Supporting Information for

Nickel-Catalyzed Thioallylation of Alkynes with Allyl Phenyl Sulfides

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General Comments.

All manipulations were carried out under nitrogen atmosphere. THF and dioxane were dried (Na) and distilled before use. ¹H-, ¹³C- and ³¹P-NMR spectra were recorded on a Bruker ARX-300 spectrometer (¹H: 300 MHz; ¹³C: 75 MHz and ³¹P: 121.5 MHz) and referenced to SiMe₄ (¹H), appropriate solvent resonances (¹³C) and 85% H₃PO₄ (³¹P). IR spectra were measured on a JASCO FT/IR-5000 spectrometer. GC-MS spectra were obtained on a Shimadzu GC-17A/QP-5000 mass spectrometer by using EI technique (70 eV). High-resolution mass spectra were obtained with a JEOL JMS-BU20 mass spectrometer at an ionization energy of 70 eV. Melting points were measured on a Yanagimoto Micro Melting Point apparatus and were uncorrected.

Ni(CO)₃(PPh₃),¹ Ni(CO)₂(PPh₃)₂,¹ Ni[P(OPh)₃]₄,² (4*S*)-(-)-2-(2'-diphenylphosphino-phenyl)-4-isopropylloxazoline,³ and 1,2-bis[(4*S*)-4-isopropyl-2-oxazolin-2-yl]ethane,⁴ 2,3-di-(phenylimino)butane,⁵ and allylic sulfides **2c**,⁶ **2b**,⁷ **2d**,⁶ **2d'**⁶ and **2e**⁶ were prepared according to the literature procedures. All the other metal complexes and ligands were commercial products and were used as received. Alkynes were also obtained from commercial source and were dried over molecular sieves 4A and degassed before use.

Addition of Allyl Phenyl Sulfide (2a) to 1-Octyne (1a); Typical Procedure (Entry 1, Table 1).

To a solution of Ni(cod)₂ (0.02 mmol) in THF (0.5 mL) were added ally phenyl sulfide (0.5 mmol) and 1-octyne (1.5 mmol) and the resulting mixture was heated at 60 °C for 8 h. An

appropriate amount of docosane (C₂₂H₄₆) was then added as internal standard for GC analyses. The GC and GC-MS analyses revealed the formation of two adducts **3aa** and **4aa** in 98% total yield (**3aa** : **4aa** = 89 : 11). After removal of volatiles under reduced pressure, the residue was subjected to silica-gel column chromatography (eluted with hexane) to afford an adduct mixture **3aa** and **4aa** as a colorless oil (87% yield, **3aa** : **4aa** = 89 : 11). Further careful separation of the adduct mixture by preparative TLC (silica gel, eluted with a 10 : 1 hexane-diethyl ether mixture) gave pure **3aa** in 73 % yield, and a fraction comprising of **3aa** and **4aa** (**3aa** : **4aa** = 14 : 86) in 9 % yield.

Physical and/or Spectral data of Products.

5-Phenylthioundeca-1,4(Z)-diene (3aa): Colorless oil, bp 50 °C (0.15 Torr). ¹H NMR (CDCl₃) δ 7.27-7.13 (m, 5H), 5.89 (t, 1H, *J* = 7.0 Hz), 5.88-5.77 (m, 1H), 5.06 (dd, 1H, *J* = 17.0, 1.6 Hz), 5.01 (dd, 1H, *J* = 10.0, 1.6 Hz), 3.11 (virtual t, 2H, *J* = 7.0 Hz), 2.17 (t, 2H, *J* = 7.4 Hz), 1.50-1.21 (m, 8H), 0.85 (t, 3H *J* = 6.8 Hz). ¹³C NMR (CDCl₃) δ 136.4, 135.4, 134.9, 133.0, 129.6, 128.8, 125.9, 115.2, 37.5, 34.2, 31.6, 28.5, 28.4, 22.6, 14.1. IR (thin film): 2956, 2929, 2856, 1639, 1583, 1477, 1438, 1024, 991, 912, 740, 690 cm⁻¹. GCMS *m/z* (% relative intensity.) 260 (M⁺, 28), 245 (4), 203 (5), 183 (51), 147 (23), 135 (17), 109 (47), 95 (53), 79 (66), 67 (100), 55 (52). Anal. Calcd for C₁₇H₂₄S (a mixture of adducts): C, 78.46; H, 9.23; S, 12.30. Found: C, 78.84; H, 9.49; S, 12.16. **3aa** is a cis-adduct as evidenced by an NOE experiment; irradiation at δ 2.17 ppm assignable to the allylic protons in *n*-hexyl moiety resulted in a 5% enhancement of the olefinic proton signal at δ 5.89 ppm. For ¹H and ¹³C NMR spectra of the compound, see appendixes 1 and 2.

2-Hexyl-1-phenylthiopenta-1(Z),4-diene (4aa): ¹H NMR (CDCl₃) δ 7.29-7.13 (m, 5H), 5.99 (s, 1H), 5.82-5.71 (m, 1H), 5.09 (dd, 1H, *J* = 17.2, 1.4 Hz), 5.04 (dd, 1H, *J* = 11.4, 1.4 Hz), 3.04 (d, 2H, *J* = 6.6 Hz), 2.17 (t, 2H, *J* = 7.3 Hz), 1.49-1.24 (m, 8H), 0.89 (t, 3H *J* = 6.7 Hz). ¹³C NMR (CDCl₃) δ 144.6, 137.3, 135.1, 128.8, 128.1, 125.7, 116.7, 116.0, 36.8, 36.7, 31.6, 29.0, 27.6, 22.6, 14.1. GCMS *m/z* (% relative intensity.) 260 (M⁺, 65), 245 (4), 217 (2), 189 (14), 183 (36), 175 (13), 147 (60), 109 (35), 91 (65), 79 (100), 67 (75), 55 (42). **4aa** is a cis-adduct as evidenced by an NOE experiment; irradiation at δ 2.17 ppm assignable to the allylic protons in *n*-hexyl moiety resulted in a 8% enhancement of the olefinic proton signal at δ 5.99 ppm. For ¹H NMR spectrum of the compound, see appendix 3.

5-Phenylthiohexa-1,4(Z)-diene (3ba) and 2-methyl-1-phenylthiopenta-1(E),4-diene (4ba): The isolated yield was 17% (catalyst B). Colorless oil, bp 50 °C (0.6 Torr). **3ba:** ¹H NMR (CDCl₃) δ 7.32-7.16 (m, 5H), 5.90-5.77 (m, 2H), 5.05 (dd, 1H, *J* = 17.0, 1.5 Hz), 5.02 (dd, 1H, *J* = 10.0, 1.5 Hz), 3.10 (virtual t, 2H, *J* = 6.2 Hz), 1.92 (d, 3H, *J* = 0.9 Hz). ¹³C NMR (CDCl₃) δ 136.3, 135.7, 134.6, 132.3, 130.4, 128.9, 126.4, 115.2, 34.3, 24.4. IR (thin film): 3075, 3002, 2964, 2915, 1637, 1583, 1477, 1438, 1024, 993, 912, 740, 690 cm⁻¹. GCMS *m/z* (% relative intensity.) 190 (M⁺, 24), 175 (9), 157 (15), 113 (85), 109 (11), 81 (92), 79 (100), 77 (40),

53 (45). HRMS (m/z) calcd for $C_{12}H_{14}S$: 190.0815, found: 190.0812. **4ba**: 1H NMR ($CDCl_3$) δ 7.29-7.16 (m, 5H), 5.95 (s, 1H), 5.84-5.71 (m, 1H), 5.10 (dd, 1H, $J = 17.0, 1.5$ Hz), 5.05 (dd, 1H, $J = 10.0, 1.5$ Hz), 3.04 (d, 2H, $J = 6.6$ Hz), 1.87 (d, 3H, $J = 0.9$ Hz). GCMS m/z (% relative intensity.) 190 (M^+ , 47), 175 (24), 157 (18), 113 (61), 81 (92), 79 (100), 77 (40), 53 (40). For 1H and ^{13}C NMR spectra of these compounds, see appendixes 4-7.

6,6-Dimethyl-5-phenylthiohepta-1,4(Z)-diene (3ca): Isolated yield: 58% (catalyst B), colorless oil, bp 60 °C (0.25 Torr). 1H NMR ($CDCl_3$) δ 7.23-7.03 (m, 5H), 6.18 (t, 1H, $J = 6.8$ Hz), 5.84-5.70 (m, 1H), 5.00-4.94 (m, 2H), 2.95 (virtual t, 2H, $J = 6.6$ Hz), 1.18 (s, 9H). ^{13}C NMR ($CDCl_3$) δ 142.4, 138.2, 136.2, 134.2, 128.7, 126.0, 124.5, 115.4, 39.4, 35.1, 29.4. IR (thin film): 2962, 2952, 2904, 2867, 1639, 1583, 1477, 1361, 1081, 993, 738, 690 cm^{-1} . GCMS m/z (% relative intensity.) 232 (M^+ , 8), 175 (9), 217 (2), 175 (5), 155 (16), 109 (5), 81 (18), 79 (10), 77 (10), 57 (100). HRMS (m/z) calcd for $C_{15}H_{20}S$: 232.1284, found: 232.1276. For 1H and ^{13}C NMR spectra of the compound, see appendixes 8 and 9.

8-Chloro-5-phenylthioocta-1,4(Z)-diene (3da) and 2-(3-chloropropyl)-1-phenylthiopenta-1(Z),4-diene (4da): The isolated yield was 87% (catalyst A). Colorless oil, bp 70 °C (0.3 Torr). **3da**: 1H NMR ($CDCl_3$) δ 7.28-7.18 (m, 5H), 5.97 (t, 1H, $J = 7.2$ Hz), 5.88-5.77 (m, 1H), 5.05 (dd, 1H, $J = 17.0, 1.5$ Hz), 5.03 (dd, 1H, $J = 10.0, 1.5$ Hz), 3.47 (t, 2H, $J = 6.4$ Hz), 3.13 (virtual t, 2H, $J = 6.8$ Hz), 2.34 (t, 2H, $J = 7.1$ Hz), 1.94 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 136.0, 134.6, 134.5, 133.1, 129.9, 129.0, 126.4, 115.4, 44.1, 34.3, 34.2, 30.9. IR (thin film): 3002, 2956, 2913, 1637, 1583, 1477, 1438, 1024, 993, 916, 742, 692 cm^{-1} . GCMS m/z (% relative intensity.) 252 (M^+ , 37), 237 (7), 175 (100), 143 (14), 109 (20), 91 (47), 79 (64), 77 (55). Anal. Calcd for $C_{14}H_{17}ClS$ (a mixture of adducts): C, 66.53; H, 6.73; S, 12.67. Found: C, 66.22; H, 6.68; S, 12.39. **4da**: 1H NMR ($CDCl_3$) δ 7.31-7.16 (m, 5H), 6.07 (s, 1H), 5.84-5.71 (m, 1H), 5.15-5.06 (m, 2H), 3.55 (t, 2H, $J = 6.4$ Hz), 3.05 (d, 2H, $J = 6.6$ Hz), 2.34 (t, 2H, $J = 7.1$ Hz), 1.95 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 141.3, 136.7, 134.7, 129.0, 128.4, 126.1, 118.9, 116.5, 44.4, 36.7, 33.8, 30.5. GCMS m/z (% relative intensity.) 252 (M^+ , 44), 175 (100), 143 (17), 109 (29), 91 (49), 79 (59), 77 (57). For 1H and ^{13}C NMR spectra of these compounds, see appendixes 10-13.

8-Cyano-5-phenylthioocta-1,4(Z)-diene (3ea) and 2-(3'-cyanopropyl)-1-phenylthiopenta-1(Z),4-diene (4ea): The isolated yield was 77% (catalyst B). Colorless oil, bp 85 °C (0.3 Torr). **3ea**: 1H NMR ($CDCl_3$) δ 7.26-7.18 (m, 5H), 5.98 (t, 1H, $J = 7.2$ Hz), 5.90-5.76 (m, 1H), 5.11-5.07 (m, 2H), 3.14 (virtual t, 2H, $J = 6.7$ Hz), 2.32 (t, 2H, $J = 7.1$ Hz), 2.26 (t, 2H, $J = 7.1$ Hz), 1.82 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 135.8, 135.2, 134.1, 132.5, 130.1, 129.1, 126.6, 119.5, 115.6, 35.6, 34.1, 23.7, 15.9. IR (thin film): 3075, 3004, 2938, 2246, 1637, 1581, 1477, 1438, 1024, 997, 916, 744, 692 cm^{-1} . GCMS m/z (% relative intensity.) 243 (M^+ , 38), 210 (9), 189 (4), 175 (10), 166 (96), 147 (20), 134 (100), 110 (48), 93 (61), 91 (74), 77 (75), 65 (51). Anal. Calcd for $C_{15}H_{17}NS$ (a mixture of adducts): C, 74.07; H, 6.70; N, 5.76; S, 13.16. Found: C, 73.81; H, 6.71; N, 5.38; S, 13.48. **4ea**: 1H NMR ($CDCl_3$) δ 7.31-7.17 (m, 5H), 6.09 (s, 1H), 5.83-5.07 (m, 1H), 5.15-5.05 (m, 2H), 3.03 (d, 2H, $J = 6.6$ Hz), 2.35 (t, 2H, $J = 7.0$ Hz), 2.33 (t,

2H, $J = 7.0$ Hz), 1.84 (m, 2H). ^{13}C NMR (CDCl_3) δ 139.7, 136.3, 134.4, 129.1, 128.7, 126.3, 120.2, 119.4, 116.7, 36.5, 35.5, 23.5, 16.6. GCMS m/z (% relative intensity.) 243 (M^+ , 31), 210 (6), 189 (4), 175 (17), 166 (40), 147 (47), 134 (75), 110 (56), 93 (100), 91 (82), 77 (75), 65 (68). For ^1H and ^{13}C NMR spectra of these compounds, see appendixes 14-17.

9-*t*-Butyldimethylsiloxy-5-phenylthionona-1,4(*Z*)-diene (3fa): The isolated yield was 72% (catalyst B). Colorless oil, bp 85 °C (1.5×10^{-2} Torr). ^1H NMR (CDCl_3) δ 7.28-7.13 (m, 5H), 5.90 (t, 1H, $J = 7.3$ Hz), 5.86-5.76 (m, 1H), 5.05 (dd, 1H, $J = 18.0, 1.4$ Hz), 5.00 (dd, 1H, $J = 10.0, 1.4$ Hz), 3.54 (t, 2H, $J = 6.2$ Hz), 3.11 (virtual t, 2H, $J = 6.6$ Hz), 2.19 (t, 2H, $J = 6.9$ Hz), 1.55-1.39 (m, 4H), 0.87 (s, 9H), 0.02 (s, 6H). ^{13}C NMR (CDCl_3) δ 136.3, 135.2, 134.7, 133.2, 129.6, 128.8, 126.0, 115.2, 63.0, 37.2, 34.2, 32.0, 25.9, 24.7, 18.4, -5.3. IR (thin film): 3075, 3004, 2952, 2929, 2896, 2857, 1639, 1583, 1475, 1438, 1255, 1103, 1024, 912, 836, 775, 740, 690 cm^{-1} . GCMS m/z (% relative intensity.) 362 (M^+ , 4), 347 (2), 305 (64), 253 (18), 231 (4), 195 (48), 167 (42), 145 (10), 115 (27), 109 (8), 93 (36), 91 (58), 77 (37), 75 (100). Anal. Calcd for $\text{C}_{21}\text{H}_{34}\text{OSSi}$ (a mixture of adducts): C, 69.61; H, 9.39; S, 8.84. Found: C, 69.77; H, 9.18; S, 8.77. For ^1H and ^{13}C NMR spectra of the compound, see appendixes 18 and 19.

6-Hydroxy-6-methyl-5-phenylthiohepta-1,4(*Z*)-diene (3ga): Isolated yield: 74% (catalyst B), colorless oil, bp 70 °C (0.2 Torr). ^1H NMR (CDCl_3) δ 7.25-7.08 (m, 5H), 6.45 (t, 1H, $J = 7.0$ Hz), 5.82-5.68 (m, 1H), 5.01-4.95 (m, 2H), 2.99 (virtual t, 2H, $J = 6.6$ Hz), 2.29 (s, 1H), 1.44 (s, 6H). ^{13}C NMR (CDCl_3) δ 140.3, 136.8, 135.4 (2C), 128.9, 126.6, 125.3, 116.0, 74.4, 34.9, 29.2. IR (thin film): 3421, 3075, 3060, 2977, 2931, 1639, 1583, 1477, 1438, 1363, 1124, 1024, 995, 916, 738, 690 cm^{-1} . GCMS m/z (% relative intensity.) 234 (M^+ , 11), 219 (2), 217 (8), 216 (63), 201 (100), 175 (7), 147 (11), 125 (3), 109 (28), 107 (48), 91 (88), 77 (26), 59 (60). Anal. Calcd for $\text{C}_{14}\text{H}_{18}\text{OS}$: C, 71.79; H, 7.69; S, 13.67. Found: C, 71.59; H, 7.76; S, 13.65. For ^1H and ^{13}C NMR spectra of the compound, see appendixes 20 and 21.

6-Methoxy-5-phenylthiohexa-1,4(*Z*)-diene (3ha) and 2-methoxymethyl-1-phenylthiopenta-1(*E*),4-diene (4ha): The isolated yield was 58% (catalyst A). Colorless oil, bp 55 °C (0.2 Torr). **3ha:** ^1H NMR (CDCl_3) δ 7.29-7.18 (m, 5H), 6.24 (tt, 1H, $J = 7.3, 0.8$ Hz), 5.90-5.77 (m, 1H), 5.11-5.01 (m, 2H), 3.89 (d, 2H, $J = 0.8$ Hz), 3.28 (s, 3H), 3.17 (virtual t, 2H, $J = 6.7$ Hz). ^{13}C NMR (CDCl_3) δ 135.6, 135.4, 134.5, 130.6, 129.5, 128.9, 126.3, 115.7, 74.9, 57.9, 33.8. IR (thin film): 3075, 3058, 2981, 2925, 2888, 2821, 1637, 1583, 1477, 1438, 1112, 1072, 1024, 993, 916, 740, 690 cm^{-1} . GCMS m/z (% relative intensity.) 220 (M^+ , 25), 205 (1), 188 (53), 173 (54), 147 (31), 110 (65), 109 (34), 97 (77), 79 (86), 77 (100), 65 (38). Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{OS}$ (a mixture of adducts): C, 70.90; H, 7.27; S, 14.54. Found: C, 71.07; H, 7.05; S, 14.40. **4ha:** ^1H NMR (CDCl_3) δ 7.36-7.16 (m, 5H), 6.32 (s, 1H), 5.88-5.74 (m, 1H), 5.16-5.09 (m, 2H), 3.93 (s, 2H), 3.33 (s, 3H), 3.04 (d, 2H, $J = 6.6$ Hz). ^{13}C NMR (CDCl_3) δ 137.3, 136.1, 134.2, 129.1, 129.0, 126.4, 121.9, 116.3, 75.0, 57.9, 34.3. GCMS m/z (% relative intensity.) 220 (M^+ , 34), 205 (1), 175 (3), 147 (50), 110 (17), 109 (15), 97 (7), 79 (100), 77 (46), 65 (23). For ^1H and ^{13}C NMR spectra of these compounds, see appendixes 22-25.

7-Ethoxycarbonyl-5-phenylthiohepta-1,4(*Z*)-diene (3ia) and 2-(2-ethoxycarbon-

ylethyl)-1-phenylthiopenta-1(Z),4-diene (4ia): The isolated yield was 89% (catalyst A). Colorless oil, bp 95 °C (0.25 Torr). **3ia:** ^1H NMR (CDCl_3) δ 7.27-7.16 (m, 5H), 5.99 (t, 1H, J = 7.2 Hz), 5.87-5.74 (m, 1H), 5.07-4.99 (m, 2H), 4.08 (q, 2H, J = 7.1 Hz), 3.10 (virtual t, 2H, J = 6.6 Hz), 2.51 (m, 4H), 1.21 (t, 3H, J = 7.1). ^{13}C NMR (CDCl_3) δ 172.9, 135.9, 134.9, 134.7, 133.0, 129.5, 129.0, 126.2, 115.4, 60.3, 34.2, 33.4, 32.8, 14.2. IR (thin film): 3075, 2979, 2933, 1735, 1637, 1583, 1477, 1438, 1160, 1037, 1024, 995, 916, 742, 692 cm^{-1} . GCMS m/z (% relative intensity.) 276 (M^+ , 4), 231 (1), 203 (2), 189 (2), 175 (3), 167 (31), 121 (79), 109 (15), 93 (87), 79 (100), 77 (52). Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_2\text{S}$ (a mixture of adducts): C, 69.56; H, 7.26; S, 11.59. Found: C, 69.18; H, 7.19; S, 11.51. **4ia:** ^1H NMR (CDCl_3) δ 7.29-7.16 (m, 5H), 6.05 (s, 1H), 5.84-5.70 (m, 1H), 5.14-5.02 (m, 2H), 4.13 (q, 2H, J = 7.1 Hz), 3.05 (d, 2H, J = 6.5 Hz), 2.49 (m, 4H), 1.24 (t, 3H, J = 7.1). GCMS m/z (% relative intensity.) 276 (M^+ , 22), 231 (3), 203 (1), 189 (5), 175 (1), 167 (13), 121 (65), 109 (14), 93 (100), 79 (67), 77 (38). For ^1H and ^{13}C NMR spectra of these compounds, see appendixes 26-28.

6-Methyl-5-phenylthiohepta-1,4(Z),6-triene (3ja): Isolated yield: 10 % (catalyst B), colorless oil, bp 55 °C (0.3 Torr). ^1H NMR (CDCl_3) δ 7.24-7.09 (m, 5H), 6.33 (t, 1H, J = 7.3 Hz), 5.86-5.75 (m, 1H), 5.52 (d, 1H, J = 0.9 Hz), 5.09-4.99 (m, 3H), 3.26-3.20 (m, 2H), 1.97 (s, 3H). ^{13}C NMR (CDCl_3) δ 141.7, 137.0, 136.7, 135.7, 134.9, 128.7, 127.3, 125.1, 116.7, 115.8, 35.2, 21.2. IR (thin film): 2971, 2921, 2854, 1637, 1583, 1477, 1438, 1124, 900, 738, 688 cm^{-1} . GCMS m/z (% relative intensity.) 216 (M^+ , 86), 201 (75), 187 (12), 175 (10), 139 (45), 123 (45), 110 (40), 107 (60), 105 (64), 91 (100), 79 (69), 77 (59), 65 (54), 51 (35). HRMS (m/z) calcd for $\text{C}_{14}\text{H}_{16}\text{S}$: 216.0971, found: 216.0976. For ^1H and ^{13}C NMR spectra of the compound, see appendixes 29 and 30.

6-Phenyl-5-phenylthiohexa-1,4(Z)-diene (3ka) and 2-benzyl-1-phenylthiopenta-1(E),4-diene (4ka): The isolated yield was 90% (catalyst A). Colorless oil, bp 80 °C (0.2 Torr). ^1H NMR (CDCl_3) δ 7.29-7.08 (m, 10H), 5.89 (t, 1H, J = 7.2 Hz), 5.86-5.75 (m, 1H), 5.05 (dd, 1H, J = 16, 1.5 Hz), 5.01 (dd, 1H, J = 10, 1.5 Hz), 3.47 (s, 2H), 3.14 (virtual t, 2H, J = 6.6 Hz). ^{13}C NMR (CDCl_3) δ 138.9, 136.0, 134.5, 134.4, 130.2, 129.1, 128.9, 128.5, 128.3, 126.4, 126.3, 115.4, 43.6, 34.2. IR (thin film): 3060, 3027, 3002, 2977, 2902, 1637, 1583, 1492, 1475, 1452, 1438, 1076, 1024, 993, 914, 740, 690 cm^{-1} . GCMS m/z (% relative intensity.) 266 (M^+ , 14), 189 (10), 175 (5), 156 (9), 109 (4), 91 (100), 77 (9). Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{S}$ (a mixture of adducts): C, 81.20; H, 6.77; S, 12.03. Found: C, 80.71; H, 6.78; S, 11.90. **4ka:** ^1H NMR (CDCl_3) δ 7.29-7.07 (m, 10H), 6.04 (s, 1H), 5.87-5.71 (m, 1H), 5.11-5.06 (m, 2H), 3.47 (s, 2H), 2.98 (d, 2H, J = 6.6 Hz). GCMS m/z (% relative intensity.) 266 (M^+ , 39), 189 (6), 175 (9), 157 (9), 109 (6), 91 (100), 77 (14). For ^1H and ^{13}C NMR spectra of these compounds, see appendixes 31-33.

1-Phenyl-1-phenylthiopenta-1(Z),4-diene (3la): Isolated yield: 78% (catalyst A), colorless oil, bp 110 °C (0.9 Torr). ^1H NMR (CDCl_3) δ 7.58-7.10 (m, 10H), 6.42 (t, 1H, J = 7.3 Hz), 5.97-5.84 (m, 1H), 5.14 (dd, 1H, J = 17, 1.5 Hz), 5.07 (dd, 1H, J = 10, 1.5 Hz), 3.32 (m, 2H). ^{13}C NMR (CDCl_3) δ 140.2, 136.5, 135.7, 134.7, 128.7, 128.4, 128.2, 127.7, 127.6, 125.5, 115.8, 35.2. IR (thin film): 3075, 3058, 3004, 2977, 2917, 1637, 1581, 1477, 1440, 1076, 1024,

993, 914, 740, 696 cm^{-1} . GCMS m/z (% relative intensity.) 252 (M^+ , 33), 211 (6), 175 (82), 143 (56), 141 (75), 128 (100), 115 (57), 109 (5), 91 (28), 77 (17). Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{S}$: C, 80.95; H, 6.35; S, 12.69. Found: C, 80.61; H, 6.25; S, 12.74. For ^1H and ^{13}C NMR spectra of the compound, see appendixes 34 and 35.

1-(4'-Fluorophenyl)-1-phenylthiopenta-1(Z),4-diene (3ma): Isolated yield: 76% (catalyst A), colorless oil, bp 65 °C (0.4 Torr). ^1H NMR (CDCl_3) δ 7.53-7.49 (m, 2H), 7.14-7.03 (m, 5H), 6.93-6.87 (m, 2H), 6.33 (t, 1H, $J = 7.3$ Hz), 5.96-5.83 (m, 1H), 5.16-5.05 (m, 2H), 3.32-3.28 (m, 2H). ^{13}C NMR (CDCl_3) δ 162.3 (d, $J_{\text{F-C}} = 247$ Hz), 136.2 (d, $J_{\text{F-C}} = 3.1$ Hz), 136.1, 135.6, 135.3, 133.9, 129.2 (d, $J_{\text{F-C}} = 8.0$ Hz), 128.7, 128.6, 125.7, 115.9, 115.0 (d, $J_{\text{F-C}} = 21.5$ Hz), 35.2. IR (thin film): 3075, 3004, 1637, 1598, 1504, 1477, 1232, 1157, 916, 833, 804, 740, 719 cm^{-1} . GCMS m/z (% relative intensity.) 270 (M^+ , 25), 229 (5), 193 (90), 161 (40), 159 (63), 146 (100), 133 (48), 109 (31), 95 (6), 65 (22). HRMS (m/z) calcd for $\text{C}_{17}\text{H}_{15}\text{FS}$: 270.0877, found: 270.0875. For ^1H and ^{13}C NMR spectra of the compound, see appendixes 36 and 37.

1-Phenylthio-1-(p-tolyl)penta-1(Z),4-diene (3na): Isolated yield: 35% (catalyst A), colorless oil, bp 60 °C (0.25 Torr). ^1H NMR (CDCl_3) δ 7.46 (d, 2H, $J = 8.0$ Hz), 7.16-7.10 (m, 5H), 7.04 (d, 2H, $J = 8.0$ Hz), 6.39 (t, 1H, $J = 7.3$ Hz), 5.95-5.82 (m, 1H), 5.14-5.03 (m, 2H), 3.30 (m, 2H), 2.27 (s, 3H). ^{13}C NMR (CDCl_3) δ 137.5, 137.3, 136.0, 135.8, 134.4, 129.1, 128.9, 128.7, 128.2, 127.4, 125.4, 115.7, 35.2, 21.1. IR (thin film): 3075, 3002, 2977, 2919, 1477, 1438, 1024, 815, 738, 690 cm^{-1} . GCMS m/z (% relative intensity.) 266 (M^+ , 22), 251 (6), 224 (5), 189 (67), 175 (2), 157 (46), 142 (100), 141 (75), 129 (30), 115 (44), 91 (17), 77 (14). Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{S}$: C, 81.20; H, 6.77; S, 12.03. Found: C, 81.59; H, 6.71; S, 11.94. For ^1H and ^{13}C NMR spectra of the compound, see appendixes 38 and 39.

1-(4-Methoxyphenyl)-1-phenylthiopenta-1(Z),4-diene (3oa): Isolated yield: 42% (catalyst A), colorless oil, bp 70 °C (0.25 Torr). ^1H NMR (CDCl_3) δ 7.49 (d, 2H, $J = 8.7$ Hz), 7.14-7.02 (m, 5H), 6.76 (d, 2H, $J = 8.7$ Hz), 6.32 (t, 1H, $J = 7.2$ Hz), 5.96-5.82 (m, 1H), 5.16-5.04 (m, 2H), 3.75 (s, 3H), 3.29 (m, 2H). ^{13}C NMR (CDCl_3) δ 159.2, 135.9, 134.9, 134.0, 132.7, 128.7 (2C), 128.3, 125.4, 115.6, 113.5, 55.2, 35.2. IR (thin film): 3002, 2834, 1604, 1506, 1249, 1174, 1035, 829, 740, 690 cm^{-1} . GCMS m/z (% relative intensity.) 282 (M^+ , 34), 267 (3), 251 (2), 240 (5), 205 (60), 189 (2), 173 (82), 158 (100), 141 (28), 128 (35), 115 (37), 109 (5), 91 (5), 77 (19). Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{OS}$: C, 76.59; H, 6.38; S, 11.34. Found: C, 76.56; H, 6.28; S, 11.11. For ^1H and ^{13}C NMR spectra of the compound, see appendixes 40 and 41.

5-Phenylthio-4-propyl-octa-1,4(Z)-diene (3pa): Isolated yield: 75%, colorless oil, bp 55 °C (0.4 Torr). ^1H NMR (CDCl_3) δ 7.27-7.10 (m, 5H), 5.84-5.70 (m, 1H), 5.06-4.98 (m, 2H), 3.21 (d, 2H, $J = 6.4$ Hz), 2.24-2.18 (m, 4H), 1.57-1.49 (m, 4H), 0.98 (t, 3H $J = 7.3$ Hz), 0.86 (t, 3H $J = 7.3$ Hz). ^{13}C NMR (CDCl_3) δ 146.0, 137.2, 136.4, 128.8, 128.6, 128.1, 125.2, 115.5, 39.0, 34.9, 34.5, 22.4, 21.9, 14.3, 13.8. IR (thin film): 2960, 2931, 2869, 1637, 1583, 1475, 1085, 1024, 993, 910, 738, 690 cm^{-1} . GCMS m/z (% relative intensity.) 260 (M^+ , 23), 245 (3), 231 (9), 183 (100), 141 (26), 109 (21), 77 (37), 55 (35). Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{S}$: C, 78.46; H, 9.23; S,

12.30. Found: C, 78.43; H, 9.42; S, 12.13. For ^1H and ^{13}C NMR spectra of the compound, see appendixes 42 and 43.

1,2-Diphenyl-1-phenylthiopenta-1(*E*),4-diene (3qa): Isolated yield: 41%, colorless needle crystals, mp 76.5-77.0 °C. ^1H NMR (CDCl_3) δ 7.21-6.90 (m, 15H), 5.90-5.77 (m, 1H), 5.11 (dd, 1H, $J = 17.0, 1.5$ Hz), 5.04 (dd, 1H, $J = 10.0, 1.5$ Hz), 3.79 (d, 2H, $J = 6.3$ Hz). ^{13}C NMR (CDCl_3) δ 163.1, 144.6, 142.0, 139.4, 134.9, 133.3, 130.9, 130.1, 129.5, 128.5, 127.8, 127.2, 126.5, 126.4, 126.0, 116.1, 42.5. IR (thin film): 3072, 3031, 2915, 1635, 1579, 1477, 1438, 1085, 1025, 997, 902, 755, 738, 709, 694 cm^{-1} . GCMS m/z (% relative intensity.) 328 (M^+ , 57), 251 (85), 237 (6), 217 (43), 202 (43), 141 (28), 115 (34), 91 (100), 77 (13). Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{S}$: C, 84.14; H, 6.10; S, 9.76. Found: C, 84.31; H, 6.21; S, 9.46. For ^1H and ^{13}C NMR spectra of the compound, see appendixes 44 and 45.

4-Methyl-5-phenyl-5-phenylthiopenta-1,4(*Z*)-diene (3ra) and 4-phenyl-5-phenylthiohexa-1(*E*),4-diene (4ra): The isolated yield was 67% (**3ra** : **4ra** = 84 : 16). Colorless oil, bp 70.0 °C (0.3 Torr). **3ra**: ^1H NMR (CDCl_3) δ 7.25-7.03 (m, 10H), 5.96-5.83 (m, 1H), 5.18-5.09 (m, 2H), 3.39 (d, 2H, $J = 6.0$ Hz), 1.81 (s, 3H). ^{13}C NMR (CDCl_3) δ 142.1, 140.3, 135.8, 135.4, 129.8, 129.5, 129.0, 128.4, 127.6, 126.7, 125.7, 116.1, 41.5, 20.8. IR (thin film): 3075, 2908, 1637, 1581, 1477, 1438, 1024, 914, 759, 740, 690 cm^{-1} . GCMS m/z (% relative intensity.) 266 (M^+ , 30), 251 (5), 189 (100), 157 (37), 141 (47), 129 (62), 115 (53), 91 (40), 77 (27), 65 (13). Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{S}$ (a mixture of adducts): C, 81.20; H, 6.77; S, 12.03. Found: C, 81.23; H, 6.82; S, 12.19. **4ra**: ^1H NMR (CDCl_3) δ 7.37-7.20 (m, 10H), 5.82-5.69 (m, 1H), 5.04-4.96 (m, 2H), 3.54 (d, 2H, $J = 6.4$ Hz), 1.80 (s, 3H). GCMS m/z (% relative intensity.) 266 (M^+ , 28), 251 (6), 189 (100), 157 (13), 141 (27), 129 (43), 115 (41), 91 (31), 77 (23), 65 (12). For ^1H and ^{13}C NMR spectra of these compounds, see appendixes 46-48.

4-Isopropenyl-8-methyl-5-phenylthionona-1,4(*E*)-diene (3sa) and 2-methyl-4-(3-methylbutyl)-3-phenylthiohepta-1,3(*Z*),6-triene (4sa): The isolated yield was 41% (**3sa** : **4sa** = 68 : 32). Colorless oil, bp 70.0 °C (0.2 Torr). **3sa**: ^1H NMR (CDCl_3) δ 7.23-7.12 (m, 5H), 5.87-5.74 (m, 1H), 5.10-5.03 (m, 2H), 4.83 (s, 1H), 4.63 (s, 1H), 3.24 (d, 2H, $J = 6.5$ Hz), 2.27-2.22 (m, 2H), 1.80 (s, 3H), 1.58-1.45 (m, 1H), 1.36-1.29 (m, 2H), 0.88 (d, 6H, $J = 6.5$ Hz). ^{13}C NMR (CDCl_3) δ 144.8, 142.3, 136.0, 131.5, 130.1, 128.5, 125.9, 115.8 (2C), 38.6, 37.7, 31.6, 28.5, 22.8, 22.5. IR (thin film): 2952, 2921, 2869, 1635, 1583, 1477, 1438, 1024, 908, 896, 740, 690 cm^{-1} . GCMS m/z (% relative intensity.) 286 (M^+ , 18), 271 (4), 243 (4), 230 (14), 215 (26), 209 (42), 187 (10), 137 (12), 121 (47), 109 (21), 107 (37), 105 (80), 91 (100), 77 (77), 71 (15), 65 (43), 55 (60). Anal. Calcd for $\text{C}_{19}\text{H}_{26}\text{S}$ (a mixture of adducts): C, 79.72; H, 9.09; S, 11.18. Found: C, 79.81; H, 8.88; S, 11.10. **4sa**: ^1H NMR (CDCl_3) δ 7.24-7.12 (m, 5H), 5.82-5.67 (m, 1H), 5.04-4.97 (m, 2H), 4.99 (s, 1H), 4.70 (s, 1H), 3.25 (d, 2H, $J = 6.5$ Hz), 2.22-2.17 (m, 2H), 1.87 (s, 3H), 1.56-1.52 (m, 1H), 1.39-1.31 (m, 2H), 0.89 (d, 3H, $J = 6.5$ Hz), 0.76 (d, 3H, $J = 5.9$ Hz). GCMS m/z (% relative intensity.) 286 (M^+ , 7), 209 (100), 167 (6), 153 (8), 111 (30), 91 (27), 77 (26). For ^1H and ^{13}C NMR spectra of these compounds, see appendixes 49-51.

4-Hydroxymethyl-5-phenyl-5-phenylthiopenta-1,4(E)-diene (3ta): Isolated yield: 79%, colorless oil, bp 100.0 °C (0.1 Torr). ^1H NMR (CDCl_3) δ 7.22-7.03 (m, 10H), 6.06-5.93 (m, 1H), 5.25-5.13 (m, 2H), 4.08 (s, 2H), 3.53-3.50 (m, 2H), 1.49 (s, 1H). ^{13}C NMR (CDCl_3) δ 140.7, 138.4, 135.7, 134.0, 131.4, 129.7, 128.4, 127.7, 127.4, 126.6, 116.4, 62.9, 37.0. IR (thin film): 3272, 3075, 3058, 1637, 1581, 1477, 1440, 1024, 761, 742, 700, 690 cm^{-1} . GCMS m/z (% relative intensity.) 282 (M^+ , 20), 264 (22), 241 (7), 223 (28), 205 (13), 175 (10), 155 (100), 141 (41), 128 (49), 109 (7), 91 (52), 77 (33). Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{OS}$: C, 76.59; H, 6.38; S, 11.34. Found: C, 76.69; H, 6.42; S, 11.69. For ^1H and ^{13}C NMR spectra of the compound, see appendixes 52 and 53.

5-Methylthioundeca-1,4(Z)-diene (3ab) and 1-methylthio-2-hexyl-1-penta-1(Z),4-diene (4ab): The isolated yield: 28%, colorless oil, bp 55 °C (0.20 Torr). **3ab:** ^1H NMR (CDCl_3) δ 5.87-5.74 (m, 1H), 5.52 (t, 1H, $J = 7.1$ Hz), 5.03 (dm, 1H, $J = 17$ Hz), 4.97 (dm, 1H, $J = 10.0$), 2.98 (t, 2H, $J = 6.6$ Hz), 2.24 (t, 2H, $J = 7.7$ Hz), 2.17 (s, 3H), 1.53-1.48 (m, 2H), 1.31-1.27 (m, 6H), 0.88 (t, 3H $J = 6.5$ Hz). ^{13}C NMR (CDCl_3) δ 136.6 (2C), 126.5, 114.7, 36.2, 33.5, 31.7, 28.7, 28.5, 22.7, 14.7, 14.1. IR (thin film): 2954, 2925, 2871, 2856, 1639, 1619, 991, 910 cm^{-1} . GCMS m/z (% relative intensity.) 198 (M^+ , 20), 183 (100), 113 (13), 85 (17), 79 (49), 71 (10), 57 (23). HRMS (m/z) calcd for $\text{C}_{12}\text{H}_{22}\text{S}$: 198.1441, found: 198.1434. **4ab:** ^1H NMR (CDCl_3) δ 5.80-5.67 (m, 1H), 5.65 (s, 1H), 5.09-4.99 (m, 2H), 2.88 (d, 2H, $J = 6.8$ Hz), 2.24 (s, 3H), 2.04 (t, 2H, $J = 7.5$ Hz), 1.41-1.27 (m, 8H), 0.87 (t, 3H $J = 6.5$ Hz). GCMS m/z (% relative intensity.) 198 (M^+ , 28), 183 (82), 113 (14), 85 (13), 79 (100), 57 (17). For ^1H and ^{13}C NMR spectra of these compounds, see appendixes 54-56.

2-Methyl-5-phenylthioundeca-1,4(Z)-diene (3ac) and 4-methyl-2-hexyl-1-phenylthiopenta-1(Z),4-diene (4ac): Isolated yield: 68%, colorless oil, bp 70 °C (0.25 Torr). **3ac:** ^1H NMR (CDCl_3) δ 7.32-7.15 (m, 5H), 5.91 (t, 1H, $J = 7.3$ Hz), 4.74 (s, 1H), 4.72 (s, 1H), 3.06 (d, 2H, $J = 7.2$ Hz), 2.17 (t, 2H, $J = 7.5$ Hz), 1.75 (s, 3H), 1.49-1.20 (m, 8H), 0.84 (t, 3H $J = 6.8$ Hz). ^{13}C NMR (CDCl_3) δ 133.2, 129.6, 128.9, 128.8, 125.9, 125.8, 110.5, 110.1, 38.3, 37.4, 31.6, 28.5, 28.4, 22.8, 22.5, 14.0. IR (thin film): 2956, 2929, 2856, 1650, 1585, 1477, 1438, 1024, 889, 740, 690 cm^{-1} . GCMS m/z (% relative intensity.) 274 (M^+ , 67), 197 (45), 189 (6), 147 (18), 109 (37), 95 (96), 93 (62), 91 (67), 81 (100), 77 (70), 57 (10). HRMS (m/z) calcd for $\text{C}_{18}\text{H}_{26}\text{S}$: 274.1753, found: 274.1757. **4ac:** ^1H NMR (CDCl_3) δ 7.31-7.13 (m, 5H), 6.06 (s, 1H), 4.80 (s, 1H), 4.71 (s, 1H), 3.02 (s, 2H), 2.13 (t, 2H, $J = 7.4$ Hz), 1.72 (s, 3H), 1.47-1.20 (m, 8H), 0.89 (t, 3H $J = 6.6$ Hz). ^{13}C NMR (CDCl_3) δ 144.4, 140.0, 128.8, 128.7, 128.0, 125.6, 117.5, 111.7, 40.5, 36.4, 31.7, 29.0, 27.7, 22.6, 22.3, 14.1. GCMS m/z (% relative intensity.) 274 (M^+ , 47), 197 (13), 189 (9), 147 (17), 109 (32), 95 (44), 93 (100), 91 (91), 81 (81), 77 (68), 57 (6). For ^1H and ^{13}C NMR spectra of these compounds, see appendixes 57-59.

6-Phenylthio-dodeca-2(Z or E),5(Z)-diene (6), 2-hexyl-1-phenylthiohexa-1(Z),4-diene (7) and 3-methyl-5-phenylthioundeca-1,4(Z)-diene (5): Colorless oil, bp 70 °C (0.25 Torr). Anal. Calcd for $\text{C}_{18}\text{H}_{26}\text{S}$ (a mixture of adducts): C, 78.83; H, 9.50; S, 11.68.

Found: C, 78.73; H, 9.29; S, 11.57. **6**: ^1H NMR (CDCl_3) δ 7.31-7.14 (m, 5H), 5.87 (t, 1H, $J = 7.1$ Hz), 5.51-5.38 (m, 2H), 3.03 (t, 2H, $J = 5.9$ Hz), 2.15 (t, 2H, $J = 7.4$ Hz), 1.66 (d, 3H, $J = 4.8$ Hz), 1.48-1.20 (m, 8H), 0.85 (t, 3H, $J = 7.4$ Hz). IR (thin film): 2952, 2911, 2867, 2854, 1619, 1588, 1477, 1438, 1024, 964, 738, 690 cm^{-1} . GCMS m/z (% relative intensity.) 274 (M^+ , 67), 245 (6), 197 (77), 123 (10), 109 (37), 95 (70), 93 (26), 91 (39), 81 (100), 79 (52), 77 (38), 67 (38), 55 (56). **7**: ^1H NMR (CDCl_3) δ 7.29-7.25 (m, 5H), 5.94 (s, 1H), 5.57-5.33 (m, 2H), 2.96 (d, 2H, $J = 6.5$ Hz), 2.15 (t, 2H, $J = 7.2$ Hz), 1.66 (dd, 3H, $J = 6.1, 1.2$ Hz), 1.48-1.20 (m, 8H), 0.89 (t, 3H, $J = 6.6$ Hz). GCMS m/z (% relative intensity.) 274 (M^+ , 100), 245 (12), 197 (33), 147 (22), 123 (23), 109 (41), 95 (66), 93 (48), 91 (50), 81 (73), 79 (42), 77 (37), 67 (32), 55 (61). **5**: ^1H NMR (CDCl_3) δ 5.71 (d, 1H, $J = 6.1$ Hz), 5.01 (dm, 1H, $J = 16$ Hz), 4.96 (dm, 1H, $J = 10.4$ Hz), 3.69-3.58 (m, 1H), other signals are overlapping with the signals of the other adducts **6** and **7**. GCMS m/z (% relative intensity.) 274 (M^+ , 10), 197 (100), 123 (5), 113 (16), 95 (14), 93 (13), 91 (16), 81 (23), 79 (21), 77 (17), 67 (12), 55 (24). For ^1H NMR spectra of these compounds, see appendixes 60-62.

Synthesis of $\text{Ni}(\eta^3\text{-C}_3\text{H}_5)(\text{SPh})(\text{PMe}_3)$ (**8a**).

$\text{Ni}(\text{cod})_2$ (0.75 mmol) was dissolved in 10 mL of THF and the mixture was cooled to -60 $^\circ\text{C}$. PMe_3 (1.5 mmol) and **2a** (0.75 mmol) were added to the mixture, which was then gradually warmed to room temperature overnight. Resulting brown solution was evaporated under vacuum and hexane was added to result in precipitation of orange solid, which was separated and washed three times with cold hexane and recrystallized from octane to afford 46% yield. **8a**: ^1H NMR ($\text{C}_6\text{D}_5\text{CD}_3$) δ 7.74 (d, 2H, $J = 7.3$ Hz), 7.10-6.90 (m, 3H), 4.80 (m, 1H), 2.28 (br, 2H), 2.09 (br, 2H, partially overlapping with a solvent signal), 0.85 (d, 9H, $J = 8.6$ Hz). ^{31}P NMR ($\text{C}_6\text{D}_5\text{CD}_3$) δ -12.5. This complex was extremely air-sensitive and satisfactory elemental analysis could not be obtained. The structure was confirmed by X-ray diffraction analysis.

Synthesis of $\text{Ni}(\eta^3\text{-C}_3\text{H}_5)(\text{SPh})(\text{PPh}_3)$ (**8b**).

To $\text{Ni}(\text{cod})_2$ (0.1 mmol) placed in an NMR tube were added a toluene- d_8 solution of **2a** (0.1 mmol) and PPh_3 (0.1 mmol) at -60 $^\circ\text{C}$, and the mixture was gradually warmed to room temperature (overnight) to form a homogeneous orange solution. ^1H NMR of this reaction mixture showed that the conversion of **2a** was *ca.* 80%. Evaporation of volatiles and recrystallization from toluene and hexane, which accompanied extensive decomposition of the product, gave **8b** in only 6% yield. Another experiment using THF as reaction solvent and THF-hexane as recrystallization solvent afforded **8b** in 61% yield. **8b**: ^{31}P NMR ($\text{C}_6\text{D}_5\text{CD}_3$) δ 24.3 ppm

References

- (1) (a) Edgell, W. F.; Dunkle, M. P. *Inorg. Chem.* **1965**, *4*, 1629-1637. (b) Bodner, G. M. *Inorg. Chem.* **1975**, *14*, 1932-1935.
- (2) Ittel, S. D. *Inorg. Synth.* **1977**, *17*, 117-124.
- (3) Koch, G.; Lloy-J. G.; Loiselrur, O.; Pfaltz, A.; Pretot, R.; Schaffner, S.; Schnider, P; Matt, P. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 206-210.
- (4) Bolm, C.; Weickhardt, K.; Zehnder, M.; Ranff, T. *Chem. Ber.* **1991**, *124*, 1173-1180.
- (5) Alcaide, B.; Gomez, A.; Plumet, J.; Rodriguez-L., J. *Tetrahedron* **1989**, *45*, 2751-2762.
- (6) Furuta, K.; Ikeda, Y.; Meguriya, N.; Ikeda, N.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2781-2790.
- (7) Price, C. C.; Gillis, R. G. *J. Am. Chem. Soc.* **1953**, *75*, 4750-4753.

Appendix 1: ^1H NMR spectrum of 5-phenylthioundeca-1,4(Z)-diene (**3aa**)

Appendix 2: ^{13}C NMR spectrum of 5-phenylthioundeca-1,4(Z)-diene (**3aa**)

Appendix 3: ^1H NMR spectrum of 2-hexyl-1-phenylthiopenta-1(Z),4-diene (**4aa**) as a mixture containing a small amount of 5-phenylthioundeca-1,4(Z)-diene (**3aa**)

Appendix 4: ^1H NMR spectrum of 5-phenylthiohexa-1,4(Z)-diene (**3ba**)

Appendix 5: ^{13}C NMR spectrum of 5-phenylthiohexa-1,4(Z)-diene (**3ba**) as a mixture containing 2-methyl-1-phenylthiopenta-1(E),4-diene (**4ba**)

Appendix 6: Expanded ^{13}C NMR spectrum of 5-phenylthiohexa-1,4(Z)-diene (**3ba**)

Appendix 7: ^1H NMR spectrum of 2-methyl-1-phenylthiopenta-1(E),4-diene (**4ba**) as a mixture containing 5-phenylthiohexa-1,4(Z)-diene (**3ba**)

Appendix 8: ^1H NMR spectrum of 6,6-dimethyl-5-phenylthiohepta-1,4(Z)-diene

Appendix 9: ^{13}C NMR spectrum of 6,6-dimethyl-5-phenylthiohepta-1,4(Z)-diene (**3ca**)

Appendix 10: ^1H NMR spectrum of 8-chloro-5-phenylthioocta-1,4(Z)-diene (3da)

Appendix 11: ^{13}C NMR spectrum of 8-chloro-5-phenylthioocta-1,4(Z)-diene (3da)

Appendix 12: ^1H NMR spectrum of 2-(3-chloropropyl)-1-phenylthiopenta-1(Z),4-diene (**4da**)

Appendix 13: ^{13}C NMR spectrum of 2-(3-chloropropyl)-1-phenylthiopenta-1(Z),4-diene (**4da**)

Appendix 14: ^1H NMR spectrum of 8-cyano-5-phenylthioocta-1,4(Z)-diene (**3ea**)

Appendix 15: ^{13}C NMR spectrum of 8-cyano-5-phenylthioocta-1,4(Z)-diene (**3ea**)

Appendix 16: ^1H NMR spectrum of 2-(3'-cyanopropyl)-1-phenylthiopenta-1(Z),4-diene (**4ea**)

Appendix 17: ^{13}C NMR spectrum of 2-(3'-cyanopropyl)-1-phenylthiopenta-1(Z),4-diene (**4ea**)

Appendix 18: ^1H NMR spectrum of 9-*t*-butyldimethylsiloxy-5-phenylthionona-1,4(*Z*)-diene (**3fa**)

Appendix 19: ^1H NMR spectrum of 9-*t*-butyldimethylsiloxy-5-phenylthionona-1,4(*Z*)-diene (**3fa**)

Appendix 20: ^1H NMR spectrum of 6-hydroxy-6-methyl-5-phenylthiohepta-1,4(Z)-diene (**3ga**)

Appendix 21: ^{13}C NMR spectrum of 6-hydroxy-6-methyl-5-phenylthiohepta-1,4(Z)-diene (**3ga**)

Appendix 22: ^1H NMR spectrum of 6-methoxy-5-phenylthiohexa-1,4(Z)-diene (**3ha**)

Appendix 23: ^{13}C NMR spectrum of 6-methoxy-5-phenylthiohexa-1,4(Z)-diene (**3ha**)

Appendix 24: ^1H NMR spectrum of 2-methoxymethyl-1-phenylthiopenta-1(*E*),4-diene (**4ha**) as a mixture containing 6-methoxy-5-phenylthiohexa-1,4(*Z*)-diene (**3ha**)

Appendix 25: ^{13}C NMR spectrum of 2-methoxymethyl-1-phenylthiopenta-1(*E*),4-diene (**4ha**) as a mixture containing 6-methoxy-5-phenylthiohexa-1,4(*Z*)-diene (**3ha**)

Appendix 26: ^1H NMR spectrum of 7-ethoxycarbonyl-5-phenylthiohepta-1,4(Z)-diene (3ia)

Appendix 27: ^{13}C NMR spectrum of 7-ethoxycarbonyl-5-phenylthiohepta-1,4(Z)-diene (3ia)

Appendix 28: ^1H NMR spectrum of 2-(2-ethoxycarbonyl-1-phenylthio)pent-1(Z),4-diene (**4ia**) as a mixture containing 7-ethoxycarbonyl-5-phenylthiohepta-1,4(Z)-diene (**3ia**)

Appendix 29: ^1H NMR spectrum of 6-methyl-5-phenylthiohepta-1,4(Z),6-triene (**3ja**)

Appendix 30: ^{13}C NMR spectrum of 6-methyl-5-phenylthiohepta-1,4(Z),6-triene

Appendix 31: ^1H NMR spectrum of 6-phenyl-5-phenylthiohexa-1,4(Z)-diene (3ka)

Appendix 32: ^{13}C NMR spectrum of 6-phenyl-5-phenylthiohexa-1,4(Z)-diene (**3ka**)

Appendix 33: ^1H NMR spectrum of 2-benzyl-1-phenylthiopenta-1(E),4-diene (**4ka**) as a mixture containing 6-phenyl-5-phenylthiohexa-1,4(Z)-diene (**3ka**)

Appendix 34: ^1H NMR spectrum of 1-phenyl-1-phenylthiopenta-1(Z),4-diene (**3la**)

Appendix 35: ^{13}C NMR spectrum of 1-phenyl-1-phenylthiopenta-1(Z),4-diene (**3la**)

Appendix 36: ^1H NMR spectrum of 1-(4'-fluorophenyl)-1-phenylthiopenta-1(Z),4-diene (**3ma**)

Appendix 37: ^{13}C NMR spectrum of 1-(4'-fluorophenyl)-1-phenylthiopenta-1(Z),4-diene (**3ma**)

Appendix 38: ^1H NMR spectrum of 1-phenylthio-1-(*p*-tolyl)penta-1(*Z*),4-diene (**3na**)

Appendix 39: ^{13}C NMR spectrum of 1-phenylthio-1-(*p*-tolyl)penta-1(*Z*),4-diene (**3na**)

Appendix 40: ^1H NMR spectrum of 1-(4-methoxyphenyl)-1-phenylthiopenta-1(Z),4-diene (**30a**)

Appendix 41: ^{13}C NMR spectrum of 1-(4-methoxyphenyl)-1-phenylthiopenta-1(Z),4-diene (**30a**)

Appendix 42: ^1H NMR spectrum of 5-phenylthio-4-propyl-octa-1,4(Z)-diene (**3pa**)

Appendix 43: ^{13}C NMR spectrum of 5-phenylthio-4-propyl-octa-1,4(Z)-diene (**3pa**)

Appendix 44: ^1H NMR spectrum of 1,2-diphenyl-1-phenylthiopenta-1(*E*),4-diene (3qa)

Appendix 45: ^{13}C NMR spectrum of 1,2-diphenyl-1-phenylthiopenta-1(*E*),4-diene (3qa)

Appendix 46: ^1H NMR spectrum of 4-methyl-5-phenyl-5-phenylthiopenta-1,4(Z)-diene (**39a**)

Appendix 47: ^{13}C NMR spectrum of 4-methyl-5-phenyl-5-phenylthiopenta-1,4(Z)-diene (**39a**)

Appendix 48: ^1H NMR spectrum of 4-phenyl-5-phenylthiohexa-1(*E*),4-diene (**4ra**) as a mixture containing 4-methyl-5-phenyl-5-phenylthiopenta-1,4(*Z*)-diene (**3ra**)

Appendix 49: ^1H NMR spectrum of 4-isopropenyl-8-methyl-5-phenylthionona-1,4(*E*)-

diene (**3sa**)

Appendix 50: ^{13}C NMR spectrum of 4-isopropenyl-8-methyl-5-phenylthionona-1,4(*E*)-diene (**3sa**)

Appendix 54: ^1H NMR spectrum of 5-methylthioundeca-1,4(Z)-diene (**3ab**)

Appendix 55: ^{13}C NMR spectrum of 5-methylthioundeca-1,4(Z)-diene (**3ab**)

Appendix 56: ^{13}C NMR spectrum of 1-methylthio-2-hexyl-1-penta-1(Z),4-diene (**4ab**) as a mixture containing 5-methylthioundeca-1,4(Z)-diene (**3ab**)

Appendix 57: ^1H NMR spectrum of 2-methyl-5-phenylthioundeca-1,4(Z)-diene (**3ac**)

Appendix 58: ^{13}C NMR spectrum of 2-methyl-5-phenylthioundeca-1,4(Z)-diene (**3ac**)

Appendix 59: ^1H NMR spectrum of 4-methyl-2-hexyl-1-phenylthiopenta-1(Z),4-diene (**4ac**)

Appendix 62: ^1H NMR spectrum of 2-hexyl-1-phenylthiohexa-1(Z),4-diene (7)