Electronic Supplementary Material (ESI) for ChemComm.

Mesomeric Betaine – N-Heterocyclic Carbene Interconversions of 1,2,4-Triazolium-phenolates. Sulfur, Selenium, and Borane Adduct Formations

Ming Liu,[a] Martin Nieger,[b] and Andreas Schmidt[a]*

[a] Clausthal University of Technology, Institute of Organic Chemistry, Leibnizstrasse 6, D-38678 Clausthal-Zellerfeld, Germany. E-mail: schmidt@ioc.tu-clausthal.de

[b] University of Helsinki, Laboratory of Inorganic Chemistry, Department of Chemistry, P.O. Box 55 (A.I. Virtasen aukio1), FIN-00014 University of Helsinki, Finland.

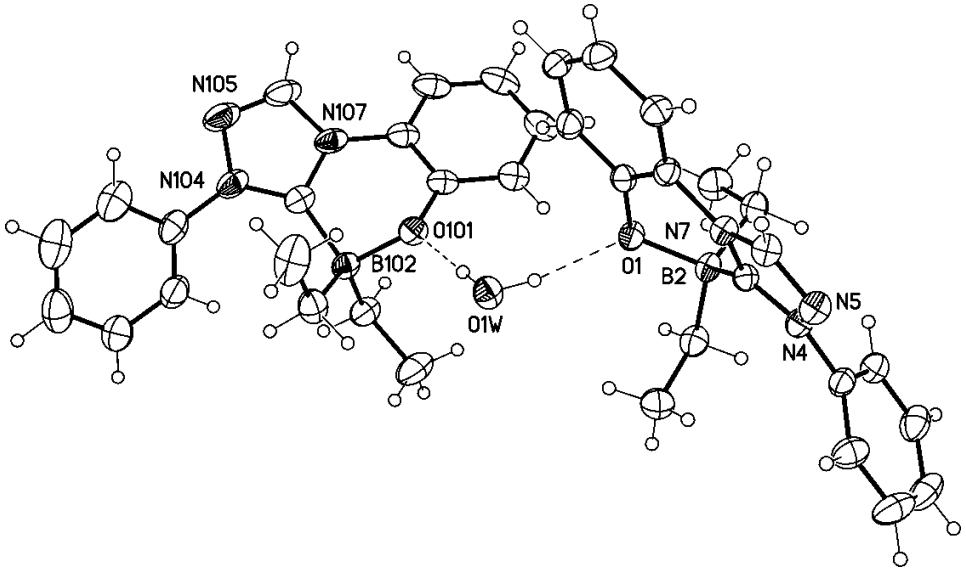
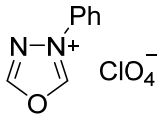


Fig. 5. Molecular drawing of the new heterocyclic ring system **15a** showing the two crystallographic independent molecules linked by a water molecule (displacement parameters are drawn at 50% probability level).

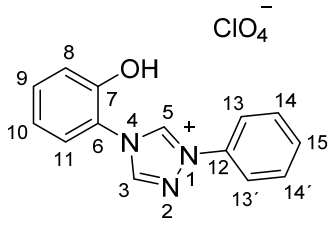
General considerations. Flash-chromatography was performed with silica gel 60 (0.040-0.063 mm). Nuclear magnetic resonance (NMR) spectra were obtained with a Bruker Avance 400 and Bruker Avance III 600 MHz. ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz. ^{13}C NMR spectra were recorded at 100 MHz or 150 MHz, with the solvent peak or tetramethylsilane used as the internal reference. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Signal orientations in DEPT experiments were described as follows: o = no signal; + = up (CH, CH_3); - = down (CH_2). The numbering of the compounds is not always in accordance with IUPAC rules to allow comparisons ("spectroscopic numbering"). FT-IR spectra were obtained on a Bruker Alpha T in the range of 400 to 4000 cm^{-1}. The mass spectra were measured with a Varian 320 MS Triple Quad GC/MS/MS with a Varian 450-GC. The electrospray ionisation mass spectra (ESIMS) were measured with an Agilent LCMSD series HP 1100 with APIES at fragmentor voltages as indicated. Samples were sprayed from MeOH at 4000 V capillary voltage and fragmentor voltages of 30 V, unless otherwise noted. Melting points are uncorrected and were determined in an apparatus according to Dr. Tottoli (Büchi). The HR-MS spectra were measured on a Bruker Daltonik Tesla-Fourier transform - ion cyclotron resonance mass spectrometer with electrospray ionisation.

3-Phenyl-1,3,4-oxadiazolium perchlorate 10.[1]

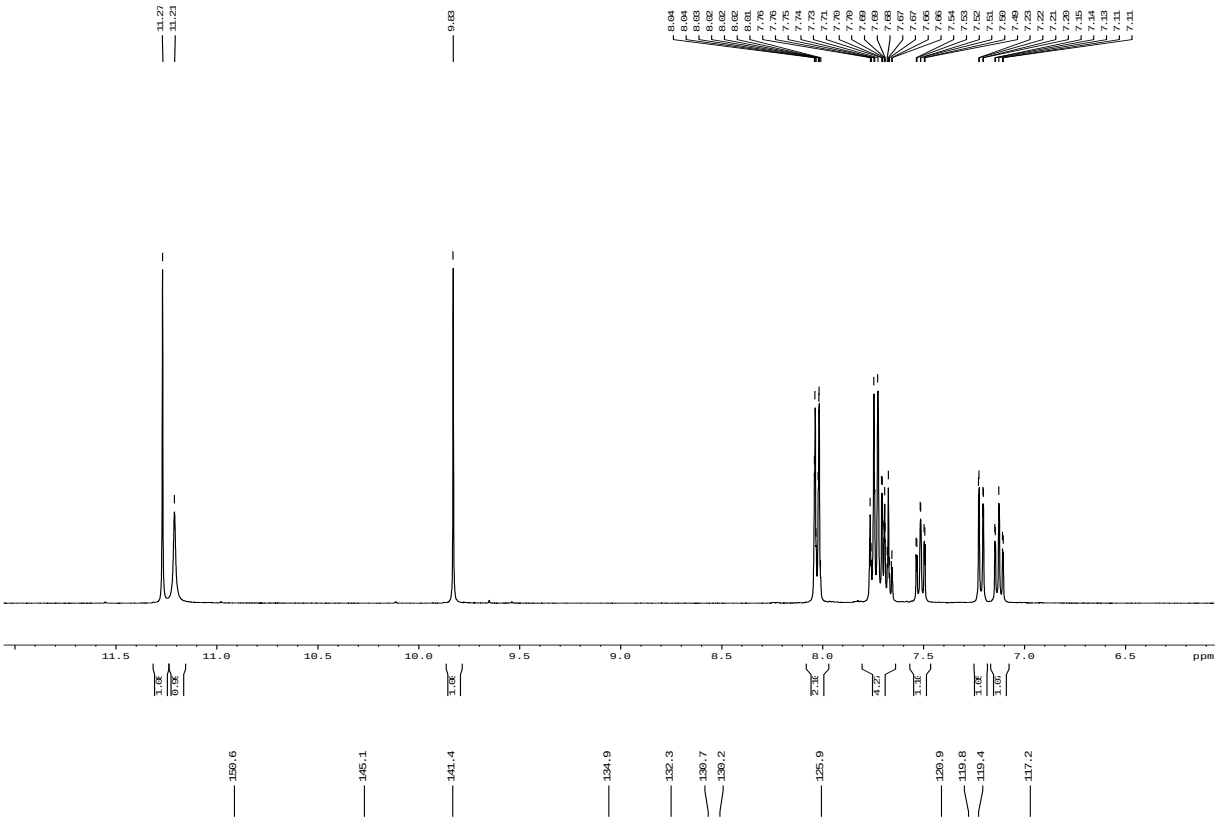


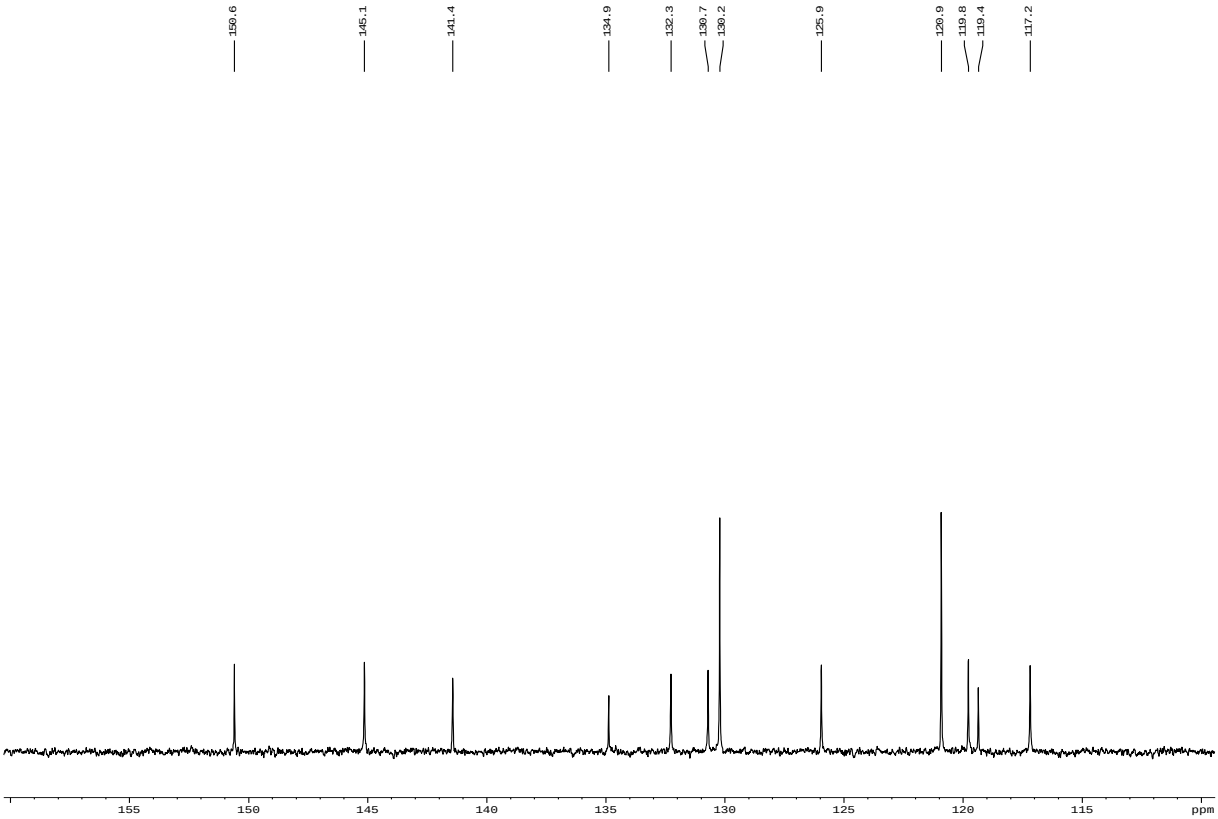
A sample of 0.893 g (5.44 mmol) of N,N'-diformyl-N-phenylhydrazine was treated under an inert atmosphere with 5.2 mL (54.4 mmol) of acetic anhydride. After cooling to 0 °C, 0.37 mL (6.5 mmol) of perchloric acid (70%) were added dropwise, whereupon a precipitate formed. Stirring was continued for one additional hour at rt. Then, 20 mL of anhyd. diethyl ether was added to the mixture. The precipitate was filtered off under an inert atmosphere and washed with Et_2O. Yield: 0.994 g (74%) of a colorless solid. This compound is hygroscopic and was continuously kept under an inert atmosphere.

4-(2-Hydroxyphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate 11a:

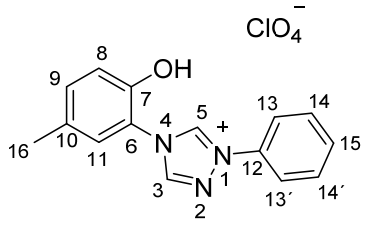


A solution of 0.450 g (4.12 mmol) of 2-aminophenol and 1.016 g (4.12 mmol) of 3-phenyl-1,3,4-oxadiazolium perchlorate in 20 mL of anhydrous THF was heated at 100 °C overnight. Then the solvent was distilled off and the residue was treated with 20 mL of diethyl ether. The precipitated solid was filtered off and dried *in vacuo*. Yield: 0.833 g (60%) of a yellowish solid, mp: 154 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.27 (s, 1 H, 5-H), 11.21 (s, 1 H, OH), 9.83 (s, 1 H, 3-H), 8.01 - 8.04 (m, 2 H, 13/13´-H), 7.66 - 7.76 (m, 4 H, 14/14´/15/11-H), 7.52 (ddd, J_1 = 1.6 Hz, J_2 = 7.7 Hz, J_3 = 8.2 Hz, 1 H, 9-H), 7.22 (dd, J_1 = 1.1 Hz, J_2 = 8.2 Hz, 1 H, 8-H), 7.13 (td, J_1 = 1.1 Hz, J_2 = 7.7 Hz, 1 H, 10-H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 150.6 (o, C-7), 145.1 (+, C-3), 141.4 (+, C-5), 134.9 (o, C-12), 132.3 (+, C-9), 130.7 (+, C-15), 130.2 (+, C-14/C-14´), 125.9 (+, C-11), 120.9 (+, C-13/C-13´), 119.8 (+, C-10), 119.4 (o, C-6), 117.2 (+, C-8) ppm; IR (ATR): $\tilde{\nu}$ = 3167, 1565, 1338, 1093, 1074, 1034, 999, 773, 755, 741, 639, 551, 499, 468 cm^{-1}; MS (ESI 10 V): *m/z* (%) = 436.0 (100) $[M^+ + 2ClO_4]^-$. HR-ESI-MS: calcd for $C_{14}H_{12}N_3O^+$ 238.0980. Found 238.0975.

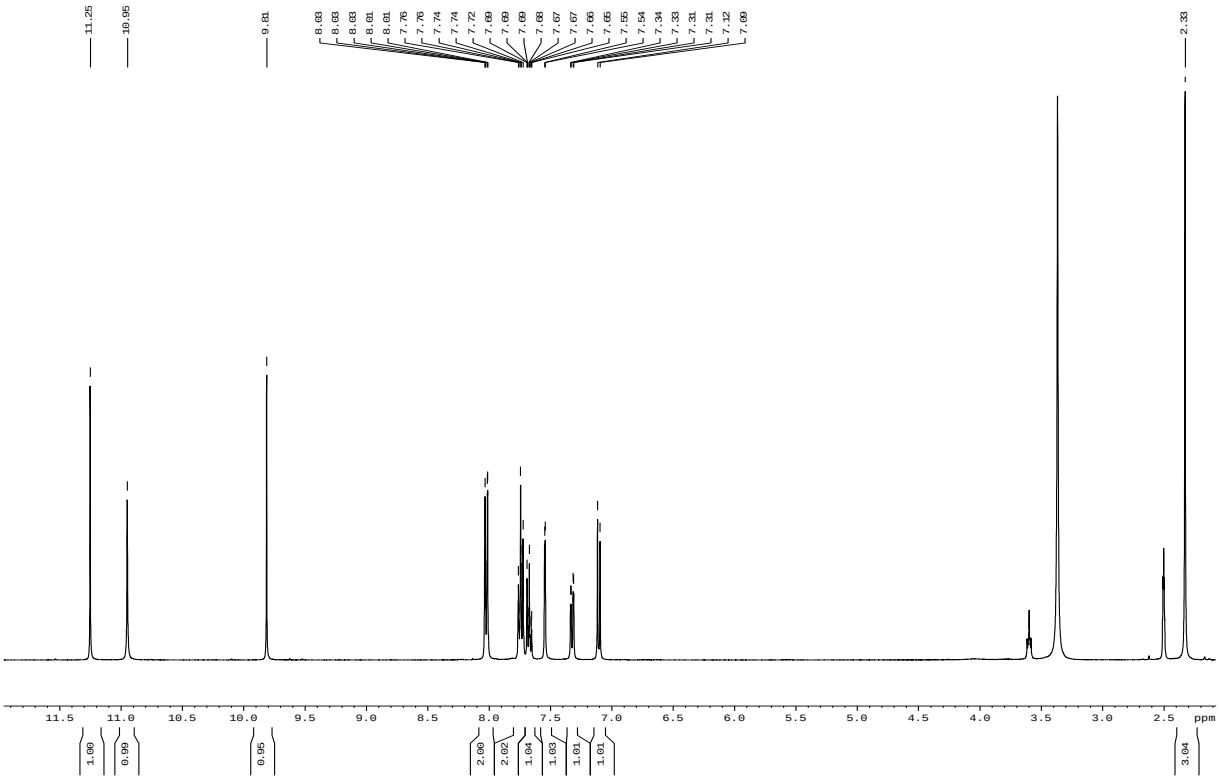

11.27
11.21
9.83
8.04
8.04
8.03
8.02
8.02
8.02
8.01
7.76
7.76
7.75
7.74
7.73
7.71
7.70
7.69
7.69
7.68
7.67
7.67
7.66
7.66
7.64
7.63
7.52
7.51
7.50
7.49
7.23
7.22
7.21
7.20
7.15
7.14
7.13
7.11
7.11
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
ppm
1.08
1.08
0.98
1.06
2.38
4.27
1.38
1.08
1.06

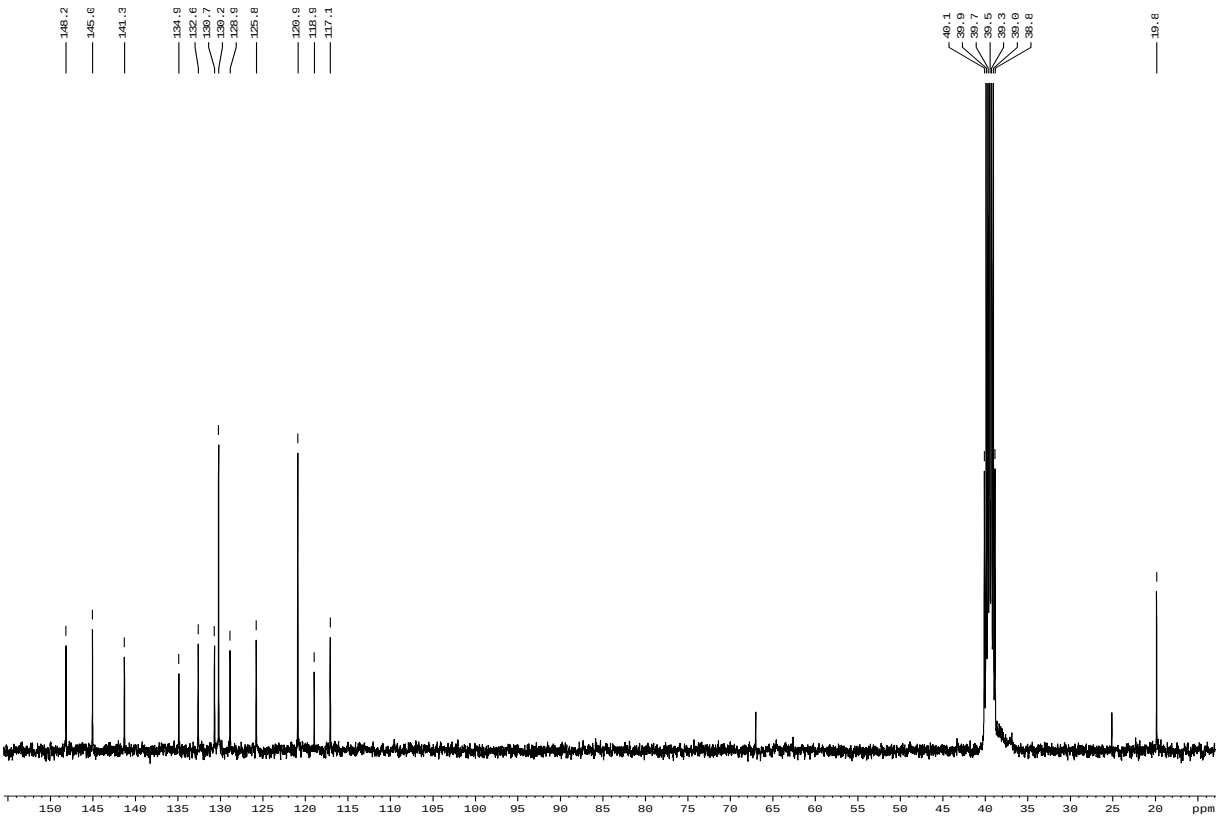

150.6
145.1
141.4
134.9
132.3
130.7
130.2
125.9
120.9
119.8
119.4
117.2
155
150
145
140
135
130
125
120
115
ppm

4-(2-Hydroxy-5-methylphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate 11b:

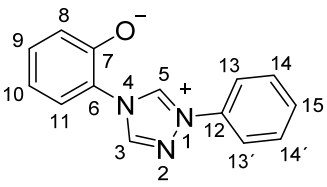


A solution of 0.530 g (4.30 mmol) of 2-amino-4-methylphenol and 1.060 g (4.30 mmol) of 3-phenyl-1,3,4-oxadiazolium perchlorate in 20 mL of anhydrous THF was heated at 100 °C overnight under an inert atmosphere. Then the solvent was distilled off and the residue was treated with 20 mL of diethyl ether. The precipitated solid was filtered off and dried *in vacuo.* Yield: 0.935 g (62%) of a yellowish solid, mp: 156 °C; ^{1}H NMR (400 MHz, DMSO-d$_6$): δ = 11.25 (s, 1 H, 5-H), 10.95 (s, 1 H, OH), 9.81 (s, 1 H, 3-H), 8.01 - 8.03 (m, 2 H, 13/13´-H), 7.72 - 7.76 (m, 2 H, 14/14´-H), 7.67 (tt, J_1 = 1.1 Hz, J_2 = 7.3 Hz, 1 H, 15-H), 7.54 (d, J = 1.6 Hz, 1 H, 11-H), 7.32 (dd, J_1 = 1.6 Hz, J_2 = 8.4 Hz, 1 H, 9-H), 7.11 (d, J = 8.4 Hz, 1 H, 8-H), 2.33 (s, 3 H, 16-H) ppm; ^{13}C NMR (100 MHz, DMSO-d$_6$): δ = 148.2 (o, C-7), 145.0 (+, C-3), 141.3 (+, C-5), 134.9 (o, C-12), 132.6 (+, C-9), 130.7 (+, C-15), 130.2 (+, C-14/C-14´), 128.9 (o, C-10), 125.8 (+, C-11), 120.9 (+, C-13/C-13´), 118.9 (o, C-6), 117.1 (+, C-8), 19.8 (+, C-16) ppm; IR (ATR): $\bar{\nu}$ = 3241, 1567, 1522, 1289, 1268, 1144, 1123, 1108, 1095, 1046, 759, 666, 620, 475 cm^{-1}; MS (ESI 10 V): *m/z* (%) = 450.0 (100) $[M^+ + 2ClO_4]^-$. HR-ESI-MS: calcd for $C_{15}H_{14}N_3O^+$ 252.1137. Found 252.1137.

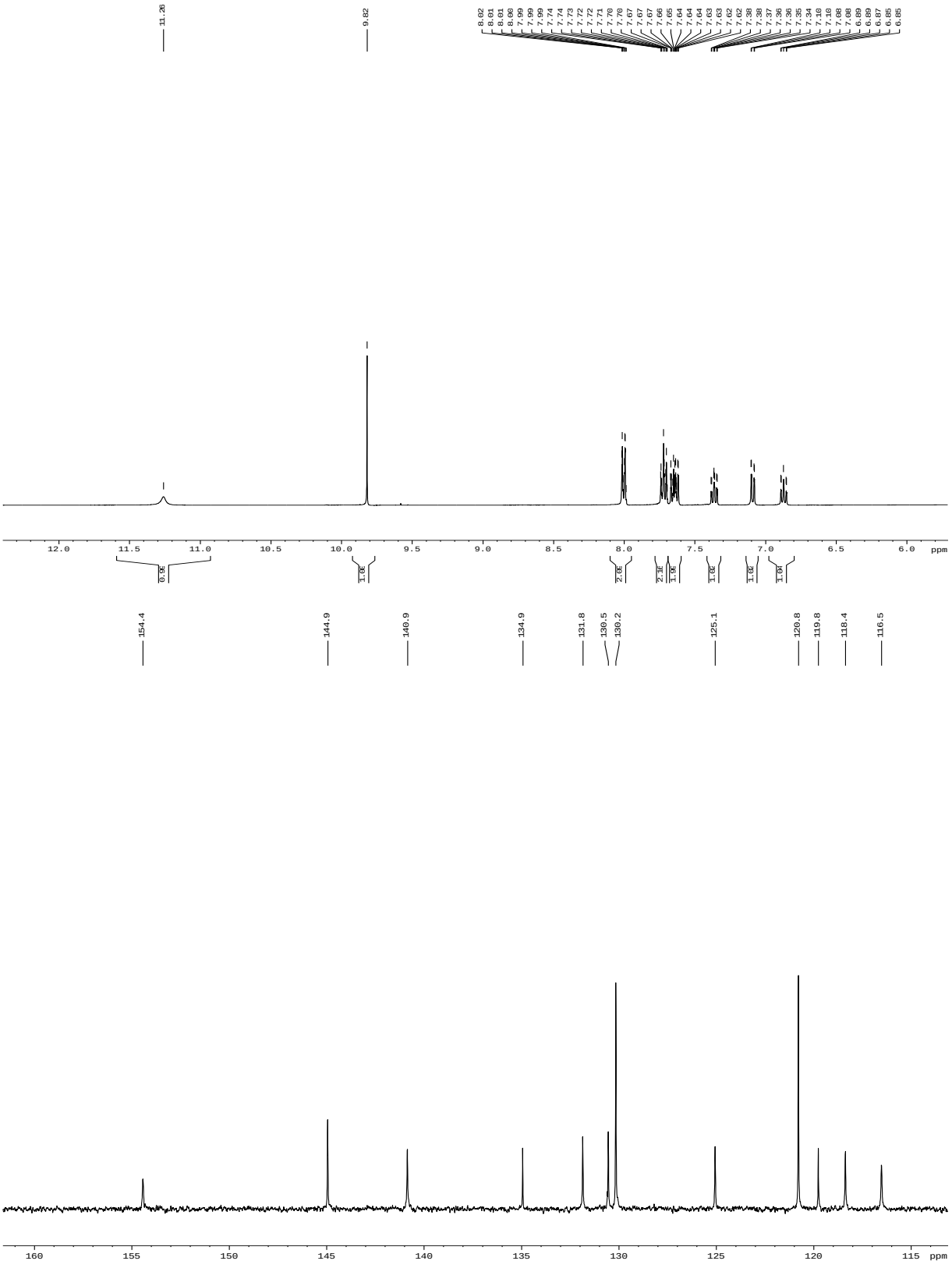

11.25
10.95
9.81
8.03
8.03
8.03
8.01
8.01
7.76
7.76
7.74
7.74
7.72
7.69
7.69
7.68
7.67
7.67
7.66
7.65
7.55
7.54
7.34
7.33
7.31
7.31
7.12
7.09
2.33
ppm
1.00
0.99
0.95
2.00
2.02
1.04
1.03
1.01
1.01
3.04


148.2
145.6
141.3
134.9
132.6
130.7
130.2
128.9
125.8
120.9
118.9
117.1
40.1
39.9
39.7
39.5
39.3
39.0
38.8
19.8
ppm

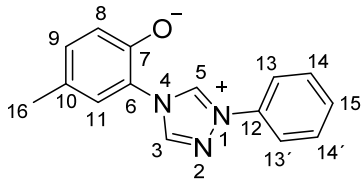
2-(1-Phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate 12a:



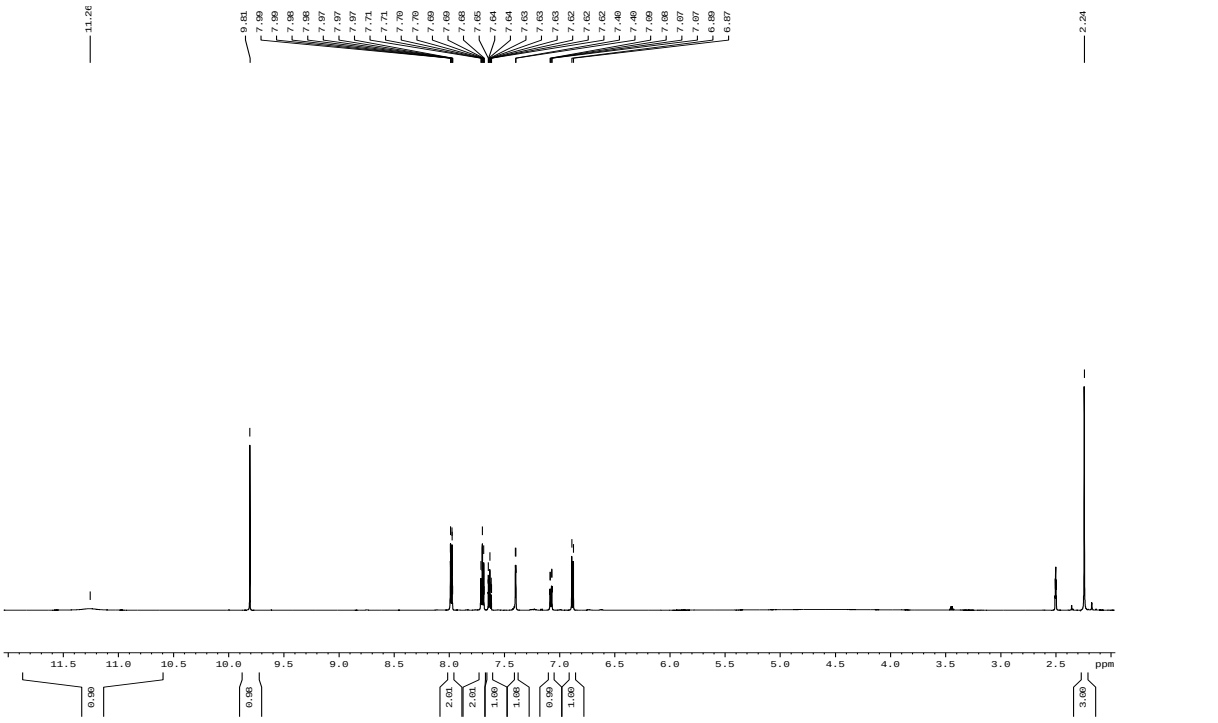
A sample of 0.338 g (1.00 mmol) of 4-(2-hydroxyphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate in 10 mL of MeOH was cooled to 0 °C. Then, 1.2 equiv of a 3 M solution of KOH in MeOH was added dropwise. The resulting precipitate was filtered off and the organic phase was concentrated *in vacuo*. The resulting solid was filtered off and dried *in vacuo.* Yield: 0.206 g (87%) of a yellow solid, mp: 155 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.26 (s, 1 H, 5-H), 9.82 (s, 1 H, 3-H), 7.99 - 8.02 (m, 2 H, 13/13´-H), 7.70 - 7.74 (m, 2 H, 14/14´-H), 7.62 - 7.67 (overlapped signals, 2 H, 15/11-H), 7.37 (ddd, J_1 = 1.7 Hz, J_2 = 7.7 Hz, J_3 = 8.4 Hz, 1 H, 9-H), 7.09 (dd, J_1 = 1.1 Hz, J_2 = 8.4 Hz, 1 H, 8-H), 6.87 (td, J_1 = 1.1 Hz, J_2 = 7.7 Hz, 1 H, 10-H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 154.4 (o, C-7), 144.9 (+, C-3), 140.9 (+, C-5), 134.9 (o, C-12), 131.8 (+, C-9), 130.5 (+, C-15), 130.2 (+, C-14/C-14´), 125.1 (+, C-11), 120.8 (+, C-13/C-13´), 119.8 (o, C-6), 118.4 (+, C-8), 116.5 (+, C-10) ppm; IR (ATR): $\bar{\nu}$ = 2902, 1592, 1564, 1479, 1450,1334, 1327, 1270, 977, 848, 746, 733, 629, 477, 458 cm^{-1}; MS (ESI 30 V): *m/z* (%) = 238.1 (100) $[M+H]^+$. HR-ESI-MS calcd for $C_{14}H_{13}N_3O^+$: 238.0980. Found 238.0984.

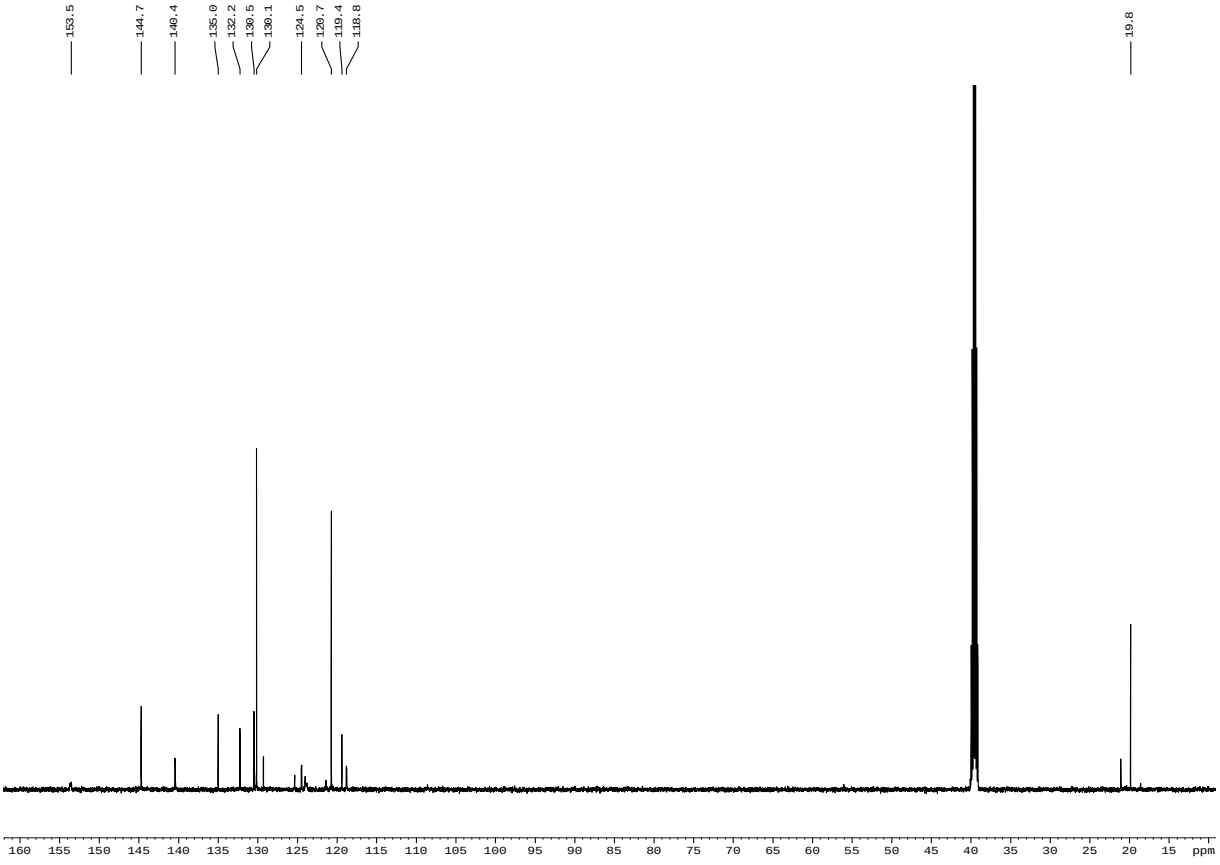

11.26
9.82
8.02
8.01
8.01
8.00
7.99
7.99
7.99
7.74
7.74
7.73
7.72
7.72
7.71
7.70
7.70
7.67
7.67
7.67
7.66
7.65
7.64
7.64
7.64
7.63
7.63
7.62
7.62
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.10
7.10
7.08
7.08
6.89
6.89
6.87
6.85
6.85
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
ppm
0.98
1.00
2.86
2.16
1.00
1.00
1.00
1.00
154.4
144.9
140.9
134.9
131.8
130.5
130.2
125.1
120.8
119.8
118.4
116.5
160
155
150
145
140
135
130
125
120
115
ppm

4-Methyl-2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate 12b:

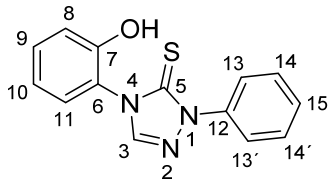


A sample of 0.351 g (1.00 mmol) of 4-(2-hydroxy-5-methylphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate in 10 mL of MeOH was cooled to 0 °C. Then, 1.2 equiv of a 3 M solution of KOH in MeOH was added dropwise. The resulting precipitate was filtered off and the organic phase was evaporated to dryness. The resulting solid was dried *in vacuo*. Yield: 0.153 g (61%) of a yellow solid, mp: 188°C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 11.26 (s, 1 H, 5-H), 9.81(s, 1 H, 3-H), 7.97 - 7.99 (m, 2 H, 13/13´-H), 7.68 - 7.71 (m, 2 H, 14/14´-H), 7.63 (tt, , J_1 = 1.1 Hz, J_2 = 7.4 Hz, 1 H, 15-H), 7.40 (d, J = 1.8 Hz, 1 H, 11-H), 7.08 (dd, J_1 = 1.8 Hz, J_2 = 8.5 Hz, 1 H, 9-H), 6.88 (d, J = 8.5 Hz, 1 H, 8-H), 2.24 (s, 3 H, 16-H) ppm; ^{13}C NMR (150 MHz, DMSO-d_6): δ = 153.5 (o, C-7), 144.7 (+, C-3), 140.4 (+, C-5), 135.0 (o, C-12), 132.2 (+, C-9), 130.5 (+, C-15), 130.1 (+, C-14/C-14´), 124.5 (+, C-11), 120.7 (+, C-13/C-13´), 119.4 (o, C-6), 118.8 (+, C-8), 19.8 (+, C-16) ppm; IR (ATR): $\bar{\nu}$ = 3136, 1569, 1275, 1100, 1082, 1047, 988, 872, 757, 665, 629, 619, 455 cm^{-1}; MS (ESI 30 V): *m/z* (%) = 252.1 (100) $[M+H]^-$. HR-ESI-MS calcd for $C_{15}H_{15}N_3O^+$: 252.1137. Found 252.1129.


11.26
9.81
7.99
7.99
7.98
7.98
7.97
7.97
7.97
7.71
7.71
7.70
7.70
7.69
7.69
7.68
7.65
7.64
7.64
7.63
7.63
7.63
7.62
7.62
7.62
7.40
7.40
7.09
7.08
7.07
7.07
6.89
6.87
2.24
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 ppm
0.90
0.98
2.01
2.01
1.00
1.00
0.99
1.00
3.00


153.5
144.7
140.4
135.0
132.2
130.5
130.1
124.5
120.7
119.4
118.8
19.8
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 ppm

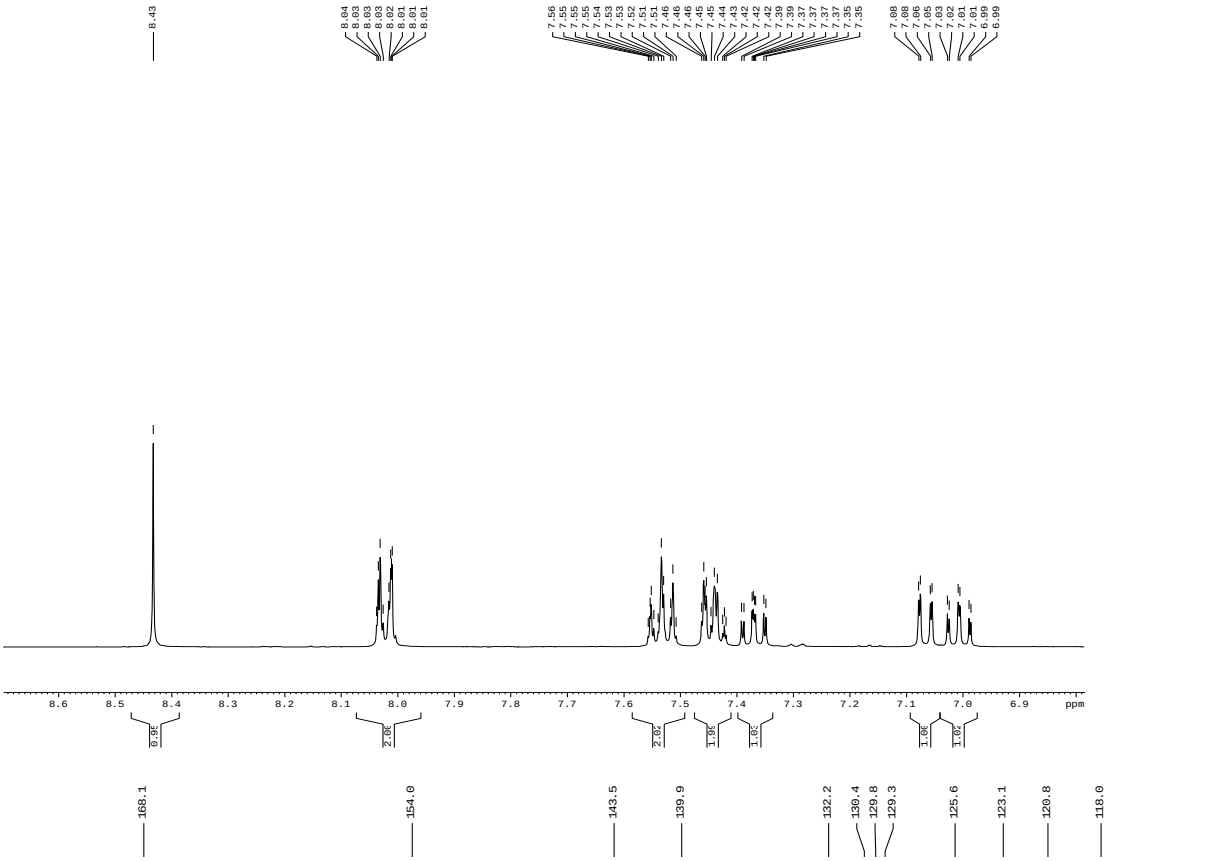
4-(2-Hydroxyphenyl)-2-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione 13a

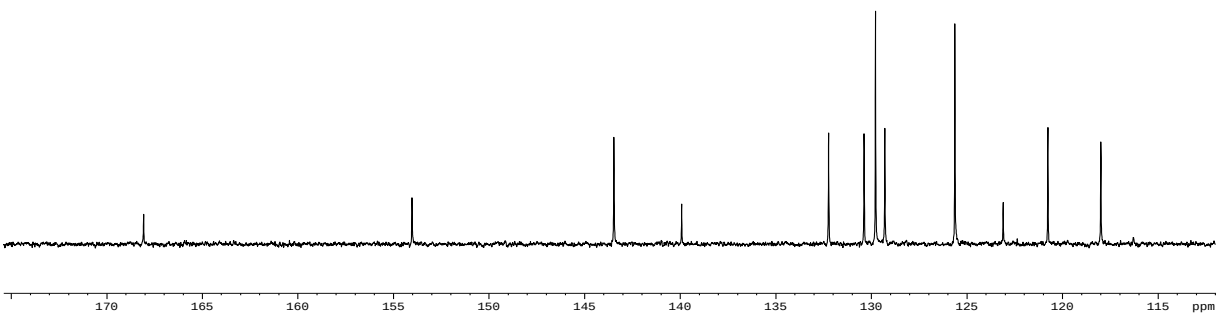


Method B: Under a nitrogen atmosphere a solution of 0.169 g (0.50 mmol) of 4-(2-hydroxyphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate and 19.2 mg (0.6 mmol) of sulfur in 10 mL of dry THF was cooled to 0 °C. Then, a solution of potassium 2-methylbutan-2-olate (0.32 mL, 0.55 mmol) was added slowly by using a syringe. The mixture was stirred at rt for 30 min and heated at 100 °C for 3 h. After cooling, the solvent was evaporated *in vacuo*. The product was separated by column chromatography (silica gel, ethyl acetate/petroleum ether). Yield: 0.079 g (59%) of a yellow solid, mp: 182 °C.

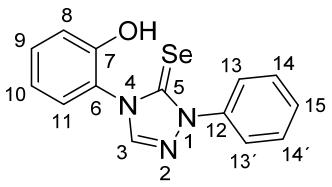
Method D: A flask was charged with 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate (0.119 g, 0.5 mmol), sulfur (32 mg, 1.0 mmol), and dry toluene (10 mL). Then, the mixture was stirred at reflux temperature for 8 h. After evaporation, the resulting precipitate was purified by column chromatography (silica gel, ethyl acetate/petroleum ether). Yield: 0.135 g (50 %), mp: 182 °C.

^{1}H NMR (400 MHz, MeOD-d_4): δ = 8.43 (s, 1 H, 3-H), 8.01 - 8.04 (m, 2 H, 13/13´-H), 7.51 - 7.56 (m, 2 H, 14/14´-H), 7.42 - 7.46 (overlapped signals, 2 H, 15/11-H), 7.37 (ddd, J_1 = 1.7 Hz, J_2 = 7.5 Hz, J_3 = 8.3 Hz, 1 H, 9-H), 7.07 (dd, J_1 = 1.2 Hz, J_2 = 8.3 Hz, 1 H, 8-H), 7.01 (td, J_1 = 1.2 Hz, J_2 = 7.5 Hz, 1H, 10-H) ppm; ^{13}C NMR (100 MHz, MeOD-d_4): δ = 168.1 (o, C-5), 154.0 (o, C-7), 143.5 (+, C-3), 139.9 (o, C-12), 132.2 (+ C-9), 130.4 (+, C-15), 129.8 (+, C-14/C-14´), 129.3 (+, C-11), 125.6 (+, C-13/C-13´), 123.1 (o, C-6), 120.8 (+, C-8), 118.0 (+, C-10) ppm; IR (ATR): $\bar{\nu}$ = 3080, 1598, 1541, 1499, 1467, 1403, 1324, 1295, 1160, 961, 748, 715, 574 cm^{-1}; MS (ESI 30 V): *m/z* (%) = 292.0 (100) $[M+Na]^+$. HR-ESI-MS: calcd for $C_{14}H_{12}N_3OS^+$ 270.0701. Found 270.0704.

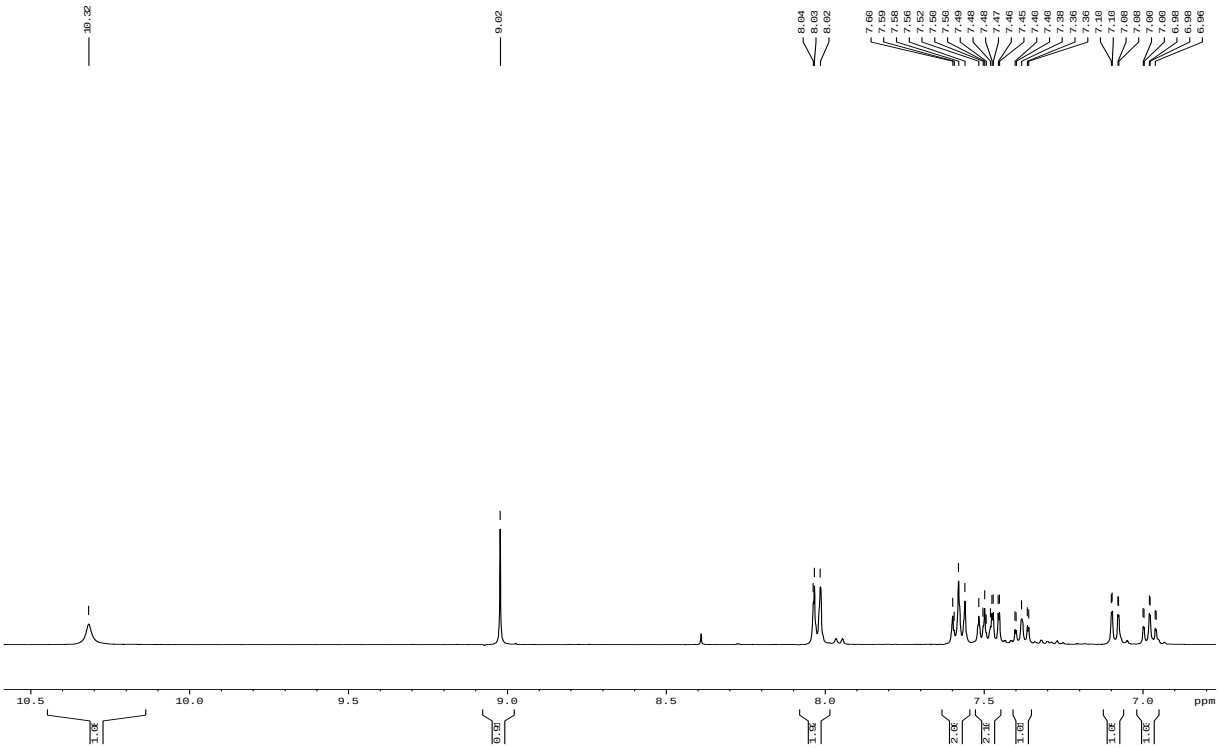

8.43
8.04 8.03 8.03 8.03 8.02 8.01 8.01 8.01
7.56 7.55 7.55 7.55 7.54 7.53 7.53 7.52 7.51 7.51 7.46 7.46 7.46 7.45 7.45 7.44 7.43 7.42 7.42 7.42 7.39 7.39 7.37 7.37 7.37 7.37 7.35 7.35
7.08 7.08 7.06 7.05 7.03 7.02 7.01 7.01 6.99 6.99
8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 ppm
0.94 2.06 2.07 1.00 1.02 1.06 1.02
168.1 154.0 143.5 139.9 132.2 130.4 129.8 129.3 125.6 123.1 120.8 118.0

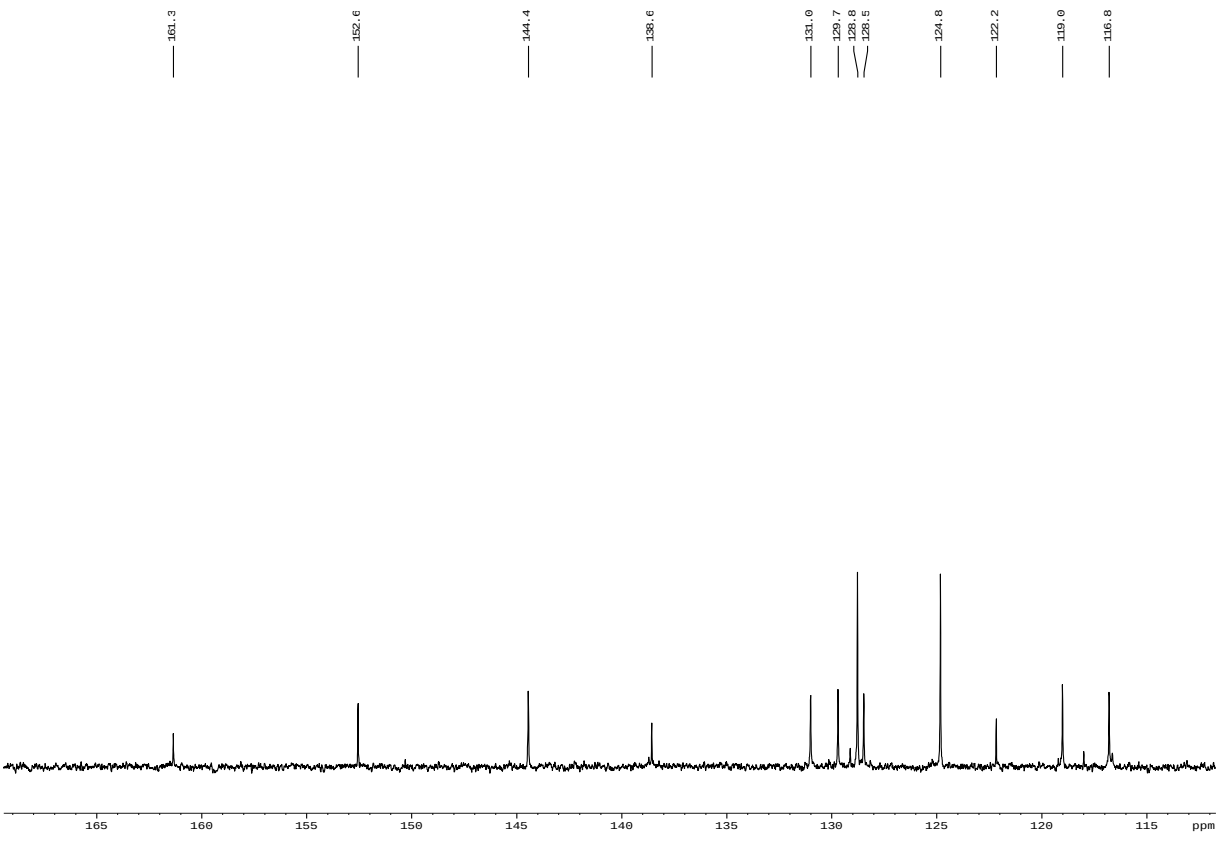

170 165 160 155 150 145 140 135 130 125 120 115 ppm

4-(2-Hydroxyphenyl)-2-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-selenone 13b

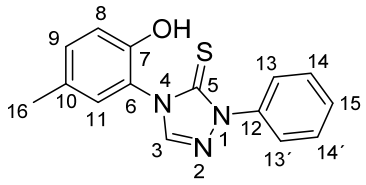


Under a nitrogen atmosphere a solution of 0.169 g (0.50 mmol) of 4-(2-hydroxyphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate and 47 mg (0.6 mmol) of selenium in 10 mL of dry THF was cooled to 0 °C. Then, a solution of potassium 2-methylbutan-2-olate (0.32 mL, 0.55 mmol) was added slowly by using a syringe. The mixture was stirred at rt for 30 min and then heated at 100 °C for 3 h. After cooling, the solvent was evaporated *in vacuo*. The product was separated by column chromatography (silica gel, ethyl acetate/petroleum ether). Yield: 0.079 g (50%) of a yellow solid, mp: 168 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ =10.32 (s, 1H, OH), 9.02 (s, 1H, 3-H), 8.02 - 8.04 (m, 2 H, 13/13´-H), 7.56 - 7.60 (m, 2 H, 14/14´-H), 7.45 - 7.52 (overlap, 2 H, 15/11-H), 7.38 (ddd, J_1 = 1.6 Hz, J_2 = 7.7 Hz, J_3 = 8.2 Hz, 1 H, 9-H), 7.09 (dd, J_1 = 1.1 Hz, J_2 = 8.2 Hz, 1 H, 8-H), 6.98 (td, J_1 = 1.1 Hz, J_2 = 7.7 Hz, 1 H, 10-H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 161.3 (o, C-5), 152.6 (o, C-7), 144.4 (+, C-3), 138.6 (o, C-12), 131.0 (+, C-9), 129.7 (+, C-15), 128.8 (+, C-14/C-14´), 128.5 (+, C-11), 124.8 (+, C-13/C-13´), 122.2 (o, C-6), 119.0 (+, C-8), 116.8 (+, C-10) ppm; IR (ATR): $\bar{\nu}$ = 3069, 1694, 1598, 1500, 1457, 1409,1322, 1316, 1303, 962, 747, 692, 684, 549, 498 cm^{-1}; MS (ESI 10 V): *m/z* (%) = 316.0 (100) [M-H]$^-$. HR-ESI-MS: calcd for $C_{14}H_{13}N_3OSe^+$ 318.0146. Found 318.0147.


10.32
9.02
8.04
8.03
8.02
7.60
7.59
7.58
7.56
7.52
7.50
7.50
7.49
7.48
7.48
7.47
7.46
7.45
7.40
7.40
7.38
7.36
7.36
7.10
7.10
7.08
7.08
7.00
7.00
6.98
6.98
6.96
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
ppm
1.00
0.97
1.00
2.08
2.14
1.08
1.02
1.08


161.3
152.6
144.4
138.6
131.0
129.7
128.8
128.5
124.8
122.2
119.0
116.8
165
160
155
150
145
140
135
130
125
120
115
ppm

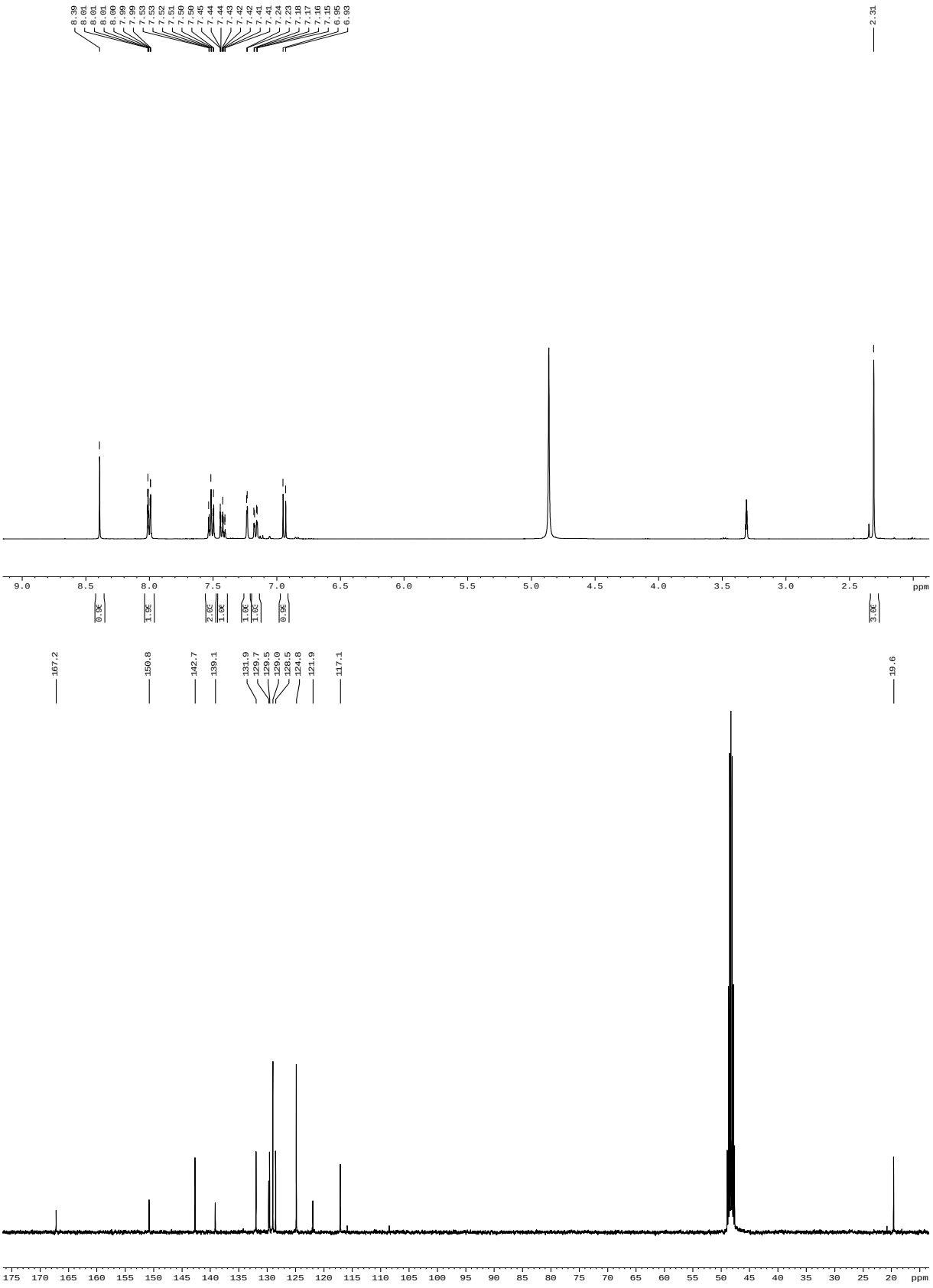
4-(2-Hydroxy-5-methylphenyl)-2-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-thione 13c



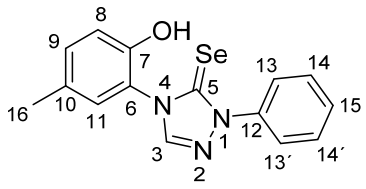
Method B: Under a nitrogen atmosphere a solution of 0.176 g (0.50 mmol) of 4-(2-hydroxy-5-methylphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate and 19.2 mg (0.6 mmol) of sulfur in 10 mL of dry THF was cooled to 0 °C. Then, a solution of potassium 2-methylbutan-2-olate (0.32 mL, 0.55 mmol) was added slowly by using a syringe. The mixture was stirred at rt for 30 min and then heated at 100 °C for 3 h. Then, the solvent was distilled off *in vacuo*. The product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether). Yield: 0.112 g (79%) of a yellow solid, mp: 177 °C.

Method D: A flask was charged with 4-methyl-2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate (0.126 g, 0.5 mmol), sulfur (32 mg, 1.0 mmol), and dry toluene (10 mL), and then the mixture was stirred at reflux temperature for 8 h. After evaporation, the resulting precipitate was purified by column chromatography (silica gel, ethyl acetate/petroleum ether). Yield: 0.085 g (60%) of a yellow solid, mp: 177 °C.

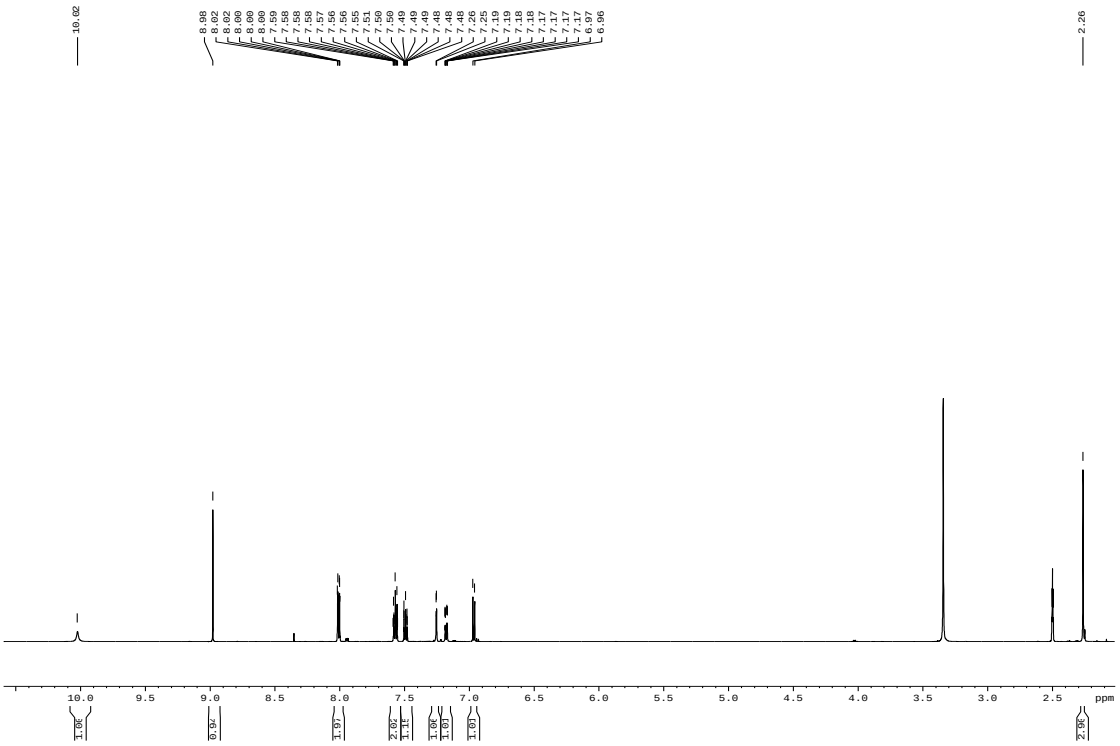
^{1}H NMR (400 MHz, MeOD-d_4): δ = 8.391 (s, 1H, 3-H), 7.99 - 8.01 (m, 2 H, 13/13´-H), 7.50 - 7.53 (m, 2 H, 14/14´-H), 7.43 (tt, J_1 = 1.1 Hz, J_2 = 7.4 Hz, 1 H, 15-H), 7.23 (d, J = 1.9 Hz, 1 H, 11-H), 7.17 (dd, J_1 = 1.9 Hz, J_2 = 8.5 Hz, 1 H, 9-H), 6.94 (d, J = 8.5 Hz, 1 H, 8-H) ppm; ^{13}C NMR (100 MHz, MeOD-d_4): δ = 167.2 (o, C-5), 150.8 (o, C-7), 142.7 (+, C-3), 139.1 (o, C-12), 131.9 (+, C-9), 129.7 (o, C-10), 129.5 (+, C-15), 129.0 (+, C-14/C-14´), 128.5 (+, C-11), 124.8 (+, C-13/ C-13´), 121.9 (o, C-6), 117.1 (+, C-8), 19.6 (+, C-16) ppm; IR (ATR): $\bar{\nu}$ = 3145, 1542, 1517, 1501, 1400, 1311, 1288, 1261, 1183, 967, 807, 759, 692, 578, 548 cm^{-1}. MS (ESI 30 V) m/z (%) = 306.0 (100) $[M+Na]^+$. HR-ESI-MS: calcd for $C_{15}H_{14}N_3OS^+$ 284.0858. Found 284.0860.

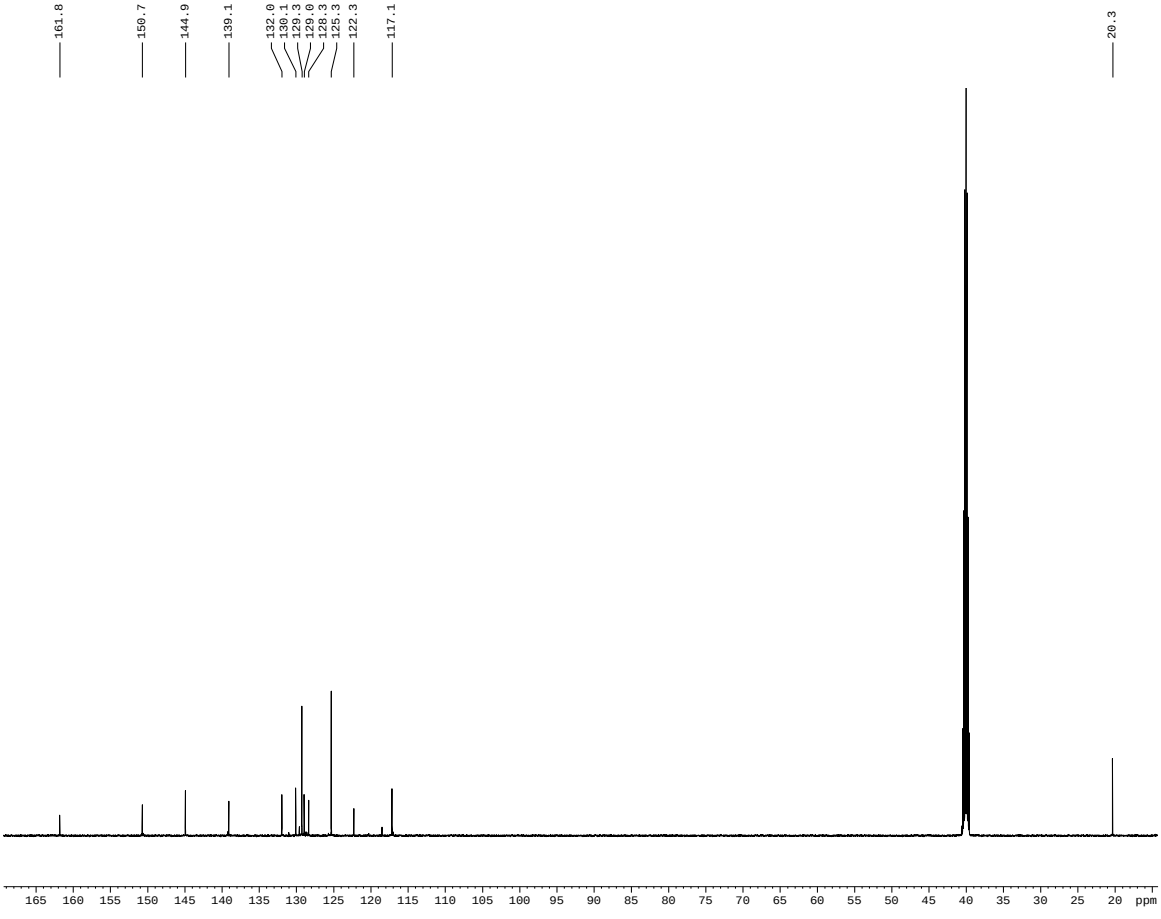

8.39
8.01
8.01
8.01
8.00
7.99
7.99
7.53
7.52
7.51
7.50
7.50
7.45
7.44
7.43
7.42
7.42
7.41
7.41
7.24
7.23
7.18
7.17
7.16
7.15
6.95
6.93
2.31
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
0.96
1.98
2.02
1.00
1.08
1.02
0.96
3.06
167.2
150.8
142.7
139.1
131.9
129.7
129.5
129.0
128.5
124.8
121.9
117.1
19.6
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
ppm

4-(2-Hydroxy-5-methylphenyl)-2-phenyl-2,4-dihydro-3*H*-1,2,4-triazole-3-selenone 13d

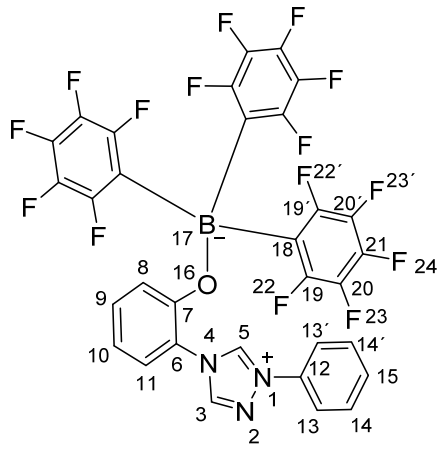


Under a nitrogen atmosphere a solution of 0.176 g (0.50 mmol) of 4-(2-hydroxy-5-methylphenyl)-1-phenyl-4*H*-1,2,4-triazolium perchlorate and 47 mg (0.6 mmol) of selenium in 10 mL of dry THF was cooled to 0 °C. Then, a solution of potassium 2-methylbutan-2-olate (0.32 mL, 0.55 mmol) was added slowly by using a syringe. The mixture was stirred at rt for 30 min and then heated at 100 °C for 3 h. After cooling, the solvent was evaporated *in vacuo*. The product was separated by column chromatography (silica gel, ethyl acetate/petroleum ether). Yield: 0.089 g (54%) of a yellow solid, mp: 137 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 10.02 (s, 1 H, OH), 8.98 (s, 1 H, 3-H), 8.00 - 8.02 (m, 2 H, 13/13´-H), 7.56 - 7.59 (m, 2 H, 14/14´-H), 7.50 (tt, J_1 = 1.1 Hz, J_2 = 7.4 Hz, 1 H, 15-H), 7.25 (d, J = 1.9 Hz, 1 H, 11-H), 7.18 (ddd, J_1 = 0.5 Hz, J_2 = 1.9 Hz, J_3 = 8.3 Hz, 1 H, 9-H), 6.97 (d, J = 8.3 Hz, 1 H, 8-H), 2.26 (s, 3 H, 16-H) ppm; ^{13}C NMR (150 MHz, DMSO-d_6): δ = 161.8 (o, C-5), 150.7 (o, C-7), 144.9 (+, C-3), 139.1 (o, C-12), 132.0 (+, C-9), 130.1 (+, C-11), 129.3 (+, C-14/C-14´), 129.0 (+, C-15), 128.3 (o, C-10), 125.3 (+, C-13/C-13´), 122.3 (o, C-6), 117.1 (+, C-8), 20.3 (+, C-16) ppm; IR (ATR): $\bar{\nu}$ = 3067, 1694, 1516, 1500, 1405, 1309, 1273, 1181, 965, 811, 760, 693, 486 cm^{-1}; MS (ESI 10 V) m/z (%) = 330.0 (100) $[M-H]^-$.

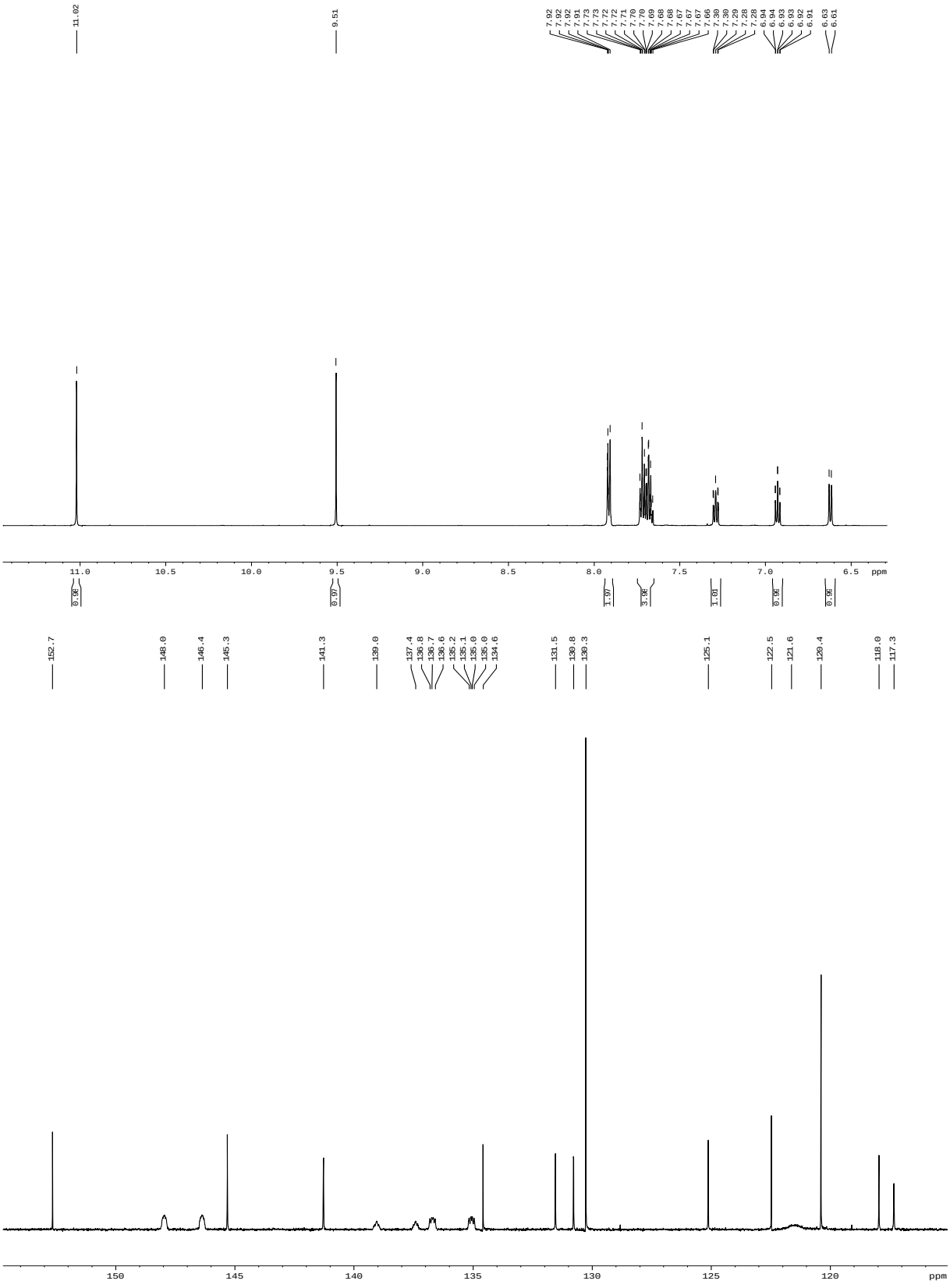

10.02
8.98
8.02
8.02
8.00
8.00
8.00
7.59
7.58
7.58
7.57
7.56
7.56
7.55
7.51
7.50
7.50
7.49
7.49
7.49
7.48
7.48
7.48
7.26
7.25
7.19
7.19
7.18
7.18
7.17
7.17
7.17
6.97
6.96
2.26
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
1.06
0.94
1.97
2.02
1.71
1.04
1.03
1.03
2.06

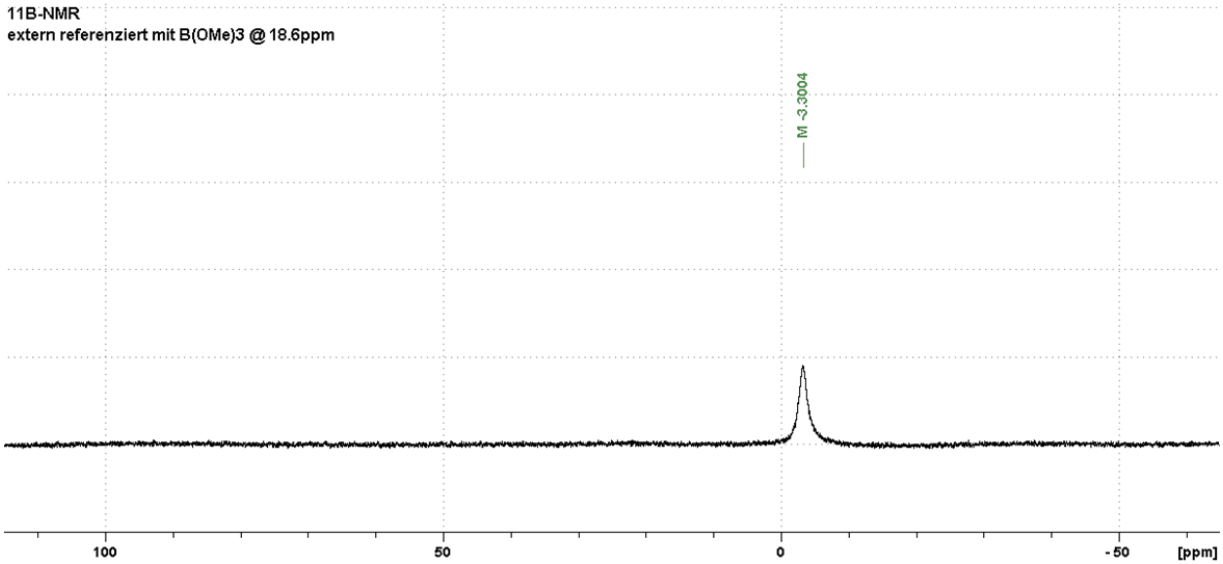

161.8
150.7
144.9
139.1
132.0
130.1
129.3
129.0
128.3
125.3
122.3
117.1
20.3
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
ppm

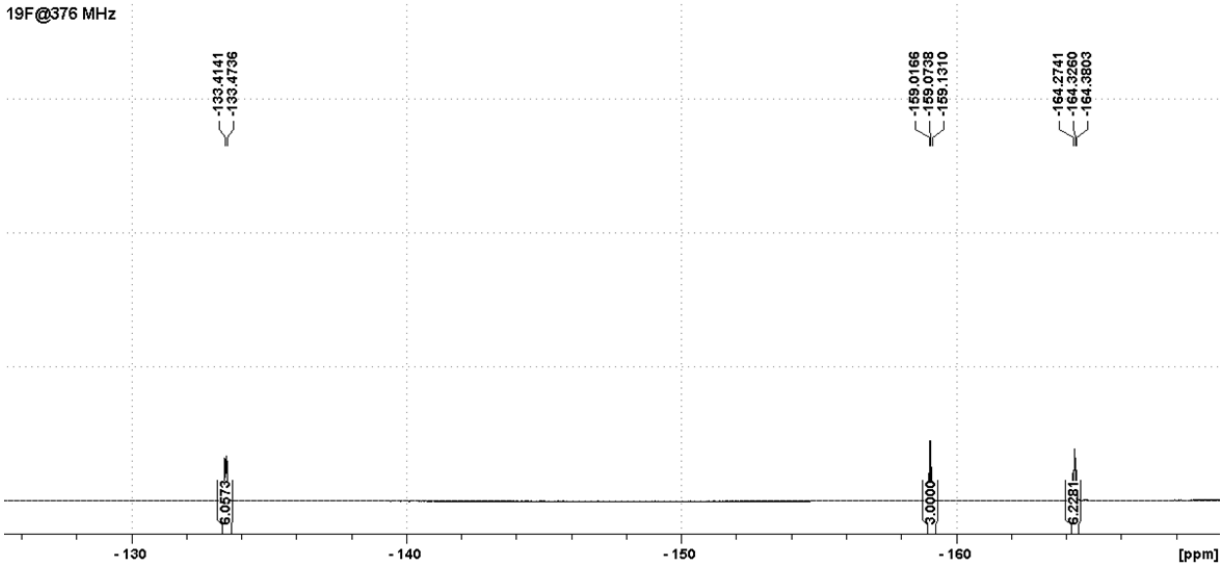
Tris(perfluorophenyl)(2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenoxy)borate 14a



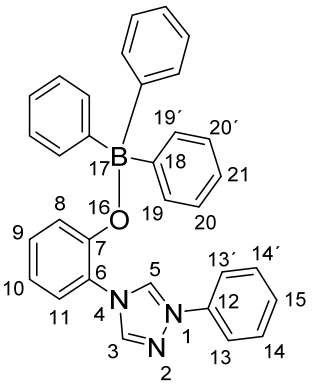
Under an inert atmosphere a solution of 0.119 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate and 0.512 mg (1.0 mmol) of tris(pentafluorophenyl)borane in 10 mL of dry dioxane was stirred at rt for 2 h in a bomb tube. Then, the solvent was distilled off *in vacuo*. The product was separated by column chromatography (silica gel, ethyl acetate/petroleum ether). Yield: 0.281 g (75%) of a colorless solid, mp: 260 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 11.02 (s, 1 H, 5-H), 9.51 (s, 1 H, 3-H), 7.91 - 7.92 (m, 2 H, 13/13´-H), 7.66 - 7.73 (overlapped signals, 4 H, 14/14´/15/11-H), 7.29 (ddd, J_1 = 1.7 Hz, J_2 = 7.8 Hz, J_3 = 8.5 Hz, 1 H, 9-H), 6.93 (dt, J_1 = 1.0 Hz, J_2 = 7.8 Hz, 1 H, 10-H), 6.62 (d, J = 8.5 Hz, 1 H, 8-H) ppm; ^{13}C NMR (150 MHz, DMSO-d_6): δ = 152.7 (o, C-7), 148.0 (o, C-19), 146.4 (o, C-19´), 145.3 (+, C-3), 141.3 (+, C-5), 137.4 - 139.0 (C-21), 136.6 - 136.8 (C-20), 135.0-135.2 (C-20´), 134.6 (o, C-12), 131.5 (+, C-9), 130.8 (+, C-15), 130.3 (+, C-14/C-14´), 125.1 (+, C-11), 122.5 (o, C-6), 121.6 (o, C-18), 120.4 (+, C-13/C-13´), 118.0 (+, C-10), 117.3 (+, C-8) ppm; ^{11}B NMR (DMSO, 193 MHz, $B(OMe)_3$): δ = -3.30 ppm; ^{19}F NMR (DMSO, 376 MHz, Cl_3CF): δ = -133.44 (d, J = 22.37 Hz, 6 F, FC-22/FC-22´), -159.07 (t, J = 21.51 Hz, 3F, FC-24), -164.33 (t, J = 19.51 Hz, 6 F, FC-23/FC-23´) ppm; IR (ATR): $\bar{\nu}$ = 3150, 1565, 1512, 1483, 1277, 1087, 975, 965, 929, 764, 749, 690, 669, 549 cm^{-1}; GC-MS: 237.0 (100) [M-$B(C_6F_5)_3$].


11.02
9.51
7.92
7.92
7.92
7.91
7.73
7.73
7.72
7.72
7.71
7.70
7.70
7.69
7.68
7.68
7.67
7.67
7.67
7.66
7.30
7.30
7.29
7.28
7.28
6.94
6.94
6.93
6.93
6.92
6.91
6.63
6.61
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
ppm
0.98
0.97
1.97
3.98
1.01
0.96
0.96
152.7
148.0
146.4
145.3
141.3
139.0
137.4
136.8
136.7
136.6
135.2
135.1
135.0
135.0
134.6
131.5
130.8
130.3
125.1
122.5
121.6
120.4
118.0
117.3
150
145
140
135
130
125
120
ppm

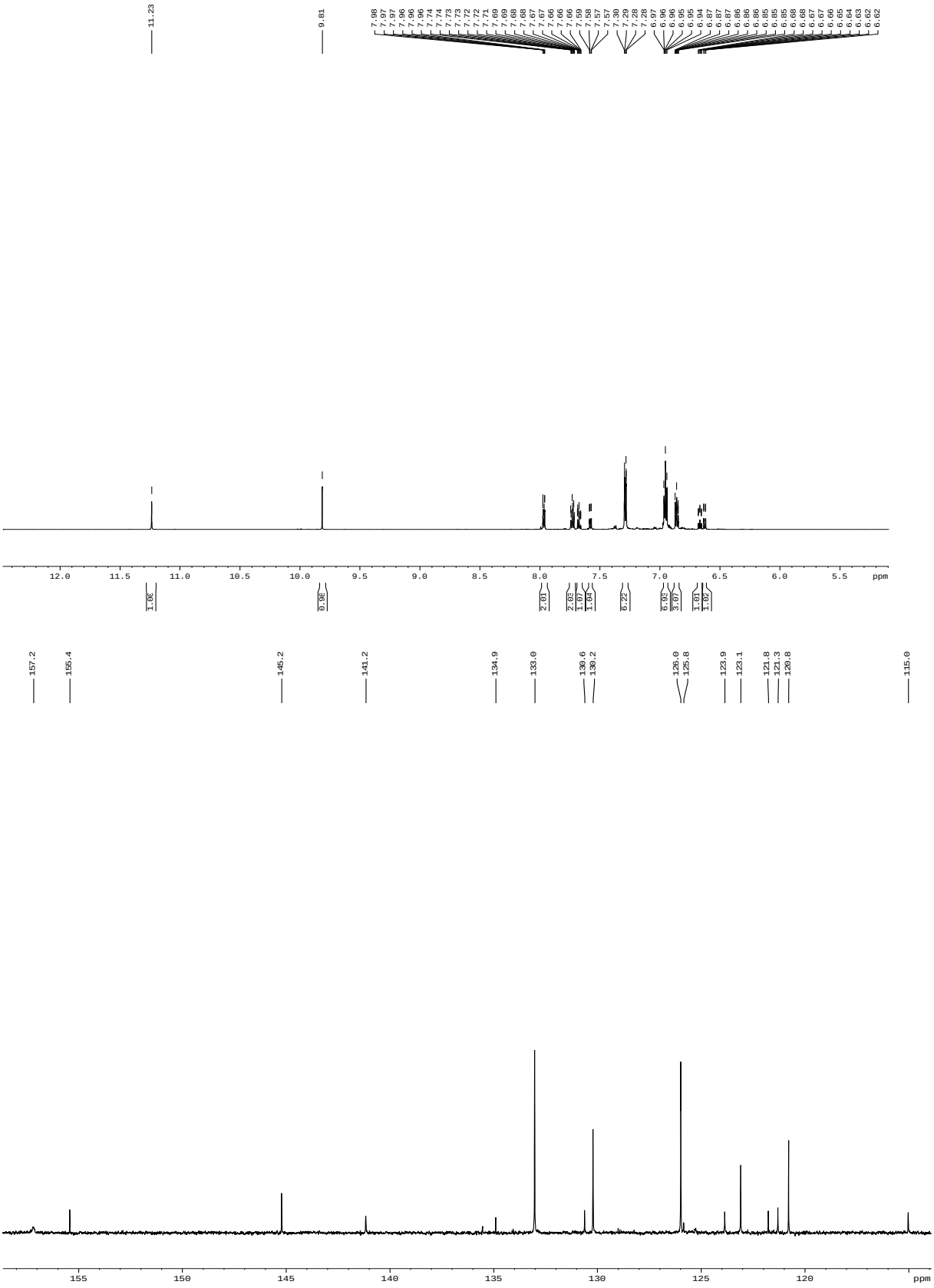

11B-NMR
extern referenziert mit B(OMe)3 @ 18.6ppm
M -3.3004
100
50
0
-50
[ppm]

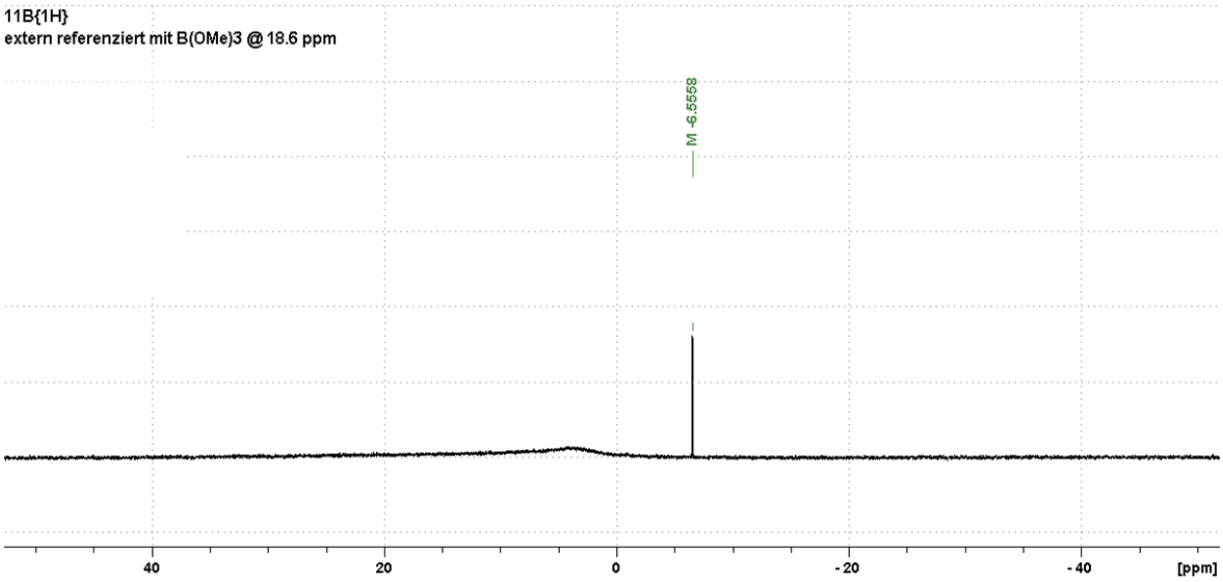

19F@376 MHz
-133.4141
-133.4736
-159.0166
-159.0738
-159.1310
-164.2741
-164.3260
-164.3803
6.0573
3.0000
6.2281
-130
-140
-150
-160
[ppm]

Triphenyl(2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenoxy)borate 14b

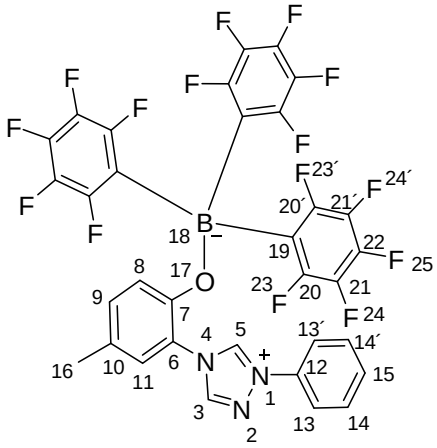


Under an inert atmosphere a solution of 0.242 g (1.0 mmol) of triphenylborane in 2 mL of dioxane was added to a suspension of 0.119 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate in 5 mL of dry dioxane. The mixture was stirred at rt in a Schlenk-tube for 2 h. Then, the solvent was evaporated *in vacuo*. The resulting solid was purified by column chromatography (silica gel, ethyl acetate/petroleum ether). Yield: 0.321 g (67%) of a colorless solid, mp: 158 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 11.23 (s, 1 H, 5-H), 9.81 (s, 1 H, 3-H), 7.96 - 7.98 (m, 2 H, 13/13´-H), 7.71 - 7.74 (m, 2 H, 14/14´-H), 7.68 (tt, J_1 = 1.1 Hz, J_2 = 7.4 Hz, 1 H, 15-H), 7.58 (dd, J_1 = 1.7 Hz, J_2 = 7.9 Hz, 1 H, 11-H), 7.29 (dd, J_1 = 1.3 Hz, J_2 = 8.0 Hz, 6 H, 19/19´-H), 6.94 - 6.97 (overlapped signals, 7 H, 20/20´/9-H), 6.86 (tt, J_1 = 1.3 Hz, J_2 = 7.3 Hz, 3 H, 21-H), 6.67 (dd, J_1 = 1.2 Hz, J_2 = J_3 = 7.9 Hz, 1 H, 10-H), 6.62 (dd, J_1 = 1.2 Hz, J_2 = 8.5 Hz, 1 H, 8-H) ppm; ^{13}C NMR (150 MHz, DMSO-d_6): δ = 157.2 (o, C-18), 155.4 (o, C-7), 145.2 (+, C-3), 141.2 (+, C-5), 134.9 (o, C-12), 133.0 (+, C-19/C-19´), 130.6 (+, C-15), 130.2 (+, C-14/C-14´), 126.0 (+, C-20/C-20´), 125.8 (+, C-9), 123.9 (+, C-11), 123.1 (+, C-21), 121.8 (o, C-6), 121.3 (+, C-8), 120.8 (+, C-13/C-13´), 115.0 (+, C-10) ppm; ^{11}B NMR (DMSO, 193 MHz, $B(OMe)_3$): δ = −6.56 ppm; IR (ATR): $\bar{\nu}$ = 1601, 1557, 1497, 1311, 1115, 827, 806, 702, 684, 667, 612 cm^{-1}; MS (ESI 30 V): *m/z* (%) = 238.1 (100) $[M\text{-}B(C_6H_5)_3+H]^+$.


11.23
9.81
7.98 7.97 7.97 7.96 7.96 7.96 7.74 7.74 7.73 7.73 7.72 7.72 7.71 7.69 7.69 7.68 7.68 7.67 7.67 7.66 7.66 7.59 7.58 7.57 7.57 7.30 7.29 7.28 7.28 6.97 6.96 6.96 6.95 6.95 6.94 6.87 6.87 6.87 6.86 6.86 6.86 6.85 6.85 6.85 6.68 6.68 6.67 6.67 6.66 6.65 6.64 6.63 6.62 6.62
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 ppm
1.06 0.96 2.01 2.03 1.07 1.06 6.22 6.03 3.07 1.01 1.02
157.2 155.4 145.2 141.2 134.9 133.0 130.6 130.2 126.0 125.8 123.9 123.1 121.8 121.3 120.8 115.0
155 150 145 140 135 130 125 120 ppm

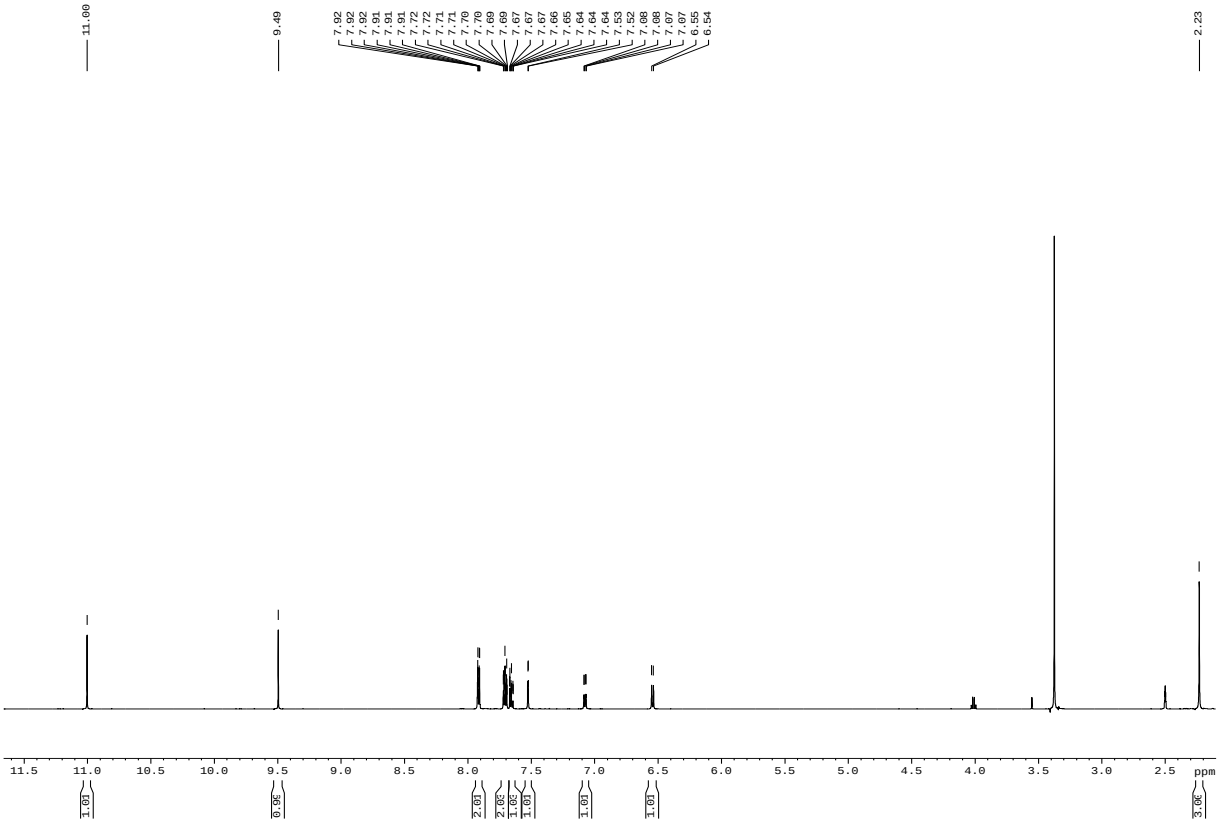


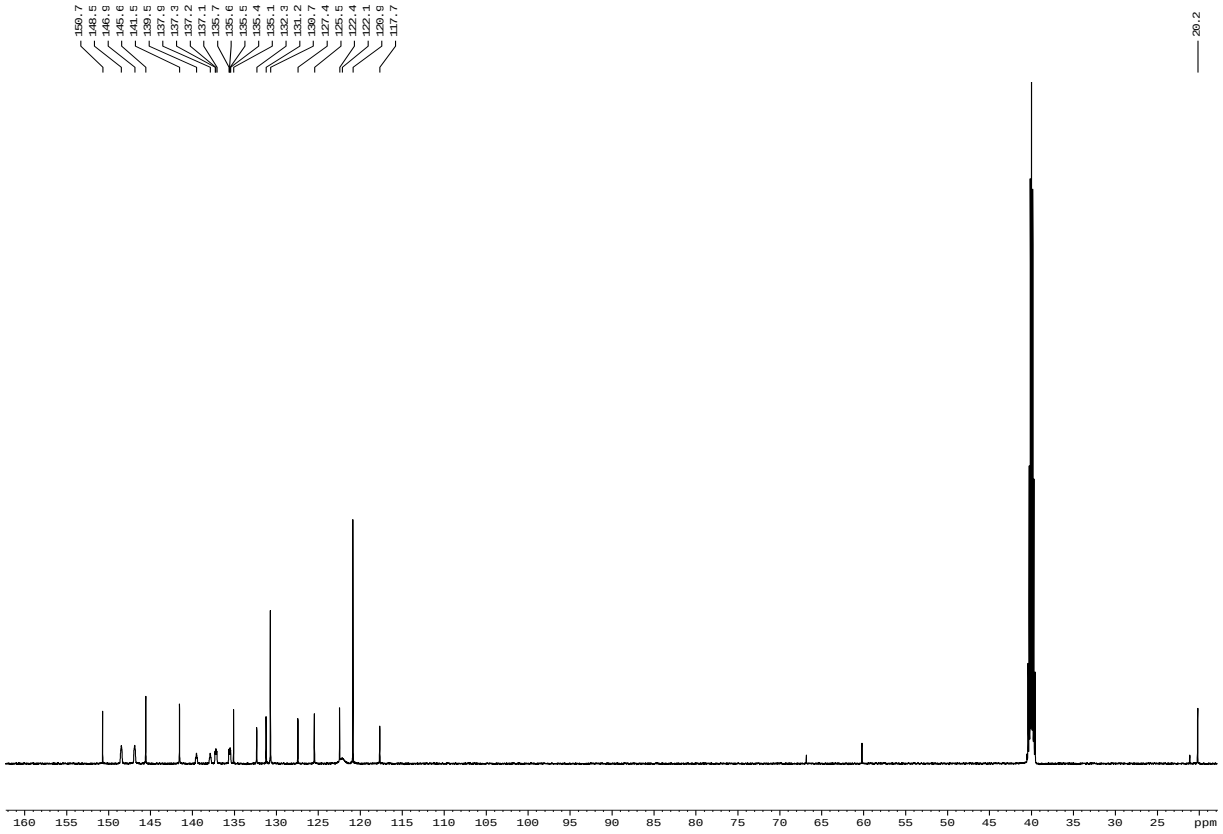
(4-Methyl-2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenoxy)tris(perfluorophenyl)borate 14c

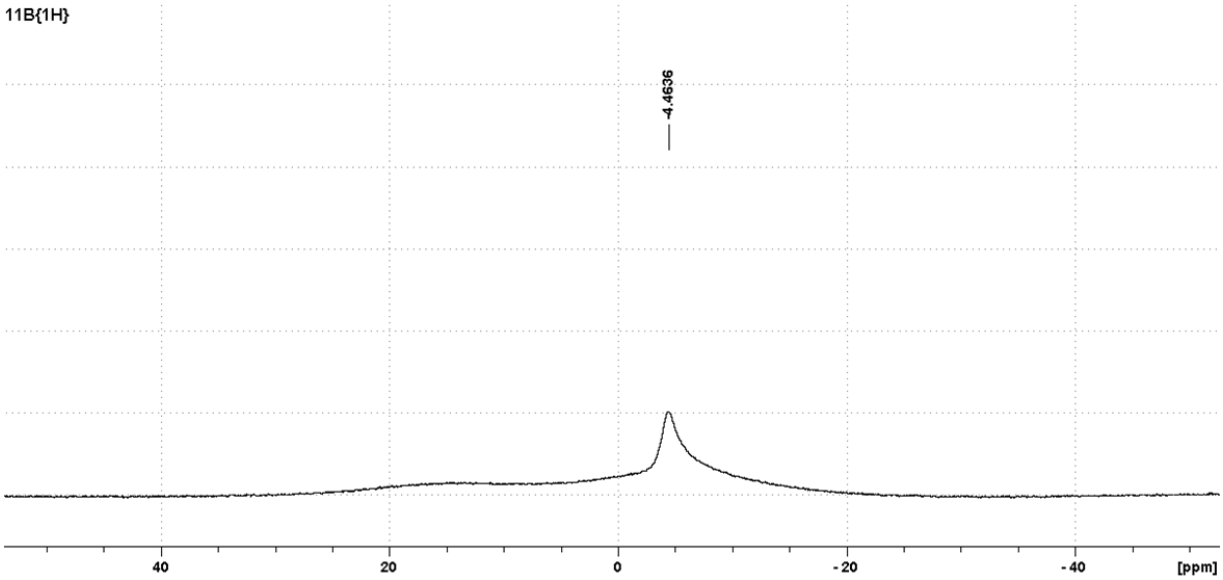


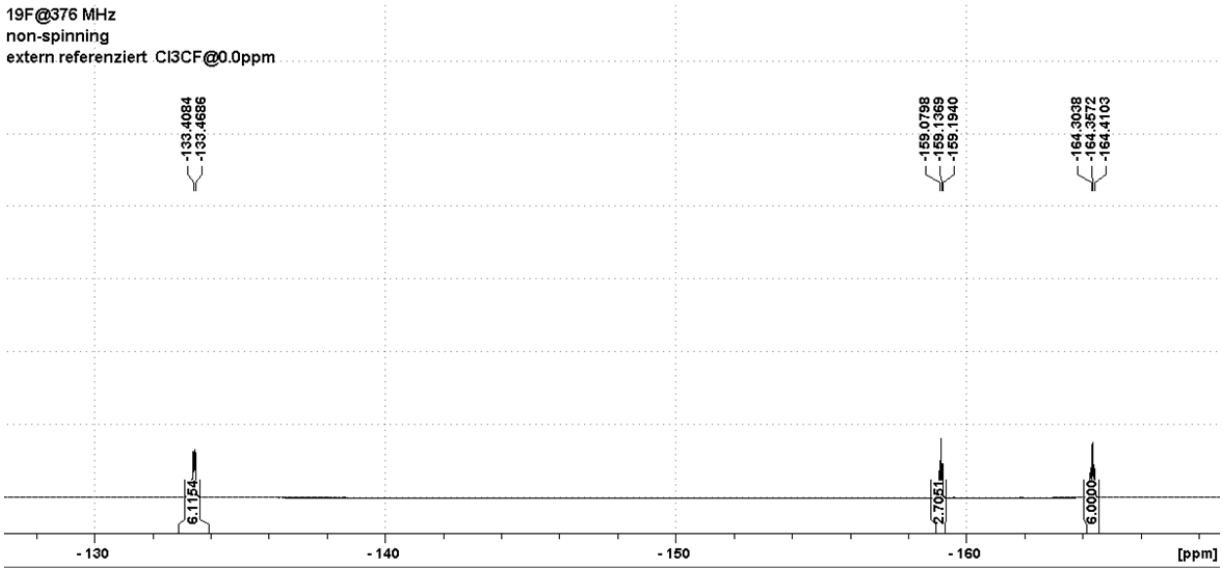
Under an inert atmosphere a solution of 0.126 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate and 0.512 mg (1.0 mmol) of tris(pentafluorophenyl)borane in 10 mL of dry dioxane was stirred at rt for 2 h in a bomb tube. Then, the solvent was evaporated *in vacuo*. The resulting solid was purified by column chromatography (silica gel, ethyl acetate/petroleum ether). Yield: 0.298 g (78%) of a colorless solid, mp: 281 °C; ^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 11.00 (s, 1 H, 5-H), 9.49 (s, 1 H, 3-H), 7.91 - 7.92 (m, 2 H, 13/13´-H), 7.69 - 7.72 (m, 2 H, 14/14´-H), 7.66 (tt, , J_1 = 1.1 Hz, J_2 = 7.4 Hz, 1 H, 15-

H), 7.53 (d, J = 2.0 Hz, 1 H, 11-H), 7.08 (dd, J_1 = 2.0 Hz, J_2 = 8.8 Hz, 2 H, 9-H), 6.55 (d, J = 8.8 Hz, 1 H, 8-H) ppm; ^{13}C NMR (150 MHz, DMSO-d_6): δ = 150.7 (o, C-7), 148.5 (o, C-20), 146.9 (o, C-20´), 145.6 (+, C-3), 141.5 (+, C-5), 137.9 - 139.5 (o, C-22), 137.1 - 137.3 (o, C-21), 135.4 - 135.7 (o, C-21´), 135.1 (o, C-12), 132.3 (+, C-9), 131.2 (+, C-15), 130.7 (+, C-14/C-14´), 127.4 (o, C-10), 125.5 (+, C-11), 122.4 (o, C-6), 122.1 (o, C-19), 120.9 (+, C-13/C-13´), 117.7 (+, C-8), 20.2 (+, C-16) ppm; ^{11}B NMR (DMSO, 193 MHz, $BF_3 \cdot Et_2O$): δ = −4.46 ppm; ^{19}F NMR (DMSO, 376 MHz, Cl_3CF): δ = -133.44 (d, J = 22.64 Hz, 6 F, FC-23 /FC-23´), -159.14 (t, J = 21.47 Hz, 3F, FC-25), -164.36 (t, J = 20.08 Hz, 6 F, FC-24/FC-24´) ppm; IR (ATR): $\bar{\nu}$ = 3163, 1514, 1457, 1277, 1089, 975, 965, 949, 941, 929, 916, 767, 759, 753, 667 cm^{-1}; MS (ESI 30 V): *m/z* (%) = 252.1 (100) $[M\text{-}B(C_6F_5)_3+H]^+$.

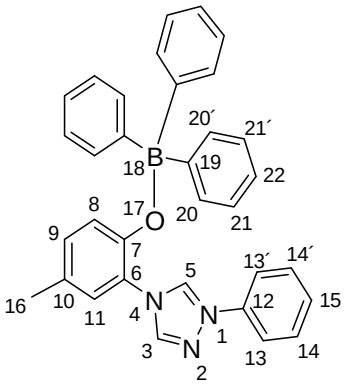



159.7
148.5
146.9
145.6
141.5
139.5
137.9
137.3
137.2
137.1
135.7
135.6
135.5
135.4
135.1
132.3
131.2
130.7
127.4
125.5
122.4
122.1
120.9
117.7
20.2
160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 ppm


11B{1H}
-4.4636
40
20
0
-20
-40
[ppm]

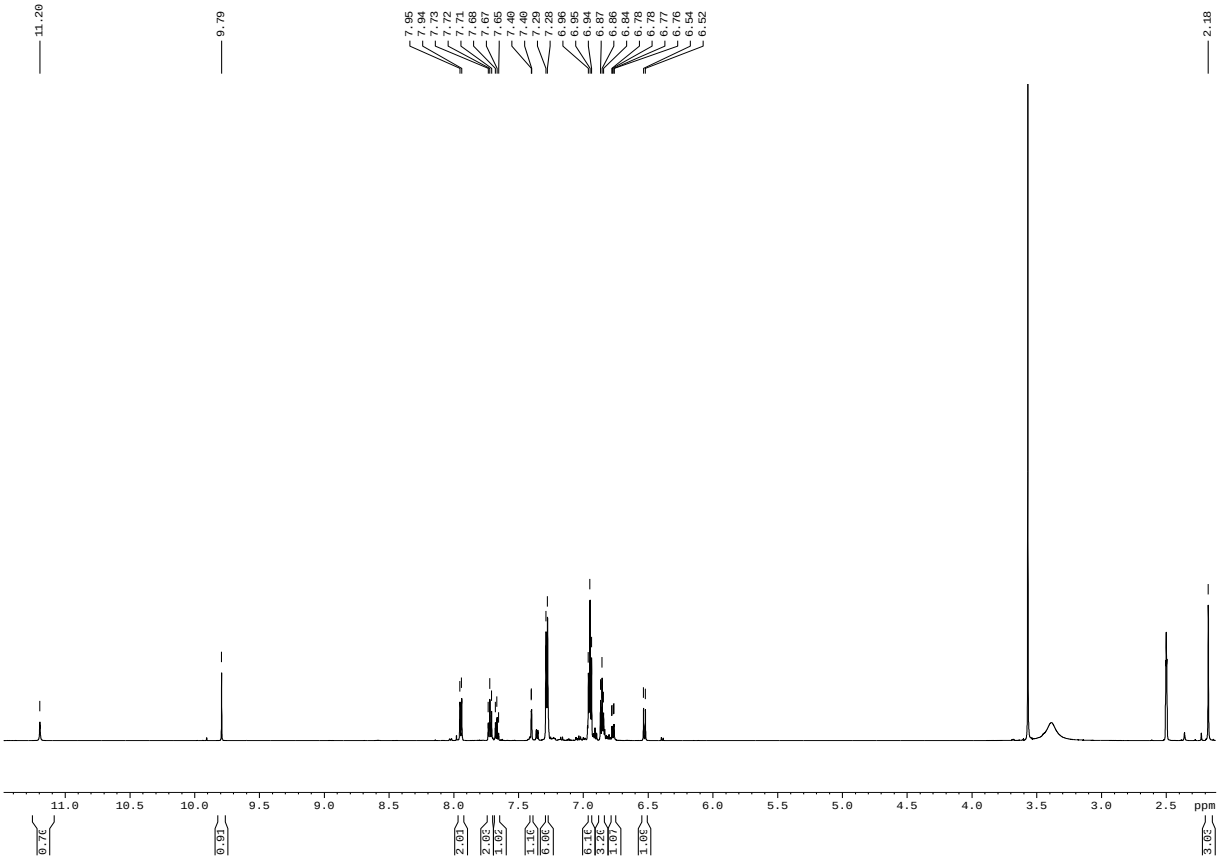


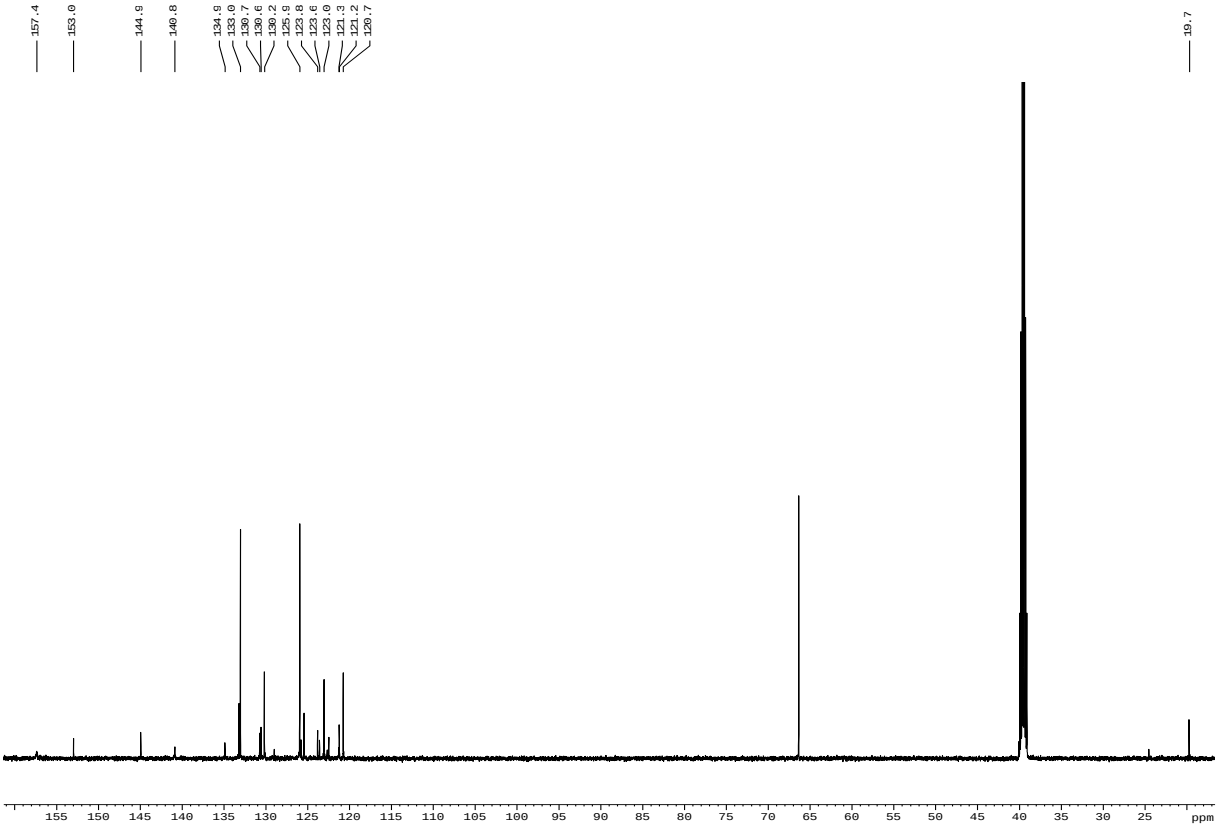
(4-Methyl-2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenoxy)triphenylborate 14d

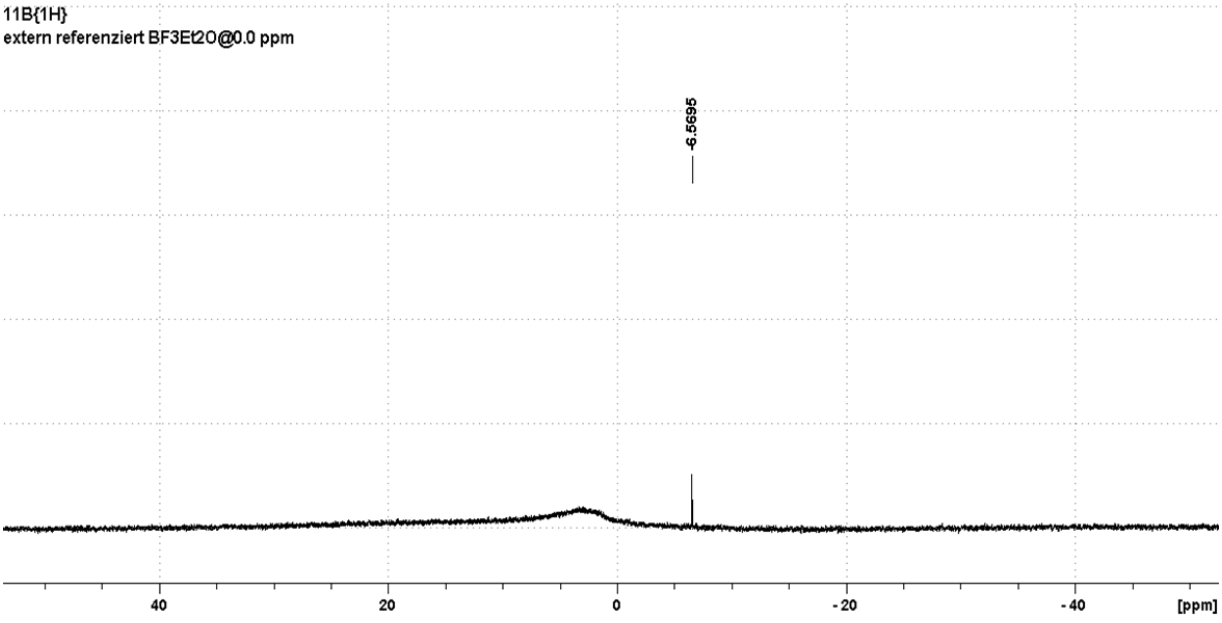


Under an inert atmosphere a solution of 0.242 g (1.0 mmol) of triphenylborane in 2 mL of anhydrous dioxane was added to a suspension of 0.126 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate in 5 mL of anhydrous dioxane. The mixture was stirred at rt in a Schlenk-tube for 2 h. Then, the solvent was evaporated *in vacuo*. The resulting residue was purified by column chromatography (silica gel, ethyl acetate/petroleum ether). Yield: 0.355 g (72%) of a colorless solid, mp: 148 °C; ^{1}H NMR (600 MHz, DMSO-d$_6$): δ = 11.20 (s, 1 H, 5-H), 9.79 (s, 1 H, 3-H), 7.95 (d, J = 7.9 Hz, 2 H, 13/13´-H), 7.71 - 7.73 (m, 2 H, 14/14´-H), 7.67 (tt, J_1 = 1.1 Hz, J_2 = 7.4 Hz, 1 H, 15-H), 7.40 (d, J = 1.83 Hz, 1 H, 11-H), 7.28 (dd, J_1 = 1.1 Hz, J_2 = 7.1 Hz, 6 H, 20/20´-H), 6.95 (t, J = 7.1 Hz, 6 H, 21/21´-H), 6.86 (tt, J_1 = 1.1 Hz, J_2 = 7.1 Hz, 3 H, 22-H), 6.77 (dd, 1 H, J_1 = 1.8 Hz, J_2 = 8.7 Hz, 9-H), 6.53 (d, J = 8.7 Hz, 1 H, 8-

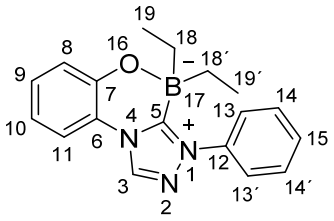
H), 2.18 (s, 3H, 16-H) ppm; ^{13}C NMR (150 MHz, DMSO-d_6): δ = 157.4 (o, C-19), 156.0 (o, C-7), 144.9 (+, C-3), 140.8 (+, C-5), 134.9 (o, C-12), 133.0 (+, C-20/C-20´), 130.7 (+, C-9), 130.6 (+, C-15), 130.2 (+, C-14/C-14´), 125.9 (+, C-21/C-21´), 123.8 (o, C-10), 123.6 (+, C-11), 123.0 (+, C-22), 121.3 (o, C-6), 121.2 (+, C-8), 120.7 (+, C-13/C-13´), 19.7 (+, C-16) ppm; ^{11}B NMR (DMSO, 193 MHz, $BF_3 \cdot Et_2O$): δ = −6.57 ppm; IR (ATR): $\tilde{\nu}$ = 3120, 1566, 1520, 1292, 1284, 1094, 1072, 870, 845, 752, 699, 684, 666, 621, 482 cm^{-1}; MS (ESI 30 V): *m/z* (%) = 252.1 (100) $[M\text{-}B(C_6H_5)_3+H]^+$.



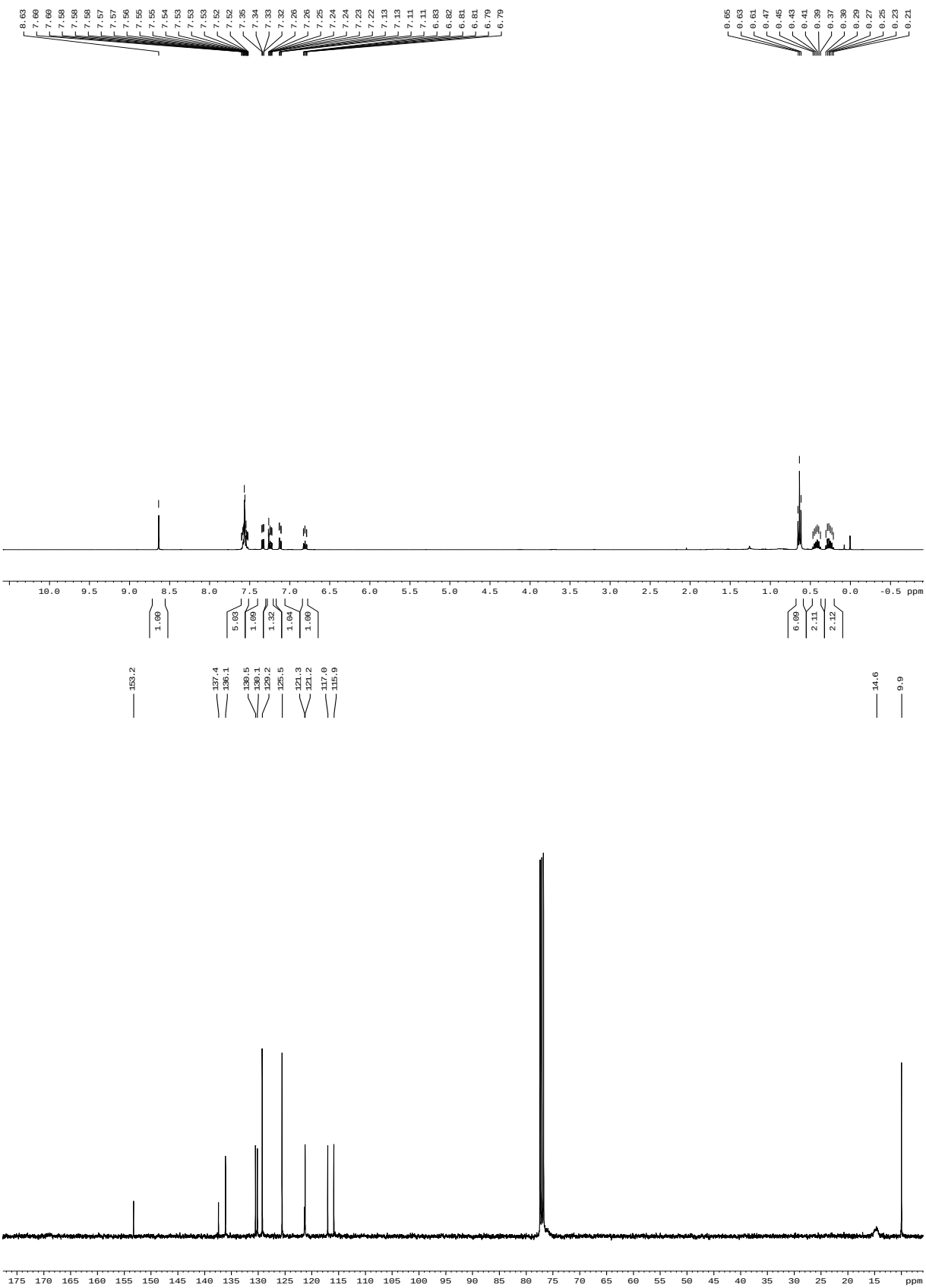

157.4
153.0
144.9
140.8
134.9
133.0
130.7
130.6
130.2
125.9
123.8
123.6
123.0
121.3
121.2
120.7
19.7
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
ppm

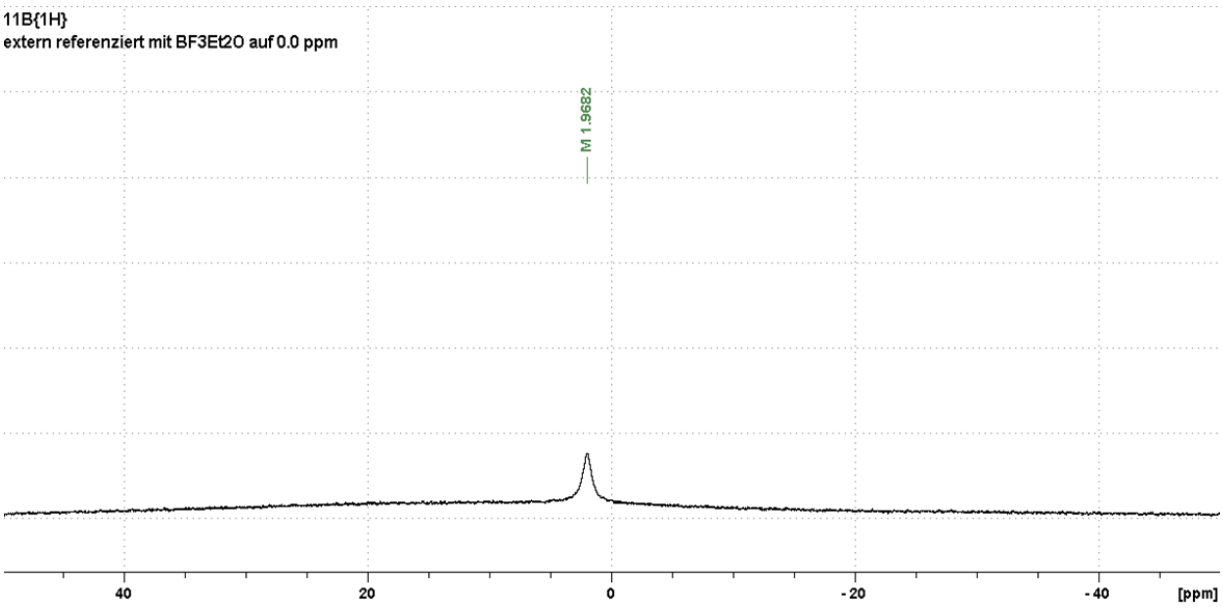

11B{1H}
extern referenziert BF3Et2O@0.0 ppm
-6.5695
40
20
0
-20
-40
[ppm]

4,4-Diethyl-3-phenyl-4*H*-benzo[*e*][1,2,4]triazolo[3,4-*c*][1,4,2]oxazaborinin-3-ium-4-ide 15a

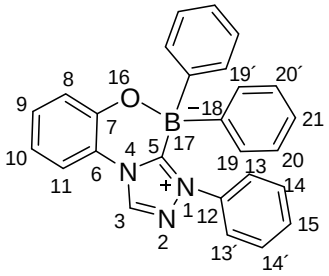


Under an inert atmosphere a solution of 460 mg (5 mmol) of triethylborane in 2 mL of anhydrous dioxane was added to a suspension of 0.119 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate in 5 mL of anhydrous dioxane. The mixture was stirred at 100 °C in a Schlenk-tube for 8 h. After cooling to rt the mixture was diluted with dioxane and subjected to column chromatography (silica gel, ethyl acetate/petroleum ether). Yield: 0.122 g (80%) of a colorless solid, mp: 143 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (s, 1 H, 3-H), 7.52 - 7.60 (m, 5 H, 13/13´/14/14´/15-H), 7.33 (dd, J_1 = 1.7 Hz, J_2 = 7.8 Hz, 1 H, 11-H), 7.24 (ddd, J_1 = 1.7 Hz, J_2 = 7.8 Hz, J_3 = 8.3 Hz, 1 H, 9-H), 7.12 (dd, J_1 = 1.3 Hz, J_2 = 8.3 Hz, 1 H, 8-H), 6.81 (td, J_1 = 1.3 Hz, J_2 = 7.8 Hz, 1 H, 10-H), 0.63 (t, J = 7.7 Hz, 6 H, 19/19´-H), 0.37 - 0.47 (overlapped signals, 2 H, 18/18´-H), 0.21 - 0.30 (overlap, 2 H, 18/18´-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.2 (o, C-7), 137.4 (o, C-12), 136.1 (+, C-13), 130.5 (+, C-15), 130.1 (+, C-9), 129.2 (+, C-13/C-13´), 125.5 (+, C-14/C-14´), 121.3 (o, C-6), 121.2 (+, C-8), 117.0 (+, C-10), 115.9 (+, C-11), 14.6 (-, C-18/C-18´), 9.9 (+, C-19/C-19´) ppm; ^{11}B NMR ($CDCl_3$, 193 MHz, $BF_3 \cdot Et_2O$): δ = -1.97 ppm; IR (ATR): $\bar{\nu}$ = 2864, 1506, 1460, 1306, 1292, 1146, 1036, 978, 883, 816, 750, 688, 659 cm^{-1}; MS (ESI 30 V): *m/z* (%) = 238.1 (100) [M+Na]$^+$. HR-ESI-MS: calcd for $C_{18}H_{21}N_3OB^+$ 306.1778. Found 306.1775 .


8.63 7.60 7.60 7.58 7.58 7.58 7.57 7.57 7.56 7.55 7.55 7.54 7.53 7.53 7.53 7.52 7.52 7.35 7.34 7.33 7.32 7.26 7.26 7.25 7.24 7.24 7.23 7.22 7.13 7.13 7.11 7.11 6.83 6.82 6.81 6.81 6.79 6.79
0.65 0.63 0.61 0.47 0.45 0.43 0.41 0.39 0.37 0.30 0.29 0.27 0.25 0.23 0.21
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.00 5.03 1.09 1.32 1.04 1.00 6.00 2.11 2.12
153.2 137.4 136.1 130.5 130.1 129.2 125.5 121.3 121.2 117.0 115.9 14.6 9.9
175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 ppm



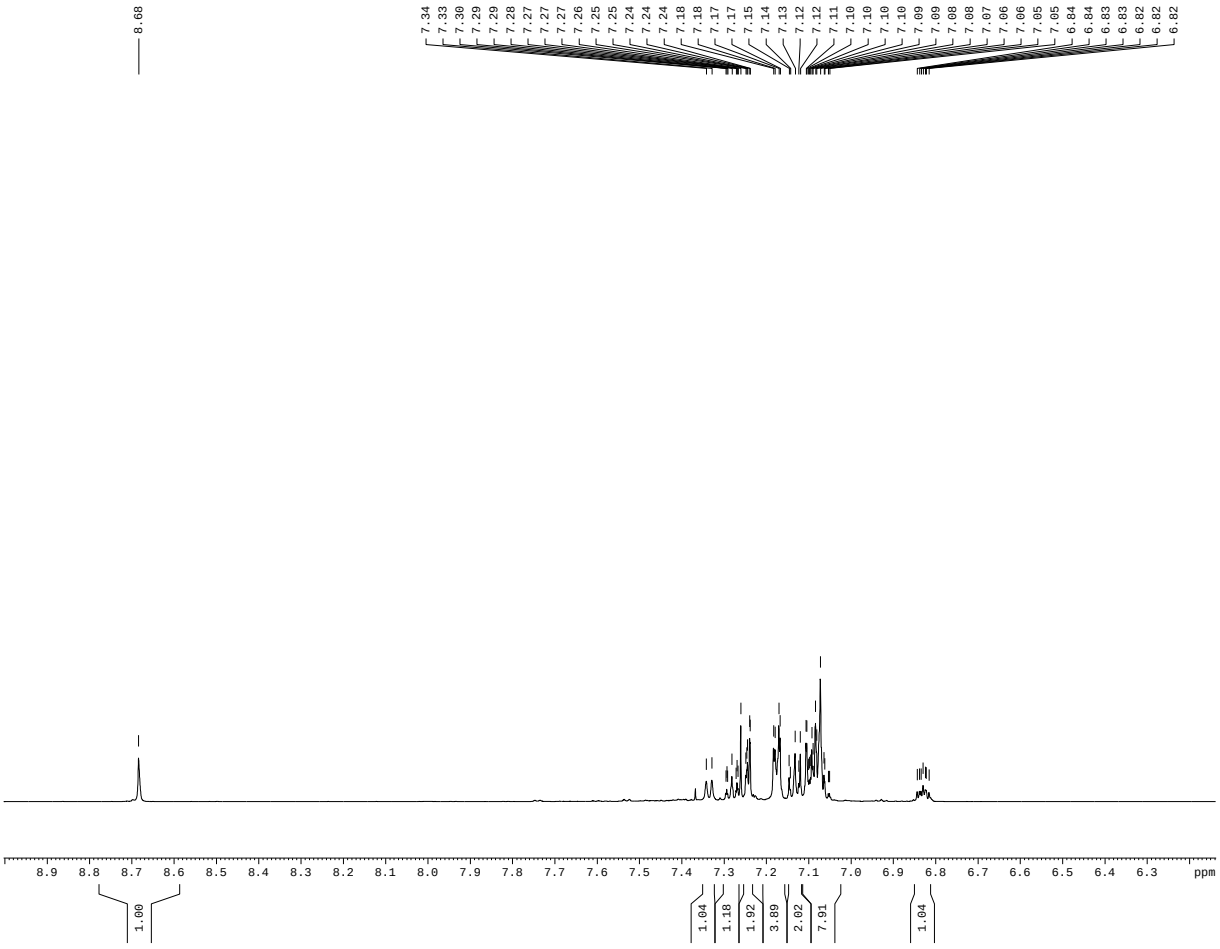
3,4,4-Triphenyl-4*H*-benzo[*e*][1,2,4]triazolo[3,4-*c*][1,4,2]oxazaborinin-3-ium-4-ide 15b

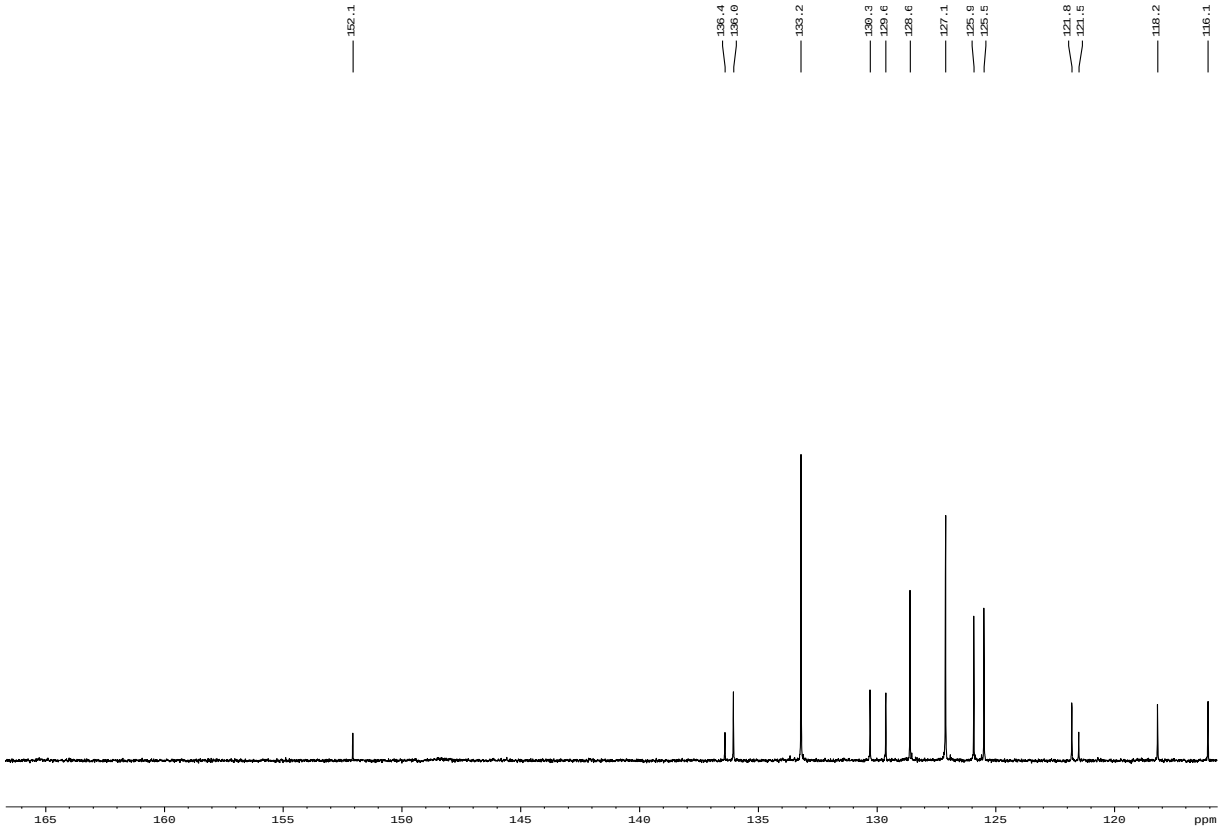


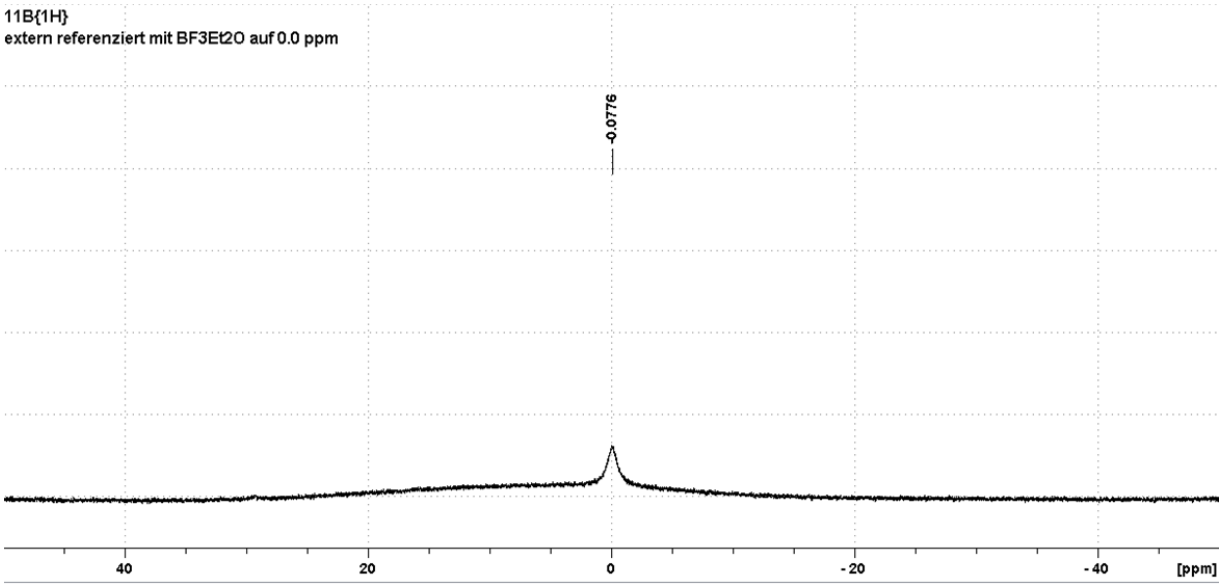
Method A: Under an inert atmosphere a solution of 0.242 g (1.0 mmol) of triphenylborane in 2 mL of anhydrous dioxane was added to a suspension of 0.119 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate in 5 mL of the same solvent. The mixture was stirred at 100 °C in a Schlenk-tube for 8 h. After cooling to rt, the mixture was diluted with dioxane and subjected to column chromatography (ethyl acetate/petroleum ether). Yield: 0.050 g (25%) of a colorless solid, mp: 86 °C;

Method B: Under an inert atmosphere a flask was charged with triphenyl(2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenoxy)borate (0.240 g, 0.5 mmol) and dry dioxane (10 mL). The mixture was then stirred at 100 °C for 8 h. After evaporation, the resulting precipitate was purified by column chromatography (silica gel, ethyl acetate/petroleum ether). Yield: 0.178 g (89%), mp: 86 °C.

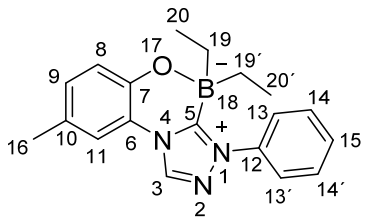
^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.68 (s, 1 H, 3-H), 7.34 (d, J = 7.9 Hz, 1 H, 11-H), 7.29 (tt, J_1 = 1.4 Hz, J_2 = 3.1 Hz, 1 H, 15-H), 7.24 - 7.25 (m, 2 H, 9/10-H), 7.18 (dd, J_1 = 2.0 Hz, J_2 = 7.7 Hz, 4 H, 19/19´-H), 7.12 - 7.15 (m, 2 H, 14/14´-H), 7.05 - 7.11 (m, 8 H, 13/13´/20/20´/21-H), 6.82 - 6.84 (m, 1 H, 8-H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 152.1 (o, C-7), 136.4 (o, C-12), 136.0 (+, C-3), 133.2 (+, C-19/C-19´), 130.3 (+, C-9), 129.6 (+, C-15), 128.6 (+, C-13/C-13´), 127.1 (+, C-20/C-20´), 125.9 (+, C-21), 125.5 (+, C-14/C-14´), 121.8 (+, C-10), 121.5 (o, C-6), 118.2 (+, C-8), 116.1 (+, C-11) ppm; ^{11}B NMR ($CDCl_3$, 193 MHz, $BF_3{\cdot}Et_2O$): δ = -0.08 ppm; IR (ATR): $\bar{\nu}$ = 3042, 1530, 1305,1279, 1181, 979, 926, 898, 739, 701, 688, 660, 650 cm^{-1}; MS (ESI 30 V): *m/z* (%) = 424.1 (100) $[M+Na]^+$. HR-ESI-MS: calcd for $C_{26}H_{20}N_3OBNa^+$ 424.1597. Found 424.1598.



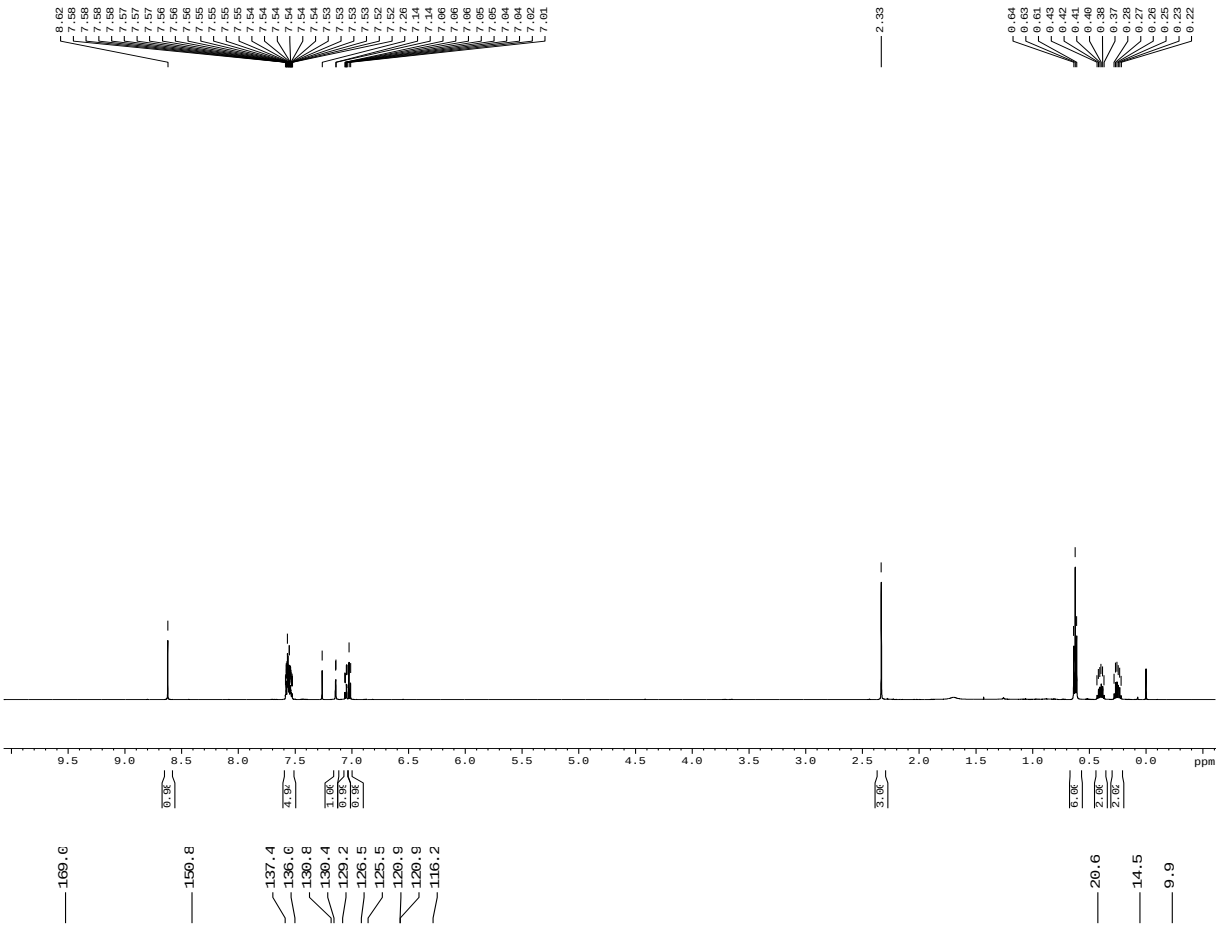

152.1
136.4
136.0
133.2
130.3
129.6
128.6
127.1
125.9
125.5
121.8
121.5
118.2
116.1
165
160
155
150
145
140
135
130
125
120
ppm

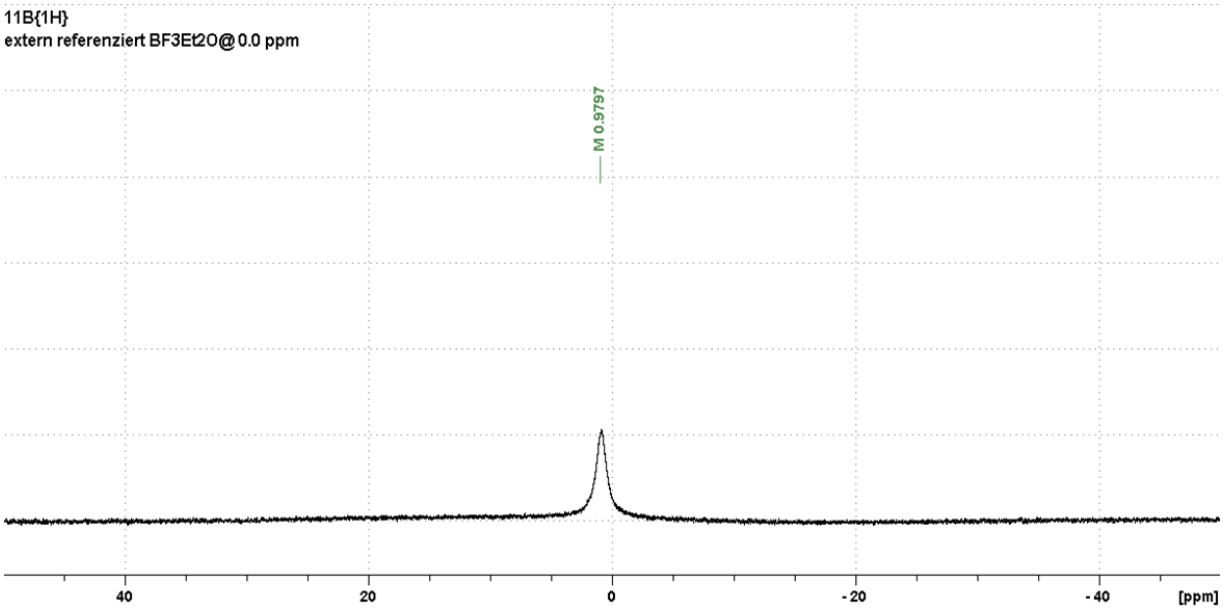

11B{1H}
extern referenziert mit BF3Et2O auf 0.0 ppm
-0.0776
40
20
0
-20
-40
[ppm]

4,4-Diethyl-3-phenyl-4*H*-benzo[*e*][1,2,4]triazolo[3,4-*c*][1,4,2]oxazaborinin-3-ium-4-ide 15c

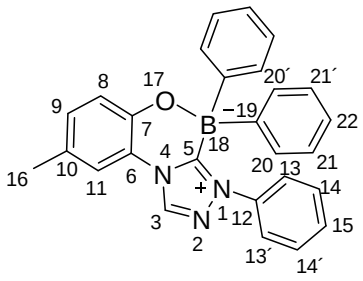


Under an inert atmosphere a solution of 460 mg (5 mmol) of triethylborane in 2 mL of anhydrous dioxane was added to a suspension of 0.126 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate in 5 mL of the same solvent. The mixture was stirred at 100 °C in a Schlenk-tube for 8 h. After cooling to rt, the mixture was treated with dioxane and subjected to column chromatography (ethyl acetate/petroleum ether). Yield: 0.120 g (75%) of a colorless solid, mp: 114 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.62 (s, 1 H, 3-H), 7.52 - 7.58 (m, 5 H, 13/13´/14/14´/15-H), 7.14 (d, J = 1.6 Hz, 1 H, 11-H), 7.05 (dd, J_1 = 1.6 Hz, J_2 = 8.3 Hz, 1 H, 9-H), 7.02 (d, J = 8.3 Hz, 1 H, 8-H), 2.33 (s, 3 H, 16-H), 0.63 (t, J = 7.7 Hz, 6 H, 20/20´-H), 0.37 - 0.43 (overlapped signals, 2 H, 19/19´-H), 0.22 - 0.28 (overlap, 2 H, 19/19´-H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 169.0 (o, C-5), 150.8 (o, C-7), 137.4 (o, C-12), 136.0 (+, C-3), 130.8 (+, C-9), 130.4 (+, C-15), 129.2 (+, C-13/C-13´), 126.5 (o, C-10), 125.5 (+, C-14/C-14´), 120.9 (o, C-6), 120.9 (+, C-8), 116.2(+, C-11), 20.6 (+, C-16), 14.5 (-, C-19/C-19´), 9.9 (+, C-20/C-20´) ppm; ^{11}B NMR ($CDCl_3$, 193 MHz, $BF_3 \cdot Et_2O$): δ = - 0.98 ppm; IR (ATR): $\tilde{\nu}$ = 2864, 1513, 1456, 1305, 1117, 913, 897, 868, 821, 763, 689, 661 cm^{-1}; MS (ESI 30 V): *m/z* (%) = 342.1 (100) $[M+Na]^+$. HR-ESI-MS: calcd for $C_{19}H_{22}N_3OBNa^+$ 342.1754. Found 342.1758.


8.62
7.58
7.58
7.58
7.58
7.57
7.57
7.57
7.56
7.56
7.56
7.55
7.55
7.55
7.55
7.54
7.54
7.54
7.54
7.54
7.54
7.53
7.53
7.53
7.53
7.52
7.52
7.26
7.14
7.06
7.06
7.06
7.05
7.05
7.04
7.04
7.02
7.01
2.33
0.64
0.63
0.61
0.43
0.42
0.41
0.40
0.38
0.37
0.28
0.27
0.26
0.25
0.23
0.22
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.9K
4.9K
1.0K
0.9K
0.9K
3.0K
6.0K
2.0K
2.0K
169.6
150.8
137.4
136.6
130.8
130.4
129.2
126.5
125.5
120.9
120.9
116.2
20.6
14.5
9.9
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



8-Methyl-3,4,4-triphenyl-4*H*-benzo[*e*][1,2,4]triazolo[3,4-*c*][1,4,2]oxazaborinin-3-ium-4-ide 15d

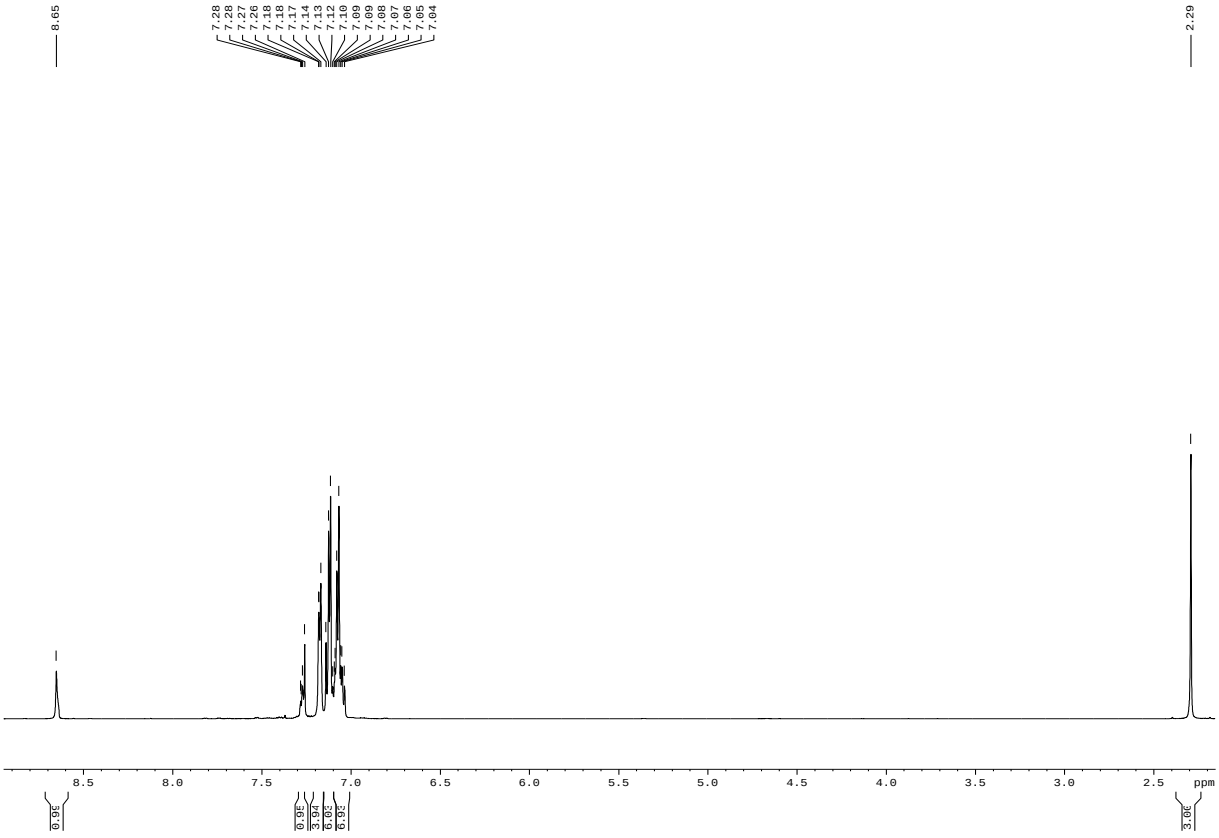


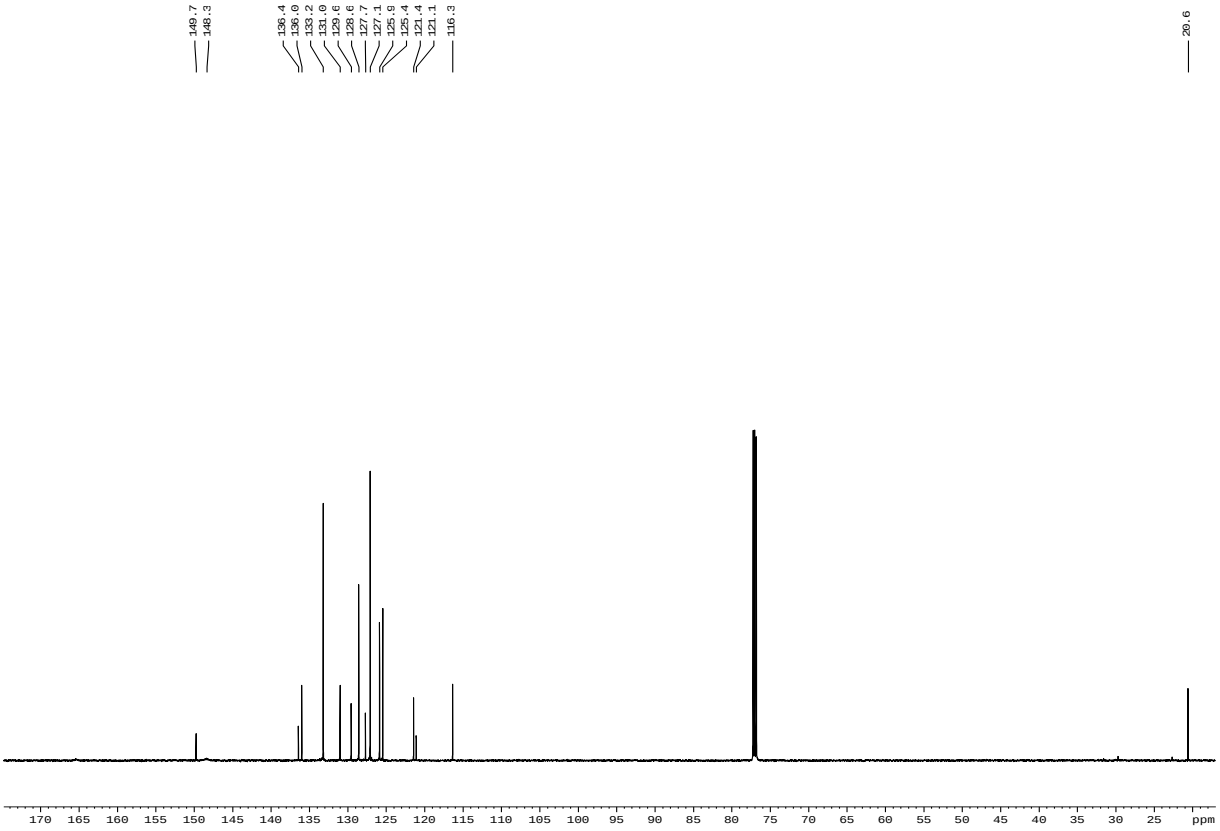
Method A: Under an inert atmosphere a solution of 0.242 g (1.0 mmol) of triphenylborane in 2 mL of anhydrous dioxane was added to a suspension of 0.126 g (0.50 mmol) of 2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenolate in 5 mL of the same solvent. The mixture was stirred at 100 °C in a Schlenk-tube for 8 h. After cooling to rt, the mixture was treated with dioxane and subjected to column chromatography (ethyl acetate/petroleum ether). Yield: 0.093 g (45%) of a colorless solid, mp: 182 °C;

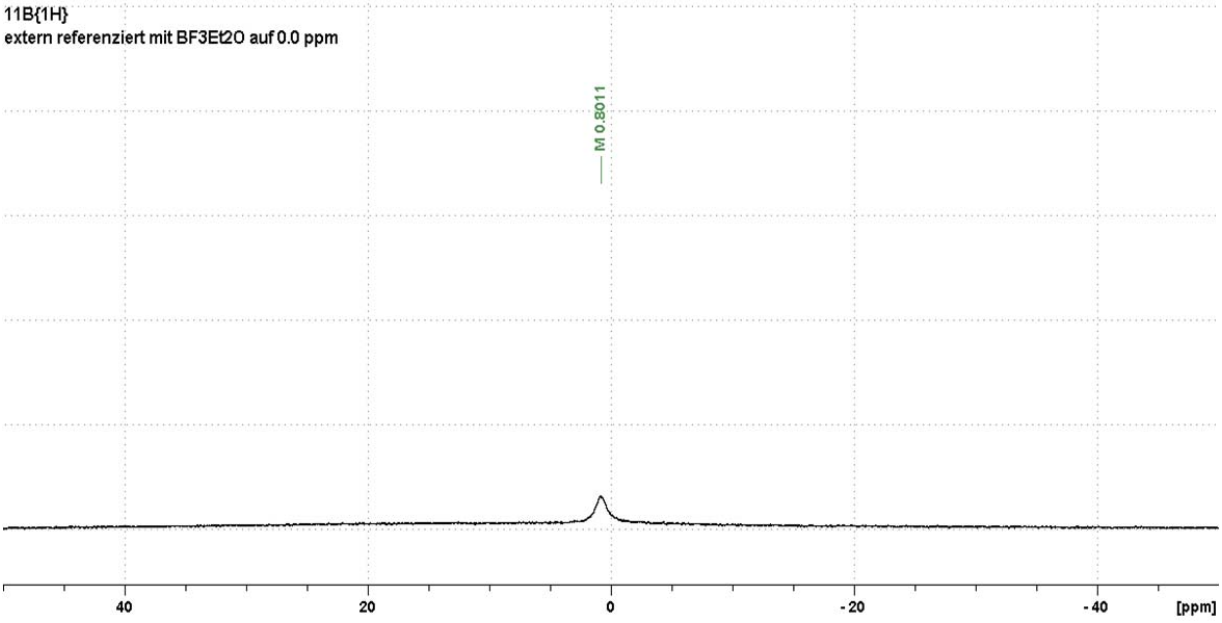
Method B: Under an inert atmosphere a flask was charged with (4-methyl-2-(1-phenyl-4*H*-1,2,4-triazolium-4-yl)phenoxy)triphenylborate (0.247 g, 0.5 mmol) and dry dioxane (10 mL), and the mixture was stirred at 100 °C for 8 h. After evaporation, the resulting precipitate was purified by column chromatography (silica gel, ethyl acetate/petroleum ether). Yield: 0.187 g (90%) of a colorless solid, mp: 182 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.65 (s, 1 H, 3-H), 7.27 (tt, J_1 = 2.3 Hz, J_2 = 6.5 Hz 1 H, 15-H), 7.18 (dd, J_1 = 0.9 Hz, J_2 = 7.2 Hz, 4 H, 20/20´-H), 7.10 - 7.14 (m, 6 H, 13/13´/14/14´/11/8-H), 7.04 - 7.09 (m, 7 H,

21/21´/22/9-H), 2.29 (s, 3 H, 16-H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 149.7 (o, C-19), 148.3 (o, C-7), 136.4 (o, C-12), 136.0 (+, C-3), 133.2 (+, C-20/C-20´), 130.0 (+, C-9), 129.6 (+, C-15), 128.6 (+, C-13/C-13´), 127.7 (o, C-10), 127.1 (+, C-21/C-21´), 125.9 (+, C-22), 125.4 (+, C-14/C-14´), 121.4 (+, C-8), 121.1 (o, C-6), 116.3 (+, C-11), 20.6 (+, C-16) ppm; ^{11}B NMR ($CDCl_3$, 193 MHz, $BF_3 \cdot Et_2O$): δ = −0.80 ppm; IR (ATR): $\bar{\nu}$ = 1511, 1301, 1177, 1145, 927, 907, 872, 823, 739, 689, 660 cm^{-1}; MS (ESI 30 V): *m/z* (%) = 438.1 (100) $[M+Na]^+$. HR-ESI-MS: calcd for $C_{27}H_{22}N_3OBNa^+$ 438.1754. Found 438.1758**.**







[1] S. E. O'Toole, S. J. Connon, *Org. Biomol. Chem.* **2009**, *7*, 3584 - 3593.