Two-step-one-pot synthesis of visible-light-responsive 6-azopurines

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Materials and methods

General Reagent Information: Preparation of commercially unavailable compounds: unless stated otherwise, all reactions were carried out in oven- and flame-dried glassware using standard Schlenk techniques and were run under nitrogen atmosphere. The reaction progress was monitored by TLC. Starting materials, reagents and solvents were purchased from Sigma–Aldrich, Acros, Fluka, Fischer, TCI, J.T. Baker or Macron and were used as received, unless stated otherwise. Solvents for the reactions were of quality puriss., p.a.. Anhydrous solvents were purified by passage through solvent purification columns[i] (MBraun SPS-800). For aqueous solutions, deionized water was used.

General Considerations: Thin Layer Chromatography analyses were performed on commercial Kieselgel 60, F254 silica gel plates with fluorescence-indicator UV254 (Merck, TLC silica gel 60 F254). For detection of components, UV light at λ = 254 nm or λ = 365 nm was used. Alternatively, oxidative staining using aqueous basic potassium permanganate solution ($KMnO_4$) or aqueous acidic cerium phosphomolybdic acid solution (Seebach's stain[ii]) was used. Drying of solutions was performed with $MgSO_4$ and volatiles were removed with a rotary evaporator.

General Analytical Information: Nuclear Magnetic Resonance spectra were measured with an Agilent Technologies 400-MR (400/54 Premium Shielded) spectrometer (400 MHz). All spectra were measured at room temperature (22–24 °C). Chemical shifts for the specific NMR spectra were reported relative to the residual solvent peak [in ppm; $CDCl_3$: δ_H = 7.26; $CDCl_3$: δ_C = 77.16; d_6-DMSO: δ_H = 2.50; d_6-DMSO: δ_C = 39.52][iii]. The multiplicities of the signals are denoted by s (singlet), d (doublet), t (triplet), q (quartet), hept (heptet), m (multiplet), br (broad signal). All ^{13}C-NMR spectra are 1H-broadband decoupled.

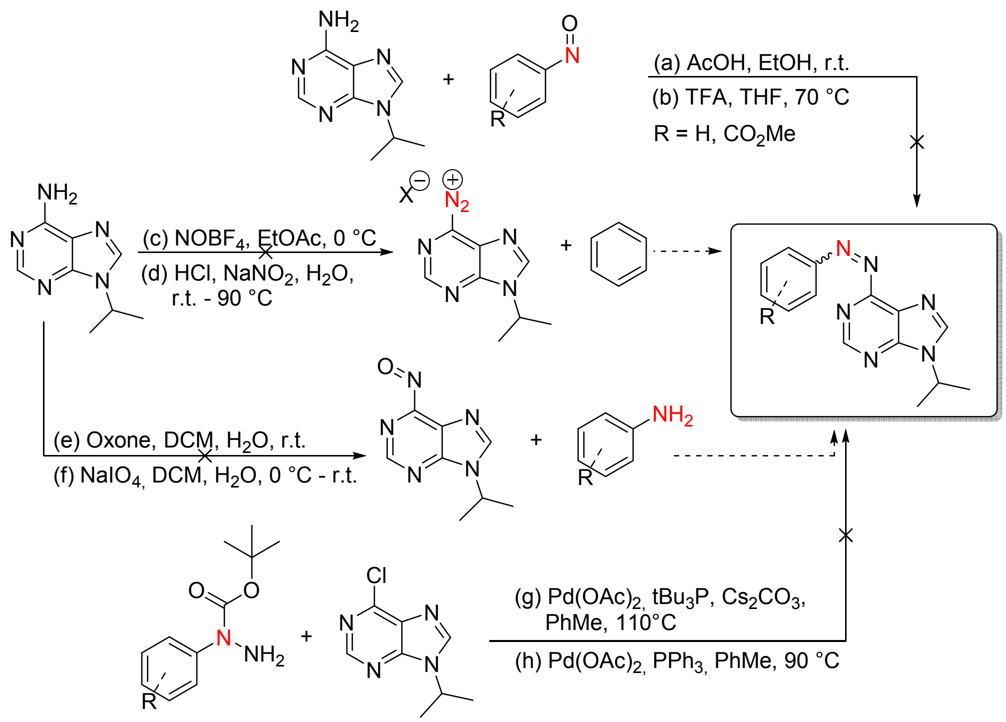
High-resolution mass spectrometric measurements were performed using a Thermo scientific LTQ OrbitrapXL spectrometer with ESI ionization. Melting points were recorded using a Stuart analogue capillary melting point SMP11 apparatus.

All the reactions were performed in CEM Discover SP-D microwave reactor.

Room temperature UV-Vis absorption spectra were recorded on an Agilent 8453 UV-Visible Spectrophotometer using Uvasol grade solvents. Irradiation experiments were performed with 530 nm LED system (3 x 270 mW, λmax = 526 nm, FWHM 35.1 nm, Sahlmann Photochemical Solutions).

Data-analysis of and UV-Vis kinetic measurements was performed using Spectrogryph and Origin Software.

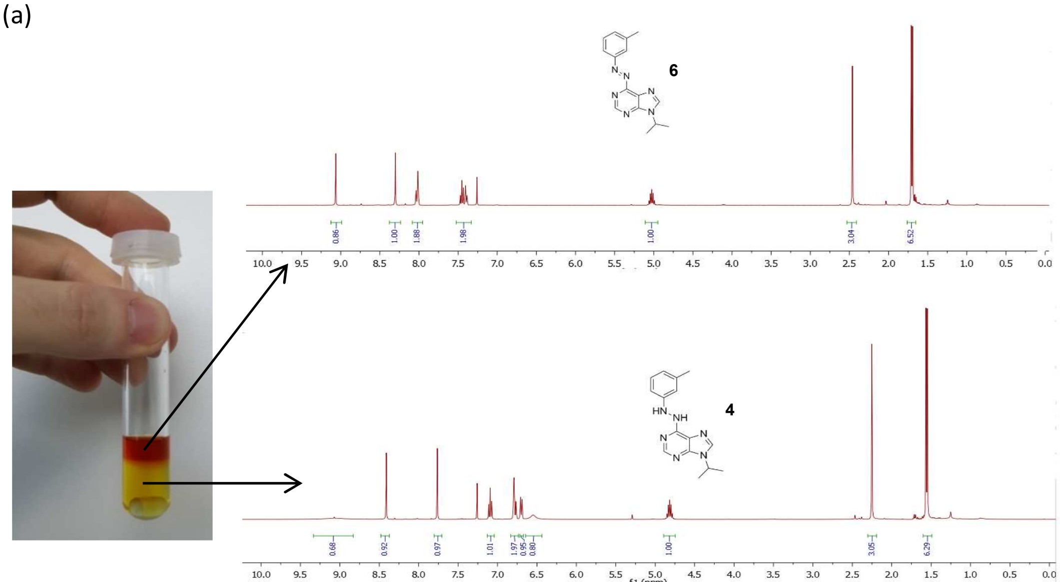
Initial attempts toobtain 6-azopurines



Scheme S1. Unsuccessful attempts to obtain 9-isopropyl-6-azoadenine.

Reaction Analysis

(a)



(b)

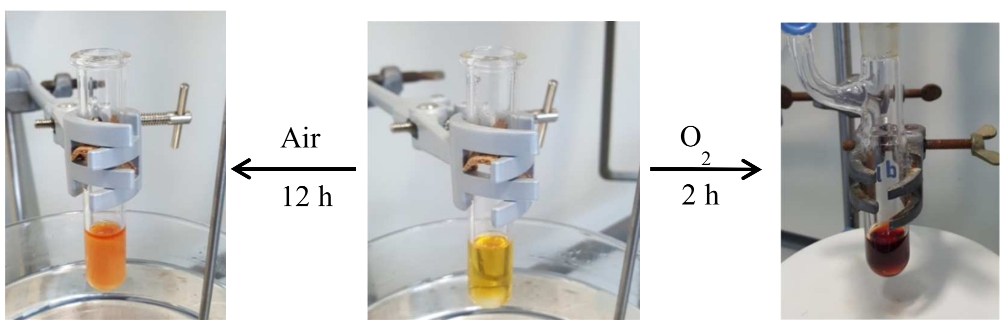
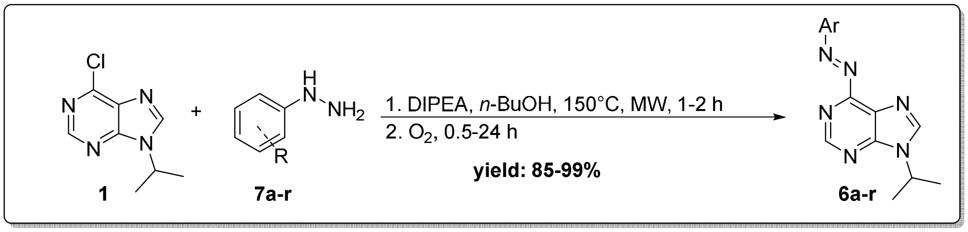
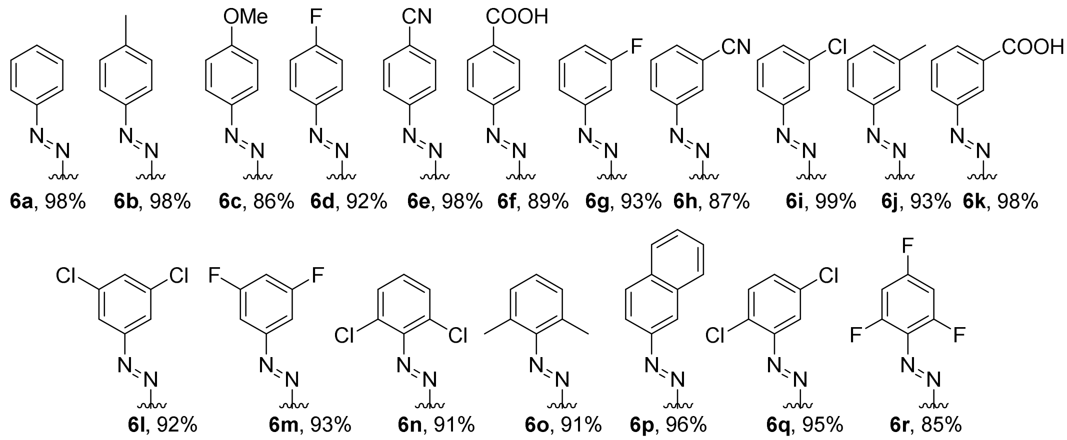


Figure S1. (a) Microwave vessel with NMR analysis of bothlayers of*n*BuOH (compound **6** in the red layer, and **4** in the yellow layer of the reaction mixture); (b) Different oxidation time of hydrazine **4** by using air or oxygen *in situ*.

General Procedure for the Synthesis of 6-Azoadenines (6a-r)





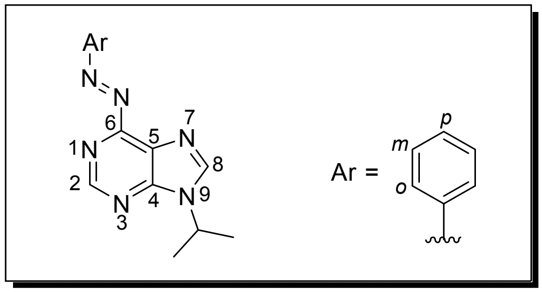
The reaction was carried out using a microwave vessel (10 mL) equipped with a magnetic stirring bar, in the presence of air. 6-Chloro-9-isopropyl-*9H*-purine **1** (59 mg, 0.30 mmol, 1.0 equiv), hydrazine (0.36 mmol, 1.2 equiv), DIPEA (0.26mL,1.5 mmol, 5 equiv in case of hydrazine, or 0.31 mL, 1.8 mmol, 6 equiv in case of hydrazine hydrochloride) and *n*-BuOH (2.0 mL) were added in sequence. The resulting mixture was reacted under microwave irradiation (200 W) at 150 ℃ for 1-2 h. After the substitution was completed (followed by TLC), the reaction mixture was exposed to a pure oxygen for 30 min – 24 h. After the reaction was finished (followed by TLC), the solvent was removed under reduced pressure and the product was purified by flash column chromatography (SiO_2, DCM/MeOH 98:2) to give **6a-r** as the orange-red solids.

When needed, additional recrystallization was performed from ethyl acetate/pentane or acetone in case of **6k** and **6f**.

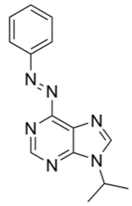
Scale-up synthesis of a representative example **6a**:

The reaction was carried out using a microwave vessel (30 mL) equipped with a magnetic stirring bar, in the presence of air. 6-Chloro-9-isopropyl-*9H*-purine **1** (555 mg, 2.8 mmol, 1.0 equiv), phenylhydrazine hydrochloride (490 mg, 3.4 mmol, 1.2 equiv), DIPEA (2.4 mL, 17 mmol, 6 equiv) and *n*-BuOH (12.0 mL) were added in sequence. The resulting mixture was reacted under microwave irradiation (200 W) at 150 ℃ for 1 h. After the substitution was completed (followed by TLC), the reaction mixture was exposed to a pure oxygen for 3 h. After the reaction was finished (followed by TLC), the solvent was removed under reduced pressure and the product was purified by flash column chromatography (SiO_2, DCM/MeOH 98:2) to give **6a** (582 mg, 2.2 mmol, 78%) as the dark orange solids.

^{1}H, ^{13}C and ^{19}F NMR Spectra of 6-Azoadenines (6a-r)

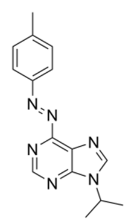


(*E*)-9-isopropyl-6-(phenyldiazenyl)-*9H*-purine (**6a**):



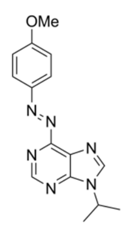
Dark orange solid; Yield: 78 mg (0.29 mmol, 98%); m.p. = 111-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (d, *J* = 6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 5.04 (hept, *J* = 6.8 Hz, 1H; C*H*(CH$_3$)$_2$), 7.54 – 7.61 (m, 3H; *o*-Ar, *p*-Ar), 8.21 (dd, *J* = 7.8, 2.0 Hz, 2H; *m*-Ar), 8.31 (s, 1H; C8-H), 9.08 (s, 1H; C2-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.5, 47.9, 124.3, 127.2, 129.2, 133.3, 144.5, 152.3, 153.1, 154.8, 157.3; IR (ATR) $\tilde{\nu}$3429, 3043, 2978, 1892, 1657, 1601, 1752, 1406, 1330, 1228, 1175, 1145, 986, 773, 650 cm^{-1};HRMS (ESI$^+$) calc. for $C_{14}H_{15}N_6$ [M+H]$^+$: 267.1353, found: 267.1353.

(*E*)-9-isopropyl-6-(*p*-tolyldiazenyl)-*9H*-purine (**6b**):



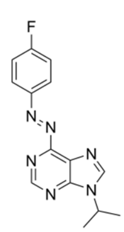
Dark orange solid; Yield: 82 mg (0.29 mmol, 98%); m.p. = 97-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 (d, *J* = 6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 2.46 (s, 3H; Ar-C*H*$_3$), 5.02 (hept, *J* = 6.8 Hz, 1H; C*H*(CH$_3$)$_2$), 7.36 (d, *J* = 8.2 Hz, 2H; *o*-Ar), 8.11 (d, *J* = 8.2 Hz, 2H; *m*-Ar), 8.29 (s, 1H; C8-H), 9.06 (s, 1H; C2-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.7, 22.5, 47.8, 124.4, 127.5, 129.8, 144.3, 144.5, 151.4, 152.2, 154.8, 157.4; IR (ATR) $\tilde{\nu}$3050, 2978, 2928, 1857, 1572, 1498, 1427, 1318 1222, 1148, 985, 826, 684 cm^{-1};HRMS (ESI$^+$) calc. for $C_{15}H_{17}N_6$ [M+H]$^+$: 281.1509, found: 281.1509.

(*E*)-9-isopropyl-6-((4-methoxyphenyl)diazenyl)-*9H*-purine (**6c**):



Dark red solid; Yield: 76 mg (0.26 mmol, 86%); m.p. = 94-96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 (d, *J* = 6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 3.93 (s, 3H; Ar-C*H*$_3$), 5.03 (hept, *J* = 6.8 Hz, 1H; C*H*(CH$_3$)$_2$), 7.05 (d, *J* = 9.1 Hz, 2H; *o*-Ar), 8.23 (d, *J* = 9.1 Hz, 2H; *m*-Ar), 8.28 (s, 1H; C8-H), 9.05 (s, 1H; C2-H);^{13}C NMR (101 MHz, $CDCl_3$) δ 22.6, 47.8, 55.7, 114.4, 114.8, 126.8, 144.0, 147.9, 152.4, 154.7, 157.4, 164.2. IR (ATR) $\tilde{\nu}$3058, 2977, 2840, 1568, 1498, 1463, 1319, 1255, 1212, 1028, 985, 833, 641 cm^{-1};HRMS (ESI$^+$) calc. for $C_{15}H_{17}N_6O$ [M+H]$^+$: 297.1458, found: 297.1458.

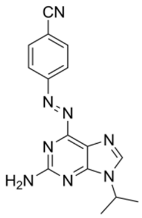
(*E*)-6-((4-fluorophenyl)diazenyl)-9-isopropyl-*9H*-purine (**6d**):



Red solid; Yield: 79 mg (0.28 mmol, 92%); m.p. = 112-114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (d, *J* = 6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 5.03 (hept, *J* = 6.8 Hz, 1H; C*H*(CH$_3$)$_2$), 7.19 – 7.29 (m, 2H; *m*-Ar), 8.20 – 8.29 (m, 2H; *o*-Ar), 8.33 (s, 1H; C8-H), 9.07 (s, 1H; C2-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.5, 48.0, 116.3 (d, *J* = 23.1 Hz), 126.6 (d, *J* = 9.5 Hz), 127.1, 144.5, 149.8 (d, *J* = 3.0 Hz), 152.3, 154.8, 157.1, 165.9 (d, *J* = 256.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.02 (ddd, *J*

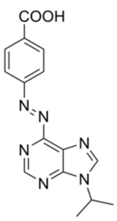
= 13.4, 8.2, 5.2 Hz); IR (ATR) $\tilde{\nu}$ 3049, 2982, 1594, 1569, 1499, 11414, 1225, 1137, 987, 844, 821, 641 cm^{-1};HRMS (ESI^+) calc. for $C_{14}H_{14}N_6F$ $[M+H]^+$: 285.1259, found: 285.1261.

(*E*)-4-((9-isopropyl-*9H*-purin-6-yl)diazenyl)benzonitrile (**6e**):



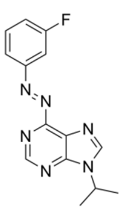
Dark orange solid; Yield: 86 mg (0.29 mmol, 98%); m.p. = 195-197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (d, J = 6.8 Hz, 6H; $CH(CH_3)_2$), 5.02 (hept, J = 6.8 Hz, 1H; $CH(CH_3)_2$), 7.85 (d, J = 8.5 Hz, 2H; *m*-Ar), 8.23 (d, J = 8.5 Hz, 2H; *o*-Ar), 8.34 (s, 1H; C8-H), 9.07 (s, 1H; C2-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.5, 48.1, 116.0, 118.0, 124.4, 127.6, 133.3, 145.2, 152.1, 154.5, 155.3, 156.4; IR (ATR) $\tilde{\nu}$ 3111, 3064, 2229, 1792, 1573, 1392, 1323, 1318, 1149, 988, 851, 642 cm^{-1};HRMS (ESI^+) calc. for $C_{15}H_{14}N_7$ $[M+H]^+$: 292.1305, found: 292.1307.

(*E*)-4-((9-isopropyl-*9H*-purin-6-yl)diazenyl)benzoic acid (**6f**):



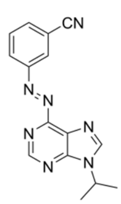
Red solid; Yield: 83 mg (0.27 mmol, 89%); m.p. = 248-250 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.61 (d, J = 6.8 Hz, 6H; $CH(CH_3)_2$), 4.96 (hept, J = 6.8 Hz, 1H; $CH(CH_3)_2$), 8.09 (d, J = 8.5 Hz, 2H; *m*-Ar), 8.20 (d, J = 8.5 Hz, 2H; *o*-Ar), 8.86 (s, 1H; C8-H), 9.00 (s, 1H; C2-H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 22.3, 48.0, 123.7, 126.2, 131.3, 135.0, 147.5, 151.8, 154.9, 155.0, 157.8, 167.0; IR (ATR) $\tilde{\nu}$3107, 2983, 2935, 2762, 2616, 2495, 2835, 1698, 1574, 1495, 1435, 1391, 1329, 1266, 1224, 1116, 996, 942, 865, 772, 696, 644 cm^{-1};HRMS (ESI^+) calc. for $C_{15}H_{13}N_6O_2$ $[M+H]^+$: 309.1095, found: 309.1101.

(*E*)-6-((3-fluorophenyl)diazenyl)-9-isopropyl-*9H*-purine (**6g**):



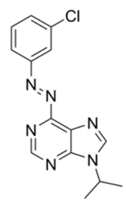
Red solid; Yield: 79 mg (0.28 mmol, 93%); m.p. = 164-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 (d, J = 6.8 Hz, 6H; $CH(CH_3)_2$), 5.03 (hept, J = 6.8 Hz, 1H; $CH(CH_3)_2$), 7.29 (tdd, J = 8.1, 2.6, 1.0 Hz, 1H; *o*-Ar), 7.55 (td, J = 8.1, 5.8 Hz, 1H; *o*-Ar), 7.84 – 7.89 (m, 1H; *p*-Ar), 8.06 (ddd, J = 7.9, 1.8, 1.0 Hz, 1H; *m*-Ar), 8.33 (s, 1H; C8-H), 9.07 (s, 1H; C2-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.5, 48.0, 108.9 (d, J = 23.0 Hz), 120.0 (d, J = 22.0 Hz), 122.3 (d, J = 3.0 Hz), 127.5, 130.4 (d, J = 8.4 Hz), 144.7, 152.2, 154.4 (d, J = 7.0 Hz), 156.0 (d, J = 184.9 Hz), 161.9, 164.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.59 (ddd, J = 9.6, 7.9, 5.8 Hz); IR (ATR) $\tilde{\nu}$ 3051, 2992, 1849, 1735, 1592, 1568, 1475, 1415, 1320, 1224, 1160, 1108, 986, 882, 798, 731, 697, 640 cm^{-1};HRMS (ESI^+) calc. for $C_{14}H_{14}N_6F$ $[M+H]^+$: 285.1289, found: 285.1260.

(*E*)-3-((9-isopropyl-*9H*-purin-6-yl)diazenyl)benzonitrile (**6h**):



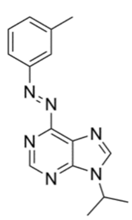
Dark orange solid; Yield: 76 mg (0.26 mmol, 87%); m.p. = 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 (d, J = 6.8 Hz, 6H; $CH(CH_3)_2$), 5.02 (hept, J = 6.8 Hz, 1H; $CH(CH_3)_2$), 7.69 (t, J = 7.8 Hz, 1H; *m*-Ar), 7.84 (d, J = 7.8 Hz, 1H; *o*-Ar), 8.33 (s, 1H; *o*-Ar), 8.40 (d, J = 8.1 Hz, 1H; *p*-Ar), 8.44 (s, 1H; C8-H), 9.07 (s, 1H; C2-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.5, 48.1, 113.7, 117.7, 127.0, 127.7, 128.5, 130.3, 135.7, 145.1, 152.1, 152.7, 155.3, 156.4; IR (ATR) $\tilde{\nu}$ 3102, 3053, 2938, 2234, 1737, 1591, 1566, 1490, 1432, 1321, 1224, 1129, 1065, 988, 914, 815, 695, 642 cm^{-1};HRMS (ESI^+) calc. for $C_{15}H_{14}N_7$ $[M+H]^+$: 292.1305, found: 292.1306.

(E)-6-((3-chlorophenyl)diazenyl)-9-isopropyl-*9H*-purine (**6i**):



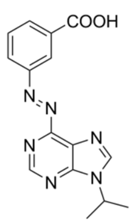
Yield: 89 mg (0.3 mmol, 99%); m.p. = 139-141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (d, J = 6.8 Hz, 6H; CH(CH_3)$_2$), 4.97 (hept, J = 6.8 Hz, 1H; CH(CH_3)$_2$), 7.42 – 7.51 (m, 2H; *m*-,*p*-Ar), 8.06 (dt, J = 7.3, 1.8 Hz, 1H; *o*-Ar), 8.11 (t, J = 2.0 Hz, 1H; *o*-Ar), 8.28 (s, 1H; C8-H), 9.02 (s, 1H; C2-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.5, 47.9, 122.4, 124.1, 127.5, 130.2, 132.8, 135.3, 144.8, 152.1, 153.7, 155.0, 156.7; IR (ATR) $\tilde{\nu}$ 3096, 3053, 2967, 2876, 1945, 1802, 1559, 1494, 1392, 1320, 1279, 1229, 1182, 1097, 919, 878, 784, 689 cm^{-1};HRMS (ESI$^+$) calc. for $C_{14}H_{14}N_6Cl$ [M+H]$^+$: 301.0963, found: 301.0966.

(E)-9-isopropyl-6-(*m*-tolyldiazenyl)-*9H*-purine (**6j**):



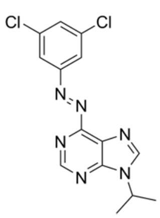
Red solid; Yield: 78 mg (0.28 mmol, 93%); m.p. = 69-72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (d, J = 6.8 Hz, 6H; CH(CH_3)$_2$), 2.47 (s, 3H; CH3), 5.03 (hept, J = 6.8 Hz, 1H; CH(CH_3)$_2$), 7.40 (d, J = 7.5 Hz, 1H; *p*-Ar), 7.46 (t, J = 7.5 Hz, 1H; *m*-Ar), 8.04 (m, 2H; *o*-,*o*-Ar), 8.31 (s, 1H; C8-H), 9.07 (s, 1H; C2-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 21.2, 22.6, 47.9, 122.6, 123.7, 127.4, 129.0, 134.2, 139.1, 144.4, 152.3, 153.3, 154.9, 157.3; IR (ATR) $\tilde{\nu}$ 3052, 2978, 1854, 1737, 1594, 1570, 1476, 1418, 1383, 1322, 1263, 1223, 1188, 1126, 986, 926, 790, 698, 640 cm^{-1};HRMS (ESI$^+$) calc. for $C_{15}H_{17}N_6$ [M+H]$^+$: 281.1509, found: 281.1511.

(E)-3-((9-isopropyl-*9H*-purin-6-yl)diazenyl)benzoic acid (**6k**):



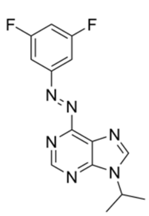
Dark orange solid; Yield: 91 mg (0.29 mmol, 98%); m.p. = 225-228 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.61 (d, J = 6.8 Hz, 6H; CH(CH_3)$_2$), 4.96 (hept, J = 6.8 Hz, 1H; CH(CH_3)$_2$), 7.82 (t, J = 7.8 Hz, 1H; *p*-Ar), 8.23 (dt, J = 7.8, 1.5 Hz, 1H; *m*-Ar), 8.28 (dt, J = 7.8, 1.5 Hz, 1H; *o*-Ar), 8.46 (t, J = 1.9 Hz, 1H; *o*-Ar), 8.85 (s, 1H; C8-H), 9.00 (s, 1H; C2-H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 22.3, 48.0, 123.0, 126.3, 128.7, 130.8, 132.9, 134.1, 147.4, 151.8, 152.7, 154.9, 157.7, 166.9; IR (ATR) $\tilde{\nu}$ 3123, 2972, 1841, 1694, 1492, 1407, 1327, 1294, 1213, 1150, 1068, 1016, 760, 682, 642 cm^{-1};HRMS (ESI$^+$) calc. for $C_{15}H_{15}N_6O_2$ [M+H]$^+$: 311.1251, found: 311.1253.

(E)-6-((3,5-dichlorophenyl)diazenyl)-9-isopropyl-*9H*-purine (**6l**):



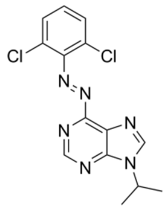
Dark red solid; Yield: 93 mg (0.28 mmol, 92%); m.p. = 155-157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (d, J = 6.8 Hz, 6H; CH(CH_3)$_2$), 5.04 (hept, J = 6.8 Hz, 1H; CH(CH_3)$_2$), 7.56 (t, J = 1.9 Hz, 1H; *p*-Ar), 8.10 (d, J = 1.9 Hz, 2H; *o*-Ar), 8.36 (s, 1H; C8-H), 9.08 (s, 1H; C2-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.5, 48.1, 122.6, 127.3, 132.4, 135.9, 145.0, 152.2, 153.9, 155.2, 156.4; IR (ATR) $\tilde{\nu}$ 3056, 2976, 1861, 1738, 1564, 1496, 1391, 1322, 1201, 1157, 1104, 986, 935, 870, 799, 642 cm^{-1};HRMS (ESI$^+$) calc. for $C_{14}H_{13}N_6Cl_2$ [M+H]$^+$: 335.0573, found: 335.0576.

(E)-6-((3,5-difluorophenyl)diazenyl)-9-isopropyl-*9H*-purine (**6m**):



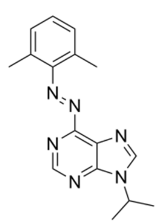
Dark orange solid; Yield: 84 mg (0.28 mmol, 93%); m.p. = 210-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (d, J = 6.8 Hz, 6H; CH(CH_3)$_2$), 5.01 (hept, J = 6.8 Hz, 1H; CH(CH_3)$_2$), 7.02 (tt, J = 8.3, 2.4 Hz, 1H; *p*-Ar), 7.72 (dd, J = 7.5, 2.4 Hz, 2H; *o*-Ar), 8.31 (s, 1H; C8-H), 9.05 (s, 1H; C2-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.5, 48.0, 107.2, 107.3 (d, J = 12.1 Hz), 107.5 , 107.9 (t, J = 25.9 Hz), 127.6, 145.0, 152.1, 154.6 (t, J = 9.2 Hz), 155.2, 156.4 , 161.9 (d, J = 12.7 Hz), 164.4 (d, J = 12.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.22 (t, J = 7.5 Hz); IR (ATR) $\tilde{\nu}$ 3103, 3053, 3027, 1853, 1760, 1598, 1566, 1497, 1446, 1379, 1320, 1295, 1184, 1130, 995,874, 696, 641 cm^{-1};HRMS (ESI$^+$) calc. for $C_{14}H_{13}N_6F_2$ [M+H]$^+$: 303.1164, found: 303.1166.

(E)-6-((2,6-dichlorophenyl)diazenyl)-9-isopropyl-*9H*-purine (**6n**):



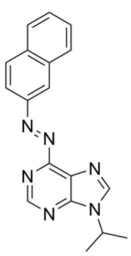
Dark orange solid; Yield: 92 mg (0.27 mmol, 91%); m.p. = 110-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (d, J = 6.8 Hz, 6H; CH(CH_3)$_2$), 5.05 (hept, J = 6.8 Hz, 1H; CH(CH_3)$_2$), 7.27 (t, 1H, J = 8.1 Hz; *p*-Ar), 7.45 (d, J = 8.1 Hz, 2H; *m*-Ar), 8.38 (s, 1H; C8-H), 9.13 (s, 1H; C2-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.5, 48.1, 126.7, 127.3, 129.2, 129.8, 145.4, 148.7, 152.2, 155.3, 156.1; IR (ATR) $\tilde{\nu}$3071, 2982, 1563, 1490, 1405, 1377, 1324, 1213, 1156, 1101, 1057, 982, 941, 888, 785, 641 cm^{-1};HRMS (ESI^{+}) calc. for $C_{14}H_{13}N_6Cl_2$ [M+H]$^{+}$: 335.0573, found: 335.0579.

(E)-6-((2,6-dimethylphenyl)diazenyl)-9-isopropyl-*9H*-purine (**6o**):



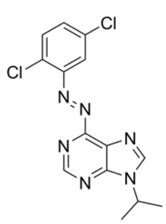
Dark orange solid; Yield: 80 mg (0.27 mmol, 91%); m.p. = 84-85 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (d, J = 6.8 Hz, 6H; CH(CH_3)$_2$), 2.53 (s, 6H; CH3), 5.01 (hept, J = 6.8 Hz, 1H; CH(CH_3)$_2$), 7.15 (d, J = 7.4 Hz, 2H; *m*-Ar), 7.23 (dd, J = 7.4, 6.4 Hz, 1H; *p*-Ar), 8.26 (s, 1H; C8-H), 9.05 (s, 1H; C2-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 19.5, 22.6, 47.8, 126.1, 129.3, 130.3, 132.7, 144.4, 151.7, 152.1, 154.6, 158.3; IR (ATR) $\tilde{\nu}$3049, 2971, 1563, 1492, 1461, 1321, 1185, 1007, 883, 764, 646 cm^{-1};HRMS (ESI^{+}) calc. for $C_{16}H_{19}N_6$ [M+H]$^{+}$: 295.1666, found: 295.1666.

(E)-9-isopropyl-6-(naphthalen-2-yldiazenyl)-*9H*-purine (**6p**):



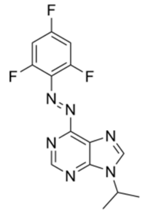
Dark red solid; Yield: 91 mg (0.29 mmol, 96%); m.p. = 133-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 (d, J = 6.8 Hz, 6H; CH(CH_3)$_2$), 5.04 (hept, J = 6.8 Hz, 1H; CH(CH_3)$_2$), 7.52 – 7.63 (m, 2H; Ar), 7.89 (d, J = 8.3 Hz, 1H; Ar), 7.92 (d, J = 9.1 Hz, 1H; Ar), 8.05 (d, J = 7.8 Hz, 1H; Ar), 8.26 (dd, J = 8.9, 2.0 Hz, 1H; Ar), 8.38 (s, 1H; C8-H), 8.85 (d, J = 1.9 Hz, 1H; Ar), 9.09 (s, 1H; C2-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.5, 48.0, 116.6, 127.0, 128.0, 128.8, 129.3, 130.1, 132.2, 133.3, 136.0, 144.5, 150.9, 152.4, 154.8, 157.3(one signal missing due to overlap); IR (ATR) $\tilde{\nu}$3047, 2934, 1735, 1571, 1419, 1250, 1153, 953, 919, 721, 644 cm^{-1};HRMS (ESI^{+}) calc. for $C_{18}H_{17}N_6$ [M+H]$^{+}$: 317.1509, found: 317.1511.

(E)-6-((2,5-dichlorophenyl)diazenyl)-9-isopropyl-*9H*-purine (**6q**):



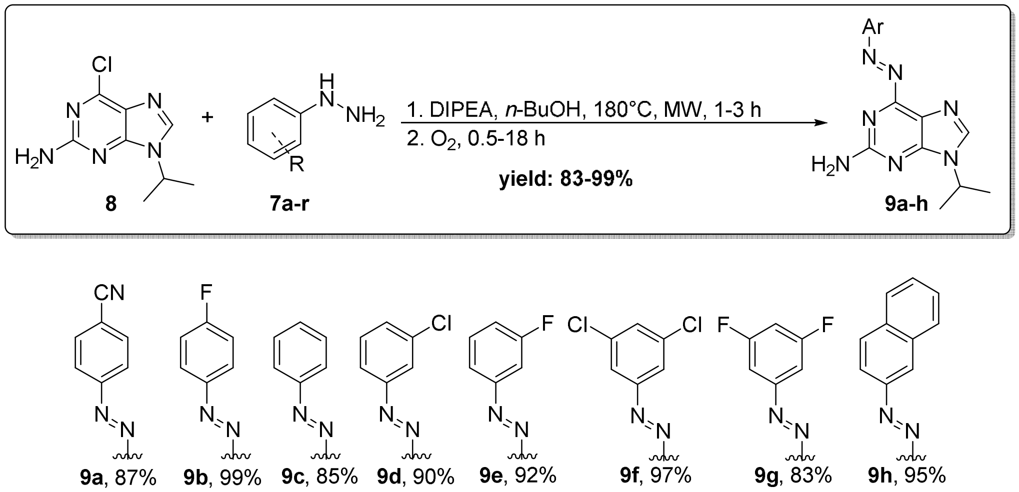
Dark orange solid; Yield: 95 mg (0.28 mmol, 95%); m.p. = 128-131 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.70 (d, J = 6.8 Hz, 6H; CH(CH_3)$_2$), 5.03 (hept, J = 6.8 Hz, 1H; CH(CH_3)$_2$), 7.47 (dd, J = 8.6, 2.5 Hz, 1H; *P*-Ar), 7.56 (d, J = 8.6 Hz, 1H; *m*-Ar), 7.91 (d, J = 2.5 Hz, 1H; *o*-Ar), 8.32 (s, 1H; C8-H), 9.09 (s, 1H; C2-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.5, 48.0, 118.0, 127.0, 131.8, 133.4, 133.7, 135.6, 145.1, 149.7, 152.2, 155.1, 157.0; IR (ATR) $\tilde{\nu}$3120, 3084, 2980, 2935, 1600, 1586, 1456, 1393, 1367, 1329, 1302, 1217, 1159, 1056, 990, 889, 807, 617 cm^{-1};HRMS (ESI^{+}) calc. for $C_{14}H_{13}N_6Cl_2$ [M+H]$^{+}$: 335.0573, found: 335.0576.

(E)-9-isopropyl-6-((2,4,6-trifluorophenyl)diazenyl)-*9H*-purine (**6r**):



Dark red solid; Yield: 82 mg (0.28 mmol, 95%); m.p. = 119-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.68 (d, J = 6.8 Hz, 6H; CH(CH_3)$_2$), 4.99 (hept, J = 6.8 Hz, 1H; CH(CH_3)$_2$), 6.74 – 6.95 (m, 2H; *m*-Ar), 8.30 (s, 1H; C8-H), 9.06 (s, 1H; C2-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.5, 47.9, 101.7 (ddd, J = 26.1, 24.2, 4.0 Hz), 126.7, 145.1, 152.1, 155.9 (dd, J = 15.4, 6.2 Hz), 156.2 (d, J = 224.9 Hz), 158.5 (dd, J = 15.4, 6.2 Hz), 162.9 (t, J = 15.0 Hz), 165.5 (t, J = 15.0 Hz); 3098, 3058, 2984, 2941, 1736, 1597, 1445, 1325, 1177, 1126, 1070, 1001, 842, 649 cm^{-1};HRMS (ESI^{+}) calc. for $C_{14}H_{12}N_6F_3$ [M+H]$^{+}$: 321.1070, found: 321.1073.

General Procedure for the Synthesis of 6-Azoguanines (9a-h)



The reaction was carried out using a microwave vessel (10 mL) equipped with a magnetic stirring bar, in the presence of air. 6-Chloro-9-isopropyl-*9H*-purin-2-amine **8** (64 mg, 0.30 mmol, 1.0 equiv), hydrazine (0.36 mmol, 1.2 equiv), DIPEA (0.26 mL, 1.5 mmol, 5 equiv in case of hydrazine, or 0.31 mL, 1.8 mmol, 6 equiv in case of hydrazine hydrochloride) and *n*-BuOH (2.0 mL) were added in sequence. The resulting mixture was reacted under microwave irradiation (200 W) at 180 ℃ for 1-3 h. After the substitution was completed (followed by TLC), the reaction mixture was exposed to a pure oxygen for 30 min – 18 h. After the reaction was finished (followed by TLC), the solvent was removed under reduced pressure and the product was purified by flash column chromatography (SiO_2, DCM/MeOH 96:4) to give **9a-h** as the red-brown solids.

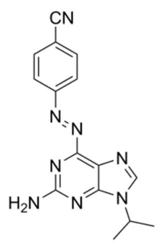
When needed, additional recrystallization was done from ethyl acetate/pentane.

Scale-up synthesis of a representative example **9c**:

The reaction was carried out using a microwave vessel (30 mL) equipped with a magnetic stirring bar, in the presence of air. 6-Chloro-9-isopropyl-*9H*-purin-2-amine **8** (592 mg, 2.8 mmol, 1.0 equiv), phenylhydrazine hydrochloride (490 mg, 3.4 mmol, 1.2 equiv), DIPEA (2.4 mL, 17 mmol, 6 equiv) and *n*-BuOH (12.0 mL) were added in sequence. The resulting mixture was reacted under microwave irradiation (200 W) at 180 ℃ for 2 h. After the substitution was completed (followed by TLC), the reaction mixture was exposed to a pure oxygen for 4 h. After the reaction was finished (followed by TLC), the solvent was removed under reduced pressure and the product was purified by flash column chromatography (SiO_2, DCM/MeOH 96:4) to give **9c (**611 mg, 0.26 mmol, 87%) as the red solids.

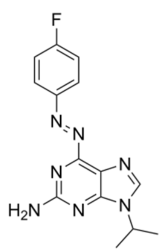
^{1}H, ^{13}C and ^{19}F NMR Spectra of 6-Azoguanines (9a-h)

(*E*)-4-((2-amino-9-isopropyl-*9H*-purin-6-yl)diazenyl)benzonitrile (**9a**):



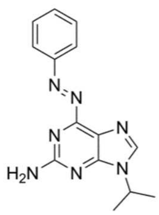
Dark red solid; Yield: 80 mg (0.26 mmol, 87%); m.p. = >250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (d, J = 6.8 Hz, 6H; $CH(CH_3)_2$), 4.83 (hept, J = 6.8 Hz, 1H; $CH(CH_3)_2$), 5.46 (br, 2H; NH_2), 7.86 (d, J = 8.5 Hz, 2H; *m*-Ar), 8.09 (s, 1H; C8-H), 8.28 (d, J = 8.5 Hz, 2H; *o*-Ar). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.4, 47.2, 115.8, 118.1, 121.7, 124.3, 133.2, 142.7, 154.6, 157.1, 159.3(one signal missing due to overlap); IR (ATR) $\tilde{\nu}$ 3299, 3193, 2222, 1629, 1615, 1574, 1501, 1363, 1277, 1143, 1087, 993, 847, 630 cm^{-1};HRMS (ESI^+) calc. for $C_{15}H_{15}N_8$ $[M+H]^+$: 307.1414, found: 307.1414.

(*E*)-6-((4-fluorophenyl)diazenyl)-9-isopropyl-*9H*-purin-2-amine (**9b**):



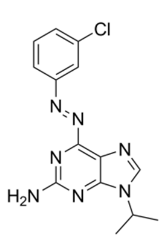
Dark red solid; Yield: 89 mg (0.3 mmol, 99%); m.p. = 199-202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (d, J = 6.8 Hz, 6H; $CH(CH_3)_2$), 4.81 (hept, J = 6.8 Hz, 1H; $CH(CH_3)_2$), 5.76 (br, 2H; NH_2), 7.14 – 7.29 (m, 2H; *m*-Ar), 8.11 (s, 1H; C8-H), 8.21 – 8.33 (m, 2H; *o*-Ar). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.3, 47.4, 116.4 (d, J = 23.1 Hz), 120.66, 127.0 (d, J = 9.6 Hz), 140.0, 142.9, 149.5 (d, J = 2.9 Hz), 157.0, 158.7, 166.2 (d, J = 257.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.17 (s); IR (ATR) $\tilde{\nu}$3312, 3190, 3097, 2984, 1635, 1592, 1562, 1499, 1458, 1369, 1313, 1222, 1137, 1001, 792, 636 cm^{-1};HRMS (ESI^+) calc. for $C_{14}H_{15}N_7F$ $[M+H]^+$: 300.1368, found: 300.1370.

(*E*)-9-isopropyl-6-(phenyldiazenyl)-*9H*-purin-2-amine (**9c**):



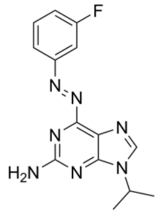
Red solid; Yield: 72 mg (0.26 mmol, 85%); m.p. = 192-195 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.61 (d, J = 6.8 Hz, 6H; $CH(CH_3)_2$), 4.79 (hept, J = 6.8 Hz, 1H; $CH(CH_3)_2$), 5.52 (br, 2H; NH_2), 7.45 – 7.61 (m, 3H; *p*-,*m*-Ar), 8.02 (s, 1H; C8-H), 8.11 – 8.23 (m, 2H; *o*-Ar). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.4, 47.1, 121.1, 124.3, 129.1, 133.3, 142.3, 153.0, 156.8, 157.4, 159.1; IR (ATR) $\tilde{\nu}$ 3346, 3305, 3188, 2968, 1727, 1613, 1572, 1472, 1365, 1235, 1082, 991, 880, 772, 694, 634 cm^{-1};HRMS (ESI^+) calc. for $C_{14}H_{16}N_7$ $[M+H]^+$: 282.1462, found: 282.1465.

(*E*)-6-((3-chlorophenyl)diazenyl)-9-isopropyl-*9H*-purin-2-amine (**9d**):



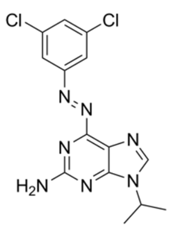
Dark red solid; Yield: 85 mg (0.27 mmol, 90%); m.p. = 89-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63 (d, J = 6.8 Hz, 6H; $CH(CH_3)_2$), 4.81 (hept, J = 6.8 Hz, 1H; $CH(CH_3)_2$), 5.44 (br, 2H; NH_2), 7.45 – 7.61 (m, 2H; *o*-,*p*-Ar), 8.06 (s, 1H; C8-H), 8.09 – 8.17 (m, 2H; *o*-,*m*-Ar). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.4, 47.2, 122.4, 124.4, 130.2, 133.0, 135.3, 142.6, 153.6, 157.0, 159.0; IR (ATR) $\tilde{\nu}$ 3497, 3307, 3198, 2977, 1710, 1628, 1601, 1574, 1421, 1371, 1273, 1235, 1069, 993, 880, 796, 680, 637 cm^{-1};HRMS (ESI$^+$) calc. for $C_{14}H_{15}N_7Cl$ $[M+H]^+$: 316.1072, found: 316.1075.

(*E*)-6-((3-fluorophenyl)diazenyl)-9-isopropyl-*9H*-purin-2-amine (**9e**):



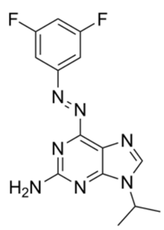
Dark red solid; Yield: 83 mg (0.27 mmol, 92%); m.p. = 160-163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.59 (d, *J* = 6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 4.77 (hept, *J* = 6.8 Hz, 1H; C*H*(CH$_3$)$_2$), 5.40 (br, 2H; NH_2), 7.18 – 7.31 (m, 1H; *p*-Ar), 7.43 – 7.56 (m, 1H; *m*-Ar), 7.79 (d, *J* = 9.6 Hz, 1H; *o*-Ar), 7.92 – 8.02 (m, 2H; *o*-Ar, C8-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.4, 46.9, 108.7, 108.9, 119.6, 119.8, 121.9, 122.0, 130.2, 130.3, 142.1, 154.4, 156.8, 157.8, 159.4, 161.9, 164.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.69 – -112.84 (m); IR (ATR) $\tilde{\nu}$ 3309, 3197, 2977, 2935, 1711, 1604, 1572, 1506, 1441, 1370, 1280, 1226, 1188, 992, 877, 635 cm^{-1};HRMS (ESI$^+$) calc. for $C_{14}H_{15}N_7F$ $[M+H]^+$: 300.1368, found: 300.1370.

(*E*)-6-((3,5-dichlorophenyl)diazenyl)-9-isopropyl-*9H*-purin-2-amine (**9f**):



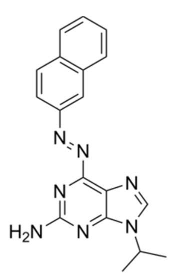
Dark red solid; Yield: 102 mg (0.29 mmol, 97%); m.p. = 101-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.61 (d, *J* = 6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 4.79 (hept, *J* = 6.8 Hz, 1H; C*H*(CH$_3$)$_2$), 5.35 (br, 2H; NH_2), 7.53 (s, 1H; *p*-Ar), 8.02 (s, 1H; C8-H), 8.05 (d, *J* = 1.9 Hz, 2H; *o*-Ar). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.4, 47.1, 121.5, 122.5, 132.2, 135.8, 142.5, 153.8, 157.0, 157.1, 159.3; IR (ATR) $\tilde{\nu}$ 3370, 3316, 3209, 3106, 2949, 1741, 1614, 1568, 1508, 1464, 1367, 1285, 1215, 994, 862, 798, 634 cm^{-1};HRMS (ESI$^+$) calc. for $C_{14}H_{14}N_7Cl_2$ $[M+H]^+$: 350.0682, found: 350.0684.

(*E*)-6-((3,5-difluorophenyl)diazenyl)-9-isopropyl-*9H*-purin-2-amine (**9g**):



Dark red solid; Yield: 79 mg (0.25 mmol, 83%); m.p. = 190-192 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63 (d, *J* = 6.8 Hz, 6H; CH(C*H*$_3$)$_2$), 4.81 (hept, *J* = 6.8 Hz, 1H; C*H*(CH$_3$)$_2$), 5.39 (br, 2H; NH_2), 7.03 (tt, *J* = 8.3, 2.4 Hz, 1H; *p*-Ar), 7.69 – 7.78 (m, 2H; *o*-Ar), 8.05 (s, 1H; C8-H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.4, 47.2, 107.1 – 107.4 (m), 107.8 (t, *J* = 26.0 Hz), 121.3, 142.6, 154.5 (t, *J*= 9.1 Hz), 156.9 (d, *J* = 15.1 Hz), 159.3, 161.8 (d, *J* = 12.8 Hz), 164.3 (d, *J* = 12.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.21 (t, *J* = 7.6 Hz); IR (ATR) $\tilde{\nu}$ 3449, 3282, 3097, 2934, 1713, 1598, 1504, 1439, 1405, 1368, 1298, 1228, 1118, 851, 631 cm^{-1};HRMS (ESI$^+$) calc. for $C_{14}H_{14}N_7F_2$ $[M+H]^+$: 318.1273, found: 318.1275.

(*E*)-9-isopropyl-6-(naphthalen-2-yldiazenyl)-*9H*-purin-2-amine (**9h**):



Brown solid; Yield: 94 mg (0.28 mmol, 95%); m.p. = 209-212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.63 (d, *J* = 7.7 Hz, 6H; CH(C*H*$_3$)$_2$), 4.81 (hept, *J* = 6.8 Hz, 1H; C*H*(CH$_3$)$_2$), 5.40 (br, 2H; NH_2), 7.50 – 7.69 (m, 2H; Ar), 7.87 – 7.95 (m, 2H; Ar), 8.03 (s, 1H; Ar), 8.06 (d, *J* = 7.9 Hz, 1H; Ar), 8.23 (dd, *J* = 9.0, 1.7 Hz, 1H; Ar), 8.83 (d, *J* = 1.9 Hz, 1H; Ar). ^{13}C NMR (101 MHz, $CDCl_3$) δ 22.5, 46.9, 116.8, 121.4, 126.9, 128.0, 128.6, 129.2, 130.0, 131.7, 133.3, 135.8, 142.0, 150.8, 156.7, 158.2, 159.4; IR (ATR) $\tilde{\nu}$3407, 3301, 3231, 3104, 1978, 1629, 1574, 1509, 1464, 1394, 1286, 1219, 1109, 992, 866, 819, 757, 634 cm^{-1};HRMS (ESI$^+$) calc. for $C_{18}H_{18}N_7$ $[M+H]^+$: 332.1618, found: 332.1620.

UV-Vis spectroscopy: thermally adapted and PSS spectra

6-Azoadenines

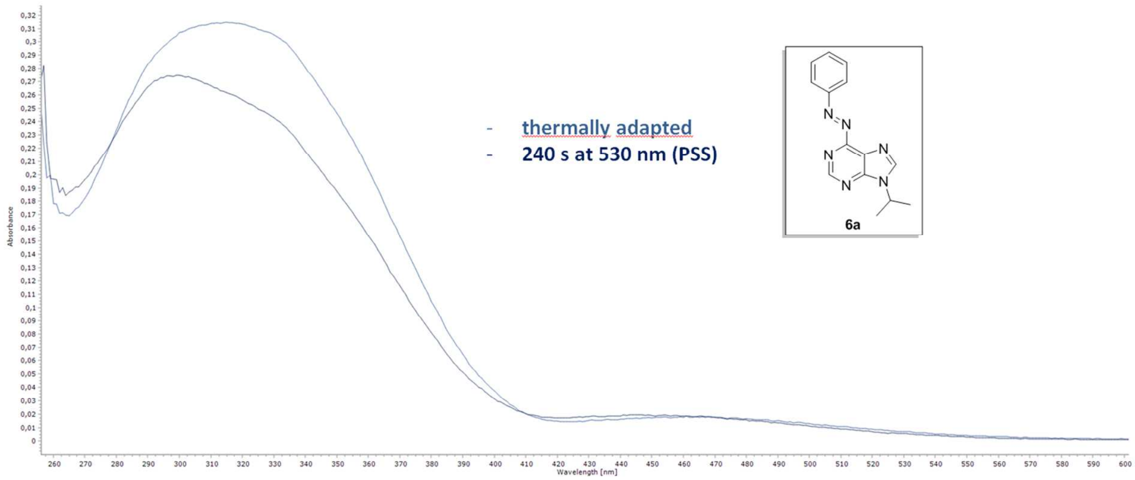


Figure S2. Thermally adapted and photostationary state spectra of compound **6a** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

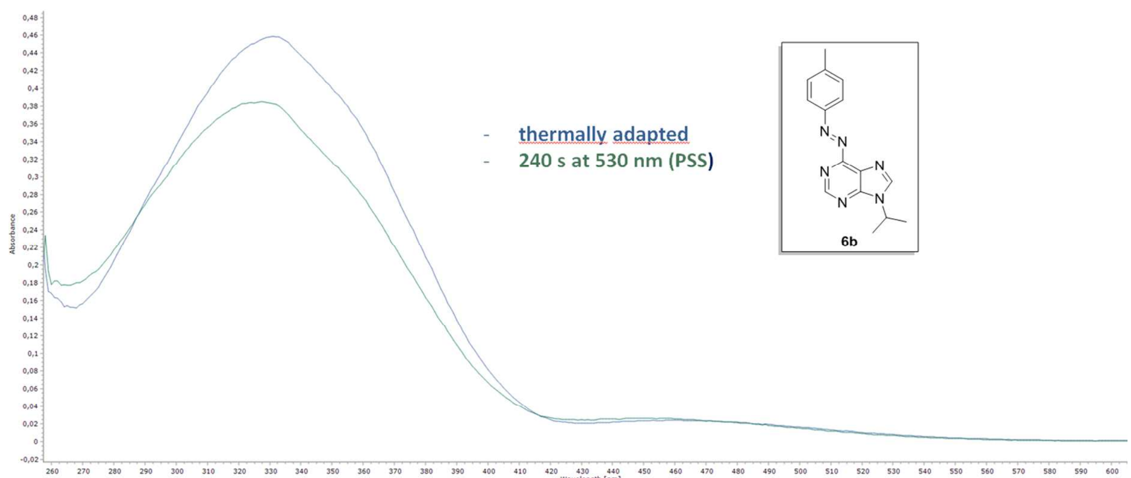


Figure S3. Thermally adapted and photostationary state spectra of compound **6b** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

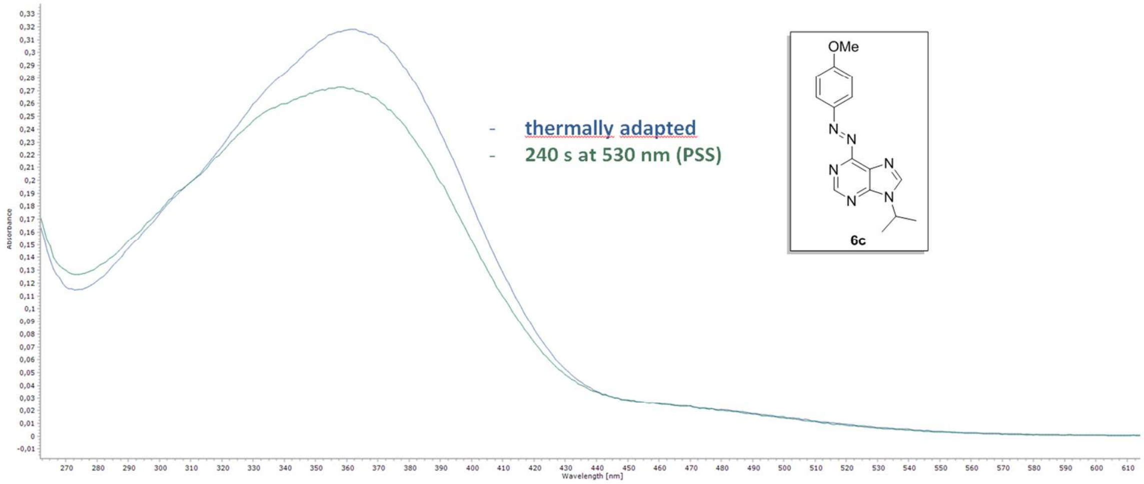


Figure S4. Thermally adapted and photostationary state spectra of compound **6c** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

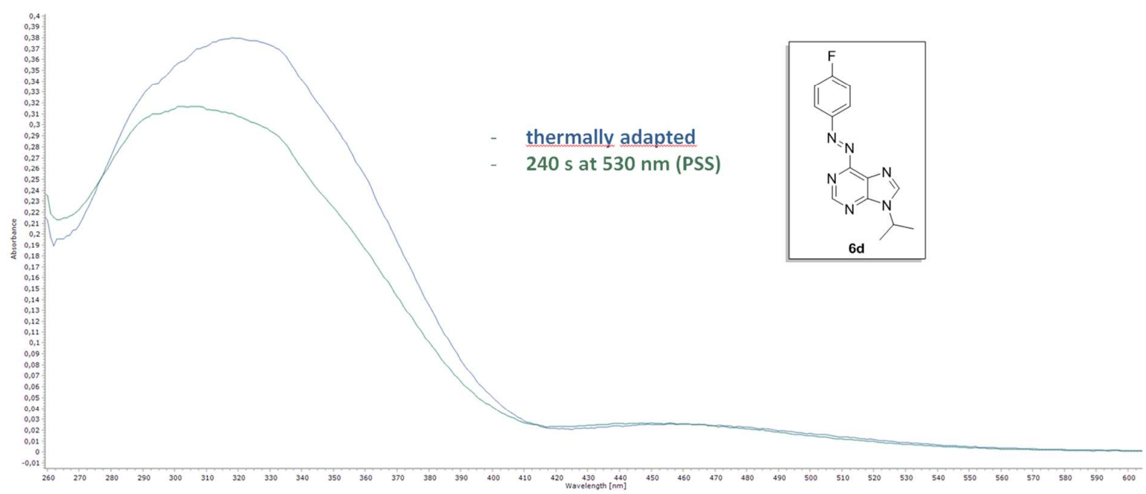


Figure S5. Thermally adapted and photostationary state spectra of compound **6d** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

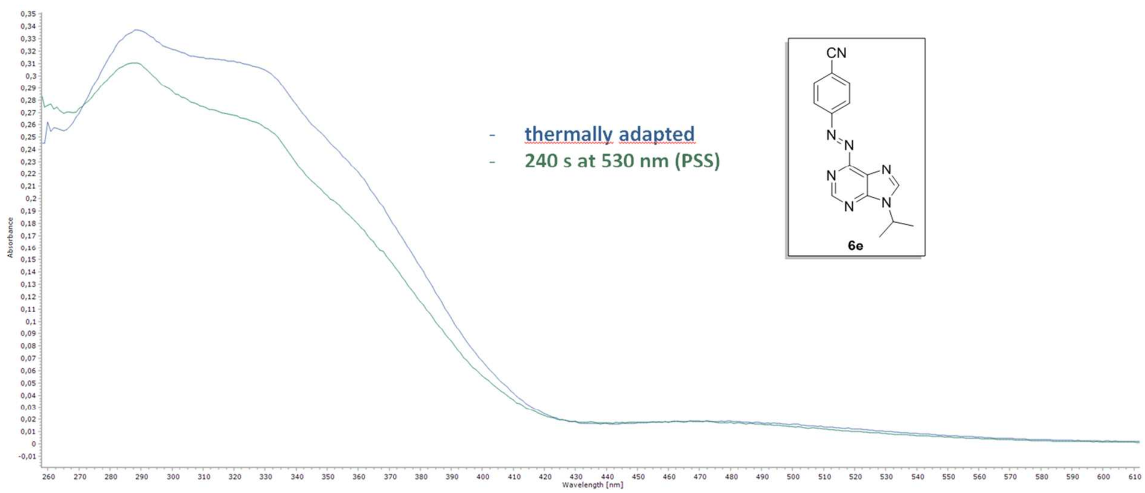


Figure S6. Thermally adapted and photostationary state spectra of compound **6e** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

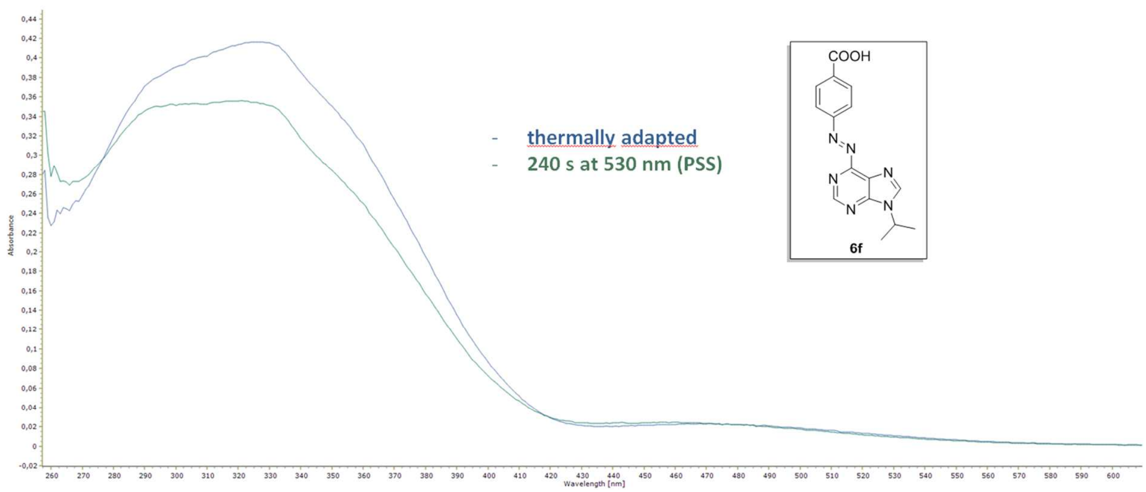


Figure S7. Thermally adapted and photostationary state spectra of compound **6f** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

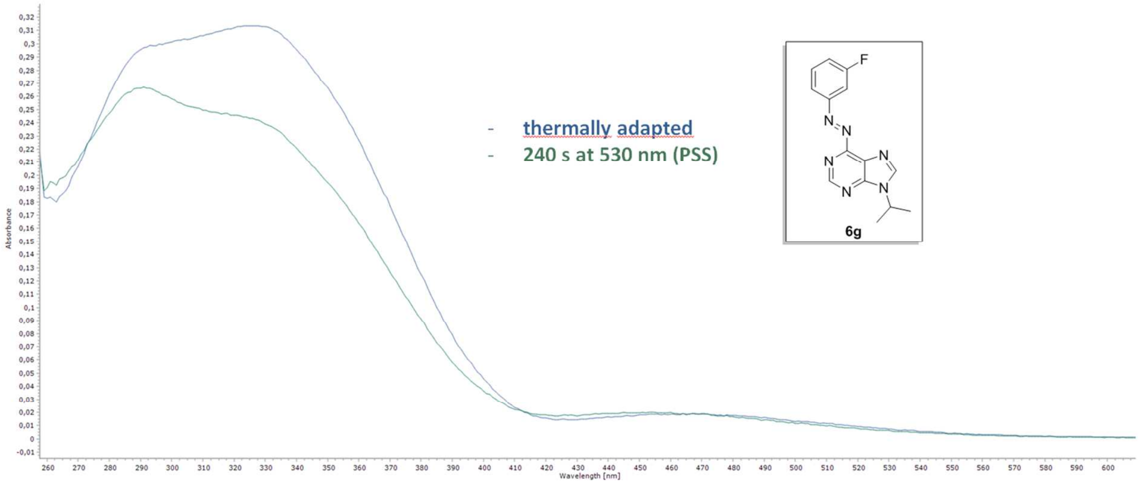


Figure S8. Thermally adapted and photostationary state spectra of compound **6g** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

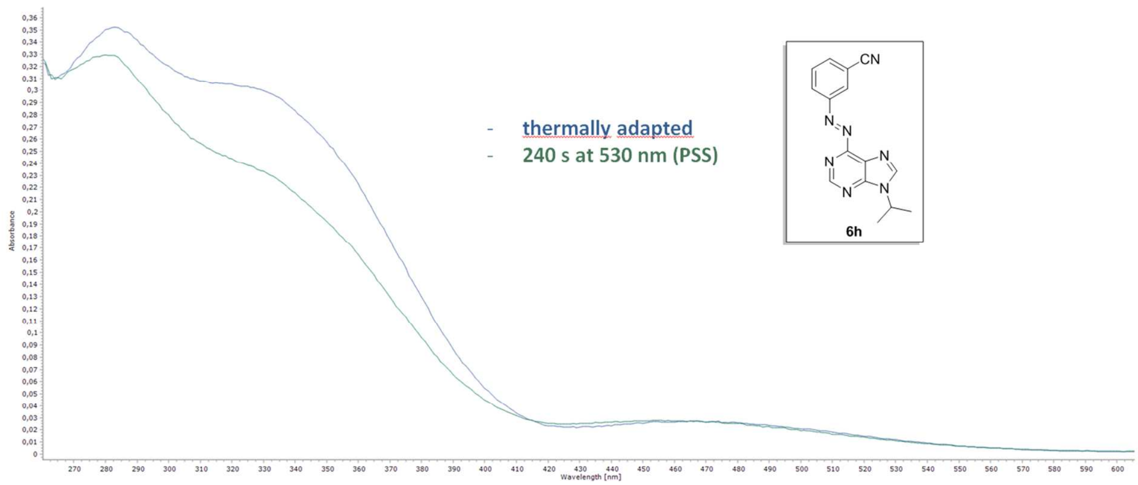


Figure S9. Thermally adapted and photostationary state spectra of compound **6h** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

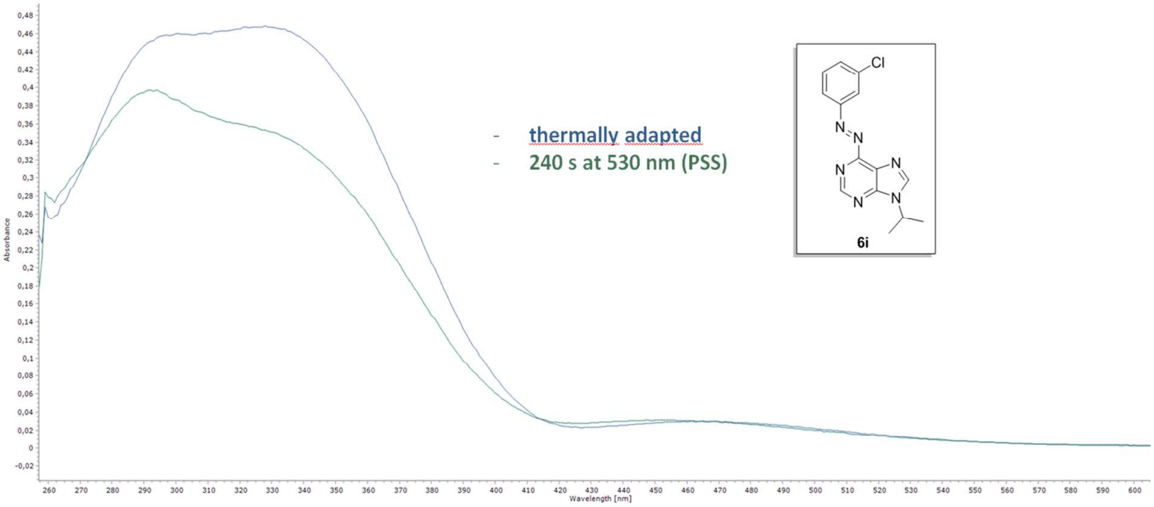


Figure S10. Thermally adapted and photostationary state spectra of compound **6i** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

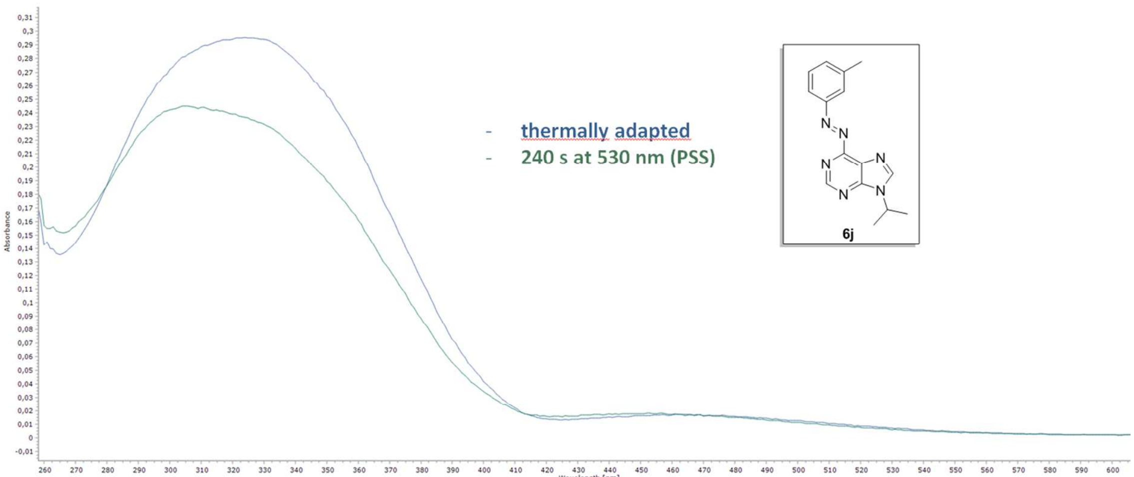


Figure S11. Thermally adapted and photostationary state spectra of compound **6j** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

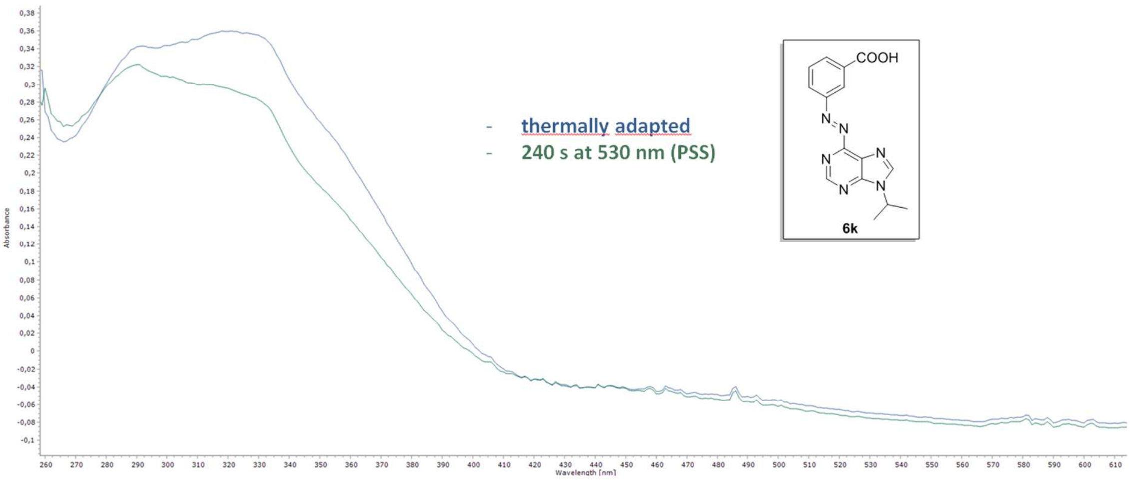


Figure S12. Thermally adapted and photostationary state spectra of compound **6k** (~40 μM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

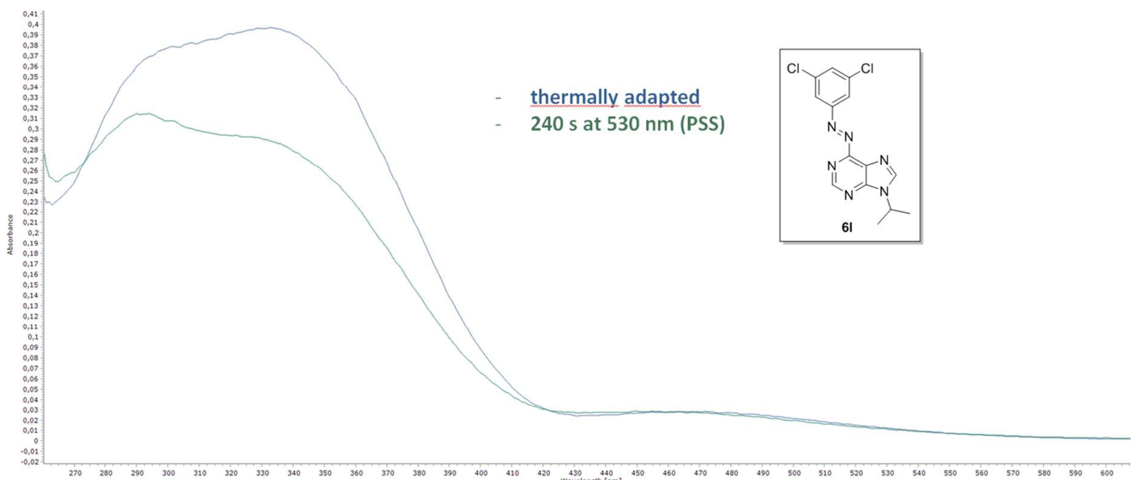


Figure S13. Thermally adapted and photostationary state spectra of compound **6l** (~40 μM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

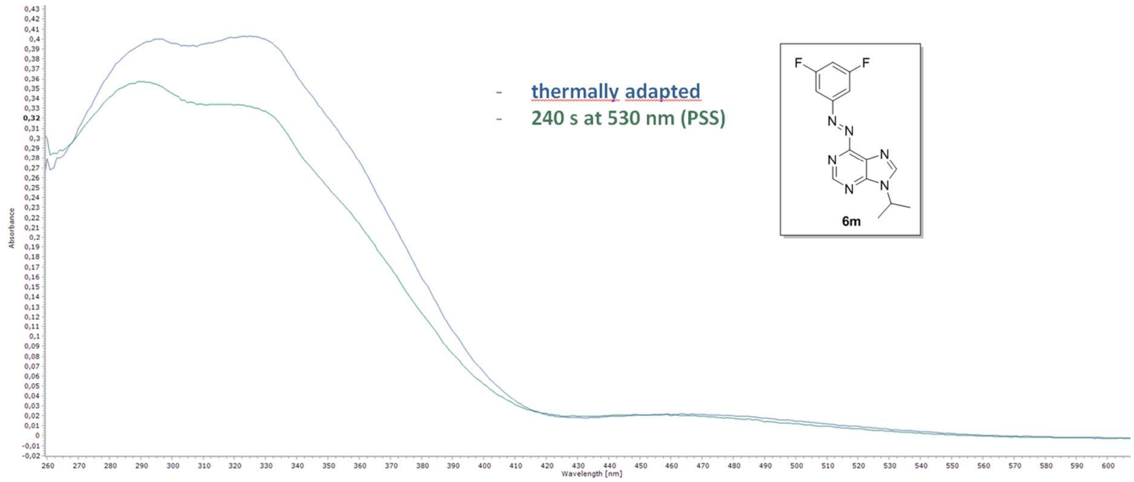


Figure S14. Thermally adapted and photostationary state spectra of compound **6m** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

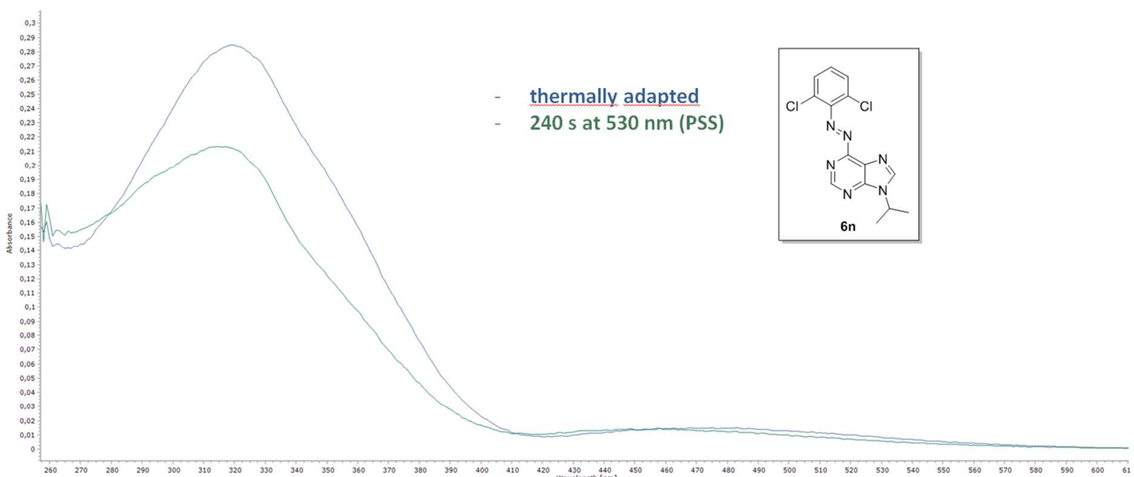


Figure S15. Thermally adapted and photostationary state spectra of compound **6n** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

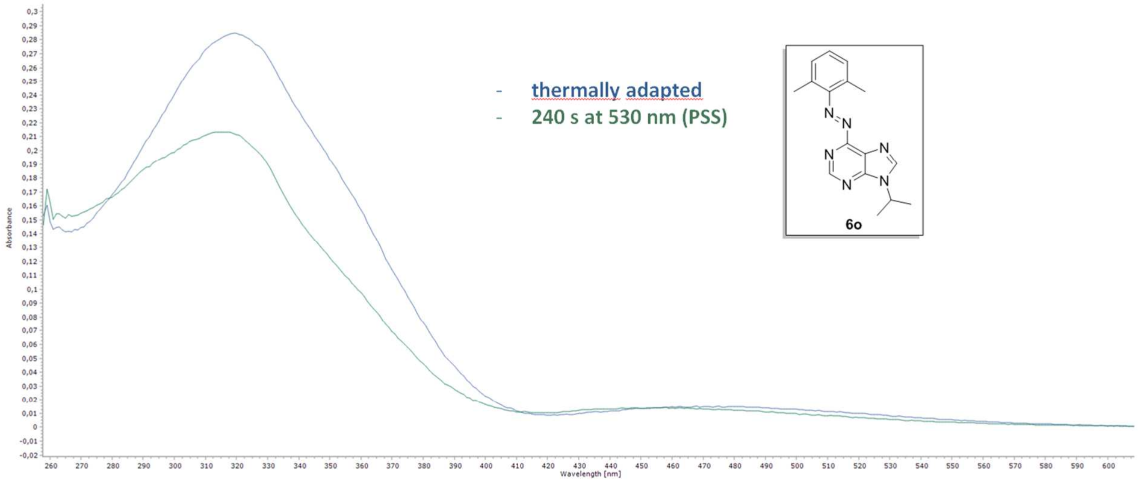


Figure S16. Thermally adapted and photostationary state spectra of compound **6o** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

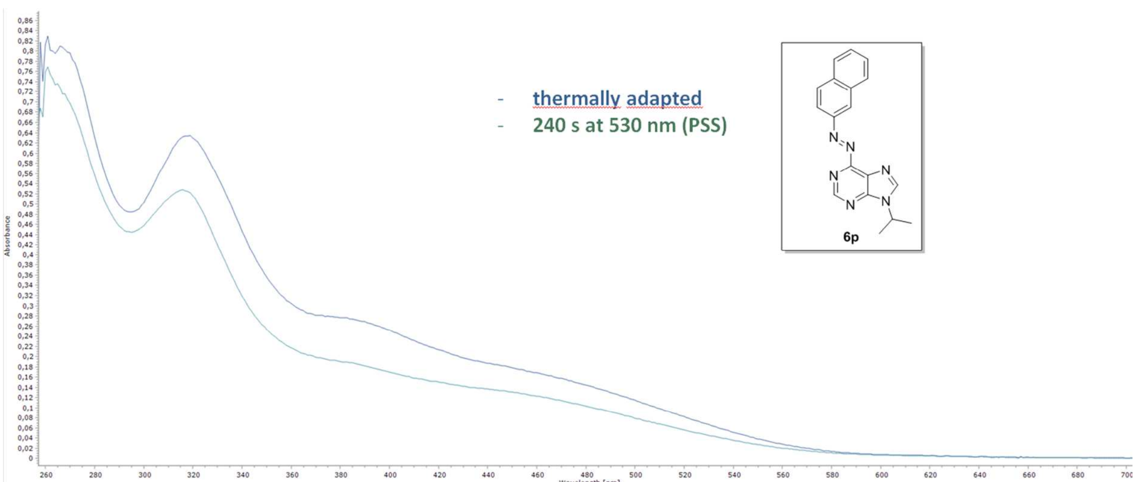


Figure S17. Thermally adapted and photostationary state spectra of compound **6p** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

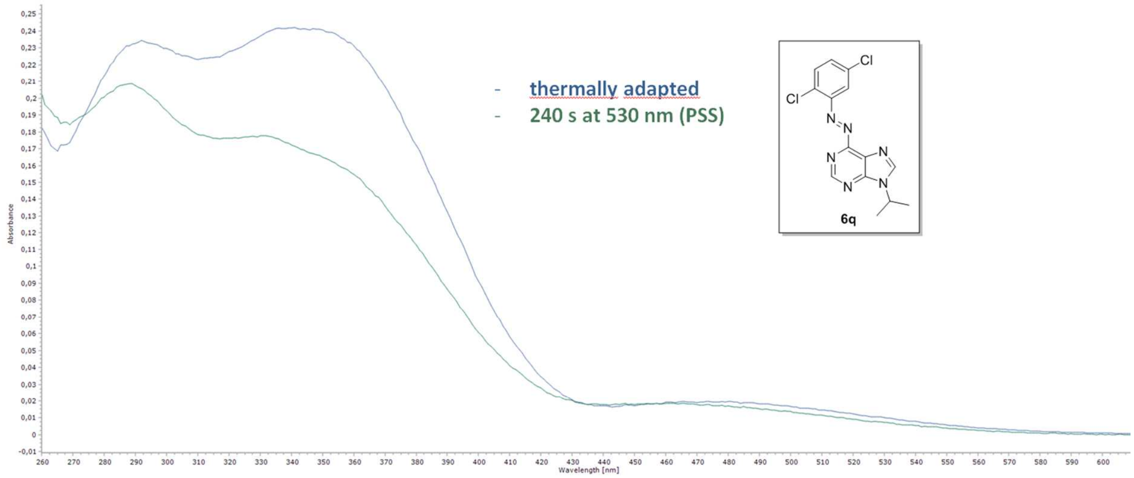


Figure S18. Thermally adapted and photostationary state spectra of compound **6q** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

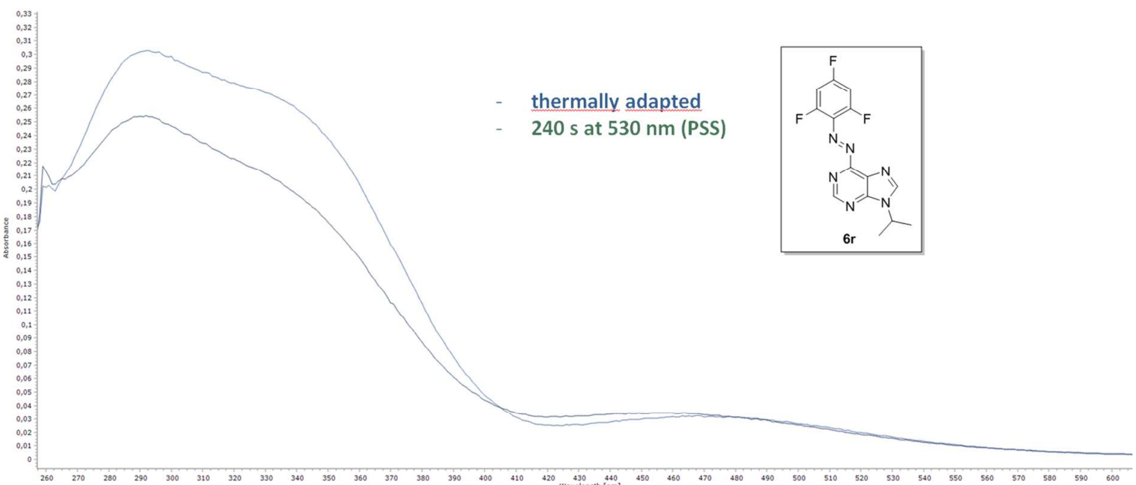


Figure S19. Thermally adapted and photostationary state spectra of compound **6r** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

6-Azoguanines

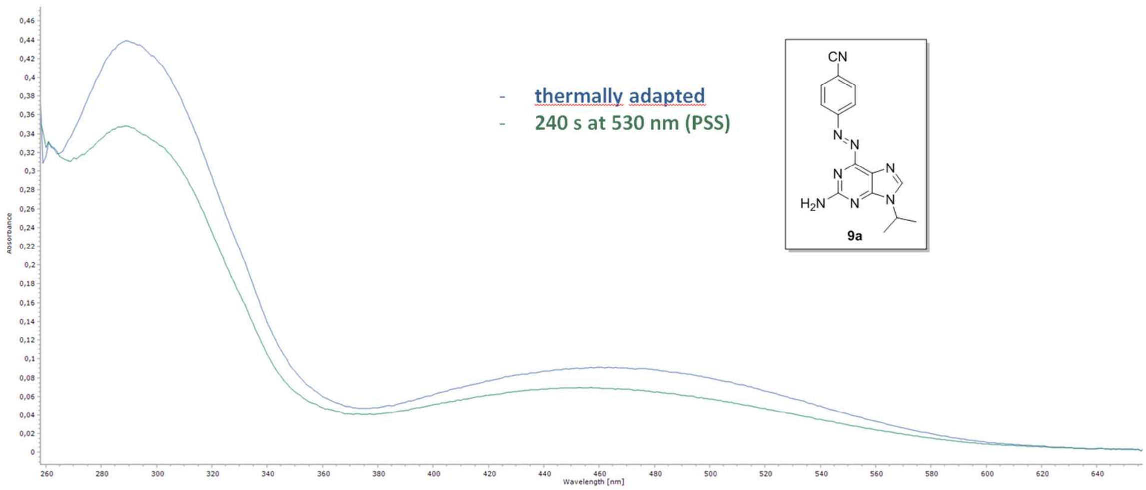


Figure S20. Thermally adapted and photostationary state spectra of compound **9a** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

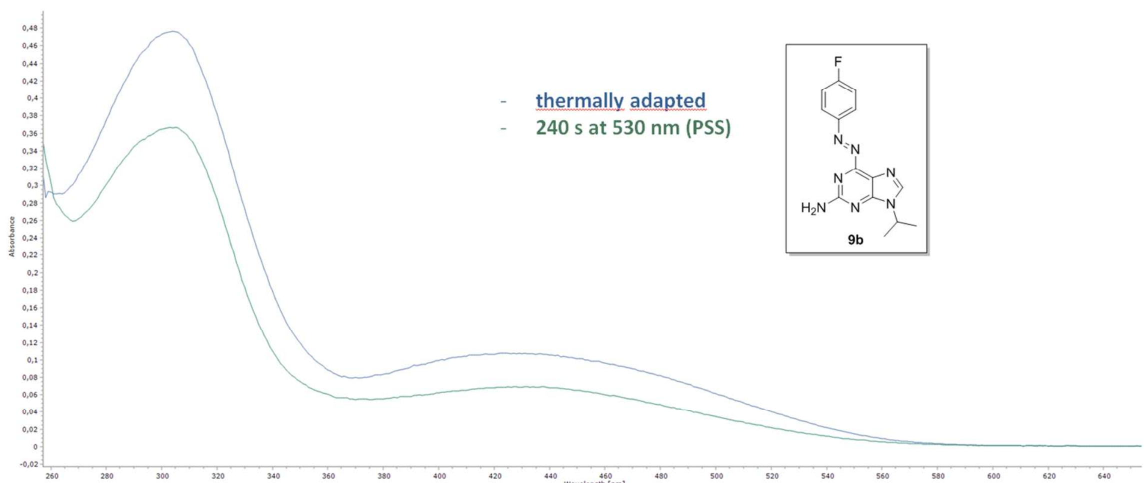


Figure S21. Thermally adapted and photostationary state spectra of compound **9b** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

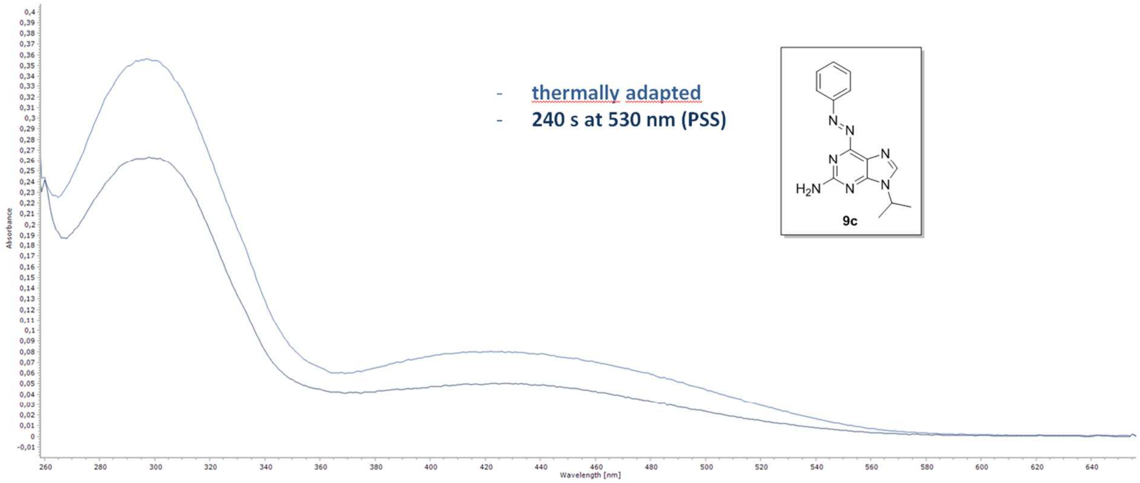


Figure S22. Thermally adapted and photostationary state spectra of compound **9c** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

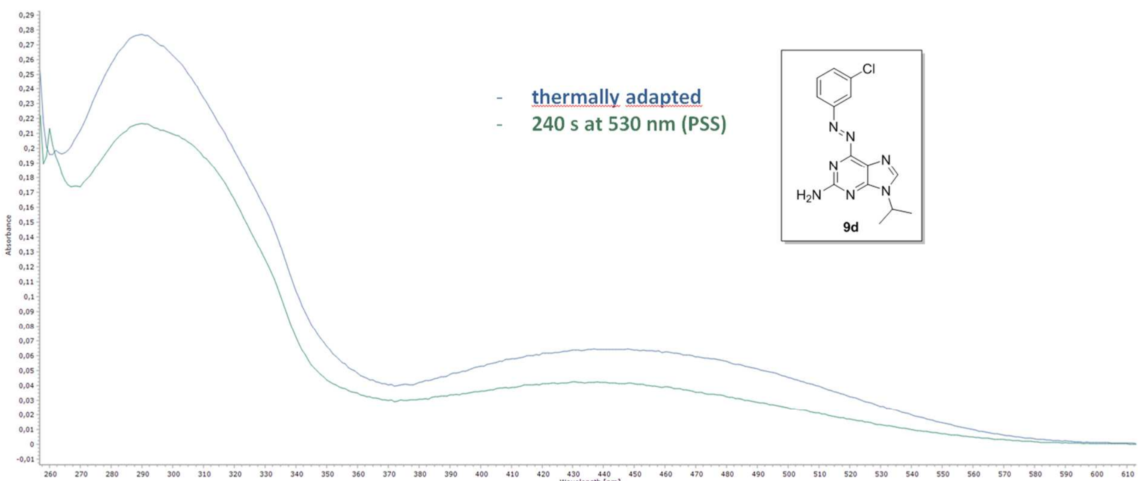


Figure S23. Thermally adapted and photostationary state spectra of compound **9d** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

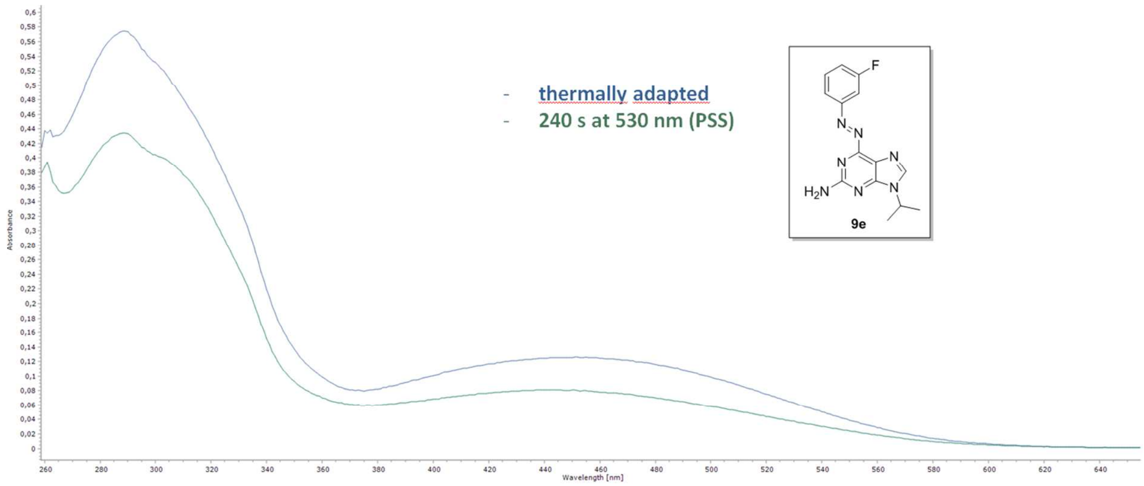


Figure S24. Thermally adapted and photostationary state spectra of compound **9e** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 4 min irradiation with green light (λ = 530 nm).

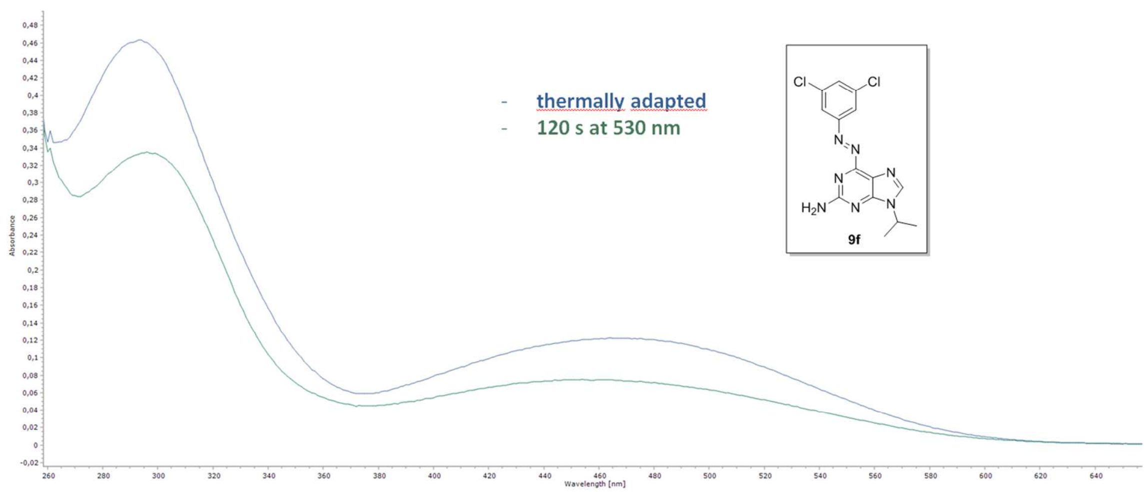


Figure S25. Thermally adapted and photostationary state spectra of compound **9f** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 2 min irradiation with green light (λ = 530 nm).

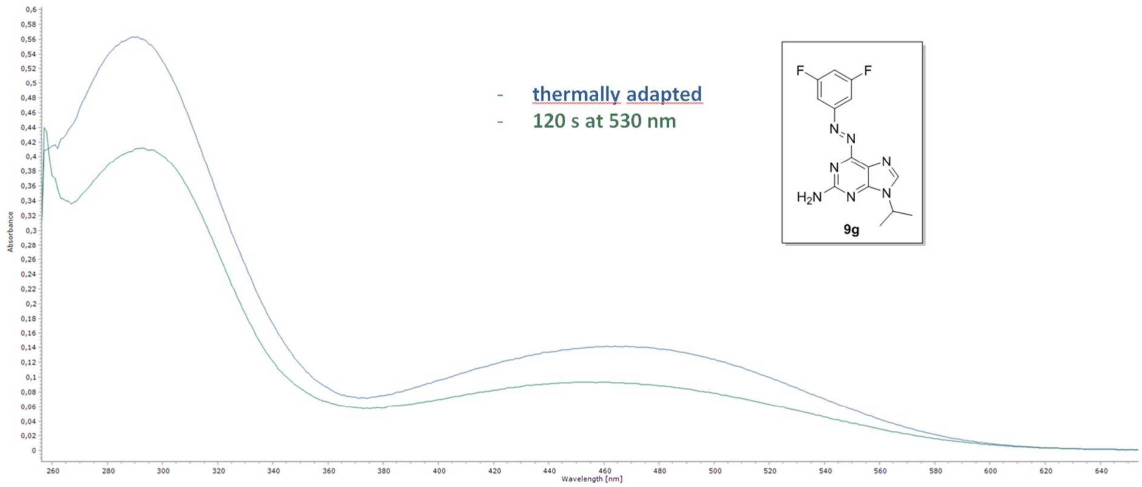


Figure S26. Thermally adapted and photostationary state spectra of compound **9g** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 2 min irradiation with green light (λ = 530 nm).

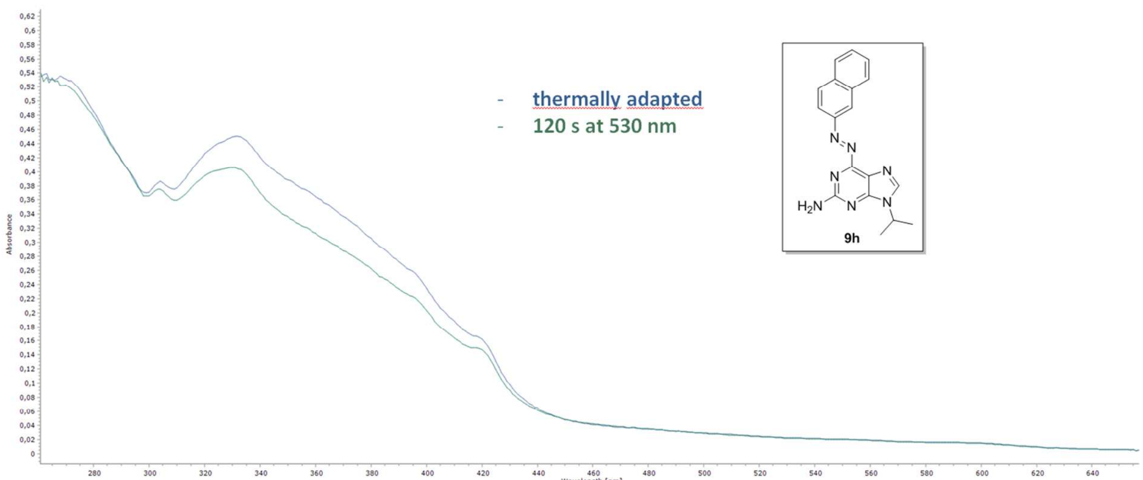


Figure S27. Thermally adapted and photostationary state spectra of compound **9h** (~40 µM in DMSO, 25 °C). Photostationary state was achieved after 2 min irradiation with green light (λ = 530 nm).

Determination of half-life

6-Azoadenines

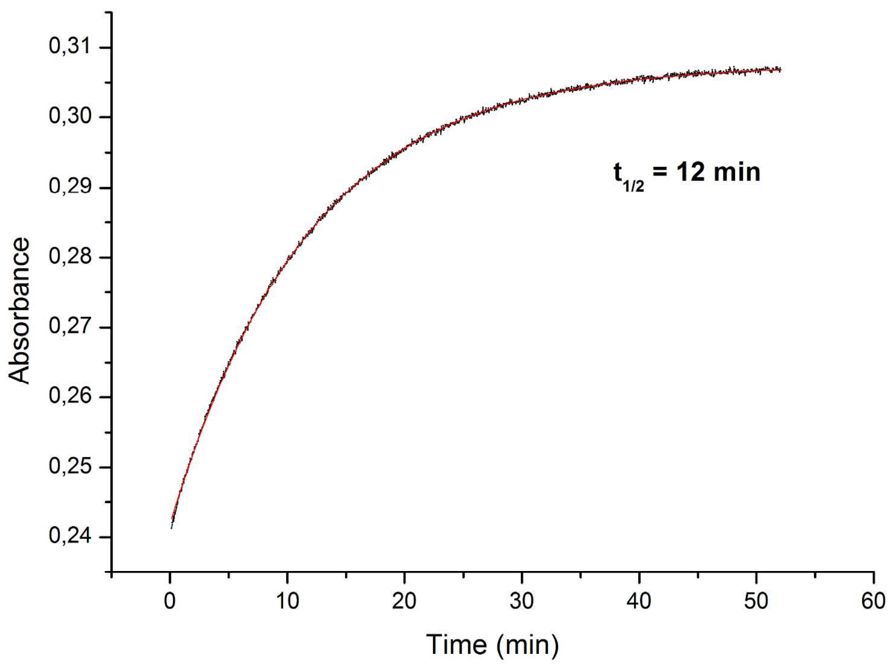


Figure S28. Determination of half-life for **6g** at 25 °C in DMSO (~40 μM). Photostationary state was reached upon irradiation with λ = 530 nm. Line presents the fitting with single exponential process.

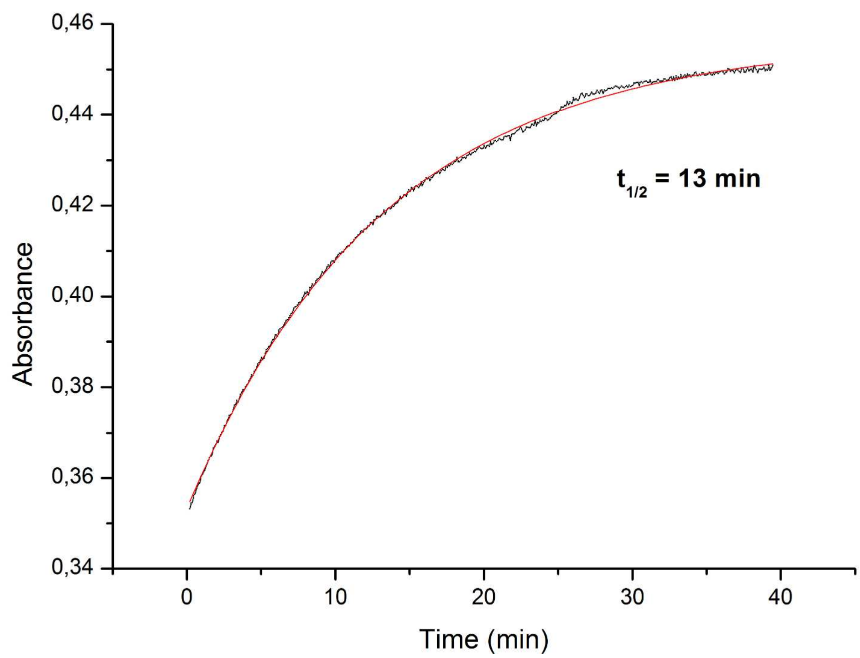


Figure S29. Determination of half-life for **6i** at 25 °C in DMSO (~40 μM). Photostationary state was reached upon irradiation with λ = 530 nm. Line presents the fitting with single exponential process.

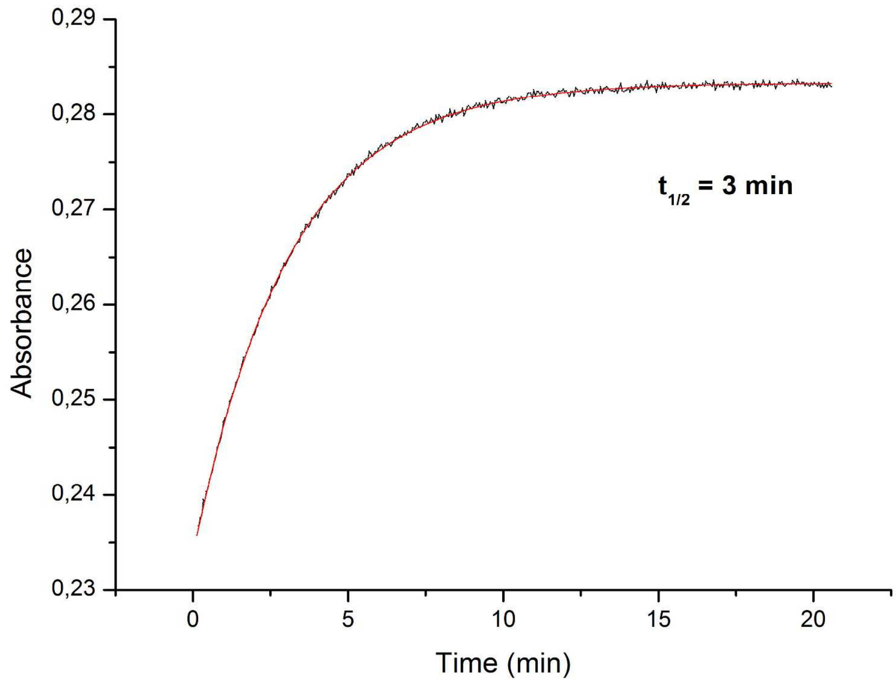


Figure S30. Determination of half-life for **6j** at 25 °C in DMSO (~40 μM). Photostationary state was reached upon irradiation with λ = 530 nm. Line presents the fitting with single exponential process.

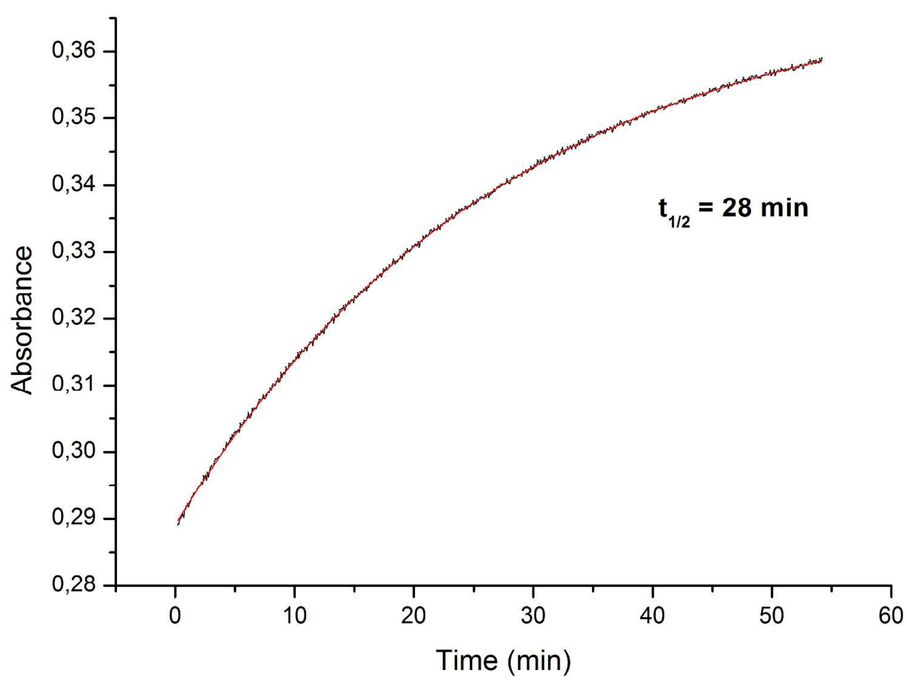


Figure S31. Determination of half-life for **6l** at 25 °C in DMSO (~40 μM). Photostationary state was reached upon irradiation with λ = 530 nm. Line presents the fitting with single exponential process.

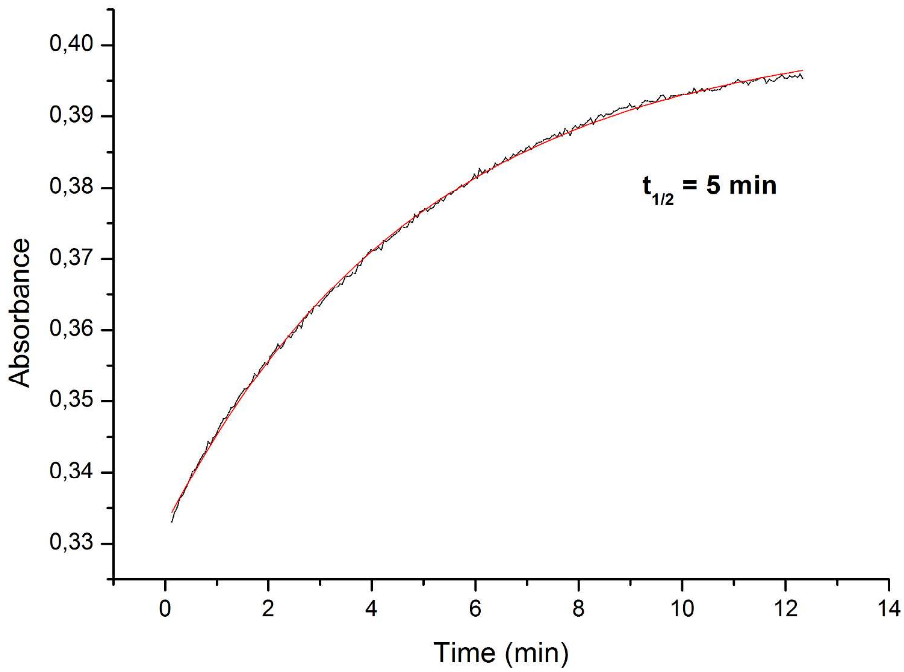


Figure S32. Determination of half-life for **6m** at 25 °C in DMSO (~40 µM). Photostationary state was reached upon irradiation with λ = 530 nm. Line presents the fitting with single exponential process.

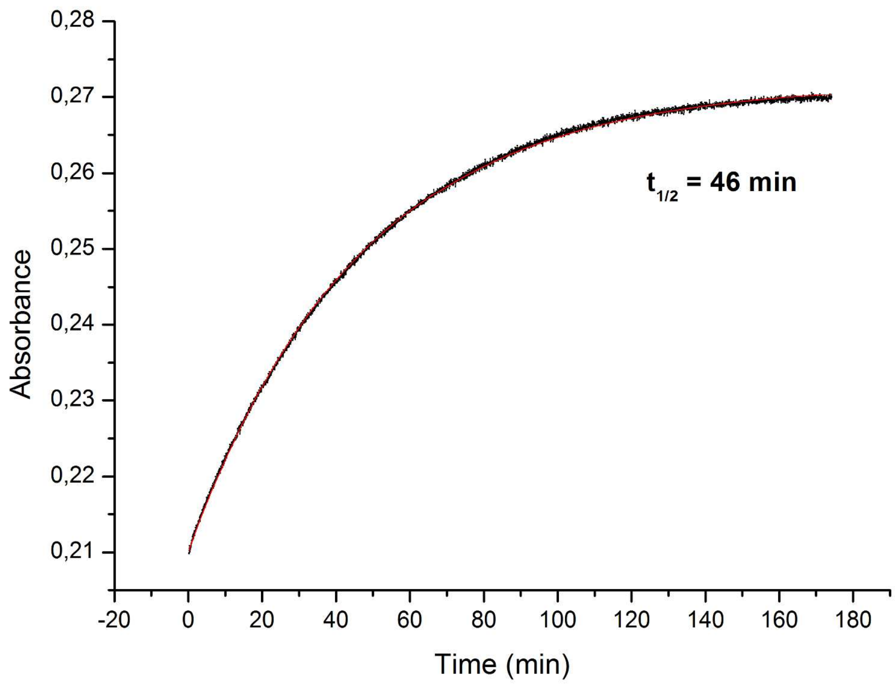


Figure S33. Determination of half-life for **6o** at 25 °C in DMSO (~40 µM). Photostationary state was reached upon irradiation with λ = 530 nm. Line presents the fitting with single exponential process.

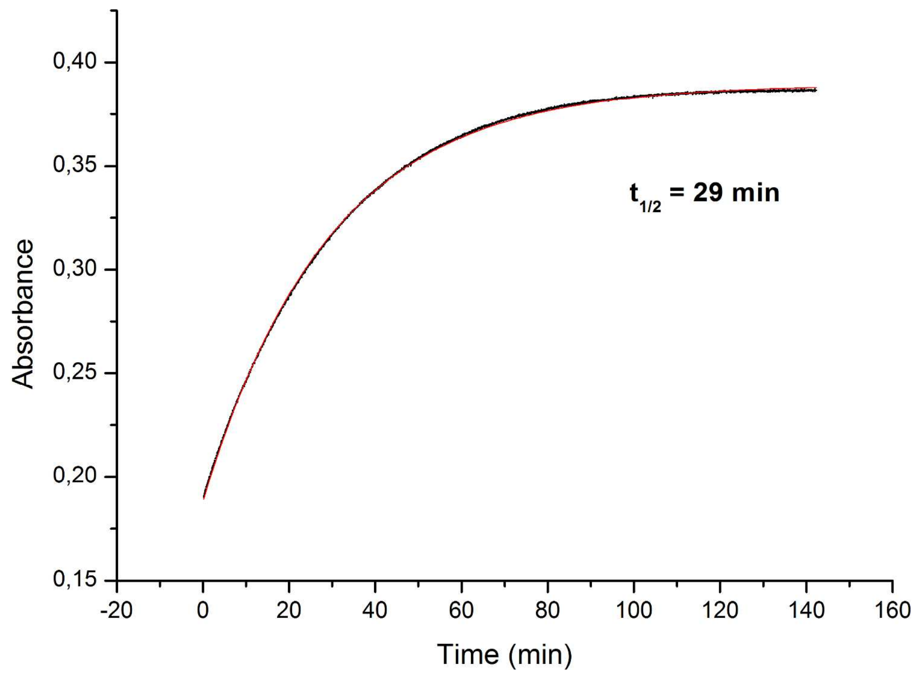


Figure S34. Determination of half-life for **6q** at 25 °C in DMSO (~40 µM). Photostationary state was reached upon irradiation with λ = 530 nm. Line presents the fitting with single exponential process.

6-Azoguanines

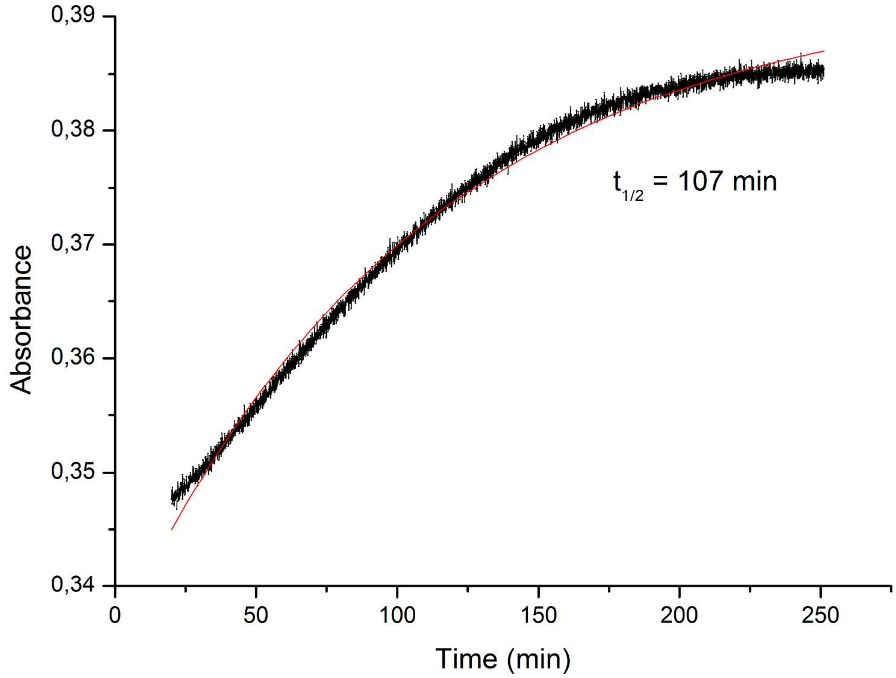


Figure S35. Determination of half-life for **9a** at 25 °C in DMSO (~40 µM). Photostationary state was reached upon irradiation with λ = 530 nm. Line presents the fitting with single exponential process.

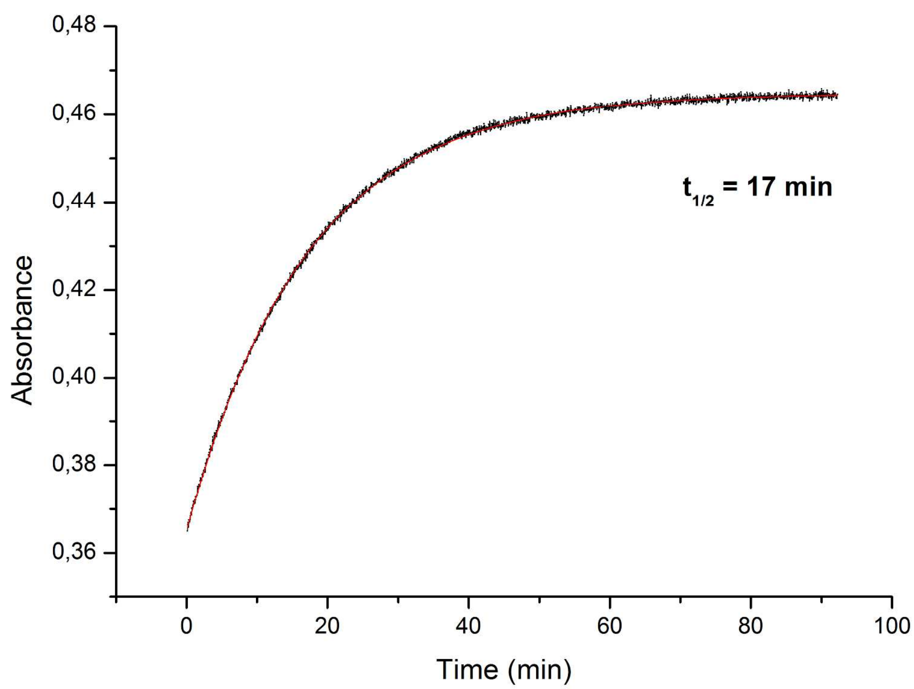


Figure S36. Determination of half-life for **9b** at 25 °C in DMSO (~40 µM). Photostationary state was reached upon irradiation with λ = 530 nm. Line presents the fitting with single exponential process.

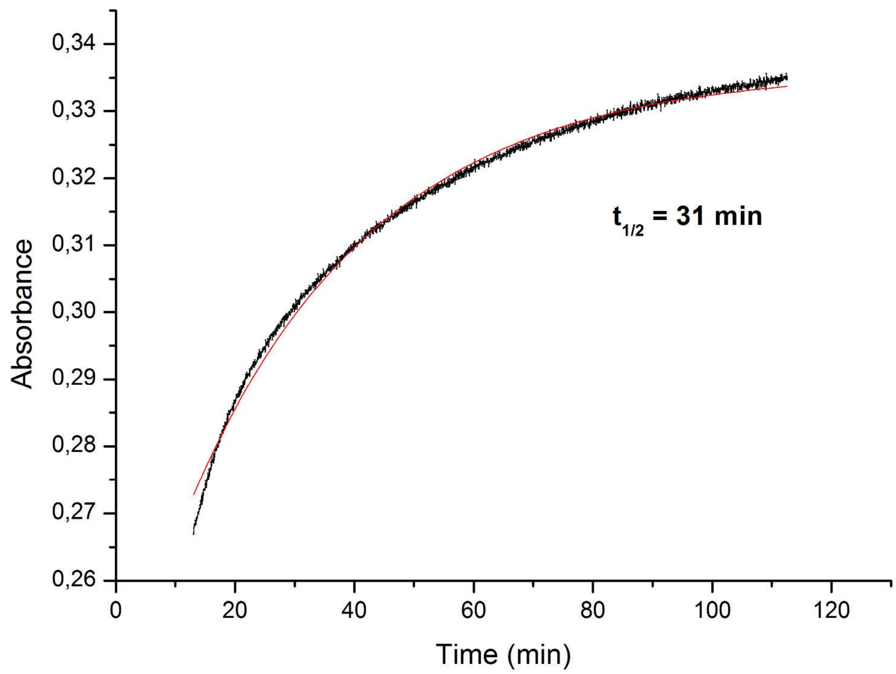


Figure S37. Determination of half-life for **9d** at 25 °C in DMSO (~40 μM). Photostationary state was reached upon irradiation with λ = 530 nm. Line presents the fitting with single exponential process.

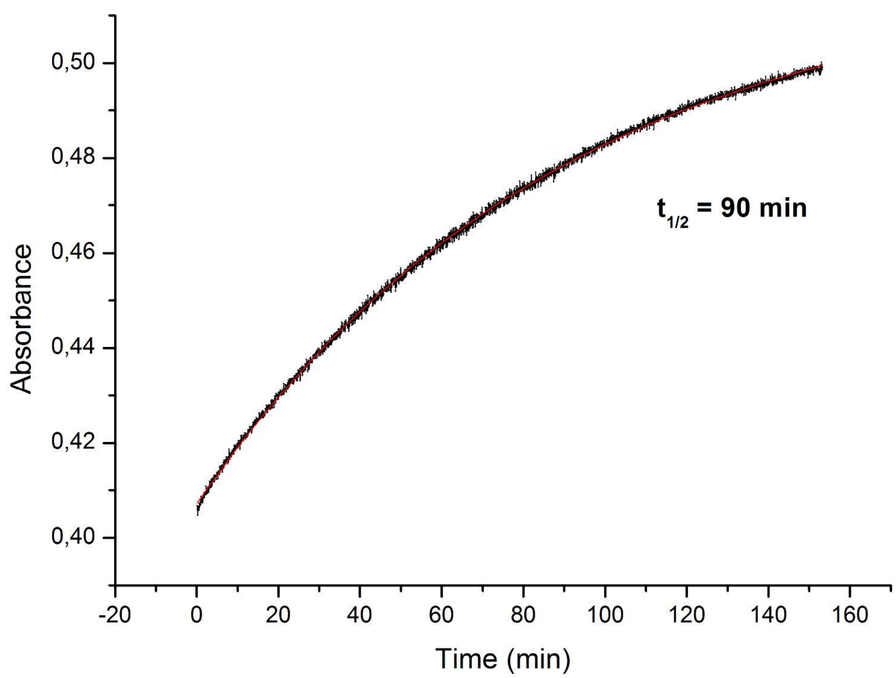


Figure S38. Determination of half-life for **9g** at 25 °C in DMSO (~40 μM). Photostationary state was reached upon irradiation with λ = 530 nm. Line presents the fitting with single exponential process.

Long-term photochromism

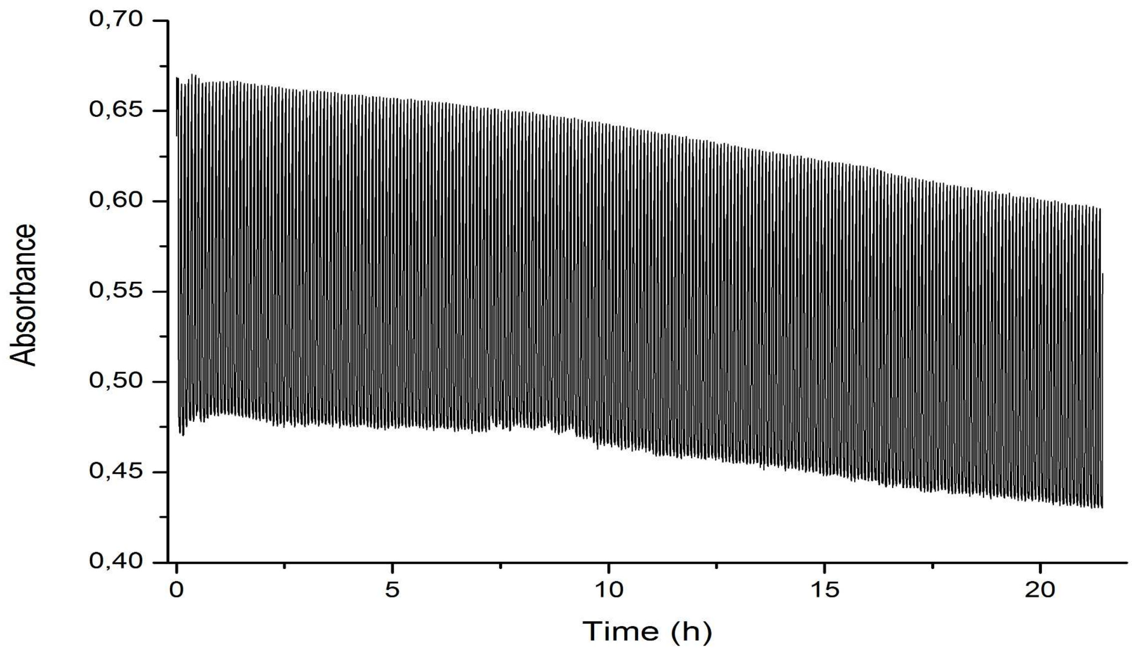


Figure S39. Long-term photochromism for **6a** at 35 °C in PBS buffer with 2 vol% DMSO, pH 7.4 (~40 µM). More than hundred cycles of 530 nm/thermal relaxation.

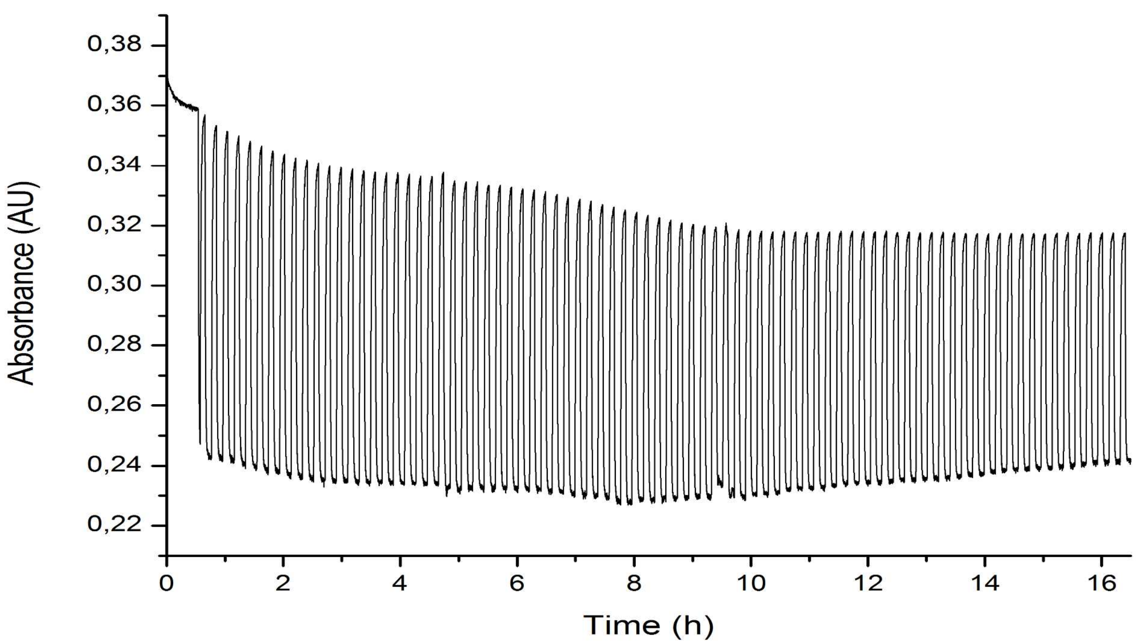


Figure S40. Long-term photochromism for **6g** at 35 °C in PBS buffer with 2 vol% DMSO, pH 7.4 (~40 µM). More than 70 cycles of 530 nm/thermal relaxation.

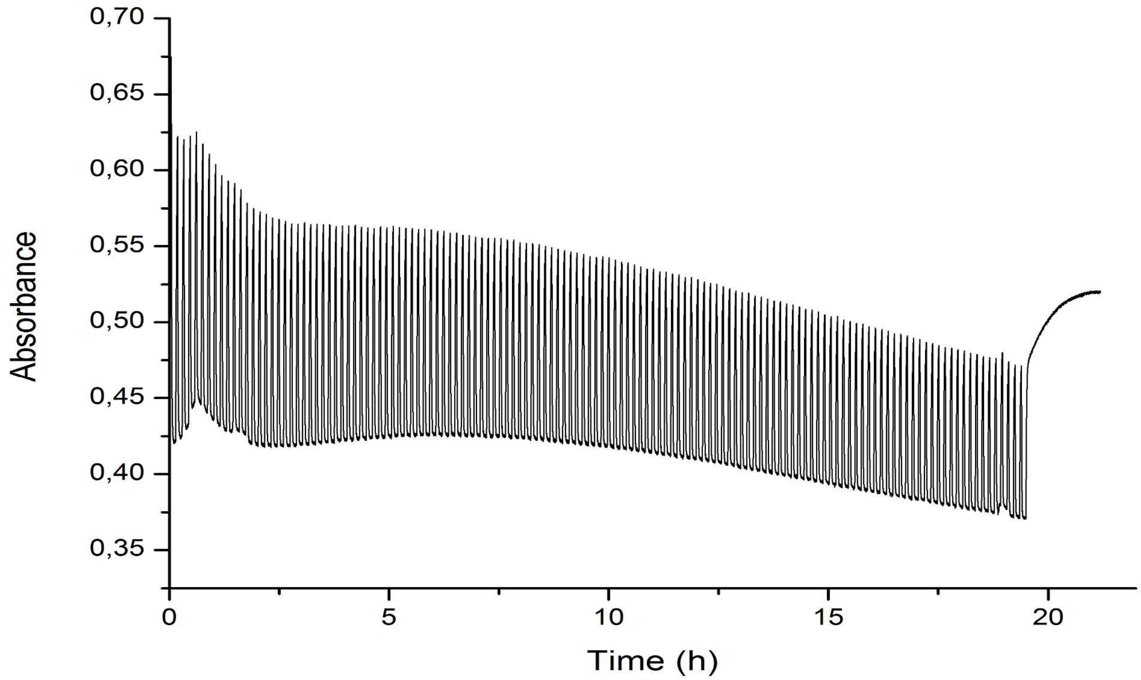


Figure S41. Long-term photochromism for **6h** at 35 °C in PBS buffer with 2 vol% DMSO, pH 7.4 (~40 µM). More than hundred cycles of 530 nm/thermal relaxation.

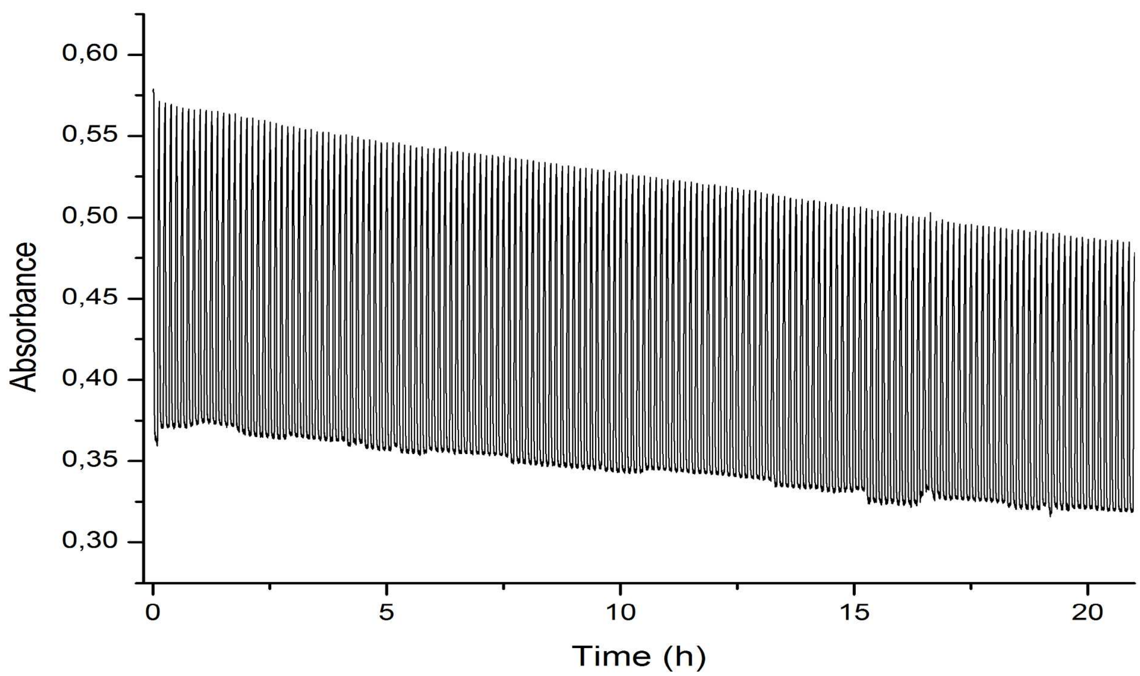


Figure S42. Long-term photochromism for **6k** at 35 °C in PBS buffer with 2 vol% DMSO, pH 7.4 (~40 µM). More than hundred cycles of 530 nm/thermal relaxation.

Reversible photochromism of 6o and 9f

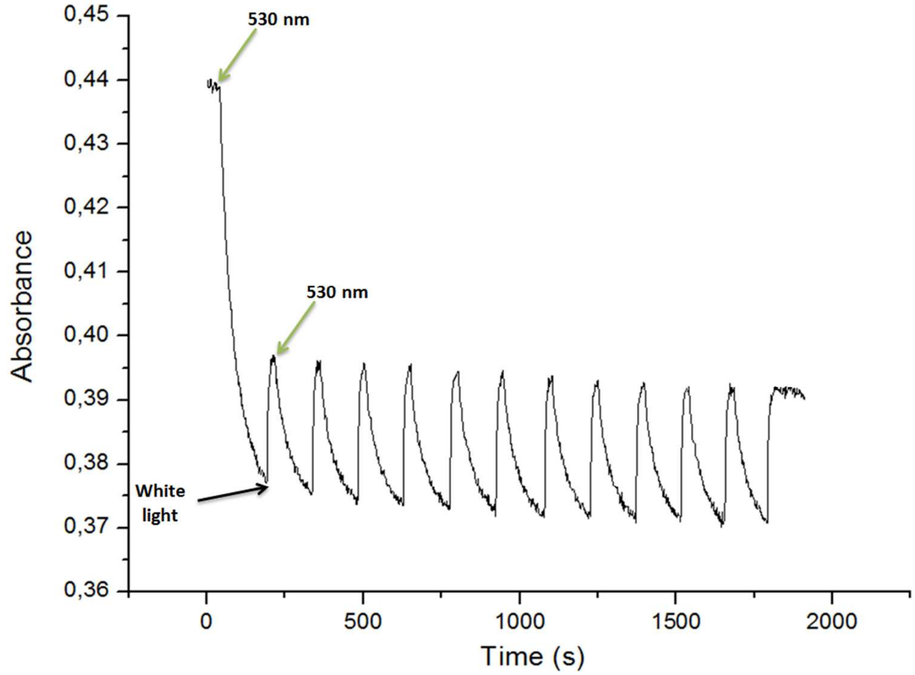


Figure S43. Reversible photochromism for 10 repeated switching cycles of compound **6o** (~40 µM in DMSO; room temperature) observed at λ_{max} = 282 nm: Switching with λ = 530 nm and white light.

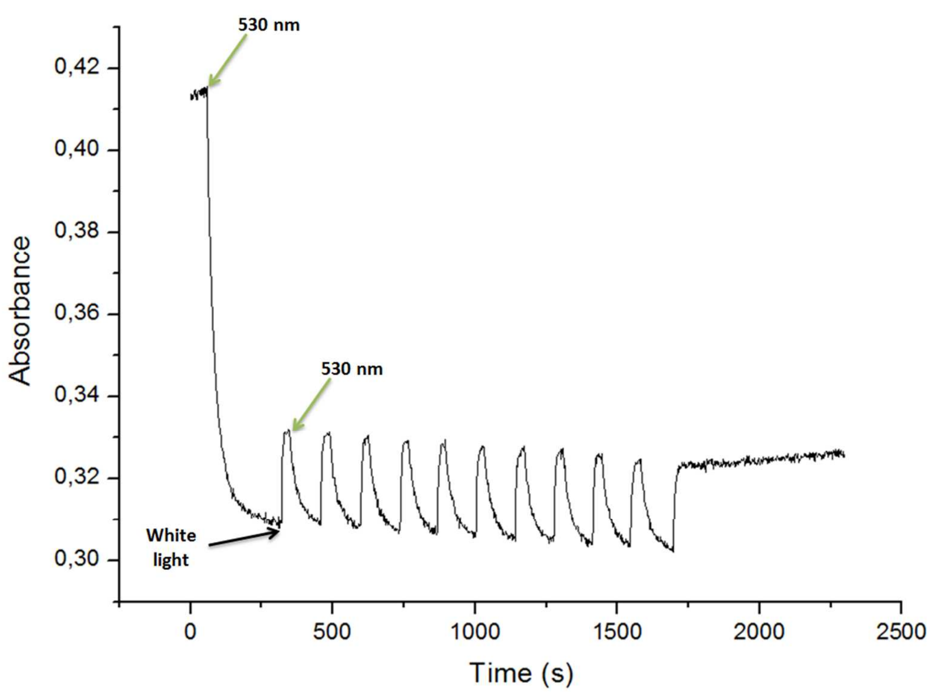


Figure S44. Reversible photochromism for 10 repeated switching cycles of compound **9f** (~40 µM in DMSO; room temperature) observed at λ_{max} = 292 nm: Switching with λ = 530 nm and white light.

Determination of PSS by NMR and UV-Vis

NMR and UV-Vis studies of 6o

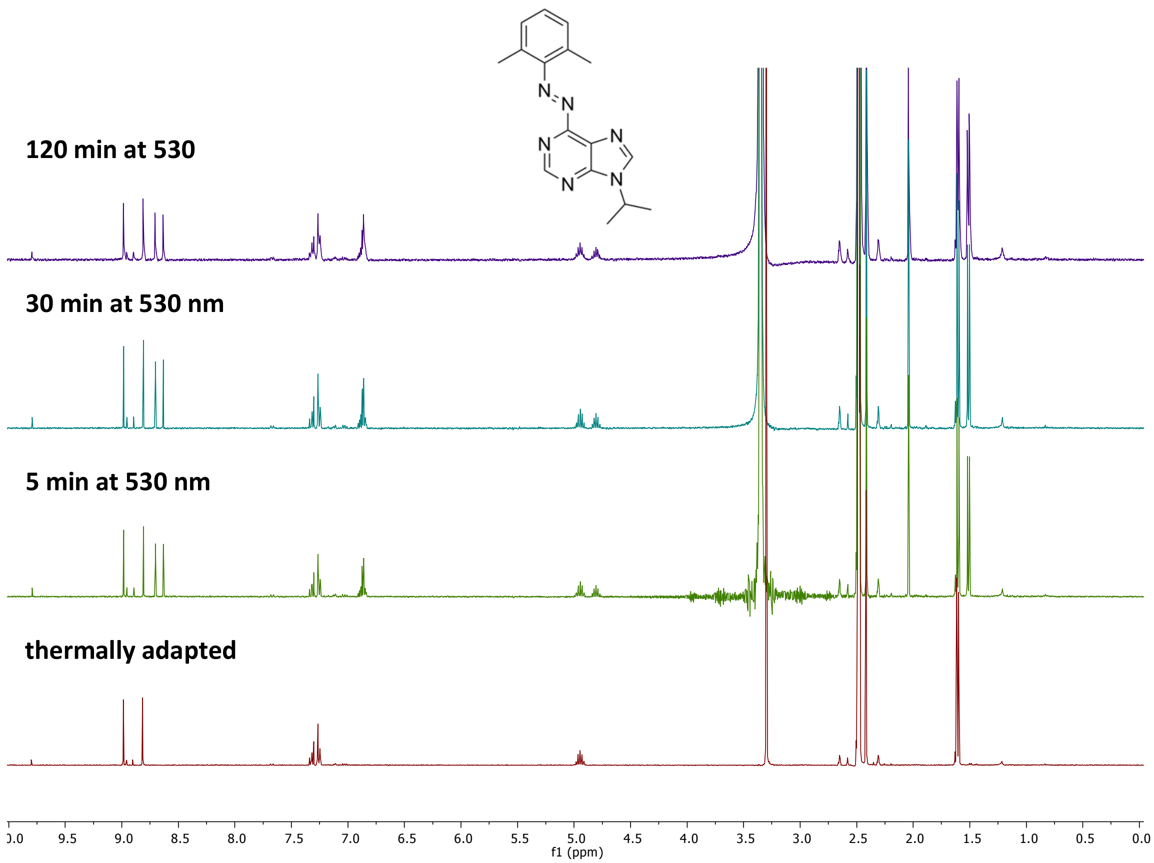


Figure S45. [1]H-NMR studies of the photochemical isomerization of **6o**(1 mg/mL, 25 °C). Photostationary state was reached upon irradiation with 530 nm (measured point: thermally adapted – 0 min, 5 min, 30 min, and 120 min).

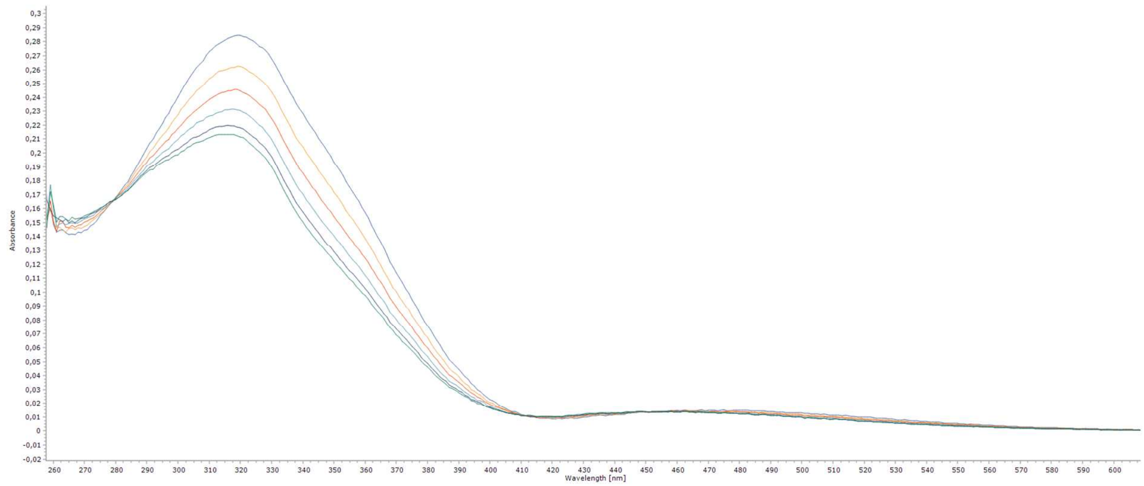


Figure 46. UV-Vis studies of the photochemical isomerization of **6o** (~40 µM in DMSO, 25 °C). Photostationary state was reached after 4 min upon irradiation with 530 nm (measured points: thermally adapted – 0 s, 10 s, 30 s, 60 s, 120 s, and 240 s).

NMR and UV-Vis studies of 9f

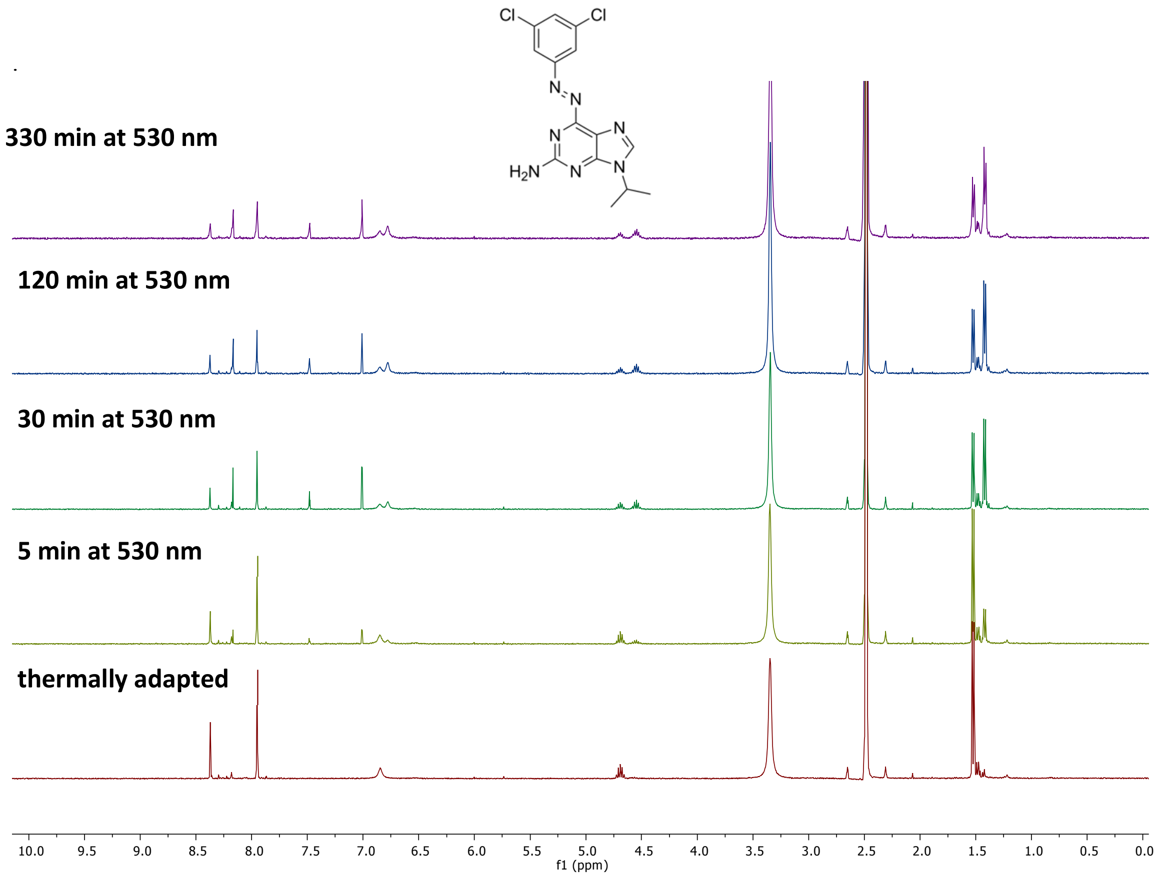


Figure S47. [1]H-NMR studies of the photochemical isomerization of **9f** (1 mg/mL, 25 °C). Photostationary state was reached upon irradiation with 530 nm (measured points: thermally adapted – 0 min, 5 min, 30 min, 120 s, and 330 min).

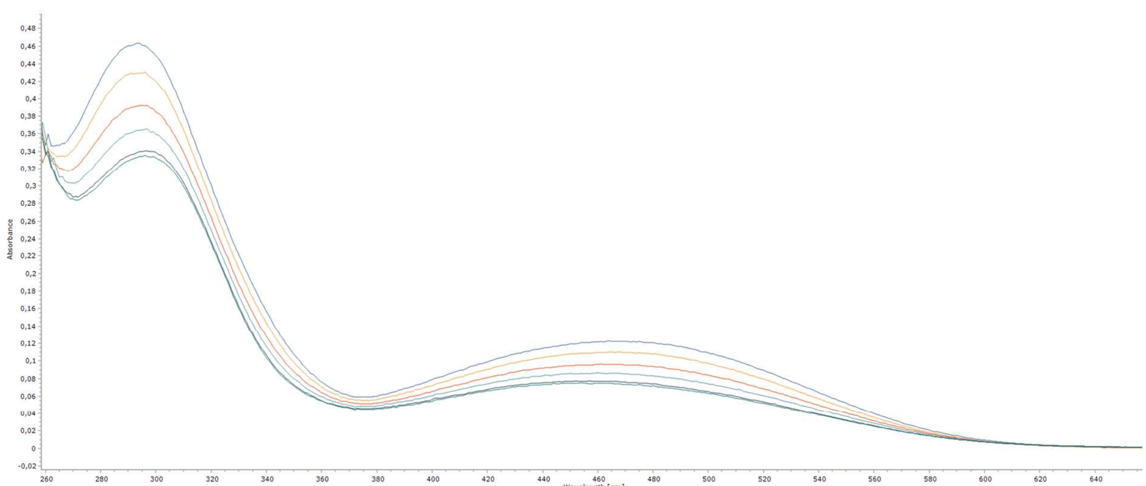
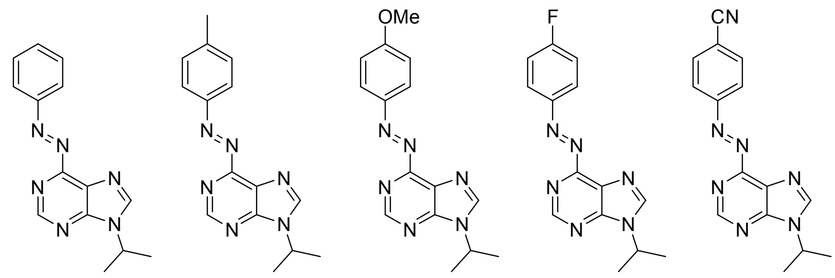


Figure 48. UV-Vis studies of the photochemical isomerization of **9f** (~40 µM in DMSO, 25 °C). Photostationary state was reached after 4 min upon irradiation with 530 nm (measured points: thermally adapted – 0 s, 10 s, 30 s, 60 s, 120 s, and 240 s).

Hammett Plot ofπ-π* lambda max for*p*-Substituted 6-Azoadenines



6a 6b 6c 6d 6e

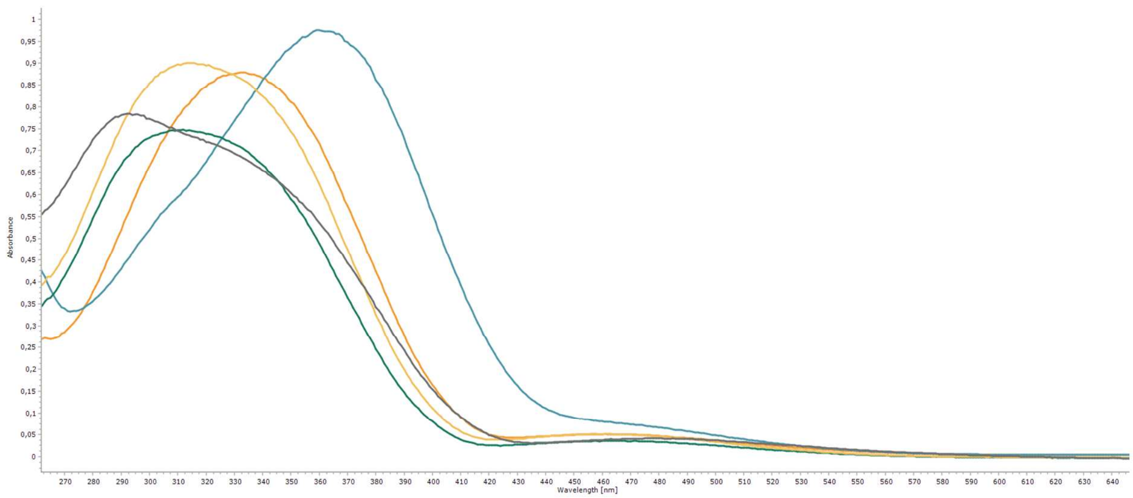


Figure S49. Absorption spectra of **6a** (●), **6c** (●), **6c** (●), **6d** (●), and **6e** (●) (60μM in DMSO, 25 °C).

Table 1. λ_1 (π → π*) (nm) and λ_2 (n → π*) (nm) forthe compounds **6a-e**.

compound	λ_1 (π → π*) (nm)	λ_2 (n → π*) (nm)
6a	309	462
6b	333	460
6c	360	/
6d	313	460
6e	292	484

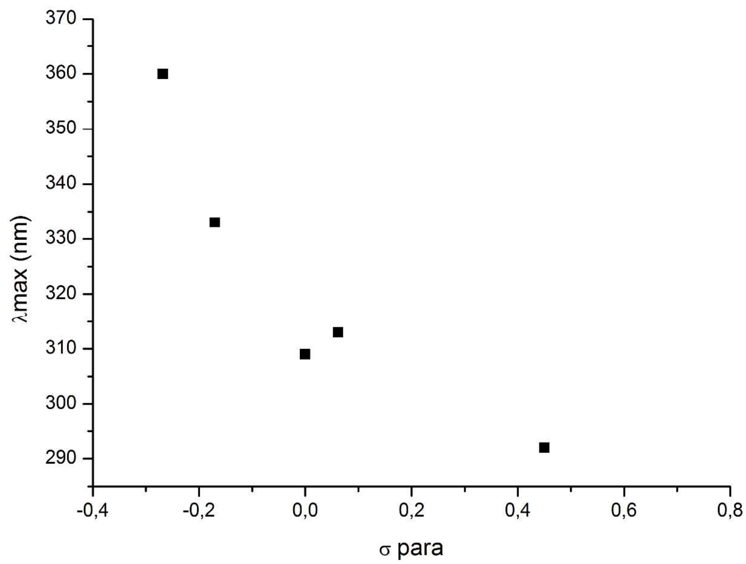


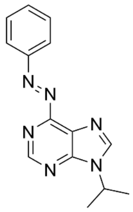
Figure S50. Hammett plot of λ_{max} (π-π*) for *p*-substituted 6-azoadenines (**6a-e**).

Solubility of 6-azopurines in water and PBS buffer (pH = 7.4)

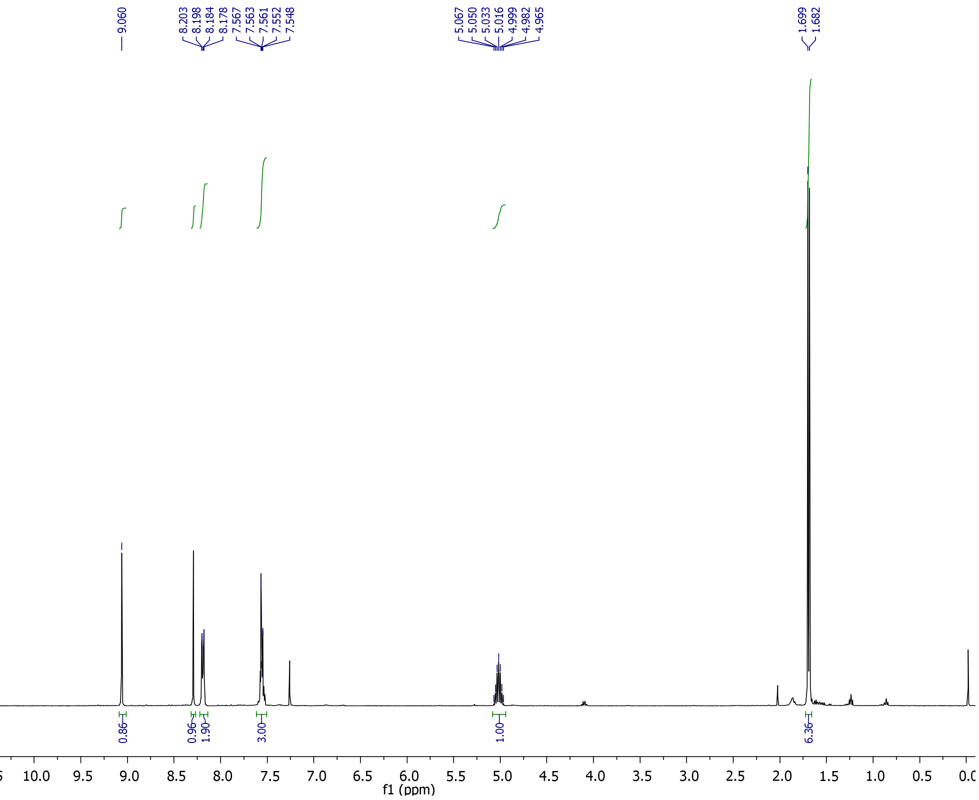
Table 2. Water and PBS buffer solubility of all 26 6-azopurines. Solubility is given at 5 different concentrations: 20, 40, 60, 80, and 100 µM, where '✓' represents clear solution, and 'X' appearance of milky solution.

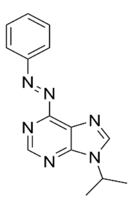
compound	water (µM)					PBS buffer (µM)				
	20	40	60	80	100	20	40	60	80	100
6a	✓	✓	✓	✓	✓	✓	✓	✓	✓	X
6b	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
6c	✓	✓	✓	✓	✓	✓	✓	✓	✓	X
6d	✓	✓	✓	✓	✓	✓	✓	✓	✓	X
6e	✓	✓	✓	✓	✓	✓	✓	✓	✓	X
6f	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
6g	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
6h	✓	✓	✓	✓	✓	✓	✓	✓	✓	X
6i	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
6j	✓	✓	✓	✓	✓	✓	✓	✓	✓	X
6k	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
6l	✓	✓	✓	X	X	✓	✓	✓	X	X
6m	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
6n	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
6o	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
6p	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
6q	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
6r	✓	✓	✓	✓	✓	✓	✓	X	X	X
9a	✓	✓	✓	✓	X	✓	✓	✓	✓	✓
9b	✓	✓	✓	X	X	✓	✓	✓	✓	✓
9c	✓	✓	X	X	X	✓	✓	✓	✓	✓
9d	✓	✓	✓	✓	X	✓	✓	✓	X	X
9e	✓	✓	✓	✓	X	✓	✓	✓	✓	✓
9f	✓	✓	✓	X	X	✓	✓	✓	✓	✓
9g	✓	✓	✓	✓	X	✓	✓	✓	✓	✓
9h	✓	X	X	X	X	✓	✓	X	X	X

NMR data for 6-azoadenines

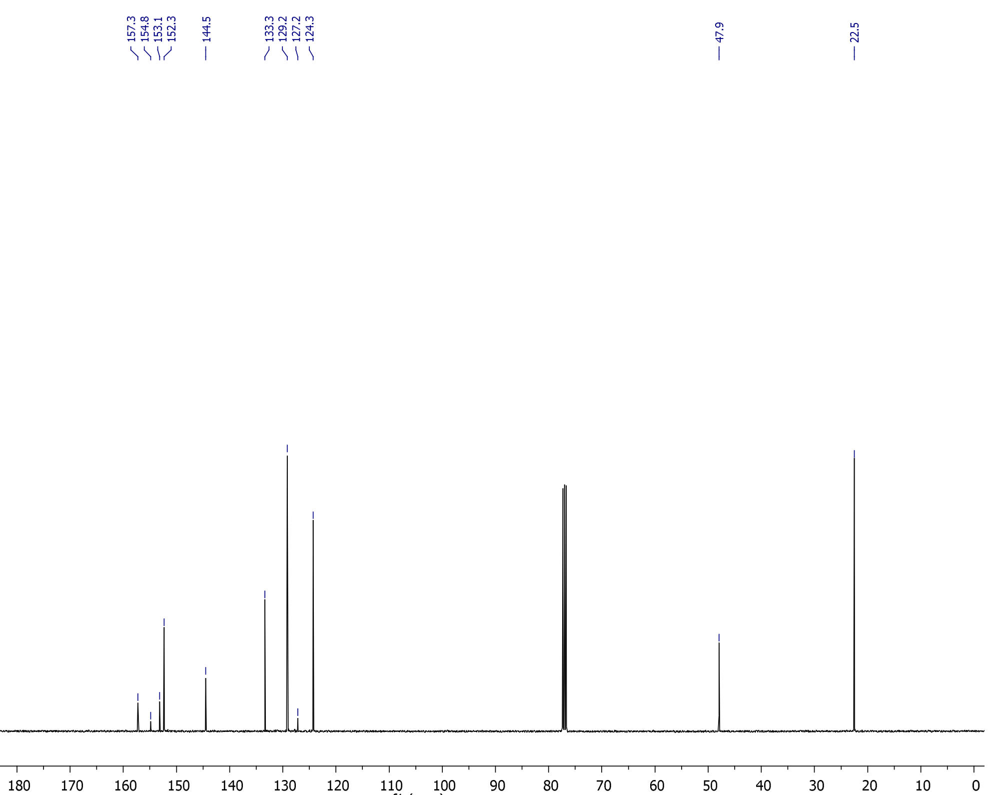


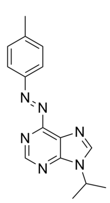
6a



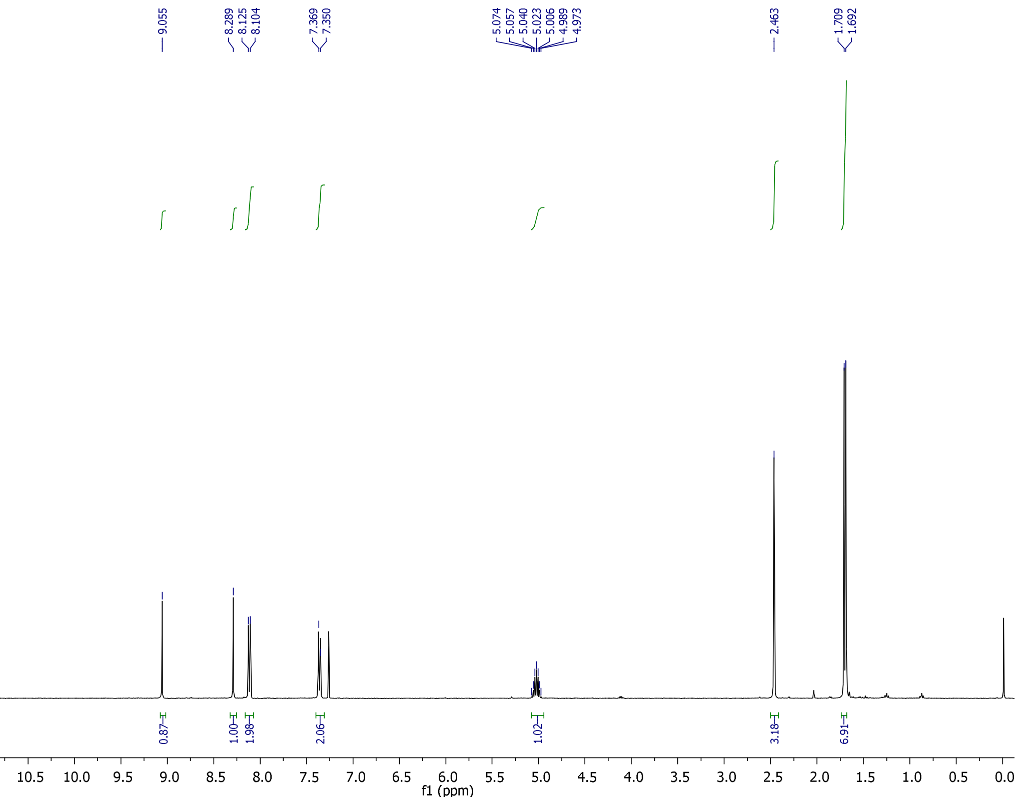


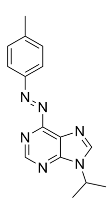
6a



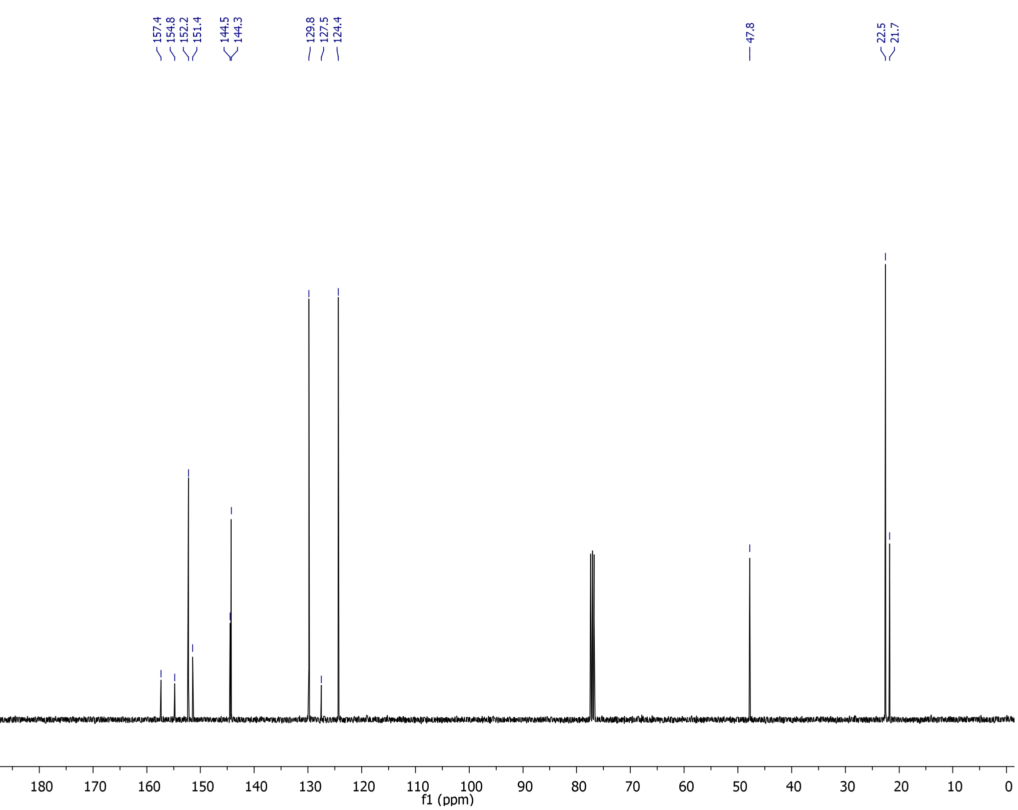


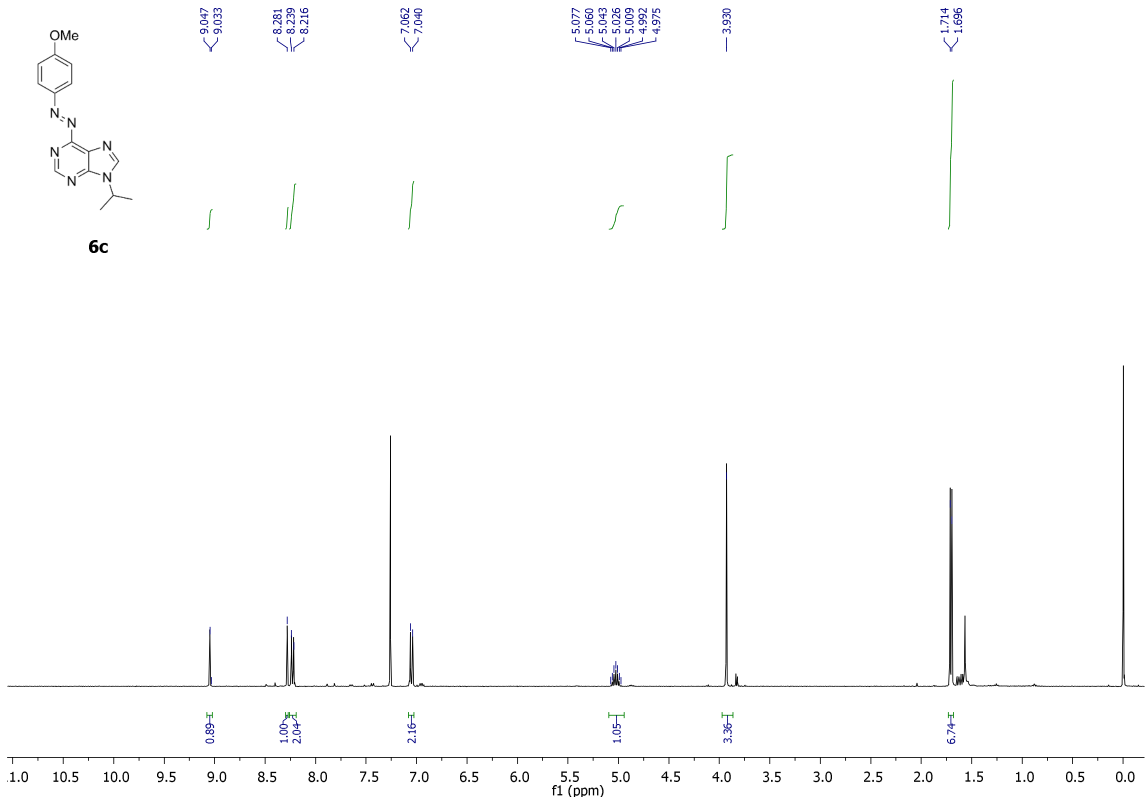
6b


9.055
8.289
8.125
8.104
7.369
7.350
5.074
5.057
5.040
5.023
5.006
4.989
4.973
2.463
1.709
1.692
0.87
1.00
1.98
2.06
1.02
3.18
6.91
f1 (ppm)

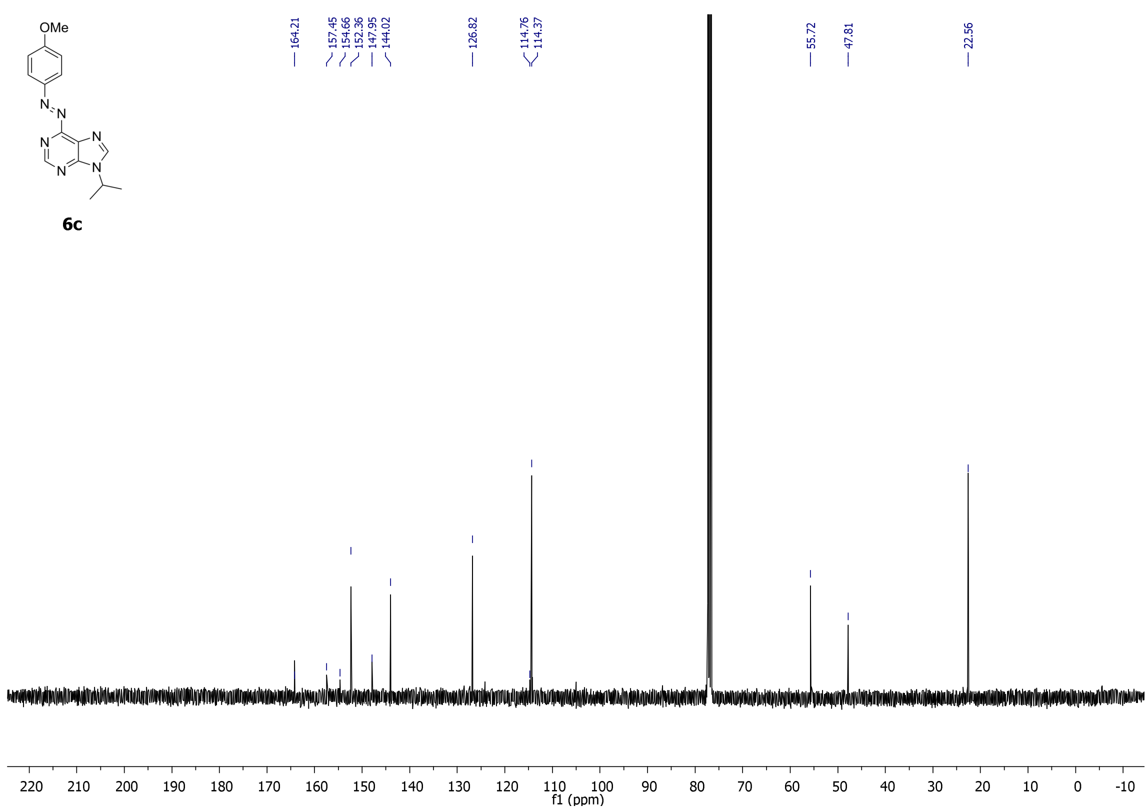


6b


157.4
154.8
152.2
151.4
144.5
144.3
129.8
127.5
124.4
47.8
22.5
21.7
f1 (ppm)


OMe
N
N
N
N
N
N
9.047
9.033
8.281
8.239
8.216
7.062
7.040
5.077
5.060
5.043
5.026
5.009
4.992
4.975
3.930
1.714
1.696
0.89
1.00
2.04
2.16
1.05
3.36
6.74
f1 (ppm)

6c


OMe
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N
N
N
N
N
164.21
157.45
154.66
152.36
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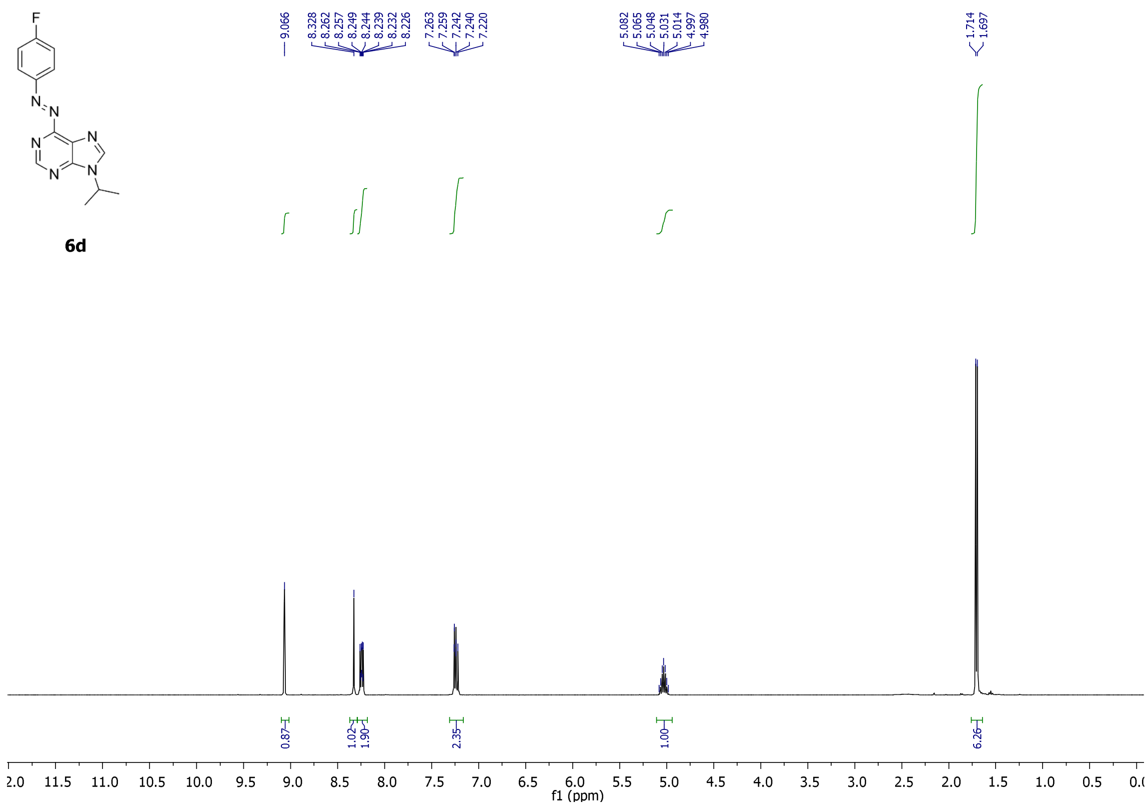
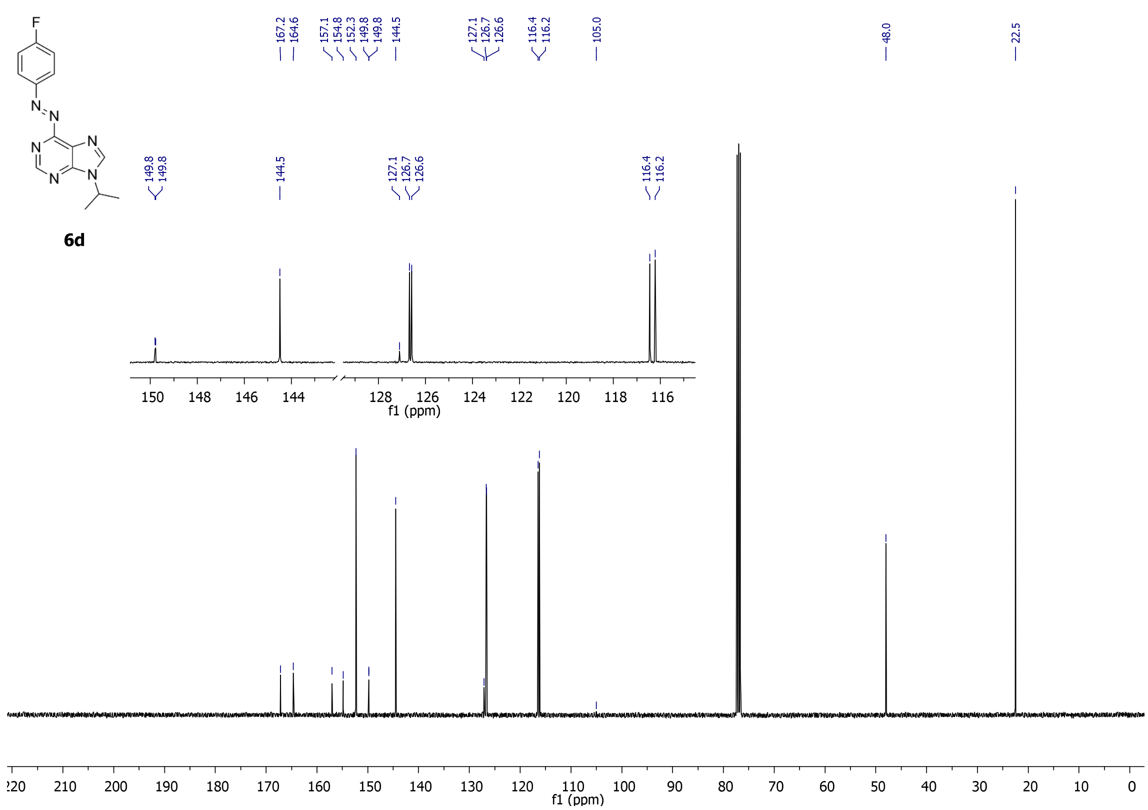
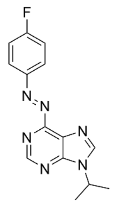
126.82
114.76
114.37
55.72
47.81
22.56
f1 (ppm)

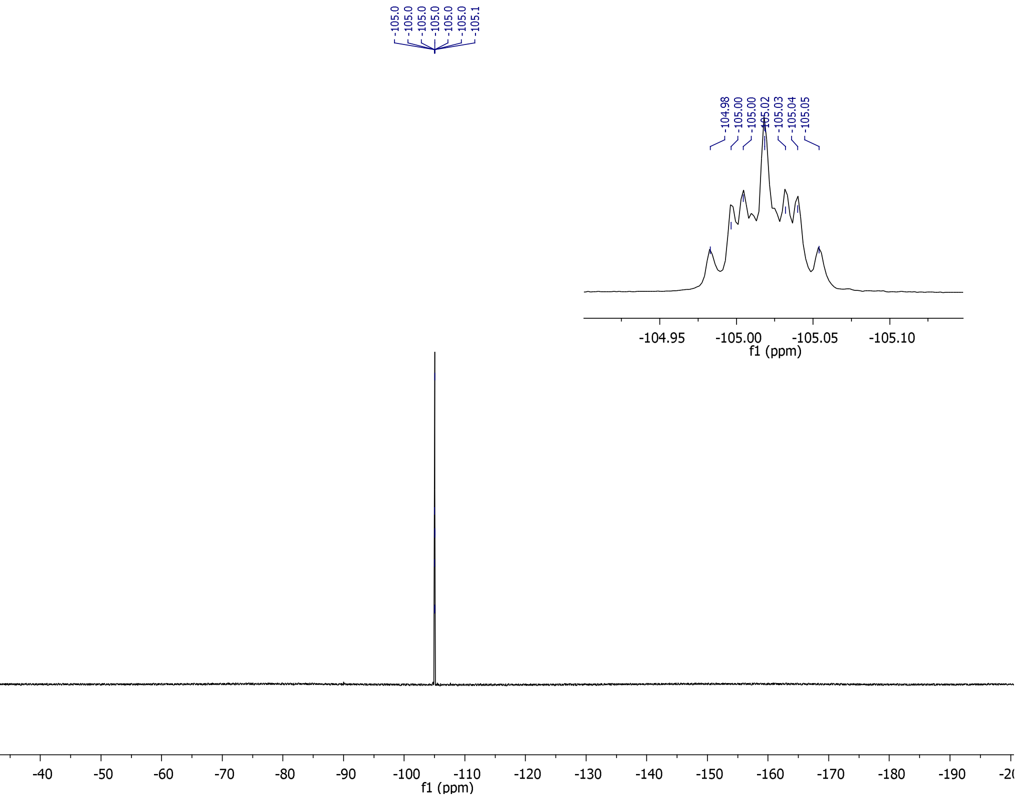
6c

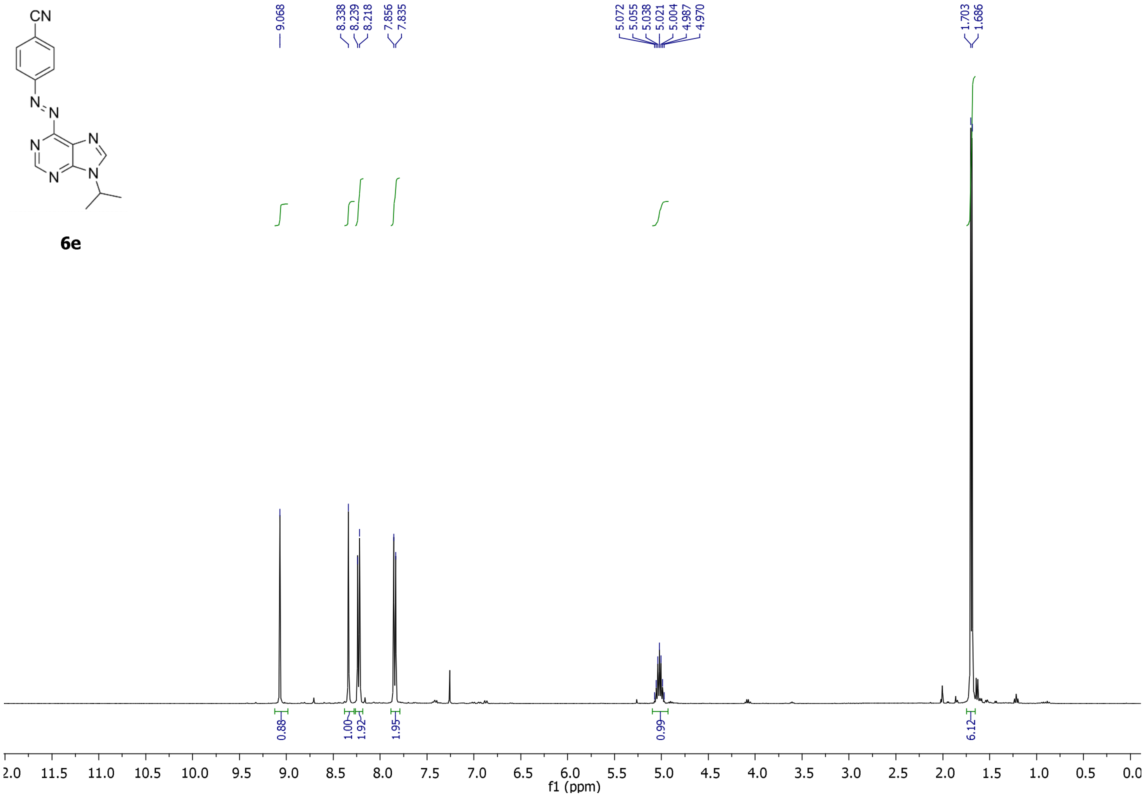

F
N
N
N
N
N
N
6d
9.066
8.328
8.262
8.257
8.249
8.244
8.239
8.232
8.226
7.263
7.259
7.242
7.240
7.220
5.082
5.065
5.048
5.031
5.014
4.997
4.980
1.714
1.697
0.87
1.02
1.90
2.35
1.00
6.26
f1 (ppm)


F
N
N
N
N
N
N
6d
167.2
164.6
157.1
154.8
152.3
149.8
149.8
144.5
127.1
126.7
126.6
116.4
116.2
105.0
48.0
22.5
f1 (ppm)



6d


-105.0
-105.0
-105.0
-105.0
-105.0
-105.1
-104.98
-105.00
-105.00
-105.02
-105.03
-105.04
-105.05
-104.95
-105.00
-105.05
-105.10
f1 (ppm)
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)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N
N
N
N
N
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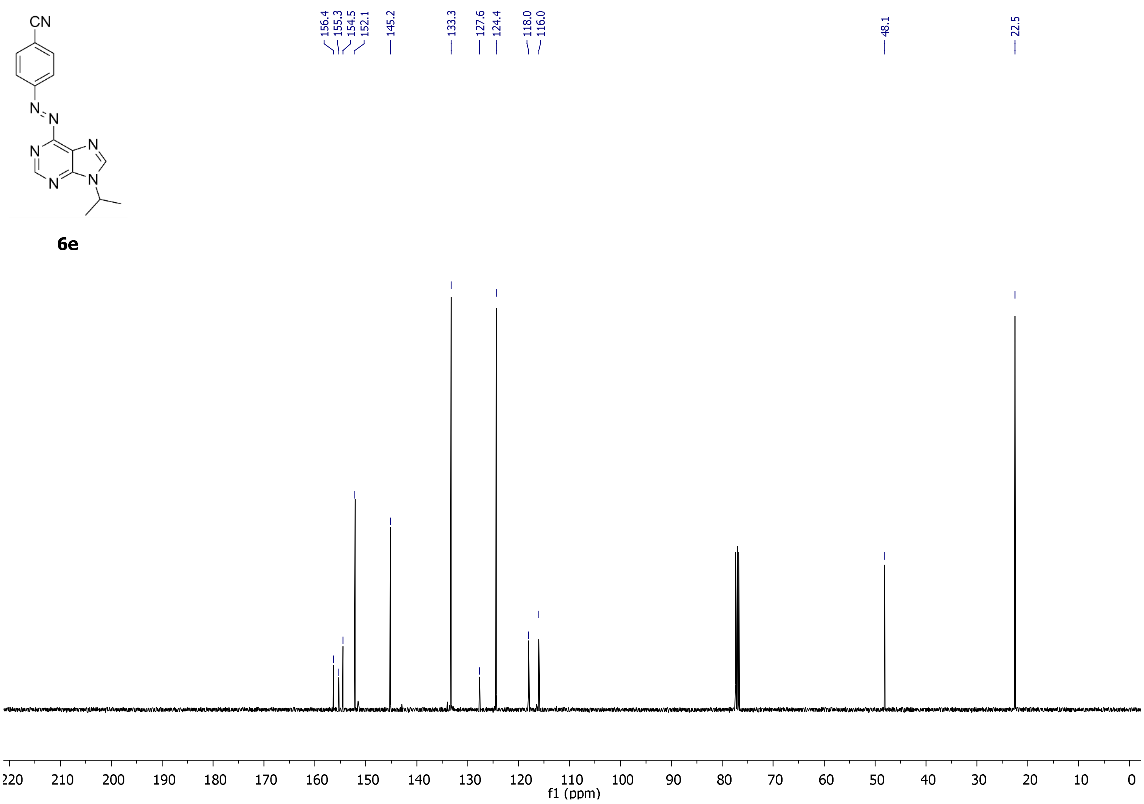
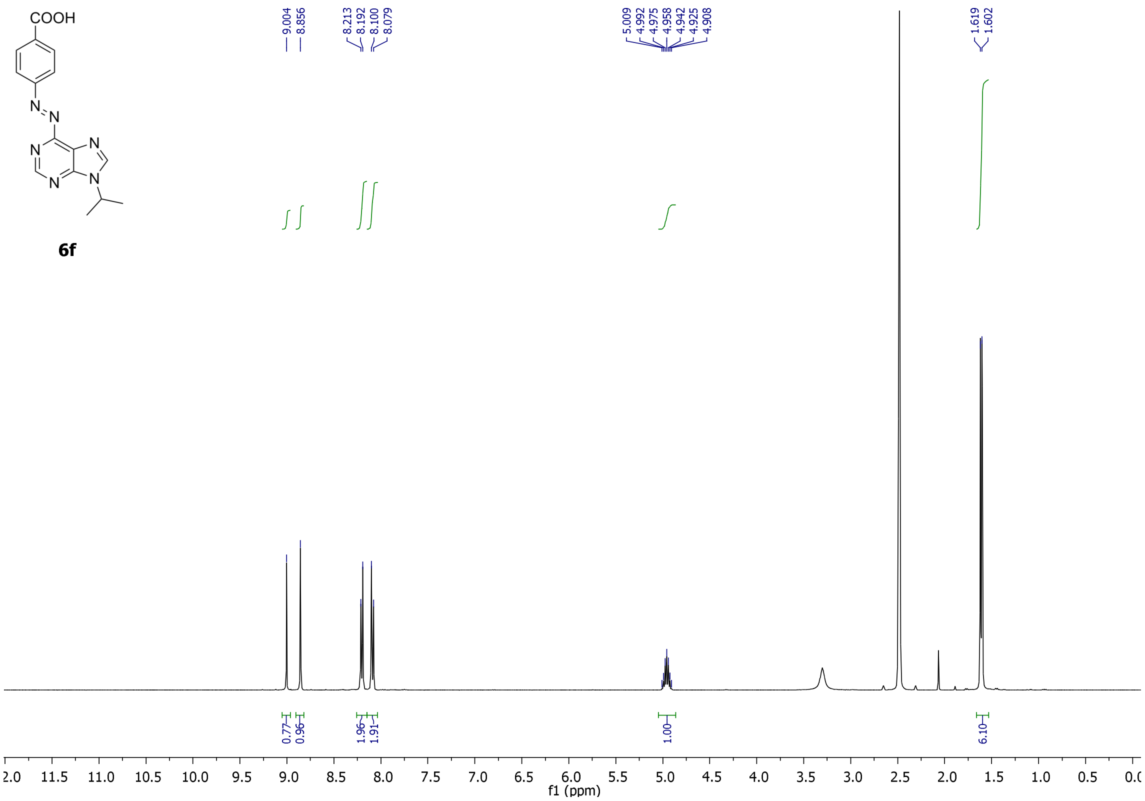
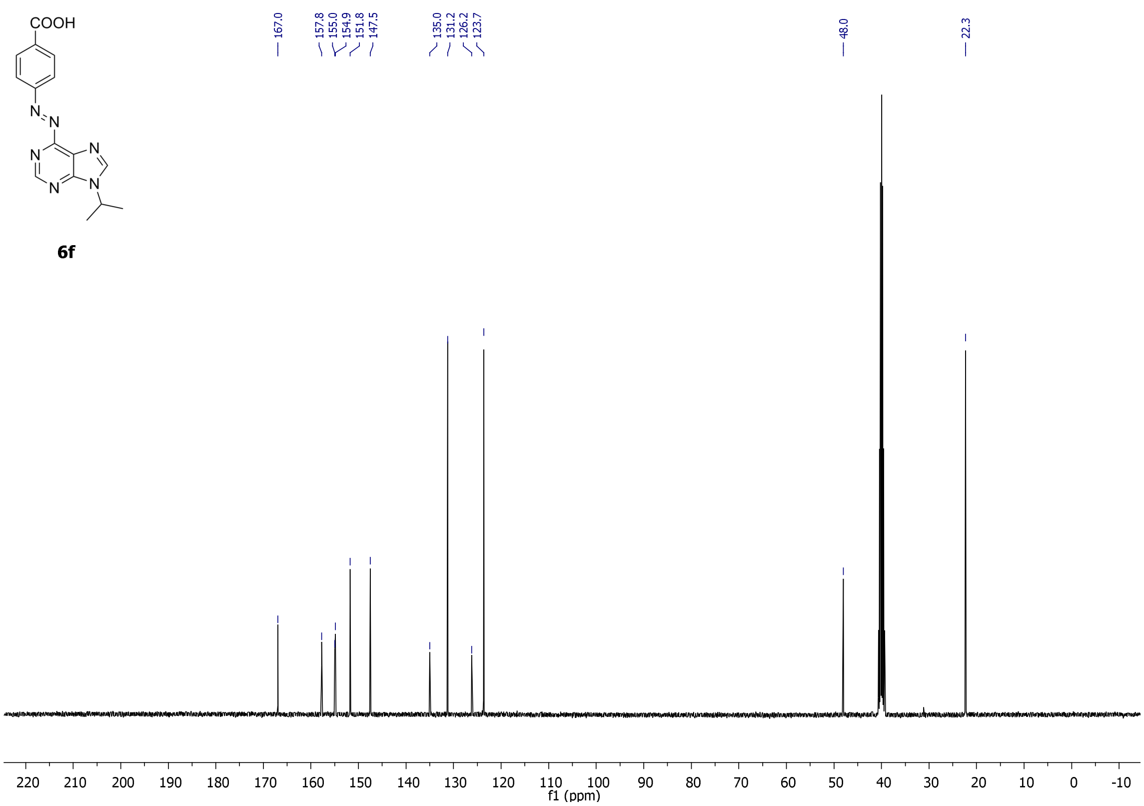
8.338
8.239
8.218
7.856
7.835
5.072
5.055
5.038
5.021
5.004
4.987
4.970
1.703
1.686
0.88
1.00
1.92
1.95
0.99
6.12
f1 (ppm)

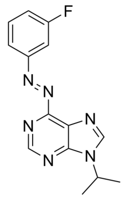
6e


CN
N
N
N
N
N
N
156.4
155.3
154.5
152.1
145.2
133.3
127.6
124.4
118.0
116.0
48.1
22.5
f1 (ppm)

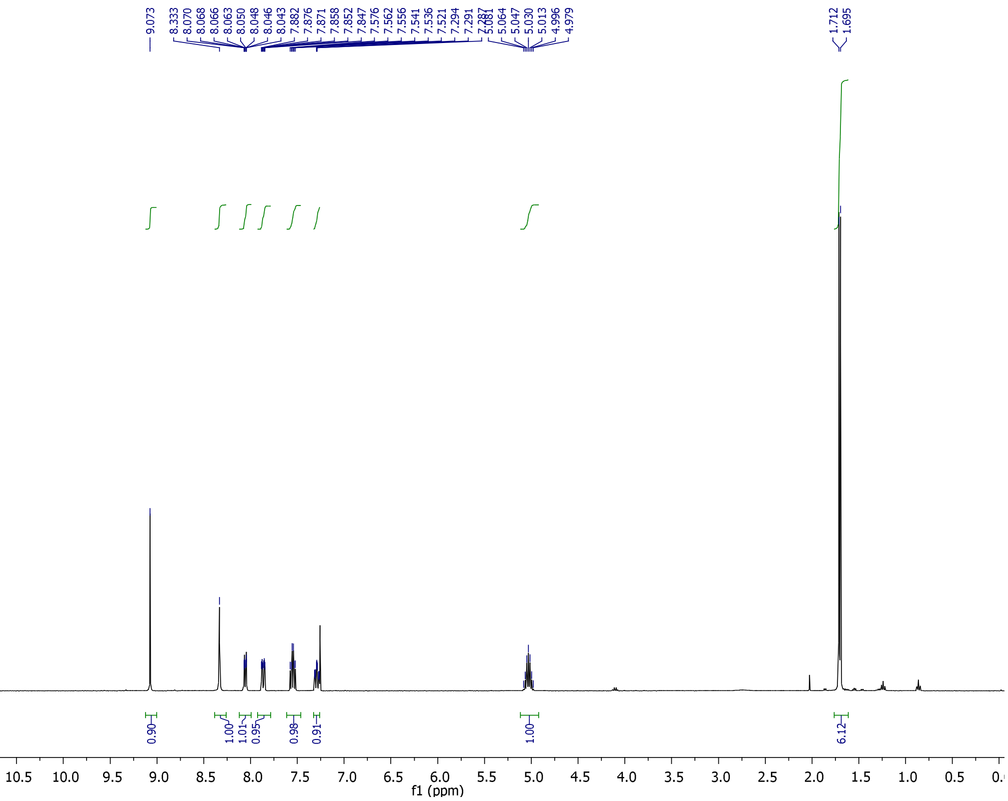
6e

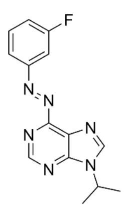

COOH
N
N
N
N
N
N
6f
9.004
8.856
8.213
8.192
8.100
8.079
5.009
4.992
4.975
4.958
4.942
4.925
4.908
1.619
1.602
0.77
0.96
1.96
1.91
1.00
6.10
f1 (ppm)


COOH
N
N
N
N
N
N
6f
167.0
157.8
155.0
154.9
151.8
147.5
135.0
131.2
126.2
123.7
48.0
22.3
f1 (ppm)

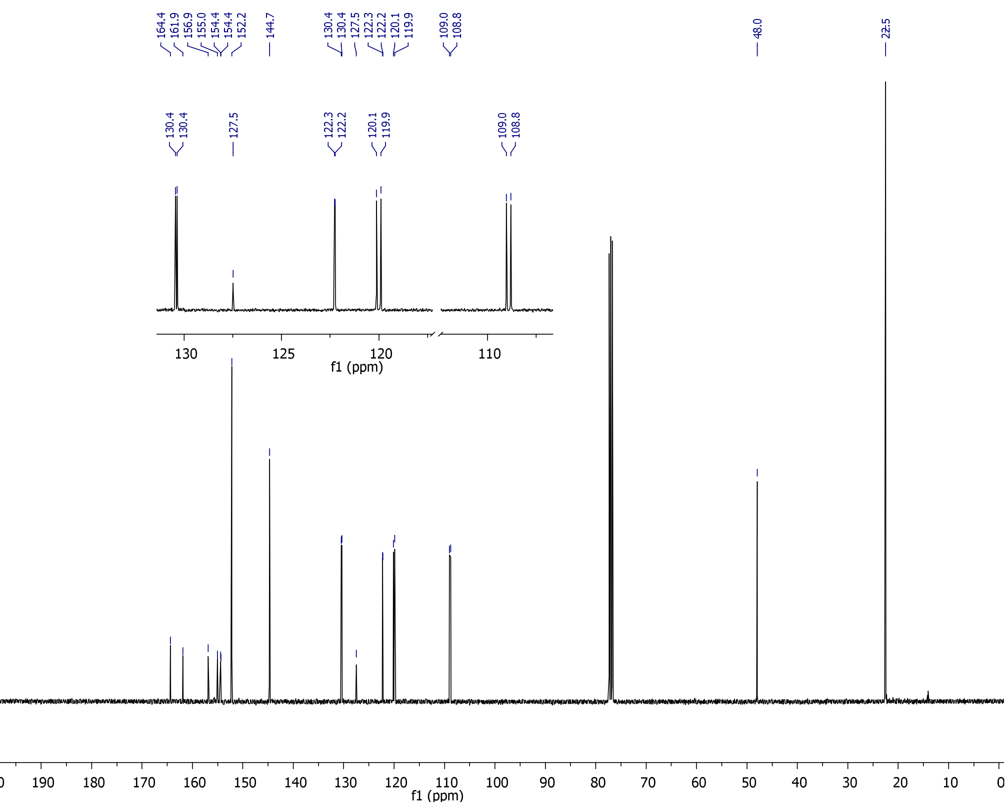


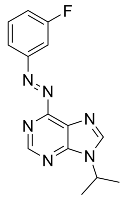
6g



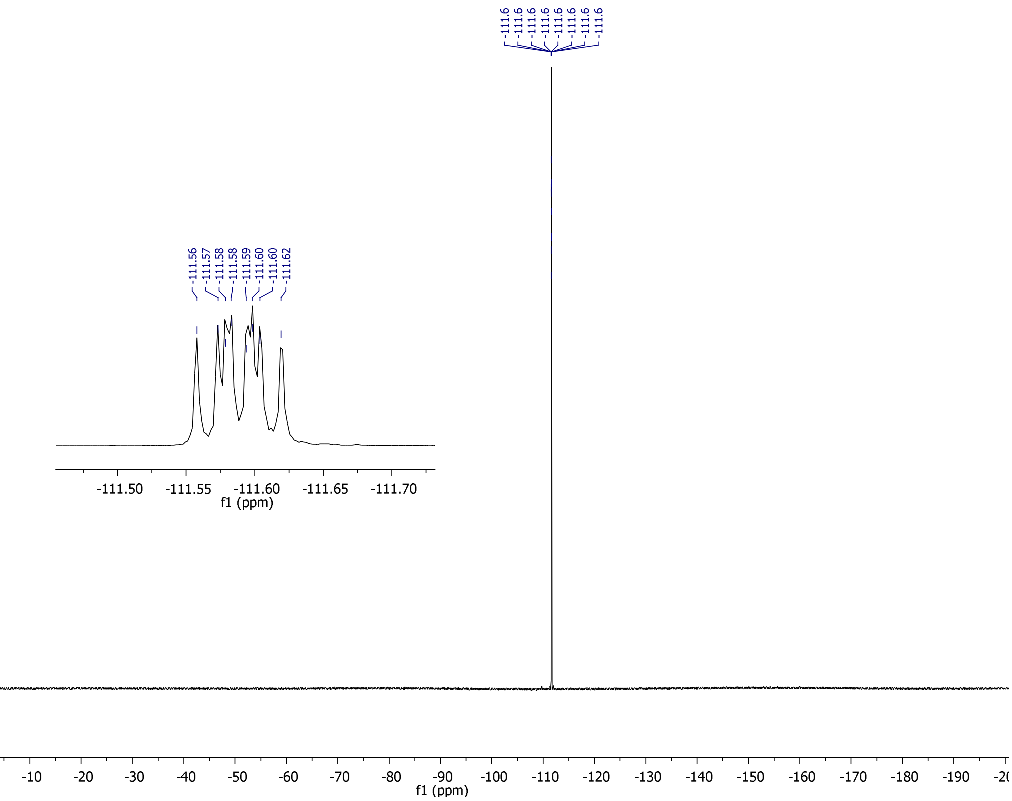


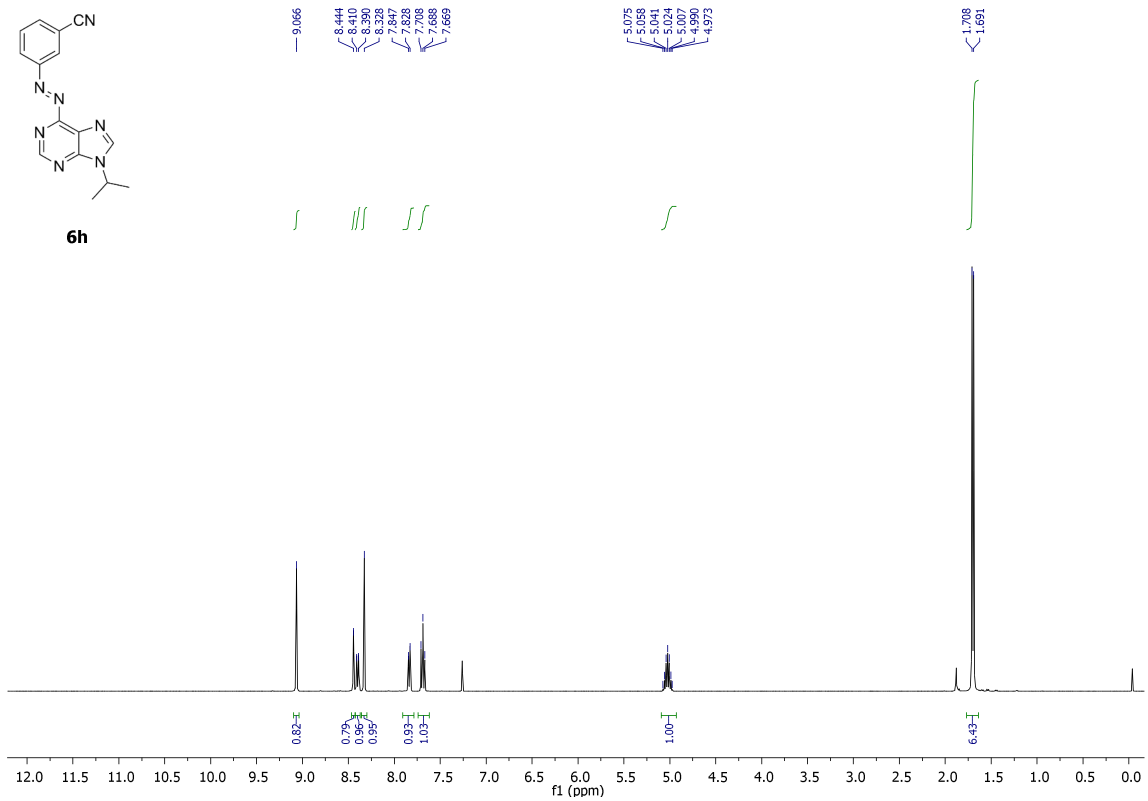
6g





6g


-111.56
-111.57
-111.58
-111.58
-111.59
-111.60
-111.60
-111.62
-111.50 -111.55 -111.60 -111.65 -111.70
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)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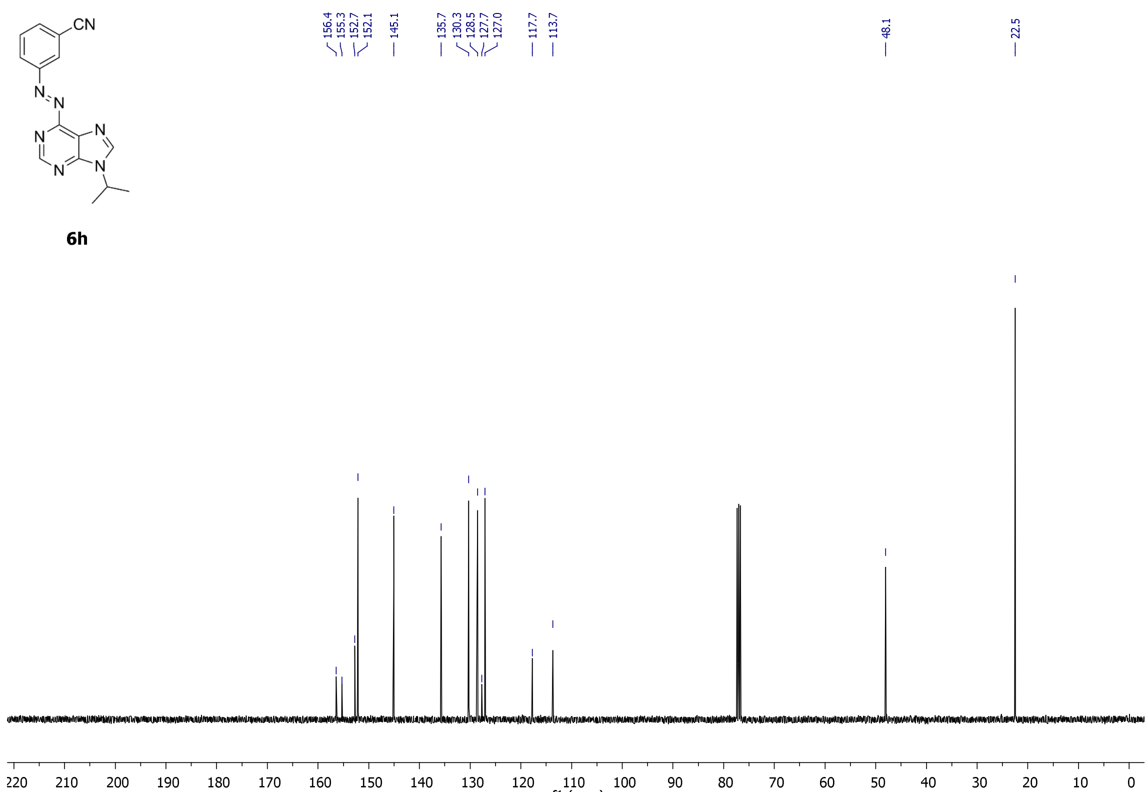
N
N
N
N
N
N
9.066
8.444
8.410
8.390
8.328
7.847
7.828
7.708
7.688
7.669
5.075
5.058
5.041
5.024
5.007
4.990
4.973
1.708
1.691
0.82
0.79
0.96
0.95
0.93
1.03
1.00
6.43
f1 (ppm)

6h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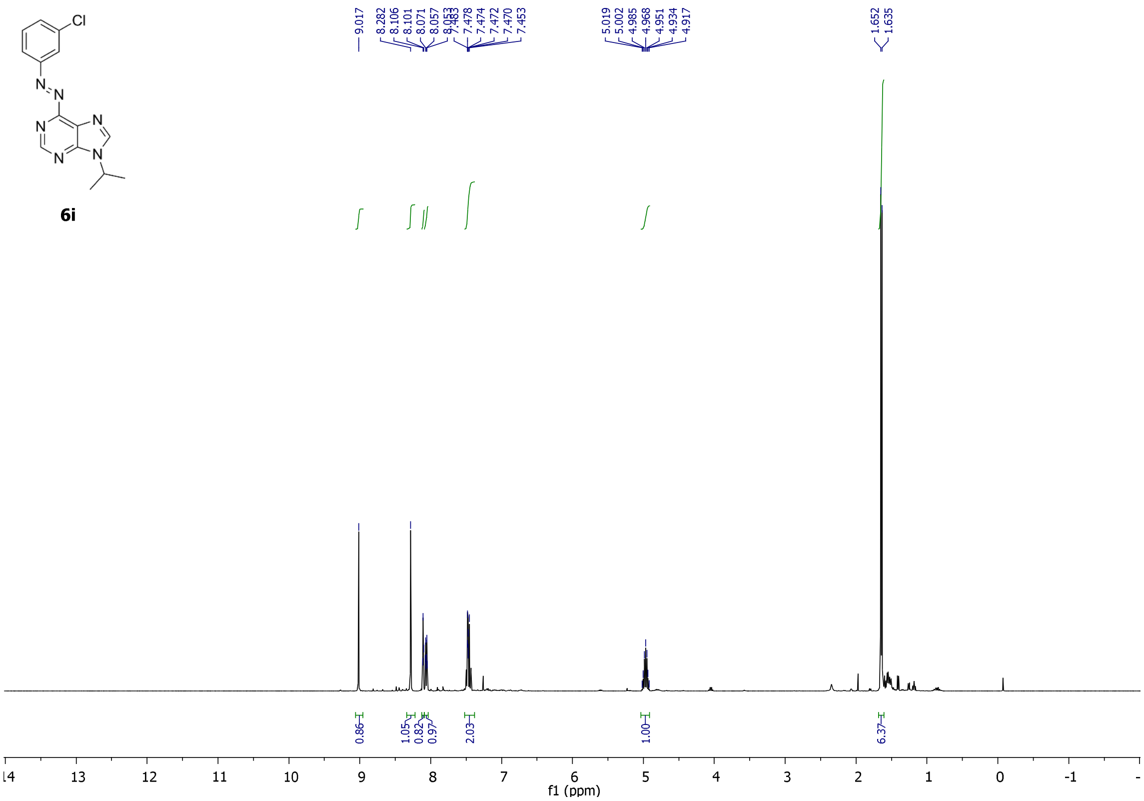
N
N
N
N
N
N
156.4
155.3
152.7
152.1
145.1
135.7
130.3
128.5
127.7
127.0
117.7
113.7
48.1
22.5
f1 (ppm)

6h


Cl
N
6i
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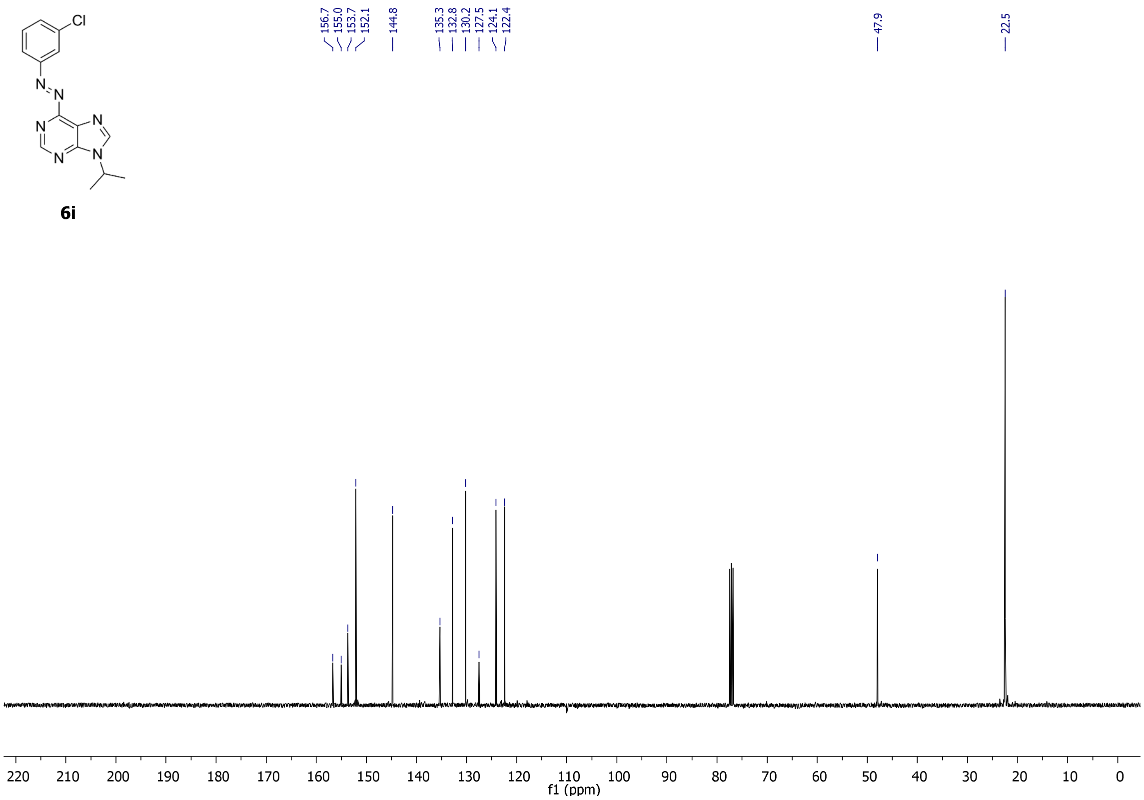
8.282
8.106
8.101
8.071
8.057
7.483
7.478
7.474
7.472
7.470
7.453
5.019
5.002
4.985
4.968
4.951
4.934
4.917
1.652
1.635
0.86
1.05
0.82
0.97
2.03
1.00
6.37
f1 (ppm)


Cl
N
6i
156.7
155.0
153.7
152.1
144.8
135.3
132.8
130.2
127.5
124.1
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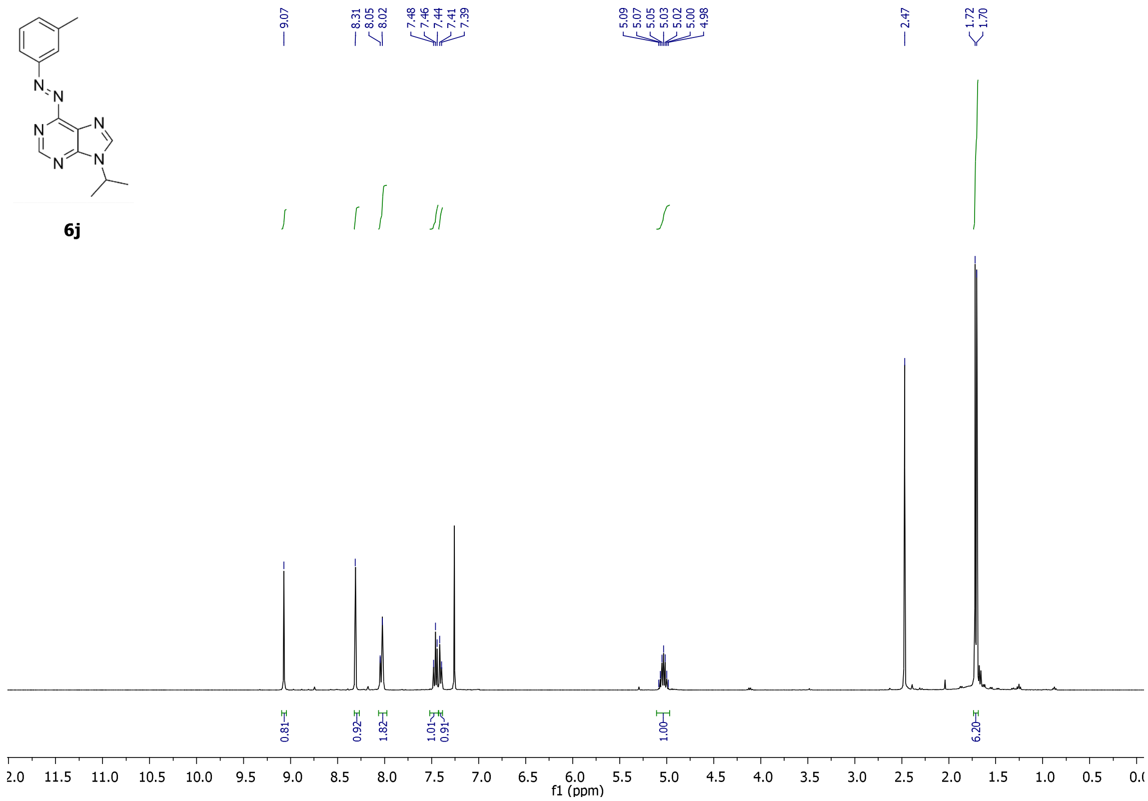
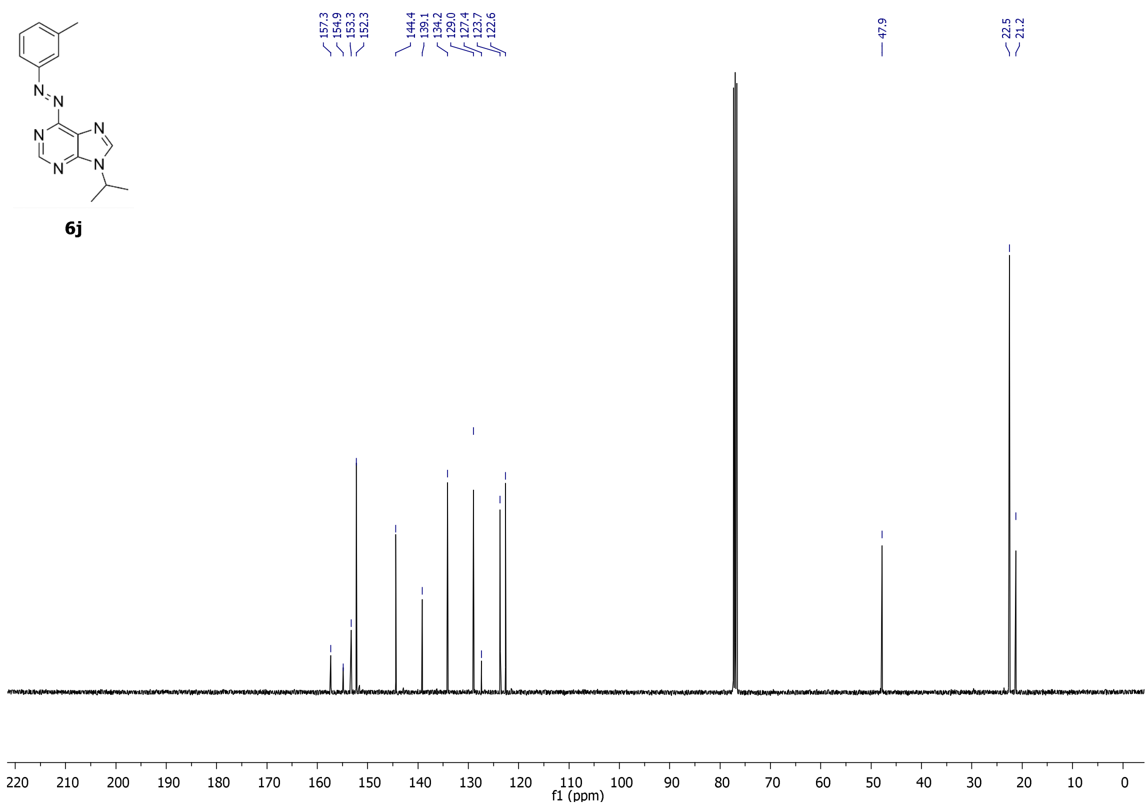
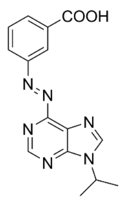
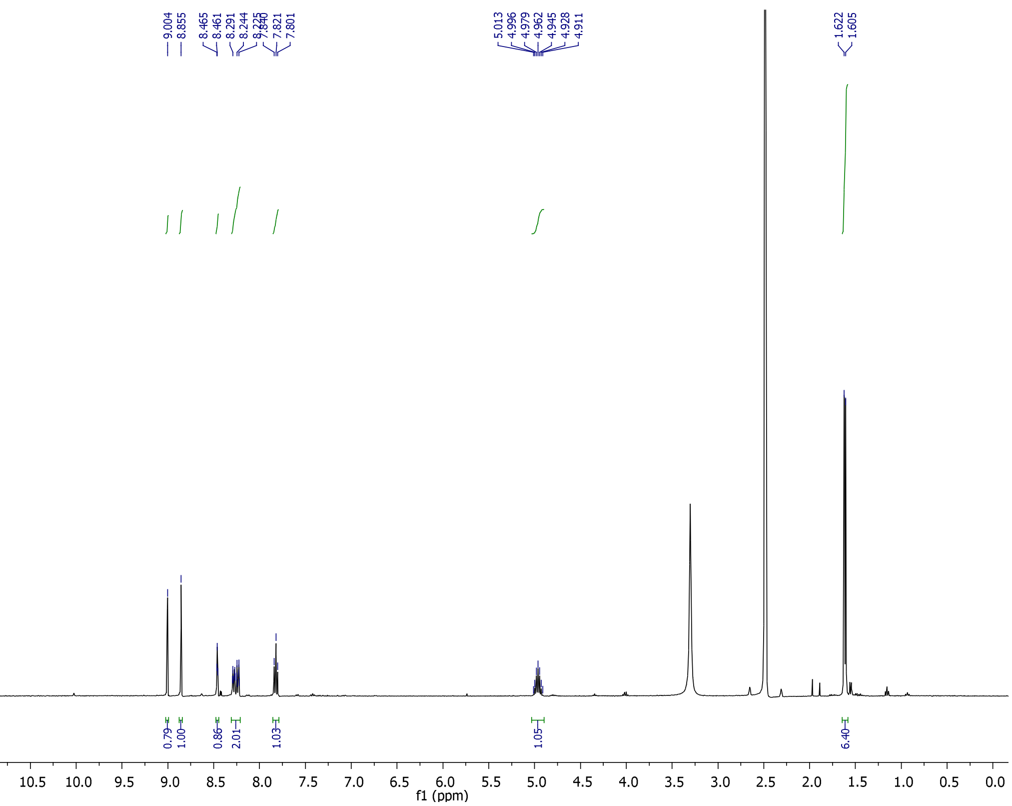
47.9
22.5
f1 (ppm)

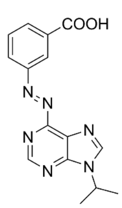

6j
9.07
8.31
8.05
8.02
7.48
7.46
7.44
7.41
7.39
5.09
5.07
5.05
5.03
5.02
5.00
4.98
2.47
1.72
1.70
0.81
0.92
1.82
1.01
0.91
1.00
6.20
f1 (ppm)


6j
157.3
154.9
153.3
152.3
144.4
139.1
134.2
129.0
127.4
123.7
122.6
47.9
22.5
21.2
f1 (ppm)

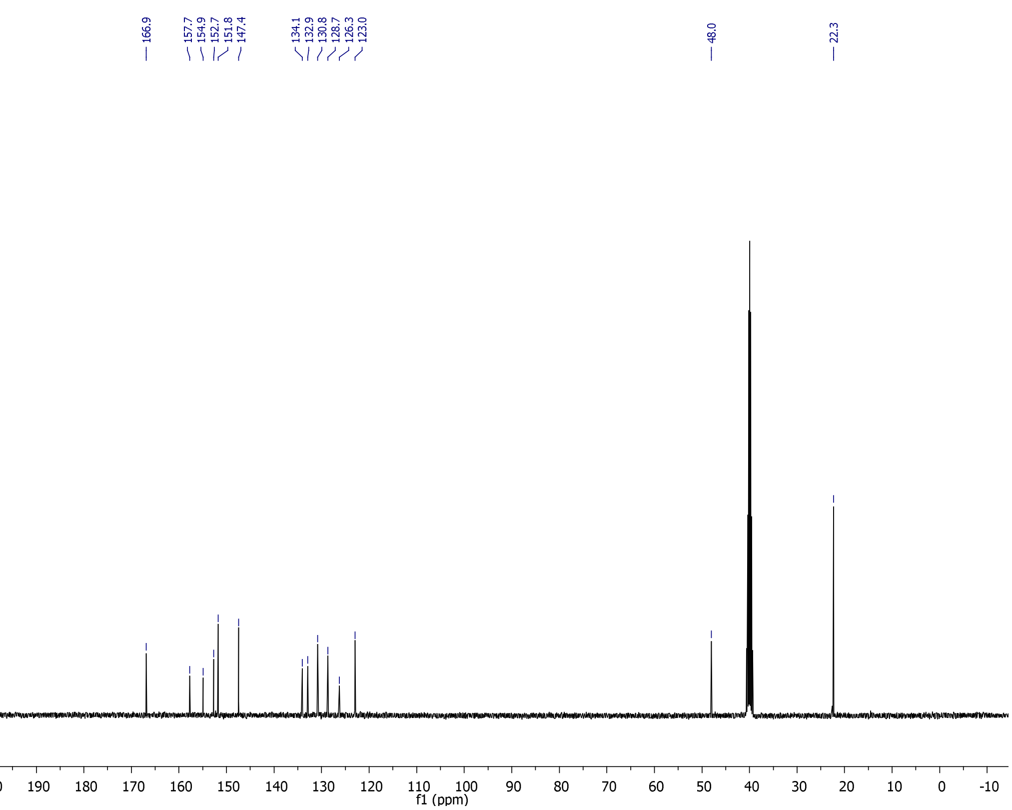

COOH
N
N
N
N
N
N

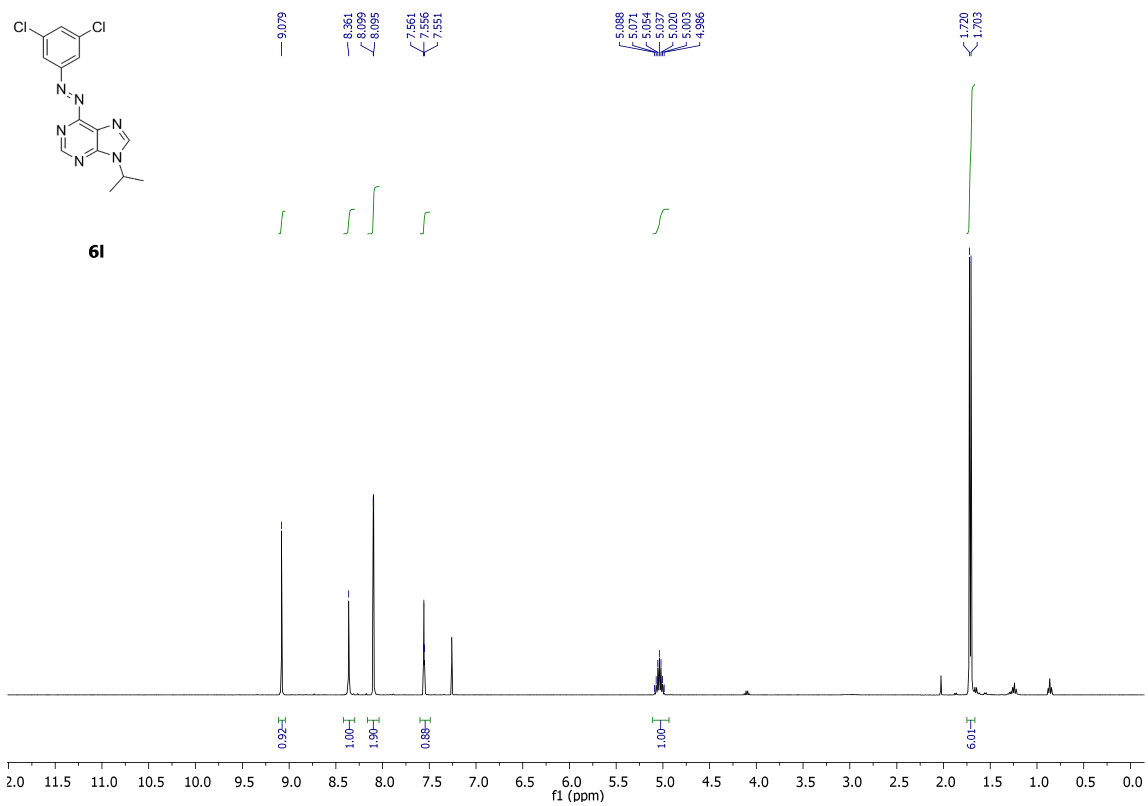
6k


9.004
8.855
8.465
8.461
8.291
8.244
8.225
7.840
7.821
7.801
5.013
4.996
4.979
4.962
4.945
4.928
4.911
1.622
1.605
0.79
1.00
0.86
2.01
1.03
1.05
6.40
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


COOH
N
N
N
N
N
N

6k


166.9
157.7
154.9
152.7
151.8
147.4
134.1
132.9
130.8
128.7
126.3
123.0
48.0
22.3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



Cl
Cl
N
N
N
N
N
N
6l
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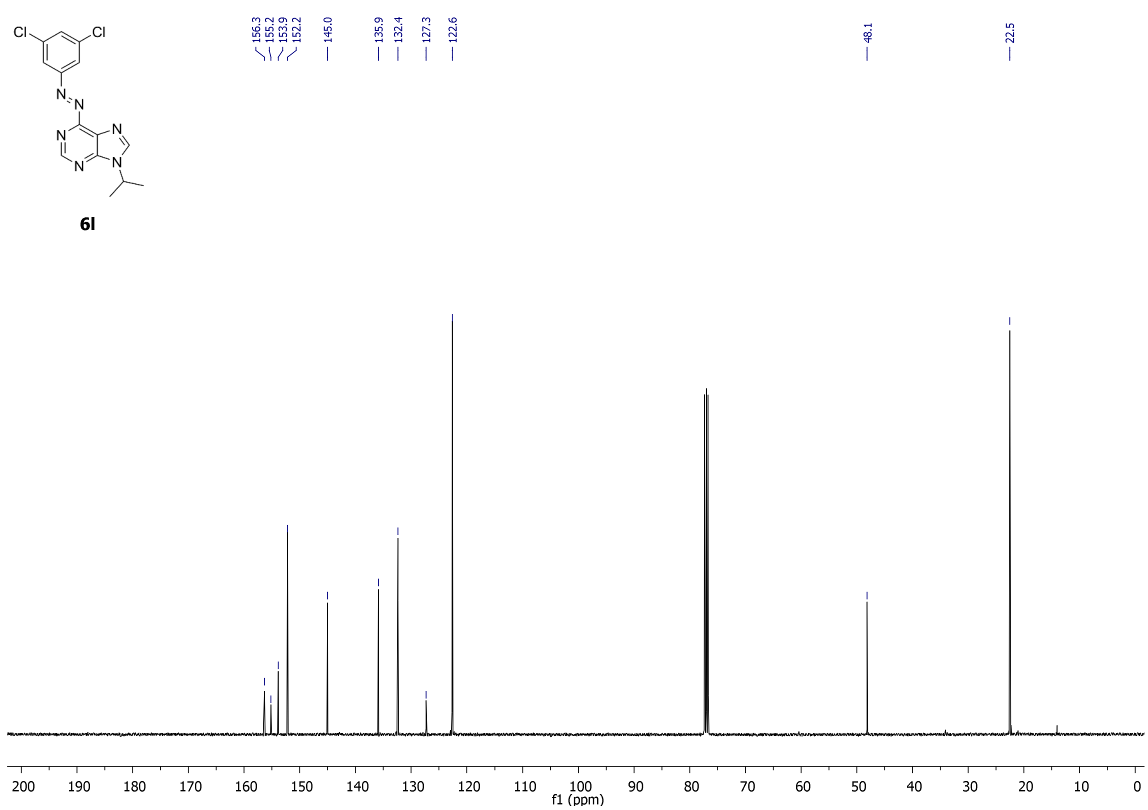
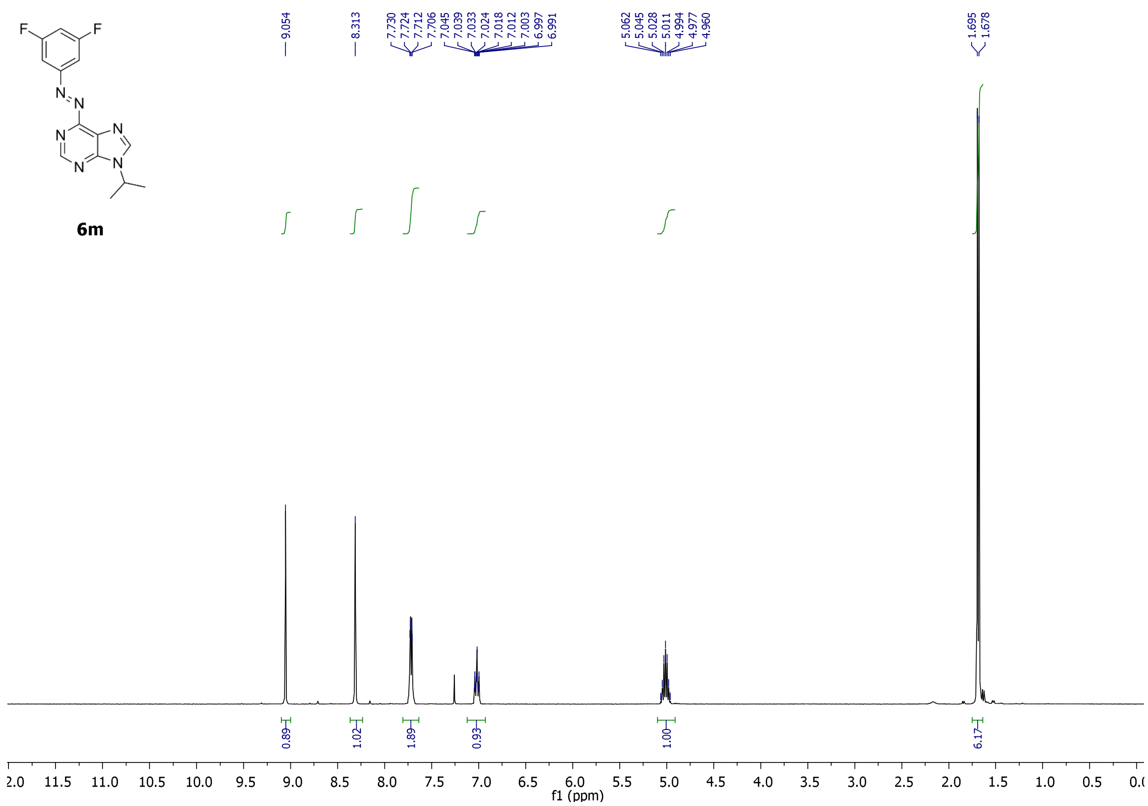
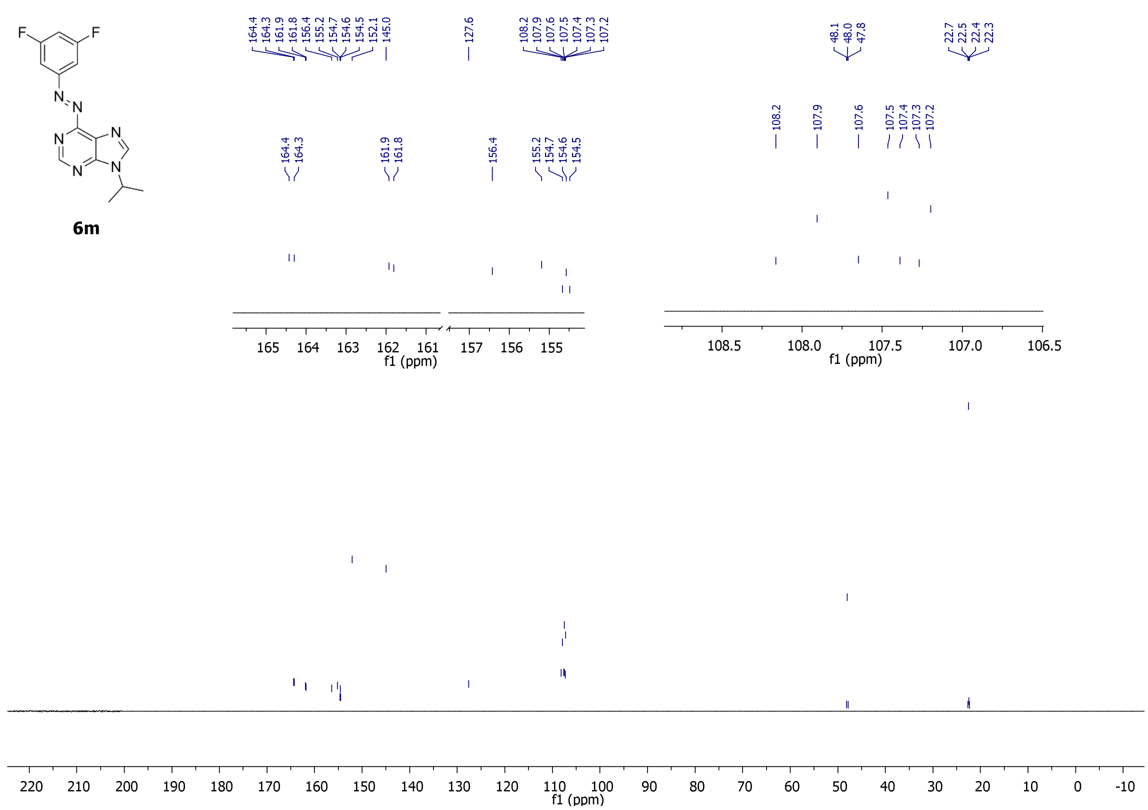
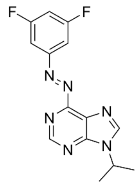
8.361
8.099
8.095
7.561
7.556
7.551
5.088
5.071
5.054
5.037
5.020
5.003
4.986
1.720
1.703
0.92
1.00
1.90
0.88
1.00
6.01
f1 (ppm)



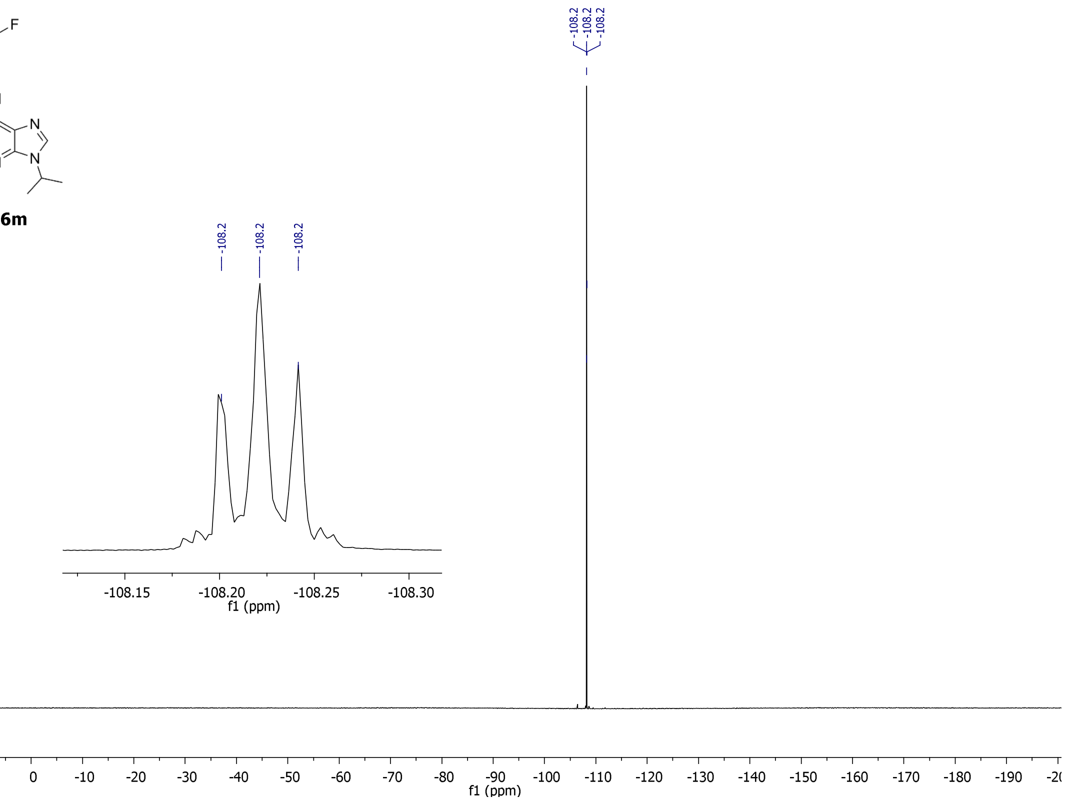
Cl
Cl
N
N
N
N
N
N
6l
156.3
155.2
153.9
152.2
145.0
135.9
132.4
127.3
122.6
48.1
22.5
f1 (ppm)

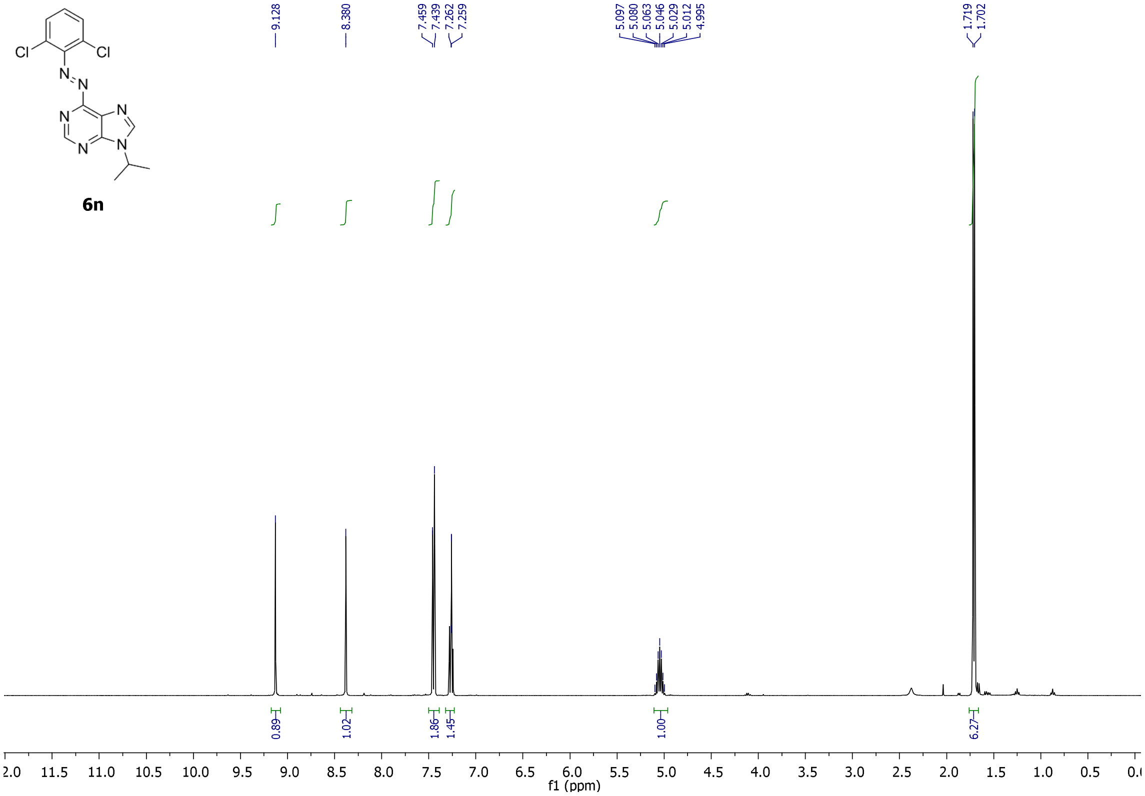


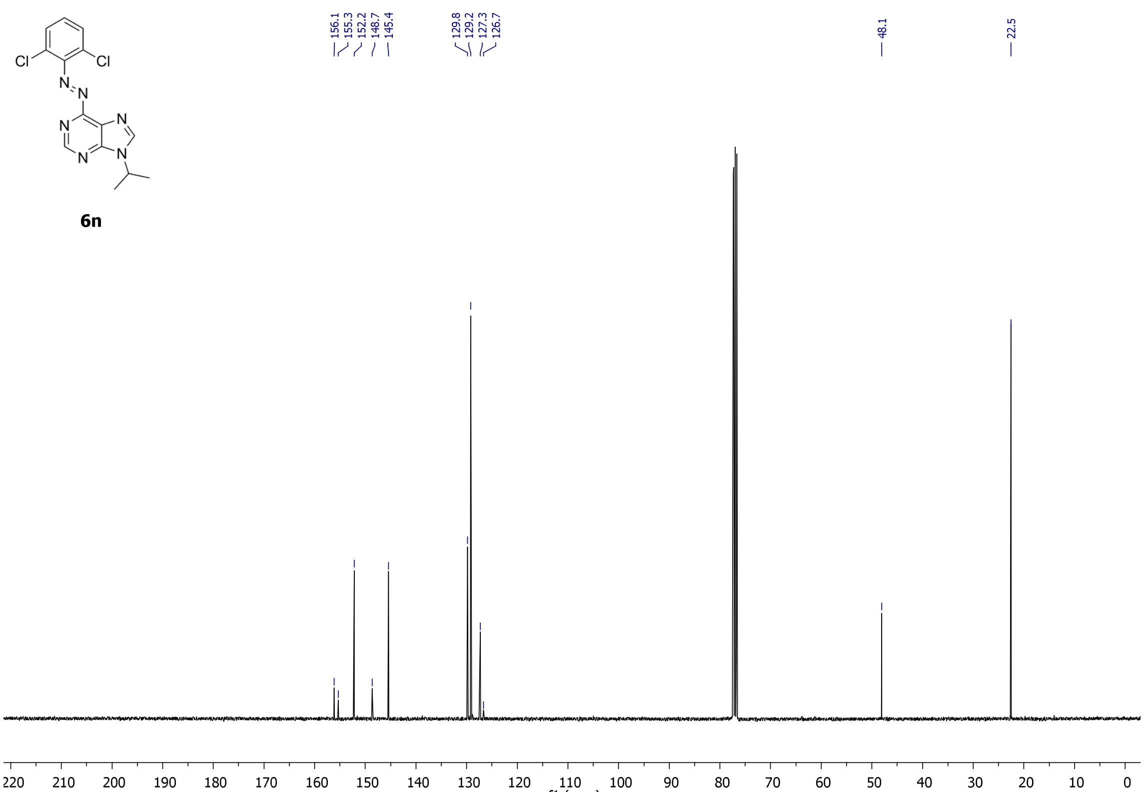


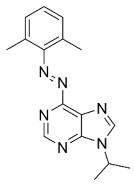


6m

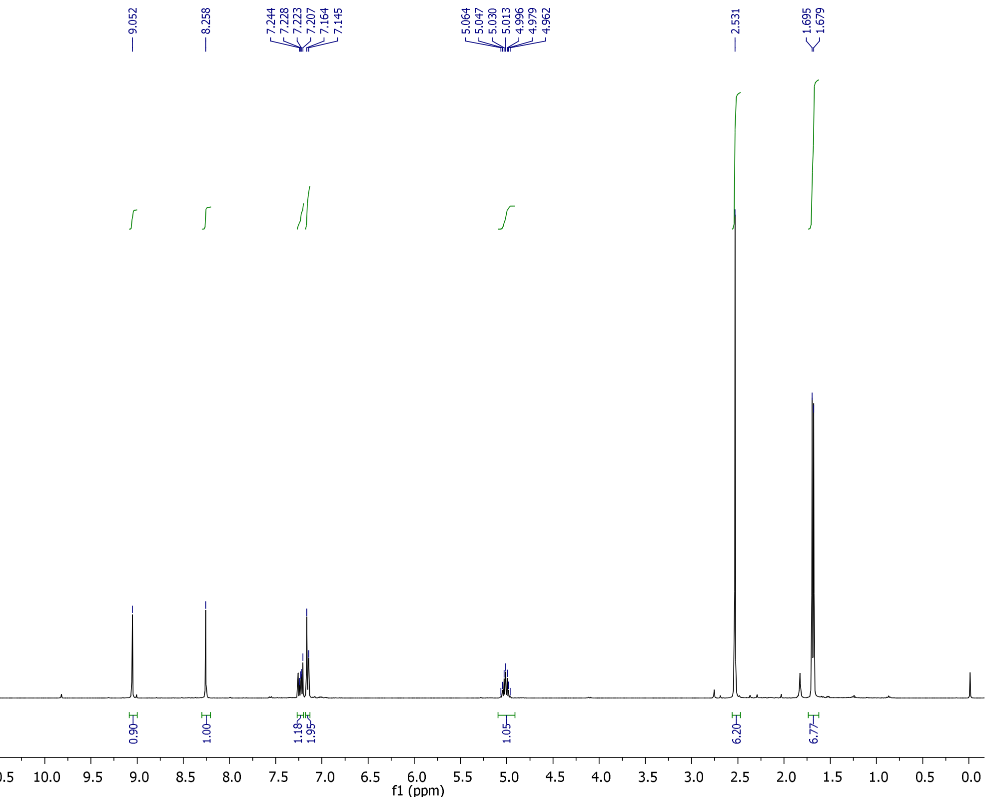

-108.2
-108.2
-108.2
-108.15
-108.20
-108.25
-108.30
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)


Cl
Cl
N
N
6n
9.128
8.380
7.459
7.439
7.262
7.259
5.097
5.080
5.063
5.046
5.029
5.012
4.995
1.719
1.702
0.89
1.02
1.86
1.45
1.00
6.27
f1 (ppm)

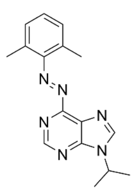

Cl
Cl
N
N
6n
156.1
155.3
152.2
148.7
145.4
129.8
129.2
127.3
126.7
48.1
22.5
f1 (ppm)



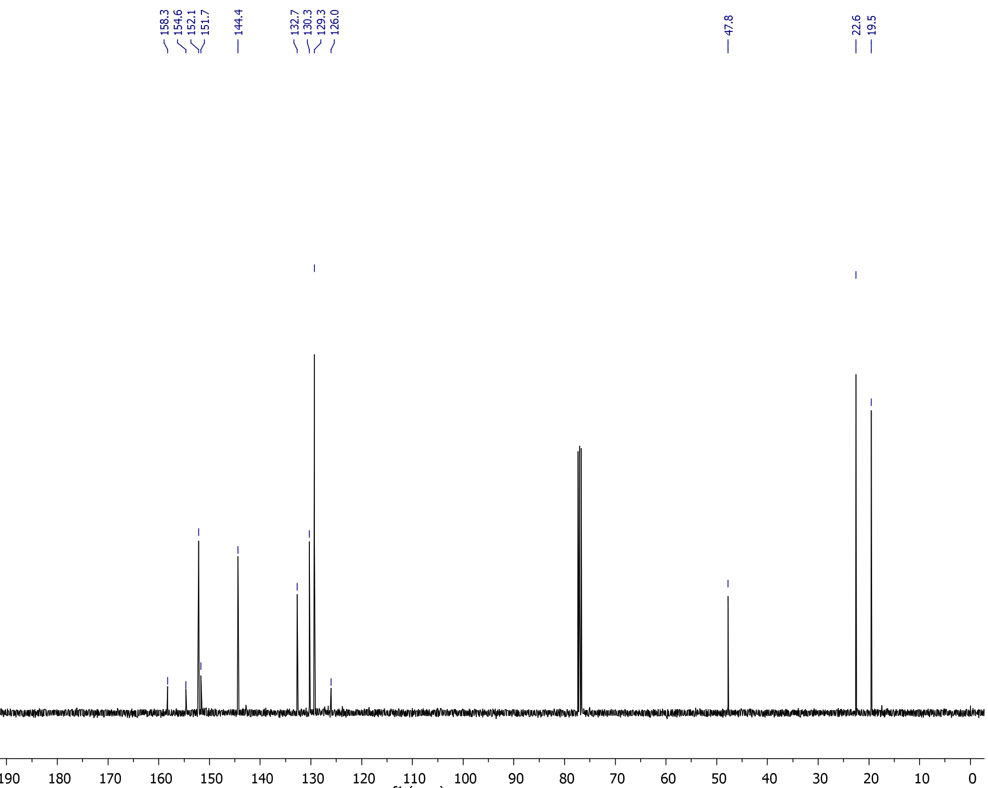
6o



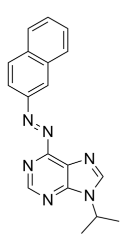
9.052
8.258
7.244
7.228
7.223
7.207
7.164
7.145
5.064
5.047
5.030
5.013
4.996
4.979
4.962
2.531
1.695
1.679
0.90
1.00
1.18
1.95
1.05
6.20
6.77
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



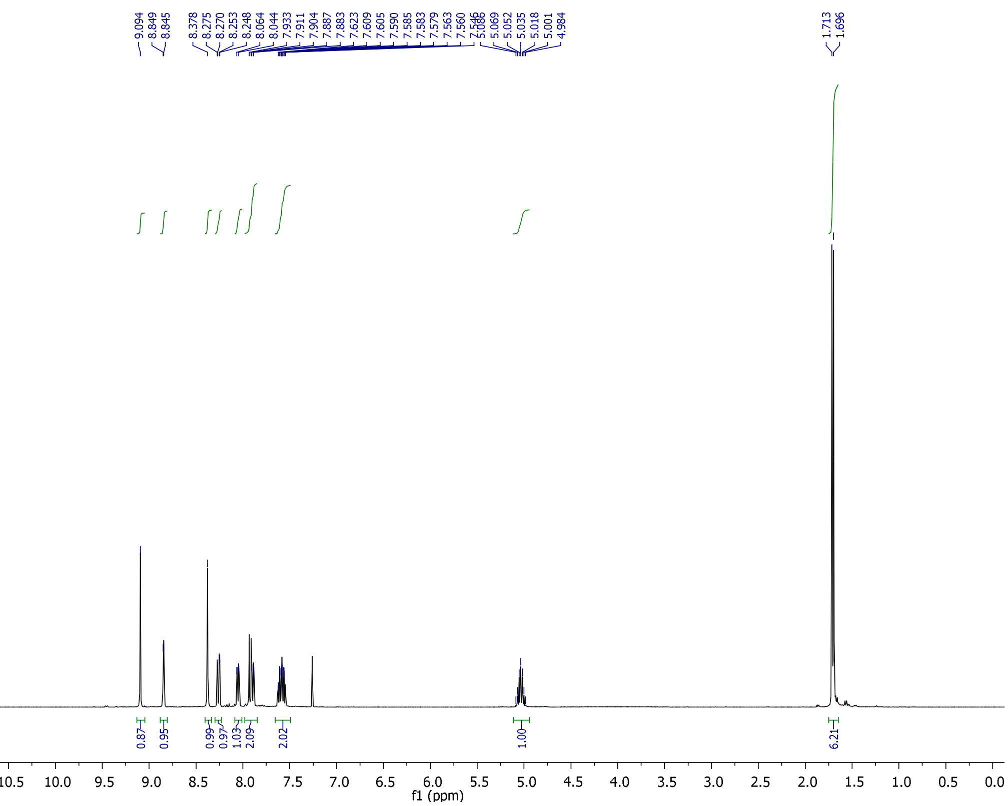
6o

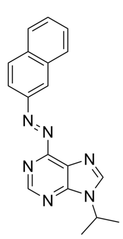


158.3
154.6
152.1
151.7
144.4
132.7
130.3
129.3
126.0
47.8
22.6
19.5
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

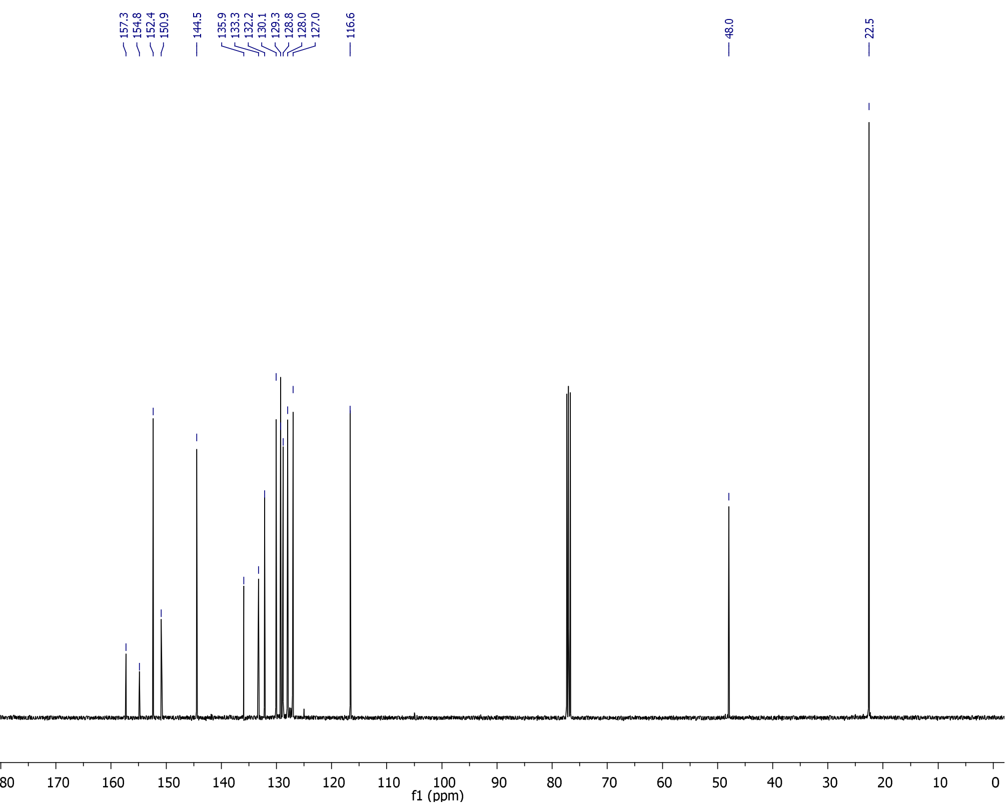


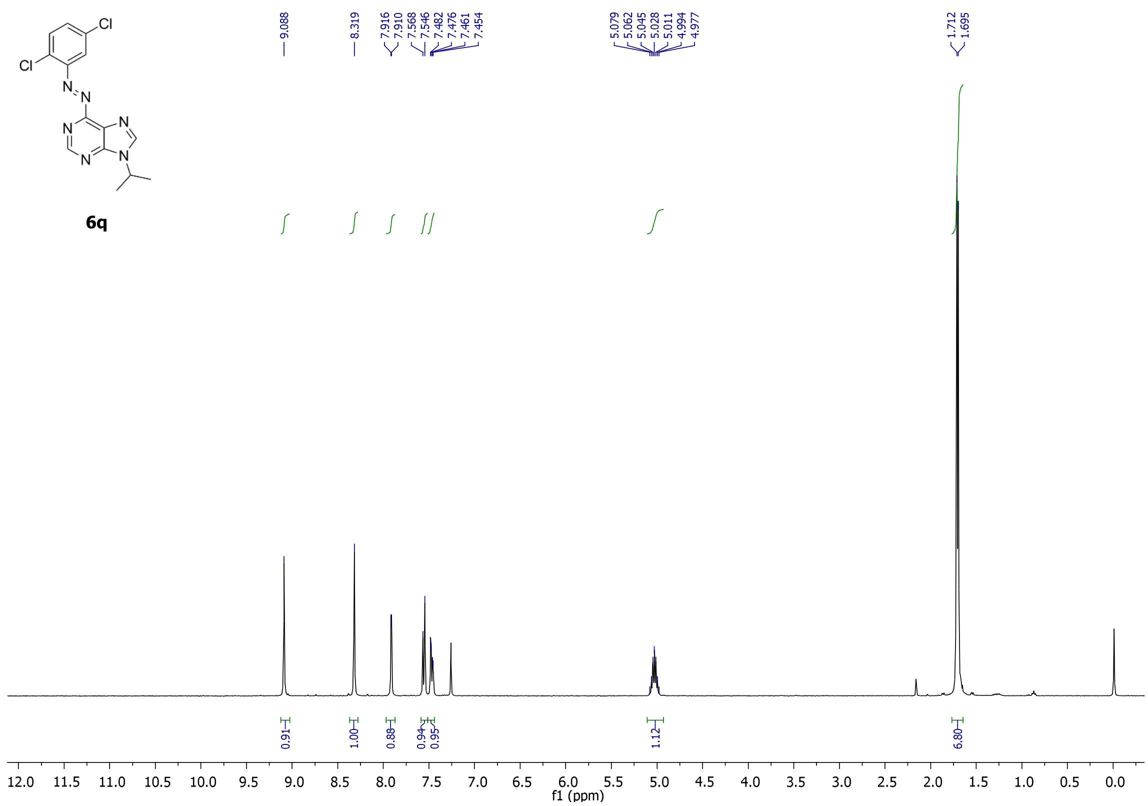
6p

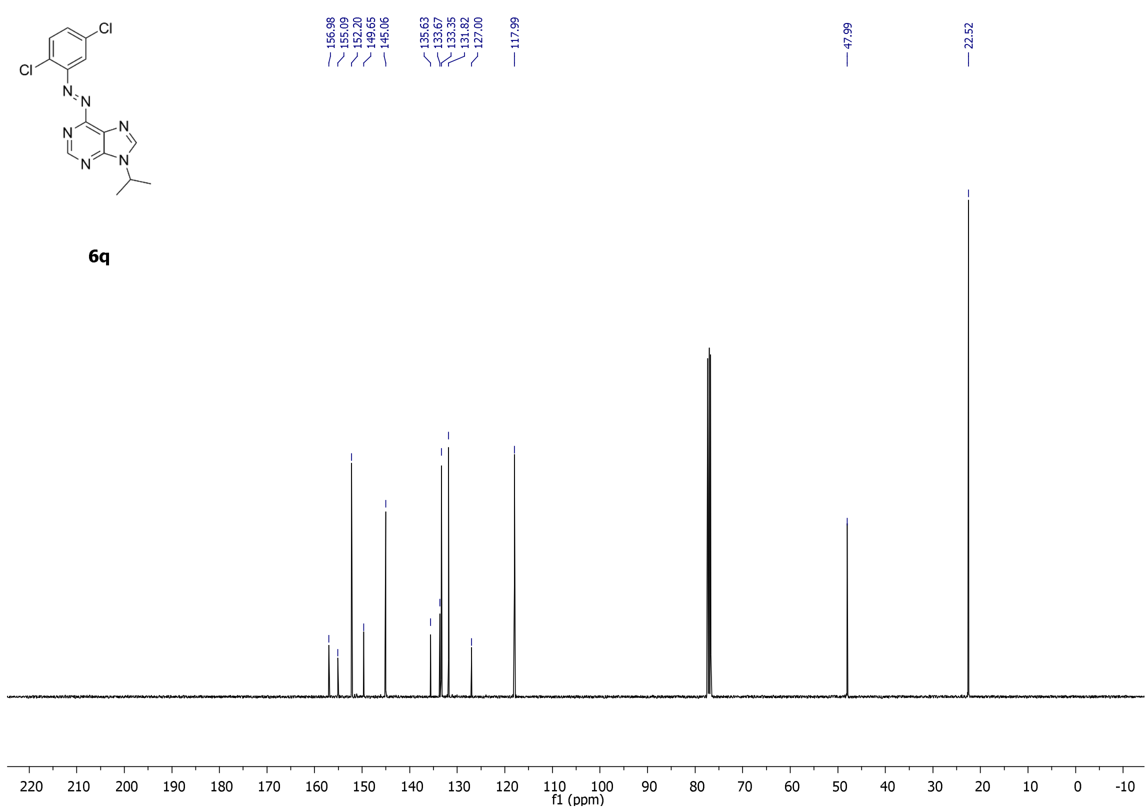


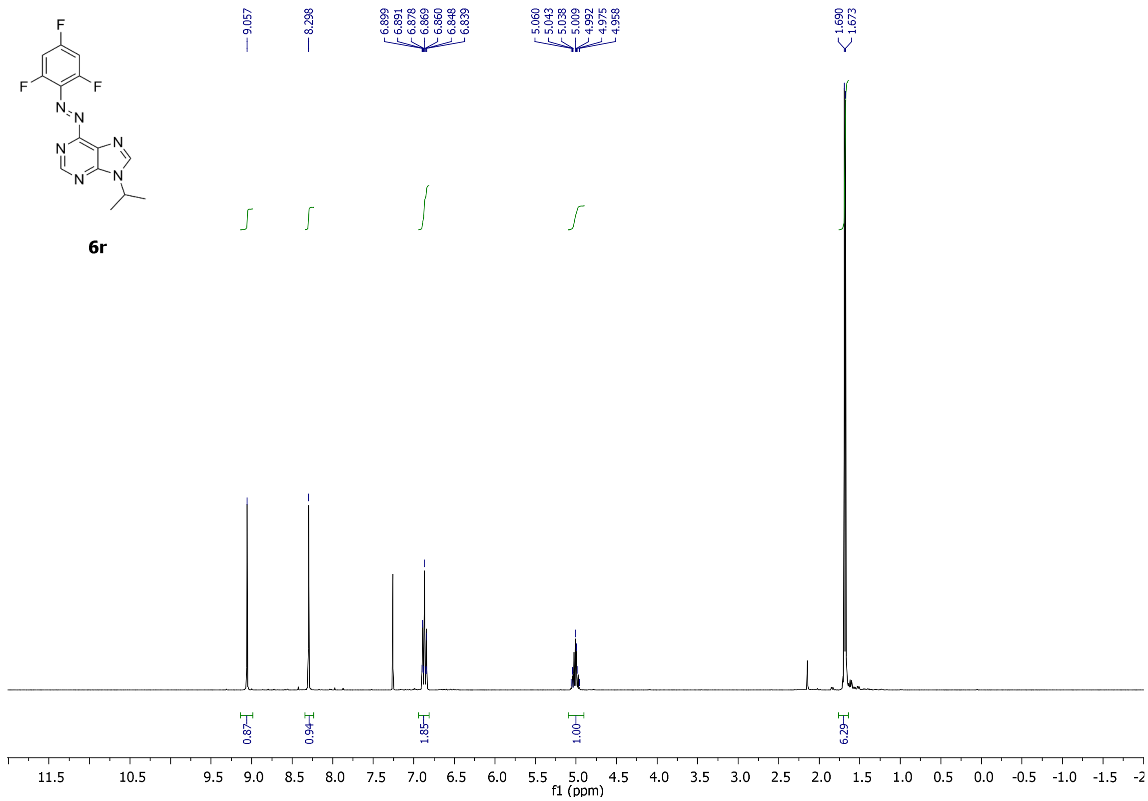


6p



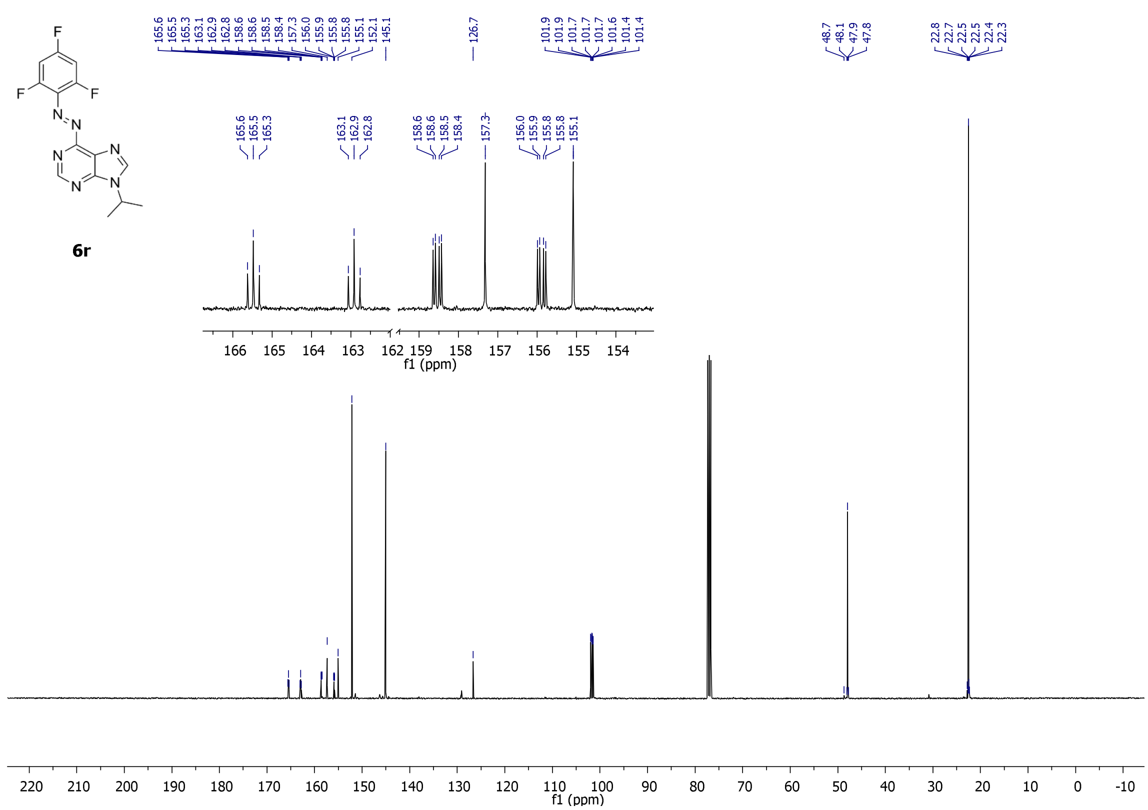

6q
9.088
8.319
7.916
7.910
7.568
7.546
7.482
7.476
7.461
7.454
5.079
5.062
5.045
5.028
5.011
4.994
4.977
1.712
1.695
0.91
1.00
0.88
0.94
0.95
1.12
6.80
f1 (ppm)


6q
156.98
155.09
152.20
149.65
145.06
135.63
133.67
133.35
131.82
127.00
117.99
47.99
22.52
f1 (ppm)



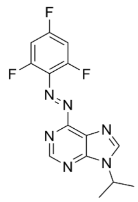
9.057
8.298
6.899
6.891
6.878
6.869
6.860
6.848
6.839
5.060
5.043
5.038
5.009
4.992
4.975
4.958
1.690
1.673
0.87
0.94
1.85
1.00
6.29
f1 (ppm)

6r

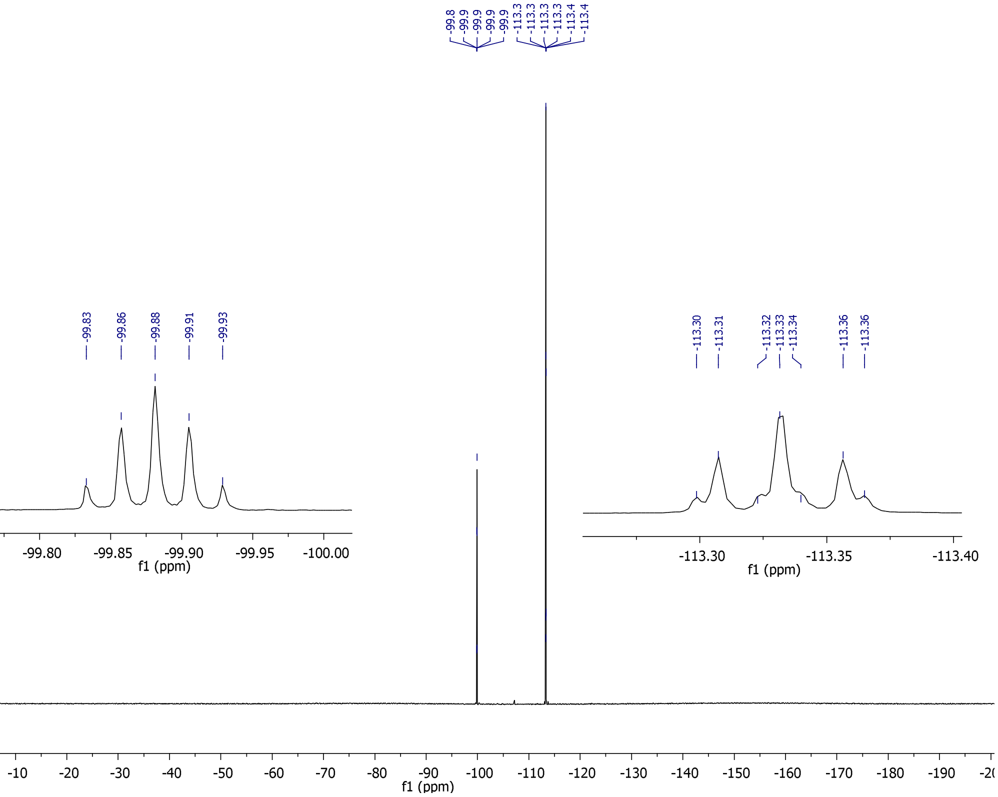


165.6
165.5
165.3
163.1
162.9
162.8
158.6
158.6
158.5
158.4
157.3
156.0
155.9
155.8
155.8
155.1
152.1
145.1
126.7
101.9
101.9
101.7
101.7
101.7
101.6
101.4
101.4
48.7
48.1
47.9
47.8
22.8
22.7
22.5
22.5
22.4
22.3
f1 (ppm)

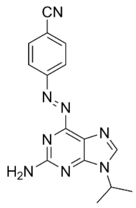
6r



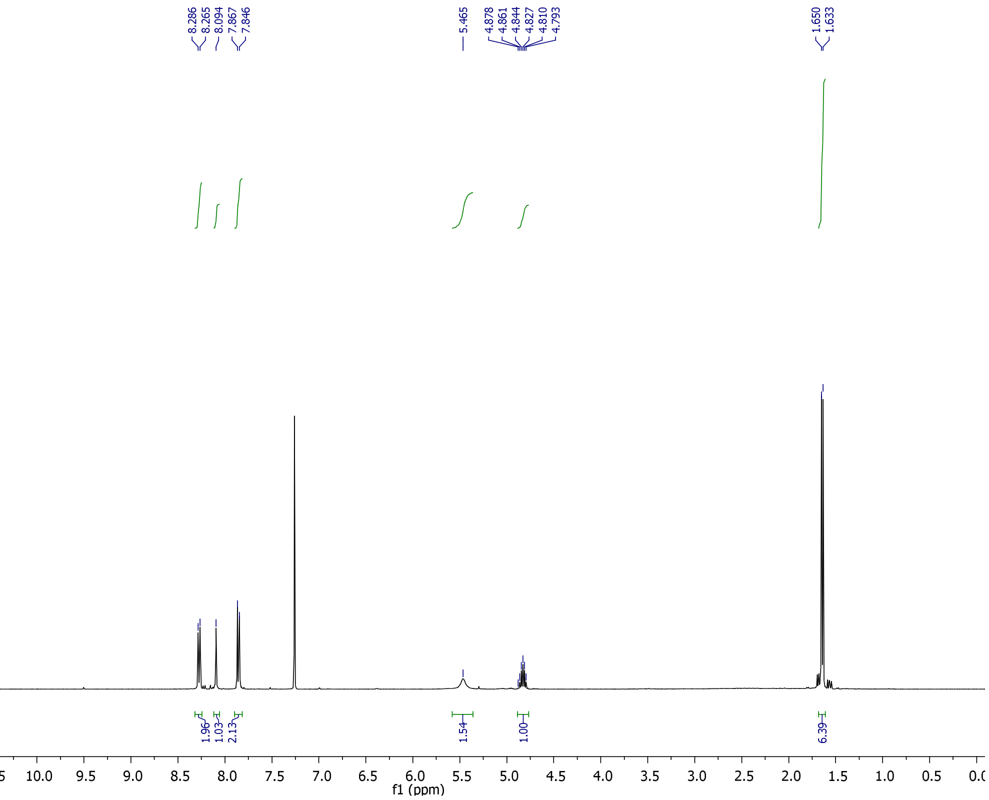
6r

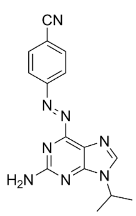

-99.83
-99.86
-99.88
-99.91
-99.93
-113.30
-113.31
-113.32
-113.33
-113.34
-113.36
-113.36
f1 (ppm)

NMR data for 6-azoguanines

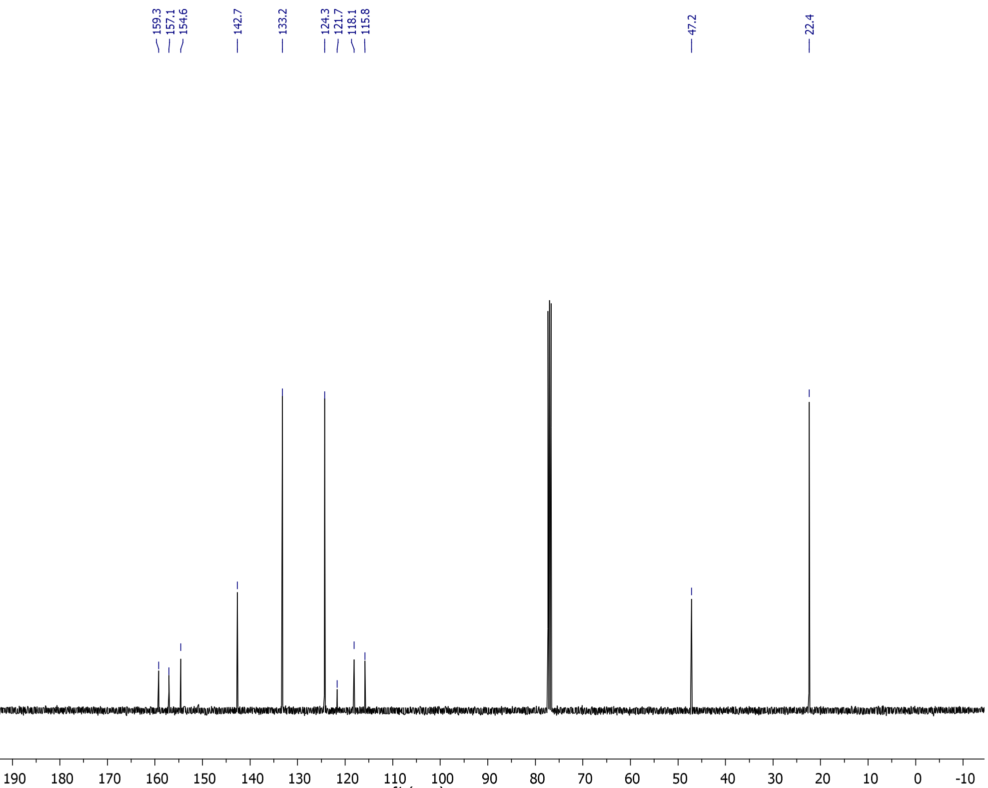


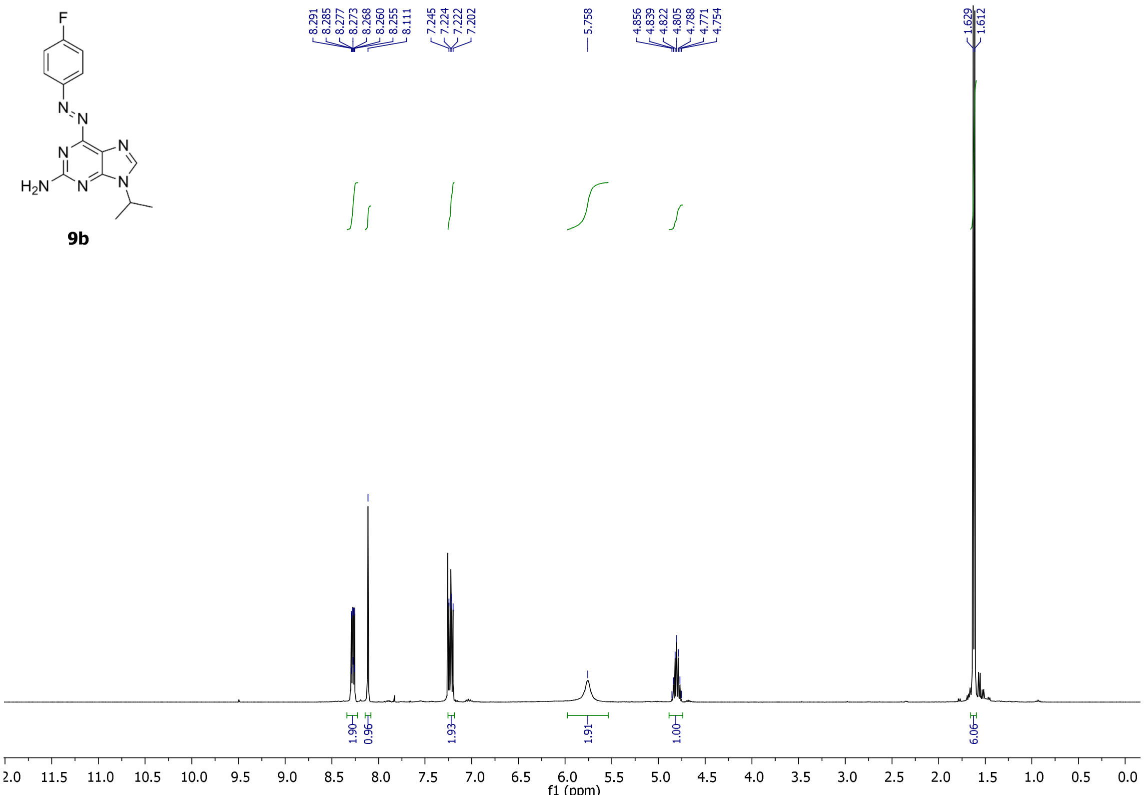
9a

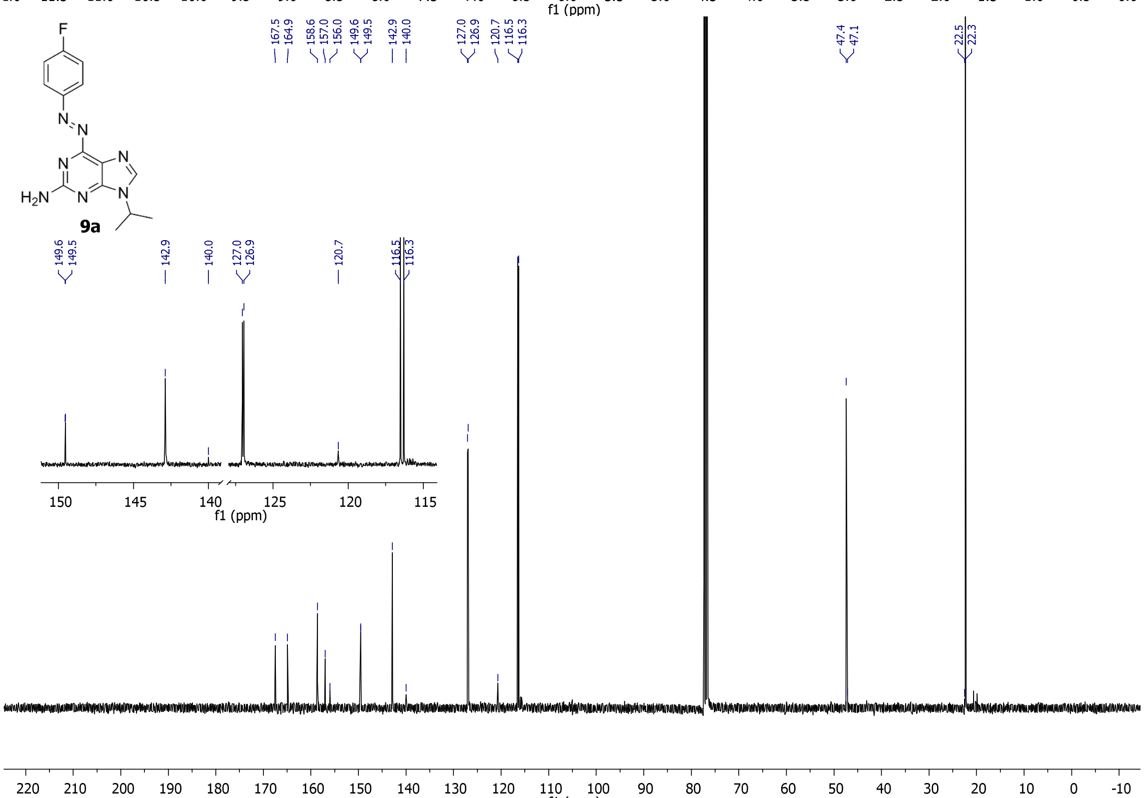


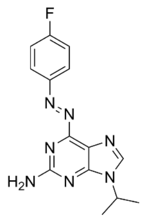


9a

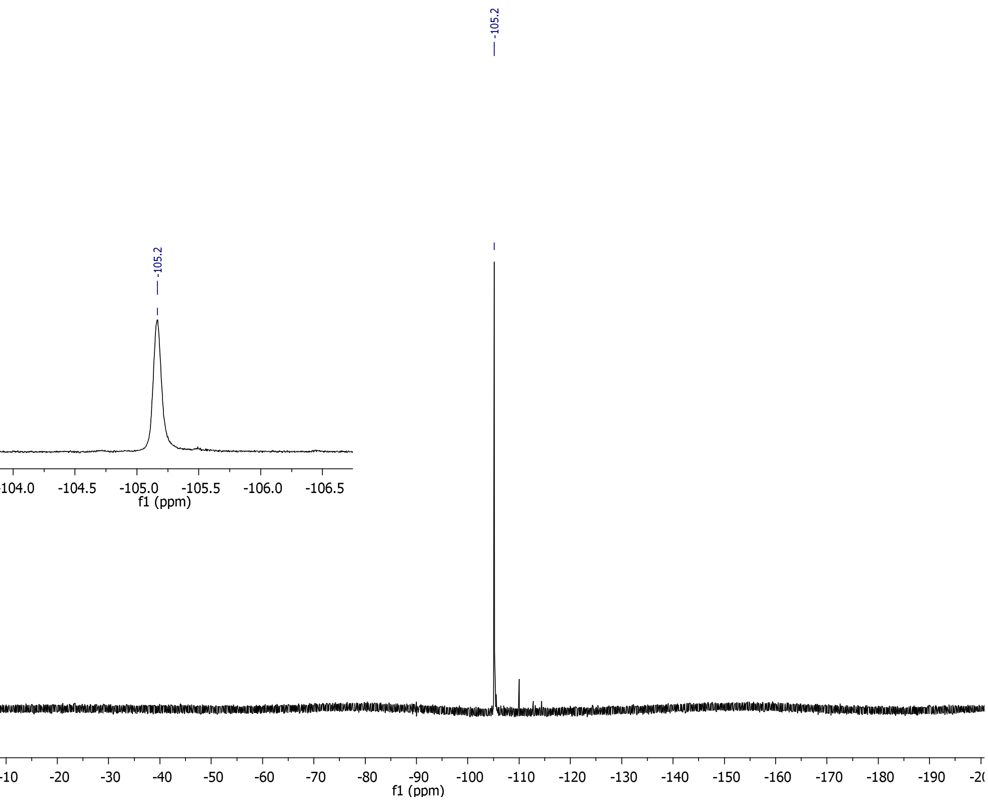


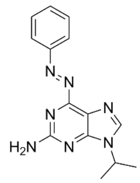

9b
8.291
8.285
8.277
8.273
8.268
8.260
8.255
8.111
7.245
7.224
7.222
7.202
5.758
4.856
4.839
4.822
4.805
4.788
4.771
4.754
1.629
1.612
1.90
0.96
1.93
1.91
1.00
6.06
f1 (ppm)


9a
167.5
164.9
158.6
157.0
156.0
149.6
149.5
142.9
140.0
127.0
126.9
120.7
116.5
116.3
47.4
47.1
22.5
22.3
f1 (ppm)

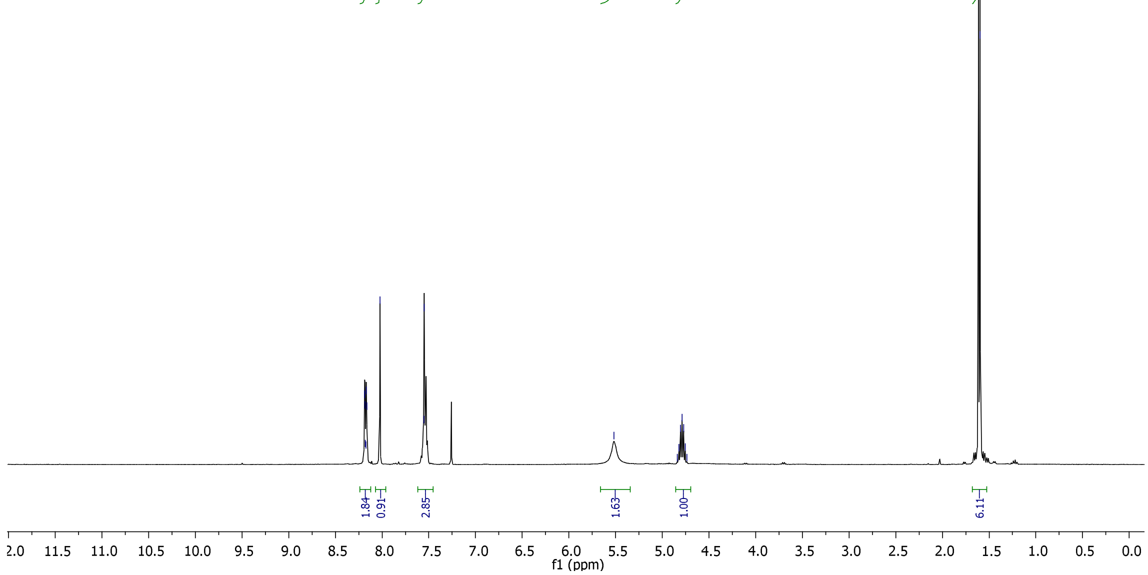


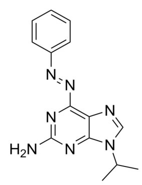
9a


-105.2
-105.2
-104.0
-104.5
-105.0
-105.5
-106.0
-106.5
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

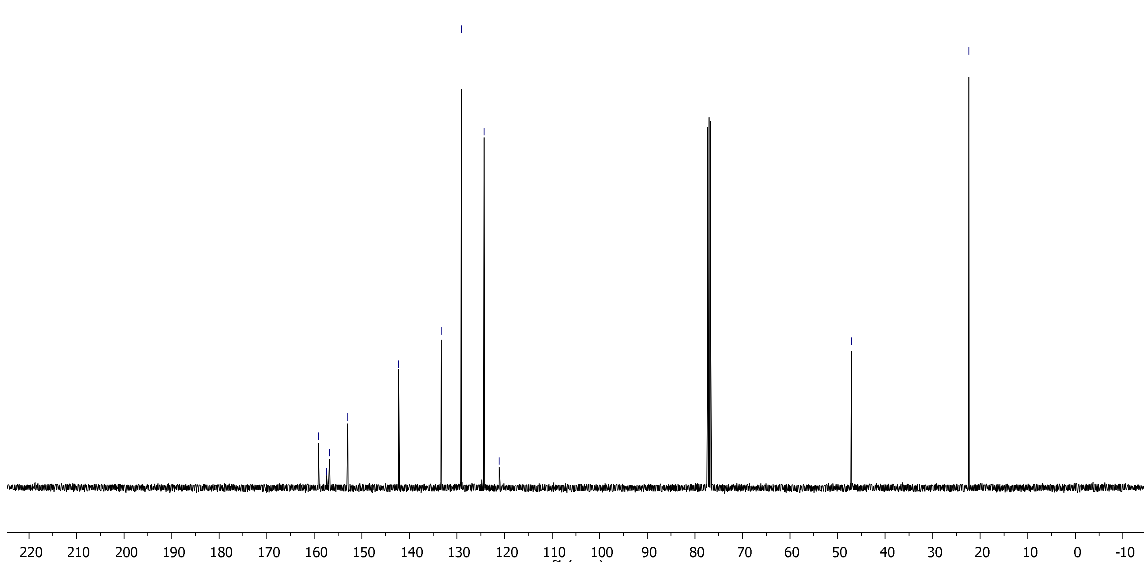


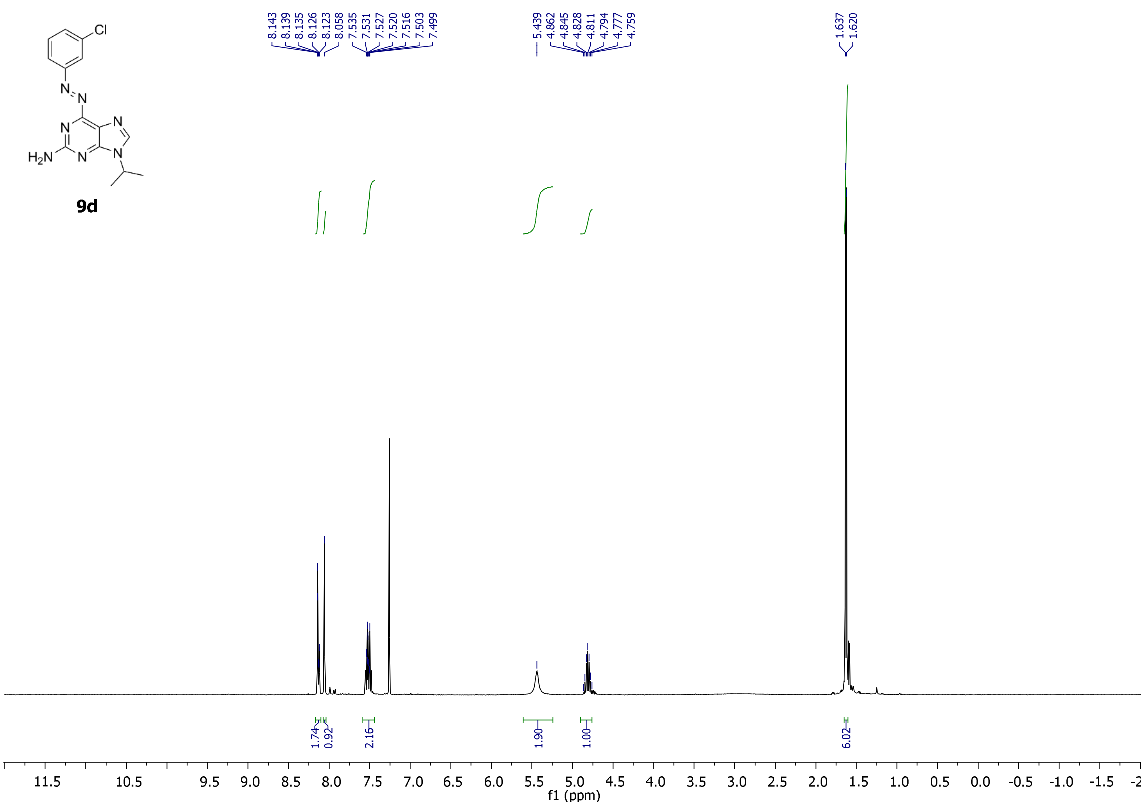
9c

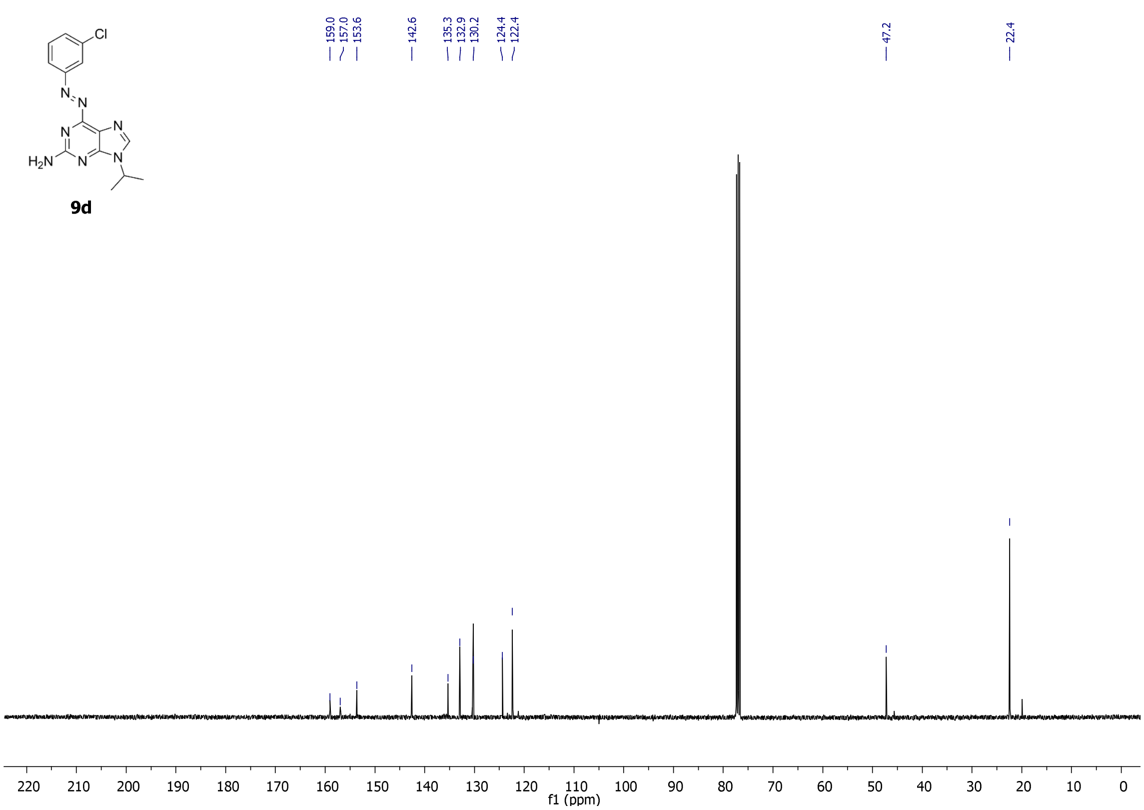

8.188
8.184
8.179
8.173
8.169
8.164
8.023
7.552
7.549
5.516
4.840
4.823
4.806
4.789
4.772
4.755
4.738
1.615
1.597
1.84
0.91
2.85
1.63
1.00
6.11
f1 (ppm)



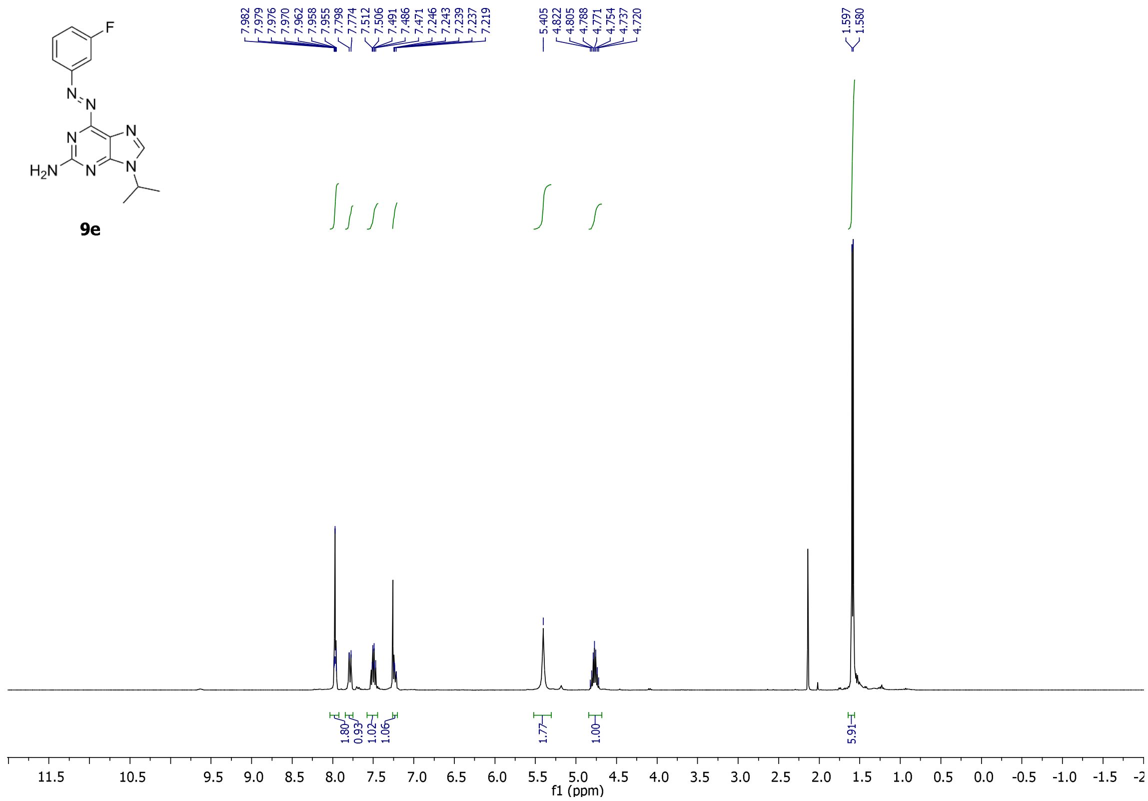
9c


159.1
157.4
156.8
153.0
142.3
133.3
129.1
124.3
121.1
47.1
22.4
f1 (ppm)

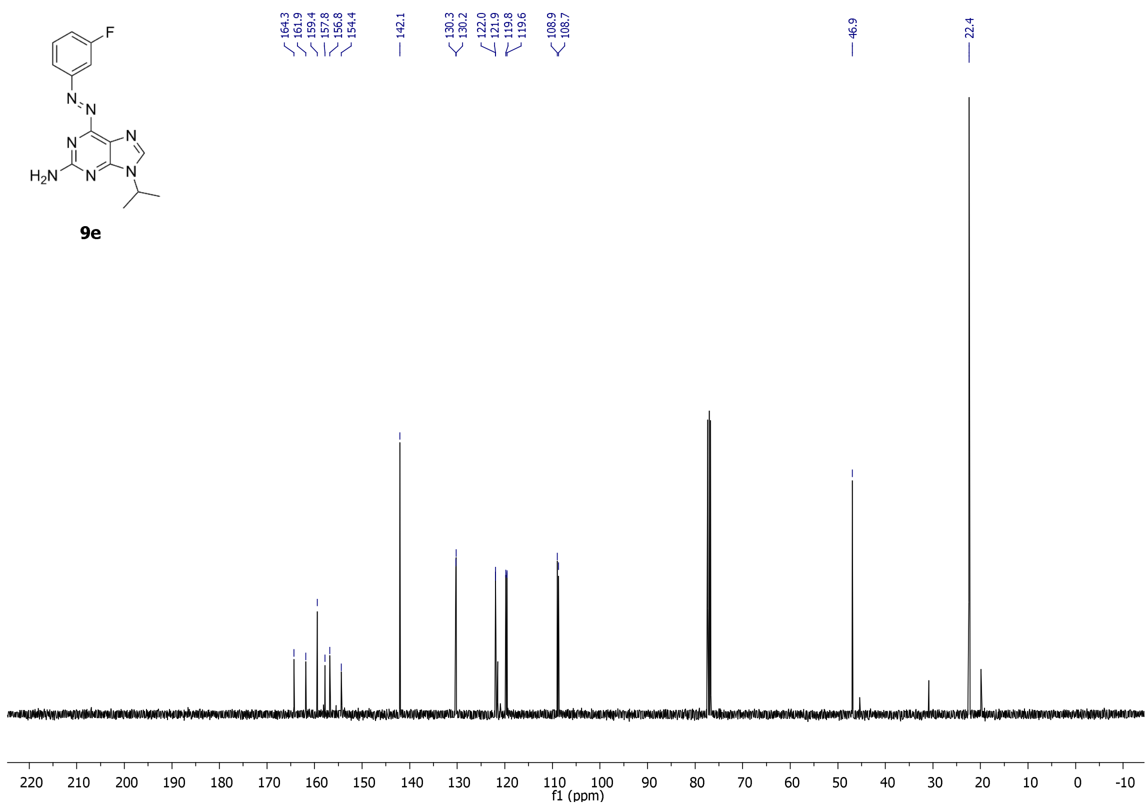

9d
8.143
8.139
8.135
8.126
8.123
8.058
7.535
7.531
7.527
7.520
7.516
7.503
7.499
5.439
4.862
4.845
4.828
4.811
4.794
4.777
4.759
1.637
1.620
1.74
0.92
2.16
1.90
1.00
6.02
f1 (ppm)

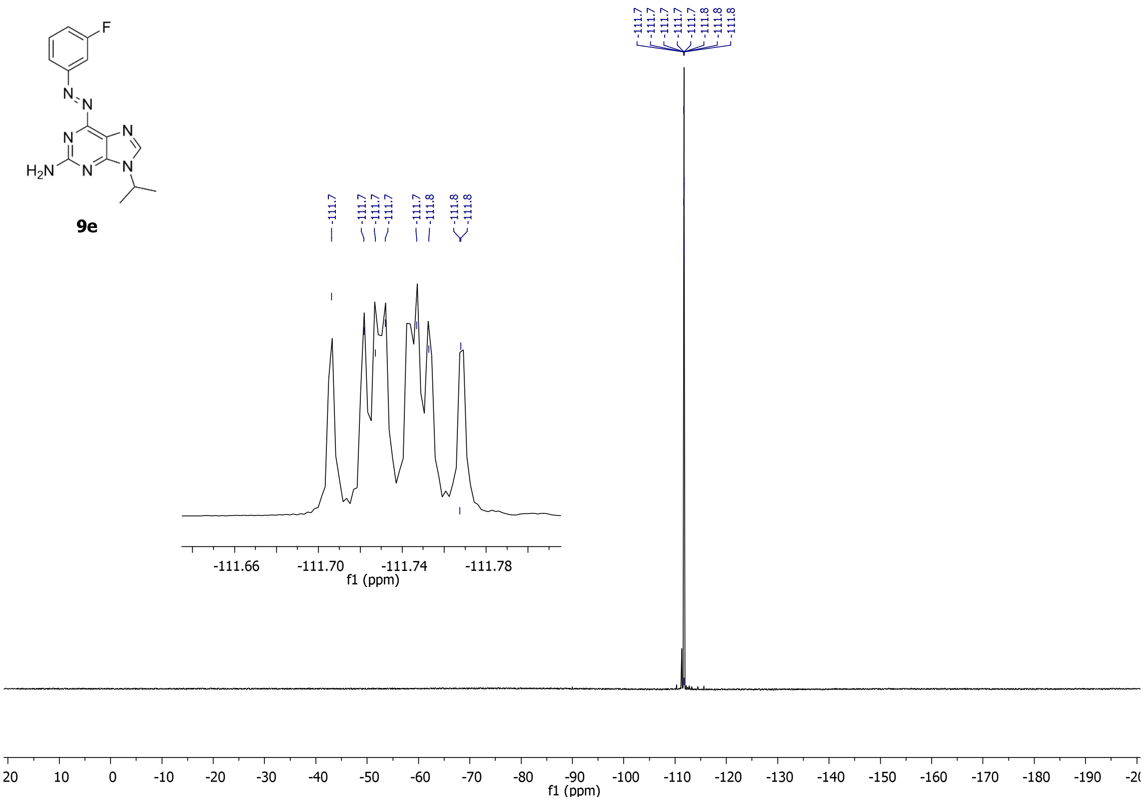

9d
159.0
157.0
153.6
142.6
135.3
132.9
130.2
124.4
122.4
47.2
22.4
f1 (ppm)

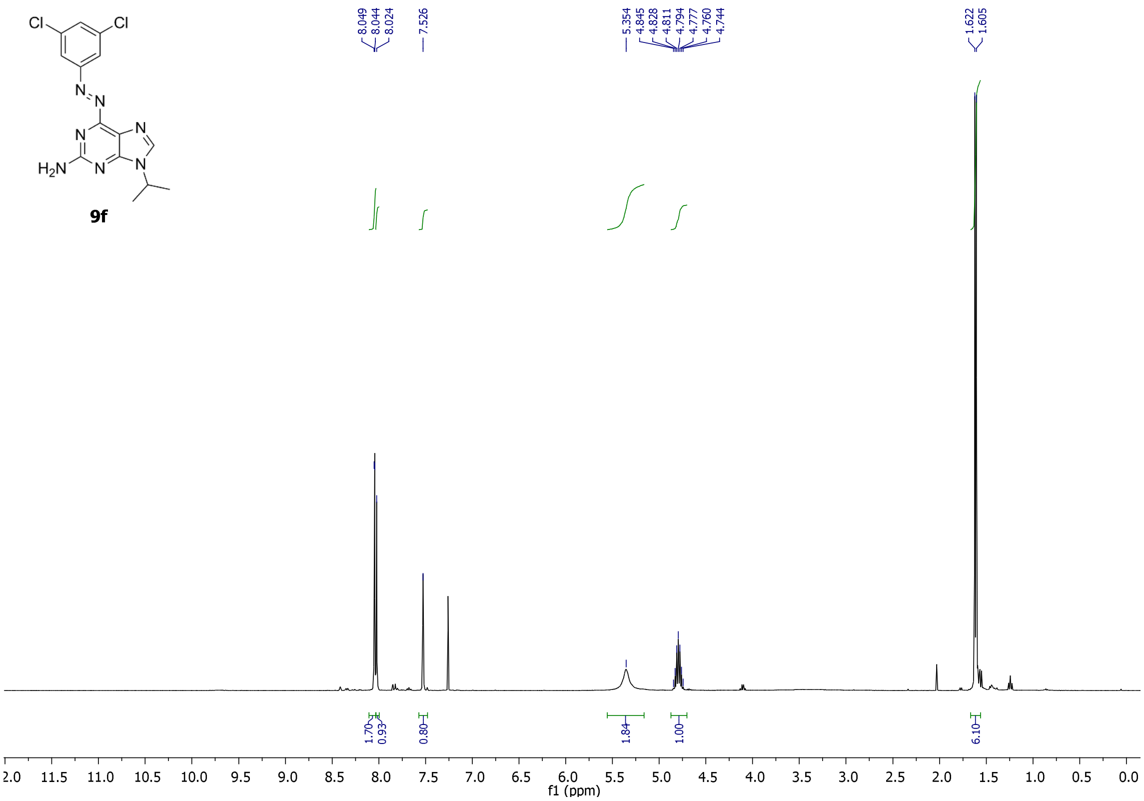
9e

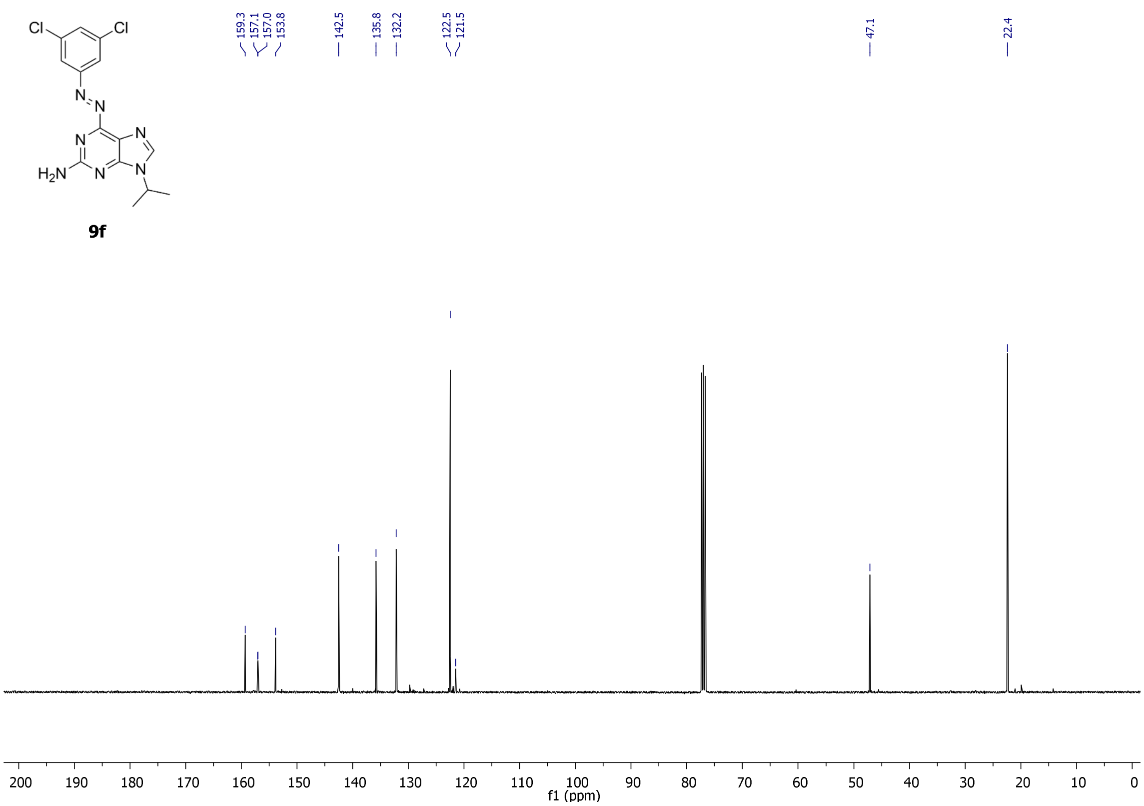


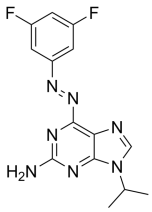
9e



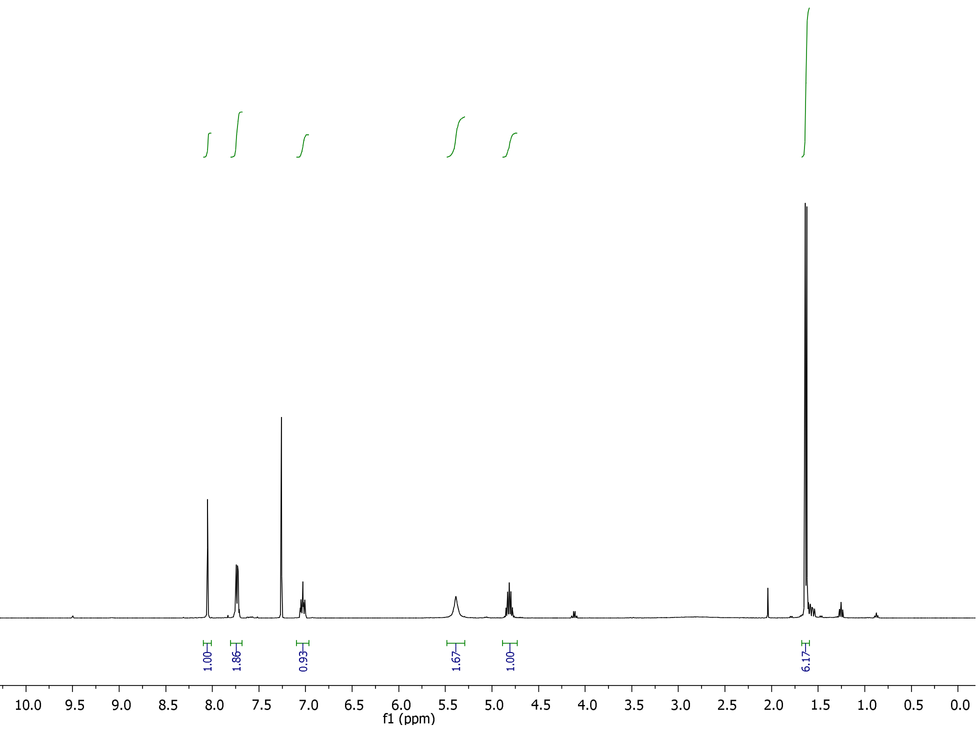

F
N
N
N
N
N
N
H2N
9e
-111.7
-111.7
-111.7
-111.7
-111.7
-111.8
-111.8
-111.8
-111.66
-111.70
-111.74
-111.78
f1 (ppm)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

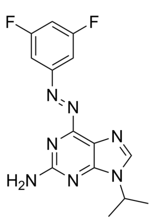

9f
8.049
8.044
8.024
7.526
5.354
4.845
4.828
4.811
4.794
4.777
4.760
4.744
1.622
1.605
1.70
0.93
0.80
1.84
1.00
6.10
f1 (ppm)


9f
159.3
157.1
157.0
153.8
142.5
135.8
132.2
122.5
121.5
47.1
22.4
f1 (ppm)

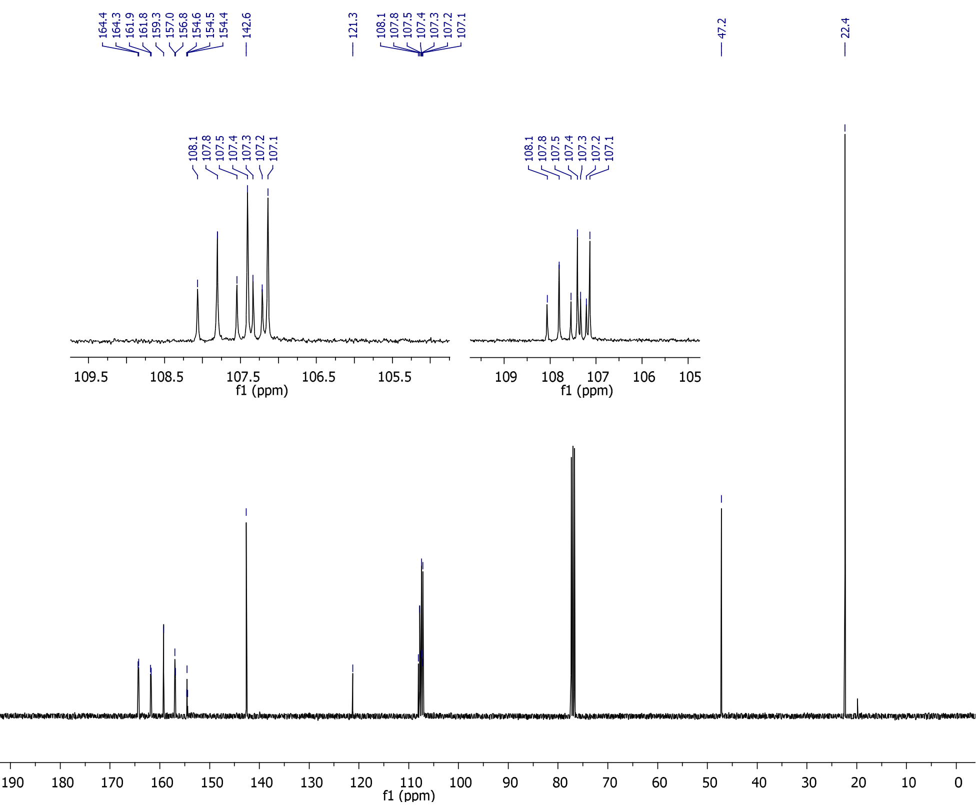

F
F
N
N
N
N
N
N
H_2N

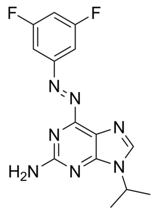
9g


1.00
1.86
0.93
1.67
1.00
6.17
f1 (ppm)

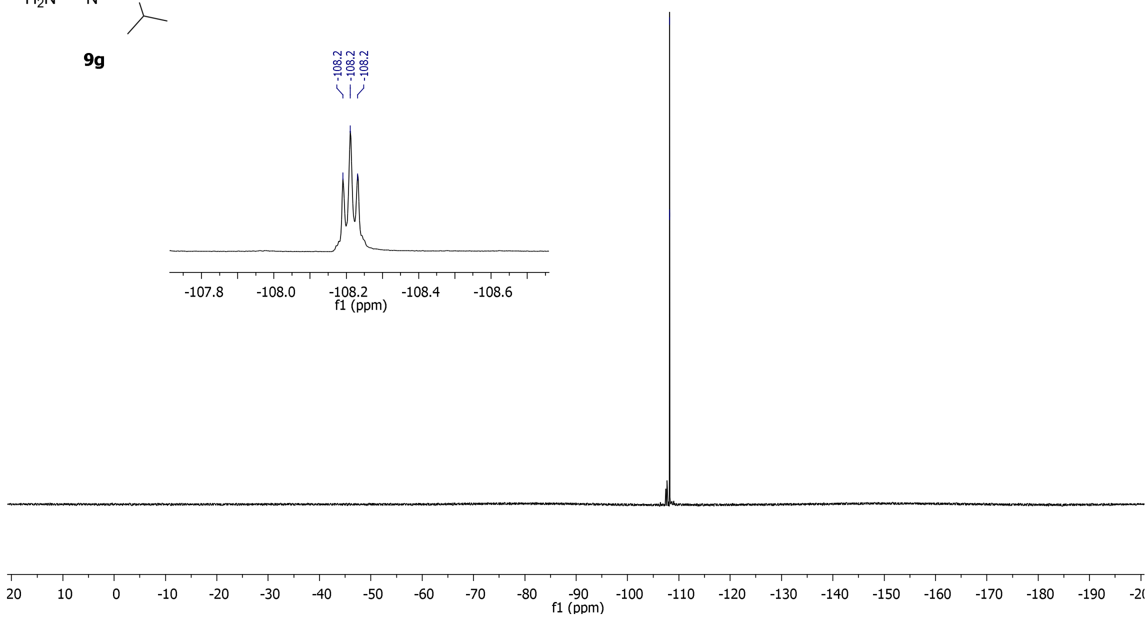

F
F
N
N
N
N
N
N
H_2N

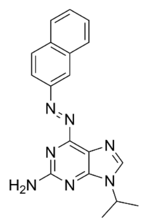
9g


164.4
164.3
161.9
161.8
159.3
157.0
156.8
154.6
154.5
154.4
142.6
121.3
108.1
107.8
107.5
107.4
107.3
107.2
107.1
47.2
22.4
f1 (ppm)

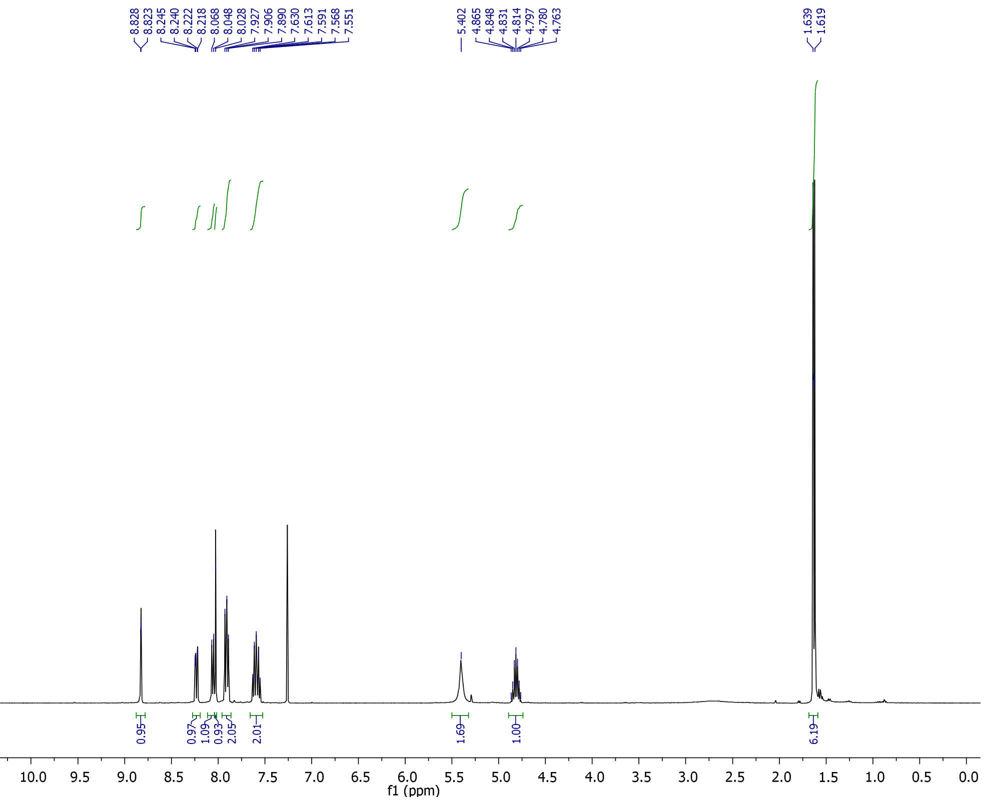

F
F
N
N
N
N
N
N
H2N
N

9g

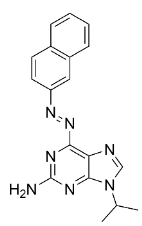

-108.2
-108.2
-108.2
-107.8
-108.0
-108.2
-108.4
-108.6
f1 (ppm)
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)



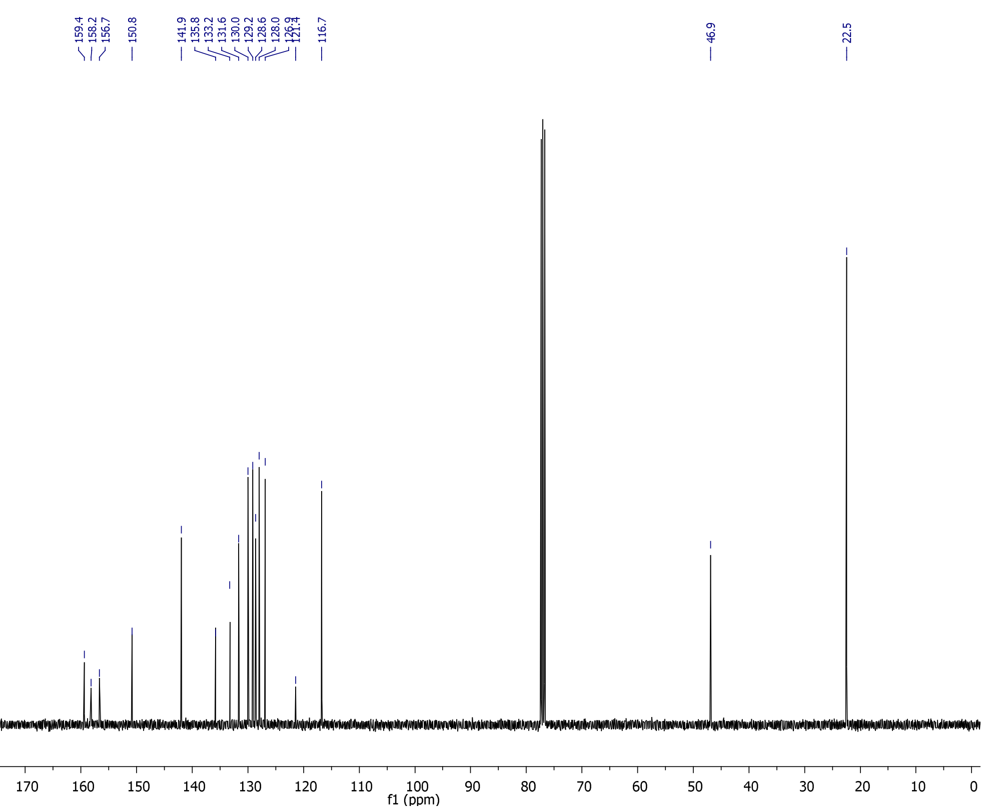
9h



8.828
8.823
8.245
8.240
8.222
8.218
8.068
8.048
8.028
7.927
7.906
7.890
7.630
7.613
7.591
7.568
7.551
5.402
4.865
4.848
4.831
4.814
4.797
4.780
4.763
1.639
1.619
0.95
0.97
1.09
0.93
2.05
2.01
1.69
1.00
6.19
f1 (ppm)



9h



159.4
158.2
156.7
150.8
141.9
135.8
133.2
131.6
130.0
129.2
128.6
128.0
126.9
121.4
116.7
46.9
22.5
f1 (ppm)

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