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+Supporting Information

Rongalite in PEG-400 as a general and reusable system for the synthesis of 2,5-disubstituted chalcogenophenes

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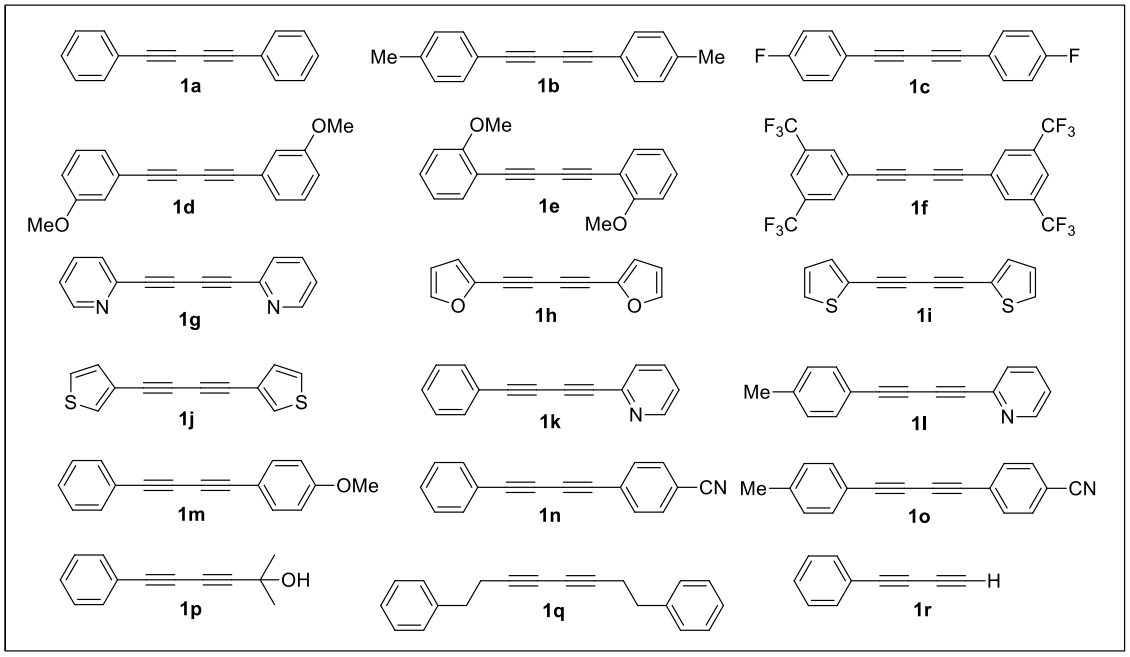
1. General Information

Unless otherwise stated, all glassware was flame-dried before use and all the reactions were performed under an argon atmosphere and heated in an oil bath. All reagents were purchased from commercial suppliers and used without further purification. DMF (*N*,*N*-dimethylformamide), DMSO (dimethyl sulfoxide), MeCN (acetonitrile), THF (tetrahydrofuran), DCM (dichloromethane), toluene and ethanol were purified and dried under classical methods.[1] Elemental tellurium was oven-dried at 150 ºC for 20 minutes always just before use. The reactions were monitored by thin-layer chromatography (TLC) using silica gel 60 F_{254} aluminum sheets, and the visualization of the spots were done under UV light (254 nm), stained with iodine, or by the mixture between 5% of vanillin in 10% of H_2SO_4 and heat as developing agents. Column chromatography was performed on silica gel (230-400 mesh). ^{1}H NMR and ^{13}C{^{1}H} NMR were recorded on 400 MHz spectrometer Varian Inova 400 and Bruker Avance 400. Chemical shifts (δ) are expressed in ppm downfield from TMS as internal standard in spectra made in $CDCl_3$. Coupling constants are reported in Hz. Hydrogen coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of doublet of doublets (ddd), multiplet (m) and broad signal (bs) as soon as appears. Melting points were recorded on a Buchi Melting Point M-560 equipment. High resolution mass spectra (HRMS) were recorded on a Micromass Q-Tof spectrometer, using electrospray ionization (ESI).

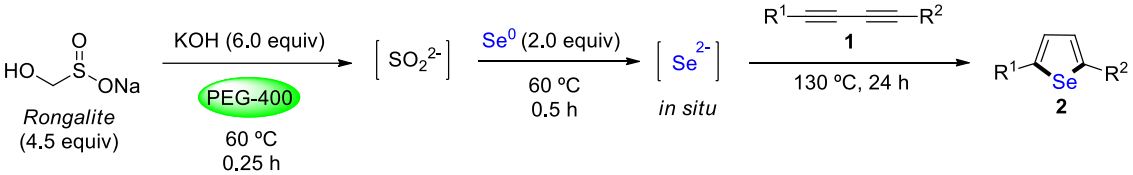
2. Synthesis of Starting Materials 1,3-diynes

Starting materials **1a-1j** and **1q** were prepared by oxidative homocoupling and substrates **1k-1p** were prepared by cross coupling from their corresponding terminal alkynes according to the literature.[2] Substrate **1r** was obtained from **1p** by retro-Favorskii reaction.[3]



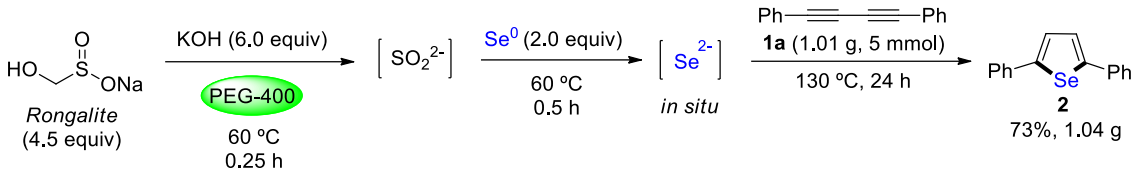
3. General Procedure and Spectral Data of Products 2, 3 and 4

3.1 General procedure for the synthesis of selenophenes 2



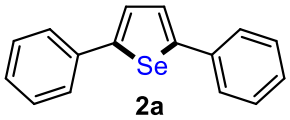
In a flame-dried Schlenk tube under argon atmosphere, PEG-400 (3.0 mL) was added and degassed with argon for 10 minutes. Next, rongalite (sodium hydroxymethanesulfinate hydrate, 4.5 equiv., 1.12 mmol) and KOH powder (6.0 equiv., 1.50 mmol) were added and the mixture was stirred at 60 ºC for 15 minutes. To this solution, elemental selenium (2.0 equiv., 0.50 mmol) was added and the reaction mixture was stirred at 60 ºC for 30 minutes. Next, the respective 1,3-diyne **1** (0.25 mmol) was added and the reaction mixture was stirred at 130 ºC for 24 h. The Schlenk tube was cooled to room temperature and a mixture of hexane/ethyl acetate (75:25 v:v, 20.0 mL) was added. After vigorous stirring, two layers were generated, and the upper layer containing the organic solvents was collected and this process was repeated until the complete extraction of the desired product **2** (monitored by TLC). The collected organic phase was concentrated under reduced pressure and further purified by column chromatography (hexane/ethyl acetate) on silica gel to give the respective 2,5-disubstituted selenophenes **2**.

3.1.1 Gram-scale synthesis of 2a

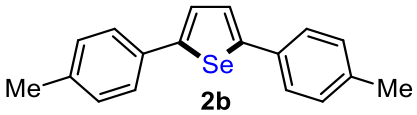


In a flame-dried Schlenk tube under argon atmosphere, PEG-400 (60 mL) was added and degassed with argon for 20 minutes. Next, rongalite (sodium hydroxymethanesulfinate hydrate, 4.5 equiv., 22.5 mmol) and KOH powder (6.0 equiv., 30 mmol) were added and the mixture was stirred at 60 ºC for 15 minutes. To this yellow homogenous solution, elemental selenium (2.0 equiv., 10 mmol) was added and the reaction mixture was stirred at 60 ºC for 30 minutes. Next, the respective 1,3-diyne **1a** (5 mmol) was added and the reaction mixture was stirred at 130 ºC for 24 h. The Schlenk tube was cooled to room temperature and the mixture was extracted 4 times with ethyl acetate and saturated aqueous NH_4Cl solution. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. The crude was further purified by column chromatography on silica gel to give the desired 2,5-diphenylselenophene **2a** in 73% yield (1.04 g).

3.2 Spectral Data of selenophenes 2

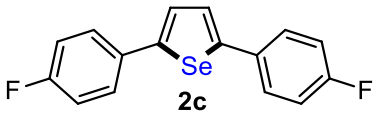


2,5-Diphenylselenophene (2a).[4] The product was isolated by column chromatography (hexane) as a white solid in 87% yield. mp 175–177 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (d, J = 7.3 Hz, 4H), 7.45 (s, 2H), 7.37 (t, J = 7.5 Hz, 4H), 7.28 (t, J = 7.3 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.8, 136.3, 128.9, 127.6, 126.2, 126.0.



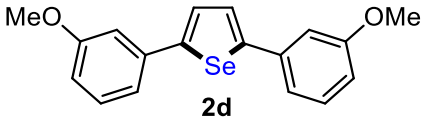
2,5-Bis-*p*-tolylselenophene (2b).[5] The product was isolated by column chromatography (hexane) as a white solid in 77% yield. mp 203–205 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ

7.44 (d, J = 7.9 Hz, 4H), 7.37 (s, 2H), 7.16 (d, J = 7.9 Hz, 4H), 2.35 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.3, 137.4, 133.6, 129.5, 125.9, 125.6, 21.2.



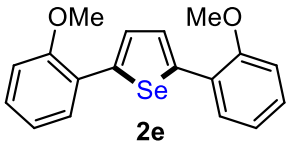
2c

2,5-Bis(4-fluorophenyl)selenophene (2c):[5] The product was isolated by column chromatography (hexane) as a yellow solid in 70% yield. mp 169–171 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 – 7.48 (m, 4H), 7.35 (s, 2H), 7.10 – 7.03 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 162.4 (d, $^1J_{C–F}$ = 247.7 Hz), 148.6, 132.5 (d, $^4J_{C–F}$ = 3.4 Hz), 127.6 (d, $^3J_{C–F}$ = 8.0 Hz), 126.2, 115.9 (d, $^2J_{C–F}$ = 21.9 Hz).



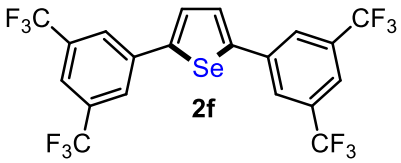
2d

2,5-bis(3-methoxyphenyl)selenophene (2d):[5] The product was isolated by column chromatography (hexane 90:10 ethyl acetate) as a light-yellow solid in 95% yield. mp 67–69 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 (s, 2H), 7.27 (t, J = 7.9 Hz, 2H), 7.15 (d, J = 7.7 Hz, 2H), 7.13 – 7.06 (m, 2H), 6.83 (dd, J = 8.1, 1.9 Hz, 2H), 3.84 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.9, 149.7, 137.6, 129.9, 126.3, 118.7, 113.0, 111.6, 55.3.



2e

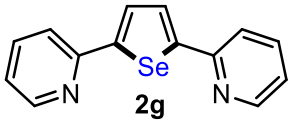
2,5-bis(2-methoxyphenyl)selenophene (2e):[5] The product was isolated by column chromatography (hexane 90:10 ethyl acetate) as a yellow solid in 30% yield. mp 94–96 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.74 (dd, J = 7.7, 1.5 Hz, 2H), 7.71 (s, 2H), 7.27 – 7.21 (m, 2H), 7.04 – 6.96 (m, 4H), 3.96 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.0, 143.9, 127.9, 127.0, 126.1, 125.5, 120.9, 111.6, 55.5.



2f

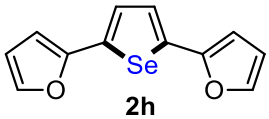
2,5-bis(3,5-bis(trifluoromethyl)phenyl)selenophene (2f):[5] The product was isolated by column chromatography (hexane) as a white solid in 56% yield. mp 158–160 °C. **^{1}H**

NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 4H), 7.82 (s, 2H), 7.64 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 148.3, 137.7, 132.6 (q, $^2J_{C–F}$ = 33.5 Hz), 128.7, 125.9, 123.1 (q, $^1J_{C–F}$ = 272.9 Hz) 121.4.



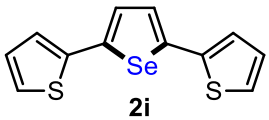
2g

2,5-di(pyridin-2-yl)selenophene (2g): The product was isolated by column chromatography (hexane 60:40 ethyl acetate) as a red solid in 52% yield. mp 177–179 ^oC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.57 – 8.54 (m, 2H), 7.78 (s, 2H), 7.69 – 7.65 (m, 4H), 7.18 – 7.12 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.9, 152.8, 149.7, 136.4, 127.3, 122.0, 117.9. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{11}N_2Se$ 287.0082; found 287.0087.



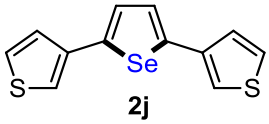
2h

2,5-di(furan-2-yl)selenophene (2h): The product was isolated by column chromatography (hexane) as a brown solid in 51% yield. mp 50–52 ^oC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.40 (dd, J = 1.8, 0.7 Hz, 2H), 7.32 (s, 2H), 6.50 (dd, J = 3.4, 0.7 Hz, 2H), 6.45 (dd, J = 3.4, 1.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.1, 141.8, 136.5, 124.7, 112.0, 105.1. **HRMS** (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{12}H_8O_2SeNa$ 286.9582; found 286.9588.



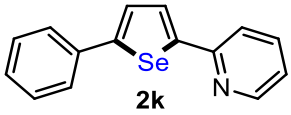
2i

2,5-di(thiophen-2-yl)selenophene (2i):[5] The product was isolated by column chromatography (hexane) as a yellow solid in 81% yield. mp 198–200 ^oC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.24 – 7.18 (m, 4H), 7.10 (dd, J = 3.6, 0.7 Hz, 2H), 6.99 (dd, J = 5.0, 3.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 141.0, 139.3, 127.9, 126.3, 124.6, 124.3.



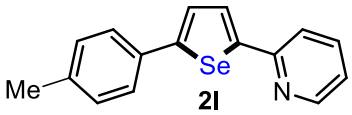
2j

2,5-di(thiophen-3-yl)selenophene (2j): The product was isolated by column chromatography (hexane) as a white solid in 73% yield. mp 185-187 ºC. **^{1}H NMR** (400 MHz, DMSO-d_6): δ 7.69 (dd, J = 2.9, 1.2 Hz, 2H), 7.63 (dd, J = 5.0, 2.9 Hz, 2H), 7.49 (s, 2H), 7.43 (dd, J = 5.0, 1.2 Hz, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 142.6, 137.5, 127.9, 127.0, 126.4, 120.9. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{12}H_9S_2Se$ 296.9306; found 296.9312.



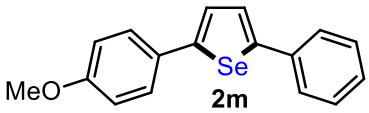
2k

2-(5-phenylselenophen-2-yl)pyridine (2k): The product was isolated by column chromatography (hexane 95:5 ethyl acetate) as an orange solid in 74% yield. mp 123-125 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.54 – 8.52 (m, 1H), 7.71 (d, J = 4.1 Hz, 1H), 7.67 – 7.64 (m, 2H), 7.63 – 7.58 (m, 2H), 7.50 (d, J = 4.1 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.33 – 7.27 (m, 1H), 7.15 – 7.10 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.9, 152.4, 150.5, 149.6, 136.45, 136.40, 128.9, 127.8, 127.1, 126.3, 126.1, 121.8, 117.5. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{12}NSe$ 286.0130; found 286.0132.



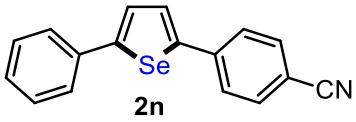
2l

2-(5-(p-tolyl)selenophen-2-yl)pyridine (2l): The product was isolated by column chromatography (hexane 95:5 ethyl acetate) as an orange solid in 89% yield. mp 156–158 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.54 – 8.51 (m, 1H), 7.70 (d, J = 4.1 Hz, 1H), 7.67 – 7.64 (m, 2H), 7.50 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 4.1 Hz, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.15 – 7.09 (m, 1H), 2.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.0, 152.6, 149.9, 149.6, 137.8, 136.4, 133.7, 129.6, 127.1, 126.0, 125.8, 121.7, 117.5, 21.2. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{14}NSe$ 300.0287; found 300.0296.



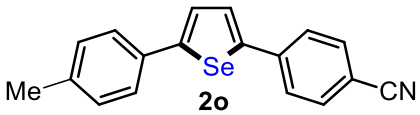
2m

2-(4-methoxyphenyl)-5-phenylselenophene (2m):[5] The product was isolated by column chromatography (hexane 90:10 ethyl acetate) as a light-yellow solid in 80% yield. mp 144–146 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 – 7.53 (m, 2H), 7.50 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 4.0 Hz, 1H), 7.36 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 4.0 Hz, 1H), 7.30 – 7.26 (m, 1H), 6.91 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.3, 149.7, 148.6, 136.4, 129.2, 128.9, 127.4, 127.3, 126.2, 125.9, 125.1, 114.3, 55.4.



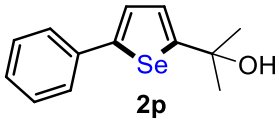
2n

4-(5-phenylselenophen-2-yl)benzonitrile (2n):[6] The product was isolated by column chromatography (hexane 95:5 ethyl acetate) as a light-yellow solid in 60% yield. mp 174-176 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65 – 7.61 (m, 4H), 7.59 – 7.55 (m, 3H), 7.48 (d, J = 4.1 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.36 – 7.30 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ: 152.5, 146.9, 140.5, 135.7, 132.7, 129.0, 128.4, 128.2, 126.4, 126.1, 126.1, 118.8, 110.5.



2o

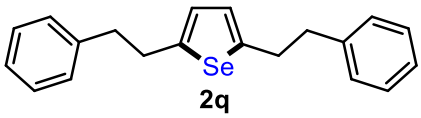
4-(5-(p-tolyl)selenophen-2-yl)benzonitrile (2o):[6] The product was isolated by column chromatography (hexane 90:10 ethyl acetate) as a light yellow solid in 45% yield. mp 228-230 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.67 – 7.59 (m, 4H), 7.55 (d, J = 4.0 Hz, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 4.0 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 2.37 (s, J = 6.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.8, 146.2, 140.6, 138.3, 133.0, 132.7, 129.7, 128.4, 126.1, 126.0, 125.9, 118.9, 110.3, 21.2.



2p

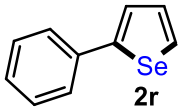
2-(5-phenylselenophen-2-yl)propan-2-ol (2p): The product was isolated by column chromatography (hexane 85:15 ethyl acetate) as a yellow oil in 52% yield. **^{1}H NMR** (400

MHz, $CDCl_3$): δ 7.51 (d, J = 7.2 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.29 (d, J = 3.9 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.04 (d, J = 3.9 Hz, 1H), 2.23 (bs, 1H), 1.68 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.7, 149.0, 136.5, 128.8, 127.4, 126.0, 124.8, 124.6, 72.9, 32.3. **HRMS** (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{13}H_{14}OSeNa$ 289.0103; found 289.0108.



2q

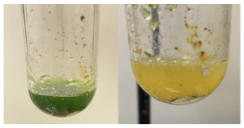
2,5-diphenethylselenophene (2q): The product was isolated by column chromatography (hexane 95:5 ethyl acetate) as a yellow oil in 88% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 4H), 7.23 – 7.17 (m, 6H), 6.70 (s, 2H), 3.16 – 3.10 (m, 4H), 2.98 – 2.92 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.6, 141.1, 128.4, 128.3, 126.1, 126.0, 38.7, 34.7. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{21}Se$ 341.0804; found 341.0798.

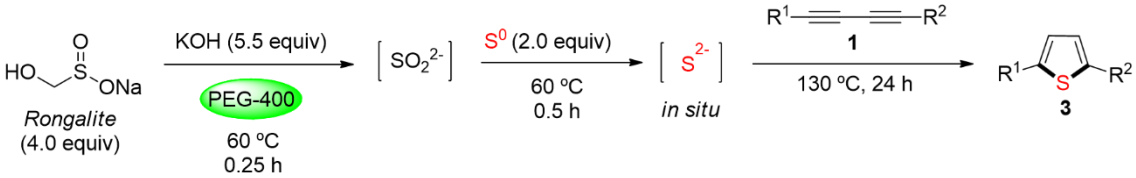


2r

2-phenylselenophene (2r).[7] The product was isolated by column chromatography (hexane) as a white solid in 40% yield. mp 40–42 ºC **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.93 (dd, J = 5.6, 1.1 Hz, 1H), 7.59 – 7.54 (m, 2H), 7.46 (dd, J = 3.8, 1.1 Hz, 1H), 7.38 – 7.33 (m, 2H), 7.31 (dd, J = 5.6, 3.8 Hz, 1H), 7.30 – 7.25 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.8, 136.4, 130.6, 129.9, 128.9, 127.5, 126.4, 125.2.

3.3 General Procedure for the Synthesis of Thiophenes 3





In a flame-dried Schlenk tube under argon atmosphere, PEG-400 (3.0 mL) was added and degassed with argon for 10 minutes. Next, rongalite (sodium hydroxymethanesulfinate hydrate, 4.0 equiv., 1 mmol) and KOH powder (5.5 equiv., 1.375 mmol) were added and the mixture was stirred at 60 ºC for 15 minutes. To this solution, elemental sulfur (2.0 equiv., 0.50 mmol) was added (instantly producing a dark green solution) and the reaction

mixture was stirred at 60 ºC for 30 minutes, and then became a yellow solution. The respective 1,3-diyne **1** (0.25 mmol) was added and the reaction mixture was stirred at 130 ºC for 24 h. The Schlenk tube was cooled to room temperature and a mixture of hexane/ethyl acetate (75:25 v:v, 20.0 mL) was added. After vigorous stirring, two layers were generated, and the upper layer containing the organic solvents was collected and this process was repeated until complete the extraction of the desired products **3** (monitored by TLC). The collected organic phase was concentrated under reduced pressure and further purified by column chromatography (hexanes/ethyl acetate) on silica gel to give the respective 2,5-disubstituted thiophenes **3**.

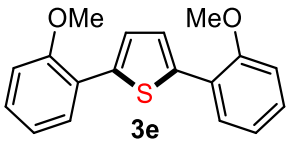
3.4 Spectral Data of Thiophenes 3

2,5-Diphenylthiophene (3a).[8] The product was isolated by column chromatography (hexane) as a white solid in 95% yield. mp 149–151 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.64 – 7.60 (m, 4H), 7.40 – 7.34 (m, 4H), 7.31 – 7.24 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 143.6, 134.3, 128.9, 127.5, 125.6, 124.0.

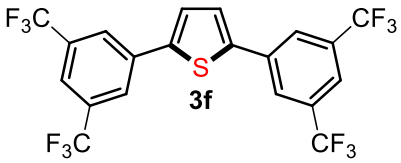
2,5-Di-*p*-tolylthiophene (3b).[8] The product was isolated by column chromatography (hexane) as a white solid in 76% yield. 177–179 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.50 (d, J = 8.2 Hz, 4H), 7.21 (s, 2H), 7.18 (d, J = 8.2 Hz, 4H), 2.36 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 143.2, 137.3, 131.6, 129.6, 125.5, 123.4, 21.2.

2,5-Bis(4-fluorophenyl)thiophene (3c).[8] The product was isolated by column chromatography (hexane) as a white solid in 70% yield. mp 177–179 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.60 – 7.54 (m, 4H), 7.18 (s, 2H), 7.12 – 7.04 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 162.3 (d, $^1J_{C-F}$ = 247.5 Hz), 142.5, 130.5 (d, $^4J_{C-F}$ = 3.5 Hz), 127.3 (d, $^3J_{C-F}$ = 8.0 Hz), 124.0, 115.9 (d, $^2J_{C-F}$ = 21.9 Hz).

2,5-bis(3-methoxyphenyl)thiophene (3d).[8] The product was isolated by column chromatography (hexane 90:10 ethyl acetate) as a light-yellow solid in 68% yield. mp 74–76 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 (t, J = 7.9 Hz, 2H), 7.27 (s, 2H), 7.24 – 7.21 (m, 2H), 7.17 – 7.15 (m, 2H), 6.84 (ddd, J = 8.2, 2.5, 1.0 Hz, 2H), 3.86 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.9, 143.5, 135.6, 129.9, 124.1, 118.2, 113.1, 111.3, 55.3.



2,5-bis(2-methoxyphenyl)thiophene (3e).[8] The product was isolated by column chromatography as a yellow solid in 17% yield. mp 90–92 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (dd, J = 7.5, 1.9 Hz, 2H), 7.49 (s, 2H), 7.28 – 7.23 (m, 2H), 7.03 – 6.97 (m, 4H), 3.94 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.7, 139.2, 128.4, 128.1, 125.7, 123.6, 120.9, 111.6, 55.6.



2,5-bis(3,5-bis(trifluoromethyl)phenyl)thiophene (3f).[8] The product was isolated by column chromatography (hexane) as a light-yellow solid in 43% yield. mp 163–165 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04 (s, 4H), 7.82 (s, 2H), 7.49 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 142.1, 135.6, 132.6 (q, $^2J_{C\text{-}F}$ = 33.5 Hz), 126.4, 125.5, 123.1 (q, $^1J_{C\text{-}F}$ = 273 Hz), 121.4.

2,5-di(pyridin-2-yl)thiophene (3g): The product was isolated by column chromatography (hexane 70:30 ethyl acetate) as a yellow solid in 80% yield. mp 172-174 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.61 – 8.58 (m, 2H), 7.72 – 7.66 (m, 4H), 7.63 (s, 2H), 7.16 (ddd, J = 6.3, 4.9, 2.3 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.3, 149.6,

145.9, 136.6, 125.6, 122.1, 118.9. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{11}N_2S$ 239.0638; found 239.0642.

3h

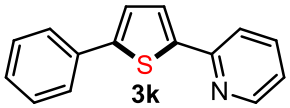
2,5-di(furan-2-yl)thiophene (3h): The product was isolated by column chromatography (hexane) as a yellow solid in 42% yield. mp 64-66 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.41 (dd, J = 1.8, 0.8 Hz, 2H), 7.16 (s, 2H), 6.50 (dd, J = 3.4, 0.8 Hz, 2H), 6.44 (dd, J = 3.4, 1.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.1, 141.7, 132.2, 123.0, 111.8, 105.2. **HRMS** (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{12}H_8O_2SNa$ 239.0138; found 239.0143.

3i

2,2':5',2''-terthiophene (3i).[8] The product was isolated by column chromatography (hexane) as a yellow solid in 64% yield. mp 93-95 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.22 (dd, J = 5.1, 1.0 Hz, 2H), 7.17 (dd, J = 3.6, 1.1 Hz, 2H), 7.08 (s, 2H), 7.02 (dd, J = 5.1, 3.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.1, 136.2, 127.9, 124.4, 124.3, 123.7.

3j

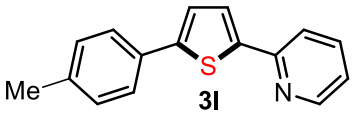
3,2':5',3''-terthiophene (3j):[9] The product was isolated by column chromatography (hexane) as a white solid in 42% yield. mp 190-192 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.39 – 7.33 (m, 4H), 7.31 (dd, J = 5.0, 1.4 Hz, 2H), 7.12 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.5, 135.5, 126.4, 125.9, 123.7, 119.3.



3k

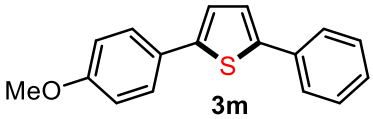
2-(5-phenylthiophen-2-yl)pyridine (3k):[10] The product was isolated by column chromatography (hexane 80:20 ethyl acetate) as a yellow solid in 62% yield. mp 109-111 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.58 (ddd, J = 4.9, 1.6, 1.1 Hz, 1H), 7.72 – 7.63 (m, 4H), 7.54 (d, J = 3.9 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.35 – 7.27 (m, 2H), 7.17 – 7.10 (m,

1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.4, 149.5, 146.1, 143.8, 136.6, 134.2, 128.9, 127.8, 125.7, 125.4, 123.9, 121.8, 118.5.



3l

2-(5-(p-tolyl)thiophen-2-yl)pyridine (3l):[11] The product was isolated by column chromatography (hexane 80:20 ethyl acetate) as a yellow solid in 86% yield. mp 128–130 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.57 (ddd, J = 4.9, 1.6, 1.1 Hz, 1H), 7.70 – 7.62 (m, 2H), 7.59 – 7.55 (m, 2H), 7.53 (d, J = 3.8 Hz, 1H), 7.28 (d, J = 3.9 Hz, 1H), 7.23 – 7.18 (m, 2H), 7.15 – 7.10 (m, 1H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.6, 149.5, 146.4, 143.2, 137.8, 136.5, 131.5, 129.6, 125.6, 125.4, 123.4, 121.7, 118.4, 21.2.

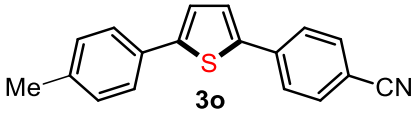


3m

2-(4-methoxyphenyl)-5-phenylthiophene (3m):[8] The product was isolated by column chromatography (hexane 90:10 ethyl acetate) as a light-yellow solid in 80% yield. mp 166–168 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 – 7.59 (m, 2H), 7.56 (d, J = 8.9 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.16 (d, J = 3.7 Hz, 1H), 6.93 (d, J = 8.9 Hz, 2H), 3.84 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.2, 143.6, 142.5, 134.4, 128.9, 127.3, 127.2, 126.9, 125.5, 123.9, 122.9, 114.3, 55.3.

3n

4-(5-phenylthiophen-2-yl)benzonitrile (3n).[8] The product was isolated by column chromatography (hexane 90:10 ethyl acetate) as a light yellow solid in 97% yield. mp 173-175 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72 – 7.68 (m, 2H), 7.67 – 7.61 (m, 4H), 7.44 – 7.38 (m, 3H), 7.36 – 7.30 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.1, 140.9, 138.5, 133.6, 132.7, 129.0, 128.1, 126.0, 125.8, 125.7, 124.3, 118.8, 110.4.



3o

4-(5-(p-tolyl)thiophen-2-yl)benzonitrile (3o):[12] The product was isolated by column chromatography (hexane 90:10 ethyl acetate) as a light yellow solid in 51% yield. mp 198-200 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.71 – 7.61 (m, 4H), 7.52 (d, J = 8.2 Hz, 2H), 7.38 (d, J = 3.8 Hz, 1H), 7.27 (d, J = 3.8 Hz, 1H), 7.21 (d, J = 8.2 Hz, 2H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 146.3, 140.4, 138.6, 138.2, 132.7, 130.9, 129.7, 126.0, 125.7, 125.6, 123.8, 118.9, 110.2, 21.2.

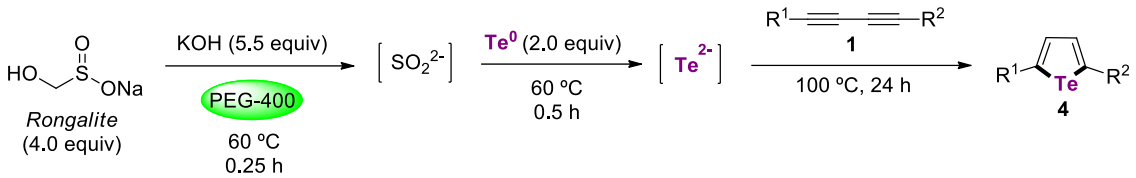
3p

2-(5-phenylthiophen-2-yl)propan-2-ol (3p): The product was isolated by column chromatography (hexane 90:10 ethyl acetate) as a brown oil in 33% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 – 7.47 (m, 2H), 7.28 (t, J = 7.6 Hz, 2H), 7.22 – 7.16 (m, 1H), 7.06 (d, J = 3.7 Hz, 1H), 6.84 (d, J = 3.7 Hz, 1H), 2.04 (bs, 1H), 1.62 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.7, 142.7, 134.4, 128.8, 127.3, 125.6, 122.9, 122.5, 71.4, 32.0. **HRMS** (ESI) *m/z*: $[M - OH]^+$ calcd for $C_{13}H_{13}S$ 201.0732; found 201.0750.

3q

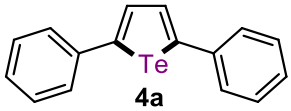
2,5-diphenethylthiophene (3q): The product was isolated by column chromatography (hexane 95:5 ethyl acetate) as a yellow oil in 70% yield. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 4H), 7.23 – 7.17 (m, 6H), 6.54 (s, 2H), 3.09 – 3.03 (m, 4H), 2.98 – 2.92 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 142.3, 141.2, 128.4, 128.3, 126.0, 123.8, 38.0, 32.1. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{21}S$ 293.1358; found 293.1363.

3.5 General Procedure for the Synthesis of Tellurophenes 4

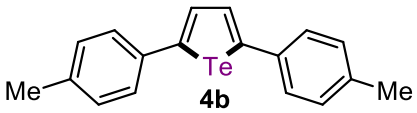


In a flame-dried Schlenk tube under argon atmosphere, PEG-400 (3.0 mL) was added and degassed with argon for 10 minutes. Next, rongalite (sodium hydroxymethanesulfinate hydrate, 4.0 equiv., 1 mmol) and KOH powder (5.5 equiv., 1.375 mmol) were added and the mixture was stirred at 60 ºC for 15 minutes. To this solution, elemental tellurium (2.0 equiv., 0.50 mmol) was added and the mixture was stirred at 60 ºC for 30 minutes, which then became a dark purple solution. The respective 1,3-diyne **1** (0.25 mmol) was added and the reaction mixture was stirred at 100 ºC for 24 h. The Schlenk tube was cooled to room temperature and a mixture of hexane/ethyl acetate (75:25 v:v, 20.0 mL) was added. After vigorous stirring, two layers were generated, and the upper layer containing the organic solvents was collected and this process was repeated until complete extraction of the desired products **4** (monitored by TLC). The collected organic phase was concentrated under reduced pressure and further purified by column chromatography (hexanes/ethyl acetate) on silica gel to give the respective 2,5-disubstituted tellurophenes **4**.

3.6 Spectral Data of Tellurophenes 4

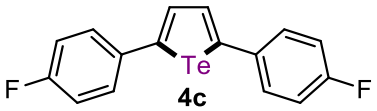


2,5-diphenyltellurophene (4a):[13] The product was isolated by column chromatography (hexane) as a yellow solid in 94% yield. mp 223-225 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (ppm): 7.82 (s, 2H), 7.48 (d, *J* = 7.3 Hz, 4H), 7.34 (t, *J* = 7.4 Hz, 4H), 7.27 (t, *J* = 7.2 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ (ppm): 148.2, 139.9, 133.9, 128.9, 127.6, 126.7.



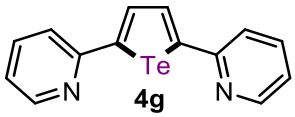
2,5-Bis-*p*-tolyltellurophene (4b).[13] The product was isolated by column chromatography (hexane) as a yellow solid in 60% yield. mp 246-248 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$) δ:

7.75 (s, 2H), 7.37 (d, J = 7.9 Hz, 4H), 7.14 (d, J = 7.9 Hz, 4H), 2.34 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 147.6, 137.4, 137.3, 133.3, 129.6, 126.6, 21.1.



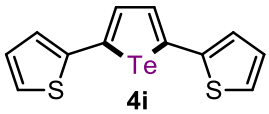
4c

2,5-bis(4-fluorophenyl)tellurophene (4c): The product was isolated by column chromatography (hexane) as a white solid in 52% yield. mp 176-178 ºC. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.96 (s, 2H), 7.64 – 7.58 (m, 4H), 7.25 – 7.18 (m, 4H). **^{13}C NMR** (100 MHz, DMSO-d_6) δ 161.8 (d, $^1J_{C\text{-}F}$ = 245.4 Hz), 146.3, 135.9 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 134.7, 128.3 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 116.0 (d, $^2J_{C\text{-}F}$ = 21.8 Hz). **HRMS** (ESI) *m/z*: $[M + OH]^+$ calcd for $C_{16}H_{11}F_2OTe$ 386.9835; found 386.9844.



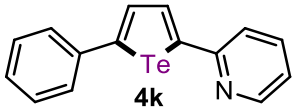
4g

2,5-di(pyridin-2-yl)tellurophene (4g): The product was isolated by column chromatography (hexane 80:20 ethyl acetate) as a light-yellow solid in 32% yield. mp 197-199 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.47 (ddd, J = 4.9, 1.6, 1.0 Hz, 2H), 8.25 (s, J = 3.2 Hz, 2H), 7.71 – 7.61 (m, 4H), 7.16 – 7.11 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.8, 153.7, 149.8, 136.3, 134.0, 122.1, 116.0. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{11}N_2Te$ 336.9979; found 336.9988.



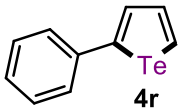
4i

2,5-di(thiophen-2-yl)tellurophene (4i).[13] The product was isolated by column chromatography (hexane) as a yellow solid in 44% yield. mp 128-130 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (s, 2H), 7.18 (dd, J = 5.1, 1.2 Hz, 2H), 7.00 (dd, J = 3.6, 1.2 Hz, 2H), 6.96 (dd, J = 5.1, 3.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.7, 137.3, 133.6, 127.8, 125.0, 124.7.



4k

2-(5-phenyltellurophen-2-yl)pyridine (4k): The product was isolated by column chromatography (hexane 90:10 ethyl acetate) as a light-yellow solid in 25% yield. mp 148-150 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.47 – 8.41 (m, 1H), 8.13 (d, J = 4.4 Hz, 1H), 7.96 (d, J = 4.4 Hz, 1H), 7.71 – 7.62 (m, 2H), 7.55 – 7.51 (m, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.27 (m, 1H), 7.13 (ddd, J = 6.7, 4.9, 1.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.5, 151.2, 151.1, 149.7, 140.3, 136.3, 134.5, 133.5, 128.9, 127.7, 126.7, 122.0, 115.9. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{12}NTe$ 336.0027; found 336.0021.



4r

2-phenyltellurophene (4r):[14] The product was isolated by column chromatography (hexane) as a white solid in 66% yield. mp 47-49 ºC. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.83 – 8.77 (m, 1H), 7.83 – 7.79 (m, 2H), 7.49 (d, J = 7.1 Hz, 2H), 7.33 (t, J = 7.3 Hz, 2H), 7.28 (d, J = 7.1 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.7, 140.0, 138.6, 133.3, 128.9, 127.5, 127.0, 125.5.

4. References

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5. NMR Spectra

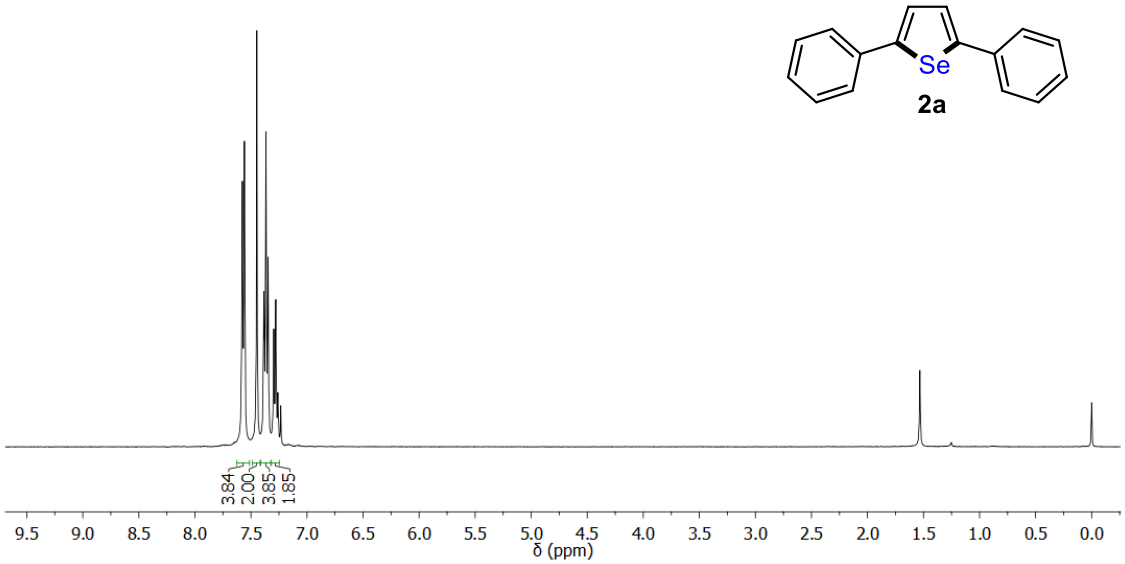

Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2a**.

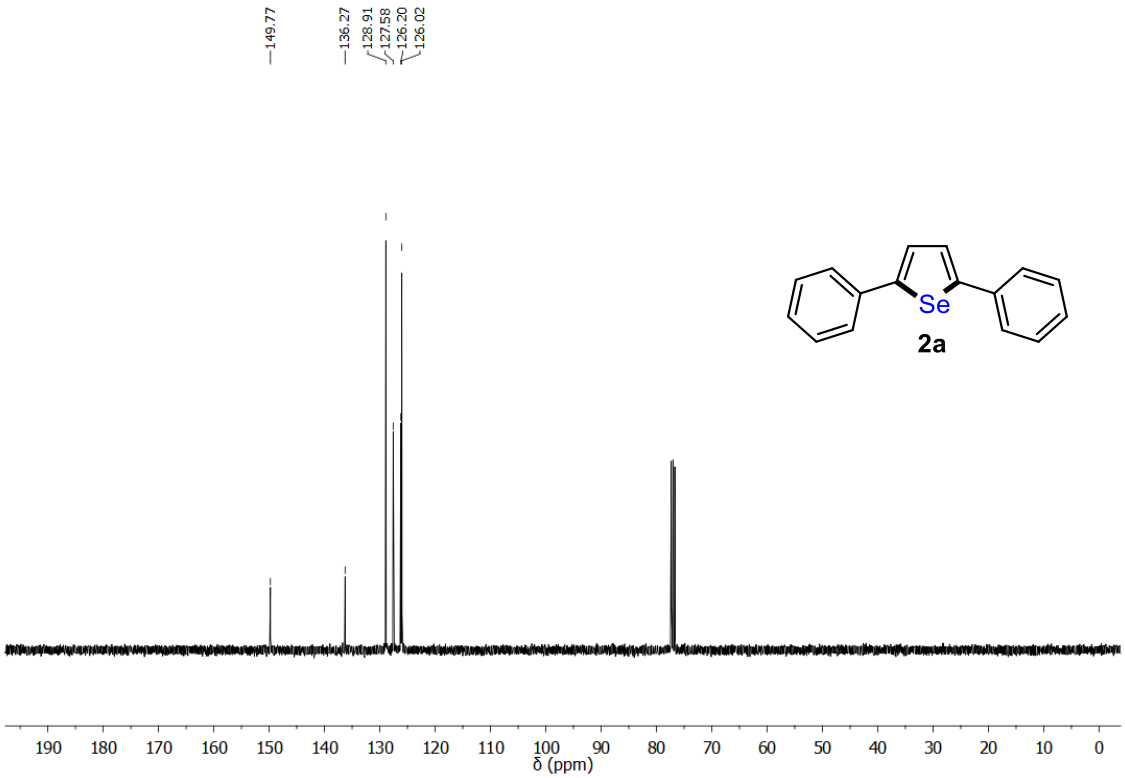

Figure S2. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **2a**.

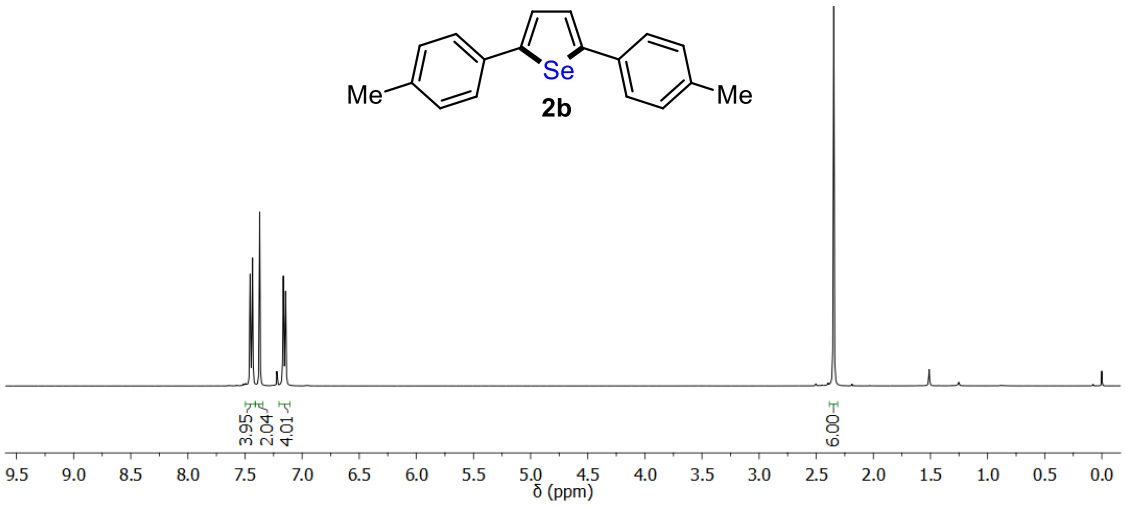

Figure S3. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2b**.

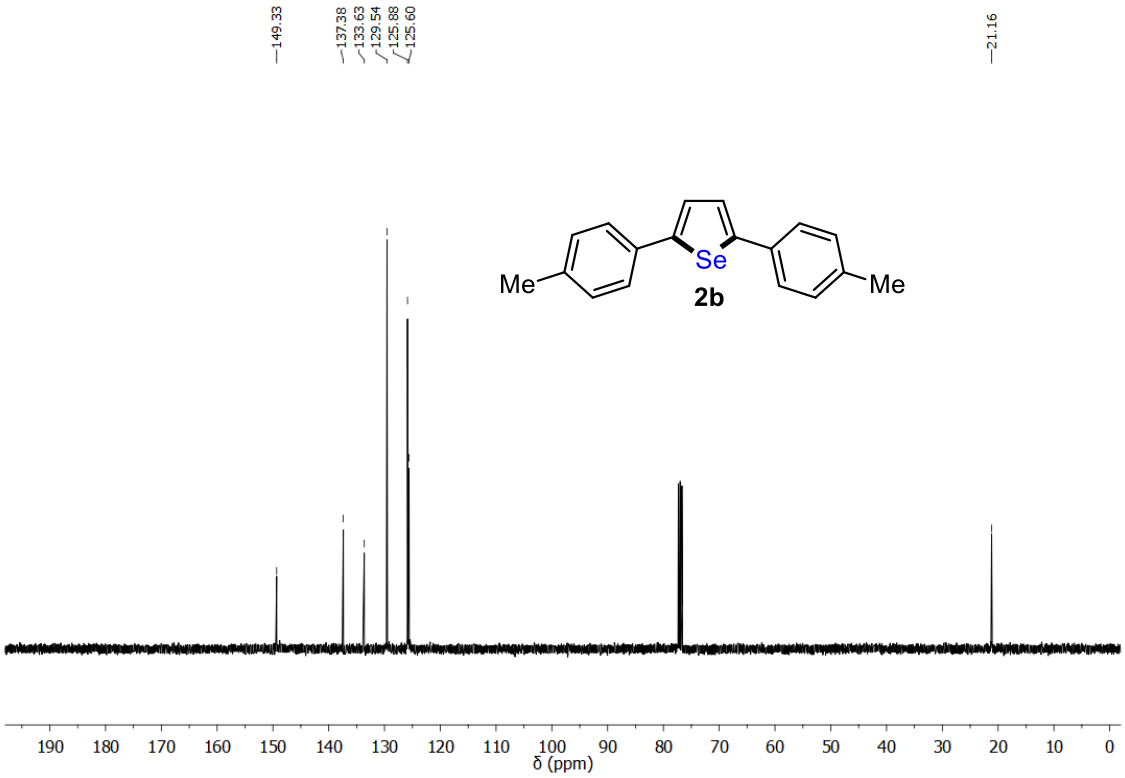

Figure S4. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **2b**.

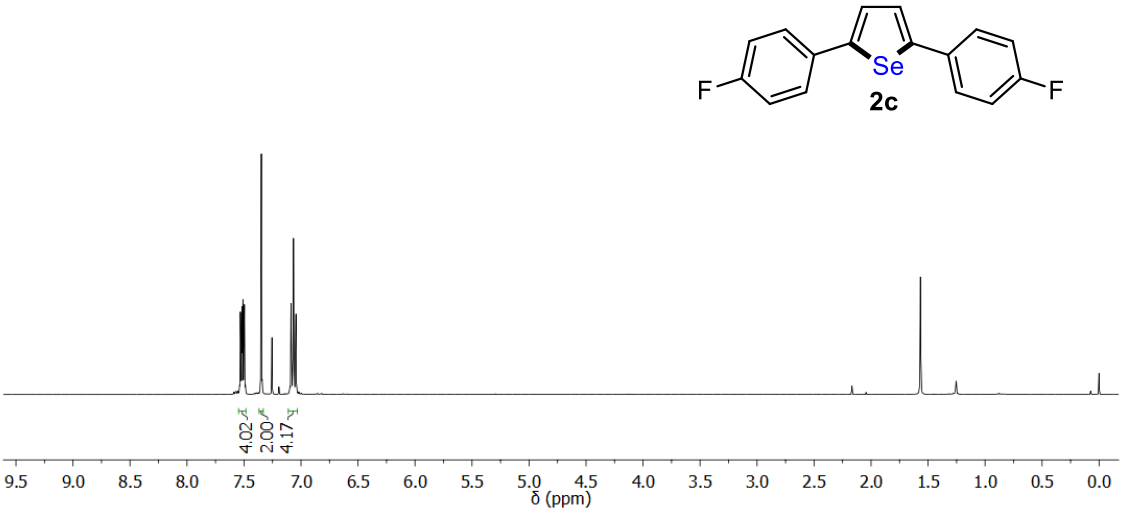

Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2c**.

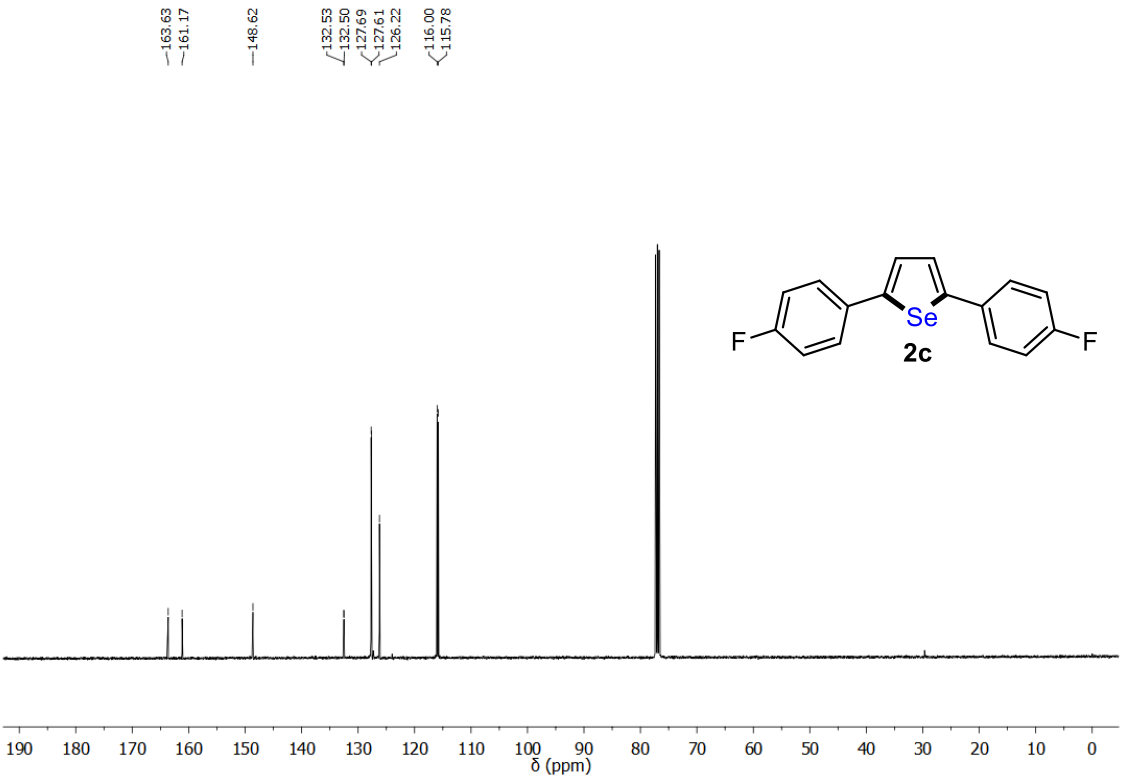

Figure S6. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **2c**.

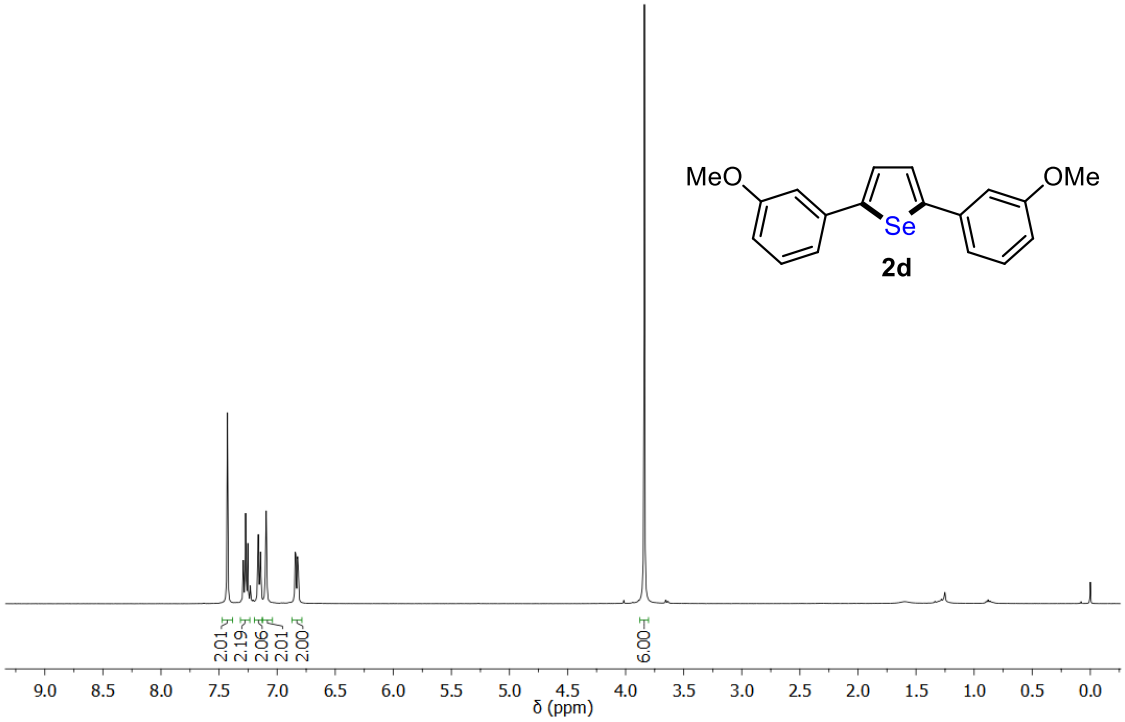

Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2d**.

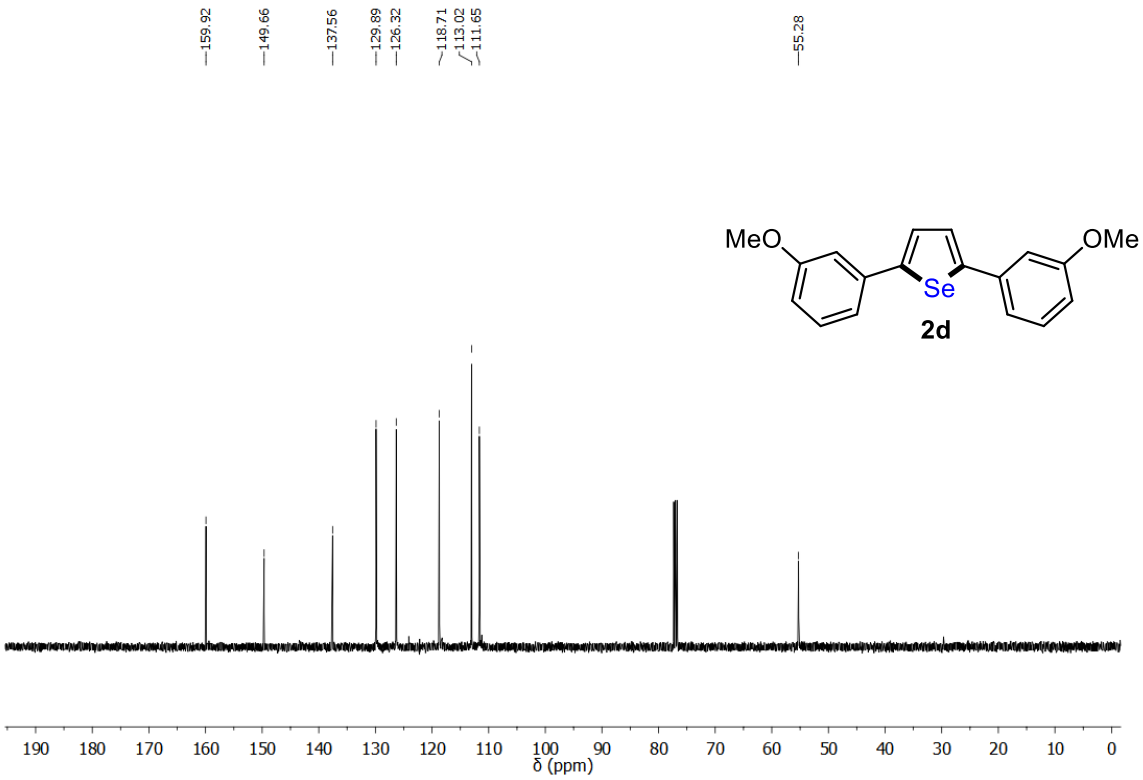

Figure S8. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **2d**.

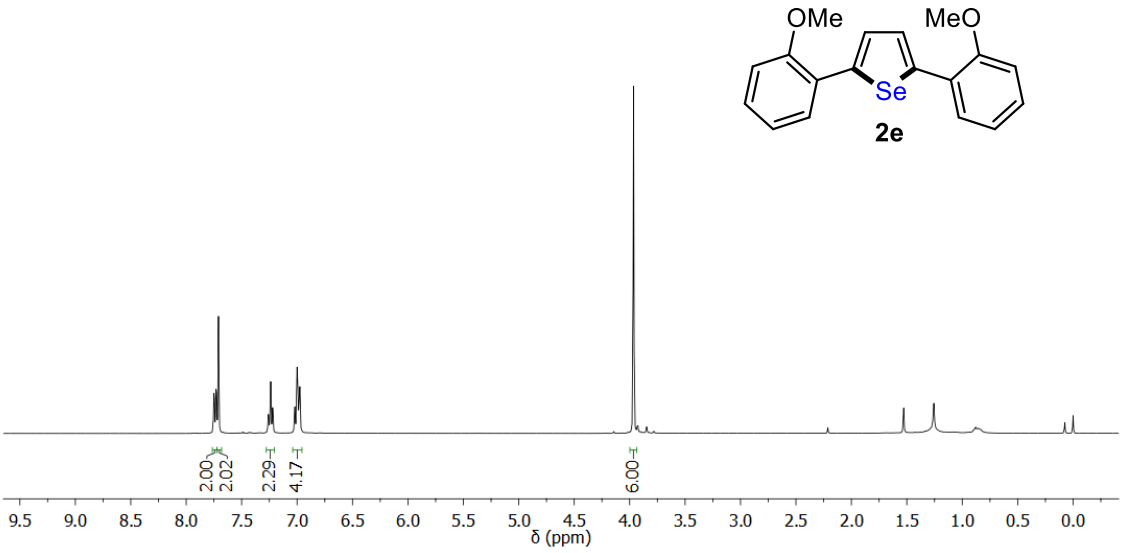

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2e**.

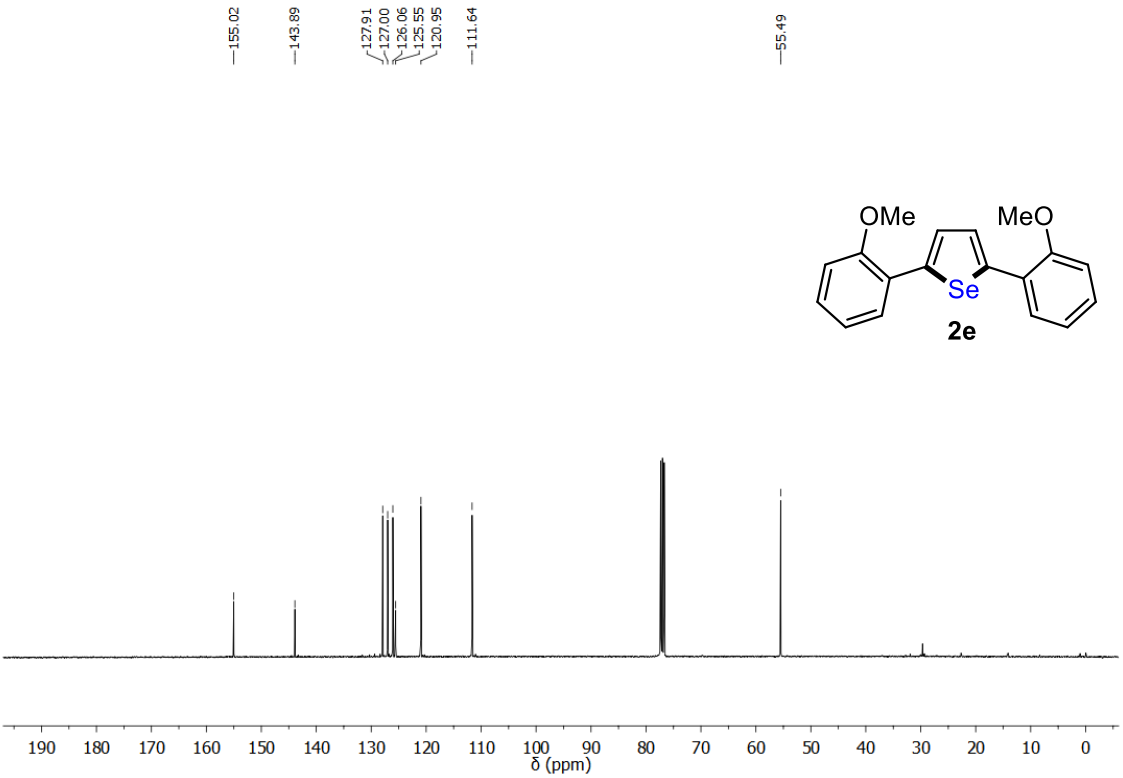

Figure S10. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2e**.

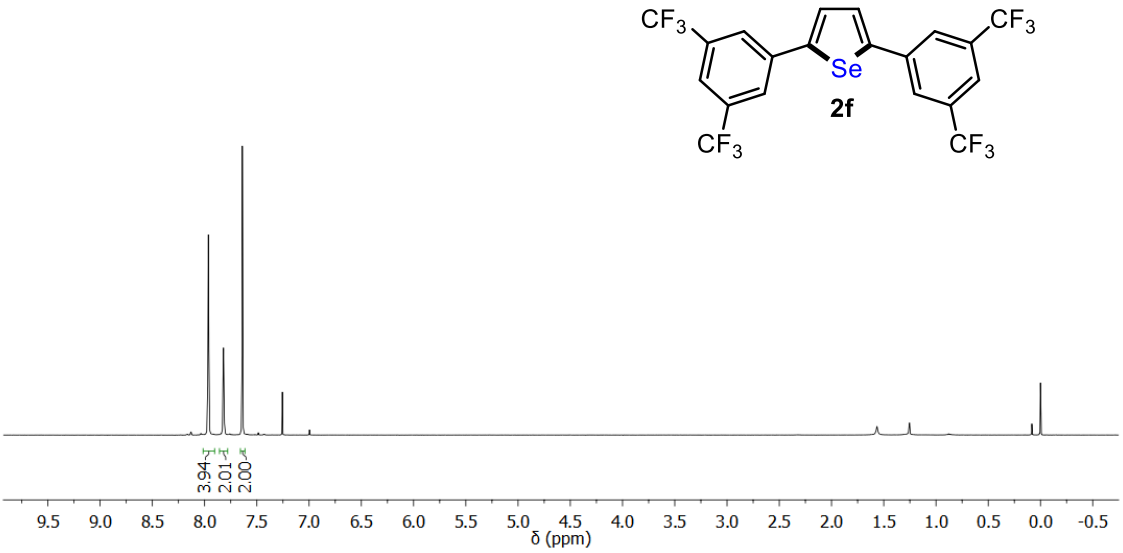

Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2f**.

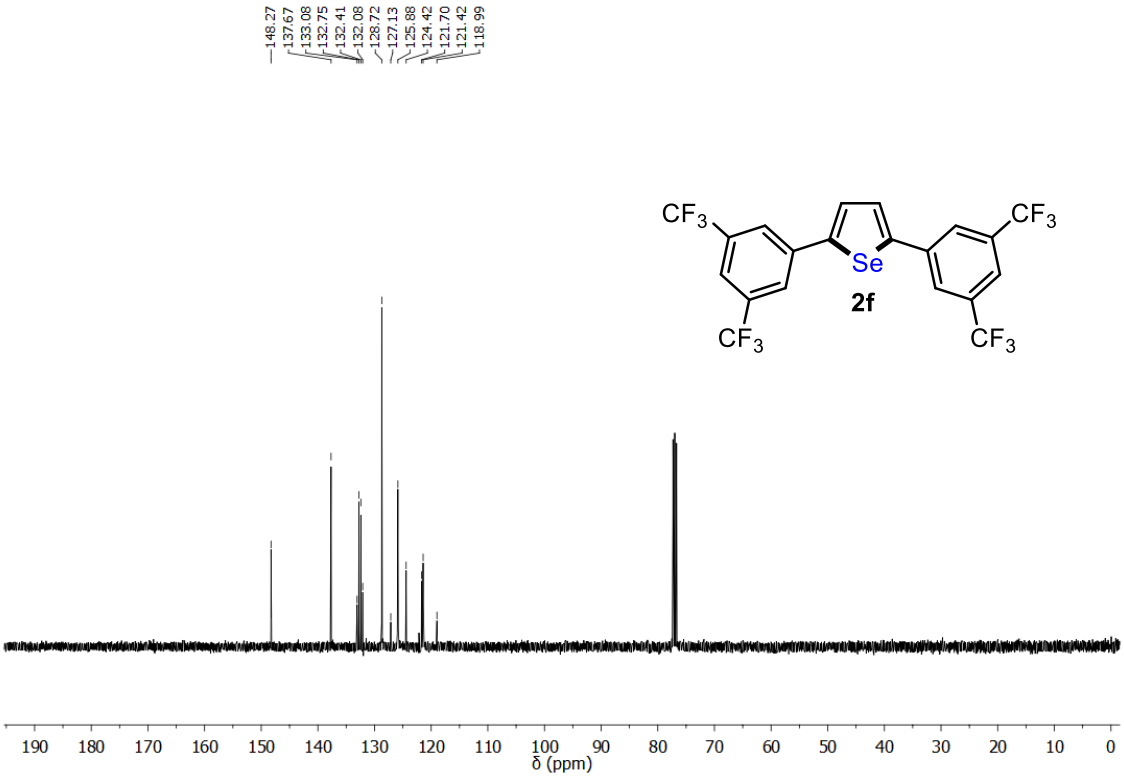

Figure S12. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **2f**.

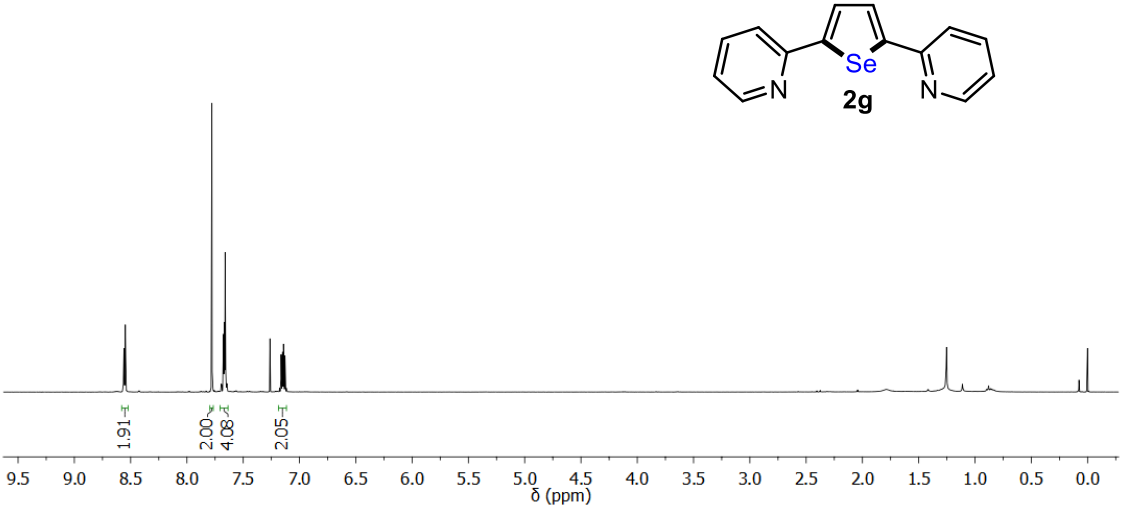

Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2g**.

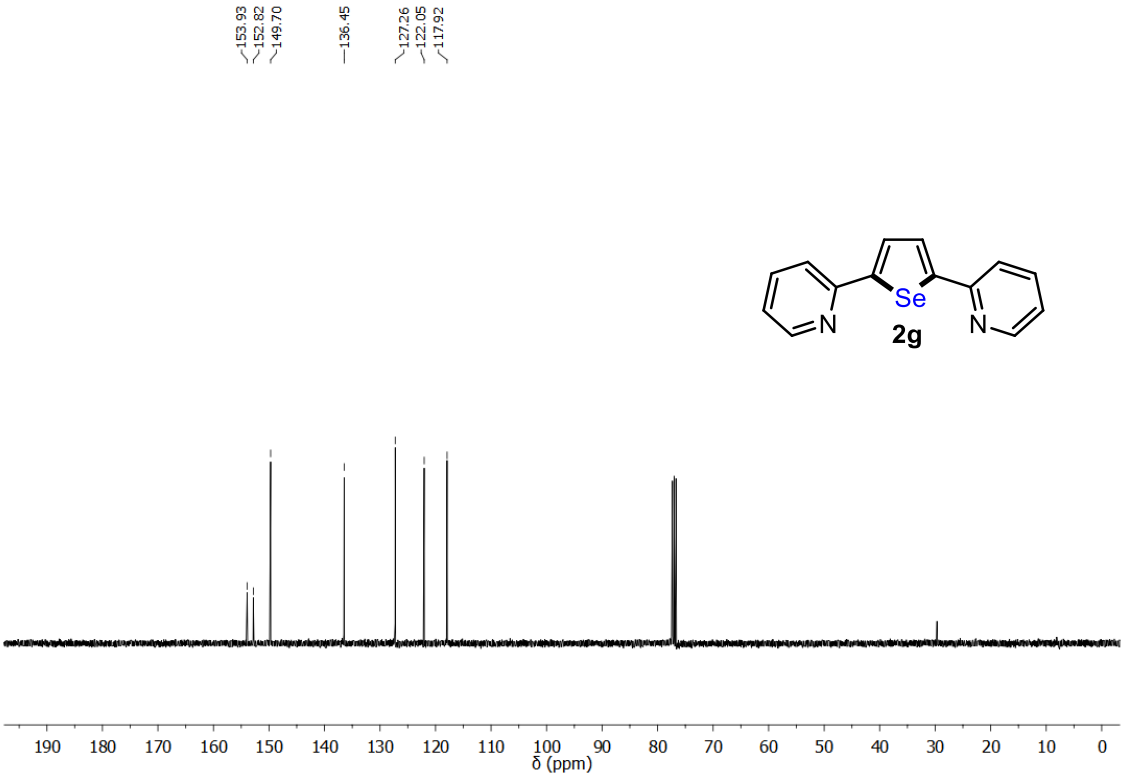

Figure S14. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2g**.

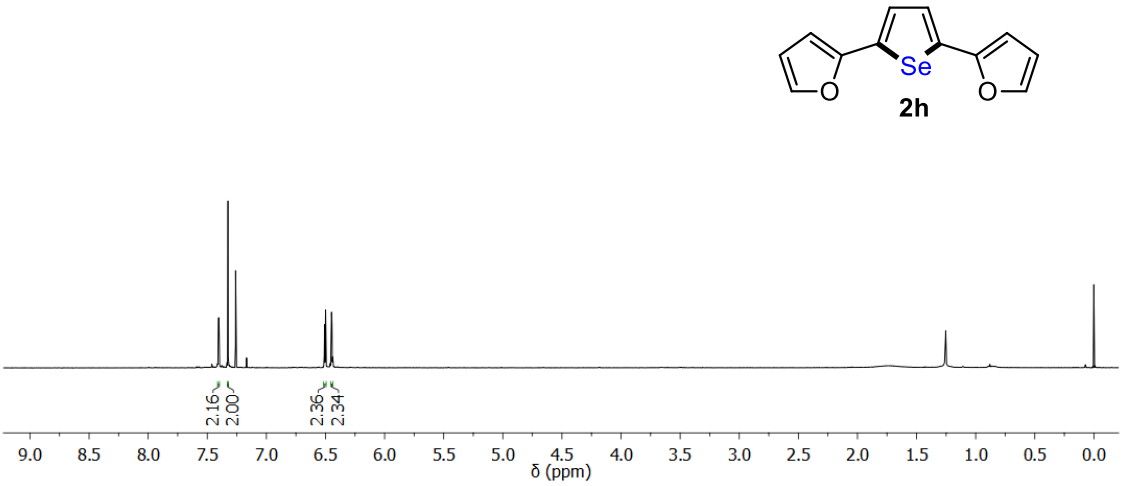

Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2h**.

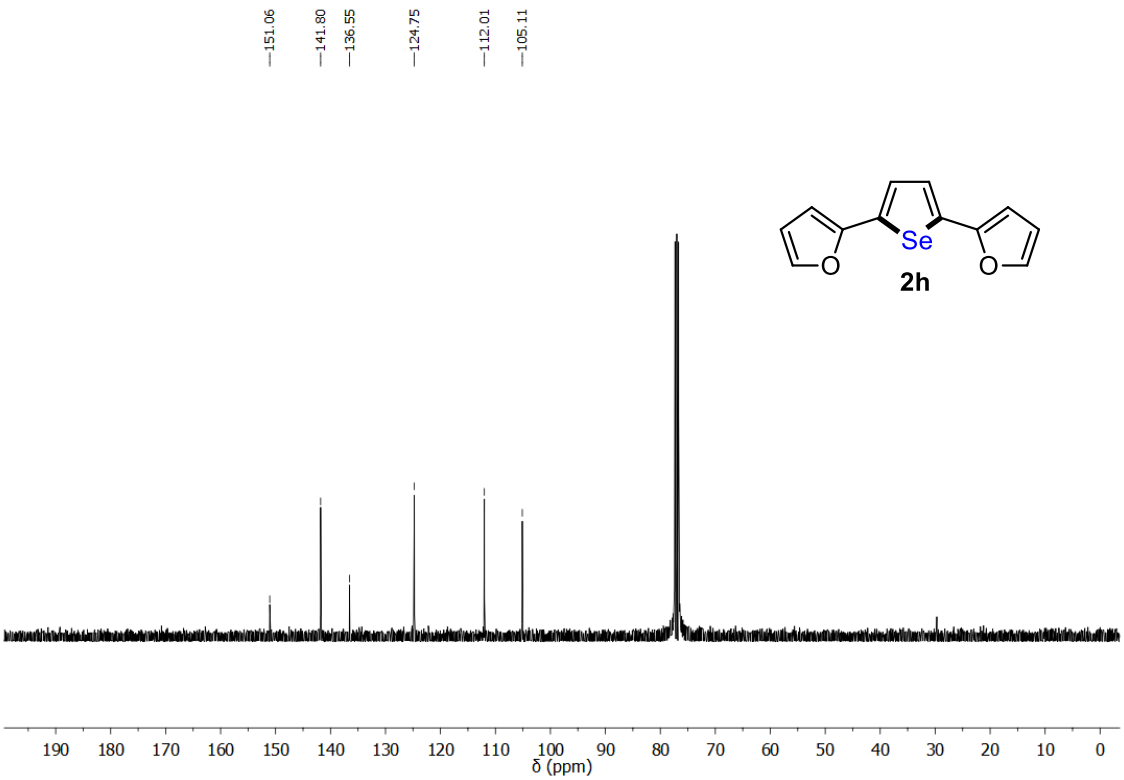

Figure S16. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) spectrum of **2h**.

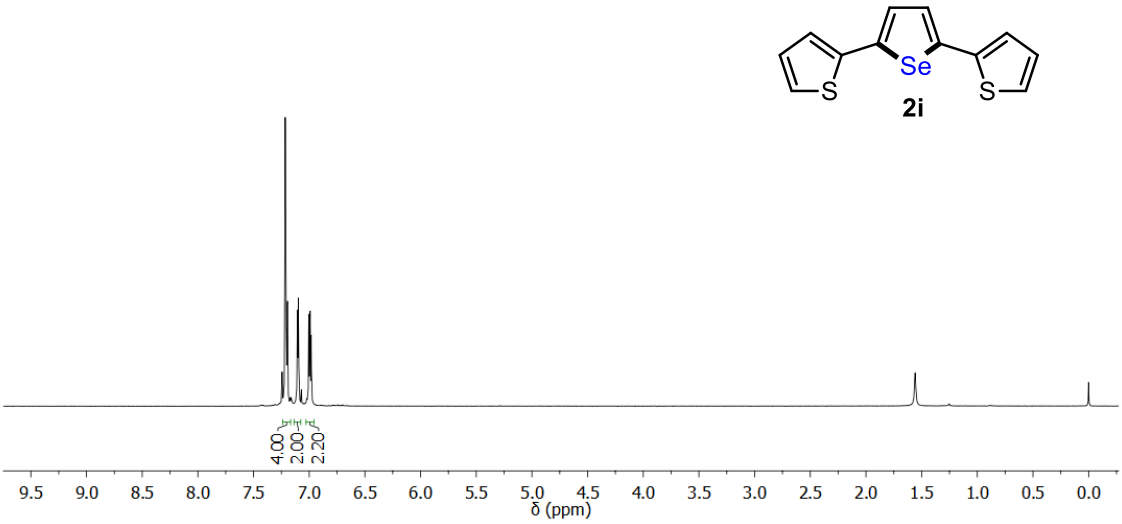

Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2i**.

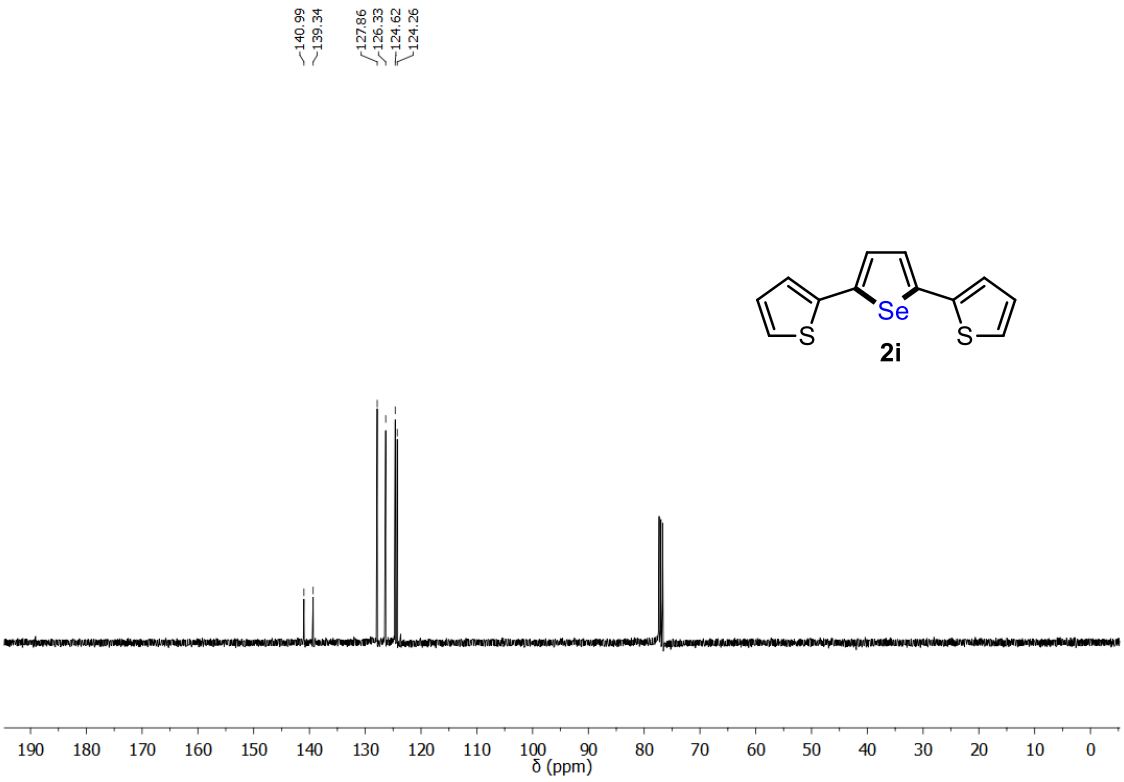

Figure S18. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) spectrum of **2i**.

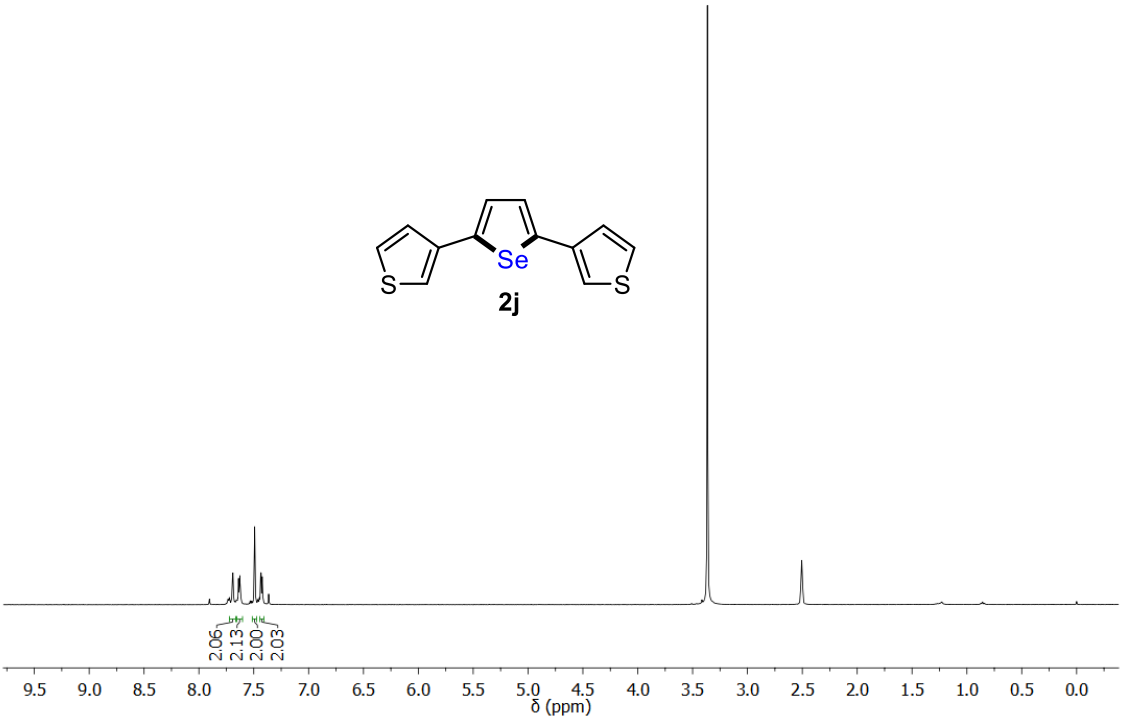

Figure S19. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **2j**.

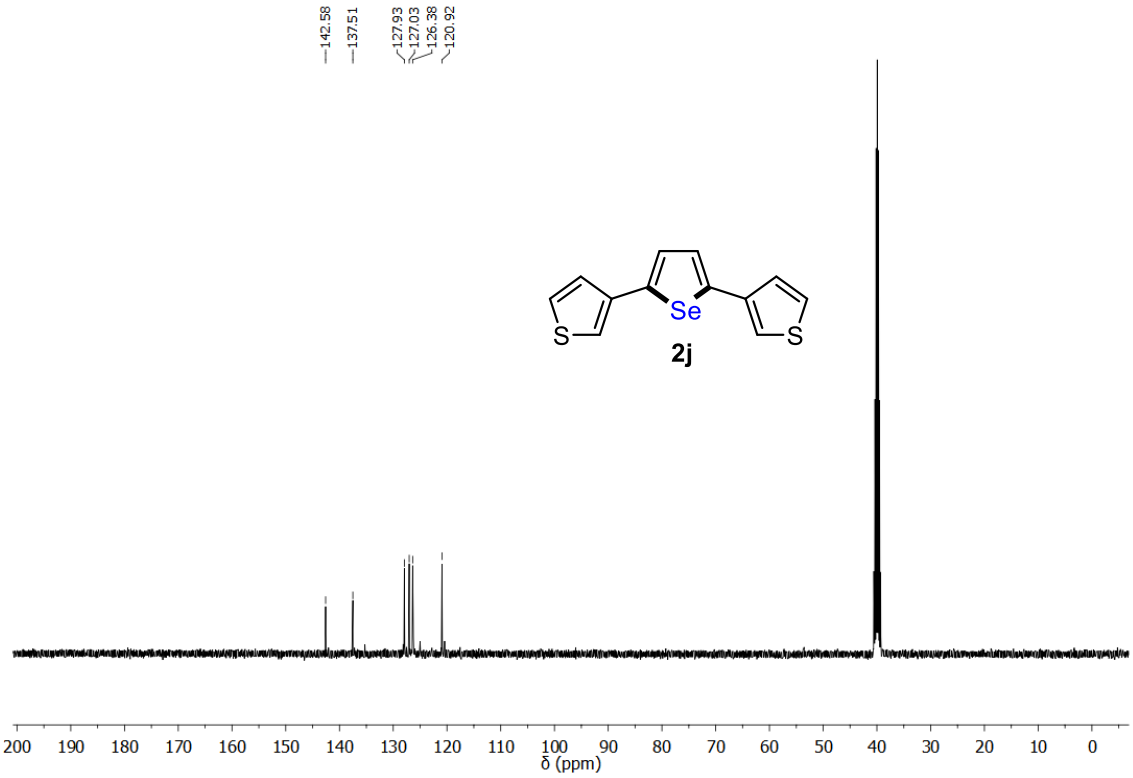

Figure S20. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of **2j**.

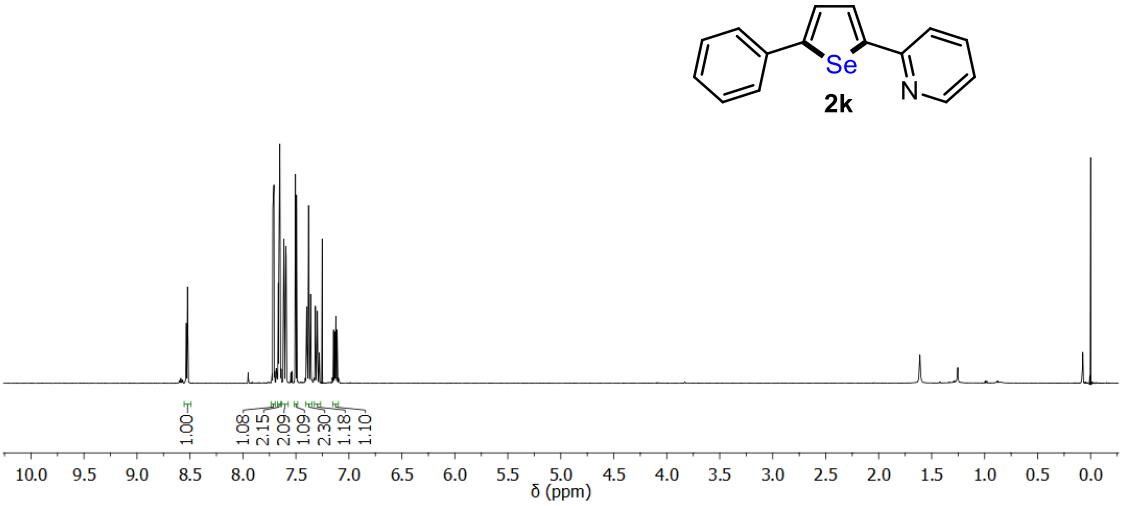

Figure S21. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2k**.

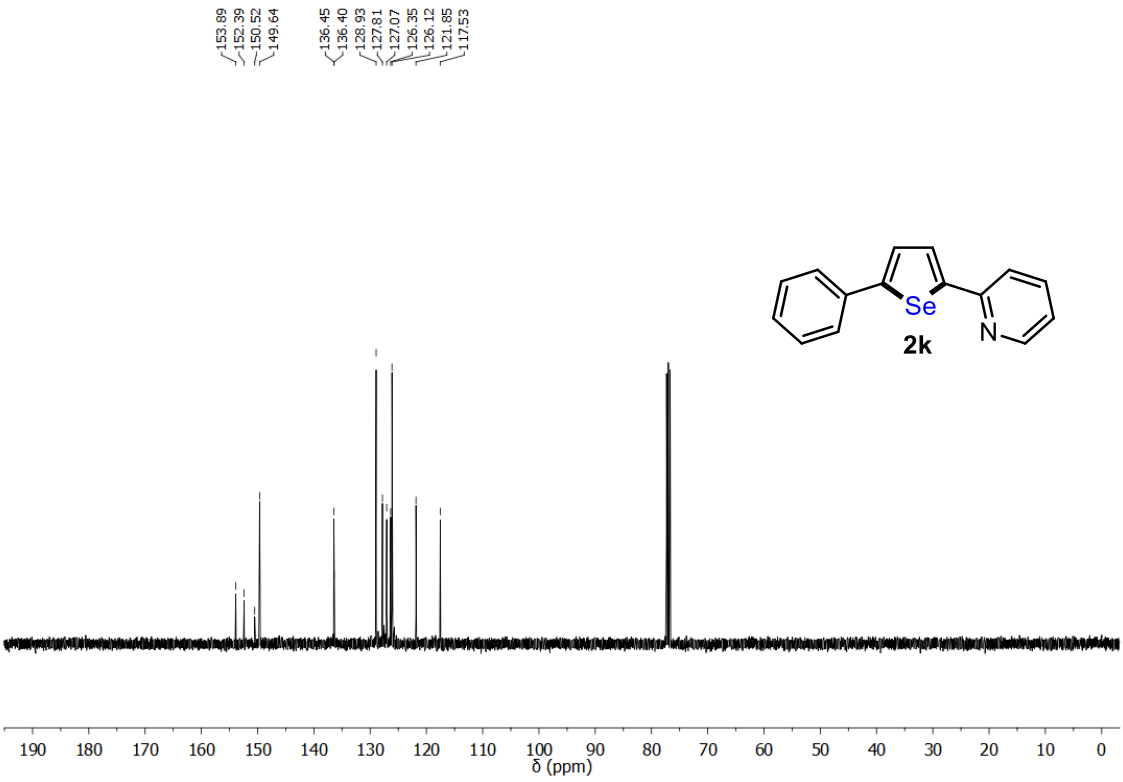

Figure S22. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2k**.

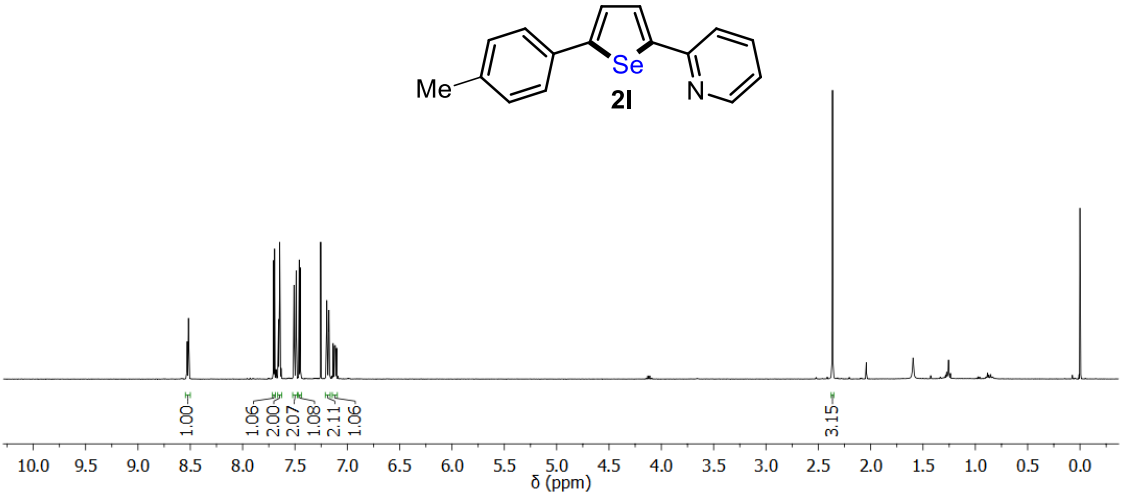

Figure S23. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2l**.

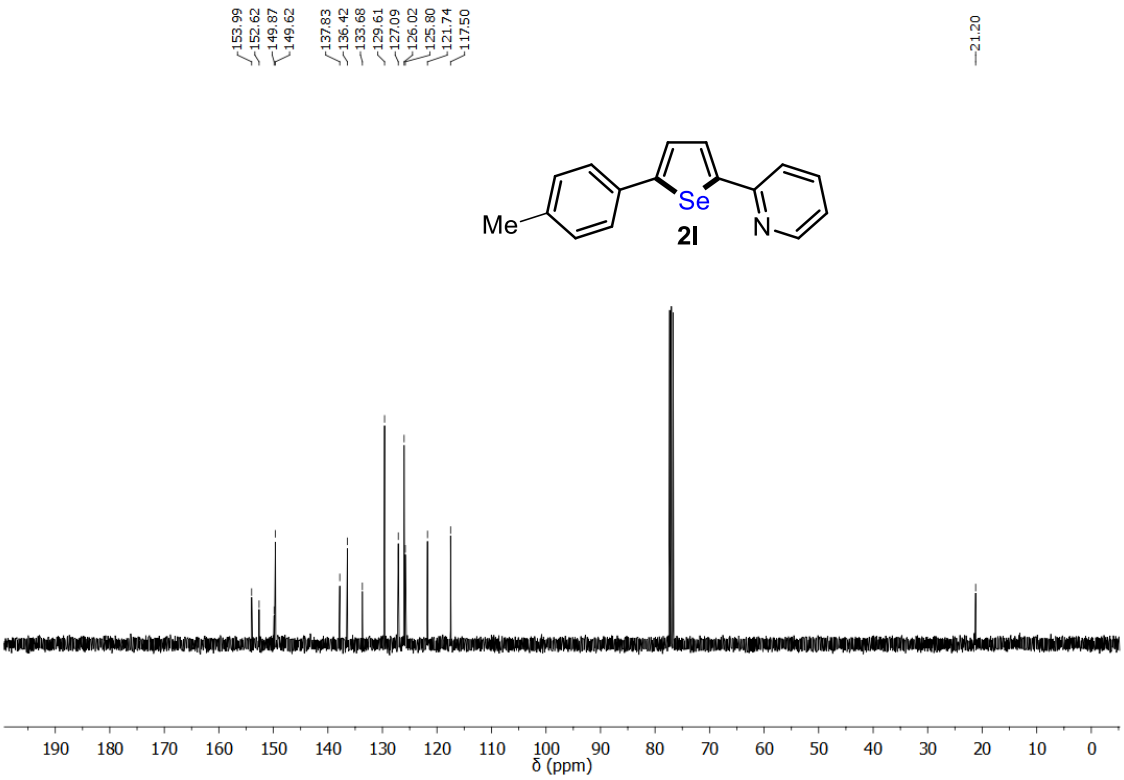

Figure S24. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **2l**.

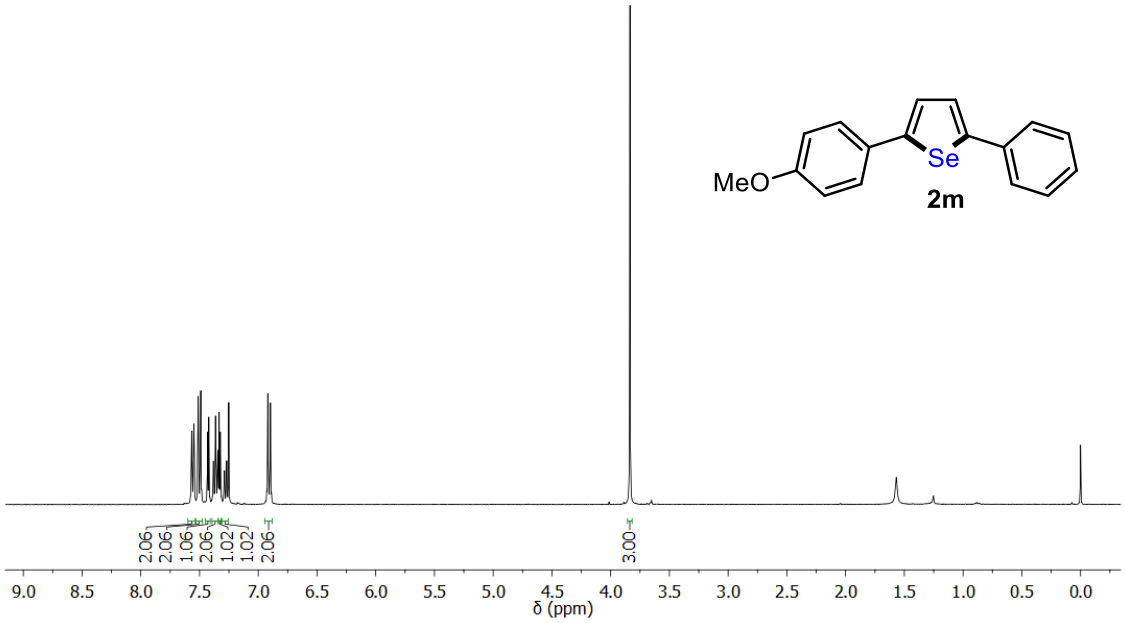

Figure S25. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2m**.

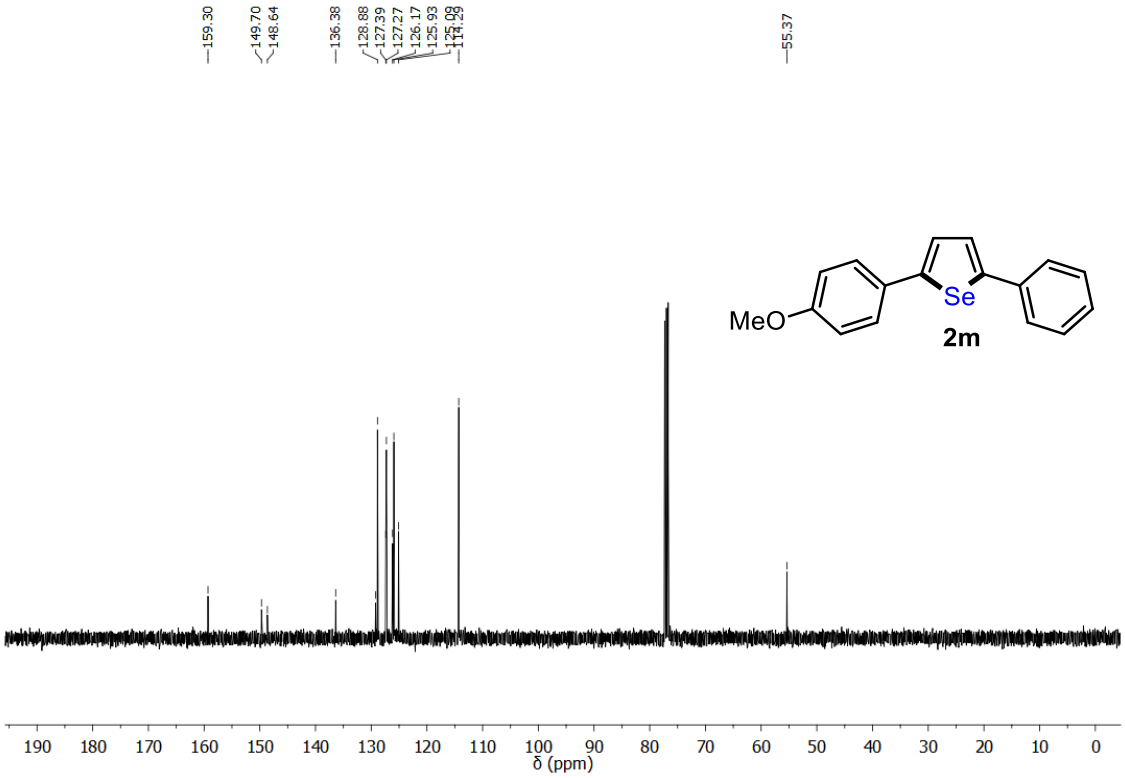

Figure S26. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **2m**.

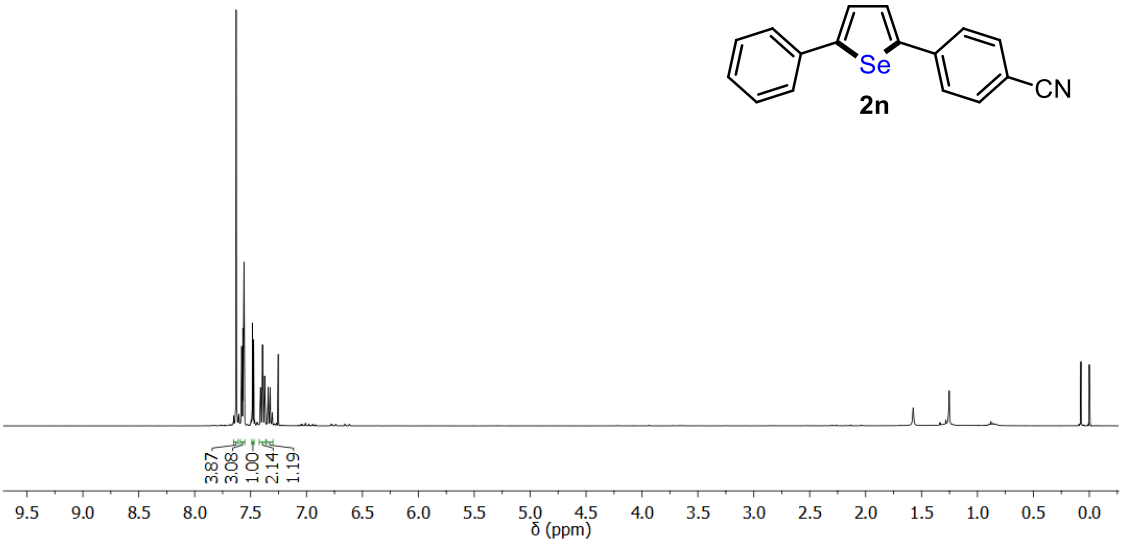

Figure S27. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2n**.

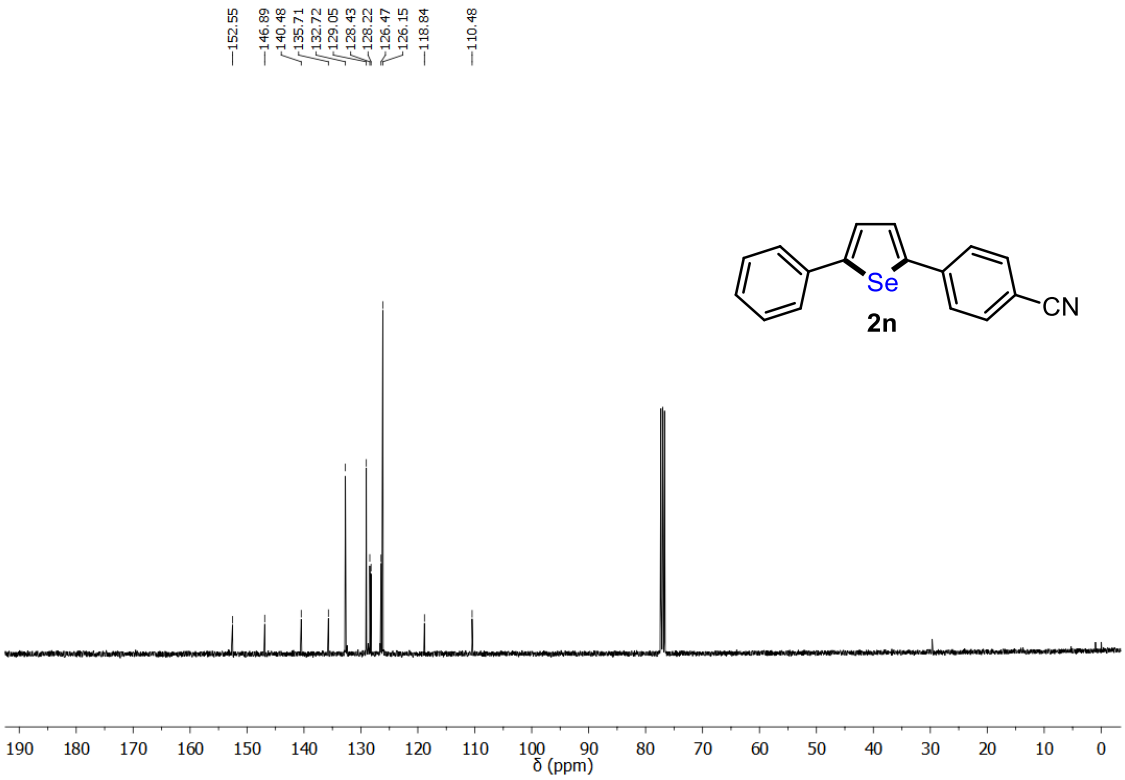

Figure S28. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2n**.

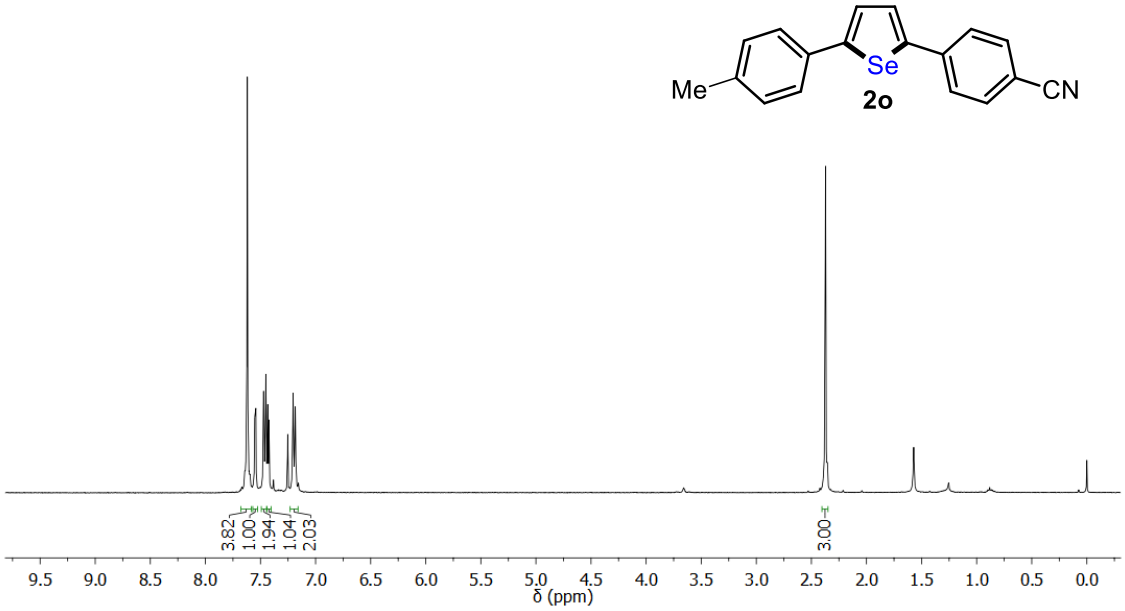

Figure S29. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2o**.

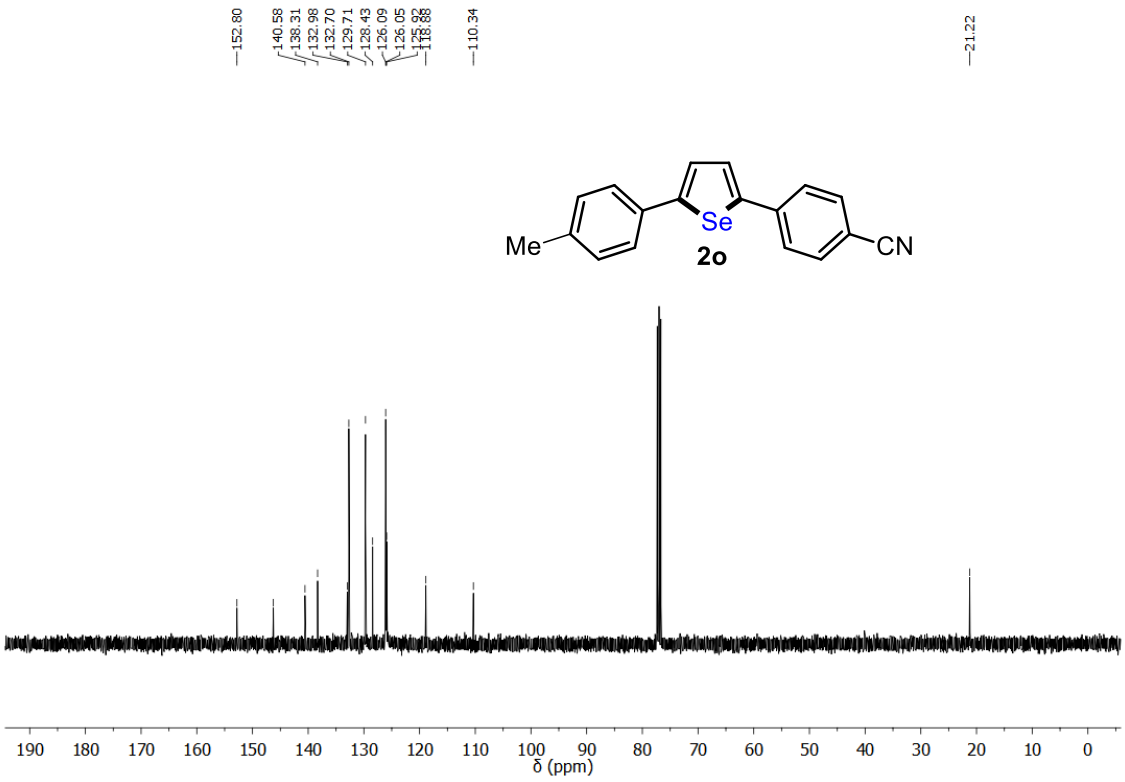

Figure S30. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **2o**.

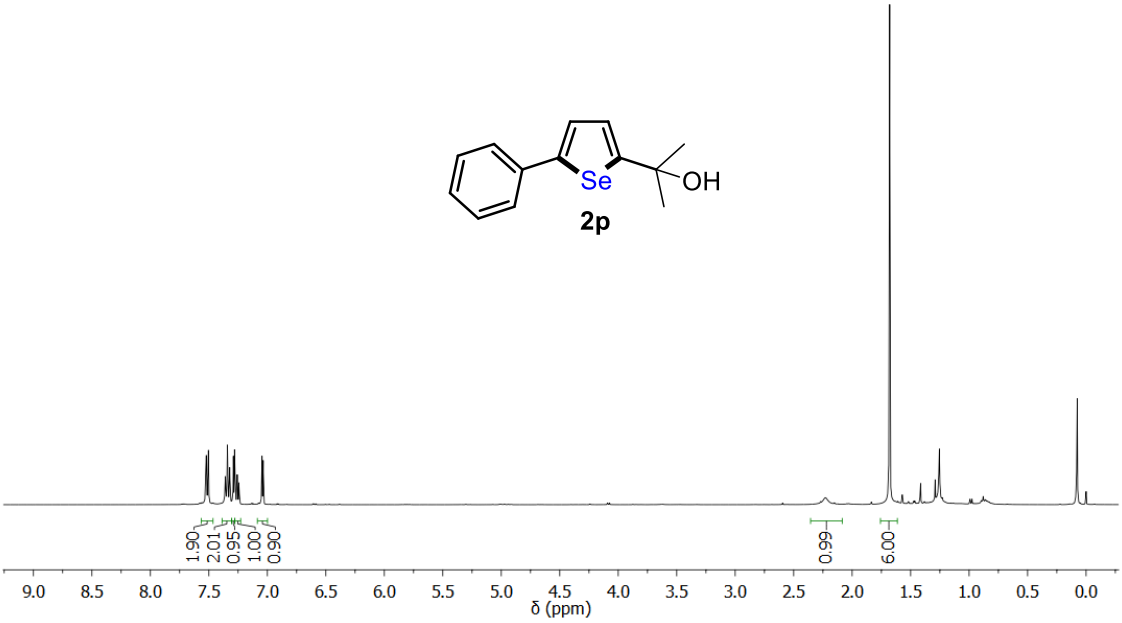

Figure S31. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2p**.

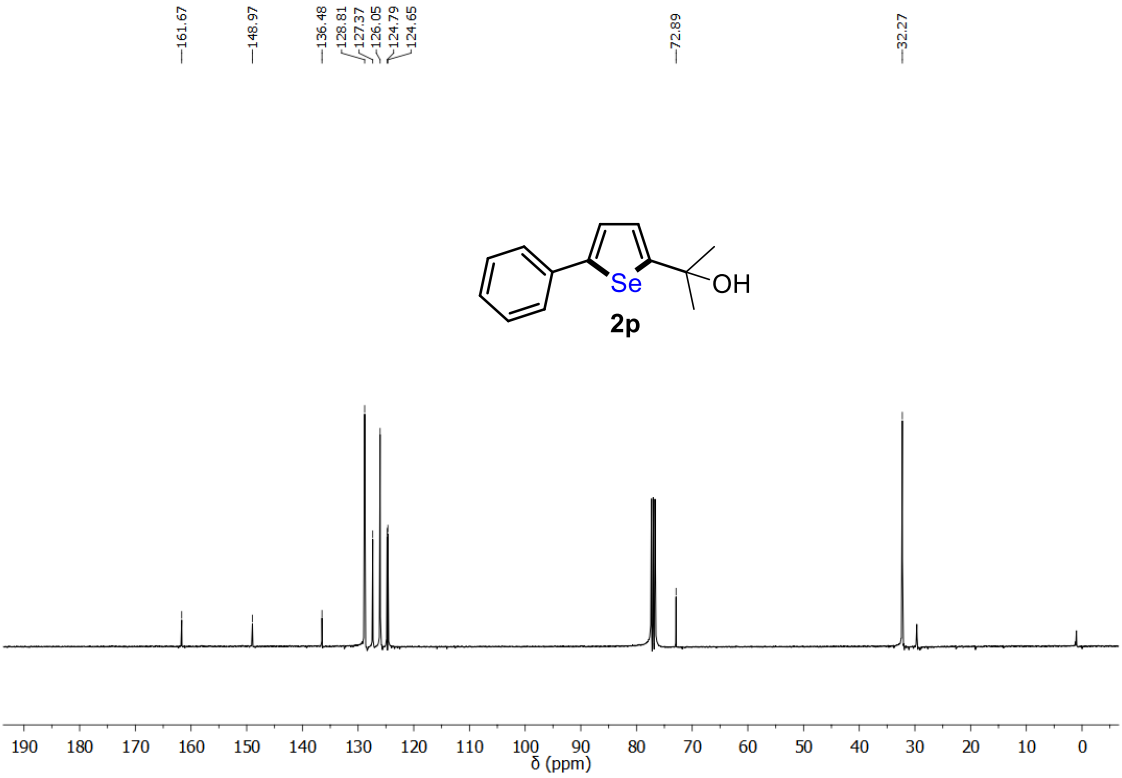

Figure S32. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2p**.

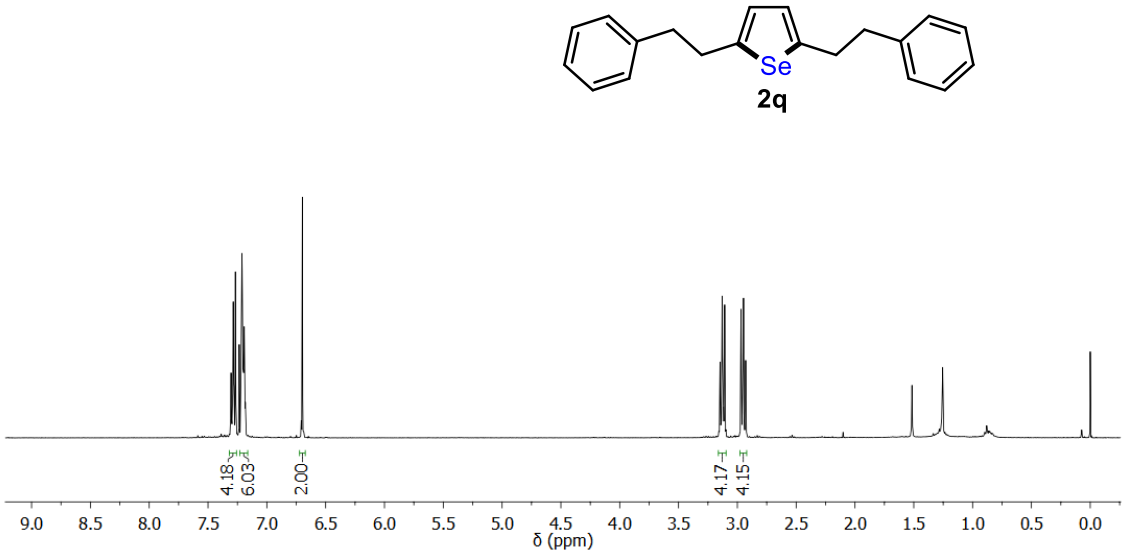

Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2q**.

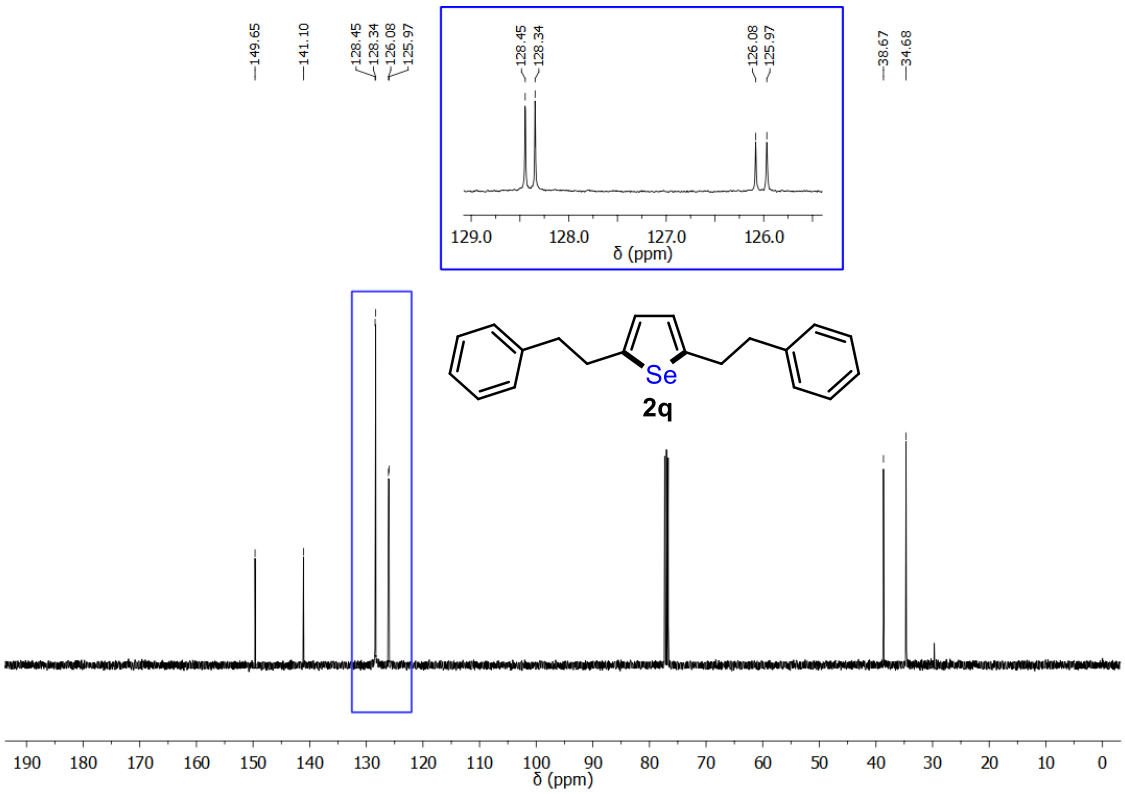

Figure S34. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **2q**.

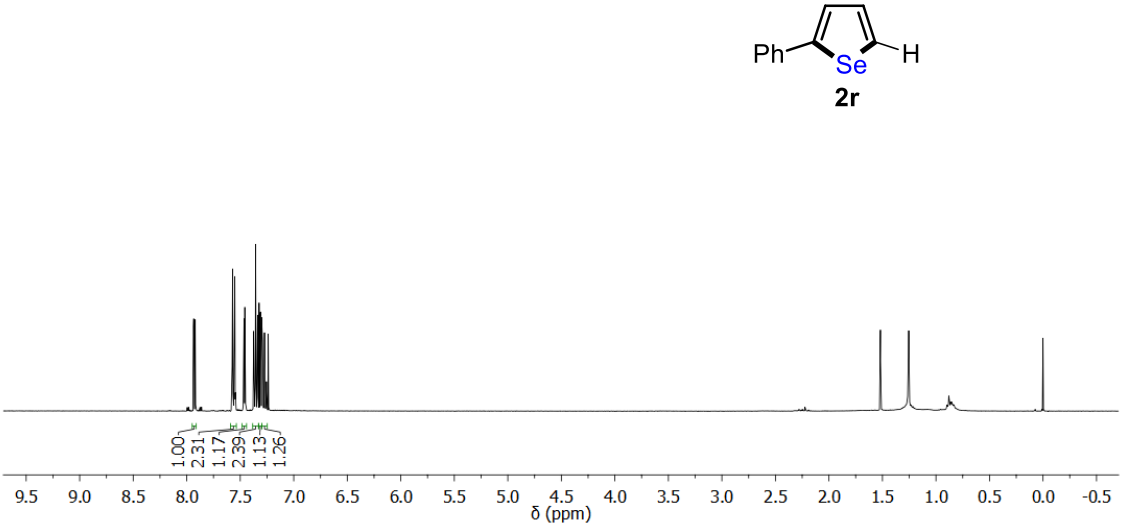

Figure S35. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2r**.

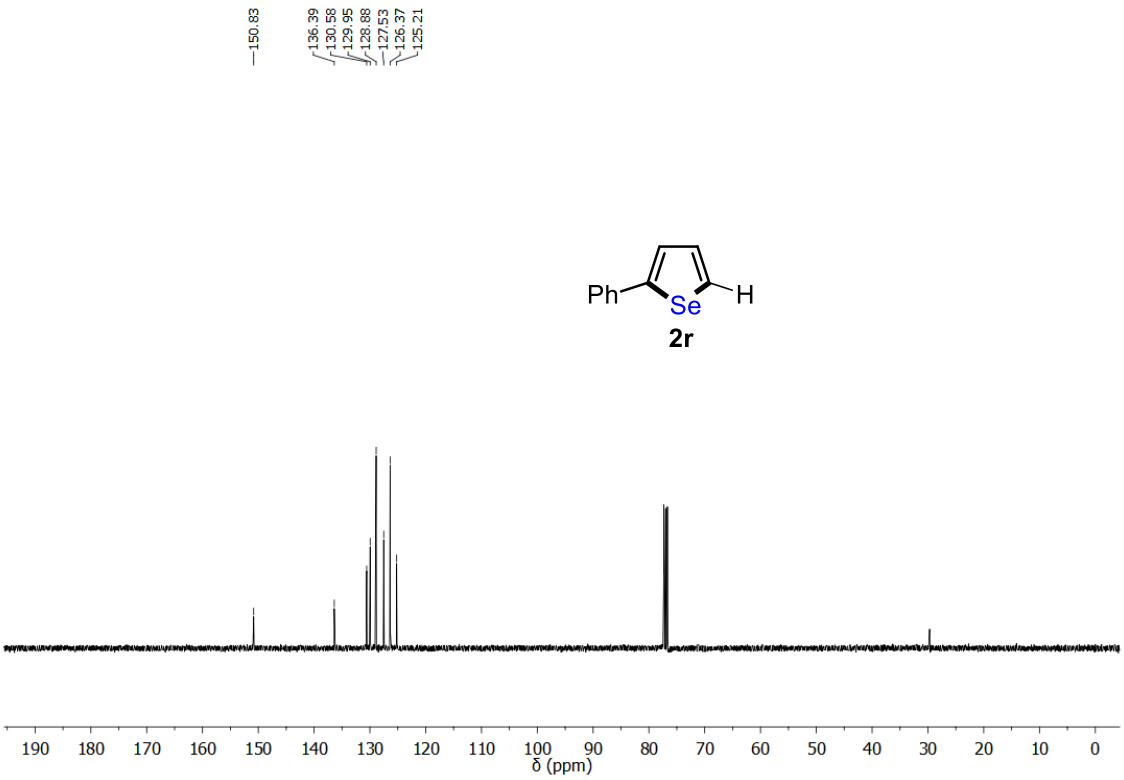

Figure S36. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **2r**.

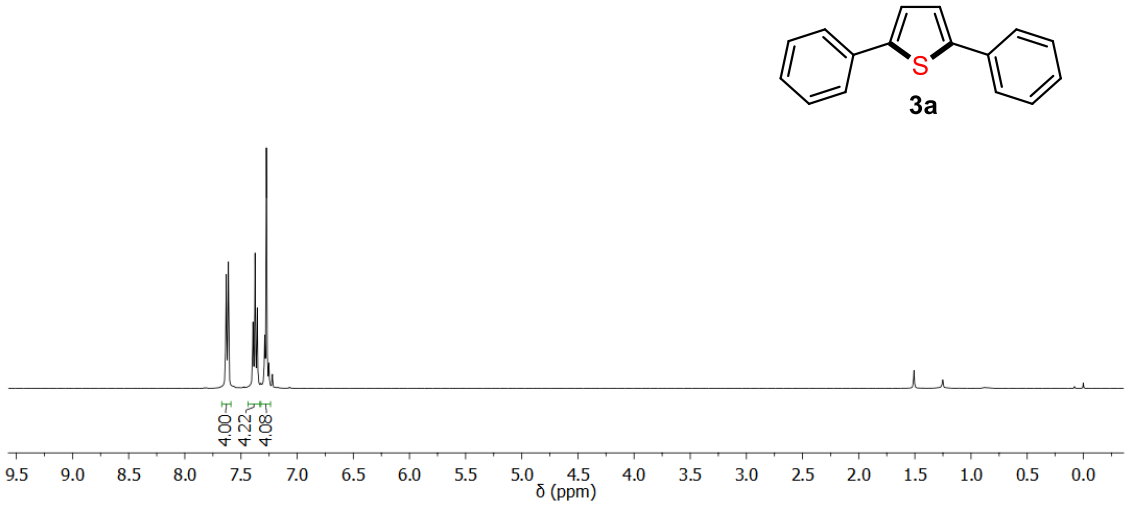

Figure S37. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**.

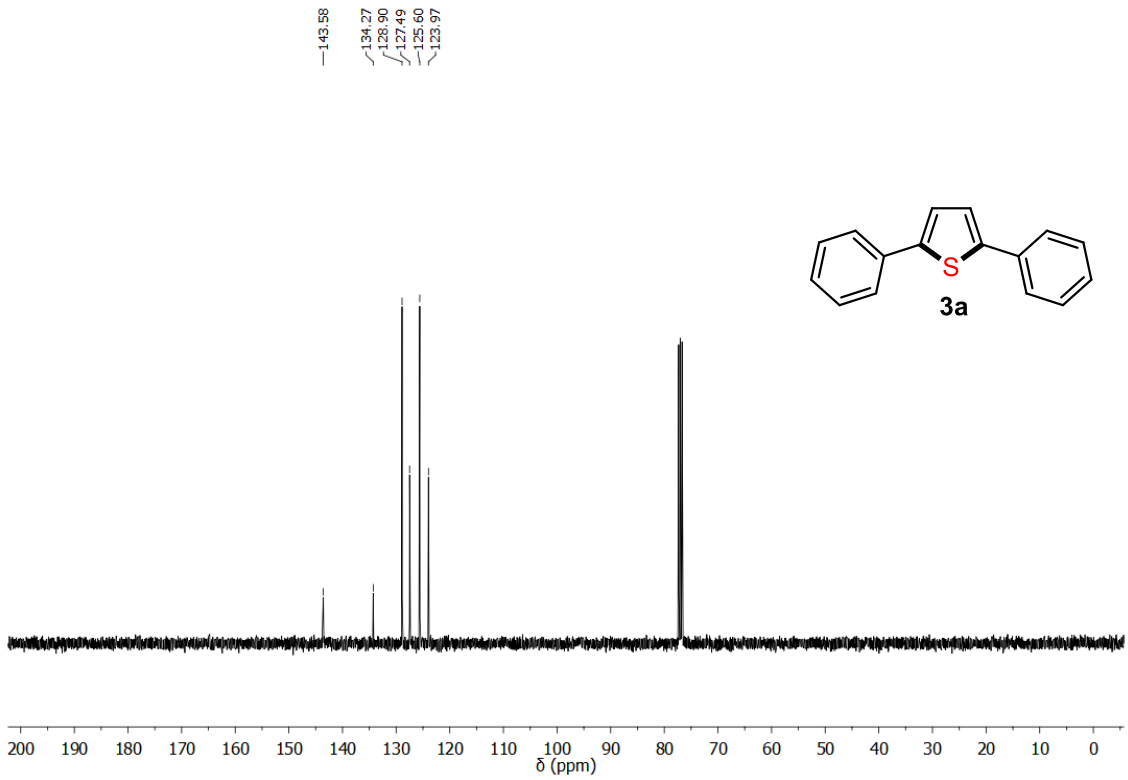

Figure S38. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3a**.

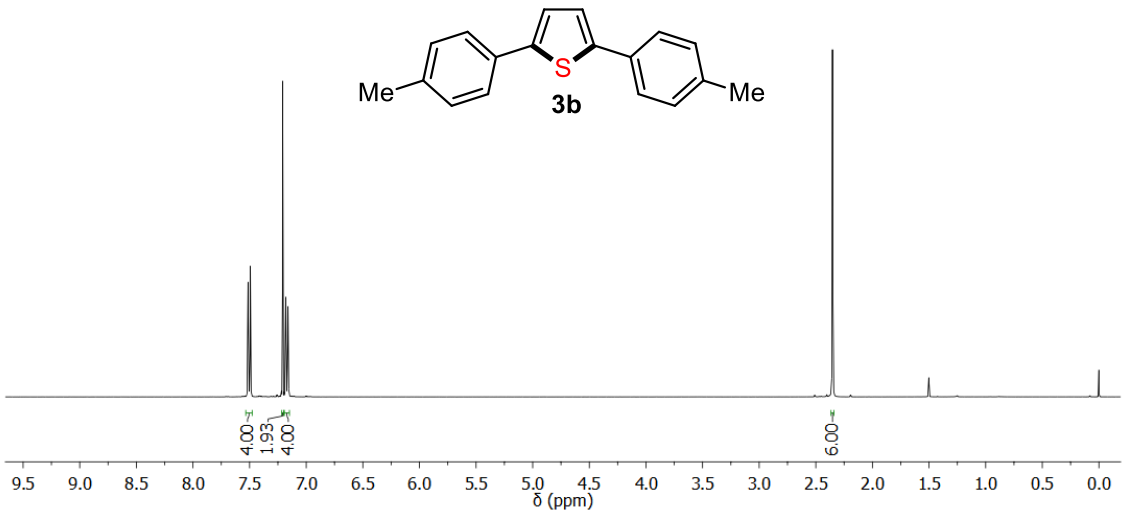

Figure S39. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b**.

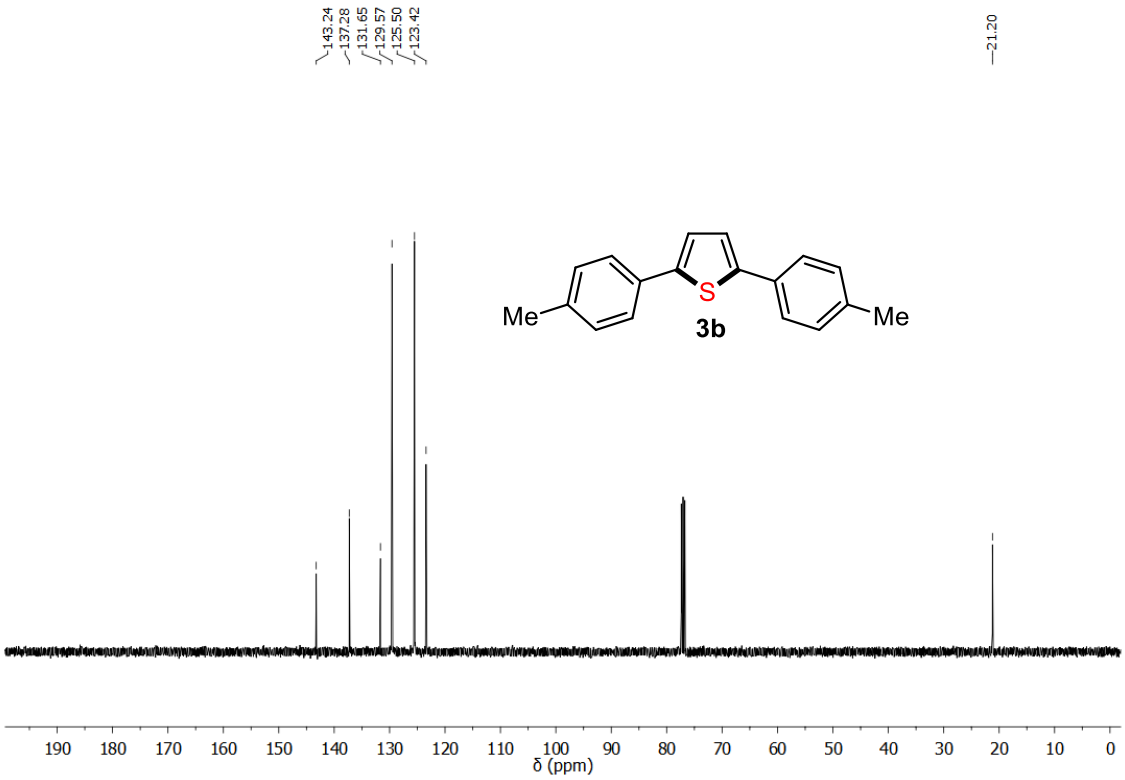

Figure S40. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3b**.

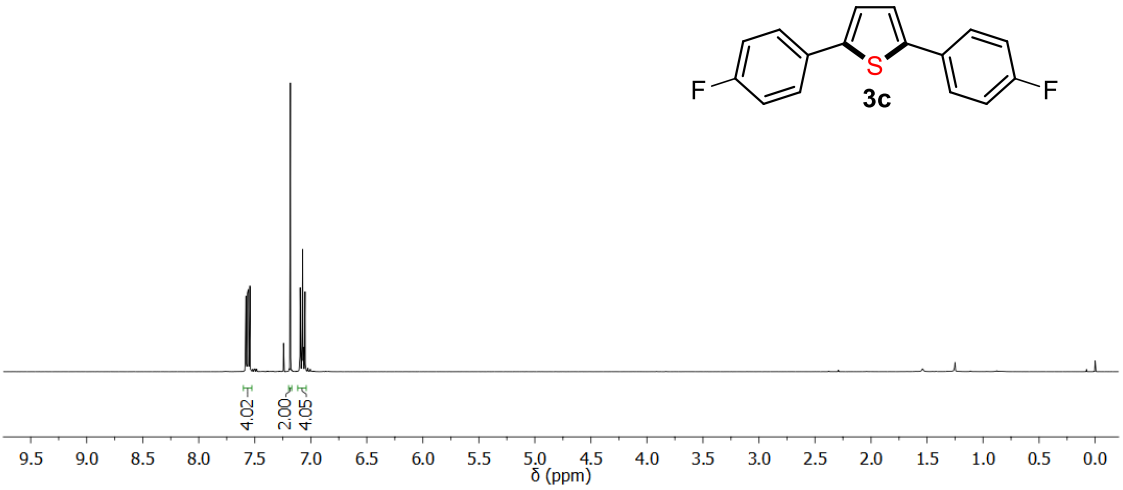

Figure S41. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c**.

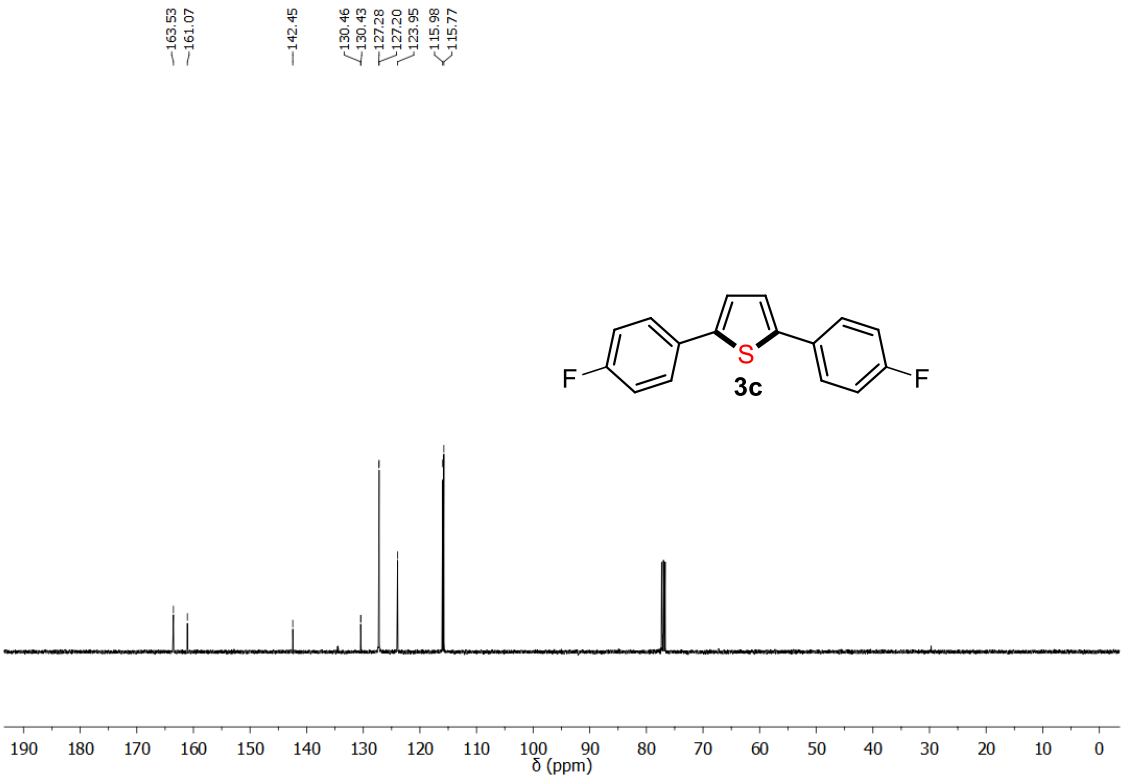

Figure S42. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) spectrum of **3c**.

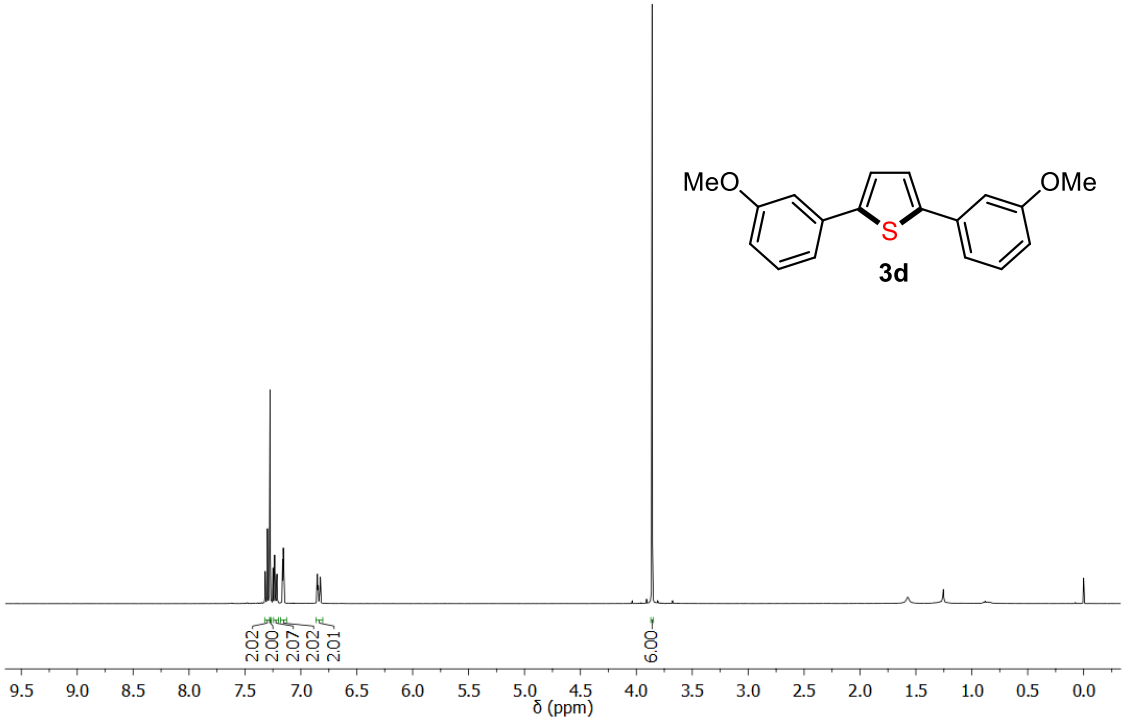

Figure S43. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3d**.

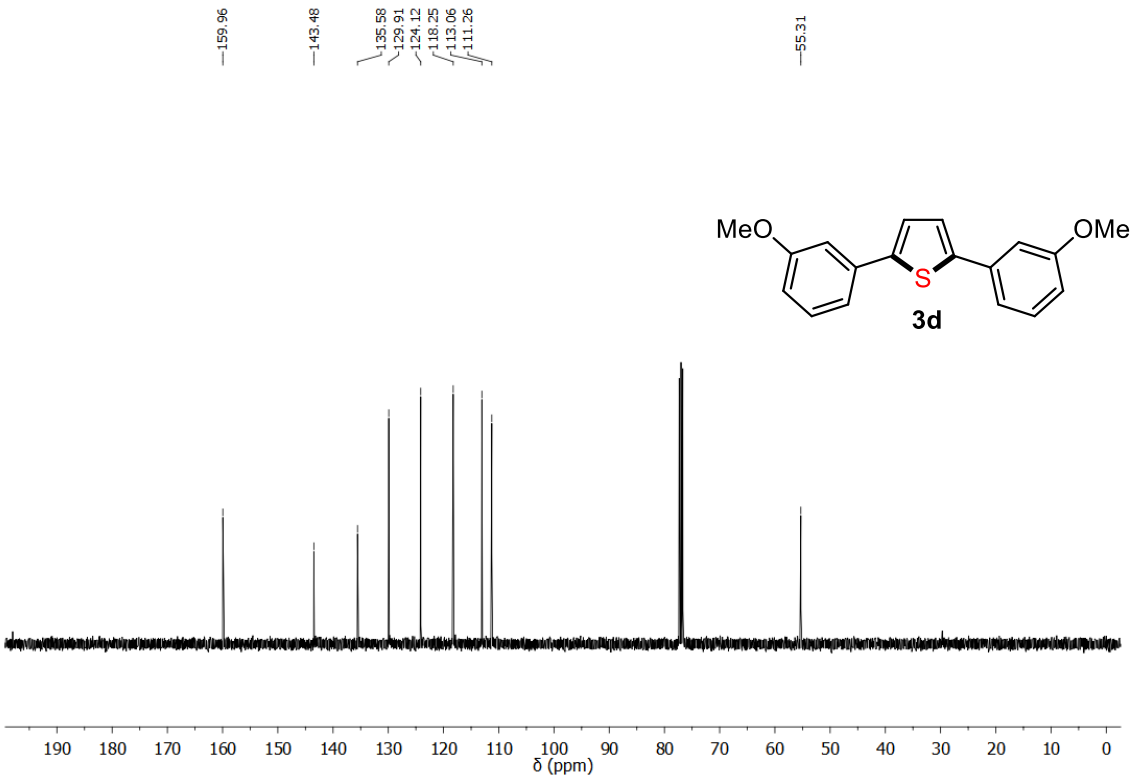

Figure S44. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3d**.

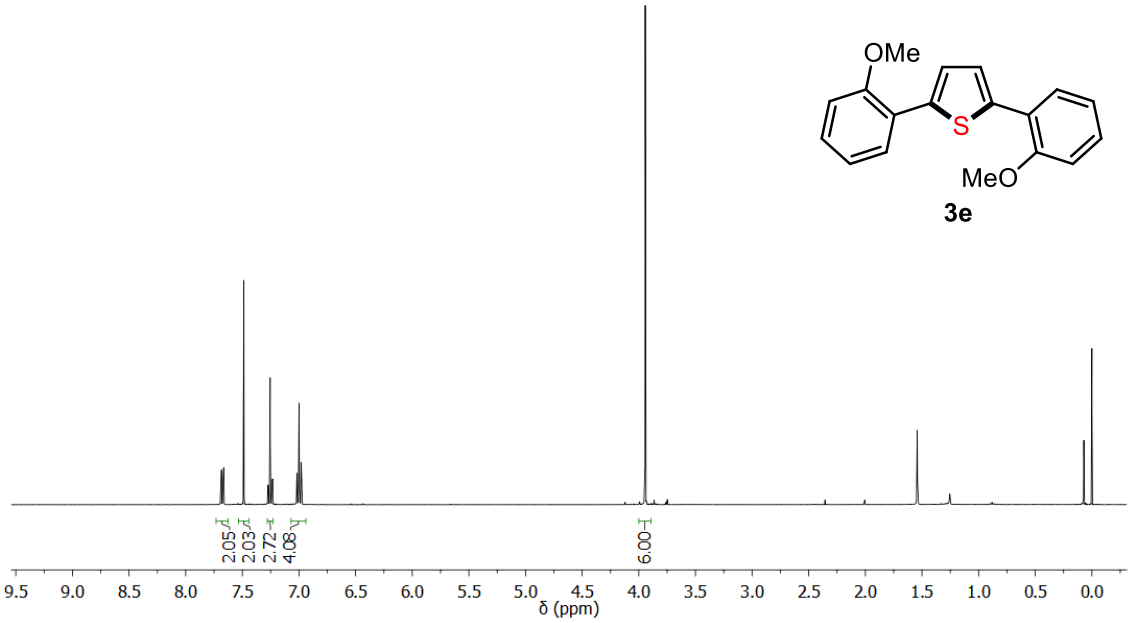

Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3e**.

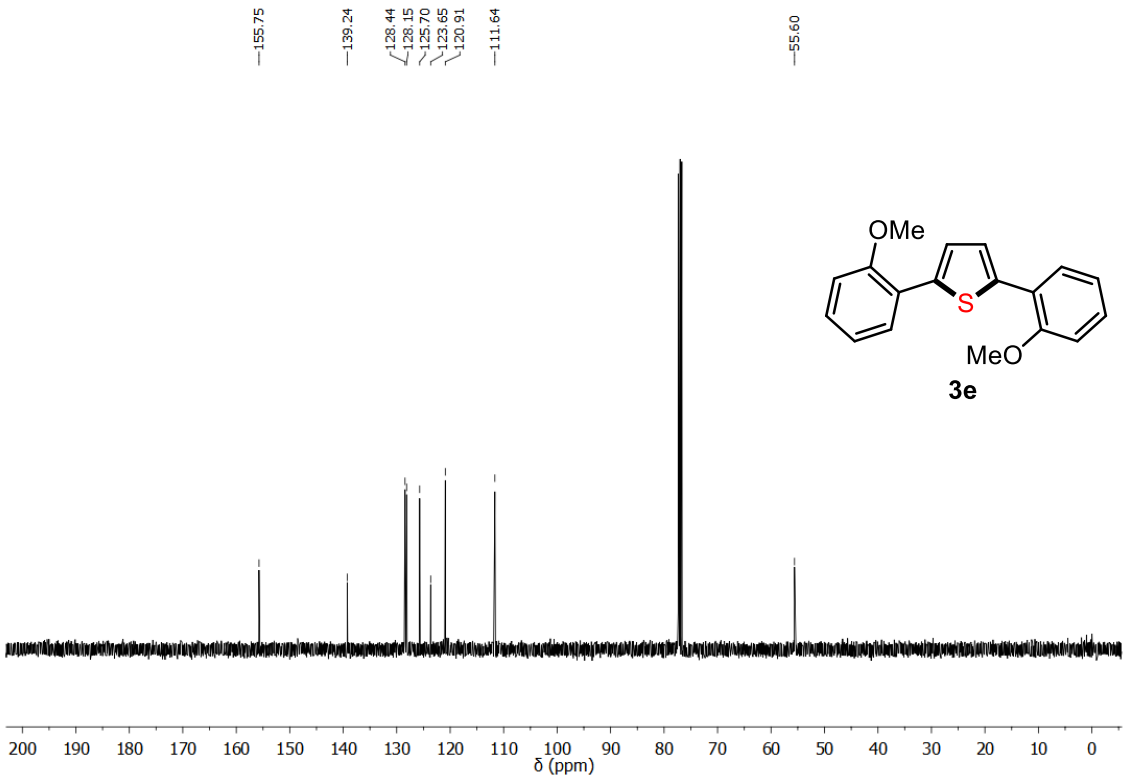

Figure S46. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3e**.

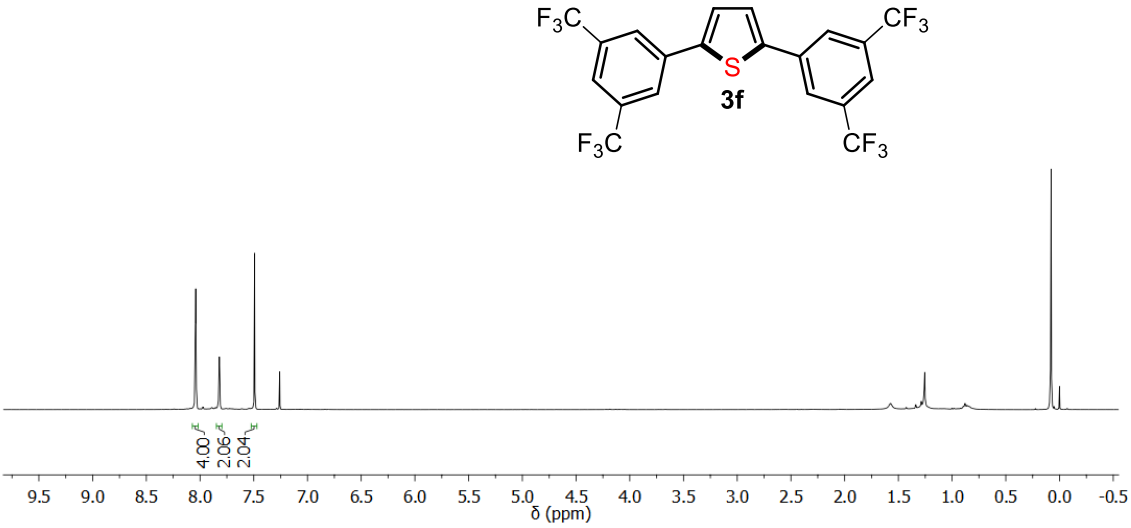

Figure S47. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3f**.

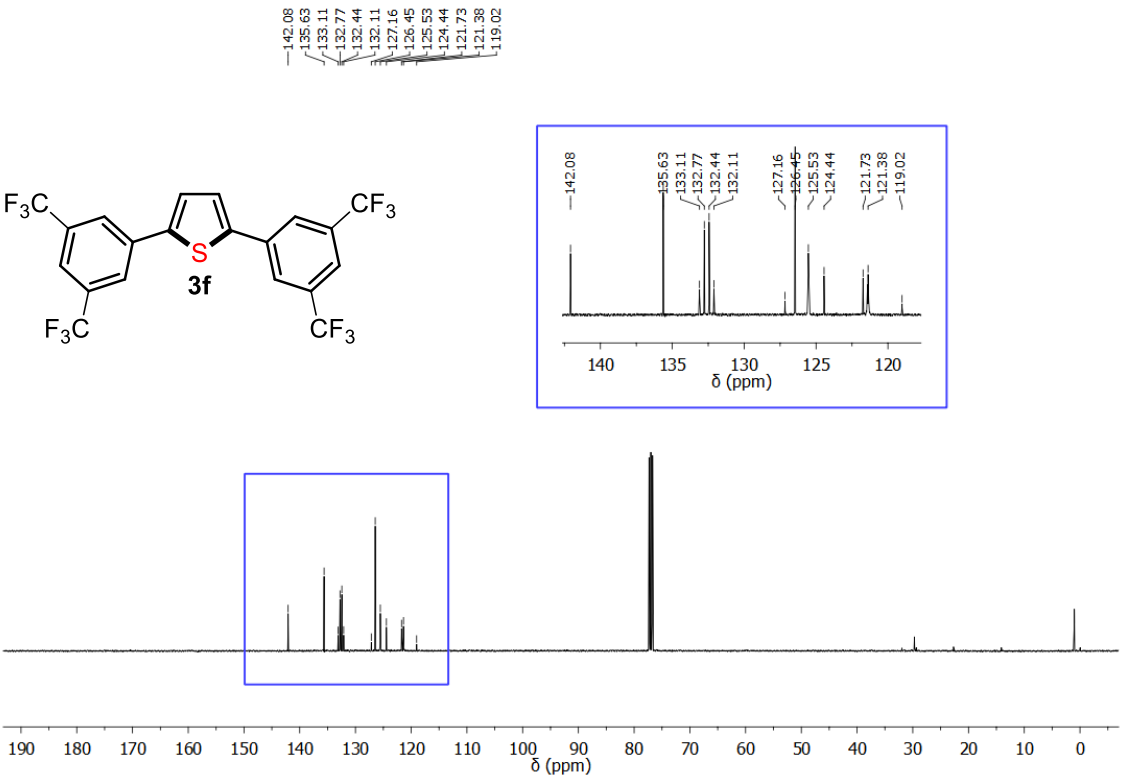

Figure S48. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) spectrum of **3f**.

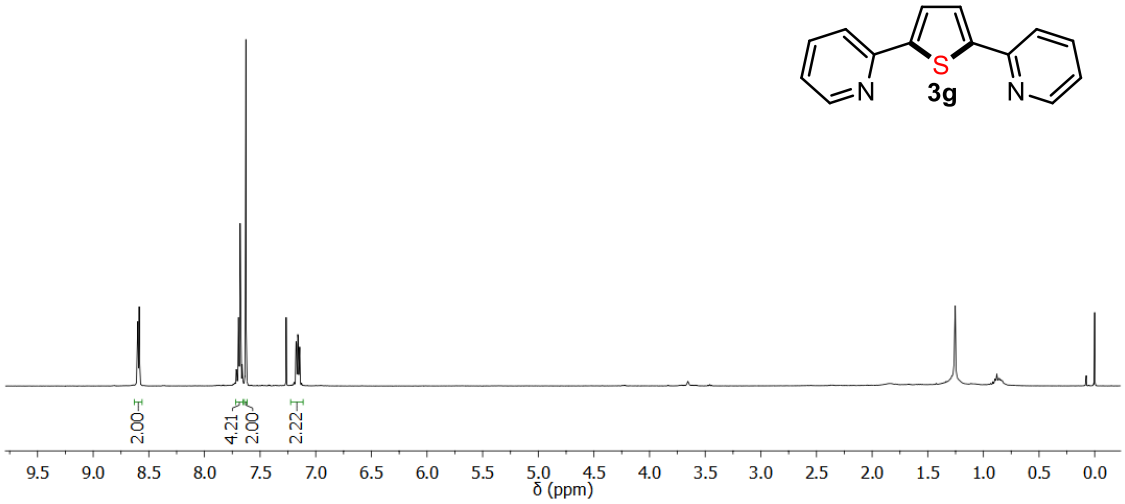

Figure S49. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3g**.

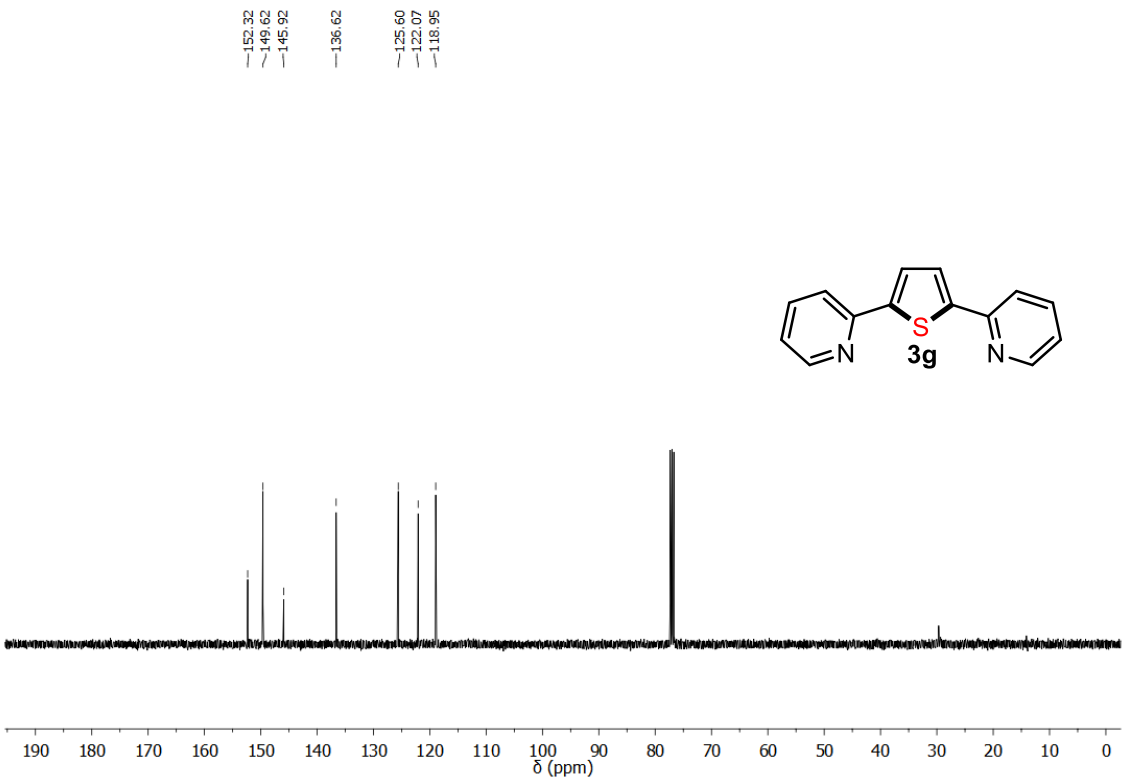

Figure S50. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) spectrum of **3g**.

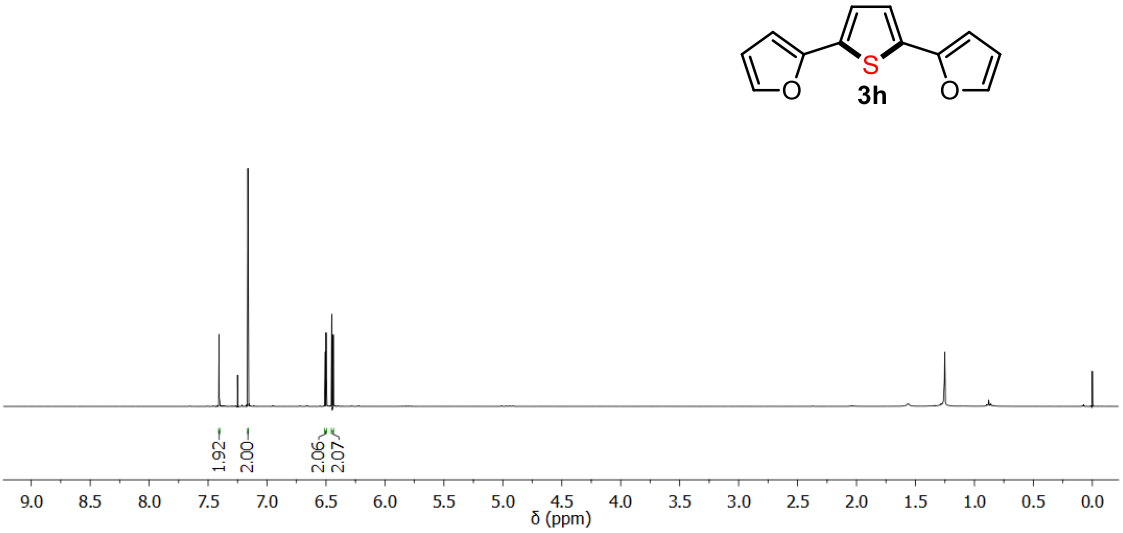

Figure S51. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3h**.

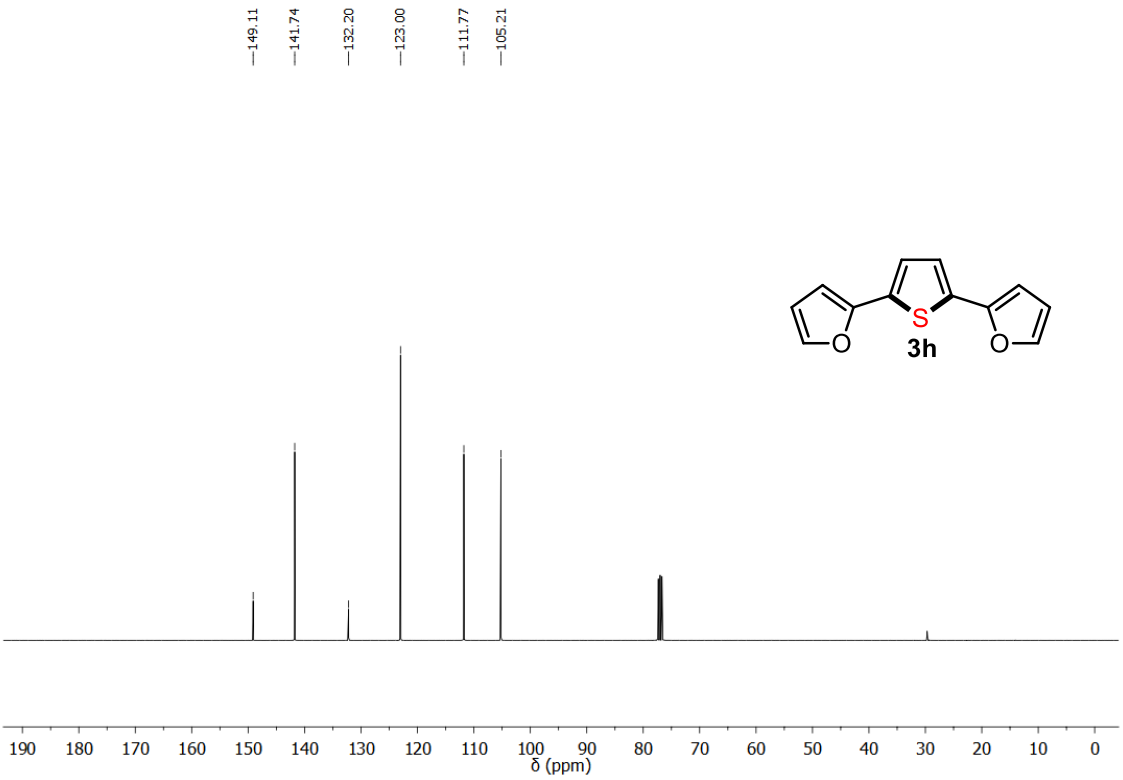

Figure S52. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) spectrum of **3h**.

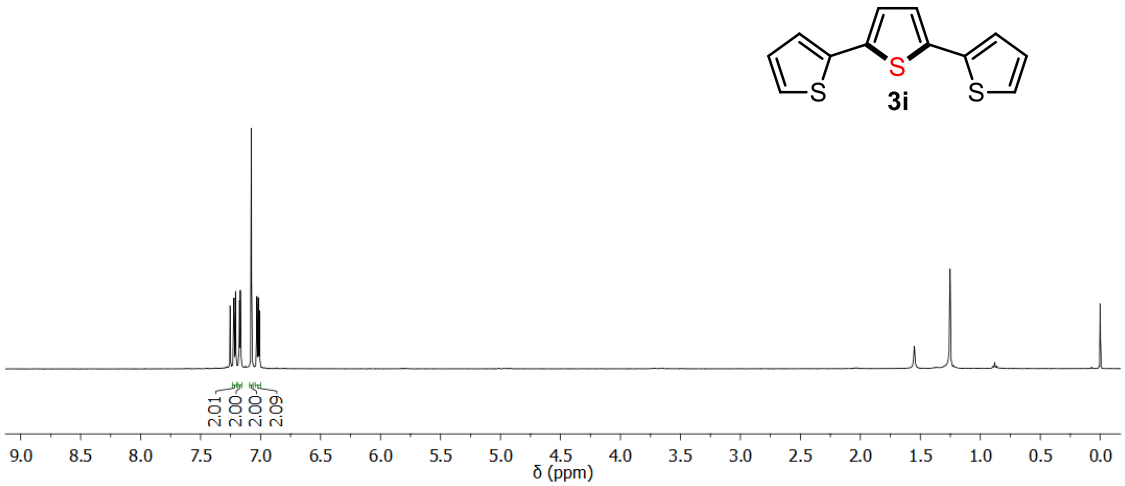

Figure S53. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3i**.

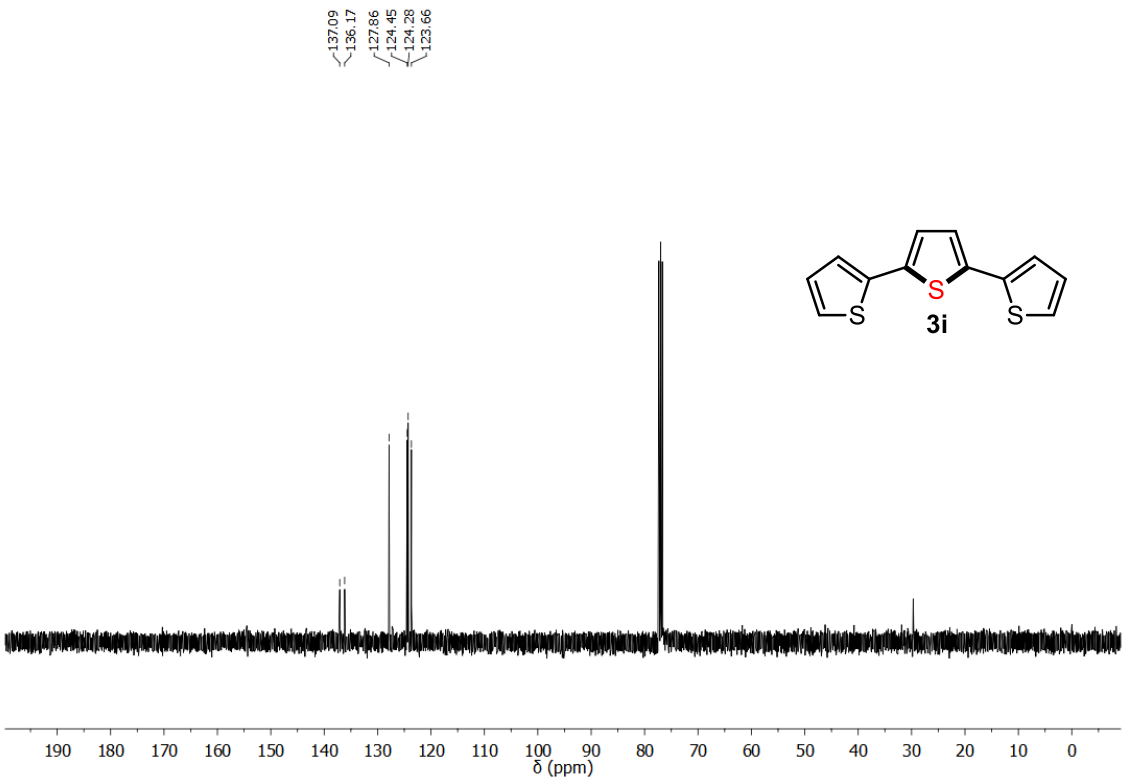

Figure S54. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) spectrum of **3i**.

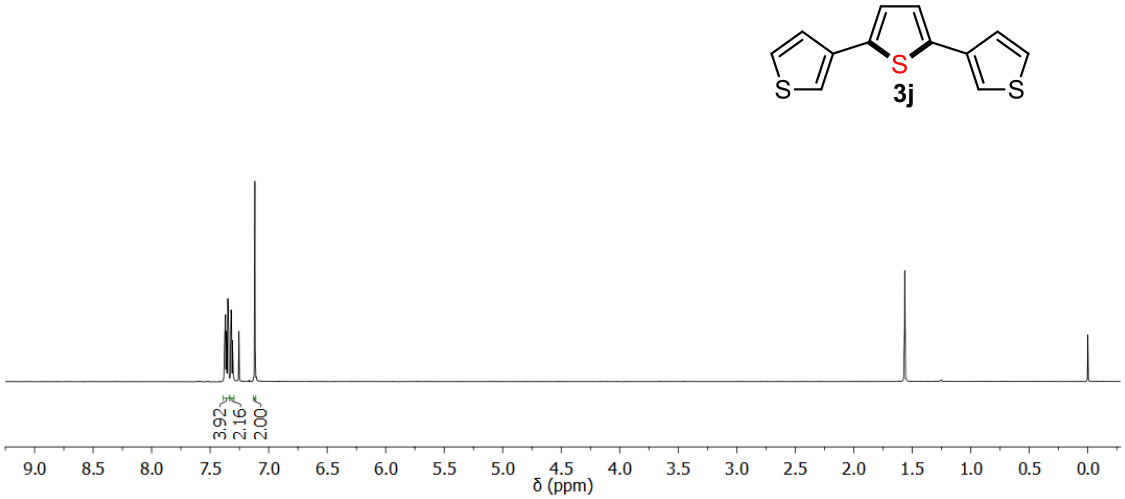

Figure S55. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3j**.

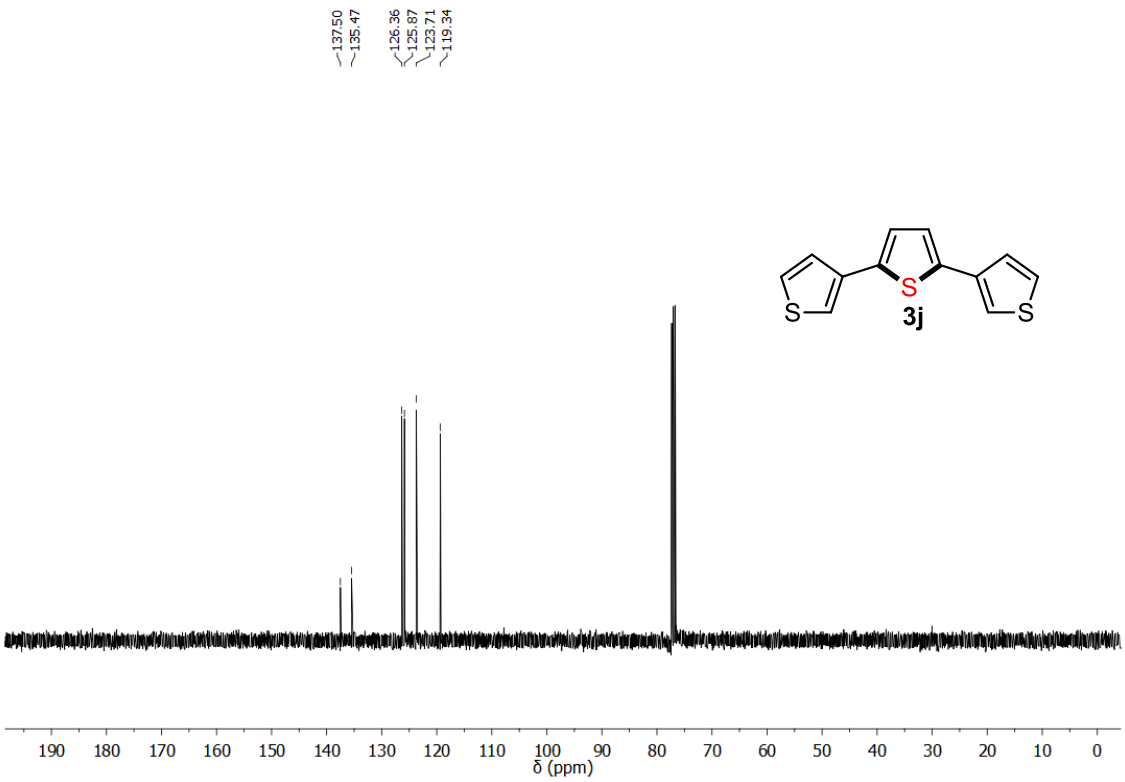

Figure S56. ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) spectrum of **3j**.

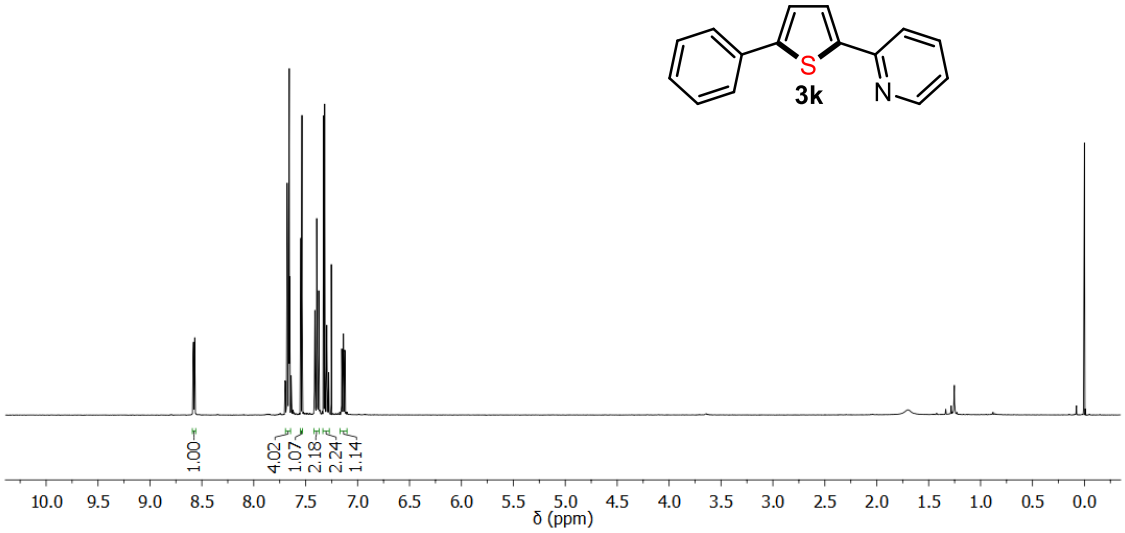

Figure S57. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3k**.

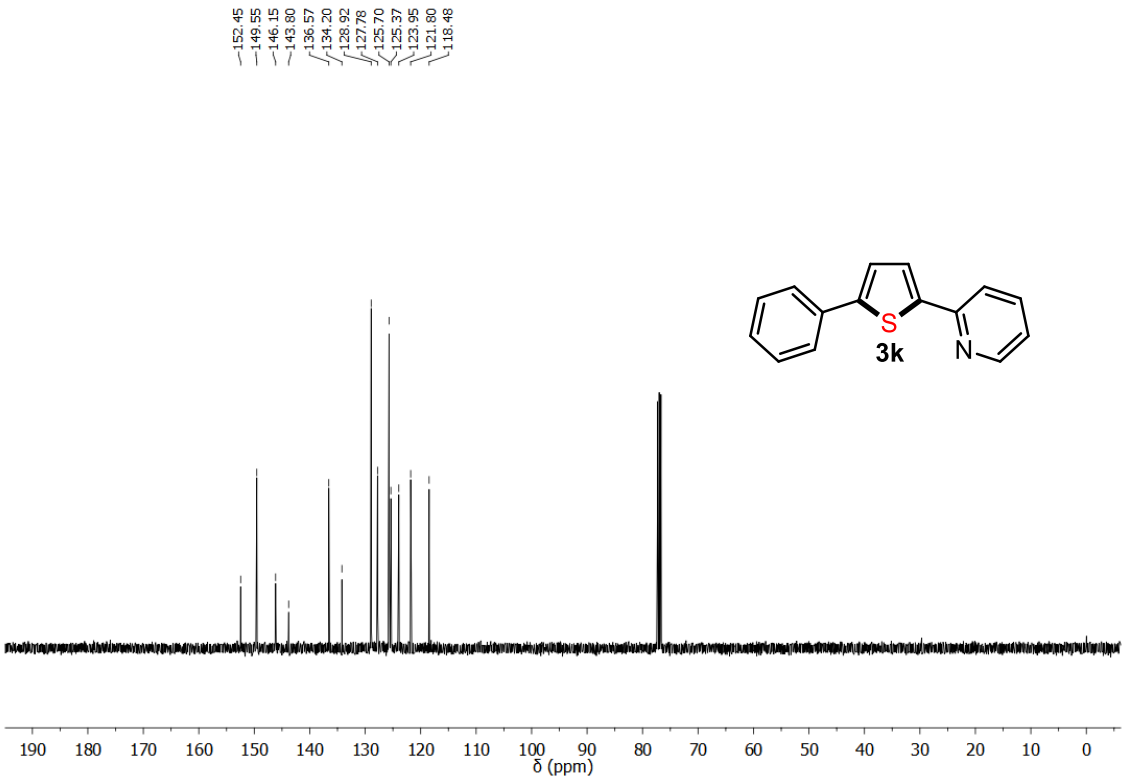

Figure S58. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **3k**.

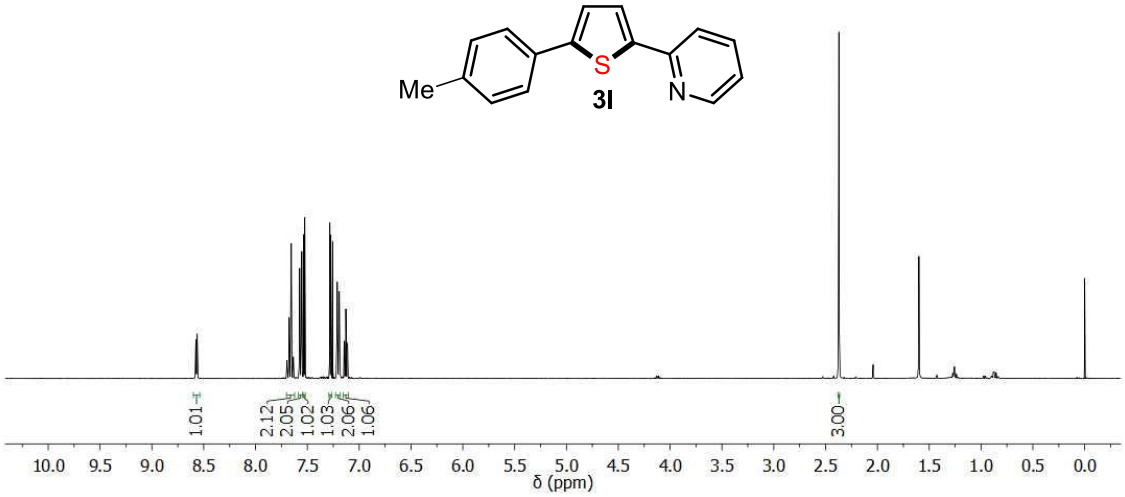

Figure S59. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3l**.

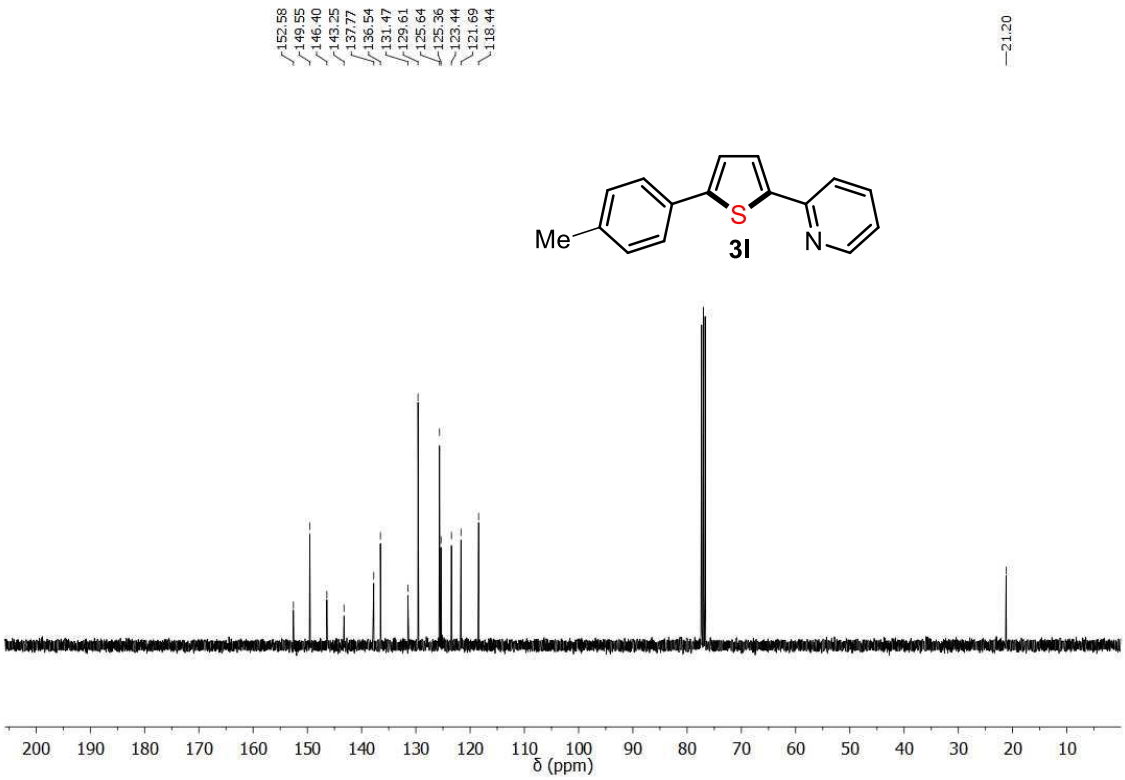

Figure S60. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3l**.

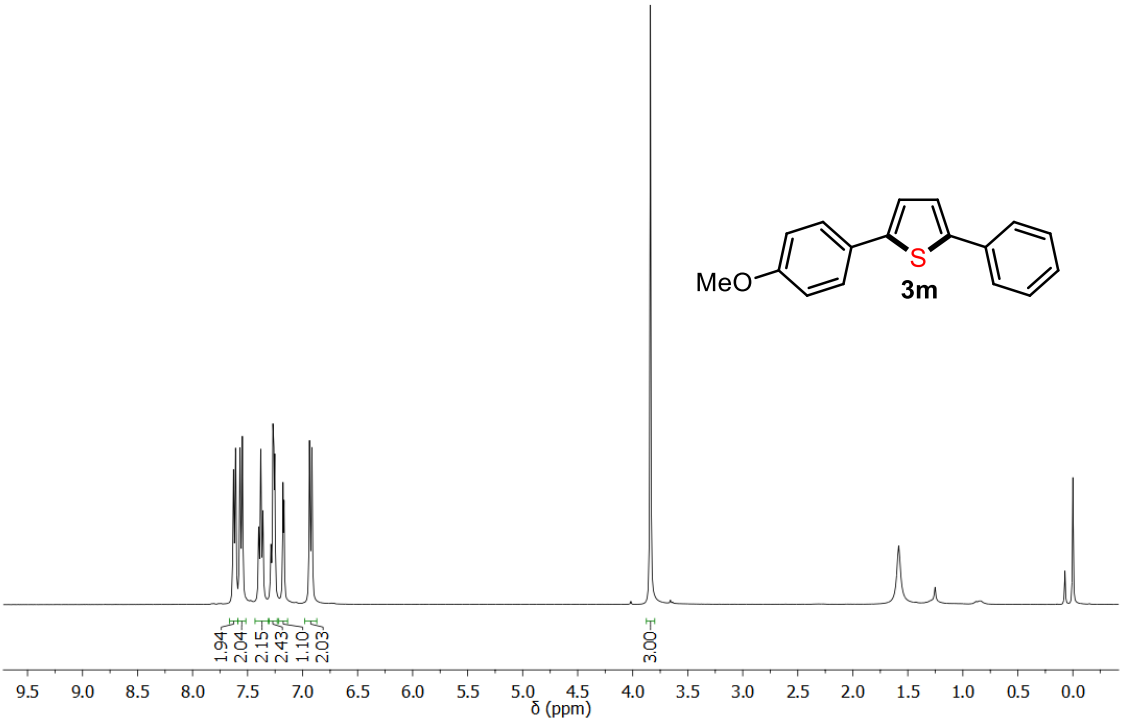

Figure S61. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3m**.

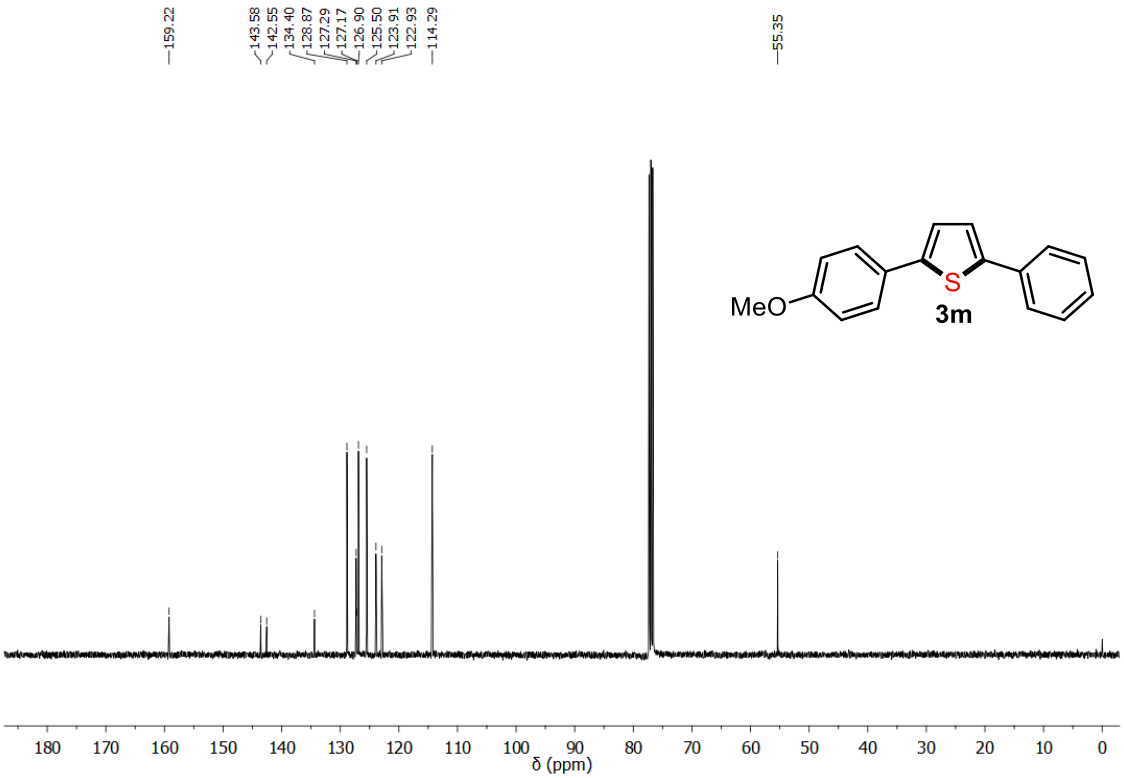

Figure S62. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3m**.

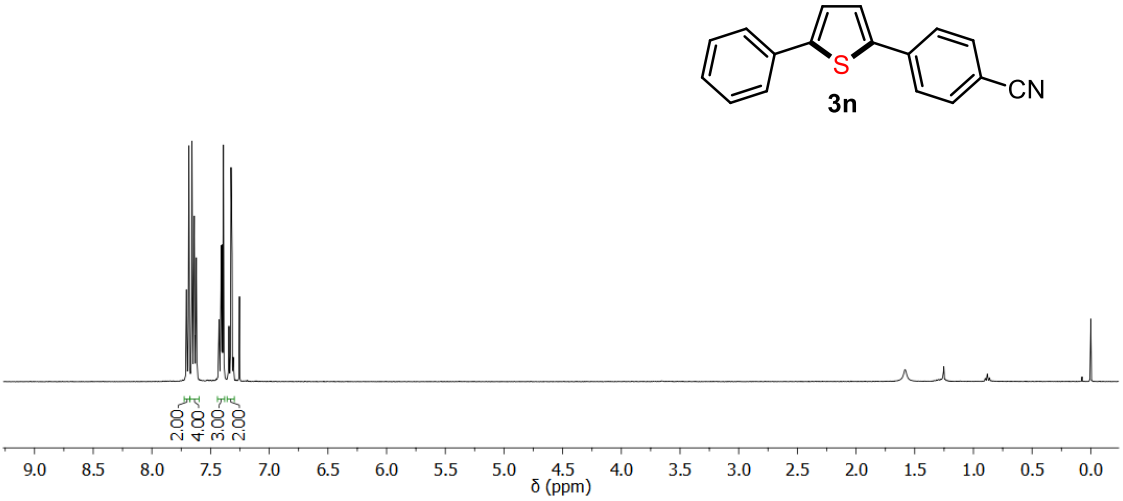

Figure S63. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3n**.

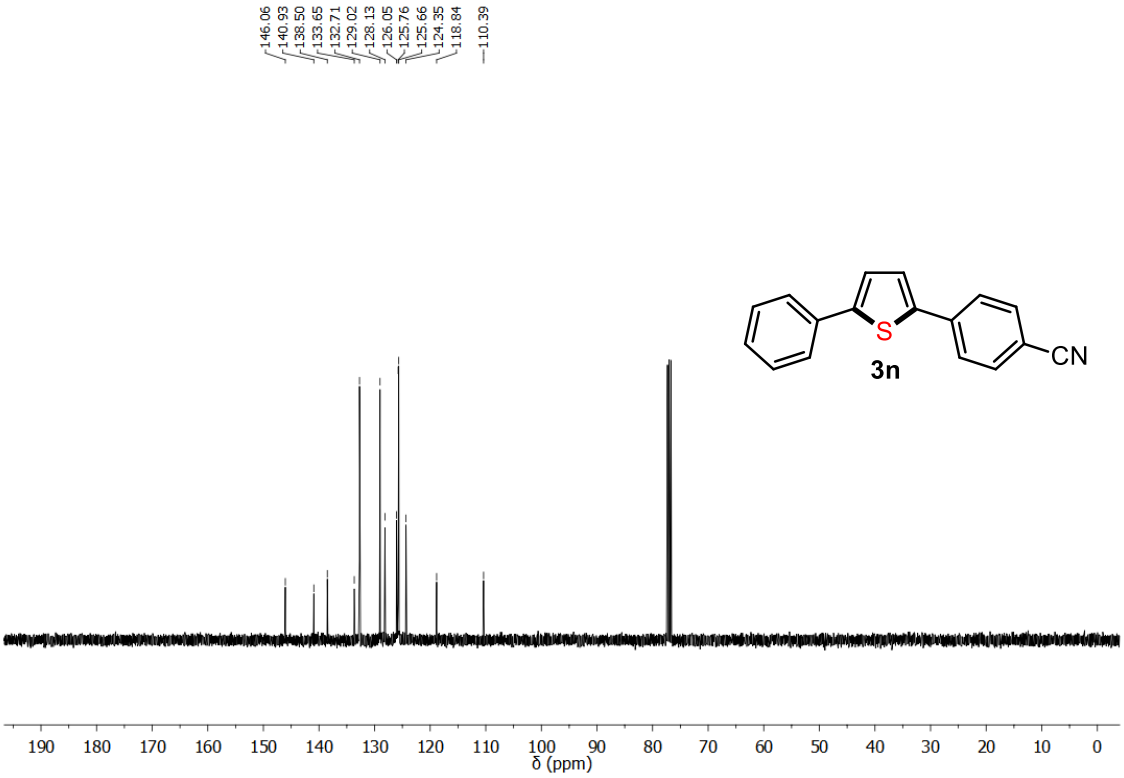

Figure S64. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3n**.

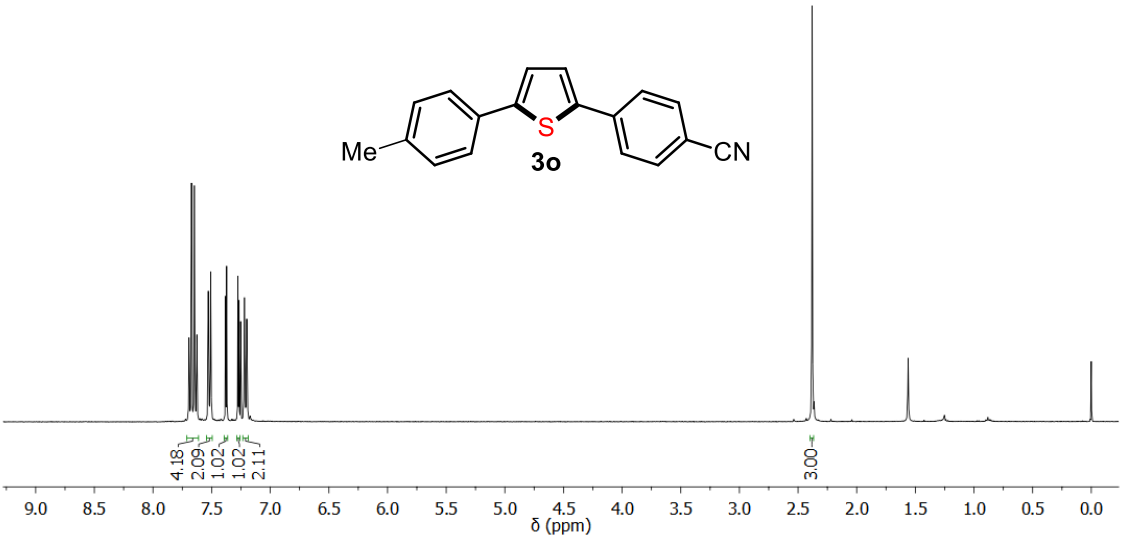

Figure S65. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3o**.

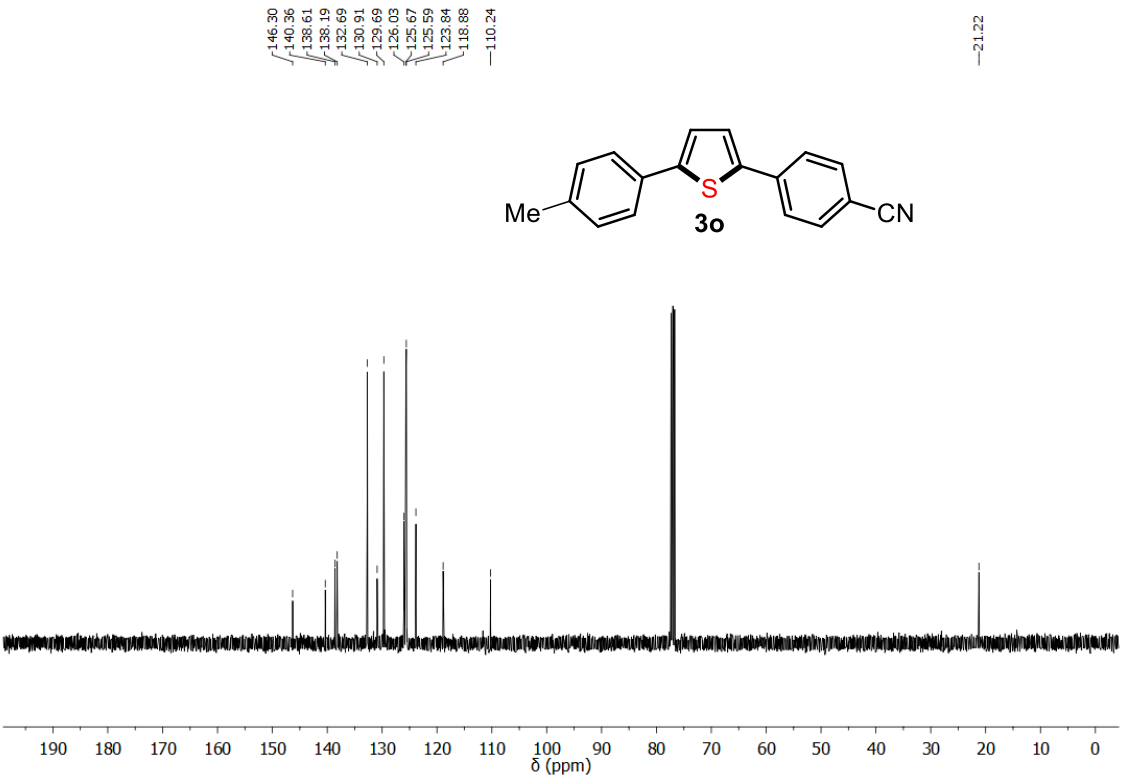

Figure S66. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3o**.

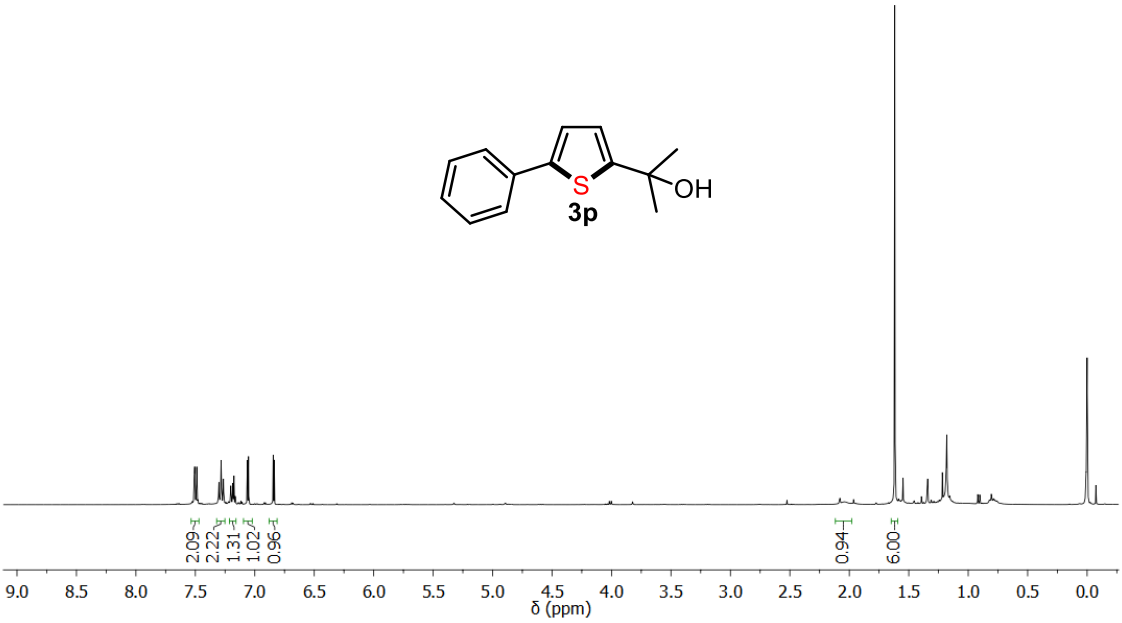

Figure S67. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3p**.

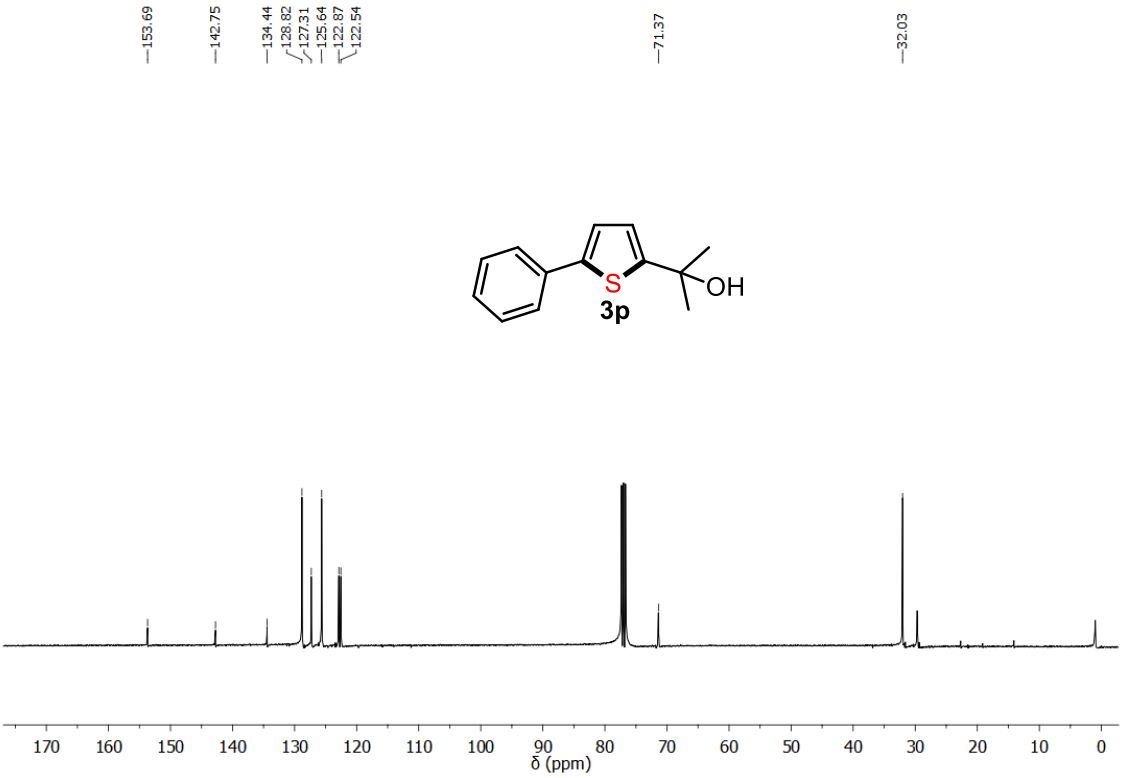

Figure S68. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3p**.

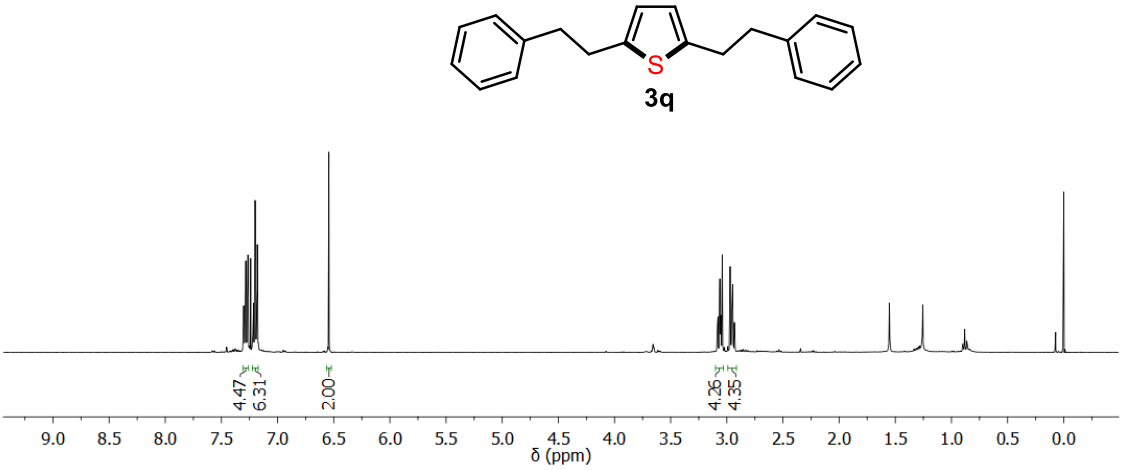

Figure S69. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3q**.

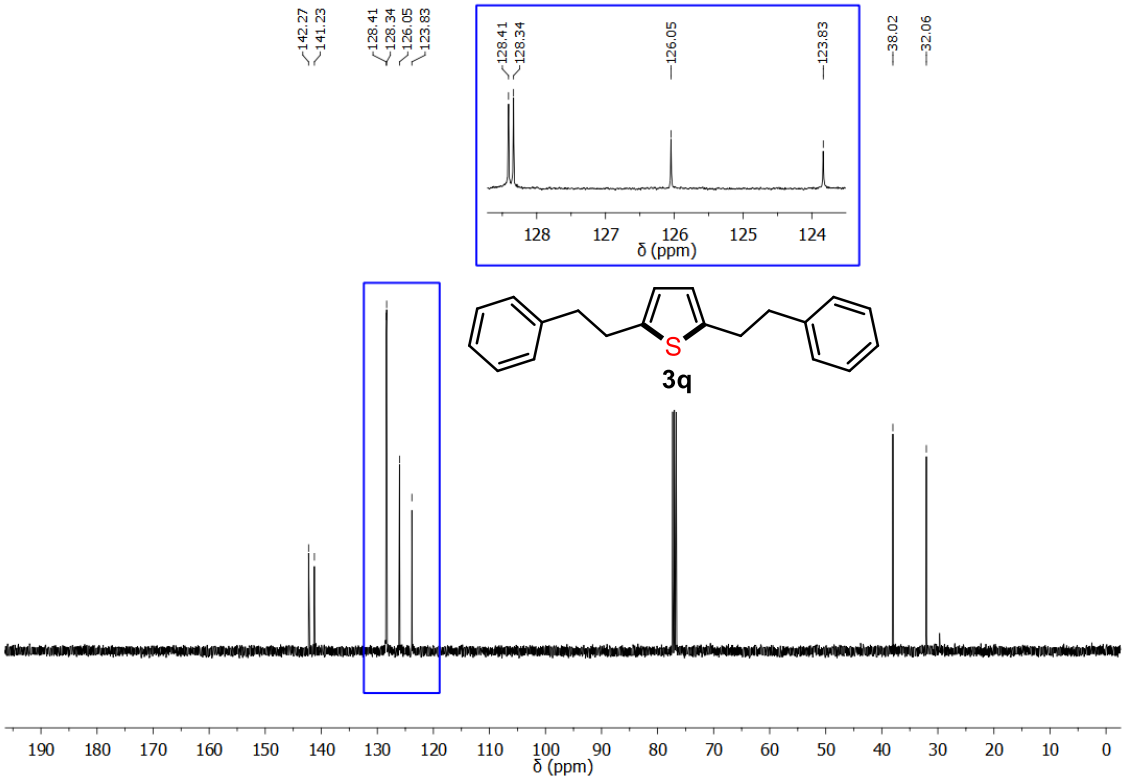

Figure S70. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **3q**.

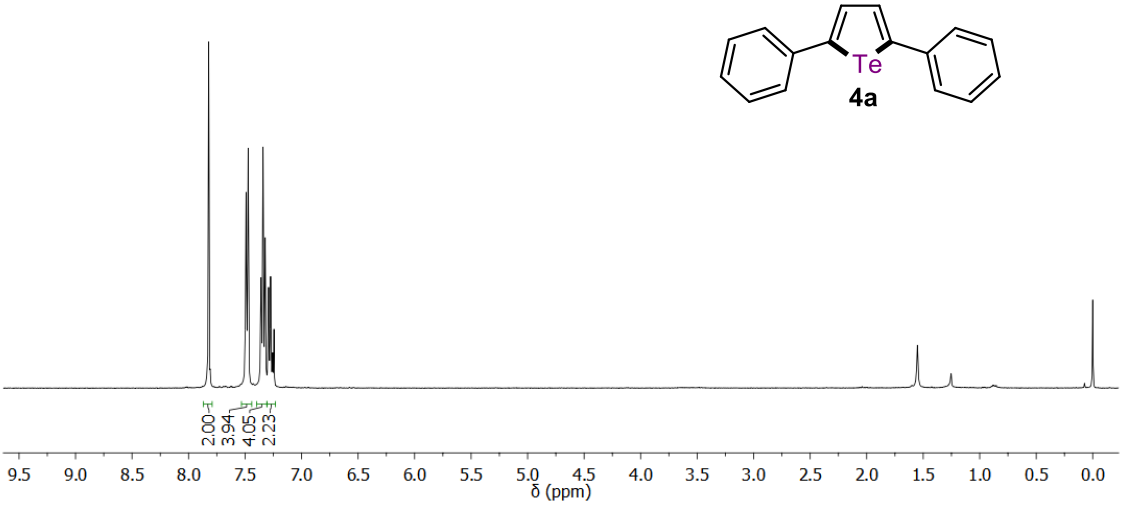

Figure S71. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4a**.

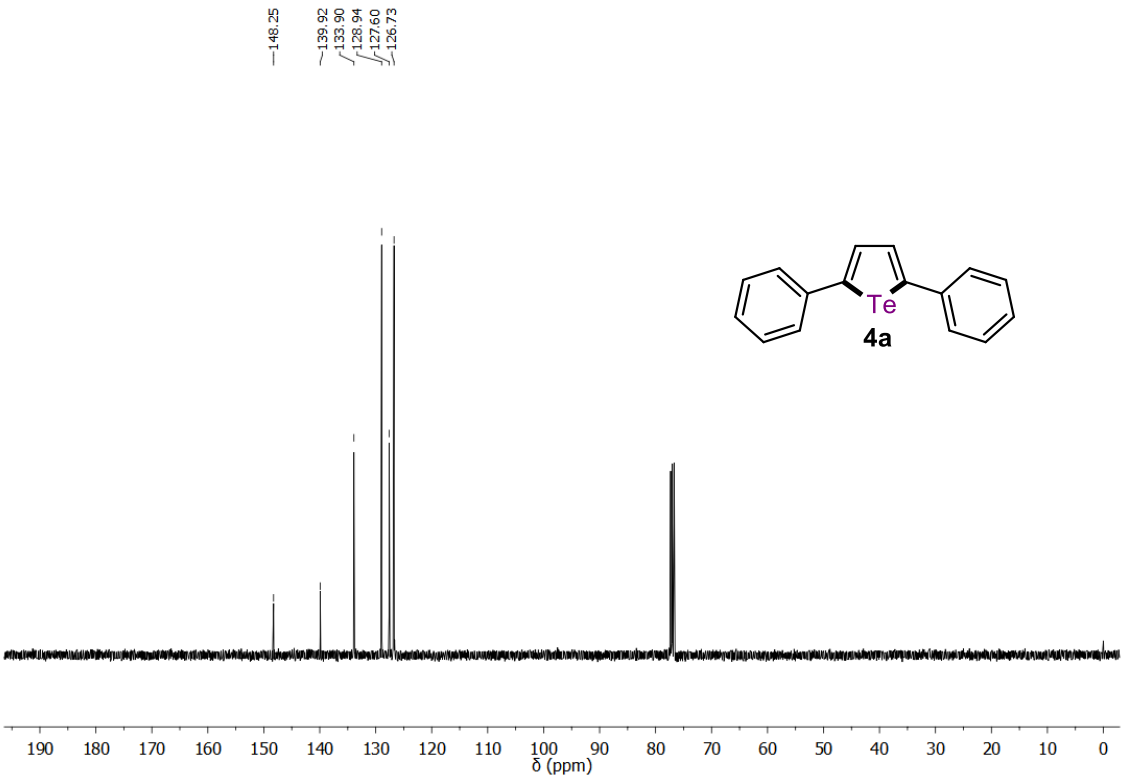

Figure S72. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **4a**.

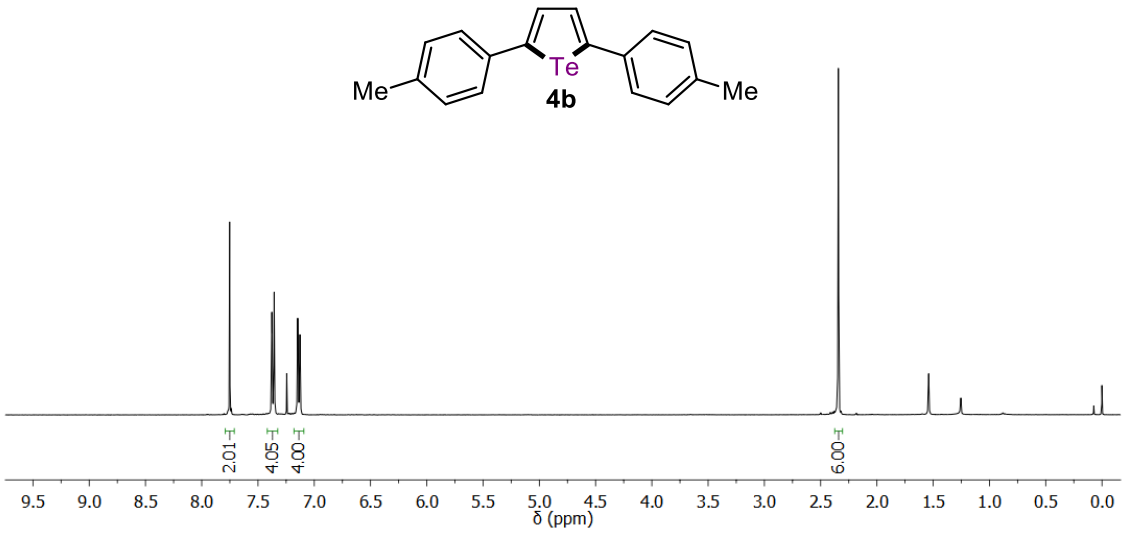

Figure S73. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4b**.

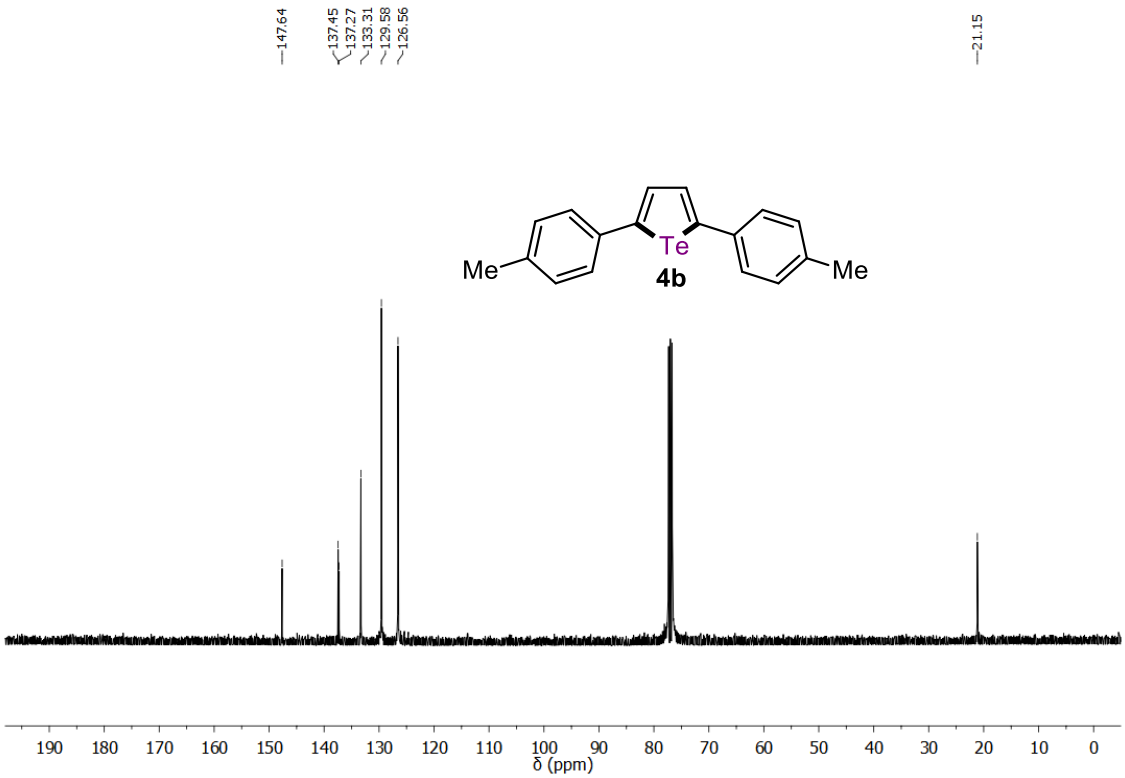

Figure S74. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **4b**.

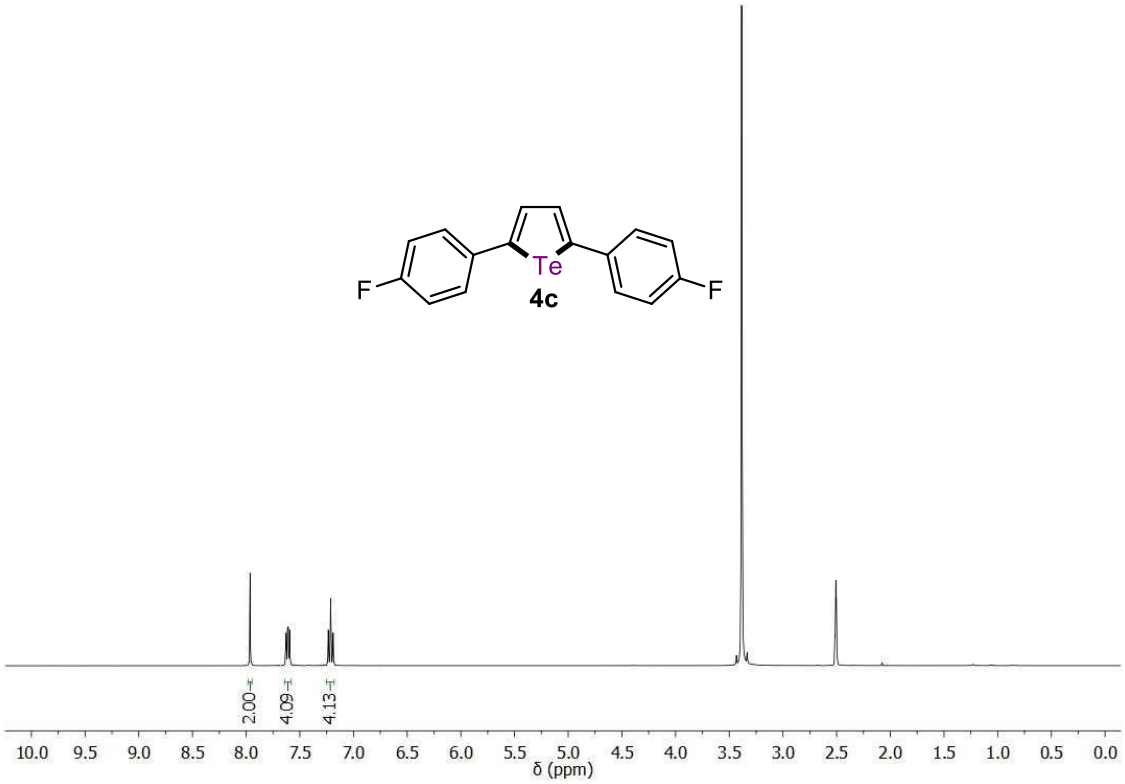

Figure S75. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **4c**.

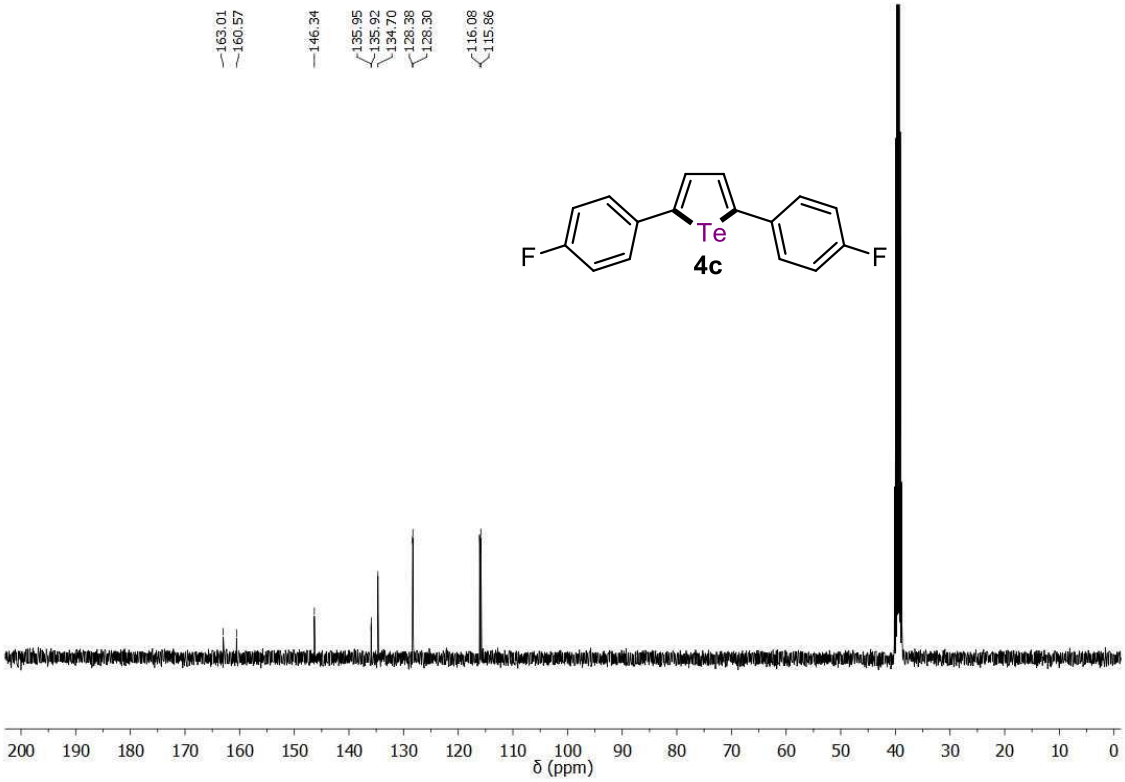

Figure S76. ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) spectrum of **4c**.

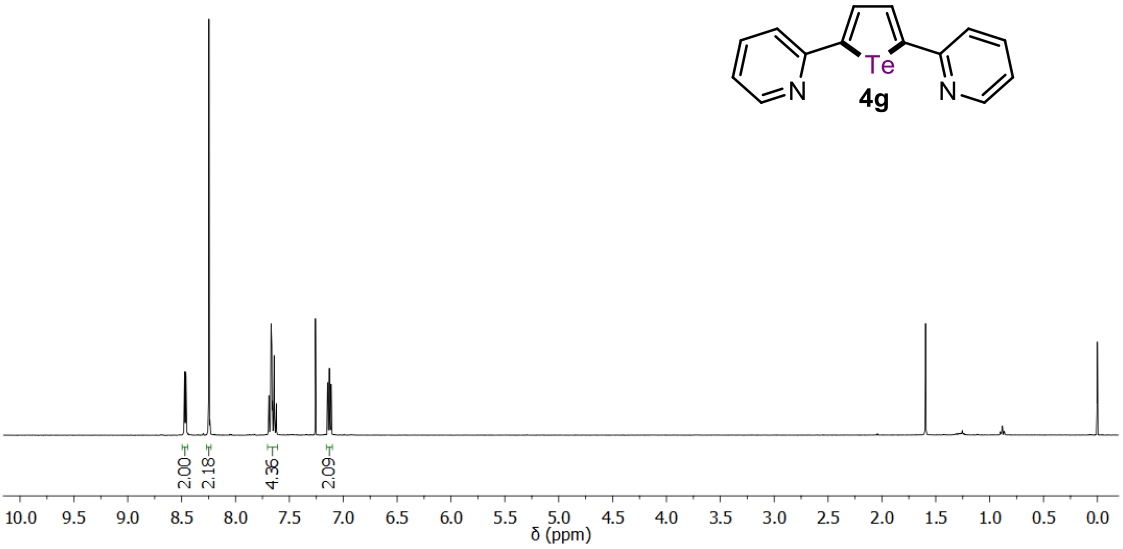

Figure S77. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4g**.

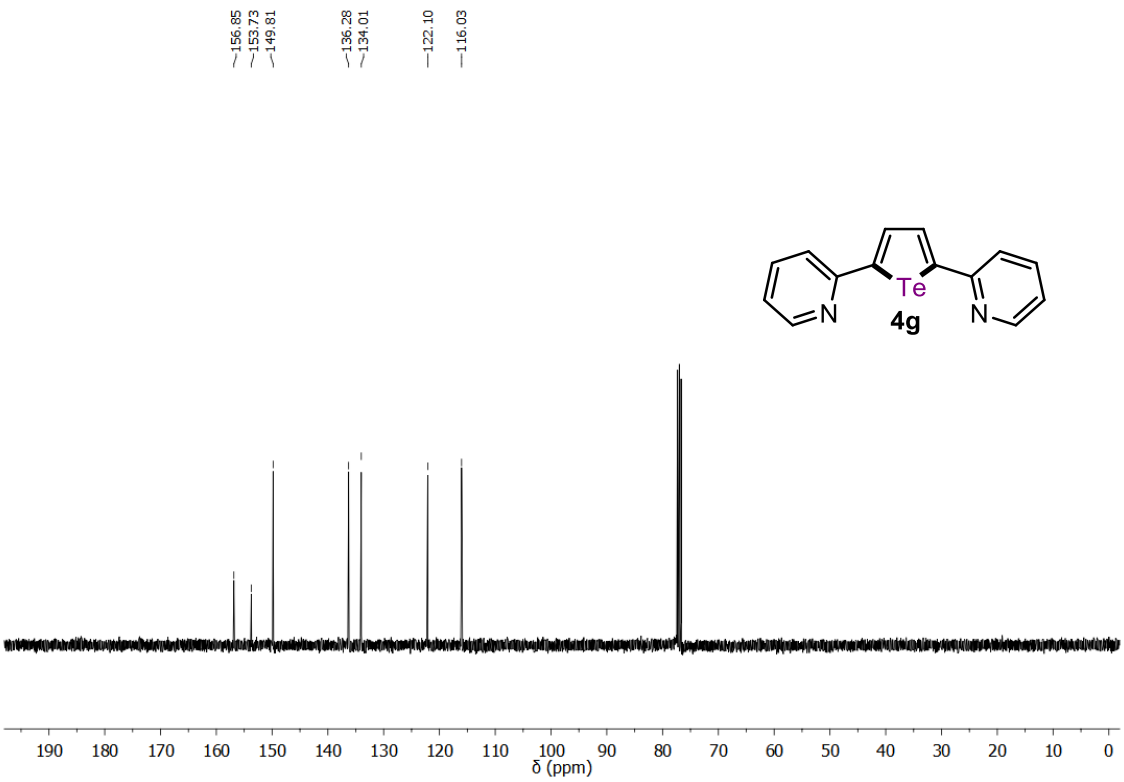

Figure S78. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **4g**.

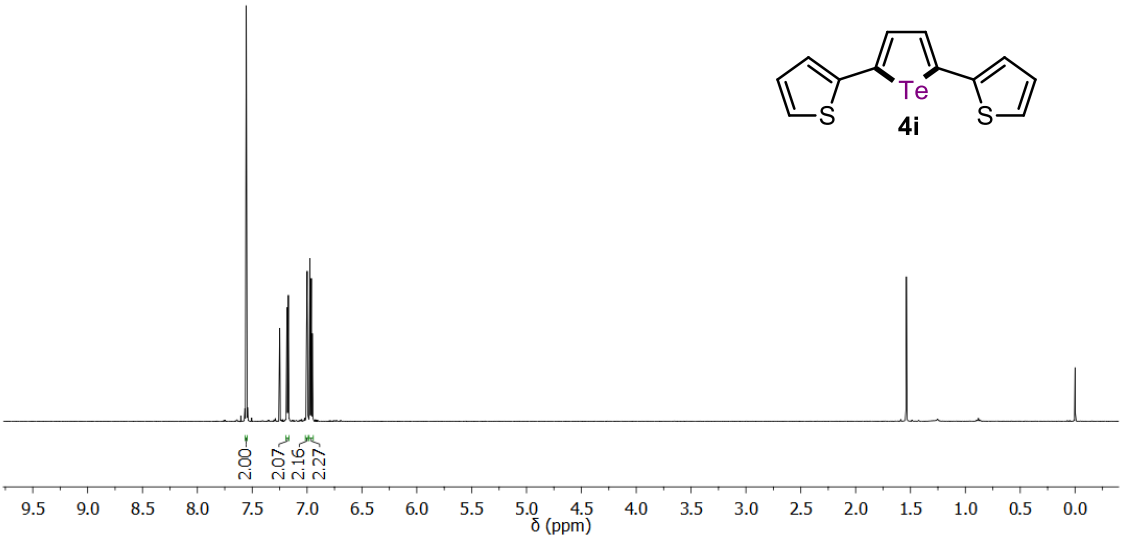

Figure S79. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4i**.

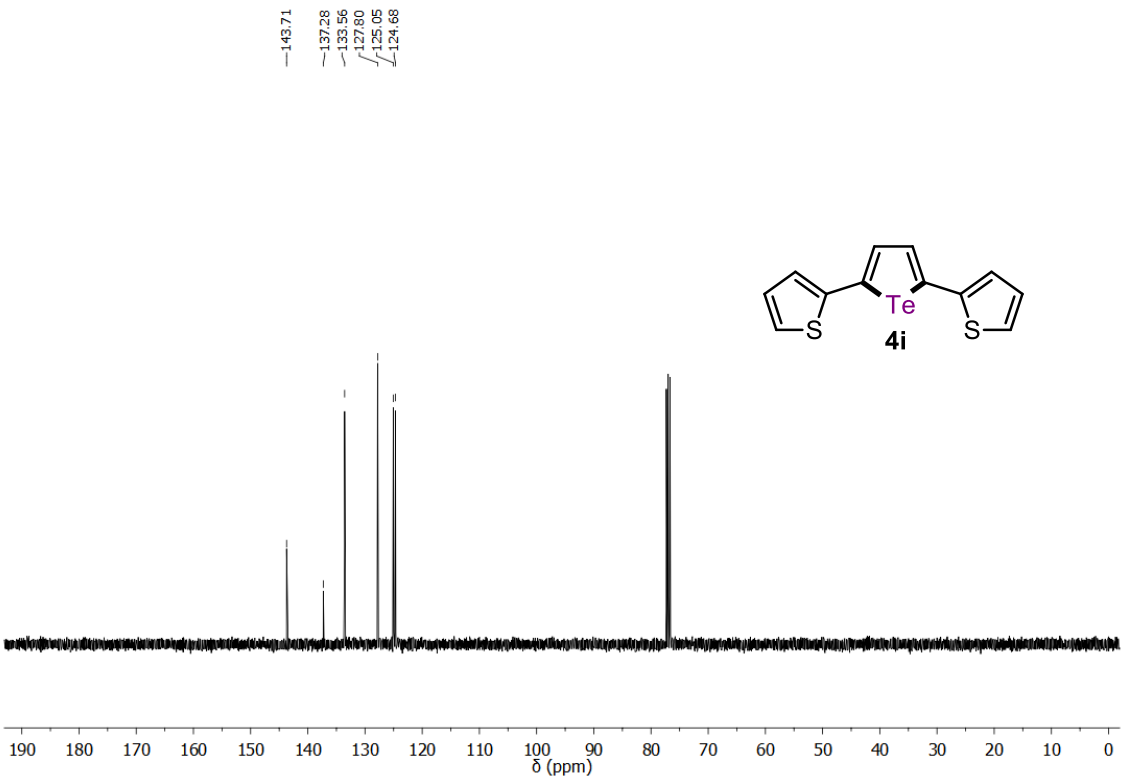

Figure S80. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **4i**.

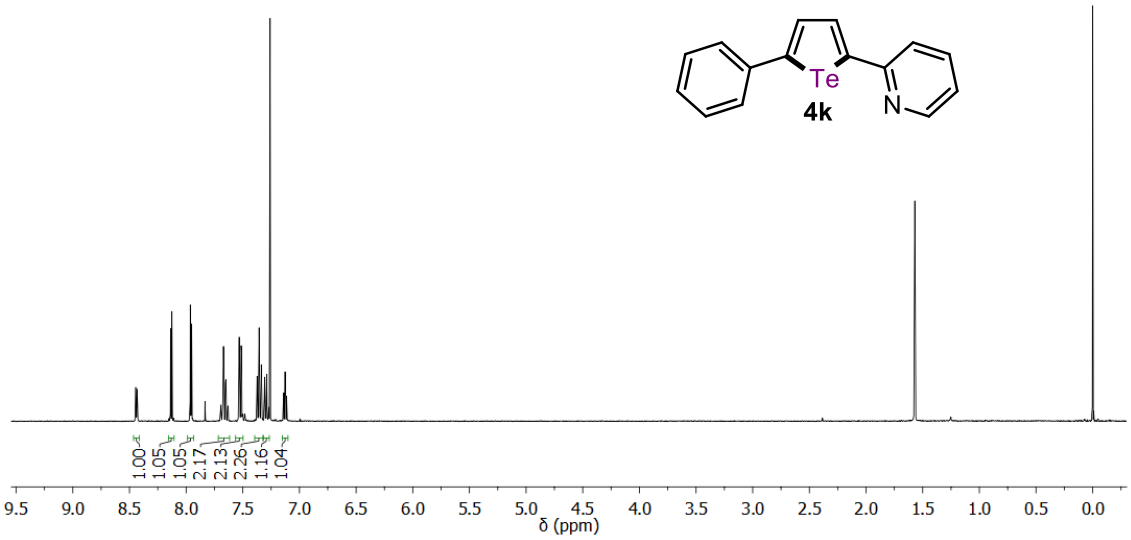

Figure S81. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4k**.

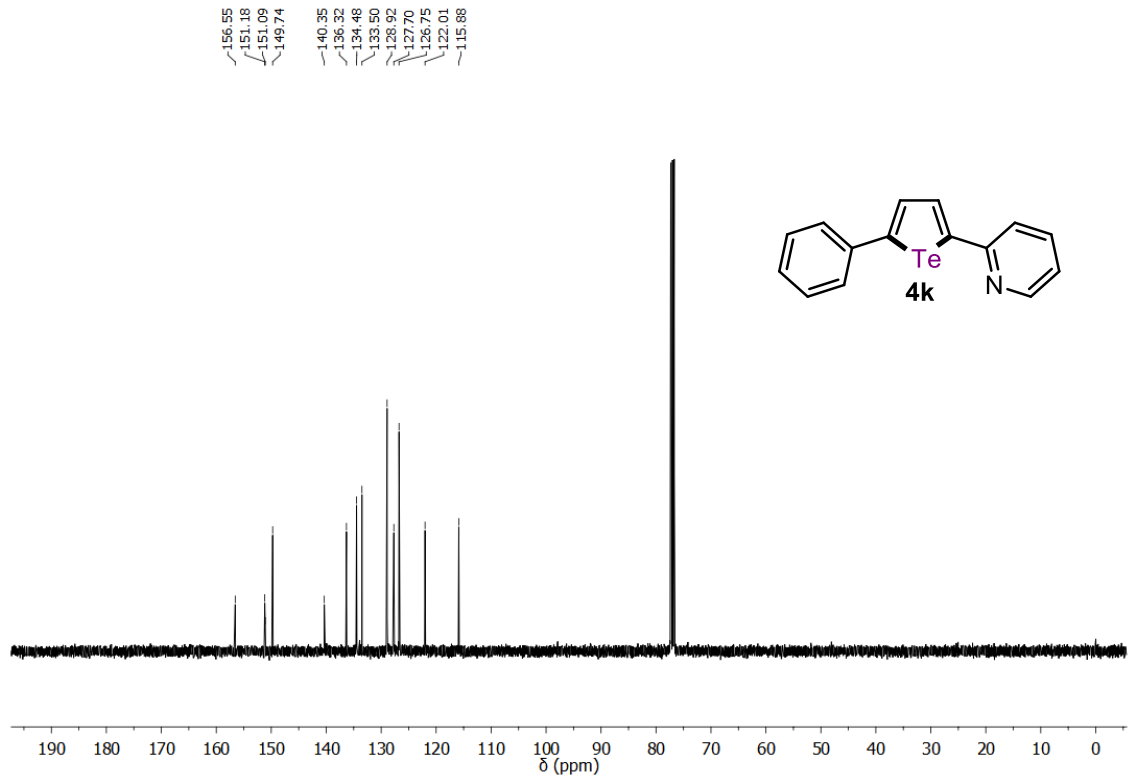

Figure S82. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) spectrum of **4k**.

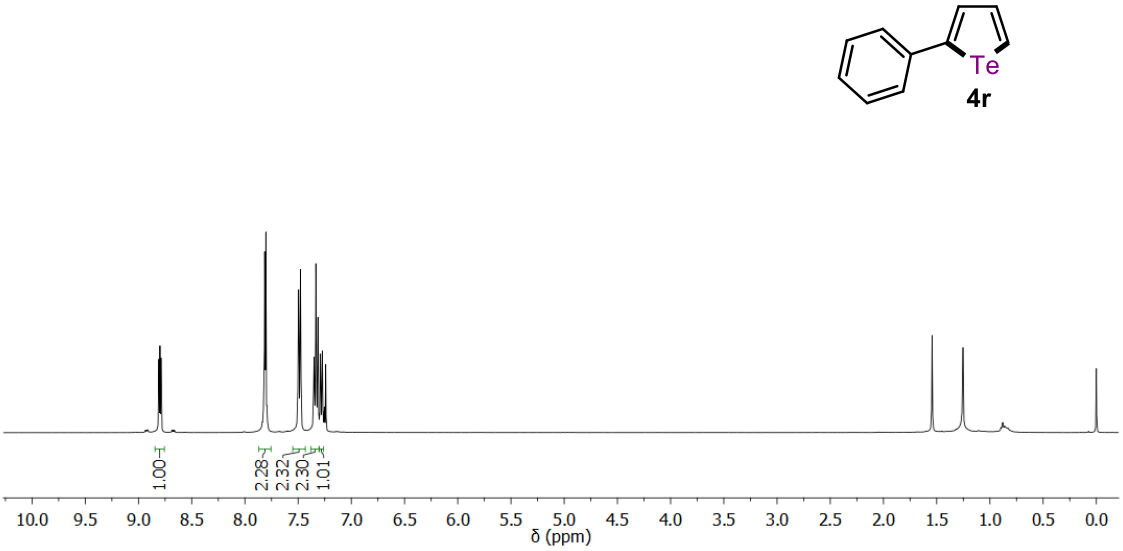

Figure S83. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4r**.

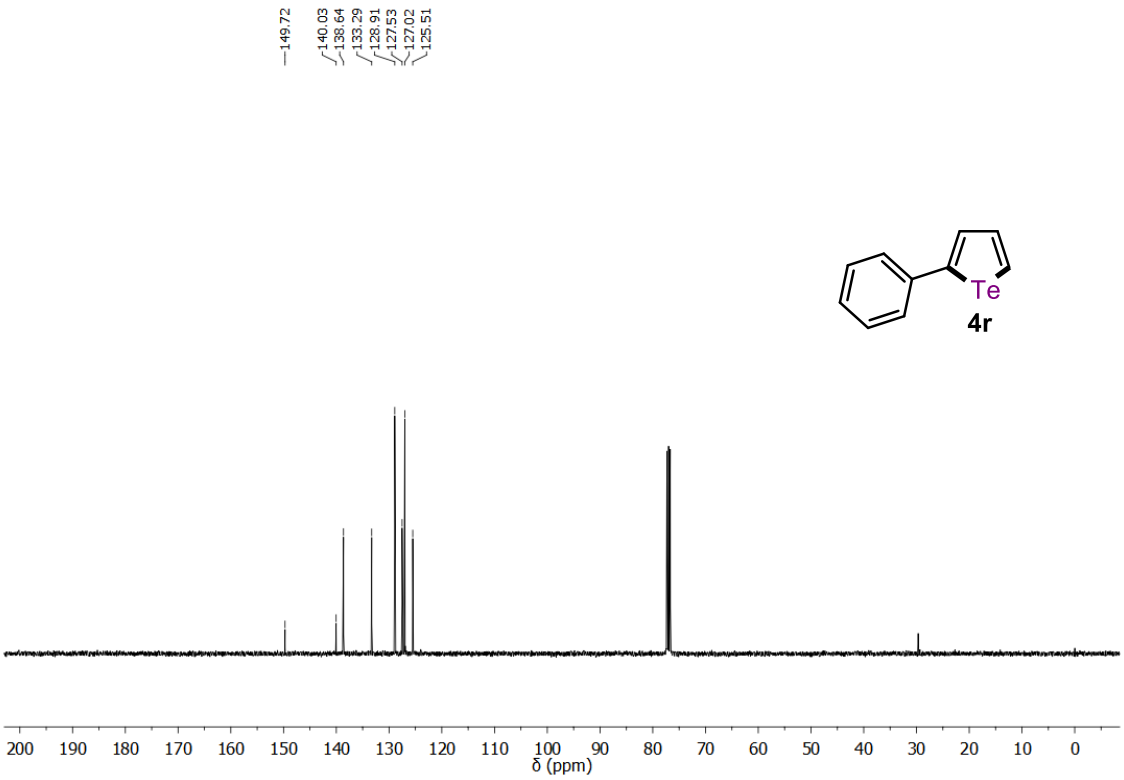

Figure S84. ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of **4r**.