

Electronic supplementary information

for

Optimized trade-offs between triplet emission and transparency in Pt(II) acetylides through phenylsulfonyl units for achieving good optical power limiting performances †

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Experimental

General synthetic procedure for S-0F-Br, S-1F-Br and S-3F-Br.

Under N₂ atmosphere, the corresponding iodobenzene compound (1.1 equiv) and 4-bromobenzenethiol (1.0 equiv) were mixed in dioxane. Then, KOH (2.0 equiv), CuI (0.05) and glycine (0.2 equiv) were added. The reaction was allowed to proceed at 110 °C for 16 h under stirring. After cooling to room temperature, water was added and the mixture was extracted three times with CH₂Cl₂. The organic layer was collected and dried over MgSO₄. After the solvent was removed under reduced pressure, the residue was dissolved in CHCl₃ and m-chloroperoxybenzoic acid (mCPBA, 4.5 equiv) was added slowly at 0 °C. Then, the reaction mixture was warmed to room temperature and stirred for 2 days to ensure completion of the reaction. Chloroform was added and the white precipitate was removed by filtration. The filtrate was washed with NaOH solution (*ca.* 20%) successively. The organic phase was separated and dried over MgSO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography using CH₂Cl₂/petroleum ether as eluent. The product was obtained as white crystals.

S-0F-Br: (Yield: 82%). ¹H NMR (270 MHz, CDCl₃): δ (ppm) 7.93–7.91 (m, 2H), 7.80–7.78 (m, 2H), 7.63–7.48 (m, 5H); ¹³C NMR (67.5 MHz, CDCl₃): δ (ppm) 140.98, 140.53, 133.40, 132.50, 129.34, 129.09, 128.36, 127.54. FAB-MS (m/z): 296, 298 [M]⁺. Elemental analysis calcd (%) for C₁₂H₉BrO₂S: C 48.50, H 3.05; found: C 48.39, H 2.89.

S-1F-Br: (Yield: 78%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.96–7.93 (m, 2H), 7.80–7.77 (m, 2H), 7.66–7.64 (m, 2H), 7.21–7.17 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 140.51, 132.70, 130.55, 130.45, 129.09, 128.63, 116.88, 116.65; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -104.10 (s, 1F). FAB-MS (m/z): 314, 316 [M]⁺. Elemental analysis calcd (%) for C₁₂H₈BrFO₂S:

C 45.73, H 2.56; found: C 45.65, H 2.47.

S-3F-Br: (Yield: 76%). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.78 (d, $J = 8.4$ Hz, 2H), 7.70 (d, $J = 8.4$ Hz, 2H), 7.60 (t, $J = 6.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 136.16, 133.03, 129.55, 129.32, 113.02, 112.95, 112.85, 112.78; ^{19}F NMR (376 MHz, CDCl_3): δ (ppm) -128.47 (d, 2F), -150.01 (t, 1F). FAB-MS (m/z): 350, 352 $[\text{M}]^+$. Elemental analysis calcd (%) for $\text{C}_{12}\text{H}_6\text{BrF}_3\text{O}_2\text{S}$: C 41.05, H 1.72; found: C 40.93, H 1.68.

General synthetic procedure for S-0F-TMS, S-1F-TMS and S-3F-TMS

To the mixture of corresponding brominated phenylsulfonyl compound (1.0 equiv), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (0.05 equiv), CuI (0.025 equiv) and the solvent Et_3N , trimethylsilylacetylene (2.0 equiv) was added at room temperature. After stirring 1 h at room temperature, the reaction mixture was allowed to proceed at 70 °C for 24 h. After cooling to room temperature, the reaction mixture was concentrated under vacuum to give the crude product, which was further purified by silica gel column chromatography with CH_2Cl_2 /hexane as eluent to get the pure product as white solid.

S-0F-TMS: (Yield: 89%). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.92 (d, $J = 8.0$ Hz, 2H), 7.86 (d, $J = 8.0$ Hz, 2H), 7.59–7.48 (m, 5H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 141.31, 140.88, 133.36, 132.61, 129.36, 128.41, 127.65, 127.55, 102.99, 99.02, -0.26. FAB-MS (m/z): 314 $[\text{M}]^+$. Elemental analysis calcd (%) for $\text{C}_{17}\text{H}_{18}\text{O}_2\text{SSi}$: C 64.93, H 5.77; found: C 64.90, H 5.73.

S-1F-TMS: (Yield: 87%). ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.95–7.92 (m, 2H), 7.85 (d, $J = 8.0$ Hz, 2H), 7.56 (d, $J = 8.0$ Hz, 2H), 7.18 (t, $J = 8.0$ Hz, 2H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 140.68, 132.67, 130.52, 130.43, 128.56, 127.43, 116.79, 116.56, 102.85, 99.21, -0.30; ^{19}F NMR (376 MHz, CDCl_3): δ (ppm) -103.81 (s, 1F). FAB-MS (m/z): 332 $[\text{M}]^+$.

Elemental analysis calcd (%) for C₁₇H₁₇FO₂SSi: C 61.41, H 5.15; found: C 64.38, H 5.03.

S-3F-TMS: (Yield: 85%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.84 (d, *J* = 8.0 Hz, 2H), 7.60–7.57 (m, 4H), 0.25 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 139.26, 132.92, 129.40, 127.71, 112.99, 112.92, 112.82, 112.75, 102.59, 100.03, -0.32; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -128.68 (d, 2F), -150.29 (t, 1F). FAB-MS (*m/z*): 378 [M]⁺. Elemental analysis calcd (%) for C₁₇H₁₅F₃O₂SSi: C 55.42, H 4.10; found: C 55.40, H 3.97.

General synthetic procedure for the organic ligands

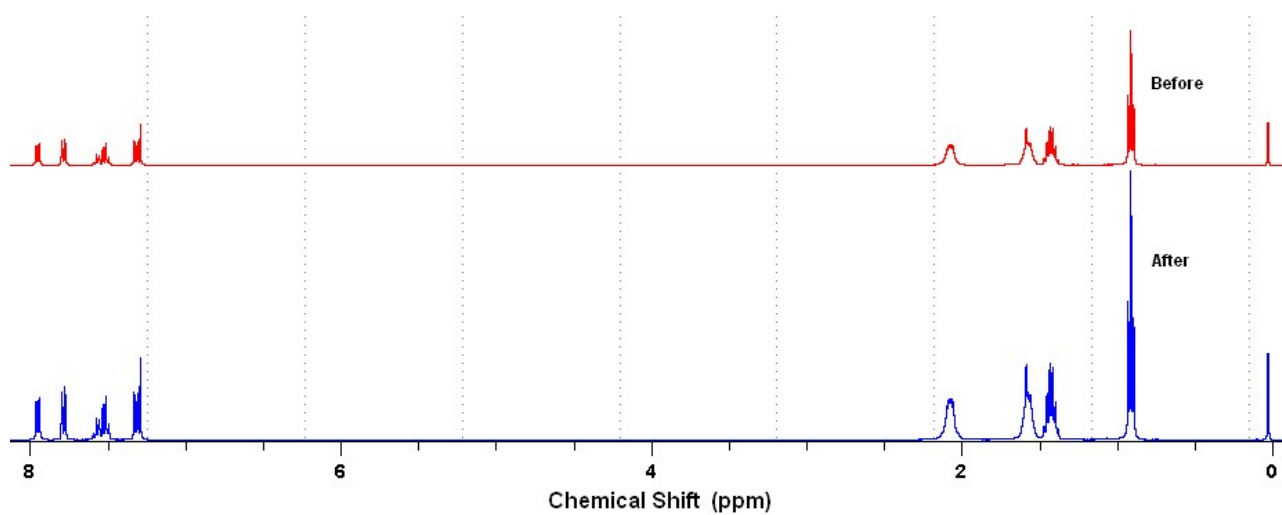
To the solution of **S-0F-TMS/S-1F-TMS/S-3F-TMS** (1.0 equiv) in CH₂Cl₂, tetrabutylammonium fluoride trihydrate (1.1 equiv) was added. The reaction mixture was stirred at room temperature for 30 min and then was washed with water. The organic phase was dried over MgSO₄ and concentrated under vacuum. After concentration, the residue was purified by silica gel column chromatography with CH₂Cl₂/hexane as eluent to get the pure product as white solid.

L-0F (Yield: 93%) ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.94 (d, *J* = 7.6 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.60–7.49 (m, 5H), 3.24 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 141.46, 141.13, 133.41, 132.83, 129.37, 127.69, 127.59, 127.33, 81.83, 80.99. FAB-MS (*m/z*): 242 [M]⁺. Elemental analysis calcd (%) for C₁₄H₁₀O₂S: C 69.40, H 4.16; found: C 69.28, H 4.07.

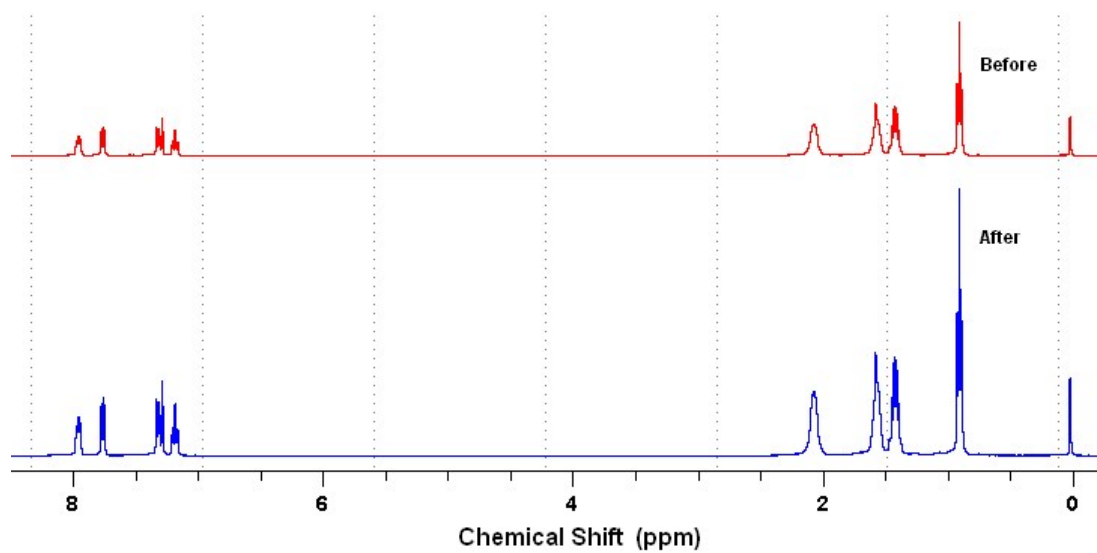
L-1F (Yield: 92%) ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.97–7.93 (m, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 8.0 Hz, 2H), 3.25 (s, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 141.31, 132.92, 130.59, 130.50, 127.52, 116.84, 116.61, 81.76, 81.15; ¹⁹F NMR (376 MHz, CDCl₃): δ (ppm) -103.64 (s, 1F). FAB-MS (*m/z*): 260 [M]⁺. Elemental analysis calcd (%) for C₁₄H₉FO₂S: C 64.60, H 3.49; found: C 64.51, H 3.51.

L-3F (Yield: 91%) ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.88 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* =

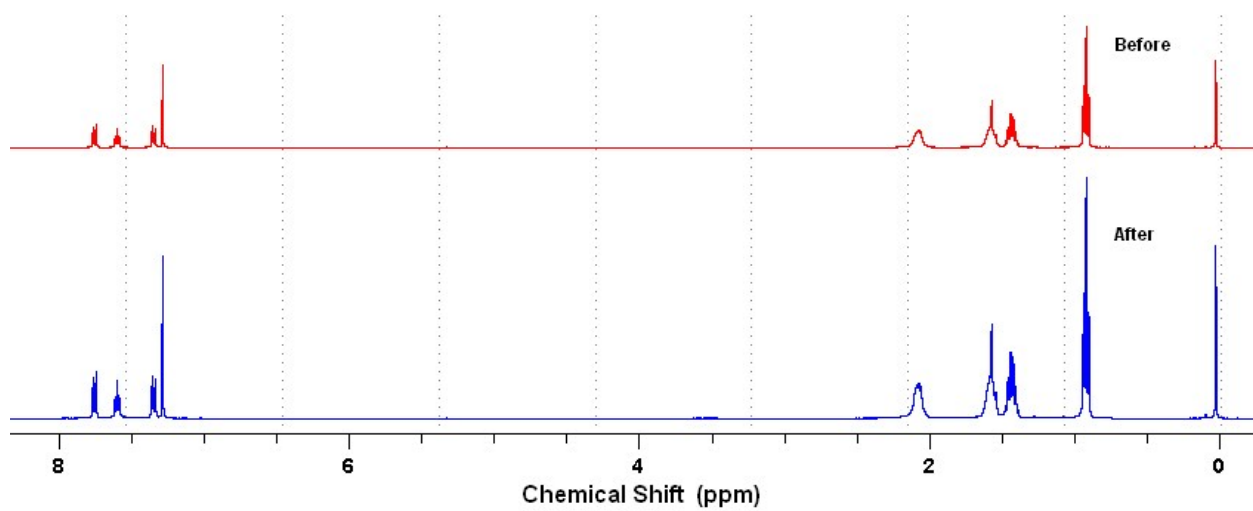
8.0 Hz, 2H), 7.60 (t, $J = 4.0$ Hz, 2H), 3.29 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 139.26, 132.92, 129.40, 127.71, 112.99, 112.92, 112.82, 112.75, 102.59, 100.03, -0.32; ^{19}F NMR (376 MHz, CDCl_3): δ (ppm) -128.57 (d, 2F), -150.12 (t, 1F). FAB-MS (m/z): 296 $[\text{M}]^+$.
Elemental analysis calcd (%) for $\text{C}_{14}\text{H}_7\text{F}_3\text{O}_2\text{S}$: C 56.76, H 2.38; found: C 56.81, H 2.32.



(a) Pt-S-0F



(b) Pt-S-1F



(c) Pt-S-3F

Fig. S1 ¹H-NMR spectra for these Pt(II) acetylides before and after Z-scan measurement.