Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

A new anchoring group to fabricate single-molecule junctions：diphenyl sulfide

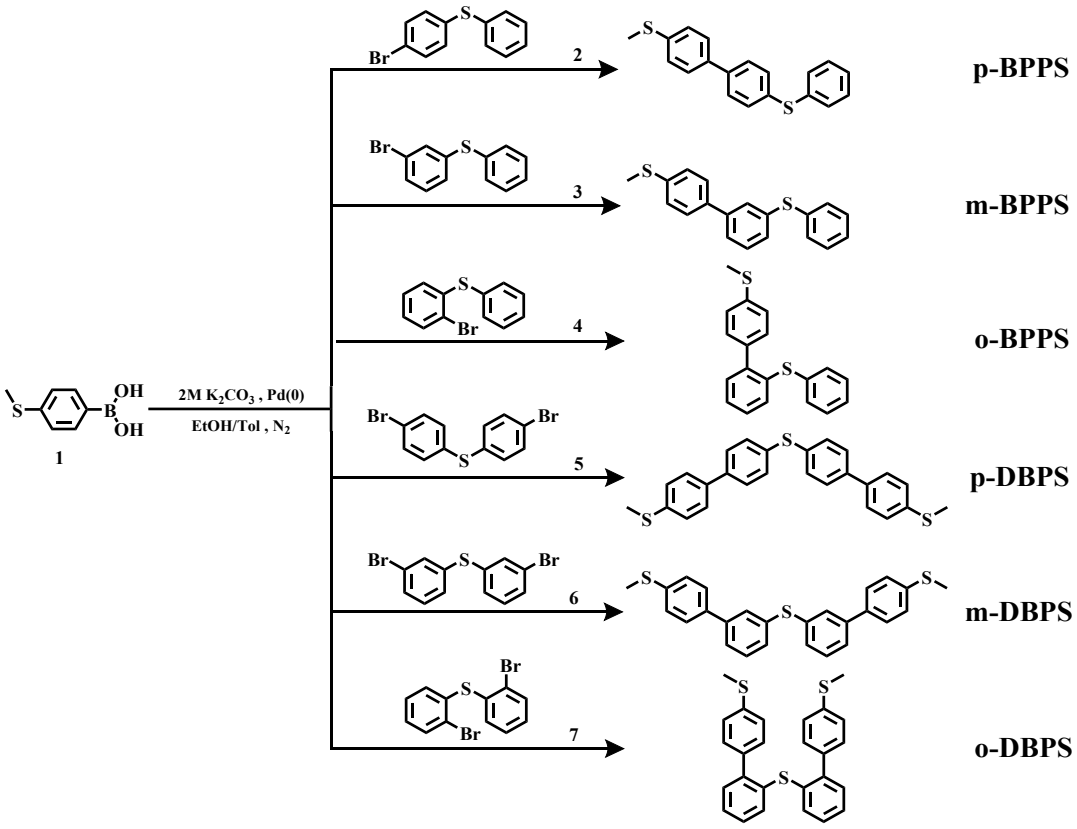
Zhonghao Hu, Yanze Wang, Lei Liang, Mingzhen Wang, Bohuai Xiao*, Yunchuan Li*

Pages:

Experimental section

General information

^{1}H NMR & ^{13}C NMR spectra were obtained on a Bruker NMR spectrometer operating at 600 and 150 MHz, respectively, in deuterated DMSO. Materials: all solvents and reagents were used as received from commercial suppliers. Reagent 2-7 was prepared according to the description in the references[1-2] Synthetic routes of the target compounds are outlined in **Scheme S1-S2**.

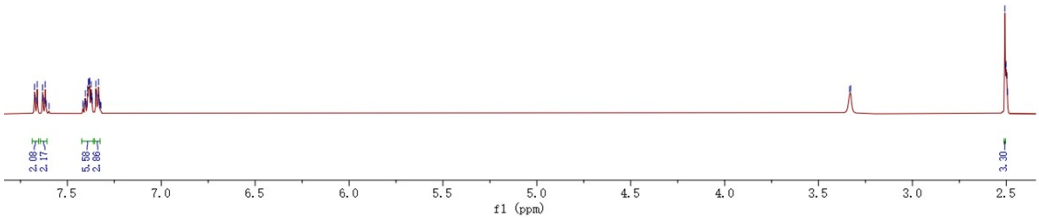


Scheme S1 The synthetic routes of the above sis target molecules.

p-BPPS:

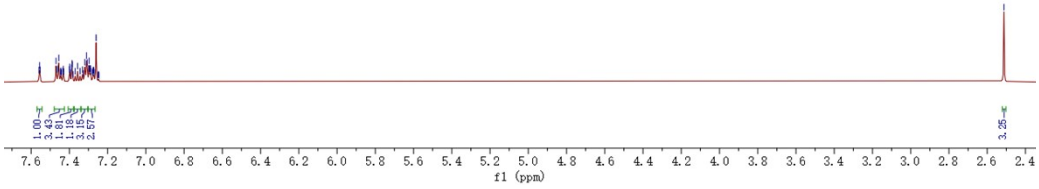
Toluene (60 mL), ethanol (40 mL), 2 M aqueous K_2CO_3 (15 mL) and a mixture of 1 (0.565 g, 3.36 mmol), 2 (0.742 g, 2.8 mmol) were added into three necks flask, the reaction mixture was bubbled for 15 minutes before adding $Pd(PPh_3)_4$ (97 mg, 3 mol%). The reaction was bubbled for another 15 minutes, and then the suspension was stirred at 90 °C overnight under a nitrogen atmosphere. When cooled to room temperature, the

mixture was extracted with CH_2Cl_2 and dried over $MgSO_4$. After theremoval of solvent, the residue was purified by column chromatography on silica gel to afford p-BPPS (0.426 g, yield 49%) as a white solid. ^{1}H NMR (600 MHz, DMSO-d6) δ 7.69 – 7.65 (m, 2H), 7.62 (dd, J = 9.2, 2.5 Hz, 2H), 7.42 – 7.36 (m, 6H), 7.36 – 7.33 (m, 3H), 2.51 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 139.39, 138.09, 137.15, 135.79, 134.94, 131.48, 131.27, 129.38, 127.62, 127.38, 127.28, 127.04, 15.95. MS (MALDI-TOF): m/z calcd for C19H16S2, 308.07; found 308.073.



m-BPPS:

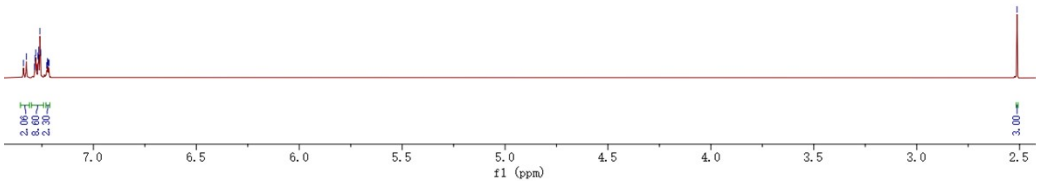
m-BPPS (0.526 g, yield 60%) was synthesized as a white solid in a similar procedure of p-BPPS with 3 instead of 2. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.56 (t, J = 1.9 Hz, 1H), 7.48 – 7.43 (m, 3H), 7.41 – 7.38 (m, 2H), 7.36 (t, J = 7.7 Hz, 1H), 7.34 – 7.30 (m, 3H), 7.30 – 7.27 (m, 3H), 2.51 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 141.68, 138.27, 137.20, 136.64, 135.64, 131.32, 129.71, 129.69, 129.38, 129.29, 127.54, 127.32, 126.98, 125.64, 15.92. MS (MALDI-TOF): m/z calcd for C19H16S2, 308.07; found 308.085.



o-BPPS:

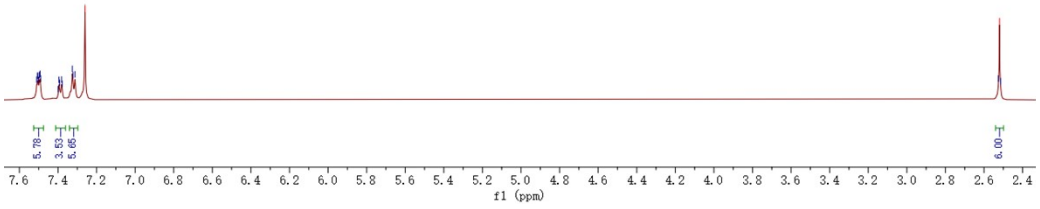
o-BPPS (0.335 g, yield 66%) was synthesized as a white solid in a similar procedure of p-BPPS with 4 instead of 2. 11 ^{1}H NMR (600 MHz, Chloroform-d) δ 7.33 (d, J = 8.4 Hz, 2H), 7.30 – 7.24 (m, 9H), 7.23 – 7.21 (m, 2H), 2.51 (s, 3H). ^{13}C NMR (151 MHz, Chloroform-d) δ 142.55, 137.91, 137.49, 135.70, 135.07, 131.91, 131.47, 130.64,

129.92, 129.29, 128.17, 127.28, 127.00, 126.11, 15.87. MS (MALDI-TOF): m/z calcd for C19H16S2, 308.07; found 308.083.



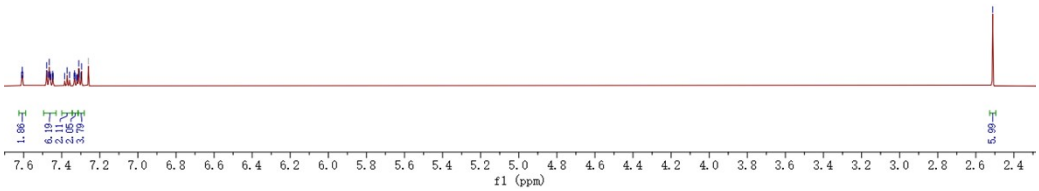
P-DBPS:

Doubling the usage of 1, p-DBPS (0.16 g, yield 16%) was synthesized as a white solid in a similar procedure of p-BPPS with 5 instead of 2. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.53 – 7.47 (m, 6H), 7.39 (dd, J = 8.2, 2.1 Hz, 4H), 7.34 – 7.30 (m, 6H), 2.52 (d, J = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, Chloroform-d) δ 139.39, 138.09, 137.16, 134.94, 131.48, 129.38, 127.62, 127.38, 15.95. MS (MALDI-TOF): m/z calcd for C26H22S3, 430.09; found 430.096.



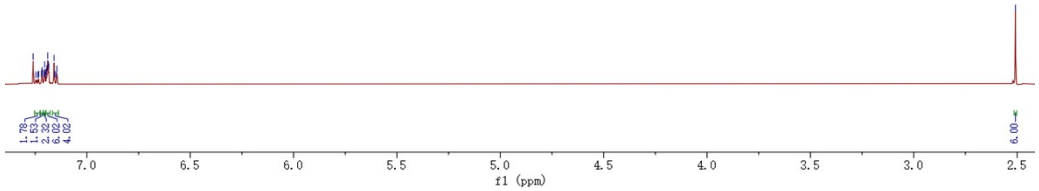
m-DBPS:

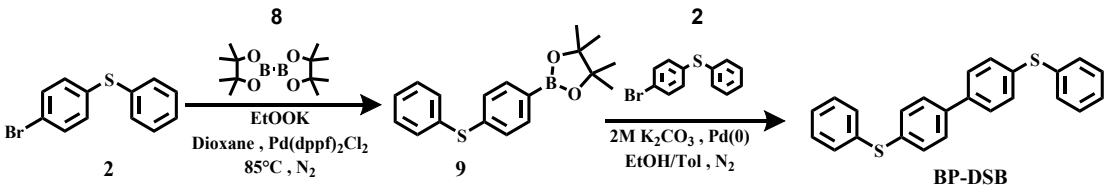
Doubling the usage of 1, m-DBPS (1 g, yield 80%) was synthesized as a white solid in a similar procedure of p-BPPS with 6 instead of 2. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.61 (t, J = 1.8 Hz, 2H), 7.49 – 7.43 (m, 6H), 7.37 (t, J = 7.7 Hz, 2H), 7.33 (dt, J = 7.7, 1.5 Hz, 2H), 7.31 – 7.28 (m, 4H), 2.51 (s, 6H). ^{13}C NMR (151 MHz, Chloroform-d) δ 141.77, 138.33, 137.19, 136.40, 129.85, 129.79, 129.47, 127.56, 127.01, 125.82, 15.94. MS (MALDI-TOF): m/z calcd for C26H22S3, 430.09; found 430.089.



o-DBPS:

Doubling the usage of 1, o-DBPS (0.54 g, yield 43%) was synthesized as a white solid in a similar procedure of p-BPPS with 7 instead of 2. ^{1}H NMR (600 MHz, Chloroform-d) δ 7.25 – 7.23 (m, 2H), 7.22 (dd, J = 1.7, 0.8 Hz, 2H), 7.21 (d, J = 1.7 Hz, 2H), 7.20 – 7.18 (m, 6H), 7.15 (d, J = 8.3 Hz, 4H), 2.51 (s, 6H). ^{13}C NMR (151 MHz, Chloroform-d) δ 143.13, 137.58, 137.50, 134.98, 132.64, 130.61, 129.82, 128.08, 127.20, 125.95, 15.89. MS (MALDI-TOF): m/z calcd for C26H22S3, 430.09; found 430.090.





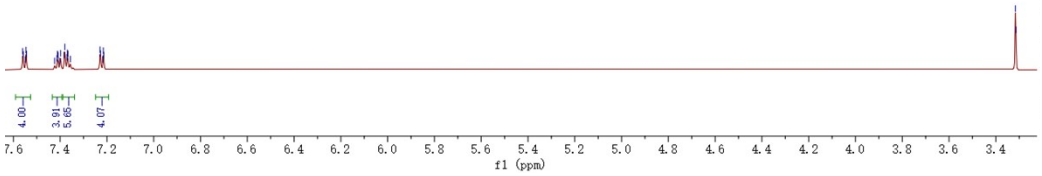
Scheme S2 The synthetic routes of BP-DSB.

13:

A mixture of 2 (0.45 g, 1.7 mmol), 8 (0.65 g, 2.55 mmol), Potassium Acetate (500 mg, 5.1 mmol), dioxane (25 mL) were added into three necks flask, the reaction mixture was bubbled for 15 minutes before adding $Pd(dppf)_2Cl_2$ (70 mg). The reaction was bubbled for another 15 minutes, and then the suspension was stirred at 85 °C overnight under a nitrogen atmosphere. When cooled to room temperature, the mixture was extracted with CH_2Cl_2 and dried over $MgSO_4$. After removing solvent, the residue was purified by column chromatography on silica gel to afford 9 (0.17 g, yield 32%) as a white solid.

BP-DSB:

BP-DSB (0.15 g, yield 43%) was synthesized as a yellow oil in a similar procedure of p-BPPS with 9 instead of 2. ^{1}H NMR (600 MHz, DMSO-d6) δ 7.55 (dd, J = 8.2, 1.4 Hz, 4H), 7.41 (dd, J = 8.3, 6.9 Hz, 4H), 7.39 – 7.34 (m, 6H), 7.22 (dd, J = 8.3, 1.4 Hz, 4H). ^{13}C NMR (151 MHz, Chloroform-d) δ 135.65, 134.97, 132.37, 132.22, 131.69, 129.51, 127.70, 121.00. MS (MALDI-TOF): m/z calcd for C24H18S2, 370.5; found 370.54.



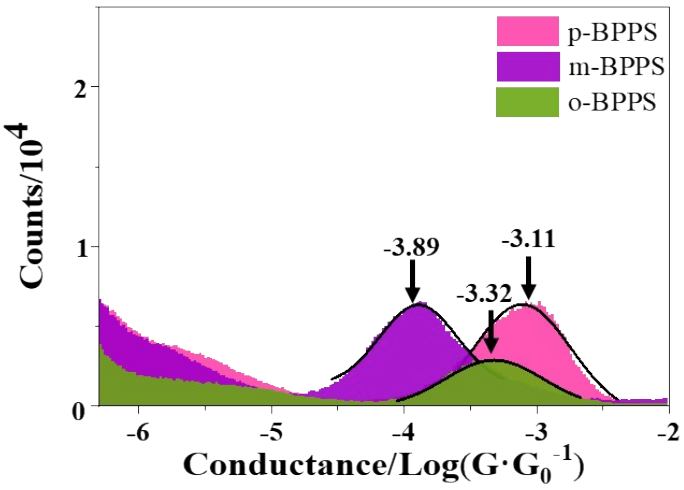


Figure S1 The conductance histograms for diphenyl sulfide substituted molecules at one end with different connectivity.

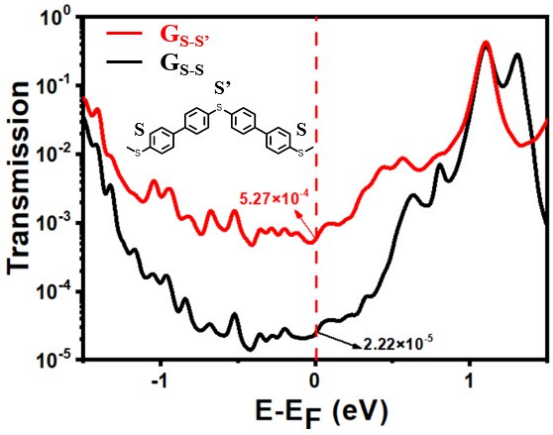


Figure S2 The transmission spectra for p-DBPS with two types of junction geometries.

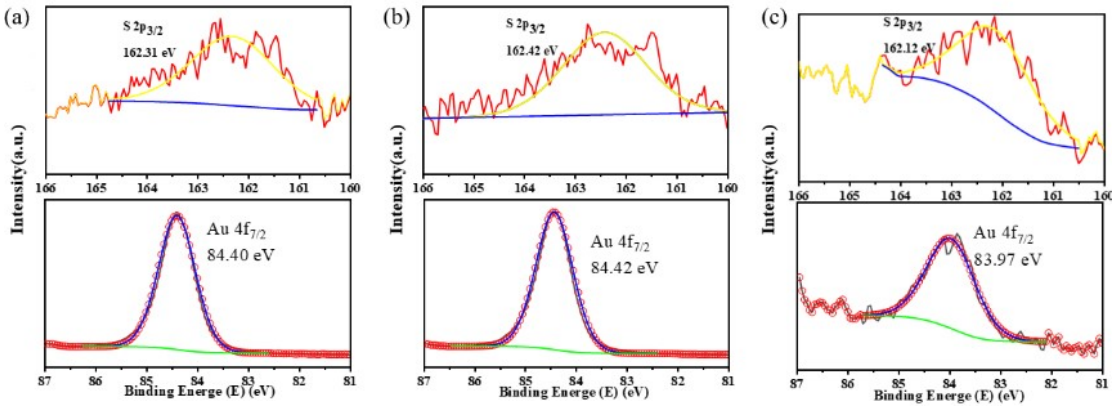


Figure S3 XPS study of p-DBPS (a), p-BPPS (b), and BP-DSB (c) on Au electrode. Well-defined peaks at 84.62 eV for Au $4f_{7/2}$and 162.48 eV for S $2p_{3/2}$ are characteristic of Au-S binding [3, 4]. But the kind of sulfur (S or S') for p-DBPS or p-BPPS can't be readily distinguished from the measurement here.

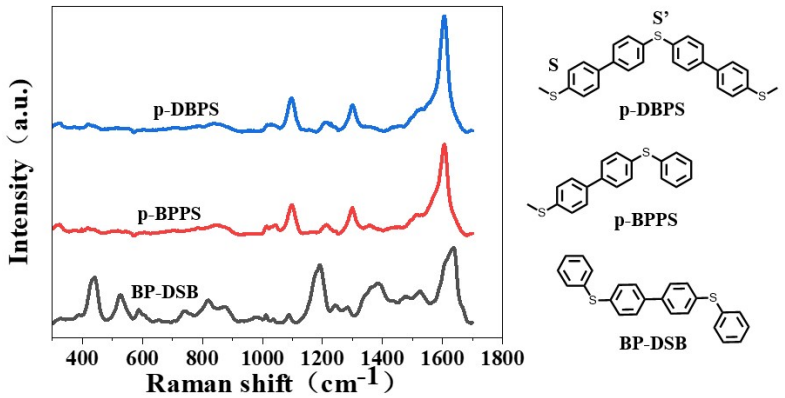


Figure S4 Surface enhanced Raman scattering of p-DBPS (a), p-BPPS (b), and BP-

DSB (c) on Au tip.

The electrochemically ethed gold tip of about several tenths of nm was immersed in a solution (10 mM) containing p-DBPS, p-BPPS, or BP-DSB for 6 hours. Subsequently, the modified tip was kept in a gold particle solution for another 6 hours for secondary modification. As a consequence, an Au (tip)-molecule-Au (particle) structure was formed. Finally, the prepared tip samples were irradiated with a 15mW laser and Raman data was collected. The experimental data was analyze using Matlab software and OriginPro was used to generate corresponding graphs.

The results are showed in Figure S4. It shows that p-DBPS and p-BPPS gives rise to almost the same Raman spectra, indicating that p-DBPS might form the same Au-molecule-Au structure as p-BPPS, with two types of Sulphur atoms used in it. But the reason why p-DBPS didn't bind to Au electrodes with two -SMe anchors simultaneously is currently unclear, given that -SMe has stronger binding ability towards Au than -SPh. Meanwhile, the Raman spectrum of p-BPPS is remarkably different with that of BP-DSB, and this difference indicates that the characteristics of the Raman spectra are highly associated with the types of Sulphur atoms in forming the Au-molecule-Au structure. Through comparing the Raman spectra of p-DBPS, p-BPPS, and BP-DSB, we are sure that the *Ph-S-Au* binding is formed, and is responsible for the observation of the high conductance in our single-molecule conductance measurement.

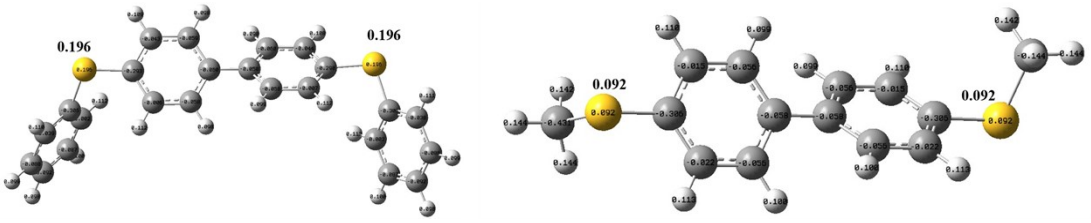
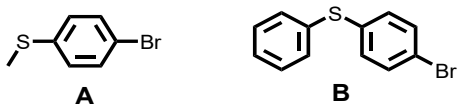


Figure S5 The Mulliken charge number shown on different types of S atoms.

Oxidation experiment



A **B**

0.015 mmol A was added to a single-ended flask containing 30 mL of dichloromethane and 10 mL of acetic acid, respectively, and then 5 drops (approximately 1.76 mmol) of 30% wt hydrogen peroxide solution was added to the flask under stirring at room temperature. Meanwhile, the same procedured was performed for B. Thin-layer chromatography (TLC) was used to monitor the oxidation reaction of A and B. The TLC analysis shows A begins to oxdize after 46 minutes, while B began the reaction after 2h. Additionally, it takes 2h and 39 minutes for A to be completely consumed. However, the specific time for compound B to reach complete consumption is 15h and 20 minutes. This experiment demonstrates –SPh group exhibits significantly higher chemical stability compared to the –SMe group.

[1] W. Fu, T. Liu, Z. Fang, Y. Ma, X. Zheng, W. Wang, X. Ni, M. Hu and T. Tang, *Chemical Communications*, 2015, **51**, 5890-5893.

[2] H.-Y. Chen, W. Peng, Y.-H. Lee, Y. L. Chang, Y.-J. Chen, Y.-C. Lai, N.-Y. Jheng and H. Y. Chen, *Organometallics*, 2013, **32**, 5514-5522.

[3] M. C. Bourg, A. Badia, R. B. Lennox, Gold Sulfur Bonding in 2D and 3D Self-Assembled Monolayers: XPS Characterization. *Journal of Physical Chemistry B*, 2000, **104**, 6562-6567.

[4] Y. Zhang, J. He, Y. Zhu, H. Chen, H. Ma, Directly observed Au–S bond breakage due to swelling of the anchored polyelectrolyte. *Chemical Communications*, 2011, **47**, 1190-1192.