

Supplementary information

Kinetic Investigation of Thermal and Photoinduced Homolysis of Alkylated Verdazyls

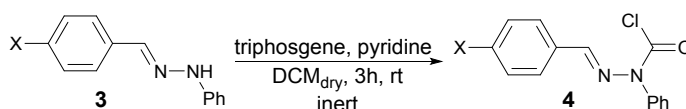
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Section S1. Experimental part

General procedure for preparation of chlorocarbamoyl derivatives of hydrazones 4a–4c. Hydrazone **3** (5 mmol) was dissolved in dry CH₂Cl₂ (50 mL) in a Schlenk flask under an argon atmosphere. Anhydrous pyridine (495 μ L, 6.1 mmol) and a solution of triphosgene (1.484 g, 5 mmol) in 15 mL of CH₂Cl₂ were added, and the resulting solution was stirred for 3 hours at room temperature. 1 M HCl (20 mL) was added to the mixture, and the product was extracted with CH₂Cl₂, washed with water (3 \times 35 mL), and dried with MgSO₄. Chlorocarbamoyls **4a–4c** were purified by flash-chromatography (CH₂Cl₂ as the eluent).



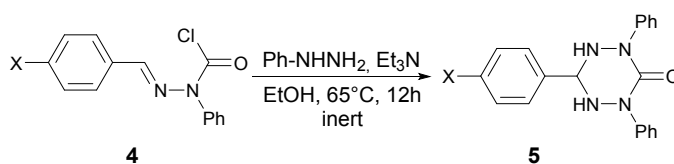
2-(4-methoxyphenyl)- α -chloroformyl-4-phenylhydrazone 4a. According to the general procedure, the reaction of 1-(4-methoxybenzylidene)-2-phenylhydrazine **3a** (1.131 g, 5 mmol) with triphosgene afforded compound **4a** as a yellow-white solid (1.227 g, 85% yield), **mp** = 97.8 – 99.0°C. **¹H NMR** (DMSO-d₆, 400 MHz): δ 3.76 (s, 3H), 6.70 (t, 1H, J = 7.2 Hz), 6.95 (d, 2H, J = 8.8 Hz), 7.05 (d, 2H, J = 8.6 Hz), 7.16 – 7.21 (m, 2H), 7.57 (d, 2H, J = 7.0 Hz), 7.85 (s, 1H) ppm. **¹³C{¹H} NMR** (DMSO-d₆, 101 MHz): 55.23, 111.85, 114.22, 118.32, 127.06, 127.57, 128.60, 129.09, 136.57, 145.67, 159.33 ppm. **FT-IR** (ATR): λ = 3052, 3002, 2928, 1730, 1597, 1516, 1492, 1457, 1370, 1316, 1302, 1260, 1187, 1162, 1018, 865 cm⁻¹. Anal. calcd. for C₁₅H₁₃ClN₂O₂: C, 62.40; H, 4.54; N, 9.70. Found: C, 62.42; H, 4.58; N, 9.79.

2-phenyl- α -chloroformyl-4-phenylhydrazone 4b. According to the general procedure, the reaction of 1-benzylidene-2-phenylhydrazine **3b** (0.981 g, 5 mmol) with triphosgene afforded compound **4b** as a yellow solid (1.203 g, 93% yield), **mp** = 98.5 °C. **¹H NMR** (DMSO-d₆, 400 MHz): δ 6.73 (t, 1H, J = 7.2 Hz), 7.08 (d, 2H, J = 7.9 Hz), 7.21 (t, 2H, J = 7.8 Hz), 7.27 (t, 1H, J = 7.3 Hz), 7.37 (t, 2H, J = 7.5 Hz), 7.63 (d, 2H, J = 7.5 Hz), 7.88 (s, 1H) ppm. **¹³C{¹H} NMR** (DMSO-d₆, 101 MHz): 112.03, 118.75, 124.27, 125.65, 127.94, 128.72, 129.16, 135.94, 136.39, 145.39 ppm. **FT-IR** (ATR): λ = 1722, 1489, 1392, 1323, 1280, 1230, 1184, 959, 878, 814, 755, 719, 689 cm⁻¹. Anal. calcd. for C₁₄H₁₁ClN₂O: C, 65.00; H, 4.29; N, 10.83. Found: C, 64.96; H, 4.33; N, 10.84.

2-(4-nitrophenyl)- α -chloroformyl-4-phenylhydrazone 4c. According to the general procedure, the reaction of 1-(4-nitrobenzylidene)-2-phenylhydrazine **3c** (1.206 g, 5 mmol) with triphosgene afforded compound **4c** as a yellow solid (1.382 g, 91% yield), **mp** = 134.5 °C. **¹H NMR** (DMSO-d₆, 400 MHz): δ 6.82 (t, 1H, J = 7.2 Hz), 7.16 (d, 2H, J = 8.5 Hz), 7.21 – 7.29 (m, 2H),

7.86 (d, 2H, $J = 8.9$ Hz), 7.97 (s, 1H), 8.21 (d, 2H, $J = 8.9$ Hz,) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 101 MHz): 112.62, 119.94, 124.13, 124.20, 126.02, 129.27, 133.56, 142.74, 144.55, 146.01 ppm. **FT-IR** (ATR): $\lambda = 1734, 1587, 1511, 1490, 1336, 1319, 1250, 1163, 1105, 944, 848, 733, 709$ cm^{-1} . Anal. calcd. for $\text{C}_{14}\text{H}_{10}\text{ClN}_3\text{O}_3$: C, 55.37; H, 3.32; N, 13.84. Found: C, 55.40; H, 3.29; N, 13.89.

General procedure for 2,4,6-Substituted-1,2,4,5-tetrazinane-3-ones 5a–5c. Chlorocarbamoyl hydrazone **4a–4c** (4 mmol) was dissolved in deoxygenated EtOH (40 mL), and Et_3N (608 μL , 4.4 mmol) and phenylhydrazine (472 μL , 4.4 mmol) were added. The mixture was heated at 65 °C for 8 hours under an argon atmosphere and cooled to 0 °C, water (4 mL) was added, and the precipitate was filtered and washed with cold EtOH (10 mL).



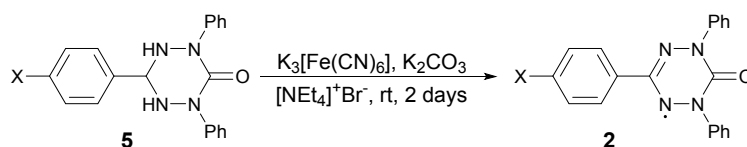
6-(4-methoxyphenyl)-2,4-diphenyl-1,2,4,5-tetrazinane-3-one 5a. According to the general procedure, the reaction of 2-(4-methoxyphenyl)- α -chloroformyl-4-phenylhydrazone **4a** (1.155 g, 4 mmol) with phenylhydrazine afforded compound **5a** as white solid (1.254 g, 87% yield), **mp** = 216.7-217.4 °C. ^1H NMR (DMSO- d_6 , 400 MHz): δ 3.72 (s, 3H), 5.31 (t, 1H, $J = 9.1$ Hz), 6.32 (d, 2H, $J = 9.1$ Hz), 6.90 (d, 2H, $J = 8.7$ Hz), 7.06 (t, 2H, $J = 7.3$ Hz), 7.32 (t, 4H, $J = 7.9$ Hz), 7.44 (d, 2H, $J = 8.6$ Hz), 7.59 (d, 4H, $J = 7.7$ Hz,) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 101 MHz): δ 55.12, 72.49, 113.66, 121.20, 123.26, 128.01, 128.20, 129.76, 142.84, 156.88, 159.12 ppm. **FT-IR** (ATR): $\lambda = 3240, 3224, 1669, 1635, 1613, 1593, 1490, 1398, 1295, 1245, 1170, 1027, 946, 693$ cm^{-1} . Anal. calcd. for $\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_2$: C, 69.98; H, 5.59; N, 15.55. Found: C, 69.96; H, 5.62; N, 15.56.

2,4,6-triphenyl-1,2,4,5-tetrazinane-3-one 5b. According to the general procedure, the reaction of 2-phenyl- α -chloroformyl-4-phenylhydrazone **4b** (1.035 g, 4 mmol) with phenylhydrazine afforded compound **5b** as white solid (1.229 g, 93% yield), **mp** = 213.9-215 °C. ^1H NMR (DMSO- d_6 , 400 MHz): δ 5.36 (t, 1H, $J = 9.0$ Hz), 6.37 (d, 2H, $J = 9.1$ Hz), 7.04 (t, 2H, $J = 7.3$ Hz), 7.26 – 7.37 (m, 7H), 7.52 (d, 2H, $J = 7.7$ Hz), 7.58 (d, 4H, $J = 7.7$ Hz) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 101 MHz): δ 72.93, 121.16, 123.30, 127.00, 128.05, 128.19, 128.34, 137.79, 142.80, 157.11 ppm. **FT-IR** (ATR): $\lambda = 3227, 3212, 3062, 3039, 1617, 1595, 1490, 1447, 1376, 1307, 1226, 1027, 909, 743, 690$ cm^{-1} . Anal. calcd. for $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}$: C, 72.71; H, 5.49; N, 16.96. Found: C, 72.69; H, 5.46; N, 16.95.

6-(4-nitrophenyl)-2,4-diphenyl-1,2,4,5-tetrazinane-3-one 5c. According to the general procedure, the reaction of 2-(4-methoxyphenyl)- α -chloroformyl-4-phenylhydrazone **4c** (1.215 g,

4 mmol) with phenylhydrazine afforded compound **5c** as yellow solid (1.336 g, 89% yield), **mp** = 206.7-208 °C. **¹H NMR** (DMSO-*d*₆, 400 MHz): δ 5.58 (t, 1H, *J* = 8.3 Hz), 6.61 (d, 2H, *J* = 8.4 Hz), 7.08 (t, 2H, *J* = 7.2 Hz), 7.31 – 7.36 (m, 4H), 7.60 (d, 4H, *J* = 7.4 Hz), 7.80 (d, 2H, *J* = 8.4 Hz), 8.23 (d, 2H, *J* = 8.5 Hz) ppm. **¹³C{¹H} NMR** (DMSO-*d*₆, 101 MHz): δ 72.22, 121.11, 123.54, 128.17, 128.53, 130.12, 142.57, 145.23, 147.43, 157.26 ppm. **FT-IR** (ATR): λ = 3220, 1647, 1595, 1582, 1521, 1490, 1477, 1371, 1338, 1308, 1107, 923, 911, 853, 745, 691 cm⁻¹. Anal. calcd. for C₂₀H₁₇N₅O₃: C, 63.99; H, 4.56; N, 18.66. Found: C, 64.01; H, 4.60; N, 18.61.

General procedure for preparation of 1,3,5-substituted-6-oxoverdazyl radicals 2a–2c. A solution of K₂CO₃ (5.52 g, 40 mmol) and K₃[Fe(CN)₆] (5.926 g, 18 mmol) in 40 mL of water was added to a solution (100 mL) of tetrazinan-3-ones **5a–5c** (4 mmol) and Et₄NBr (84 mg, 0.4 mmol) in CH₂Cl₂ (100 mL). Radicals **2a–2c** were extracted with CH₂Cl₂ (2 × 60 mL), washed with water, dried over Na₂SO₄, and purified by flash-chromatography (hexane : CH₂Cl₂ = 2 : 1). Pure radicals **5a–5c** were obtained after evaporation of the eluate *in vacuo*.



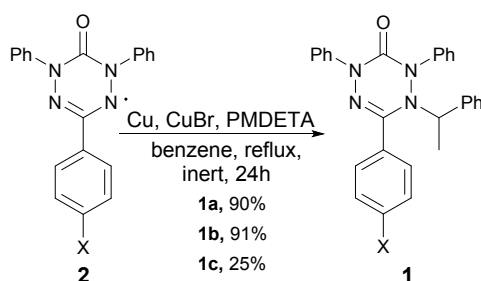
1,5-diphenyl-3-(4-methoxyphenyl)-6-oxoverdazyl radical 2a. Oxidation of 6-(4-methoxyphenyl)-2,4-diphenyl-1,2,4,5-tetrazinan-3-one **5a** (1.442 g, 4 mmol) according to general procedure afforded compound **2a** as deep-violet solid (1.043 g, 73%), **mp** = 155.3-156.7 °C. **UV-vis** (CH₂Cl₂): λ_{max} (log ε) = 421 (3.02), 573 (3.22) nm. **FT-IR** (ATR): λ = 3063, 2967, 2840, 1690, 1609, 1489, 1408, 1357, 1301, 1249, 1166, 1123, 1027, 834, 766, 691 cm⁻¹. **ESR** (toluene, 9.5 GHz): nonet, a_N = 6.45 G (N₂, N₄), a_N = 4.45 G (N₁, N₅). Anal. calcd. for C₂₁H₁₇N₄O₂: C, 70.58; H, 4.79; N, 15.68. Found: C, 70.56; H, 4.77; N, 15.73.

1,3,5-triphenyl-6-oxoverdazyl radical 2b. Oxidation of 2,4,6-triphenyl-1,2,4,5-tetrazinan-3-one **5b** (1.322 g, 4 mmol) according to general procedure afforded compound **2b** as deep-violet solid (1.231 g, 94%), **mp** = 209.6-210 °C. **UV-vis** (CH₂Cl₂): λ_{max} (log ε) = 415 (3.03), 530 (3.29), 560 (3.30) nm. **FT-IR** (ATR): λ = 3063, 3023, 1692, 1587, 1483, 1401, 1364, 1308, 1237, 1170, 1025, 752, 685 cm⁻¹. **ESR** (toluene, 9.5 GHz): nonet, a_N = 6.42 G (N₂, N₄), a_N = 4.48 G (N₁, N₅). Anal. calcd. for C₂₀H₁₅N₄O: C, 73.38; H, 4.62; N, 17.11. Found: C, 73.31; H, 4.61; N, 17.06.

1,5-diphenyl-3-(4-nitrophenyl)-6-oxoverdazyl radical 2c. Oxidation of 6-(4-nitrophenyl)-2,4-diphenyl-1,2,4,5-tetrazinan-3-one **5c** (1.501 g, 4 mmol) according to general procedure afforded compound **2c** as brown-violet solid (1.400 g, 94%), **mp** = 259-260.1 °C. **UV-vis** (CH₂Cl₂): λ_{max} (log ε) = 453 (3.25), 543 (3.16) nm. **FT-IR** (ATR): λ = 3070, 3037, 1696, 1601, 1519,

1487, 1457, 1346, 1312, 1241, 1102, 1014, 854, 743, 673 cm^{-1} . **ESR** (toluene, 9.5 GHz): nonet, $a_{\text{N}} = 6.33$ G (N2, N4), $a_{\text{N}} = 4.58$ G (N1, N5). Anal. calcd. for $\text{C}_{20}\text{H}_{14}\text{N}_5\text{O}_3$: C, 64.51; H, 3.79; N, 18.81. Found: C, 64.52; H, 3.81; N, 18.77.

General procedure for 2,4,6-substituted-5-(1-phenylethyl)-4,5-dihydro-1,2,4,5-tetrazin-3(2H)-ones 1a-1c. To a solution of Cu (153 mg, 2.4 mmol), CuBr (172 mg, 1.2 mmol), PMDETA (N,N,N',N'',N''-pentamethyldiethylenetriamine) (251 μL , 1.2 mmol) in degassed benzene (15 mL), the mixture of verdazyl radical **2** (2 mmol) and 1-bromoethylbenzene (328 μL , 2.4 mmol) in degassed benzene (15 mL) was added. The reaction solution was degassed again, put under argon and heated to 80 $^{\circ}\text{C}$ until full conversion of the starting material (monitored by TLC). The mixture was cooled to room temperature, filtered over celite. Removal of the benzene *in vacuo* provided the crude product, which was purified by FC (hexane : EtOAc = 10 : 1) to afford alkylated verdazyl **1**.



6-(4-methoxyphenyl)-2,4-diphenyl-5-(1-phenylethyl)-4,5-dihydro-1,2,4,5-tetrazin-3(2H)-

one 1a. According to the general procedure, the reaction of 1,5-diphenyl-3-(4-methoxyphenyl)-6-oxoverdazyl radical **2a** (715 mg, 2 mmol) with 1-bromoethylbenzene afforded compound **1a** as yellow-white solid (832 mg, 90% yield), **mp** = 119.3-120.8 $^{\circ}\text{C}$. **^1H NMR** (CDCl_3 , 400 MHz): two rotamers are visible in a ratio of 0.84 : 0.16, δ 1.53 (d, 3H, $J = 7.2$ Hz, major), 1.61 (d, 3H, $J = 7.1$ Hz, minor), 3.92 (s, 3H, minor), 3.95 (s, 3H, major), 4.66 (q, 1H, $J = 7.1$ Hz, major), 4.93 (q, 1H, $J = 6.5$ Hz, minor), 6.99 (d, 1H, $J = 7.6$ Hz, major), 7.03 (d, 1H, $J = 8.7$ Hz, minor), 7.08 – 7.30 (m, 6H), 7.31 – 7.48 (m, 7H), 7.67 (d, 2H, $J = 8.1$ Hz, minor), 7.91 (d, 2H, $J = 7.9$ Hz, major), 7.98 (d, 2H, $J = 8.6$ Hz, minor), 8.05 (d, 2H, $J = 8.8$ Hz, major) ppm. **$^{13}\text{C}\{^1\text{H}\}$ NMR** (CDCl_3 , 101 MHz): δ 18.26, 55.62, 63.31, 114.72, 121.40, 123.37, 123.63, 124.85, 125.71, 127.80, 128.04, 128.69, 128.81, 129.33, 129.83, 138.81, 140.17, 144.83, 150.13, 153.09, 162.09 ppm. **FT-IR** (ATR): $\lambda = 2978, 2929, 1740, 1684, 1591, 1493, 1454, 1330, 1248, 1166, 1032, 834, 752, 693$ cm^{-1} . **UV-vis** (CH_2Cl_2): λ_{max} (log ϵ) = 329 (3.59) nm. **HRMS** (ESI): $m/z = 463.2129$ calcd. for $[\text{M}+\text{H}]^+$, found: 463.2121. Anal. calcd. for $\text{C}_{29}\text{H}_{26}\text{N}_4\text{O}_2$: C, 75.30; H, 5.67; N, 12.11. Found: C, 75.31; H, 5.69; N, 12.09.

2,4,6-triphenyl-5-(1-phenylethyl)-4,5-dihydro-1,2,4,5-tetrazin-3(2H)-one 1b. According to the general procedure, the reaction of 1,3,5-triphenyl-6-oxoverdazyl radical **2b** (655 mg, 2 mmol) with 1-bromoethylbenzene afforded compound **1b** as white solid (787 mg, 91% yield),

mp = 145.4 - 147.1 °C. **¹H NMR** (CDCl₃, 400 MHz): two rotamers are visible in a ratio of 0.84 : 0.16, δ 1.51 (d, 3H, *J* = 7.2 Hz, major), 1.57 (d, 3H, *J* = 7.1 Hz, minor), 4.61 (q, 1H, *J* = 7.1 Hz), 6.95 – 7.10 (m, 2H), 7.11 – 7.25 (m, 4H), 7.29 – 7.42 (m, 7H), 7.45 – 7.58 (m, 3H), 7.67 (d, 2H, *J* = 7.9 Hz, minor), 7.89 (d, 2H, *J* = 7.8 Hz, major), 8.00 – 8.09 (m, 2H) ppm. **¹³C{¹H} NMR** (CDCl₃, 101 MHz): δ 18.14, 63.40, 121.52, 123.70, 124.97, 125.86, 127.70, 127.81, 128.09, 128.73, 128.78, 128.85, 129.31, 131.15, 131.19, 138.74, 140.11, 144.75, 149.90, 152.97 ppm. **FT-IR** (ATR): λ = 3063, 3037, 2929, 1692, 1591, 1483, 1454, 1330, 1300, 1166, 1129, 1095, 1028, 758, 736, 691 cm⁻¹. **UV-vis** (CH₂Cl₂): λ_{max} (log ε) = 331 (3.51) nm. **HRMS** (ESI): *m/z* = 433.2023 calcd. for [M+H]⁺, found: 433.2016. Anal. calcd. for C₂₈H₂₄N₄O: C, 77.75; H, 5.59; N, 12.95. Found: C, 77.72; H, 5.58; N, 12.93.

6-(4-nitrophenyl)-2,4-diphenyl-5-(1-phenylethyl)-4,5-dihydro-1,2,4,5-tetrazin-3(2H)-one 1c. According to the general procedure, the reaction of 1,5-diphenyl-3-(4-nitrophenyl)-6-oxoverdazyl radical **2c** (744 mg, 2 mmol) with 1-bromoethylbenzene afforded compound **1c** as yellow solid (763 mg, 80% yield). Purification of this compound was carried out *via* washing of crude products with hexane (20 mL). **mp** = 215-216.2 °C °C. **¹H NMR** (CDCl₃, 400 MHz): two rotamers are visible in a ratio of 0.68 : 0.12, δ 1.44 (d, 3H, *J* = 7.2 Hz, major), 1.48 (d, 3H, *J* = 7.2 Hz, minor), 4.41 – 4.48 (m, 1H, major), 4.50 – 4.54 (m, 1H, minor), 6.84 (d, 2H, *J* = 8.0 Hz, major), 6.98 - 7.43 (m, 12H), 7.64 (d, 2H, *J* = 7.6 Hz, minor), 7.74 (d, 2H, *J* = 7.6 Hz, major), 7.98 (d, 2H, *J* = 7.6 Hz, minor), 8.13 (d, 2H, *J* = 8.8 Hz), 8.31 (d, 2H, *J* = 8.4 Hz, major) ppm. **¹³C{¹H} NMR** (DMSO-d₆, 101 MHz): δ 18.20, 64.04, 121.61, 123.85, 124.54, 125.43, 126.42, 127.79, 128.20, 128.27, 128.90, 129.03, 129.12, 137.47, 138.23, 139.74, 144.13, 147.06, 149.19, 152.37 ppm. **FT-IR** (ATR): λ = 1744, 1684, 1595, 1513, 1483, 1453, 1342, 861, 693 cm⁻¹. **UV-vis** (CH₂Cl₂): λ_{max} (log ε) = 323 (3.61), 366 (4.00), 388 (3.59) nm. **HRMS** (ESI): *m/z* = 478.1874 calcd. for [M+H]⁺, found: 478.1842. Anal. calcd. for C₂₈H₂₃N₅O₃: C, 70.43; H, 4.86; N, 14.67. Found: C, 70.44; H, 4.68; N, 14.65.

Section S2. NMR spectra

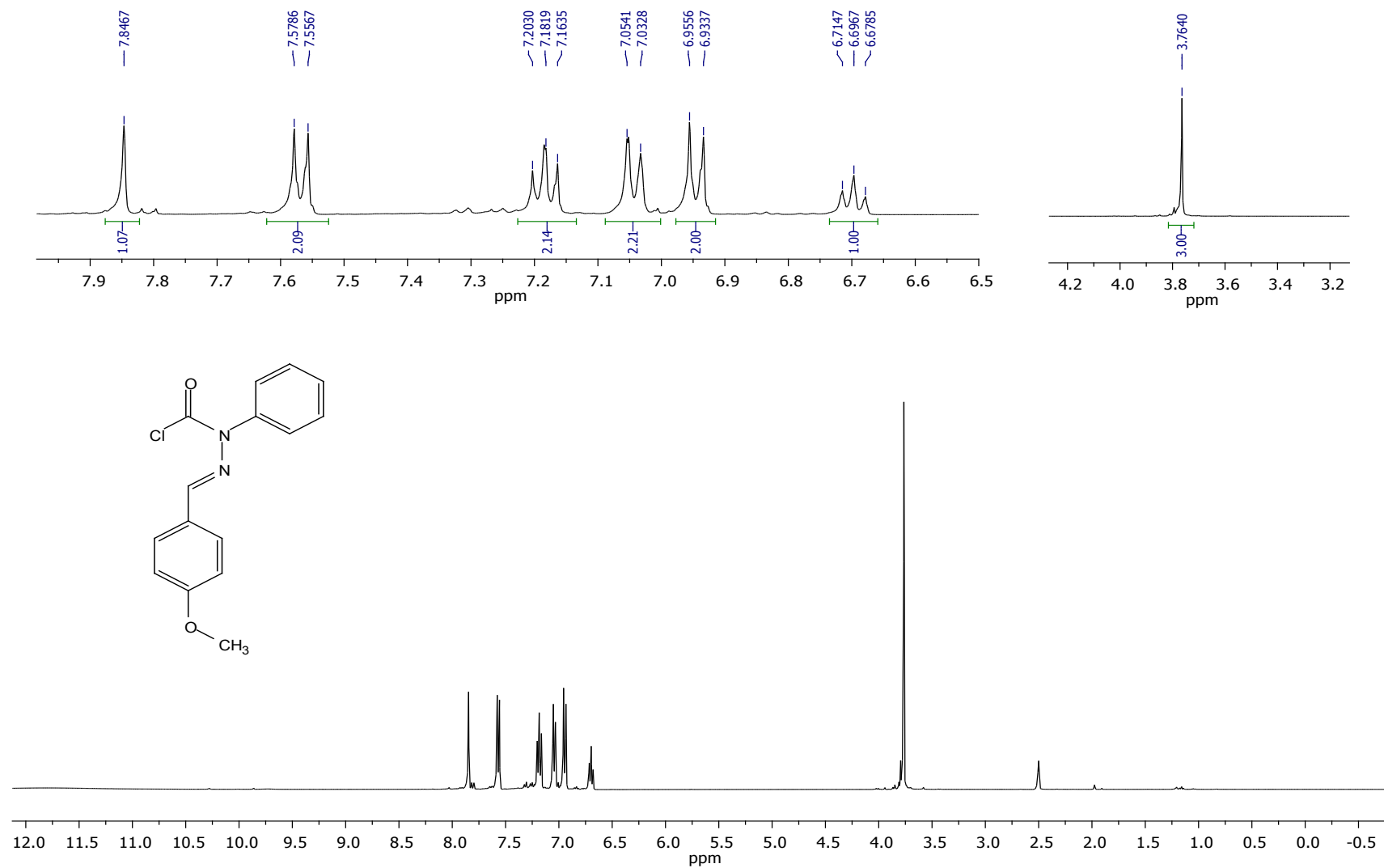


Fig. S2.1. ¹H NMR spectrum (DMSO-d₆) of 2-(4-methoxyphenyl)- α -chloroformyl-4-phenylhydrazone **4a**.

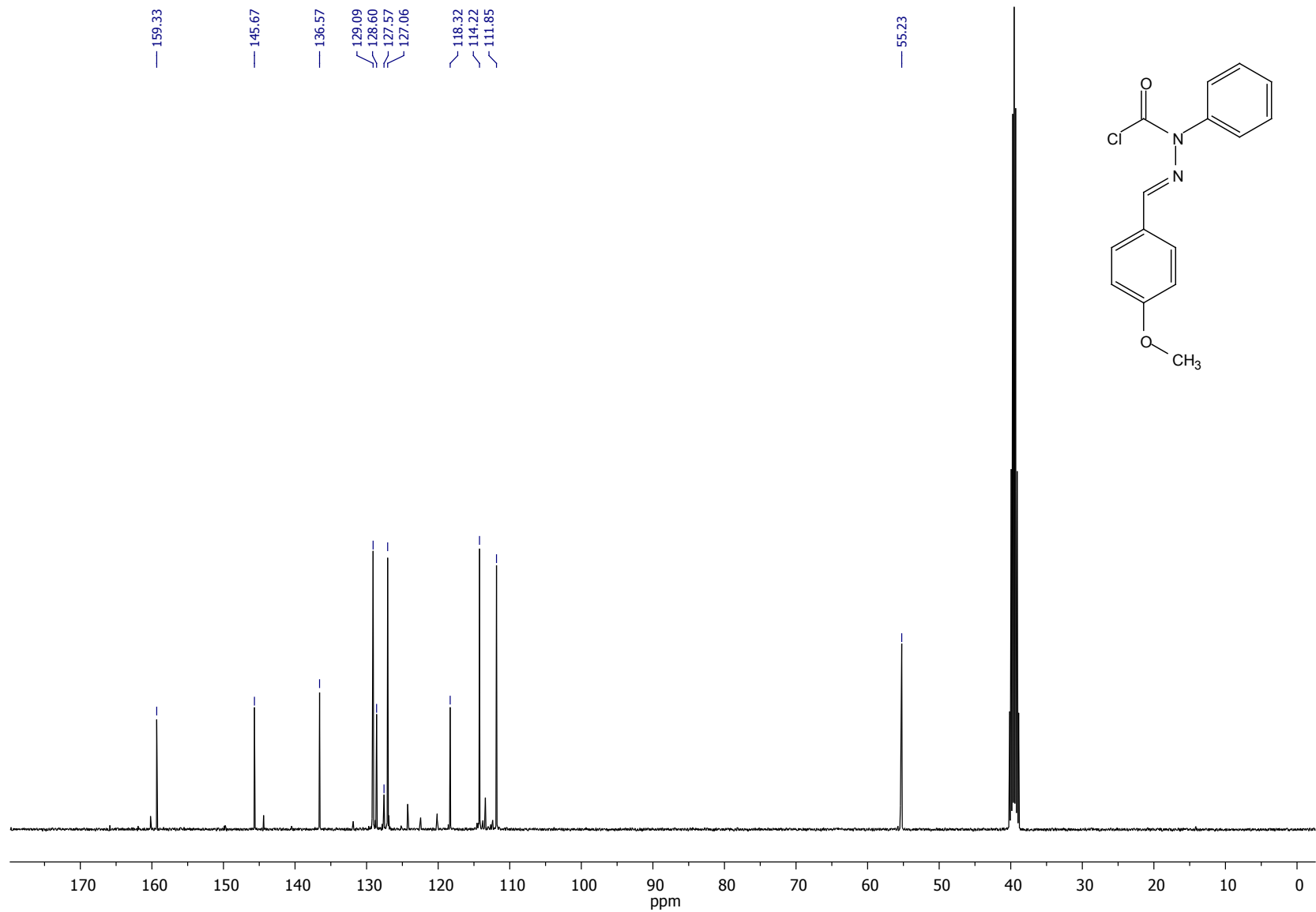


Fig. S2.2. ^{13}C NMR spectrum (DMSO- d_6) of 2-(4-methoxyphenyl)- α -chloroformyl-4-phenylhydrazone **4a**.

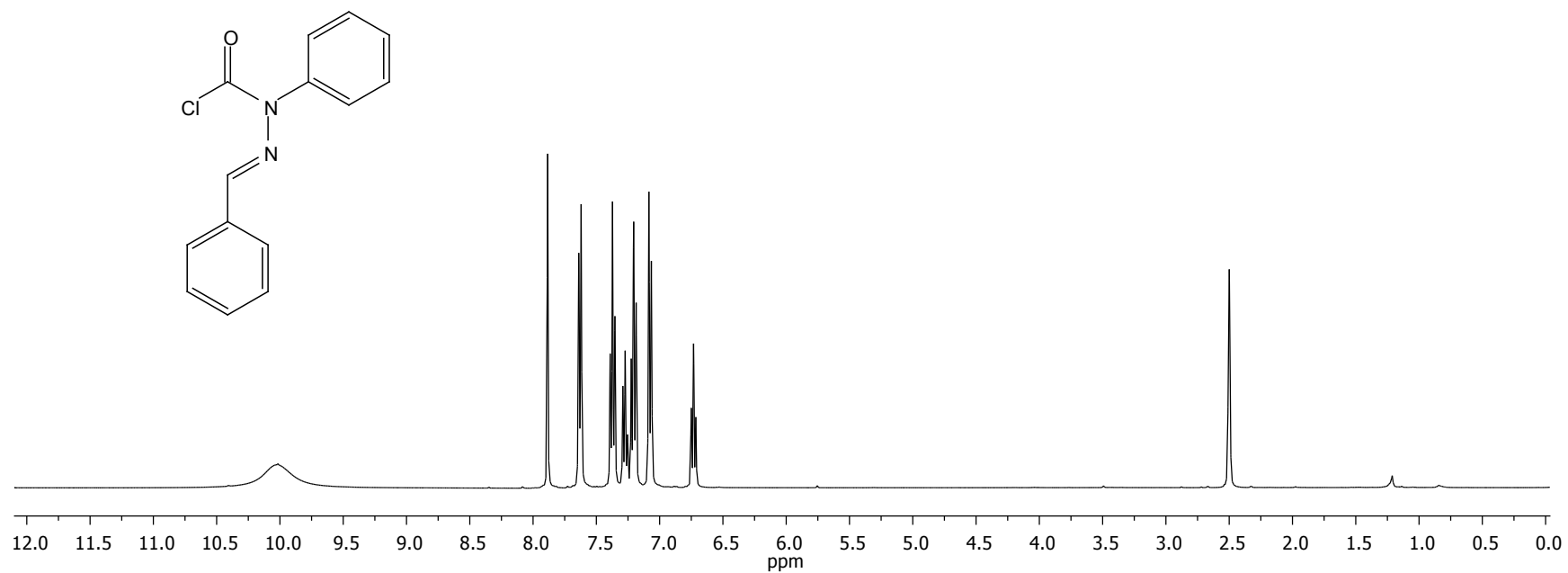
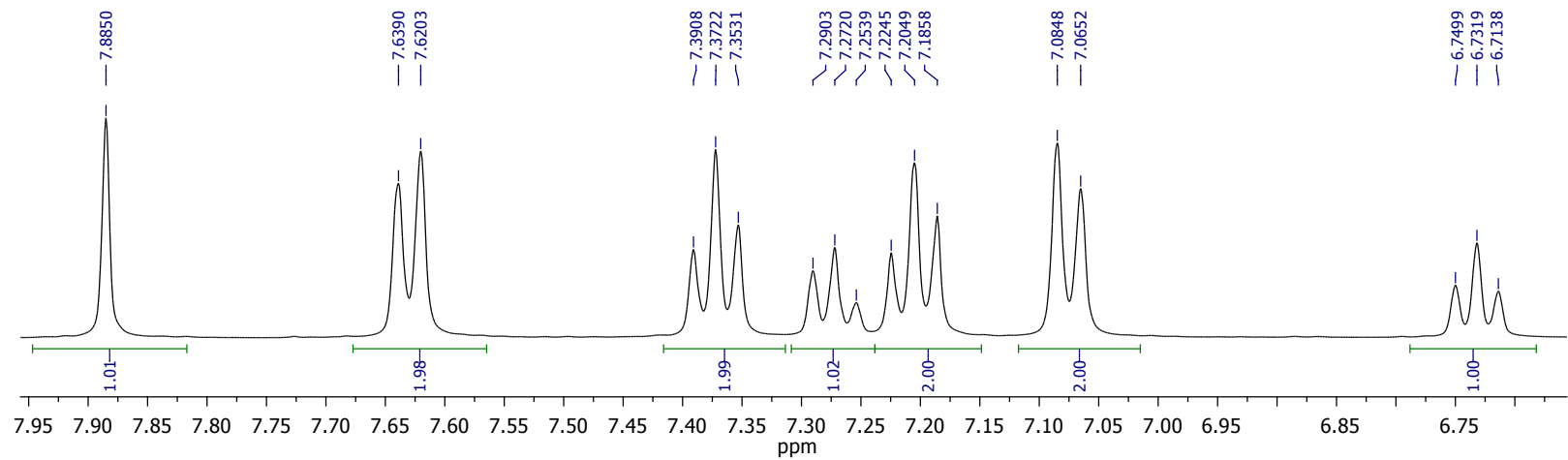


Fig. S2.3. ^1H NMR spectrum (DMSO-d_6) of 2-phenyl- α -chloroformyl-4-phenylhydrazone **4b**.

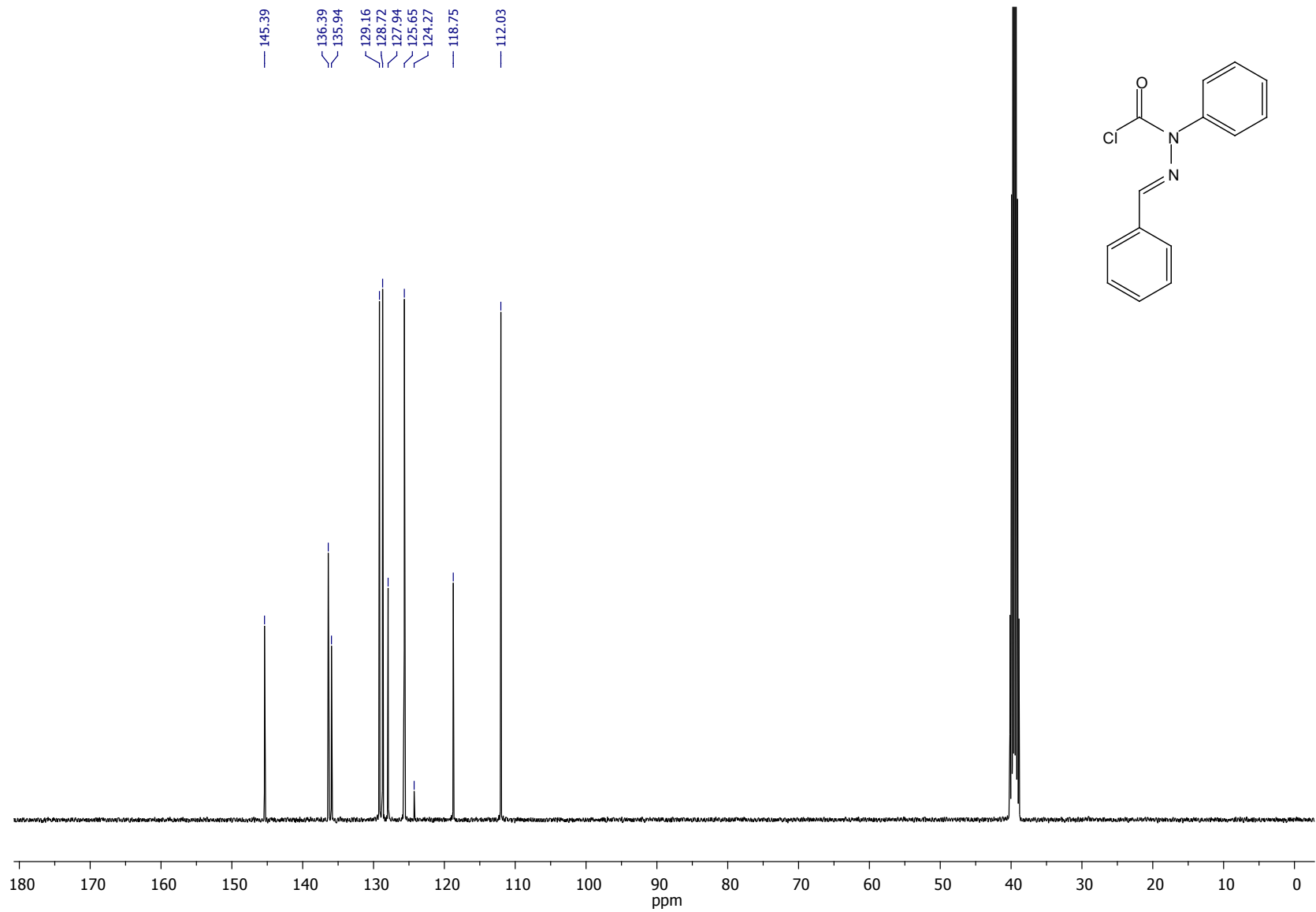


Fig. S2.4. ^{13}C NMR spectrum (DMSO-d_6) of 2-phenyl- α -chloroformyl-4-phenylhydrazone **4b**.

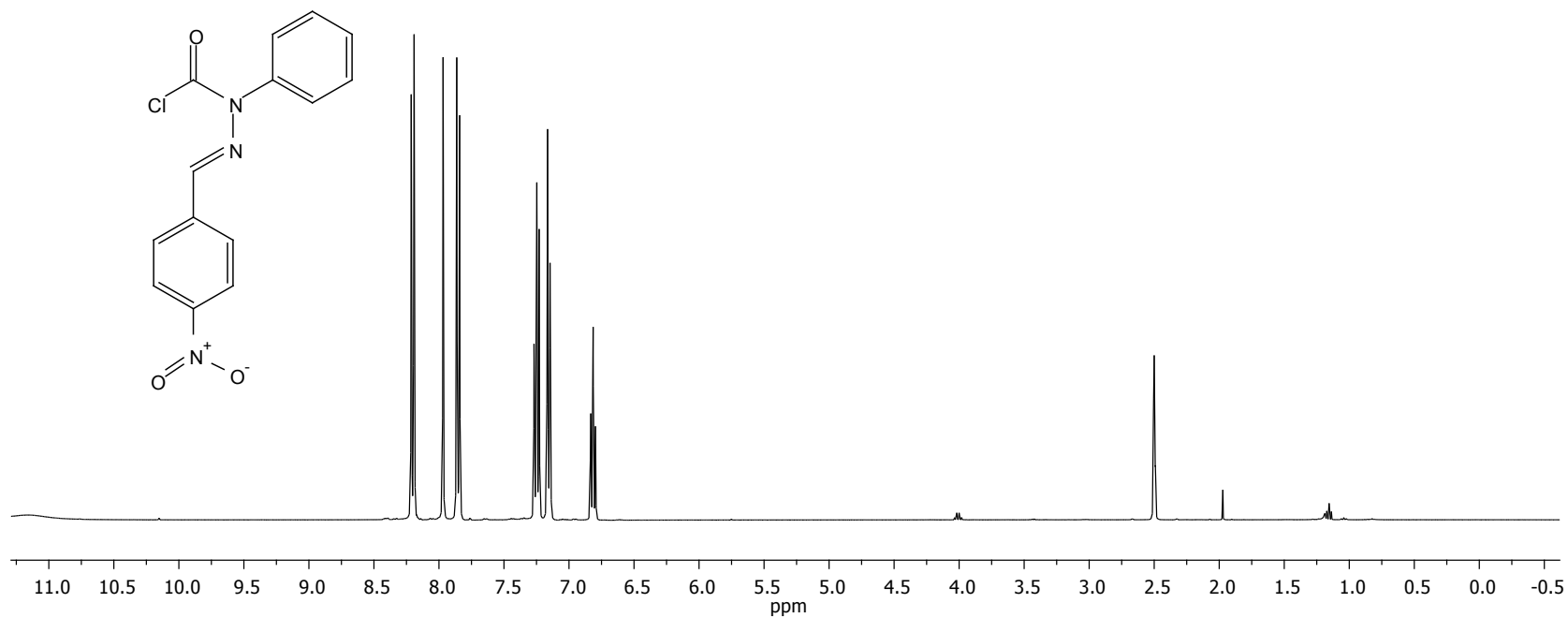
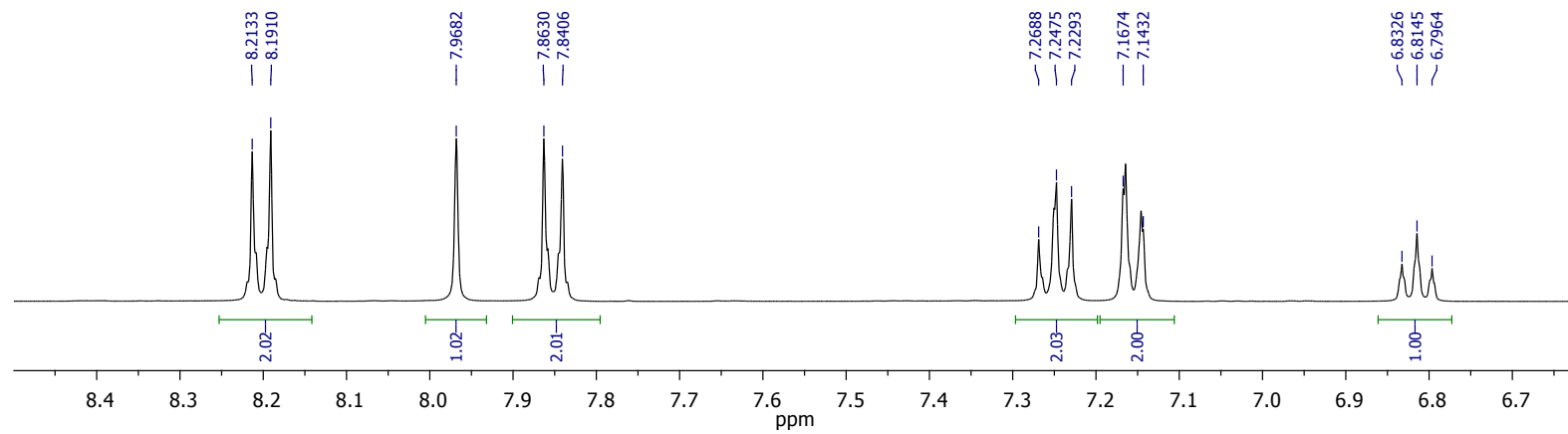


Fig. S2.5. ^1H NMR spectrum (DMSO-d_6) of 2-(4-nitrophenyl)- α -chloroformyl-4-phenylhydrazone **4c**.

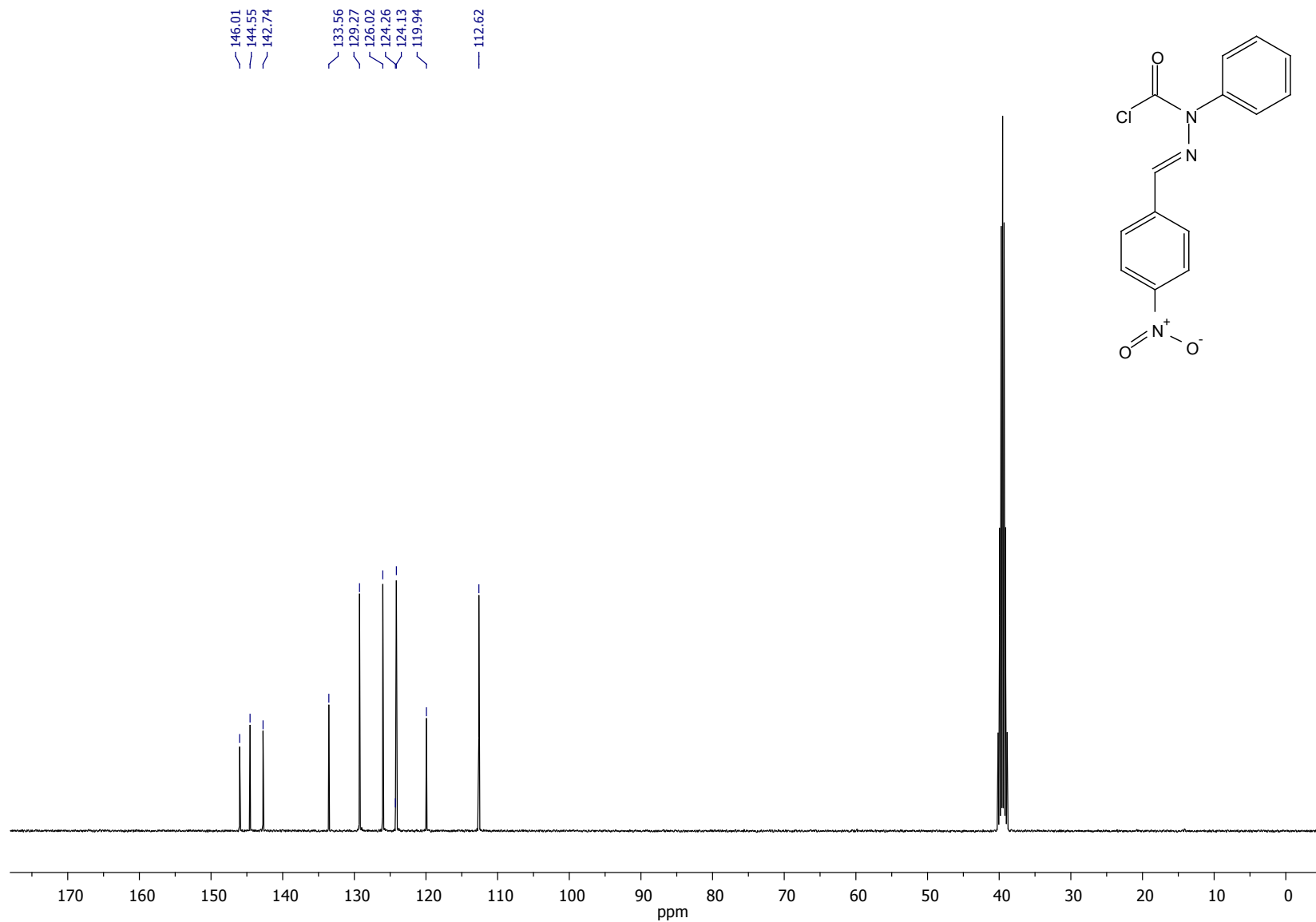


Fig. S2.6. ^{13}C NMR spectrum (DMSO-d_6) of 2-(4-nitrophenyl)- α -chloroformyl-4-phenylhydrazone **4c**.

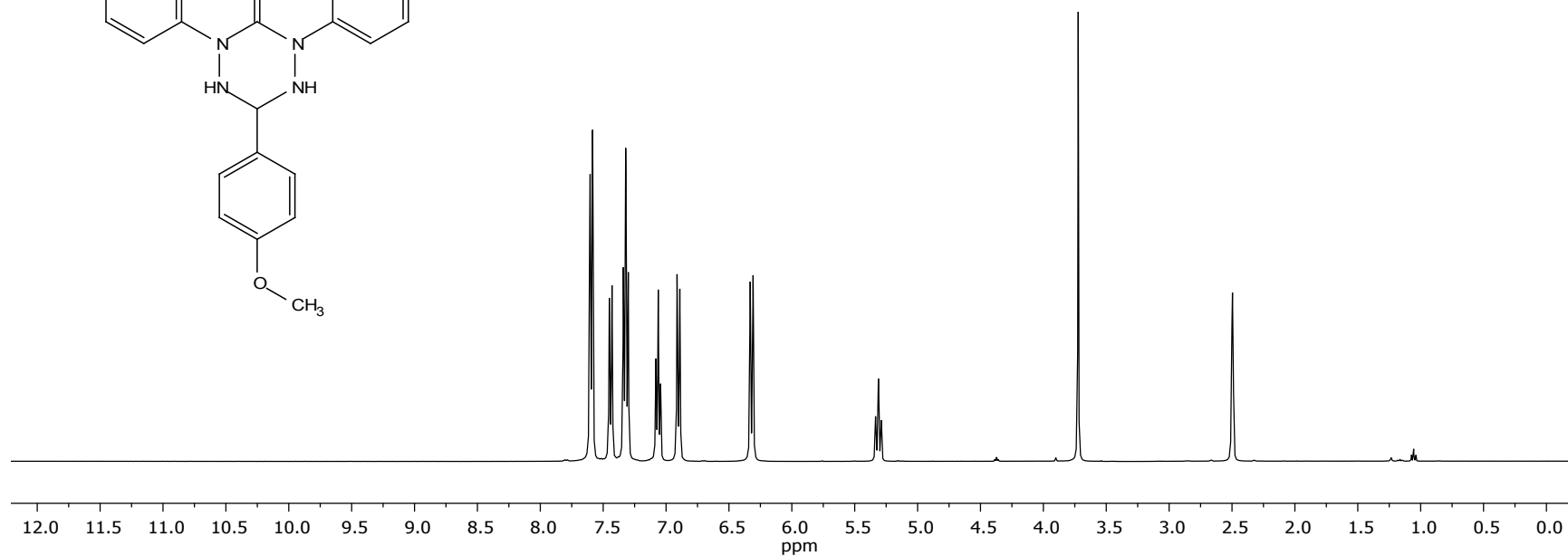
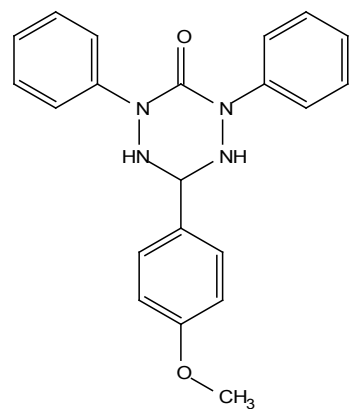
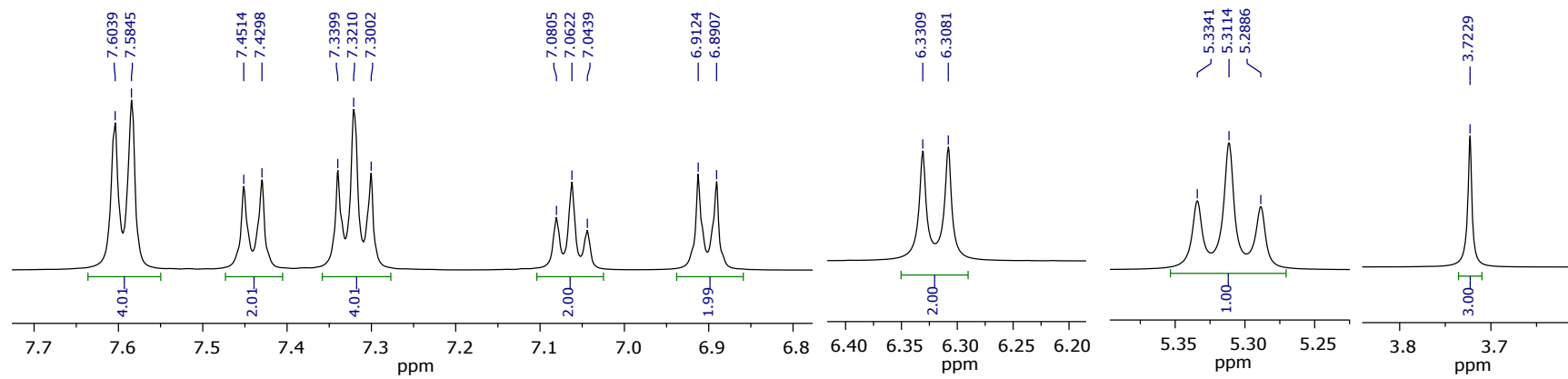


Fig. S2.7. ¹H NMR spectrum (DMSO-d₆) of 6-(4-methoxyphenyl)-2,4-diphenyl-1,2,4,5-tetrazinan-3-one **5a**.

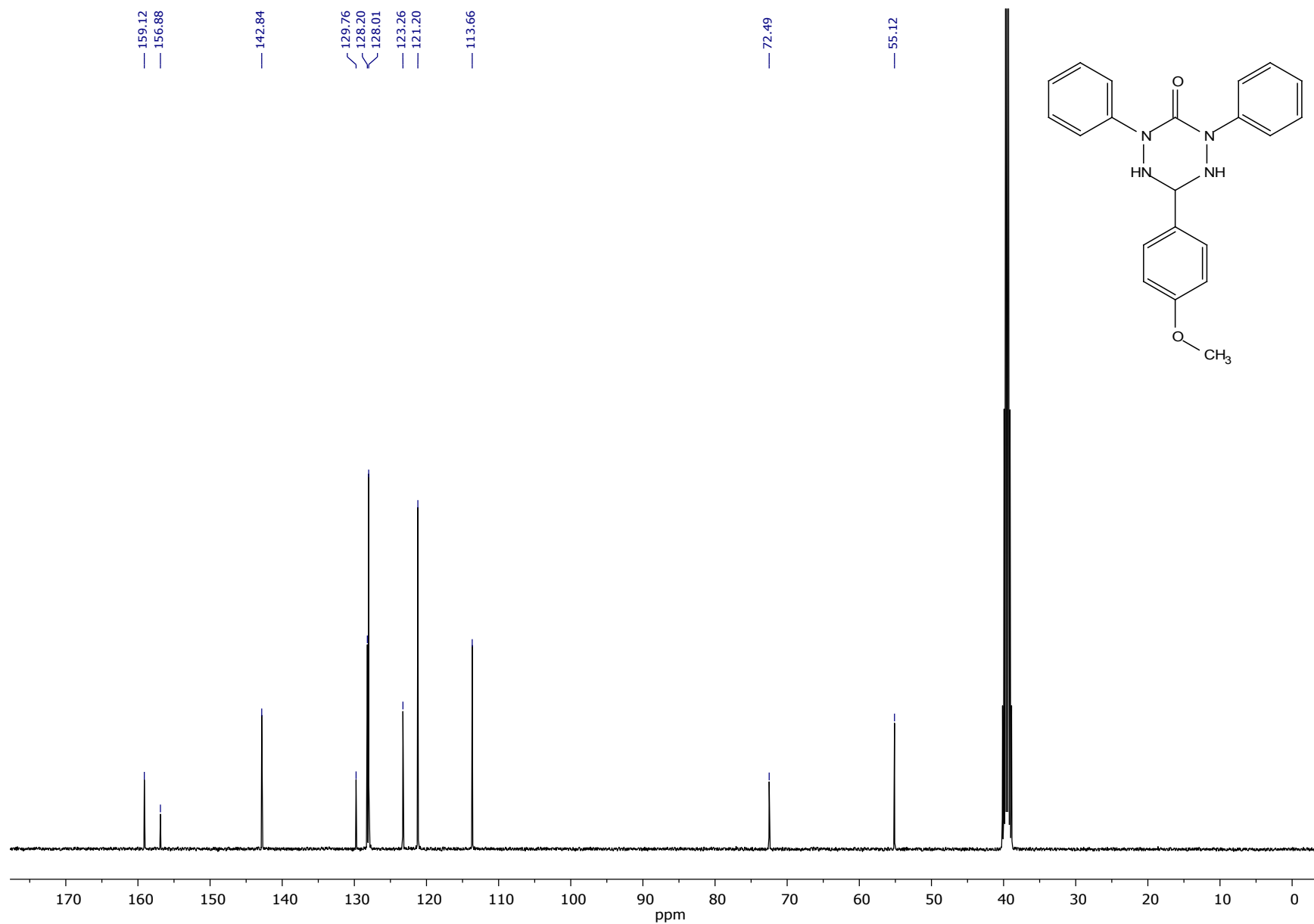


Fig. S2.8. ^{13}C NMR spectrum (DMSO-d_6) of 6-(4-methoxyphenyl)-2,4-diphenyl-1,2,4,5-tetrazinan-3-one **5a**.

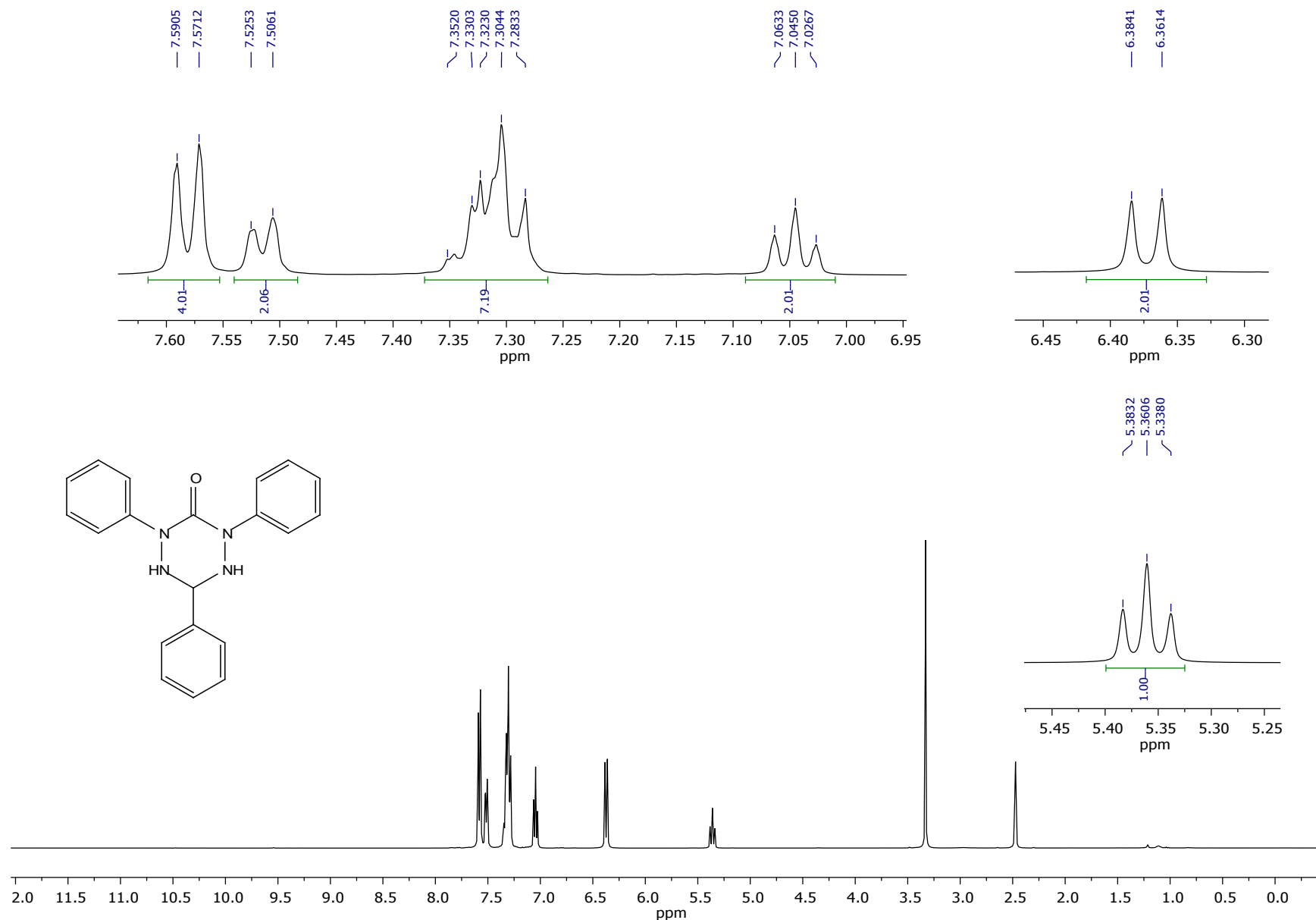


Fig. S2.9. ¹H NMR spectrum (DMSO-d₆) of 2,4,6-triphenyl-1,2,4,5-tetrazinan-3-one **5b**.

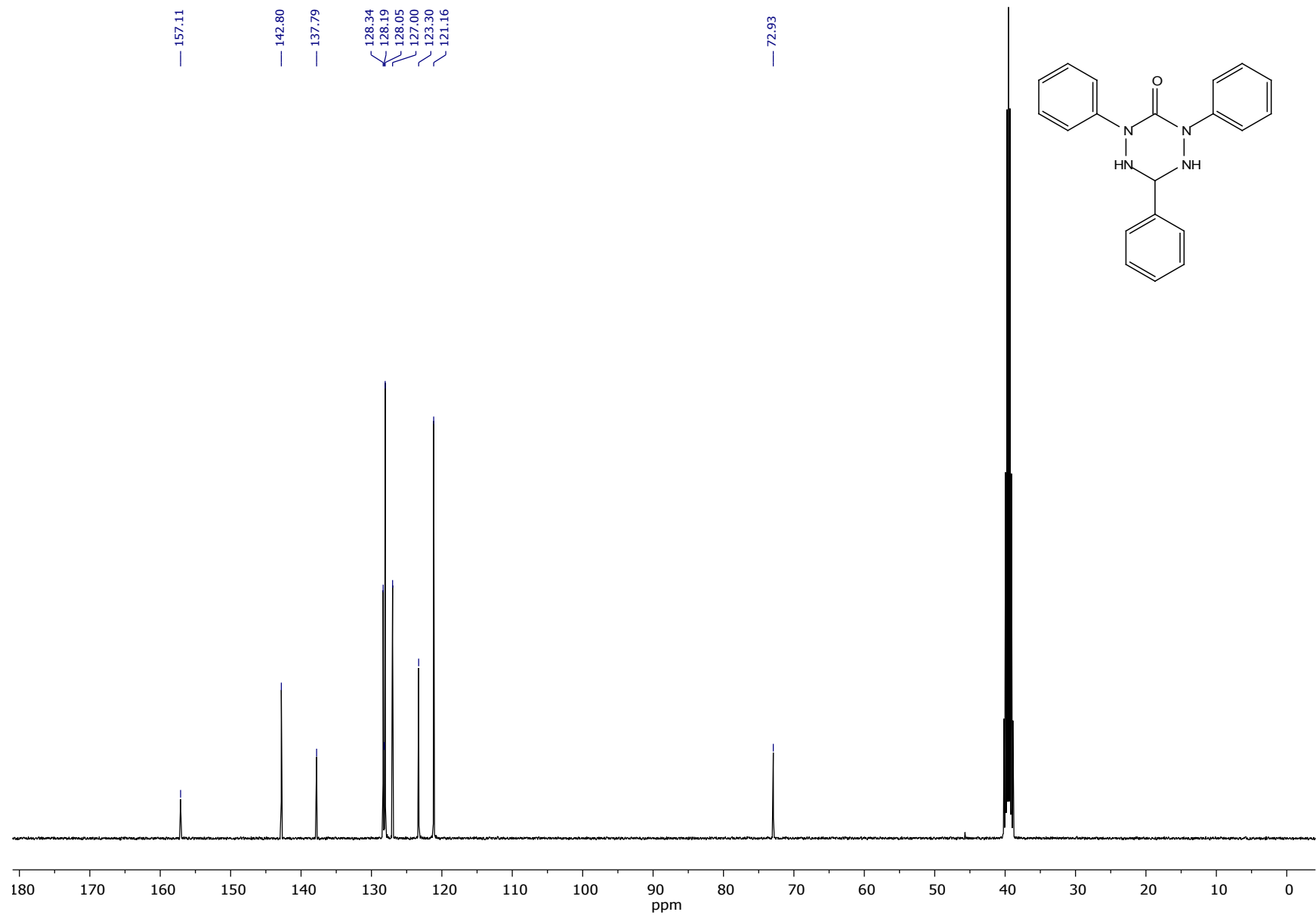


Fig. S2.10. ^{13}C NMR spectrum (DMSO-d_6) of 2,4,6-triphenyl-1,2,4,5-tetrazin-3-one **5b**.

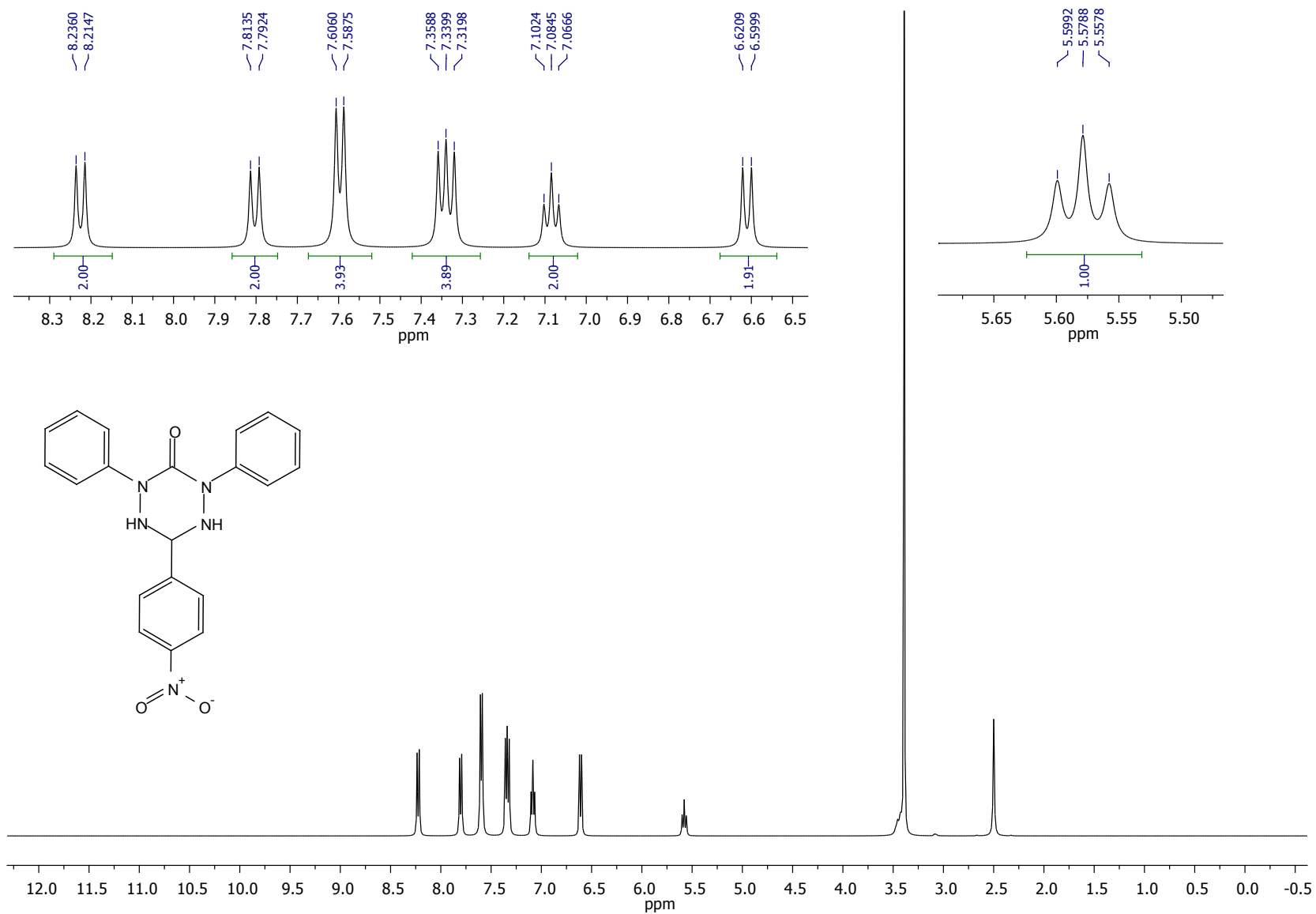


Fig. S2.11 ¹H NMR spectrum (DMSO-d₆) of 6-(4-nitrophenyl)-2,4-diphenyl-1,2,4,5-tetrazin-3-one **5c**.

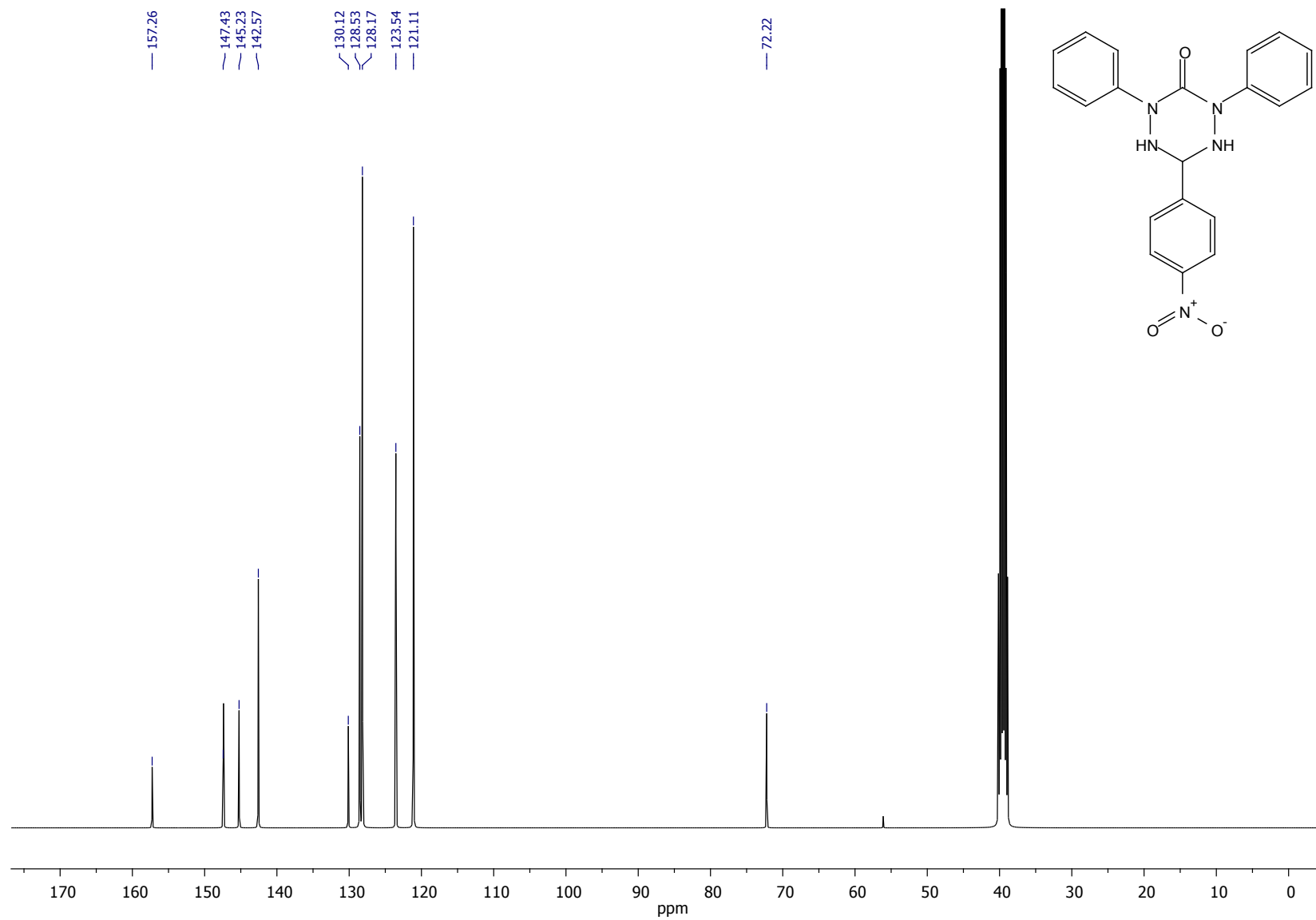


Fig. S2.12. ^{13}C NMR spectrum (DMSO-d_6) of 6-(4-nitrophenyl)-2,4-diphenyl-1,2,4,5-tetrazinan-3-one **5c**.

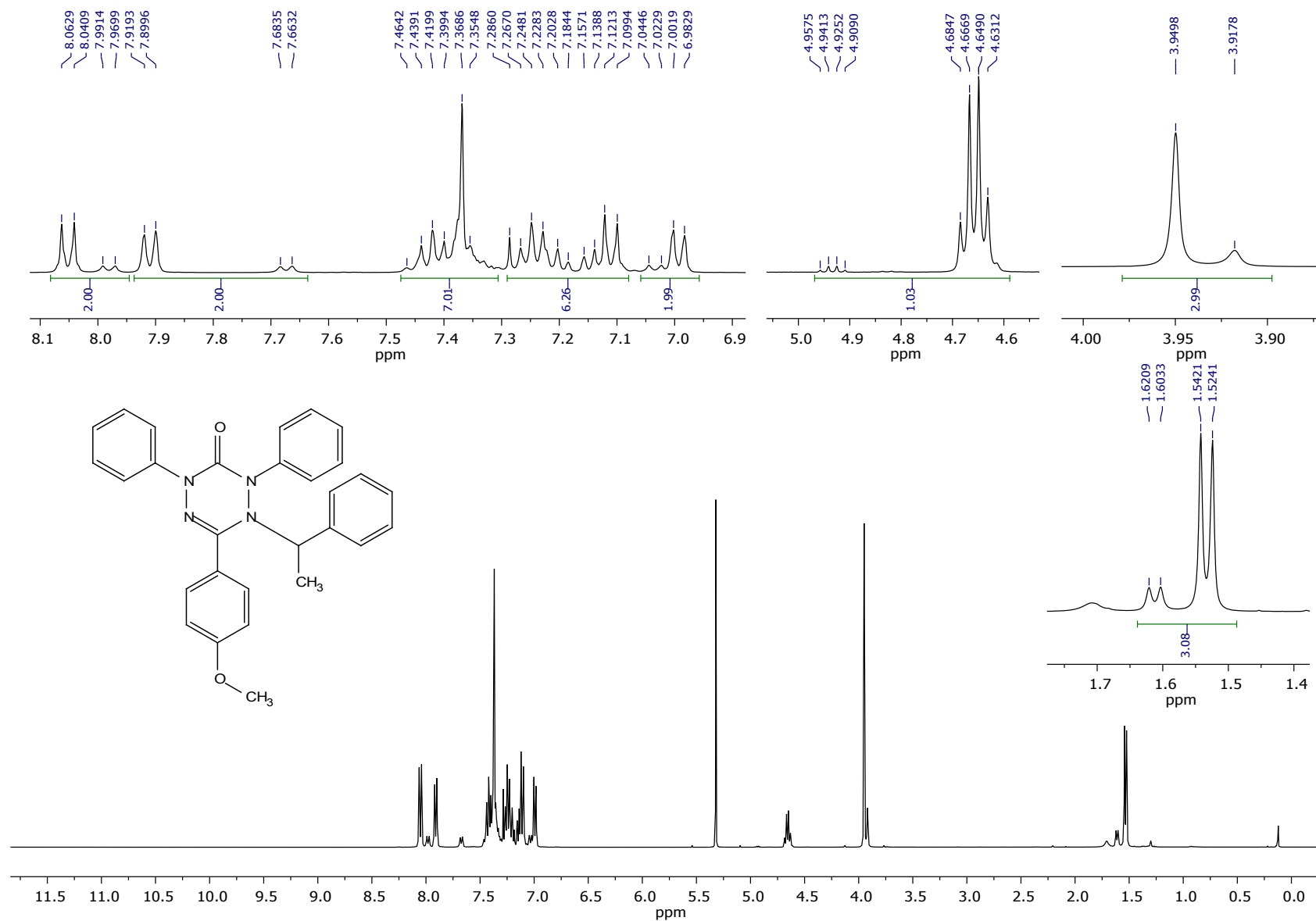


Fig. S2.13. ¹H NMR spectrum (DMSO-d₆) of 6-(4-methoxyphenyl)-2,4-diphenyl-5-(1-phenylethyl)-4,5-dihydro-1,2,4,5-tetrazin-3(2H)-one **1a**.

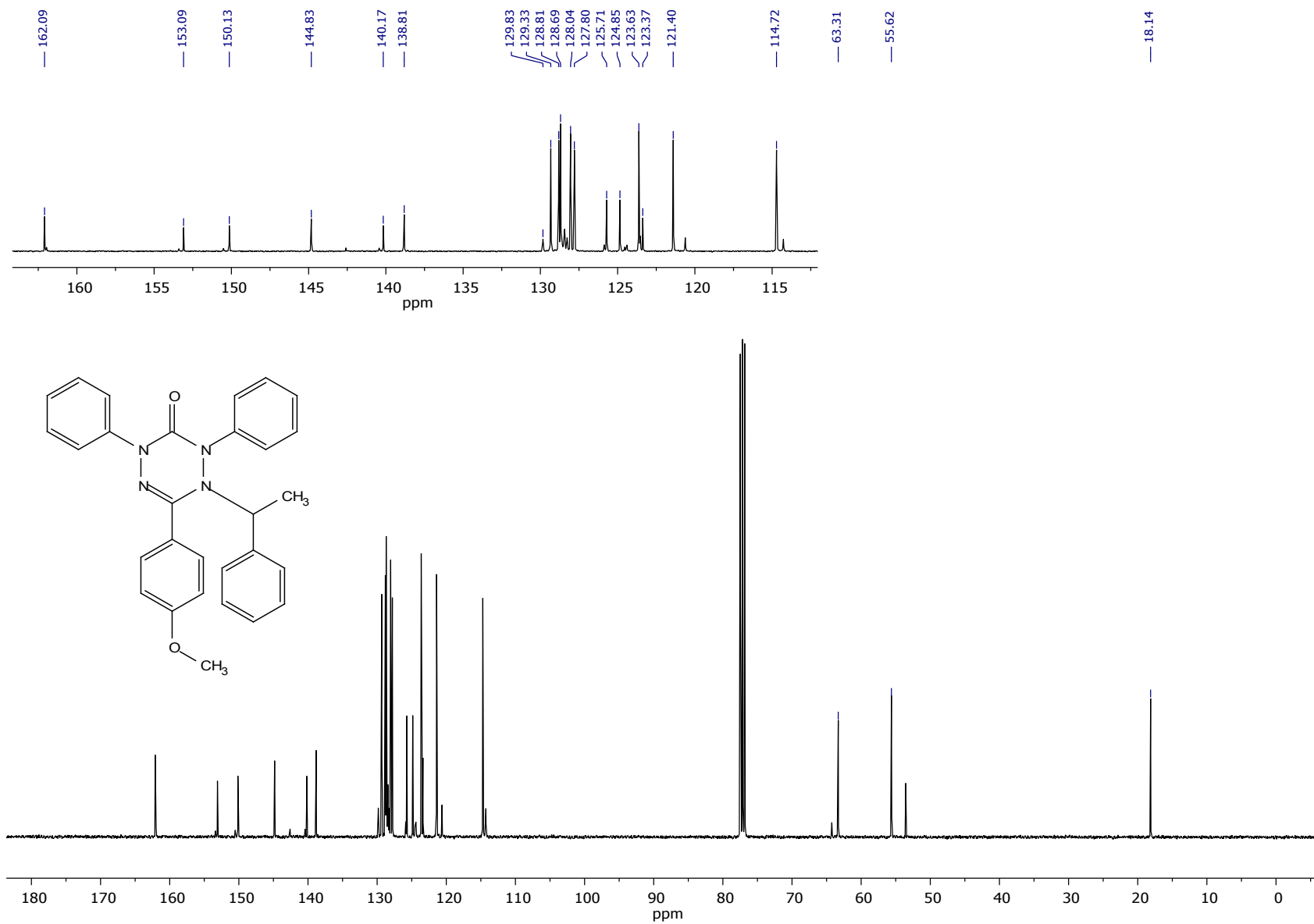


Fig. S2.14. ¹³C NMR spectrum (DMSO-d₆) of 6-(4-methoxyphenyl)-2,4-diphenyl-5-(1-phenylethyl)-4,5-dihydro-1,2,4,5-tetrazin-3(2H)-one **1a**.

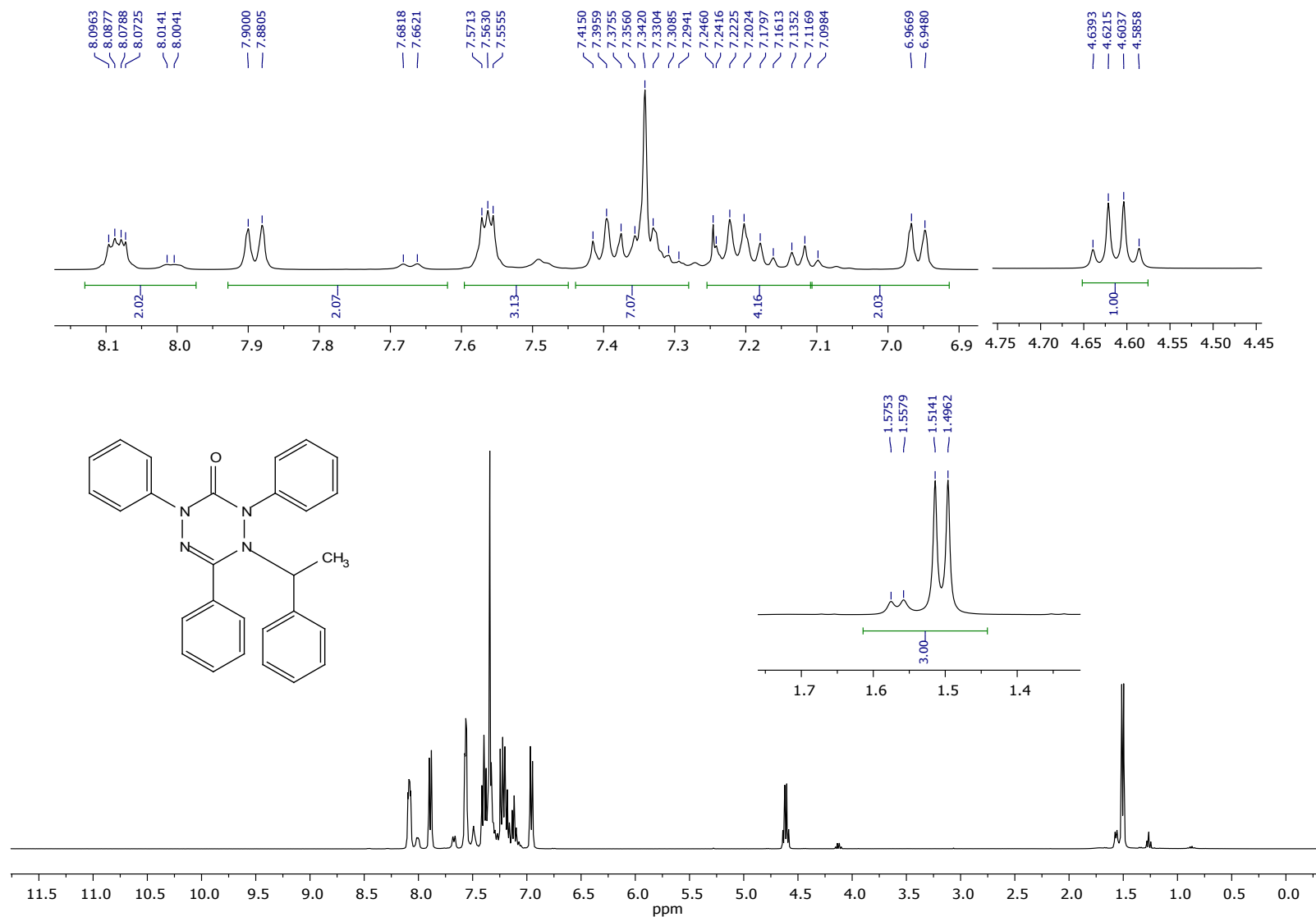


Fig. S2.15. ¹H NMR spectrum (DMSO-d₆) of 2,4,6-triphenyl-5-(1-phenylethyl)-4,5-dihydro-1,2,4,5-tetrazin-3(2H)-one **1b**.

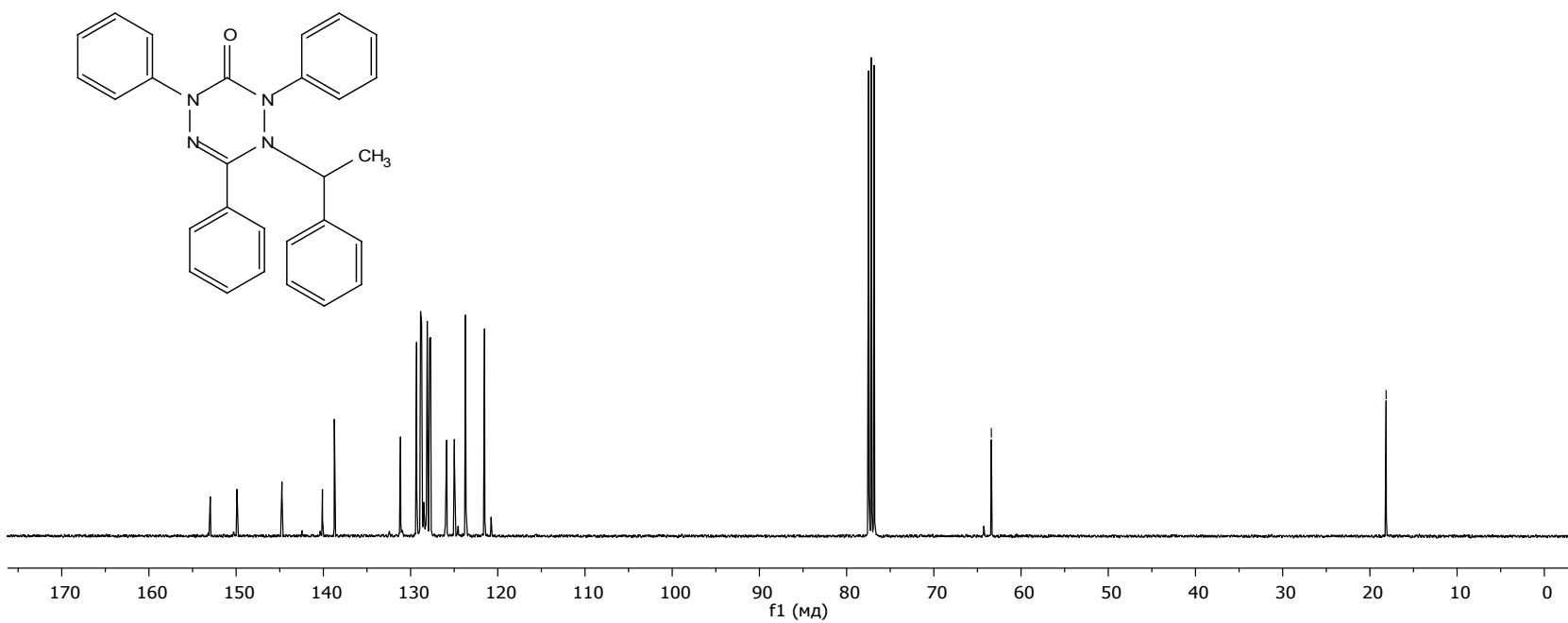
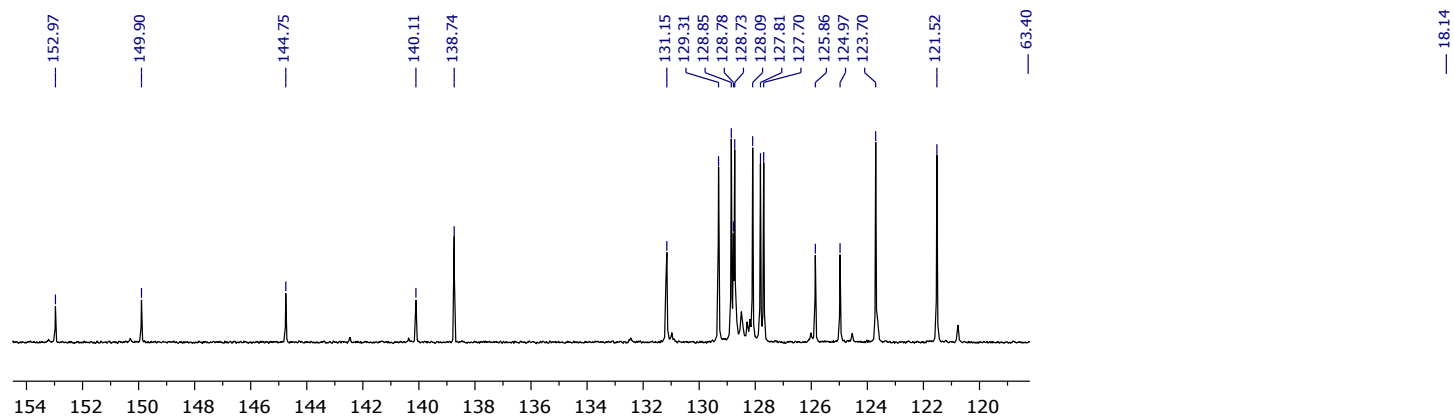


Fig. S2.16. ^{13}C NMR spectrum (DMSO- d_6) of 2,4,6-triphenyl-5-(1-phenylethyl)-4,5-dihydro-1,2,4,5-tetrazin-3(2H)-one **1b**.

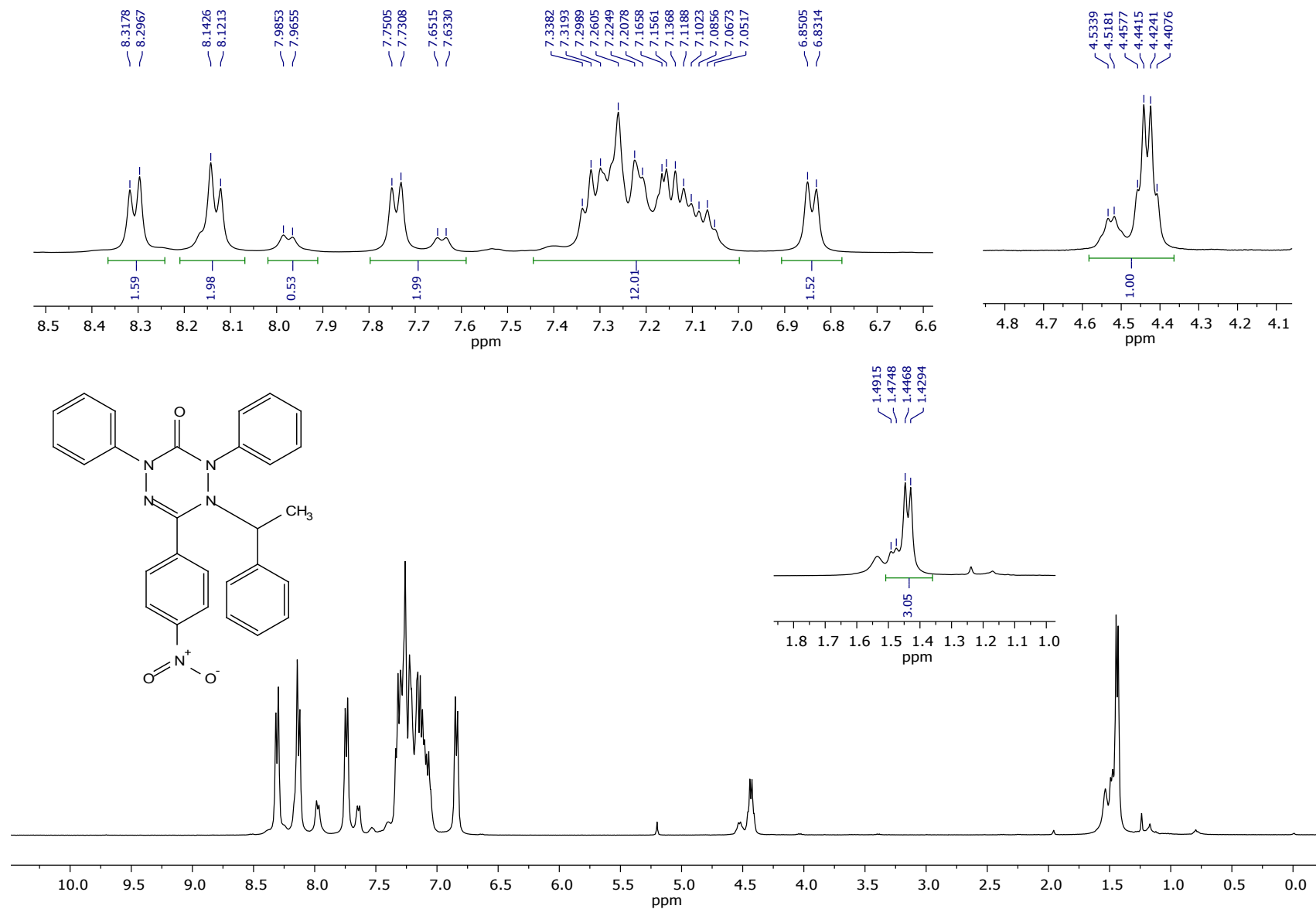


Fig. S2.17. ¹H NMR spectrum (DMSO-d₆) of 6-(4-nitrophenyl)-2,4-diphenyl-5-(1-phenylethyl)-4,5-dihydro-1,2,4,5-tetrazin-3(2H)-one **1c**.

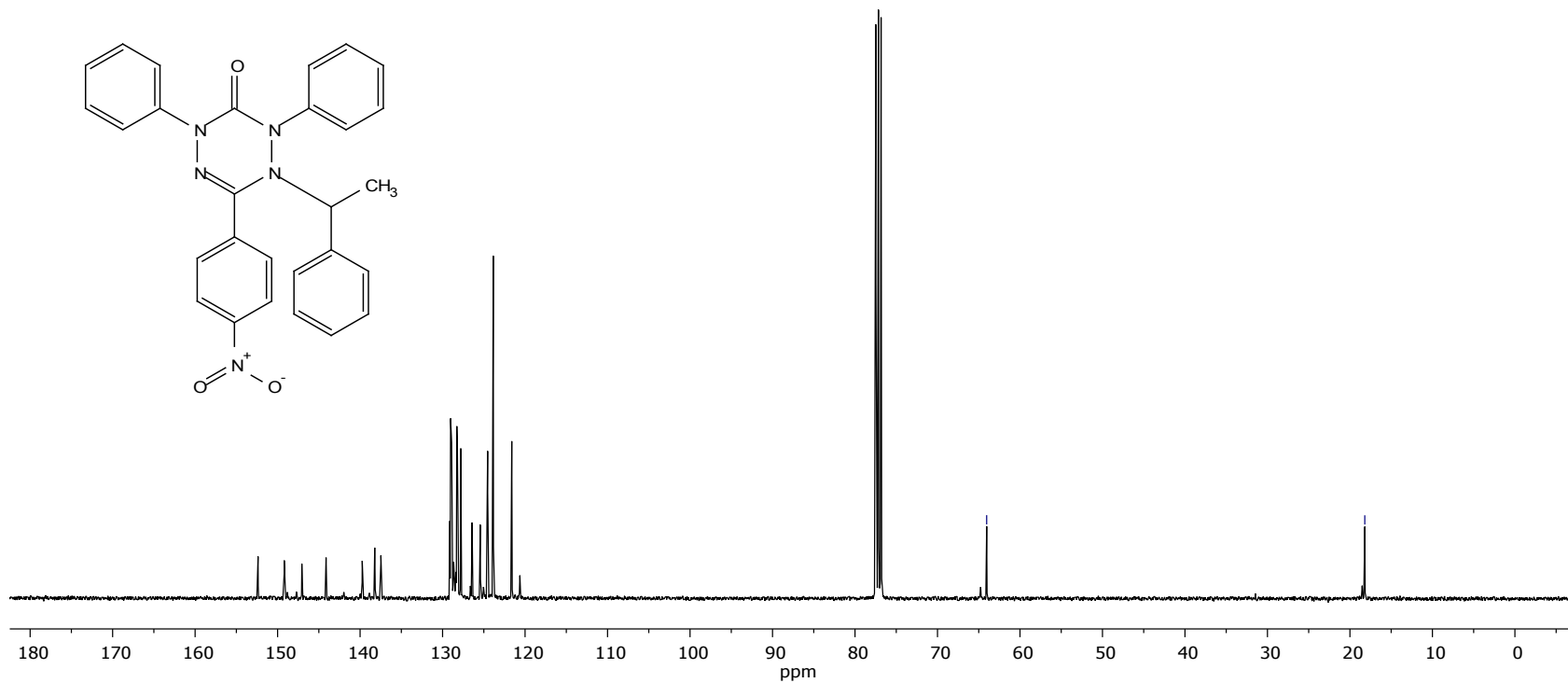
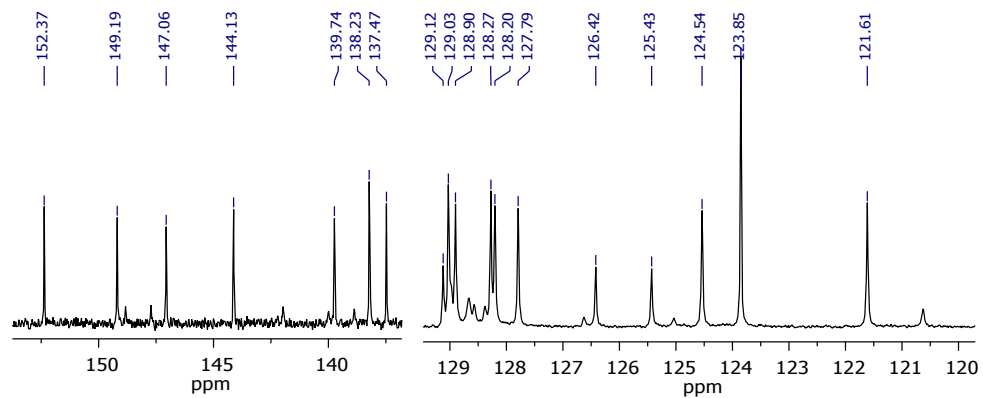


Fig. S2.18 ^{13}C NMR spectrum (DMSO-d_6) of 6-(4-nitrophenyl)-2,4-diphenyl-5-(1-phenylethyl)-4,5-dihydro-1,2,4,5-tetrazin-3(2H)-one **1c**.

Section S3. EPR spectra

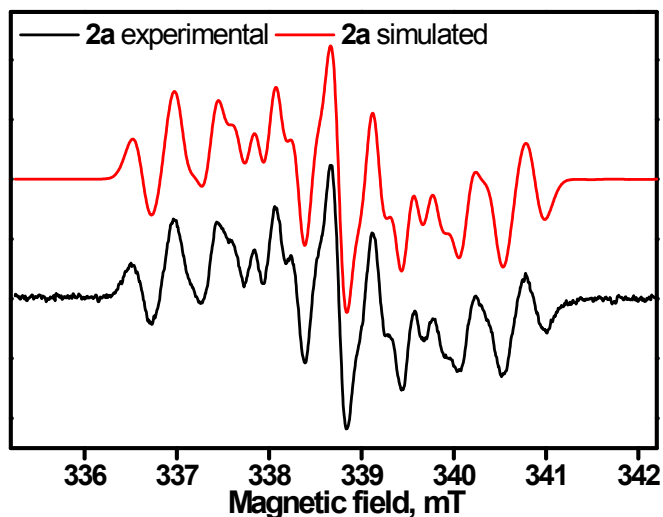


Fig. S3.1. ESR spectra of 2a (black – experimental, red – simulated) in deoxygenated toluene solution.

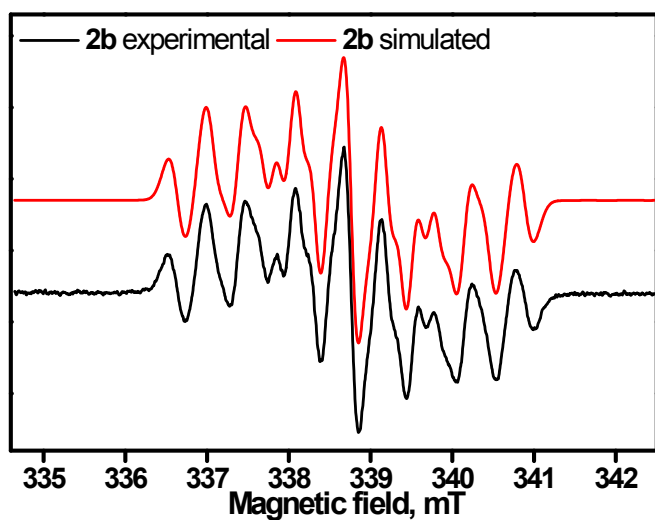


Fig. S3.2. ESR spectra of 2b (black – experimental, red – simulated) in deoxygenated toluene solution.

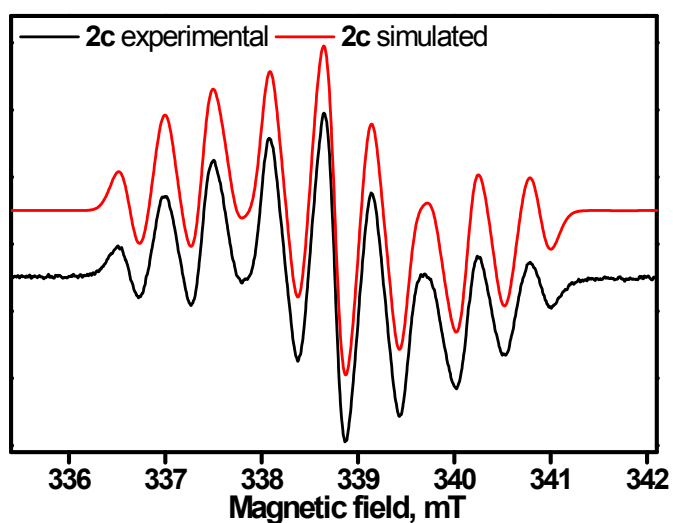


Fig. S3.3. ESR spectra of 2c (black – experimental, red – simulated) in deoxygenated toluene solution.

Section S4. UV-Vis spectra

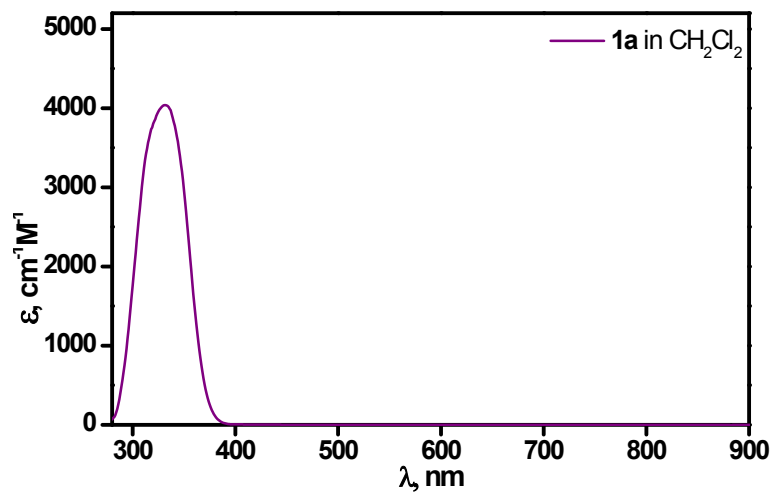


Fig. S4.1. UV-Vis spectrum of **1a** in CH_2Cl_2

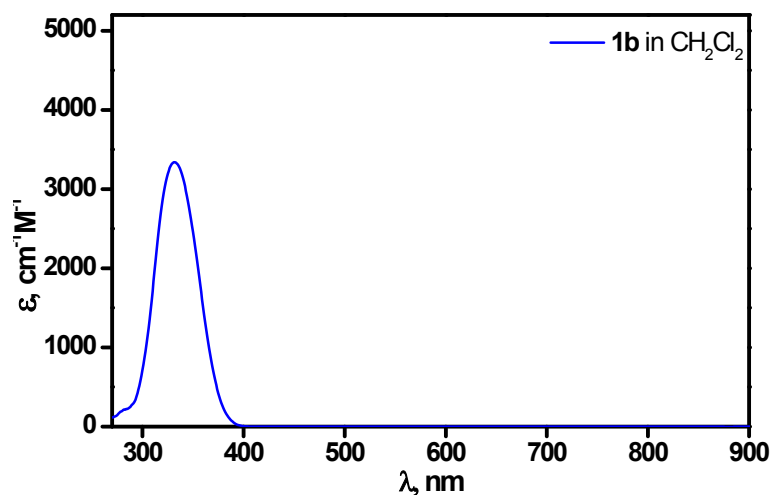


Fig. S4.2. UV-Vis spectrum of **1b** in CH_2Cl_2

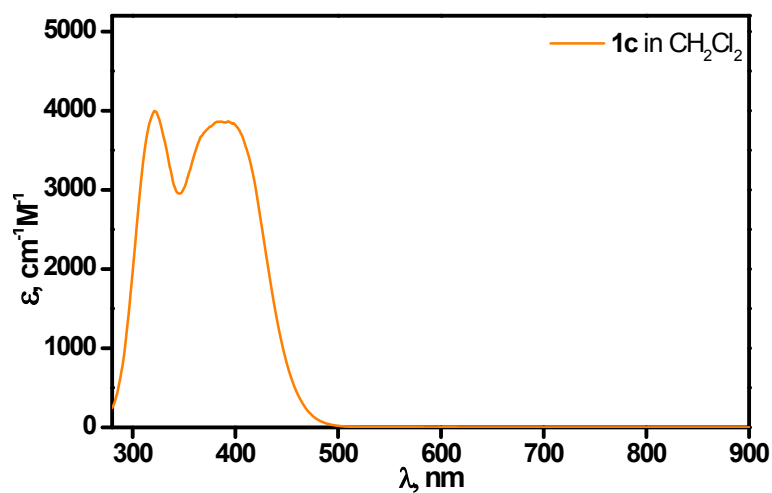


Fig. S4.3. UV-Vis spectrum of **1c** in CH_2Cl_2

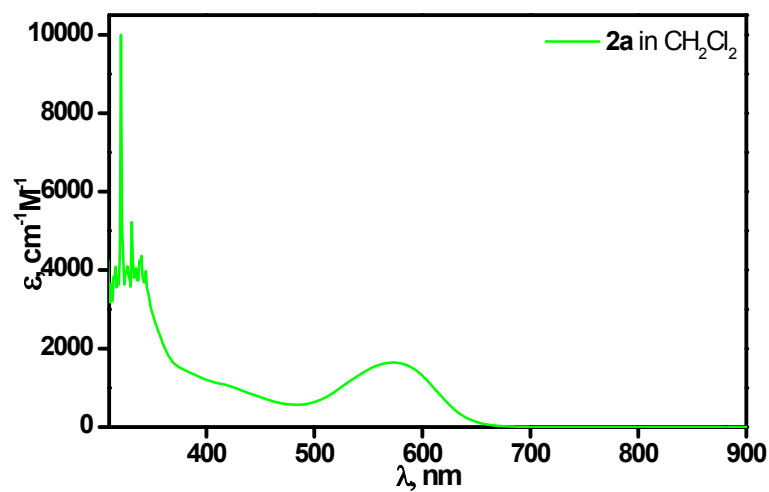


Fig. S4.4. UV-Vis spectrum of 2a in CH₂Cl₂

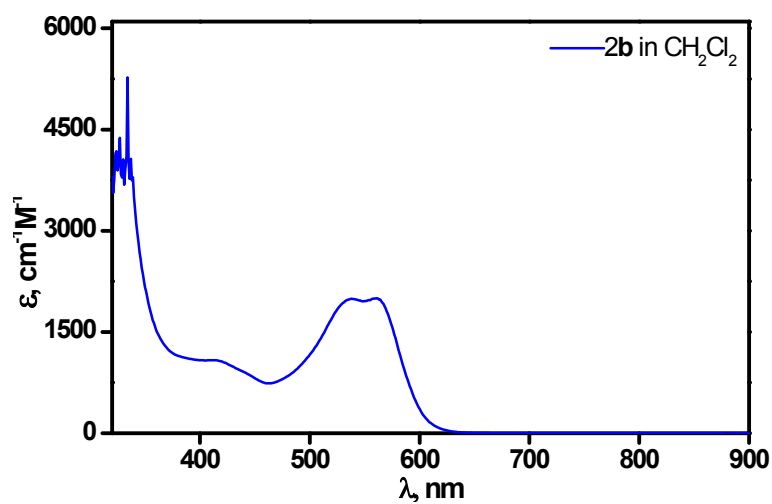


Fig. S4.5. UV-Vis spectrum of 2b in CH₂Cl₂

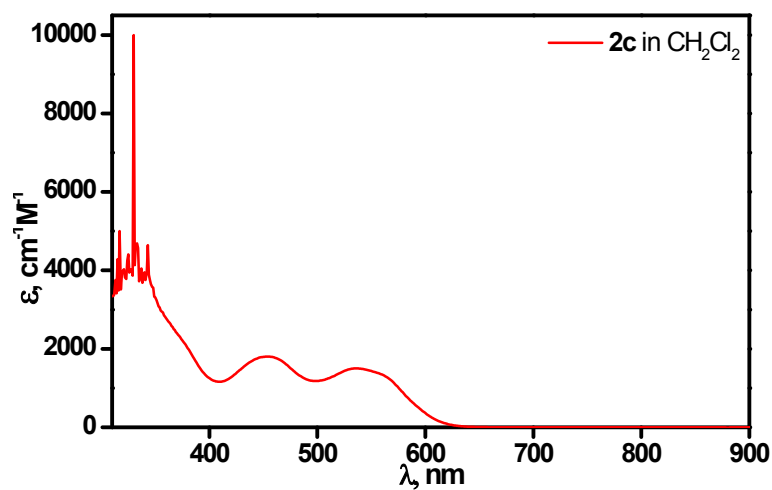


Fig. S4.6. UV-Vis spectrum of 2c in CH₂Cl₂

Section S5. Thermal induced kinetic data

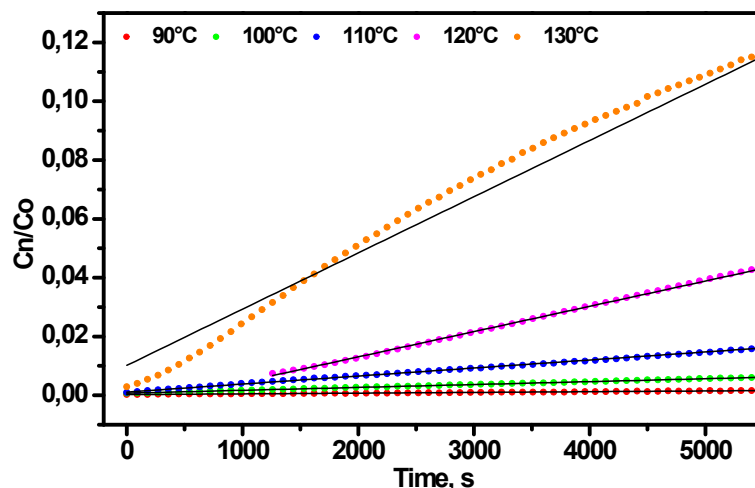


Fig. S5.1. Homolysis of **1a** in tert-butylbenzene under heat

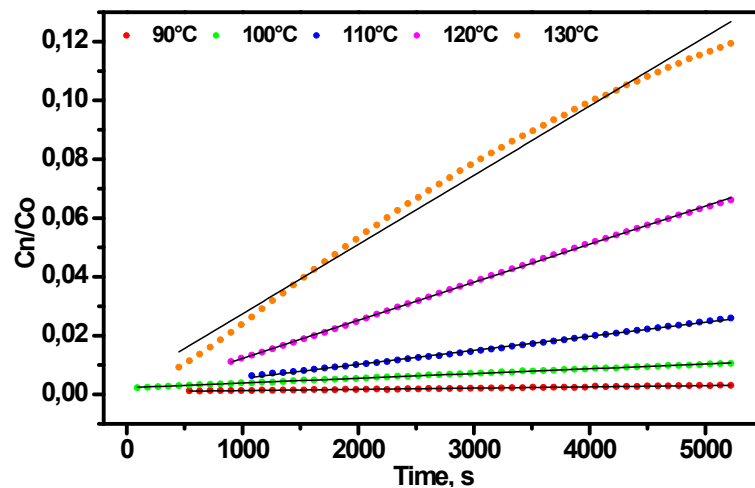


Fig. S5.2. Homolysis of **1b** in tert-butylbenzene under heat

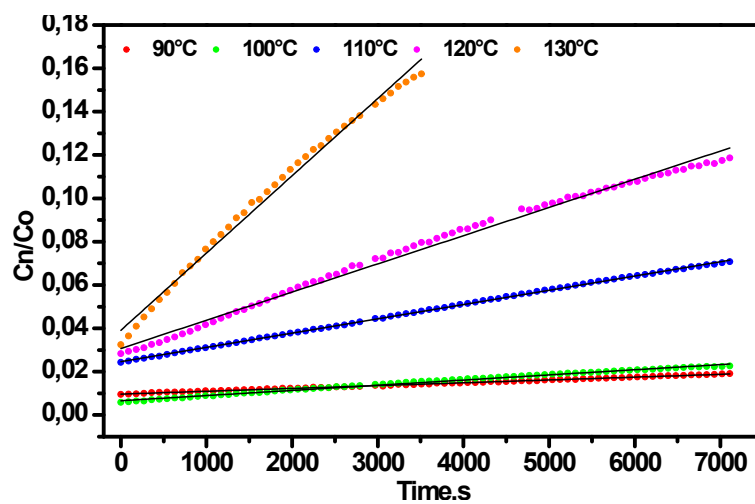


Fig. S5.3. Homolysis of **1c** in tert-butylbenzene under heat

Section S6. Photo-induced kinetic data

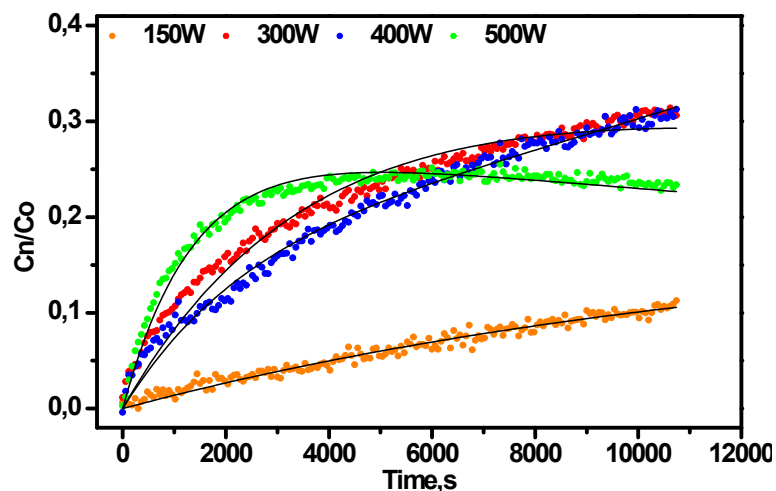


Fig. S6.1. Homolysis of **1a** in tert-butylbenzene under light

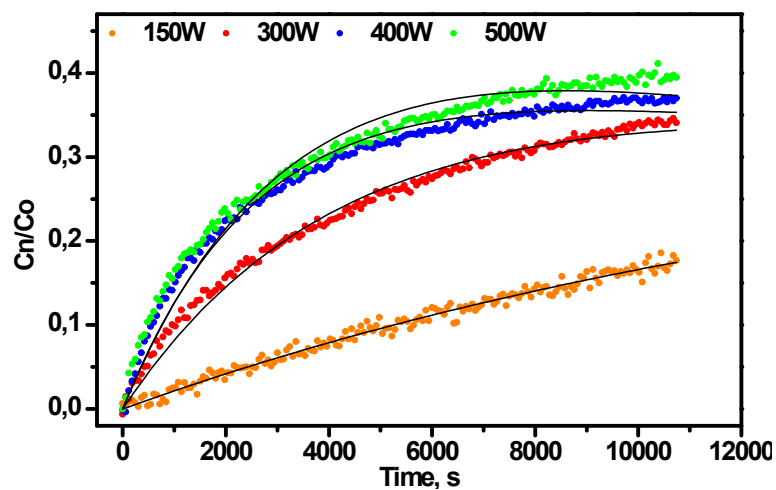


Fig. S6.2. Homolysis of **1b** in tert-butylbenzene under light

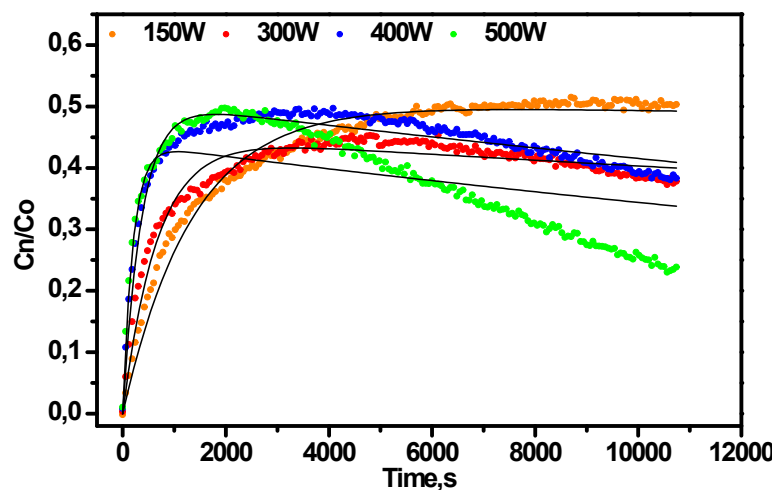


Fig. S6.3. Homolysis of **1c** in tert-butylbenzene under light

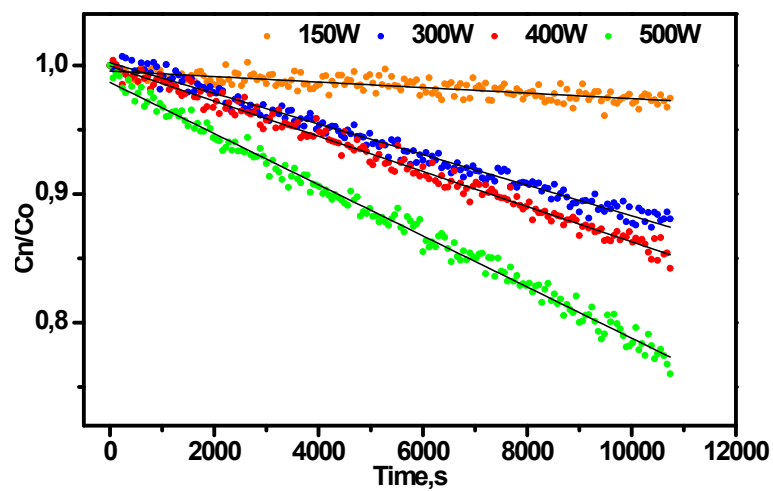


Fig. S6.4. Decomposition of 2a in tert-butylbenzene under light

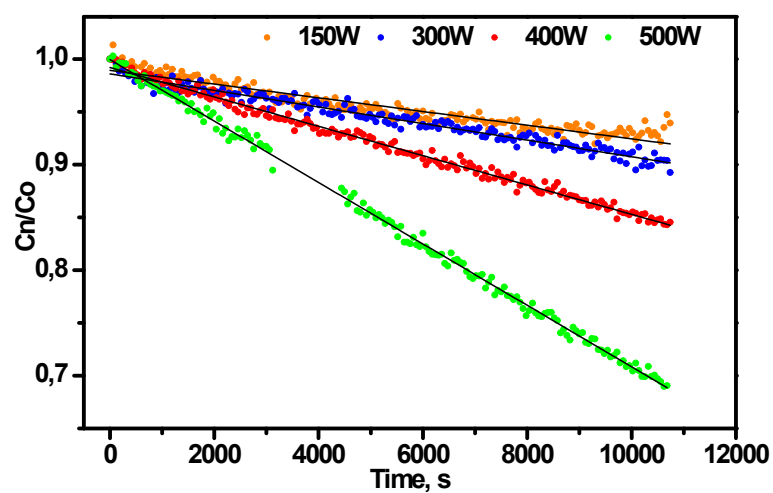


Fig. S6.5. Decomposition of 2b in tert-butylbenzene under light

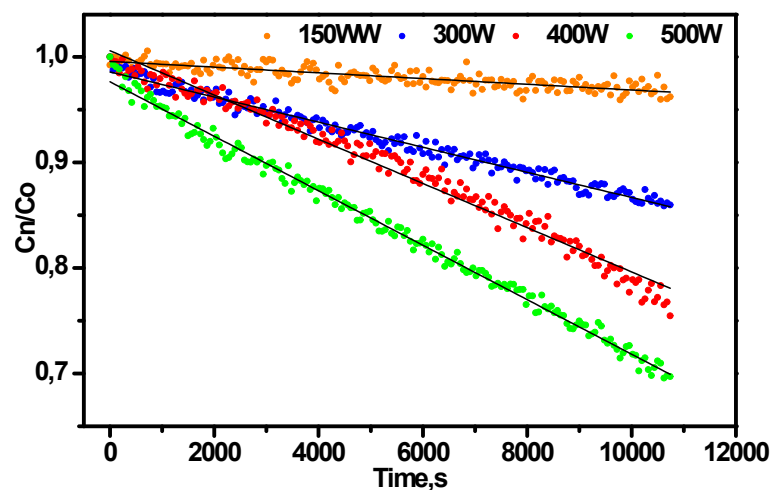


Fig. S6.6. Decomposition of 2c in tert-butylbenzene under light

Table S6.1. The fitting of homolysis kinetic curve

Entry	Kinetic scheme ^[a,b]	Comments	Equations ^[c]
1	A $\xrightarrow{0}$ B $\xrightarrow{0}$ C	No fit	$[B] = (k_1 - k_2) \cdot t$
2	A $\xrightarrow{1}$ B $\xrightarrow{0}$ C	No fit	$[B] = [A]_0 \cdot (1 - e^{-k_1 \cdot t}) - k_2 \cdot t$
3	A $\xrightarrow{0}$ B $\xrightarrow{1}$ C	No fit	$[B] = (1 - e^{-k_2 \cdot t})$
4	A $\xrightarrow{1}$ B $\xrightarrow{1}$ C	No fit	$[B] = [A]_0 \cdot \frac{k_1}{k_2 - k_1} (e^{-k_1 \cdot t} - e^{-k_2 \cdot t})$
5	A $\begin{matrix} \xrightarrow{1} \\ \xrightarrow{0} \end{matrix}$ B $\xrightarrow{1}$ C D	Good fit	$[B] = \frac{k_1}{k_2} \cdot [A]_0 \cdot (1 - e^{-k_2 \cdot t}) - \frac{k_3}{k_2} \cdot (1 - e^{-k_2 \cdot t}) + \frac{k_3}{k_2(k_2 - k_1)} \cdot (e^{-k_1 \cdot t} - e^{-k_2 \cdot t})$
6	A $\begin{matrix} \xrightarrow{1} \\ \xrightarrow{1} \end{matrix}$ B $\xrightarrow{1}$ C D	No fit	$[B] = [A]_0 \cdot \frac{k_1}{k_2 - k_1} (e^{-k_1 \cdot t} - e^{-k_2 \cdot t})$
7	A $\begin{matrix} \xrightarrow{0} \\ \xrightarrow{1} \end{matrix}$ B $\xrightarrow{1}$ C D	No fit	$[B] = \frac{k_1}{k_2} \cdot (1 - e^{-k_2 \cdot t})$
8	A $\xrightarrow{1}$ B $\begin{matrix} \xrightarrow{1} \\ \xrightarrow{0} \end{matrix}$ C D	No fit	$[B] = \frac{k_1}{k_2 - k_1} \cdot [A]_0 \cdot (e^{-k_1 \cdot t} - e^{-k_2 \cdot t}) - \frac{k_3}{k_2} \cdot (1 - e^{-k_2 \cdot t})$
9	A $\xrightarrow{1}$ B $\begin{matrix} \xrightarrow{1} \\ \xrightarrow{1} \end{matrix}$ C D	No fit	$[B] = \frac{k_1}{k_3 + k_2 - k_1} [A]_0 (e^{-k_1 t} - e^{-(k_2 + k_3)t})$
10	A $\xrightarrow{0}$ B $\begin{matrix} \xrightarrow{0} \\ \xrightarrow{1} \end{matrix}$ C D	Fit, except 1c homolysis	$[B] = \frac{k_1 - k_2}{k_3} (1 - e^{-k_3 t})$
11	A $\xrightarrow{0}$ B $\begin{matrix} \xrightarrow{1} \\ \xrightarrow{0} \end{matrix}$ C D	No fit	$[B] = \frac{k_1 - k_3}{k_2} (1 - e^{-k_2 t})$
12	A $\xrightarrow{1}$ B $\begin{matrix} \xrightarrow{0} \\ \xrightarrow{1} \end{matrix}$ C D	Very poor fit	$[B] = \frac{k_1}{k_3 - k_1} [A]_0 (e^{-k_1 t} - e^{-k_3 t}) - \frac{k_2}{k_3} (1 - e^{-k_3 t})$
13	A $\xrightarrow{0}$ B $\begin{matrix} \xrightarrow{1} \\ \xrightarrow{1} \end{matrix}$ C D	Fit, except 1c homolysis	$[B] = \frac{k_1}{k_3 + k_2} (1 - e^{-(k_2 + k_3)t})$
14	A $\xrightarrow{1}$ B $\begin{matrix} \xrightarrow{0} \\ \xrightarrow{0} \end{matrix}$ C D	Very poor fit	$[B] = k_1 [A]_0 (1 - e^{-k_1 t}) - (k_2 + k_3)t$

^[a]A-alkylated verdazyl **1**, B-verdazyl radical **2**, C- product of verdazyl degradation, D-product of side-reaction during homolysis of alkylated verdazyl **1** or during degradation of verdazyl **2**.

^[b]“0” means zero-order of reaction, “1” – first-order reaction.

^[c] k_1 – rate constant for homolysis, k_2 – rate constant for verdazyl degradation, k_3 - rate constant for side reaction