

Supporting Information
for
**Diradical reaction mechanisms in [3 + 2]-
cycloadditions of hetaryl thioketones with alkyl- or
trimethylsilyl-substituted diazomethanes**

Grzegorz Mloston^{*1}, Paulina Pipiak¹ and Heinz Heimgartner²

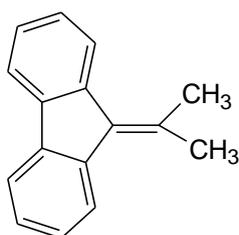
Address: ¹Department of Organic and Applied Chemistry, University of Łódź,
Tamka 12, PL 91-403 Łódź, Poland and ²Department of Chemistry,
University of Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

Email: Grzegorz Mloston - gmloston@uni.lodz.pl

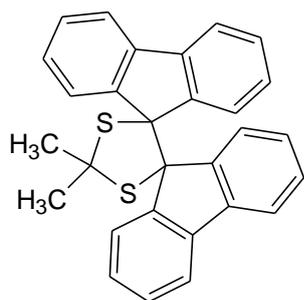
*Corresponding author

**Experimental data for compounds 8, 9, 10 and the original ¹H and
¹³C NMR spectra**

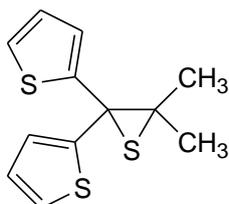
1. Experimental data for compound **8**, **9** and **10**.



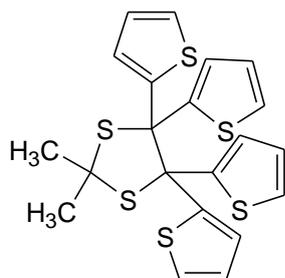
9-Isopropylidene fluorene (9b) [S1]: Yield: 85 mg (41%). White crystals; m.p. 114 – 115 °C (chromatographic purification; lit. m.p. 114 °C [S1]). ¹H NMR (600 MHz, CDCl₃): δ = 7.78–7.89 (m, 4 H_{arom}), 7.30–7.35 (m, 4 H_{arom}), 2.58 (s, 2 CH₃) ppm. C₁₆H₁₄(206.28): calcd. C 93.16 H 6.84; found C 93.13 H 6.98.



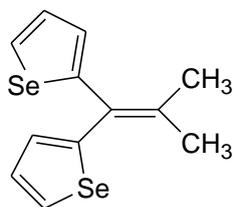
2,2'-Dimethyldispiro[9H-fluorene-9,4'-(1,3)dithiolane-5'9''-[9H]fluorene] (10b): Yield: 27 mg (12%). White crystals; m.p. 258 – 260 °C (MeOH/CHCl₃). IR (KBr): $\nu = 2918$ (w), 1445 (m), 1279 (w), 1149 (m), 1108 (w), 1033 (w), 760 (m), 744 (s) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): $\delta = 7.97$ (br. s, 4 H_{arom}), 7.42 (t, $J = 7.8$ Hz, 4 H_{arom}), 7.25 (t, $J = 7.2$ Hz, 4 H_{arom}), 7.12 (t, $J = 7.2$ Hz, 4 H_{arom}), 2.37 (s, 2 CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 140.1$ (for 8 C_{arom}), 128.5, 127.8, 126.3, 119.3 (for 16 CH_{arom}), 59.4 (C-2), 78.4 (C-4, C-5), 35.2 (2 CH₃) ppm. C₂₉H₂₂S₂ (434.61): calcd. C 80.14, 5.10, 14.76; found C 80.0, 5.27, 14.95.



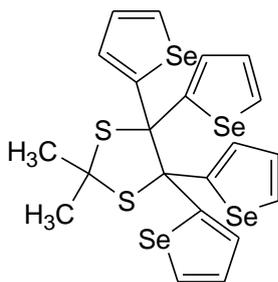
2,2-Dimethyl-3,3-di(thiophen-2-yl)thiirane (8d): Yield: 190 mg (75%). Yellow crystals; m.p. 50 – 51 °C (chromatographic purification). IR (KBr): $\nu = 3099$ (w), 2955 (w), 2917 (w), 1429 (m), 1367 (m), 1244 (m), 1231 (m), 1085 (m), 1077 (m), 849 (m), 833 (s), 783 (m), 705 (s), 560 (m) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): $\delta = 7.07$ (dd, $J = 1.2$ Hz, $J = 4.8$ Hz, 2 H_{arom}), 7.00 (dd, $J = 1.2$ Hz, $J = 3.6$ Hz, 2 H_{arom}), 6.80–6.81 (m, 2 H_{arom}), 1.64 (s, 2 CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 146.2$ (for 2 C_{arom}), 127.4, 126.5, 125.2 (for 6 CH_{arom}), 56.0, 54.8 (C-2, C-3), 26.7 (2 CH₃) ppm. MS (ESI): m/z (%) = 253 (100, [M+H]⁺). C₁₂H₁₂S₃ (252.42): calcd. C 57.10, H 4.79, S 38.11; found C 56.91, H 4.80, S 38.12.



2,2-Dimethyl-4,4,5,5-tetra(thiophen-2-yl)-1,3-dithiolane (10d): Yield: 74 mg (32%). White crystals; m.p. 150 – 151 °C (MeOH/CHCl₃). IR (KBr): ν = 3101 (w), 3085 (w), 2916 (w), 1423 (m), 1234 (m), 1226 (m), 1156 (m), 1106 (m), 1048 (m), 856 (m), 758 (m), 707 (s) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ = 7.24 (dd, J = 1.2 Hz, J = 5.4 Hz, 4 H_{arom}), 7.05 (dd, J = 1.2 Hz, J = 3.6 Hz, 4 H_{arom}), 6.86–6.87 (m, 4 H_{arom}), 1.76 (s, 2 CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 147.7 (for 4 C_{arom}), 130.3, 126.3, 125.3 (for 12 CH_{arom}), 76.1 (C-4, C-5), 57.5 (C-2), 33.1 (2 CH₃) ppm. MS (ESI): m/z (%) = 485 (100, [M+Na]⁺). C₂₁H₁₈S₆ (462.76): calcd. C 54.50, H 3.92, S 41.57; found C 54.44, H 3.76, S 41.82.

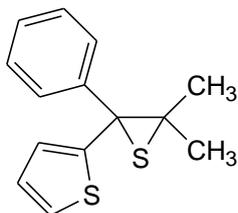


1,1-Di(selenophen-2-yl)-2-methylpropene (9e): Yield: 192 mg (61%) – After desulfurization of tiirane **8d**. Colorless oil that crystallized in the refrigerator. IR (film): ν = 3054 (m), 2926 (m), 2905 (m), 2850 (w), 1448 (m), 1368 (w), 1267 (w), 1225 (m), 1168 (w), 1078 (w), 1000 (w), 829 (w), 783 (w), 681 (s) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ = 7.98 (d, J = 6.0 Hz, 2 H_{arom}), 7.22–7.23 (m, 2 H_{arom}), 7.05 (d, J = 3.6 Hz, 2 H_{arom}), 1.98 (s, 2 CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 151.8, 135.6 (C_{arom}, C_{arom}-C=), 130.7, 129.0, 128.6 (for 6 CH_{arom}), 127.3 (C=C(CH₃)₂) 23.5 (2 CH₃) ppm. MS (ESI): m/z (%) = 315 (100, [M+H]⁺). C₁₂H₁₂Se₂ (314.14): calcd. C 45.88, H 3.85; found C 46.14, H 3.70.

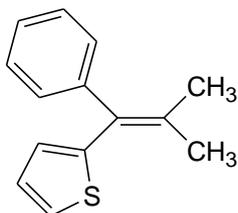


2,2-Dimethyl-4,4,5,5-tetra(selenophen-2-yl)-1,3-dithiolane (10e): Yield: 56 mg (17%). White crystals; m.p. 123 – 124 °C (MeOH/CHCl₃). IR (KBr): ν = 2952 (w), 2917 (w), 1434 (m), 1362 (w), 1230 (s), 1154 (m), 1103 (m), 1025 (m), 797 (m), 688 (s) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ = 7.96 (dd, J = 1.2 Hz, J = 6.0 Hz, 4 H_{arom}), 7.39 (dd, J = 1.2 Hz, J = 4.2 Hz, 4 H_{arom}), 7.11–7.13 (m, 4 H_{arom}), 1.77 (s, 2 CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 154.8 (for 4 C_{arom}), 133.3, 133.2, 127.9 (for 12 CH_{arom}), 79.8

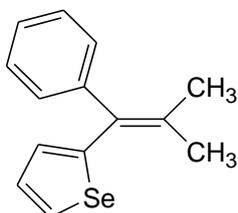
(C-4, C-5), 58.1 (C-2), 33.2 (2 CH₃) ppm. C₂₁H₁₈S₂Se₄ (650.34): calcd. C 38.78, H 2.79, S 9.86; found C 38.56, H 2.93, S 9.78.



2,2-Dimethyl-3-phenyl-3-(thiophen-2-yl)thiirane (8f): Yield: 42 mg (17%). White crystals; m.p. 44 – 45 °C (chromatographic purification). IR (KBr): $\nu = 2997$ (w), 2919 (w), 1491 (w), 1443 (m), 1369 (w), 1228 (m), 1075 (m), 753 (m), 702 (s) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): $\delta = 7.55\text{--}7.56$ (m, 2 H_{arom}), 7.32–7.35 (m, 2 H_{arom}), 7.27–7.28 (m, 1 H_{arom}), 7.14 (dd, $J = 1.2$ Hz, $J = 5.4$ Hz, 1 H_{arom}), 7.02 (dd, $J = 1.2$ Hz, $J = 3.6$ Hz, 1 H_{arom}), 6.87 (dd, $J = 3.6$ Hz, $J = 4.8$ Hz, 1 H_{arom}), 1.68 (s, CH₃), 1.53 (s, CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 147.3$, 141.7 (2 C_{arom}), 129.5, 127.9, 127.3, 127.2, 126.5, 125.3 (for 8 CH_{arom}), 61.5, 54.4, (C-2, C-3), 26.3 (CH₃), 28.3 (CH₃) ppm. MS (ESI): m/z (%) = 247 (100, [M+H]⁺). C₁₄H₁₄S₂ (246.39): calcd. C 68.25, H 5.73, S 26.03; found C 68.37, H 5.56, S 26.23.

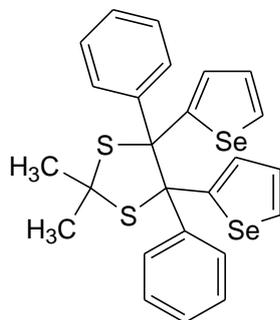


1-Phenyl-1-(thiophen-2-yl)-2-methylpropene (9f) [S2]: Yield 15 mg (7%). Pale yellow oil (lit. [S2]: colorless liquid). ¹H NMR (600 MHz, CDCl₃): $\delta = 7.21\text{--}7.36$ (m, 6 H_{arom}), 6.97–6.98 (m, 1 H_{arom}), 6.79–6.80 (m, 1 H_{arom}), 2.06 (s, CH₃), 1.79 (s, CH₃) ppm.

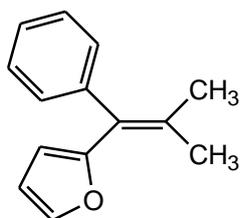


1-Phenyl-1-(selenophen-2-yl)-2-methylpropene (9c): Yield 148 mg (57%) – After desulfurization of thiirane **8f**. Yellow oil. IR (film): $\nu = 3055$ (m), 2907 (m), 2853 (m), 1598 (w), 1491 (m), 1442 (s), 1369 (m), 1218 (m), 1019 (m), 757 (m), 700 (s), 685 (s) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): $\delta = 7.91$ (dd, $J = 1.2$ Hz, $J = 6.0$ Hz, 1 H_{arom}), 7.21–7.36 (m, 6 H_{arom}), 6.97 (dd, $J = 1.2$ Hz, $J = 3.6$ Hz, 1 H_{arom}), 2.06 (s, CH₃), 1.77 (s, CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 151.9$, 143.7, 132.7, 132.5 (2 C_{arom},

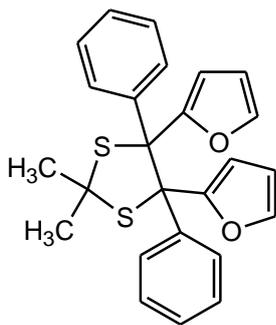
$C_{\text{arom}}-C=C(\text{CH}_3)_2$, 130.3, 129.4, 129.0, 128.6, 128.0, 126.5 (for 8 CH_{arom}), 23.5 (CH_3), 22.8 (CH_3) ppm. MS (ESI): m/z (%) = 263 (100, $[M+2H]^+$), 261 (40, $[M]^+$). $\text{C}_{14}\text{H}_{14}\text{Se}$ (261.22): calcd. C 64.37, H 5.40; found C 64.41, H 5.61.



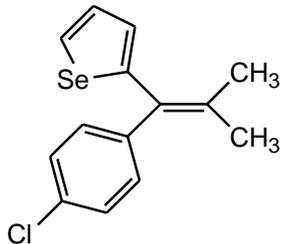
2,2-Dimethyl-4,5-diphenyl-4,5-di(selenophen-2-yl)-1,3-dithiolane (10c): Isolated as a mixture of *cis*, *trans*-isomers (crude product ratio 72 : 28). Yield: 30 mg (11%). White crystals; m.p. 137 – 138 °C (MeOH/ CHCl_3). IR (KBr): ν = 3057 (w), 2922 (w), 2853 (w), 1596 (w), 1490 (m), 1444 (s), 1364 (m), 1232 (m), 1181 (m), 1155 (m), 1033 (m), 931 (m), 692 (s) cm^{-1} . ^1H NMR (600 MHz, CDCl_3): δ = 7.93–7.24 (m, 32 H_{arom}), 1.87 (s, CH_3 *cis*), 1.74 (s, 2 CH_3 *trans*), 1.36 (s, CH_3 *cis*) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 144.6 br., 143.2 br. (for 8 C_{arom}), 133.1, 132.9, 132.8, 131.6, 131.2, 130.8, 128.0, 127.9, 127.6, 127.1, 127.0, 126.7 (for 32 CH_{arom}), 80.5, 80.0 (C-4 + C-5, for *cis* and *trans*), 55.6, 55.3 (C-2, *cis* and *trans*), 33.2 (2 CH_3 *trans*), 33.0 (CH_3 *cis*), 32.7 (CH_3 *cis*) ppm. $\text{C}_{25}\text{H}_{22}\text{S}_2\text{Se}_2$ (544.49): calcd. C 55.15, H 4.07, S 11.78; found C 55.32, H 4.26, S 11.63.



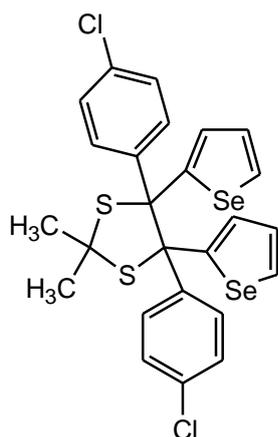
1-Phenyl-1-(furan-2-yl)-2-methylpropene (9g) [S2b]: Yield 79 mg (40%) – After desulfurization of tiirane **8g**. Pale yellow oil (lit. [S2b]: a liquid isolated by distillation under reduced pressure). ^1H NMR (600 MHz, CDCl_3): δ = 7.29–7.39 (m, 4 H_{arom}), 7.20–7.21 (m, 2 H_{arom}), 6.37–6.38 (m, 1 H_{arom}), 5.96 (d, J = 3.0 Hz, 1 H_{arom}), 2.17 (s, CH_3), 1.75 (s, CH_3) ppm. ^{13}C NMR (150 MHz, CDCl_3): δ = 155.5, 141.2, 133.3, 127.3 (2 C_{arom} , $\text{C}_{\text{arom}}\text{C}=\text{C}(\text{CH}_3)_2$), 140.9, 129.9, 128.0, 126.6, 110.4, 109.4 (for 8 CH_{arom}), 23.3 (CH_3), 22.4 (CH_3) ppm.



2,2-Dimethyl-4,5-diphenyl-4,5-di(furan-2-yl)-1,3-dithiolane (10g): Isolated as a mixture of *cis,trans*-isomers (crude product ratio 58:42). Yield: 59 mg (28%). White crystals; m.p. 144 – 145 °C (MeOH/CHCl₃). IR (KBr): $\nu = 3110$ (w), 3058 (w), 2921 (m), 2855 (w), 1598 (w), 1490 (s), 1445 (s), 1149 (s), 1037 (m), 1017 (s), 932 (m), 795 (m), 750 (s), 718 (s), 696 (s), 595 (m) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): $\delta = 7.37\text{--}5.94$ (m, 32 CH_{arom}) 1.99 (s, CH₃ *cis*), 1.72 (s, 2 CH₃ *trans*), 1.53 (s, CH₃ *cis*) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 155.0, 154.9, 140.0, 139.9$ (for 8 C_{arom}), 141.0, 140.6, 130.5, 129.8, 127.6, 127.3, 127.2, 126.5, 112.9, 110.9, 110.3, 110.1 (for 32 CH_{arom}), 76.1, 76.0 (C-4 + C-5, for *cis* and *trans*), 55.8, 54.9 (C-2, *cis* and *trans*), 34.8 (CH₃ *cis*), 33.7 (2 CH₃ *trans*), 32.3 (CH₃ *cis*) ppm. C₂₅H₂₂O₂S₂ (418.57): calcd. C 71.74, H 5.30, S 15.32; found C 71.87, H 5.28, S 15.54.

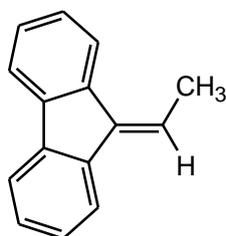


1-(4-Chlorophenyl)-1-(selenophen-2-yl)-2-methylpropene (9h): Yield: 168 mg (65%) – After desulfurization of tiirane **8h**. Yellow oil. IR (film): $\nu = 3056$ (w), 2908 (m), 2852 (m), 1901 (w), 1590 (w), 1488 (s), 1448 (m), 1229 (m), 1218 (m), 1091 (s), 1014 (s), 855 (m), 833 (m), 817 (s), 776 (s), 685 (s) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): $\delta = 7.95\text{--}7.96$ (m, 1 H_{arom}), 7.16–7.33 (m, 5 H_{arom}), 6.96–6.97 (m, 1 H_{arom}), 2.05 (s, CH₃), 1.77 (s, CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 151.3, 142.0, 133.5, 132.4, 131.1$ (3 C_{arom}, C_{arom}C=C(CH₃)₂), 130.9, 130.6, 129.1, 128.9, 128.3 (for 7 CH_{arom}), 22.8 (CH₃), 22.3 (CH₃) ppm. C₁₄H₁₃ClSe (259.67): calcd. C 56.87, H 4.43; found C 56.96, H 4.55.

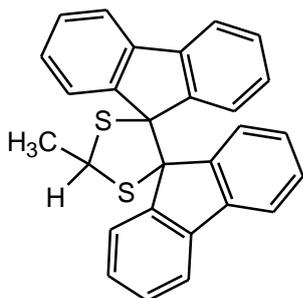


2,2-Dimethyl-4,5-di(4-chlorophenyl)-4,5-di(selenophen-2-yl)-1,3-dithiolane (10h):

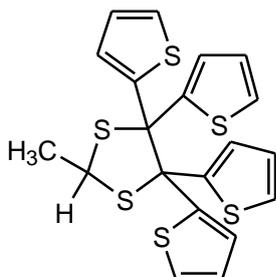
Isolated as a mixture of *cis,trans*-isomers (crude product ratio 70:30). Yield: 53 mg (17%). White crystals; m.p. 86 – 87 °C (MeOH/CHCl₃). IR (KBr): $\nu = 2919$ (w), 2851 (w), 1587 (w), 1489 (s), 1230 (m), 1095 (s), 1012 (s), 785 (m), 688 (s) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): $\delta = 7.94\text{--}6.98$ (m, 28 H_{arom}), 1.85 (s, CH₃ *cis*), 1.72 (s, 2 CH₃ *trans*), 1.44 (s, CH₃ *cis*) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 157.3, 156.6, 142.6, 141.9$ (for 8 C_{arom}), 133.6, 133.2, 133.1, 132.9, 132.8, 132.5, 132.3, 132.1, 128.0, 127.1, 126.9 (for 32 CH_{arom}), 79.7, 79.4 (C-4 + C-5, for *cis* and *trans*), 56.0, 55.9 (C-2, *cis* and *trans*), 33.1 (CH₃ *cis*), 33.0 (2 CH₃ *trans*), 32.7 (CH₃ *cis*) ppm. C₂₅H₂₀Cl₂S₂Se₂ (613.38): calcd. C 48.95, H 3.29, S 10.45; found C 48.73, H 3.50, S 10.48.



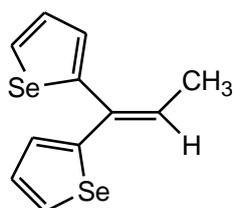
9-Ethylidene fluorene (9j) [S3]: Yield: 6 mg (6%). Pale yellow crystals; m.p. 97 – 98 °C (isolated by PLC). (Lit. [S3a], m.p. 76.5 – 78.0); lit. [S3b], m. p. 103 – 104 °C). ¹H NMR (600 MHz, CDCl₃): $\delta = 7.92$ (d, $J = 7.2$ Hz, 1 H_{arom}), 7.79 (d, $J = 7.2$ Hz, 1 H_{arom}), 7.73 (d, $J = 7.2$ Hz, 1 H_{arom}), 7.68 (d, $J = 7.2$ Hz, 1 H_{arom}), 7.30–7.40 (m, 4 H_{arom}), 6.89 (q, $J = 7.2$ Hz, =CH), 2.43 (d, $J = 7.2$ Hz, CH₃) ppm.



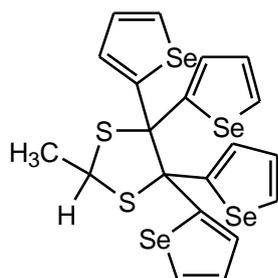
2'-Methyldispiro[9H-fluorene-9,4'-(1,3)dithiolane-5'9''-[9H]fluorene] (**10j**): Yield: 65 mg (61%). White crystals; m.p. 251 – 252 °C (MeOH/CHCl₃). IR (KBr): ν = 3052 (w), 3028 (w), 1474 (w), 1445 (m), 1279 (w), 1157 (w), 1033 (w), 739 (s) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ = 7.55–7.28 (m, 8 H_{arom}), 7.16–7.11 (m, 4 H_{arom}), 7.00 (s br., 4 H_{arom}), 5.51 (q, J = 6.0 Hz, =CH) 2.00 (d, J = 6.0 Hz, CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 140.2, 140.0 (for 8 C_{arom}), 128.5, 128.4, 127.2, 126.6, 126.5, 126.4, 119.4, 119.1 (for 16 CH_{arom}), 76.1 (C-4, C-5), 46.8 (C-2), 22.2 (CH₃) ppm. C₂₈H₂₀S₂ (420.59): calcd. C 79.96, 4.79, 15.25; found C 79.73, H 4.77, S 15.15.



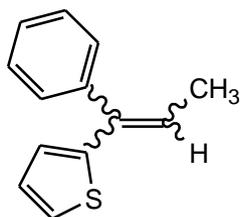
2-Methyl-4,4,5,5-tetra(thiophen-2-yl)-1,3-dithiolane (**10k**): Yield: 160 mg (72%). Yellow crystals; m.p. 155 – 156 °C (MeOH/CHCl₃). IR (KBr): ν = 3097 (w), 3070 (w), 2918 (w), 1424 (m), 1227 (s), 1187 (w), 1045 (m), 856 (m), 753 (m), 703 (s) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ = 7.23–7.25 (m, 4 H_{arom}), 7.09–7.10 (m, 2 H_{arom}), 6.89–6.90 (m, 2 H_{arom}), 6.85–6.87 (m, 4 H_{arom}), 4.77 (q, J = 6.6 Hz, CH(CH₃)), 1.79 (d, J = 6.6 Hz, CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 146.2, 147.4 (for 4 C_{arom}), 130.3, 129.4, 126.9, 126.1, 125.8, 125.6 (for 12 CH_{arom}), 74.8 (C-4, C-5), 45.0 (C-2), 18.9 (CH₃) ppm. C₂₀H₁₆S₆ (448.73): calcd. C 53.53, H 3.59, S 42.87; found C 53.62, H 3.83, S 42.88.



1,1-Di(selenophen-2-yl)propene (9l): Yield: 10 mg (3 %). Pale yellow oil. IR (film): $\nu = 3055$ (w), 2926 (w), 1724 (w), 1444 (m), 1246 (m), 1221 (m), 1022 (w), 841 (w), 816 (m), 793 (w), 742 (w), 684 (s) cm^{-1} . ^1H NMR (600 MHz, CDCl_3): $\delta = 8.07\text{--}8.08$ (m, 1 H_{arom}), 7.79–7.80 (m, 1 H_{arom}), 7.30–7.31 (m, 1 H_{arom}), 7.14–7.17 (m, 2 H_{arom}), 7.02–7.03 (m, 1 H_{arom}), 6.24 (q, $J = 7.2$ Hz, =CH), 1.82 (d, $J = 7.2$ Hz, CH_3) ppm. ^{13}C NMR (150 MHz, CDCl_3): $\delta = 153.3, 145.9, 133.7$ (2 C_{arom} , $\text{C}_{\text{arom}}\text{-C=}$), 131.3, 129.9, 129.8, 129.1, 128.7, 127.0, 126.6 (6 CH_{arom} , =CH), 15.9 (CH_3) ppm. $\text{C}_{11}\text{H}_{10}\text{Se}_2$ (300.12): calcd. C 44.02, H 3.36; found C 44.00, H 3.66.

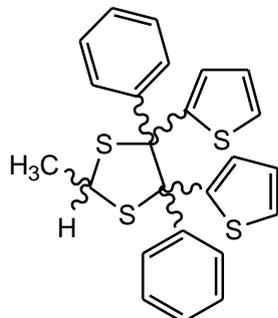


2-Methyl-4,4,5,5-tetra(selenophen-2-yl)-1,3-dithiolane (10l): Yield: 252 mg (79%). White crystals; m.p. 152 – 153 °C (MeOH/ CHCl_3). IR (KBr): $\nu = 3088$ (w), 3048 (w), 2914 (w), 1439 (m), 1375 (w), 1230 (s), 1022 (m), 829 (w), 787 (w), 682 (s) cm^{-1} . ^1H NMR (600 MHz, CDCl_3): $\delta = 7.99\text{--}8.01$ (m, 4 H_{arom}), 7.47–7.48 (m, 2 H_{arom}), 7.17–7.19 (m, 2 H_{arom}), 7.10–7.13 (m, 4 H_{arom}), 4.8 (q, $J = 6.6$ Hz, $\text{CH}(\text{CH}_3)$), 1.76 (d, $J = 6.6$ Hz, CH_3) ppm. ^{13}C NMR (150 MHz, CDCl_3): $\delta = 154.5, 152.7$ (for 4 C_{arom}), 134.1, 133.2 br., 132.3, 128.2, 128.0 (for 12 CH_{arom}), 78.4 (C-4, C-5), 45.6 (C-2), 19.1 (CH_3) ppm. $\text{C}_{20}\text{H}_{16}\text{S}_2\text{Se}_4$ (636.31): calcd. C 37.75, H 2.53, S 10.08; found C 37.67, H 2.65, S 10.23.

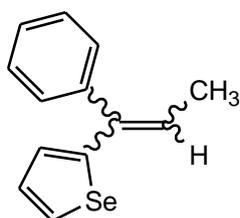


1-Phenyl-1-(thiophen-2-yl)propene (9m): Isolated as a mixture of (*E/Z*)-isomers (53:47). Yield: 96 mg (48%) – After desulfurization of tiirane **8m**. Yellow oil. IR (film): $\nu = 3062$ (w), 2931 (w), 1716 (m), 1682 (m), 1635 (s), 1599 (m), 1578 (m), 1515 (m), 1447 (m), 1413 (s), 1354 (m), 1288 (s), 1232 (m), 1053 (m), 843 (m), 717 (s), 700 (s), 649 (m) cm^{-1} . ^1H NMR (600 MHz, CDCl_3): $\delta = 6.48\text{--}7.32$ (m, 16 H_{arom}), 6.17 (q, $J = 7.2$ Hz, =CH), 6.02 (q, $J = 7.2$ Hz, =CH), 1.86 (d, $J = 7.2$ Hz, CH_3), 1.60 (d, $J = 7.2$

Hz, CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 147.4, 143.2, 141.6, 139.1, 136.7, 135.8 (4 C_{arom}, 2 C_{arom}-C=), 129.7, 128.2, 128.0, 127.8, 127.5, 127.3, 127.1, 126.8, 126.6, 125.4, 124.6, 123.4, 123.1 (for 16 CH_{arom}, 2 (=CH)), 16.0 (CH₃), 15.2 (CH₃). C₁₃H₁₂S (200.30): calcd. C 77.95, H 6.04, S 16.01; found C 78.0, H 5.79, S 16.29.

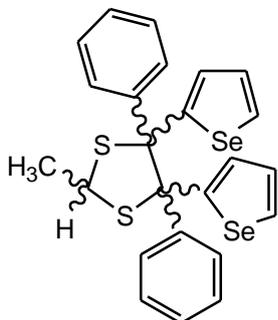


2-Methyl-4,5-diphenyl-4,5-di(thiophen-2-yl)-1,3-dithiolane (10m): Isolated as a mixture of two *cis,trans*-isomers in a ratio of 56:44 (from three isomers possible). Yield: 58 mg (27%). Yellow crystals; m.p. 137 – 139 °C (MeOH/CHCl₃). IR (KBr): ν = 3055 (w), 2922 (w), 1597 (w), 1488 (s), 1443 (s), 1371 (w), 1233 (w), 1187 (m), 1052 (m), 1034 (m), 850 (w), 695 (s) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ = 6.48–7.54 (m, 32 H_{arom}), 4.38 (q, *J* = 6.6 Hz, CH(CH₃)), 4.09 (q, *J* = 6.6 Hz, CH(CH₃)), 1.68 (d, *J* = 6.6 Hz, CH₃), 1.61 (d, *J* = 6.6 Hz, CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 151.1, 149.8, 148.7, 143.4, 143.3, 141.3 (for 8 C_{arom}), 131.2, 130.8, 130.6, 130.4, 130.3, 130.2, 127.7, 127.3, 127.2, 126.8, 126.7, 126.4, 126.2, 126.1, 125.5, 125.4, 125.3, 124.9 (for 32 CH_{arom}), 77.7, 77.6, 76.4, 76.9 (2 C-4, 2 C-5), 43.3, 43.1 (2 C-2), 17.8 (CH₃), 18.7 (CH₃) ppm. C₂₄H₂₀S₄ (436.68): calcd. C 66.01, H 4.62, S 29.37; found C 66.00, H 4.71, S 29.27.

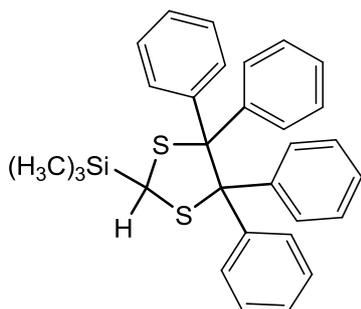


1-Phenyl-1-(selenophen-2-yl)propene (9n): Isolated as a mixture of (*E/Z*)-isomers (73:27). Yield: 176 mg (71%) – After desulfurization of tiirane **8n**. Red oil. IR (film): ν = 3055 (w), 3020 (w), 2928 (w), 2909 (w), 2852 (w), 1491 (m), 1441 (m), 1220 (m), 819 (m), 787 (m), 702 (s), 685 (s). ¹H NMR (600 MHz, CDCl₃): δ = 6.70–8.04 (m, 16 H_{arom}), 6.17 (q, *J* = 7.2 Hz, =CH), 6.09 (q, *J* = 7.2 Hz, =CH), 1.93 (d, *J* = 7.2 Hz, CH₃), 1.65 (d, *J* = 7.2 Hz, CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): δ = 153.7, 147.8, 143.4,

139.2, 138.8, 137.9 (4 C_{arom}, 2 C_{arom}C=), 131.1, 130.0, 129.9, 129.6, 129.1, 128.2, 128.1, 128.0, 127.6, 127.2, 127.1, 126.0, 124.2 (for 16 CH_{arom}, 2 =CH), 16.0 (CH₃), 15.4 (CH₃). C₁₃H₁₂Se (247.19): calcd. C 63.16, H 4.89; fund C 62.98, 4.84.

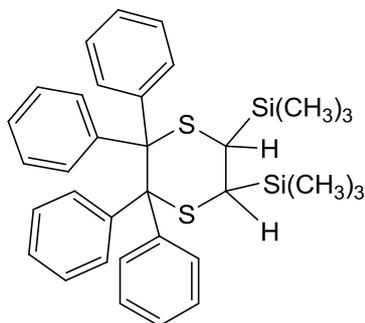


2-Methyl-4,5-diphenyl-4,5-di(selenophen-2-yl)-1,3-dithiolane (10n): Isolated as a mixture of two *cis/trans*-isomers in a ratio of 52:48 (from three isomers possible). Yield: 74 mg (28%). Yellow crystals: m.p. 144 – 146 °C (MeOH/CHCl₃). IR (KBr): $\nu = 3053$ (w), 2922 (w), 1596 (w), 1486 (s), 1441 (s), 1371 (m), 1232 (s), 1185 (m), 1032 (m), 685 (s) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): δ 6.63–7.92 (m, 32 H_{arom}), 4.54 (q, *J* = 6.6 Hz, CH(CH₃)), 4.12 (q, *J* = 6.6 Hz, CH(CH₃)), 1.78 (d, *J* = 6.6 Hz, CH₃), 1.68 (d, *J* = 6.6 Hz, CH₃) ppm. ¹³C NMR (150 MHz, CDCl₃): $\delta = 160.2, 157.9, 156.2, 143.7, 143.4, 140.9$ (for 8 C_{arom}), 133.2, 132.7, 132.6, 132.5, 132.4, 131.6, 131.0, 130.6, 130.3, 128.2, 128.0, 127.8, 127.6, 127.5, 127.3, 126.9, 126.8, 126.7 (for 32 CH_{arom}), 79.3, 79.2, 78.7, 78.1 (2 C-4, 2 C-5), 43.4, 43.3 (2 C-2), 18.6 (CH₃), 17.7 (CH₃) ppm. C₂₄H₂₀S₂Se₂ (530.47): calcd. C 54.34, H 3.80, S 12.09; found C 54.39, H 3.77, 12.19.

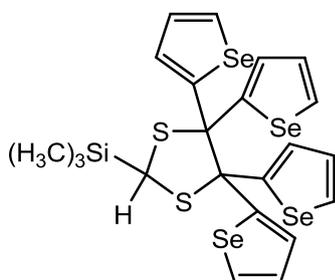


4,4,5,5-Tetraphenyl-2-trimethylsilyl-1,3-dithiolane (10o): Yield: 79 mg (33%). Colorless crystals: m.p. 87 – 88 °C (CH₃OH/CH₂Cl₂). IR (KBr): $\nu = 3054$ (w), 2952 (w), 2842 (w), 1603 (w), 1494 (m), 1437 (m), 1246 (m), 864 (s), 835 (s), 722 (s), 694 (s) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): 6.94–7.64 (m, 20 H_{arom}), 3.36 (s, ((CH₃)₃Si)HC), 0.34 (s, (CH₃)₃Si) ppm. ¹³C NMR (150 MHz, CDCl₃): 142.5 (for 4 C_{arom}), 131.7 br., 131.3 br., 129.2, 128.1, 127.8, 126.4 br., 126.1 br. (for 20 CH_{arom}), 79.5 (C-4,C-5),

33.4 (C-2), -1.55 ((CH₃)₃Si) ppm. HR-EI-MS: 482.155825 (calcd. 482.154830 for C₃₀H₃₀S₂Si [M]⁺).



2,2,3,3-Tetraphenyl-5,6-bis(trimethylsilyl)-1,4-dithiane (4c) (in analogy to **4d** tentatively described as a *trans*-isomer): Yield: 65 mg (22%). Colorless crystals: m.p. 185 – 186 °C (CH₃OH/CH₂Cl₂). IR (KBr): $\nu = 3058$ (w), 2941 (w), 2860 (w), 1487 (m), 1434 (m), 1250 (s), 1108 (w), 857 (s), 718 (s), 694 (s) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): 7.56–7.57 (m, 4 H_{arom}), 7.32–7.33 (m, 4 H_{arom}), 7.03–7.17 (m, 12 H_{arom}), 2.97 (s, (2 (CH₃)₃Si)HC), 0.14 (s, 2 (CH₃)₃Si) ppm. ¹³C NMR (150 MHz, CDCl₃): 146.7, 145.2 (for 4 C_{arom}), 135.0, 132.0, 126.5, 126.2, 125.8, 124.9 (for 20 CH_{arom}), 63.9 (C-5, C-6), 36.3 (2 CHSi), 0.17 (2 (CH₃)₃Si) ppm. C₃₄H₄₀S₂Si (568.98): calcd. C 71.77, H 7.09, S 11.27; found C 71.77, H 7.13, S 11.38.ESI-MS (MeOH): 591(100, [M+Na]).



4,4,5,5-Tetra(selenophen-2-yl)-2-trimethylsilyl-1,3-dithiolane (10s): Yield: 265 mg (76%). Yellow crystals: m.p. 140 – 142 °C (hexane/CH₂Cl₂). IR (KBr): $\nu = 2949$ (w), 1439 (m), 1251 (s), 1225 (s), 1156 (w), 1120 (m), 1104 (w), 844 (s), 805 (m), 694 (s) cm⁻¹. ¹H NMR (600 MHz, CDCl₃): 7.09–7.10 (m, 2 H_{arom}), 7.14–7.16 (m, 2 H_{arom}), 7.19–7.20 (m, 2 H_{arom}), 7.51–7.52 (m, 2 H_{arom}), 7.93–7.93 (m, 4 H_{arom}), 4.02 (s, ((CH₃)₃Si)HC), 0.31 (s, (CH₃)₃Si) ppm. ¹³C NMR (150 MHz, CDCl₃): 156.0, 153.3 (for 4 arom. C), 133.8, 132.8, 132.2, 131.9, 128.3, 128.1 (for 12 CH_{arom}), 78.2 (C-4, C-5), 37.4 (C-2), -1.46 ((CH₃)₃Si) ppm. C₂₂H₂₂S₂Se₄Si (694.47): calcd. C 38.05, H 3.19, S 9.23; found C 38.08, H 3.21, 9.55.

References

[S1] Rabinovitz, M.; Agranat, I.; Bergmann, E. D., *J. Chem. Soc.*, **1967**, 1281–1284. doi: 10.1039/J29670001281.

[S2] a) Ganapathy, D.; Sekar G.; *Org. Lett.* **2014**, *16*, 3856–3859, doi: 10.1021/ol5017367 b) Cantrell, T. S.; *J. Org. Chem.*, **1974**, *3*, 2242–2246. doi: 10.1021/jo00929a024.

[S3] a) Bell, T. W.; Catalano, V. J.; Drew, M. G. B.; Phillips, D. J.; *Chem. Eur. J.*, **2002**, *8*, 5001–5006, doi: 10.1002/1521-3765. b) Boyce, R.; Hayes, B. A.; Murphy, W. S., *J. Chem. Soc. Perkin Trans. 1*, **1975**, 531–534. doi: 10.1039/P19750000531.

2. Collection of the ^1H - and ^{13}C -NMR for the described compounds **8**, **9**, and **10**

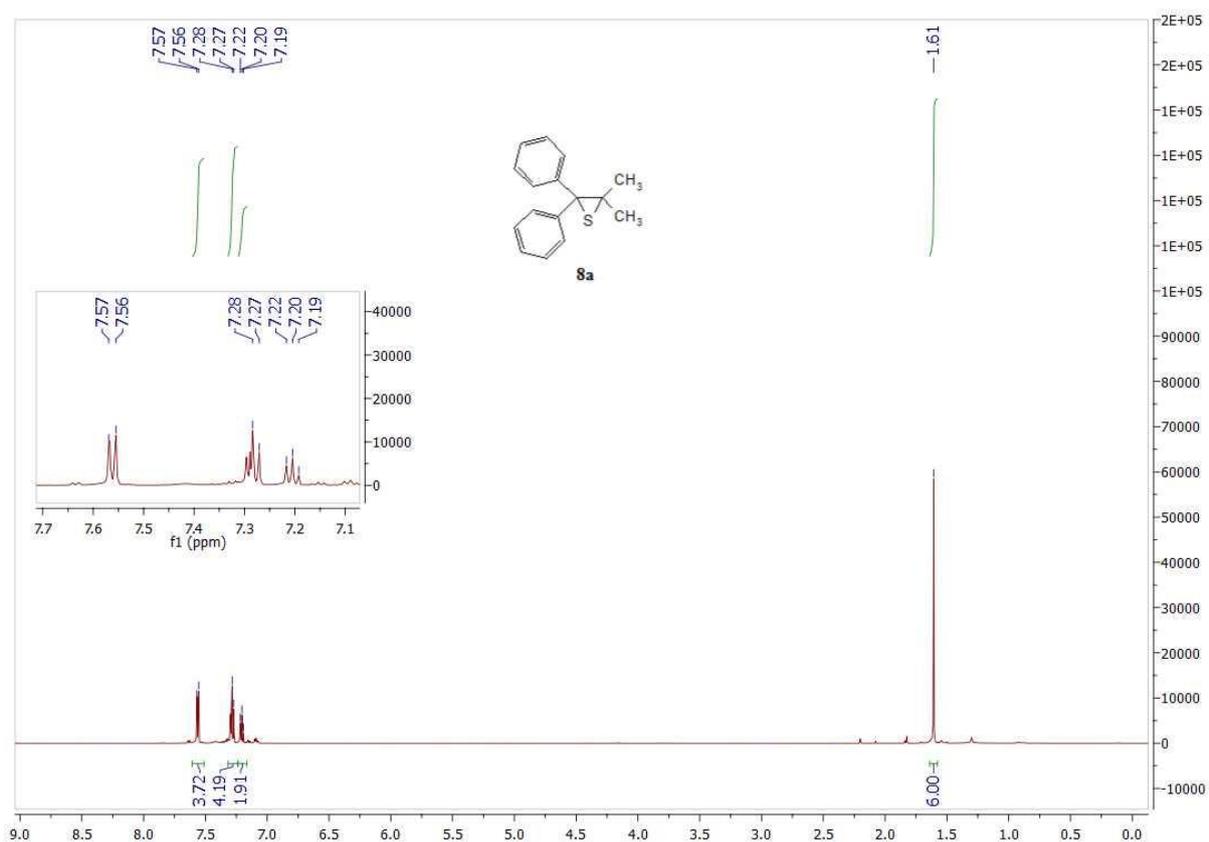


Figure S1: The ^1H NMR spectrum of compound **8a**.

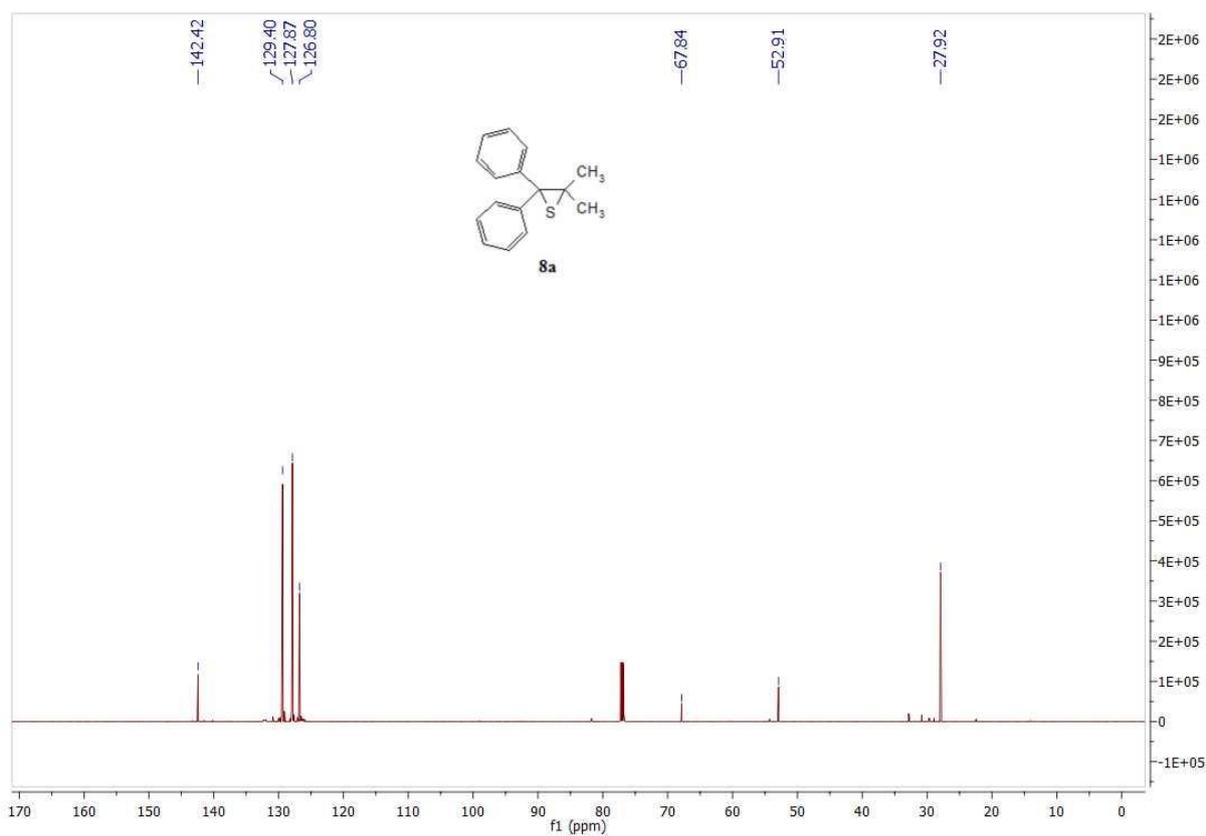


Figure S2: The ^{13}C NMR spectrum of compound **8a**.

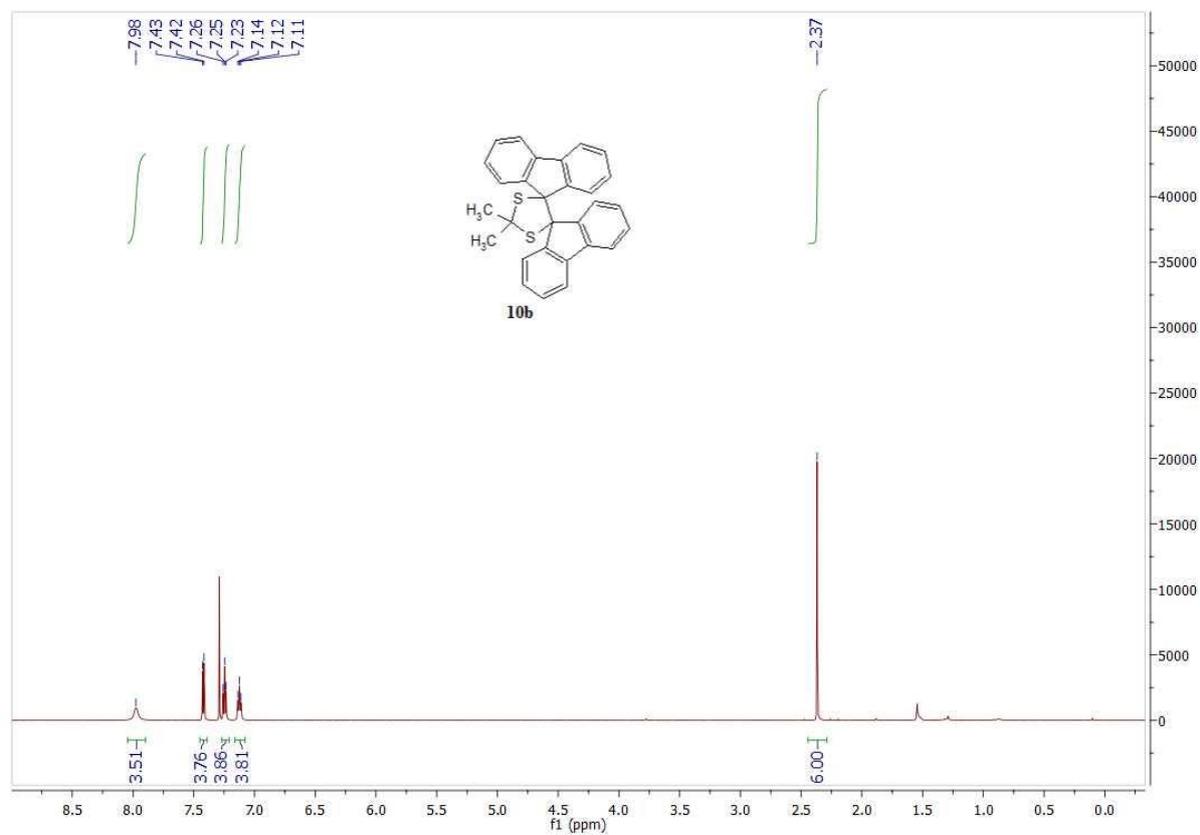


Figure S3: The ^1H NMR spectrum of compound **10b**.

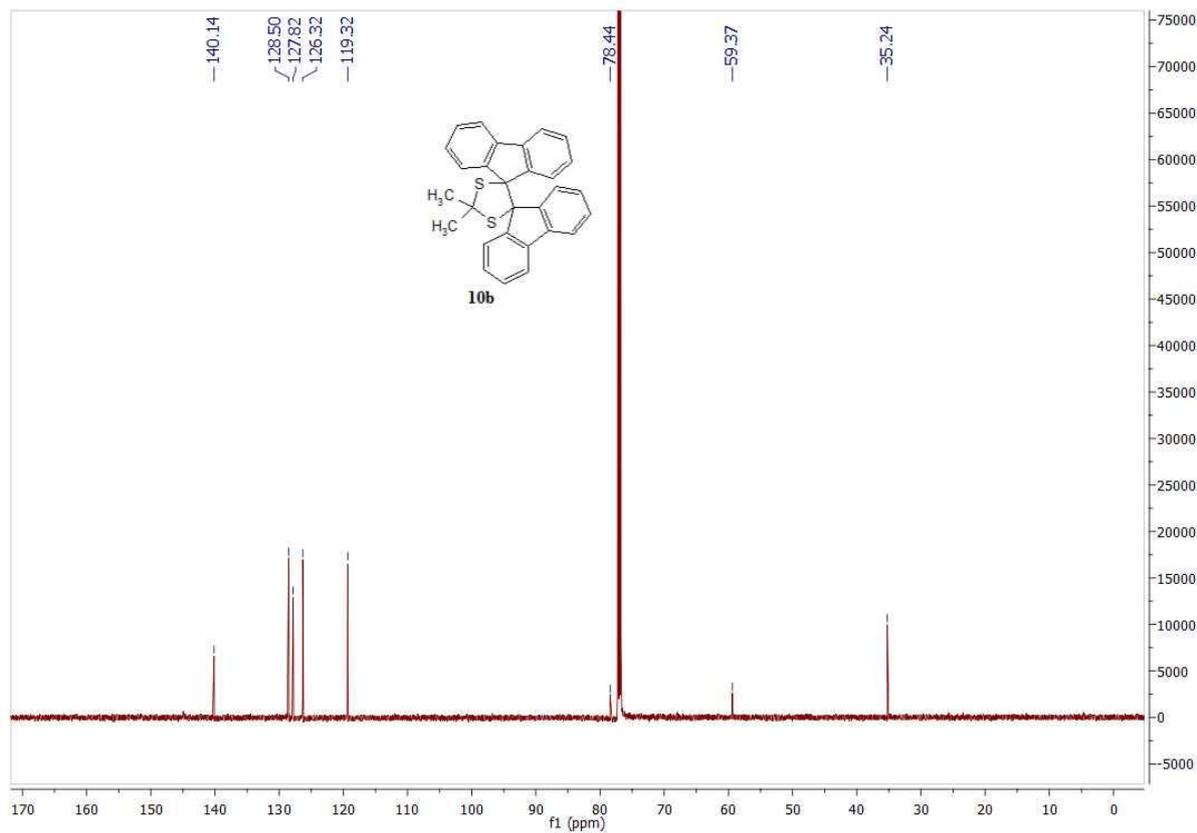


Figure S4: The ^{13}C NMR spectrum of compound **10b**.

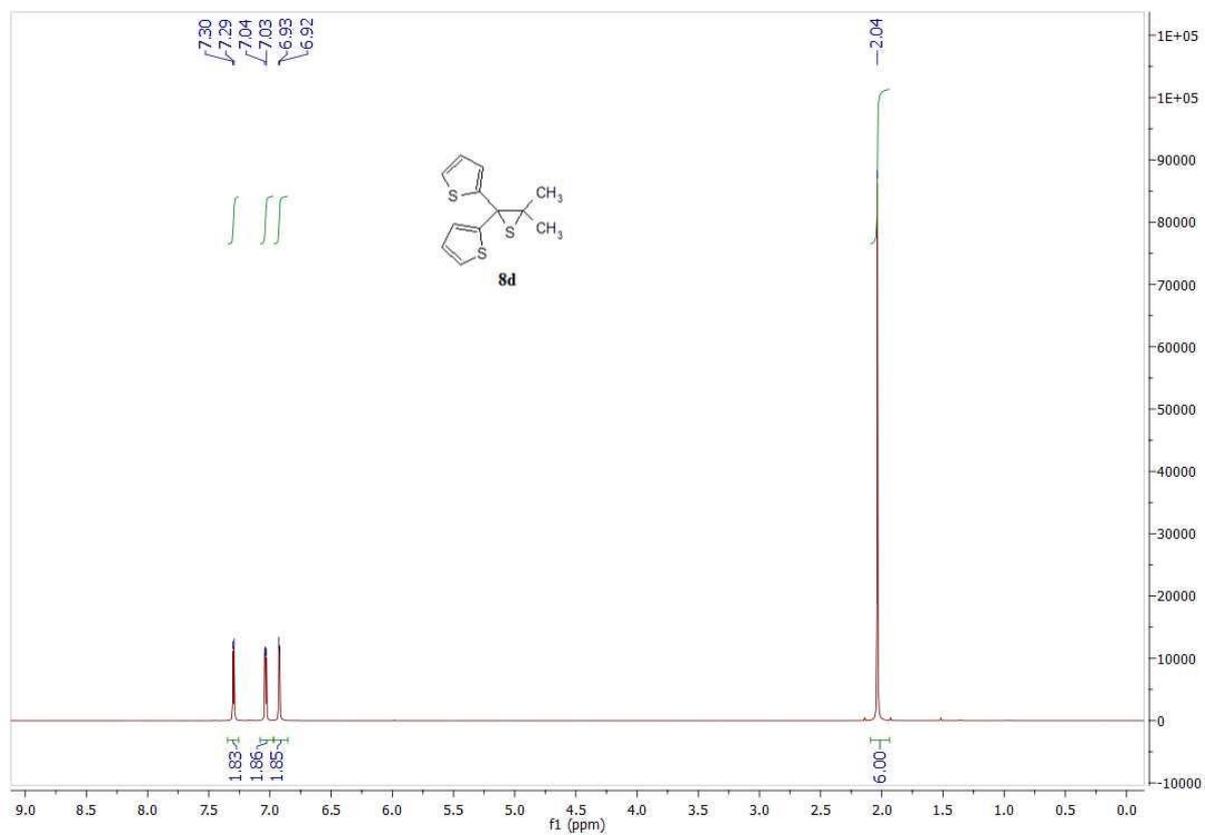


Figure S5: The ^1H NMR spectrum of compound **8d**.

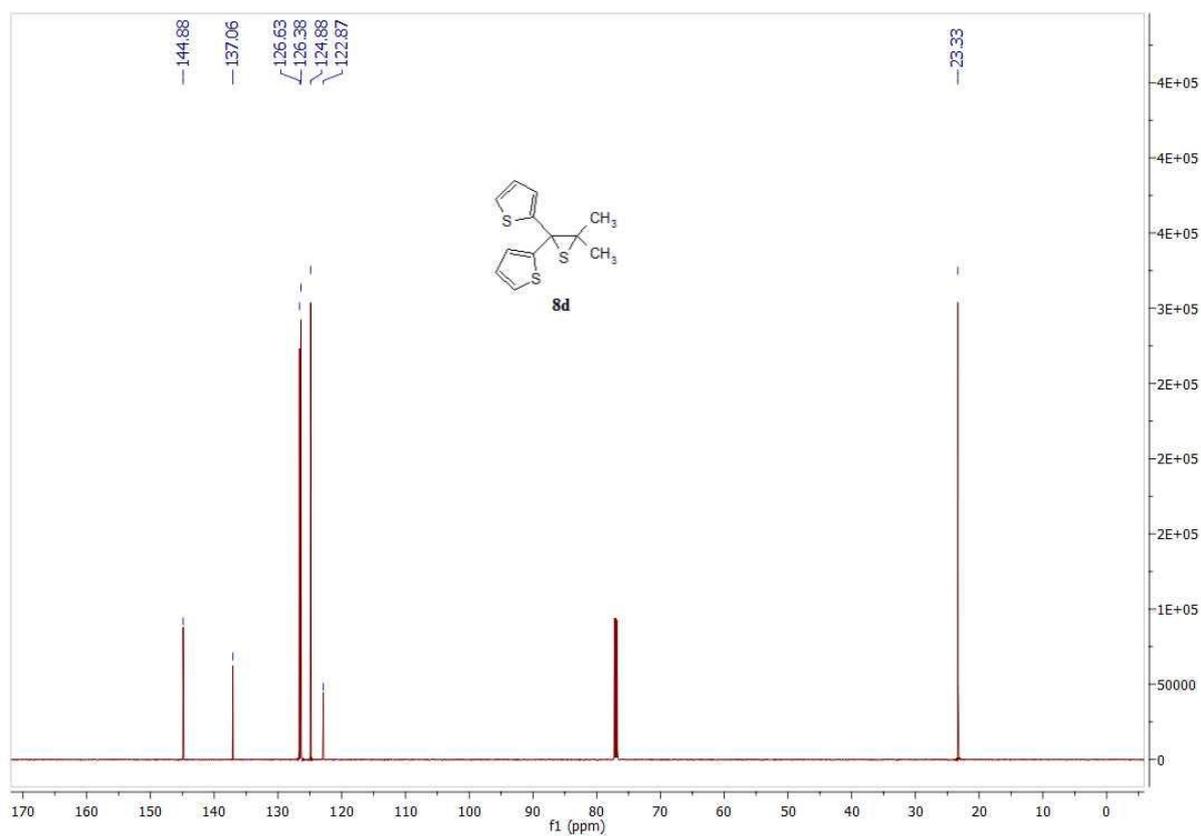


Figure S6: The ^{13}C NMR spectrum of compound **8d**.

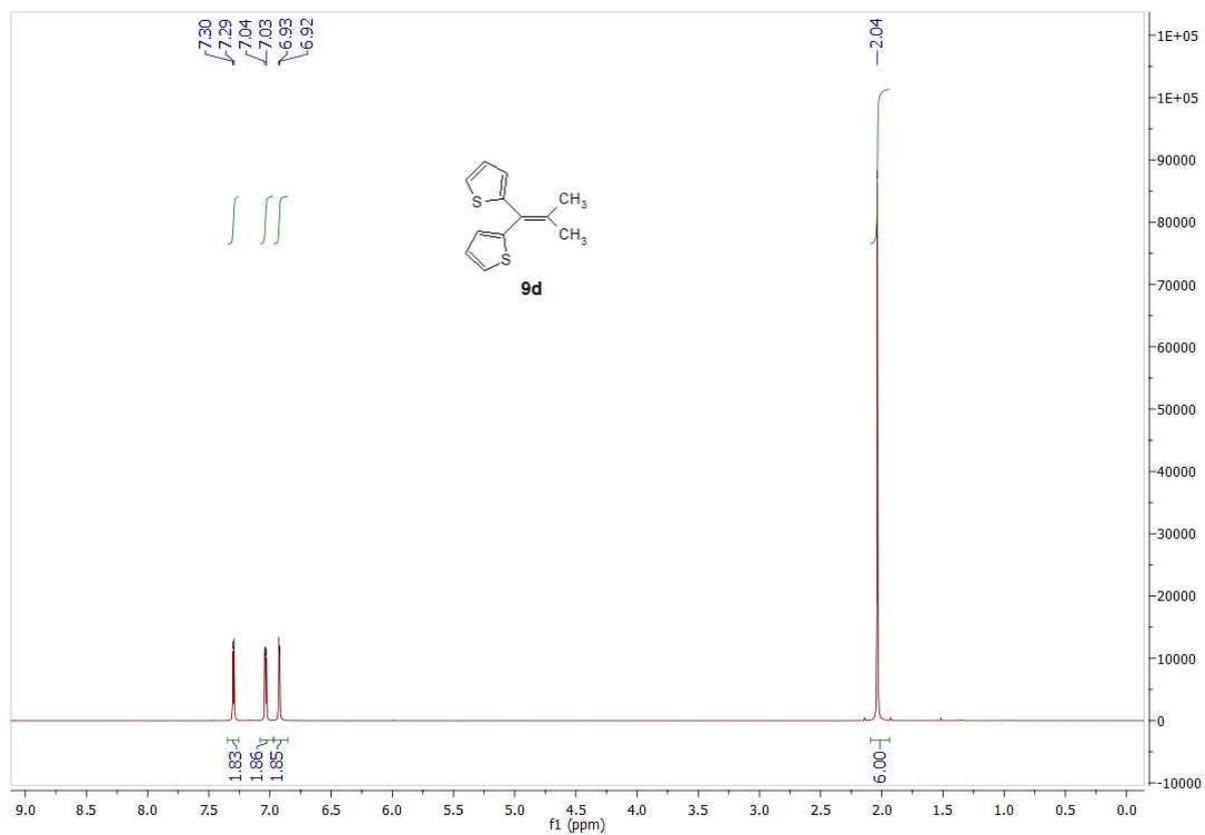


Figure S7: The ^1H NMR spectrum of compound **9d**.

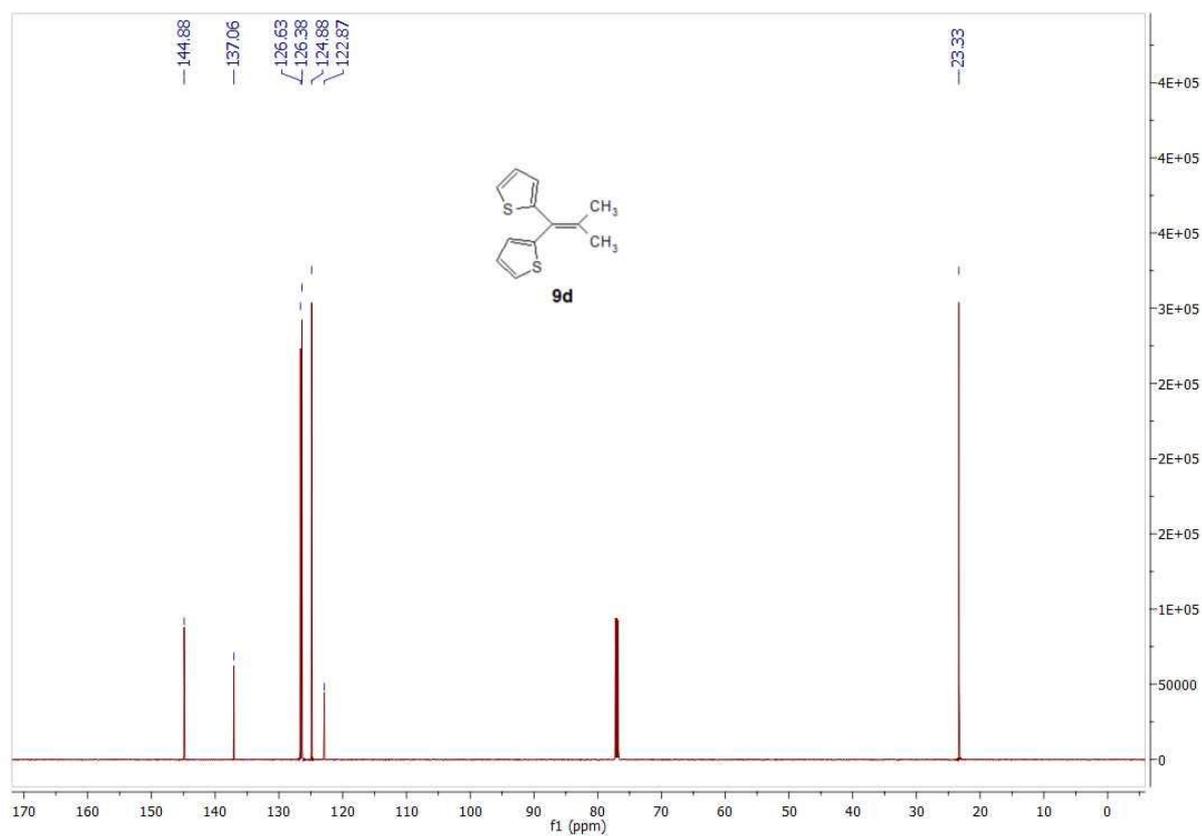


Figure S8: The ^{13}C NMR spectrum of compound **9d**.

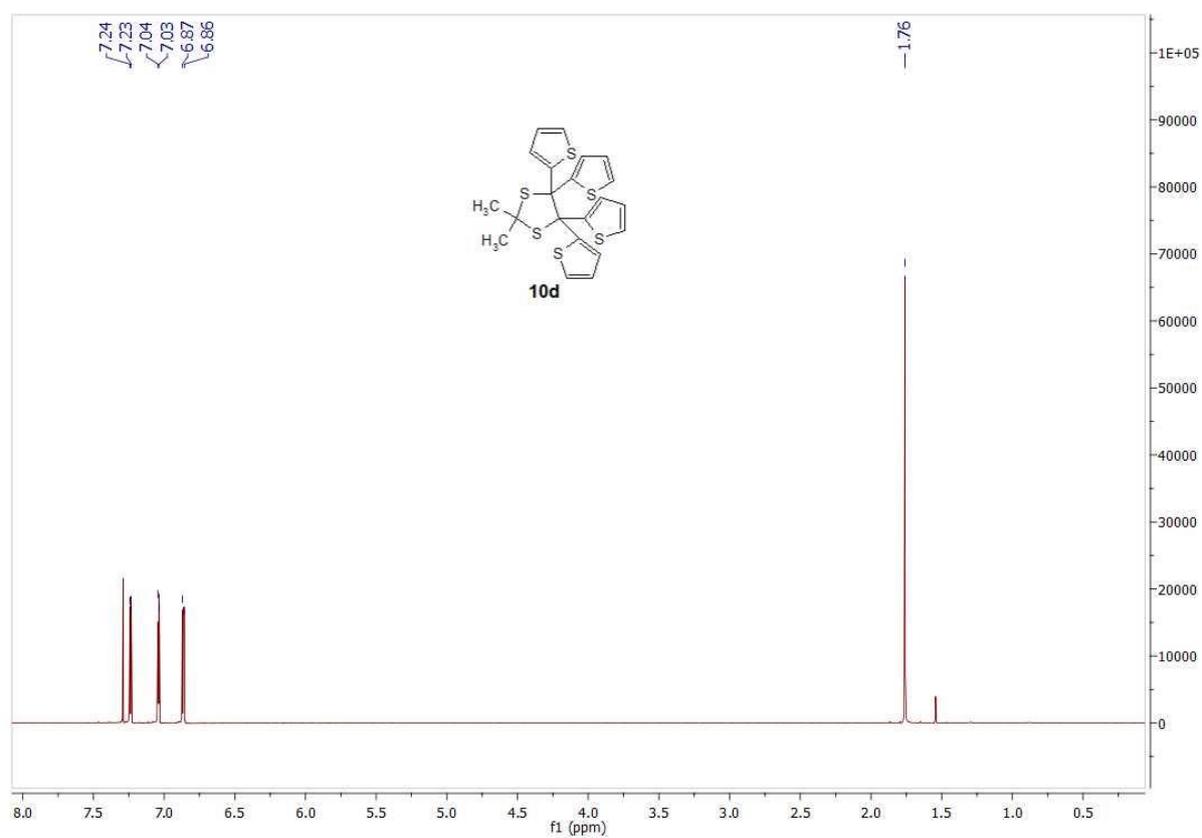


Figure S9: The ^1H NMR spectrum of compound **10d**.

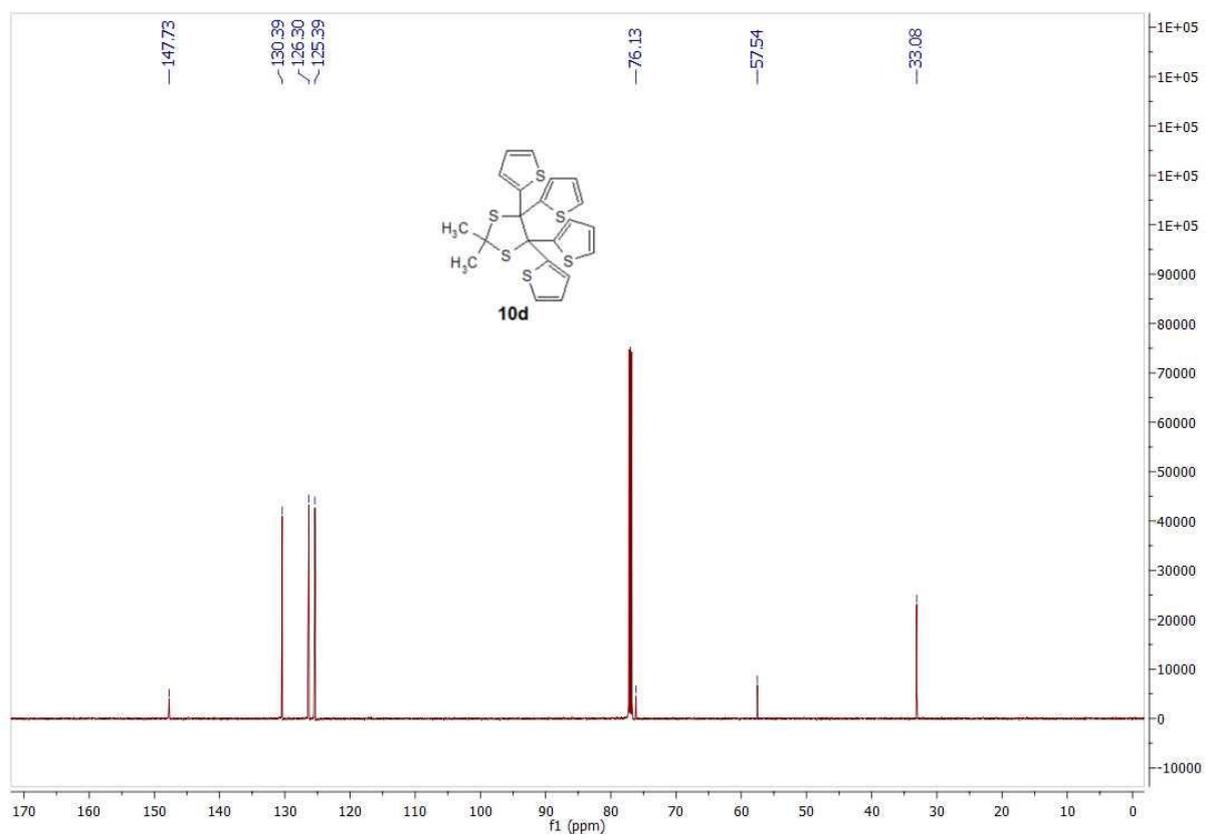


Figure S10: The ^{13}C NMR spectrum of compound **10d**.

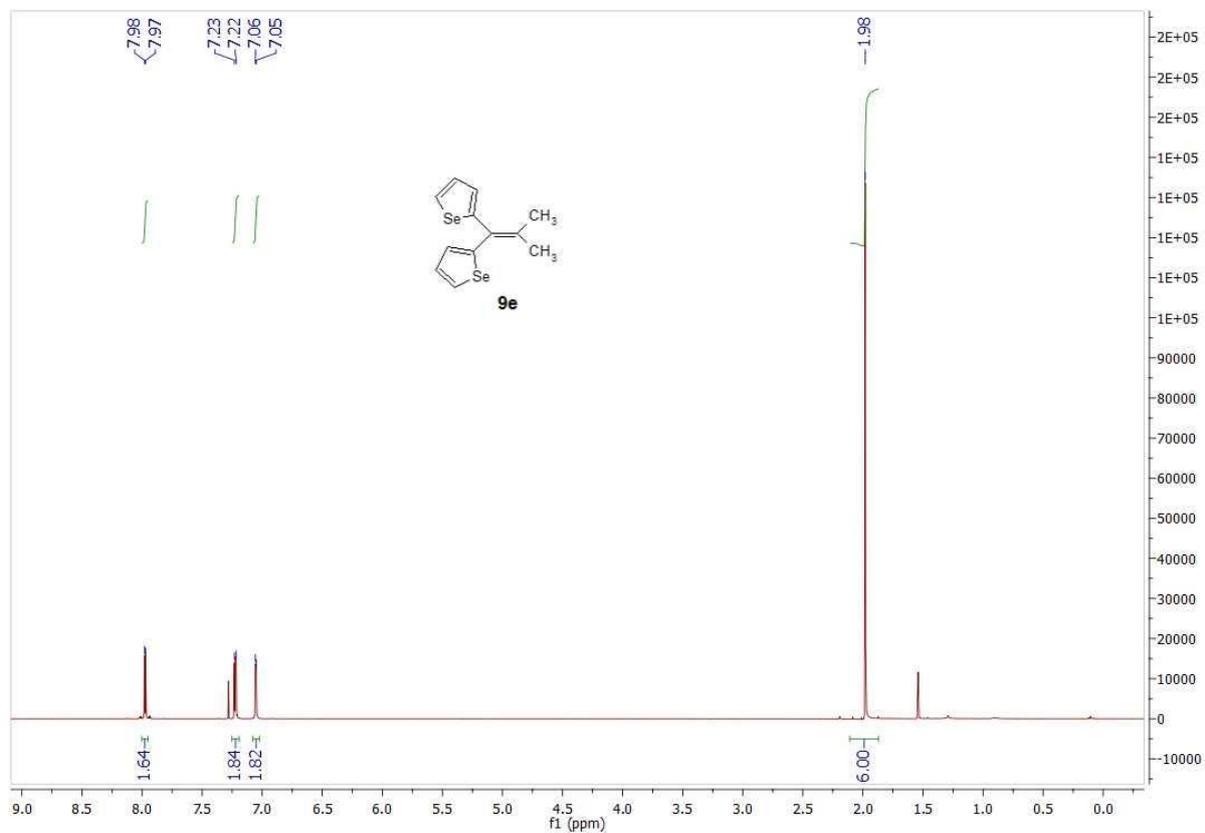


Figure S11: The ^1H NMR spectrum of compound **9e**.

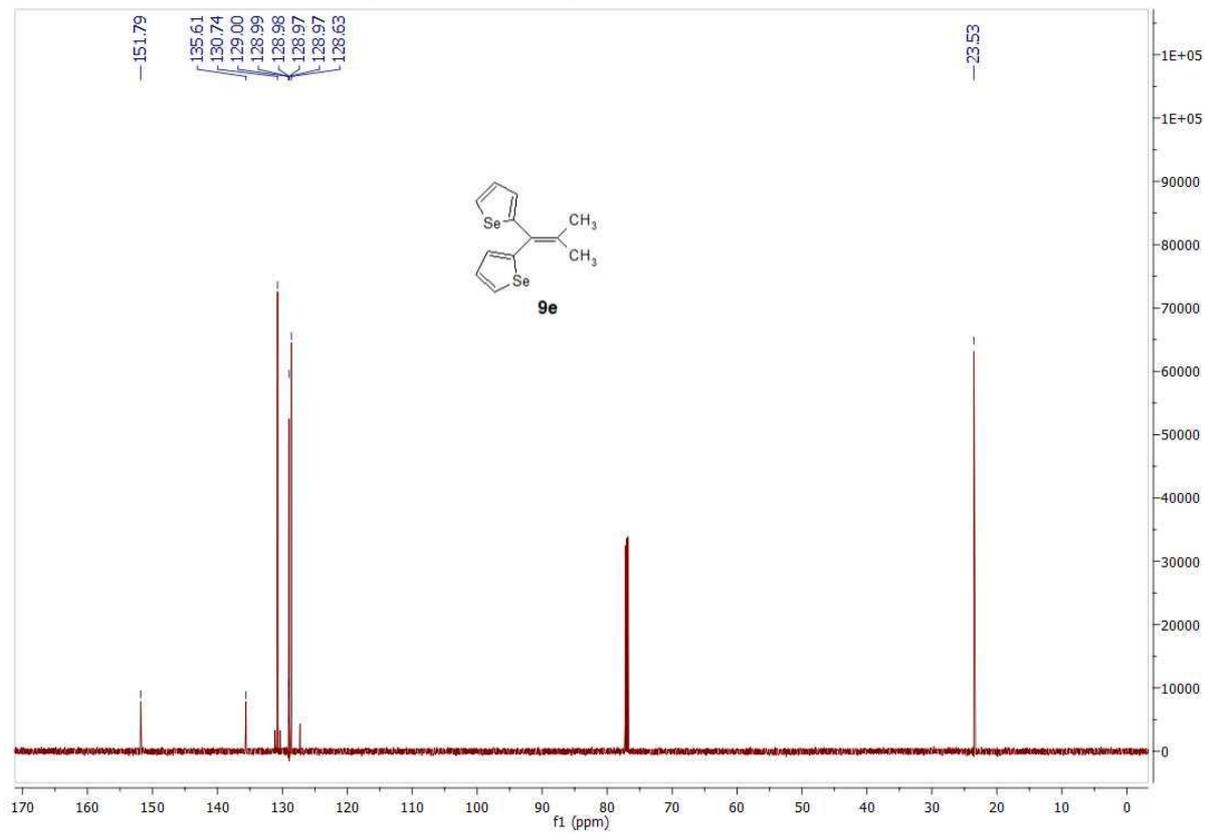


Figure S12: The ^{13}C NMR spectrum of compound **9e**.

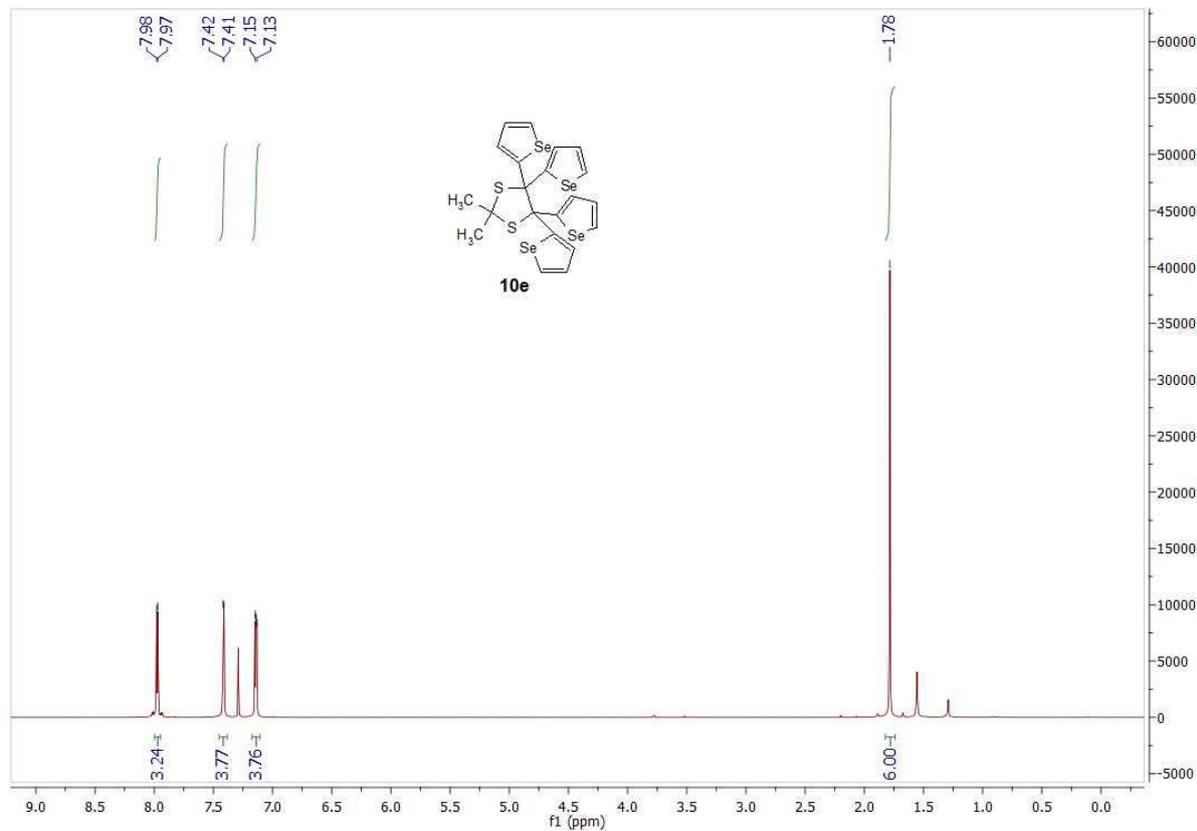


Figure S13: The ^1H NMR spectrum of compound **10e**.

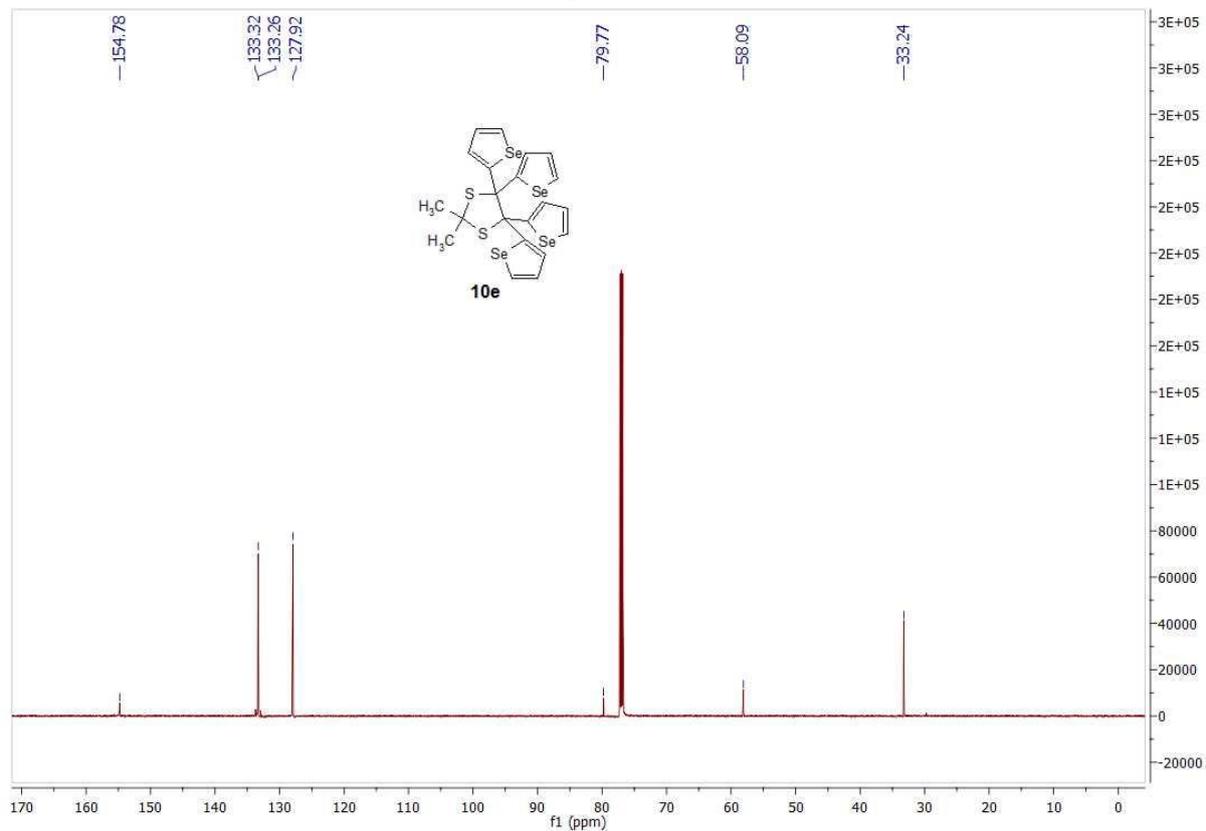


Figure S14: The ^{13}C NMR spectrum of compound **10e**.

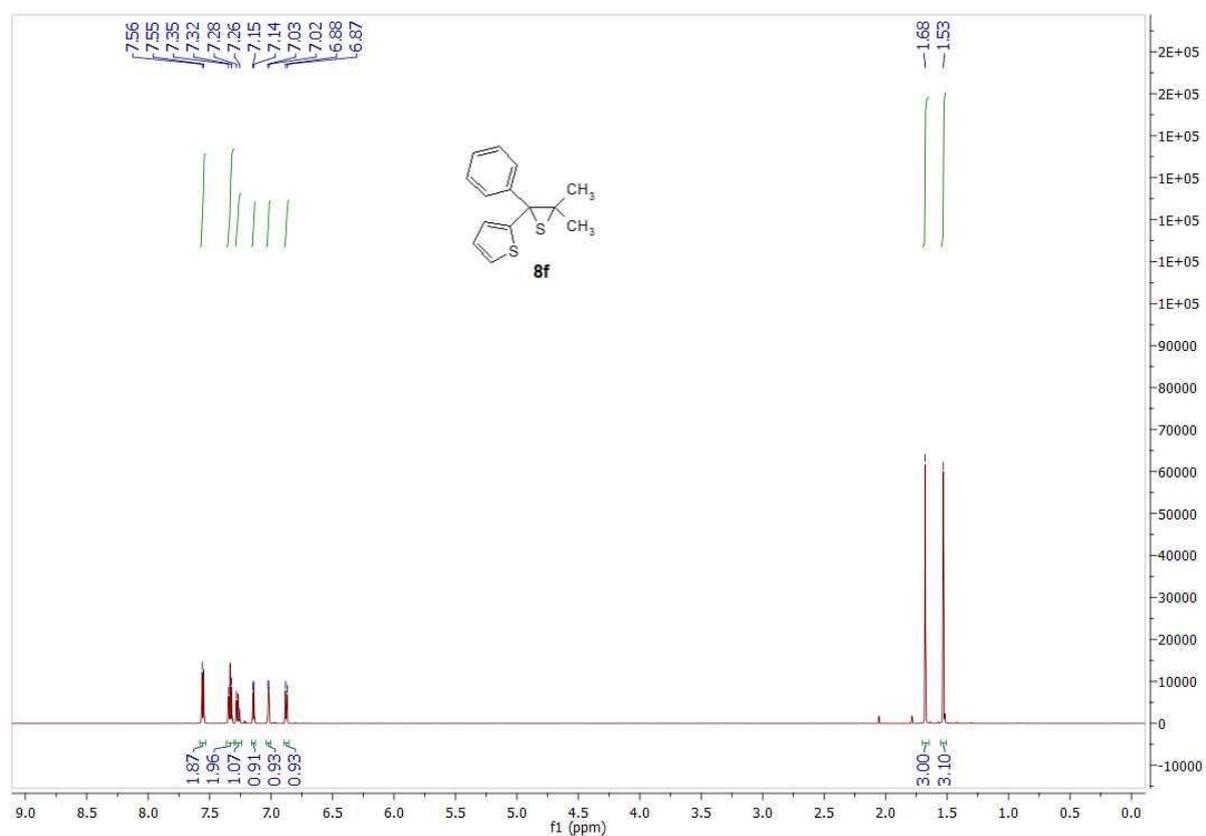


Figure S15: The ^1H NMR spectrum of compound **8f**.

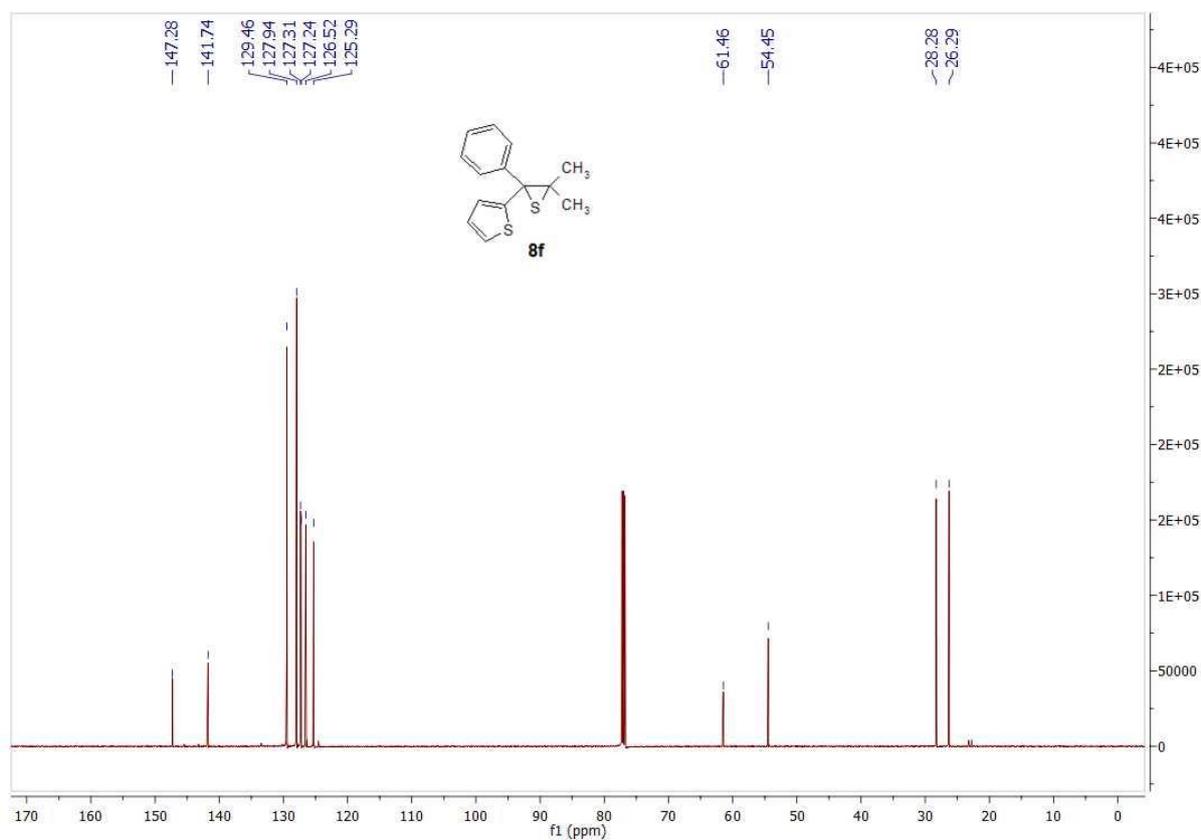


Figure S16: The ^{13}C NMR spectrum of compound **8f**.

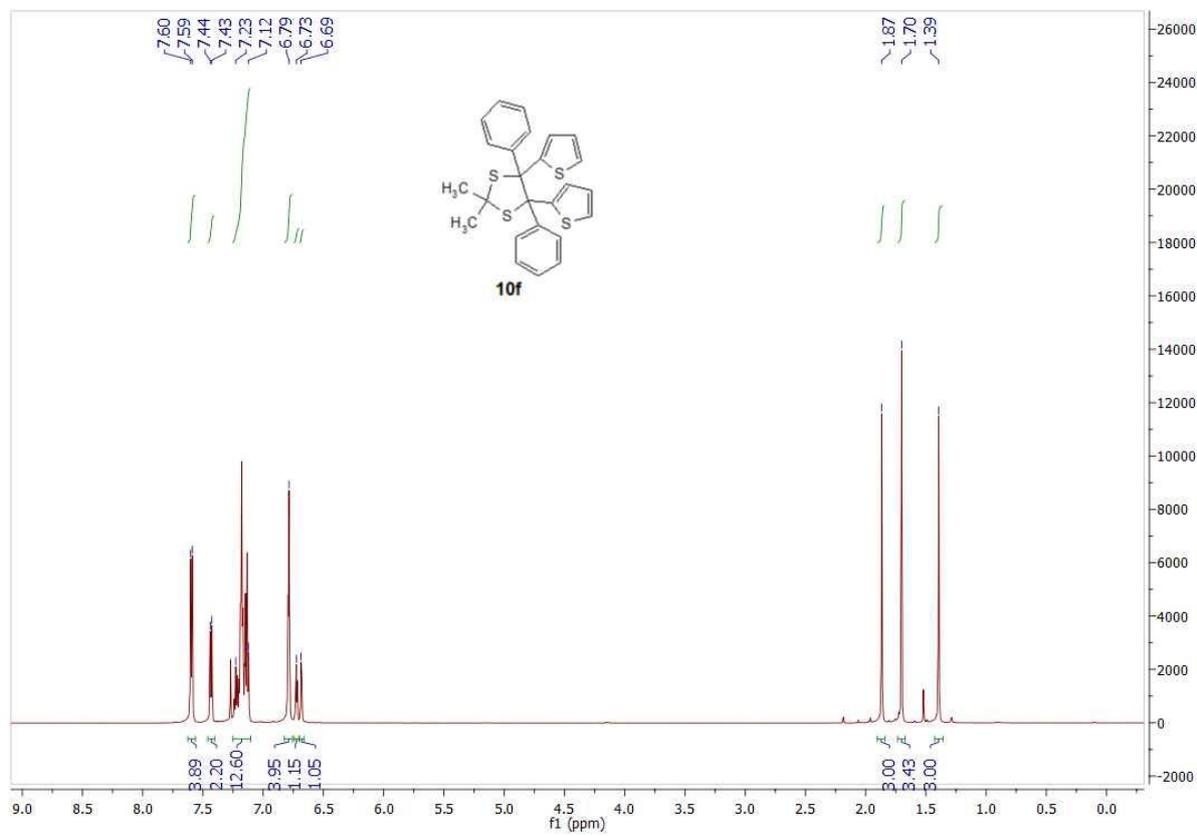


Figure S17: The ^1H NMR spectrum of compound **10f**.

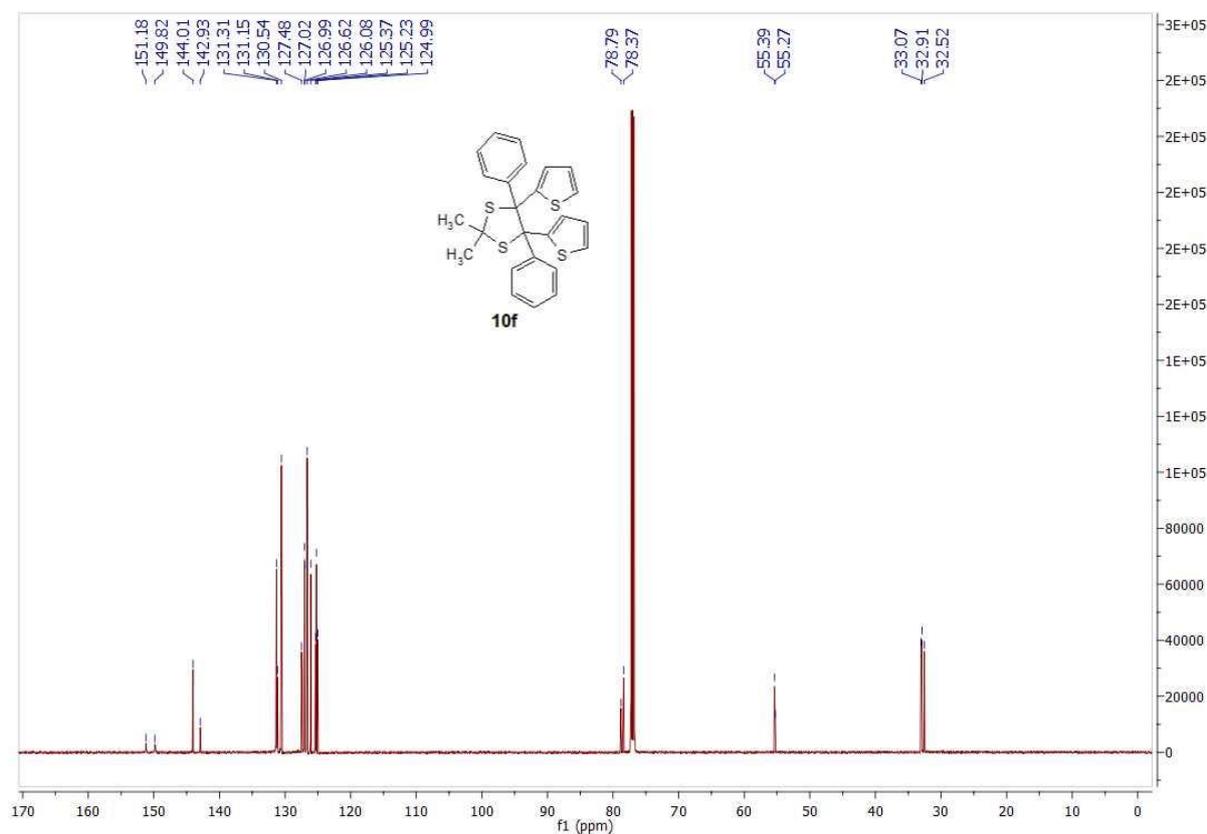


Figure S18: The ^{13}C NMR spectrum of compound **10f**.

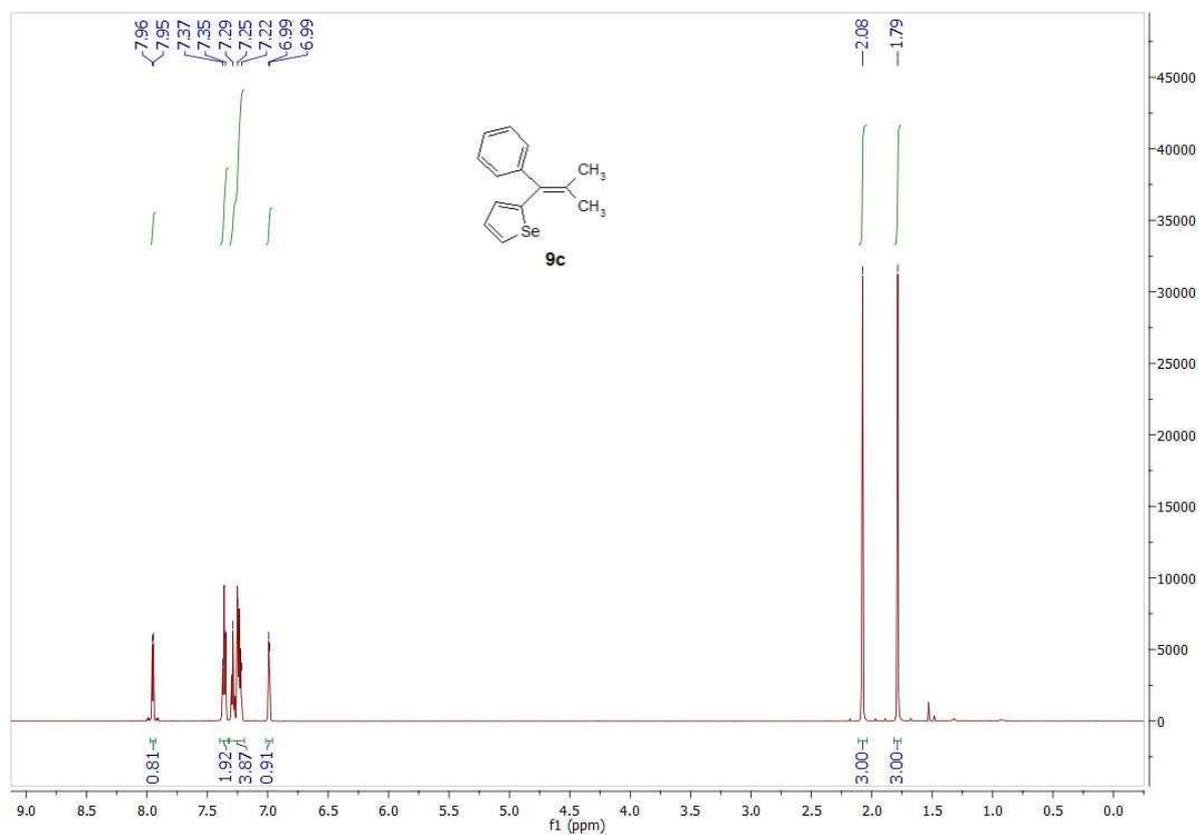


Figure S19: The ^1H NMR spectrum of compound **9c**.

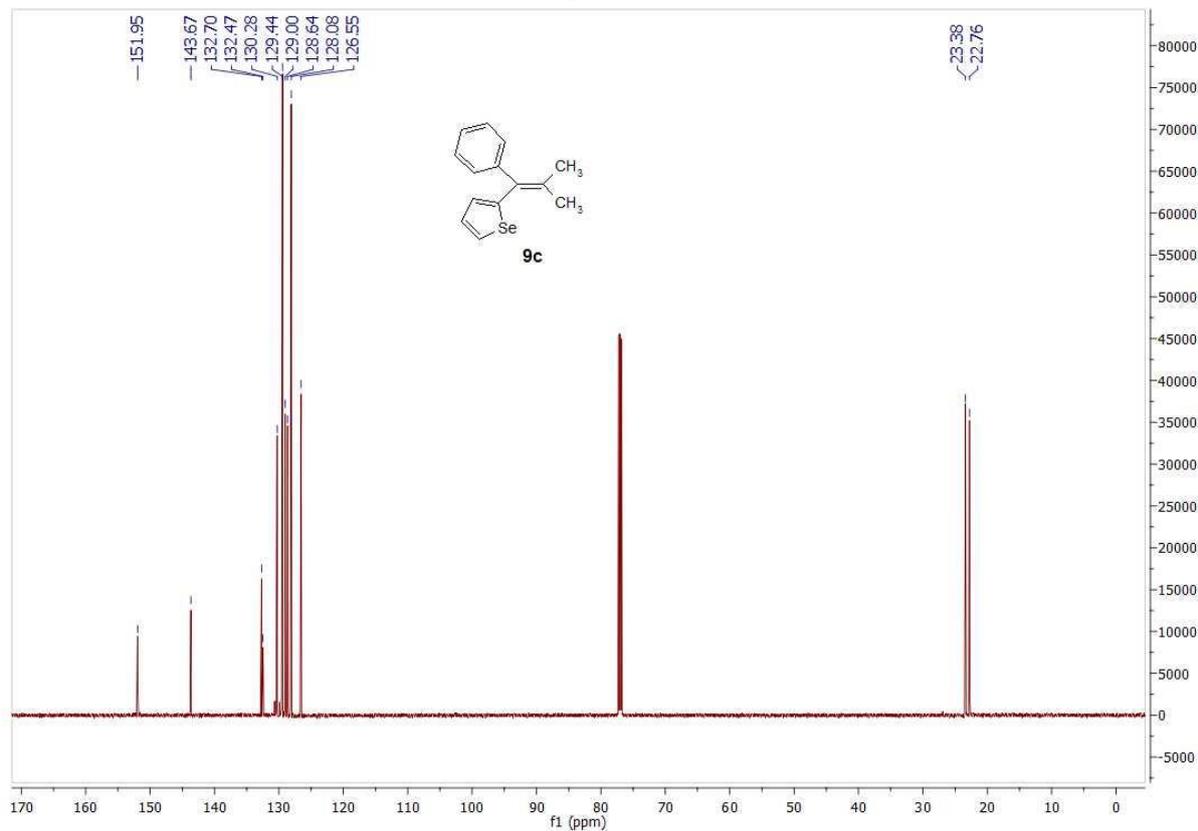


Figure S20: The ^{13}C NMR spectrum of compound **9c**.

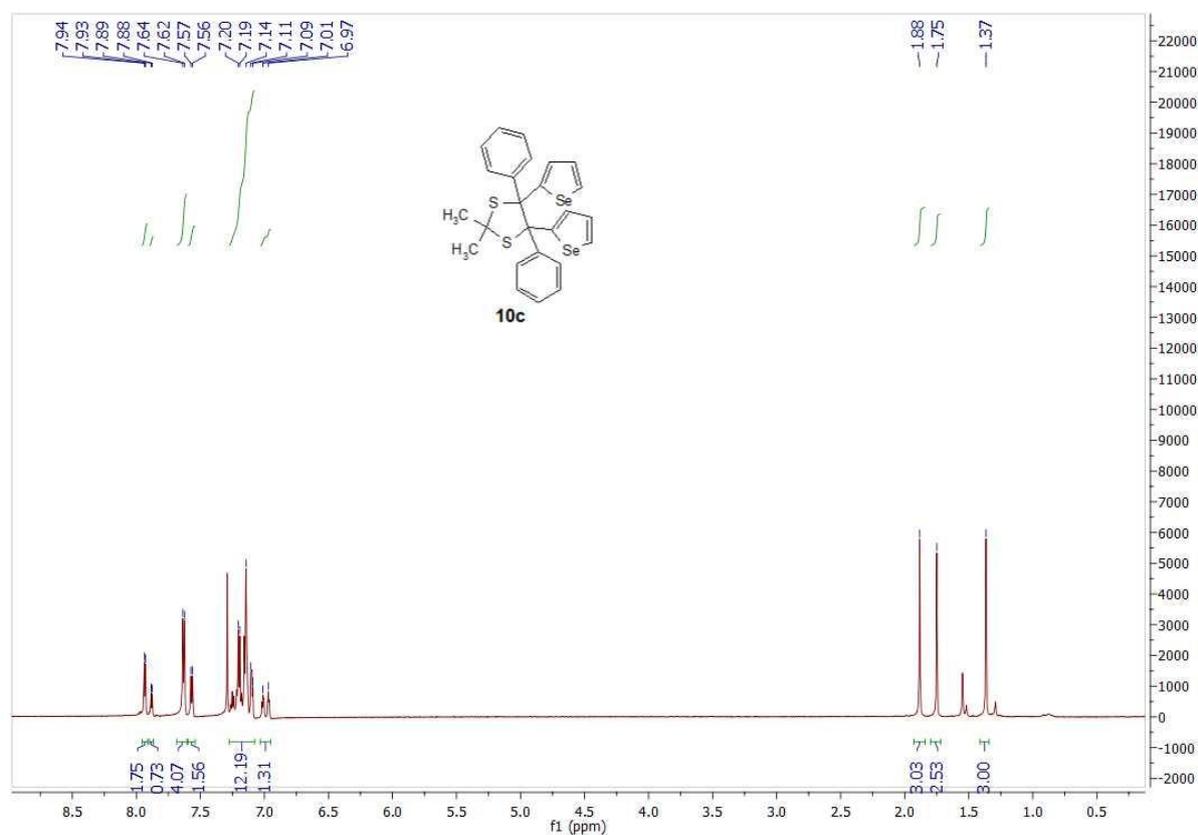


Figure S21: The ^1H NMR spectrum of compound **10c**.

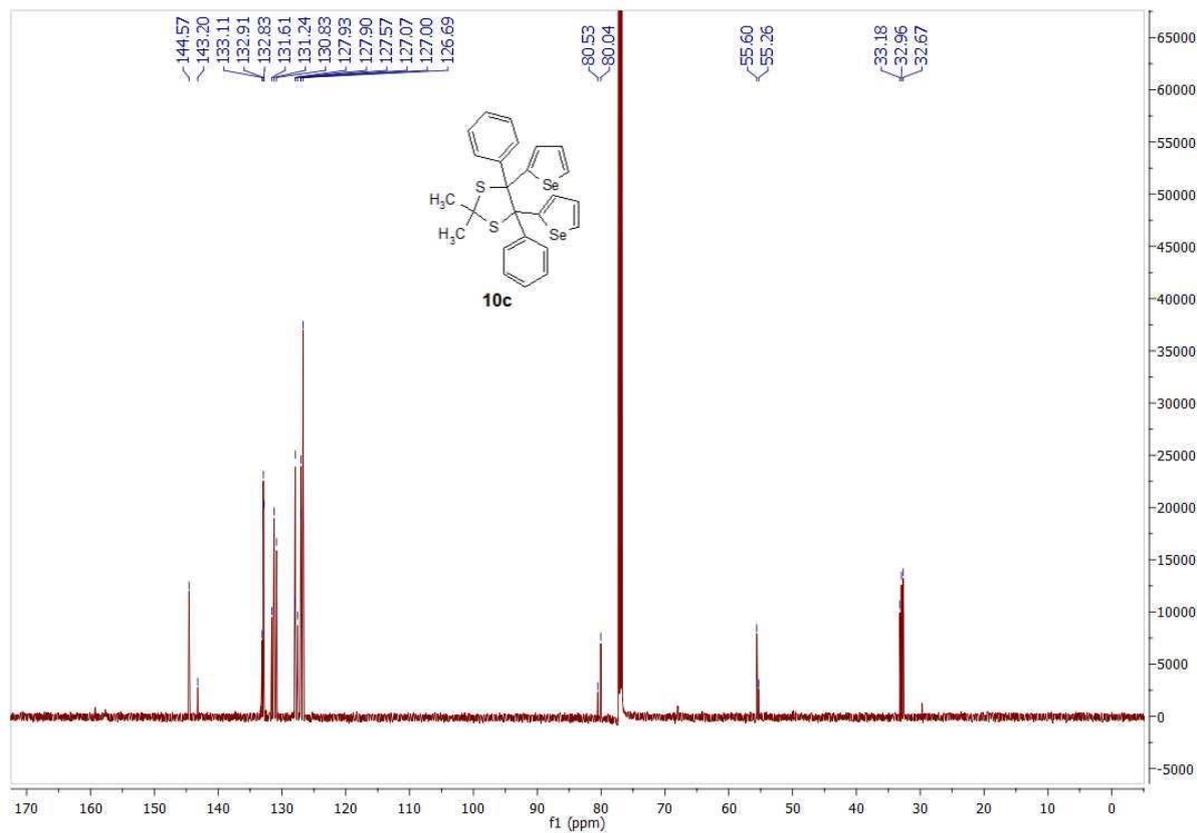


Figure S22: The ^{13}C NMR spectrum of compound **10c**.

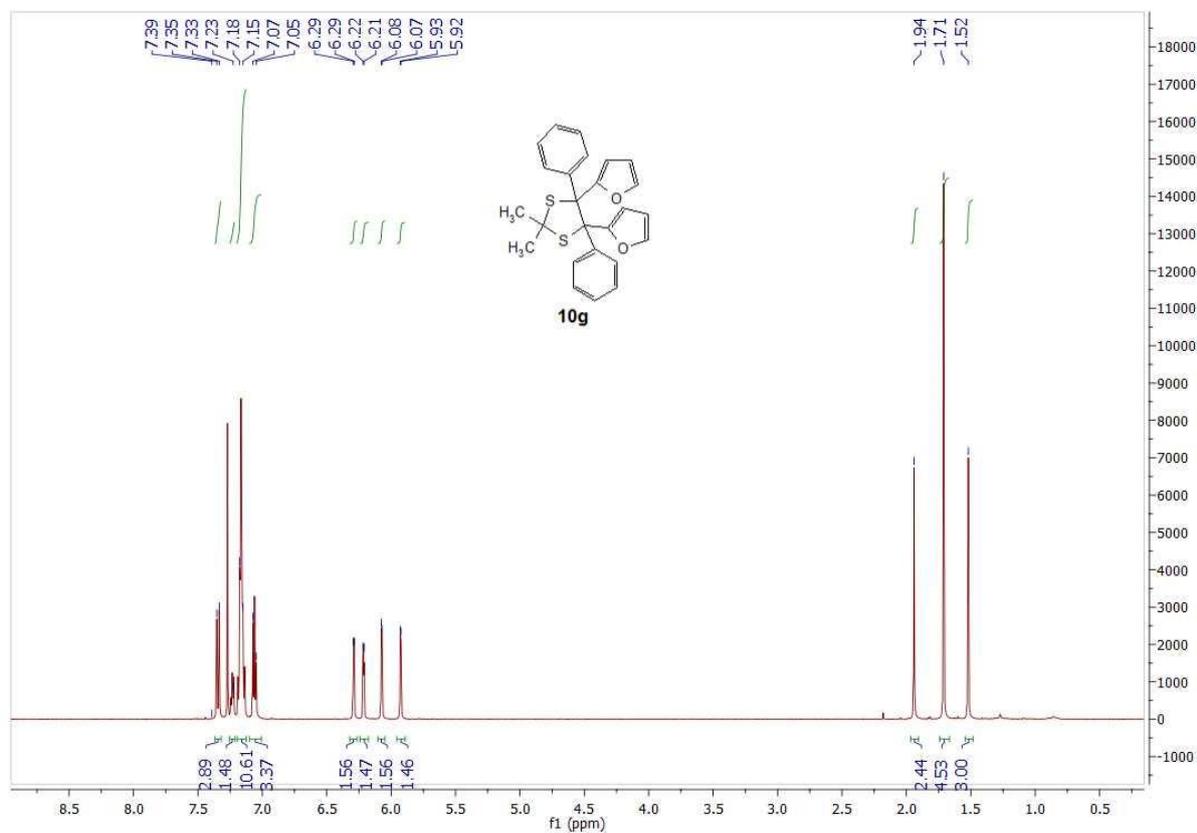


Figure S23: The ^1H NMR spectrum of compound **10g**.

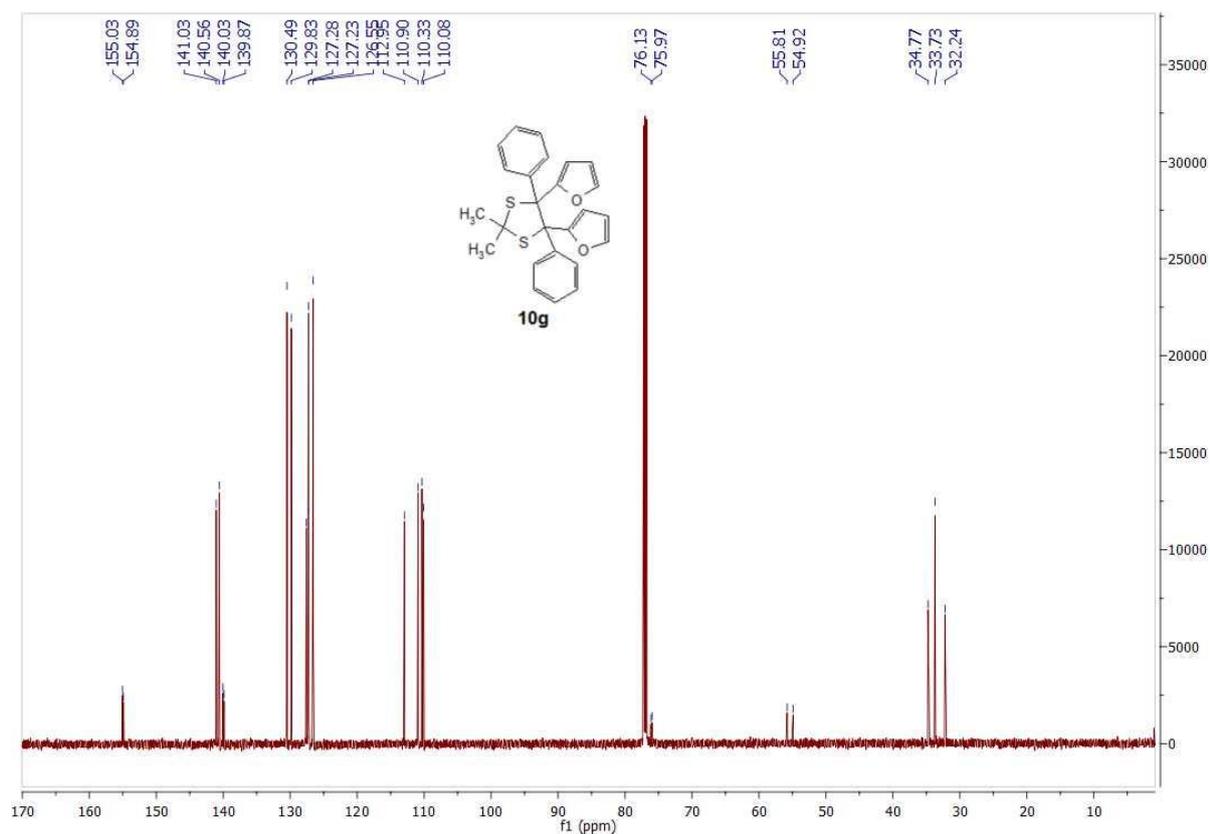


Figure S24: The ^{13}C NMR spectrum of compound **10g**.

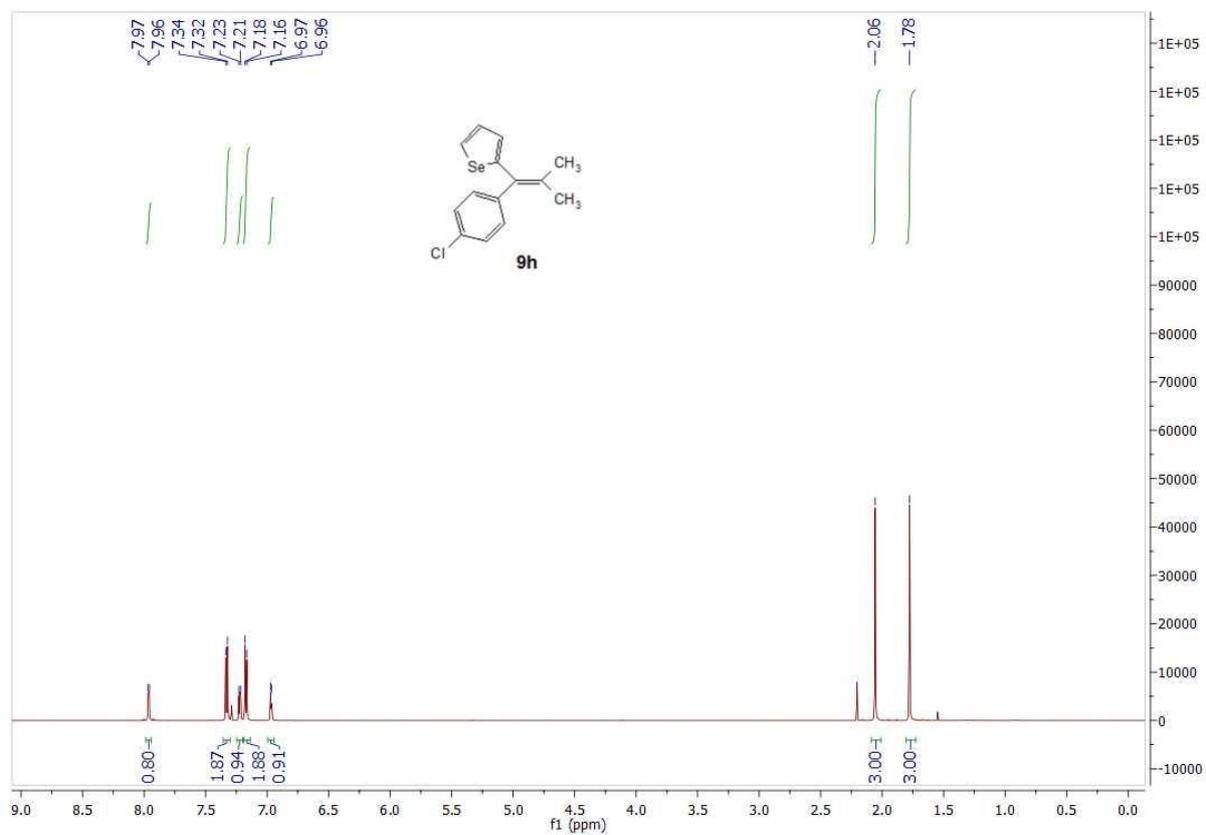


Figure S25: The ^1H NMR spectrum of compound **9h**.

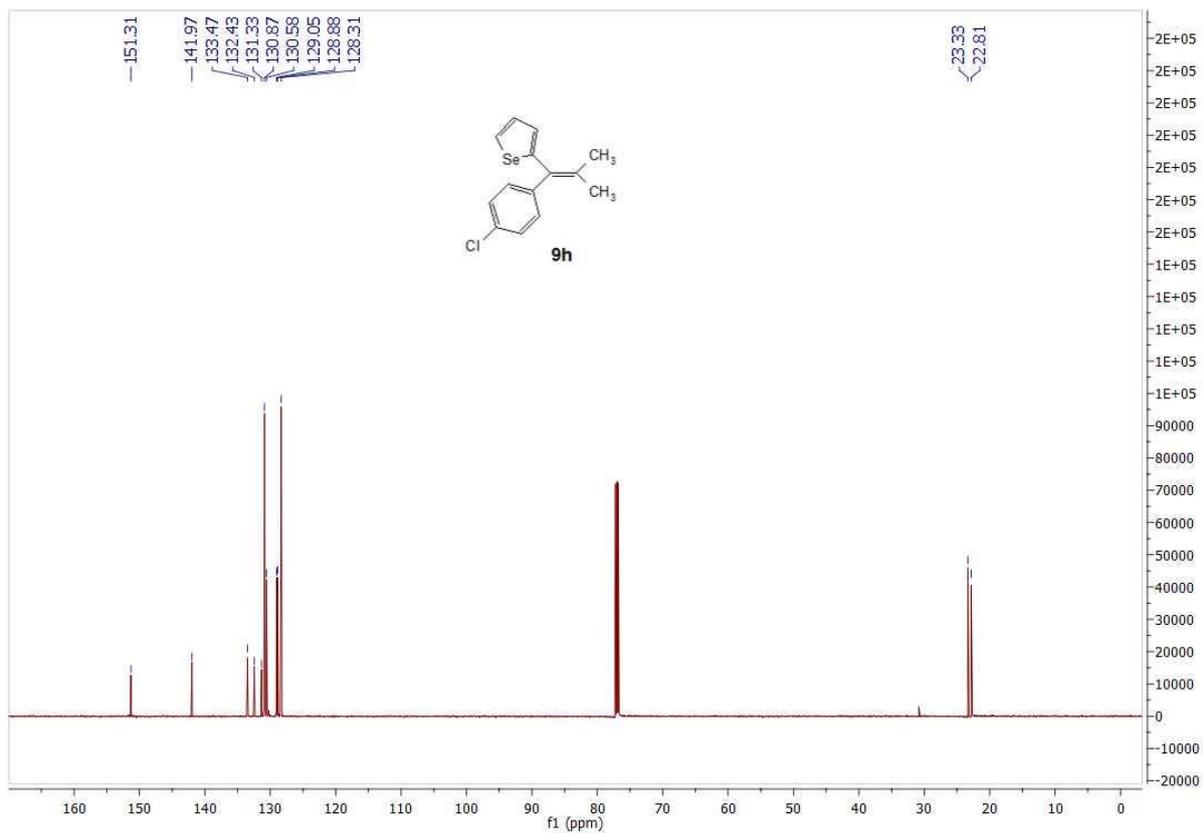


Figure S26: The ¹³C NMR spectrum of compound **9h**.

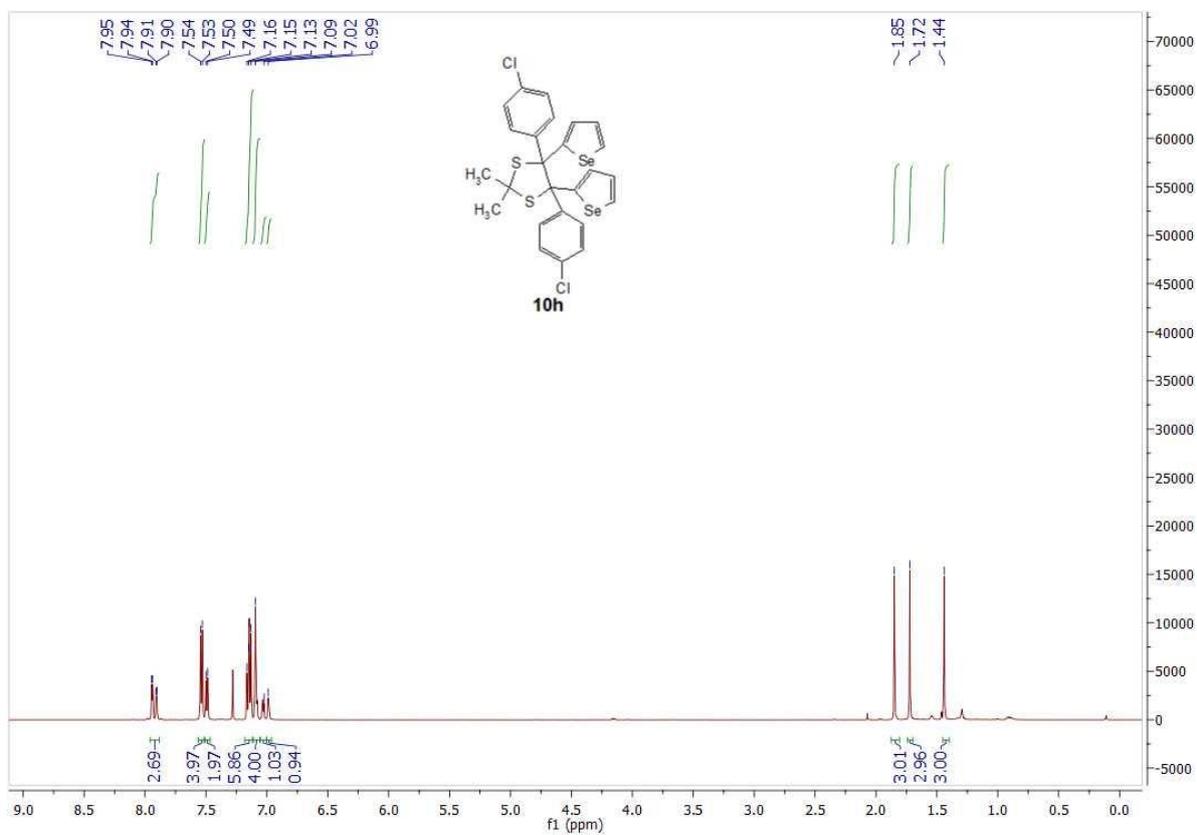


Figure S27: The ¹H NMR spectrum of compound **10h**.

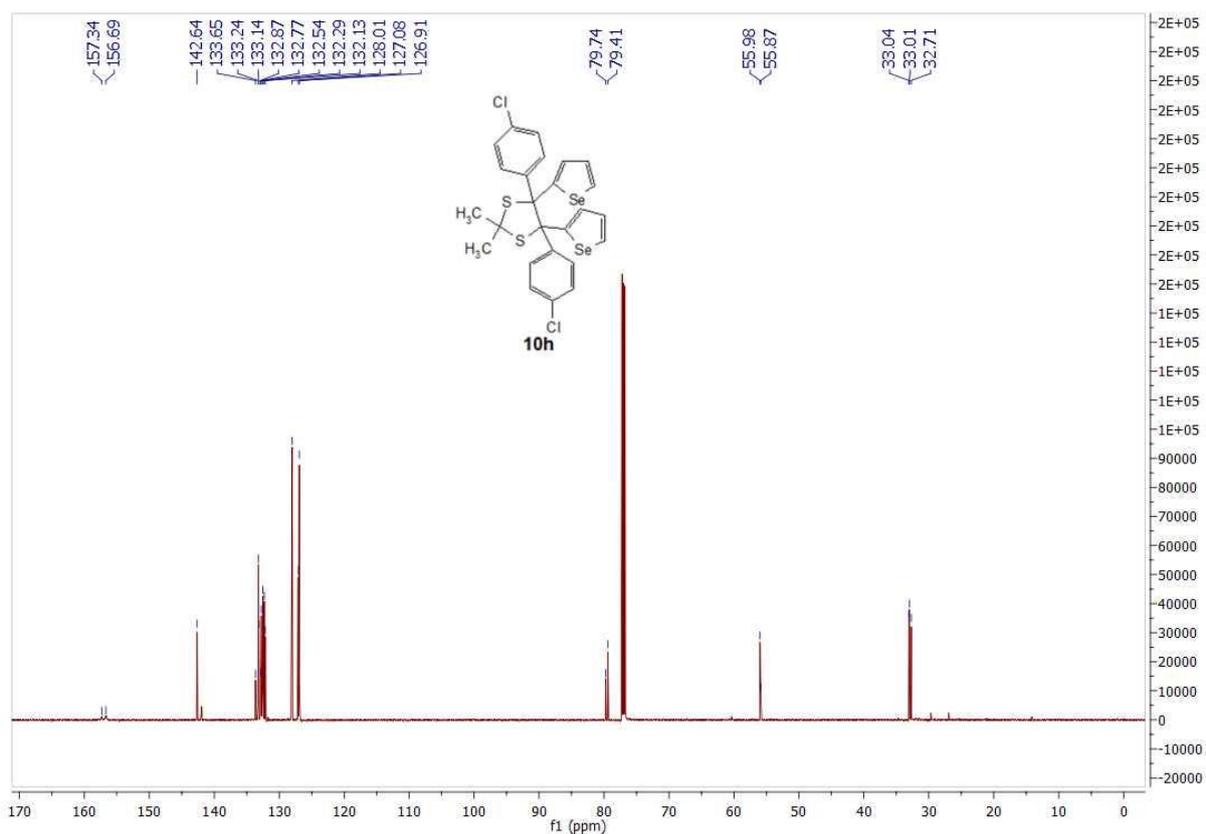


Figure S28: The ^{13}C NMR spectrum of compound **10h**.

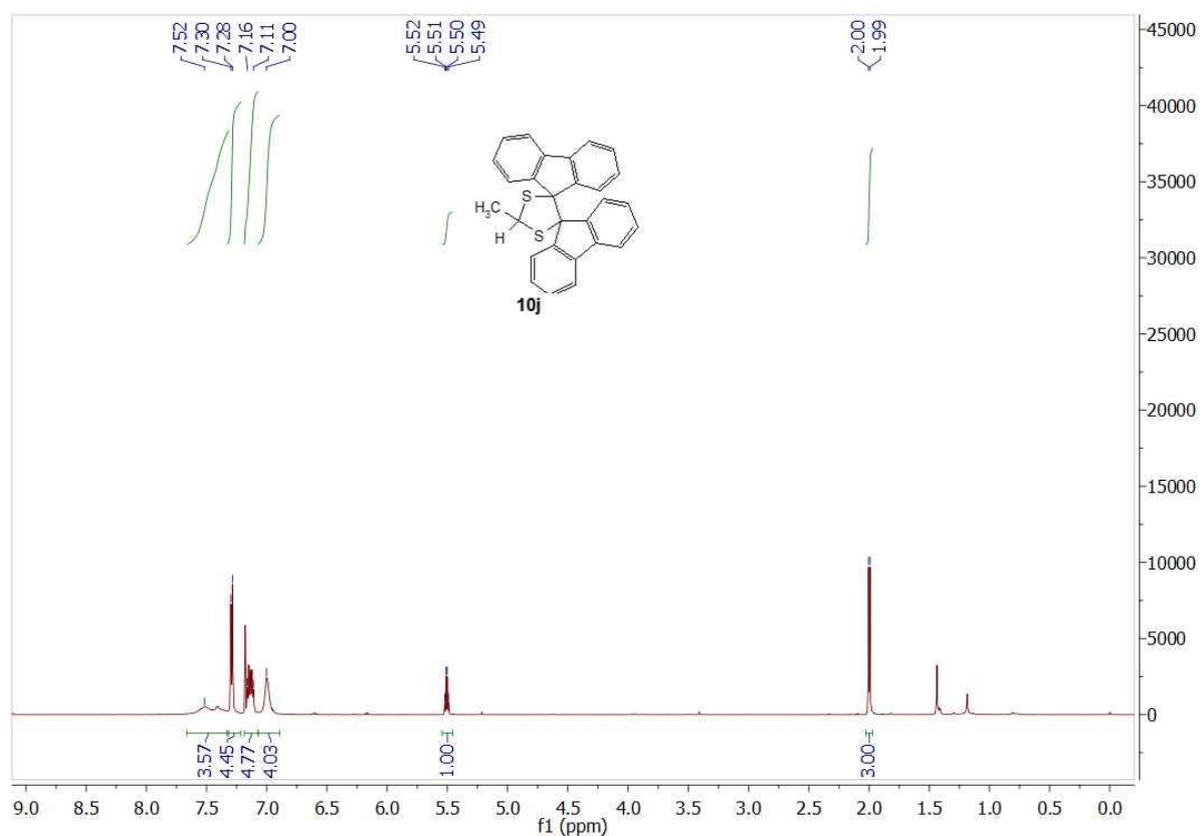


Figure S29: The ^1H NMR spectrum of compound **10j**.

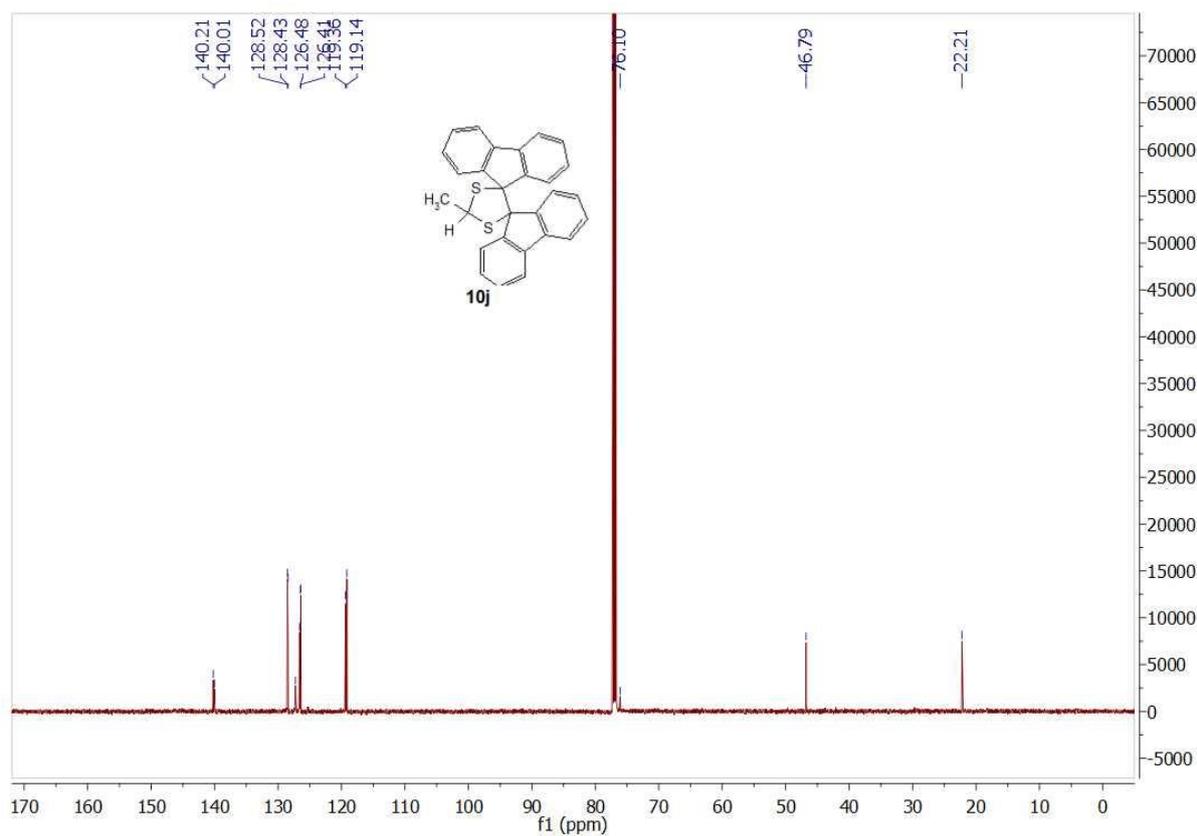


Figure S30: The ^{13}C NMR spectrum of compound **10j**.

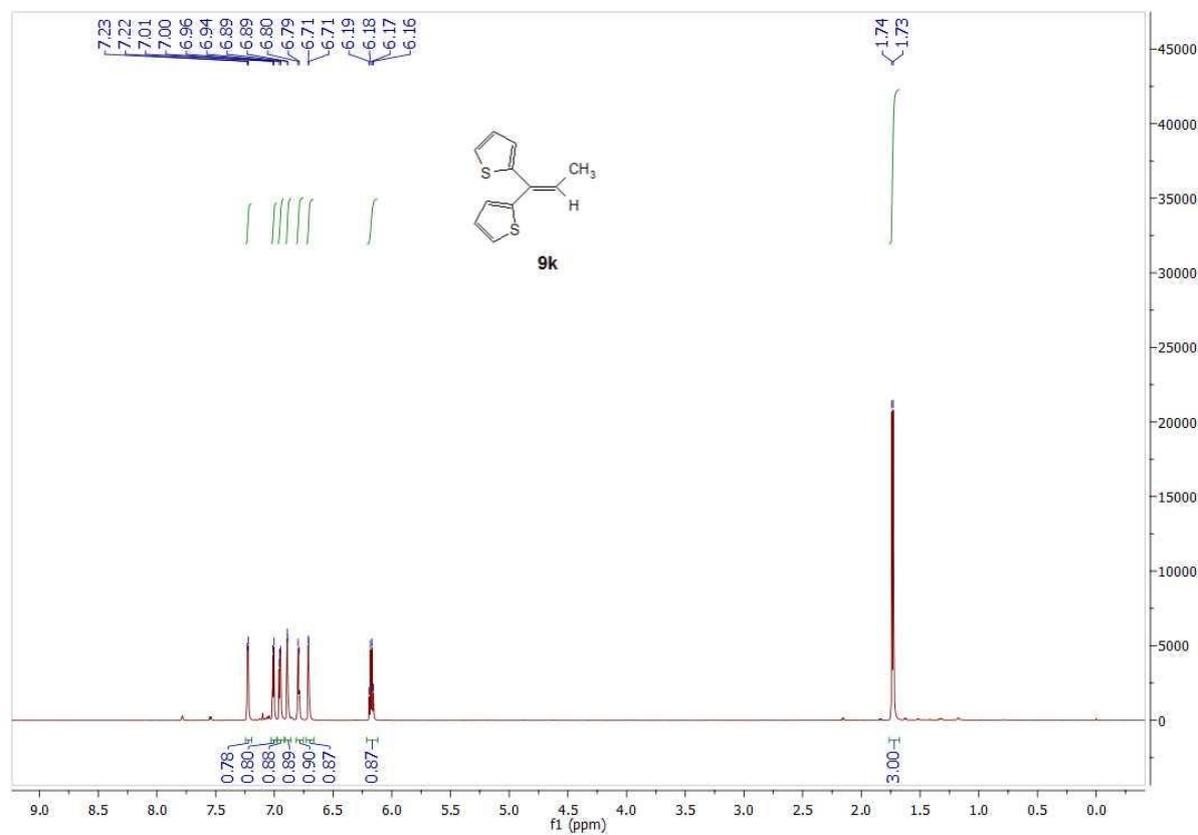


Figure S31: The ^1H NMR spectrum of compound **9k**.

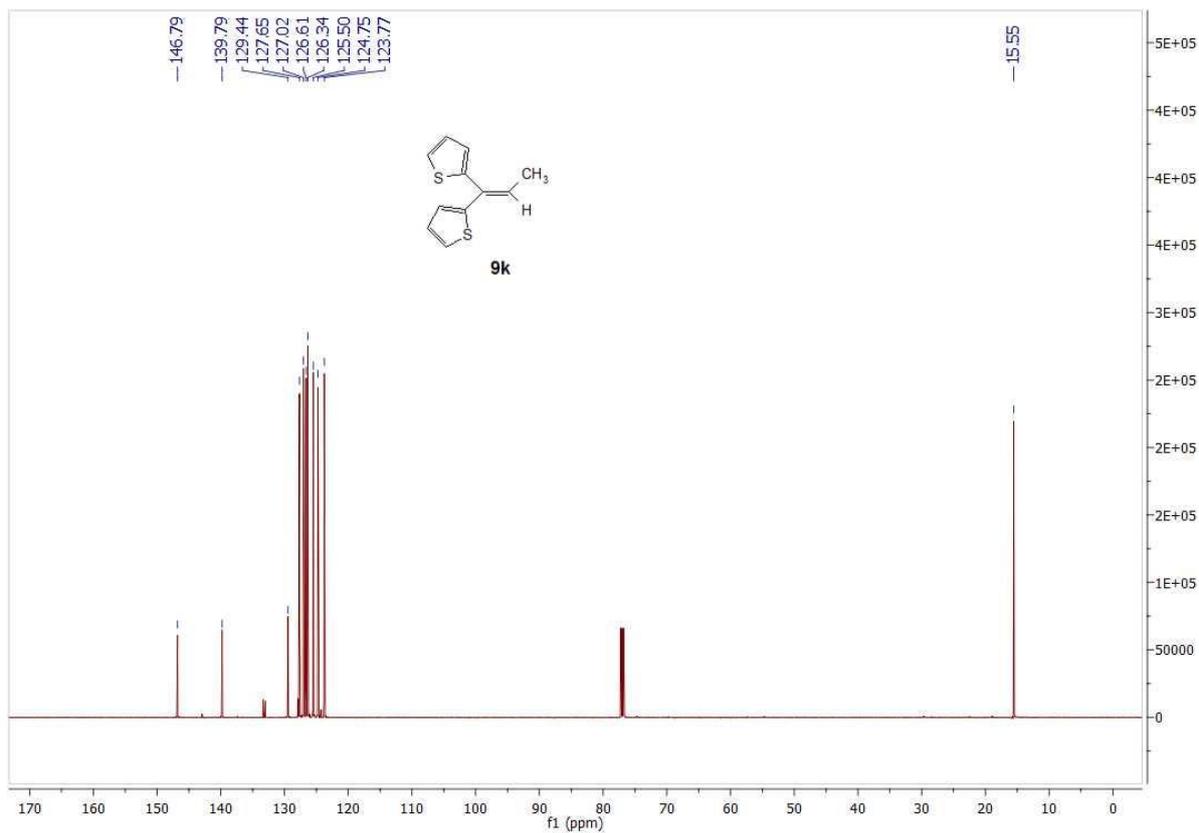


Figure S32: The ^{13}C NMR spectrum of compound **9k**.

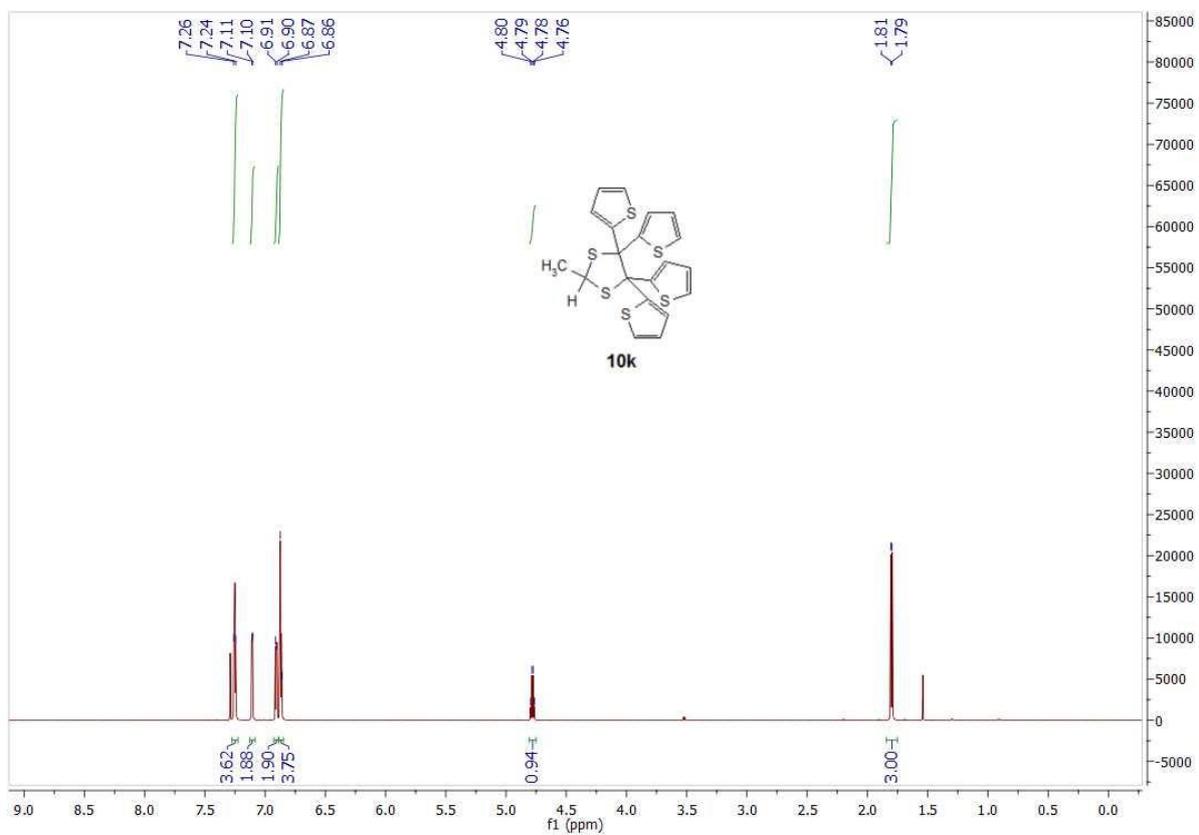


Figure S33: The ^1H NMR spectrum of compound **10k**.

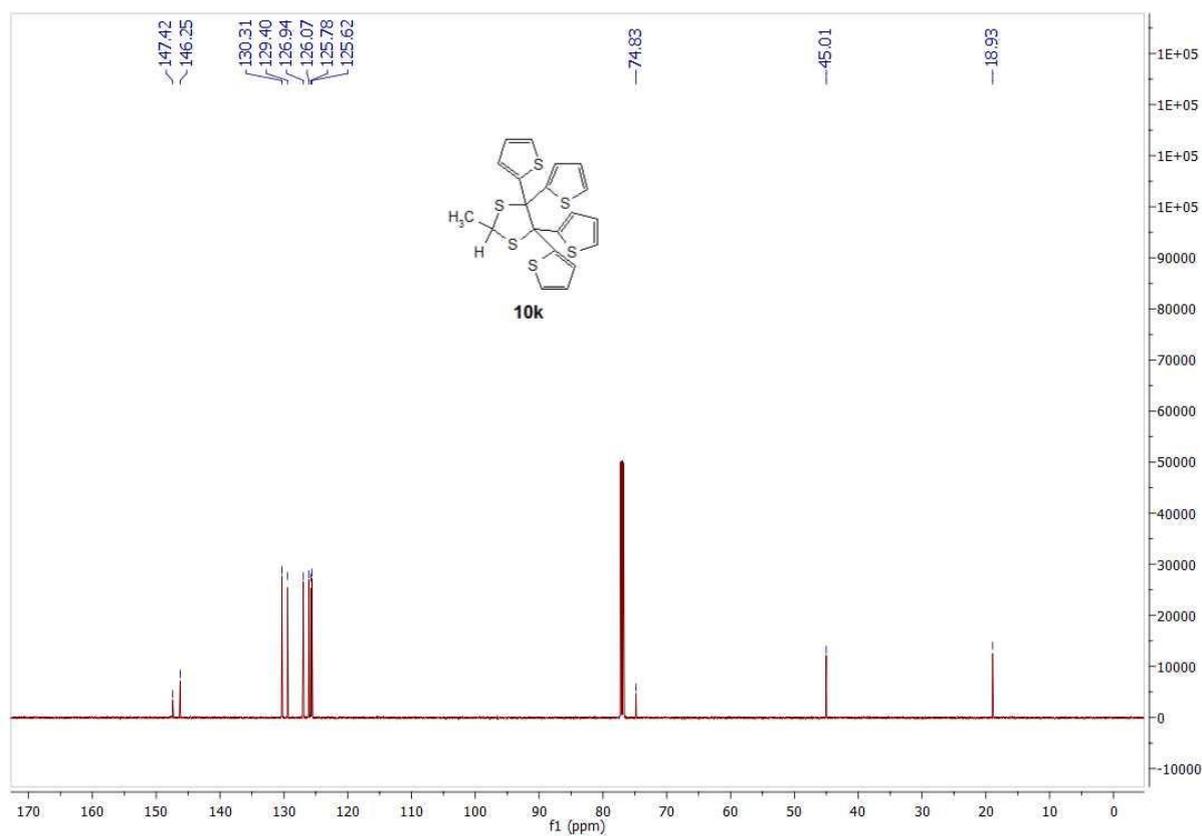


Figure S34: The ^{13}C NMR spectrum of compound **10k**.

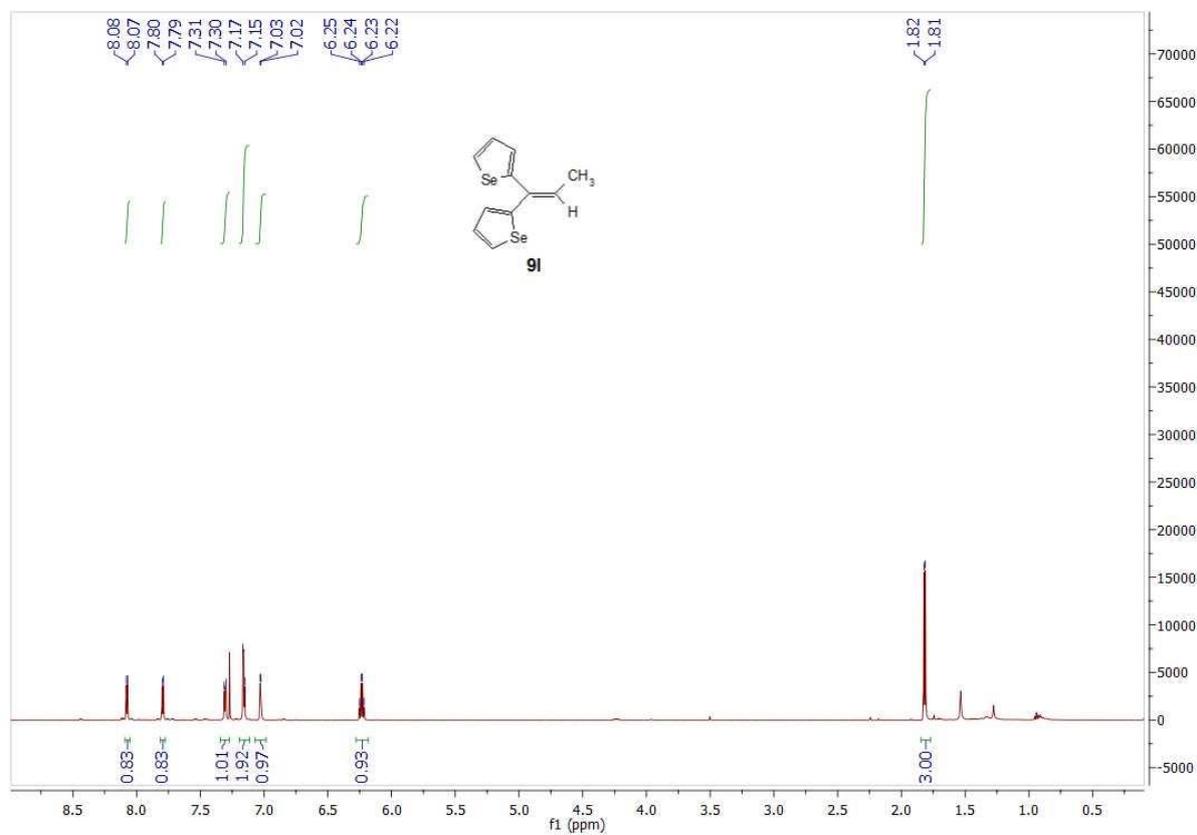


Figure S35: The ^1H NMR spectrum of compound **9l**.

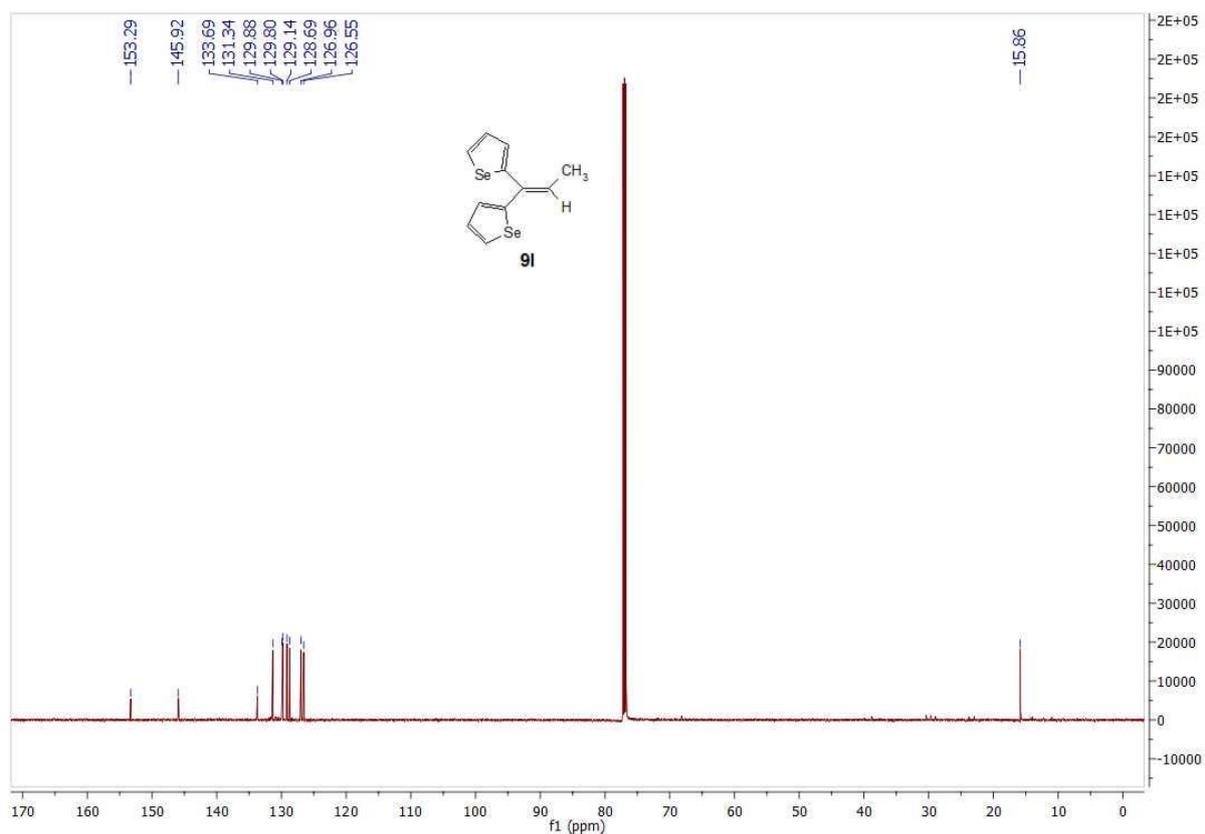


Figure S36: The ^{13}C NMR spectrum of compound **9I**.

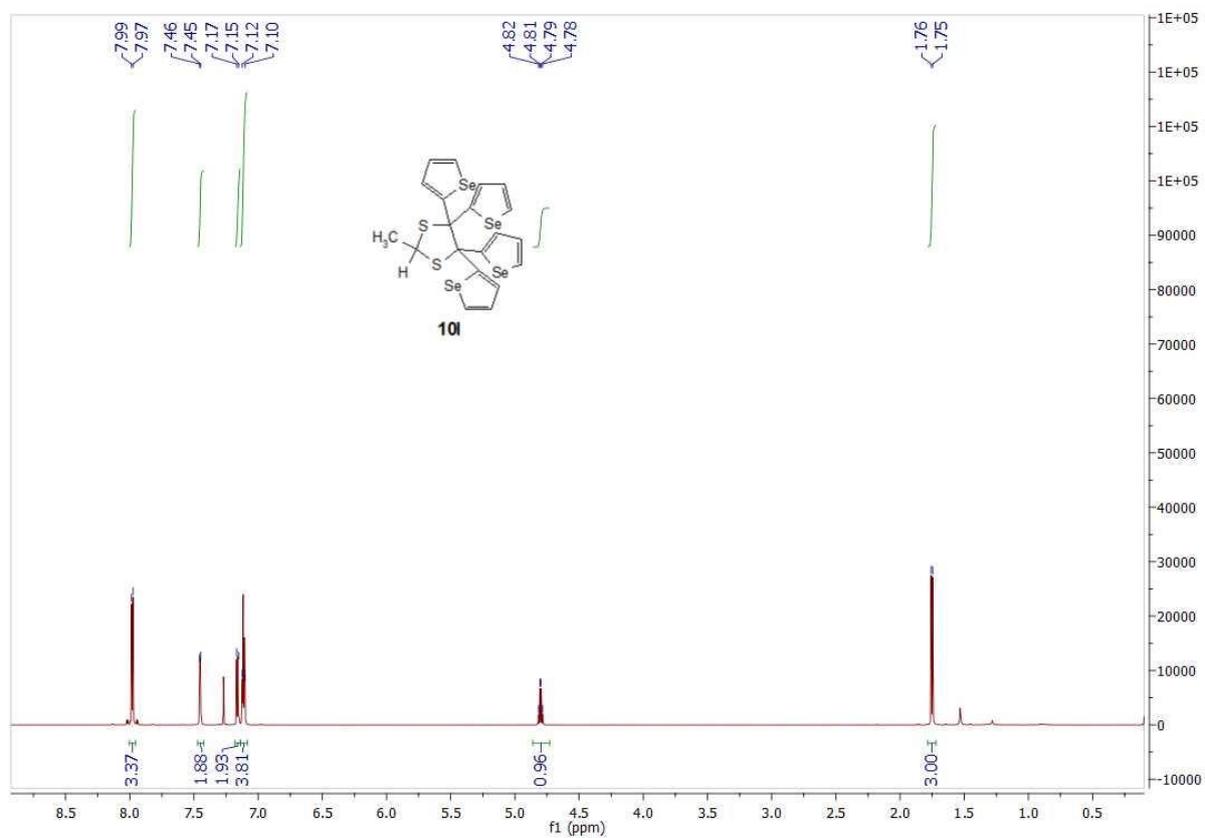


Figure S37: The ^1H NMR spectrum of compound **10I**.

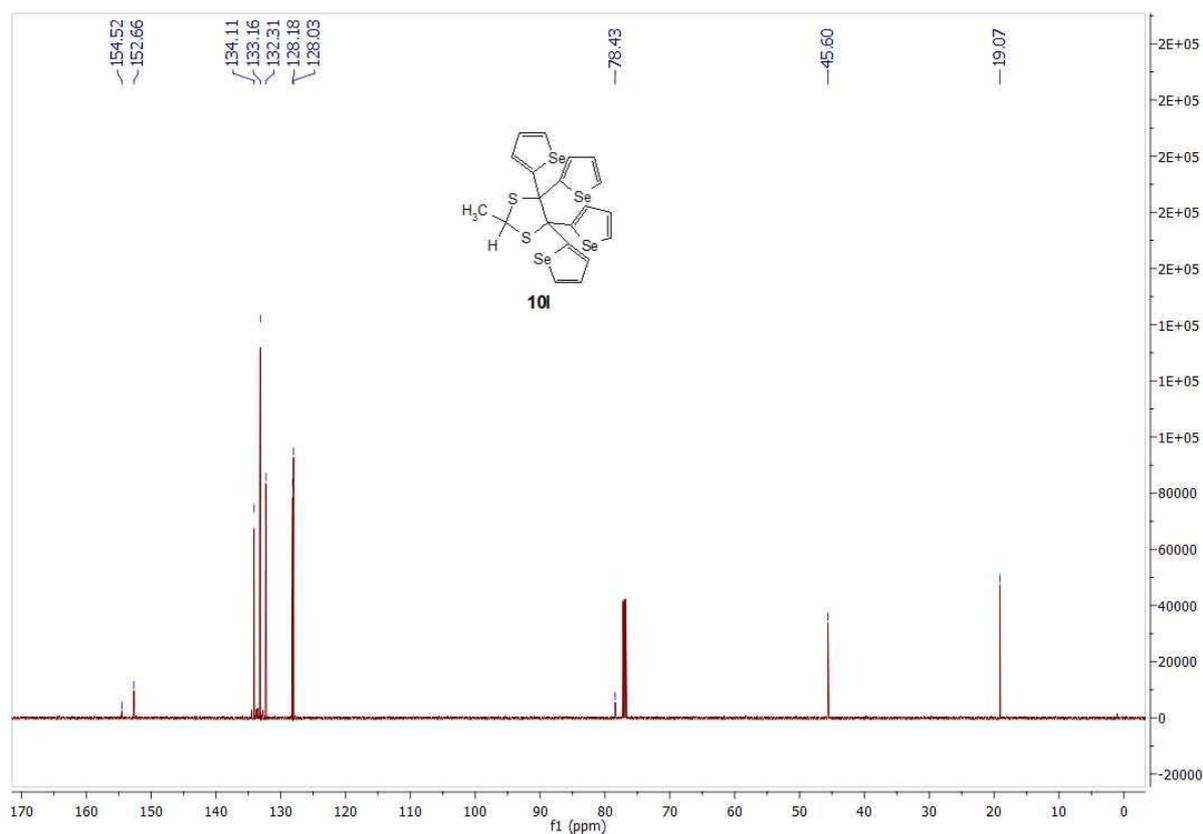


Figure S38: The ^{13}C NMR spectrum of compound **10l**.

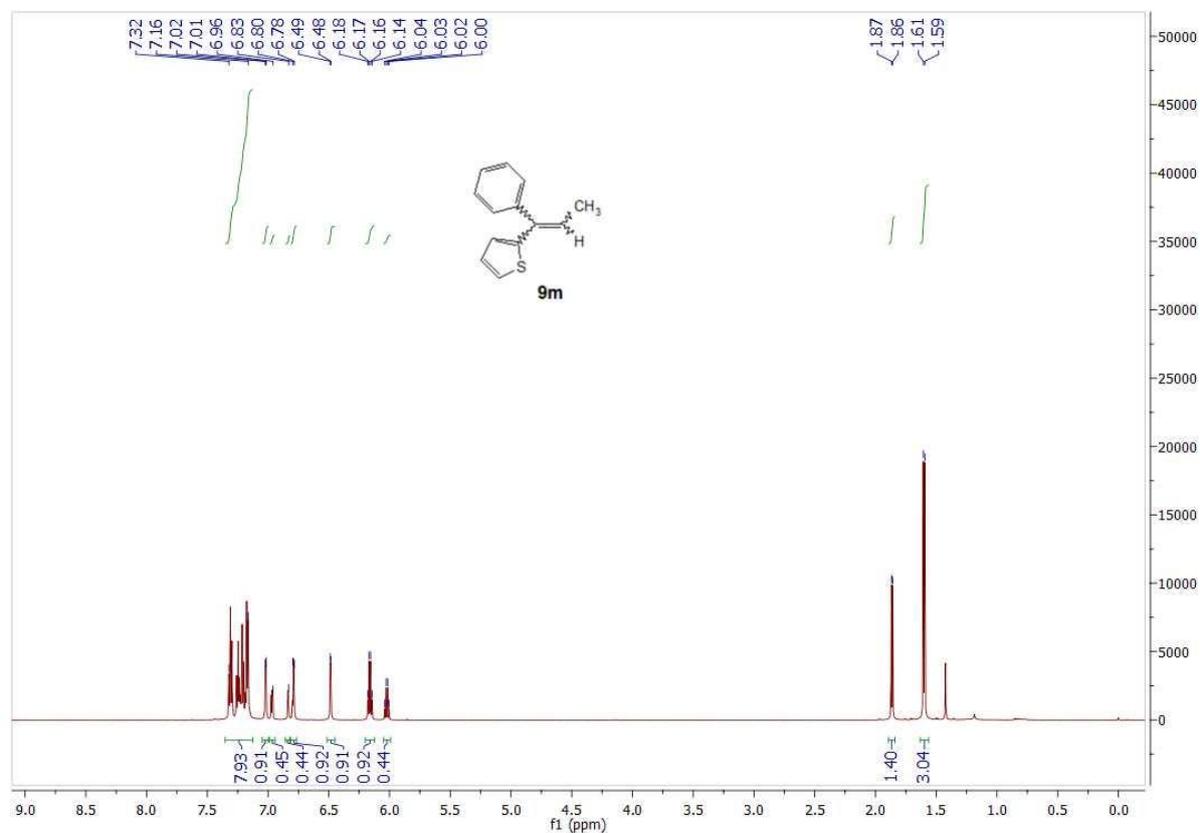


Figure S39: The ^1H NMR spectrum of compound **9m**.

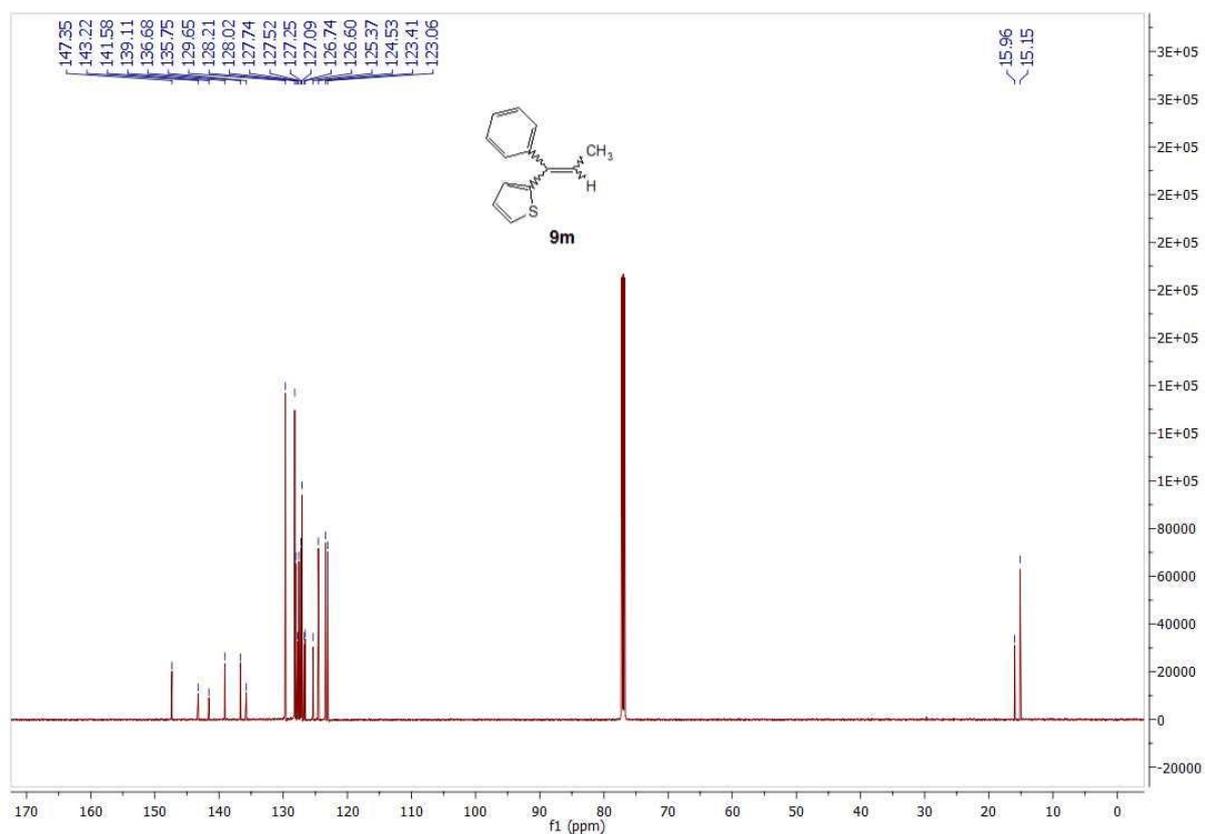


Figure S40: The ^{13}C NMR spectrum of compound **9m**.

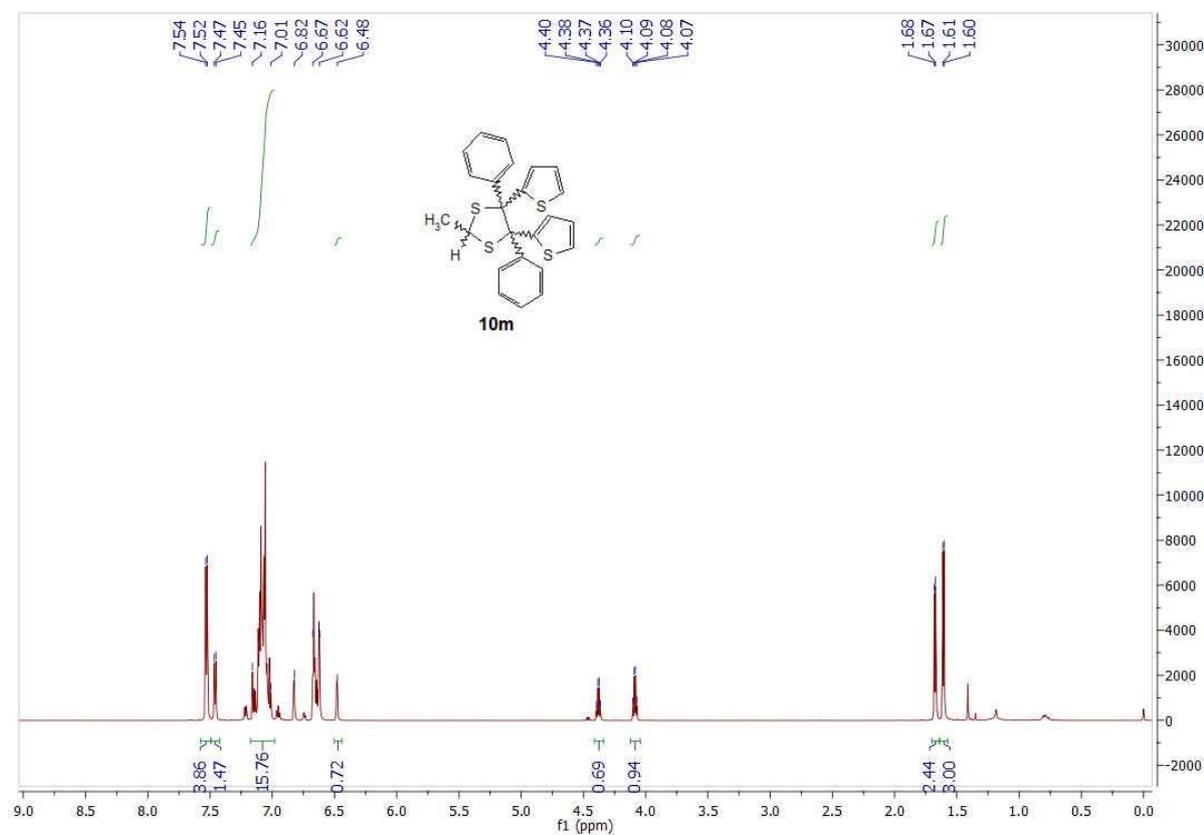


Figure S41: The ^1H NMR spectrum of compound **10m**.

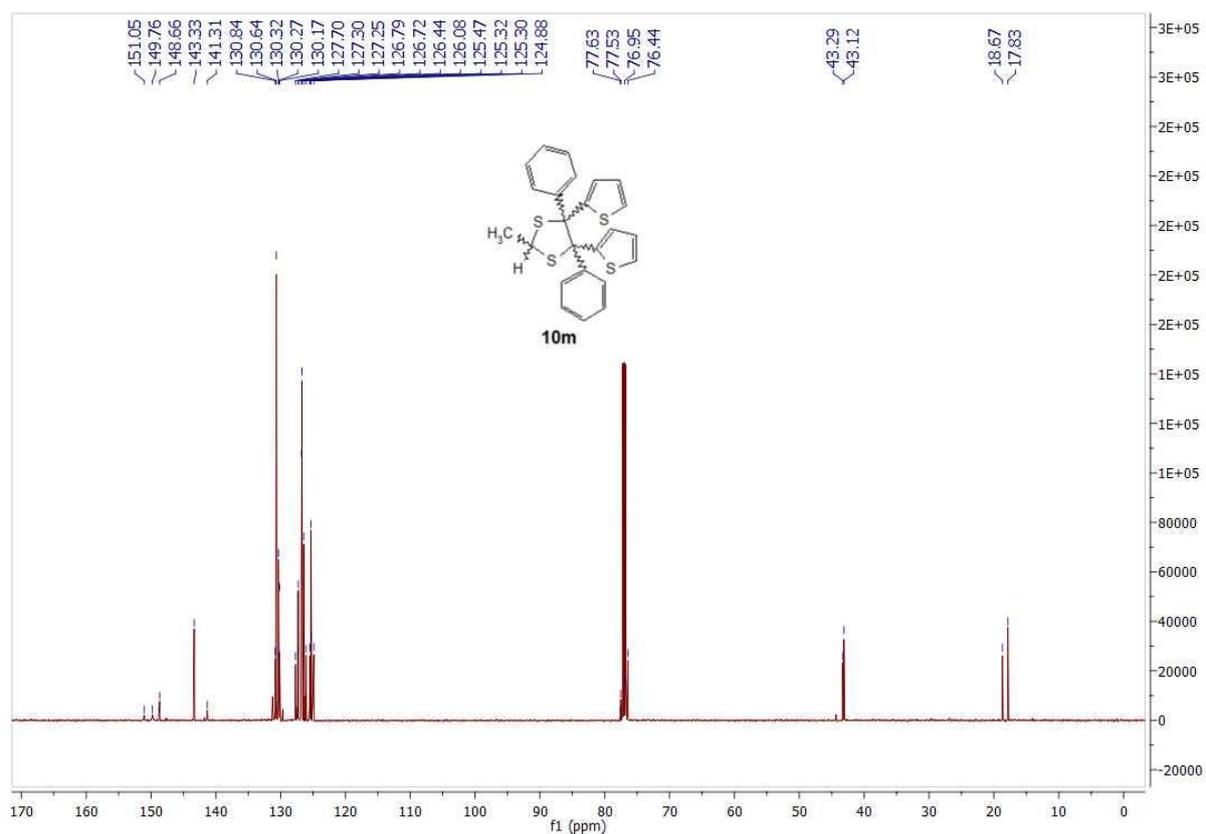


Figure S42: The ¹³C NMR spectrum of compound **10m**.

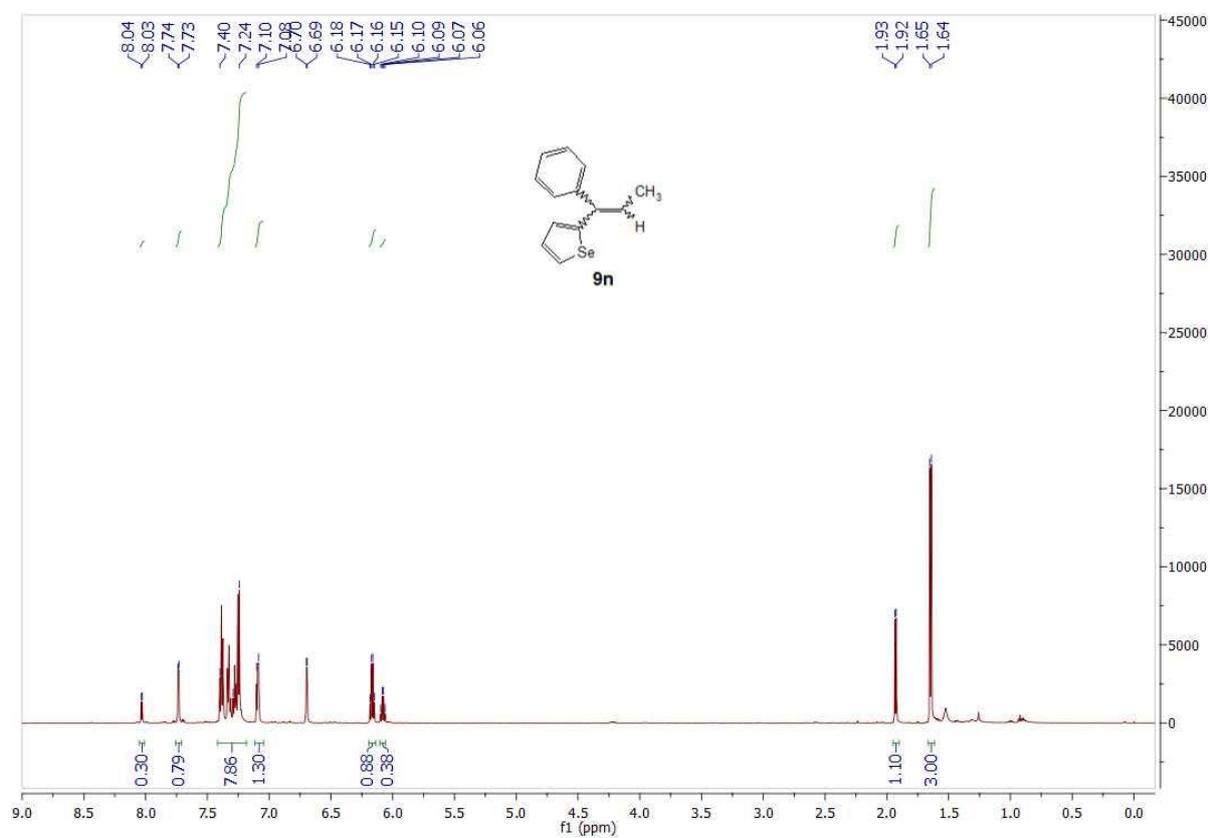


Figure S43: The ¹H NMR spectrum of compound **9n**.

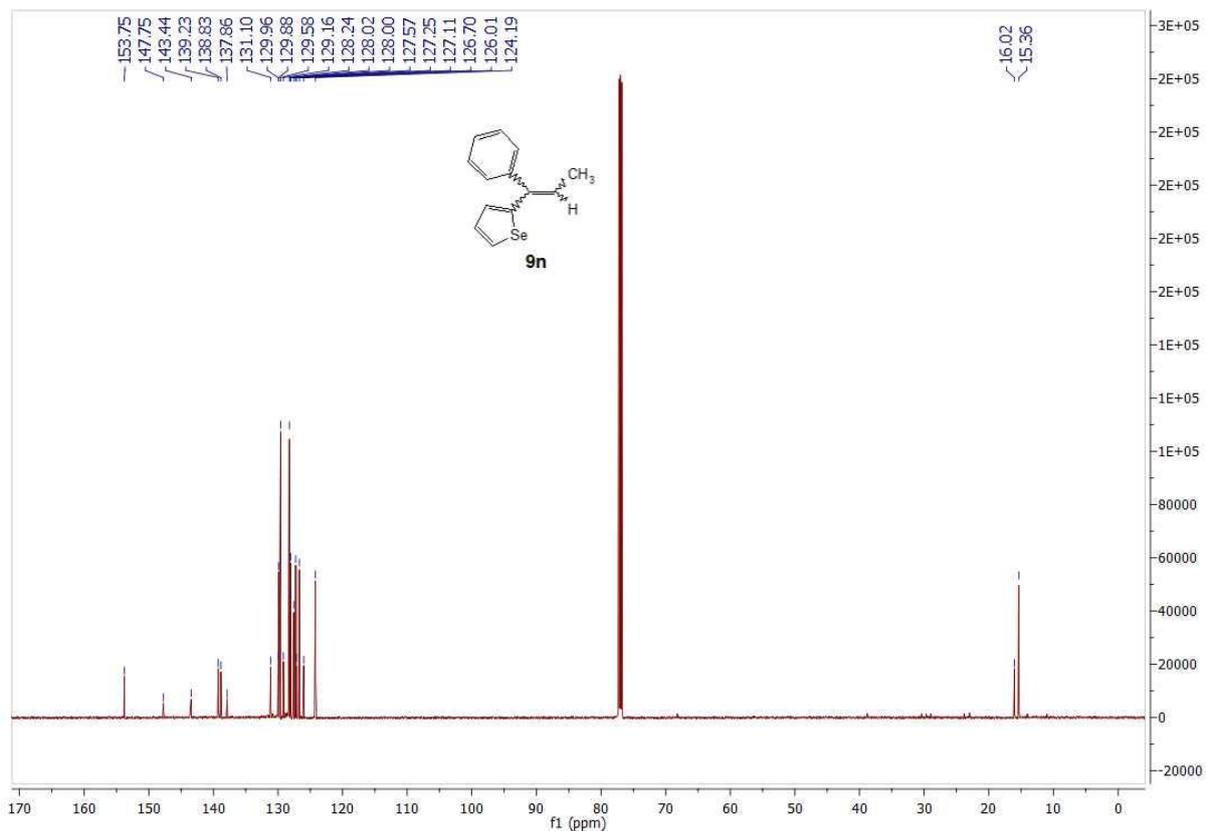


Figure S44: The ^{13}C NMR spectrum of compound **9n**.

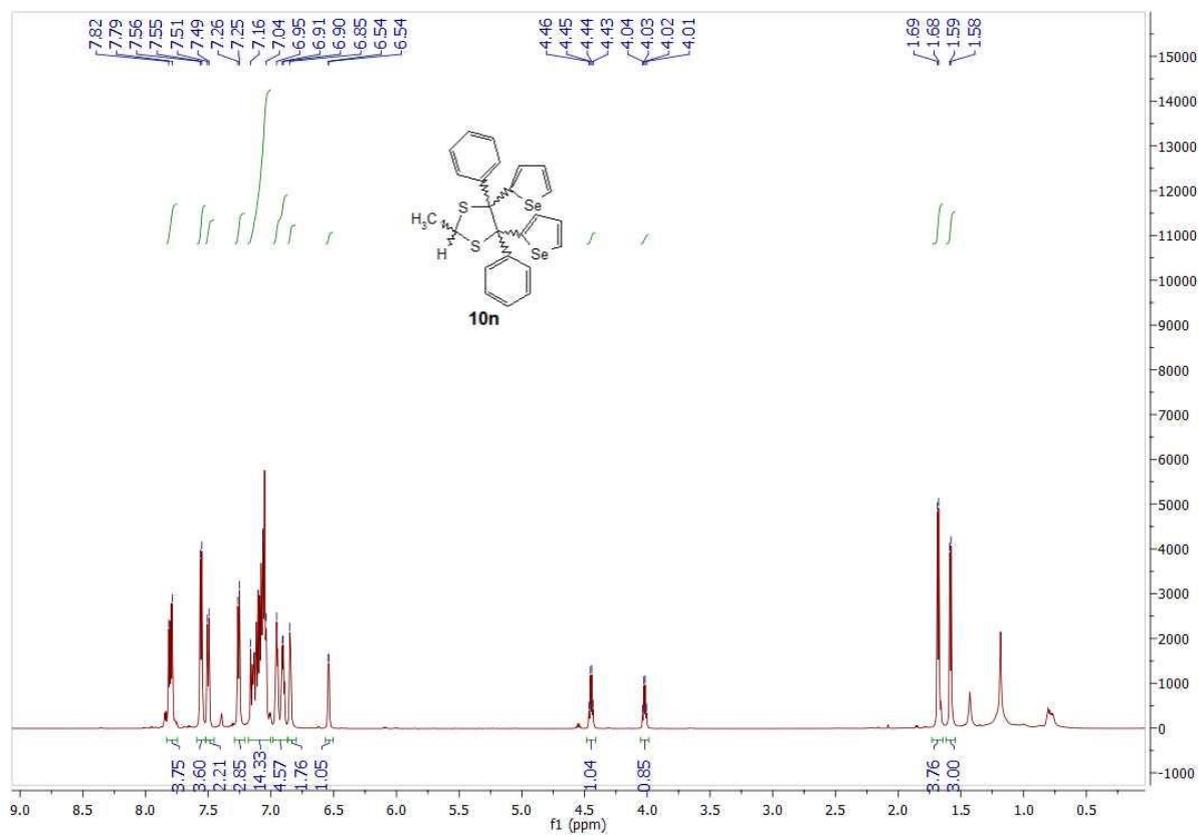


Figure S45: The ^1H NMR spectrum of compound **10n**.

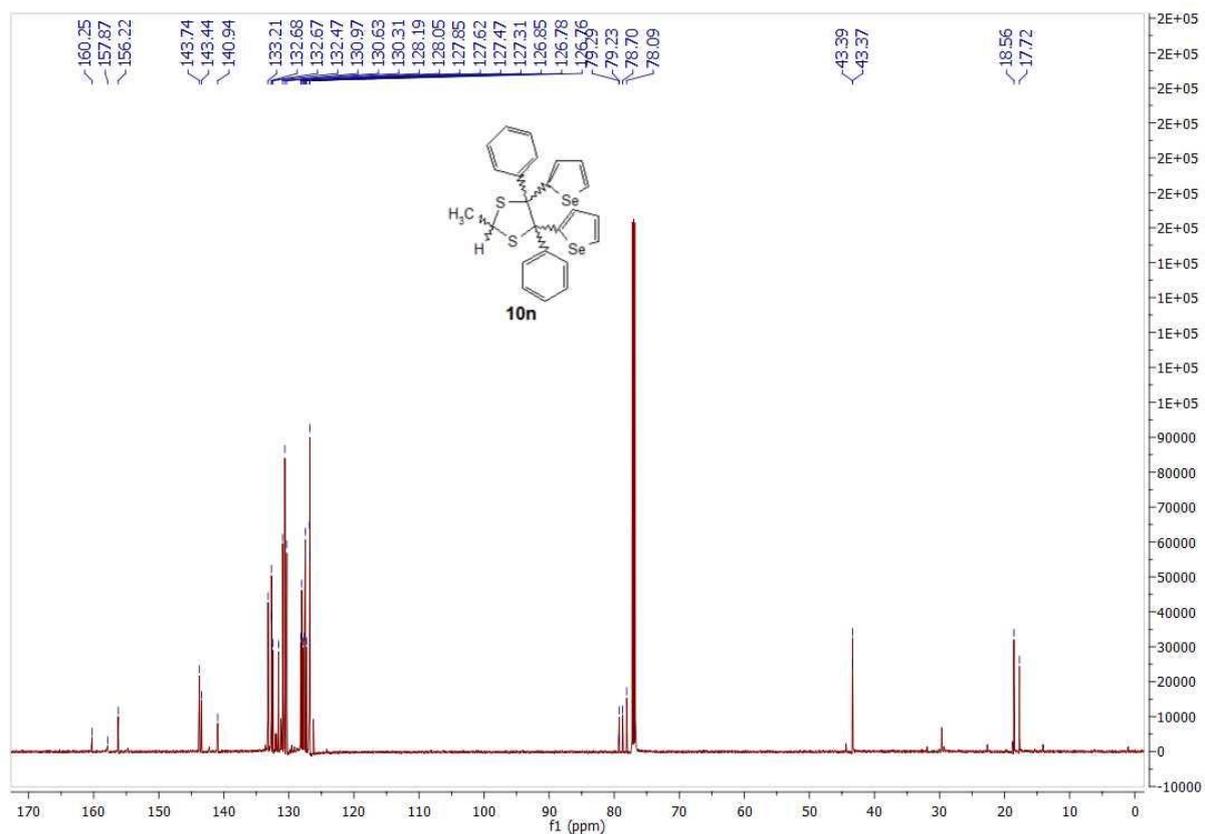


Figure S46: The ¹³C NMR spectrum of compound **10n**.

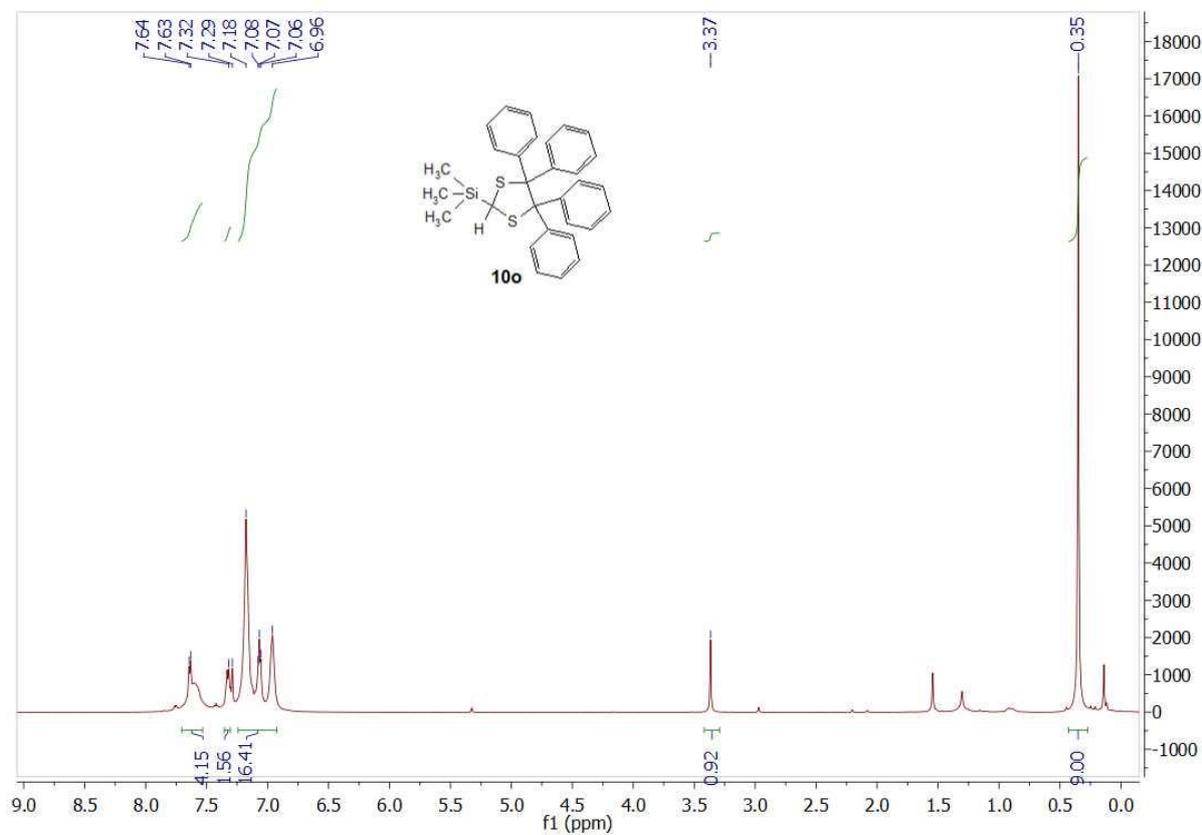


Figure S47: The ¹H NMR spectrum of compound **10o**.

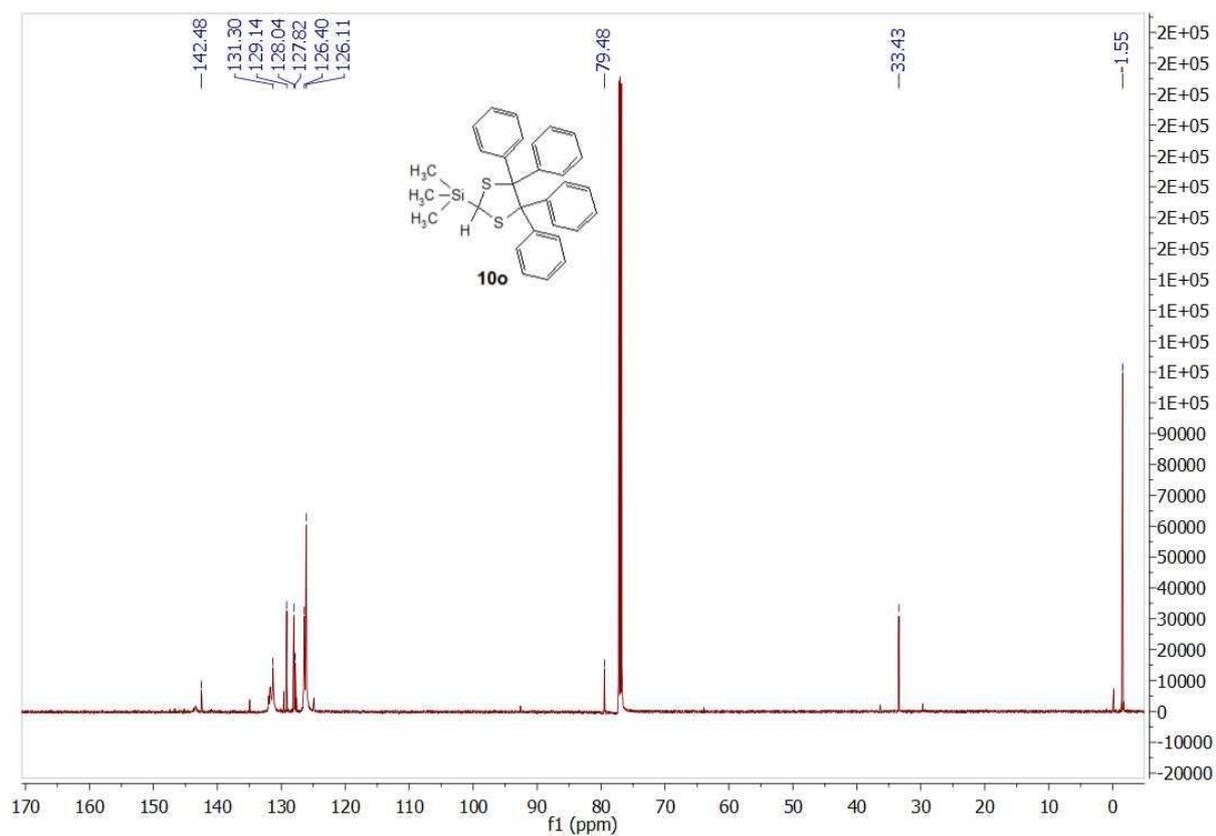


Figure S48: The ¹³C NMR spectrum of compound **10o**.

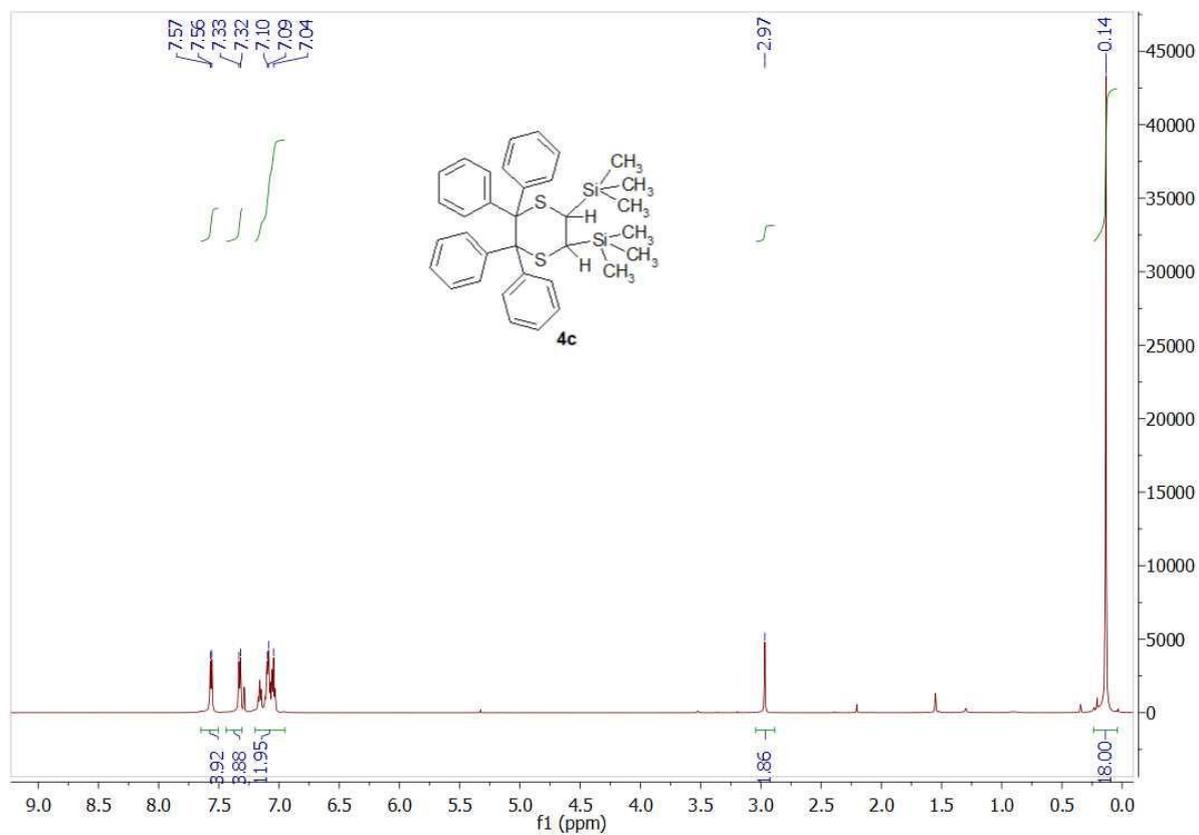


Figure S49: The ¹H NMR spectrum of compound **4c**.

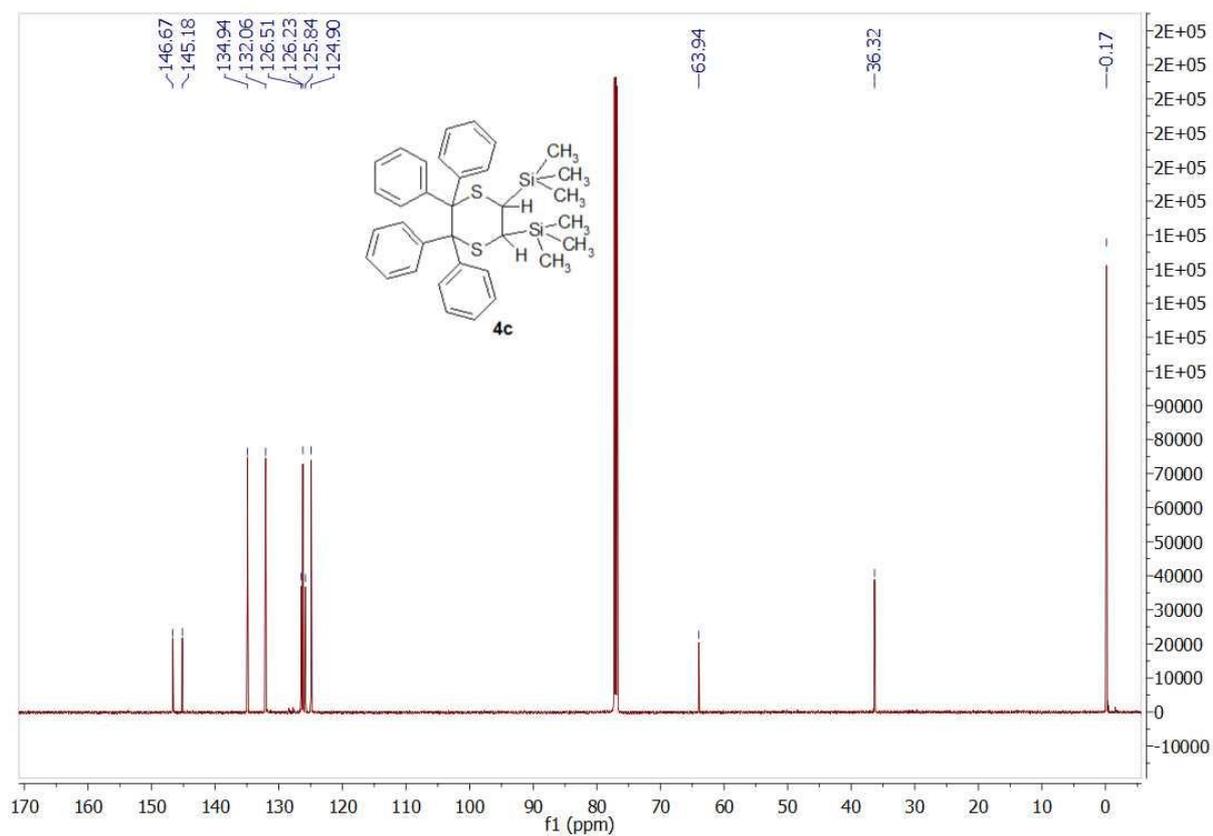


Figure S50: The ^{13}C NMR spectrum of compound **4c**.

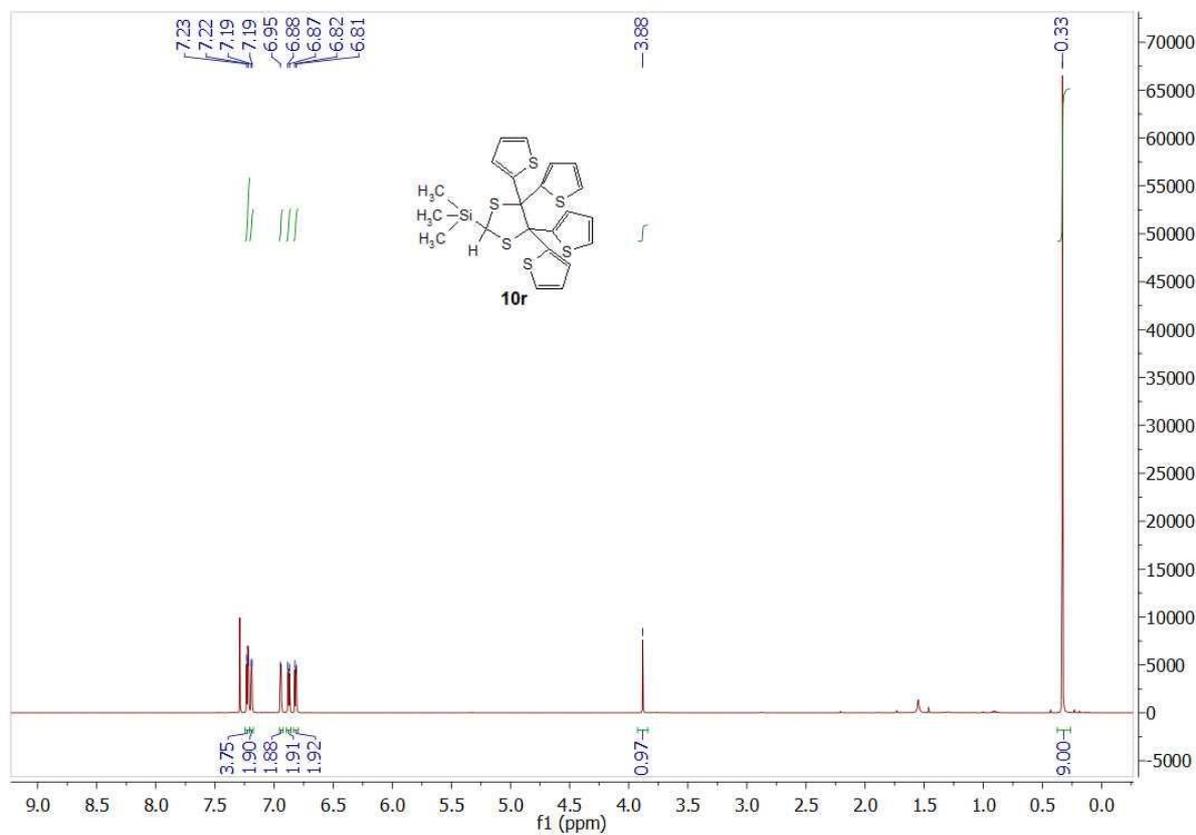


Figure S51: The ^1H NMR spectrum of compound **10r**.

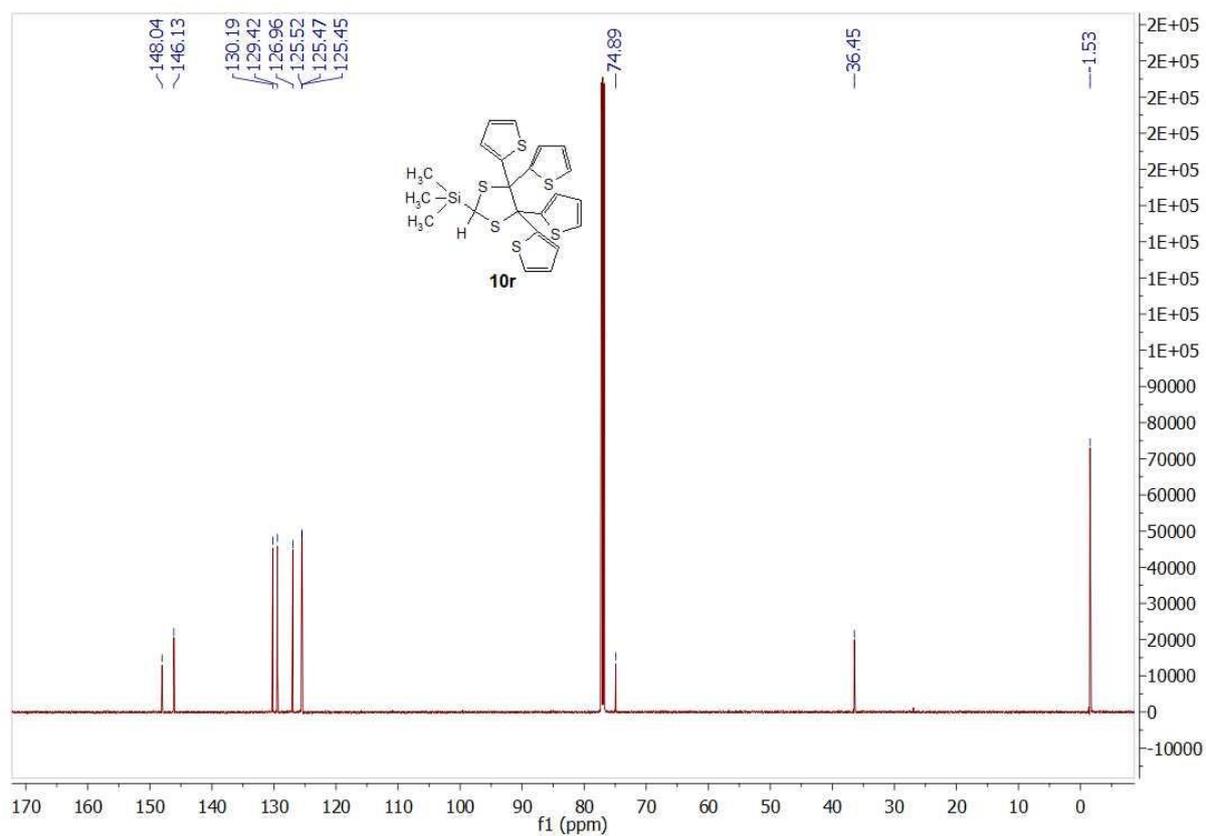


Figure S52: The ^{13}C NMR spectrum of compound **10r**.

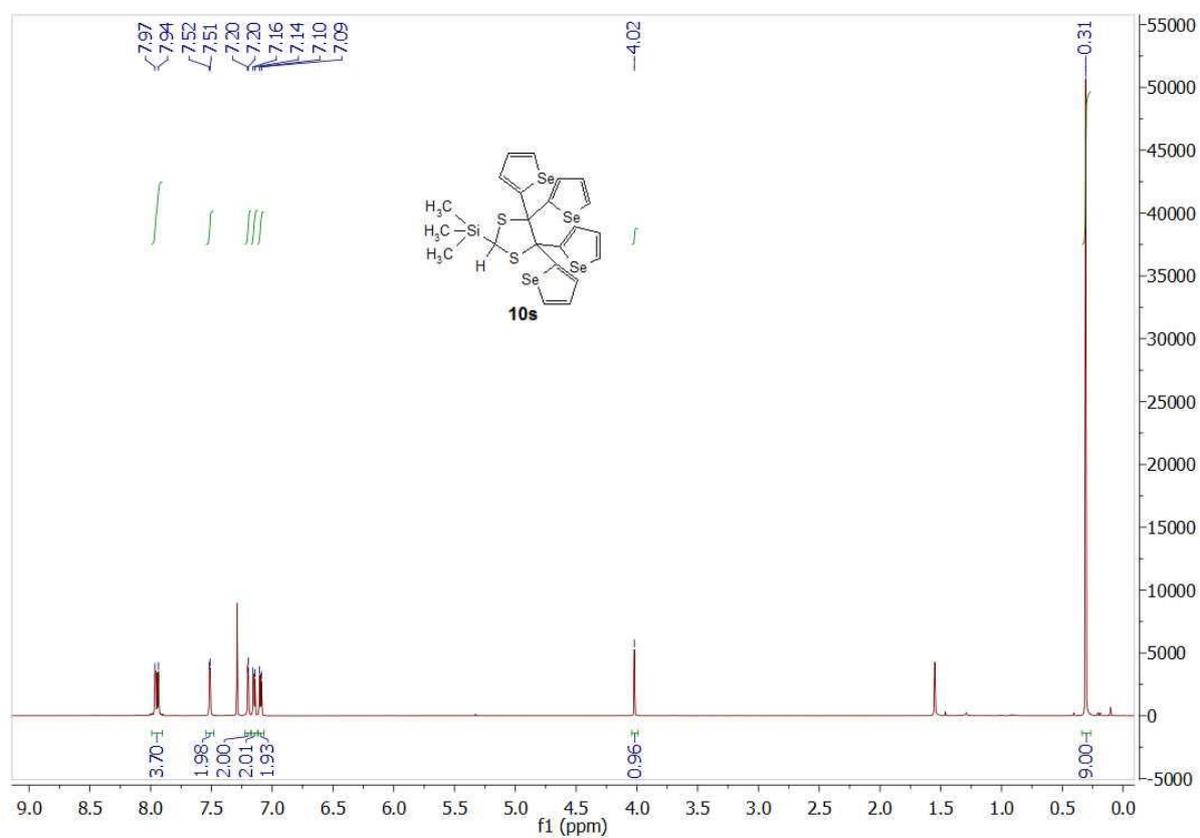


Figure S53: The ^1H NMR spectrum of compound **10s**.

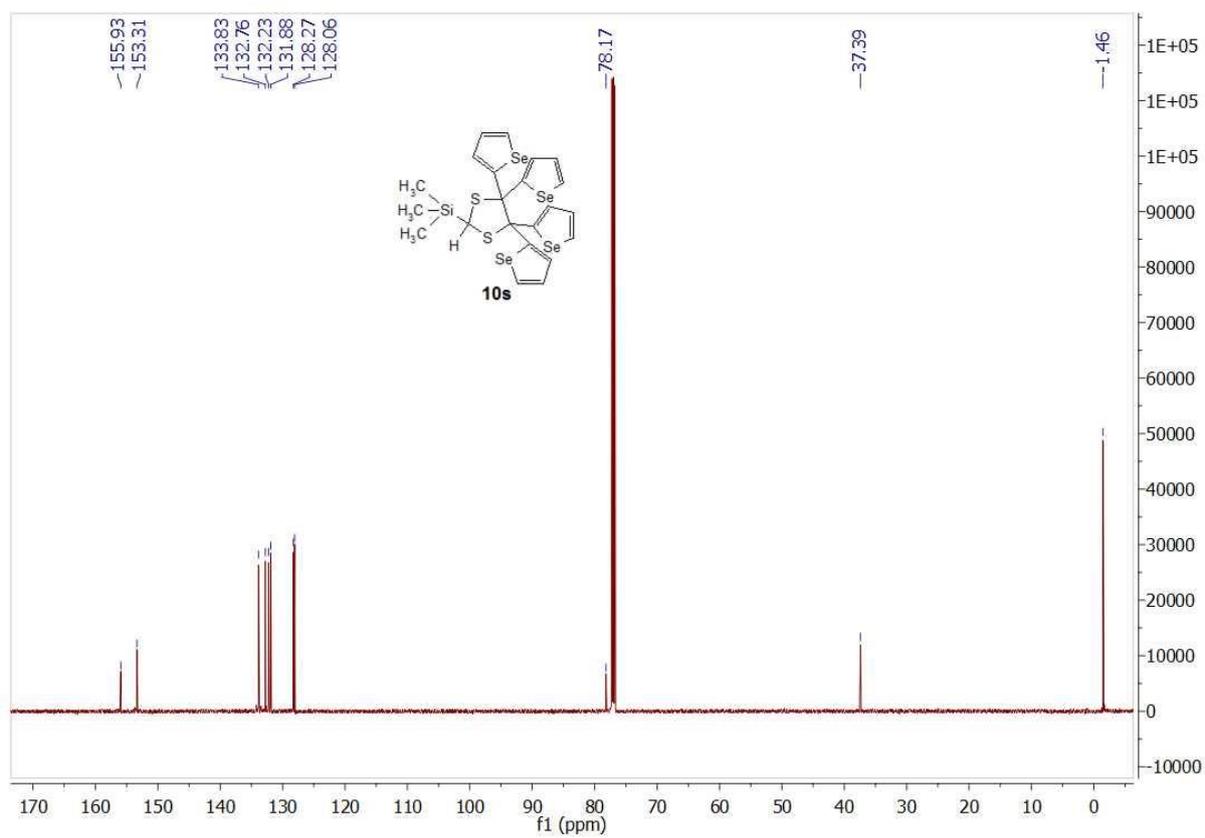


Figure S54: The ^{13}C NMR spectrum of compound **10s**.