Electronic Supplementary Material (ESI) for ChemComm.

Sydnone anions and abnormal N-heterocyclic carbenes of O-ethylsydnones. Characterizations, calculations and catalyses

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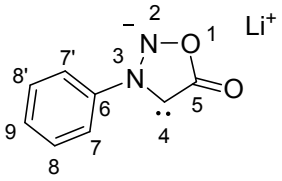
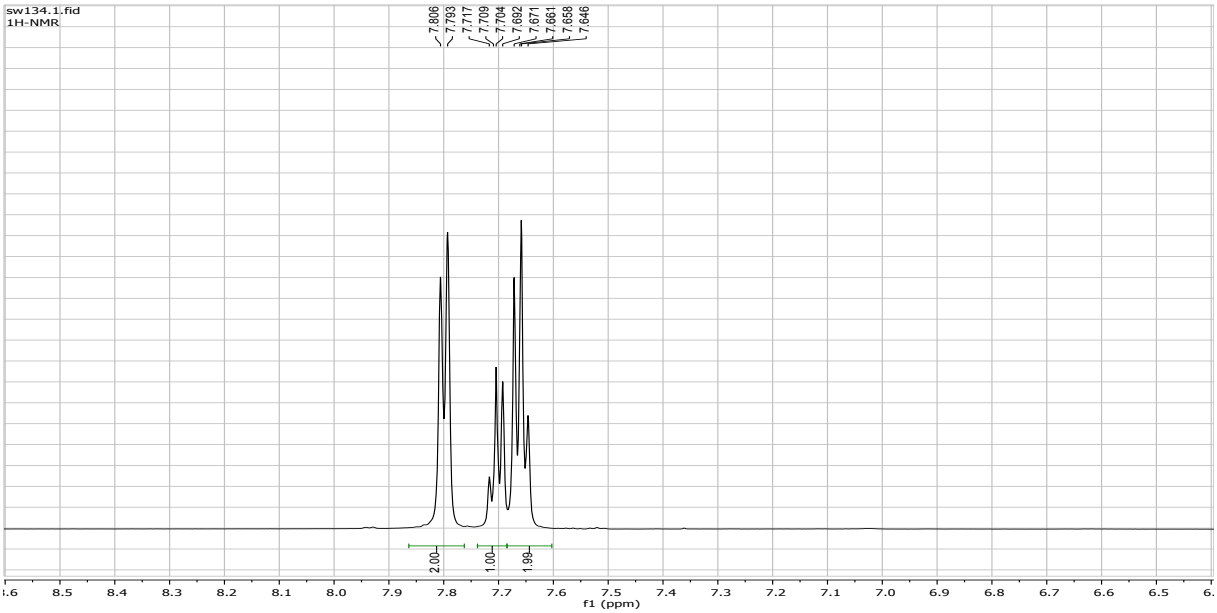
General considerations. Flash-chromatography was performed with silica gel 60 (0.040-0.063 mm). Nuclear magnetic resonance (NMR) spectra were obtained with a Bruker Avance 400 and Bruker Avance III 600 MHz. ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz. ^{13}C NMR spectra were recorded at 100 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 Vector 22 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. 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. Yields are not optimized. All density-functional theory (DFT)-calculations were carried out by using the Jaguar 7.7.107 software (Jaguar, version 7.7, Schrodinger, LLC, New York, NY, 2010) running on Linux 2.6.18-238.el5 SMP (x86_64) on two AMD Phenom II X6 1090T processor workstations (Beowulf-cluster) parallelized with OpenMPI 1.3.4. MM2 optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the implemented LACVP* (Hay-Wadt effective core potential (ECP) basis on heavy atoms, N31G6* for all other atoms) basis set and with the B3LYP density functional. All calculated structures were proven to be true minima by the absence of imaginary frequencies or transition states by the occurrence of one negative frequency. Plots were obtained using Maestro 9.1.207, the graphical interface of Jaguar. Inversion barriers have been calculated fully relaxed, fixating one torsion angle around the inverted center, and optimizing all remaining degrees of freedom. Torsion angles were modified in steps of 10°. Thermodynamic corrections were estimated from unscaled frequencies, using standard formulae in the ideal gas harmonic oscillator approximation as implemented in Jaguar, and refer to a standard state of 298.15 K and 1 mol/dm^3 concentration.

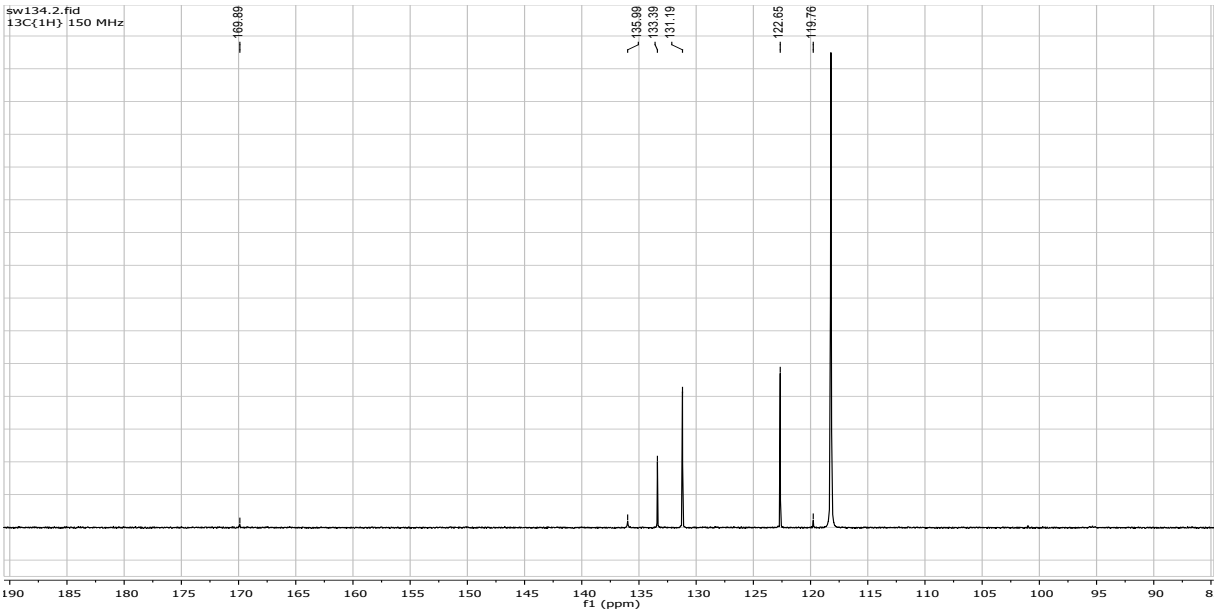
Anion of N-phenyl-1,2,3-oxadiazolium-5-olate 5a:



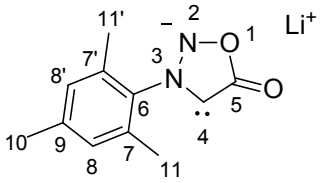
A sample of 11 mg (68 µmol) of N-phenylsydnone **2a**[1] was dissolved in 0.3 mL of anhydrous CD_3CN under an inert atmosphere. Then, a freshly prepared solution of 0.2 mL of anhydrous CD_3CN and 0.03 mL (73 µmol) of a 24% solution of nBuLi in hexanes was added to give **5a** in quantitative yields (protocol 1). ^{1}H NMR (600 MHz, MeCN-d_3): δ = 7.81-7.79[1] (m, 2 H, *H*C-7 + *H*C-7'), 7.69-7.72 (m, 1 H, *H*C-9), 7.65-7.67[1] (m, 2 H, *H*C-8 + *H*C-8') ppm; ^{13}C NMR (150 MHz, MeCN-d_3)[2]: δ = 169.9 (o, *C*-5), 136.0 (o, *C*-6), 133.4 (+, H*C*-9), 131.2 (+), 122.7 (+) ppm.



[1] Assignment exchangeable.
[2] *C*-4 is not detectable.

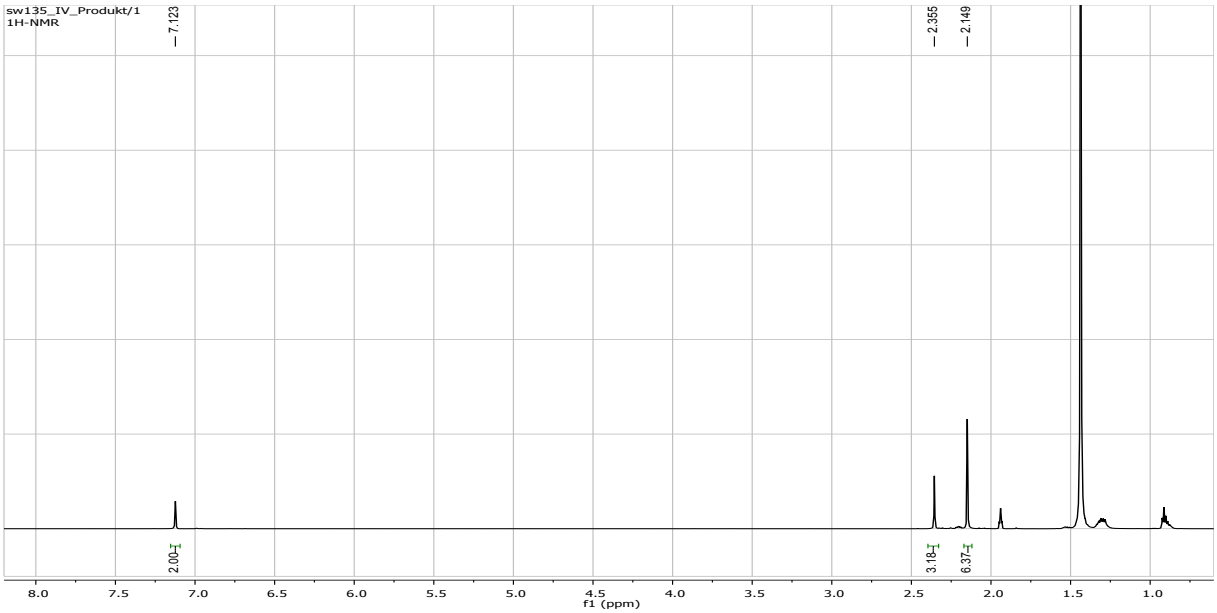


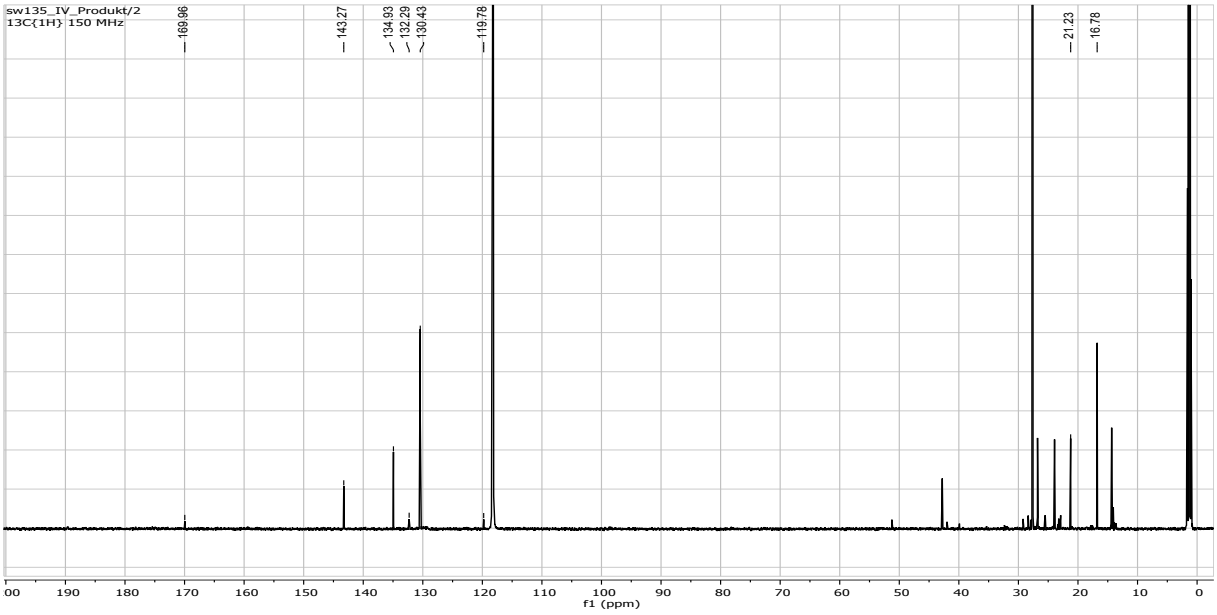
Anion of N-mesityl-1,2,3-oxadiazolium-5-olate 5b:



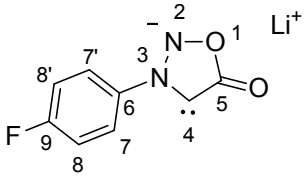
A sample of 11 mg (54 µmol) of N-mesitylsydnone **2b**[2] was dissolved in 0.3 mL of anhydrous CD_3CN under an inert atmosphere. Then, a freshly prepared solution of 0.2 mL of anhydrous CD_3CN and 0.03 mL (73 µmol) of a 24% solution of nBuLi in cyclohexane was added to give **5b** in quantitative yields (protocol 2). ^{1}H NMR (600 MHz, MeCN-d_3): δ = 7.12 (s, 2 H, *H*C-8 + *H*C-8'), 2.36 (s, 3 H, H_3C-10), 2.15 (s, 6 H, H_3C-11 + H_3C-11') ppm; ^{13}C NMR (150 MHz, MeCN-d_3)[3]: δ = 170.0 (o, *C*-5), 143.3 (o, *C*-9), 134.9 (o, *C*-7 + *C*-7'), 132.3 (o, *C*-6), 130.4 (+, H*C*-8 + H*C*-8'), 21.2 (+, H*C*-10), 16.8 (+, H*C*-11 + H*C*-11') ppm.

[3] *C*-4 is not detectable.



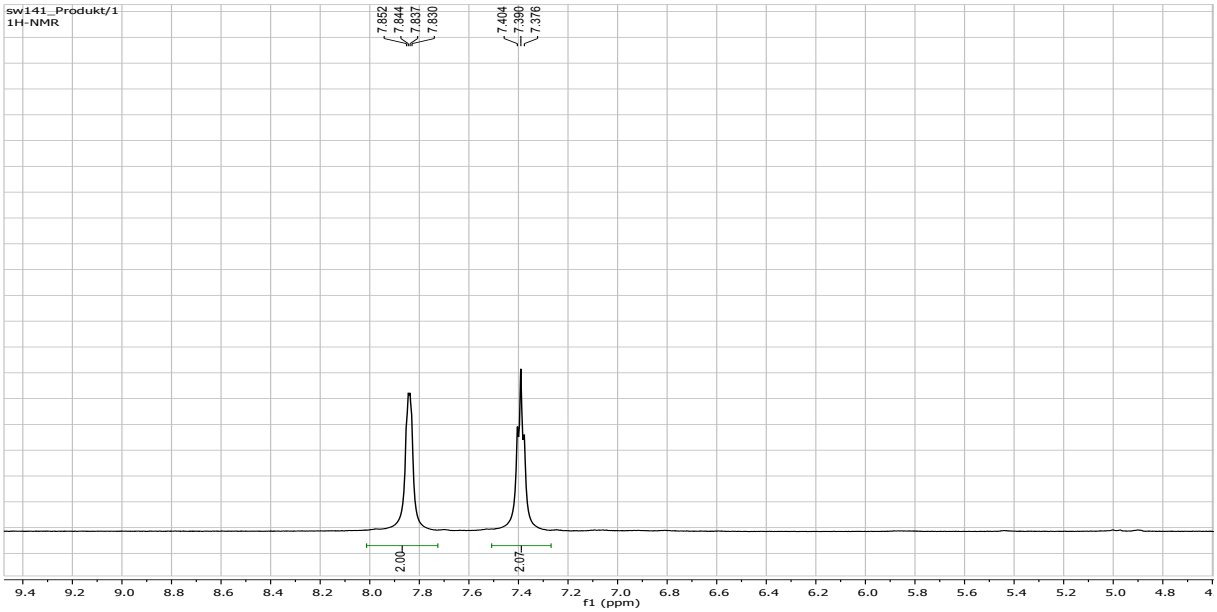


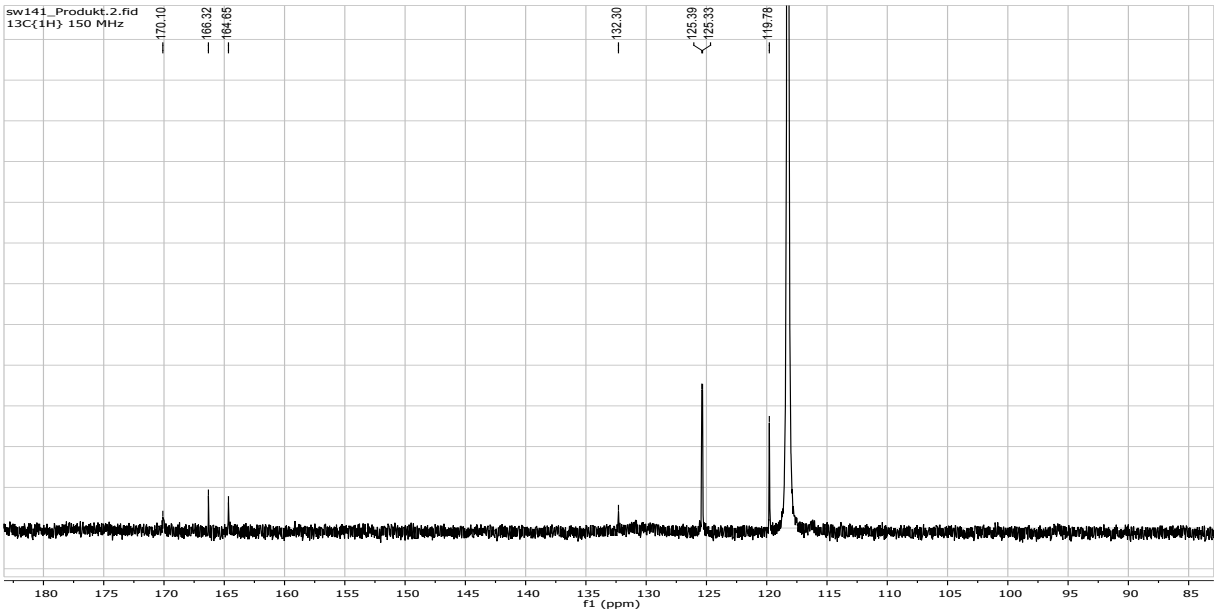
Anion of N-(4-fluorophenyl)-1,2,3-oxadiazolium-5-olate 5c:



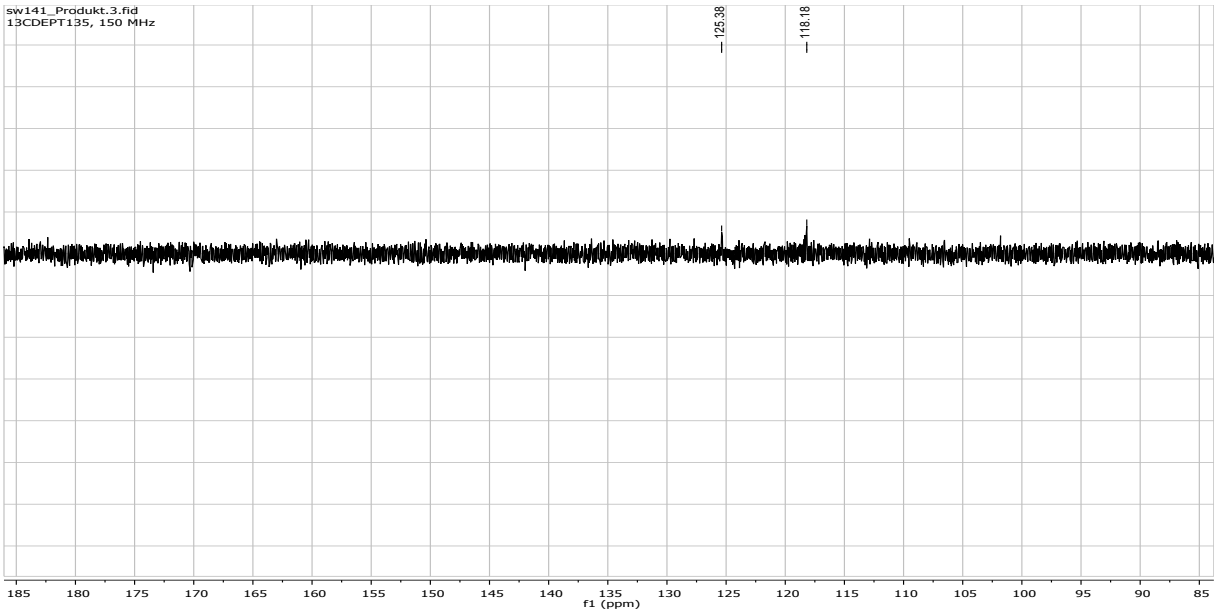
A sample of 11 mg (61 µmol) of N-(4-fluorophenyl)sydnone **2c**[1,3] was used following protocol 1 (*c.f.* **5a**). ^{1}H NMR (600 MHz, MeCN-d_3): δ = 7.84-7.85[4] (m, 2 H, *H*C-7 + *H*C-7'), 7.38-7.40[4] (m, 2 H, *H*C-8 + *H*C-8') ppm; ^{13}C NMR (150 MHz, MeCN-d_3)[5]: δ = 169.7 (o, *C*-5), 165.5 (d, *J* = 258.3 Hz, o, *C*-9), 132.3 (o, *C*-6), 125.4 (d, *J* = 9.4 Hz, +, H*C*-7 + H*C*-7'), 118.0 (+, H*C*-8 + H*C*-8') ppm.

[4] Assignment exchangeable.
[5] *C*-4 is not detectable.

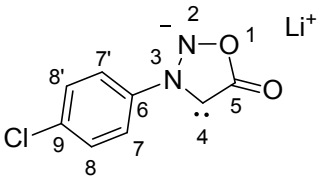




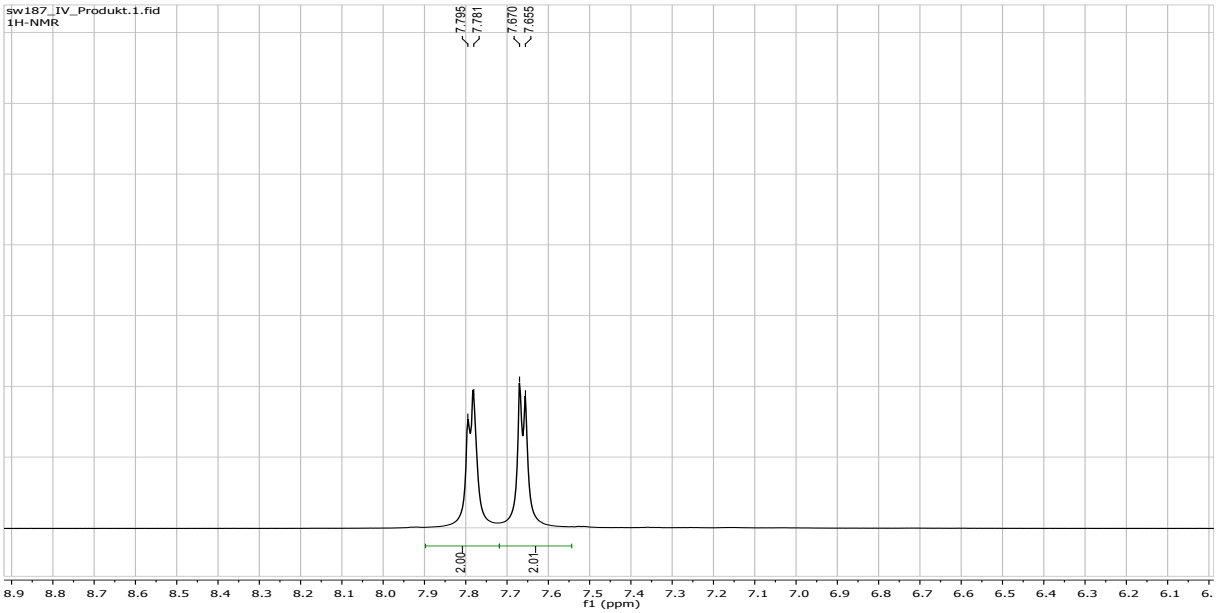
Signals of C-8/C8´were overlapped by CN signal.



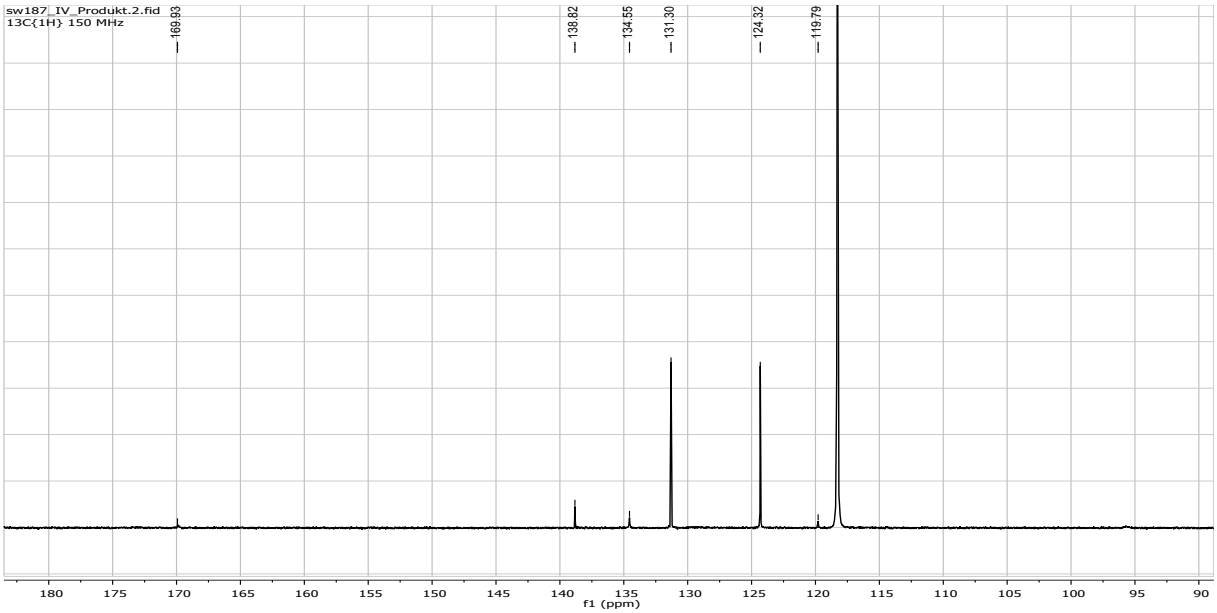
Anion of N-(4-chlorophenyl)-1,2,3-oxadiazolium-5-olate 5d:



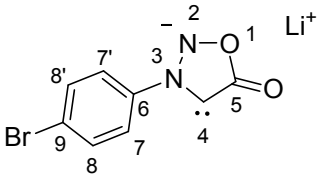
A sample of 11 mg (56 µmol) of N-(4-chlorophenyl)sydnone **2d**[1,4] was used following protocol 1 (*c.f.* **5a**). ^{1}H NMR (600 MHz, MeCN-d_3): δ = 7.78-7.79[6] (m, 2 H, *H*C-8 + *H*C-8'), 7.66-7.67[6] (m, 2 H, *H*C-7 + *H*C-7') ppm; ^{13}C NMR (150 MHz, MeCN-d_3)[7]: δ = 169.9 (o, *C*-5), 138.8 (o, *C*-9), 134.6 (o, *C*-6), 131.3 (+, H*C*-8 + H*C*-8'), 124.3 (+, H*C*-7 + H*C*-7') ppm.



[6] Assignment exchangeable.
[7] *C*-4 is not detectable.

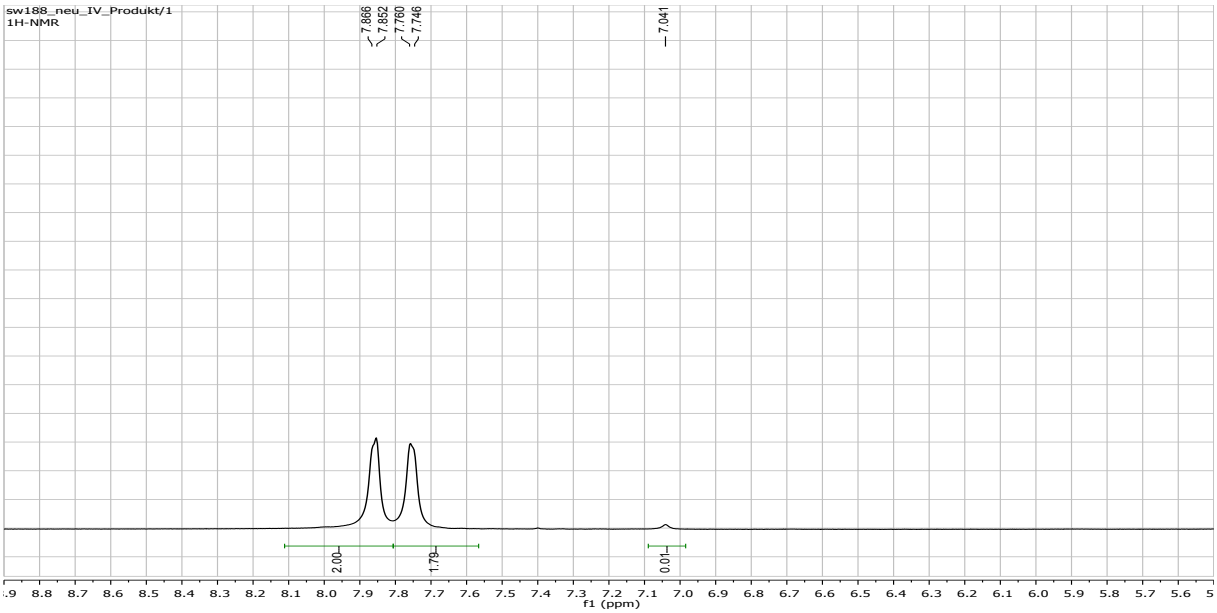


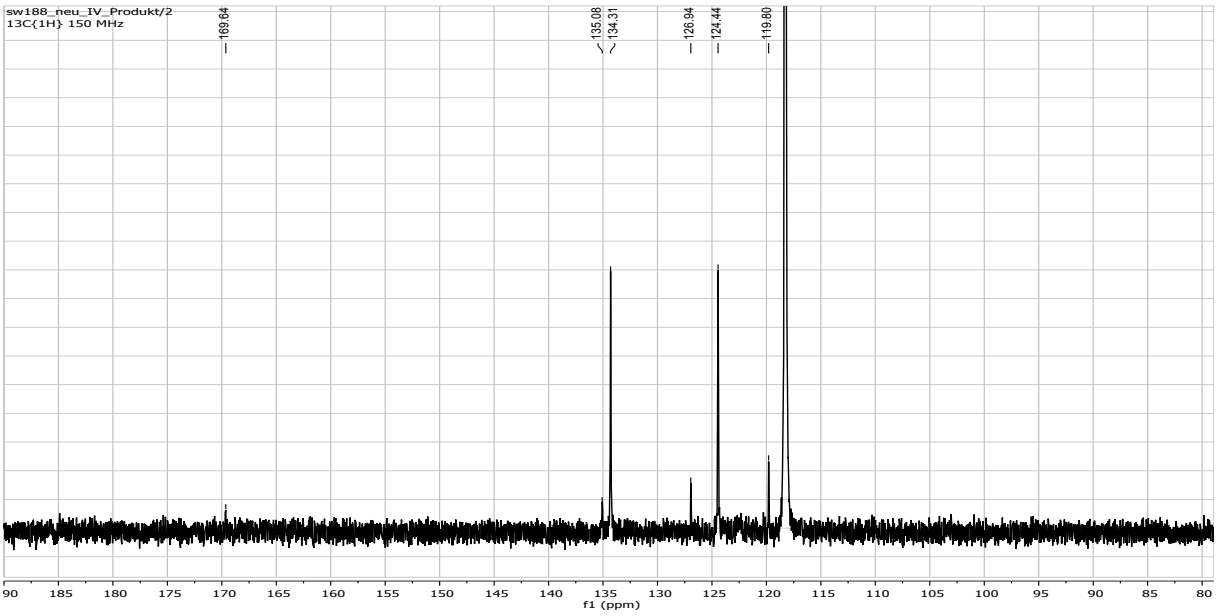
Anion of N-(4-bromophenyl)-1,2,3-oxadiazolium-5-olate 5e:



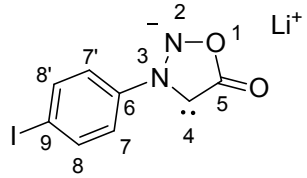
A sample of 11 mg (46 µmol) of N-(4-bromophenyl)sydnone **2e**[1,5] was used following protocol 1 (*c.f.* **5a**). ^{1}H NMR (600 MHz, MeCN-d_3): δ = 7.82-7.83[8] (m, 2 H, *H*C-8 + *H*C-8'), 7.71-7.72[8] (m, 2 H, *H*C-7 + *H*C-7') ppm; ^{13}C NMR (150 MHz, MeCN-d_3)[9]: δ = 169.6 (*C*-5, o), 135.1 (o, *C*-6), 134.3 (+), 126.9 (o, *C*-9), 124.4 (+) ppm.

[8] Assignment exchangeable.
[9] *C*-4 is not detectable.



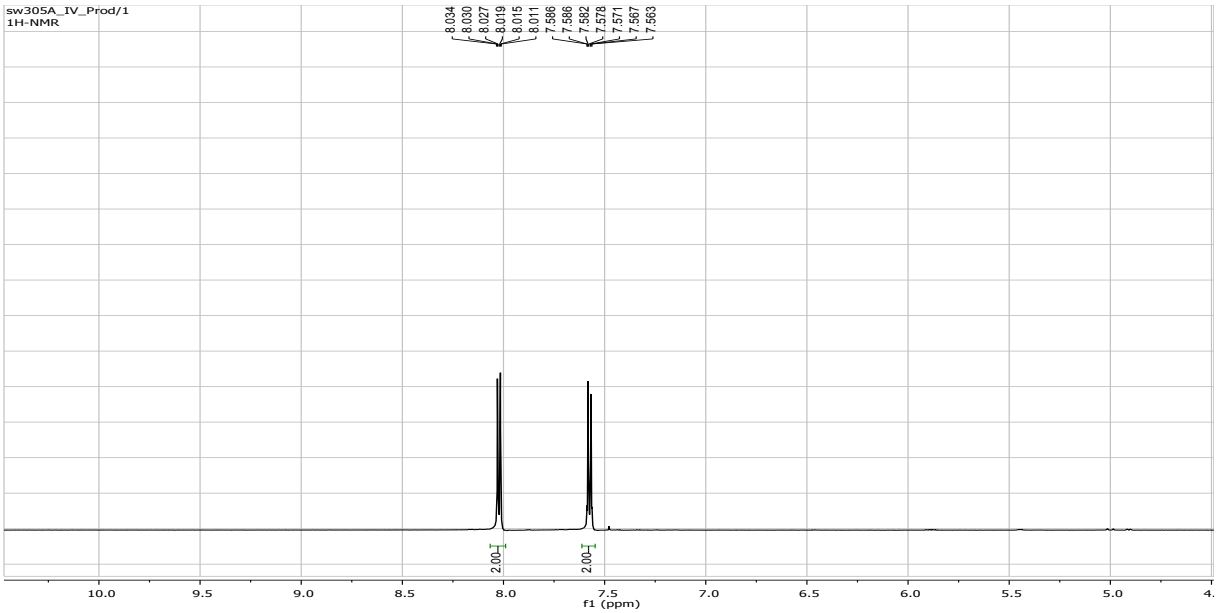


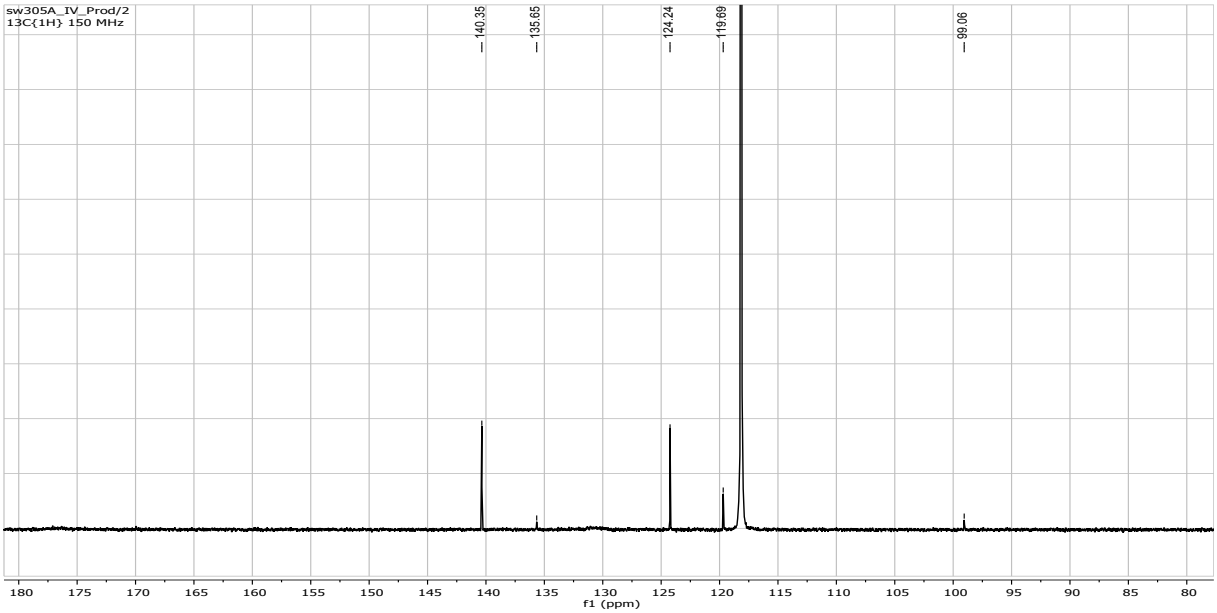
Anion of N-(4-iodophenyl)-1,2,3-oxadiazolium-5-olate 5f:



A sample of 11 mg (38 µmol) of N-(4-iodophenyl)sydnone **2f** was used following protocol 2 (*c.f.* **5b**). ^{1}H NMR (600 MHz, MeCN-d_3): δ = 8.01-8.03[10] (m, 2 H, *H*C-8 + *H*C-8'), 7.56-7.59[10] (m, 2 H, *H*C-7 + *H*C-7') ppm; ^{13}C NMR (150 MHz, MeCN-d_3) [11]: δ = 140.4 (+), 135.7 (o, *C*-6), 124.3 (+), 99.0 (*C*-9, o) ppm.

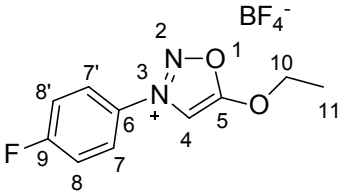
[10] Assignment exchangeable.
[11] *C*-5 and *C*-4 were not detectable.



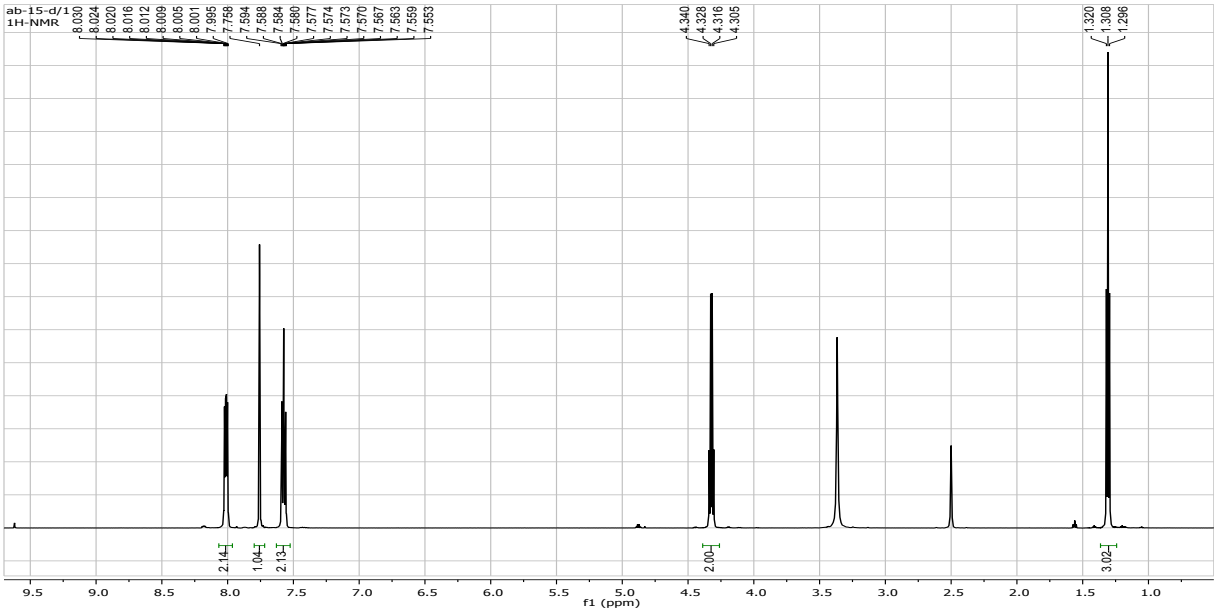


Decomposition observable after approximately 1 h. C-5 is not detectable after 2 k.

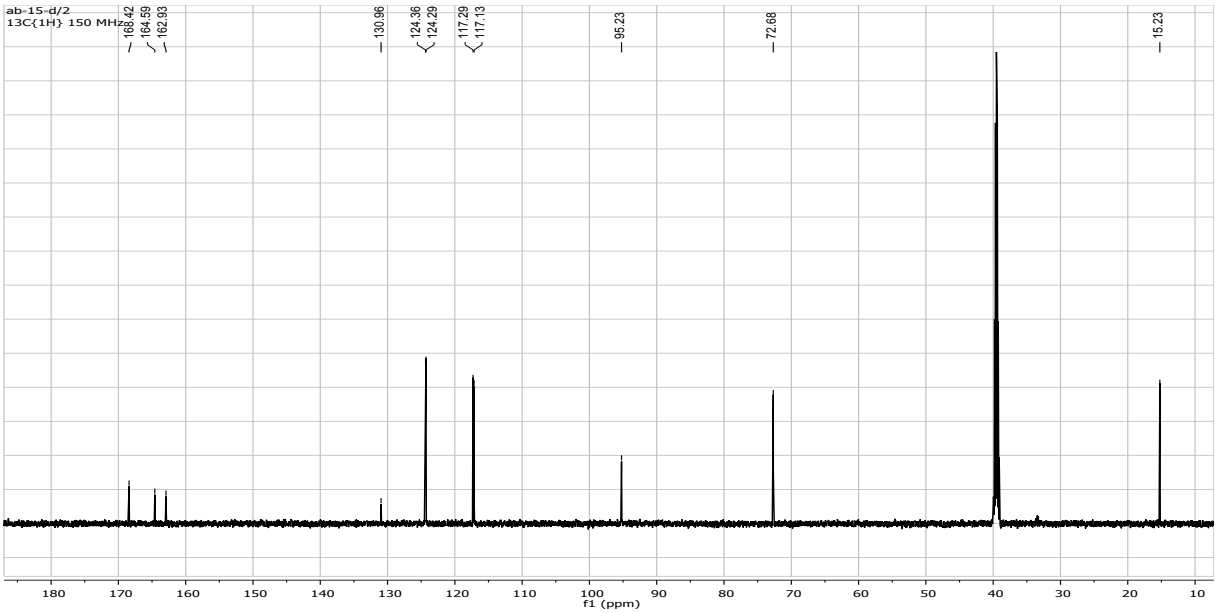
5-Ethoxy-N-(4-fluorophenyl)-1,2,3-oxadiazolium tetrafluoroborate 6c.



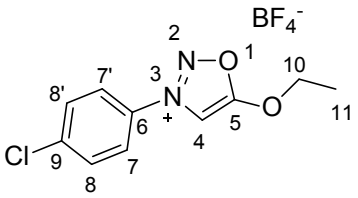
Under an inert atmosphere a sample of 1.12 g (6.2 mmol) of N-(4-fluorophenyl)sydnone[6] in 10 mL of anhydrous dichloromethane was treated dropwise with 9.3 mL (9.3 mmol) of triethyloxonium tetrafluoroborate (1 M in CH_2Cl_2) and stirred at rt for 5 days. On addition of diethylether a precipitate formed which was filtered off and dried *in vacuo*. Yield: 1.05 g (57 %) of a colorless solid, mp. 98 °C; ^{1}H NMR (600 MHz, DMSO-d_6): δ = 8.00-8.03[12] (m, 2H, *H*C-7/*H*C-7‘), 7.76 (s, 1H, *H*C-4), 7.59-7.55[12] (m, 2H, *H*C-8/*H*C-8‘), 4.32 (q, $J_{H,H}$ = 7.1 Hz, 2H, H_2C-10), 1.31 (t, $J_{H,H}$ = 7.1 Hz, 3H, H_3C-11) ppm; ^{13}C NMR (150 MHz, DMSO-d_6): δ = 168.4 (o, *C*-5), 163.8 (o, d, $^1J_{C,F}$ = 248.9 Hz, *C*-9), 131.0 (o, *C*-6), 124.3 (+, d, $^3J_{C,F}$ = 9.5 Hz, H*C*-7/H*C*-7‘), 117.2 (+, d, $^2J_{C,F}$ = 23.7 Hz, H*C*-8/H*C*-8‘), 95.2 (+, H*C*-4), 72.7 (-, H_2C-10), 15.2 (+, H_3C-11) ppm; IR (ATR): $\tilde{\nu}$ = 3141, 3098, 2993, 1719, 1638, 1611, 1596, 1506, 1473, 1446, 1425, 1386, 1348, 1300, 1261, 1243, 1164, 1054, 1030, 1013, 1003, 962, 881, 840, 817, 781, 767, 710, 669, 597, 541, 521, 497 cm^{-1}; MS (ESI 30V) *m/z* (%) = 209 (33) [M^+], 505 (100) [$2M^+$+BF_4^-]. HRMS: Calcd 209.0721. Found 209.0723.



[12] Assignment exchangeable.

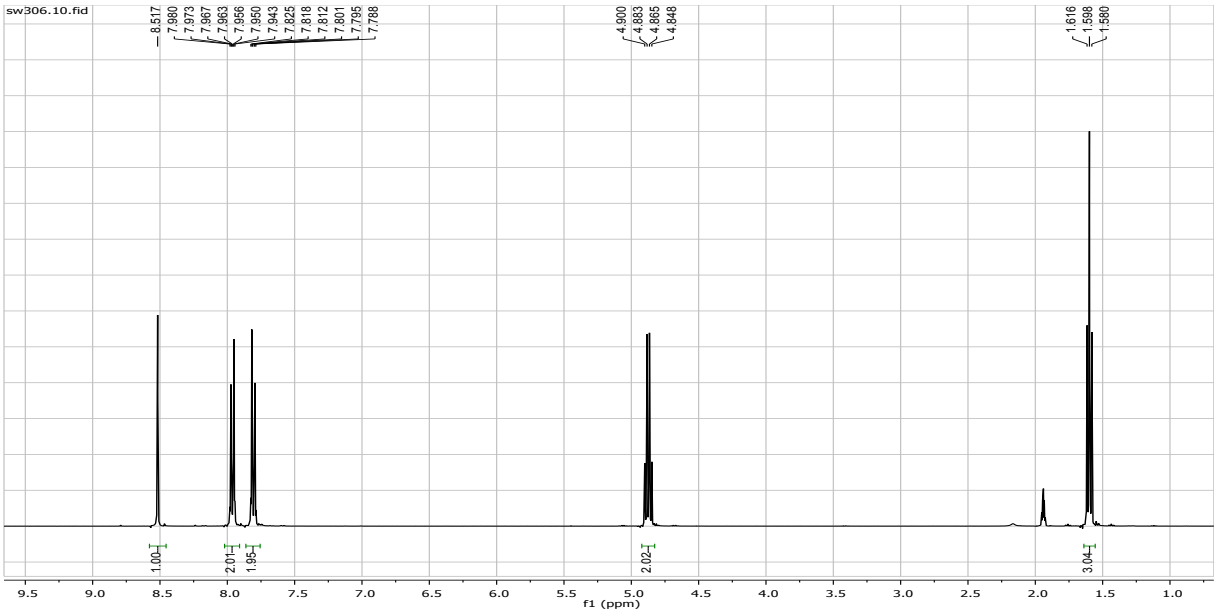


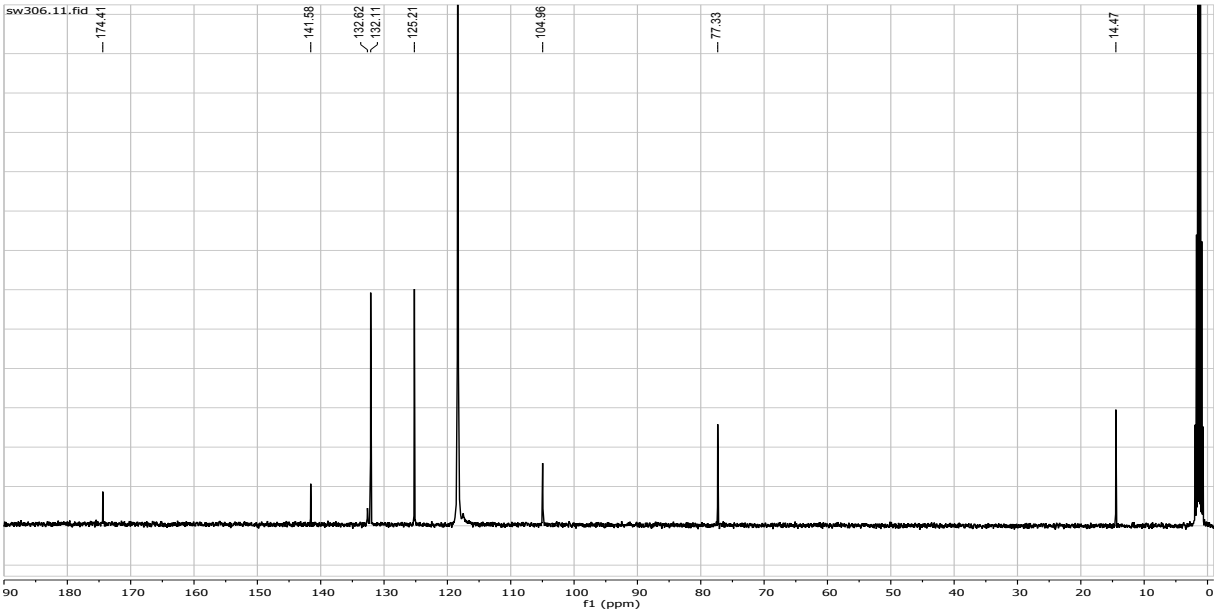
5-Ethoxy-N-(4-chlorophenyl)-1,2,3-oxadiazolium tetrafluoroborate 6d.



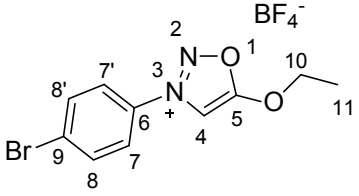
A sample of 2.79 g (14.2 mmol) N-(4-chlorophenyl)sydnone[6] dissolved in 20 mL of anhydrous CH_2Cl_2 was treated dropwise with 17 mL (17.0 mmol) of triethyloxonium tetrafluoroborate (1 M in CH_2Cl_2) and then stirred for 96 h at rt. On addition of diethylether a precipitate formed which was filtered off and dried *in vacuo*. Yield: 2.42 g (55 %), mp. 117 °C. ^{1}H NMR (400 MHz, MeCN-d_3): δ = 8.52 (s, 1H, *H*C-4), 7.94-7.98[13] (m, 2H, *H*C-7/*H*C-7‘), 7.79-7.83[13] (m, 2H, *H*C-8/*H*C-8‘), 4.87 (q, $J_{H,H}$ = 7.1 Hz, 2H, H_2C-10), 1.60 (t, $J_{H,H}$ = 7.1 Hz, 3H, H_3C-11) ppm. ^{13}C NMR (100 MHz, MeCN-d_3): δ = 174.4 (o, *C*-5), 141.6 (o, *C*-9), 132.6 (o, *C*-6), 132.1 (+), 125.2 (+), 105.0 (+, H*C*-4), 77.3 (-, H_2C-10), 14.5 (+, H_3C-11) ppm; IR (ATR): $\tilde{\nu}$ = 3148, 3105, 2994, 1639, 1596, 1585, 1485, 1438, 1411, 1394, 1382, 1347, 1306, 1286, 1264, 1219, 1186, 1098, 1060, 1024, 992, 962, 883, 839, 761, 750, 705, 696, 662, 544, 519, 514, 500, 453, 423 cm^{-1}; MS (ESI 30 V) *m/z* (%) = 225 (100) [M^+], 537 (13) [$2M^+$+BF_4^-]. HRMS: Calcd 225.0425. Found 225.0432.

[13] Assignment exchangeable.



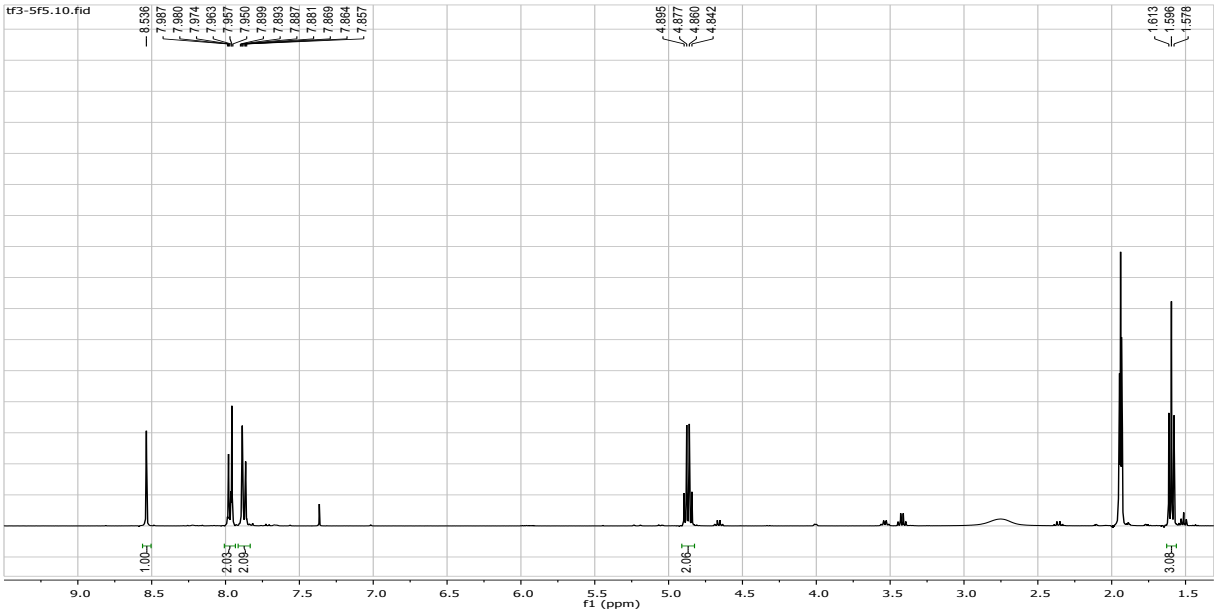


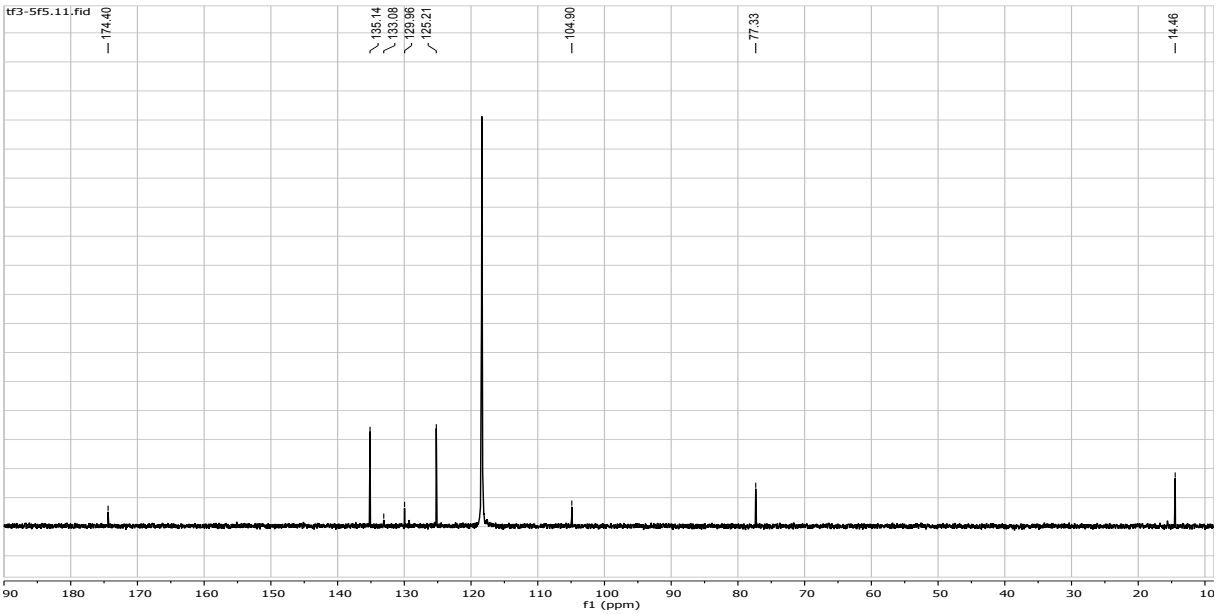
5-Ethoxy-N-(4-bromophenyl)-1,2,3-oxadiazolium tetrafluoroborate 6e.



A sample of 0.19 g (0.76 mmol) N-(4-bromophenyl)Sydnone[6] in 10 mL of anhydrous CH_2Cl_2 was treated dropwise with 1.2 mL (1.20 mmol) of triethyloxonium tetrafluoroborate (1 M in CH_2Cl_2) and then stirred at rt for 72 h. On addition of diethylether a precipitate formed which was filtered off and dried *in vacuo*. Yield: 0.167 g (58 %), mp: 102 °C. ^{1}H NMR (400 MHz, MeCN-d_3: δ = 8.54 (s, 1H, *H*C-4), 7.95-7.99[14] (m, 2H, *H*C-8/*H*C-8‘), 7.86-7.90[14] (m, 2H, *H*C-7/*H*C-7‘), 4.87 (q, $J_{H,H}$ = 7.1 Hz,

2H, H_2C-10), 1.60 (t, $J_{H,H}$ = 7.1 Hz, 3H, H_3C-11) ppm; ^{13}C NMR (100 MHz, MeCN-d_3): δ = 174.4 (o, *C*-5), 135.1 (+), 133.1 (o, *C*-6), 130.0 (o, *C*-9), 125.2 (+), 104.9 (+, H*C*-4), 77.3 (-, H_2C-10), 14.5 (+, H_3C-11) ppm; IR (ATR): $\tilde{\nu}$ = 3146, 3103, 2994, 1638, 1592, 1580, 1484, 1449, 1435, 1395, 1380, 1345, 1305, 1284, 1262, 1187, 1124, 1099, 1057, 1025, 991, 961, 882, 834, 760, 736, 701, 687, 661, 623, 538, 520, 509, 442, 417, 407 cm^{-1}; MS (ESI 30 V) *m/z* (%) = 271.0 (100) [M^+], 627.0 (10) [$2M^+$+BF_4^-]. HRMS: calcd. 268.9920. Found 268.9962.





5-Ethoxy-N-(4-iodophenyl)-1,2,3-oxadiazolium tetrafluoroborate 6f.

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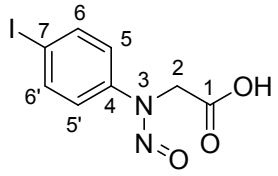
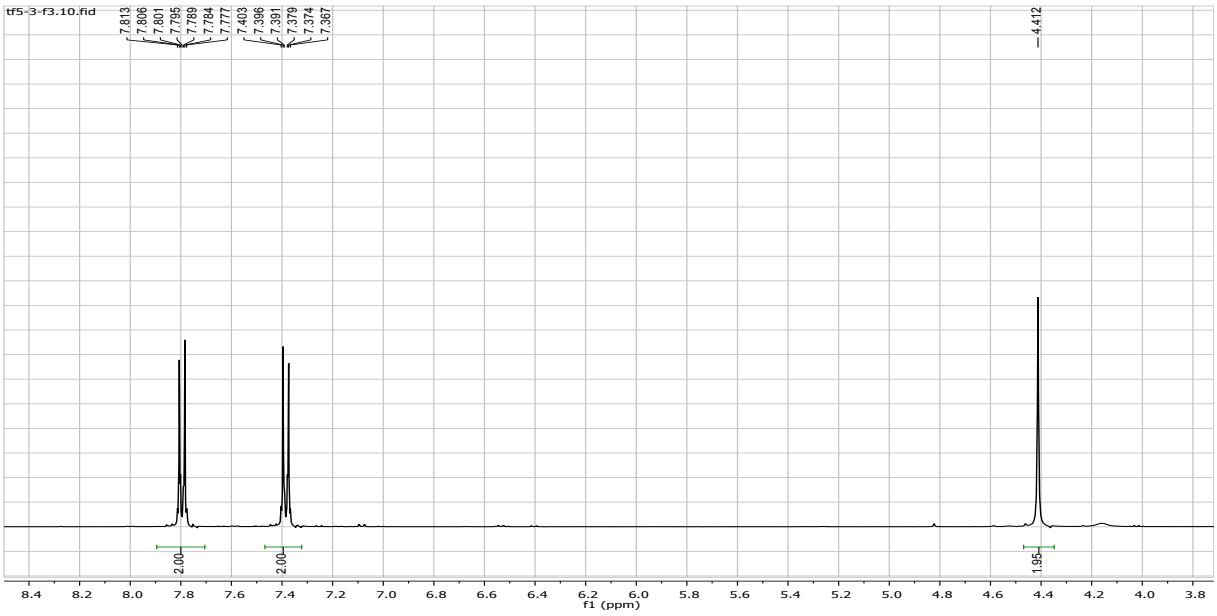
[14] Assignment exchangeable.

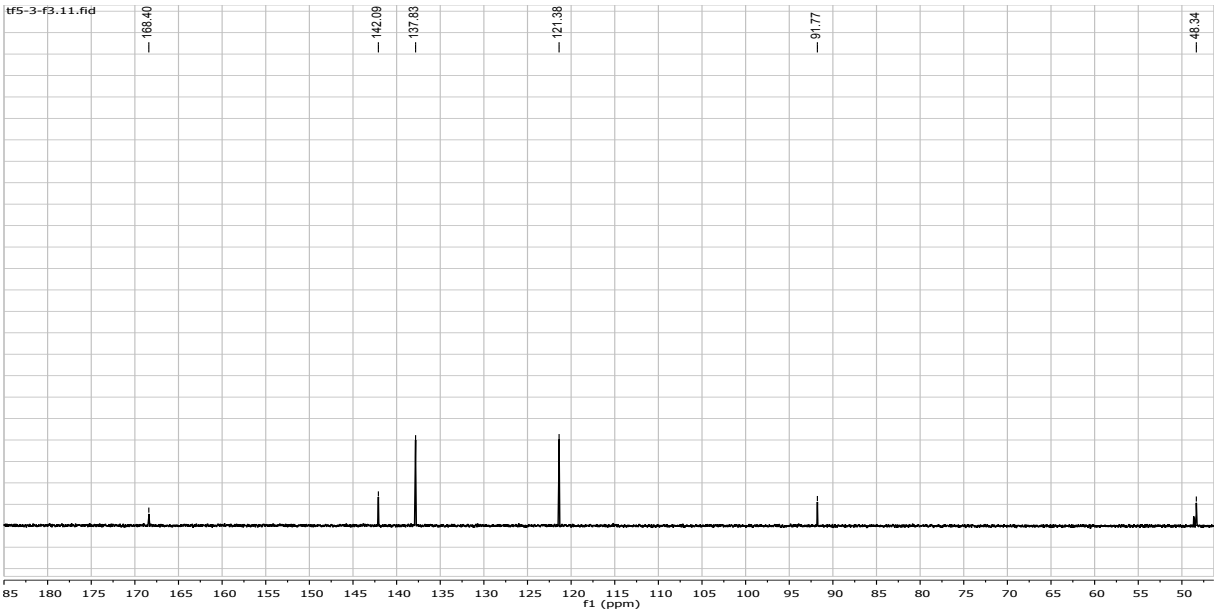
a) **N-Nitroso-N-(4-iodophenyl)-glycine**



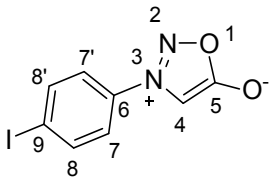
A sample of 2.19 g (7.89 mmol) of N-(4-iodophenyl)glycine[1] in 15 mL of hydrochloric acid (12.5 %) was cooled to 0°C. Then a solution of 0.82 g (11.8 mmol) of $NaNO_2$ in 10 mL of water was added dropwise. After 30 min 15 mL of Et_2O were added and stirring at that temperature was continued for 1.5 h. After warming to rt, additional 20 mL of Et_2O were added and the two phases were separated. The aqueous layer was extracted three times with $CHCl_3$. The combined organic phases were dried over $MgSO_4$ and then the solvent mixture was distilled off. The resulting solid was dried *in vacuo* and purified by column chromatography (1. petroleum ether / ethyl acetate = 10 / 1; 2. EtOAc; 3. MeOH). Yield: 1.33 g (55 %), mp 133 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.78-7.82[15] (m, 2H, *H*C-6/*H*C-6') 7.37-7.41[15] (m, 2H, *H*C-5/*H*C-5'), 4.42 (s, 2H, H_2C-2) ppm[16]; ^{13}C NMR (100 MHz, DMSO-d_6): δ = 168.4 (o, *C*-1), 142.1 (o, *C*-4), 137.8 (+), 121.4 (+), 91.8 (o, *C*-7), 48.3 (-, H_2C-2) ppm; IR (ATR): $\tilde{\nu}$ = 3405, 3086, 3011, 2967, 1611, 1576, 1487, 1431, 1401, 1381, 1354, 1308, 1277, 1242, 1187, 1134, 1117, 1064, 1039, 1013, 1002, 957, 931, 919, 861, 815, 720, 699, 589, 557, 519, 466, 414, 405 cm^{-1}; MS (ESI 50 V) *m/z* (%) = 305 (100) $[M-H]^-$ (anion detection mode). HRMS: Calcd. 304.9429. Found 304.9267.



[15] Assignment exchangeable.
[16] O*H* is not observable.

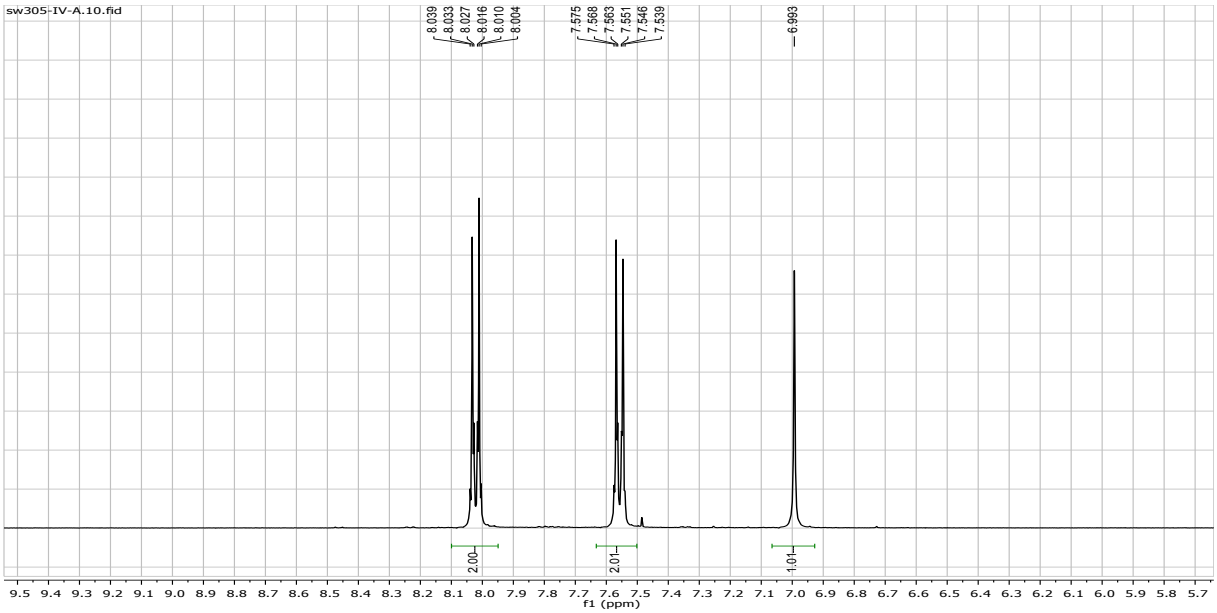


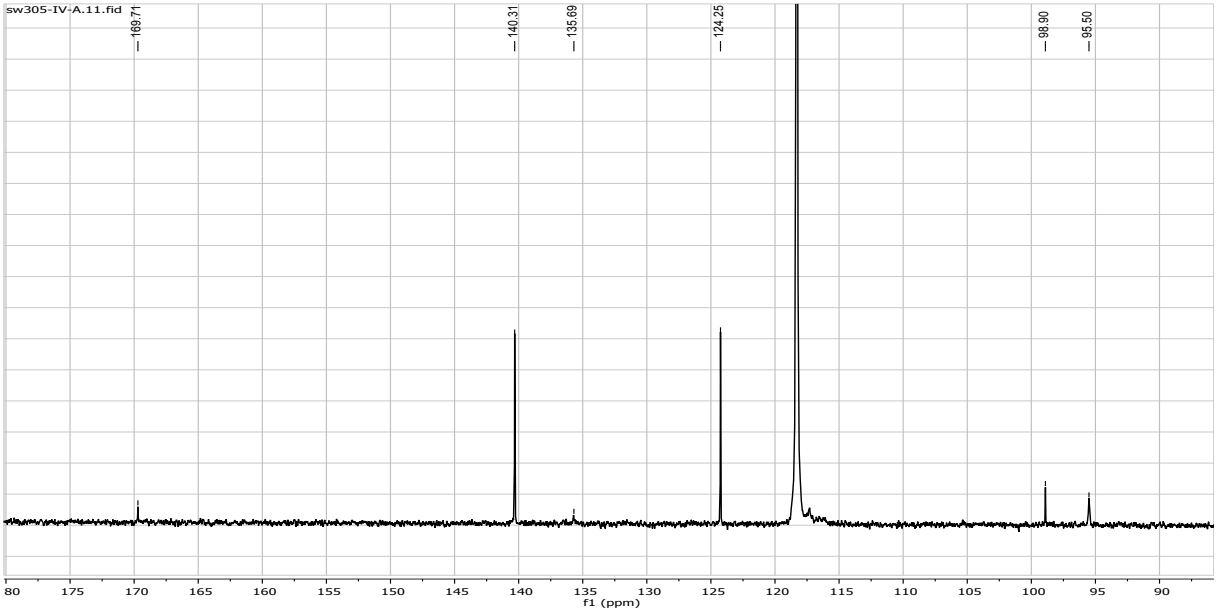
b) **N-(4-Iodophenyl)sydnone 2f:**



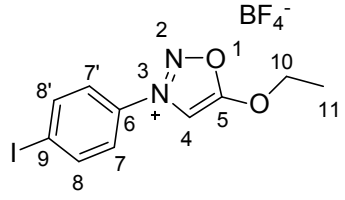
A sample of 1.33 g (4.35 mmol) of N-nitroso-N-(4-iodophenyl)glycine in 25 mL of Ac_2O was heated at reflux temperature for 2.5 h. After cooling to rt the reaction mixture was poured on 200 mL of ice. The aqueous layer was extracted three times with $CHCl_3$, then the combined organic phases were dried over $MgSO_4$ and finally the solvent was distilled off *in vacuo*. The resulting solid was dried *in vacuo* and then recrystallized from EtOH and dried. Yield: 0.90 g (72 %), mp. 198 °C. ^{1}H NMR (400 MHz, MeCN-d_3): δ = 6.99 (s, 1H, *H*C-4), 7.54-7.57[17] (m, 2H, *H*C-8/*H*C-8'), 8.00-8.04[17] (m, 2H, *H*C-7/*H*C-7') ppm; ^{13}C NMR (100 MHz, MeCN-d_3): δ = 169.7 (o, *C*-5), 140.3 (+), 135.7 (o, *C*-6), 124.3 (+), 98.9 (o, *C*-9), 95.5 (+, *C*-4) ppm; IR (ATR): $\tilde{\nu}$ = 3130, 3088, 3064, 1892, 1743, 1580, 1492, 1440, 1411, 1355, 1299, 1275, 1230, 1187, 1174, 1116, 1087, 1059, 1017, 1002, 944, 853, 828, 819, 725, 692, 644, 621, 552, 496, 465, 425 cm^{-1}; MS (ESI 30 V) *m/z* (%) = 311 (43) [M+Na] $^+$, 599 (100) [2M+Na]$^+$. HRMS: Calcd 288.9468. Found 288.9540.

[17] Assignment exchangeable.





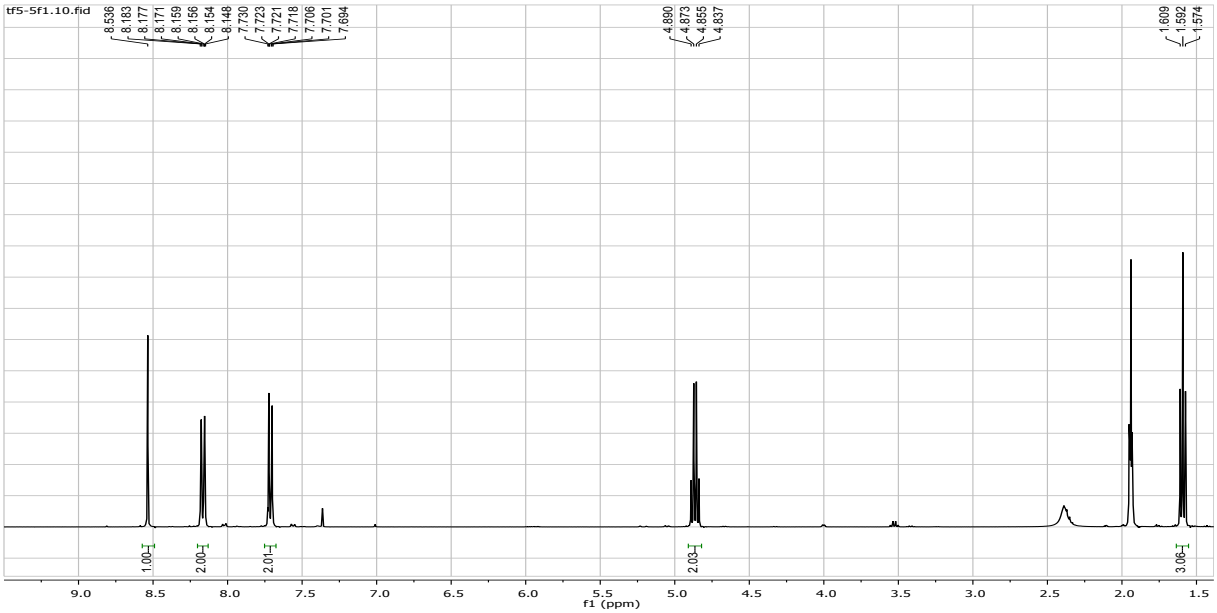
c) Ethylation of N-(4-iodophenyl)sydnone to give 6f:

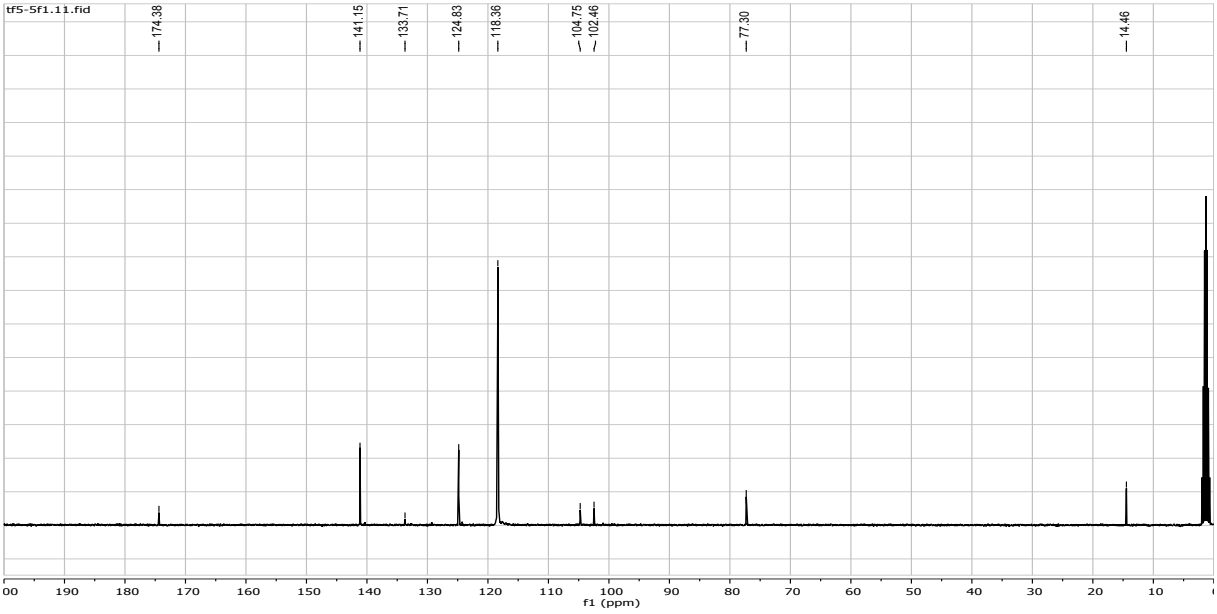


A sample of 0.80 g (2.77 mmol) of N-(4-iodophenyl)sydnone in 10 mL of anhydrous CH_2Cl_2 was treated dropwise with 4.2 mL (4.20 mmol) of triethyloxonium tetrafluoroborate (1 M in CH_2Cl_2) and stirred for 72 h at rt. On addition of diethylether a colorless precipitate formed which was filtered off and dried. Yield: 0.753 g (67 %), mp: 111 °C. ^{1}H NMR (400 MHz, MeCN-d_3): δ = 8.54 (s, 1H, *H*C-4), 8.15-8.18[18] (m, 2H, *H*C-8/*H*C-8‘), 7.70-7.73[18] (m, 2H, *H*C-7/*H*C-7), 4.86 (q, $J_{H,H}$ = 7.1 Hz, 2H, H_2C-

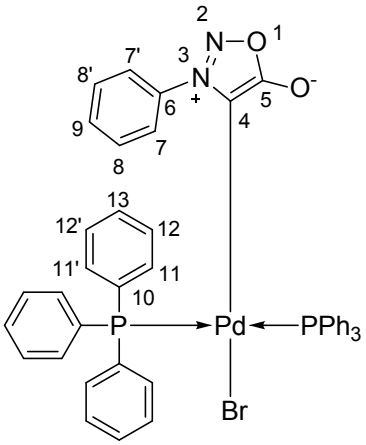
[18] Assignment exchangeable.

10), 1.59 (t, $J_{H,H}$ = 7.1 Hz, 3H, H_3C-11) ppm; ^{13}C NMR (100 MHz, MeCN-d_3): δ = 174.0 (o, *C*-5), 141.1 (+), 133.7 (o, *C*-6), 124.8 (+), 104.7 (+, H*C*-4), 102.5 (o, *C*-9), 77.3 (-, H_2C-10), 13.1 (+, H_3C-11) ppm; IR (ATR): $\tilde{\nu}$ = 3145, 3104, 2984, 2938, 1627, 1587, 1489, 1469, 1435, 1420, 1402, 1375, 1361, 1310, 1290, 1279, 1261, 1191, 1101, 1033, 1001, 958, 884, 833, 817, 771, 748, 698, 664, 622, 577, 534, 519, 490, 440, 427 cm^{-1}; MS (ESI 30 V) *m/z* (%) = 317.0 (100) [M$^+$]. HRMS: Calcd 316.9781. Found: 316.9781.

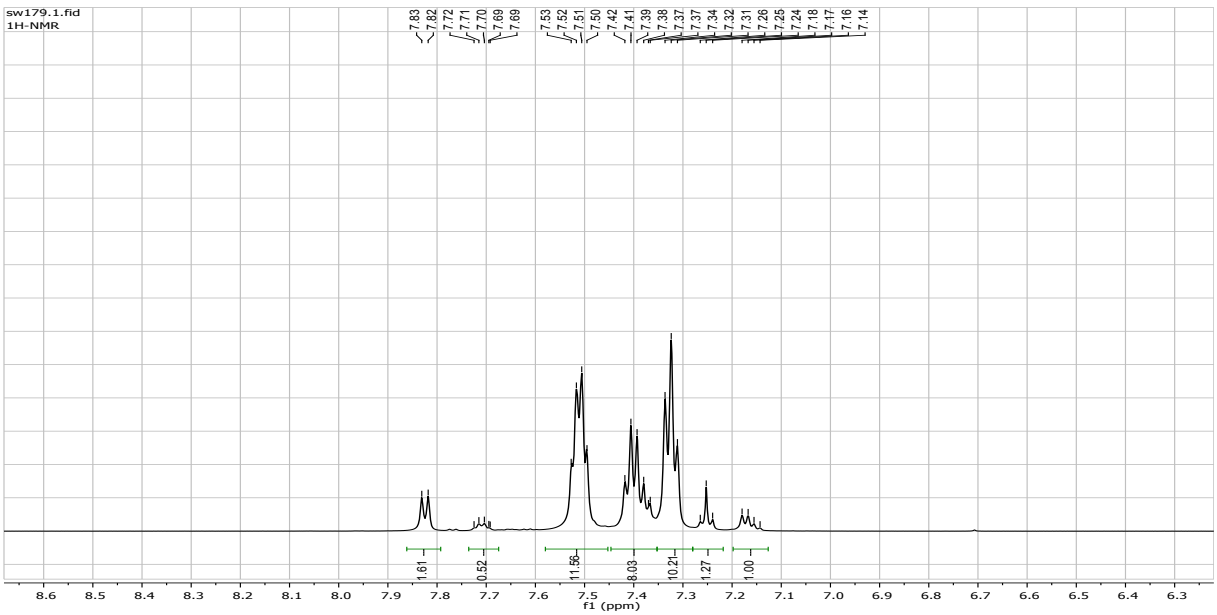




(*cis*-/*trans*-)-Bromo-(5-oxy-N-phenyl-1,2,3-oxadiazolium-4-yl)-bis-(triphenylphosphine)-palladium(II) 16:

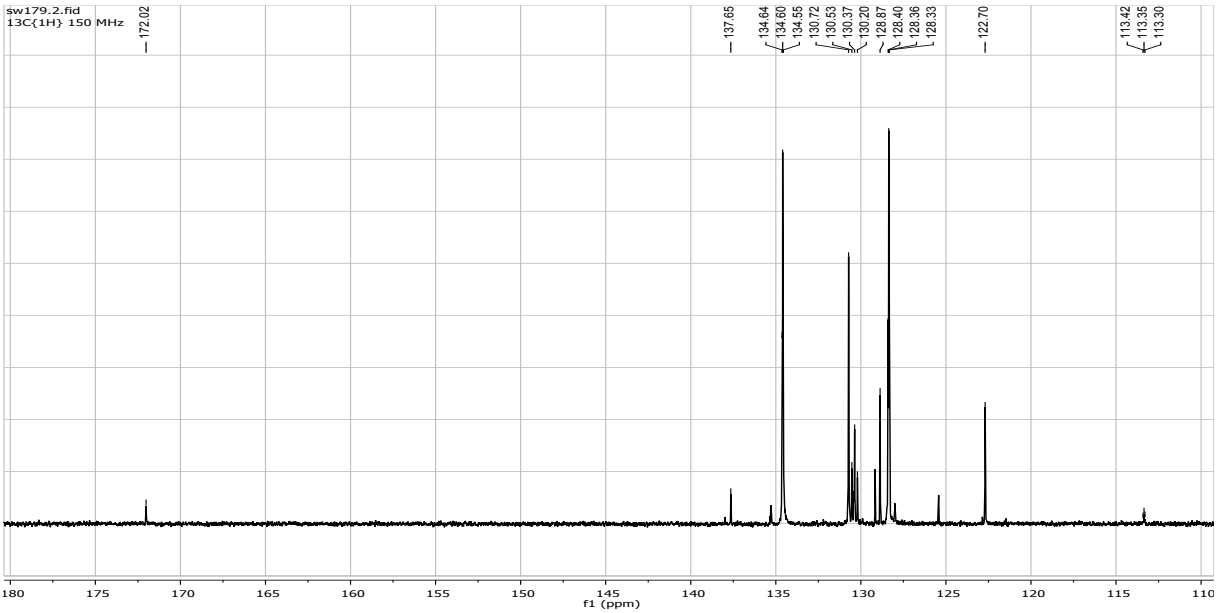


Under an inert atmosphere at rt a solution of 4-bromo-N-phenylsydnone[7] (0.1 g, 0.4 mmol) in approximately 7 mL of anhydrous THF was treated with 0.479 g of tetrakis-(triphenylphosphine)-palladium(0) (0.4 mmol). The mixture was stirred at rt for 35 min and then the resulting solid was filtered off, washed with THF and dried. Yield: 0.24 g (67 %). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.14 – 7.18 (m, 1 H), 7.24 – 7.53 (m, 31 H), 7.69 – 7.72 (m, 1 H), 7.82 – 7.83 (m, 2 H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 113.4 (t, *J* = 9.2 Hz, o, *C*-4), 122.6 (+, H*C*-7 + H*C*-7‘), 128.3 (t, *J* = 5.2 Hz, +, H*C*-12 + H*C*-12‘), 128.8 (+, H*C*-13), 130.26 (t, *J* = 24.6 Hz, o, *C*-10), 130.31 (+, H*C*-9), 130.6 (+, H*C*-8 + H*C*-8‘), 134.5 (t, *J* = 6.4 Hz, +, H*C*-11 + H*C*-11‘), 137.5 (o, *C*-6), 171.9 (o, *C*-5) ppm; signals are overlapped by signals of the cis isomer. ^{31}P NMR (243 MHz, $CDCl_3$): δ = 21.3 (s, *trans*), 21.9 (d, *J* = 36.8 Hz, *cis*) ppm; IR (ATR): $\tilde{\nu}$ = 1698, 1097, 933, 695 cm^{-1}.[19]

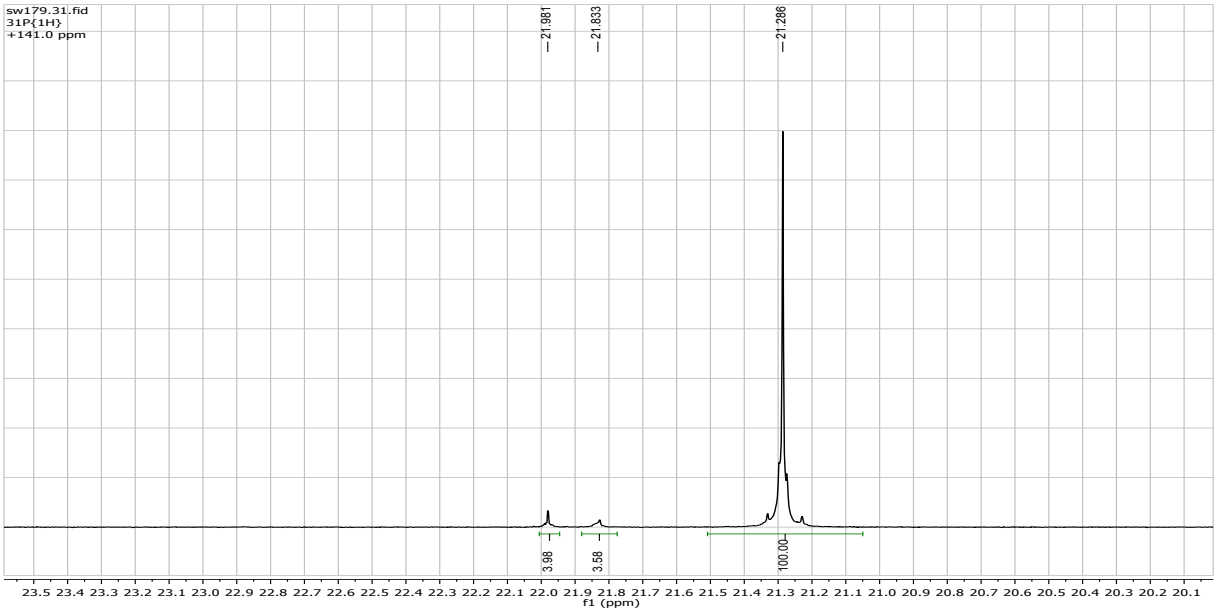


The *trans*-product is overlapped by the *cis*-product in ^{1}H-nmr.

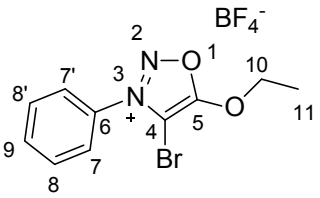
[19] The *cis*/*trans*-ratio was determined by an ^{31}P-NMR experiment.



Only the *trans*-product is marked in ^{13}C-nmr, the *cis*-product is visible.

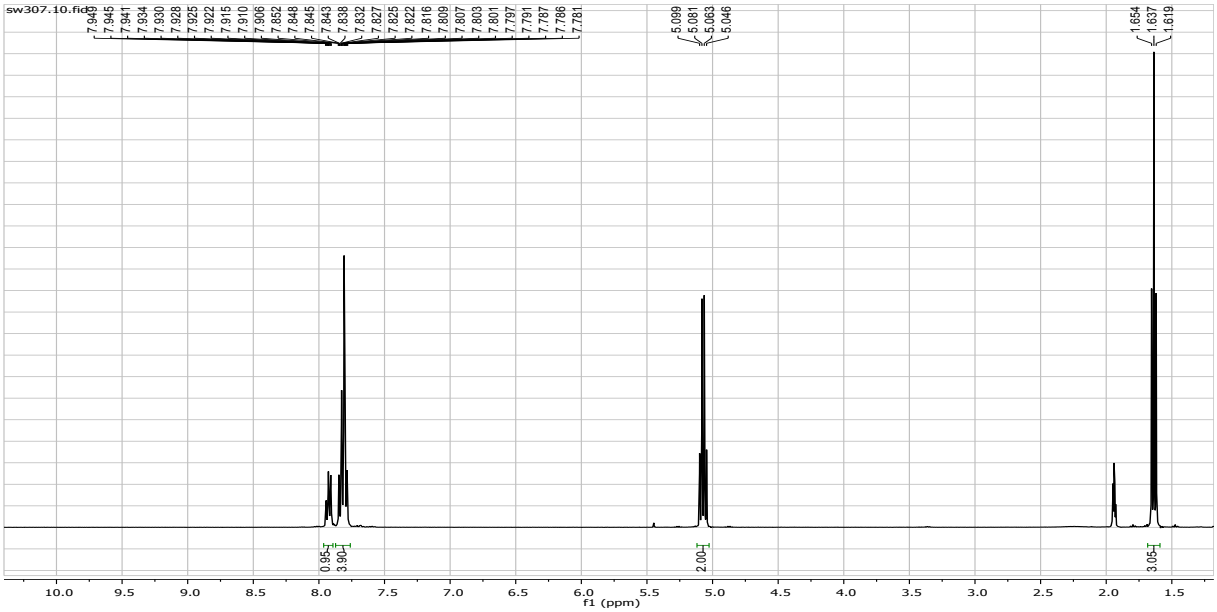


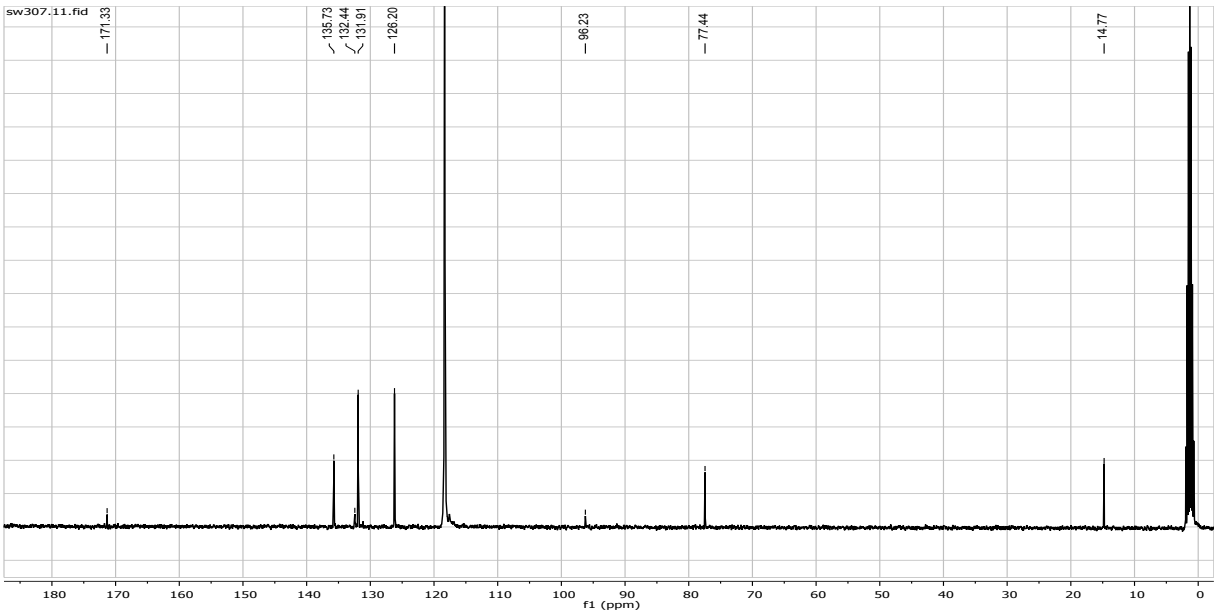
4-Bromo-5-ethoxy-N-phenylsydnone 17:



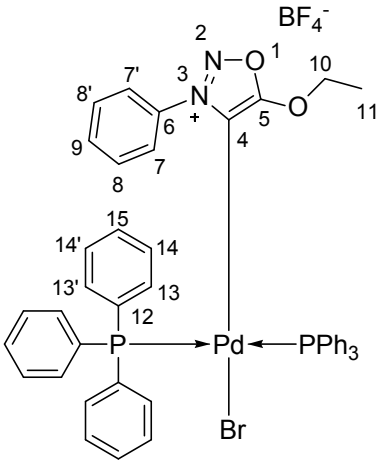
A sample of 1.48 g (6.14 mmol) of 4-bromo-N-(phenyl)sydnone[8] in 10 mL of anhydrous CH_2Cl_2 was treated dropwise with 9.2 mL (9.20 mmol) of triethyloxonium tetrafluoroborate (1 M in CH_2Cl_2) and stirred at rt for 72 h. On addition of Et_2O a precipitate formed which was filtered off and dried. Yield: 1.637 g (75 %), mp 156 °C. ^{1}H NMR (600 MHz, MeCN-d_3): δ = 7.91-7.95 (m, 1H, *H*C-9), 7.78-7.85 (m, 4H, *H*C-7/*H*C-7‘/*H*C-8/*H*C-8‘), 5.07 (q, $J_{H,H}$ = 7.1 Hz, 2H, H_2-C10), 1.64 (t, $J_{H,H}$ = 7.1 Hz, 3H, H_3-

C11) ppm; ^{13}C NMR (150 MHz, MeCN-d_3): δ = 171.3 (o, *C*-5), 135.7 (+, H*C*-9), 132.4 (o, H*C*-6), 131.9 (+), 126.2 (+), 96.2 (o, *C*4), 77.4 (-, H_2C-10), 14.8 (+, H_3C-11) ppm; IR (ATR): $\tilde{\nu}$ = 2995, 1641, 1596, 1491, 1467, 1441, 1419, 1389, 1355, 1301, 1291, 1249, 1166, 1119, 1060, 1042, 1019, 987, 939, 924, 859, 811, 759, 742, 703, 686, 660, 609, 594, 522, 509, 489, 452, 405 cm^{-1}; MS (ESI 30 V) *m/z* (%) = 269.0 (100) [M$^+$]. HRMS: Calcd 268.9920. Found: 268.9925.



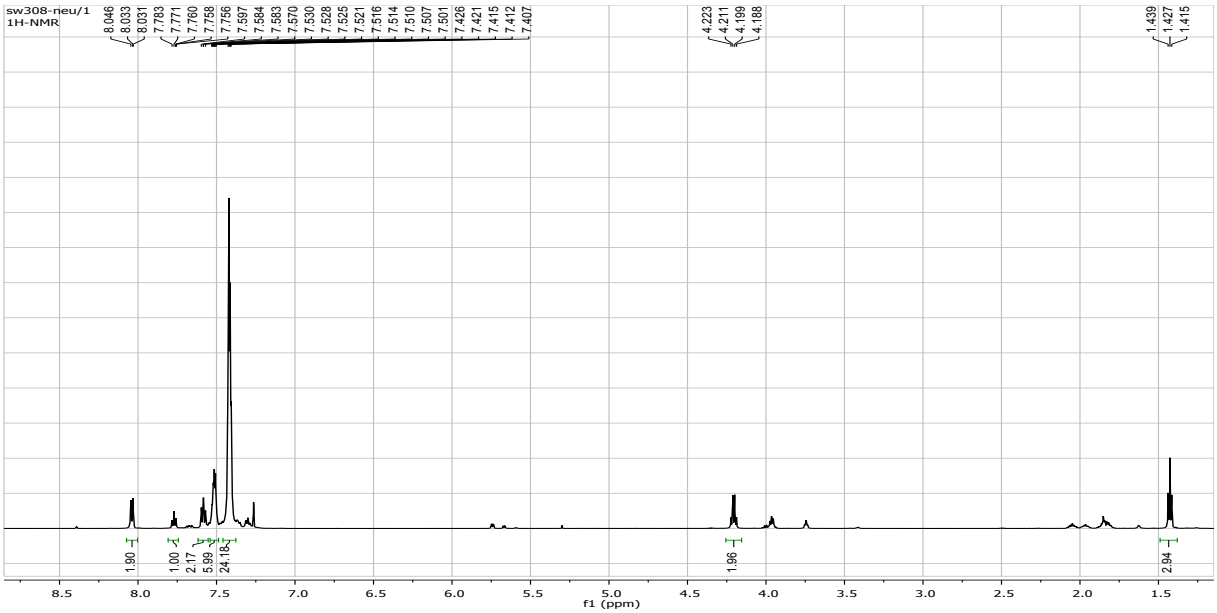


(*cis*-/*trans*-)-Bromo-(N-(phenyl)-5-ethoxysydnone-4-yl)-bis-(triphenylphosphine)-palladium(II) 18:

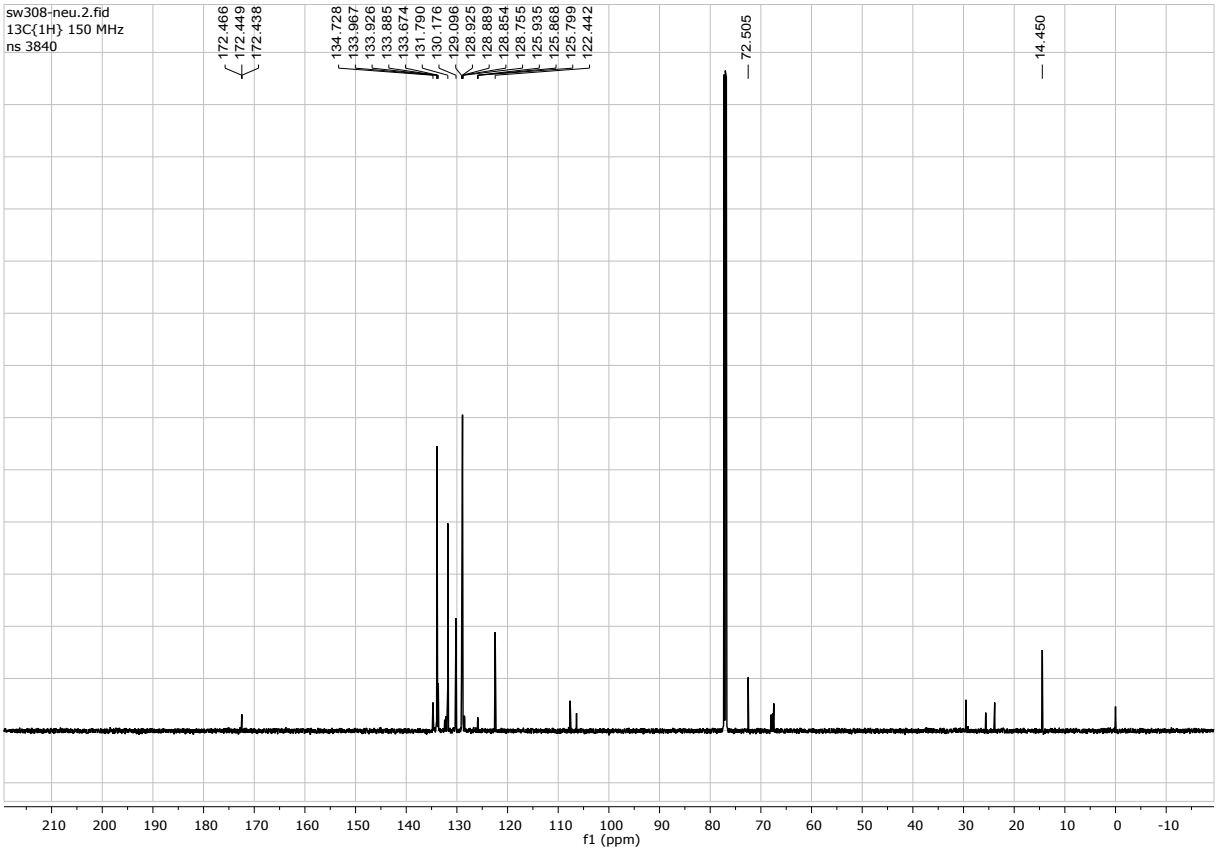


A solution of 0.06 g (0.17 mmol) of 4-bromo-5-ethoxy-N-phenylsydnone in 5 mL of anhydrous THF was treated with 0.20 g (0.17 mmol) of tetrakis(triphenylphosphine)palladium(0) and stirred under an inert atmosphere for 4 h at rt. The resulting yellow solid was filtered off, washed with THF and dried *in vacuo*. Yield: 0.150 g (88 %), mp. 205 °C (dec.). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.02-8.04 (m, 2H), 7.76-7.80 (m, 1H), 7.26-7.61 (m, 31H), 7.14-7.18 (m, 1H), 4.19 (q, $J_{H,H}$ = 7.1 Hz, 2H, C10-*H*$_2$), 1.43 (t, $J_{H,H}$ = 7.1 Hz, 3H, C11-*H*$_3$) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 172.4 (o, C5), 133.9 (+, t, *J* = 6.2 Hz, C13/C13‘), 131.8 (+, C8/C8‘), 131.3 (+, C9), 130.2 (+, C15), 129.7 (o, t, *J* = 25.8 Hz, C12), 129.1 (o, C6), 128.9 (+, t, *J* = 5.2 Hz, C14/C14‘), 125.9 (o, t, *J* = 10.2 Hz, C4), 122.4 (+, C7/C7‘), 72.4 (-, C10), 14.4 (+, C11) ppm; signals are overlapped by signals of the cis isomer. ^{31}P NMR (243 MHz, $CDCl_3$): δ = 25.4 (d, *J* = 1667.9 Hz, *cis*), 20.8 (s, *trans*) ppm; IR (ATR): $\bar{\nu}$ = 3057, 1602, 1579, 1482, 1466, 1434, 1381, 1351, 1310, 1282, 1199, 1162, 1094, 1052, 990, 869, 824, 763, 744, 692, 617, 578, 533, 522, 510, 497, 460, 445, 431, 421 cm^{-1}; MS (ESI 30 V) *m/z* (%) = 903.0 (100) [M$^+$]. HRMS: Calcd 899.0778. Found: 899.0779.[20]

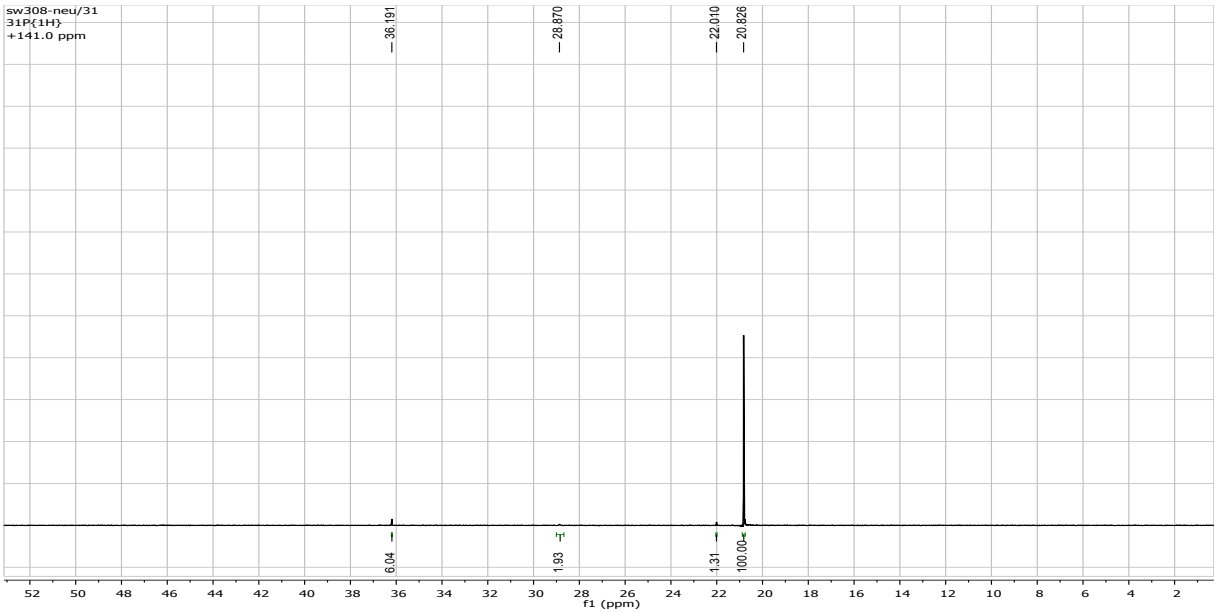
[20] The *cis*/*trans*-ratio was determined by an ^{31}P-NMR experiment.



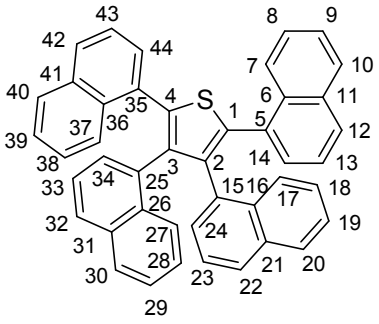
Traces of THF are visible and the *trans*-product is overlapped by the *cis*-product in ^{1}H-NMR.



Only the *trans*-product is marked in ^{13}C-nmr, the *cis*-product is visible.



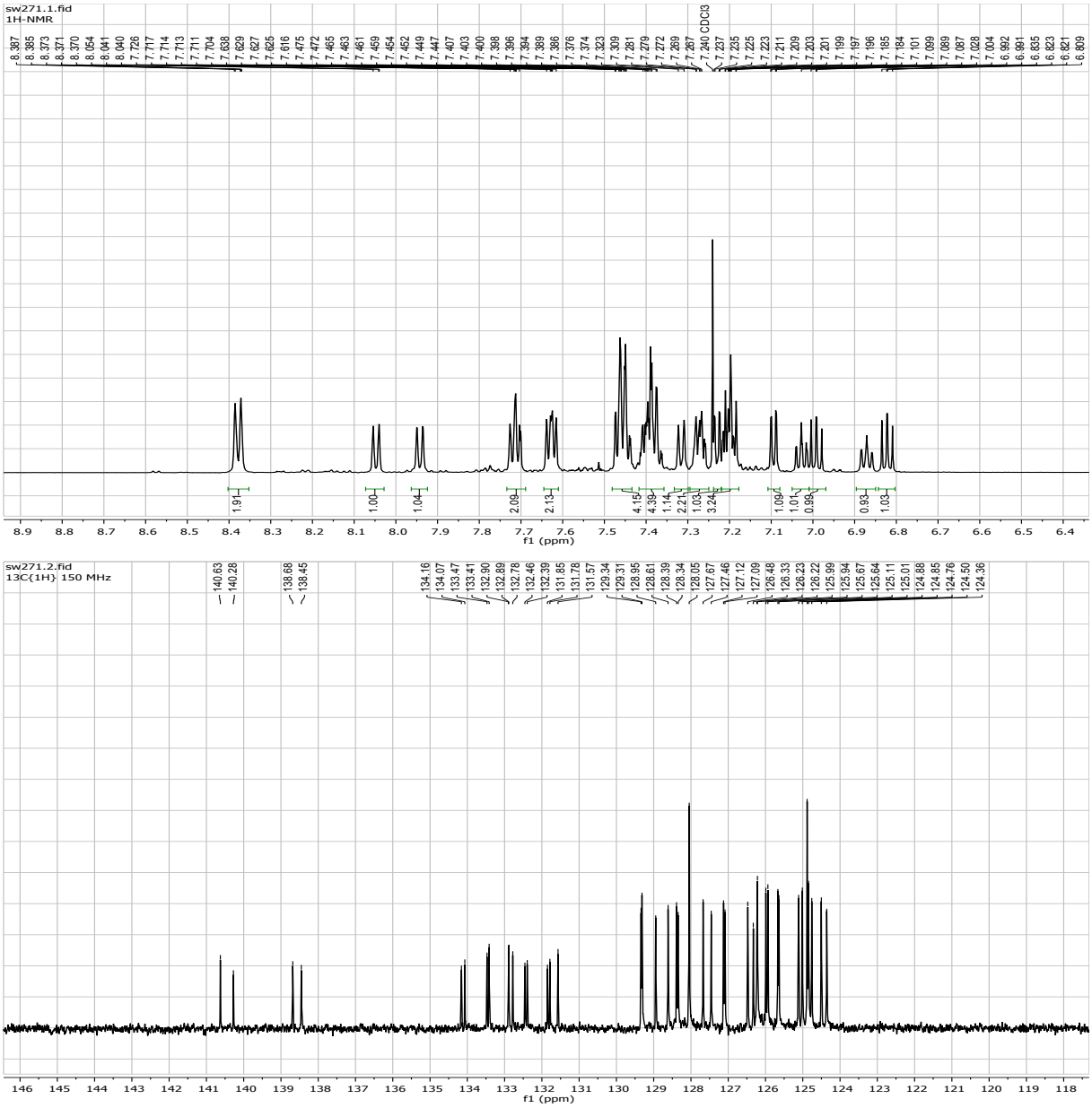
2,3,4,5-Tetra(naphthalen-1-yl)thiophene 20b:

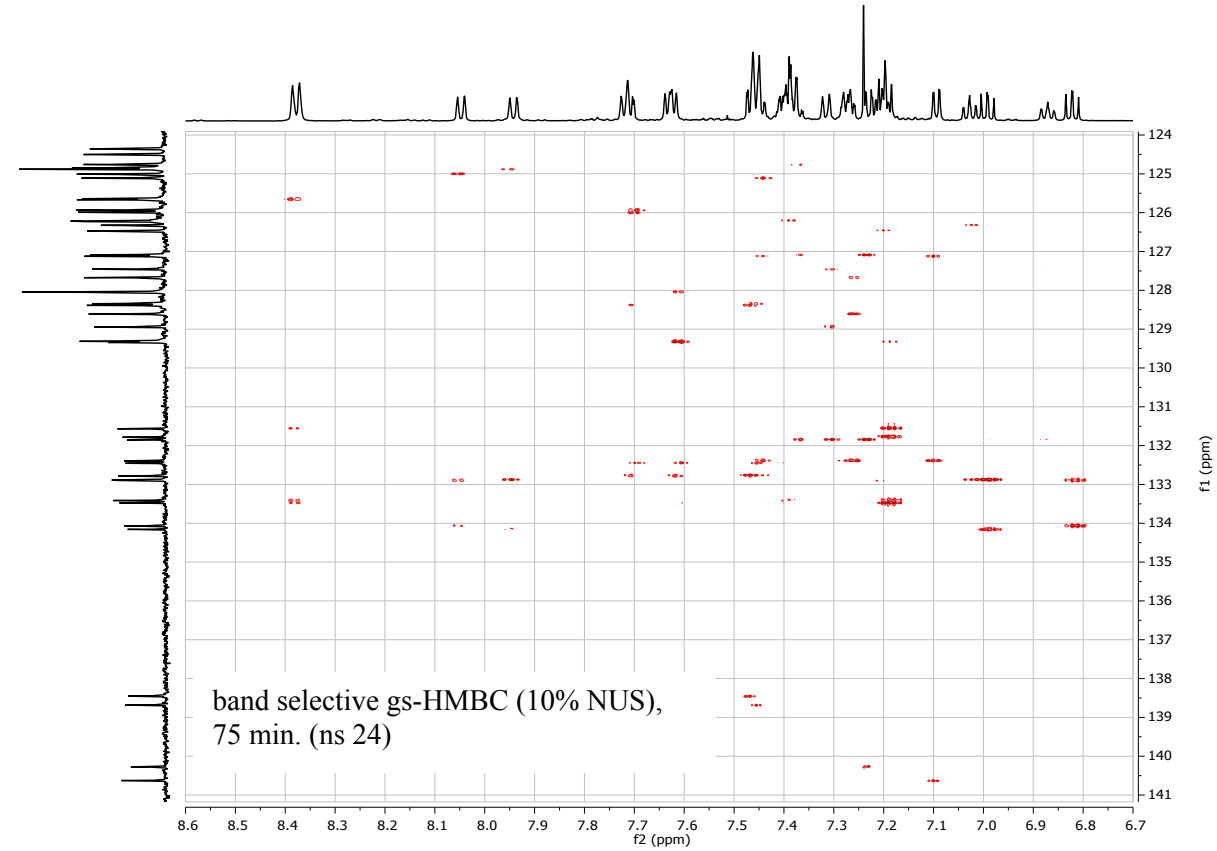


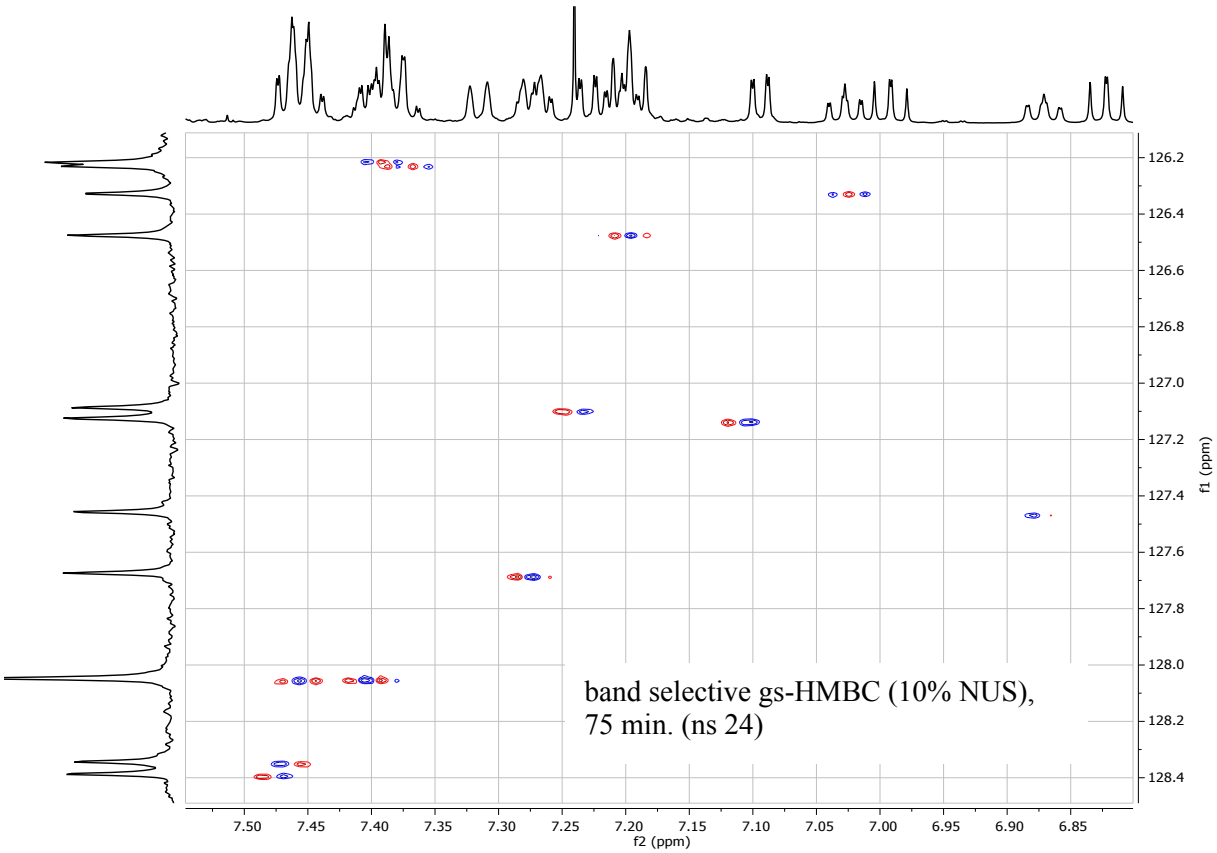
A sample of 75 mg (188 µmol) of tetrabromothiophene was dissolved in 8 mL of anhydrous toluene under an inert atmosphere. Then a portion of 10 mol-% of the catalyst (**15**/**17**) was added, the mixture was degassed by ultrasound, and then stirred for 30 minutes at rt. After that time 161 mg (0.94 mmol) of 1-naphthylboronic acid, 319 mg (1.50 mmol) of potassium phosphate and 2 mL of water were added. The mixture was heated to 100 °C for 22 h. The crude product was extracted with ethyl acetate and purified by column chromatography using petroleum ether.[21] Yield: 59 mg (53 %), mp. 230 °C (dec.). ^{1}H NMR (600 MHz, $CDCl_3$)[22]: δ = 8.39-8.37 (m, 2 H, *H*C-7 + *H*C-37), 8.06-8.05 (m, 1 H, *H*C-27), 7.95-7.93 (m, 1 H, *H*C-17), 7.73-7.70 (m, 2 H, *H*C-12 + *H*C-44), 7.64-7.61 (m, 2 H, *H*C-10 + *H*C-40), 7.48-7.44 (m, 4 *H*, *H*C-8 + *H*C-14 + *H*C-20 + *H*C-38), 7.41-7.37 (m, 4 *H*, *H*C-9 + *H*C-30 + *H*C-39 + *H*C-42), 7.33-7.31 (m, 1 *H*, *H*C-32), 7.39-7.26 (m, 2 *H*, *H*C-18 + *H*C-22), 7.24-7.22 (m, 1 *H*, *H*C-34), 7.21-7.18 (m, 3 *H*, *H*C-43 + *H*C-29 + *H*C-13), 7.10-7.09 (m, 1 *H*, *H*C-24), 7.04-7.01 (m, 1 *H*, *H*C-19), 7.00-6.98 (m, 1 *H*, *H*C-33), 6.89-6.86 (m, 1 *H*, *H*C-28), 6.84-6.81 (m, 1*H*, *H*C-23) ppm; ^{13}C NMR

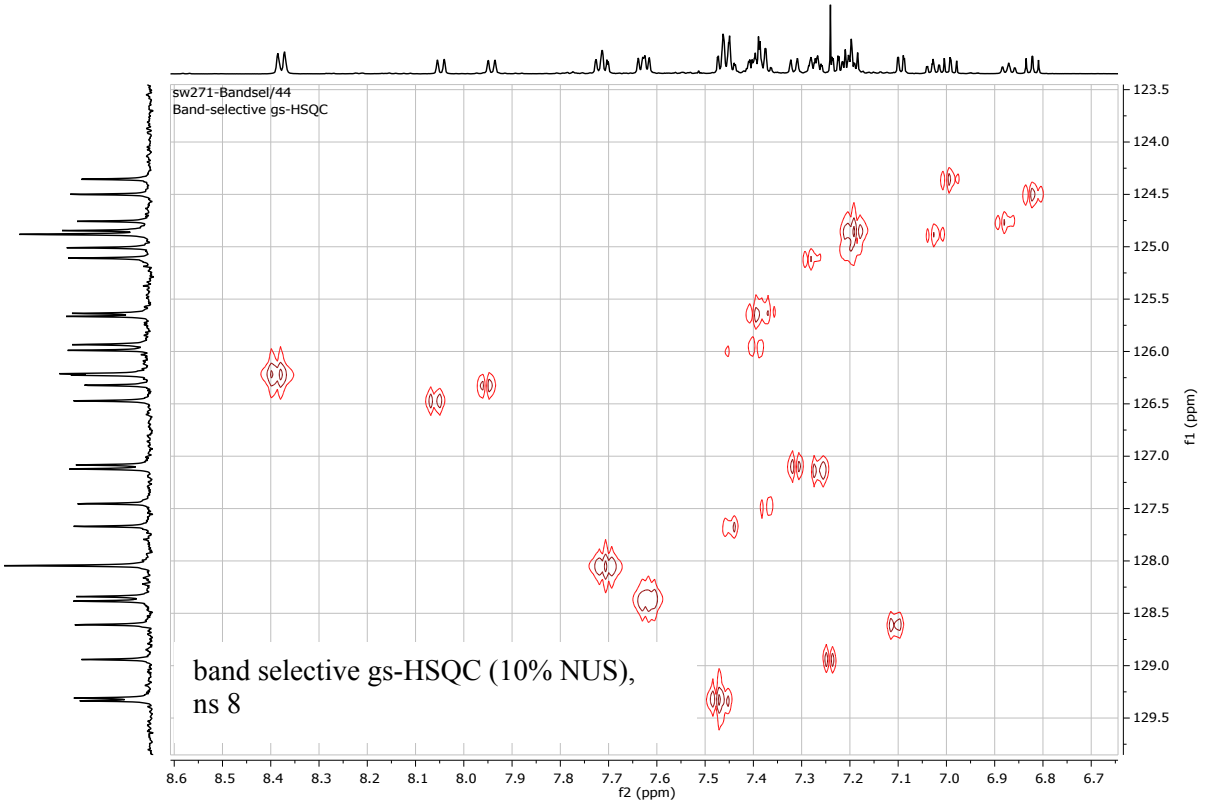
[21] This is our typical procedure for Suzuki-Miyaura-reactions with tetrabromothiophene.
[22] Due to the symmetry the peak assignments of C1/C-4 and C-2/C-3 are exchangeable, respectively.

(150 MHz, $CDCl_3$)[22]: δ = 140.6 (o, *C*-2), 140.3 (o, *C*-3), 138.7 (o, *C*-1), 138.5 (o, *C*-4), 134.2 (o, *C*-25), 134.1 (o, *C*-15), 133.5 (o, *C*-5 / *C*-35), 133.4 (o, *C*-35 / *C*-5), 132.9 (o, *C*-21), 132.9 (o, *C*-31), 132.8 (o, *C*-36), 132.5 (o, *C*-6), 132.4 (o, *C*-16), 131.9 (o, *C*-26), 131.8 (o, *C*-41), 131.6 (o, *C*-11), 129.3 (+, H*C*-38), 129.3 (+, H*C*-8), 129.0 (+, H*C*-34), 128.6 (+, H*C*-24), 128.4 (+, H*C*-10 / H*C*-40), 128.3 (+, H*C*-40 / H*C*-10), 128.0 (+, H*C*-12 + H*C*-44), 127.7 (+, H*C*-20), 127.5 (+, H*C*-30), 127.1 (+, H*C*-22), 127.1 (+, H*C*-32), 126.5 (+, H*C*-27), 126.3 (+, H*C*-17), 126.2 (+, H*C*-7 / H*C*-37), 126.2 (+, H*C*-37 / H*C*-7), 126.0 (+, H*C*-14), 125.9 (+, H*C*-42), 125.7 (+, H*C*-9 / H*C*-39), 125.6 (+, H*C*-39 / H*C*-9), 125.1 (+, H*C*-18), 125.0 (+, H*C*-29), 128.9 (+, H*C*-19 + H*C*-43), 124.9 (+, H*C*-13), 124.8 (+, H*C*-28), 124.5 (+, H*C*-23), 124.4 (+, H*C*-33) ppm; IR (ATR): $\tilde{\nu}$ = 3043, 2962, 1591, 1505, 1258, 1086, 1012, 790, 769 cm^{-1}; MS (EI, DEP, 70 eV) *m/z* (%) = 588.4 (100) [M^+]. HRMS: Calcd 588.1912. Found 588.1909.

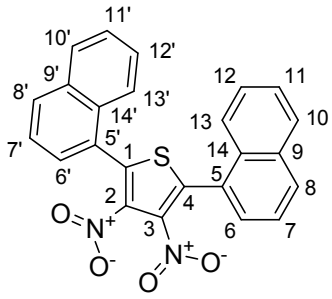



band selective gs-HMBC (10% NUS),
75 min. (ns 24)
f2 (ppm)
f1 (ppm)


band selective gs-HMBC (10% NUS),
75 min. (ns 24)
f2 (ppm)
f1 (ppm)



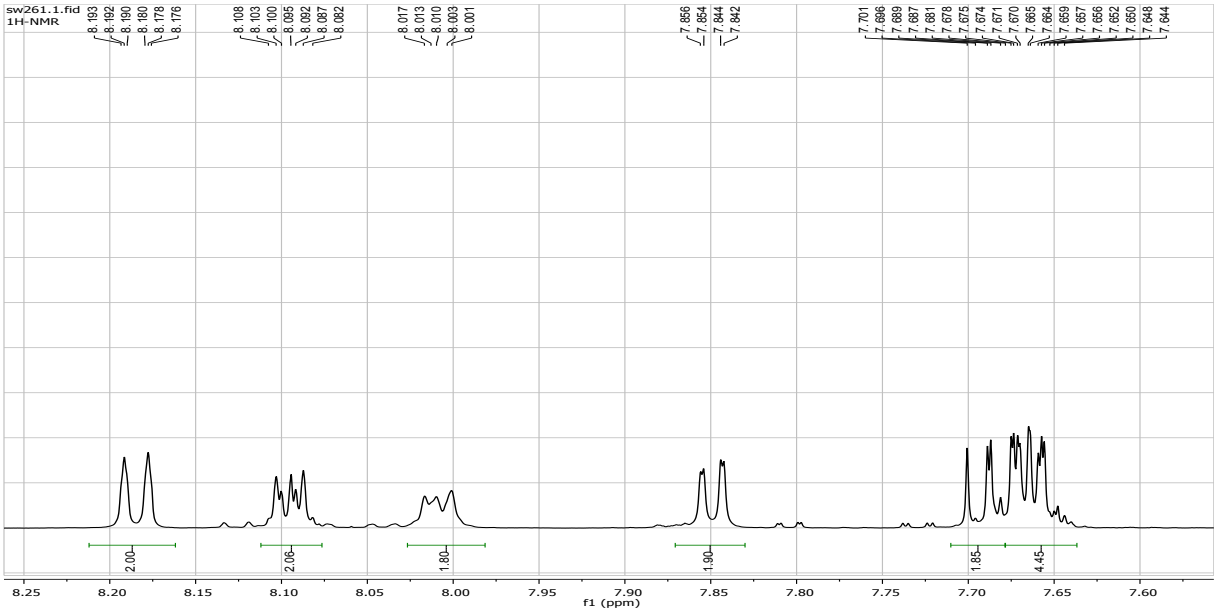
2,5-Di(naphthalen-1-yl)-3,4-dinitrothiophene 20d:



A sample of 75 mg (226 µmol) of 2,5-dibromo-3,4-dinitrothiophene was dissolved in 8 mL of anhydrous toluene under an inert atmosphere. Then 10 mol-% of the catalyst (**15**/**17**) were added, the mixture was degassed by ultrasound and then stirred for 30 minutes at rt. After that time a portion of 178 mg (1.03 mmol) of 1-naphthalylboronic acid, 384 mg (1.81 mmol) of potassium phosphate and 2 mL of water were added. The mixture was heated to 100 °C for 72 h. The crude product was extracted with ethyl acetate and purified by column chromatography using a solvent mixture of petroleum ether and dichloromethane.[23] Yield: 77 mg (80%; with catalyst **15**), 76 mg (80%; with catalyst **17**), mp. 261 °C. ^{1}H NMR (600 MHz, DMSO-d_6)[24]: δ = 8.18-8.19 (m, 2H, *H*C-8/ *H*C-8'), 8.08-8.11 (m, 2H, *H*C-

[23] This is our typical procedure for Suzuki-Miyaura-reactions with 2,5-dibromo-3,4-dinitrothiophene.
[24] Due to the symmetry the peak assignments of C1/C-4 and C-2/C-3 are exchangeable, respectively.

10/*H*C-10‘), 8.00-8.02 (m, 2H, *H*C-13/*H*C-13’), 7.85 (dd, $J_{H,H}$ = 7.2, 1.2 Hz, 2H, *H*C-6/*H*C-6‘), 7.68-7.70 (m, 2H, *H*C-7/ *H*C-7’), 7.64-7.68 (m, 4H, *H*C-11/*H*C-11’/*H*C-12/*H*C-12’) ppm; ^{13}C NMR (150 MHz, DMSO-d_6)[24]: δ = 141.1 (o, *C*-1/*C*-4), 137.8 (o, *C*-3/*C*-2), 133.0 (o, *C*-9/*C*-9’), 131.3 (+, H*C*-8/H*C*-8’), 131.2 (o, *C*-14/*C*-14’), 129.4 (+, H*C*-6/H*C*-6’), 128.7 (+, H*C*-10/H*C*-10’), 127.9 (+, H*C*-11/H*C*-11’/H*C*-12/H*C*-12’), 127.0 (+, H*C*-11/H*C*-11’/H*C*-12/H*C*-12’), 125.4 (+, H*C*-7/H*C*-7’), 125.0 (o, *C*-5/*C*-5’), 124.8 (+, H*C*-13/H*C*-13’) ppm; IR (ATR): $\bar{\nu}$ = 3049, 1552, 1538, 1514, 1503, 1384, 1341, 1324, 1272, 545 cm^{-1}; MS (EI, DEP, 70 eV) *m/z* (%) = 426.3 (100) [M$^+$]. HRMS: Calcd 426.0674. Found 426.0674.



Results of the single crystal X-ray analysis of sydnone 2b

Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 987516 (**2b**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int.code+(1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

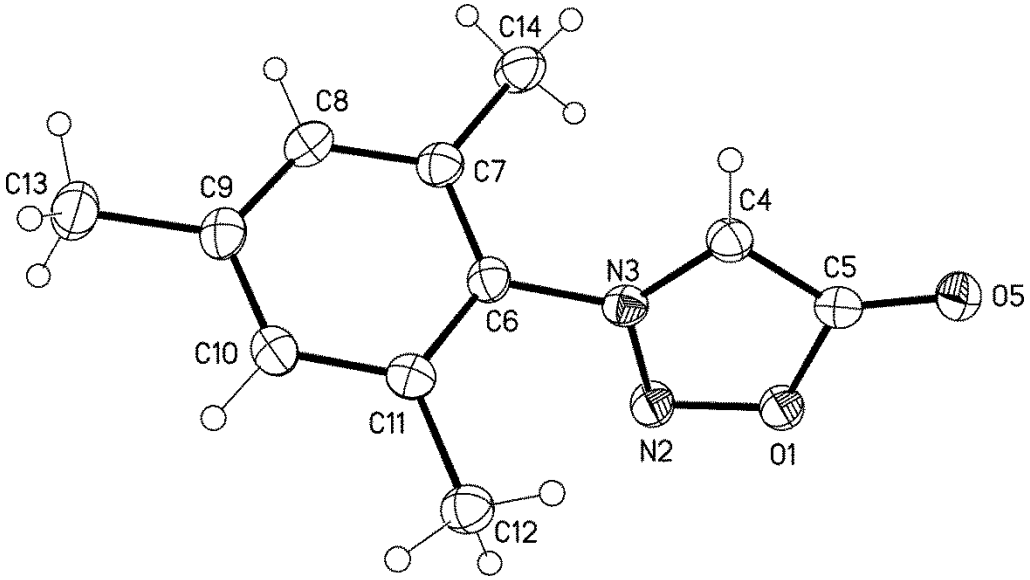


Fig. S1. Molecular structure of **2b** (displacement parameters are drawn at 50 % probability level).

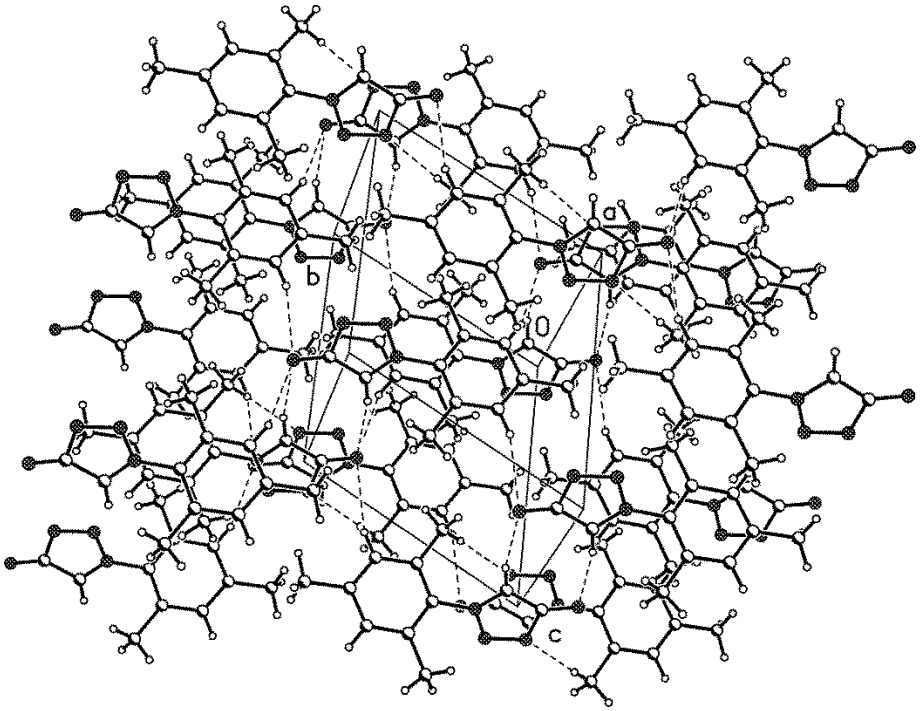


Fig. S2. Crystal packing of **2b**.

3-Mesityl-1,2,3-oxadiazol-3-ium-5-olate – 2b

Crystal data for **2b**

$C_{11}H_{12}N_2O_2$	$Z = 2$
$M_r = 204.23$	$F(000) = 216$
Triclinic, $P\bar{1}$	$D_x = 1.322$ Mg m^{-3}
$a = 7.423$ (1) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 8.934$ (2) Å	Cell parameters from 536 reflections
$c = 9.001$ (2) Å	$\theta = 2$–$25°$
$\alpha = 118.77$ (1)°	$\mu = 0.09$ mm^{-1}
$\beta = 97.71$ (1)°	$T = 123$ K
$\gamma = 93.62$ (1)°	Blocks, colourless
$V = 512.87$ (18) Å^3	0.24 × 0.18 × 0.06 mm

Data collection for **2b**

Bruker-Nonius KappaCCD diffractometer	2343 independent reflections
Radiation source: fine-focus sealed tube	1983 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.057$
rotation in phi and ω, 2 deg. scans	$\theta_{max} = 27.5°$, $\theta_{min} = 3.6°$
Absorption correction: multi-scan *SADABS* (Sheldrick, 2008)	$h = -9 \rightarrow 9$
$T_{min} = 0.686$, $T_{max} = 0.997$	$k = -11 \rightarrow 11$
11031 measured reflections	$l = -11 \rightarrow 11$

Refinement for **2b**

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.049$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.138$	H-atom parameters constrained
$S = 1.08$	$w = 1/[\sigma^2(F_o^2) + (0.0732P)^2 + 0.182P]$ where $P = (F_o^2 + 2F_c^2)/3$
2343 reflections	$(\Delta/\sigma)_{max} < 0.001$
139 parameters	$\Delta\rangle_{max} = 0.38$ e Å^{-3}
0 restraints	$\Delta\rangle_{min} = -0.23$ e Å^{-3}

Computing details

Data collection: Collect (Nonius, 1998); cell refinement: *EVALCCD* (Duisenberg *et al.*, 2003); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

Special details

Experimental. dx = 35 mm, 50 sec./deg., 2 deg., 10 sets, 410 frames
Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.
Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for **2b**

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.09931 (13)	-0.02430 (12)	0.14908 (13)	0.0249 (3)
N2	0.07280 (16)	0.14583 (15)	0.23446 (16)	0.0244 (3)
N3	0.21619 (15)	0.22844 (15)	0.21963 (14)	0.0205 (3)
C4	0.33387 (18)	0.12822 (17)	0.13106 (17)	0.0223 (3)
H4	0.4436	0.1651	0.1068	0.027*
C5	0.26288 (18)	-0.04205 (18)	0.08123 (17)	0.0219 (3)
O5	0.30877 (14)	-0.18438 (13)	0.00302 (13)	0.0273 (3)
C6	0.23405 (18)	0.41559 (17)	0.30634 (17)	0.0211 (3)
C7	0.23630 (19)	0.49744 (18)	0.20754 (18)	0.0236 (3)
C8	0.25044 (19)	0.67699 (18)	0.29566 (19)	0.0252 (3)
H8	0.2531	0.7367	0.2324	0.030*
C9	0.26071 (19)	0.77127 (18)	0.47327 (19)	0.0248 (3)
C10	0.26085 (18)	0.68288 (18)	0.56561 (18)	0.0231 (3)
H10	0.2692	0.7469	0.6871	0.028*
C11	0.24920 (17)	0.50461 (18)	0.48598 (17)	0.0214 (3)
C12	0.2561 (2)	0.41605 (19)	0.59279 (18)	0.0258 (3)
H12A	0.2986	0.5020	0.7148	0.039*
H12B	0.3411	0.3310	0.5557	0.039*

H12C	0.1331	0.3577	0.5772	0.039*
C13	0.2706 (2)	0.96498 (19)	0.5657 (2)	0.0333 (4)
H13A	0.1592	0.9967	0.6139	0.050*
H13B	0.2805	1.0068	0.4840	0.050*
H13C	0.3785	1.0173	0.6591	0.050*
C14	0.2255 (2)	0.4013 (2)	0.01465 (19)	0.0310 (4)
H14A	0.1966	0.4779	-0.0319	0.047*
H14B	0.1291	0.3008	-0.0382	0.047*
H14C	0.3439	0.3627	-0.0111	0.047*

Atomic displacement parameters (Å^2) for **2b**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0235 (5)	0.0206 (5)	0.0284 (5)	-0.0007 (4)	0.0077 (4)	0.0103 (4)
N2	0.0212 (6)	0.0204 (6)	0.0282 (6)	-0.0014 (4)	0.0065 (5)	0.0095 (5)
N3	0.0177 (5)	0.0218 (6)	0.0210 (6)	-0.0009 (4)	0.0028 (4)	0.0104 (5)
C4	0.0203 (6)	0.0222 (7)	0.0232 (7)	0.0011 (5)	0.0053 (5)	0.0104 (6)
C5	0.0208 (6)	0.0247 (7)	0.0200 (6)	0.0009 (5)	0.0035 (5)	0.0114 (6)
O5	0.0313 (6)	0.0214 (5)	0.0285 (5)	0.0038 (4)	0.0095 (4)	0.0109 (4)
C6	0.0179 (6)	0.0191 (7)	0.0234 (7)	0.0001 (5)	0.0032 (5)	0.0087 (5)
C7	0.0213 (6)	0.0244 (7)	0.0237 (7)	-0.0006 (5)	0.0029 (5)	0.0115 (6)
C8	0.0238 (7)	0.0249 (7)	0.0288 (7)	-0.0005 (5)	0.0025 (5)	0.0159 (6)
C9	0.0182 (6)	0.0226 (7)	0.0295 (7)	0.0000 (5)	0.0026 (5)	0.0105 (6)
C10	0.0184 (6)	0.0236 (7)	0.0223 (7)	0.0009 (5)	0.0034 (5)	0.0077 (6)
C11	0.0149 (6)	0.0256 (7)	0.0232 (7)	0.0014 (5)	0.0031 (5)	0.0120 (6)
C12	0.0261 (7)	0.0271 (7)	0.0240 (7)	0.0007 (6)	0.0030 (6)	0.0132 (6)
C13	0.0357 (8)	0.0233 (8)	0.0371 (9)	0.0022 (6)	0.0068 (7)	0.0123 (7)
C14	0.0409 (9)	0.0272 (8)	0.0237 (7)	-0.0029 (6)	0.0033 (6)	0.0133 (6)

Geometric parameters (Å, º) for **2b**

O1—N2	1.3761 (15)	C9—C10	1.395 (2)
O1—C5	1.4151 (17)	C9—C13	1.508 (2)
N2—N3	1.3150 (16)	C10—C11	1.3874 (19)
N3—C4	1.3412 (17)	C10—H10	0.9500
N3—C6	1.4527 (17)	C11—C12	1.5090 (19)
C4—C5	1.4041 (19)	C12—H12A	0.9800
C4—H4	0.9500	C12—H12B	0.9800
C5—O5	1.2190 (17)	C12—H12C	0.9800
C6—C7	1.3980 (19)	C13—H13A	0.9800
C6—C11	1.4006 (19)	C13—H13B	0.9800

C7—C8	1.395 (2)	C13—H13C	0.9800
C7—C14	1.509 (2)	C14—H14A	0.9800
C8—C9	1.391 (2)	C14—H14B	0.9800
C8—H8	0.9500	C14—H14C	0.9800
N2—O1—C5	111.18 (10)	C11—C10—H10	118.9
N3—N2—O1	103.69 (10)	C9—C10—H10	118.9
N2—N3—C4	115.17 (12)	C10—C11—C6	116.80 (12)
N2—N3—C6	117.21 (11)	C10—C11—C12	120.02 (12)
C4—N3—C6	127.55 (11)	C6—C11—C12	123.17 (12)
N3—C4—C5	106.43 (12)	C11—C12—H12A	109.5
N3—C4—H4	126.8	C11—C12—H12B	109.5
C5—C4—H4	126.8	H12A—C12—H12B	109.5
O5—C5—C4	136.51 (13)	C11—C12—H12C	109.5
O5—C5—O1	119.95 (12)	H12A—C12—H12C	109.5
C4—C5—O1	103.53 (11)	H12B—C12—H12C	109.5
C7—C6—C11	123.45 (13)	C9—C13—H13A	109.5
C7—C6—N3	118.79 (12)	C9—C13—H13B	109.5
C11—C6—N3	117.76 (12)	H13A—C13—H13B	109.5
C8—C7—C6	116.87 (13)	C9—C13—H13C	109.5
C8—C7—C14	119.88 (13)	H13A—C13—H13C	109.5
C6—C7—C14	123.25 (13)	H13B—C13—H13C	109.5
C9—C8—C7	121.99 (13)	C7—C14—H14A	109.5
C9—C8—H8	119.0	C7—C14—H14B	109.5
C7—C8—H8	119.0	H14A—C14—H14B	109.5
C8—C9—C10	118.62 (13)	C7—C14—H14C	109.5
C8—C9—C13	121.24 (13)	H14A—C14—H14C	109.5
C10—C9—C13	120.14 (13)	H14B—C14—H14C	109.5
C11—C10—C9	122.22 (13)		
C5—O1—N2—N3	-0.34 (14)	C11—C6—C7—C14	178.15 (13)
O1—N2—N3—C4	0.55 (15)	N3—C6—C7—C14	-1.5 (2)
O1—N2—N3—C6	-176.65 (10)	C6—C7—C8—C9	-0.4 (2)
N2—N3—C4—C5	-0.54 (16)	C14—C7—C8—C9	179.98 (13)
C6—N3—C4—C5	176.32 (12)	C7—C8—C9—C10	1.4 (2)
N3—C4—C5—O5	-178.66 (16)	C7—C8—C9—C13	-178.26 (13)
N3—C4—C5—O1	0.28 (14)	C8—C9—C10—C11	-0.7 (2)
N2—O1—C5—O5	179.20 (12)	C13—C9—C10—C11	179.01 (13)
N2—O1—C5—C4	0.04 (14)	C9—C10—C11—C6	-1.0 (2)
N2—N3—C6—C7	-119.78 (14)	C9—C10—C11—C12	178.01 (12)
C4—N3—C6—C7	63.41 (18)	C7—C6—C11—C10	2.1 (2)

N2—N3—C6—C11	60.57 (16)	N3—C6—C11—C10	-178.22 (11)
C4—N3—C6—C11	-116.24 (15)	C7—C6—C11—C12	-176.87 (13)
C11—C6—C7—C8	-1.5 (2)	N3—C6—C11—C12	2.77 (19)
N3—C6—C7—C8	178.91 (11)		

Hydrogen-bond geometry (Å, º) for **2b**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O5^{i}	0.95	2.24	3.1652 (17)	166
C8—H8···O5^{ii}	0.95	2.55	3.4696 (19)	162
C10—H10···O5^{iii}	0.95	2.57	3.480 (2)	160
C14—H14*B*···O1^{iv}	0.98	2.57	3.546 (2)	172

Symmetry codes: (i) -*x*+1, -*y*, -*z*; (ii) *x*, *y*+1, *z*; (iii) *x*, *y*+1, *z*+1; (iv) -*x*, -*y*, -*z*.

Results of the single crystal X-ray analysis of trans-16

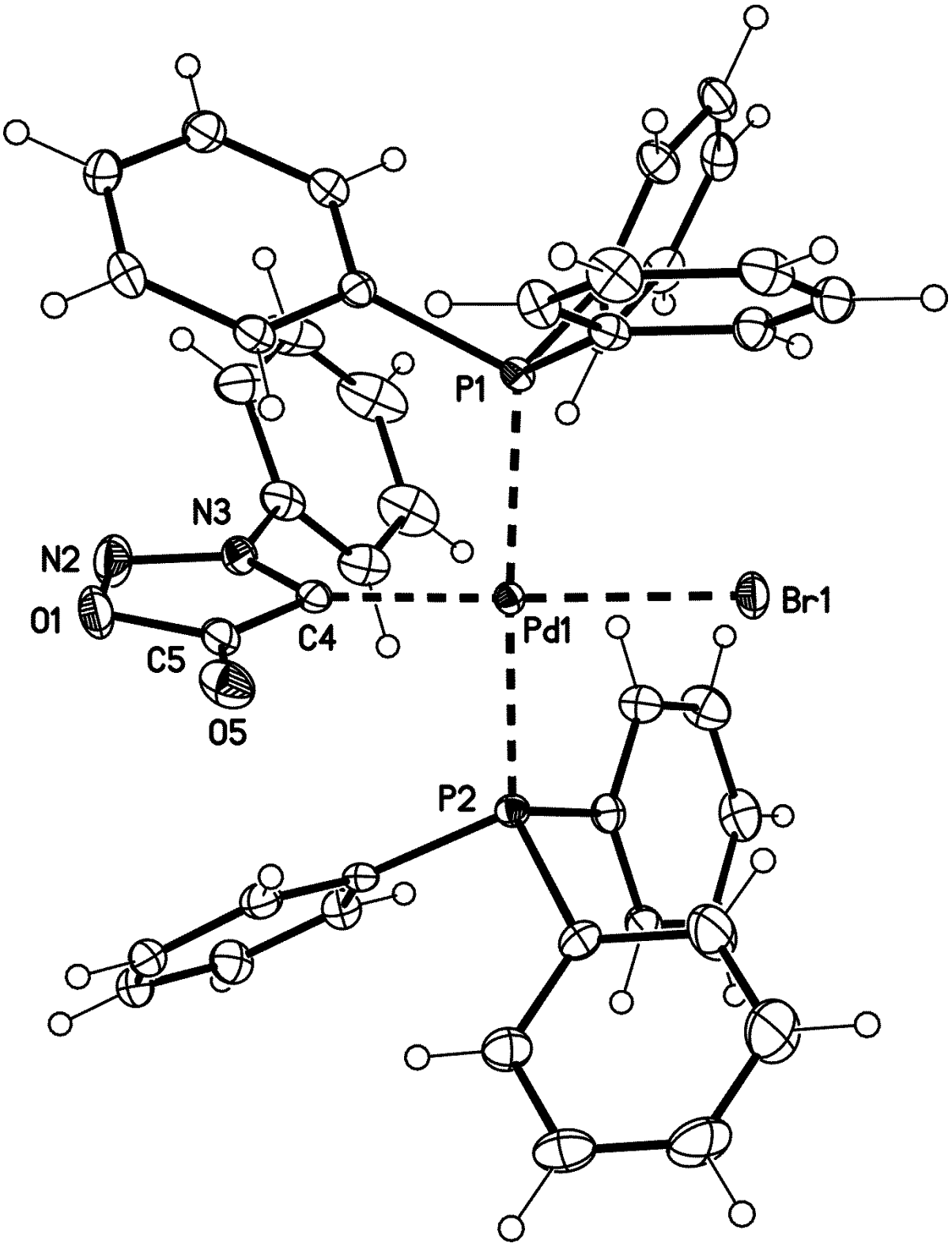


Fig. S3. Molecular structure of trans-**16** (displacement parameters are drawn at 50 % probability level).

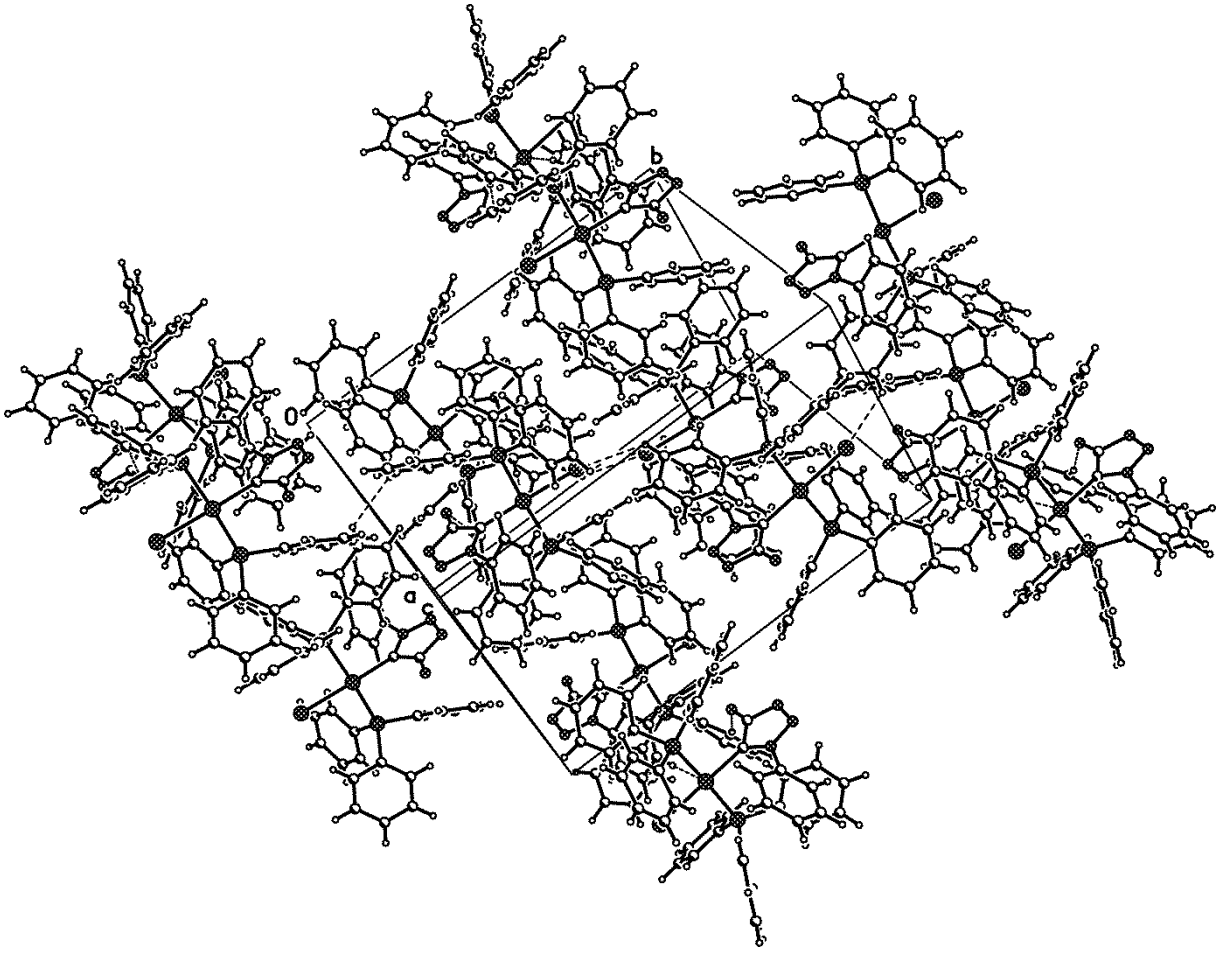


Fig. S4. Crystal packing of trans-**16**.

trans_16

Crystal data for trans-**16**

$C_{44}H_{35}BrN_2O_2P_2Pd$	$F(000) = 1760$
$M_r = 871.99$	$D_x = 1.614$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 11.8099$ (9) Å	Cell parameters from 320 reflections
$b = 17.9947$ (14) Å	$\theta = 1–25°$
$c = 17.1796$ (7) Å	$\mu = 1.76$ mm^{-1}
$\alpha = 100.544$ (7)°	$T = 123$ K
$V = 3589.3$ (4) Å^3	Blocks, yellow
$Z = 4$	0.35 × 0.30 × 0.20 mm

Data collection for trans-**16**

Bruker-Nonius KappaCCD diffractometer	8212 independent reflections
Radiation source: fine-focus sealed tube	7323 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.024$
rotation in phi and ω, 2 deg. scans	$\theta_{max} = 27.5°$, $\theta_{min} = 2.9°$
Absorption correction: multi-scan *SADABS* (Sheldrick, 2008)	$h = -15 \rightarrow 15$
$T_{min} = 0.634$, $T_{max} = 0.694$	$k = -23 \rightarrow 23$
69335 measured reflections	$l = -22 \rightarrow 22$

Refinement for trans-**16**

Refinement on F^2	Primary atom site location: heavy-atom method
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.023$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.051$	H-atom parameters constrained
$S = 1.15$	$w = 1/[\sigma^2(F_o^2) + (0.0112P)^2 + 4.4724P]$ where $P = (F_o^2 + 2F_c^2)/3$
8212 reflections	$(\Delta/\sigma)_{max} = 0.003$
469 parameters	$\Delta\rangle_{max} = 0.43$ e Å^{-3}
0 restraints	$\Delta\rangle_{min} = -0.43$ e Å^{-3}

Computing details

Data collection: Collect (Nonius, 1998); cell refinement: *EVALCCD* (Duisenberg *et al.*, 2003); data reduction: *EVALCCD* (Duisenberg *et al.*, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 1997).

Special details for trans-**16**

Experimental. dx = 40 mm, 60 sec./deg., 2 deg., 10 sets, 430 frames
Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$) for trans-**16**

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.305494 (17)	0.411083 (10)	0.619966 (12)	0.02015 (5)
Pd1	0.280505 (11)	0.274341 (7)	0.615665 (8)	0.01042 (4)
O1	0.25105 (13)	0.04379 (8)	0.57343 (9)	0.0256 (3)
N2	0.25328 (16)	0.04409 (10)	0.65431 (11)	0.0257 (4)
N3	0.26133 (14)	0.11584 (9)	0.67157 (10)	0.0169 (3)
C4	0.26475 (15)	0.16373 (10)	0.61159 (11)	0.0132 (3)
C5	0.25776 (16)	0.11646 (11)	0.54461 (12)	0.0182 (4)
O5	0.25875 (13)	0.12639 (9)	0.47434 (8)	0.0246 (3)
C6	0.27297 (17)	0.13438 (11)	0.75440 (12)	0.0199 (4)
C7	0.19858 (18)	0.18508 (12)	0.77792 (12)	0.0234 (4)
H7	0.1364	0.2047	0.7406	0.028*
C8	0.2152 (2)	0.20728 (15)	0.85676 (13)	0.0325 (5)
H8	0.1653	0.2430	0.8733	0.039*
C9	0.3040 (2)	0.17741 (17)	0.91078 (13)	0.0386 (6)
H9	0.3163	0.1933	0.9644	0.046*
C10	0.3751 (2)	0.12461 (16)	0.88739 (14)	0.0380 (6)
H10	0.4347	0.1032	0.9254	0.046*
C11	0.36079 (19)	0.10216 (13)	0.80836 (14)	0.0294 (5)
H11	0.4099	0.0658	0.7921	0.035*
P1	0.48194 (4)	0.26612 (3)	0.65362 (3)	0.01131 (9)
C12	0.56527 (16)	0.31294 (10)	0.58782 (10)	0.0143 (4)
C13	0.61229 (17)	0.27337 (11)	0.53177 (11)	0.0183 (4)
H13	0.6046	0.2208	0.5292	0.022*
C14	0.67033 (18)	0.30974 (12)	0.47961 (12)	0.0220 (4)
H14	0.7006	0.2821	0.4410	0.026*

C15	0.68422 (17)	0.38620 (12)	0.48369 (12)	0.0213 (4)
H15	0.7247	0.4110	0.4484	0.026*
C16	0.63874 (17)	0.42621 (11)	0.53959 (12)	0.0208 (4)
H16	0.6482	0.4786	0.5425	0.025*
C17	0.57952 (16)	0.39035 (11)	0.59143 (11)	0.0174 (4)
H17	0.5485	0.4183	0.6295	0.021*
C18	0.52967 (16)	0.30977 (10)	0.74931 (10)	0.0134 (3)
C19	0.45310 (17)	0.31583 (10)	0.80168 (11)	0.0162 (4)
H19	0.3764	0.2981	0.7867	0.019*
C20	0.48839 (18)	0.34772 (11)	0.87596 (11)	0.0199 (4)
H20	0.4359	0.3518	0.9116	0.024*
C21	0.60005 (19)	0.37343 (11)	0.89774 (11)	0.0208 (4)
H21	0.6237	0.3963	0.9479	0.025*
C22	0.67767 (18)	0.36605 (11)	0.84662 (12)	0.0208 (4)
H22	0.7547	0.3830	0.8622	0.025*
C23	0.64293 (17)	0.33387 (11)	0.77257 (11)	0.0184 (4)
H23	0.6964	0.3283	0.7378	0.022*
C24	0.54093 (15)	0.17225 (10)	0.66792 (11)	0.0136 (3)
C25	0.52021 (16)	0.12050 (10)	0.60590 (11)	0.0155 (4)
H25	0.4793	0.1354	0.5555	0.019*
C26	0.55849 (17)	0.04806 (11)	0.61719 (12)	0.0192 (4)
H26	0.5449	0.0138	0.5744	0.023*
C27	0.61695 (17)	0.02502 (11)	0.69108 (12)	0.0205 (4)
H27	0.6427	-0.0249	0.6990	0.025*
C28	0.63714 (17)	0.07525 (11)	0.75277 (12)	0.0192 (4)
H28	0.6769	0.0597	0.8033	0.023*
C29	0.59984 (16)	0.14856 (11)	0.74175 (11)	0.0160 (4)
H29	0.6145	0.1826	0.7847	0.019*
P2	0.07863 (4)	0.28859 (3)	0.58723 (3)	0.01219 (9)
C30	0.03123 (16)	0.34658 (10)	0.66239 (11)	0.0150 (4)
C31	-0.08020 (17)	0.37588 (11)	0.65036 (12)	0.0187 (4)
H31	-0.1322	0.3660	0.6024	0.022*
C32	-0.11498 (18)	0.41955 (11)	0.70852 (13)	0.0227 (4)

H32	-0.1904	0.4401	0.6997	0.027*
C33	-0.04037 (19)	0.43331 (12)	0.77926 (13)	0.0250 (4)
H33	-0.0647	0.4631	0.8188	0.030*
C34	0.06928 (19)	0.40364 (12)	0.79221 (12)	0.0250 (4)
H34	0.1200	0.4123	0.8410	0.030*
C35	0.10537 (17)	0.36105 (11)	0.73370 (11)	0.0189 (4)
H35	0.1814	0.3416	0.7425	0.023*
C36	-0.00819 (15)	0.20449 (10)	0.58453 (11)	0.0135 (3)
C37	0.00010 (16)	0.15028 (11)	0.52732 (11)	0.0174 (4)
H37	0.0537	0.1565	0.4928	0.021*
C38	-0.06925 (17)	0.08758 (11)	0.52071 (12)	0.0200 (4)
H38	-0.0642	0.0518	0.4809	0.024*
C39	-0.14581 (18)	0.07689 (11)	0.57189 (12)	0.0217 (4)
H39	-0.1927	0.0337	0.5675	0.026*
C40	-0.15366 (18)	0.12964 (11)	0.62954 (12)	0.0217 (4)
H40	-0.2058	0.1223	0.6649	0.026*
C41	-0.08551 (17)	0.19324 (11)	0.63580 (11)	0.0180 (4)
H41	-0.0917	0.2292	0.6753	0.022*
C42	0.01985 (17)	0.33321 (11)	0.49255 (11)	0.0170 (4)
C43	-0.05423 (18)	0.29798 (12)	0.43166 (12)	0.0222 (4)
H43	-0.0787	0.2486	0.4389	0.027*
C44	-0.09312 (19)	0.33402 (13)	0.36014 (12)	0.0271 (5)
H44	-0.1434	0.3090	0.3190	0.032*
C45	-0.0594 (2)	0.40528 (14)	0.34870 (14)	0.0329 (5)
H45	-0.0853	0.4298	0.2997	0.039*
C46	0.0123 (3)	0.44092 (16)	0.40899 (17)	0.0544 (9)
H46	0.0353	0.4906	0.4017	0.065*
C47	0.0517 (3)	0.40546 (14)	0.48041 (16)	0.0438 (7)
H47	0.1013	0.4312	0.5215	0.053*

Atomic displacement parameters (Å^2) for trans-**16**

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02062	0.01120 (9)	0.02902	-0.00117 (7)	0.00553 (8)	-0.00181 (7)

	(10)		(11)			
Pd1	0.01155 (6)	0.00990 (6)	0.00973 (6)	-0.00078 (5)	0.00173 (5)	-0.00024 (5)
O1	0.0244 (8)	0.0142 (7)	0.0385 (9)	-0.0042 (6)	0.0069 (7)	-0.0073 (6)
N2	0.0273 (10)	0.0146 (8)	0.0360 (10)	-0.0017 (7)	0.0075 (8)	0.0025 (7)
N3	0.0143 (8)	0.0136 (8)	0.0229 (8)	-0.0028 (6)	0.0036 (6)	0.0027 (6)
C4	0.0101 (8)	0.0135 (8)	0.0158 (9)	-0.0011 (7)	0.0016 (7)	0.0014 (7)
C5	0.0123 (9)	0.0161 (9)	0.0253 (10)	-0.0006 (7)	0.0011 (7)	-0.0052 (8)
O5	0.0225 (8)	0.0316 (8)	0.0196 (7)	-0.0017 (6)	0.0037 (6)	-0.0099 (6)
C6	0.0184 (10)	0.0229 (10)	0.0179 (9)	-0.0075 (8)	0.0021 (8)	0.0083 (8)
C7	0.0209 (10)	0.0325 (11)	0.0170 (10)	-0.0030 (9)	0.0034 (8)	0.0055 (8)
C8	0.0320 (12)	0.0489 (15)	0.0185 (10)	-0.0084 (11)	0.0096 (9)	0.0009 (10)
C9	0.0330 (13)	0.0667 (18)	0.0157 (10)	-0.0174 (13)	0.0036 (9)	0.0073 (11)
C10	0.0270 (12)	0.0565 (16)	0.0258 (12)	-0.0116 (11)	-0.0074 (10)	0.0244 (11)
C11	0.0186 (10)	0.0340 (12)	0.0344 (12)	-0.0039 (9)	0.0020 (9)	0.0177 (10)
P1	0.0115 (2)	0.0122 (2)	0.0103 (2)	-0.00163 (17)	0.00211 (16)	-0.00038 (16)
C12	0.0128 (8)	0.0178 (9)	0.0119 (8)	-0.0023 (7)	0.0014 (7)	0.0025 (7)
C13	0.0210 (10)	0.0175 (9)	0.0167 (9)	-0.0035 (8)	0.0042 (7)	-0.0009 (7)
C14	0.0230 (10)	0.0277 (11)	0.0173 (9)	-0.0025 (8)	0.0086 (8)	-0.0017 (8)
C15	0.0185 (10)	0.0287 (11)	0.0169 (9)	-0.0052 (8)	0.0035 (8)	0.0065 (8)
C16	0.0200 (10)	0.0180 (9)	0.0233 (10)	-0.0024 (8)	0.0012 (8)	0.0051 (8)
C17	0.0176 (9)	0.0173 (9)	0.0174 (9)	-0.0003 (7)	0.0037 (7)	0.0004 (7)
C18	0.0171 (9)	0.0112 (8)	0.0111 (8)	-0.0012 (7)	0.0004 (7)	-0.0003 (6)
C19	0.0173 (9)	0.0162 (9)	0.0145 (9)	0.0007 (7)	0.0019 (7)	0.0011 (7)
C20	0.0277 (11)	0.0202 (10)	0.0122 (9)	0.0046 (8)	0.0047 (8)	0.0004 (7)
C21	0.0326 (11)	0.0151 (9)	0.0129 (9)	-0.0014 (8)	-0.0006 (8)	-0.0014 (7)
C22	0.0233 (10)	0.0179 (9)	0.0190 (10)	-0.0078 (8)	-0.0025 (8)	0.0000 (8)
C23	0.0191 (10)	0.0202 (9)	0.0163 (9)	-0.0048 (8)	0.0041 (7)	0.0002 (7)
C24	0.0121 (8)	0.0142 (8)	0.0152 (9)	-0.0013 (7)	0.0038 (7)	0.0014 (7)
C25	0.0140 (9)	0.0173 (9)	0.0148 (9)	-0.0029 (7)	0.0015 (7)	0.0009 (7)
C26	0.0208 (10)	0.0154 (9)	0.0212 (10)	-0.0052 (8)	0.0030 (8)	-0.0036 (7)
C27	0.0201 (10)	0.0136 (9)	0.0272 (10)	-0.0002 (7)	0.0032 (8)	0.0036 (8)
C28	0.0197 (10)	0.0191 (9)	0.0179 (9)	-0.0012 (8)	0.0009 (7)	0.0048 (7)

C29	0.0154 (9)	0.0178 (9)	0.0149 (9)	-0.0029 (7)	0.0025 (7)	-0.0003 (7)
P2	0.0124 (2)	0.0130 (2)	0.0110 (2)	0.00016 (17)	0.00164 (17)	-0.00011 (16)
C30	0.0165 (9)	0.0137 (8)	0.0154 (9)	-0.0008 (7)	0.0048 (7)	-0.0009 (7)
C31	0.0161 (9)	0.0173 (9)	0.0224 (10)	-0.0016 (7)	0.0031 (8)	-0.0020 (8)
C32	0.0186 (10)	0.0178 (9)	0.0338 (12)	0.0005 (8)	0.0103 (9)	-0.0017 (8)
C33	0.0290 (11)	0.0227 (10)	0.0267 (11)	-0.0016 (9)	0.0142 (9)	-0.0071 (8)
C34	0.0253 (11)	0.0314 (12)	0.0185 (10)	-0.0024 (9)	0.0048 (8)	-0.0071 (8)
C35	0.0167 (9)	0.0231 (10)	0.0169 (9)	0.0009 (8)	0.0031 (7)	-0.0020 (8)
C36	0.0107 (8)	0.0145 (8)	0.0139 (8)	0.0001 (7)	-0.0015 (7)	0.0010 (7)
C37	0.0148 (9)	0.0193 (9)	0.0175 (9)	0.0030 (7)	0.0012 (7)	-0.0010 (7)
C38	0.0195 (10)	0.0163 (9)	0.0217 (10)	0.0023 (8)	-0.0031 (8)	-0.0044 (8)
C39	0.0202 (10)	0.0154 (9)	0.0274 (11)	-0.0029 (8)	-0.0012 (8)	0.0028 (8)
C40	0.0213 (10)	0.0224 (10)	0.0222 (10)	-0.0044 (8)	0.0057 (8)	0.0039 (8)
C41	0.0201 (10)	0.0184 (9)	0.0158 (9)	-0.0007 (8)	0.0042 (8)	0.0000 (7)
C42	0.0176 (9)	0.0179 (9)	0.0153 (9)	0.0028 (7)	0.0026 (7)	0.0035 (7)
C43	0.0229 (10)	0.0253 (10)	0.0177 (10)	0.0009 (8)	0.0014 (8)	0.0023 (8)
C44	0.0255 (11)	0.0382 (13)	0.0158 (10)	0.0049 (9)	-0.0006 (8)	0.0017 (9)
C45	0.0335 (13)	0.0401 (13)	0.0229 (11)	0.0033 (11)	-0.0008 (9)	0.0155 (10)
C46	0.070 (2)	0.0350 (15)	0.0465 (16)	-0.0179 (14)	-0.0198 (15)	0.0258 (13)
C47	0.0559 (17)	0.0286 (13)	0.0365 (14)	-0.0169 (12)	-0.0191 (12)	0.0123 (11)

Geometric parameters (Å, º) for trans-**16**

Br1—Pd1	2.4778 (3)	C24—C29	1.397 (3)
Pd1—C4	1.9991 (18)	C24—C25	1.402 (3)
Pd1—P1	2.3534 (5)	C25—C26	1.382 (3)
Pd1—P2	2.3584 (5)	C25—H25	0.9500
O1—N2	1.385 (2)	C26—C27	1.393 (3)
O1—C5	1.406 (2)	C26—H26	0.9500
N2—N3	1.324 (2)	C27—C28	1.380 (3)
N3—C4	1.350 (2)	C27—H27	0.9500
N3—C6	1.443 (3)	C28—C29	1.393 (3)
C4—C5	1.421 (3)	C28—H28	0.9500

C5—O5	1.222 (2)	C29—H29	0.9500
C6—C7	1.377 (3)	P2—C36	1.8238 (19)
C6—C11	1.385 (3)	P2—C30	1.8259 (19)
C7—C8	1.391 (3)	P2—C42	1.8329 (19)
C7—H7	0.9500	C30—C35	1.394 (3)
C8—C9	1.377 (3)	C30—C31	1.398 (3)
C8—H8	0.9500	C31—C32	1.391 (3)
C9—C10	1.376 (4)	C31—H31	0.9500
C9—H9	0.9500	C32—C33	1.387 (3)
C10—C11	1.397 (4)	C32—H32	0.9500
C10—H10	0.9500	C33—C34	1.381 (3)
C11—H11	0.9500	C33—H33	0.9500
P1—C18	1.8161 (18)	C34—C35	1.391 (3)
P1—C24	1.8266 (19)	C34—H34	0.9500
P1—C12	1.8339 (19)	C35—H35	0.9500
C12—C13	1.392 (3)	C36—C41	1.395 (3)
C12—C17	1.403 (3)	C36—C37	1.401 (3)
C13—C14	1.388 (3)	C37—C38	1.387 (3)
C13—H13	0.9500	C37—H37	0.9500
C14—C15	1.386 (3)	C38—C39	1.385 (3)
C14—H14	0.9500	C38—H38	0.9500
C15—C16	1.385 (3)	C39—C40	1.387 (3)
C15—H15	0.9500	C39—H39	0.9500
C16—C17	1.388 (3)	C40—C41	1.392 (3)
C16—H16	0.9500	C40—H40	0.9500
C17—H17	0.9500	C41—H41	0.9500
C18—C19	1.392 (3)	C42—C47	1.380 (3)
C18—C23	1.393 (3)	C42—C43	1.388 (3)
C19—C20	1.392 (3)	C43—C44	1.391 (3)
C19—H19	0.9500	C43—H43	0.9500
C20—C21	1.383 (3)	C44—C45	1.368 (3)
C20—H20	0.9500	C44—H44	0.9500
C21—C22	1.387 (3)	C45—C46	1.371 (4)

C21—H21	0.9500	C45—H45	0.9500
C22—C23	1.390 (3)	C46—C47	1.386 (3)
C22—H22	0.9500	C46—H46	0.9500
C23—H23	0.9500	C47—H47	0.9500
C4—Pd1—P1	91.72 (5)	C29—C24—P1	121.24 (14)
C4—Pd1—P2	90.97 (5)	C25—C24—P1	120.17 (14)
P1—Pd1—P2	175.208 (17)	C26—C25—C24	120.84 (17)
C4—Pd1—Br1	178.42 (5)	C26—C25—H25	119.6
P1—Pd1—Br1	86.865 (13)	C24—C25—H25	119.6
P2—Pd1—Br1	90.494 (13)	C25—C26—C27	120.25 (18)
N2—O1—C5	110.97 (14)	C25—C26—H26	119.9
N3—N2—O1	102.46 (15)	C27—C26—H26	119.9
N2—N3—C4	117.55 (17)	C28—C27—C26	119.48 (18)
N2—N3—C6	115.85 (16)	C28—C27—H27	120.3
C4—N3—C6	126.47 (16)	C26—C27—H27	120.3
N3—C4—C5	103.33 (16)	C27—C28—C29	120.68 (18)
N3—C4—Pd1	128.65 (14)	C27—C28—H28	119.7
C5—C4—Pd1	127.99 (14)	C29—C28—H28	119.7
O5—C5—O1	119.68 (17)	C28—C29—C24	120.33 (18)
O5—C5—C4	134.62 (19)	C28—C29—H29	119.8
O1—C5—C4	105.68 (16)	C24—C29—H29	119.8
C7—C6—C11	121.4 (2)	C36—P2—C30	104.39 (9)
C7—C6—N3	119.44 (18)	C36—P2—C42	102.77 (9)
C11—C6—N3	119.2 (2)	C30—P2—C42	105.18 (9)
C6—C7—C8	119.5 (2)	C36—P2—Pd1	117.22 (6)
C6—C7—H7	120.3	C30—P2—Pd1	110.17 (6)
C8—C7—H7	120.3	C42—P2—Pd1	115.84 (6)
C9—C8—C7	119.9 (2)	C35—C30—C31	118.85 (17)
C9—C8—H8	120.1	C35—C30—P2	120.25 (14)
C7—C8—H8	120.1	C31—C30—P2	120.89 (15)
C10—C9—C8	120.2 (2)	C32—C31—C30	120.06 (19)
C10—C9—H9	119.9	C32—C31—H31	120.0

C8—C9—H9	119.9	C30—C31—H31	120.0
C9—C10—C11	120.8 (2)	C33—C32—C31	120.44 (19)
C9—C10—H10	119.6	C33—C32—H32	119.8
C11—C10—H10	119.6	C31—C32—H32	119.8
C6—C11—C10	118.2 (2)	C34—C33—C32	119.94 (19)
C6—C11—H11	120.9	C34—C33—H33	120.0
C10—C11—H11	120.9	C32—C33—H33	120.0
C18—P1—C24	103.33 (8)	C33—C34—C35	119.92 (19)
C18—P1—C12	104.28 (8)	C33—C34—H34	120.0
C24—P1—C12	105.86 (8)	C35—C34—H34	120.0
C18—P1—Pd1	110.74 (6)	C34—C35—C30	120.78 (19)
C24—P1—Pd1	115.89 (6)	C34—C35—H35	119.6
C12—P1—Pd1	115.44 (6)	C30—C35—H35	119.6
C13—C12—C17	118.59 (17)	C41—C36—C37	118.68 (17)
C13—C12—P1	121.22 (14)	C41—C36—P2	122.30 (14)
C17—C12—P1	120.16 (15)	C37—C36—P2	118.98 (14)
C14—C13—C12	120.80 (18)	C38—C37—C36	120.54 (18)
C14—C13—H13	119.6	C38—C37—H37	119.7
C12—C13—H13	119.6	C36—C37—H37	119.7
C15—C14—C13	120.22 (19)	C39—C38—C37	120.35 (18)
C15—C14—H14	119.9	C39—C38—H38	119.8
C13—C14—H14	119.9	C37—C38—H38	119.8
C16—C15—C14	119.60 (19)	C38—C39—C40	119.67 (19)
C16—C15—H15	120.2	C38—C39—H39	120.2
C14—C15—H15	120.2	C40—C39—H39	120.2
C15—C16—C17	120.54 (19)	C39—C40—C41	120.30 (19)
C15—C16—H16	119.7	C39—C40—H40	119.9
C17—C16—H16	119.7	C41—C40—H40	119.9
C16—C17—C12	120.24 (18)	C40—C41—C36	120.44 (18)
C16—C17—H17	119.9	C40—C41—H41	119.8
C12—C17—H17	119.9	C36—C41—H41	119.8
C19—C18—C23	119.57 (17)	C47—C42—C43	117.92 (19)
C19—C18—P1	119.23 (14)	C47—C42—P2	118.51 (16)

C23—C18—P1	121.12 (14)	C43—C42—P2	123.57 (15)
C20—C19—C18	120.27 (18)	C42—C43—C44	120.9 (2)
C20—C19—H19	119.9	C42—C43—H43	119.6
C18—C19—H19	119.9	C44—C43—H43	119.6
C21—C20—C19	119.79 (19)	C45—C44—C43	120.4 (2)
C21—C20—H20	120.1	C45—C44—H44	119.8
C19—C20—H20	120.1	C43—C44—H44	119.8
C20—C21—C22	120.31 (18)	C44—C45—C46	119.1 (2)
C20—C21—H21	119.8	C44—C45—H45	120.5
C22—C21—H21	119.8	C46—C45—H45	120.5
C21—C22—C23	120.06 (19)	C45—C46—C47	121.0 (2)
C21—C22—H22	120.0	C45—C46—H46	119.5
C23—C22—H22	120.0	C47—C46—H46	119.5
C22—C23—C18	119.96 (18)	C42—C47—C46	120.7 (2)
C22—C23—H23	120.0	C42—C47—H47	119.6
C18—C23—H23	120.0	C46—C47—H47	119.6
C29—C24—C25	118.42 (17)		
C5—O1—N2—N3	-0.1 (2)	P1—C18—C23—C22	-179.00 (15)
O1—N2—N3—C4	0.0 (2)	C18—P1—C24—C29	3.87 (17)
O1—N2—N3—C6	-176.18 (15)	C12—P1—C24—C29	113.18 (16)
N2—N3—C4—C5	0.1 (2)	Pd1—P1—C24—C29	-117.44 (14)
C6—N3—C4—C5	175.82 (17)	C18—P1—C24—C25	179.04 (15)
N2—N3—C4—Pd1	-178.31 (14)	C12—P1—C24—C25	-71.64 (16)
C6—N3—C4—Pd1	-2.6 (3)	Pd1—P1—C24—C25	57.73 (16)
P1—Pd1—C4—N3	82.61 (16)	C29—C24—C25—C26	-0.9 (3)
P2—Pd1—C4—N3	-93.42 (16)	P1—C24—C25—C26	-176.18 (15)
Br1—Pd1—C4—N3	109.1 (19)	C24—C25—C26—C27	1.0 (3)
P1—Pd1—C4—C5	-95.41 (16)	C25—C26—C27—C28	-0.5 (3)
P2—Pd1—C4—C5	88.56 (16)	C26—C27—C28—C29	-0.1 (3)

Br1—Pd1—C4—C5	-69 (2)	C27—C28—C29—C24	0.2 (3)
N2—O1—C5—O5	178.83 (17)	C25—C24—C29—C28	0.3 (3)
N2—O1—C5—C4	0.1 (2)	P1—C24—C29—C28	175.52 (15)
N3—C4—C5—O5	-178.5 (2)	C4—Pd1—P2—C36	6.71 (9)
Pd1—C4—C5—O5	-0.1 (3)	P1—Pd1—P2—C36	-117.4 (2)
N3—C4—C5—O1	-0.13 (19)	Br1—Pd1—P2—C36	-173.90 (7)
Pd1—C4—C5—O1	178.28 (13)	C4—Pd1—P2—C30	125.83 (8)
N2—N3—C6—C7	-127.2 (2)	P1—Pd1—P2—C30	1.7 (2)
C4—N3—C6—C7	57.0 (3)	Br1—Pd1—P2—C30	-54.78 (6)
N2—N3—C6—C11	54.5 (2)	C4—Pd1—P2—C42	-114.98 (9)
C4—N3—C6—C11	-121.3 (2)	P1—Pd1—P2—C42	120.9 (2)
C11—C6—C7—C8	3.2 (3)	Br1—Pd1—P2—C42	64.42 (7)
N3—C6—C7—C8	-175.09 (19)	C36—P2—C30—C35	111.89 (16)
C6—C7—C8—C9	-1.3 (3)	C42—P2—C30—C35	-140.29 (16)
C7—C8—C9—C10	-1.3 (4)	Pd1—P2—C30—C35	-14.79 (17)
C8—C9—C10—C11	2.0 (4)	C36—P2—C30—C31	-66.75 (17)
C7—C6—C11—C10	-2.5 (3)	C42—P2—C30—C31	41.07 (18)
N3—C6—C11—C10	175.84 (19)	Pd1—P2—C30—C31	166.57 (14)
C9—C10—C11—C6	-0.2 (3)	C35—C30—C31—C32	0.9 (3)
C4—Pd1—P1—C18	-119.70 (8)	P2—C30—C31—C32	179.58 (15)
P2—Pd1—P1—C18	4.4 (2)	C30—C31—C32—C33	-1.1 (3)
Br1—Pd1—P1—C18	61.00 (6)	C31—C32—C33—C34	0.1 (3)
C4—Pd1—P1—C24	-2.45 (8)	C32—C33—C34—C35	1.1 (3)
P2—Pd1—P1—C24	121.6 (2)	C33—C34—C35—C30	-1.3 (3)
Br1—Pd1—P1—C24	178.26 (7)	C31—C30—C35—C34	0.3 (3)
C4—Pd1—P1—C12	122.12 (9)	P2—C30—C35—C34	-178.41 (16)
P2—Pd1—P1—C12	-113.8 (2)	C30—P2—C36—C41	-3.29 (18)

Br1—Pd1—P1—C12	-57.17 (7)	C42—P2—C36—C41	-112.88 (16)
C18—P1—C12—C13	138.68 (16)	Pd1—P2—C36—C41	118.87 (15)
C24—P1—C12—C13	30.04 (18)	C30—P2—C36—C37	174.56 (14)
Pd1—P1—C12—C13	-99.60 (15)	C42—P2—C36—C37	64.97 (16)
C18—P1—C12—C17	-43.47 (17)	Pd1—P2—C36—C37	-63.28 (16)
C24—P1—C12—C17	-152.11 (15)	C41—C36—C37—C38	1.5 (3)
Pd1—P1—C12—C17	78.25 (16)	P2—C36—C37—C38	-176.42 (14)
C17—C12—C13—C14	-1.1 (3)	C36—C37—C38—C39	-1.5 (3)
P1—C12—C13—C14	176.78 (15)	C37—C38—C39—C40	0.6 (3)
C12—C13—C14—C15	1.3 (3)	C38—C39—C40—C41	0.4 (3)
C13—C14—C15—C16	-0.7 (3)	C39—C40—C41—C36	-0.3 (3)
C14—C15—C16—C17	0.0 (3)	C37—C36—C41—C40	-0.6 (3)
C15—C16—C17—C12	0.1 (3)	P2—C36—C41—C40	177.28 (15)
C13—C12—C17—C16	0.4 (3)	C36—P2—C42—C47	168.6 (2)
P1—C12—C17—C16	-177.49 (15)	C30—P2—C42—C47	59.6 (2)
C24—P1—C18—C19	-100.17 (16)	Pd1—P2—C42—C47	-62.3 (2)
C12—P1—C18—C19	149.34 (15)	C36—P2—C42—C43	-12.21 (19)
Pd1—P1—C18—C19	24.56 (16)	C30—P2—C42—C43	-121.21 (18)
C24—P1—C18—C23	76.65 (17)	Pd1—P2—C42—C43	116.91 (16)
C12—P1—C18—C23	-33.85 (17)	C47—C42—C43—C44	1.3 (3)
Pd1—P1—C18—C23	-158.63 (14)	P2—C42—C43—C44	-177.94 (16)
C23—C18—C19—C20	1.9 (3)	C42—C43—C44—C45	-0.4 (3)
P1—C18—C19—C20	178.72 (14)	C43—C44—C45—C46	-0.7 (4)
C18—C19—C20—C21	0.0 (3)	C44—C45—C46—C47	0.8 (5)
C19—C20—C21—	-1.5 (3)	C43—C42—C47—	-1.1 (4)

C22		C46	
C20—C21—C22—C23	1.1 (3)	P2—C42—C47—C46	178.1 (3)
C21—C22—C23—C18	0.7 (3)	C45—C46—C47—C42	0.1 (5)
C19—C18—C23—C22	-2.2 (3)		

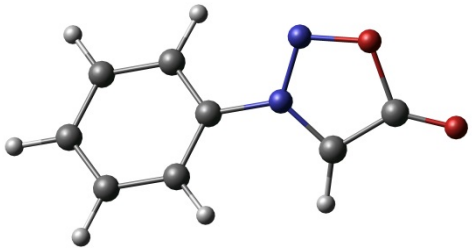
Hydrogen-bond geometry (Å, º) for trans-**16**

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C20—H20···O5^{i}	0.95	2.55	3.479 (3)	165

Symmetry code: (i) *x*, -*y*+1/2, *z*+1/2.

DFT-calculations

2aA



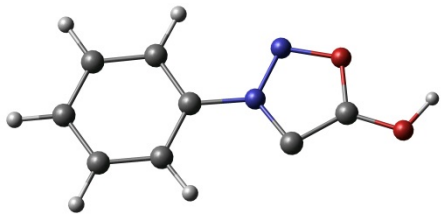
Negative frequencies: 0

Energy: -568.315217 Hartree

NICS(1): -6.8

N1	0.4214755013	-0.5855401487	0.1268292873
N2	0.3873061738	-1.8007596944	-0.3714790982
O3	1.6380976178	-2.2882386429	-0.1781827692
C4	2.4988386644	-1.3146655464	0.4647038584
C5	1.6167065024	-0.2129600991	0.6303769475
C6	-0.7807769266	0.1958388870	0.0833535782
C7	-0.6939081615	1.5714274152	-0.1302672957
C8	-1.8677713739	2.3226055176	-0.1626156954
C9	-3.1060777267	1.7004347536	0.0067130724
C10	-3.1738734997	0.3204445785	0.2108683813
C11	-2.0093556333	-0.4430531602	0.2552087502
O12	3.6506692219	-1.5647249199	0.7216439171
H13	1.7817836237	0.7307863873	1.1183878543
H14	0.2708934448	2.0414369892	-0.2912446161
H15	-1.8120898424	3.3938088624	-0.3313967628
H16	-4.0176145833	2.2904331596	-0.0214603706
H17	-4.1357459922	-0.1652560873	0.3452467275
H18	-2.0393132557	-1.5135932904	0.4230551891

2aB

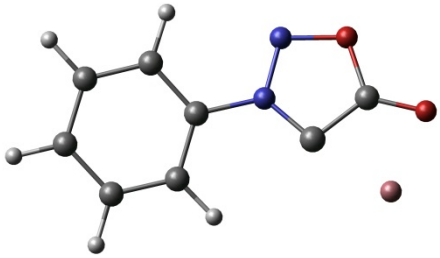


Negative frequencies: 0

Energy: -568.242452 Hartree

N1	0.7215295482	1.8268410441	-0.0706199129
N2	0.5506036874	0.5201236584	0.1387457250
C3	1.6488403467	-0.2602552534	0.4281646837
C4	2.5924525740	0.7521394291	0.3788553369
O5	2.0616916883	1.9733672356	0.0900119052
O6	3.9119580468	0.7092344853	0.5691544966
C7	-0.7946811163	0.0186580833	0.0421666087
C8	-1.8613925579	0.8867430653	-0.2055208877
C9	-3.1491631346	0.3620575299	-0.2935444158
C10	-3.3685480248	-1.0082235225	-0.1360100513
C11	-2.2907862749	-1.8603769576	0.1121003544
C12	-0.9965719522	-1.3526570661	0.2026729988
H13	4.2867475837	1.5998971571	0.4608411158
H14	-1.6848040903	1.9490891993	-0.3248639186
H15	-3.9840852033	1.0301822904	-0.4846410195
H16	-4.3760733019	-1.4091187615	-0.2054055706
H17	-2.4551001130	-2.9270169775	0.2360250840
H18	-0.1356950740	-1.9822195964	0.3963308239

5a with Li

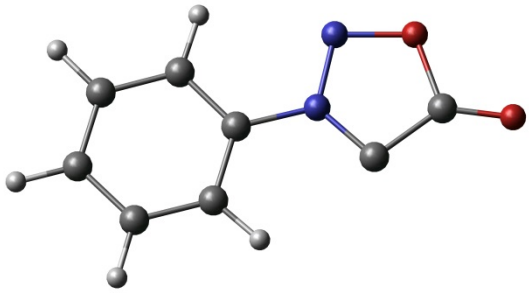


Negative frequencies: 0

Energy: -575.265401 Hartree

C1	-1.0123748970	1.1734220833	0.7920574467
C2	-0.8337261328	0.0476690218	-0.0113666566
C3	-2.2669727598	1.7773553594	0.8466846685
C4	-1.8883951518	-0.4806739184	-0.7595220939
C5	-3.3322187196	1.2597249272	0.1077022071
C6	-3.1383266014	0.1317716018	-0.6918383455
N7	0.4638991907	-0.5673291730	-0.0647060909
C8	1.6335965860	0.0052359315	0.2966273529
N9	0.5021713351	-1.8249541507	-0.5170454633
C10	2.5355574649	-1.0526972284	0.0134912315
O11	1.8372096864	-2.1341533427	-0.4764130862
O12	3.7929801001	-1.0468424675	0.1511938687
Li13	3.4914758478	0.7224627460	0.6967836528
H14	-0.1713208302	1.5563197499	1.3582083272
H15	-2.4114933947	2.6536473608	1.4724481755
H16	-1.7238737537	-1.3518222232	-1.3823055308
H17	-4.3087837234	1.7339795034	0.1532109080
H18	-3.9620015406	-0.2731929280	-1.2730371561

5a without Li



Negative frequencies: 0

Energy: -567.708371 Hartree

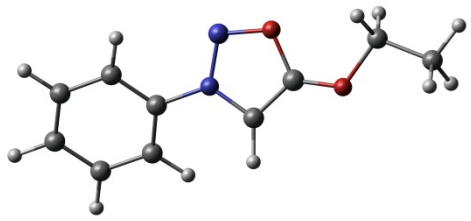
NICS(1): -7.9

Energy HOMO: -0.005809 Hartree

Energy HOMO-1: -0.033816 Hartree

C1	-0.7426828930	1.4216885359	0.3939375405
C2	-0.6812561805	0.0808723014	0.0013263997
C3	-1.9702083253	2.0799824536	0.4159152733
C4	-1.8480769618	-0.5979923290	-0.3683782917
C5	-3.1424707074	1.4118715192	0.0487061762
C6	-3.0716784879	0.0732043639	-0.3419988598
N7	0.5834256803	-0.5752842976	-0.0150312488
C8	1.7473631104	0.0274470884	0.3189831385
N9	0.5605007931	-1.8823049265	-0.3968997056
C10	2.6682844190	-1.0769754634	0.1244907367
O11	1.8909743129	-2.2130384070	-0.3109730077
O12	3.8811970619	-1.2178327037	0.2490047277
H13	0.1966441821	1.8916008417	0.6678084552
H14	-2.0119478537	3.1235227101	0.7225710648
H15	-1.7768365670	-1.6360327879	-0.6694429687
H16	-4.0998199102	1.9292631428	0.0667696219
H17	-3.9770149097	-0.4577872975	-0.6303605885

6a without BF_4^-



Negative frequencies: 0

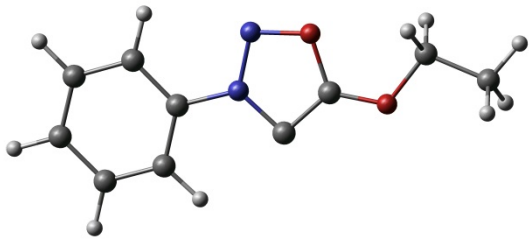
Energy: -647.303538 Hartree

NICS(1): -8.9

C1	0.1040315120	0.2432231369	1.1177239598
N2	0.5059205304	-0.6460847563	-0.8885119804
N3	-0.6489504509	-0.0364531809	-0.8912930665
C4	-0.9741530292	0.5309436914	0.3053390975
O5	0.9916239722	-0.4591136588	0.3769802411
O6	0.3362831700	0.5455595546	2.3486273669
C7	-1.4226800315	-0.0107171486	-2.1044480897
C8	-0.7496850392	0.0413231104	-3.3281411213
C9	-1.5092448149	0.0620724262	-4.4944950969
C10	-2.9052011386	0.0344861801	-4.4279214571
C11	-3.5555124824	-0.0190830065	-3.1918958624
C12	-2.8164911502	-0.0447292831	-2.0122974017
C13	1.6142307398	0.1231679865	2.9892270399
C14	1.5738365392	0.6237007608	4.4132241607
H15	0.3335768392	0.0800601795	-3.3624819490
H16	-1.0084816208	0.1098530405	-5.4560337142
H17	-3.4890606873	0.0547106777	-5.3429984947
H18	-4.6390625736	-0.0527335375	-3.1444121366
H19	-3.3157789693	-0.1230206719	-1.0515597400
H20	1.6605441398	-0.9667913588	2.9201607019
H21	2.4252810886	0.5641351419	2.4037685737
H22	2.5027718297	0.3287635384	4.9124090839

H23	1.4969305894	1.7139799838	4.4468399688
H24	0.7351743586	0.1864519229	4.9620574763
H25	-1.8671724451	1.1062258852	0.4792122314

7a



Negative frequencies: 0

Energy: -646.868716 Hartree

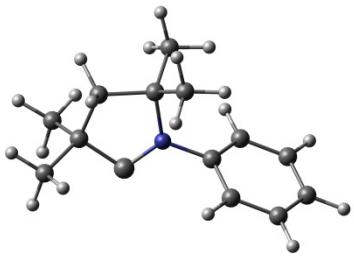
NICS(1): -10.3

Energy HOMO: -0.212233 Hartree

N1	0.7048227712	0.0000000000	-0.9748337212
N2	-0.6268477636	-0.0007236799	-0.8593104234
C3	-1.1873581506	-0.0020937335	0.3954582196
C4	0.0000000000	0.0000000000	1.1172758614
O5	1.1093831429	0.0028174134	0.3214100635
O6	0.1783114499	0.0011389241	2.4301709108
C7	-1.3845803637	-0.0023043637	-2.0824049639
C8	-0.7400415319	0.0675559372	-3.3201273940
C9	-1.5099923592	0.0622205581	-4.4818265633
C10	-2.9026512896	-0.0108582322	-4.4092811748
C11	-3.5300567100	-0.0788157438	-3.1638065976
C12	-2.7754034015	-0.0751608725	-1.9928480446
C13	1.5278602779	-0.0019365074	2.9456386150
C14	1.4268643471	-0.0061608571	4.4587640577
H15	0.3407531003	0.1262653700	-3.3696868570
H16	-1.0160436285	0.1174862177	-5.4478008699
H17	-3.4956712274	-0.0136716690	-5.3198272681
H18	-4.6131331170	-0.1353895419	-3.1000584945
H19	-3.2267279473	-0.1237523581	-1.0084799779
H20	2.0515163475	-0.8889252250	2.5699374458
H21	2.0534674454	0.8860719415	2.5750586331

H22	2.4307981596	-0.0082602865	4.8965897878
H23	0.8938650251	0.8812621358	4.8136931222
H24	0.8923698937	-0.8947285317	4.8086025445

9



Negative frequencies: 0

Energy: -599.608566 Hartree

C1	-0.0778459591	1.6214146951	-0.5205293335
N2	0.0731859411	0.2246227967	0.0881674631
C3	1.2738705800	-0.2121577798	0.4070677685
C4	2.2331149793	0.9328357548	0.0895556551
C5	1.4107008491	2.0030275158	-0.6968416988
C6	-0.8303151521	1.5370784546	-1.8552856161
C7	-0.8185317083	2.5637094908	0.4416458351
C8	-1.0778210161	-0.6312763191	0.2470891813
C9	3.4130032098	0.3910221538	-0.7371196959
C10	2.7582925723	1.4743855368	1.4375654614
C11	-1.9961315395	-0.4247887266	1.2800204752
C12	-3.0984781114	-1.2717926228	1.4106796170
C13	-3.2865529363	-2.3262437208	0.5168625101
C14	-2.3601041752	-2.5391316632	-0.5059860665
C15	-1.2588742213	-1.6952507212	-0.6408442942
H16	1.6037652474	3.0218719803	-0.3438997131
H17	1.6764082041	1.9776234285	-1.7599485578
H18	-0.8654399960	2.5269801902	-2.3252216484
H19	-0.3284072211	0.8512887855	-2.5465813071
H20	-1.8612088934	1.1933490552	-1.7185123629
H21	-1.8555776748	2.2490721410	0.5963606016
H22	-0.3202169195	2.6106743375	1.4158390630
H23	-0.8393584061	3.5766450063	0.0229341781

H24	4.1240297672	1.1931879415	-0.9745631206
H25	3.9422665278	-0.3917099097	-0.1841482685
H26	3.0673823333	-0.0445699939	-1.6825680394
H27	3.2311498715	0.6730964653	2.0146473891
H28	3.4986728215	2.2668839064	1.2701390182
H29	1.9494254409	1.8916422505	2.0492132730
H30	-1.8339590908	0.3754338402	1.9945174812
H31	-3.8048332592	-1.1113538450	2.2209179967
H32	-4.1448848196	-2.9845056886	0.6218979854
H33	-2.4919351389	-3.3663161881	-1.1984824774
H34	-0.5210814371	-1.8603915199	-1.4198713009

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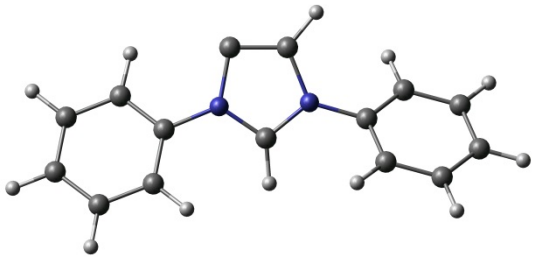

Negative frequencies: 0

Energy: -688.227083 Hartree

C1	-1.1956520588	1.7433949650	-0.5263813033
N2	-1.3139339172	0.4586058548	0.0416120267
C3	-0.1522121819	0.1894045901	0.6553120137
N4	0.6524820762	1.2557756683	0.4698589639
C5	0.0438206159	2.2979338148	-0.2877736417
C6	-2.4459702289	-0.4033643425	0.0039803902
C7	1.9770388260	1.3525547133	0.9939574533
C8	2.5315907582	2.6258678422	1.1508696186
C9	3.8159568281	2.7565445206	1.6717312660
C10	4.5522602767	1.6270521222	2.0376673076
C11	3.9967580398	0.3586572473	1.8667527360
C12	2.7132876440	0.2153142625	1.3388854370
C13	-3.7241093958	0.1416465016	0.1632099290
C14	-4.8389815128	-0.6930789913	0.1120066250
C15	-4.6847609998	-2.0667323778	-0.0840417558
C16	-3.4060053574	-2.6044596330	-0.2401628208
C17	-2.2849616723	-1.7764150798	-0.2079099948
H18	-2.0236433948	2.1228592264	-1.1079986388
H19	0.0330037139	-0.6847252844	1.2584094618
H20	1.9356658333	3.4769085975	0.8403587111
H21	4.2430771818	3.7484907655	1.7935070576
H22	5.5539683739	1.7341115542	2.4448285570
H23	4.5668583857	-0.5278391222	2.1312600789

H24	2.3060854469	-0.7782887344	1.1751802812
H25	-3.8340348692	1.2065025118	0.3420924924
H26	-5.8307603577	-0.2675469897	0.2370485322
H27	-5.5563530933	-2.7141855355	-0.1185200117
H28	-3.2783039395	-3.6708495908	-0.4039708996
H29	-1.2914988963	-2.1844259362	-0.3690556345

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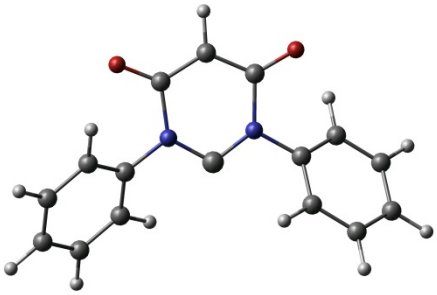

Negative frequencies: 0

Energy: -876.285216 Hartree

C1	-1.1868766480	2.0455804531	-0.4635871644
N2	-1.1586444992	0.6749651493	0.0788558903
C3	-0.0941812344	0.0676061138	0.6667955302
N4	1.0217190796	0.8339083531	0.7925809255
C5	1.1555004798	2.2463509048	0.3914240236
C6	0.0073478634	2.7542820526	-0.2422219228
O7	2.2102935821	2.8505313584	0.6322048772
O8	-2.2038662020	2.4485951976	-1.0455726340
C9	2.1327569436	0.1878264145	1.4332075476
C10	-2.3256259128	-0.1496356356	-0.0656217531
C11	-3.6180159520	0.3618198773	0.1170422058
C12	-4.7241367990	-0.4822015564	0.0095790502
C13	-4.5671615230	-1.8383397677	-0.2805115488
C14	-3.2795670720	-2.3470332836	-0.4622306182
C15	-2.1698345935	-1.5108846209	-0.3596435320
C16	1.8898681312	-0.7097261039	2.4817058131
C17	2.9416628081	-1.3872591435	3.0945684780
C18	4.2572683779	-1.1757251468	2.6773763085
C19	4.5009865127	-0.2799063377	1.6353100358
C20	3.4532683569	0.4002702658	1.0132614683
H21	0.0464032302	3.7794377062	-0.5909651773
H22	-3.7469900018	1.4146145562	0.3258206479
H23	-5.7204218142	-0.0700966972	0.1584152883

H24	-5.4351576558	-2.4895918187	-0.3632953758
H25	-3.1348498081	-3.4016477978	-0.6895634095
H26	-1.1621054491	-1.8942964968	-0.4720631589
H27	0.8605392903	-0.8815146354	2.7751281405
H28	2.7294126773	-2.0814438466	3.9056610852
H29	5.0803929427	-1.7013080472	3.1575428141
H30	5.5200872464	-0.1063902024	1.2949793232
H31	3.6496579112	1.1053955545	0.2178591155

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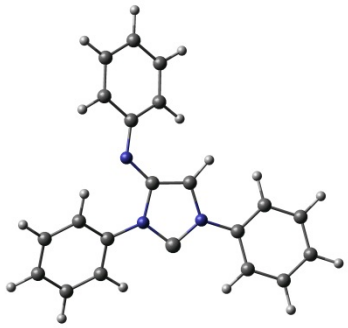

Negative frequencies: 0

Energy: -974.089388 Hartree

C1	-1.0210396530	0.5457064260	0.1612751421
N2	-0.5521187020	-0.7502269876	0.6238204069
C3	0.8136814595	-0.8904922842	0.5764733934
N4	1.2211424372	0.3172319746	0.0836383186
C5	0.1491870004	1.1899969684	-0.2016212585
N6	-2.3210321126	0.8545823198	0.2160406094
C7	-1.3550611816	-1.8417404096	1.0581988632
C8	2.5761213200	0.6028185697	-0.1637476522
C9	-2.8572880336	1.9289538147	-0.4346843724
C10	-4.2015401180	2.2774803136	-0.1073732462
C11	-4.8667050723	3.3284516529	-0.7200391574
C12	-4.2414587402	4.1010717370	-1.7106773431
C13	-2.9316201285	3.7704801500	-2.0663002850
C14	-2.2464641005	2.7252860854	-1.4489908820
C15	-2.6402095185	-1.6627317340	1.5920056310
C16	-3.3732364884	-2.7696350523	2.0235562995
C17	-2.8495118112	-4.0597976482	1.9426554315
C18	-1.5675240898	-4.2348186114	1.4149973997
C19	-0.8280084182	-3.1420561187	0.9720862799
C20	3.5789578256	-0.2254074596	0.3721911954
C21	4.9192301306	0.0564627679	0.1384897058
C22	5.2988449881	1.1678321307	-0.6252570701
C23	4.3046802112	1.9864597539	-1.1592098644

C24	2.9538075251	1.7118074752	-0.9375005744
H25	0.2982557657	2.2318523014	-0.4208526596
H26	-4.6972104771	1.6766364999	0.6521512569
H27	-5.8918704751	3.5529162751	-0.4242614663
H28	-4.7616673954	4.9283875583	-2.1885677900
H29	-2.4250785819	4.3402463937	-2.8463813503
H30	-1.2460324558	2.4788405013	-1.7857015700
H31	-3.0463005388	-0.6606809088	1.6258469088
H32	-4.3701718127	-2.6128489648	2.4316085430
H33	-3.4298805285	-4.9159401816	2.2812313610
H34	-1.1393355106	-5.2328731736	1.3390376400
H35	0.1716569826	-3.2594407453	0.5706437851
H36	3.2615169711	-1.0813197018	0.9570904187
H37	5.6799156311	-0.5960838950	0.5630349759
H38	6.3495980531	1.3874259856	-0.7990676841
H39	4.5757349979	2.8497871247	-1.7637307773
H40	2.1934299417	2.3421386709	-1.3844890228

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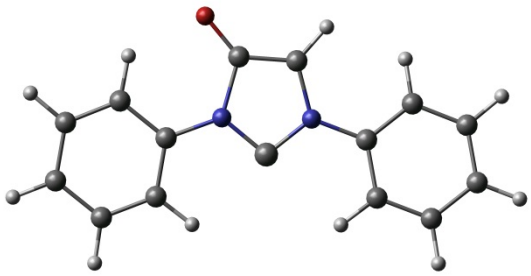

Negative frequencies: 0

Energy: -762.923220 Hartree

C1	-1.3631967888	2.0014583667	-0.2189316178
N2	-1.3220709353	0.5460592981	0.1216480571
C3	-0.0675426753	0.0913873721	0.4447916138
N4	0.7019283766	1.2167897207	0.3164771169
C5	-0.0282212149	2.3570925834	-0.0941002688
C6	2.0859685138	1.1830651802	0.5332254165
C7	-2.4321410940	-0.3285248835	0.1227449839
C8	-3.7342506100	0.1315018370	-0.1459160838
C9	-4.8045484270	-0.7639814259	-0.1335734809
C10	-4.6154269551	-2.1187051058	0.1420148513
C11	-3.3204244882	-2.5737570841	0.4087353899
C12	-2.2411859050	-1.6965049231	0.3995720359
C13	2.6891252316	0.0464860645	1.1066282646
C14	4.0588340534	0.0147535613	1.3315064152
C15	4.8710338943	1.1083522980	0.9997189343
C16	4.2772775677	2.2326242464	0.4290730799
C17	2.9018757853	2.2773610057	0.1936831337
O18	-2.4031898163	2.6278055024	-0.5231485689
H19	0.3923534330	3.3461282007	-0.1461797741
H20	-3.8643640050	1.1848506239	-0.3608215031
H21	-5.8050363805	-0.3883282620	-0.3439163582
H22	-5.4577724012	-2.8080920292	0.1489888215
H23	-3.1466024760	-3.6269712380	0.6257546722

H24	-1.2303332437	-2.0298472336	0.6046274660
H25	2.0410964211	-0.7872826581	1.3520909378
H26	4.5023139142	-0.8738713453	1.7778370076
H27	5.9427992126	1.0800059493	1.1839164572
H28	4.8878402146	3.0917733641	0.1558008144
H29	2.4641668224	3.1523399102	-0.2723278386

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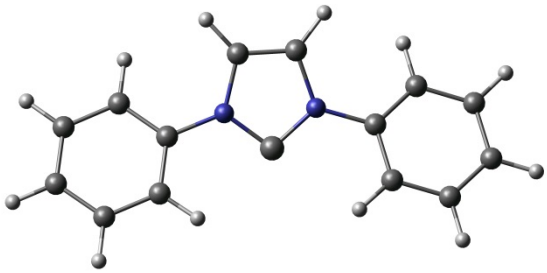

Negative frequencies: 0

Energy: -688.257491 Hartree

C1	-1.2605812944	1.7240739058	0.6556699144
N2	-1.2820488223	0.4295040875	0.1247980877
C3	-0.1012384164	0.0871308280	-0.4877997279
N4	0.6506205149	1.2238595921	-0.3158526991
C5	-0.0367955262	2.2273696115	0.3762152045
C6	1.9901988785	1.3308066382	-0.7940601488
C7	-2.3868809253	-0.4688890039	0.2050368672
C8	-3.6918023684	0.0095576372	0.3571415653
C9	-4.7545430131	-0.8915516263	0.4470665556
C10	-4.5257285522	-2.2654372115	0.3733053684
C11	-3.2201011310	-2.7359101778	0.2075918238
C12	-2.1513920395	-1.8470537487	0.1279816035
C13	2.7365610288	0.1634908568	-0.9975680346
C14	4.0468864771	0.2531321922	-1.4596009992
C15	4.6280433574	1.4985978820	-1.7137422958
C16	3.8788210322	2.6576195201	-1.5126077926
C17	2.5602478193	2.5794264097	-1.0600268954
H18	-2.0799233933	2.1517968371	1.2106674598
H19	0.4053077514	3.1732581725	0.6446350367
H20	-3.8865491607	1.0770751522	0.3792258660
H21	-5.7657973417	-0.5119862524	0.5625983445
H22	-5.3553735864	-2.9632188778	0.4407194412
H23	-3.0295328088	-3.8038660874	0.1468102006

H24	-1.1325981588	-2.1910380769	-0.0047550099
H25	2.2664674139	-0.7921090478	-0.7984305961
H26	4.6196819951	-0.6570216075	-1.6147317943
H27	5.6525404892	1.5633197800	-2.0686422629
H28	4.3135772259	3.6314626210	-1.7191601022
H29	1.9761710128	3.4865531530	-0.9421952652

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