TANDEM [4+2] CYCLOADDITION/AROMATIZATION SEQUENCE OF ALLENYL 2-BROMO-3-VINYLCYCLOHEX-2-ENYL THIOETHER TO NAPHTHO[1,8-*bc*]THIOPHENE.

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Supporting Information

Experimental Procedures

General

All non-aqueous reactions were carried out under a positive argon atmosphere in dried glassware unless stated otherwise. The solvents were dried and distilled according to standard protocols. Analytical thin-layer chromatography was performed with Silica gel $60PF_{254}$ (Merck). Silica gel column chromatography was performed with PSQ100B (Fuji Silysia). Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a JEOL EX-400 (400 MHz). Chemical shifts are reported relative to Me_4Si (δ = 0.00). Multiplicity is indicated by one or more of the following: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), or br (broad). Carbon nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on a JEOL EX-400 spectrometer (100 MHz). Chemical shifts are reported relative to $CDCl_3$ (δ = 77.0). Infrared spectra of solids (KBr) and liquids (NaCl) were recorded on a JASCO FT/IR-460 PLUS spectrophotometer. ESI-MS were recorded on a JEOL JMS-T100LP mass spectrometer.

Synthesis route and spectral data for 1,3-cyclohexanedione (**4**) to 2-Bromo-3-vinylcyclohex-2-en-1-ol (**5**) was reported previously.[1]

***S*-(2-bromo-3-vinylcyclohex-2-en-1-yl) ethanethioate (6).** To a solution of alcohol **5** (248 mg, 1.22 mmol) in dry toluene (2.44 mL) at 0 °C were added *N,N*-dimethylformamide dineopentyl acetal (0.682 mL, 2.44 mmol) and thioacetic acid (0.175 mL, 2.44 mmol). After the reaction mixture was stirred for 1 h at 0 °C, the reaction mixture was poured into sat. $NaHCO_3$ *aq*. and extracted three times with ethyl acetate. The combined organic layers were washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography with hexane/ethyl acetate (20:1) to give *S*-(2-bromo-3-vinylcyclohex-2-en-1-yl) ethanethioate (**6**) as a colorless oil in 92% yield. IR (NaCl): ν = 2931, 1693; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.70-1.77 (1H, m), 1.86-1.97 (2H, m), 2.10-2.17 (1H, m), 2.19-2.28 (1H, m), 2.36 (3H, s), 2.39-2.43 (1H, m), 4.56 (1H, brs), 5.23 (1H, d, *J* = 11.5 Hz), 5.36 (1H, d, *J* = 17.1 Hz), 6.88 (1H, dd, *J* = 11.5 and 17.1 Hz); ^{13}C NMR (100 MHz,

$CDCl_3$): δ = 19.0, 27.14, 30.80, 31.99, 51.30, 117.05, 122.71, 136.54, 137.15, 195.17; HRMS (ESI) Calcd for $C_{10}H_{13}BrNaOS$ [$(M+Na)^+$]: 282.97682. Found: 282.97682.

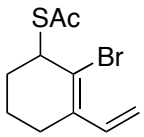
(2-bromo-3-vinylcyclohex-2-en-1-yl)(prop-2-yn-1-yl)sulfane (7). To a solution of thioacetate **6** (620 mg, 2.38 mmol) in ethanol (2.38 mL) was added an ethanolic solution of 0.2 mol/L KOH (47.5 mL, 9.52 mmol). After the reaction mixture was stirred for 20 min at room temperature, the reaction mixture was poured into sat. NH_4Cl *aq.* and extracted three times with ethyl acetate. The combined organic layers were washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. To a solution of the residue and catalytic amount of tetrabutylammonium hydrogensulfate (80.6 mg, 0.238 mmol) in 6% sodium hydroxide *aq.* (5.0 mL) and THF (5.0 mL) was added propargyl bromide (0.368 mL, 4.75 mmol) and the mixture was then stirred at room temperature for 1 h. The reaction mixture was poured into sat. NH_4Cl *aq.* and extracted three times with ethyl acetate. The combined organic layers were washed with water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography with hexane/ethyl acetate (30:1) to give (2-bromo-3-vinylcyclohex-2-en-1-yl)(prop-2-yn-1-yl)sulfane (**7**) as a colorless oil in 84% yield. IR (NaCl): ν = 3295, 2937; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.79-1.84 (1H, m), 1.91-2.00 (1H, m), 2.03-2.15 (2H, m), 2.20-2.28 (1H, m), 2.28 (1H, dd, *J* = 2.8 and 2.9 Hz), 2.38-2.42 (1H, m), 3.37 (1H, dd, *J* = 2.8 and 17.0 Hz), 3.42 (1H, dd, *J* = 2.9 and 17.0 Hz), 3.89 (1H, brs), 5.22 (1H, d, *J* = 11.5 Hz), 5.35 (1H, d, *J* = 17.5 Hz), 6.89 (1H, dd, *J* = 11.5 and 17.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.3, 20.9, 27.3, 31.2, 52.7, 71.9, 80.2, 116.9, 124.4, 135.5, 137.3; HRMS (ESI) Calcd for $C_{11}H_{14}BrS$ [$(M+H)^+$]: 256.99996. Found: 256.99851.

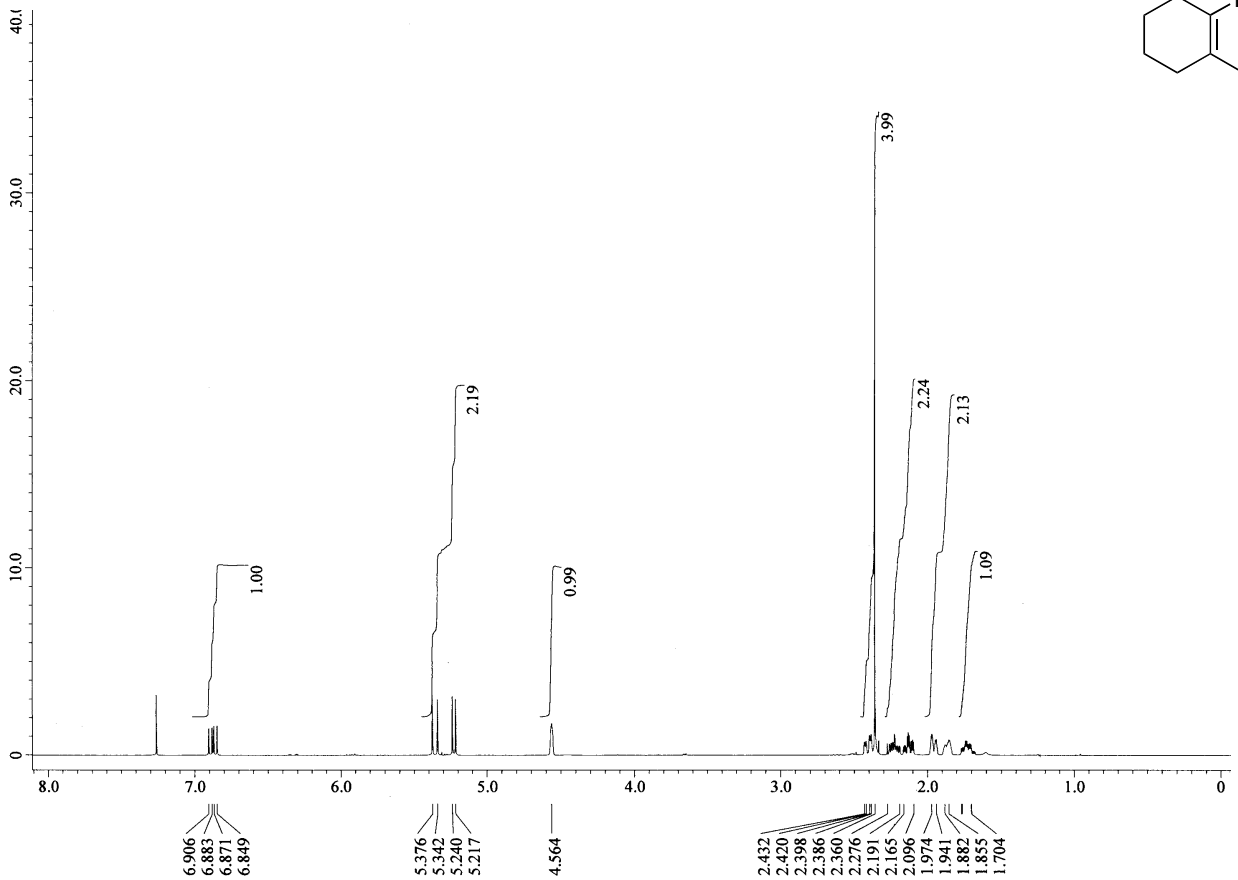
(2-bromo-3-vinylcyclohex-2-en-1-yl)(propa-1,2-dien-1-yl)sulfane (8). A solution of propargyl thioether **7** (232 mg, 0.902 mmol) in *t*-BuOH (9.0 mL) was added 10% sodium hydroxide *aq.* (0.361 mL, 0.902 mmol) and refluxed for 2 h. The reaction mixture was poured into water and extracted three times with ethyl acetate. The combined organic layers were washed with brine,

dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography with hexane to give (2-bromo-3-vinylcyclohex-2-en-1-yl)(propa-1,2-dien-1-yl)sulfane (**8**) as a colorless oil in 91% yield. IR (NaCl): ν = 2936, 1939; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.77-1.84 (1H, m), 1.97-2.12 (3H, m), 2.19-2.26 (1H, m), 2.39-2.42 (1H, m), 3.85 (1H, brs), 5.00 (2H, d, J = 6.8 Hz), 5.23 (1H, d, J = 10.7 Hz), 5.37 (1H, d, J = 17.0 Hz), 5.81 (1H, t, J = 6.8 Hz), 6.90 (1H, dd, J = 10.7 and 17.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.1, 27.4, 31.1, 53.9, 80.4, 87.1, 117.0, 123.3, 136.4, 137.3, 207.1; HRMS (ESI) Calcd for $C_{11}H_{114}BrS$ [$(M+H)^+$]: 256.99996. Found: 257.00029.

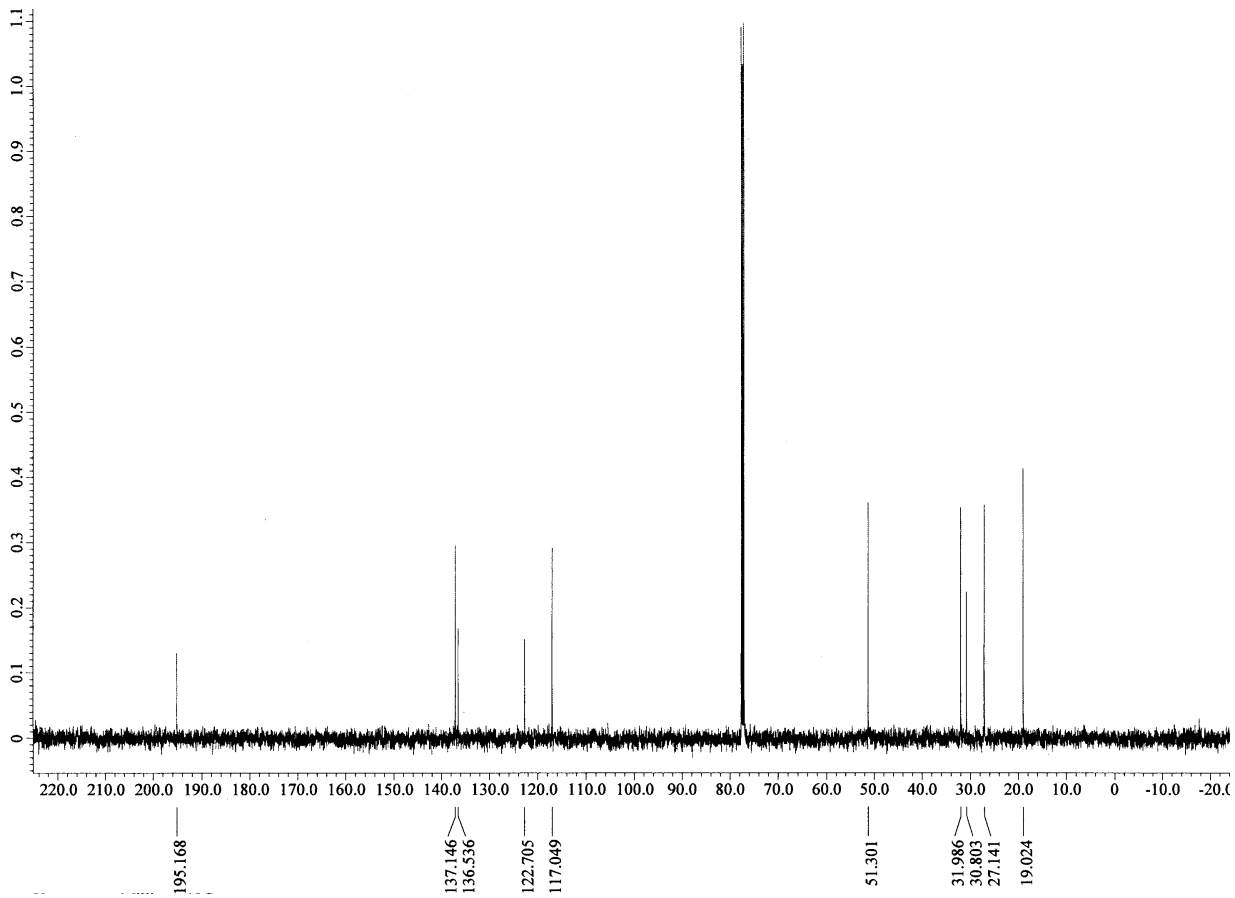
General procedures for synthesis 4,6,7,8-tetrahydro-*3H*-naphtho[1,8-*bc*]thiophene (9). To a solution of allenyl thioether **8** (212 mg, 0.82 mmol) in dry toluene (8.2 mL) was added pyridine (0.078 mL, 0.988 mmol) at room temperature under atmosphere of N_2 and the mixture was then refluxed for 20 h. The reaction mixture was poured into water and extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography with hexane to give 4,6,7,8-tetrahydro-*3H*-naphtho[1,8-*bc*]thiophene (**9**) as a colorless oil in 94% yield. IR (NaCl): ν = 2929, 1433; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.93 (2H, tt, J = 6.2 and 6.2 Hz), 2.32-2.35 (2H, m), 2.38-2.41 (2H, m), 2.72 (2H, t, J = 6.2 Hz), 2.80 (2H, t, J = 6.2 Hz), 5.43 (1H, t, J = 3.9 Hz), 6.62 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 24.5, 25.0, 25.2, 25.5, 28.8, 115.2, 117.8, 132.4, 134.2, 134.4, 136.1; HRMS (ESI) Calcd for $C_{11}H_{13}S$ [$(M+H)^+$]: 177.07380. Found: 177.07458.

[1]H-NMR for *S*-(2-bromo-3-vinylcyclohex-2-en-1-yl) ethanethioate (6)





[13]C-NMR for *S*-(2-bromo-3-vinylcyclohex-2-en-1-yl) ethanethioate (6)



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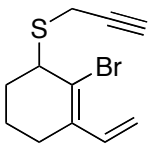

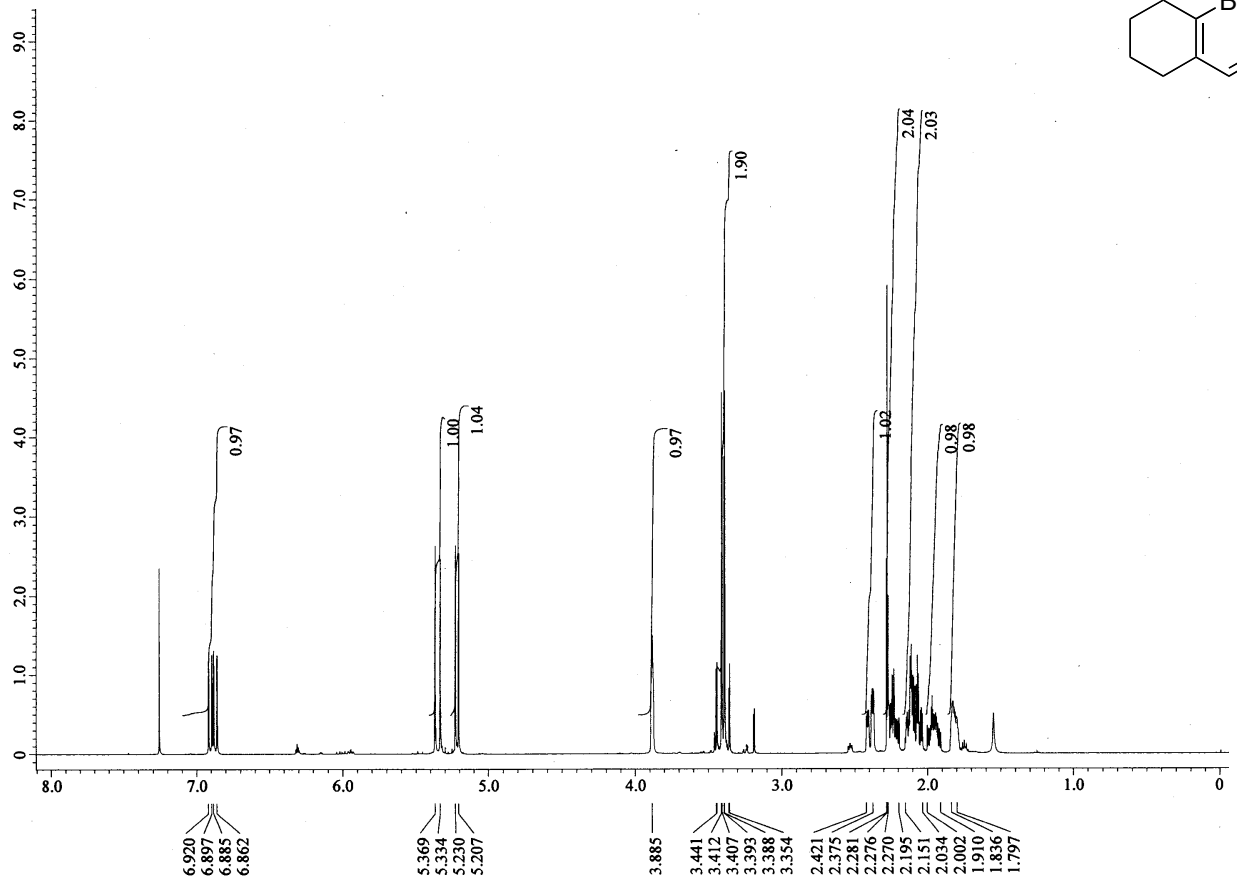

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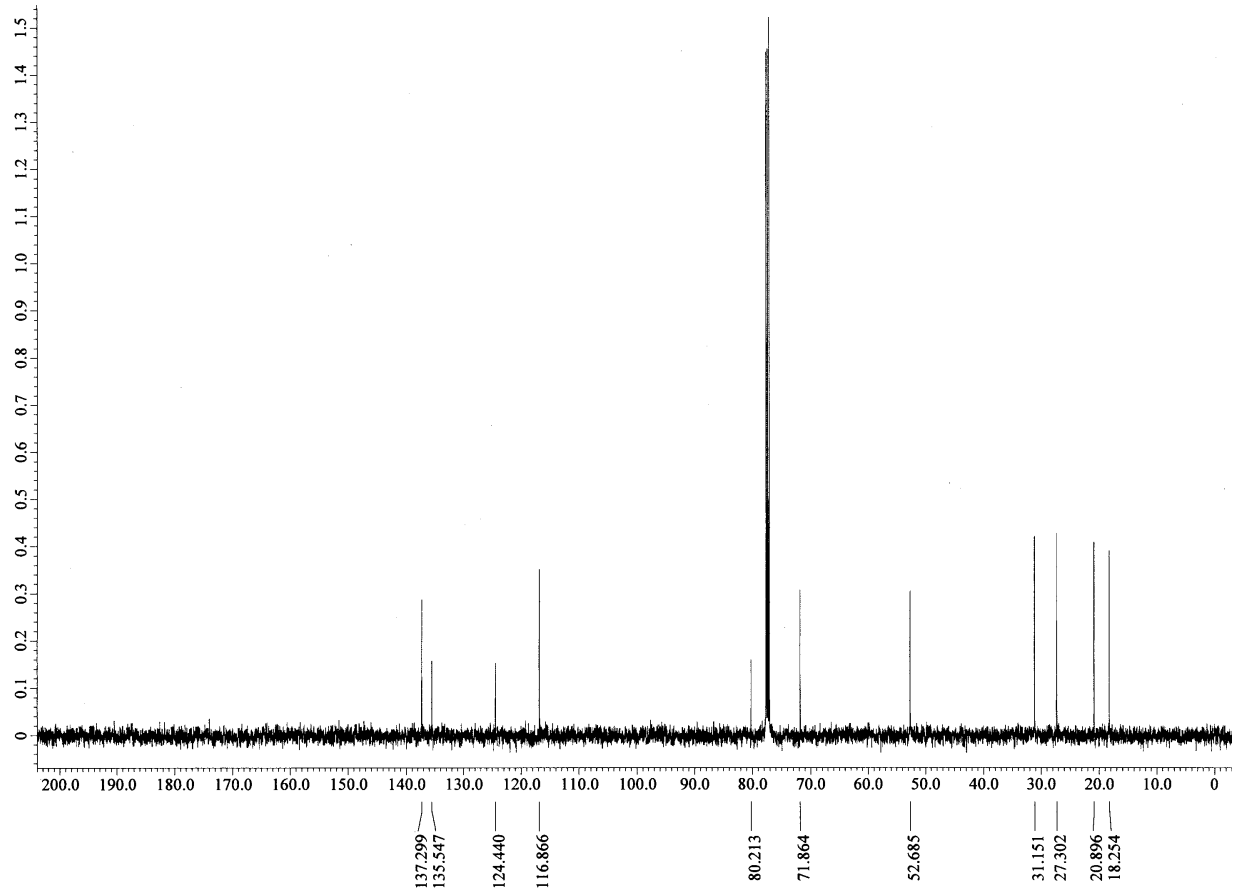

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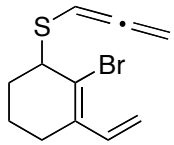
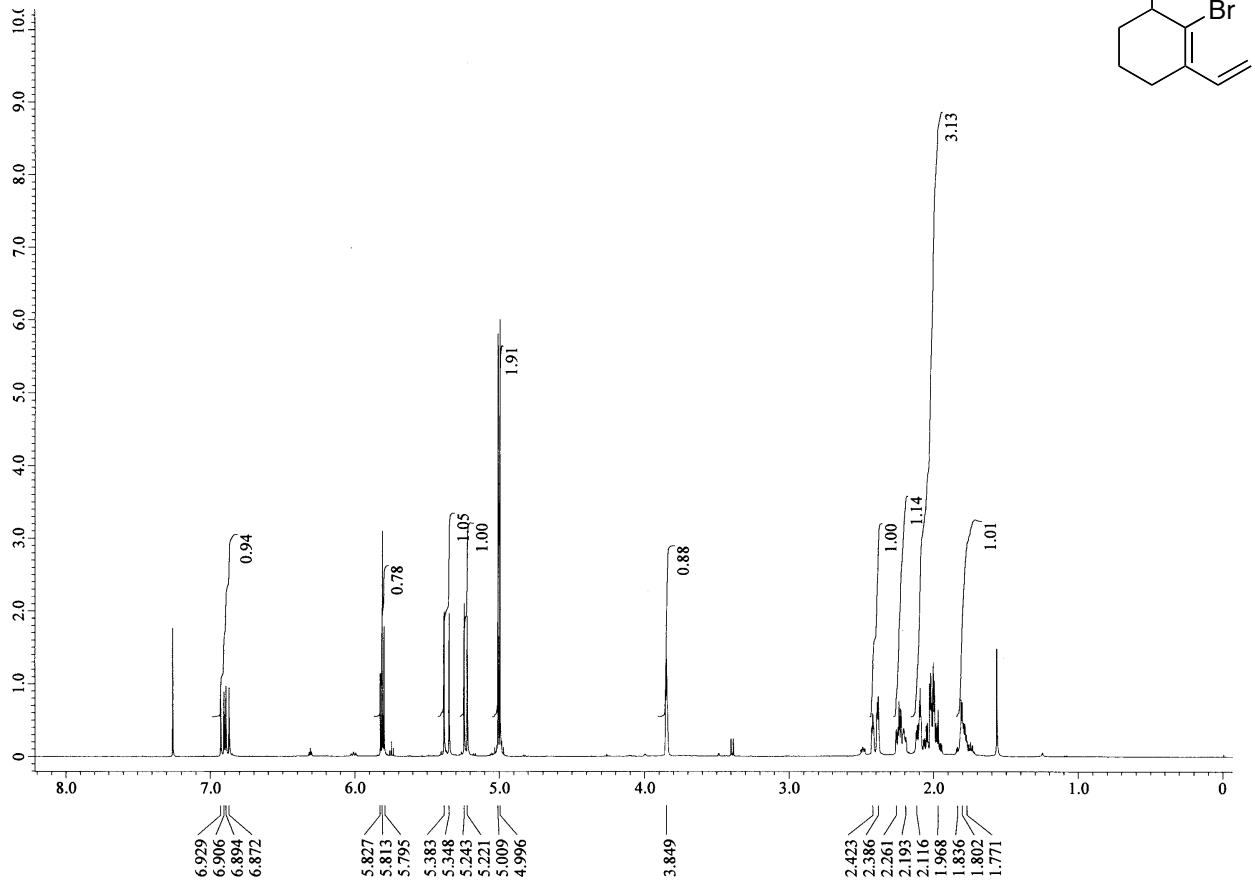
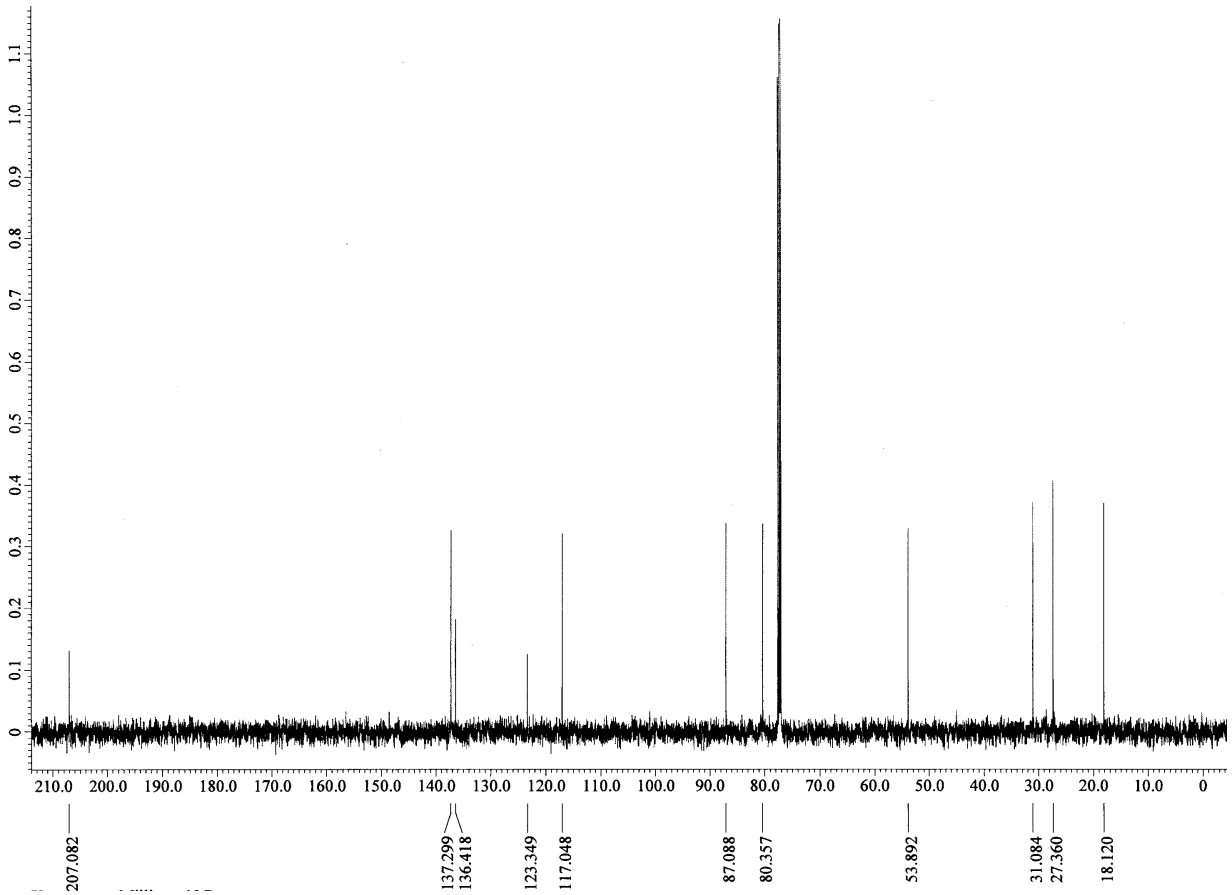




^{13}C-NMR for (2-bromo-3-vinylcyclohex-2-en-1-yl)(propa-1,2-dien-1-yl)sulfane (8)



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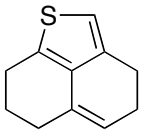
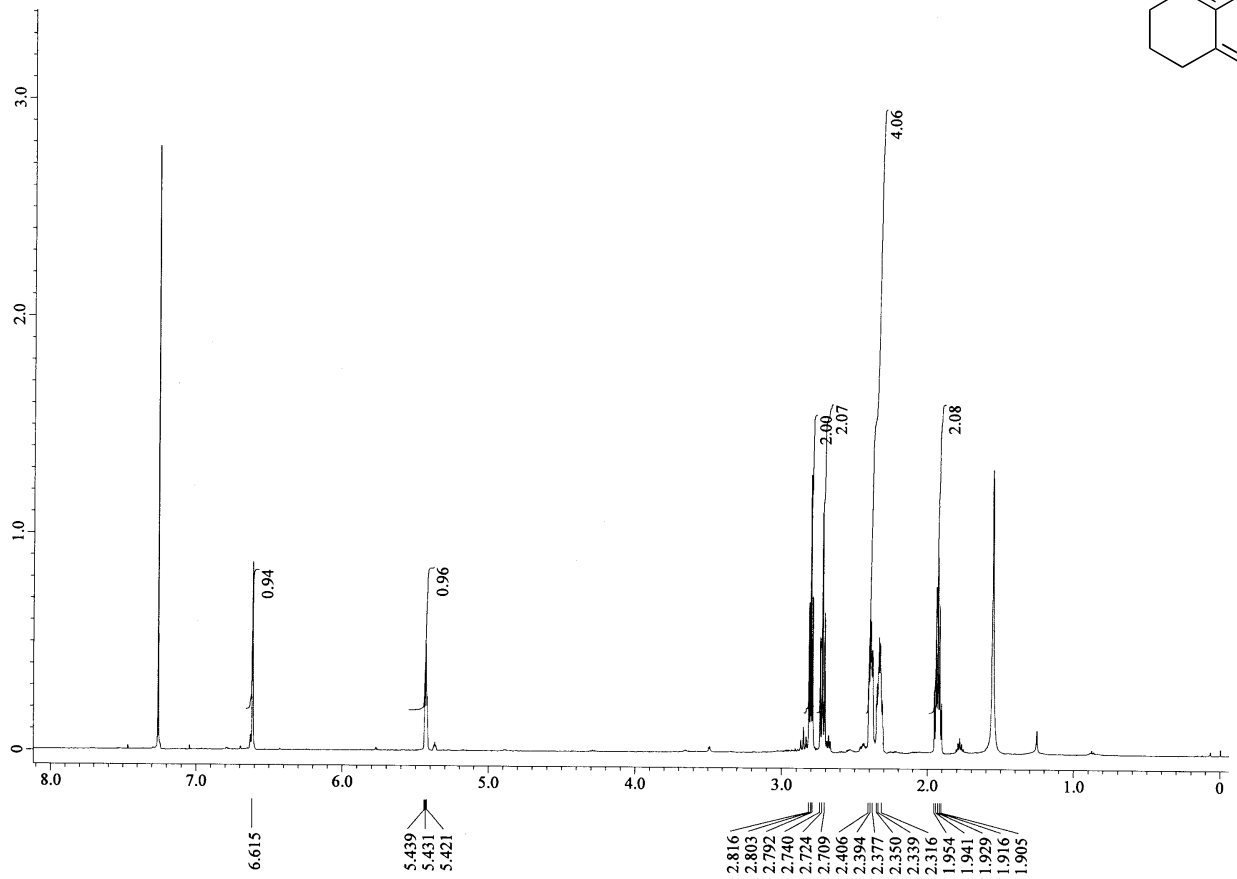
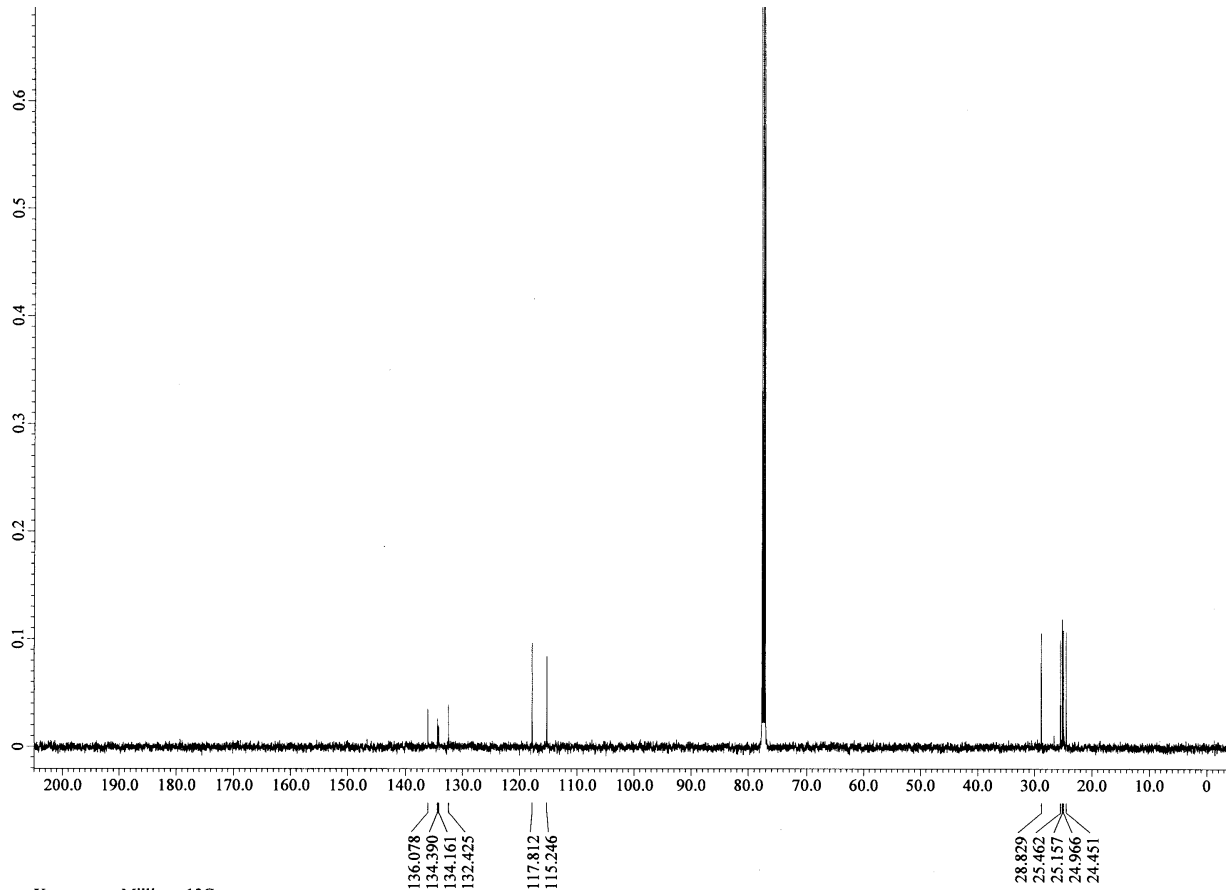




^{13}C-NMR for 4,6,7,8-tetrahydro-*3H*-naphtho[1,8-*bc*]thiophene (9)



References

1. N. Hatae, I. Suzuki, T. Choshi, S. Hibino, C. Okada, and E. Toyota, *Tetrahedron Lett.,* 2014, **55**, 4146.