Electronic Supplementary Material (ESI) for ChemComm.

Supporting information for:

A catalytic intramolecular nitrene insertion into a copper(I)–*N*-heterocyclic carbene bond yielding fused nitrogen heterocycles

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SI 1- General considerations

NMR spectra were recorded in Fourier Transform mode with a Bruker AVANCE 400 (^{1}H at 400 MHz, ^{13}C at 100 MHz), at 298K. Data are reported as chemical shifts (δ) in ppm. Residual solvent signals were used as internal references (^{1}H, ^{13}C). NMR assignments were supported by multidimensional experiments when needed. For the final cyclized compounds, the assignment was also supported by a previous experimental and computational report.[1]

Electrospray (positive mode) high-resolution mass spectra were recorded on a Thermo Scientific Q-exactive spectrometer (Orbitrap technology).

IR spectra were recorded on a Shimadzu Fourier Transform Infrared Spectrophotometer FTIR-8400S, equipped with a PIKE MIRacle Attenuated Total Reflectance (ATR) accessory (ATR crystal plate: germanium).

Elemental analyses were performed with a Flash EA 1112 (Thermofinnigan), in the elemental analysis facility of SRSMC (Vandoeuvre-lès-Nancy, France)

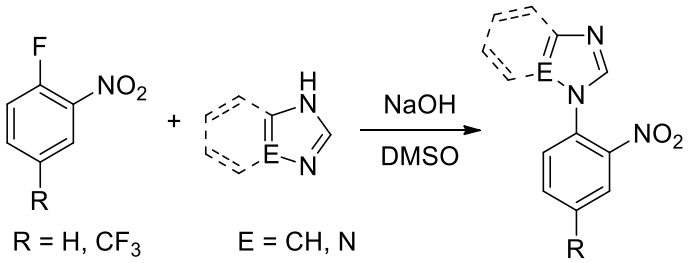
1-fluoro-2-nitrobenzene, 1-fluoro-4-trifluoromethyl-2-nitrobenzene were purchased from Acros and Fluorochem respectively. **1-(2-nitrophenyl)-4-phenyl-1H-1,2,3-triazole** was synthetized according to literature.[2]

All calculations were conducted using density functional theory (DFT) as implemented in the Gaussian 09.revD program. Geometry optimizations, transitions states (TS) and intrinsic reaction coordinates (IRC) calculations were performed using the B3LYP functional and the 6-31g** basis set for all atoms. Harmonic frequency analysis based on analytical second derivatives was used to characterize the optimized geometries as local minima.

[1] T. Mas, R. M. Claramunt; M. D. Santa María, D. Sanz, S. H. Alarcón, M. Pérez-Torralba, J. Elguero, *ARKIVOC*, **2002**, *5*, 48-61.
[2] D. B. Ramachary, A. B. Shashank, S. S. Karthik, *Angew. Chem. Int. Ed.* **2014**, 53, 10420-10424.

SI 2- Preparation of *N*-(2-azidophenyl)azoles starting materials

General procedure for the synthesis of *N*-(2-nitrophenyl)azoles from fluorinated aromatics



1-fluoro-2-nitrobenzene or 1-fluoro-4-trifluoromethyl-2-nitrobenzene (48.0 mmol) and azole (48.0 mmol) were dissolved in DMSO (10 mL). Powdered NaOH (2.88 g, 72.0 mmol) was added (caution: exothermic reaction) and the mixture was stirred at room temperature. After completion, 30 mL of ether were added to the resulting pasty mixture, which was triturated. Ether was removed and 40 mL of water were added resulting in the precipitation of a solid. The mixture was filtered, the crude residue washed with a minimum of ether, then *n*-pentane to furnish a solid.

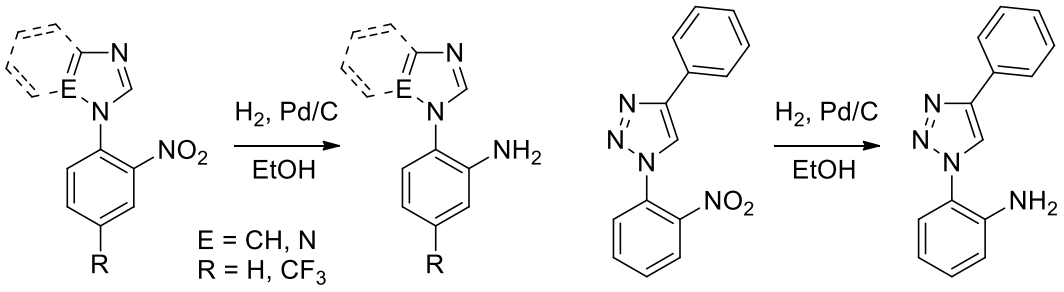
1-(2-nitrophenyl)imidazole: 3.5 h reaction time. Yellow solid. Yield: 87%, data identical to literature.[3]

1-(2-nitrophenyl)benzimidazole: 3.5 h reaction time. Yellow solid. Yield: 75%, data identical to literature.[4]

1-(2-nitro-4-(trifluoromethyl)phenyl)imidazole: 19 h reaction time. After completion, the mixture was diluted with water (100 mL), and extracted with ethyl acetate, dried on $MgSO_4$. Orange solid. Yield: 94%, data identical to literature.[5]

1-(2-nitrophenyl)-1,2,4-triazole: 2 h reaction time. After completion, the mixture was diluted with water (100 mL), and extracted with ethyl acetate, dried on $MgSO_4$. Beige solid. Yield: 91%, data identical to literature.[6]

General procedure for the synthesis of *N*-(2-aminophenyl)azoles by reduction



[3] A. J. Blake, B. A. J. Clark, H. McNab and C. C. Sommerville, *J. Chem. Soc. Perkin Trans. 1* **1997**, 1605-1608.

[4] B. D. Palmer, J. B. Smaill, M. Boyd, D. H. Boschelli, A. M. Doherty, J. M. Hamby, S. S. Khatana, J. B. Kramer, A. J. Kraker, R. L. Panek, G. H. Lu, T. K. Dahring, R. T. Winters, H. D. H. Showalter and W.A. Denny, *J. Med. Chem.* **1998**, *41*, 5457-5465.

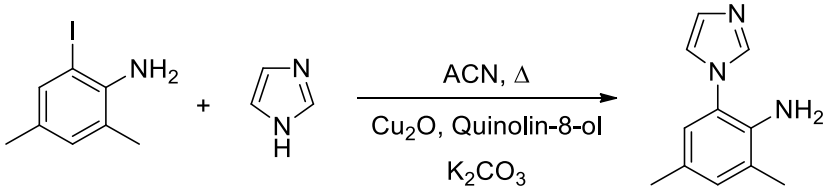
[5] V. V. Ivanov, A.A. Yurchenko, A.N. Chernega, A.M. Pinchuk, A. A.Tolmachev, *Heteroatom Chem.* **2002**, *13*, 84-92.

[6] P. Subramanian, K. P. Kaliappan, *Eur. J. Org. Chem.* **2014**, 5986-5989

N-(2-nitrophenyl)azole (16.0 mmol) and Pd/C (10% Pd, 400 mg) were added to ethanol (80 mL). The mixture was stirred at RT under hydrogen (4 bar) during 6-24 h. Heating the reaction mixture to 50 °C in the case of the 1,2,3-triazole starting material proved beneficial to reduce the reaction time from 24 h to 9 h. Then, it was filtered on celite, the solvents were evaporated and the oily residue was placed under high vacuum (0.05 mbar) for 2h to furnish the aminophenyl azole.

1-(2-aminophenyl)imidazole: yield: 93%, data identical to literature.[3]
1-(2-aminophenyl)benzimidazole: yield: 70%, data identical to literature.[4]
1-(2-amino-4-(trifluoromethyl)phenyl)imidazole: yield: quantitative, data identical to literature.[5]
1-(2-aminophenyl)-1,2,4-triazole: methanol used instead of ethanol, yield: quantitative, data identical to literature.[6]
1-(2-aminophenyl)-4-phenyl-1H-1,2,3-triazole: yield: 98%, data identical to literature.[7]

Preparation of 1-(2-amino-3,5-dimethylphenyl)imidazole[8]

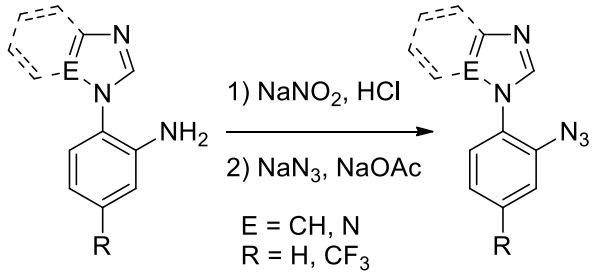


6-iodo-2,4-dimethylaniline[9] (1.236 g, 5.00 mmol) and imidazole (408.6 mg, 6.00 mmol) were added to 10 mL acetonitrile in an Ace Pressure Tube. Cu_2O (36.0 mg, 0.25 mmol) and K_2CO_3 (1.728 g, 12.50 mmol) were added. The solution was dearated by argon bubbling (5 min), quinolin-8-ol (145.2 mg, 1.00 mmol) was added and the vessel was closed. The mixture was stirred 3 days at 110 °C. Then, the solids were removed by filtration, the solvent was evaporated and the crude oily residue was purified by SiO_2 column chromatography (elution with AcOEt/MeOH *v*/*v* 20 : 1) to obtain 860.1 mg (77% yield) of an off-white solid.

^{1}H NMR (DMSO-d_6): δ = 7.71 (bs, 1H)[10], 7.28 (bs, 1H), 7.11 (bs, 1H), 6.91 (s, 1H), 6.74 (s, 1H), 4.33 (bs, 2H), 2.16 (s, 3H), 2.13 (s, 3H).
^{13}C NMR (DMSO-d_6): δ = 138.6, 137.7 (very broad)[10], 130.9, 129.0[10], 124.9, 124.8, 123.5, 122.5, 120.6 (broad, 2C)[10], 19.7, 17.8.
IR (neat): $\bar{\nu}$ (cm^{-1}) = 3408, 1636, 1503, 1062, 865, 829.
ESI-HRMS: calcd for $C_{11}H_{14}N_3$ $[M+H]^+$ 188.1182, found 188.1192.

[7] B. Saha, S. Sharma, D. Sawant, B. Kundu, *Tetrahedron* **2008**, *64*, 8676-8684.
[8] Conditions adapted from: A. Sathyanarayana and G. Prabusankar, *New J. Chem.* **2014**, *38*, 3613-3621.
[9] R. Adepu, A. Rajitha, D. Ahuja, A. K. Sharma, B. Ramudu, R. Kapavarapu, K. V. L. Parsa and M. Pal, *Org. Biomol. Chem.* **2014**, *12*, 2514-2518.
[10] Imidazole signals were more or less broadened in ^{1}H and ^{13}C NMR, probably due to dynamic exchange.

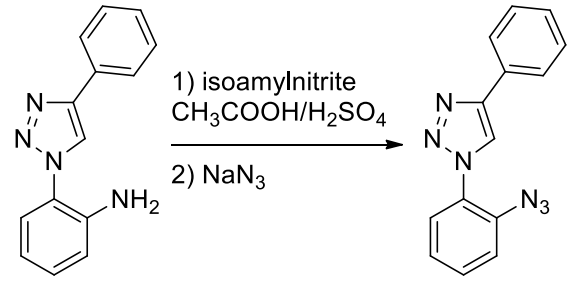
General procedure for the synthesis of *N*-(2-azidophenyl)azoles *via* diazonium salts



N-(2-aminophenyl)azole (13.0 mmol) was dissolved in 25-30 mL ice-cooled concentrated HCl/water (*v*/*v* 1 : 4). A solution of $NaNO_2$ (1.00 g, 14.5 mmol) in 6-7 mL of water was added dropwise under stirring and the resulting solution was stirred for 30 minutes at 0°C. NaN_3 (943 mg, 14.5 mmol) and sodium acetate (~5 g) were dissolved in water (30 mL). The diazonium salt solution was added dropwise to the azide solution. Gaseous evolution was observed immediately. After 30 min-1 h stirring at room temperature, an extraction with ether (3×100mL) was performed. The joint organic layers were washed with NaOH (1 mol L^{-1}, 50 mL) and water (50 mL), then dried over $MgSO_4$. Evaporation under reduced pressure afforded the pure azidophenyl azoles as off-white or beige solids.

1-(2-azidophenyl)imidazole: yield: quantitative, data identical to literature.[3]
1-(2-azidophenyl)benzimidazole: 93%, ^{1}H NMR ($CDCl_3$): δ = 8.08 (s, 1H), 7.90 (m, 1H), 7.56 (ddd, 1H, J_1 = 9.0 Hz, J_2 = 8.1 Hz, J_3 = 1.7 Hz), 7.46 (ddd, 1H, J_1 = 7.9 Hz, J_2 = 1.5 Hz, J_3 = 0.4 Hz), 7.41 (ddd, 1H, J_1 = 8.1 Hz, J_2 = 1.3 Hz, J_3 = 0.4 Hz), 7.34 (m, 4H).
^{13}C NMR ($CDCl_3$): δ = 144.1, 131.7, 131.4, 131.4, 128.4, 126.2, 126.2, 117.6, 117.0, 116.6, 115.1, 113.2 (one ^{13}C missing).
IR (neat): $\bar{\nu}$ (cm^{-1}) = 2130, 1505, 1459, 1307, 1284, 1230, 742.
ESI-HRMS: calcd for $C_{13}H_{10}N_5$ $[M+H]^+$ 236.0931, found 236.0928
1-(2-azido-4-(trifluoromethyl)phenyl)imidazole: 88%, ^{1}H NMR ($CDCl_3$): δ = 7.87 (s, 1H), 7.55 (s, 1H), 7.53 (d, 1H, J = 8.4 Hz), 7.47 (d, 1H, J = 8.4 Hz), 7.25 (s, 1H), 7.23 (s, 1H).
^{13}C NMR ($CDCl_3$): δ = 137.2, 135.0, 131.3 (q, $^2J_{C\text{-}F}$ = 34 Hz), 130.9, 129.5, 126.8, 122.9 (q, $^1J_{C\text{-}F}$ = 273 Hz), 122.2 (q, $^3J_{C\text{-}F}$ = 4 Hz), 119.9 (CH_{im}), 116.7 (q, $^3J_{C\text{-}F}$ = 4 Hz).
IR (neat): $\bar{\nu}$ (cm^{-1}) = 2120 (st), 1522, 1429, 1331, 1281, 1128.
ESI-HRMS: calcd for $C_{10}H_7F_3N_5$ $[M+H]^+$ 254.0654, found 254.0640
1-(2-azidophenyl)-1,2,4-triazole. yield: 96%, ^{1}H NMR ($CDCl_3$): δ = 8.69 (s, 1H, $H_{triazole}$), 8.12 (s, 1H), 7.72 (dd, 1H, J_1 = 8.1 Hz, J_2 =1.5 Hz), 7.48 (td, 1H, J_1 = 8.1 Hz, J_2 =1.5 Hz), 7.36-7.28 (m, 2H).
^{13}C NMR ($CDCl_3$): δ = 151.0, 143.8, 131.6, 128.7, 127.3, 125.0, 124.8, 118.7.
IR (neat): $\bar{\nu}$ (cm^{-1}) = 2129 (st), 1501, 1281, 1144, 984, 756.
ESI-HRMS: calcd for $C_8H_7N_6$ $[M+H]^+$ 187.0732, found: 187.0741.
1-(2-azido-3,5-dimethyl phenyl)imidazole: yield: 91%. ^{1}H NMR (DMSO-d_6): δ = 7.92 (s, 1H), 7.48 (s, 1H), 7.19 (s, 1H), 7.10 (m, 2H), 2.31 (s, 3H), 2.29 (s, 3H).
^{13}C NMR (DMSO-d_6): 138.4 (very broad), 135.5, 132.3, 131.7, 130.5, 130.3, 129.1, 125.9, 121.6 (broad), 20.0, 17.5.
IR (neat): $\bar{\nu}$ (cm^{-1}) = 2118, 1495, 1095, 1062, 801.
ESI-HRMS: calcd. for $C_{11}H_{12}N_5$ $[M+H]^+$ 214.1087, found 214.1102.

Preparation of 1-(2-azidophenyl)-4-phenyl-1H-1,2,3-triazole:[11]



The amine (1.146 g, 4,85 mmol) starting material was dissolved in 30 mL CH_3COOH/H_2SO_4 (*v*/*v* 5:1). The solution was cooled at -20°C with an ice-salt bath and isoamylnitrite (0.72 mL, 0.63 g, 5.30 mmol) was added dropwise. The reaction mixture was kept 30 minutes at -20 °C, then stirred 1 h at RT. Then, it was diluted with 30 mL H_2O and urea (2.052 g, 34.0 mmol) was added. After cooling the mixture again to -20 °C, a solution of NaN_3, (631 mg, 9.71 mmol) in 15 mL H_2O was added resulting in gaseous evolution and stirred during 1.5 h. After reverting to RT, the mixture was added to a sodium carbonate solution (34 g in 100 mL H_2O). Extraction with 3×100 mL ethyl acetate was performed. The joint organic phases were washed with 100 mL aqueous saturated $NaHCO_3$ and with 2×100 mL H_2O, dried on $MgSO_4$ and evaporated. The resulting brown solid was purified by SiO_2 column chromatography (toluene/ether *v*/*v* 9:1) to yield the 705 mg of the pure compound as a light brown solid (56% yield).

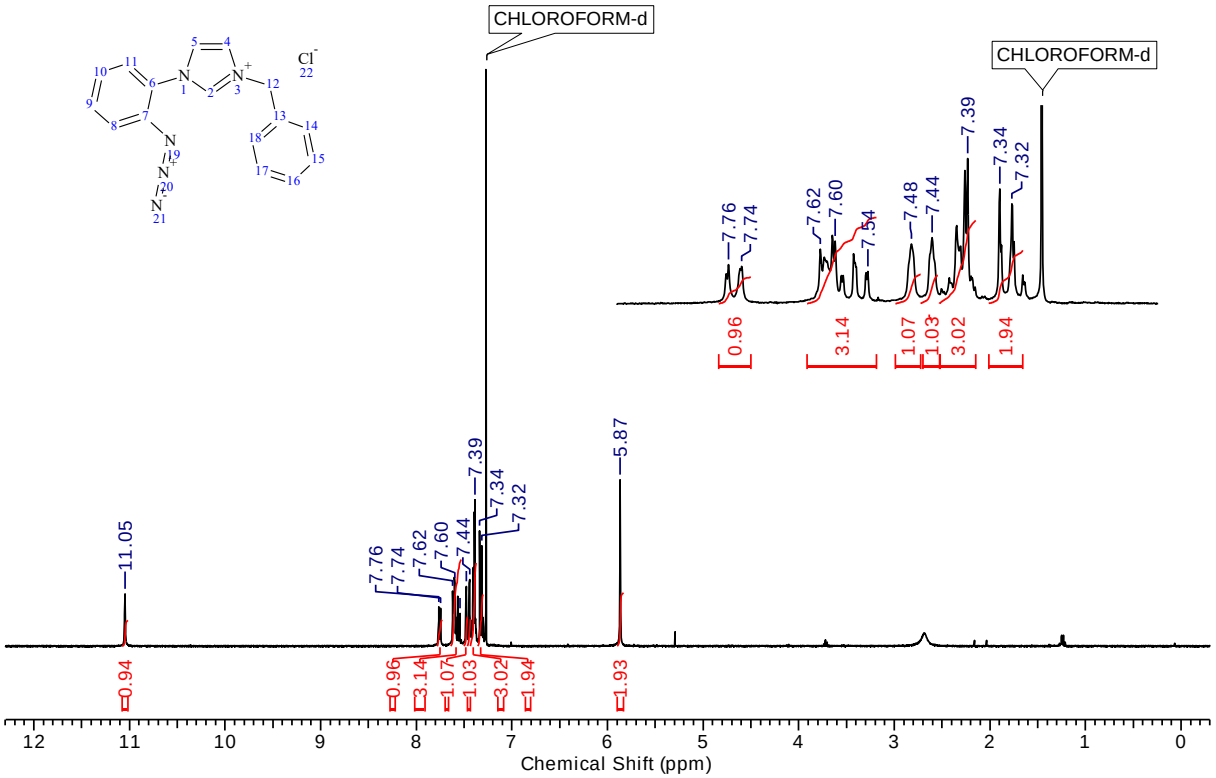
^{1}H NMR (DMSO-d_6): δ = 9.03 (s, 1H, $H_{triazole}$), 7.96-7.93 (m, 2H, H_{ar}), 7.73 (dd, 1H, J_1 = 8.1 Hz, J_2 = 1.5 Hz, H_{ar}), 7.69-7.62 (m, 2H, H_{ar}), 7.51-7.48 (m, 2H, H_{ar}), 7.44-7.36 (m, 2H, H_{ar}).
^{13}C NMR (DMSO-d_6): δ = 146.4 ($Cq_{triazole}$), 133.7 (Cq), 131.1 ($CH_{triazole}$), 130.3 (Cq), 129.0 (CH_{ar}), 128.2 (CH_{ar}), 127.7 (Cq), 126.9 (CH_{ar}), 125.7 (CH_{ar}), 125.4 (CH_{ar}), 123.6 (CH_{ar}), 120.5 (CH_{ar}).
IR (neat): $\bar{\nu}$ (cm^{-1}) = 2137 (m), 2106 (m), 1504, 1471, 1304, 1240, 1034, 1022, 808, 760 (st).
ESI-HRMS: calcd. for $C_{14}H_{11}N_6$ $[M+H]^+$ 263.1039, found 263.1051.

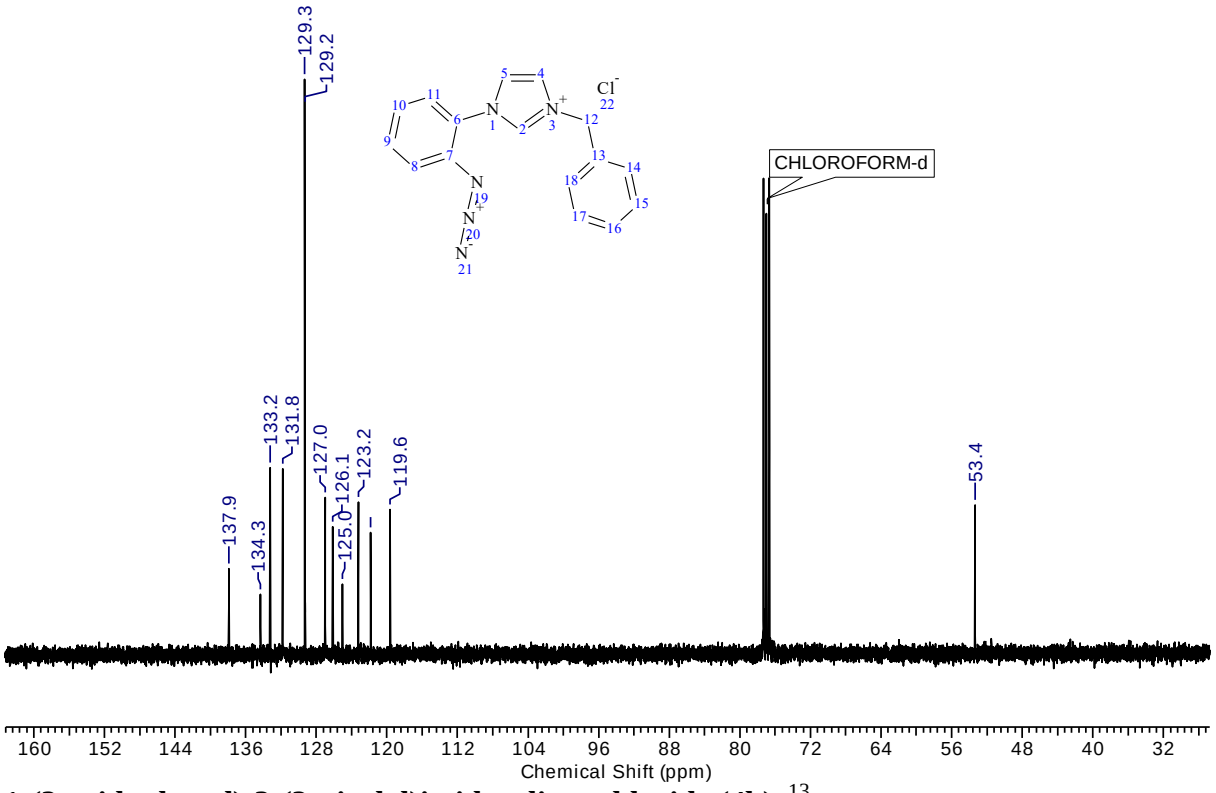
SI 3- Preparation of azolium salts

1-(2-azidophenyl)-3-benzylimidazolium chloride (4a)
1-(2-azidophenyl)imidazole (2.69 g, 14.5 mmol) was dissolved in 15 mL acetonitrile in an Ace Tube Pressure. Benzyl chloride (2.0 mL, 17 mmol) was added. The mixture was heated at 80°C overnight. When cooling down to RT, a solid precipitated. The mixture was filtered and the product was washed with acetone to afford 4.038 g (89% yield) of a light brown solid.

^{1}H NMR ($CDCl_3$): δ = 11.05 (s, 1H, H_{im}), 7.75 (d, 1H, *J* = 8.2 Hz, H_{ar}), 7.62-7.54 (m, 3H, H_{ar}), 7.48 (s, 1H, H_{im}), 7.44 (s, 1H, H_{im}), 7.41-7.35 (m, 3H, H_{ar}), 7.33 (d, 2H, *J* = 7.7 Hz, H_{ar}), 5.87 (s, 2H, CH_2),
^{13}C NMR ($CDCl_3$): δ = 137.9 (CH_{im}), 134.3 (C_q), 133.2 (C_q), 131.8 (CH_{ar}), 129.3 (CH_{ar})[12], 129.2 (CH_{ar}), 127.0 (CH_{ar}), 126.1 (CH_{ar}), 125.0 (C_q), 123.2 (CH_{im}), 121.8 (CH_{im}), 119.6 (CH_{ar}), 53.4 (CH_2).
ESI-HRMS: calcd for $C_{16}H_{14}N_5^+$ $[M]^+$ 276.1244, found: 276.1260.
IR (neat): $\bar{\nu}$ (cm^{-1}) = 2145 (st), 1546, 1501, 145,, 1306, 1215, 762, 708.
EA: calcd. for $C_{16}H_{14}ClN_5$ + $1H_2O$ (%): C, 58.27; H: 4.89; N, 21.24. Found C, 58.86; H, 4.79; N, 21.25.

[11] Inspired from published azidation conditions: H. Jian, J. M. Tour, *J. Org. Chem.*, **2003**, *68*, 5091-5103.
[12] Two signals were overlapped.



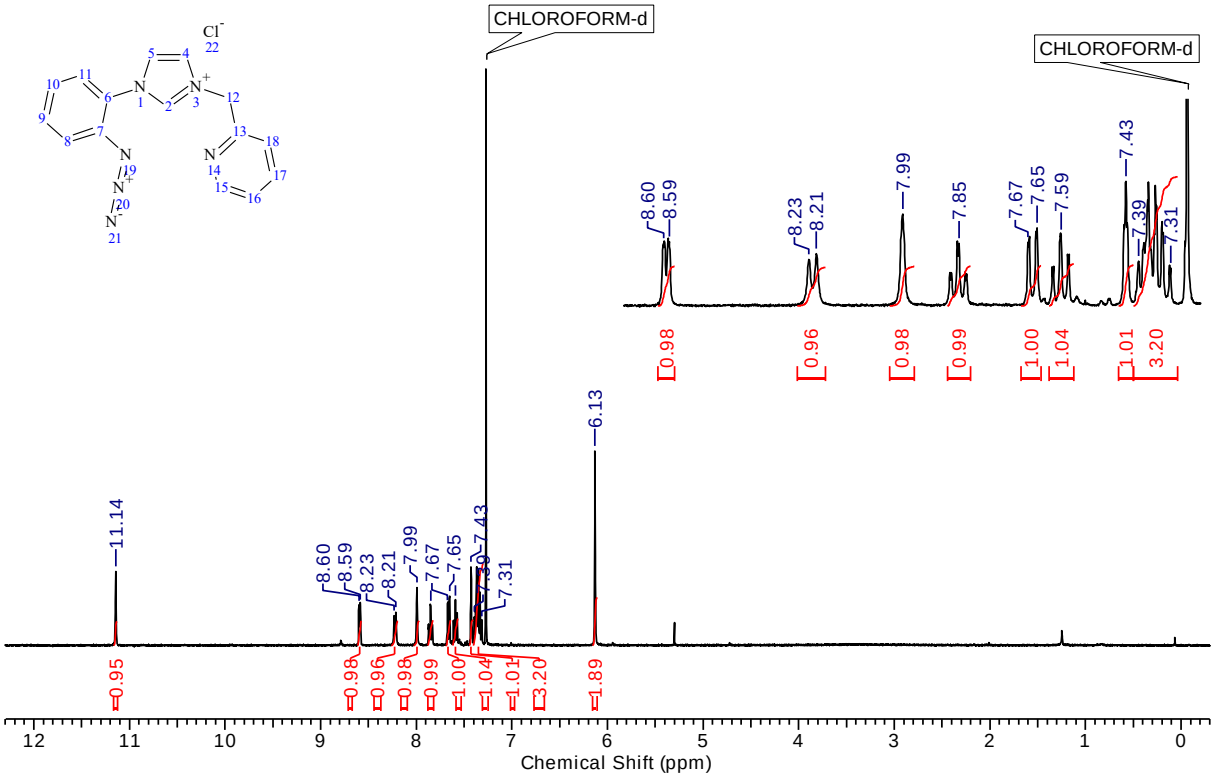


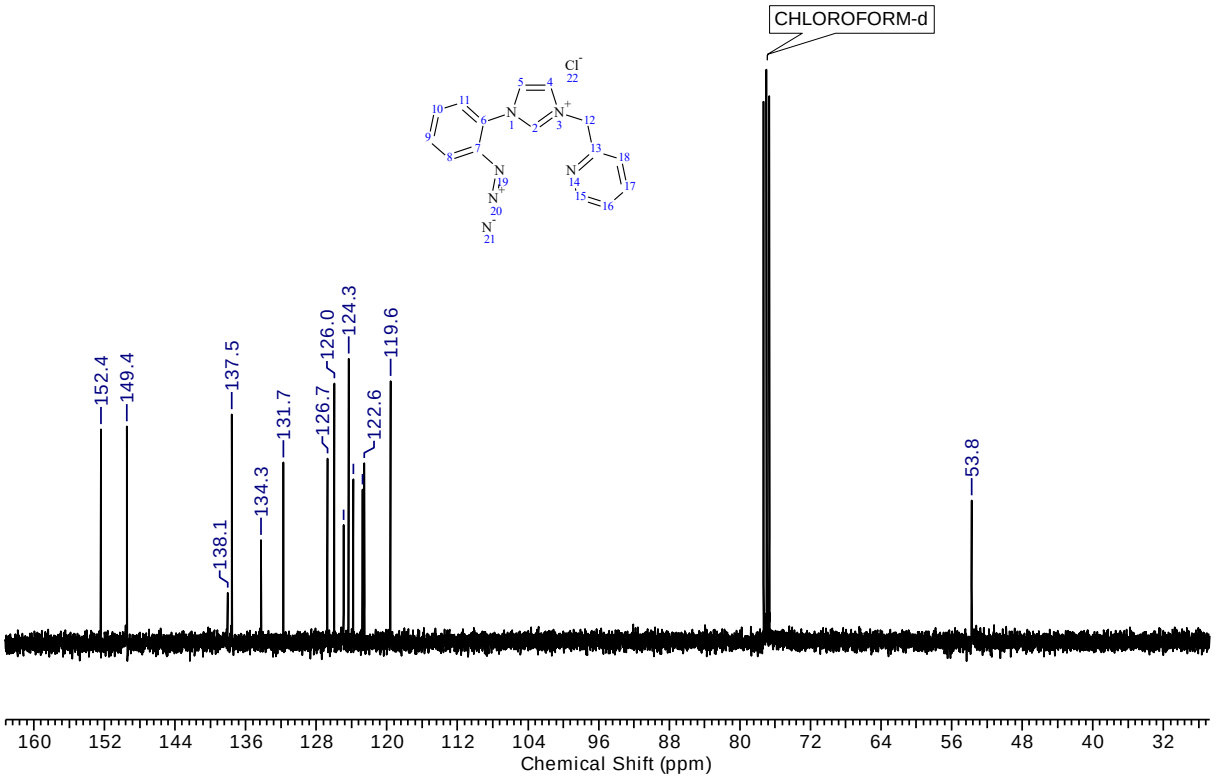
1-(2-azidophenyl)-3-(2-picolyl)imidazolium chloride (4b): [13]
2-picolyl chloride hydrochloride (2.21 g, 13.5 mmol) was dissolved in 20 mL of acetonitrile. Solid Na_2CO_3 was added until neutralization. The reaction flask was charged with 1-(2-azidophenyl)imidazole (2.24 g, 12.1 mmol). The solution containing 2-picolyl chloride was

[13] Protocol adapted from: F. Cisnetti, P. Lemoine, M. El-Ghozzi, D. Avignant, A. Gautier, *Tetrahedron Lett.* **2010**, *51*, 5226

filtered through cotton directly in the flask. 10 mL of acetonitrile were used to rinse the glassware and added similarly. The mixture was refluxed overnight, then the solvents were evaporated under reduce pressure. The brown oil was triturated with acetone until a beige solid formed. It was filtered and washed with acetone to yield a beige solid (m = 2.89 g, 74% yield).

^{1}H NMR ($CDCl_3$): δ = 11.14 (s, 1H, H_{im}), 8.60 (dd, 1H, J_1 = 5.0 Hz, J_2 = 1.1 Hz, $H_{py,}$), 8.22 (d, 1H, J = 7.7 Hz, H_{ar}), 7.99 (s, 1H, H_{im}), 7.85 (td, 1H, J_1 = 7.7 Hz, J_2 = 1.8 Hz, H_{py}), 7.66 (dd, 1H, J_1 = 8.1 Hz, J_2 = 1.5 Hz, H_{py}), 7.59 (td, 1H, J_1 = 8.1 Hz, J_2 = 1.5 Hz, H_{py}), 7.43 (t, 1H, J = 1.5 Hz, H_{im}), 7.39-7.31 (m, 3H, H_{ar}), 6.13 (s, 2H, CH_2),
^{13}C NMR ($CDCl_3$): δ = 152.4 (CH_{im}), 149.4 (CH_{pic}), 138.1 (Cq_{pic}), 137.5 (CH_{pic}), 134.3 (Cq_{ar}), 131.7 (CH_{ar}), 126.7 (CH_{ar}), 126.0 (CH_{ar}), 124.9 (Cq_{ar}), 124.3 (CH_{pic}), 123.8 (CH_{pic}), 122.7 (CH_{im}), 122.6 (CH_{im}), 119.6 (CH_{ar}), 53.8 (CH_2).
IR (neat): $\bar{\nu}$ (cm^{-1}) = 2141 (st), 1546, 1500, 1304, 1215, 756.
ESI-HRMS: calcd. for $C_{15}H_{13}N_6$ $[M]^+$ 277.1196, found: 277.1202.
EA: calcd. for $C_{15}H_{13}ClN_6$ (%): C, 57.60; H, 4.19; N, 26.87. Found C, 57.49; H, 4.18; N, 26.32.

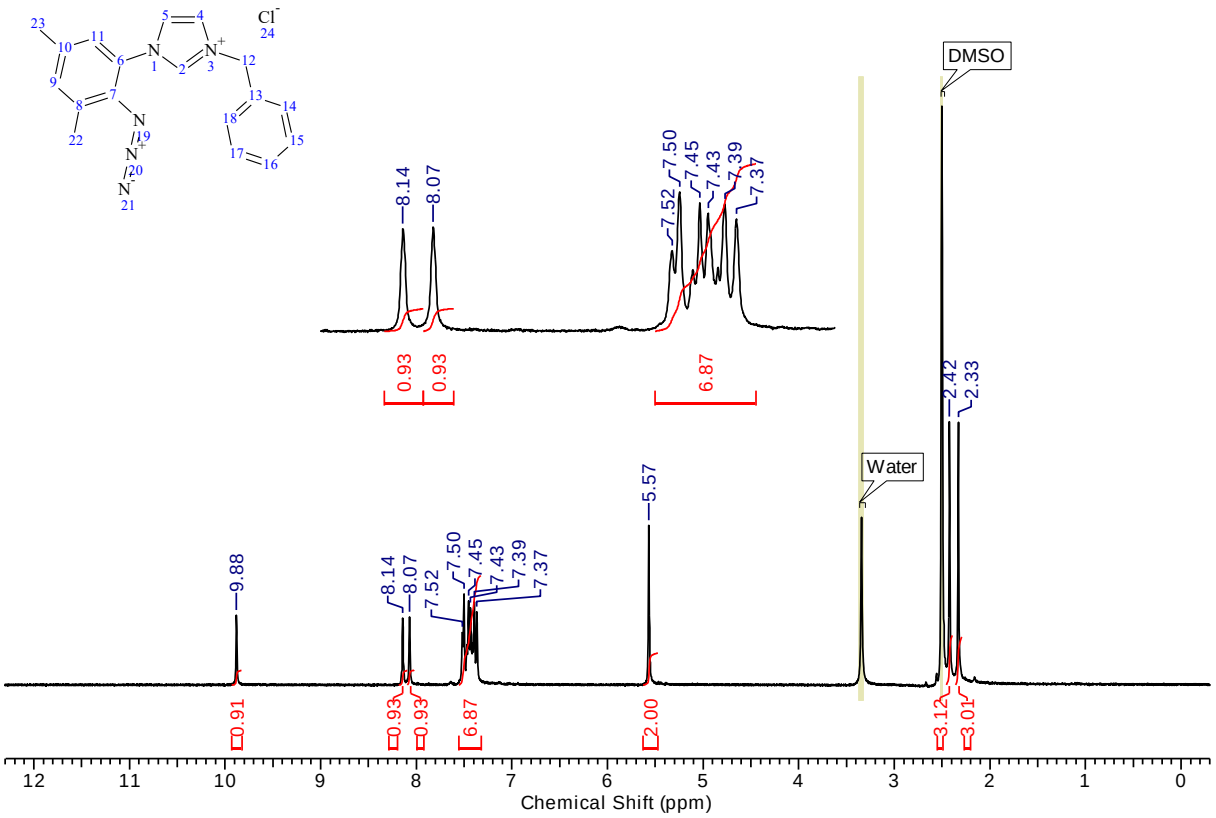


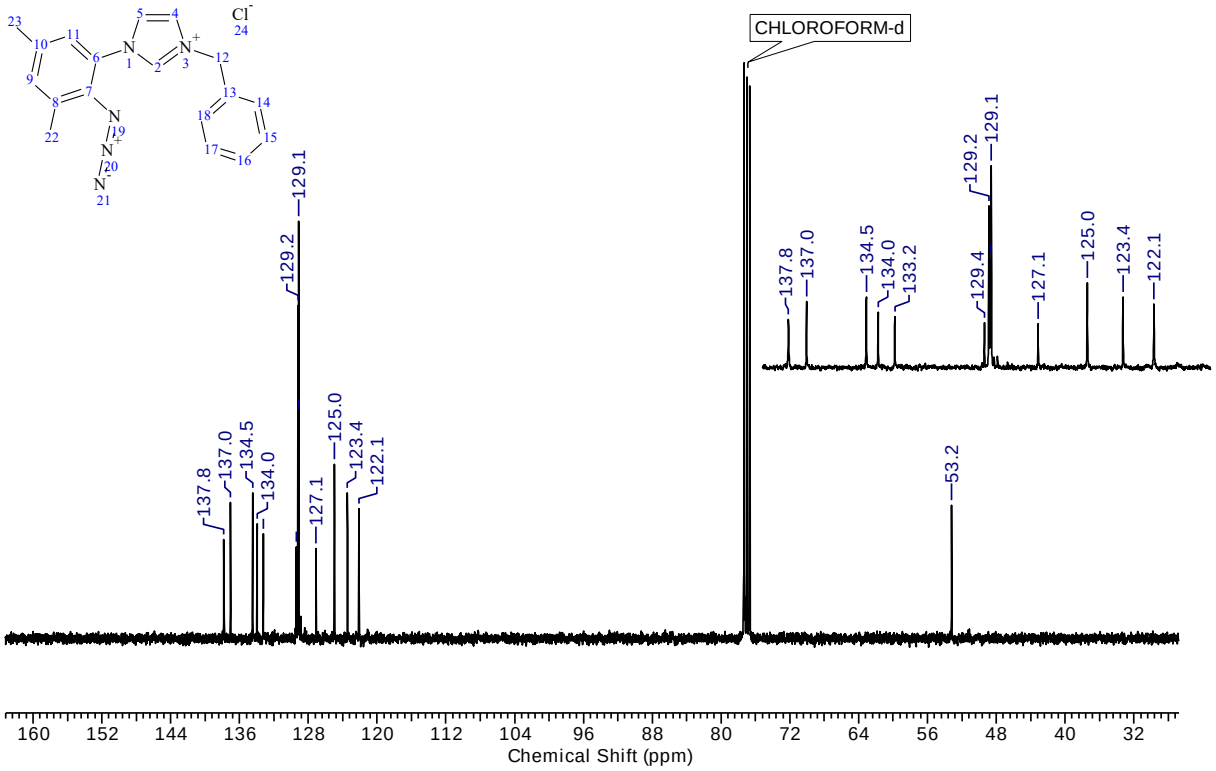


1-(2-azido-3,5-dimethylphenyl)-3-benzylimidazolium chloride (4c):
1-(2-azido-3,5-dimethylphenyl)imidazole (1.31 g, 6.14 mmol) was dissolved in acetonitrile (8 mL) and introduced in an Ace pressure tube. Benzyl chloride (780 µL, 6.67 mmol) was added and the resulting solution stirred overnight at 80°C. The solvent was evaporated. Trituration with 15 mL ether/ethanol (v/v 19:1) of the resulting oil furnishes a brownish solid. The solution was kept in a freezer overnight, filtered, washed with the same cold solvent mixture, then with diethyl ether to afford 1.96 g (74% yield) of a light brown solid.

^{1}H NMR (DMSO-d_6): 11.14 (s, 1H, H_{im}), [8.14 (s, 1H), 8.07 (s, 1H), (H_{im}, H_{ar})], 7.52-7.37 (m, 7H, H_{ar}, H_{im}), 5.57 (s, 2H, CH_2), 2.42 (s, 3H, CH_3), 2.33 (s, 3H, CH_3).
^{13}C NMR ($CDCl_3$): 137.8 ($C2_{im}$), 137.0 (C_q), 134.5 (CH_{ar}), 134.0 (C_q), 133.2 (CH_{ar}), 129.4 (C_q), [129.4, 129.2, 129.1 (CH_{ar})][14], 127.1 (C_q), 125.0 (CH_{ar}), 123.4 (C_{im}), 122.1 (C_{im}), 53.2 (CH_2), 20.4 (CH_3), 17.8 (CH_3).
IR (neat): $\bar{\nu}$ (cm^{-1}) = 2135, 1546, 1489, 1325, 1136, 868, 779.
ESI-HRMS: calcd. for $C_{18}H_{18}N_5$ $[M]^+$ 304.1557, found 304.1555
EA : calcd. for $C_{18}H_{18}N_5Cl$ + $1H_2O$ (%): C, 60.42; H, 5.63; N, 19.57. Found C, 60.32; H, 5.35; N, 19.66.

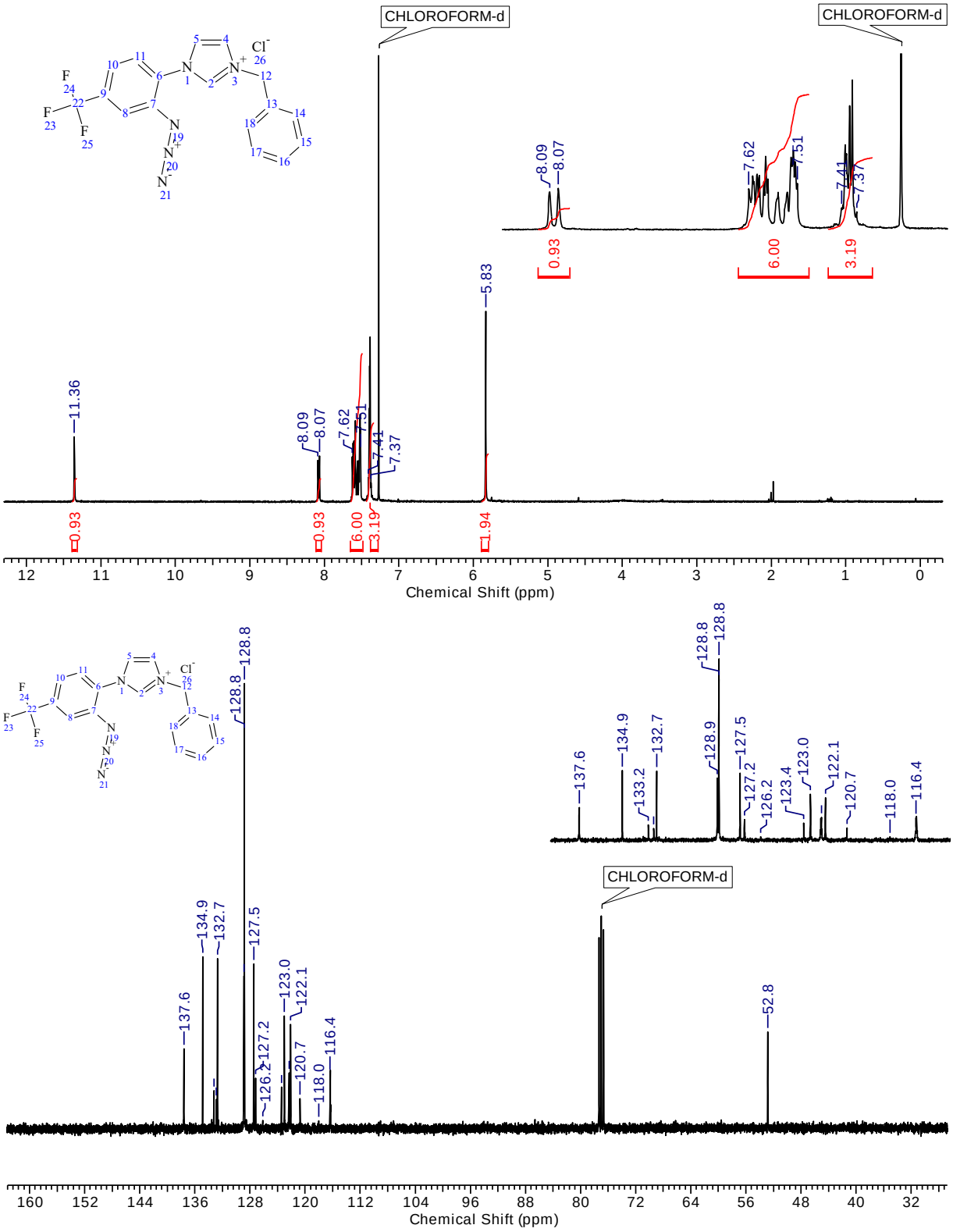
[14] Benzyl aromatic signals partly overlayed.





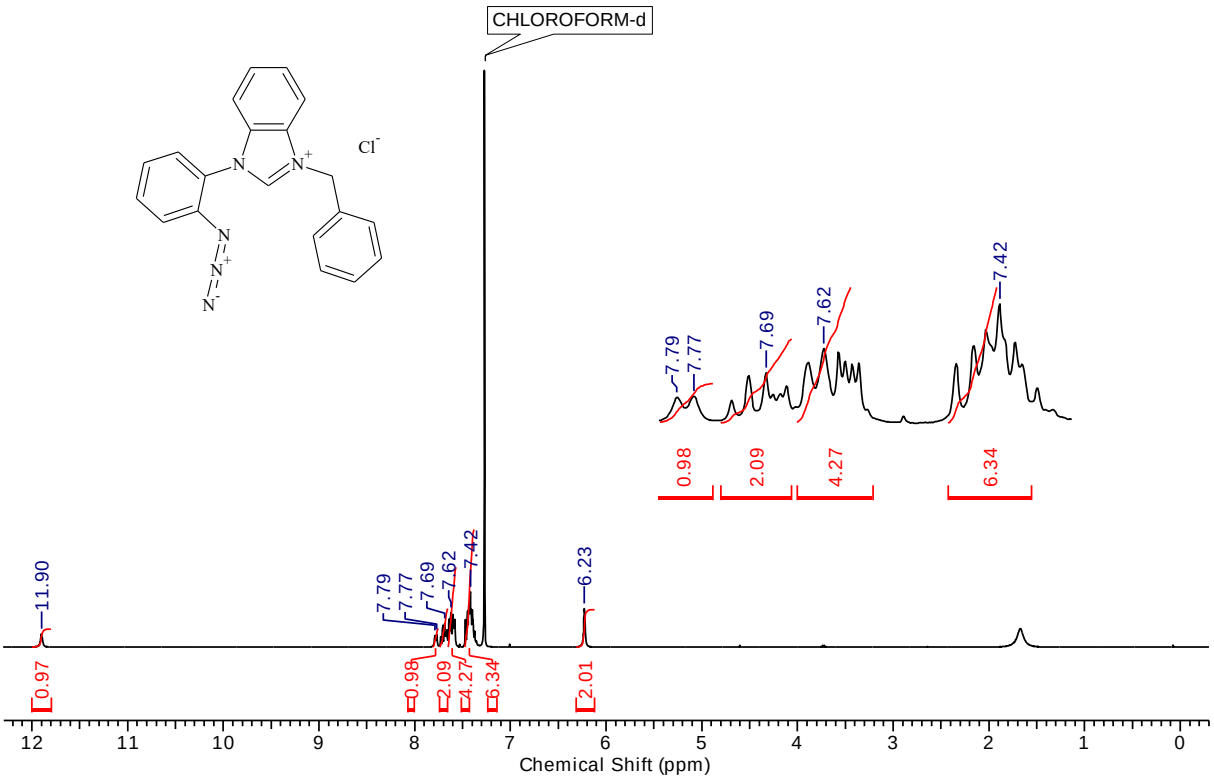
1-(2-azido-4-(trifluoromethyl)phenyl)-3-benzylimidazolium chloride (4d):
1-(2-azido-4-(trifluoromethyl)phenyl)imidazole (250 mg, 0.987 mmol) and benzyl chloride (140 µL, 1.22 mmol) were dissolved in acetonitrile (1 mL) in an Ace pressure tube. The mixture was stirred at 80°C overnight and the solvents evaporated under reduced pressure. The orange residue was triturated in ether to give a yellow solid (m = 332 mg, yield = 89%).

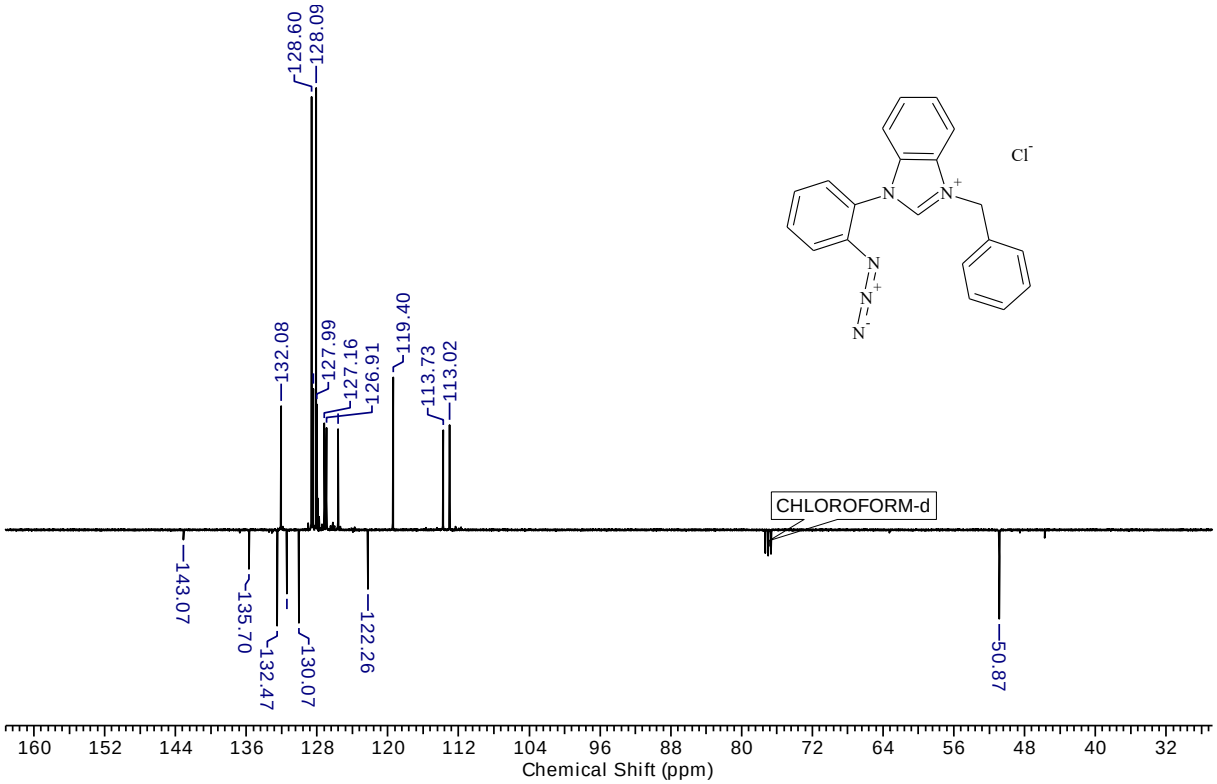
^{1}H NMR ($CDCl_3$): δ = 11.36 (s, 1H, H_{im}), 8.08 (d, 1H, *J* = 8.1 Hz, H_{ar}), 7.62-7.51 (m, 6H), 7.41-7.37 (m, 3H), 5.83 (s, 2H, CH_2).
^{13}C NMR ($CDCl_3$): δ = 137.6 (CH_{im}), 134.9 (Cq), 133.2 (q, $^{2}J_{C\text{-}F}$ = 33.7 Hz, C-CF_3), 132.7 (Cq), 128.9 (CH_{ar}), 128.8 (CH_{ar}), 127.5 (CH_{ar}), 127.2 (Cq), 123.0 (CH_{im}), 122.3 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz, CH_{ar}), 122.1 (CH_{im}), 122.1 (q, $^{1}J_{C\text{-}F}$ = 273.7 Hz, CF_3), 116.4 (q, $^{3}J_{C\text{-}F}$ = 3.8 Hz, CH_{ar}), 52.8 (CH_2).
IR (neat): $\bar{\nu}$ (cm^{-1}) = 2127 (st), 1548, 1433, 1331, 1280, 1132.
ESI-HRMS: calcd. for $C_{17}H_{13}N_5F_3$ $[M]^+$ 344.1129, found: 344.1123.
EA: calcd. for $C_{17}H_{13}ClN_5F_3$ (%): C, 53.77; H, 3.45; N, 18.44. Found C, 53.56; H, 3.34; N, 18.09.



1-(2-azidophenyl)-3-benzylbenzimidazolium chloride (4e):
1-(2-azidophenyl)benzimidazole (470 mg, 2.00 mmol) was dissolved in MeCN (8 mL) in an Ace pressure tube. Benzyl chloride (506 mg, 4.00 mmol) was added. The solution was stirred 24 h at 85°C. Evaporation and elimination of volatiles under high vacuum for 24 h affords a viscous oil. The latter was triturated several times in ethyl acetate to obtain a viscous brown solid (m = 514 mg, yield =71%).

^{1}H NMR ($CDCl_3$): δ = 11.90 (s, 1H), 7.78 (d, 1H, *J* = 7.8 Hz), 7.73-7.66 (m, 2H), 7.64-7.58 (m, 4H), 7.47-7.38 (m, 6H), 6.23 (s, 2H).
^{13}C NMR ($CDCl_3$): δ = 143.1(C_{Im}), 135.7 (Cq), 132.5 (Cq), 132.1 (CH), 131.5 (Cq), 130.1 (Cq), 128.6 (CH), 128.5 (CH), 128.1 (CH), 128.0 (CH), 127.2 (CH), 127.0 (CH), 125.7 (CH), 122.3 (Cq), 119.4 (CH), 113.8 (CH), 113.1 (CH), 50.9 (CH_2).
IR (neat): $\bar{\nu}$ (cm^{-1}) = 2136 (st), 1553, 1498, 1474, 1456, 1413, 1301, 750.
ESI-HRMS: calcd. for $C_{20}H_{16}ClN_5$ $[M]^+$ 326.1400, found 326.1404.
EA: calcd. for $C_{10}H_{16}ClN_5$ (%): C, 66.39; H, 4.46; N, 19.36. Found C, 66.56; H, 4.70; N, 19.12.





1-(2-azidophenyl)-3-ethylimidazolium bromide (4f):

1-(2-azidophenyl)-imidazole (370 mg, 2.00 mmol) was dissolved in THF (2 mL) in an Ace Tube Pressure. Ethyl bromide (164 µL, 2.20 mmol) was added. The mixture was heated at 90°C for 24 h. A brownish oil separated. The solvent was removed by evaporation. The oil was washed with *n*-pentane (5 mL), then taken up in chloroform (5 mL). Solvent evaporation under reduced pressure gave the product as a solid (m = 563 mg, yield = 92%).

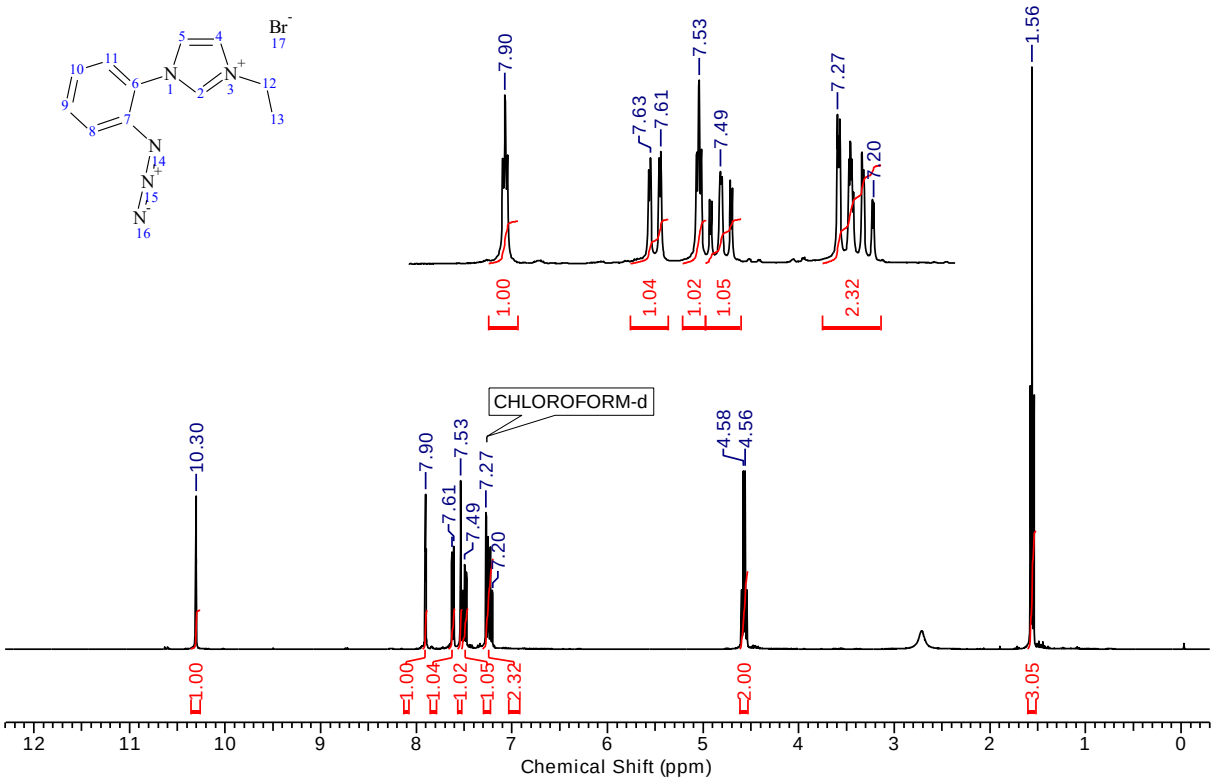
^{1}H NMR ($CDCl_3$): δ = 10.30 (s, 1H, H_{im}), 7.90 (t, 1H, J = 1.8 Hz, H_{im}), 7.62 (dd, 1H, J_1 = 8.1 Hz, J_2 = 1.5 Hz, H_{ar}), 7.53 (t, 1H, J = 1.8 Hz, H_{im}), 7.49 (td, 1H, J_1 = 8.1 Hz, J_2 = 1.5 Hz, $H_{ar)}$, 7.27-7.20 (m, 2H, H_{ar}), 4.66 (q, 2H, J = 7.3 Hz, CH_2), 1.63 (t, 3H, J = 7.3 Hz, CH_3),

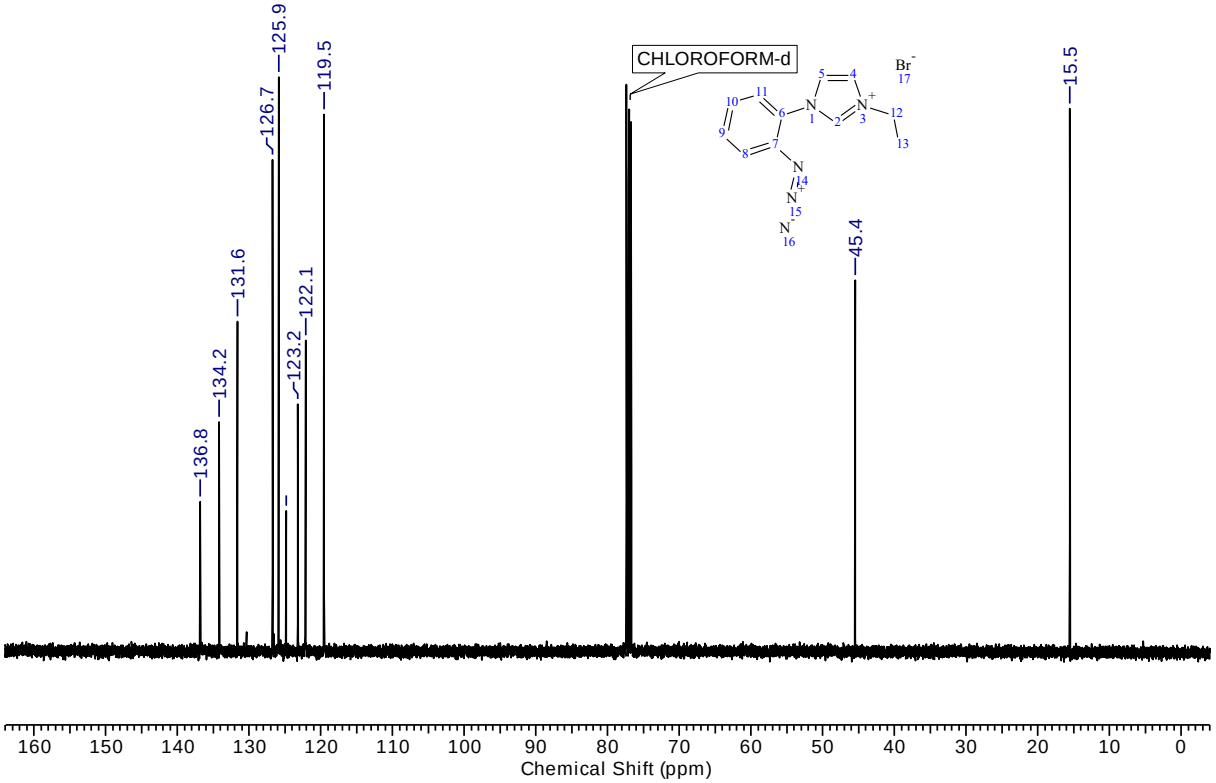
^{13}C NMR ($CDCl_3$): δ = 136.8 (CH_{im}), 134.2 (Cq), 131.6 (CH_{ar}), 126.7 (CH_{ar}), 125.9 (CH_{ar}), 124.8 (Cq), 123.2 (CH_{im}), 122.1 (CH_{im}), 119.5 (CH_{ar}), 45.4 (CH_2CH_3), 15.5 (CH_2CH_3).

IR (neat): $\bar{\nu}$ (cm^{-1}) = 2120 (st), 1510, 1320, 840, 760

ESI-HRMS: calcd for $C_{11}H_{12}N_5$ $[M]^+$ 214.1087, found: 214.1089.

EA: calcd. for $C_{11}H_{12}BrN_5$ + ⅓H_2O (%): C, 44.02; H, 4.25; N, 23.33. Found C, 44.01; H, 4.35; N, 22.86.

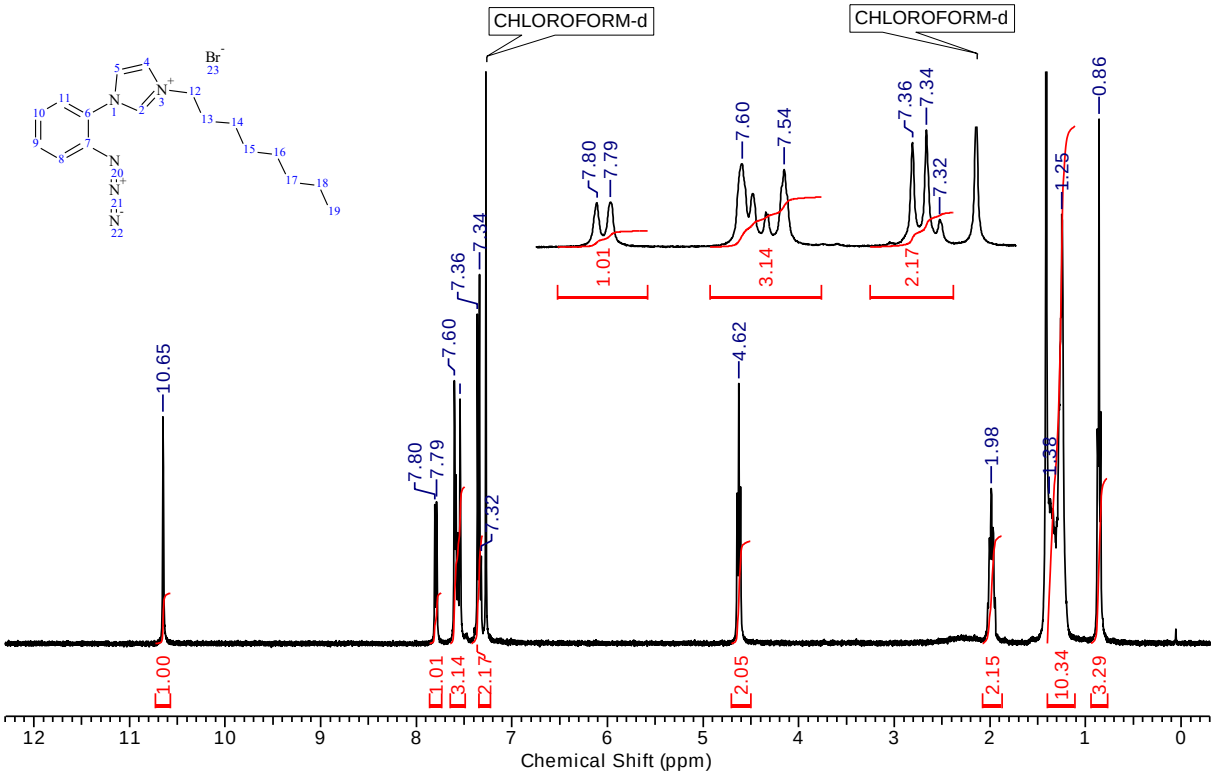




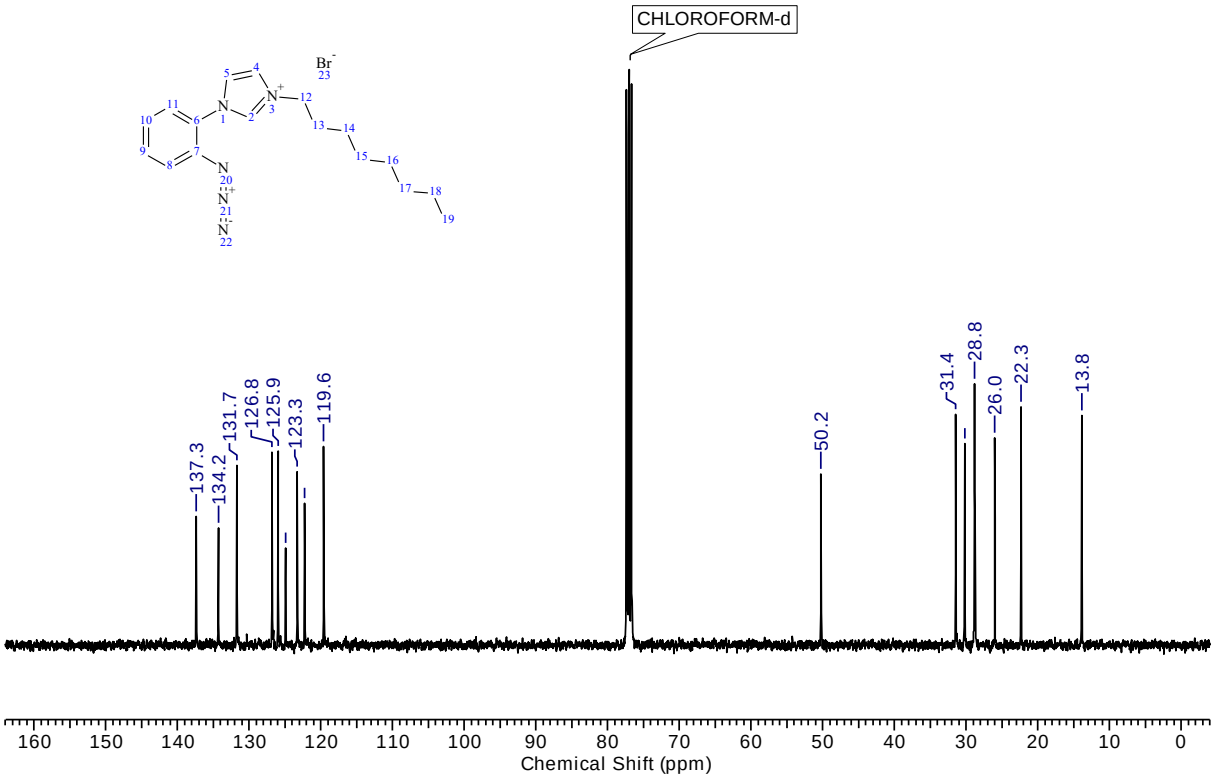
1-(2-azidophenyl)-3-octylimidazolium bromide (4g):

1-(2-azidophenyl)imidazole (1.11 g, 5.99 mmol) was dissolved in THF (6 mL) in an Ace pressure tube. 1-bromooctane (1.15 mL, 6.66 mmol) was added. The reaction mixture was stirred at 90°C during 36 h. The resulting solution was cooled in an ice-water bath. After 4 h, a thick paste deposited. 8 mL of cyclohexane were added to afford a solid, which was isolated by filtration. 1.603 g (72% yield) of a beige solid were obtained.

^{1}H NMR ($CDCl_3$): δ = 10.65 (s, 1H, H_{im}), 7.80 (d, 1H, *J* = 7.7 Hz, H_{ar}), 7.60-7.54 (m, 3H, H_{ar} + H_{im}), 7.34 (m, 2H, H_{ar}+H_{im}), 4.62 (t, 2H, *J* = 7.3 Hz, CH_2), 1.98 (qt, 2H, *J* = 7.3 Hz, CH_2), 1.38-1.25 (m, 10H, CH_2)[15], 0.86 (t, 3H, *J* = 7.3 Hz, CH_3).
^{13}C NMR ($CDCl_3$): δ = 137.3 ($C2_{Im}$), 134.2 (Cq), 131.7 (CH_{ar}), 126.8 (CH_{ar}), 125.9 (CH_{ar}), 124.9 (Cq), 123.3(CH_{im}), 122.2 (CH_{im}), 119.6 (CH_{ar}), 50.2 (CH_2), 31.4 (CH_2), 30.2 (CH_2), 28.8 (CH_2), 28.8 (CH_2), 26.0 (CH_2), 22.3 (CH_2), 13.8 (CH_3).
IR (neat): $\bar{\nu}$ (cm^{-1}) = 2918, 2128, 1545, 1499, 1300, 818, 754.
ESI-HRMS: calcd. for $C_{17}H_{24}N_5$ $[M]^+$ 280.2026, found 280.2032.
EA: calcd. for $C_{17}H_{24}BrN_5$ (%): C, 53.97; H, 6.39; N, 18.51. Found C, 53.73; H, 6.33; N, 18.63.

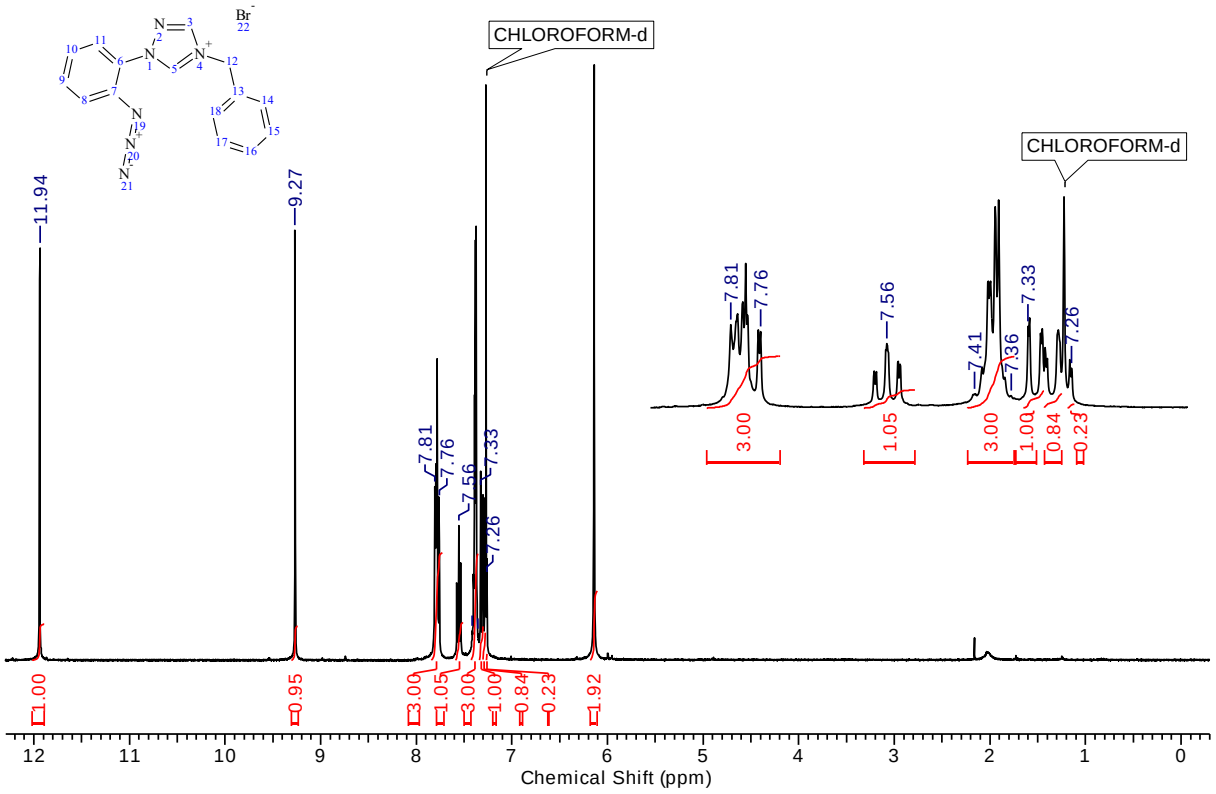


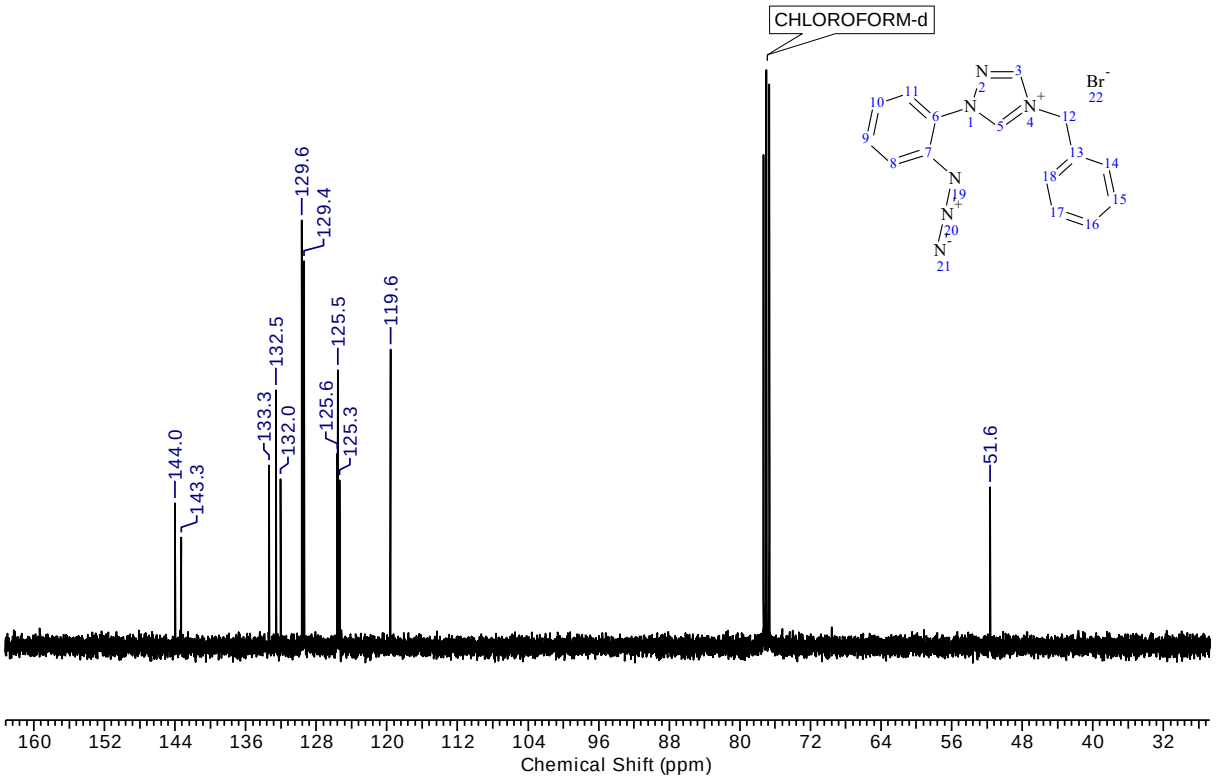
[15] Partly overlayed with the residual water signal.



1-(2-azidophenyl)-4-benzyl-1,2,4-triazolium bromide (4h):
1-(2-azidophenyl)-1,2,4-triazole (751 mg, 4.03 mmol) was dissolved in 4 mL of acetonitrile. Benzyl bromide (0.58 mL, 4.88 mmol) was added. The mixture was stirred at 80°C overnight and the solvents evaporated under reduce pressure. The residue was triturated with ether to give a brown solid (m = 1.408, yield = 98%).
^{1}H NMR ($CDCl_3$): δ = 11.94 (s, 1H, H_{triaz}), 9.27 (s, 1H, H_{triaz}), 7.81-7.76 (m, 3H, H_{ar}), 7.56 (td, 1H, J_1 = 8.1 Hz, J_2 = 1.5Hz, H_{ar}), 7.41-7.36 (m, 3H, H_{ar}), 7.33-7.26 (m, 2H, H_{ar}), 6.14 (s, 2H, CH_2).
^{13}C NMR ($CDCl_3$): δ = 144.0 (CH_{triaz}), 143.3 (CH_{triaz}), 133.3 (Cq), 132.5 (Cq), 132.0 (CH_{ar}), 129.6 (CH_{ar})[16], 129.4 (CH_{ar}), 125.6 (CH_{ar}), 125.5 (CH_{ar}), 125.3 (Cq), 119.6 (CH_{ar}), 51.6 (CH_2).
IR (neat): $\bar{\nu}$ (cm^{-1}) = 2125 (st), 1560, 1505, 1321, 1194, 959, 754.
ESI-HRMS: calcd for $C_{15}H_{13}N_6$ $[M]^+$ 277.1196, found: 277.1194.
EA: calcd. for $C_{15}H_{13}BrN_6$ (%): C, 50.44; H, 3.67; N, 23.53. Found C, 50.56; H, 3.78; N, 23.68.

[16] Two signals were overlapped





1-(2-azidophenyl)-4-ethyl-1,2,4-triazolium iodide (4i):
1-(2-azidophenyl)-1,2,4-triazole (377 mg, 2.03 mmol) and ethyl iodide (0.20 mL, 2.5 mmol) were dissolved in acetonitrile (1 mL). The mixture was heated at 80°C for 40 h. A precipitate

was formed. The liquid phase was removed and the solid was triturated with ether to furnish a yellow solid (m = 467 mg, yield = 67 %)[17].

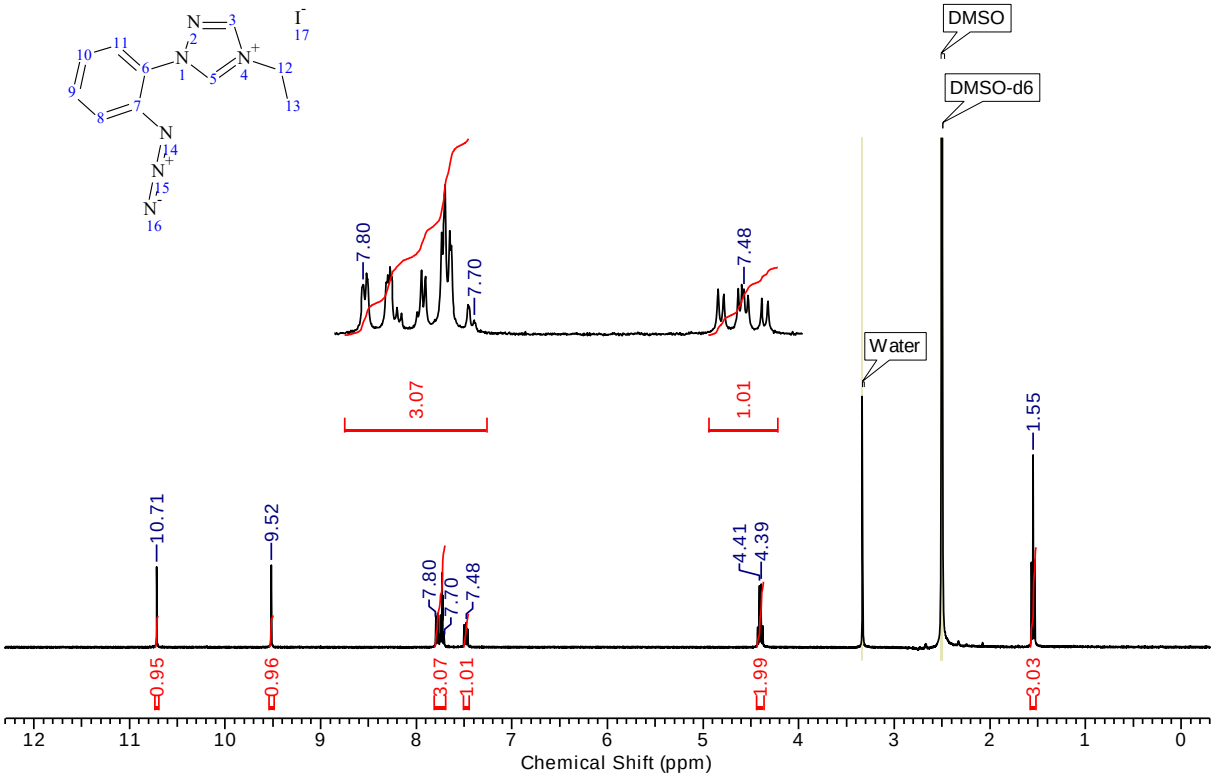
^{1}H NMR (DMSO-d_6): δ = 10.71 (s, 1H, H_{triaz}), 9.52 (s, 1H, H_{triaz}), 7.80-7.70 (m, 3H, H_{ar}), 7.48 (ddd, 1H, J_1 = 8.1 Hz, J_2 = 6.8 Hz, J_3 = 2.0 Hz, H_{ar}), 4.40 (q, 2H, J = 7.3 Hz, CH_2), 1.55 (t, 3H, J = 7.3 Hz, CH_3).

^{13}C NMR (DMSO-d_6): δ = 144.7 (CH_{triaz}), 144.1 (CH_{triaz}), 133.7 (Cq), 132.4 (CH_{ar}), 126.5 (CH_{ar}), 125.9 (CH_{ar}), 125.4 (Cq), 120.8 (CH_{ar}), 43.7 (CH_2), 14.3 (CH_3).

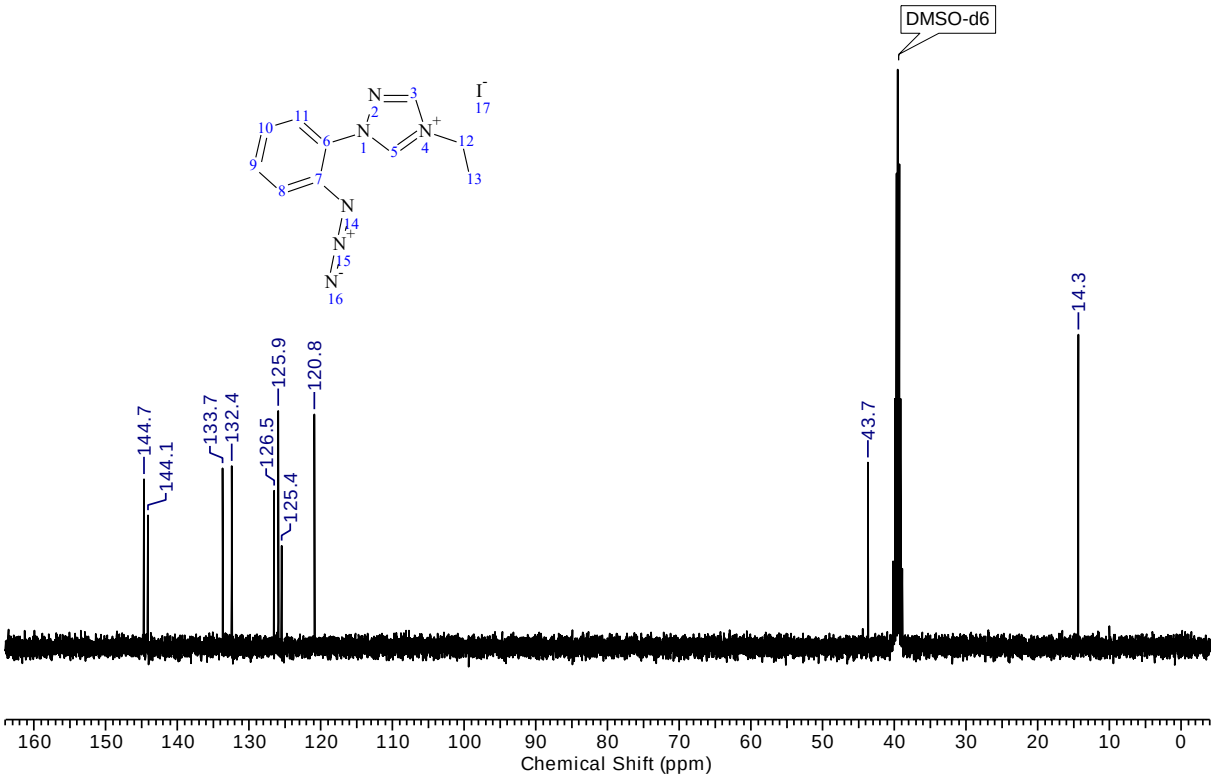
IR (neat): $\bar{\nu}$ (cm^{-1}) = 2131 (st), 1578, 1493, 1298, 1198, 968, 762.

ESI-HRMS: calcd. for $C_{10}H_{11}N_6$ $[M]^+$ 215.1040, found: 215.1038.

EA: calcd. for $C_{10}H_{11}IN_6$ (%): C, 35.10; H, 3.24; N, 24.56. Found C, 35.85; H, 3.17; N, 25.54.

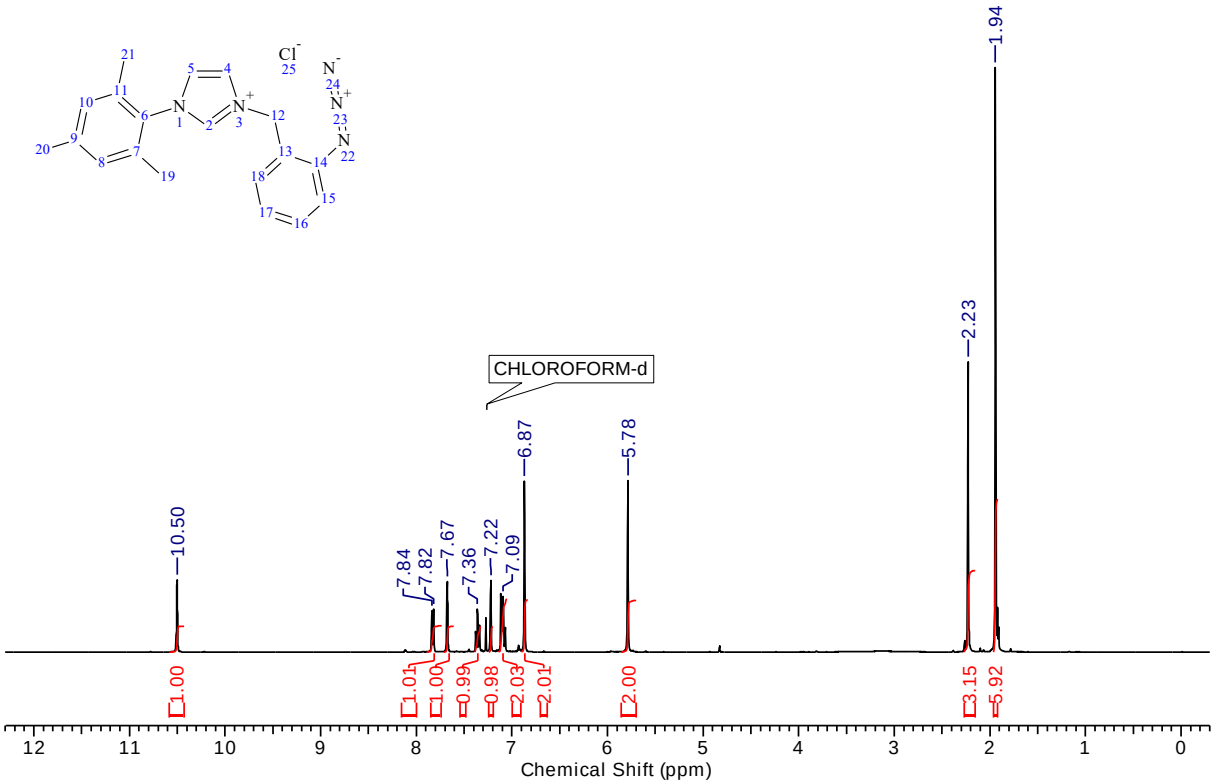


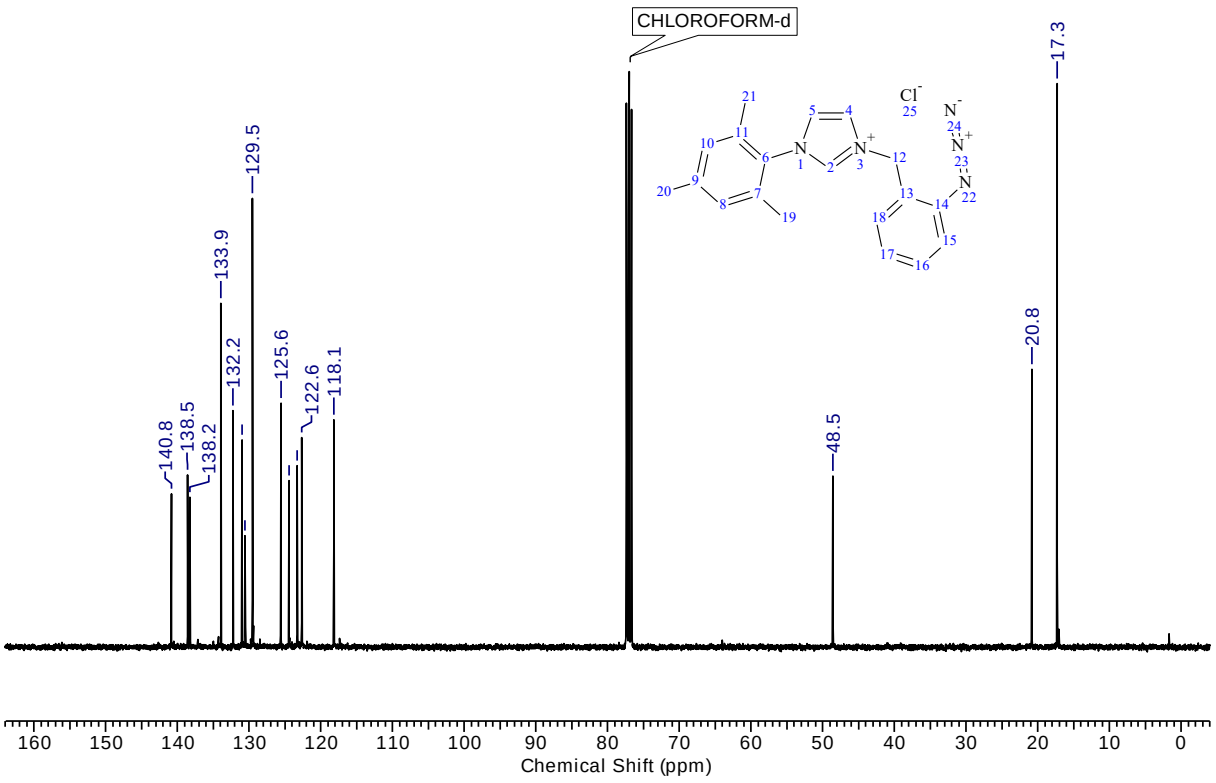
[17] Increasing the reaction time lead to a degradation of the product.



1-(2-azidobenzyl)-3-mesitylimidazolium chloride (4j):
2-azidobenzylmethanol (1.00 g, 6.75 mmol) was dissolved in 20 mL dichloromethane. Excess $SOCl_2$ (8 mL) was added dropwise while maintaining the temperature of the reaction medium with a water bath. After 30 minutes, the reaction medium was concentrated and then coevaporated with 3×20 mL cyclohexane. The resulting oil was dissolved in 10 mL acetonitrile in an Ace pressure tube. Mesitylimidazole (1.257 g, 6.75 mmol) was added and the resulting solution was heated at 80°C overnight. After cooling to RT, a solid appeared. It was triturated in 3×10 mL cyclohexane until 2.01 g (84% yield) of **4j** as a beige powder were obtained.

^{1}H NMR (DMSO-d_6): δ = 10.50 (s, 1H, H_{im}), 7.83 (d, 2H, *J* = 7.3 Hz, H_{ar}), 7.67 (bs, 1H, H_{im}), 7.36 (t, 1H, *J* = 7.5 Hz, H_{ar}), 7.22 (bs, 1H, H_{im}), 7.09 (m, 2H, H_{ar}), 6.87 (s, 2H, H_{ar}), 5.78 (s, 2H, CH_2), 2.23 (s, 3H, CH_3), 1.94 (s, 6H, CH_3) .
^{13}C NMR ($CDCl_3$): δ = 141.1 (Cq), 138.8 (Cq), 138.4 (CH_{im}), 134.1 (Cq), 132.4 (CH_{ar}), 131.2 (CH_{ar}), 130.8 (Cq), 125.8 (CH_{ar}), 124.7 (Cq), 123.5(CH_{im}), 122.8 (CH_{im}), 118.3 (CH_{ar}), 48.8 (CH_2), 21.0 (CH_3), 17.5 (CH_3).
IR (neat): $\bar{\nu}$ (cm^{-1}) = 2942, 2120 (very strong), 1562, 1541, 1495, 1283, 1213, 1165, 858, 775.
ESI-HRMS: calcd. for $C_{19}H_{20}N_4$ $[M]^+$: 318.1713, found: 318.1716
EA: calcd. for $C_{19}H_{20}ClN_5$ (%): C, 64.49; H, 5.70; N, 19.79. Found C, 64.71; H, 5.42; N, 19.56.





1-(2-azidophenyl)-3-ethyl-4-phenyl-1H-1,2,3-triazol-3-ium tetrafluoroborate (4k):
Triethyloxonium tetrafluoroborate was synthesized according a modified procedure by Meerwein.[18] $BF_3.OEt_2$ (0.65 mL, 5.18 mmol) and 12 mL of ether were introduced in a dried flask under argon. Epichlorohydrin (0.31 mL, 3.96 mmol) was added dropwise and the reaction was refluxed during 1 h, then stirred 2.5 h at room temperature during which a white

[18] Meerwein, H., *Org. Synth*. **1966**, 46, 113

solid deposited. The solvent was removed with a syringe and the solid was washed with diethyl ether (10 mL), which was eliminated similarly. The resulting white solid was dissolved in 10 mL of anh. CH_2Cl_2. 1-(2-azidophenyl)-4-phenyl-1*H*-1,2,3-triazole (575 mg, 2.19 mmol) dissolved in 10 mL of anh. CH_2Cl_2 was added dropwise to the Meerwein salt's solution and the mixture was stirred overnight. The resulting dark solution was quenched with 5 mL of absolute ethanol and evaporated to furnish a brown solid. Trituration with ethyl acetate, filtration and evaporation under high vacuum affords 553 mg (67%) of **4k** as a brownish solid.

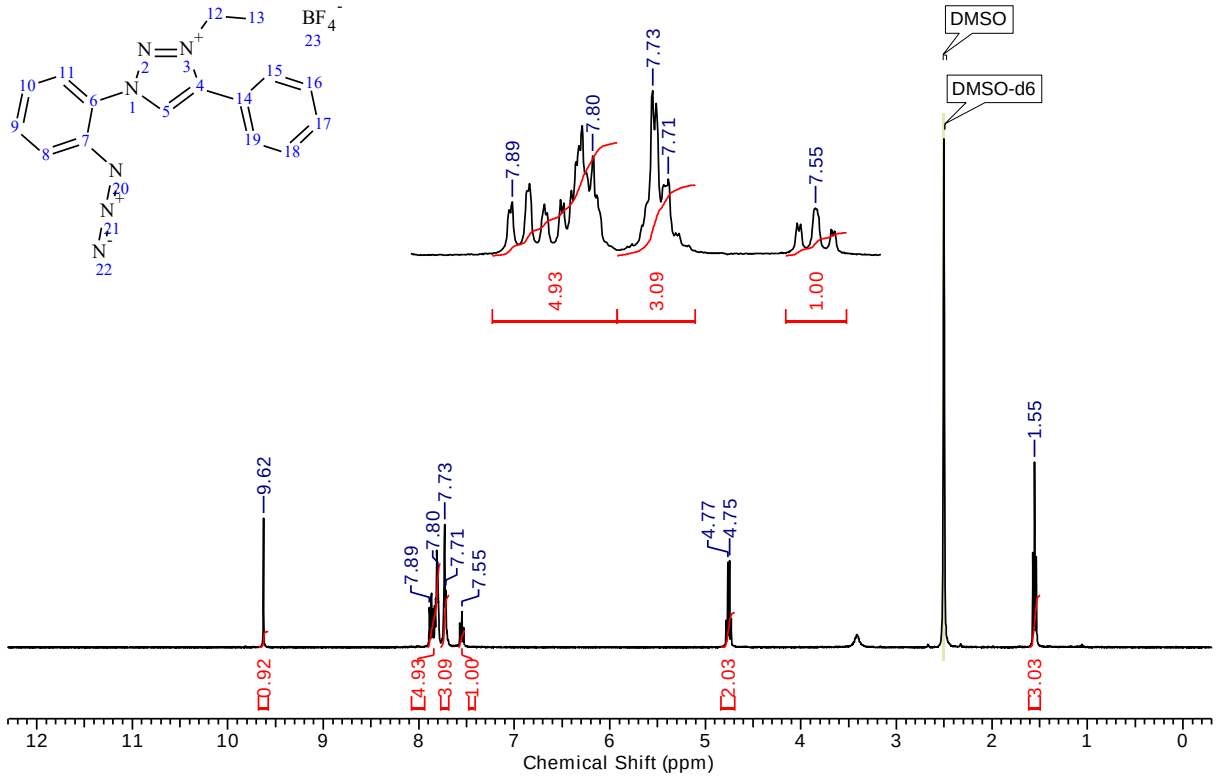
^{1}H NMR (DMSO-d_6): δ = 9.62 (s, 1H, $H_{triazole}$), 7.89-7.80 (m, 5H, H_{ar}), 7.74-7.69 (m, 3H, H_{ar}), 7.55 (td, 1H, J_1 = 8.1 Hz, J_2 = 1.5 Hz, H_{ar}), 4.76 (q, 2H, J = 7.3 Hz, CH_2), 1.55 (t, 3H, J = 7.3 Hz, CH_3).

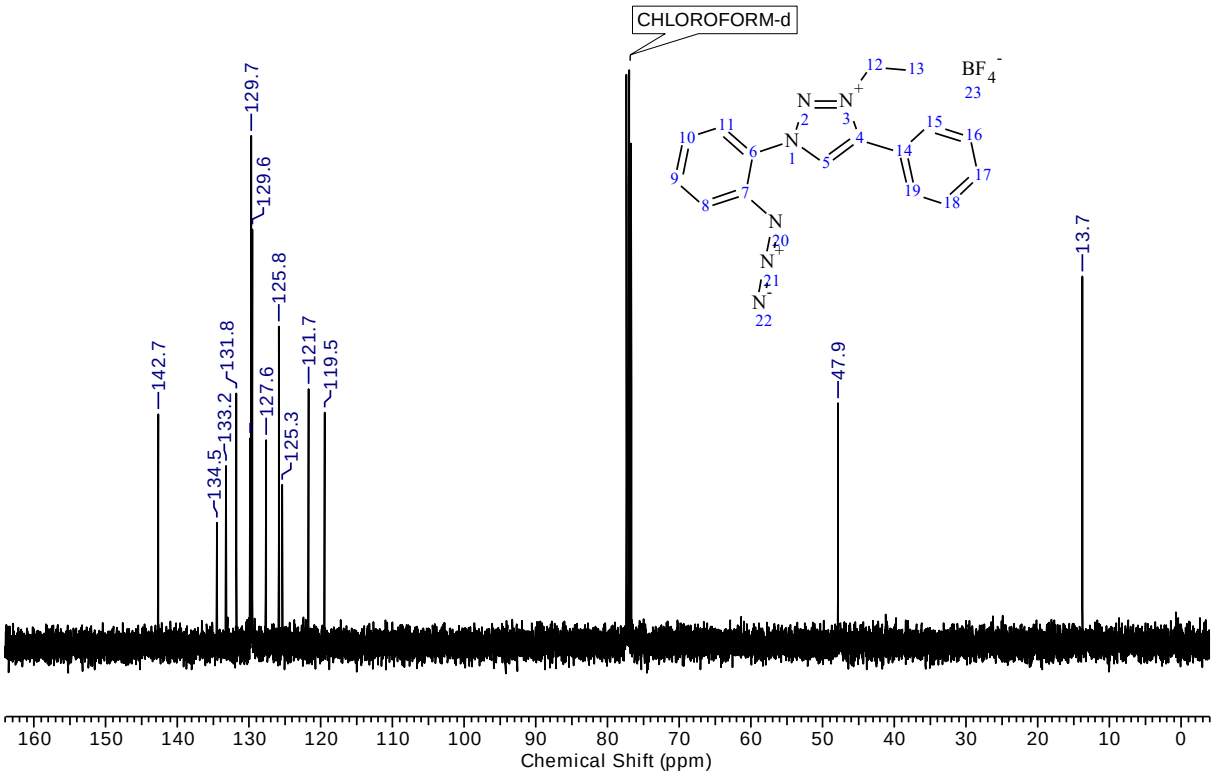
^{13}C NMR ($CDCl_3$): δ = 142.7 ($Cq_{triazole}$), 134.5 (Cq), 133.2 (CH_{ar}), 131.8 (CH_{ar}), 129.9 (CH_{ar}), 129.7 (CH_{ar}), 129.5 (CH_{ar}), 127.6 (CH_{ar}), 125.8 (CH_{ar}), 125.3 (Cq), 121.7 (Cq), 119.5 (CH_{ar}), 47.9 (CH_2), 13.7 (CH_3).

IR (neat): $\bar{\nu}$ (cm^{-1}) = 2141 (st), 1505, 1491, 1310, 1059 (very strong), 766.

ESI-HRMS: calcd. for $C_{16}H_{14}N_6$ $[M]^+$ 291.1353, found 291.1351.

EA: calcd. for $C_{16}H_{15}BF_4N_6$ (%): C, 50.82; H, 4.00; N, 22.22. Found C, 50.97; H, 4.09; N, 22.21.



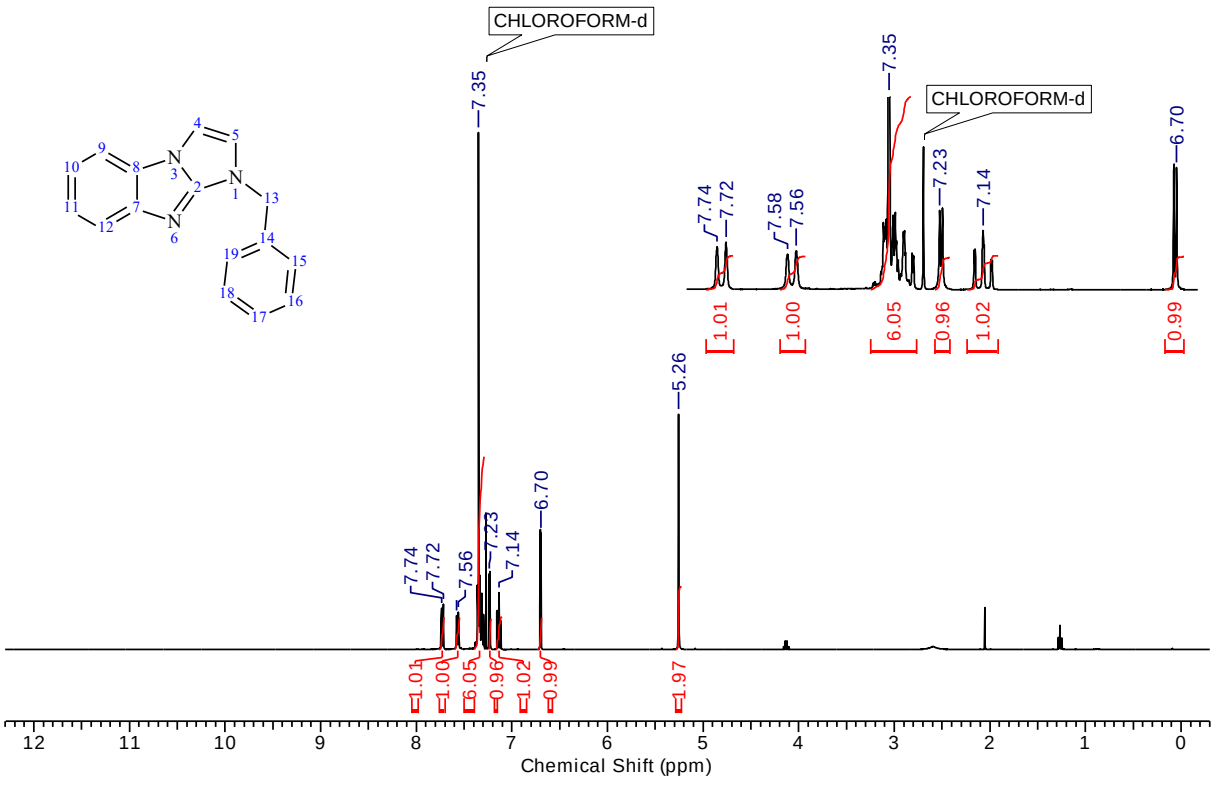

CHLOROFORM-d
142.7
134.5
133.2
131.8
129.7
129.6
127.6
125.8
125.3
121.7
119.5
47.9
13.7
BF4
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

SI 4- Cyclization reactions

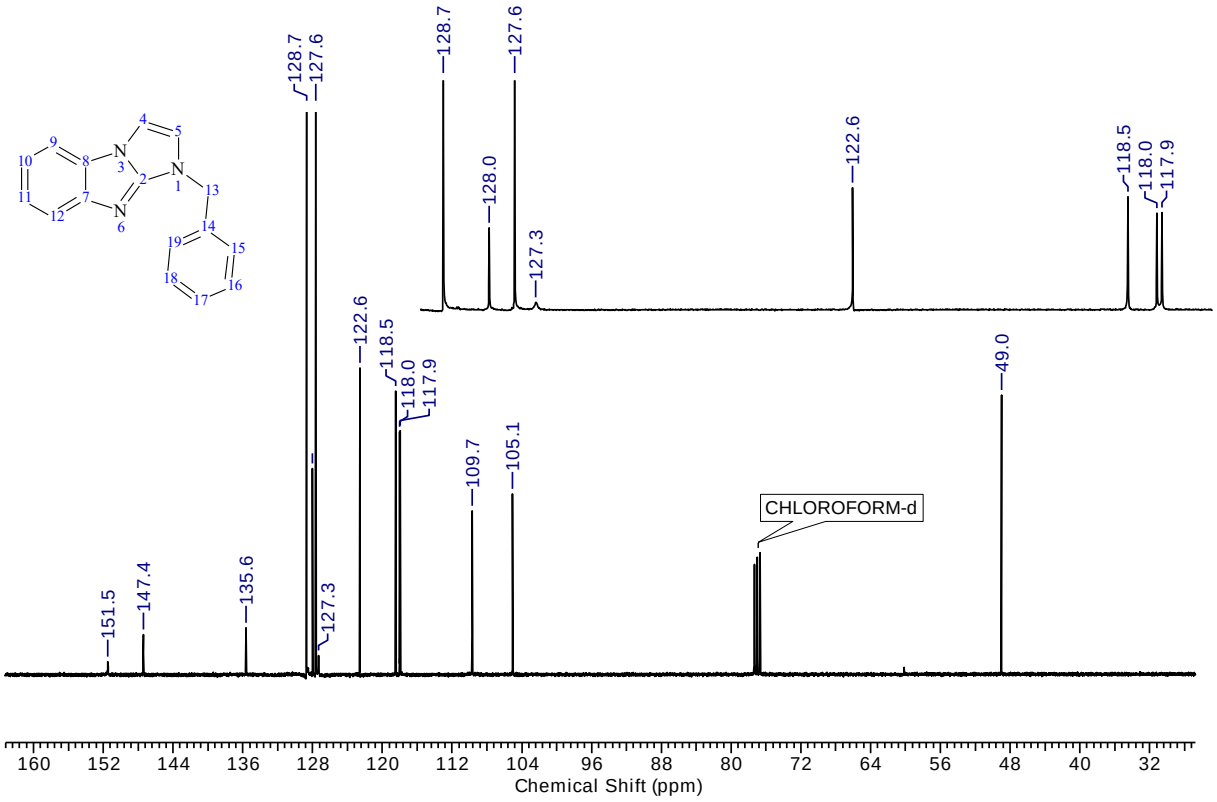
General procedure for the cyclization (CuCl-ammonia method)

The azolium salt (1.0 mmol) was dissolved in 10 mL of absolute ethanol. The mixture was degassed by argon bubbling (~ 5 min). Copper(I) chloride (9.9 mg, 0.10 mmol), followed by aqueous NH_3 (83 µL, 12 mol L^{-1}, 1.0 mmol) were added and the mixture was stirred at room temperature during 1 h (unless otherwise specified). A gaseous release was observed. After completion, the mixture was diluted with 10 mL of AcOEt and 10 mL of brine. The mixture was stirred open-flask to oxidize copper(I). The phases were separated and the aqueous layer was extracted twice with 10 mL of AcOEt. The combined organic layers were washed with 10 mL of water, dried over $MgSO_4$ and K_2CO_3 and condensed under reduced pressure to give the pure product[19].

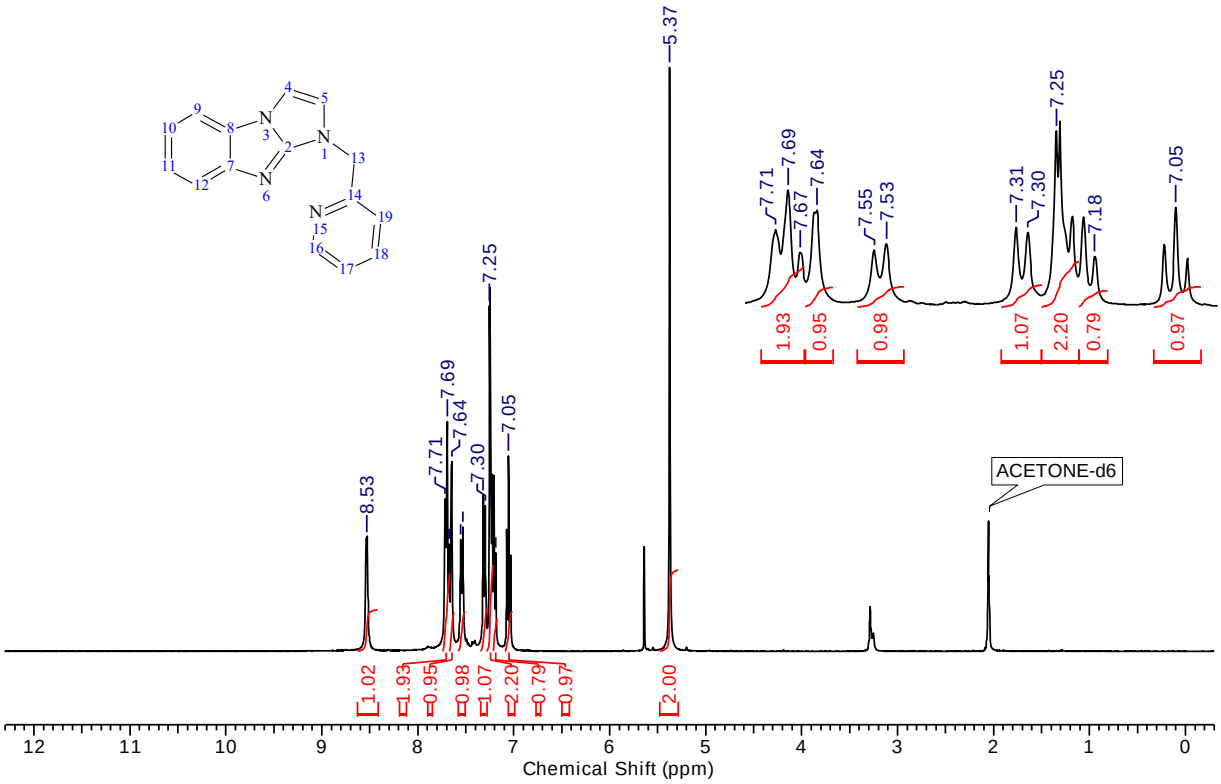
1-(2-benzyl)-benzo[d]imidazo[1,2-a]imidazole(6a): Light brown solid. Yield: 94%^{1}H NMR ($CDCl_3$): δ = 7.73 (d, 1H, *J* = 8.1 Hz, H_{ar}), 7.57 (d, 1H, *J* = 7.9 Hz, H_{ar}), 7.38-7.29 (m, 6H, H_{ar}), 7.23 (d, 1H, *J* = 2.6 Hz, $H_{imidazole}$), 7.14 (t, 1H, J_1 = 8.1 Hz, J_2 = 1.1 Hz, H_{ar}), 6.70 (d, 1H, *J* = 2.6 Hz, $H_{imidazole}$), 5.26 (s, 2H, CH_2).
^{13}C NMR ($CDCl_3$): δ = 151.5 (CN_3), 147.4 (Cq), 135.6 (Cq), 128.7 (CH_{ar}), 128.0 (CH_{ar}), 127.6 (CH_{ar}), 127.3 (Cq), 122.6 (CH_{ar}), 118.5 (CH_{im}), 118.0 (CH_{ar}), 117.9 (CH_{ar}), 109.7 (CH_{ar}), 105.1 (CH_{im}), 49.0 (CH_2).
IR (neat): $\bar{\nu}$ (cm^{-1}) = 1638, 1593, 1560, 1456, 1263, 1217, 1165, 1148, 849, 741, 716.
ESI-HRMS: calcd for $C_{16}H_{14}N_3$ $[M+H]^+$ 248.1182, found: 248.1179.
EA: calcd for $C_{16}H_{13}N_3$ + ⅓ H_2O (%): C, 75.87; H, 5.44; N, 16.59. Found C, 75.72; H, 5.45; N, 16.54.

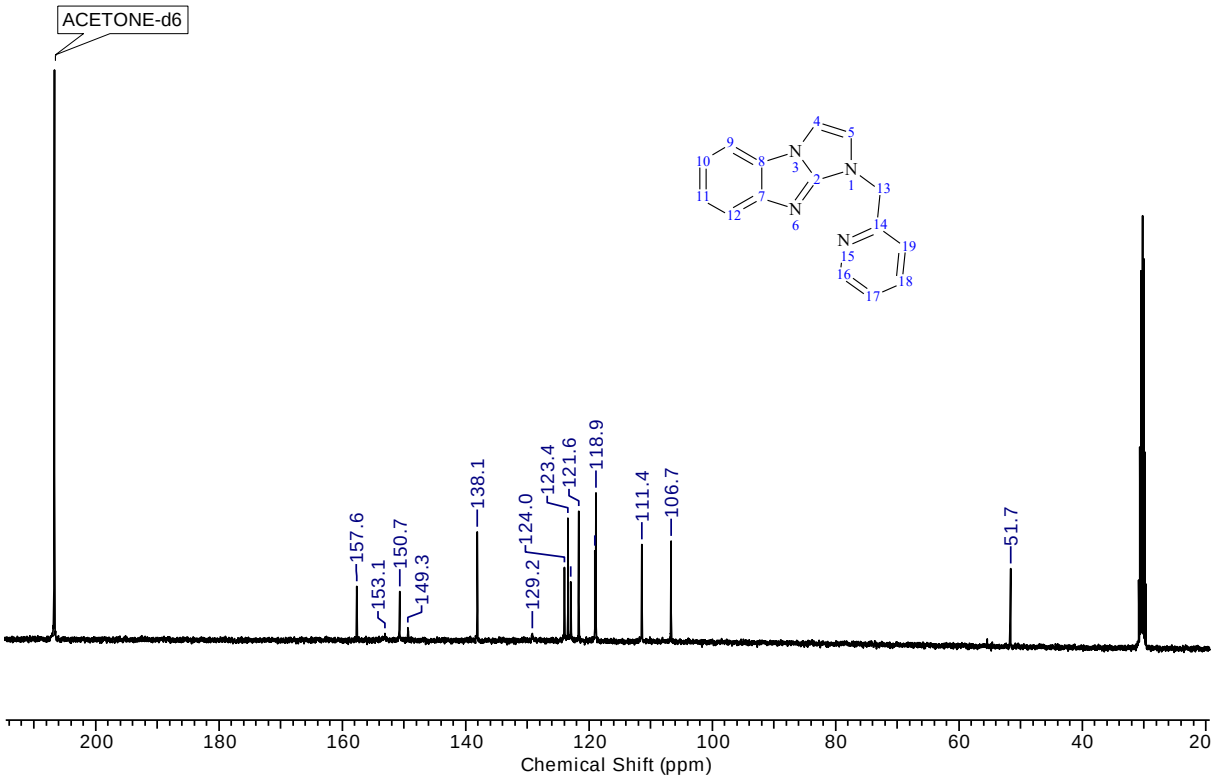


[19] If the product is contaminated with traces of copper(II), this contaminant could be easily removed by taking up the product in dichloromethane and washing with an aqueous solution of Na_2EDTA (1 mol L^{-1}).



1-(2-pycolyl)-benzo[d]imidazo[1,2-a]imidazole (6b): Brown solid. Yield: 95%.
^{1}H NMR ($(CD_3)_2CO$): δ = 8.53 (d, 1H, *J* = 3.3 Hz, H_{py}), 7.74-7.66 (m, 2H, $H_{ar + py}$), 7.65 (s, 1H, H_{im}), 7.54 (d, 1H, *J* = 8.1 Hz, H_{ar}), 7.30 (d, 1H, *J* = 7.7 Hz, $H_{py)}$, 7.27-7.17 (m, 3H, $H_{ar + py + im}$), 7.05 (t, 1H, *J* = 7.7 Hz, H_{ar}), 5.37 (s, 2H, CH_2),
^{13}C NMR ($(CD_3)_2CO$): δ = 157.6 (Cq), 153.1 (CN_3), 150.7 (C_{py}), 149.3 (Cq), 138.1 (C_{py}), 129.2 (Cq), 124.0 (C_{py}), 123.4 (C_{ar}), 122.9 (C_{py}), 121.6 ($C_{imidazole}$), 119.0(C_{ar}), 118.9 (C_{ar}), 111.4 (C_{ar}), 106.7 ($C_{imidazole}$), 51.7 (CH_2).
ESI-HRMS: calcd for $C_{15}H_{13}N_4$ $[M+H]^+$ 249.1135, found: 249.1130.
IR (neat): $\bar{\nu}$ (cm^{-1}) = 1640, 1590, 1560, 1450, 1250, 1215, 1150, 1140, 990, 850, 760.
EA: calcd for $C_{15}H_{12}N_4$ + ⅓H_2O (%): C, 70.85; H, 5.02; N, 22.03. Found C, 70.79; H, 4.79; N, 22.11.

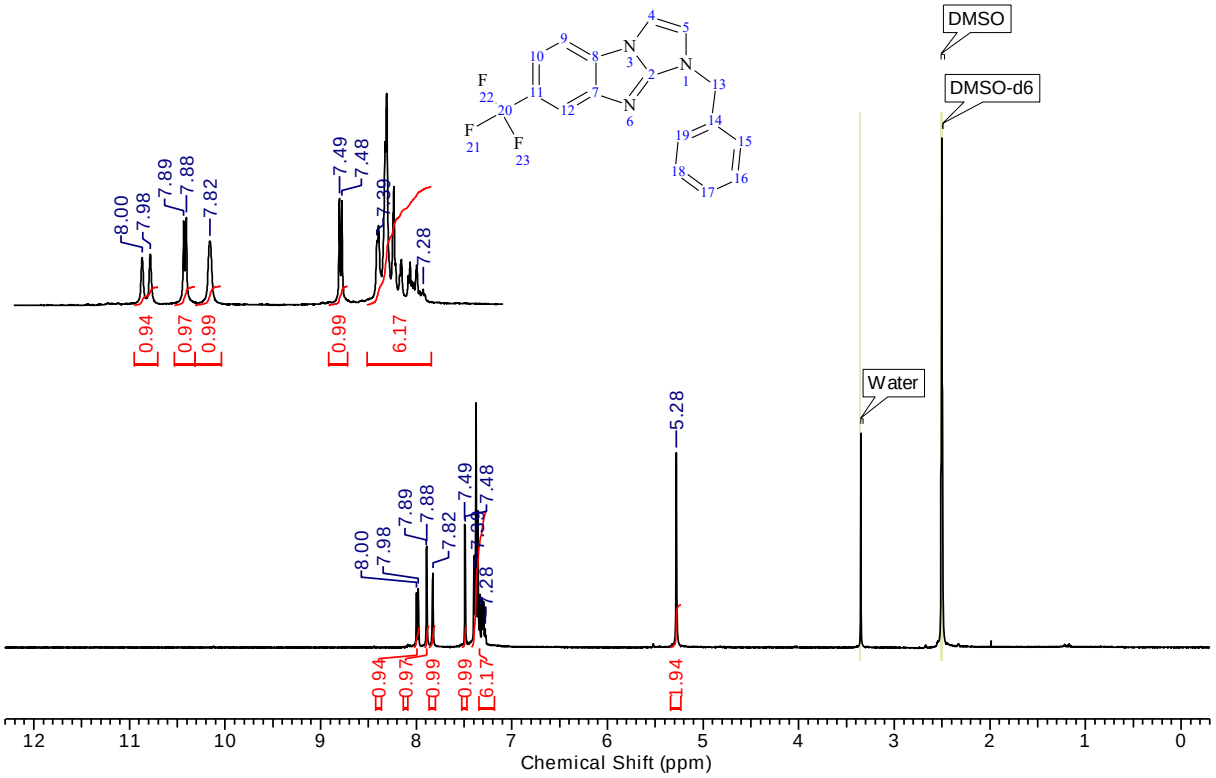


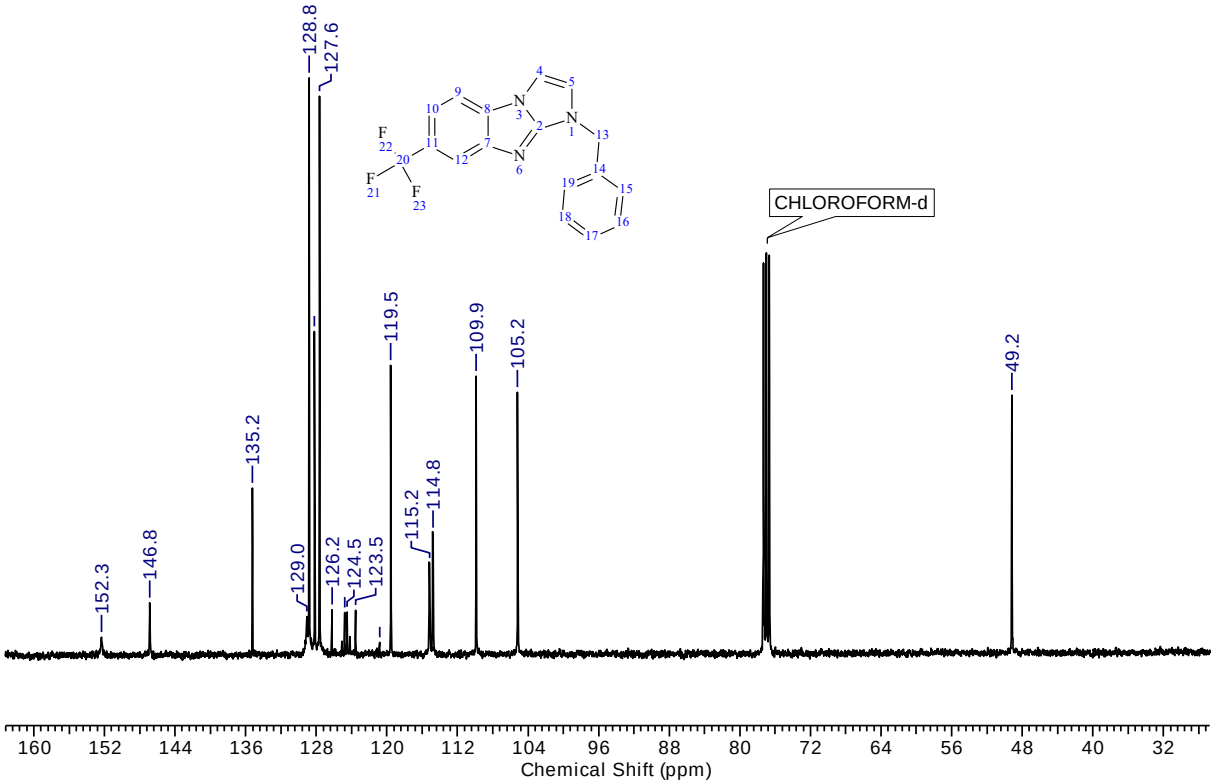


1-benzyl-7-(trifluoromethyl)-1H-benzo[d]imidazo[1,2-a]imidazole (6d): Brown solid. Yield 93%.

^{1}H NMR (DMSO-d_6): δ = 7.99 (d, 1H, *J* = 8.2 Hz, H_{ar}), 7.89 (d, 1H, *J* = 2.6 Hz, H_{im}), 7.82 (s, 1H, H_{ar}), 7.49 (d, 1H, *J* = 2.6 Hz, H_{im}), 7.39-7.27 (m, 6H, H_{ar}), 5.28 (s, 2H, CH_2).

^{13}C NMR ($CDCl_3$): δ = 152.3 (CN_3), 146.8 (Cq), 135.2 (Cq), 129.0 (Cq), 128.8 (CH_{ar}), 128.2 (CH_{ar}), 127.6 (CH_{ar}), 129.4 (q, *J* = 271 Hz, CF_3), 124.7 (q, *J* = 31 Hz, Cq), 119.5 (CH_{ar}), 115.2 (d, *J* = 3 Hz, CH_{ar}), 114.5 (d, *J* = 4 Hz, CH_{ar}), 109.9 (CH_{im}), 105.2 (CH_{im}), 49.2 (CH_2).
IR (ν, cm^{-1}): 1649, 1578, 1321, 1152, 1109, 1047, 914, 812.
ESI-HRMS: calcd for $C_{17}H_{13}F_3N_3$ $[M+H]^+$ 316.1056, found 316.1062.
EA: calcd for $C_{17}H_{12}F_3N_3$ + ½ H_2O (%): C, 62.96; H, 4.04; N, 12.96. Found C, 62.40; H, 3.95; N, 13.11.





1-(2-benzyl)-benzo[d]imidazo[1,2-a]benzimidazole (6e): Brown solid. Yield: 61%

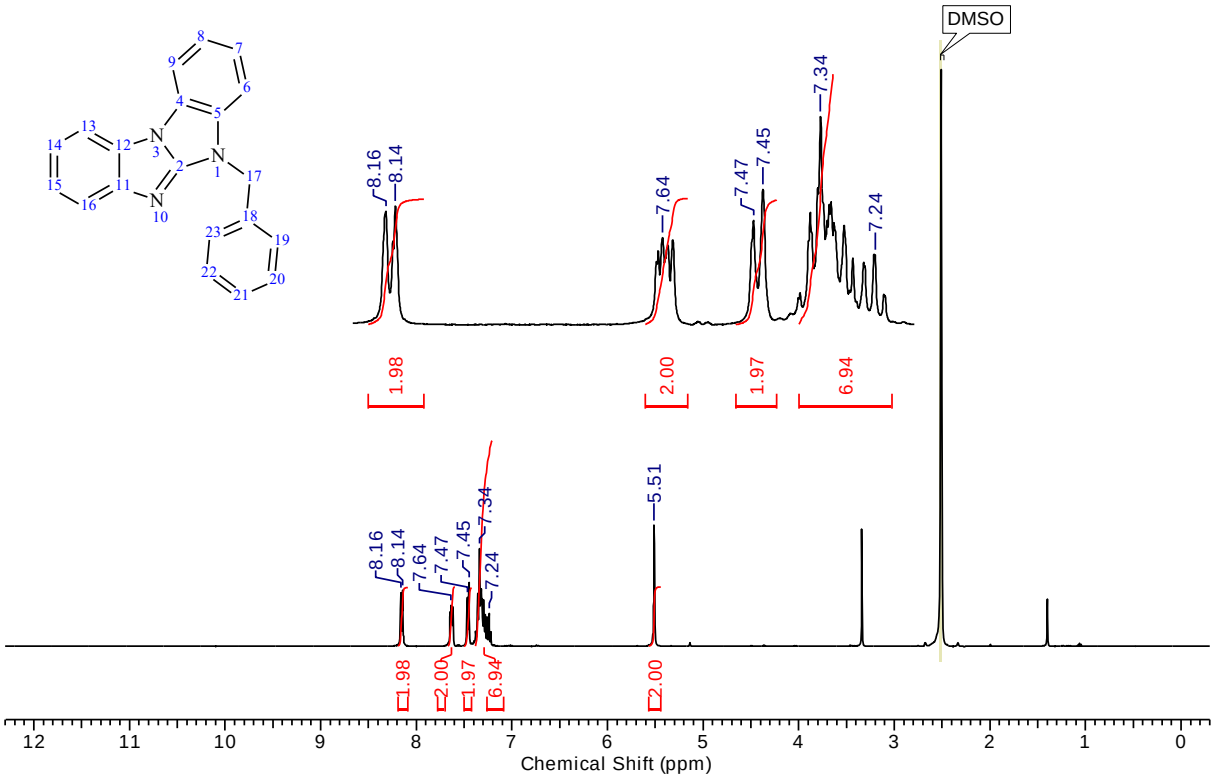
^{1}H NMR (DMSO-d_6): δ = 8.15 (d, 2H, *J* = 7.1 Hz, H_{ar}), 7.67 (m, 2H, H_{ar}), 7.46 (d, 2H, *J* = 7.1 Hz, H_{ar}), 7.38-7.24 (m, 7H, H_{ar}), 5.51 (s, 2H, CH_2).

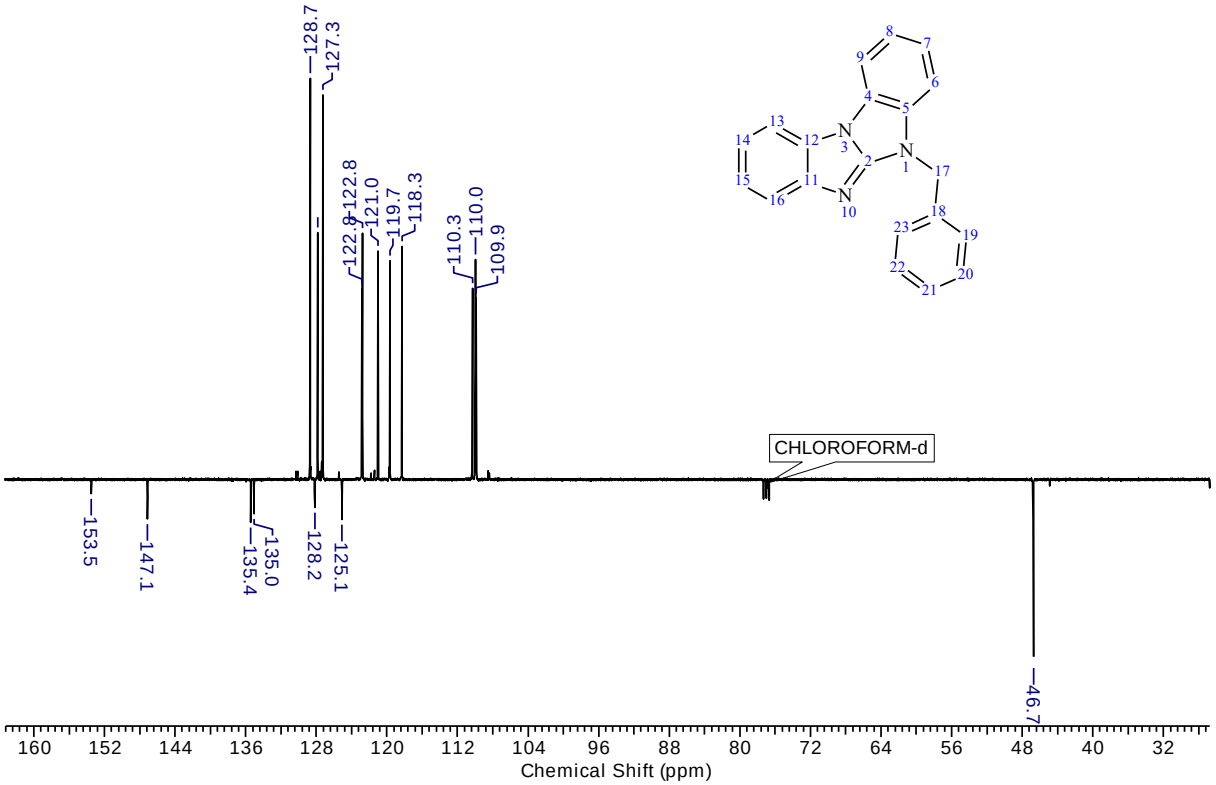
^{13}C NMR ($CDCl_3$): δ = 153.7 (CN_3), 147.3(Cq), 135.6 (Cq), 135.2 (Cq), 128.9 (CH_{ar}), 128.4 (Cq), 128.1 (CH_{ar}), 127.5 (CH_{ar}), 127.2 (CH_{ar}), 125.3 (Cq), 123.0 (CH_{ar}), 121.2 (CH_{ar}), 119.9 (CH_{ar}), 118.8 (CH_{ar}), 110.5 (CH_{ar}), 110.2 (CH_{ar}), 110.1 (CH_{ar}), 46.9 (CH_2).

ESI-HRMS: calcd for $C_{20}H_{16}N_3$ $[M+H]^+$ 298.1339, found 298.1335

IR (neat): $\bar{\nu}$ (cm^{-1}) = 1638, 1563, 1496, 1454, 735

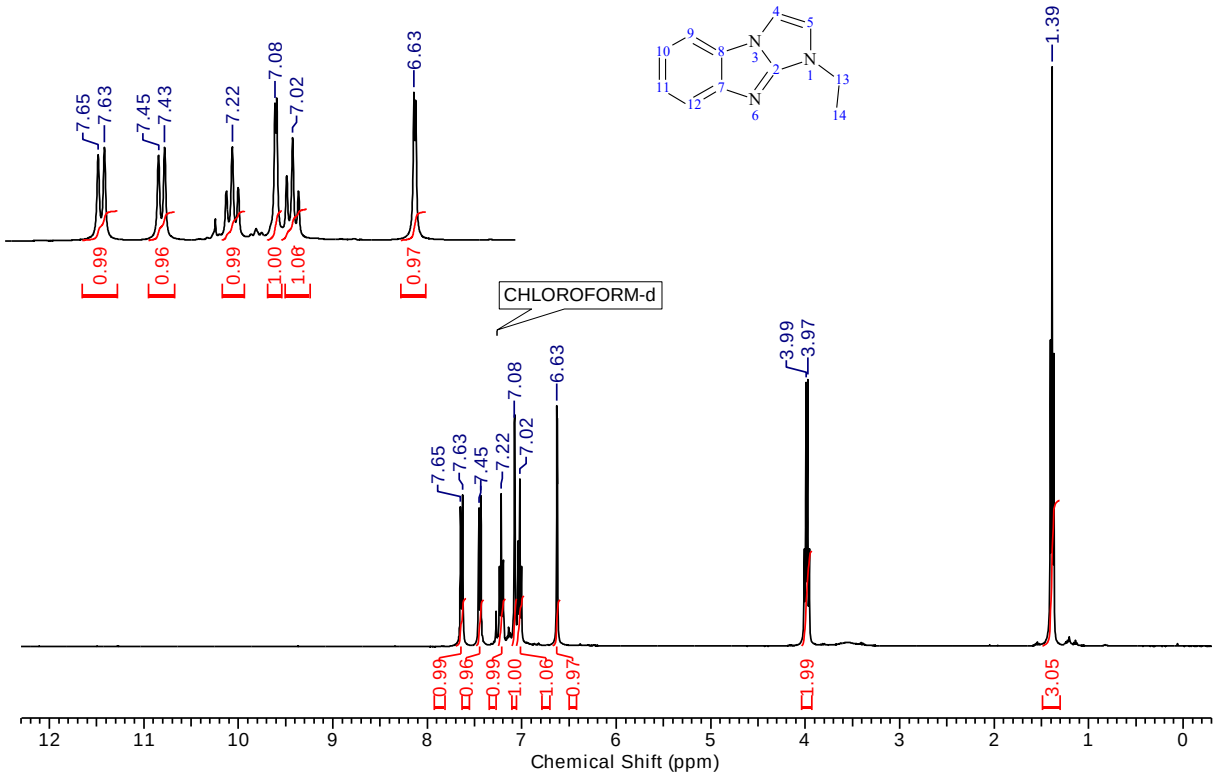
EA: calcd for $C_{20}H_{15}N_3$ + ¼ H_2O (%): C, 79.58; H, 5.18; N, 13.92. Found C, 79.15; H, 5.07; N, 14.38



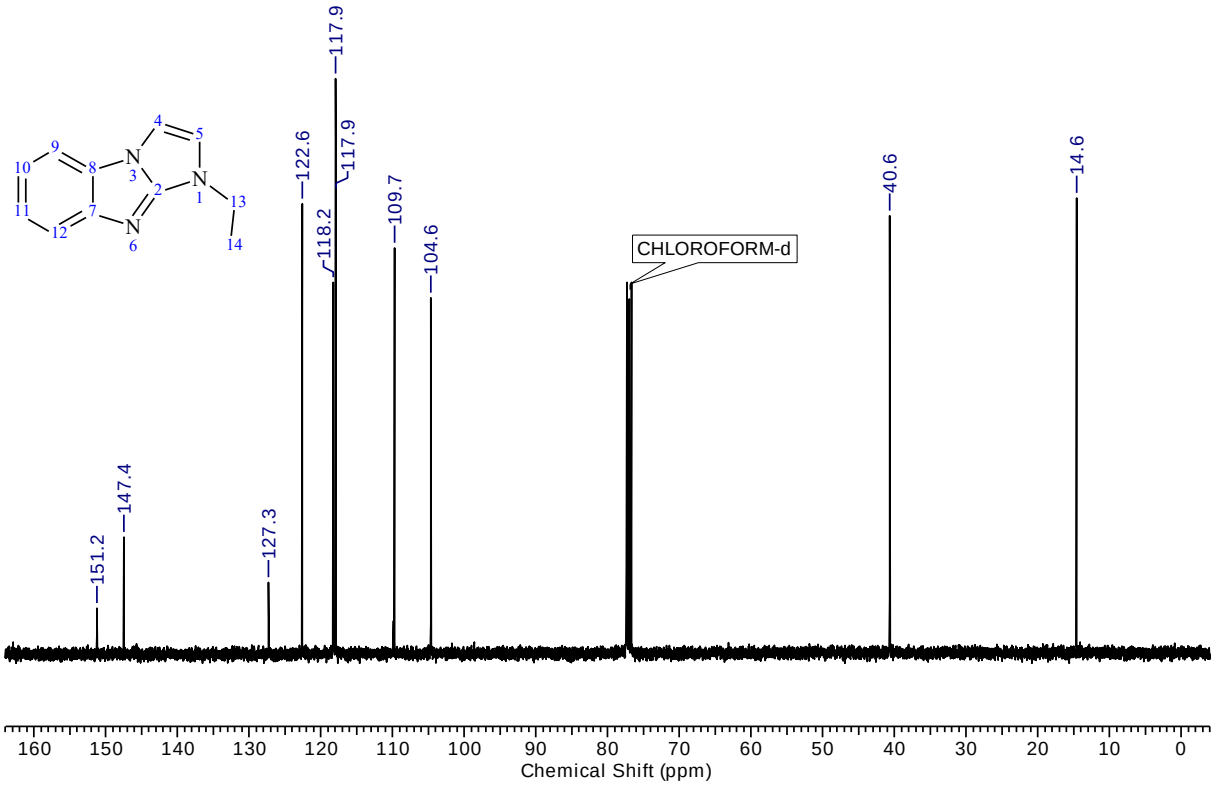


1-(2-ethyl)-benzo[d]imidazo[1,2-a]imidazole (6f): Brown oil. Yield: 83%.
^{1}H NMR ($CDCl_3$): δ = 7.66 (d, 1H, *J* = 8.1 Hz, H_{ar}), 7.50 (d, 1H, *J* = 8.1 Hz, H_{ar}), 7.24 (t, 1H, *J* = 8.1 Hz, H_{ar}), 7.16 (d, 1H, *J* = 2.2 Hz, H_{im}), 7.05 (t, 1H, *J* = 7.7 Hz, H_{ar}), 6.72 (d, 1H, *J* = 2.6 Hz, H_{im}), 4.07 (q, 2H, *J* = 7.0 Hz, CH_2), 1.45 (t, 3H, *J* = 7.0 Hz, CH_3).

^{13}C NMR ($CDCl_3$): δ = 151.2 (CN_3), 147.4 (Cq), 127.3 (Cq), 122.6 (CH_{ar}), 118.2 (CH_{im}), 117.9 (CH_{ar})[20], 109.7 (CH_{ar}), 104.6 (CH_{im}), 40.6 (CH_2), 14.6 (CH_3).
ESI-HRMS: calcd for $C_{11}H_{12}N_3$ $[M+H]^+$ 186.1026 , found 186.1020.
IR (neat): $\bar{\nu}$ (cm^{-1}) = 1640, 1590, 1550, 1460, 1440, 1270, 1220, 740.
EA: calcd for $C_{11}H_{11}N_3$ + ⅓ H_2O (%): C, 69.09; H, 6.15; N, 21.97. Found C, 69.10; H, 5.96; N, 22.73.

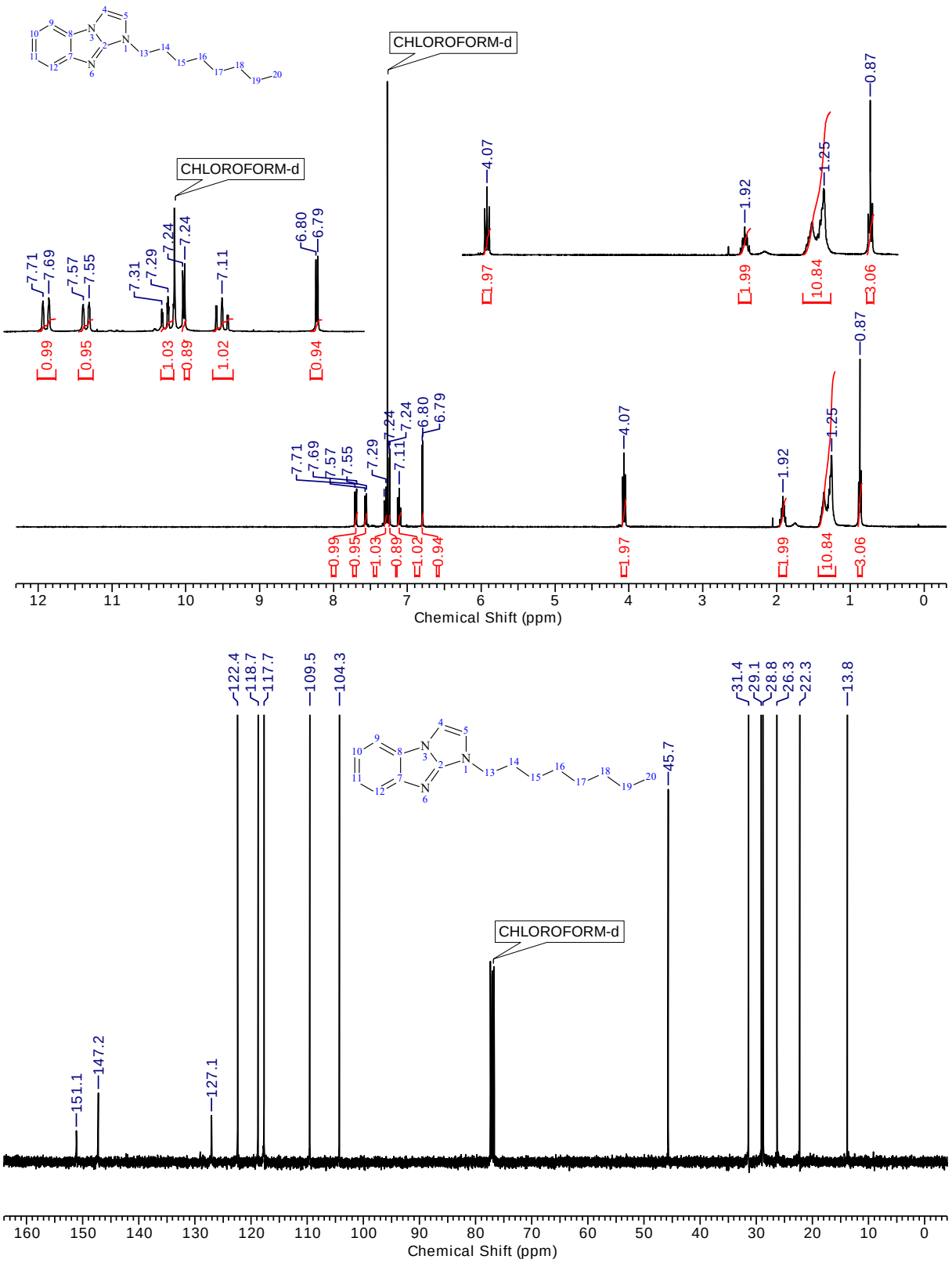


[20] Two signals were overlapped



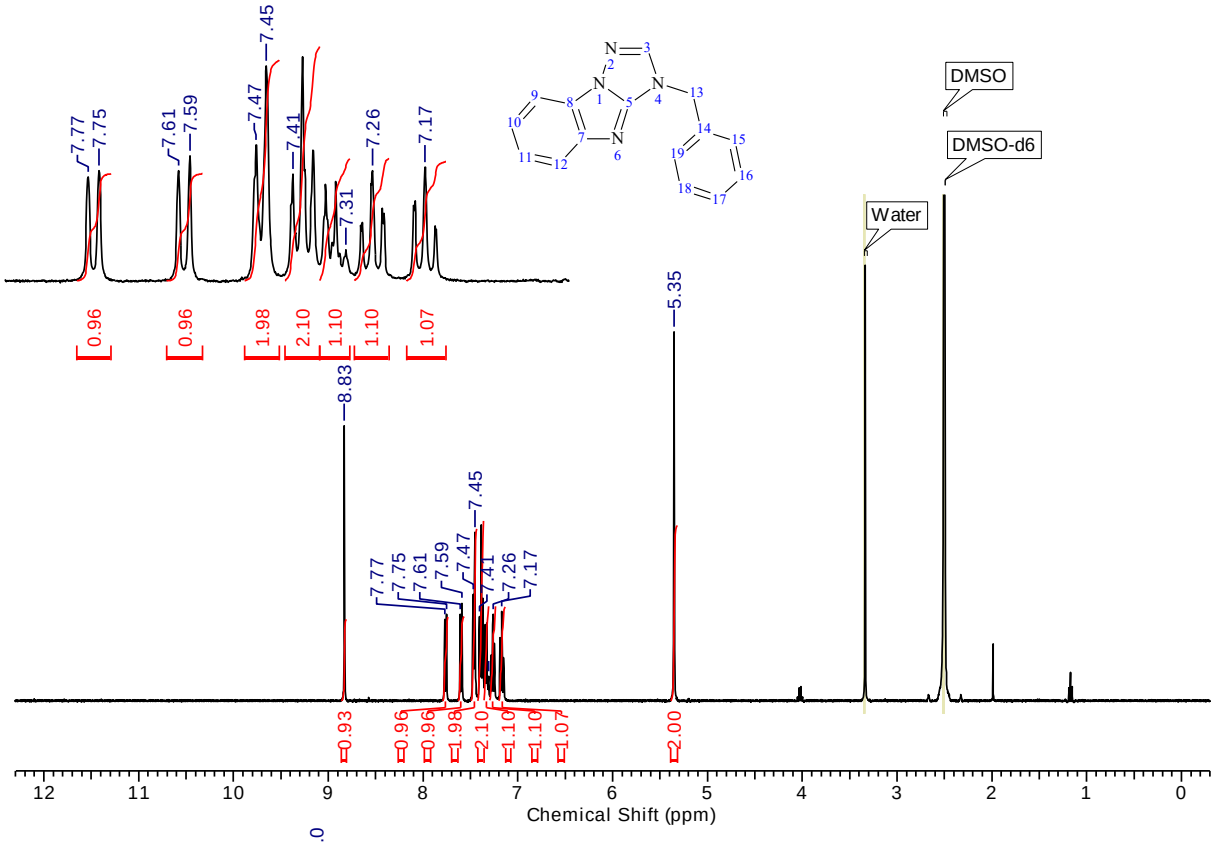
1-(2-octyl)-benzo[d]imidazo[1,2-a]imidazole (6g): 50°C overnight. Brown oil. Yield: 94%.
^{1}H NMR ($CDCl_3$): δ = 7.70 (d, 1H, *J* = 8.1 Hz, H_{ar}), 7.56 (d, 1H, *J* = 8.1 Hz, H_{ar}), 7.29 (td, 1H, J_1 = 1.5 Hz, J_2 = 7.3 Hz, H_{ar}), 7.24 (d, 1H, *J* = 2.6 Hz, H_{im}), 7.11 (t, 1H, *J* = 8.1 Hz, H_{ar}), 6.80 (d, 1H, *J* = 2.6 Hz, H_{im}), 4.07 (t, 2H, *J* = 7.3 Hz, CH_2), 1.92 (quint, 2H, *J* = 7.3 Hz, CH_2), 1.42-1.21 (m, 10 H, CH_2), 0.87 (t, 3H, *J* = 7.0 Hz, CH_3),
^{13}C NMR ($CDCl_3$): δ = 151.1 (CN_3), 147.2 (Cq), 127.1 (Cq), 122.4 (CH_{ar}), 118.7 (CH_{im}), 117.7 (CH_{ar})[21], 109.5 (CH_{ar}), 104.3 (CH_{im}), 45.7 (CH_2-N), 31.4 (CH_2), 29.1 (CH_2), 28.8 (CH_2), 26.3 (CH_2), 22.3 (CH_2), 13.8 (CH_3).
ESI-HRMS: calcd for $C_{17}H_{24}N_3$ $[M+H]^+$ 270.1965, found 270.1966.
IR (neat): $\bar{\nu}$ (cm^{-1}) = 2926, 1638, 1562, 1456, 1263, 1217, 741.
EA: calcd for $C_{17}H_{23}N_3$ + 0.8H_2O (%): C, 71.95; H, 8.74; N, 14.81. Found C, 71.88; H, 8.34; N, 15.26.

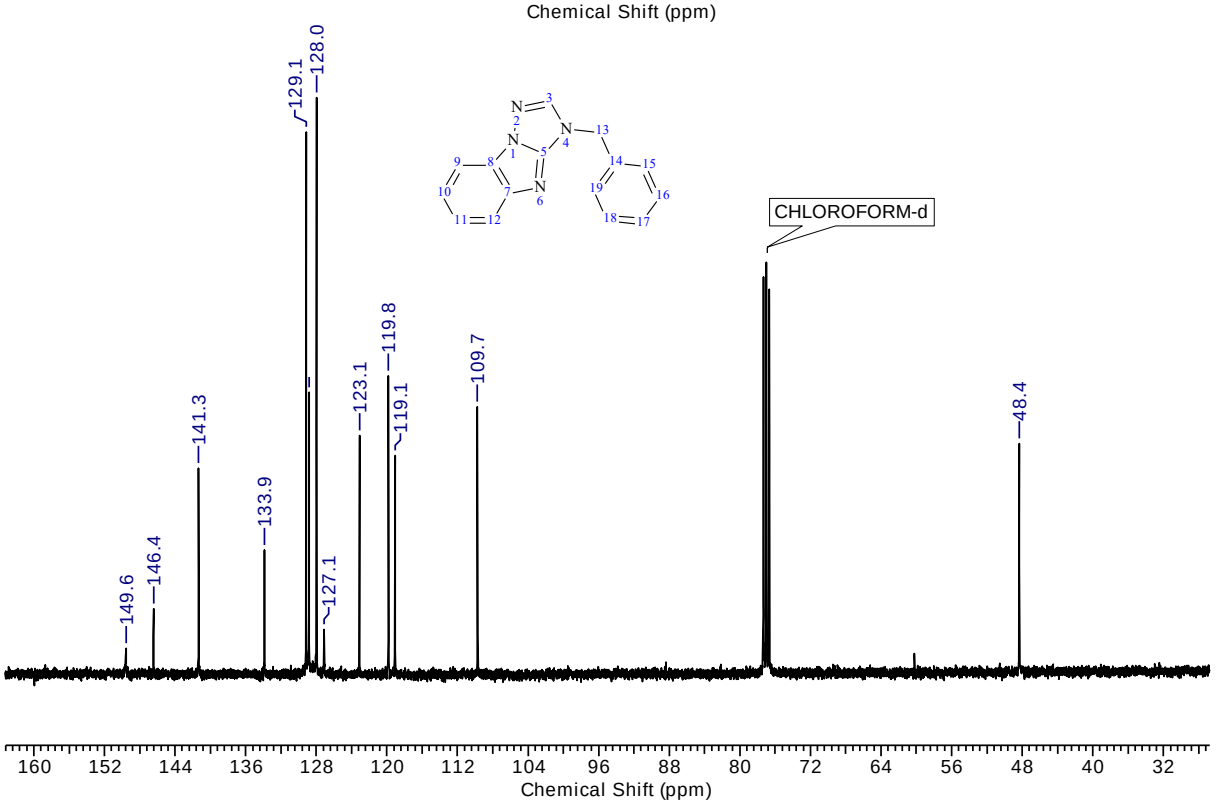
[21] Two signals were overlapped.



3-benzyl-3H-benzo[4,5]imidazo[1,2-b]-1,2,4-triazole (6h): Brown solid. Yield: 96%
^{1}H NMR (DMSO-d_6): δ = 8.83 (s, 1H, $H_{triazole}$), 7.76 (d, 1H, J = 7.7 Hz, H_{ar}), 7.60 (d, 1H, J = 8.1 Hz, H_{ar}), 7.47-7.45 (m, 2H, $H_{ar + triazole}$), 7.41-7.31 (m, 3H, $H_{ar + triazole}$), 7.26 (td, 1H, J_1 = 8.1 Hz, J_2 = 1.1 Hz, H_{ar}), 7.17 (td, 1H, J_1 = 8.1 Hz, J_2 = 1.1 Hz, H_{ar}), 5.35 (s, 2H, CH_2).
^{13}C NMR ($CDCl_3$): δ = 149.6 (CN_3), 146.4 (Cq), 141.3 ($CH_{triazole}$), 133.9 (Cq), 129.1(CH_{ar}), 128.8 (CH_{ar}), 128.0 (CH_{ar}), 127.1 (Cq), 123.1 (CH_{ar}), 119.8 (CH_{ar}), 119.1 (CH_{ar}), 109.7 (CH_{ar}), 48.4 (CH_2).

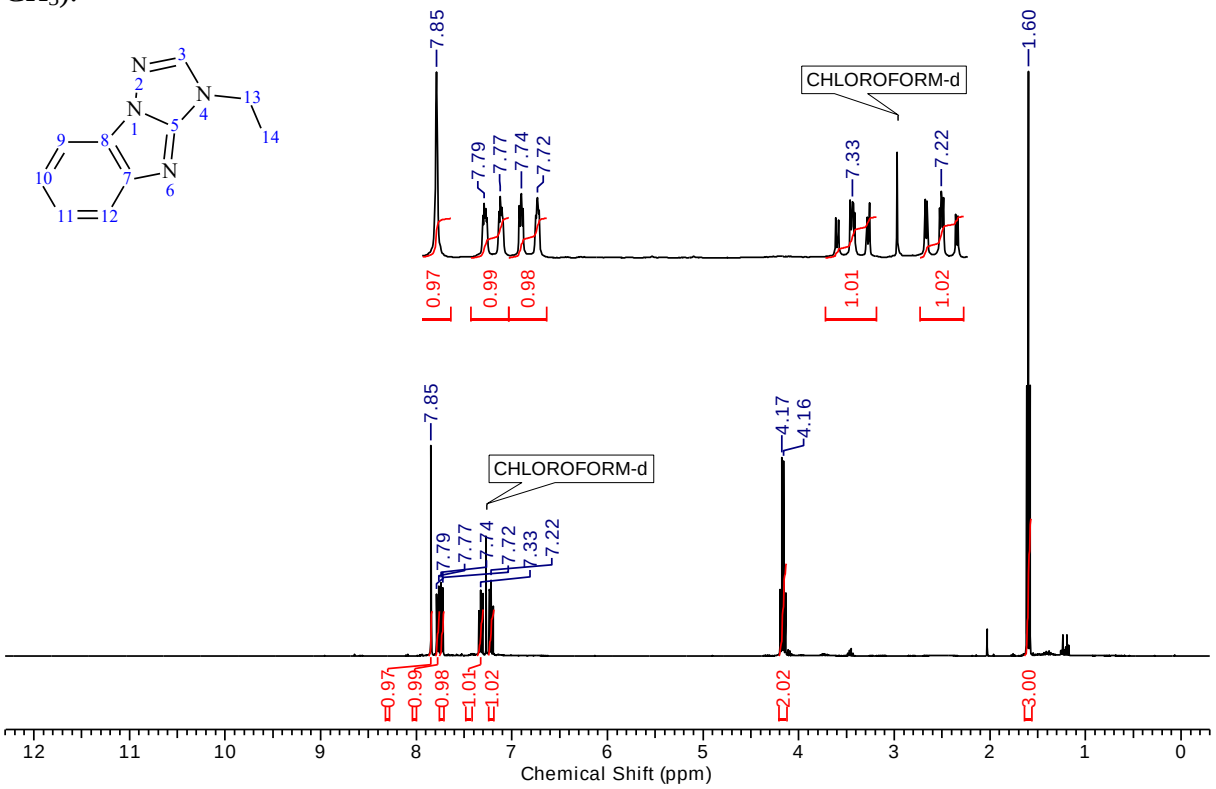
IR (neat): $\bar{\nu}$ (cm^{-1}) = 1634, 1593, 1560, 1419, 1445, 1211, 725 (s).
ESI-HRMS: calcd for $C_{15}H_{13}N_4$ $[M+H]^+$ 249.1135, found 249.1139.
EA: calcd for $C_{15}H_{12}N_4$ + ⅓ H_2O (%): C, 70.85; H, 5.02; N, 22.03. Found C, 70.40; H, 4.64; N, 22.60.





3-ethyl-3H-benzo[4,5]imidazo[1,2-b]-1,2,4-triazole (6i): Blackish solid. Yield: 84%. NMR data in accordance to previous low resolution report.[22]

^{1}H NMR (DMSO-d_6): δ = 7.85 (s, 1H, $H_{triazole}$), 7.78 (dd, 1H, J_1 = 8.1 Hz, J_2 = 1.5 Hz, H_{ar}), 7.73 (dd, 1H, J_1 = 8.1 Hz, J_2 = 1.1 Hz, H_{ar}), 7.33 (td, 1H, J_1 = 8.4 Hz, J_2 = 1.1 Hz, H_{ar}), 7.22 (dd, 1H, J_1 = 8.1 Hz, J_2 = 1.1 Hz, H_{ar}), 4.16 (q, 2H, J = 7.3 Hz, CH_2), 1.60 (t, 3H, J = 7.3 Hz, CH_3).



2-ethyl-3-phenyl-4H-benzo[4,5]imidazo[1,2-c][1,2,3]triazol-2-ium tetrafluoroborate (6k): Obtained following an alternate procedure involving silver transmetalation. Silver metalation[23] was performed by dissolving **4k** (383 mg, 1.01 mmol) in 50 mL MeCN/CH_2Cl_2 (*v*/*v* 1:1) and treating the resulting solution with Ag_2O (168 mg, 0.725 mmol) and NEt_4Cl (70%, 312 mg, 1.32 mmol) overnight at 30 °C. The intermediated silver complex was isolated by filtration over celite and evaporation. ^{1}H NMR showed the disappearance of the deshielded triazolium proton and the formation of a major and a minor species (probably homoleptic and heterolectic complexes). Tetraethylammonium salts were removed by taking up the resulting oil in 10 mL CH_2Cl_2 and washing with 3×30 mL H_2O. The resulting solid (390 mg) was dissolved in 50 mL of MeCN/CH_2Cl_2 1:1. CuCl (10.4 mg, 0.105, mmol) was added. After 1 h stirring at RT, the reaction mixture was filtered on celite, and evaporated to dryness to yield a brown solid (m = 302 mg, 85% yield).

^{1}H NMR (DMSO-d_6):[24] δ = 8.26 (d, 1H, J = 8.3 Hz, H_{ar}), 7.77-7.74 (m, 3H, H_{ar}), 7.71-7.64 (m, 4H, H_{ar}), 7.50 (t, 1H, J = 7.3 Hz, H_{ar}), 4.72 (q, 2H, J = 7.3 Hz, CH_2), 1.53 (t, 3H, J = 7.3 Hz, CH_3).

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[22] V. V. Kuz'menko, T. A. Kuz'menko, A. F. Pozharskii, V. N. Doron'kin, N. L. Chikina, S. S. Pozharskaya, *Chem. Heterocycl. Compd.***1989**, *25*, 168-179.

[23] Inspired from the conditions reported by: T. Nakamura, T. Terashima, K. Ogata, S.-I Fukuzawa, *Org. Lett.* **2011**, *13*, 620-623.

[24] TFA is added to fully protonate the product (0.5 mL of DMSO-d_6/TFA 9:1 *v*/*v*)

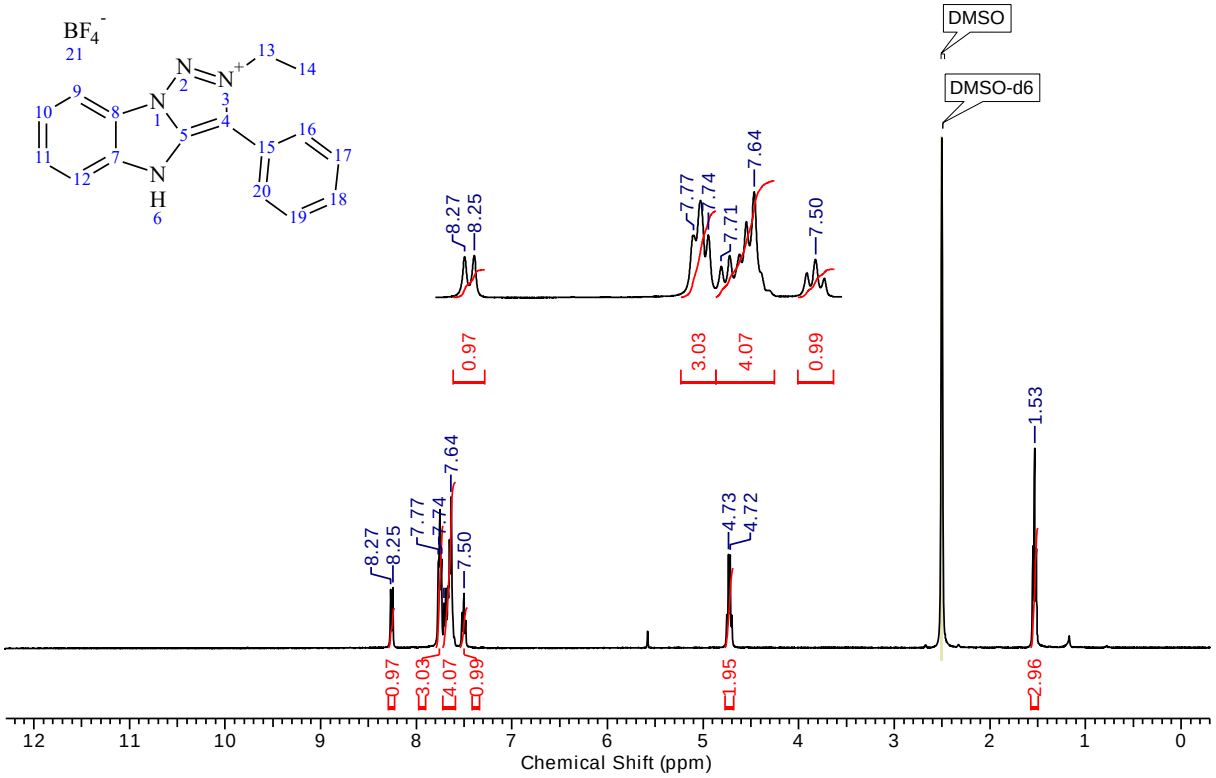
^{13}C NMR (DMSO-d$_6$):[25] δ = 137.6 (Cq), 136.6 (Cq), 130.7 (CH_{ar}), 129.2 (CH_{ar}), 129.1 (CH_{ar}), 122.6 (CH_{ar}), 122.4 (Cq), 121.2 (Cq), 119.7 (Cq), 114.0 (CH_{ar}), 113.0 (CH_{ar}), 47.5 (CH_2), 13.8 (CH_3).

IR (neat): $\bar{\nu}$ (cm^{-1}) = 1466, 1098, 1051 (st), 1040, 754.

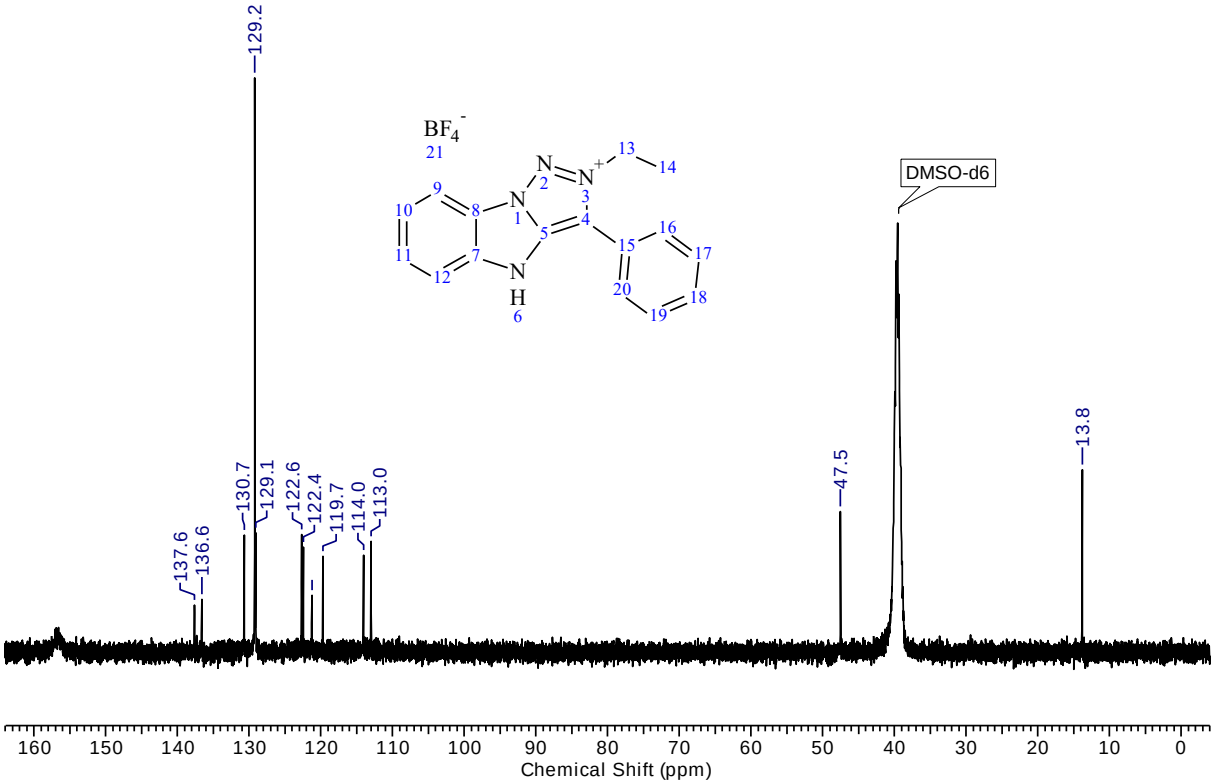
ESI-HRMS: calcd. for $C_{16}H_{15}N_4$ $[M]^+$ 263.1291, found 263.1290.

EA: calcd for $C_{16}H_{15}N_4$ BF_4 (%): C, 54.89; H, 4.32; N, 16.00. Found C, 56.95; H, 4.41; N, 16.31.

The higher content of C,H,N consistently obtained by microanalysis could be rationalized by considering that the sample is ~4 : 1 mixture of a BF_4 salt and a zwitterionic form. Indeed this type of compound was previously reported to be zwitterionic.[25]



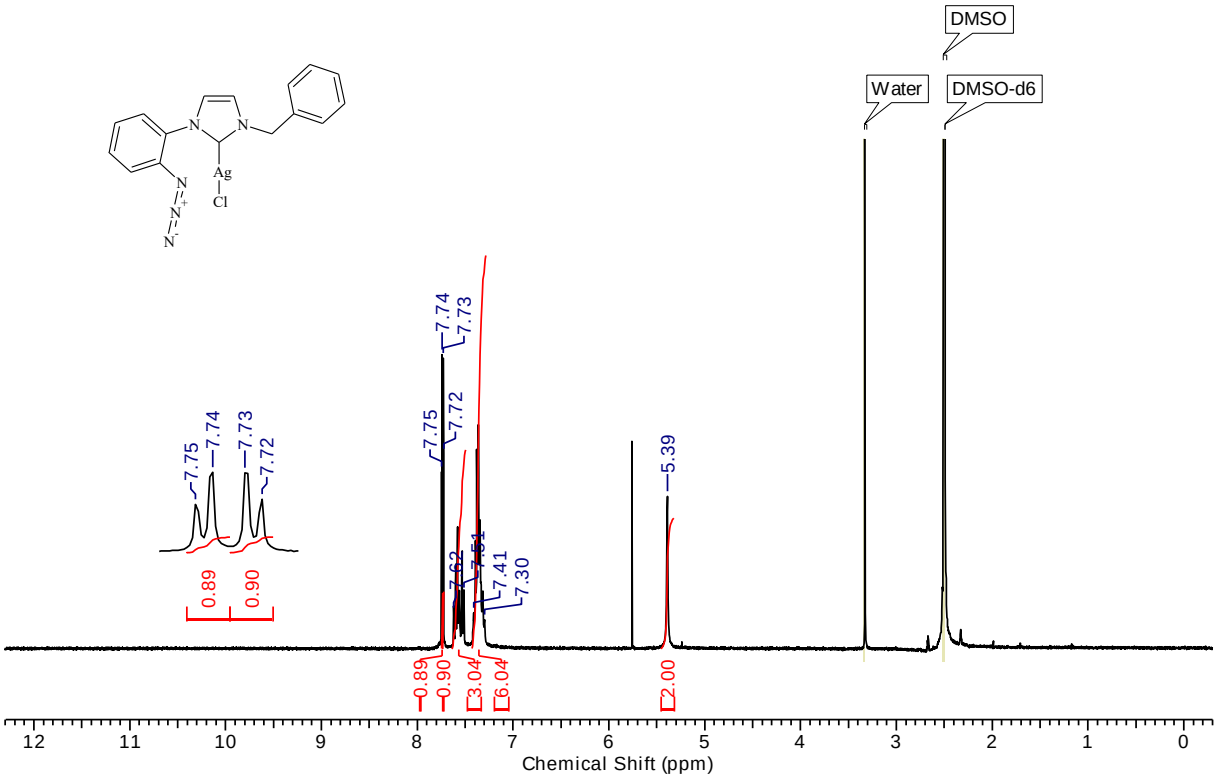
[25] V. A. Chuiguk, A. G. Maidannik, *Khim. Geterotsikl. Soedin.* **1980**, *12*, 1695-1696

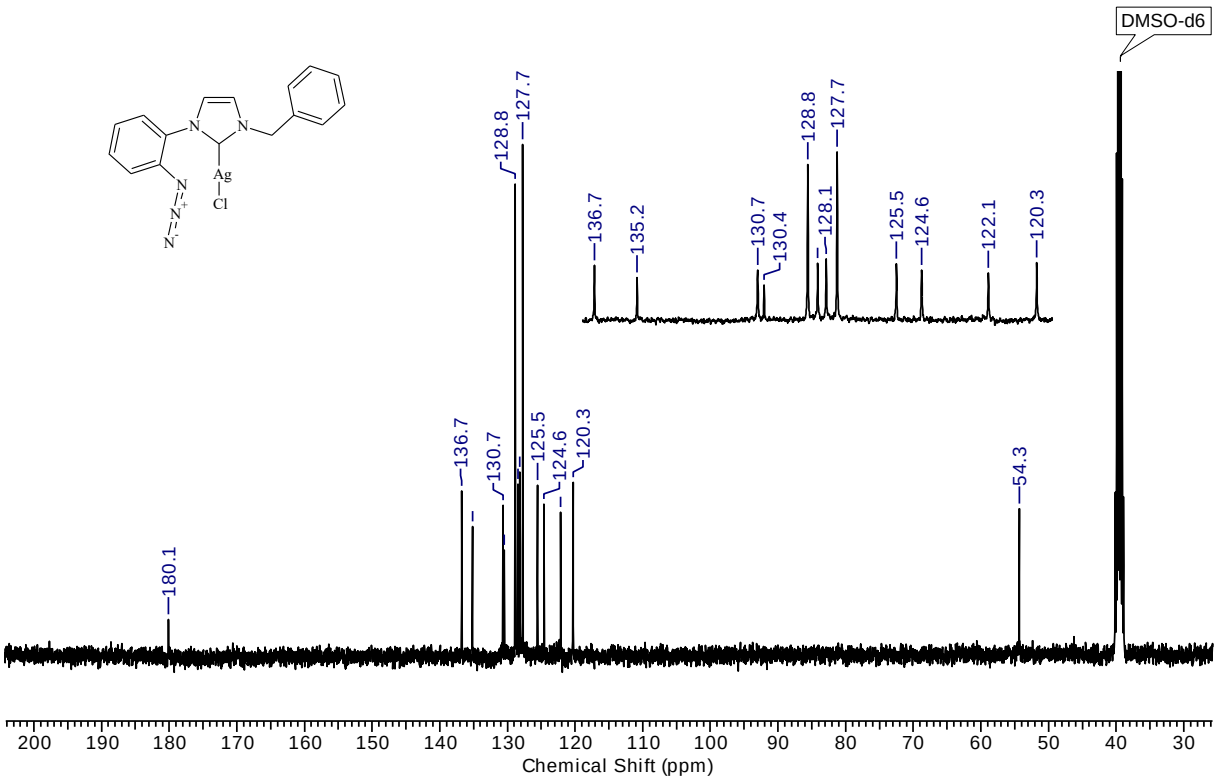


The application of the general procedure (CuCl, 3 days, 80°C) yields a quantitative conversion to a species showing the same spectral analyses as above.
The procedure was also performed with Cu_2O: copper(I) oxide (3.6 mg, 0.025 mmol) was added to Ace Pressure tube containing a solution of **4k** (96 mg, 0.25 mmol) in 2.5 mL absolute ethanol degassed by argon bubbling. Ammonia (13 mol L^{-1}, 20 µL, 0.26 mmol) was added, the tube stoppered and the reaction mixture stirred at 90°C for 4 days. ^{1}H NMR indicated a total conversion. The solvent was evaporated, the resulting solid was taken up in 5 mL CH_2Cl_2, washed with 5 mL of an EDTA solution (5 mmol L^{-1} of Na_4EDTA), 5 mL of water, dried over $MgSO_4$ and evaporated. The spectral analysis data were identical to those reported above. Elemental analysis also showed a CHN excess (see above for justification). Yellow solid. Isolated mass: 57 mg, yield = 64%.

SI 5- Synthesis of the intermediate silver complex

(1-(2-azidophenyl)-3-benzyl-1H-imidazol-2(3H)-ylidene)silver(I) chloride (7):
The imidazolium salt **4a** (316 mg, 1.01 mmol) is dissolved in 30 mL CH_2Cl_2. Silver(I) oxide (135 mg, 0.583 mmol) is added and the mixture is stirred at room temperature for 1.5 h. The product is isolated as a yellow solid by filtration over celite and evaporation (414 mg, 98%).^{1}H NMR (DMSO-d_6): δ = 7.74 (d, 2H, *J* = 2.2 Hz, H_{imi}), 7.72 (d, 2H, *J* = 2.2 Hz, H_{imi}), 7.62-7.51 (m, 3H, H_{ar}), 7.41-7.30 (m, 6H, H_{ar}), 5.39 (s, 2H, CH_2).
^{13}C NMR (DMSO-d_6): δ = 180.1, 136.7, 135.2, 130.7, 130.4, 128.8, 128.4, 128.1, 127.7, 125.5, 124.6, 122.1, 120.3, 54.3.
IR (neat): $\bar{\nu}$ (cm^{-1}) = 2129, 2099, 1503, 1456, 1300, 1238, 758, 725.
EA: calcd for $C_{16}H_{13}AgClN_5$ (%): C, 45.90; H, 3.13; N, 16.73. Found C, 45.90; H, 3.13; N, 16.73, C, 45.72; H, 3.09; N, 16.47.



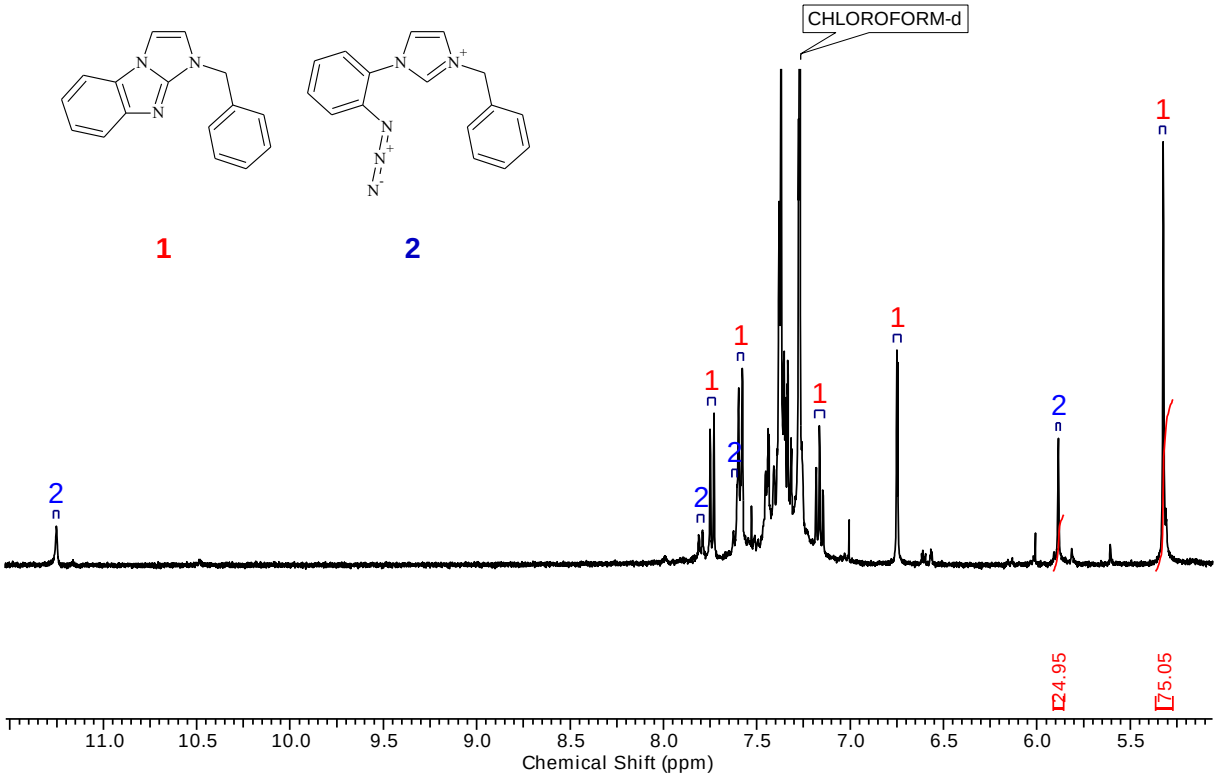


Alternative procedure for the synthesis of 1-(2-benzyl)-benzo[d]imidazo[1,2-a]imidazole(6a) using trasmetalation:

156 mg (0.500 mmol) of **4a** were dissolved in 15 mL CH_2Cl_2 under argon. Ag_2O (63.7 mg, 0.275 mmol) was added. The reaction mixture was stirred 1 h at RT after which it turned

nearly limpid.[26] Then, CuCl (5.0 mg, 0.050 mmol) was added and gaseous evolution was observed. After 1 h stirring at RT, the reaction mixture was filtered on celite, and evaporated to dryness. Light brown solid. Yield: 100%.

Thermal cyclization of the silver complex (7):
The silver complex **7** (51.5 mg, 0.123 mmol) is suspended in 4 mL 1,2-dichloroethane. The mixture is refluxed for 22 h. An aliquot is filtered over celite, condensed under reduced pressure and dissolved in DMSO-d_6 for a ^{1}H NMR spectrum. A mixture of 25% imidazolium salt **4a** and 75% of the tricycle product **6a** is obtained.



SI 6- X-ray crystallography

6b:

A specimen of **6b**, approximate dimensions 0.140 mm x 0.390 mm x 0.710 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.
The total exposure time was 19.54 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the numerical method (SADABS).

Table S1. Sample and crystal data for 6b

[26] An aliquot of the metalation step displayed a strong IR band at 2100 cm^{-1}, the complete disappearance of the deshielded ^{1}H NMR signal corresponding to the imidazolium proton was observed.

Chemical formula	$C_{15}H_{12}N_4$	
Formula weight	248.29 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.140 x 0.390 x 0.710 mm	
Crystal system	Orthorhombic	
Space group	P 2_1 2_1 2_1	
Unit cell dimensions	a = 5.8271(7) Å	α = 90°
	b = 12.4492(14) Å	β = 90°
	c = 16.779(2) Å	γ = 90°
Volume	1217.2(2) $Å^3$	
Z	4	
Density (calculated)	1.355 g/cm^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	520	

Table S2. Data collection and structure refinement for 6b.

Theta range for data collection	2.273 to 33.207°	
Index ranges	-8<=h<=8, -18<=k<=19, -25<=l<=25	
Reflections collected	73330	
Independent reflections	4485 [R(int) = 0.0376]	
Coverage of independent reflections	96.4%	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	4485 / 0 / 172	
Goodness-of-fit on F^2	1.068	
Δ/σ_{max}	0.001	
Final R indices	4255 data; I>2σ(I)	R1 = 0.0340, wR2 = 0.0923
	all data	R1 = 0.0369, wR2 = 0.0949
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0647P)^2+0.1038P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	-0.2(4)	
Largest diff. peak and hole	0.328 and -0.268 $eÅ^{-3}$	
R.M.S. deviation from mean	0.052 $eÅ^{-3}$	

7:

A specimen of the dimer of **7**, approximate dimensions 0.120 mm x 0.392 mm x 0.903 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 18.55 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the numerical method (SADABS).

Table S4. Sample and crystal data for the dimer of 7

Chemical formula	$C_{32}H_{26}Ag_2Cl_2N_{10}$	
Formula weight	812.7 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.120 x 0.392 x 0.903 mm	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	A = 8.4826(14) Å	α = 65.594(9)°
	b = 9.7874(17) Å	β = 73.444(9)°
	c = 11.235(2) Å	γ = 86.297(9)°
Volume	812.7(3) $Å^3$	
Z	1	
Density (calculated)	1.711 g/cm^3	
Absorption coefficient	1.41 mm^{-1}	
F(000)	416	

Table S5. Data collection and structure refinement for the dimer of 7.

Theta range for data collection	3.109 to 33.491°	
Index ranges	-13<=h<=13, -14<=k<=14, -16<=l<=16	
Reflections collected	55075	
Independent reflections	5749 [R(int) = 0.0417]	
Coverage of independent reflections	90.0%	
Absorption correction	Empirical	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5749 / 0 / 208	
Goodness-of-fit on F^2	1.055	
Δ/σ_{max}	0.001	
Final R indices	5013 data; I>2σ(I)	R1 = 0.0330, wR2 = 0.0758
	all data	R1 = 0.0429, wR2 = 0.0814
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0327P)^2+1.4748P]$	

	where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	2.74 and -1.30 eÅ^{-3}
R.M.S. deviation from mean	0.115 eÅ^{-3}

SI 7- DFT

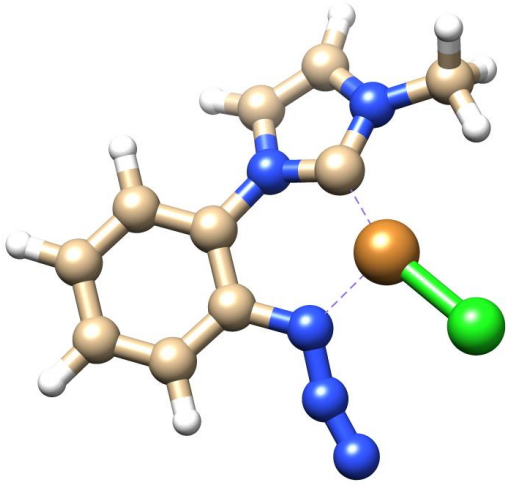
All calculations was performed by Gaussian G09 rev D at DFT level of theory using the B3LYP functional and 6-31g(d,p) basis set (DFT/B3LYP/6-31g(d,p)).

1-(2-azidophenyl)-4-methyl imidazolium (Mol 1)

initial state step 1 : this state corresponds to the optimization of IRC

1-(2-azidophenyl)-4-methyl imidazolium IRC 1 reactant optimisation

C	2.62400	-1.75100	0.07300
C	1.56700	-0.83500	0.17700
C	1.84700	0.54200	0.01500
C	3.15500	0.94300	-0.28000
C	4.19300	0.02200	-0.37300
C	3.92400	-1.33300	-0.18700
H	2.41200	-2.80800	0.19600
H	5.19800	0.36200	-0.60100
N	0.84900	1.55000	0.16200
C	-0.47700	1.39800	-0.16200
C	1.09900	2.83800	0.63900
C	-0.08400	3.49800	0.60900
H	2.06800	3.15500	0.98700
H	-0.33200	4.50400	0.90500
N	-1.02700	2.60600	0.12400
N	0.23300	-1.25500	0.40400
N	0.07400	-2.44100	0.80400
N	-0.40000	-3.43500	1.10200
H	3.35300	1.99500	-0.45600
H	4.71800	-2.06900	-0.25900
Cu	-1.34000	-0.19500	-0.45200
Cl	-2.90700	-1.64400	-0.65600
C	-2.44700	2.88900	-0.05100
H	-2.93300	1.93900	-0.27600
H	-2.86500	3.30400	0.87000
H	-2.60500	3.59100	-0.87500

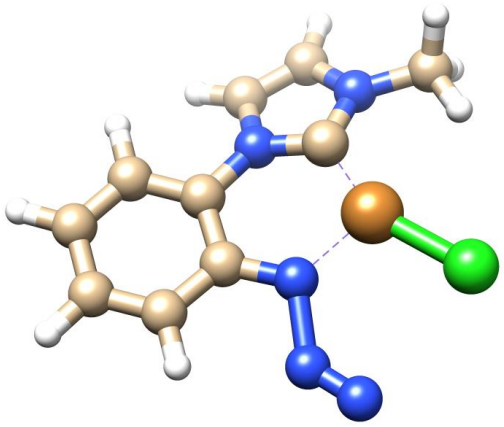


Sum of electronic and thermal Free Energies = -2760.599834 Ha
Freq mode 1 = 27.86 cm $^{-1}$

Transition state step 1

1-(2-azidophenyl)-4-methyl imidazolium TS Step 1 optimisation

C	2.53400	-1.74800	0.01500
C	1.44700	-0.84000	0.07300
C	1.78000	0.54300	-0.03200
C	3.10100	0.94900	-0.25300
C	4.14100	0.03200	-0.30200
C	3.84200	-1.32500	-0.15100
H	2.31700	-2.80500	0.10600
H	5.15900	0.36700	-0.46700
N	0.76900	1.55100	0.06500
C	-0.55900	1.34900	-0.16600
C	0.99600	2.87400	0.43500
C	-0.20900	3.49700	0.42800
H	1.96800	3.24700	0.70500
H	-0.47300	4.51700	0.66200
N	-1.14900	2.54900	0.06800
N	0.12500	-1.23000	0.19700
N	0.01900	-2.80200	0.60500
N	-0.88000	-3.48900	0.65800
H	3.31300	2.00200	-0.40200
H	4.63400	-2.06700	-0.18300
Cu	-1.37400	-0.30200	-0.35100
Cl	-3.07400	-1.59500	-0.39800
C	-2.58400	2.78400	-0.05000
H	-3.07500	1.81400	-0.13200
H	-2.95000	3.30100	0.84000
H	-2.80600	3.38200	-0.93900

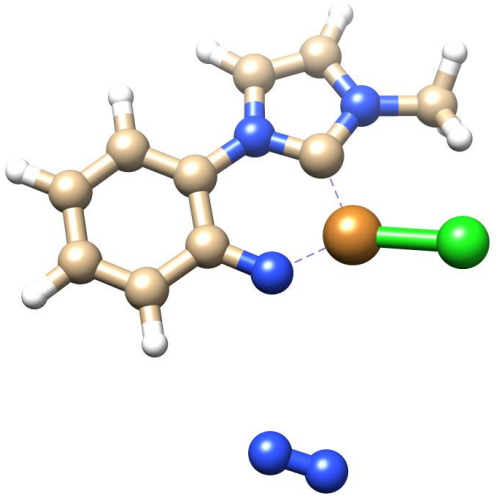


Sum of electronic and thermal Free Energies = -2760.586086 Ha
Freq mode 1 : - 512.12 cm^{-1}
Freq mode 2 : 37.67 cm^{-1}

Product state step 1

26
1-(2-azidophenyl)-4-methyl imidazolium IRC 1 product optimisation

C	2.64600	-1.56500	0.17100
C	1.58600	-0.60800	0.13700
C	1.96400	0.75700	-0.03100
C	3.29900	1.13300	-0.20400
C	4.30500	0.17900	-0.17400
C	3.96100	-1.17000	0.02400
H	2.38200	-2.60700	0.30900
H	5.34000	0.47400	-0.30800
N	0.90900	1.70500	-0.01100
C	-0.41600	1.39100	-0.01600
C	1.06200	3.08200	0.09300
C	-0.18400	3.61600	0.15800
H	2.02500	3.55800	0.13000
H	-0.50400	4.64200	0.25000
N	-1.08400	2.57300	0.09400
N	0.31800	-0.99800	0.28000
N	0.02100	-4.46600	0.62000
N	-1.03500	-4.64500	0.89200
H	3.55500	2.17400	-0.37200
H	4.74100	-1.92600	0.05100
Cu	-1.17400	-0.29900	-0.20400
Cl	-3.25000	-0.51900	-0.75700
C	-2.53100	2.75100	0.21900
H	-3.04200	1.88100	-0.19200
H	-2.80400	2.87000	1.27100
H	-2.82400	3.64400	-0.33600

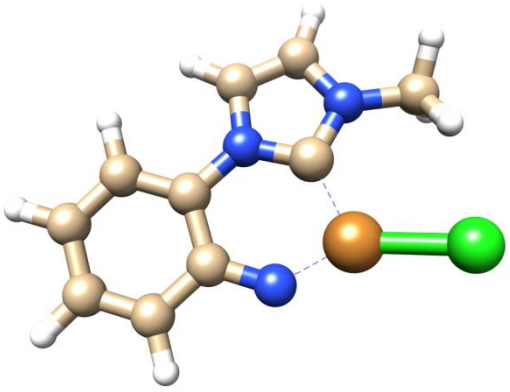


Sum of electronic and thermal Free Energies= -2760.645993 Ha
Freq mode 1 : 9.80 cm^{-1}

initial State step 2

24
1-(2-azidophenyl)-4-methyl imidazolium IRC 2 reactant optimisation

C	2.86700	-1.68000	0.37700
C	1.68100	-0.88400	0.32100
C	1.84400	0.47500	-0.07700
C	3.09300	0.98900	-0.43900
C	4.22400	0.18800	-0.38300
C	4.09400	-1.14700	0.03700
H	2.76800	-2.71300	0.68900
H	5.19000	0.59000	-0.66500
N	0.67200	1.27400	-0.07800
C	-0.59100	0.79800	0.11300
C	0.63600	2.65700	-0.20300
C	-0.66200	3.03300	-0.08300
H	1.52100	3.25000	-0.34900
H	-1.11400	4.01100	-0.11400
N	-1.40800	1.89000	0.11300
N	0.50000	-1.40900	0.64900
H	3.18400	2.01600	-0.77700
H	4.97300	-1.78400	0.08800
Cu	-1.11800	-0.98000	0.27300
Cl	-3.19200	-1.53300	0.02900
C	-2.84800	1.90300	0.37300
H	-3.28200	0.94900	0.07800
H	-3.03700	2.07100	1.43700
H	-3.29800	2.70900	-0.20800

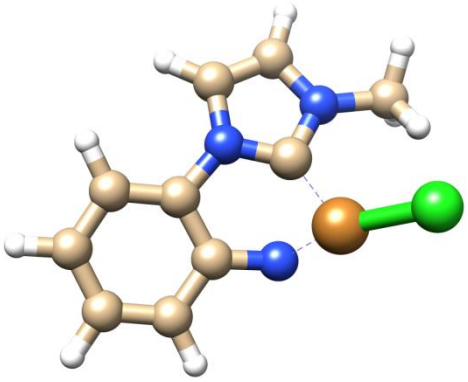


Sum of electronic and thermal Free Energies= -2651.116744 Ha
Freq mode 1 = 21.39 cm^{-1}

Transition State step 2

24
1-(2-azidophenyl)-4-methyl imidazolium TS Step 2 optimisation

C	2.66400	-1.60700	0.67900
C	1.55700	-0.74000	0.49300
C	1.80300	0.46900	-0.20700
C	3.05000	0.81100	-0.72600
C	4.11600	-0.05800	-0.52300
C	3.91100	-1.25400	0.18600
H	2.51300	-2.53800	1.21400
H	5.09600	0.18500	-0.91800
N	0.64500	1.26400	-0.25700
C	-0.53500	0.72200	0.14900
C	0.52300	2.64200	-0.37000
C	-0.74600	2.95100	0.00300
H	1.34300	3.27100	-0.67100
H	-1.25100	3.90300	0.05000
N	-1.38800	1.76800	0.33200
N	0.32500	-0.99800	1.01100
H	3.18400	1.73600	-1.27900
H	4.74700	-1.93100	0.34100
Cu	-1.14200	-1.05100	0.05000
Cl	-3.04900	-1.59300	-0.76400
C	-2.76600	1.67100	0.80500
H	-3.17500	0.70400	0.50800
H	-2.80300	1.77200	1.89400
H	-3.35800	2.46400	0.34500

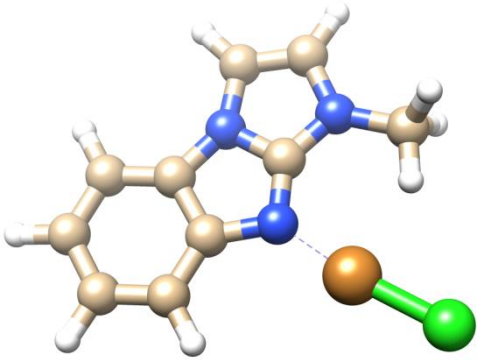


Sum of electronic and thermal Free Energies= -2651.109209 Ha
Freq mode 1 : -198.25 cm^{-1}
Freq mode 2 : 58.78 cm^{-1}

Product state Step 2

24
1-(2-azidophenyl)-4-methyl imidazolium IRC 2 product optimisation

C	2.28500	-1.54100	0.18900
C	1.48100	-0.40000	0.14500
C	2.06800	0.85800	-0.15200
C	3.42700	1.01300	-0.40400
C	4.21200	-0.13800	-0.35500
C	3.64700	-1.39200	-0.06300
H	1.85200	-2.51000	0.41400
H	5.27800	-0.06300	-0.54500
N	1.00100	1.76100	-0.11500
C	-0.11700	1.03400	0.18700
C	0.64000	3.10100	-0.26500
C	-0.70300	3.15900	-0.04900
H	1.34600	3.87700	-0.50600
H	-1.36800	4.00700	-0.07100
N	-1.18100	1.87600	0.23300
N	0.10100	-0.27000	0.35600
H	3.85800	1.98300	-0.62900
H	4.28800	-2.26700	-0.03300
Cu	-1.25700	-1.41600	0.76300
Cl	-2.97400	-2.50700	1.22200
C	-2.54700	1.46000	0.52800
H	-2.51700	0.37700	0.69300
H	-2.91500	1.95200	1.43100
H	-3.20800	1.67700	-0.31500



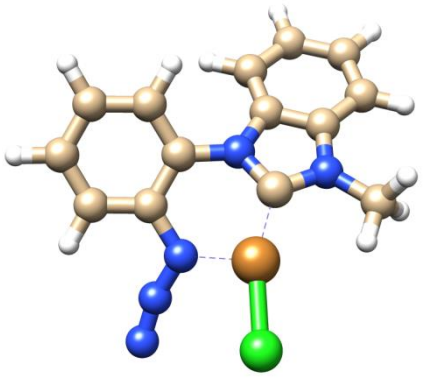
Sum of electronic and thermal Free Energies= -2651.175326 Ha
Freq mode 1 : 38.09 cm^{-1}

1-(2-azidophenyl)-4-methylbenzimidazolium (Mol 2)

initial state step 1 : this state corresponding to the optimization of IRC

32
1-(2-azidophenyl)-4-methylbenzimidazolium IRC 1 reactant optimisation

C	1.74200	2.94800	0.19900
C	1.08100	1.71300	0.22000
C	-0.26000	1.64900	-0.22300
C	-0.86900	2.80500	-0.72400
C	-0.20000	4.02600	-0.73600
C	1.10800	4.09700	-0.26000
H	2.77200	2.99700	0.53800
H	-0.69600	4.90800	-1.12600
N	-1.01100	0.43800	-0.17800
C	-0.48400	-0.79300	-0.49100
N	-1.51000	-1.67300	-0.36200
N	1.73000	0.51600	0.61800
N	2.78700	0.63600	1.28600
N	3.76900	0.45400	1.83700
H	-1.87500	2.73300	-1.12000
H	1.64600	5.04000	-0.26300
Cu	1.30100	-1.19600	-0.54800
Cl	3.14900	-2.27800	-0.57300
C	-1.35800	-3.10500	-0.57300
H	-0.29400	-3.29000	-0.72700
H	-1.70000	-3.65500	0.30900
H	-1.92600	-3.43200	-1.44900
C	-2.68200	-1.03800	0.03700
C	-2.36900	0.32500	0.17400
C	-3.32100	1.23400	0.63600
H	-3.08400	2.28100	0.78400
C	-4.59400	0.74000	0.92200
H	-5.35500	1.42400	1.28400
C	-4.91000	-0.61800	0.75800
H	-5.91300	-0.96400	0.98700
C	-3.95500	-1.53200	0.31800
H	-4.18900	-2.58500	0.20800

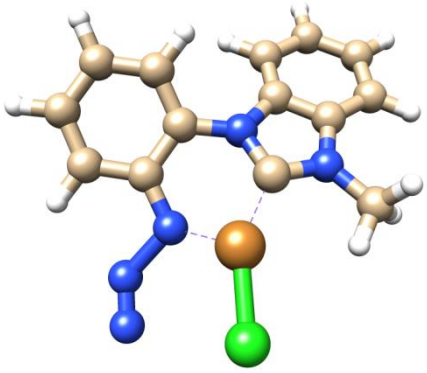


Sum of electronic and thermal Free Energies= -2914.210600 Ha
Freq mode 1 : 27.49 cm^{-1}

Transition state step 1

32
1-(2-azidophenyl)-4-methylbenzimidazolium TS Step 1 optimisation

C	1.80800	2.89400	0.12300
C	1.16900	1.63000	0.10400
C	-0.21000	1.62400	-0.25500
C	-0.84300	2.79400	-0.68700
C	-0.18500	4.01700	-0.66300
C	1.14200	4.05700	-0.22800
H	2.84900	2.93400	0.42000
H	-0.69400	4.91800	-0.98900
N	-0.95200	0.40100	-0.24000
C	-0.39800	-0.82200	-0.48400
N	-1.39200	-1.73700	-0.36000
N	1.81400	0.43100	0.35700
N	3.24700	0.68500	1.10100
N	4.11800	-0.01400	1.28500
H	-1.85800	2.73400	-1.06100
H	1.67800	5.00100	-0.19000
Cu	1.42100	-1.18100	-0.46000
Cl	3.08100	-2.52500	-0.36000
C	-1.20000	-3.17300	-0.50900
H	-0.12900	-3.35900	-0.59000
H	-1.59000	-3.69400	0.37000
H	-1.70800	-3.54000	-1.40500
C	-2.59200	-1.11800	-0.03100
C	-2.31700	0.25600	0.07200
C	-3.31000	1.14800	0.48700
H	-3.10700	2.20200	0.62500
C	-4.57500	0.62600	0.74600
H	-5.36300	1.29600	1.07100
C	-4.85200	-0.74400	0.60300
H	-5.85300	-1.11100	0.80800
C	-3.86000	-1.64200	0.21900
H	-4.06200	-2.70400	0.12800

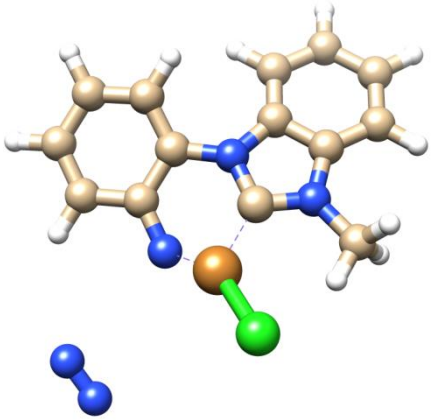


Sum of electronic and thermal Free Energies= -2914.194162 Ha
Freq Mode 1 : -518.60 cm $^{-1}$
Freq Mode 2 : 39.32 cm $^{-1}$

Product state step 1

32
1-(2-azidophenyl)-4-methylbenzimidazolium IRC 1 product optimisation

C	1.63900	2.92500	0.21200
C	0.92200	1.69400	0.14100
C	-0.46300	1.77600	-0.19400
C	-1.05400	2.98700	-0.56300
C	-0.32900	4.16900	-0.48600
C	1.01200	4.12500	-0.07000
H	2.68700	2.88700	0.48600
H	-0.79100	5.10800	-0.76600
N	-1.15500	0.53700	-0.20200
C	-0.51900	-0.66600	-0.27100
N	-1.44900	-1.64100	-0.10600
N	1.53100	0.52700	0.38900
N	4.91000	0.93400	1.17100
N	5.18400	-0.05800	1.57500
H	-2.06900	3.00200	-0.94000
H	1.58500	5.04500	-0.00200
Cu	1.31500	-0.96500	-0.45200
Cl	2.09300	-2.79100	-1.30300
C	-1.21200	-3.08100	-0.09100
H	-0.15500	-3.26900	-0.27500
H	-1.50200	-3.49100	0.88000
H	-1.80000	-3.56000	-0.87900
C	-2.70300	-1.07000	0.06100
C	-2.52800	0.32300	0.02300
C	-3.60800	1.17900	0.25500
H	-3.49000	2.25300	0.29300
C	-4.85300	0.59600	0.47400
H	-5.70800	1.23800	0.65900
C	-5.02800	-0.79900	0.47000
H	-6.01700	-1.21300	0.63800
C	-3.95200	-1.65700	0.27200
H	-4.07500	-2.73400	0.29100

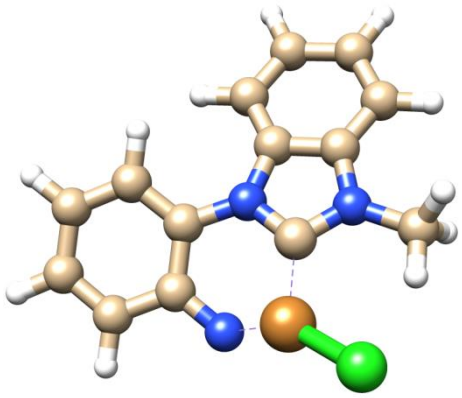


Sum of electronic and thermal Free Energies= -2914.251526 Ha
Freq Mode 1 : 6.64 cm^{-1}

initial State step 2

30
1-(2-azidophenyl)-4-methylbenzimidazolium IRC 2 Reactant optimisation

C	1.89300	3.09800	0.57100
C	1.25700	1.82500	0.48700
C	-0.05600	1.80000	-0.07200
C	-0.63300	2.94300	-0.63200
C	0.01600	4.16800	-0.53900
C	1.26900	4.23500	0.09100
H	2.88100	3.14400	1.01500
H	-0.43600	5.05500	-0.96900
N	-0.68300	0.52600	-0.08600
C	0.00800	-0.64000	0.05200
N	-0.89300	-1.65100	0.14700
N	1.87000	0.71700	0.92400
H	-1.57100	2.87000	-1.16800
H	1.78000	5.18900	0.17400
Cu	1.85900	-0.84600	0.19100
Cl	2.83800	-2.68500	-0.37400
C	-0.60000	-3.07000	0.32500
H	0.47900	-3.21300	0.32500
H	-1.02400	-3.41700	1.27100
H	-1.03300	-3.64100	-0.50000
C	-2.18100	-1.14100	0.06000
C	-2.06300	0.25200	-0.06800
C	-3.20300	1.06100	-0.08800
H	-3.14000	2.13900	-0.12300
C	-4.44000	0.42600	-0.02400
H	-5.34100	1.03000	-0.03600
C	-4.55100	-0.97300	0.06300
H	-5.53500	-1.42900	0.10500
C	-3.42100	-1.78100	0.11600
H	-3.49700	-2.85900	0.20700

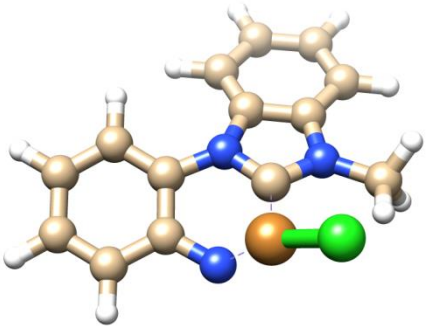


Sum of electronic and thermal Free Energies= -2804.720673 Ha
Freq Mode 1 : 35.72 cm $^{-1}$

Transition State step 2

30
1-(2-azidophenyl)-4-methylbenzimidazolium Step 2 TS optimisation

C	1.96300	2.94400	0.70100
C	1.26200	1.72200	0.53400
C	0.00600	1.78400	-0.13000
C	-0.49200	2.96600	-0.67800
C	0.21800	4.14800	-0.49400
C	1.43100	4.12700	0.21300
H	2.91800	2.92600	1.21600
H	-0.15900	5.07500	-0.91200
N	-0.62600	0.52200	-0.17600
C	0.09600	-0.59100	0.13300
N	-0.77600	-1.60900	0.35700
N	1.73500	0.54700	1.02000
H	-1.40500	2.96400	-1.26100
H	1.98400	5.05100	0.35600
Cu	1.94400	-0.87400	0.02000
Cl	2.81100	-2.62700	-0.86000
C	-0.42700	-2.98000	0.70900
H	0.65400	-3.09400	0.63800
H	-0.76400	-3.20400	1.72500
H	-0.89500	-3.67300	0.00600
C	-2.07800	-1.15600	0.16600
C	-1.99600	0.20700	-0.16700
C	-3.15100	0.96200	-0.37200
H	-3.11200	2.02000	-0.59000
C	-4.37400	0.30300	-0.26400
H	-5.28900	0.86500	-0.41800
C	-4.44900	-1.06600	0.04200
H	-5.42100	-1.54400	0.11200
C	-3.30100	-1.81900	0.26800
H	-3.35400	-2.87300	0.52000

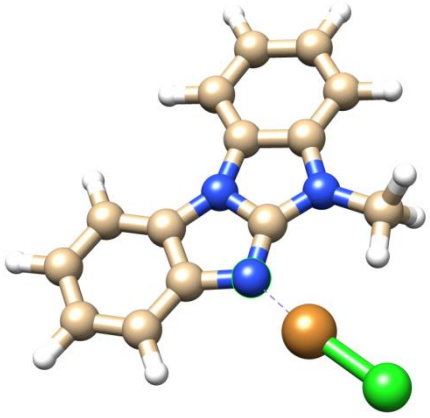


Sum of electronic and thermal Free Energies= -2804.718635 Ha
Freq Mode 1 : -131.69 cm^{-1}
Freq Mode 2 : 55.79 cm^{-1}

Product state Step 2

30
1-(2-azidophenyl)-4-methylbenzimidazolium IRC Step 2 product optimisation

C	2.03800	2.51900	0.15200
C	0.99100	1.59900	0.16000
C	-0.34100	2.04400	-0.04300
C	-0.65700	3.38200	-0.25400
C	0.40400	4.28800	-0.25900
C	1.72700	3.86100	-0.05900
H	3.06000	2.18900	0.30600
H	0.20000	5.34100	-0.42000
N	-1.11400	0.88000	0.02600
C	-0.24700	-0.15700	0.25700
N	-0.93700	-1.32800	0.33700
N	1.02500	0.20500	0.34700
H	-1.67900	3.71000	-0.40800
H	2.52800	4.59400	-0.06900
Cu	2.36400	-0.99400	0.65100
Cl	3.72500	-2.53300	1.00100
C	-0.33100	-2.62900	0.57400
H	0.74800	-2.46300	0.66900
H	-0.71000	-3.07100	1.50000
H	-0.51900	-3.30300	-0.26600
C	-2.29200	-1.02300	0.15000
C	-2.41600	0.37400	-0.04800
C	-3.65100	0.97100	-0.26100
H	-3.74300	2.04100	-0.41200
C	-4.77300	0.13700	-0.27200
H	-5.75300	0.57200	-0.43600
C	-4.65400	-1.24500	-0.07700
H	-5.54500	-1.86400	-0.09200
C	-3.41100	-1.84800	0.13700
H	-3.32400	-2.91900	0.28800



Sum of electronic and thermal Free Energies= -2804.792379 Ha
Freq Mode 1 : 31.94 cm^{-1}

Table S5. Summary of DFT calculations

		Step 1			Step 2		
		Reactant	TS	Product	Reactant	TS	Product
Mol 1	Energies (Ha)	-2760.599834	-2760.586086	-2760.645993	-2651.116744	-2651.109209	-2651.175326
	Relative energies ($kJ.mol^{-1}$)	0	36.1	-121.2	0	19.8	-153.8
	Relative energies ($kcal.mol^{-1}$)	0	8.6	-29.0	0	4.7	-36.8
	Frequencies (cm^{-1})	27.86	- 512.12	9.80	21.39	-198.25	38.09
Mol 2	Energies (Ha)	-2914.210600	-2914.194162	-2914.251526	-2804.720673	-2804.718635	-2804.792379
	Relative energies ($kJ.mol^{-1}$)	0	43.2	-107.5	0	5.4	-188.3
	Relative energies ($kcal.mol^{-1}$)	0	10.3	-25.7	0	1.3	-45.0
	Frequencies (cm^{-1})	27.49	-518.60	6.64	35.72	-131.69	31.94

Free energies.