Supporting Information

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I) Syntheses and Experimental Data

A) General Information

A.1) Chemicals

Chemicals were obtained from *ABCR*, *Acros Organics*, *Alfa Aesar*, *Merck*, *Sigma-Aldrich* or *VWR*. Commercially available reagents and starting materials were, unless mentioned otherwise, used without further purification. Solvents which were to be used in moisture-sensitive experiments were taken from a solvent drying system by *M. Braun* (type: *MB SPS-800*) and stored under an argon atmosphere. Other solvents were used after single distillation.

For reactions including oxygen- or moisture-sensitive reagents, glassware was baked out under high-vacuum conditions and procedures carried out under an argon atmosphere. Reagents were injected via a septum or added under argon counterflow.

A.2) Appliances and Materials

Thin layer chromatography (TLC) was performed on plates from *Merck* (silica gel 60, F_{254}). Detection of the substances was obtained by fluorescence detection under UV light (wavelength $\lambda = 254$ nm). The corresponding R_f values and solvents used as eluents are listed in the experimental part. Column chromatographies were performed with silica gel (grain size 0.04-0.063 cm, *Merck, Si60*) at approximately 1.5 atm (hand pump). The used eluent relations are listed with the respective experiments.

Nuclear magnetic resonance spectra (NMR-spectra) were obtained on instruments of the type *AV-250* (for ^{1}H-spectra), *AV-360* (for ^{1}H- and ^{13}C-spectra), *AV-500* (for ^{1}H-spectra) or *AV-500c* (for ^{1}H- and ^{13}C-spectra) from *Bruker*. Chemical shifts (δ) are given as parts per million (ppm) and refer to the shift of the hydrogen or carbon atoms in the solvents used ($CDCl_3$, CD_3CN). The following abbreviations were used for the assignment of the signals and their multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). The given coupling constants *J* are listed as the average of the experimental findings.

Mass spectrometry spectra (MS-spectra) were obtained by using electron ionization (EI) or electrospray ionization (ESI). Assigned m/z-relations are listed in ascending order. ESI-spectra were measured on a *Finnigan LCQ classic* or a *500-MS LC Ion Trap Mass Spectrometer* by *Varian*. EI-spectra were measured on a *MAT 8200* by *Finnigan.*

Infrared-spectra (IR-spectra) were measured on a *JASCO IR-4100* spectrometer directly from the substance via attenuated total reflectance (ATR-IR). The signals are labelled with the following abbreviations: vs (very strong), s (strong), m (medium), w (weak), vw (very weak).

B) Syntheses

B.1) Starting Materials

N-iodomorpholine-hydrogen iodide[I-1], *N*-ocytlazide[I-2], (*R*)-1-phenyl-azidoethane[I-3], tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA)[I-4], 1,3-bis(ethyny1)benzene[I-5] and 1,3,5-tris(ethyny1)benzene[I-6-1][I-5b] were prepared according to previously reported procedures.

B.2) General Methods

General procedure A for the synthesis of the applied iodoalkynes:

1,3-bis(iodoethynyl)benzene:

1,3-diethynylbenzene (0.63 g, 5 mmol) was dissolved in THF (20 mL) and treated with CuI (0.96 g, 0.5 mmol, 10 mol%) and *N*-iodomorpholine (3.74 g, 11 mmol, 2.2 eq.). The reaction mixture was stirred at room temperature for 2 hours, after which a fine white precipitate had formed. The suspension was poured onto a pad of neutral alumina and the filtrate was collected under vacuum. The solid phase was washed with DCM (4x100mL) the organic fractions were combined, washed with 20 mL of saturated $Na_2S_2O_3$ and dried over sodium sulfate. The organic fraction were concentrated in vacuo and recrystalized from hexane to afford 1.58 g (83%) of 1,3-bis(iodoethynyl)benzene as a yellow solid.

General procedure B for the synthesis of bis- or tris(iodotriazolyl)benzenes:

1,3-bis(1-benzyl-5-iodo-1*H*-1,2,3-triazol-4-yl)benzene (1,3-I^{Bn}):

Following a modified procedure of Sharpless and Fokin et al.[I-7], CuI (0.03 g, 0.16 mmol, 10 mol%) and TBTA (0.83 g, 0.16 mmol, 10 mol%) were dissolved in 8 mL of dry and degassed THF. The reaction mixture was stirred for 2 hours at room temperature until a homogeneous clear solution was obtained. The above solution was added to a solution of 1,3-bis(2-iodoethynyl)benzene (0.60 g, 1.58 mmol) in 2 ml THF. Benzyl azide (0.396 mL, 3.17 mmol, 2 eq.), dissloved in 2 mL THF were added to this reaction mixture over a period of 10 to 20 minutes. The sample was allowed to stir for 18 hours at room temperature in the dark. After removal of the solvent, the residue was taken up in 20 mL ethyl acetate, washed subsequently with 2 mL of 5 % NH_4OH solution, 20 mL water and 20 mL brine and dried over sodium sulfate. The solvent was removed in vacuo and the residue was purified by flash column chromatography. Recrystalization of the crude product from ethyl acetate and diethyl ether yields 0.66 g (65%) 1,3-bis(1-benzyl-5-iodo-1*H*-1,2,3-triazol-4-yl)benzene as a white solid.

General procedure C for the methylation of bis- or tris(iodotriazolyl)benzenes:

4,4'-(1,3-phenylene)bis(1-benzyl-5-iodo-3-methyl-1*H*-1,2,3-triazol-3-ium) triflate (1,3-I^{Bn}/OTf):

To a solution of 1,3-bis(1-benzyl-5-iodo-1*H*-1,2,3-triazol-4-yl)benzene (0.13 g, 0.2 mmol) in 5 mL of dry dichloromethane was added methyl triflate (88.00 µL, 0.80 mmol, 4 eq.) over a period of 10 to 20 minutes. The sample was allowed to stir for 2 days at room temperature in the dark. The solvent was removed in vacuo and the residue was recrystallized twice from acetonitrile and diethyl ether to afford 0.12 g (61%) 4,4'-(1,3-phenylene)bis(1-benzyl-5-iodo-3-methyl-1*H*-1,2,3-triazol-3-ium) triflate as a white solid.

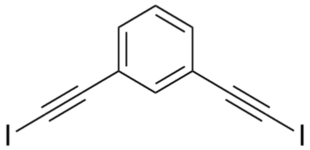
General procedure D for anion-cross-metathesis:

4,4'-(1,3-phenylene)bis(1-benzyl-5-iodo-3-methyl-1*H*-1,2,3-triazol-3-ium) hexafluorophosphate (1,3-I^{Bn}/PF$_6$):

To a solution of 4,4'-(1,3-phenylene)bis(1-benzyl-5-iodo-3-methyl-1*H*-1,2,3-triazol-3-ium) triflate (0.12 g, 0.12 mmol) in 1.5 mL freshly distilled methanol was added sodium hexafluorophosphate (0.06 g, 3eq). The sample was allowed to stir for 2 days at room temperature in the dark. The white precipitate was filtered, washed with small amounts of cold diethyl ether and methanol, and recrystallized from acetonitrile and diethyl ether to afford 0.09 g (82%) 4,4'-(1,3-phenylene)bis(1-benzyl-5-iodo-3-methyl-1*H*-1,2,3-triazol-3-ium) hexafluorophosphate as a white solid.

C) **Experimental Data**

C.1) 1,3-bis(iodoethynyl)benzene



The compound was synthesized by general procedure A.

Yield: 83% (yellow solid)

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.50 (s, 1 H), 7.40-7.35 (m. 2H), 7.29-7.23 (m, 1H) ppm.

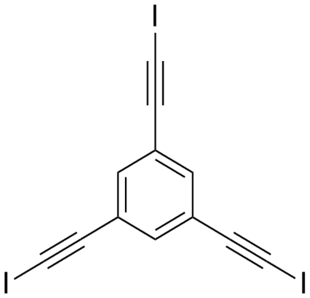
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 136.1, 132.1, 128.3, 123.6, 110.6, 93.1 ppm.

Elemental analysis:	*calc.*:	C: 31.78	H: 1.07
	found:	C: 31.83	H: 1.04

IR (ATR): υ = 3292, 2928, 2856, 1679, 1649, 1588, 1569, 1478, 1411, 1249, 1091, 937, 898, 847, 789, 688 cm^{-1}.

EI-MS: m/z = 377.82 [M]$^+$

C.2) 1,3,5-tris(iodoethynyl)benzene



The compound was synthesized by general procedure A. 20 mol% of copper iodide and 3.3 equivalents of *N*-iodomorpholine were used. The sample was stirred for 3h.

Yield: 90% (yellow solid)

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.42 (s, 3 H) ppm.

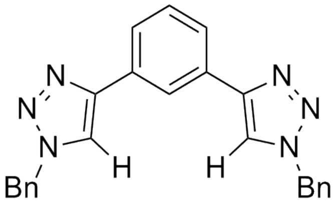
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 135.8, 123.9, 92.4 ppm.

Elemental analysis:	*calc.*:	C: 27.30	H: 0.57
	found:	C: 27.33	H: 0.51

IR (ATR): υ = 2837, 2344, 2103, 1697, 1572, 1413, 1356, 1220, 1167, 979, 872, 669 cm^{-1}.

EI-MS: m/z = 276.1 $[M - 2I^-]^{2+}$

C.3) 1,3-bis(1-benzyl-1*H*-1,2,3-triazol-4-yl)benzene (**1,3-H$^{\mathbf{Bn}}$**)



The compound was synthesized by general procedure B.

Yield: 64% (white solid)

R$_f$ (pentane/EtOAc = 1:1): 0.52

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.10 (m, 1H); 7.82-7.82 (m, 2H), 7.76 (s, 2H); 7.43-7.40 (m, 1H), 7.41-7.35 (m, 10H), 5.62 (s, 4H) ppm.

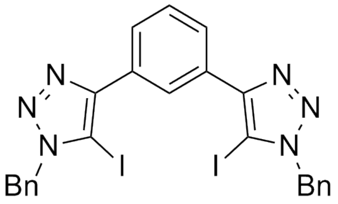
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 147.8, 134.6, 131.2, 129.2, 128.9, 128.2, 125.4, 122.8, 119.7, 54.3 ppm.

Elemental analysis:	*calc.*:	C: 73.45	H: 5.14	N: 21.41
	found:	C: 73.40	H: 5.20	N: 21.40

IR (ATR): υ = 2363, 2252, 1620, 1504, 1466, 1345, 1225, 1046, 910, 847, 794, 722, 678 cm^{-1}.

ESI-MS: m/z = 393.2 $[M + H]^+$

C.4) 1,3-bis(1-benzyl-5-iodo-1*H*-1,2,3-triazol-4-yl)benzene (**1,3-I**$^{\mathbf{Bn}}$)



The compound was synthesized by general procedure B.

Yield: 65% (white solid)

R_f (pentane/EtOAc = 1:1): 0.30

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.57 (m, 1H), 8.03-8.00 (m, 2H), 7.60-7.56 (m, 1H), 7.41-7.34 (m, 10H), 5.71 (s, 4H) ppm.

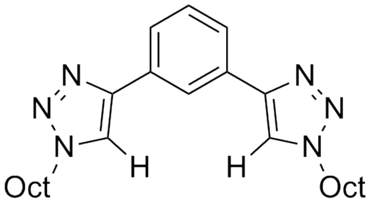
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 134.3, 130.6, 128.9, 128.5, 127.8, 127.6, 126.2, 54.5 ppm.

Elemental analysis:	*calc.*:	C: 44.74	H: 2.82	N: 13.04
	found:	C: 44.72	H: 2.83	N: 13.10

IR (ATR): υ = 3058, 3030, 2923, 2851, 2088, 1702, 1601, 1494, 1455, 1331, 1229, 1065, 1026, 974, 886, 846, 794, 727, 688 cm^{-1}.

ESI-MS: m/z = 644.9 $[M - H]^+$

C.5) 1,3-bis(1-octyl-1*H*-1,2,3-triazol-4-yl)benzene (**1,3-H^{Oct}**)



The compound was synthesized by general procedure B.

Yield: 65% (white solid)

R$_f$ (pentane/EtOAc = 1:1): 0.70

^{1}H-NMR (500 MHz, CDCl$_3$): δ = 8.29 (m, 1H), 7.85 (s, 2H), 7.84-7.82 (m, 2H), 7.49 (m, 1H), 4.41 (t, 4H, ^3J = 7.0 Hz), 2.01-1.90 (m, 4H), 1.41-1.17 (m, 20H), 0.87 (t, 6H, ^3J = 7.0 Hz) ppm.

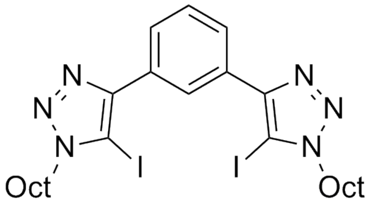
^{13}C-NMR (125 MHz, CDCl$_3$): δ = 147.5, 131.4, 129.5, 125.4, 123.0, 119.8, 50.6, 30.5, 29.2, 29.1, 26.6, 22.7, 14.2 ppm.

Elemental analysis:				
	calc.:	C: 71.52	H: 9.23	N: 19.25
	found:	C: 71.48	H: 9.18	N: 19.16

IR (ATR): υ = 2947, 2918, 2846, 1465, 1431, 1369, 1345, 1219, 1195, 1166, 1084, 1046, 964, 876, 808, 784, 755, 722, 678 cm^{-1}.

ESI-MS: m/z = 437.3 [M + H]$^+$, 873.3 [2M + H]$^+$

C.6) 1,3-bis(1-octyl-5-iodo-1*H*-1,2,3-triazol-4-yl)benzene (**1,3-I^{Oct}**)



The compound was synthesized by general procedure B.

Yield: 66% (white solid)

R_f (pentane/EtOAc = 4:1): 0.34

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.54 (m, 1H), 8.00-7.98 (m, 2H), 7.57 (m, 1H), 4.45 (t, 4H, ^3J = 7.0 Hz), 2.01-1.90 (m, 4H), 1.46-1.17 (m, 20H), 0.88 (t, 6H, ^3J = 7.0 Hz) ppm.

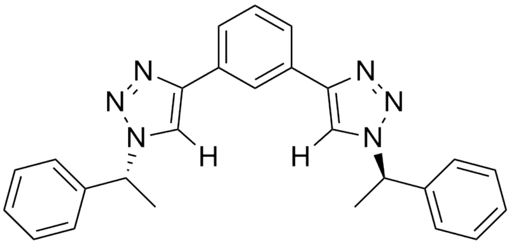
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 149.5, 130.8, 129.0, 127.7, 126.4, 51.2, 31.9, 30.1, 29.2, 29.1, 26.6, 22.8, 14.2 ppm.

Elemental analysis:				
	calc.:	C: 45.36	H: 5.56	N: 12.21
	found:	C: 45.26	H: 5.45	N: 12.25

IR (ATR): υ = 2952, 2923, 2851, 1451, 1378, 1330, 1224, 1161, 1070, 1036, 983, 886, 818, 789, 722, 698 cm^{-1}.

ESI-MS: m/z = 689.0 $[M + H]^+$, 1376.6 $[2M + H]^+$

C.7) 1,3-bis(1-((*R*)-1-phenylethyl)-1*H*-1,2,3-triazol-4-yl)benzene (**1,3-H$^{R\text{-}MeBn}$**)



The compound was synthesized by general procedure B.

Yield: 87% (white solid)

$[\alpha]_D^{25}$ = - 70° (EtOAc, *c* 0.024)

R_f (pentane/EtOAc = 4:1): 0.31

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.18 (m, 1H), 7.80-7.76 (m, 2H), 7.72 (s, 2H), 7.43 (m, 1H), 7.43-7.29 (m, 10H), 5.88 (q, 2H, ^3J = 7.1 Hz), 2.03 (d, 6H, ^3J = 7.1 Hz) ppm.

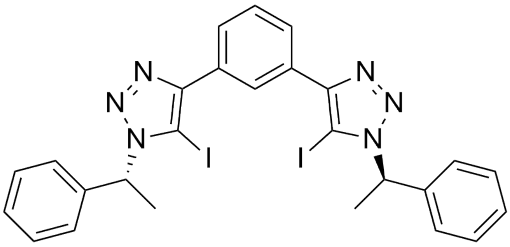
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 147.5, 139.9, 131.3, 129.5, 129.2, 128.8, 126.7, 125.4, 122.3, 118.8, 60.4, 21.4 ppm.

Elemental analysis:	*calc.*:	C: 74.26	H: 5.75	N: 19.99
	found:	C: 73.99	H: 5.69	N: 19.46

IR (ATR): υ = 1610, 1494, 1441, 1214, 1157, 1079, 1026, 973, 905, 799, 760, 698 cm^{-1}.

ESI-MS: m/z = 421.1 $[M + H]^+$, 841.0 $[2M + H]^+$

C.8) 1,3-bis(5-iodo-1-((*R*)-1-phenylethyl)-1*H*-1,2,3-triazol-4-yl)benzene (**1,3-I$^{R\text{-MeBn}}$**)



The compound was synthesized by general procedure B. 3.0 equivalents of (*R*)-1-Phenyl-azidoethane were used.

Yield: 42% (pale yellow solid)

$[\alpha]_D^{25}$ = + 38° (EtOAc, *c* 0.015)

R_f (pentane/EtOAc = 1:1): 0.56

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.53 (m, 1H), 7.99-7.96 (m, 2H), 7.54 (m, 1H), 7.38-7.29 (m, 10H), 5.81 (q, 2H, ^3J = 7.1 Hz), 2.12 (d, 6H, ^3J = 7.1 Hz) ppm.

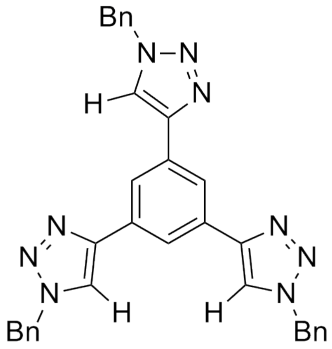
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 149.5, 140.2, 130.7, 129.0, 128.9, 128.4, 127.8, 126.7, 126.6, 61.6, 22.4 ppm.

Elemental analysis:	*calc.*:	C: 46.45	H: 3.30	N: 12.50
	found:	C: 46.40	H: 3.32	N: 11.98

IR (ATR): υ = 1537, 1509, 1460, 1388, 1330, 1263, 1234, 1161, 1026, 978, 804, 760, 693 cm^{-1}.

ESI-MS: m/z = 672.8 $[M + H]^+$, 1344.5 $[2M + H]^+$

C.9) 1,3,5-tris(1-benzyl-1*H*-1,2,3-triazol-4-yl)benzene (**1,3,5-H$^{\mathbf{Bn}}$**)



The compound was synthesized by general procedure B. 20 mol% of copper iodide and 20 mol% of TBTA were used. 3.0 equivalents of benzyl azide were added.

Yield: 55% (white solid)

R_f (pentane/EtOAc = 1:1): 0.20

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.22 (s, 3H), 7.85 (s, 3H), 7.43-7.34 (m, 15H), 5.60 (s, 6H) ppm.

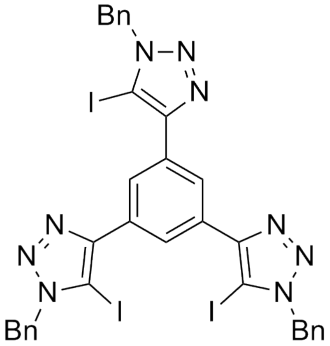
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 147.4, 134.4, 131.6, 129.3, 129.0, 128.7, 128.3, 128.2, 122.2, 120.2, 54.4 ppm.

Elemental analysis:	*calc.*:	C: 72.11	H: 4.95	N: 22.94
	found:	C: 72.13	H: 4.93	N: 22.93

IR (ATR): υ = 2928, 2851, 2358, 2209, 2161, 2035, 1973, 1610, 1499, 1456, 1408, 1350, 1229, 1051, 1012, 881, 799, 760, 712, 683 cm^{-1}.

ESI-MS: m/z = 550.2 $[M + H]^+$, 1099.2 $[2M + H]^+$

C.10) 1,3,5-tris(1-benzyl-5-iodo-1*H*-1,2,3-triazol-4-yl)benzene (**1,3,5-I$^{\mathbf{Bn}}$**)



CuI (0.04 g, 0.23 mmol, 20 mol%) and TBTA (0.12 g, 0.23 mmol, 20 mol%) were dissolved in 6 mL of dry and degassed THF. The reaction mixture was stirred for 2 hours at room temperature until a homogeneous clear solution was obtained. The above solution was added to a solution of 1,3,5-tris(iodoethynyl)benzene (0.611 g, 1.16 mmol) in 2 ml THF. Benzyl azide (0.43 mL, 3.44 mmol, 3 eq.), dissloved in 2 mL THF were added to this reaction mixture over a period of 20 minutes. The sample was allowed to stir for 18 hours at room temperature in the dark. The reaction was quenched with 2 mL of 5 % NH_4OH solution, the solvent as removed in vacuo and the residue was suspended in water and diethylether. A precipitate formed upon vigorous stirring, which was filtrated, dried, dissolved in acetone and again filtrated. The solvent was removed in vacuo and the residue was further purified by flash column chromatography yielding 0.57 g (54%) 1,3,5-tris(1-benzyl-5-iodo-1*H*-1,2,3-triazol-4-yl)benzene as an off-white solid.

Yield: 54% (off-white solid)

R_f (EtOAc/MeOH = 10:1): 0.19

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 8.64 (s, 3H); 7.41-7.33 (m, 10H), 5.72 (s, 6H) ppm.

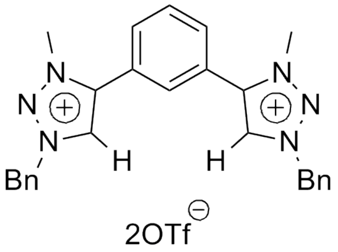
^{13}C-NMR (125 MHz, $CDCl_3$): δ = 134.4, 131.1, 128.9, 128.5, 127.8, 126.3, 54.5 ppm.

Elemental analysis:	*calc.*:	C: 42.74	H: 2.61	N: 13.59
	found:	C: 42.72	H: 2.65	N: 13.58

IR (ATR): υ = 2368, 2339, 2324, 1605, 1499, 1456, 1403, 1355, 1321, 1229, 1138, 1080, 1022, 983, 886, 823, 761, 717, 654 cm^{-1}.

ESI-MS: m/z = 927.7 $[M + H]^+$

C.11) 4,4'-(1,3-phenylene)bis(1-benzyl-3-methyl-1*H*-1,2,3-triazol-3-ium) triflate (**1,3-H^{Bn}/OTf**)



The compound was synthesized by general procedure C.

Yield: 80% (white, highly hydroscopic solid)

^{1}H-NMR (500 MHz, CD_3CN): δ = 8.85 (s, 2H), 8.15 (m, 1H), 7.89-7.87 (m, 2H), 7.61-7.59 (m, 1H), 7.54-7.37 (m, 10H), 5.73 (s, 4H), 4.33 (s, 6H) ppm.

^{13}C-NMR (125 MHz, CD_3CN): δ = 140.0, 132.4, 131.1, 130.1, 130.2, 129.6, 129.4, 123.6, 57.9 39.2 ppm.

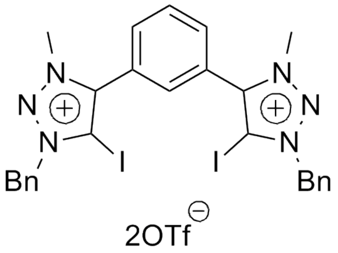
^{19}F-NMR (471 MHz, CD_3CN): δ = -79.33 (s, 3F) ppm.

Elemental analysis:	*calc.*:	C: 46.67	H: 3.64	N: 11.66	S: 8.90
	found:	C: 46.66	H: 3.65	N: 11.65	S: 8.91

IR (ATR): υ = 2358, 2166, 1968, 1576, 1499, 1456, 1253, 1229, 1152, 1080, 1027, 814, 756, 703 cm^{-1}.

ESI-MS: m/z = 571.1 $[M^{2+} + OTf]^+$, 1290.9 $[2M^{2+} + 3OTf]^+$

C.12) 4,4'-(1,3-phenylene)bis(1-benzyl-5-iodo-3-methyl-1*H*-1,2,3-triazol-3-ium) triflate (**1,3-I^{Bn}/OTf**)



The compound was synthesized by general procedure C.

Yield: 63% (white solid)

^{1}H-NMR (500 MHz, CD$_3$CN): δ = 8.00-7.95 (m, 1H), 7.91-7.88 (m, 2H), 7.76 (m, 1H); 7.56-7.51 (m, 10H), 5.88 (s, 4H), 4.22 (s, 6H) ppm.

^{13}C-NMR (125 MHz, CD$_3$CN): δ = 146.1, 133.8, 132.1, 131.5, 131.1, 129.2, 124.1, 122.28, 119.73, 90.3, 57.9, 39.4 ppm.

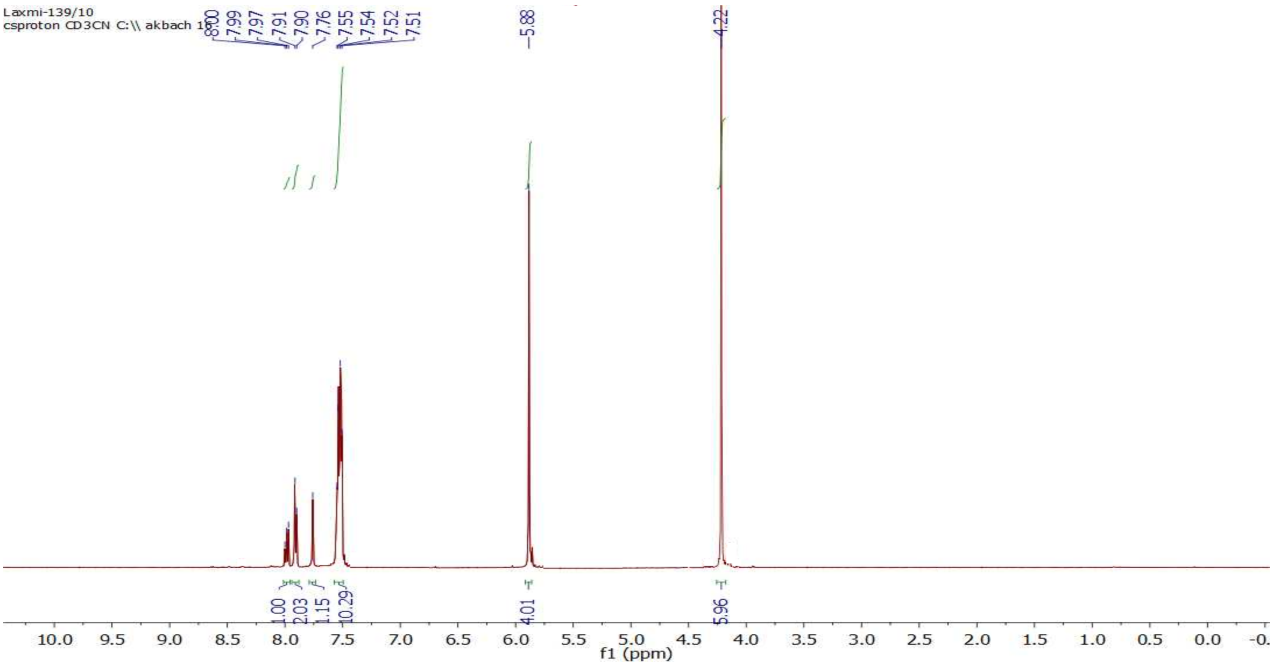
^{19}F-NMR (471 MHz, CD$_3$CN): δ = -79.33 (s, 3F) ppm.

Elemental analysis:	*calc.*:	C: 34.58	H: 2.49	N: 8.64	S: 6.59
	found:	C: 34.61	H: 2.50	N: 8.62	S: 6.56

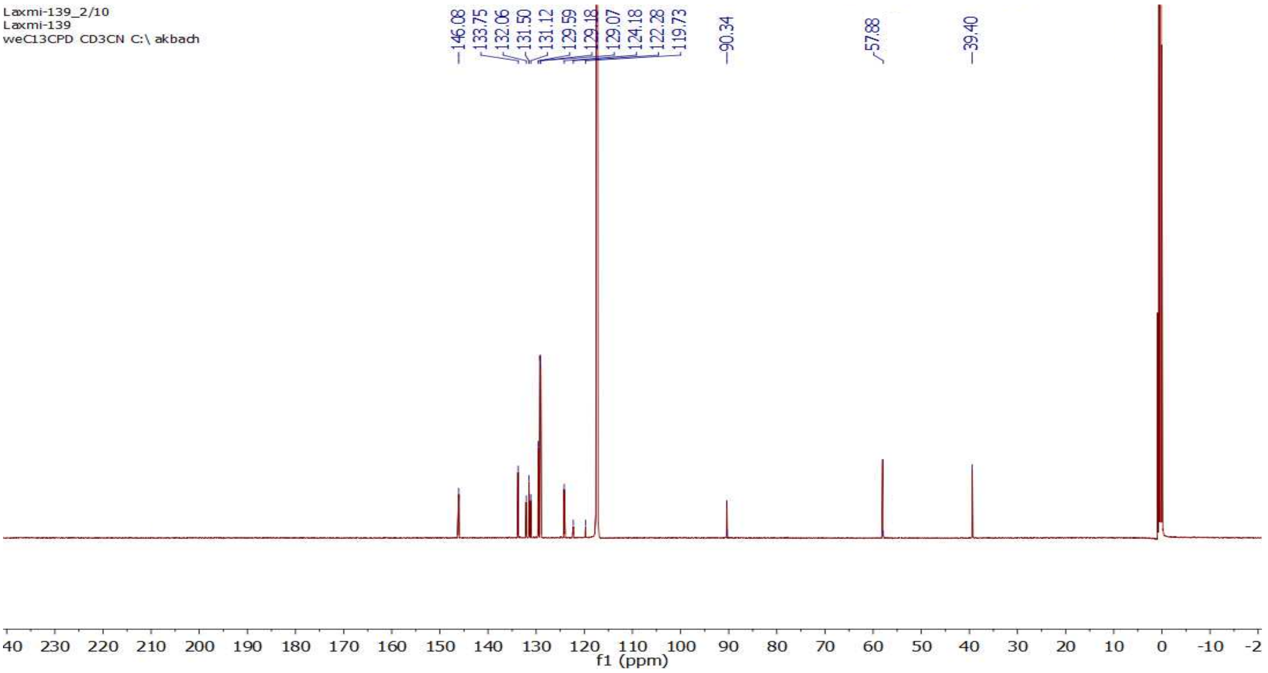
IR (ATR): υ = 3047, 2521, 2167, 2037,1971, 1578, 1502, 1478, 1459, 1429, 1330, 1277, 1234, 1176, 1143, 1095, 1028, 865, 803, 736, 703 cm^{-1}.

ESI-MS: m/z = 822.8 [M^{2+} + OTf^{-}]$^{+}$, 1794.4 [2M^{2+} + 3OTf^{-}]$^{+}$

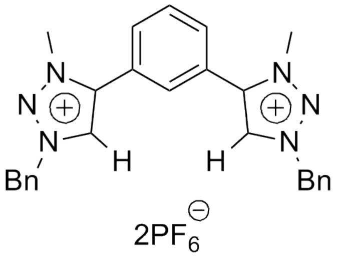
^{1}H-spectrum of 1,3-I^{Bn}/OTf



^{13}C-spectrum of 1,3-I^{Bn}/OTf



C.13) 4,4'-(1,3-phenylene)bis(1-benzyl-3-methyl-1*H*-1,2,3-triazol-3-ium) hexafluorophosphate **(1,3-H^{Bn}/PF$_6$)**



The compound was synthesized by general procedure D. The exchange is 90% complete.

Yield: 88% (white, highly hydroscopic solid)

^{1}H-NMR (500 MHz, CD_3CN): δ = 8.51 (s, 2H), 7.88-7.80 (m, 3H), 7.72 (m, 1H), 7.56-7.47 (m, 10H), 5.79 (s, 4H), 4.18 (s, 6H) ppm.

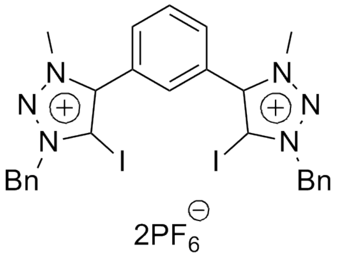
^{13}C-NMR (125 MHz, CD_3CN): δ = 143.1, 133.7, 132.9, 131.7, 131.2, 130.8, 130.4, 130.3, 129.8, 124.7, 58.2, 39.7 ppm.

^{19}F-NMR (471 MHz, CD_3CN): δ = -72.1 (s, 3F), -73.7 (s, 3F) ppm.

IR (ATR): υ = 2360, 2155, 1954, 1580, 1500, 1455, 1277, 1219, 1161, 1031, 828, 799, 760, 717, 639 cm^{-1}.

ESI-MS: m/z = 567.1 $[M^{2+} + PF_6^-]^+$, 1279.0 $[2M^{2+} + 3PF_6^-]^+$

C.14) 4,4'-(1,3-phenylene)bis(1-benzyl-5-iodo-3-methyl-1*H*-1,2,3-triazol-3-ium) hexafluorophosphate **(1,3-I^{Bn}/PF$_6$)**



The compound was synthesized by general procedure D. The exchange is 98% complete.

Yield: 82% (white solid)

^{1}H-NMR (500 MHz, CD$_3$CN): δ = 8.00-7.96 (m, 1H), 7.9-7.88 (m, 2H), 7.73 (m, 1H), 7.55-7.49 (m, 10H), 5.87 (s, 4H), 4.20 (s, 6H) ppm.

^{13}C-NMR (125 MHz, CD$_3$CN): δ = 146.1, 133.7, 131.8, 131.4, 129.8, 129.2, 124.2, 117.3, 90.2, 65.3, 58.1, 54.0, 39.2, 14.4 ppm.

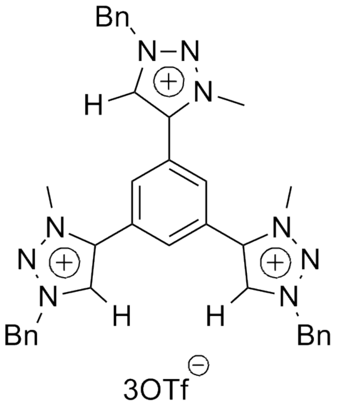
^{19}F-NMR (471 MHz, CD$_3$CN): δ = -71.47 (s, 3F), -74.74 (s, 3F) ppm.

Elemental analysis:	*calc.*:	C: 32.39	H: 2.51	N: 8.72
	found:	C: 32.35	H: 2.54	N: 8.70

IR (ATR): υ = 2336, 2324, 2163, 2029, 1971, 1493, 1454, 1435, 1286, 1224, 1171, 1023, 861, 803, 727, 698 cm^{-1}.

ESI-MS: m/z = 818.9 [M^{2+} + PF$_6^-$]$^+$

C.15) 4,4',4''-(benzene-1,3,5-triyl)tris(1-benzyl-3-methyl-1*H*-1,2,3-triazol-3-ium) triflate **(1,3,5-H^{Bn}/OTf)**



The compound was synthesized by general procedure C. 6.0 equivalents of methyl triflate were used.

Yield: 78% (white, highly hydroscopic solid)

^{1}H-NMR (500 MHz, CD_3CN): δ = 8.90 (s, 3H), 8.47 (s, 3H), 7.52-7.43 (m, 15H), 5.73 (s, 6H), 4.33 (s, 9H) ppm.

^{13}C-NMR (125 MHz, CD_3CN): δ = 140.7, 130.5, 130.3, 130.0, 129.7, 129.6, 125.2, 58.1, 39.2 ppm.

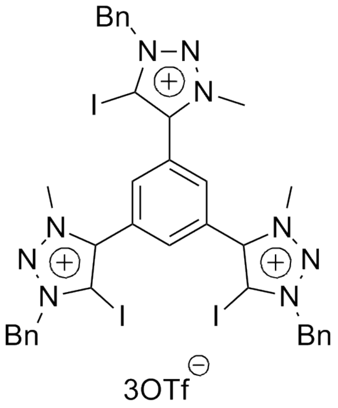
^{19}F-NMR (471 MHz, CD_3CN): δ = -79.33 (s, 3F) ppm.

Elemental analysis:					
	calc.:	C: 44.96	H: 3.48	N: 12.12	S: 9.23
	found:	C: 44.94	H: 3.51	N: 12.11	S: 9.24

IR (ATR): υ = 2363, 2325, 2156, 2040, 1963, 1562, 1504, 1456, 1249, 1225, 1147, 1027, 896, 823, 741, 703 cm^{-1}.

ESI-MS: m/z = 892.1 $[M^{3+} + 2OTf]^+$, 1932.9 $[2M^{3+} + 5OTf]^+$

C.16) 4,4',4''-(benzene-1,3,5-triyl)tris(1-benzyl-5-iodo-3-methyl-1H-1,2,3-triazol-3-ium) triflate **(1,3,5-I^{Bn}/OTf)**



The compound was synthesized by general procedure C. 6.0 equivalents of methyl triflate were used.

Yield: 61% (off-white solid)

^{1}H-NMR (500 MHz, CD_3CN): δ = 8.08 (s, 3H), 7.56-7.49 (m, 15H), 5.9 (s, 6H), 4.3 (s, 9H) ppm.

^{13}C-NMR (125 MHz, CD_3CN): δ = 144.9, 135.4, 131.4, 129.6, 129.2, 129.1, 90.7, 58.4, 39.5 ppm.

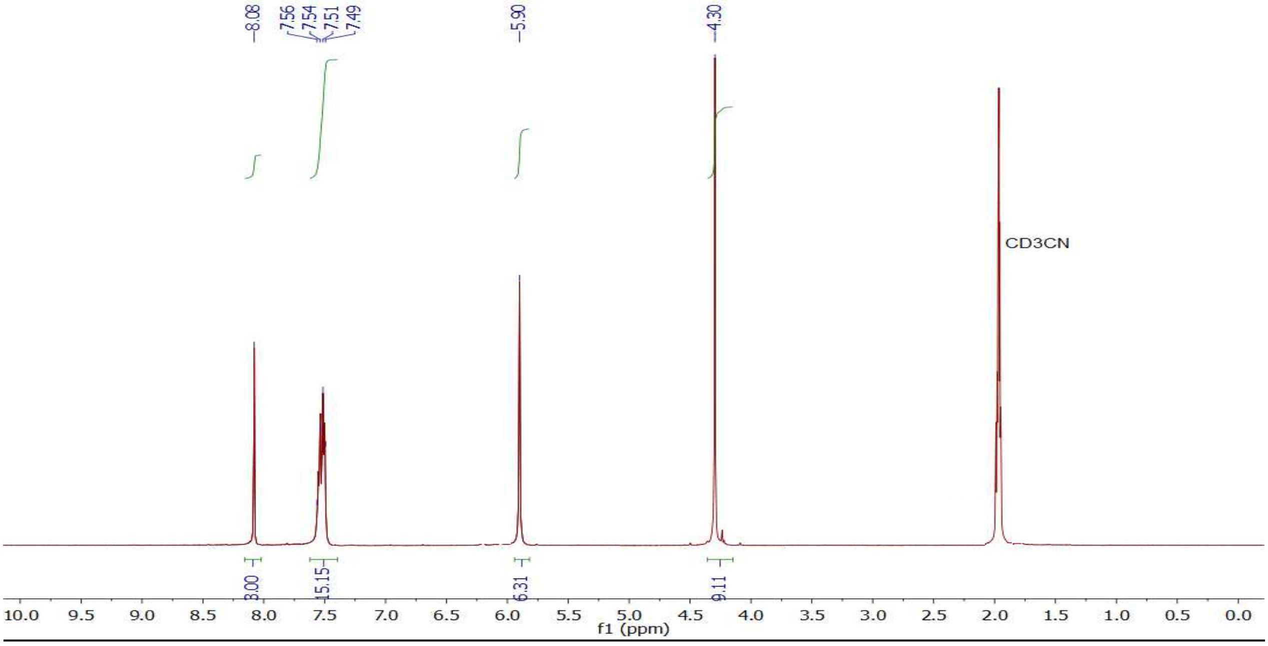
^{19}F-NMR (471 MHz, CD_3CN): δ = -79.33 (s, 3F) ppm.

Elemental analysis:					
	calc.:	C: 33.00	H: 2.34	N: 8.88	S: 6.78
	found:	C: 33.03	H: 2.32	N: 8.86	S: 6.77

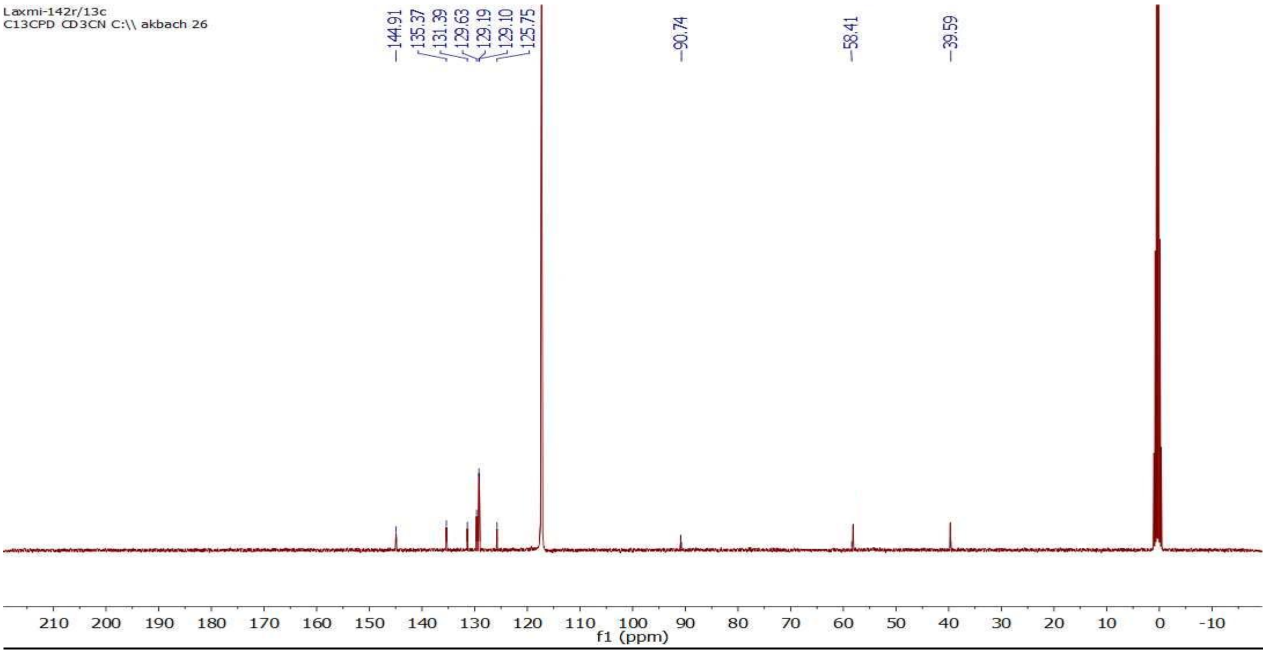
IR (ATR): υ = 2358, 2339, 2165, 2031, 1968, 1456, 1273, 1200, 1162, 1027, 905, 876, 737, 712 cm^{-1}.

ESI-MS: m/z = 1119.8 $[M^{3+} + OTf^{-}]^{2+}$, 1269.7 $[M^{3+} + 2OTf^{-}]^{+}$

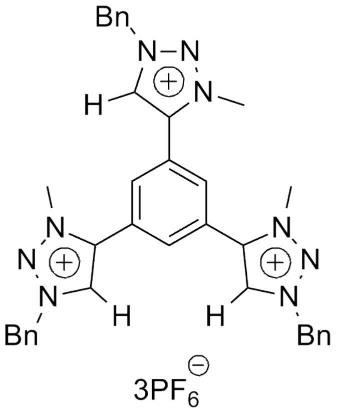
^{1}H-spectrum of 1,3,5-I^{Bn}/OTf



^{13}C-spectrum of 1,3,5-I^{Bn}/OTf



C.17) 4,4',4''-(benzene-1,3,5-triyl)tris(1-benzyl-3-methyl-1*H*-1,2,3-triazol-3-ium) hexafluorophosphate **(1,3,5-H$^{\mathbf{Bn}}$/PF$_6$)**



The compound was synthesized by general procedure D. 4.5 equivalents of sodium hexafluorophosphate were used. The exchange is 90% complete.

Yield: 89% (white, highly hydroscopic solid)

^{1}H-NMR (500 MHz, CD_3CN): δ = 8.61 (s, 3H), 7.96 (s, 3H), 7.57-7.46 (m, 15H), 5.82 (s, 6H), 4.21 (s, 9H) ppm.

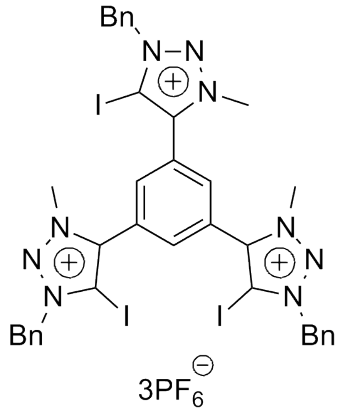
^{13}C-NMR (125 MHz, CD_3CN): δ = 140.9, 133.4, 131.8, 129.9, 129.3, 125.0, 57.4, 38.8 ppm.

^{19}F-NMR (471 MHz, CD_3CN): δ = -71.56 (s, 3F), -74.33 (s, 3F) ppm.

IR (ATR): υ = 2354, 2318, 2161, 2042, 1960, 1549, 1541, 1444, 1263, 1229, 1166, 1041, 823, 765, 731, 702 cm^{-1}.

ESI-MS: m/z = 884.2 $[M^{2+} + PF_6^-]^+$, 1921.0 $[2M^{2+} + 5PF_6^-]^+$

C.18) 4,4',4''-(benzene-1,3,5-triyl)tris(1-benzyl-5-iodo-3-methyl-1H-1,2,3-triazol-3-ium) hexafluorophosphate (**1,3,5-I^{Bn}/PF$_6$**)



The compound was synthesized by general procedure D. 4.5 equivalents of sodium hexafluorophosphate were used. The exchange is 98% complete.

Yield: 95% (off-white solid)

^{1}H-NMR (500 MHz, CD$_3$CN): δ = 8.03 (s, 3H), 7.54-7.51(m, 15H), 5.90 (s, 6H), 4.28 (s, 9H) ppm.

^{13}C-NMR (125 MHz, CD$_3$CN): δ = 144.9, 135.3, 131.4, 129.6, 129.2, 129.1, 125.7, 90.6, 58.1, 39.6 ppm.

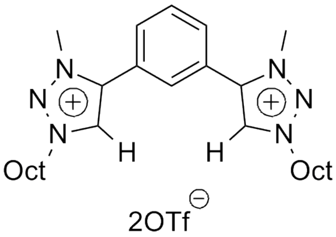
^{19}F-NMR (471 MHz, CD$_3$CN): δ = -71.47 (s, 3F), -74.47 (s, 3F) ppm.

Elemental analysis:	*calc.*:	C: 30.72	H: 2.36	N: 8.96
	found:	C: 30.71	H: 2.39	N: 8.95

IR (ATR): υ = 3043, 2363, 2163, 2029, 1970, 1267, 1234, 1171, 1042, 832, 736, 708 cm^{-1}.

ESI-MS: m/z = 1116.9 [M^{3+} + PF$_6^-$]$^{2+}$, 1261.7 [M^{3+} + 2PF$_6^-$]$^+$

C.19) 4,4'-(1,3-phenylene)bis(1-octyl-3-methyl-1*H*-1,2,3-triazol-3-ium) triflate (**1,3-H$^{\mathbf{Oct}}$/OTf**)



The compound was synthesized by general procedure C.

Yield: 91% (white, highly hydroscopic solid)

^{1}H-NMR (500 MHz, CDCl$_3$): δ = 8.85 (s, 2H), 8.11 (m, 1H), 7.90-7.89 (m, 2H), 7.69 (m, 1H), 4.56 (t, 4H, ^3J = 7.0 Hz), 4.30 (s, 6H), 2.10-1.99 (m, 4H), 1.45-1.20 (m, 20H), 0.88 (t, 6H, ^3J = 7.0 Hz) ppm.

^{13}C-NMR (125 MHz, CDCl$_3$): δ = 141.9, 132.2, 131.1, 131.0, 129.3, 123.6, 120.2, 54.4, 38.9, 31.7, 29.0, 28.9, 28.8, 26.1, 22.6, 14.0 ppm.

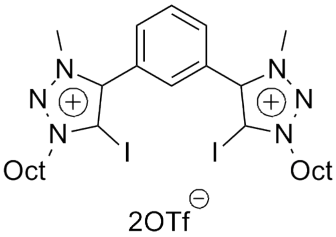
^{19}F-NMR (471 MHz, CDCl$_3$): δ = -78.77 (s, 3F) ppm.

Elemental analysis:	*calc.*: C: 47.11	H: 6.06	N: 10.99	S: 8.38
	found: C: 47.03	H: 5.99	N: 10.89	S: 8.31

IR (ATR): υ = 2962, 2928, 2865, 1460, 1263, 1219, 1147, 1079, 1026, 862, 837, 804, 751, 722, 698 cm^{-1}.

ESI-MS: m/z = 615.3 [M^{2+} + OTf]$^+$, 1379 [2M^{2+} + 3OTf]$^+$

C.20) 4,4'-(1,3-phenylene)bis(1-octyl-5-iodo-3-methyl-1*H*-1,2,3-triazol-3-ium) triflate (**1,3-I^{Oct}/OTf**)



The compound was synthesized by general procedure C.

Yield: 92% (white solid)

^{1}H-NMR (500 MHz, CDCl$_3$): δ = 7.93-7.92 (m, 2H), 7.86 (m, 1H), 7.37 (m, 1H), 4.53 (t, 4H, ^3J = 7.0 Hz), 2.10-2.00 (m, 4H), 1.51-1.23 (m, 20H), 0.89 (t, 6H, ^3J = 7.0 Hz) ppm.

^{13}C-NMR (125 MHz, CDCl$_3$): δ = 145.9, 133.7, 133.4, 131.3, 124.2, 120.3, 90.5, 55.2, 39.7, 31.8, 29.0, 28.9, 28.8, 26.3, 22.7, 14.2 ppm.

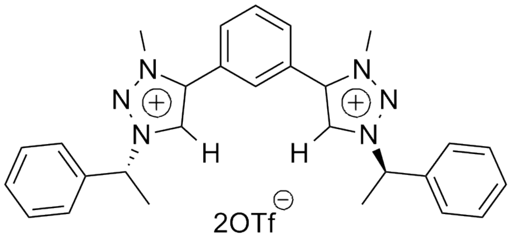
^{19}F-NMR (471 MHz, CDCl$_3$): δ = -78.77 (s, 3F) ppm.

Elemental analysis:	*calc.*:	C: 35.44	H: 4.36	N: 8.27	S: 6.31
	found:	C: 35.41	H: 4.30	N: 8.18	S: 6.40

IR (ATR): υ = 2947, 2918, 2860, 1451, 1321, 1243, 1219, 1152, 915, 842, 808, 755, 702 cm^{-1}.

ESI-MS: m/z = 867.1[M^{2+} + OTf]$^+$, 1882.4 [2M^{2+} + 3OTf]$^+$

C.21) (*R*)-4,4'-(1,3-phenylene)bis(3-methyl-1-((R)-1-phenylethyl)-1*H*-1,2,3-triazol-3-ium) triflate **(1,3-H$^{R\text{-MeBn}}$/OTf)**



The compound was synthesized by general procedure C.

Yield: 83% (white, highly hydroscopic solid)

$[\alpha]_D^{25}$ = - 68° (CH_3CN, c 0.013)

^{1}H-NMR (500 MHz, CD_3CN): δ = 8.57 (s, 2H), 7.84 (m, 3H), 7.76 (m, 1H), 7.57-7.44 (m, 10H), 6.11 (q, 2H, ^3J = 7.1 Hz), 4.19 (s, 6H), 2.07 (d, 6H, ^3J = 7.1 Hz) ppm.

^{13}C-NMR (125 MHz, CD_3CN): δ = 142.9, 138.1, 133.5, 131.7, 131.4, 130.6, 130.2, 129.0, 128.2, 124.8, 122.0, 65.7, 39.7, 20.9 ppm.

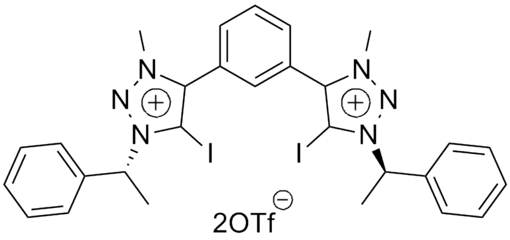
^{19}F-NMR (471 MHz, CD_3CN): δ = -79.33 (s, 3F) ppm.

Elemental analysis:	*calc.*:	C: 48.13	H: 4.04	N: 11.22	S: 8.57
	found:	C: 47.86	H: 4.15	N: 10.96	S: 8.43

IR (ATR): υ = 1465, 1253, 1224, 1147, 1075, 1022, 988, 915, 866, 808, 765, 746, 702 cm^{-1}.

ESI-MS: m/z = 599.0 $[M^{2+} + OTf]^+$, 1347.0 $[2M^{2+} + 3OTf]^+$

C.22) (*R*)-4,4'-(1,3-phenylene)bis(5-iodo-3-methyl-1-((R)-1-phenylethyl)-1*H*-1,2,3-triazol-3-ium) triflate (**1,3-I$^{R\text{-}MeBn}$/OTf**)



The compound was synthesized by general procedure C. 3.0 equivalents of (*R*)-1-Phenyl-azidoethane were used.

Yield: 85% (white solid)

$[\alpha]_D^{25}$ = + 37° (CH_3CN, c 0.010)

^{1}H-NMR (500 MHz, CD_3CN): δ = 7.98-7.90 (m, 1H), 7.87-7.80 (m, 2H), 7.65 (m, 1H), 7.52-7.41 (m, 10H), 6.14 (q, 2H, ^3J = 7.1 Hz), 4.19 (s, 6H), 2.06 (d, 6H, ^3J = 7.1 Hz) ppm.

^{13}C-NMR (125 MHz, CD_3CN): δ = 146.7, 137.8, 134.7, 132.9, 132.1, 130.4, 130.2, 128.3, 125.1, 122.1, 91.0, 66.9, 40.5, 22.0 ppm.

^{19}F-NMR (471 MHz, CD_3CN): δ = -79.33 (s, 3F) ppm.

Elemental analysis:					
	calc.:	C: 36.01	H: 2.82	N: 8.40	S: 6.41
	found:	C: 36.10	H: 2.73	N: 8.18	S: 6.33

IR (ATR): υ = 1542, 1509, 1460, 1277, 1243, 1224, 1157, 1031, 818, 760, 698 cm^{-1}.

ESI-MS: m/z = 850.7 $[M^{2+} + OTf]^+$, 1850.4 $[2M^{2+} + 3OTf]^+$

References:

[I-1] M. Koyama, N. Ohtani, F. Kai, I. Moriguchi, S. Inouye, *J. Med. Chem.* 1987, **30**, 552.

[I-2] S. G. Alvarez, M. H. Alvarez, *Synthesis* 1997, **4**, 413.

[I-3] A. S. Thompson, G. R. Humphrey, A. M. DeMarco, D. J. Mathre, E. J. J. Grabowski, *J. Org. Chem.* 1993, **58**, 5886.

[I-4] M. von Delius, E. M. Geertsema; D. A. Leigh, *Nature Chemistry* 2010, **2**, 96.

[I-5] a) T. X. Neenan; G. M. Whitesides, *J. Org. Chem.* 1988**, 53,** 2489; b) K. Yoosaf, *Chem. Eur. J.* 2011, **11**, 3262.

[I-6] L. Jie, H. Pengcheng, *Beil. J. Org. Chem.* 2011, **7**, 426.

[I-7] J. E. Hein, J. C. Tripp, L. B. Krasnova, K. B. Sharpless, V. V. Fokin, *Angew. Chem. Int. Ed.* 2009, **48**, 8018.

D) NMR Experiments

General procedure for the NMR experiments of Table X

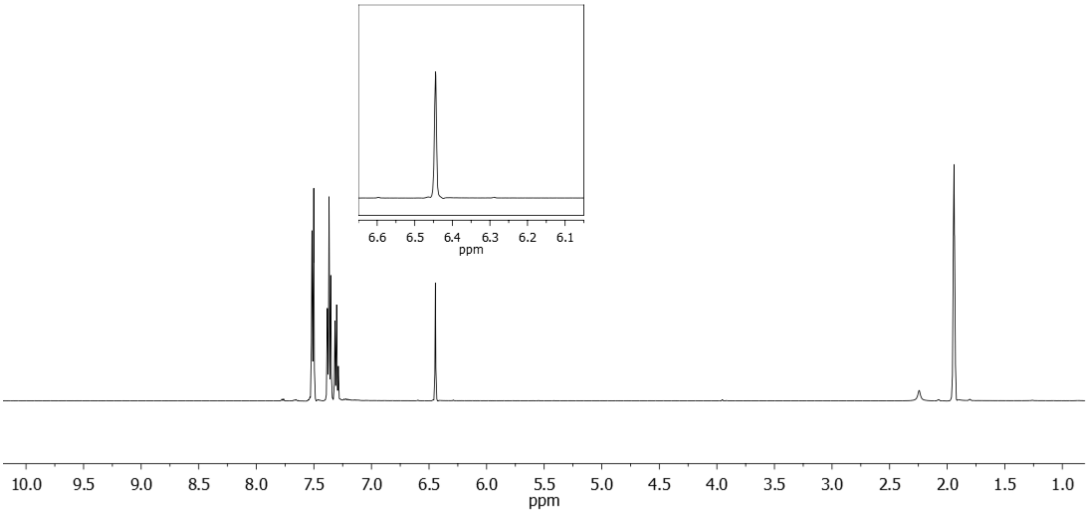
From stock solutions (in CD_3CN), the respective substrate (10.0 µmol, 1.0 equiv.) and, if applicable, the activating reagent (10.0 µmol, 1.0 equiv.) as well as pyridine (1.0 µmol, 0.1 equiv.) were mixed in an NMR tube, and the solution was filled up to an overall volume of 0.60 mL. All experiments were started simultaneously and the yield was determined by NMR spectroscopy after approx. 0, 3, 6, 12, 18, 24, 36, 48, 72, and 96 h of reaction time.

Analysis of the spectra (determination of the yield of X)

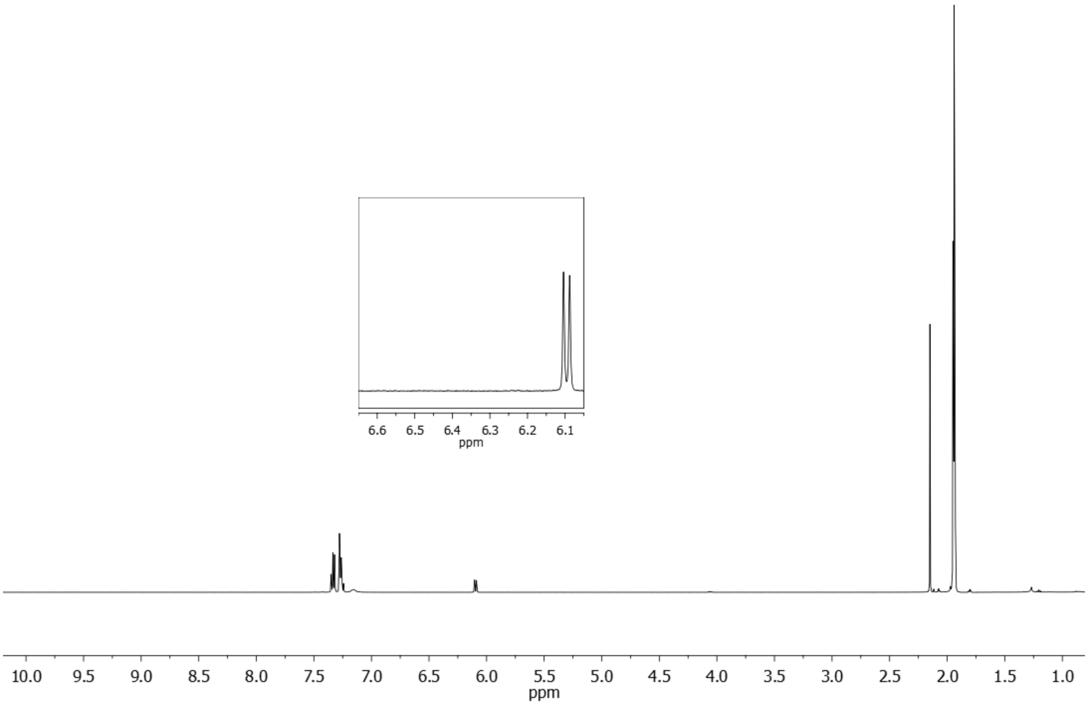
The yield was determined from the ratio of the product peak (doublet between 6.15 and 6.30 ppm, depending on the coordination with activating reagent or H^+) to the methylene peak of tetraethylsilane (quartet at 0.52 ppm). In the experiments with pyridine, the additional formation of trace amounts of benzhydryl pyridinium salt was accounted for.

E) Selected ^{1}H-NMR Spectra of the Ritter-like Reaction

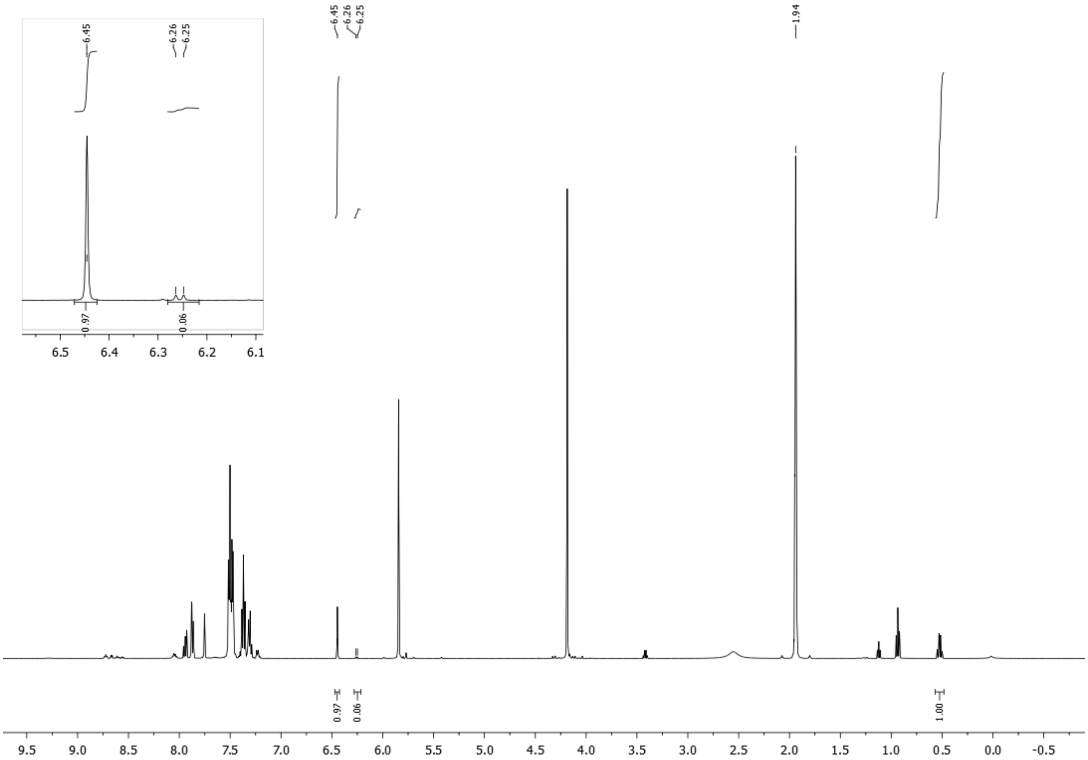
Benzhydryl bromide



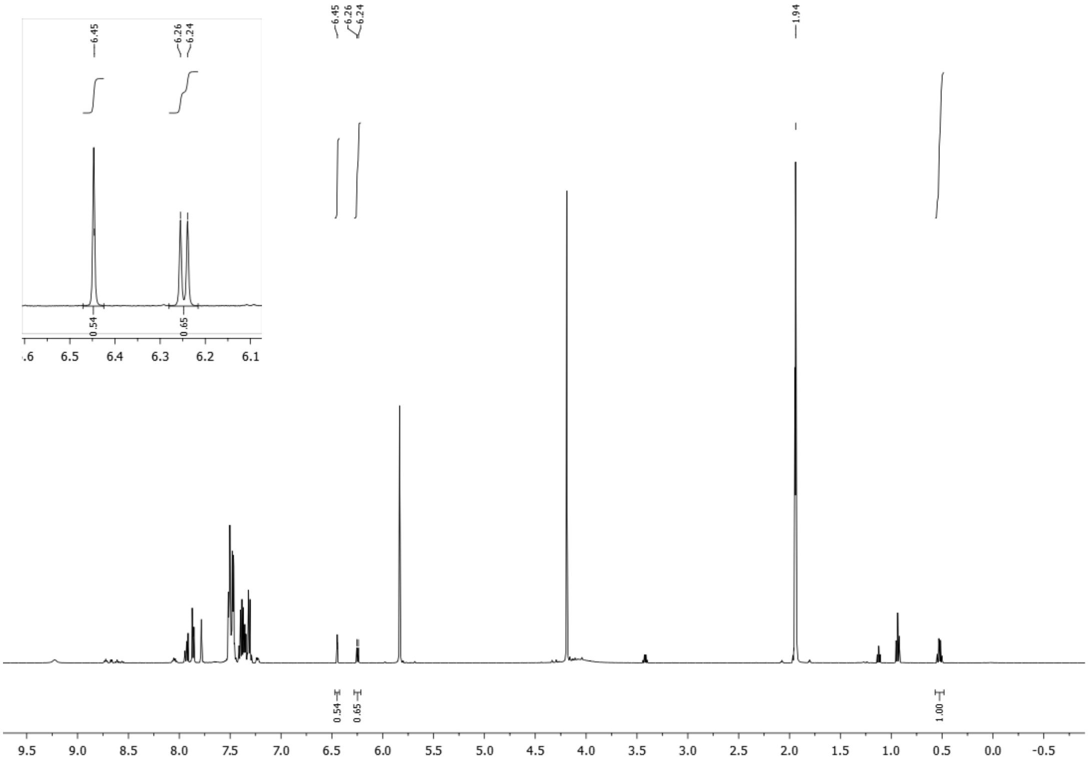
N-Benzyhdryl acetamide



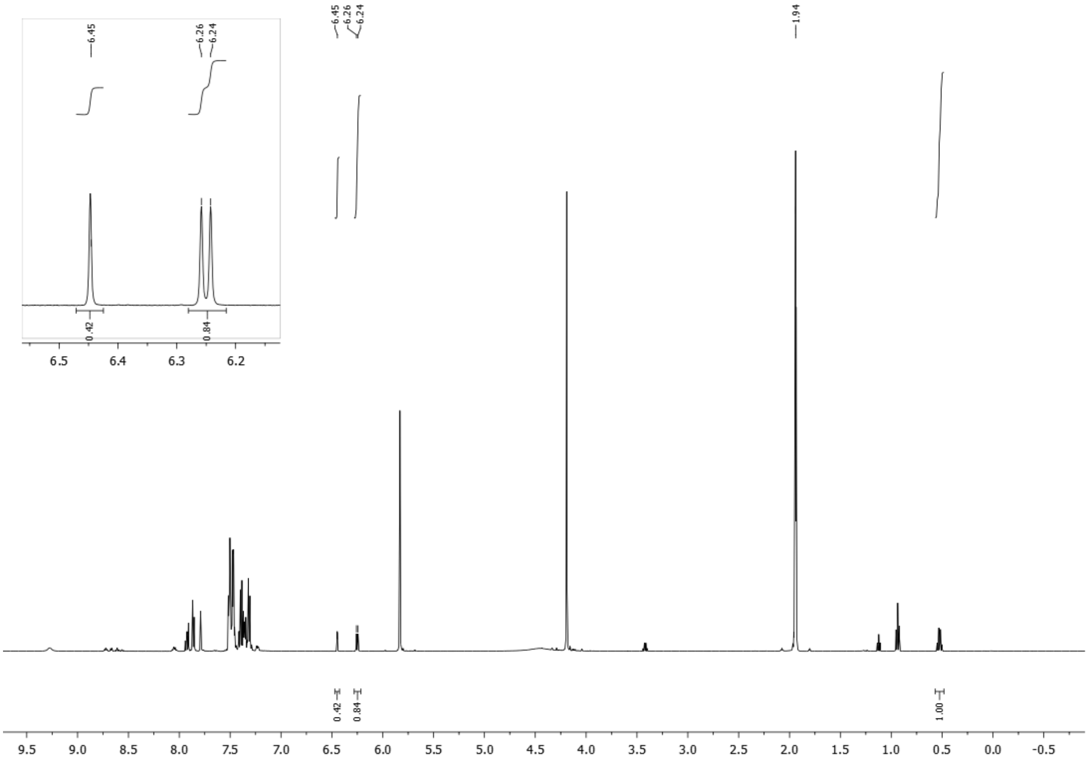
3 (see Table 1) after 0 h



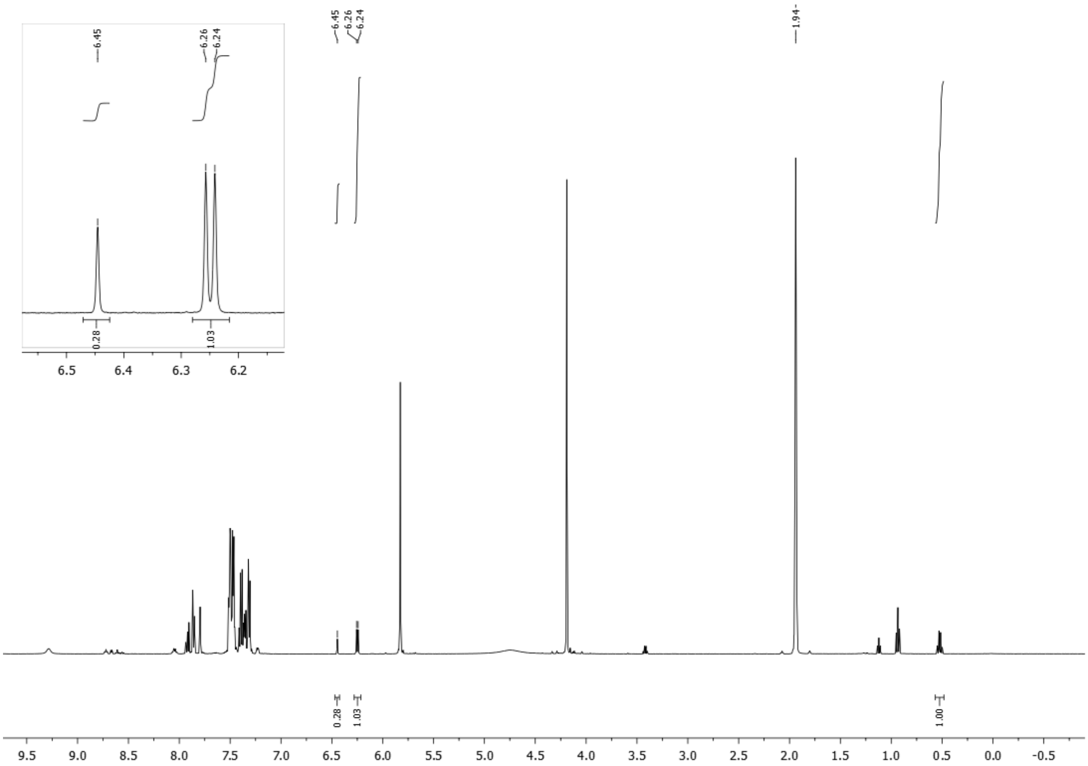
3 (see Table 1) after 24 h



3 (see Table 1) after 48 h



3 (see Table 1) after 96 h



II) Kinetics of the Ritter-like Reactions (Graphic representations)

All important experiments have been replicated several times. The estimated error of measurement is approx. 5%.

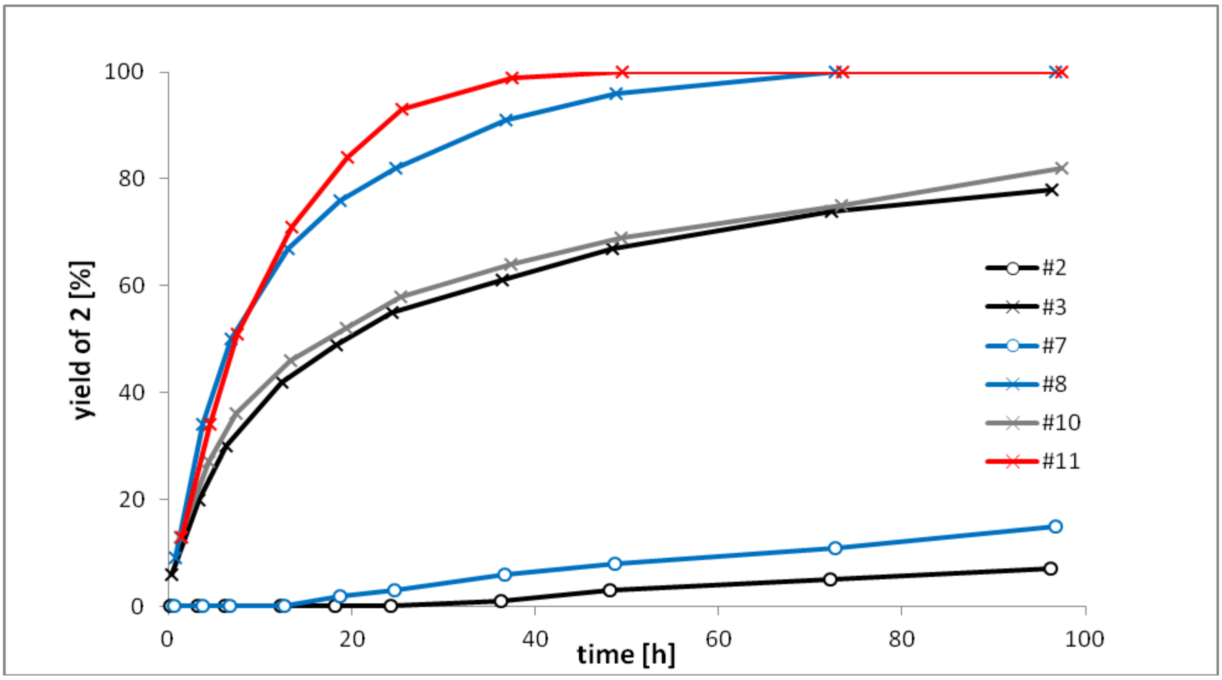


Figure II-1: Graphic Representation of NMR experiments # 2, 3, 7, 8, 10 and 11 (see Table 1 and Figure 3)

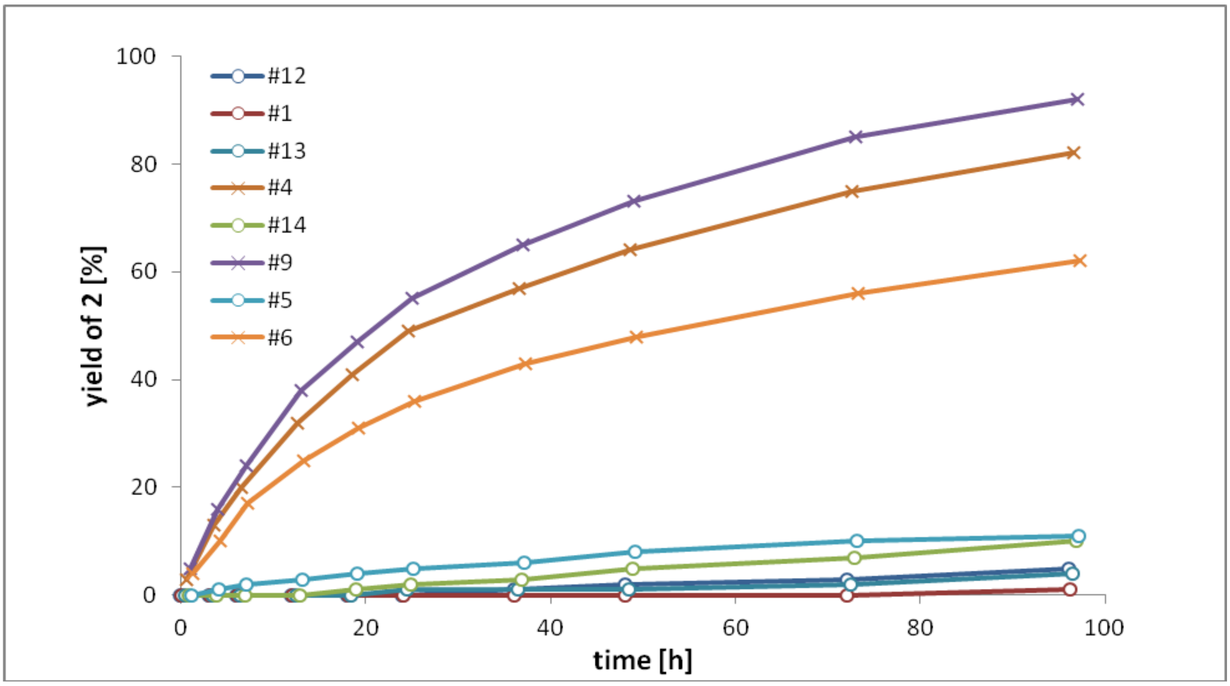


Figure II-2: Graphic Representation of NMR experiments # 1, 4, 5, 6, 9, 12, 13 and 14 (see Table 1)

III) Kinetics of the Ritter-like Reactions (Table)

#	Activating reagent	Add.[a]	Yield of **2** ([%], 48 h)	Yield of **2** ([%], 96 h)
1	-	py	≤ 5	≤ 5
2	**1,3-H^{Bn}/OTf**	py	≤ 5	7
3	**1,3-I^{Bn}/OTf**	py	67	78
4	**1,3-I^{Bn}/PF$_6$**	py	64	82
5	**1,3-H^{Oct}/OTf**	py	8	11
6	**1,3-I^{Oct}/OTf**	py	48	62
7	**1,3,5-H^{Bn}/OTf**	py	8	15
8	**1,3,5-I^{Bn}/OTf**	py	96	100
9	**1,3,5-I^{Bn}/PF$_6$**	py	73	92
10	**3**	py	69	82
11	**4**	py, 1 eq. cyc[b]	100	100
12	**-**	-	≤ 5	≤ 5
13	**1,3-H^{Bn}/PF$_6$**	py	≤ 5	≤ 5
14	**1,3,5-H^{Bn}/PF$_6$**	py	≤ 5	10

[a] Additive: 0.1 equivalents of pyridine (relative to **1**). [b] 1 eq. cyclohexene to quench the forming elemental bromine[I-8].

[I-8] F. Kniep, S. M. Walter, E. Herdtweck, S. M. Huber, *Chem. Eur. J.* 2012, **18**, 1306.

IV) X-Ray Structural Analysis

General:

The data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (APEX II, κ–CCD), a rotating anode (Bruker AXS, FR591) with MoK_{α} radiation (λ = 0.71073 Å), and a graphite monochromator by using the SMART software package.[I-8] The measurements were performed on single crystals coated with perfluorinated ether. The crystal was fixed on the top of a glass fiber and transferred to the diffractometer. A crystal from **1,3-$\mathbf{I^{Bn}}$/OTf** was frozen under a stream of cold nitrogen. A matrix scan using three short runs was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorenz and polarization effects, scan speed, and background using SAINT.[I-9] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.[I-9] Space group assignments were based upon systematic absences, *E* statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using WinGX[I-14] based on SIR-92.[I-10] Methyl hydrogen atoms treated as a part of rigid rotating groups, with C–H = 0.98 Å and $U_{\mathrm{iso(H)}} = 1.5 \cdot U_{\mathrm{eq(C)}}$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 Å and 0.95 Å, respectively, and $U_{\mathrm{iso(H)}} = 1.2 \cdot U_{\mathrm{eq(C)}}$. If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with SHELXL-97[I-12] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[I-11] Images of the crystal structures were generated by PLATON.[I-13]

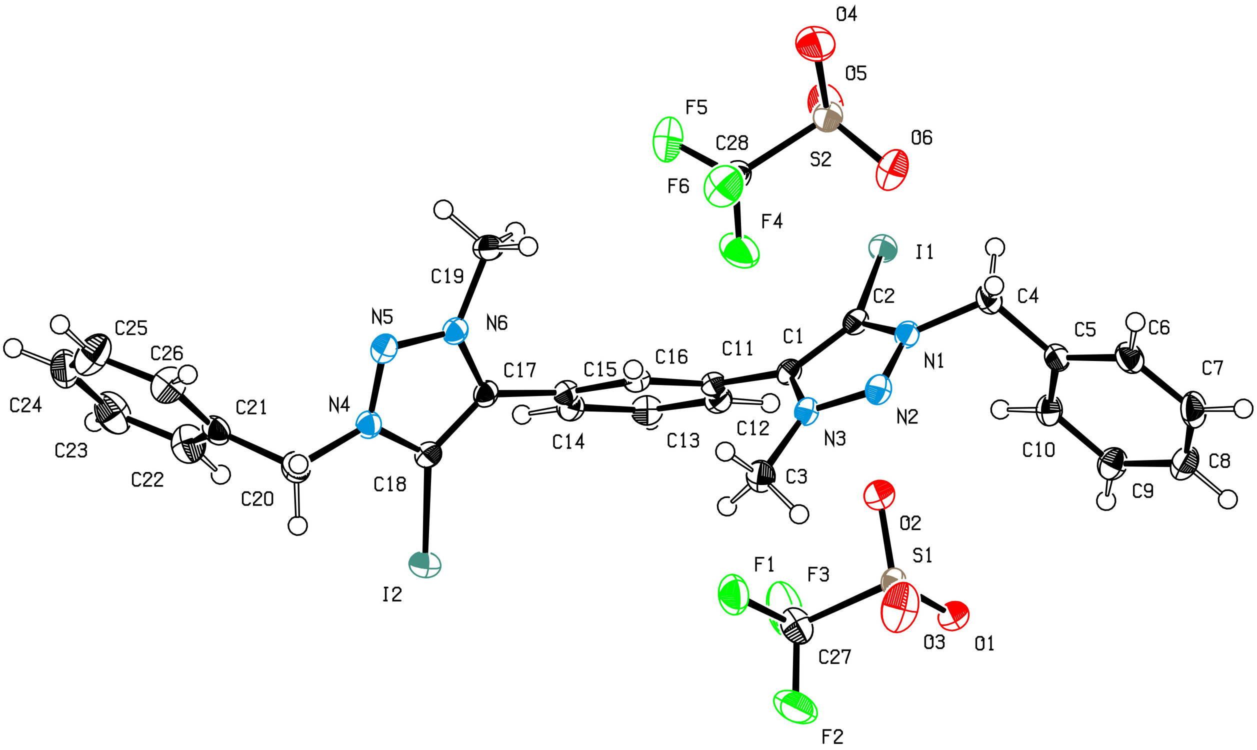


Figure F1 – Ortep drawing drawing of compound **1,3-I^{Bn}/OTf** with 50% ellipsoids.[I-13]

Operator:	*** Herdtweck ***
Molecular Formula:	$C_{28}\ H_{24}\ F_6\ I_2\ N_6\ O_6\ S_2$ $[(C_{26}\ H_{24}\ I_2\ N_6)^{2+}]$, $2[(C\ F_3\ O_3\ S)^-]$
Crystal Color / Shape	Colorless column
Crystal Size	Approximate size of crystal fragment used for data collection: 0.05 × 0.05 × 0.15 mm
Molecular Weight:	972.47 a.m.u.
F_{000}:	1896
Systematic Absences:	h0l: l≠2n; 0k0: k≠2n
Space Group:	Monoclinic $P\ 2_1/c$ (I.T.-No.: 14)
Cell Constants:	Least-squares refinement of 9689 reflections with the programs "APEX suite" and "SAINT"[I-8,I-9]; theta range 1.44° < θ < 25.44°; Mo(K$\overline{\alpha}$); λ = 71.073 pm a = 1020.00(2) pm b = 2829.19(6) pm β = 101.2130(8)° c = 1208.16(2) pm V = 3419.92(11)· 10^6 pm^3; Z = 4; D_{calc} = 1.889 g cm^{-3}; Mos. = 0.71
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; λ = 71.073 pm; Mo(K$\overline{\alpha}$)
Temperature:	(-150±1) °C; (123±1) K
Measurement Range:	1.44° < θ < 25.44°; h: -12/12, k: -34/34, l: -14/14
Measurement Time:	2 × 5 s per film
Measurement Mode:	measured: 7 runs; 3278 films / scaled: 7 runs; 3278 films φ– and ω–movement; Increment: $\Delta\varphi/\Delta\omega$ = 0.50°; dx = 55.0 mm
LP - Correction:	Yes[I-9]
Intensity Correction	No/Yes; during scaling[I-9]
Absorption Correction:	Multi-scan; during scaling; μ = 2.045 mm^{-1} [I-9] Correction Factors: T_{min} = 0.6173 T_{max} = 0.7452

Reflection Data:	65121	reflections were integrated and scaled
	935	reflections systematic absent and rejected
	64186	reflections to be merged
	6311	independent reflections
	0.026	R_{int}: (basis F_o^2)

	6311	independent reflections (all) were used in refinements
	6137	independent reflections with $I_o > 2\sigma(I_o)$
	99.7 %	completeness of the data set
	453	parameter full-matrix refinement
	13.9	reflections per parameter
Solution:	Direct Methods[I-10]; Difference Fourier syntheses	
Refinement Parameters:	In the asymmetric unit:	
	50	Non-hydrogen atoms with anisotropic displacement parameters
Hydrogen Atoms:	In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the hydrogen atoms were placed in calculated positions ($d_{C\text{-}H}$ = 95, 98, 99 pm). Isotropic displacement parameters were calculated from the parent carbon atom (U_H = 1.2/1.5 U_C). The hydrogen atoms were included in the structure factor calculations but not refined.	
Atomic Form Factors:	For neutral atoms and anomalous dispersion [I-11]	
Extinction Correction:	no	
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2)+(a*P)^2+b*P$ with a: 0.0175; b: 6.2834; P: [Maximum(0 or F_o^2)+2*F_c^2]/3	
Shift/Err:	Less than 0.001 in the last cycle of refinement:	
Resid. Electron Density:	$+1.51\ e_{0;}^{-}/\text{Å}^3$; $-0.69\ e_{0;}^{-}/\text{Å}^3$	
R1:	$\Sigma(\|\|F_o\|-\|F_c\|\|)/\Sigma\|F_o\|$	
[$F_o > 4\sigma(F_o)$]; N=6137]:		= 0.0223
[all reflctns; N=6311]:		= 0.0230
wR2:	$[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$	
[$F_o > 4\sigma(F_o)$]; N=6137]:		= 0.0526
[all reflctns; N=6311]:		= 0.0530
Goodness of fit:	$[\Sigma w(F_o^2-F_c^2)^2/(NO-NV)]^{1/2}$	= 1.107
Remarks:	Refinement expression $\Sigma w(F_o^2-F_c^2)^2$	

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V) DFT Calculations on the possible Threefold Coordination of Bromide to the Tridentate Activator

In order test the viability of a threefold coordination of the substrate to tridentate activators like **1,3,5-I^{Bn}/OTf**, we performed orientating DFT calculations on model systems. To this end, we replaced the benzyl substituents on the triazolium moieties of 1,3,5-IBn/OTf with methyl groups and we also used bromide as a prototypical XB acceptor(i.e. as a replacement for benzhydryl bromide; this, at the same time, represents the complex formed after the abstraction of bromide from the substrate). For these orientating investigations, the M06-2X functional[I-15] was used with the triple-zeta TZVPP basis set[I-16] on all atoms (employing the corresponding pseudopotential on the iodine atoms). The Gaussian09[I-17] suite of programs was used for the calculations.

A tridentate minimum structure was obtained that is shown in Figures F2 and F3 below. The identity of the minimum was confirmed by the absence of imaginary frequencies. The corresponding I-Br distances are 3.13 Å, with C-I-Br angles of 163°. The triazolium moieties are slightly bent towards the bromide (with an angle of about 13°), but the energetic penalty for this seems to be less than the interaction energy gained by the third complexation.

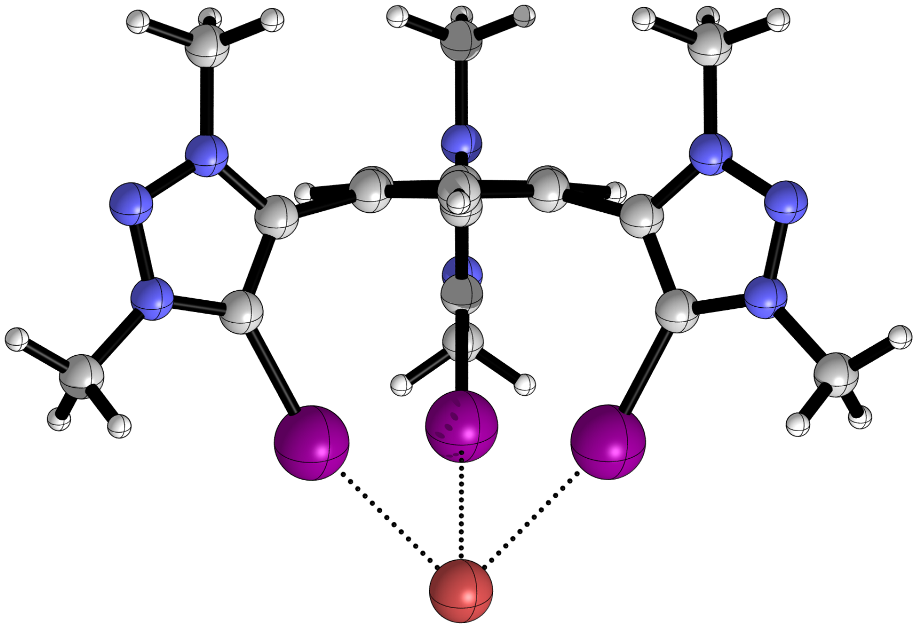

Figure F2 – CYLview plot[I-18] of the tridentate minimum structure (side view).

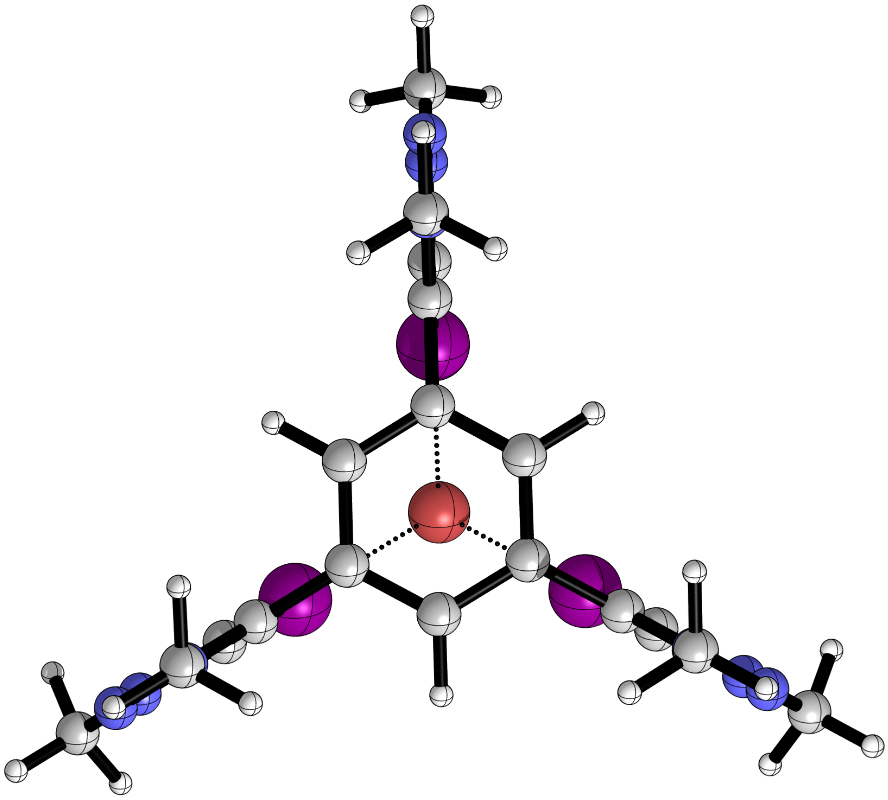

Figure F3 – CYLview plot[I-18] of the tridentate minimum structure (top view).

Coordinates of the complex:

H	2.45676300	0.24955100	1.96385200
C	1.38402900	0.14050600	2.06585900
C	-1.38560500	-0.14115100	2.06516100
C	0.81731200	-1.13087000	2.06474800
C	0.57297000	1.27170500	2.06504300
C	-0.81137900	1.12681200	2.06613600
C	-0.56789700	-1.26754300	2.06483500
H	-1.44217600	2.00132200	1.96419400
H	-1.00977300	-2.25100700	1.96192700
N	2.94413300	-4.08067100	1.95070000
N	2.27979100	-3.15888500	2.58501100
C	1.66049300	-2.29998400	1.73630000
C	1.97911200	-2.74197800	0.47027200
N	2.76203700	-3.82845500	0.68264800
N	-3.87204000	-0.39425400	2.58881900
C	-2.82000600	-0.28674300	1.73836800
C	-3.36417200	-0.34171300	0.47326300
N	-4.69617000	-0.47687700	0.68780600
N	-5.00353100	-0.50870000	1.95636700
C	1.16355500	2.58663300	1.73712800
C	1.38634000	3.08423700	0.47131700
N	1.93488300	4.30583500	0.68417200

N	2.06327400	4.58872200	1.95235700
N	1.59823000	3.55177000	2.58629200
C	-5.75033100	-0.58370700	-0.32136000
H	-5.55629500	-1.45841100	-0.93661400
H	-5.73680000	0.31286800	-0.93555400
H	-6.69574900	-0.68038900	0.20103600
I	-2.30311300	-0.23408300	-1.32603100
I	1.35217500	-1.87412400	-1.32701800
I	0.94668300	2.10801800	-1.32606300
C	3.38060000	-4.68669900	-0.32823900
H	3.93670200	-5.45841900	0.19256800
H	4.04123800	-4.08072100	-0.94269600
H	2.59683200	-5.12170000	-0.94286400
C	2.36796900	5.27149900	-0.32631700
H	2.75649500	6.13951600	0.19489200
H	1.51278700	5.53930400	-0.94130100
H	3.13775600	4.81153800	-0.94042900
C	-3.85916400	-0.39404200	4.04992900
H	-3.26020800	-1.23016800	4.40062500
H	-3.43998400	0.54466500	4.40201400
H	-4.88595100	-0.49835400	4.38394300
C	1.59454000	3.54120600	4.04740500
H	0.57151300	3.44120300	4.39994800
H	2.19806900	2.70865900	4.39877800
H	2.01869200	4.48246600	4.38032600
C	2.27353000	-3.15044600	4.04612900
H	2.69768200	-2.21407300	4.39846300
H	1.25110400	-3.25804600	4.39819000
H	2.87773100	-3.98780200	4.37852400
Br	-0.00018600	0.00120800	-3.43776900

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