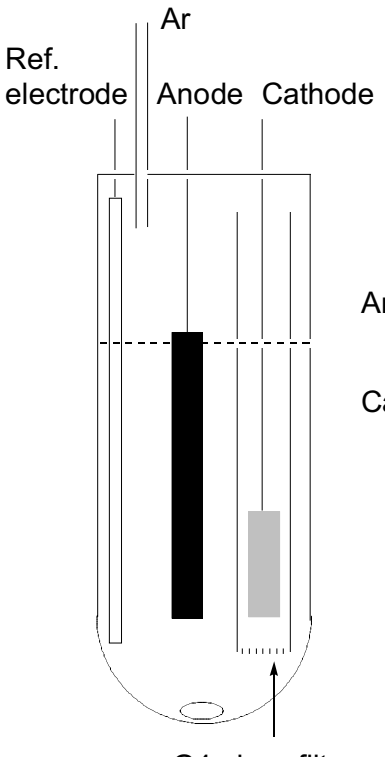
Supporting Information

Benzylic Intermolecular Carbon-Carbon Bond Formation by Selective Anodic Oxidation of Dithioacetals

Kazuhiro Chiba,* Rikiya Uchiyama, Shokaku Kim, Yoshikazu Kitano, Masahiro Tada

General procedure: Dithioacetals (0.5 mmol) was dissolved in 20 ml of 3.0 M $LiClO_4$ + dry nitromethane. This solution was then electrolysed in the presence of 2 equimolar of alkene at a constant potential [0.95 V *vs.* Ag|AgCl|KCl(sat)] by using a divided cell equipped with a glassy carbon anode (60 mm x 20 mm) and a Pt cathode (10 mm x 10 mm) under Ar atmosphere, and it was quenched at 1.2 F/mole. After addition of water, the solution was extracted with AcOEt. The extract was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by using *n*-hexane-AcOEt (silica-gel) to afford the products._



Anodic cell: 3 M $LiClO_4$+CH_3NO_2
dithioacetal, alkene

Cathodic cell: 3 M $LiClO_4$+CH_3NO_2

Spectral ...LPHA-600
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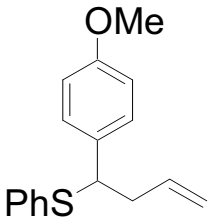
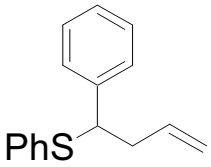
FT-IR spectrometer. Mass spectra were recorded on a JEOL JMS-SX-102A spectrometer at 70 eV.

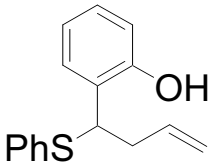
Spectroscopic data:



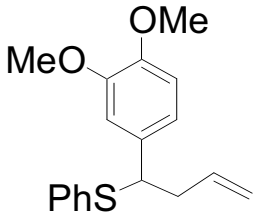
Compound **6** Colorless oil, HRMS calcd. for $C_{17}H_{18}OS$ *m/z* 270.1078, Found *m/z* 270.1074; MS *m/z*(%) 270(M^+, 11), 229(17) and 161(100); δ_C 158.50, 135.20, 134.82, 133.28, 132.37, 128.84, 128.58, 126.97, 117.03, 113.62, 55.22, 52.57 and 40.55; δ_H 7.27-7.19(5H, m), 7.16(2H, d, *J*=8.79), 6.80(2H, d, *J*=8.79), 5.71(1H, ddt, *J*=17.33, 10.25, 7.08Hz), 5.02(1H, ddt, *J*=17.33, 1.71, 1.47), 4.99(1H, ddt, *J*=10.25, 1.71, 0.98), 4.17(1H, dd, *J*=8.30, 6.59), 3.78(3H, s) and 2.73-2.61(2H, m); IR(ν cm^{-1}) 3075, 3058, 3002, 2958, 2929, 2858, 2836, 1610, 1585, 1511, 1463, 1438, 1288, 1249, 1176, 1122, 1037, 917, 831, 742 and 692.



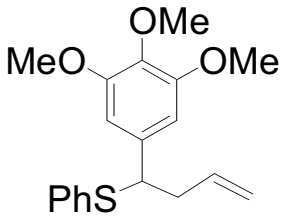
Compound **12** Colorless oil, HRMS calcd. for $C_{16}H_{16}S$ *m/z* 240.0973, Found *m/z* 240.0978; MS *m/z*(%) 240(M^+, 13), 199(75) and 131(100);δ_C 141.33, 135.09, 134.66, 132.41, 128.58, 128.23, 127.80, 127.08, 127.04, 117.13, 53.27 and 40.46; δ_H 7.29-7.13(10H, m), 5.72(1H, ddt, *J*=17.15, 10.22, 6.92), 5.04(1H, ddt, *J*=17.15, 1.81, 1.48), 4.99(1H, ddt, *J*=10.22, 1.81, 0.99), 4.19(1H, dd, *J*=7.91, 6.92) and 2.73-2.61(2H, m); IR(ν cm^{-1}) 3074, 3060, 3027, 3002, 2977, 2925, 2852, 1641, 1585, 1481, 1442, 1263, 1178, 1025, 917, 746 and 696.



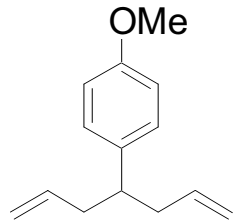
Compound **14** Colorless oil, HRMS calcd. for $C_{16}H_{16}OS$ *m/z* 256.0922, Found *m/z* 256.0929; MS *m/z*(%) 256(M^+,16), 215(7), 147(51) and 109(100); δ_C 154.14, 134.93, 132.85, 132.64, 129.32, 128.71, 128.62, 127.65, 125.94, 120.53, 117.43, 117.15, 50.03 and 38.45; δ_H 7.31-7.28(2H, m), 7.20-7.17(3H, m), 7.11(1H, ddd, *J*=8.79, 8.06, 1.71), 6.96(1H, dd, *J*=7.57, 1.71), 6.83(1H, dd, *J*=8.06, 1.22), 6.77(1H, ddd, *J*=8.79, 7.57, 1.22), 6.37(1H, s), 5.76(1H, ddt, *J*=17.09, 10.25, 7.08), 5.08(1H, ddt, *J*=17.09, 1.71, 1.47), 5.04(1H, ddt, *J*=10.25, 1.71, 0.98), 4.44(1H, dd, *J*=8.55, 7.57) and 2.77-2.69(2H, m); IR(ν cm^{-1}) 3396, 3074, 3037, 3004, 2977, 2925, 2852, 1641, 1583, 1483, 1456, 1440, 1259, 1224, 1174, 1155, 1024, 917, 836, 750 and 690



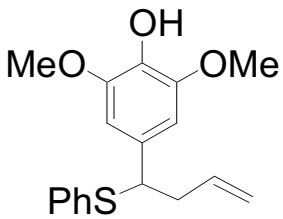
Compound **16** Colorless oil, HRMS calcd. for $C_{18}H_{20}O_2S$ *m/z* 300.1184, Found *m/z* 300.1208; MS *m/z*(%) 300(M^+,18), 259(26) and 191(100); δ_C 148.64, 147.96, 135.18, 134.66, 133.78, 132.63, 128.59, 127.10, 120.02, 117.06, 110.82, 110.68, 55.86, 55.82, 53.11 and 40.49; δ_H 7.28-7.19(5H, m), 6.77-6.73(3H, m), 5.73(1H, ddt, *J*=17.09, 10.01, 6.84), 5.04(1H, d, *J*=17.09), 5.00(1H, d, *J*=10.01), 4.15(1H, dd, *J*=8.55, 6.84), 3.85(3H, s), 3.82(3H, s) and 2.74-2.62(2H, m); IR(ν cm^{-1}) 3074, 3058, 3000, 2975, 2954, 2933, 2908, 2873, 2832, 1639, 1604, 1591, 1515, 1463, 1438, 1417, 1263, 1238, 1141, 1027, 917 and 744.



Compound **18** Colorless oil, HRMS calcd. for $C_{19}H_{22}O_3S$ *m/z* 330.1290, Found *m/z* 330.1284; MS *m/z*(%) 330(M^+, 15), 289(8) and 221(100); δ_C 152.80, 136.88, 136.84, 135.02, 134.42, 132.81, 128.58, 117.12, 104.74, 60.81, 56.04, 56.01, 53.71 and 40.29; δ_H 7.29-7.20(5H, m), 6.42(1H, s), 5.75(1H, ddt, *J*=17.33, 10.25, 7.08Hz), 5.07(1H, ddt, *J*=17.33, 1.71, 1.47Hz), 5.03(1H, ddt, *J*=10.25, 1.71, 0.98), 4.10(1H, dd, *J*=7.81, 6.84), 3.82(3H, s), 3.79, (6H, s) and 2.74-2.63(2H, m); IR(ν cm^{-1}) 3074, 3058, 3002, 2960, 2935, 2836, 1589, 1506, 1457, 1419, 1240, 1128, 1008, 917, 835, 746 and 692.

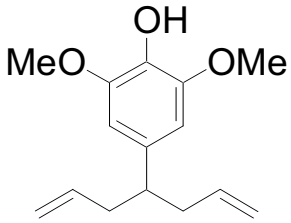


Compound **19** Colorless oil, HRMS calcd. for $C_{14}H_{18}O$, 202.1358, Found 202.1362; MS *m/z*(%) 202(M^+, 10), 161(100) and 134(12); δ_C 157.72, 136.86, 136.59, 128.47, 115.87, 113.55, 55.20, 44.77 and 40.52; δ_H 7.07(2H, d, *J*=8.79), 6.83(2H, d, *J*=8.79), 5.66(2H, ddt, *J*=17.09, 10.25, 7.08), 4.96(2H, ddt, *J*=17.09, 1.95, 1.47), 4.92(2H, ddt, *J*=10.25, 1.95, 0.98), 2.66(1H, dddd, *J*=8.55, 8.30, 6.35, 6.10) and 2.43-2.27(4H, m); IR(ν cm^{-1}) 3074, 3031, 2998, 2975, 2952, 2919, 2910, 2856, 2834, 1610, 1511, 1442, 1247, 1178, 1037, 912 and 827.

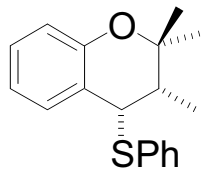


Compound **21** Colorless oil, HRMS calcd. for $C_{19}H_{22}O_3S$ *m/z* 316.1133, Found *m/z* 316.1138; MS *m/z*(%) 316(M^+, 19), 273(36) and 206(46), 173(100); δ_C 146.64, 135.17, 134.54, 133.64, 132.88,

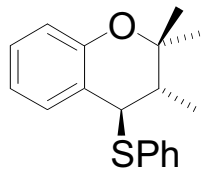
132.37, 128.62, 127.24, 117.10, 104.49, 56.27, 53.76 and 40.45; δ_H 7.28-7.19(5H, m), 6.43(1H, s), 5.747(1H, ddt, *J*=17.09, 10.25, 6.84Hz), 5.42(1H, s), 5.05(1H, ddt, *J*=17.09, 1.71, 1.47Hz), 5.02(1H, ddt, *J*=10.25, 1.71, 0.98), 4.10(1H, dd, *J*=8.30, 6.84), 3.82(6H, s) and 2.67-2.65(2H, m); IR(ν cm^{-1}) 3469, 3072, 3060, 3000, 2956, 2935, 2838, 1612, 1515, 1459, 1330, 1214, 1114, 914, 740 and 696.



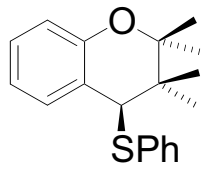
Compound **22** Colorless oil, HRMS calcd. for $C_{15}H_{20}O_3$ *m/z* 248.1412, Found *m/z* 248.1410; MS *m/z*(%) 248(M^+, 54), 207(91), 175(100) and 147(80); δ_C 146.74, 136.75, 135.77, 115.99, 105.08, 104.22, 56.28, 45.85 and 40.53; δ_H 6.37(2H, s), 5.67(2H, ddt, *J*=17.09, 10.25, 7.08), 5.37(1H, s), 4.98(2H, ddt, *J*=17.09, 1.95, 1.47), 4.95(2H, ddt, *J*=10.25, 1.95, 0.98), 3.88(6H, s), 2.62(1H, dddd, *J*=8.30, 8.06, 6.35, 6.10), 2.42-2.27(4H, m); IR(ν cm^{-1}) 3498, 3074, 3000, 2973, 2935, 2838, 1612, 1517, 1461, 1214, 1114 and 912.



Compound **26** Colorless oil, HRMS calcd. for $C_{18}H_{20}OS$ *m/z* 284.1235, Found *m/z* 284.1233; MS *m/z*(%) 284(M^+,13), 175(100), 145(27) and 133(46); δ_C 153.67, 134.14, 132.06, 130.40, 128.68, 128.19, 127.08, 123.17, 120.18, 117.25, 78.27, 50.04, 41.46, 28.23, 19.32 and 15.45; δ_H 7.73(1H, dd, *J*=7.81, 1.22), 7.25-7.18(5H, m), 7.12(1H, ddd, *J*=8.30, 8.06, 1.22), 6.92(1H, ddd, *J*=8.06, 7.81, 1.22), 6.73(1H, dd, *J*=8.30, 1.22), 3.87(1H, d, *J*=10.74), 1.95(1H, dq, *J*=10.74, 6.84), 1.39(3H, s), 1.22(3H, d, *J*=6.84) and 1.14(3H, s); IR(ν cm^{-1}) 3072, 3058, 3031, 2973, 2933, 2877, 2854, 1650, 1558, 1479, 1454, 1249, 1120, 948, 754 and 690.

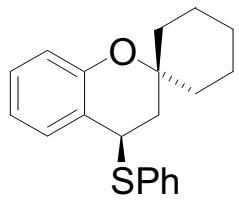


Compound **27** Colorless oil, HRMS calcd. for $C_{18}H_{20}OS$ *m/z* 284.1235, Found *m/z* 284.1233; MS *m/z*(%) 284(M^+,13), 175(100), 145(27) and 133(46); δ_C 152.88, 137.01, 132.52, 129.40, 129.03, 128.53, 126.57, 121.25, 120.06, 116.95, 77.46, 49.18, 39.37, 26.71, 25.60 and 11.41; δ_H 7.55-7.49(3H, m), 7.36-7.32(2H, m), 7.28-7.25(1H, m), 7.15(1H, ddd, *J*=8.30, 7.57, 1.22), 6.88(1H, ddd, *J*=7.81, 7.57, 1.22), 6.78(1H, dd, *J*=8.30, 1.22), 4.69(1H, d, *J*=5.13), 2.09(1H, dq, J=6.84, 5.13), 1.40(3H, s), 1.34(3H, s) and 1.12(3H, d, *J*=6.84); IR(ν cm^{-1}) 3074, 3058, 3031, 2977, 2927, 2877, 2854, 1646, 1515, 1483, 1249, 1149, 946, 752 and 690.

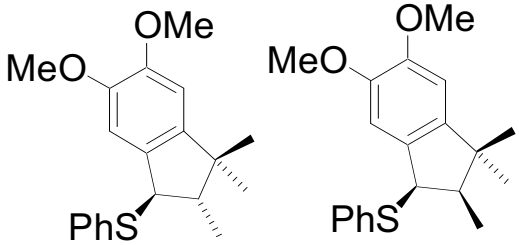


Compound **28** Colorless oil, HRMS calcd. for $C_{19}H_{22}OS$ *m/z* 298.1391, Found *m/z* 298.1387; MS

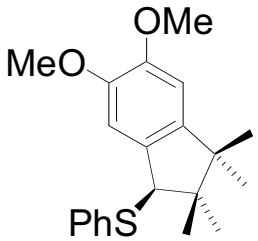
m/z(%) 298(M^+, 3), 189(100), 147(57) and 133(31);δ_C 152.88, 139.19, 130.57, 129.54, 128.44, 126.17, 123.40, 120.13, 116.80, 80.63, 57.38, 39.19, 24.41, 23.61, 22.03 and 18.56; δ_H 7.67(1H, dd, *J*=7.75, 1.32), 7.52(2H, dd, *J*=7.42, 1.32), 7.33(2H, ddd, *J*=7.42, 7.09, 1.32), 7.23(1H, dd, 7.09, 1.32), 7.15(1H, ddd, *J*=8.24, 8.08, 1.32), 6.89(1H, ddd, *J*=8.24, 7.75, 1.32), 6.76(1H, dd, *J*=8.08, 1.32), 4.28(1H, s), 1.43(3H, s), 1.28(3H, s), 1.22(3H, s) and 1.07(3H, s); IR(ν cm^{-1}) 3072, 3058, 3031, 2977, 2939, 2875, 1646, 1579, 1479, 1454, 1247, 1137, 950, 752 and 690.



Compound **29** Colorless oil, HRMS calcd. for $C_{20}H_{22}OS$ *m/z* 310.1391, Found *m/z* 310.1390; MS *m/z*(%) 310(M^+, 8), 201(100),157(18) and 133(46);δ_C 153.53, 134.67, 131.70, 129.39, 128.85, 128.50, 127.01, 121.71, 120.03, 117.57, 75.48, 40.76, 39.93, 37.32, 33.10, 25.69, 21.62 and 21.57; δ_H 7.67(1H, dd, *J*=8.06, 1.22), 7.43-7.38(2H, m), 7.31-7.22(3H), 7.15(1H, ddd, *J*=8.30, 7.57, 1.22), 6.90(1H, ddd, *J*=8.06, 7.57, 1.22), 6.83(1H, dd, *J*=8.30, 1.22), 4.47(1H, dd, *J*=10.01, 6.59), 2.17(1H, dd, 13.92, 6.59), 1.99(1H, dd, *J*=13.92, 10.01) and 1.86-1.27(10H, m); IR(ν cm^{-1}) 3072, 3058, 3033, 3002, 2931, 2858, 1643, 1579, 1481, 1446, 1236, 754 and 692.

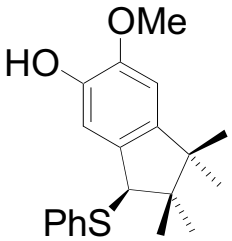


Compound **33** and **34** (a mixture of *trans* **33** and *cis* **34** isomers, t/c=10). Colorless oil, HRMS calcd. for $C_{20}H_{24}O_2S$ *m/z* 328.1497, Found *m/z* 328.1494; MS *m/z*(%) 328(M^+, 68), 257(27), 243(100) and 227(69); δ_C (**33**) 148.94, 147.44, 138.84, 136.98, 132.94, 131.38, 126.92, 125.98, 124.11, 121.76, 112.02, 110.76, 55.93, 55.84, 51.36, 47.45, 45.02, 28.35, 22.23 and 14.56; δ_H(**33**) 7.08(1H, dd, *J*=7.81, 1.22), 7.00(1H, ddd, *J*=7.81, 7.57, 1.22), 6.89-6.72(4H, m), 6.59(1H, d, *J*=1.95), 3.87(3H, s), 3.80(3H, s), 3.61(1H, d, *J*=11.23), 2.36(1H, dq, *J*=11.23), 1.39(3H, s), 1.35(3H, s) and 0.82(3H, d, *J*=6.84); δ_H(**34**) 3.68(1H, d, *J*= 11.23), 2.13(1H, dq, *J*=11.23, 6.89), 1.28(3H, s), 1.26(3H, s), 0.72(3H, d, *J*=6.59); IR(ν cm^{-1}) 3058, 3002, 2962, 2929, 2865, 2832, 1589, 1513, 1259, 1238, 1139, 1027 and 744.

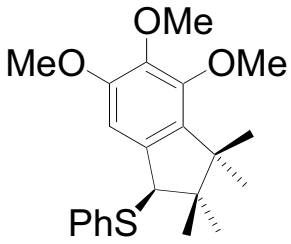


Compound **35**_Colorless oil, HRMS calcd. for $C_{21}H_{26}O_2S$ *m/z* 342.1653, Found *m/z* 342.1648; MS *m/z*(%) 342(M^+,74), 285(36), 243(34), 182(40) and 148(100);δ_C 148.46, 148.01, 141.50, 134.17, 131.37, 126.13, 125.63, 125.21, 123.84, 123.38, 114.09, 110.23, 55.99, 55.88, 51.86, 41.50, 37.64, 25.88, 22.63, 22.38 and 18.22; δ_H 7.36(1H, dd, *J*=7.57, 1.47), 7.15(1H, dd, *J*=7.32, 1.95), 7.09-6.99(4H, m), 6.82(1H, d, *J*=8.30), 4.52(1H, s), 3.89(6H, s), 1.43(3H, s), 1.30(3H, s), 0.88(3H, s) and

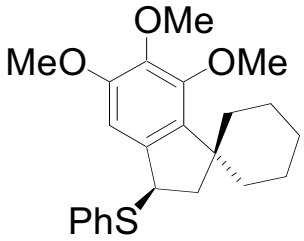
0.79(3H, s); IR(ν cm^{-1})3087, 3056, 2973, 2937, 2910, 2832, 1589, 1515, 1463, 1261, 1141, 1027 and 754.



Compound **37** Colorless oil, HRMS calcd. for $C_{20}H_{24}O_2S$ *m/z* 328.1497, Found *m/z* 328.1495; MS *m/z*(%) 328(M^+,95), 285(41), 227(59) and 168(100);δ_C 145.93, 144.68, 141.52, 134.22, 132.18, 126.10, 125.61, 125.22, 123.79, 122.62, 117.19, 109.68, 55.94, 51.61, 41.47, 37.58, 25.78, 22.64, 22.39 and 18.18; δ_H 7.35(1H, dd, *J*=7.57, 1.71), 7.13(1H, dd, *J*=7.32, 1.95), 7.09-6.95(4H, m), 6.79(1H, d, *J*=8.30), 5.55(1H, s), 3.89(1H, s), 3.89(3H,s), 1.42(3H, s), 1.29(3H, s), 0.87(3H, s) and 0.78(3H, s); IR(ν cm^{-1})3457, 3091, 3060, 2973, 2940, 2879, 2840, 1589, 1508, 1469, 1440, 1270, 1124, 1027 and 754.



Compound **39** Colorless oil, HRMS calcd. for $C_{22}H_{28}O_3S$, 372.1759, Found 372.1757; MS *m/z*(%) 372(M^+, 82), 315(28), 207(23), 181(24) and 168(100); δ_C 152.29, 146.63, 141.43, 137.66, 134.49, 133.89, 129.47, 126.19, 125.65, 125.22, 123.92, 108.22, 60.90, 56.23 (2C), 52.45, 41.56, 37.63, 26.08, 22.65, 22.51 and 18.33; δ_H 7.38-7.29(2H, m), 7.16-7.02(3H, m), 6.71(1H, s), 4.50(1H, s), 3.87(3H, s), 3.86(6H, s), 1.44(3H, s), 1.31(3H, s), 0.90(3H, s) and 0.83(3H, s); IR(ν cm^{-1}) 3077, 3054, 2975, 2937, 2881, 2834, 1589, 1504, 1465, 1421, 1326, 1240, 1128 and 754.



Compound **40** Colorless oil, HRMS calcd. for $C_{23}H_{28}O_3S$ *m/z* 384.1759, Found *m/z* 384.1755; MS *m/z*(%) 384(M^+, 21), 275(100), 181(33) and 149(74);δ_C 152.74, 141.31, 137.68 (2C), 134.26, 132.48, 128.56, 126.98, 124.61, 104.84, 60.88, 56.11 (2C), 52.63, 45.01, 28.37, 25.33, 22.93 and 22.29; δ_H 7.30(5H, m), 6.43(1H, s), 4.21(1H, dd, *J*=8.30, 7.08), 3.81(3H, s), 3.78(6H, s), 2.59(1H, dd, *J*=14.16, 7.08), 2.49(1H, dd, *J*=14.16, 8.30), 1.93-1.44(10H, m); IR(ν cm^{-1}) 3056, 2994, 2929, 2854, 2834, 1589, 1506, 1459, 1419, 1330, 1238, 1126, 1008 and 746.