

Supporting Information

for

N-Acetyl Diazocine Derivatives via Cross-Coupling

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I. Analytical Equipment

NMR spectroscopy

NMR spectra were measured in deuterated solvents (Deutero). The spectra were referenced to the following solvent residual signals:

solvent	degree of deuteration	¹ H signal ppm	¹³ C-signal ppm
acetone-d ₆	99.8%	2.05 (quintet)	29.84 (septet)
chloroform-d ₁	99.8%	7.26 (singlet)	77.16 (triplet)
acetonitrile-d ₃	99.8%	1.94 (singlet)	1.32 (septet), 118.26 (multiplet)
water-d ₂	99.9%	4.79 (singlet)	-

The spectra were recorded with a Bruker DRX 500 (¹H-NMR: 500 MHz, ¹³C-NMR: 125 MHz) and a Bruker AV 600 (¹H-NMR: 600 MHz, ¹³C-NMR: 150 MHz). The Multiplicities of the signals were abbreviated with s (singlet), d (doublet), t (triplet), q (quartet), quint. (quintet), m (multiplet), and br. (broad) in addition for broad signals. DEPT data were used to assign carbon types. Structural assignments were made with additional information from HSQC and HMBC experiments. Baseline correction of the spectra in D₂O was performed with Baseline Correction "Withaker Smoother" tool and Signal Suppression tool in MestReNova 14.3.1 NMR analytic software by Mestrelab Research. Spectra were plotted with TopSpin 4.1.0 NMR analytic software by Bruker. Major impurities in the 1D-NMR spectra used for compound characterization have been identified as far as possible and labeled accordingly.

Melting Point

Melting Points were measured with a Melting Point B-560 (Büchi) in melting point tubes without further correction.

Mass spectrometry

Mass spectra (EI) and high-resolution mass spectra (HR-EI) were measured with an AccuTOF GCv 4G EI-time of flight mass spectrometer from the company Joel. An ionization energy of 70 eV was used.

HR-ESI mass spectra were measured with a Q Exactive Plus Hybrid Quadrupole-Orbitrap ESI-mass spectrometer of the company Thermo Scientific was used.

IR spectroscopy

Infrared spectra were measured with a Perkin-Elmer 1600 FT-IR spectrometer with an A531-G Golden-Gate-Diamond-ATR-unit. Signals were abbreviated with w (weak), m (medium) or s (strong) for its intensity.

UV-vis spectroscopy

UV-vis spectra were measured with a Shimadzu UV-2600 i UV-vis spectrometer. Quartz cuvettes of 10 mm optical path length were used.

Chromatography

Silica gel (Merck, particle size 0.040-0.063 mm) was used for column chromatography purifications. *R_f* values were determined via thin layer chromatography on Polygram® SiLG/UV254 (Macherey Nagel, 0.2 mm particle size).

Chemicals

All commercially available chemicals were used without further purification.

Light sources

For irradiation different custom-built light sources with a wavelength of 405 nm and 530 nm were used (Sahlmann Photochemistry Solutions & in-house built). Irradiation wavelengths for all (405 nm and 530 nm) LED units were measured via a mobile UV-vis spectrometer (USB4000-UV-VIS, Ocean Optics, Largo, FL, USA). All emission spectra were normalized. Figure S11 shows the normalized emission spectra of all LED units used.

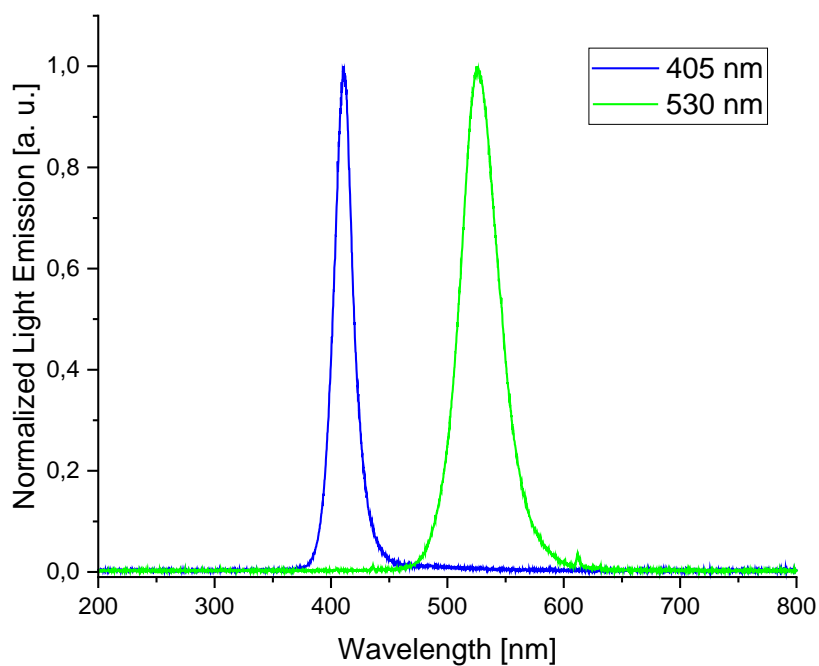


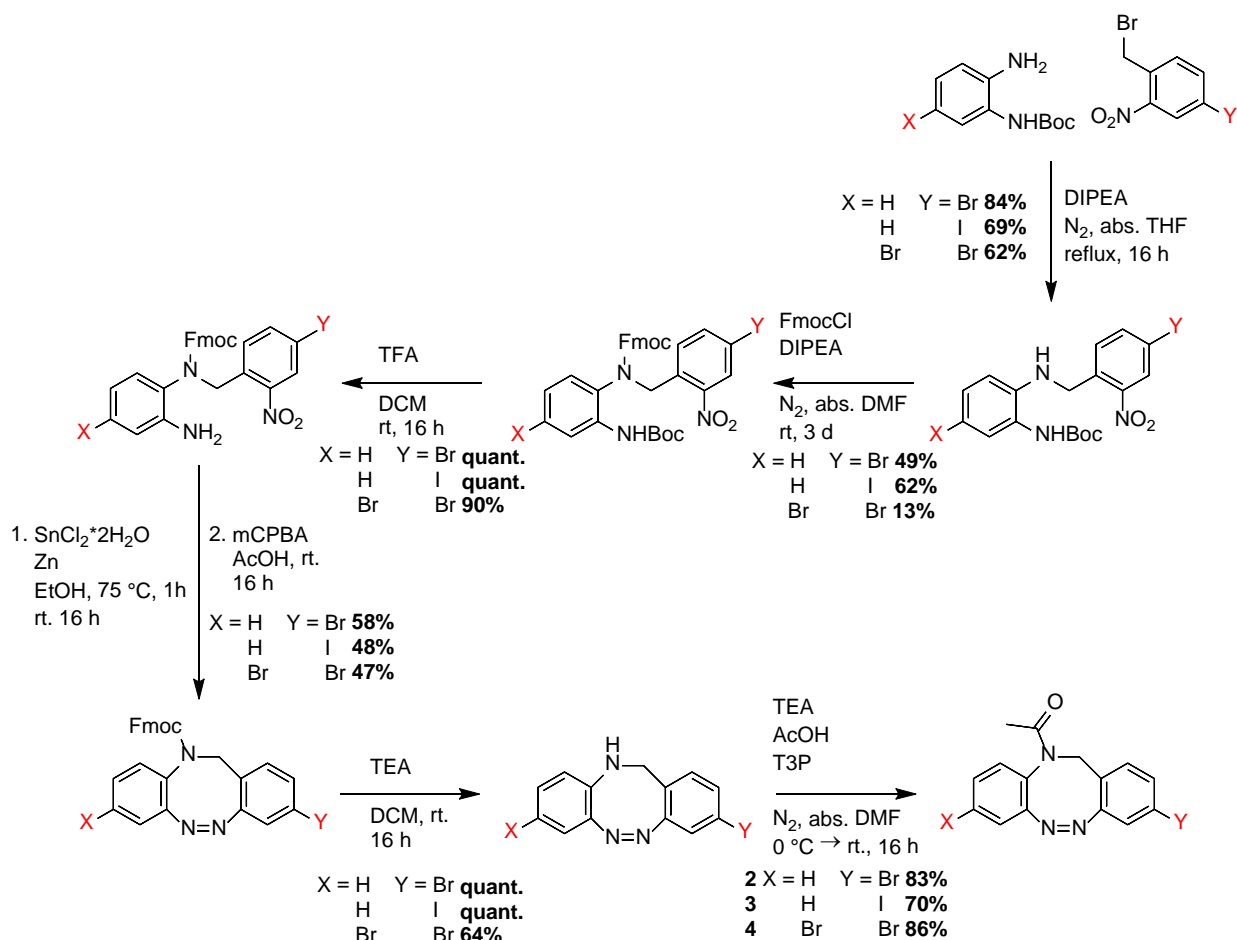
Figure SI.1: Emission spectra of all LED units used. For better comparison all datasets were normalized to its maximum.

The full width at half maximum (FWHM) amounts to 19 nm (401-420 nm, maximum at 410 nm) for the 405 nm LED unit and to 38 nm (509-547 nm, maximum at 525 nm) for the 530 nm LED unit.

II. Syntheses

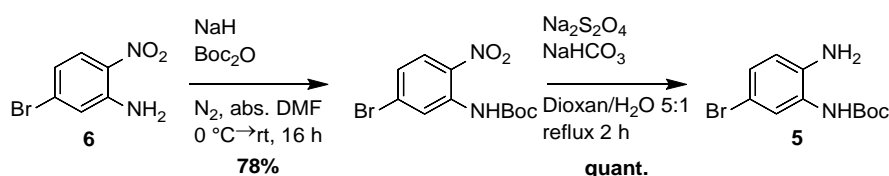
II.1 Synthesis of halogenated *N*-acetyl diazocines

The halogenated *N*-acetyl diazocine precursors **2-4** were synthesized following the procedure of LENTES *et al.*^[1] (Scheme 1). Therefore, the dianiline and bromide building blocks were connected in a nucleophile substitution in the first step followed by Fmoc-protection of the secondary amine. After cleaving the Boc-protecting group the nitro-group was reduced using stannous chloride and zink. In the following the oxidative azo-cyclization adapted from the procedure of MAIER *et al.*^[2] was performed to receive the Fmoc-protected *N*-acetyl diazocine intermediates. After the Fmoc-group was cleaved the acetyl protecting group was introduced as final step.



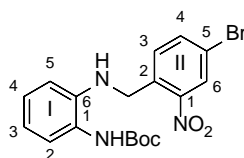
Scheme S1: Synthesis of the halogenated *N*-acetyl diazocine precursors **2-4** for the cross-coupling reactions according to the procedure of LENTES *et al.*^[1]

For the synthesis of dibromo-*N*-acetyl diazocine **4** the Boc-protected dianiline building block **5** was prepared from commercially available 5-bromo-2-nitroaniline **6**. In the first step the Boc protecting group was introduced after deprotonation of the aniline with sodium hydride. The nitro group was reduced with sodium dithionite and sodium hydrogencarbonate subsequently to obtain dianiline building block **5**.



Scheme S2: Synthesis of dianiline building block **5** from *o*-nitroaniline **6**.

II.1.1 Synthesis of *tert*-butyl-(2-((4-bromo-2-nitrobenzyl)amino)phenyl)carbamate^[1]



Under a nitrogen atmosphere triethylamine (3.87 mL, 27.9 mmol) and 4-bromo-1-(bromomethyl)-2-nitrobenzene (7.50 g, 25.4 mmol) were added to solution of *tert*-butyl-(2-aminophenyl)carbamate (5.30 g, 25.4 mmol) in 100 mL abs. THF. The reaction mixture was heated to reflux with an oil bath and stirred for 16 h at that temperature. Afterwards the solvent was evaporated and 100 mL of deionized water and 100 mL DCM were added to the residue. The organic layer was separated and the aqueous layer was extracted twice with 50 mL of DCM. The combined organic layers were dried over MgSO₄ and the solvent was evaporated. Recrystallization from cyclohexane/ethyl acetate (1:1) gave the product as yellow solid (9.06 g, 21.4 mmol, 84%, lit. 71%^[1]).

melting point: 147 °C

¹H-NMR (500 MHz, acetone-*d*₆, 298 K): δ = 8.24 (d, ⁴*J* = 2.0 Hz, 1 H, Ar^{II}-H-6), 7.83 (dd, ³*J* = 8.4 Hz, ⁴*J* = 2.1 Hz, 1 H, Ar^{II}-H-4), 7.73 (d, ³*J* = 8.4 Hz, 1 H, Ar^{II}-H-3), 7.63 (br. s, 1 H, NH), 7.25 (d, ³*J* = 7.7 Hz, 1 H, Ar^I-H-2), 6.93 (td, ³*J* = 7.8 Hz, ⁴*J* = 1.5 Hz, 1 H, Ar^I-H-4), 6.64 (td, ³*J* = 7.6 Hz, ⁴*J* = 1.3 Hz, 1 H, Ar^I-H-3), 6.50 (dd, ³*J* = 7.6 Hz, ⁴*J* = 2.1 Hz, 1 H, Ar^I-H-5), 5.51 (br. s, 1 H, NH), 4.76 (s, 2 H, CH₂), 1.47 (s, 9 H, CH₃) ppm.

¹³C{¹H}-NMR (125 MHz, acetone-*d*₆, 298 K): δ = 155.0 (C=O), 150.0 (Ar^{II}-C-1), 142.7 (Ar^I-C-6), 137.1 (Ar^{II}-C-4), 136.2 (Ar^{II}-C-6), 132.4 (Ar^{II}-C-3), 128.3 (Ar^{II}-C-6), 127.1 (Ar^I-C-4), 126.8 (Ar^I-C-2), 125.5 (Ar^I-C-1), 120.9 (Ar^{II}-C-5), 118.0 (Ar^I-C-3), 112.4 (Ar^I-C-5), 79.9 (C-(CH₃)₃), 45.1 (-CH₂), 28.6 (-CH₃) ppm.

IR (ATR): $\tilde{\nu}$ = 3398 (m), 3270 (m), 2975 (w), 1707 (w), 1684 (s), 1604 (m), 1528 (s), 1502 (s), 1462 (m), 1421 (w), 1393 (w), 1346 (m), 1336 (m), 1307 (w), 1242 (s), 1153 (s), 1083 (w), 1066 (w), 1052 (m), 1028 (w), 906 (w), 874 (w), 845 (w), 831 (m), 792 (w), 754 (s), 717 (w), 647 (w), 616 (w) cm⁻¹.

HR-MS (ESI, DCM): *m/z* [M+H]⁺ calculated for C₁₈H₂₀O₄N₃⁷⁹Br+H⁺: 422.0710; found: 422.0700 ± 2.36 ppm.

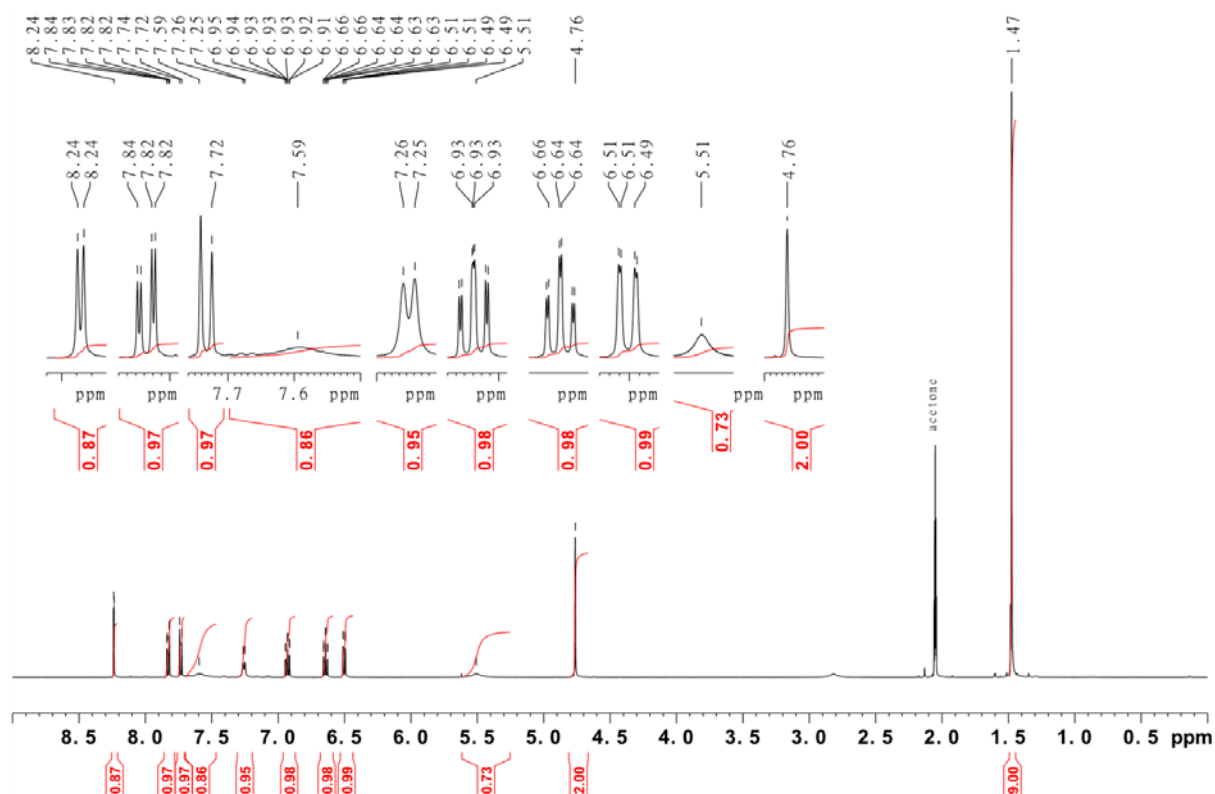


Figure SII.1: 500 MHz ^1H -NMR spectrum of *tert*-butyl-(2-((4-bromo-2-nitrobenzyl)amino)phenyl)carbamate.

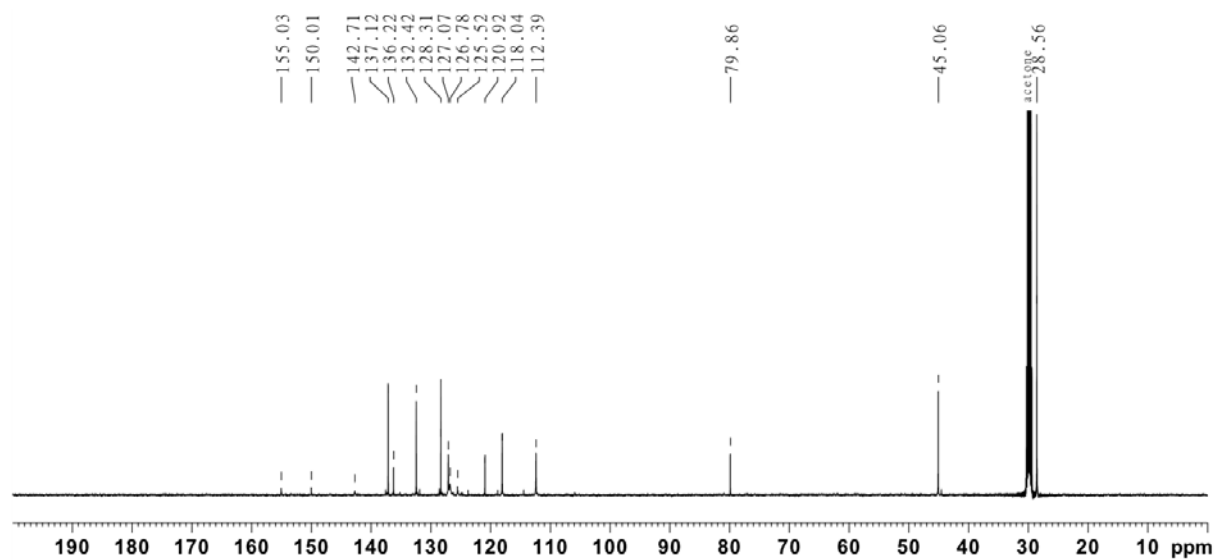


Figure SII.2: 125 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of *tert*-butyl-(2-((4-bromo-2-nitrobenzyl)amino)phenyl)carbamate.

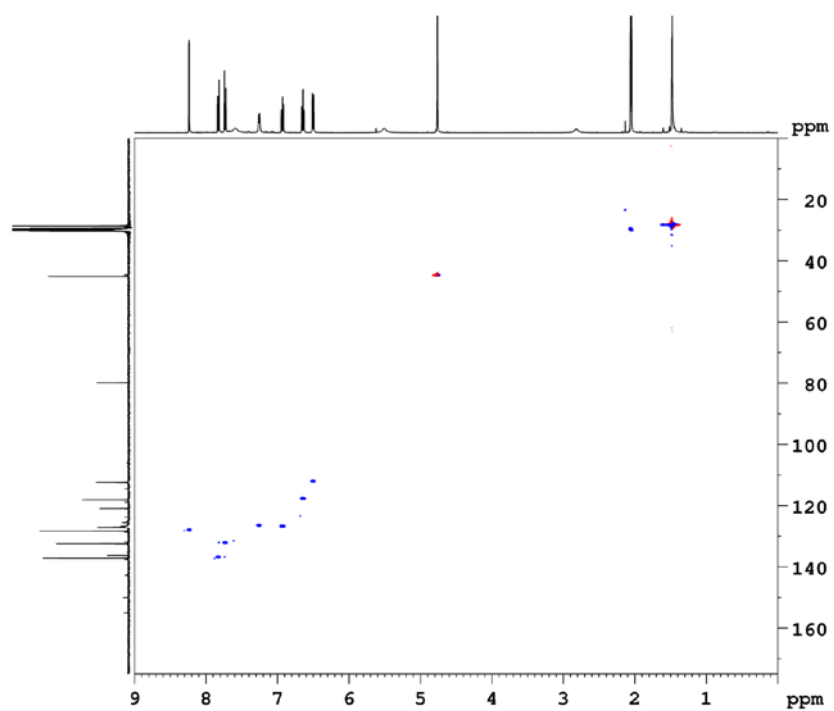


Figure SII.3: 500 MHz ^1H - ^{13}C HSQC spectrum of *tert*-butyl-(2-((4-bromo-2-nitrobenzyl)amino)phenyl)carbamate.

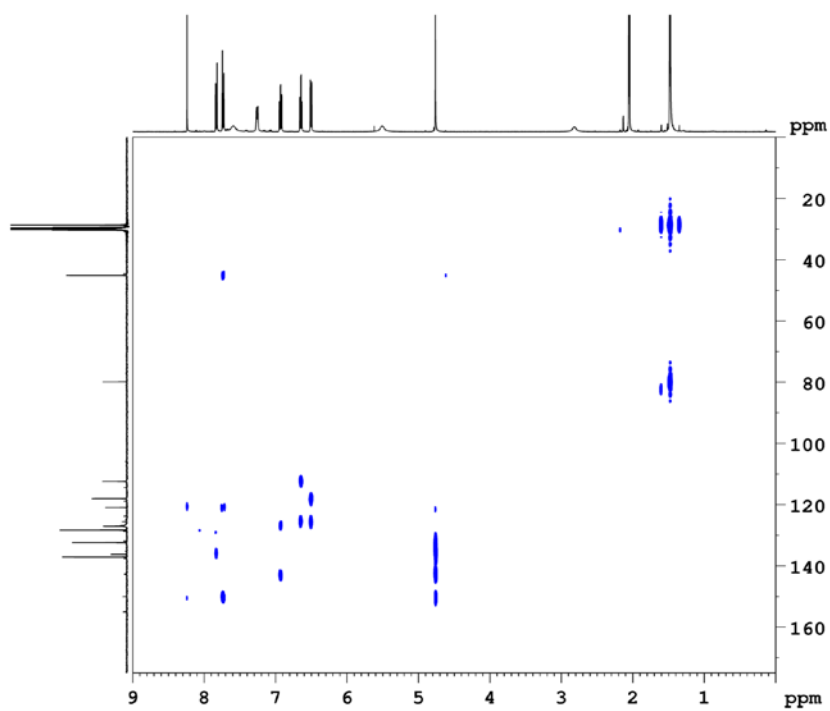
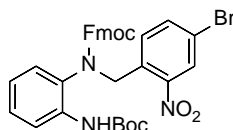


Figure SII.4: 500 MHz HMBC spectrum of *tert*-butyl-(2-((4-bromo-2-nitrobenzyl)amino)phenyl)carbamate.

II.1.2 Synthesis of (9H-fluoren-9-yl)methyl-(4-bromo-2-nitrobenzyl)(2-((tert-butoxycarbonyl)amino)phenyl)carbamate^[1]



DIPEA (3.21 mL, 18.9 mmol) and 9-Fluorenylmethoxycarbonyl chlorid (9.77 g, 37.8 mmol) were added to a solution of *tert*-butyl-(2-((4-bromo-2-nitrobenzyl)amino)phenyl)carbamate (8.00 g, 18.9 mmol) in 50 mL abs. DMF under a nitrogen atmosphere. The reaction mixture was stirred for 48 h at rt. and the solvent was evaporated subsequently. 100 mL of deionized water and 100 mL of DCM were added to the residue. The organic layer was separated and the aqueous layer was extracted twice with 100 mL DCM. The combined organic layers were dried over MgSO₄ and the solvent was evaporated. Column chromatography on silica (ethyl acetate/cyclohexane 1:4, *R*_f = 0.34) gave a colorless solid (5.91 g, 9.18 mmol, 49%, lit. 56%^[1]).

melting point: 157 °C

¹H-NMR (500 MHz, acetone-*d*₆, 298 K): δ = 8.14 (d, ⁴*J* = 2.1 Hz, 1 H), 8.05-7.61 (m, 5 H), 7.53-7.01 (m, 10 H), 5.24-4.92 (m, 2 H, aliph.-*H*), 4.56-4.00 (m, 3 H, aliph.-*H*), 1.45 (s, 9 H, CH₃) ppm.

¹³C{¹H}-NMR (125 MHz, acetone-*d*₆, 298 K): δ = 153.5 (C=O), 142.1, 137.0, 129.2, 128.5, 128.2, 127.8, 126.1, 124.4, 120.7, 80.4, 68.4, 47.8, 28.5 (CH₃) ppm.

IR (ATR): $\tilde{\nu}$ = 3381 (m), 2974 (w), 2348 (w), 2253 (w), 1717 (s), 1596 (m), 1536 (m), 1518 (s), 1450 (m), 1390 (m), 1365 (w), 1292 (m), 1278 (w), 1234 (m), 1217 (w), 1152 (s), 1042 (w), 1024 (w), 976 (m), 942 (w), 884 (m), 842 (w), 756 (s), 739 (w), 634 (w), 617 (m), 543 (m) cm⁻¹.

HR-MS (ESI, DCM): *m/z* [M+H]⁺ calculated for C₃₃H₃₀O₆N₃⁷⁹Br+H⁺: 644.1391; found: 644.1393 ± 0.41 ppm.

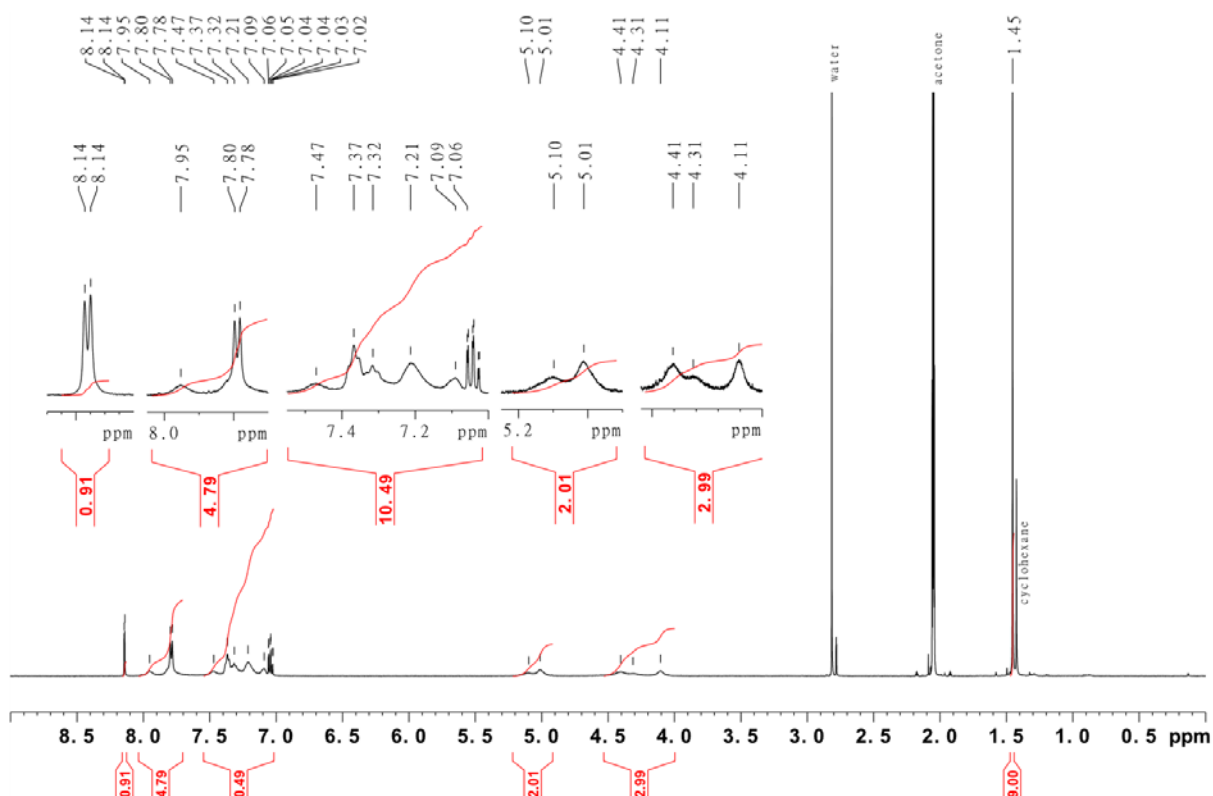


Figure SII.5: 500 MHz ^1H -NMR spectrum of (9*H*-fluoren-9-yl)methyl-(4-bromo-2-nitrobenzyl)(2-((*tert*-butoxycarbonyl)amino)phenyl)carbamate.

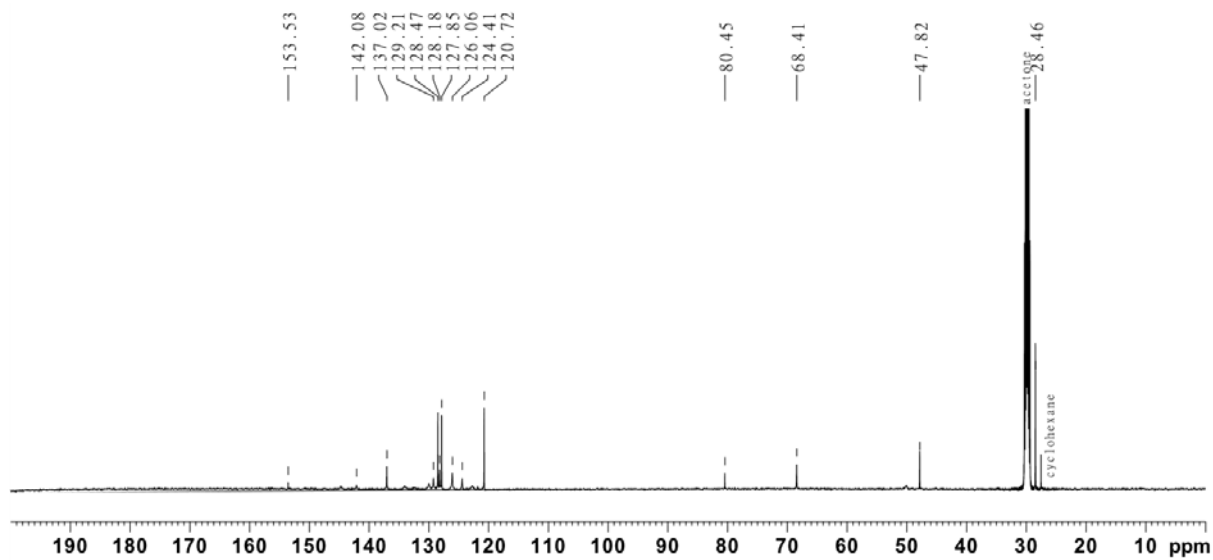


Figure SII.6: 125 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (9*H*-fluoren-9-yl)methyl-(4-bromo-2-nitrobenzyl)(2-((*tert*-butoxycarbonyl)amino)phenyl)carbamate.

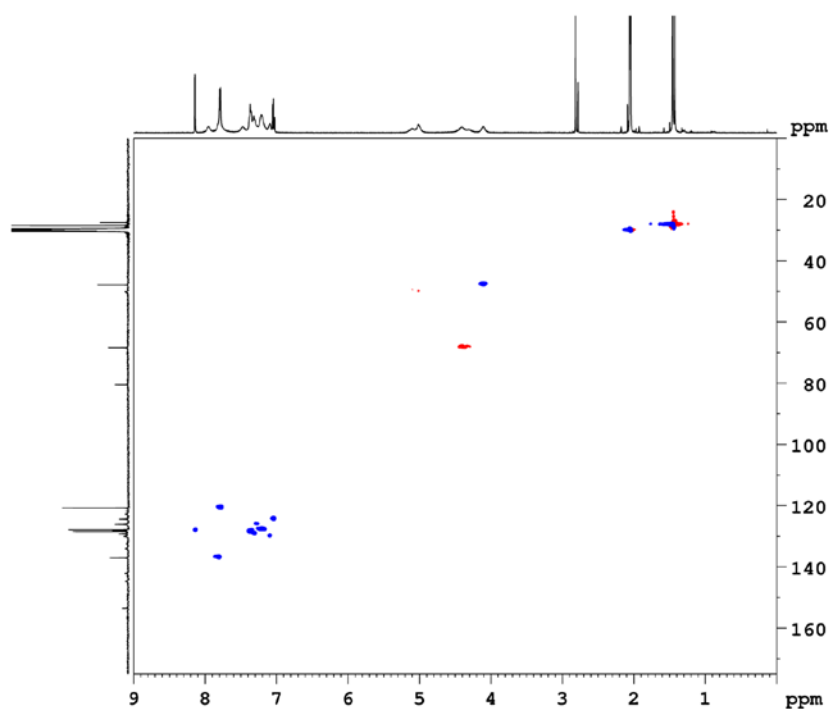


Figure SII.7: 500 MHz ^1H - ^{13}C HSQC spectrum of (9*H*-fluoren-9-yl)methyl-(4-bromo-2-nitrobenzyl)(2-((*tert*-butoxycarbonyl)amino)phenyl)carbamate.

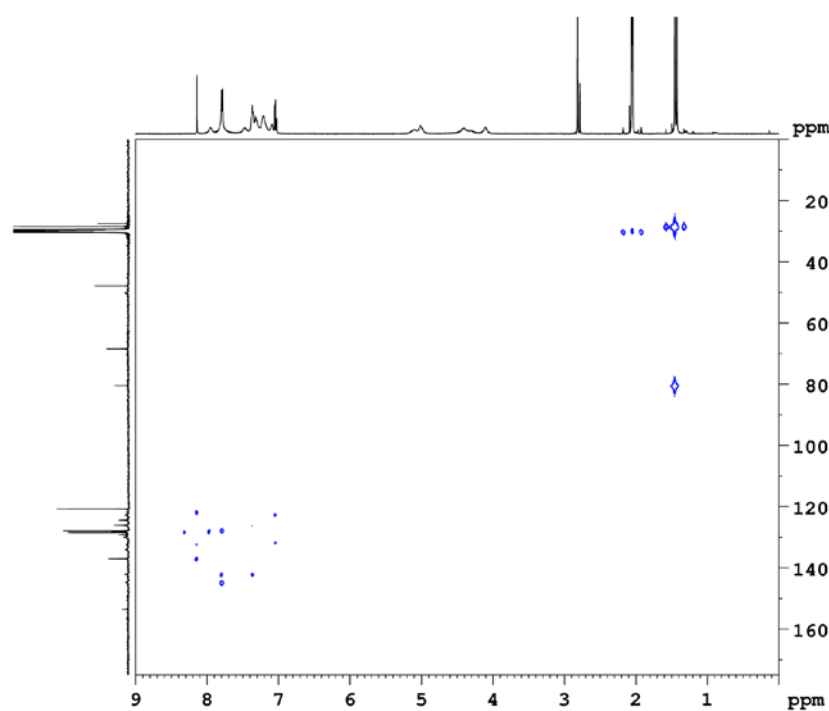
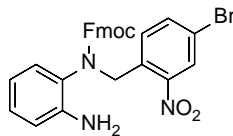


Figure SII.8: 500 MHz HMBC spectrum of (9*H*-fluoren-9-yl)methyl-(4-bromo-2-nitrobenzyl)(2-((*tert*-butoxycarbonyl)amino)phenyl)carbamate.

II.1.3 Synthesis of (9H-fluoren-9-yl)methyl-(2-aminophenyl)(4-bromo-2-nitrobenzyl)carbamate^[1]



(9H-fluoren-9-yl)methyl-(4-bromo-2-nitrobenzyl)(2-((*tert*-butoxycarbonyl)amino)phenyl)carbamate (5.00 g, 7.76 mol) was dissolved in 100 mL DCM and 30 mL TFA was added. The reaction mixture was stirred at rt. for 16 h and neutralized with saturated aqueous NaHCO₃ subsequently. The organic layer was separated and the aqueous layer was extracted twice with 100 mL. The combined organic layers were dried over MgSO₄ and the solvent was evaporated to obtain a pale yellow solid (4.22 g, 7.75 mmol, quant., lit. quant.^[1]) which was used without further purification.

melting point: 156 °C

¹H-NMR (600 MHz, acetone-*d*₆, 298 K): δ = 8.12 (s, 1 H), 7.92-7.63 (m, 4 H), 7.50-6.52 (m, 10 H), 5.60-4.02 (m, 5 H, aliph.-H) ppm.

¹³C{¹H}-NMR (150 MHz, acetone-*d*₆, 298 K): δ = 144.7, 142.1, 136.9, 133.2, 130.3, 129.0, 128.4, 127.84, 127.79, 126.1, 124.4, 121.5, 120.72, 120.67, 68.0, 49.66, 47.97, 47.89 ppm.

IR (ATR): $\tilde{\nu}$ = 3425 (w), 3353 (w), 2348 (w), 2185 (w), 2163 (s), 2052 (m), 1978 (m), 1712 (s), 1619 (m), 1521 (s), 1503 (w), 1451 (w), 1433 (m), 1340 (m), 1253 (s), 1189 (w), 1172 (m), 1150 (w), 1102 (m), 1063 (m), 1051 (w), 876 (m), 764 (m), 745 (s), 659 (m), 638 (w), 621 (m), 568 (w), 543 (m) cm⁻¹.

HR-MS (ESI, DCM): m/z [M+H]⁺ calculated for C₂₈H₂₂O₄N₃⁷⁹Br+H⁺: 544.0867; found: 544.0870 \pm 0.58 ppm.

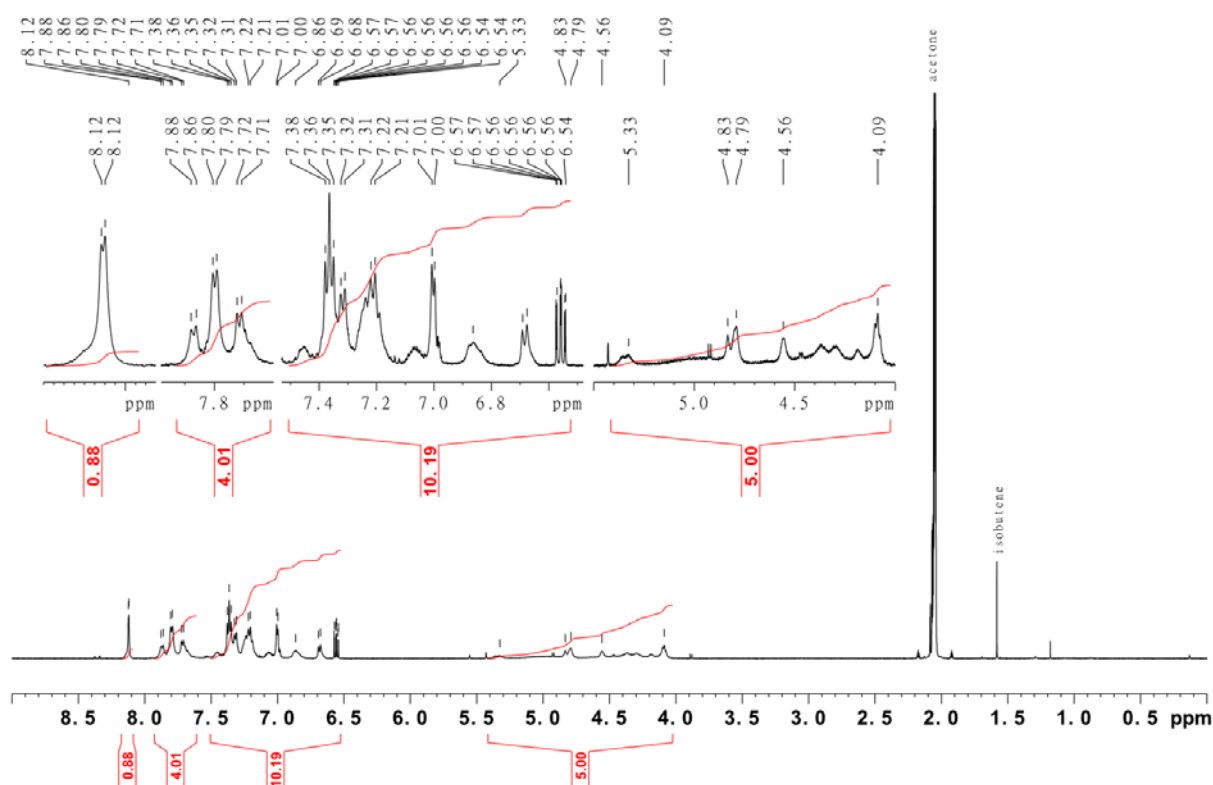


Figure SII.9: 600 MHz ^1H -NMR spectrum of (9*H*-fluoren-9-yl)methyl-(2-aminophenyl)(4-bromo-2-nitrobenzyl)carbamate.

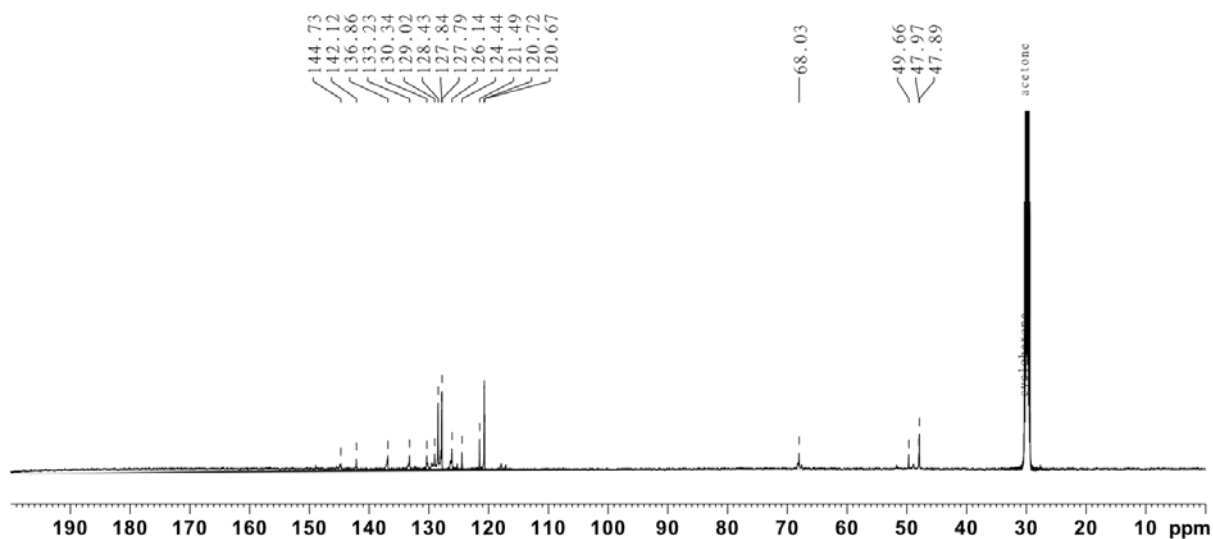


Figure SII.10: 150 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (9*H*-fluoren-9-yl)methyl-(2-aminophenyl)(4-bromo-2-nitrobenzyl)carbamate.

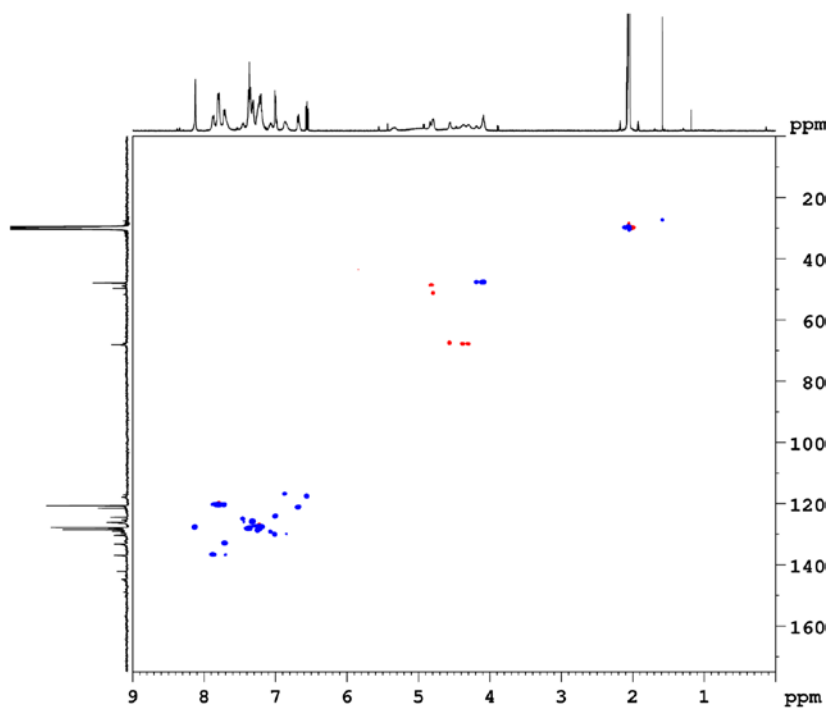


Figure SII.11: 600 MHz ^1H - ^{13}C HSQC spectrum of (9*H*-fluoren-9-yl)methyl-(2-aminophenyl)(4-bromo-2-nitrobenzyl)carbamate.

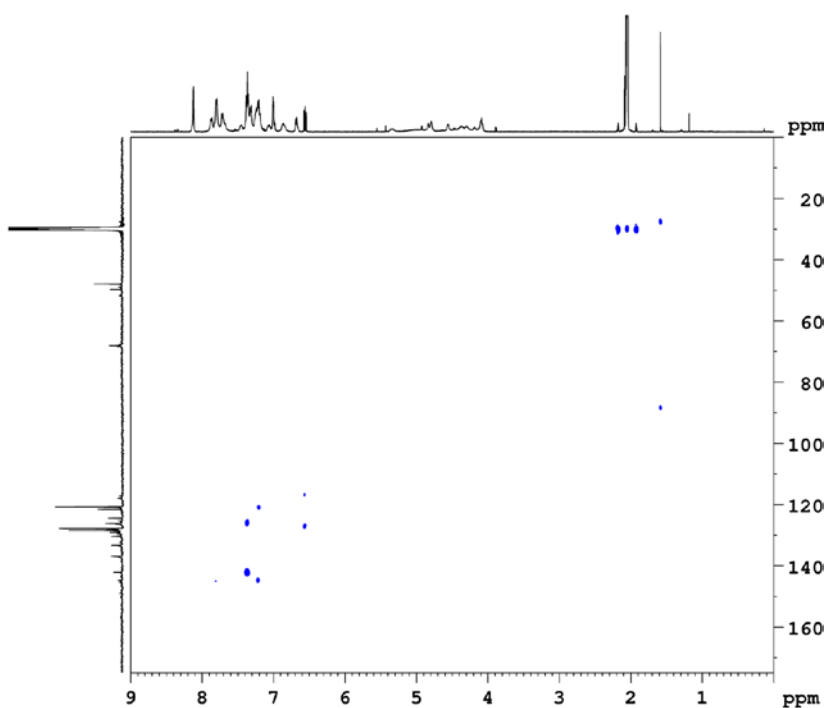
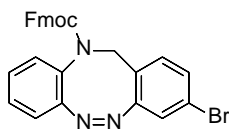


Figure SII.12: 600 MHz HMBC spectrum of (9*H*-fluoren-9-yl)methyl-(2-aminophenyl)(4-bromo-2-nitrobenzyl)carbamate.

II.1.4 Synthesis of (9*H*-fluoren-9-yl)methyl-(*Z*)-3-bromodibenzo[*c,g*][1,2,5]triazocin-11-(12*H*)-carboxylate^[1]



(9*H*-fluoren-9-yl)methyl-(2-aminophenyl)(4-bromo-2-nitrobenzyl)carbamate (4.18 g, 7.68 mmol) was suspended in 250 mL EtOH and SnCl₂ · 2 H₂O (10.4 g, 46.1 mmol) was added. The reaction mixture was heated to 75 °C with an oil bath and zinc-powder (4.02 g, 61.4 mmol) was added. The reaction mixture was stirred at 75 °C for 1 h and cooled to rt. afterwards. It was stirred at rt. for 16 h and neutralized with saturated aqueous NaHCO₃ solution subsequently. The solvent was evaporated and 100 mL water and 100 mL DCM were added to the residue. The organic layer was separated and the aqueous layer was extracted twice with 100 mL DCM. The combined organic layers were dried over MgSO₄ and the solvent was evaporated. The residue was dissolved in 300 mL of acetic acid and *m*CPBA (2.66 g, 15.4 mmol) dissolved in 300 mL acetic acid was added dropwise to the reaction mixture. The reaction mixture was stirred at rt. for 16 h and the solvent was evaporated in the following. 100 mL DCM and 100 mL half-concentrated aqueous NaHCO₃ solution were added to the residue. The organic layer was separated and the aqueous layer was extracted twice with 100 mL DCM. The combined organic layers were dried over MgSO₄ and the solvent was evaporated. After column chromatography on silica (ethyl acetate/cyclohexane = 1:4, *R*_f = 0.43) the product could be obtained as yellow solid (2.27 g, 4.45 mmol, 58%, lit. 56%^[1]).

melting point: 175 °C

¹H-NMR (600 MHz, acetone-*d*₆, 298 K): δ = 7.99-7.77 (s, 2 H, Ar-*H*), 7.50-6.95 (m, 13 H, Ar-*H*), 4.99-3.95 (m, 5 H, aliph.-*H*) ppm.

¹³C{¹H}-NMR (150 MHz, acetone-*d*₆, 298 K): δ = 154.7, 142.1, 132.7, 131.3, 130.5, 129.5, 129.1, 128.5, 127.9, 126.1, 124.2, 122.6, 120.8, 119.7, 68.5, 52.7, 47.8 ppm.

IR (ATR): $\tilde{\nu}$ = 2946 (w), 2320 (w), 2256 (w), 2178 (w), 2038 (w), 1999 (w), 1701 (s), 1591 (m), 1475 (m), 1447 (m), 1389 (s), 1316 (s), 1243 (m), 1132 (m), 1074 (w), 1042 (m), 1023 (m), 1003 (w), 976 (w), 864 (w), 843 (w), 822 (m), 755 (s), 736 (s), 698 (m), 622 (m), 547 (m), 515 (w), 503 (m) cm^{-1} .

HR-MS (ESI, DCM): m/z $[M+H]^+$ calculated for $C_{28}H_{22}O_3N_2^{79}Br+H^+$: 510.0812, found: 510.0817 \pm 0.55 ppm.

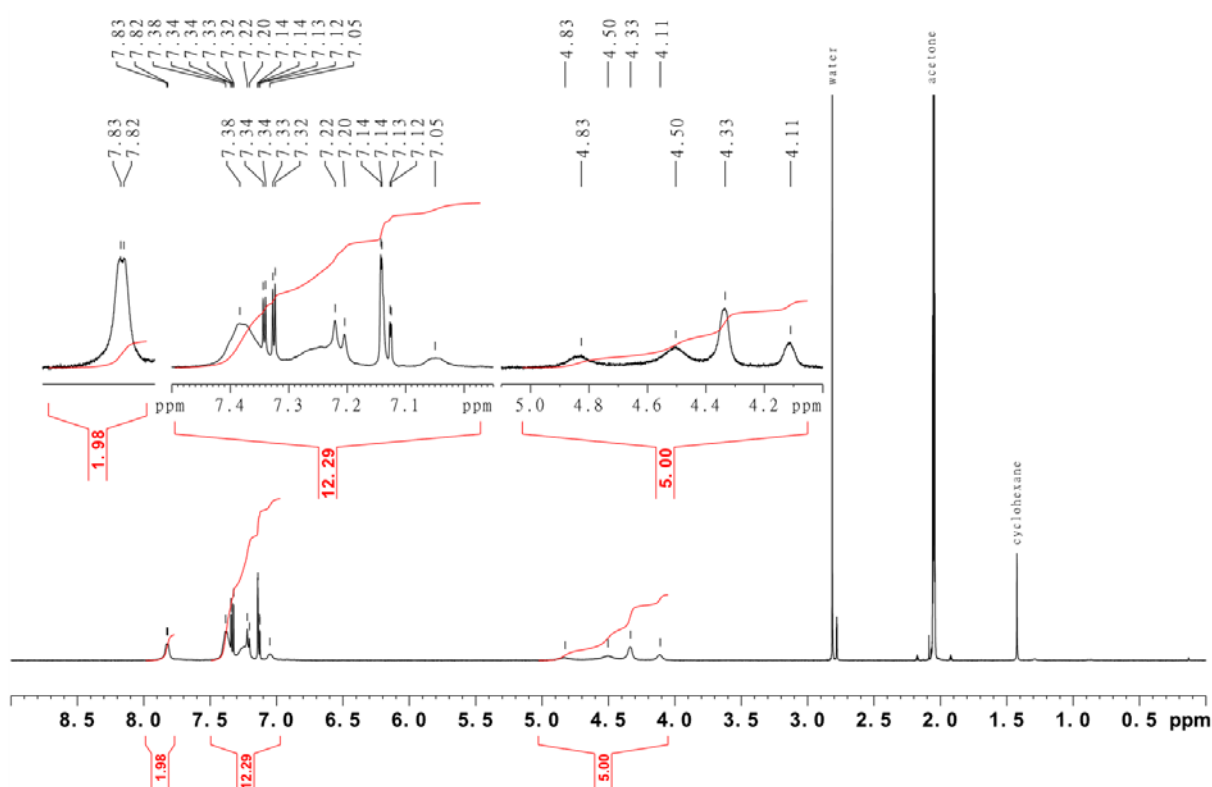


Figure SII.13: 600 MHz ^1H -NMR spectrum of (9H-fluoren-9-yl)methyl-(Z)-3-bromodibenzo[c,g][1,2,5]triazocin-11-(12H)-carboxylate.

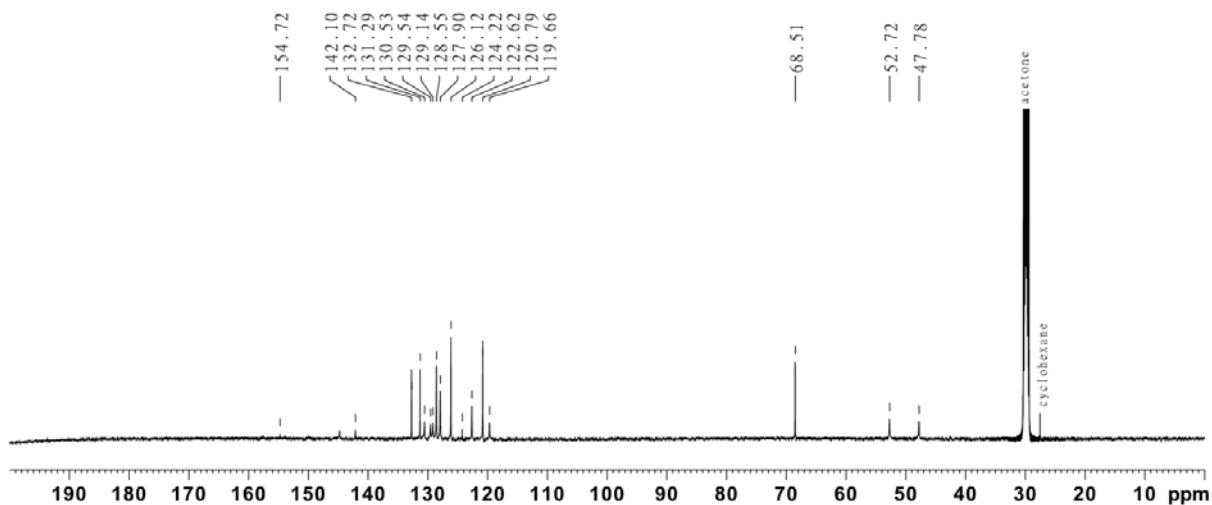


Figure SII.14: 150 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (9H-fluoren-9-yl)methyl-(Z)-3-bromodibenzo[c,g][1,2,5]triazocin-11-(12H)-carboxylate.

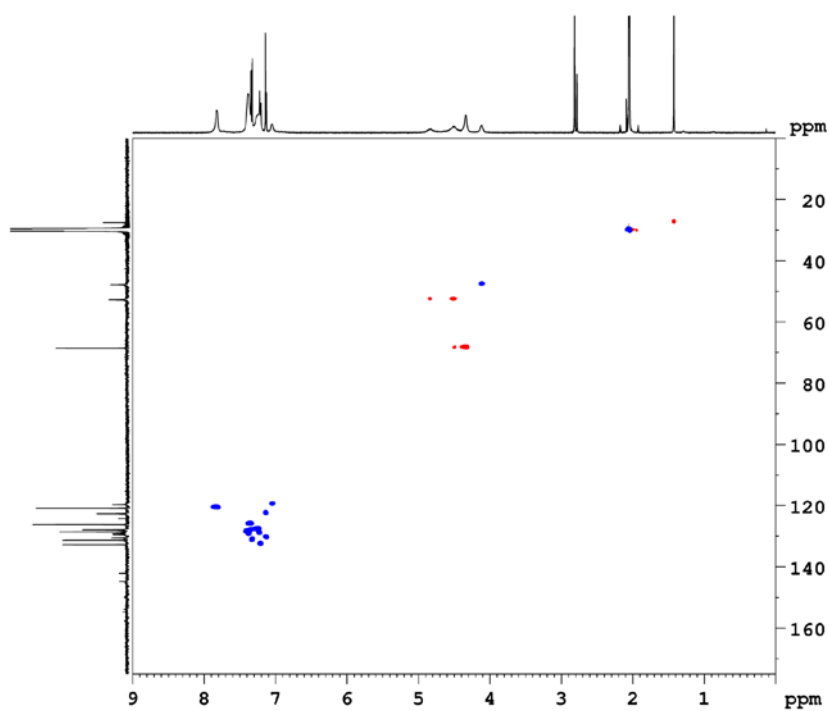


Figure SII.15: 600 MHz ^1H - ^{13}C HSQC spectrum of (9*H*-fluoren-9-yl)methyl-(*Z*)-3-bromodibenzo[*c,g*][1,2,5]triazocin-11-(12*H*)-carboxylate.

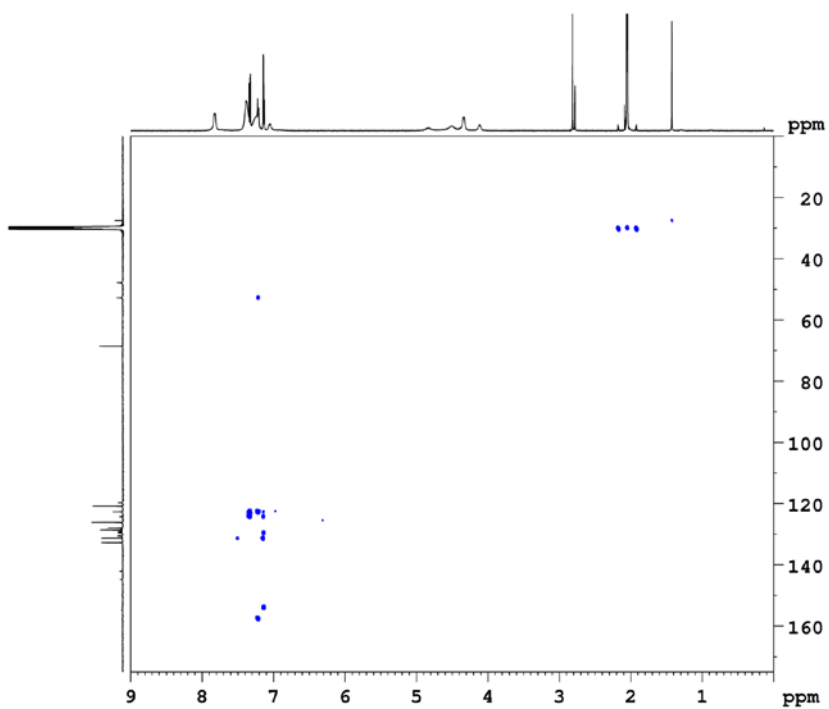
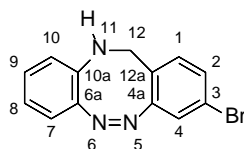


Figure SII.16: 600 MHz HMBC spectrum of (9*H*-fluoren-9-yl)methyl-(*Z*)-3-bromodibenzo[*c,g*][1,2,5]triazocin-11-(12*H*)-carboxylate.

II.1.5 Synthesis of (Z)-bromo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine^[1]



9*H*-fluoren-9-yl)methyl-(*Z*)-3-bromodibenzo[c,g][1,2,5]triazocin-11-(12*H*)-carboxylate (1.63 g, 3.19 mmol) was dissolved in 50 mL of DCM and 50 mL NEt_3 was added. The reaction mixture was stirred at rt. for 16 h. the solvent was evaporated and column chromatography on silica (ethyl acetate/cyclohexane 1:2, R_f = 0.32) gave a red solid (893 mg, 3.17 mmol, quant., lit. 93%^[1]).

melting point: 149 °C

$^1\text{H-NMR}$ (500 MHz, acetone- d_6 , 298 K): δ = 7.42 (dd, 3J = 8.1 Hz, 4J = 2.0 Hz, 1 H, *H*-2), 7.33 (d, 4J = 2.1 Hz, 1 H, *H*-4), 7.31 (d, 3J = 8.1 Hz, 1 H, *H*-1), 6.87 (td, 3J = 7.7 Hz, 4J = 1.6 Hz, 1 H, *H*-9), 6.74 (dd, 3J = 8.0 Hz, 4J = 1.6 Hz, 1 H, *H*-7), 6.64 (td, 3J = 7.4 Hz, 4J = 1.2 Hz, 1 H, *H*-8), 6.56 (dd, 3J = 8.1 Hz, 4J = 1.1 Hz, 1 H, *H*-10), 5.51 (s, 1 H, *NH*-), 4.04 (s, 1 H, -*H*-12), 3.88 (s, 1 H, -*H*-12') ppm.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (125 MHz, acetone- d_6 , 298 K): δ = 160.1 (C-4a), 144.5 (C-6a), 137.0 (C-10a), 132.4 (C-1), 131.8 (C-2), 129.1 (C-9), 124.0 (C-3), 123.5 (C-7), 122.6 (C-4), 121.7 (C-12a), 119.9 (C-10), 118.2 (C-8), 47.0 (C-12) ppm.

IR (ATR): $\tilde{\nu}$ = 3317 (s), 3026 (w), 2959 (w), 2878 (w), 1601 (m), 1587 (m), 1567 (w), 1511 (m), 1481 (s), 1455 (w), 1389 (m), 1363 (w), 1321 (s), 1272 (w), 1251 (s), 1191 (w), 1161 (m), 1139 (w), 1119 (w), 1093 (m), 1072 (m), 1034 (w), 956 (w), 898 (m), 831 (m), 812 (s), 740 (s), 720 (m), 702 (w), 651 (w), 603 (w) cm^{-1} .

HR-MS (ESI, DCM): m/z $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{13}\text{H}_{10}\text{N}_3^{79}\text{Br}+\text{H}^+$: 288.01301; found: 288.0127 \pm 1.44 ppm.

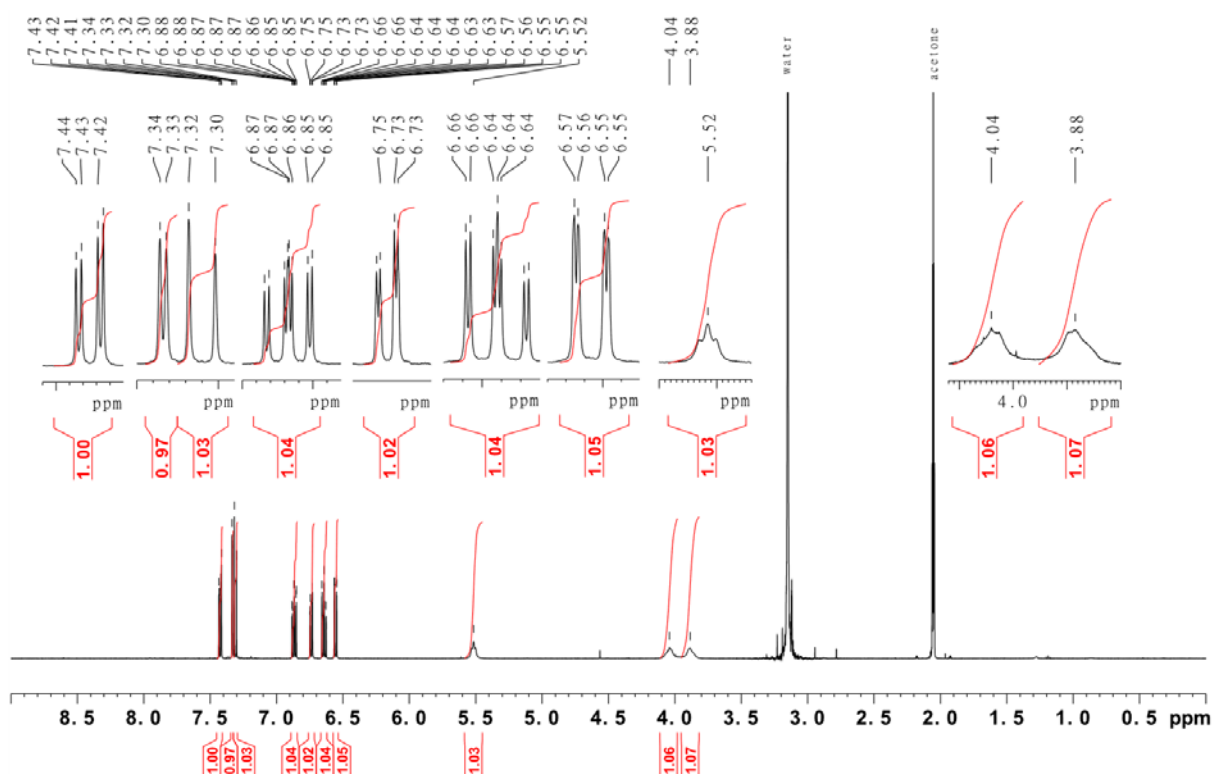


Figure SII.17: 500 MHz ^1H -NMR spectrum of (Z)-bromo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine.

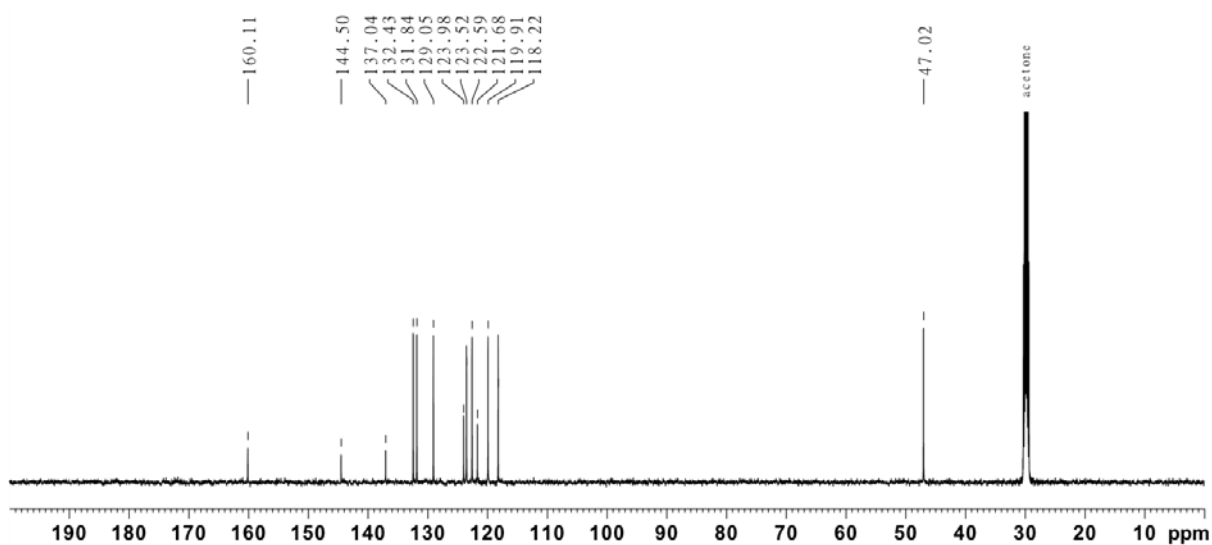


Figure SII.18: 125 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (Z)-bromo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine.

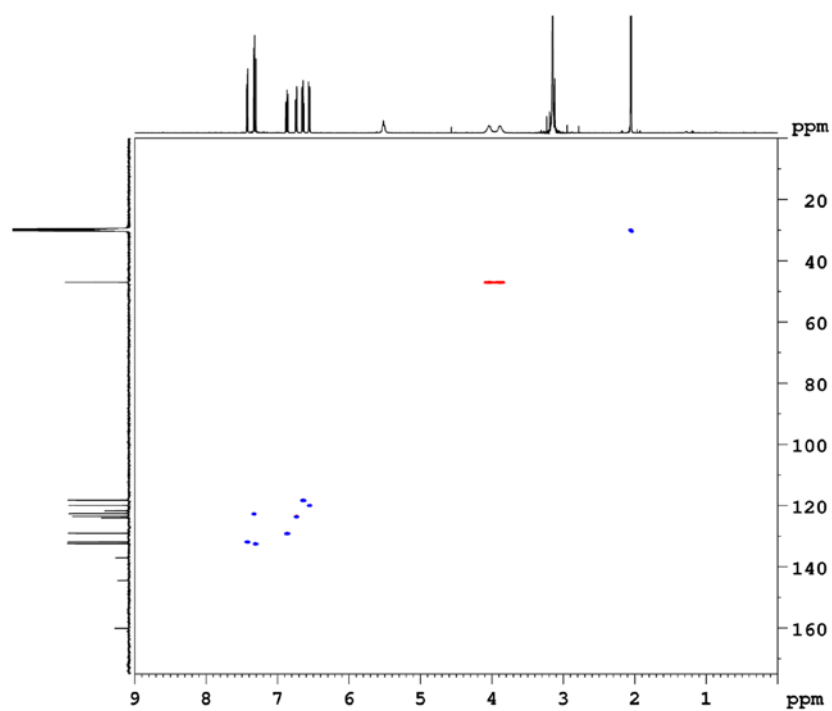


Figure SII.19: 500 MHz ^1H - ^{13}C HSQC spectrum of (Z)-bromo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine.

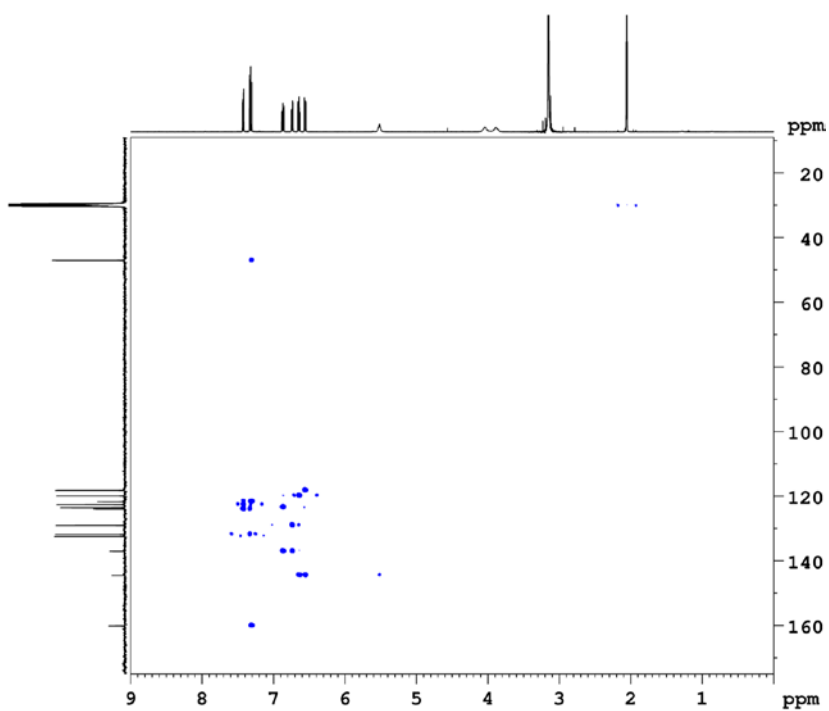
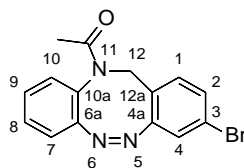


Figure SII.20: 500 MHz HMBC spectrum of (Z)-bromo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine.

II.1.6 Synthesis of (Z)-1-(3-bromodibenzo[c,g][1,2,5]triazocin-11(12*H*)-yl)-ethan-1-one (2)^[1]



(Z)-bromo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine (500 mg, 1.8 mmol) were dissolved in 50 mL anhydrous DMF under a nitrogen atmosphere. NEt_3 (5 mL, 36 mmol) and AcOH (1.03 mL, 18 mmol) were added. The reaction mixture was cooled to 0 °C and T3P (10 mL, 18 mmol, 50% in ethyl acetate) was added dropwise. The reaction mixture was stirred at rt. for 16 h. 100 mL DCM and 100 mL deionized water were added and the organic layer was separated. The aqueous layer was extracted twice with 100 mL DCM and the combined organic layers were dried over MgSO_4 . The solvent was removed and column chromatography on silica (ethyl acetate/cyclohexane 1:1, R_f = 0.39) gave a yellow solid (492 mg, 1.49 mmol, 83%, lit. 86%^[1]).

melting point: 163 °C

$^1\text{H-NMR}$ (600 MHz, acetone- d_6 , 298 K): δ = 7.40 (dd, 3J = 7.4 Hz, 4J = 1.6 Hz, 1 H, *H*-8/9), 7.34-7.27 (m, 3 H, *H*-2, *H*-7/10, *H*-8/9), 7.18 (d, 3J = 8.2 Hz, 1 H, *H*-1), 7.11 (d, 4J = 2.0 Hz, 1 H, *H*-4), 7.06 (dd, 3J = 7.8 Hz, 4J = 0.9 Hz, 1 H, *H*-10), 5.02 (d, 2J = 14.8 Hz, 1 H, *H*-12a), 4.32 (d, 2J = 14.7 Hz, 1 H, *H*-12b), 1.79 (s, 3 H, CH_3) ppm.

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (150 MHz, acetone- d_6 , 198 K): δ = 169.4 (C=O), 157.2 (C-4a), 154.1 (C-6a/10a), 132.8 (C-1), 131.3 (C-2), 130.28 (C-8/9), 130.22 (C-8/9), 129.56 (C-7/10), 129.44 (C-6a/10a), 124.7 (C-12a), 122.7 (C-4), 122.3 (C-3), 120.0 (C-7/10), 51.5 (C-12), 23.0 (CH_3) ppm.

IR (ATR): $\tilde{\nu}$ = 3049 (m), 2928 (m), 1658 (s), 1590 (m), 1518 (w), 1475 (m), 1380 (s), 1338 (s), 1294 (m), 1242 (w), 1161 (m), 1115 (w), 1085 (m), 1031 (m), 1007 (w), 962 (m), 925 (w), 887 (w), 872 (w), 847 (m), 815 (s), 782 (w), 762 (s), 738 (m), 689 (w), 659 (m), 629 (w), 584s (w), 532 (w), 441 (s), 405 (m) cm^{-1} .

HR-MS (ESI, DCM): m/z [$\text{M}+\text{H}$]⁺ calculated for $\text{C}_{15}\text{H}_{12}\text{N}_3\text{O}^{79}\text{Br}+\text{H}^+$: 330.0237; found: 330.0233 \pm 1.18 ppm.

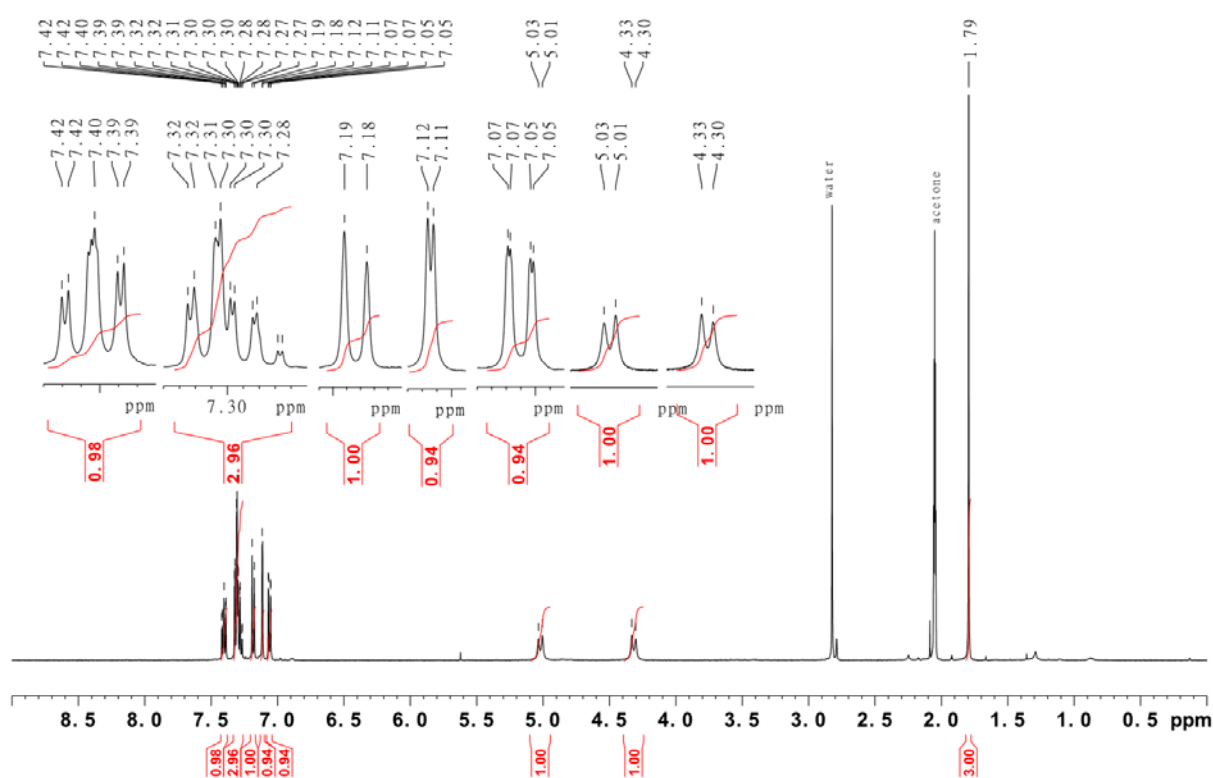


Figure SII.21: 600 MHz ^1H -NMR spectrum of (Z)-1-(3-bromodibenzo[c,g][1,2,5]triazocin-11(12*H*)-yl)-ethan-1-one (**2**).

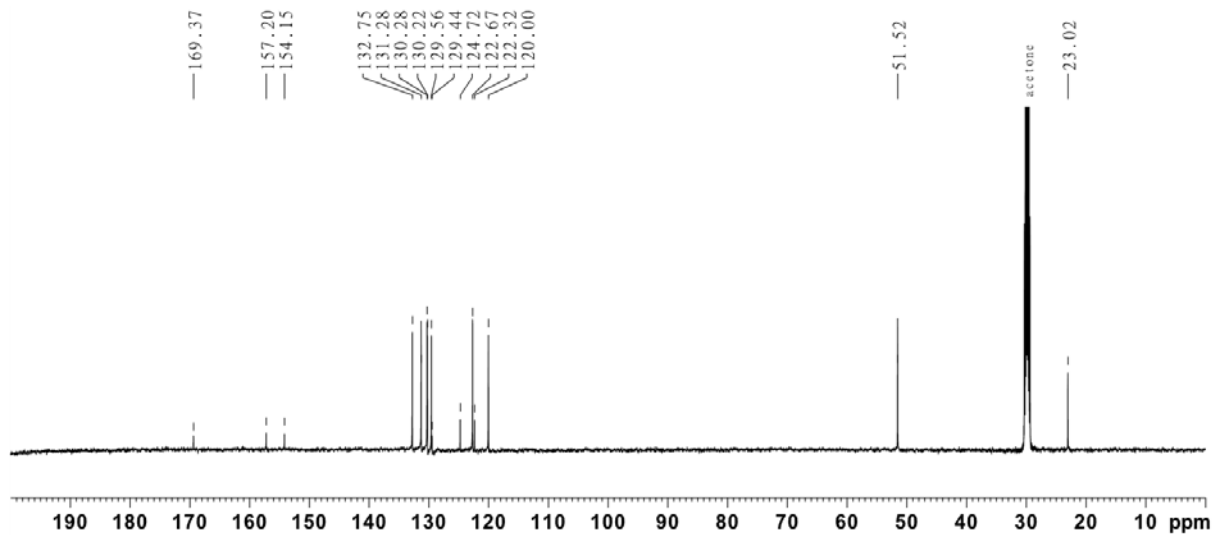


Figure SII.22: 150 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (Z)-1-(3-bromodibenzo[c,g][1,2,5]triazocin-11(12*H*)-yl)-ethan-1-one (**2**).

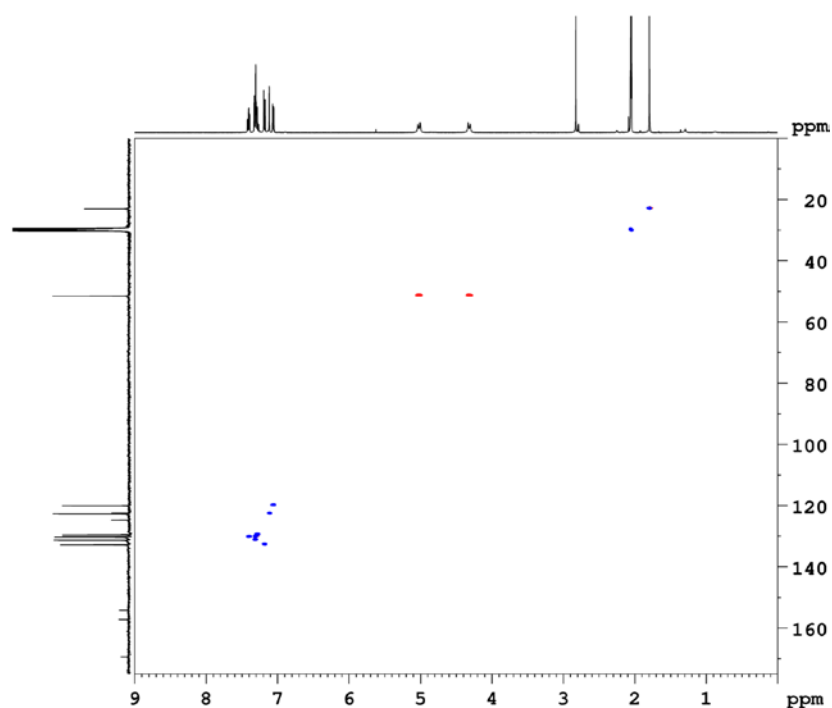


Figure SII.23: 600 MHz ^1H - ^{13}C HSQC spectrum of (*Z*)-1-(3-bromodibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-yl)-ethan-1-one (**2**).

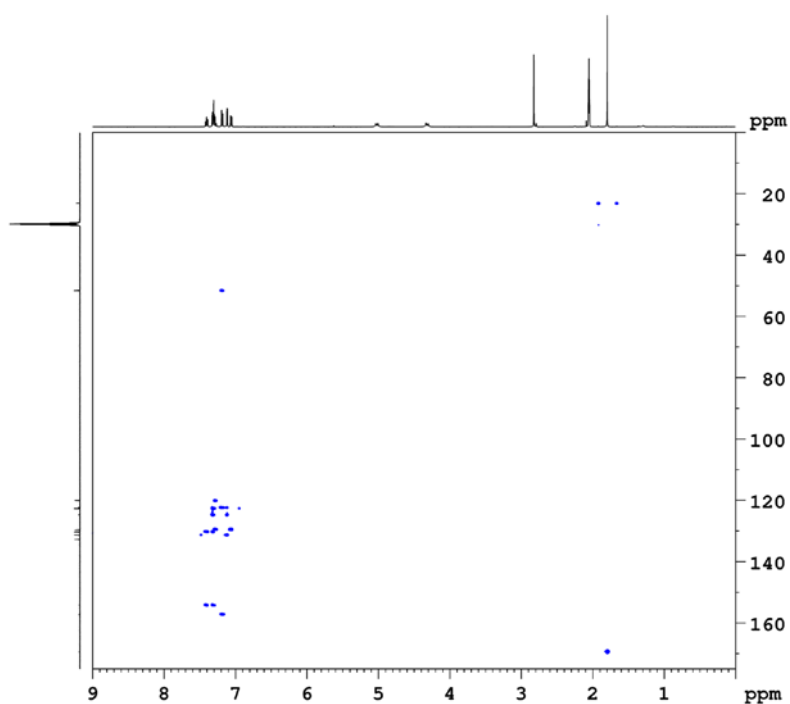
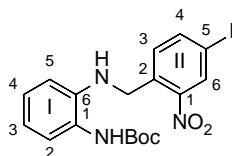


Figure SII.24: 600 MHz HMBC spectrum of (*Z*)-1-(3-bromodibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-yl)-ethan-1-one (**2**).

II.1.7 Synthesis of *tert*-butyl-(2-((4-iodo-2-nitrobenzyl)amino)phenyl)carbamate^[1]



Under a nitrogen atmosphere triethylamine (4.25 mL, 24.9 mmol) and 1-(bromomethyl)-4-iodo-2-nitrobenzene (7.81 g, 22.9 mmol) were added to solution of *tert*-butyl-(2-aminophenyl)carbamate (4.77 g, 22.9 mmol) in 100 mL abs. THF. The reaction mixture was heated to reflux with an oil bath and stirred for 16 h at that temperature. Afterwards the solvent was evaporated and 100 mL of deionized water and 100 mL DCM were added to the residue. The organic layer was separated and the aqueous layer was extracted twice with 50 mL of DCM. The combined organic layers were dried over MgSO₄ and the solvent was evaporated. Recrystallization from cyclohexane/ethyl acetate (1:1) gave the product as yellow solid (7.39 g, 15.7 mmol, 69%, lit. 96%^[1]).

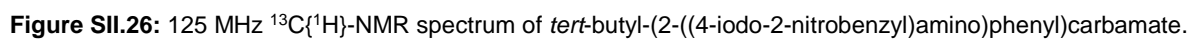
melting point: 109 °C

¹H-NMR (500 MHz, CDCl₃, 298 K): δ = 8.37 (d, ⁴*J* = 1.7 Hz, 1 H, Ar^{II}-*H*-3), 7.85 (dd, ³*J* = 8.3 Hz, ⁴*J* = 1.6 Hz, 1 H, Ar^{II}-*H*-5), 7.38 (d, ³*J* = 8.2 Hz, 1 H, Ar^{II}-*H*-6), 7.24 (d, ³*J* = 7.6 Hz, 1 H, Ar^I-*H*-6), 7.00 (td, ³*J* = 8.0 Hz, ⁴*J* = 1.3 Hz, 1 H, Ar^I-*H*-4), 6.75 (t, ³*J* = 7.6 Hz, 1 H, Ar^I-*H*-5), 6.43 (d, ³*J* = 8.0 Hz, 1 H, Ar^I-*H*-3), 6.18 (br. s, 1 H, NH), 4.68 (s, 2 H, CH₂), 1.51 (s, 9 H, *t*Bu-*H*) ppm.

¹³C{¹H}-NMR (125 MHz, CDCl₃, 298 K): δ = 154.4 (C=O), 148.6 (Ar^{II}-C-2), 142.7 (Ar^{II}-C-5), 141.5 (Ar^I-C-2), 135.3 (Ar^{II}-C-1), 133.8 (Ar^{II}-C-3), 131.5 (Ar^{II}-C-6), 127.1 (Ar^I-C-4), 126.0 (Ar^I-C-6), 124.3 (Ar^I-C-1), 118.9 (Ar^I-C-5), 112.9 (Ar^I-C-3), 91.6 (Ar^{II}-C-4), 81.0 (-C(CH₃)₃), 45.4 (-CH₂), 28.5 (-CH₃), ppm.

IR (ATR): $\tilde{\nu}$ = 3374 (m), 2974 (m), 2931 (w), 2169 (w), 2051 (w), 1978 (w), 1684 (m), 1605 (m), 1509 (s), 1446 (m), 1391 (w), 1366 (w), 1342 (m), 1307 (w), 1272 (w), 1244 (m), 1152 (s), 1047 (m), 1024 (m), 934 (w), 869 (w), 823 (w), 743 (s), 715 (w), 637 (w) cm⁻¹.

HR-MS (ESI, DCM): *m/z* [M+H]⁺ calculated for C₁₈H₂₀O₄N₃¹²⁷I+H⁺: 470.0571; found: 470.0572 ± 0.08 ppm.



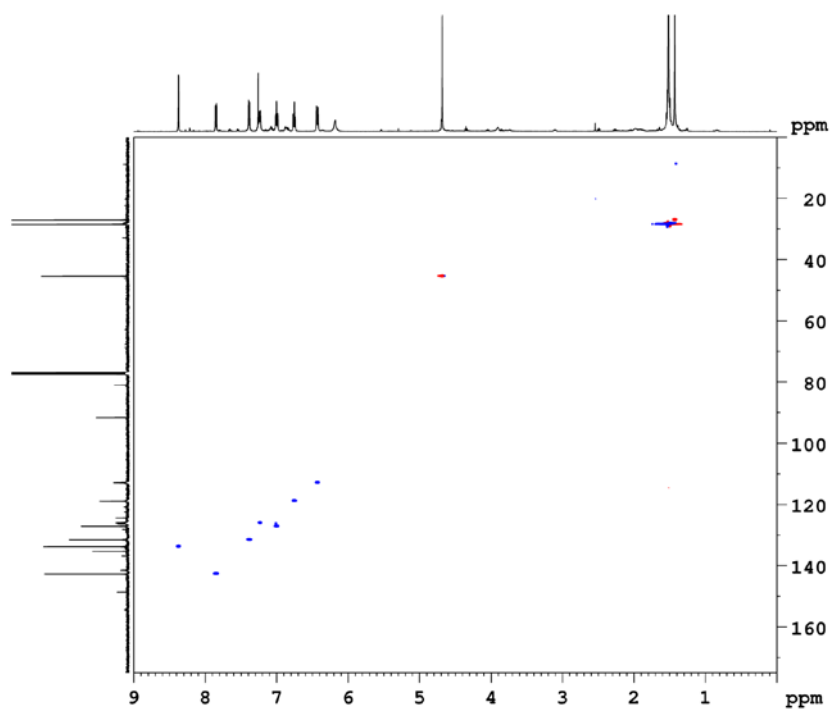


Figure SII.27: 500 MHz ^1H - ^{13}C HSQC spectrum of *tert*-butyl-(2-((4-iodo-2-nitrobenzyl)amino)phenyl)carbamate.

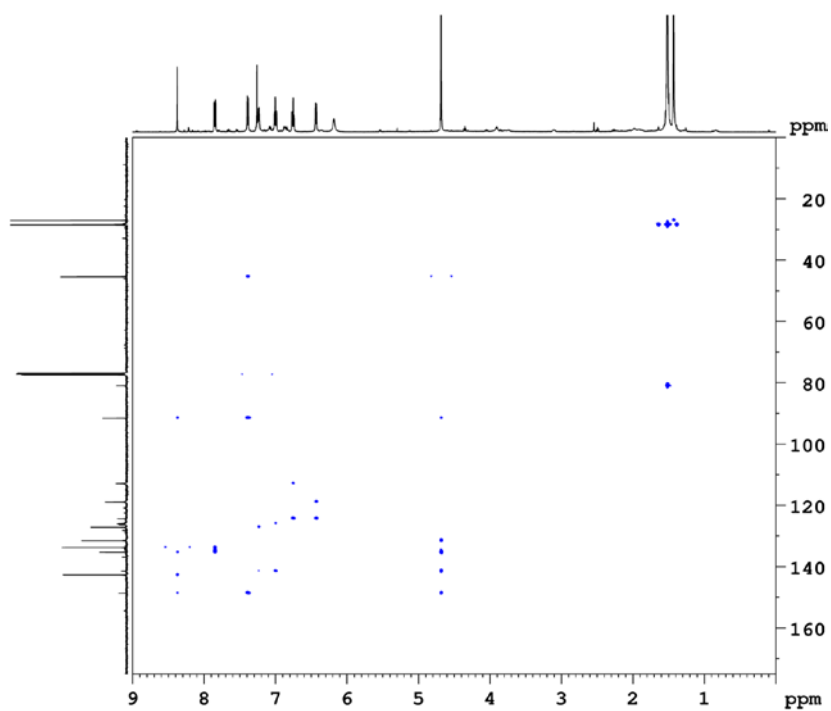
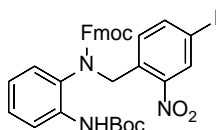


Figure SII.28: 500 MHz HMBC spectrum of *tert*-butyl-(2-((4-iodo-2-nitrobenzyl)amino)phenyl)carbamate.

II.1.8 Synthesis of (9H-fluoren-9-yl)methyl-(4-iodo-2-nitrobenzyl)(2-((tert-butoxycarbonyl)amino)phenyl)carbamate^[1]



DIPEA (2.67 mL, 15.7 mmol) and 9-Fluorenylmethoxycarbonyl chlorid (8.12 g, 31.4 mmol) were added to a solution of *tert*-butyl-(2-((4-iodo-2-nitrobenzyl)amino)phenyl)carbamate (7.39 g, 15.7 mmol) in 50 mL abs. DMF under a nitrogen atmosphere. The reaction mixture was stirred for 48 h at rt. and the solvent was evaporated subsequently. 100 mL of deionized water and 100 mL of DCM were added to the residue. The organic layer was separated and the aqueous layer was extracted twice with 100 mL DCM. The combined organic layers were dried over MgSO₄ and the solvent was evaporated. Column chromatography on silica (ethyl acetate/cyclohexane 1:4, *R_f* = 0.48) gave a slightly yellow solid (6.66 g, 9.63 mmol, 62%, lit. 33%^[1]).

melting point: 99 °C

¹H-NMR (600 MHz, acetone-*d*₆, 298 K): δ = 8.29 (d, ⁴*J* = 1.8 Hz, 1 H, Ar-*H*), 8.08-7.70 (m, 5 H), 7.40-7.02 (m, 10 H), 5.18-4.93 (m, 2 H), 4.53-4.01 (m, 3 H), 1.45 (s, 9 H, *t*Bu-*H*) ppm.

¹³C{¹H}-NMR (150 MHz, acetone-*d*₆, 298 K): δ = 153.5, 143.0, 133.9, 129.2, 128.5, 127.9, 126.1, 124.4, 120.7, 92.7, 80.4, 68.4, 47.8, 28.5 ppm.

IR (ATR): $\tilde{\nu}$ = 3314 (w), 3066 (w), 2051 (w), 2024 (w), 2012 (w), 1709 (s), 1595 (m), 1525 (s), 1477 (w), 1449 (s), 1401 (m), 1345 (m), 1296 (m), 1216 (m), 1155 (m), 1043 (m), 981 (w), 940 (w), 870 (m), 838 (w), 757 (w), 749 (w), 738 (s), 620 (m), 573 (w), 538 (m), 494 (w) cm⁻¹.

HR-MS (ESI, DCM): *m/z* [M+H]⁺ calculated for C₃₀H₃₀O₆N₃¹²⁷I+H⁺: 692.1252; found: 692.1259 ± 1.00 ppm.

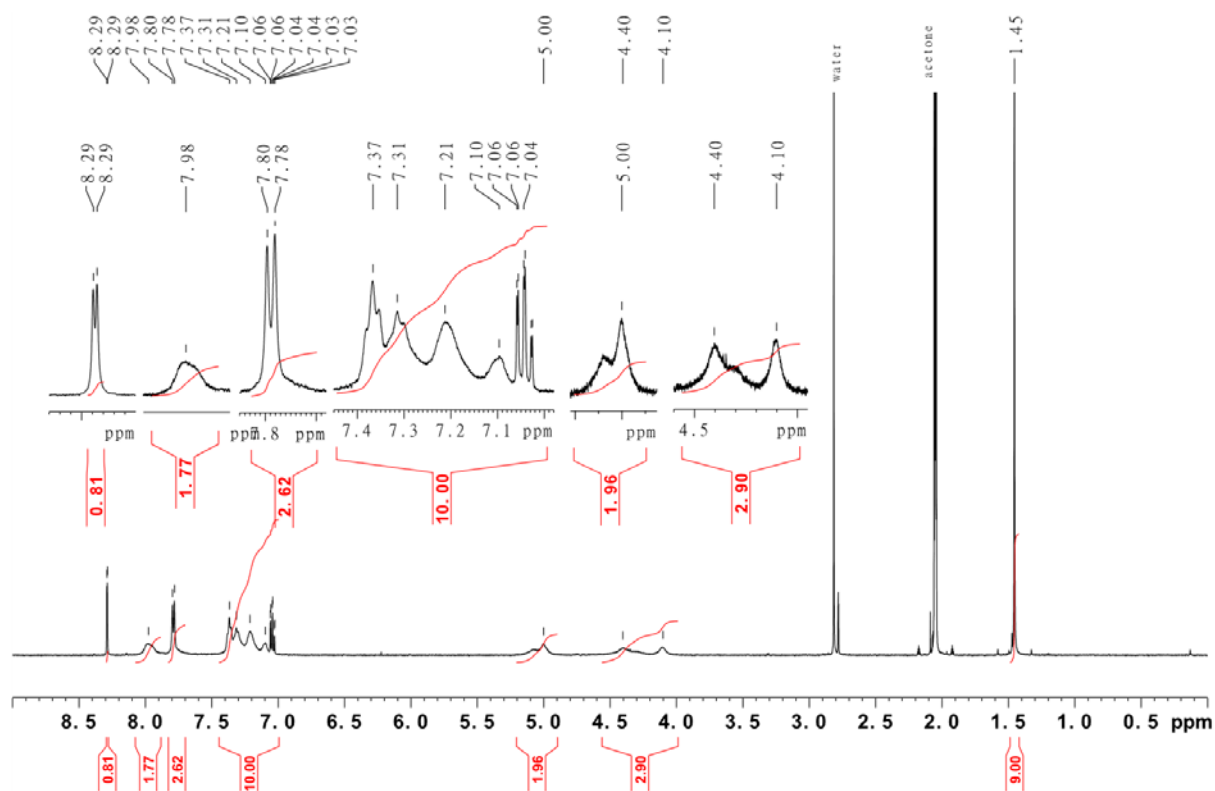


Figure SII.29: 600 MHz ^1H -NMR spectrum of (9*H*-fluoren-9-yl)methyl-(4-iodo-2-nitrobenzyl)(2-((*tert*-butoxycarbonyl)amino)phenyl)carbamate.

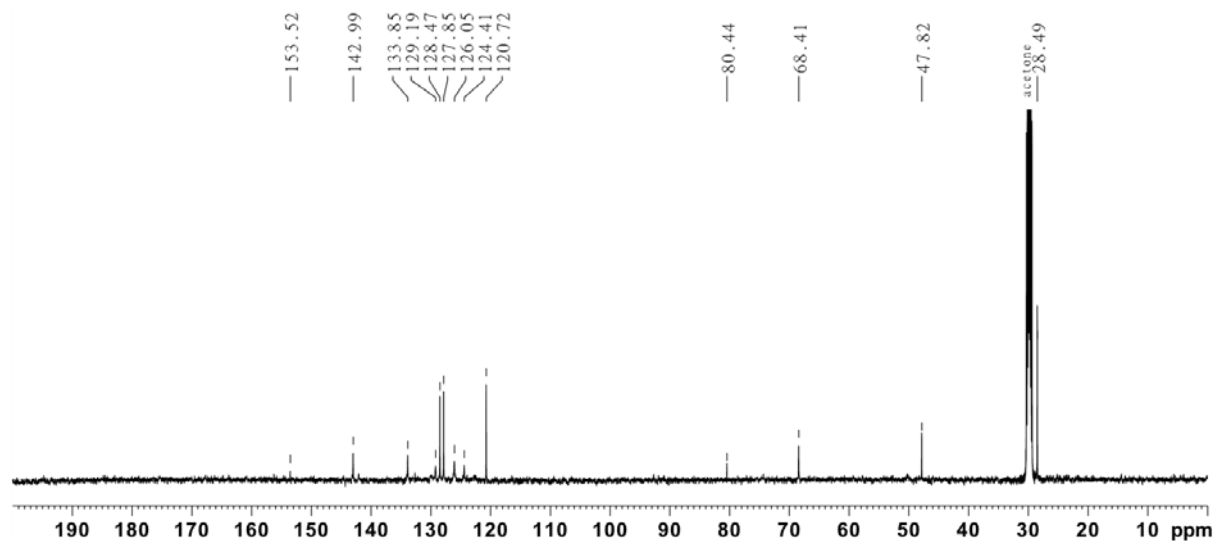


Figure SII.30: 150 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (9*H*-fluoren-9-yl)methyl-(4-iodo-2-nitrobenzyl)(2-((*tert*-butoxycarbonyl)amino)phenyl)carbamate.

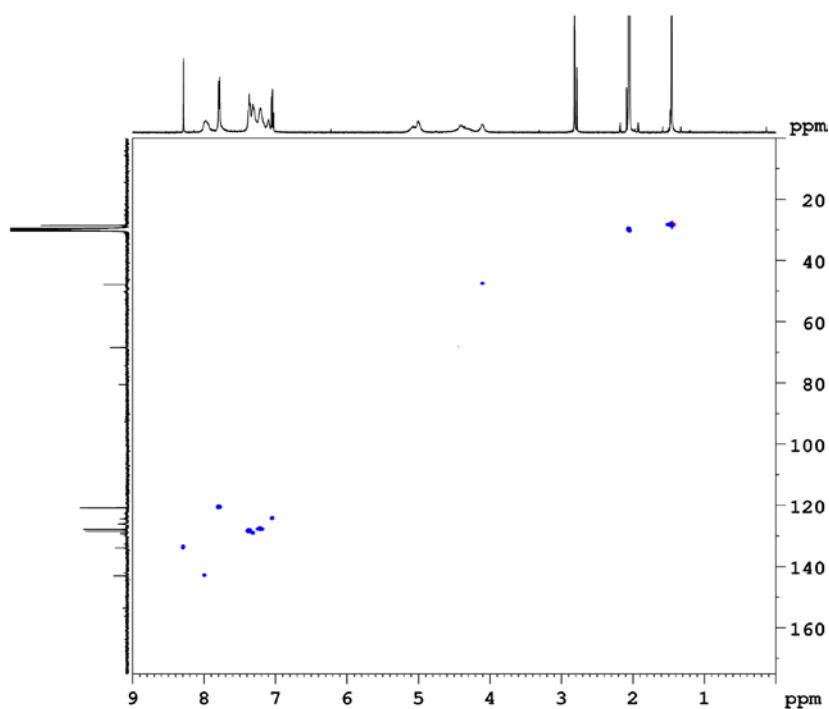


Figure SII.31: 600 MHz ^1H - ^{13}C HSQC spectrum of (9*H*-fluoren-9-yl)methyl-(4-iodo-2-nitrobenzyl)(2-((*tert*-butoxycarbonyl)amino)phenyl)carbamate.

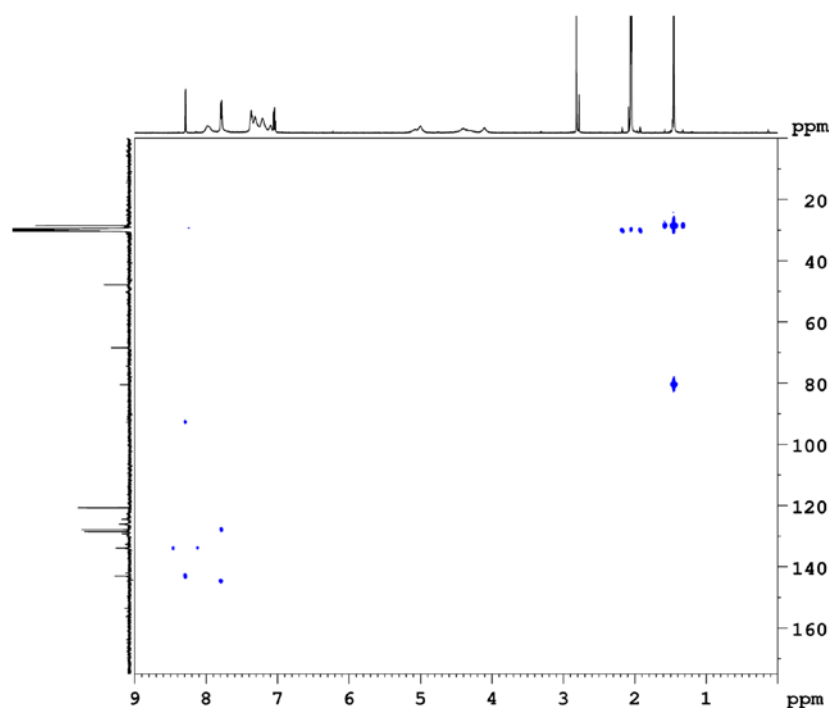
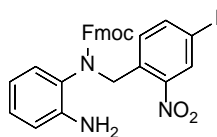


Figure SII.32: 600 MHz HMBC spectrum of (9*H*-fluoren-9-yl)methyl-(4-iodo-2-nitrobenzyl)(2-((*tert*-butoxycarbonyl)amino)phenyl)carbamate.

II.1.9 Synthesis of (9*H*-fluoren-9-yl)methyl-(2-aminophenyl)(4-iodo-2-nitrobenzyl)carbamate^[1]



(9*H*-fluoren-9-yl)methyl-(4-iodo-2-nitrobenzyl)(2-((*tert*-butoxycarbonyl)amino)phenyl)carbamate (6.66 g, 9.63 mol) was dissolved in 100 mL DCM and 30 mL TFA was added. The reaction mixture was stirred at rt. for 16 h and neutralized with saturated aqueous NaHCO₃ subsequently. The organic layer was separated and the aqueous layer was extracted twice with 100 mL. The combined organic layers were dried over MgSO₄ and the solvent was evaporated to obtain a pale yellow solid (5.74 g, 9.60 mmol, quant., lit. 96%^[1]) which was used without further purification.

melting point: 86 °C

¹H-NMR (500 MHz, CDCl₃, 298 K): δ = 8.24 (d, ⁴*J* = 1.5 Hz, 1 H), 7.87 (br. s, 1 H), 7.72-7.62 (m, 2 H), 7.38-7.32 (m, 3 H), 7.22-7.10 (m, 5 H), 6.78-6.72 (m, 2 H), 6.69-6.65 (m, 1 H), 5.21 (br. s, 1 H, -CH₂), 5.04-3.98 (m, 4 H) ppm.

¹³C{¹H}-NMR (125 MHz, CDCl₃, 298 K): δ = 155.2, 143.6, 142.3, 141.4, 133.5, 132.4, 129.2, 128.8, 127.8, 127.1, 125.3, 120.0, 119.0, 92.16, 68.0, 47.2 ppm.

IR (ATR): $\tilde{\nu}$ = 3370 (w), 3039 (w), 2252 (w), 2168 (w), 1978 (w), 1695 (s), 1620 (m), 1525 (s), 1503 (w), 1477 (w), 1449 (m), 1402 (w), 1339 (m), 1297 (m), 1156 (w), 1136 (w), 1043 (w), 987 (w), 870 (m), 795 (w), 756 (w), 738 (s), 692 (w), 620 (m), 534 (w), 501 (w), 480 (w) cm⁻¹.

HR-MS (ESI, DCM): *m/z* [M+H]⁺ calculated for C₂₈H₂₂O₄N₃¹²⁷I+H⁺: 592,0729; found: 592.0732 ± 0.78 ppm.

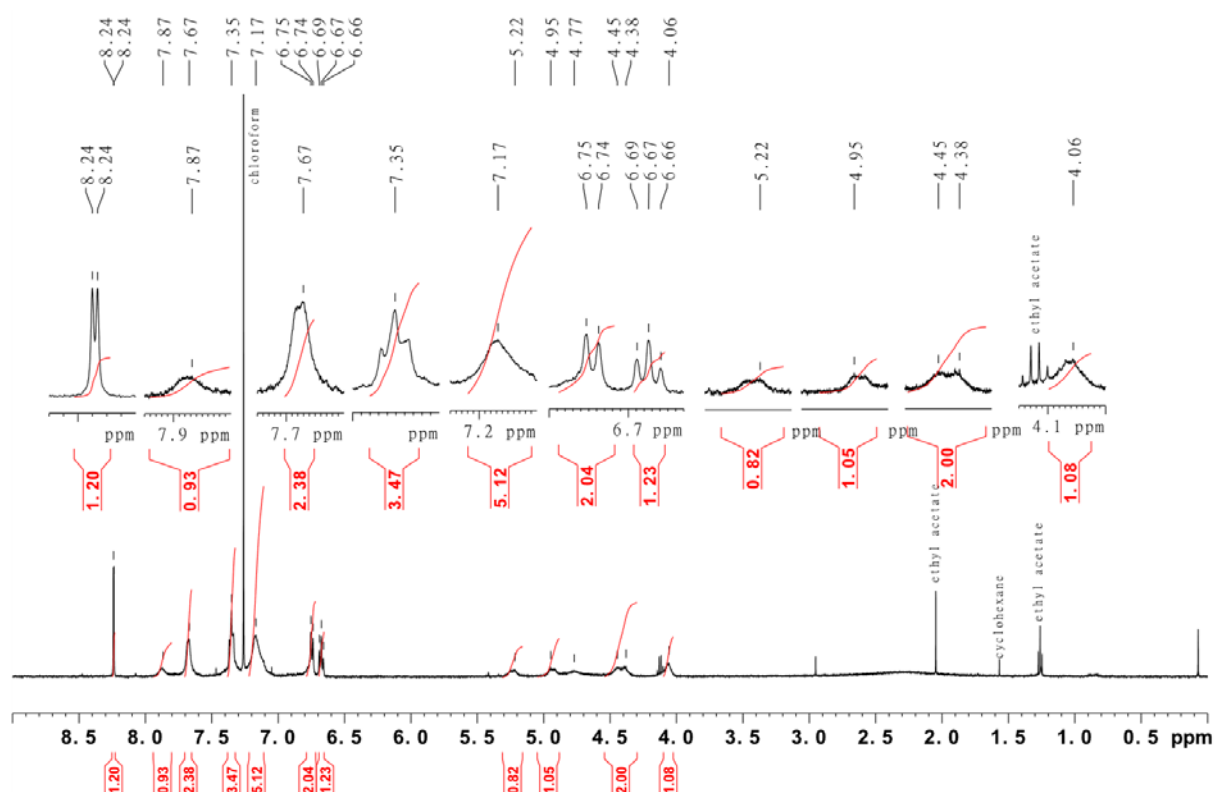


Figure SII.33: 500 MHz ^1H -NMR spectrum of (9*H*-fluoren-9-yl)methyl-(2-aminophenyl)(4-iodo-2-nitrobenzyl)carbamate.

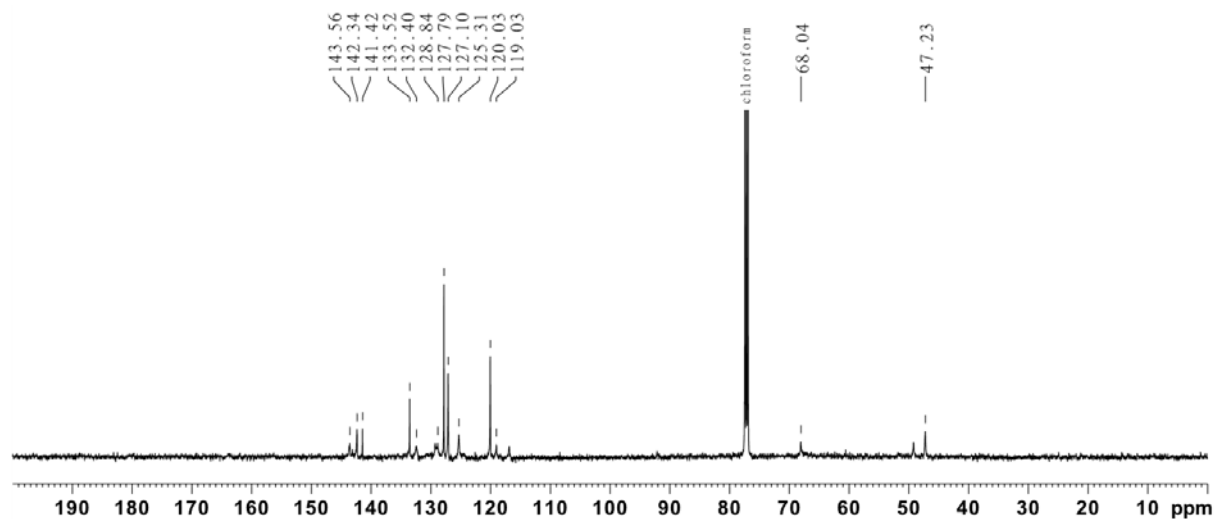


Figure SII.34: 125 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (9*H*-fluoren-9-yl)methyl-(2-aminophenyl)(4-iodo-2-nitrobenzyl)carbamate.

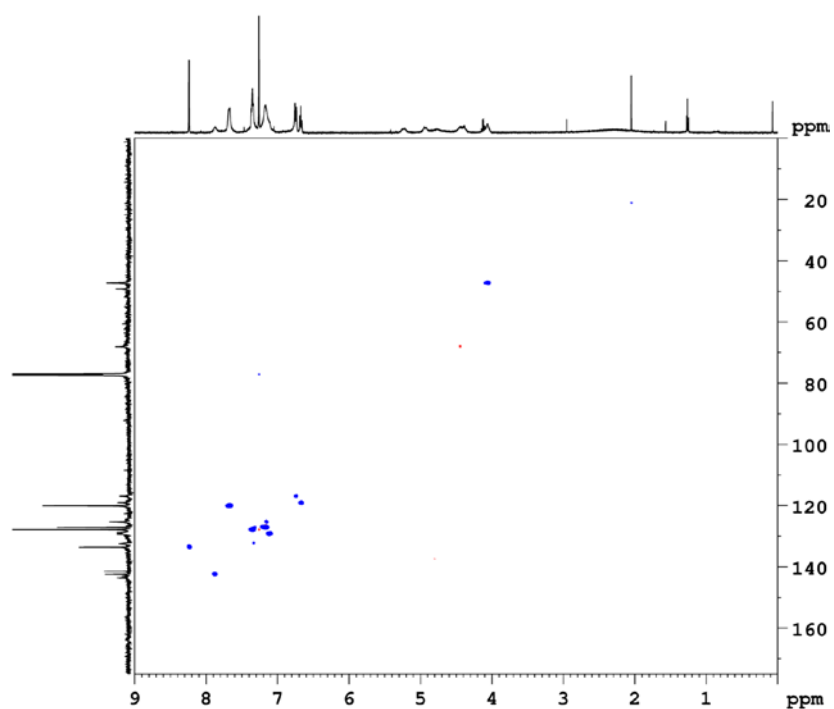


Figure SII.35: 500 MHz ^1H - ^{13}C HSQC spectrum of (9*H*-fluoren-9-yl)methyl-(2-aminophenyl)(4-iodo-2-nitrobenzyl)carbamate.

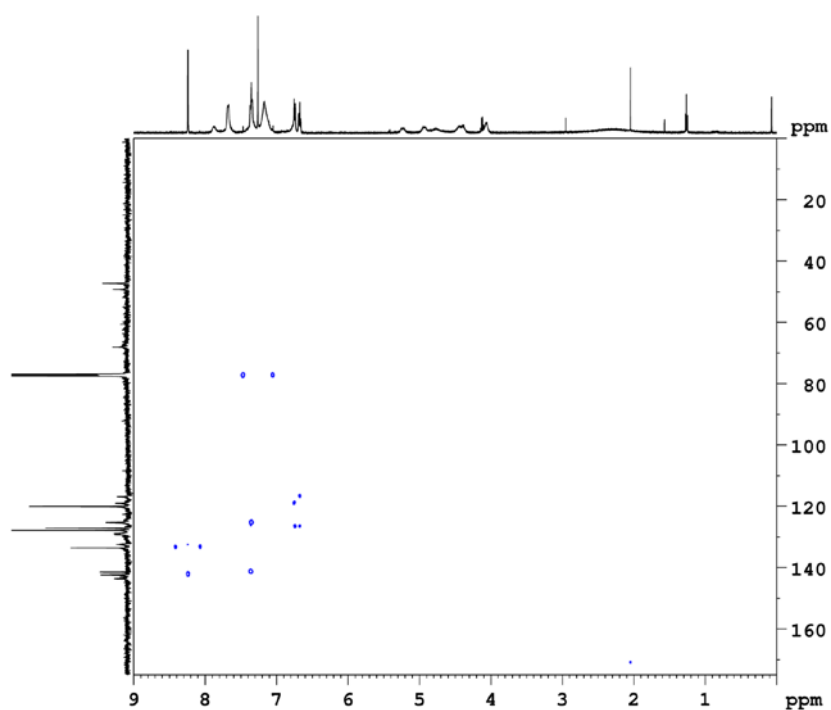
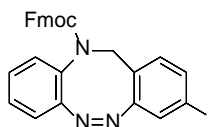


Figure SII.36: 500 MHz HMBC spectrum of (9*H*-fluoren-9-yl)methyl-(2-aminophenyl)(4-iodo-2-nitrobenzyl)carbamate.

II.1.10 Synthesis of (9*H*-fluoren-9-yl)methyl-(*Z*)-3-iododibenzo[*c,g*][1,2,5]triazocin-11-(12*H*)-carboxylate^[1]



(9*H*-fluoren-9-yl)methyl-(2-aminophenyl)(4-iodo-2-nitrobenzyl)carbamate (5.74 g, 9.71 mmol) was suspended in 250 mL EtOH and SnCl₂ · 2 H₂O (13.2 g, 46.1 mmol) was added. The reaction mixture was heated to 75 °C with an oil bath and zinc-powder (5.08 g, 77.7 mmol) was added. The reaction mixture was stirred at that temperature for 1 h and then cooled to rt. It was stirred at rt. for 16 h and neutralized with saturated aqueous NaHCO₃ solution subsequently. The solvent was evaporated and 100 mL water and 100 mL DCM were added to the residue. The organic layer was separated and the aqueous layer was extracted twice with 100 mL DCM. The combined organic layers were dried over MgSO₄ and the solvent was evaporated. The residue was dissolved in 300 mL of acetic acid and *m*CPBA (3.35 g, 19.42 mmol) dissolved in 300 mL acetic acid was added dropwise to the reaction mixture. The reaction mixture was stirred at rt. for 16 h and the solvent was evaporated in the following. 100 mL DCM and 100 mL half-concentrated aqueous NaHCO₃ solution were added to the residue. The organic layer was separated and the aqueous layer was extracted twice with 100 mL DCM. The combined organic layers were dried over MgSO₄ and the solvent was evaporated. After column chromatography on silica (ethyl acetate/cyclohexane = 1:4, *R_f* = 0.38) the product could be obtained as yellow solid (2.59 g, 4.66 mmol, 48%, lit. 56%^[1]).

melting point: 167 °C

¹H-NMR (500 MHz, CDCl₃, 298 K): δ = 7.97-6.98 (m, 15 H, Ar-*H*), 4.99-3.99 (m, 5 H, aliph. H), ppm.

¹³C{¹H}-NMR (125 MHz, CDCl₃, 298 K): δ = 154.4, 152.6, 144.7, 142.1, 137.4, 132.6, 130.5, 129.5, 129.1, 128.54, 128.36, 127.9, 126.1, 124.8, 120.8, 119.7, 93.4, 68.5, 52.8, 47.8 ppm.

IR (ATR): $\tilde{\nu}$ = 3071 (w), 2945 (w), 2255 (w), 2037 (w), 1700 (s), 1585 (m), 1485 (m), 1448 (s), 1315 (s), 1130 (s), 1072 (m), 1041 (m), 1021 (m), 976 (w), 878 (w), 863 (m), 820 (m), 753 (s), 735 (s), 696 (m), 670 (w), 640 (w), 546 (s), 512 (m), 487 (w), 464 (w), 434 (m) cm⁻¹.

HR-MS (ESI, DCM): *m/z* [M+H]⁺ calculated for C₂₈H₂₀O₂N₃¹²⁷I+H⁺: 558.0673; found: 558.0667 ± 1.09 ppm.

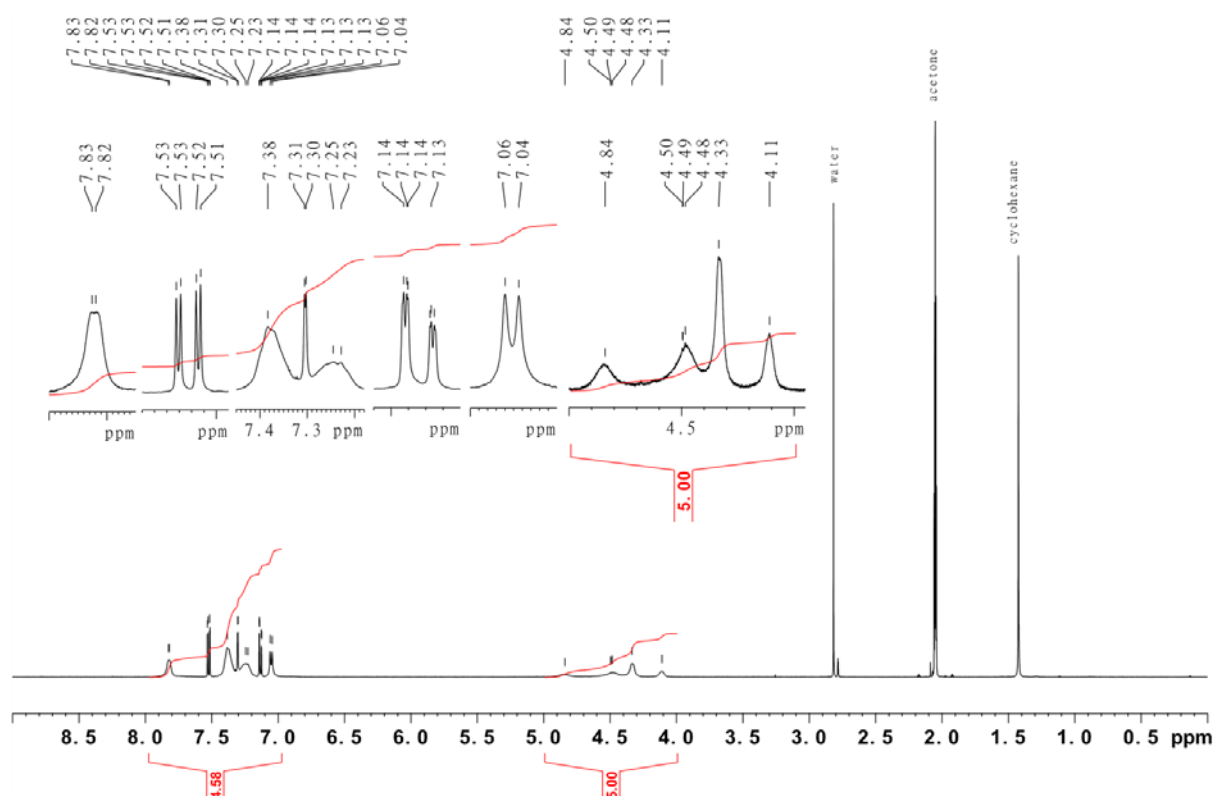


Figure SII.37: 500 MHz ^1H -NMR spectrum of (9*H*-fluoren-9-yl)methyl-(*Z*)-3-iododibenzo[*c,g*][1,2,5]triazocin-11-(12*H*)-carboxylate.

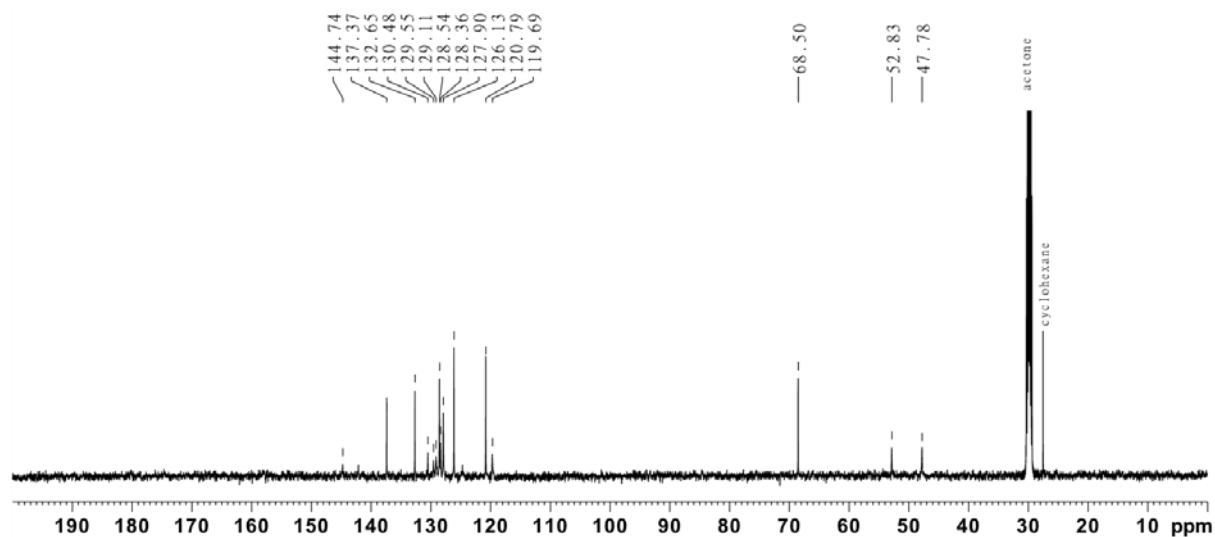


Figure SII.38: 125 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (9*H*-fluoren-9-yl)methyl-(*Z*)-3-iododibenzo[*c,g*][1,2,5]triazocin-11-(12*H*)-carboxylate.

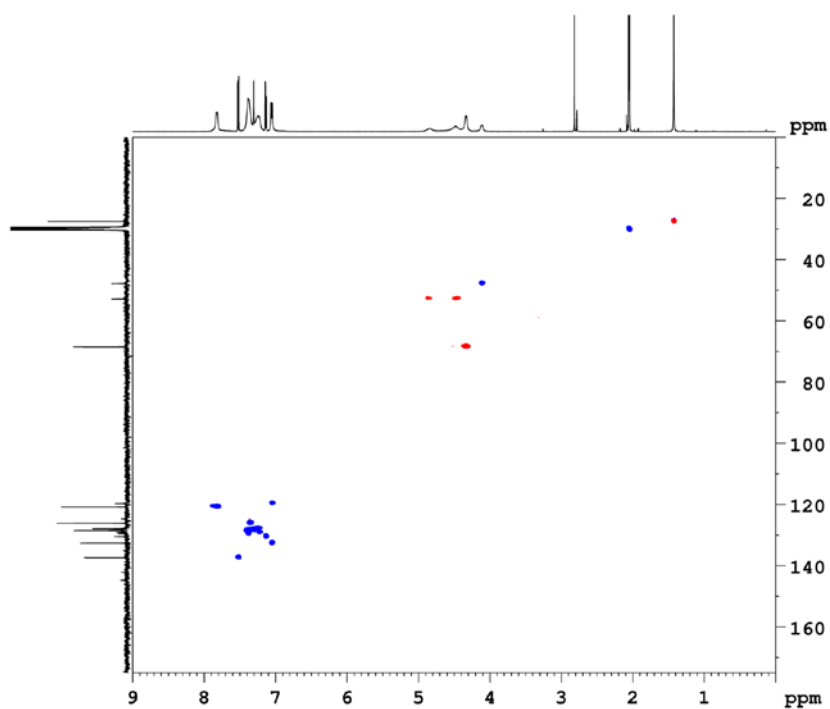


Figure SII.39: 500 MHz ^1H - ^{13}C HSQC spectrum of (9*H*-fluoren-9-yl)methyl-(*Z*)-3-iododibenzo[*c,g*][1,2,5]triazocin-11-(12*H*)-carboxylate.

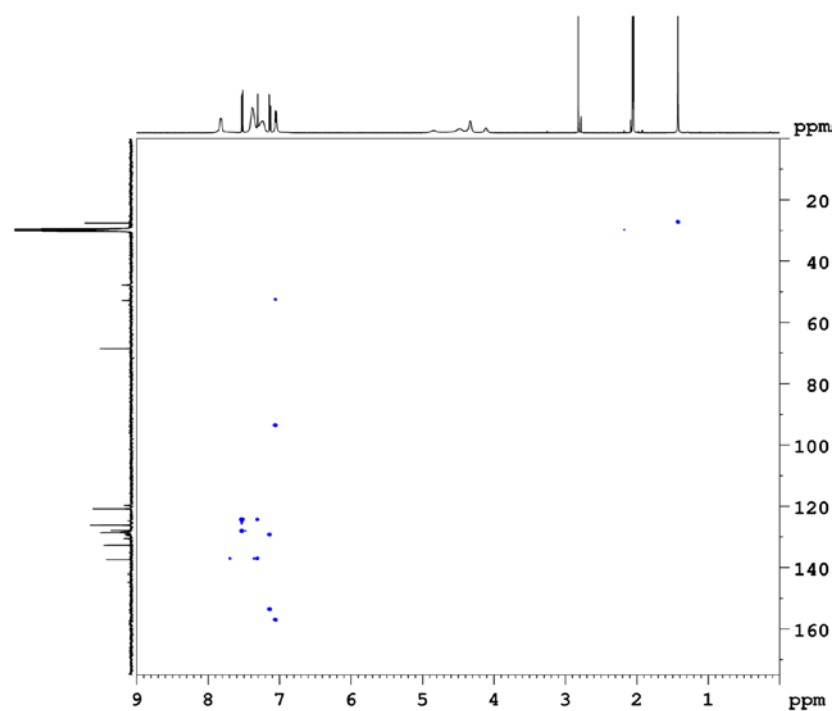
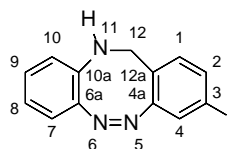


Figure SII.40: 500 MHz HMBC spectrum of (9*H*-fluoren-9-yl)methyl-(*Z*)-3-iododibenzo[*c,g*][1,2,5]triazocin-11-(12*H*)-carboxylate.

II.1.11 Synthesis of (Z)-3-iodo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine^[1]



(9*H*-fluoren-9-yl)methyl-(*Z*)-3-iododibenzo[*c,g*][1,2,5]triazocin-11-(12*H*)-carboxylate (2.09 g, 3.75 mmol) was dissolved in 50 mL of DCM and 50 mL NEt_3 was added. The reaction mixture was stirred at rt. for 16 h. the solvent was evaporated and column chromatography on silica (ethyl acetate/cyclohexane 1:3, R_f = 0.25) gave a red solid (1.25 g, 3.72 mmol, quant., lit. 84%^[1]).

melting point: 151 °C

$^1\text{H-NMR}$ (500 MHz, acetone- d_6 , 298 K): δ = 7.63 (dd, 3J = 8.0 Hz, 4J = 1.8 Hz, 1 H, *H*-2), 7.52 (d, 4J = 1.6 Hz, 1 H, *H*-4), 7.16 (d, 3J = 7.8 Hz, 1 H, *H*-1), 6.88 (td, 3J = 8.3 Hz, 4J = 1.6 Hz, 1 H, *H*-9), 6.75 (dd, 3J = 8.0 Hz, 4J = 1.6 Hz, 1 H, *H*-7), 6.65 (td, 3J = 7.9 Hz, 4J = 1.2 Hz, 1 H, *H*-8), 6.56 (dd, 3J = 8.2 Hz, 4J = 1.0 Hz, 1 H, *H*-10), 5.42 (mc, 1 H, -NH), 3.97 (mc, 2 H, -CH₂) ppm.

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (125 MHz, acetone- d_6 , 298 K): δ = 160.3 (C-4a), 144.6 (C-6a), 137.9 (C-2), 137.1 (C-10a), 131.8 (C-1), 129.0 (C-9), 128.5 (C-4), 124.5 (C-12a), 123.6 (C-7), 119.9 (C-10), 118.3 (C-8), 93.1 (C-3), 47.2 (CH₂) ppm.

IR (ATR): $\tilde{\nu}$ = 3381 (m), 3042 (w), 2255 (w), 2169 (w), 1597 (m), 1582 (m), 1514 (w), 1479 (s), 1385 (w), 1315 (m), 1246 (w), 1161 (m), 1145 (w), 1117 (w), 1066 (m), 970 (w), 938 (w), 912 (m), 875 (w), 835 (m), 810 (m), 749 (s), 721 (w), 703 (w), 650 (w), 601 (m), 543 (w), 501 (w), 466 (m), 454 (w) cm^{-1} .

HR-MS (ESI, DCM): m/z [M+H]⁺ calculated for $\text{C}_{13}\text{H}_{10}\text{N}_3^{127}\text{I}+\text{H}^+$: 335.9992; found: 335.9986 \pm 0.57 ppm.

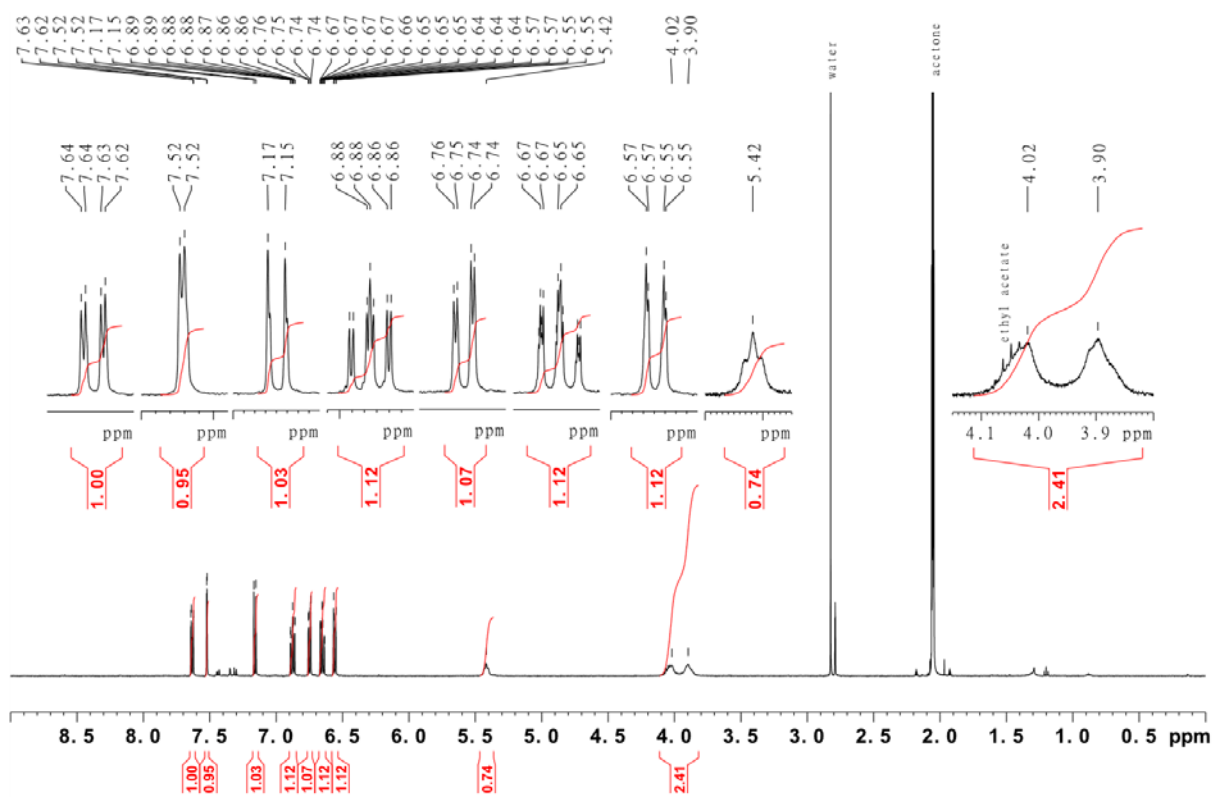


Figure SII.41: 500 MHz ^1H -NMR spectrum of (Z)-3-iodo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine.

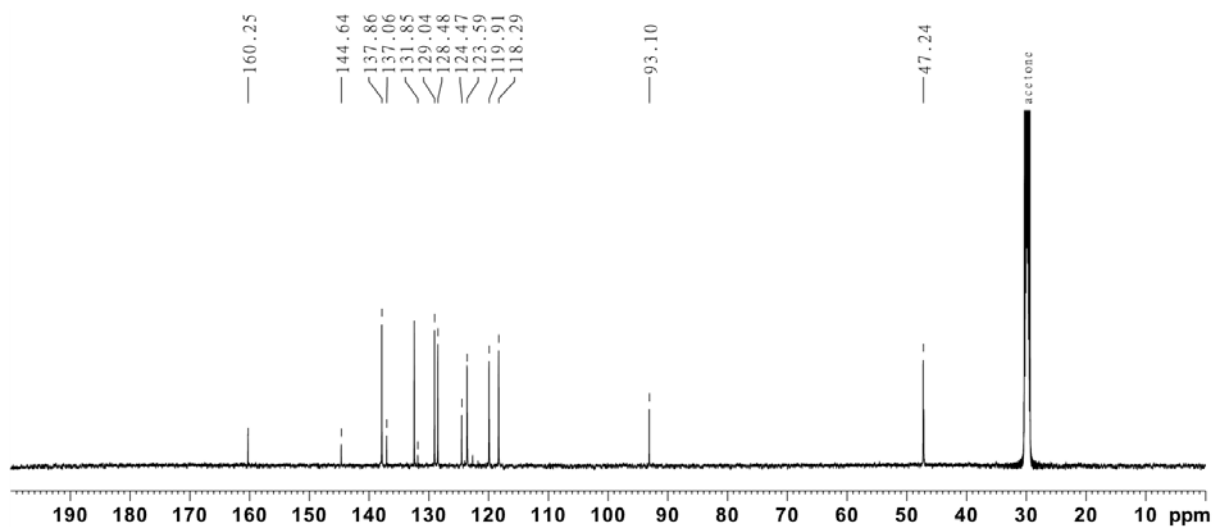


Figure SII.42: 125 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (Z)-3-iodo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine.

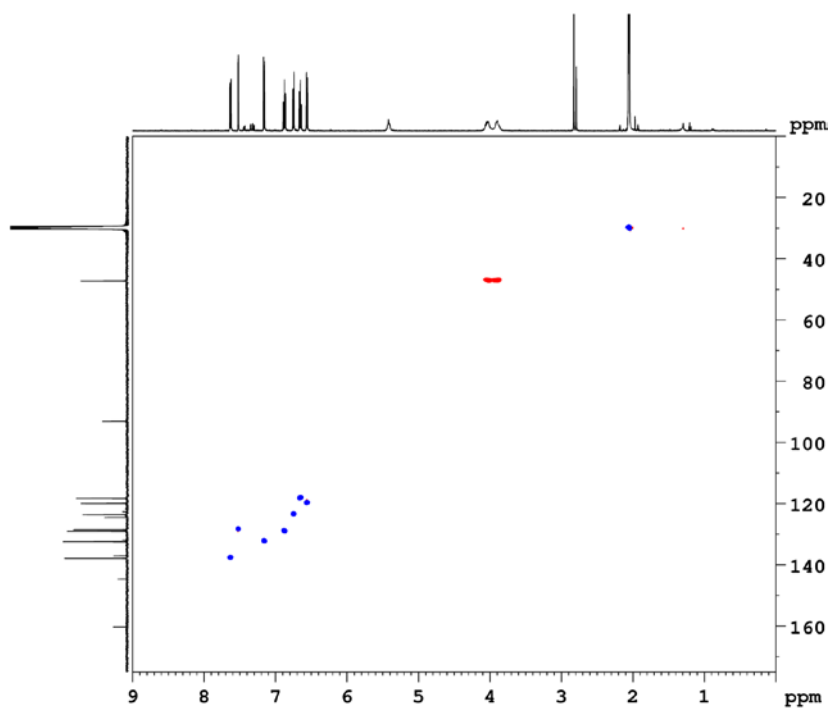


Figure SII.43: 500 MHz ^1H - ^{13}C HSQC spectrum of (Z)-3-iodo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine.

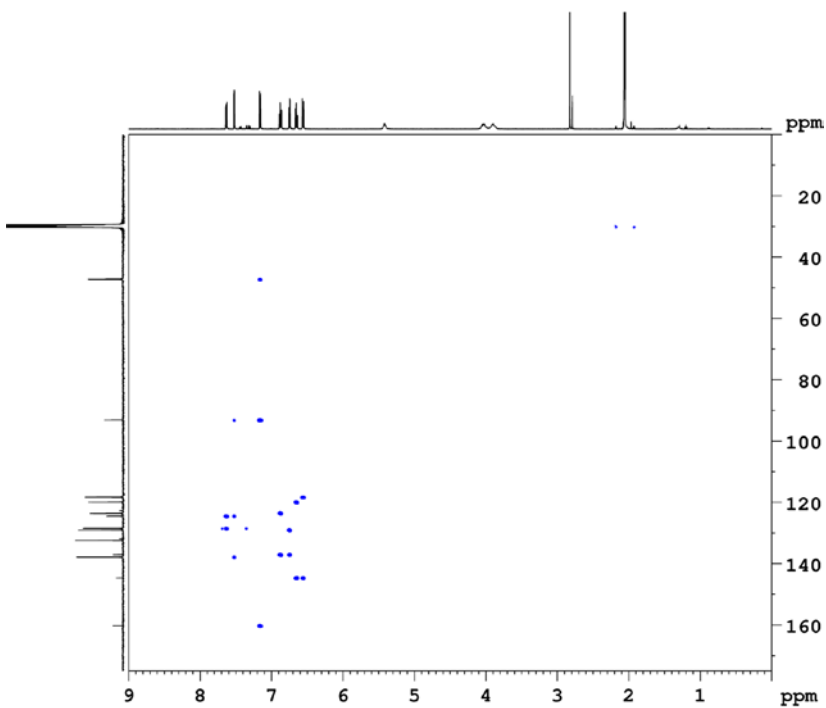
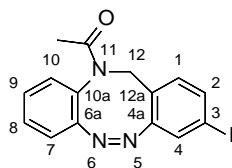


Figure SII.44: 500 MHz HMBC spectrum of (Z)-3-iodo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine.

II.1.12 Synthesis of (Z)-1-(3-iododibenzo[c,g][1,2,5]triazocin-11(12*H*)-yl)-ethan-1-one (3)^[1]



(Z)-3-iodo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine (603 mg, 1.8 mmol) were dissolved in 50 mL anhydrous DMF under a nitrogen atmosphere. NEt₃ (2.5 mL, 3.6 mmol) and AcOH (1.03 mL, 18 mmol) were added. The reaction mixture was cooled to 0 °C and T3P (10 mL, 18 mmol, 50% in ethyl acetate) was added dropwise. The reaction mixture was stirred at rt. for 16 h. 100 mL DCM and 100 mL deionized water were added and the organic layer was separated. The aqueous layer was extracted twice with 100 mL DCM and the combined organic layers were dried over MgSO₄. The solvent was removed and column chromatography on silica (ethyl acetate/cyclohexane 1:1, *R_f* = 0.39) gave a yellow solid (476 mg, 1.26 mmol, 70%, lit. 60%^[1]).

melting point: 179 °C

¹H-NMR (600 MHz, acetone-*d*₆, 298 K): δ = 7.51 (dd, ³*J* = 8.0 Hz, ⁴*J* = 1.8 Hz, 1 H, *H*-2), 7.40 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.6 Hz, 1 H, *H*-8/9), 7.32-7.26 (m, 3 H, *H*-4, *H*-7/10, *H*-8/9), 7.06 (dd, ³*J* = 7.8 Hz, ⁴*J* = 1.1 Hz, 1 H, *H*-7/10), 7.03 (d, ³*J* = 8.1 Hz, 1 H, *H*-1), 5.02 (d, ²*J* = 14.6 Hz, 1 H, *H*-12), 4.29 (d, ²*J* = 14.7 Hz, 1 H, *H*-12'), 1.79 (s, 3 H, CH₃), ppm.

¹³C{¹H}-NMR (150 MHz, acetone-*d*₆, 298 K): δ = 169.4 (C=O), 157.1 (C-4a), 154.2 (C-6a/10a), 137.4 (C-2), 132.7 (C-1), 130.28 (C-7/10), 130.18 (C-8/9), 129.54 (C-8/9), 129.45 (C-6a/10a), 128.4 (C-4), 125.2 (C-12a), 120.0 (C-7/10), 93.5 (C-3), 51.6 (C-12), 23.0 (CH₃) ppm.

IR (ATR): $\tilde{\nu}$ = 3057 (w), 3010 (w), 2930 (w), 2021 (w), 1654 (s), 1582 (m), 1554 (w), 1513 (w), 1473 (m), 1432 (w), 1377 (s), 1336 (s), 1296 (m), 1250 (w), 1110 (m), 1084 (m), 1030 (m), 1009 (w), 970 (m), 917 (w), 842 (m), 823 (s), 767 (s), 735 (w), 652 (m), 598 (m), 582 (m), 514 (m), 485 (m), 470 (w), 437 (s) cm⁻¹.

HR-MS (ESI, DCM): *m/z* [M+H]⁺ calculated for C₁₅H₁₁ON₃¹²⁷I+H⁺: 378.0098; found: 378.0090 ± 2.03 ppm.

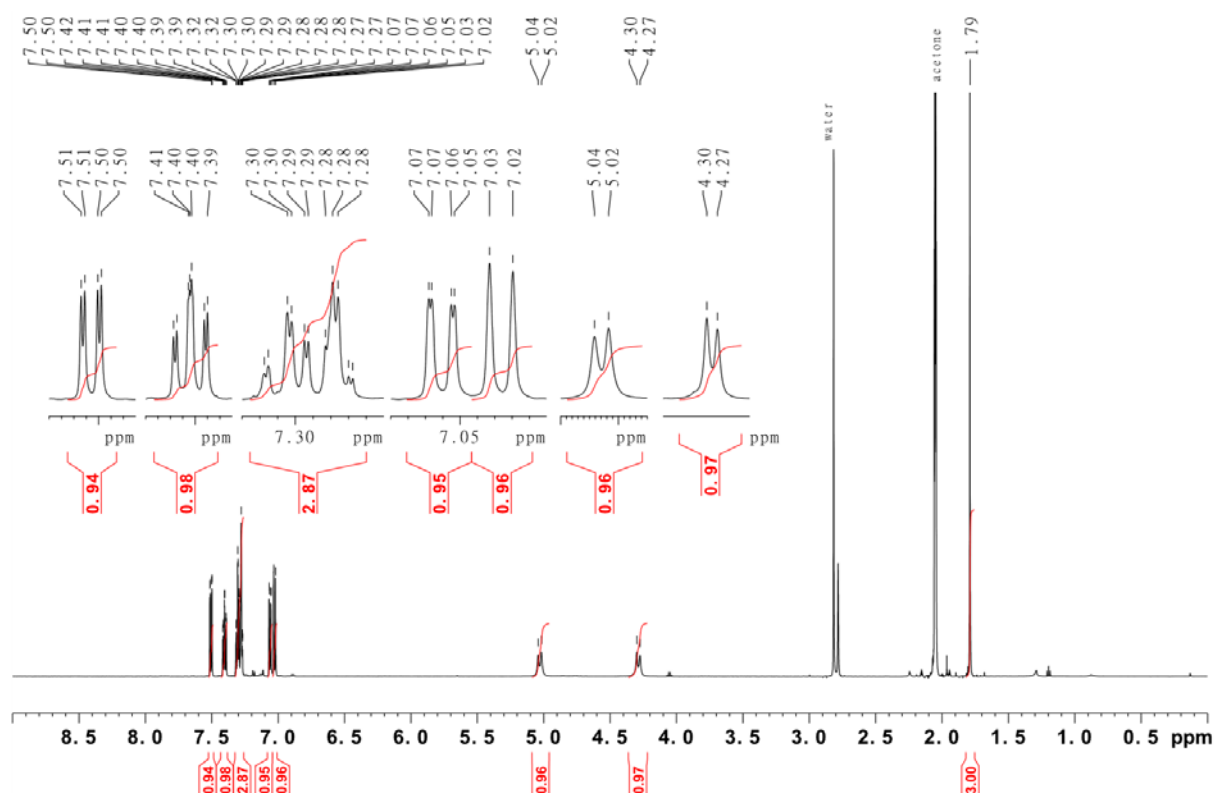


Figure SII.45: 600 MHz ^1H -NMR spectrum of (Z)-1-(3-iododibenzo[c,g][1,2,5]triazocin-11(12*H*)-yl)-ethan-1-one (**3**).

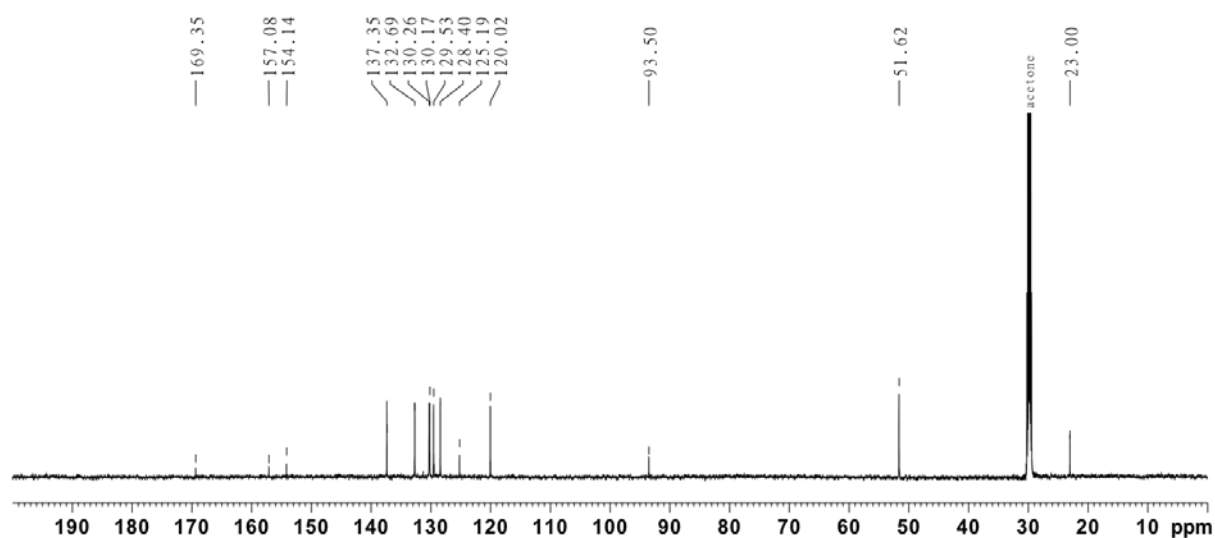


Figure SII.46: 150 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (Z)-1-(3-iododibenzo[c,g][1,2,5]triazocin-11(12*H*)-yl)-ethan-1-one (**3**).

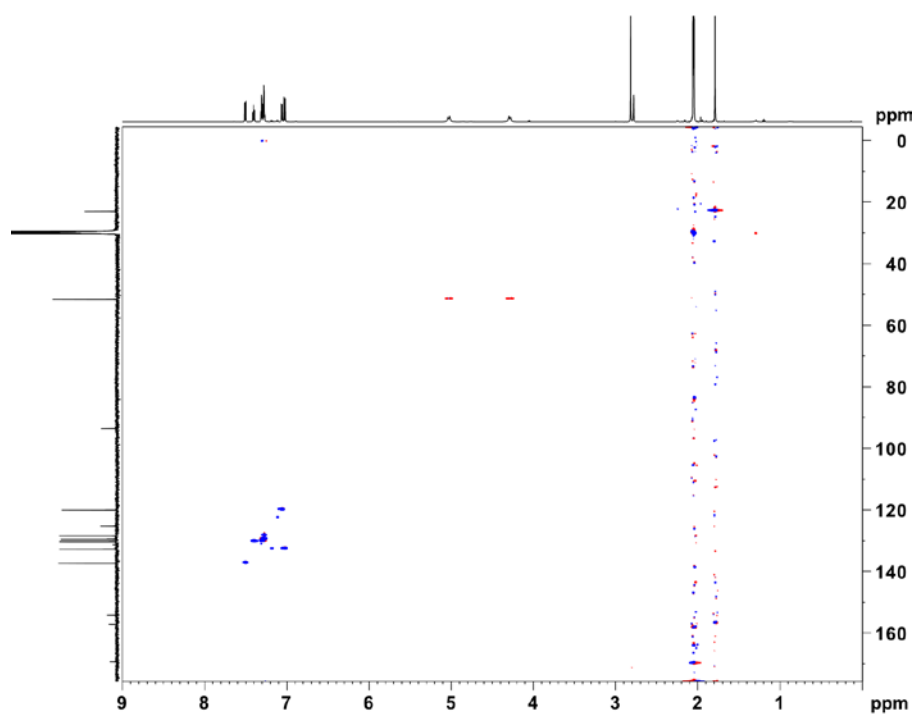


Figure SII.47: 600 MHz ^1H - ^{13}C HSQC spectrum of (Z)-1-(3-iododibenzo[c,g][1,2,5]triazocin-11(12*H*)-yl)-ethan-1-one (**3**).

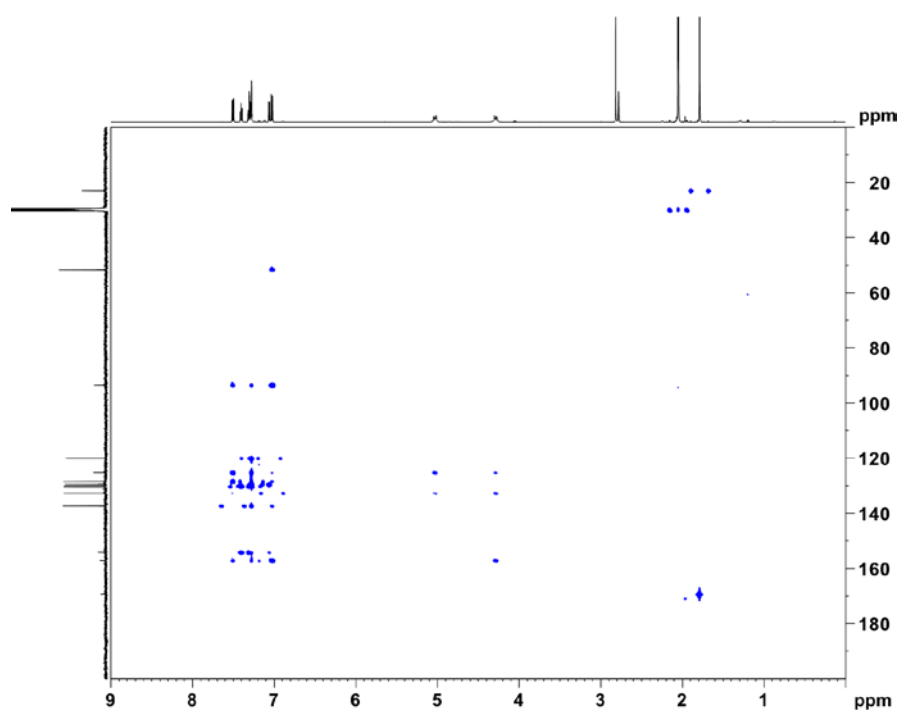
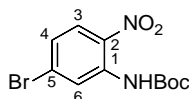


Figure SII.48: 600 MHz HMBC spectrum of (Z)-1-(3-iododibenzo[c,g][1,2,5]triazocin-11(12*H*)-yl)-ethan-1-one (**3**).

II.1.13 Synthesis of *tert*-butyl-(5-bromo-2-nitrophenyl)carbamate



Under a nitrogen atmosphere NaH (444 mg, 18.5 mmol, 60% in mineral oil) was suspended in 10 mL anhydrous DMF and 5-bromo-2-nitroaniline (**6**, 1.00 g, 4.61 mmol) was added at 0 °C. The reaction mixture was stirred at 0 °C for 10 min. and at rt. for 30 min. Di-*tert*-butyldicarbonate (1.00 g, 4.66 mmol) dissolved in 10 mL anhydrous DMF was added dropwise and the reaction mixture was stirred at rt. for 16 h and poured on ice subsequently. The organic layer was separated and the aqueous layer was extracted twice with 50 mL ethyl acetate. The combined organic layers were dried over MgSO₄ and the solvent was evaporated. After column chromatography on silica (ethyl acetate/cyclohexane 1:10, *R_f* = 0.70) the product could be obtained as pale green solid (1.14 g, 3.60 mmol, 78%).

melting point: 83 °C

¹H-NMR (500 MHz, CDCl₃, 298 K): δ = 9.73 (br. s, 1 H, NH), 8.85 (d, ⁴*J* = 2.1 Hz, 1 H, *H*-6), 8.06 (d, ³*J* = 9.1 Hz, 1 H, *H*-3), 7.21 (dd, ³*J* = 9.0 Hz, ⁴*J* = 2.2 Hz, 1 H, *H*-4), 1.55 (s, 10 H, CH₃) ppm.

¹³C{¹H}-NMR (125 MHz, CDCl₃, 198 K): δ = 151.9 (C=O), 137.0 (C-1), 134.6 (C-2), 131.5 (C-4), 127.1 (C-6), 125.2 (C-5), 123.4 (C-3), 82.6 (C-(CH₃)₃), 28.3 (CH₃), ppm.

IR (ATR): $\tilde{\nu}$ = 3356 (w), 3115 (w), 2980 (w), 1729 (m), 1605 (m), 1569 (m), 1537 (w), 1489 (m), 1470 (m), 1427 (m), 1392 (w), 1368 (w), 1327 (m), 1298 (m), 1244 (m), 1204 (w), 1144 (s), 1093 (w), 1073 (m), 1049 (w), 1027 (w), 923 (w), 837 (m), 818 (m), 773 (w), 761 (w), 750 (m), 672 (m), 603 (w), 583 (w) cm⁻¹.

MS (EI, 70 eV): *m/z*(%) = 318.00 [C₁₁H₁₃⁸¹BrN₂O₄]⁺, 316.01 [C₁₁H₁₃⁷⁹BrN₂O₄]⁺, 260.95 [C₈H₈⁷⁹BrN₂O₃]⁺, 215.95 [C₆H₃⁷⁹BrN₂O₂]⁺, 185.95 [C₆H₃⁷⁹BrN₁O₁]⁺, 169.94 [C₆H₃⁷⁹BrN]⁺, 90.03 [C₆H₃⁷⁹BrN]⁺.

HR-MS (EI, 70 eV, acetone): *m/z* [M]⁺ calculated for C₁₁H₁₃N₂O₄⁷⁹Br⁺: 316.0057; found.: 316.0059 ± 0.44 ppm.

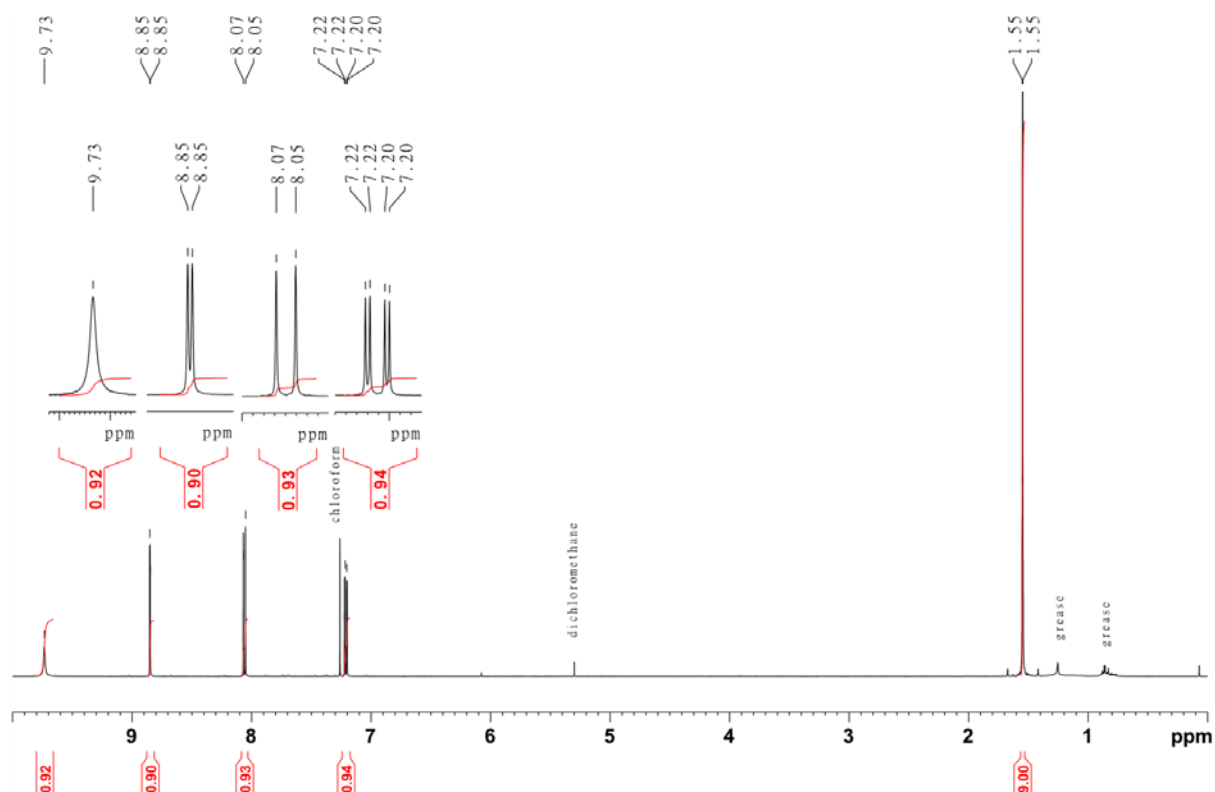


Figure SII.49: 500 MHz ^1H -NMR spectrum of *tert*-butyl-(5-bromo-2-nitrophenyl)carbamate.

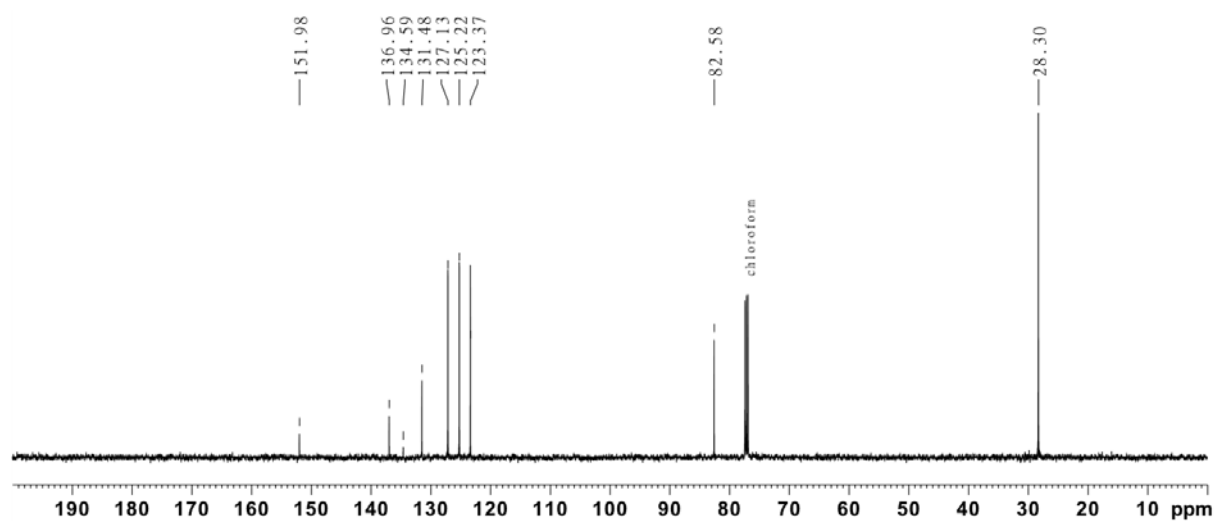


Figure SII.50: 125 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of *tert*-butyl-(5-bromo-2-nitrophenyl)carbamate.

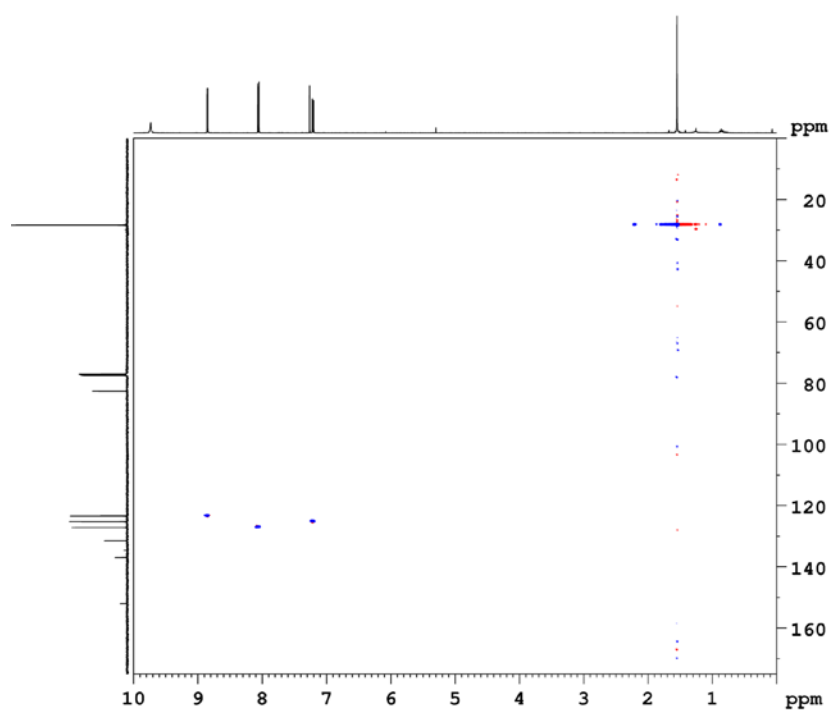


Figure SII.51: 500 MHz ^1H - ^{13}C HSQC spectrum of *tert*-butyl-(5-bromo-2-nitrophenyl)carbamate.

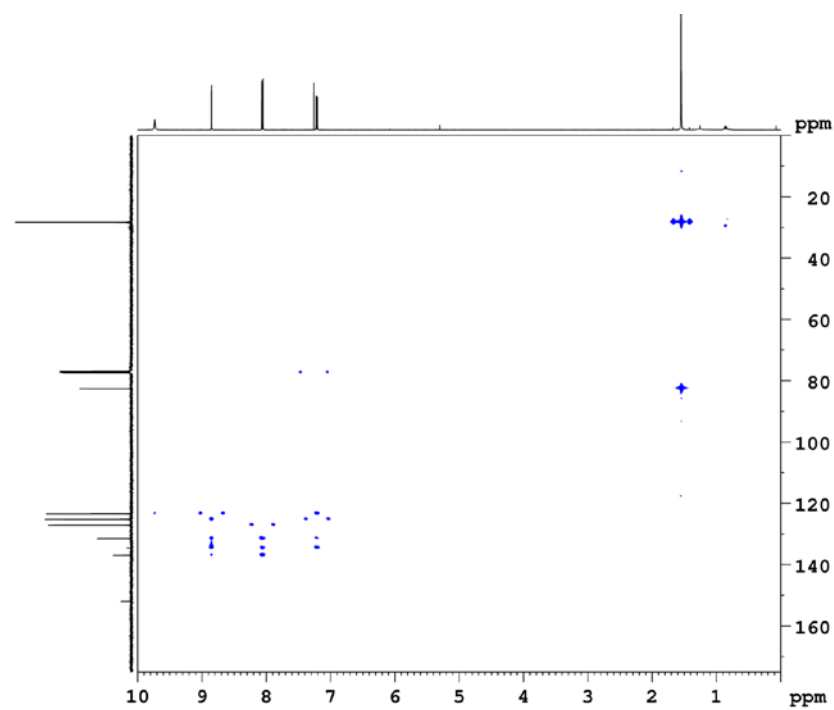
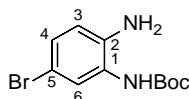


Figure SII.52: 500 MHz HMBC spectrum of *tert*-butyl-(5-bromo-2-nitrophenyl)carbamate.

II.1.14 Synthesis of *tert*-butyl-(2-amino-5-bromophenyl)carbamate (5)



tert-butyl-(5-bromo-2-nitrophenyl)carbamate (1.80 g, 5.70 mmol), sodium dithionite (3.97 g, 22.7 mmol) and sodium bicarbonate (4.79 g, 57.0 mmol) were suspended in 48 mL 1,4-dioxane/deionized water mixture (5:1), heated to reflux with an oil bath and stirred at given temperature for 2 h. After cooling down 100 mL deionized water were added and the reaction mixture was extracted three times with 50 mL ethyl acetate. After drying the combined organic layers over MgSO_4 and evaporation of the solvent the product could be obtained as yellow solid (1.58 g, 5.53 mmol, 97 %)

melting point: 141 °C

$^1\text{H-NMR}$ (500 MHz, CDCl_3 , 298 K): δ = 7.52 (s, 1 H, *H*-6), 7.08 (dd, 3J = 2.4 Hz, 4J = 8.4 Hz, 1 H, *H*-4), 6.67 (d, 4J = 8.4 Hz, 1 H, *H*-3), 6.32 (s, 1 H, -NH), 3.71 (s, 2 H, -NH₂), 1.51 (s, 9 H, -CH₃) ppm.

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (125 MHz, CDCl_3 , 298 K): δ = 153.5 (C=O), 137.8 (C-2), 128.6 (C-4), 126.8 (C-6), 119.3 (C-3), 111.8 (C-1), 81.2 (C-(CH₃)₃), 28.4 (CH₃) ppm.

IR (ATR): $\tilde{\nu}$ = 3440 (w), 3359 (m), 3295 (m), 2980 (m), 2929 (w), 2163 (w), 1980 (w), 1673 (s), 1634 (m), 1589 (m), 1515 (s), 1488 (m), 1454 (w), 1416 (s), 1389 (m), 1362 (m), 1322 (m), 1282 (s), 1248 (s), 1224 (w), 1149 (s), 1049 (m), 1024 (m), 882 (m), 857 (m), 817 (w), 807 (m), 777 (m), 760 (w), 742 (m), 627 (m), 601 (m), 556 (s) cm^{-1} .

MS (EI, 70 eV): m/z (%) = 288.02991 [$\text{C}_{11}\text{H}_{15}^{79}\text{BrN}_2\text{O}_2$]⁺, 286.03176 [$\text{C}_{11}\text{H}_{15}^{79}\text{BrN}_2\text{O}_2$]⁺, 229.97 [$\text{C}_7\text{H}_6^{79}\text{BrN}_2\text{O}_2$]⁺, 185.98 [$\text{C}_6\text{H}_6^{79}\text{BrN}_2$]⁺.

HR-MS (EI, 70 eV, acetone): m/z [M]⁺ calculated for $\text{C}_{11}\text{H}_{15}^{79}\text{BrN}_2\text{O}_2$ ⁺: 286.0318; found: 286.0317 ± 0.24 ppm.

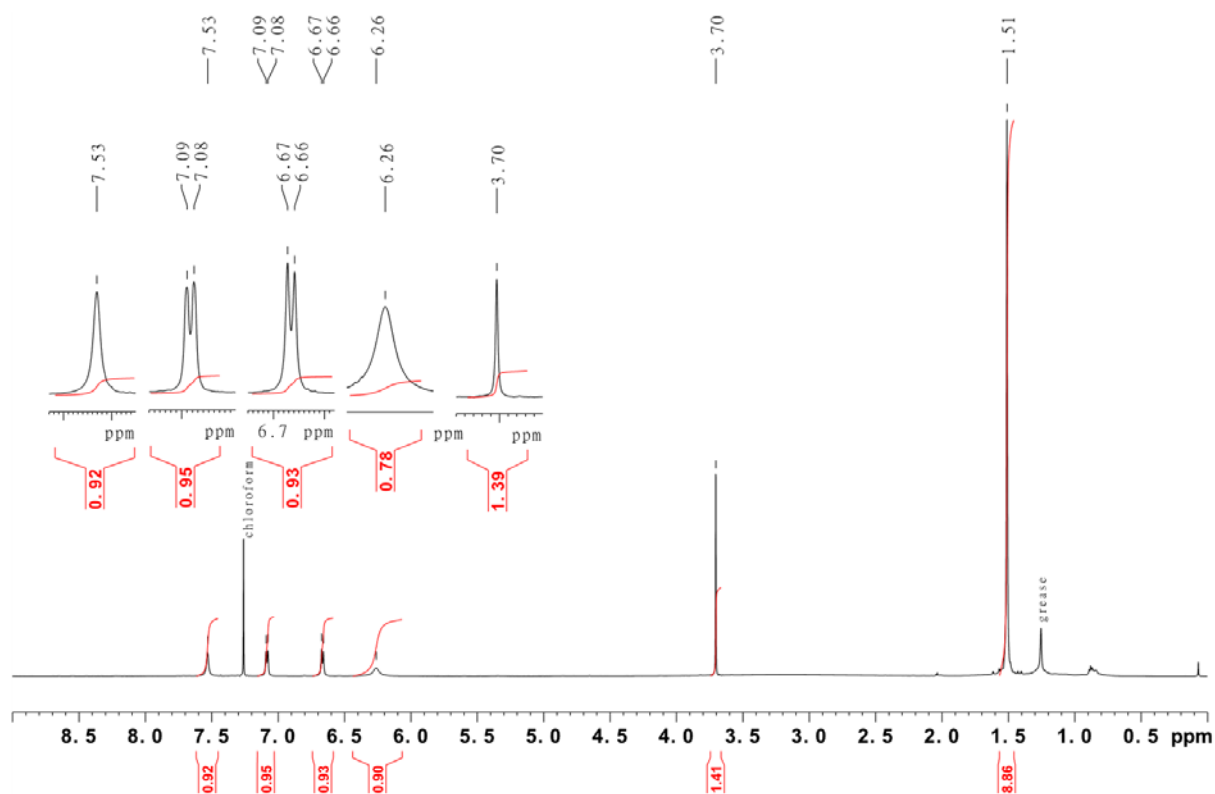


Figure SII.53: 500 MHz ^1H -NMR spectrum of *tert*-butyl-(2-amino-5-bromophenyl)carbamate (**5**).

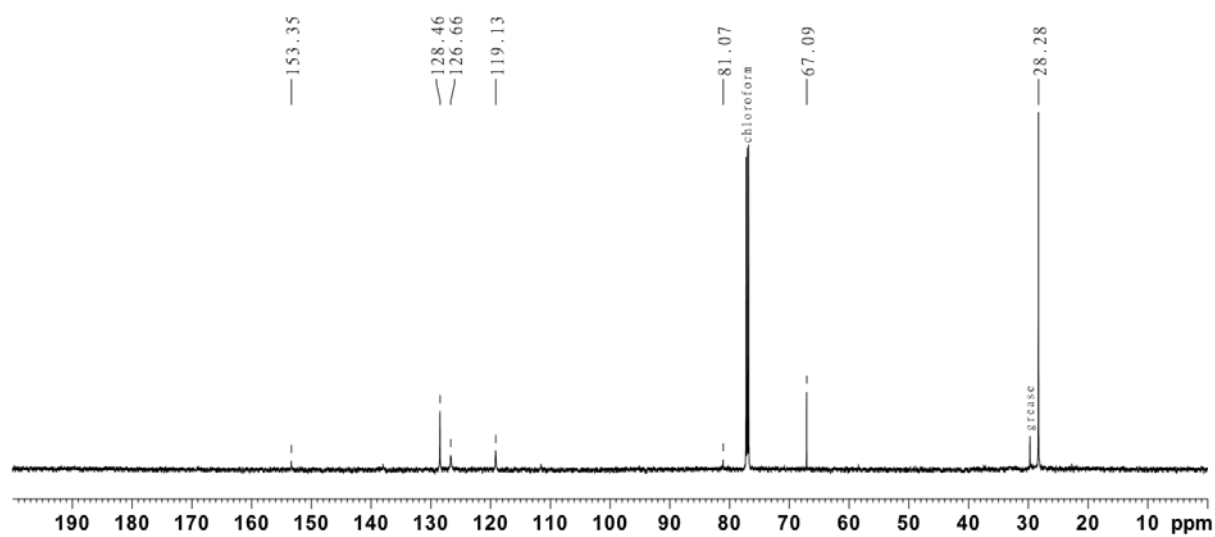


Figure SII.54: 125 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of *tert*-butyl-(2-amino-5-bromophenyl)carbamate (**5**).

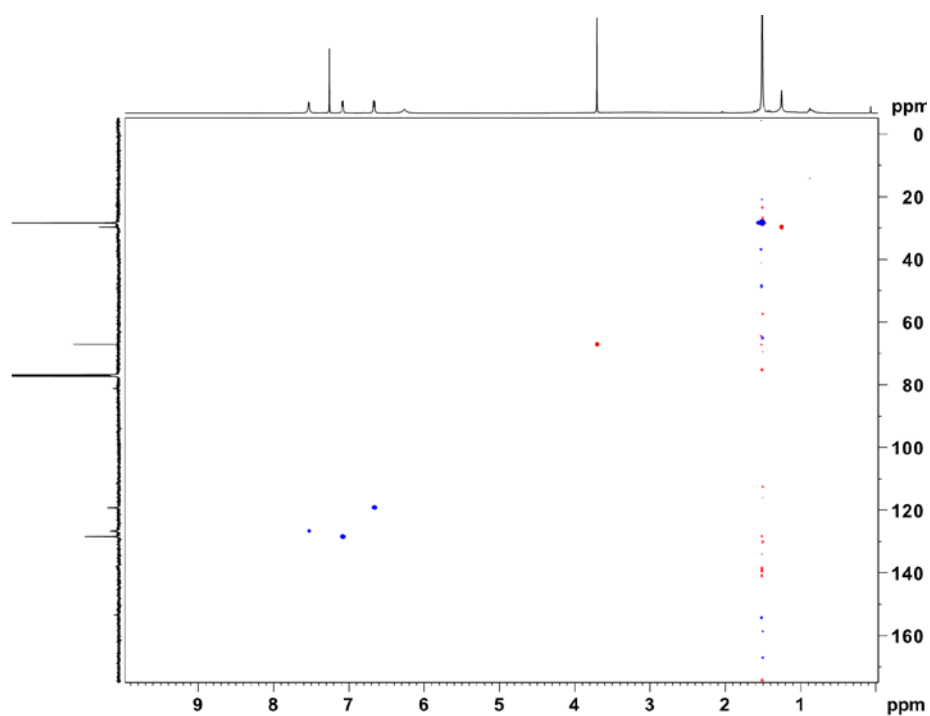


Figure SII.55: 500 MHz ^1H - ^{13}C HSQC spectrum of *tert*-butyl-(2-amino-5-bromophenyl)carbamate (**5**).

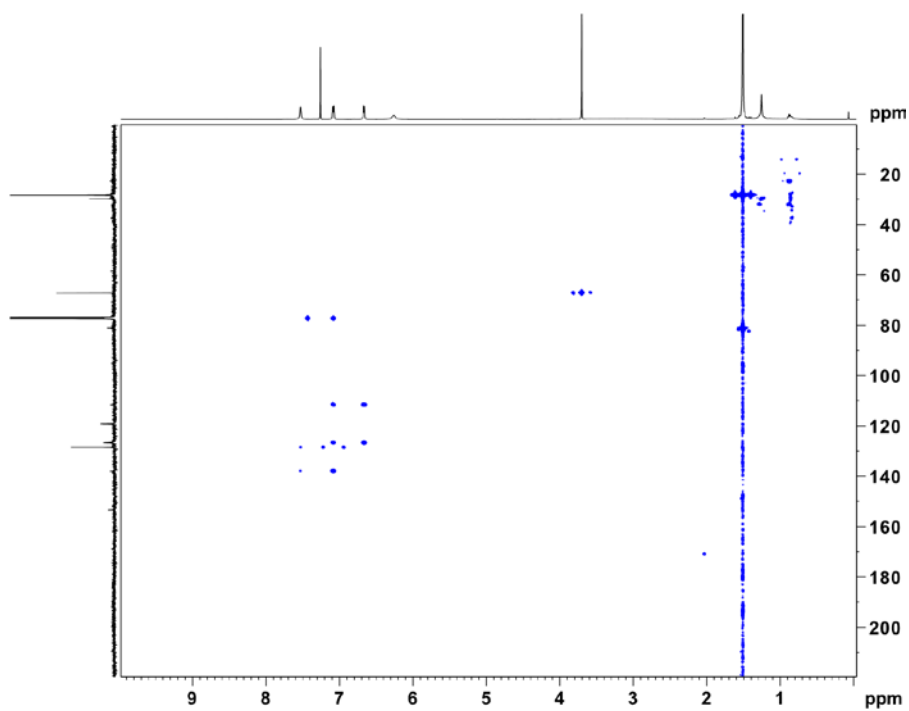
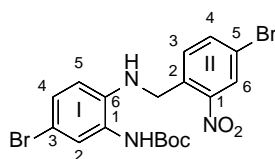


Figure SII.56: 500 MHz HMBC spectrum of *tert*-butyl-(2-amino-5-bromophenyl)carbamate (**5**).

II.1.15 Synthesis of *tert*-butyl-(5-bromo-2-((4-bromo-2-nitrobenzyl)amino)phenyl)carbamate



Under a nitrogen atmosphere triethylamine (3.06 mL, 18.0 mmol) and 1-(bromomethyl)-4-bromo-2-nitrobenzene (5.17 g, 17.5 mmol) were added to solution of *tert*-butyl-(2-amino-5-bromophenyl)carbamate (5.02 g, 17.5 mmol) in 100 mL abs. THF. The reaction mixture was heated to reflux with an oil bath and stirred for 16 h at given temperature. Afterwards the solvent was evaporated and 100 mL of deionized water and 100 mL DCM were added to the residue. The organic layer was separated and the aqueous layer was extracted twice with 50 mL of DCM. The combined organic layers were dried over MgSO₄ and the solvent was evaporated. Recrystallization from cyclohexane/ethyl acetate (1:1) gave the product as yellow solid (7.39 g, 15.7 mmol, 62%).

melting point: 186 °C

¹H-NMR (500 MHz, CDCl₃, 298 K): δ = 8.22 (d, ⁴J = 2.0 Hz, 1 H, Ar^{II}-H-3), 7.68 (dd, ⁴J = 2.1 Hz, ³J = 8.3 Hz, 1 H, Ar^{II}-H-4), 7.49-7.43 (m, 2 H, Ar^{II}-H-3, Ar^I-H-2), 7.08 (dd, ⁴J = 2.2 Hz, ³J = 8.6 Hz, 1 H, Ar^I-H-4), 6.32 (s, 1 H, Ar^I-H-5), 6.20 (br. s, 1 H, -CONH), 4.98 (br. s, 1 H, -NH), 4.74-4.41 (m, 3 H, -CH₂, -NH), 1.51 (s, 9 H, -CH₃) ppm.

¹³C{¹H}-NMR (125 MHz, CDCl₃, 198 K): δ = 153.9 (C=O), 148.8 (Ar^{II}-C-1), 140.1 (Ar^I-C-2), 136.9 (Ar^{II}-C-4), 133.9 (Ar^{II}-C-5), 131.4 (Ar^{II}-C-3), 129.5 (Ar^I-C-4), 128.30 (Ar^{II}-C-6), 128.15 (Ar^I-C-6), 126.1 (Ar^I-C-1), 121.5 (Ar^{II}-C-2), 114.6 (Ar^{II}-C-3), 110.90 (Ar^{II}-C-5), 81.5 (-C-(CH₃)₃), 45.6 (-CH₂), 28.4 (-CH₃) ppm.

IR (ATR): $\tilde{\nu}$ = 3421 (m), 2982 (m), 2211 (w), 1685 (s), 1594 (m), 1527 (s), 1497 (m), 1366 (m), 1342 (m), 1281 (m), 1243 (s), 1152 (s), 1054 (w), 875 (s), 857 (w), 831 (w), 807 (m), 790 (w), 751 (m), 627 (w), 551 (m) cm⁻¹.

HR-MS (ESI, DCM): m/z [M+H]⁺ calculated for C₁₈H₁₉⁷⁹Br₂N₃O₄+H⁺: 499.9815; found: 499.9808 ± 151 ppm.

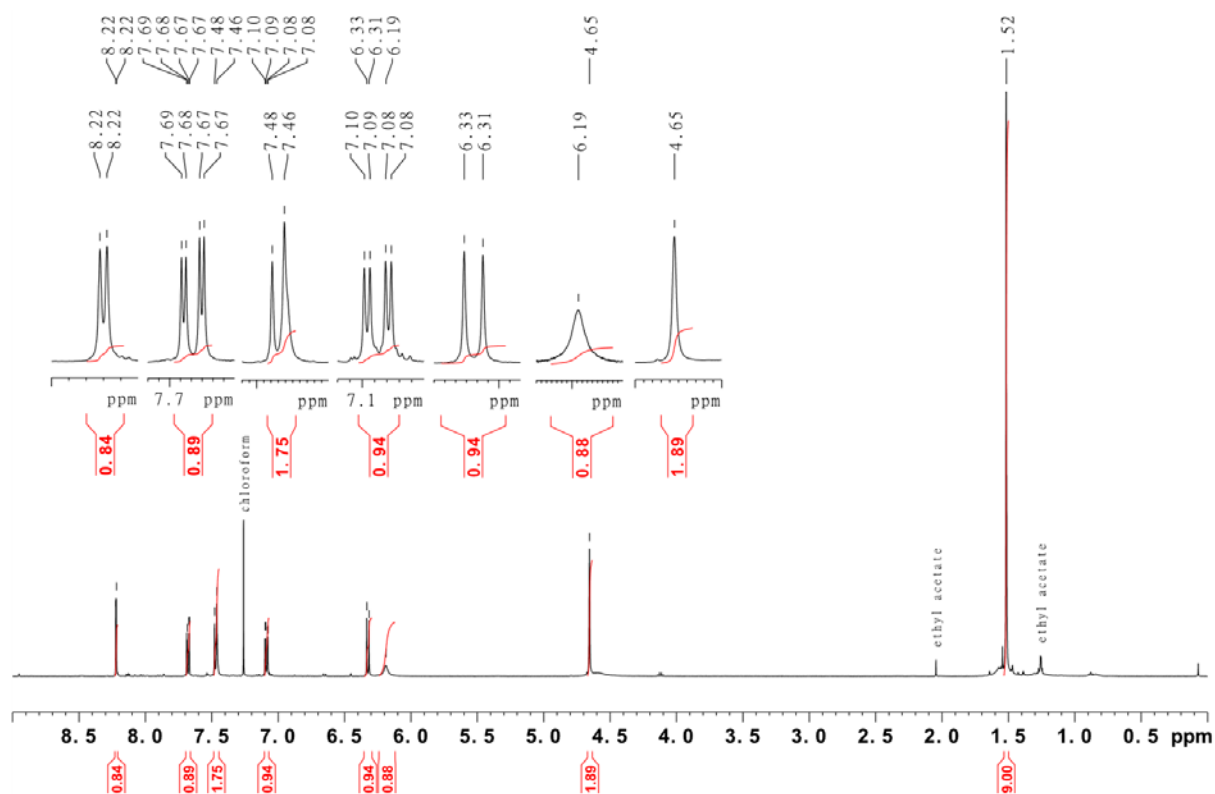


Figure SII.57: 500 MHz ¹H-NMR spectrum of *tert*-butyl-(5-bromo-2-((4-bromo-2-nitrobenzyl)amino)phenyl)carbamate.

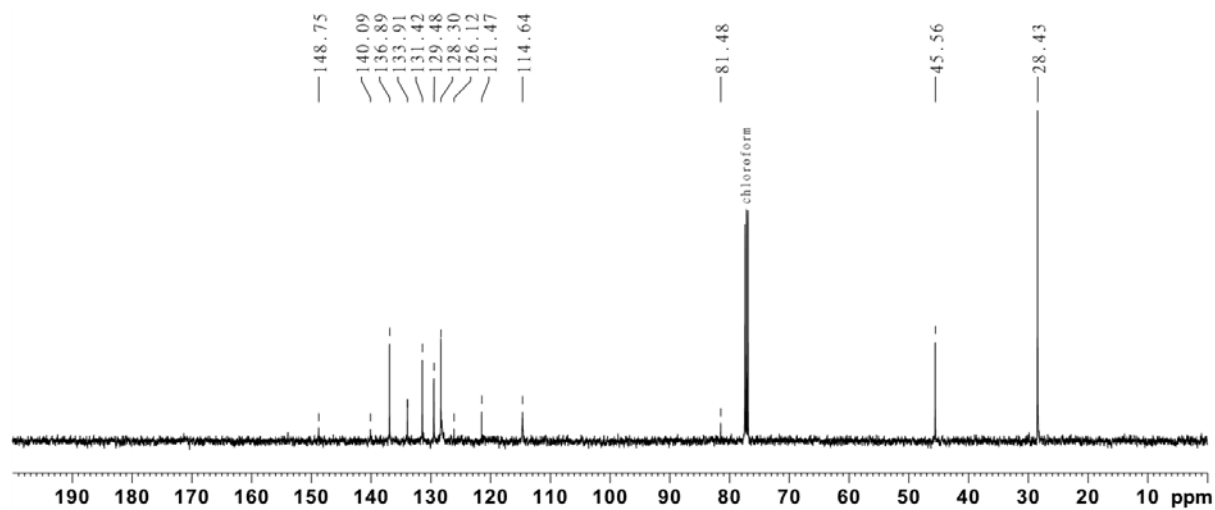


Figure SII.58: 125 MHz ¹³C{¹H}-NMR spectrum of *tert*-butyl-(5-bromo-2-((4-bromo-2-nitrobenzyl)amino)phenyl)carbamate.

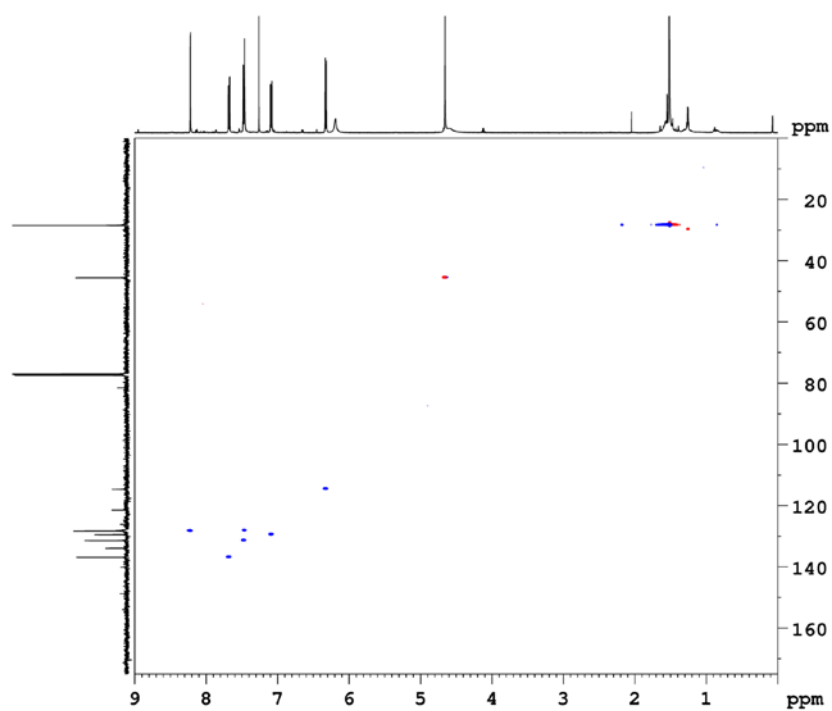


Figure SII.59: 500 MHz ^1H - ^{13}C HSQC spectrum of *tert*-butyl-(5-bromo-2-((4-bromo-2-nitrobenzyl)amino)phenyl)carbamate.

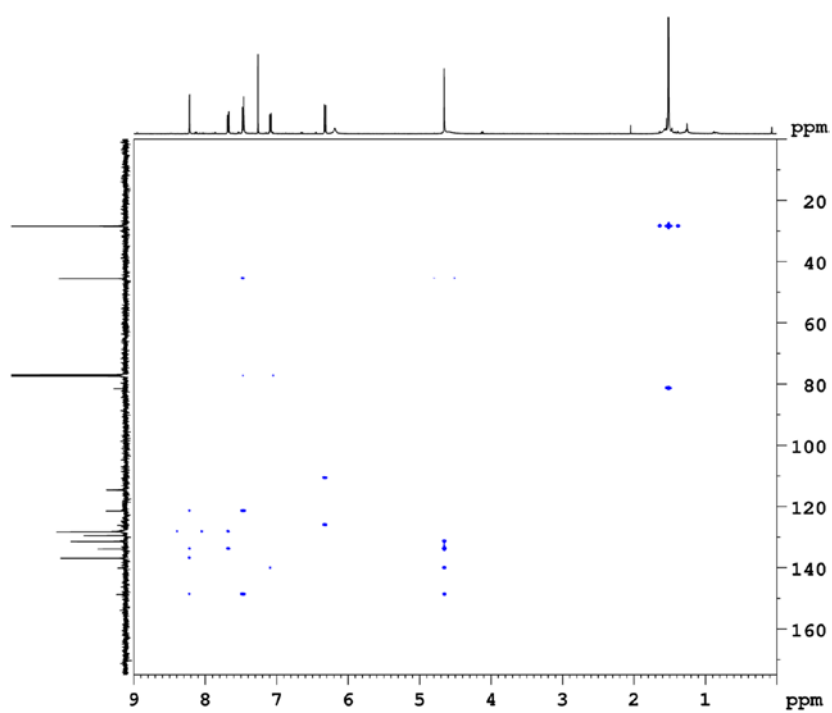
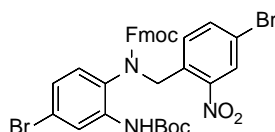


Figure SII.60: 500 MHz ^1H - ^{13}C HMBC spectrum of *tert*-butyl-(5-bromo-2-((4-bromo-2-nitrobenzyl)amino)phenyl)carbamate.

II.1.16 Synthesis of (9H-fluoren-2-yl)methyl-(4-bromo-2-((tert-butoxycarbonyl)amino)phenyl)(4-bromo-2-nitrobenzyl)carbamate



DIPEA (820 μ L, 5 mmol) and 9-Fluorenylmethoxycarbonyl chlorid (2.50 g, 4.83 mmol) were added to a solution of *tert*-butyl-(5-bromo-2-((4-bromo-2-nitrobenzyl)amino)phenyl)carbamate (2.42 g, 4.83 mmol) in 50 mL abs. DMF under a nitrogen atmosphere. The reaction mixture was stirred for 48 h at rt. and the solvent was evaporated subsequently. 100 mL of deionized water and 100 mL of DCM were added to the residue. The organic layer was separated and the aqueous layer was extracted twice with 100 mL DCM. The combined organic layers were dried over MgSO_4 and the solvent was evaporated. Column chromatography on silica (ethyl acetate/cyclohexane 1:4, R_f = 0.34) gave a colorless solid (302 mg, 418 μ mol, 13%).

melting point: 88 $^{\circ}\text{C}$

$^1\text{H-NMR}$ (500 MHz, CDCl_3 , 298 K): δ = 8.16 (br. s, 1 H, -CONH), 8.06 (s, 1 H, Ar-*H*), 7.66 (d, 3J = 7.4 Hz, 2 H, Ar-*H*), 7.58 (br. s, 1 H, Ar-*H*), 7.38-7.33 (m, 2 H, Ar-*H*), 7.25-6.98 (s, 6 H, Ar-*H*), 6.61 (br. s, 1 H, Ar-*H*), 6.32 (br. s, 1 H, Ar-*H*), 5.09 (br. s, 1 H, -CH₂), 4.78 (br. s, 1 H, -CH₂), 4.52 (br. s, 2 H, Fmoc-CH₂), 4.05 (s, 1 H, Fmoc-CH), 1.46 (s, 9 H, -CH₃) ppm.

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (125 MHz, CDCl_3 , 298 K): δ = 155.6, 143.3, 141.4, 136.5, 129.0, 128.08, 127.86, 127.1, 126.5, 124.7, 123.3, 120.1, 81.6, 68.2, 47.0, 28.4 ppm.

IR (ATR): $\tilde{\nu}$ = 2929 (w), 2166 (w), 1713 (s), 1583 (m), 1531 (s), 1512 (s), 1450 (m), 1392 (w), 1347 (w), 1276 (w), 1233 (m), 1151 (s), 1022 (w), 877 (m), 758 (s), 749 (s), 739 (s), 621 (w), 545 (w) cm^{-1} .

HR-MS (ESI, $\text{CHCl}_3/\text{MeOH}$): m/z $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{33}\text{H}_{29}\text{O}_6\text{N}_3\text{Br}_2+\text{H}^+$: 722.0496; found: 722.0490 \pm 0.82 ppm.

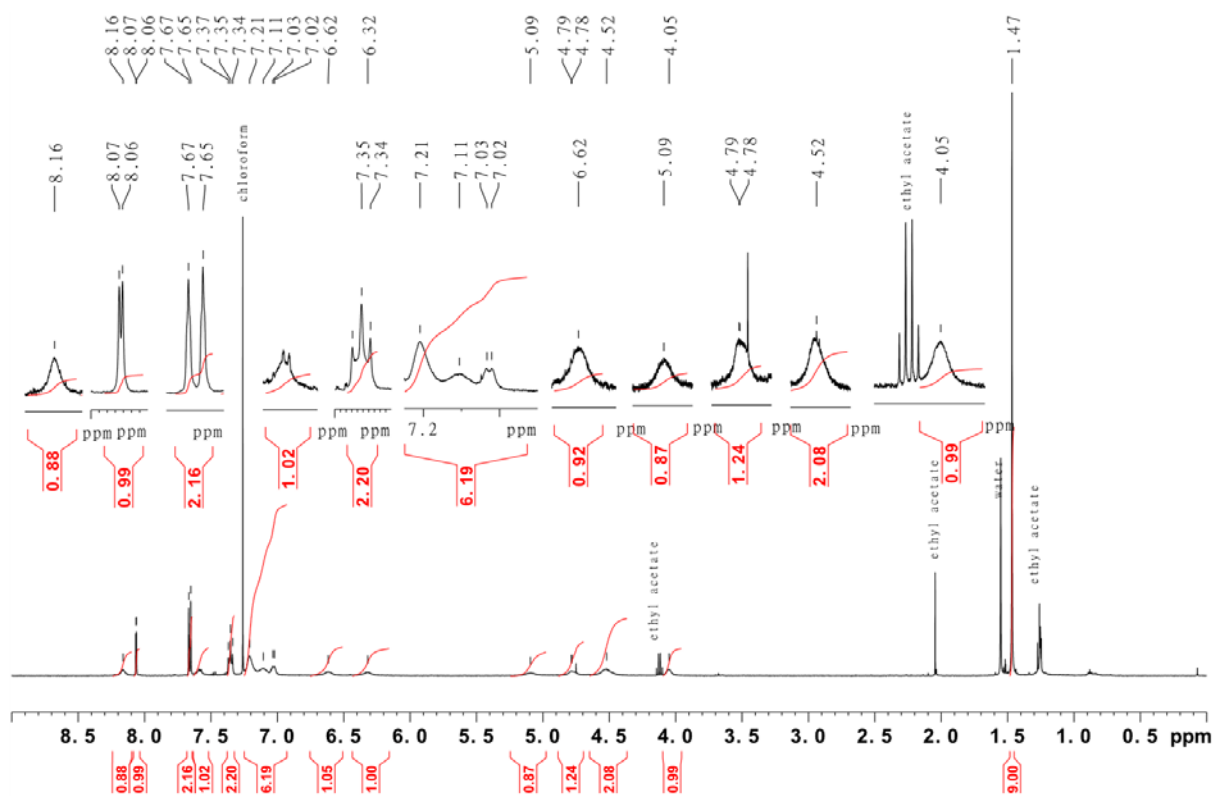


Figure SII.61: 500 MHz ^1H -NMR spectrum of (9*H*-fluoren-2-yl)methyl-(4-bromo-2-((*tert*-butoxycarbonyl)amino)phenyl)(4-bromo-2-nitrobenzyl)carbamate.

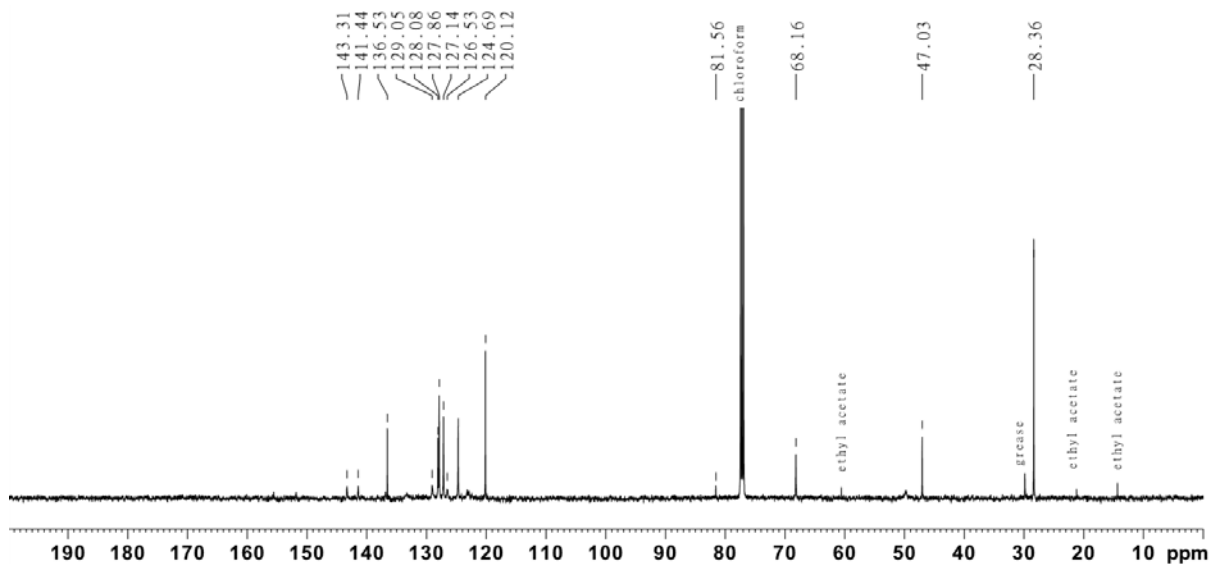


Figure SII.62: 125 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (9*H*-fluoren-2-yl)methyl-(4-bromo-2-((*tert*-butoxycarbonyl)amino)phenyl)(4-bromo-2-nitrobenzyl)carbamate.

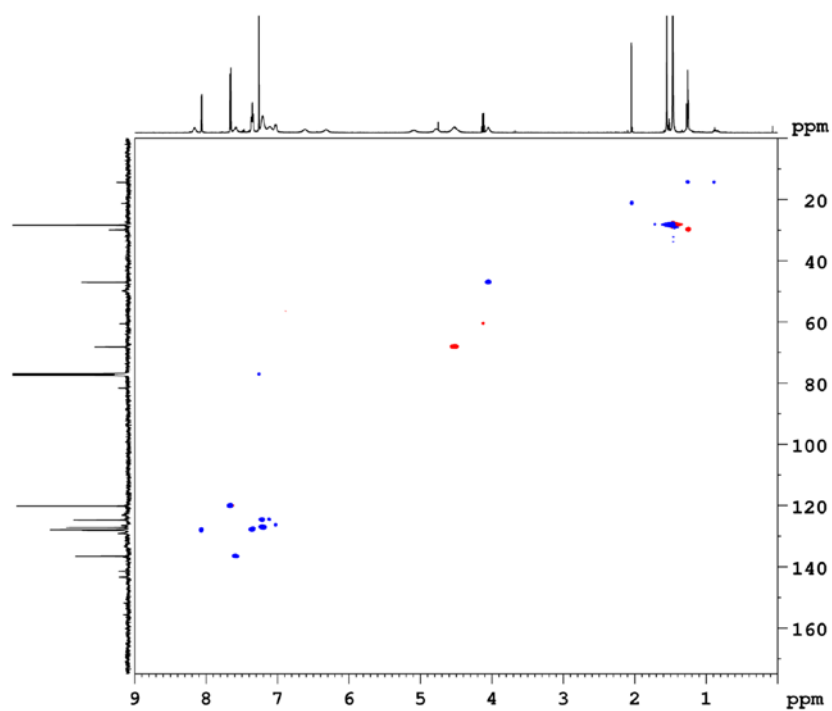


Figure SII.63: 500 MHz ^1H - ^{13}C HSQC spectrum of (9*H*-fluoren-2-yl)methyl-(4-bromo-2-((*tert*-butoxycarbonyl)amino)phenyl)(4-bromo-2-nitrobenzyl)carbamate.

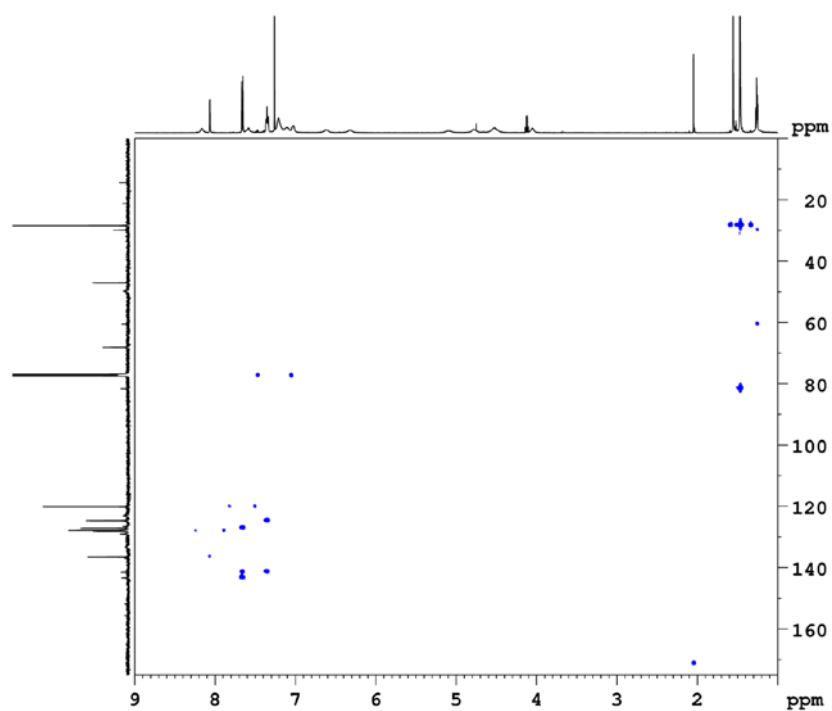
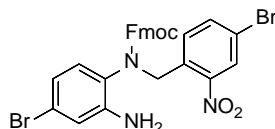


Figure SII.64: 500 MHz ^1H - ^{13}C HMBC spectrum of (9*H*-fluoren-2-yl)methyl-(4-bromo-2-((*tert*-butoxycarbonyl)amino)phenyl)(4-bromo-2-nitrobenzyl)carbamate.

II.1.17 Synthesis of (9*H*-fluoren-9-yl)methyl-(2-amino-4-bromophenyl)(4-bromo-2-nitrobenzyl)carbamate



(9*H*-fluoren-2-yl)methyl-(4-bromo-2-((*tert*-butoxycarbonyl)amino)phenyl)(4-bromo-2-nitrobenzyl)carbamate (599 mg, 828 μ mol) was dissolved in 25 mL DCM and 10 mL TFA was added. The reaction mixture was stirred at rt. for 16 h and neutralized with saturated aqueous NaHCO₃ subsequently. The organic layer was separated and the aqueous layer was extracted twice with 100 mL. The combined organic layers were dried over MgSO₄ and the solvent was evaporated to obtain a pale yellow solid (518 mg, 827 μ mol, quant.) which was used without further purification.

melting point: 185 °C

¹H-NMR (600 MHz, CDCl₃, 298 K): δ = 8.06 (d, ⁴*J* = 1.9 Hz, 1 H, Ar-*H*), 7.73-7.61 (m, 3 H, Ar-*H*), 7.39-7.33 (m, 3 H, Ar-*H*), 7.25-7.11 (m, 4 H, Ar-*H*), 6.82 (br. s, 1 H, Ar-*H*), 6.70 (br. s, 1 H, Ar-*H*), 6.47 (br. s, 1 H, Ar-*H*), 5.11 (br. s, 1 H, -CH₂), 4.88 (br. s, 1 H, -CH₂), 4.49 (d, ²*J* = 19.9 Hz 2 H, Fmoc-CH₂), 4.07 (br. s, 1 H, Fmoc-CH), 3.50 (br. s, 2 H, -NH₂) ppm.

¹³C{¹H}-NMR (150 MHz, CDCl₃, 298 K): δ = 143.2, 140.9, 135.9, 132.3, 129.8, 127.41, 127.25, 126.6, 124.4, 122.3, 119.5, 67.7, 48.3, 46.7 ppm.

IR (ATR): $\tilde{\nu}$ = 3388 (m), 2925 (m), 2850 (w), 1704 (s), 1621 (m), 1523 (s), 1496 (s), 1450 (m), 1413 (s), 1394 (w), 1351 (m), 1297 (s), 1278 (w), 1229 (m), 1198 (w), 1182 (w), 1161 (m), 1139 (m), 1101 (w), 1066 (w), 1025 (m), 992 (m), 889 (w), 877 (m), 857 (w), 792 (m), 763 (s), 738 (s), 698 (w), 620 (w), 589 (w), 538 (w), 503 (w) cm⁻¹.

HR-MS (ESI, CHCl₃/MeOH): *m/z* [M+H]⁺ calculated for C₂₈H₂₁O₄N₃Br₂+H⁺: 621.9972; found: 621.9975 \pm 0.49 ppm.

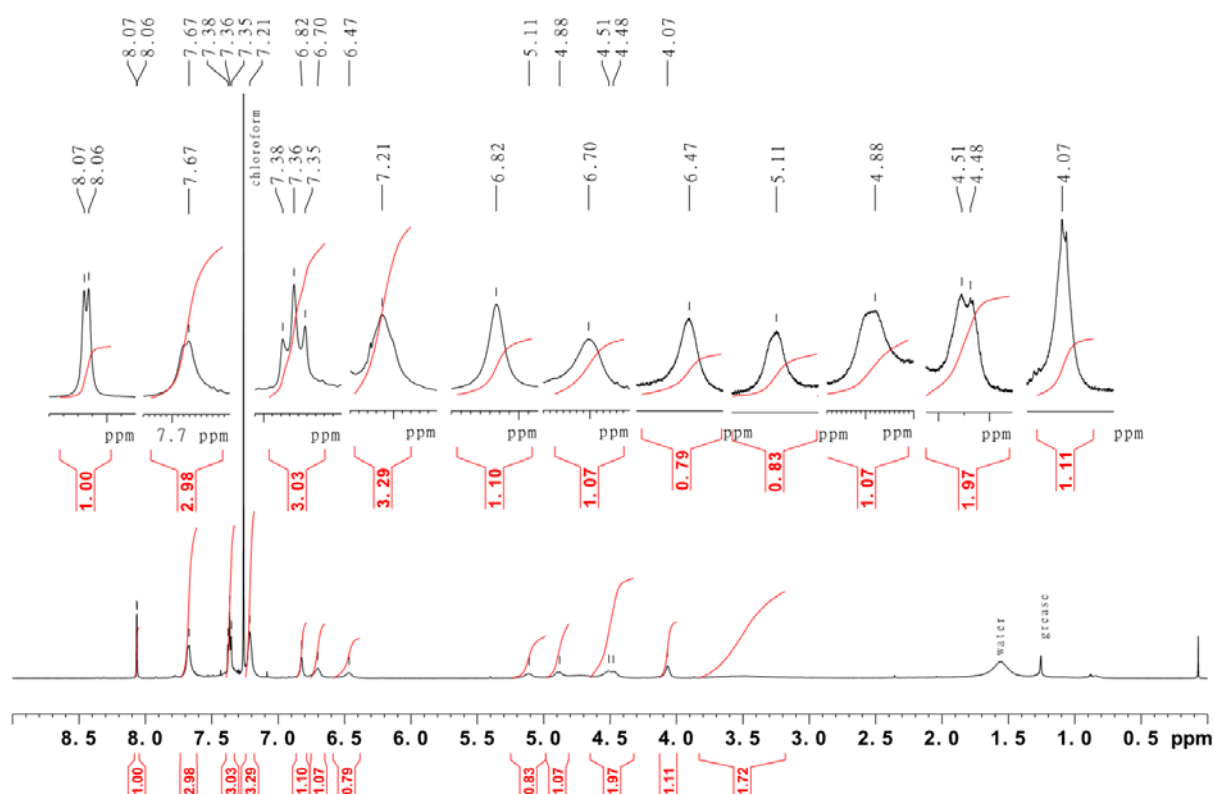


Figure SII.65: 600 MHz ^1H -NMR spectrum of (9*H*-fluoren-9-yl)methyl-(2-amino-4-bromophenyl)(4-bromo-2-nitrobenzyl)carbamate.

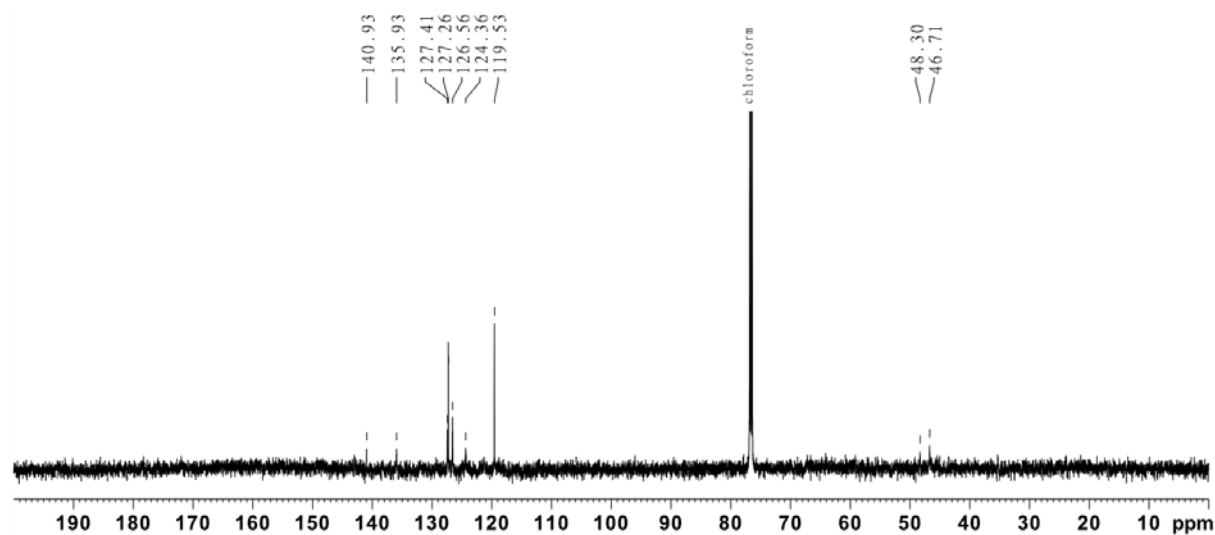


Figure SII.66: 150 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (9*H*-fluoren-9-yl)methyl-(2-amino-4-bromophenyl)(4-bromo-2-nitrobenzyl)carbamate.

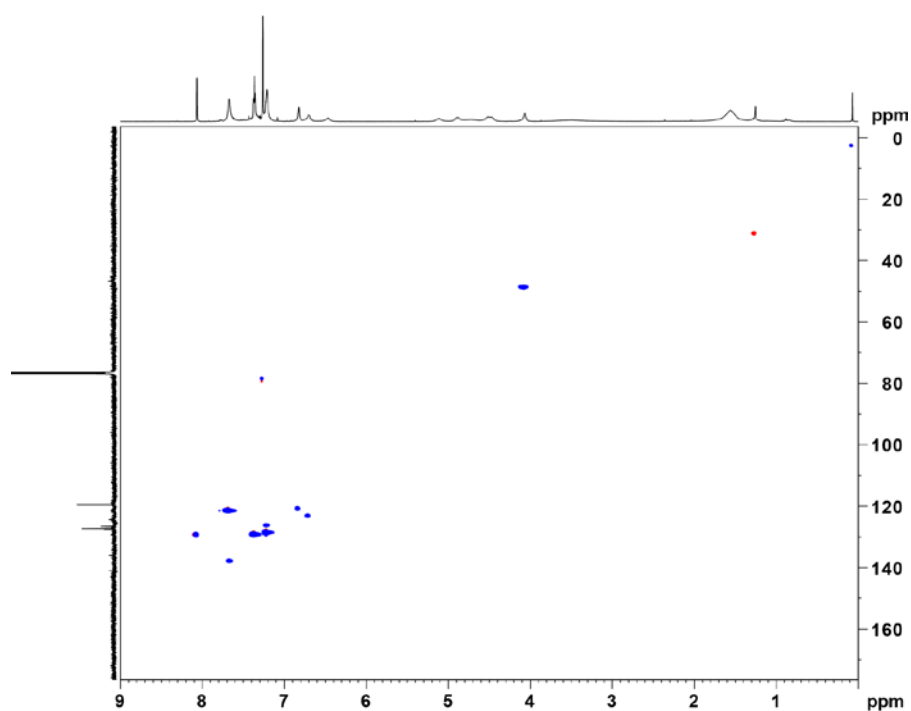


Figure SII.67: 600 MHz ^1H - ^{13}C HSQC spectrum of (9*H*-fluoren-9-yl)methyl-(2-amino-4-bromophenyl)(4-bromo-2-nitrobenzyl)carbamate.

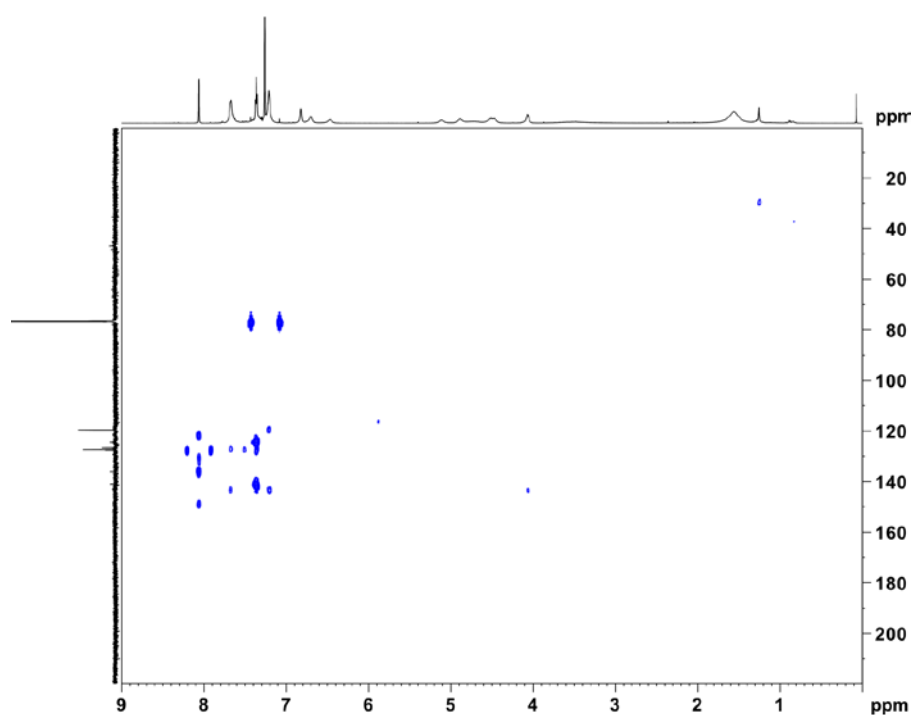
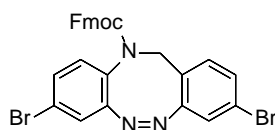


Figure SII.68: 600 MHz HMBC spectrum of (9*H*-fluoren-9-yl)methyl-(2-amino-4-bromophenyl)(4-bromo-2-nitrobenzyl)carbamate.

II.1.18 Synthesis of (9*H*-fluoren-9-yl)methyl-(*Z*)-3,8-dibromodibenzo[*c,g*][1,2,5]triazocin-11(12*H*)carboxylate



(9*H*-fluoren-9-yl)methyl-(2-amino-4-bromophenyl)(4-bromo-2-nitrobenzyl)carbamate (500 mg, 802 μ mol) was suspended in 50 mL EtOH and $\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$ (1.09 g, 4.81 mmol) was added. The reaction mixture was heated to 75 °C with an oil bath, zinc-powder (420 mg, 6.42 mmol) was added and it was stirred at given temperature. After cooling to rt the reaction mixture was stirred at for 16 h and neutralized with saturated aqueous NaHCO_3 solution subsequently. The solvent was evaporated and 100 mL water and 100 mL DCM were added to the residue. The organic layer was separated and the aqueous layer was extracted twice with 100 mL DCM. The combined organic layers were dried over MgSO_4 and the solvent was evaporated. The residue was dissolved in 25 mL of acetic acid and *m*CPBA (277 mg, 1.60 mmol) dissolved in 25 mL acetic acid was added dropwise to the reaction mixture. The reaction mixture was stirred at rt. for 16 h and the solvent was evaporated in the following. 50 mL DCM and 50 mL half-concentrated aqueous NaHCO_3 solution were added to the residue. The organic layer was separated and the aqueous layer was extracted twice with 50 mL DCM. The combined organic layers were dried over MgSO_4 and the solvent was evaporated. After column chromatography on silica (ethyl acetate/cyclohexane = 1:4, R_f = 0.58) the product could be obtained as yellow solid (63.6 mg, 108 μ mol, 14%).

melting point: 91 °C

$^1\text{H-NMR}$ (600 MHz, CDCl_3 , 298 K): δ = 7.81-6.58 (m, 14 H, Ar-*H*), 4.92-4.03 (m, 5 H, - CH_2 , - CH_2' , Fmoc- CH_2 , Fmoc- CH) ppm.

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (150 MHz, CDCl_3 , 298 K): δ = 152.8, 143.4, 141.3, 131.23, 131.19, 130.94, 130.71, 127.7, 127.0, 124.8, 122.21, 122.00, 119.9, 67.7, 52.0, 46.9 ppm.

IR (ATR): $\tilde{\nu}$ = 2922 (s), 2853 (m), 2360 (w), 2347 (w), 2228 (w), 2169 (w), 2019 (w), 1980 (w), 1961 (w), 1705 (s), 1590 (w), 1464 (w), 1450 (m), 1390 (m), 1317 (m), 1296 (w), 1228 (m), 1176 (m), 1071 (m), 1026 (m), 870 (m), 818 (m), 757 (m), 737 (s), 655 (w), 620 (m), 590 (w), 547 (m), 521 (w), 458 (m) cm^{-1} .

HR-MS (ESI, DCM): m/z [$\text{M}+\text{H}$] $^+$ calculated for $\text{C}_{28}\text{H}_{19}\text{O}_2\text{N}_3\text{Br}_2+\text{H}^+$: 587.99169; found: 587.99067 \pm 1.74 ppm.

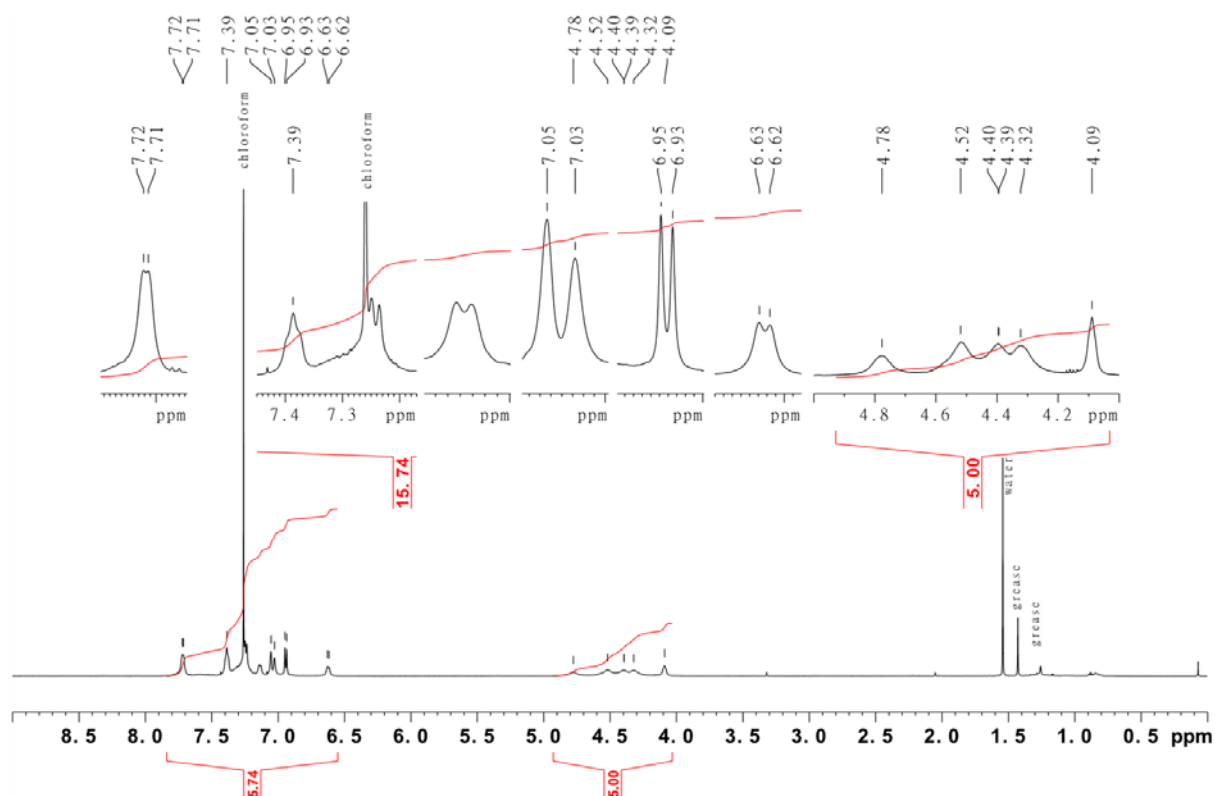


Figure SII.69: 600 MHz ^1H -NMR spectrum of (9*H*-fluoren-9-yl)methyl-(*Z*)-3,8-dibromodibenzo[*c,g*][1,2,5]triazocin-11(12*H*)carboxylate.

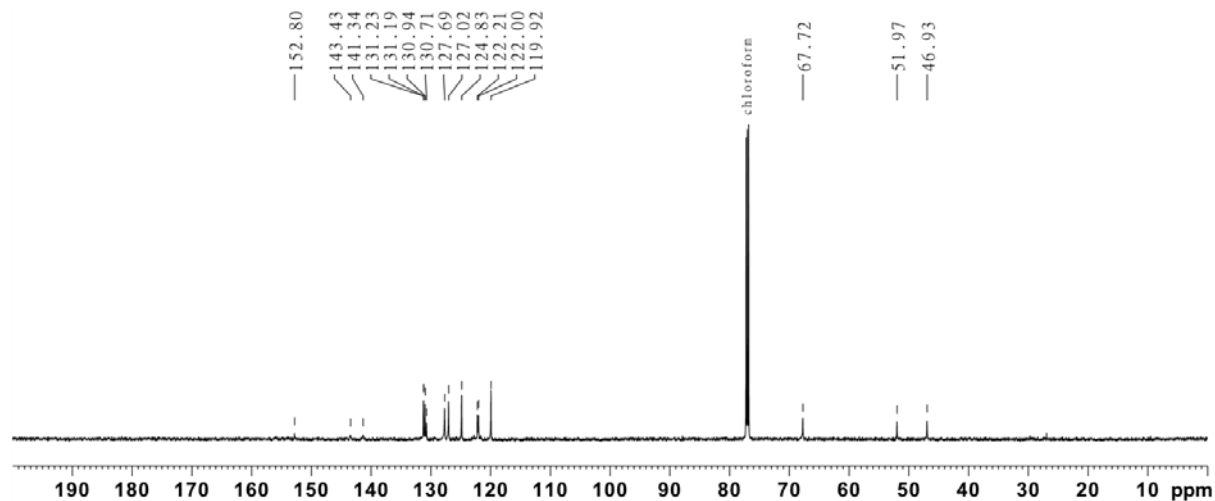


Figure SII.70: 150 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (9*H*-fluoren-9-yl)methyl-(*Z*)-3,8-dibromodibenzo[*c,g*][1,2,5]triazocin-11(12*H*)carboxylate.

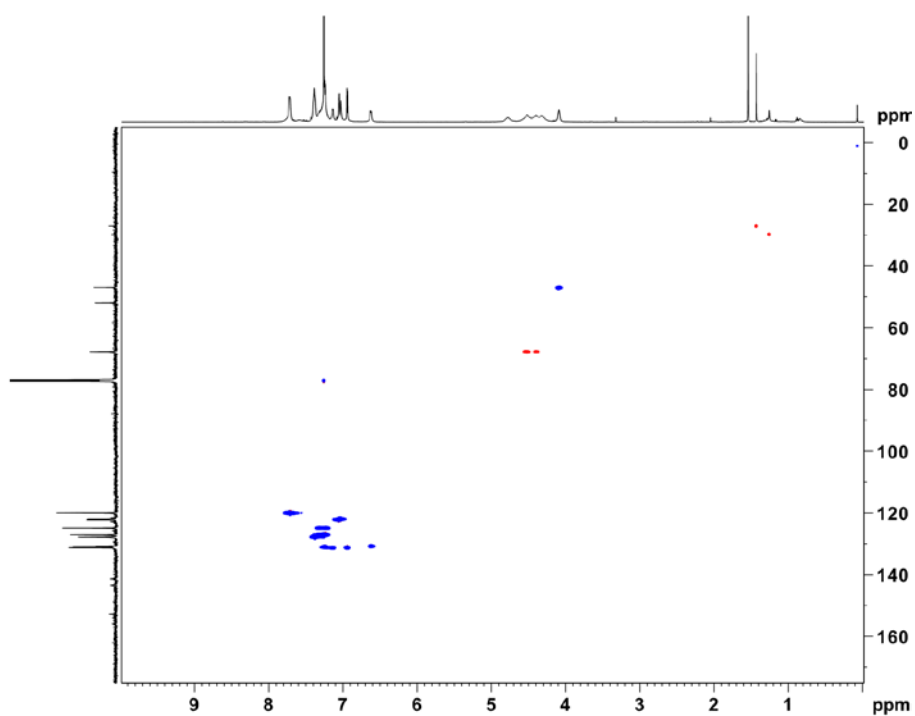


Figure SII.71: 600 MHz ^1H - ^{13}C HSQC spectrum of (9*H*-fluoren-9-yl)methyl-(*Z*)-3,8-dibromodibenzo[*c,g*][1,2,5]triazocin-11(12*H*)carboxylate.

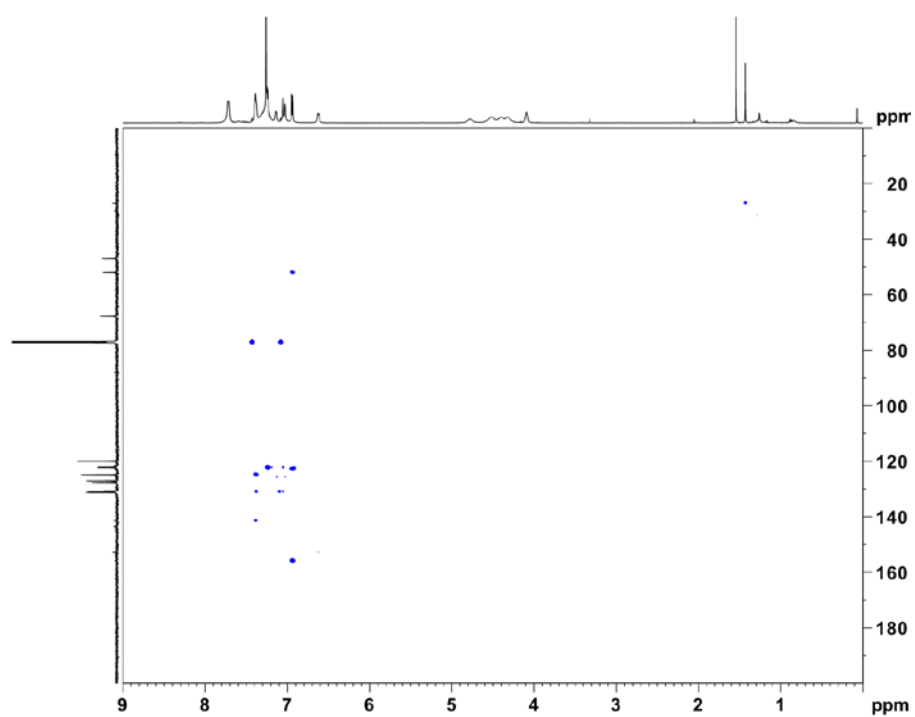
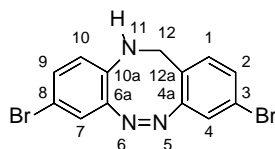


Figure SII.72: 600 MHz HMBC spectrum of (9*H*-fluoren-9-yl)methyl-(*Z*)-3,8-dibromodibenzo[*c,g*][1,2,5]triazocin-11(12*H*)carboxylate.

II.1.19 Synthesis of (Z)-3,8-dibromo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine



(9*H*-fluoren-9-yl)methyl-(*Z*)-3,8-dibromodibenzo[c,g][1,2,5]triazocin-11(12*H*)carboxylate (30.0 g, 50.9 μmol) was dissolved in 50 mL of DCM and 50 mL NEt_3 was added. The reaction mixture was stirred at rt. for 16 h. the solvent was evaporated and column chromatography on silica (ethyl acetate/cyclohexane 1:3, R_f = 0.32) gave a red solid (12.0 mg, 32.7 μmol , 64%).

melting point: 191 $^{\circ}\text{C}$

$^1\text{H-NMR}$ (600 MHz, CDCl_3 , 298 K): δ = 7.38 (dd, 3J = 8.1 Hz, 4J = 2.0 Hz, 1 H, *H*-2), 7.33 (d, 4J = 1.9 Hz, 1 H, *H*-4), 7.10 (d, 3J = 8.1 Hz, 1 H, *H*-1), 7.00 (dd, 3J = 8.6 Hz, 4J = 2.3 Hz, 1 H, *H*-9), 6.96 (d, 4J = 2.2 Hz, 1 H, *H*-10), 6.31 (d, 3J = 8.6 Hz, 1 H, *H*-7), 4.08-3.81 (m, 3 H, -NH, *H*-12) ppm.

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (150 MHz, CDCl_3 , 298 K): δ = 158.6 (C-4a), 144.4 (C-6a), 134.3 (C-10-a), 131.8 (C-2), 131.4 (C-9), 130.8 (C-1), 125.7 (C-10), 122.8 (C-4), 122.3 (C-3), 121.6 (C-12a), 120.5 (C-7), 110.3 (C-8), 47.1 (CH_2) ppm.

IR (ATR): $\tilde{\nu}$ = 3307 (m), 2920 (m), 2360 (w), 2177 (w), 2020 (w), 1735 (w), 1588 (m), 1563 (w), 1520 (w), 1501 (w), 1479 (s), 1451 (w), 1378 (m), 1316 (m), 1269 (m), 1244 (m), 1192 (w), 1160 (m), 1120 (m), 1091 (m), 1056 (m), 967 (w), 904 (w), 858 (m), 831 (m), 806 (m), 775 (m), 720 (w), 696 (w), 518 (s) cm^{-1} .

HR-MS (ESI, EtOAc): m/z [$\text{M}+\text{H}$] $^+$ calculated for $\text{C}_{13}\text{H}_9\text{N}_3^{79}\text{Br}_2+\text{H}^+$: 365.9236; found: 365.9233 \pm 0.89 ppm.

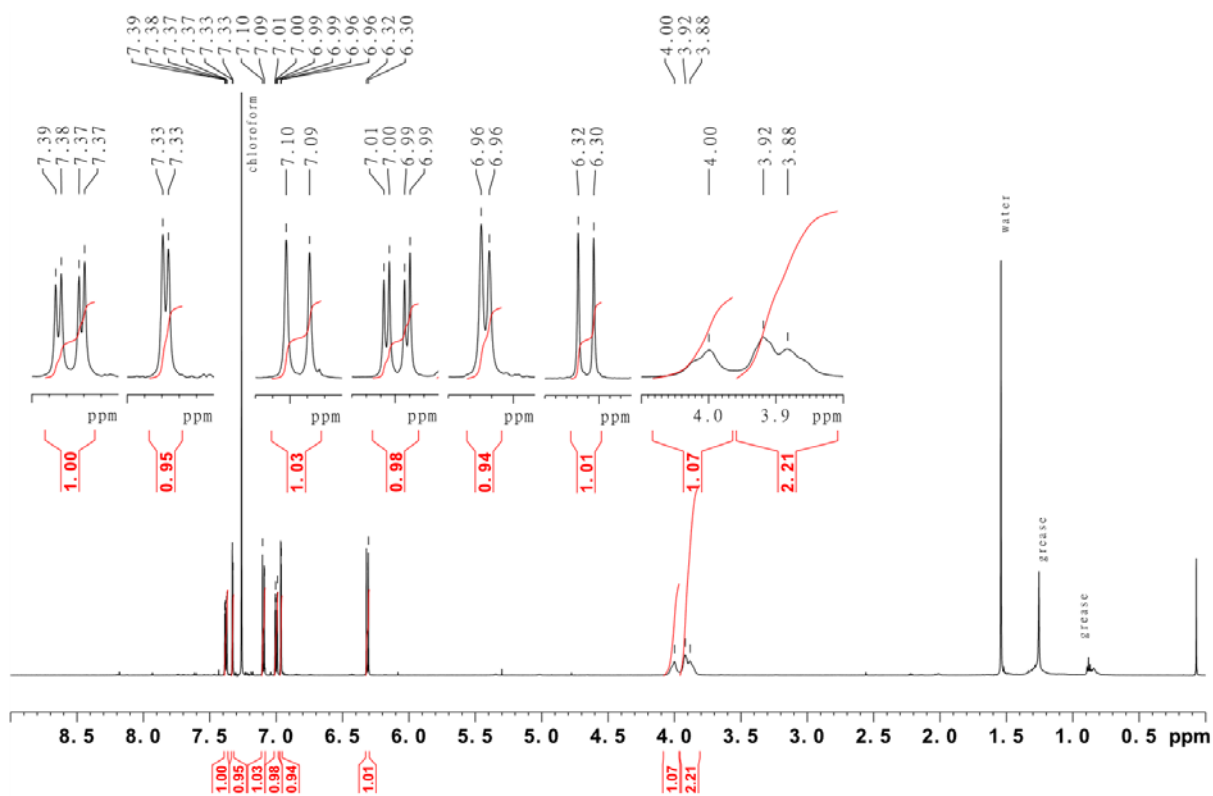


Figure SII.73: 600 MHz ^1H -NMR spectrum of (Z)-3,8-dibromo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine.

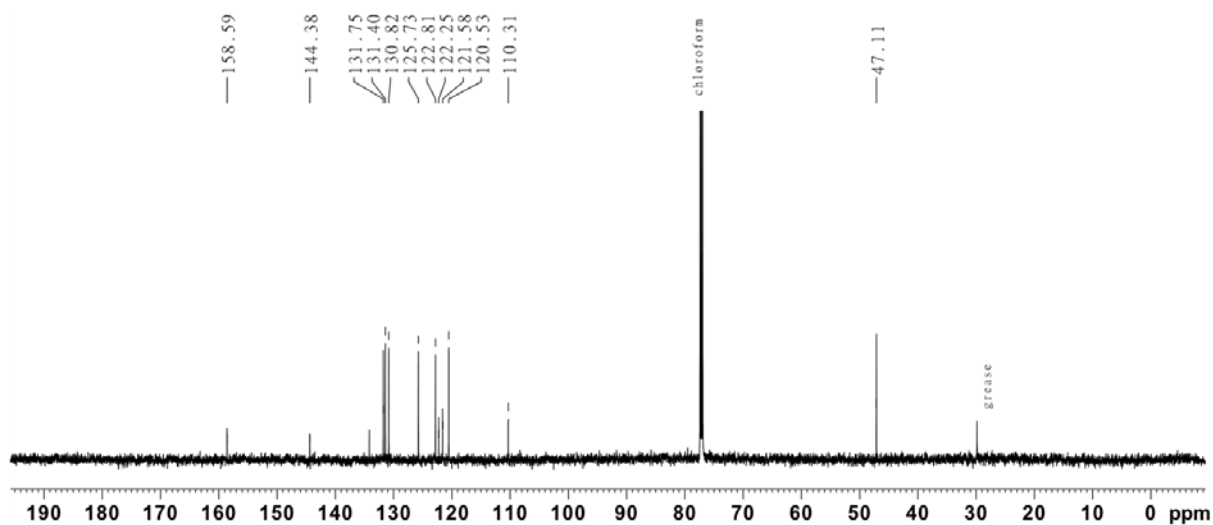


Figure SII.74: 150 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (Z)-3,8-dibromo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine.

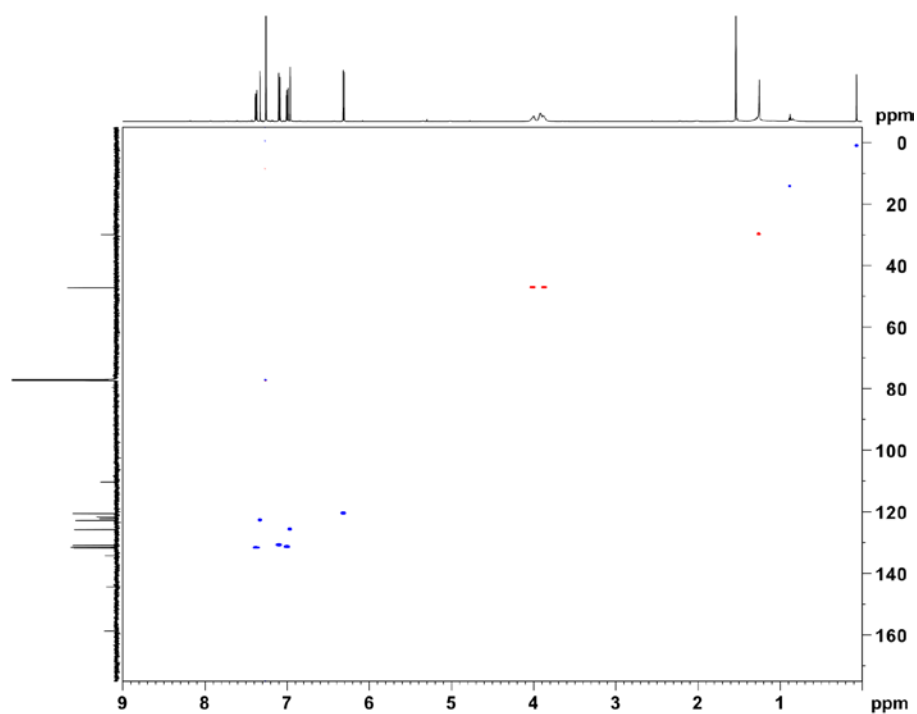


Figure SII.75: 600 MHz ^1H - ^{13}C HSQC spectrum of (Z)-3,8-dibromo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine.

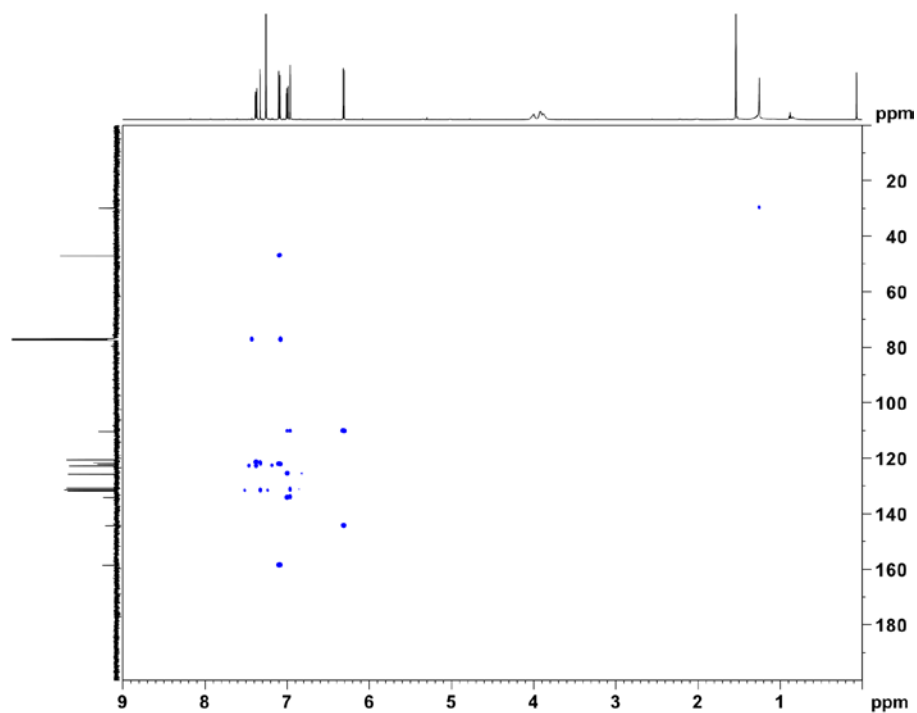
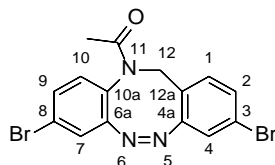


Figure SII.76: 600 MHz HMBC spectrum of (Z)-3,8-dibromo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine.

II.1.20 Synthesis of (Z)-(3,8-dibromodibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (4)



(Z)-3,8-dibromo-11,12-dihydrodibenzo[c,g][1,2,5]triazocine (12.0 mg, 32.7 μ mol) were dissolved in 1 mL anhydrous DMF under a nitrogen atmosphere. NEt₃ (36.4 μ L, 261 μ mol) and AcOH (19.0 μ L, 32.7 μ mol) were added. The reaction mixture was cooled to 0 °C and T3P (167 μ L, 327 μ mol, 50% in ethyl acetate) was added dropwise. The reaction mixture was stirred at rt. for 16 h. 10 mL DCM and 10 mL deionized water were added and the organic layer was separated. The aqueous layer was extracted twice with 10 mL DCM and the combined organic layers were dried over MgSO₄. The solvent was removed and column chromatography on silica (ethyl acetate/cyclohexane 1:1, *R_f* = 0.37) gave a yellow solid (11.5 mg, 28.1 μ mol, 86%).

melting point: 222 °C

¹H-NMR (500 MHz, CDCl₃, 298 K): δ = 7.32 (dd, ³*J* = 8.4 Hz, ⁴*J* = 2.2 Hz, 1 H, *H*-9), 7.25 (dd, ³*J* = 8.2 Hz, ⁴*J* = 2.0 Hz, 1 H, *H*-2), 7.12 (d, ⁴*J* = 2.1 Hz, 1 H, *H*-7), 7.07 (d, ⁴*J* = 1.8 Hz, 1 H, *H*-4), 6.95 (d, ³*J* = 8.2 Hz, 1 H, *H*-1), 6.92 (d, ³*J* = 8.4 Hz, 1 H, *H*-10), 5.01 (d, ²*J* = 15.2 Hz, 1 H, *H*-12), 4.28 (d, ²*J* = 14.5 Hz, 1 H, *H*-12'), 1.91 (s, 3 H, -CH₃) ppm.

¹³C{¹H}-NMR (125 MHz, CDCl₃, 198 K): δ = 169.8 (C=O), 155.8 (C-4a), 153.5 (C-6a), 131.9 (C-9), 131.44 (C-1), 131.17 (C-2), 130.3 (C-10), 127.6 (C-10a), 122.93 (C-8), 122.68 (C-7), 122.59 (C-12a), 122.44 (C-4), 51.4 (C-12), 23.2 (CH₃) ppm.

IR (ATR): $\tilde{\nu}$ = 2920 (m), 2851 (w), 1654 (s), 1589 (m), 1557 (w), 1523 (w), 1469 (m), 1372 (s), 1332 (m), 1291 (m), 1268 (w), 1241 (w), 1159 (m), 1112 (m), 1075 (m), 1034 (w), 968 (m), 940 (w), 925 (w), 882 (m), 858 (m), 844 (s), 807 (s), 760 (m), 731 (m), 689 (w), 657 (m), 601 (m), 572 (s), 465 (s) cm⁻¹.

HR-MS (ESI, DCM): *m/z* [M+H]⁺ calculated for C₁₅H₁₁O₁N₃Br₂+H⁺: 407.9342; found: 407.9335 \pm 1.62 ppm.

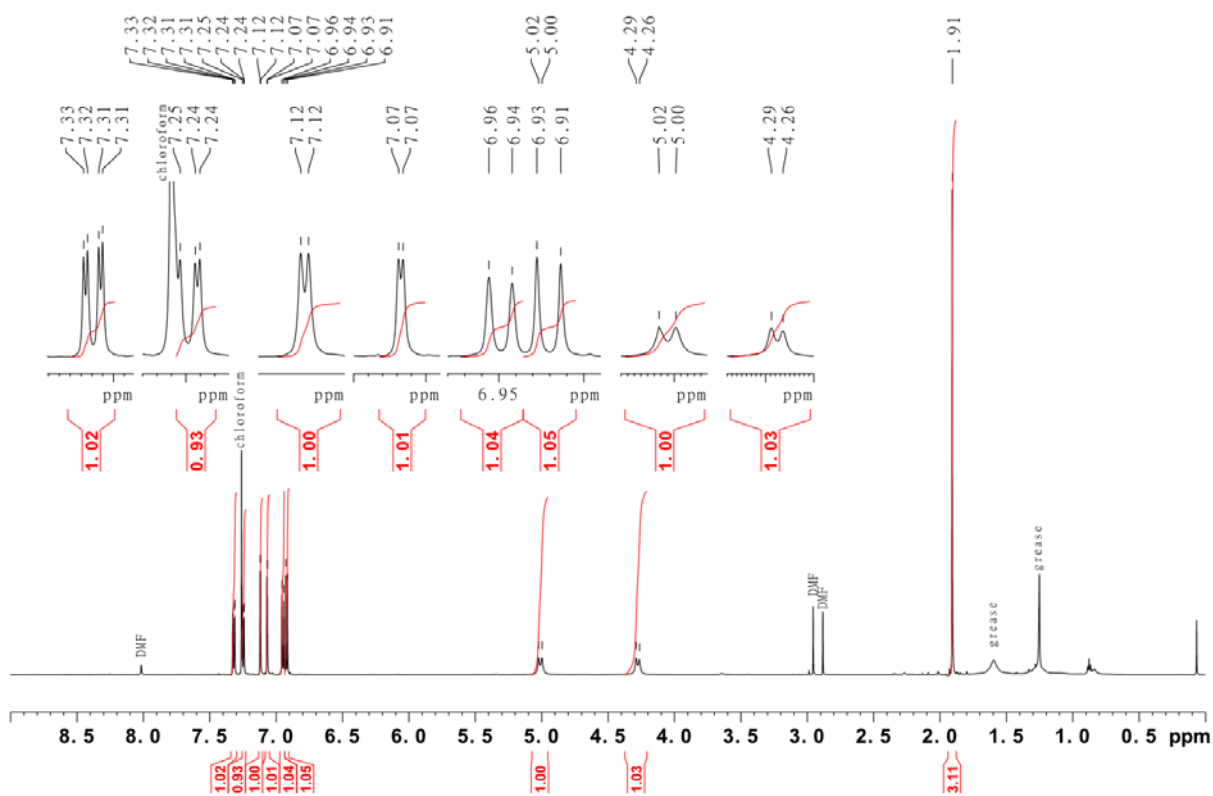


Figure SII.77: 500 MHz ^1H -NMR spectrum of (Z)-(3,8-dibromodibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**4**).

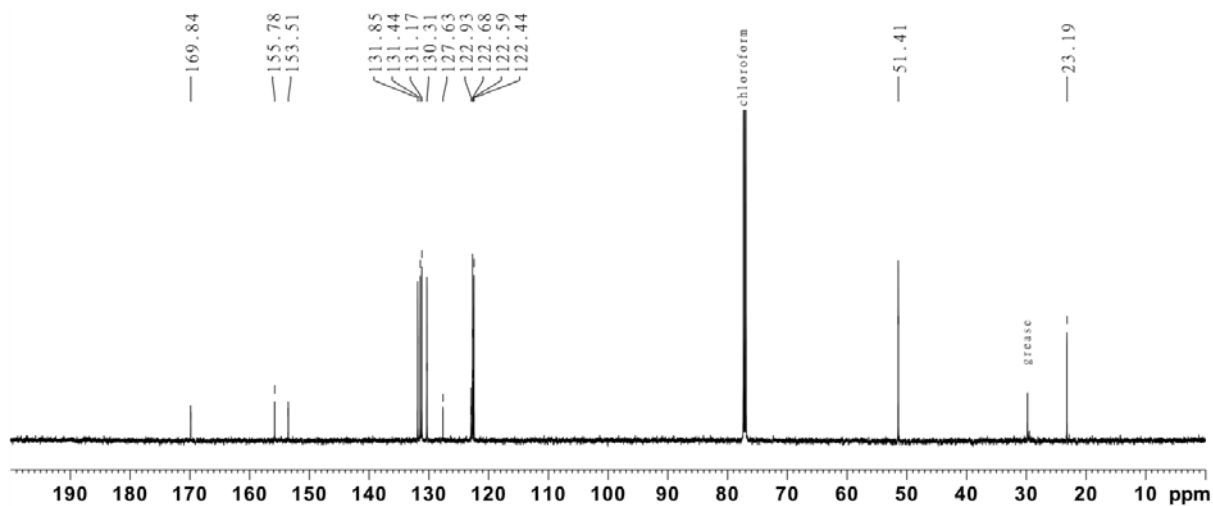


Figure SII.78: 125 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (Z)-(3,8-dibromodibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**4**).

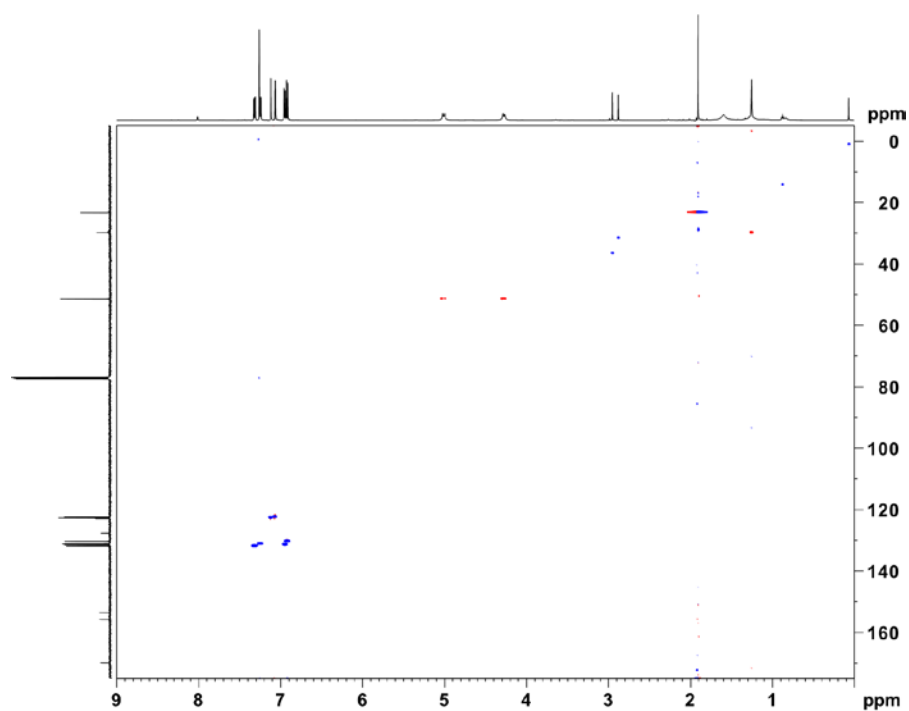


Figure SII.79: 500 MHz ^1H - ^{13}C HSQC spectrum of (Z)-(3,8-dibromodibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**4**).

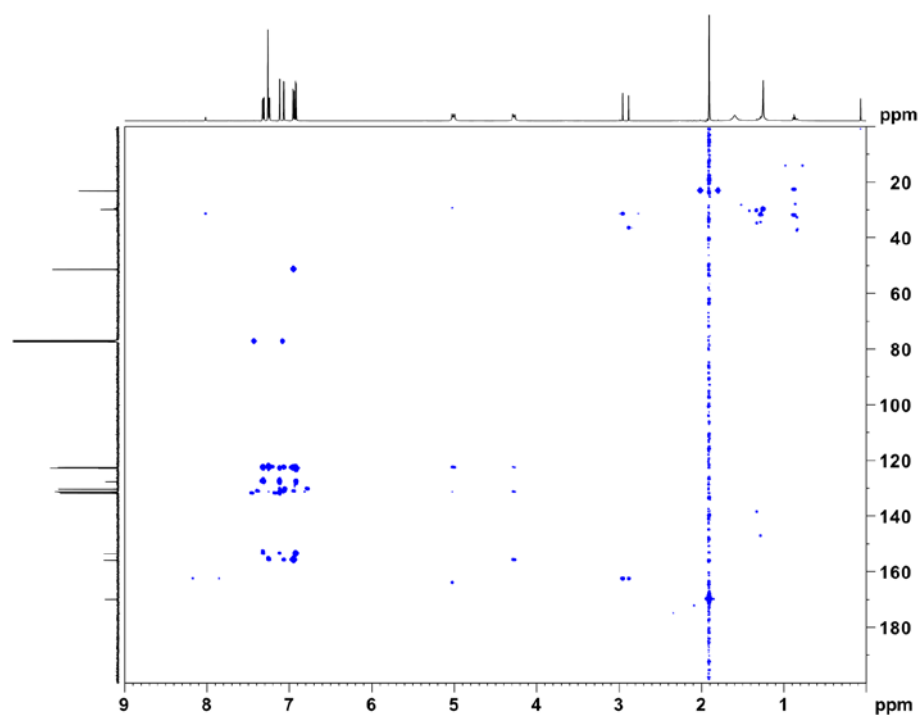
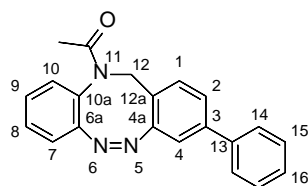


Figure SII.80: 500 MHz HMBC spectrum of (Z)-(3,8-dibromodibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**4**).

II.2 Syntheses of diazocine derivatives via cross-coupling reactions

II.2.1 Synthesis of (Z)-1-(3-phenyldibenzo[c,g][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (7)



Preparation via Stille-coupling:

Halogenated *N*-acetyl-diazocine (**2**: 20.0 mg, 60.6 μmol , **3**: 23.0 mg, 60.6 μmol) and $\text{Pd}(\text{P}t\text{Bu}_3)_2$ (3.1 mg, 6.06 μmol) were dissolved in 2 mL anhydrous THF and stirred at rt. for 10 min. Ph_3SnCl (23.4 mg, 60.6 μmol) was added and the reaction mixture was heated to 65 $^\circ\text{C}$ with an oil bath and stirred for 16 h at given temperature. After cooling to rt. deionized water and DCM were added and the reaction mixture was extracted with 10 mL DCM twice. The combined organic layers were dried over MgSO_4 and the solvent was evaporated. Column chromatography on silica (ethyl acetate/cyclohexane 1:1, R_f = 0.39) gave a mixture of starting material and product. The yield was determined via NMR (from bromide **2**: 1.9 mg, 5.67 μmol , 10%; from iodide **3**: 1.9 mg, 5.67 μmol , 10%).

Preparation via Suzuki-coupling:

Halogenated *N*-acetyl-diazocine (**2**: 20.0 mg, 60.6 μmol , **3**: 23.0 mg, 60.6 μmol), phenylboronic acid (14.8 mg, 121 μmol), $\text{Pd}(\text{PPh}_3)_4$ (2.45 mg, 2.12 μmol) and potassium carbonate (33.4 mg, 212 μmol) were dissolved in 2.4 mL of toluene/MeOH/deionized H_2O (5 : 1 : 2) under a nitrogen atmosphere, heated to 85 $^\circ\text{C}$ with an oil bath and stirred for 16 h at given temperature. After cooling to rt. the reaction mixture was extracted with 10 mL of DCM twice, dried over MgSO_4 and the solvent was evaporated. Column chromatography on silica (ethyl acetate/cyclohexane 1:1, R_f = 0.39) gave the product as yellow solid (from bromide **2**: 14.7 mg, 44.8 μmol , 74%; from iodide **3**: 16.5 mg, 50.3 μmol , 83%).

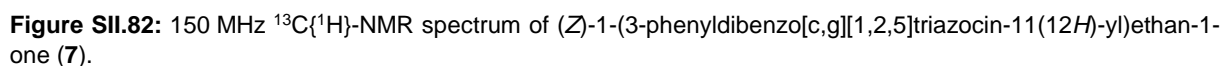
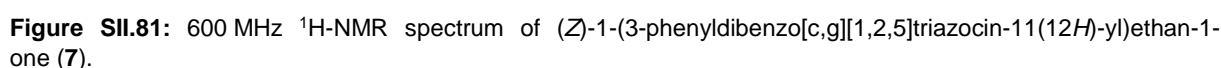
melting point: 187 $^\circ\text{C}$

^1H -NMR (600 MHz, acetone- d_6 , 298 K): δ = 7.61 (d, 3J = 8.4 Hz, 2 H, *H*-14), 7.46-7.42 (m, 3 H, *H*-2, *H*-15), 7.38-7.23 (m, 5 H, *H*-16, *H*-7/8/9/10, *H*-7/8/9/10, *H*-1, *H*-8/9), 7.18 (d, 4J = 1.8 Hz, 1 H, *H*-4), 7.04 (dd, 3J = 7.8 Hz, 4J = 1.2 Hz, 1 H, *H*-7/10), 5.11 (d, 2J = 14.6 Hz, 1 H, *H*-12), 4.35 (d, 2J = 14.6 Hz, 1 H, *H*-12'), 1.82 (s, 3 H, - CH_3) ppm.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (150 MHz, acetone- d_6 , 298 K): δ = 169.4 (C=O), 156.8 (C-4a), 154.4 (C-6a), 142.1 (C-3), 140.0 (C-13), 131.5 (C-1), 130.13 (C-7/8/9/10), 130.08 (C-7/8/9/10), 129.84 (C-15), 129.69 (C-10a), 129.26 (C-8/9), 128.9 (C-16), 127.7 (C-14), 126.6 (C-2), 124.1 (C-12a), 120.0 (C-7/10), 118.0 (C-4), 51.8 (C-12), 23.1 (CH_3), ppm.

IR (ATR): $\tilde{\nu}$ = 2925 (m), 1656 (s), 1612 (w), 1590 (w), 1478 (m), 1448 (w), 1373 (s), 1335 (m), 1287 (w), 1157 (w), 1106 (w), 1076 (w), 1035 (w), 967 (w), 950 (w), 922 (w), 891 (w), 873 (w), 835 (m), 759 (s), 702 (m), 633 (m), 600 (w), 570 (m), 542 (w), 514 (m), 491 (m), 451 (w), 439 (w), 405 (m) cm^{-1} .

HR-MS (ESI, acetone): m/z [$\text{M}+\text{H}$] $^+$ calculated for $\text{C}_{21}\text{H}_{17}\text{ON}_3+\text{H}^+$: 328.1444; found: 328.1440 \pm 1.35 ppm.



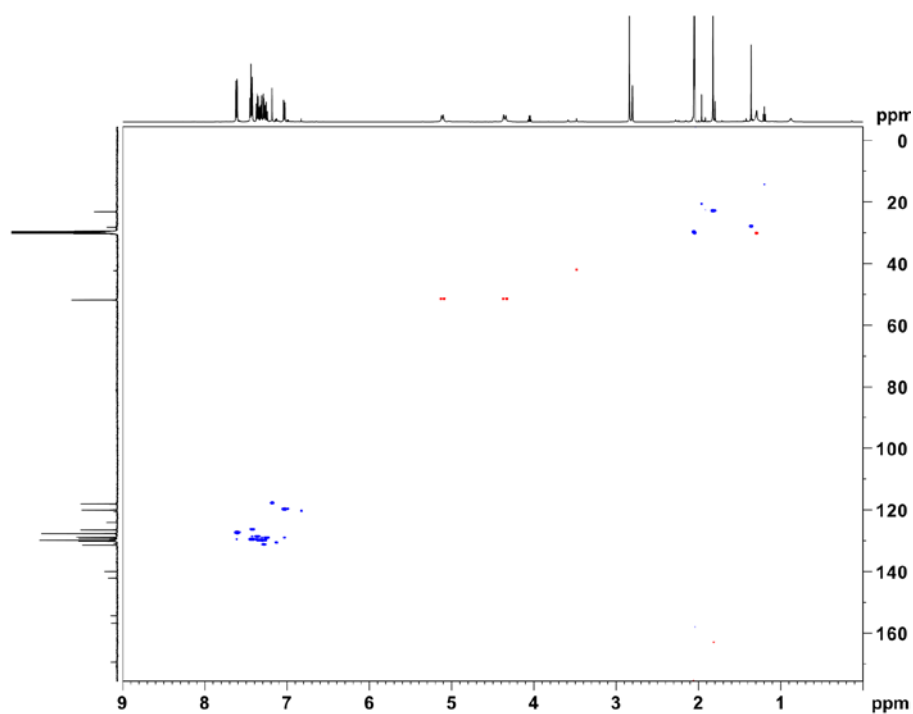


Figure SII.83: 600 MHz ^1H - ^{13}C HSQC spectrum of (Z)-1-(3-phenyldibenzo[c,g][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**7**).

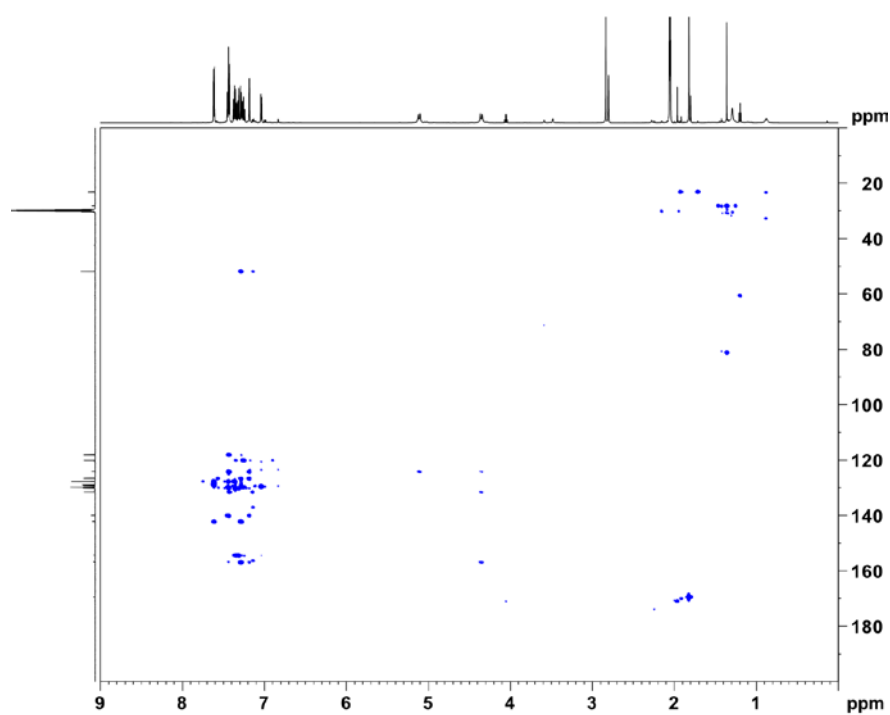
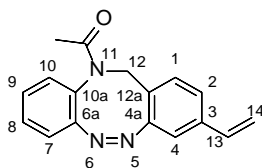


Figure SII.84: 600 MHz HMBC spectrum of (Z)-1-(3-phenyldibenzo[c,g][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**7**).

II.2.2 Synthesis of (Z)-1-(3-vinyldibenzo[c,g][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (8)



Preparation via Stille-coupling:

Halogenated *N*-acetyl-diazocine (**2**: 20.0 mg, 60.6 μmol , **3**: 23.0 mg, 60.6 μmol), $\text{Pd}(\text{OAc})_2$ and PPh_3 (12.7 mg, 48.5 μmol) were dissolved in 2 mL anhydrous DMF and stirred at rt. for 15 min. vinyltributyltin (57.7 mg, 181 μmol) was added and the reaction mixture was heated to 100 °C with an oil bath and stirred for 16 h at given temperature. After cooling to rt. brine and ethyl acetate were added and the organic layer was separated. The aqueous layer was extracted with 10 mL ethyl acetate twice. The combined organic layers were dried over MgSO_4 and the solvent was evaporated. Column chromatography on silica (ethyl acetate/cyclohexane 1:1, $R_f = 0.41$) gave the product as yellow solid (from bromide **2**: 10.9 mg, 39.4 μmol , 65%; from iodide **3**: 11.8 mg, 43.0 μmol , 71%).

Tin-free preparation following the DENMARK-procedure^[3]:

PdBr_2 (1.60 mg, 6.06 μmol) and JohnPhos (1.8 mg, 6.06 μmol) were suspended in 2 mL anhydrous THF, 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D_4^{V} , 13.4 μL , 38.8 μmol) and TBAF (1 M in THF, 242 μL , 242 μmol) were added and the reaction mixture was stirred for 10 min. at rt. The halogenated *N*-acetyl diazocine (**2**: 20.0 mg, 60.6 μmol , **3**: 23.0 mg, 60.6 μmol) was added, the reaction mixture was heated to 50 °C with an oil bath, stirred for 16 h at given temperature and the solvent was evaporated subsequently. After column chromatography on silica (ethyl acetate/cyclohexane, $R_f = 0.39$) the product could be obtained as yellow solid (from bromide **2**: 12.4 mg, 44.8 μmol , 74%; from iodide **3**: 13.0 mg, 46.9 μmol , 78%).

melting point: 144 °C

$^1\text{H-NMR}$ (500 MHz, acetone- d_6 , 298 K): $\delta = 7.35$ (td, $^3J = 7.6$ Hz, $^4J = 1.4$ Hz, 1 H, *H*-8), 7.29 (dd, $^3J = 7.9$ Hz, $^4J = 1.7$ Hz, 1 H, *H*-10), 7.25 (dd, $^3J = 7.3$ Hz, $^4J = 1.4$ Hz, 1 H, *H*-7), 7.22 (dd, $^3J = 7.9$ Hz, $^4J = 1.8$ Hz, 1 H, *H*-2), 7.17 (d, $^3J = 7.9$ Hz, 1 H, *H*-1), 7.02-6.97 (m, 2 H, *H*-4, *H*-9), 6.68 (dd, $^2J = 17.6$ Hz, $^3J = 10.9$ Hz, 1 H, *H*-13), 5.81 (dd, $^2J = 17.6$ Hz, $^4J = 0.7$ Hz, 1 H, *H*-14), 5.27 (dd, $^3J = 10.9$ Hz, $^4J = 0.7$ Hz, 1 H, *H*-14'), 5.04 (d, $^2J = 14.5$ Hz, 1 H, *H*-12), 4.30 (d, $^2J = 14.7$ Hz, 1 H, *H*-12'), 1.80 (s, 3 H, -CH₃) ppm.

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (125 MHz, acetone- d_6 , 298 K): $\delta = 169.3$ (C=O), 156.5 (C-4a), 154.3 (C-6a), 139.0 (C-3), 136.3 (C-13), 131.1 (C-1), 130.11 (C-10), 130.04 (C-8), 129.7 (C-10a), 129.2 (C-7), 126.0 (C-2), 124.5 (C-12a), 120.0 (C-9), 117.4 (C-4), 116.0 (C-14), 51.8 (C-12), 23.1 (CH₃), ppm.

IR (ATR): $\tilde{\nu} = 2956$ (w), 2922 (m), 1651 (s), 1591 (w), 1513 (w), 1479 (m), 1450 (w), 1431 (w), 1378 (s), 1339 (s), 1303 (m), 1252 (w), 1147 (w), 1109 (w), 1077 (w), 1031 (w), 995 (m), 962 (w), 926 (w), 911 (m), 885 (w), 845 (m), 766 (m), 742 (m), 665 (m), 630 (w), 601 (w), 585 (m), 570 (w), 529 (w) cm^{-1} .

HR-MS (ESI, acetone): m/z $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{15}\text{ON}_3+\text{H}^+$: 278.1288 found: 278.1287 ± 0.49 ppm.

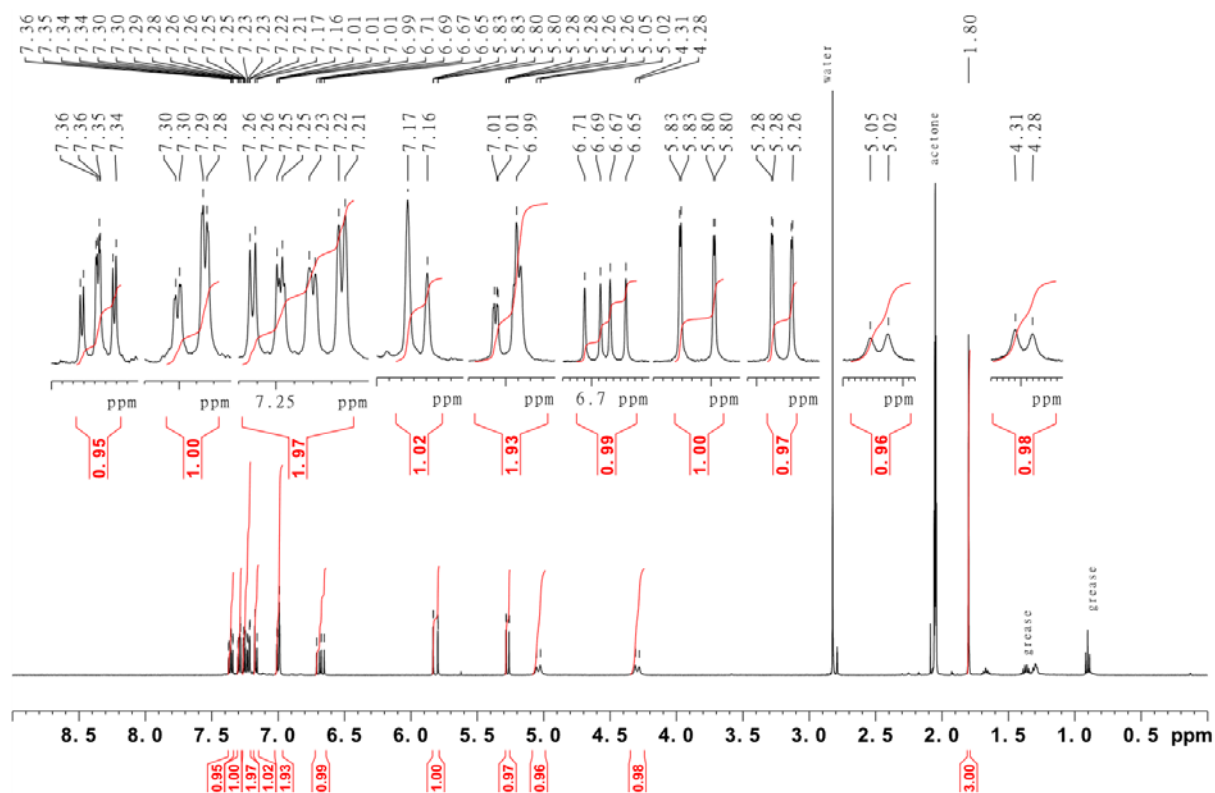


Figure SII.85: 500 MHz ^1H -NMR spectrum of (Z)-1-(3-vinyldibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**8**).

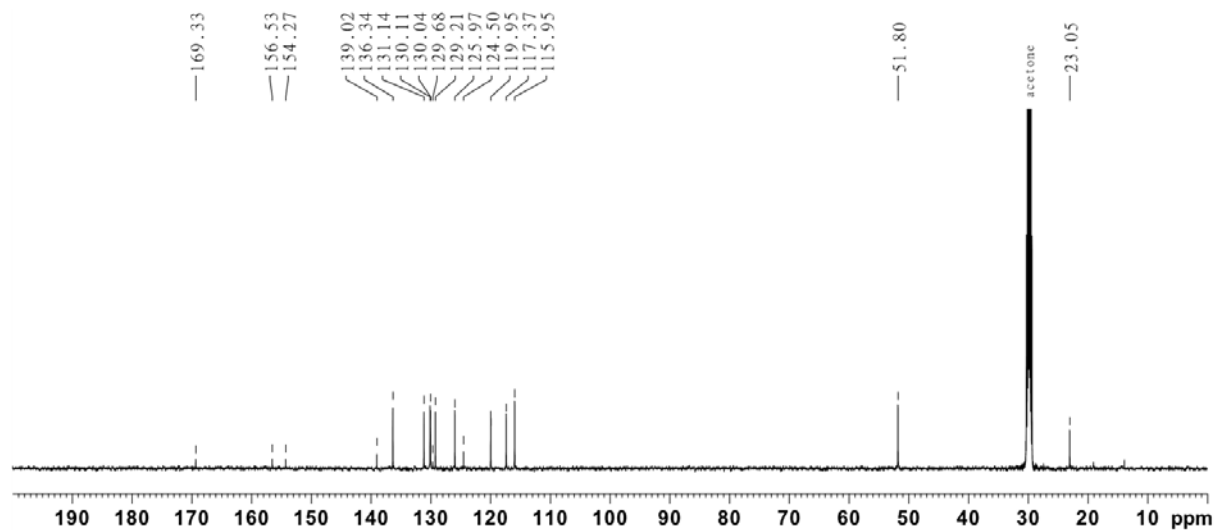


Figure SII.86: 125 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (Z)-1-(3-vinyldibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**8**).

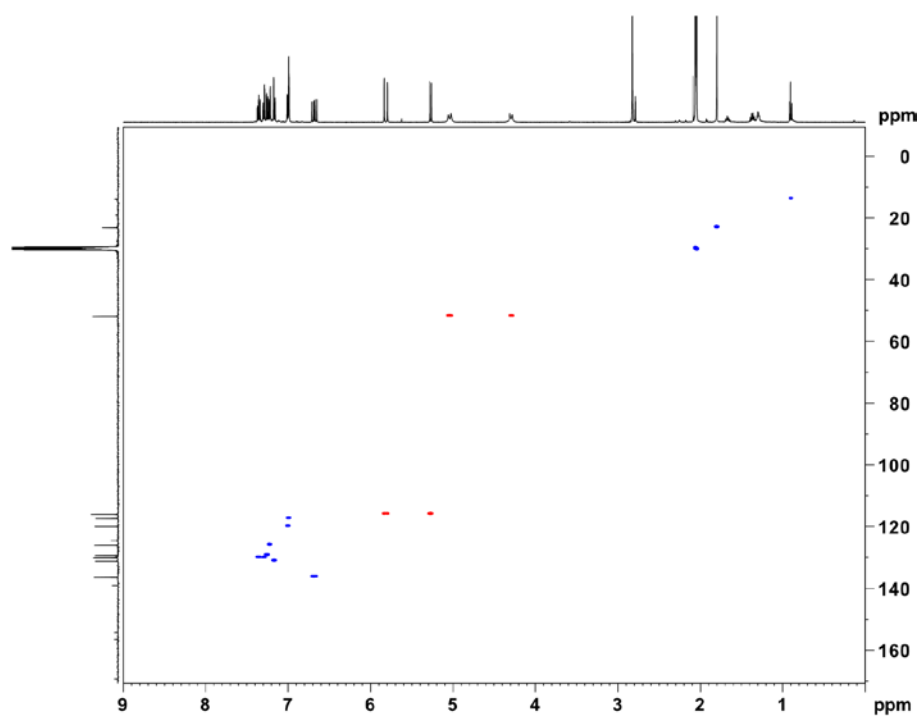


Figure SII.87: 500 MHz ^1H - ^{13}C HSQC spectrum of (*Z*)-1-(3-vinyldibenzo[c,g][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**8**).

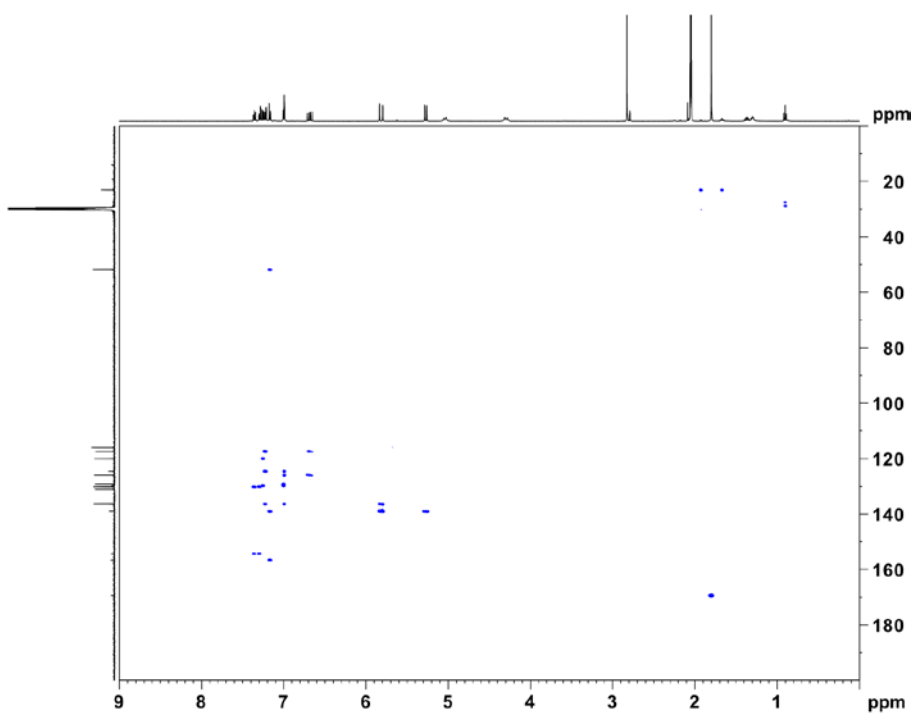
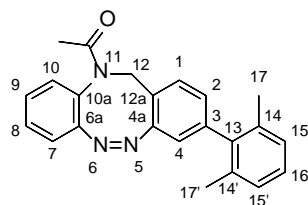


Figure SII.88: 500 MHz HMBC spectrum of (*Z*)-1-(3-vinyldibenzo[c,g][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**8**).

II.2.3 Synthesis of (Z)-1-(3-(2,6-dimethylphenyl)dibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (9)



Halogenated *N*-acetyl-diazocine (**2**: 20.0 mg, 60.6 μmol , **3**: 23.0 mg, 60.6 μmol), phenylboronic acid (18.2 mg, 121 μmol), $\text{Pd}(\text{PPh}_3)_4$ (2.45 mg, 2.12 μmol) and potassium carbonate (33.4 mg, 212 μmol) were dissolved in 2.4 mL of toluene/MeOH/deionized H_2O (5 : 1 : 2) under a nitrogen atmosphere, heated to 85 $^\circ\text{C}$ with an oil bath and stirred for 16 h at given temperature. After cooling to rt. the reaction mixture was extracted with 10 mL of DCM twice, dried over MgSO_4 and the solvent was evaporated. Column chromatography on silica (ethyl acetate/cyclohexane 1:1, R_f = 0.40) gave the product as yellow solid (from bromide **2**: 14.6 mg, 41.1 μmol , 68%; from iodide **3**: 15.9 mg, 44.8 μmol , 74%).

melting point: 203 $^\circ\text{C}$

^1H -NMR (600 MHz, acetone- d_6 , 298 K): δ = 7.35 (td, 3J = 7.5 Hz, 4J = 1.5 Hz, 1 H, *H*-8), 7.29-7.24 (m, 3 H, *H*-1, *H*-9, *H*-10), 7.12 (t, 3J = 7.3 Hz, 1 H, *H*-14), 7.10 (d, 3J = 7.2 Hz, 1 H, *H*-15), 7.01 (d, 3J = 6.6 Hz, 1 H, *H*-15'), 6.99 (dd, 3J = 7.9 Hz, 4J = 1.1 Hz, 1 H, *H*-7), 6.88 (dd, 3J = 7.7 Hz, 4J = 1.7 Hz, 1 H, *H*-2), 6.60 (d, 4J = 1.6 Hz, 1 H, *H*-4), 5.01 (d, 2J = 14.2 Hz, 1 H, *H*-12), 4.38 (d, 2J = 14.3 Hz, 1 H, *H*-12'), 2.08 (s, 3 H, *H*-17), 1.80 (s, 3 H, *-CH*₃), 1.55 (s, 3 H, *-17'*) ppm.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (150 MHz, acetone- d_6 , 298 K): δ = 169.3 (C=O), 157.1 (C-4a), 154.7 (C-6a), 142.6 (C-3), 141.0 (C-13), 136.5 (C-14'), 136.1 (C-14), 131.3 (C-1), 130.3 (C-10), 130.0 (C-10a), 129.8 (C-8), 129.0 (C-9), 128.8 (C-2), 128.30 (C-16), 128.21 (C-17), 128.17 (C-17'), 123.6 (C-12a), 119.72 (C-4), 119.64 (C-7), 52.0 (C-12), 23.2 (CH_3), 20.8 (C-17), 20.4 (C-17') ppm.

IR (ATR): $\tilde{\nu}$ = 3751 (w), 2922 (m), 2300 (w), 1728 (w), 1651 (s), 1613 (w), 1589 (w), 1509 (w), 1482 (m), 1464 (w), 1380 (s), 1339 (s), 1297 (w), 1244 (w), 1169 (w), 1104 (w), 1069 (m), 1033 (m), 987 (w), 966 (m), 928 (w), 877 (m), 856 (w), 833 (s), 777 (s), 742 (m), 663 (w), 637 (m), 599 (m), 581 (m) cm^{-1} .

HR-MS (ESI, acetone): m/z [$\text{M}+\text{H}$]⁺ calculated for $\text{C}_{23}\text{H}_{21}\text{ON}_3+\text{H}^+$: 356.1757; found: 356.1755 \pm 0.75 ppm.

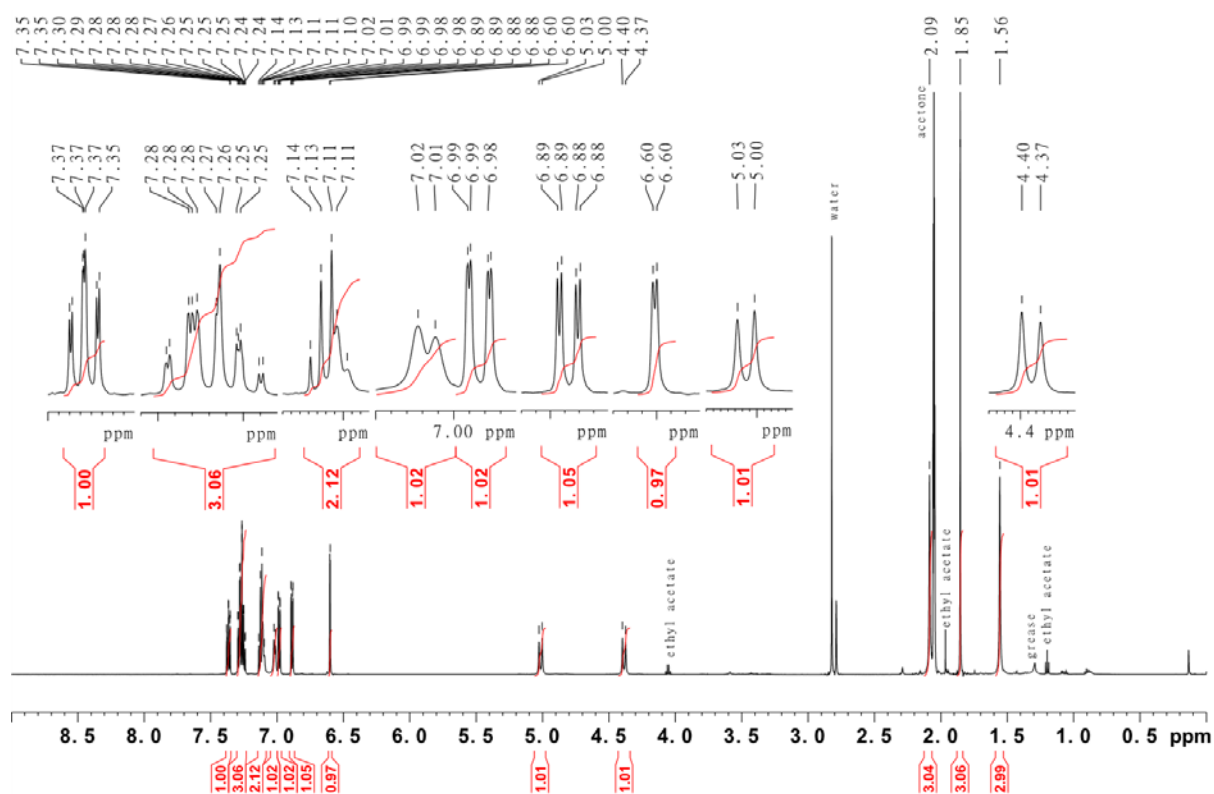


Figure SII.89: 600 MHz ^1H -NMR spectrum of (Z)-1-(3-(2,6-dimethylphenyl)dibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**9**).

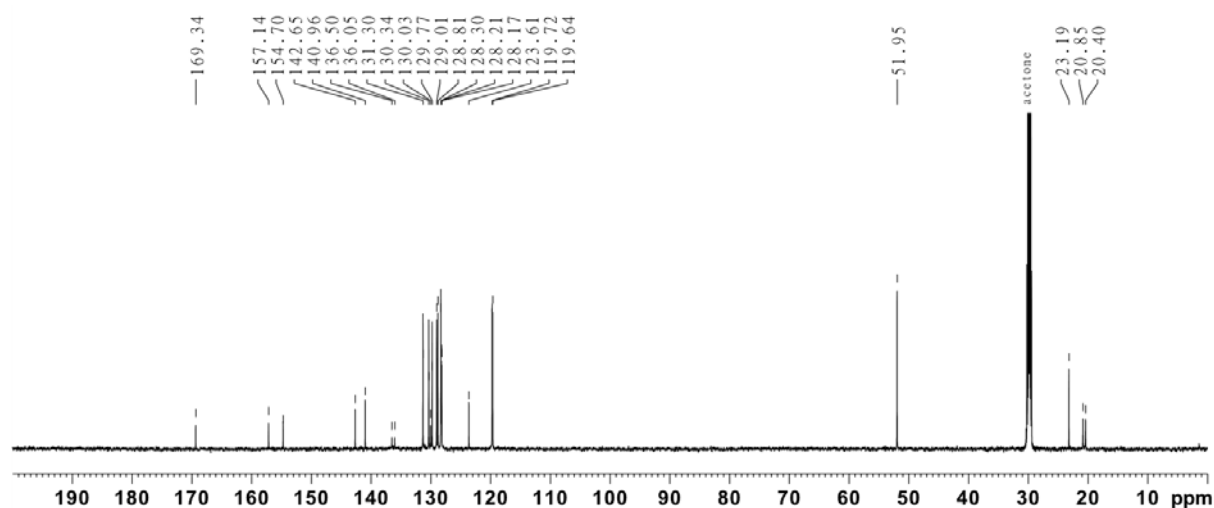


Figure SII.90: 150 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (Z)-1-(3-(2,6-dimethylphenyl)dibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**9**).

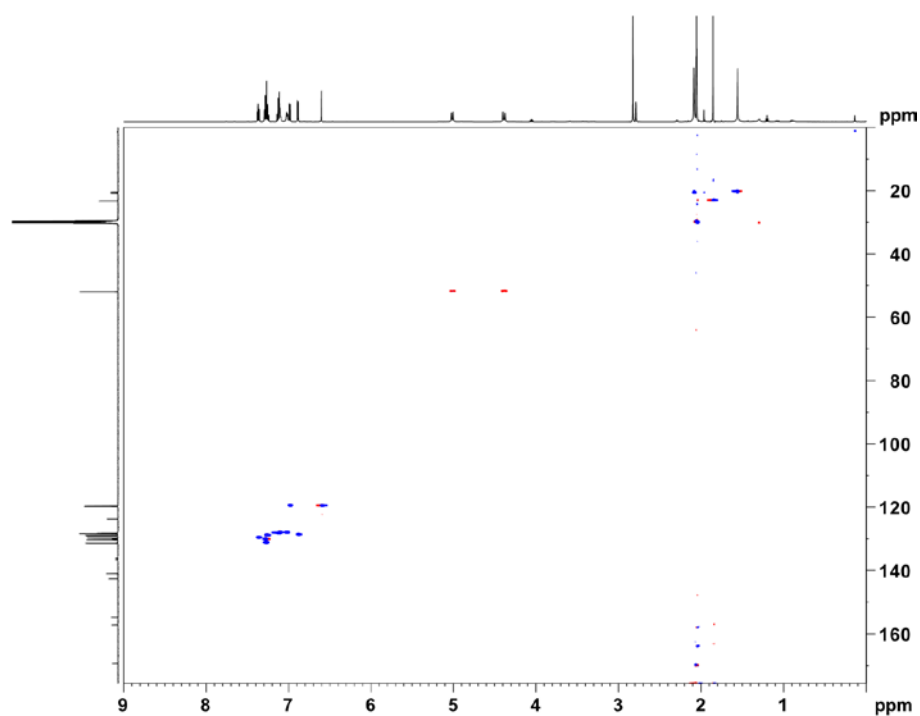


Figure SII.91: 600 MHz ^1H - ^{13}C HSQC spectrum of (*Z*)-1-(3-(2,6-dimethylphenyl)dibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**9**).

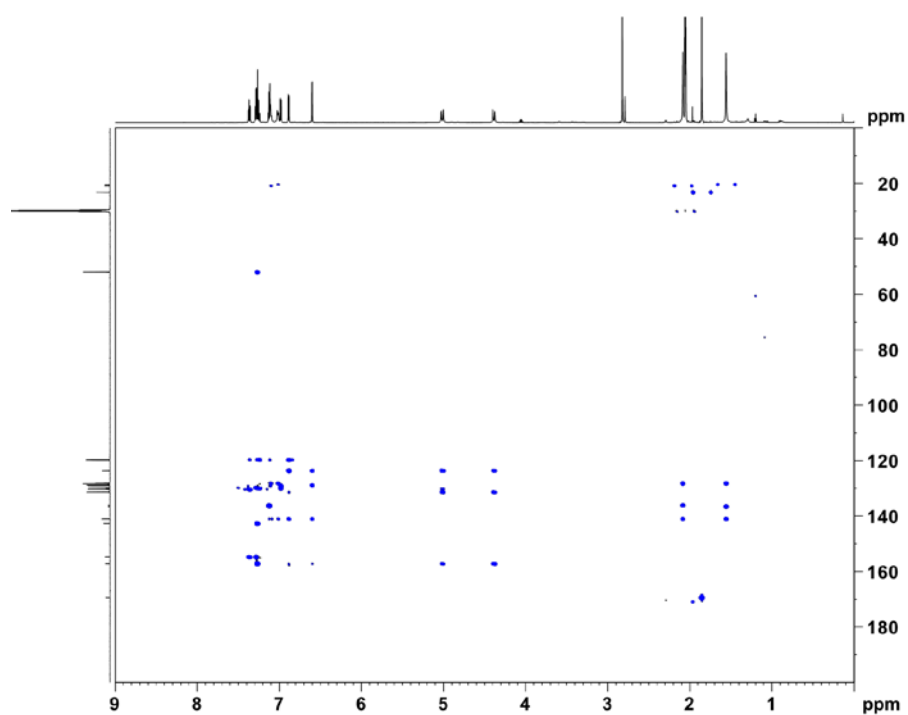
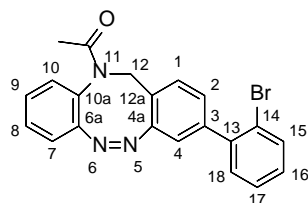


Figure SII.92: 600 MHz HMBC spectrum of (*Z*)-1-(3-(2,6-dimethylphenyl)dibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**9**).

II.2.4 Synthesis of (Z)-1-(3-(2-bromophenyl)dibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (10)



Halogenated *N*-acetyl-diazocine (**3**: 23.0 mg, 60.6 μmol), (2-bromophenyl)boronic acid (24.3 mg, 121 μmol), $\text{Pd}(\text{PPh}_3)_4$ (2.45 mg, 2.12 μmol) and potassium carbonate (33.4 mg, 212 μmol) were dissolved in 2.4 mL of toluene/MeOH/deionized H_2O (5 : 1 : 2) under a nitrogen atmosphere, heated to 85 $^\circ\text{C}$ with an oil bath and stirred for 16 h at given temperature. After cooling to rt. the reaction mixture was extracted with 10 mL of DCM twice, dried over MgSO_4 and the solvent was evaporated. Column chromatography on silica (ethyl acetate/cyclohexane 1:1, R_f = 0.45) gave the product as yellow solid (from iodide **3**: 20.2 mg, 49.7 μmol , 82%).

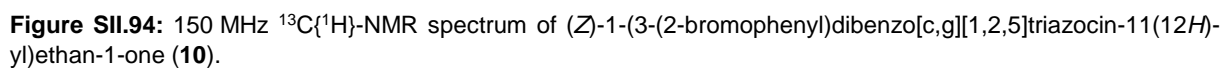
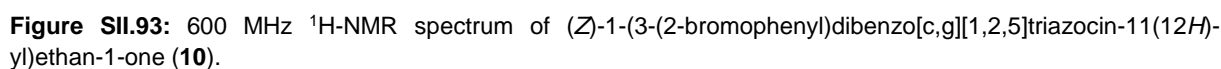
melting point: 119 $^\circ\text{C}$

$^1\text{H-NMR}$ (600 MHz, acetone- d_6 , 298 K): δ = 7.69 (d, 3J = 9.5 Hz, 1 H, Ar-*H*), 7.43 (td, 3J = 7.5 Hz, 4J = 1.2 Hz, 1 H, Ar-*H*), 7.38 (td, 3J = 7.7 Hz, 4J = 1.3 Hz, 1 H, Ar-*H*), 7.33-7.25 (m, 5 H), 7.16 (dd, 3J = 7.9 Hz, 4J = 1.8 Hz, 1 H, *H*-2), 7.04 (dd, 3J = 7.8 Hz, 4J = 1.2 Hz, 1 H, Ar-*H*), 6.94 (d, 4J = 1.7 Hz, 1 H, *H*-4), 5.11 (d, 2J = 14.4 Hz, 1 H, *H*-12), 4.37 (d, 2J = 14.6 Hz, 1 H, *H*-12'), 1.83 (s, 3 H, - CH_3) ppm.

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (150 MHz, acetone- d_6 , 298 K): δ = 169.4 (C=O), 156.0 (C-4a), 154.5 (C-6a), 142.2 (C-Ar), 141.7 (C-3), 134.1 (C-Ar), 1320 (C-Ar), 130.7 (C-1), 130.5 (C-Ar), 130.15 (C-Ar), 130.06 (C-8), 129.7 (C-Ar), 129.3 (C-Ar), 128.8 (C-Ar), 124.6 (C-12a), 122.7 (C-Ar), 120.7 (C-4), 120.0 (C-Ar), 116.6 (C-Ar), 51.9 (C-12), 23.1 (CH_3) ppm.

IR (ATR): $\tilde{\nu}$ = 2922 (m), 2852 (w), 1654 (s), 1592 (w), 1485 (m), 1464 (m), 1433 (w), 1369 (s), 1334 (s), 1288 (w), 1242 (w), 1066 (w), 1023 (m), 971 (w), 933 (w), 879 (w), 842 (m), 752 (s), 729 (w), 699 (w), 659 (m), 603 (w), 569 (m), 533 (m), 430 (m) cm^{-1} .

HR-MS (ESI, DCM): m/z [$\text{M}+\text{H}$] $^+$ calculated for $\text{C}_{21}\text{H}_{16}\text{ON}_3^{79}\text{Br}+\text{H}^+$: 406.0550 found: 406.0547 \pm 0.54 ppm.



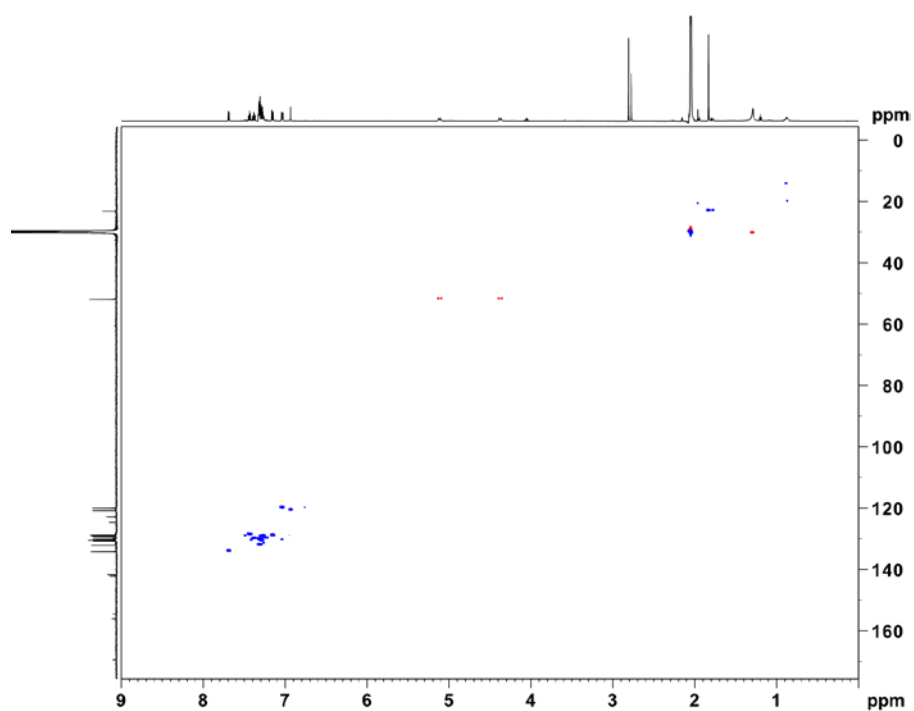


Figure SII.95: 600 MHz ^1H - ^{13}C HSQC spectrum of (*Z*)-1-(3-(2-bromophenyl)dibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**10**).

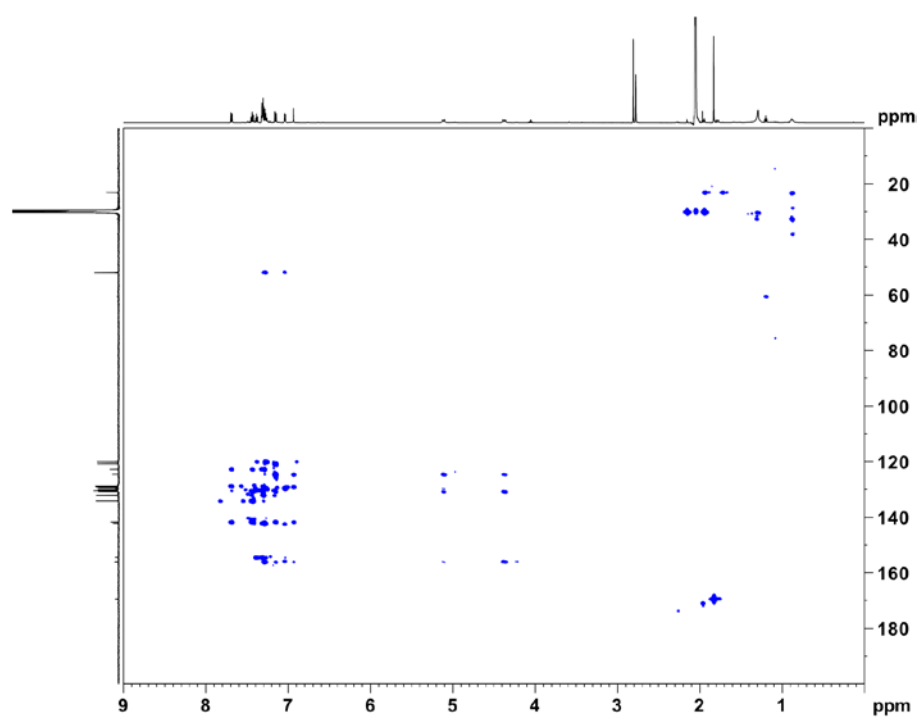
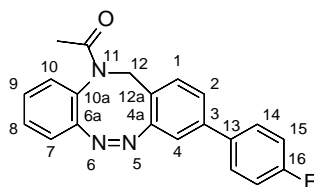


Figure SII.96: 600 MHz HMBC spectrum of (*Z*)-1-(3-(2-bromophenyl)dibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**10**).

II.2.5 Synthesis of (Z)-1-(3-(4-fluorophenyl)dibenzo[c,g][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (11)



Halogenated *N*-acetyl-diazocine (**2**: 20.0 mg, 60.6 μ mol, **3**: 23.0 mg, 60.6 μ mol), (2,6-dimethylphenyl)boronic acid (17.0 mg, 121 μ mol), Pd(PPh₃)₄ (2.45 mg, 2.12 μ mol) and potassium carbonate (33.4 mg, 212 μ mol) were dissolved in 2.4 mL of toluene/MeOH/deionized H₂O (5 : 1 : 2) under a nitrogen atmosphere, heated to 85 °C with an oil bath and stirred for 16 h at given temperature. After cooling to rt. the reaction mixture was extracted with 10 mL of DCM twice, dried over MgSO₄ and the solvent was evaporated. Column chromatography on silica (ethyl acetate/cyclohexane 1:1, *R_f* = 0.38) gave the product as yellow solid (from bromide **2**: 16.9 mg, 49.1 μ mol, 81%; from iodide **3**: 18.4 mg, 53.3 μ mol, 88%).

melting point: 203 °C

¹H-NMR (600 MHz, acetone-*d*₆, 298 K): δ = 7.67 (dd, ³*J* = 8.9 Hz, ³*J* = 5.3 Hz, 2 H, *H*-14), 7.41 (dd, ³*J* = 7.9 Hz, ⁴*J* = 1.9 Hz, 1 H, *H*-2), 7.36 (td, ³*J* = 7.6 Hz, ⁴*J* = 1.3 Hz, 1 H, *H*-8), 7.32 (dd, ³*J* = 7.9 Hz, ⁴*J* = 1.1 Hz, 1 H, *H*-10), 7.29 (d, ³*J* = 7.9 Hz, 1 H, *H*-1), 7.26 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.4 Hz, 1 H, *H*-9), 7.21 (t, ³*J* = 8.8 Hz, 2 H, *H*-15), 7.17 (d, ⁴*J* = 1.8 Hz, 1 H, *H*-4), 7.03 (dd, ³*J* = 7.8 Hz, ³*J* = 1.3 Hz, 1 H, *H*-7), 5.11 (d, ²*J* = 14.6 Hz, 1 H, *H*-12), 4.35 (d, ²*J* = 14.6 Hz, 1 H, *H*-12'), 1.81 (s, 3 H, -CH₃) ppm.

¹³C{¹H}-NMR (150 MHz, acetone-*d*₆, 298 K): δ = 169.4 (C=O), 163.7 (¹*J* = 247.3 Hz, C-16) 156.8 (C-4a), 154.4 (C-6a), 141.1 (C-3), 136.4 (C-13), 131.5 (C-1), 130.14 (C-10), 130.09 (C-8), 129.7 (³*J* = 8.2 Hz, C-14), 129.3 (C-9), 126.5 (C-2), 124.2 (C-12a), 120.0 (C-7), 118.0 (C-4), 116.6 (²*J* = 21.7 Hz, C-15), 51.8 (C-12), 23.1 (CH₃) ppm.

IR (ATR): $\tilde{\nu}$ = 3065 (w), 2924 (m), 2852 (w), 2254 (w), 2038 (w), 1654 (s), 1606 (w), 1518 (m), 1475 (m), 1382 (s), 1290 (m), 1222 (s), 1164 (m), 1107 (w), 1034 (w), 1016 (m), 974 (m), 914 (w), 878 (w), 843 (m), 809 (s), 783 (w), 759 (s), 739 (s), 703 (w), 635 (m), 593 (s), 536 (m) cm⁻¹.

HR-MS (ESI, acetone): *m/z* [M+H]⁺ calculated for C₂₁H₁₅FON₃+H⁺: 346.1350; found: 346.1347 \pm 0.33 ppm.

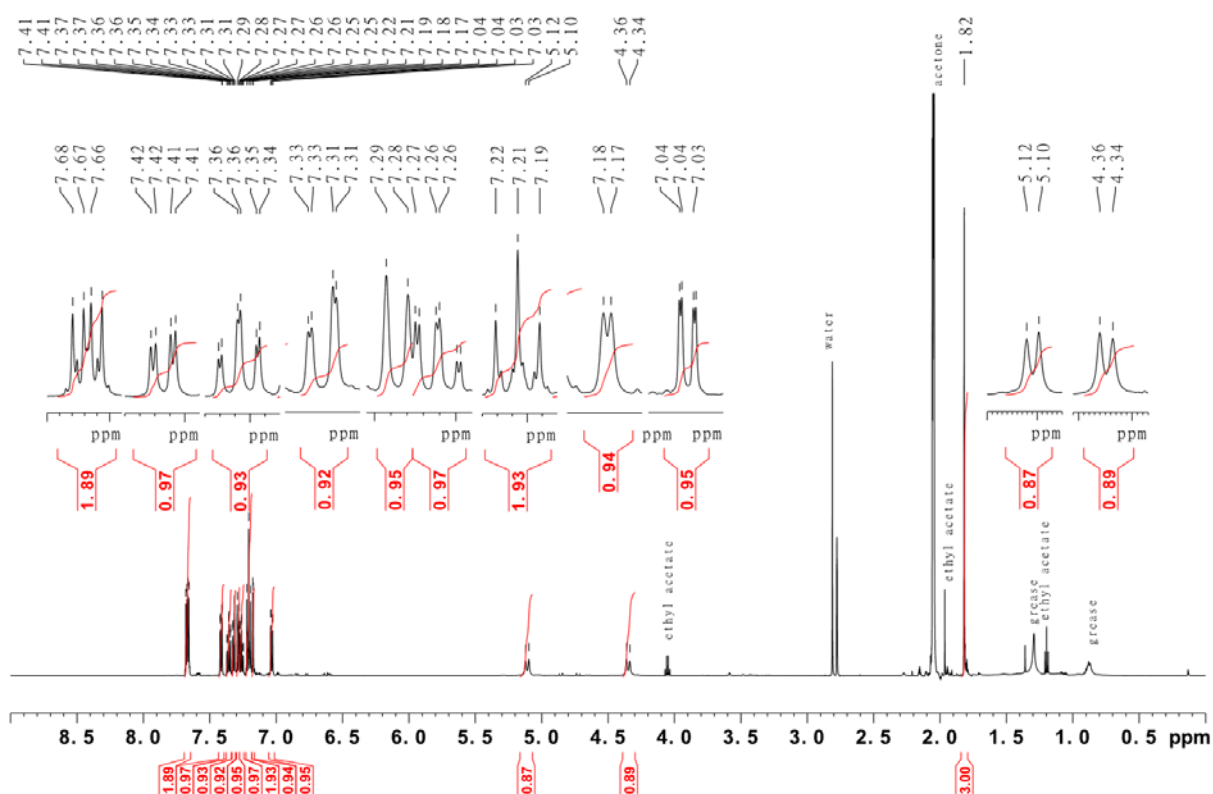


Figure SII.97: 600 MHz ^1H -NMR spectrum of (Z)-1-(3-(4-fluorophenyl)dibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**11**).

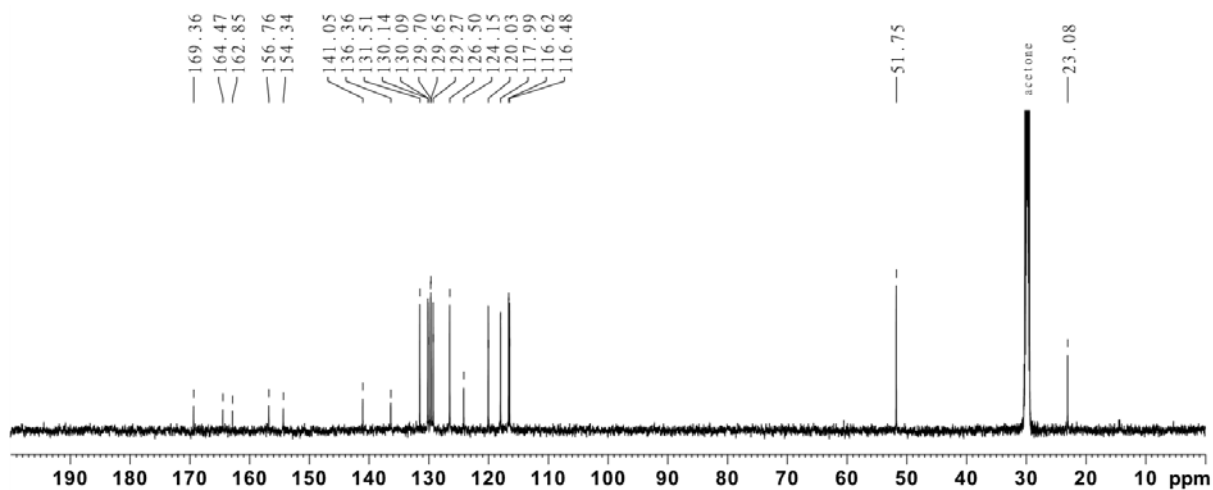


Figure SII.98: 150 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (Z)-1-(3-(4-fluorophenyl)dibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**11**).

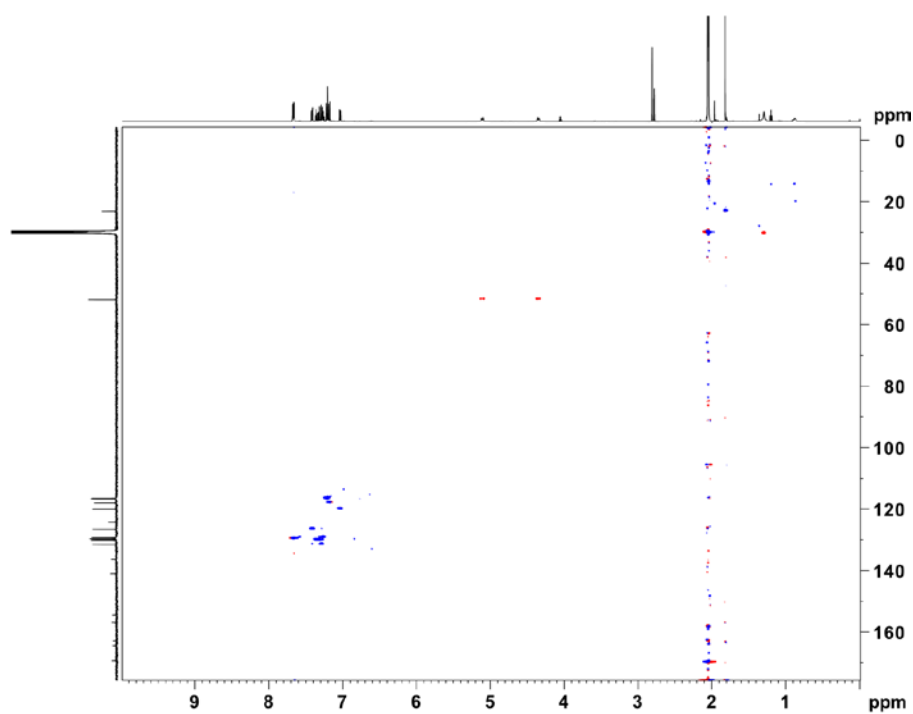


Figure SII.99: 600 MHz ^1H - ^{13}C HSQC spectrum of (Z)-1-(3-(4-fluorophenyl)dibenzo[c,g][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**11**).

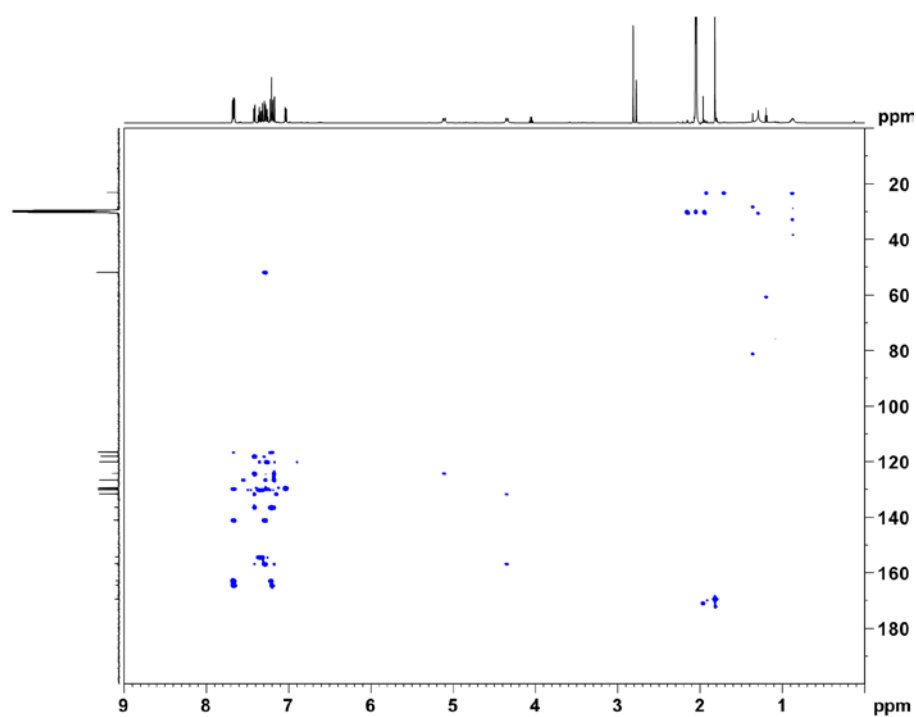
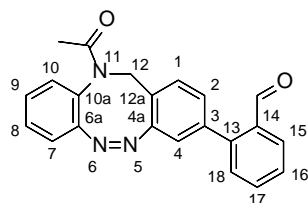


Figure SII.100: 600 MHz HMBC spectrum of (Z)-1-(3-(4-fluorophenyl)dibenzo[c,g][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**11**).

II.2.6 Synthesis of (Z)-2-(11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocin-3-yl)benzaldehyde (**12**)



Halogenated *N*-acetyl-diazocine (**2**: 20.0 mg, 60.6 μ mol, **3**: 23.0 mg, 60.6 μ mol), (2-formylphenyl)boronic acid (18.1 mg, 121 μ mol), Pd(PPh₃)₄ (2.45 mg, 2.12 μ mol) and potassium carbonate (33.4 mg, 212 μ mol) were dissolved in 2.4 mL of toluene/MeOH/deionized H₂O (5 : 1 : 2) under a nitrogen atmosphere, heated to 85 °C with an oil bath and stirred for 16 h at given temperature. After cooling to rt. the reaction mixture was extracted with 10 mL of DCM twice, dried over MgSO₄ and the solvent was evaporated. Column chromatography on silica (ethyl acetate/cyclohexane 1:1, *R_f* = 0.26) gave the product as yellow solid (from bromide **2**: 15.1 mg, 42.4 μ mol, 70%; from iodide **3**: 16.6 mg, 46.7 μ mol, 77%).

melting point: 160 °C

¹H-NMR (600 MHz, acetone-*d*₆, 298 K): δ = 9.71 (s, ³*J* = 5.3 Hz, 1 H, CHO), 7.93 (dd, ³*J* = 7.8 Hz, ⁴*J* = 1.9 Hz, 1 H, *H*-15), 7.71 (td, ³*J* = 7.6 Hz, ⁴*J* = 1.4 Hz, 1 H, *H*-17), 7.58 (td, ³*J* = 7.7 Hz, ⁴*J* = 2.0 Hz, 1 H, *H*-16), 7.44-7.38 (m, 2 H, *H*-8, *H*-18), 7.37-7.33 (m, 2 H, *H*-1, *H*-10), 7.29 (td, ³*J* = 7.3 Hz, ⁴*J* = 1.5 Hz, 1 H, *H*-9), 7.22 (dd, ³*J* = 7.8 Hz, ⁴*J* = 1.9 Hz, 1 H, *H*-2), 7.05 (dd, ³*J* = 7.8 Hz, ³*J* = 1.5 Hz, 1 H, *H*-7), 6.99 (d, ⁴*J* = 1.7 Hz, 1 H, *H*-4), 5.14 (d, ²*J* = 14.6 Hz, 1 H, *H*-12), 4.41 (d, ²*J* = 14.7 Hz, 1 H, *H*-12'), 1.83 (s, 3 H, -CH₃) ppm.

¹³C{¹H}-NMR (150 MHz, acetone-*d*₆, 298 K): δ = 191.4 (CHO), 169.4 (C=O), 156.3 (C-4a), 154.4 (C-6a), 144.7 (C-13), 139.29 (C-3), 134.62 (C-14), 134.57 (C-17), 131.6 (C-18), 131.1 (C-1), 130.26 (C-10), 130.10 (C-8), 129.85 (C-2), 129.66 (C-10a), 129.39 (C-9), 129.26 (C-16), 128.34 (C-15), 125.1 (C-12a), 121.2 (C-4), 119.9 (C-7), 51.8 (C-12), 23.1 (CH₃) ppm.

IR (ATR): $\tilde{\nu}$ = 3751 (w), 3038 (w), 2924 (m), 2855 (w), 2753 (w), 2255 (w), 1688 (s), 1661 (s), 1600 (m), 1511 (w), 1474 (m), 1456 (w), 1430 (w), 1381 (s), 1337 (s), 1295 (w), 1253 (m), 1194 (m), 1163 (w), 1107 (m), 1074 (w), 1042 (w), 1005 (w), 928 (w), 839 (m), 768 (s), 741 (m), 630 (m), 576 (m), 439 (m) cm⁻¹.

HR-MS (ESI, acetone): *m/z* [M+H]⁺ calculated for C₂₂H₁₈O₂N₃+H⁺: 356.1394 found: 356.1387 \pm 1.76 ppm.

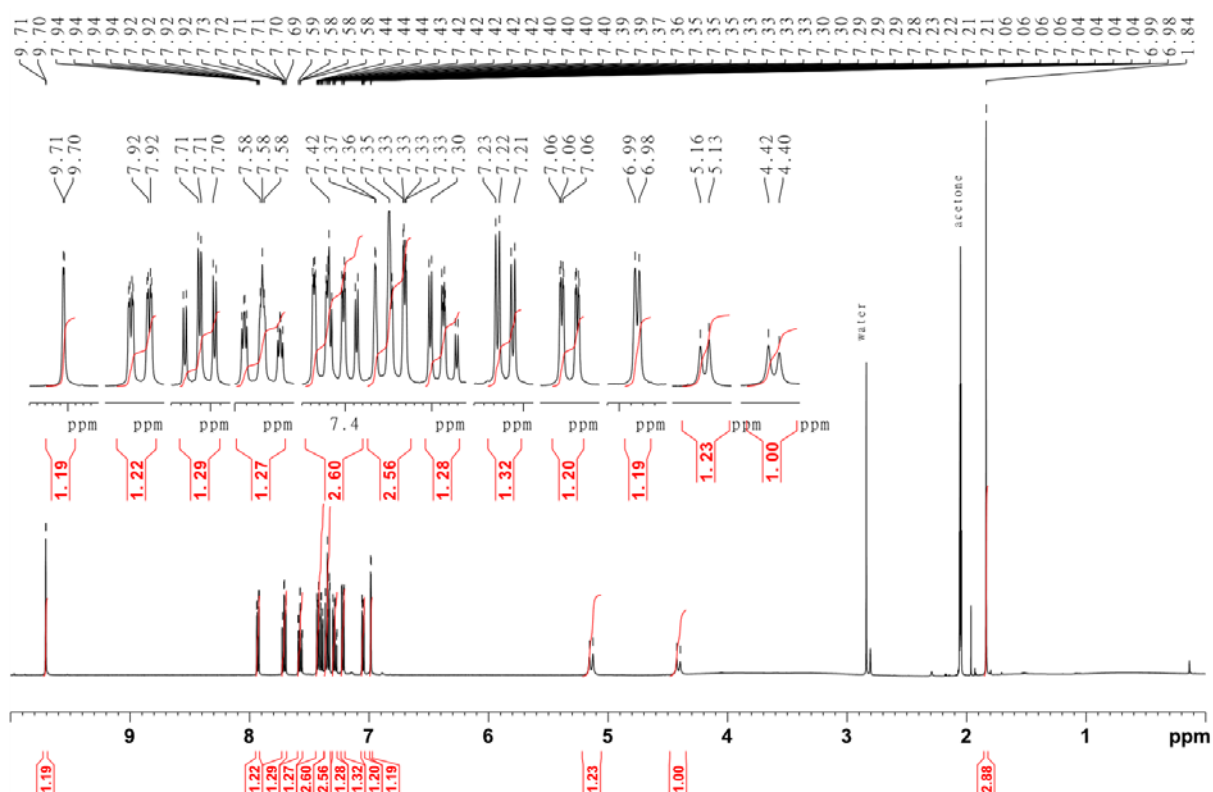


Figure SII.101: 600 MHz ^1H -NMR spectrum of (Z)-2-(11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocin-3-yl)benzaldehyde (12).

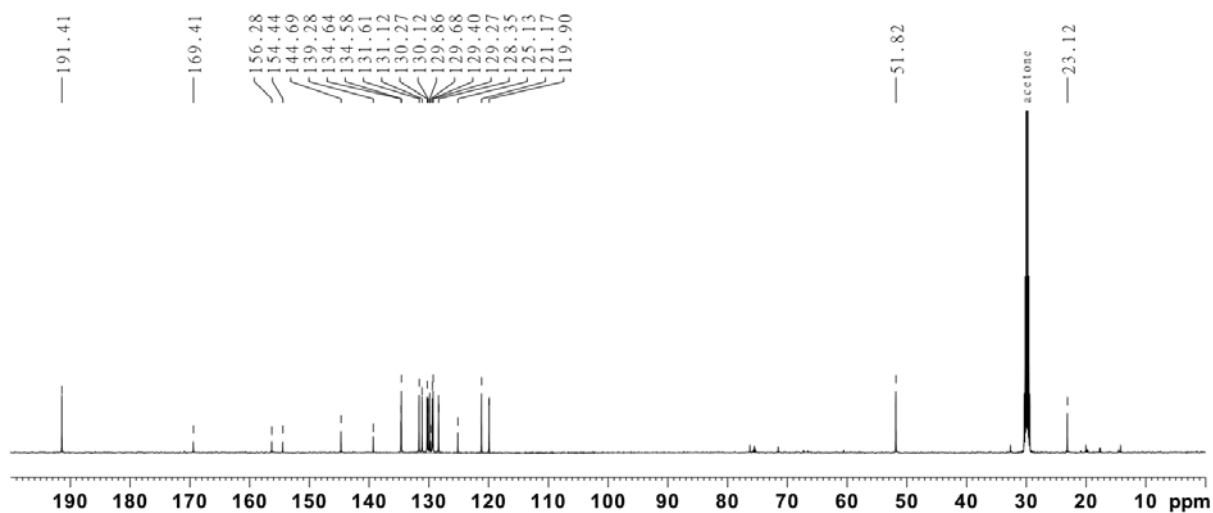


Figure SII.102: 150 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (Z)-2-(11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocin-3-yl)benzaldehyde (12).

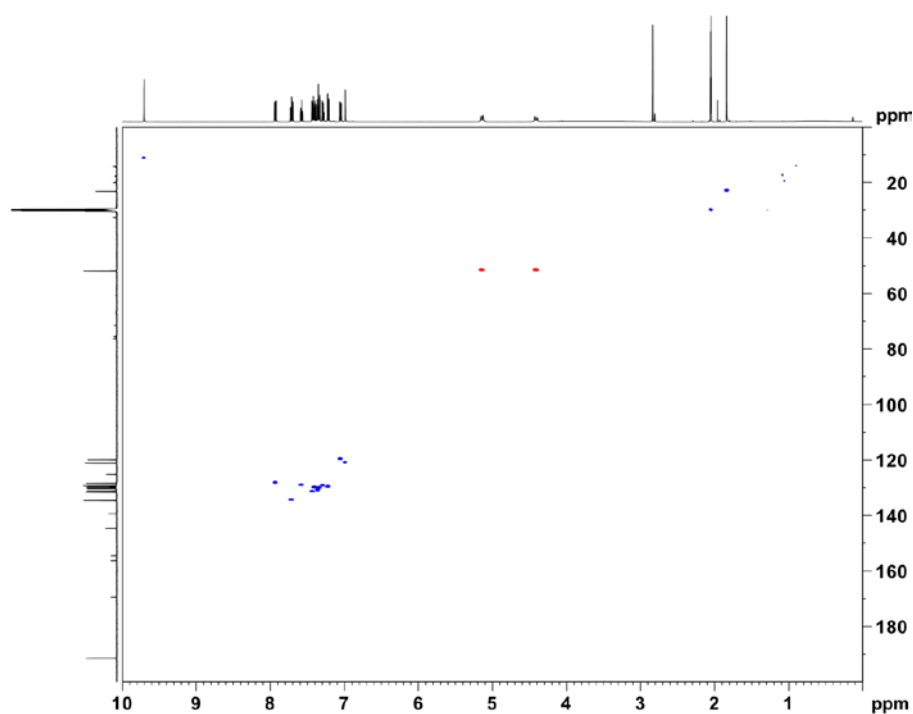


Figure SII.103: 600 MHz ^1H - ^{13}C HSQC spectrum of (*Z*)-2-(11-acetyl-11,12-dihydrodibenzo[*c,g*][1,2,5]triazocin-3-yl)benzaldehyde (**12**).

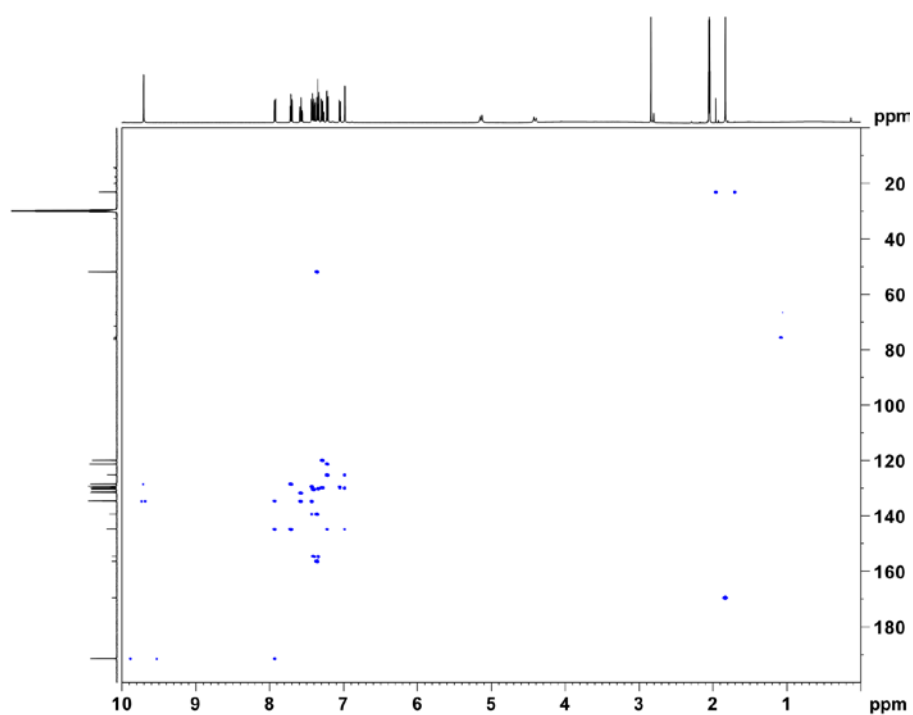
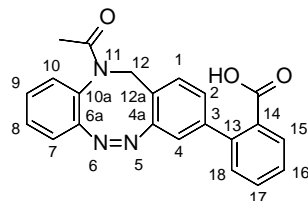


Figure SII.104: 600 MHz HMBC spectrum of (*Z*)-2-(11-acetyl-11,12-dihydrodibenzo[*c,g*][1,2,5]triazocin-3-yl)benzaldehyde (**12**).

II.2.7 Synthesis of (Z)-2-(11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocin-3-yl)benzoic acid (13)



Halogenated *N*-acetyl-diazocine (**2**: 20.0 mg, 60.6 μmol , **3**: 23.0 mg, 60.6 μmol), 2-boronobenzoic acid (20.1 mg, 121 μmol), $\text{Pd}(\text{PPh}_3)_4$ (2.45 mg, 2.12 μmol) and potassium carbonate (33.4 mg, 212 μmol) were dissolved in 2.4 mL of dry DMF under a nitrogen atmosphere, heated to 100 °C with an oil bath and stirred for 16 h at given temperature. After cooling to rt. the reaction mixture was extracted with 10 mL of DCM twice, dried over MgSO_4 and the solvent was evaporated. Column chromatography on silica (ethyl acetate/cyclohexane 1:1 + 1% AcOH, R_f = 0.33) gave the product as yellow solid (from bromide **2**: 17.1 mg, 46.1 μmol , 76%; from iodide **3**: 17.6 mg, 47.3 μmol , 79%).

melting point: 190 °C

^1H -NMR (600 MHz, acetone- d_6 , 298 K): δ = 7.84 (dd, 3J = 7.7 Hz, 4J = 1.0 Hz, 1 H, *H*-15/17), 7.56 (td, 3J = 7.6 Hz, 4J = 1.4 Hz, 1 H, *H*-15/17), 7.47 (td, 3J = 7.6 Hz, 4J = 1.2 Hz, 1 H, *H*-16), 7.36 (td, 3J = 7.7 Hz, 4J = 1.3 Hz, 1 H, *H*-8), 7.31 (dd, 3J = 7.9 Hz, 4J = 1.1 Hz, 1 H, *H*-10), 7.29-7.24 (m, 2 H, *H*-9, *H*-18), 7.21 (d, 3J = 7.9 Hz, 1 H, *H*-1), 7.12 (dd, 3J = 7.8 Hz, 4J = 1.2 Hz, 1 H, *H*-2), 7.02 (dd, 3J = 7.8 Hz, 3J = 1.2 Hz, 1 H, *H*-7), 6.89 (d, 4J = 1.6 Hz, 1 H, *H*-4), 5.11 (d, 2J = 14.5 Hz, 1 H, *H*-12), 4.33 (d, 2J = 14.5 Hz, 1 H, *H*-12'), 1.82 (s, 3 H, -CH₃) ppm.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (150 MHz, acetone- d_6 , 298 K): δ = 169.4 (C=O, COOH), 155.9 (C-4a), 154.4 (C-6a), 142.8 (C-3), 141.3 (C-13), 132.6 (C-14), 132.0 (C-15/17), 131.5 (C-18), 130.76 (C-15/17), 130.55 (C-1), 130.10 (C-10), 130.02 (C-8), 129.6 (C-10a), 129.2 (C-9), 128.6 (C-16), 128.5 (C-2), 123.9 (C-12a), 120.08 (C-7), 120.01 (C-4), 51.9 (C-12), 23.1 (CH₃) ppm.

IR (ATR): $\tilde{\nu}$ = 2921 (s), 2852 (m), 2022 (w), 1713 (m), 1613 (s), 1591 (w), 1516 (w), 1477 (s), 1448 (w), 1377 (s), 1235 (s), 1135 (m), 1078 (m), 1014 (w), 977 (w), 922 (w), 877 (w), 834 (m), 756 (s), 739 (w), 720 (w), 691 (w), 628 (m), 603 (w), 575 (m), 533 (w), 488 (w), 439 (m), 409 (m) cm^{-1} .

HR-MS (ESI, DCM): m/z [$\text{M}+\text{H}$]⁺ calculated for $\text{C}_{22}\text{H}_{17}\text{O}_3\text{N}_3+\text{H}^+$: 372.1343 found: 372.1337 \pm 1.64 ppm.

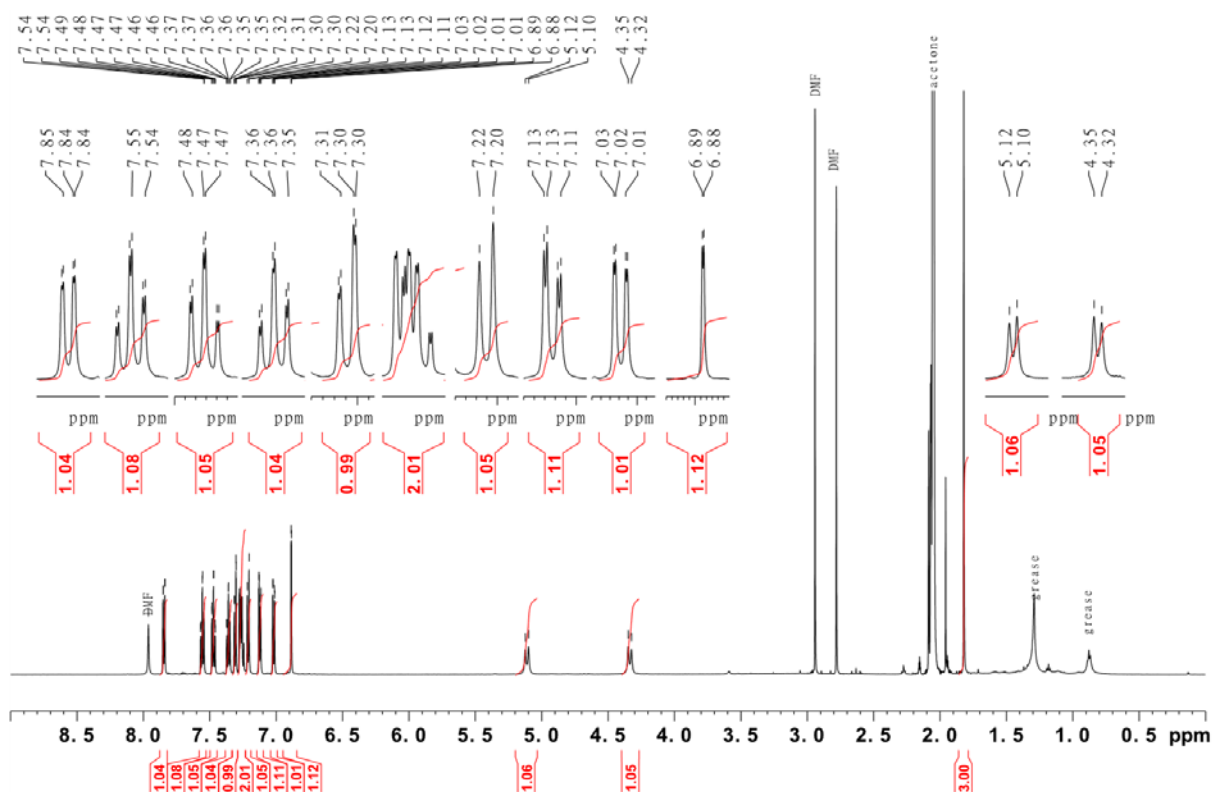


Figure SII.105: 600 MHz ^1H -NMR spectrum of (Z)-2-(11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocin-3-yl)benzoic acid (**13**).

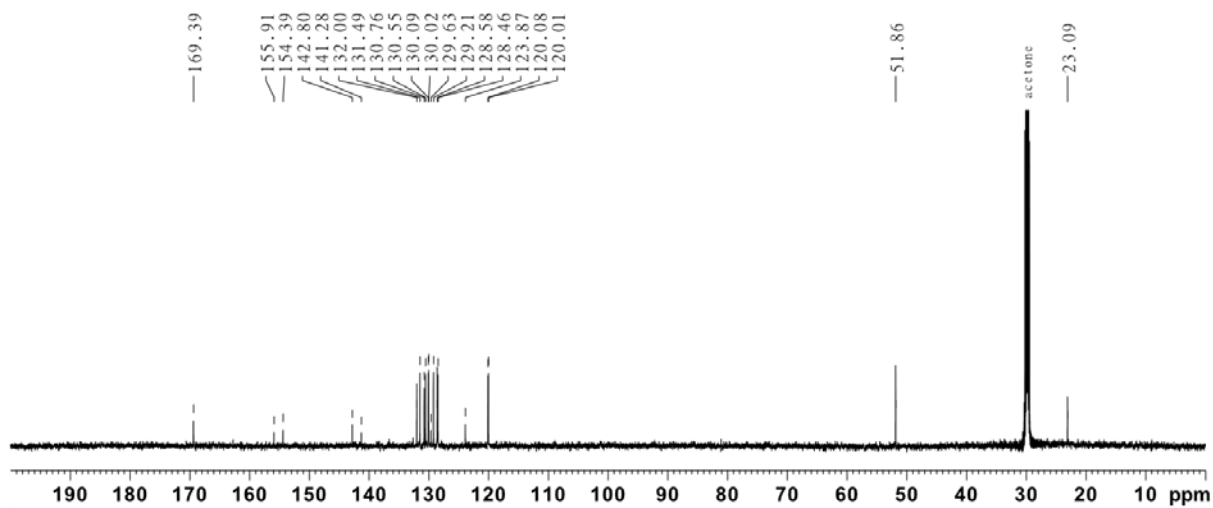


Figure SII.106: 150 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (Z)-2-(11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocin-3-yl)benzoic acid (**13**).

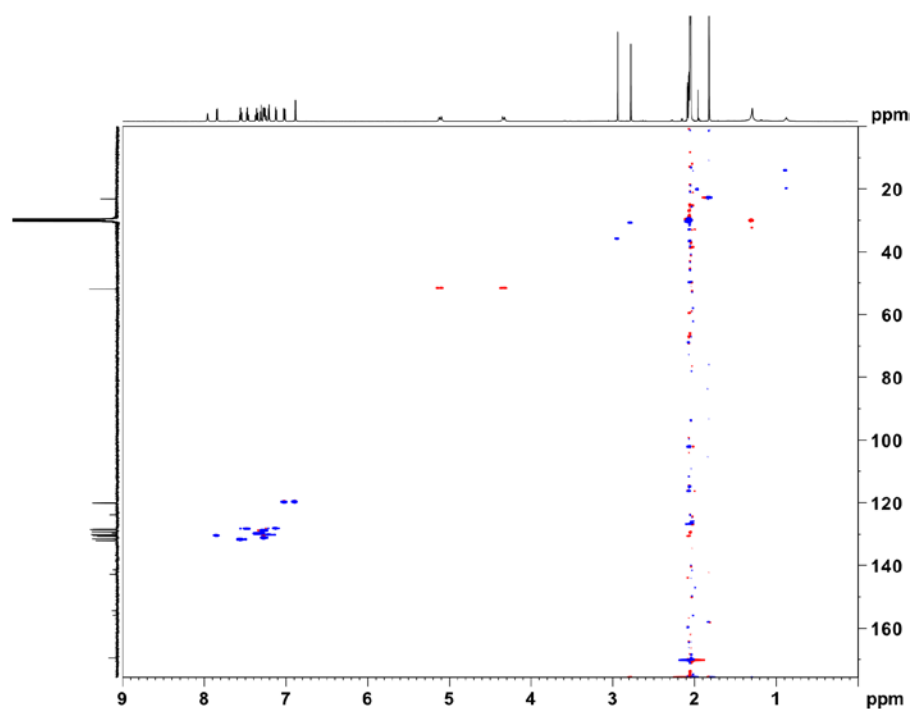


Figure SII.107: 600 MHz ^1H - ^{13}C HSQC spectrum of (Z)-2-(11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocin-3-yl)benzoic acid (**13**).

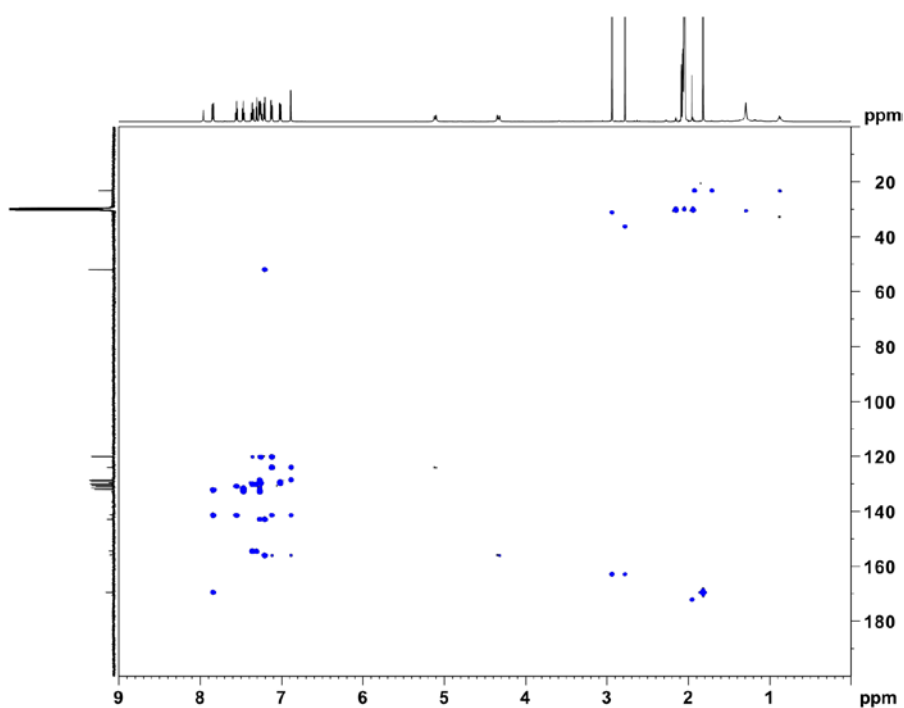
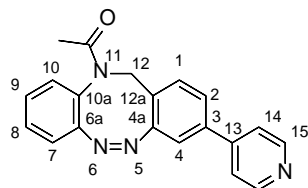


Figure SII.108: 600 MHz HMBC spectrum of (Z)-2-(11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocin-3-yl)benzoic acid (**13**).

II.2.8 Synthesis of (Z)-1-(3-(pyridine-4-yl)dibenzo[c,g][1,2,5]triazocin-11(12*H*)-ethan-1-one (14)



Halogenated *N*-acetyl-diazocine (**2**: 20.0 mg, 60.6 μmol , **3**: 23.0 mg, 60.6 μmol), pyridine-4-boronic acid (14.8 mg, 121 μmol), $\text{Pd}(\text{PPh}_3)_4$ (2.45 mg, 2.12 μmol) and potassium carbonate (33.4 mg, 212 μmol) were dissolved in 2.4 mL of toluene/MeOH/deionized H_2O (5 : 1 : 2) under a nitrogen atmosphere, heated to 85 $^\circ\text{C}$ with an oil bath and stirred for 16 h at given temperature. After cooling to rt. the reaction mixture was extracted with 10 mL of DCM twice, dried over MgSO_4 and the solvent was evaporated. Column chromatography on silica (ethyl acetate/cyclohexane 1:1, R_f = 0.07) gave the product as yellow solid (from bromide **2**: 1.4 mg, 4.26 μmol , 7%; from iodide **3**: 3.8 mg, 11.6 μmol , 19%).

melting point: 223 $^\circ\text{C}$

^1H -NMR (600 MHz, acetone- d_6 , 298 K): δ = 8.62 (dd, 3J = 6.1 Hz, 4J = 1.6 Hz, 2 H, *H*-15), 7.61 (dd, 3J = 6.1 Hz, 4J = 1.6 Hz, 2 H, *H*-14), 7.56 (dd, 3J = 8.0 Hz, 4J = 1.9 Hz, 1 H, *H*-2), 7.38-7.32 (4 H, *H*-1, *H*-4, *H*-8, *H*-9), 7.27 (dd, 3J = 7.8 Hz, 4J = 1.4 Hz, 1 H, *H*-7), 7.05 (dd, 3J = 7.8 Hz, 4J = 1.2 Hz, 1 H, *H*-10), 5.15 (d, 2J = 14.6 Hz, 1 H, *H*-12), 4.38 (d, 2J = 14.4 Hz, 1 H, *H*-12'), 1.81 (s, 3 H, - CH_3) ppm.

$^{13}\text{C}\{^1\text{H}\}$ -NMR (150 MHz, acetone- d_6 , 298 K): δ = 169.4 (C=O), 156.8 (C-4a), 154.3 (C-6a), 151.4 (C-15), 146.7 (C-13), 139.2 (C-3), 131.8 (C-1), 130.21 (C-8/9), 130.16 (C-8/9), 129.57 (C-10a), 129.41 (C-7), 126.7 (C-2), 126.1 (C-12a), 122.0 (C-14), 120.1 (C-10), 118.3 (C-4), 51.8 (C-12), 23.0 (CH_3) ppm.

IR (ATR): $\tilde{\nu}$ = 2922 (m), 2851 (w), 1726 (m), 1655 (s), 1599 (m), 1543 (w), 1513 (w), 1478 (m), 1451 (w), 1420 (w), 1379 (s), 1336 (s), 1291 (w), 1246 (w), 1074 (m), 1045 (w), 995 (w), 964 (w), 922 (w), 876 (m), 846 (w), 817 (s), 767 (m), 738 (m), 711 (m), 624 (s), 602 (w), 573 (m), 547 (m), 512 (m) cm^{-1} .

HR-MS (ESI, DCM): m/z [$\text{M}+\text{H}$] $^+$ calculated for $\text{C}_{20}\text{H}_{16}\text{ON}_4+\text{H}^+$: 329.1397; found: 329.1393 \pm 1.07 ppm.

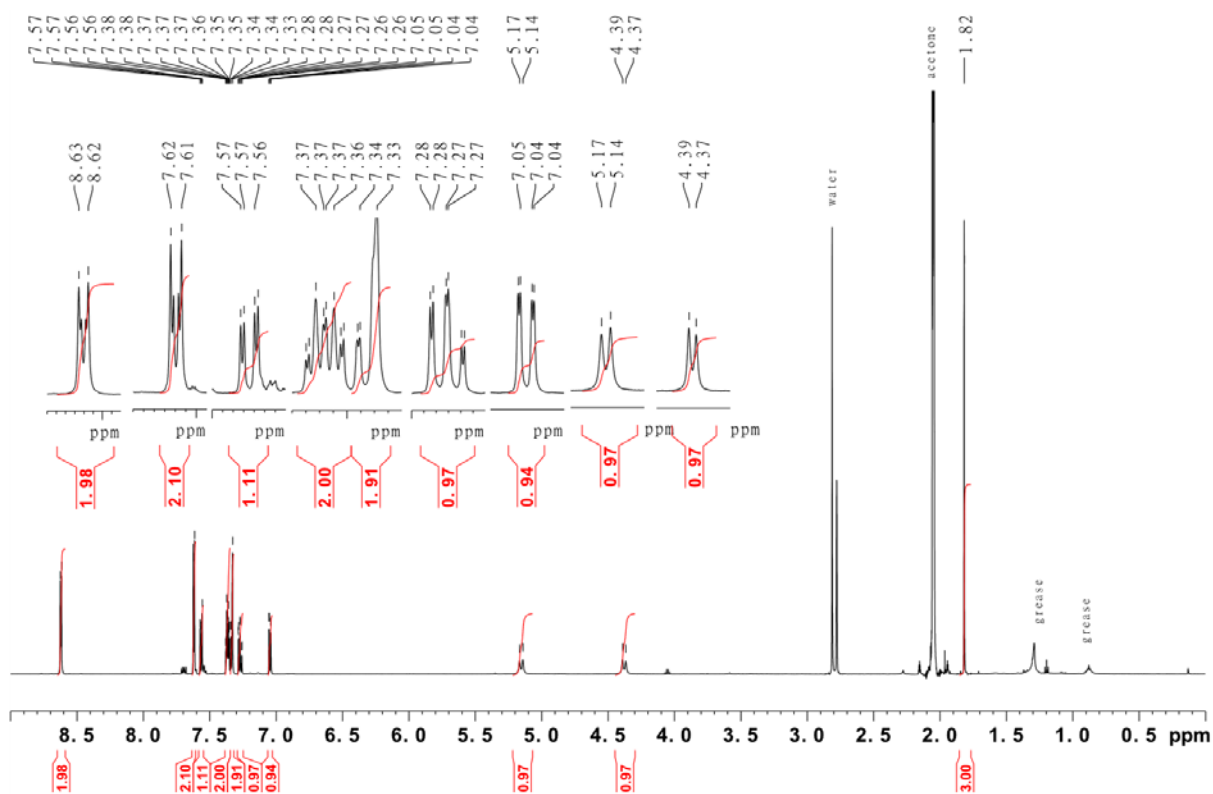


Figure SII.109: 600 MHz ^1H -NMR spectrum of (Z)-1-(3-(pyridine-4-yl)dibenzo[c,g][1,2,5]triazocin-11(12H)-ethan-1-one (**14**).

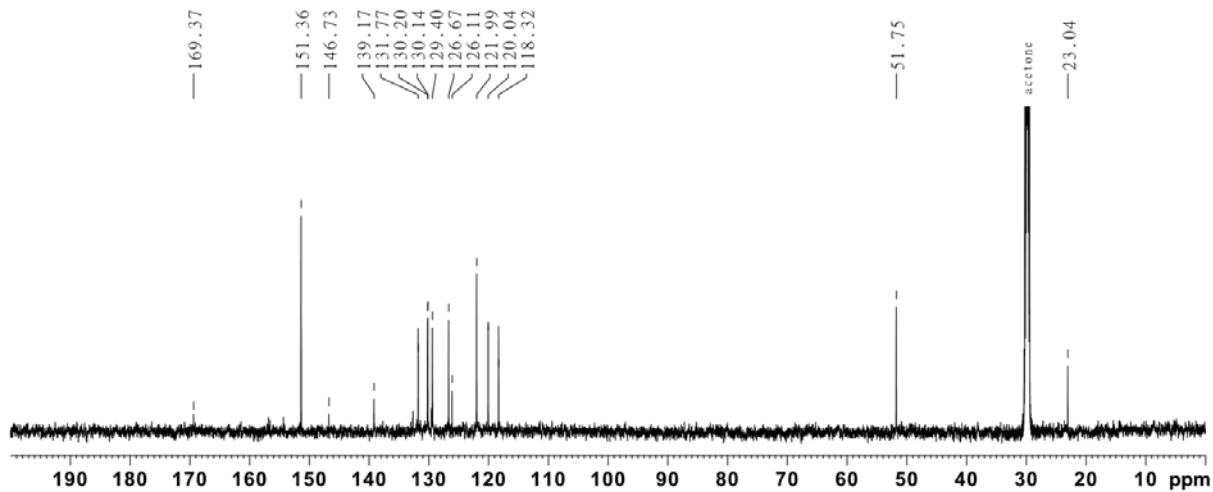


Figure SII.110: 150 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (Z)-1-(3-(pyridine-4-yl)dibenzo[c,g][1,2,5]triazocin-11(12H)-ethan-1-one (**14**).

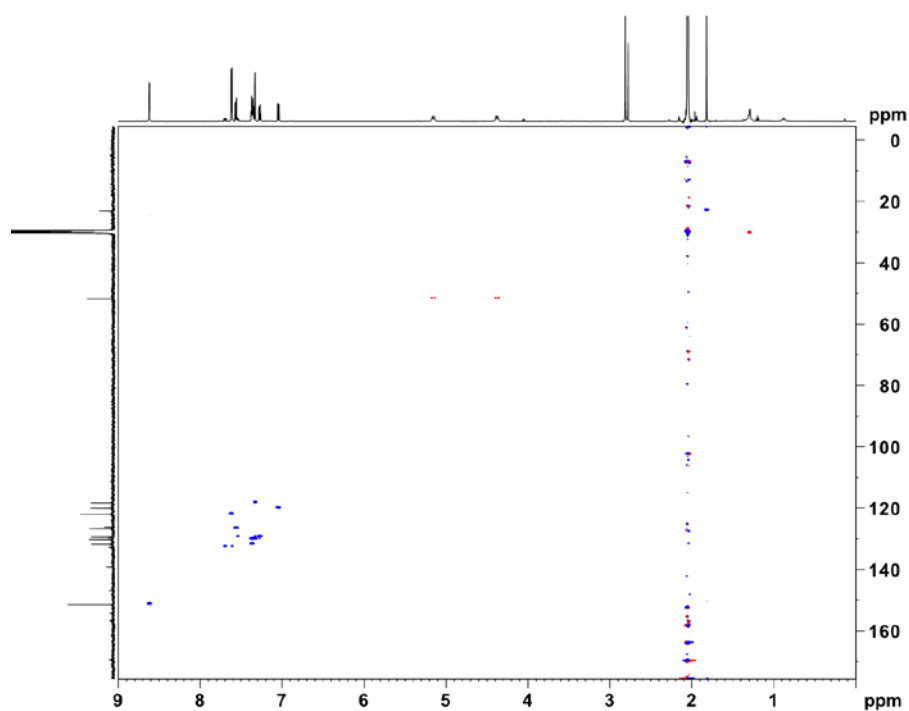


Figure SII.111: 600 MHz ^1H - ^{13}C HSQC spectrum of (*Z*)-1-(3-(pyridine-4-yl)dibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-ethan-1-one (**14**).

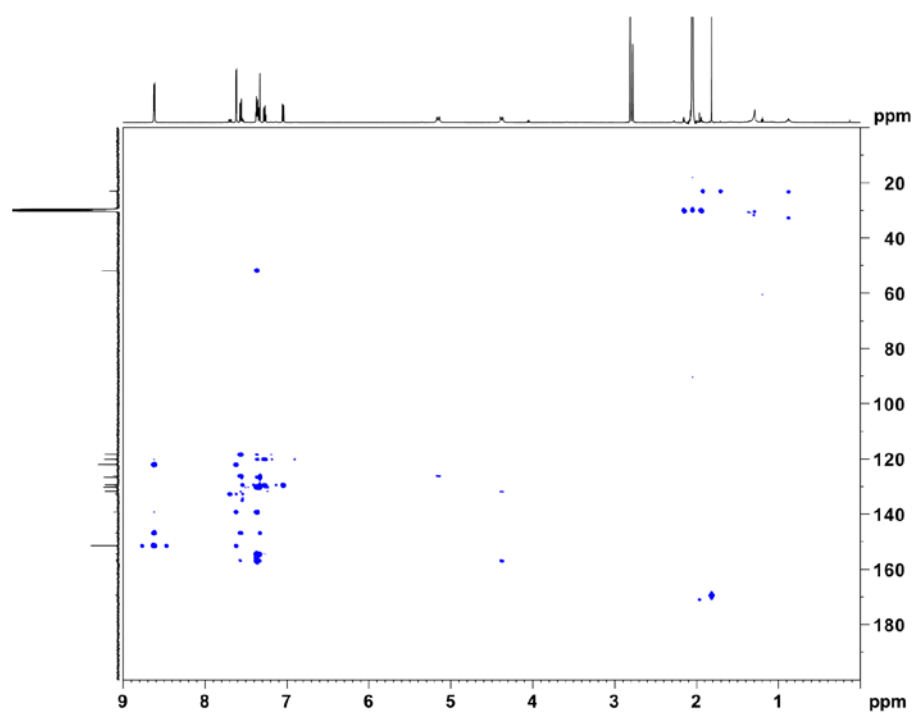
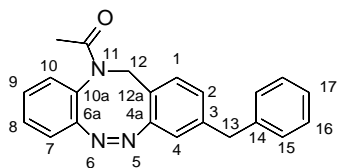


Figure SII.112: 600 MHz HMBC spectrum of (*Z*)-1-(3-(pyridine-4-yl)dibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-ethan-1-one (**14**).

II.2.9 Synthesis of (Z)-1-(3-benzyl-dibenzo[c,g][1,2,5]triazocin-11(12H)-ethan-1-one (17)



Halogenated *N*-acetyl-diazocine (**2**, 20.0 mg, 60.6 μ mol, **3**: 23.0 mg, 60.6 μ mol) 2-benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolan (26.4 mg, 121 μ mol), Pd(PPh₃)₄ (2.45 mg, 2.12 μ mol) and potassium carbonate (33.4 mg, 212 μ mol) were dissolved in 2.4 mL of toluene/MeOH/deionized H₂O (5 : 1 : 2) under a nitrogen atmosphere, heated to 85 °C with an oil bath and stirred for 16 h at given temperature. After cooling to rt. the reaction mixture was extracted with 10 mL of DCM twice, dried over MgSO₄ and the solvent was evaporated. Column chromatography on silica (ethyl acetate/cyclohexane 1:1, *R_f* = 0.33) gave the product as yellow solid (from bromide **2**: 9.4 mg, 27.5 μ mol, 45%; from iodide **3**: no product could be obtained).

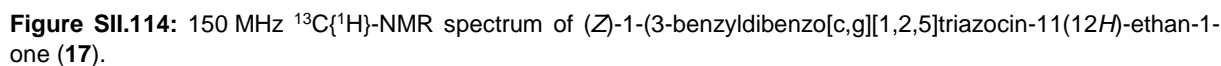
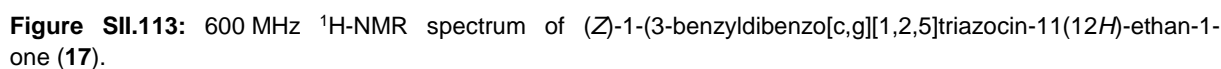
melting point: 147 °C

¹H-NMR (600 MHz, CDCl₃, 298 K): δ = 7.29-7.23 (m, 3 H, *H*-10, *H*-16), 7.19 (t, ³*J* = 7.1 Hz, 1 H, *H*-17), 7.15 (td, ³*J* = 7.7 Hz, ⁴*J* = 1.5 Hz, 1 H, *H*-8), 7.04-7.00 (m, 3 H, *H*-9, *H*-15), 6.95 (d, ³*J* = 8.1 Hz, 1 H, *H*-1), 6.88 (dd, ³*J* = 7.9 Hz, ⁴*J* = 1.4 Hz, 1 H, *H*-7), 6.86 (dd, ³*J* = 8.0 Hz, ⁴*J* = 1.7 Hz, 1 H, *H*-2), 6.68 (d, ⁴*J* = 1.3 Hz, 1 H, *H*-4), 5.02 (d, ²*J* = 14.6 Hz, 1 H, *H*-12), 4.31 (d, ²*J* = 14.4 Hz, 1 H, *H*-12'), 3.88 (s, 2 H, *H*-13), 1.91 (s, 3 H, -CH₃) ppm.

¹³C{¹H}-NMR (150 MHz, CDCl₃, 298 K): δ = 170.2 (C=O), 155.6 (C-4a), 153.2 (C-6a), 142.3 (C-3), 140.0 (C-14), 130.2 (C-1), 129.05 (C-10/16), 128.96 (C-15), 128.91 (C-9), 128.69 (C-10/16), 128.3 (C-2), 128.14 (C-8), 126.5 (C-17), 121.6 (C-12a), 119.57 (C-4), 119.46 (C-7), 51.8 (C-12), 41.4 (C-13) 23.4 (CH₃) ppm.

IR (ATR): $\tilde{\nu}$ = 2924 (m), 2853 (w), 2256 (m), 1654 (s), 1611 (w), 1593 (w), 1513 (w), 1482 (m), 1453 (m), 1437 (w), 1386 (s), 1337 (s), 1286 (w), 1245 (w), 1200 (m), 1147 (w), 1074 (m), 1040 (m), 974 (w), 914 (m), 902 (w), 772 (s), 739 (m), 723 (s), 703 (m), 644 (w), 623 (w), 607 (s), 591 (s), 462 (m) cm⁻¹.

HR-MS (ESI, EtOAc): *m/z* [M+Na]⁺ calculated for C₂₂H₁₉ON₃+Na⁺: 364.1420; found: 364.1418 \pm 0.75 ppm.



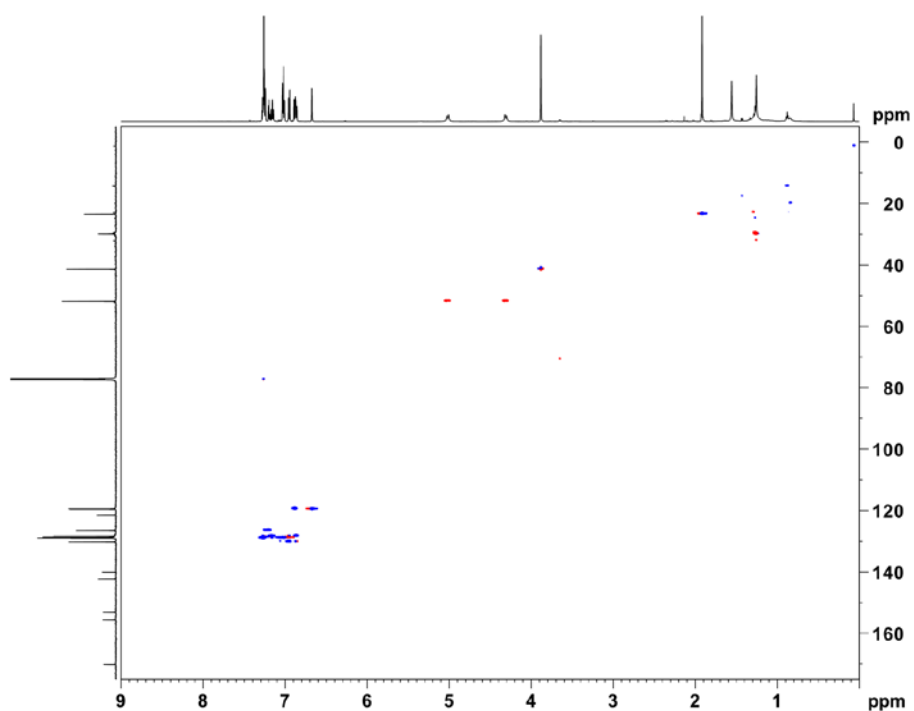


Figure SII.115: 600 MHz ^1H - ^{13}C HSQC spectrum of (*Z*)-1-(3-benzylidibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-ethan-1-one (**17**).

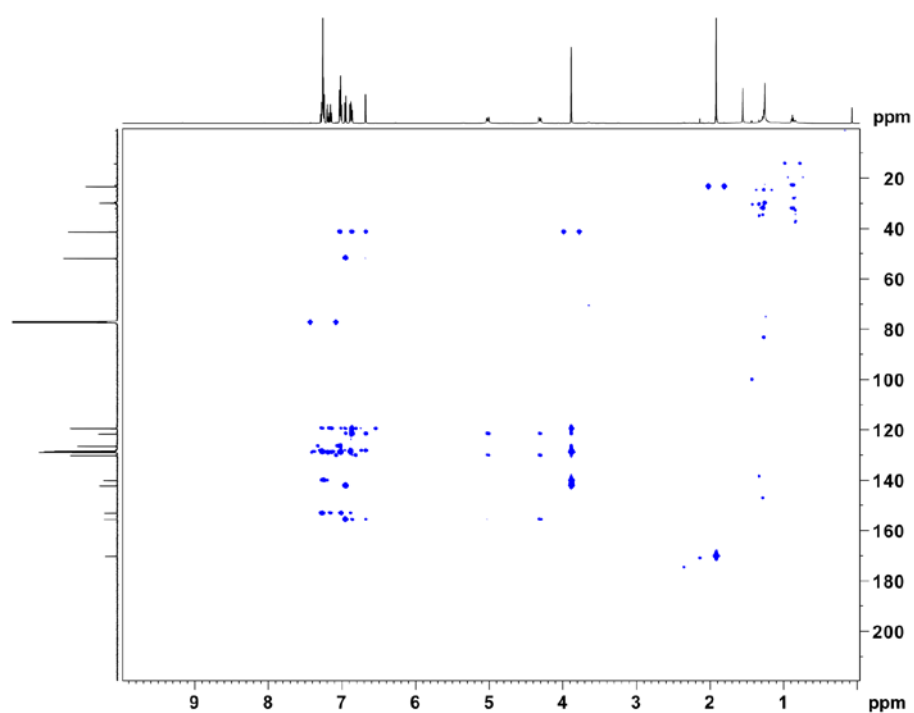
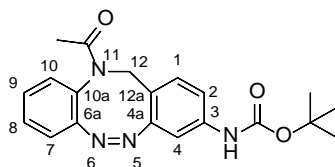


Figure SII.116: 600 MHz HMBC spectrum of (*Z*)-1-(3-benzylidibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-ethan-1-one (**17**).

II.2.11 Synthesis of *tert*-butyl-(*Z*)-(11-acetyl-11,12-dihydrodiebenzo[*c,g*][1,2,5]triazocin-3-yl)carbamate (19)



Halogenated *N*-acetyl-diazocine (**2**, 20.0 mg, 60.6 μmol , **3**: 23.0 mg, 60.6 μmol), *tert*-butyl carbamate (10.6 mg, 90.9 μmol), Xantphos Pd G3 (2.90 mg, 3.03 μmol) and caesium carbonate (19.7 mg, 60.6 μmol) were dissolved in 2.4 mL of dry 1,4-dioxane under a nitrogen atmosphere, heated to 100 °C with an oil bath and stirred for 16 h at given temperature. After cooling to rt. deionized H₂O and 5 mL ethyl acetate were added and the reaction mixture was extracted with 10 mL of ethyl acetate twice, dried over MgSO₄ and the solvent was evaporated. Column chromatography on silica (ethyl acetate/cyclohexane 1:1, *R_f* = 0.30) gave the product as yellow solid (from bromide **2**: no product could be obtained; from iodide **3**: 15.8 mg, 43.1 μmol , 72%).

melting point: 217 °C

¹H-NMR (600 MHz, acetone-*d*₆, 298 K): δ = 8.56 (s, 1 H, -NH), 7.36 (td, ³*J* = 7.6 Hz, ⁴*J* = 1.7 Hz, 1 H, *H*-8), 7.28-7.20 (m, 4 H, *H*-2, *H*-4, *H*-9, *H*-10), 7.08 (d, ³*J* = 8.2 Hz, 1 H, *H*-1), 7.00 (dd, ³*J* = 7.7 Hz, ⁴*J* = 1.3 Hz, 1 H, *H*-7), 4.93 (d, ²*J* = 14.4 Hz, 1 H, *H*-12), 4.25 (d, ²*J* = 14.5 Hz, 1 H, *H*-12'), 1.80 (s, 3 H, -CH₃), 1.45 (s, 9 H, -C(CH₃)₃) ppm.

¹³C{¹H}-NMR (150 MHz, acetone-*d*₆, 298 K): δ = 170.9 (-NHCO), 169.3 (C=O), 156.8 (C-4a), 154.2 (C-6a), 141.1 (C-3), 131.3 (C-1), 130.1 (C-10), 129.9 (C-8), 129.1 (C-9), 119.9 (C-7), 118.3 (C-12a), 117.5 (C-2/4), 108.9 (C-2/4), 80.5 (C(CH₃)₃), 51.7 (C-12), 28.4 (C(CH₃)₃) 23.2 (CH₃) ppm.

IR (ATR): $\tilde{\nu}$ = 3304 (m), 2976 (w), 2923 (m), 2164 (s), 1722 (s), 1638 (s), 1615 (m), 1590 (m), 1528 (s), 1479 (m), 1394 (s), 1367 (w), 1310 (m), 1239 (s), 1159 (s), 1075 (m), 1059 (m), 1034 (w), 974 (w), 953 (w), 917 (w), 881 (m), 856 (w), 829 (m), 796 (m), 763 (m), 694 (w), 618 (m), 570 (m), 449 (m) cm⁻¹.

HR-MS (ESI, DCM): *m/z* [M+H]⁺ calculated for C₂₀H₂₂O₃N₄+H⁺: 367.1765; found: 367.1761 ± 1.02 ppm.

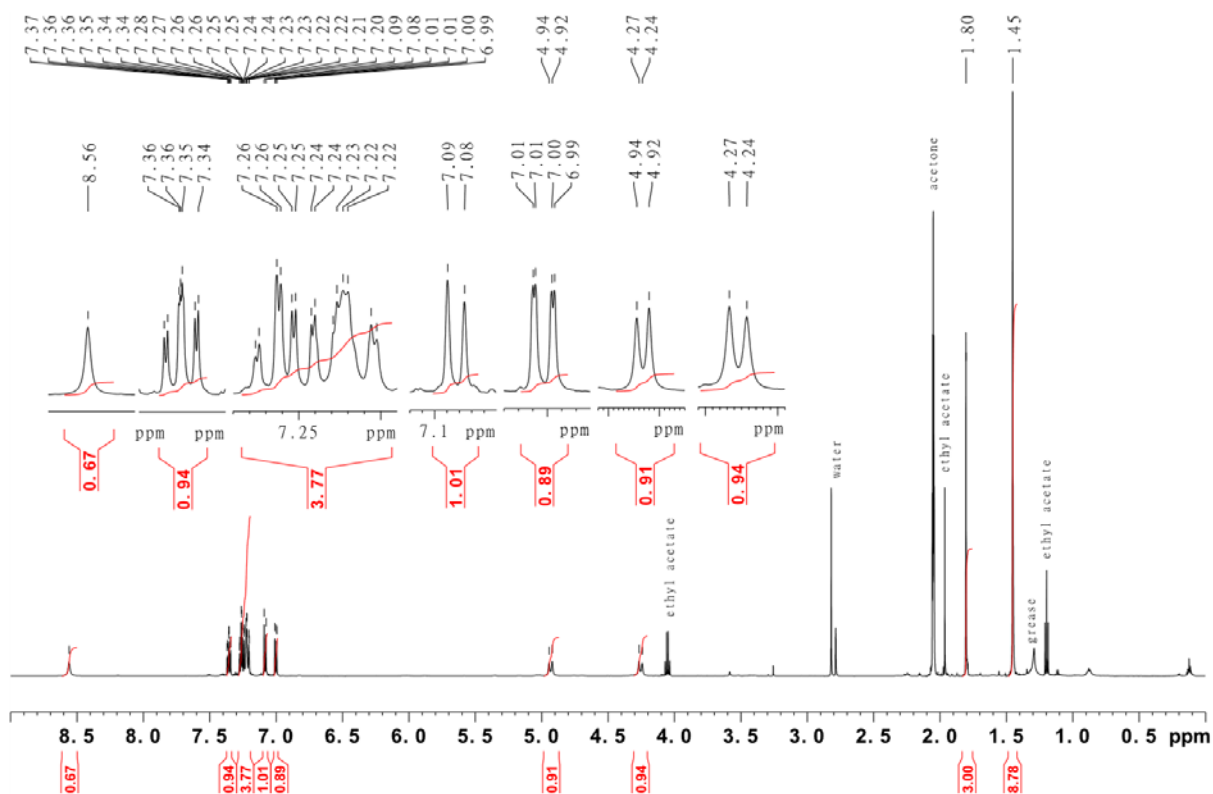


Figure SII.117: 600 MHz ^1H -NMR spectrum of *tert*-butyl-(*Z*)-(11-acetyl-11,12-dihydrodiebenzo[*c,g*][1,2,5]triazocin-3-yl)carbamate (**19**).

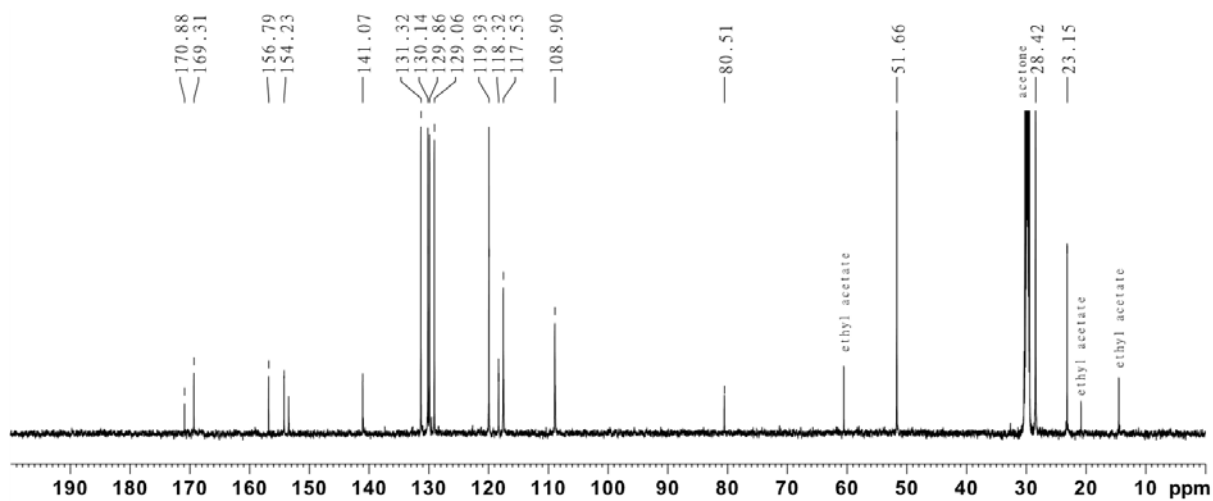


Figure SII.118: 150 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of *tert*-butyl-(*Z*)-(11-acetyl-11,12-dihydrodiebenzo[*c,g*][1,2,5]triazocin-3-yl)carbamate (**19**).

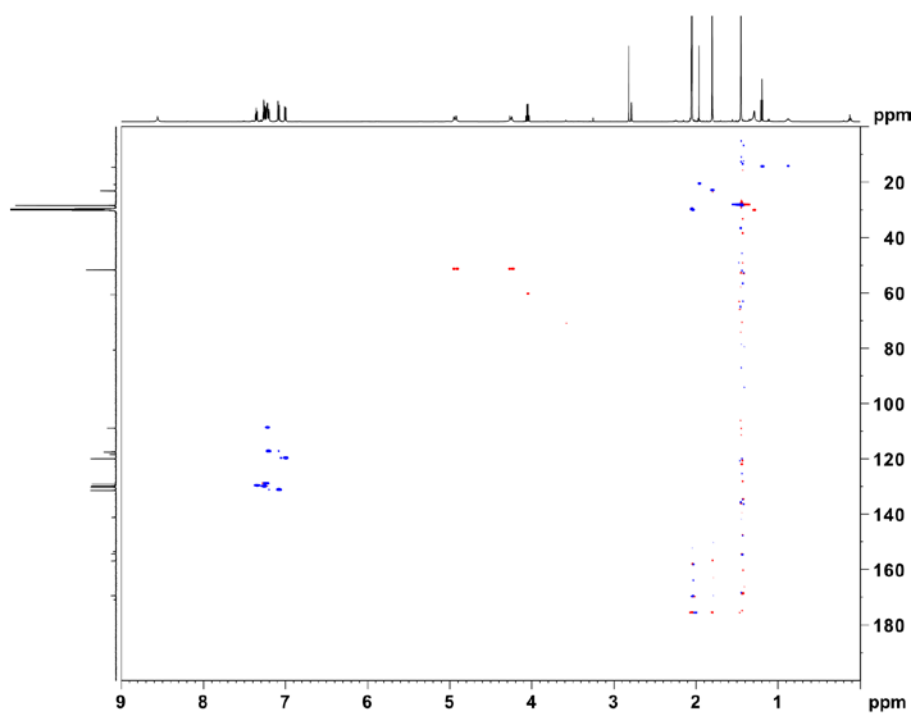


Figure SII.119: 600 MHz ^1H - ^{13}C HSQC spectrum of *tert*-butyl-(*Z*)-(11-acetyl-11,12-dihydrodiebenzo[*c,g*][1,2,5]triazocin-3-yl)carbamate (**19**).

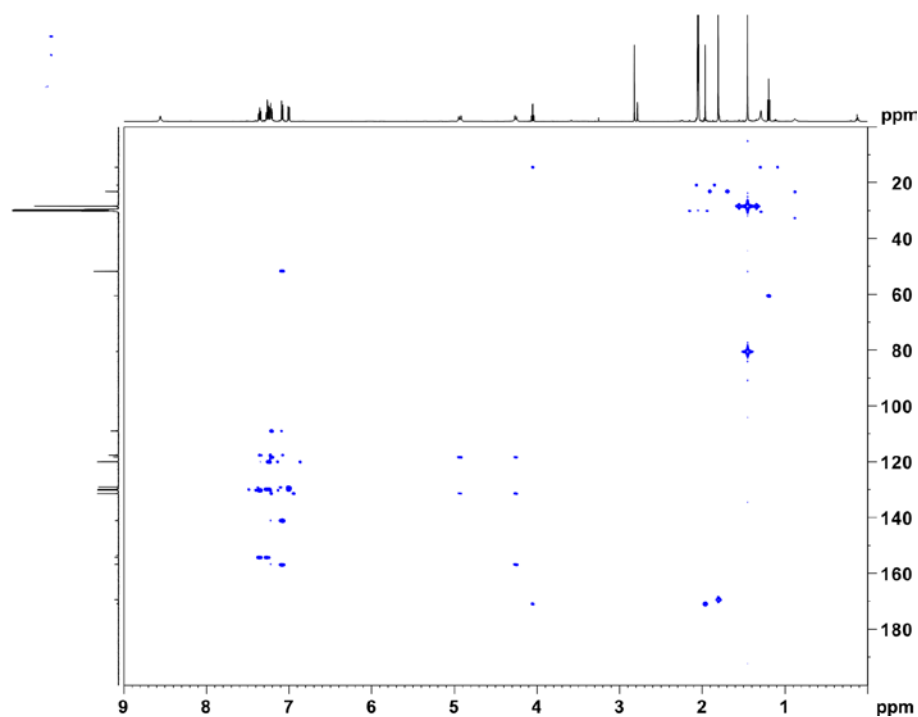
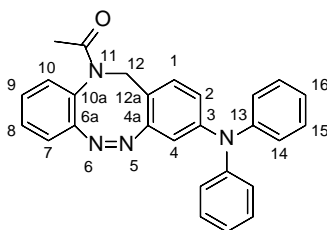


Figure SII.120: 600 MHz HMBC spectrum of *tert*-butyl-(*Z*)-(11-acetyl-11,12-dihydrodiebenzo[*c,g*][1,2,5]triazocin-3-yl)carbamate (**19**).

II.2.12 Synthesis of (Z)-1-(3-(diphenylamino)dibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (20)



Halogenated *N*-acetyl-diazocine (**2**, 20.0 mg, 60.6 μ mol, **3**: 23.0 mg, 60.6 μ mol), diphenylamine (15.4 mg, 90.9 μ mol), Xantphos Pd G3 (2.90 mg, 3.03 μ mol) and caesium carbonate (19.7 mg, 60.6 μ mol) were dissolved in 2.4 mL of dry 1,4-dioxane under a nitrogen atmosphere, heated to 100 °C with an oil bath and stirred for 16 h at given temperature. After cooling to rt. deionized H₂O and 5 mL ethyl acetate were added and the reaction mixture was extracted with 10 mL of ethyl acetate twice, dried over MgSO₄ and the solvent was evaporated. Column chromatography on silica (ethyl acetate/cyclohexane 1:1, *R_f* = 0.30) gave the product as yellow solid (from bromide **2**: 6.30 mg, 15.1 μ mol, 25%, **3**: 11.8 mg, 28.2 μ mol, 47%).

melting point: 160 °C

¹H-NMR (500 MHz, acetone-*d*₆, 298 K): δ = 7.46 (td, ³*J* = 7.9 Hz, ⁴*J* = 1.9 Hz, 1 H, *H*-9), 7.32-7.27 (m, 6 H, *H*-7, *H*-8, *H*-14/15), 7.10-7.06 (m, 2 H, *H*-16), 7.04 (d, ³*J* = 8.3 Hz, 1 H, *H*-1), 6.98-6.93 (5 H, *H*-10, *H*-14/15), 6.66 (dd, ³*J* = 8.3 Hz, ⁴*J* = 2.4 Hz, 1 H, *H*-2), 6.44 (d, ⁴*J* = 2.4 Hz, 1 H, *H*-4), 4.77 (d, ²*J* = 14.3 Hz, 1 H, *H*-12), 4.26 (d, ²*J* = 14.3 Hz, 1 H, *H*-12'), 1.81 (s, 3 H, -CH₃) ppm.

¹³C{¹H}-NMR (125 MHz, acetone-*d*₆, 298 K): δ = 169.3 (C=O), 157.4 (C-4a), 154.5 (C-6a), 149.2 (C-3), 147.9 (C-13), 131.9 (C-1), 130.42 (C-14/15), 130.34 (C-7), 130.04 (C-10a), 129.8 (C-9), 129.1 (C-8), 125.6 (C-14/15), 124.7 (C-16), 121.5 (C-2), 119.8 (C-10), 118.2 (C-12a), 112.8 (C-4), 51.6 (C-12) 23.2 (CH₃) ppm.

IR (ATR): $\tilde{\nu}$ = 2921 (w), 2228 (w), 2185 (w), 2084 (w), 2021 (w), 1659 (s), 1610 (w), 1592 (s), 1481 (s), 1384 (s), 1333 (s), 1304 (w), 1290 (m), 1265 (s), 1221 (w), 1171 (w), 1095 (w), 1075 (w), 1029 (w), 977 (w), 901 (w), 840 (w), 811 (m), 758 (m), 745 (m), 697 (s), 631 (m), 586 (m), 508 (s), 483 (m) cm⁻¹.

HR-MS (ESI, DCM): *m/z* [M+H]⁺ calculated for C₂₇H₂₂ON₄+H⁺: 419.1866; found: 419.1863 \pm 0.85 ppm.

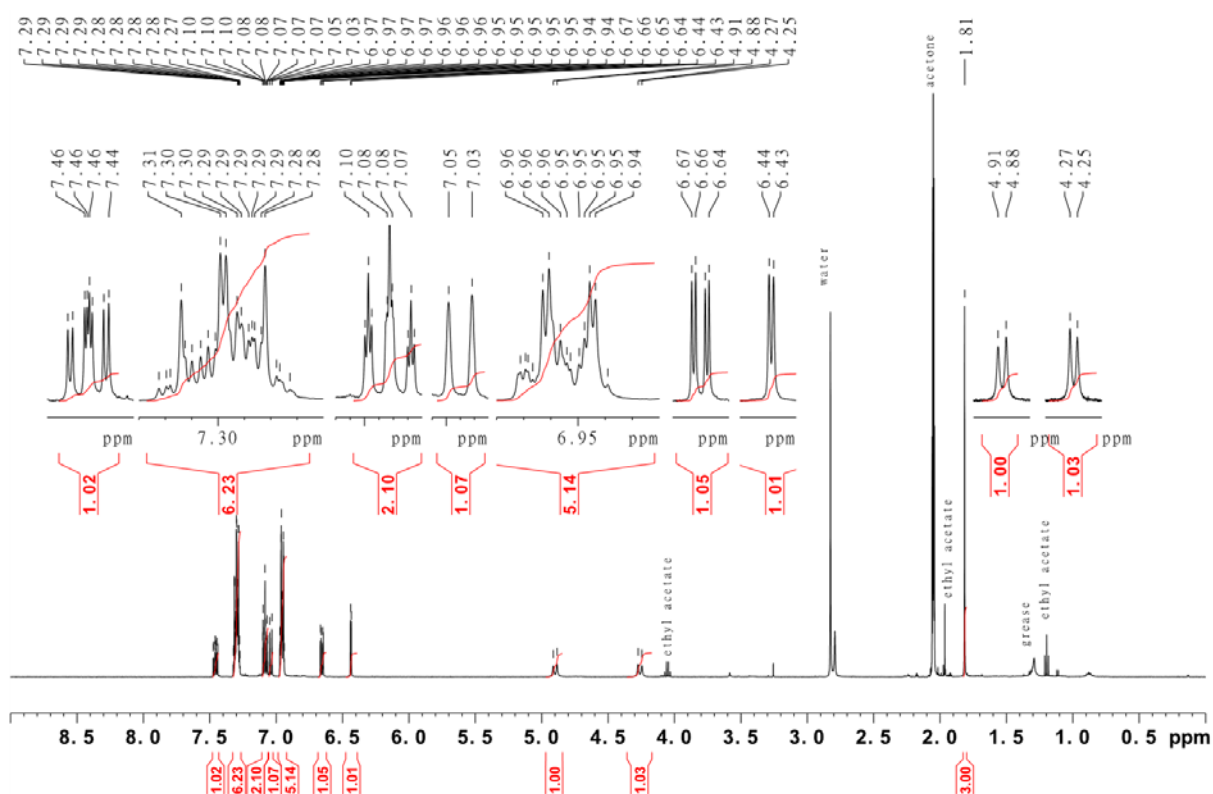


Figure SII.121: 500 MHz ^1H -NMR spectrum of (Z)-1-(3-(diphenylamino)dibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**20**).

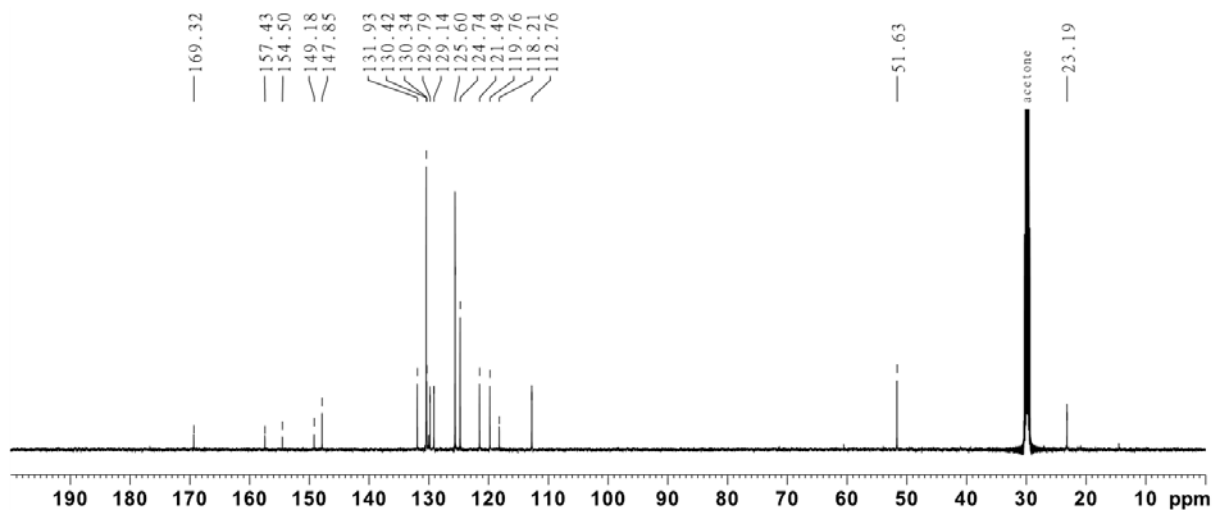


Figure SII.122: 125 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (Z)-1-(3-(diphenylamino)dibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**20**).

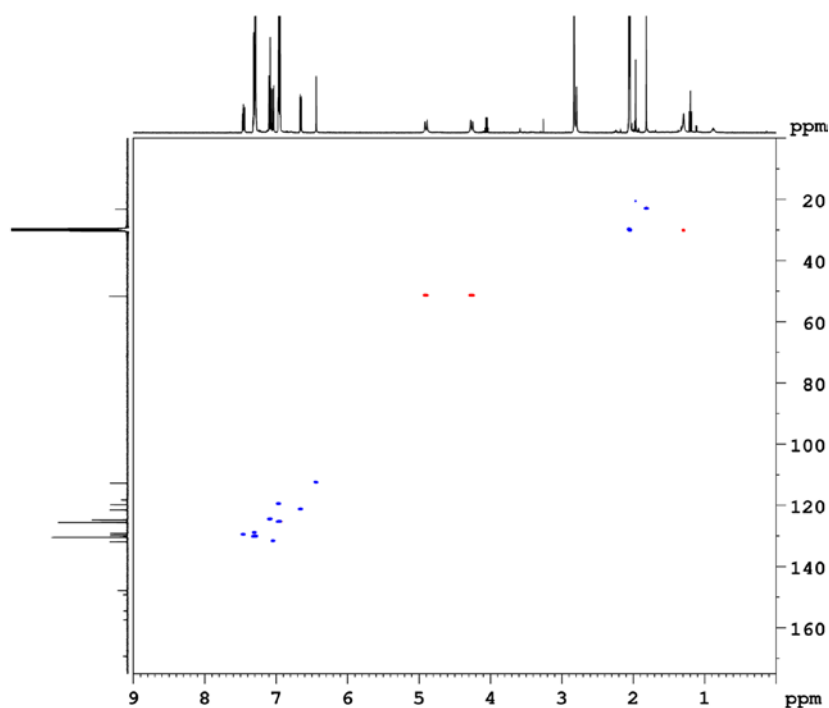


Figure SII.123: 500 MHz ^1H - ^{13}C HSQC spectrum of (*Z*)-1-(3-(diphenylamino)dibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**20**).

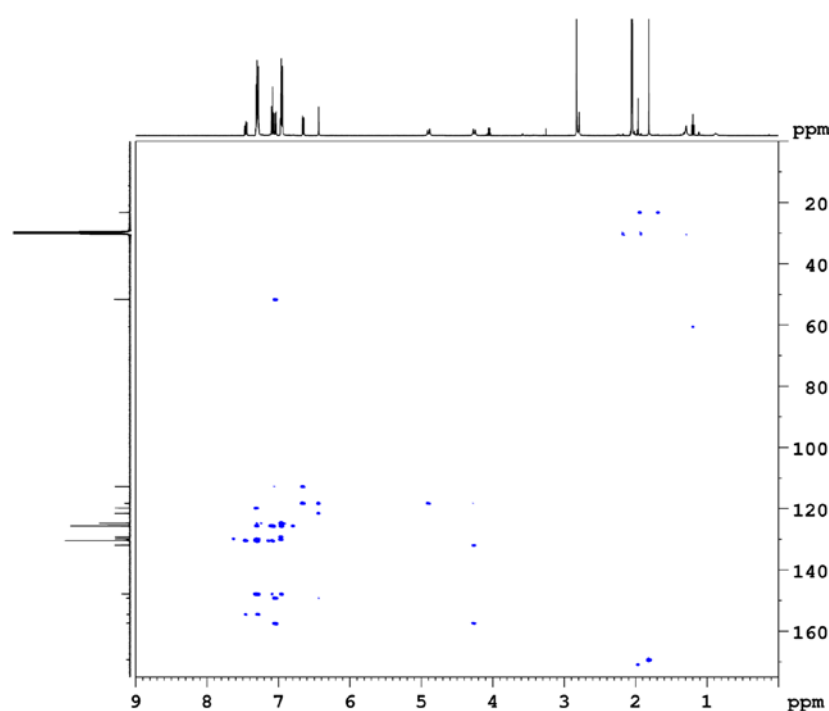
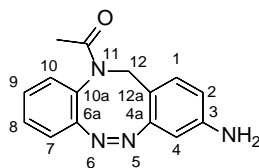


Figure SII.124: 500 MHz HMBC spectrum of (*Z*)-1-(3-(diphenylamino)dibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**20**).

II.2.13 Synthesis of (Z)-1-(3-aminodibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (21)



Tert-butyl-(*Z*)-(11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocin-3-yl)carbamate (**21**, 17.3 mg, 47.2 μ mol) was dissolved in 25 mL dichloromethane and 5 mL of trifluoroacetic acid were added. The reaction mixture was stirred at room temperature for 16 h and then neutralized with saturated aqueous NaHCO_3 solution. The organic layer was separated and the aqueous layer was extracted twice with 10 mL dichloromethane, dried over MgSO_4 and the solvent was evaporated. Column chromatography on silica (ethyl acetate/cyclohexane 1:1, R_f = 0.15) gave the product as yellow solid (7.50 mg, 28.2 μ mol, 60%).

melting point: 178 $^{\circ}\text{C}$

$^1\text{H-NMR}$ (600 MHz, CDCl_3 , 298 K): δ = 7.27-7.24 (m, 1 H, *H*-8), 7.14 (td, 3J = 7.7 Hz, 4J = 1.4 Hz, 1 H, *H*-9), 6.99 (dd, 3J = 7.9 Hz, 4J = 0.9 Hz, 1 H, *H*-10), 6.87 (dd, 3J = 7.8 Hz, 4J = 1.2 Hz, 1 H, *H*-7), 6.80 (d, 3J = 8.2 Hz, 1 H, *H*-1), 6.33 (dd, 3J = 8.1 Hz, 4J = 2.4 Hz, 1 H, *H*-2), 6.16 (d, 4J = 2.4 Hz, 1 H, *H*-4), 4.86 (d, 2J = 14.3 Hz, 1 H, *H*-12), 4.27 (d, 2J = 14.3 Hz, 1 H, *H*-12'), 3.72 (br. s, 2 H, $-\text{NH}_2$), 1.92 (s, 3 H, $-\text{CH}_3$) ppm.

$^{13}\text{C}\{^1\text{H}\}\text{-NMR}$ (150 MHz, CDCl_3 , 298 K): δ = 170.0 (C=O), 156.6 (C-4a), 152.9 (C-6a), 146.8 (C-3), 131.0 (C-1), 129.0 (C-10a), 128.82 (C-10), 128.67 (C-8), 127.9 (C-9), 119.3 (C-7), 113.9 (C-2), 113.2 (C-12a), 104.9 (C-4), 51.5 (C-12) 23.3 (CH_3) ppm.

IR (ATR): $\tilde{\nu}$ = 3346 (m), 2922 (m), 2852 (w), 1653 (s), 1608 (s), 1504 (w), 1480 (s), 1389 (s), 1372 (w), 1349 (s), 1326 (w), 1283 (m), 1241 (w), 1209 (w), 1148 (w), 1091 (w), 1071 (w), 975 (w), 907 (w), 867 (w), 827 (m), 802 (w), 760 (m), 742 (m), 718 (w), 696 (w), 605 (m), 585 (w), 541 (w), 515 (m) cm^{-1} .

HR-MS (ESI, EtOAc): m/z [$\text{M}+\text{Na}$] $^+$ calculated for $\text{C}_{15}\text{H}_{14}\text{ON}_4+\text{Na}^+$: 289.1060; found: 289.1057 \pm 0.98 ppm.

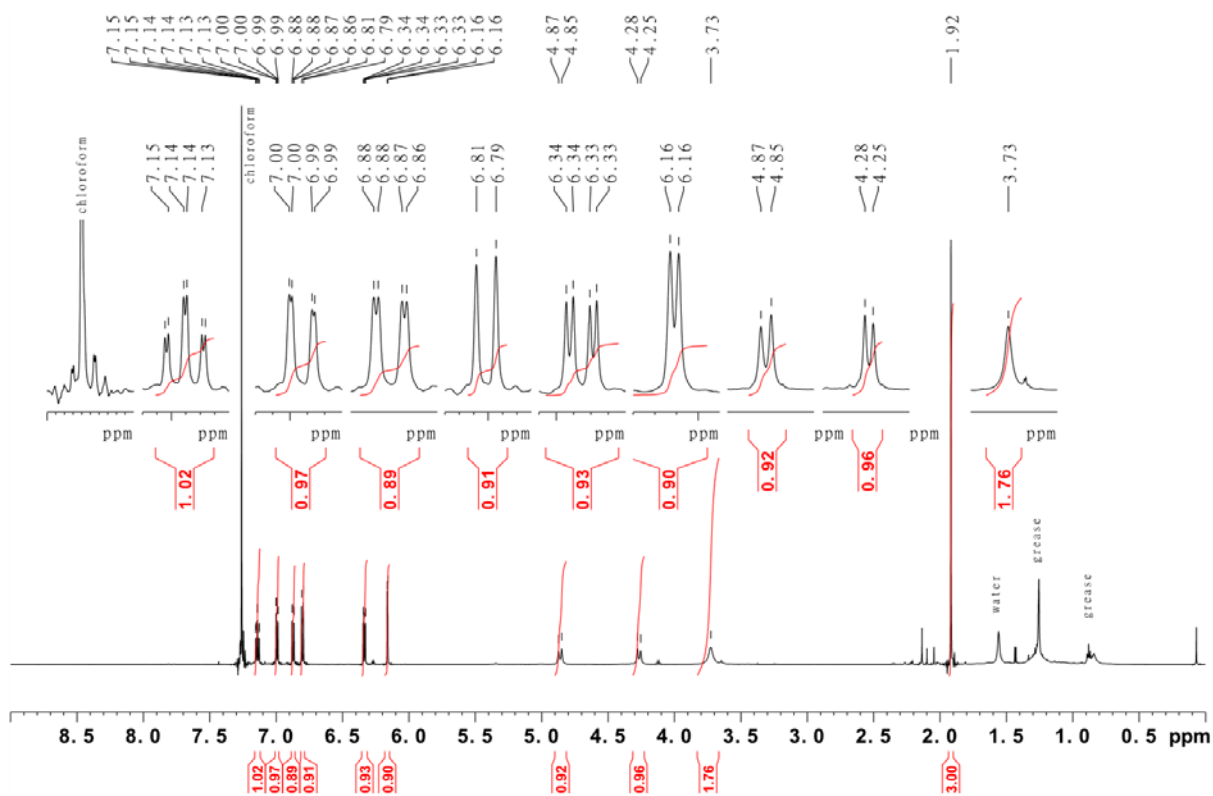


Figure SII.125: 600 MHz ^1H -NMR spectrum of (Z)-1-(3-aminodibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**21**).

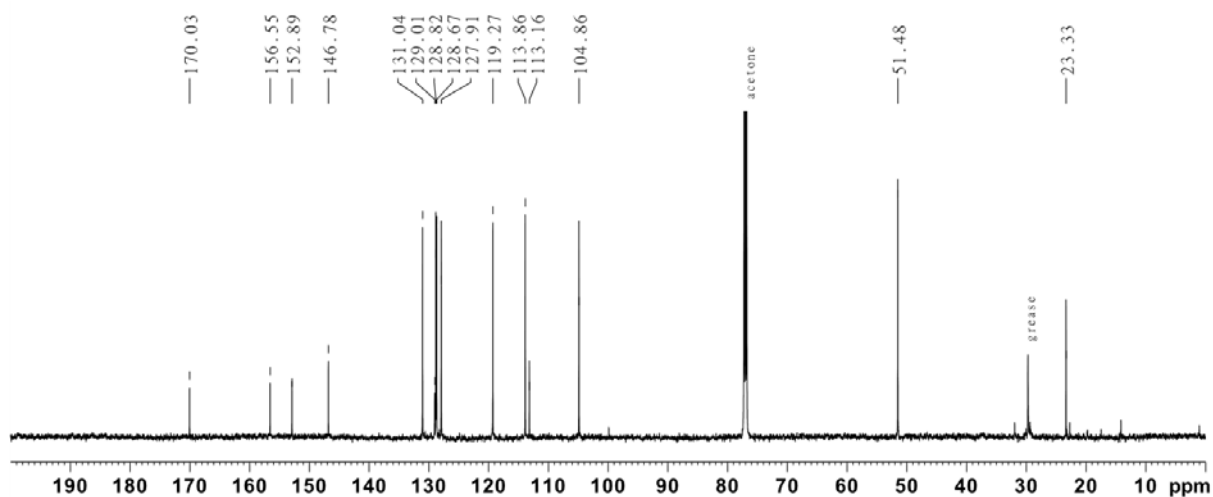


Figure SII.126: 150 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (Z)-1-(3-aminodibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**21**).

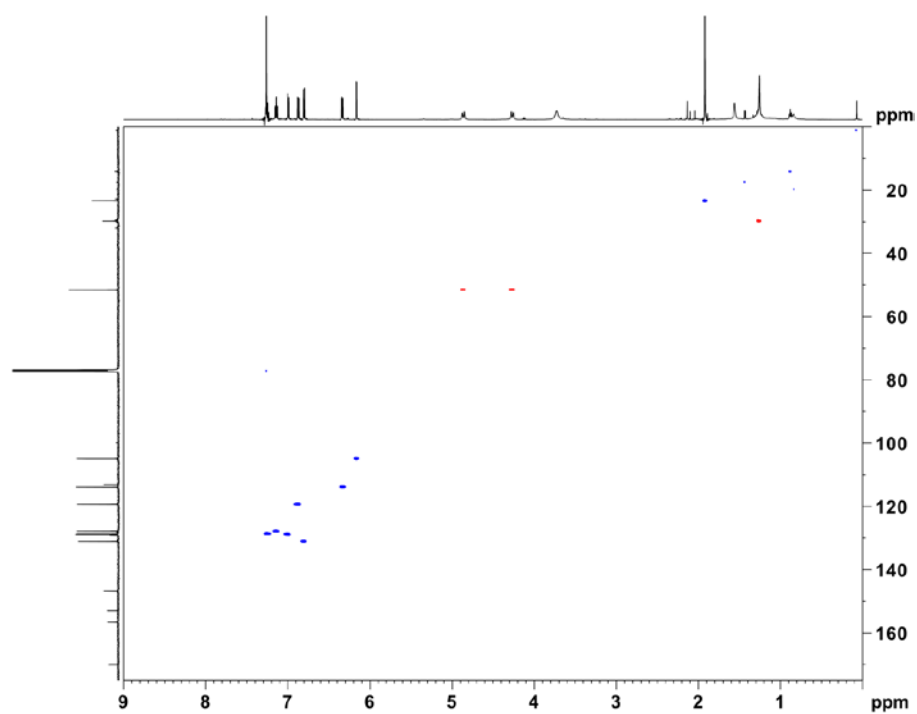


Figure SII.127: 600 MHz ^1H - ^{13}C HSQC spectrum of (*Z*)-1-(3-aminodibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**21**).

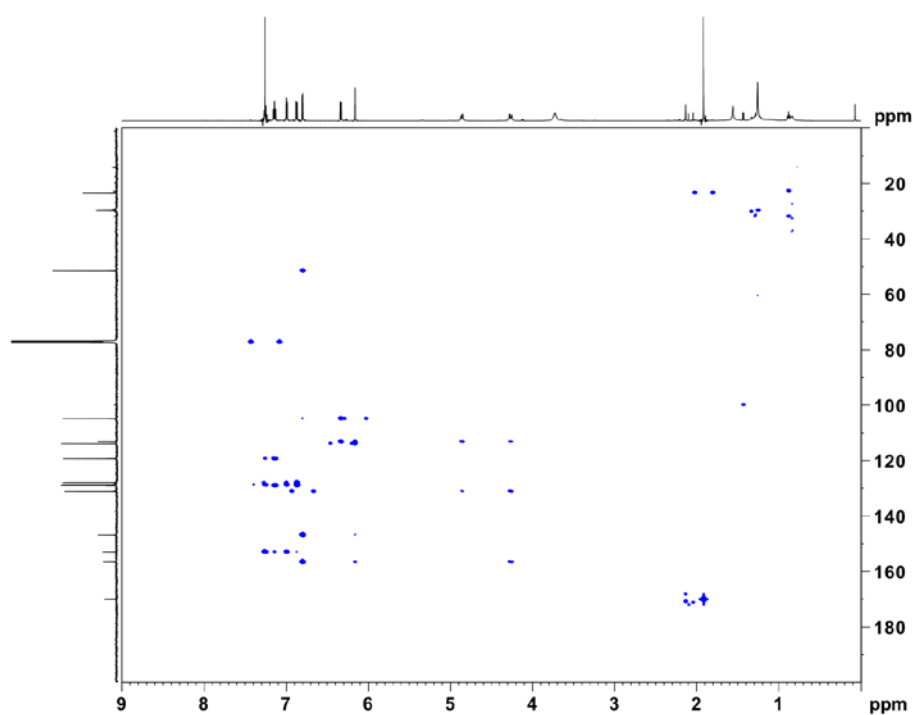
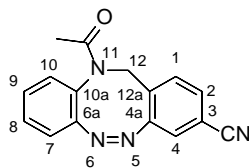


Figure SII.128: 600 MHz HMBC spectrum of (*Z*)-1-(3-aminodibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**21**).

II.2.14 Synthesis of (Z)-11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocine-3-carbonitrile (23)



Halogenated *N*-acetyl-diazocine (**2**: 20.0 mg, 60.6 μ mol, **3**: 23.0 mg, 60.6 μ mol), 1,1'-bis(diphenylphosphino)ferrocene (1.00 mg, 1.81 μ mol), Pd(dba)₂ (1.00 mg, 1.21 μ mol) and zinc cyanide (3.55 mg, 30.3 μ mol) were dissolved in 2.4 mL of dry DMAC under a nitrogen atmosphere, heated to 130 °C with an oil bath and stirred for 16 h at given temperature. After cooling to rt. the reaction mixture was extracted with 10 mL of DCM twice, dried over MgSO₄ and the solvent was evaporated. Column chromatography on silica (ethyl acetate/cyclohexane 1:1, *R_f* = 0.23) gave the product as yellow solid (from bromide **2**: 10.2 mg, 36.9 μ mol, 61%; from iodide **3**: 13.6 mg, 49.1 μ mol, 81%).

melting point: 194 °C

¹H-NMR (600 MHz, acetone-*d*₆, 298 K): δ = 7.56 (dd, ³*J* = 7.9 Hz, ⁴*J* = 1.7 Hz, 1 H, *H*-2), 7.47 (d, ³*J* = 8.0 Hz, 1 H, *H*-1), 7.42 (td, ³*J* = 7.9 Hz, ⁴*J* = 1.4 Hz, 1 H, *H*-8), 7.37 (d, ⁴*J* = 1.5 Hz, 1 H, *H*-4), 7.35 (dd, ³*J* = 8.0 Hz, ⁴*J* = 1.1 Hz, 1 H, *H*-10), 7.31 (td, ³*J* = 7.4 Hz, ⁴*J* = 1.4 Hz, 1 H, *H*-9), 7.09 (dd, ³*J* = 7.9 Hz, ⁴*J* = 1.1 Hz, 1 H, *H*-7), 5.21 (d, ²*J* = 15.1 Hz, 1 H, *H*-12), 4.41 (d, ²*J* = 15.0 Hz, 1 H, *H*-12'), 1.80 (s, 3 H, -CH₃) ppm.

¹³C{¹H}-NMR (150 MHz, acetone-*d*₆, 298 K): δ = 169.4 (C=O), 156.3 (C-4a), 154.1 (C-6a), 132.1 (C-1), 131.9 (C-2), 130.9 (C-12a), 130.6 (C-8), 130.2 (C-10), 129.8 (C-9), 129.1 (C-10a), 123.7 (C-4), 120.1 (C-7), 118.1 (-CN), 113.2 (C-3), 51.8 (C-12) 22.9 (CH₃) ppm.

IR (ATR): $\tilde{\nu}$ = 3058 (w), 2923 (m), 2853 (w), 2233 (m), 1662 (s), 1589 (w), 1556 (w), 1521 (w), 1475 (m), 1448 (w), 1377 (s), 1340 (w), 1299 (m), 1228 (w), 1148 (w), 1109 (w), 1078 (w), 1032 (w), 1019 (w), 973 (w), 930 (w), 884 (w), 844 (w), 832 (w), 813 (w), 770 (m), 741 (m), 693 (w), 634 (w), 596 (m) cm⁻¹.

HR-MS (ESI, DCM): *m/z* [M+H]⁺ calculated for C₁₆H₁₂ON₄+H⁺: 277.1084; found: 277.1080 \pm 1.40 ppm.

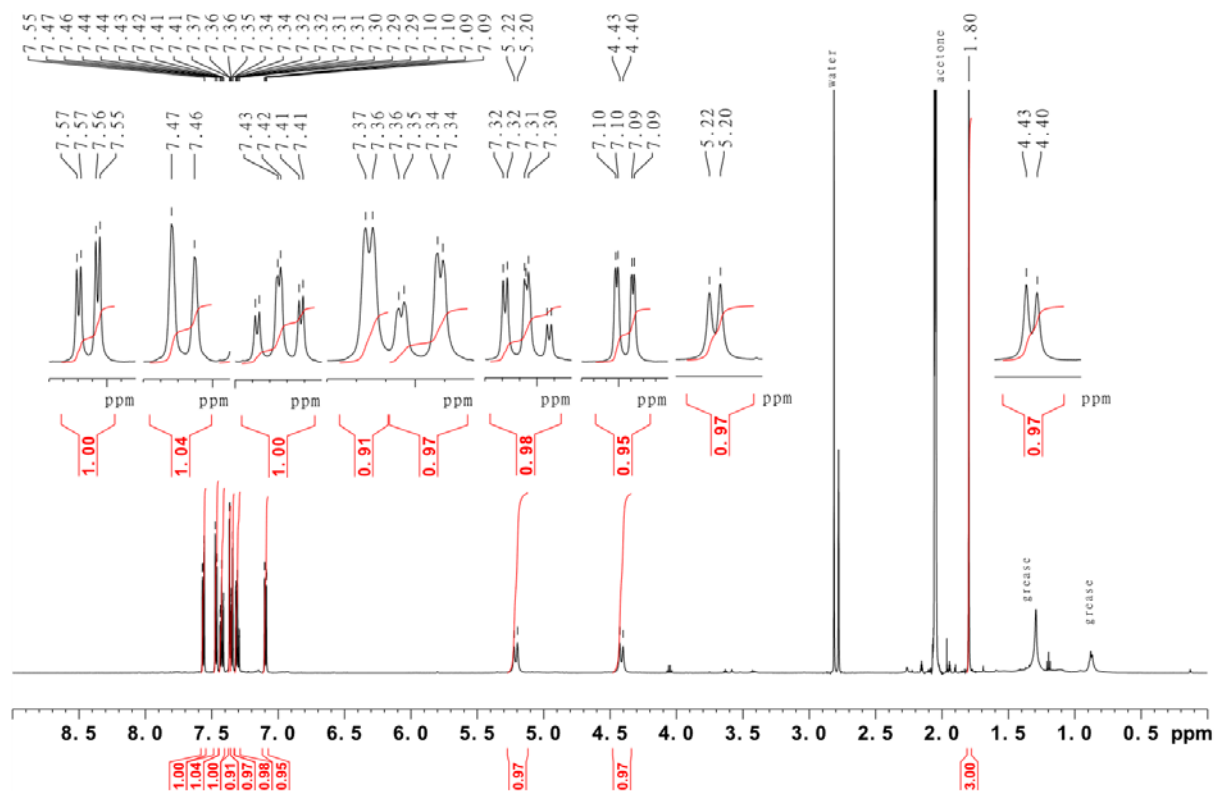


Figure SII.129: 600 MHz ^1H -NMR spectrum of (Z)-11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocine-3-carbonitrile (**23**).

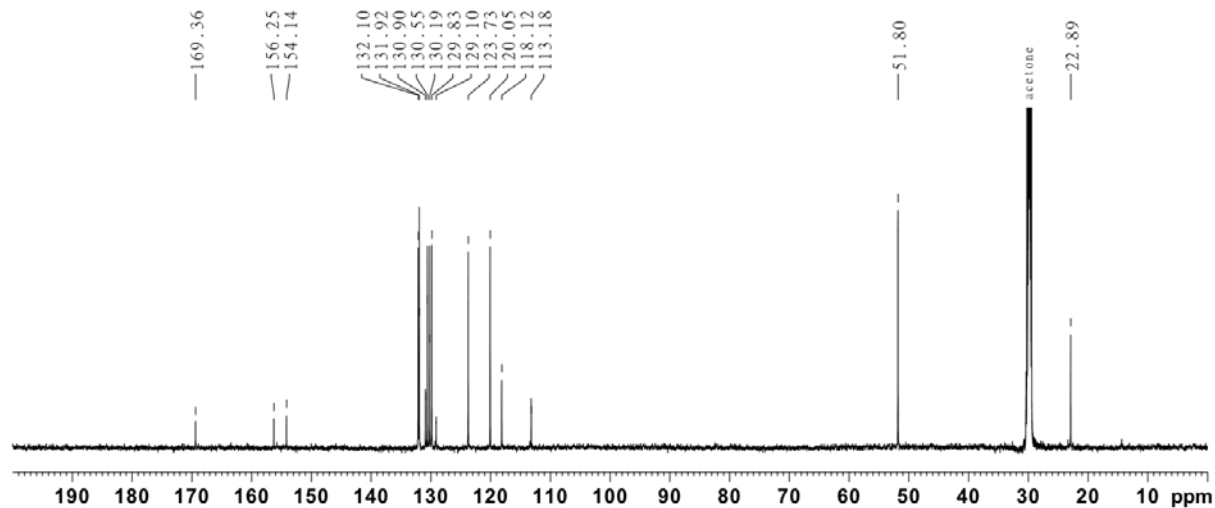


Figure SII.130: 150 MHz $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of (Z)-11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocine-3-carbonitrile (**23**).

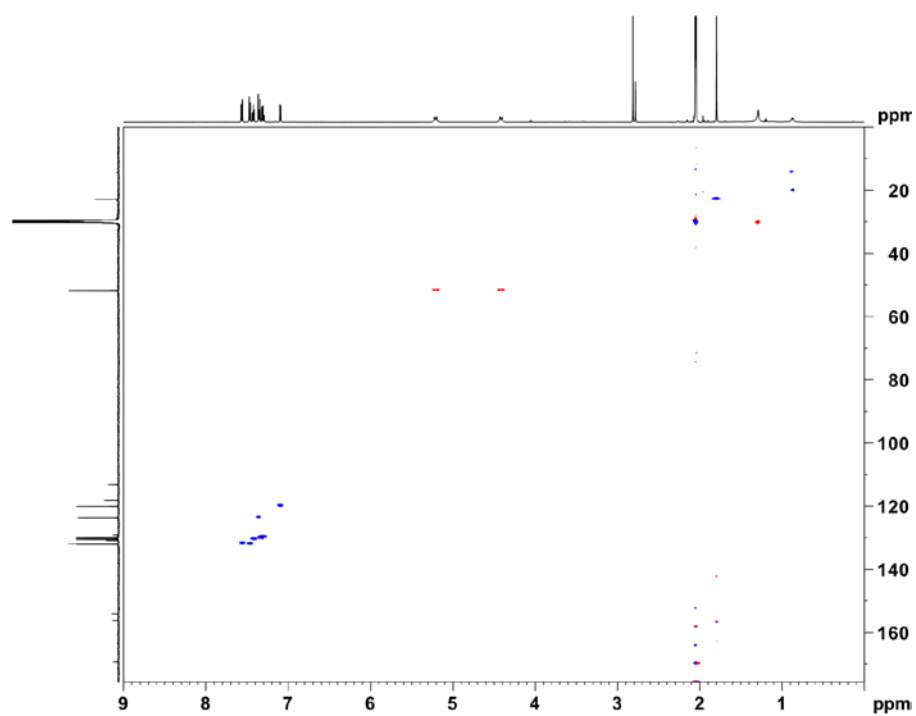


Figure SII.131: 600 MHz ^1H - ^{13}C HSQC spectrum of *Z*)-11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocine-3-carbonitrile (**23**).

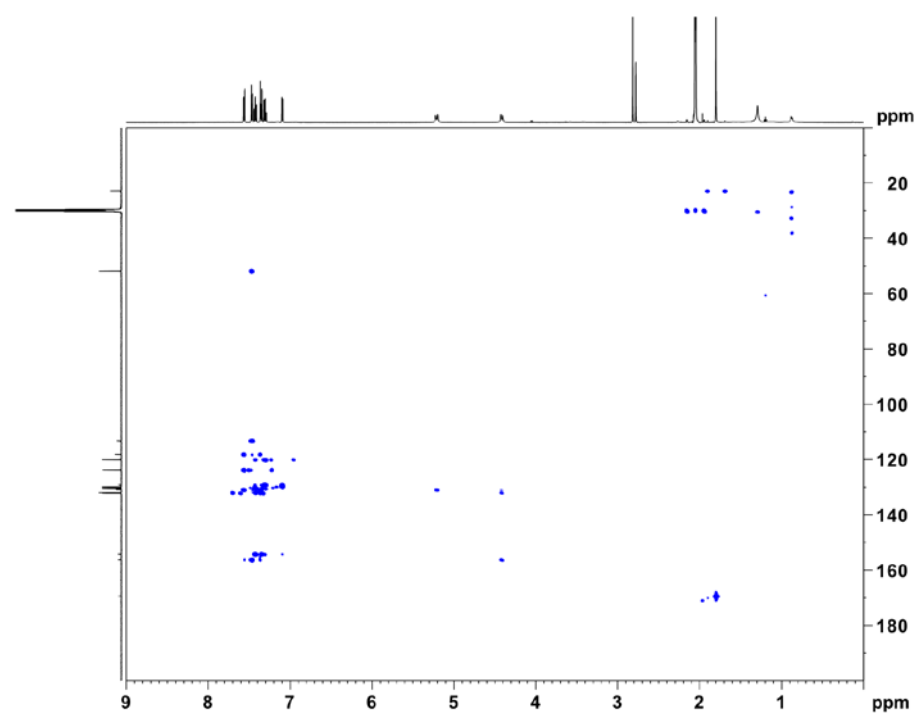


Figure SII.132: 600 MHz HMBC spectrum of *Z*)-11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocine-3-carbonitrile (**23**).

III. UV-vis switching experiments

All samples were irradiated to the photostationary state (PSS) with 405 nm in acetonitrile or water. The UV-vis spectra were measured at 250 μM concentrations at 25 $^{\circ}\text{C}$, except pyridine-substituted *N*-acetyl-diazocine **14** (2.55 mM due to low synthesis yield).

III.1 (Z)-(3,8-dibromodibenzo[*c,g*][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**4**)

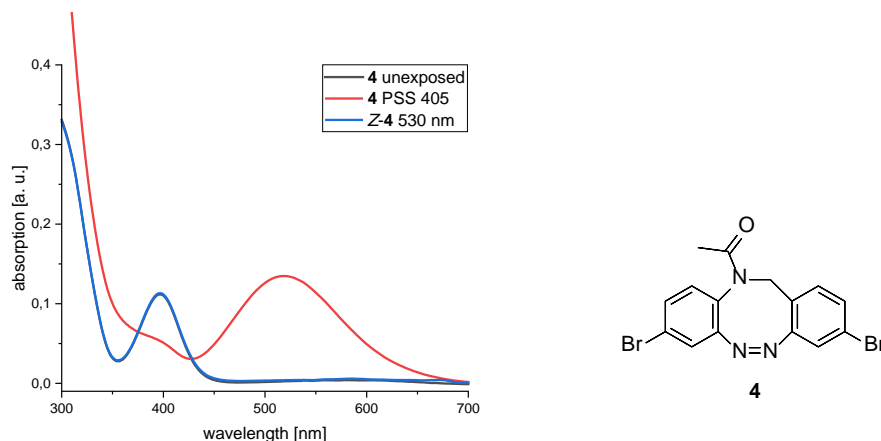


Figure SIII.1: UV-vis spectra of **4** in MeCN at 25 $^{\circ}\text{C}$. The unexposed sample is plotted in black, the spectra of the PSS between Z-4 and E-4 after irradiation with 405 nm in red and the spectra of Z-4 after irradiation with 530 nm in blue.

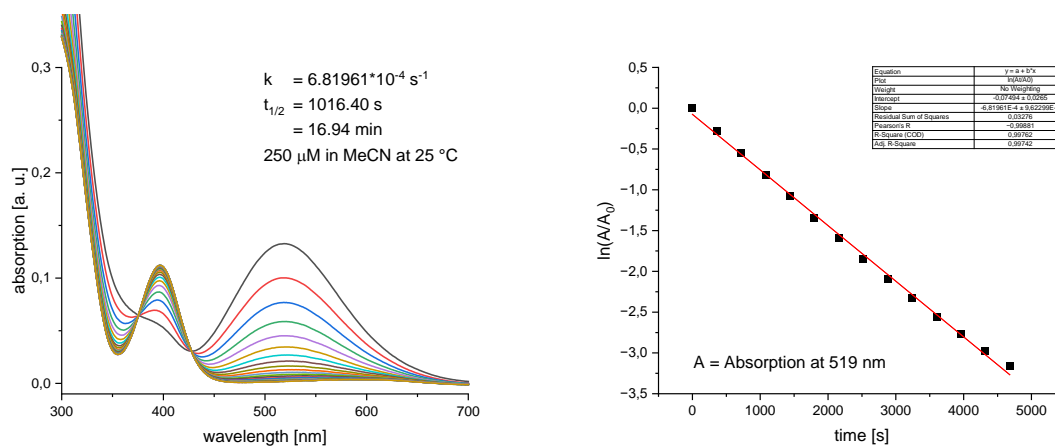


Figure SIII.2: UV-vis spectra of the half-life determination of **4** in MeCN at 25 $^{\circ}\text{C}$ (left) with the corresponding first order kinetics plot (right).

III.2 (Z)-1-(3-phenyldibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (7)

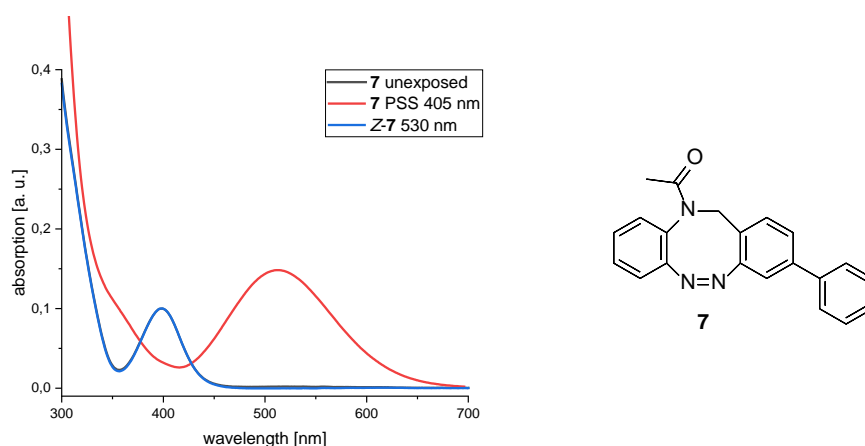


Figure SIII.3: UV-vis spectra of **7** in MeCN at 25 °C. The unexposed sample is plotted in black, the spectra of the PSS between Z-7 and E-7 after irradiation with 405 nm in red and the spectra of Z-7 after irradiation with 530 nm in blue.

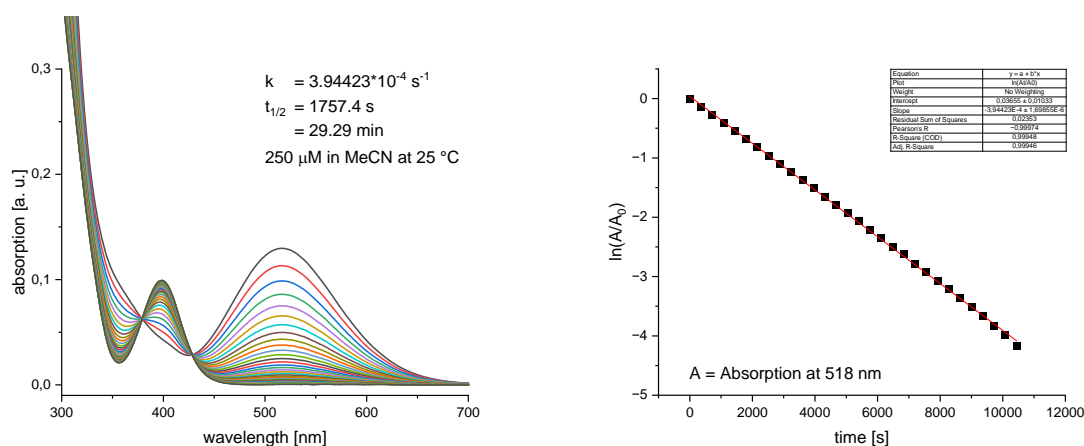


Figure SIII.4: UV-vis spectra of the half-life determination of **7** in MeCN at 25 °C (left) with the corresponding first order kinetics plot (right).

III.3 (Z)-1-(3-vinyldibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (8)

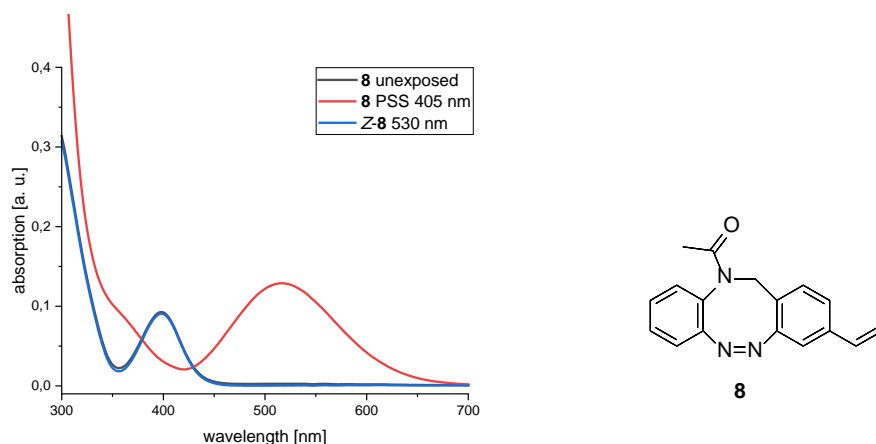


Figure SIII.5: UV-vis spectra of **8** in MeCN at 25 °C. The unexposed sample is plotted in black, the spectra of the PSS between Z-8 and E-8 after irradiation with 405 nm in red and the spectra of Z-8 after irradiation with 530 nm in blue.

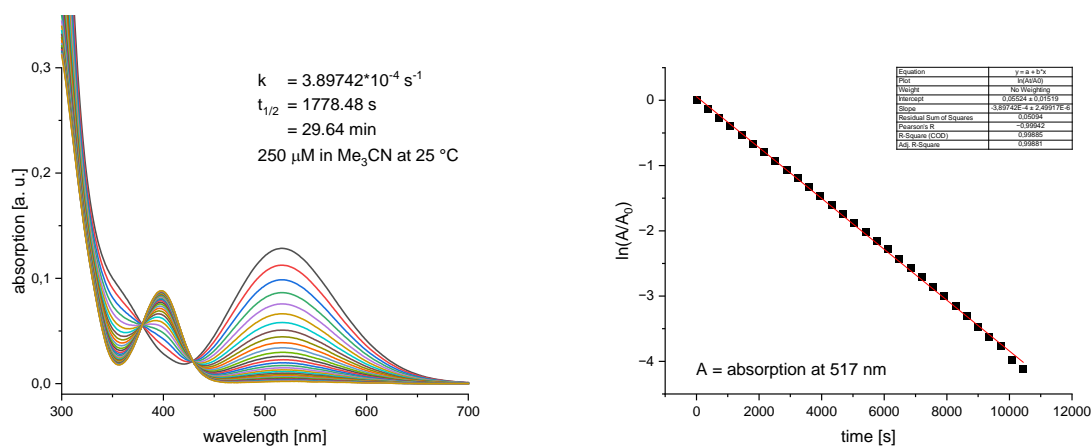


Figure SIII.6: UV-vis spectra of the half-life determination of **8** in MeCN at 25 °C (left) with the corresponding first order kinetics plot (right).

III.4 (Z)-1-(3-(2,6-dimethylphenyl)dibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**9**)

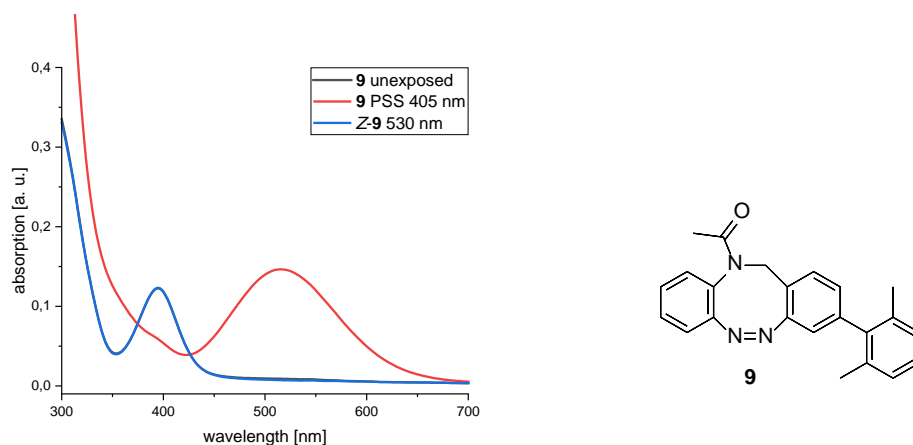


Figure SIII.7: UV-vis spectra of **9** in MeCN at 25 °C. The unexposed sample is plotted in black, the spectra of the PSS between Z-**9** and E-**9** after irradiation with 405 nm in red and the spectra of Z-**9** after irradiation with 530 nm in blue.

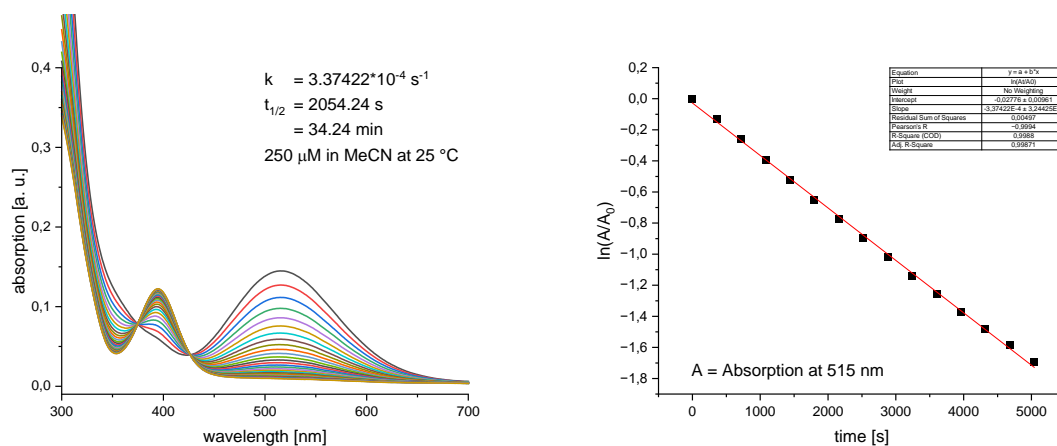


Figure SIII.8: UV-vis spectra of the half-life determination of **9** in MeCN at 25 °C (left) with the corresponding first order kinetics plot (right).

III.5 (Z)-1-(3-(2-bromophenyl)dibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (10)

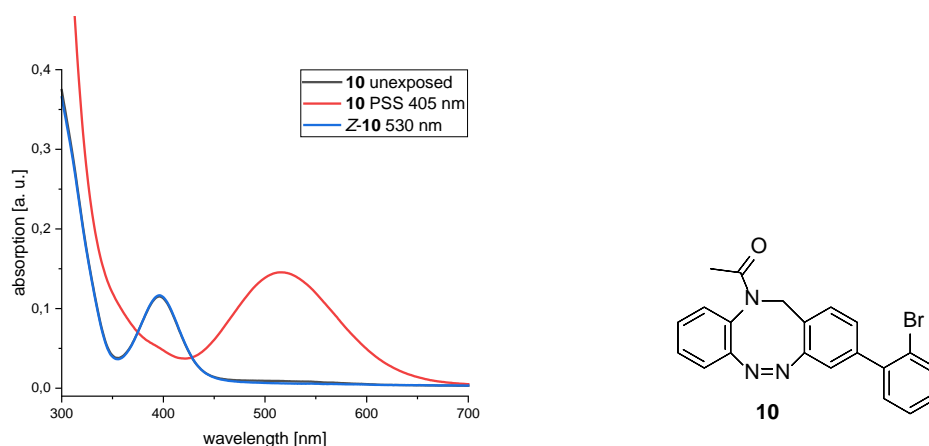


Figure SIII.9: UV-vis spectra of **10** in MeCN at 25 °C. The unexposed sample is plotted in black, the spectra of the PSS between Z-**10** and E-**10** after irradiation with 405 nm in red and the spectra of Z-**10** after irradiation with 530 nm in blue.

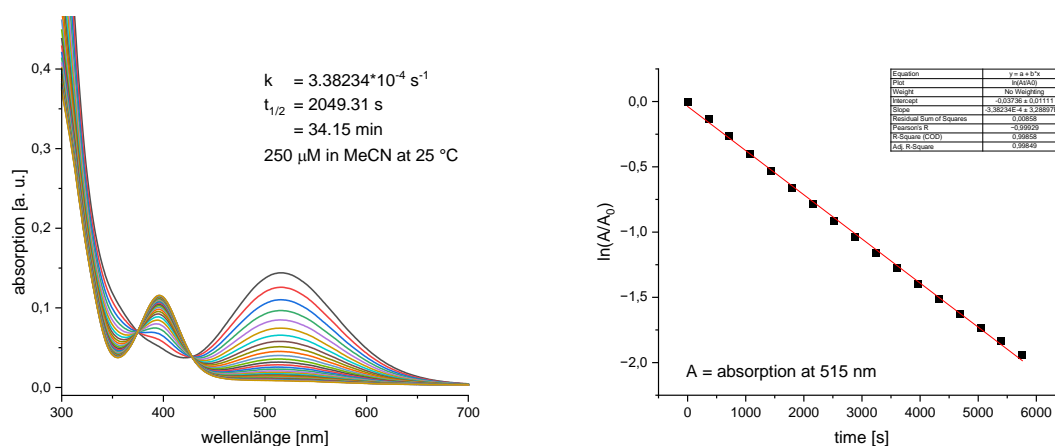


Figure SIII.10: UV-vis spectra of the half-life determination of **10** in MeCN at 25 °C (left) with the corresponding first order kinetics plot (right).

III.6 (Z)-1-(3-(4-fluorophenyl)dibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (11)

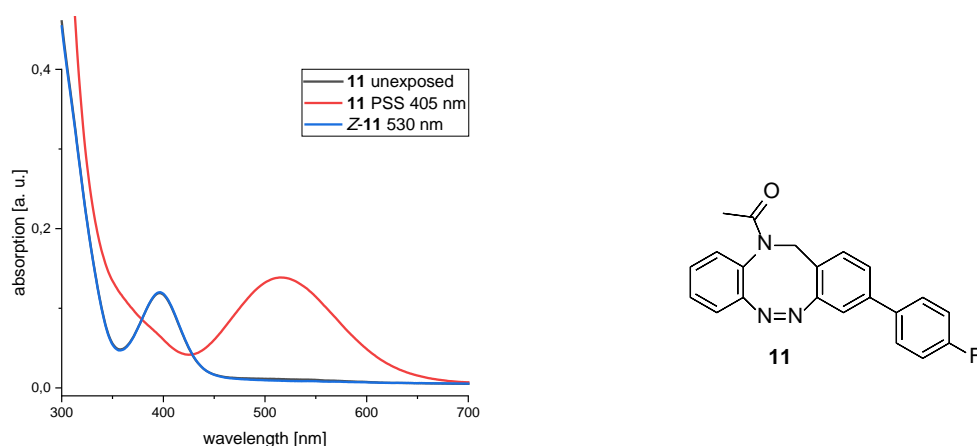


Figure SIII.11: UV-vis spectra of **11** in MeCN at 25 °C. The unexposed sample is plotted in black, the spectra of the PSS between Z-**11** and E-**11** after irradiation with 405 nm in red and the spectra of Z-**11** after irradiation with 530 nm in blue.

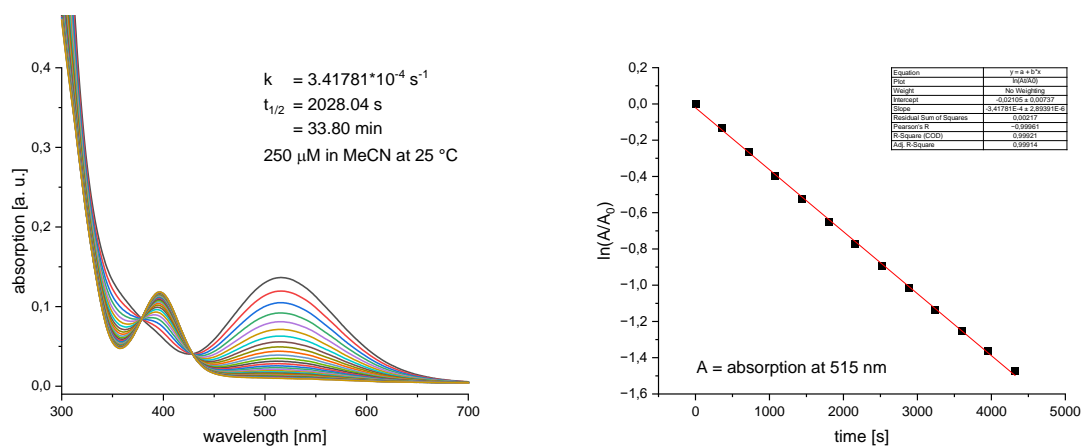


Figure SIII.12: UV-vis spectra of the half-life determination of **11** in MeCN at 25 °C (left) with the corresponding first order kinetics plot (right).

III.7 (Z)-2-(11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocin-3-yl)benzaldehyde (**12**)

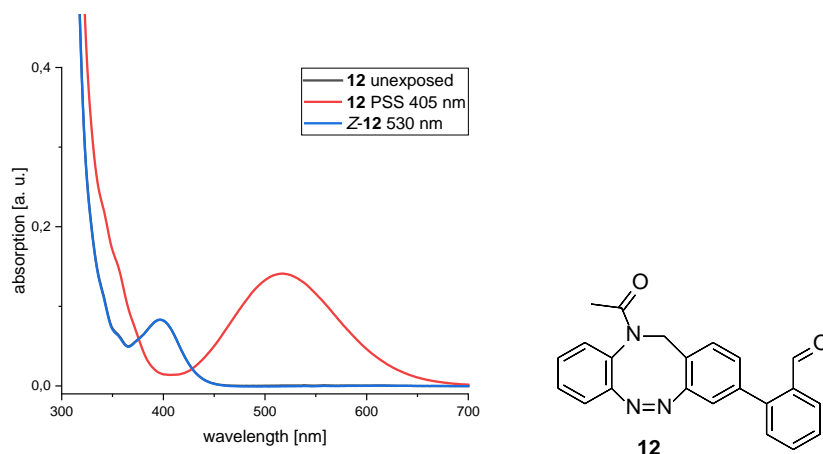


Figure SIII.13: UV-vis spectra of **12** in MeCN at 25 °C. The unexposed sample is plotted in black, the spectra of the PSS between **Z-12** and **E-12** after irradiation with 405 nm in red and the spectra of **Z-12** after irradiation with 530 nm in blue.

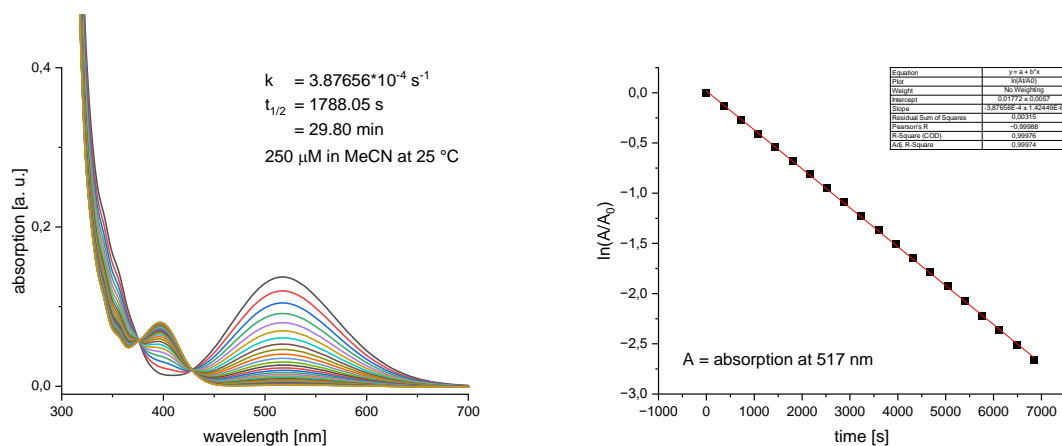


Figure SIII.14: UV-vis spectra of the half-life determination of **12** in MeCN at 25 °C (left) with the corresponding first order kinetics plot (right).

III.8 (Z)-2-(11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocin-3-yl)benzoic acid (**13**)

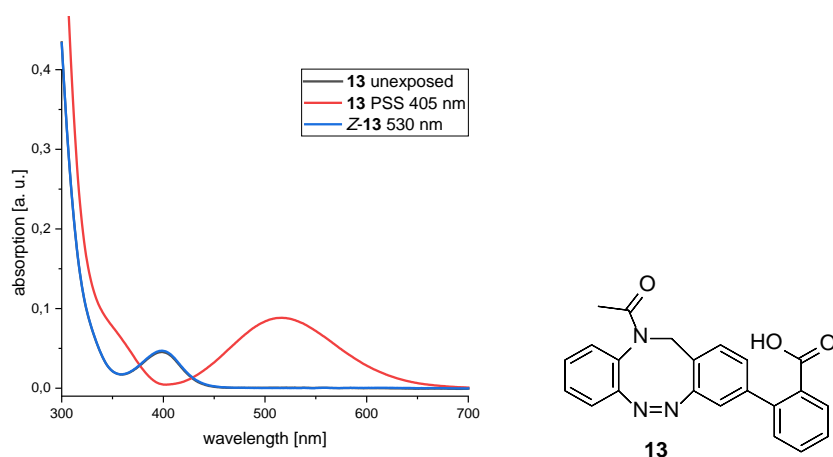


Figure SIII.15: UV-vis spectra of **13** in MeCN at 25 °C. The unexposed sample is plotted in black, the spectra of the PSS between **Z-13** and **E-13** after irradiation with 405 nm in red and the spectra of **Z-13** after irradiation with 530 nm in blue.

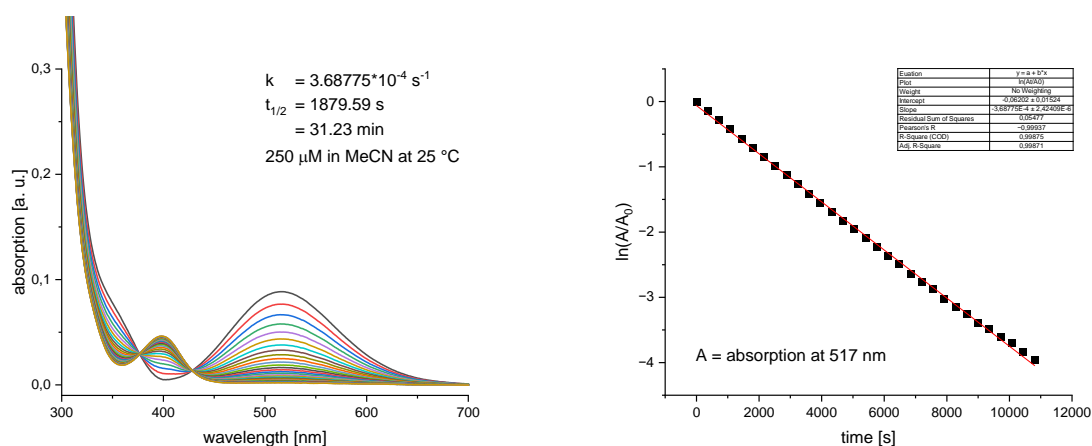


Figure SIII.16: UV-vis spectra of the half-life determination of **13** in MeCN at 25 °C (left) with the corresponding first order kinetics plot (right).

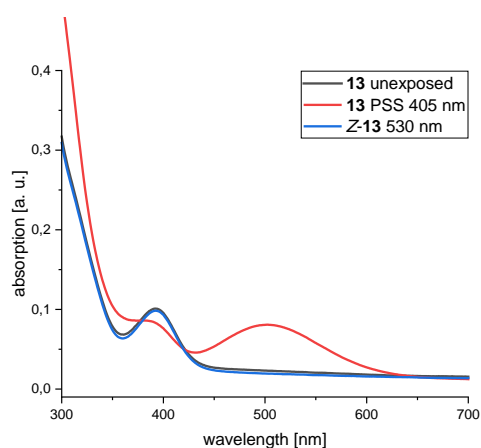


Figure SIII.17: UV-vis spectra of **13** in deionized water pH 9 at 25 °C. The unexposed sample is plotted in black, the spectra of the PSS between **Z-13** and **E-13** after irradiation with 405 nm in red and the spectra of **Z-13** after irradiation with 530 nm in blue.

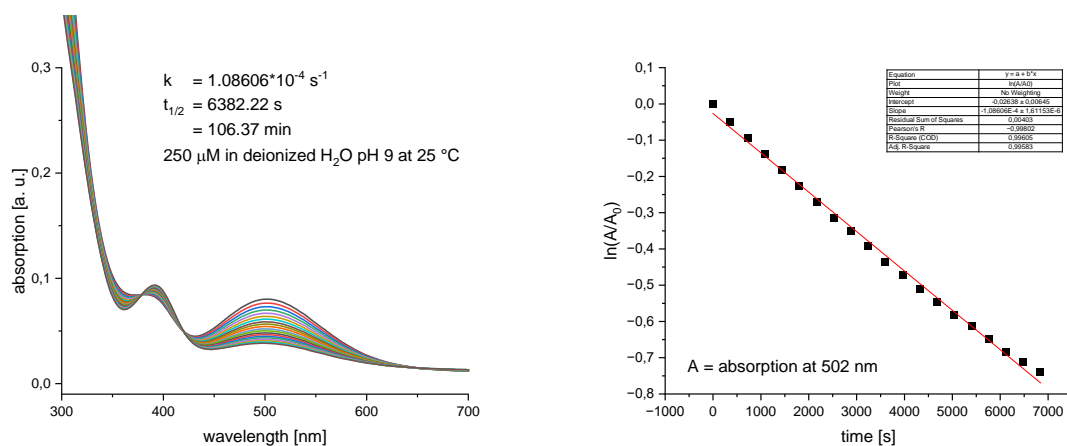


Figure SIII.18: UV-vis spectra of the half-life determination of **13** in deionized water pH 9 at 25 °C (left) with the corresponding first order kinetics plot (right).

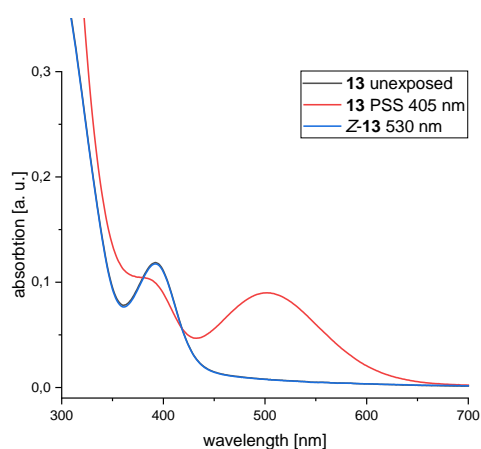


Figure SIII.19: UV-vis spectra of **13** in aqueous PBS buffer solution pH 7.4 at 25 °C. The unexposed sample is plotted in black, the spectra of the PSS between Z-**13** and E-**13** after irradiation with 405 nm in red and the spectra of Z-**13** after irradiation with 530 nm in blue.

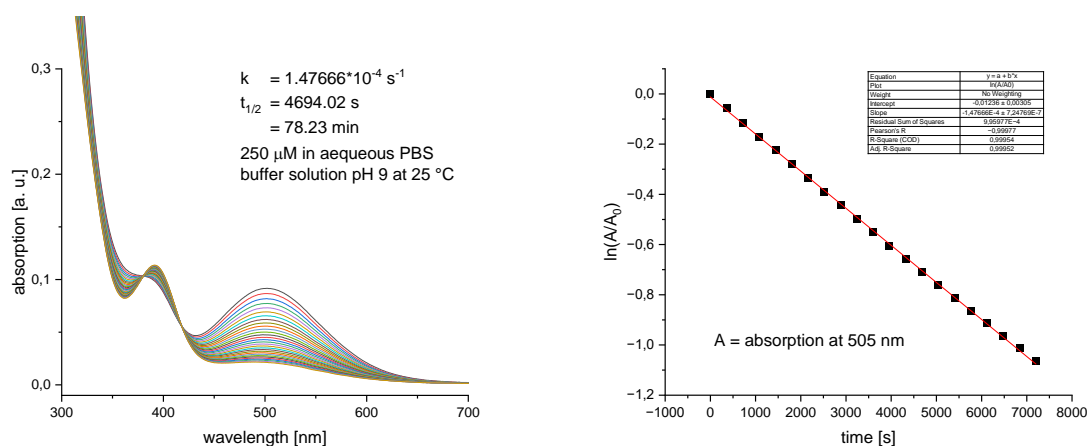


Figure SIII.20: UV-vis spectra of the half-life determination of **13** in aqueous PBS buffer solution pH 7.4 at 25 °C (left) with the corresponding first order kinetics plot (right).

III.9 (Z)-1-(3-(pyridine-4-yl)dibenzo[c,g][1,2,5]triazocin-11(12H)-ethan-1-one (14)

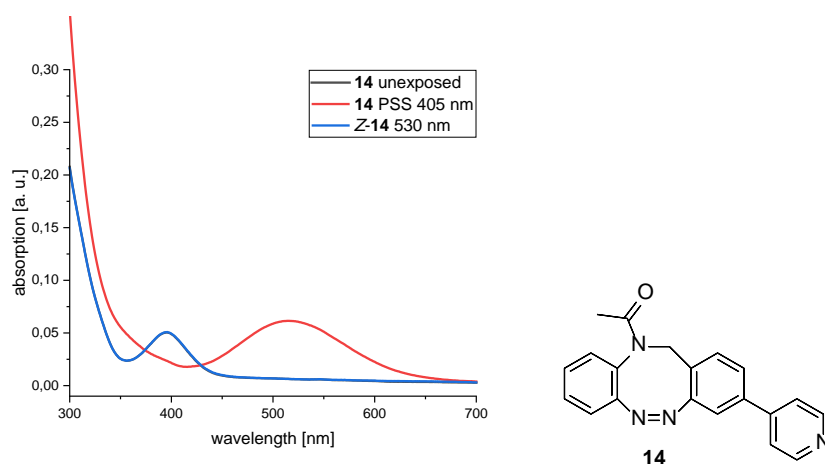


Figure SIII.21: UV-vis spectra of **14** in MeCN at 25 °C. The unexposed sample is plotted in black, the spectra of the PSS between **Z-14** and **E-14** after irradiation with 405 nm in red and the spectra of **Z-14** after irradiation with 530 nm in blue.

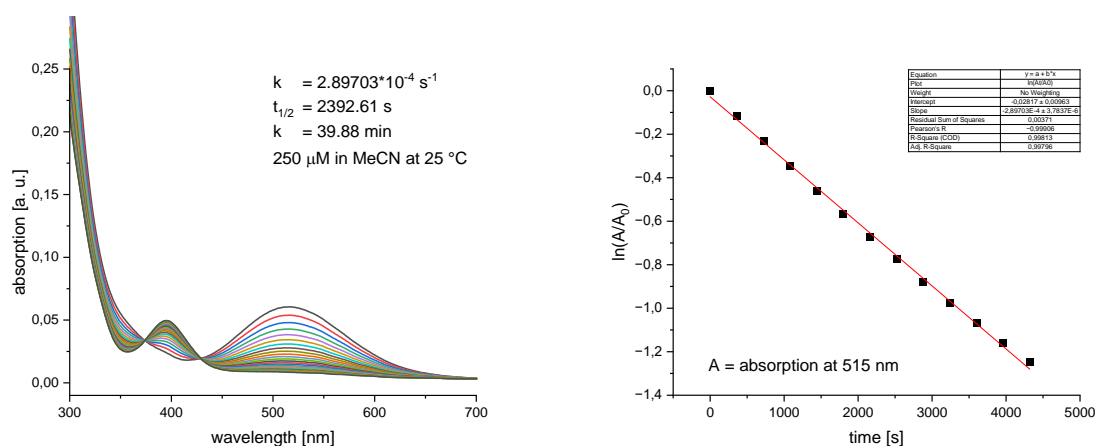


Figure SIII.22: UV-vis spectra of the half-life determination of **14** in MeCN at 25 °C (left) with the corresponding first order kinetics plot (right).

III.10 (Z)-1-(3-benzyl)dibenzo[c,g][1,2,5]triazocin-11(12H)-ethan-1-one (17)

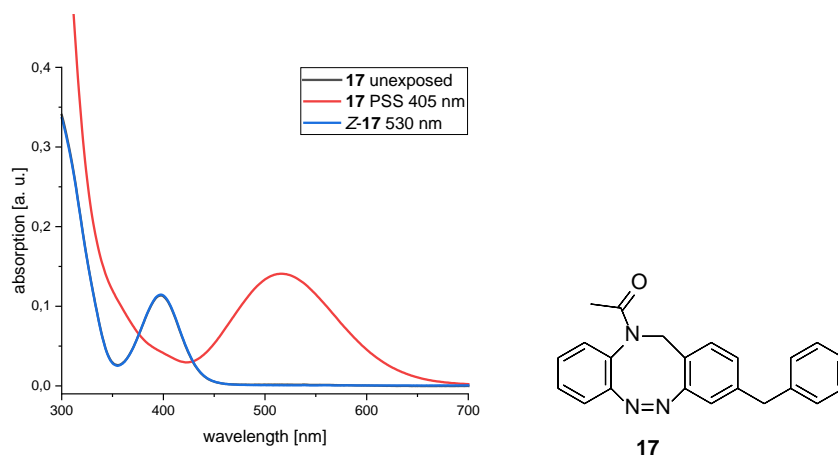


Figure SIII.23: UV-vis spectra of **17** in MeCN at 25 °C. The unexposed sample is plotted in black, the spectra of the PSS between **Z-17** and **E-17** after irradiation with 405 nm in red and the spectra of **Z-17** after irradiation with 530 nm in blue.

III.12 (Z)-1-(3-(diphenylamino)dibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (20)

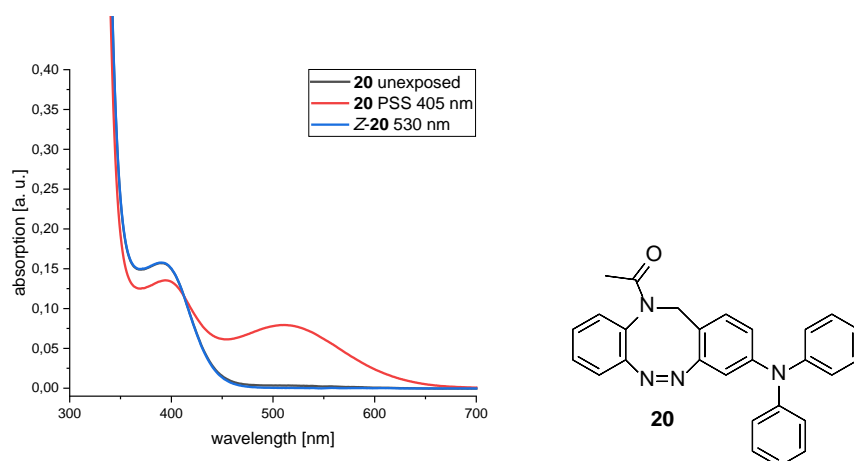


Figure SIII.27: UV-vis spectra of **20** in MeCN at 25 °C. The unexposed sample is plotted in black, the spectra of the PSS between **Z-20** and **E-20** after irradiation with 405 nm in red and the spectra of **Z-20** after irradiation with 530 nm in blue.

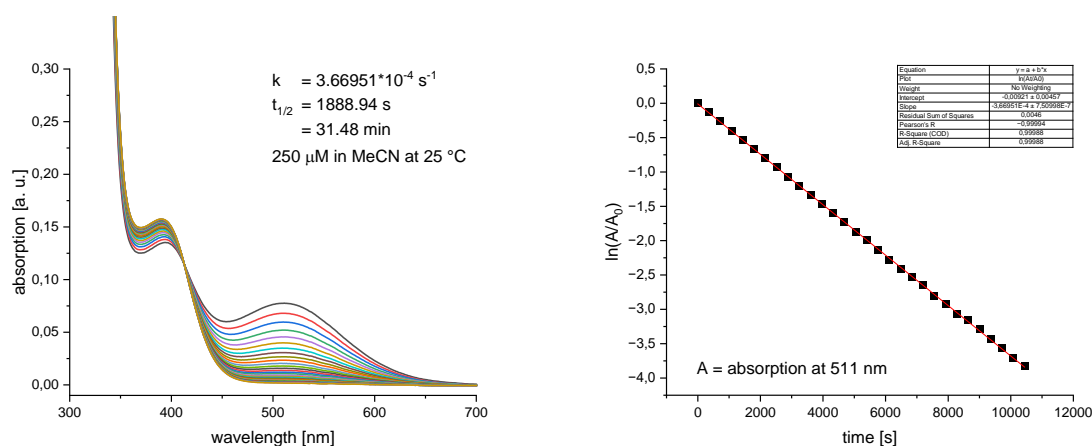


Figure SIII.28: UV-vis spectra of the half-life determination of **20** in MeCN at 25 °C (left) with the corresponding first order kinetics plot (right).

III.13 (Z)-1-(3-aminodibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (21)

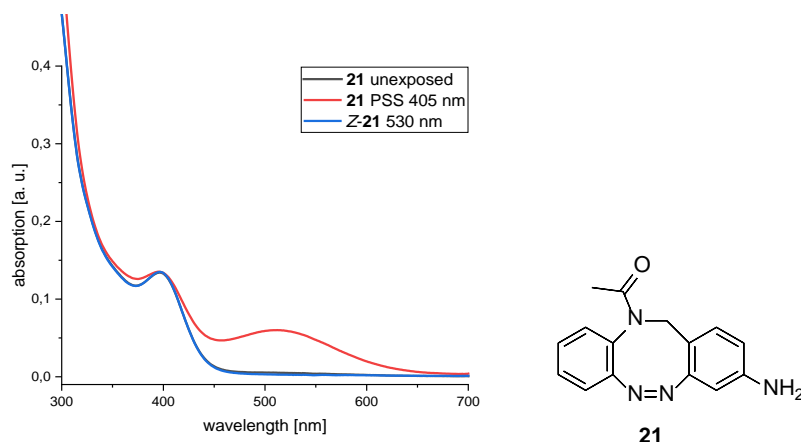


Figure SIII.29: UV-vis spectra of **21** in MeCN at 25 °C. The unexposed sample is plotted in black, the spectra of the PSS between **Z-21** and **E-21** after irradiation with 405 nm in red and the spectra of **Z-21** after irradiation with 530 nm in blue.

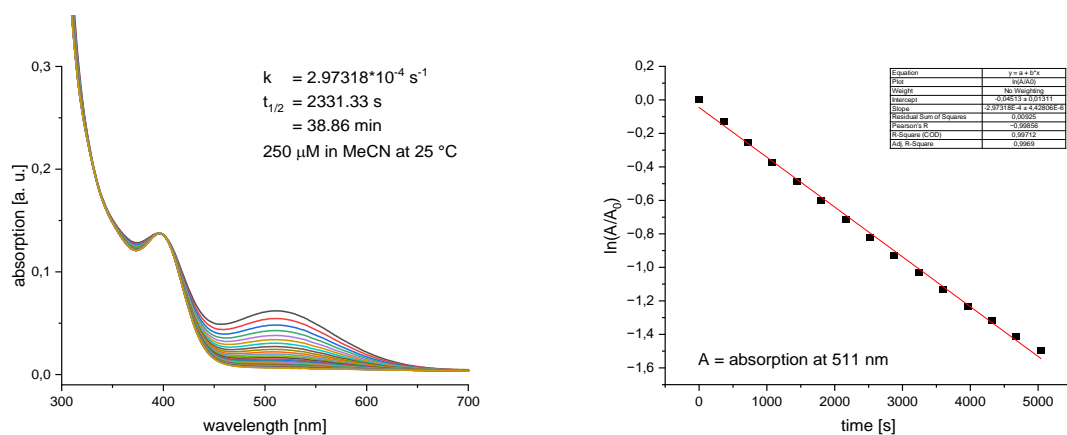


Figure SIII.30: UV-vis spectra of the half-life determination of **21** in MeCN at 25 °C (left) with the corresponding first order kinetics plot (right).

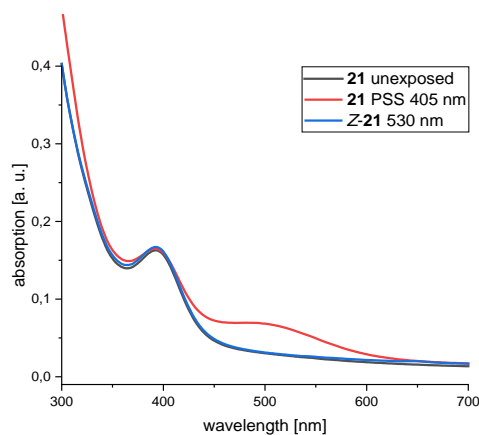


Figure SIII.31: UV-vis spectra of **21** in deionized water at 25 °C. The unexposed sample is plotted in black, the spectra of the PSS between Z-**21** and E-**21** after irradiation with 405 nm in red and the spectra of Z-**21** after irradiation with 530 nm in blue.

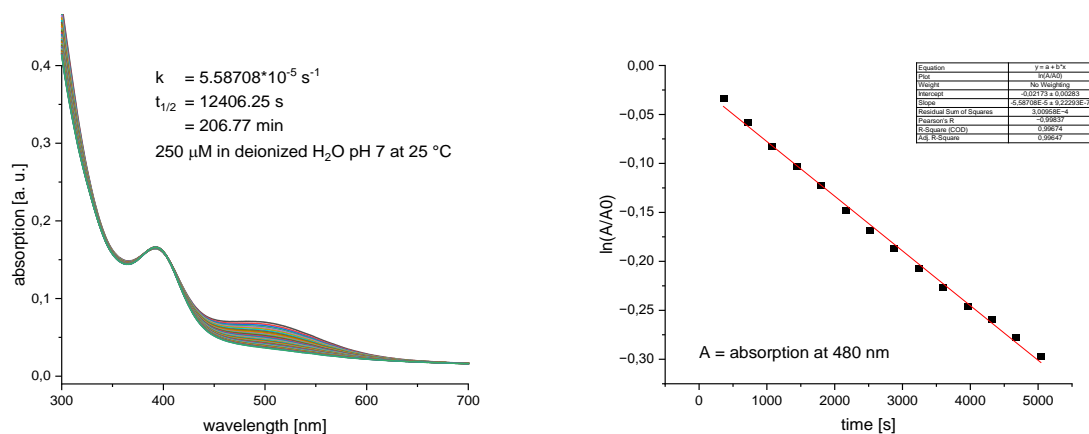


Figure SIII.32: UV-vis spectra of the half-life determination of **21** in deionized water at 25 °C (left) with the corresponding first order kinetics plot (right).

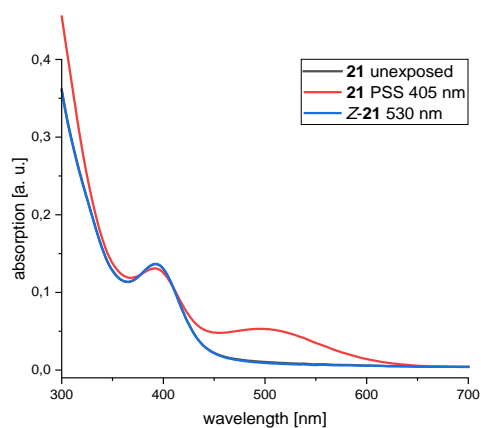


Figure SIII.33: UV-vis spectra of **21** in deionized water pH 3.5 at 25 °C. The unexposed sample is plotted in black, the spectra of the PSS between **Z-21** and **E-21** after irradiation with 405 nm in red and the spectra of **Z-21** after irradiation with 530 nm in blue.

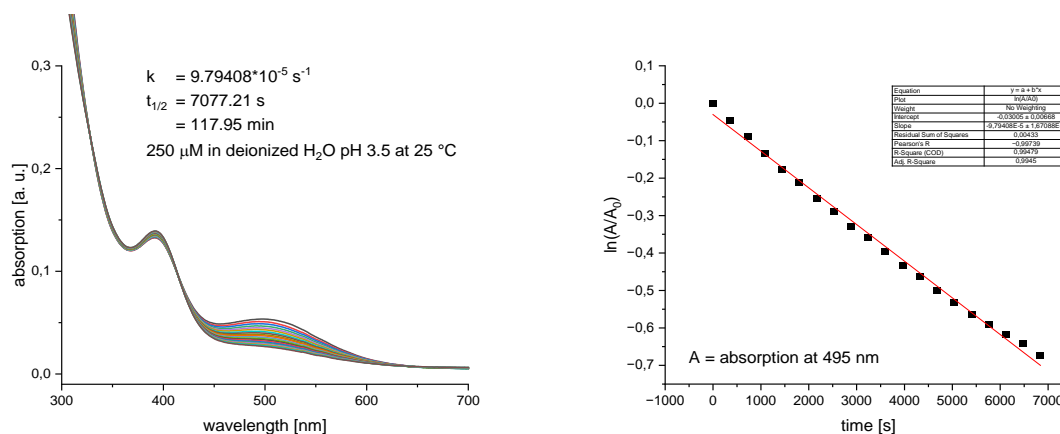


Figure SIII.34: UV-vis spectra of the half-life determination of **21** in deionized water pH 3.5 at 25 °C (left) with the corresponding first order kinetics plot (right).

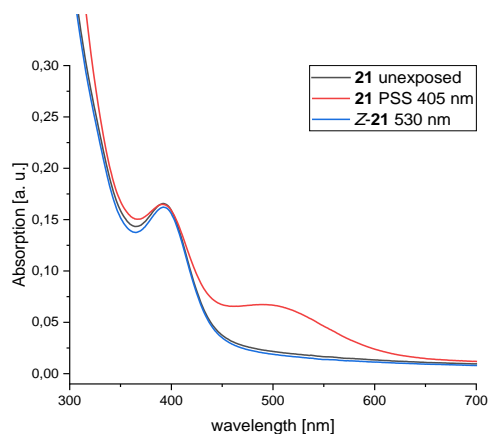


Figure SIII.35: UV-vis spectra of **21** in aqueous PBS buffer solution pH 7.4 at 25 °C. The unexposed sample is plotted in black, the spectra of the PSS between **Z-21** and **E-21** after irradiation with 405 nm in red and the spectra of **Z-21** after irradiation with 530 nm in blue.

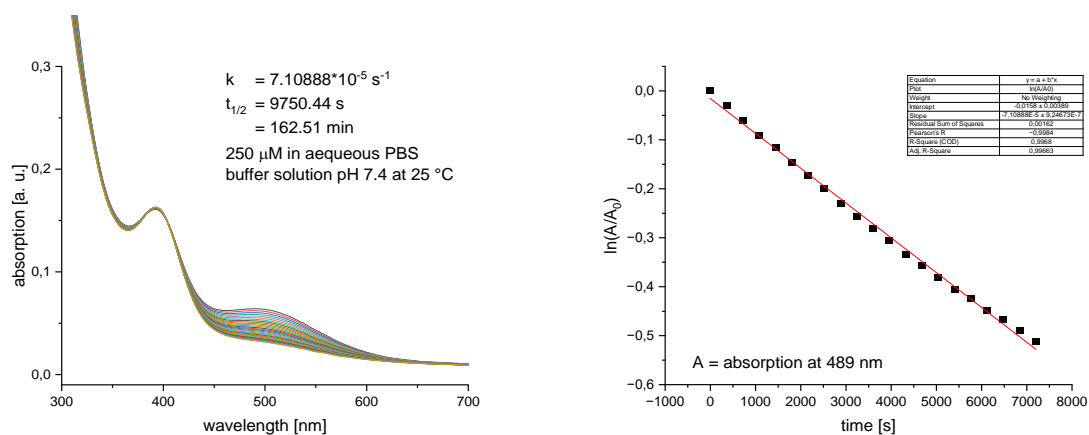


Figure SIII.36: UV-vis spectra of the half-life determination of **21** in aqueous PBS buffer solution pH 7.4 at 25 °C (left) with the corresponding first order kinetics plot (right).

III.14 (Z)-11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocine-3-carbonitrile (**23**)

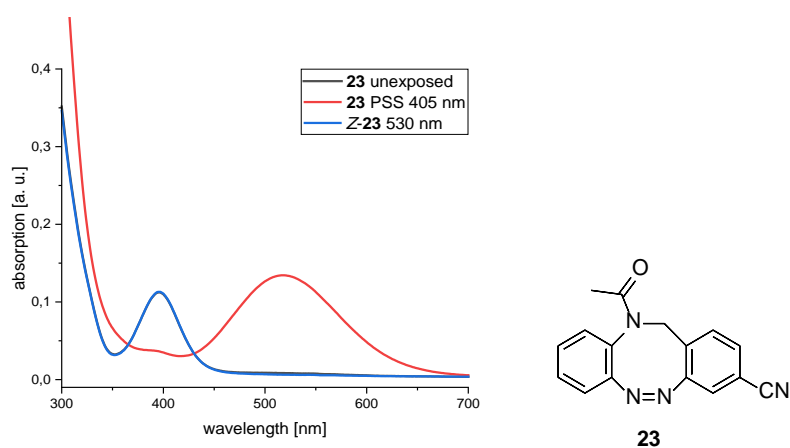


Figure SIII.37: UV-vis spectra of **23** in MeCN at 25 °C. The unexposed sample is plotted in black, the spectra of the PSS between *Z*-**23** and *E*-**23** after irradiation with 405 nm in red and the spectra of *Z*-**23** after irradiation with 530 nm in blue.

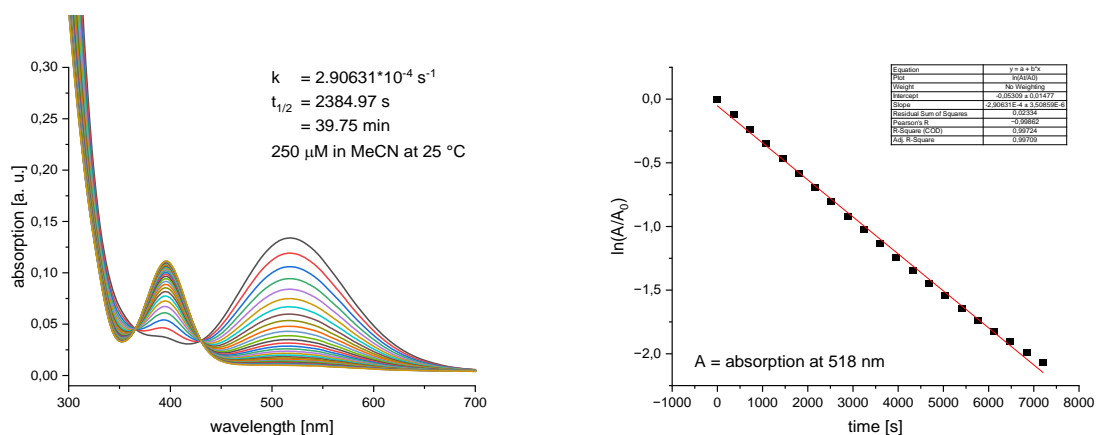


Figure SIII.38: UV-vis spectra of the half-life determination of **23** in MeCN at 25 °C (left) with the corresponding first order kinetics plot (right).

IV. ¹H-NMR switching experiments

Photostationary states (PSS) of compounds **4**, **7**, **14**, **17**, **19**–**21** and **23** were measured via ¹H-NMR by integration of the different species after irradiation with 405 nm, whereby no distinction was made between *E-twist*- and *E-chair*-conformations. The value of the integrals and the extrapolated values are given in Table SIII.1. ¹H-NMR spectra were measured at 5 mM concentrations, except pyridine-substituted *N*-acetyl-diazocine **14** (2.55 mM due to low synthesis yield). The following equation (1) was used for extrapolation of the photostationary states:

$$PSS_{extrapol.} = PSS_{measured} \cdot e^{kt} \quad (1)$$

k is the rate constant at 25 °C (see table 6 and 7) and *t* the measuring time (330 s): 120 s preparation (transfer into the spectrometer and shimming after excitation with light) and 210 s measuring time for 32 scans. All spectra were measured at a Bruker AV600 spectrometer.

Table SIV.1: Measured and extrapolated photostationary states of compounds **4**, **7**, **14**, **17**, **19**–**21** and **23** in acetonitrile.

	measured PSS	extrapolated PSS
	%	%
4	68	85
7	69	79
8	67	76
9	69	77
10	73	82
11	70	78
12	71	80
13	8	77
14	72	79
17	72	82
19	54	61
20	43	49
21	37	41
23	76	83

Table SIV.2: Measured and extrapolated photostationary states of compounds **13** and **23** in water.

	measured PSS	extrapolated PSS
	%	%
13 pH 7.4	51	53
13 pH 9	46	48
21 pH 7.4	35	37
21 pH 3.5	62	62

IV.1 (Z)-(3,8-dibromodibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**4**)

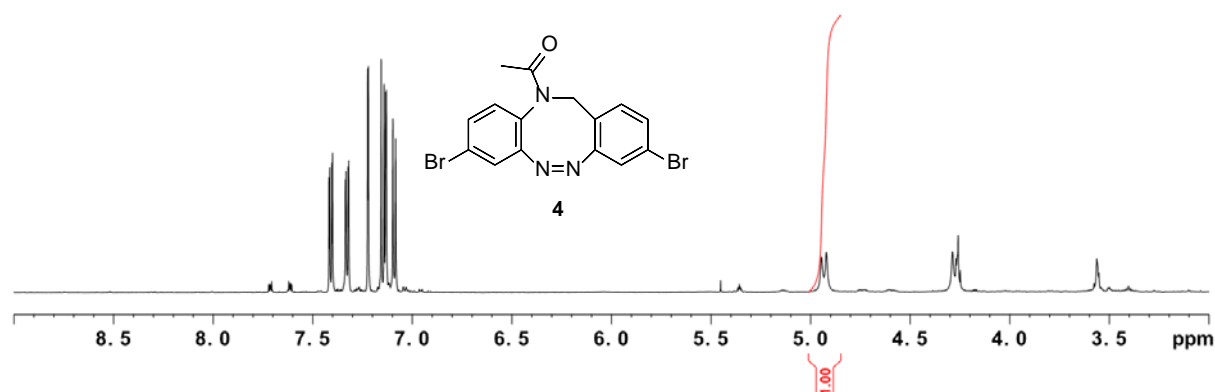


Figure SIV.1: ¹H-NMR-spectra of **Z-4** in CD₃CN at 298 K.

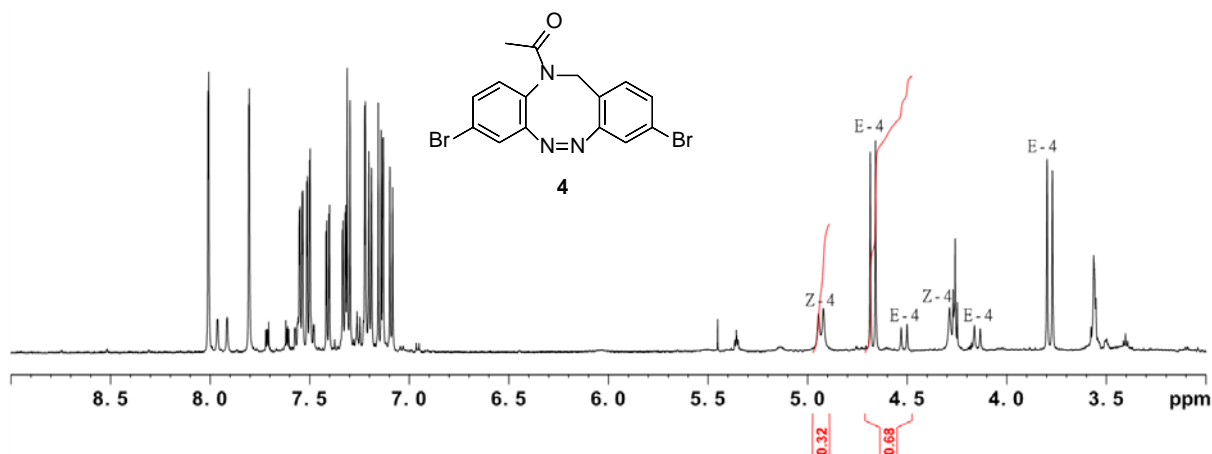


Figure SIV.2: ^1H -NMR-spectra of **4** in CD_3CN at 298 K after irradiation with 405 nm.

IV.2 (*Z*)-1-(3-phenyldibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**7**)

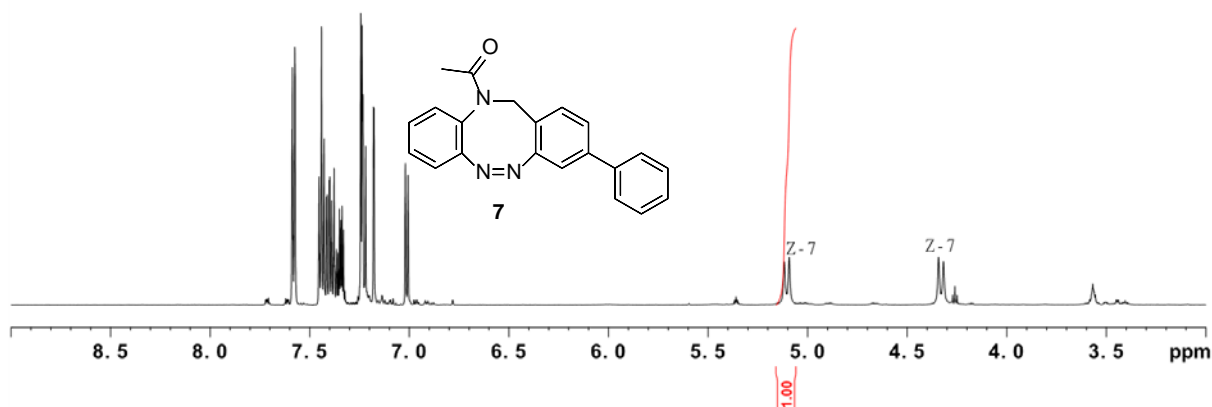


Figure SIV.3: ^1H -NMR-spectra of **Z-7** in CD_3CN at 298 K.

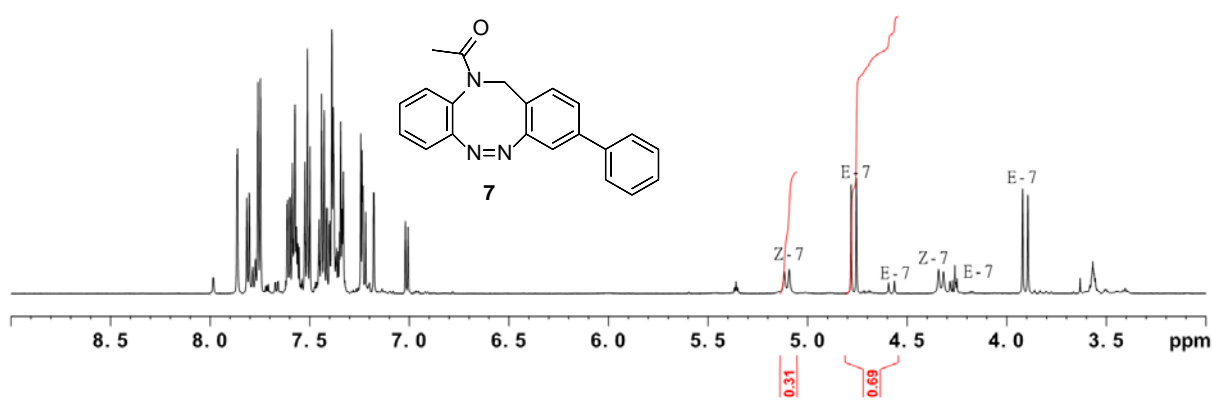


Figure SIV.4: ^1H -NMR-spectra of **7** in CD_3CN at 298 K after irradiation with 405 nm.

IV.3 (*Z*)-1-(3-vinyldibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**8**)

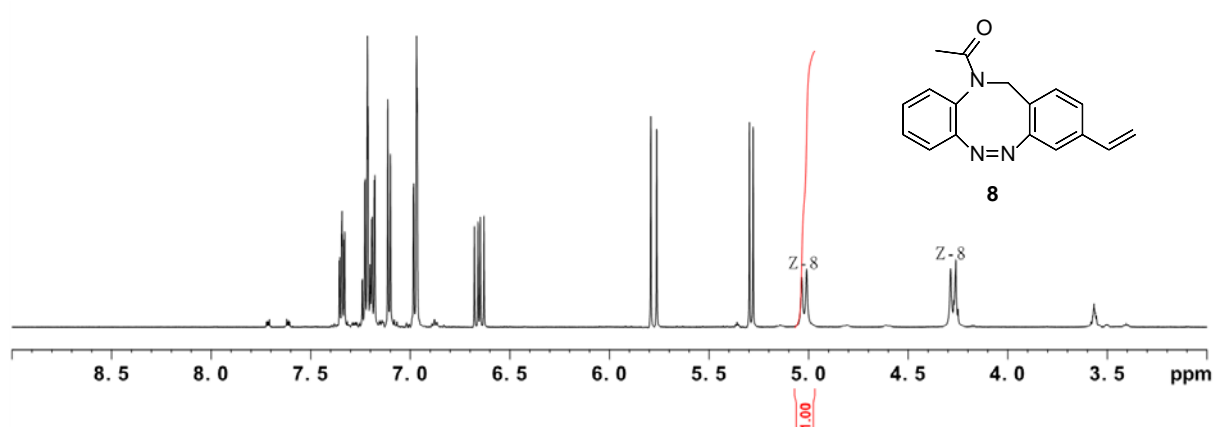


Figure SIV.5: ^1H -NMR-spectra of Z-**8** in CD_3CN at 298 K.

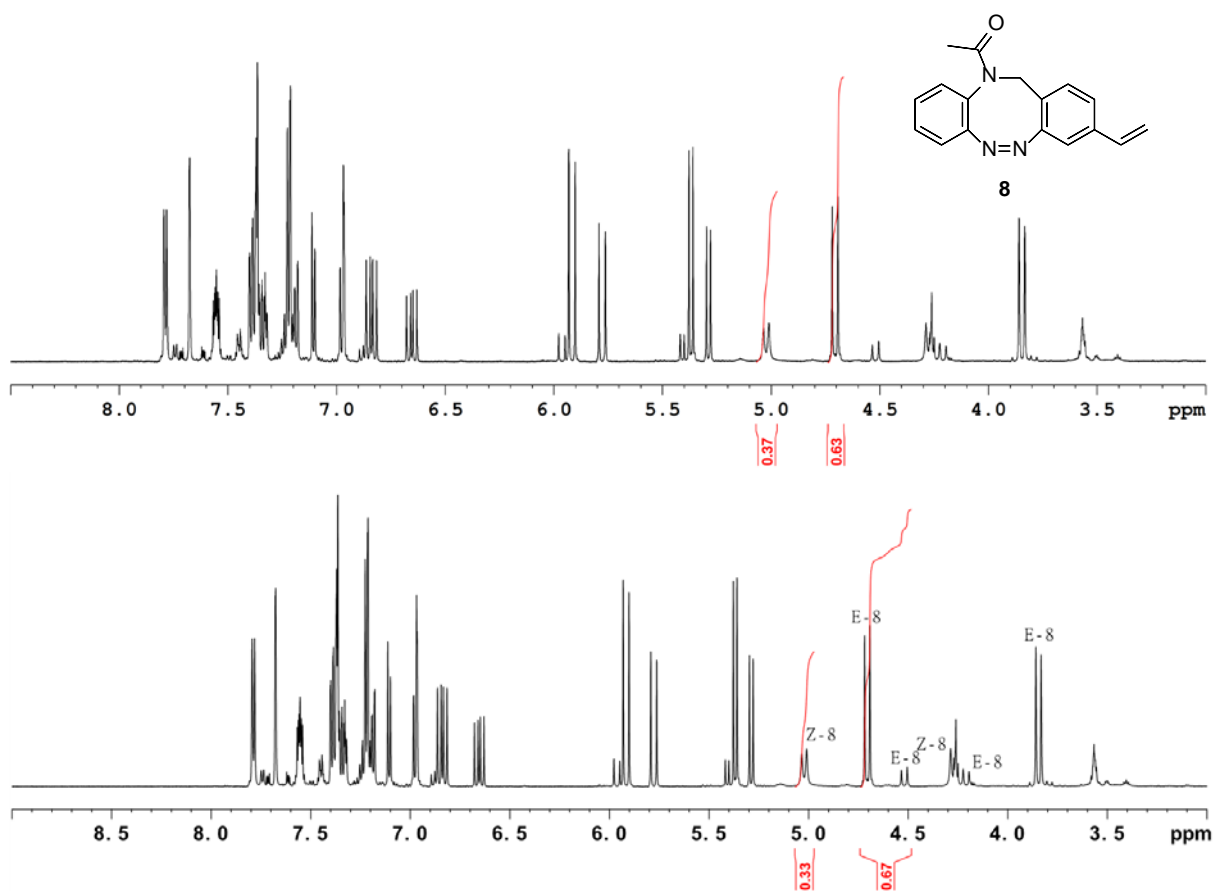


Figure SIV.6: ^1H -NMR-spectra of **8** in CD_3CN at 298 K after irradiation with 405 nm.

IV.4 (Z)-1-(3-(2,6-dimethylphenyl)dibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (9)

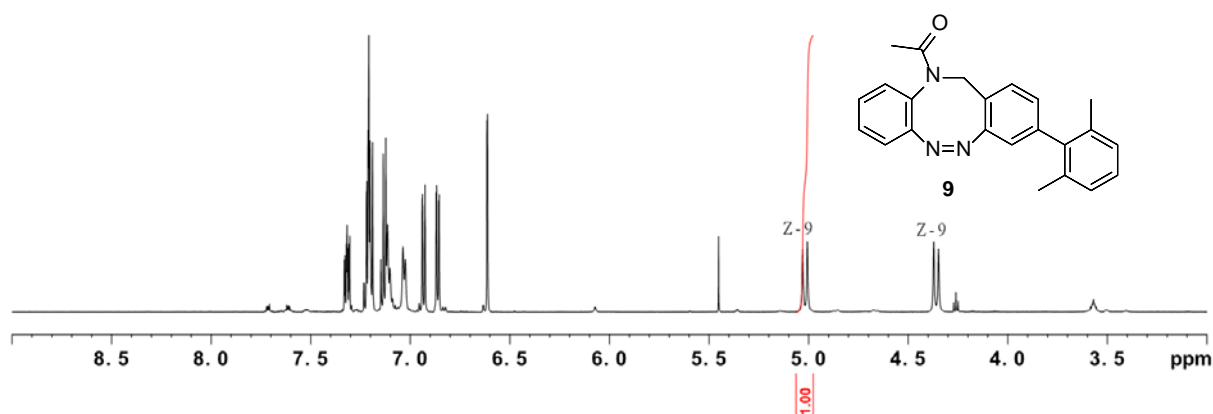


Figure SIV.7: ¹H-NMR-spectra of Z-9 in CD₃CN at 298 K.

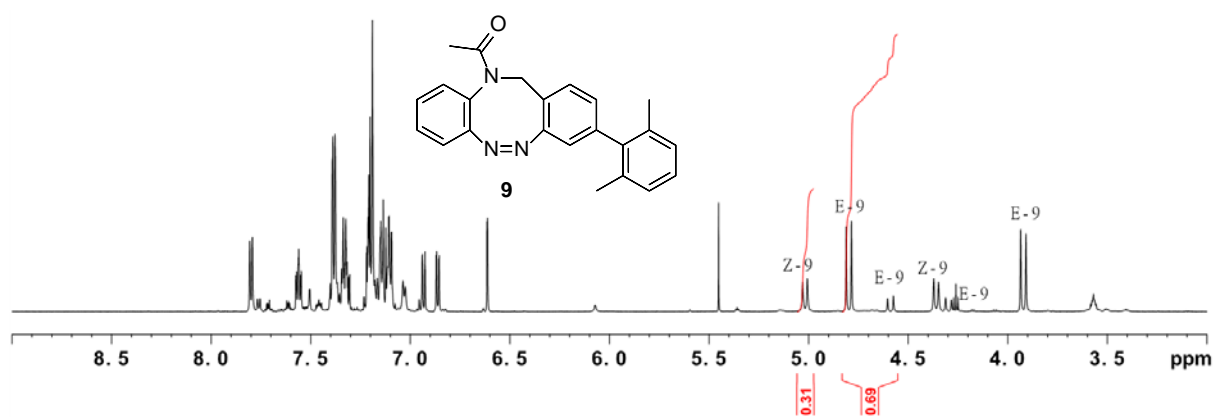


Figure SIV.8: ¹H-NMR-spectra of 9 in CD₃CN at 298 K after irradiation with 405 nm.

IV.5 (Z)-1-(3-(2-bromophenyl)dibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (10)

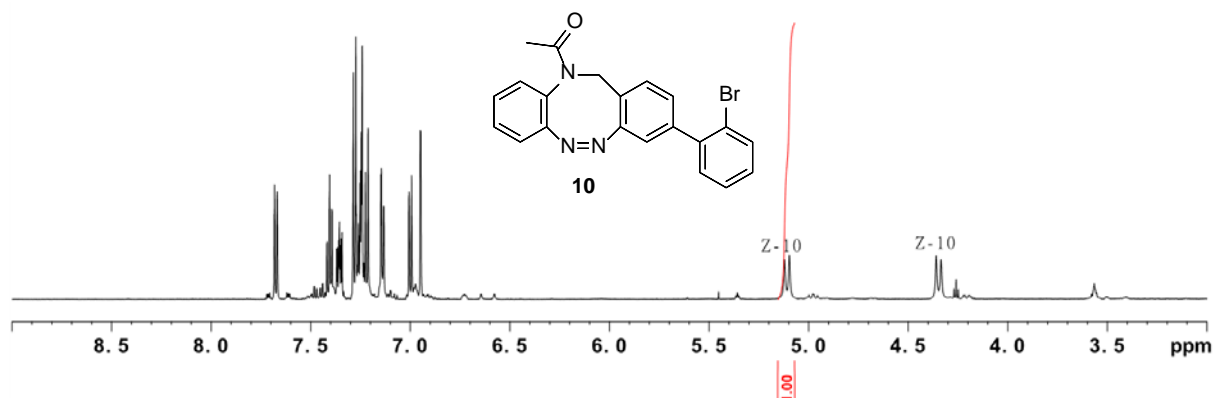


Figure SIV.9: ¹H-NMR-spectra of Z-10 in CD₃CN at 298 K.

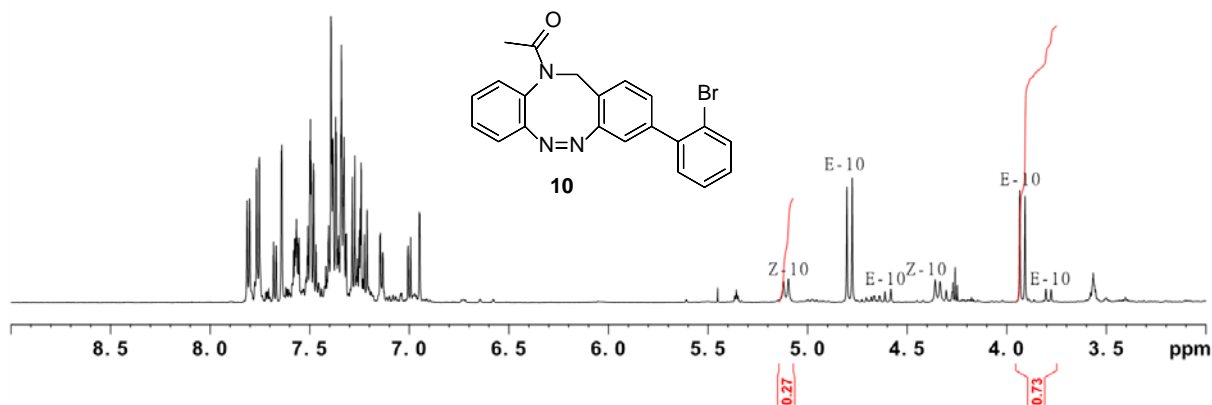


Figure SIV.10: ¹H-NMR-spectra of **10** in CD₃CN at 298 K after irradiation with 405 nm.

IV.6 (Z)-1-(3-(4-fluorophenyl)dibenzo[c,g][1,2,5]triazocin-11(12H)-yl)ethan-1-one (**11**)

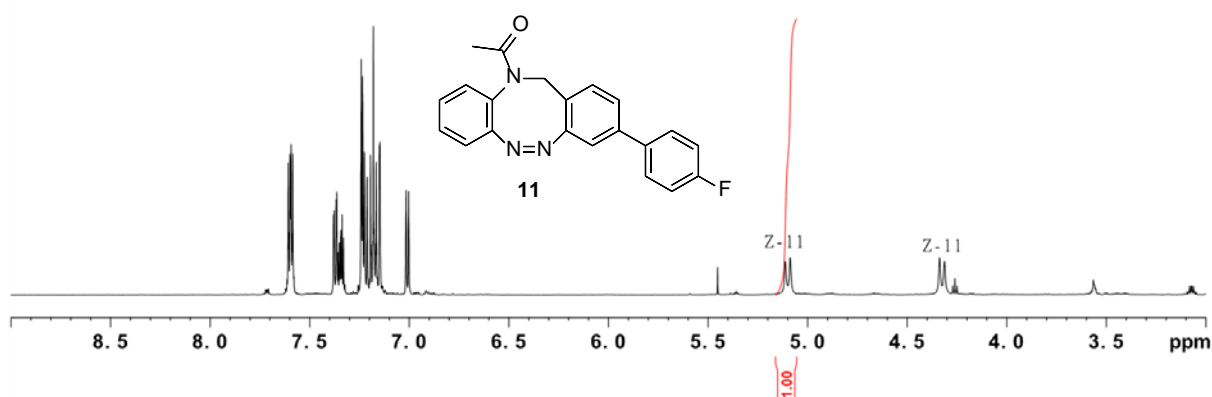


Figure SIV.11: ¹H-NMR-spectra of Z-11 in CD₃CN at 298 K.

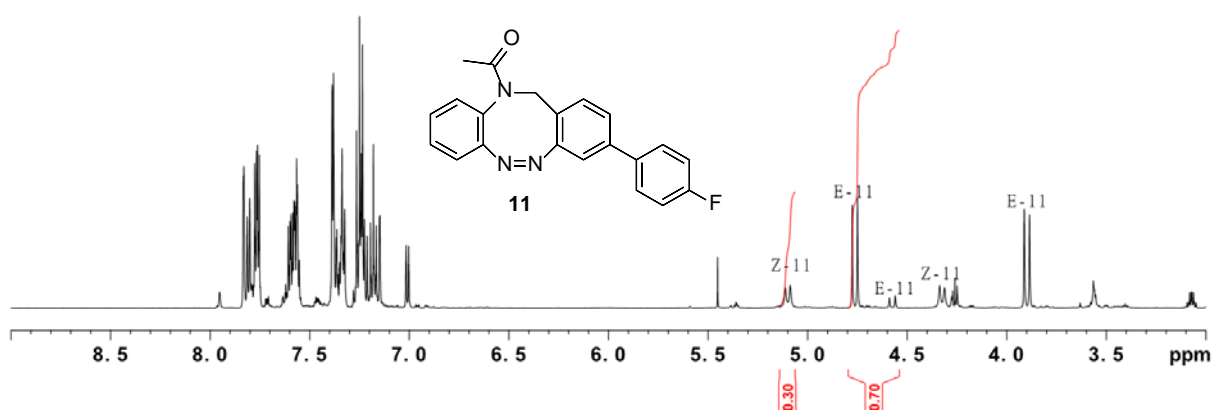


Figure SIV.12: ¹H-NMR-spectra of **11** in CD₃CN at 298 K after irradiation with 405 nm.

IV.7 (Z)-2-(11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocin-3-yl)benzaldehyde (12)

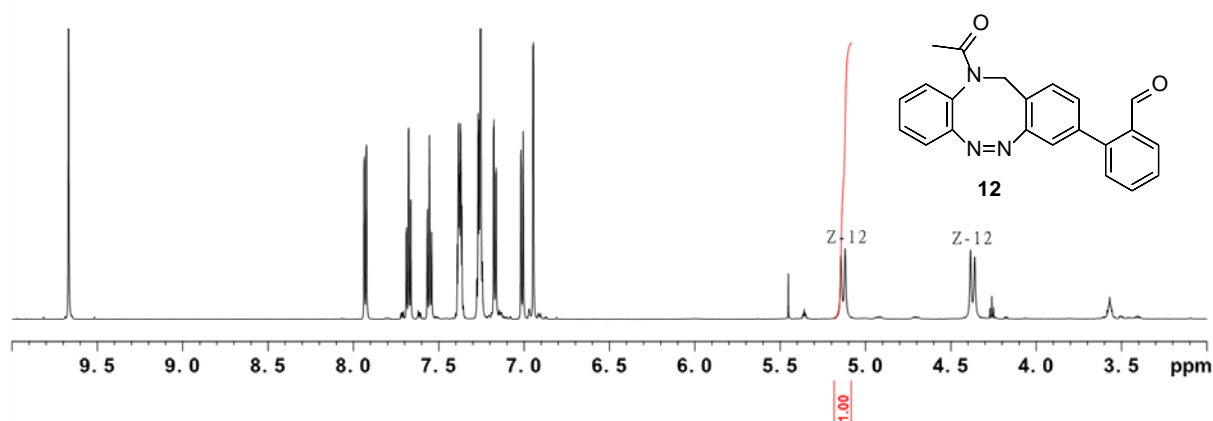


Figure SIV.13: ¹H-NMR-spectra of Z-12 in CD₃CN at 298 K.

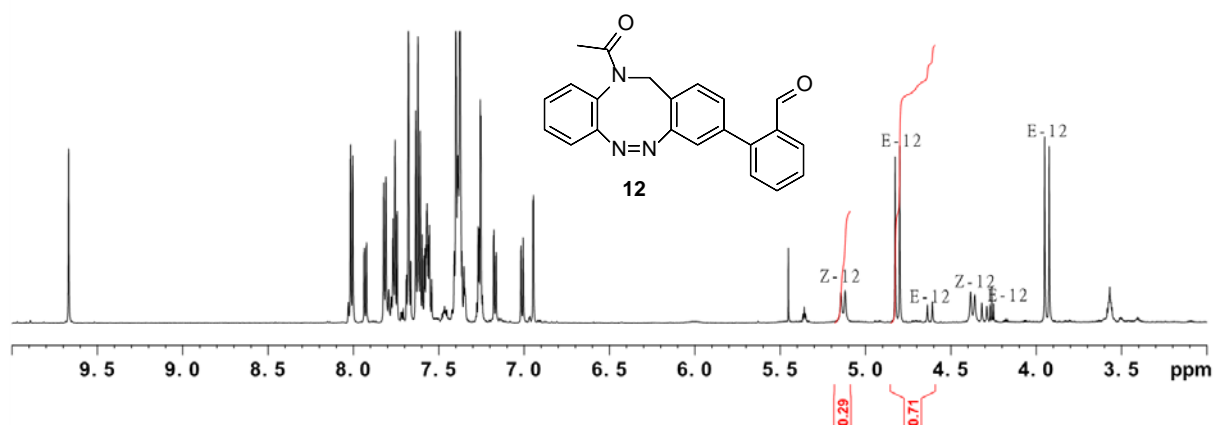


Figure SIV.14: ¹H-NMR-spectra of 12 in CD₃CN at 298 K after irradiation with 405 nm.

IV.8 (Z)-2-(11-acetyl-11,12-dihydrodibenzo[c,g][1,2,5]triazocin-3-yl)benzoic acid (13)

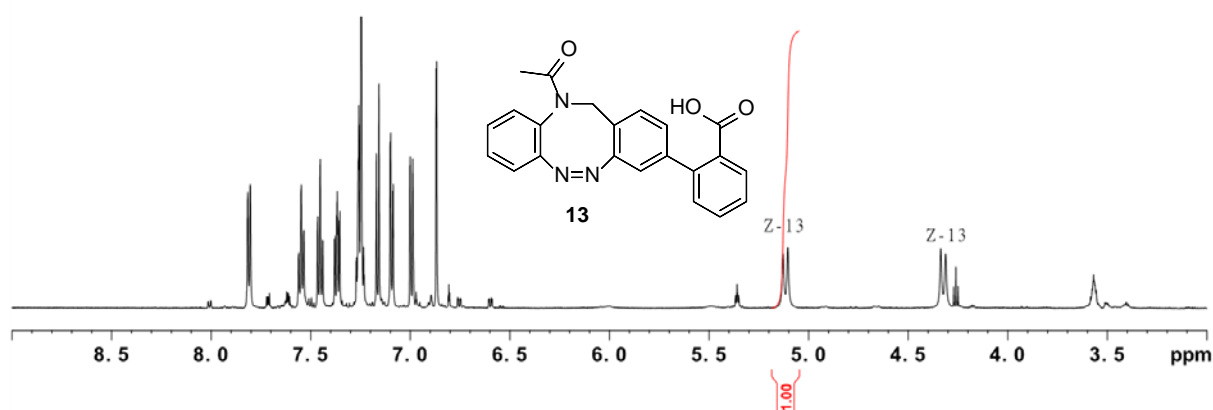


Figure SIV.15: ¹H-NMR-spectra of Z-13 in CD₃CN at 298 K.

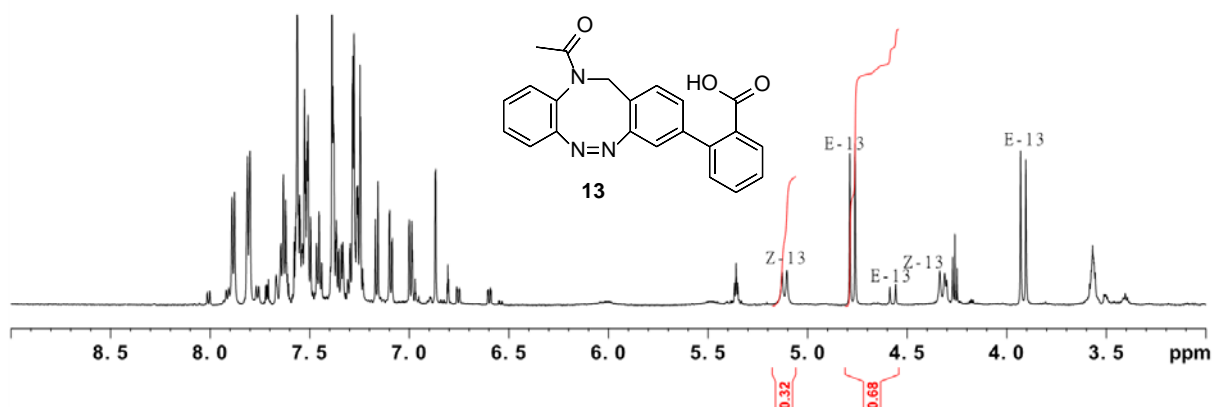


Figure SIV.16: ^1H -NMR-spectra of **13** in CD_3CN at 298 K after irradiation with 405 nm.

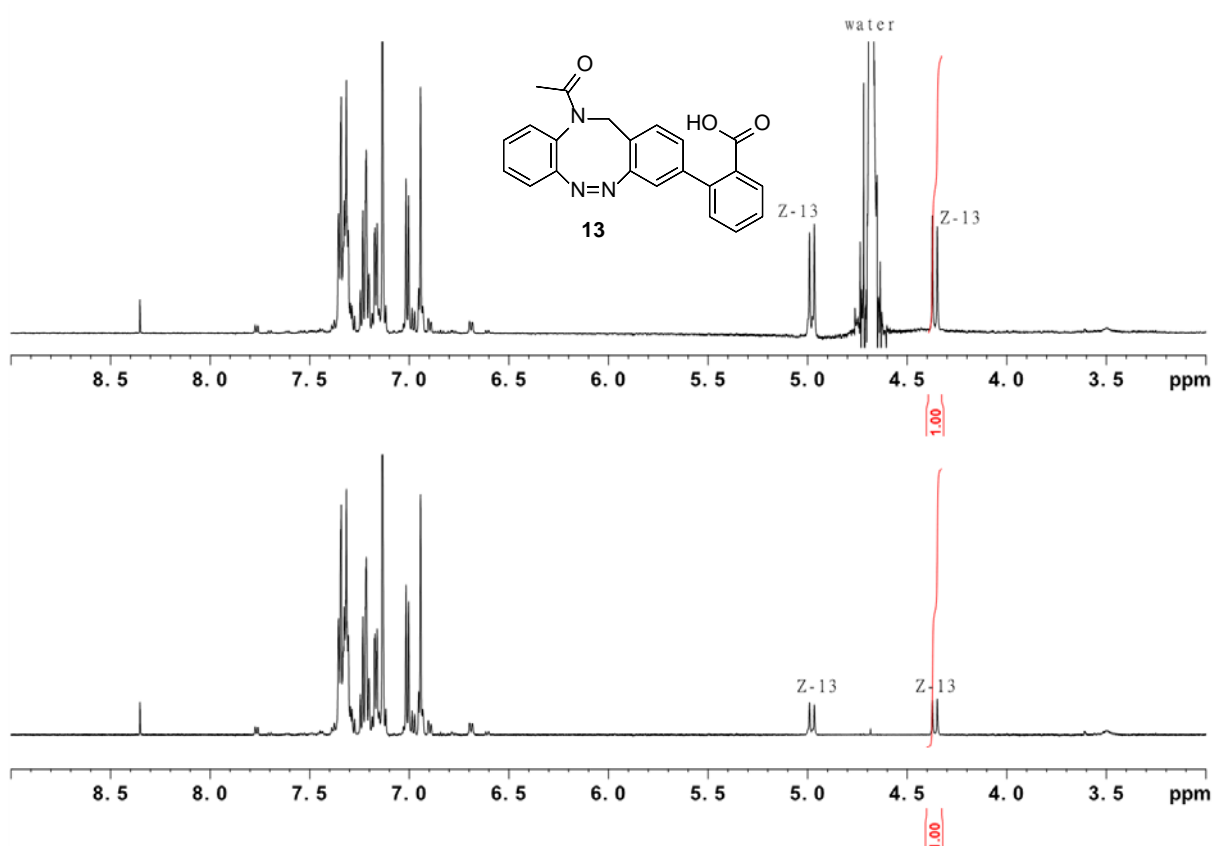


Figure SIV.17: ^1H -NMR-spectra of **Z-13** in D_2O pH 9 at 298 K (top) and the ^1H -NMR-Spektrum of **13** in D_2O pH 9 at 298 K with baseline correction and water suppression performed with MestReNova 14.3.1 NMR analysis Software by Mestrelab (bottom).

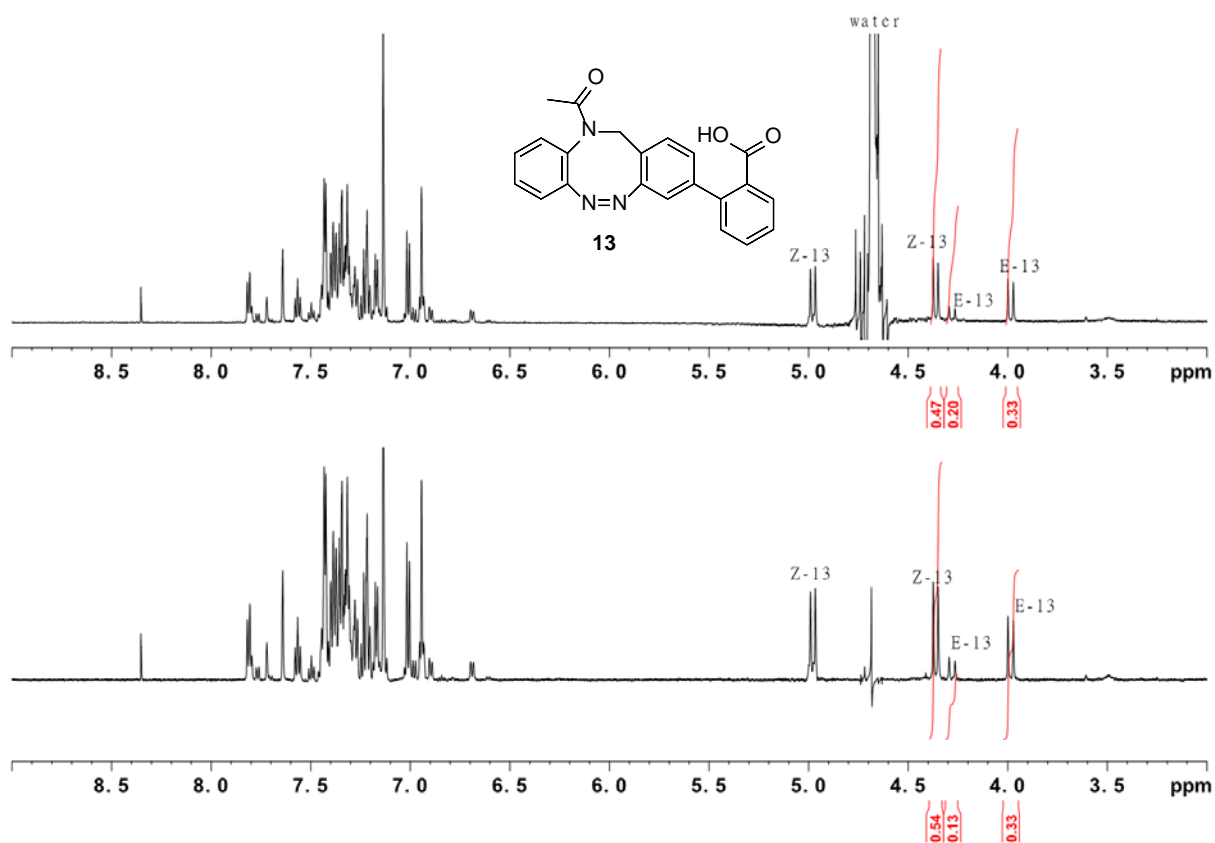


Figure SIV.18: ^1H -NMR-spectra of **13** in D_2O pH 9 at 298 K after irradiation with 405 nm (top) and the ^1H -NMR-Spektrum of **13** in D_2O pH 9 at 298 K after irradiation with 405 nm with baseline correction and water suppression performed with MestReNova 14.3.1 NMR analysis Software by Mestrelab (bottom)..

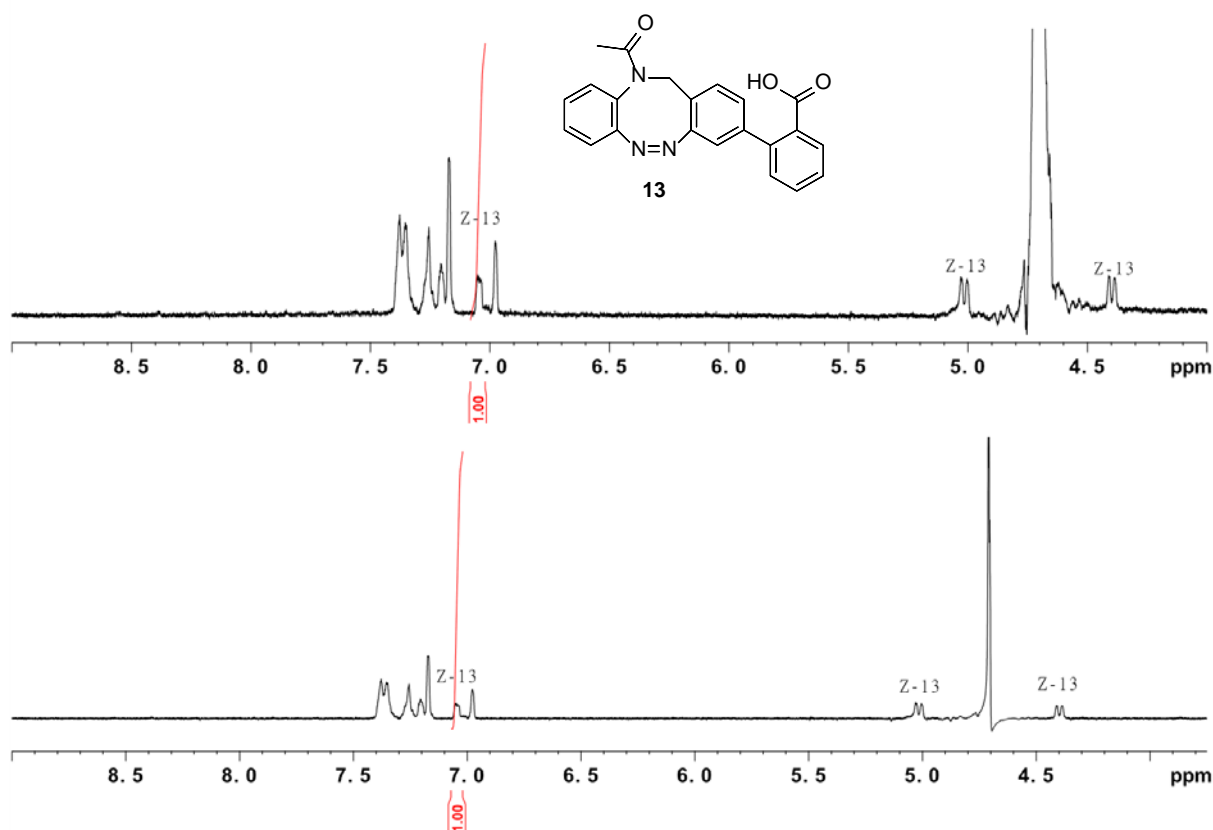


Figure SIV.19: ^1H -NMR-spectra of **13** in D_2O PBS buffer solution pH 7.4 at 298 K (top) and the ^1H -NMR-Spektrum of **13** in D_2O PBS buffer solution pH 7.4 at 298 K with baseline correction and water suppression performed with MestReNova 14.3.1 NMR analysis Software by Mestrelab (bottom).

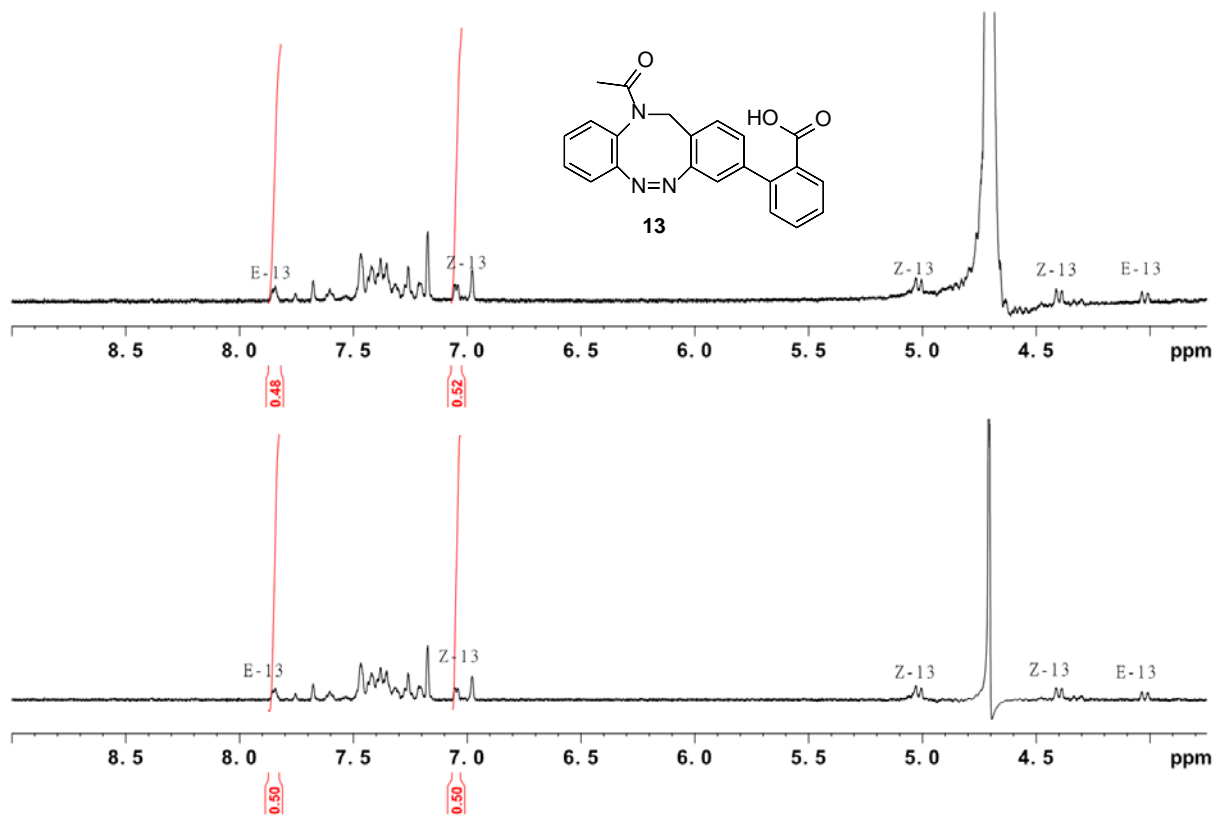


Figure SIV.20: ^1H -NMR-spectra of **13** in D_2O PBS buffer solution pH 7.4 at 298 K after irradiation with 405 nm (top) and the ^1H -NMR-Spektrum of **13** in D_2O PBS buffer solution pH 7.4 at 298 K after irradiation with 405 nm with

baseline correction and water suppression performed with MestReNova 14.3.1 NMR analysis Software by Mestrelab (bottom).

IV.9 (Z)-1-(3-(pyridine-4-yl)dibenzo[c,g][1,2,5]triazocin-11(12H)-ethan-1-one (14)

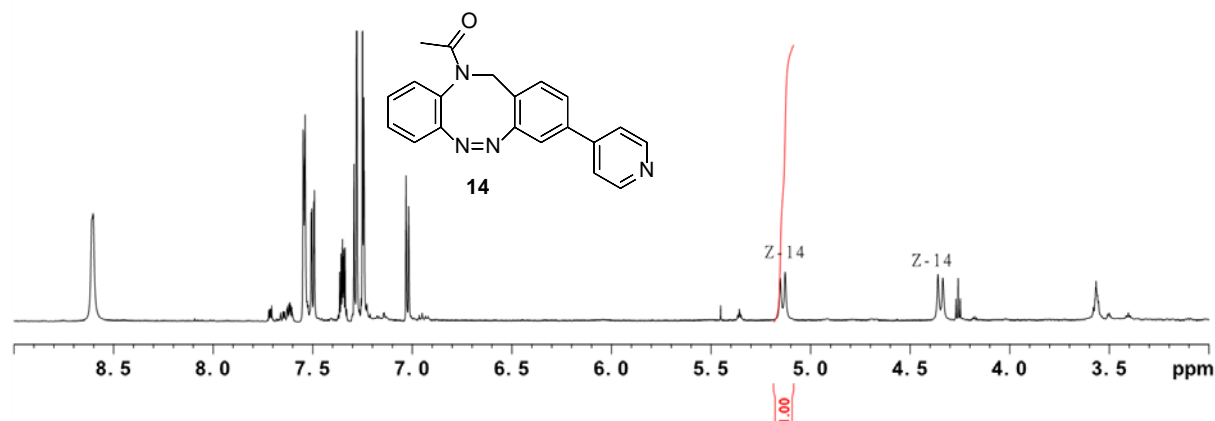


Figure SIV.21: ^1H -NMR-spectra of 14 in CD_3CN at 298 K.

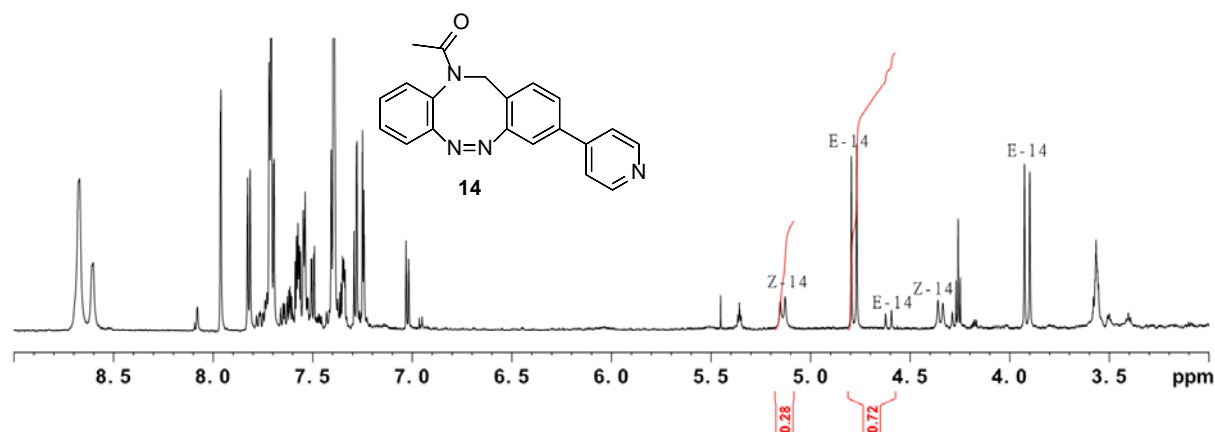


Figure SIV.22: ^1H -NMR-spectra of 14 in CD_3CN at 298 K after irradiation with 405 nm.

IV.10 (Z)-1-(3-benzyl)dibenzo[c,g][1,2,5]triazocin-11(12H)-ethan-1-one (17)

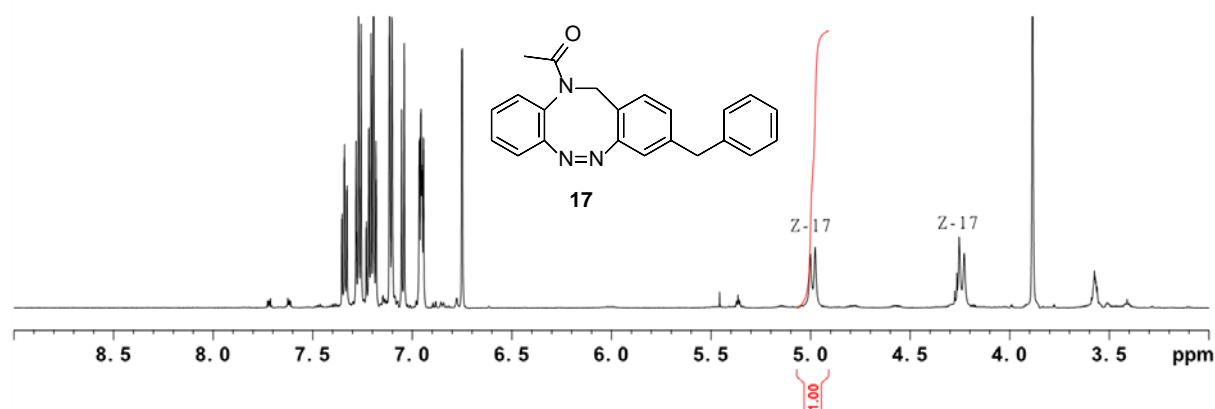


Figure SIV.23: ^1H -NMR-spectra of 17 in CD_3CN at 298 K.

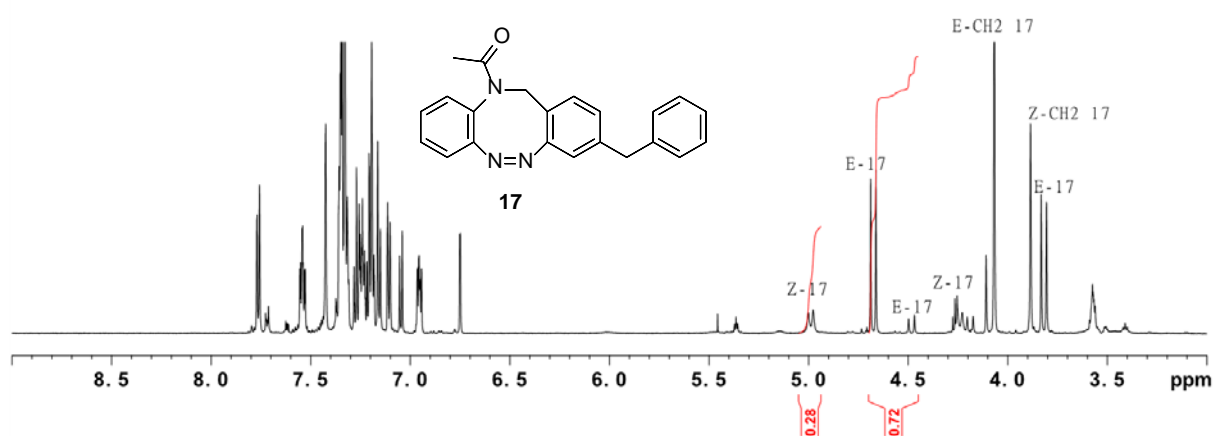


Figure SIV.24: ^1H -NMR-spectra of **17** in CD_3CN at 298 K after irradiation with 405 nm.

IV.11 ***tert*-butyl-(*Z*)-(11-acetyl-11,12-dihydrodiebenzo[*c,g*][1,2,5]triazocin-3-yl)carbamate (**19**)**

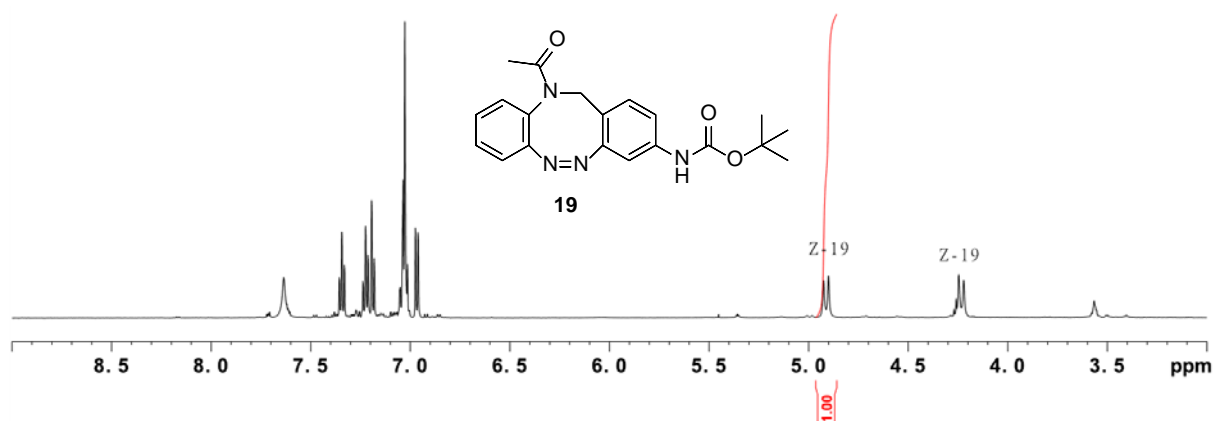


Figure SIV.25: ^1H -NMR-spectra of **19** in CD_3CN at 298 K.

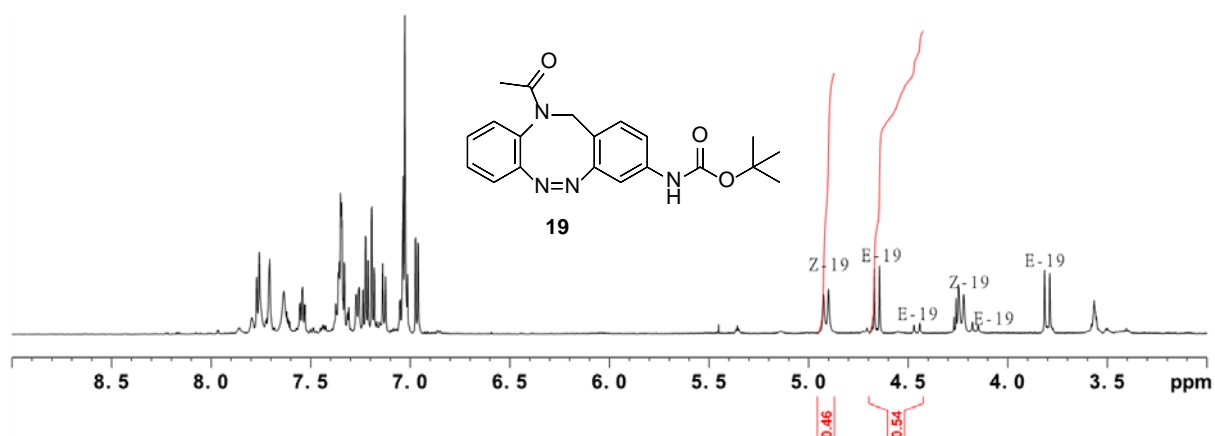


Figure SIV.26: ^1H -NMR-spectra of **19** in CD_3CN at 298 K after irradiation with 405 nm.

IV.12 (*Z*)-1-(3-(diphenylamino)dibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**20**)

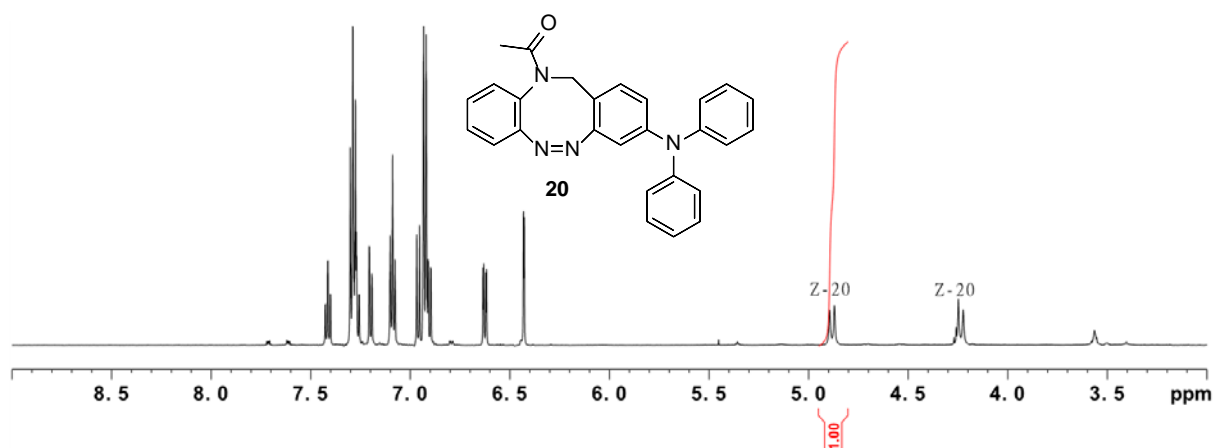


Figure SIV.27: ^1H -NMR-spectra of **20** in CD_3CN at 298 K.

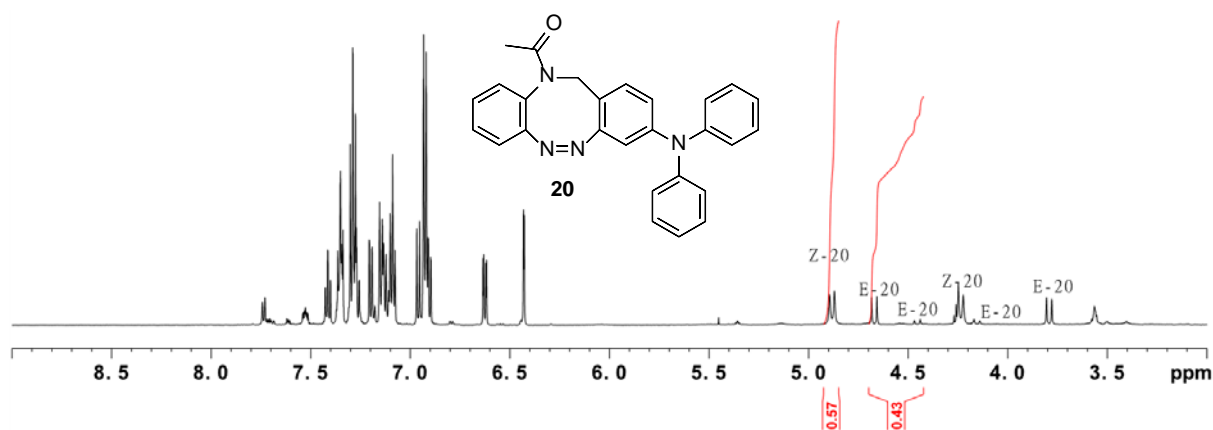


Figure SIV.28: ^1H -NMR-spectra of **20** in CD_3CN at 298 K after irradiation with 405 nm.

IV.13 (*Z*)-1-(3-aminodibenzo[*c,g*][1,2,5]triazocin-11(12*H*)-yl)ethan-1-one (**21**)

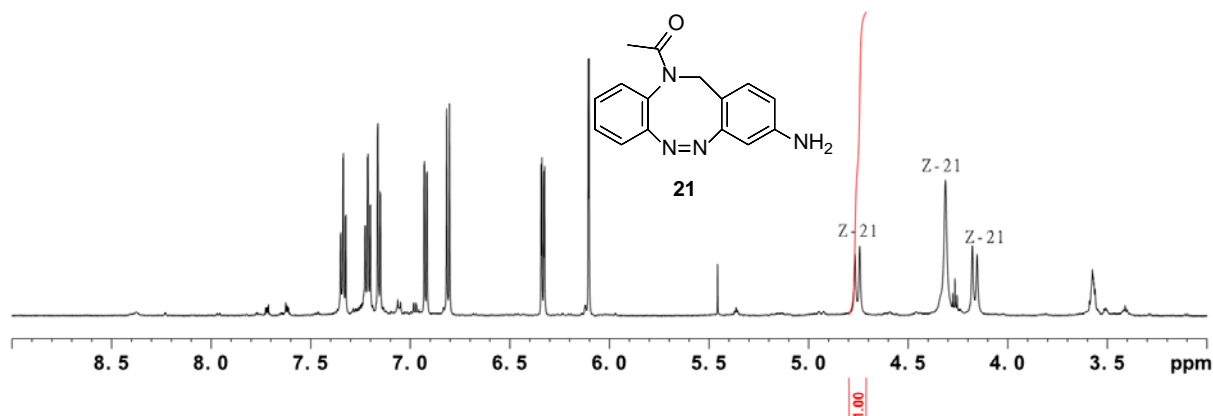


Figure SIV.29: ^1H -NMR-spectra of **21** in CD_3CN at 298 K.

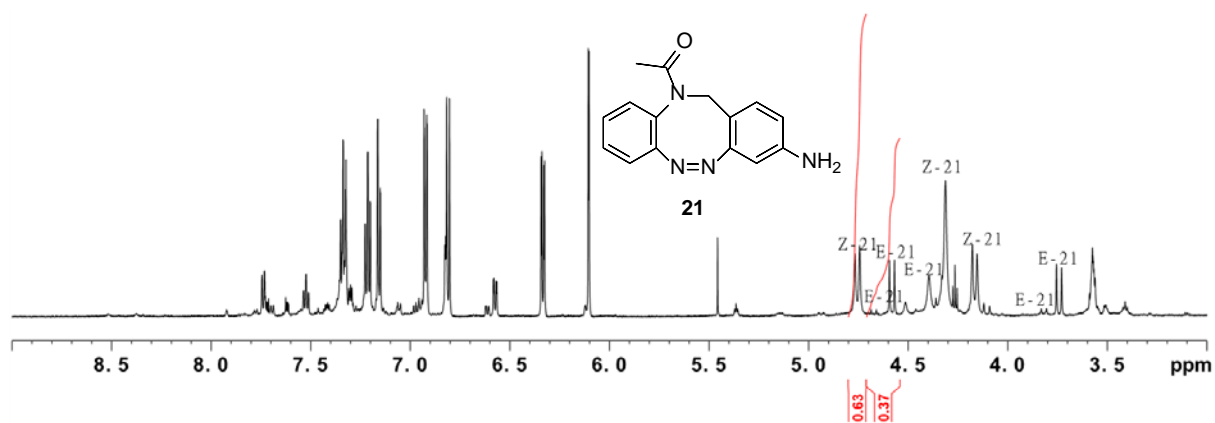


Figure SIV.30: ¹H-NMR-spectra of **21** in CD₃CN at 298 K after irradiation with 405 nm.

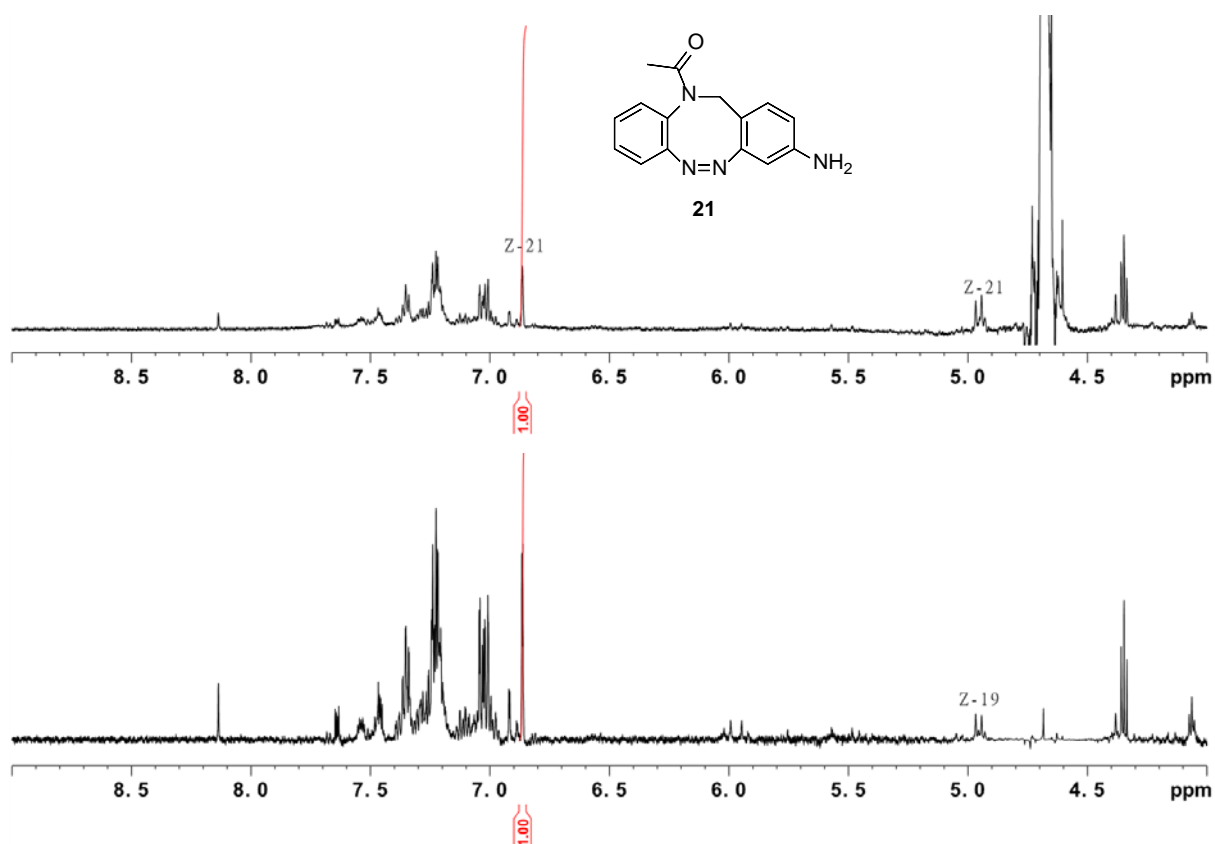


Figure SIV.33: ¹H-NMR-spectra of **21** in D₂O pH 3.5 at 298 K (top) and the ¹H-NMR-Spektrum of **23** in D₂O pH 3.5 at 298 K with baseline correction and water suppression performed with MestReNova 14.3.1 NMR analysis Software by Mestrelab (bottom).

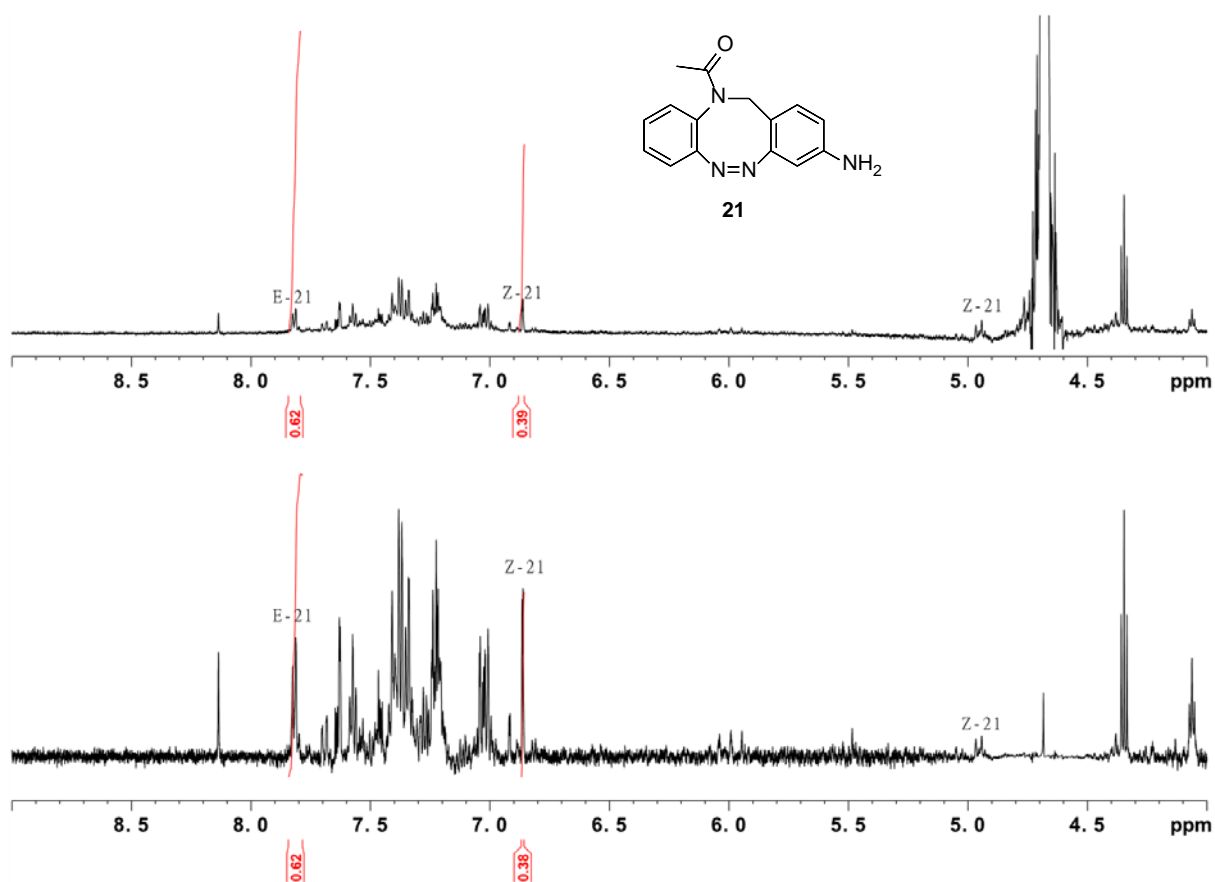


Figure SIV.34: ^1H -NMR-spectra of **21** in D_2O pH 3.5 at 298 K after irradiation with 405 nm (top) and the ^1H -NMR-Spektrum of **23** in D_2O pH 3.5 at 298 K after irradiation with 405 nm with baseline correction and water suppression performed with MestReNova 14.3.1 NMR analysis Software by Mestrelab (bottom)

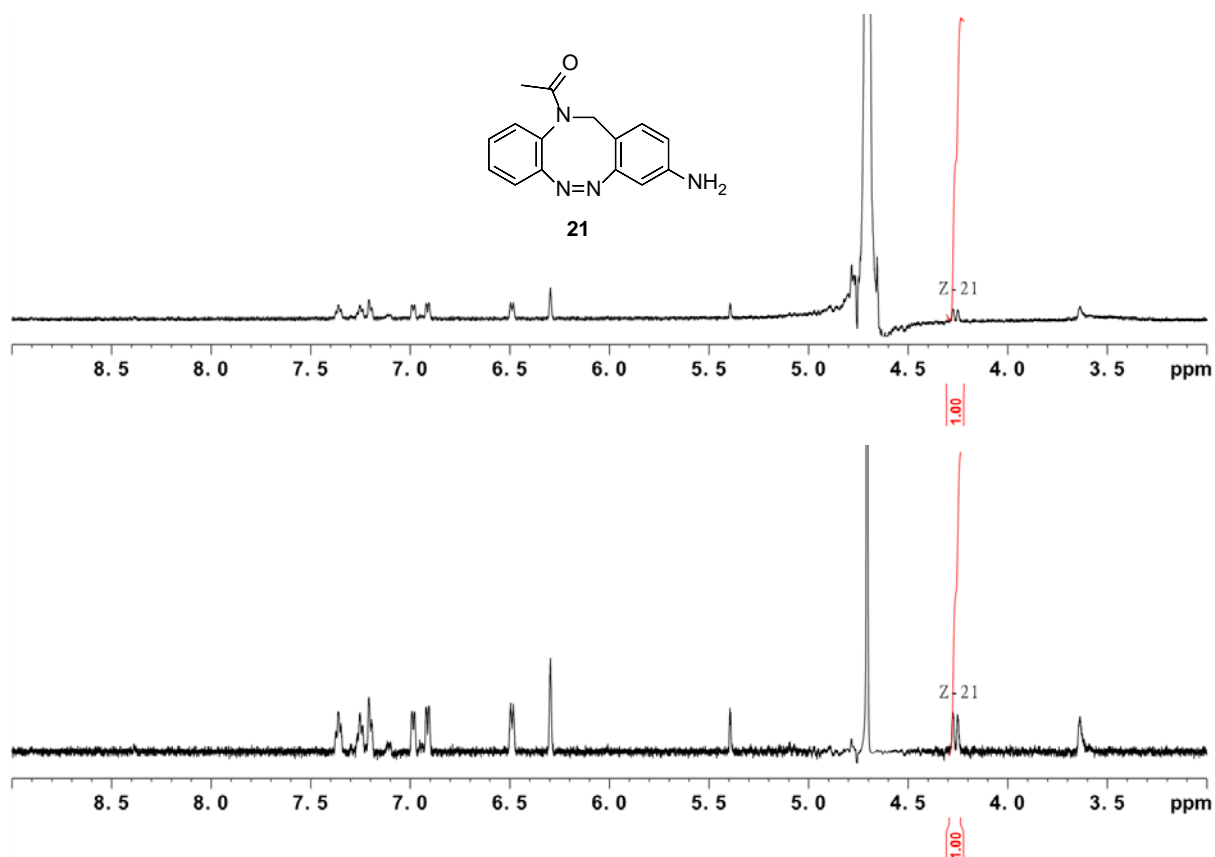


Figure SIV.35: ^1H -NMR-spectra of **21** in D_2O PBS buffer solution pH 7.4 at 298 K (top) and the ^1H -NMR-Spektrum of **23** in D_2O PBS buffer solution pH 7.4 at 298 K with baseline correction and water suppression performed with MestReNova 14.3.1 NMR analysis Software by Mestrelab (bottom).

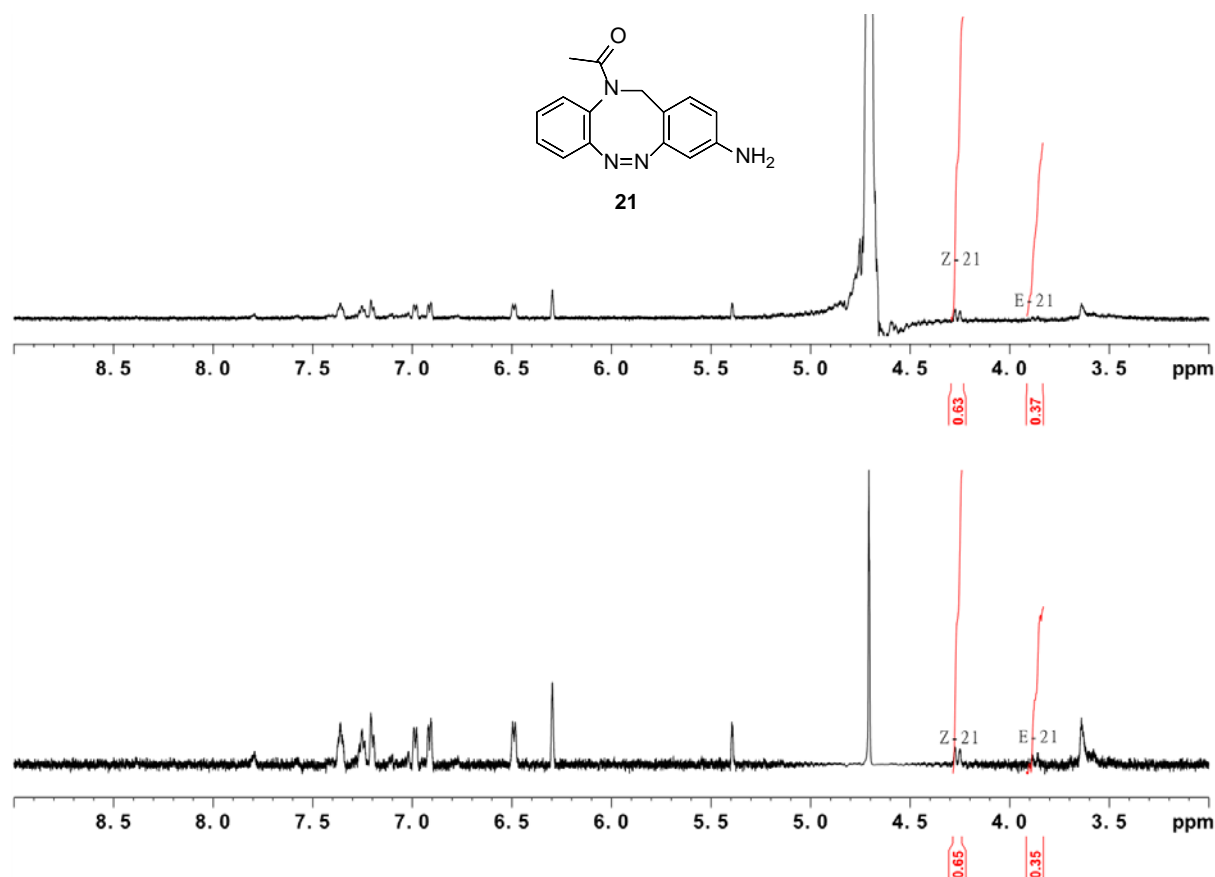


Figure SIV.36: ^1H -NMR-spectra of **21** in D_2O PBS buffer solution pH 7.4 at 298 K after irradiation with 405 nm (top) and the ^1H -NMR-Spektrum of **23** in D_2O PBS buffer solution pH 7.4 at 298 K after irradiation with 405 nm with baseline correction and water suppression performed with MestReNova 14.3.1 NMR analysis Software by Mestrelab (bottom).

IV.14 (*Z*)-11-acetyl-11,12-dihydrodibenzo[*c,g*][1,2,5]triazocine-3-carbonitrile (**23**)

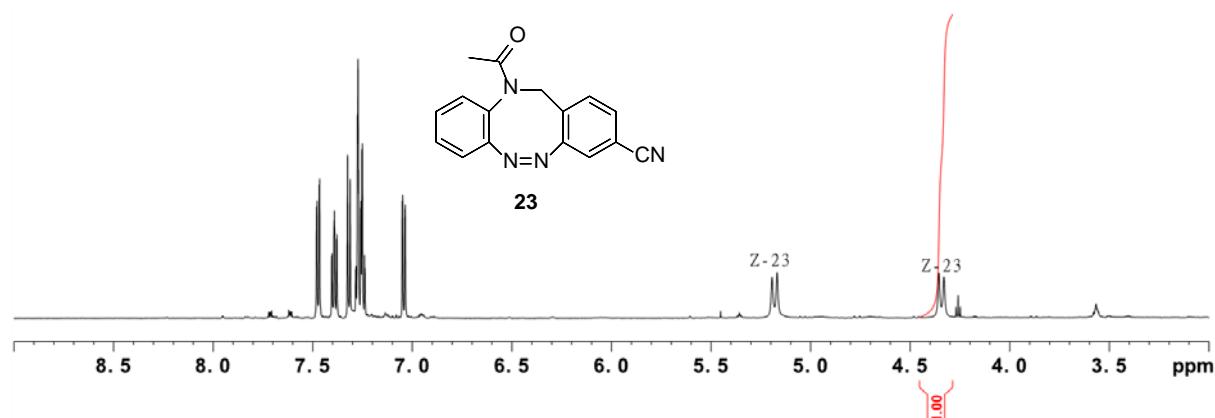


Figure SIV.37: ^1H -NMR-spectra of **23** in CD_3CN at 298 K.

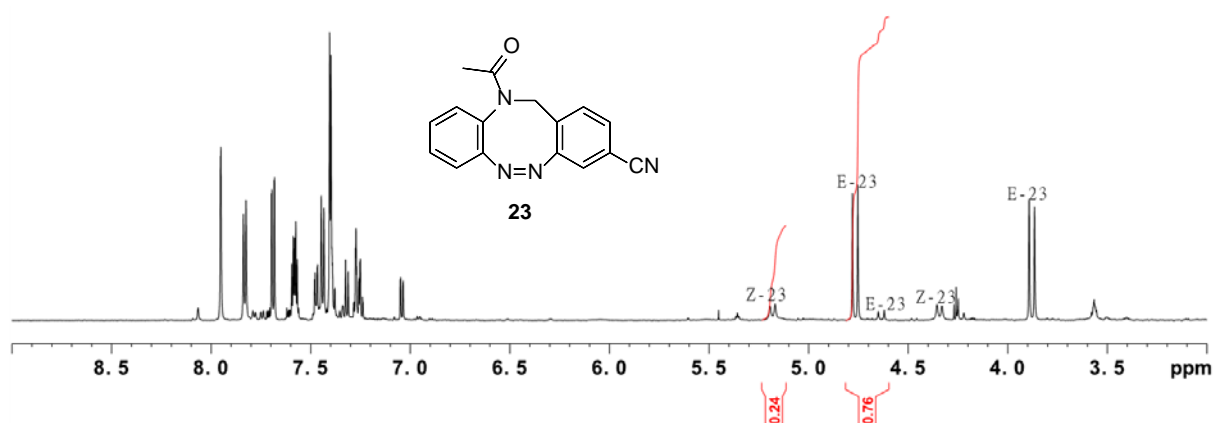


Figure SIV.38: ^1H -NMR-spectra of **23** in CD_3CN at 298 K after irradiation with 405 nm.

V. X-ray crystallographic data

Preparation of crystal samples

For crystal growth 10 mg of the given compound were dissolved in 0.2 ml acetone in a small glass vial and a drop of water was added. The vial was closed with a perforated cap and was stored in the dark for 3 weeks for slow evaporation of the solvent. Suitable crystals were selected subsequently.

General

The data collections were performed with a XtaLAB Synergy, Dualflex, HyPix diffractometer with a micro focus tube using Cu-K α radiation ($\lambda = 1.54184$ Å). The structures were solved with SHELXT [1] and refined with SHELXL-2016 [2] using Least Squares minimisation. All non-hydrogen atoms were refined anisotropic. The C-H H atoms were positioned with idealized geometry, methyl H atoms allowed to rotate but not to tip, and were refined isotropic with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ (1.5 for methyl H atoms) using a riding model. In compound **1**, the hydrogen atoms of the methyl group are disordered and were refined in two orientations, each rotated by 60 ° (AFIX 127). ORTEP plots of all compounds can be found in figure SV.1, SV.2 and SV.3.

CCDC-2329263 (**1**), CCDC-2329261 (**2**), and CCDC- 2329262 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

1. Sheldrick, G.M. (2015). *Acta Cryst.* A71, 3-8.
2. Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.

Table SV.1: Selected crystal data and details of the structure determinations for the diazocine compounds **1**, **2** and **7**.

	1	2	7
Formula	C ₁₅ H ₁₃ N ₃ O	C ₁₅ H ₁₂ BrN ₃ O	C ₂₁ H ₁₇ N ₃ O
MW /g mol ⁻¹	251.28	330.19	327.38
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	8.7563(1)	7.4471(2)	11.1465(1)
<i>b</i> /Å	8.7647(1)	9.2088(2)	13.0070(1)
<i>c</i> /Å	16.8947(1)	10.8243(2)	11.8469(1)
α /deg	90	84.031(2)	90
β /deg	101.974(1)	77.293(2)	91.709(1)
γ /deg	90	81.905(2)	90
<i>V</i> /Å ³	1268.40(2)	714.87(3)	1716.83(2)
<i>T</i> /K	293	293	293
<i>Z</i>	4	2	4
<i>D</i> _{calcd} /g cm ⁻³	1.316	1.534	1.267
μ /mm ⁻¹	0.687	3.911	0.634
2 θ_{max} /deg	159.062	160.064	159.654
Refl. collected	21811	12222	18993
Refl. unique	2704	3001	3685

R_{int}	0.0214	0.0263	0.0188
Refl. [$F_0 > 4 \sigma(F_0)$]	2592	2885	3440
Parameters	174	182	228
R_1 [$F_0 > 4 \sigma(F_0)$]	0.0342	0.0381	0.0426
wR_2 (all data)	0.0986	0.1067	0.1230
GOF	1.054	1.035	1.058
$\Delta\rho_{\text{max; min}} / e \text{ \AA}^{-3}$	0.19; -0.17	0.92; -0.70	0.20; -0.17

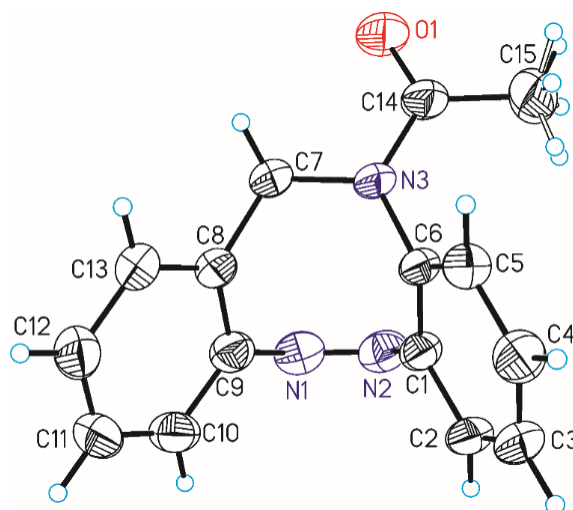


Figure SV.1: Crystal structure of *N*-acetyl diazocine **1** with labeling and displacement ellipsoids drawn at the 50% probability level.

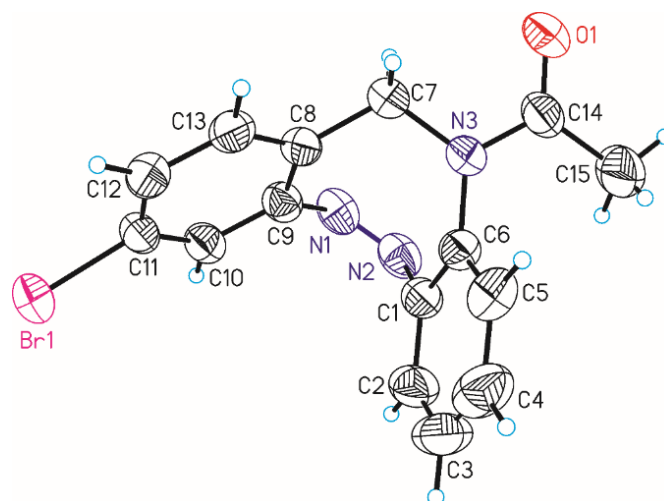


Figure SV.2: Crystal structure of bromo-*N*-acetyl diazocine **2** with labeling and displacement ellipsoids drawn at the 50% probability level.

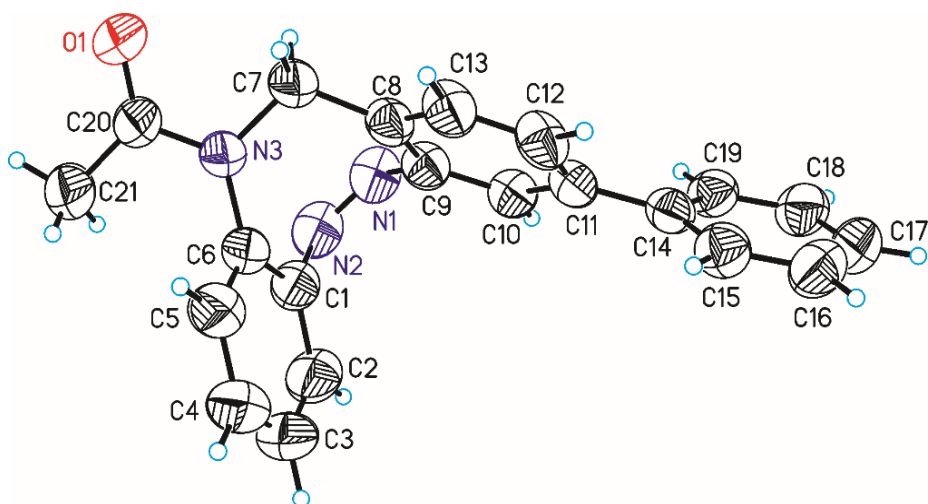


Figure SV.3: Crystal structure of phenyl-*N*-acetyl diazocine **7**.

VI. References

- [1] Lentès, P.; Rudtke, J.; Griebenow, T.; Herges, R. *Beilstein J. Org. Chem.* **2021**, *17*, 1503-1508. doi: 10.3762/bjoc.17.107.
- [2] Maier, M. S.; Hüll, K.; Reynders, M.; Matsuura, B. S.; Leippe, P.; Ko, T.; Schäffer, L.; Trauner, D. *J. Am. Chem. Soc.* **2019**, *141*, 17295-17304. doi: 10.1021/jacs.9b08794.
- [3] Denmark, S. E.; Butler, C. R. *Org. Lett.* **2006**, *8*, 63-66. doi: 10.1021/ol052517r.