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Electronic Supplementary information

An Umpolung of Lewis Acidity/Basicity at Nitrogen by Deprotonation of A Cyclic (Amino)(Aryl)Nitrenium Cation

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This PDF file includes:

1.	Materials and Methods	S3
2.	Syntheses and Spectroscopic Data	S 4
3.	Crystallographic Details	S15
4.	Computational Details	S19
5.	References	S24

1. Materials and Methods

General Remarks

All manipulations were performed in a MB Unilab glove box produced by MBraun or using standard Schlenk techniques under an inert atmosphere of anhydrous N₂. All glassware was oven-dried and cooled under vacuum before use. Dry, oxygen-free solvents (dichloromethane, toluene, *n*-pentane and *n*-hexane) were prepared using an Innovative Technologies solvent purification system. Other solvents (cyclohexane, chloroform, benzene, 1,2-dichlorobenzene) were degassed and stored over molecular sieves (4 Å) for at least two days prior to use. Deuterated chloroform (CDCl₃), dichloromethane (CD_2Cl_2) and benzene (C_6D_6) purchased from Cambridge Isotope Laboratories Inc. were degassed and stored over molecular sieves (4 Å) for at least two days prior to use. Commercial reagents were used without further purification unless indicated otherwise. Fluorene-9,3'-indazole^[S1] was prepared according to literature procedures. NMR spectra were obtained on a Bruker AvanceIII-400 MHz spectrometer or an Agilent DD2 500 MHz spectrometer. ¹H, ¹³C{¹H}, ³¹P, ¹⁹F and ¹¹B{¹H} NMR chemical shifts (δ /ppm) are referenced to Me₄Si, Me₄Si, H₃PO₄, CFCl₃ and BF₃·OEt₂, respectively. High-resolution mass spectra (HRMS) were obtained on an Agilent 6538 Q-TOF (ESI) or a JMS-T100LC JOEL (DART).

2. Syntheses and Spectroscopic Data

2: Dichloromethane solution (1 mL) of Ph₂CHCl (203 mg, 1.0 mmol) was added to dichloromethane solution (4 mL) of Ag[BF₄] (195 mg, 1.0 mmol) and fluorene-9,3'indazole 1 (268 mg, 1.0 mmol), and the mixture was stirred at room temperature for 30 minutes. The suspension was filtered. The filtrate was reduced to 1.5 mL under vacuum, and 5 mL of *n*-pentane was added with rigorous stirring to give a precipitate. After decanting the supernatant, the precipitate was washed with a component solvent (1 mL of dichloromethane and 4 mL of *n*-pentane) and dried under vacuum to give 2 as a yellow solid (502 mg, 96% yield). Single crystals of 2 were obtained by layering of pentane on a dichloromethane solution. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.89 (m, 1H, Ar-*H*), 8.05 (m, 4H, Ar-*H*), 7.63 (t, ${}^{3}J_{H-H} = 7.6$ Hz, 2H, Ar-*H*), 7.38-7.25 (m, 7H, Ar-*H*), 7.13 (t, ${}^{3}J_{H-H} = 7.6$ Hz, 2H, Ar-*H*), 7.02 (m, 4H, Ar-*H*), 6.51 (d, ${}^{3}J_{H-H} = 8.0$ Hz, 2H, Ar-H), 6.16 (s, 1H, Ph₂CH). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 152.5, 144.2, 141.1, 139.7, 133.9, 133.6, 133.3, 131.5, 130.5, 130.163, 130.159, 129.6, 128.1, 125.5, 123.7, 122.7 (Ar-C), 99.4 (fluorene-9C), 74.3 (Ph₂CH). ¹¹B{¹H} NMR (128 MHz, CDCl₃): δ (ppm) -0.9 (s). ¹⁹F NMR (377 MHz, CDCl₃): δ (ppm) -153.1 (s). MS (ESI) [M] $C_{32}H_{23}N_2^+$ calc. 435.1856 m/z found 435.1855 m/z.



¹H NMR spectrum of **2** (400 MHz, CDCl₃).



 $^{13}C\{^{1}H\}$ NMR spectrum of **2** (100 MHz, CDCl₃).



¹¹B $\{^{1}H\}$ NMR spectrum of **2** (128 MHz, CDCl₃).



¹⁹F NMR spectrum of 2 (377 MHz, CDCl₃).

3: THF solution of PMe₃ (0.40 mL, 1M, 0.40 mmol) was added to dichloromethane solution (3 mL) of 3 (104 mg, 0.20 mmol), and the mixture was stirred at room temperature for 30 minutes. The solution was reduced to 1 mL under vacuum, and 4 mL of *n*-pentane was added with rigorous stirring to give a precipitate. After decanting the supernatant, the precipitate was washed with *n*-pentane (4 mL \times 2) and dried under vacuum to give $3 \cdot (n-\text{pentane})_{0.25}$ as a pale green solid (118 mg, 96%) yield). Single crystals of **3** were obtained by slow diffusion of cyclohexane into a 1,2dichlorobenzene solution at room temperature. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.60-6.50 (br/m, 22H, Ar-H), 5.68 (s, 1H, Ph₂CH), 1.76 (d, ${}^{2}J_{H-P} = 12.8$ Hz, 9H, PMe₃), 1.30 (m, 1.5H, *n*-pentane-CH₂), 0.88 (t, ${}^{3}J_{H-H} = 7.2$ Hz, 1.5H, *n*-pentane-CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 148.3 (br), 143.0 (d, $J_{C-P} = 5.9$ Hz), 142.7 (br), 140.7 (br), 139.6 (br), 139.3 (br), 135.1 (d, $J_{C-P} = 2.1$ Hz), 132.1 (br), 130.4, 129.9 (br), 129.2 (br), 128.1 (br), 127.7 (br), 127.5 (br), 127.1 (br), 126.5 (br), 126.3, 125.2, 122.4 (br), 120.7 (br), 119.8 (br), 114.8 (Ar-C); 82.8 (d, $J_{C-P} = 1.2$ Hz, fluorene-9C); 73.4 (Ph₂CH); 34.2, 22.4, 14.1 (*n*-pentane-C); 11.5 (d, $J_{C-P} = 63.0$ Hz, PMe_3). ³¹P{¹H} NMR (162 MHz, CDCl₃): δ (ppm) 71.9 (s). MS (ESI) [M] C₃₅H₃₂N₂P⁺ calc. 511.2298 m/z found 511.2291 m/z.



¹H NMR spectrum of **3** (400 MHz, CDCl₃).



 $^{13}C{^{1}H}$ NMR spectrum of **3** (100 MHz, CDCl₃).



 ${}^{31}P{}^{1}H$ NMR spectrum of **3** (162 MHz, CDCl₃).

4: 2 (261 mg, 0.50 mmol) and KO*t*Bu (56 mg, 0.50 mmol) were mixed in 4 mL of toluene and the mixture was stirred at room temperature for 1 hour. The suspension was filtered. The volatiles of the filtrate were removed under vacuum, and the residue was washed with *n*-pentane (1.5 mL × 3) and dried under vacuum to give **4** as a red solid (186 mg, 86% yield). Single crystals of **4** were obtained by slow diffusion of *n*-pentane into a chloroform solution at room temperature. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.00 (d, ³*J*_{H-H} = 7.6 Hz, 2H, Ar-*H*), 7.32-7.11 (m, 13H, Ar-*H*), 6.84 (t, ³*J*_{H-H} = 7.6 Hz, 1H, Ar-*H*), 6.54 (t, ³*J*_{H-H} = 7.6 Hz, 2H, Ar-*H*), 6.45 (m, 1H, Ar-*H*), 6.20 (d, ³*J*_{H-H} = 7.2 Hz, 1H, Ar-*H*), 6.17 (d, ³*J*_{H-H} = 7.2 Hz, 2H, Ar-*H*). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 156.0, 146.7, 140.4, 136.8, 132.5, 132.1, 130.5, 129.8, 129.4, 129.1, 128.4, 127.8, 127.7, 127.0, 126.0, 124.6, 120.5, 120.2, 118.2, 110.5 (Ar-*C* and Ph₂*C*N), 90.5 (fluorene-9*C*). MS (DART) [M+H] C₃₂H₂₃N₂⁺ calc. 435.18612 m/z found 435.18582 m/z.



¹H NMR spectrum of 4 (400 MHz, CDCl₃).



 $^{13}C{^{1}H}$ NMR spectrum of 4 (100 MHz, CDCl₃).

5: 4 (44 mg, 0.10 mmol) and GaCl₃ (18 mg, 0.10 mmol) were mixed in 2 mL of toluene, the mixture was stirred at room temperature for 1 hour. The volatiles of the solution were removed under vacuum, and the residue was washed with *n*-pentane (0.5 mL × 2) and dried under vacuum to give $5 \cdot (\text{PhMe})_{0.5}(n\text{-pentane})_{0.25}$ as a red solid (56 mg, 83% yield). Single crystals of **5** were obtained by slow diffusion of *n*-pentane into a benzene solution at room temperature. ¹H NMR (500 MHz, C₆D₆): δ (ppm)

8.04 (d, ${}^{3}J_{\text{H-H}} = 7.5$ Hz, 1H, Ar-*H*), 7.64 (d, ${}^{3}J_{\text{H-H}} = 8.0$ Hz, 1H, Ar-*H*), 7.59 (br, 2H, Ar-*H*), 7.13 (m, 1H, *Ph*Me), 7.08-6.95 (m, 7.5H, Ar-*H* and *Ph*Me), 6.89 (m, 3H, Ar-*H*), 6.80 (m, 2H, Ar-*H*), 6.70 (t, ${}^{3}J_{\text{H-H}} = 7.0$ Hz, 1H, Ar-*H*), 6.59 (t, ${}^{3}J_{\text{H-H}} = 7.5$ Hz, 1H, Ar-*H*), 6.49 (td, ${}^{3}J_{\text{H-H}} = 7.5$ Hz, ${}^{4}J_{\text{H-H}} = 1.0$ Hz, 1H, Ar-*H*), 6.26 (td, ${}^{3}J_{\text{H-H}} = 7.5$ Hz, ${}^{4}J_{\text{H-H}} = 3.0$ Hz, 2H, Ar-*H*), 6.12 (d, ${}^{3}J_{\text{H-H}} = 7.5$ Hz, 1H, Ar-*H*), 5.69 (d, ${}^{3}J_{\text{H-H}} = 8.0$ Hz, 1H, Ar-*H*), 2.11 (s, 1.5H, Ph*Me*), 1.26 (m, 1.5H, *n*-pentane-C*H*₂), 0.87 (t, ${}^{3}J_{\text{H-H}} = 7.0$ Hz, 1.5H, *n*-pentane-C*H*₃). ${}^{13}C{}^{1}H{}$ NMR (126 MHz, C₆D₆): δ (ppm) 161.9, 147.6, 147.5, 143.9, 142.1, 138.5, 137.9, 137.0, 133.0, 132.7, 131.0, 130.7, 130.6, 130.1, 130.0, 129.9, 129.3, 128.6, 128.5, 128.4, 128.2, 128.0, 127.7, 127.5, 126.5, 126.0, 125.7, 123.2, 121.8, 121.1, 120.1, 113.7 (Ar-*C*, *Ph*Me and Ph₂*C*N), 88.9 (fluorene-*9C*), 34.4, 22.7, 14.3 (*n*-pentane-*C*), 21.4 (Ph*Me*).



¹H NMR spectrum of **5** (500 MHz, C_6D_6).



 $^{13}C{^{1}H}$ NMR spectrum of **5** (126 MHz, C₆D₆).

6: Dichloromethane solution (0.5 mL) of MeOTf (18 mg, 0.11 mmol) was added to dichloromethane solution (1.5 mL) of 4 (44 mg, 0.10 mmol), and the mixture was stirred at room temperature for 30 minutes. The solution was reduced to 0.5 mL under vacuum, and 3 mL of *n*-pentane was added with rigorous stirring to give a precipitate. After decanting the supernatant, the precipitate was washed with 2 mL of *n*-pentane and dried under vacuum to give $6 \cdot (CH_2Cl_2)_{0.25}$ as a pale orange solid (58 mg, 94%) yield). Single crystals of 6 were obtained by slow diffusion of *n*-pentane into a toluene solution at room temperature. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.65 (m, 3H, Ar-H), 7.56 (m, 2H, Ar-H), 7.48 (t, ${}^{3}J_{H-H} = 7.6$ Hz, 1H, Ar-H), 7.42-7.35 (m, 6H, Ar-*H*), 7.34-7.25 (m, 3H, Ar-*H*), 7.15 (t, ${}^{3}J_{H-H} = 7.6$ Hz, 1H, Ar-*H*), 7.03 (t, ${}^{3}J_{H-H} =$ 7.6 Hz, 1H, Ar-*H*), 6.75 (t, ${}^{3}J_{H-H} = 8.0$ Hz, 2H, Ar-*H*), 6.50 (d, ${}^{3}J_{H-H} = 7.6$ Hz, 1H, Ar-*H*), 6.37 (d, ${}^{3}J_{H-H} = 7.2$ Hz, 2H, Ar-*H*), 5.30 (s, 0.5H, CH₂Cl₂), 3.58 (s, 3H, NMe). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ (ppm) 169.1, 145.5, 144.4, 140.1, 135.4, 134.0, 132.0, 131.3, 131.1, 130.7, 130.3, 129.9, 129.8, 129.6, 127.3, 126.1, 125.8, 124.9, 122.6, 121.1, 112.2 (Ar-C and Ph₂CN), 89.6 (fluorene-9C), 53.6 (CH₂Cl₂), 45.8 (NMe). ¹⁹F NMR (377 MHz, CDCl₃): δ (ppm) -78.1 (s). MS (ESI) [M] C₃₃H₂₅N₂⁺ calc. 449.2012 m/z found 449.2008 m/z.



¹H NMR spectrum of **6** (400 MHz, CDCl₃).



 $^{13}C{^{1}H}$ NMR spectrum of **6** (100 MHz, CDCl₃).



¹⁹F NMR spectrum of **6** (377 MHz, $CDCl_3$).

7: Toluene solution (0.5 mL) of PhNCO (16 mg, 0.13 mmol) was added to toluene solution (1.5 mL) of **4** (54 mg, 0.12 mmol), and the mixture stood at room temperature for 30 minutes. The volatiles of the solution were removed under vacuum, and the residue was washed with 2 mL of *n*-pentane and dried under vacuum to give $7 \cdot (PhMe)_{0.5}$ as a pale solid (72 mg, 96% yield). Single crystals of 7 were obtained by slow diffusion of *n*-pentane into a toluene solution at room temperature. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.71 (d, ³*J*_{H-H} = 8.0 Hz, 1H, Ar-*H*), 7.43 (m, 2H, Ar-*H*), 7.31 (t, ³*J*_{H-H} = 7.6 Hz, 1H, Ar-*H*), 7.28-7.11 (m, 11.5H, Ar-*H* and *Ph*Me), 7.03-6.86 (m, 9H, Ar-*H*), 6.76 (t, ³*J*_{H-H} = 7.6 Hz, 4H, Ar-*H*), 6.35 (d, ³*J*_{H-H} = 7.6 Hz, 1H, Ar-*H*), 2.35 (s, 1.5H, Ph*Me*). ¹³C {¹H} NMR (100 MHz, CDCl₃): δ (ppm) 160.1, 147.3, 139.4, 139.1, 138.3, 138.0, 130.4, 129.9, 129.2, 128.6, 128.5, 128.4, 128.3, 127.69, 127.68, 127.64, 126.3, 126.2, 125.4, 121.5, 119.8, 117.2 (O=CN₂, Ar-*C* and *Ph*Me), 87.8, 80.3 (fluorene-*9C* and Ph₂CN), 21.6 (Ph*Me*). MS (ESI) [M+H] C₃₉H₂₈N₃O⁺ calc. 554.2227 m/z found 554.2223 m/z.



¹H NMR spectrum of 7 (400 MHz, CDCl₃).



 $^{13}C{^{1}H}$ NMR spectrum of 7 (100 MHz, CDCl₃).

3. Crystallographic Details

Single crystals were coated with Paratone-N oil, mounted using a glass fibre pin and frozen in the cold nitrogen stream of the goniometer. Data sets were collected on a Siemens Smart System CCD diffractometer which was equipped with a rotation anode using graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). Data reduction was performed using the Bruker SMART software package. Data sets were corrected for absorption effects using SADABS routine (empirical multi-scan method). The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with anisotropic thermal parameters for nonhydrogen atoms. Hydrogen atoms were placed at calculated positions and were included in the structure calculation. Calculations were carried out using the SHELXL-97, SHELXL-2014 or Olex2 program.^[S2]

	2	0.53·1,2-dichlorobenzene
formula	$C_{32}H_{23}N_2BF_4$	$C_{23.5}H_{20}B_{0.5}F_2NCl_2P_{0.5}$
formula Mass	522.33	446.19
color	yellow	colorless
cryst system	Orthorhombic	Triclinic
space group	$P2_{1}2_{1}2_{1}$	$P\bar{1}$
<i>a</i> , Å	9.9397(16)	10.6050(13)
b, Å	12.0611(19)	10.7240(12)
<i>c</i> , Å	21.140(3)	18.967(2)
α , deg	90.00	89.741(4)
β , deg	90.00	87.191(4)
γ, deg	90.00	87.511(4)
<i>V</i> , Å ³	2534.3(7)	2152.5(4)
Z	4	4
$D_{\text{calcd}}, (\text{mg/m}^3)$	1.369	1.377
<i>F</i> (000)	1080	920
<i>T</i> (K)	150(2)	150(2)
θ range, deg	2.264 to 25.359	1.075 to 27.199
no. of reflns measured	10881	31682
no. of independent reflns	4592	9505
no. of obsd reflns $(I > 2\sigma(I))$	3221	6785
No. of params	352	535
final R_I , wR (I > 2 σ (I))	0.0445, 0.0725	0.0492, 0.1143
goodness of fit on F^2	0.989	1.012
$\Delta \rho_{max, min}, e \text{Å}^{-3}$	0.167, -0.182	0.628, -0.626

 Table S1 Crystallographic data and refinement parameters for 2-7.

	4	$5 \cdot 0.5n$ -pentane
formula	$C_{32}H_{22}N_2$	$C_{37.5}H_{31}N_2GaCl_3$
formula Mass	434.51	685.71
color	red	red
cryst system	Monoclinic	Triclinic
space group	$P2_{1}/c$	PĪ
<i>a</i> , Å	13.2204(15)	10.1320(16)
b, Å	10.9447(12)	11.6757(18)
<i>c</i> , Å	17.0214(18)	15.355(2)
a, deg	90.00	85.260(4)
β , deg	112.336(3)	78.703(4)
γ, deg	90.00	68.857(5)
<i>V</i> , Å ³	2278.1(4)	1661.2(4)
Z	4	2
$D_{\text{calcd}}, (\text{mg/m}^3)$	1.267	1.371
<i>F</i> (000)	912	704
<i>T</i> (K)	150(2)	150(2)
θ range, deg	2.266 to 30.998	3.963 to 27.103
no. of reflns measured	21404	35986
no. of independent reflns	7238	7277
no. of obsd reflns $(I > 2\sigma(I))$	5524	5641
No. of params	307	415
final R_1 , wR (I > 2 σ (I))	0.0527, 0.1302	0.0367, 0.0874
goodness of fit on F^2	1.017	1.027
$\Delta \rho_{max, min}, e Å^{-3}$	0.485, -0.339	0.617, -0.426

	6	7
formula	$C_{34}H_{25}N_2O_3F_3$	C ₃₉ H ₂₇ N ₃ O
formula Mass	598.62	553.63
color	colorless	colorless
cryst system	Monoclinic	Monoclinic
space group	$P2_{1}/c$	$P2_{1}/c$
<i>a</i> , Å	8.4490(6)	16.697(4)
b, Å	17.2112(9)	9.825(2)
<i>c</i> , Å	19.6802(11)	16.948(4)
α , deg	90.00	90.00
β , deg	91.062(3)	91.627(8)
γ, deg	90.00	90.00
<i>V</i> , Å ³	2861.4(3)	2779.0(10)
Z	4	4
$D_{\text{calcd}}, (\text{mg/m}^3)$	1.390	1.323
<i>F</i> (000)	1240	1160
<i>T</i> (K)	150(2)	150(2)
θ range, deg	2.686 to 26.373	2.396 to 27.106
no. of reflns measured	17762	16132
no. of independent reflns	5831	5688
no. of obsd reflns $(I > 2\sigma(I))$	3271	3948
No. of params	389	388
final R_I , wR (I > 2 σ (I))	0.0606 0.1262	0.0440, 0.0879
goodness of fit on F^2	1.004	1.012
$\Delta \rho_{max, min}, e Å^{-3}$	0.606, -0.532	0.212, -0.244

4. Computational Details

Calculations were carried out with the Gaussian 09 package.^[S3] Optimizations of the structures with frequency calculations were carried out with the M06-2X functional^[S4] with SVP basis set for all atoms, using crystallographic coordinates as the starting geometry. Natural bond orbital (NBO) calculations were carried out using NBO 5.9 program^[S5] at the M06-2X/TZVP level of theory.



Fig. S1 HOMO of 2.

2	٠
4	٠

7	0.337273	-0.498300	0.503304
7	0.687941	-1.079359	1.542411
6	-1.590299	-1.326955	1.409472
6	-0.443601	-1.616472	2.159875
6	-1.364696	-1.187866	-1.154247
6	-1.893734	-0.235450	-2.039859
6	-2.089369	1.033910	-1.312353
6	-1.143585	-0.549754	0.213258
6	2.599613	-0.498446	-0.483532
6	-1.694806	0.858446	0.021939
6	1.345945	1.689270	0.122482
6	1.287206	0.253119	-0.366775
1	0.789142	0.247914	-1.347216

6	-0.471273	-2.340794	3.351693
1	0.444132	-2.547973	3.905694
6	-2.575897	2.269990	-1.731466
1	-2.889961	2.428283	-2.764175
6	-2.150683	-0.591862	-3.360966
1	-2.565610	0.129934	-4.065987
6	-1.094333	-2.490268	-1.545427
1	-0.692938	-3.223338	-0.841338
6	-1.873764	-1.900149	-3.767063
1	-2.073322	-2.193640	-4.798462
6	-1.793200	1.874569	0.960540
1	-1.488089	1.721578	1.997865
6	2.627213	-1.640943	-1.292950
1	1.725819	-1.946095	-1.832902
6	1.567400	1.994887	1.468783
1	1.726860	1.195712	2.197573
6	-2.281099	3.112049	0.534558
1	-2.365913	3.933151	1.246893
6	1.145766	2.719665	-0.798188
1	0.964661	2.483048	-1.849417
6	-1.355141	-2.841509	-2.874238
1	-1.158843	-3.858916	-3.213767
6	-2.833003	-1.764249	1.836999
1	-3.739449	-1.550718	1.269315
6	1.375230	4.351169	0.967465
1	1.384238	5.390456	1.298683
6	1.581069	3.323715	1.888738
1	1.755335	3.557629	2.939849
6	-1.721933	-2.775147	3.778310

1	-1.809171	-3.345517	4.703242
6	3.759611	-0.090849	0.175391
1	3.759735	0.812858	0.785137
6	-2.877772	-2.490246	3.033093
1	-3.841295	-2.847900	3.399481
6	-2.660152	3.304980	-0.797537
1	-3.038265	4.279009	-1.110961
6	1.164057	4.047815	-0.376906
1	1.006627	4.847260	-1.101993
6	3.798840	-2.378909	-1.426878
1	3.814616	-3.264288	-2.063580
6	4.934245	-0.830945	0.036870
1	5.839760	-0.505268	0.550096
6	4.955191	-1.974765	-0.757566
1	5.877172	-2.547600	-0.865116

4:

7	-0.547010	1.041065	-0.070370
7	-0.759237	2.346450	-0.102534
6	1.370688	0.006923	1.243779
6	-1.141532	-1.322297	-0.060780
6	1.432139	-0.268533	-1.107492
6	2.096850	-1.155935	0.950915
6	-1.511424	0.127556	-0.027596
6	0.950158	0.696604	-0.041707
6	0.457778	2.972441	-0.174540
6	2.127939	-1.332309	-0.512140
6	-0.899228	-2.043813	1.111723
1	-0.926081	-1.530031	2.074553
			S21

6	1.535266	2.077024	-0.170312
6	1.139327	0.414666	2.548103
1	0.578055	1.329081	2.754366
6	-2.949158	0.450958	0.007977
6	1.306048	-0.163766	-2.483926
1	0.783815	0.684020	-2.933133
6	-0.610074	-3.407708	1.053078
1	-0.407768	-3.955071	1.975116
6	-1.139699	-1.999208	-1.288423
1	-1.363437	-1.443875	-2.201263
6	2.677599	-2.337044	-1.304578
1	3.210506	-3.175576	-0.852916
6	1.848919	-1.179245	-3.275242
1	1.752005	-1.130246	-4.360765
6	2.848449	2.501619	-0.253506
1	3.669382	1.780885	-0.249488
6	1.630639	-0.384733	3.584299
1	1.455248	-0.096030	4.621515
6	2.598097	-1.941926	1.985101
1	3.158618	-2.854069	1.773190
6	0.699995	4.349865	-0.259596
1	-0.132405	5.053061	-0.264368
6	-0.575492	-4.063780	-0.175166
1	-0.346321	-5.129872	-0.219113
6	-0.850507	-3.358611	-1.348804
1	-0.836802	-3.868888	-2.313013
6	3.093204	3.876988	-0.341490
1	4.117028	4.244992	-0.409388
6	2.351595	-1.549558	3.302674

1	2.730184	-2.158135	4.125330
6	2.522157	-2.255857	-2.689618
1	2.939245	-3.037922	-3.325862
6	2.023502	4.779569	-0.342115
1	2.229290	5.849328	-0.411262
6	-3.861640	-0.629401	0.093969
1	-3.491166	-1.652384	0.136859
6	-5.233387	-0.422239	0.128916
1	-5.901492	-1.282342	0.195413
6	-3.496759	1.752948	-0.038140
1	-2.831515	2.605045	-0.101484
6	-5.755146	0.871126	0.078484
1	-6.833543	1.034764	0.103995
6	-4.876946	1.946789	-0.004388
1	-5.265274	2.965973	-0.044701

5. References:

- S1. G. Baum and H. Shechter, J. Org. Chem, 1976, 41, 2120-2124.
- S2. (a) G. M. Sheldrick, SADABS, An Empirical Absorption Correction Program for Area Detector Data; University of Göttingen, Göttingen, Germany, 1996; (b) G.
 M. Sheldrick, SHELXS-97 and SHELXL-97, University of Göttingen, Göttingen, Germany, 1997 and 2008; (c) G. M. Sheldrick, SHELXL-2014, University of Göttingen, Göttingen, German, 2014; (d) O. V. Dolomanov, L. J. Bourhis, R. J.
 Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program, J. Appl. Cryst., 2009, 42, 339-341; (e) SMART Version 5.628, Bruker AXS Inc., Madison, WI, 2002; (f) SAINT+ Version 6.22a, Bruker AXS Inc., Madison, WI, 2002; (g) SAINT+ Version v7.68A, Bruker AXS Inc., Madison, WI, 2009; (h) SHELXTL NT/2000, Version 6.1, Bruker AXS Inc., Madison, WI, 2002.
- M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford, CT, USA, 2009.
- S4. Y. Zhao and D. G. Truhlar, Theoretical Chemistry Accounts, 2007, 120, 215-224.
- S5. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann,C. M. Morales, F. Weinhold, Theoretical Chemistry Institute; University of

Wisconsin: Madison, WI, 2009.