

Supporting Information

for

**Molecular iodine-catalyzed one-pot
multicomponent synthesis of 5-amino-4-
(arylselanyl)-1*H*-pyrazoles**

Camila S. Pires¹, Daniela H. de Oliveira¹, Maria R. B. Pontel¹, Jean C. Kazmierczak², Roberta Cargnelutti², Diego Alves¹, Raquel G. Jacob¹ and Ricardo F. Schumacher^{*1,2}

Address: ¹LASOL - CCQFA - Universidade Federal de Pelotas - UFPel - P.O. Box 354 - 96010-900, Pelotas, RS, Brazil and ²Departamento de Química, Universidade Federal de Santa Maria – UFSM, 97105-900, Santa Maria, RS, Brazil

Email: Ricardo F. Schumacher - ricardo.schumacher@ufsm.br

*Corresponding author

Experimental part

Contents

General Information	S2
General procedure for the synthesis of 5-amino-4-(arylselanyl)pyrazoles (4)	S2
General procedure for the synthesis of diazo pyrazole derivative (6)	S3
Table S1. Crystallographic data and refinement parameters for 6	S8
Selected spectra	S9

General Information: Reactions were monitored by TLC carried out on Merck silica gel (60 F254) by using UV light as visualizing agent and 5% vanillin in 10% H₂SO₄ and heat as developing agents. Column chromatography was performed by using silica gel. Proton nuclear magnetic resonance spectra (¹H NMR) were obtained at 400 MHz with Bruker DPX 400 spectrometer. Spectra were recorded in CDCl₃ solutions. Chemical shifts are reported in ppm, referenced to tetramethylsilane (TMS) as the external reference. Hydrogen coupling patterns are described as singlet (s), doublet (d), triplet (t), double doublet (dd) and multiplet (m). Coupling constants (*J*) are reported in Hertz. Carbon-13 nuclear magnetic resonance spectra (¹³C NMR) were obtained at 100 MHz with Bruker DPX 400 spectrometer. Chemical shifts are reported in ppm, referenced to the solvent peak of CDCl₃ (77.0 ppm). Low resolution mass spectra (MS) were obtained with Shimadzu GCMS-QP2010 mass spectrometer 10416. High resolution mass spectra (HRMS) were recorded on a Bruker Micro TOF-QII spectrometer. Melting point (m.p.) values were measured with a Marte PFD III instrument. Infrared spectra were measured using a Shimadzu Prestige-21 IR spectrometer. A Cole Parmer-ultrasonic processor Model CPX 130, with a maximum power of 130 W, operating at amplitude of 60% and a frequency of 20 kHz was used.

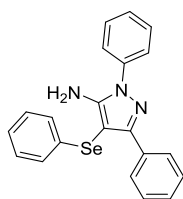
General procedure for the synthesis of 5-amino-4-(arylselanyl)pyrazoles (4)

To a 10 mL vial equipped with a reflux condenser containing a mixture of benzoylacetone nitrile **1** (0.5 mmol), arylhydrazine **2** (0.7 mmol) and diaryl diselenide **3** (0.5 mmol) in MeCN (3 mL), molecular iodine (50 mol %) was added. Then the mixture was stirred at reflux temperature for a period of 48 hours. Under these conditions the expected product **4** was obtained and the progress of the reaction was monitored by TLC. The reaction mixture was poured in water (15 mL), extracted with ethyl acetate (3 × 10 mL), dried over MgSO₄ and concentrated under vacuum. The residue was purified by column

chromatography by using silica gel and a mixture of hexane/ethyl acetate (95:05) as eluent.

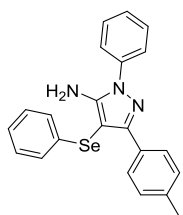
General procedure for the synthesis of diazo pyrazole derivative (6)¹

5-Amino-4-(phenylselanyl)-1*H*-pyrazol **4a** (0.5 mmol) was added to a 10 mL vial containing a mixture of 1,10-phenantroline (0.15 mmol), *tert*-butyl peroxide (1.5 mmol) and CuI (0.05 mmol) in dichloromethane (2 mL). Then, the mixture was stirred at room temperature for 2 hours and the expected product **5** was obtained. The progress of the reaction was monitored by TLC. The reaction mixture was received in water (10 mL), extracted with ethyl acetate (3 × 5 mL), dried over MgSO₄ and concentrated under vacuum. The residue was purified by column chromatography using silica gel and a mixture of hexane/ethyl acetate (90:10) as eluent.



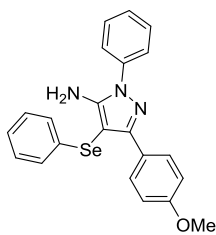
1,3-Diphenyl-4-(phenylselanyl)-1*H*-pyrazol-5-amine (4a):

Orange oil; Yield: 96%; IR (KBr, cm⁻¹): 3450 (s), 3412 (s), 3055 (m), 2922 (w), 1946 (w), 1801 (w), 1600 (s), 1500 (s), 1475 (m), 1371 (m), 1111 (w), 970 (m), 759 (s), 690 (s). ¹H NMR (CDCl₃, 400 MHz): δ=7.93-7.91 (m, 2H), 7.67-7.65 (m, 2H), 7.50-7.46 (m, 2H), 7.37-7.25 (m, 6H), 7.21-7.13 (m, 3H) 4.30 ppm (s, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ=153.6, 149.5, 138.6, 133.0, 132.9, 129.5, 129.2, 128.1, 128.1, 127.9, 127.8, 127.6, 125.8, 123.6, 82.4 ppm. ⁷⁷Se NMR (CDCl₃, 76 MHz): δ=193.9 ppm. MS *m/z* (rel. int.): 391 (43), 389 (23), 311 (100), 293 (3), 208 (15), 155 (8). HRMS calcd. for C₂₁H₁₈N₃Se: [M + H]⁺ 392.0660. Found: 392.0663.

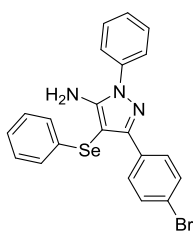


1-Phenyl-4-(phenylselanyl)-3-(*p*-tolyl)-1*H*-pyrazol-5-amine (4b):

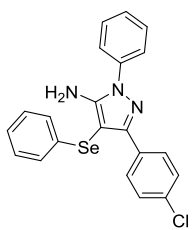
Reddish oil; Yield: 73%; IR (KBr, cm⁻¹): 3433 (s), 3057 (w), 2916 (w), 1598 (s), 1502 (s), 1473 (m), 1367 (w), 1182 (w), 1020 (m), 970 (m), 732 (s), 665 (w). ¹H NMR (CDCl₃, 400 MHz): δ=7.83-7.81 (m, 2H), 7.68-7.66 (m, 2H), 7.51-7.47 (m, 2H), 7.38-7.34 (m, 2H), 7.26-7.12 (m, 6H), 4.30 (s, 2H), 2.33 ppm (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ=153.7, 149.5, 137.9, 133.2, 130.6, 130.2, 129.6, 129.3, 128.9, 128.0, 127.8, 127.6, 125.9, 123.7, 82.6, 21.2 ppm. ⁷⁷Se NMR (CDCl₃, 76 MHz): δ=194.3 ppm. MS *m/z* (rel. int.): 405 (37), 325 (100), 307 (2), 232 (3), 208 (13), 162 (4), 132 (15), 119 (14), 77 (35). HRMS calcd. for C₂₂H₂₀N₃Se: [M + H]⁺ 406.0817. Found: 406.0820.



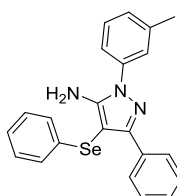
3-(4-methoxyphenyl)-1-phenyl-4-(phenylselanyl)-1H-pyrazol-5-amine (4c): Brownish oil; Yield: 35%; ^1H NMR (CDCl_3 , 400 MHz): δ = 7.89-7.85 (m, 2H), 7.66-7.63 (m, 2H), 7.48-7.44 (m, 2H), 7.34-7.30 (m, 1H), 7.26-7.24 (m, 2H), 7.21-7.16 (m, 2H), 7.14-7.10 (m, 1H), 6.87-6.83 (m, 2H), 4.28 (s, 2H), 3.75 ppm (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 159.6, 153.3, 149.4, 138.7, 133.1, 129.5, 129.2, 129.0, 127.8, 127.4, 125.8, 125.6, 123.5, 113.5, 82.1, 55.1 ppm. MS m/z (rel. int.): 421 (1), 408 (1), 345 (4), 280 (61), 265 (51), 146 (47), 131 (23), 119 (47), 104 (49), 77 (100).



3-(4-Bromophenyl)-1-phenyl-4-(phenylselanyl)-1H-pyrazol-5-amine (4d): Brown solid; m.p.: 43-45 °C; Yield: 78%; IR (KBr, cm^{-1}): 3412 (m), 3055 (w), 2920 (w), 2850 (w), 1598 (s), 1575 (m), 1498 (s), 1436 (m), 1363 (m), 1008 (m), 912 (w), 829 (s), 665 (w). ^1H NMR (CDCl_3 , 400 MHz): δ =7.76-7.74 (m, 2H), 7.56-7.54 (m, 2H), 7.41-7.35 (m, 4H), 7.28-7.25 (m, 1H), 7.16-7.04 (m, 5H), 4.14 ppm (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ =152.3, 149.7, 138.6, 132.8, 132.0, 131.2, 129.6, 129.3, 127.9, 127.8, 126.0, 123.6, 123.4, 82.5 ppm. ^{77}Se NMR (CDCl_3 , 76 MHz): δ = 192.9 ppm. MS m/z (rel. int.): $[\text{M}+2]$ 471 (40) $[\text{M}+]$ 469 (51), 389 (99), 309 (7), 267 (5), 233 (4), 208 (33), 155 (13), 127 (15), 119 (28), 77 (100). HRMS calcd. for $\text{C}_{21}\text{H}_{17}\text{BrN}_3\text{Se}$: $[\text{M} + \text{H}]^+$ 469.9766. Found: 469.9763.

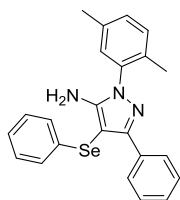


3-(4-Chlorophenyl)-1-phenyl-4-(phenylselanyl)-1H-pyrazol-5-amine (4e): Brown oil; Yield: 81%; IR (KBr, cm^{-1}): 3550 (m), 3414 (s), 3057 (m), 2920 (w), 1948 (w), 1884 (w), 1598 (s), 1531 (m), 1500 (s), 1454 (m), 1373 (m), 1087 (s), 759 (s), 659 (w). ^1H NMR (CDCl_3 , 400 MHz): δ =7.83-7.81 (m, 2H), 7.58-7.56 (m, 2H), 7.41 (t, J =7.4 Hz, 2H), 7.30-7.26 (m, 1H), 7.22-7.20 (m, 2H), 7.17-7.06 (m, 5H), 4.18 ppm (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ =152.4, 149.6, 138.6, 134.1, 132.8, 131.6, 129.6, 129.3, 129.1, 128.3, 128.0, 127.8, 126.1, 123.7, 82.5 ppm. MS m/z (rel. int.): $[\text{M}+2]$ 427 (10) 425 (31), 421 (6), 347 (35), 345 (100), 309 (4), 267 (3), 233 (2), 208 (16), 180 (2), 162 (9), 153 (3), 177 (35). HRMS calcd. for $\text{C}_{21}\text{H}_{17}\text{ClN}_3\text{Se}$: $[\text{M} + \text{H}]^+$ 426.0271. Found: 426.0262.

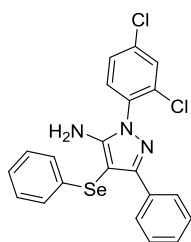


3-Phenyl-4-(phenylselanyl)-1-(m-tolyl)-1H-pyrazol-5-amine (4g): Brown oil; Yield: 63%; IR (KBr, cm^{-1}): 3473 (m), 3408 (s),

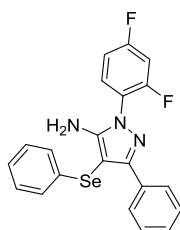
3331 (m), 3097 (w), 2922 (w), 2852 (w), 1606 (s), 1575 (m), 1541 (s), 1496 (m), 1346 (s), 1109 (w), 966 (m), 742 (s), 657 (w). ^1H NMR (CDCl_3 , 400 MHz): δ =7.92-7.90 (m, 2H), 7.48-7.12 (m, 12H), 4.28 (s, 2H), 2.39 ppm (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ =153.4, 149.4, 139.8, 138.4, 133.1, 132.9, 129.2, 128.4, 128.1, 127.8, 127.7, 125.8, 124.8, 120.4, 82.1, 21.3 ppm. MS m/z (rel. int.): 405 (31), 391 (3), 325 (100), 283 (17), 248 (3), 222 (15), 146 (17). HRMS calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_3\text{Se}$: $[\text{M} + \text{H}]^+$ 406.0817. Found: 406.0818.



1-(2,5-Dimethylphenyl)-3-phenyl-4-(phenylselanyl)-1H-pyrazol-5-amine (4h): Orange oil; Yield: 52%; IR (KBr, cm^{-1}): 3550 (s), 3415 (s), 3055 (w), 2920 (w), 2854 (w), 1616 (s), 1508 (w), 1367 (w), 1143 (w), 968 (m), 815 (m), 771 (m), 734 (m), 694 (m). ^1H NMR (CDCl_3 , 400 MHz): δ =7.84 (d, J =8.1 Hz, 2H), 7.24-7.16 (m, 6H), 7.12-7.01 (m, 5H), 3.90 (s, 2H), 2.28 (s, 3H), 2.09 ppm (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): δ =153.1, 150.3, 139.7, 136.2, 134.2, 133.5, 133.3, 132.0, 129.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 125.7, 80.3, 21.1, 17.4 ppm. MS m/z (rel. int.): 419 (85), 417 (45), 339 (100), 323 (16), 297 (5), 262 (12), 235 (38), 184 (6), 159 (15). HRMS calcd. for $\text{C}_{23}\text{H}_{22}\text{N}_3\text{Se}$: $[\text{M} + \text{H}]^+$ 420.0973. Found: 420.0982.

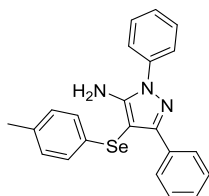


1-(2,4-Dichlorophenyl)-3-phenyl-4-(phenylselanyl)-1H-pyrazol-5-amine (4i): Brown oil; Yield: 80%; IR (KBr, cm^{-1}): 3550 (m), 3390 (s), 3248 (m), 3082 (s), 2915 (w), 2848 (w), 2362 (w), 1618 (s), 1537 (s), 1504 (s), 1469 (s), 1431 (m), 1296 (m), 1099 (m), 775 (s), 657 (m). ^1H NMR (CDCl_3 , 400 MHz): δ =7.82-7.80 (m, 2H), 7.49-7.42 (m, 2H), 7.32-7.05 (m, 9H), 4.02 ppm (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ =154.5, 150.9, 136.2, 134.6, 133.0, 132.9, 132.8, 130.8, 130.4, 129.3, 128.4, 128.3, 128.1, 127.9, 127.8, 125.9, 82.0 ppm. MS m/z (rel. int.): $[\text{M}+2]$ 461 (37), $[\text{M}+]$ 459 (55), 424 (100), 381 (50), 321 (8), 276 (17), 218 (11), 199 (14), 128 (41), 77 (60). HRMS calcd. for $\text{C}_{21}\text{H}_{16}\text{Cl}_2\text{N}_3\text{Se}$: $[\text{M} + \text{H}]^+$ 459.9881. Found: 459.9882.



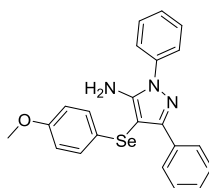
1-(2,4-Difluorophenyl)-3-phenyl-4-(phenylselanyl)-1H-pyrazol-5-amine (4j): Brown solid; m.p.: 102-103 °C; Yield: 76%; IR (KBr, cm^{-1}): 3550 (m), 3473 (s), 3412 (s), 3230 (w), 3051 (w), 2920 (w), 1637 (m), 1616 (s), 1597 (s), 1531 (m), 1363 (w), 831 (s), 723 (m), 620 (w). ^1H NMR (CDCl_3 , 400 MHz): δ =7.90-7.87 (m, 2H), 7.68-7.62 (m, 1H), 7.37-7.30 (m, 3H), 7.27-7.20 (m, 4H), 7.18-7.15 (m, 1H), 7.08-7.01 (m, 2H), 4.22 ppm (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ =162.5 (dd, J =241.2 e 11.1 Hz), 156.7 (dd, J =241.2 e 11.1 Hz), 154.7, 151.0, 147.9, 143.4, 132.9, 132.7, 130.0, 129.9, 129.3, 128.3, 128.1, 127.8,

127.7, 127.1, 125.9, 122.6 (dd, $J = 12.1, 4.0$ Hz), 112.5 (dd, $J = 22.5, 3.7$ Hz), 105.1 (dd, $J = 26.5, 23.6$ Hz), 82.3 ppm. ^{77}Se NMR (CDCl_3 , 76 MHz): $\delta = 195.2$ ppm. MS m/z (rel. int.): 427 (48), 425 (25), 383 (2), 347 (100), 305 (2), 244 (23), 218 (6), 155 (19), 128 (18). HRMS calcd. for $\text{C}_{21}\text{H}_{16}\text{F}_2\text{N}_3\text{Se}$: $[\text{M} + \text{H}]^+$ 428.0472. Found: 428.0486.



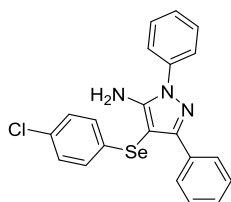
1,3-Diphenyl-4-(*p*-tolylselanyl)-1*H*-pyrazol-5-amine (4l):

Orange oil; Yield: 54%; IR (KBr, cm^{-1}): 3550 (m), 3477 (m), 3390 (s), 3250 (s), 3109 (s), 1881 (w), 1811 (w), 1743 (w), 1618 (s), 1575 (m), 1469 (s), 1431 (s), 1294 (m), 1139 (m), 1099 (s), 974 (s), 657 (m). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.94$ –7.92 (m, 2H), 7.65–7.63 (m, 2H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.35–7.28 (m, 4H), 7.15 (d, $J = 8.0$ Hz, 2H), 7.01 (d, $J = 8.0$ Hz, 2H), 4.28 (s, 2H), 2.25 ppm (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 153.5, 149.4, 138.6, 135.6, 132.9, 130.0, 129.5, 129.1, 128.1, 128.0, 127.9, 127.8, 127.5, 123.5, 82.7, 20.9$ ppm. MS m/z (rel. int.): 405 (10), 328 (100), 312 (12), 298 (22), 142 (16), 77 (61). HRMS calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_3\text{Se}$: $[\text{M} + \text{H}]^+$ 406.0817. Found 406.0822.



4-((4-Methoxyphenyl)selanyl)-1,3-diphenyl-1*H*-pyrazol-5-amine (4m):

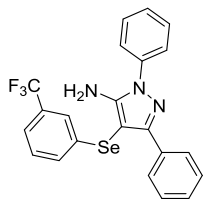
Brown solid; m.p.: 38–40 °C; Yield: 63%; IR (KBr, cm^{-1}): 3552 (w), 3442 (m), 3342 (m), 3053 (w), 2920 (w), 1884 (w), 1734 (w), 1602 (s), 1529 (m), 1600 (s), 1471 (s), 1452 (m), 1384 (m), 1170 (w), 1008 (s), 688 (s). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.86$ –7.84 (m, 2H), 7.49–7.48 (m, 2H), 7.29 (t, $J = 7.3$ Hz, 2H), 7.22–7.16 (m, 4H), 7.06 (d, $J = 7.0$ Hz, 2H), 6.60 (d, $J = 6.9$ Hz, 2H), 4.16 (s, 2H), 3.53 ppm (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz): $\delta = 158.4, 153.1, 149.3, 138.7, 133.1, 132.8, 130.0, 129.3, 127.9, 127.8, 127.3, 123.4, 122.8, 115.0, 83.7, 55.1$ ppm. MS m/z (rel. int.): 421 (6), 347 (34), 345 (100), 327 (7), 309 (8), 281 (28), 267 (8), 253 (16), 235 (7), 207 (84), 191 (12), 155 (5), 119 (25), 104, (16), 77 (82). HRMS calcd. for $\text{C}_{22}\text{H}_{20}\text{N}_3\text{OSe}$: $[\text{M} + \text{H}]^+$ 422.0766. Found: 422.0791.



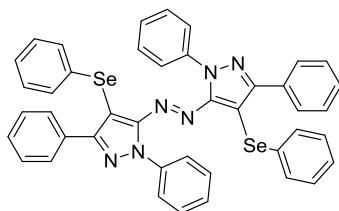
4-((4-Chlorophenyl)selanyl)-1,3-diphenyl-1*H*-pyrazol-5-amine (4n):

Reddish solid; m.p.: 41–43 °C; Yield: 80%; IR (KBr, cm^{-1}): 3435 (s), 3059 (m), 2924 (w), 2850 (w), 2733 (w), 2194 (w), 1948 (w), 1884 (w), 1600 (s), 1531 (m), 1500 (s), 1454 (m), 1373 (m), 1174 (w), 1087 (s), 759 (s), 659 (w). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.82$ (d, $J = 7.9$ Hz, 2H), 7.56 (d, $J = 7.5$ Hz, 2H), 7.39 (t, $J = 7.7$ Hz, 2H), 7.26–7.22 (m, 4H), 7.10–7.04 (m, 4H), 6.84–6.64 (m, 1H), 4.22 ppm (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz) $\delta = 153.5, 149.5, 138.6, 132.9, 131.9, 131.4, 129.6, 129.3, 129.2, 128.2, 128.1, 127.8, 123.6, 113.8, 82.2$ ppm. ^{77}Se NMR (CDCl_3 , 76 MHz): $\delta = 196.8$

ppm. MS m/z (rel. int.): [M+2] 427 (19), [M+] 425 (42), 386 (13), 345 (100), 306 (44), 267 (3), 242 (11), 217 (8), 119 (20). HRMS calcd. for $C_{21}H_{17}ClN_3Se$: [M + H]⁺ 426.0271. Found: 426.0276.



4-((3-(trifluoromethyl)phenyl)selanyl)-1,3-diphenyl-1H-pyrazol-5-amine (4o): Reddish oil; Yield: 24%; ¹H NMR (CDCl₃, 400 MHz): δ = 7.09-6.96 (m, 2H), 6.69-6.33 (m, 12H), 3.38 ppm (s, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ = 153.3, 149.5, 138.3, 134.5, 132.7, 131.8, 131.3 (d, J = 32 Hz), 130.9 (d, J = 1.5 Hz), 129.5, 128.2, 128.1, 127.7, 124.4 (d, J = 3.9 Hz), 123.6 (d, J = 272 Hz) 123.5, 122.6 (d, J = 3.9 Hz), 81.5 ppm. MS m/z (rel. int.): 459 (44), 457 (22), 379 (100), 358 (3), 341 (4), 281 (12), 253 (5), 207 (35), 180 (3), 132 (24), 119 (22), 77 (57).



(E)-1,2-bis(1,3-diphenyl-4-(phenylselanyl)-1H-pyrazol-5-yl)diazene (6): Reddish solid; m.p.: 190-193 °C; Yield: 50%; ¹H NMR (CDCl₃, 400 MHz): δ = 7.85-7.83 (m, 4H), 7.57-7.36 (m, 24H), 7.30-7.26 ppm (m, 2H). ¹³C NMR (CDCl₃, 100 MHz): δ = 151.1, 138.8, 131.6, 130.9, 129.6, 129.4, 129.3, 129.2, 129.2, 128.9, 128.7, 128.4, 128.2, 125.9, 125.8, 124.9, 124.5, 103.9. MS m/z (rel. int.): 778 (3), 621 (10), 541 (30), 311 (13), 169 (10), 155 (11), 91 (16), 77 (100).

Reference:

1. Jiang, B.; Ning, Y.; Fan, W.; Tu, S. J.; Li, G. *J. Org. Chem.* **2014**, *79*, 4018–4024.

Table S1. Crystallographic data and refinement parameters for **6**.

Crystal Data	6
Formula	C ₄₂ H ₃₀ N ₆ Se ₂
Fw (g mol ⁻¹)	776.64
T (K)	100(2)
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	12.6802(4)
<i>b</i> /Å	32.3059(11)
<i>c</i> /Å	8.5778(3)
α /°	90
β /°	105.8660(10)
γ /°	90
<i>V</i> /Å ³	3380.0(2)
<i>Z</i>	4
<i>D</i> _{calc} (g cm ⁻³)	1.526
μ (Mo K α) (mm ⁻¹)	2.230
λ /Å	0.71073
<i>F</i> (000)	1568
Collected reflns.	57449
Unique reflns.	10347
<i>Goof</i> (<i>F</i> ²)	1.065
<i>R</i> ₁ ^a	0.0548
<i>wR</i> ₂ ^b	0.1227

^a $R_1 = \sum \frac{||F_o| - |F_c||}{\sum |F_o|}$

^b $wR_2 = \{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\}^{1/2}$

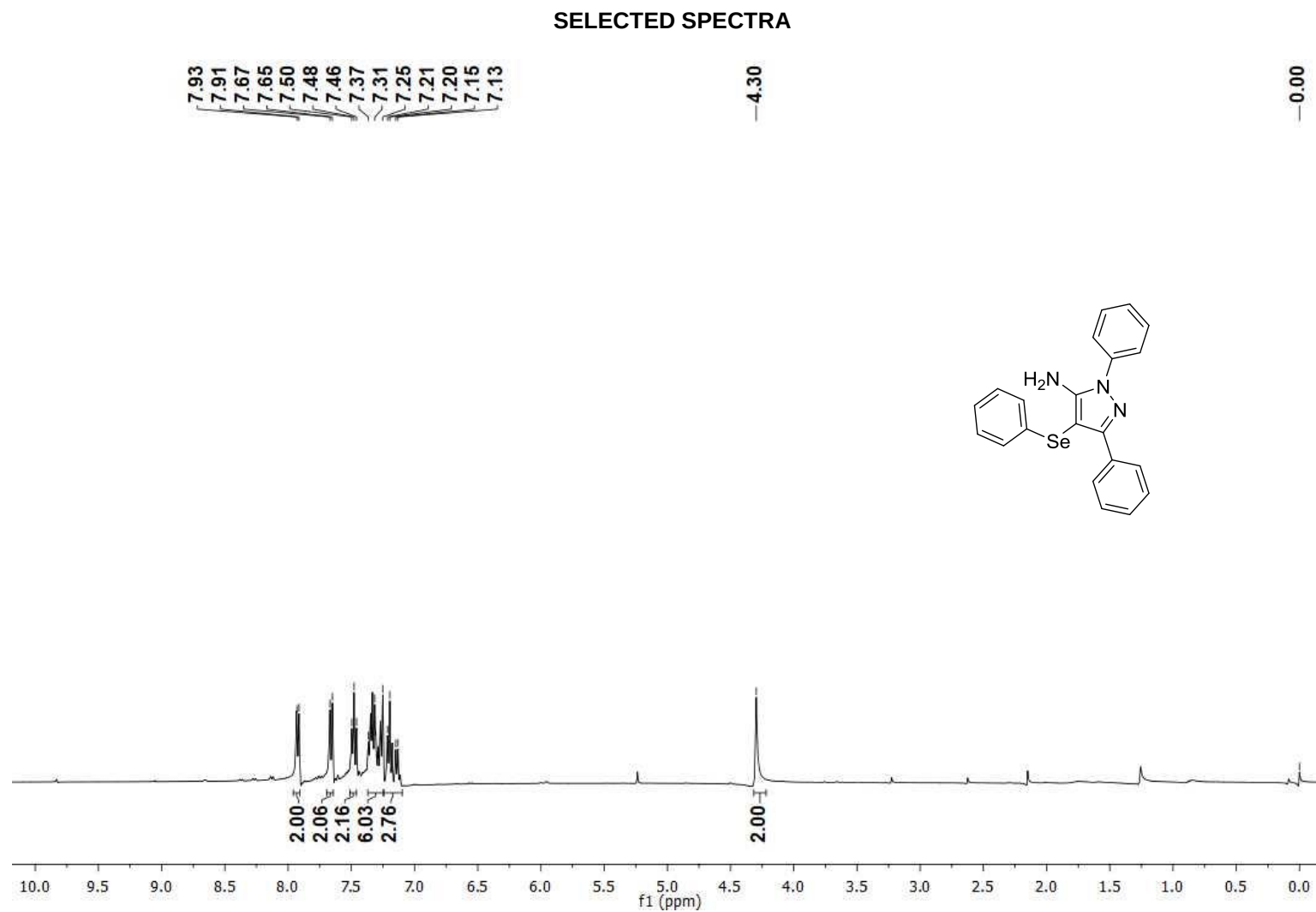


Figure S1. ^1H NMR (400 MHz, CDCl_3) of the product **4a**.

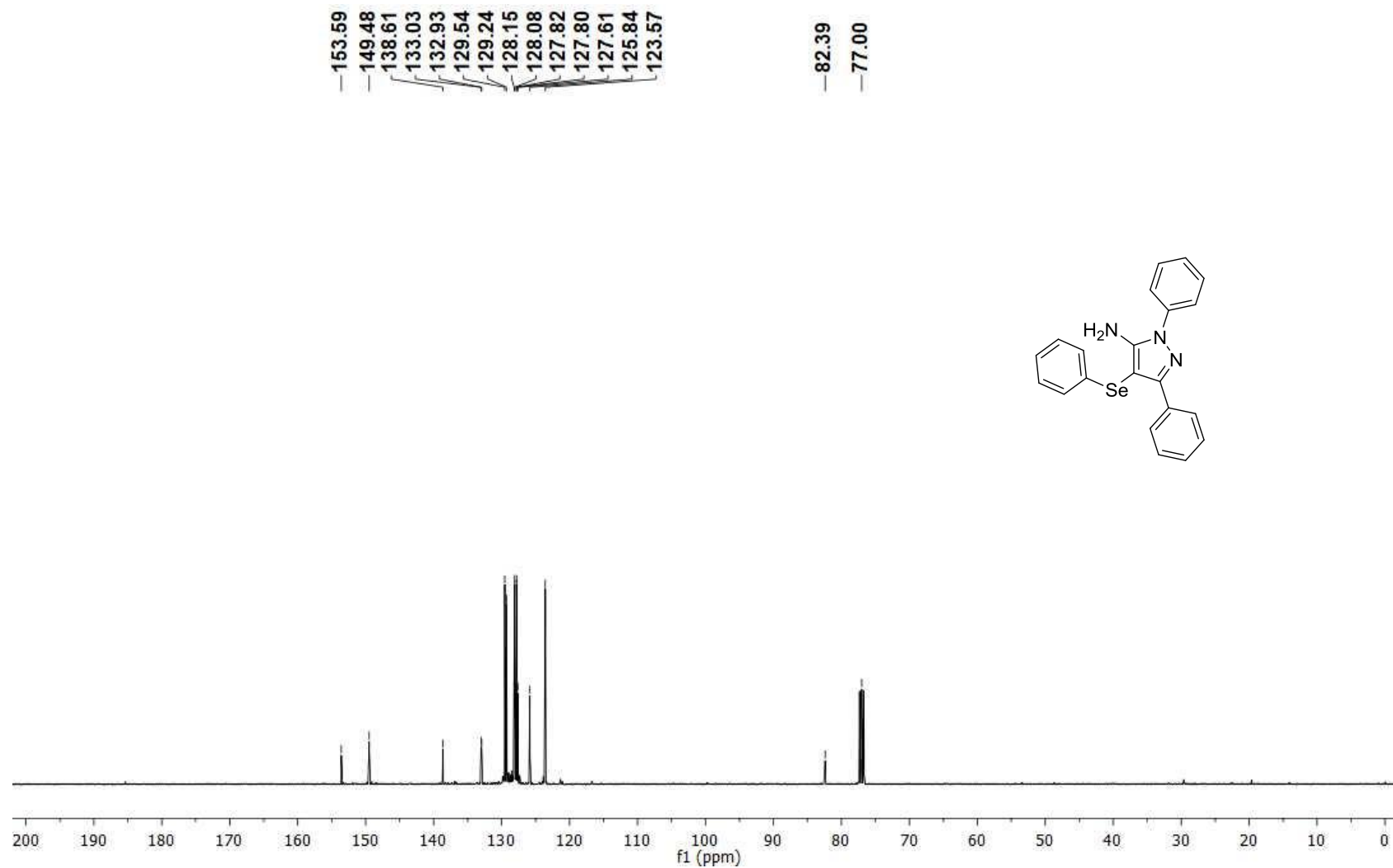


Figure S2. ¹³C NMR (100 MHz, CDCl₃) of the product **4a**.

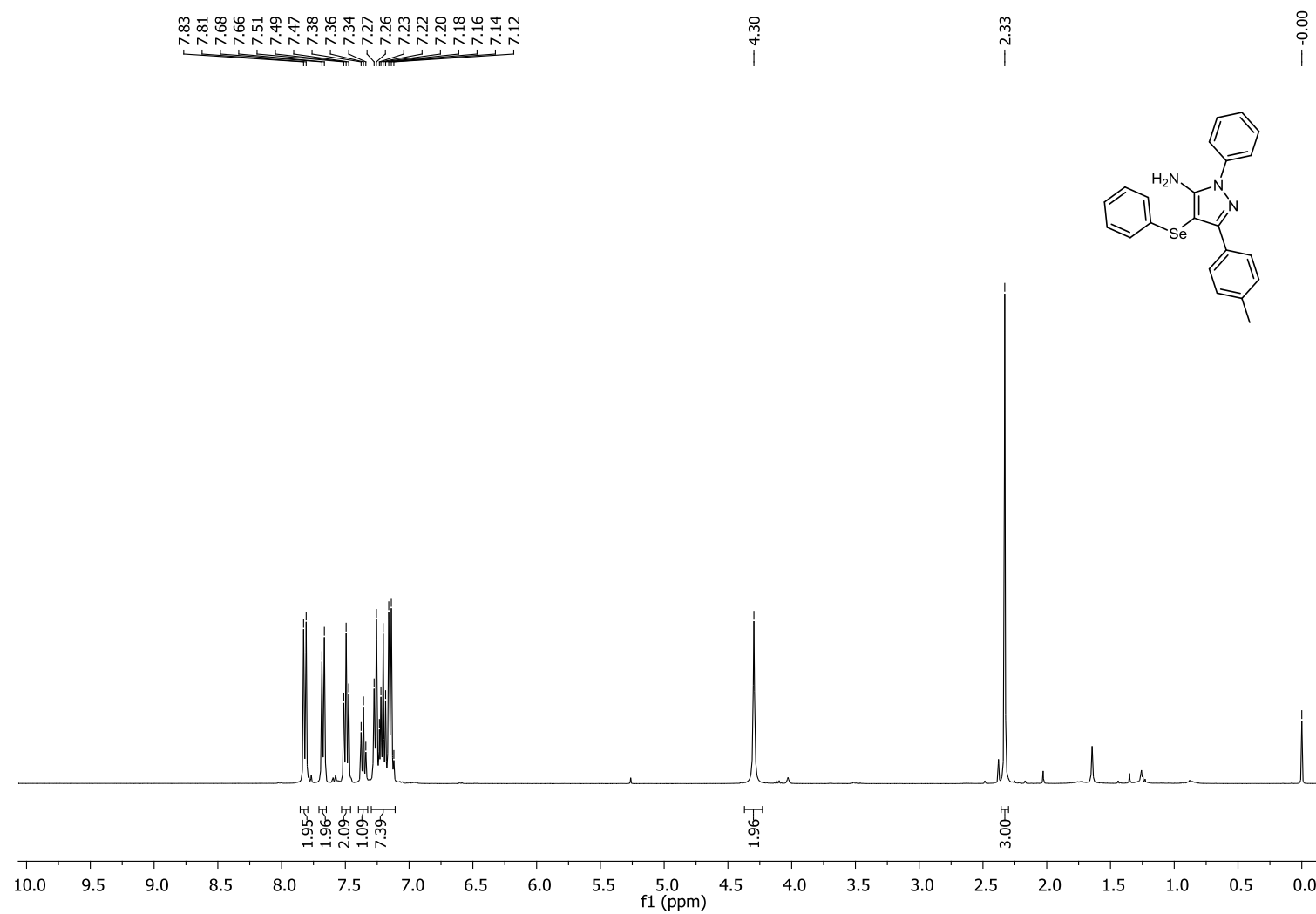


Figure S3. ¹H NMR (400 MHz, CDCl₃) of the product **4b**.

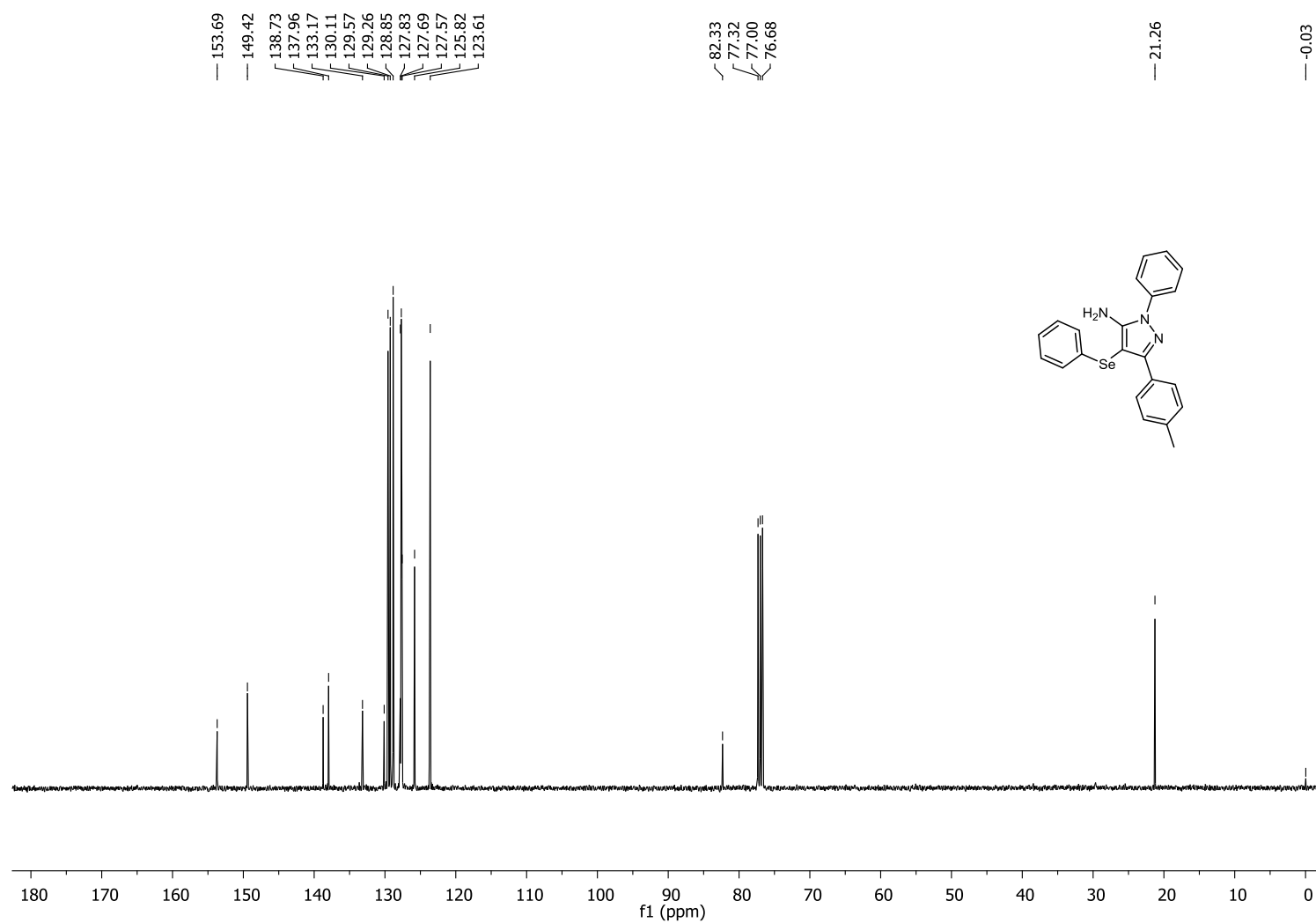


Figure S4. ¹³C NMR (100 MHz, CDCl₃) of the product **4b**.

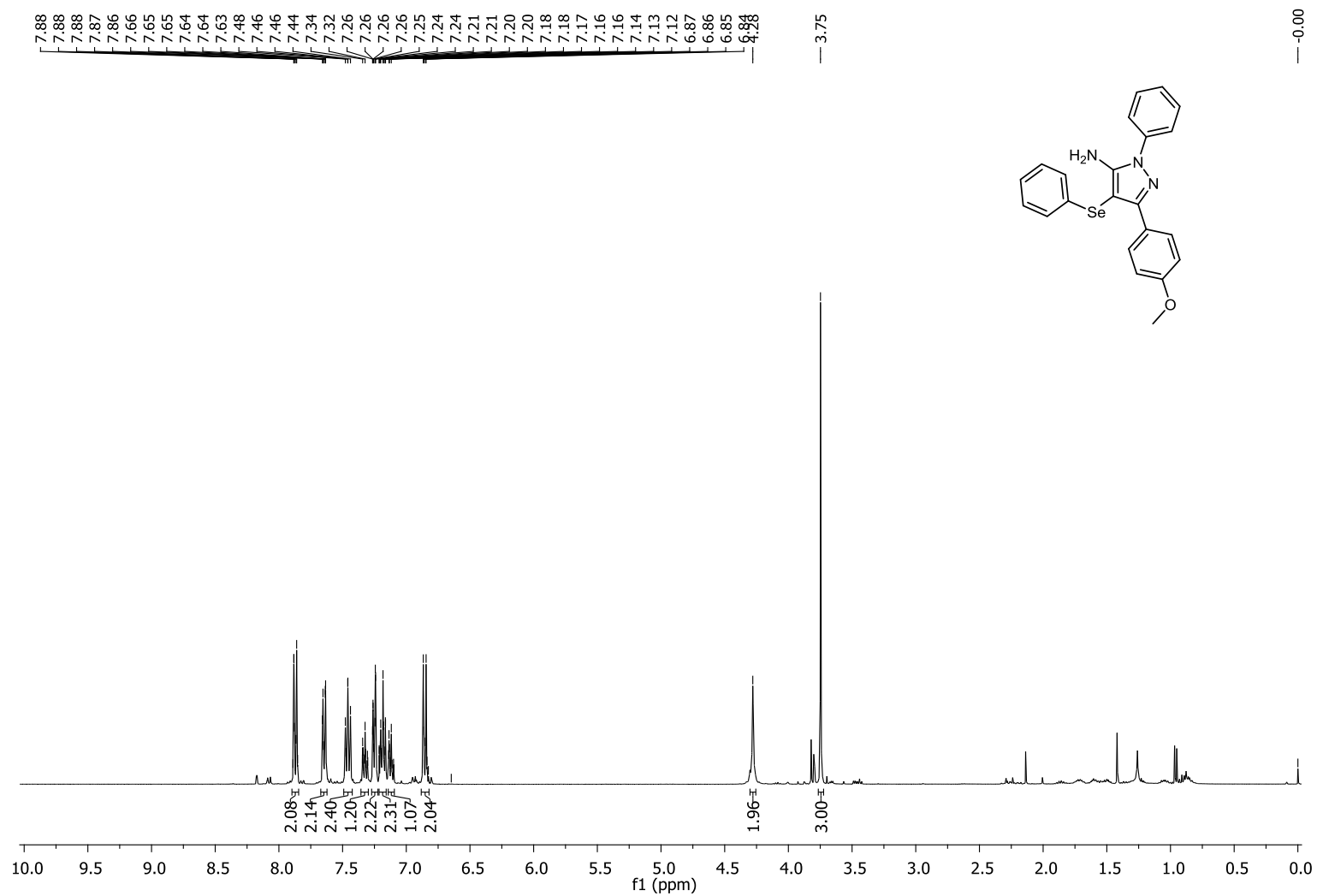


Figure S5. ¹H NMR (400 MHz, CDCl₃) of the product **4b**.

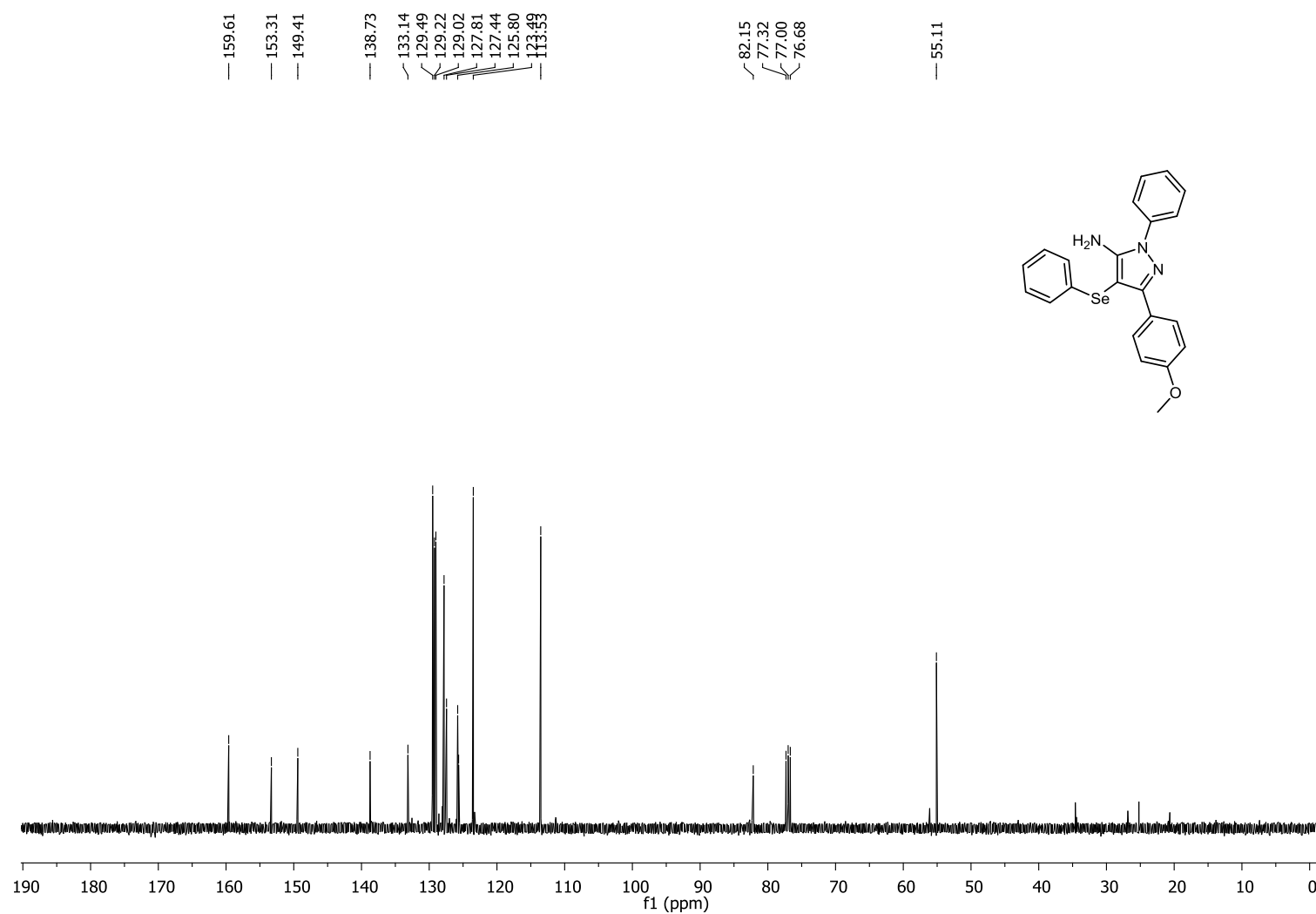


Figure S6. ¹³C NMR (100 MHz, CDCl₃) of the product **4c**.

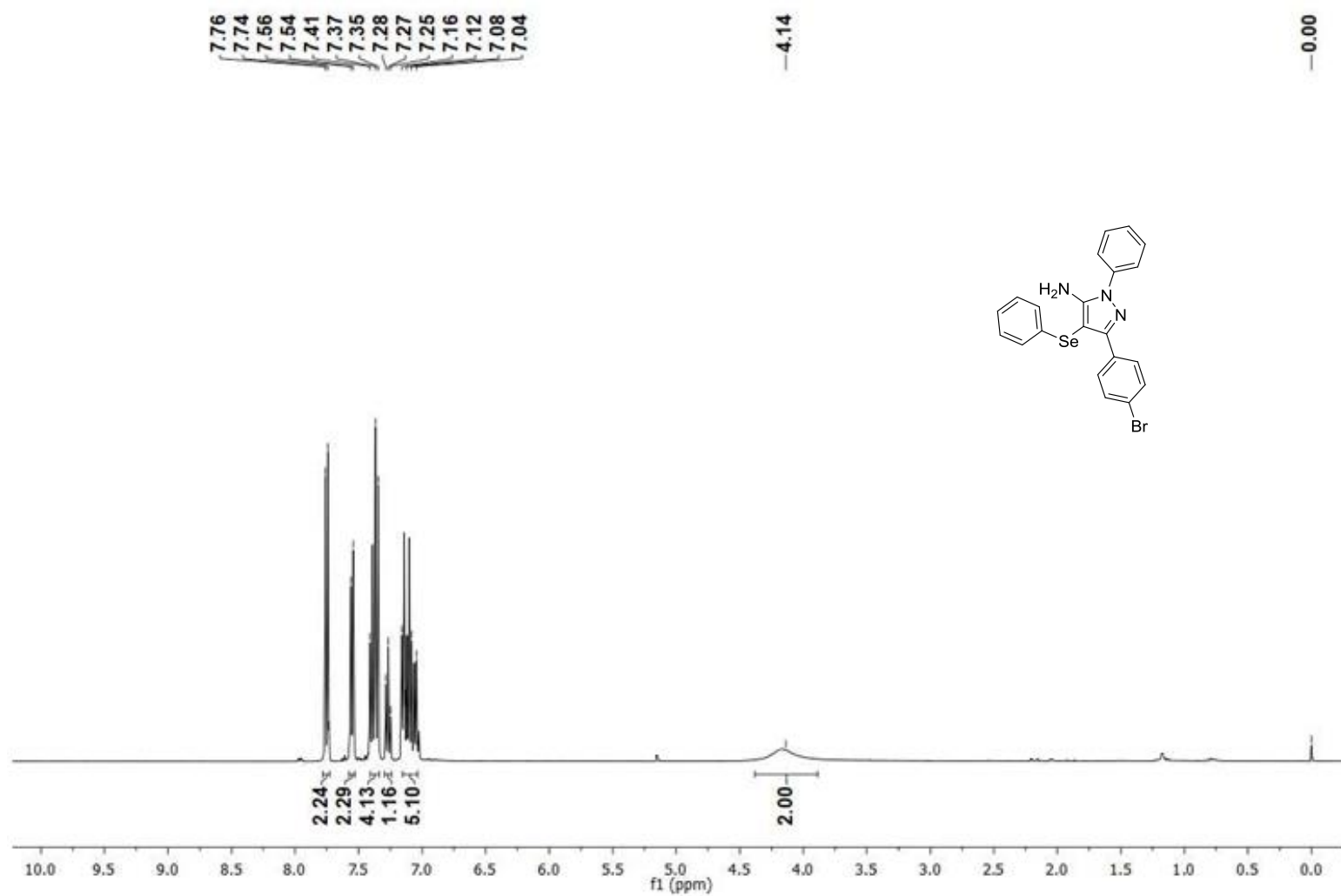


Figure S7. ¹H NMR (400 MHz, CDCl₃) of the product **4d**.

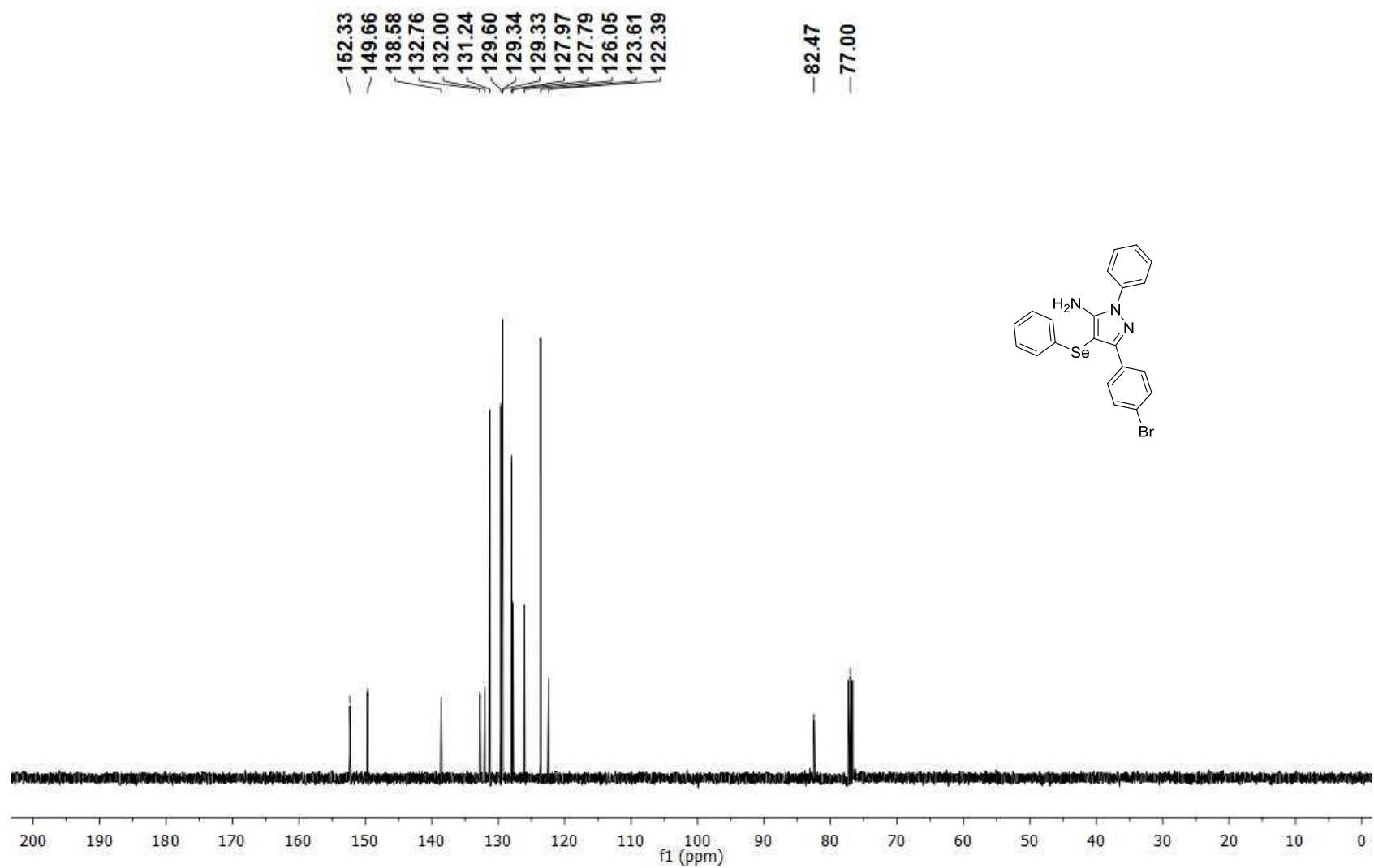


Figure S8. ¹³C NMR (100 MHz, CDCl₃) of the product **4d**.

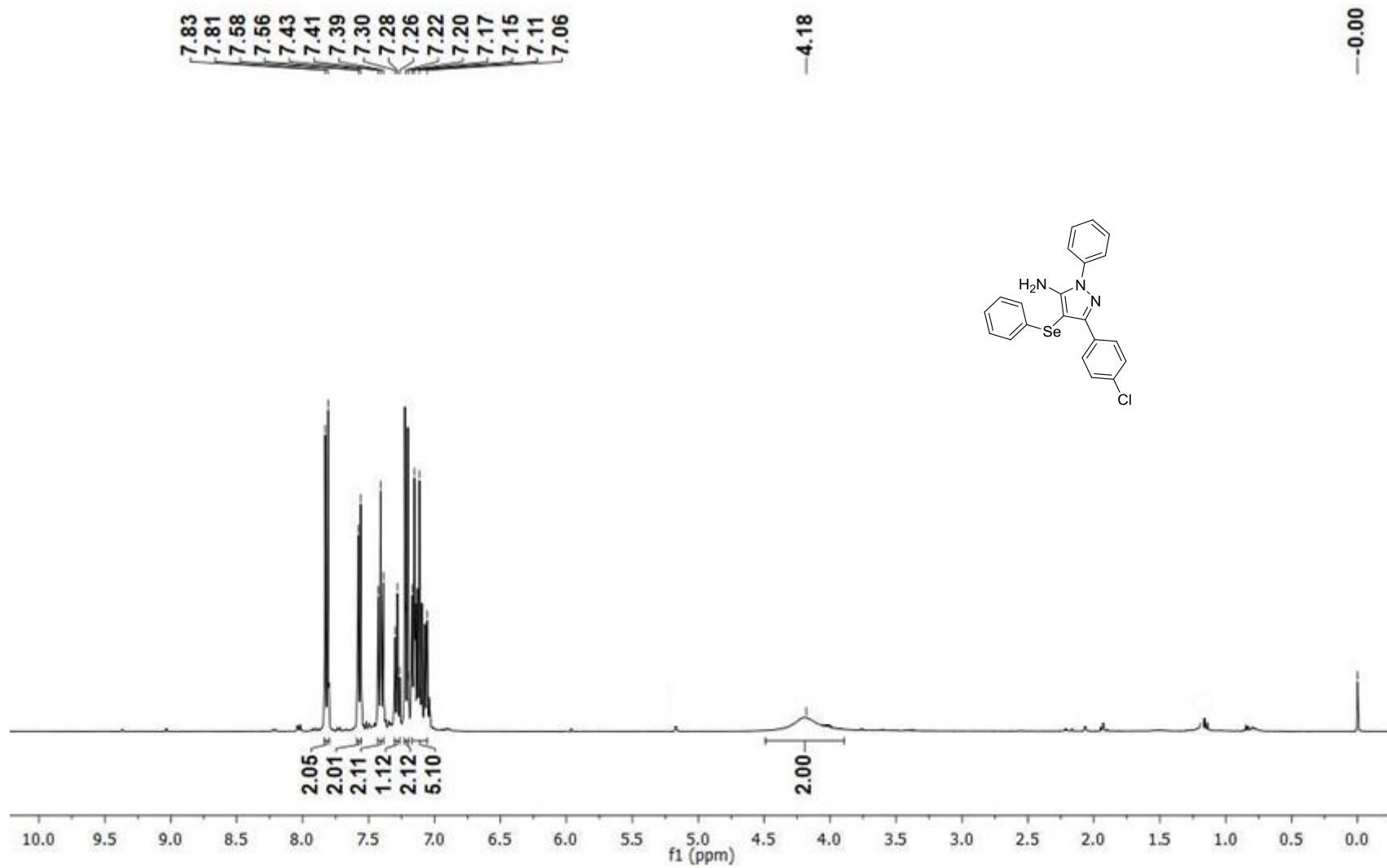


Figure S9. ¹H NMR (400 MHz, CDCl₃) of the product **4e**.

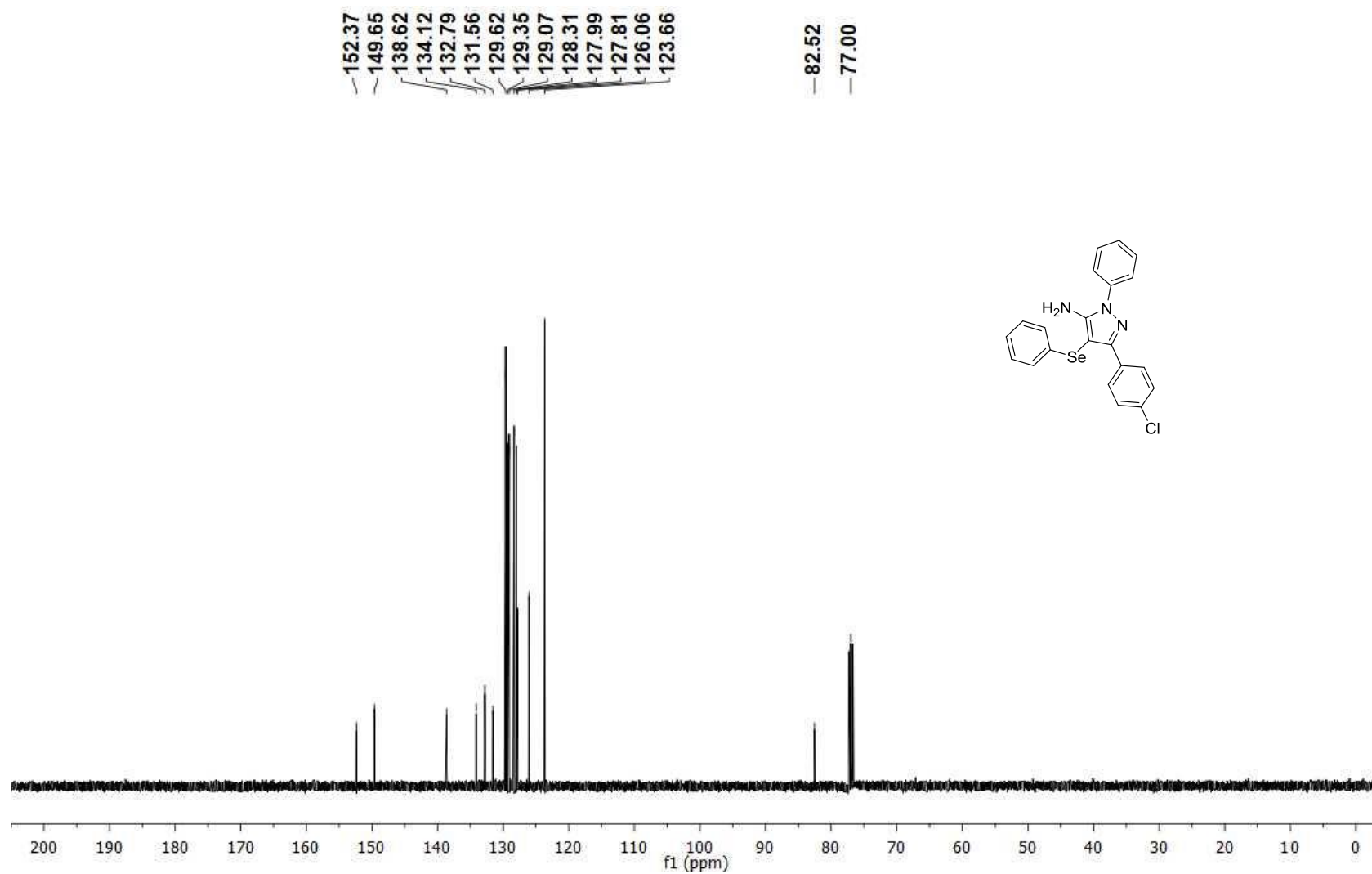


Figure S10. ¹³C NMR (100 MHz, CDCl₃) of the product **4e**.

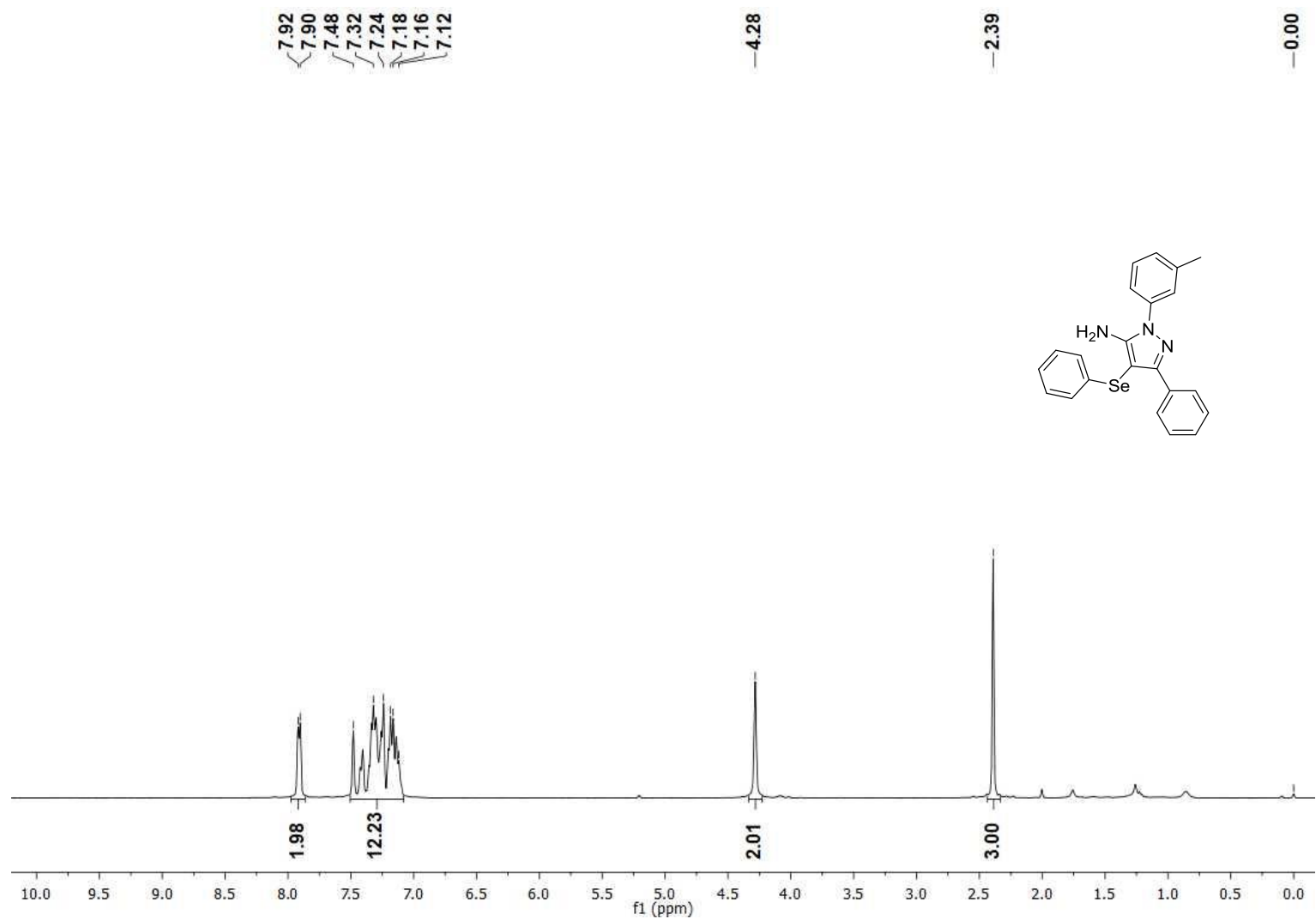


Figure S11. ^1H NMR (400 MHz, CDCl_3) of the product **4g**.

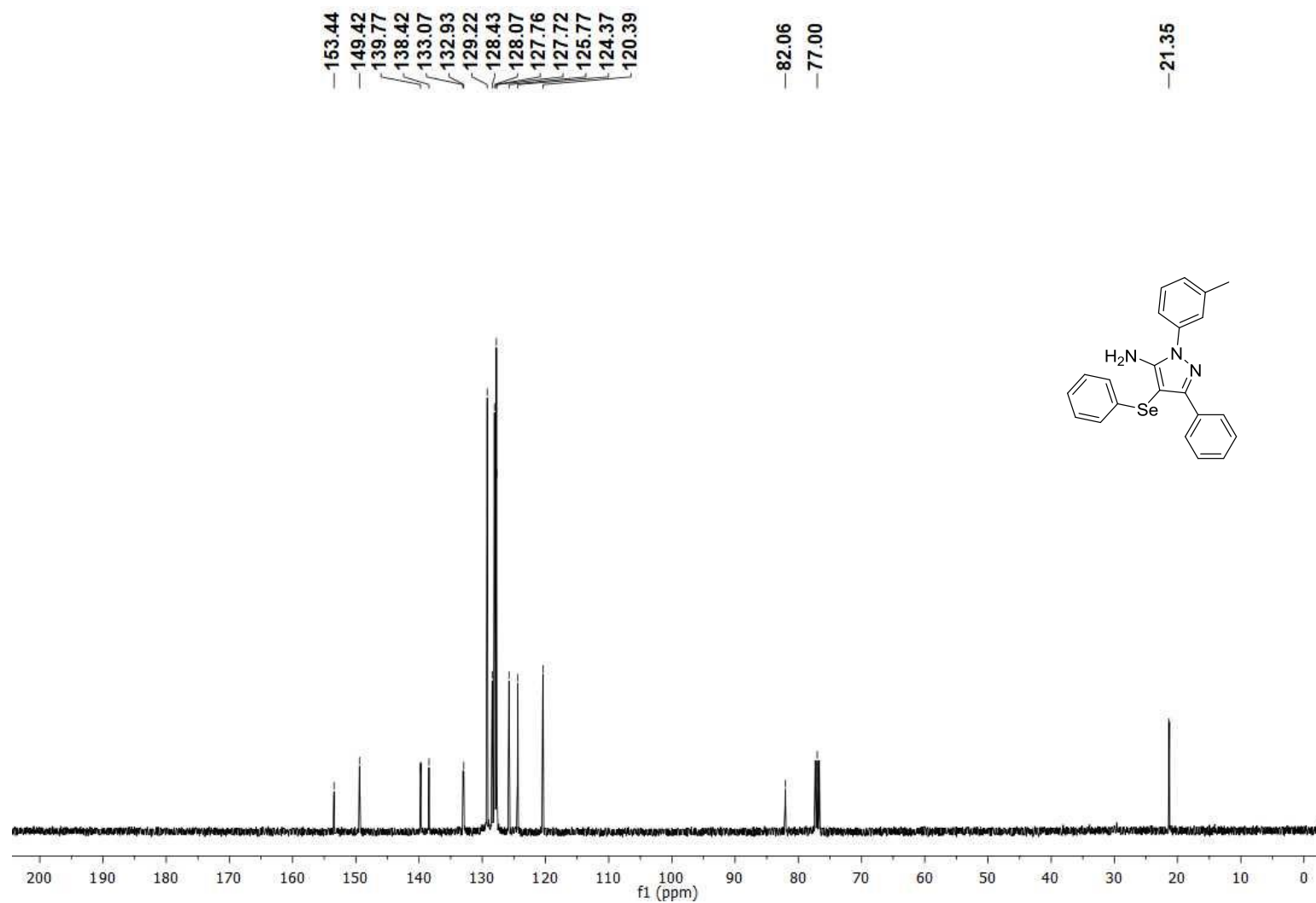


Figure S12. ¹³C NMR (100 MHz, CDCl₃) of the product **4g**.

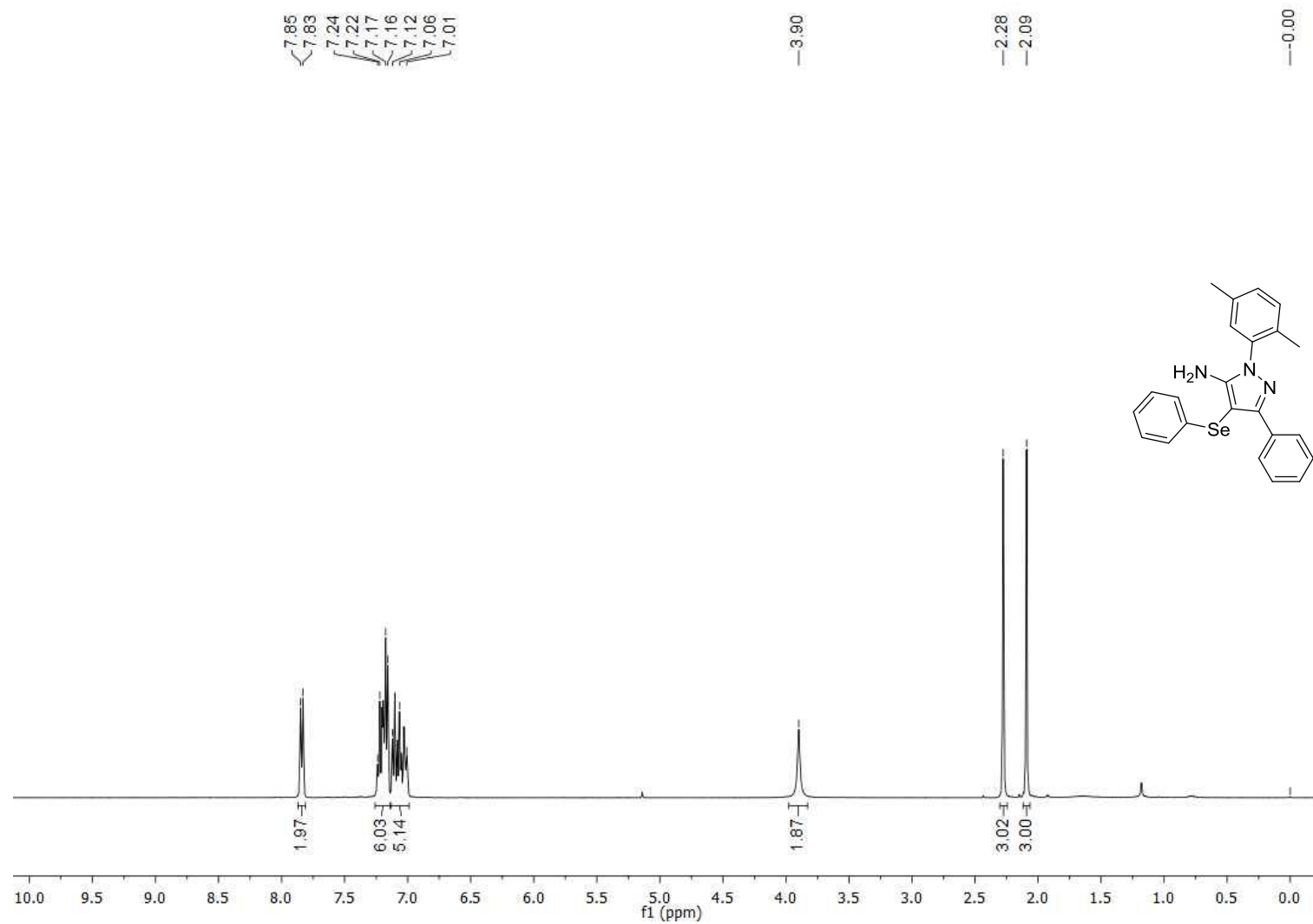


Figure S13. ¹H NMR (400 MHz, CDCl₃) of the product **4h**.

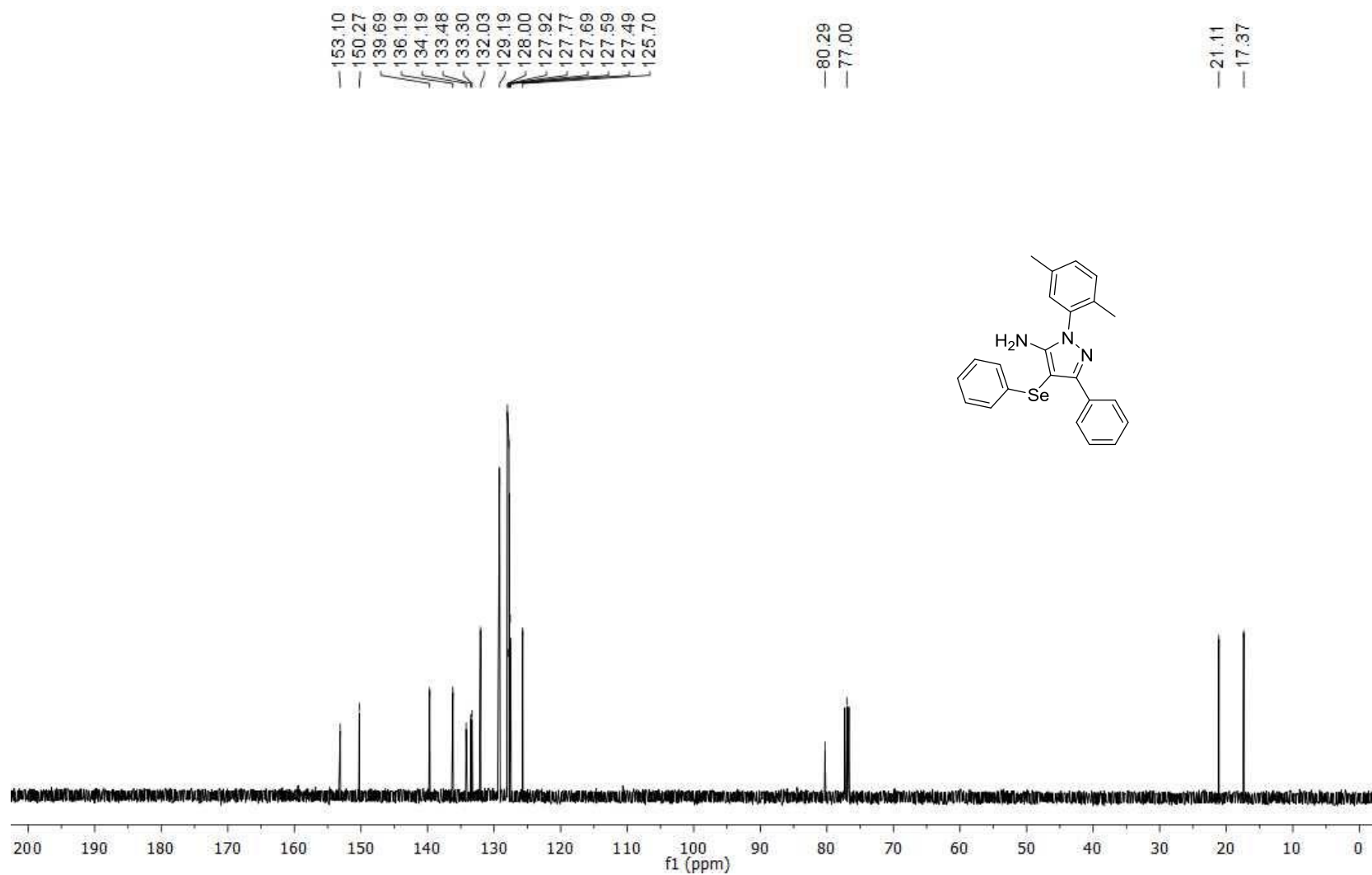


Figure S14. ¹³C NMR (100 MHz, CDCl₃) of the product 4h.

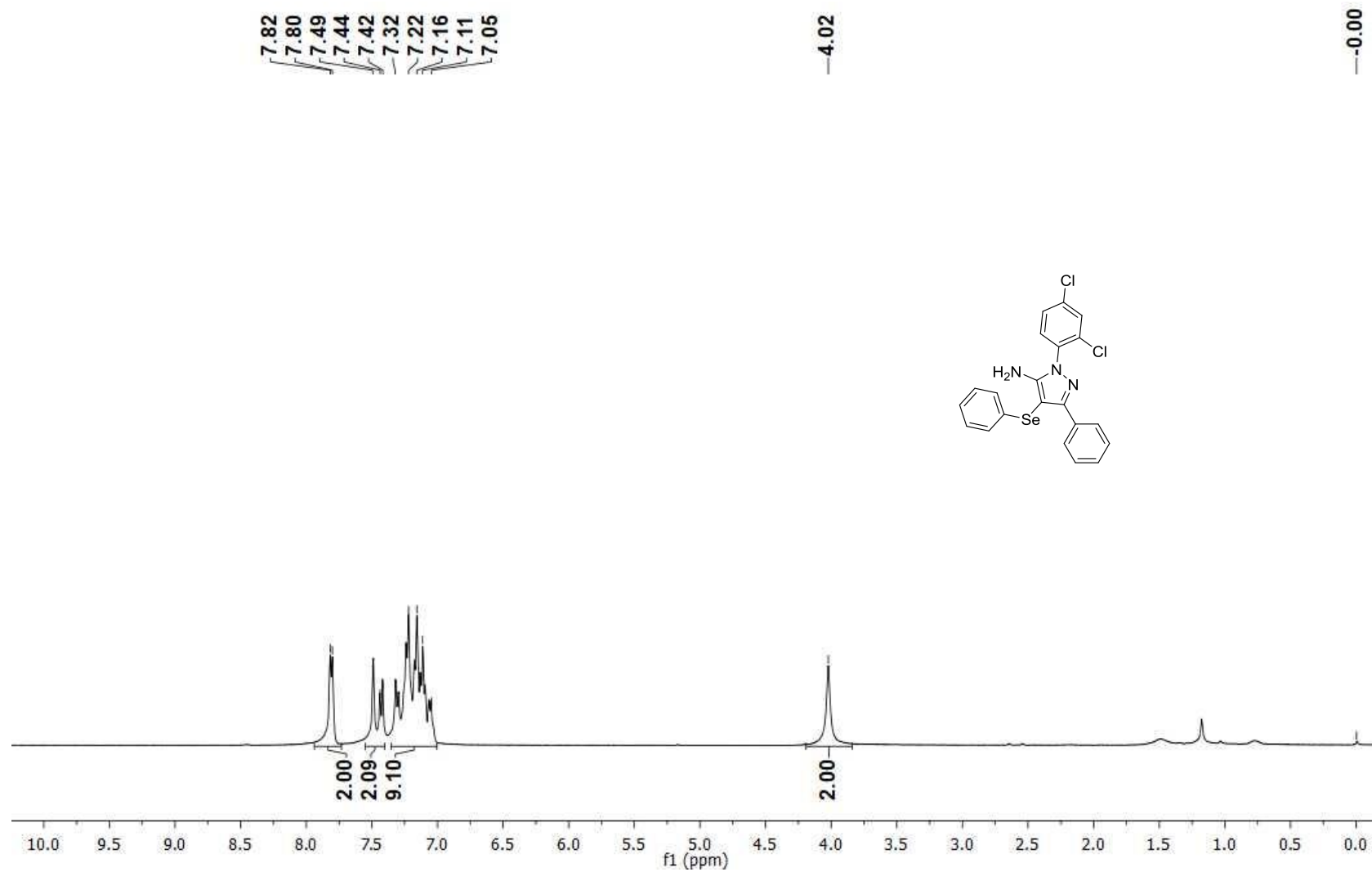


Figure S15. ^1H NMR (400 MHz, CDCl_3) of the product **4i**.

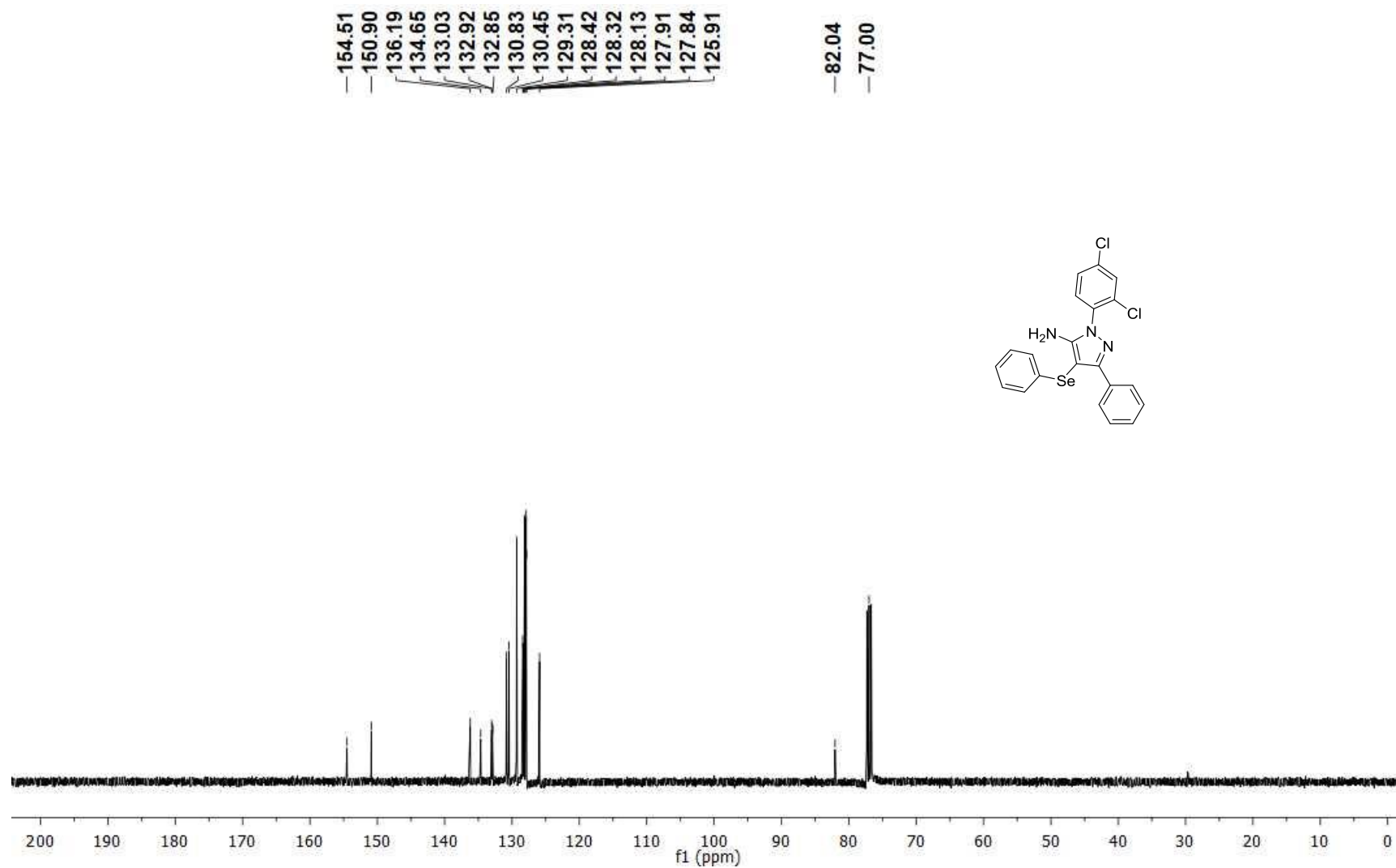


Figure S16. ¹³C NMR (100 MHz, CDCl₃) of the product 4i.

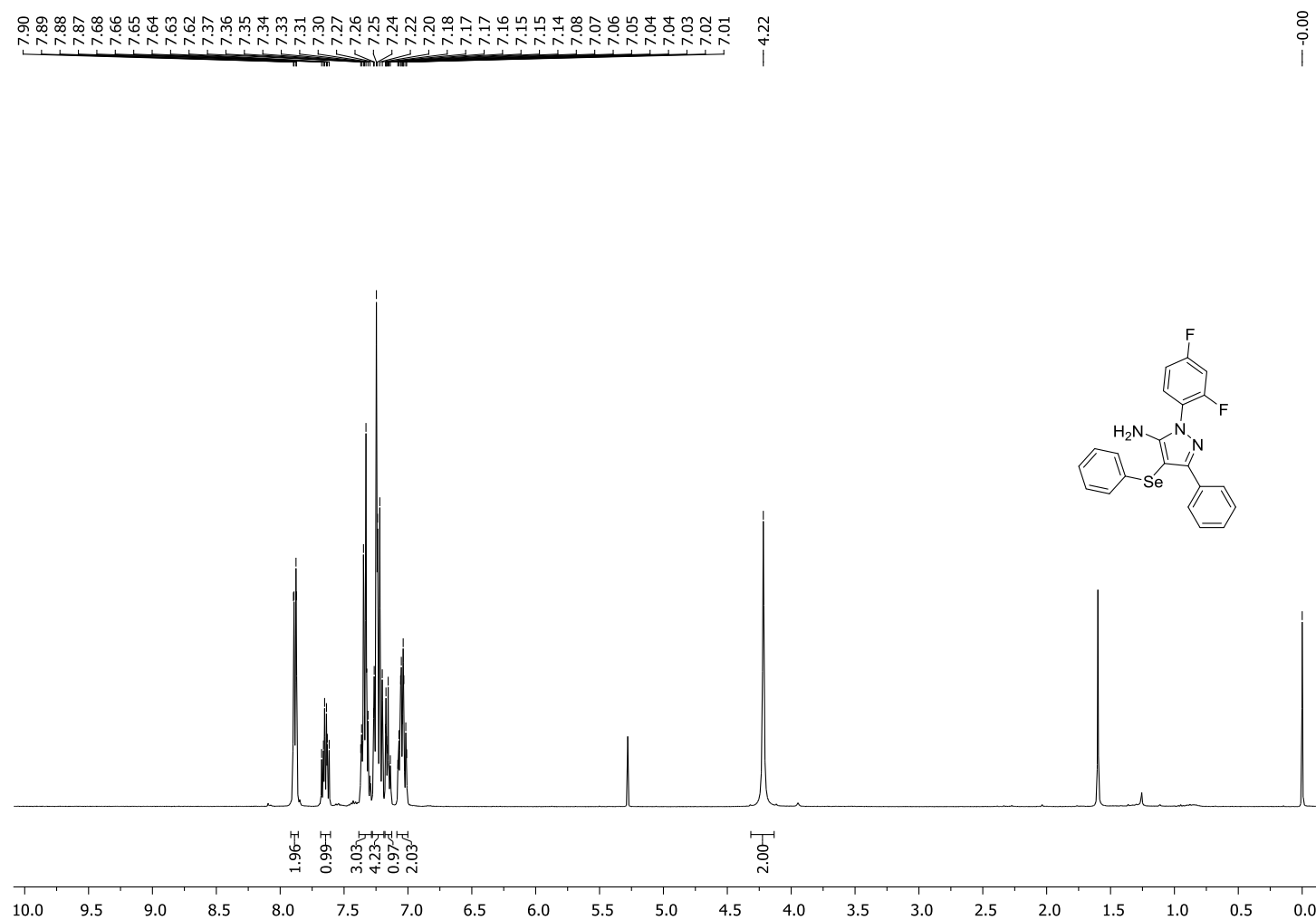


Figure S17. ¹H NMR (400 MHz, CDCl₃) of the product **4j**.

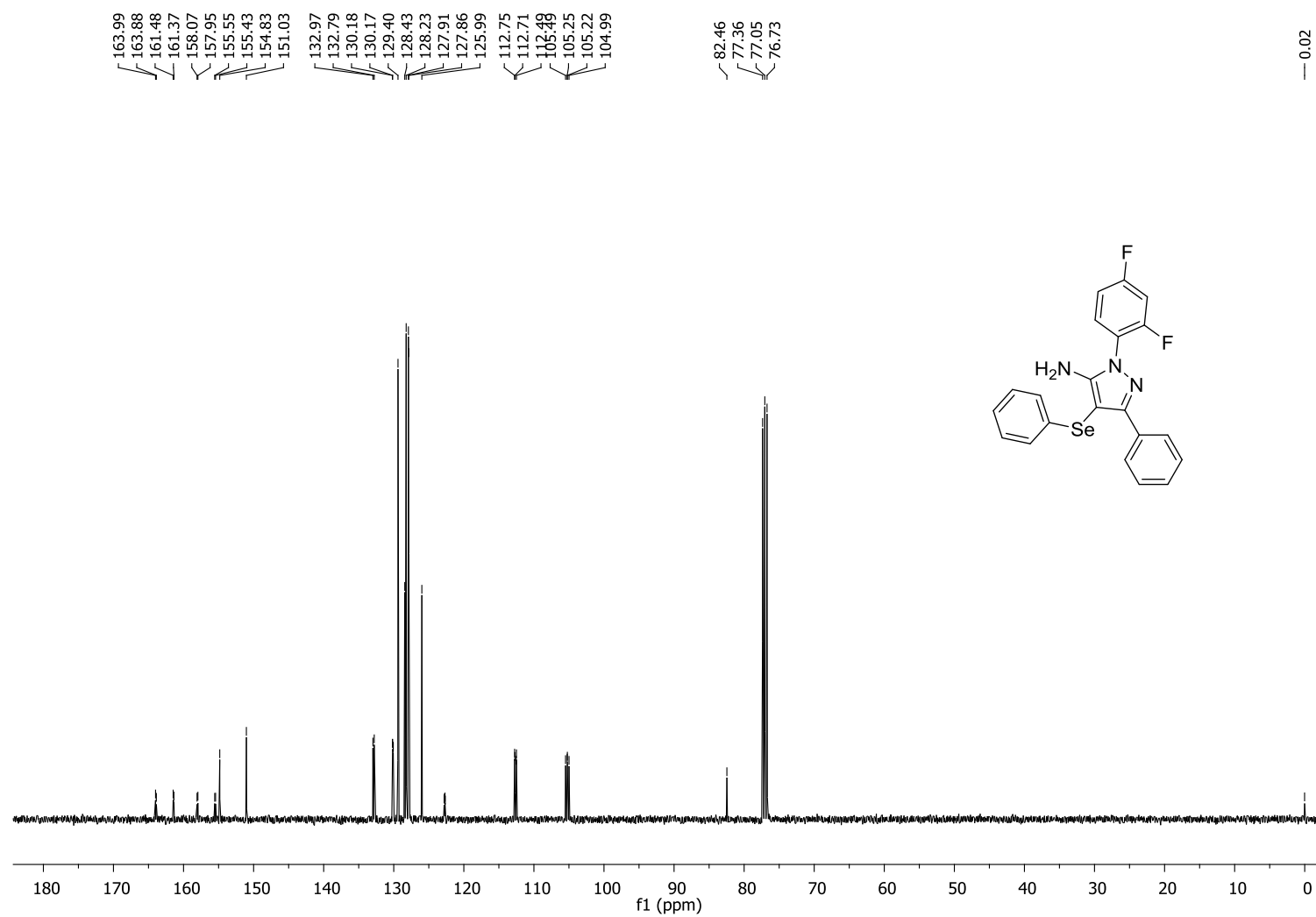


Figure S18. ¹³C NMR (100 MHz, CDCl₃) of the product **4j**.

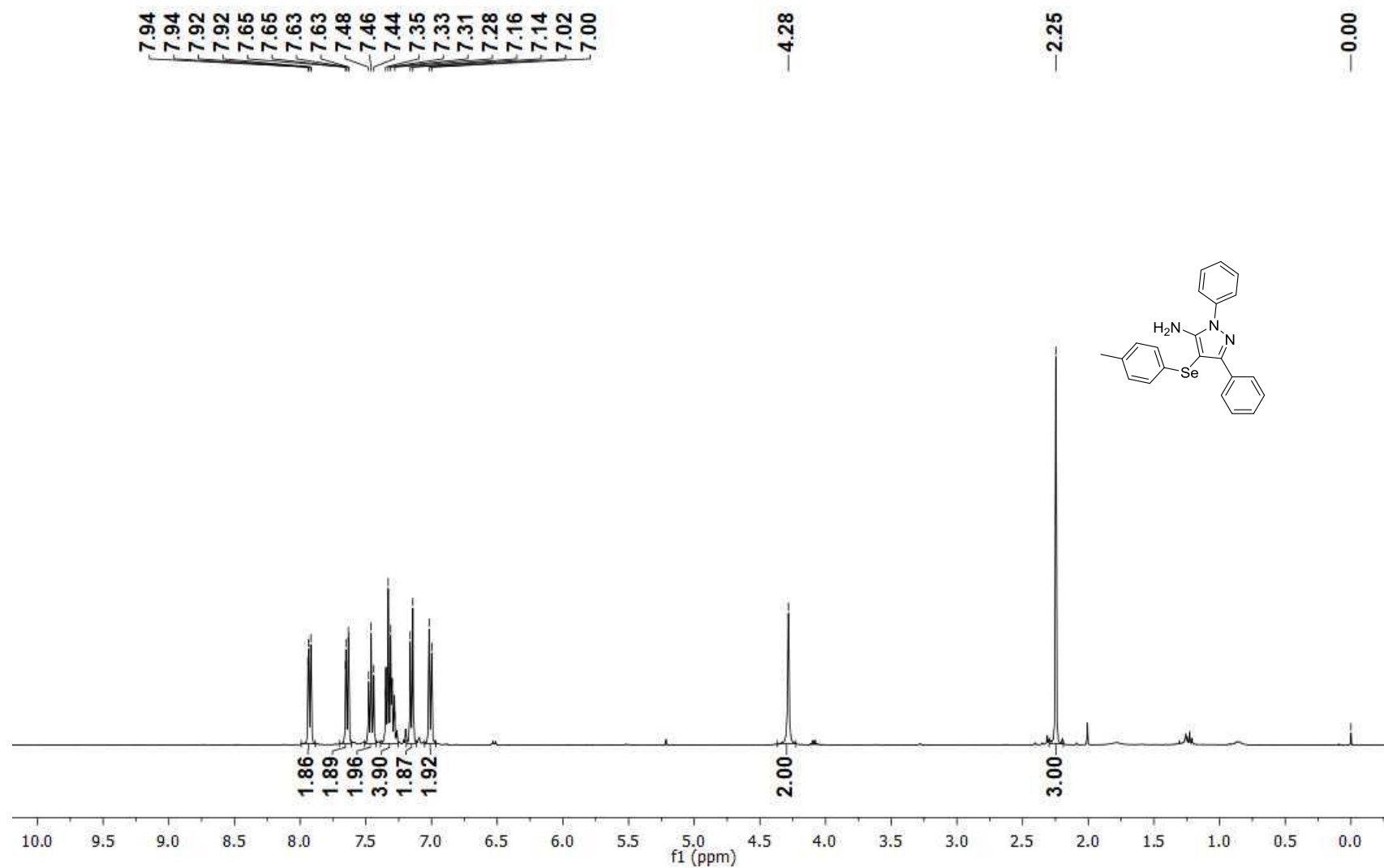


Figure S19. ¹H NMR (400 MHz, CDCl₃) of the product **4l**.

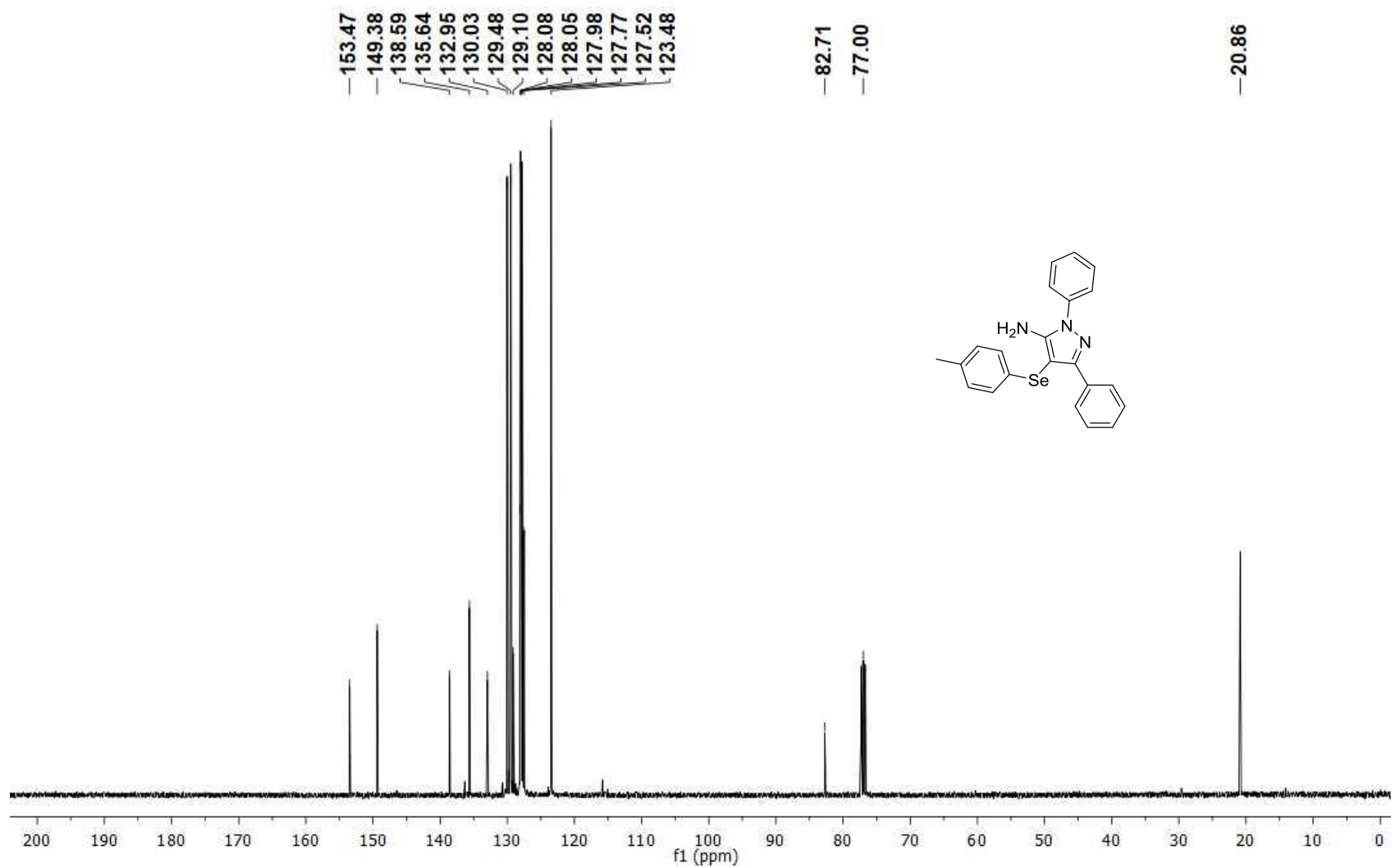


Figure S20. ¹³C NMR (100 MHz, CDCl₃) of the product 4l.

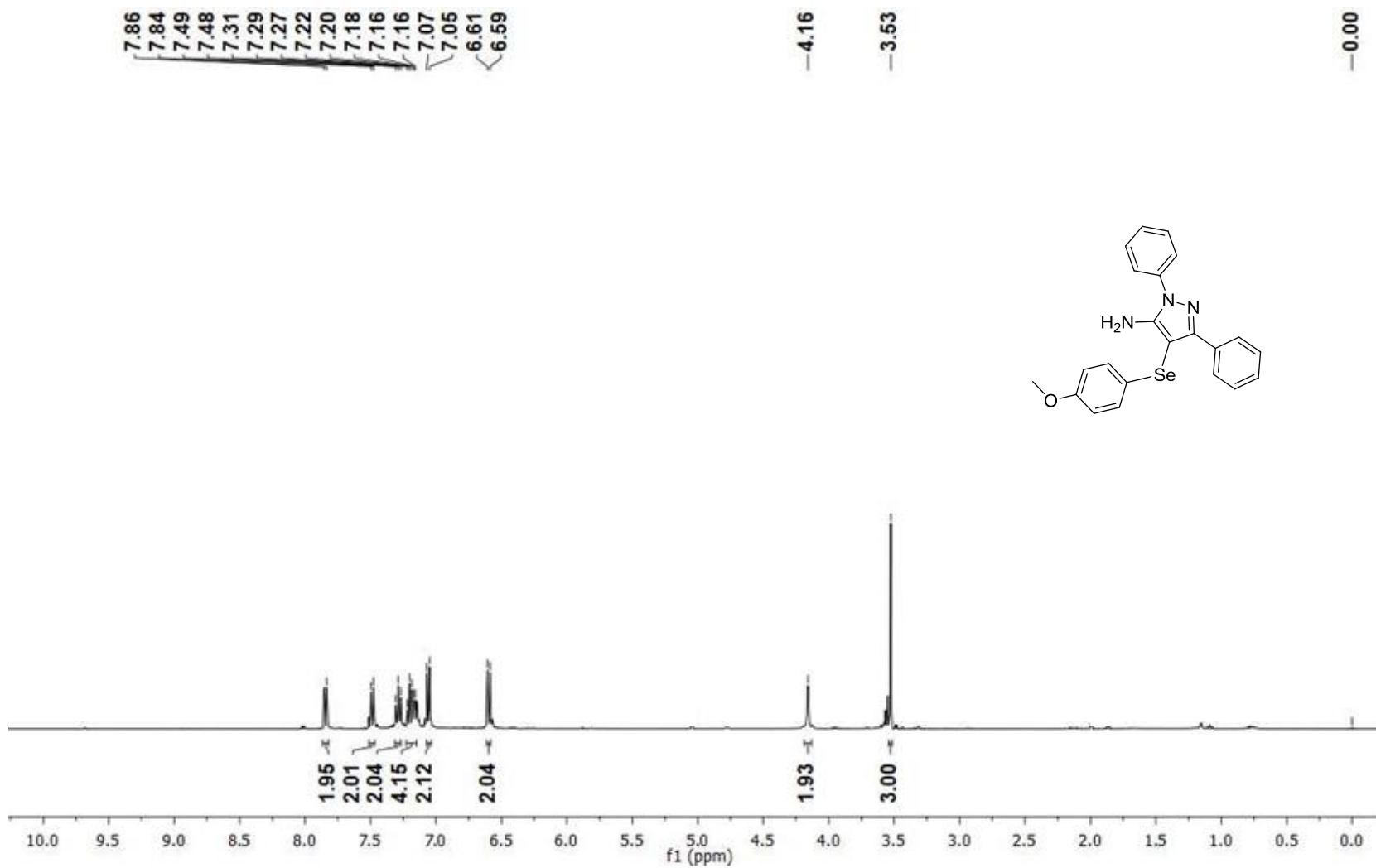


Figure S21. ¹H NMR (400 MHz, CDCl₃) of the product **4m**.

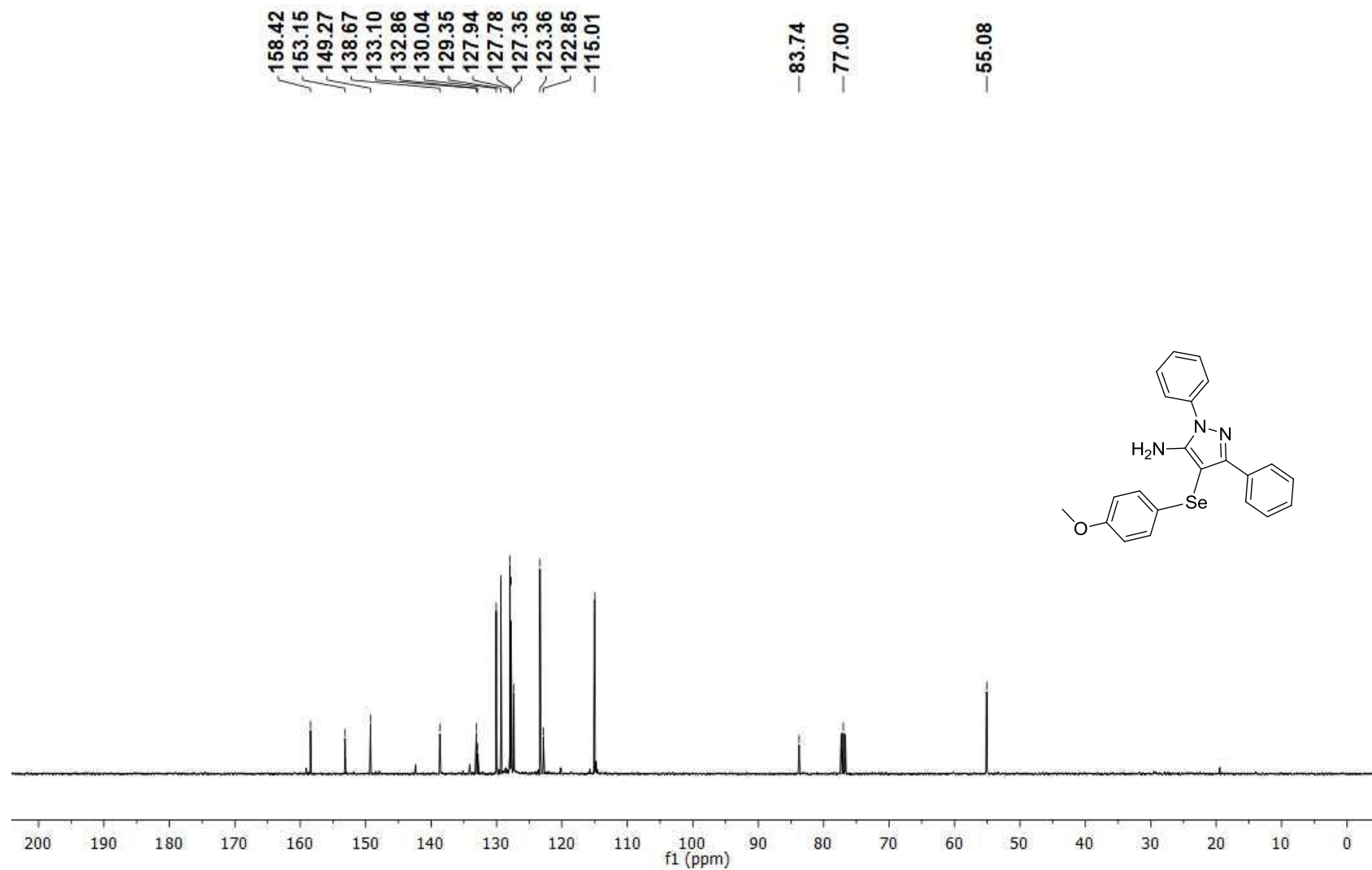


Figure S22. ¹³C NMR (100 MHz, CDCl₃) of the product **4m**.

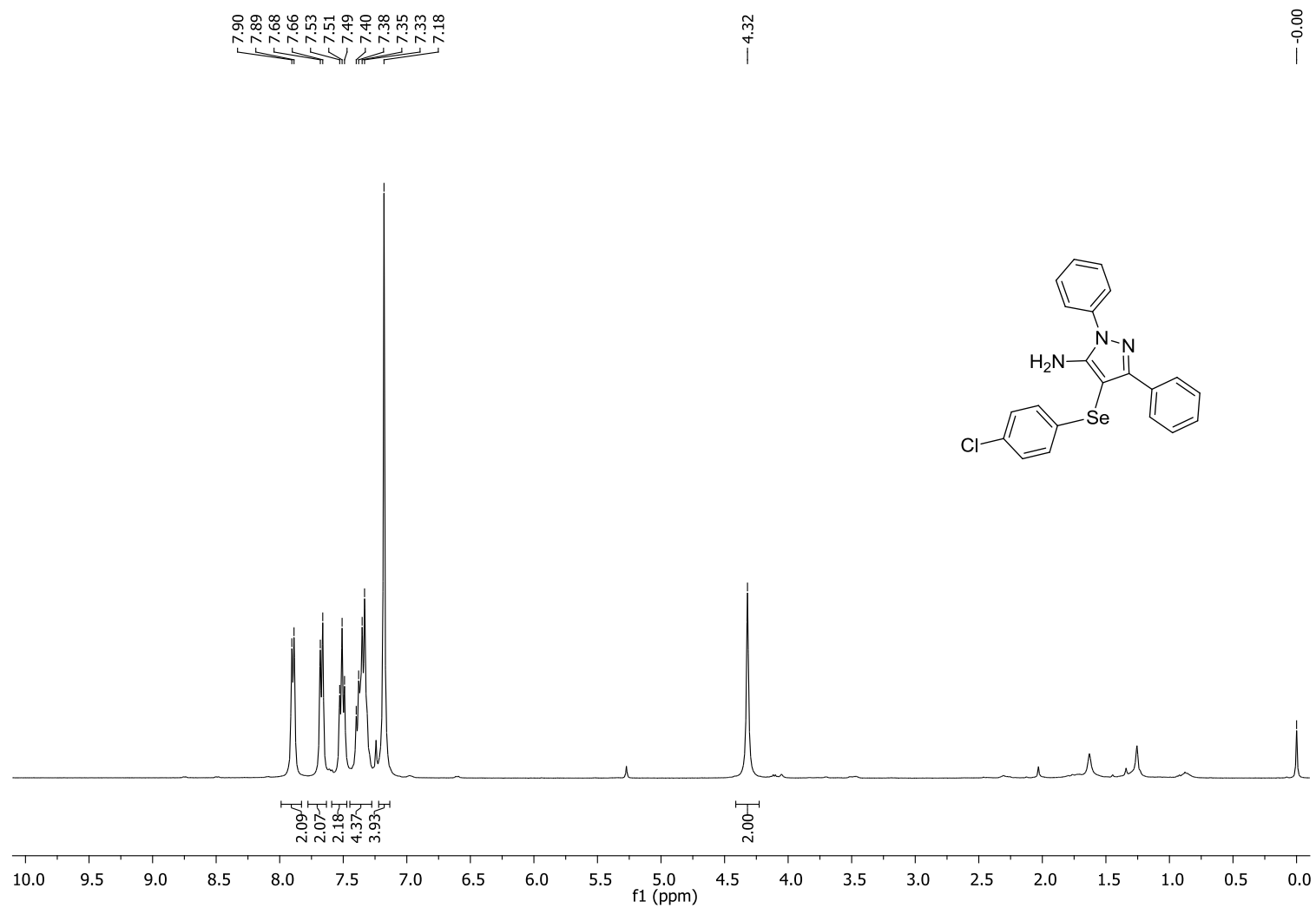


Figure S23. ¹H NMR (400 MHz, CDCl₃) of the product **4n**.

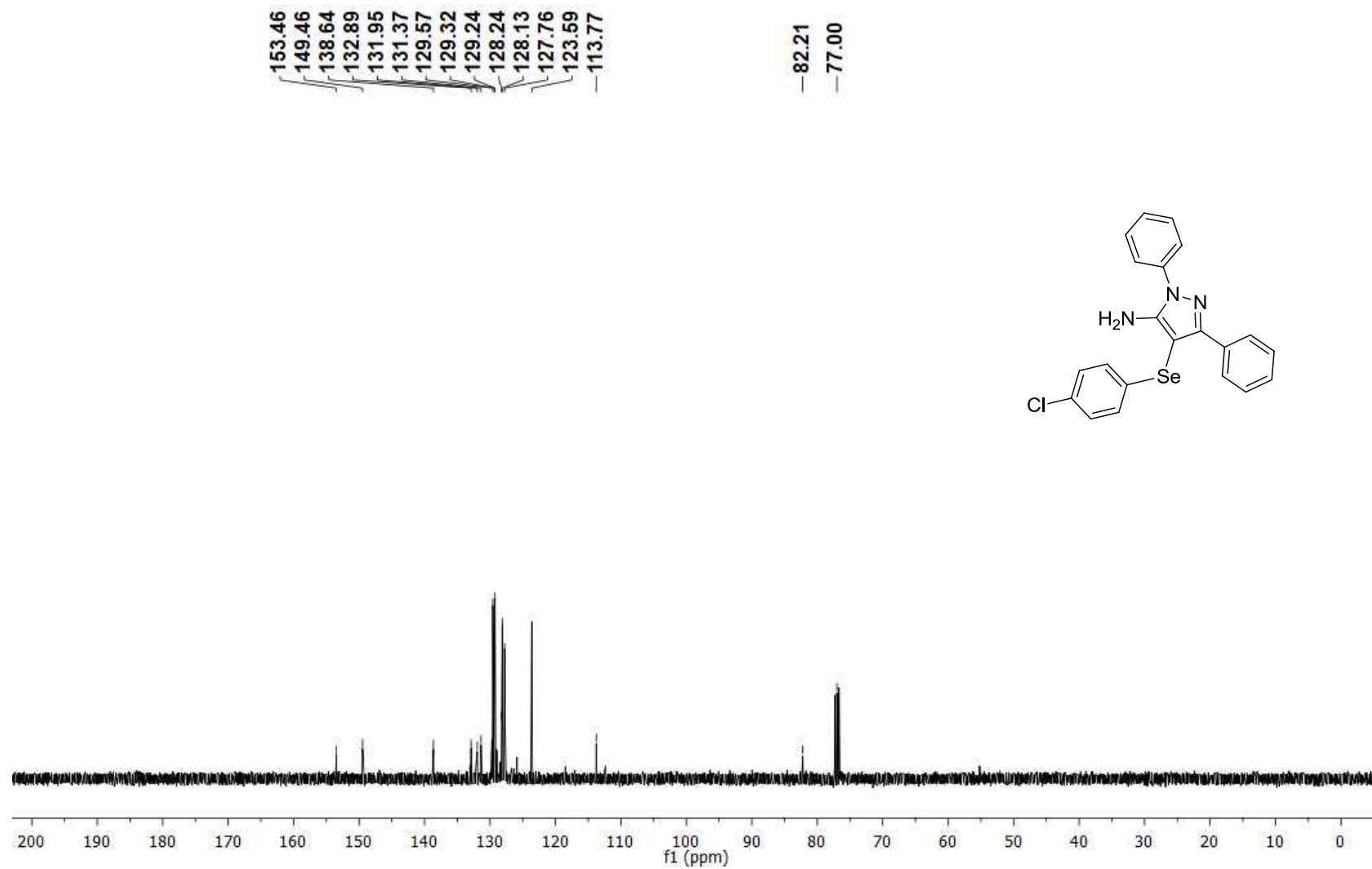


Figure S24. ^{13}C NMR (100 MHz, CDCl_3) of the product **4n**.

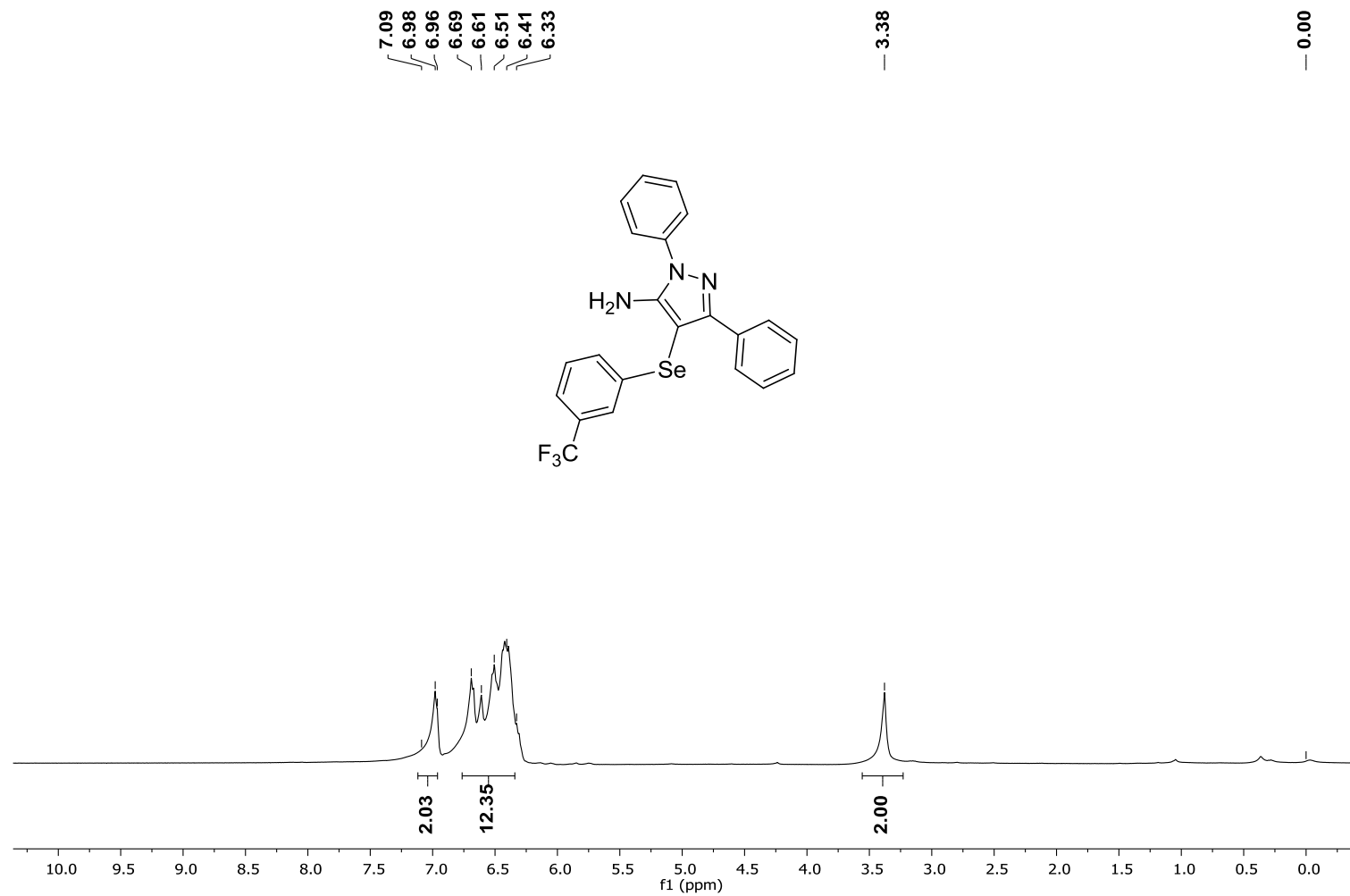


Figure S25. ^1H NMR (400 MHz, CDCl_3) of the product **4o**

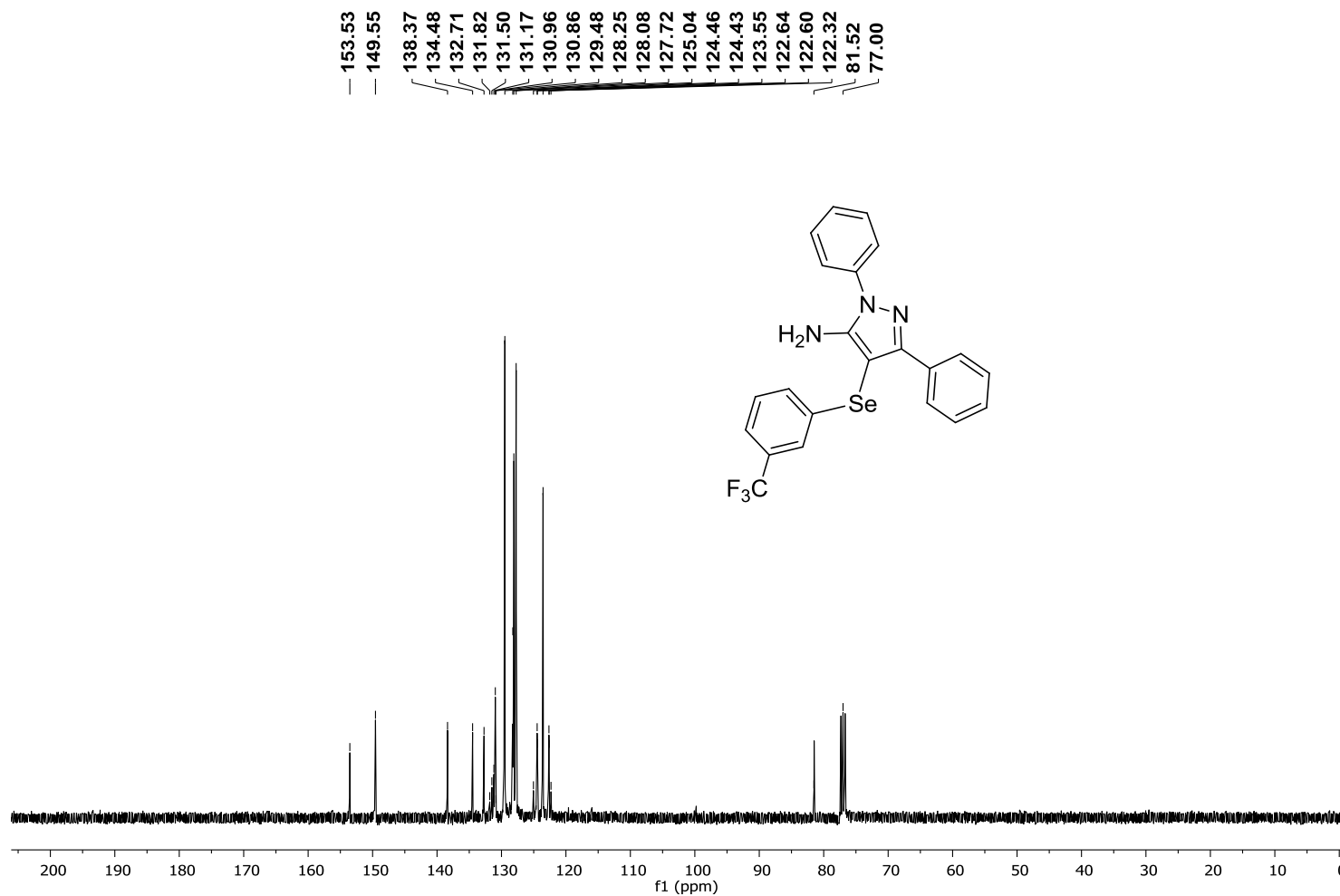


Figure S26. ¹³C NMR (100 MHz, CDCl₃) of the product **4o**.

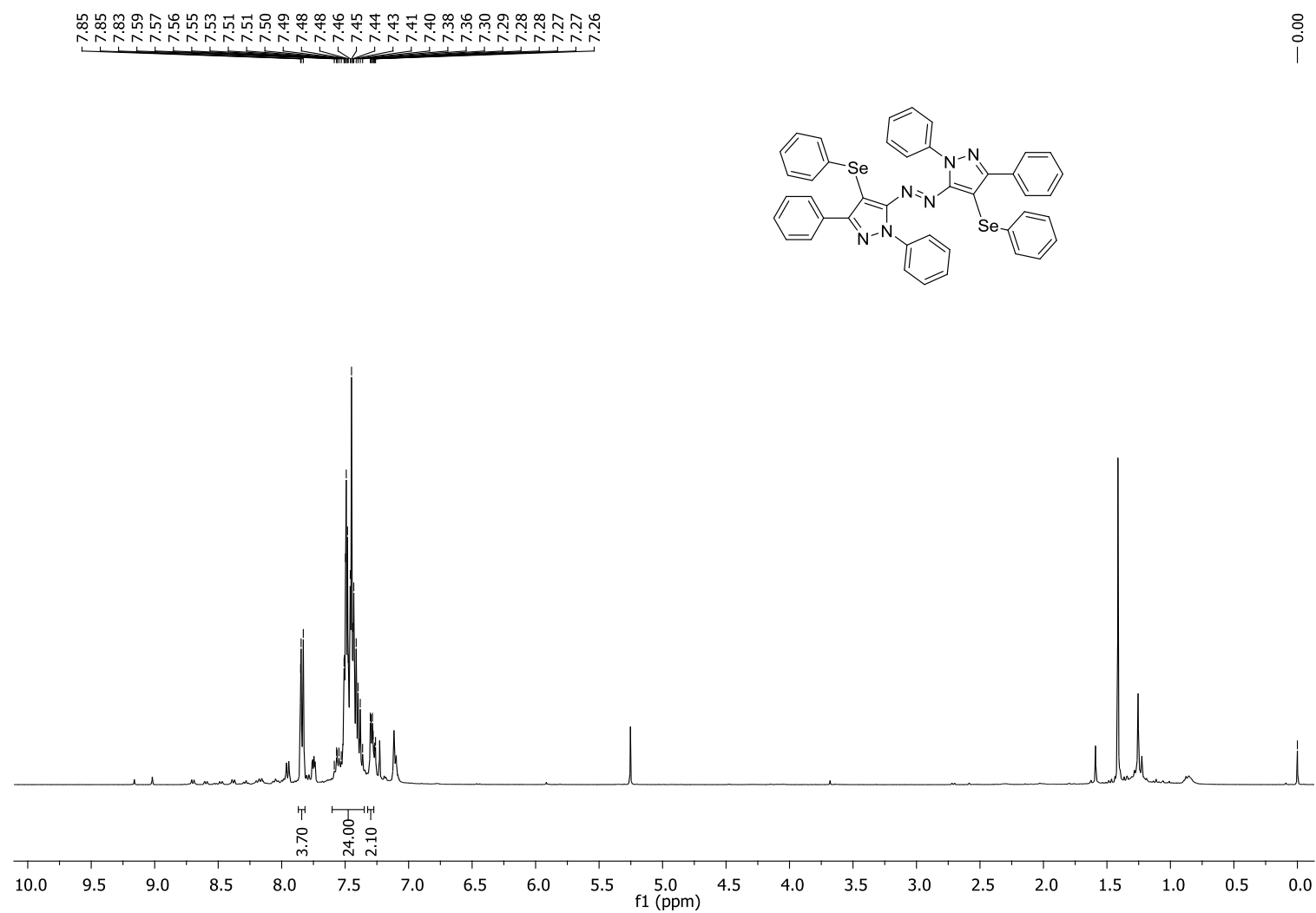


Figure S27. ^1H NMR (400 MHz, CDCl_3) of the product 6.

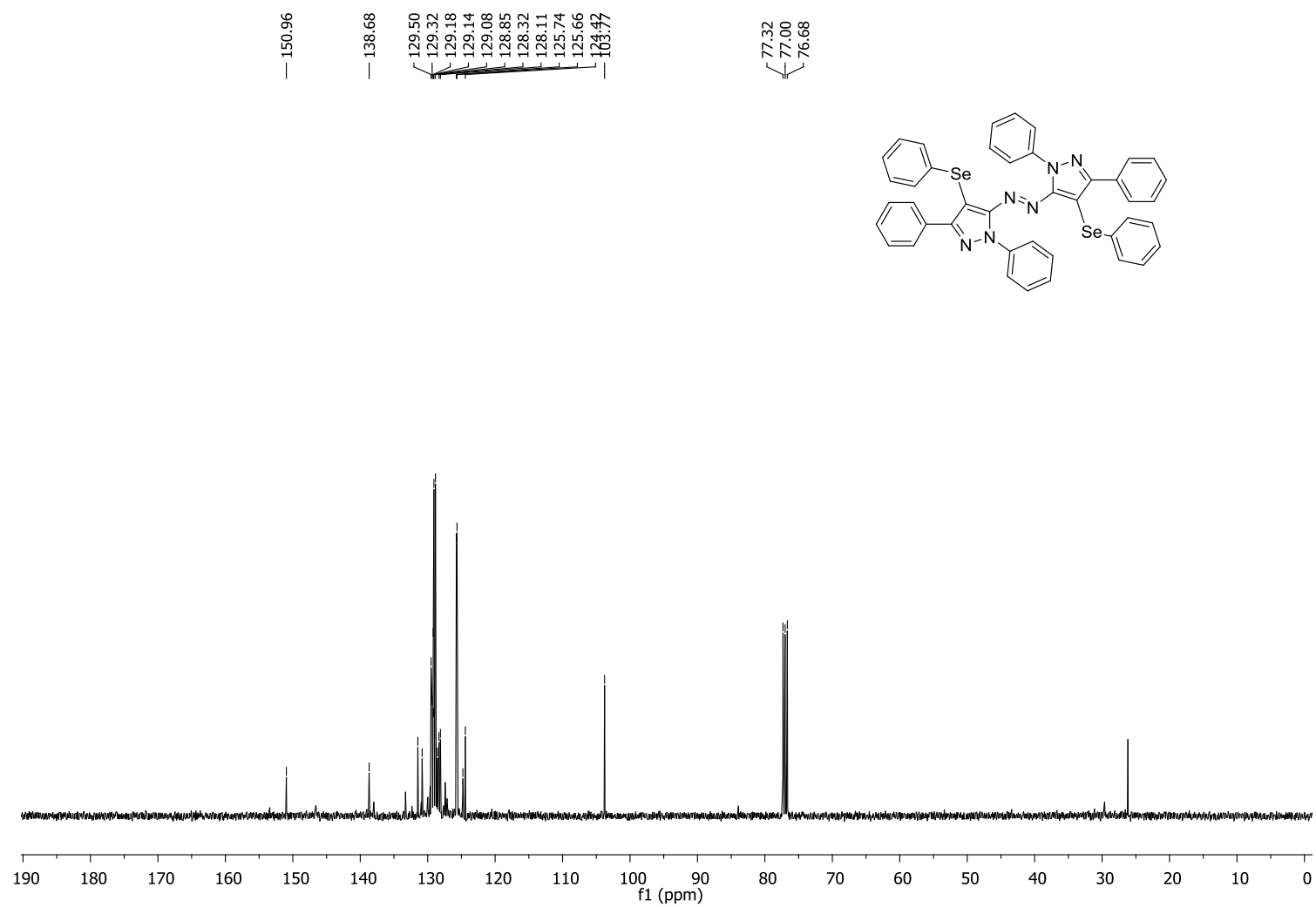


Figure S28. ¹³C NMR (100 MHz, CDCl₃) of the product 6.