Electronic Supplementary Information (ESI)

Oxidation of Diazenyl-protected *N*-Heterocycles – a New Entry to Functionalized Lactams

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Oxidant **Solvent**

1. Oxidation of 4-(piperidin-1-ylazo)-benzoic acid ethyl ester 3c{1}.

Table S1. Optimization of reaction conditions at room temperature[a]

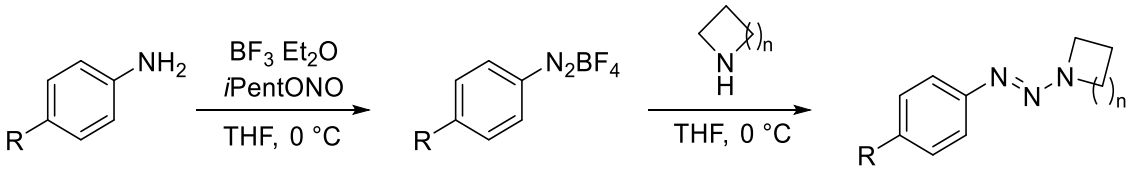
	Precatalyst	Oxidant	Solvent	Time [h]	yield[b] [%]
1	$RuCl_3$ H_2O (30%)	$NaIO_4$ (5 eq)	CCl_4/ACN/buffer (pH = 8), (2/2/3)	2	52 (61)[c]
2	$RuCl_3$ H_2O (30%)	$NaIO_4$ (5 eq)	CCl_4/ACN/H_2O (2/2/3)	2	44
3	$RuCl_3$ H_2O (15%)	$NaIO_4$ (2.5 eq)	CCl_4/ACN/H_2O (2/2/3)	2.5	39
4	$RuCl_3$ H_2O (45%)	$NaIO_4$ (5 eq)	EtOAc/ACN/H_2O (2/0.4/2)	2.5	16
5	$RuCl_3$ H_2O (30%)	$NaIO_4$ (5 eq)	DCM/H_2O (1/1)	14	10
6	$RuCl_3$ H_2O (30%)	$NaIO_4$ (3 eq)	DCM/ACN/H_2O (2/1/2)	14	16
7	$RuCl_3$ H_2O (30%)	$NaIO_4$ (3 eq)	$CHCl_3$/ACN/H_2O (2/1/2)	14	10
8	RuO_2 H_2O (30%)	$NaIO_4$ (5 eq)	CCl_4/ACN/H_2O (2/2/3)	14	47
9	(Diacetoxyiodo)benzene (4 eq)	H_2O_2 (3 eq)	CH_3CN	14	-[1]
10	(Diacetoxyiodo)benzene (4 eq)	THYDRO (3 eq)	CH_3CN	14	19
11	$Rh_2(cap)_4$ (5%)	THYDRO (20 eq)	ACN	14	22[2]
12	$Rh_2(OAc)_4$ (5%)	THYDRO (20 eq)	ACN	14	-

[a] Reaction carried out on 0.2 mmol scale. [b] Yield after chromatography. [c] Reaction carried out on 2 mmol scale.

[1] Y. Zhao, J. Q. L. Ang, A. W. T. Ng, Y.-Y. Yeung, *RSC Adv.*, **2013**, *3*, 19765 – 19768.
[2] Y. Wang, Y. Kuang, Y. Wang, *Chem. Commun*., **2015**, *51*, 5852 – 5855.

2. Experimental procedures

General Information. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-AC-250 instrument using $CDCl_3$ as solvent. The coupling constant *J* was assigned in Hertz [Hz]. MS (EI) (electron impact mass spectrometry) and EI-HRMS: Finnigan MAT 90 (70 eV). The molecular fragments are quoted as the relation between mass and charge (m/z), the intensities as a percentage value relative to the intensity of the base signal (100%). IR spectra of solids were recorded in KBr, and of oils as thin films on KBr. The deposit of the absorption band is given in wave numbers in cm^{-1}. Melting points are uncorrected. Chromatographic separations were performed under pressure on silica gel by flash-column techniques; R_f values refer to TLC carried out on 0.25-mm silica gel plates (Merck F_{254}), with the same eluent as indicated for the column chromatography. Solvents and chemicals used for reactions were purchased from commercial suppliers. Solvents and chemicals were used without further purification.



General procedure 1 (GP1) for the synthesis of triazenes.

Triazenes were prepared under basic conditions in reaction between a diazonium salt and a cyclic amine according to known procedures.[3,4]

Preparation of the diazonium salt (part 1): A solution of aniline (1 mmol) in DCM (4 mL) was rapidly added to the solution of $BF_3 \cdot Et_2O$ (2 mmol) in THF (8 mL) at 0 °C. Few minutes later, isopentyl nitrite (2 mmol) was slowly added to the reaction mixture and the ice bath was removed. The reaction mixture was stirred at room temperature for 2 h. The formed precipitate was collected by filtration, washed with Et_2O and the obtained diazonium salt was used in the next step.

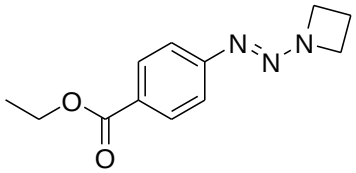
(Part 2): A solution of cyclic amine (2 mmol) and Et_3N (4 mmol) in THF (4 mL) was cooled by an ice bath and the diazonium salt (1 mmol) was added portion-wise. The ice bath was removed and the reaction was stirred at room temperature for 30 min. Water (5 mL) was added and the product was extracted with Et_2O (3 x 5 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated. The crude was purified by column chromatography.

General procedure 2 (GP2) for the oxidation of triazenes.

To a stirred mixture of phosphate buffer (pH = 8, c = 0.3 M)/CCl_4/ACN = 3:2:2 (10 mL) were added $NaIO_4$ (5 mmol) and $RuCl_3 \cdot H_2O$ (0.3 mmol). After 5 minutes the substrate (1 mmol) was slowly added and the reaction mixture was left to stir at room temperature. The progress of the reaction was monitored by TLC. Isopropanol was added and formed precipitate was removed by filtration through a Celite pad (washed with 10 mL of DCM). The mother liquid was washed with water (10 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated. The crude was purified by column chromatography.

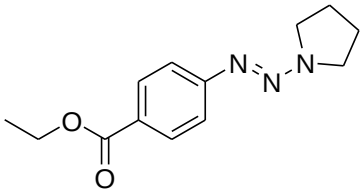
[3] Ryszard Lazny, Janusz Poplawski, Johannes Köbberling, Dieter Enders, Stefan Bräse, *Synlett* **1999**, 1304–1306.
[4] Jinlong Fu, Kelvin Lau, Mónica Barra, *JOC* **2009**, *74*, 1770-1773.

4-(Azetidin-1-ylazo)-benzoic acid ethyl ester (3a)



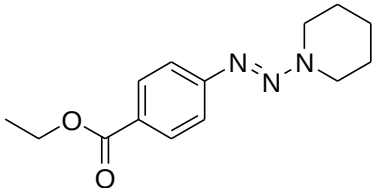
Diazonium salt, synthesized following **GP1 (part 1)** from 4-amino-benzoic acid ethyl ester (1 mmol), was slowly added to the cold solution of azetidin hydrochloride (2 mmol) in NaOH (1 M, 5 mL). The product was extracted with Et_2O (3 × 5 mL) and combined organic layers were dried over Na_2SO_4, filtered and concentrated. After chromatography (cyclohexane/EtOAc = 10:1 + 1% Et_3N), the pure compound **3a** (145 mg, 62%) was obtained as a yellow solid. - **R_f** (cyclohexane/EtOAc = 10:1) = 0.36. - **m.p. =** 54.1 – 54.8 °C. - **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 7.95 (d, *J* = 8.6 Hz, 2 H), 7.38 (d, *J* = 8.6 Hz, 2 H), 4.50 – 4.11 (m, 6 H), 2.47 – 2.16 (m, 2 H), 1.32 (t, *J* = 7.1 Hz, 3 H) ppm. - **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 166.6, 154.2, 130.7, 128.0, 120.3, 60.5, 55.7, 15.7, 14.5 ppm. **MS (EI),** m/z (%): 233 (30) $[M]^+$, 188 (9) $[C_9H_{10}N_3O]^+$, 177 (40) $[C_9H_9N_2O]^+$, 149 (100) $[C_9H_9O_2]^+$. - **HRMS** ($C_{12}H_{15}N_3O_2$): calc. 233.1159, found 233.1160. - **IR** (ATR, ṽ): 2976, 1705, 1596, 1455, 1370, 1242, 1212, 1137, 1096, 1023, 860, 773, 699, 548, 522, 503, 424 cm^{-1}. - **EA** ($C_{12}H_{15}N_3O_2$): calc. C 61.79, H 6.48, N 18.01, O 13.72; found C 61.76, H 6.38, N 17.76.

4-(Pyrrolidin-1-ylazo)-benzoic acid ethyl ester (3b)[5]



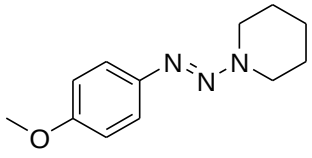
Compound **3b** was synthesized following **GP1** from 4-amino-benzoic acid ethyl ester (2 mmol) and pyrrolidine (4 mmol). After chromatography (cyclohexane/EtOAc = 20:1 + 1% Et_3N), the pure compound **3b** (384 mg, 78%) was obtained as yellow crystals. - **R_f** (cyclohexane/EtOAc = 20:1) = 0.34. - **m.p. =** 65.2 – 65.4°C. - **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.6 Hz, 2 H), 7.44 (d, *J* = 8.6 Hz, 2 H), 4.35 (q, *J* = 7.1 Hz, 2 H), 4.09 – 3.84 (m, 2 H), 3.84 – 3.58 (m, 2 H), 2.16 – 1.93 (m, 4 H), 1.39 (t, *J* = 7.1 Hz, 3 H) ppm. - **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 166.7, 154.8, 130.7, 130.5, 126.8, 120.3, 60.5, 23.7, 14.4 ppm. - **HRMS** ($C_{13}H_{17}N_3O_2$): calc. 247.1315, found 247.1317. **- IR** (ATR, ṽ): 2973, 2875, 1707, 1597, 1504, 1476, 1451, 1421, 1388, 1341, 1312, 1260, 1222, 1148, 1099, 1021, 857, 772, 698, 611, 550, 524, 500, 416 cm^{-1}. - **EA** ($C_{13}H_{17}N_3O_2$): calc. C 63.14, H 6.93, N 16.99, O 12.94; found C 63.21, H 6.92, N 16.91.

4-(Piperidin-1-ylazo)-benzoic acid ethyl ester (3c{1})



Compound **3c{1}** was synthesized following **GP1** from 4-amino-benzoic acid ethyl ester (3 mmol) and piperidine (6 mmol). After chromatography (cyclohexane/EtOAc = 10:1 + 1% Et_3N) the pure product**3c{1}** (675 mg, 85%) was obtained as a yellow solid. - **R_f** (cyclohexane/EtOAc = 10:1) = 0.21. **- m.p. =** 128.4 - 129.5 °C. - **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 8.01 (d, *J* = 8.7 Hz, 2 H), 7.45 (d, *J* = 8.7 Hz, 2 H), 4.36 (q, *J* = 7.7 Hz, 2 H), 3.90 – 3.78 (m, 4 H), 1.81 – 1.67 (m, 6 H), 1.39 (t, *J* = 7.7 Hz, 3 H) ppm. - **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 167.7, 155.4, 131.6, 128.3, 121.2, 61.7, 27.9, 26.4, 25.3, 15.4 ppm. **MS (ESI),** m/z (%): 543 (100) $[2M+Na]^+$, 284 (11) $[M+Na]^+$, 262 (30) $[M+1]^+$. - **EA** ($C_{14}H_{19}N_3O_2$): calc. C 64.35, H 7.33, N 16.08, O 12.25; found C 64.27, H 7.12, N 15.96.

(4-Methoxy-phenyl)-piperidin-1-yl-diazene[6] (3c{2})

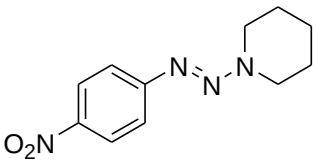


This compound was synthesized following **GP1** from 4-methoxy-aniline (1.5 mmol) and piperidine (3 mmol). After chromatography (cyclohexane/EtOAc = 10:1 + 1% Et_3N), the pure compound **3c{2}** (271 mg, 83%) was obtained as an orange solid. R_f (cyclohexane/EtOAc = 10:1) = 0.31. - **m.p. =** 50.7 – 51.3 °C. - **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 7.39 (d,

[5] Y. Zhang, Y. Li, X. Zhang, X. Jiang, *Chem. Comm*. **2015**, *51*, 941 – 944.

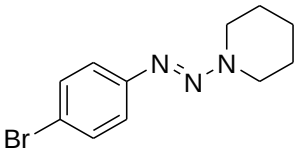
J = 9.0 Hz, 2 H), 6.88 (d, *J* = 9.0 Hz, 2 H), 3.79 (s, 3 H), 3.73 – 3.68 (m, 4 H), 1.74 – 1.68 (m, 6 H) ppm. - **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 157.9, 144.5, 121.5, 114.4, 55.6, 48.2, 25.2, 24.5 ppm.

(4-Nitro-phenyl)-piperidin-1-yl-diazene[6] **(3c{3})**



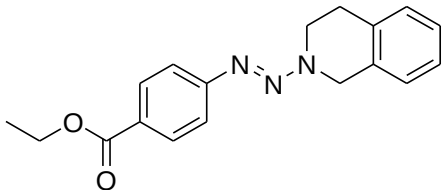
Compound **3c{3}** was synthesized following **GP1** from 4-nitro-aniline (1.5 mmol) and piperidine (3 mmol). After chromatography (cyclohexane/EtOAc = 10:1 + 1% Et_3N), the pure product **3c{3}** (234 mg, 67%) was obtained as an orange solid. - **R_f** (cyclohexane/EtOAc = 10:1) = 0.27. - **m.p. =** 89.3 – 91.6 °C. - **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.20 (d, *J* = 9.1 Hz, 2 H), 7.51 (d, *J* = 9.1 Hz, 2 H), 4.00 - 3.80 (m, 4 H), 1.87 - 1.65 (m, 6 H) ppm. - **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 156.1, 144.6, 124.8, 120.4, 53.5, 43.8, 26.4, 24.5, 24.1 ppm. - **HRMS** ($C_{11}H_{14}N_4O_2$): calc. 234.1111, found 234.1112. - **IR** (ATR, ṽ): 2947, 2858, 1585, 1508, 1401, 1317, 1287, 1220, 1186, 1101, 1015, 992, 850, 753, 692, 564, 515, 492 cm^{-1}. - **EA** ($C_{11}H_{14}N_4O_2$): calc. C 56.40, H 6.02, N 23.92, O 13.66; found C 56.33, H 6.03, N 23.85.

(4-Bromo-phenyl)-piperidin-1-yl-diazene (3c{4})



Compound **3c{4}** was synthesized following **GP1** from 4-bromo aniline (1.5 mmol) and piperidine (3 mmol). After chromatography (cyclohexane/EtOAc = 10:1 + 1% Et_3N), the pure product **3c{4}** (291 mg, 72%) was obtained as a brown solid. - **R_f** (cyclohexane/EtOAc = 10:1) = 0.27. - **m.p. =** 55.9 – 56.6 °C. - **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 7.46 - 7.41 (m, 2 H), 7.33 - 7.28 (m, 2 H), 3.82 - 3.74 (m, 4 H), 1.76 - 1.65 (m, 6 H) ppm. - **^{13}C NMR** (63 MHz, $CDCl_3$), δ = 150.1, 132.1, 122.3, 118.7, 27.3, 25.5, 24.6 ppm. - **MS (EI),** m/z (%): 267 (18) $[C_{11}H_{14}{}^{79}BrN_3]^+$, 183 (46) $[C_6H_4{}^{79}BrN_2]^+$, 155 (100) $[C_6H_4{}^{79}Br]^+$. - **HRMS** ($C_{11}H_{14}N_3{}^{79}Br$): calc. 267.0366, found 267.0364. - **IR** (ATR, ṽ): 2931, 2849, 1477, 1426, 1394, 1349, 1295, 1258, 1216, 1184, 1106, 1000, 926, 888, 828, 704, 628, 578, 544, 517, 478 cm^{-1}. - **EA** ($C_{11}H_{14}BrN_3$): calc. C 49.27, H 5.26, Br 29.80, N 15.67; found C 49.05, H 5.26, N 15.46.

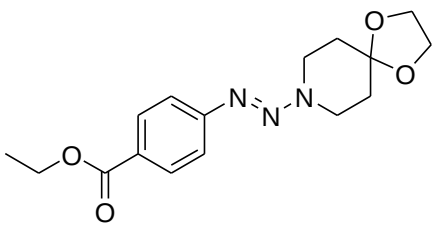
4-(3,4-Dihydro-1*H*-isoquinolin-2-ylazo)-benzoic acid ethyl ester (3c{5})



Compound **3c{5}** was synthesized following **GP1** from 4-amino-benzoic acid ethyl ester (2 mmol) and 1,2,3,4-tetrahydroisoquinoline (4 mmol). After chromatography (cyclohexane/EtOAc = 20:1 + 1% Et_3N), the pure product **3c{5}** (490 mg, 80%) was obtained as an orange solid. - **R_f** (cyclohexane/EtOAc = 20:1) = 0.26. - **m.p. =** 76.6 – 77.2 °C. - **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.96 (d, *J* = 8.4 Hz, 2 H), 7.43 (d, *J* = 8.4 Hz, 2 H), 7.26 - 7.09 (m, 4 H), 4.92 (s, 2 H), 4.29 (q, *J* = 7.1 Hz, 2 H), 4.25 - 3.98 (m, 2 H), 3.01 (t, *J* = 5.8 Hz, 2 H), 1.32 (t, *J* = 7.1 Hz, 3 H) ppm. - **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 166.6, 154.4, 130.6, 128.4, 127.2, 127.0, 126.8, 120.3, 60.7, 14.4 ppm. - **MS (EI),** m/z (%): 309 (26) $[M]^+$, 149 (100) $[C_9H_9O_2]^+$, 132 (76) $[C_9H_9N]^+$. - **HRMS** ($C_{18}H_{19}N_3O_2$): calc. 309.1472, found 309.1473. - **IR** (ATR, ṽ): 2983, 1703, 1598, 1498, 1454, 1422, 1400, 1364, 1345, 1306, 1267, 1205.3, 1157, 1099, 1042, 1012, 942, 914, 852, 773, 750, 702, 587, 560, 524, 484, 436 cm^{-1}. - **EA** ($C_{18}H_{19}N_3O_2$) calc. C 69.88, H 6.19, N 13.58, O 10.34; found C 69.80, H 6.20, N 13.37.

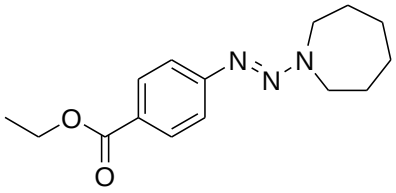
[6] Chengming Wang, Hu Chen, Zhaofeng Wang, Jiean Chen, Yong Huang, *Angew. Chem. Int. Ed.* **2012**, *51*, 7242–7245.

4-(1,4-Dioxa-8-aza-spiro[4.5]dec-8-ylazo)-benzoic acid ethyl ester (3c{6})



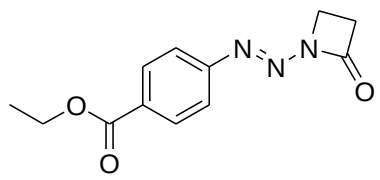
Compound **3c{6}** was synthesized following **GP1** from 4-amino-benzoic acid ethyl ester (2 mmol) and 1,4-dioxa-8-aza-spiro[4.5]decane (4 mmol). After chromatography (cyclohexane/EtOAc = 10:1 + 1% Et_3N), the pure product **3c{6}** (350 mg, 55%) was obtained as an orange solid. - **R_f** (cyclohexane/EtOAc = 10:1) = 0.34. - **m.p. =** 64.8 – 65.4 °C. - **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 8.02 (d, *J* = 8.6 Hz, 2 H), 7.46 (d, *J* = 8.6 Hz, 2 H), 4.36 (q, *J* = 7.1 Hz, 2 H), 4.02 (s, 4 H), 3.98 (m, 4 H), 1.91 – 1.79 (m, 4 H), 1.39 (t, *J* = 7.1 Hz, 3 H) ppm. - **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 166.6, 154.0, 130.2, 127.6, 120.2, 107.2, 64.8, 60.8, 14.5 ppm.- **MS (EI),** m/z (%): 319 (62) $[M]^+$, 274 (13) $[C_{14}H_{16}N_3O_3]^+$, 177 (58) $[C_9H_9N_2O]^+$, 149 (100) $[C_9H_9O_2]^+$. - **HRMS** ($C_{16}H_{21}N_3O_4$): calc. 319.1527, found 319.1527. - **IR** (ATR, ṽ): 2960, 1700, 1601, 1433, 1407, 1365, 1336, 1268, 1176, 1154, 1081, 1028, 942, 911, 856, 772, 700, 659, 604, 559, 528, 493, 460 cm^{-1}. - **EA** ($C_{16}H_{21}N_3O_4$): calc. C 60.17, H 6.63, N 13.16, O, 20.04; found C 60.14, H 6.49, N 13.20.

4-(Azepan-1-ylazo)-benzoic acid ethyl ester (3d)



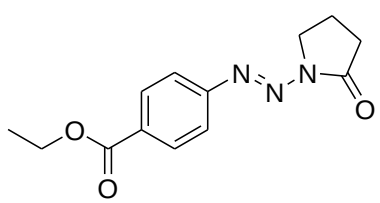
Compound **3d** was synthesized following **GP1** from 4-amino-benzoic acid ethyl ester (2 mmol) and hexamethyleneimine (4 mmol). After chromatography (cyclohexane/EtOAc = 20:1 + 1% Et_3N), the pure product **3d** (402 mg, 73%) was obtained as a red solid. - **R_f** (cyclohexane/EtOAc = 20:1) = 0.24. - **m.p. =** 60.2 – 62.1 °C. - **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.00 (d, *J* = 8.6 Hz, 2 H), 7.44 (d, *J* = 8.6 Hz, 2 H), 4.35 (q, *J* = 7.1 Hz, 2 H), 4.01 – 3.98 (m, 2 H), 3.83 – 3.79 (m, 2 H), 1.94 – 1.80 (m, 4 H), 1.62 – 1.53 (m, 4 H), 1.38 (t, *J* = 7.1 Hz, 3 H) ppm. - **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 167.2, 155.0, 130.3, 126.2, 119.6, 60.5, 54.6, 48.9, 29.9, 28.7, 28.4, 25.1, 14.2 ppm. - **MS** m/z (%): 275 (18) $[M]^+$, 149 (100) $[C_9H_9O_2]^+$. - **HRMS** ($C_{15}H_{21}N_3O_2$): calc. 275.1628, found 275.1628. – **IR** (ATR, ṽ): 2989, 2930, 2854, 1709, 1599, 1444, 1389, 1341, 1305, 1268, 1211, 1189, 1147, 1097, 1020, 990, 894, 861, 847, 798, 772, 734, 701, 557, 526, 501, 437, 394 cm^{-1}. - **EA** ($C_{15}H_{21}N_3O_2$): calc. C 65.43, H 7.69, N 15.26, O 11.62; found C 65.37, H 7.59, N 14.62.

4-(2-Oxo-azetidin-1-ylazo)-benzoic acid ethyl ester (6a)



Compound **6a** was synthesized following **GP2** from corresponding triazene **3a** (1 mmol). After chromatography (cyclohexane/EtOAc = 4:1 + 1% Et_3N), the pure product **6a** (12.8 mg, 10%) was obtained as a brown solid. - **R_f** (cyclohexane/EtOAc = 4:1) = 0.22. - **m.p. =** 97.6 – 98.2 °C. - **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 9.8 Hz, 2 H), 7.66 (d, *J* = 9.8 Hz, 2 H), 4.35 (q, *J* = 7.1 Hz, 2 H), 3.86 (t, *J* = 5.2 Hz, 2 H), 3.17 – 2.91 (t, *J* = 5.2 Hz, 2 H), 1.36 (t, *J* = 7.1 Hz, 3 H) ppm. - **MS (EI),** m/z (%): 247 (27) $[M]^+$, 177 (33) $[C_9H_9N_2O]^+$, 149 (100) $[C_9H_9O_2]^+$. - **HRMS** ($C_{12}H_{13}N_3O_3$): calc. 247.0951, found 247.0950. - **IR** (ATR, ṽ): 2977, 1773, 1702, 1602, 1453, 1408, 1368, 1322, 1273, 1242, 1184, 1098, 1044, 870, 774, 698, 541, 525, 463, 393 cm^{-1}. - **EA** ($C_{12}H_{13}N_3O_3$) calc. C 58.29, H 5.30, N 16.99, O 19.41; found C 58.39, H 5.54, N 17.12.

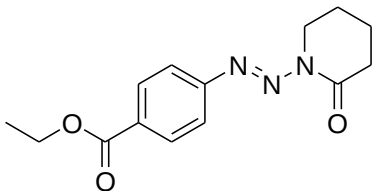
4-(2-Oxo-pyrrolidin-1-ylazo)-benzoic acid ethyl ester (6b)



Compound **6b** was synthesized following **GP2** from corresponding triazene **3b** (1 mmol). After chromatography (cyclohexane/EtOAc = 4:1 + 1% Et_3N), the pure product **6b** (169 mg, 65%) was obtained as a pale orange solid. - **R_f** (cyclohexane/EtOAc = 4:1) = 0.32. - **m.p.** 127.9 – 128.8 °C. - **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.5 Hz, 2 H), 7.65 (d, *J* = 8.5 Hz, 2 H), 4.32 (q, *J* = 7.1 Hz, 2 H), 3.98 – 3.81 (m, 2 H), 2.67 (t, *J* = 8.1 Hz,

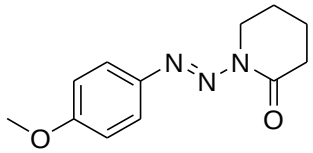
2 H), 2.25 – 2.06 (m, 2 H), 1.34 (t, *J* = 7.1 Hz, 3 H) ppm. - **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 172.9, 166.0, 152.0, 131.3, 130.3, 122.1, 61.1, 44.4, 31.1, 16.2, 13.9 ppm. - **MS (EI),** m/z (%): 261 (28) $[M]^+$, 177 (50) $[C_9H_9N_2O]^+$, 149 (100) $[C_9H_9O_2]^+$. - **HRMS** ($C_{13}H_{15}N_3O_3$): calc. 261.1108, found 261.1109. - **IR** (ATR, ṽ): 2986, 1734, 1706, 1601, 1456, 1404, 1352, 1317, 1273, 1229, 1151, 1125, 1097, 1019, 867, 775, 695, 645, 559, 503, 476, 396 cm^{-1}. - **EA** ($C_{13}H_{15}N_3O_3$) calc. C 59.76, H 5.79, N 16.08, O 18.37; found C 59.76, H 5.78, N 15.84.

4-(2-Oxo-piperidin-1-ylazo)-benzoic acid ethyl ester (6c{1})



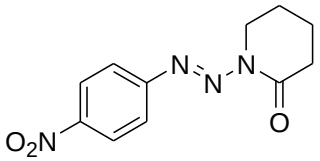
Compound **6c{1}** was synthesized following **GP2** from the corresponding triazene **3c{1}** (1.91 mmol). After chromatography (cyclohexane/EtOAc = 4:1 + 1% Et_3N), the pure product **6c{1}** (320 mg, 61%) was obtained as a yellow solid. - **R_f** (cyclohexane/EtOAc = 4:1) = 0.19. - **m.p. =** 128.4 – 129.5 °C. - **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.09 (d, *J* = 8.6 Hz, 2 H), 7.70 (d, *J* = 8.6 Hz, 2 H), 4.38 (q, *J* = 7.1 Hz, 2 H), 3.92 (t, *J* = 6.2 Hz, 2 H), 2.77 (t, *J* = 6.5 Hz, 2 H), 2.11 – 1.97 (m, 2 H), 1.92 – 1.82 (m, 2 H), 1.40 (t, *J* = 7.1 Hz, 3 H) ppm. - **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 169.2, 166.3, 151.7, 130.6, 122.5, 122.3, 61.1, 45.9, 34.1, 22.5, 20.4, 14.2 ppm. **MS** m/z (%): 275 (26) $[M]^+$, **177** (79) $[(C_9H_9N_2O_3]^+$, 164 (100) $[(C_9H_8NO_2]^+$. - **HRMS** ($C_{14}H_{19}N_3O_2$): calc. 275.1266; found 275.1264. **– IR** (ATR, ṽ): 2944, 1688, 1602, 1463, 1378, 1345, 1273, 1190, 1151, 1125, 1107, 1083, 1066, 1022, 987, 907, 864, 821, 770, 743, 698, 647, 548, 477, 383 cm^{-1}. **EA** ($C_{14}H_{17}N_3O_3$): calc. C 61.08, H 6.22, N 15.26, O 17.43; found C 60.05, H 6.17, N 15.13.

1-(4-Methoxyphenyl-diazenyl)-piperidin-2-one (6c{2})



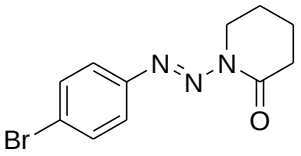
Compound **6c{2}** was synthesized following **GP2** from the corresponding triazene **3c{2}** (1 mmol). After chromatography (cyclohexane/EtOAc = 4:1 + 1% Et_3N), the pure product **3c{2}** (88 mg, 38%) was obtained as a brown solid. - **R_f** (cyclohexane/EtOAc = 4:1) = 0.20. - **m.p. =** 103.8 – 104.5 °C. - **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.68 (m, 2 H), 6.92 (m, 2 H), 3.94 – 3.84 (m, 2 H), 3.83 (s, 3 H), 2.79 – 2.71 (m, 2 H), 2.04 – 1.95 (m, 2 H), 1.92 – 1.83 (m, 2 H) ppm. - **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 168.5, 160.5, 141.8, 123.0, 113.8, 54.4, 44.3, 33.3, 21.8, 19.9 ppm. **MS** m/z (%): 233 (18) $[M]^+$, 135 (52) $[C_7H_7N_2O]^+$, 107 (100) $[C_7H_7O]^+$. - **HRMS** ($C_{12}H_{15}N_3O_2$): calc. 233.1033, found. 233.1032. - **IR** (ATR, ṽ): 2953, 1690, 1597, 1503, 1476, 1452, 1382, 1296, 1259, 1188, 1143, 1068, 1024, 986, 906, 834, 792, 713, 635, 600, 571, 518, 472, 411 cm^{-1}. - **EA** ($C_{12}H_{15}N_3O_2$): calc. C 61.79, H 6.48, N 18.01, O 13.72; found C 61.21, H 6.48, N 18.24.

1-(4-Nitrophenyl-diazenyl)-piperidin-2-one (6c{3})



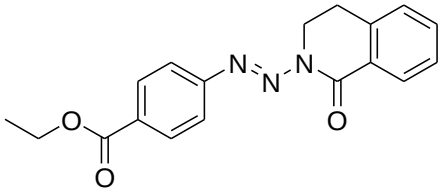
Compound **6c{3}** was synthesized following **GP2** from corresponding triazene **3c{3}** (1 mmol). After chromatography (cyclohexane/EtOAc = 4:1 + 1% Et_3N), pure product **6c{3}** (114 mg, 49%) was obtained as a yellow solid. **R_f** (cyclohexane/EtOAc = 4:1) = 0.19. - **m.p. =** 153.3 – 154.1 °C. - **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.29 (d, *J* = 8.8 Hz, 2 H), 7.79 (d, *J* = 8.8 Hz, 2 H), 3.95 (t, *J* = 6.3 Hz, 2 H), 2.80 (t, *J* = 6.5 Hz, 2 H), 2.14 – 2.00 (m, 2 H), 2.00 – 1.85 (m, 2 H) ppm. - **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 169.2, 152.9, 147.5, 124.6, 123.1, 45.9, 33.9, 21.7, 19.6 ppm. - **MS (ESI)**, m/z (%): 271 (44) $[M+Na]^+$, 519 (100) $[2M+Na]^+$. - **HRMS** ($C_{11}H_{12}N_4O_3$): calc. 248.0904, found 248.0902. - **IR** (ATR, ṽ): 3103, 2952, 2879, 1684, 1611, 1526, 1454, 1376, 1340, 1190, 1170, 1149, 1110, 1082, 1008, 986, 912, 865, 847, 755, 685, 662, 555, 520, 494, 385 cm^{-1}. - **EA** ($C_{11}H_{12}N_4O_3$): calc. C 53.22, H 4.87, N 22.57, O 19.34; found C 52.87, H 4.91, N 22.33.

1-(4-Bromophenyl-diazenyl)-piperidin-2-one (6c{4})



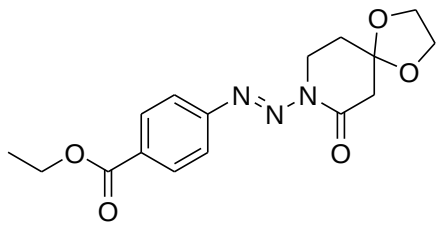
Compound **6c{4}** was synthesized following **GP2** from corresponding triazene **3c{4}** (1 mmol). After chromatography (cyclohexane/EtOAc = 4:1 + 1% Et_3N), pure product **6c{4}** (70 mg, 25%) was obtained. Recrystallisation from DCM/cyclohexane gave brownish crystals. - **R_f** (cyclohexane/EtOAc = 4:1) = 0.19. - **m.p.** 59.7 – 60.2 °C. - **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 7.66 – 7.45 (m, 4 H), 3.89 (t, *J* = 6.3 Hz, 2 H), 2.75 (t, *J* = 6.6 Hz, 2 H), 2.05 – 1.93 (m, 2 H), 1.95 – 1.79 (m, 2 H) ppm. - **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 168.6, 147.5, 132.3, 124.3, 123.17, 45.3, 34.2, 22.4, 20.3 ppm. - **MS** m/z (%): 281 (14) $[C_{11}H_{12}{}^{79}BrN_3O]^+$, 183 (47) $[C_6H_4{}^{79}BrN_2]^+$, 155 (100) $[C_6H_4{}^{79}Br]^+$. - **HRMS** ($C_{11}H_{12}N_3O^{79}Br$): calc. 281.0158, found 281.0160. - **IR** (ATR, ṽ): 2952, 2881, 1683, 1571, 1480, 1457, 1398, 1377, 1327, 1295, 1191, 1172, 1146, 1064, 1006, 988, 910, 827, 705, 659, 639, 546, 522, 473, 385 cm^{-1}. - **EA** ($C_{11}H_{12}BrN_3O$): calc. C 46.83, H 4.29, Br 28.32, N 14.89, O 5.67; found C 46.50, H 4.28, N 14.17.

4-(1-Oxo-3,4-dihydro-1*H*-isoquinolin-2-ylazo)-benzoic acid ethyl ester (6c{5})



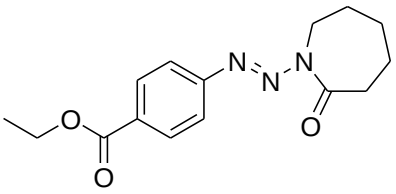
Compound **6c{5}** was synthesized following **GP2** from the corresponding triazene **3c{5}** (1 mmol). After chromatography (cyclohexane/EtOAc = 4:1 + 1% Et_3N), the pure product **6c{5}** (149 mg, 47%) was obtained as a yellow solid. - **R_f** (cyclohexane/EtOAc = 4:1) = 0.20. - **m.p. =** 137.2 – 138.0 °C. - **^{1}H NMR** (300 MHz, $CDCl_3$): δ = 8.22 (d, *J* = 7.5 Hz, 1 H), 8.07 (d, *J* = 8.5 Hz, 2 H), 7.73 (d, *J* = 8.5 Hz, 2 H), 7.49 (t, *J* = 7.5 Hz, 1 H), 7.38 (t, *J* = 7.5 Hz, 1 H), 7.25 (d, *J* = 7.5 Hz, 1 H), 4.38 – 4.26 (m, 4 H), 3.14 (t, *J* = 6.5 Hz, 2 H), 1.35 (t, *J* = 7.1 Hz, 3 H) ppm. - **^{13}C NMR** (75 MHz, $CDCl_3$): δ = 165.8, 162.7, 151.8, 138.7, 133.4, 130.8, 130.6, 130.6, 129.5, 128.7, 127.5, 127.3, 123.4, 122.4, 61.1, 41.5, 27.5, 14.1 ppm.- **MS (EI),** m/z (%): 323 (17) $[M]^+$, 177 (73) $[C_9H_9N_2O]^+$, 149 (100) $[C_9H_9O_2]^+$. - **HRMS** ($C_{18}H_{17}N_3O_3$): calc. 323.1264, found 323.1263. – **IR** (ATR, ṽ): 2978, 1713, 1682, 1603, 1460, 1410, 1367, 1310, 1270, 1227, 1185, 1125, 1091, 1009, 959, 890, 859, 789, 770, 739, 696, 643, 597, 528, 483, 414 cm^{-1}. - **EA** ($C_{18}H_{17}N_3O_3$) calc. C 66.86, H 5.30, N 13.00, O 14.84; found C 66.30, H 5.27, N 13.56.

4-(7-Oxo-1,4-dioxa-8-aza-spiro[4.5]dec-8-ylazo)-benzoic acid ethyl ester (6c{6})



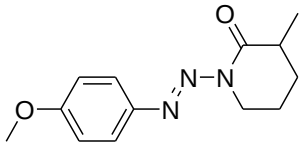
Compound **6c{6}** was synthesized following **GP2** from the corresponding triazene **3c{6}** (1 mmol). After chromatography (cyclohexane/EtOAc = 4:1 + 1% Et_3N), the pure product **6c{6}** (196 mg, 59%) was obtained as a yellow solid. - **R_f** (cyclohexane/EtOAc) = 0.19. - **m.p.** 121.2 – 122.3 °C. - **^{1}H NMR** (250 MHz, $CDCl_3$): δ = 8.04 (d, *J* = 8.6 Hz, 2 H), 7.65 (d, *J* = 8.6 Hz, 2 H), 4.33 (q, *J* = 7.1 Hz, 2 H), 4.11 – 3.71 (m, 6 H), 2.92 (s, 2 H), 2.12 (t, *J* = 6.5 Hz, 2 H), 1.34 (t, *J* = 7.1 Hz, 3 H) ppm. - **^{13}C NMR** (63 MHz, $CDCl_3$): δ = 167.0, 166.0, 152.1, 131.2, 130.5, 122.5, 105.3, 65.06, 61.2, 44.0, 41.7, 31.4, 14.4 ppm. - **MS (EI),** m/z (%): 333 (11) $[M]^+$, 177 (58) $[C_9H_9N_2O]^+$, 149 (100) $[C_9H_9O_2]^+$. - **HRMS** ($C_{16}H_{19}N_3O_5$): calc. 333.1319, found 333.1320. – **IR** (ATR, ṽ): 2900, 1694, 1604, 1465, 1368, 1269, 1173, 1131, 1094, 1057, 1000, 963, 927, 866, 774, 718, 696, 670, 568, 523, 503, 423 cm^{-1}. - **EA** ($C_{16}H_{19}N_3O_5$) calc. C 57.65, H 5.75, N 12.61, O 24.00; found C 57.76, H 5.77, N 12.37.

4-(2-Oxo-azepan-1-ylazo)-benzoic acid ethyl ester (6d)



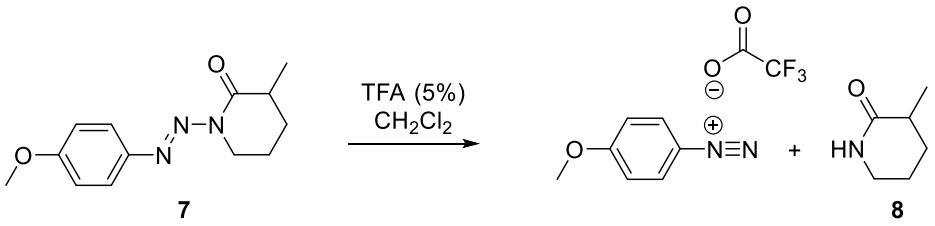
Compound **6d** was synthesized following **GP2** from the corresponding triazene **3d** (1 mmol). After chromatography (cyclohexane/EtOAc = 4:1 + 1% Et_3N), the pure product **6d** (134 mg, 47%) was obtained as an orange oil. - $\mathbf{R_f}$ (cyclohexane/EtOAc = 4:1) = 0.32. - ^{1}**H NMR** (300 MHz, $CDCl_3$): δ = 8.03 (d, *J* = 8.5 Hz, 2 H), 7.65 (d, *J* = 8.5 Hz, 2 H), 4.35 - 4.25 (m, 4 H), 2.80 - 2.77 (m, 2 H), 1.88 - 1.65 (m, 4 H), 1.87 - 1.57 (s, 2 H), 1.34 (t, *J* = 7.1 Hz, 3 H) ppm. - ^{13}**C NMR** (75 MHz, $CDCl_3$): δ = 174.2, 165.9, 151.3, 130.8, 130.4, 122.2, 60.9, 41.5, 37.8, 29.5, 27.3, 23.7, 14.4 ppm. - **MS (EI),** m/z (%): 289 (23) $[M]^+$, 177 (57) $[C_9H_9N_2O]^+$, 149 (100) $[C_9H_9O_2]^+$. - **HRMS** ($C_{15}H_{19}N_3O_3$): calc. 289.1421, found 289.1421. - **IR** (ATR, ṽ): 2930, 1706, 1603, 1477, 1377, 1269, 1137, 1096, 1077, 1014, 951, 922, 862, 845, 773, 699, 584 cm^{-1}. - **EA** ($C_{15}H_{19}N_3O_3$): calc. C 62.27, H 6.62, N 14.52, O 16.59; found C 62.01, H 6.74, N 14.34.

1-(4-Methoxy-phenyl-diazenyl)-3-methyl-piperidin-2-one (7)



Compound **6c{2}** (61 mg, 0.26 mmol) was dissolved in anhydrous THF (3.2 mL) and, after cooling to -78 °C, a 1.0 M solution of LiHMDS in THF (290 mL, 0.29 mmol) was added dropwise, keeping the temperature below -70 °C. The resulting mixture was stirred under nitrogen at -78 °C; after 1 h, MeI (18 mL, 0.29 mmol) was slowly added and, after 10 min., the cooling bath was removed and the mixture stirred at room temperature for 2 h. After dilution with Et_2O (5 mL), water was added (10 mL), the phases were separated and the aqueous layer was extracted with Et_2O (2 × 10 mL). The combined organic extracts were dried over anhydrous K_2CO_3. After filtration and evaporation of the solvent, the crude was purified by flash column chromatography (*n*-hexane/EtOAc = 3:1 + 1% Et_3N), affording the pure compound **7** (38 mg, 59%) as an orange solid. - $\mathbf{R_f}$ (*n*-hexane/EtOAc = 3:1) = 0.24. – **m.p.** = 87.7 - 89.2 °C. - ^{1}**H NMR** (400 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 9.1 Hz, 2 H), 6.92 (d, *J* = 9.1 Hz, 2 H), 4.05 (dddd, *J* = 13.5, 5.8, 4.6, 1.4 Hz, 1 H), 3.83 (s, 3 H), 3.71 (ddd, *J* = 13.5, 9.2, 5.3 Hz, 1 H), 2.78 – 2.67 (m, 1 H), 2.17 – 1.99 (m, 2 H), 1.97 – 1.84 (m, 1 H), 1.65 – 1.54 (m, 1 H), 1.39 (d, *J* = 9.2 Hz, 3 H) ppm. - ^{13}**C NMR** (100 MHz, $CDCl_3$): δ = 172.5, 160.6, 142.5, 124.0, 114.1, 55.6, 45.4, 38.6, 28.5, 21.08, 17.6 ppm. - **MS (ESI),** m/z (%): 517 (100) $[2M+Na]^+$, 270 (23) $[M+Na]^+$. – **EA** ($C_{13}H_{17}N_3O_2$) calc C 63.14, H 6.93, N 16.99; found C 62.99, H 7.38, N 17.21.

Deprotection of compound 7

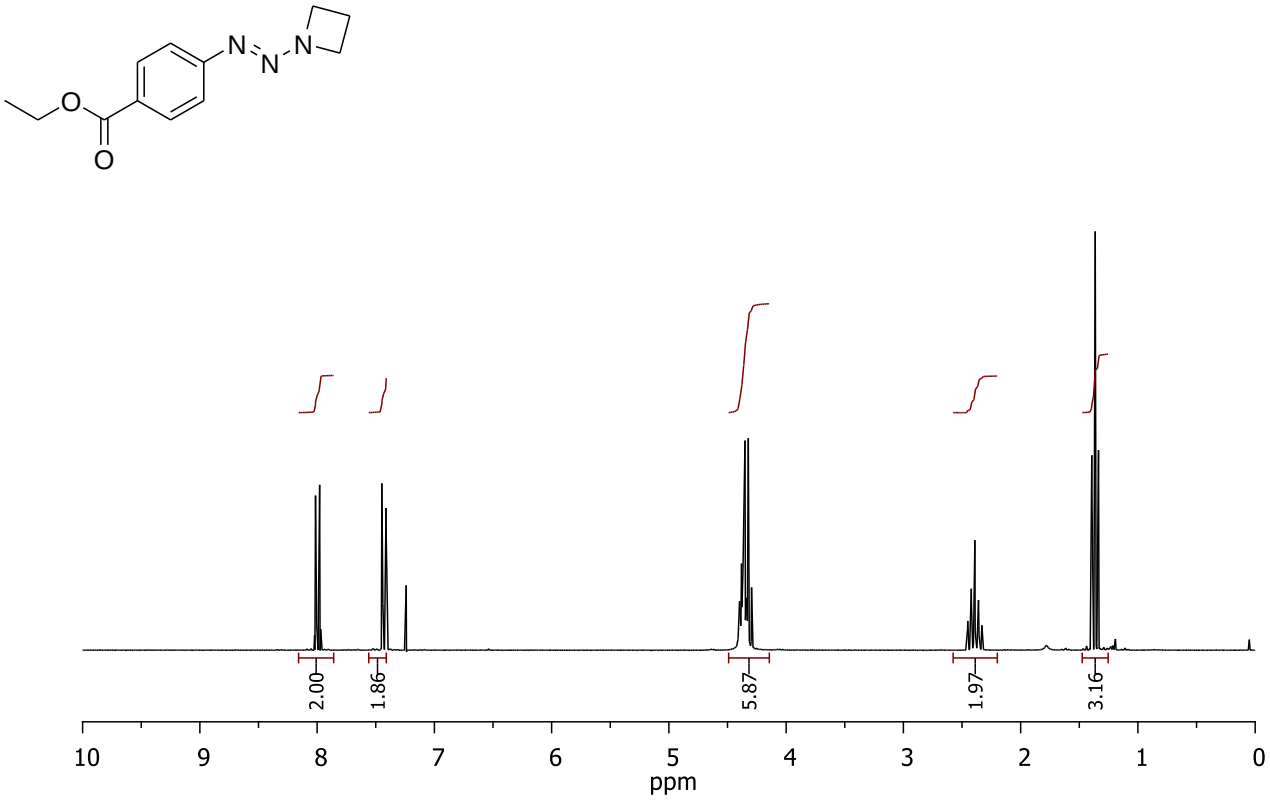


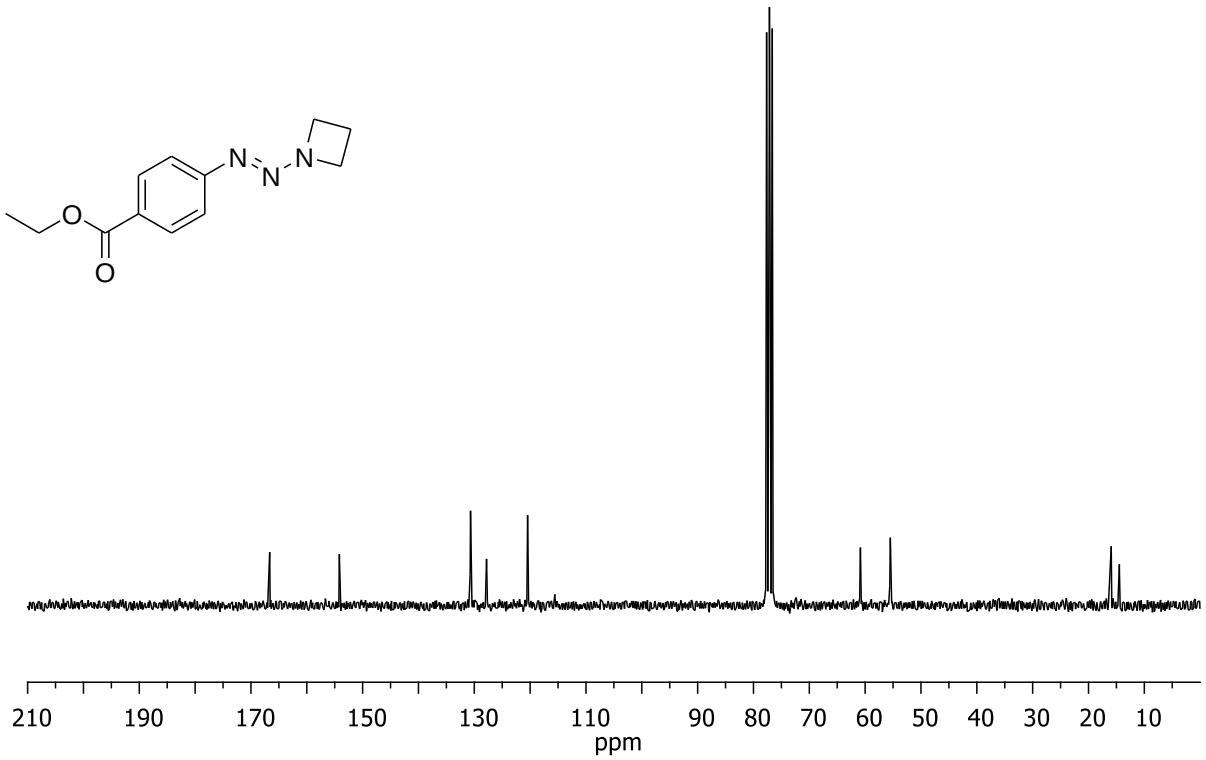
7 **8**

The diazenyl-protected lactam **7** was dissolved in 5% TFA in DCM (substrate conc. 0.1 M) and left under stirring at room temperature (25 °C). The reaction was complete within 15 min (monitored by TLC). The solvent was evaporated and the crude was analyzed by 1H NMR showing the complete conversion of the substrate into the deprotected lactam (100% conversion, see spectra part of this SI, page 27). Additionally, the crude product was purified by flash column chromatography (CH_2Cl_2/MeOH = 10:1), affording compound **7**. - R_f (CH_2Cl_2/MeOH = 10:1) = 0.26.

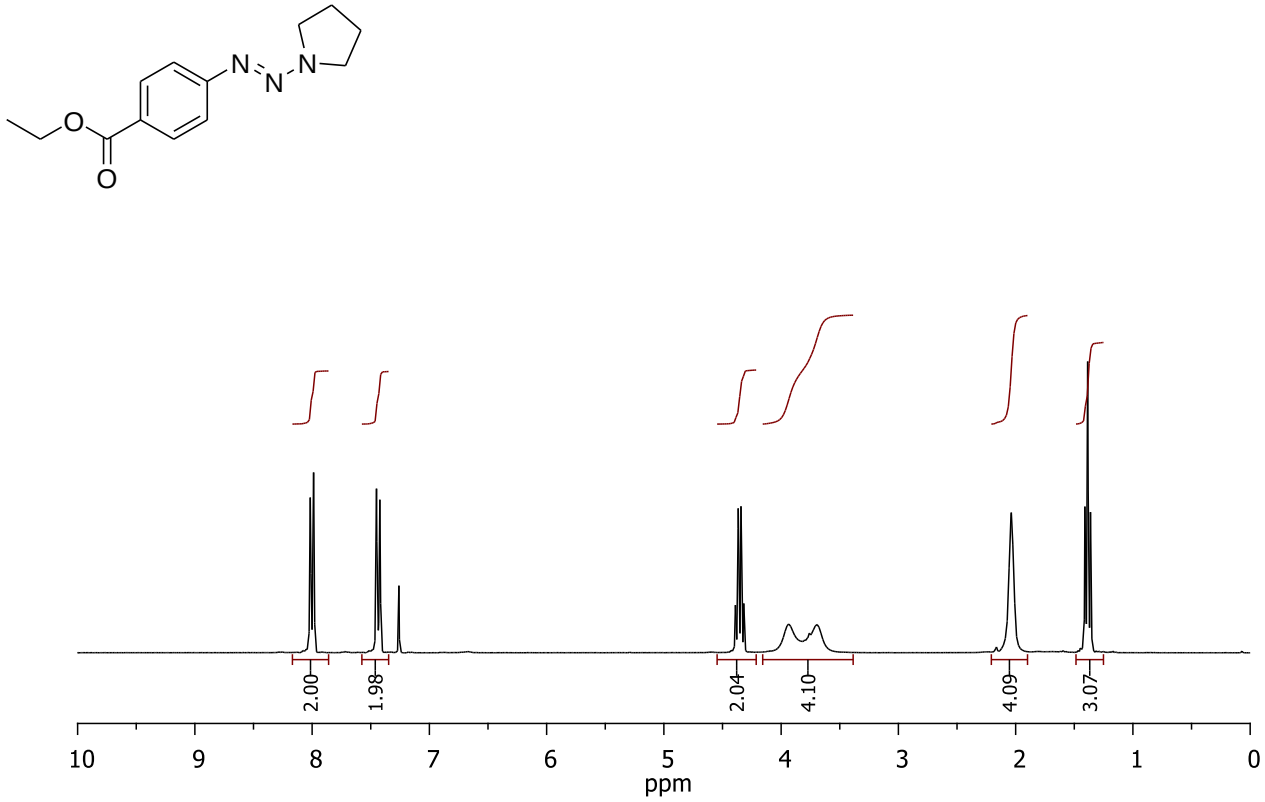
3. ^{1}H NMR and ^{13}C NMR spectra of new compounds

^{1}H NMR and ^{13}C NMR spectra of 4-(Azetidin-1-ylazo)-benzoic acid ethyl ester (**3a**)

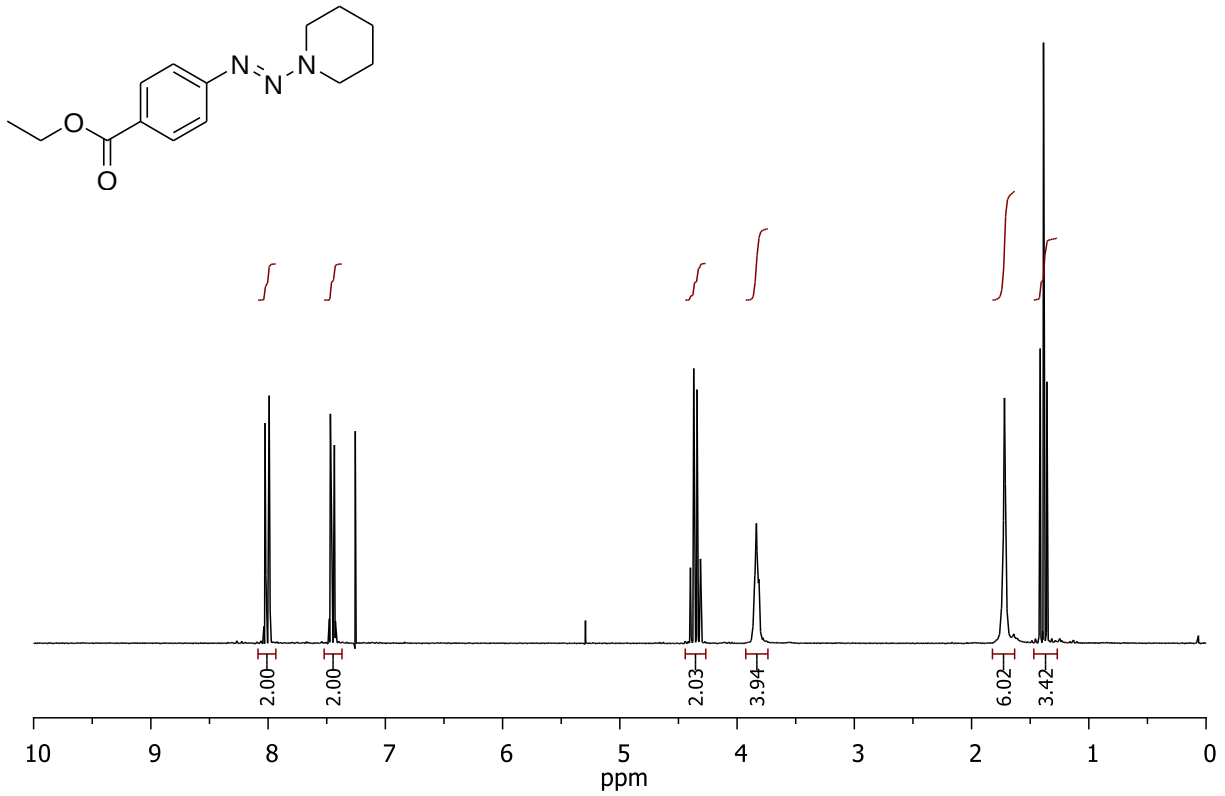


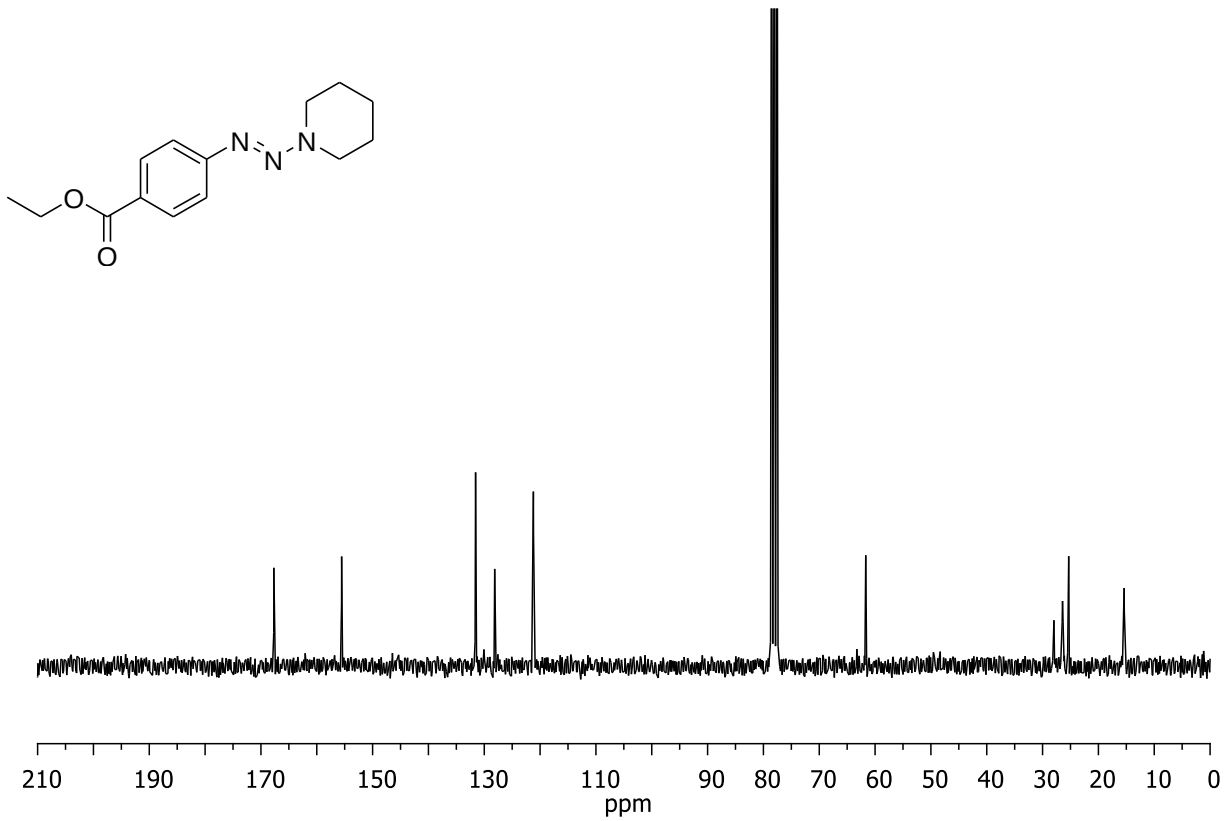


1H NMR spectrum of 4-(pyrrolidin-1-ylazo)-benzoic acid ethyl ester (**3b**)

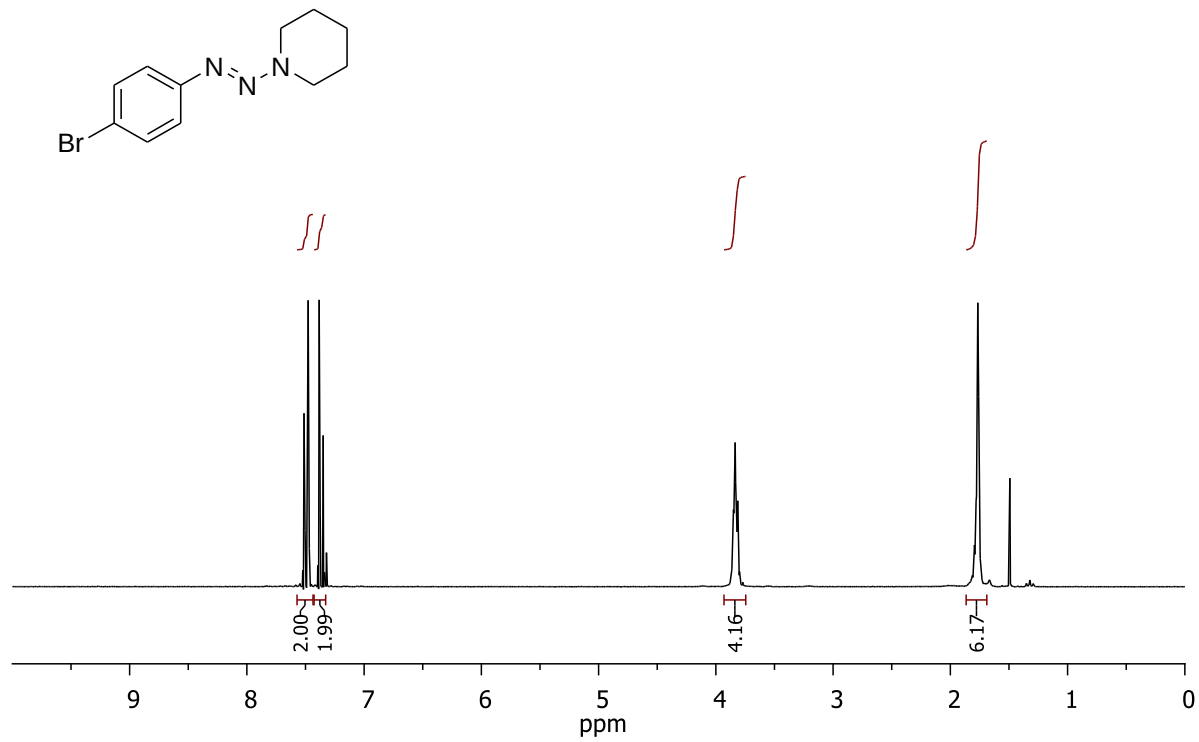


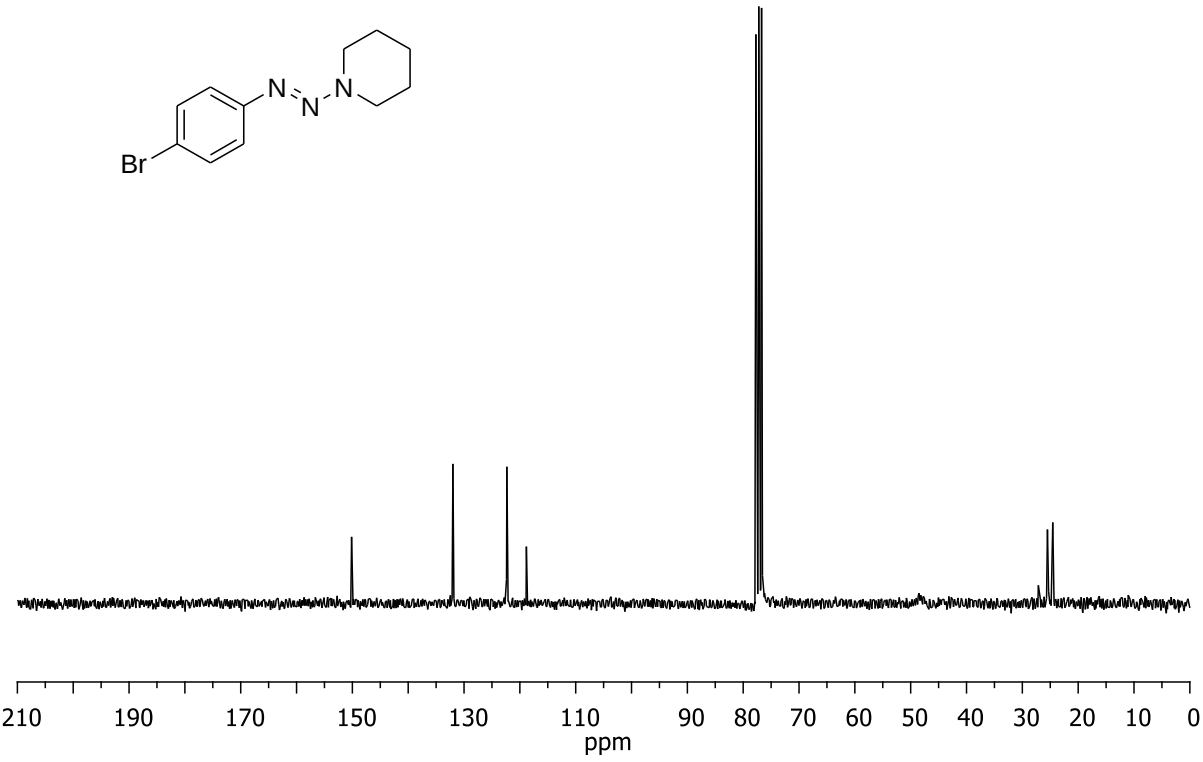
^{1}H NMR and ^{13}C NMR spectra of 4-(piperidin-1-ylazo)-benzoic acid ethyl ester (**3c{1}**)



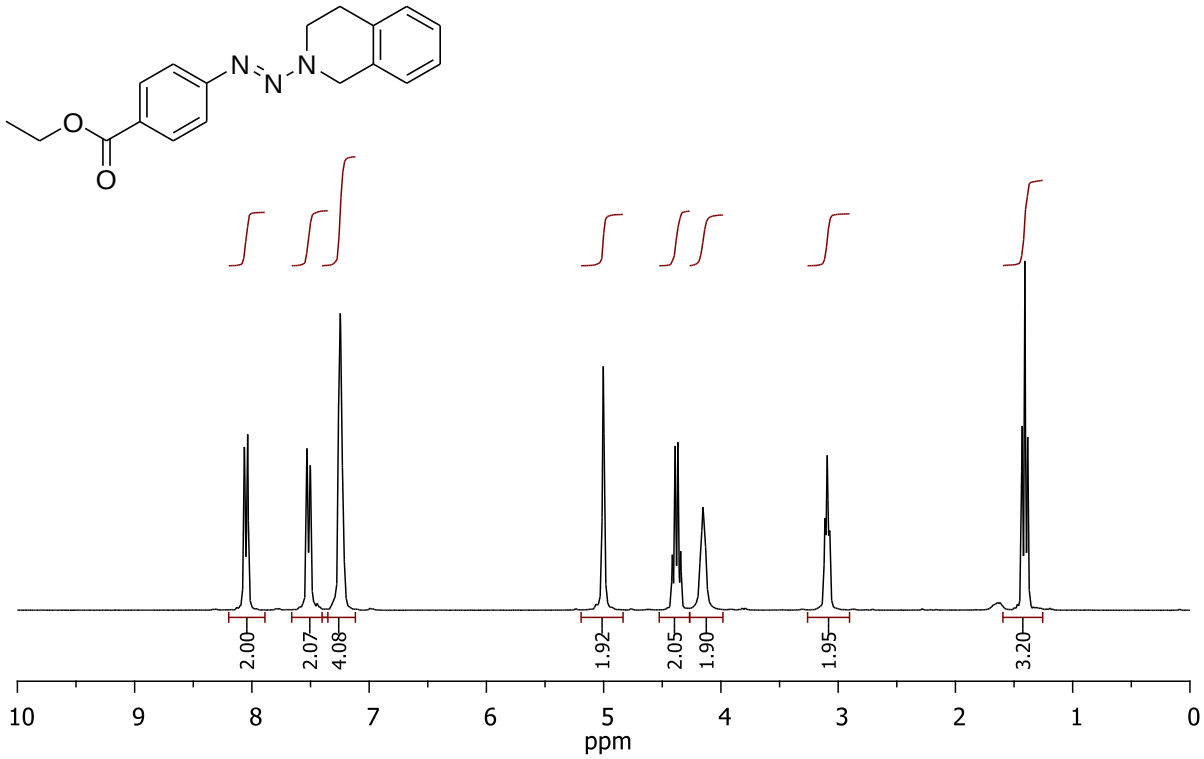


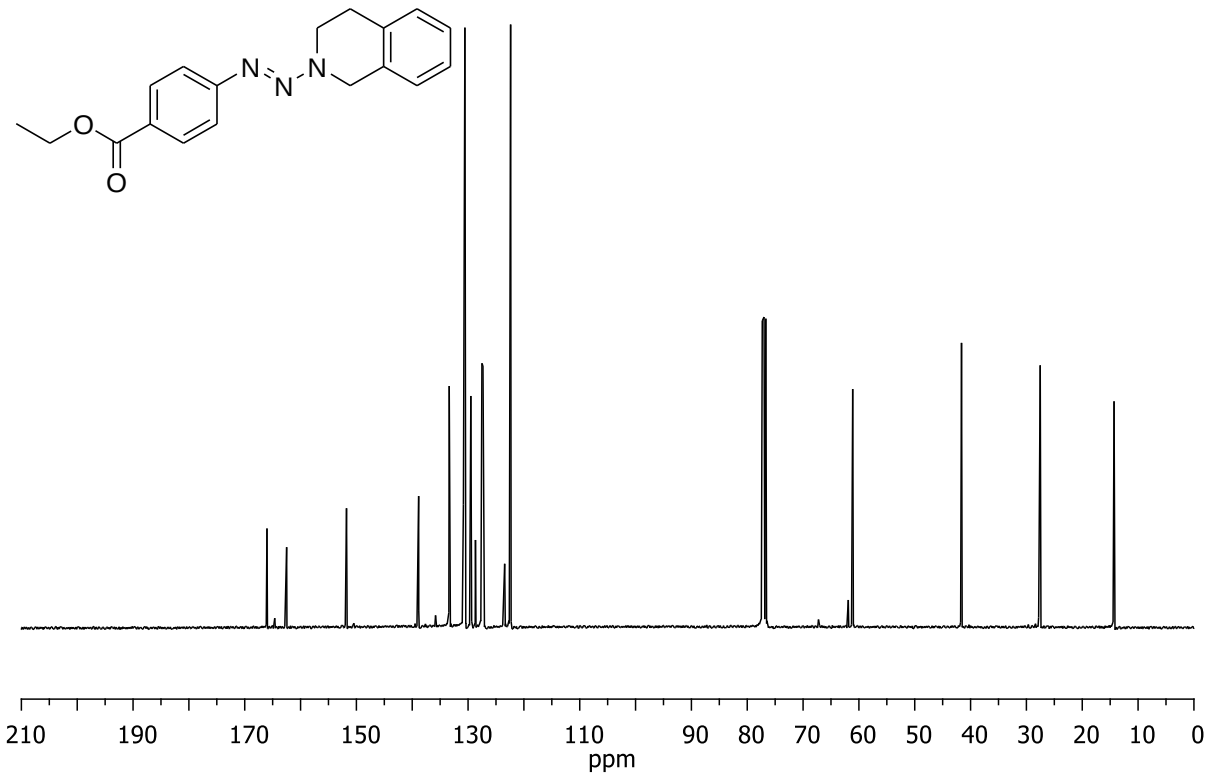
^{1}H NMR and ^{13}C NMR spectra of (4-bromo-phenyl)-piperidin-1-yl-diazene (**3c{4}**)



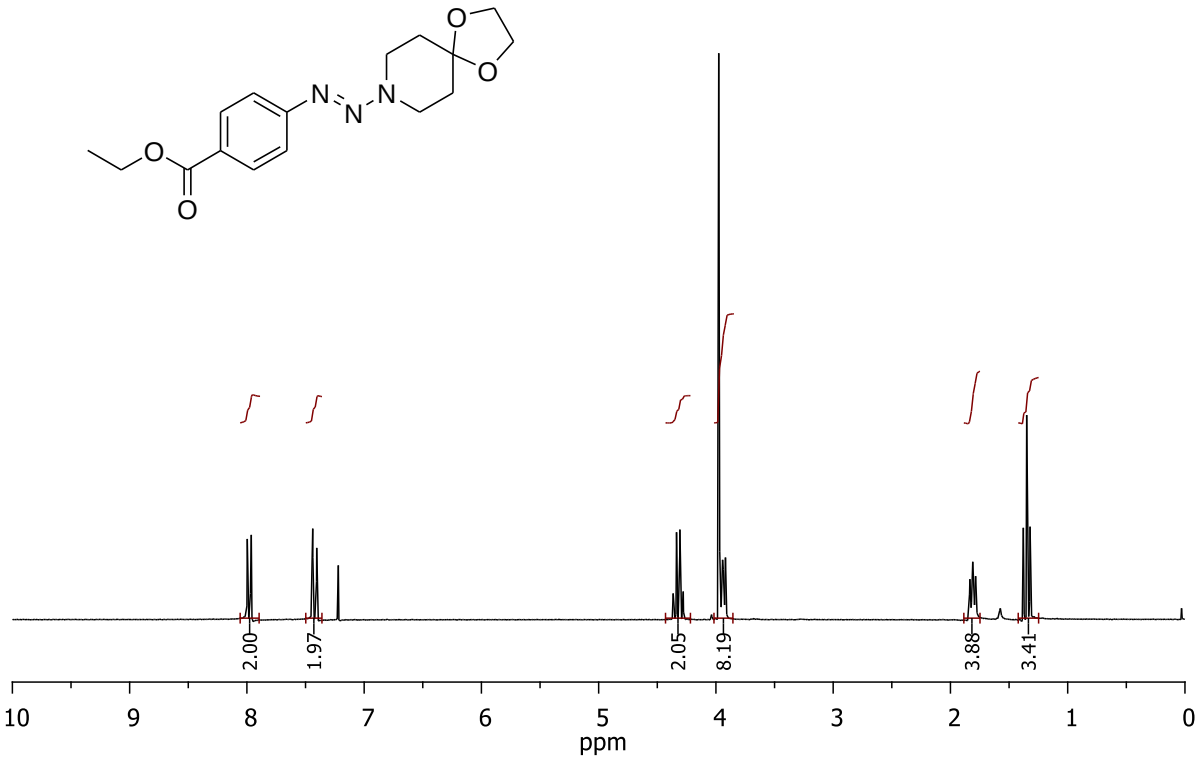


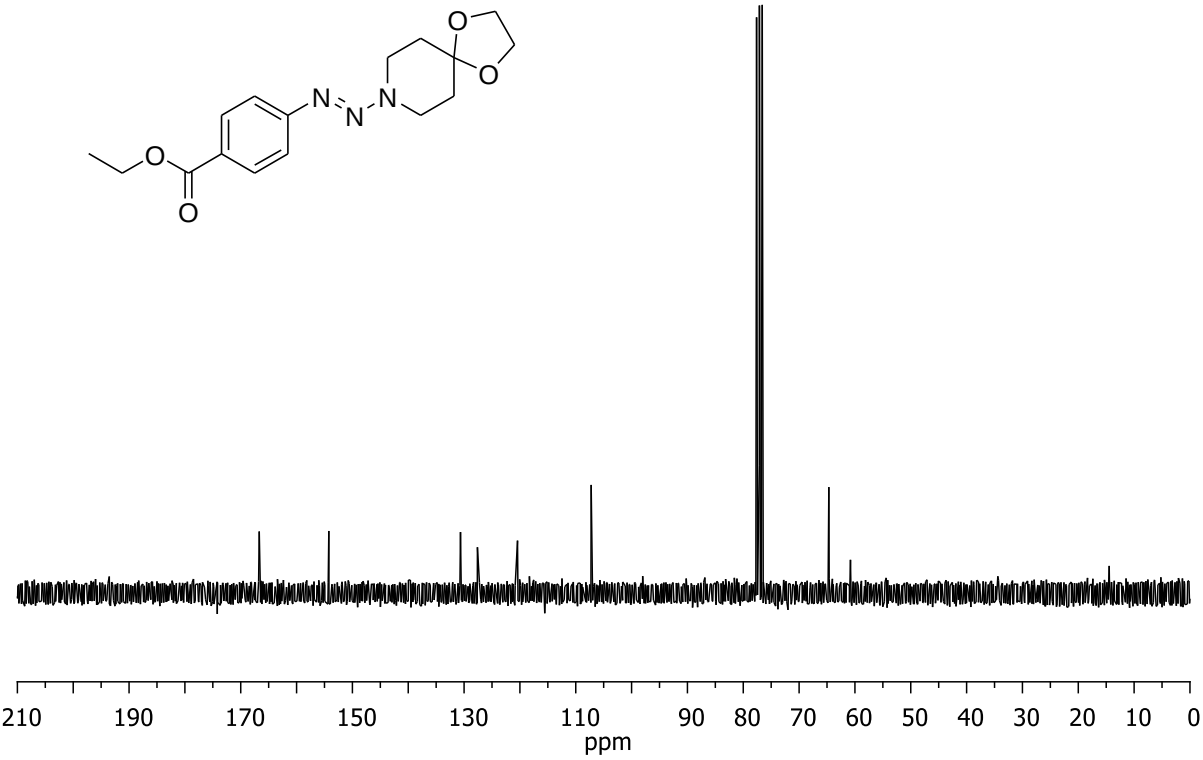
^{1}H NMR and ^{13}C NMR spectra of 4-(3,4-dihydro-1*H*-isoquinolin-2-ylazo)-benzoic acid ethyl ester (**3c{5}**)



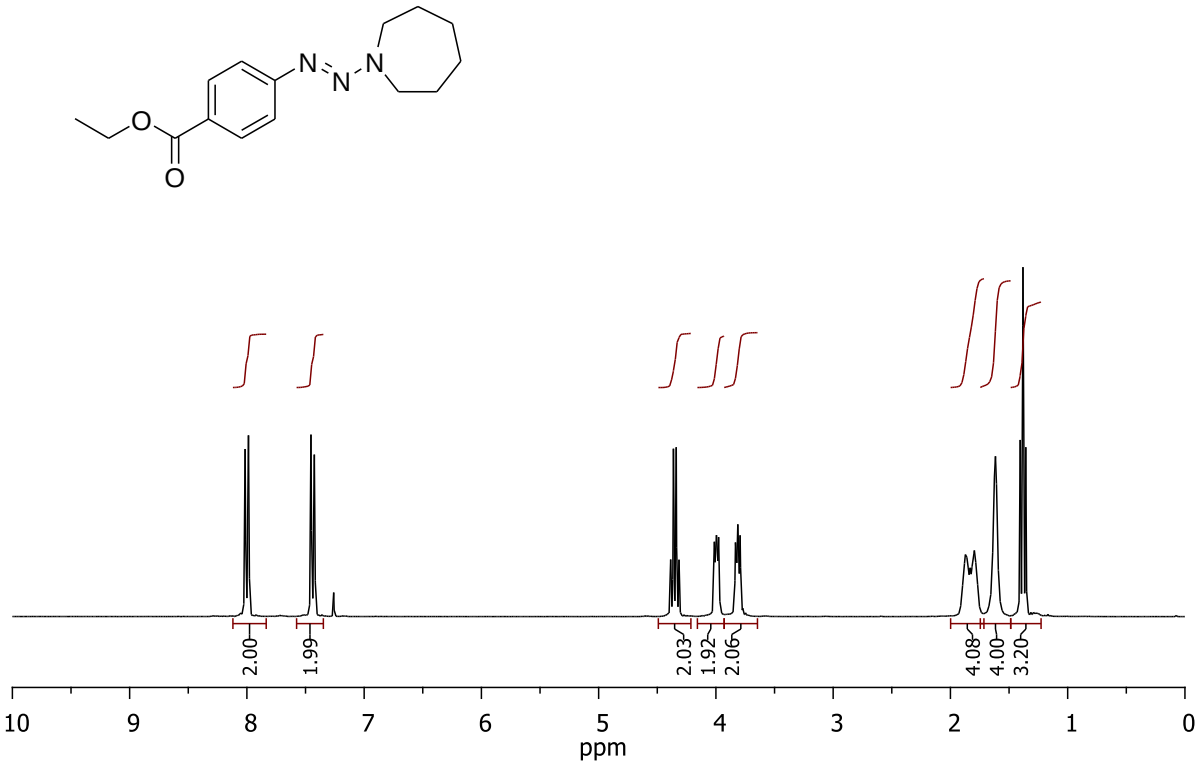


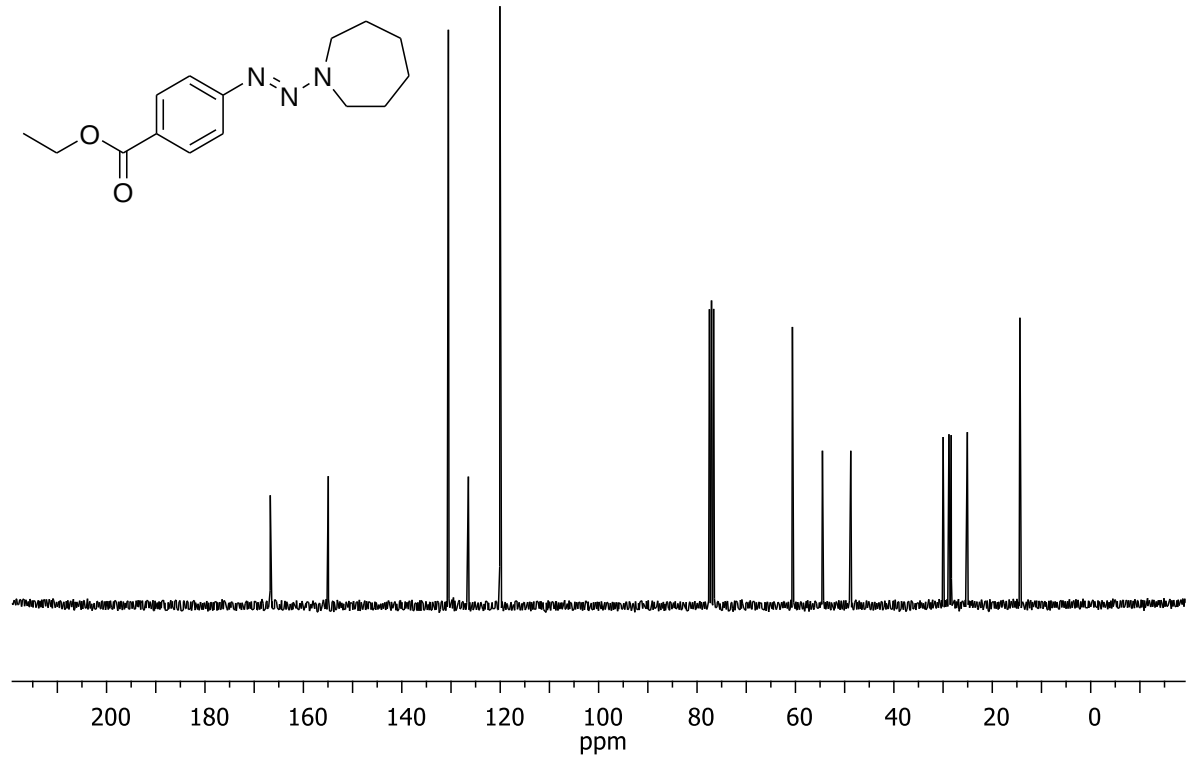
^{1}H NMR and ^{13}C NMR spectra of 4-(1,4-Dioxa-8-aza-spiro[4.5]dec-8-ylazo)-benzoic acid ethyl ester (**3c{6}**)



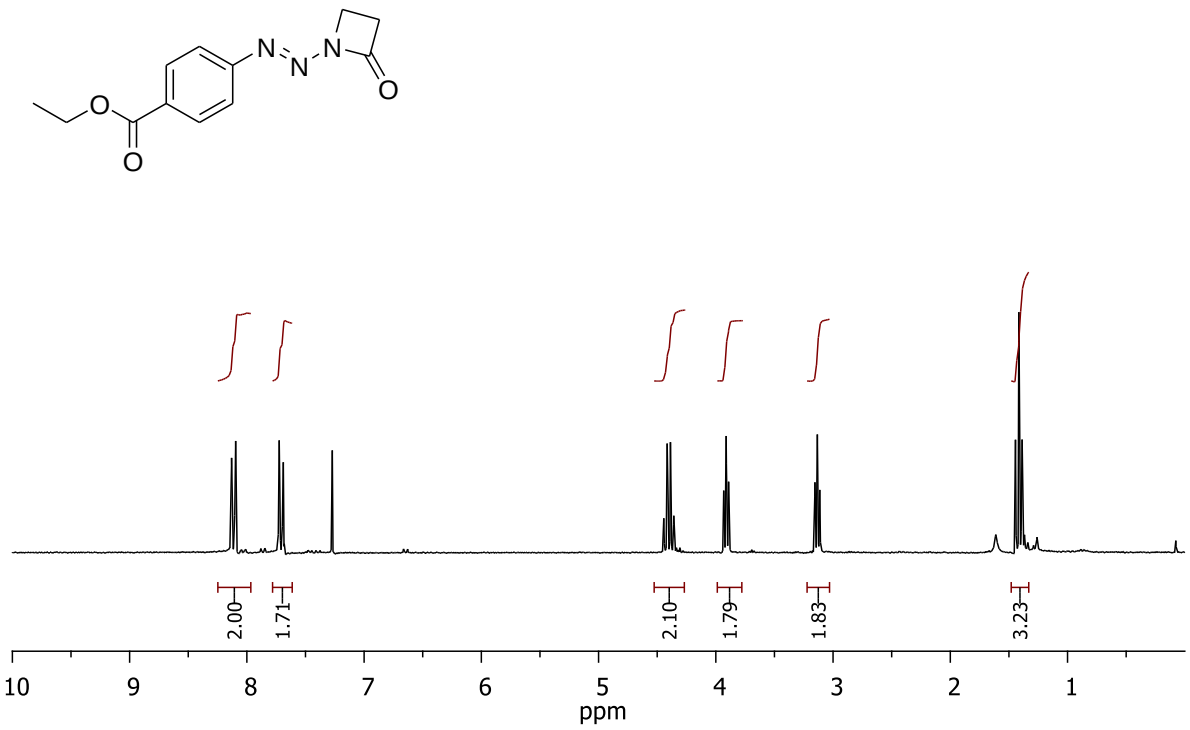


^{1}H NMR and ^{13}C NMR spectra of 4-(Azepan-1-ylazo)-benzoic acid ethyl ester (**3d**)

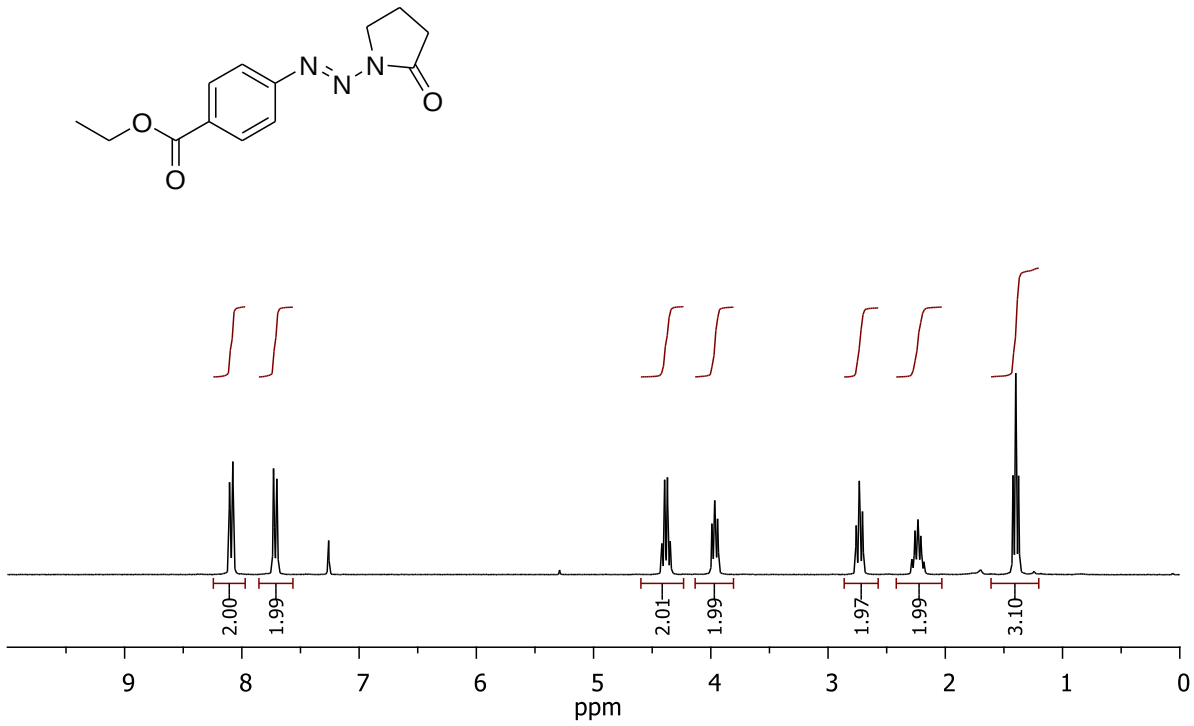


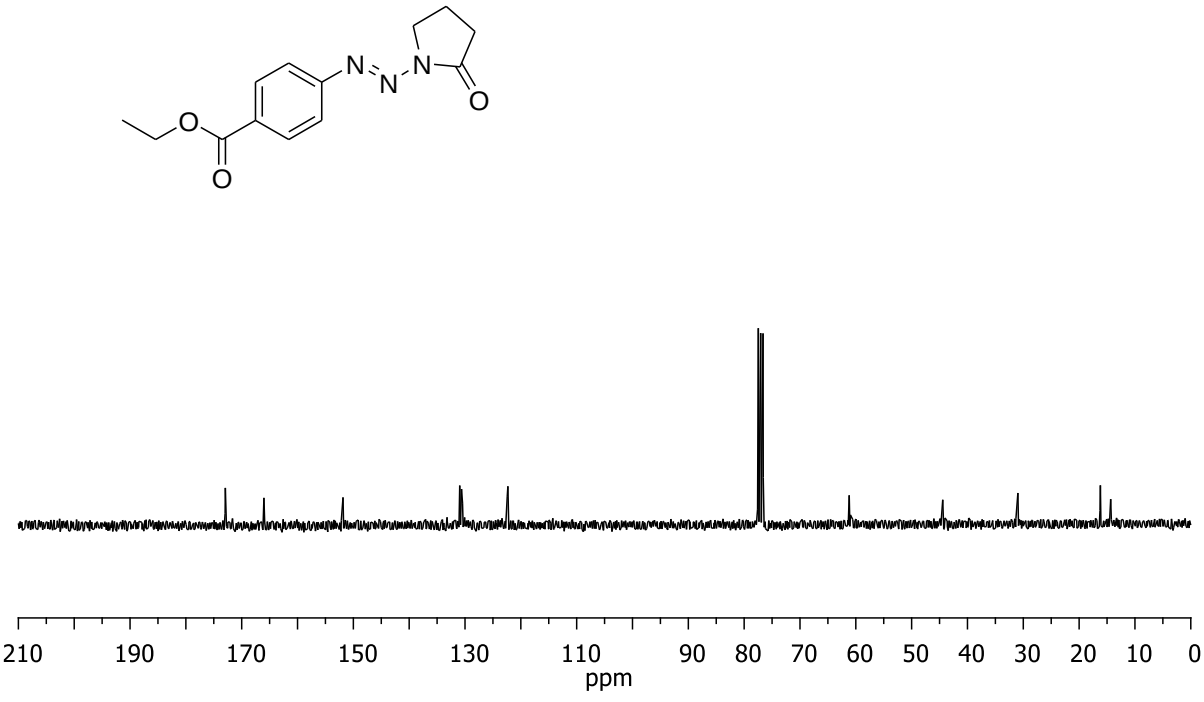


^{1}H NMR spectra of 4-(2-Oxo-azetidin-1-ylazo)-benzoic acid ethyl ester (**6a**)

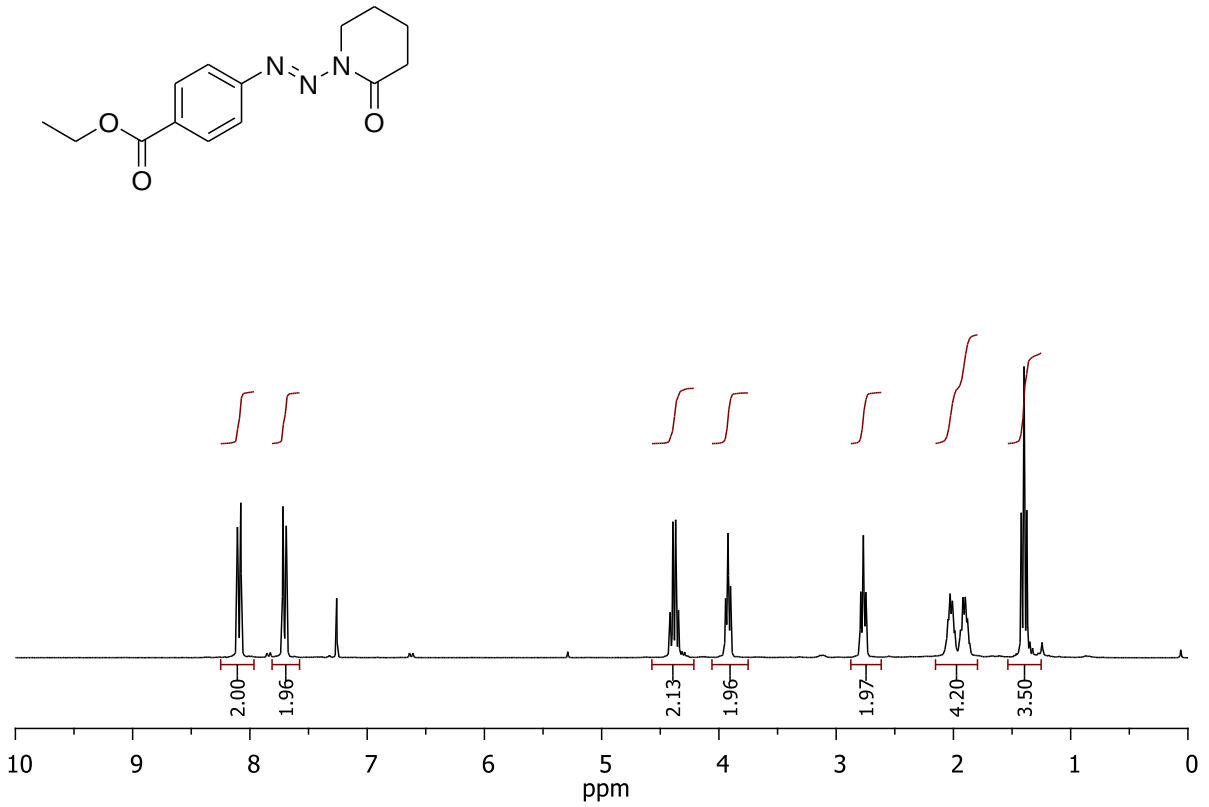


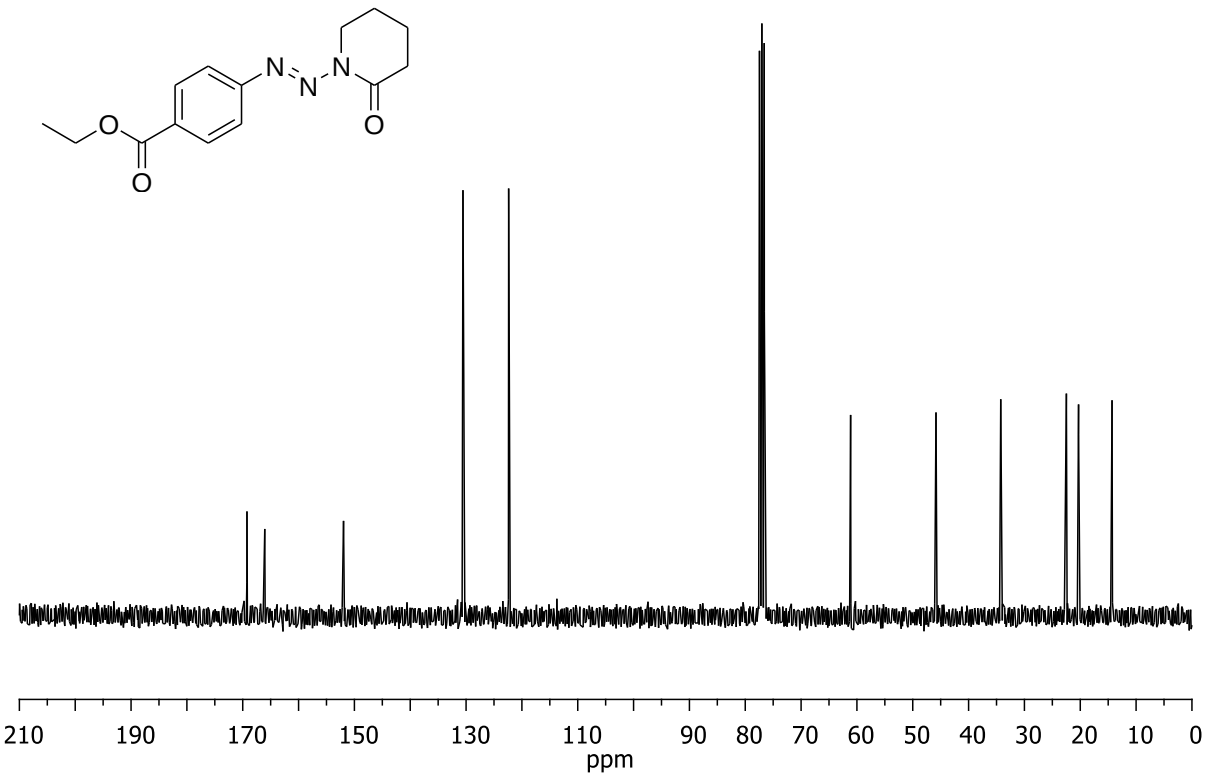
^{1}H NMR and ^{13}C NMR spectra of 4-(2-Oxo-pyrrolidin-1-ylazo)-benzoic acid ethyl ester (**6b**)



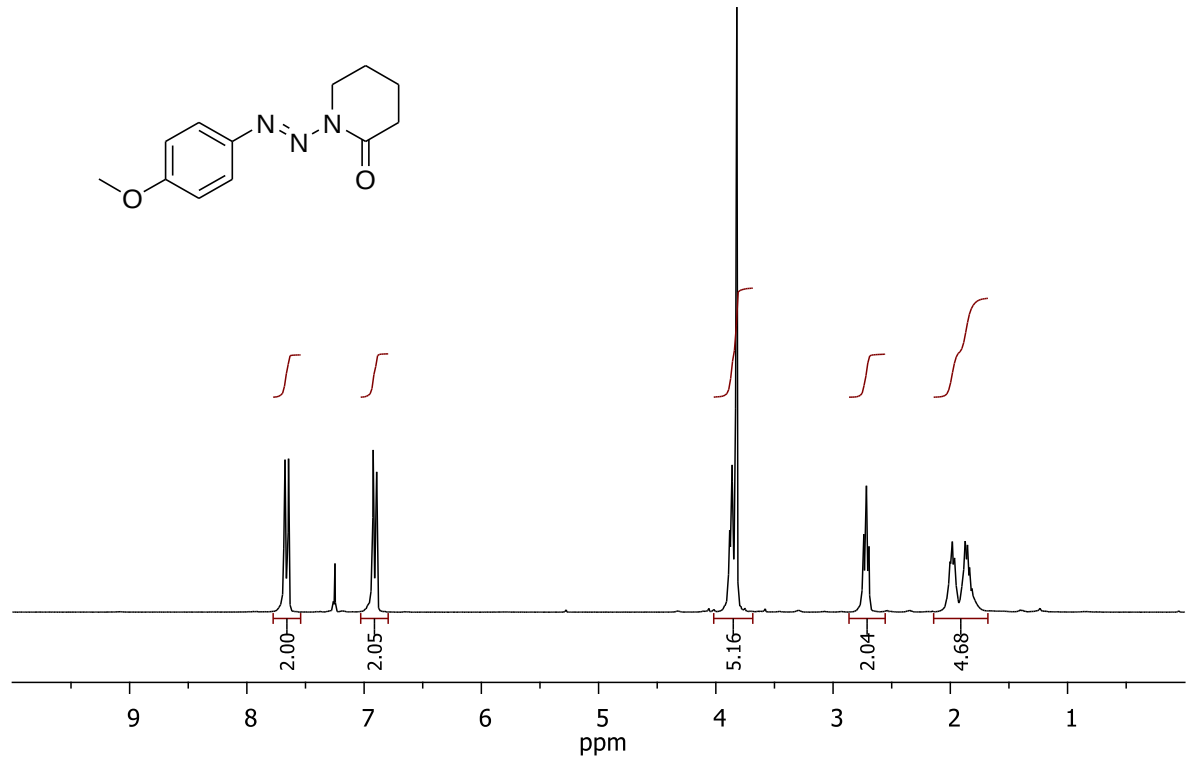


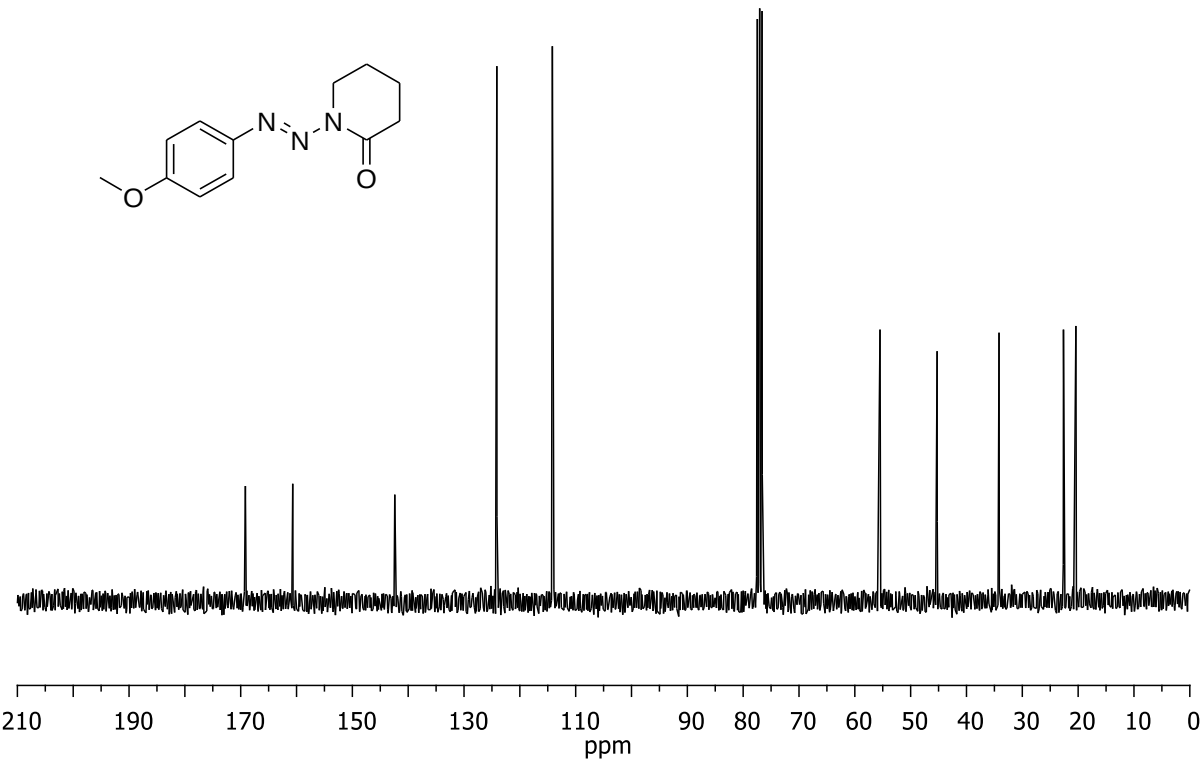
^{1}H NMR and ^{13}C NMR spectra of 4-(2-oxo-piperidin-1-ylazo)-benzoic acid ethyl ester (**6c{1}**)



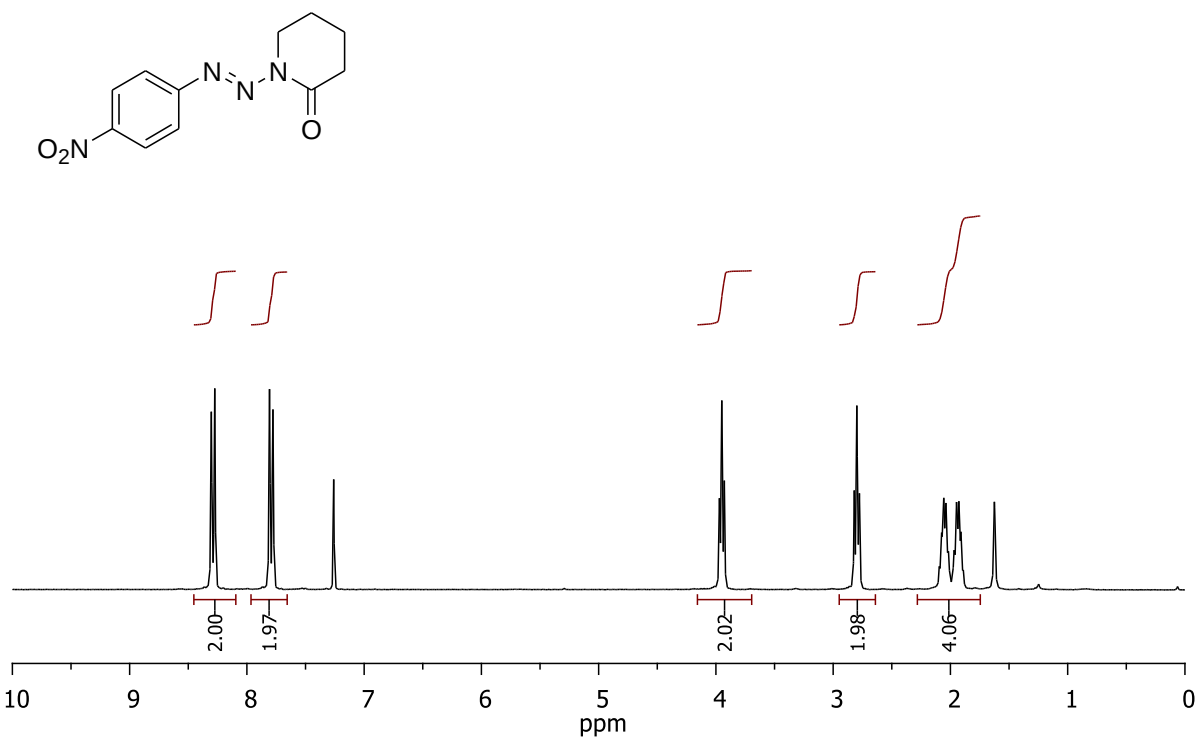


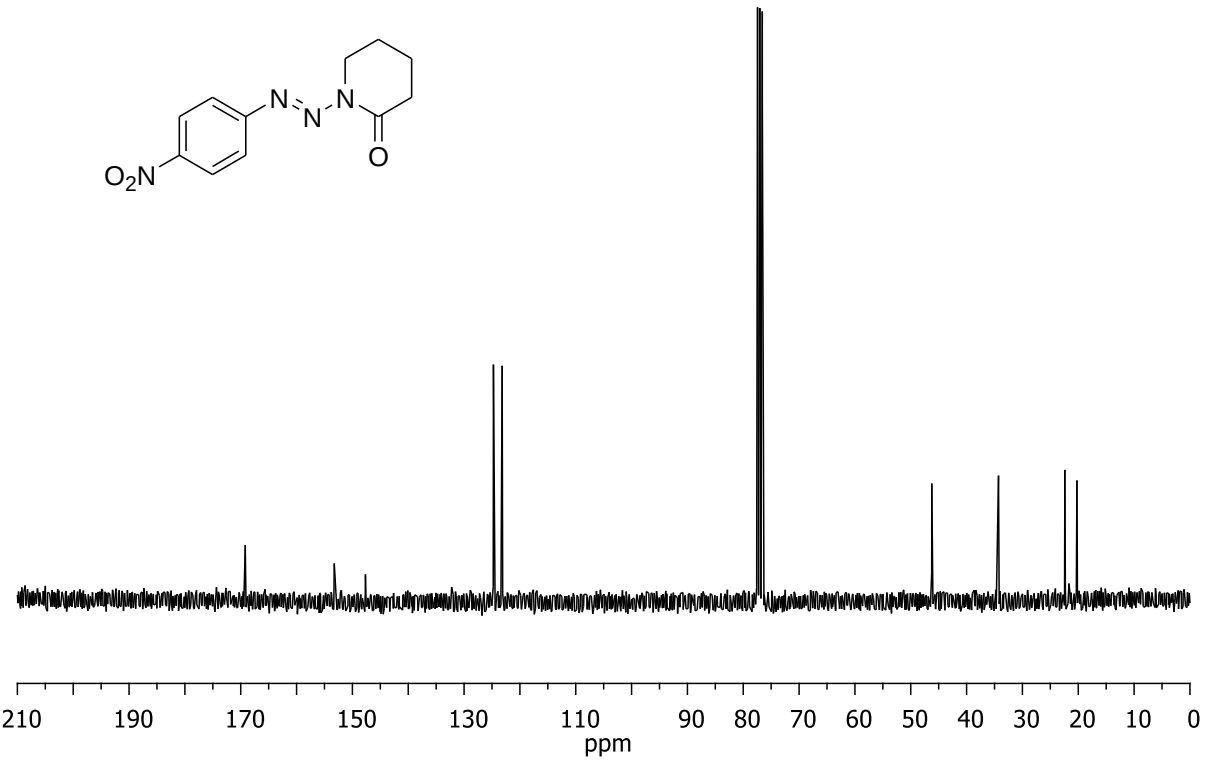
^{1}H NMR and ^{13}C NMR spectra of 1-(4-methoxy-phenyl-diazenyl)-piperidin-2-one (**6c{2}**)



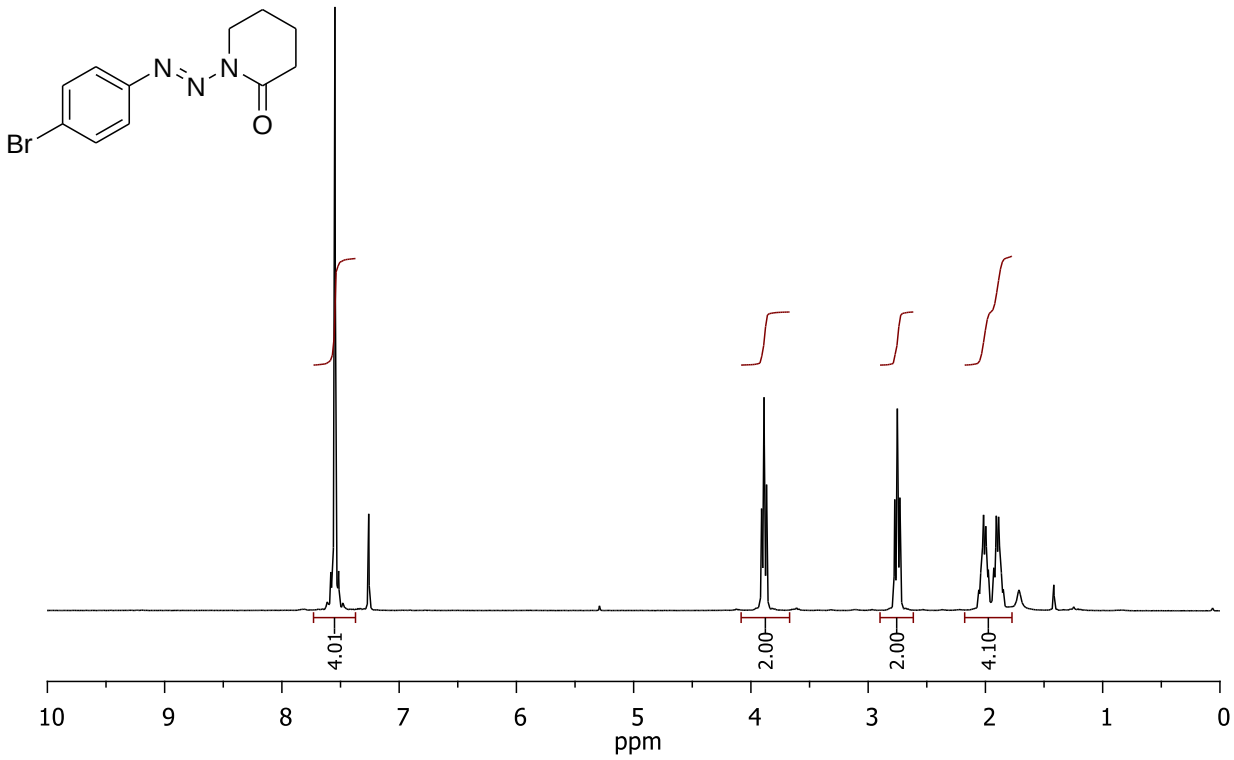


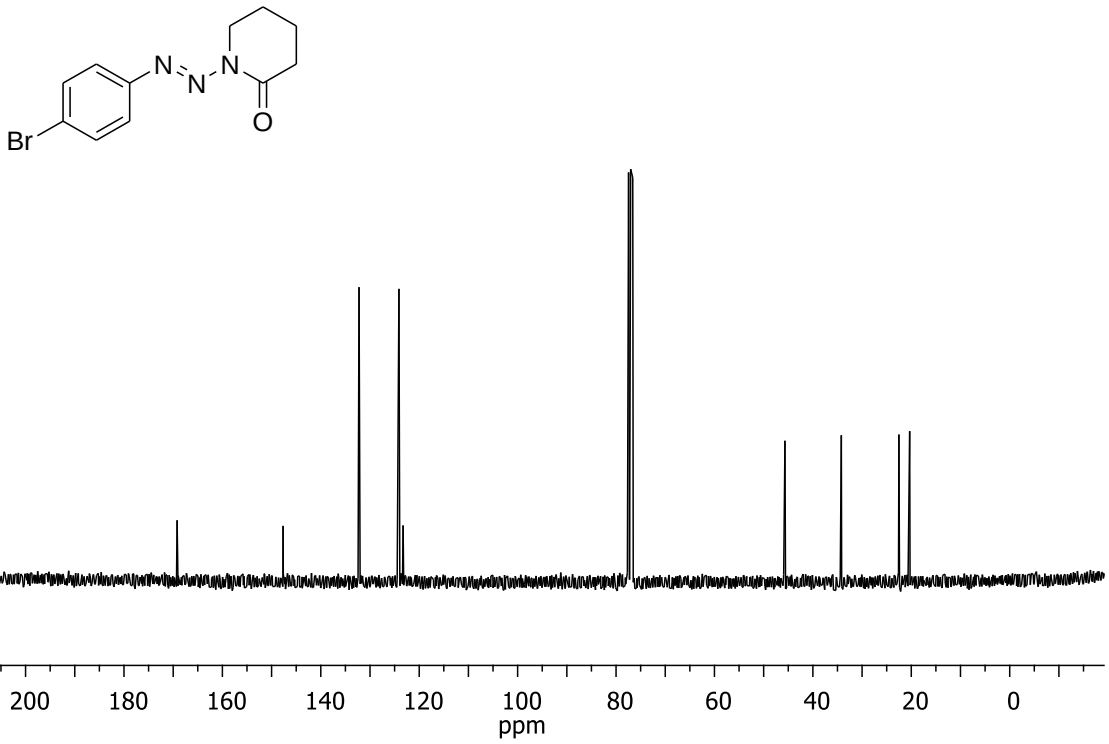
^{1}H NMR and ^{13}C NMR spectra of 1-(4-nitro-phenyl-diazenyl)-piperidin-2-one (**6c{3}**)



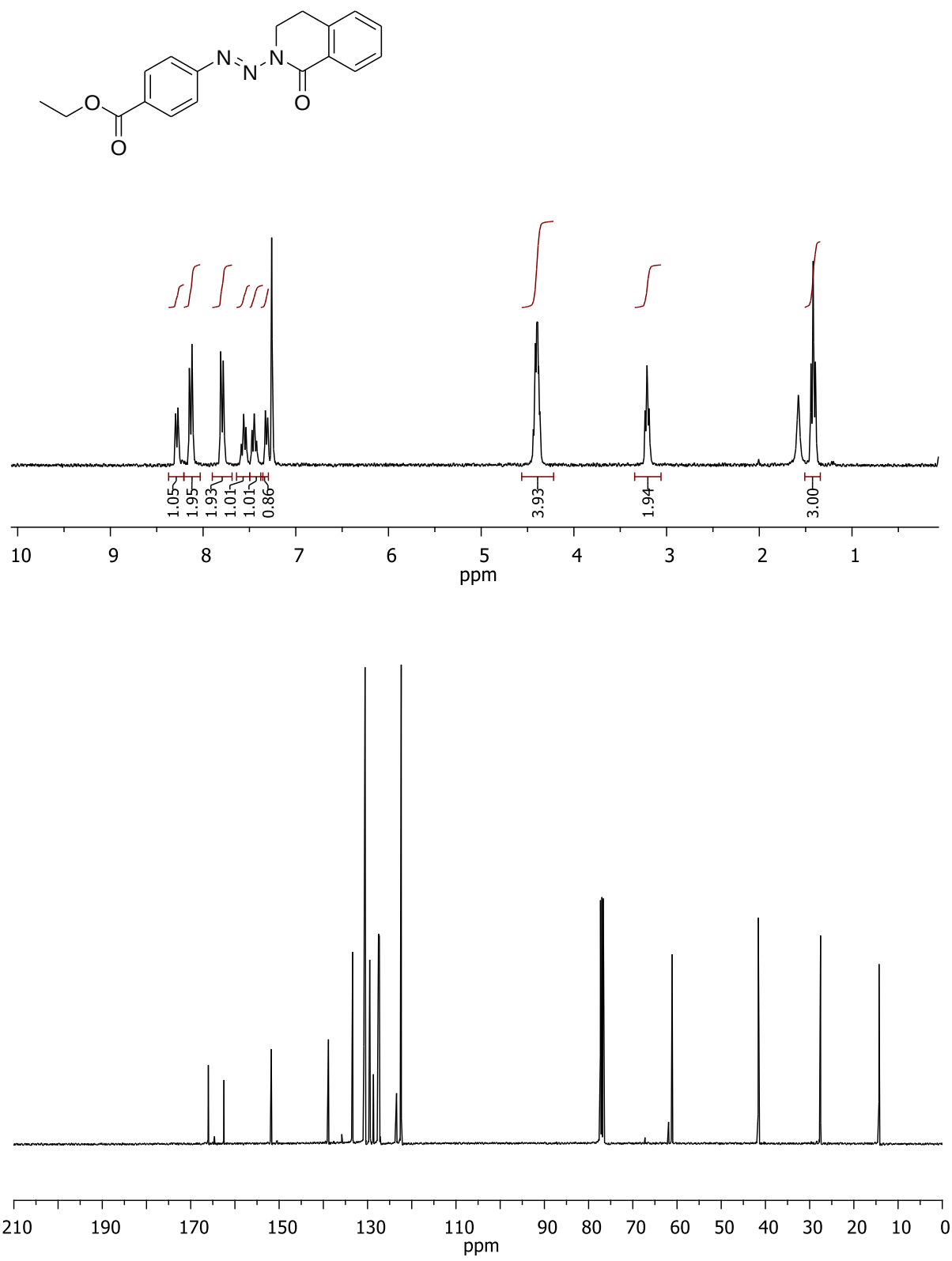


^{1}H NMR and ^{13}C NMR spectra of 1-(4-bromo-phenyl-diazenyl)-piperidin-2-one (**6c{4}**)

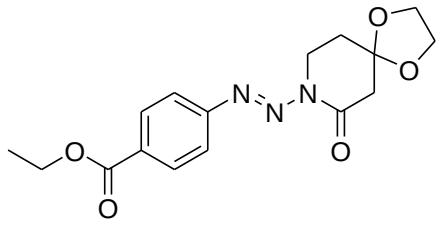


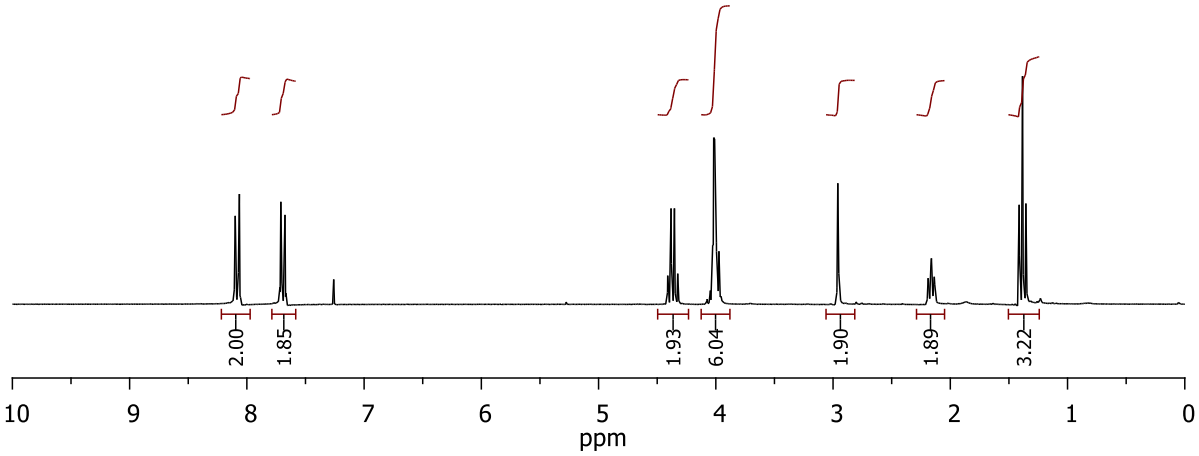


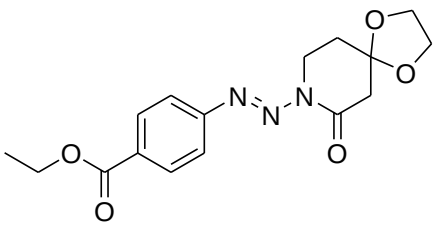
^{1}H NMR and ^{13}C NMR spectra of 4-(1-Oxo-3,4-dihydro-1*H*-isoquinolin-2-ylazo)-benzoic acid ethyl ester (**6c{5}**)

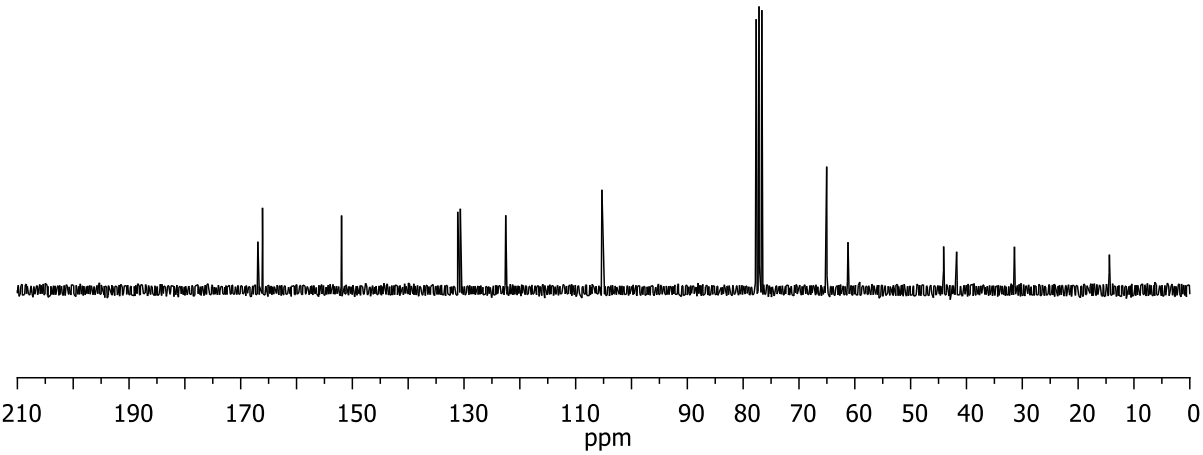


^{1}H NMR and ^{13}C NMR spectra of 4-(7-Oxo-1,4-dioxa-8-aza-spiro[4.5]dec-8-ylazo)-benzoic acid ethyl ester (**6c{6}**)

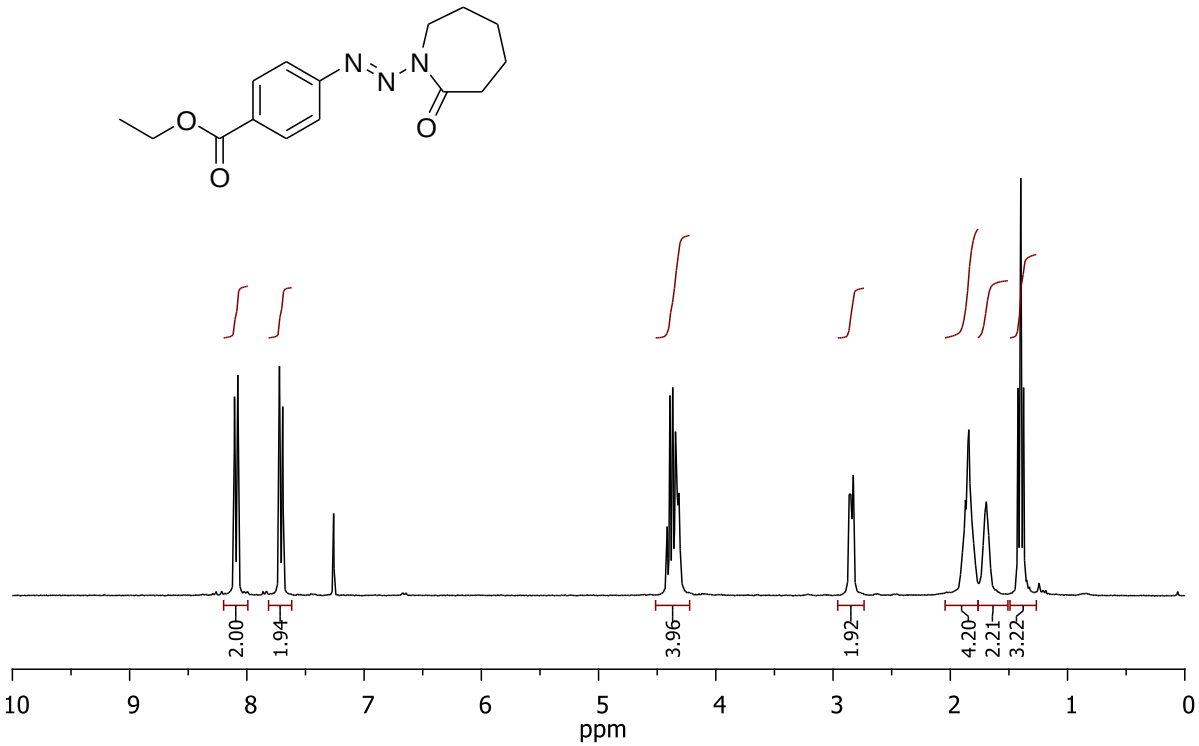


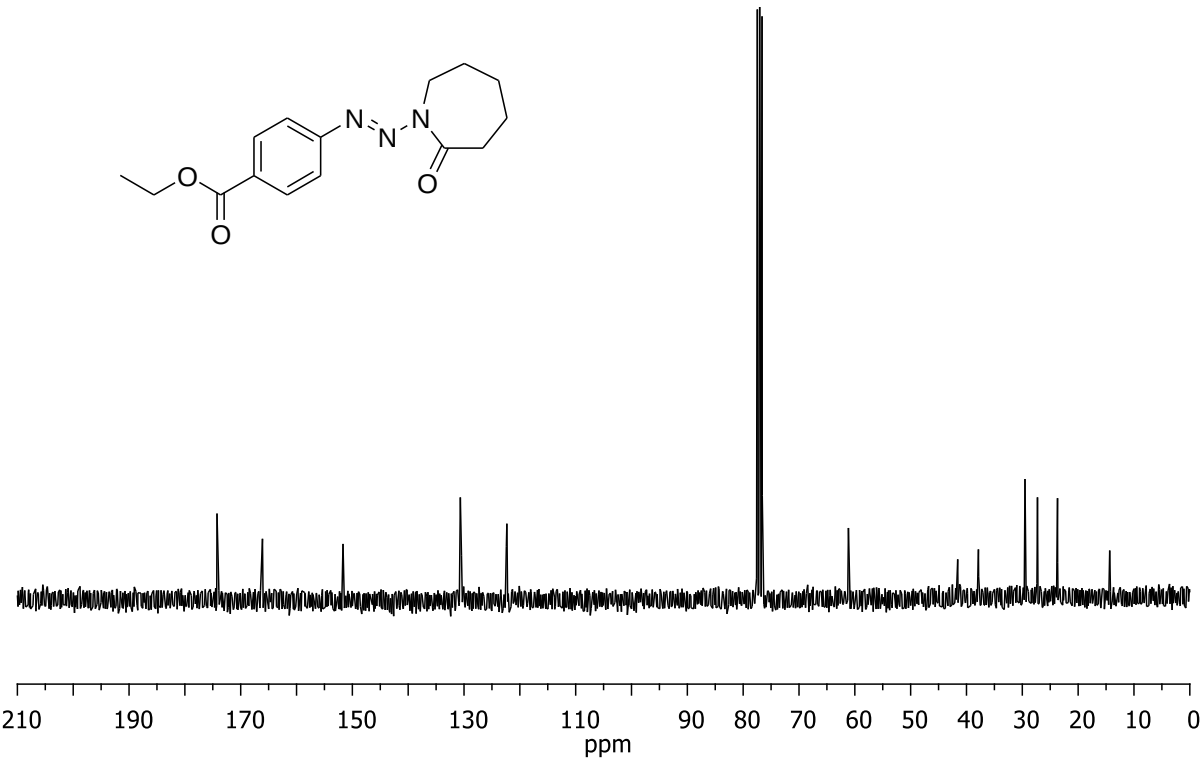




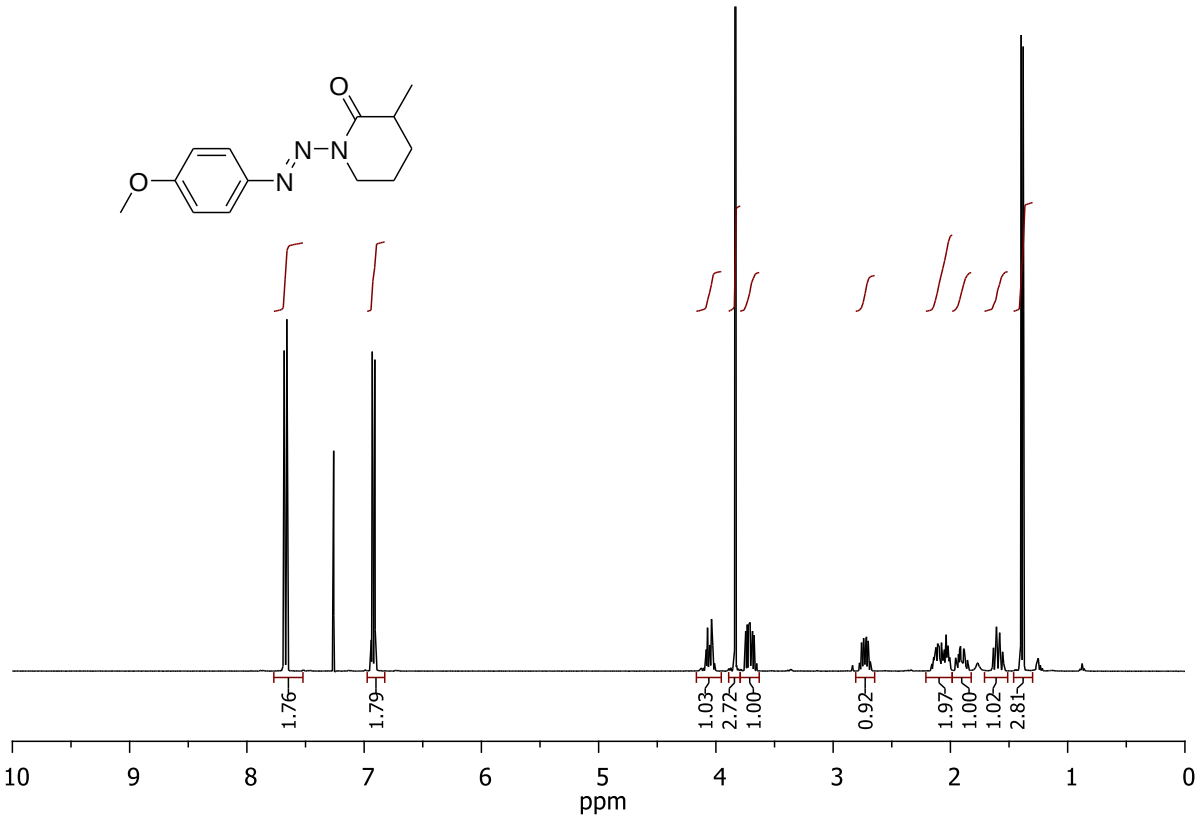


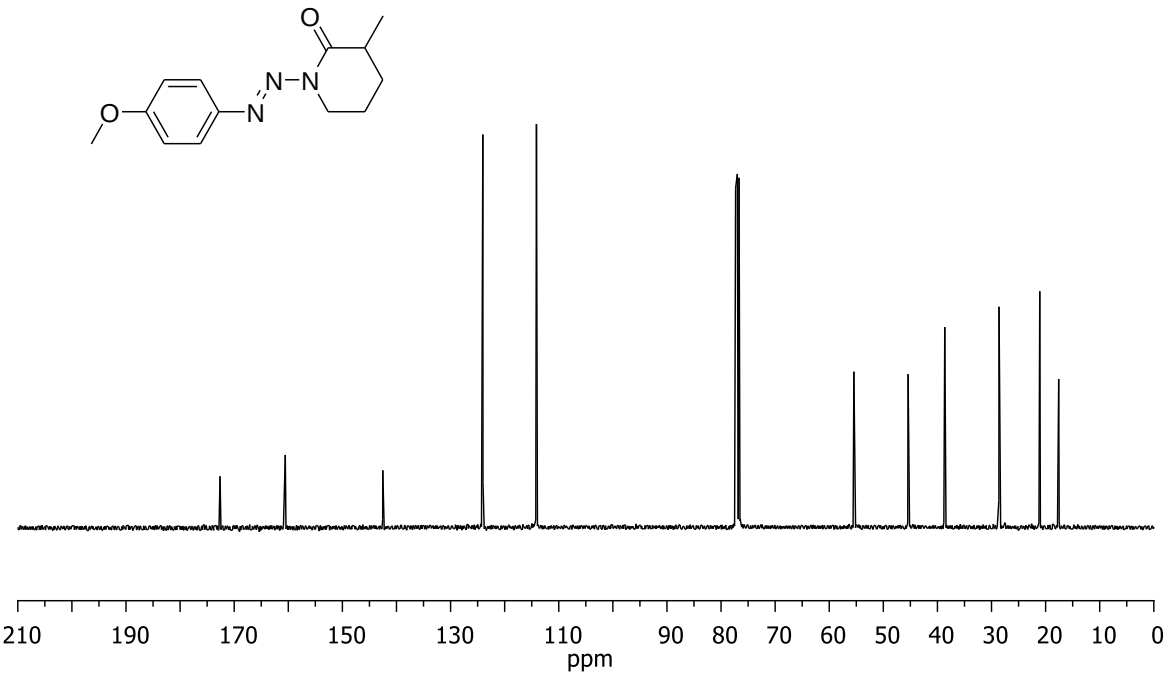
^{1}H NMR and ^{13}C NMR spectra of 4-(2-Oxo-azepan-1-ylazo)-benzoic acid ethyl ester (**6d**)



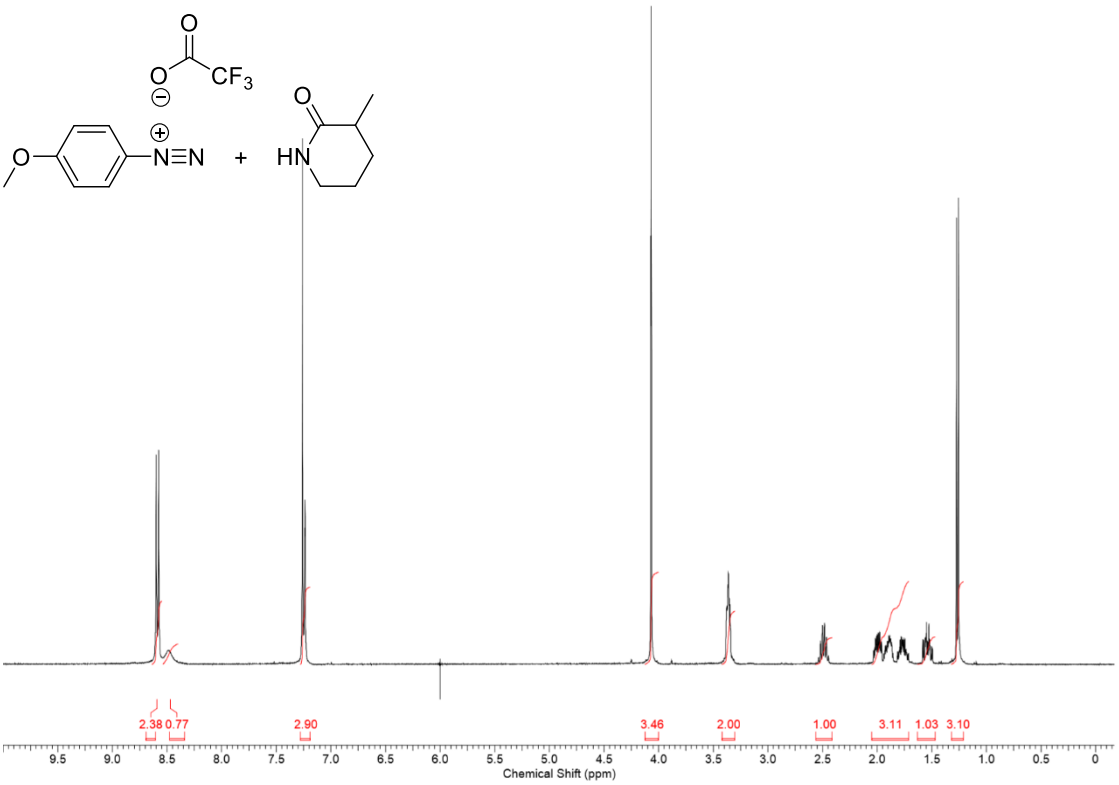


^{1}H NMR and ^{13}C NMR spectra of 1-(4-Methoxy-phenyl-diazenyl)-3-methyl-piperidin-2-one (**7**)





^{1}H NMR spectrum of the crude reaction mixture yielding the deprotected lactam **8** (1:1 mixture of liberated lactam and protecting group).



4. Crystal Structure Determinations

Crystal Structure Determinations. The single-crystal X-ray diffraction study was carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123 K using Cu-Kα radiation (λ = 1.54178 Å). Direct Methods (SHELXS-97) [G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112-122] were used for structure solution and refinement was carried out using SHELXL-2014 [G. M. Sheldrick, *Acta Crystallogr.* 2015, **C71**, 3-8.] (full-matrix least-squares on F^2). Hydrogen atoms were localized by difference Fourier map and refined using a riding model. Semi-empirical absorption corrections and extinction corrections were applied.

3b: colorless blocks, $C_{13}H_{17}N_3O_2$, Mr = 247.29, crystal size 0.10 x 0.04 x 0.02 mm, triclinic, space group *P*-1 (no.2), a = 7.8721 (3) Å, b = 8.4927 (3) Å, c = 10.4598 (4) Å, α = 68.931 (2)°, β = 89.853 (2)°, γ = 77.388 (2)°, V = 634.58 (4) $Å^3$, Z = 2, ρ = 1.294 Mgm^{-3}, μ(Cu-Kα) = 0.727 mm^{-1}, *F*(000) = 264, $2\Theta_{max}$ = 144.2°, 10221 measured reflections, of which 2484 were independent (R_{int} = 0.038), 164 parameters, R_1 = 0.037 (for 2065 I > 2σ(I)), wR_2 = 0.094 (all data), *S* = 1.04, largest diff. peak / hole = 0.244 / -0.185 e $Å^{-3}$.
3c{5} orange plates, $C_{18}H_{19}N_3O_2$, Mr = 309.36, crystal size 0.24 x 0.20 x 0.06 mm, monoclinic, space group $P2_1/n$ (no.14), a = 5.9831 (5) Å, b = 33.3076 (28) Å, c = 7.7858 (7) Å, β = 93.355 (2)°, V = 1548.9 (2) $Å^3$, Z = 4, ρ = 1.327 Mgm^{-3}, μ(Cu-Kα) = 0.712 mm^{-1}, *F*(000) = 656, $2\Theta_{max}$ = 144,4°, 22876 measured reflections, of which 3057 were independent (R_{int} = 0.024), 209 parameters, R_1 = 0.035 (for 2951 I > 2σ(I)), wR_2 = 0.090 (all data), *S* = 1.05, largest diff. peak / hole = 0.285 / -0.239 e $Å^{-3}$.
6c{1}: colorless plates, $C_{14}H_{17}N_3O_3$, Mr = 275.30, crystal size 0.14 x 0.08 x 0.02 mm, monoclinic, space group $P2_1/c$ (no.14), a = 14.7907 (3) Å, b = 7.0900 (2) Å, c = 12.8103 (3) Å, β = 98.877 (1)°, V = 1327.27 (6) $Å^3$, Z = 4, ρ = 1.378 Mgm^{-3}, μ(Cu-Kα) = 0.814 mm^{-1}, *F*(000) = 584, $2\Theta_{max}$ = 144.2°, 20424 measured reflections, of which 2610 were independent (R_{int} = 0.039), 182 parameters, R_1 = 0.034 (for 2289 I > 2σ(I)), wR_2 = 0.090 (all data), *S* = 1.06, largest diff. peak / hole = 0.325 / -0.162 e $Å^{-3}$.
CCDC 1510209 (**3b**), CCDC 1510210 (**3c{5}**) and 1510211 (**6c{1}**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

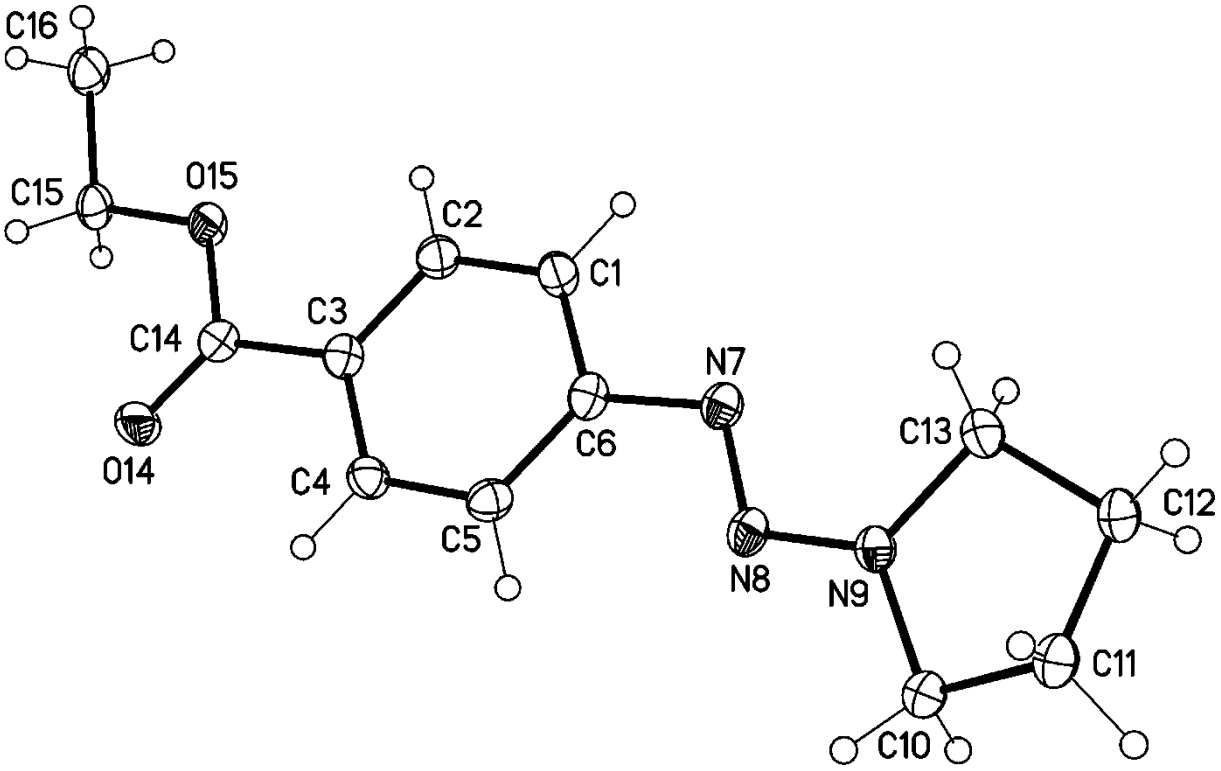


Fig. 1x. Molecular structure of **3b** (displacement parameters are drawn at 50 % probability level).

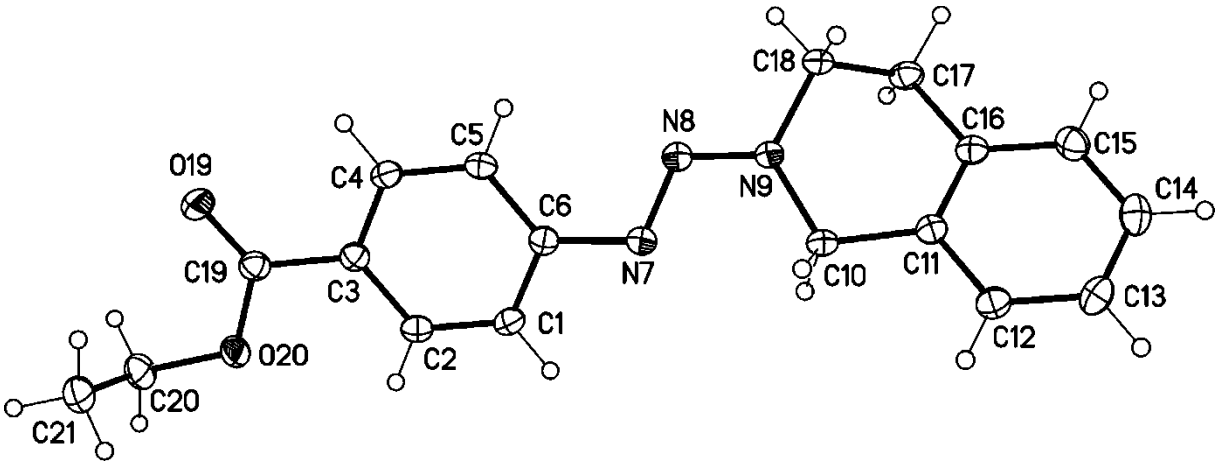


Fig. 2x. Molecular structure of **3c{5}** (displacement parameters are drawn at 50 % probability level).

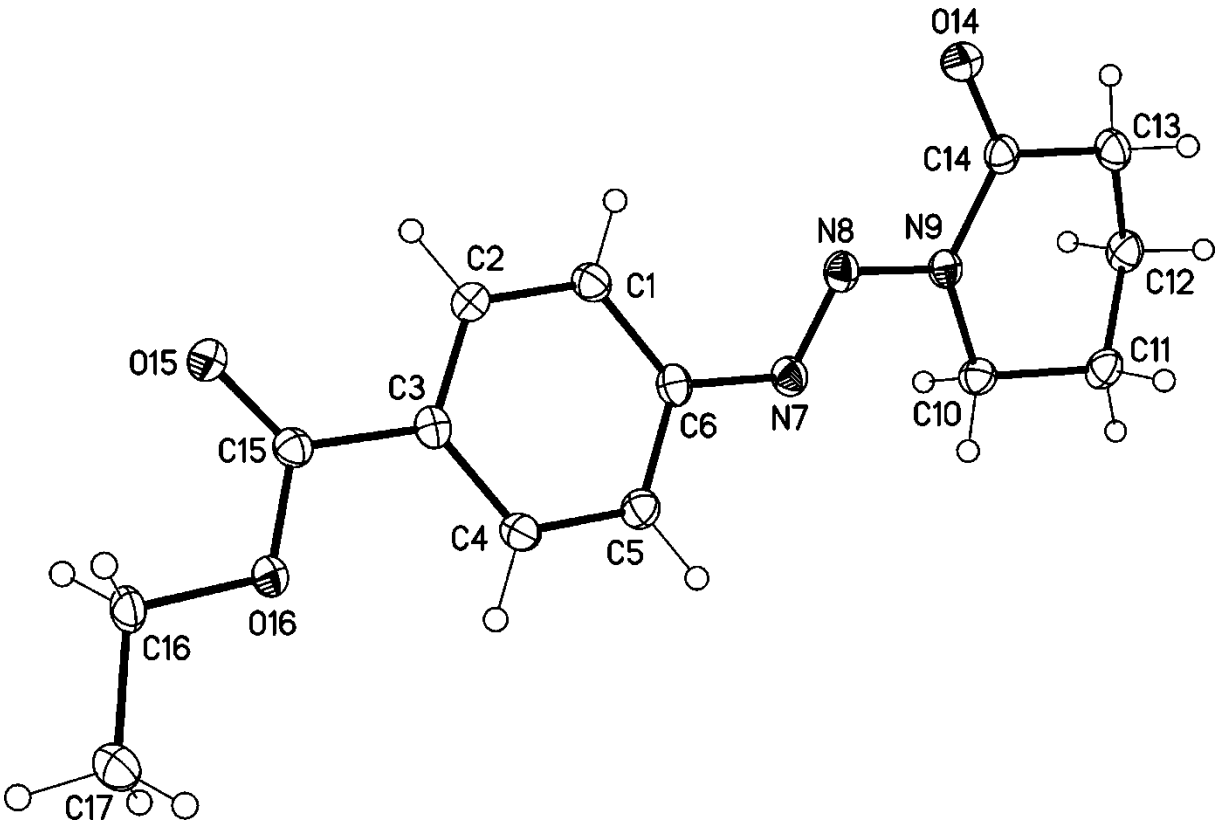


Fig. 3x. Molecular structure of **6c{1}** (displacement parameters are drawn at 50 % probability level).