Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Photo electron transfer induced desilylation of N,N-bis(trimethylsilyl)aminodibenzoborole and photodimerization of aminodibenzoborole

Constanze Keck,[a] Cäcilia Maichle-Mössmer [b] and Holger F. Bettinger [*a]

Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

Institut für Anorganische Chemie, Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

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I. Experimental and Computational Details

General procedures. All experiments were performed under anhydrous conditions using argon as protective gas. All commercially available compounds and dry solvents were purchased. ^{1}H, ^{13}C and ^{29}Si NMR spectra were referenced to tetramethylsilane, ^{11}B NMR spectra were referenced externally to BF_3•OEt_2. ^{1}H and ^{13}C spectra were calibrated to residual solvent signals. NMR spectra were recorded on Bruker AVIII HDX+600, Bruker AVIII HDX+700 and on Bruker Avance III+ 400 spectrometers. Due to the quadrupole moment, carbon atoms bound to boron could not be detected. For HR-EI-MS measurements a sector field spectrometer MAT95 (Finnigan MAT) was used. UV-Vis spectra were recorded on a Lambda 1050 spectrometer from PerkinElmer. Single crystal x-ray diffraction was performed on a Bruker Apex II diffractometer using Mo K_α radiation. For irradiation experiments a low pressure mercury lamp from Pen-Ray UVP (3SC-9 series) or a high pressure mercury lamp from Newport (500 W, dichroic mirror from 280-400 nm) were used. 9-Chloro-9-borafluorene was synthesized as described in the literature.[1]

Syntheses.

Compound 2. 9-Chloro-9-borafluorene (73 mg, 0.37 mmol) and KHMDS (78 mg, 0.39 mmol) were dissolved in 15 mL benzene. The bright yellow solution turned into yellowish green within a minute and a colorless precipitation was formed. After removal of the solvent, the dried residue was sublimed under vacuum at 95 °C. The product was obtained as a light yellow solid (82 mg, 69%). ^{1}H (400 MHz, CD_2Cl_2): 0.34 (s, 18 H), 7.11-7.15 (ddd, 2 H, J= 0.96, 7.17, 7.34 Hz), 7.27–7.31 (ddd, 2H, J=1.17, 7.45, 7.51 Hz), 7.42-7.44 (d, 2H, J=7.45 Hz), 7.61-7.63 (d, 2H, J=7.16 Hz) ppm; ^{13}C (100 MHz, CD_2Cl_2): 4.6, 119.5, 127.8, 132.3, 133.6, 152.9 ppm; ^{11}B (128 MHz, CD_2Cl_2): 53.3 ppm; ^{29}Si (80 MHz, CD_2Cl_2): 3.5 ppm (dezett, J=6.6 Hz); HR-EI-MS: calc. 323.169 Da, found 323.168 Da.

Attempted desilylation of compound 2 with CsF. 9-Bis(trimethylsilyl)amino-9-borafuorene **2** and 1, 2, 3, or 5 equivalents of cesium fluoride were dissolved in CD_2Cl_2. The mixture was shaken occasionally within the next days.

In another experiment, **2** and an excess of cesium fluoride were mixed in CD_2Cl_2 and heated to 40 °C for 2.5 hours.

Irradiation of compound 2. In a typical irradiation experiment 9-bis(trimethylsilyl)amino-9-borafluorene (5mg, 0.015 mmol) was dissolved in 1.5 mL DCM and irradiated at λ = 254 nm. If compound **3** and **4** should be obtained, irradiation was terminated after 40 minutes and four charges were combined. At 80 °C, 9-bis(trimethylsilyl)amino-9-borafluorene (compound **2**) and 9- trimethylsilylamino-9-borafluorene (compound **3**) sublime, at 125 °C 9-amino-9-borafluorene (compound **4**) sublimes. In both cases a colorless film was formed at the cold finger.

Independent synthesis of compound 3. 9-Chloro-9-borafluorene (5 mg, 0.025 mmol) was dissolved in 1.5 mL hexane-d14 and bis(trimethylsilyl)amine (5 µl, 0.025 mmol) was added. The bright yellow solution was shaken occasionally within the next hour and became colorless. NMR spectra were directly recorded. ^{1}H (600 MHz, n-hexane d-14): 0.41 (s, 9H), 4.41 (bs, 1H), 7.03-7.07 (m, 2H), 7.20 – 7.22 (ddd, 2H, J=2.25, 7.54, 8.47 Hz), 7.29-7.30 (d, 1H, J=6.90 Hz), 7.39-7.41 (d, 1H, J=7.44 Hz), 7.43-7.44 (d, 1H, J=7.37 Hz), 7.63-7.64 (d, 1H, J=7.14 Hz) ppm; ^{13}C (150 MHz, n-hexane d-14): 4.4, 120.7, 121.1, 128.5, 128.7, 130.1, 132.8, 133.0, 134.4, 153.4, 155.5 ppm; ^{11}B (193 MHz, n-hexane d-14): 44.8 ppm; ^{29}Si (80 MHz, n-hexane d-14) 6.5 ppm (dezett, J=6.6 Hz); HR-EI-MS: calc. 251.129 Da, found 251.128 Da.

Compound 4. ^{1}H (700 MHz, CD_2Cl_2): 4.65 (bs, 2H), 7.15-7.17 (ddd, 2H, J=0.91, 7.21, 7.81 Hz), 7.32-7.35 (ddd, 2H, J=1.19, 7.24, 7.53 Hz), 7.50-7.51 (d, 2H, J=7.00 Hz), 7.52-7.53 (d, 2H, J=7.50 Hz) ppm; ^{13}C (176 MHz, CD_2Cl_2): 119.9, 127.7, 130.3, 131.8, 152.4 ppm; ^{11}B (128 MHz, CD_2Cl_2): 41.2 ppm; HR-EI-MS: calc. 179.090 Da, found 179.091 Da.

Compound 6. Irradiation of compound **2** until the defined endpoint of irradiation produces compound **6**. ^{1}H (400 MHz, CD_2Cl_2): 4.29 (bs, 2H), 7.16-7.20 (m, 2H), 7.25-7.29 (m, 2H), 7.51-7.53 (d, 2H, J=6.90 Hz), 7.57-7.59 (d, 2H, J=7.50 Hz) ppm; ^{13}C (176 MHz, CD_2Cl_2): 119.9, 127.6, 129.1, 129.7, 148.5 ppm; ^{11}B (128 MHz, CD_2Cl_2): 1.0 ppm.

Compound 8. Aniline (17 mL, 186.19 mmol) was dissolved in 100 mL THF and the colorless solution was cooled to -78 °C. During the addition of n-Butyllithium (150 mL, 375 mmol) within 50 minutes, the reaction mixture became a colorless suspension. After stirring the suspension for additional two hours at -78 °C, trimethylsilylchloride (48 mL, 378 mmol) was added within 30 minutes. The suspension turned in between into a solution, but became a light yellow suspension at the end of the addition of trimethylsilylchloride. The suspension was allowed to warm up overnight. Stirring was ceased and a colorless precipitation settled. The supernatant was transferred and fractionally distilled. At 85 °C, the product was obtained as a colorless liquid (32.92 g, 74%). ^{1}H (400 MHz, CD_2Cl_2): 0.08-0.09 (bm, 18H), 6.92-6.94 (m, 2H), 7.07-7.09 (m, 1H), 7.20-7.24 (m, 2H) ppm; ^{13}C (100 MHz, CD_2Cl_2): 2.2, 123.9, 128.8, 130.7, 148.5 ppm; ^{29}Si (80 MHz, CD_2Cl_2): 4.5 ppm.

Computational Methods

The structures of stationary points were optimized using the B3LYP[2, 3] functional as implemented[4] in Gaussian 09[5] in conjunction with the 6-311+G** basis set.[6] The effects of the dichloromethane solvent were takin into account using the polarizable continuum model

(PCM) implemented in Gaussian. Harmonic vibrational frequencies were computed to verify that the optimized structures are minima and to obtain Gibbs energies using the conventional approximations. For the computation of the ionization potentials, the spin-unrestricted ansatz was used for the radical ions.

NMR spectra.

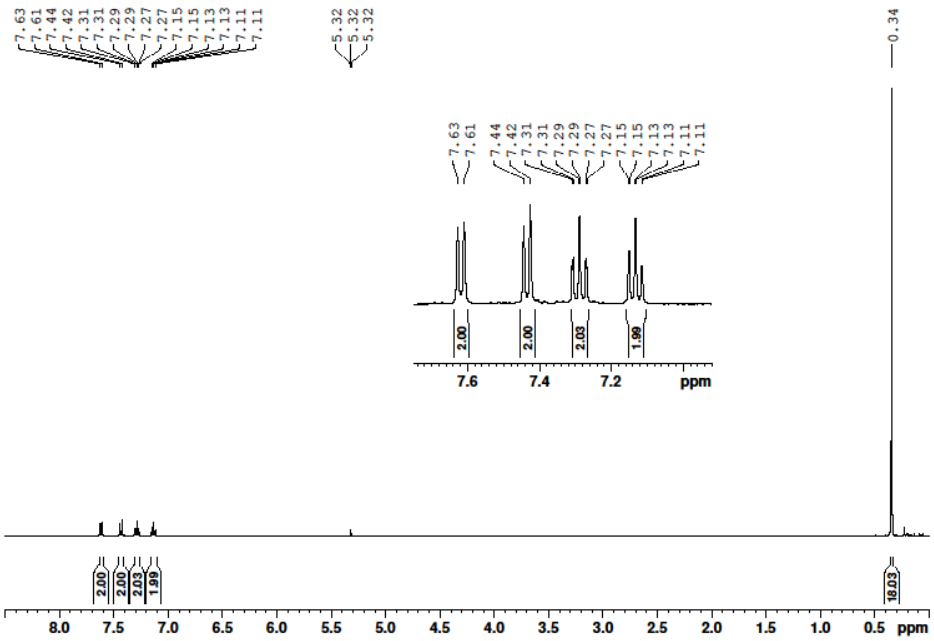

Fig S1. ^{1}H NMR (400 MHz, CD_2Cl_2) of compound **2**.

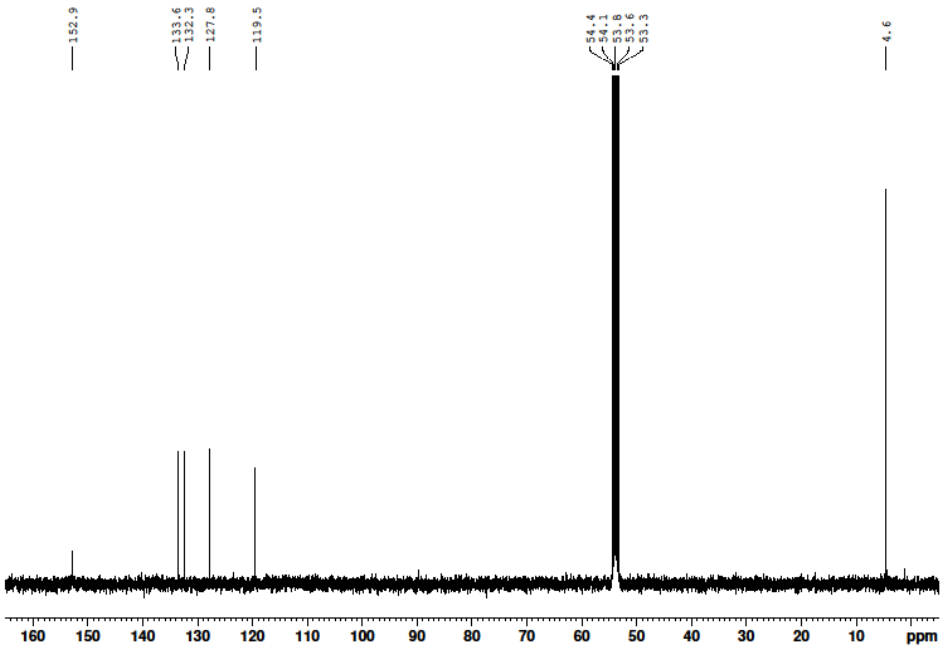

Fig S2. ^{13}C NMR (100 MHz, CD_2Cl_2) of compound **2**.

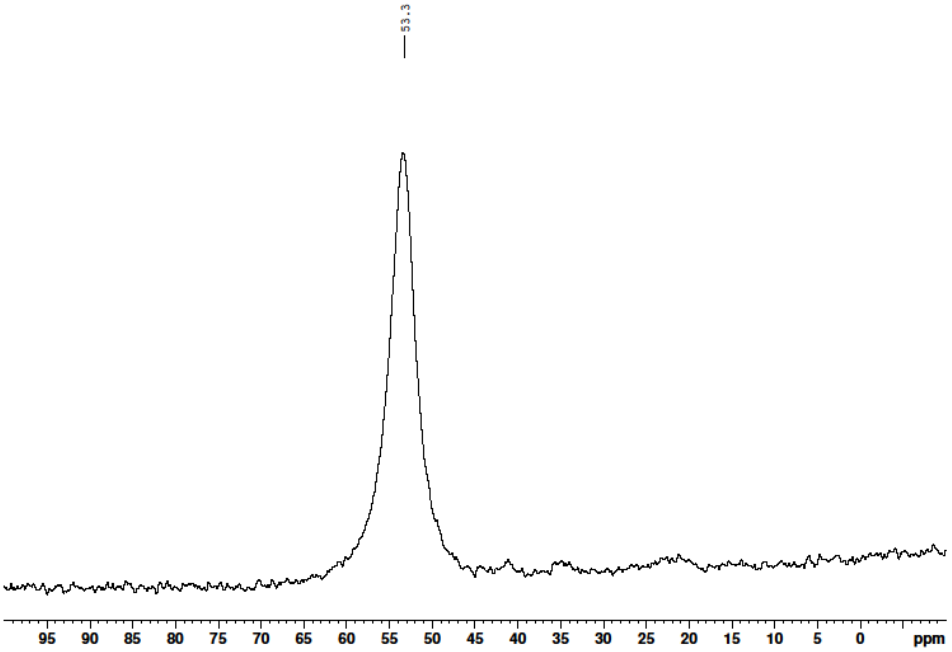

Fig S3. ^{11}B NMR (128 MHz, CD_2Cl_2) of compound **2**.

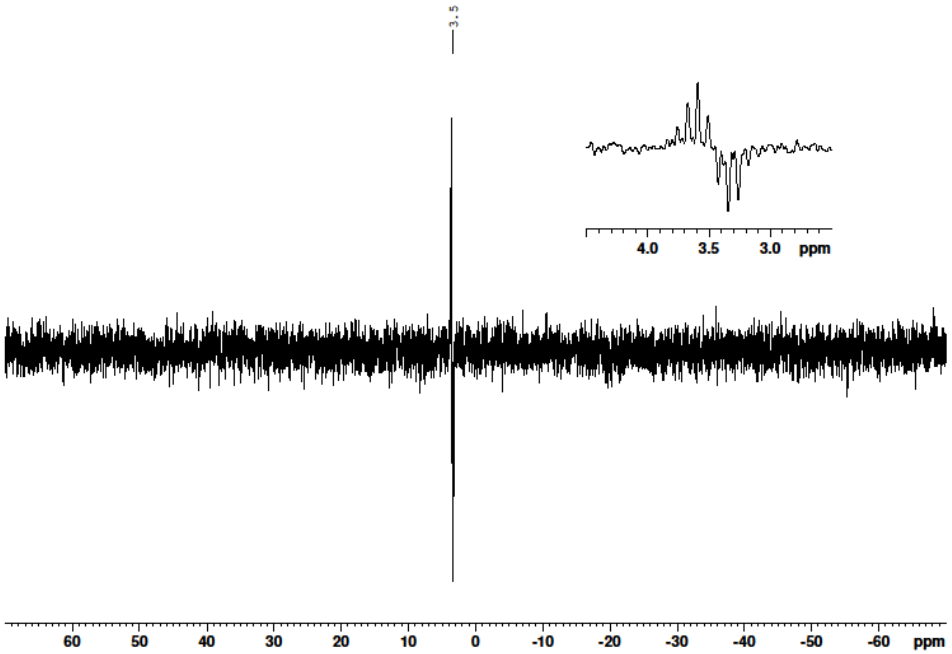

Fig S4. ^{29}Si INEPT NMR (80 MHz, CD_2Cl_2) of compound **2**.

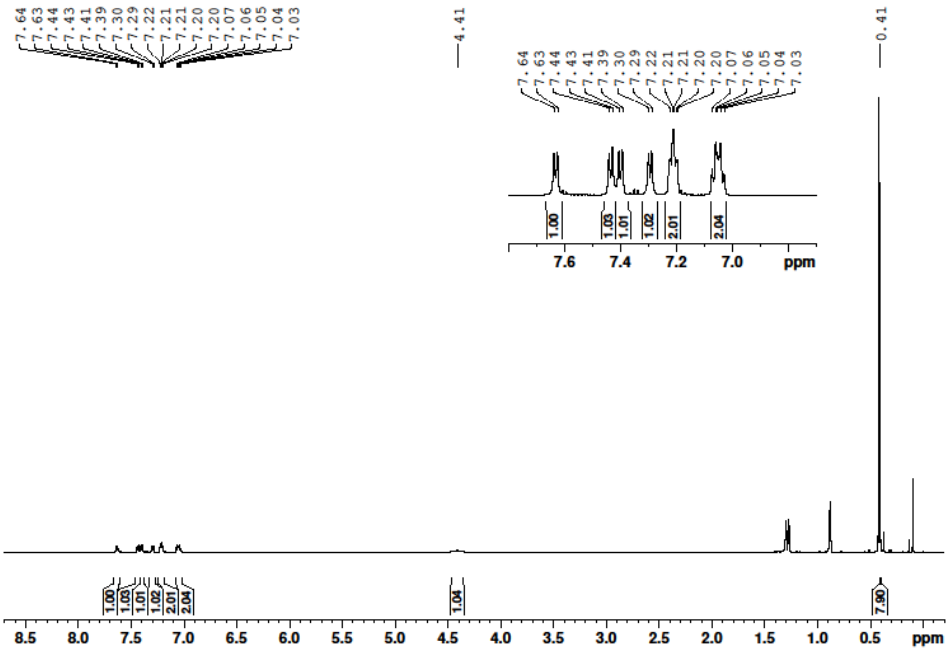

Fig S5. ^{1}H NMR (600 MHz, n-Hex-d_{14}) of compound **3**.

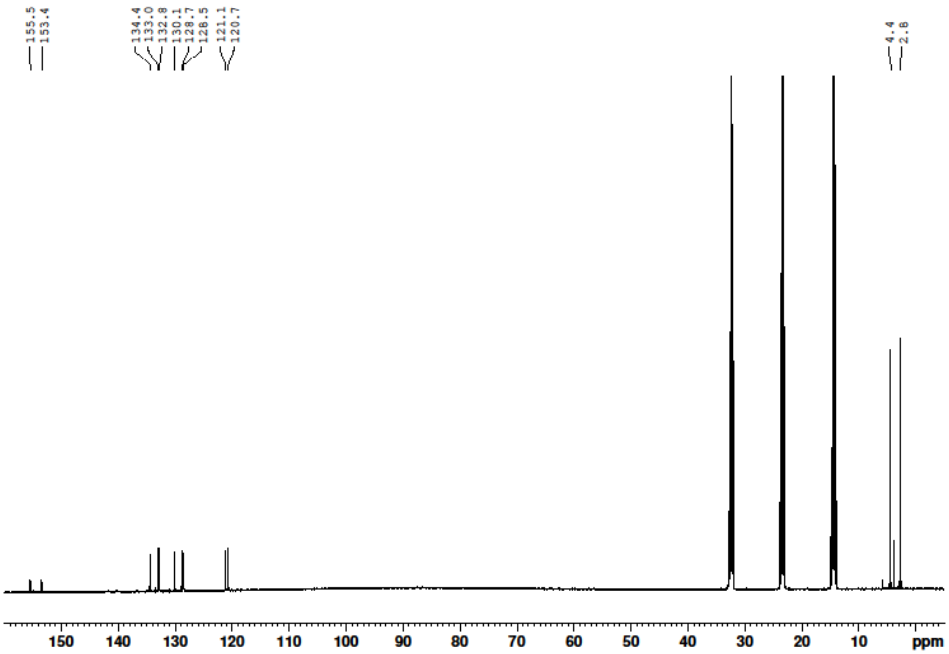

Fig S6. ^{13}C NMR (150 MHz, n-Hex-d_{14}) of compound **3**.

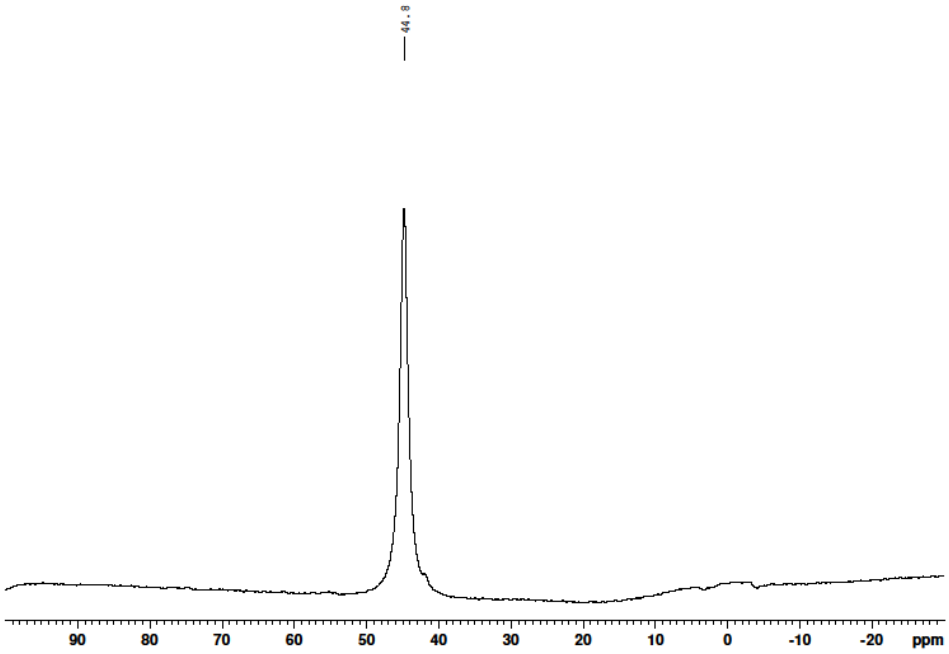

Fig S7. ^{11}B NMR (193 MHz, n-Hex-d_{14}) of compound **3**.

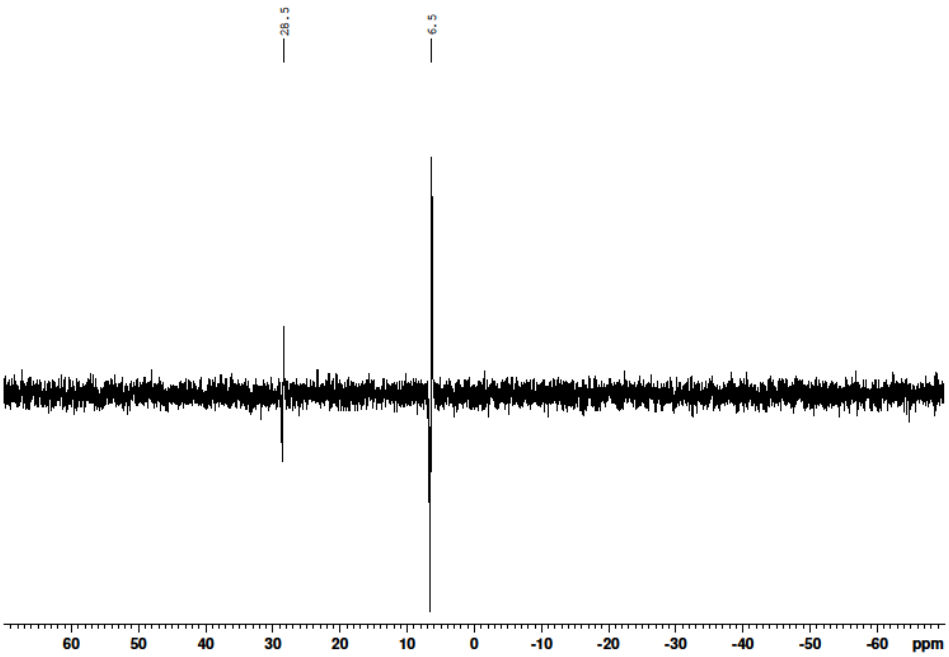

Fig S8. ^{29}Si INEPT NMR (79 MHz, n-Hex-d_{14}) of compound **3**.

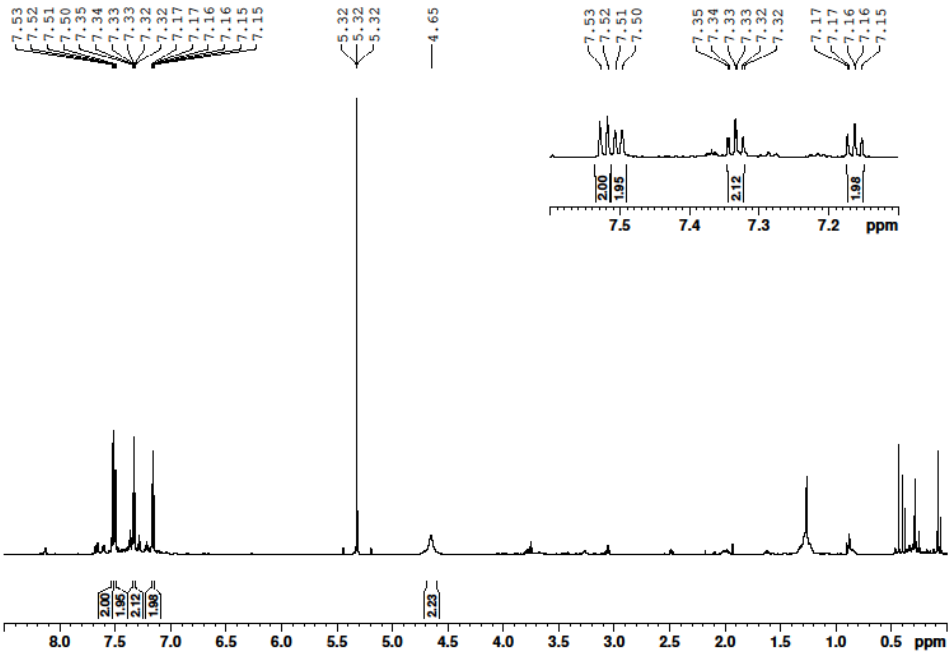

Fig S9. ^{1}H NMR (700 MHZ, CD_2Cl_2) of compound **4**.

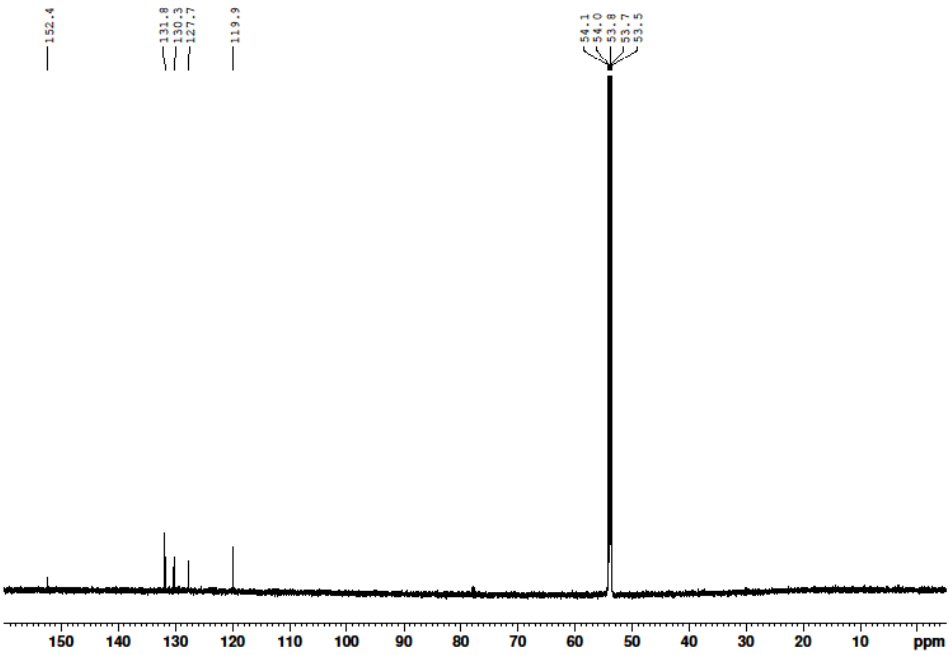

Fig S10. ^{13}C NMR (176 MHZ, CD_2Cl_2) of compound **4**.

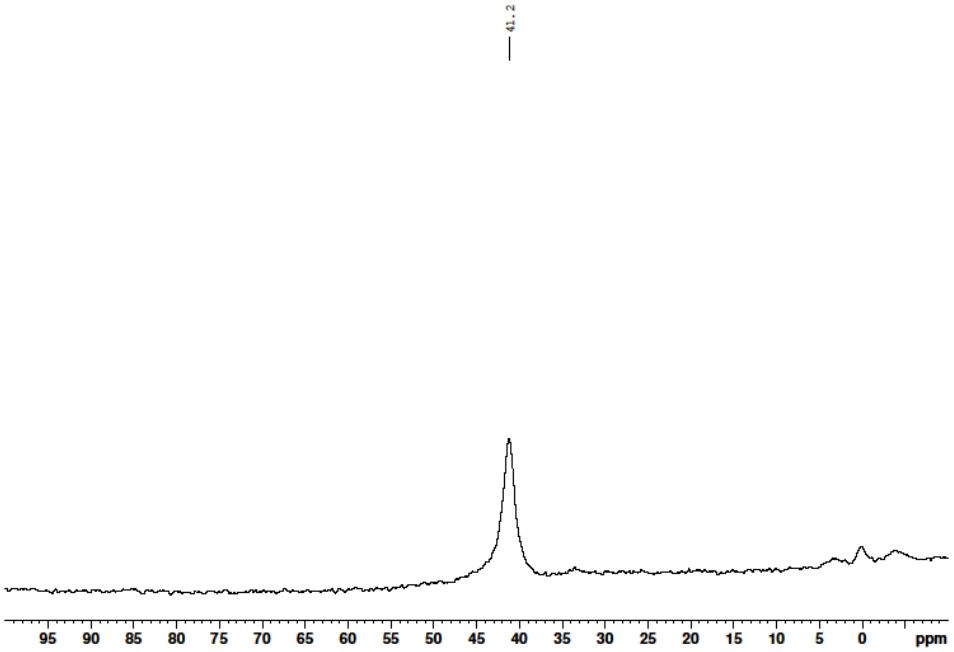

Fig S11. ^{11}B NMR (128 MHZ, CD_2Cl_2) of compound **4**.

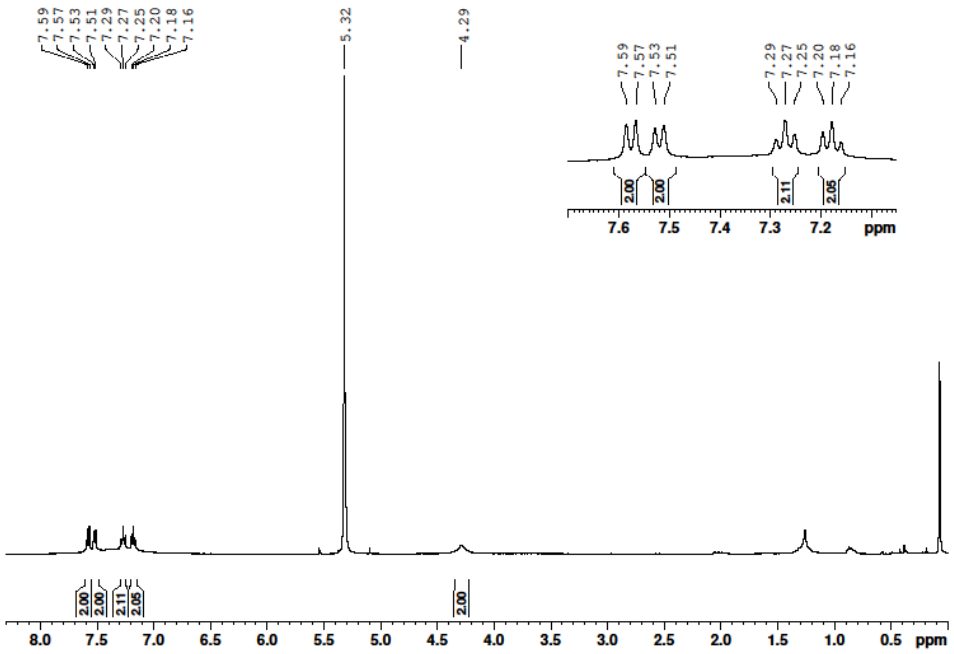

Fig S12. ^{1}H NMR (400 MHz, CD_2Cl_2) of compound **6**.

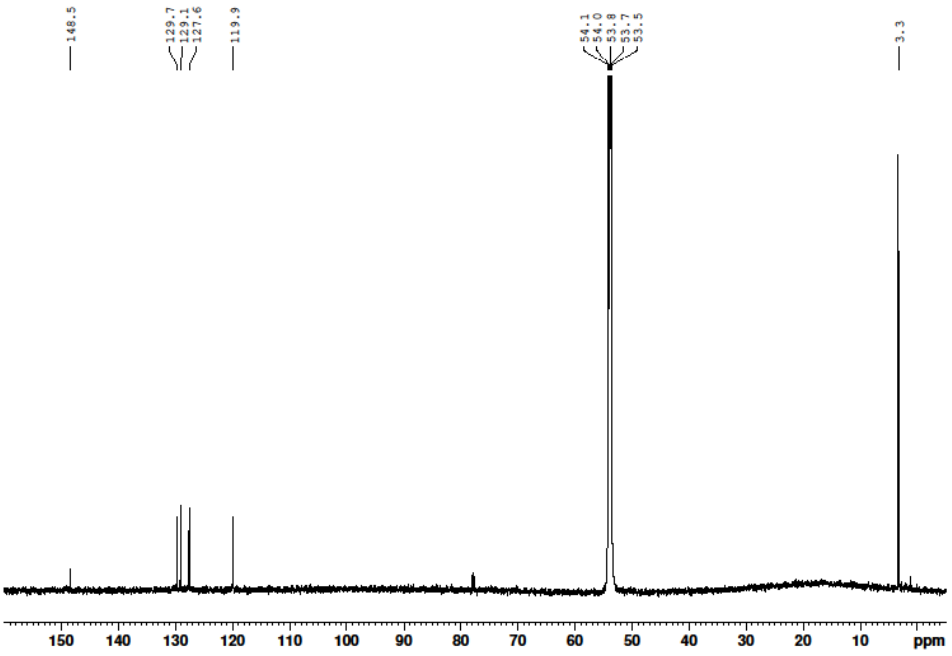

Fig S13. ^{13}C NMR (176 MHz, CD_2Cl_2) of compound **6**.

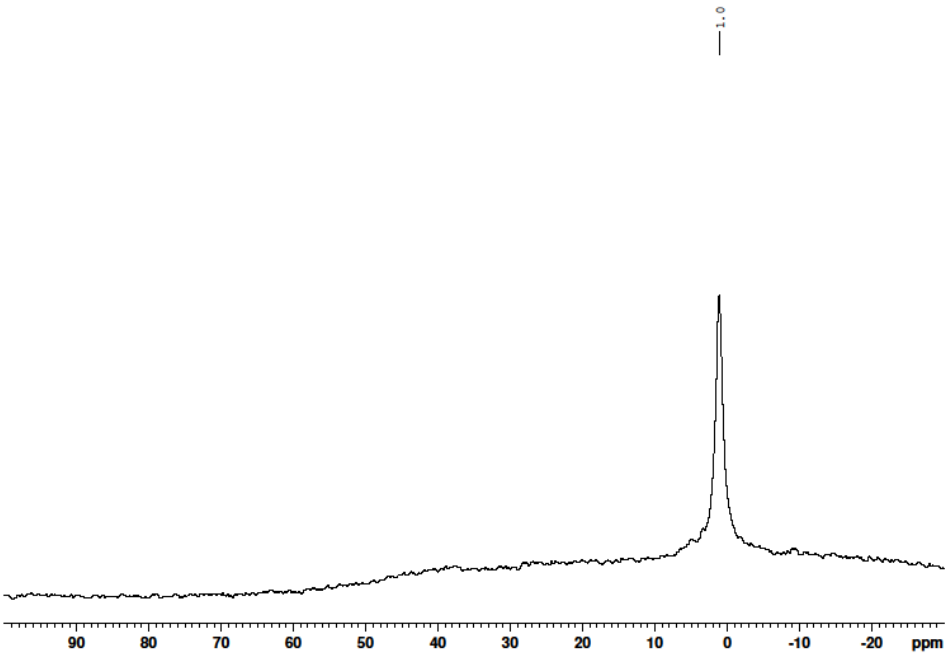

Fig S14. ^{11}B NMR (128 MHz, CD_2Cl_2) of compound **6**.

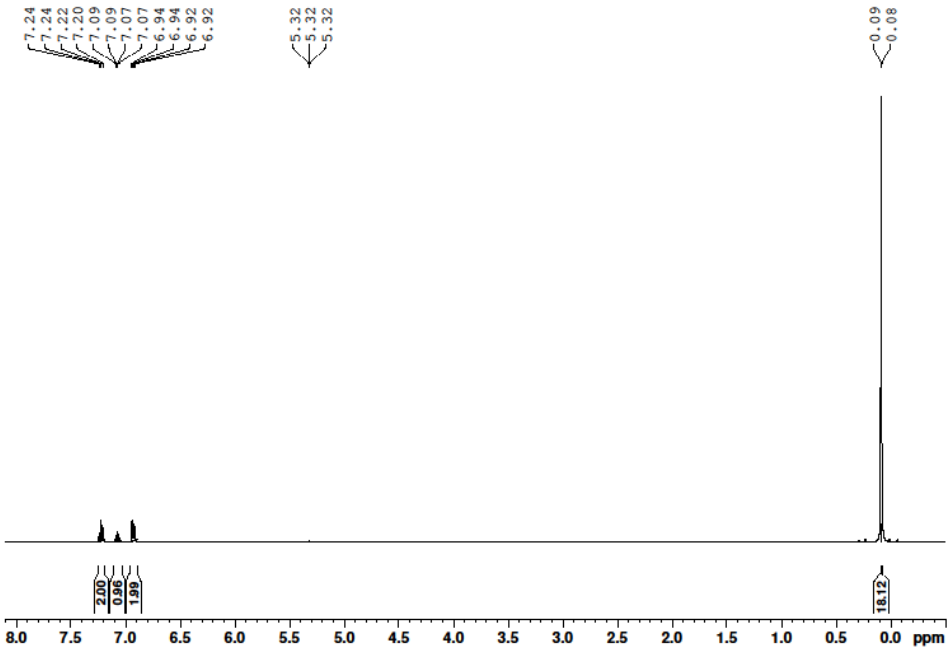

Fig S15. ^{1}H NMR (400 MHz, CD_2Cl_2) of compound **8**.

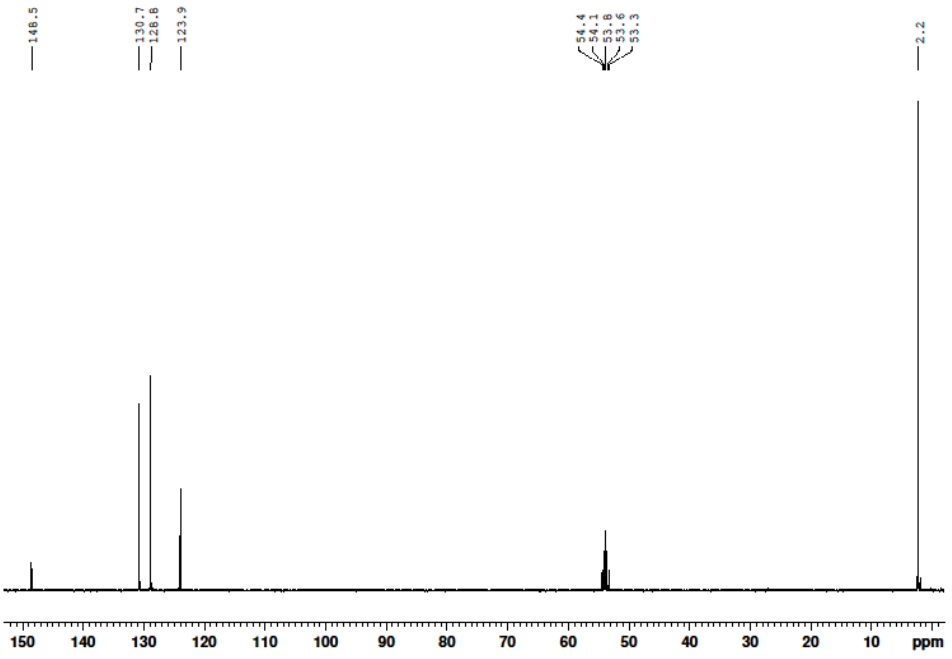

Fig S16. ^{13}C NMR (100 MHz, CD_2Cl_2) of compound **8**.

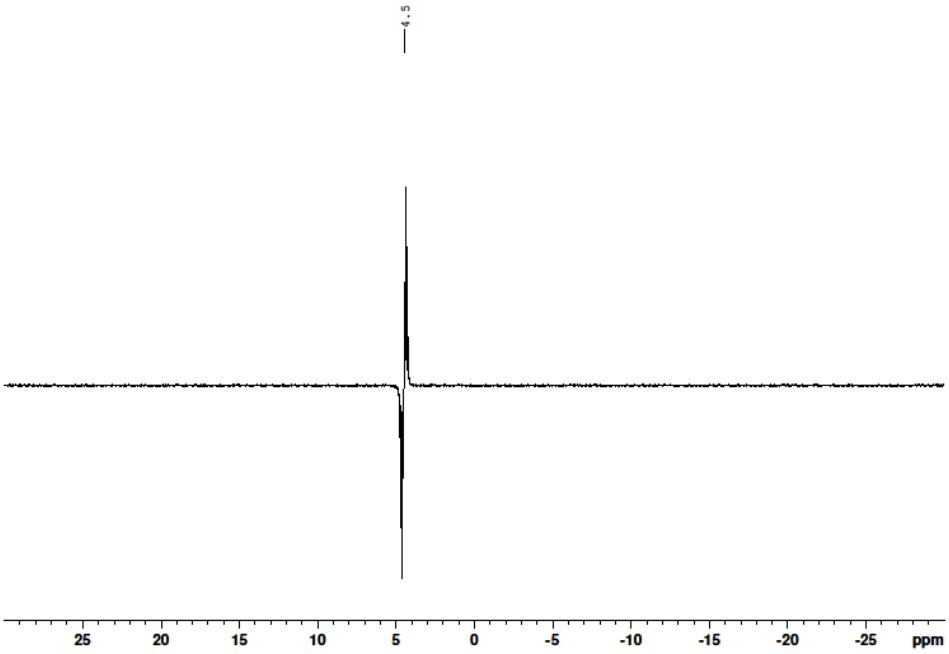

Fig S17. ^{29}Si INEPT NMR (80 MHz, CD_2Cl_2) of compound **8**.

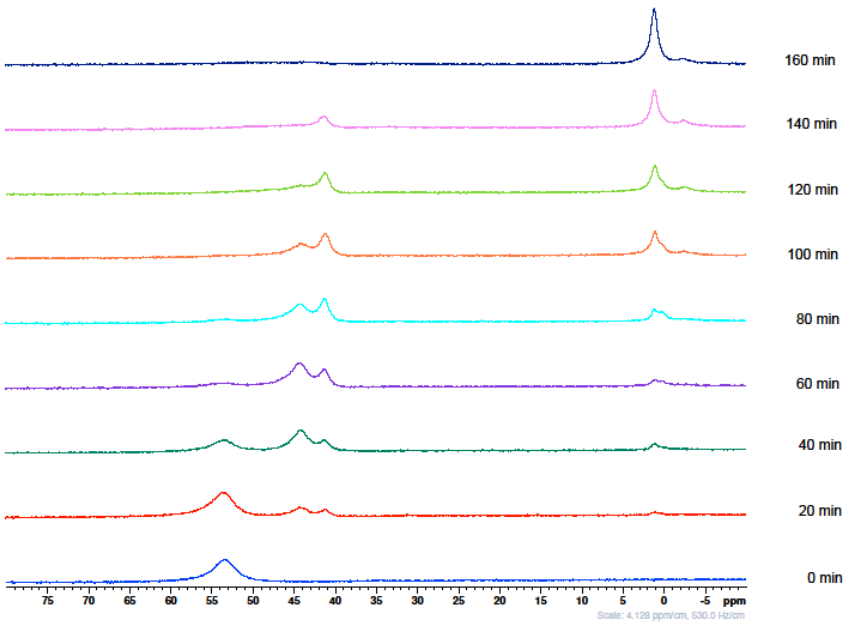

Fig S18. Changes in the ^{11}B NMR (128 MHz) during irradiation of compound **2** at λ = 254 nm.

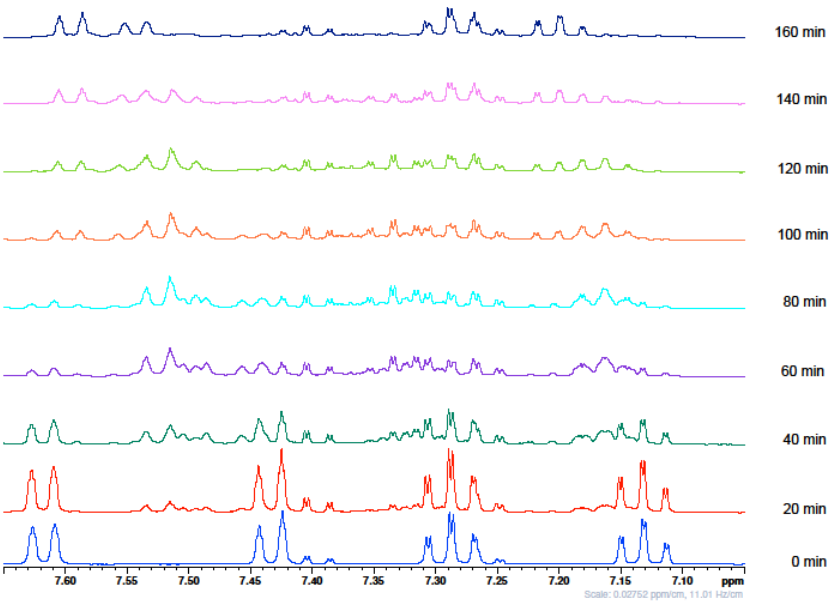

Fig S19. Changes in the ^{1}H NMR (400 MHz) in the aromatic region during Irradiation of compound **2** at λ = 254 nm.

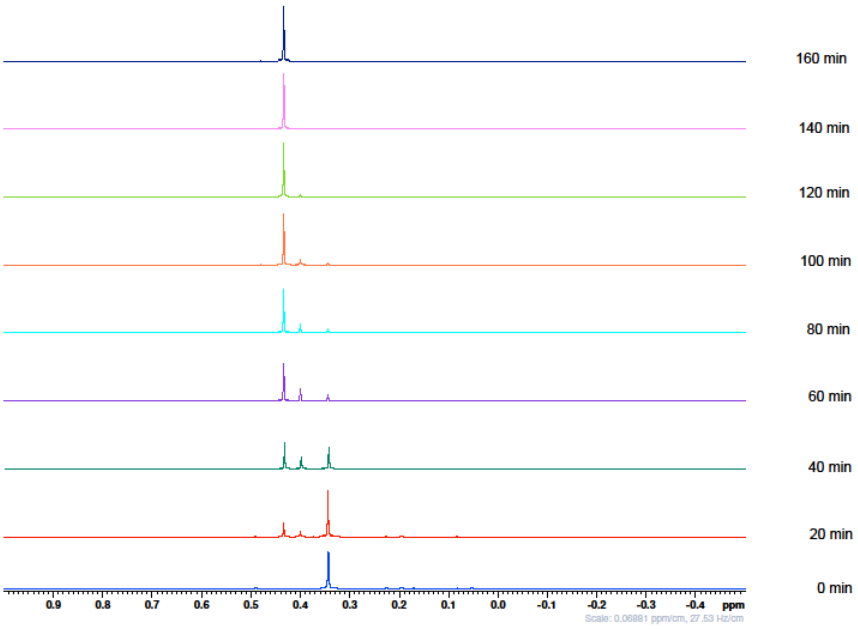

Fig S20. Changes in the ^{1}H NMR (400 MHz) in the aliphatic region during irradiation of compound **2** at λ = 254 nm.

UV-Vis Spectrum.

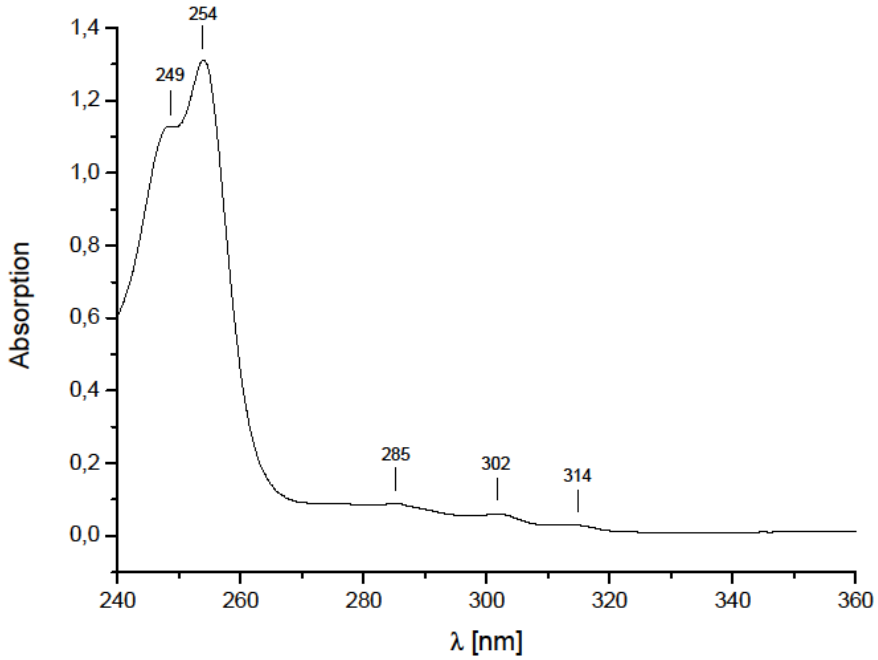

Fig S21. UV-Vis spectrum of compound **2** in DCM.

III. X-Ray Crystallography

Single crystals of compound **2** were obtained by sublimation at 80 °C in an oil pump vacuum. Data for **2** were collected on a Bruker APEX DUO instrument equipped with an IμS microfocus sealed tube and QUAZAR optics for MoK_α radiation (λ = 0.71073 Å). The data collection strategy was determined using COSMO[7] employing ω-scans. Raw data were processed using APEX[8] and SAINT,[9] corrections for absorption effects were applied using SADABS.[10] The structure was solved by direct methods and refined against all data by full-matrix least-squares methods on F^2 using SHELXTL[11] and Shelxle.[12]

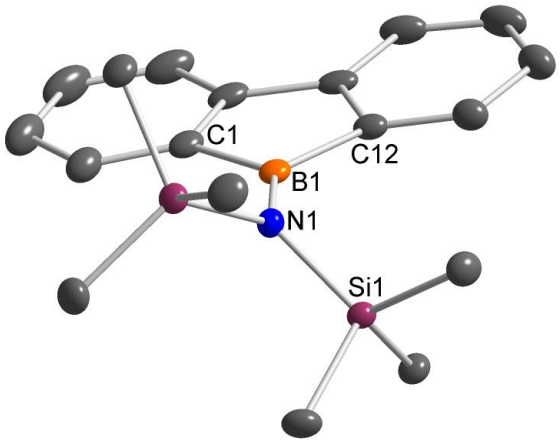

Fig S22. Molecular structure of **2** in the solid state. Anisotropic displacement parameters are depicted at the 50 % probability level. Hydrogen atoms bonded to carbon atoms are omitted for clarity. Selected bond lengths [in Å] and angles [in °]: B1-N1 1.429(1), B1-C1 1.589(2), B1-C12 1.594(2), C1-B1-C12 102.5(7), C12-B1-N1 128.2(7), C12-B1-N1-Si1 43.5(1)

Crystal Data and Structure Refinement of Compound 2

Empirical formula	$C_{18}H_{26}BNSi_2$	
CCDC	1913727	
Formula weight	323.39	
Temperature [K]	101(2)	
Crystal system	orthorhombic	
Space group	Pbca	
Unit cell dimensions	a = 8.8021(6) Å	α = 90°
	b = 15.5028(10) Å	β = 90°
	c = 27.4387(17) Å	γ = 90°
Volume [$Å^3$]	3744.2(4)	
Z	8	
Density (calculated) [Mg/m^3]	1.147	
Crystal size [mm^3]	0.166 · 0.100 · 0.046	
Theta range for data collection	1.484 – 28.340 °	
Index ranges	-11 ≤ h ≤11, -20 ≤ k ≤ 20, -36 ≤ l ≤ 36	
Reflections collected	56173	
Independent reflections	4669 [R(int) = 0.0844]	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R_1 = 0.0386, wR_2 = 0.0863	
R indices (all data)	R_1 = 0.0598, wR_2 = 0.0958	

IV. LIFDI measurement

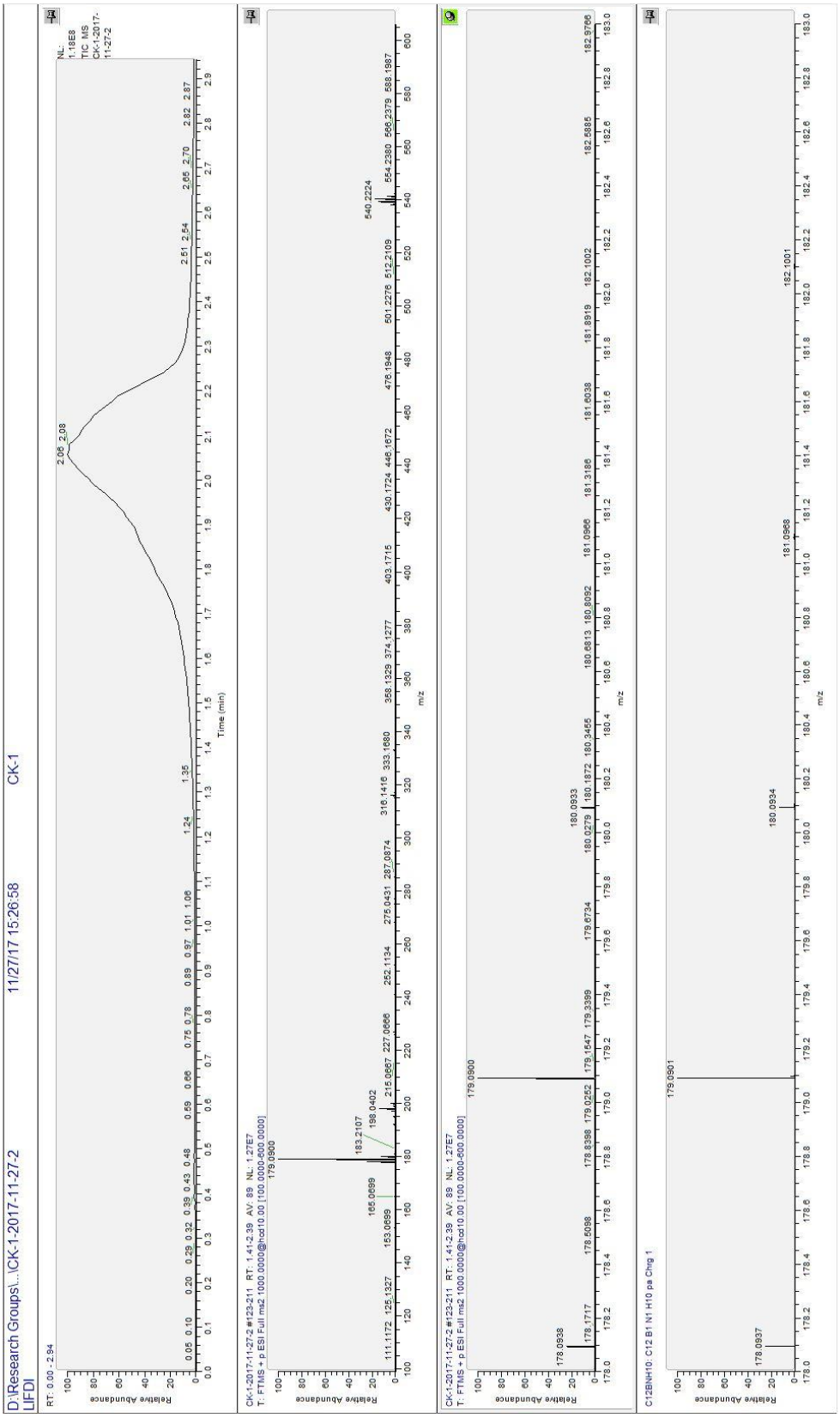

Fig S23. LIFDI measurement of compound **6**.

V. GC-MS measurements

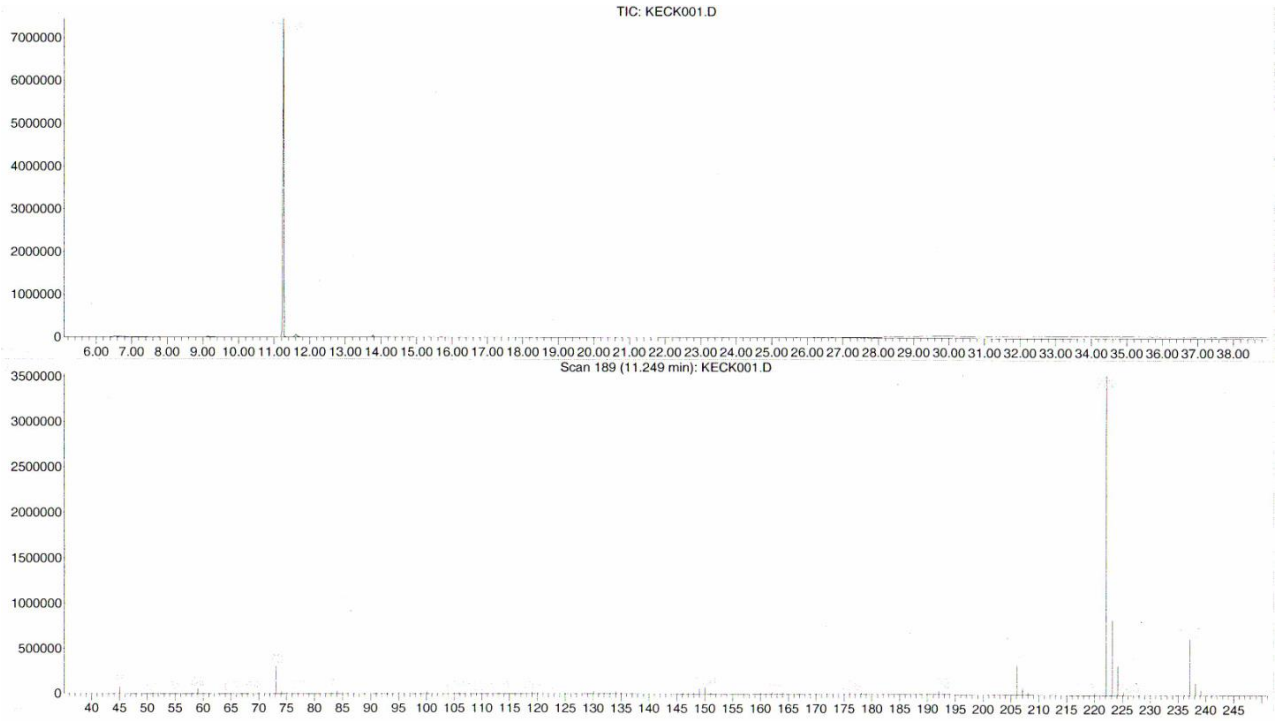

Fig S24. GC-MS measurement of compound **8**.

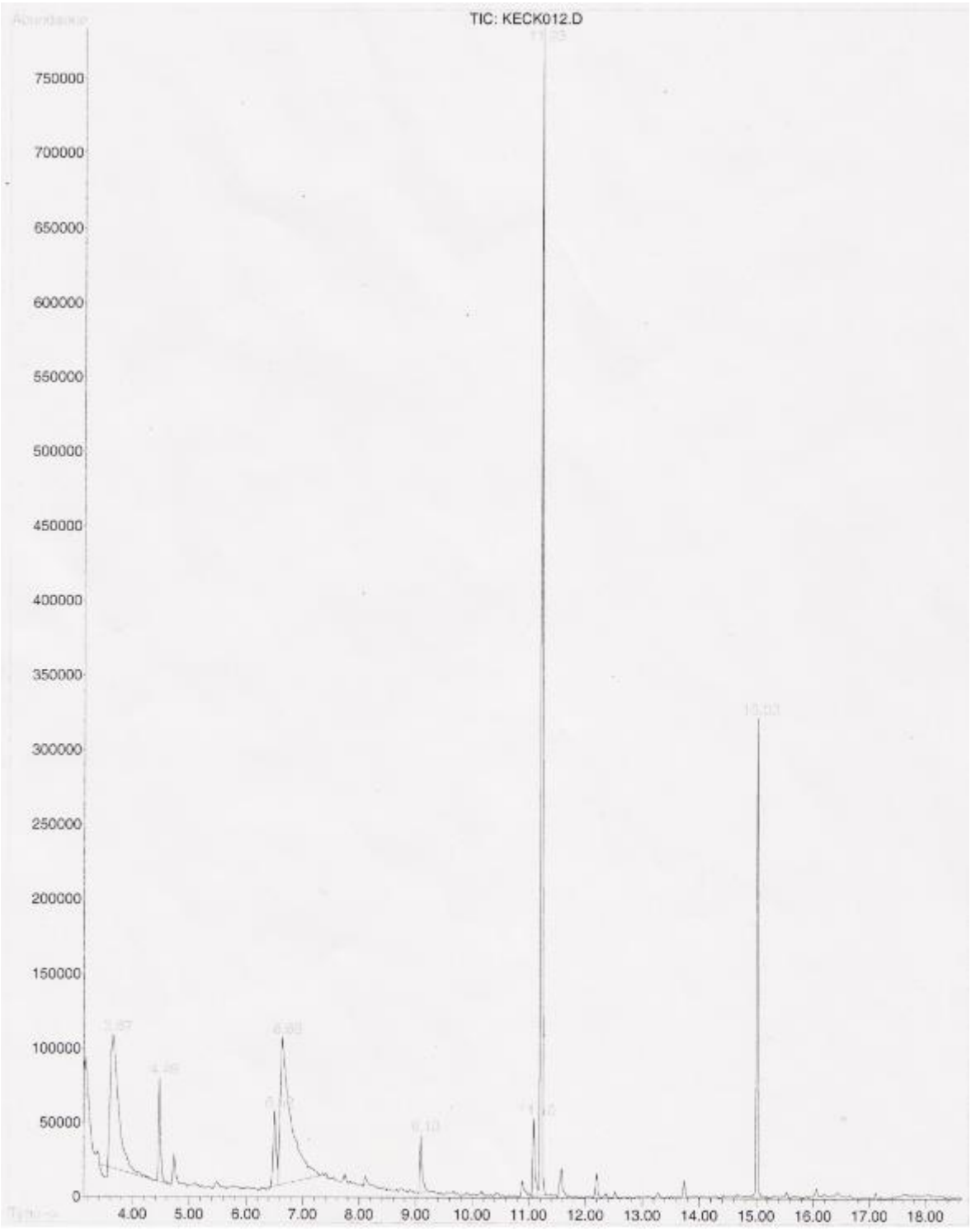

Fig S25. GC-MS measurement of compound **8** after irradiation at λ = 254 nm for 40 minutes in DCM.

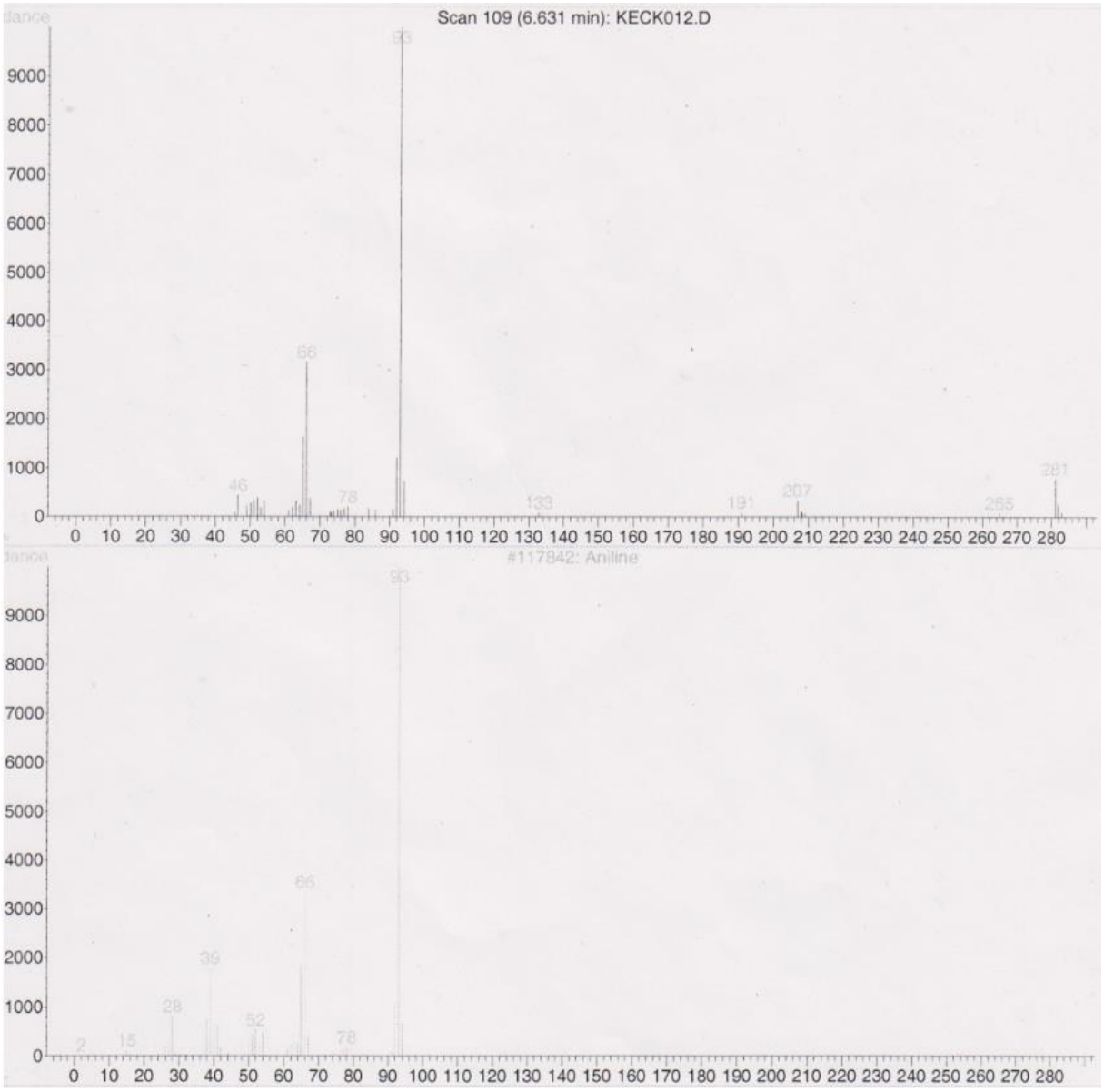

Fig S26. Measured MS spectrum of the product of irradiation of compound **8** compared to a MS spectrum of aniline in the database.

VI. Cartesian Coordinates

All coordinates are given in Å and refer to structure optimization at the B3LYP/6-311+G**/PCM(CH_2Cl_2) level of theory.

2

```
48
SCF Done:  E(RB3LYP) =  -1360.60813251
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1        -1.555443000      2.670417000      2.865813000
6        -3.491468000      0.480528000      1.825306000
1        -4.258490000      0.060995000      1.170935000
1        -3.149046000     -0.307937000      2.501063000
1        -3.972278000      1.254022000      2.433891000
```

$2^{+\cdot}$

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48
SCF Done:  E(UB3LYP) =  -1360.38607257
6        -1.267487000      1.210411000      0.249926000
6        -1.104123000      2.531818000      0.633297000
1        -0.119611000      2.965838000      0.741374000
6        -2.223712000      3.333200000      0.896866000
1        -2.083538000      4.365192000      1.196747000
6        -3.536175000      2.824479000      0.785291000
```

1	-4.378319000	3.471816000	0.995669000
6	-3.741459000	1.509410000	0.425391000
1	-4.744773000	1.108513000	0.357055000
6	-2.614113000	0.696497000	0.168486000
6	-2.614149000	-0.696408000	-0.168503000
6	-3.741541000	-1.509269000	-0.425369000
1	-4.744835000	-1.108324000	-0.357005000
6	-3.536331000	-2.824351000	-0.785262000
1	-4.378512000	-3.471651000	-0.995605000
6	-2.223895000	-3.333135000	-0.896871000
1	-2.083779000	-4.365139000	-1.196739000
6	-1.104260000	-2.531803000	-0.633346000
1	-0.119774000	-2.965875000	-0.741442000
6	-1.267548000	-1.210381000	-0.249992000
6	0.967681000	-2.102517000	2.163349000
1	0.520402000	-1.341731000	2.810277000
1	1.598478000	-2.737529000	2.794373000
1	0.166760000	-2.728893000	1.769836000
6	2.746711000	-2.627350000	-0.322570000
1	1.994386000	-3.026685000	-1.006314000
1	3.137895000	-3.464101000	0.265719000
1	3.567623000	-2.238366000	-0.928479000
6	3.512486000	-0.541234000	1.790361000
1	4.273609000	-0.094219000	1.148553000
1	4.000137000	-1.334115000	2.367405000
1	3.168095000	0.217797000	2.497718000
6	0.967871000	2.102474000	-2.163422000
1	0.520629000	1.341700000	-2.810390000
1	0.166933000	2.728863000	-1.769967000
6	2.746713000	2.627260000	0.322632000
1	1.994312000	3.026678000	1.006245000
1	3.567503000	2.238234000	0.928679000
7	1.162581000	-0.000031000	-0.000031000
14	2.072723000	-1.316361000	0.853249000
14	2.072800000	1.316290000	-0.853245000
5	-0.250766000	-0.000004000	-0.000057000
1	3.138050000	3.463961000	-0.265628000
1	1.598728000	2.737479000	-2.794394000
6	3.512622000	0.541150000	-1.790256000
1	4.273699000	0.094136000	-1.148395000
1	3.168274000	-0.217881000	-2.497632000
1	4.000315000	1.334026000	-2.367272000

3

36
SCF Done: E(RB3LYP) = -951.874803400

6	1.306166000	-1.233616000	0.000060000
6	1.635045000	-2.587462000	0.000070000
1	0.858268000	-3.347577000	0.000109000
6	2.977653000	-2.986856000	0.000022000
1	3.232156000	-4.041048000	0.000028000
6	3.991477000	-2.028316000	-0.000037000
1	5.029417000	-2.343220000	-0.000076000
6	3.682663000	-0.663038000	-0.000048000
1	4.482540000	0.069845000	-0.000094000
6	2.345857000	-0.274011000	0.000002000
6	1.783705000	1.100817000	0.000011000
6	2.482464000	2.304522000	-0.000011000
1	3.567131000	2.320846000	-0.000050000
6	1.769204000	3.507974000	0.000021000
1	2.305141000	4.450913000	0.000002000
6	0.375443000	3.501504000	0.000073000
1	-0.169525000	4.439031000	0.000095000
6	-0.321994000	2.286802000	0.000094000
1	-1.405414000	2.313562000	0.000125000
6	0.363192000	1.071865000	0.000065000
6	-3.382569000	0.506244000	1.555325000
1	-3.234449000	-0.111257000	2.446389000
1	-4.420574000	0.854390000	1.556947000
1	-2.736801000	1.382877000	1.647680000

```
6       -3.382199000      0.506416000     -1.555376000
1       -2.735926000      1.382671000     -1.647783000
1       -4.420002000      0.855158000     -1.556930000
1       -3.234490000     -0.111180000     -2.446444000
6       -4.079656000     -2.057242000     -0.000213000
1       -3.886097000     -2.669757000     -0.886299000
1       -5.143954000     -1.802858000      0.000056000
1       -3.885756000     -2.670175000      0.885511000
7       -1.340412000     -1.061947000      0.000077000
14      -3.031650000     -0.494440000     -0.000040000
5       -0.072874000     -0.454742000      0.000066000
1       -1.290010000     -2.076337000      0.000083000
```

4

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24
SCF Done:  E(RB3LYP) =  -543.121069198
6       -2.989605000     -1.507041000      0.000047000
6       -3.496943000     -0.207582000      0.000238000
6       -2.622723000      0.887007000      0.000261000
6       -1.244699000      0.683002000      0.000010000
6       -0.743608000     -0.643788000     -0.000198000
6       -1.608302000     -1.734737000     -0.000158000
1       -3.671491000     -2.350538000      0.000079000
1       -4.569470000     -0.047453000      0.000365000
1       -3.032694000      1.892762000      0.000335000
1       -1.230227000     -2.751560000     -0.000225000
6        1.244699000      0.683002000      0.000052000
6        2.622723000      0.887007000      0.000310000
6        3.496943000     -0.207581000      0.000267000
6        2.989605000     -1.507041000      0.000042000
6        1.608303000     -1.734737000     -0.000170000
6        0.743608000     -0.643788000     -0.000182000
1        3.032694000      1.892762000      0.000407000
1        4.569470000     -0.047452000      0.000403000
1        3.671491000     -2.350538000      0.000052000
1        1.230228000     -2.751560000     -0.000277000
5        0.000000000      1.652708000     -0.000321000
7        0.000000000      3.046013000     -0.000300000
1       -0.841965000      3.602801000     -0.000316000
1        0.841963000      3.602802000     -0.000232000
```

5

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35
SCF Done:  E(UB3LYP) =  -951.205675963
6        0.886688000     -1.255109000     -0.000090000
6        0.698484000     -2.633477000     -0.000107000
1       -0.302047000     -3.053285000     -0.000134000
6        1.809008000     -3.487107000     -0.000088000
1        1.667084000     -4.562179000     -0.000101000
6        3.099666000     -2.957269000     -0.000052000
1        3.954676000     -3.624485000     -0.000037000
6        3.304134000     -1.573052000     -0.000035000
1        4.314022000     -1.176884000     -0.000008000
6        2.199842000     -0.724293000     -0.000054000
6        2.172626000      0.758089000     -0.000045000
6        3.244975000      1.646933000     -0.000015000
1        4.268756000      1.288152000      0.000009000
6        2.989820000      3.022743000     -0.000016000
1        3.819783000      3.720872000      0.000008000
6        1.680601000      3.504758000     -0.000048000
1        1.499238000      4.573888000     -0.000049000
6        0.602192000      2.610884000     -0.000078000
1       -0.413157000      2.993313000     -0.000102000
```

```
6        0.840949000      1.240365000     -0.000076000
6       -3.847531000     -0.900516000      1.549144000
1       -3.515054000     -1.941936000      1.581412000
1       -4.942053000     -0.896855000      1.574311000
1       -3.484935000     -0.399485000      2.450915000
6       -3.716615000      1.786256000     -0.000463000
1       -3.338550000      2.300856000      0.886442000
1       -4.808773000      1.864513000     -0.000268000
1       -3.338908000      2.300181000     -0.887911000
6       -3.847870000     -0.901576000     -1.548200000
1       -3.485589000     -0.401075000     -2.450392000
1       -4.942400000     -0.898059000     -1.573051000
1       -3.515280000     -1.942977000     -1.579899000
7       -1.480363000     -0.051316000     -0.000123000
14      -3.224091000     -0.034479000      0.000108000
5       -0.127758000     -0.025679000     -0.000090000
```

6

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48
SCF Done:  E(RB3LYP) =  -1086.24264803
5       -1.142210000      0.000046000      0.010992000
7       -0.008847000      0.000071000     -1.145167000
1       -0.014219000     -0.816160000     -1.749853000
1       -0.014229000      0.816328000     -1.749817000
6       -2.173672000     -1.245582000      0.012229000
6       -2.001850000     -2.629736000      0.026260000
1       -1.009590000     -3.067259000      0.045935000
6       -3.105400000     -3.492721000      0.018168000
1       -2.953191000     -4.566656000      0.029556000
6       -4.399557000     -2.973840000     -0.004303000
1       -5.252181000     -3.644290000     -0.011251000
6       -4.601084000     -1.591621000     -0.015847000
1       -5.610988000     -1.195123000     -0.030575000
6       -3.496293000     -0.739471000     -0.006341000
6       -3.496332000      0.739440000     -0.006353000
6       -4.601167000      1.591533000     -0.015895000
1       -5.611051000      1.194982000     -0.030606000
6       -4.399711000      2.973762000     -0.004392000
1       -5.252371000      3.644166000     -0.011325000
6       -3.105582000      3.492711000      0.018086000
1       -2.953430000      4.566656000      0.029500000
6       -2.001988000      2.629784000      0.026227000
1       -1.009752000      3.067360000      0.045939000
6       -2.173738000      1.245621000      0.012220000
7        0.008847000      0.000071000      1.145166000
1        0.014219000     -0.816160000      1.749851000
1        0.014229000      0.816329000      1.749815000
6        2.173738000      1.245621000     -0.012221000
6        2.173672000     -1.245582000     -0.012230000
6        2.001989000      2.629784000     -0.026229000
6        3.496332000      0.739439000      0.006354000
6        2.001849000     -2.629736000     -0.026262000
6        3.496293000     -0.739471000      0.006342000
6        3.105583000      3.492711000     -0.018086000
1        1.009753000      3.067360000     -0.045943000
6        4.601168000      1.591532000      0.015898000
6        3.105399000     -3.492721000     -0.018168000
1        1.009589000     -3.067259000     -0.045939000
6        4.601084000     -1.591622000      0.015850000
6        4.399712000      2.973761000      0.004393000
1        2.953431000      4.566656000     -0.029501000
1        5.611051000      1.194981000      0.030611000
6        4.399556000     -2.973840000      0.004305000
1        2.953190000     -4.566656000     -0.029557000
1        5.610988000     -1.195123000      0.030580000
1        5.252372000      3.644165000      0.011328000
1        5.252181000     -3.644290000      0.011255000
5        1.142210000      0.000046000     -0.010994000
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7

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72
SCF Done:  E(RB3LYP) =  -1629.36888656
6       -1.501418000     -2.187351000     -1.486186000
6       -2.347182000     -1.555752000      0.764587000
6       -0.861726000     -2.479699000     -2.691038000
6       -2.789612000     -2.728978000     -1.263387000
6       -2.583490000     -1.270624000      2.108490000
6       -3.285096000     -2.368651000      0.083089000
6       -1.481066000     -3.287262000     -3.654236000
1        0.132510000     -2.096768000     -2.901443000
6       -3.417998000     -3.524537000     -2.222466000
6       -3.748784000     -1.714805000      2.746567000
1       -1.856944000     -0.713058000      2.691899000
6       -4.456798000     -2.802442000      0.704775000
6       -2.756652000     -3.801034000     -3.421627000
1       -0.967870000     -3.514030000     -4.582613000
1       -4.407416000     -3.933961000     -2.046293000
6       -4.690827000     -2.460776000      2.038946000
1       -3.918052000     -1.480940000      3.792156000
1       -5.174131000     -3.419087000      0.173281000
1       -3.235566000     -4.421304000     -4.171528000
1       -5.596482000     -2.797242000      2.531872000
6        2.627103000     -0.708734000     -0.562405000
6        2.461769000     -0.894711000      1.913052000
6        2.542944000     -0.673197000     -1.953824000
6        3.886515000     -1.014486000      0.014152000
6        2.175200000     -0.964637000      3.275880000
6        3.790527000     -1.111110000      1.487450000
6        3.669107000     -0.896127000     -2.756280000
1        1.596934000     -0.477309000     -2.447560000
6        5.016210000     -1.229453000     -0.776502000
6        3.186909000     -1.249085000      4.202342000
1        1.163675000     -0.800620000      3.642615000
6        4.805512000     -1.390449000      2.404067000
6        4.903903000     -1.163202000     -2.166902000
1        3.580260000     -0.861893000     -3.836748000
1        5.975277000     -1.459306000     -0.324044000
6        4.495470000     -1.458853000      3.764893000
1        2.955566000     -1.305457000      5.260588000
1        5.826519000     -1.555362000      2.075692000
1        5.776379000     -1.332054000     -2.788681000
1        5.276827000     -1.676552000      4.484988000
6       -1.294185000      2.475764000      0.827957000
6        0.200566000      2.633618000     -1.159420000
6       -2.029489000      2.251173000      1.991814000
6       -1.352807000      3.766783000      0.250160000
6        1.101499000      2.574382000     -2.224089000
6       -0.473518000      3.857692000     -0.932944000
6       -2.814741000      3.263321000      2.558833000
1       -2.012076000      1.284262000      2.478297000
6       -2.136505000      4.780259000      0.803954000
6        1.322026000      3.687186000     -3.046465000
1        1.660351000      1.668887000     -2.426482000
6       -0.263889000      4.969572000     -1.750106000
6       -2.872371000      4.522074000      1.962272000
1       -3.381027000      3.066335000      3.462912000
1       -2.173358000      5.765695000      0.351277000
6        0.637625000      4.879067000     -2.812565000
1        2.029849000      3.621471000     -3.865980000
1       -0.788582000      5.901599000     -1.567250000
1       -3.483231000      5.303777000      2.400858000
1        0.808368000      5.738336000     -3.452164000
1        0.077247000     -1.919486000      1.416618000
1        0.688007000     -2.411360000      0.020018000
1       -2.009568000      0.577077000     -0.909356000
1       -0.671921000      0.242725000     -1.716853000
1        0.607789000      0.972875000      1.804286000
1        1.682187000      1.571684000      0.780239000
5        1.528851000     -0.552879000      0.628402000
5       -0.293525000      1.537065000     -0.054473000
5       -1.099253000     -1.236353000     -0.227190000
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7       -1.040504000      0.293174000     -0.767586000
7        0.901077000      0.918372000      0.828907000
7        0.306530000     -1.586934000      0.481346000
```

8

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38
SCF Done:  E(RB3LYP) =  -1105.19544006
6       -3.263766000      0.161140000      1.191971000
6       -1.869056000      0.167062000      1.183429000
6       -1.155885000     -0.015242000     -0.009692000
6       -1.881300000     -0.207573000     -1.193843000
6       -3.275554000     -0.220705000     -1.185214000
6       -3.974338000     -0.034401000      0.007811000
1       -3.794700000      0.304868000      2.126916000
1       -1.319464000      0.307565000      2.107340000
1       -1.340439000     -0.342271000     -2.123903000
1       -3.816046000     -0.372539000     -2.113372000
1       -5.058410000     -0.041638000      0.014408000
7        0.281611000     -0.003031000     -0.021029000
14       1.113699000     -1.572536000      0.046054000
14       1.061244000      1.593123000     -0.050615000
6        1.426998000      2.220158000      1.694588000
1        1.907518000      3.203772000      1.655889000
1        0.508665000      2.321730000      2.280909000
1        2.095444000      1.542130000      2.233060000
6        2.679484000      1.513985000     -1.020217000
1        2.503964000      1.223137000     -2.059686000
1        3.135516000      2.509830000     -1.026049000
1        3.412724000      0.825386000     -0.593797000
6       -0.079495000      2.827272000     -0.905091000
1        0.414263000      3.803576000     -0.952500000
1       -0.313304000      2.518427000     -1.927839000
1       -1.023165000      2.956358000     -0.368882000
6        1.797122000     -2.067656000     -1.644582000
1        2.536019000     -1.350541000     -2.012068000
1        2.282456000     -3.048025000     -1.587932000
1        0.995852000     -2.134778000     -2.386998000
6       -0.105237000     -2.895508000      0.609063000
1       -0.525850000     -2.666805000      1.592124000
1       -0.935531000     -3.018839000     -0.090890000
1        0.416853000     -3.855437000      0.681337000
6        2.534957000     -1.514326000      1.289475000
1        3.292375000     -0.765707000      1.045558000
1        2.165712000     -1.304190000      2.297632000
1        3.035491000     -2.488254000      1.313612000
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38
SCF Done:  E(UB3LYP) =  -1104.98292031
6        3.302258000      1.002441000      0.689381000
6        1.925385000      1.022818000      0.673979000
6        1.184615000     -0.000078000     -0.000204000
6        1.925819000     -1.022725000     -0.674319000
6        3.302670000     -1.002014000     -0.689225000
6        4.003109000      0.000276000      0.000243000
1        3.844964000      1.760377000      1.240194000
1        1.395168000      1.776206000      1.238321000
1        1.395941000     -1.776123000     -1.238978000
1        3.845799000     -1.759737000     -1.239916000
1        5.086165000      0.000324000      0.000445000
6       -2.567524000     -1.313046000      1.266706000
1       -3.081247000     -2.273944000      1.380390000
1       -2.232505000     -1.003628000      2.259486000
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1       -3.301040000     -0.594710000      0.902694000
6       -1.638787000     -2.180659000     -1.582981000
1       -2.340908000     -1.486101000     -2.046656000
1       -0.791678000     -2.315262000     -2.259654000
1       -2.141413000     -3.148464000     -1.483958000
6       -0.001267000     -2.877549000      0.979991000
1       -0.650923000     -3.672253000      1.361360000
1        0.736774000     -3.344058000      0.326934000
1        0.519388000     -2.441795000      1.836842000
6       -1.636631000      2.181733000      1.583028000
1       -2.138719000      3.149792000      1.483632000
1       -2.339063000      1.488023000      2.047536000
1       -0.789138000      2.316185000      2.259226000
6       -0.001725000      2.876353000     -0.982219000
1       -0.651502000      3.670947000     -1.363602000
1        0.736964000      3.343207000     -0.330134000
1        0.518103000      2.439780000     -1.839154000
6       -2.569670000      1.313096000     -1.264095000
1       -2.237062000      1.003350000     -2.257553000
1       -3.302646000      0.595161000     -0.898190000
1       -3.083286000      2.274173000     -1.376767000
7       -0.182023000     -0.000252000     -0.000253000
14      -1.110481000     -1.625960000      0.127392000
14      -1.110483000      1.625706000     -0.127567000
```

10

```
29
SCF Done:  E(RB3LYP) =  -718.738667981
6        2.585408000     -1.419796000      0.114350000
6        1.144341000     -0.966356000      0.150622000
6        0.780264000      0.319568000      0.059501000
6        1.766320000      1.454046000     -0.052556000
6        3.202051000      1.021012000      0.273009000
6        3.531545000     -0.321068000     -0.387921000
1        0.387250000     -1.736469000      0.256155000
1        2.898408000     -1.746714000      1.116517000
1        2.673076000     -2.306893000     -0.523677000
1        1.709669000      1.867497000     -1.068348000
1        1.442797000      2.257744000      0.617330000
1        3.904781000      1.795577000     -0.048056000
1        3.314146000      0.923304000      1.359556000
1        3.426821000     -0.220889000     -1.475210000
1        4.571100000     -0.601935000     -0.193197000
6       -2.307516000     -1.022852000      1.542478000
1       -3.331186000     -1.411980000      1.548697000
1       -1.628688000     -1.875305000      1.624978000
1       -2.181838000     -0.402483000      2.434917000
6       -3.234974000      1.408896000     -0.111397000
1       -3.050454000      2.028629000     -0.993510000
1       -4.262388000      1.036164000     -0.169744000
1       -3.158836000      2.047286000      0.773474000
6       -2.117345000     -1.089828000     -1.556148000
1       -3.126264000     -1.503616000     -1.655316000
1       -1.906544000     -0.504746000     -2.456223000
1       -1.415603000     -1.926912000     -1.523937000
14      -2.018220000     -0.013659000     -0.017878000
8       -0.513968000      0.771405000      0.054283000
```

10$^{+\cdot}$

```
29
SCF Done:  E(UB3LYP) =  -718.527173263
6        3.182152000     -1.156102000      0.050684000
6        1.729023000     -1.404746000      0.084624000
```

```
6         0.765693000     -0.367737000      0.022676000
6         1.179901000      1.065518000     -0.079503000
6         2.644035000      1.293159000      0.331234000
6         3.567450000      0.275967000     -0.343073000
1         1.352471000     -2.417835000      0.181581000
1         3.560166000     -1.394813000      1.061643000
1         3.657935000     -1.910426000     -0.588088000
1         1.034568000      1.361319000     -1.128301000
1         0.496657000      1.683579000      0.507748000
1         2.929657000      2.311427000      0.061887000
1         2.733133000      1.214163000      1.419579000
1         3.501178000      0.382840000     -1.430798000
1         4.607122000      0.460732000     -0.068214000
6        -2.096273000      1.266351000     -1.408704000
1        -3.132242000      1.573384000     -1.586636000
1        -1.519887000      2.166479000     -1.185682000
1        -1.720457000      0.825451000     -2.335743000
6        -3.155756000     -1.459692000     -0.337161000
1        -3.038720000     -2.208052000      0.450620000
1        -4.208695000     -1.163890000     -0.368844000
1        -2.906776000     -1.922075000     -1.295537000
6        -2.332874000      0.770872000      1.684111000
1        -3.360414000      1.140858000      1.760609000
1        -2.188447000      0.021119000      2.465827000
1        -1.662409000      1.611572000      1.876454000
14       -2.091184000      0.029657000     -0.011014000
8        -0.469796000     -0.731570000      0.040846000
```

11

```
31
SCF Done:  E(RB3LYP) =  -719.964994297
6         2.895036000     -1.261609000      0.265225000
6         1.499250000     -1.270189000     -0.378622000
6         0.703572000     -0.014700000     -0.014852000
6         1.476564000      1.254640000     -0.379951000
6         2.871951000      1.272541000      0.264270000
6         3.672829000      0.012503000     -0.093046000
1         1.592936000     -1.308271000     -1.470949000
1         0.937196000     -2.158565000     -0.073884000
1         2.792773000     -1.327436000      1.356319000
1         3.452910000     -2.149997000     -0.047249000
1         1.569698000      1.292968000     -1.472317000
1         0.898511000      2.133101000     -0.076480000
1         3.413618000      2.170745000     -0.048607000
1         2.768038000      1.337072000      1.355293000
1         3.887492000      0.014127000     -1.169490000
1         4.640180000      0.021302000      0.419733000
1         0.533596000     -0.016004000      1.072654000
8        -0.556232000     -0.027149000     -0.702169000
14       -2.073576000     -0.000012000      0.025315000
6        -3.285595000      0.005338000     -1.406021000
1        -4.318249000      0.017105000     -1.043293000
1        -3.141662000      0.885782000     -2.038979000
1        -3.158741000     -0.884347000     -2.029688000
6        -2.303628000     -1.529273000      1.102174000
1        -2.225780000     -2.444868000      0.508270000
1        -1.553296000     -1.578904000      1.897325000
1        -3.288949000     -1.521766000      1.579723000
6        -2.262830000      1.549938000      1.080388000
1        -2.151997000      2.455454000      0.476400000
1        -3.252316000      1.578200000      1.548571000
1        -1.518926000      1.586523000      1.882212000
```

11$^{+\cdot}$

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31
SCF Done:  E(UB3LYP) =  -719.707989517
6       -3.032094000     -1.193069000     -0.252567000
6       -1.638778000     -1.331334000      0.346763000
6       -0.687597000     -0.213921000     -0.123841000
6       -1.400990000      1.227391000      0.365290000
6       -2.776538000      1.303142000     -0.257365000
6       -3.692414000      0.141084000      0.128779000
1       -1.666194000     -1.340250000      1.439594000
1       -1.164698000     -2.264704000      0.020675000
1       -2.980398000     -1.287404000     -1.342387000
1       -3.648168000     -2.022967000      0.107250000
1       -1.412499000      1.190641000      1.454218000
1       -0.718723000      1.999596000      0.014585000
1       -3.200399000      2.249520000      0.115611000
1       -2.699819000      1.397728000     -1.344180000
1       -3.884866000      0.164833000      1.206359000
1       -4.656192000      0.240623000     -0.374571000
1       -0.605983000     -0.128217000     -1.212472000
8        0.505141000     -0.253988000      0.500578000
14       2.165749000      0.019998000     -0.052684000
6        2.782453000      1.337721000      1.118026000
1        3.840793000      1.522982000      0.909791000
1        2.239125000      2.276113000      0.987134000
1        2.688787000      1.015234000      2.157339000
6        2.936794000     -1.659640000      0.247620000
1        2.831154000     -1.962085000      1.291232000
1        2.490021000     -2.422507000     -0.393231000
1        4.003930000     -1.591775000      0.012040000
6        2.131391000      0.525551000     -1.846590000
1        1.626864000      1.482564000     -2.001280000
1        3.164024000      0.640083000     -2.191822000
1        1.658268000     -0.229626000     -2.479637000
```

CH_2Cl_2

```
5
SCF Done:  E(RB3LYP) =  -959.771589435
6         0.000000000      0.000000000      0.777388000
1         0.900523000      0.000000000      1.379448000
1        -0.900523000      0.000000000      1.379448000
17        0.000000000      1.493236000     -0.218330000
17        0.000000000     -1.493236000     -0.218330000
```

$CH_2Cl^{\cdot}$

```
4
SCF Done:  E(UB3LYP) =  -499.483209004
6        0.000236000      1.129362000      0.000000000
1       -0.002715000      1.623146000      0.957969000
1       -0.002715000      1.623146000     -0.957969000
17       0.000236000     -0.589557000      0.000000000
```

Cl^{-}

```
1
SCF Done:  E(UB3LYP) =  -460.403535171
17       0.000000000      0.000000000      0.000000000
```

$CHCl_2^{\cdot}$

```
4
SCF Done:  E(UB3LYP) =  -959.106154420
6        0.012229000      0.702530000      0.000000000
1       -0.489149000      1.659149000      0.000000000
17       0.012229000     -0.172774000      1.482204000
17       0.012229000     -0.172774000     -1.482204000
```

$SiMe_3^+$

```
13
SCF Done:  E(UB3LYP) =  -409.123113968
6       -1.494722000      1.066417000     -0.002524000
1       -1.386386000      1.873706000     -0.732673000
1       -2.404223000      0.499038000     -0.200930000
1       -1.579718000      1.539019000      0.984443000
6        1.675321000      0.754529000      0.002559000
1        1.645731000      1.843863000      0.014715000
1        2.228728000      0.390236000      0.875486000
1        2.223228000      0.412902000     -0.883455000
6       -0.180653000     -1.823212000      0.002735000
1        0.779663000     -2.337235000      0.039542000
1       -0.791675000     -2.122371000      0.861673000
1       -0.727255000     -2.133752000     -0.895125000
14       0.000874000      0.003442000     -0.005735000
```

$SiMe_3Cl$

```
14
SCF Done:  E(RB3LYP) =  -869.621094822
17      -1.774669000     -0.001753000     -0.001282000
14       0.363673000      0.000612000      0.000798000
6        0.892289000     -0.339790000     -1.763188000
1        0.522200000      0.431781000     -2.443172000
1        1.985387000     -0.352475000     -1.827537000
1        0.521646000     -1.308869000     -2.106910000
6        0.886573000      1.699489000      0.587550000
1        0.513577000      1.902656000      1.594647000
1        1.979403000      1.763823000      0.610753000
```

1	0.515058000	2.479820000	-0.081509000
6	0.890654000	-1.357239000	1.177078000
1	1.983671000	-1.406618000	1.220727000
1	0.519207000	-1.172389000	2.188226000
1	0.520698000	-2.331247000	0.846777000

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