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Extraordinary sulfur/oxygen exchange between P=S and C=O bonds during the reaction of γ-amino ynones with secondary phosphine sulfides

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1. General information

All reactions were carried out under an argon atmosphere. Amino ynones **1a-m** were prepared from propargylic amines and acyl chlorides as previously described.[S1] Diphenylphosphine sulfide **2a** was prepared by oxidation of commercially available diphenylphosphine (Aldrich) with elemental sulfur.[S2] Phosphine sulfides **2b,c** were prepared from styrene and elemental phosphorus as previously described.[S3] The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 and Bruker AV-400 spectrometers (400.13 and 100.62 MHz, respectively) in $CDCl_3$ solutions and referenced to HMDS (^{1}H, ^{13}C). The assignment of signals in ^{1}H spectra was performed using 2D homonuclear correlation method COSY. Resonance signals of ^{13}C were assigned with application of 2D heteronuclear correlation methods HSQC and HMBC. Mass spectra were recorded on an Agilent 6210 HRMS−TOF−ESI Mass spectrometer. Electrostatic sputtering, registration of positive ions. Sample solvent − MeCN with the addition of 0.1% formic acid and with the addition of calibration mixture for mass spectrometer.

2. Synthesis of 1,2-dihydro-3*H*-pyrrole-3-thiones 3a-m: General procedure.

Synthesis of 1,2,5-trisubstituted-1,2-dihydro-3*H*-pyrrole-3-thiones 3: General procedure. A solution of bis(2-phenylethyl)phosphine sulfide **2b** (0.137 g, 0.5 mmol), amino ynones **1a-m** (0.5 mmol) and 5 eq. H_2O in MeCN (2 ml) was stirred under an argon atmosphere at 80-85 °C for 41-72 h (see also Table 1, Schemes 1,2 of the main text). After completion of the reaction (^{31}P NMR monitoring or TLC, eluent: benzene/Et_2O, 10:1), the solvent was removed under the reduced pressure. The residue was purified by column chromatography on SiO_2 (eluent: benzene/Et_2O, 10:1), the solution was dried *in vacuo* to obtain the corresponding 1,2-dihydro-3*H*-pyrrole-3-thiones **3a-m**.

2-Methyl-1,2,5-triphenyl-1,2-dihydro-3*H*-pyrrole-3-thione (3a). Reaction time 48 h. Yield: 90 mg (53%); crimson powder, mp 153–156 °C (reprecipitated from CCl_4 to hexane). The ^{1}H and ^{13}C NMR spectra are in accordance with the published[S4] data. HRMS (ESI-TOF) calcd for $[C_{23}H_{19}NS + H]^+$ 342.13164, found 342.13179.

5-(4-Chlorophenyl)-2-methyl-1,2-diphenyl-1,2-dihydro-3*H*-pyrrole-3-thione (3b). Reaction time 42 h. Yield: 66 mg (35%); dark red powder, mp 87–88 °C (reprecipitated from CCl_4 to hexane). The ^{1}H and ^{13}C NMR spectra are in accordance

with the published[S4] data. HRMS (ESI-TOF) calcd for $[C_{23}H_{18}ClNS + H]^+$ 376.09267, found 376.09218.

5-(4-Ethylphenyl)-2-methyl-1,2-diphenyl-1,2-dihydro-3*H*-pyrrole-3-thione (3c). Reaction time 48 h. Yield: 77 mg (42%); red powder, mp 150–151 °C (reprecipitated from CCl_4 to hexane). The ^1H and ^{13}C NMR spectra are in accordance with the published[S4] data. HRMS (ESI-TOF) calcd for $[C_{25}H_{23}NS + H]^+$ 370.16294, found 370.16284.

5-(Furan-2-yl)-2-methyl-1,2-diphenyl-1,2-dihydro-3*H*-pyrrole-3-thione (3d). Reaction time 42 h. Yield: 33 mg (20%); waxy product. The ^1H and ^{13}C NMR spectra are in accordance with the published[S4] data. HRMS (ESI-TOF) calcd for $[C_{21}H_{17}NOS + H]^+$ 332.11091, found 332.11066.

2-Methyl-1,2-diphenyl-5-(thiophen-2-yl)-1,2-dihydro-3*H*-pyrrole-3-thione (3e). Reaction time 41 h. Yield: 43 mg (25%); burgundy powder, mp 153–155 °C (reprecipitated from CCl_4 to hexane). The ^1H and ^{13}C NMR spectra are in accordance with the published[S4] data. HRMS (ESI-TOF) calcd for $[C_{21}H_{17}NS_2 + H]^+$ 348.08807, found 348.08838.

5-Cyclohexyl-2-methyl-1,2-diphenyl-1,2-dihydro-3*H*-pyrrole-3-thione (3f).[S4] Reaction time 72 h. Yield: 5% (according to ^1H NMR). ^1H NMR (400.13 MHz, $CDCl_3$): δ 1.75 (s, 3H, Me); 6.48 (s, 1H, H-4, pyrrolethione); 6.72–6.73 (m, 2H, H_o, NPh); 7.26–7.36 (m, 6H, $H_{m,p}$, NPh; $H_{m,p}$, PhC-2). Other signals of 1,2-dihydro-3*H*-pyrrole-3-thione **3f** are overlapped with signals of side products.

2-Methyl-1,5-diphenyl-2-(thiophen-2-yl)-1,2-dihydro-3*H*-pyrrole-3-thione (3g). Reaction time 48 h. Yield: 81 mg (47%); waxy product. The ^1H and ^{13}C NMR spectra are in accordance with the published[S4] data. HRMS (ESI-TOF) calcd for $[C_{21}H_{17}NS_2 + H]^+$ 348.08807, found 348.08820.

1,2-Diphenyl-1-azaspiro[4.5]dec-2-ene-4-thione (3h). Reaction time 56 h. Yield: 51 mg (32%); waxy product. The ^1H and ^{13}C NMR spectra are in accordance with the published[S4] data. HRMS (ESI-TOF) calcd for $[C_{21}H_{21}NS + H]^+$ 320.14730, found 320.14720.

2-(Furan-2-yl)-1-phenyl-1-azaspiro[4.5]dec-2-ene-4-thione (3i). Reaction time 52 h. Yield: 54 mg (35%); waxy product. The ^1H and ^{13}C NMR spectra are in accordance with the published[S4] data. HRMS (ESI-TOF) calcd for $[C_{19}H_{19}NOS + H]^+$ 310.12656, found 310.12672.

1-Phenyl-2-(thiophen-2-yl)-1-azaspiro[4.5]dec-2-ene-4-thione (3j). Reaction time 52 h. Yield: 54 mg (33%); waxy product. The ^1H and ^{13}C NMR spectra are in

accordance with the published[S4] data. HRMS (ESI-TOF) calcd for $[C_{19}H_{19}NS_2 + H]+$ 326.10372, found 326.10359.

1-Phenyl-2-(thiophen-2-yl)-1-azaspiro[4.6]undec-2-ene-4-thione (3k). Reaction time 51 h. Yield: 66 mg (38%); waxy product. The ^1H and ^{13}C NMR spectra are in accordance with the published[S4] data. HRMS (ESI-TOF) calcd for $[C_{20}H_{21}NS_2 + H]^+$ 340.11937, found 340.11958.

2-Methyl-2-(naphthalen-2-yl)-1,5-diphenyl-1,2-dihydro-3*H*-pyrrole-3-thione(3l). Reaction time 72 h. **Yield**: 7% (according to ^1H NMR). ^1H NMR (400.13 MHz, $CDCl_3$): 1.78 (s, 3H, Me); 6.46 (s, 1H, H-4, pyrrolethione); 6.60-6.64 (m, 2H, H_o, NPh); 7.50–7.55 (m, 2H, H-3,7, napht); 7.85–7.88 (m, 4H, H-1,4,6,8, napht). Other signals of 1,2-dihydro-3*H*-pyrrole-3-thione **3l** are overlapped with signals of side products.

1-(4-Chlorophenyl)-2-(furan-2-yl)-2-methyl-5-phenyl-1,2-dihydro-3*H*-pyrrole-3-thione (3m). Reaction time 50 h. Yield: 9% (according to ^1H NMR). ^1H NMR (400.13 MHz, $CDCl_3$): δ 1.82 (s, 3H, Me); 6.28-6.31 (m, 2H, H-3,4, furyl); 6.80-6.85 (m, 3H, H-2,6, NC_6H_4Cl; H-4, pyrrolethione); 7.39-7.41 (m, 1H, H-5, furyl). Other signals of 1,2-dihydro-3*H*-pyrrole-3-thione **3m** are overlapped with signals of side products.

References

S1. (*a*) P. A. Volkov, K. O. Khrapova, I. A. Bidusenko, A. A. Telezhkin, E. Yu. Schmidt, A. I. Albanov and B. A. Trofimov, *Russ. Chem. Bull.*, 2022, **71**, 1514; https://doi.org/10.1007/s11172-022-3558-3; (*b*) P. A. Volkov, K. O. Khrapova, A. A. Telezhkin, I. A. Bidusenko, E. Yu. Schmidt, A. I. Albanov and B. A. Trofimov, *Adv. Synth. Catal.*, 2023, **365**, 53; https://doi.org/10.1002/adsc.202201179.

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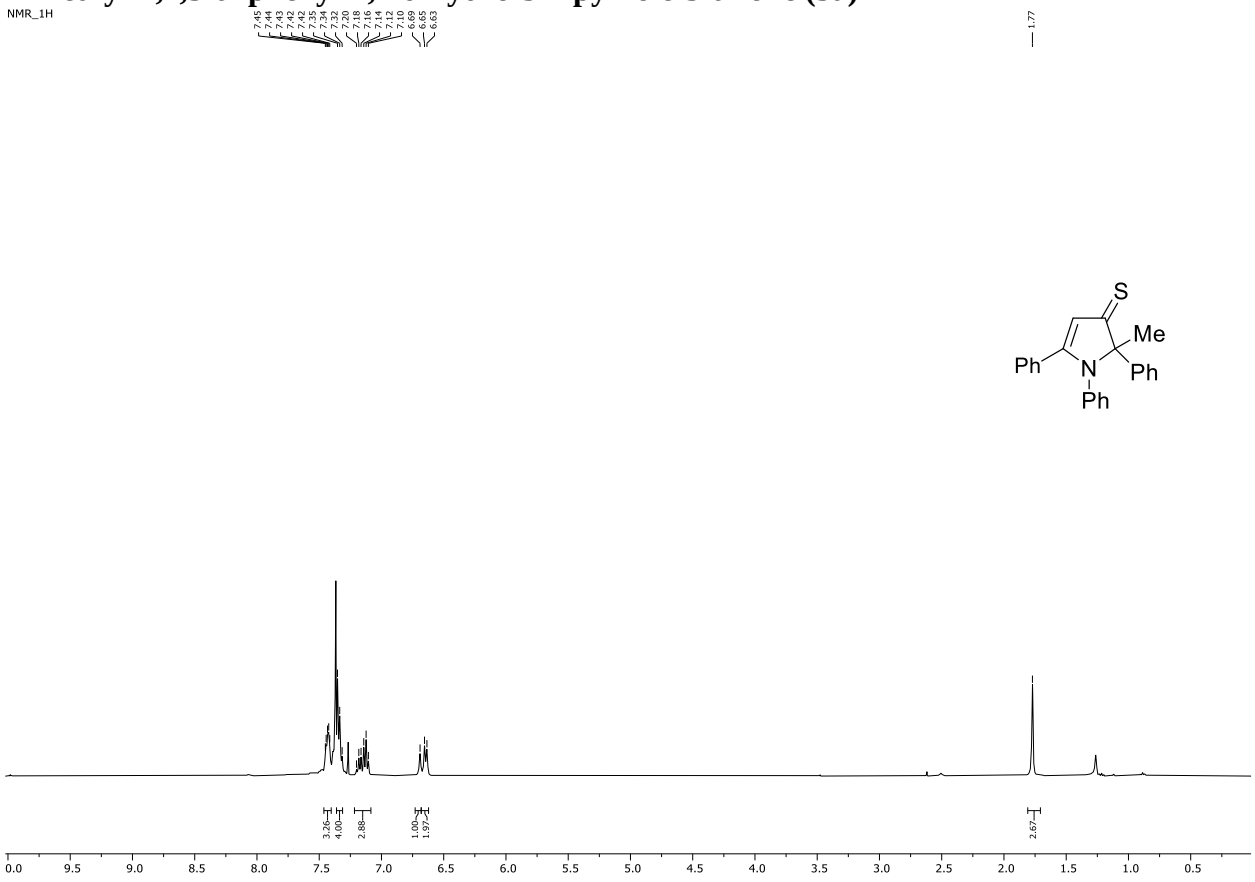
S3. (*a*) N. K. Gusarova, M. V. Bogdanova, N. I. Ivanova, N. A. Chernysheva, B. G. Sukhov, L. M. Sinegovskaya, O. N. Kazheva, G. G. Alexandrov, O. A. D'yachenko and B. A. Trofimov, *Synthesis*, 2005**,** 3103; https://doi.org/10.1055/s-2005-918408; (*b*) N. K. Gusarova and B. A. Trofimov, *Russ. Chem. Rev.*, 2020, **89**, 225; https://doi.org/10.1070/RCR4903.

S4. P. A. Volkov, K. O. Khrapova, E. M. Vyi, A. A. Telezhkin, I. A. Bidusenko, A. I. Albanov, E. Yu. Schmidt and B. A. Trofimov, *Org. Biomol. Chem.*, 2023, **21**, 6903; https://doi.org/10.1039/D3OB01061A.

3. NMR Spectra

2-Methyl-1,2,5-triphenyl-1,2-dihydro-3*H*-pyrrole-3-thione (3a)



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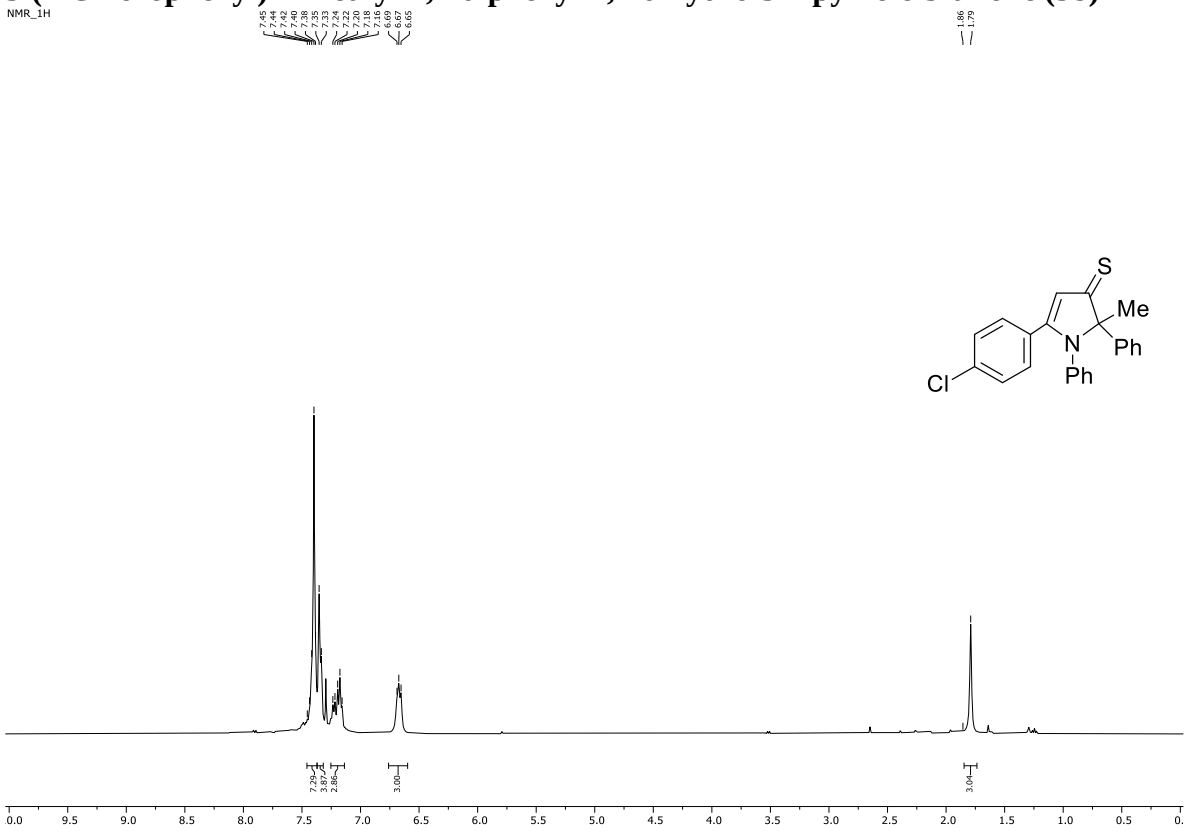

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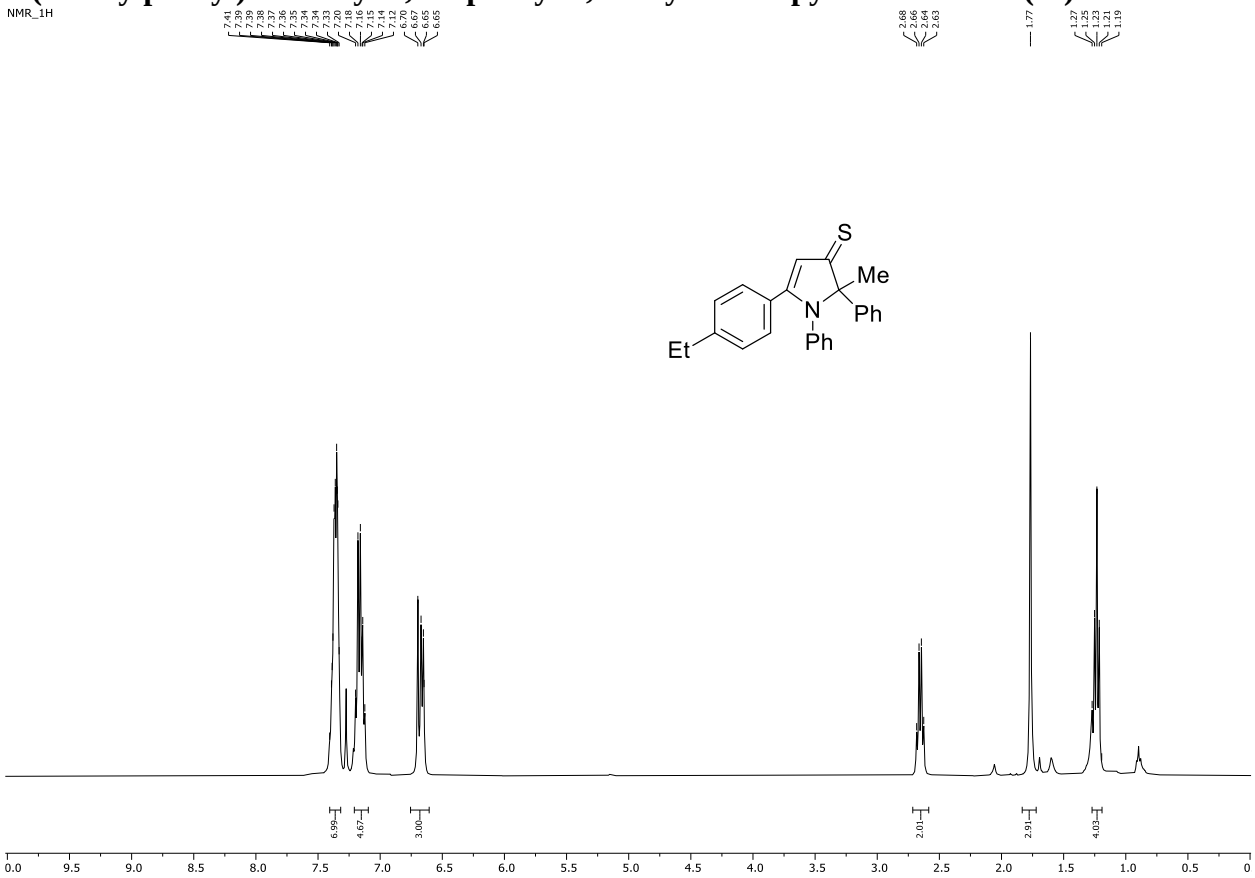

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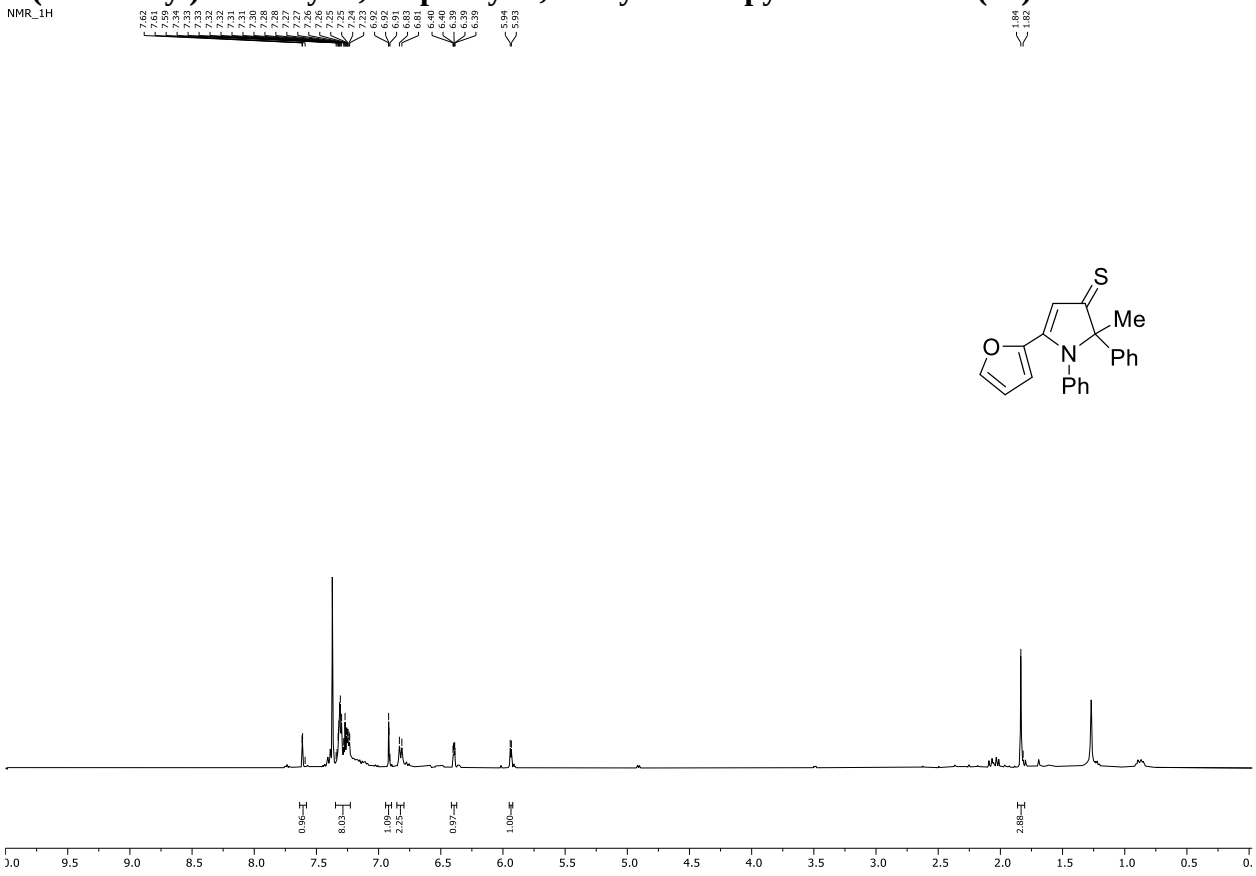

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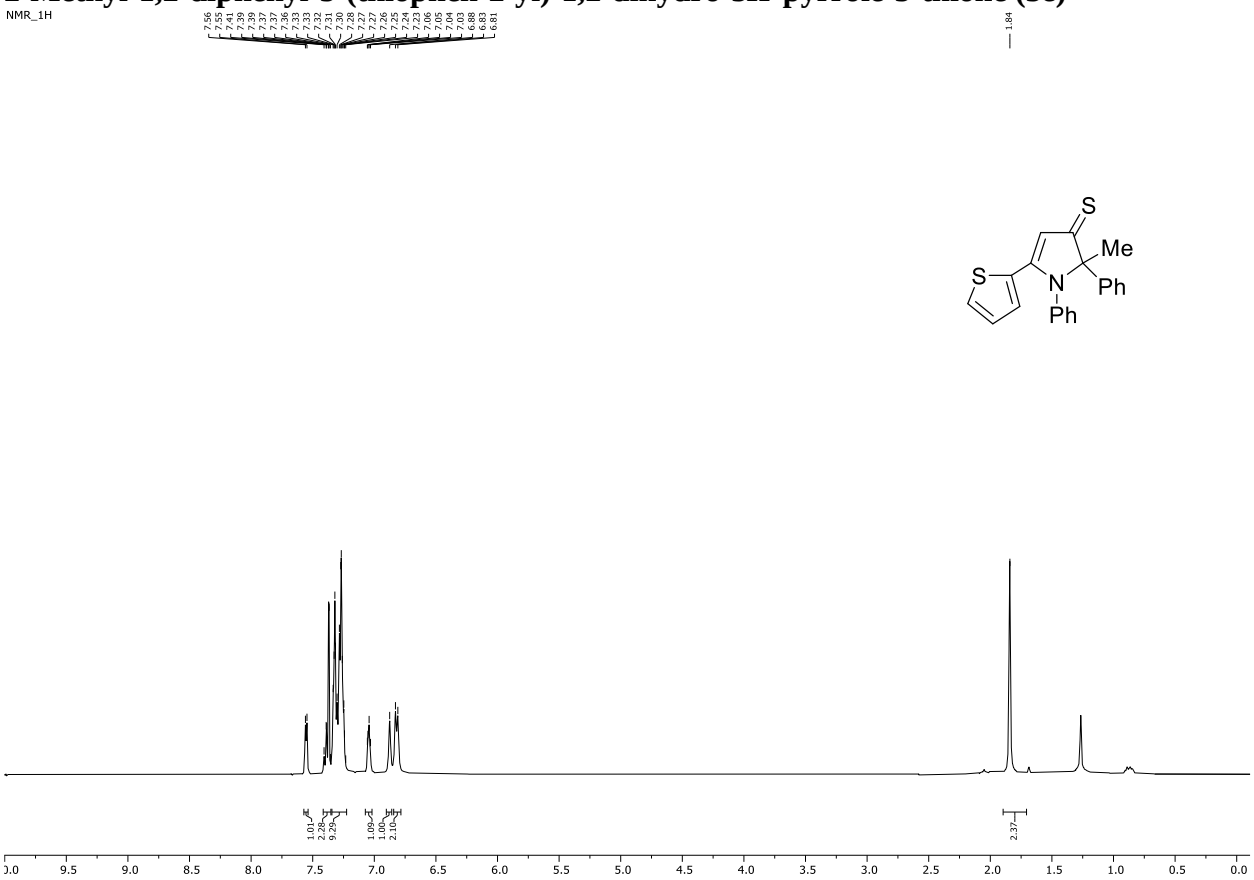

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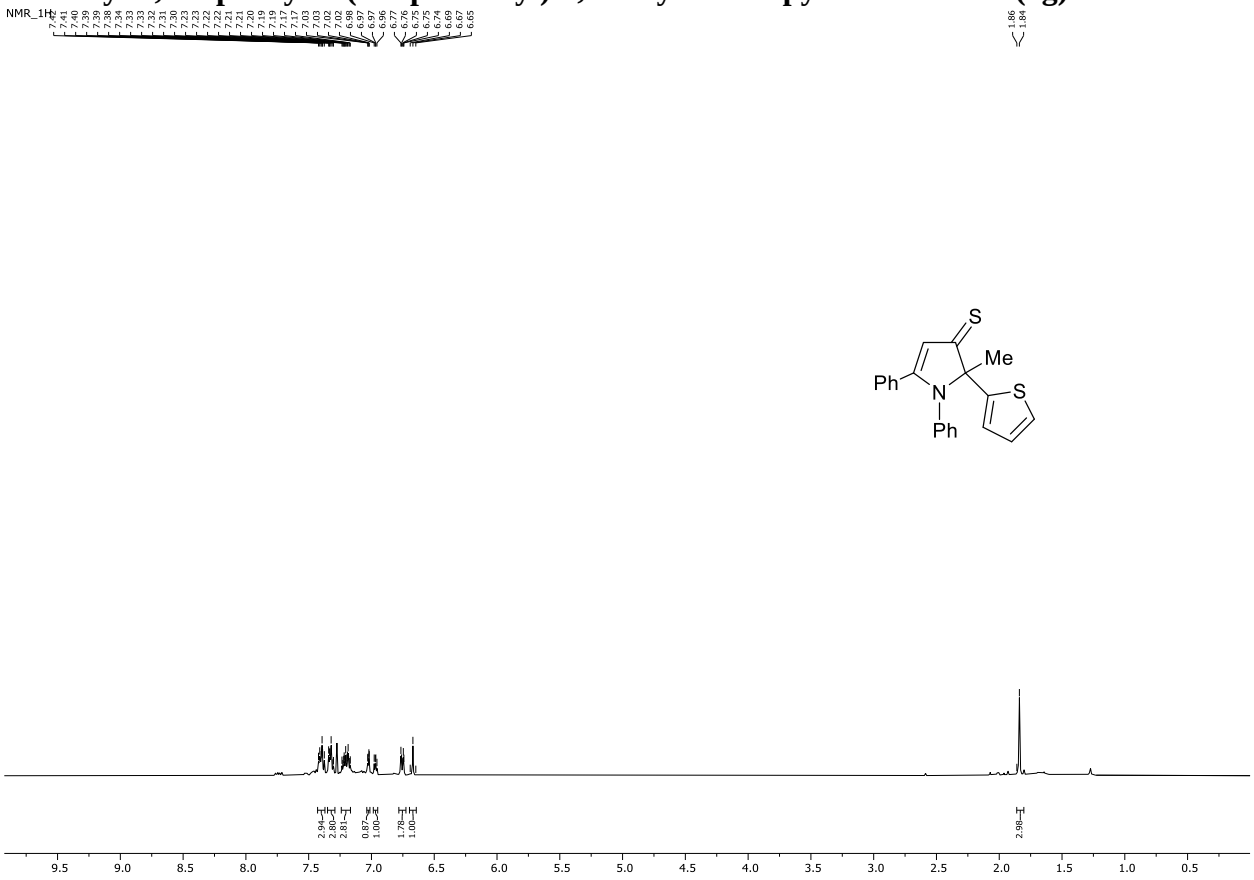

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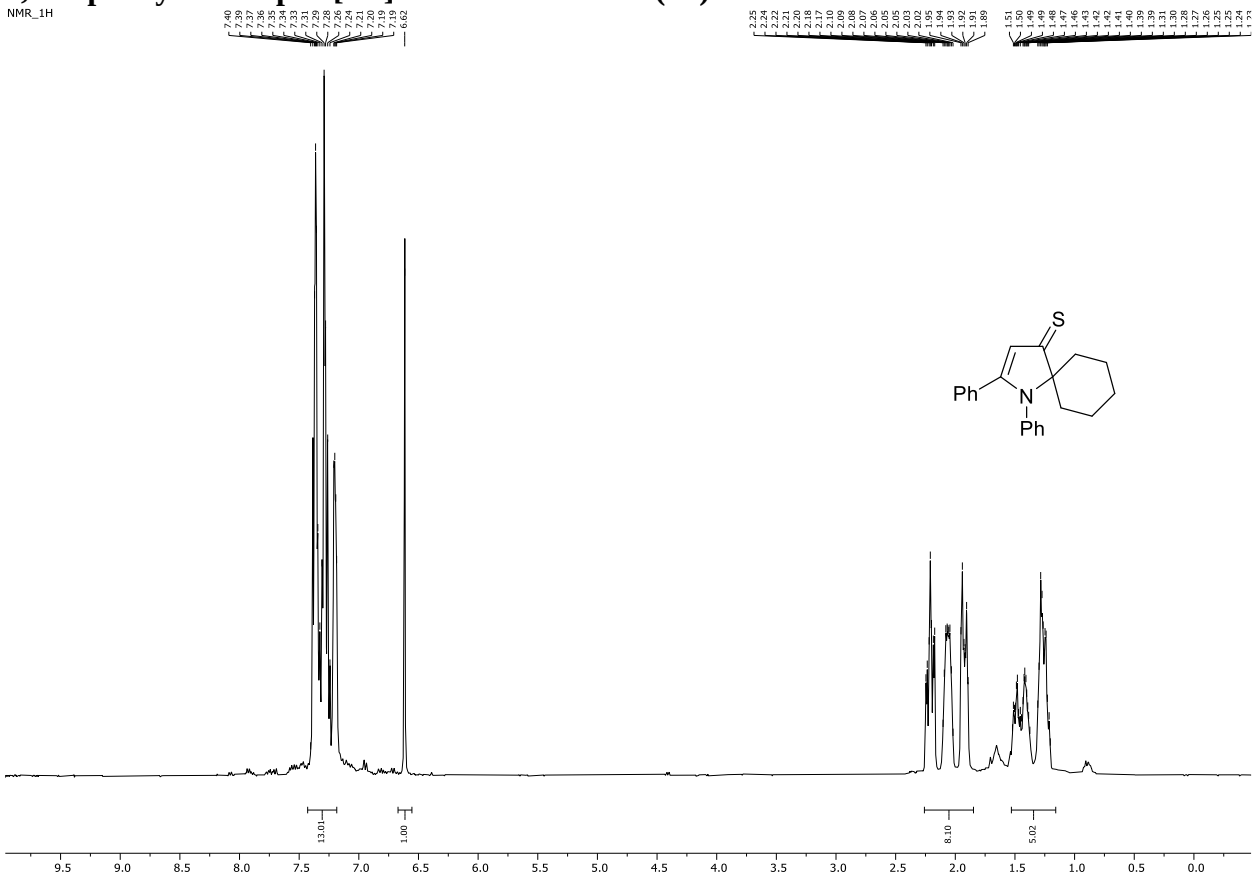

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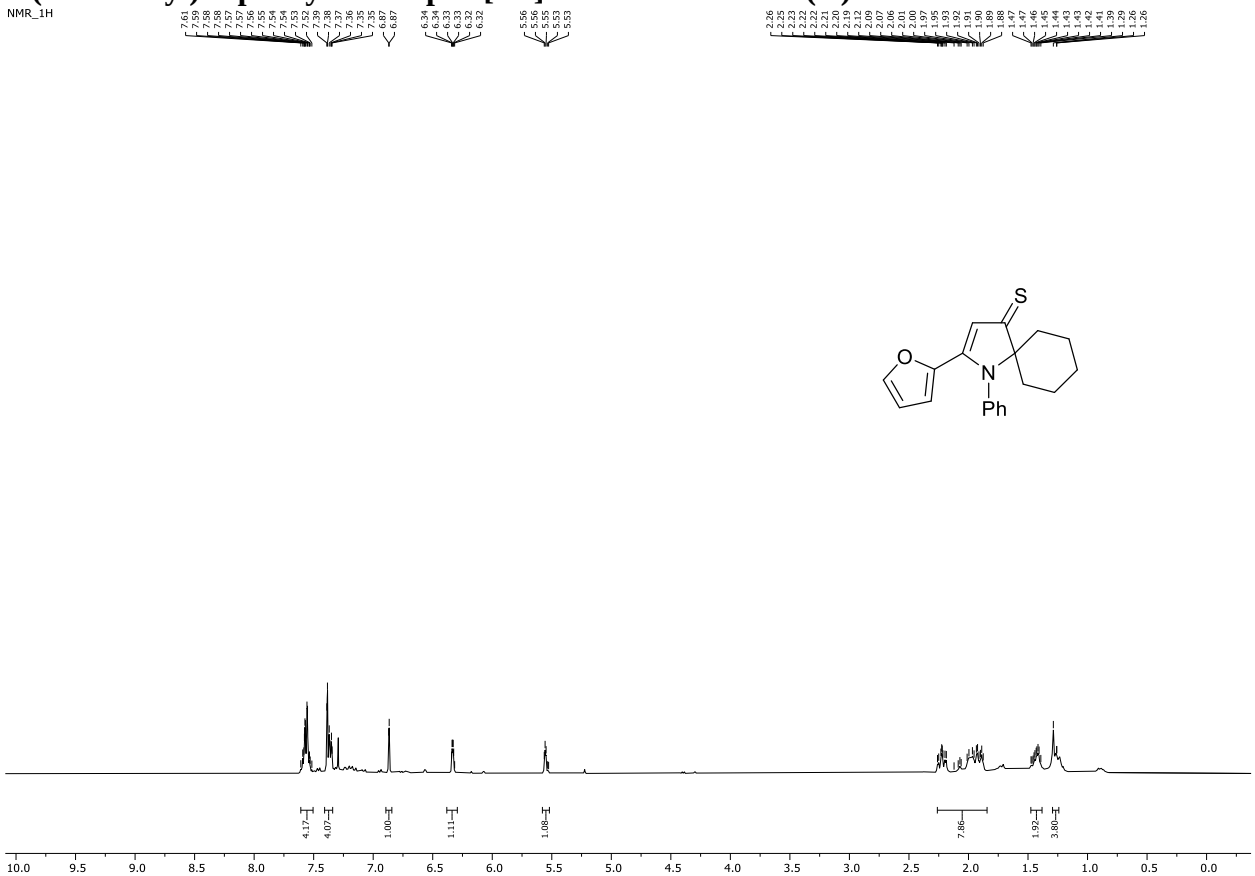

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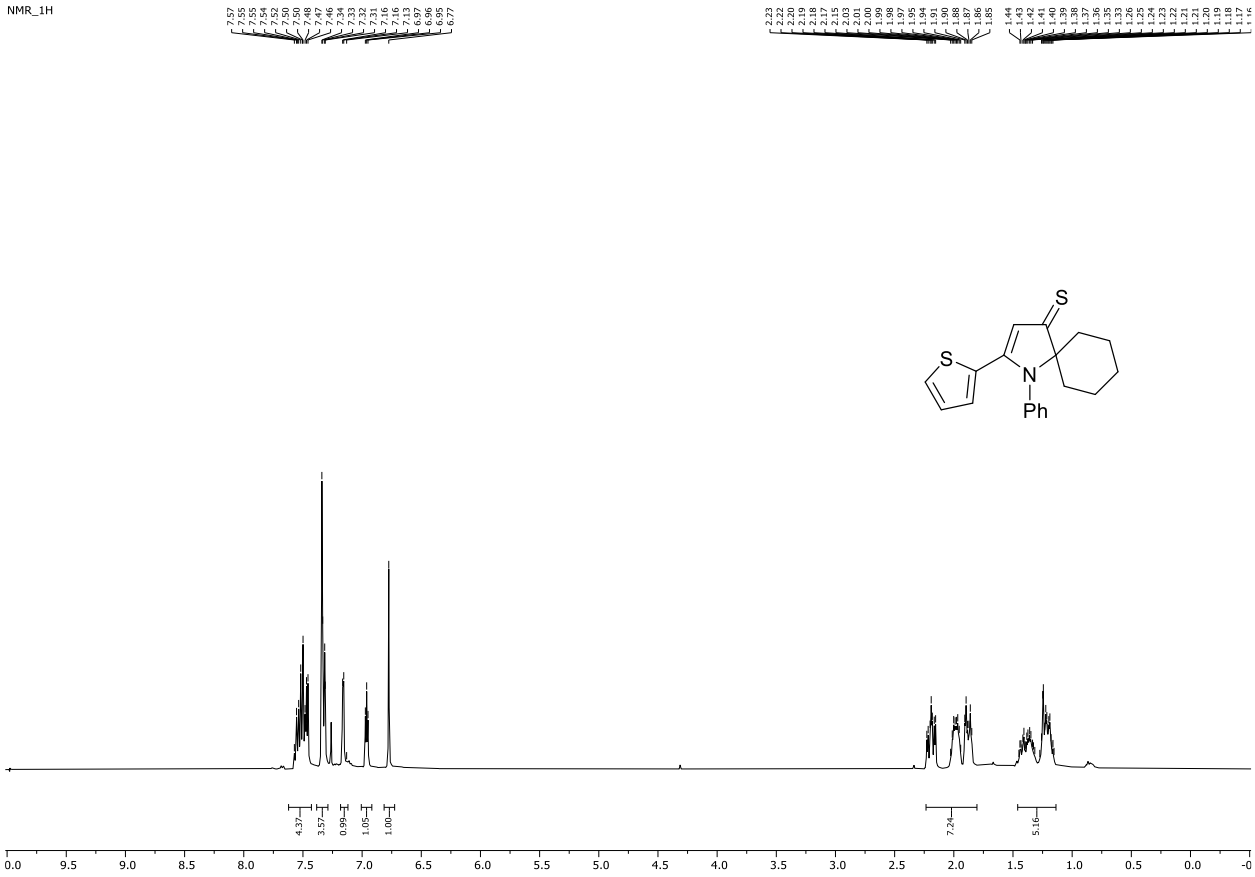

1-Phenyl-2-(thiophen-2-yl)-1-azaspiro[4.6]undec-2-ene-4-thione (3k)