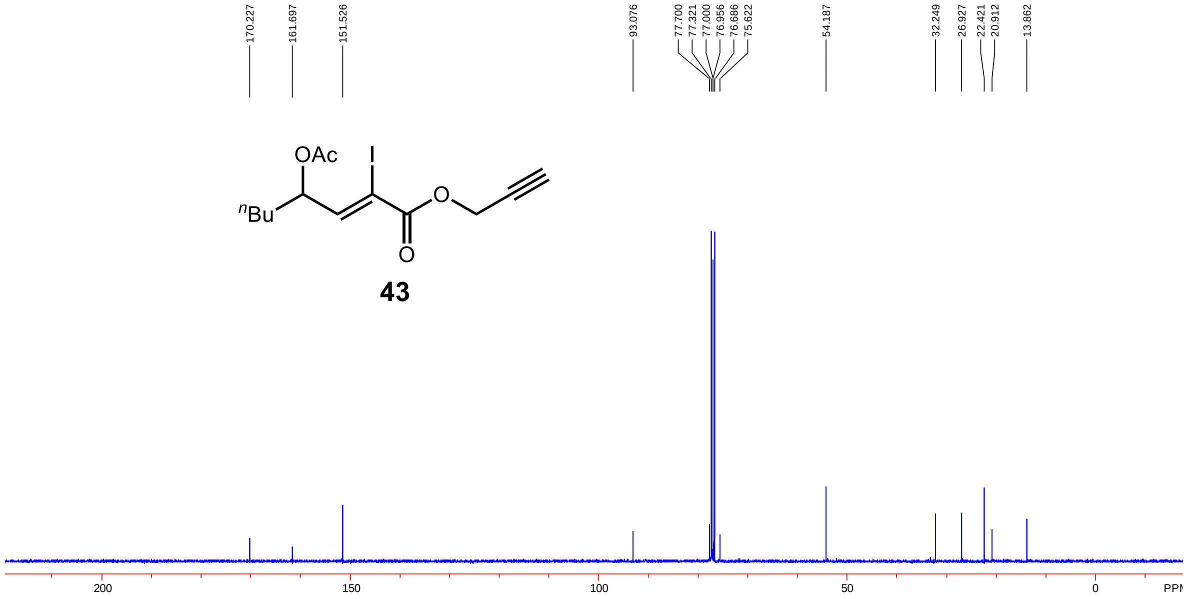
7.260
7.158
7.139
5.446
5.432
5.427
5.414
5.407
5.399
5.394
5.392
5.385
5.381
5.377
5.374
5.370
5.363
5.359
5.356
4.713
4.695
2.078
2.070
2.038
1.772
1.770
1.735
1.733
1.721
1.718
1.704
1.701
1.698
1.693
1.684
1.679
1.671
1.666
1.649
1.551
1.382
1.380
1.377
1.372
1.366
1.361
1.359
1.354
1.348
1.342
1.331
1.328
0.928
0.921
0.916
0.911
0.901
0.896
0.893
OAc
I
O
O
ⁿBu
1.00
2.07
2.15
3.11
6.95
1.74
4.41
3.32
8
6
4
2
0
PPM


**42**

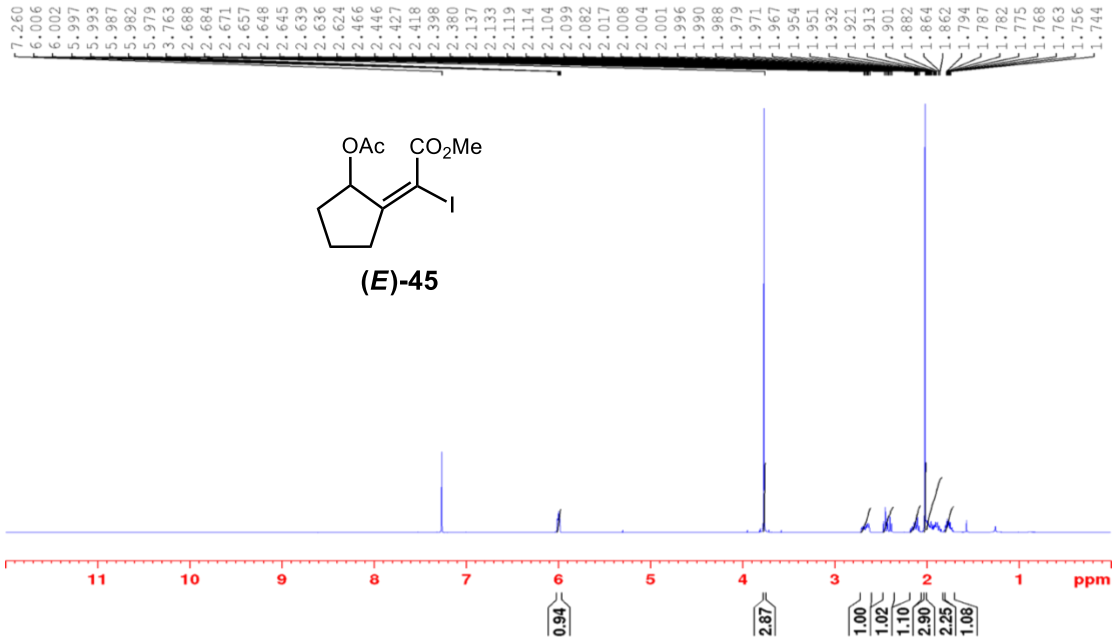
170.198
162.448
149.988
139.854
117.996
94.979
77.736
77.321
77.000
76.687
63.833
32.351
26.920
25.782
22.429
20.934
18.120
13.869
OAc
I
O
O
ⁿBu
200
150
100
50
0
PPM

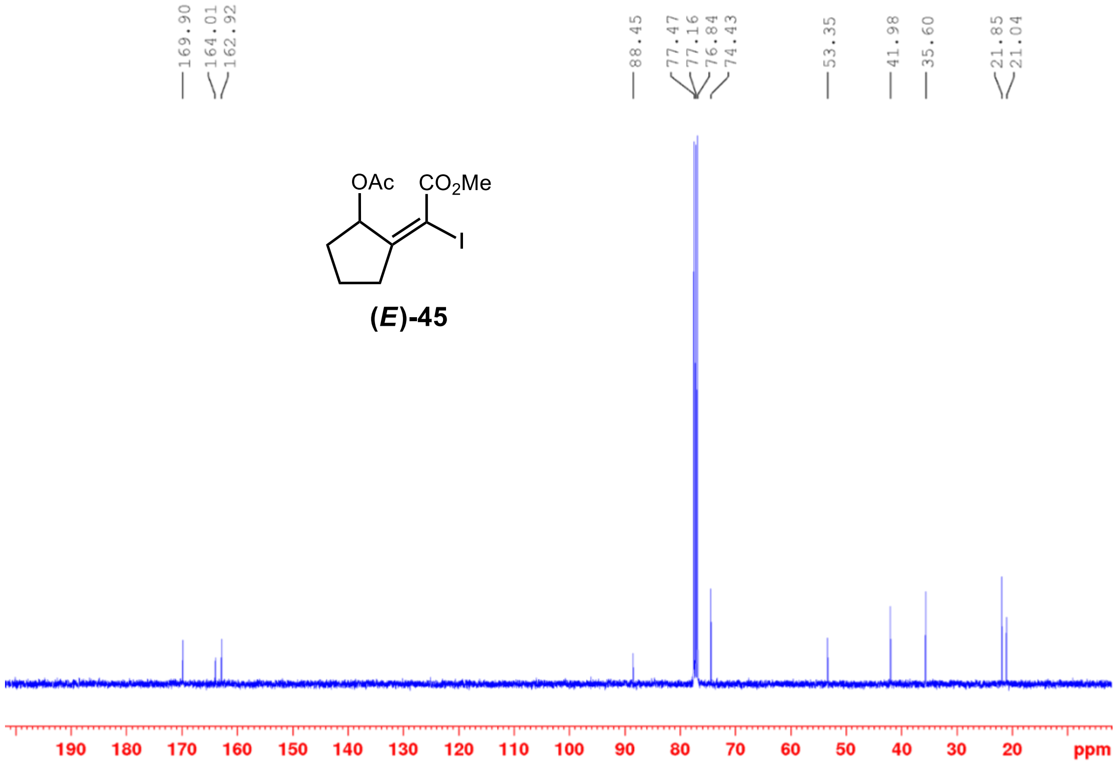

7.260
7.237
7.218
5.418
5.405
4.810
4.808
4.804
4.803
2.532
2.526
2.520
2.078
1.379
1.551
1.372
1.366
1.361
1.355
1.349
0.933
0.926
0.922
0.916
0.897
OAc
I
$^n$Bu
O
O
0.94
1.00
1.95
0.90
2.98
2.27
4.44
3.34
8
6
4
2
0
PP

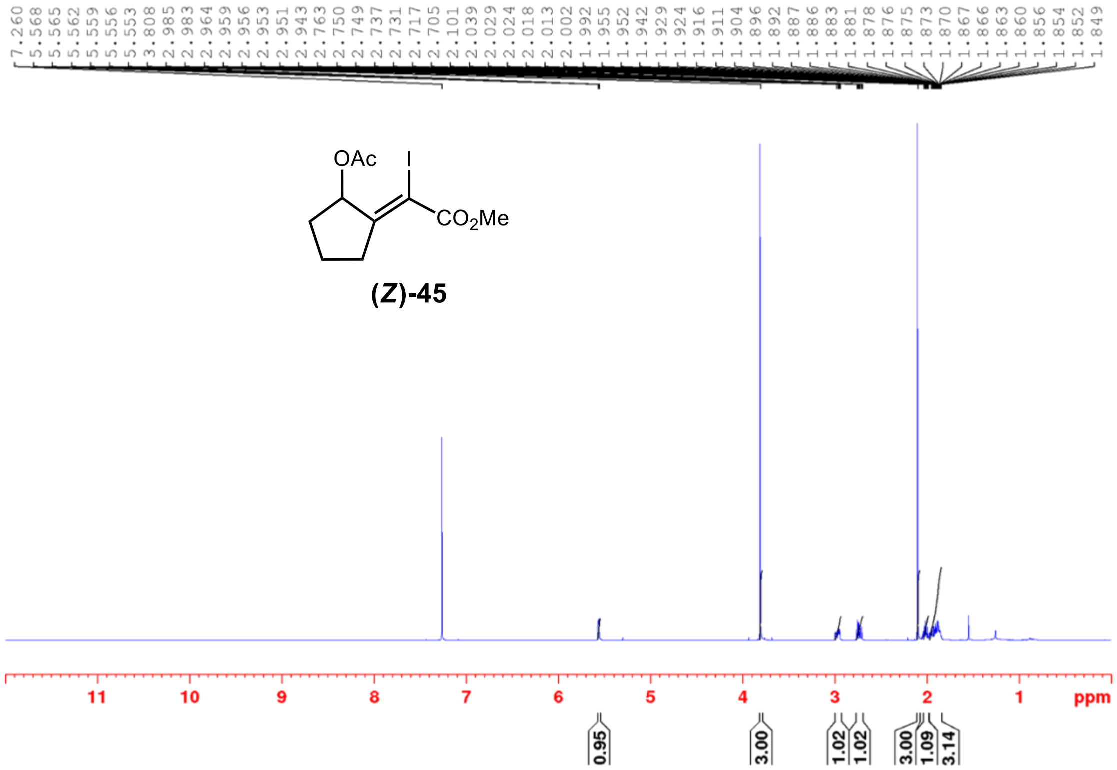
**43**

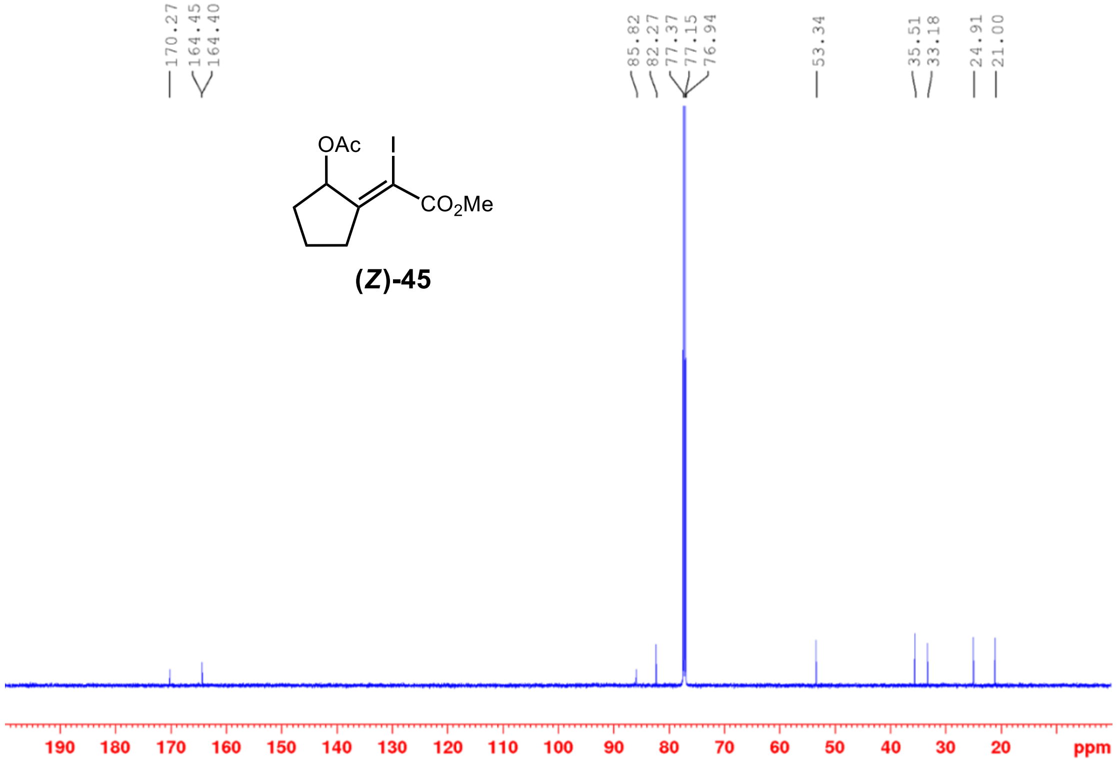

170.227
161.697
151.526
93.076
77.700
77.321
77.000
76.956
76.686
75.622
54.187
32.249
26.927
22.421
20.912
13.862
OAc
I
$^n$Bu
O
O
200
150
100
50
0
PP

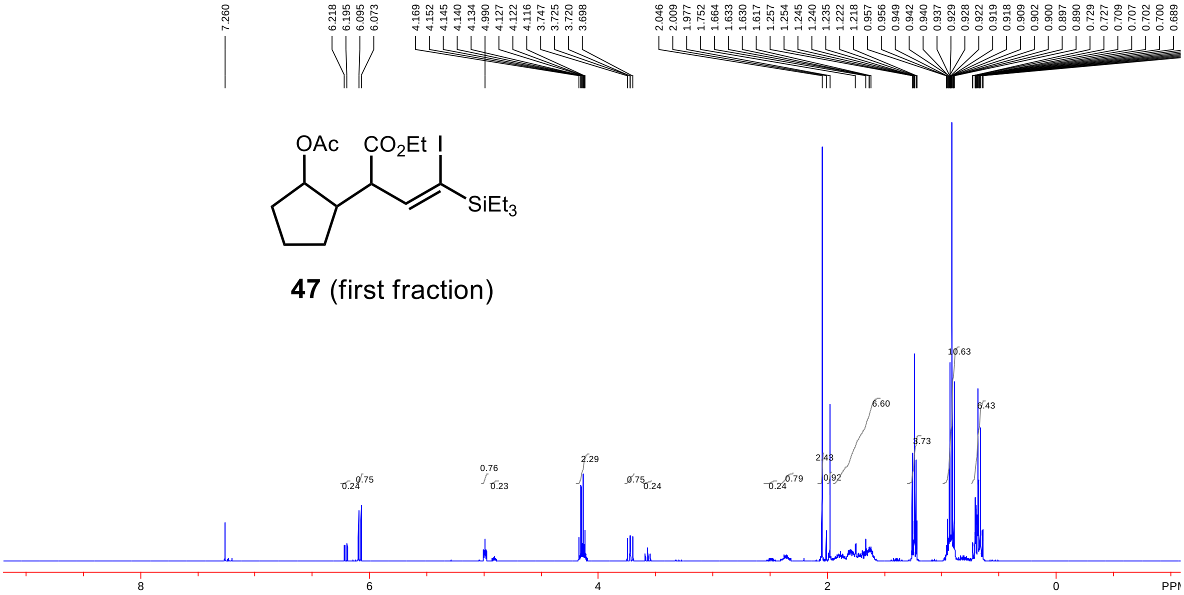
**43**


7.260
6.006
6.002
5.997
5.993
5.987
5.982
5.979
3.763
2.688
2.684
2.671
2.657
2.648
2.645
2.639
2.636
2.624
2.466
2.446
2.427
2.418
2.398
2.380
2.137
2.133
2.119
2.114
2.104
2.099
2.082
2.017
2.008
2.004
2.001
1.996
1.990
1.988
1.979
1.971
1.967
1.954
1.951
1.932
1.921
1.913
1.901
1.882
1.864
1.862
1.794
1.787
1.782
1.775
1.768
1.763
1.756
1.744
OAc
CO2Me
I
(E)-45
11
10
9
8
7
6
5
4
3
2
1
ppm
0.94
2.87
1.00
1.02
1.10
2.90
2.25
1.08

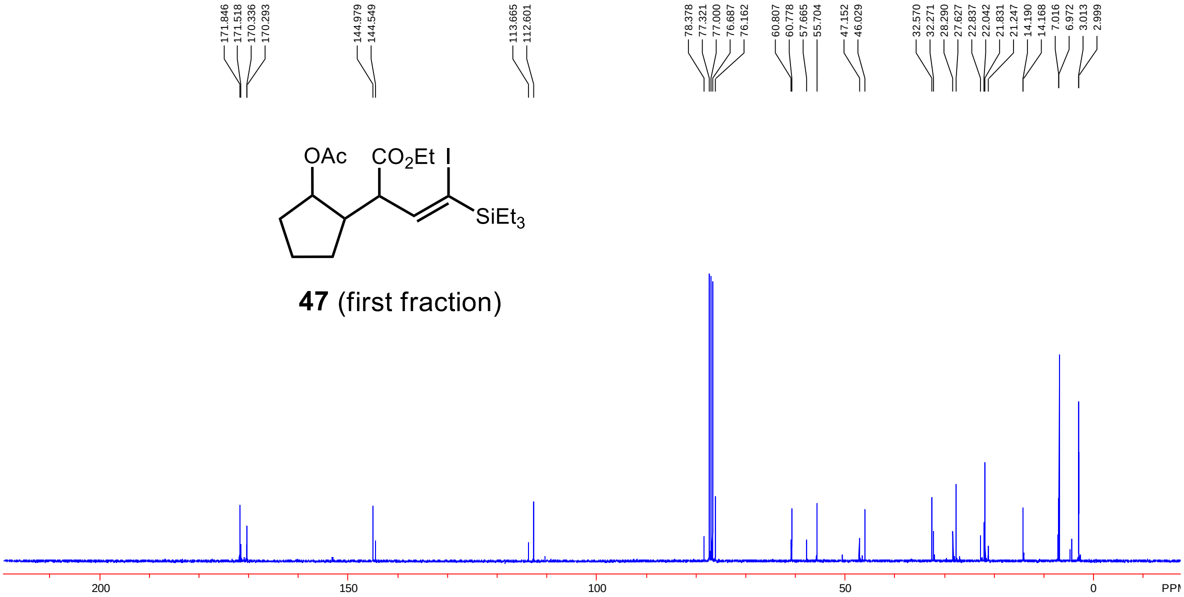

169.90
164.01
162.92
88.45
77.47
77.16
76.84
74.43
53.35
41.98
35.60
21.85
21.04
OAc
CO2Me
I
(E)-45
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


7.260
5.568
5.565
5.562
5.559
5.556
5.553
3.808
2.985
2.983
2.964
2.959
2.956
2.953
2.951
2.943
2.763
2.750
2.749
2.737
2.731
2.717
2.705
2.101
2.039
2.029
2.024
2.018
2.013
2.002
1.992
1.955
1.952
1.942
1.929
1.924
1.916
1.911
1.904
1.896
1.892
1.887
1.886
1.883
1.881
1.878
1.876
1.875
1.873
1.870
1.867
1.866
1.863
1.860
1.856
1.854
1.852
1.849
OAc
I
CO2Me
(Z)-45
11
10
9
8
7
6
5
4
3
2
1
ppm
0.95
3.00
1.02
1.02
3.00
1.09
3.14

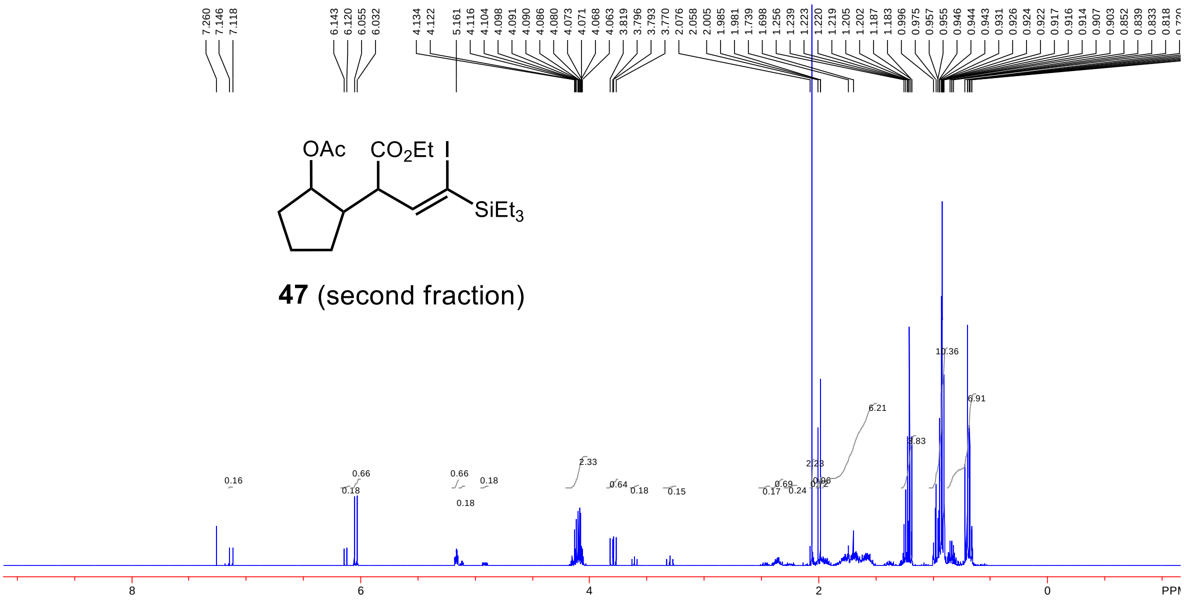

170.27
164.45
164.40
85.82
82.27
77.37
77.15
76.94
53.34
35.51
33.18
24.91
21.00
OAc
I
CO2Me
(Z)-45
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



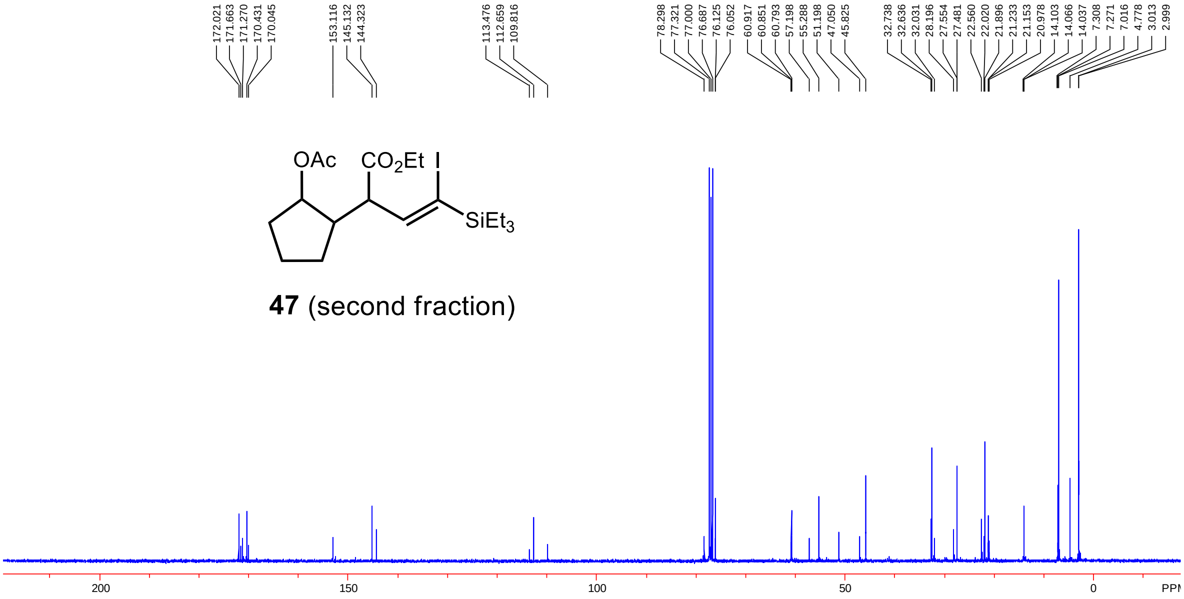
**47** (first fraction)



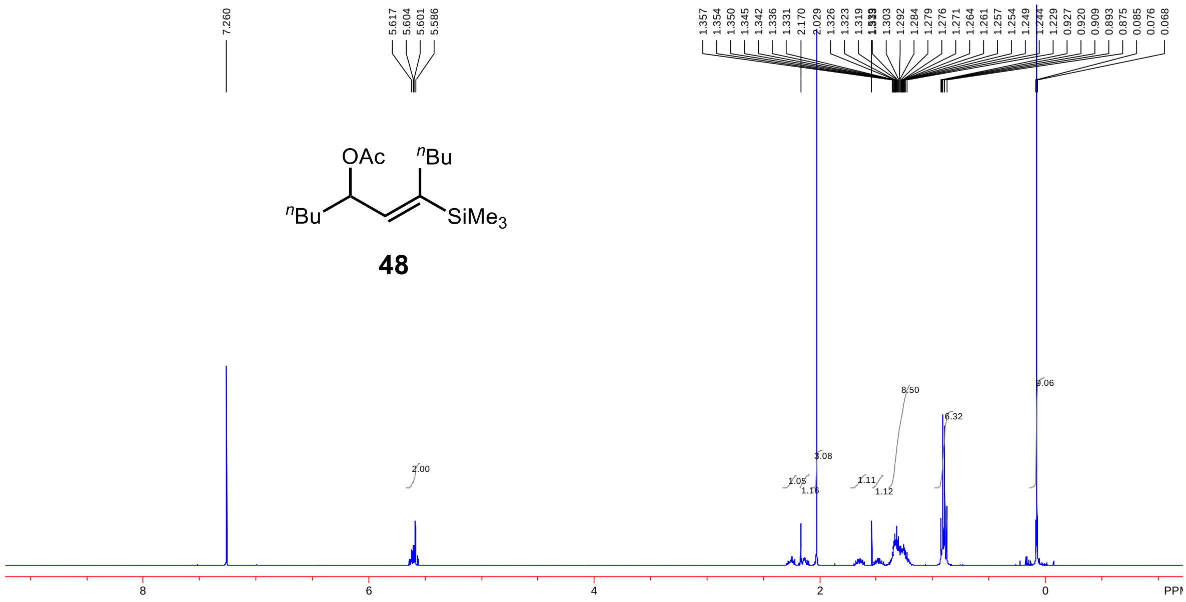
**47** (first fraction)

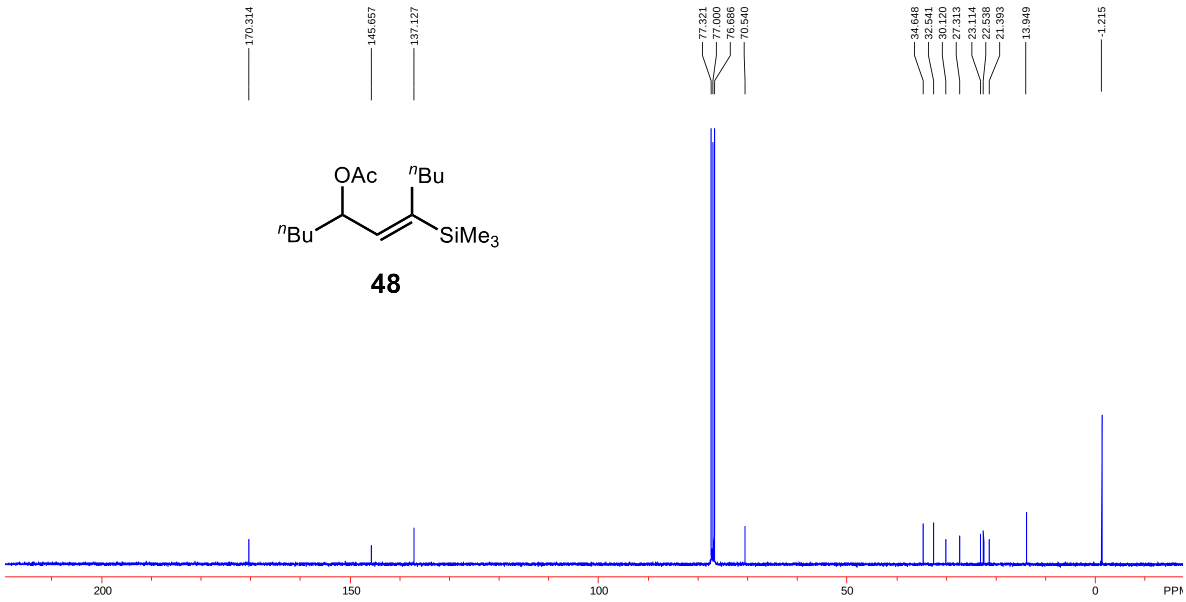


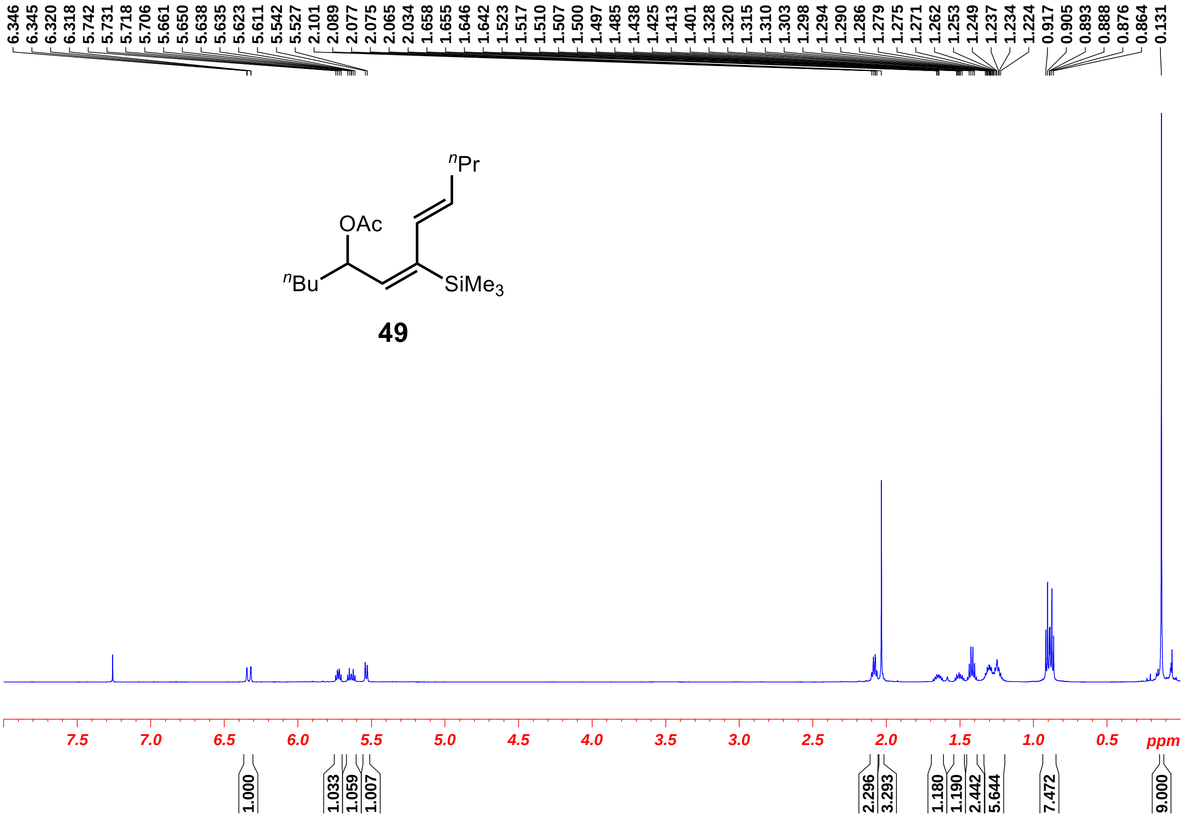
**47** (second fraction)

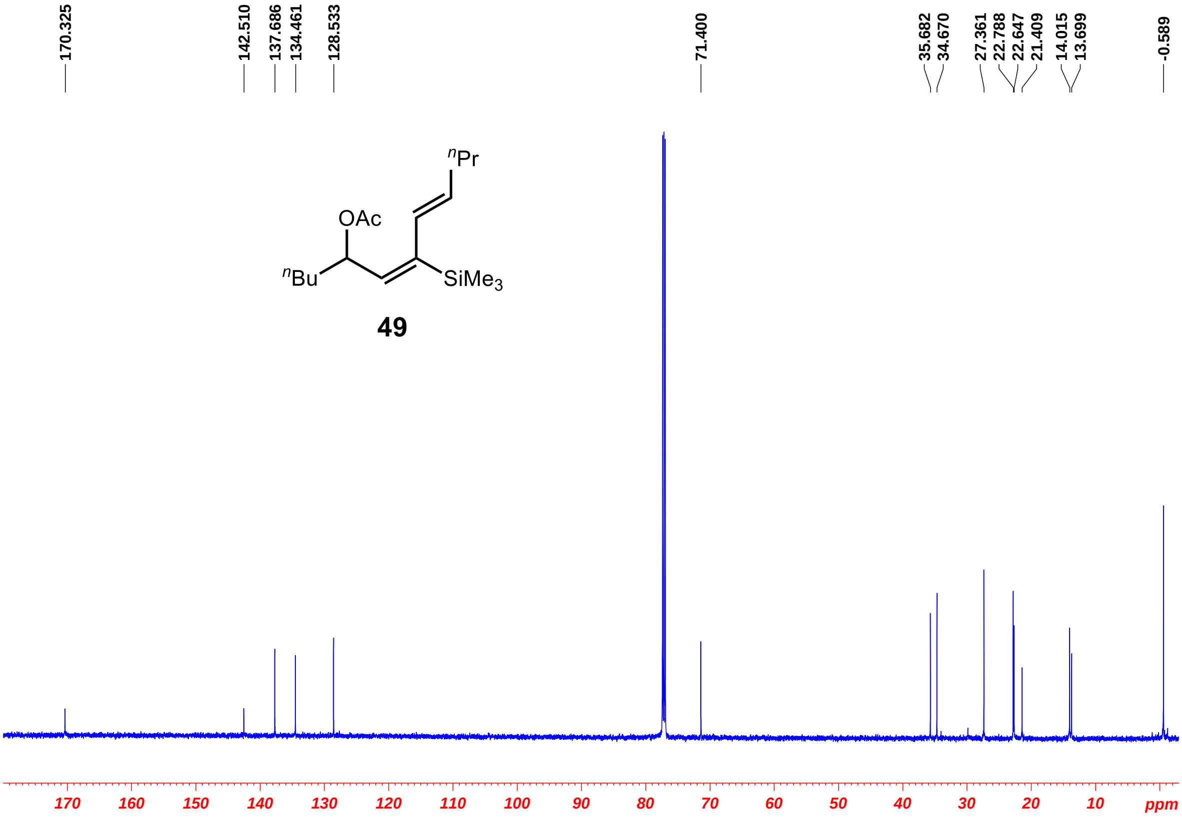


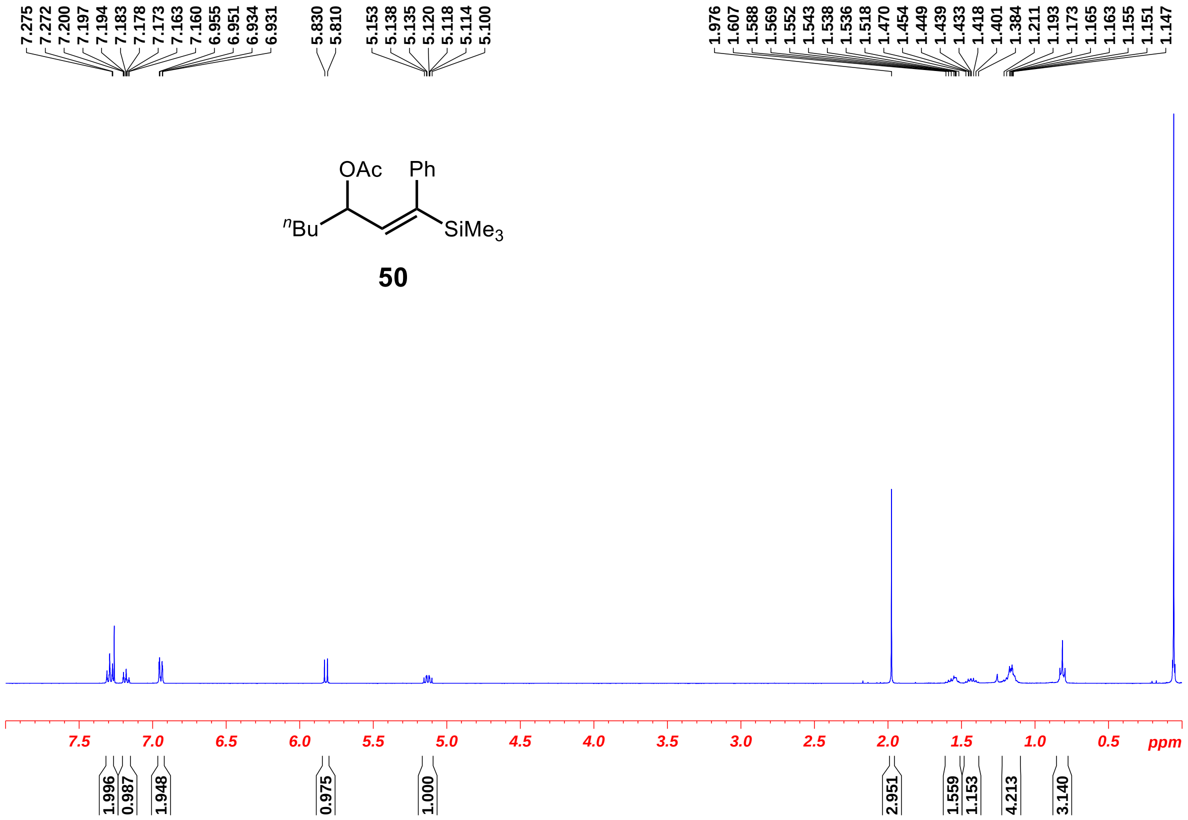
**47** (second fraction)


7.260
5.617
5.604
5.601
5.586
1.357
1.354
1.350
1.345
1.342
1.336
1.331
2.170
2.029
1.326
1.323
1.319
1.533
1.313
1.303
1.292
1.284
1.279
1.276
1.271
1.264
1.261
1.257
1.254
1.249
1.244
1.229
0.927
0.920
0.909
0.893
0.875
0.085
0.076
0.068
OAc
nBu
nBu
SiMe3
48
2.00
1.05
1.16
3.08
1.11
1.12
8.50
6.32
9.06
8
6
4
2
0
PPM

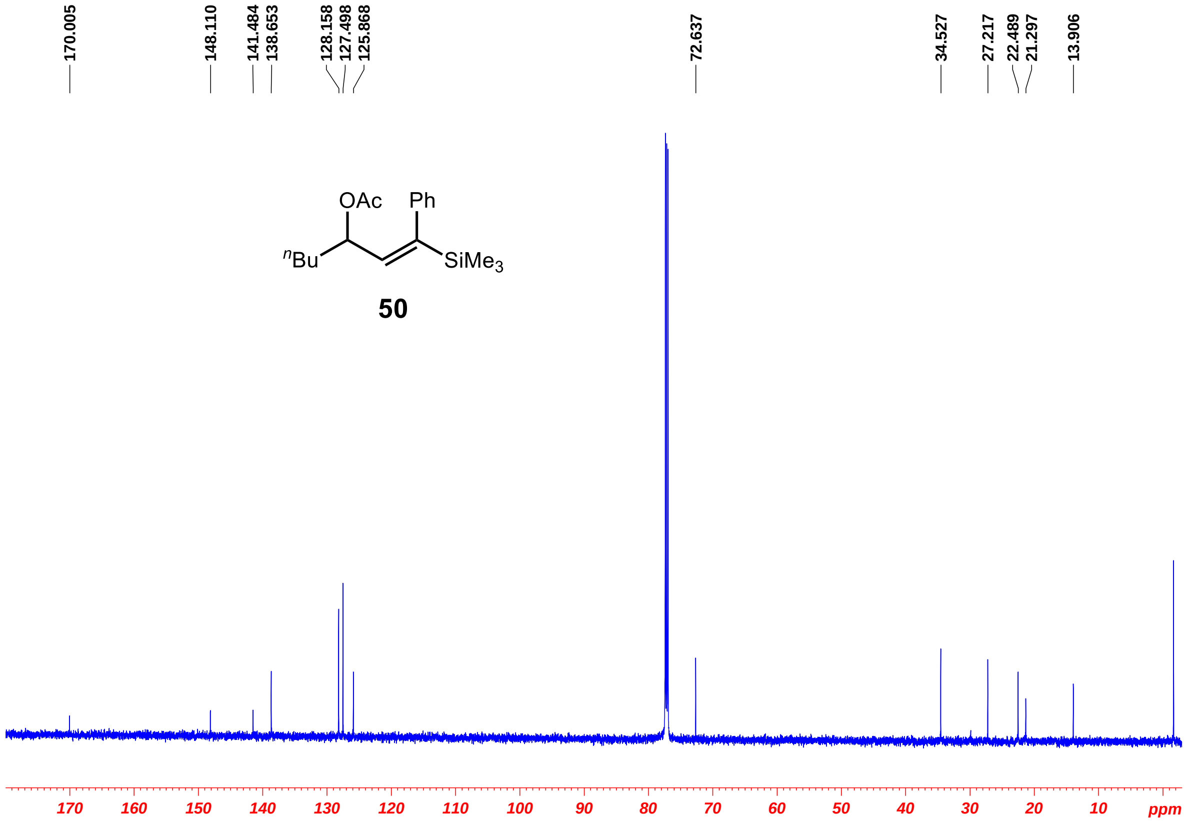

170.314
145.657
137.127
77.321
77.000
76.686
70.540
34.648
32.541
30.120
27.313
23.114
22.538
21.393
13.949
-1.215
OAc
nBu
nBu
SiMe3
48
200
150
100
50
0
PPM


6.346
6.345
6.320
6.318
5.742
5.731
5.718
5.706
5.661
5.650
5.638
5.635
5.623
5.611
5.542
5.527
2.101
2.089
2.077
2.075
2.065
2.034
1.658
1.655
1.646
1.642
1.523
1.517
1.510
1.507
1.500
1.497
1.485
1.438
1.425
1.413
1.401
1.328
1.320
1.315
1.310
1.303
1.298
1.294
1.290
1.286
1.279
1.275
1.271
1.262
1.253
1.249
1.237
1.234
1.224
0.917
0.905
0.893
0.888
0.876
0.864
0.131
$^n$Pr
OAc
$^n$Bu
SiMe$_3$
49
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.033
1.059
1.007
2.296
3.293
1.180
1.190
2.442
5.644
7.472
9.000

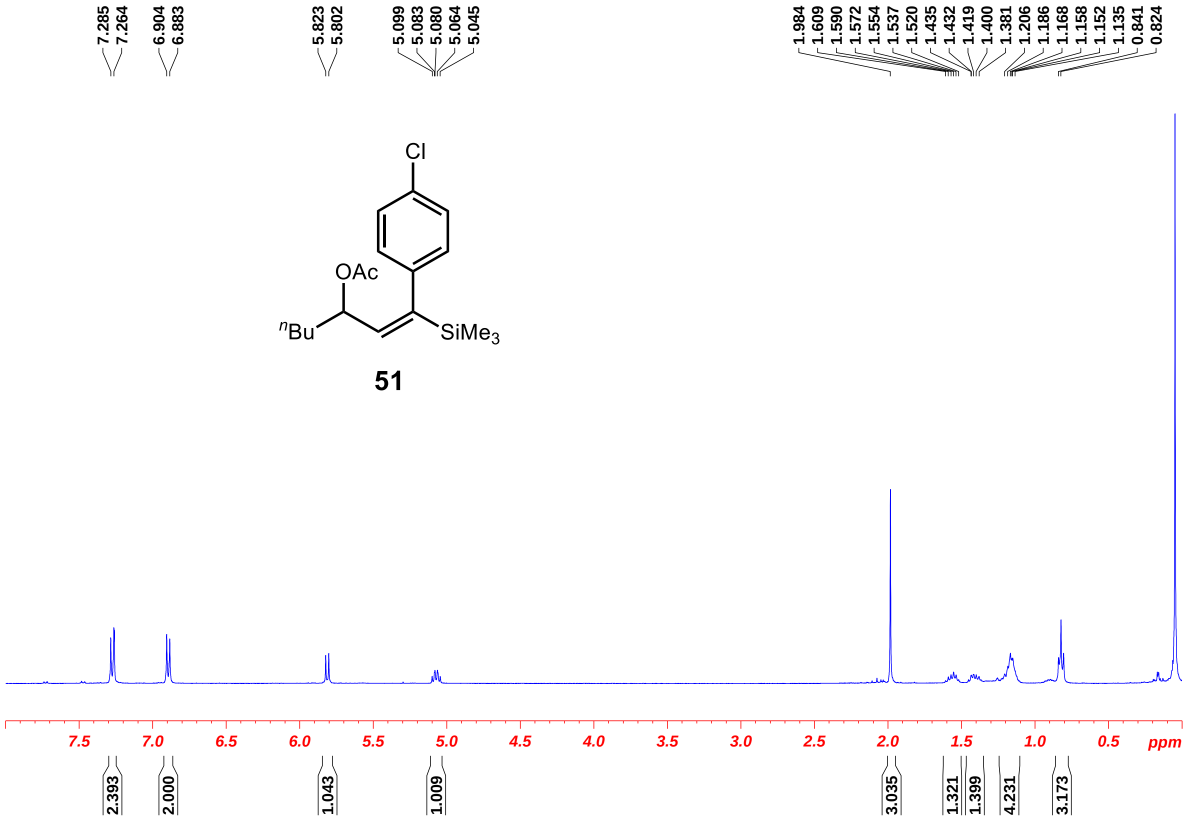

170.325
142.510
137.686
134.461
128.533
71.400
35.682
34.670
27.361
22.788
22.647
21.409
14.015
13.699
-0.589
$^n$Pr
OAc
$^n$Bu
SiMe$_3$
49
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.275
7.272
7.200
7.197
7.194
7.183
7.178
7.173
7.163
7.160
6.955
6.951
6.934
6.931
5.830
5.810
5.153
5.138
5.135
5.120
5.118
5.114
5.100
1.976
1.607
1.588
1.569
1.552
1.543
1.538
1.536
1.518
1.470
1.454
1.449
1.439
1.433
1.418
1.401
1.384
1.211
1.193
1.173
1.165
1.163
1.155
1.151
1.147
OAc
Ph
$^n$Bu
SiMe$_3$
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.996
0.987
1.948
0.975
1.000
2.951
1.559
1.153
4.213
3.140

**50**


170.005
148.110
141.484
138.653
128.158
127.498
125.868
72.637
34.527
27.217
22.489
21.297
13.906
OAc
Ph
$^n$Bu
SiMe$_3$
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

**50**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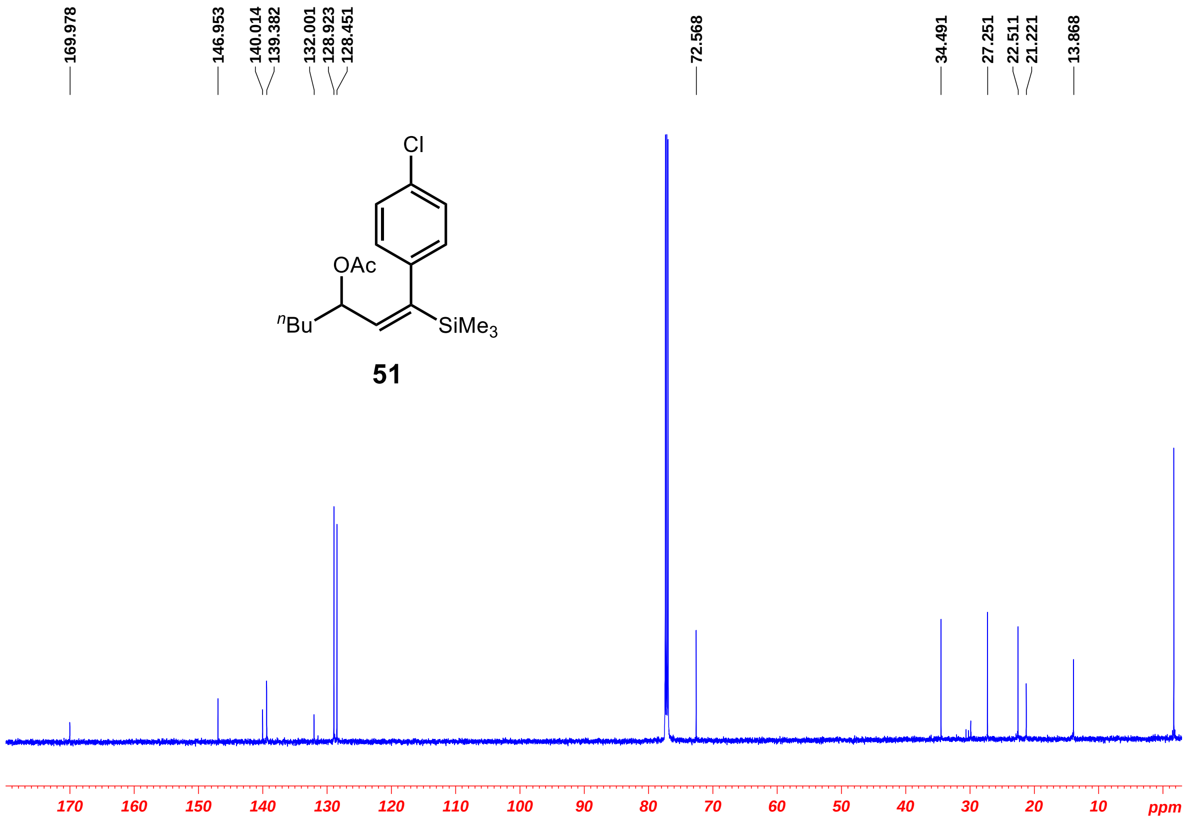
7.264
6.904
6.883
5.823
5.802
5.099
5.083
5.080
5.064
5.045
1.984
1.609
1.590
1.572
1.554
1.537
1.520
1.435
1.432
1.419
1.400
1.381
1.206
1.186
1.168
1.158
1.152
1.135
0.841
0.824
Cl
OAc
$^{n}$Bu
SiMe$_3$
51
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.393
2.000
1.043
1.009
3.035
1.321
1.399
4.231
3.173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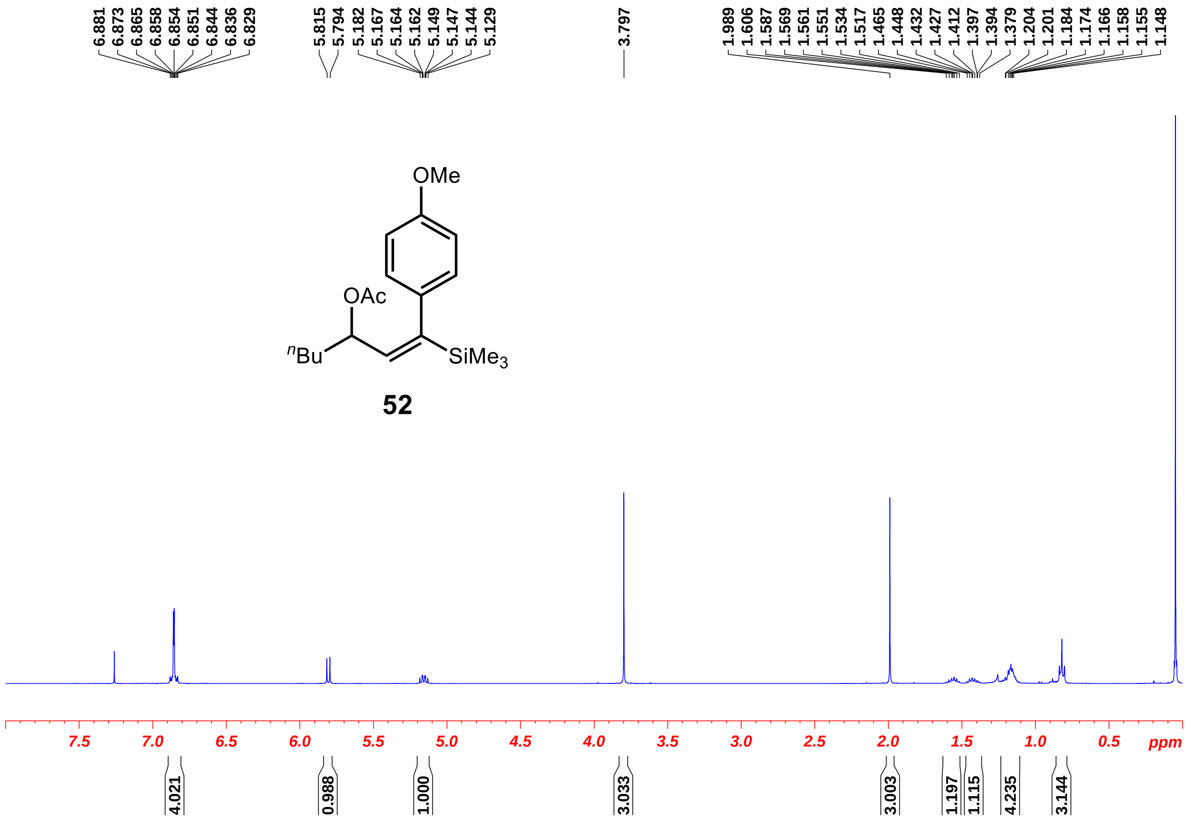
146.953
140.014
139.382
132.001
128.923
128.451
72.568
34.491
27.251
22.511
21.221
13.868
Cl
OAc
$^{n}$Bu
SiMe$_3$
51
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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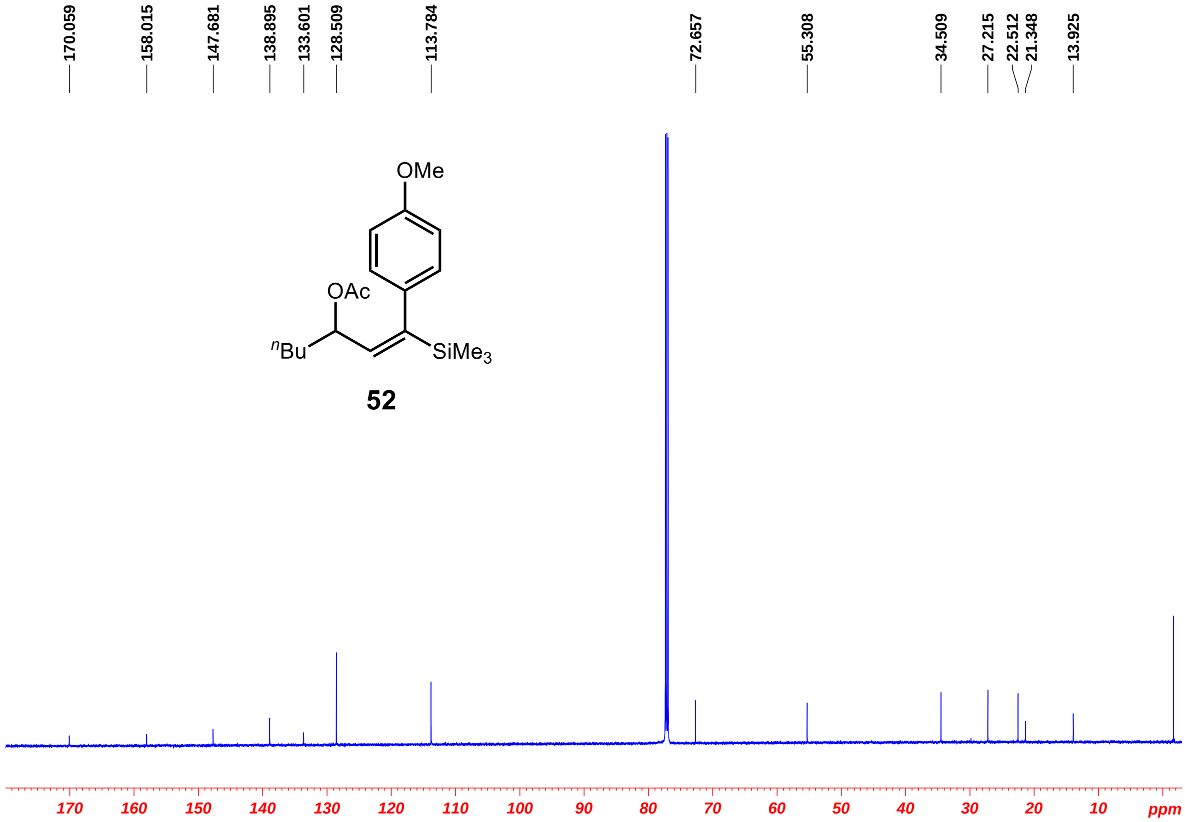
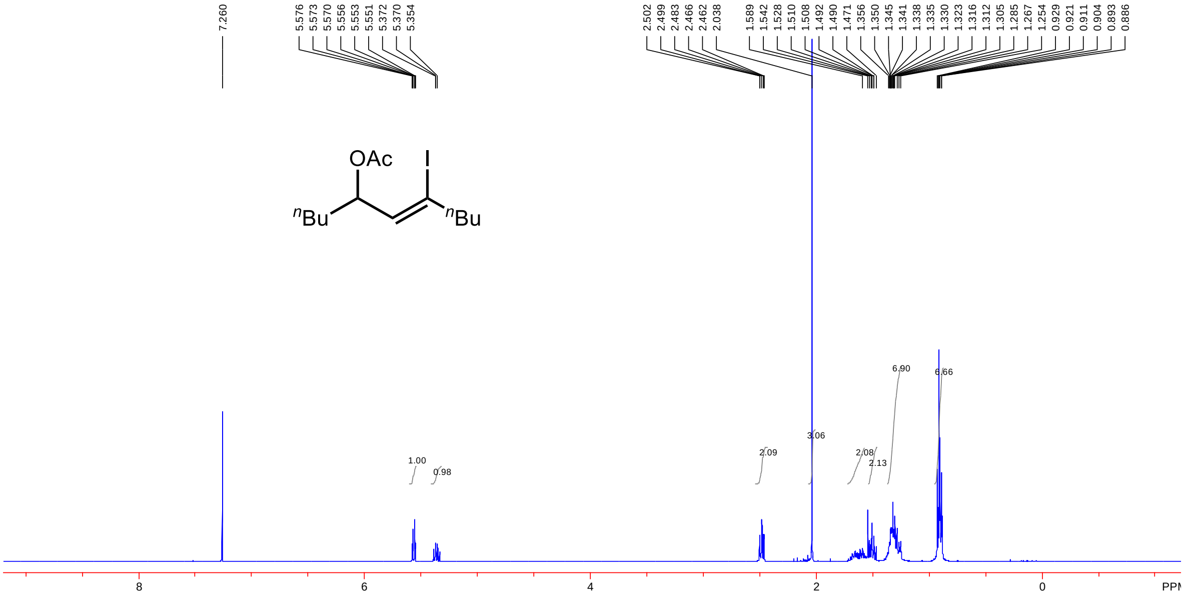
6.873
6.865
6.858
6.854
6.851
6.844
6.836
6.829
5.815
5.794
5.182
5.167
5.164
5.162
5.149
5.147
5.144
5.129
3.797
1.989
1.606
1.587
1.569
1.561
1.551
1.534
1.517
1.465
1.448
1.432
1.427
1.412
1.397
1.394
1.379
1.204
1.201
1.184
1.174
1.166
1.158
1.155
1.148
OMe
OAc
nBu
SiMe3
52
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.021
0.988
1.000
3.033
3.003
1.197
1.115
4.235
3.144


170.059
158.015
147.681
138.895
133.601
128.509
113.784
72.657
55.308
34.509
27.215
22.512
21.348
13.925
OMe
OAc
nBu
SiMe3
52
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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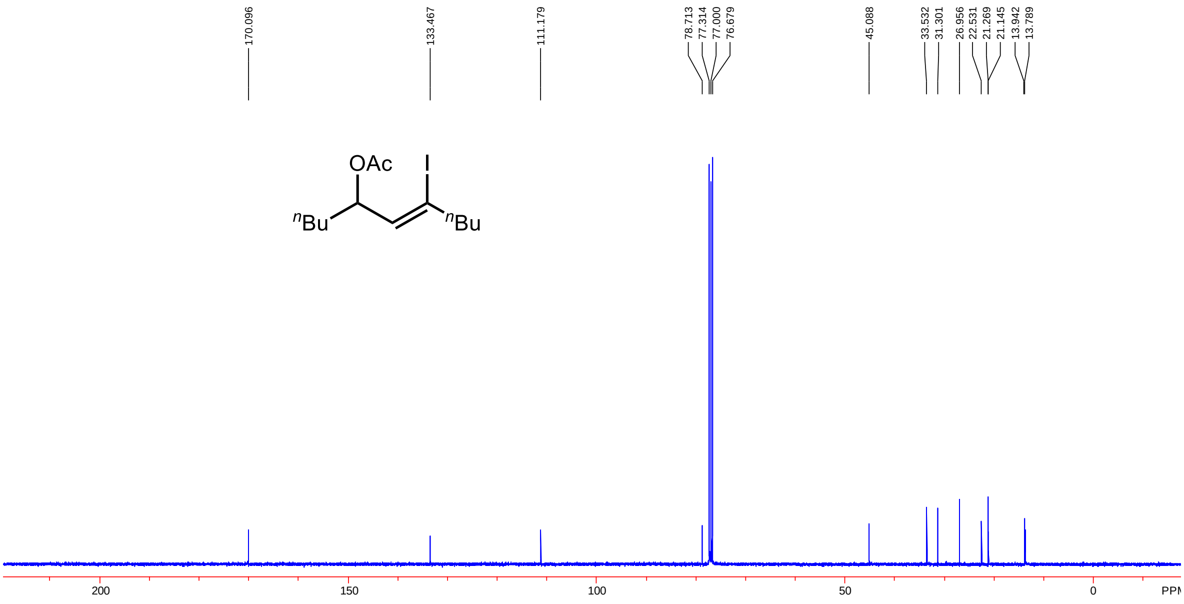
5.573
5.570
5.556
5.553
5.551
5.372
5.370
5.354
2.502
2.499
2.483
2.466
2.462
2.038
1.589
1.542
1.528
1.510
1.508
1.492
1.490
1.471
1.356
1.350
1.345
1.341
1.338
1.335
1.330
1.323
1.316
1.312
1.305
1.285
1.267
1.254
0.929
0.921
0.911
0.904
0.893
0.886
OAc
I
nBu
nBu
1.00
0.98
2.09
3.06
2.08
2.13
6.90
6.66
8
6
4
2
0
PP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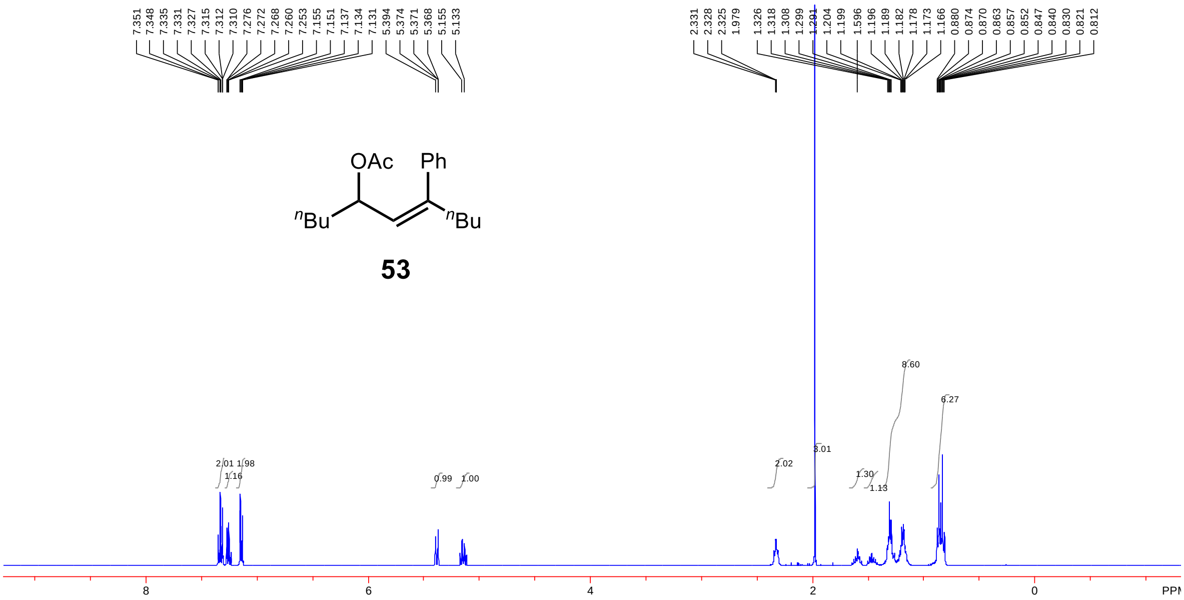
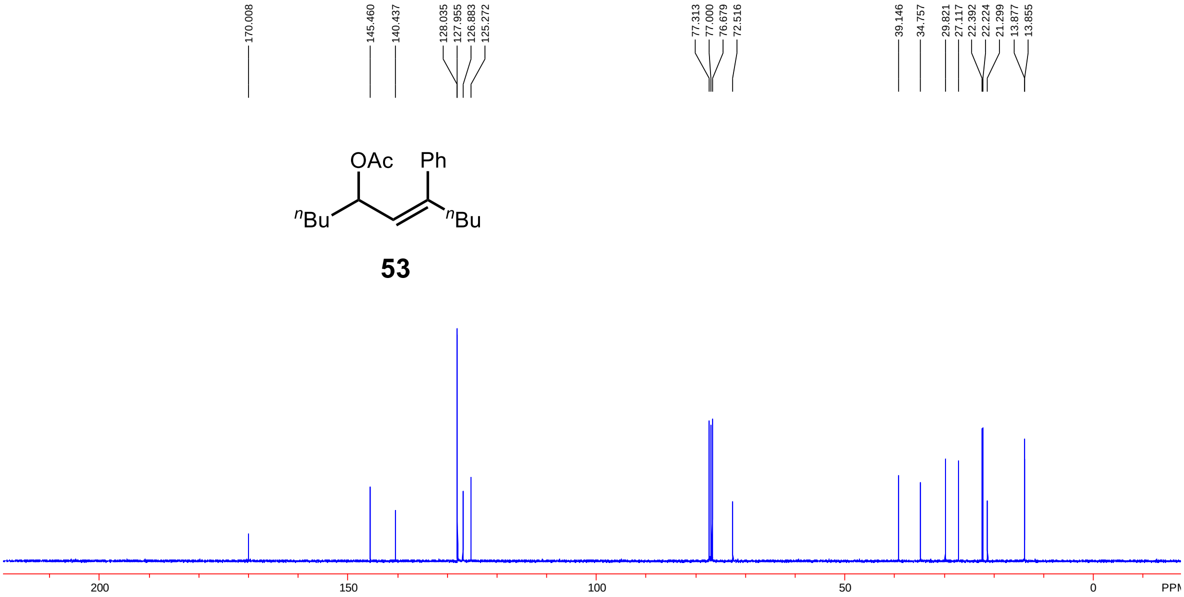
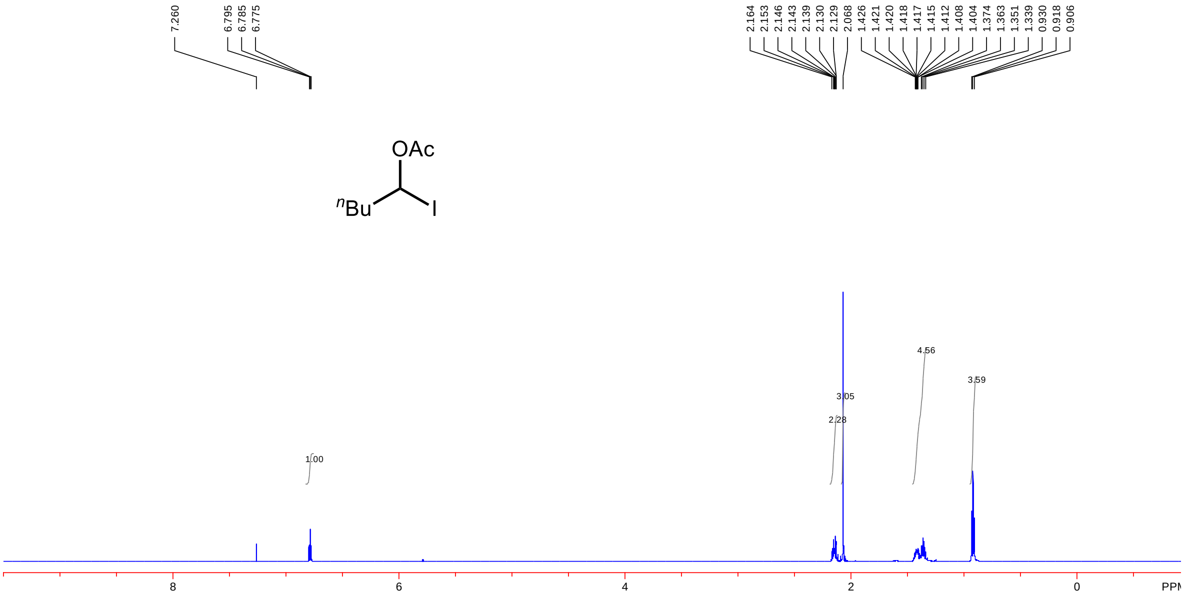
133.467
111.179
78.713
77.314
77.000
76.679
45.088
33.532
31.301
26.956
22.531
21.269
21.145
13.942
13.789
OAc
I
nBu
nBu
200
150
100
50
0
PP


7.351
7.348
7.335
7.331
7.327
7.315
7.312
7.310
7.276
7.272
7.268
7.260
7.253
7.155
7.151
7.137
7.134
7.131
5.394
5.374
5.371
5.368
5.155
5.133
2.331
2.328
2.325
1.979
1.326
1.318
1.308
1.299
1.291
1.204
1.199
1.596
1.196
1.189
1.182
1.178
1.173
1.166
0.880
0.874
0.870
0.863
0.857
0.852
0.847
0.840
0.830
0.821
0.812
OAc
Ph
$^n$Bu
$^n$Bu
2.01
1.16
1.98
0.99
1.00
2.02
3.01
1.30
1.13
8.60
6.27
8
6
4
2
0
PPM

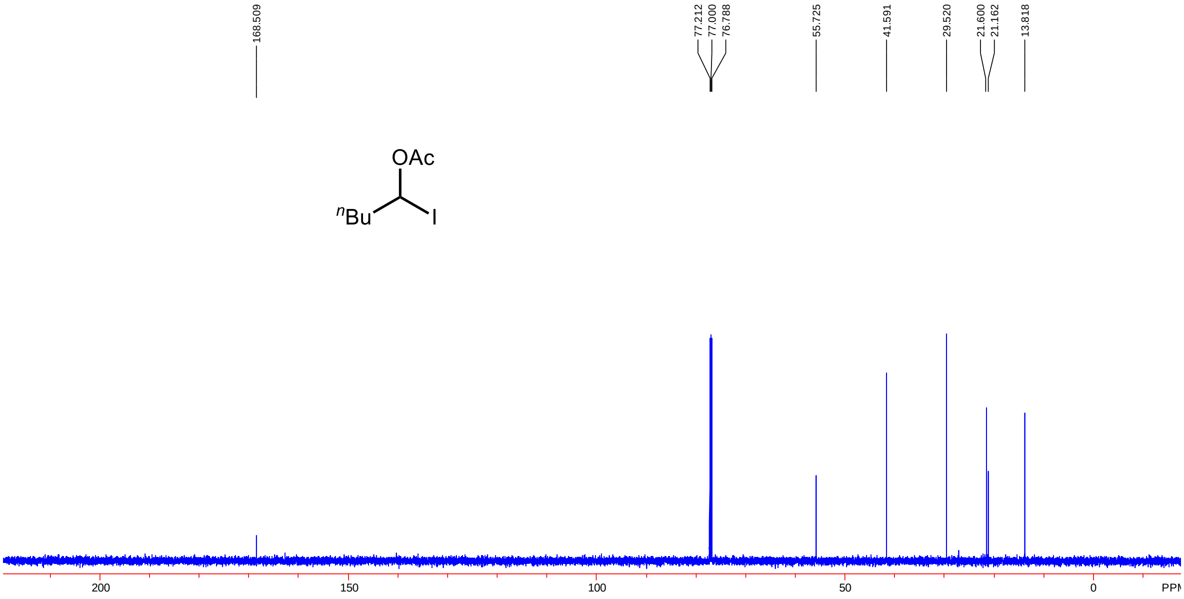
**53**


170.008
145.460
140.437
128.035
127.955
126.883
125.272
77.313
77.000
76.679
72.516
39.146
34.757
29.821
27.117
22.392
22.224
21.299
13.877
13.855
OAc
Ph
$^n$Bu
$^n$Bu
200
150
100
50
0
PPM

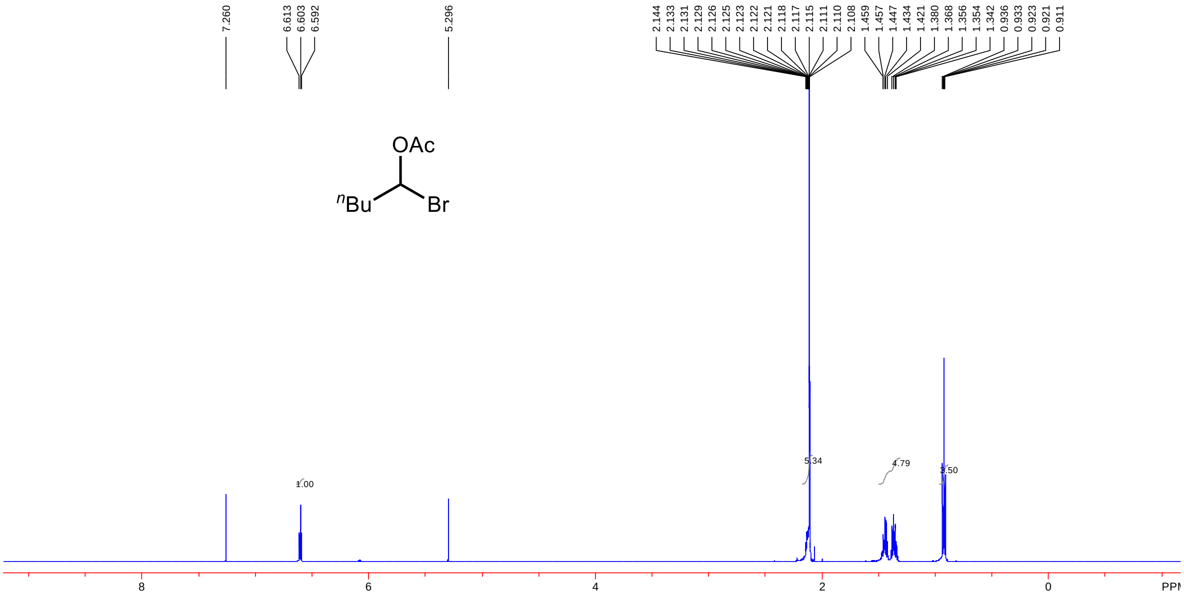
**53**

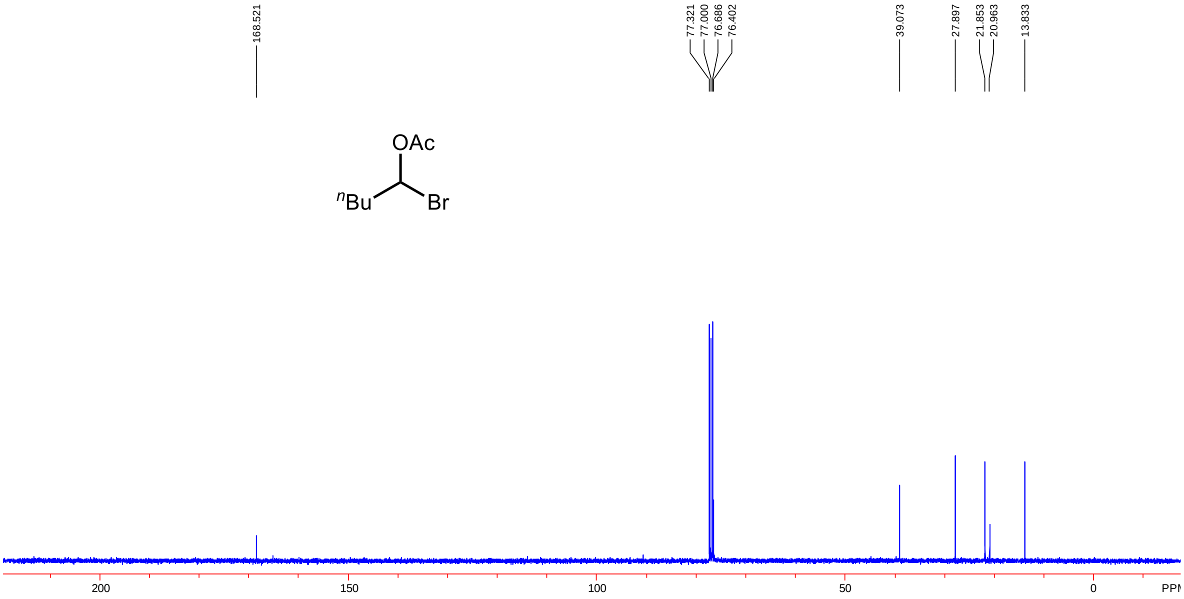


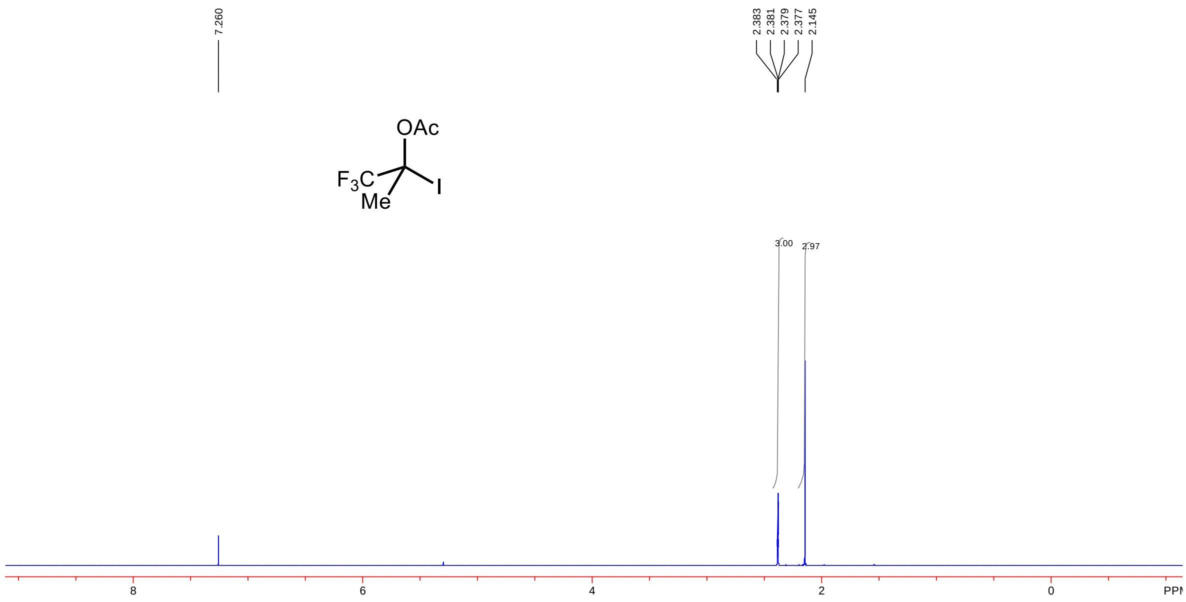
7.260
6.795
6.785
6.775
2.164
2.153
2.146
2.143
2.139
2.130
2.129
2.068
1.426
1.421
1.420
1.418
1.417
1.415
1.412
1.408
1.404
1.374
1.363
1.351
1.339
0.930
0.918
0.906
OAc
$^n$Bu
I
1.00
2.28
3.05
4.56
3.59
8
6
4
2
0
PP

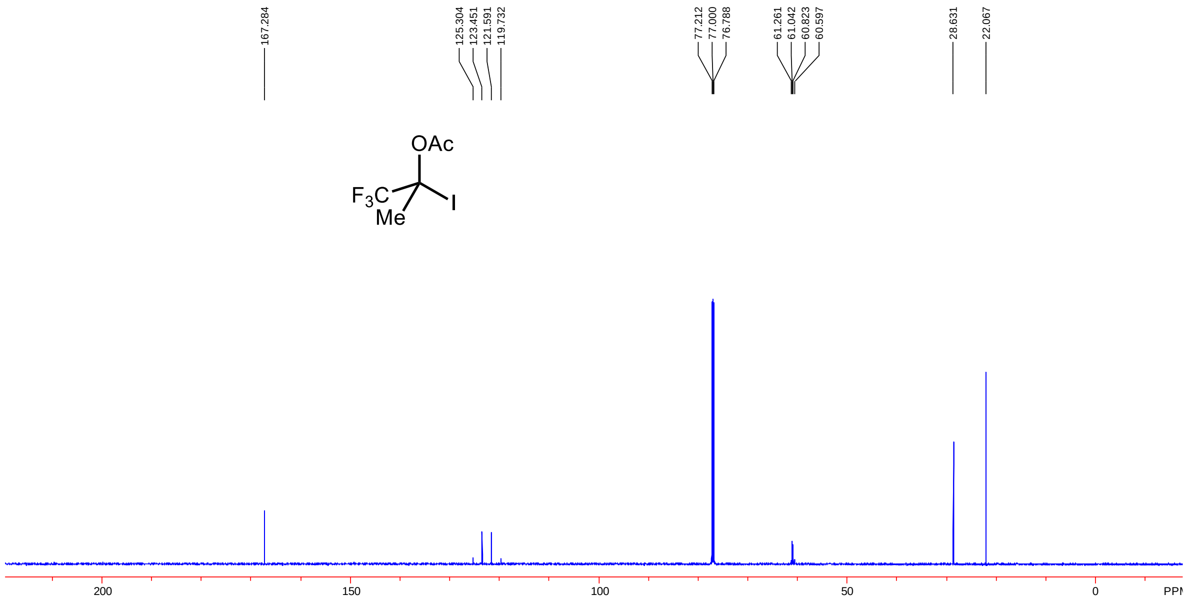


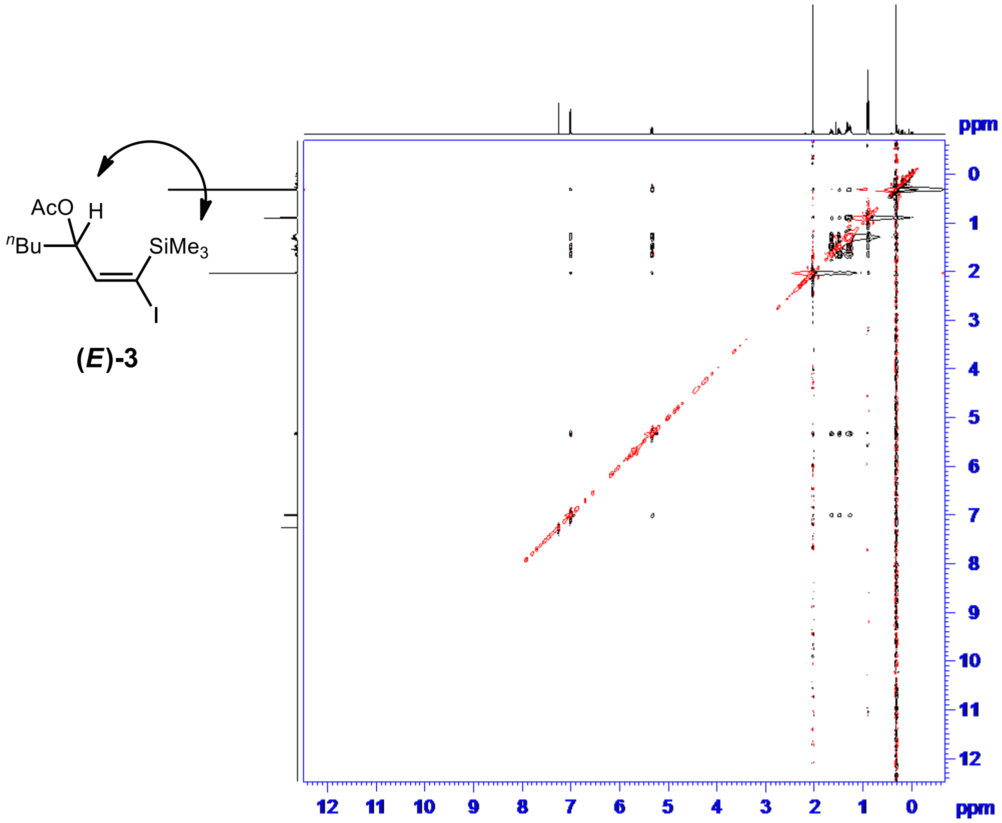
168.509
77.212
77.000
76.788
55.725
41.591
29.520
21.600
21.162
13.818
OAc
$^n$Bu
I
200
150
100
50
0
PP


7.260
6.613
6.603
6.592
5.296
2.144
2.133
2.131
2.129
2.126
2.125
2.123
2.122
2.121
2.118
2.117
2.115
2.111
2.110
2.108
1.459
1.457
1.447
1.434
1.421
1.380
1.368
1.356
1.354
1.342
0.936
0.933
0.923
0.921
0.911
OAc
$^n$Bu
Br
1.00
5.34
4.79
3.50
8
6
4
2
0
PPM

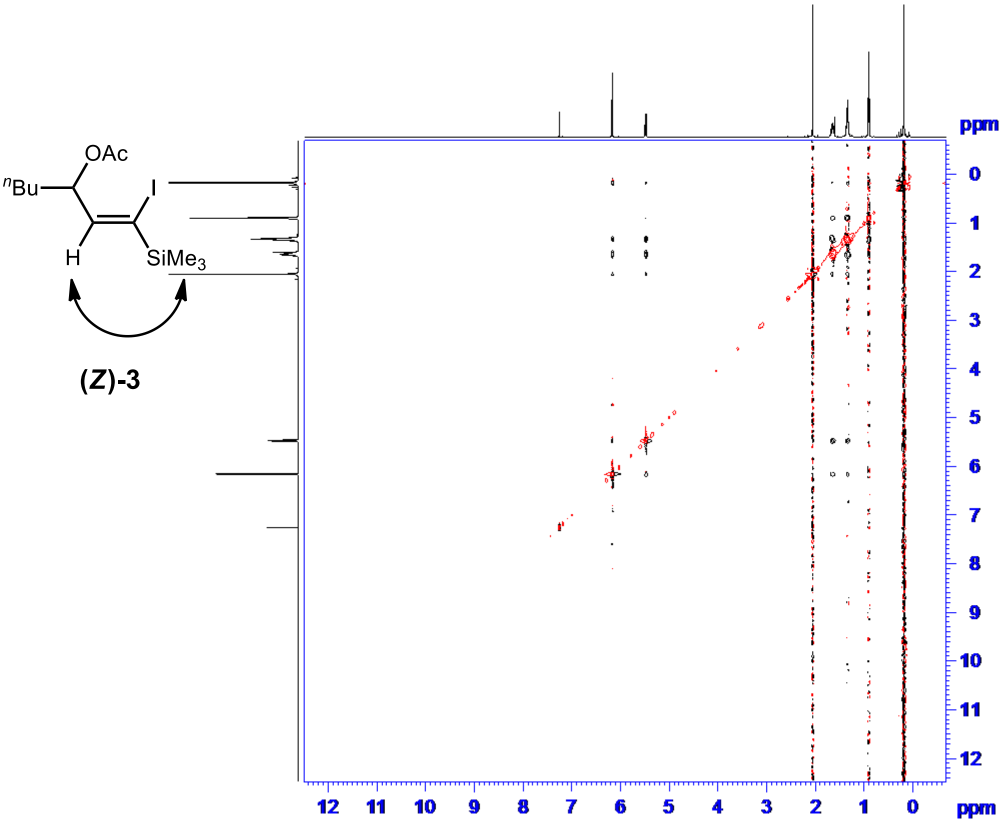

168.521
77.321
77.000
76.686
76.402
39.073
27.897
21.853
20.963
13.833
OAc
$^n$Bu
Br
200
150
100
50
0
PPM


7.260
2.383
2.381
2.379
2.377
2.145
OAc
F3C
Me
I
3.00
2.97
8
6
4
2
0
PPM

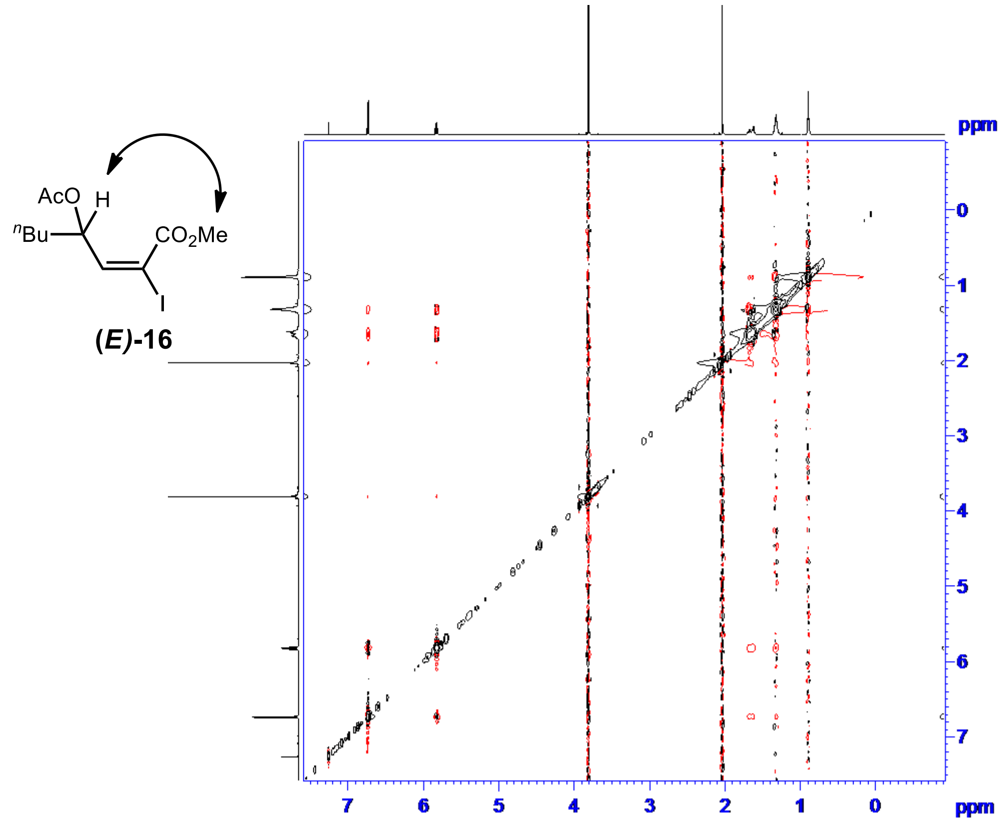

167.284
125.304
123.451
121.591
119.732
77.212
77.000
76.788
61.261
61.042
60.823
60.597
28.631
22.067
OAc
F3C
Me
I
200
150
100
50
0
PPM


AcO
H
$^n$Bu
SiMe$_3$
I
ppm
0
1
2
3
4
5
6
7
8
9
10
11
12
12 11 10 9 8 7 6 5 4 3 2 1 0
ppm

**(*E*)-3**

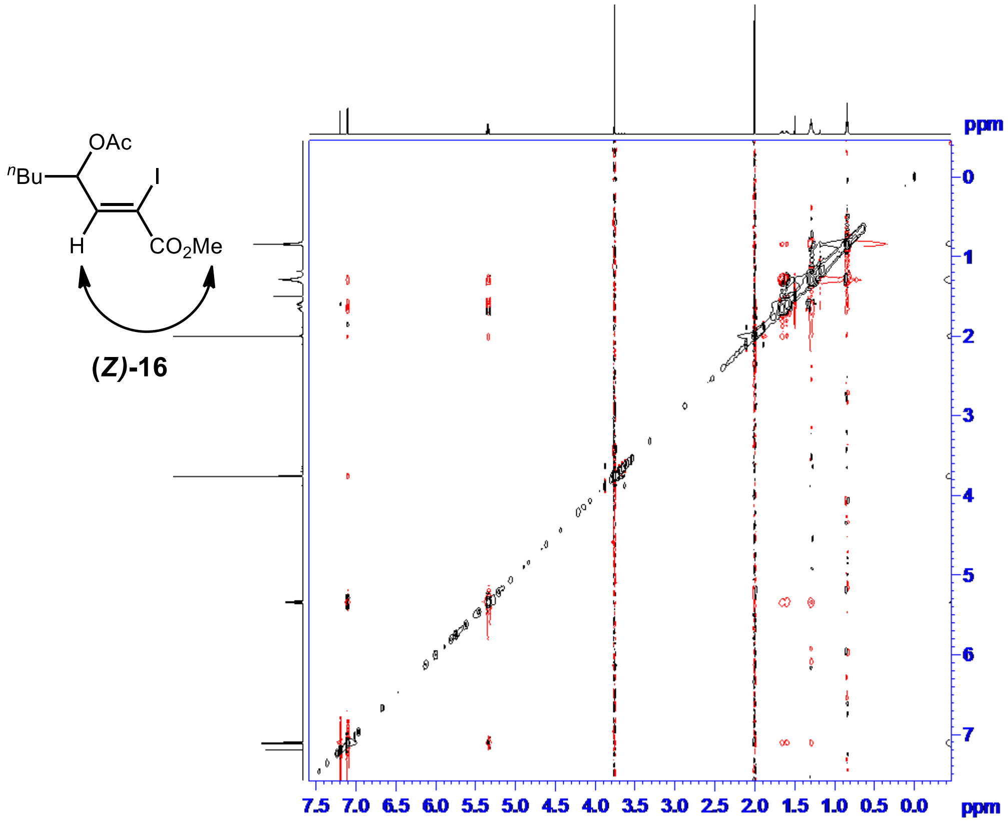

OAc
$^n$Bu
I
H
SiMe$_3$
ppm
0
1
2
3
4
5
6
7
8
9
10
11
12
12 11 10 9 8 7 6 5 4 3 2 1 0
ppm

**(*Z*)-3**



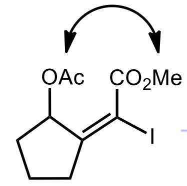
**(*E*)-16**

AcO
H
$^n$Bu
CO$_2$Me
I
ppm
0
1
2
3
4
5
6
7
7
6
5
4
3
2
1
0
ppm

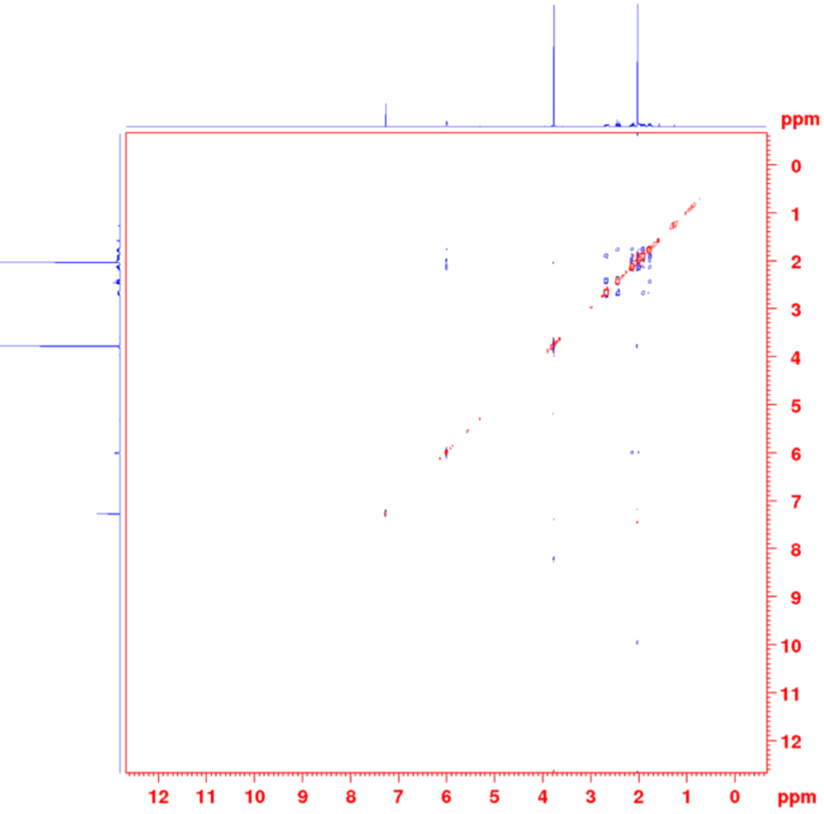


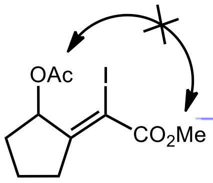
**(*Z*)-16**

OAc
$^n$Bu
I
H
CO$_2$Me
ppm
0
1
2
3
4
5
6
7
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

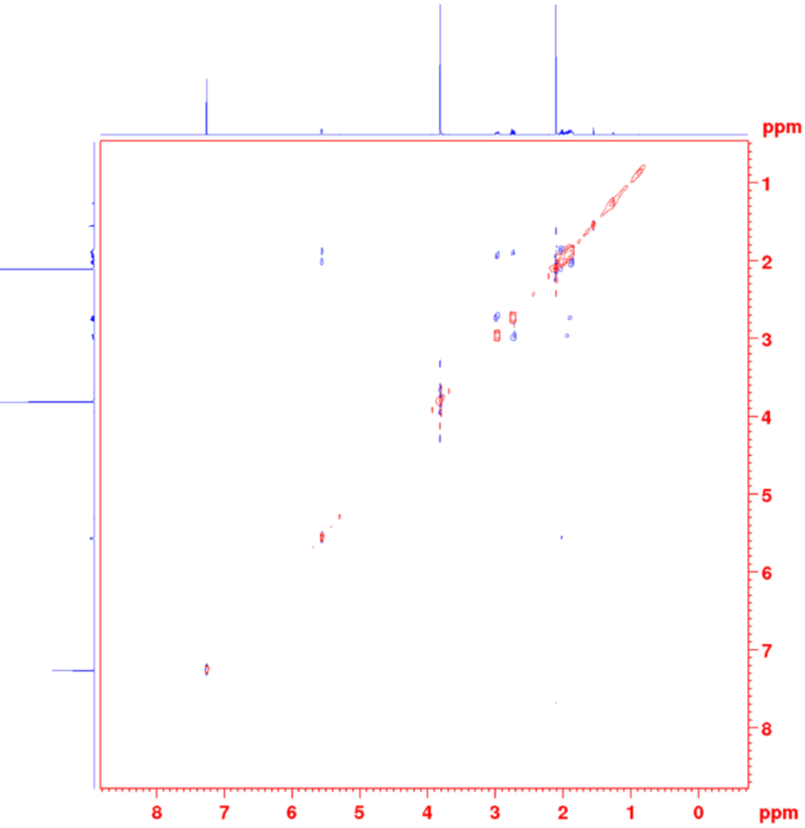

OAc
CO2Me
I

**(*E*)-45**


ppm
0
1
2
3
4
5
6
7
8
9
10
11
12
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm


OAc
I
CO2Me

**(*Z*)-45**


ppm
1
2
3
4
5
6
7
8
8
7
6
5
4
3
2
1
0
ppm

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