

Carbenoid Chain Reactions through Proton, Deuteron, or Bromine Transfer from Unactivated 1-Bromo-1- alkenes to Organolithium Compounds

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Note: Formulae and literature references taken over from the Main Text are utilized with their unchanged numbers, whereas those cited here for the first time are denominated beginning with S.

1. Table S1. Survey of Reaction Conditions and Products, as reported in the Main Text

equivalents of RLi			reagent	solvent	time [min] at $\approx +22\text{ }^{\circ}\text{C}^a$	products in situ	isolated products
applied	consumed						
2.1	PhLi	< 1.4	2a	Et ₂ O	≈ 20	PhLi + 11 + 12 + 2a = 64 : 15 : 67 : 18	mainly 11 ; 7% 9d ; traces of 4a + 9a
1	PhLi	1.0	2a	THF	< 15	almost exclusively 11	no acids 9
4.1	MeLi	1.0	2c	Et ₂ O	≤ 4	exclusively 5c	no acid 9c
2.0	PhC \equiv CLi ^b	–	2c	Et ₂ O	< 5	–	4% 5c , 71% 13c , 2% 13b , 6% 13a , no 5a ; no 9c
≈ 2	MeLi	–	2c	THF	< 7	MeBr + 16 + 5c + 5a = 67 : 36 : 26 : 2	trace of acid 9c
10.0	MeLi	≈ 1	2a	Et ₂ O	$t_{1/2} \approx 20$	–	85% 5a , 16% 9c , no 5c
13.6	MeLi	1	2b	Et ₂ O	$t_{1/2} > 140$	5a + 5b + 5c + 4c + 4b = 43 : 48 : 5 : 3 : 1	–
2.5	MeLi	0.9	2a	THF	< 12	5a + 5c + 4a + 17a = 45 : 27 : 21 : 7	–
2.2	MeLi	0.7	2b	THF	$t_{1/2} \approx 5$	5b + 5c + 4c + 17b = 13 : 44 : 40 : 3	11% acid 9b

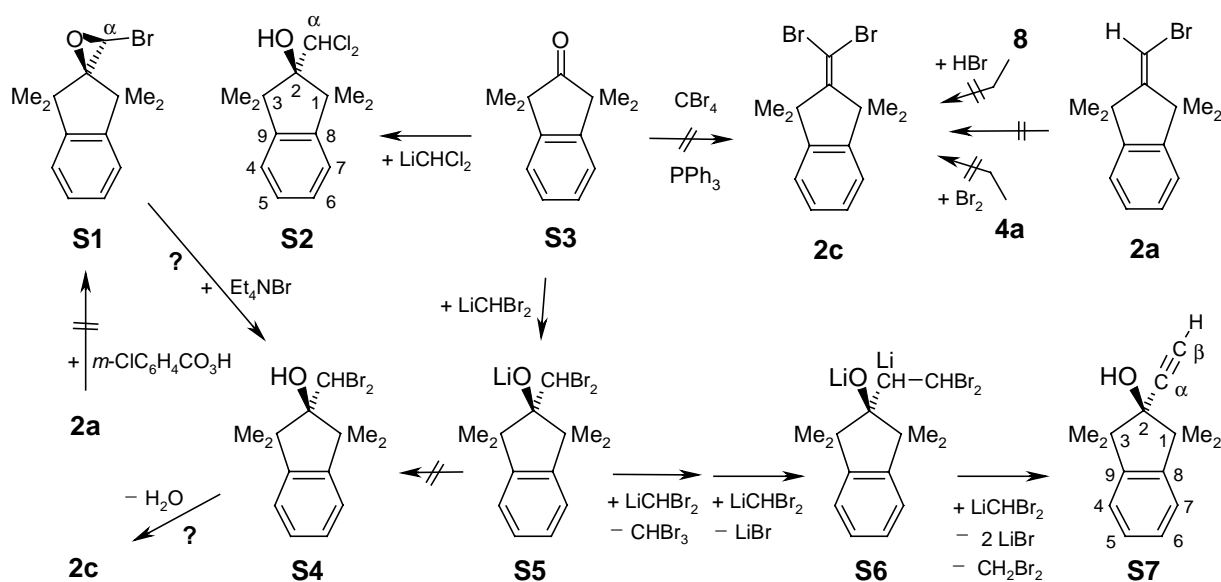
^a $t_{1/2}$ = estimated first half-reaction time. ^b Initiated by 0.1 + 0.1 equiv of MeLi.

2. Further Attempts toward the Dibromo Reagent **2c**

A synthesis of the dibromo reagent **2c** was presented in the Main Text. The shortest possible alternative route from 1,1,3,3-tetramethyl-2-indanone^{S1} (**S3**) to **2c** with the CBr₄/PPh₃ reagent in 1,2-dichlorobenzene at +156 °C led to the reisolation of **S3** after 22 hours, as anticipated from previous experience^{24,S2} with other sterically congested ketones. The bromoalkene **2a** did not react with *N*-

bromosuccinimide or with *m*-chloroperbenzoic acid, the latter in an attempt to form the α -bromo-derivative of oxirane **S1**, which was supposed to give the dibromide **S4** by nucleophilic bromination, with the intention of a final conversion of **S4** to **2c**. Elemental bromine converted **2a** to a mixture of unidentified products, and Hg(OAc)₂ plus F₃CCO₂H reacted slowly at the aromatic part of **2a**. In a further search of **2c** (or the analogous α,α -diiodoalkene), the dichloroalkene **8** was recovered unchanged from treatment with conc. HBr in dioxane (one day at +80 °C) or with Et₄N⁺Br⁻ (or NaI) in

Scheme S1



N,N-dimethylformamide at +110 °C (> 15 h). In spite of model reactions in the literature,^{S3} the chlorine atoms in **S2**⁶ could not be exchanged with iodide (by NaI) or bromide (by Et₄N⁺Br⁻ to give **S4**) in *N,N*-dimethylformamide at +110 °C (> 15 h). In analogy with **S2** ← **S3**,⁶ the preparation of **S4** was also tried from ketone **S3** with dibromomethyl lithium (LiCHBr₂). Although the expected alcoholate **S5** was probably^{S4} formed, it could not be converted to **S4** but was presumably consumed in a more rapid Br/Li interchange reaction with another equivalent of LiCHBr₂ to give the Br,Li-carbenoid of **S5**, which is thought to pick up LiCHBr₂ in the fast substitution reaction affording **S6**. Two further equivalents of LiCHBr₂ would be required in forming the O,C-dilithio derivative of the only isolated

product **S7**, in accord with the mediocre yield of **S7** and the amount of recovered ketone **S3**. This unwelcome sequence did not disturb the successful preparation⁶ of the dichloride **S2** from **S3**, because its initiation would have involved a usually more difficult Cl/Li interchange reaction of **S2**.

2-Ethynyl-1,1,3,3-tetramethyl-2-indanol (S7). *n*-Butyllithium (3.80 mL, 9.50 mmol) in hexane was added slowly to *N,N*-dicyclohexylamine (1.90 mL, 9.54 mmol) in anhydrous THF (10 mL), cooled at -70 °C. The precipitated lithium dicyclohexylamide was dissolved through warming to room temperature. This solution was added over one hour with stirring to the cooled (-70 °C) solution of CH_2Br_2 (0.60 mL, 8.60 mmol) and 1,1,3,3-tetramethyl-2-indanone^{S1} (**S3**, 400 mg, 2.13 mmol) in anhydrous THF (5 mL). After another 90 min at -70 °C, the mixture was poured onto 2 M HCl (30 mL) and diethylether (Et_2O , 30 mL). The precipitated *N,N*-dicyclohexylammonium chloride was washed thoroughly with Et_2O and then discarded. The Et_2O phases were combined, washed until neutral, dried over Na_2SO_4 , and concentrated to furnish a brown oil (706 mg) containing **S7** as the main product and residual ketone **S3** in a 41:59 ratio (41% conversion). After separation from **S3** on a small column of silicagel (4.0 g) by washing with petroleum ether containing some CHCl_3 , 144 mg (32%) of crude **S7** were obtained by elution with CHCl_3 and with ethanol. Pure **S7** distilled at $92\text{--}118$ °C (bath temp.)/0.014 mbar as a colorless oil: ^1H NMR (400 MHz, CDCl_3) δ 1.40 and 1.42 (2 s, 2 + 2 1-/3- CH_3), 1.99 (broad s, OH), 2.62 (s, $\equiv\text{CH}$), \approx 7.15 (m, 4-/7-H), \approx 7.20 (m, 5-/6-H); ^{13}C NMR (100.6 MHz, CDCl_3) δ 23.2 and 30.2 (2 qq, $^1J = 127.3$ Hz, $^3J = 4.9$ Hz, 2 + 2 1-/3- CH_3), 50.8 (unresolved, $\text{C}^{1,3}$), 76.0 (d, $^1J = 249.9$ Hz, C^β), 83.2 (d, $^2J = 48.8$ Hz, C^α), 85.2 (unresolved, C^2), 122.8 (dm, $^1J = 157$ Hz, $\text{C}^{4,7}$), 127.3 (ddm, $^1J = 159.6$ Hz, $^3J = 7.1$ Hz, $\text{C}^{5,6}$), 147.5 (m, $^3J \approx 3.6$ Hz, $\text{C}^{8,9}$), assigned by comparison with 2-ethynyl-1,1,3,3-tetramethylindan;^{S5} IR (film) 3560 and 3484 (2 broad O–H), 3305 ($\equiv\text{C}\text{--H}$), 2987, 2965, 2928, 2868, 2110 (vw, $\text{C}\equiv\text{C}$), 1482, 1021, and 754 cm^{-1} . Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}$ (214.3): C, 84.07; H, 8.47. Found: C, 83.47; H, 8.41.

3. Preparation of a THF Solution of Trimethylstannyl lithium

Trimethylstannyl lithium.²⁰⁻²² Elemental lithium (850 mg, 122.5 mmol) was hammered to flat sheets which were then cut into small pieces (diameter 2–3 mm) in a stream of dry argon gas escaping from a dried Schlenk flask (50 mL), so that the Li pieces fell down into the flask that contained a magnetic bar and the dried fragments of a freshly crushed glass tube (≈ 1 g). Anhydrous THF was added to the flask in an amount (2–4 mL) that was sufficiently small to allow the Li pieces to be scratched (hence activated) by the sharp glass fragments^{S6} when stirred rapidly. The solvent became opaque after several min and was withdrawn through a pipet. Stirring was continued after the addition of fresh THF (3 mL) plus four drops of methanol which etched the Li surface within the next 15 min. The solvent was withdrawn, and the Li pieces (now with a silvery surface) were stirred vigorously with pure THF (3 mL) for 5 min. Such washing was repeated (3 \times) until the solution remained clear after 5 min of stirring, whereupon fresh THF (7 mL) was added to the activated lithium. The flask was fitted to a pressure-equalizing dropping funnel containing chlorotrimethylstannane (2.35 g, 11.8 mmol) in anhydrous THF (10 mL), and 2 mL of this solution were dropped into the flask with stirring. As soon as the mixture turned green³⁰ (30–40 min), the flask was cooled in ice, and the remaining ClSnMe_3 solution was added slowly (30 min) with vigorous stirring so that the glass fragments could shave the precipitating LiCl from the Li pieces. After another 30 min, the olive-colored solution was separated from the insoluble components through pipeting into another dried Schlenk flask; it should now contain LiSnMe_3 ($^1\text{H NMR } \delta -0.33$)^{S7} in a concentration < 0.7 M and is stable at -20 °C²² but will lose 30% of LiSnMe_3 when stored at $+5$ °C for seven days.

4. References

- (≠) Sterically Congested Molecules, 19. – Part 18: Ref 6.
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- (S1) Knorr, R.; Mehlstäubl, J.; Böhler, P. *Chem. Ber.* **1989**, *122*, 1791–1793 and refs therein.
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- (S4) Taguchi, H.; Yamamoto, H.; Nozaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 3010–3011.
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4. The ^1H and ^{13}C NMR Spectra of **2c**, **5c**, **9c**, **13c**, **16**, **19**, and **S7**

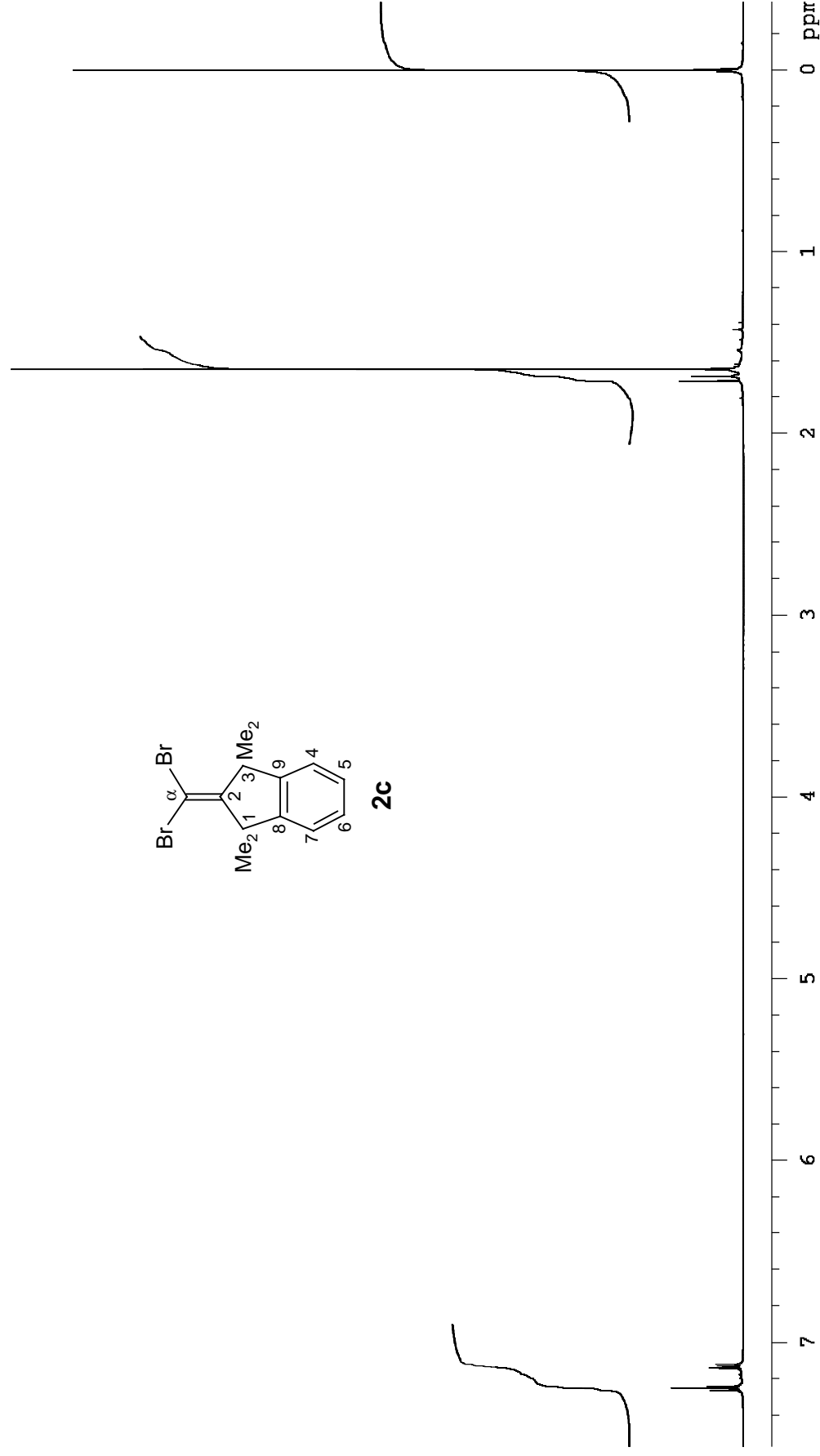


Figure S1. ^1H NMR spectrum of 2-(dibromomethylidene)-1,1,3,3-tetramethylindan (**2c**) in CDCl_3 at $+25\text{ }^\circ\text{C}$ and 400 MHz .

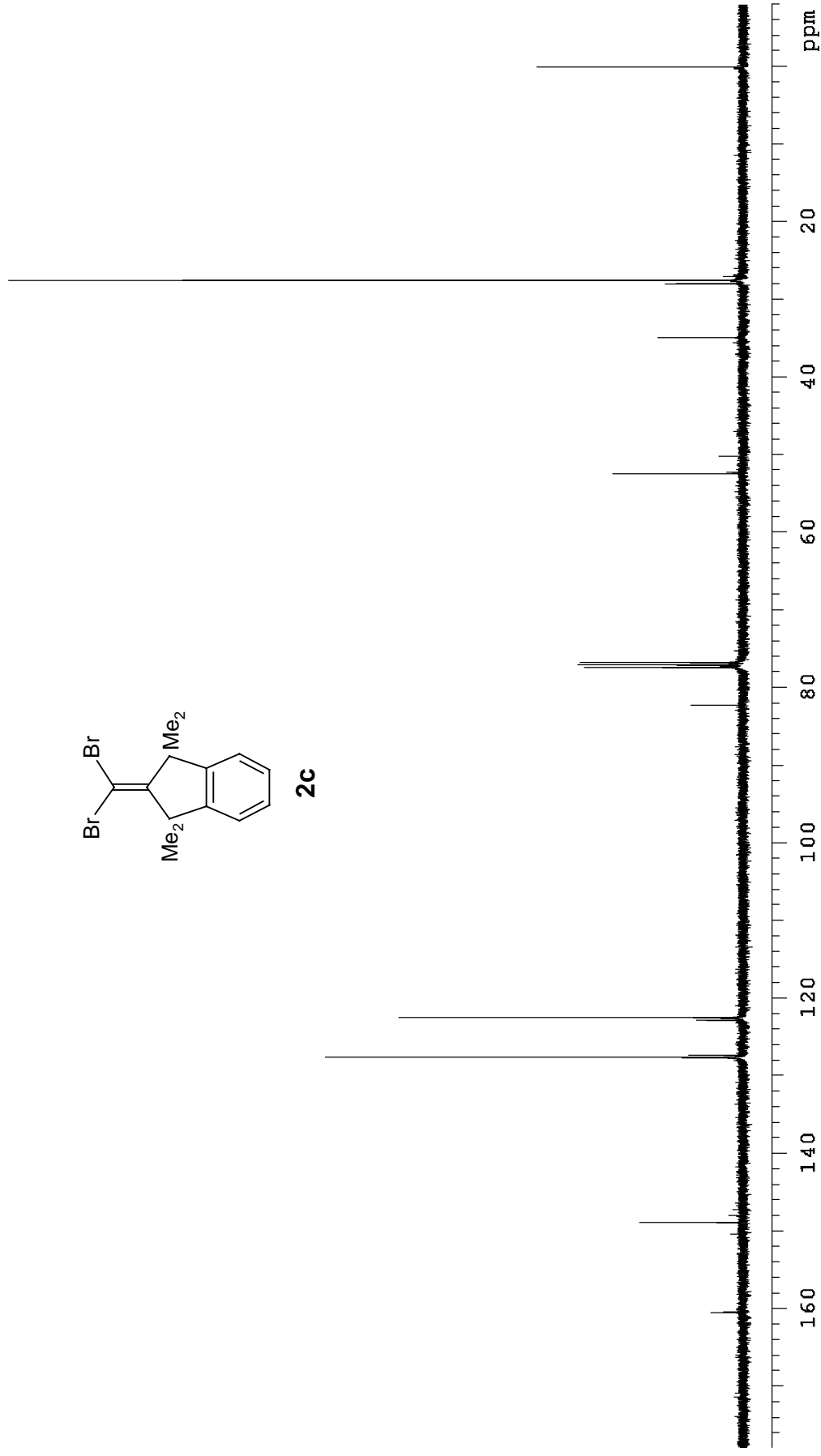


Figure S2. $\{^1\text{H}\}$ decoupled ^{13}C NMR spectrum of 2-(dibromomethylidene)-1,1,3,3-tetramethylindane (**2c**) in CDCl_3 at $+25^\circ\text{C}$, 100.6 MHz .

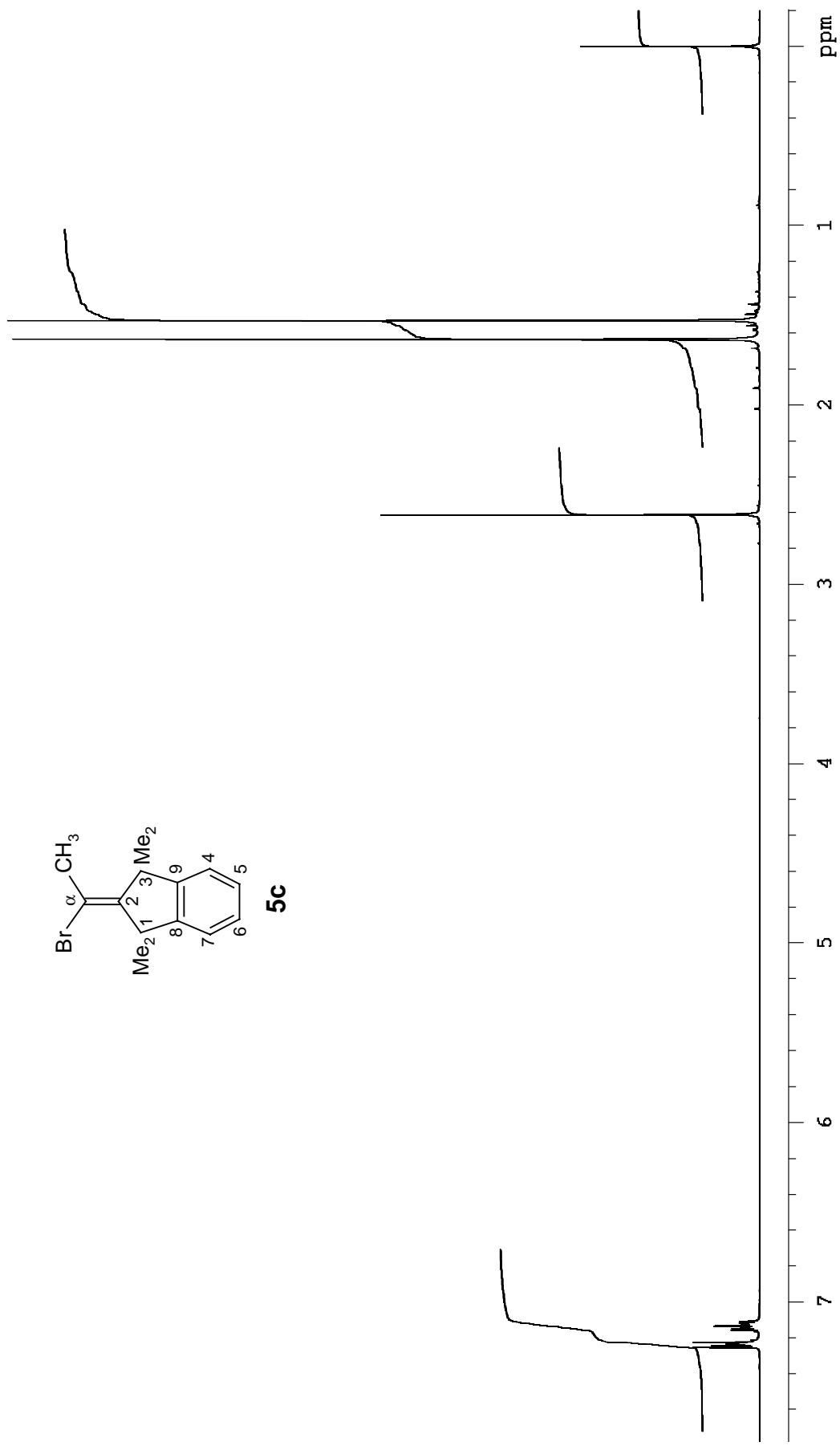


Figure S3. ¹H NMR spectrum of 2-(1-bromoethylidene)-1,1,3,3-tetramethylindan (**5c**) in CDCl₃ at +27 °C and 400 MHz.

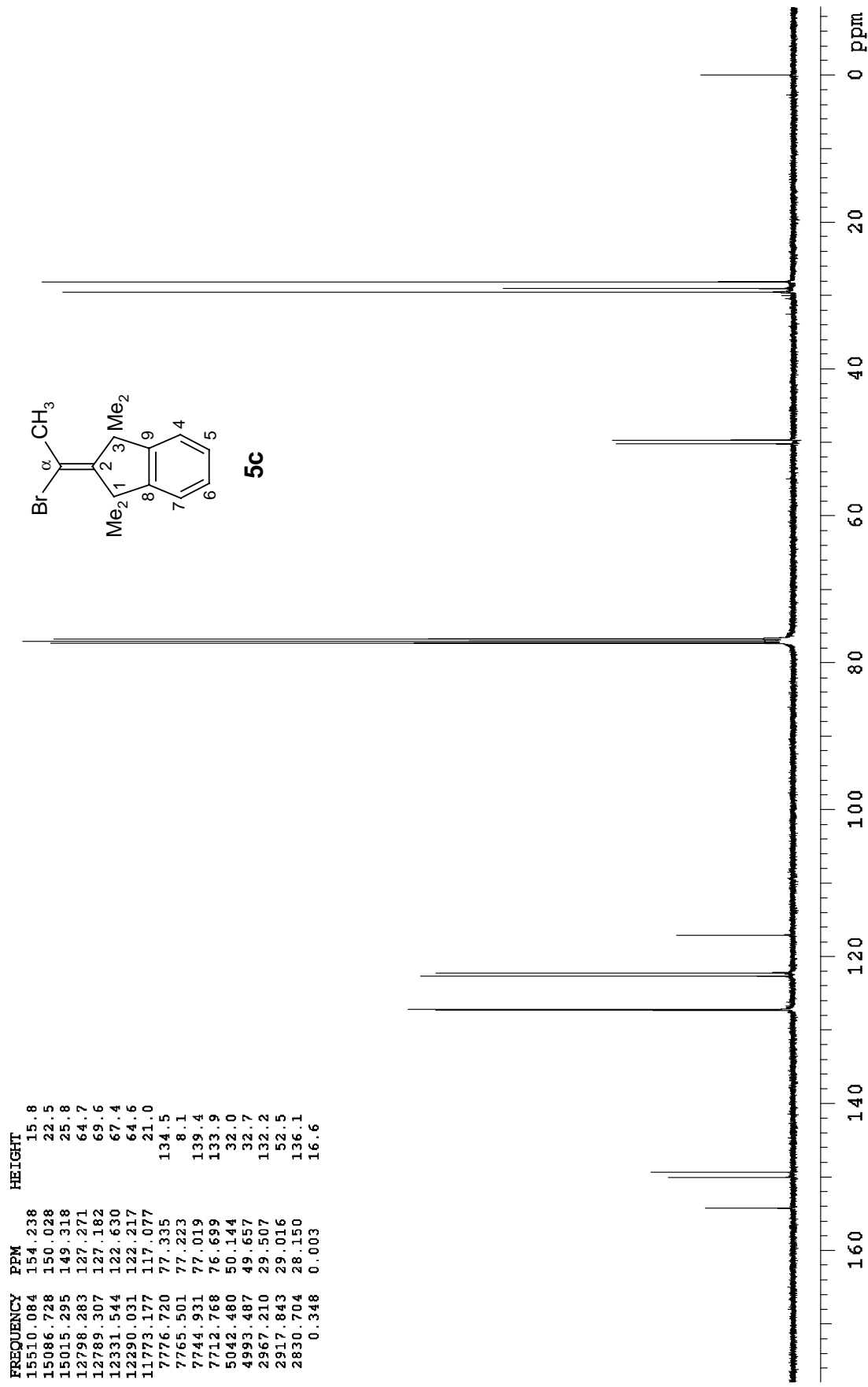


Figure S4. $\{^1\text{H}\}$ decoupled ^{13}C NMR spectrum of 2-(1-bromoethylidene)-1,1,3,3-tetramethylindane (**5c**) in CDCl_3 at $+27^\circ\text{C}$ and 100.6 MHz.

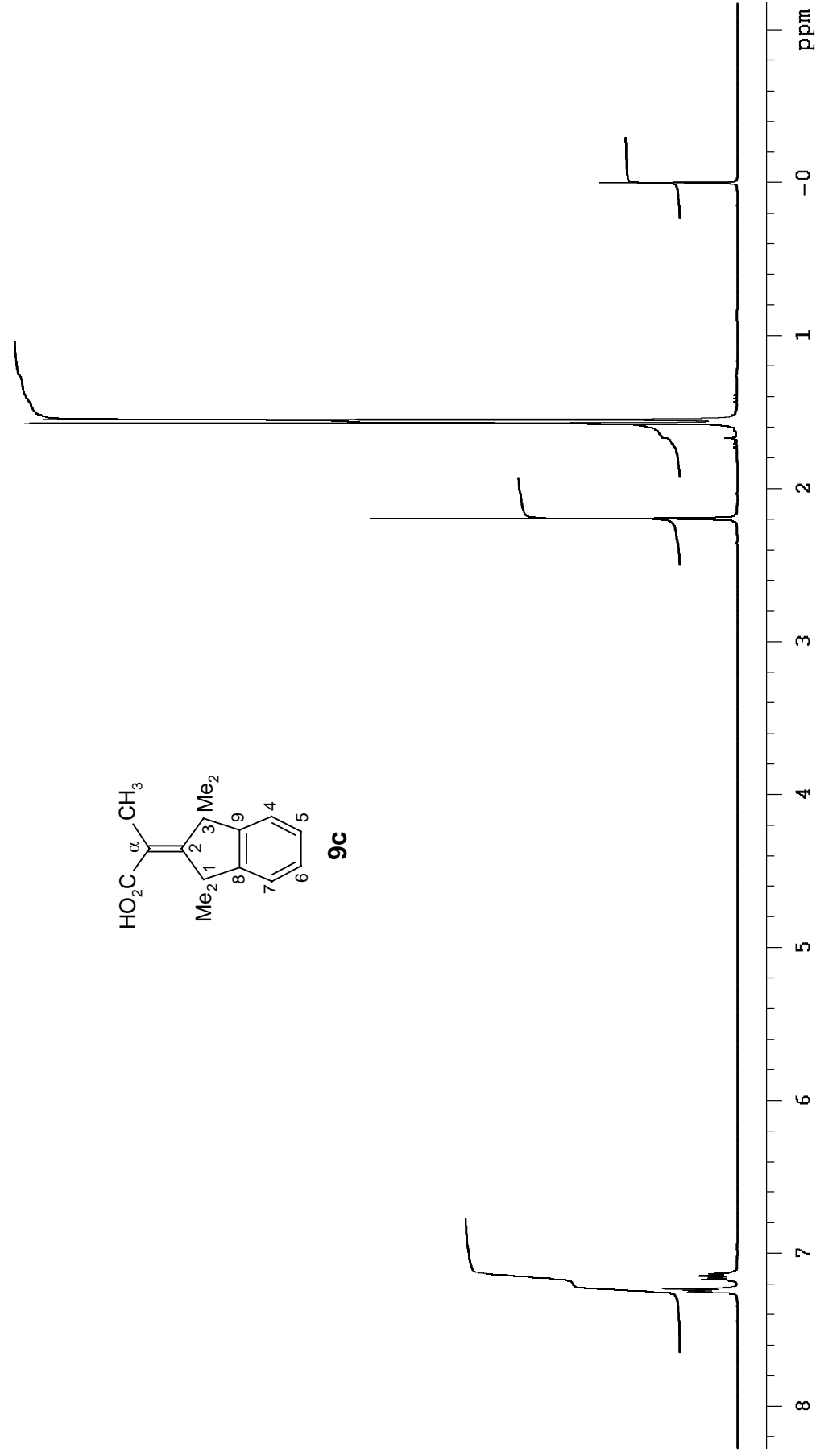


Figure S5. ¹H NMR spectrum of 2-(1,1,3,3-tetramethyl-2-indanylidene)propanoic acid (**9c**) in CDCl₃ at +27 °C and 400 MHz.

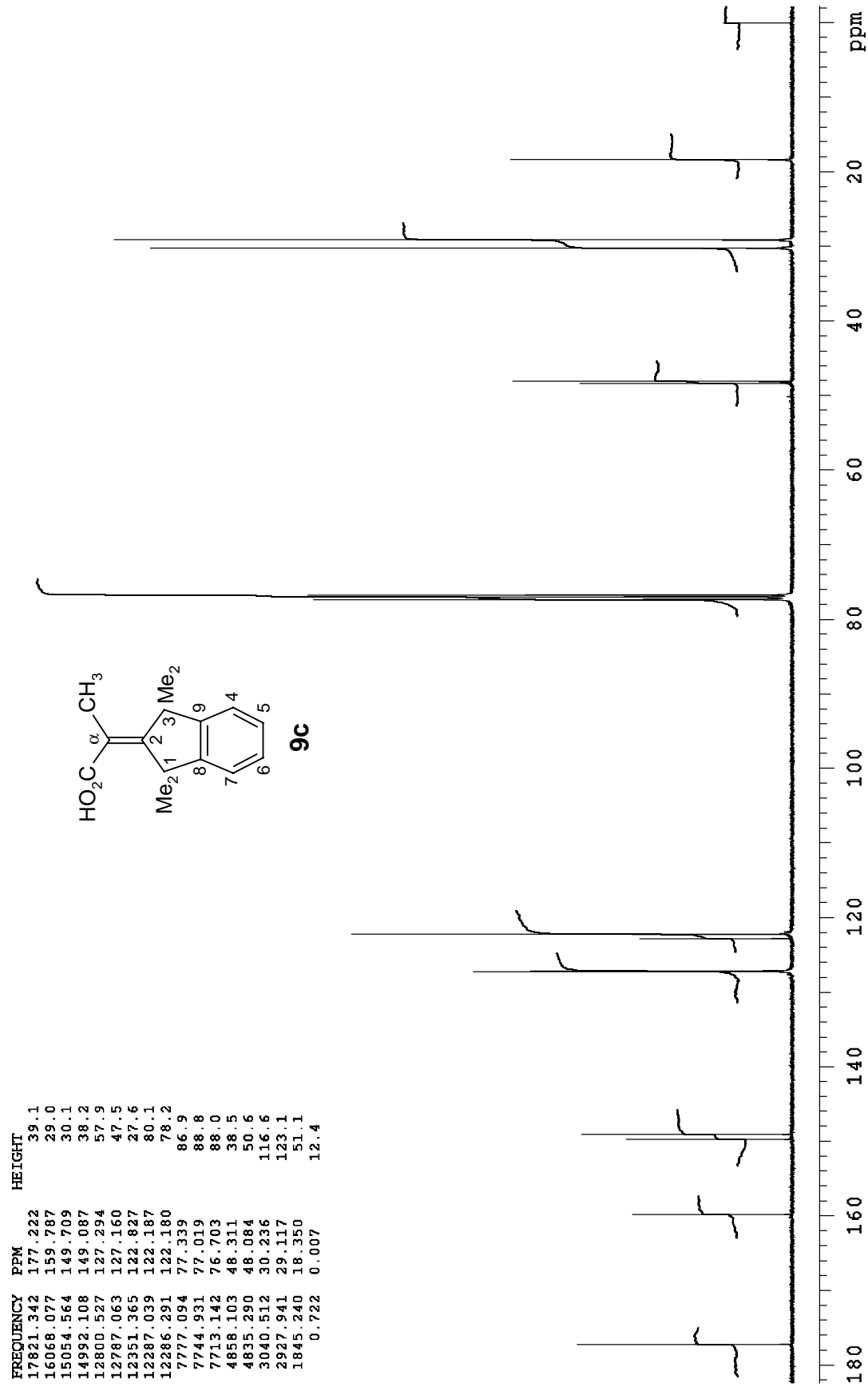


Figure S6. $\{^1\text{H}\}$ decoupled ^{13}C NMR spectrum of 2-(1,1,3,3-tetramethyl-2-indanylidene)propanoic acid (**9c**) in CDCl_3 at $+27\text{ }^\circ\text{C}$, 100.6 MHz.

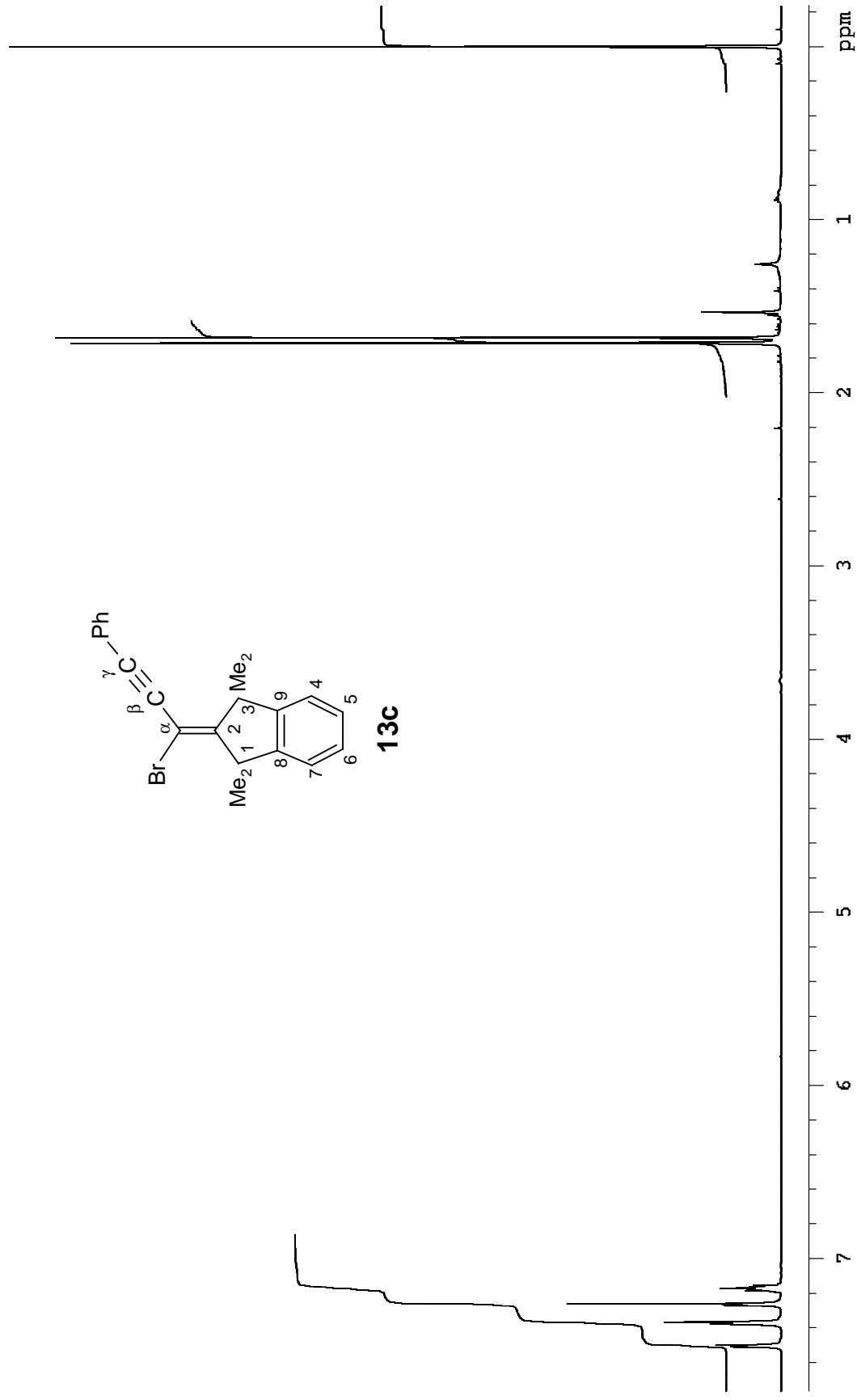


Figure S7. ¹H NMR spectrum of 2-(1-bromo-3-phenyl-2-propyn-1-ylidene)-1,1,3,3,3-tetramethylindane (**13c**) in CDCl₃ at +25 °C, 600 MHz.

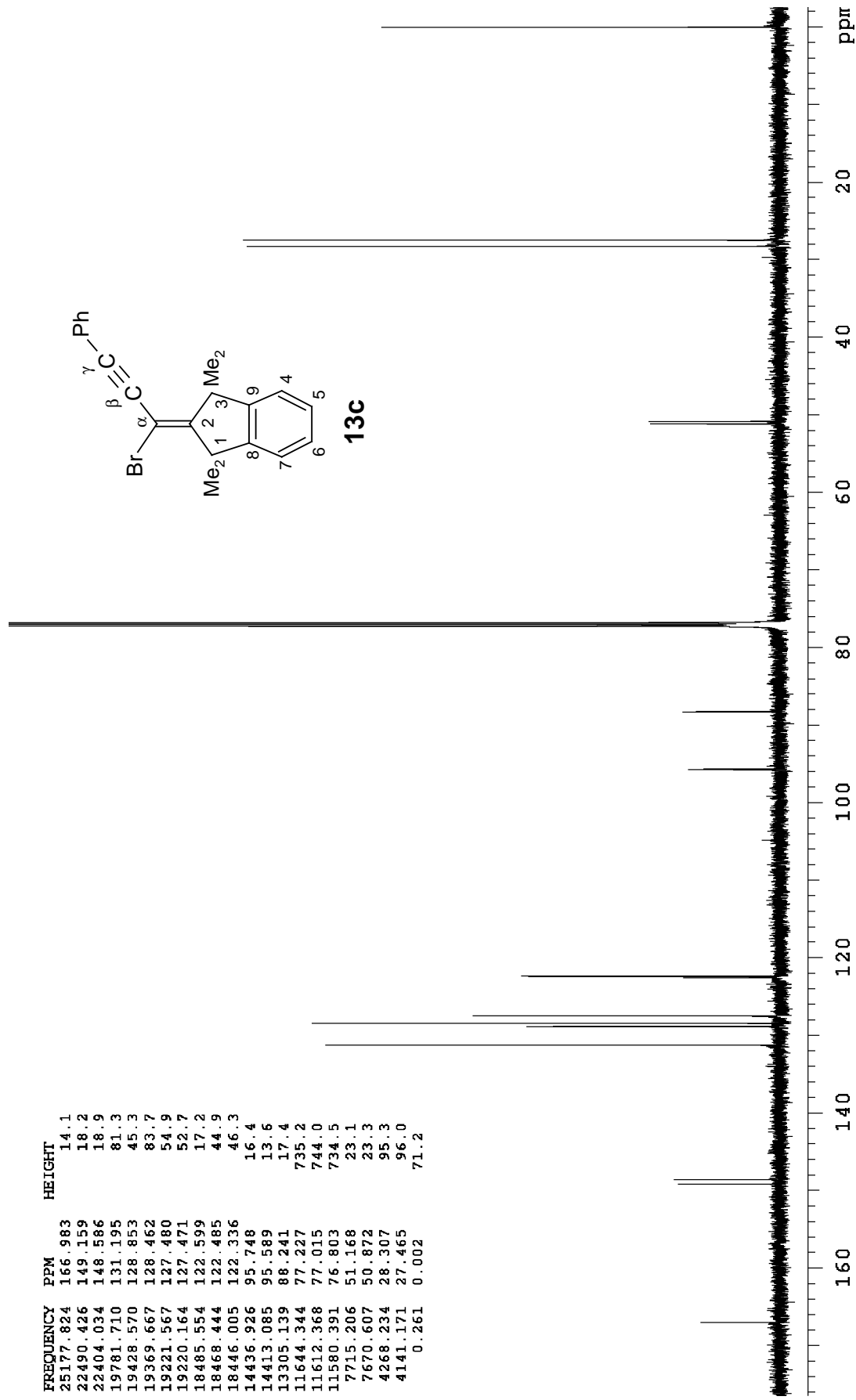


Figure S8. $\{^1\text{H}\}$ decoupled ^{13}C NMR spectrum of 2-(1-bromo-3-phenyl-2-propyn-1-ylidene)-1,1,3,3-tetramethylindane (**13c**) in CDCl_3 at $+25\text{ }^\circ\text{C}$ and 150.8 MHz.

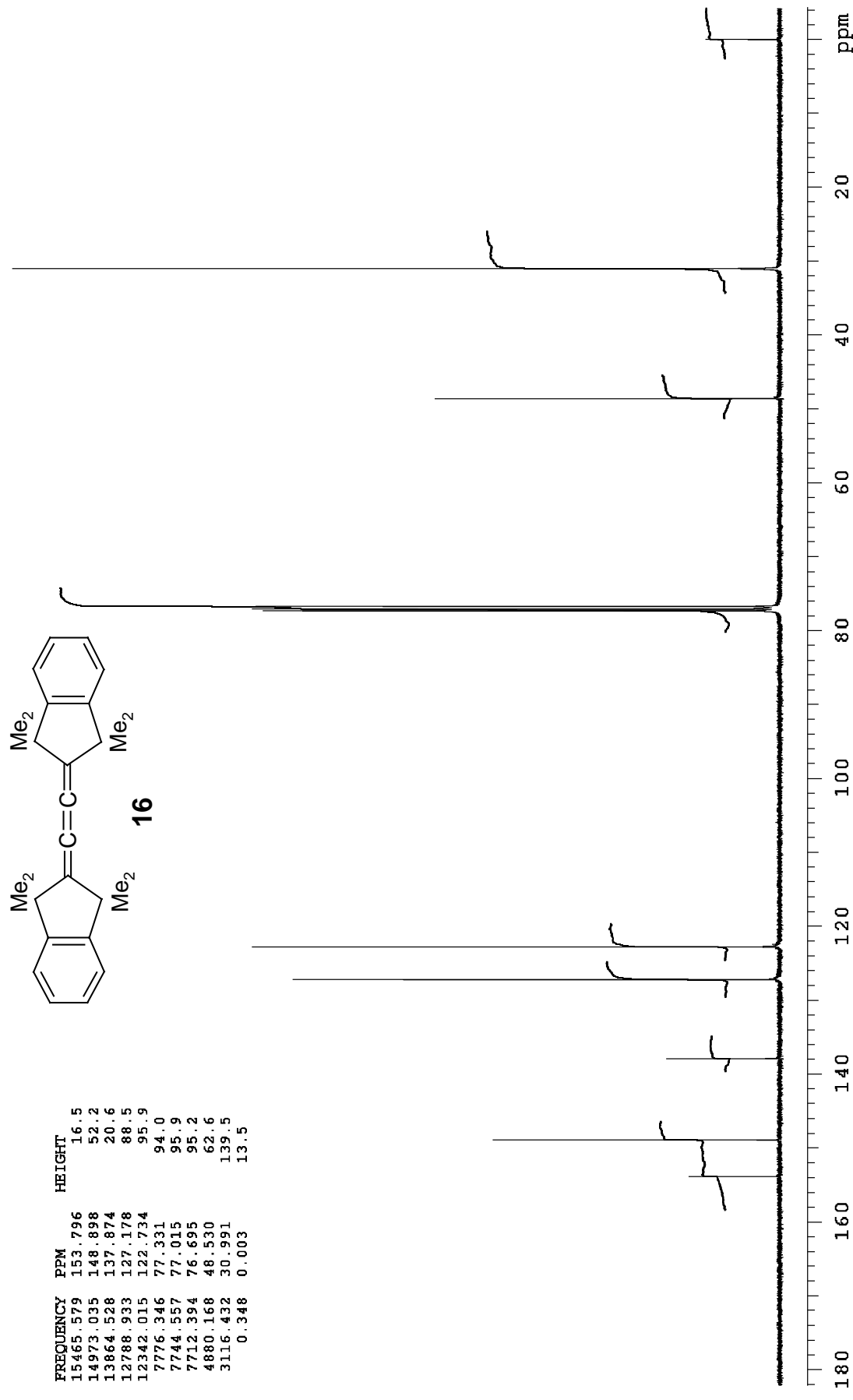
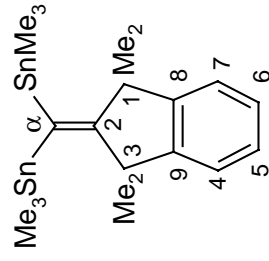


Figure S10. $\{^1\text{H}\}$ decoupled ^{13}C NMR spectrum of 1,2-bis(1,1,3,3-tetramethyl-2-indanylidene)ethene (**16**) in CDCl_3 at $+27\text{ }^\circ\text{C}$, 100.6 MHz.



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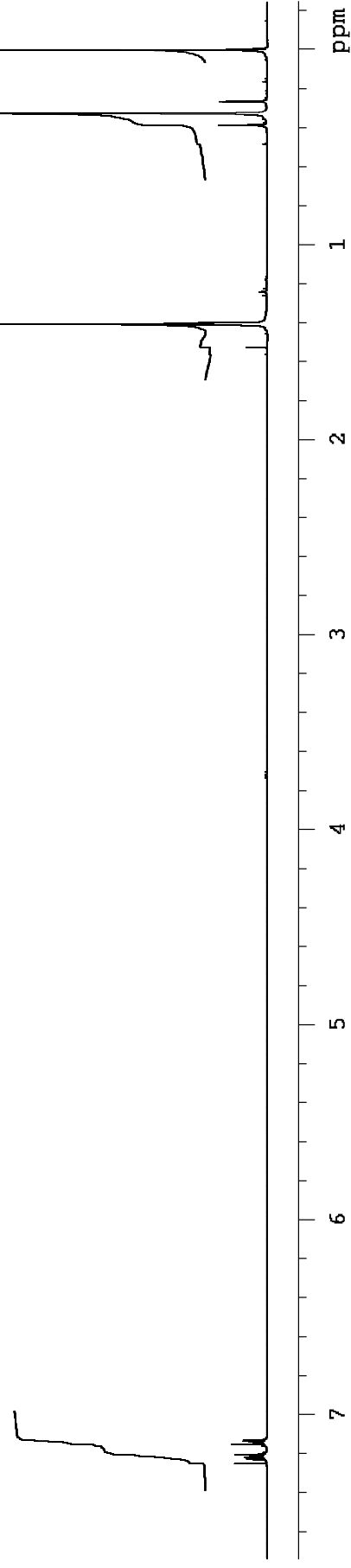


Figure S11. ¹H NMR spectrum of 2-[bis(trimethylstanny)methylidene]-1,1,3,3-tetramethylindan (**19**) in CDCl₃ at +25 °C and 400 MHz.

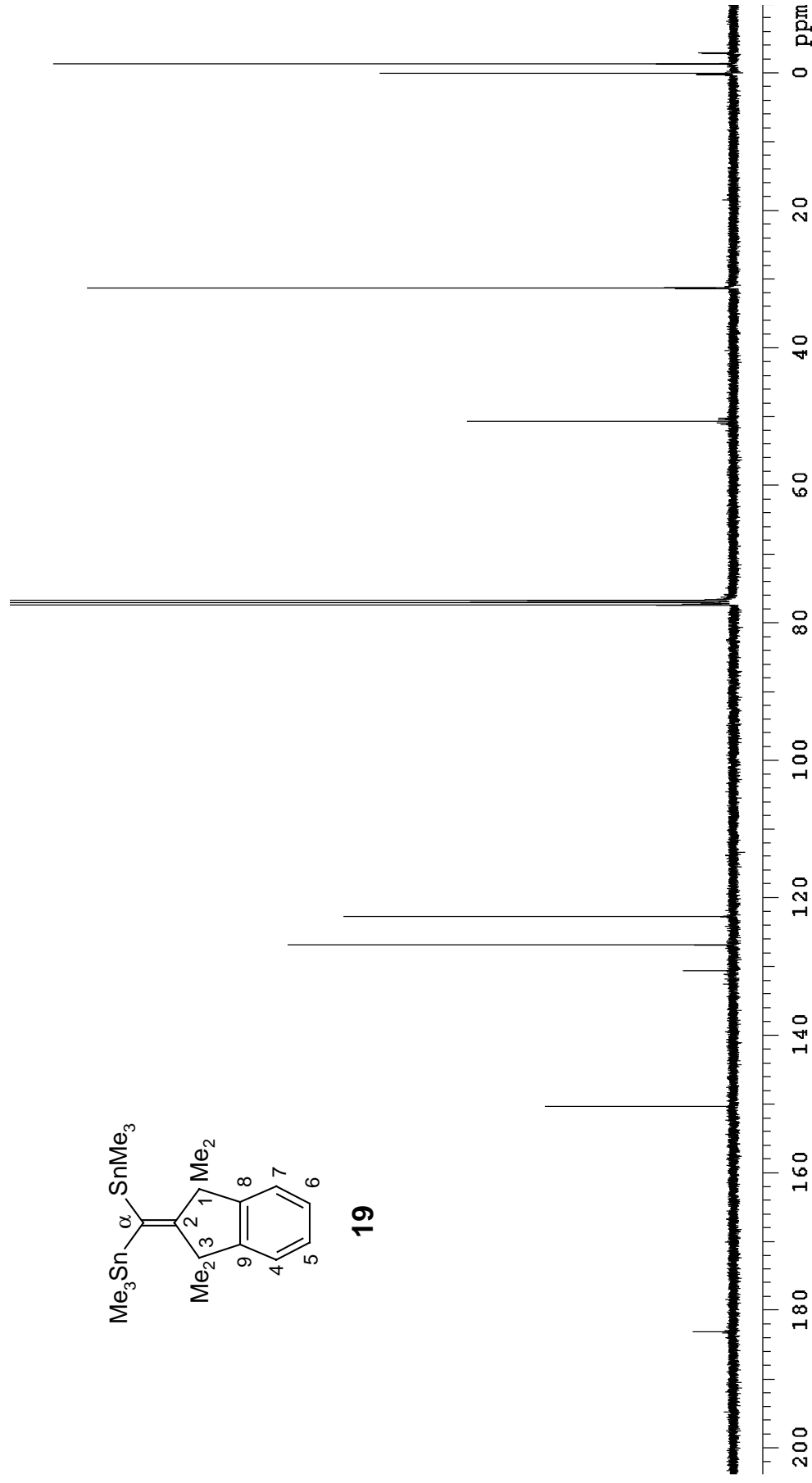


Figure S12. $\{^1\text{H}\}$ decoupled ^{13}C NMR spectrum of 2-[bis(trimethylstannylmethylene)-1,1,3,3-tetramethylindan (**19**) in CDCl_3 at $+25^\circ\text{C}$ and 100.6 MHz.

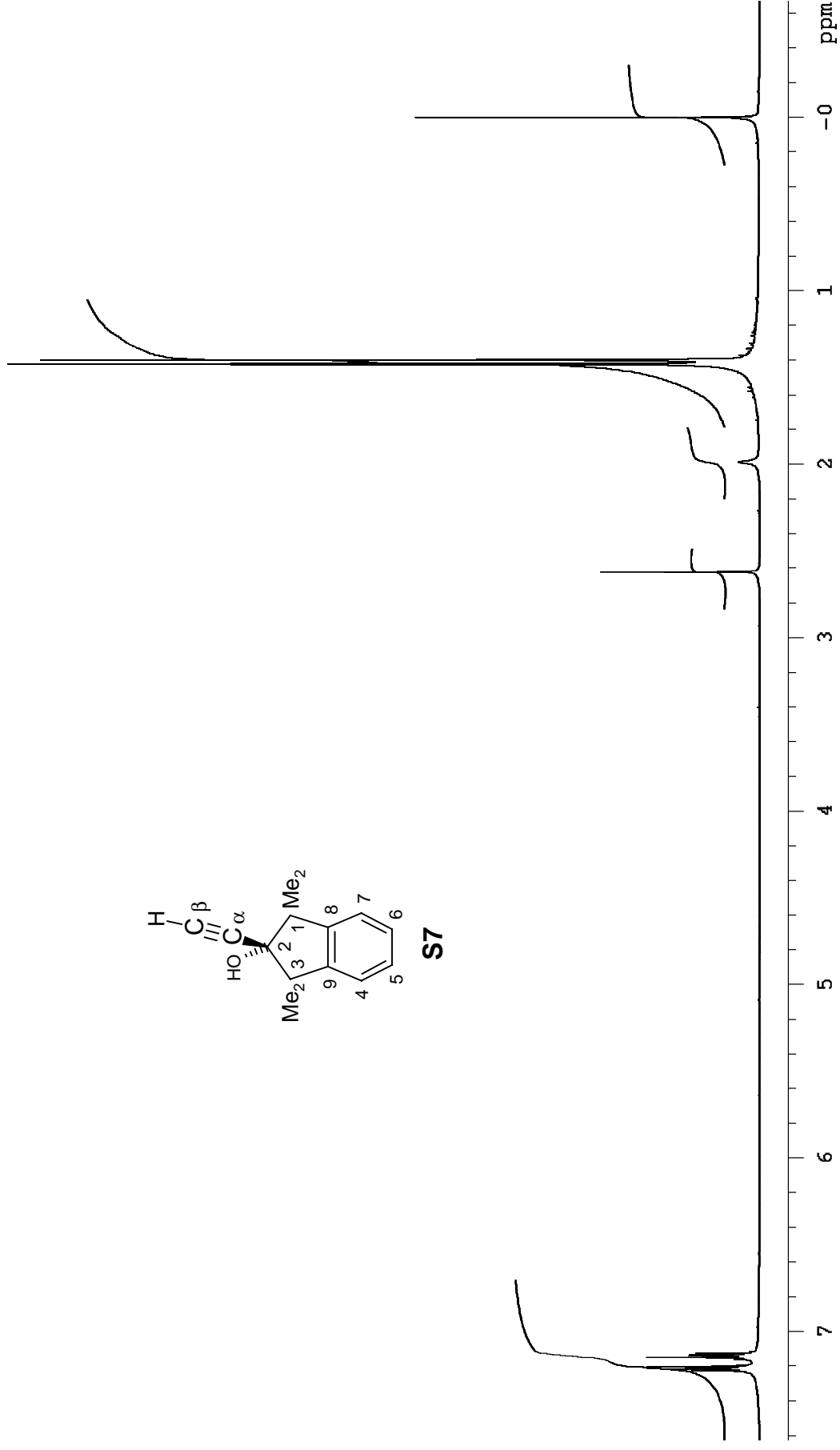


Figure S13. ¹H NMR spectrum of 2-ethynyl-1,1,3,3,3-tetramethyl-2-indanol (S7) in CDCl₃ at +25 °C and 400 MHz.

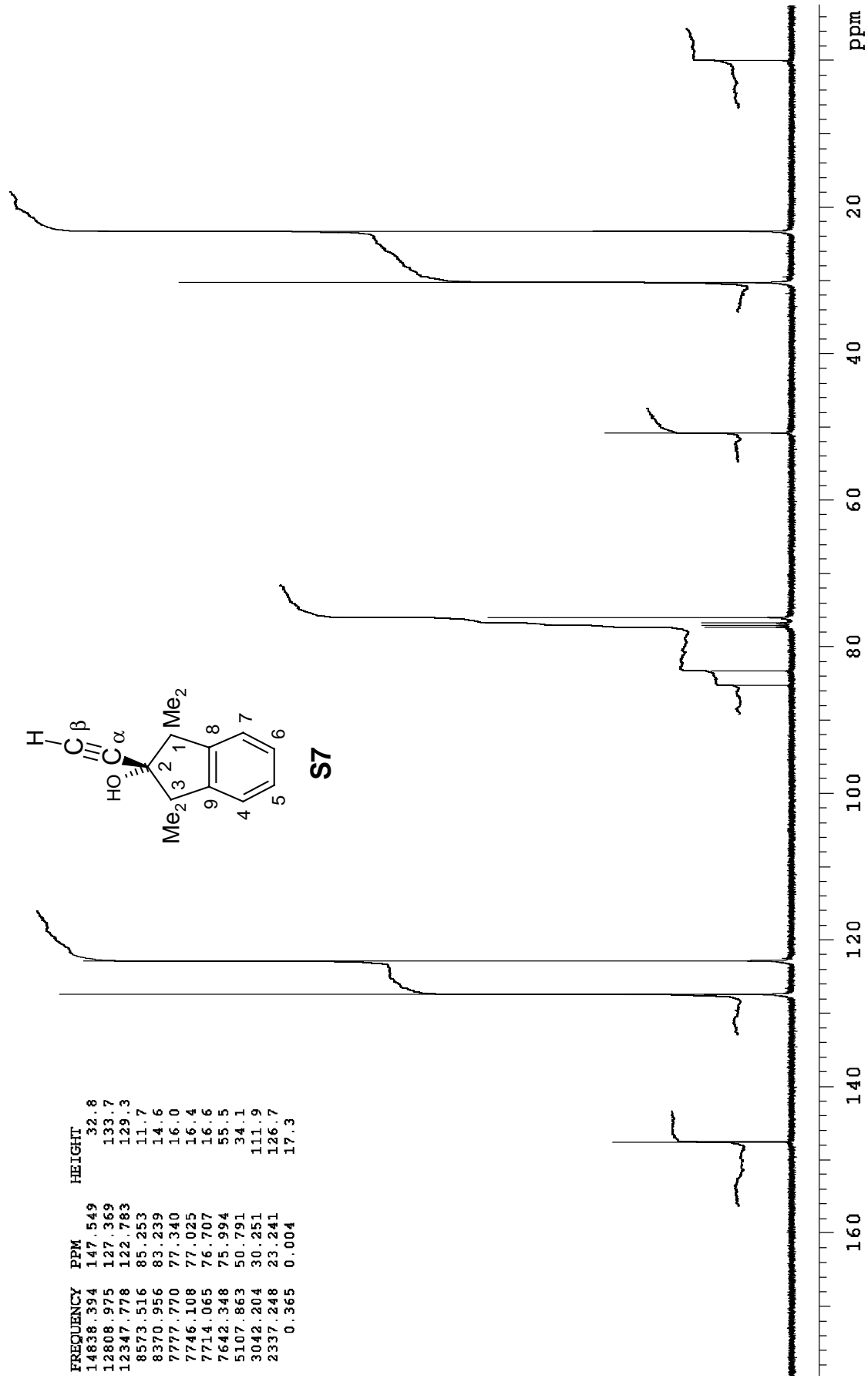


Figure S14. $\{^1\text{H}\}$ decoupled ^{13}C NMR spectrum of 2-ethynyl-1,1,3,3-tetramethyl-2-indanol (**S7**) in CDCl_3 at $+25\text{ }^\circ\text{C}$ and 100.6 MHz.