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Pd(Quinox)-Catalyzed Allylic Relay Suzuki Reactions of Secondary Homostyrenyl Tosylates via Alkene-Assisted Oxidative Addition

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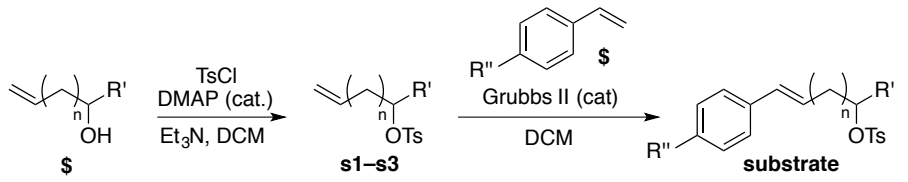
I. General Information

*i*PrOH and NEt_3 were dried by distilling from CaH_2; DCM, Et_2O, and PhMe were dried by passing through a column of activated alumina. Degassed H_2O was prepared using three freeze-pump-thaw cycles in a Schlenk flask. Flash column chromatography was performed using EM Reagent silica 60 (230-400 mesh) unless otherwise noted. ^{1}H NMR spectra were obtained at 300, 400, or 500 MHz and referenced to the residual $CHCl_3$ singlet at 7.26 ppm. ^{13}C NMR spectra were obtained at 75, 100, or 125 MHz and referenced to the center line of the $CDCl_3$ triplet at 77.23 ppm. ^{19}F NMR spectra were obtained at 282 MHz and were unreferenced. The abbreviations s, d, t, q, quint, sep, dd, dt, td, and m stand for the resonance multiplicities singlet, doublet, triplet, quartet, quintet, septet, doublet of doublets, doublet of triplets, triplet of doublets, and multiplet, respectively. GC/MS data were obtained on a HP 5890 (EI) 20:1 split. ATR-FTIR spectra were obtained as neat samples or as thin films evaporated from CH_2Cl_2 on a Bruker Tensor 37 FTIR spectrometer. Melting points were obtained on an electrothermal melting point apparatus and are uncorrected. HRMS data were obtained on an Agilent LC-TOF. Unless otherwise noted, glassware for all reactions was oven-dried at 110 °C and cooled in a dry atmosphere prior to use.

II. Preparation of Substrates

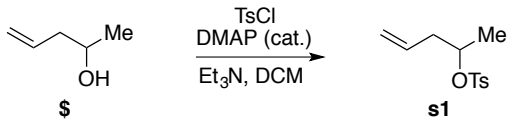
Scheme s1. General synthetic route to substrates.



substrate	n	R'	R''
1	1	Me	H
5a	1	Me	CF_3
5b	1	Me	Cl
5c	1	Me	F
5d	1	Me	Me
5e	1	Me	OMe
5f	1	Me	Br
12	2	H	H
13	3	H	H

Substrates **1**, **5a**–**5f**, **12** and **13** were prepared using a two-step sequence of alcohol tosylation and alkene cross-metathesis (Scheme s1). Neither the tosylation nor the cross-metathesis reaction were optimized.

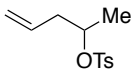
a. General Procedure for Alcohol Tosylation



(s1)

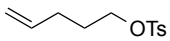
To a dry 500 mL round-bottom flask equipped with a stirbar were added 12.58 g of TsCl (66.0 mmol, 1.10 equiv) and 1.83 g of DMAP (15.0 mmol, 0.250 equiv). After purging under N_2, 150 mL of DCM and 16.7 mL of NEt_3 (120.0 mmol, 2.00 equiv) were added. The resulting mixture was cooled to 0 °C, and a solution of 6.2 mL of 4-penten-2-ol (60.0 mmol, 1.00 equiv) in 150 mL of DCM was added dropwise through an addition funnel. The mixture was allowed to warm to room temperature and was stirred overnight. The solution was then washed with saturated aqueous $NaHCO_3$ (1 × 300 mL) and H_2O (1 × 300 mL). The combined aqueous layers were extracted with DCM (1 × 300 mL) and the combined organic layers were dried over Na_2SO_4, decanted, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography.

b. Vinyl-Containing Tosylate Synthesis



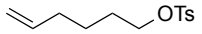
s1

Pent-4-en-2-yl 4-methylbenzenesulfonate s1. The general tosylation procedure was followed using 6.2 mL of 4-penten-2-ol (60.0 mmol), 16.7 mL of Et_3N (120.0 mmol), 12.58 g of tosyl chloride (66.0 mmol), and 1.83 g of DMAP (15.0 mmol) in 300 mL of DCM. Purification by flash column chromatography (0:100 → 30:70 EtOAc:hexanes) afforded **s1** as a colorless oil (13.43 g, 93%), R_f = 0.47 (20:80 EtOAc:hexanes, visualized by 254 nm light). The spectral data matched those reported by Stokes and coworkers.[1]



s2

Pent-4-en-1-yl 4-methylbenzenesulfonate s2. The general tosylation procedure was followed using 2.4 mL of 4-penten-1-ol (22.8 mmol), 6.3 mL of Et_3N (45.5 mmol), 4.77 g of tosyl chloride (25.0 mmol), and 278 mg of DMAP (2.3 mmol) in 115 mL of DCM. Purification by flash column chromatography (0:100 → 30:70 EtOAc/hexanes) afforded **s2** as a colorless oil (5.17 g, 94%), R_f = 0.47 (20:80 EtOAc:hexanes). The spectral data matched those reported by Stokes and coworkers.[1]

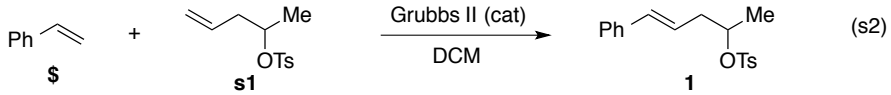


s3

Hex-5-en-1-yl 4-methylbenzenesulfonate s3. The general tosylation procedure was followed using 2.4 mL of 5-hexen-1-ol (20.0 mmol), 5.6 mL of Et_3N (40.0 mmol), 4.19 g of tosyl chloride (22.0 mmol), and 245 mg of DMAP (2.0 mmol) in 100 mL of DCM. Purification by flash column chromatography (0:100 → 30:70 EtOAc:hexanes) afforded **s3** as a colorless oil (4.54 g, 89%), R_f = 0.50 (20:80 EtOAc:hexanes, visualized by 254 nm light). The spectral data matched those reported by Kalyani and Sanford.[2] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 5.69 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 4.96-4.91 (m, 1H), 4.91-4.88 (m, 1H), 4.00 (t, *J* = 6.4 Hz, 2H), 2.42 (s, 3H), 2.01-1.93 (m, 2H), 1.67-1.58 (m, 2H), 1.43-1.33 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.0, 138.1, 133.3, 130.1, 128.1, 115.3, 70.7, 33.1, 28.4, 24.7, 21.8; ATR-FTIR (neat): 2932, 1641, 1598, 1355, 1173, 1097 cm^{-1}.

A. Preparation of Styrene-Containing Tosylates

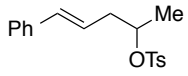
a. General Procedure for Alkene Cross-Metathesis



$ s1 1

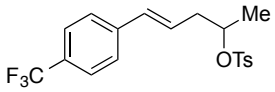
Into a dry 100 mL round-bottom flask equipped with a stirbar were added 4.78 g of secondary homoallyl tosylate **s1** (20.0 mmol, 1.00 equiv), followed by 10.4 mL of styrene (100.0 mmol, 5.00 equiv), 40 mL of DCM, and finally 74 mg of Grubbs's 2nd generation catalyst (0.10 mmol, 0.5 mol %). The flask was equipped with a condenser and refluxed for 2 hours at 40 °C under N_2, at which time TLC revealed the consumption of tosylate **s1**. ***Caution:*** *Ensure adequate venting of the reaction to avoid pressurization due to the release of ethylene gas.* After cooling to ambient temperature, 0.05 mL of di(ethylene glycol) vinyl ether (0.40 mmol, 4 equiv with respect to catalyst) was added and the reaction stirred for 30 minutes to quench active ruthenium catalyst.[3] The reaction was partially concentrated in vacuo and loaded onto a silica gel flash column using CH_2Cl_2, leaving a substantial amount of stilbene in the reaction flask. Chromatography was performed by first flushing with hexanes to remove excess stilbene byproduct (as determined by TLC analysis). Gradient addition of ethyl acetate was then used to elute the product. **Note:** Styrene was passed through basic alumina immediately prior to use.

b. Styrene-Containing Tosylate Synthesis



1

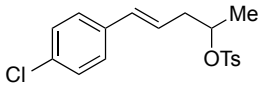
(*E*)-5-Phenylpent-4-en-2-yl 4-methylbenzenesulfonate 1. The general procedure was followed using 4.78 g of tosylate **s1** (20.0 mmol), 10.4 mL of styrene (100.0 mmol), and 74 mg of Grubbs's 2nd generation catalyst (0.10 mmol) in 40 mL of CH_2Cl_2. Purification by flash column chromatography (0:100 → 30:70 EtOAc:hexanes) afforded **1** as a white powder (3.34 g, 53%), R_f = 0.33 (20:80 EtOAc:hexanes, visualized by 254 nm light). The spectral data matched those reported by Stokes and coworkers.[1]



5a

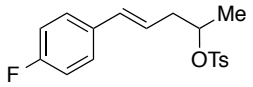
(*E*)-5-(4-(trifluoromethyl)phenyl)pent-4-en-2-yl 4-methylbenzenesulfonate 5a. The general procedure for alkene cross-metathesis was followed using 0.96 g of secondary homoallyl tosylate **s1** (4.0 mmol), 0.59 mL of 4-(trifluoromethyl)styrene (4.0 mmol), and 17 mg of Grubbs's 2nd generation catalyst (0.02 mmol) in 8.0 mL of DCM at 45 °C. Purification by flash column chromatography (0:100 → 50:50 EtOAc:hexanes) afforded **5a** as a white powder (216 mg, 14%), mp 100 °C, R_f = 0.50 (20:80 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H

NMR ($CDCl_3$, 500 MHz): δ 7.75 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 7.7 Hz, 2H), 6.36 (d, J = 15.8 Hz, 1H), 6.00 (dt, J = 15.5, 7.6 Hz, 1H), 4.69 (sextet, J = 6.5 Hz, 1H), 2.55-2.41 (m, 2H), 2.34 (s, 3H), 1.35 (d, J = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.8, 140.6, 134.4, 132.5, 129.9, 129.4 (q, $J_{C–F}$ = 32.5 Hz), 127.9, 127.2, 126.5, 125.6 (q, $J_{C–F}$ = 3.9 Hz), 124.4 (q, $J_{C–F}$ = 270.3), 79.5, 40.2, 21.7, 21.1; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –62.87; ATR-FTIR (thin film): 2933, 1614, 1324, 1169, 1117, 1067, 1016 cm^{-1}; HRMS (ESI-TOF) m / z calculated for $C_{19}H_{19}O_3F_3NaS$ [M+Na]$^+$: 407.0905, found 407.0904.



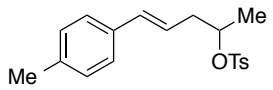
5b

(*E*)-5-(4-chlorophenyl)pent-4-en-2-yl 4-methylbenzenesulfonate 5b. The general procedure for alkene cross-metathesis was followed using 1.08 g of secondary homoallyl tosylate **s1** (4.5 mmol), 2.7 mL of 4-chlorostyrene (22.5 mmol), and 38 mg of Grubbs's 2nd generation catalyst (0.05 mmol) in 9.0 mL of DCM at 45 °C. Purification by flash column chromatography (0:100 → 50:50 EtOAc:hexanes) afforded **5b** as a white powder (591 mg, 37%), mp 92 °C, R_f = 0.15 (20:80 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.5 (d, J = 8.4 Hz, 2H), 7.27-7.18 (m, 4H), 7.13 (d, J = 8.4 Hz, 2H), 6.28 (d, J = 15.8 Hz, 1H), 5.85 (dt, J = 15.8, 7.3 Hz, 1H), 4.67 (sextet, J = 5.7 Hz, 1H), 2.54-2.38 (m, 2H), 2.36 (s, 3H), 1.34 (d, J = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.7, 135.7, 134.3, 133.2, 132.5, 129.9, 128.8, 127.9, 127.6, 125.0, 79.7, 40.2, 21.8, 21.1; ATR-FTIR (thin film): 2980, 1596, 1490, 1349, 1172, 1093 cm^{-1}; HRMS (ESI-TOF) m / z calculated for $C_{18}H_{19}ClO_3NaS$ [M+Na]$^+$: 373.0641, found 373.0645.



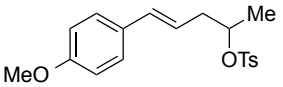
5c

(*E*)-5-(4-fluorophenyl)pent-4-en-2-yl 4-methylbenzenesulfonate 5c. The general procedure for alkene cross-metathesis was followed using 1.00 g of secondary homoallyl tosylate **s1** (4.2 mmol), 2.5 mL of 4-fluorostyrene (21.5 mmol), and 18 mg of Grubbs's 2nd generation catalyst (0.02 mmol) in 8.0 mL of DCM at 45 °C. Purification by flash column chromatography (0:100 → 50:50 EtOAc:hexanes) afforded **5c** as a white powder (357 mg, 26%), mp 103 °C, R_f = 0.34 (20:80 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.75 (d, J = 8.1 Hz, 2H), 7.23-7.14 (m, 4H), 6.98-6.94 (m, 2H), 6.28 (d, J = 15.8 Hz, 1H), 5.79 (dt, J = 15.5, 7.6 Hz, 1H), 4.66 (sextet, J = 6.2 Hz, 1H), 2.49-2.40 (m, 2H), 2.36 (s, 3H), 1.33 (d, J = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.3 (d, $J_{C–F}$ = 245 Hz), 144.7, 134.4, 133.4 (d, $J_{C–F}$ = 3.1 Hz), 132.6, 129.9, 127.9, 127.8, 123.9 (d, $J_{C–F}$ = 2.1 Hz), 115.5 (d, $J_{C–F}$ = 21.4 Hz), 79.9, 40.1, 21.8, 21.0; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –115.2; ATR-FTIR (thin film): 2933, 1599, 1507, 1349, 1225, 1173, 1096 cm^{-1}; HRMS (ESI-TOF) m / z calculated for $C_{18}H_{19}FO_3NaS$ [M+Na]$^+$: 357.0937, found 357.0945.



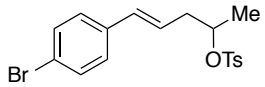
5d

(*E*)-5-(4-Tolyl)pent-4-en-2-yl 4-methylbenzenesulfonate 5d. The general procedure for alkene cross-metathesis was followed using 0.500 g of secondary homoallyl tosylate **s1** (2.0 mmol), 2.7 mL of 4-methylstyrene (21.0 mmol), and 17 mg of Grubbs's 2nd generation catalyst (0.02 mmol) in 4.0 mL of DCM at 45 °C. Purification by flash column chromatography (0:100 → 50:50 EtOAc:hexanes) afforded **5d** as a white powder (250 mg, 38%), mp 47 °C, R_f = 0.44 (20:80 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.77 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.14-7.06 (m, 4H), 6.30 (d, J = 15.8 Hz, 1H), 5.82 (dt, J = 15.8, 7.3 Hz, 1H), 4.66 (sextet, J = 6.2 Hz, 1H), 2.51-2.40 (m, 2H), 2.37 (s, 3H), 2.34 (s, 3H), 1.35 (d, J = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.7, 137.4, 134.4, 133.7, 130.0, 129.9, 129.4, 128.0, 126.3, 123.0, 80.0, 40.2, 21.8, 21.4, 21.0; ATR-FTIR (thin film): 2980, 2923, 1598, 1513, 1449, 1351, 1173, 1097 cm^{-1}; HRMS (ESI-TOF) m / z calculated for $C_{19}H_{22}O_3NaS$ [M+Na]$^+$: 353.1187, found 353.1197.



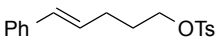
5e

(*E*)-5-(4-methoxyphenyl)pent-4-en-2-yl 4-methylbenzenesulfonate 5e. The general procedure for alkene cross-metathesis was followed using 0.96 g of secondary homoallyl tosylate **s1** (4.0 mmol), 1.1 mL of 4-methoxystyrene (8.0 mmol), and 34 mg of Grubbs's 2nd generation catalyst (0.04 mmol) in 8.0 mL of DCM at 25 °C. Purification by flash column chromatography (0:100 → 50:50 EtOAc:hexanes) afforded **5e** as a white powder (264 mg, 19%), mp 47 °C, R_f = 0.34 (20:80 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.26 (d, *J* = 15.8 Hz, 1H), 5.72 (dt, *J* = 15.8, 7.3 Hz, 1H), 4.65 (sextet, *J* = 6.1 Hz, 1H), 3.80 (s, 3H), 2.52-2.32 (m, 2H), 2.37 (s, 3H), 1.34 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 159.3, 144.7, 134.4, 133.2, 130.0, 129.9, 128.0, 127.5, 121.8, 114.1, 80.1, 55.5, 40.2, 21.8, 21.0; ATR-FTIR (thin film): 2934, 2836, 1607, 1510, 1456, 1349, 1292, 1245, 1171, 1032 cm^{-1}; HRMS (ESI-TOF) *m* / *z* calculated for $C_{19}H_{22}O_4NaS$ [M+Na]$^+$: 369.1137, found 369.1141.



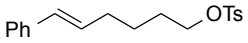
5f

(*E*)-5-(4-Bromophenyl)pent-4-en-2-yl 4-methylbenzenesulfonate 5f. The general procedure for alkene cross-metathesis was followed using 1.00 g of secondary homoallyl tosylate **s1** (4.2 mmol), 2.7 mL of 4-bromostyrene (21.0 mmol), and 18 mg of Grubbs's 2nd generation catalyst (0.02 mmol) in 8.0 mL of DCM at 45 °C. Purification by flash column chromatography (0:100 → 50:50 EtOAc:hexanes) afforded **5f** as a white powder (353 mg, 21%), mp 53 °C, R_f = 0.34 (20:80 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.26 (d, *J* = 15.8 Hz, 1H), 5.87 (dt, *J* = 15.8, 7.3 Hz, 1H), 4.67 (sextet, *J* = 6.3 Hz 1H), 2.50-2.39 (m, 2H), 2.36 (s, 3H), 1.34 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.7, 136.1, 134.3, 132.6, 131.7, 129.9, 128.0, 127.9, 125.1, 121.3, 79.7, 40.2, 21.9, 21.1; ATR-FTIR (thin film): 2980, 2932, 1597, 1486, 1448, 1349, 1172, 1097, 1071 cm^{-1}; HRMS (ESI-TOF) *m* / *z* calculated for $C_{18}H_{19}BrO_3NaS$ [M+Na]$^+$: 417.0136, found 417.0141.



12

(*E*)-5-Phenylpent-4-en-1-yl 4-methylbenzenesulfonate 12 The general procedure for alkene cross-metathesis was followed using 2.40 g of tosylate **s2** (10.0 mmol), 5.7 mL of styrene (50.0 mmol), and 42 mg of Grubbs's 2nd generation catalyst (0.05 mmol) in 20 mL of DCM. Purification by flash column chromatography (0:100 → 50:50 EtOAc:hexanes) afforded **12** as a white solid (1.58 g, 50%), R_f = 0.44 (20:80 EtOAc:hexanes, visualized by 254 nm light). The spectral data matched those reported by Stokes and coworkers.[1]

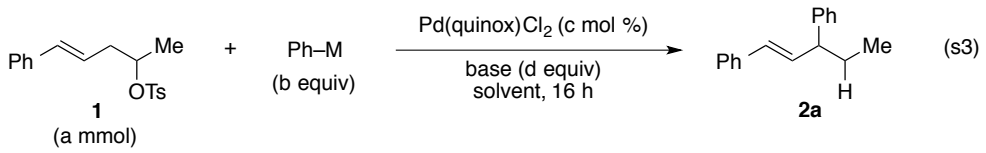


13

(*E*)-6-Phenylhex-5-en-1-yl 4-methylbenzenesulfonate 13. The general procedure for alkene cross-metathesis was followed using 1.27 g of tosylate **s3** (5.0 mmol), 2.8 mL of styrene (25.0 mmol), and 30 mg of Grubbs's 2nd generation catalyst (0.04 mmol) in 10 mL of DCM. Purification by flash column chromatography (0:100 → 30:70 EtOAc:hexanes) afforded **13** as a tan oil (956 mg, 58%), R_f = 0.47 (20:80 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.34-7.18 (m, 7H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.12 (dt, *J* = 15.3, 7.4 Hz, 1H), 4.06 (t, *J* = 6.0 Hz, 2H), 2.43 (s, 3H), 2.17 (q, *J* = 7.1 Hz, 2H), 1.70 (quint, *J* = 7.1 Hz, 2H), 1.50 (quint, *J* = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.7, 137.5, 133.2, 130.5, 129.8, 129.7, 128.5, 127.9, 127.0, 125.9, 70.4, 31.2, 28.3, 25.0, 21.6; ATR-FTIR (neat): 2936, 1597, 1494, 1448, 1354, 1173, 1097, 1019 cm^{-1}; HRMS (ESI-TOF) *m* / *z* calculated for $C_{19}H_{22}O_3NaS$ [M+Na]$^+$: 353.1187, found 353.1195.

III. Pd-Catalyzed Allylic Relay Suzuki Reactions

A. General Procedure for the Optimization of the Relay Cross-Coupling of Secondary Homostyrenyl Tosylates



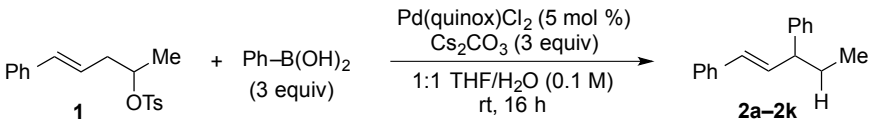
General procedure. Into a dry 4 mL vial were added base (0.15 mmol, 3.00 equiv), 9 mg of phenylboronic acid (0.08 mmol, 1.50 equiv), 16 mg of tosylate **1** (0.05 mmol, 1.00 equiv), and 2 mg of Pd(quinox)Cl_2 (0.005 mmol, 10 mol %). The vial was capped with a septum and purged under a stream of dry N_2 for approximately 3 min. To the solids was then injected 0.5 mL of solvent and the mixture was stirred for 16 h under N_2. The reaction was then filtered through a plug of silica gel using EtOAc, concentrated *in vacuo*, and the residue fully taken up in 0.75 mL of a $1x10^{-5}$ M solution of 2-methoxynaphthalene in $CDCl_3$, which was then analyzed by ^{1}H NMR spectroscopy. **Note:** 2-methoxynaphthalene solution in $CDCl_3$ was stored in the freezer when not in use.

B. Tabular Summary of Selected Optimization Experiments

Table s1. Reaction optimization experiments.

entry	a	b	M	c	d	base	solvent system	solvent ratio	[**1**] (mol/L)	% NMR conv.	% NMR yield
1	0.05	1.5	$B(OH)_2$	10	3	$KF.2H_2O$	IPA	n.a.	0.1	83	70
2	0.27	1.5	$B(OH)_2$	10	3	$KF.2H_2O$	IPA	n.a.	0.1	75	62
3	0.05	1.5	$B(OH)_2$	10	3	K_2CO_3	IPA/H_2O	1:1	0.05	trace	trace
4	0.05	1.5	$B(OH)_2$	10	3	K_2CO_3	THF/H_2O	1:1	0.05	73	54
5	0.05	1.5	$B(OH)_2$	10	3	K_2CO_3	IPA/THF/H_2O	1:1:1	0.05	37	27
6	0.05	1.5	$B(OH)_2$	5	3	K_2CO_3	THF/H_2O	1:1	0.1	55	40
7	0.05	1.5	$B(OH)_2$	5	3	Li_2CO_3	THF/H_2O	1:1	0.1	38	19
8	0.05	1.5	$B(OH)_2$	5	3	NaOAc	THF/H_2O	1:1	0.1	0	n.a.
9	0.05	1.5	$B(OH)_2$	5	3	KF	THF/H_2O	1:1	0.1	10	9
10	0.05	1.5	$B(OH)_2$	5	3	CsF	THF/H_2O	1:1	0.1	10	6
11	0.05	1.5	$B(OH)_2$	5	3	NaOH	THF/H_2O	1:1	0.1	18	17
12	0.05	1.5	$B(OH)_2$	5	3	$NaHCO_3$	THF/H_2O	1:1	0.1	0	n.a.
13	0.05	1.5	$B(OH)_2$	5	3	Na_2CO_3	THF/H_2O	1:1	0.1	58	41
14	0.05	1.5	$B(OH)_2$	5	3	Cs_2CO_3	THF/H_2O	1:1	0.1	54	41
15	0.1	1.5	Bpin	5	3	Cs_2CO_3	THF/H_2O	1:1	0.1	68	56
16	0.1	3	B(MIDA)	5	3	Cs_2CO_3	THF/H_2O	1:1	0.1	0	n.a.
17	0.1	3	BF_3K	5	3	Cs_2CO_3	THF/H_2O	1:1	0.1	76	21
18	0.05	1.5	$B(OH)_2$	5	2	Cs_2CO_3	THF/H_2O	1:1	0.1	45	39
19	0.05	3	$B(OH)_2$	5	2	Cs_2CO_3	THF/H_2O	1:1	0.1	35	31
20	0.05	3	$B(OH)_2$	5	3	Cs_2CO_3	THF/H_2O	1:2	0.17	58	54
21	0.05	3	$B(OH)_2$	5	3	Cs_2CO_3	THF/H_2O	1:1	0.1	>95	80
22	0.05	2	$B(OH)_2$	5	3	Cs_2CO_3	THF/H_2O	1:1	0.1	40	35
23	0.05	4	$B(OH)_2$	5	3	Cs_2CO_3	THF/H_2O	1:1	0.1	66	56
24	0.05	3	$B(OH)_2$	10	5	Cs_2CO_3	THF/H_2O	1:1	0.1	92	70
25	0.5	3	$B(OH)_2$	10	3	Cs_2CO_3	THF/H_2O	2:1	0.07	63	53
26	0.5	3	$B(OH)_2$	5	3	Cs_2CO_3	THF/H_2O	10:1	0.18	68	68
27	0.5	6	$B(OH)_2$	5	6	Cs_2CO_3	THF/H_2O	2:1	0.07	n.d.	65
28	0.5	6	$B(OH)_2$	10	6	Cs_2CO_3	THF/H_2O	4:1	0.04	90	74

C. Optimized General Procedure

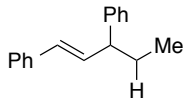


(s4)

Into a dry 20 mL scintillation equipped with a PTFE-coated stirbar were added 158 mg of tosylate **1** (0.50 mmol, 1.00 equiv), 489 mg of Cs_2CO_3 (1.50 mmol, 3.00 equiv), 183 mg of $PhB(OH)_2$ (1.50 mmol, 3.00 equiv), and 9 mg of $Pd(quinox)Cl_2$ (0.025 mmol, 5 mol %). The vial was capped with a septum, an N_2 line was added, and the vial was flushed with N_2 for approximately 3 min. To the solids were then added 2.5 mL of THF and 2.5 mL of H_2O simultaneously, and the mixture was stirred vigorously for 16 h. The resultant mixture was then partitioned between EtOAc and saturated aqueous NH_4Cl (20 mL each) and the organic layer was washed consecutively with saturated aqueous $NaHCO_3$ (1 × 20 mL) and brine (1 x 20 mL). The combined aqueous layers were extracted with EtOAc (1 × 20 mL) and the combined organic layers were concentrated, dissolved in

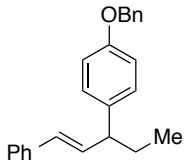
a portion of CH_2Cl_2, then dried over Na_2SO_4, decanted, and concentrated *in vacuo*. After analysis by ^{1}H NMR spectroscopy, the crude residue was purified by silica gel flash column chromatography to afford analytically pure product.

D. Scope and Limitations of the Relay Cross-Coupling Reaction



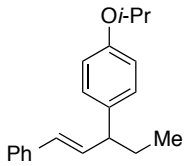
2a

(*E*)-Pent-1-ene-1,3-diyldibenzene 2a. The general procedure was followed using 158 mg of secondary homoallylic tosylate **1** (0.50 mmol), 183 mg of phenylboronic acid (1.50 mmol), 489 mg of Cs_2CO_3 (1.50 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. Purification by flash column chromatography (100% hexanes) afforded **2a** as a colorless oil (78 mg, 70%), R_f = 0.17 (hexanes, visualized by 254 nm light). The spectral data matched those reported by Stokes and coworkers.[1] ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.43–7.20 (m, 10H), 6.47 (d, *J* = 16 Hz, 1H), 6.39 (dd, *J* = 16, 6.9 Hz, 1H), 3.35 (q, *J* = 7.2 Hz, 1H), 1.95-1.79 (m, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.8, 137.9, 134.5, 129.7, 128.7 (2 C), 128.0, 127.3, 126.5, 126.4, 51.27, 29.07, 12.61; ATR-FTIR (thin film): 3028, 2963, 2925, 2874, 1723, 1494, 1451, 1268, 1026 cm^{-1}.



2b

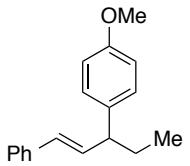
(*E*)-1-(Benzyloxy)-4-(1-phenylpent-1-en-3-yl)benzene 2b. The general procedure was followed using 158 mg of homostyrenyl tosylate **1** (0.50 mmol), 340 mg of 4-benzyloxyphenylboronic acid (1.5 mmol), 490 mg of Cs_2CO_3 (1.5 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. Purification by flash column chromatography (0:100 → 30:70 benzene:hexanes) afforded **2b** as a colorless solid (128 mg, 78%), mp 60 °C, R_f = 0.43 (20% benzene:hexanes, visualized by 254 nm light). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.50-7.29 (m, 9H), 7.25-7.18 (m, 3H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.35 (dd, *J* = 15.8, 6.9 Hz, 1H), 5.08 (s, 2H), 3.31 (q, *J* = 7.2 Hz, 1H), 1.90-1.79 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 157.5, 137.9, 137.4, 137.1, 134.8, 129.4, 128.9, 128.8, 128.7, 128.2, 127.8, 127.2, 126.4, 115.0, 70.3, 50.3, 29.1, 12.6; ATR-FTIR (thin film): 3027, 2959, 2927, 2870, 1607, 1508, 1453, 1379, 1236, 1175, 1024 cm^{-1}; HRMS (ESI-TOF) m / z calculated for $C_{24}H_{24}ONa$ $[M+Na]^+$: 351.1725, found 351.1738.



2c

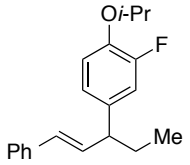
(*E*)-1-Isopropoxy-4-(1-phenylpent-1-en-3-yl)benzene 2c. The general procedure was followed using 158 mg of homostyrenyl tosylate **1** (0.50 mmol), 270 mg of 4-isopropoxyphenylboronic acid (1.5 mmol), 490 mg of Cs_2CO_3 (1.5 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. Purification by flash column chromatography (0:100 → 30:70 benzene:hexanes) afforded **2c** a colorless oil (104 mg, 74%), R_f = 0.21 (20:80 benzene:hexanes, visualized by 254 nm light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40-7.38 (m, 2H), 7.34-7.30 (m, 2H), 7.24-7.21 (m, 1H), 7.20-7.17 (m, 2H), 6.91-6.88 (m, 2H), 6.43 (d, *J* = 15.9 Hz, 1H), 6.36 (dd, *J* = 15.8, 7.4 Hz, 1H), 4.56 (sep, *J* = 6.1 Hz, 1H), 3.30 (q, *J* = 7.4 Hz, 1H), 1.89-1.80 (m, 2H), 1.37 (d, *J* = 6.0 Hz, 6H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 156.5, 138.0, 136.6, 134.9, 129.3, 128.8, 128.7, 127.2, 126.4, 116.1, 70.1, 50.3, 29.1, 22.4, 12.6; ATR-FTIR (neat): 3025, 2972, 2929, 2872, 1608, 1506,

1449, 1382, 1371, 1295, 1239, 1181, 1118 cm^{-1}; HRMS (API-TOF) m / z calculated for $C_{20}H_{25}O$ $[M+H]^+$: 281.1905, found 281.1901.



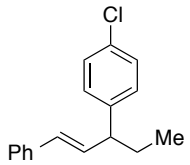
2d

(*E*)-1-Methoxy-4-(1-phenylpent-1-en-3-yl)benzene 2d. The general procedure was followed using 158 mg of homostyrenyl tosylate **1** (0.50 mmol), 230 mg of 4-methoxyphenylboronic acid (1.5 mmol), 490 mg of Cs_2CO_3 (1.5 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. Purification by flash column chromatography (0:100 → 30:70 benzene:hexanes) afforded **2d** as a colorless oil (77 mg, 61%), R_f = 0.30 (20% benzene:hexanes, visualized by 254 nm light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40-7.38 (m, 2H), 7.33-7.30 (m, 2H), 7.24-7.19 (m, 3H), 6.92-6.89 (m, 2H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.36 (dd, *J* = 15.8, 7.3 Hz, 1H), 3.83 (s, 3H), 3.31 (q, *J* = 7.4 Hz, 1H), 1.88-1.81 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 158.2, 137.9, 136.8, 134.8, 129.3, 128.8, 128.7, 127.2, 126.4, 114.1, 55.5, 50.3, 29.1, 12.6; ATR-FTIR (neat): 3025, 2957, 2929, 2871, 2833, 1609, 1509, 1461, 1448, 1300, 1245, 1176, 1034 cm^{-1}; HRMS (ESI-TOF) m / z calculated for $C_{18}H_{20}ONa$ $[M+Na]^+$: 275.1412, found 275.1425.



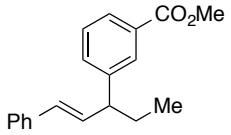
2e

(*E*)-2-Fluoro-1-isopropoxy-4-(1-phenylpent-1-en-3-yl)benzene 2e. The general procedure was followed using 158 mg of homostyrenyl tosylate **1** (0.50 mmol), 297 mg of 3-fluoro-4-isopropoxyphenylboronic acid (1.5 mmol), 490 mg of Cs_2CO_3 (1.5 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. Purification by flash column chromatography (0:100 → 30:70 benzene:hexanes) afforded **2e** as a colorless oil (54 mg, 36%), R_f = 0.37 (20% benzene:hexanes, visualized by 254 nm light). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.37-7.35 (m, 2H), 7.32-7.28 (m, 2H), 7.23-7.19 (m, 1H), 7.00-6.90 (m, 3H), 6.40 (d, *J* = 15.9 Hz, 1H), 6.28 (dd, *J* = 15.8, 7.7 Hz, 1H), 4.50 (septet, *J* = 6.1 Hz, 1H), 3.26 (q, *J* = 7.5 Hz, 1H), 1.86-1.74 (m, 2H), 1.36 (d, *J* = 6.1 Hz, 6H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 153.8 (d, $J_{C–F}$ = 244 Hz), 143.9 (d, $J_{C–F}$ = 11.1 Hz), 138.3 (d, $J_{C–F}$ = 5.9 Hz), 137.4, 133.8, 129.6, 128.5, 127.1, 126.1, 123.1 (d, $J_{C–F}$ = 3.5 Hz), 118.0 (d, $J_{C–F}$ = 2.2 Hz), 115.4 (d, $J_{C–F}$ = 18.9 Hz), 72.5, 50.0, 28.7, 22.1, 12.2; ^{19}F NMR ($CDCl_3$, 282 MHz): δ –133.5; ATR-FTIR (neat): 3025, 2973, 2929, 2873, 1580, 1506, 1449, 1428, 1383, 1373, 1270, 1214, 1109 cm^{-1}; HRMS (ESI-TOF) m / z calculated for $C_{20}H_{23}ONaF$ $[M+Na]^+$: 321.1631, found 321.1635.



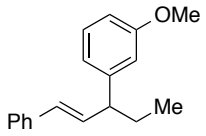
2f

(*E*)-1-Chloro-4-(1-phenylpent-1-en-3-yl)benzene 2f. The general procedure was followed using 158 mg of homostyrenyl tosylate **1** (0.50 mmol), 235 mg of 4-chlorophenylboronic acid (1.5 mmol), 490 mg of Cs_2CO_3 (1.5 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. Purification by flash column chromatography (hexanes) afforded **2f** as a colorless oil (54 mg, 42%), R_f = 0.39 (hexanes, visualized by 254 nm light). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.38-7.28 (m, 6H), 7.24-7.17 (m, 3H), 6.40 (d, *J* = 15.9 Hz, 1H), 6.29 (dd, *J* = 15.8, 7.3 Hz, 1H), 3.31 (q, *J* = 7.4 Hz, 1H), 1.90-1.74 (m, 2H), 0.91 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 143.2, 137.6, 133.8, 132.1, 130.0, 129.3, 128.8, 128.7, 127.4, 126.4, 50.5, 29.0, 12.5; ATR-FTIR (neat): 3025, 2961, 2927, 2872, 1491, 1448, 1090, 1014 cm^{-1}.



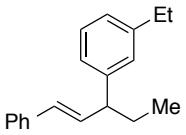
2g

Methyl (*E*)-3-(1-phenylpent-1-en-3-yl)benzoate 2g. The general procedure was followed using 158 mg of homostyrenyl tosylate **1** (0.50 mmol), 270 mg of 3-carbomethoxyphenylboronic acid (1.5 mmol), 490 mg of Cs_2CO_3 (1.5 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. Purification by flash column chromatography (100% hexanes on basic Al_2O_3) afforded **2g** as a colorless oil (58 mg, 41%), R_f = 0.65 (20% EtOAc:hexanes, visualized by 254 nm light). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.96 (t, *J* = 1.7 Hz, 1H), 7.91 (dt, *J* = 7.4, 1.6 Hz, 1H), 7.46 (dt, *J* = 7.7, 1.7 Hz, 1H), 7.42-7.27 (m, 5H), 7.24-7.18 (m, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.34 (dd, *J* = 15.8, 7.2 Hz, 1H), 3.92 (s, 3H), 3.39 (q, *J* = 7.3 Hz, 1H), 1.93-1.82 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 167.5, 145.2, 137.6, 133.8, 132.7, 130.6, 130.2, 129.0, 128.8, 128.7, 127.8, 127.4, 126.4, 52.4, 51.1, 29.0, 12.5; ATR-FTIR (neat): 3025, 2958, 2928, 2872, 1718, 1600, 1587, 1494, 1444, 1432, 1276, 1194, 1107 cm^{-1}; HRMS (ESI-TOF) m / z calculated for $C_{19}H_{20}O_2Na$ $[M+Na]^+$: 303.1361, found 303.1360.



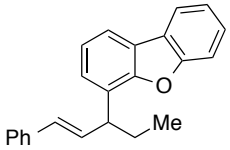
2h

(*E*)-1-Methoxy-3-(1-phenylpent-1-en-3-yl)benzene 2h. The general procedure was followed using 158 mg of homostyrenyl tosylate **1** (0.50 mmol), 230 mg of 3-methoxyphenylboronic acid (1.5 mmol), 490 mg of Cs_2CO_3 (1.5 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. Purification by flash column chromatography (0:100 → 30:70 benzene:hexanes) afforded **2h** as a colorless oil (78 mg, 62%), R_f = 0.30 (20% benzene:hexanes, visualized by 254 nm light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40-7.38 (m, 2H), 7.31 (t, *J* = 7.0 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.24-7.21 (m, 1H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.85 (t, *J* = 2.0 Hz, 1H), 6.79 (dd, *J* = 8.2, 2.6 Hz, 1H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.36 (dd, *J* = 15.8, 7.7 Hz, 1H), 3.84 (s, 3H), 3.32 (q, *J* = 7.5 Hz, 1H), 1.91-1.81 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 160.0, 146.9, 137.8, 134.3, 129.8, 129.7, 128.7, 127.3, 126.4, 120.4, 113.9, 111.4, 55.4, 51.3, 29.0, 12.6; ATR-FTIR (neat): 3024, 2958, 2929, 2871, 2833, 1598, 1583, 1485, 1450, 1435, 1257, 1152, 1044 cm^{-1}; HRMS (API-TOF) m / z calculated for $C_{18}H_{21}O$ $[M+H]^+$: 253.1592, found 253.1594.



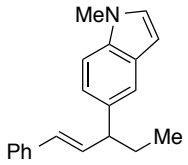
2i

(*E*)-1-Ethyl-3-(1-phenylpent-1-en-3-yl)benzene 2i. The general procedure was followed using 158 mg of homostyrenyl tosylate **1** (0.50 mmol), 230 mg of 3-ethylboronic acid (1.5 mmol), 490 mg of Cs_2CO_3 (1.5 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. Purification by flash column chromatography (100% hexanes on activated basic Al_2O_3) afforded **2i** as a colorless oil (95 mg, 76%), R_f = 0.34 (hexanes, visualized by 254 nm light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.37 (d, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.26-7.23 (m, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.10-7.04 (m, 3H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.35 (dd, *J* = 15.8, 7.7 Hz, 1H), 3.30 (q, *J* = 7.5 Hz, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.90-1.79 (m, 2H), 1.27-1.24 (t, *J* = 7.5 Hz, 3H), 0.92 (q, *J* = 7.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.5, 144.4, 137.7, 134.3, 129.3, 128.4, 128.3, 127.3, 126.9, 126.1, 125.6, 124.9, 51.0, 28.9, 28.8, 15.6, 12.3; ATR-FTIR (neat): 3024, 2962, 2928, 2871, 1602, 1493, 1448, 1376 cm^{-1}; HRMS (ESI-TOF) m / z calculated for $C_{19}H_{22}Ag$ $[M+Ag]^+$: 357.0772, found 357.0768.



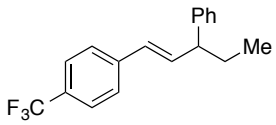
2j

(*E*)-4-(1-Phenylpent-1-en-3-yl)dibenzo[b,d]furan 2j. The general procedure was followed using 158 mg of homostyrenyl tosylate **1** (0.50 mmol), 318 mg of dibenzofuran-4-boronic acid (1.5 mmol), 490 mg of Cs_2CO_3 (1.5 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. Purification by flash column chromatography (hexanes) afforded **2j** as a slightly yellow oil (77 mg, 49%), R_f = 0.21 (20:80 benzene:hexanes, visualized by 254 nm light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.94 (d, *J* = 7.6 Hz, 1H), 7.80 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.47-7.42 (m, 1H), 7.37-7.23 (m, 7H), 7.19-7.15 (m, 1H), 6.58 (dd, *J* = 15.8, 7.0 Hz, 1H), 6.52 (d, *J* = 15.8 Hz, 1H), 3.98 (q, *J* = 7.3 Hz, 1H), 2.11-2.03 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 169.0, 156.0, 154.3, 137.6, 132.7, 130.1, 128.4, 127.0, 126.9, 126.2, 125.7, 124.6, 124.2, 122.9, 122.5, 120.6, 118.4, 111.7, 45.7, 28.1, 12.4; ATR-FTIR (neat): 3025, 2960, 2926, 2871, 1493, 1449, 1421, 1181 cm^{-1}; HRMS (ESI-TOF) m / z calculated for $C_{23}H_{20}OAg$ $[M+Ag]^+$: 419.0565, found 419.0582. Note: a small amount of 2,2'-bidibenzofuran (m.w. = 334.1g/mol) coeluted with the product and is present in the NMR spectra for this compound.



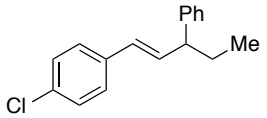
2k

(*E*)-1-Methyl-5-(1-phenylpent-1-en-3-yl)-1H-indole 2k. The general procedure was followed using 158 mg of homostyrenyl tosylate **1** (0.50 mmol), 260 mg of *N*-methylindole-5-boronic acid (1.5 mmol), 490 mg of Cs_2CO_3 (1.5 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. Purification by flash column chromatography (0:100 → 30:70 benzene:hexanes) afforded **2k** as a colorless oil (83 mg, 60%), R_f = 0.22 (20% benzene:hexanes, visualized by 254 nm light). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.60 (s, 1H), 7.45-7.42 (m, 2H), 7.38-7.33 (m, 3H), 7.28-7.20 (m, 2H), 7.08 (d, *J* = 3.1 Hz, 1H), 6.54-6.51 (m, 3H), 3.81 (s, 3H), 3.52-3.49 (m, 1H), 2.05-1.94 (m, 2H), 1.03 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 138.2, 135.9, 135.8, 135.6, 129.3, 129.0, 128.7, 128.6, 127.1, 126.4, 122.1, 119.7, 109.5, 101.0, 51.3, 33.1, 29.4, 12.8; ATR-FTIR (thin film): 3022, 2957, 2923, 2870, 1512, 1489, 1446, 1421, 1334, 1301, 1244, 1155, 1078 cm^{-1}; HRMS (API-TOF) m / z calculated for $C_{20}H_{22}N$ $[M+H]^+$: 276.1752, found 276.1755.



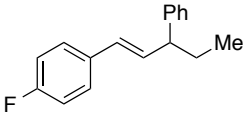
6a

(*E*)-1-(3-Phenylpent-1-en-1-yl)-4-(trifluoromethyl)benzene 6a. The general procedure was followed using 192 mg of *p*-(trifluoromethyl)homostyrenyl tosylate **5a** (0.50 mmol), 187 mg of phenylboronic acid (1.5 mmol), 490 mg of Cs_2CO_3 (1.5 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. Purification by flash column chromatography (hexanes) afforded **6a** as a colorless oil (70 mg, 48%), R_f = 0.38 (hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.37-7.29 (m, 2H), 7.28-7.19 (m, 3H), 6.50-6.38 (m, 2H), 3.33 (q, *J* = 5.7 Hz, 1H), 1.91-1.80 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.1, 141.2, 137.2, 129.0 (q, $J_{C–F}$ = 32.3 Hz), 128.7, 128.4, 127.8, 126.6, 126.4, 125.6 (q, $J_{C–F}$ = 3.8 Hz), 124.4 (q, $J_{C–F}$ = 270 Hz), 51.2, 28.8, 12.4; ^{19}F NMR ($CDCl_3$, 282 MHz) δ –62.82; ATR-FTIR (neat): 3028, 2963, 2930, 2874, 1614, 1493, 1452, 1414, 1321, 1162, 1118, 1106, 1065, 1015; HRMS (ESI-TOF) *m* / *z* calculated for $C_{18}H_{17}F_3Ag$ $[M+Ag]^+$: 397.0333, found 397.0366.



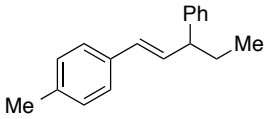
6b

(*E*)-1-Chloro-4-(3-phenylpent-1-en-1-yl)benzene 6b. The general procedure was followed using 175 mg of *p*-chlorohomostyrenyl tosylate **5b** (0.50 mmol), 183 mg of phenylboronic acid (1.5 mmol), 490 mg of Cs_2CO_3 (1.5 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. Purification by flash column chromatography (hexanes on activated basic Al_2O_3) afforded **6b** as a colorless oil (65 mg, 51%), R_f = 0.29 (hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.34-7.27 (m, 2H), 7.27-7.17 (m, 7H), 6.34 (d, *J* = 15.6 Hz, 1H), 6.29 (dd, *J* = 16.0, 6.4 Hz, 1H), 3.29 (q, *J* = 6.4 Hz, 1H), 1.87-1.76 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.4, 136.3, 135.2, 132.7, 128.8, 128.7, 128.4, 127.8, 127.5, 126.5, 51.2, 28.9, 12.5; ATR-FTIR (neat): 3026, 2960, 2927, 2872, 1600, 1489, 1451, 1403, 1090, 1012 cm^{-1}; HRMS (ESI-TOF) *m* / *z* calculated for $C_{17}H_{17}ClAg$ [M+Ag]$^+$: 363.0070, found 363.0083.



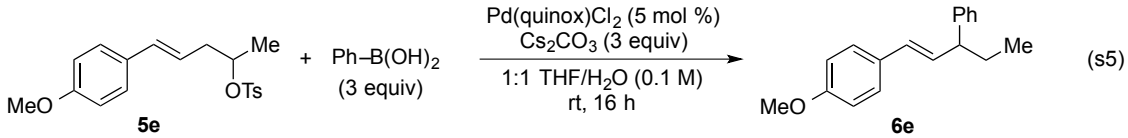
6c

(*E*)-1-Fluoro-4-(3-phenylpent-1-en-1-yl)benzene 6c. The general procedure was followed using 167 mg of *p*-fluorohomostyrenyl tosylate **5c** (0.50 mmol), 183 mg of phenylboronic acid (1.5 mmol), 490 mg of Cs_2CO_3 (1.5 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. Purification by flash column chromatography (hexanes on SiO_2) afforded **6c** as a colorless oil (50 mg, 42%), R_f = 0.16 (hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.37-7.20 (m, 7H), 7.02-6.94 (m, 2H), 6.38 (d, *J* = 15.9 Hz, 1H), 6.26 (dd, *J* = 15.8, 7.5 Hz, 1H), 3.32 (q, *J* = 7.4 Hz, 1H), 1.91-1.79 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.2 (d, $J_{C–F}$ = 244 Hz), 144.6, 134.2 (d, $J_{C–F}$ = 2.4 Hz), 134.0 (d, $J_{C–F}$ = 3.4 Hz), 128.7, 128.5, 127.9, 127.8 (d, $J_{C–F}$ = 8.0 Hz), 126.5, 115.5 (d, $J_{C–F}$ = 21.3 Hz), 51.2, 21.0, 12.5; ^{19}F NMR ($CDCl_3$, 282 MHz) δ –115.9; ATR-FTIR (neat): 3026, 2961, 2927, 2872, 1601, 1507, 1451, 1224, 1157, 1094 cm^{-1}; HRMS (ESI-TOF) *m* / *z* calculated for $C_{17}H_{17}FAg$ [M+Ag]$^+$: 347.0365, found 347.0368.



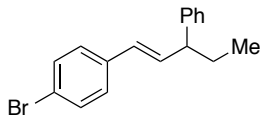
6d

(*E*)-1-Methyl-4-(3-phenylpent-1-en-1-yl)benzene 6d. The general procedure was followed using 165 mg of *p*-methylhomostyrenyl tosylate **5d** (0.50 mmol), 183 mg of phenylboronic acid (1.5 mmol), 490 mg of Cs_2CO_3 (1.5 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. Purification by flash column chromatography (hexanes on SiO_2) afforded **6d** as a colorless oil (47 mg, 40%), R_f = 0.11 (hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.37-7.19 (m, 7H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.31 (dd, J = 15.8, 7.3 Hz, 1H), 3.33 (q, *J* = 7.5 Hz, 1H), 2.35 (s, 3H), 1.93-1.80 (m, 2H), 0.95 (t, *J* = 8.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.9, 137.0, 135.1, 133.4, 129.5, 129.4, 128.7, 127.9, 126.4, 126.3, 51.2, 29.1, 21.4, 12.5; ATR-FTIR (neat): 3024, 2959, 2923, 2871, 1600, 1512, 1492, 1451, 1377, 1029 cm^{-1}; HRMS (ESI-TOF) *m* / *z* calculated for $C_{18}H_{20}Ag$ [M+Ag]$^+$: 343.0616, found 343.0622.



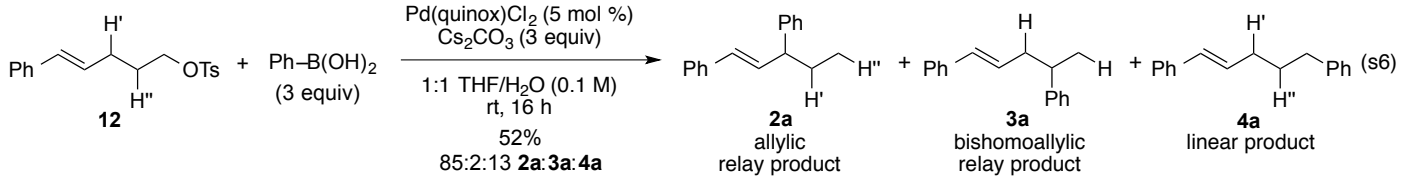
(*E*)-1-Methoxy-4-(3-phenylpent-1-en-1-yl)benzene 6e. The general procedure was followed using 82 mg of homostyrenyl tosylate **5e** (0.24 mmol), 87 mg of phenylboronic acid (0.71 mmol), 232 mg of Cs_2CO_3 (0.71 mmol), and 5 mg of Pd(quinox)Cl_2 (0.01 mmol) in 1.2 mL each of THF and H_2O. ^{1}H NMR analysis (300 MHz,

$CDCl_3$) using 2-methoxynaphthalene (0.01 mmol) as an *ex situ* internal standard revealed 29% consumption of **5e** and <5% yield of **6e** based on comparison to the spectral data of the aforementioned relay cross-coupling products. Selected physical data for **6e**: R_f = 0.27 (hexanes, visualized by 254 nm light). Selected spectral data for **6e**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.30 (q, *J* = 7.5 Hz, 1H) 0.94 (t, *J* = 7.5 Hz, 3H).

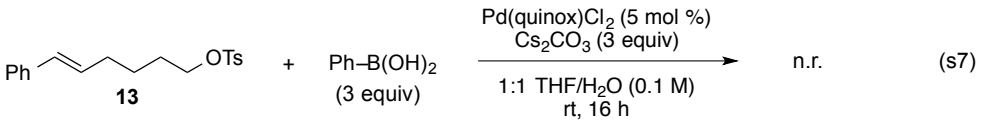


6f

(*E*)-1-Bromo-4-(3-phenylpent-1-en-1-yl)benzene 6f. The general procedure was followed using 198 mg of *p*-bromohomostyrenyl tosylate **5f** (0.50 mmol), 183 mg of phenylboronic acid (1.5 mmol), 490 mg of Cs_2CO_3 (1.5 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. Purification by flash column chromatography (hexanes on SiO_2) afforded **6f** as a colorless oil (30 mg, 20%), R_f = 0.15 (hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.24-7.19 (m, 5H), 6.34 (d, *J* = 16.0 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 3.34-3.26 (m, 1H), 1.87-1.79 (m, 2H), 0.92 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.3, 136.7, 135.3, 131.7, 128.7, 128.5, 127.8 (2C), 126.5, 120.8, 51.1, 26.7, 12.4; ATR-FTIR (thin film): 3025, 2959, 2924, 2871, 1486, 1451, 1377, 1072, 1008 cm^{-1}; HRMS (ESI-TOF) *m / z* calculated for $C_{17}H_{17}BrAg$ $[M+Ag]^+$: 406.9565, found 406.9555.

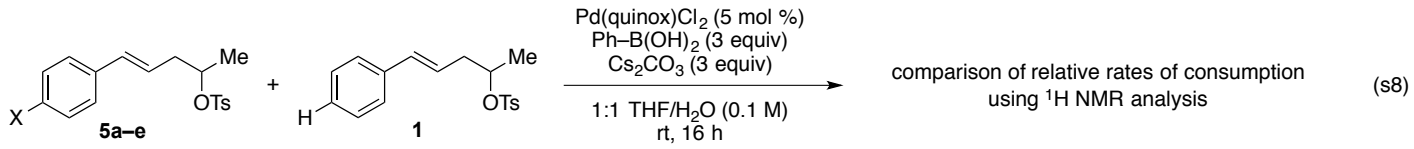


The general procedure was followed using 158 mg of bis-homostyrenyl tosylate **5** (0.50 mmol), 183 mg of phenylboronic acid (1.5 mmol), 490 mg of Cs_2CO_3 (1.5 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. ^{1}H NMR analysis (400 MHz, $CDCl_3$) using CH_2Br_2 (0.1 mmol) as an *ex situ* internal standard revealed a 52% yield of products **2a, 3a**, and **4a** in a ratio of 85:2:13. Product **2a** was quantified by comparison to the spectral data reported above using the peak at 3.35 ppm (q, *J* = 7.2 Hz, 1H). Product **3a** was assigned and quantified based on the benzylic signal at 3.00 ppm (sextet, *J* = 6.4 Hz, 2H). Product **4a** was assigned and quantified based on the report of Tarasov and coworkers using the benzylic signal at 2.72 ppm (t, *J* = 7.6 Hz, 2H).[4]



The general procedure was followed using 165 mg of tosylate **13** (0.50 mmol), 183 mg of phenylboronic acid (1.5 mmol), 490 mg of Cs_2CO_3 (1.5 mmol), and 9 mg of Pd(quinox)Cl_2 (0.03 mmol) in 2.5 mL each of THF and H_2O. ^{1}H NMR analysis (400 MHz, $CDCl_3$) using CH_2Br_2 (0.1 mmol) as an *ex situ* internal standard revealed no consumption of **13** based on the integration of the tosylate methyl peak.

IV. Hammett–Relative Rate Correlation Study



Into a dry 4 mL vial equipped with a PTFE-coated stirbar were added 16 mg of tosylate **1** (0.05 mmol, 0.5 equiv) and 0.5 equiv of tosylate **5a**, **5b**, **5c**, **5d**, or **5e** (0.5 equiv), 98 mg of Cs_2CO_3 (0.30 mmol, 3.00 equiv), 37 mg of $PhB(OH)_2$ (0.30 mmol, 3.00 equiv), and 2 mg of $Pd(quinox)Cl_2$ (0.005 mmol, 5 mol %). The vial was capped with a septum, an N_2 line was added, and the vial was flushed with N_2 for approximately 3 min. To the solids were then added 0.5 mL of THF and 0.5 mL of H_2O simultaneously, and the mixture was stirred vigorously for 16 h. The reaction was then filtered through a plug of silica gel using EtOAc, concentrated *in vacuo*, and the residue fully taken up in 0.75 mL of a $1x10^{-5}$ M solution of 2-methoxynaphthalene in $CDCl_3$ for analysis by ^1H NMR spectroscopy. **Note:** 2-methoxynaphthalene solution in $CDCl_3$ was stored in the freezer when not in use.

V. References

1. B. J. Stokes, S. M. Opra and M. S. Sigman. *J. Am. Chem. Soc.* 2012, **134**, 11408.
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3. W. Liu, P. J. Nichols and N. Smith. *Tetrahedron Lett.* 2009, **50**, 6103.
4. V. F. Tarasov, B. B. Kilimenok, D. B. Askerov and A. L. Burchachenko. *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, 1985, 361.

5a

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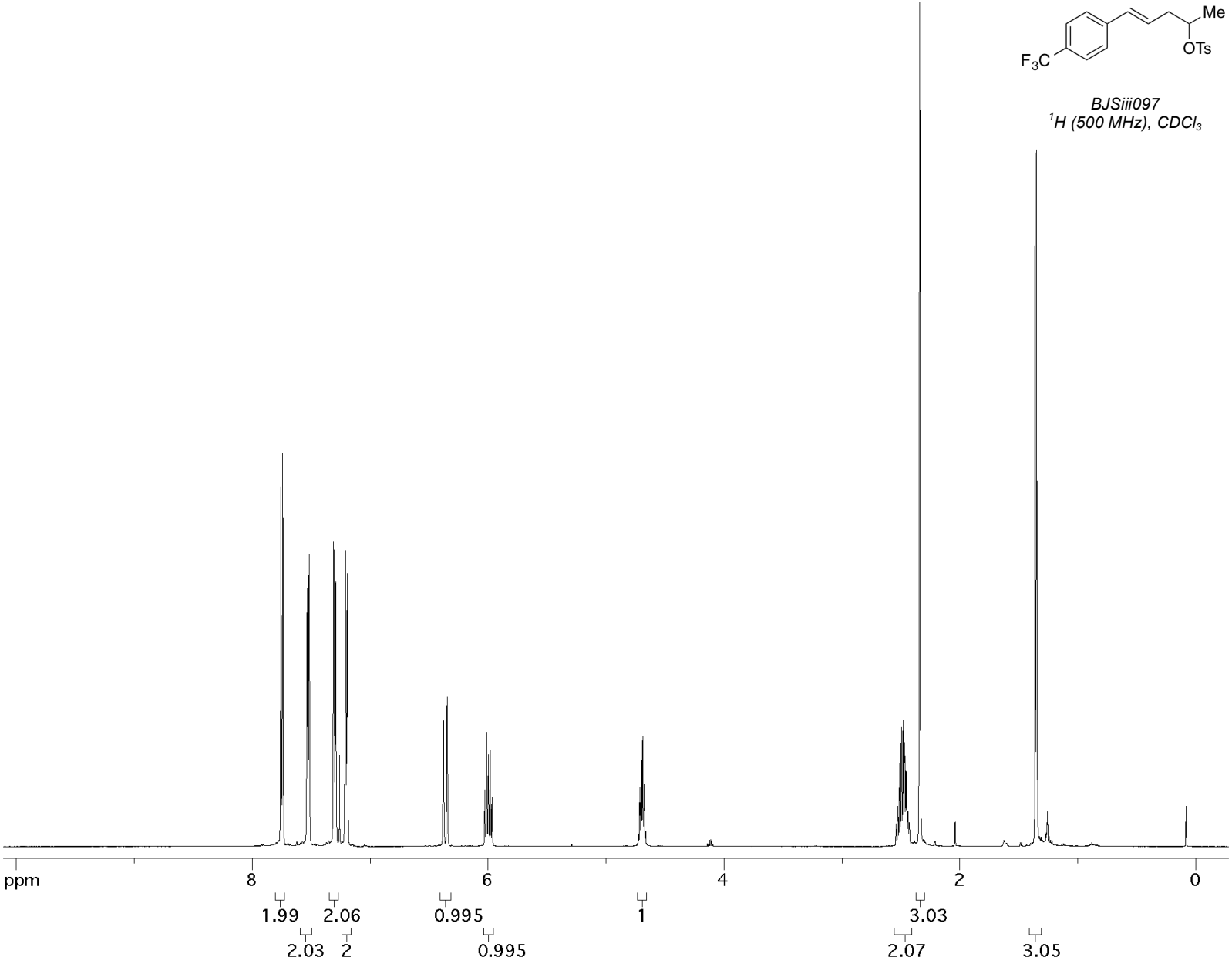
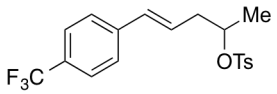
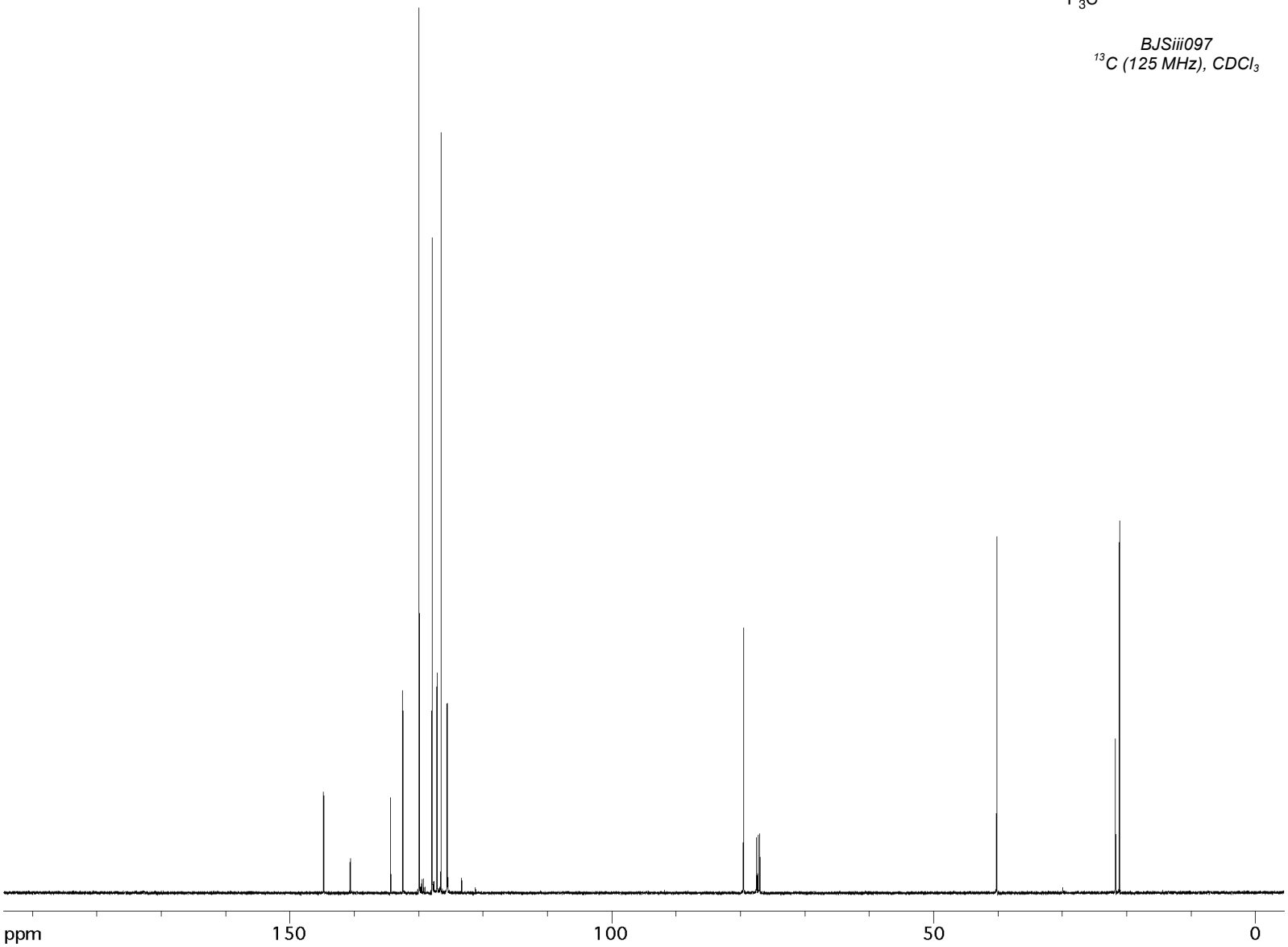
^{1}H (500 MHz), $CDCl_3$



5a

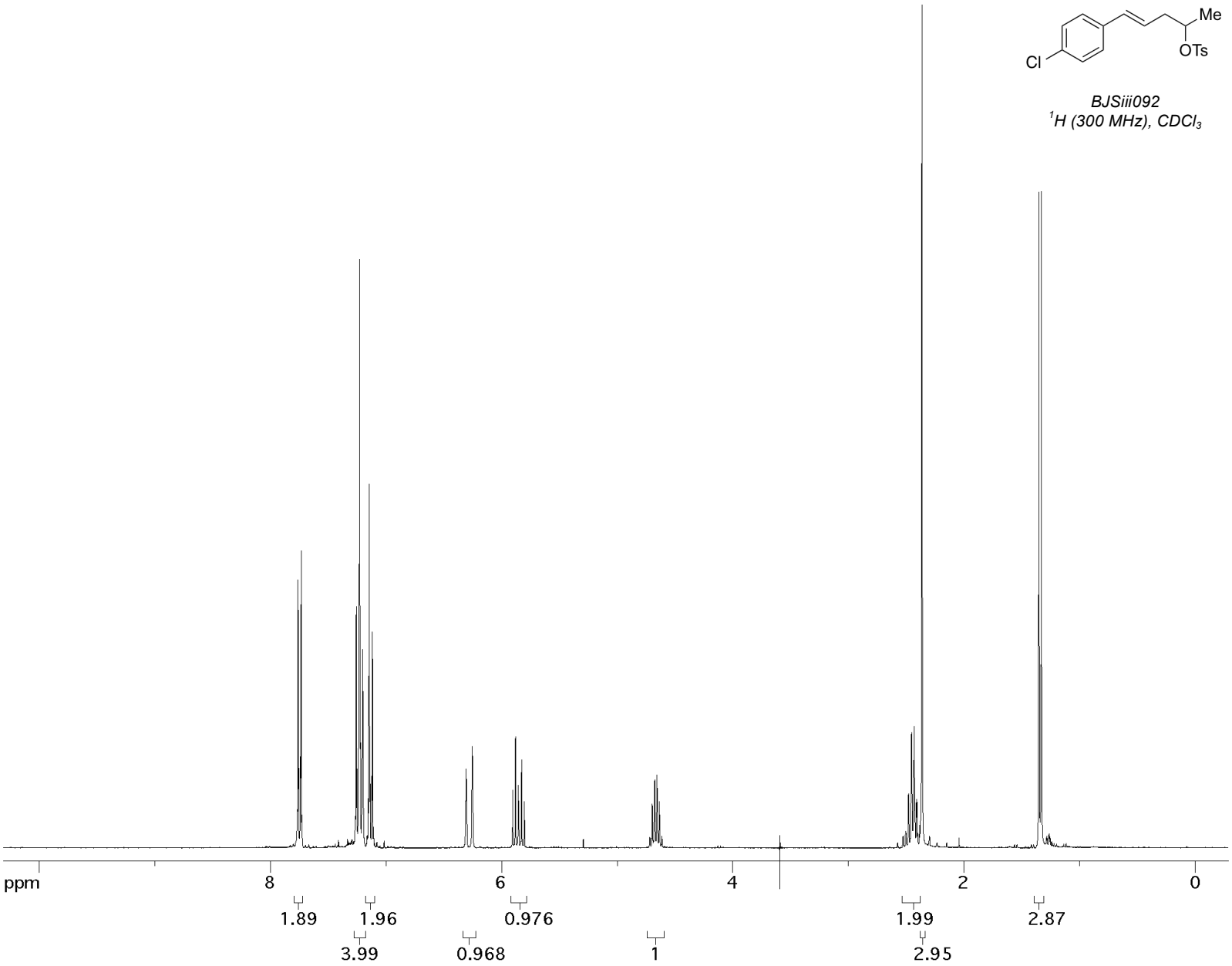


BJSiii097
^{13}C (125 MHz), $CDCl_3$

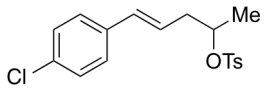


5b

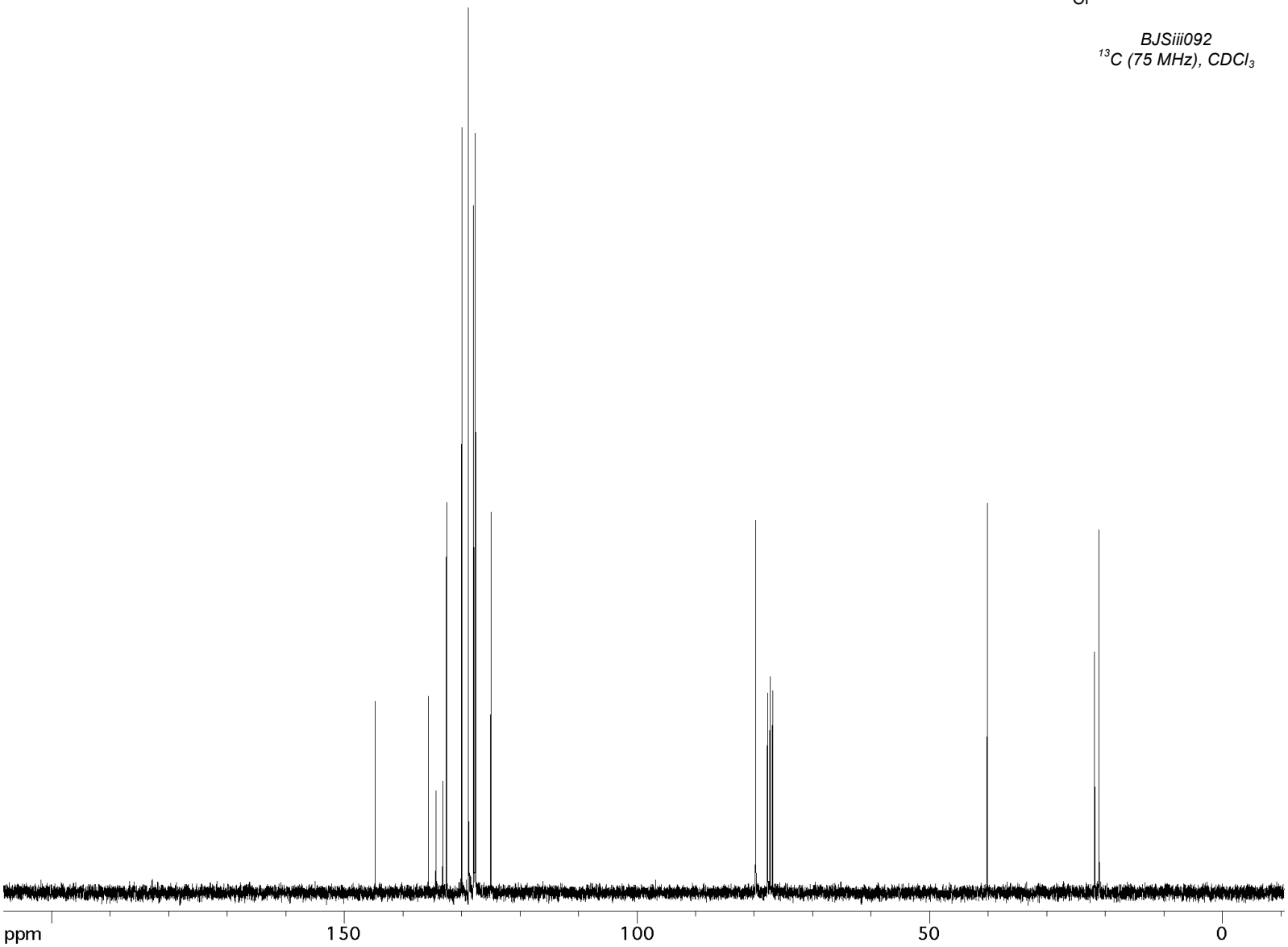
BJSiii092
^{1}H (300 MHz), $CDCl_3$



5b

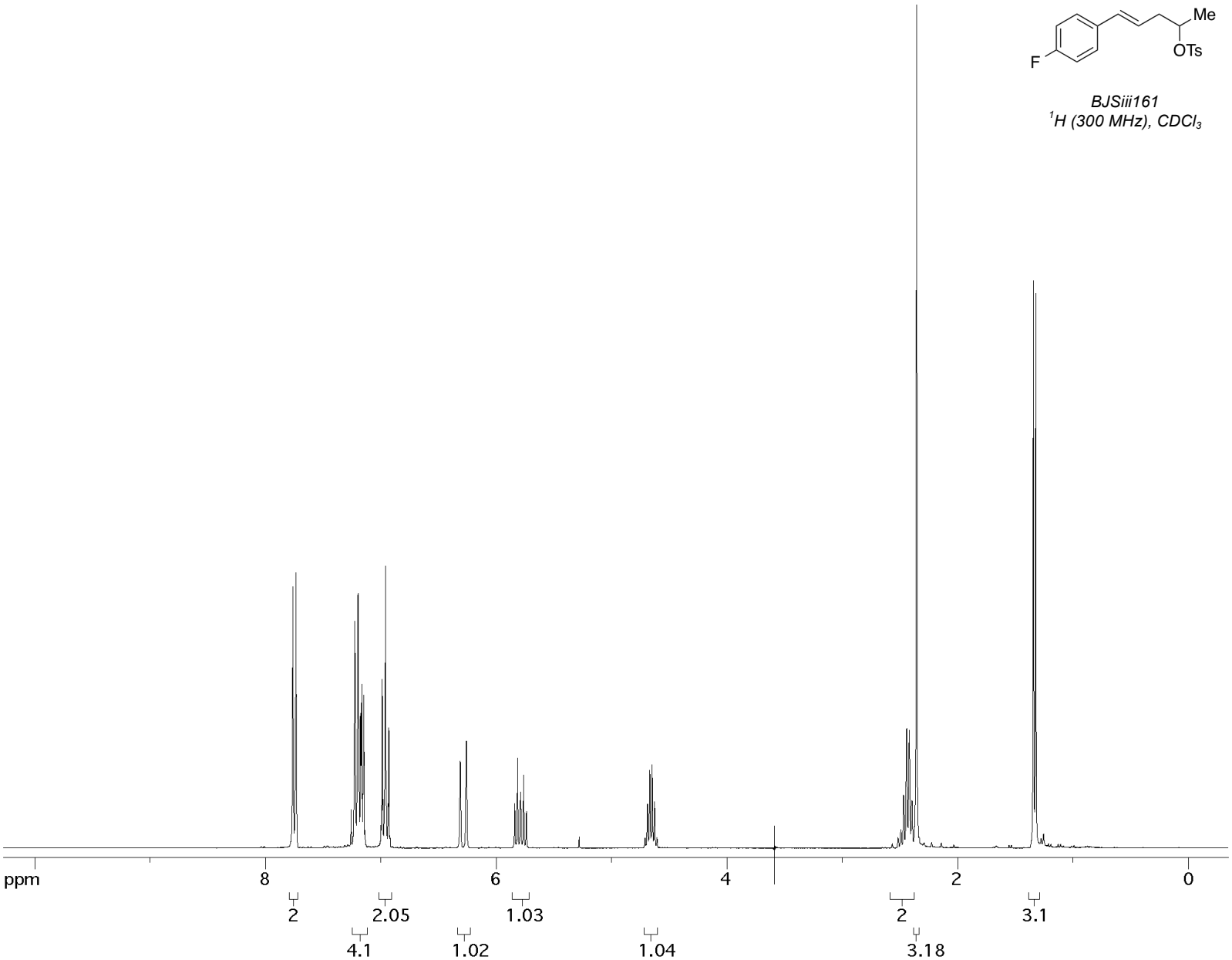


BJSiii092
^{13}C (75 MHz), $CDCl_3$



5c

BJSiii161
^{1}H (300 MHz), $CDCl_3$



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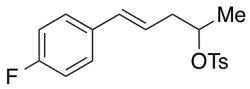
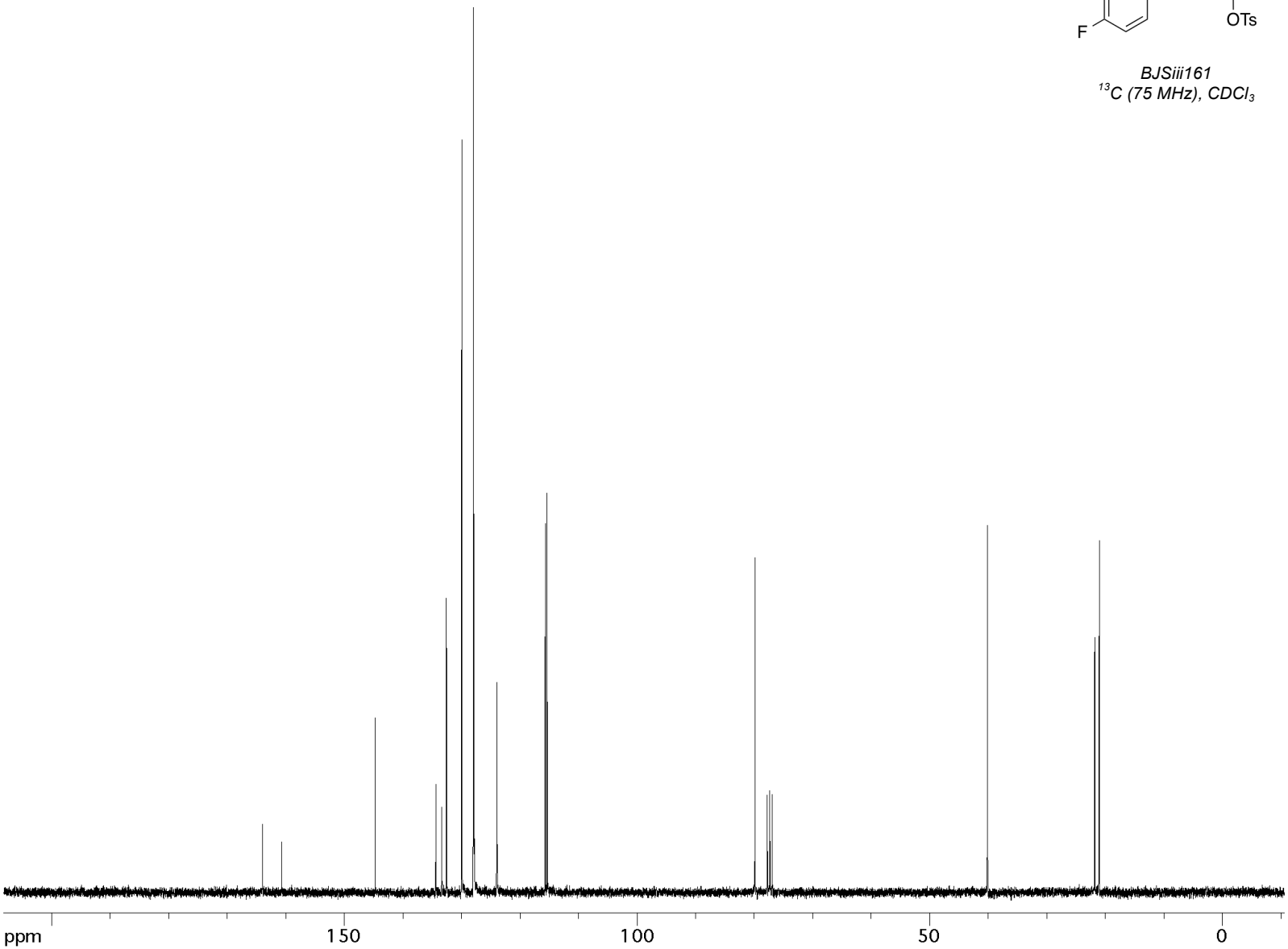
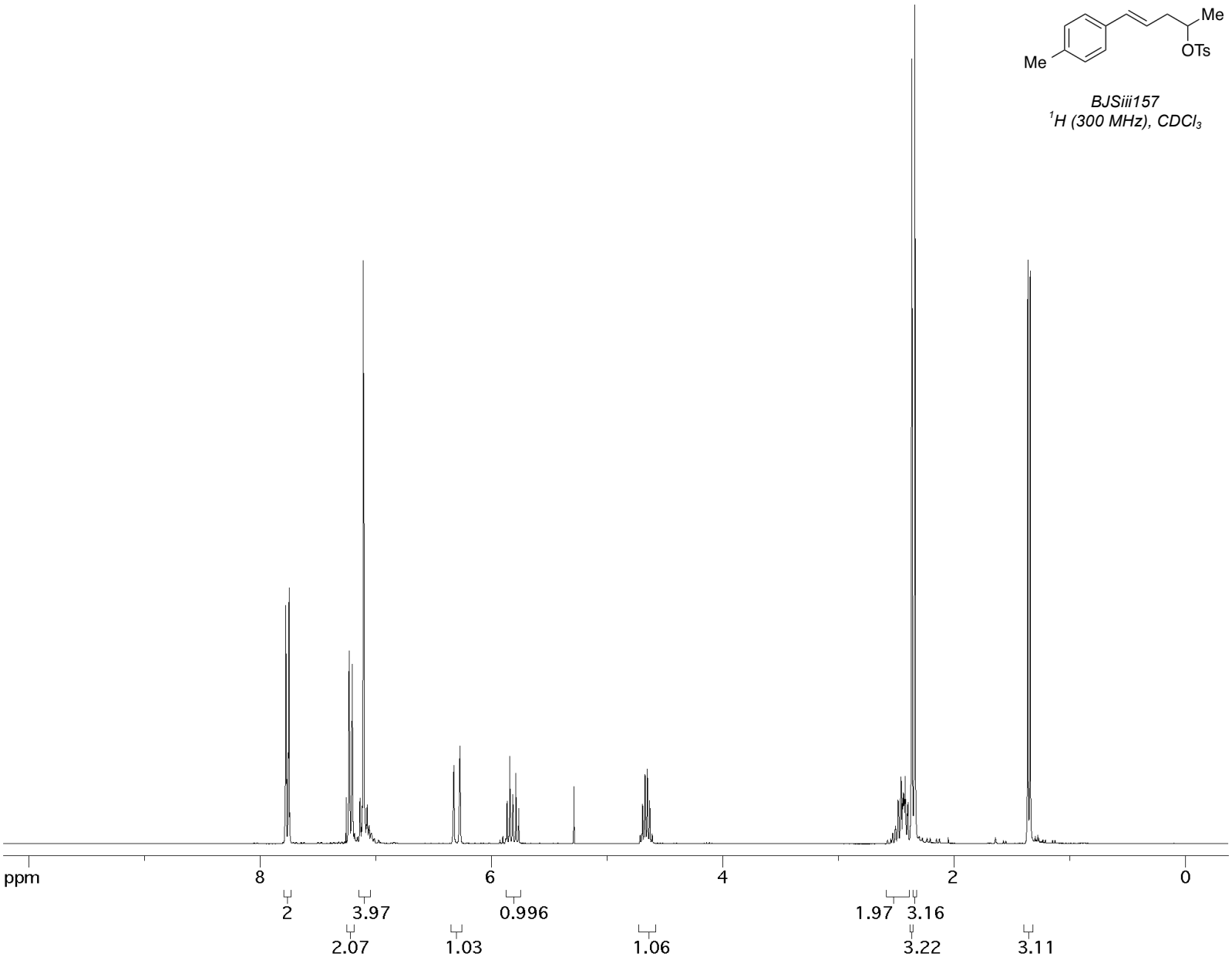


BJSiii161
^{13}C (75 MHz), $CDCl_3$



5d

BJSiii157
^{1}H (300 MHz), $CDCl_3$



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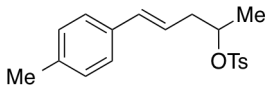
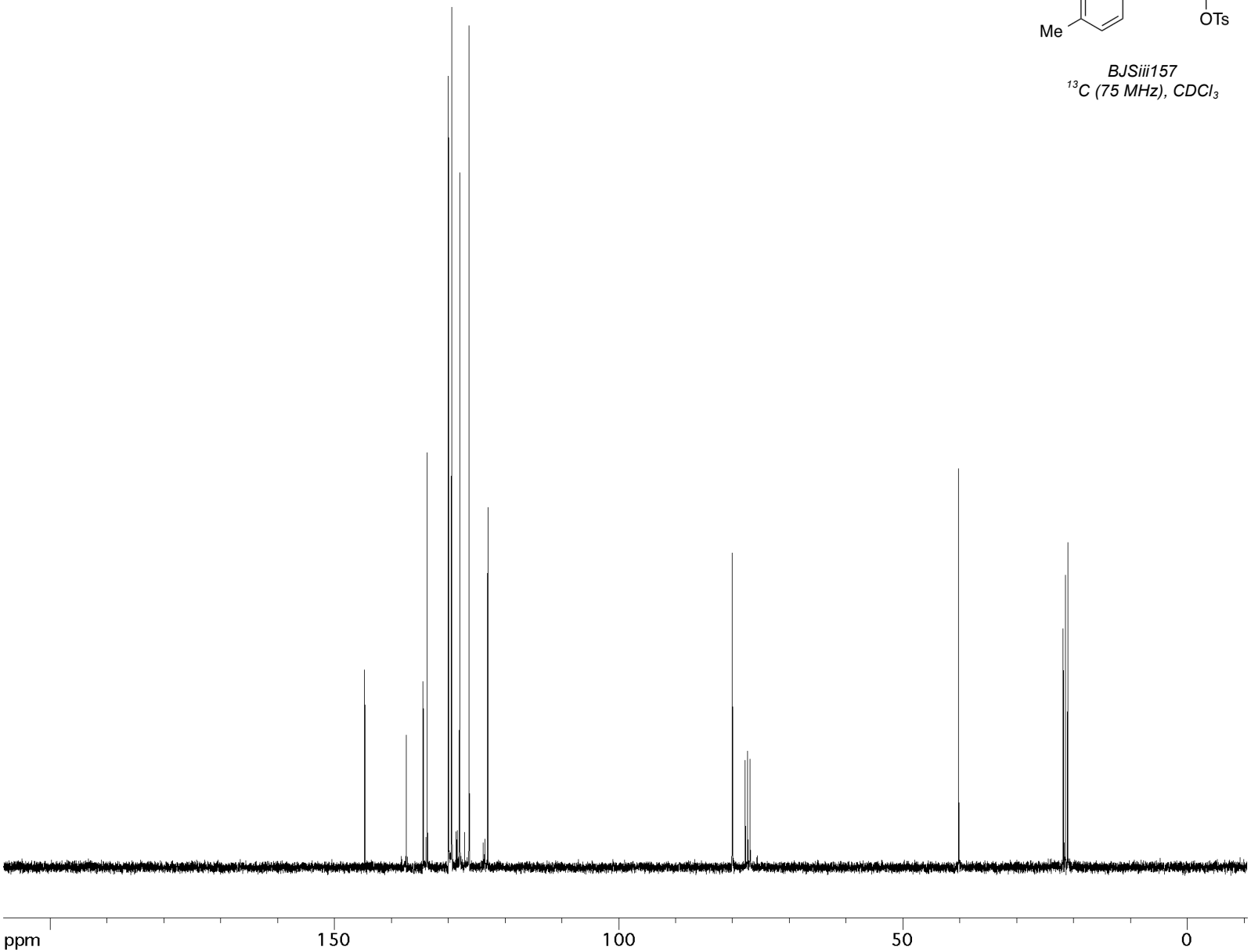
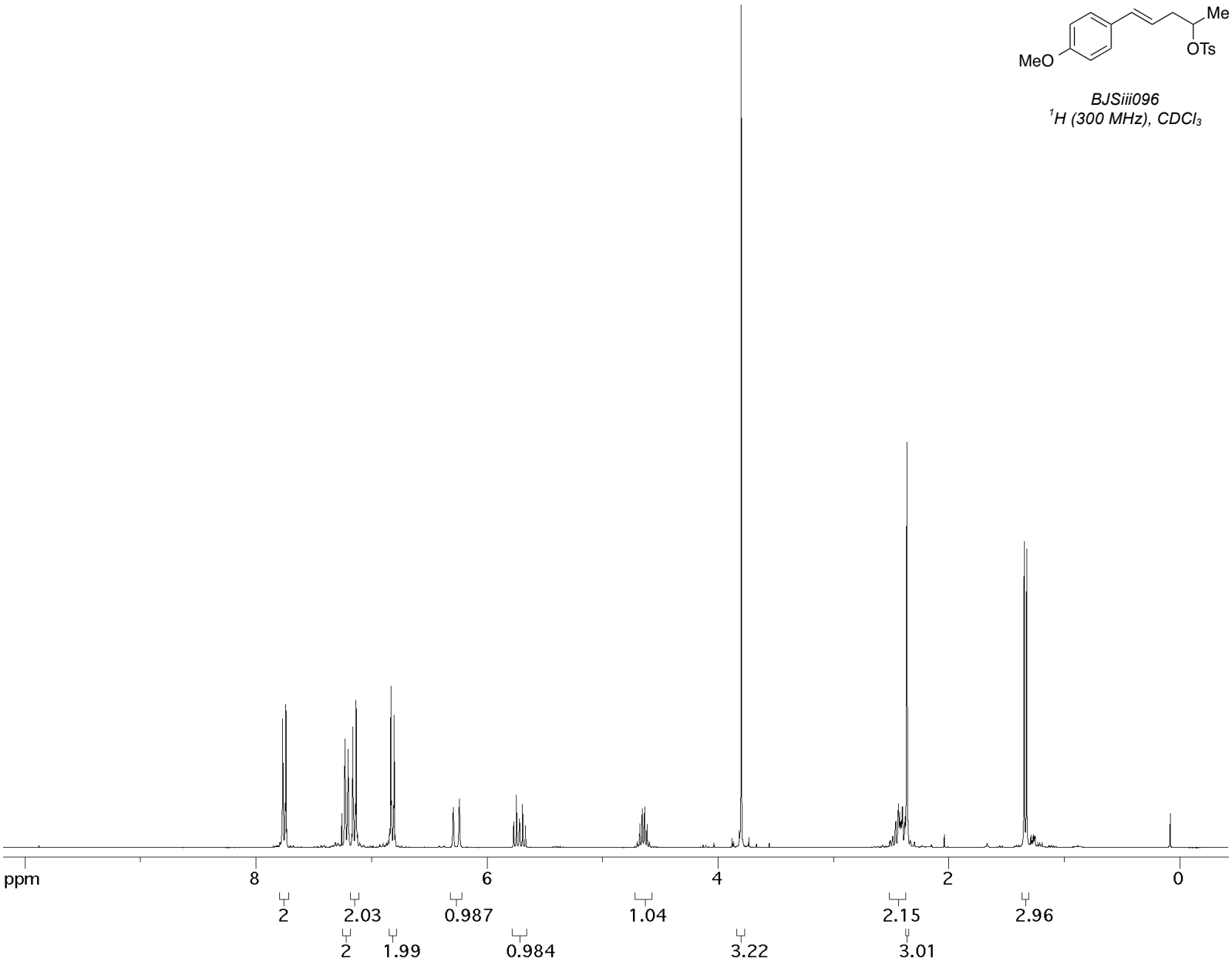


BJSiii157
^{13}C (75 MHz), $CDCl_3$



5e

BJSiii096
^{1}H (300 MHz), $CDCl_3$



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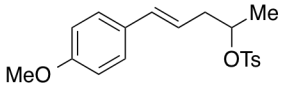

BJSiii096
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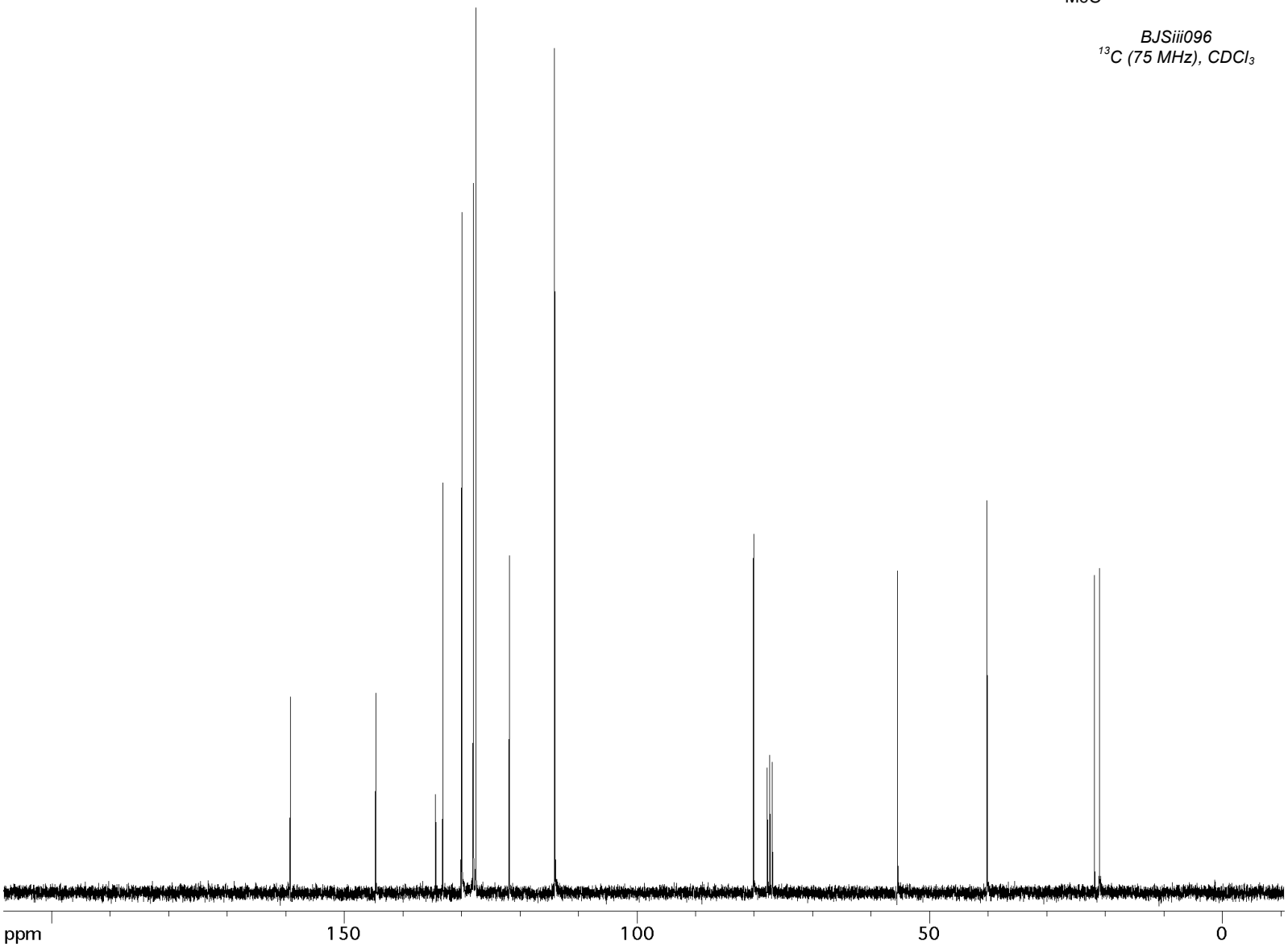
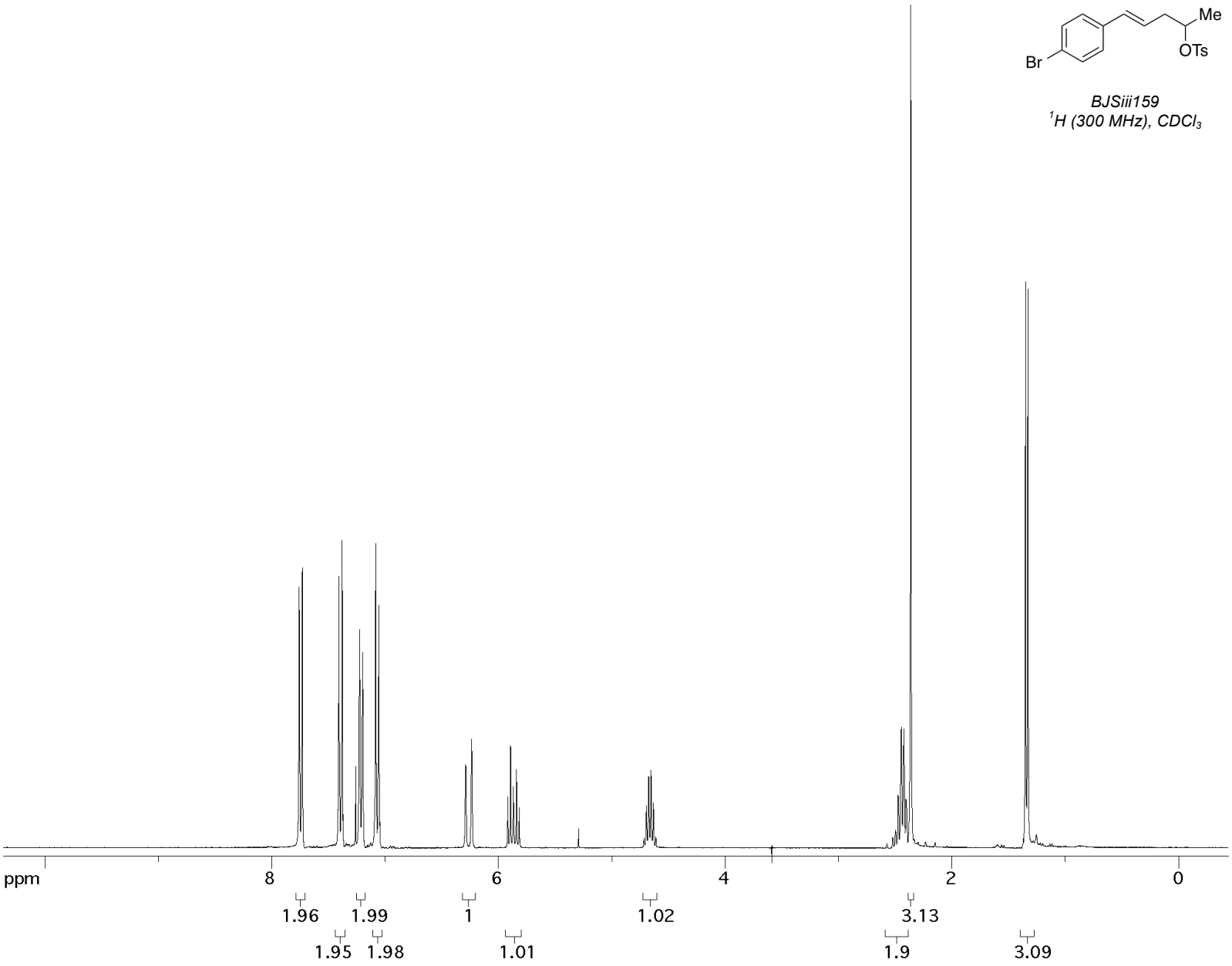


5f

BJSiii159
^{1}H (300 MHz), $CDCl_3$



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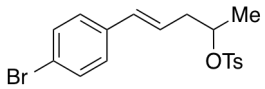
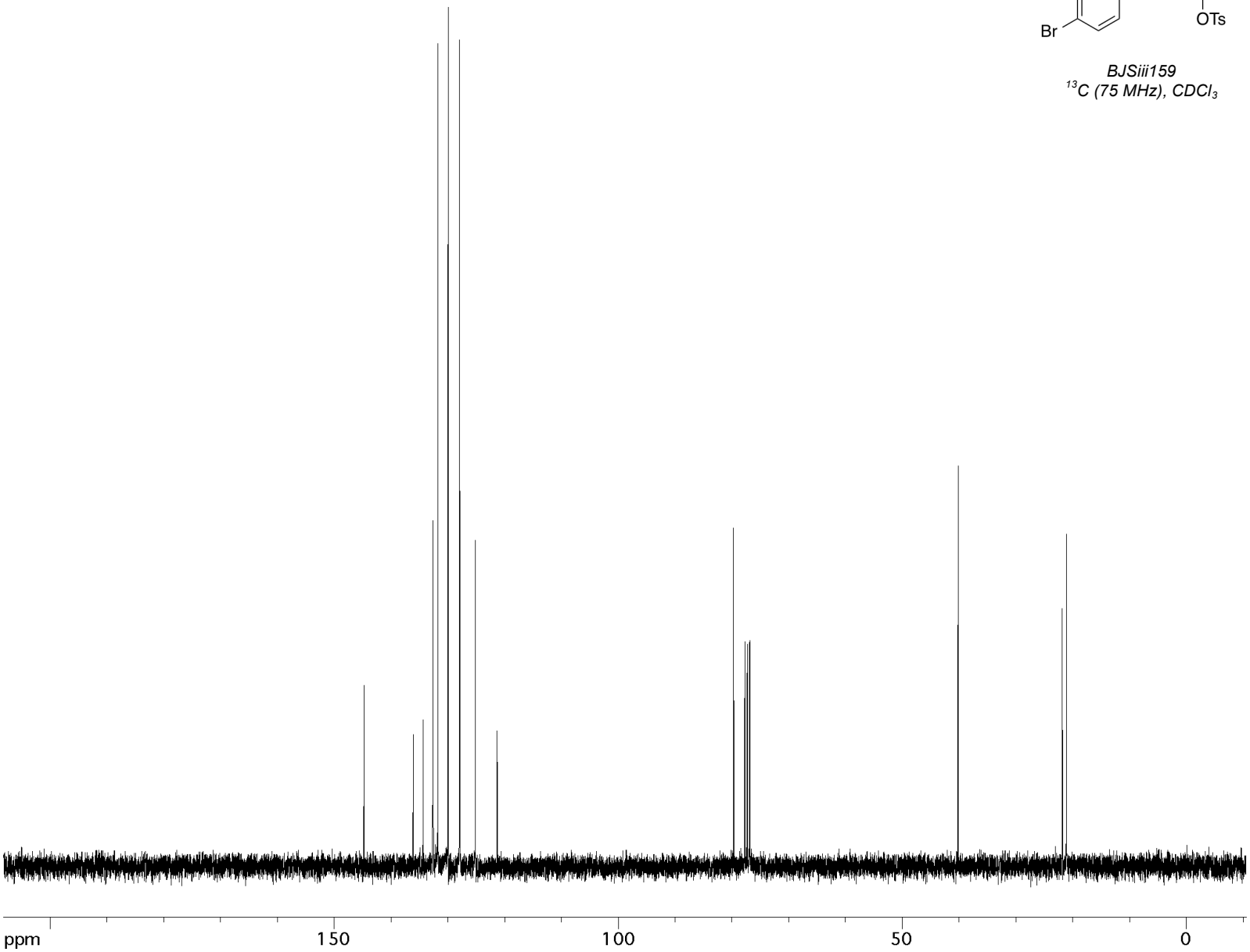
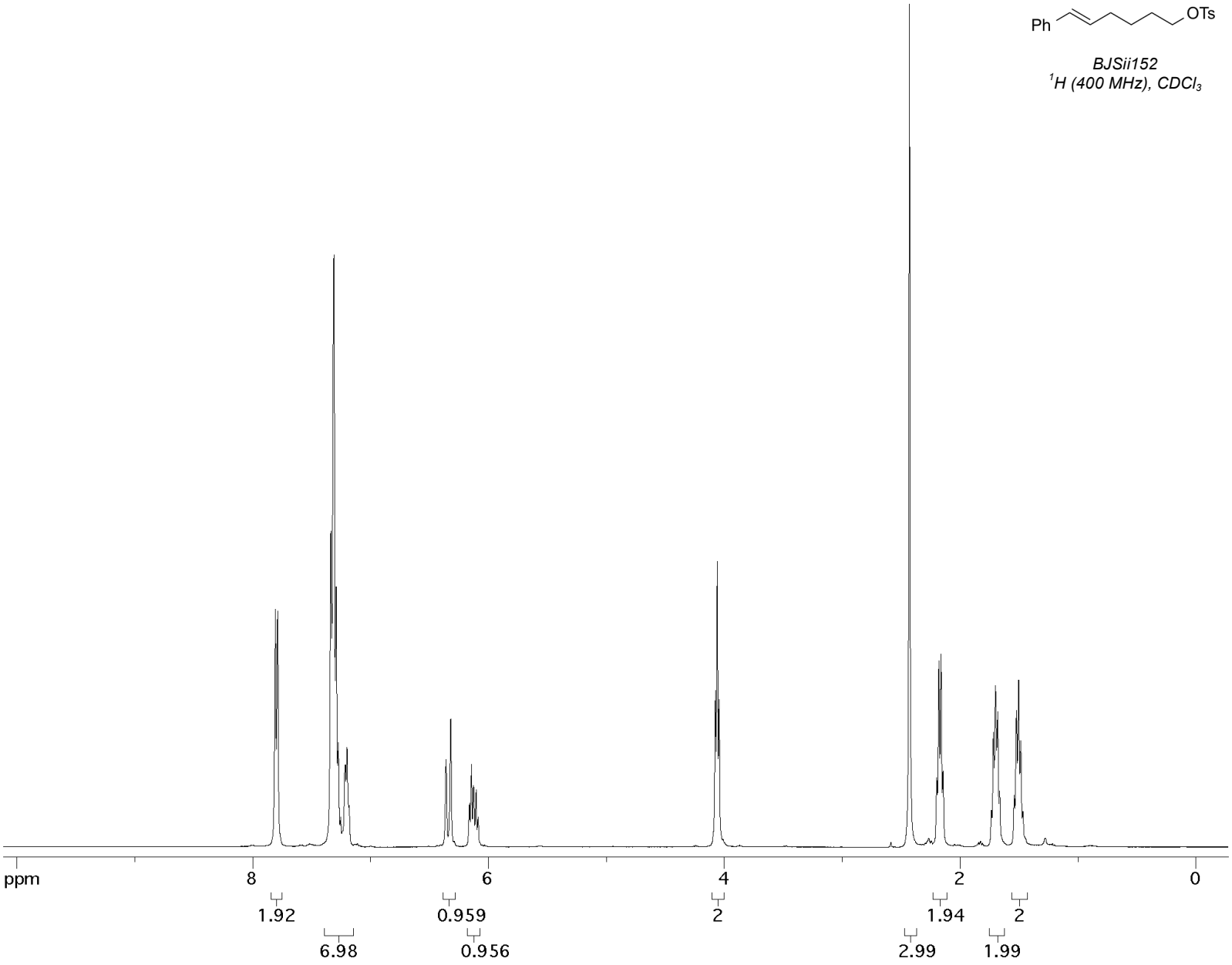


BJSiii159
^{13}C (75 MHz), $CDCl_3$

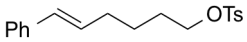


13

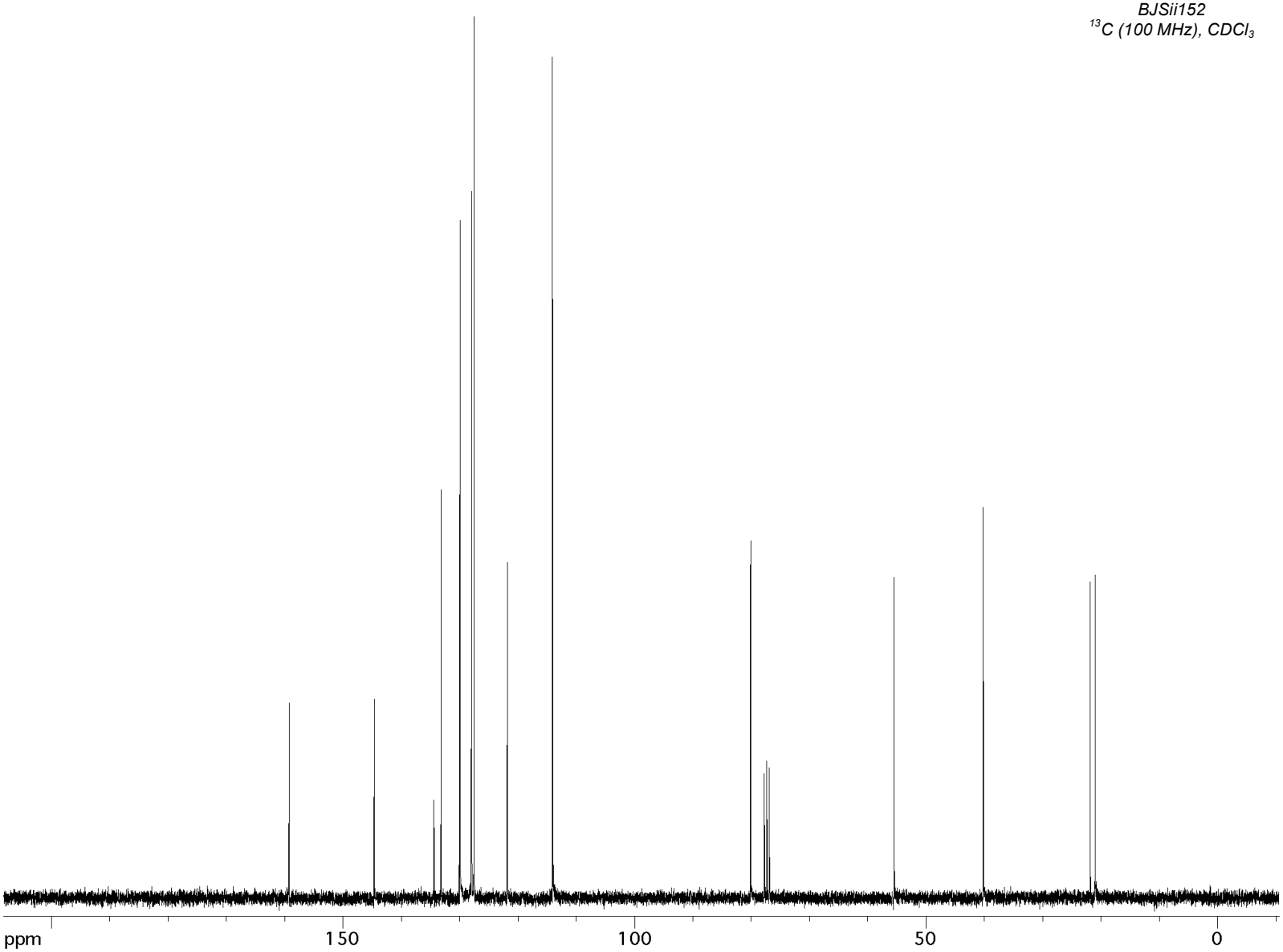
BJSii152
^{1}H (400 MHz), $CDCl_3$



13

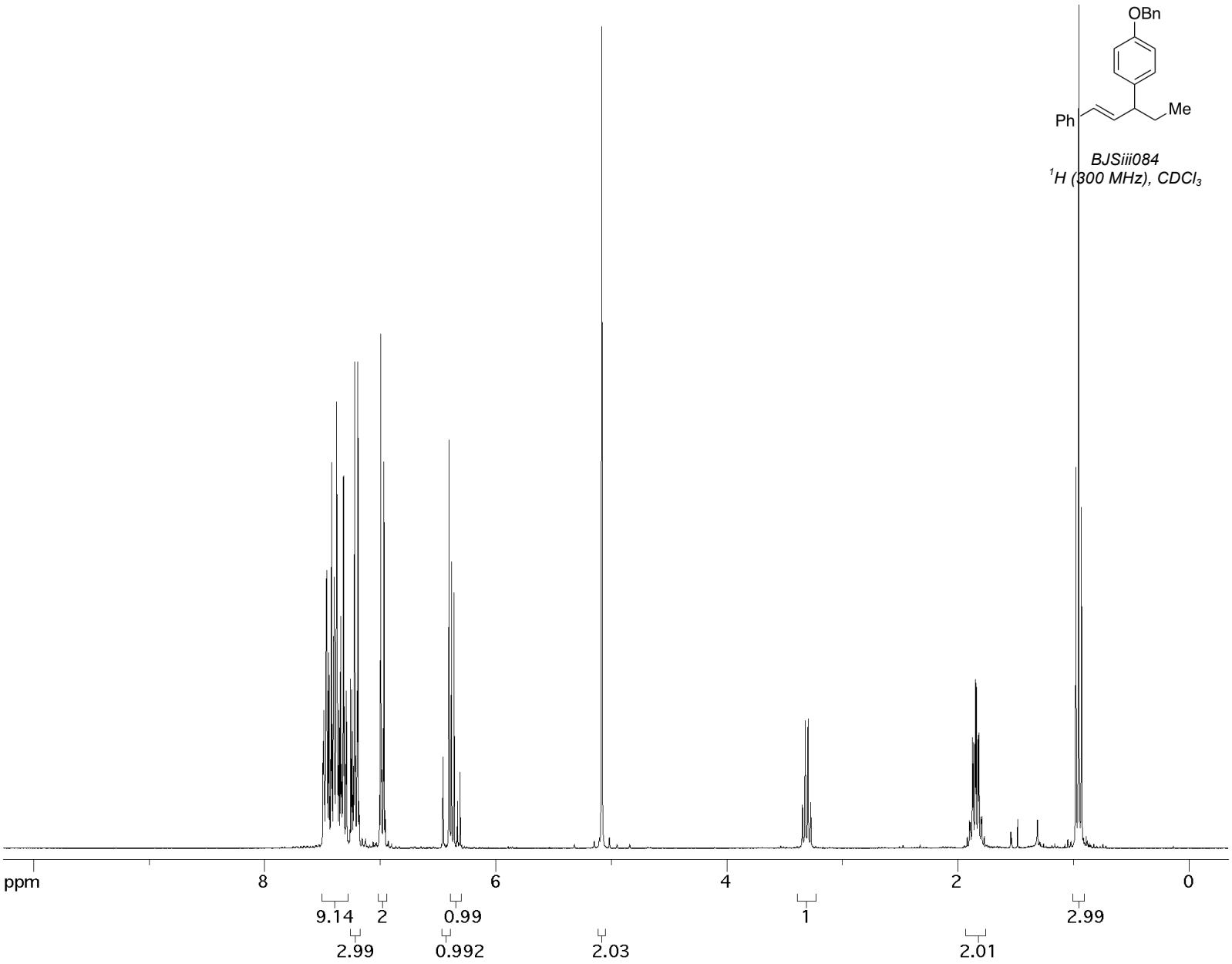


BJSii152
^{13}C (100 MHz), $CDCl_3$

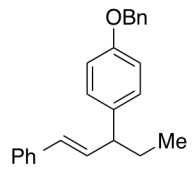


2b

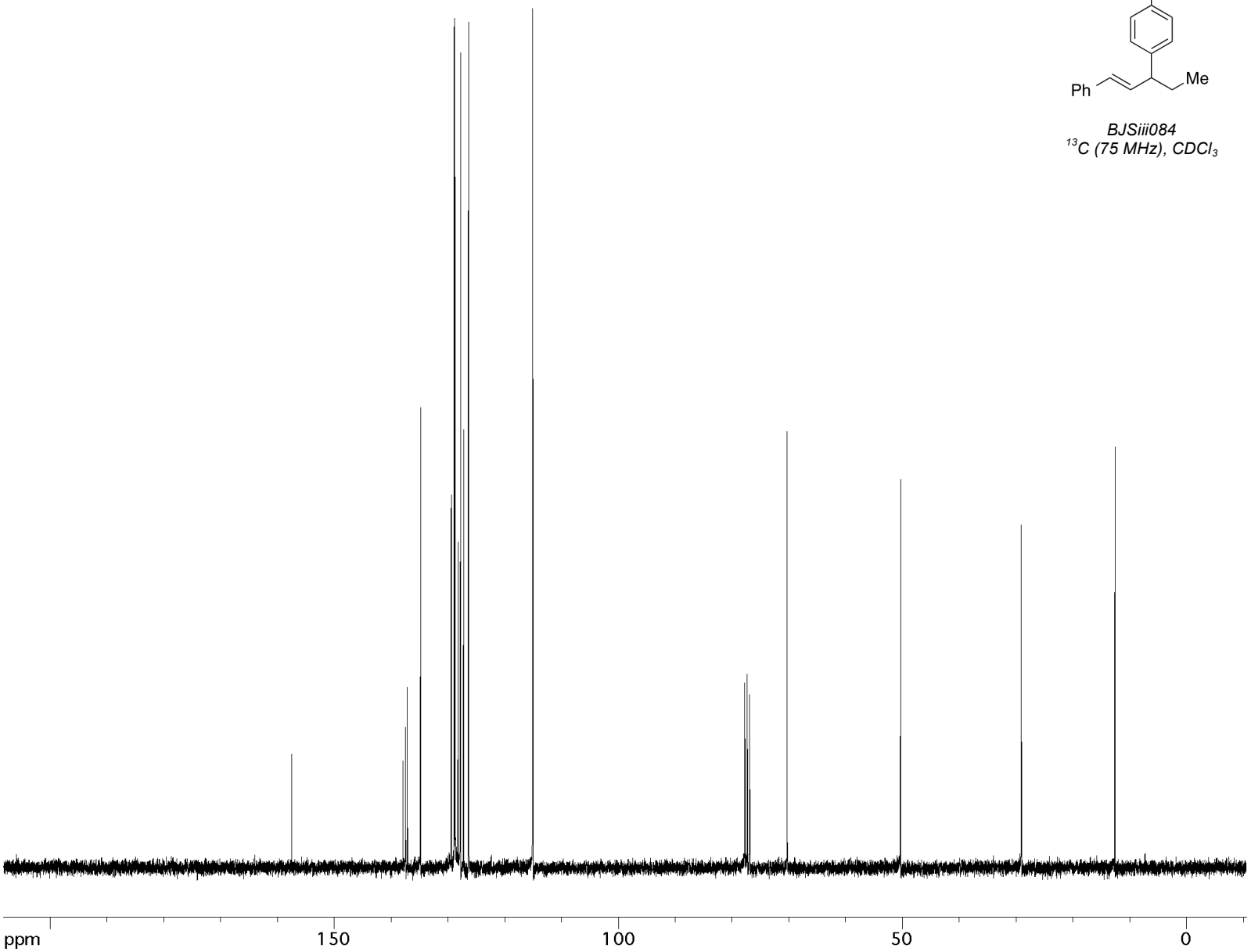
BJSiii084
^{1}H (300 MHz), $CDCl_3$



2b



BJSiii084
^{13}C (75 MHz), $CDCl_3$



2c

BJSiii077
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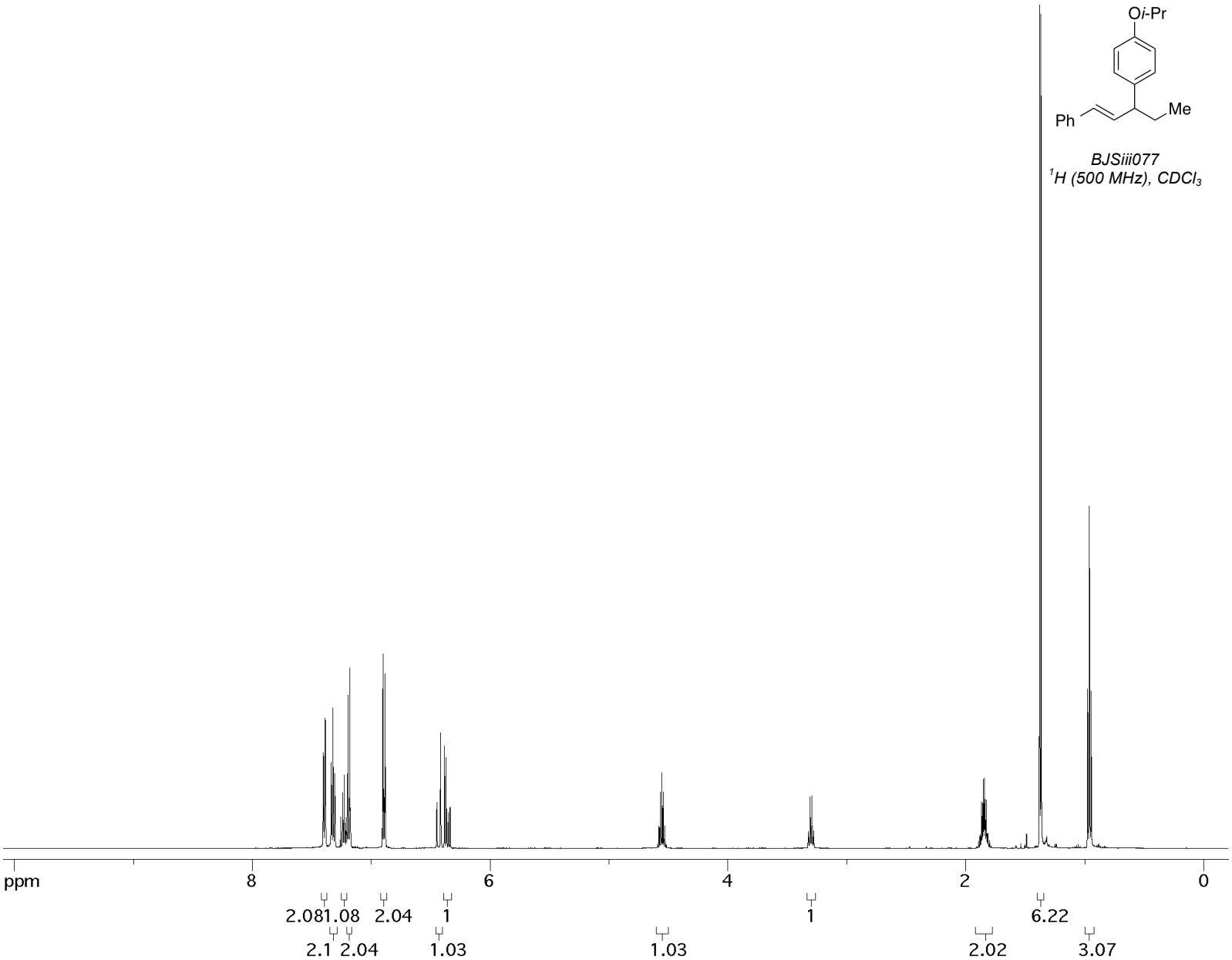
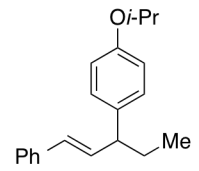
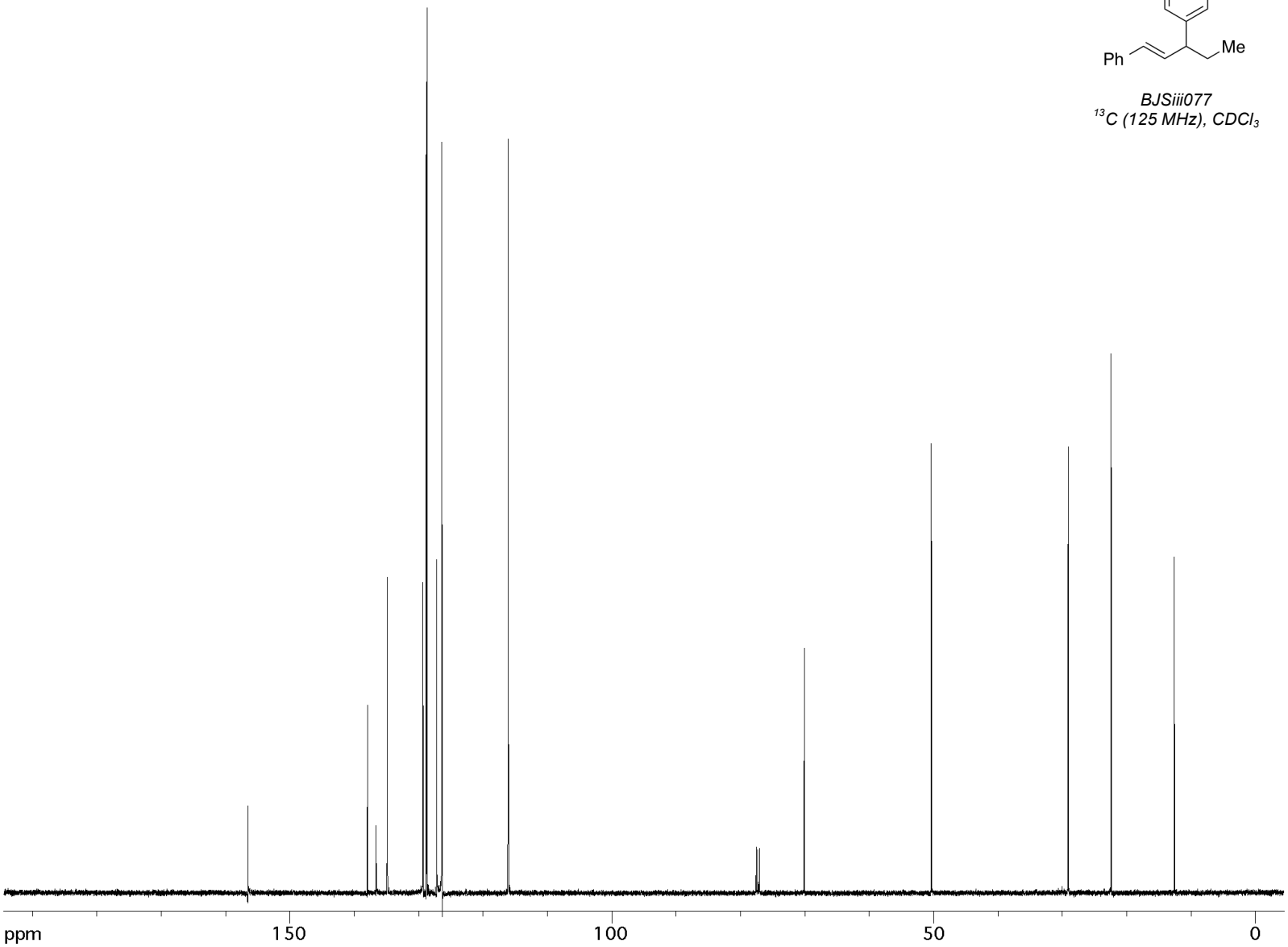


2c

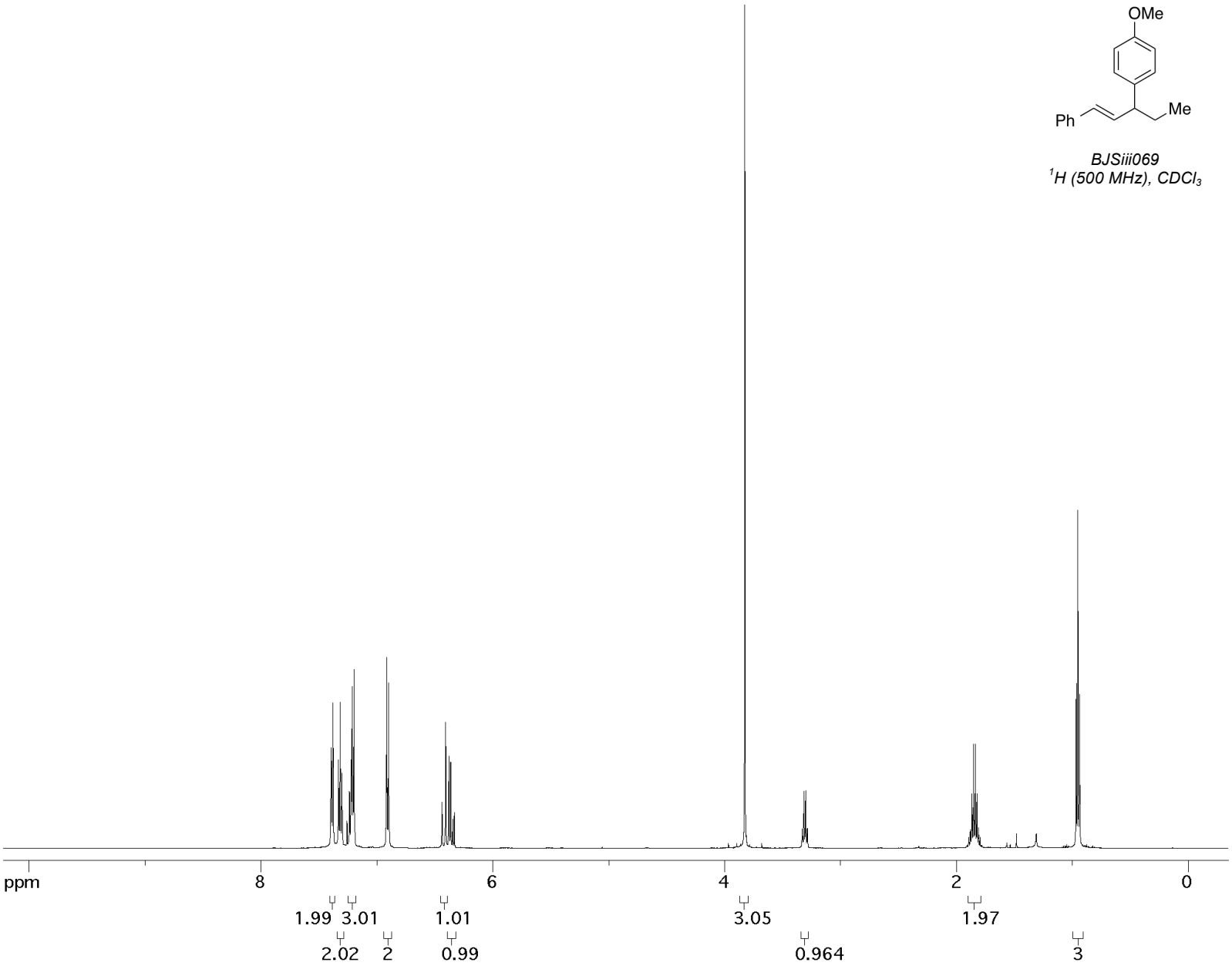


BJSiii077
^{13}C (125 MHz), $CDCl_3$

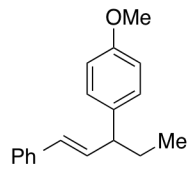


2d

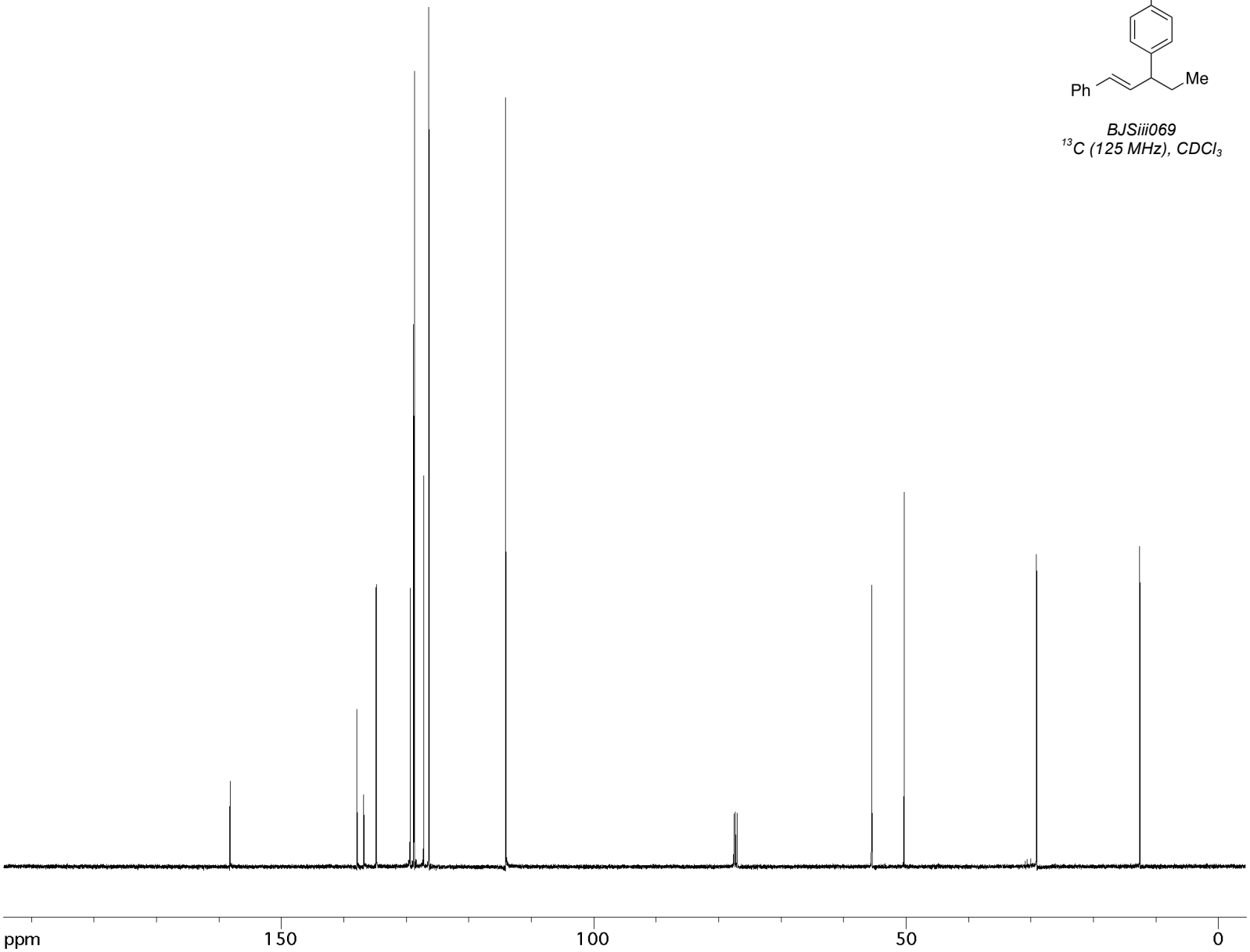
BJSiii069
^{1}H (500 MHz), $CDCl_3$



2d

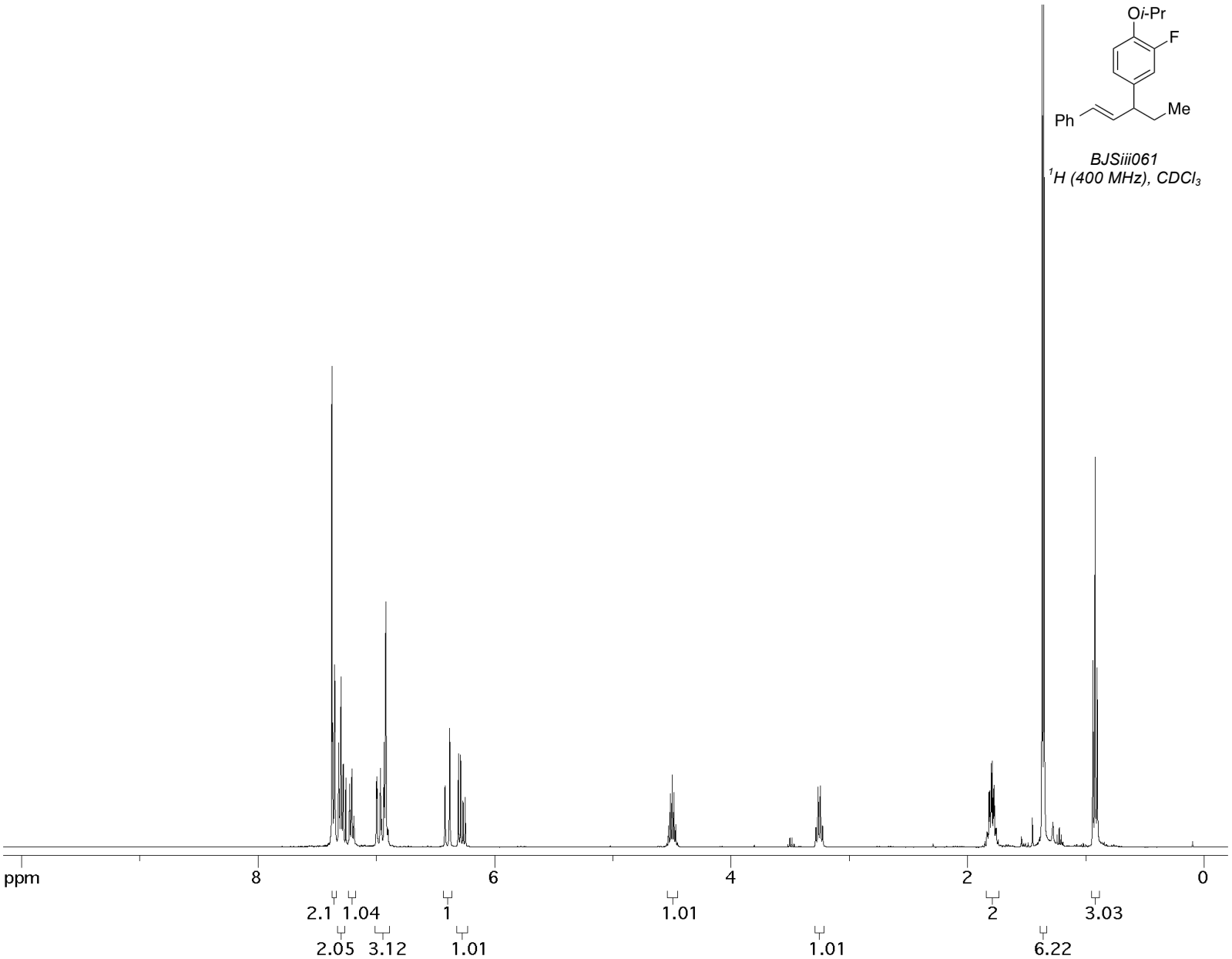


BJSiii069
^{13}C (125 MHz), $CDCl_3$



2e

BJSiii061
^{1}H (400 MHz), $CDCl_3$



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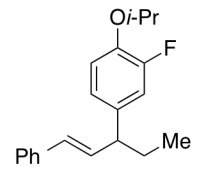
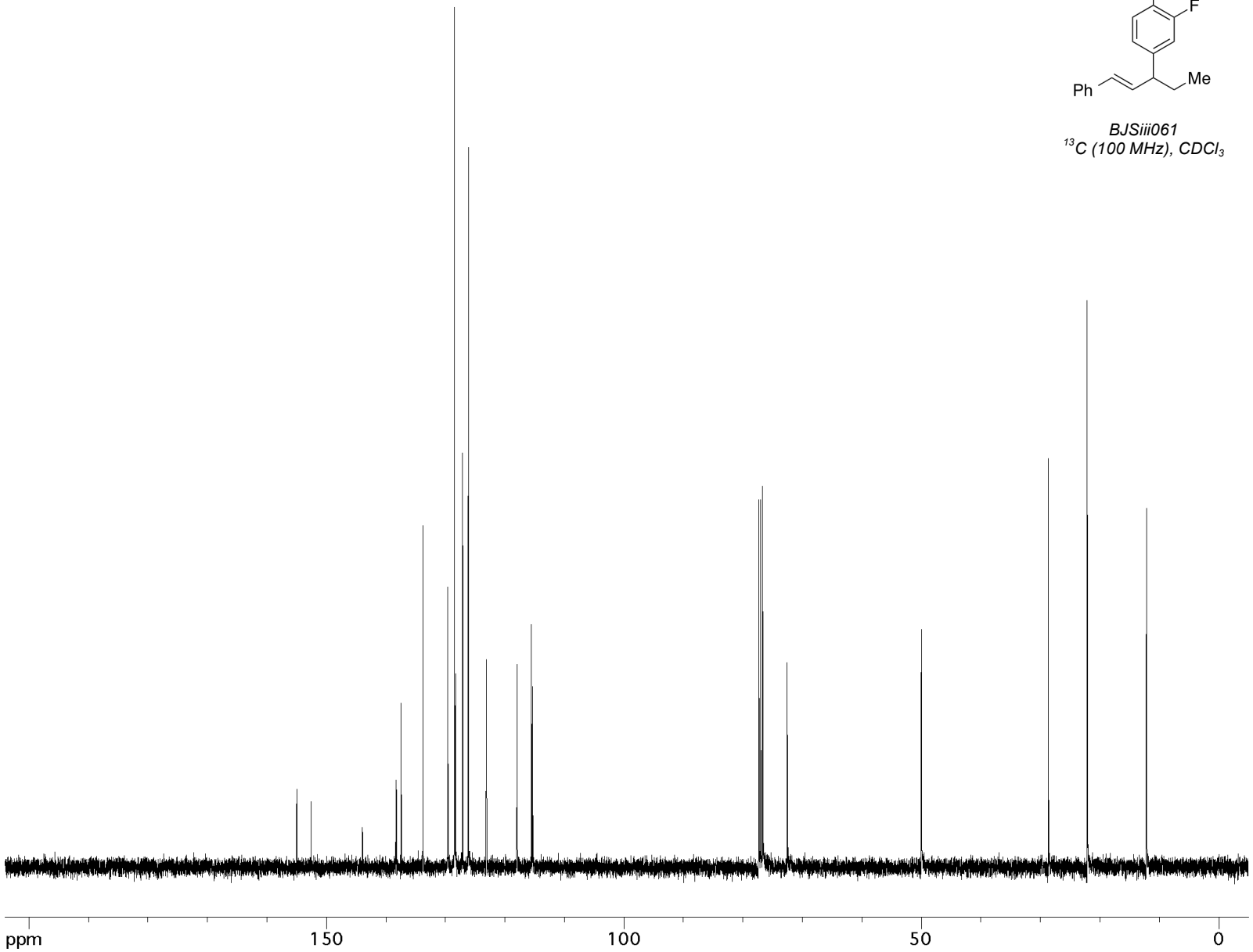
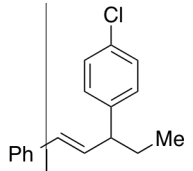


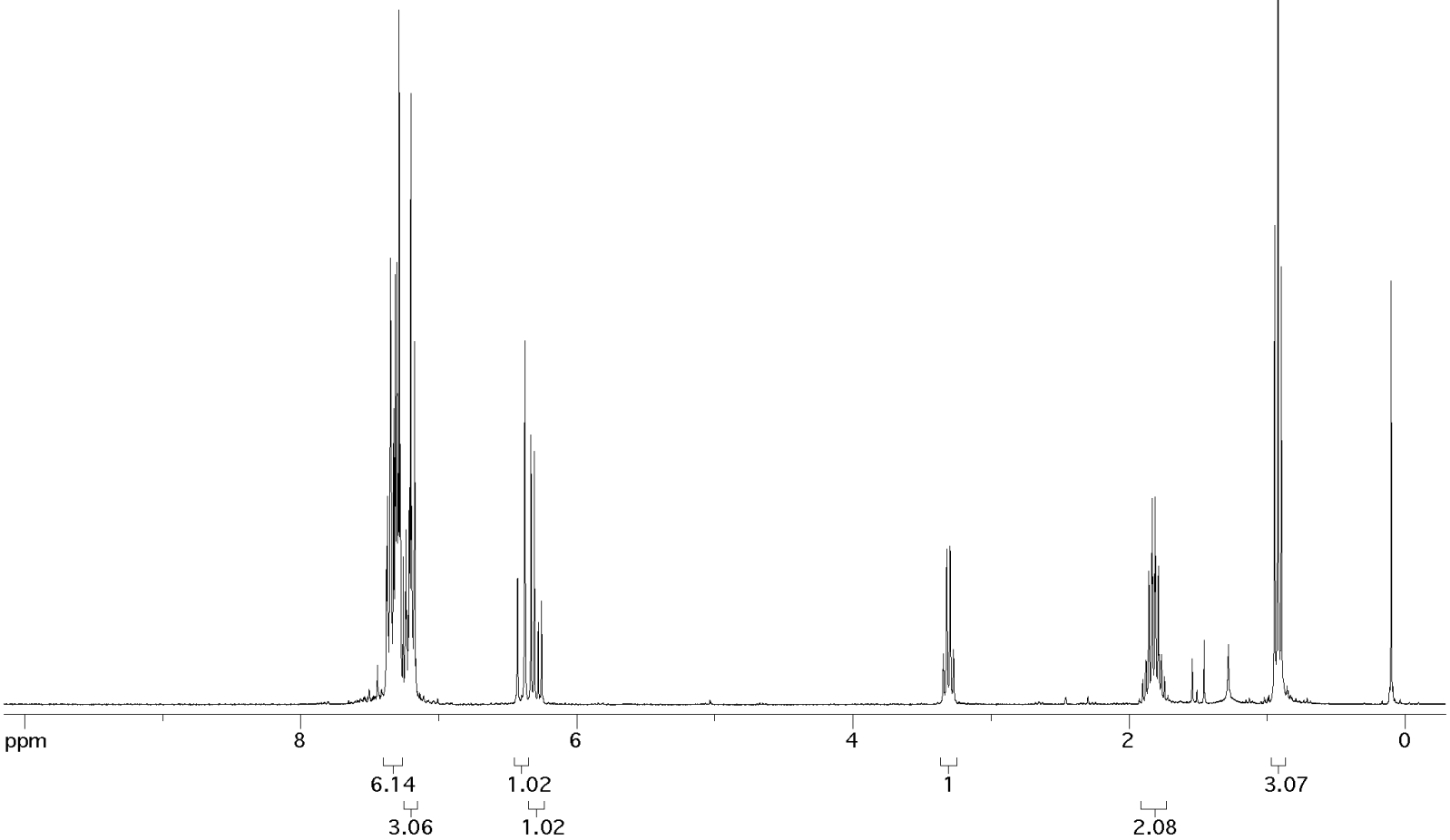
BJSiii061
^{13}C (100 MHz), $CDCl_3$



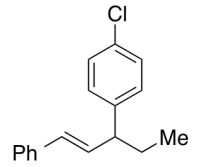
2f



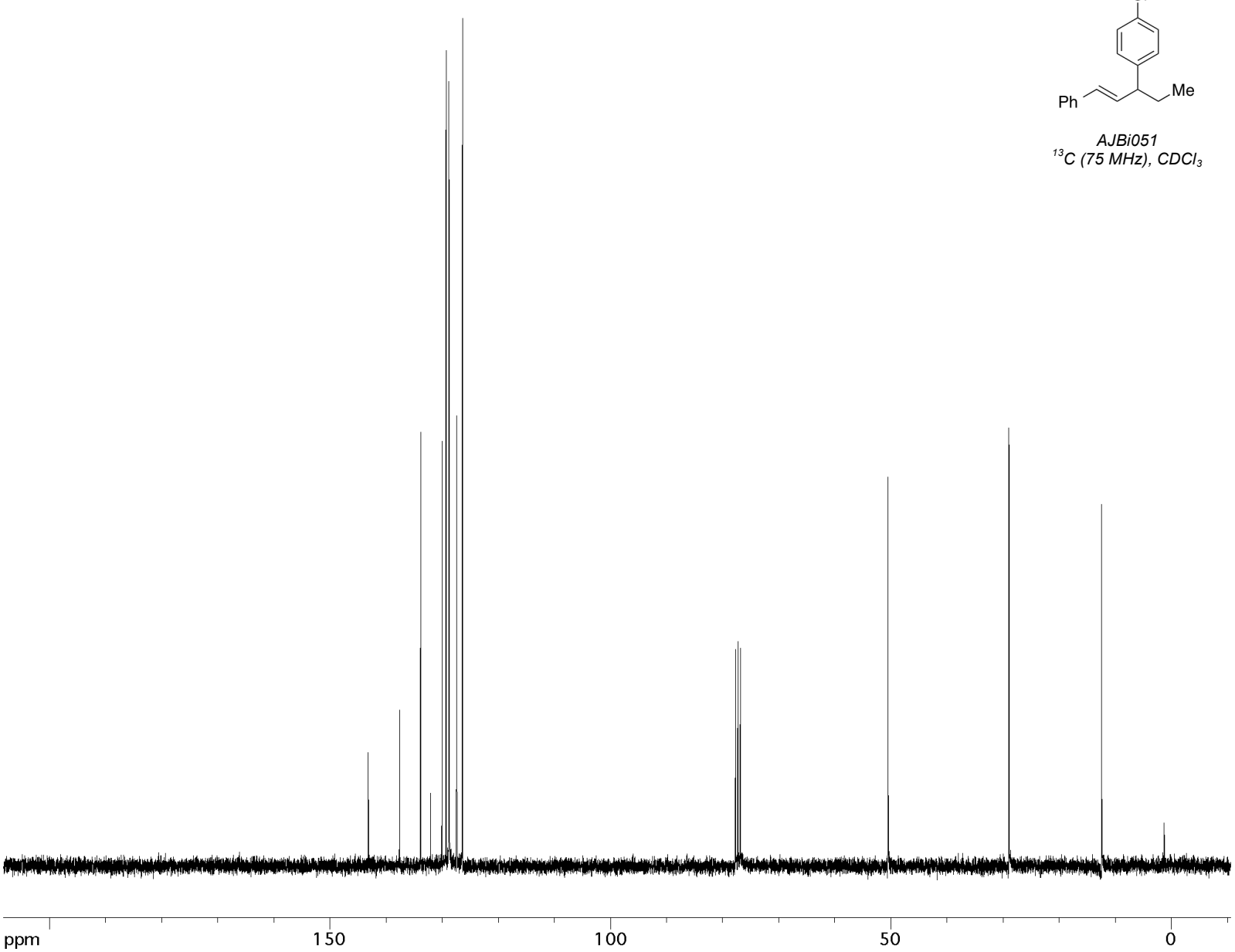
AJBi051
^{1}H (300 MHz), $CDCl_3$



2f

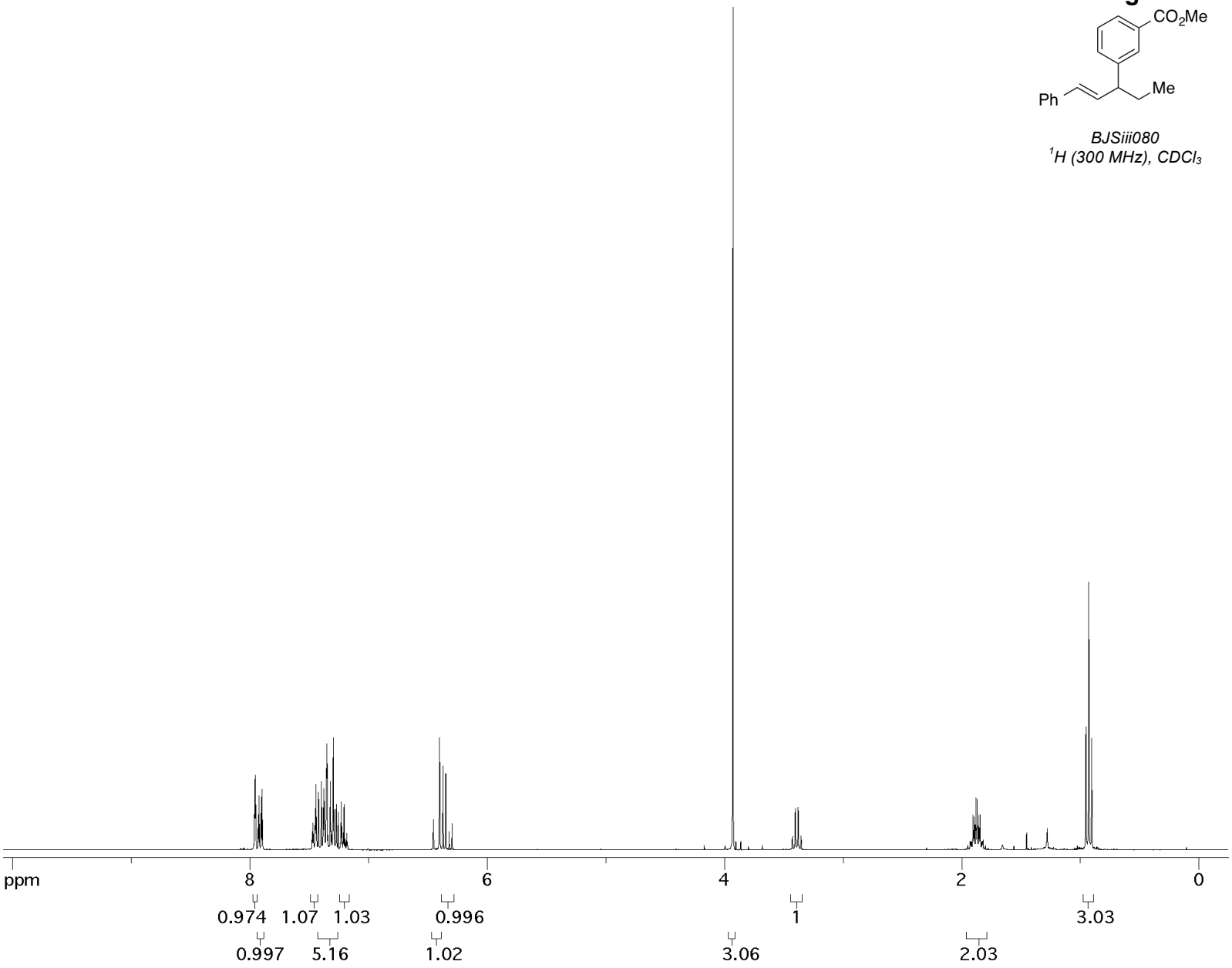


AJBi051
^{13}C (75 MHz), $CDCl_3$

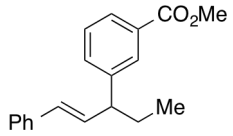


2g

BJSiii080
^{1}H (300 MHz), $CDCl_3$



2g



BJSiii080
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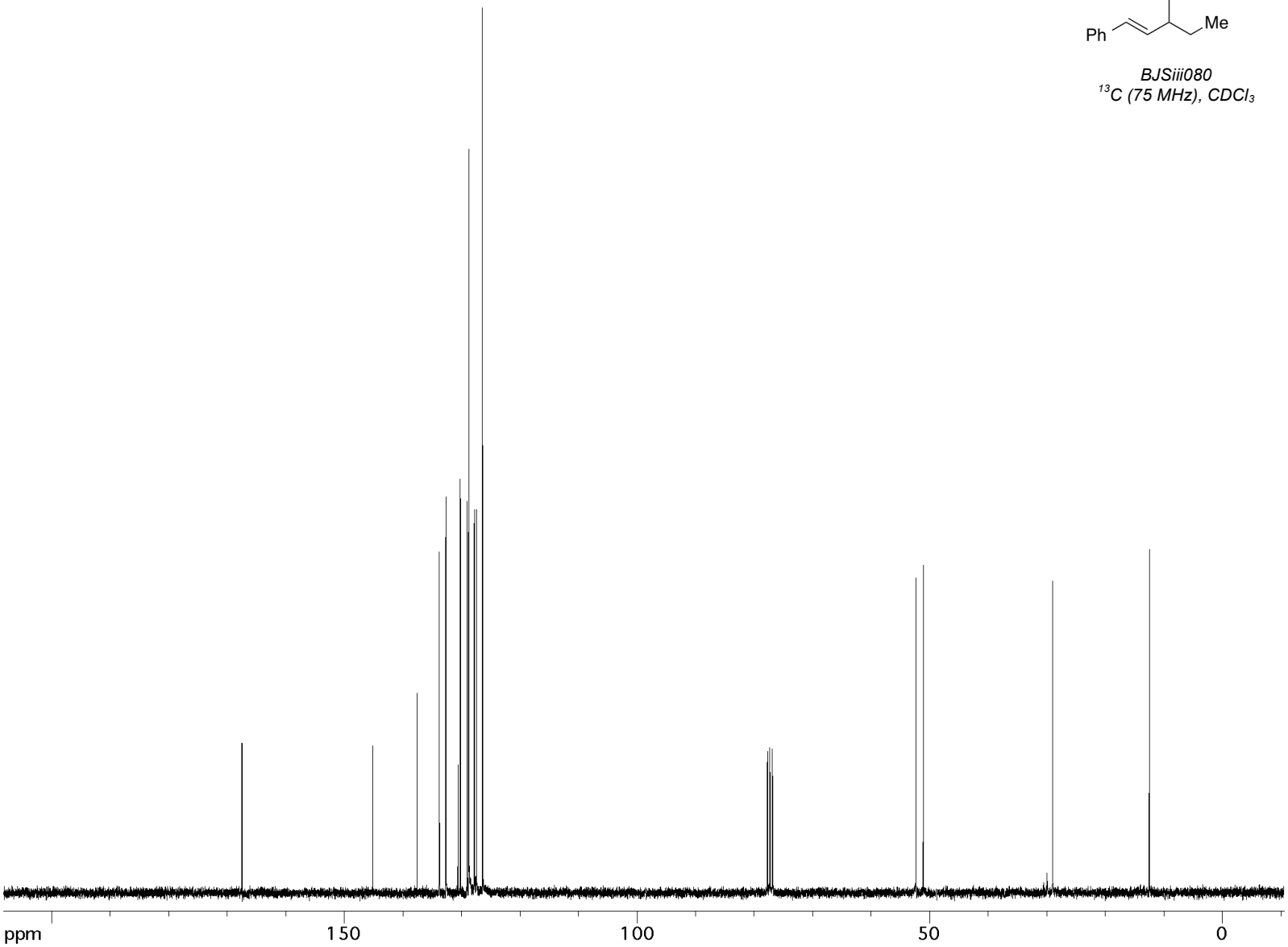
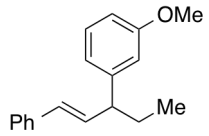
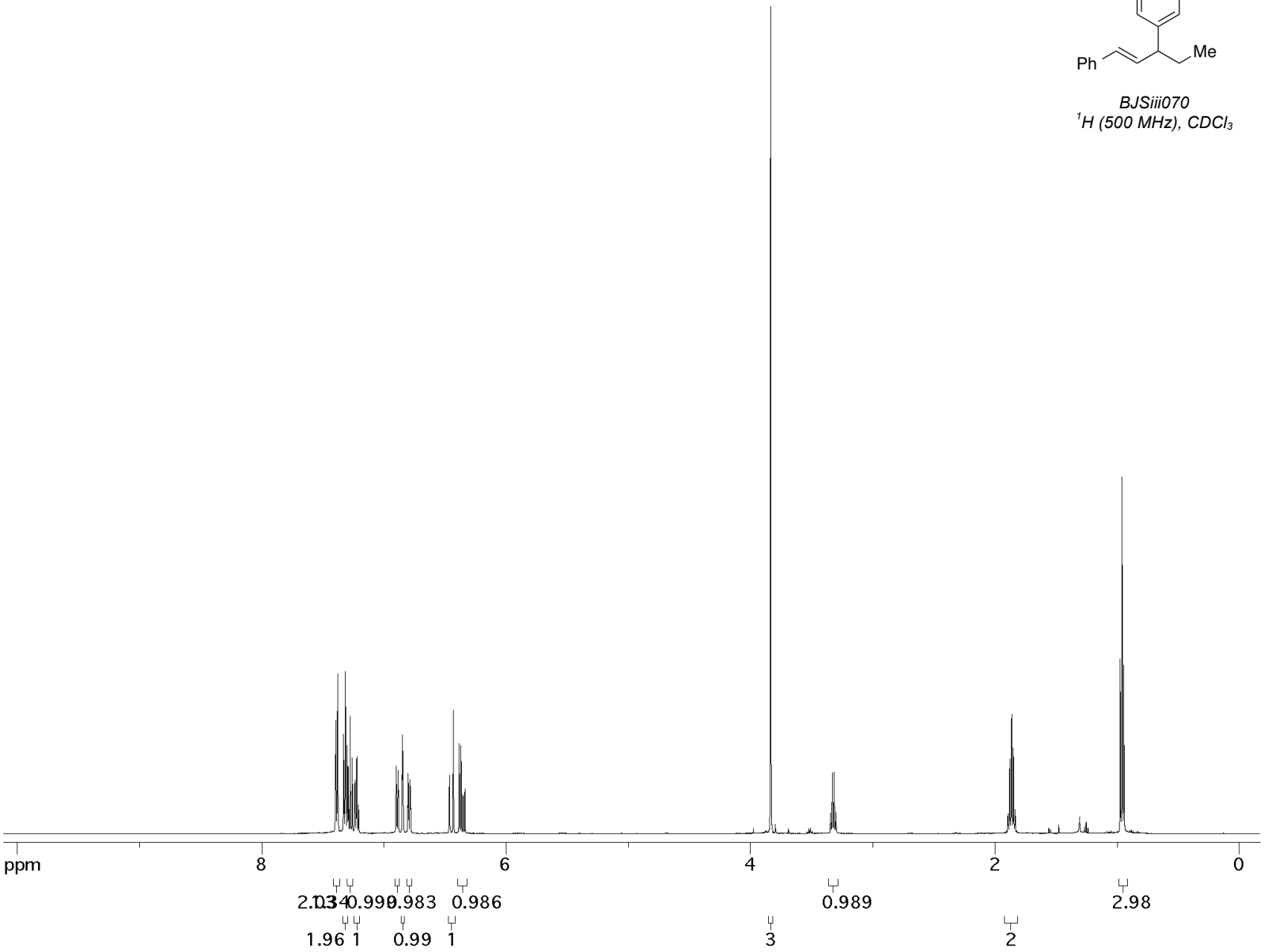


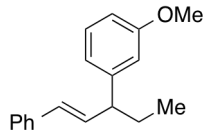
2h



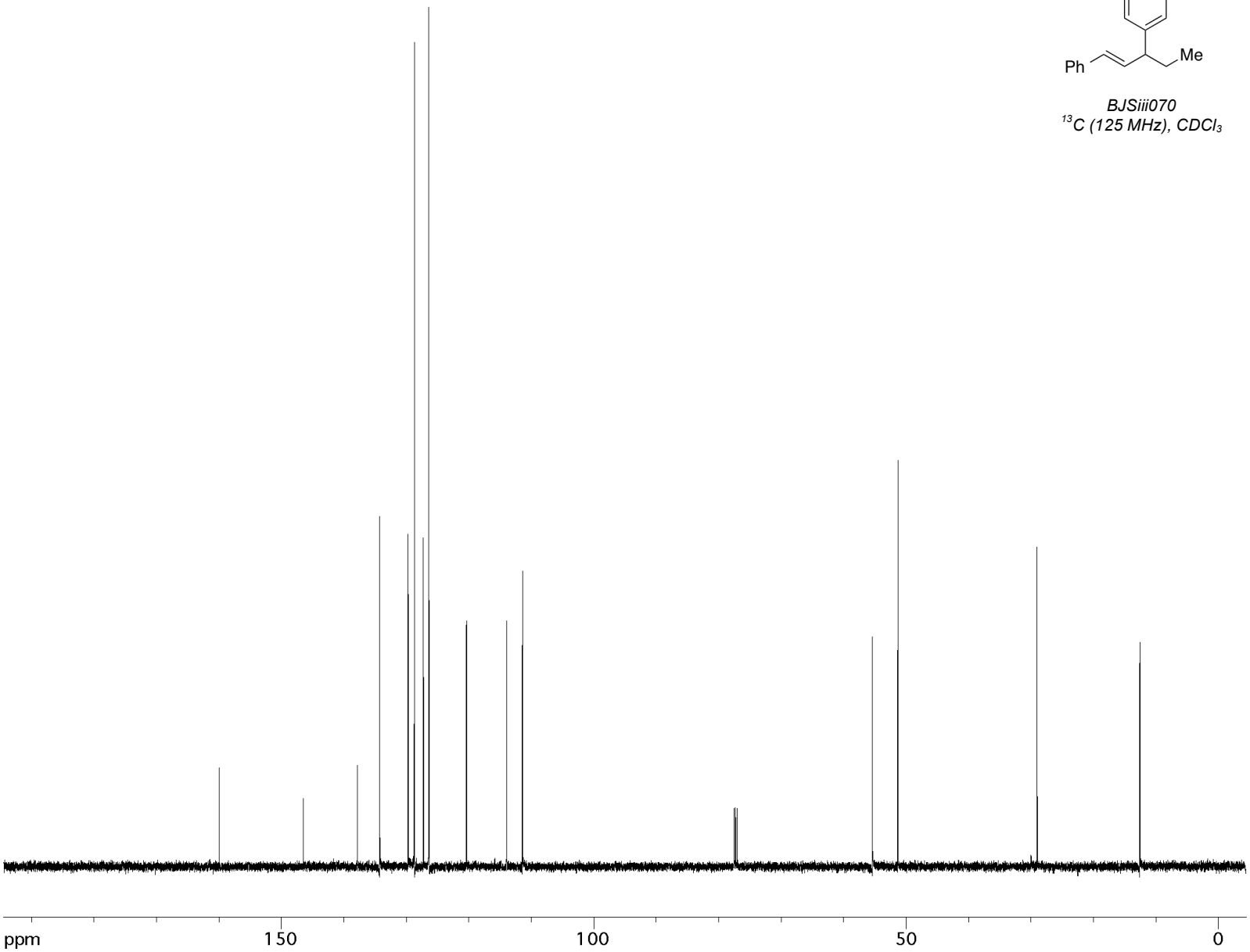
BJSiii070
^{1}H (500 MHz), $CDCl_3$



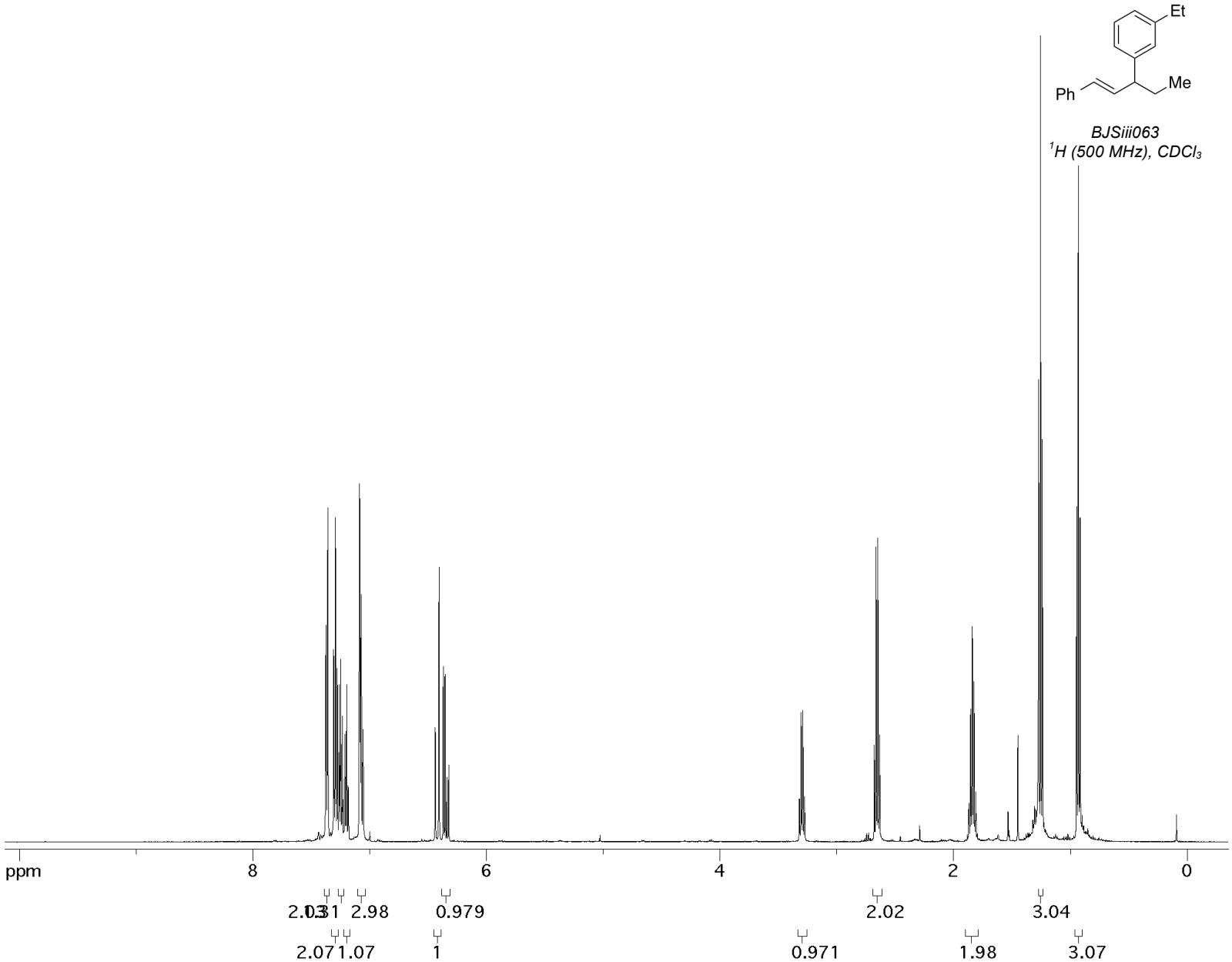
2h



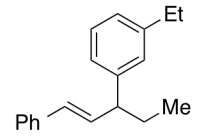
BJSiii070
^{13}C (125 MHz), $CDCl_3$



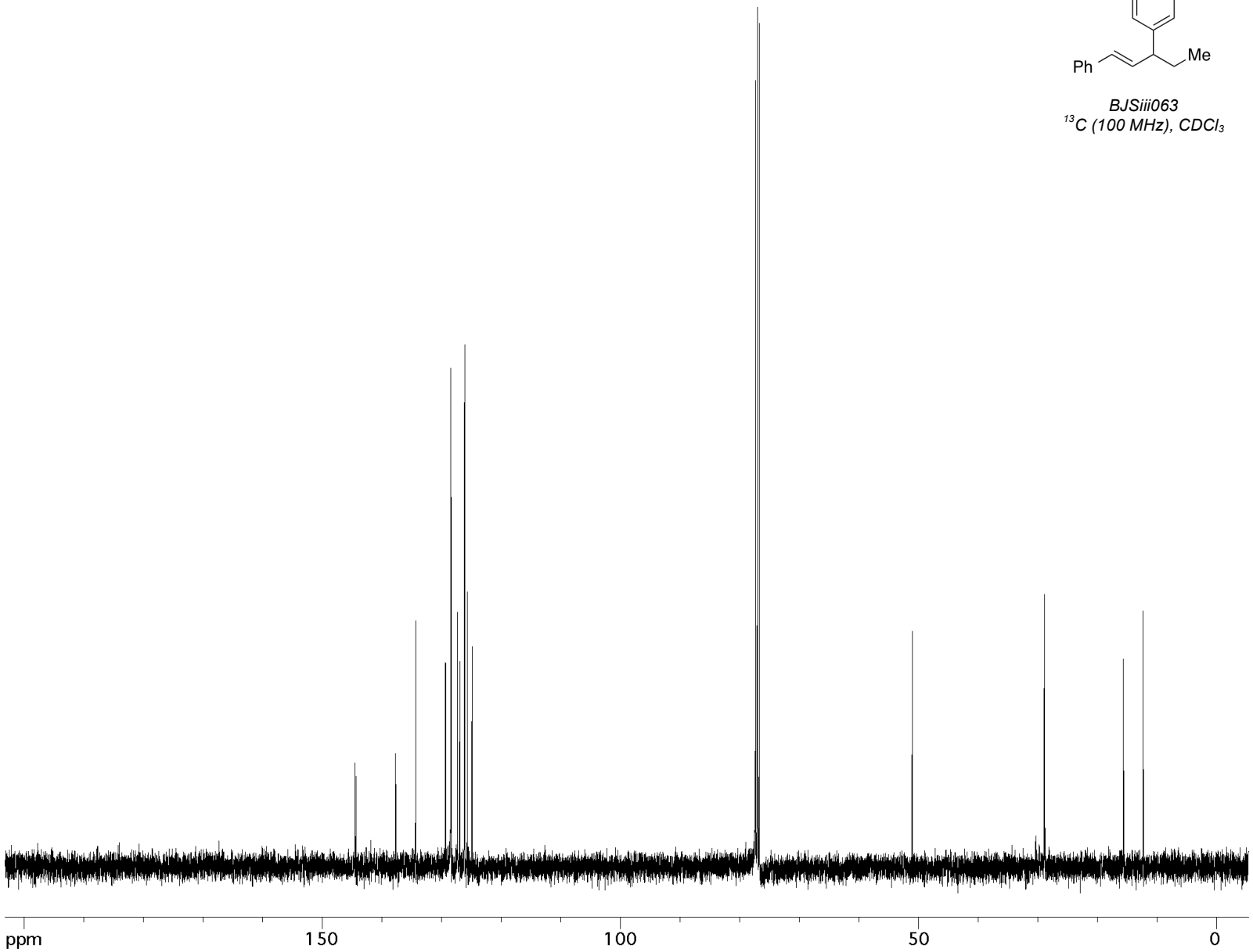
2i


Et
Me
Ph
BJSiii063
^1H (500 MHz), $CDCl_3$
ppm
8
6
4
2
0
2.03
1
2.98
0.979
2.02
3.04
2.07
1.07
1
0.971
1.98
3.07

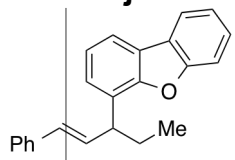
2i



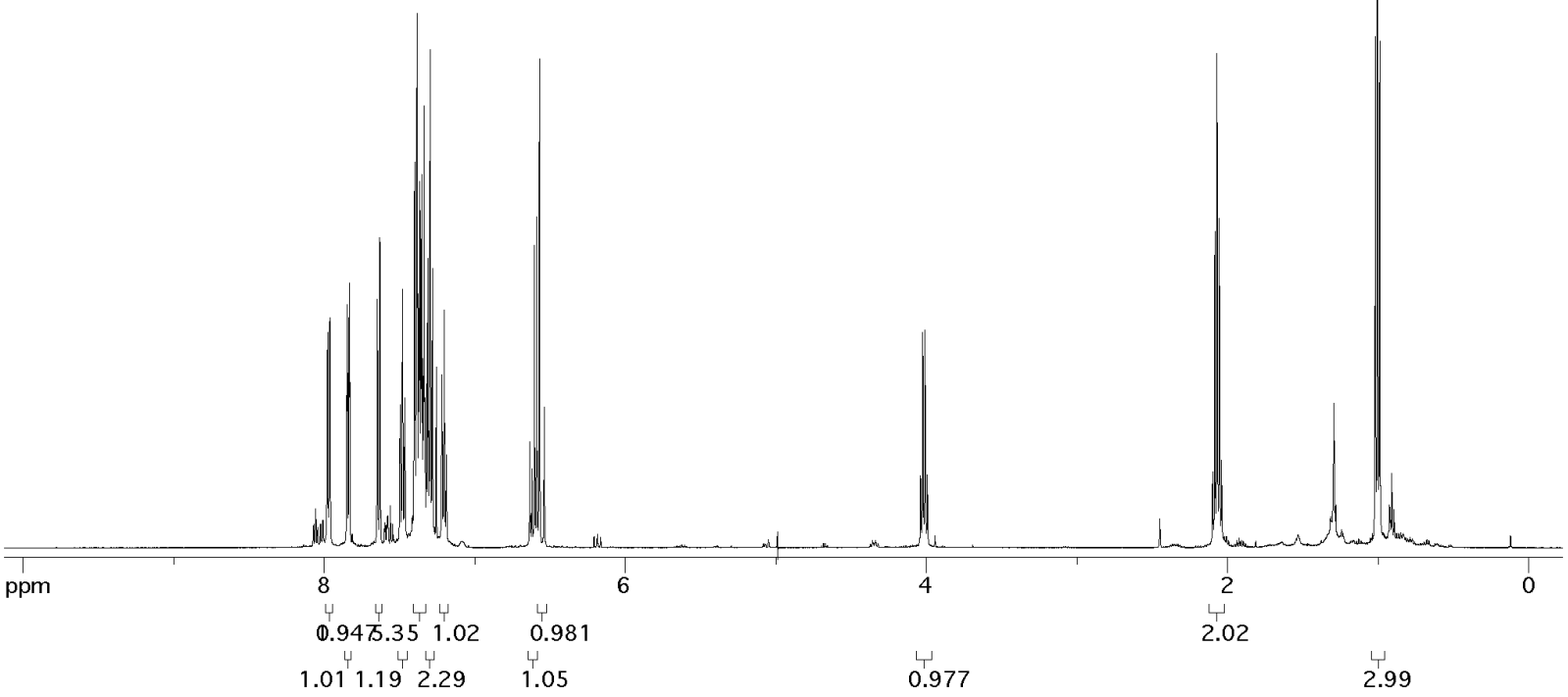
BJSiii063
^{13}C (100 MHz), $CDCl_3$



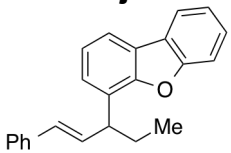
2j



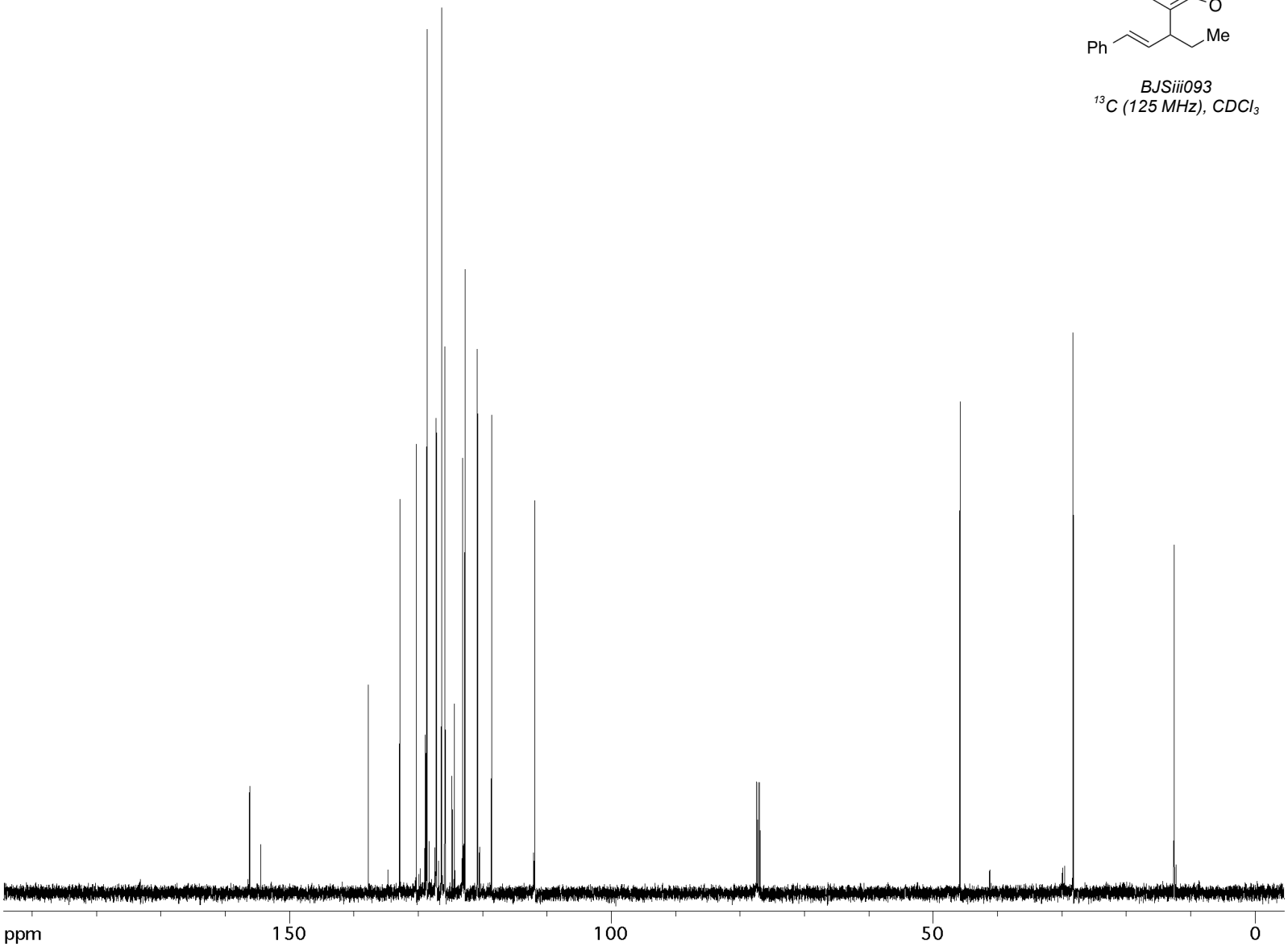
BJSiii093
^{1}H (500 MHz), $CDCl_3$



2j

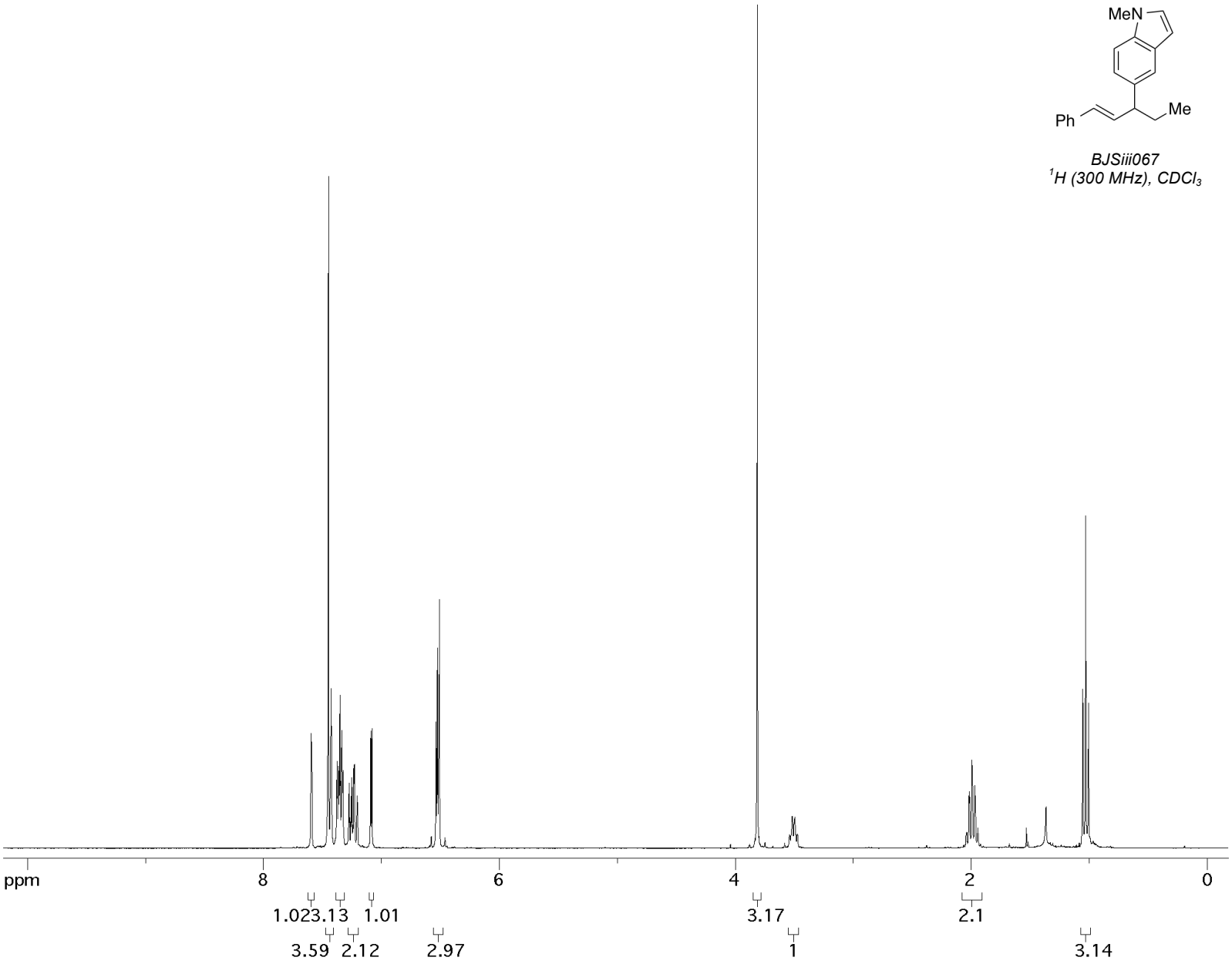


BJSiii093
^{13}C (125 MHz), $CDCl_3$

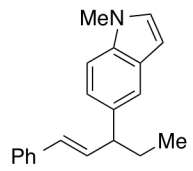


2k

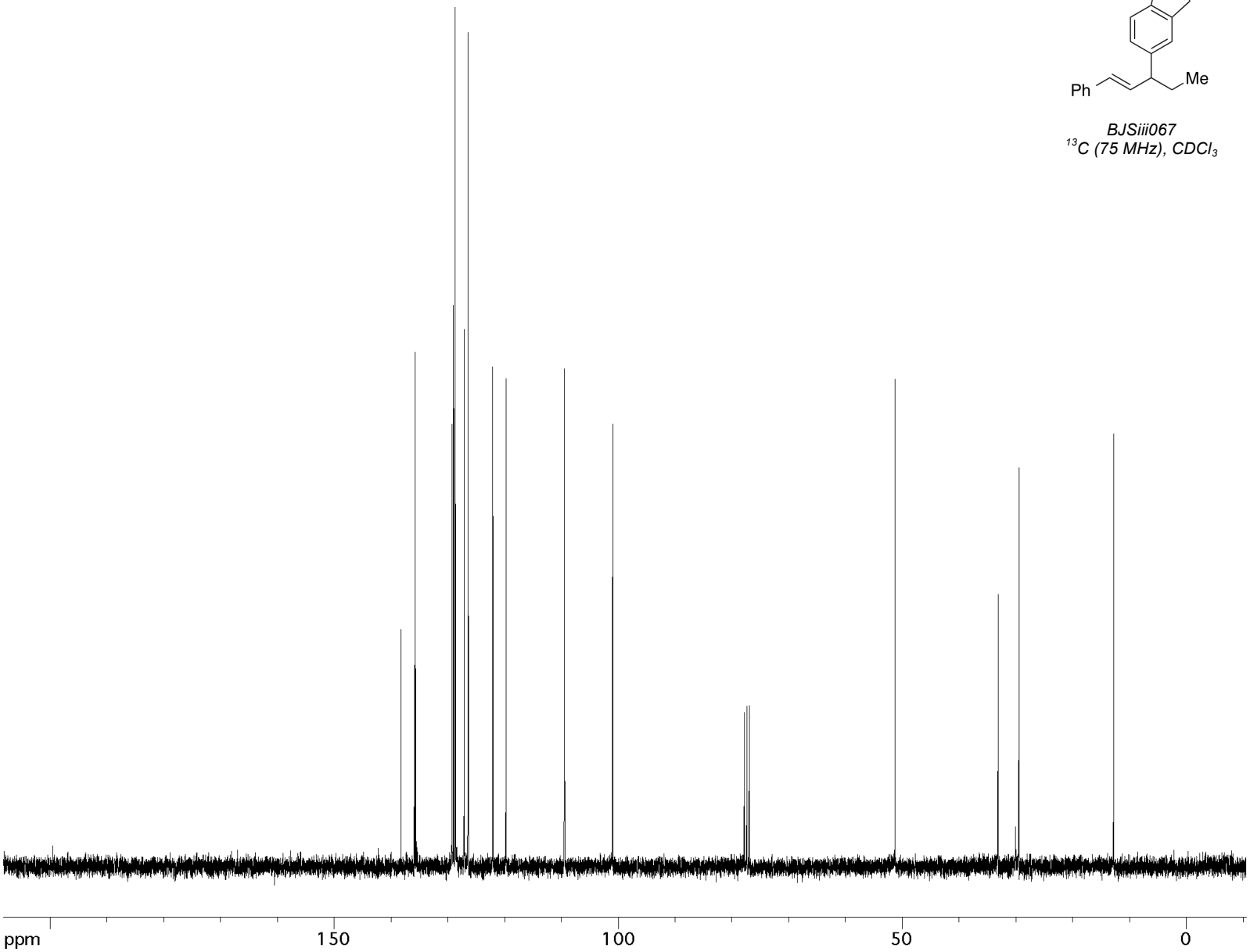
BJSiii067
^{1}H (300 MHz), $CDCl_3$



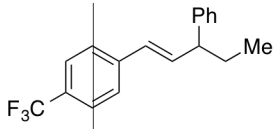
2k



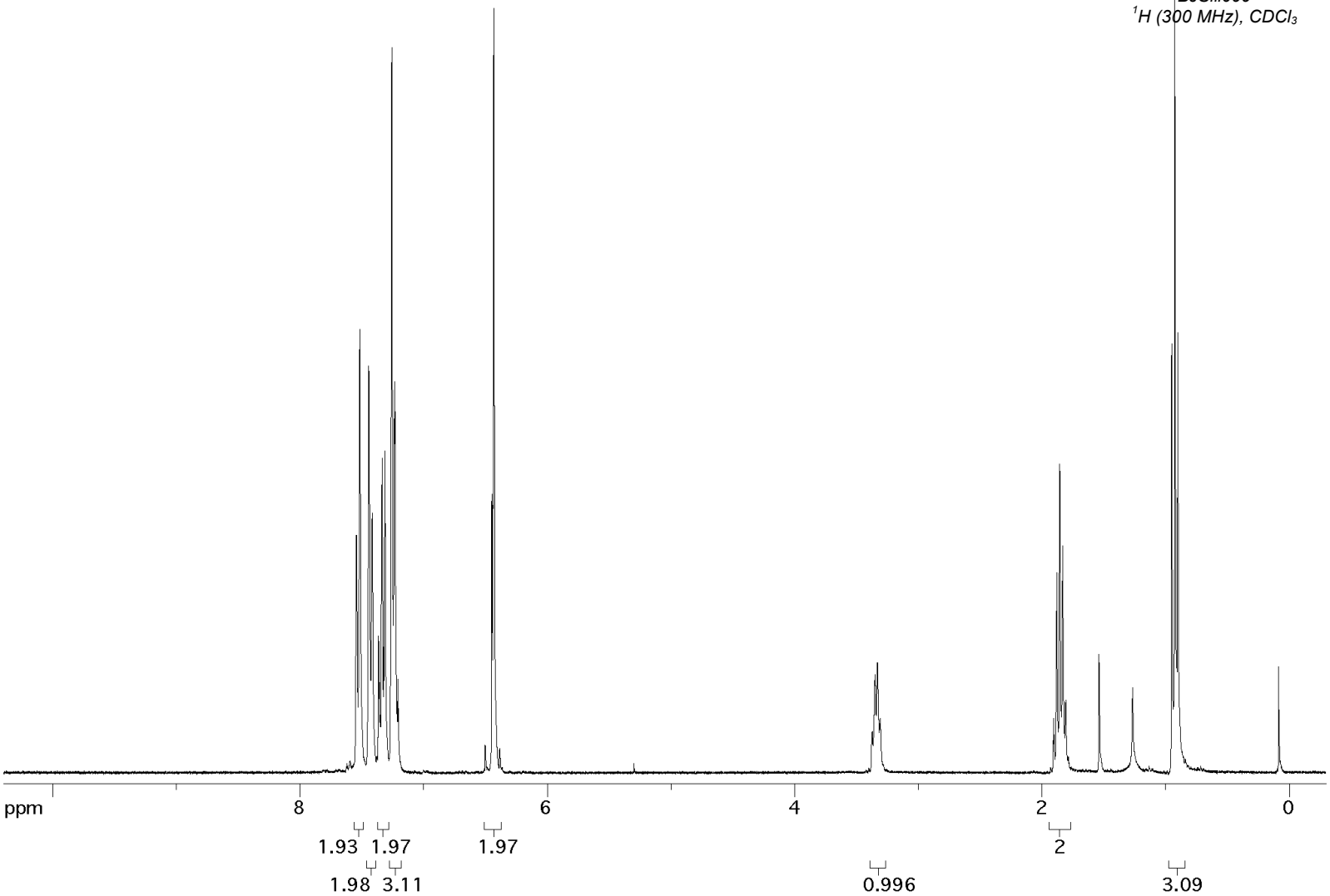
BJSiii067
^{13}C (75 MHz), $CDCl_3$



6a



BJSiii099
^{1}H (300 MHz), $CDCl_3$



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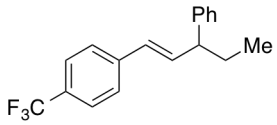
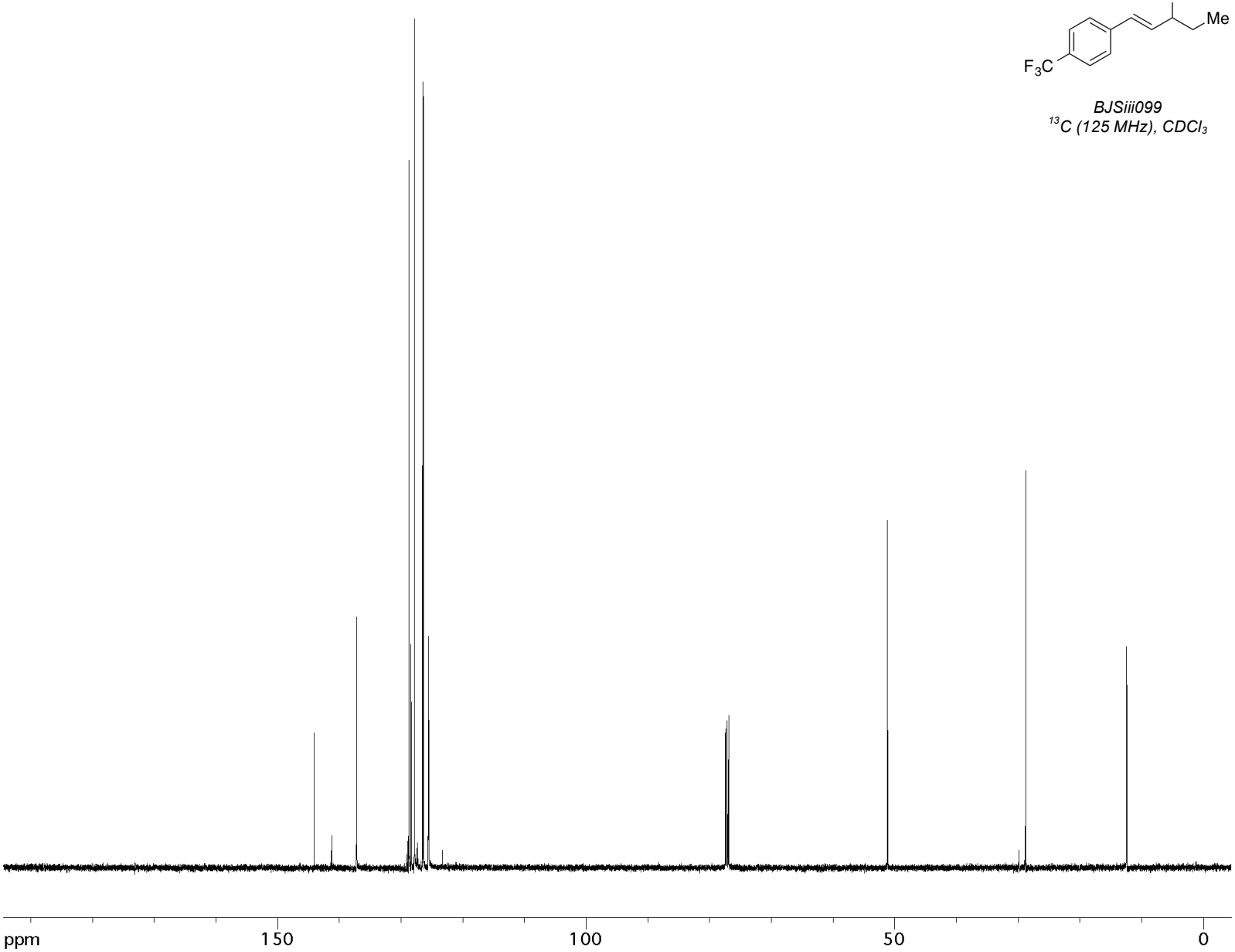
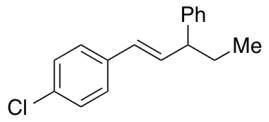


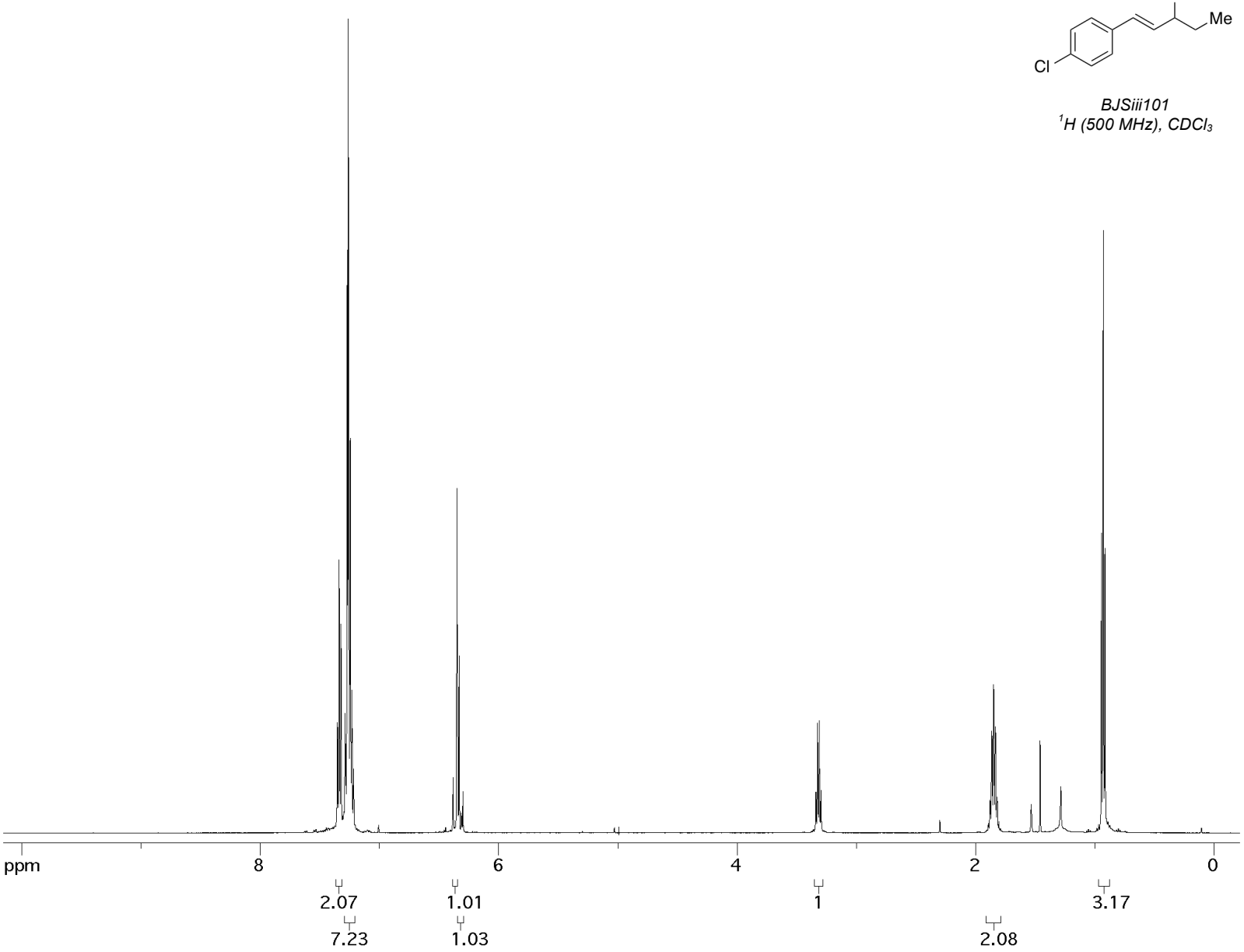
BJSiii099
^{13}C (125 MHz), $CDCl_3$



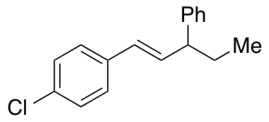
6b



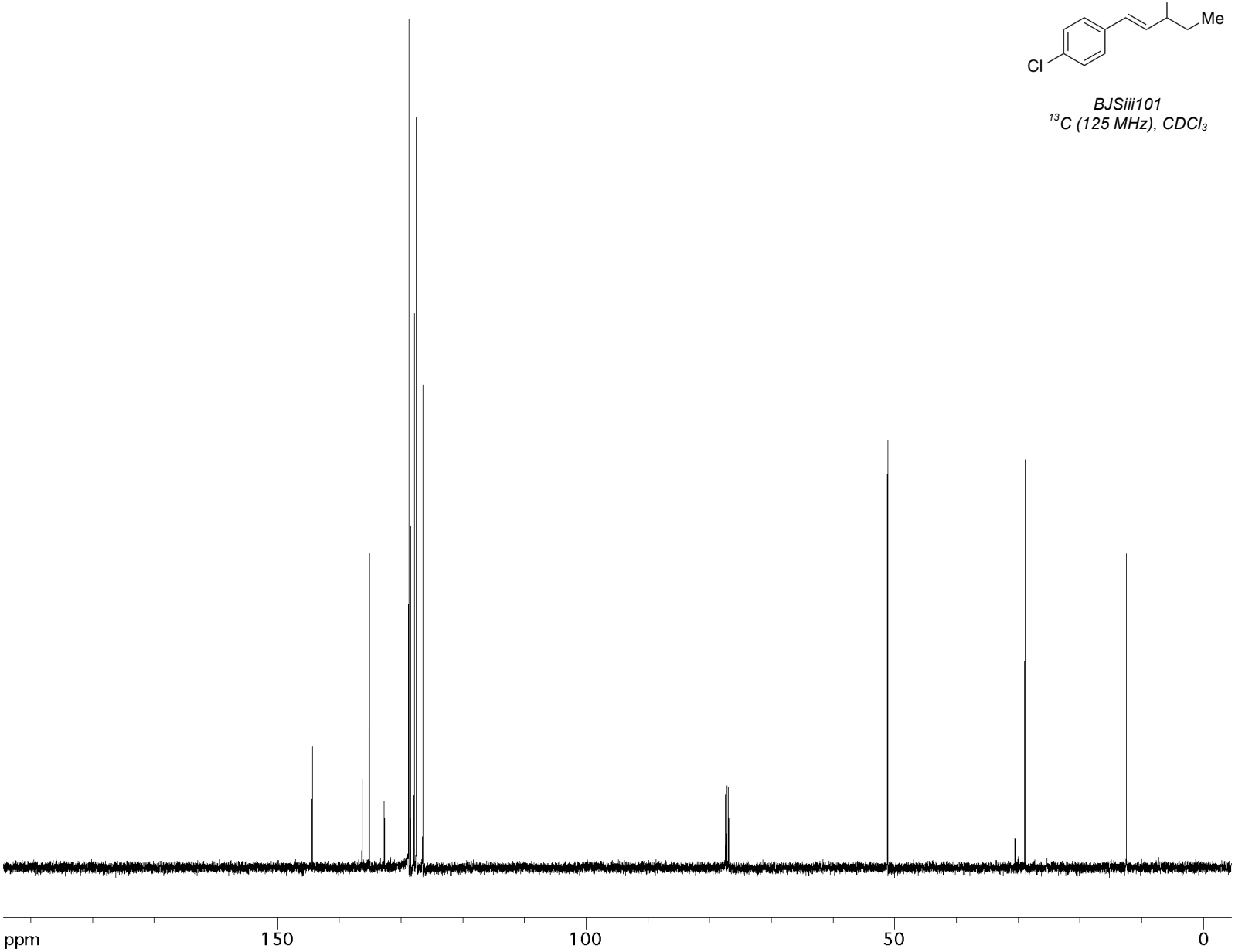
BJSiii101
^{1}H (500 MHz), $CDCl_3$



6b



BJSiii101
^{13}C (125 MHz), $CDCl_3$



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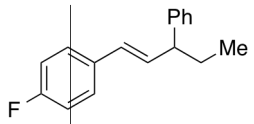
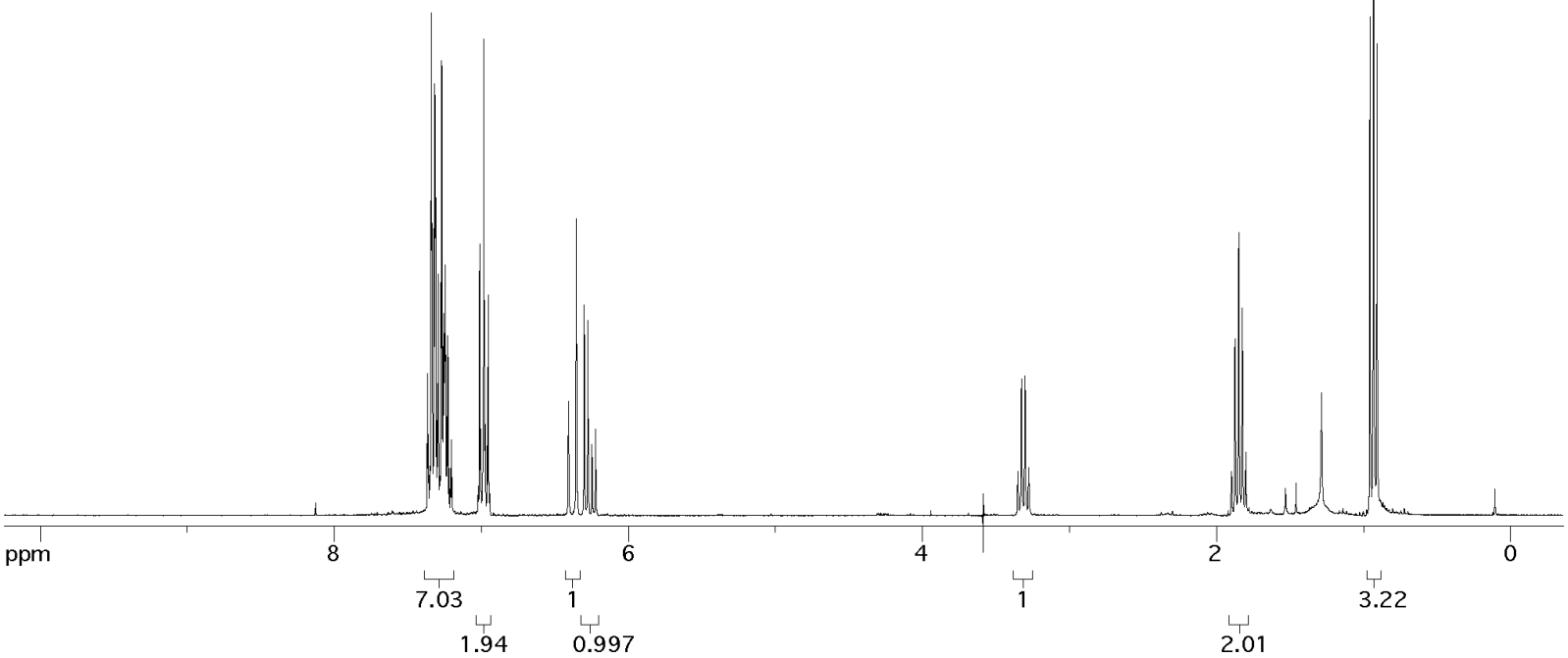
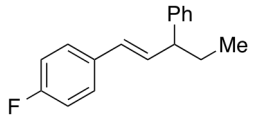


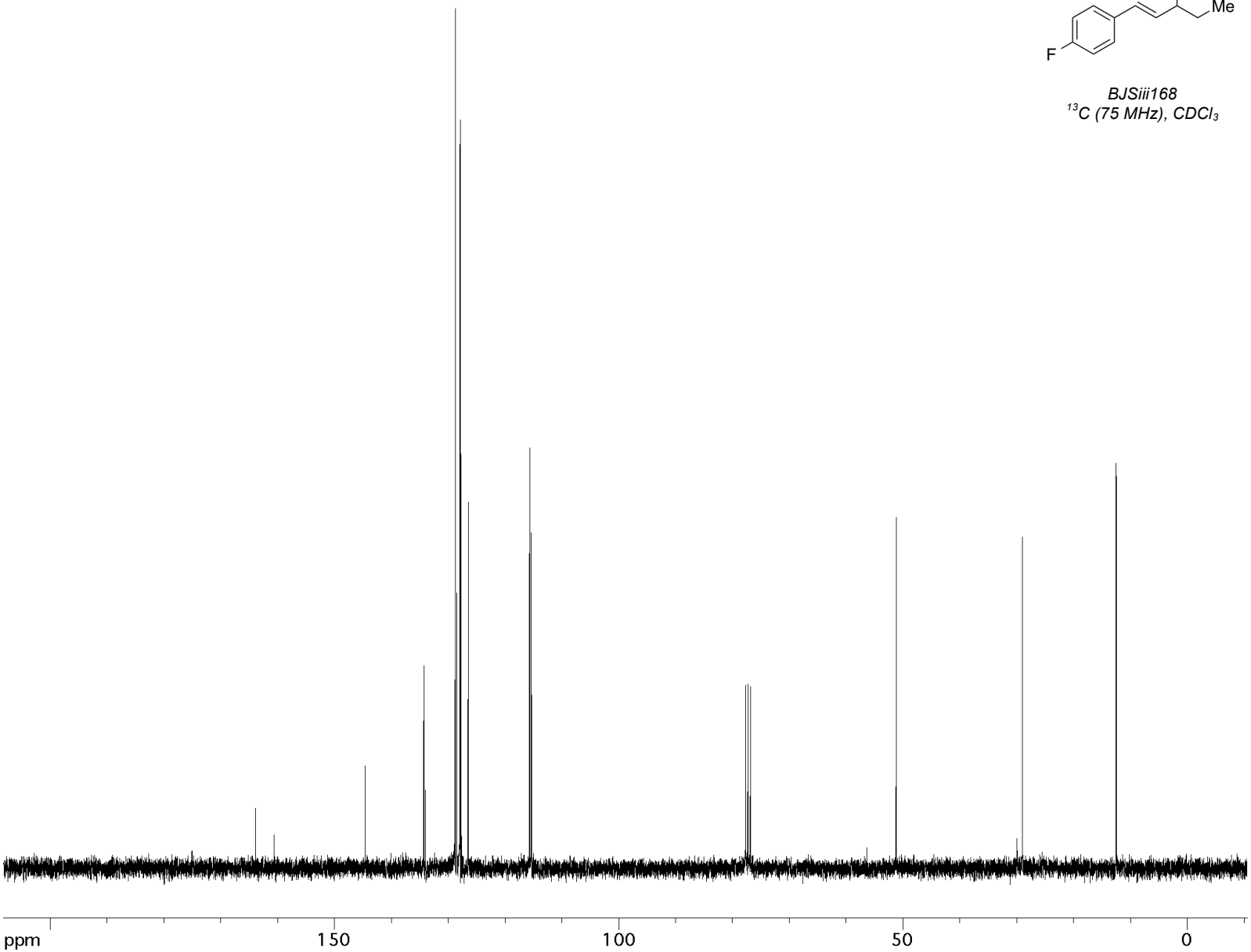
BJSiii168
^{1}H (300 MHz), $CDCl_3$



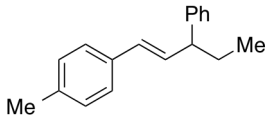
6c



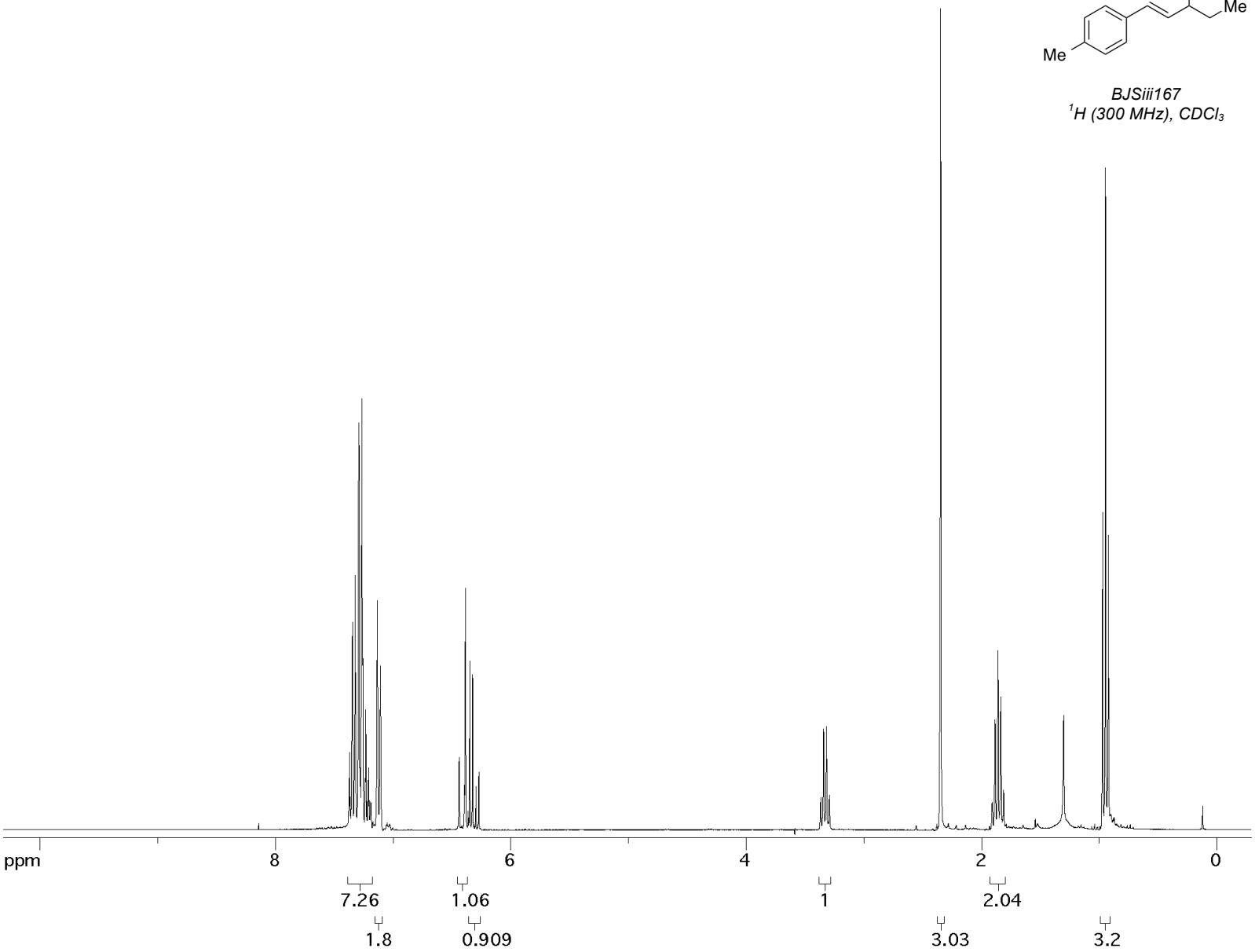
BJSiii168
^{13}C (75 MHz), $CDCl_3$



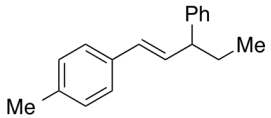
6d



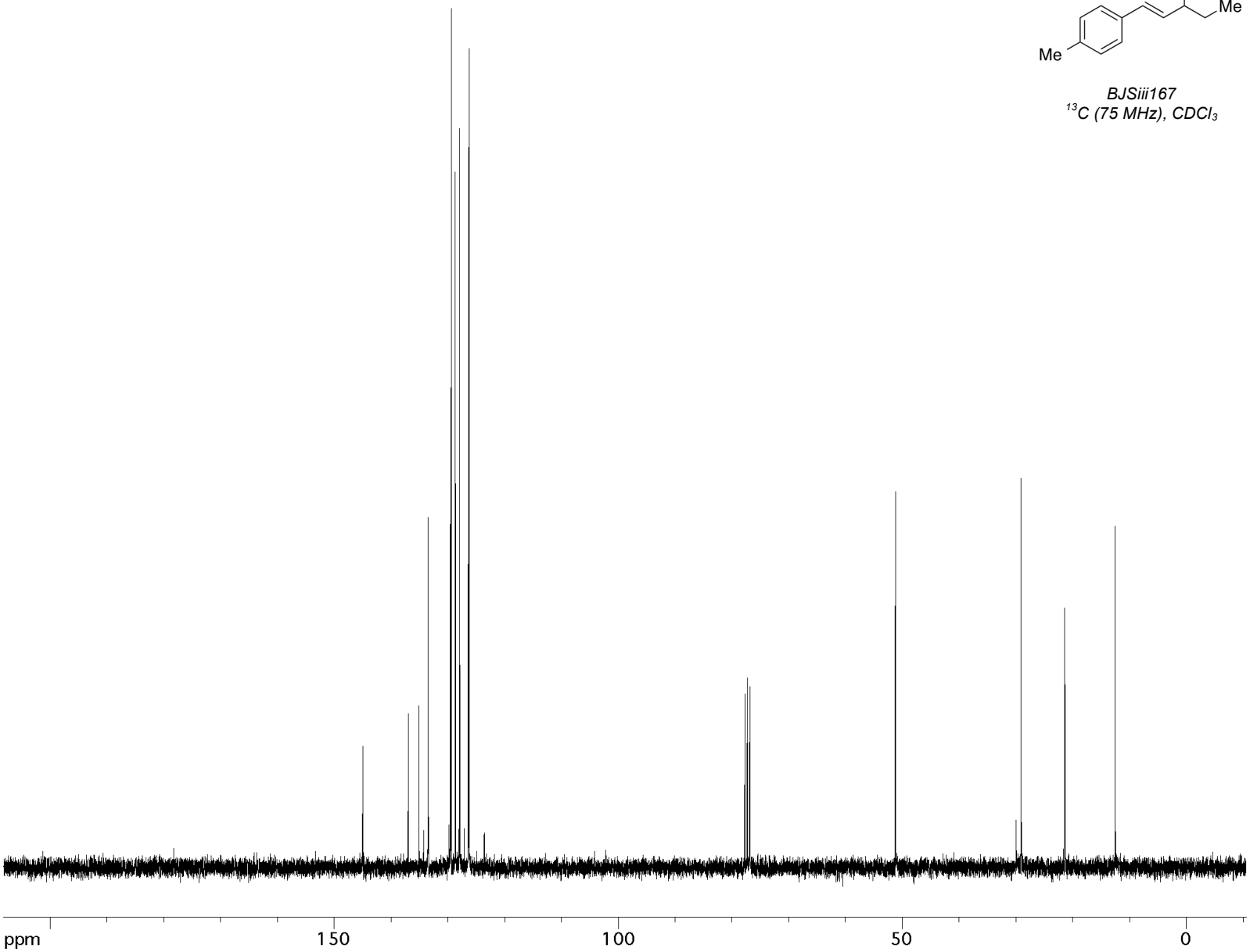
BJSiii167
^{1}H (300 MHz), $CDCl_3$



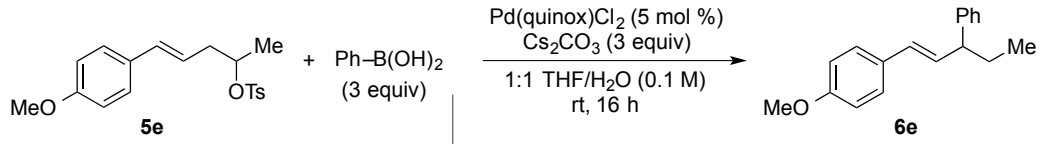
6d



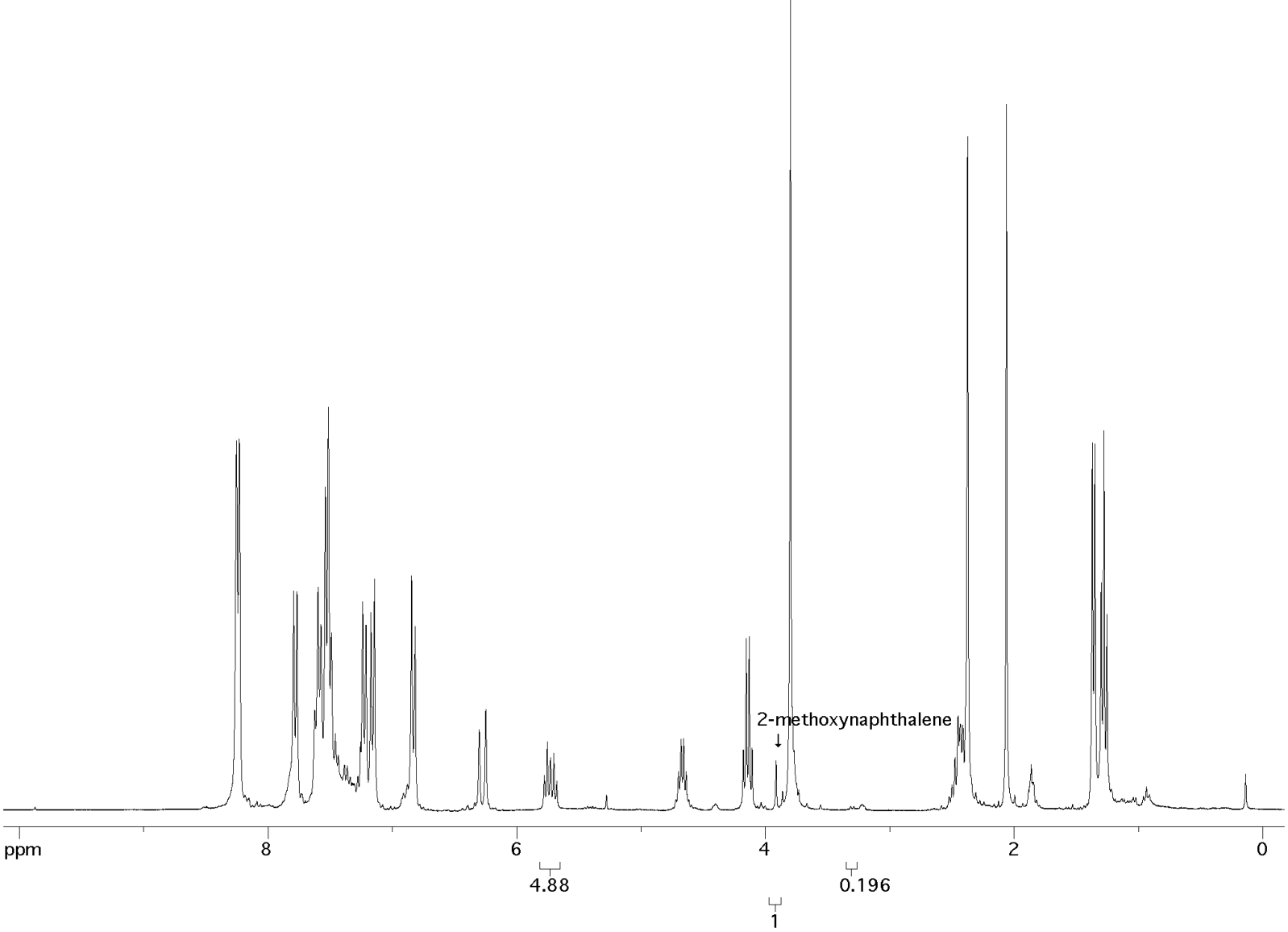
BJSiii167
^{13}C (75 MHz), $CDCl_3$



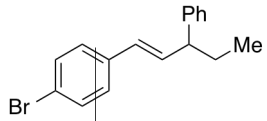
BJSiii100
^{1}H (300 MHz), $CDCl_3$



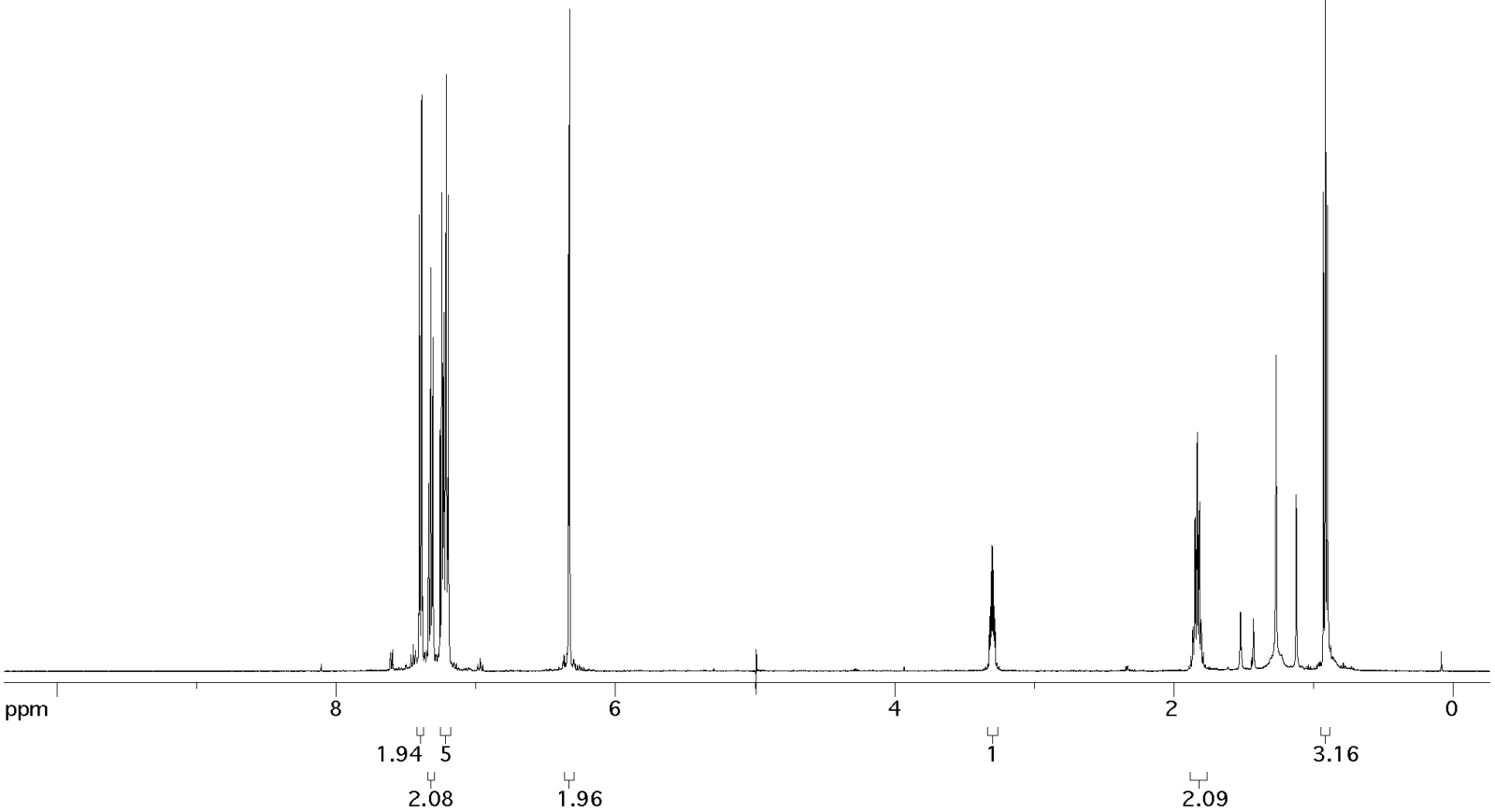
(s5)



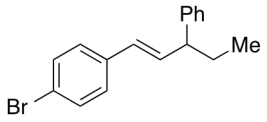
6f



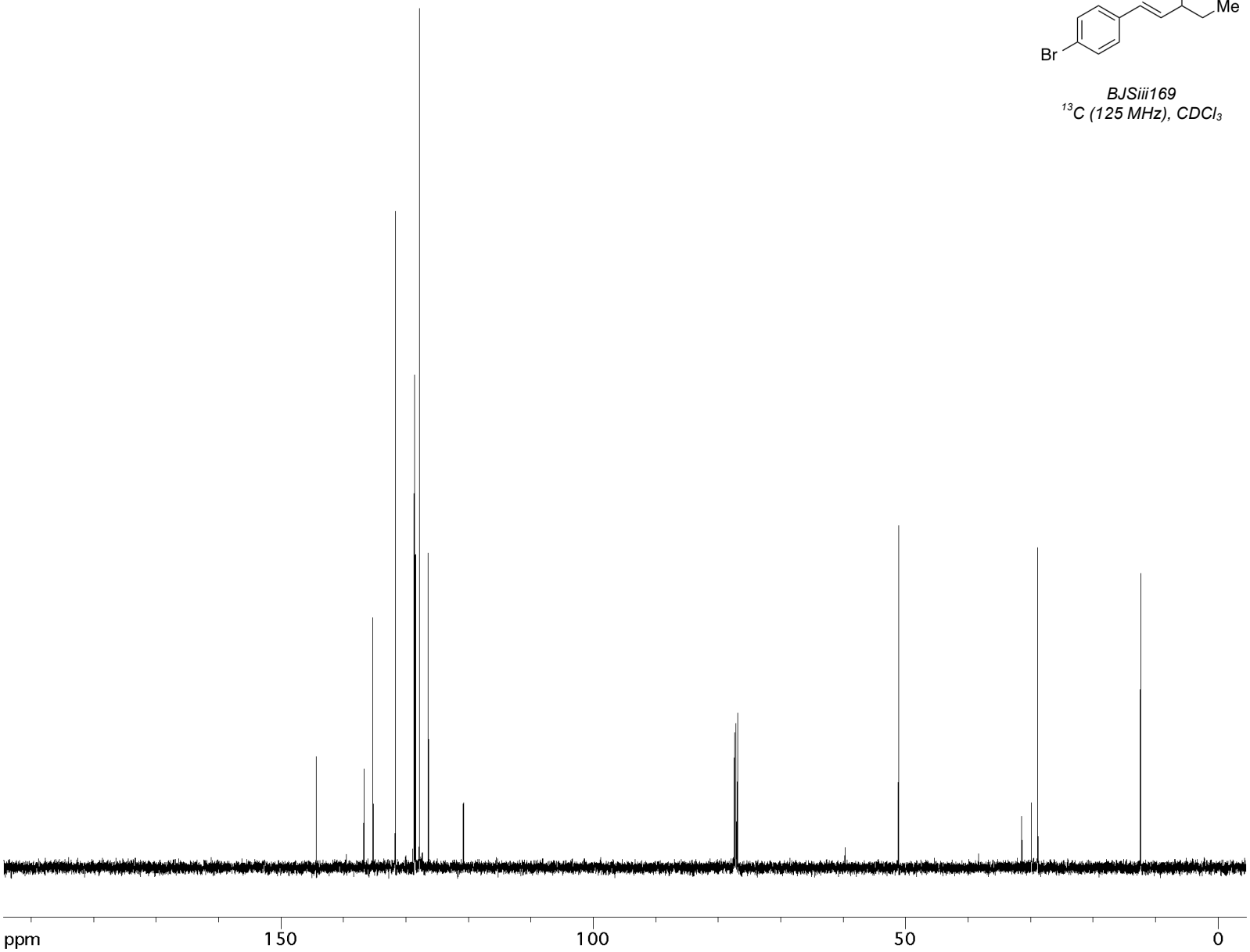
BJSiii169
^{1}H (500 MHz), $CDCl_3$



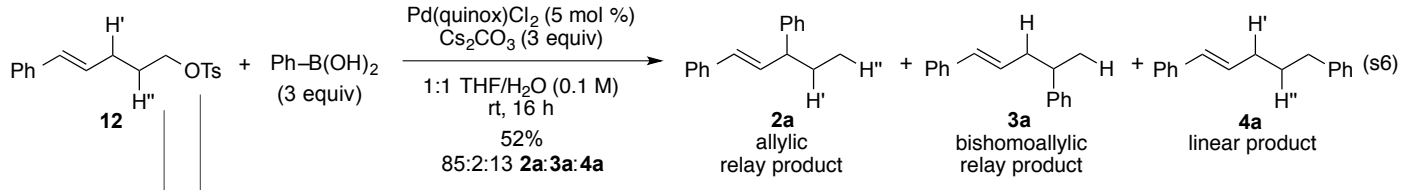
6f

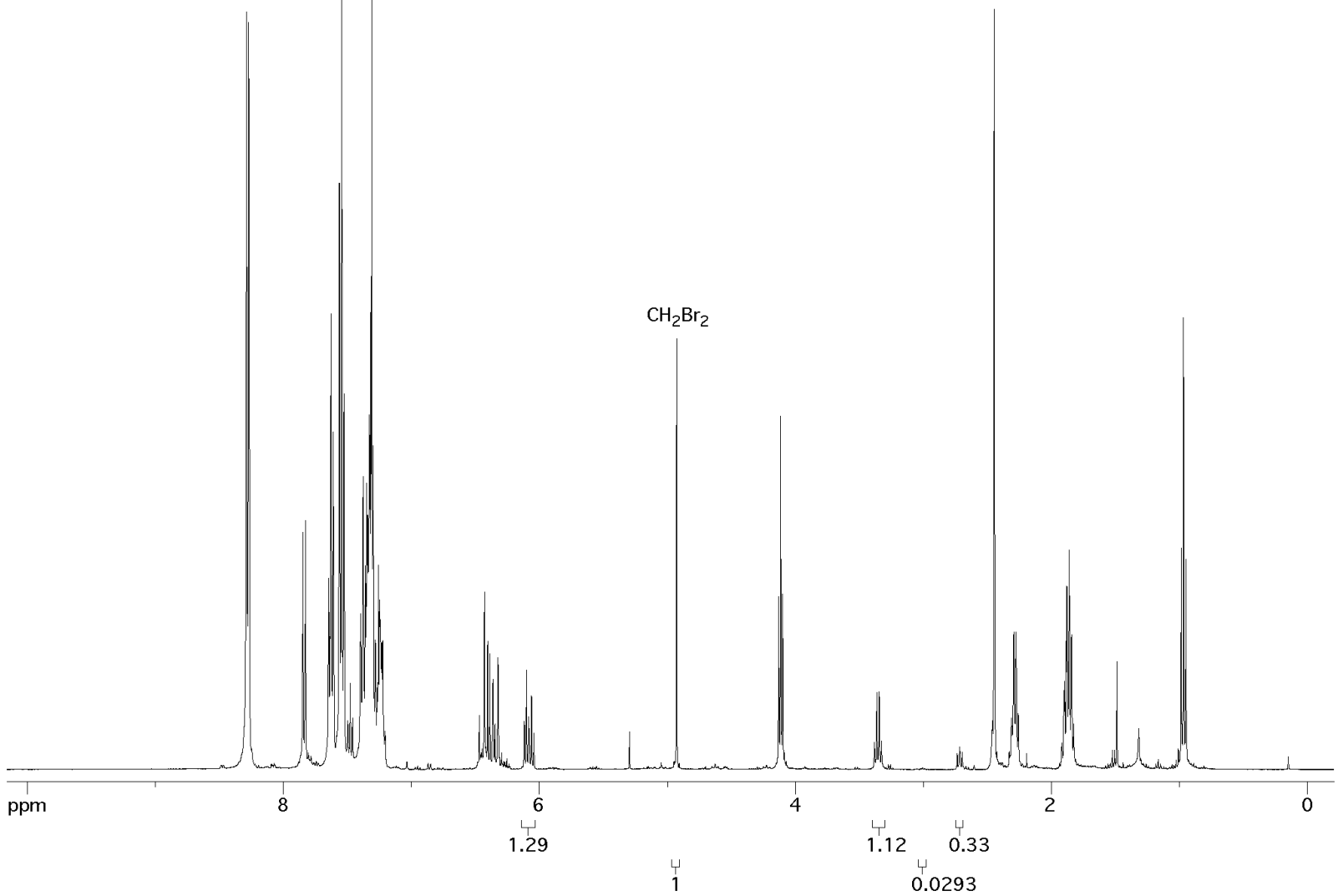


BJSiii169
^{13}C (125 MHz), $CDCl_3$

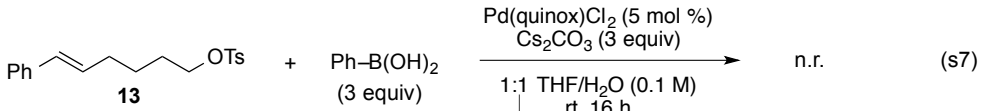


BJSiii059
^{1}H (400 MHz), $CDCl_3$

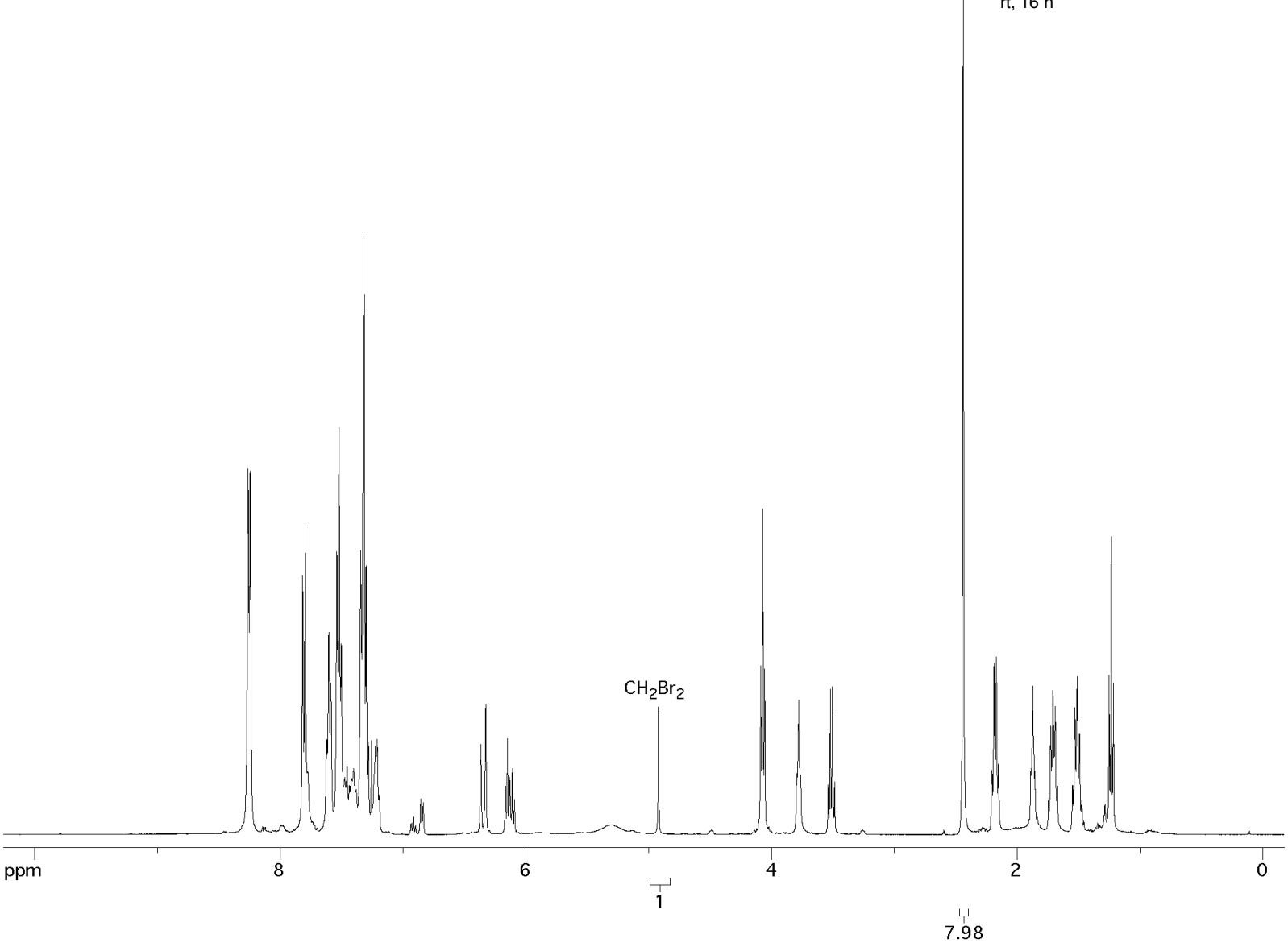




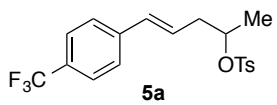
BJSiii100
^{1}H (300 MHz), $CDCl_3$



(s7)

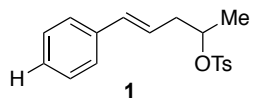


BJSiii109
^{1}H (400 MHz), $CDCl_3$



5a

+



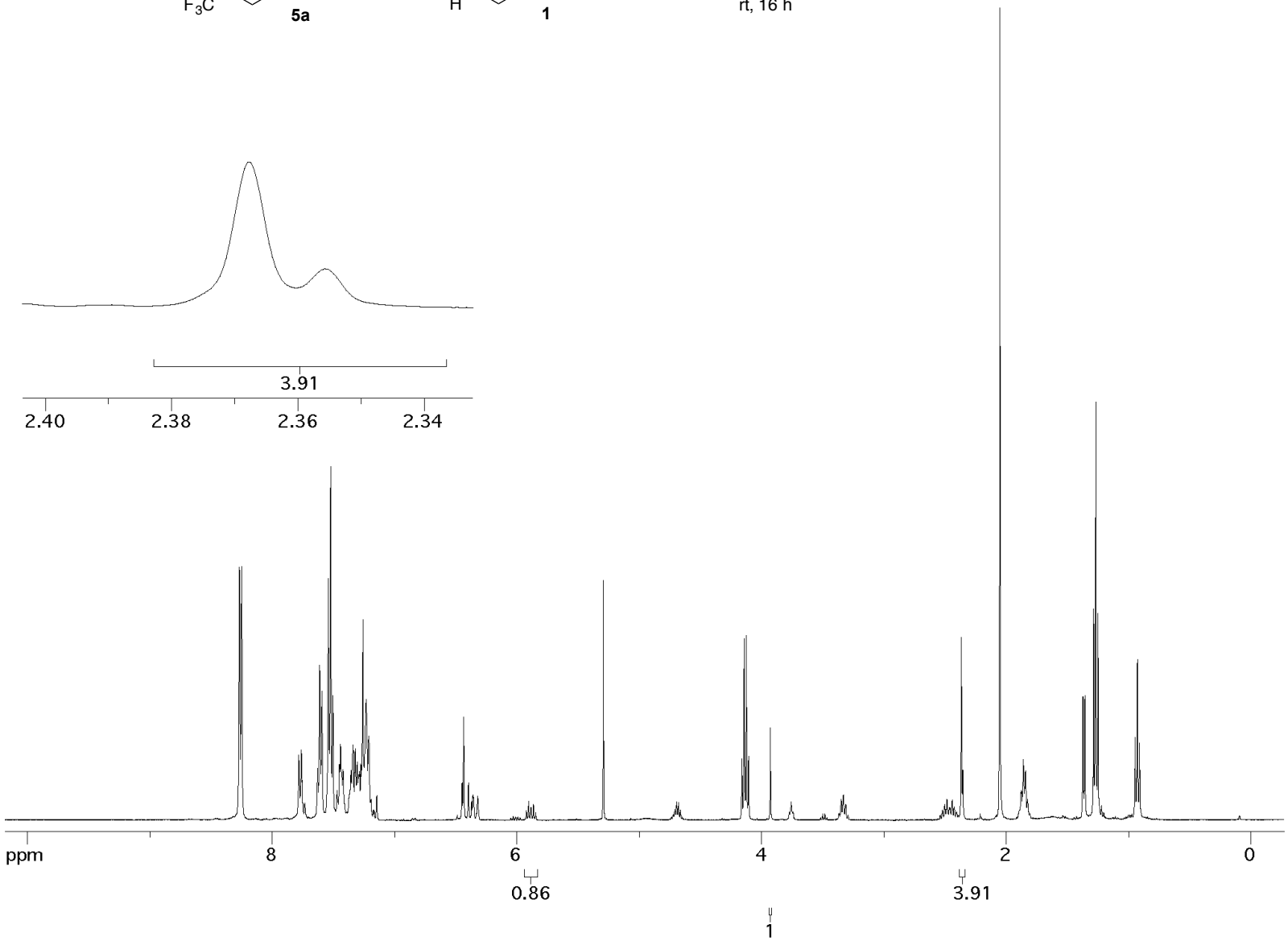
1

$Pd(quinox)Cl_2$ (5 mol %)
Ph–$B(OH)_2$ (3 equiv)
Cs_2CO_3 (3 equiv)

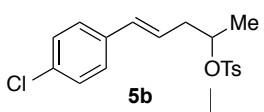
1:1 THF/H_2O (0.1 M)
rt, 16 h

comparison of relative rates of consumption using ^{1}H NMR analysis

(s9)

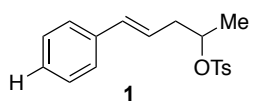


BJSiii110
^{1}H (500 MHz), $CDCl_3$



5b

+



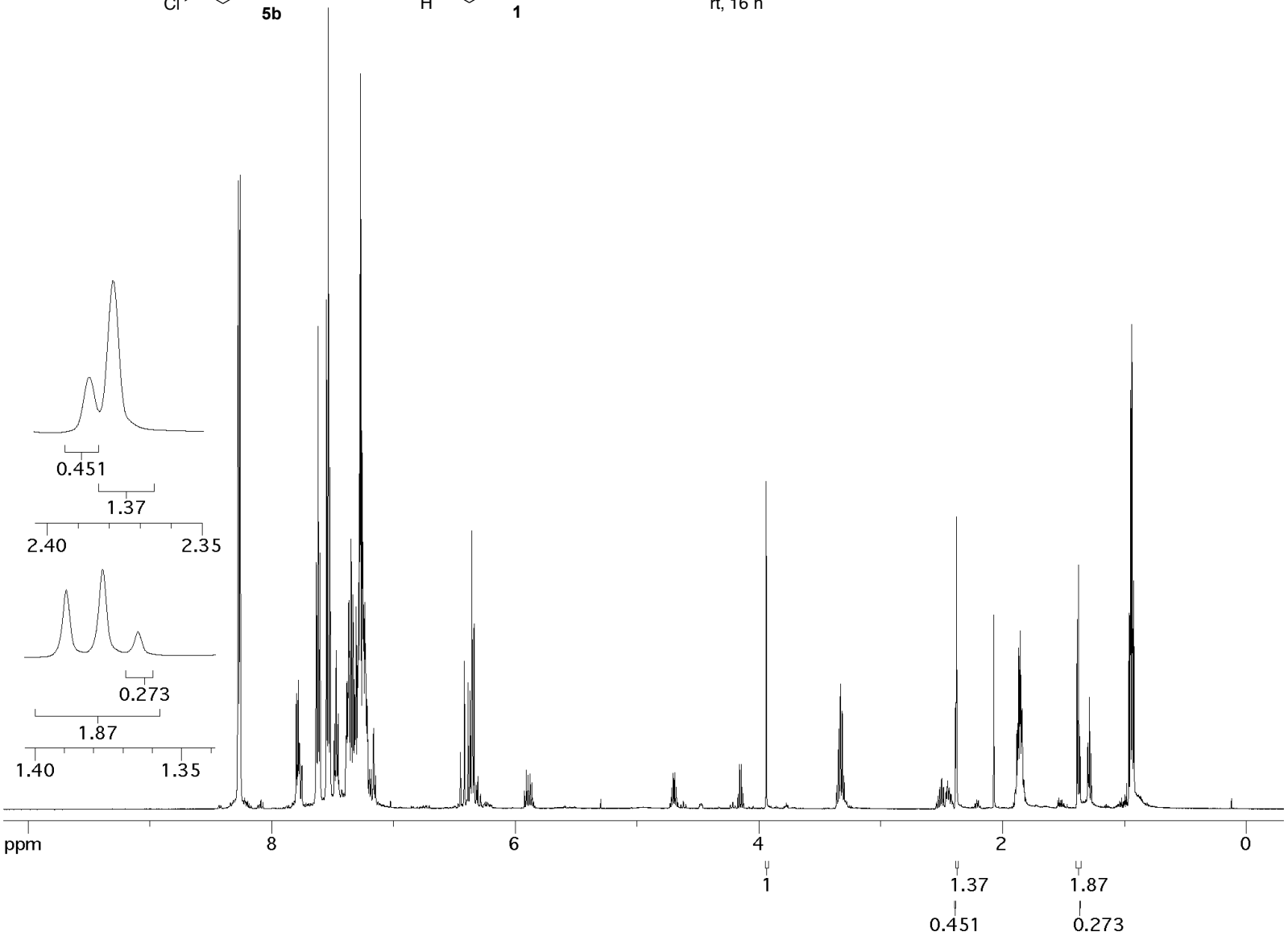
1

$Pd(quinox)Cl_2$ (5 mol %)
Ph–$B(OH)_2$ (3 equiv)
Cs_2CO_3 (3 equiv)

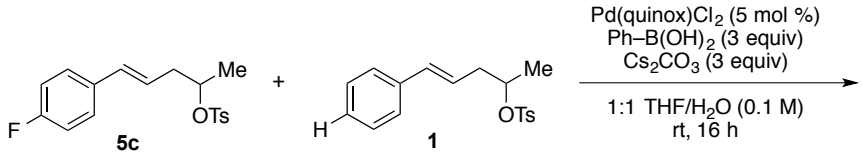
1:1 THF/H_2O (0.1 M)
rt, 16 h

comparison of relative rates of consumption using ^{1}H NMR analysis

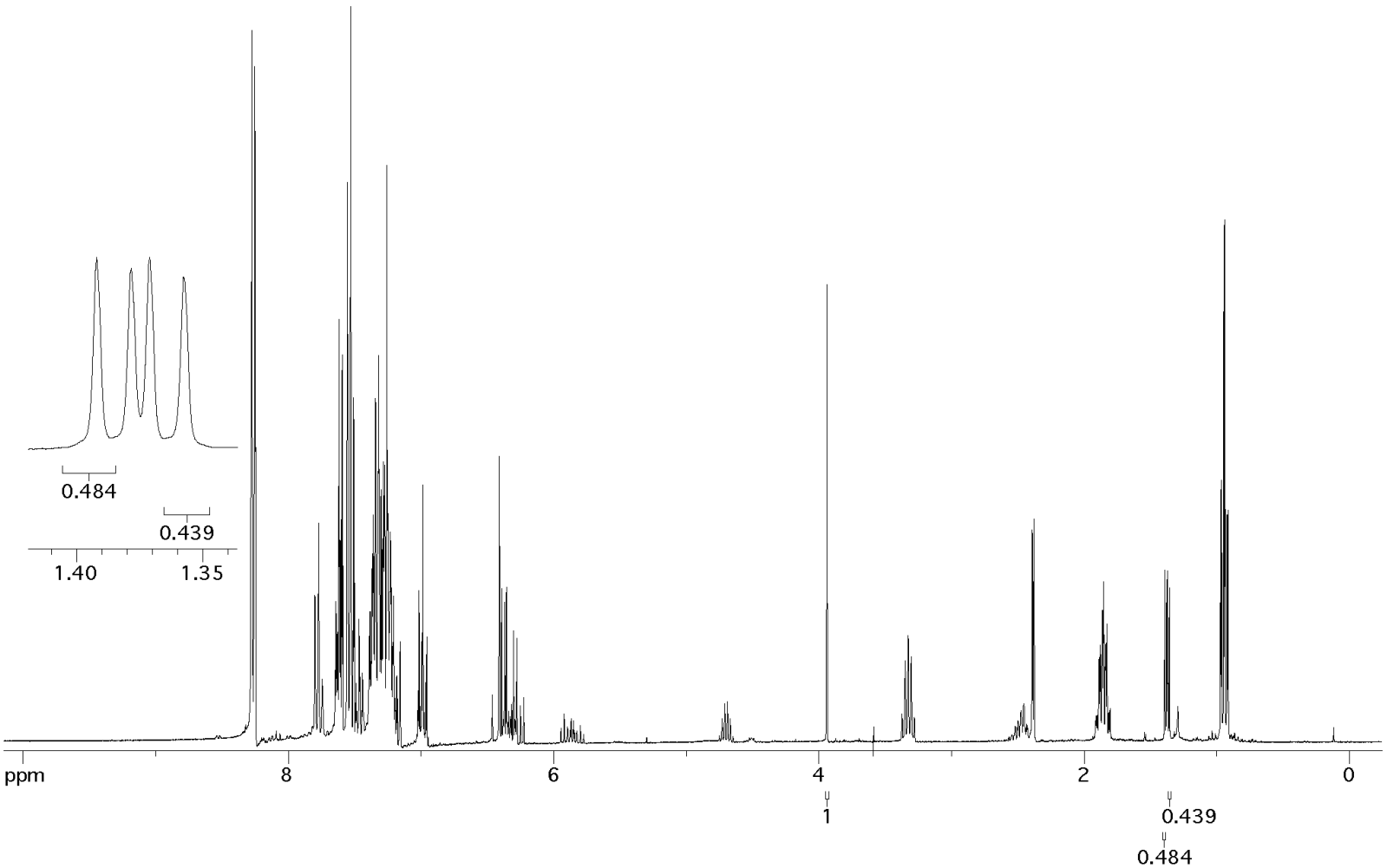
(s10)



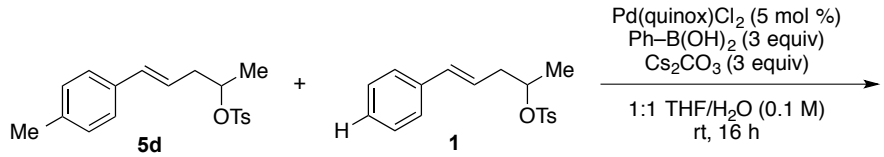
BJSiii173
^{1}H (300 MHz), $CDCl_3$



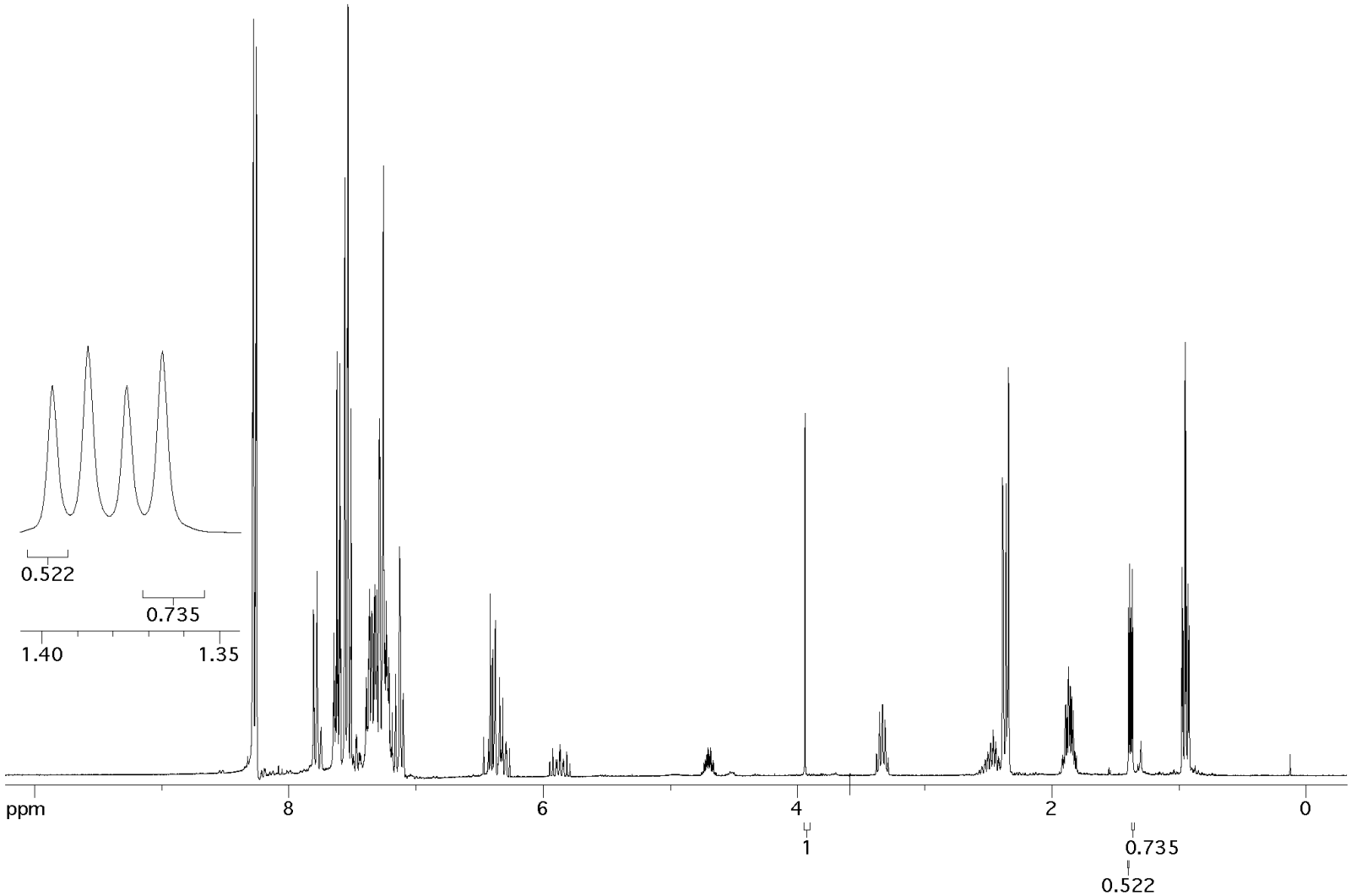
comparison of relative rates of consumption using ^{1}H NMR analysis (s11)



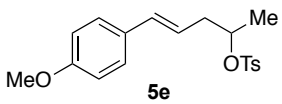
BJSiii172
^{1}H (300 MHz), $CDCl_3$



comparison of relative rates of consumption using ^{1}H NMR analysis (s12)



BJSiii121
^{1}H (400 MHz), $CDCl_3$



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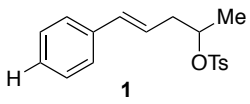
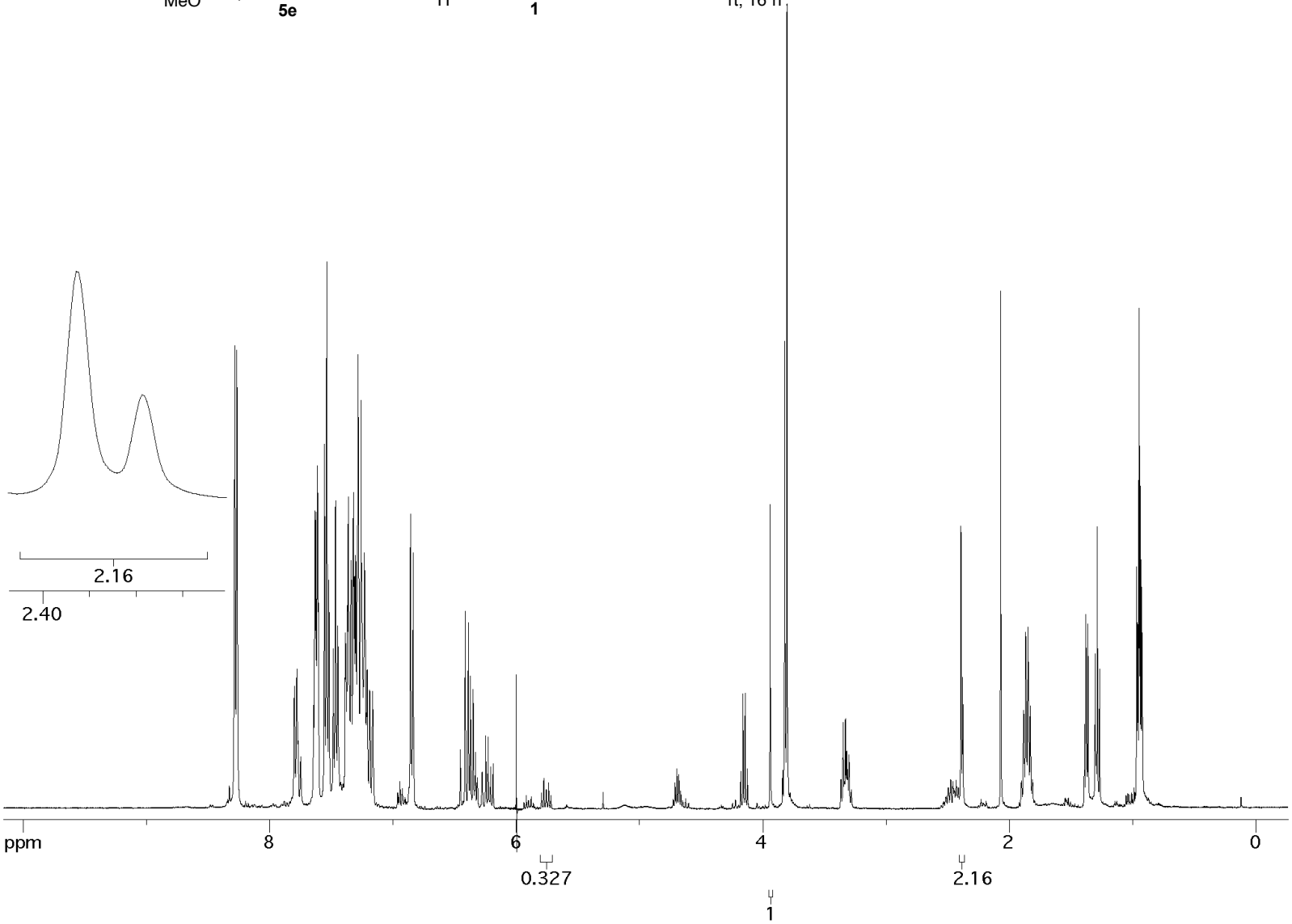
$\xrightarrow[\text{1:1 THF/H}_2\text{O (0.1 M)}, \text{ rt, 16 h}]{\text{Pd(quinox)Cl}_2\text{ (5 mol \%)}, \text{ Ph–B(OH)}_2\text{ (3 equiv)}, \text{ Cs}_2\text{CO}_3\text{ (3 equiv)}}$ comparison of relative rates of consumption using ^{1}H NMR analysis (s13)