

Supporting Information

Synthesis of Benzo[*b*]thiophenes by Cyclization of Arylketene Dithioacetal Monoxides under Pummerer-like Conditions

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Cautions

All the experiments should be performed in a fume hood with standard precautions. Trifluoromethanesulfonic anhydride is highly corrosive. Trifluoroacetophenone and ethyl trifluoroacetate irritate eyes and skin.

Characterization Data of New Compounds

methyl 1-methylsulfinyl-2,2-diphenylethenyl sulfide (1a): Mp 106–107 °C; IR (nujol) 2855, 1442, 1318, 1029, 943, 765, 696 cm⁻¹; ¹H NMR (CDCl₃) δ 2.24 (s, 3H), 2.74 (s, 3H), 7.14–7.16 (m, 2H), 7.35–7.38 (m, 8H); ¹³C NMR (CDCl₃) δ 20.3, 38.6, 128.5, 128.6, 129.0, 129.2, 129.6, 129.7, 139.9, 140.4, 143.5, 156.6. Found: C, 66.76; H, 5.62%. Calcd for C₁₆H₁₆OS₂: C, 66.63; H, 5.59%.

methyl (*E*)-3,3,3-trifluoro-1-methylsulfinyl-2-phenyl-1-propenyl sulfide (1b): (*E*)-isomer: Mp 104–105 °C; IR (nujol) 2854, 1447, 1378, 1296, 1114, 1046, 701 cm⁻¹; ¹H NMR (CDCl₃) δ 2.56 (s, 3H), 2.69 (s, 3H), 7.10–7.25 (br, 2H), 7.45–7.48 (m, 3H); ¹³C NMR (CDCl₃) δ 21.9, 38.8, 121.6 (q, *J*_{C-F} = 276 Hz), 129.0, 129.1, 130.1, 131.7, 143.7 (q, *J*_{C-F} = 31.0 Hz), 155.7. (*Z*)-isomer: IR (neat) 2928, 1564, 1489, 1444, 1293, 1124, 1074, 847, 704, 676 cm⁻¹; ¹H NMR (CDCl₃) δ 2.08 (s, 3H), 2.80 (s, 3H), 7.30–7.32 (m, 2H), 7.43–7.46 (m, 3H); ¹³C NMR

(CDCl₃) δ 19.1, 40.2, 122.0 (q, J_{C-F} = 276 Hz), 128.9, 129.2, 129.6, 133.1, 138.1 (q, J_{C-F} = 32.5 Hz), 157.8. Found: C, 47.02; H, 3.96%. Calcd for C₁₁H₁₁F₃OS₂: C, 47.13; H, 3.96%.

methyl 2-(2-methoxyphenyl)-1-methylsulfinyl-2-phenylethenyl sulfide (1c, 1:1 mixture of stereoisomers): Mp 118–119 °C; IR (nujol) 2923, 1488, 1248, 1035, 1020, 758, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 2.20–2.40 (br, 3H), 2.50–2.74 (br, 3H), 3.65–3.90 (br, 3H), 6.80–7.22 (br, 3H), 7.28–7.36 (m, 4H), 7.40 (dd, J = 1.5, 8.0 Hz, 2H); ¹³C NMR (CDCl₃) δ 20.3 (× 2C), 38.4 (× 2C), 55.4, 55.8, 111.0, 111.5, 120.4, 121.0, 128.1 (× 3C), 128.4 (× 4C), 128.7 (br, × 2C), 129.9 (br), 130.3 (× 2C), 140.0 (× 2C), 143.4 (br), 144.6 (br), 151.6 (br), 152.6 (br), 155.5 (br), 156.1 (br). Found: C, 64.19; H, 5.71%. Calcd for C₁₇H₁₈O₂S₂: C, 64.12; H, 5.70%.

methyl 2-(3-methoxyphenyl)-1-methylsulfinyl-2-phenylethenyl sulfide (1d, 3:2 mixture of stereoisomers): Mp 105–106 °C; IR (nujol) 2854, 1576, 1486, 1226, 1034, 941, 779 cm⁻¹; ¹H NMR (CDCl₃) δ 2.24 (s, 0.4 × 3H), 2.27 (s, 0.6 × 3H), 2.74 (s, 0.4 × 3H), 2.75 (s, 0.6 × 3H), 3.79 (s, 0.4 × 3H), 3.80 (s, 0.6 × 3H), 6.64–6.65 (m, 0.4 × 1H), 6.74–6.76 (m, 0.4 × 1H), 6.89–6.92 (m, 0.6 × 2H, 0.4 × 1H), 6.95–6.96 (m, 0.6 × 1H), 7.14–7.16 (m, 0.4 × 3H), 7.29 (dd, J = 7.5, 7.5 Hz, 0.6 × 2H), 7.35–7.40 (m, 0.6 × 4H, 0.4 × 3H); ¹³C NMR (CDCl₃) δ 20.2, 20.3, 38.6 (× 2C), 55.5 (× 2C), 114.3, 114.5, 115.2 (× 2C), 122.0 (× 2C), 128.5, 128.6, 129.0, 129.2, 129.4, 129.5, 129.6 (× 2C), 139.8, 140.1, 141.2, 141.6, 143.6 (× 2C), 156.0, 156.2, 159.5, 159.7. Found: C, 63.85; H, 5.66%. Calcd for C₁₇H₁₈O₂S₂: C, 64.12; H, 5.70%.

methyl 2-(4-methoxyphenyl)-1-methylsulfinyl-2-phenylethenyl sulfide (1e, 3:2 mixture of stereoisomers): Mp 111–112 °C; IR (nujol) 2854, 1604, 1507, 1253, 1027, 775, 691 cm⁻¹; ¹H NMR (CDCl₃) δ 2.22 (s, 0.4 × 3H), 2.26 (s, 0.6 × 3H), 2.73 (s, 0.6 × 3H), 2.76 (s, 0.4 × 3H), 3.83 (s, 3H), 6.86–6.89 (m, 2H), 7.06–7.07 (m, 0.4 × 2H), 7.13–7.15 (m, 0.6 × 2H), 7.33–7.39 (m, 5H); ¹³C NMR (CDCl₃) δ 20.2, 20.4, 38.5, 38.6, 55.5 (× 2C), 113.7, 113.9, 128.4, 128.5, 128.9, 129.1, 129.7, 129.8, 131.4, 131.5, 132.2, 132.5, 140.3, 140.8, 142.0, 142.2, 156.0, 156.8, 160.2, 160.5. Found: C, 63.94; H, 5.86%. Calcd for C₁₇H₁₈O₂S₂: C, 64.12; H, 5.70%.

methyl 1-methylsulfinyl-2-(2-naphthyl)-2-phenylethenyl sulfide (1f, 4:3 mixture of stereoisomers): Mp 116–117 °C; IR (nujol) 2922, 1442, 1377, 1028, 693 cm⁻¹; ¹H NMR

(CDCl₃) δ 2.22 (s, 0.45 × 3H), 2.29 (s, 0.55 × 3H), 2.78 (s, 0.55 × 3H), 2.80 (s, 0.45 × 3H), 7.19–7.22 (m, 0.45 × 2H, 0.55 × 1H), 7.37–7.43 (m, 4H), 7.48–7.57 (m, 0.45 × 3H, 0.55 × 2H), 7.67 (d, *J* = 1.5 Hz, 0.55 × 1H), 7.78–7.86 (m, 0.45 × 3H, 0.55 × 4H); ¹³C NMR (CDCl₃) δ 20.3 (× 2C), 38.5, 38.6, 126.7, 126.9 (× 2C), 127.0, 127.2, 127.3, 127.9, 128.0 (× 2C), 128.1, 128.5 (× 3C), 128.6, 129.1, 129.3 (× 2C), 129.6, 129.7, 129.9, 132.8, 133.0, 133.4, 133.4, 137.2, 137.8, 139.9, 140.2, 143.5, 143.6, 156.7 (× 2C). Found: C, 70.89; H, 5.36%. Calcd for C₂₀H₁₈OS₂: C, 70.97; H, 5.36%.

methyl 2-(4-trifluoromethylphenyl)-1-methylsulfinyl-2-phenylethenyl sulfide (1g, the major isomer): Mp 119–121 °C; IR (nujol) 2920, 1329, 1126, 1034, 706 cm⁻¹; ¹H NMR (CDCl₃) δ 2.27 (s, 3H), 2.76 (s, 3H), 7.13 (dd, *J* = 2.0, 7.5 Hz, 2H), 7.34–7.41 (m, 3H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (CDCl₃) δ 20.4, 38.6, 124.0 (q, *J*_{C-F} = 263 Hz), 125.5 (q, *J*_{C-F} = 3.9 Hz), 128.8, 129.5, 129.6, 129.9, 130.8 (q, *J*_{C-F} = 32.5 Hz), 139.0, 143.9, 145.2, 155.1. Found: C, 57.31; H, 4.33%. Calcd for C₁₇H₁₅F₃OS₂: C, 57.29; H, 4.24%.

2-methylthio-3-phenylbenzo[*b*]thiophene (5a): IR (neat) 2918, 1423, 1314, 1071, 965, 767, 732, 699 cm⁻¹; ¹H NMR (CDCl₃) δ 2.50 (s, 3H), 7.31–7.36 (m, 2H), 7.44–7.58 (m, 6H), 7.79–7.83 (m, 1H); ¹³C NMR (CDCl₃) δ 20.2, 122.0, 122.9, 124.5, 124.8, 128.0, 128.7, 130.2, 134.8, 135.5, 137.6, 139.9, 140.1. Found: C, 70.41; H, 4.98%. Calcd for C₁₅H₁₂OS₂: C, 70.27; H, 4.98%.

3-trifluoromethyl-2-methylthiobenzo[*b*]thiophene (5b): IR (neat) 1507, 1463, 1367, 1219, 1156, 1111, 757, 730 cm⁻¹; ¹H NMR (CDCl₃) δ 2.68 (s, 3H), 7.33 (ddd, *J* = 1.0, 7.5, 7.5 Hz, 1H), 7.42 (ddd, *J* = 1.0, 7.5, 7.5 Hz, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 7.5 Hz, 1H); ¹³C NMR (CDCl₃) δ 18.7 (q, *J*_{C-F} = 1.5 Hz), 120.0 (q, *J*_{C-F} = 34 Hz), 121.6, 122.0 (q, *J*_{C-F} = 2.9 Hz), 123.5 (q, *J*_{C-F} = 271 Hz), 124.4, 125.7, 137.2 (q, *J*_{C-F} = 1.5 Hz), 138.1, 145.8 (q, *J*_{C-F} = 2.9 Hz). Found: C, 48.63; H, 2.94%. Calcd for C₁₀H₇F₃S₂: C, 48.37; H, 2.84%.

4-methoxy-2-methylthio-3-phenylbenzo[*b*]thiophene (5c): IR (neat) 2919, 1600, 1423, 1245, 1114, 1027, 755, 731 cm⁻¹; ¹H NMR (CDCl₃) δ 2.49 (s, 3H), 3.78 (s, 3H), 7.07–7.12 (m, 2H), 7.28–7.36 (m, 4H), 7.45 (ddd, *J* = 2.0, 7.5, 7.5 Hz, 1H), 7.79 (dd, *J* = 1.0, 7.5 Hz, 1H); ¹³C

NMR (CDCl₃) δ 20.0, 55.5, 111.3, 120.5, 121.7, 123.0, 123.4, 124.1, 124.2, 129.6, 131.9, 134.6, 136.0, 139.7, 140.0, 157.5. Found: C, 66.86; H, 4.91%. Calcd for C₁₆H₁₄OS₂: C, 67.10; H, 4.93%.

5-methoxy-2-methylthio-3-phenylbenzo[*b*]thiophene (5d): IR (neat) 1596, 1421, 1264, 1229, 1140, 1036, 700 cm⁻¹; ¹H NMR (CDCl₃) δ 2.49 (s, 3H), 3.79 (s, 3H), 6.98–7.01 (m, 2H), 7.44–7.56 (m, 5H), 7.67 (d, *J* = 8.5 Hz, 1H); ¹³C NMR (CDCl₃) δ 20.1, 55.7, 105.3, 114.3, 122.7, 128.0, 128.8, 130.1, 132.2, 134.9, 136.8, 137.2, 141.1, 158.0. Found: C, 66.81; H, 5.00%. Calcd for C₁₆H₁₄OS₂: C, 67.10; H, 4.93%.

6-methoxy-2-methylthio-3-phenylbenzo[*b*]thiophene (5e): IR (neat) 2919, 1600, 1468, 1233, 1061, 804, 701, 645 cm⁻¹; ¹H NMR (CDCl₃) δ 2.43 (s, 3H), 3.89 (s, 3H), 6.94 (dd, *J* = 2.0, 8.5 Hz, 1H), 7.28 (d, *J* = 2.0 Hz, 1H), 7.42–7.54 (m, 6H); ¹³C NMR (CDCl₃) δ 20.9, 55.9, 104.7, 114.6, 123.9, 128.0, 128.6, 130.2, 131.7, 134.1, 135.0, 138.7, 141.6, 157.8. Found: C, 67.33; H, 4.91%. Calcd for C₁₆H₁₄OS₂: C, 67.10; H, 4.93%.

2-methylthio-3-phenylnaphtho[1,2-*b*]thiophene (5f): Mp 87–88 °C; IR (nujol) 2924, 1507, 1458, 1378, 809, 745, 690 cm⁻¹; ¹H NMR (CDCl₃) δ 2.52 (s, 3H), 7.46–7.49 (m, 1H), 7.51–7.61 (m, 7H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 20.9, 121.5, 123.7, 125.8, 126.0, 126.9, 128.0, 128.6, 128.7, 129.1, 130.4, 131.1, 134.2, 134.9, 137.5, 137.7, 139.8. Found: C, 74.22; H, 4.80%. Calcd for C₁₉H₁₄S₂: C, 74.47; H, 4.60%.

3-(4-trifluoromethylphenyl)-2-methylthiobenzo[*b*]thiophene (5g): IR (neat) 2922, 1617, 1425, 1324, 1166, 1107, 1066, 852, 732 cm⁻¹; ¹H NMR (CDCl₃) δ 2.52 (s, 3H), 7.32–7.38 (m, 2H), 7.50–7.53 (m, 1H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.80–7.83 (m, 1H); ¹³C NMR (CDCl₃) δ 20.1, 122.1, 122.5, 124.4 (q, *J*_{C-F} = 271 Hz), 124.7, 125.1, 125.7 (q, *J*_{C-F} = 3.8 Hz), 130.0 (q, *J*_{C-F} = 65 Hz), 130.7, 135.8, 136.8, 138.6, 139.6, 139.9. Found: C, 59.04; H, 3.50%. Calcd for C₁₆H₁₁F₃S₂: C, 59.24; H, 3.42%.

methyl 2,2-diphenylethenyl sulfoxide (9): Mp 88–89 °C; IR (nujol) 2925, 1448, 1020, 974, 763, 693 cm⁻¹; ¹H NMR (CDCl₃) δ 2.74 (s, 3H), 6.83 (s, 1H), 7.22–7.24 (m, 2H), 7.32–7.45 (m,

8H); ^{13}C NMR (CDCl_3) δ 41.0, 128.5 (\times 2C), 128.8, 129.4, 129.9, 130.0, 133.8, 137.3, 139.2, 152.6. Found: C, 74.29; H, 5.96%. Calcd for $\text{C}_{15}\text{H}_{14}\text{OS}$: C, 74.34; H, 5.82%.

methyl 1,2,2-triphenylethenyl sulfoxide (10): Mp 178–180 °C; IR (nujol) 2925, 1445, 1377, 1023, 740, 696 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.37 (s, 3H), 6.97–7.00 (m, 2H), 7.06–7.12 (m, 3H), 7.17–7.20 (m, 2H), 7.30–7.32 (m, 3H), 7.35–7.38 (m, 2H), 7.39–7.42 (m, 3H); ^{13}C NMR (CDCl_3) δ 37.4, 128.0, 128.2, 128.3 (\times 2C), 128.4, 128.9, 130.4, 130.5, 131.6, 132.3, 139.2, 140.0, 142.4, 150.3. Found: C, 79.20; H, 5.74%. Calcd for $\text{C}_{21}\text{H}_{18}\text{OS}$: C, 79.21; H, 5.70%.

methyl 2-(3-chloro-4-methoxyphenyl)-3,3,3-trifluoro-1-methylsulfinyl-1-propenyl sulfide (17, the major isomer): Mp 67–69 °C; IR (nujol) 2923, 1600, 1459, 1377, 1293, 1259, 1121, 815, 727, 665 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.59 (s, 3H), 2.68 (s, 3H), 3.96 (s, 3H), 6.97–7.01 (m, 1H), 7.01–7.15 (br, 1H), 7.15–7.26 (m, 1H); ^{13}C NMR (CDCl_3) δ 21.2, 38.9, 56.5, 112.2, 121.5 (q, $J_{\text{C-F}} = 276$ Hz), 123.4, 124.4, 129.0, 130.9, 142.0 (q, $J_{\text{C-F}} = 31.5$ Hz), 156.4, 156.6.

5-chloro-3-trifluoromethyl-6-methoxy-2-methylthiobenzo[*b*]thiophene (18): Mp 135–136 °C; IR (nujol) 2923, 1460, 1266, 1141, 1098, 1048, 866, 824, 704 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.65 (s, 3H), 3.96 (s, 3H), 7.23 (s, 1H), 7.83 (q, $J_{\text{H-F}} = 1.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 19.0 (q, $J_{\text{C-F}} = 1.5$ Hz), 56.4, 103.8, 119.9 (q, $J_{\text{C-F}} = 33.4$ Hz), 122.5, 122.8 (q, $J_{\text{C-F}} = 271$ Hz), 123.0 (q, $J_{\text{C-F}} = 2.9$ Hz), 130.8 (q, $J_{\text{C-F}} = 2.0$ Hz), 137.7, 143.4 (q, $J_{\text{C-F}} = 2.8$ Hz), 152.6.

Figure S2. ^{13}C NMR spectrum of 17

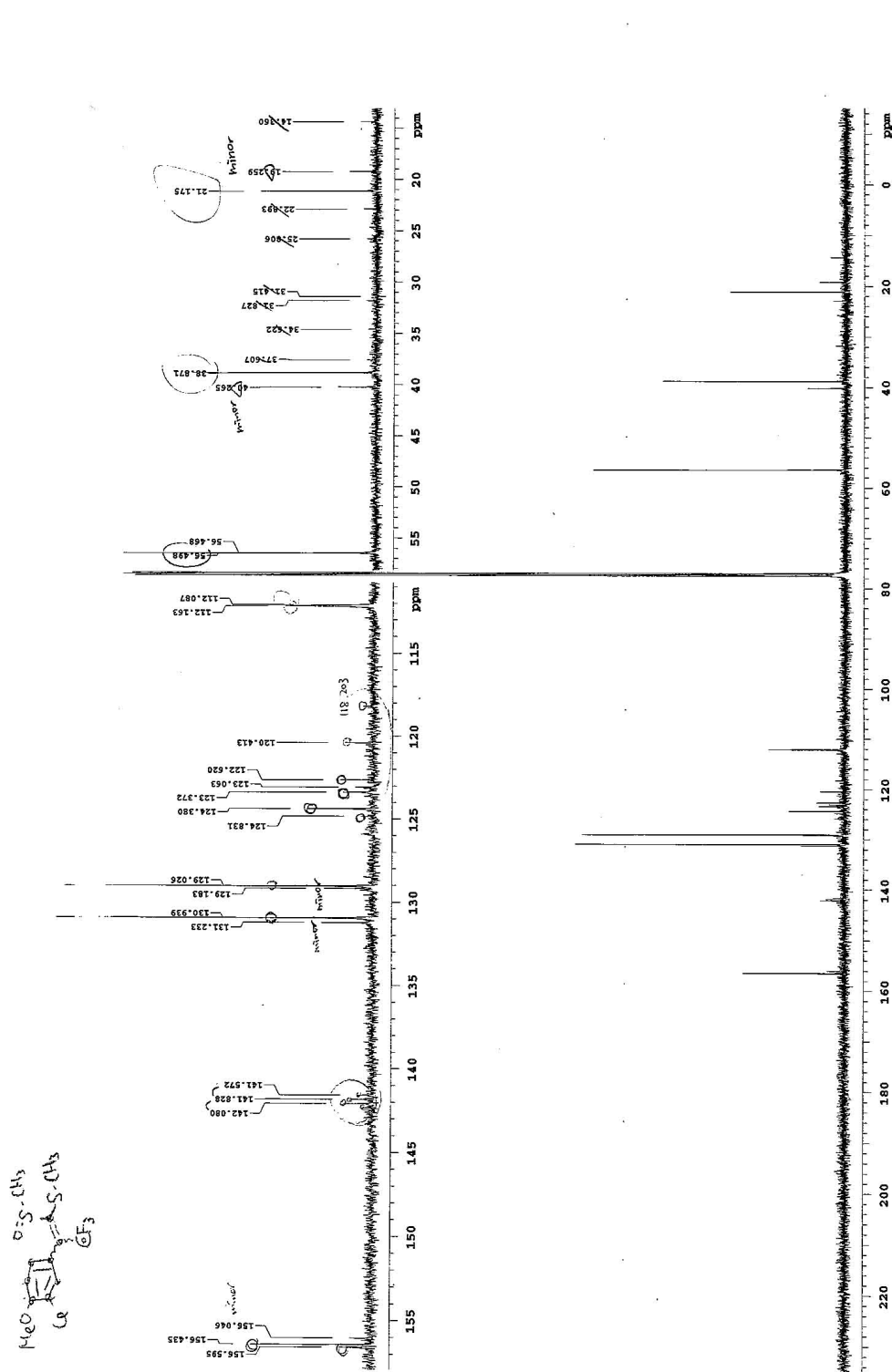


Figure S3. ¹H NMR spectrum of 18

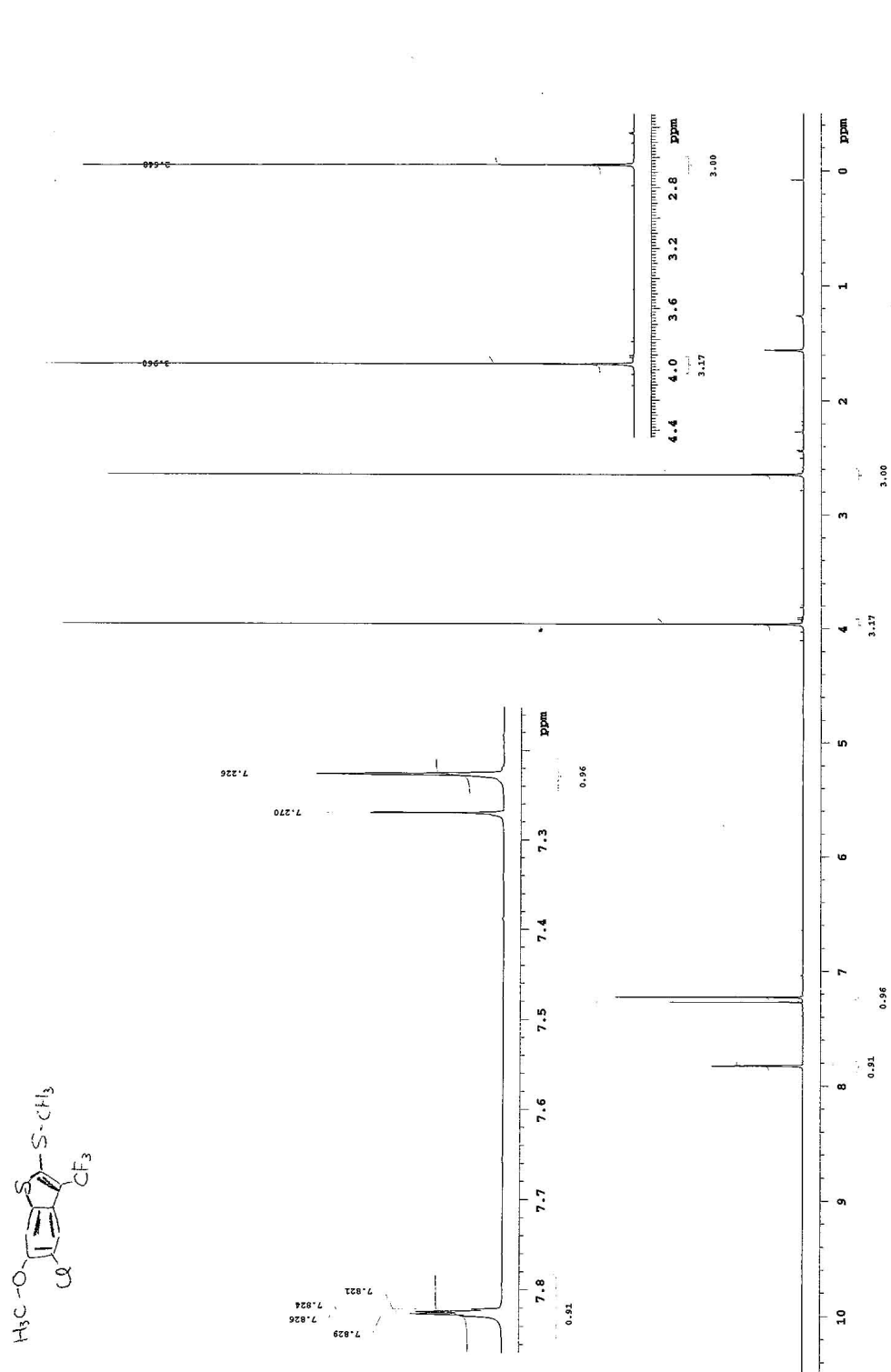
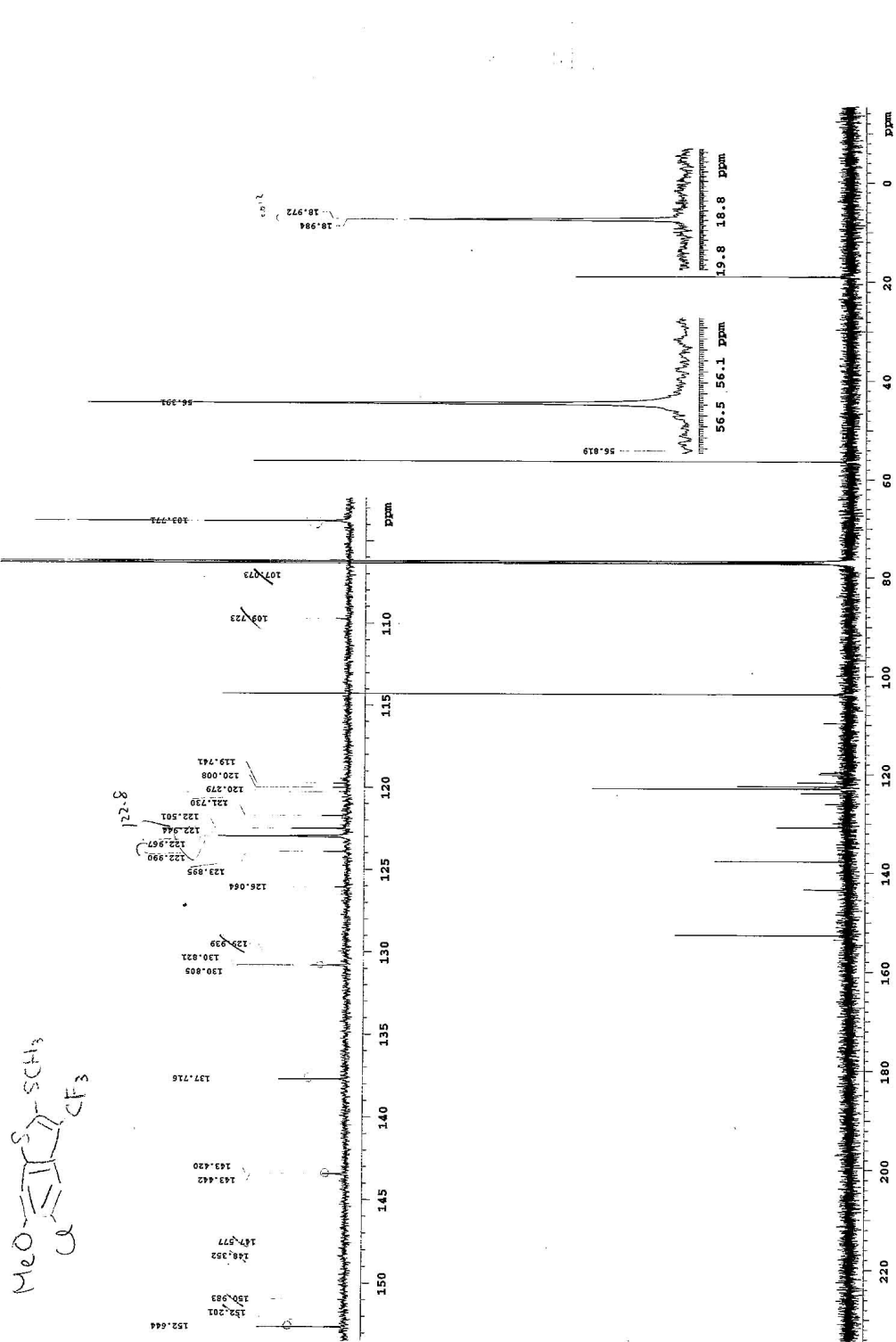


Figure S4. ¹³C NMR spectrum of 18



NMR Spectra for Known Compounds

Figure S5. ^1H NMR spectrum of **12** (Nakano, M.; Satoh, T.; Miura, M. *J. Org. Chem.* **2006**, *71*, 8309)

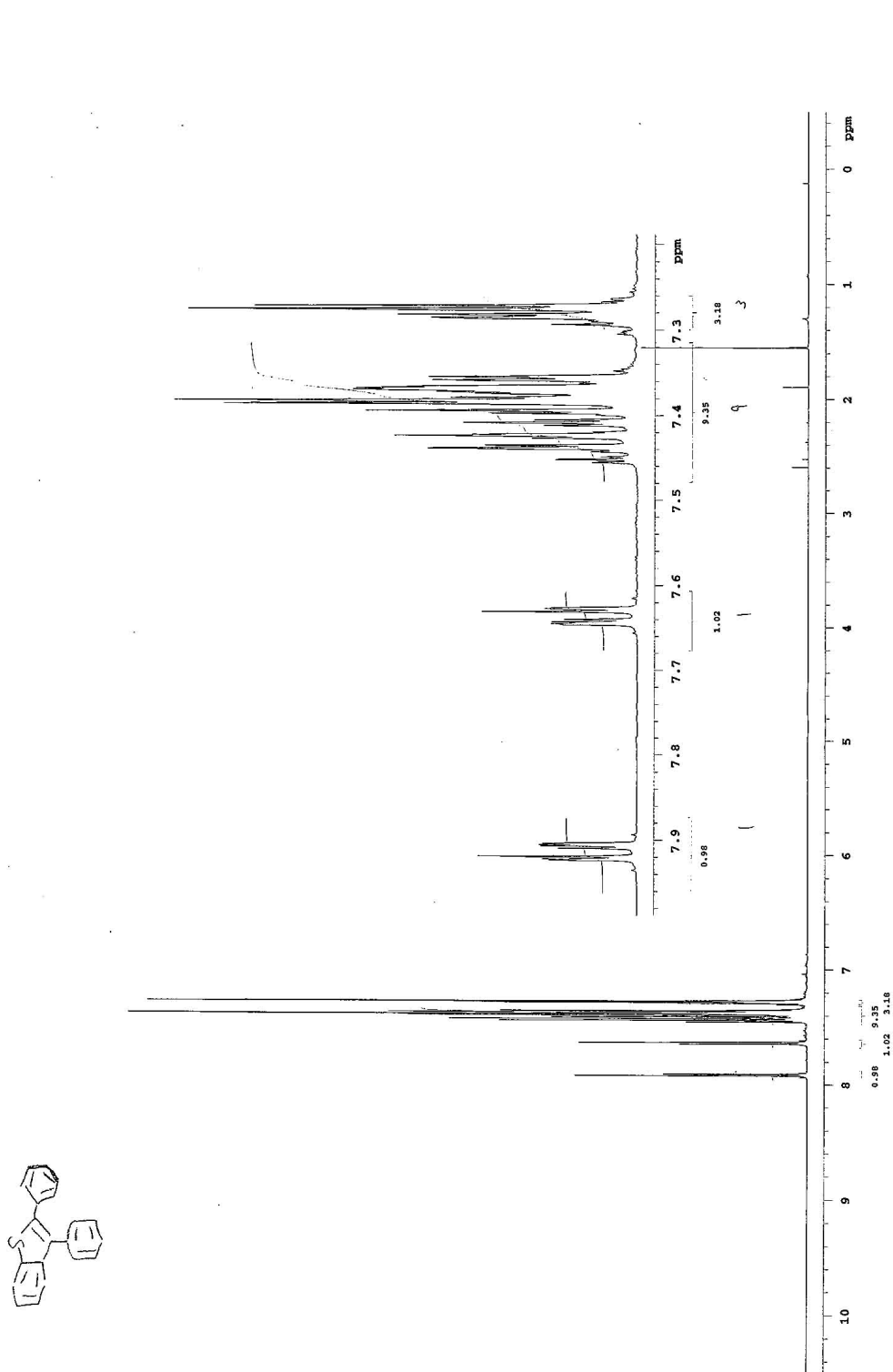


Figure S6. ^{13}C NMR spectrum of **12**

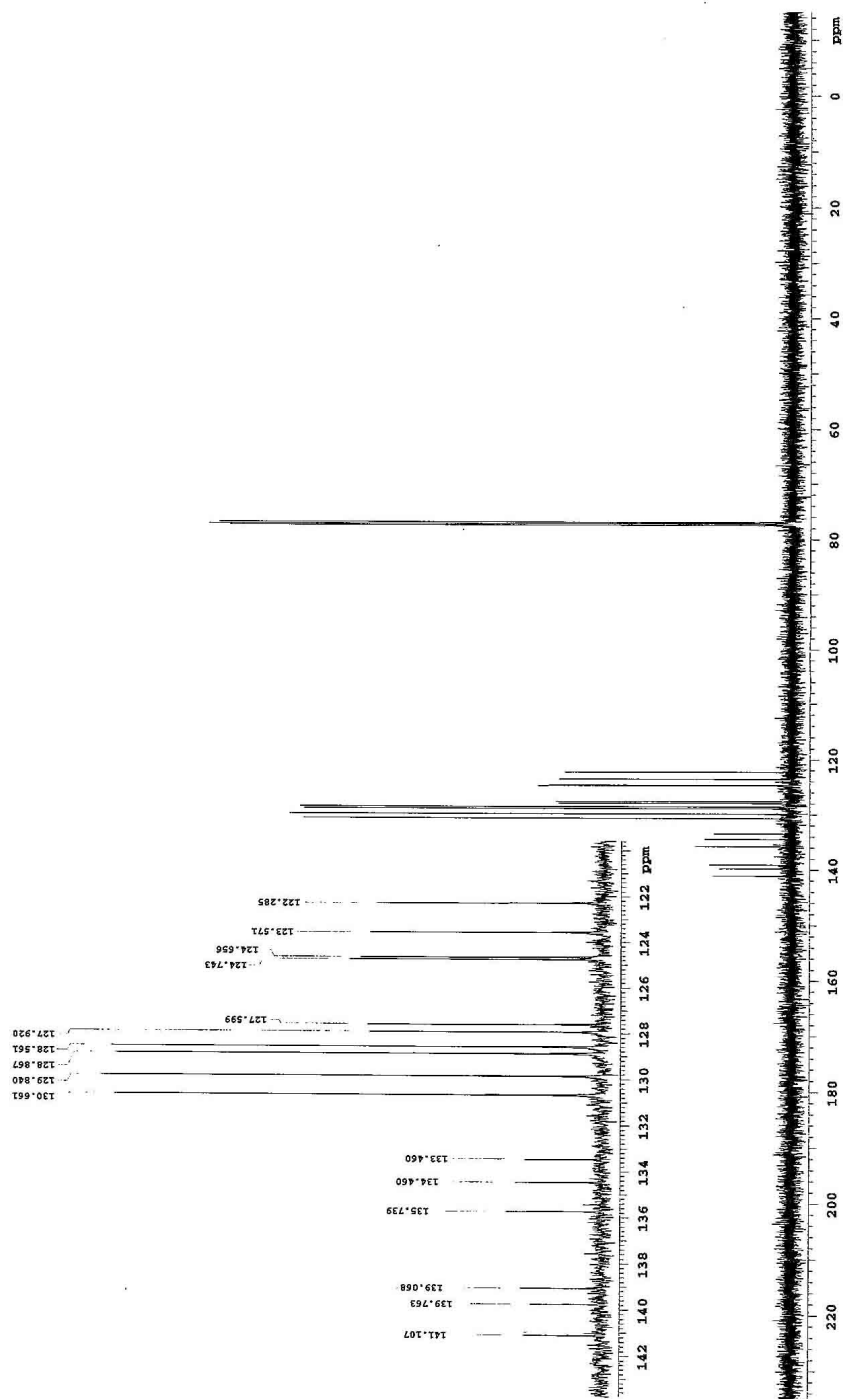


Figure S7. ¹H NMR spectrum of **15** (Oberhauser, T. J. *Org. Chem.* **1997**, 62, 4504)

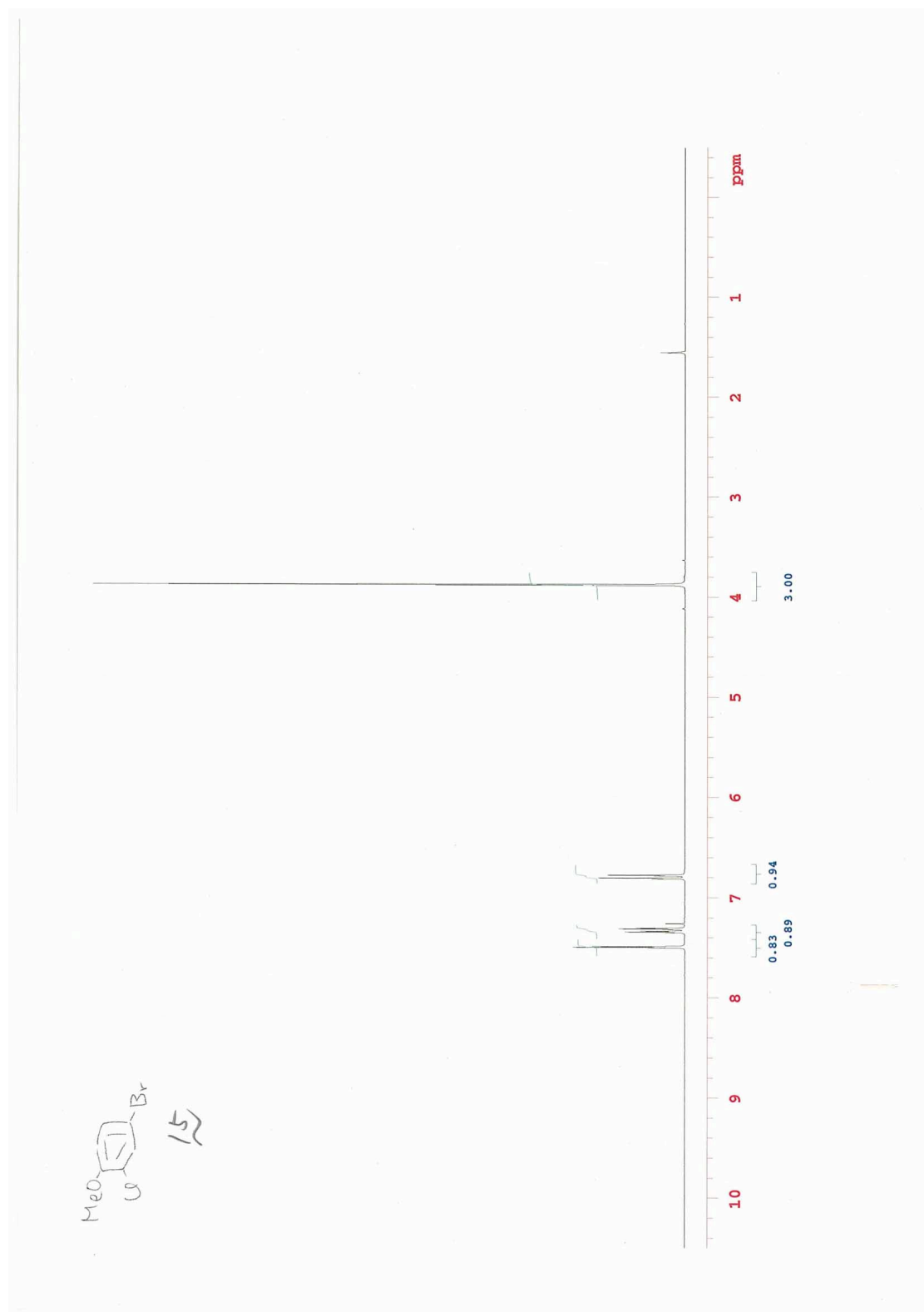


Figure S8. ^1H NMR spectrum of **16** (Konno, T.; Takehana, T.; Mishima, M.; Ishihara, T. *J. Org. Chem.* **2006**, *71*, 3545. Impurity: *o*-chloroanisole)

