

Supplemental Information

[3+2] Radical Sulfuration of Alkenes by Organic Photocatalysis

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1. General Information

If no special indicated, commercially available reagents and dry solvents were used without further purification. Column chromatographic purification of all products was conducted using 200-300 dry mesh silica gel. ^1H and ^{13}C NMR spectra were measured on a JEOL JNM-ECZ400S/L1 spectrometers, NMR (400 MHz for ^1H NMR, 101 MHz for ^{13}C NMR). Multiplicity (s = singlet, D = doublet, t = triplet, m = multiplet, Q = quartet, Coupling Constant (J) in Hz). CHCl_3 (δ = 7.26 ppm) served as the internal standard for ^1H NMR, and CDCl_3 (δ = 77.16 ppm) served as the internal standard for ^{13}C NMR. Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. High-resolution mass spectra (HRSM) were obtained on a Waters I-Class VION IMS QTof and are reported as m/z (relative intensity). UV-vis spectra experiments were measured on an Ultraviolet-visible Spectrophotometer (YOKE T2600). Fluorescence emission spectrums were recorded using an Edinburgh FLS9 Fluorescence Spectrometer.

2. General Experimental Procedure

A 10 mL of Schlenk tube equipped with magnetic bar was added rhodamine 6G (5.8 mg, 6% equiv.), the tube was evacuated and backfilled with N_2 (3 times). Then, 4-methylstyrene (0.2 mmol, 1 equiv.), 2,4,6-trimethylbenzenethiol (0.4 mmol, 2 equiv.), carbon disulfide (1 mmol, 5 equiv.), *N,N*-diisopropylethylamine (0.05 mmol, 0.25 equiv.), 1.0 mL CH_2Cl_2 as a solvent were added. The Schlenk tube was sealed with a Teflon lined cap and degassed by three freeze-pump-thaw cycles. The reaction mixture was irradiated with green light (520-530 nm) for 12 h at room temperature. The solvent was removed under reduced pressure and purified by column chromatography (petroleum ether/ CH_2Cl_2 = 20/1) to afford the title product.

3. Light On-off Experiments

A 10 mL of Schlenk tube equipped with magnetic bar was added rhodamine 6G (5.8 mg, 6% equiv.), the tube was evacuated and backfilled with N₂ (3 times). Then, 4-methylstyrene (0.2 mmol, 1 equiv.), 2,4,6-trimethylbenzenethiol (0.4 mmol, 2 equiv.), carbon disulfide (1 mmol, 5 equiv.), *N,N*-diisopropylethylamine (0.05 mmol, 0.25 equiv.), 1.0 mL CH₂Cl₂ as a solvent were added. The Schlenk tube was sealed with a Teflon lined cap and degassed by three freeze-pump-thaw cycles. Six reactions were setup in parallel under green light. After 1 h, the light was turned off, one reaction was isolated by flash column chromatography to give the desired product, the remaining five were kept stirring for another 1 h without irradiation. The experiments were cycled as above. Finally, the sixth reaction was ended after stirring for 2 h without irradiation.

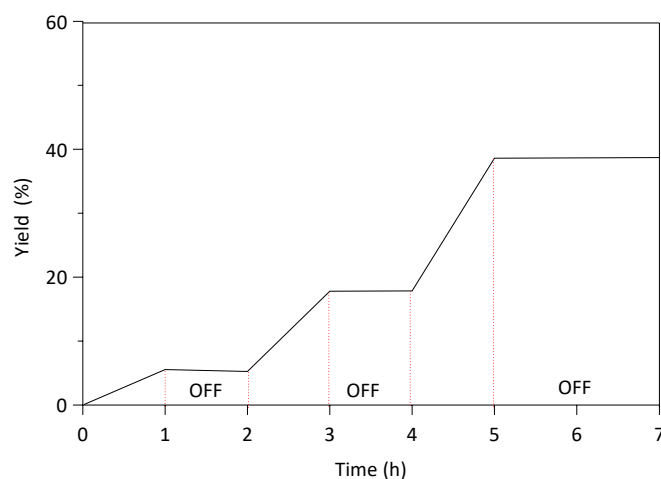


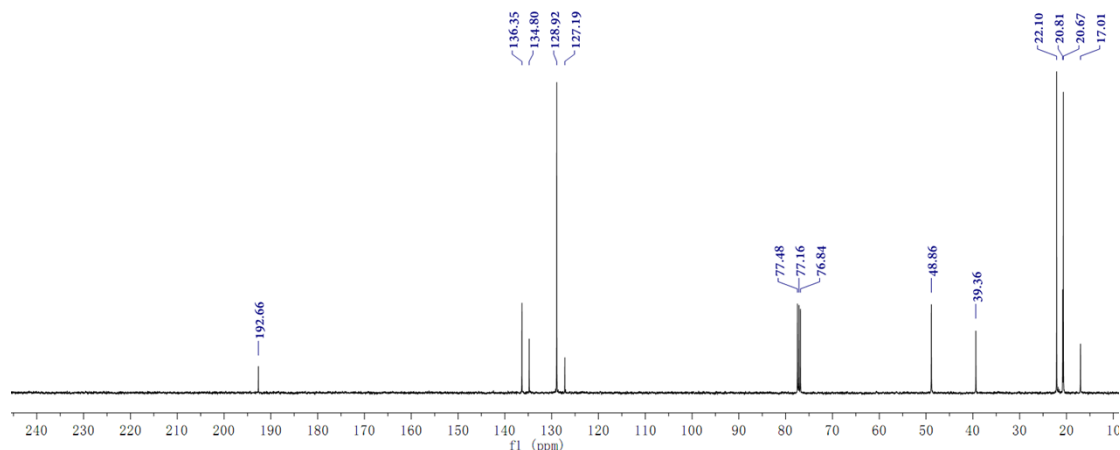
Figure S1: Light on-off experiments of the standard reaction. All yields are isolated.

4. Stern-Volmer Fluorescence Quenching

In a typical experiment, a 20 μ M solution of rhodamine 6G in CH₂Cl₂ was added to variable concentrations of quenchers in a screw-top 1.0 cm quartz cuvette, after degassing by bubbling a stream of nitrogen, the emission spectrum of the sample was collected. All solutions were excited at $\lambda = 490$ nm and their maximum emission intensity were recorded. The ratio of I_0/I was plotted as a function of the quencher concentration (I_0 = emission intensity of the Rhodamine 6G; I = observed emission intensity of the mixed solution).

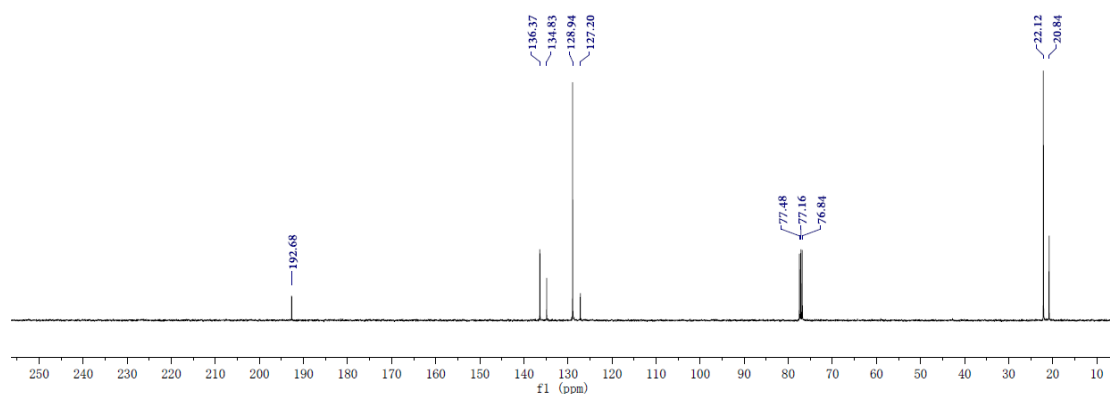
5. ^{13}C NMR Experiments

A 10 mL of Schlenk tube equipped with magnetic bar was evacuated and backfilled with N_2 (3 times). Then, 2,4,6-trimethylbenzenethiol (0.2 mmol, 1 equiv.), carbon disulfide (0.2 mmol, 1 equiv.), *N,N*-diisopropylethylamine (0.1 mmol, 0.5 equiv.), CDCl_3 as a solvent (0.6 mL) were added subsequently. The Schlenk tube was then sealed with a Teflon lined cap, and was degassed by three freeze-pump-thaw cycles. After stirring in room temperature for 12 h, the products were analyzed by ^{13}C NMR (Fig. S2). According to the same procedure, 2,4,6-trimethylbenzenethiol (0.2 mmol, 1 equiv.), carbon disulfide (0.2 mmol, 1 equiv.), CDCl_3 as a solvent (0.6 mL) were added to a 10 mL of Schlenk tube. After stirring in room temperature for 12 h, the products were analyzed by ^{13}C NMR (Fig. S3).



Note: ^{13}C NMR: CS_2 (δ 192.66), 2,4,6-trimethylbenzenethiol (δ 136.35, 134.80, 128.92, 127.19, 22.10, 20.81), *N,N*-diisopropylethylamine (δ 48.86, 39.36, 20.67, 17.01), and no new peaks appeared.

Figure S2: The ^{13}C NMR of the reaction mixture 2,4,6-trimethylbenzenethiol, carbon disulfide and *N,N*-diisopropylethylamine in CDCl_3 .



Note: ^{13}C NMR: CS_2 (δ 192.68), 2,4,6-trimethylbenzenethiol (δ 136.37, 134.83, 128.94, 127.20, 22.12, 20.84), and no new peaks appeared.

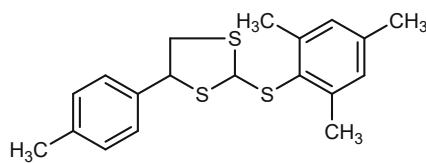
Figure S3: The ^{13}C NMR of the reaction mixture 2,4,6-trimethylbenzenethiol, carbon disulfide in CDCl_3 .

6. Uv-vis Absorption Spectrum

In order to detect EDA complex, Uv-vis absorption spectra were recorded using the mixed solution in CH_2Cl_2 at room temperature. ($[\text{Rh-6G}^+] = 1.6 \times 10^{-5} \text{ M}$, $[\text{15}] = 3.2 \times 10^{-4} \text{ M}$, $[\text{14}] = 3.2 \times 10^{-4} \text{ M}$, $[\text{CS}_2] = 3.2 \times 10^{-4} \text{ M}$, $[\text{DIPEA}] = 3.2 \times 10^{-4} \text{ M}$)

In order to detect Rh-6G^* , Uv-vis absorption spectra were recorded using the mixed solution ($[\text{Rh-6G}^+] = 1.6 \times 10^{-5} \text{ M}$, $[\text{DIPEA}] = 3.2 \times 10^{-4} \text{ M}$) in CH_2Cl_2 at different times using green light irradiation.

7. Characterization of Products



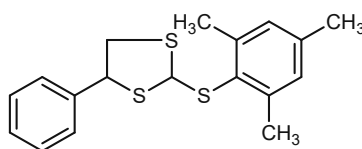
According to the general procedure, the title product was obtained in 86% yield as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, J = 8.0 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.17 (dd, J = 10.3, 8.1 Hz, 2H), 6.97 and 6.96 (s, 1H), 5.73 (s, 0.46), 5.65 (s, 0.48), 5.04 (dd, J = 8.7, 5.3 Hz, 0.52H), 4.88 (dd, J = 11.1, 4.9 Hz, 0.49), 3.74 – 3.58 (m, 1H), 3.43 – 3.34 (m, 1H), 2.59 and 2.58 (s, 6H), 2.37 and 2.35 (s, 3H), 2.29 and 2.28 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.18, 139.36, 138.12, 138.03, 134.46, 134.29, 129.51, 129.48, 129.26, 128.07, 127.85, 62.33, 62.20, 61.36, 57.13, 45.52, 43.83, 22.34, 22.31, 21.23.

HRMS (ESI) m/z Calcd. for C₁₉H₂₃S₃ [M+H]⁺ 347.0956, found: 347.0974.

IR (film) $\nu_{\max}$ (cm⁻¹) 2917, 1599, 1511, 1455, 1425, 1374, 1174, 1021, 854, 816, 731, 552, 515.



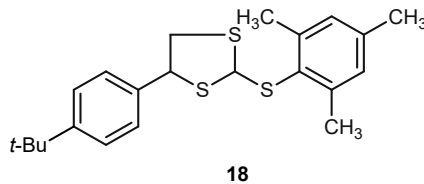
According to the general procedure, the title product was obtained in 81% yield as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.59 – 7.54 (m, 1H), 7.49 – 7.44 (m, 1H), 7.40 – 7.30 (m, 3H), 6.98 and 6.97 (s, 2H), 5.75 (s, 0.45H), 5.66 (s, 0.46H), 5.10 – 5.01 (m, 0.53H), 4.92 – 4.88 (m, 0.50H), 3.77 – 3.60 (m, 1H), 3.45 – 3.38 (m, 1H), 2.60 and 2.59 (s, 6H), 2.30 and 2.29 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.19, 139.40, 137.66, 137.47, 130.70, 130.65, 129.29, 129.27, 128.86, 128.82, 128.31, 128.22, 128.00, 62.48, 62.26, 61.42, 57.35, 45.49, 43.88, 22.35, 22.32, 21.25.

HRMS (ESI) m/z Calcd. for $C_{18}H_{20}S_3$ $[M]^+$ 332.0722, found: 332.0685.

IR (film) $\nu_{\max}$ (cm^{-1}) 2916, 1599, 1453, 1372, 1028, 852, 769, 723, 698, 596, 511.



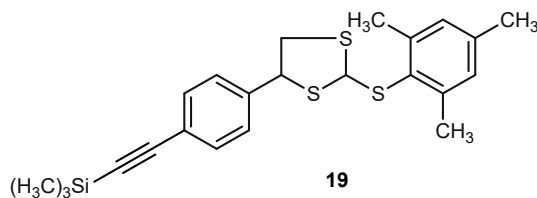
According to the general procedure, the title product was obtained in 61% yield as a yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, J = 8.4 Hz, 1H), 7.42 – 7.35 (m, 3H), 6.98 and 6.97 (s, 2H), 5.73 (s, 0.47H), 5.65 (s, 0.48H), 5.08 – 5.02 (m, 0.52H), 4.90 (dd, J = 11.1, 4.9 Hz, 0.51H), 3.75 – 3.61 (m, 1H), 3.41 (ddd, J = 10.8, 7.0, 4.0 Hz, 1H), 2.59 (s, 6H), 2.30 and 2.28 (s, 3H), 1.34 and 1.32 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 151.35, 151.26, 143.19, 139.35, 134.50, 134.20, 130.76, 130.71, 129.27, 129.25, 127.89, 127.68, 125.78, 125.76, 62.23, 62.17, 61.37, 57.01, 45.45, 43.79, 34.71, 34.68, 31.41, 31.40, 22.36, 22.33, 21.25.

HRMS (ESI) m/z Calcd. for $C_{22}H_{32}NS_3$ $[M+\text{NH}_4]^+$ 406.1691, found: 406.1701.

IR (film) $\nu_{\max}$ (cm^{-1}) 2962, 2919, 1601, 1501, 1458, 1363, 1269, 1019, 850, 826, 732, 708, 563, 553.



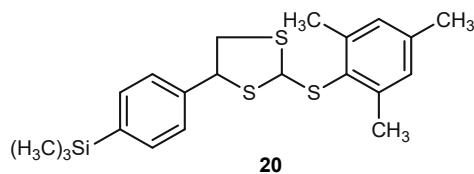
According to the general procedure, the title product was obtained in 41% yield as a white solid.

^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.35 (m, 4H), 6.97 and 6.96 (s, 2H), 5.73 (s, 0.46H), 5.64 (s, 0.44H), 5.03 (dd, J = 8.2, 5.3 Hz, 0.49H), 4.86 (dd, J = 10.9, 5.0 Hz, 0.50H), 3.72 (dd, J = 11.2, 5.3 Hz, 0.51H), 3.59 (dd, J = 12.1, 11.1 Hz, 0.54H), 3.42 – 3.32 (m, 1H), 2.58 and 2.57 (s, 6H), 2.29 and 2.28 (s, 3H), 0.27 and 0.25 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 143.19, 139.48, 138.21, 132.40, 132.31, 130.59, 129.32, 128.11, 127.89, 123.15, 123.07, 104.73, 104.64, 95.00, 62.35, 62.12, 61.54, 57.23, 45.32, 43.80, 22.35, 21.25, 0.09.

HRMS (ESI) m/z Calcd. for $C_{23}H_{28}LiS_3Si$ $[M+Li]^+$ 435.1277, found: 435.1295.

IR (film) ν_{max} (cm^{-1}) 2954, 2920, 2160, 1601, 1501, 1410, 1247, 838, 759, 641, 551.



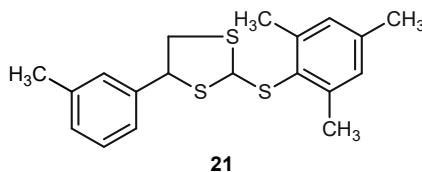
According to the general procedure, the title product was obtained in 80% yield as a light yellow oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.43 (m, 4H), 6.98 and 6.96 (s, 2H), 5.74 (s, 0.48H), 5.67 (s, 0.50H), 5.09 – 5.02 (m, 0.58H), 4.90 (dd, J = 11.0, 5.0 Hz, 0.52H), 3.77 – 3.61 (m, 1H), 3.47 – 3.35 (m, 1H), 2.60 and 2.59 (s, 6H), 2.30 and 2.29 (s, 3H), 0.30 and 0.28 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.21, 140.82, 140.72, 139.42, 139.40, 138.25, 137.98, 133.89, 133.85, 130.73, 130.68, 129.30, 129.28, 127.57, 127.36, 62.47, 62.28, 61.48, 57.36, 45.42, 43.87, 22.36, 22.34, 21.26, -1.02, -1.04.

HRMS (ESI) m/z Calcd. for $C_{21}H_{28}NaS_3Si$ $[M+Na]^+$ 427.1015, found: 427.1005.

IR (film) ν_{max} (cm^{-1}) 2953, 2919, 1600, 1247, 1110, 908, 836, 816, 729, 552, 527.



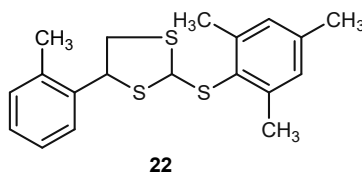
According to the general procedure, the title product was obtained in 72% yield as a yellow oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 1H), 7.29 – 7.21 (m, 2H), 7.13 (dd, J = 10.0, 3.4 Hz, 1H), 6.98 and 6.96 (s, 2H), 5.74 (s, 0.50H), 5.66 (s, 0.51H), 5.07 – 5.00 (m, 0.50H), 4.87 (dd, J = 11.1, 4.9 Hz, 0.54H), 3.75 – 3.60 (m, 1H), 3.44 – 3.36 (m, 1H), 2.60 and 2.59 (s, 6H), 2.39 and 2.36 (s, 3H), 2.30 and 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.20, 139.38, 138.55, 137.43, 137.26, 130.68, 129.29, 129.26, 129.09, 129.00, 128.82, 128.75, 128.71, 128.67, 125.28, 125.05, 62.54, 62.22, 61.38, 57.34, 45.50, 43.80, 22.36, 22.33, 21.53, 21.25.

HRMS (ESI) m/z Calcd. for $C_{19}H_{23}S_3$ $[M+H]^+$ 347.0956, found: 347.0953.

IR (film) $\nu_{\max}$ (cm⁻¹) 2916, 2851, 1600, 1455, 1434, 1374, 1032, 852, 768, 727, 711, 693, 551.



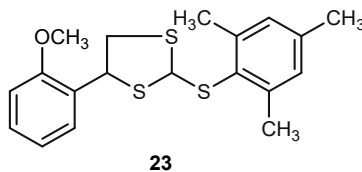
According to the general procedure, the title product was obtained in 43% yield as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.81 (m, 0.46H), 7.56 – 7.50 (m, 0.52H), 7.30 – 7.13 (m, 3H), 6.97 and 6.96 (s, 2H), 5.75 (s, 0.50H), 5.66 (s, 0.44H), 5.26 (dd, J = 9.0, 5.1 Hz, 0.51H), 5.15 (dd, J = 11.0, 4.7 Hz, 0.45H), 3.74 – 3.59 (m, 1H), 3.44 – 3.33 (m, 1H), 2.58 (s, 6H), 2.50 and 2.40 (s, 3H), 2.29 and 2.28 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.21, 143.17, 139.40, 136.26, 136.20, 135.42, 135.16, 130.82, 130.74, 130.69, 130.62, 129.29, 127.95, 127.53, 127.31, 126.73, 126.52, 61.99, 61.30, 58.18, 53.23, 44.59, 42.44, 22.34, 21.25, 19.81, 19.75.

HRMS (ESI) m/z Calcd. for C₁₉H₂₃S₃ [M+H]⁺ 347.0956, found: 347.0946.

IR (film) $\nu_{\max}$ (cm⁻¹) 2920, 1601, 1459, 1374, 1032, 906, 850, 757, 726, 648, 552.



According to the general procedure, the title product was obtained in 78% yield as a light yellow oil.

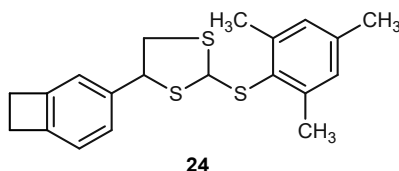
¹H NMR (400 MHz, CDCl₃) δ 7.81 (dd, J = 7.7, 1.6 Hz, 0.39H), 7.51 (dd, J = 7.6, 1.6 Hz, 0.47H), 7.32 – 7.23 (m, 1H), 7.06 – 6.86 (m, 4H), 5.76 (s, 0.47 H), 5.66 (s, 0.44H), 5.55 (dd, J = 7.2, 5.3 Hz, 0.45H), 5.41 (dd, J = 10.5, 5.0 Hz, 0.44H), 3.89 and 3.86 (s, 3H), 3.77 (dd, J = 11.2, 5.3 Hz, 0.48H), 3.53 (ddd, J = 17.1, 12.0, 7.8 Hz, 1H), 3.37 (dd, J = 11.2, 7.3 Hz, 0.44H), 2.60 and 2.59 (s, 6H), 2.30 and 2.29 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 157.19, 156.85, 143.24, 143.20, 139.29, 130.84, 129.25, 129.21, 129.06, 128.98, 128.59, 128.42, 126.22, 125.93, 120.88, 120.55, 110.68, 110.59, 61.83, 61.20, 55.60, 55.57, 54.89, 50.70, 43.81, 42.11, 22.33, 22.27,

21.23.

HRMS (ESI) m/z Calcd. for $C_{19}H_{22}OS_3$ $[M]^+$ 362.0827, found: 362.0780.

IR (film) $\nu_{\max}$ (cm^{-1}) 2921, 2836, 1735, 1560, 1490, 1461, 1437, 1242, 1103, 1049, 1028, 850, 751, 735, 705, 552.



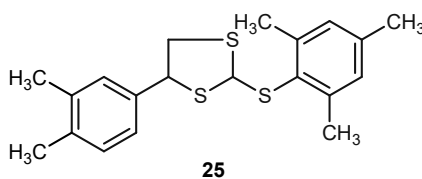
According to the general procedure, the title product was obtained in 91% yield as a yellow solid.

1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 1.5H), 7.21 (s, 0.49H), 7.05 (t, J = 6.9 Hz, 1H), 7.00 and 6.98 (s, 2H), 5.75 (s, 0.45H), 5.67 (s, 0.48H), 5.10 – 5.02 (m, 0.52H), 4.89 (dd, J = 11.1, 4.9 Hz, 0.50H), 3.76 – 3.60 (m, 1H), 3.45 – 3.36 (m, 1H), 3.21 and 3.19 (s, 4H), 2.62 and 2.61 (s, 6H), 2.32 and 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.30, 146.04, 145.94, 143.16, 139.32, 135.93, 135.72, 130.73, 130.68, 129.24, 126.96, 126.69, 122.83, 122.29, 122.13, 63.36, 62.23, 61.35, 58.05, 45.75, 44.00, 29.50, 22.33, 22.30, 21.22.

HRMS (ESI) m/z Calcd. for $C_{20}H_{26}NS_3$ $[M+NH_4]^+$ 376.1222, found: 376.1229.

IR (film) $\nu_{\max}$ (cm^{-1}) 2917, 1600, 1470, 1456, 1432, 1418, 1373, 1032, 843, 817, 725, 706, 550.



According to the general procedure, the title product was obtained in 66% yield as a light brown oil.

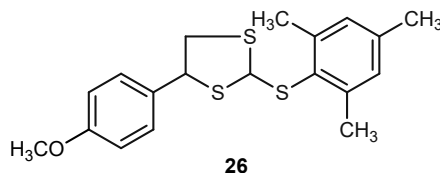
1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 1H), 7.26 – 7.19 (m, 1H), 7.13 (dd, J = 10.2, 7.8 Hz, 1H), 6.99 and 6.97 (s, 2H), 5.74 (s, 0.38H), 5.66 (s, 0.42H), 5.03 (dd, J = 9.2, 5.2 Hz, 0.45H), 4.86 (dd, J = 11.1, 4.8 Hz, 0.44H), 3.75 – 3.61 (m, 1H), 3.44 – 3.36 (m, 1H), 2.61 and 2.60 (s, 6H), 2.34 – 2.25 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.19, 139.33, 137.07, 136.78, 136.70, 134.73,

134.59, 130.71, 130.05, 130.02, 129.27, 129.14, 125.55, 125.33, 62.41, 62.18, 61.37, 57.16, 45.55, 43.80, 22.35, 22.32, 21.23, 19.90, 19.59, 19.55.

HRMS (ESI) m/z Calcd. for $C_{20}H_{28}NS_3$ $[M+NH_4]^+$ 378.1378, found: 378.1356.

IR (film) ν_{max} (cm^{-1}) 2919, 1600, 1499, 1451, 1374, 1029, 851, 823, 725, 712, 552.



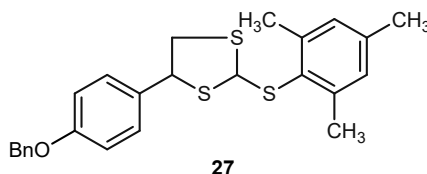
According to the general procedure, the title product was obtained in 51% yield as a white solid.

1H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.45 (m, 1H), 7.41 – 7.36 (m, 1H), 6.98 and 6.96 (s, 2H), 6.93 – 6.85 (m, 2H), 5.72 (s, 0.50H), 5.64 (s, 0.47H), 5.04 (dd, J = 8.9, 5.1 Hz, 0.50H), 4.88 (dd, J = 11.0, 4.9 Hz, 0.49H), 3.82 and 3.80 (s, 3H), 3.69 (dd, J = 11.0, 5.2 Hz, 0.51H), 3.61 (dd, J = 12.0, 11.3 Hz, 0.50H), 3.41 – 3.33 (m, 1H), 2.594 and 2.586 (s, 6H), 2.30 and 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.56, 159.50, 143.18, 139.37, 130.72, 130.69, 129.28, 129.07, 114.21, 114.18, 62.13, 61.32, 56.90, 55.43, 55.42, 45.57, 43.83, 22.34, 22.31, 21.23.

HRMS (ESI) m/z Calcd. for $C_{19}H_{22}NaOS_3$ $[M+Na]^+$ 385.5532, found: 385.0743.

IR (film) ν_{max} (cm^{-1}) 2910, 1612, 1511, 1253, 1172, 1033, 856, 825, 735, 547, 528.



According to the general procedure, the title product was obtained in 54% yield as a white solid.

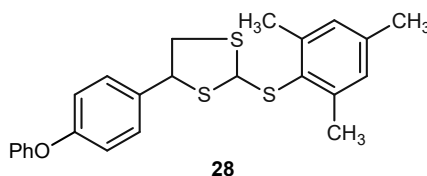
1H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.32 (m, 7H), 7.02 – 6.91 (m, 4H), 5.73 (s, 0.49H), 5.64 (s, 0.46H), 5.09 and 5.07 (s, 2H), 5.04 (dd, J = 8.9, 5.2 Hz, 0.54H), 4.88 (dd, J = 11.0, 4.9 Hz, 0.48H), 3.75 – 3.56 (m, 1H), 3.43 – 3.33 (m, 1H), 2.60 and 2.59 (s, 6H), 2.30 and 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.77, 158.71, 143.19, 139.38, 136.94, 136.91,

130.73, 130.69, 129.62, 129.54, 129.34, 129.27, 129.11, 128.72, 128.13, 127.55, 115.15, 115.11, 77.48, 62.15, 62.12, 61.34, 56.90, 45.56, 43.81, 22.35, 22.32, 21.24.

HRMS (ESI) m/z Calcd. for $C_{25}H_{26}OS_3$ $[M]^+$ 438.1140, found: 438.1121.

IR (film) $\nu_{\max}$ (cm^{-1}) 2917, 1608, 1509, 1455, 1379, 1294, 1239, 1174, 1007, 854, 824, 739, 727, 528.



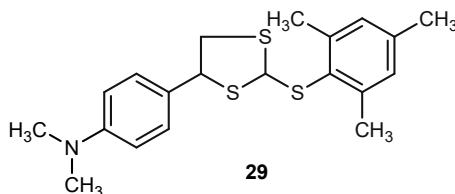
According to the general procedure, the title product was obtained in 75% yield as a white solid.

1H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.49 (m, 1H), 7.45 – 7.40 (m, 1H), 7.40 – 7.33 (m, 2H), 7.18 – 7.11 (m, 1H), 7.08 – 6.95 (m, 6H), 5.75 (s, 0.50H), 5.66 (s, 0.46H), 5.06 (dd, J = 8.7, 5.2 Hz, 0.50H), 4.90 (dd, J = 11.0, 4.9 Hz, 0.47H), 3.73 (dd, J = 11.1, 5.2 Hz, 0.51H), 3.68 – 3.60 (m, 0.47H), 3.46 – 3.34 (m, 1H), 2.600 and 2.596 (s, 6H), 2.301 and 2.293 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.34, 157.33, 156.95, 156.89, 143.16, 139.40, 132.14, 132.03, 130.65, 129.90, 129.56, 129.33, 129.28, 123.64, 123.63, 119.22, 119.21, 118.91, 118.83, 62.19, 61.92, 61.39, 56.83, 45.52, 43.88, 22.34, 22.31, 21.23.

HRMS (ESI) m/z Calcd. for $C_{24}H_{24}OS_3$ $[M]^+$ 424.0984, found: 424.0955.

IR (film) $\nu_{\max}$ (cm^{-1}) 2918, 1586, 1504, 1488, 1237, 1165, 873, 847, 749, 731, 690, 517.



According to the general procedure, the title product was obtained in 86% yield as a yellow solid.

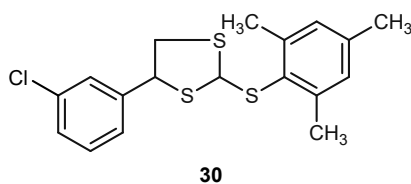
1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 0.78H), 7.34 – 7.28 (m, 1.22H), 6.96 and 6.94 (s, 2H), 6.70 (t, J = 9.9 Hz, 2H), 5.69 (s, 0.56H), 5.61 (s, 0.35H), 5.01 (dd, J = 9.4, 5.1 Hz, 0.58H), 4.86 (dd, J = 11.2, 4.8 Hz, 0.36H), 3.67 – 3.57 (m, 1H), 3.40 –

3.29 (m, 1H), 2.96 and 2.94 (s, 3H), 2.58 and 2.57 (s, 3H), 2.28 and 2.26 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 150.56, 150.48, 143.24, 143.21, 139.32, 130.84, 130.80, 129.25, 129.23, 128.94, 128.72, 112.61, 112.58, 62.65, 62.02, 61.21, 57.17, 45.55, 43.67, 40.66, 40.63, 22.37, 22.34, 21.25.

HRMS (ESI) m/z Calcd. for C₂₀H₂₆NS₃ [M+H]⁺ 376.1222, found: 376.1230.

IR (film) ν_{max} (cm⁻¹) 2918, 2851, 1613, 1520, 1444, 1349, 1166, 1059, 1046, 948, 853, 811, 709, 544, 527.



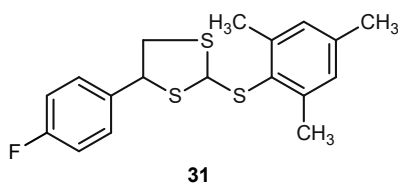
According to the general procedure, the title product was obtained in 65% yield as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.23 (m, 4H), 6.96 and 6.95 (s, 2 H), 5.73 (s, 0.42H), 5.64 (s, 0.51H), 5.00 (dd, *J* = 8.1, 5.7 Hz, 0.52H), 4.82 (dd, *J* = 10.8, 5.0 Hz, 0.54H), 3.74 (dd, *J* = 11.1, 5.2 Hz, 0.45H), 3.62 – 3.52 (m, 0.55H), 3.46 – 3.29 (m, 1H), 2.57 and 2.56 (s, 3H), 2.28 and 2.27 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.22, 143.20, 140.20, 140.00, 139.53, 134.64, 134.60, 130.51, 130.13, 130.02, 129.35, 129.33, 128.51, 128.37, 128.36, 128.20, 126.47, 126.22, 62.31, 61.66, 61.54, 56.87, 45.33, 43.88, 22.37, 22.33, 21.26.

HRMS (ESI) m/z Calcd. for C₁₈H₁₉ClLiS₃ [M+Li]⁺ 373.0492, found: 373.0487.

IR (film) ν_{max} (cm⁻¹) 2920, 1594, 1572, 1474, 1430, 1032, 906, 851, 788, 729, 691, 552.



According to the general procedure, the title product was obtained in 64% yield as a light yellow solid.

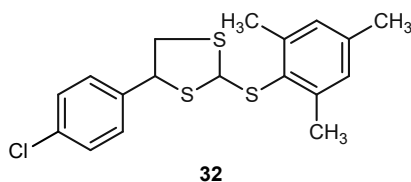
¹H NMR (400 MHz, CDCl₃) δ 7.56 – 7.49 (m, 1H), 7.47 – 7.39 (m, 1H), 7.09 – 6.99 (m, 2H), 6.98 and 6.96 (s, 2H), 5.73 (s, 0.48H), 5.65 (s, 0.46H), 5.10 – 5.00 (m,

0.55H), 4.88 (dd, $J = 10.9, 5.0$ Hz, 0.48H), 3.73 (dd, $J = 11.2, 5.3$ Hz, 0.51H), 3.59 (dd, $J = 12.2, 11.0$ Hz, 0.49H), 3.38 (ddd, $J = 19.5, 11.7, 6.7$ Hz, 1H), 2.59 and 2.58 (s, 6H), 2.29 and 2.28 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 163.76, 161.27, 143.16, 139.46, 133.56, 130.58, 129.87, 129.79, 129.64, 129.56, 129.30, 115.84, 115.79, 115.63, 115.57, 62.25, 61.61, 61.44, 56.67, 45.55, 43.99, 22.32, 21.23.

HRMS (ESI) m/z Calcd. for $\text{C}_{18}\text{H}_{19}\text{FNaS}_3$ $[\text{M}+\text{Na}]^+$ 373.0525, found: 373.0517.

IR (film) ν_{max} (cm^{-1}) 2919, 1599, 1506, 1457, 1223, 1157, 837, 820, 792, 724, 710, 528.



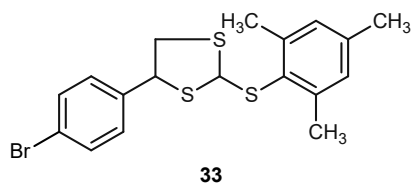
According to the general procedure, the title product was obtained in 56% yield as a light yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 7.49 (d, $J = 8.5$ Hz, 1H), 7.39 (d, $J = 8.5$ Hz, 1H), 7.36 – 7.27 (m, 2H), 6.97 and 6.96 (s, 2H), 5.73 (s, 0.48H), 5.65 (s, 0.46H), 5.06 – 5.00 (m, 0.57H), 4.86 (dd, $J = 10.8, 5.0$ Hz, 0.48H), 3.73 (dd, $J = 11.2, 5.3$ Hz, 0.50H), 3.64 – 3.54 (m, 0.48H), 3.38 (ddd, $J = 19.3, 11.8, 6.5$ Hz, 1H), 2.58 and 2.57 (s, 6H), 2.29 and 2.28 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 143.18, 139.51, 136.51, 136.40, 133.99, 130.55, 129.57, 129.33, 129.01, 128.94, 62.33, 61.59, 61.53, 56.76, 45.41, 43.94, 22.34, 22.31, 21.25.

HRMS (ESI) m/z Calcd. for $\text{C}_{18}\text{H}_{19}\text{ClLiS}_3$ $[\text{M}+\text{Li}]^+$ 373.0492, found: 373.0459.

IR (film) ν_{max} (cm^{-1}) 2917, 2850, 1600, 1488, 1456, 1374, 1086, 1040, 1014, 851, 814, 725, 710, 552, 518.



According to the general procedure, the title product was obtained in 54% yield as a

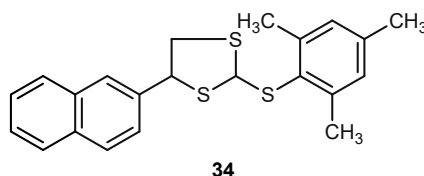
light yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.51 – 7.40 (m, 3H), 7.36 – 7.30 (m, 1H), 6.97 and 6.96 (s, 2H), 5.73 (s, 0.46H), 5.64 (s, 0.49H), 5.04 – 4.98 (m, 0.54H), 4.84 (dd, *J* = 10.8, 5.0 Hz, 0.49H), 3.73 (dd, *J* = 11.2, 5.3 Hz, 0.49H), 3.62 – 3.51 (m, 0.52H), 3.37 (ddd, *J* = 19.2, 11.8, 6.5 Hz, 1H), 2.574 and 2.566 (s, 6H), 2.29 and 2.28 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.16, 139.49, 137.07, 136.95, 131.96, 131.88, 130.53, 130.52, 129.89, 129.65, 129.31, 122.08, 62.33, 61.61, 61.55, 56.80, 45.34, 43.90, 22.34, 22.30, 21.25.

HRMS (ESI) *m/z* Calcd. for C₁₈H₁₉BrLiS₃ [M+Li]⁺ 416.9987, found: 417.0104.

IR (film) ν_{max} (cm⁻¹) 2954, 2919, 2850, 1598, 1487, 1456, 1431, 1402, 1376, 1074, 1008, 852, 816, 721, 551, 508.



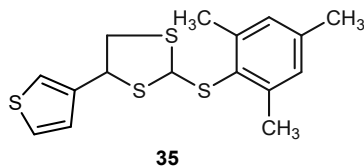
According to the general procedure, the title product was obtained in 57% yield as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.94 – 7.79 (m, 4H), 7.74 (dd, *J* = 8.5, 1.8 Hz, 0.55H), 7.58 (dd, *J* = 8.6, 1.8 Hz, 0.46H), 7.53 – 7.46 (m, 2H), 6.99 and 6.97 (s, 2H), 5.80 (s, 0.43H), 5.71 (s, 0.53H), 5.24 (dd, *J* = 8.4, 5.3 Hz, 0.44H), 5.08 (dd, *J* = 11.0, 5.0 Hz, 0.55H), 3.86 – 3.70 (m, 1H), 3.55 – 3.43 (m, 1H), 2.62 and 2.61 (s, 6H), 2.30 and 2.29 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.24, 139.46, 135.01, 134.97, 133.38, 133.30, 133.16, 130.70, 130.66, 129.33, 128.75, 128.64, 127.98, 127.92, 127.84, 127.78, 127.32, 126.99, 126.53, 126.39, 125.71, 62.75, 62.44, 61.62, 57.69, 45.45, 43.77, 22.39, 22.37, 21.27.

HRMS (ESI) *m/z* Calcd. for C₂₂H₂₆NS₃ [M+NH₄]⁺ 400.1222, found: 400.1237.

IR (film) ν_{max} (cm⁻¹) 2918, 1598, 1508, 1455, 1430, 1373, 1173, 1125, 1030, 1014, 854, 823, 748, 711, 551, 479.



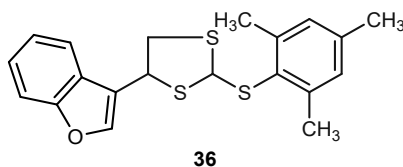
According to the general procedure, the title product was obtained in 75% yield as a yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.36 – 7.12 (m, 3H), 6.97 (s, 2H), 5.72 (s, 0.44H), 5.63 (s, 0.51H), 5.17 (dd, J = 8.0, 5.2 Hz, 0.45H), 5.04 – 4.97 (m, 0.57H), 3.73 (dd, J = 11.1, 5.2 Hz, 0.46H), 3.63 (dd, J = 12.0, 10.9 Hz, 0.54H), 3.41 (ddd, J = 19.2, 11.6, 6.5 Hz, 1H), 2.58 (s, 6H), 2.291 and 2.286 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.17, 139.42, 139.40, 138.60, 138.57, 130.61, 130.59, 129.27, 127.05, 127.03, 126.51, 126.43, 123.02, 122.70, 61.93, 61.28, 57.13, 52.69, 44.82, 43.15, 22.33, 22.31, 21.24.

HRMS (ESI) m/z Calcd. for C₁₆H₁₈KS₃ [M+K]⁺ 376.9923, found: 377.0135.

IR (film) ν_{max} (cm⁻¹) 2917, 2849, 1599, 1455, 1372, 1031, 849, 840, 784, 753, 726, 689, 626, 552.



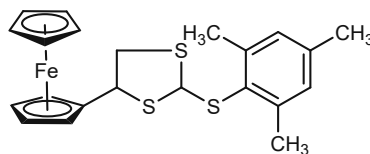
According to the general procedure, the title product was obtained in 52% yield as a light yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.95 – 7.90 (m, 0.62H), 7.73 (s, 0.6H), 7.72 – 7.67 (m, 0.43H), 7.65 (s, 0.31H), 7.54 – 7.47 (m, 1H), 7.32 (tdd, J = 14.8, 7.4, 1.3 Hz, 2H), 6.97 (s, 2H), 5.76 (s, 0.31H), 5.69 (s, 0.51H), 5.28 (dd, J = 7.2, 5.3 Hz, 0.31H), 5.09 (dd, J = 10.6, 4.9 Hz, 0.57H), 3.81 (ddd, J = 10.5, 8.4, 3.1 Hz, 1H), 3.52 (ddd, J = 12.2, 7.5, 6.1 Hz, 1H), 2.59 and 2.58 (s, 6H), 2.29 and 2.28 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 155.89, 155.73, 143.22, 142.96, 142.92, 139.51, 130.61, 129.34, 126.28, 124.92, 122.89, 120.70, 120.06, 118.34, 117.65, 111.94, 61.97, 61.35, 52.41, 48.28, 43.44, 41.63, 22.34, 21.26.

HRMS (ESI) m/z Calcd. for $C_{20}H_{24}NOS_3$ $[M+NH_4]^+$ 390.1015, found: 390.1022.

IR (film) $\nu_{\max}$ (cm^{-1}) 2918, 1600, 1451, 1176, 1099, 854, 743, 552.



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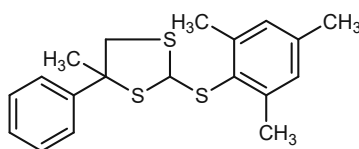
According to the general procedure, the title product was obtained in 42% yield as a brown oil.

1H NMR (400 MHz, $CDCl_3$) δ 6.96 and 6.95 (s, 2H), 5.64 (s, 0.40H), 5.53 (s, 0.52H), 4.92 (dd, J = 8.1, 5.2 Hz, 0.43H), 4.77 (dd, J = 10.8, 4.9 Hz, 0.56H), 4.55 – 4.11 (m, 9H), 3.64 (dd, J = 11.0, 5.2 Hz, 0.42H), 3.44 – 3.35 (m, 0.58H), 3.30 – 3.18 (m, 1H), 2.58 and 2.56 (s, 6H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.17, 143.16, 139.35, 139.30, 130.76, 130.72, 129.25, 85.61, 84.67, 69.12, 68.54, 68.26, 68.22, 68.20, 68.09, 67.76, 67.66, 67.30, 61.32, 61.10, 59.15, 54.21, 44.87, 42.85, 22.34, 21.25.

HRMS (ESI) m/z Calcd. for $C_{22}H_{24}FeS_3$ $[M]^+$, 440.0384, found: 440.0384.

IR (film) $\nu_{\max}$ (cm^{-1}) 2952, 2919, 2851, 1658, 1601, 1456, 1374, 1105, 1025, 1000, 850, 816, 734, 707, 552, 484.



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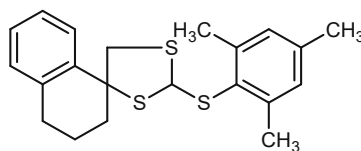
According to the general procedure, the title product was obtained in 43% yield as a light yellow oil.

1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.5 Hz, 0.72H), 7.55 – 7.49 (m, 1.22H), 7.40 – 7.21 (m, 3H), 6.95 (s, 2H), 5.65 (s, 0.34H), 5.61 (s, 0.57H), 3.93 (d, J = 12.2 Hz, 0.37H), 3.64 – 3.59 (m, 1.22H), 3.19 (d, J = 12.2 Hz, 0.35H), 2.57 and 2.54 (s, 6H), 2.28 and 2.27 (s, 3), 2.05 (s, 2H), 1.91 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.27, 143.65, 143.28, 143.25, 139.41, 139.36, 130.57, 130.32, 129.30, 129.27, 128.53, 128.44, 127.45, 127.27, 127.14, 126.50, 68.63, 67.95, 62.05, 61.77, 50.73, 49.95, 30.29, 30.09, 22.39, 22.32, 21.25.

HRMS (ESI) m/z Calcd. for $C_{19}H_{23}S_3$ $[M+H]^+$ 347.0956, found: 347.0953.

IR (film) $\nu_{\max}$ (cm^{-1}) 2920, 1600, 1493, 1443, 1374, 1058, 1028, 907, 850, 763, 729, 695, 552.



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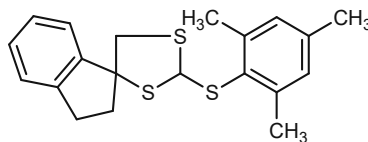
According to the general procedure, the title product was obtained in 50% yield as a yellow solid.

^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, J = 8.0 Hz, 0.21H), 7.78 – 7.71 (m, 0.78H), 7.30 – 7.12 (m, 2H), 7.11 – 7.02 (m, 1H), 6.98 and 6.97 (s, 2H), 5.81 (s, 0.74H), 5.63 (s, 0.20H), 3.96 (d, J = 12.7 Hz, 0.21H), 3.67 (d, J = 12.0 Hz, 0.79H), 3.52 (d, J = 12.0 Hz, 0.78H), 3.24 (d, J = 12.7 Hz, 0.21H), 2.93 – 2.78 (m, 2H), 2.75 – 2.66 (m, 1H), 2.60 and 2.59 (s, 6H), 2.50 – 2.39 (m, 1H), 2.30 and 2.29 (s, 3H), 2.13 – 2.01 (m, 1H), 2.01 – 1.90 (m, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ 143.27, 143.22, 139.36, 139.34, 138.46, 137.68, 137.54, 136.75, 130.69, 130.46, 129.79, 129.70, 129.39, 129.29, 128.70, 127.39, 127.36, 126.48, 126.25, 68.80, 66.78, 62.12, 62.07, 52.43, 49.34, 38.81, 38.55, 30.34, 30.07, 22.34, 21.78, 21.26, 21.22.

HRMS (ESI) m/z Calcd. for $C_{21}H_{25}S_3$ $[M+H]^+$ 373.1113, found: 373.1139.

IR (film) $\nu_{\max}$ (cm^{-1}) 2919, 2854, 1599, 1483, 1445, 1435, 1372, 1188, 1040, 852, 751, 717, 712, 658, 552.



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According to the general procedure, the title product was obtained in 66% yield as a light green oil.

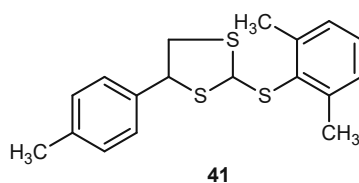
^1H NMR (400 MHz, CDCl_3) δ 7.70 – 7.43 (m, 1H), 7.33 – 7.17 (m, 3H), 6.96 (s, 2H), 5.77 (s, 0.70H), 5.67 (s, 0.24H), 3.74 (dd, J = 12.2, 0.8 Hz, 0.27H), 3.51 (s, 1.47H), 3.14 (d, J = 12.2 Hz, 0.28H), 3.10 – 2.86 (m, 3H), 2.64 – 2.56 (m, 7H), 2.29 and 2.28

(s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.93, 143.34, 143.22, 139.36, 139.33, 130.45, 129.78, 129.30, 128.44, 128.39, 127.16, 126.92, 125.04, 124.91, 124.34, 124.04, 75.21, 73.13, 62.02, 61.93, 50.28, 47.61, 42.90, 41.14, 30.64, 30.02, 22.35, 21.23.

HRMS (ESI) m/z Calcd. for C₂₀H₂₂LiS₃ [M+Li]⁺ 365.1038, found: 365.1076.

IR (film) ν_{max} (cm⁻¹) 2916, 2848, 1601, 1458, 1373, 1174, 1031, 850, 758, 735, 552.



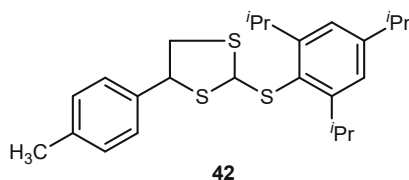
According to the general procedure, the title product was obtained in 60% yield as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.25 – 7.12 (m, 5H), 5.77 (s, 0.39H), 5.69 (s, 0.36H), 5.05 (dd, *J* = 8.9, 5.1 Hz, 0.49H), 4.89 (dd, *J* = 11.0, 4.9 Hz, 0.46H), 3.68 (ddd, *J* = 23.3, 11.5, 8.2 Hz, 1H), 3.48 – 3.33 (m, 1H), 2.64 and 2.63 (s, 6H), 2.37 and 2.35 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 143.39, 138.17, 138.09, 134.38, 134.21, 133.93, 133.88, 129.54, 129.50, 129.39, 129.38, 128.42, 128.40, 128.07, 127.86, 62.39, 62.07, 61.25, 57.20, 45.57, 43.88, 22.48, 22.45, 21.28, 21.24.

HRMS (ESI) m/z Calcd. for C₁₈H₂₄NS₃ [M+NH₄]⁺ 350.1065, found: 350.1070.

IR (film) ν_{max} (cm⁻¹) 2953, 2919, 2851, 1514, 1457, 1425, 1376, 1163, 1022, 816, 769, 731, 714, 514.



According to the general procedure, the title product was obtained in 53% yield as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 7.45 (dd, *J* = 8.1, 1.9 Hz, 1.11H), 7.36 (dd, *J* = 8.1, 2.0 Hz, 0.81H), 7.17 (dd, *J* = 13.7, 4.7 Hz, 2H), 7.07 (dd, *J* = 5.5, 2.5 Hz, 2H), 5.66 –

5.61 (m, 0.37H), 5.57 – 5.52 (m, 0.54H), 5.04 – 4.97 (m, 0.37H), 4.88 (ddd, $J = 10.9$, 4.7, 2.1 Hz, 0.54H), 4.10 – 3.94 (m, 2H), 3.69 (ddd, $J = 11.1$, 5.1, 1.7 Hz, 0.38H), 3.63 – 3.53 (m, 0.58H), 3.45 – 3.34 (m, 1H), 2.98 – 2.85 (m, 1H), 2.38 and 2.35 (s, 3H), 1.33 – 1.24 (m, 18H).

^{13}C NMR (101 MHz, CDCl_3) δ 153.36, 150.65, 138.15, 138.04, 134.39, 134.25, 129.52, 128.69, 128.63, 128.08, 127.86, 122.02, 63.92, 63.22, 62.36, 57.35, 45.64, 44.09, 34.44, 31.72, 24.76, 24.53, 24.48, 23.99, 21.29, 21.25.

HRMS (ESI) m/z Calcd. for $\text{C}_{25}\text{H}_{34}\text{LiS}_3$ $[\text{M}+\text{Li}]^+$ 437.1977, found: 437.1944.

IR (film) ν_{max} (cm^{-1}) 2959, 2924, 2866, 1597, 1513, 1461, 1425, 1382, 1361, 1102, 1059, 908, 878, 816, 734, 648, 516.

8. NMR Spectral Data

