Electronic supplementary information

Unraveling Factors Leading to Efficient Norbornadiene-Quadricyclane Molecular Solar-Thermal Energy Storage Systems

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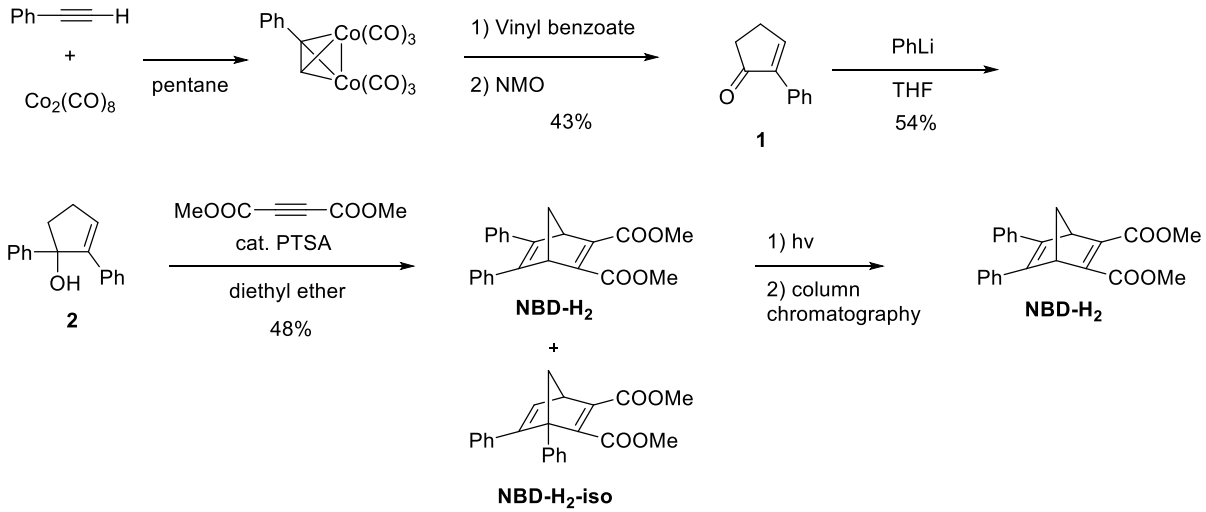
1 Contents

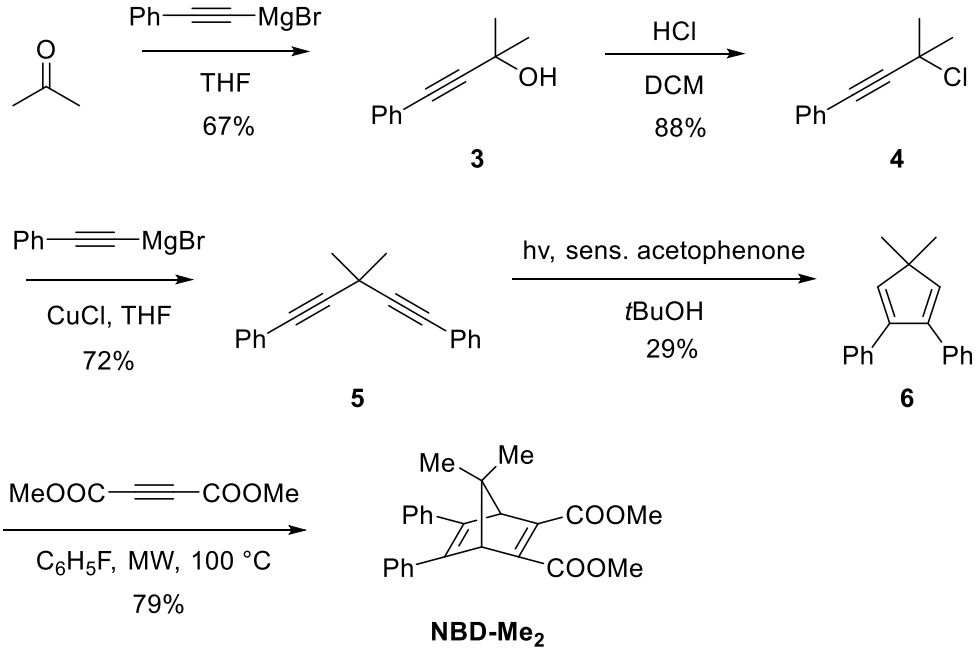
2 Synthesis

2.1 NBD-H₂



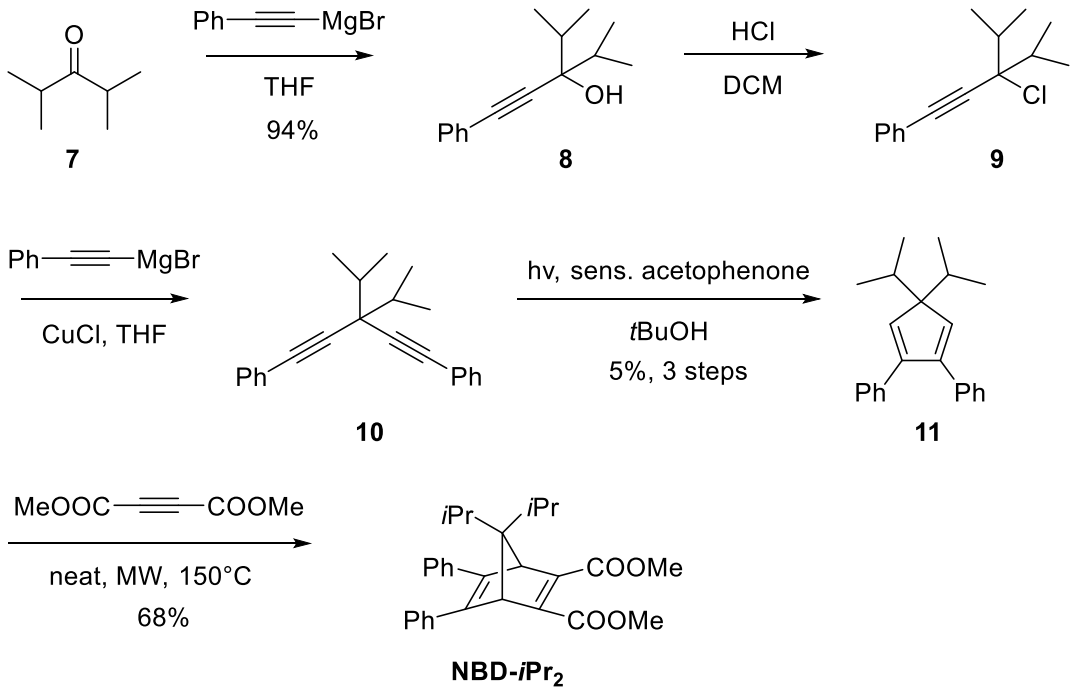
Cyclopentenone **1** was prepared in 43% yield by a Pauson-Khand reaction according to the procedure of Kerr *et. al.*[1] Reaction with PhLi in THF gave the alcohol **2**,[2] which was dehydrated to afford the corresponding cyclopentadienes, which reacted in situ with dimethyl acetylenedicarboxylate (DMAD) in a Diels-Alder reaction, giving most likely the two isomers **NBD-H2** and **NBD-H2-iso**. Spectral data were consistent with that reported by Dalkılıç and Daştan.[3] Conversion into the quadricyclane form by illumination at 366 nm allowed separation by column chromatography, and thermal back-conversion by heating in ethyl acetate followed by column chromatography afforded **NBD-H2** in 7% yield from the alcohol **2**.

2.2 NBD-Me$_2$



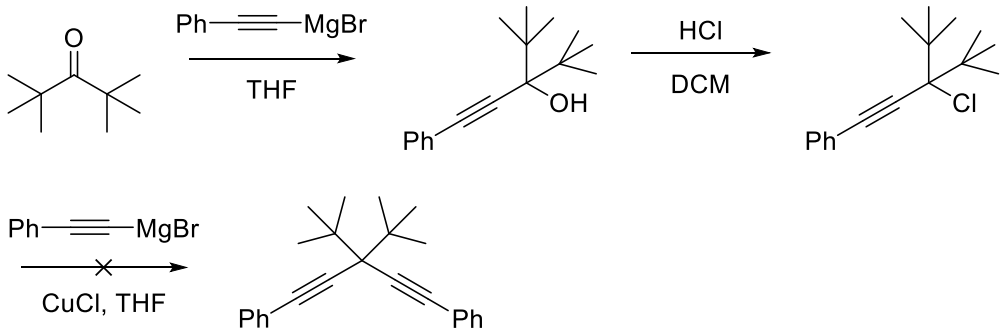
Cyclopentadiene **5** was synthesized according to the procedure of Zimmerman *et al.*[4] A Diels-Alder reaction with DMAD afforded **NBD-Me$_2$** in 79% yield.[5]

2.3 NBD-iPr$_2$



The alcohol **8**[6] was prepared in a Grignard reaction starting from commercially available ketone **7**. Exchange of OH for Cl by use of HCl afforded a mixture, probably due to competing dehydration, which was used in the next step without purification to give the diacetylene **10**, which could also not be purified. Photochemical ring closure in an analogous way as for **3** afforded the cyclopentadiene **11** in an overall yield of 5% over three steps. Diels-Alder reaction with DMAD then gave **NBD-*i*Pr$_2$** in 68% yield.

2.4 Attempted synthesis of NBD-tBu$_2$



The synthesis of NBD-*t*Bu was attempted using the same methodology as for **NBD-H$_2$** and **NBD-*i*Pr$_2$**, but the Cu-catalyzed reaction of the chloride to the acetylene did not produce the wanted diacetylene, probably due to the excessive steric repulsion.

2.5 Procedures and characterization

2.5.1 General experimental procedures

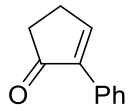
Dry conditions below indicate reactions using standard Schlenk techniques under an atmosphere of argon. Glassware were dried by the use of a heat gun at 650 °C under high vacuum. Dry solvents were obtained from a Pure Solv MD-4-EN solvent purification system. Microwave-assisted chemistry was carried out in a Biotage Initiator Sixty scientific microwave reactor. The NMR spectra were recorded on a Varian 300 MHz spectrometer, a Varian 400 MHz spectrometer or a Varian 500 MHz spectrometer. The ^{1}H spectra were recorded at 300

MHz, 400 MHz and 500 MHz, respectively. The ^{13}C spectra were recorded at 75.4 MHz or 100.6 MHz, respectively. Referencing was done to tetramethylsilane via the residual solvent peaks (^{1}H, $CDCl_3$ at 7.26 ppm, toluene-d_8 at 2.09 ppm; ^{13}C, $CDCl_3$ at 77.16 ppm). High-resolution mass spectrometry (HRMS) was performed using a high-resolution orbitrapXL mass spectrometer.

General procedure to prepare the Grignard reagent of phenylacetylene

To a well-stirred mixture of Mg turnings in dry THF, ethyl bromide (1 eq.) was added at a rate that kept reflux temperature. If needed, a small crystal of iodine was added to initiate the reaction. After the Mg had dissolved, phenylacetylene (1 eq.) was added dropwise and the reaction mixture was stirred until gas evaporation ceased. The Grignard reagent was used directly after preparation.

2.5.2 Specific procedures and characterization

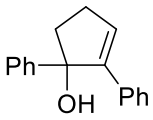


2-Phenylcyclopent-2-en-1-one (1)

Preparation of hexacarbonyldicobalt complex of phenylacetylene. Phenylacetylene (1.6 mL, 14.7 mmol) in dry pentane was added dropwise to a solution of $Co_2(CO)_8$ (6.1 g of 90% complex moistured by hexane, 16.1 mmol) in dry pentane under argon atmosphere. After of cessation of the initial gas evolution, the solution was stirred for 2 h before being poured onto a silica plug. After elution with petroleum ether/ethyl acetate (9:1), solvents were removed under reduced pressure and the resulting complex was used directly in the next step.

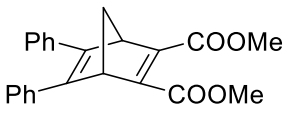
Preparation of cyclopentenone. The previously prepared hexacarbonyldicobalt complex of phenylacetylene was dissolved in vinyl benzoate (4.07 ml) and put under N_2 atmosphere. *N*-methylmorpholine *N*-oxide (NMO) (19.87 g, 147 mmol) dissolved in dry DCM (300 mL) was

added by syringe pump over 3 h. The resulting mixture was filtered repeatedly through celite and silica and excess vinyl benzoate was evaporated under reduced pressure. Purification by silica flash chromatography (petroleum ether/ethyl acetate, 3:1) afforded **1** (1.005 g, 6.35 mmol, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.59-2.63 (m, 2H), 2.70-2.75 (m, 2H), 7.31-7.41 (m, 3H), 7.67-7.71 (m, 2H), 7.83 (t, *J* = 3.0 Hz, 1H). The spectral data were consistent with the literature.[7]



1,2-Diphenylcyclopent-2-en-1-ol (2)

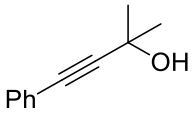
Compound **1** (0.956 g, 6.0 mmol) was dissolved in dry THF (30 mL) under argon atmosphere and cooled to -78°C. To this solution, PhLi (1.8 M in *t*-butylether, 4.4 mL, 7.9 mmol) was added dropwise, and the solution was allowed to reach room temperature under stirring overnight. The reaction mixture was quenched with sat. NH_4Cl (aq), extracted twice with diethyl ether and dried over $MgSO_4$. Purification by silica flash chromatography (petroleum ether/ethyl acetate, 3:1) afforded **2** as a yellow oil (0.771 g, 3.26 mmol, 54%).^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (s, 1H), 2.39 (t, *J* = 6.4 Hz, 2H), 2.46-2.56 (m, 1H), 2.59-2.69 (m, 1H), 6.48 (t, *J* = 2.5 Hz, 1H), 7.11-7.25 (m, 4H), 7.28-7.34 (m, 4H), 7.46 (d, *J* = 7.5 Hz, 2H). The spectral data were consistent with the literature.[2]



2,3-Dimethyl-5,6-diphenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (NBD-H_2)

Compound **2** (0.771 g, 3.26 mmol) was dissolved together with DMAD (0.5 mL, 4.1 mmol) in diethyl ether (10 mL). The solution was cooled to -78 °C and *p*-toluenesulfonic acid (0.621 g,

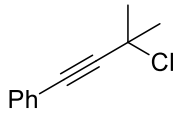
3.26 mmol) in diethyl ether (10 mL) was added dropwise. The reaction vessel was taken off the cooling bath and stirred for 1 h before being quenched by sat. $NaHCO_3$ (aq). The organic phases were separated and the water phase extracted once with diethyl ether. The organic phases were dried with $MgSO_4$ and evaporated under reduced pressure to give 1.343 g of crude product as a viscous oil. Purification by silica flash chromatography (petroleum ether/ethyl acetate, 3:1) yielded 0.327 g of viscous yellow oil. Remaining DMAD was distilled off by Kugelrohr distillation (150-175 °C at 0.1-1 mbar) to yield 0.263 mg of yellow viscous oil, most likely containing the isomers **NBD-H2** and **NBD-H2-iso**.[3] The oil was dissolved in chloroform and irradiated at 366 nm to convert into the quadricyclane isomers. Separation with silica flash chromatography (petroleum ether/ethyl acetate, 3:1), and thermal back conversion in ethyl acetate at 50 °C overnight followed by a second column afforded **NBD-H2** as pale yellow crystals (87 mg, 0.24 mmol, 7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (dt, J_1 = 7.0 Hz, J_2 = 1.6 Hz, 1H), 2.52 (dt, J_1 = 7.0 Hz, J_2 = 1.6 Hz, 1H), 3.80 (s, 6H), 4.27 (t, J = 1.6 Hz, 2H), 7.18-7.29 (m, 6H), 7.32-7.36 (m, 4H). ^{13}C NMR (100 MHz, CDCl3) δ 52.2, 59.6, 69.9, 127.4, 127.5, 128.5, 136.3, 147.7, 151.9, 165.5. HRMS calculated for $C_{23}H_{20}O_4$ $[M+Na]^+$: *m/z* 383.1254, found 383.1256.



2-Methyl-4-phenylbut-3-yn-2-ol (3)

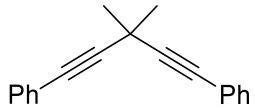
To a solution of phenylacetylene magnesium bromide (66 mmol) in dry THF (40 mL), acetone (4.41 mL, 60 mmol) in dry THF (10 mL) was added dropwise. The reaction mixture was stirred overnight at room temperature before being poured into a mixture of sat. NH_4Cl (aq) and ice. The phases were separated and the water phase was extracted twice with diethyl ether. The combined organic phases were washed with sat. NH_4Cl (aq) and brine and dried over $MgSO_4$.

Evaporation of solvent and excess starting material yielded **3** (8.54 g, 53 mmol, 67%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.62 (s, 6H), 7.28-7.32 (m, 3H), 7.40-7.44 (m, 2H). The spectral data were consistent with the literature.[8]



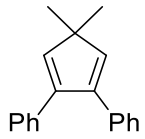
(3-Chloro-3-methylbut-1-yn-1-yl)benzene (4)

Compound **3** (8.54 g, 54.3 mmol), was dissolved in DCM (30 mL) and conc. HCl (30 mL) was added. The mixture was stirred for 3 h and thereafter quenched with sat. $NaHCO_3$ (aq.). The phases were separated and the water phase was extracted twice with DCM. The combined organic phases were washed with sat. $NaHCO_3$ (aq.) and brine and dried over $MgSO_4$. Evaporation of solvent yielded **4** as a yellow oil (8.39 g, 46.9 mmol, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.96 (s, 6H), 7.29-7.36 (m, 3H), 7.42-7.47 (m, 2H). Compound **4** proved sensitive to silica and could not be definitively purified by flash chromatography and was therefore used directly in the next step following Zimmerman *et al.*[4]



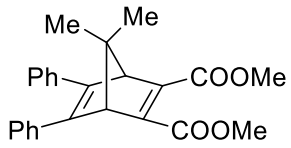
(3,3-Dimethyl-5-phenylpenta-1,4-diyn-1-yl)benzene (5)

Compound **4** (8.39 g, 46.9 mmol) was added to a solution of phenylacetylene magnesium bromide (70.4 mmol) and CuCl (232 mg, 2.4 mmol), and the reaction mixture was stirred overnight. The crude product was obtained as a dark brown solid that was recrystallized in ethanol to yield **5** as off-white crystals (8.29 g, 33.9 mmol, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70 (s, 6H), 7.27-7.31 (m, 6H), 7.43-7.47 (m, 4H). The spectral data were consistent with the literature.[9]



(3,3-Dimethyl-5-phenylcyclopenta-1,4-dien-1-yl)benzene (6)

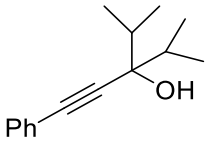
Compound **5** (0.50 g, 2.1 mmol) was dissolved in *t*BuOH (500 mL) in an immersion well photo reactor powered by a 450 W medium-pressure mercury lamp and stirred by a magnetic stirring bar. Acetophenone (10 mL) was added as triplet sensitizer, the solution was bubbled with argon for 15 min and an argon atmosphere was kept for the whole of the experiment. The mixture was illuminated for 7 h. The solvent was evaporated and most of the acetophenone was removed by a silica plug (pentane), before the resulting oil was purified by silica flash chromatography (pentane) to yield **6** (0.15 g, 0.6 mmol, 29%) as white crystals. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (s, 6H), 6.34 (2H), 7.13-7.16 (m, 4H), 7.21-7.24 (m, 6H). ^{13}C NMR (100 MHz, CDCl3) δ 22.8, 50.8, 126.9, 128.0, 128.3, 136.7, 142.5, 155.5.



2,3-Dimethyl-7,7-dimethyl-5,6-diphenylbicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (NBD-Me$_2$)

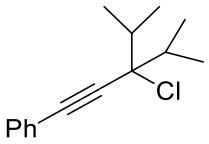
Compound **6** (100 mg, 0.4 mmol) and dimethyl acetylenedicarboxylate (1.05 mL, 1.21 g, 8.5 mmol) were dissolved in fluorobenzene (5 mL). The reaction mixture was heated at 100 °C in a microwave reactor for 260 min. Evaporation of solvent and silica flash chromatography (pentane/DCM, 1:1) gave **NBD-H$_2$** (125 mg, 0.3 mmol, 79%) as a pale yellow crystals. ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.29 (s, 3H), 1.39 (s, 3H), 3.79 (s, 6H), 3.81 (s, 2H), 7.17-7.25 (m, 5H), 7.27-7.30 (m, 5H). ^{13}C NMR (100 MHz, CDCl3) δ 22.8, 23.0, 52.3, 69.1, 82.1, 127.4,

127.5, 128.5, 137.0, 146.2, 150.3, 165.9. ^{1}H NMR data were consistent with the literature (^{13}C data is new).[5] HRMS calculated for $C_{25}H_{24}O_4$ $[M+Na]^+$: *m/z* 411.1567, found 411.1564.



4-Methyl-1-phenyl-3-(propan-2-yl)pent-1-yn-3-ol (8)

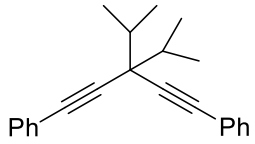
2,4-Dimethyl-3-pentanone (**7**, 6.85 g, 60 mmol) in dry THF (10 mL) was added to a solution of phenylacetylene magnesium bromide (66 mmol) in THF (40 mL) under argon atmosphere. The reaction mixture was stirred at room temperature overnight before being poured into a mixture of sat. NH_4Cl (aq.) and ice. The phases were separated and the water phase was extracted twice with diethyl ether. The combined organic phases were washed with sat. NH_4Cl (aq.) and brine and dried over $MgSO_4$. Evaporation of solvent and excess starting material yielded **8** (12.23 g, 56.5 mmol, 94%) as off-white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 (d, 6H, *J* = 6.7 Hz), 1.10 (d, 6H, *J* = 6.7 Hz), 2.05 (h, *J* = 6.7 Hz, 2H), 7.28-7.32 (m, 3H), 7.41-7.45 (m, 2H). Spectral data were consistent with the literature.[6]



[3-Chloro-4-methyl-3-(propan-2-yl)pent-1-yn-1-yl]benzene (9)

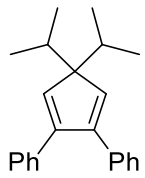
Compound **8** (12.23 g, 56.5 mmol), was dissolved in DCM (20 mL) and conc. HCl (30 mL) was added. The mixture was stirred for 2 h and thereafter quenched with sat. $NaHCO_3$ (aq). The phases were separated and the water phase was extracted twice with DCM. The combined organic phases were washed with sat. $NaHCO_3$ (aq) and brine and dried over $MgSO_4$. Evaporation of solvent yielded a crude oil (11.98 g) that was believed to contain a mixture of

the chloride **9** and the elimination product. An NMR yield of 63% (35.88 mmol) was estimated. As the corresponding methyl compound (**4**) proved sensitive to silica, no further purification or characterization was attempted and the crude oil was used directly in the next step.



[5-Phenyl-3,3-bis(propan-2-yl)penta-1,4-diyn-1-yl]benzene (10)

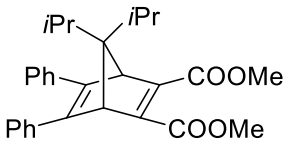
The crude product containing compound **9** was added to a solution of phenylacetylene magnesium bromide (53.8 mmol) and CuCl (178 mg, 1.8 mmol) in THF (50 mL) and the reaction mixture was stirred overnight and thereafter refluxed for 5 h and stirred for 72 h at room temperature after which it was poured into a mixture of sat. NH_4Cl (aq) and ice. The phases were separated and the water phase was extracted twice with diethyl ether. The combined organic phases were washed with sat. NH_4Cl (aq) and brine and dried over $MgSO_4$. Evaporation of solvent and excess starting material yielded a crude oil that was purified by silica flash chromatography (pentane) to yield a mixture of two compounds with the same retention time. No further purification was attempted, and the oil was used in the next step.



[5-Phenyl-3,3-bis(propan-2-yl)cyclopenta-1,4-dien-1-yl]benzene (11)

The crude product containing compound **10** was dissolved in *t*BuOH (500 mL) in an immersion well photo reactor powered by a 450 W medium-pressure mercury lamp (lower effect due to lamp malfunction) and stirred by a magnetic stirring bar. Acetophenone (20 mL) was added as triplet sensitizer, the solution was bubbled with argon for 15 min and an argon atmosphere was

kept for the whole of the experiment. The mixture was illuminated for 48 h after which the solvent was evaporated. Most of the acetophenone was removed by a silica plug (pentane/DCM, 9:1), before the resulting oil was purified by silica flash chromatography (pentane/DCM, 9:1) to yield **11** (0.86 g, 2.9 mmol, 5% over three steps) as a transparent oil that solidified on standing. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (d, *J* = 6.7 Hz, 12H), 2.30 (h, *J* = 6.7 Hz, 2H), 6.26 (s, 2H) 7.12-7.17 (m, 4H), 7.20-7.25 (m, 6H). ^{13}C NMR (100 MHz, CDCl3) δ 18.7, 30.2, 65.5, 126.8, 127.9, 128.2, 137.0, 140.2, 145.8. HRMS calculated for $C_{23}H_{26}$ $[M]^+$: *m/z* 302.2029, found 302.2025.



2,3-Dimethyl-5,6-diphenyl-7,7-bis(propan-2-yl)bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (NBD-*i*Pr$_2$)

Compound **11** (260 mg, 0.86 mmol) was dissolved in dimethyl acetylenedicarboxylate (2.5 mL, 2.89 g, 20 mmol). The reaction mixture was heated at 150 °C in a microwave reactor for 10 h. Evaporation of the acetylene by Kugelrohr vacuum distillation at 125 °C and 0.7 mbar yielded a solid that was purified by silica flash chromatography to yield crude yellow crystals. Further evaporation of remaining acetylene yielded **NBD-*i*Pr$_2$** as yellow crystals (260 mg, 0.58 mmol, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94(br. d, *J* = 7.0 Hz, 6H), 2.21 (br. m, 1H), 2.60 (m, 1H), 3.78 (s, 6H), 4.08 (s, 2H), 7.15-7.26 (m, 6H), 7.30-7.35 (m, 4H). ^{13}C NMR (100 MHz, CDCl3) δ 52.2, 65.7, 93.3, 127.3, 127.6, 128.5, 136.8, 147.2, 151.1, 165.6. The peaks associated with the *i*Pr substituents are missing in the ^{13}C NMR spectrum and broadened in the ^{1}H NMR spectrum. It is probable that this is due to hindered rotation. A broad hump in the δ 19.5-32.4 region of the ^{13}C NMR spectrum may harbour the missing peaks. HRMS calculated for $C_{29}H_{32}O_4$ $[M+Na]^+$: *m/z* 467.2193, found 467.2193.

3 Variable temperature NMR experiments

Variable temperature NMR spectra were recorded in $CDCl_3$ on a Bruker Avance III HD 18.8 T NMR spectrometer (Rheinstetten, Germany) equipped with a 5 mm TXO Cryoprobe.

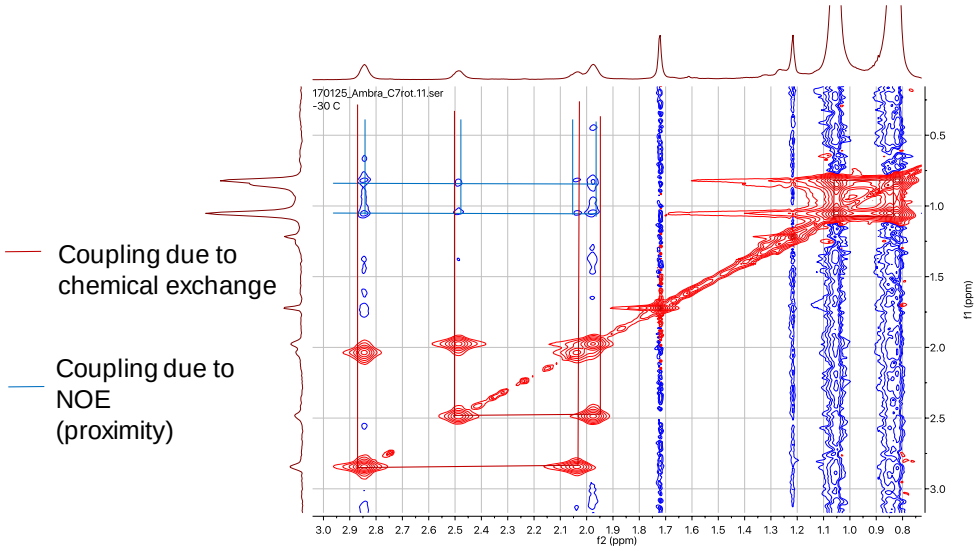


Figure S1. NOESY spectrum at -30°C for **NBD-*i*Pr$_2$**. Chemical exchange peaks in red and peaks due proximity and the nuclear Overhauser effect in blue.

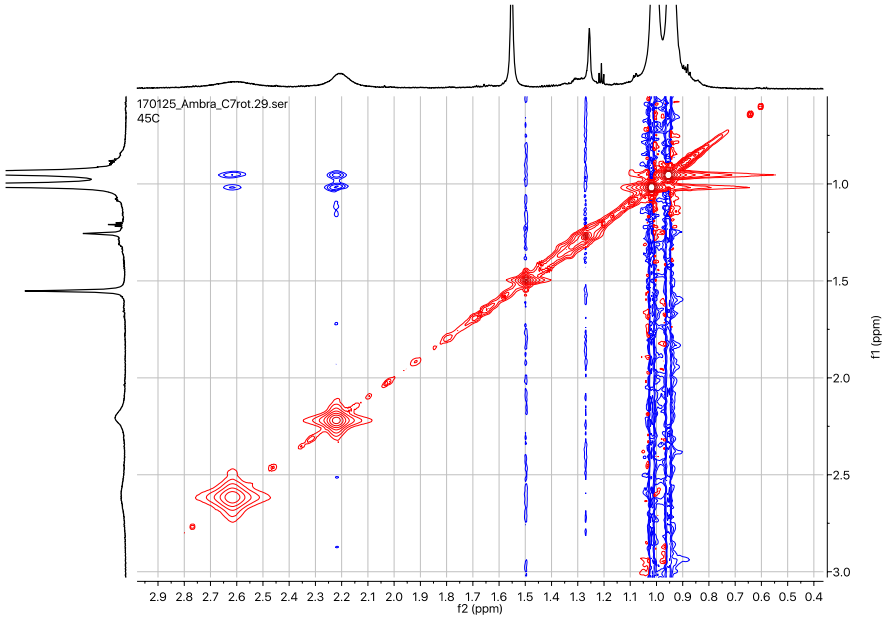


Figure S2. NOESY spectrum at 45°C for **NBD-*i*Pr$_2$**. Chemical exchange peaks in red and peaks due proximity and the nuclear Overhauser effect in blue.

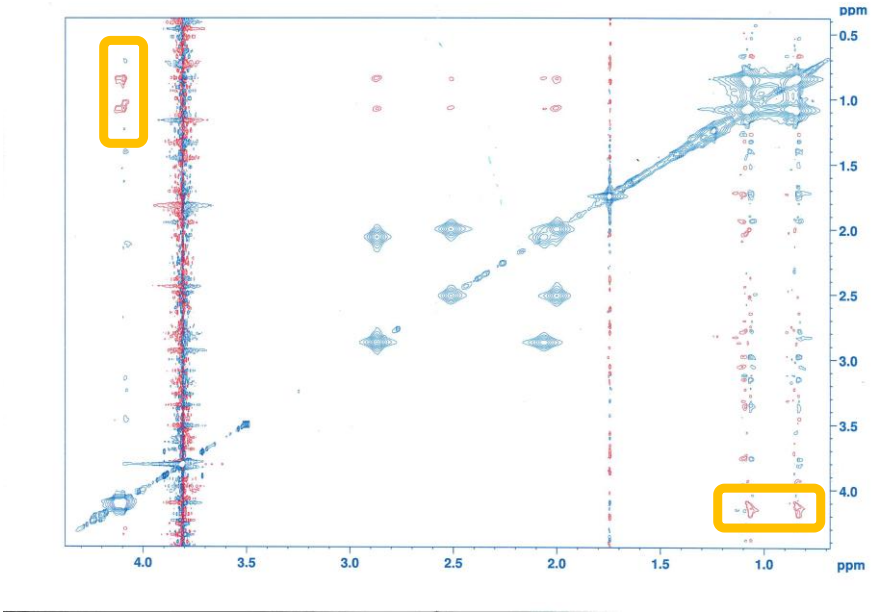


Figure S3. NOESY spectrum at -30°C for **NBD-*i*Pr$_2$** between 0 and 4.5 ppm. Yellow boxes indicate weak cross peaks between bridgehead protons and the methyl protons of the *i*Pr groups that are not present in the corresponding QC spectra. Chemical exchange peaks in blue and peaks due proximity and the nuclear Overhauser effect in red.

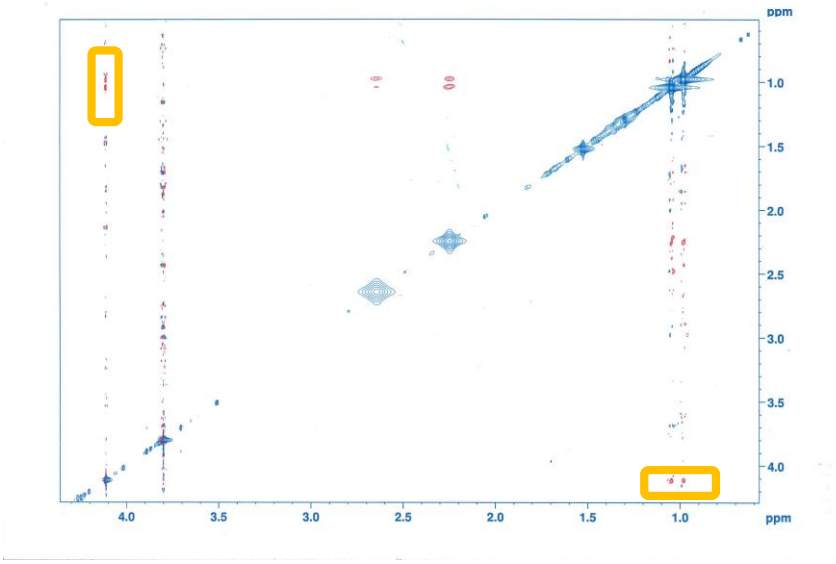


Figure S4. NOESY spectrum at 45°C for **NBD-*i*Pr$_2$** between 0 and 4.5 ppm. Yellow boxes indicate weak cross peaks between bridgehead protons and the methyl protons of the *i*Pr groups that are not present in the corresponding QC spectra. Chemical exchange peaks in blue and peaks due proximity and the nuclear Overhauser effect in red.

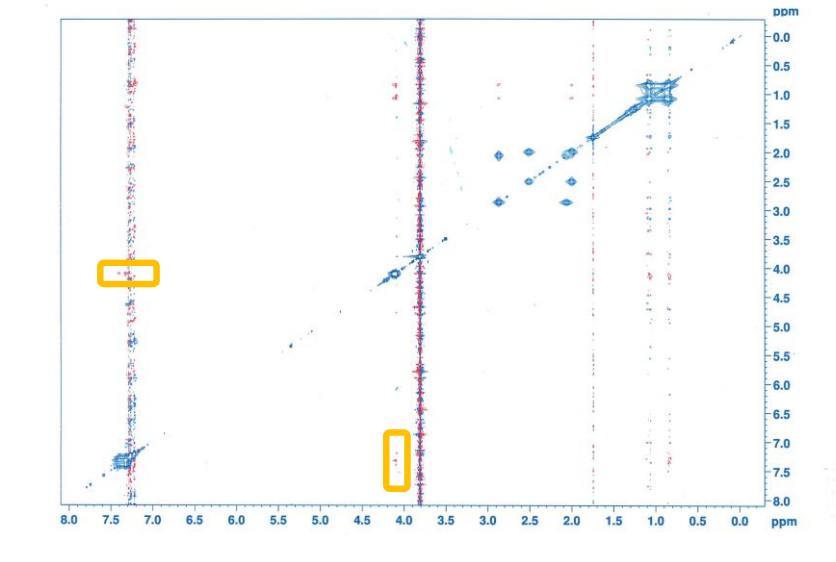


Figure S5. NOESY spectrum at -30°C for **NBD-*i*Pr$_2$** between ca 0 and 8 ppm. Yellow boxes indicate weak cross peaks between bridgehead protons and aromatic protons that are not present in the corresponding QC spectra. Chemical exchange peaks in blue and peaks due proximity and the nuclear Overhauser effect in red.

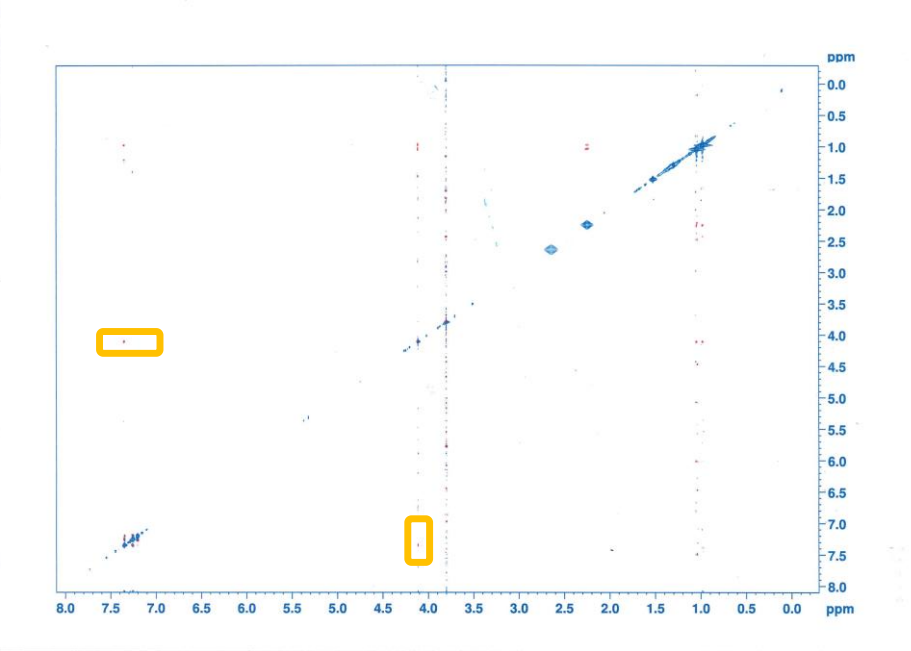


Figure S6. NOESY spectrum at 45°C for **NBD-*i*Pr$_2$** between ca 0 and 8 ppm. Yellow boxes indicate weak cross peaks between bridgehead protons and aromatic protons that are not present in the corresponding QC spectra. Chemical exchange peaks in blue and peaks due proximity and the nuclear Overhauser effect in red.

4 Quantum yields

NBD-H$_2$, **NBD-Me$_2$** and **NBD-*i*Pr$_2$** were irradiated under magnetic stirring at 334 nm using a Fluorolog 3 instrument (Horiba Jobin Yvon) equipped with a double-grating excitation monochromator (slit width of 2 nm) and a 450 W Xe lamp as the light source. Irradiation was interrupted with 30-240 seconds intervals and absorption at 334 nm was measured by a Varian Cary 5000 UV-Vis spectrometer. A total of 10-11 points were taken for each experiment. Total experiment times varied from 9 to 20 min. The resulting spectra show isosbestic points, indicating clean photoreaction (Figure S7 to Figure S9). For these short experiment times, the thermal back conversion to the QC form can be neglected (*cf.* experimental half-life values). As the QC isomer does not absorb at 334 nm, the quantum yield could be determined following Wirz and Klan by linear fitting according to:[10]

$$\Phi = \frac{V \log\left(\frac{10^{A_0} - 1}{10^{A_t} - 1}\right)}{l t q^0_{m,p} \varepsilon}$$

where V is the volume in cm^3, t is the time in seconds $q^0_{m,p}$ is the photon flux in amount basis in mol s^{-1}, e is the molar absorption coefficient in mol^{-1} dm^3 cm^{-1}, A_0 is the absorbance at t = 0 s and A_t is the absorbance at time t.

The photon flux was measured by the azobenzene actinometer through the method of Gauglitz and Hubig.[11] The photon flux in amount basis, $q^0_{m,p}$ in mol s^{-1} was determined by a linear fit to the formula

$$q^0_{m,p} = F(\lambda) \times \frac{|\Delta A(358)|}{t} \times \frac{V}{l}$$

where t is the time in s, V is the volume of the sample solution in cm^3 and l is the length of the cell in cm. The factor $F(\lambda)$ has the value of 3.60 10^{-6} mol s^{-1} cm^{-2} for 334 nm. A methanol solution of commercially available *trans*-azobenzene (Sigma Aldrich) with absorbance of ca 1.0 at 358 nm was irradiated at 334 nm under the same conditions as detailed above. The change in absorbance at 358 nm was monitored with illumination times that changed the absorbance with ca 0.02 units per interval with ca 8 data points taken in total. Total experiment time was ca 21 min. Photon flux was measured before and after each measurement series (length of up to 4 h) and the average photon flux was used. The values varied at most 3%. The light intensity at 334 nm was also monitored by an internal reference detector in the Fluorolog 3 instrument and this variation was consistent with that of the measured photon flux values.

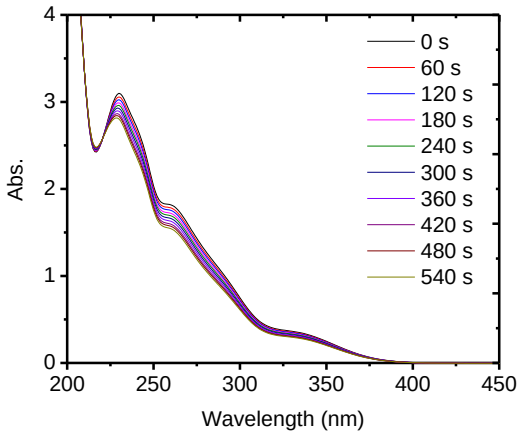


Figure S7. Absorption spectrum of **NBD-H$_2$** during irradiation at 334 nm.

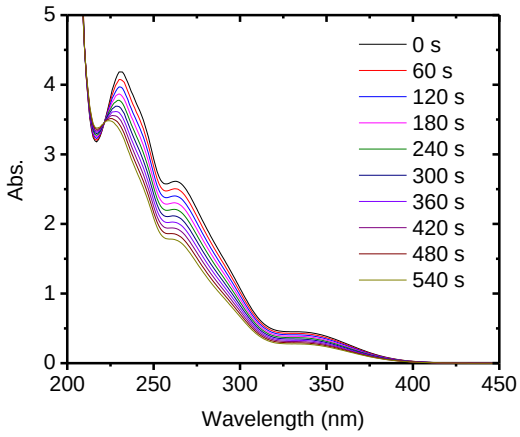


Figure S8. Absorption spectrum of **NBD-Me$_2$** during irradiation at 334 nm.

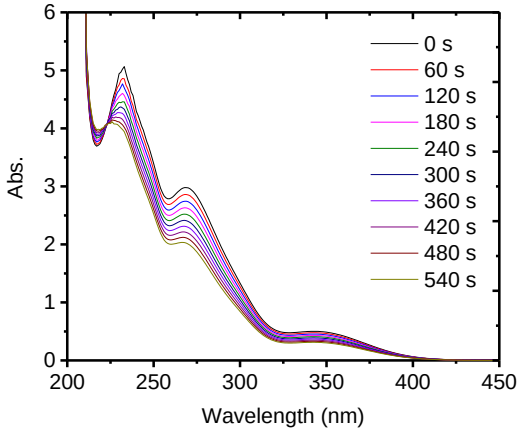


Figure S9. Absorption spectrum of **NBD-*i*Pr$_2$** during irradiation at 334 nm.

5 Kinetics of thermal back-conversion

Toluene solutions containing **NBD-R$_2$** (R = H, Me, *i*Pr) were irradiated at 365 nm using a 365 nm LED (Thorlabs, M365F1 - 365 nm, 3.0 mW (Min), 700 mA), and the thermal back-reaction was followed with a Cary 100 UV-Vis spectrophotometer at 350 nm, where the temperature was monitored on the block holding the cells. The resulting data were fitted to first-order kinetics. From the rate constants at 5 different temperatures (25, 40, 50, 60, 70 °C), the enthalpies and entropies of activation were calculated using the Eyring equation.

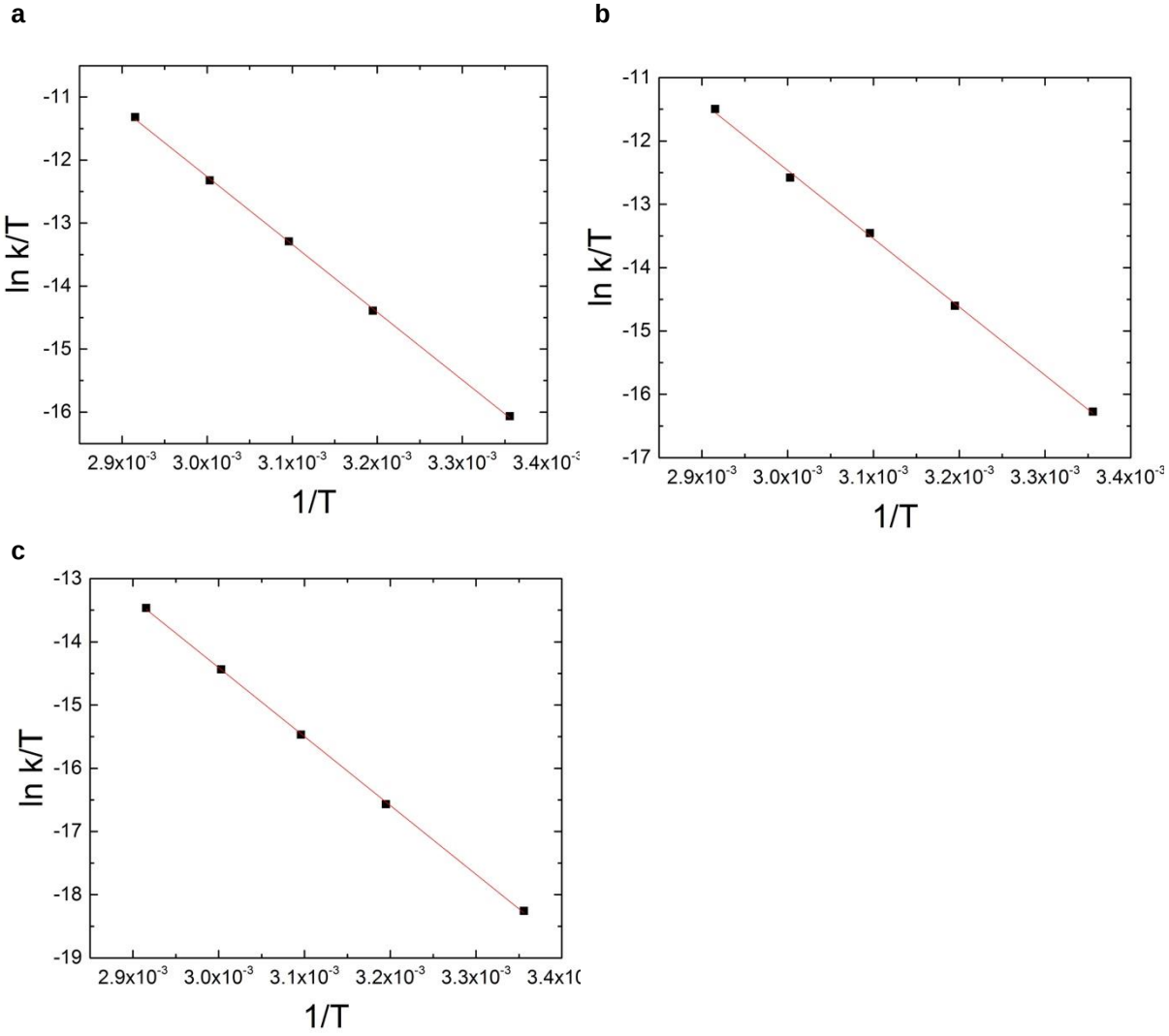


Figure S10. Eyring plots of the thermal back conversion of QC to NBD in toluene (a: **NBD-H$_2$**, b: **NBD-Me$_2$**, c: **NBD-iPr$_2$**).

Table S1. Eyring parameters and half-lives at 25°C for the thermal back conversion of QC-H_2, QC-Me_2, and QC-iPr_2 to NBD-H_2, NBD-Me_2, and NBD-iPr_2 in toluene.

Compound	$t_{1/2}$ @298K	$\Delta H^{\ddagger}$ (kJ/mol)	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (J/K mol)
NBD-H_2	6.3 hours	89.5	21.40	-31.1
NBD-Me_2	7.7 hours	89.7	21.45	-32.2
NBD-*i*Pr_2	56 hours	90.7	21.69	-45.3

6 Extinction coefficients

Absorption coefficients were determined by repeated measurement. The data are found in the Table S2.

Table S2. Measured values of the absorption coefficients in M^{-1} cm^{-1}.

	NBD-H_2	NBD-Me_2	NBD-*i*Pr_2
	2359	2196	1951
	2372	2142	1977
	2315	2200	1962
Average	2349	2179	1958
Std. dev.	30	32	15

7 Differential scanning calorimetry of quadricyclanes

NBD-H_2, **NBD-Me_2** and **NBD-iPr_2** (ca. 15 mg) were dissolved in deuterated acetonitrile or chloroform (ca. 3 mL). The solution was irradiated for ca. 2 hours using a Osram Powerstar HQI-R 150 W metal halide lamp, and the conversion to QC monitored using ^{1}H NMR spectroscopy. The solvent was evaporated, and ca. 1 mg of the obtained quadricyclane was sealed in a 40 µl aluminum pan. DSC was run performing a double cycle of heating (at 10 °C/min from 0 to 180°C) and cooling (at 40 °C/min from 180 to 0°C). Each measurement was performed twice with good agreement. The endothermic peaks were integrated, and the value normalized by the mass of QC to give the values reported in the main text. DSC thermograms are shown in Figure S11 to Figure S13.

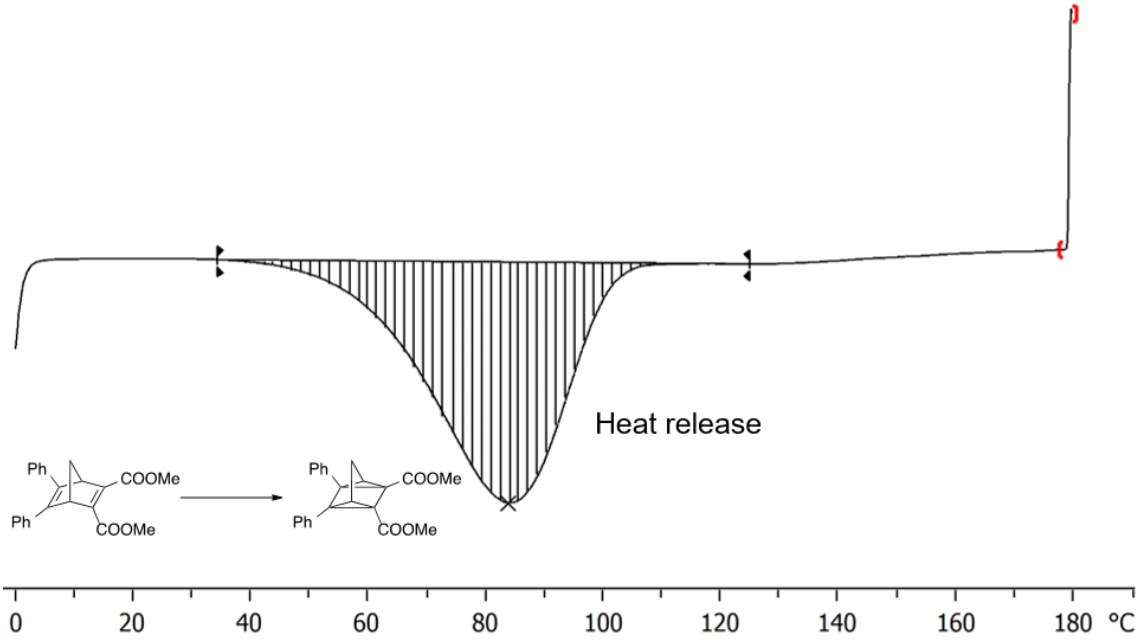


Figure S11. DSC thermogram showing the heat release peak for the thermal back-conversion of **QC-H2** to **NBD-H2**.

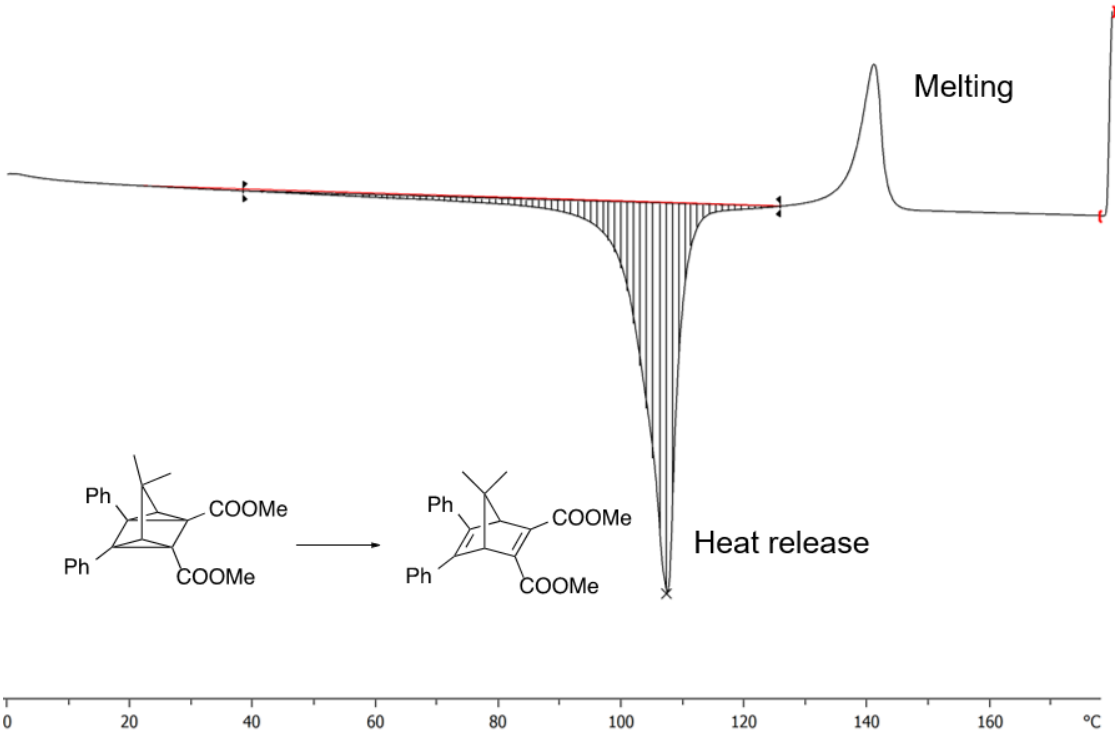


Figure S12. DSC thermogram showing the heat release peak for the thermal back-conversion of **QC-Me2** to **NBD-Me2**.

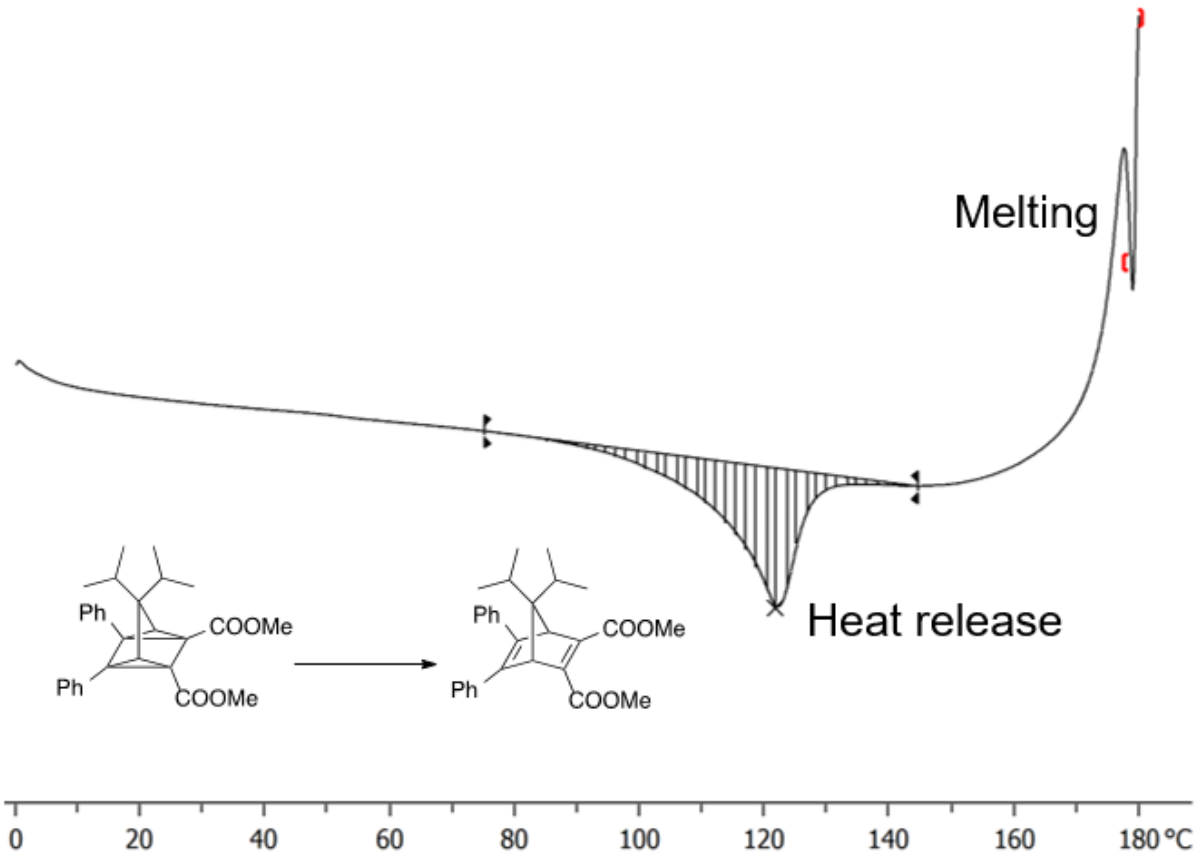


Figure S13. DSC thermogram showing the heat release peak for the thermal back-conversion of **QC-*i*Pr2** to **NBD- *i*Pr 2**.

8 Test of photoconversion in sun-like conditions in a demonstrative device

The testing device functions as a flow reactor that allows for continuous harvesting of solar energy (Figure S14). It is made of a fused silica chip (Litcon) containing a 60 μm deep and 3.5 mm wide winding channel, forming a total irradiated area of about 400 mm^2. The chip was held in place with a custom made 3D printed holder. A full spectrum solar simulator (EYE Solar Simulation System, Class B/C) was used during the experiments to reproduce the solar irradiation (≈1 sun, AM 1.5). A Sciencetech sun calibrated reference detector was used to

measure the intensity of the solar simulator lamp. A syringe pump (Fisher Scientific) was used to regulate the flow.

NBD-iPr$_2$ was dissolved in deuterated toluene (50 mM) and the conversion to the QC isomer after passing through the collector (2 mL/h, 41 s residence time) was measured by comparing the relative intensity of the ^{1}H NMR peaks associated to the two isomers (64% conversion to QC, measured in two independent experiments).

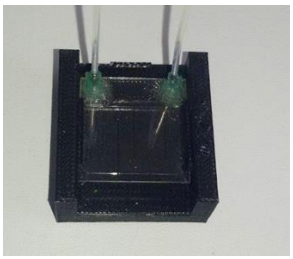


Figure S14. Photo of the fabricated device, which was used to test the performance of **NBD-*i*Pr$_2$**.

To calculate the solar energy storage efficiency (η_{MOST}), the following equation was used:[12]

$$\eta_{MOST} = \frac{\dot{n}_{NBD} \cdot \alpha_{QC} \cdot \Delta H_{storage}}{A \times E_{AM1.5}}$$

Where α_{QC} is the measured conversion to the QC isomer after irradiation, $\Delta H_{storage}$ is the stored energy of the QC isomer relative to the NBD isomer (in J/mol), $\dot{n}$ is the flow speed (in mol s^{-1}), A the irradiated area (in m^{-2}), and $E_{AM1.5}$ is the energy of incoming solar radiation (in W m^{-2}).

9 Computational

9.1 Photochemical calculations

9.1.1 Methods

For the photochemical calculations, we employed state-average CASSCF using a development version of Molcas 8.1 and the 6-31G(d) basis set. **P-R$_2$** has four π molecular orbitals and the

natural choice of an active space would therefore be four electrons in four orbitals, as was done by Roos in studying the absorption spectrum and Antol in studying the photorelaxation pathways of P-H_2.[13,14] However, we found that a 4in4 active space lead to near-state-degeneracies or state crossings that disappeared at the MS-CASPT2[15,16] level and caused problems during optimizations (Figure S15). This problem was not present for Antol using MR-CIS optimizations. An active space of 2in2 did not generate this problem and gave results that were similar to those obtained from MS-CASPT2(4in4). A 2in2 active space should be sufficient to describe the CIs as the NBD system can be described within the two-electron two-orbital model of homosymmetric and heterosymmetric biradicaloids established by Michl and co-workers.[17] The smaller active space also allowed us to treat **NBD-H_2** and **NBD-Me_2**.

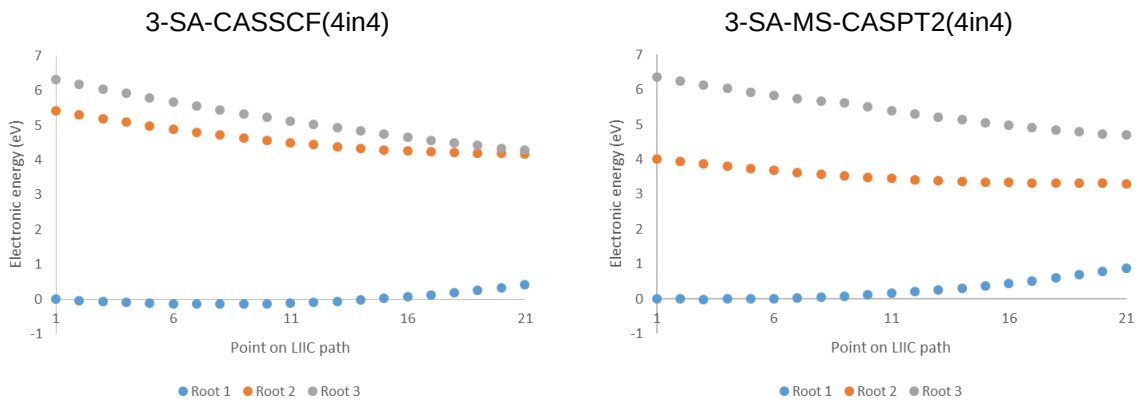
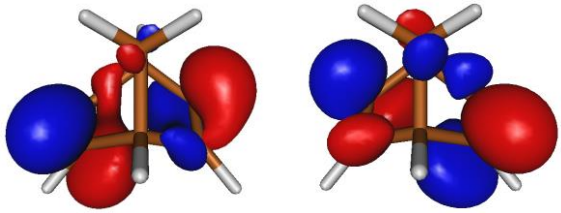


Figure S15. Comparison of CASSCF and MS-CASPT2 with 4in4 active space on linear interpolation path between FC geometry to the S_1 minimum geometry for **NBD-H$_2$**.

Conical intersections (CIs) were optimized and characterized at the 2-SA-CASSCF(2in2)/6-31G(d) level using a development version of Molcas 8.1 and the procedures described by Lindh and co-workers.[18] Relaxation from the CI structures to the NBD and QC minima were confirmed by minor perturbation from the CI structure along the relaxation vector obtained from the CI characterization followed by minimum energy path calculations on the lower surface. Minima on the S_1 surface were instead optimized with 3-SA-CASSCF(2in2) as comparison to MS-CASPT2(4in4) showed that the these minima were too deep at the 2-SA-CASSCF(2in2) level.

The orbitals included in the active space are shown in Figure S16 to Figure S18 for active spaces of 2in2 and 4in4. Note that the active space orbitals of the 2in2 set can be equally well described as localized or delocalized.[17] During our calculations different sets of delocalized and localized orbitals could be obtained for very similar structures. Although this shift does not affect the energies, the character of the states (doubly excited, singly excited etc.) changes when the orbital set is transformed and care has to be taken to ensure the identity of the states.

3-SA-CASSCF(2in2)



3-SA-CASSCF(4in4)

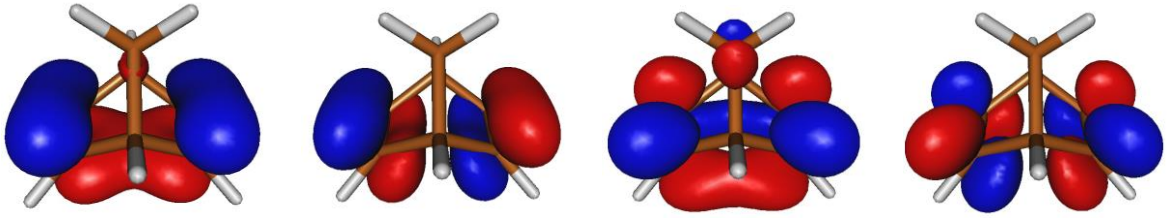
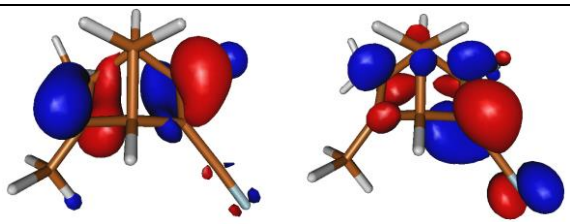


Figure S16. State-average active space orbitals for **P-H$_2$** with 2in2 and 4in4 active spaces plotted at 0.05 isodensity surface. The DFT-optimized geometry of the ground state NBD isomer is used.

3-SA-CASSCF(2in2)



3-SA-CASSCF(4in4)

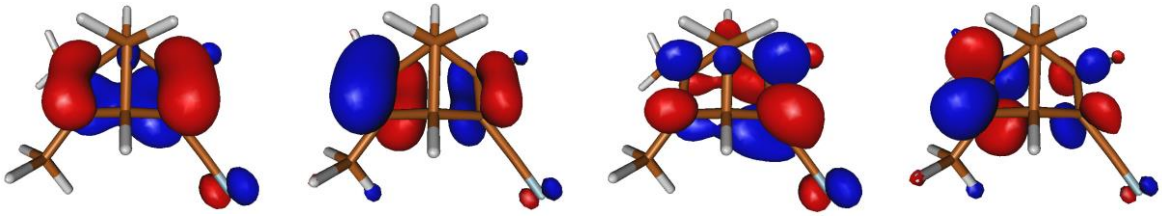
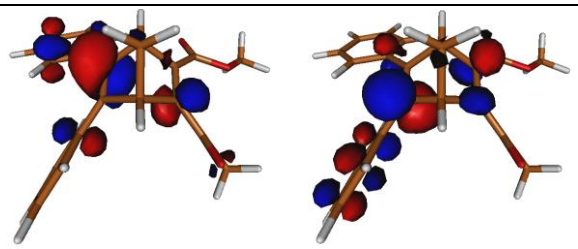


Figure S17. State-average active space orbitals for **DA-H$_2$** with 2in2 and 4in4 active spaces plotted at 0.05 isodensity surface. The DFT-optimized geometry of the ground state NBD isomer is used.

3-SA-CASSCF(2in2)



3-SA-CASSCF(4in4)

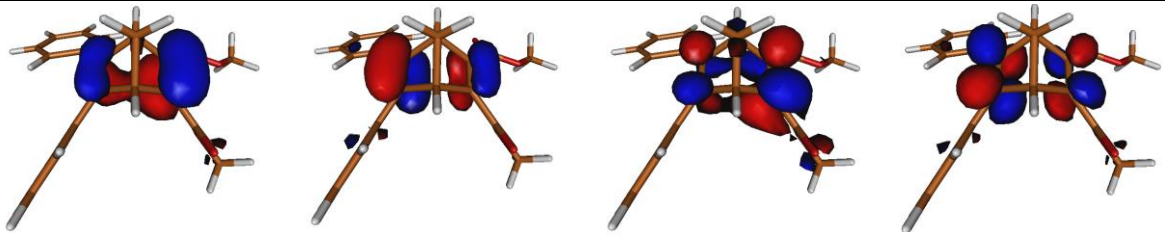


Figure S18. State-average active space orbitals for **NBD-H$_2$** with 2in2 and 4in4 active spaces plotted at 0.05 isodensity surface. The DFT-optimized geometry of the ground state NBD isomer is used.

The calculated excitation energy for **NBD-H$_2$** is 4.01 eV with 3-SA-MS-CASPT2(4in4)/6-31G(d) and 3.75 eV with 3-SA-MS-CASPT2(2in2)/6-31G(d), in fair agreement with the experimental value of 3.64 considering the small basis set and that no solvent model was used. We are thus confident that an active space of 2in2 is sufficient for describing the S_1 PES from the Franck-Condon region to the CI for the compounds considered.

NPA charges were calculated from the densities of the state-specific natural spin orbitals from Molcas using the Molden2aim 4.0.2 program[19] and NBO6.[20]

9.1.2 Conical intersections

Characterization

To characterize the conical intersections (CIs), we used the methodology described by Lindh and co-workers.[18] This description can be used to investigate relaxation pathways from a CI in the absence of dynamic effects. In particular, the gradients of the electronic states at the conical

intersection can be plotted as a function of the polar coordinates *r* and θ of the branching plane (the plane for which the degeneracy of the states is broken). We focused on the gradients of the lower state, which gives information on the relaxation pathways from the CI. In particular, the CI can be described as single-path or bifurcating, depending on if there is only one preferred direction of relaxation or two (within the linear model). The relaxation pathways show up as minima in the plot and the θ value at the minimum gives the direction of relaxation. Minimum energy path calculations on the lower energy surface starting from small displacements along the relaxation directions can then confirm that the pathway leads to the correct minimum on the lower energy surface. The relative height of the two minima for a bifurcating CI gives an indication of which pathway is preferred over the other.

For **P-R$_2$**, relaxation to the NBD isomer is preferred (Figure S19), in agreement with the experimental quantum yield of ca. 0.05 for **P-H$_2$**. As R changes from H to *t*Bu, the gradient difference between the two pathways decreases, indicating that the increased steric pressure favors the pathway forming the QC isomer. For **DA-R$_2$**, the gradient difference is much smaller, in line with the experimental quantum yield of 0.68 for **DA-H$_2$** (Figure S20). Increasing steric bulk again favors relaxation to the QC isomer, and for **DA-*t*Bu$_2$** it is actually preferred. For **NBD-R$_2$**, the NBD isomer is preferred for R = H and the QC isomer for R = Me (Figure S21). This relative change in gradients is consistent with the increase in experimental quantum yield going from **NBD-H$_2$** to **NBD-Me$_2$**.

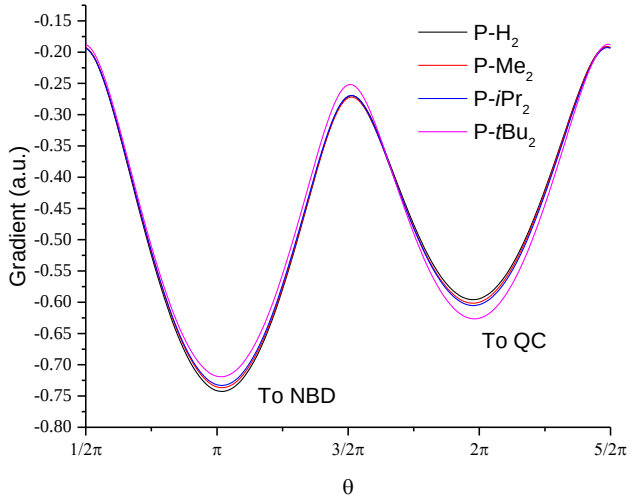


Figure S19. Gradient of the lower electronic state as a function of the angular coordinate θ for the CI of **P-R2**. Relaxation from minimum close to π leads to NBD and from minimum close to 2π to QC.

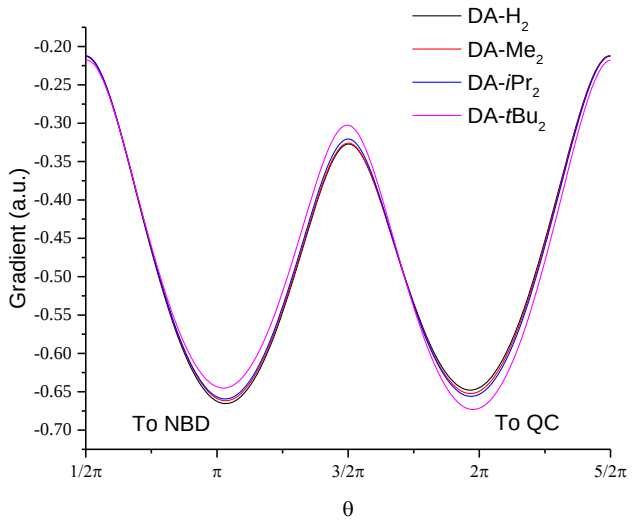


Figure S20. Gradient of the lower electronic state as a function of the angular coordinate θ for the CI of **DA-R2**. Relaxation from minimum close to π leads to NBD and from minimum close to 2π to QC.

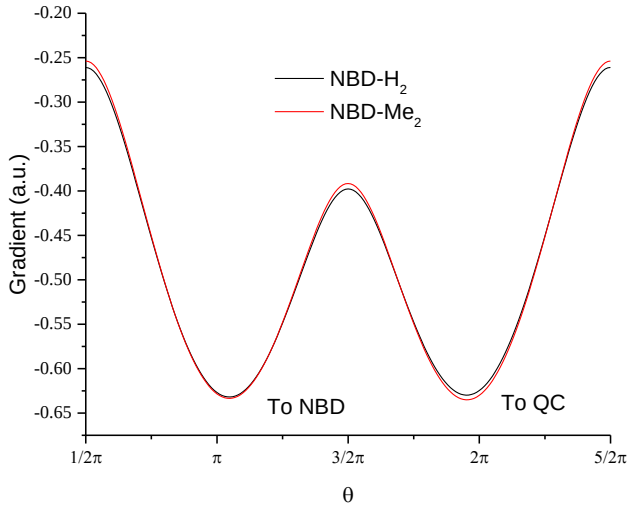


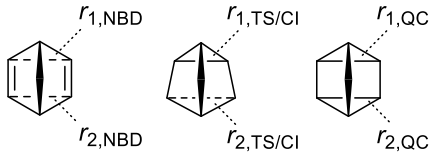
Figure S21. Gradient of the lower electronic state as a function of the angular coordinate θ for the CI of **NBD-R2** with R = H and Me. Relaxation from minimum close to π leads to NBD and from minimum close to 2π to QC.

Relation to energy storage and extent of bond formation

The difference in gradient between the minima can be correlated to the storage energy and extent of bond formation according to the Hammond postulate (see also section 9.4.2.1). The extent of bond formation was calculated as an average of the two forming bonds at the TS and CI structures for **P-R2**, **DA-R2** and **NBD-R2** (Table S3). These were calculated according to the formula in Figure S22. Note that these values are given at different levels of theory (DFT for the TS and CASSCF for the CI) and that comparison of absolute values should therefore be made with caution. The trend is, however, that the CI structure is less affected than the TS structure by the steric bulk.

Table S3. Extent of average bond formation in TS and CI structures. TS geometries at the PBE-D3(BJ)/6-31+G(d,p) and the CI geometries at the CASSCF(2in2)/6-31G(d) levels. Both evaluated against PBE-D3(BJ)/6-31+G(d,p) NBD and QC geometries.

P-R_2	H	Me	iPr	tBu
TS	50%	48%	47%	43%
CI	56%	55%	54%	51%
DA-R_2				
TS	54%	53%	52%	46%
CI	53%	53%	52%	49%
NBD-R_2				
TS	53%	52%	50%	45%
CI	55%	54%	-	-



Avg. bond formation =
$(|r_{1,TS} - r_{1,NBD}|/|r_{1,QC} - r_{1,NBD}| + |r_{2,TS} - r_{2,NBD}|/|r_{2,QC} - r_{2,NBD}|)/2$

Figure S22. Formula for calculation of average bond formation.

The gradient difference is linearly correlated to the extent of bond formation (Figure S23). As discussed in the manuscript, this is probably due to that the ground state TS position on the reaction coordinate is more affected by the steric bulk than the CI position. Correlation between gradient difference and storage energy is very similar (Figure S24).

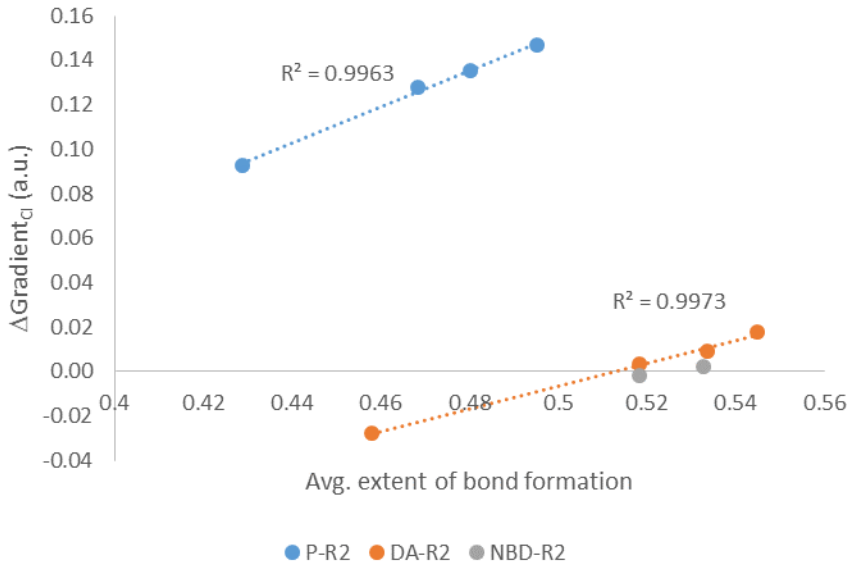


Figure S23. Correlation between bond formation in the TS at the PBE-D3(BJ)/6-31+G(d,p) level and gradient difference between the relaxation minima at the CI geometry at the CASSCF/6-31G(d) level.

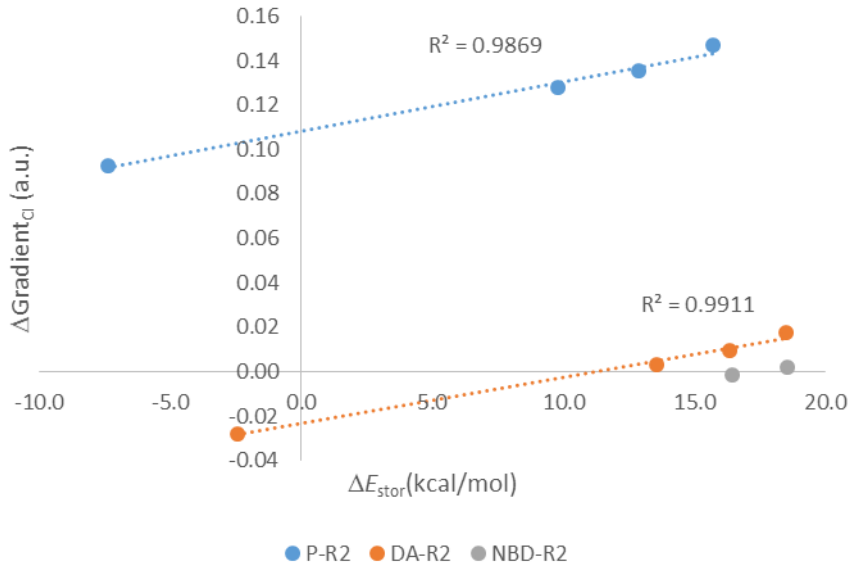


Figure S24. Correlation between storage energy at the PBE-D3(BJ)/6-31+G(d,p) level and gradient difference between the relaxation minima at the CI geometry at the CASSCF/6-31G(d) level.

9.2 MEPs and linear interpolations

Minimum energy structure and its photochemical influence

A minimum energy path calculation for **DA-H$_2$** at the 3-SA-CASSCF(2in2)/6-31G(d) level led to a S_1 minimum energy structure that was confirmed by numerical frequency calculations. Although two imaginary frequencies associated with rotation of the vinylic methyl groups were found, perturbation of the molecule along these modes and subsequent optimization lead back to the same minimum structure. We conclude that the imaginary frequencies associated with this methyl group rotations are due to the small energy barrier for rotation caused by lack of dispersion forces in CASSCF and/or inaccuracies in the numerical frequencies. Therefore, they can be excluded for the purpose of confirming the minimum structure.

Corresponding minima were found also for **DA-Me$_2$** and **DA-*i*Pr$_2$** but not for **DA-*t*Bu$_2$**, for which all minimizations instead lead to the CI structure region. For **NBD-H$_2$** and **NBD-Me$_2$** the optimization also lead to a similar structure, although these structures could not be confirmed by frequency calculations due to the large size of the systems. We also located a minimum for **P-H$_2$**.

As the excess energy from vertical excitation to the FC region is always much larger than the well-depth both with and without dynamical correlation, the minimum is not likely to be populated and should not affect the photochemistry (Table S4).

Table S4. Excess energies from vertical excitation and well depths at 3-SA-CASSCF(2in2) and 3-SA-CASPT2(2in2) in kcal/mol.

	CASSCF	CASPT2
Excess energy		
P-H$_2$	29.0	24.4
DA-H$_2$	28.2	12.6
NBD-H$_2$	30.1	14.5
Depth of well		
P-H$_2$	0.4	0
DA-H$_2$	2.1	0.3
NBD-H$_2$	3.2	2.1

Linear interpolations

Linear interpolation in internal coordinates (LIIC) was carried out on structures that had first been aligned using the RMSD procedure in VMD 1.9.2.[21] Including initial and final structures, 21 structures were generated.

The LIICs from the FC points (DFT-optimized ground state geometries) to the CI structures (optimized with 2-SA-CASSCF(2in2)) for **P-H$_2$**, **DA-H$_2$** and **NBD-H$_2$** are shown in Figure S25 to Figure S27. The results at the 3-SA-CASSCF(2in2) 3-SA-MS-CASPT2(4in4) levels show that the S_1 state is consistently well-separated from the S_2 state along this path and that 3-SA-CASSCF(2in2) is qualitatively correct. There is also no barrier present.

The LIICs from the optimized S_1 minimum structures for **P-H$_2$**, **DA-H$_2$** and **NBD-H$_2$** are shown in Figure S28 to Figure S30. At the 3-SA-CASSCF(2in2) level there is a small barrier of ca 2-3 kcal/mol which mostly disappears at the 3-SA-CASPT2(2in2) level. We opt to use this level of theory near the minimum region as the state interaction is very large for 3-SA-MS-CASPT2(4in4) and that the results are therefore not reliable. Increased steric bulk in **DA-Me$_2$**, **DA-*i*Pr$_2$** and **NBD-Me$_2$** reduces the barrier height (Figure S31 and Figure S32), but this is unlikely to have any effect on the experimental outcome as the barrier is small compared to the excess thermal energy received upon vertical excitation. Also, as shown in the FC-CI interpolations, there are barrier-less pathways from FC to the CI and the barrier on the interpolation is an upper bound for the minimum barrier to the CI.

Finally, the combined LIICs from the FC point to the S_1 minimum and from there to the CI point give a full picture of the S_1 relaxation of the system (Figure S33 to Figure S35).

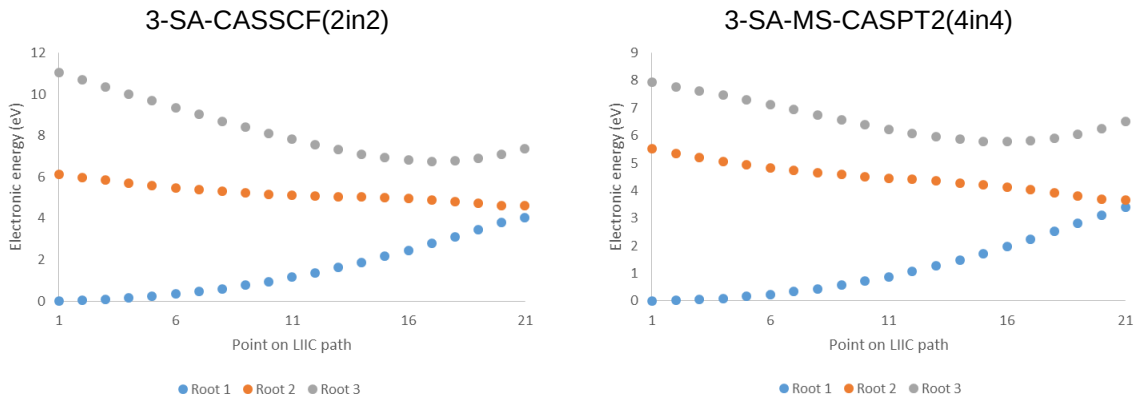


Figure S25. LIIC pathway from FC geometry to the optimized CI geometry for **P-H$_2$**.

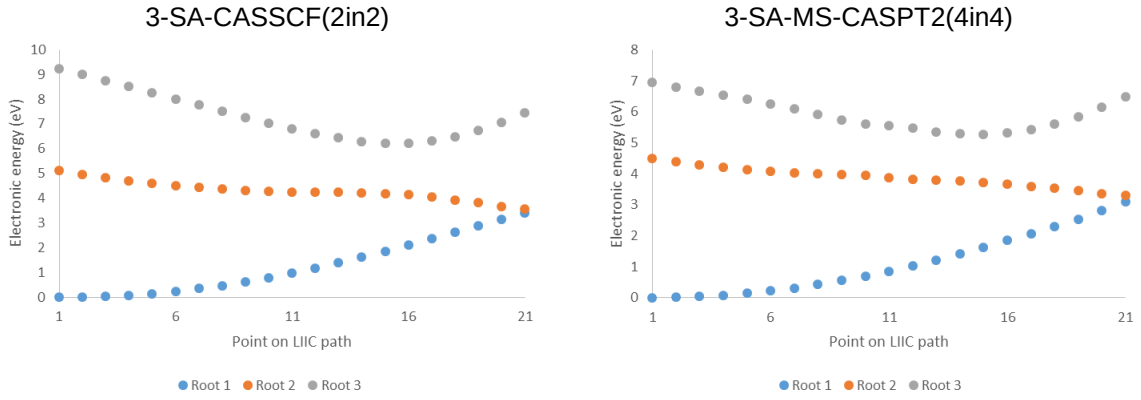


Figure S26. LIIC pathway from FC geometry to the optimized CI geometry for **DA-H$_2$**.

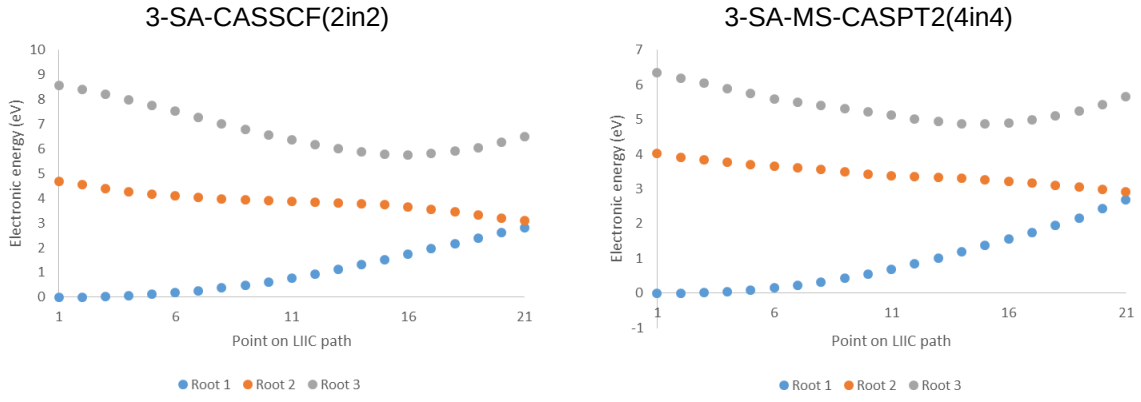


Figure S27. LIIC pathway from FC geometry to the optimized CI geometry for **NBD-H$_2$**.

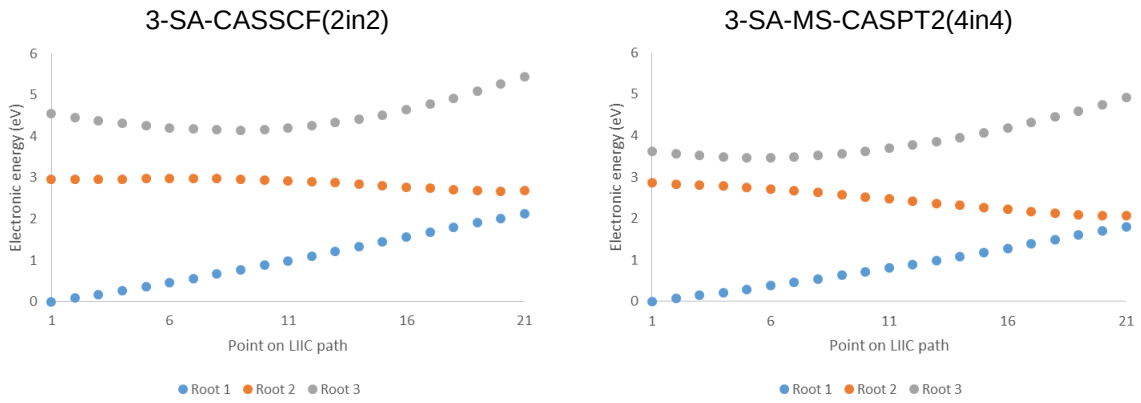


Figure S28. LIIC pathway from S_1 minimum geometry to the optimized CI geometry for **P-H$_2$**.

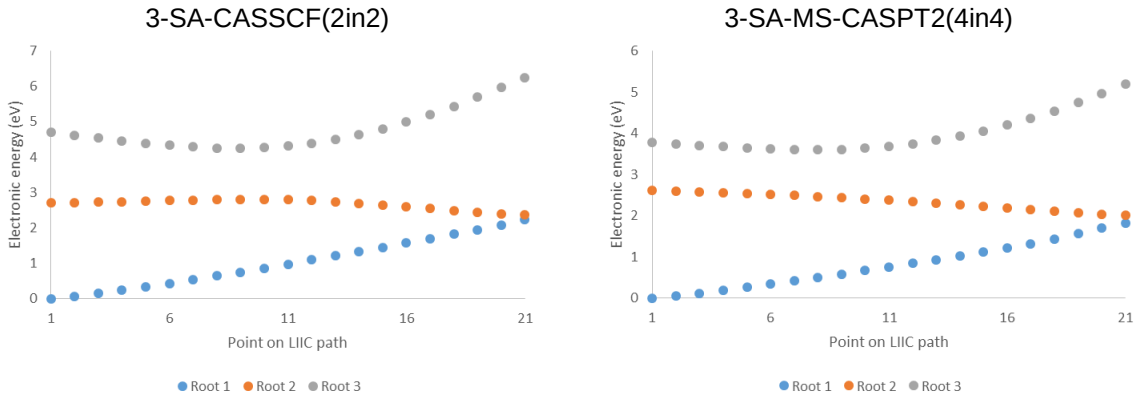


Figure S29. LIIC pathway from S_1 minimum geometry to the optimized CI geometry for **DA-H$_2$**.

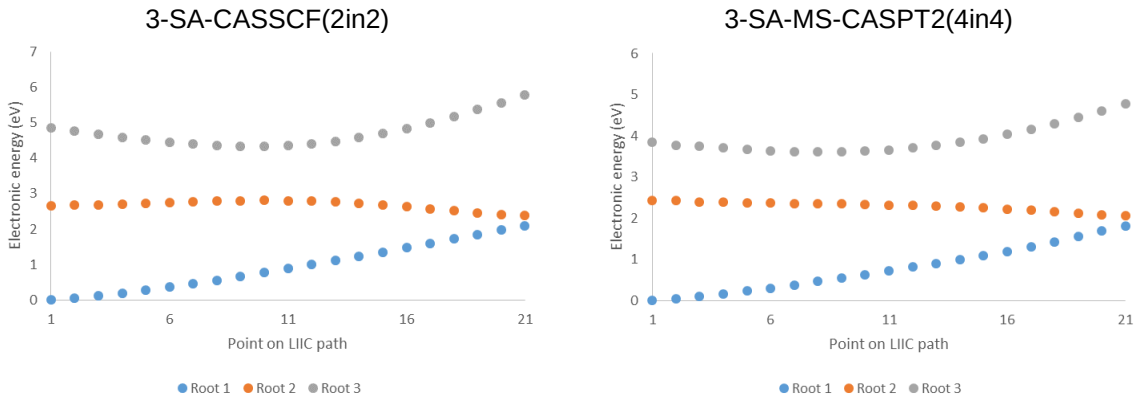


Figure S30. LIIC pathway from S_1 minimum geometry to the optimized CI geometry for **NBD-H$_2$**.

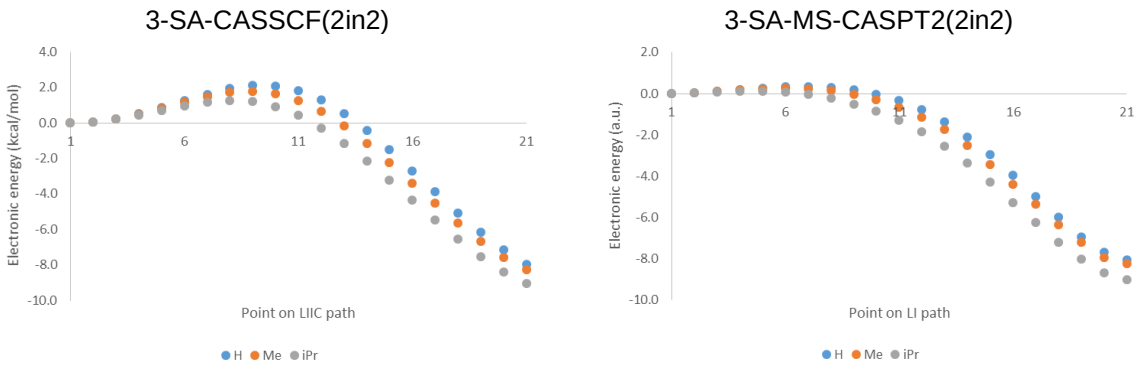


Figure S31. LIIC pathway for the S_1 state from the S_1 minimum geometry to the optimized CI geometry for **DA-R2** with R=H, Me and *i*Pr.

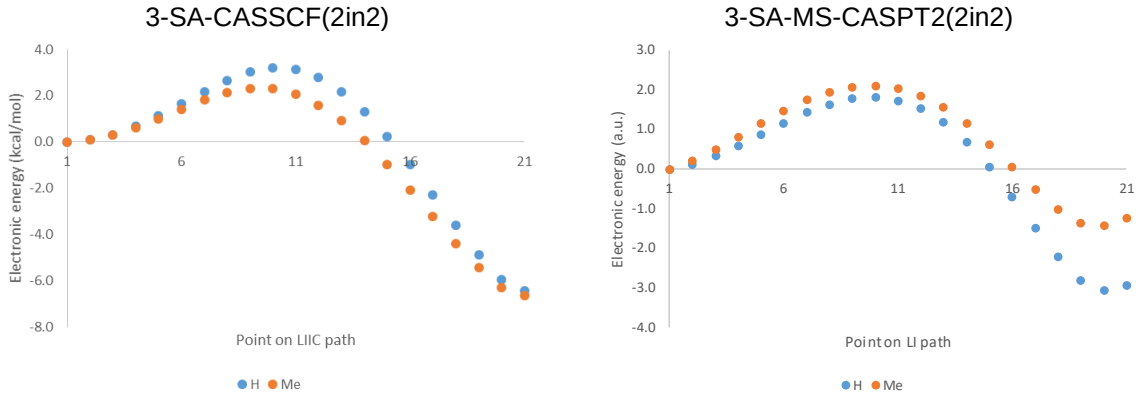


Figure S32. LIIC pathway for the S_1 state from the S_1 minimum geometry to the optimized CI geometry for **NBD-R2** with R=H and Me. The energy rise at the last points at the CASPT2 level is due to that the CI position has a slightly different geometry at this level than that used for optimization.

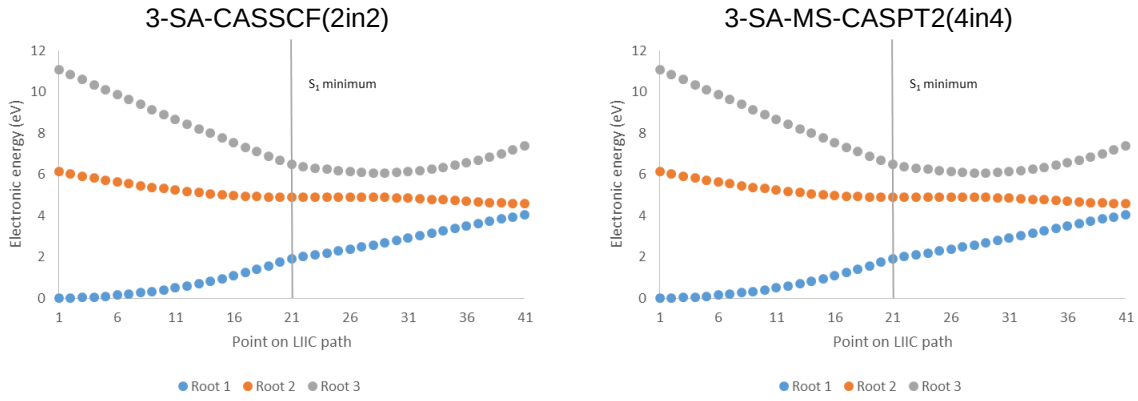


Figure S33. LIIC pathway from the FC geometry to the optimized CI geometry via the S_1 minimum for **P-H2**. The vertical bar represents the S_1 minimum geometry.

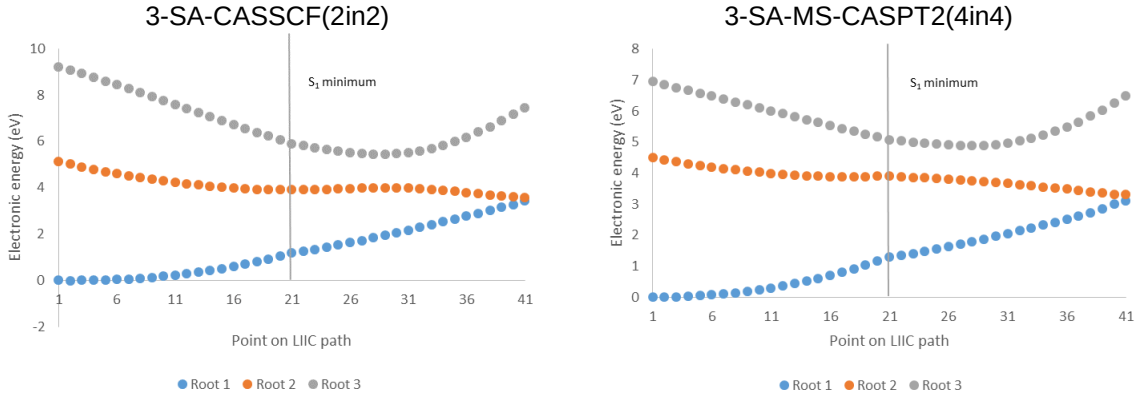


Figure S34. LIIC pathway from the FC geometry to the optimized CI geometry via the S_1 minimum for **DA-NBD-H2**. The vertical bar represents the S_1 minimum geometry.

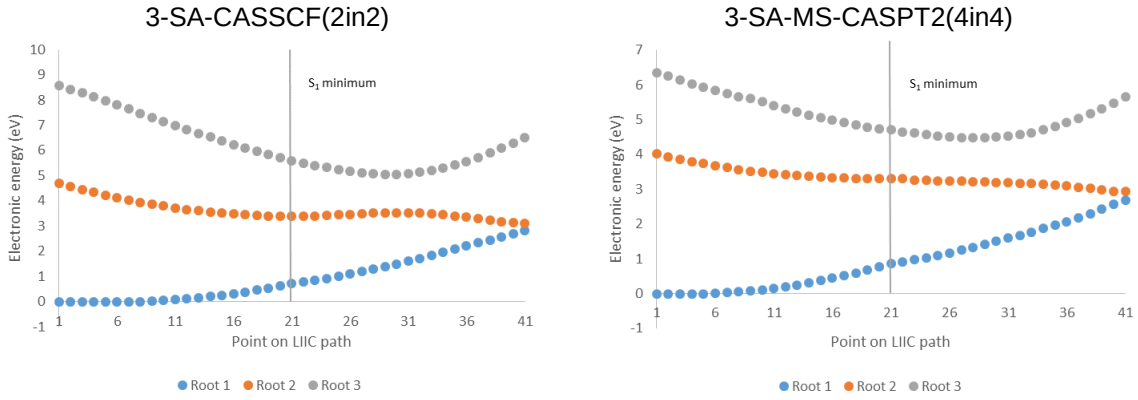


Figure S35. LIIC pathway from the FC geometry to the optimized CI geometry via the S_1 minimum for **NBD-H2**. The vertical bar represents the S_1 minimum geometry.

9.3 TD-DFT calculations

We benchmarked our TD-DFT method against the excitation energies of the NBD compounds reported by Gray *et al.* compounds (Table S5).[22] Geometries were optimized with PBE-D3(BJ)/6-31+G(d,p) and TD-DFT calculations were performed using the CAM-B3LYP and LC-τHCTH functionals with the 6-311+G(2d,p) basis set. The experimental data were taken from the ε_{max} values of ref 22. The performance of LC-τHCTH is very good with a MAD of only 0.11 kcal/mol over the set, which is below half the error of CAM-B3LYP. While CAM-B3LYP consistently underestimates the absorption energies, LC-τHCTH is more balanced with some overestimations and some underestimations.

Table S5. Calculated $S_0 \rightarrow S_1$ excitation energies in eV with TD-DFT and different functionals compared to experiment (Δ = Exc. (Exp.) – Exc. (TD-DFT)). Solvent effects were included by the SMD solvent model and toluene as the solvent.

	CAM-B3LYP		LC-τHCTH		Exp.
Compound	Exc.	Δ	Exc.	Δ	Exc.
a	3.75	-0.28	3.95	-0.08	4.03
b	3.66	-0.35	3.87	-0.14	4.01
c	3.53	-0.37	3.77	-0.13	3.90
d	3.35	-0.19	3.61	0.07	3.54
e	3.28	-0.12	3.55	0.15	3.40
MAD	0.26		0.11		
MSD	-0.26		-0.03		

9.4 Storage energies and transition state calculations

9.4.1 Storage energies

To validate our computational scheme for storage energies, we compared against the high-level composite method CBS-QB3.[23] Unfortunately, this method cannot be used for the **NBD-R2** series as the molecules are too big. Instead we chose the DFT method which performed best for **P-R2** and for **DA-R2** with R = H and Me. In this way we assess both the effects of increasing steric bulk, and the presence of donor and acceptor groups. The results (Table S6) show that

PBE-D3(BJ) heavily underestimates Δ*H* for the parent system. B3LYP[24] does a good job for the parent system but overestimates Δ*H* for the DA model. On average, CAM-B3LYP has a small underestimation of Δ*H* for the parent system (2.2-3.3 kcal/mol) but is accurate for the DA model (1.2-1.3 kcal/mol underestimation). As it is also a good performer for the activation energies, we chose CAM-B3LYP-D3(BJ) for the calculations on the **NBD-R$_2$** compounds.

Table S6. Storage enthalpies with different methods and the difference to the reference CBS-QB3 data. Geometries are optimized with PBE-D3(BJ)/6-31+G(d,p). B3LYP and CAM-B3LYP-D3(BJ) use the 6-311+G(d,p) basis set and the vibrational contributions from PBE-D3(BJ). Values in kcal/mol.

	CAM-B3LYP-D3(BJ)		PBE-D3(BJ)		B3LYP		CBS-QB3	Exp.
P-R$_2$	Δ*H*	Δ	Δ*H*	Δ	Δ*H*	Δ		
H	20.6	-2.2	15.7	-7.1	23.1	0.3	22.8	22.0 ± 0.3
Me	16.5	-2.4	12.8	-6.1	18.7	-0.2	18.9	
*i*Pr	13.2	-2.3	9.7	-5.9	15.0	-0.6	15.6	
*t*Bu	-5.0	-3.3	-7.6	-5.9	-2.6	-0.9	-1.7	
DA-R$_2$								
H	20.0	-1.2	18.0	-3.2	24.3	3.1	21.3	
Me	17.1	-1.3	16.1	-2.3	22.7	4.2	18.5	

9.4.2 Transition state calculations

9.4.2.1 Transition state optimizations

Activation energies were calculated by broken-symmetry unrestricted DFT. This method can treat biradical transition states in some cases but should be properly benchmarked against multi-reference high-level methods.[25] We located the TS for **P-H$_2$** with UB3LYP/6-31G(d) and calculated the intrinsic reaction coordinate (IRC) leading from the TS to the NBD and QC isomers. In Figure S36 we display the S_0 IRC together with the energy of the T_1 state and the spin contamination ($<S^2>$) of the UDFT wave function. The spin contamination increases to ca 1 in the area of the TS, where the S_0 and T_1 states become degenerate. This spin contamination affects the calculated S_0 energy and makes it artificially high. As a consequence, the TS area is

too flat with B3LYP. Application of Yamaguchi's spin-projection formula[26] removes some of this spin contamination and reveals a sharper TS, although it does not give a smooth curve.

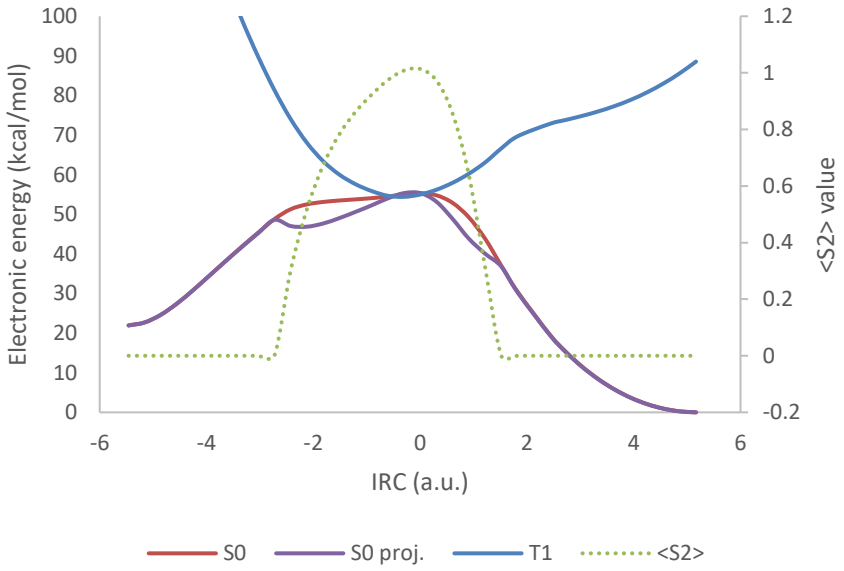


Figure S36. S_0 and T_1 energies along the IRC for **P-H$_2$** from TS structure to QC (left) and NBD (right) with (U)B3LYP/6-31G(d). Spin-projected energies for the S_0 state are also given.

The shape of the IRC was validated by computing it also using CASSCF(4in4)/6-31G(d) (Figure S37). The position of the TS is the same, as revealed by the almost identical curves using the CASSCF IRC and doing single-point CASSCF calculations on the B3LYP IRC. However, B3LYP gives a to flat TS region, especially on the QC side, due to spin contamination (*vide supra*). That the CASSCF single-point energies on the B3LYP IRC gives nearly the same result as the true CASSCF IRC confirms the reliability of using UDFT for obtaining the IRC.

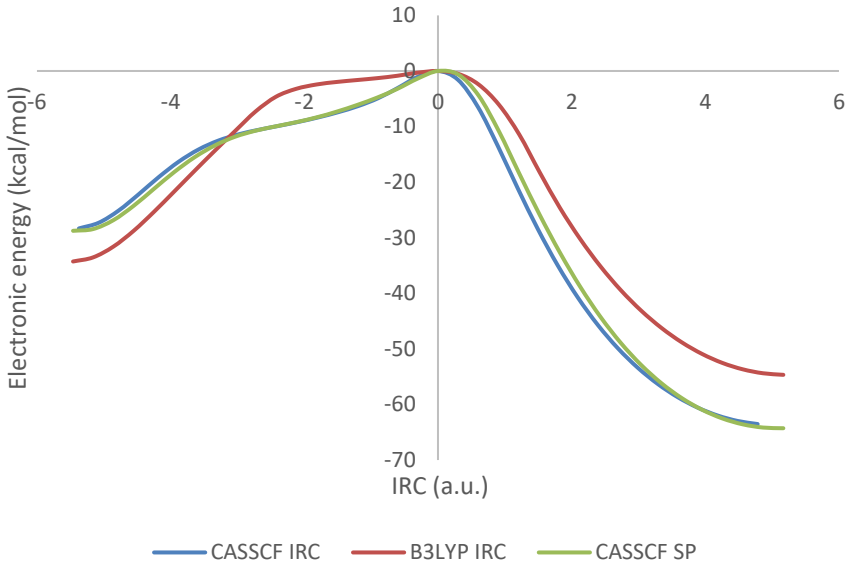


Figure S37. IRC for **P-H$_2$** from TS structure to QC (left) and NBD (right) computed with CASSCF and B3LYP. CASSCF single-point energies are computed at the B3LYP IRC coordinates.

Comparison between UB3LYP and UPBE and CASPT2(4in4)/6-31G(d) single-point energies on the UB3LYP IRC shows that UPBE has an IRC shape which is closer to that from CASPT2 (Figure S38). This is probably due to a lower amount of spin contamination for the pure DFT functional as compared to the hybrid UB3LYP. In addition, the IRC is less flat, which facilitates finding the transition state computationally. Therefore, we chose UPBE as the method of choice for TS optimizations.

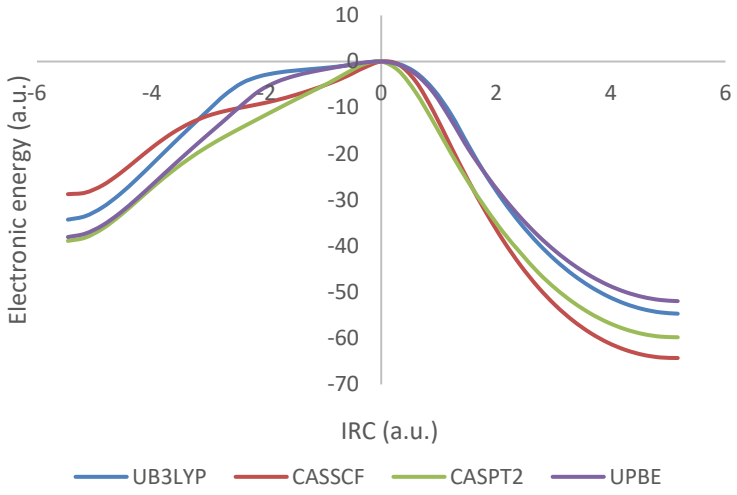


Figure S38. IRC shapes for **P-H$_2$** with various methods from single-point calculations on the UB3LYP IRC.

We then validated the UPBE method by calculating the IRC for **DA-H$_2$** (Figure S39). Also here the IRCs from UDFT are too flat as compared to CASPT2 (in this case, multi-state CASPT2(4in4)/6-31G(d) with a state-average over the lowest three singlet states). As for **P-H$_2$**, UPBE gives an IRC more similar to CASPT2 and the position of the TS is also correct.

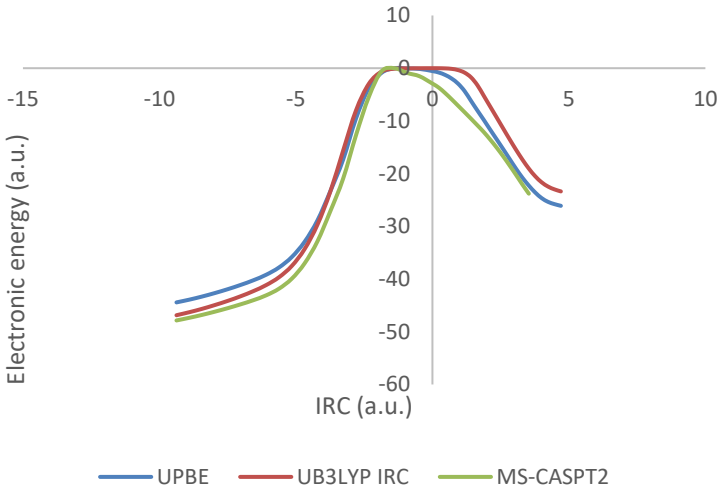


Figure S39. IRC shapes for **DA-H$_2$** with various methods from single-point calculations on the UB3LYP IRC.

The position of the TSs can be correlated to the energy difference between the two isomers at the same level of theory (Figure S40). This is in accordance with the Hammond postulate that states that the structure of the TS is closer to that minimum which is higher in energy. As the energy of the QC isomer moves closer to the energy of the NBD isomer, the structure also changes to be more like the NBD isomer. This takes expression as a lower extent of C---C bond formation in the TS as evidenced in Figure S40.

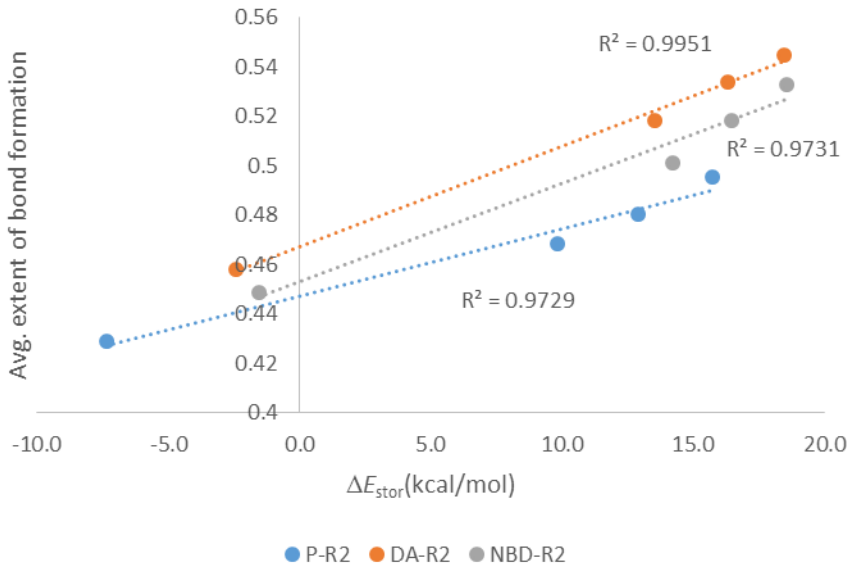


Figure S40. Correlation between storage energy and average bond formation at the TS at the PBE-D3(BJ)/6-31+G(d,p) level.

9.4.2.2 Activation energies

We compared the computed activation energies against high-level UBD(T)[27] calculations which can properly handle biradical transition states (Table S7).[25] A broken-symmetry HF orbital guess for the UBD(T) calculations was obtained with the guess=mix keyword in Gaussian. The experimental activation *enthalpy* for the parent system is included for comparison.[28] On balance, the DFT methods give reasonable activation energies, with UCAM-

B3LYP-D3(BJ) and UB3LYP-D3(BJ) underestimating the activing energy by 1-4 kcal/mol. UPBE-D3(BJ) is slightly more accurate.

Table S7. Calculated activation energies for QC→NBD reaction with different computational methods. UPBE-D3(BJ)/6-31+G(d,p) geometries were used. The 6-311+G(d,p) basis set was used for UB3LYP, UCAM-B3LYP-D3(BJ) and UBD(T).

	UCAM-B3LYP-D3(BJ)		UPBE-D3(BJ)		UB3LYP		UBD(T)	Exp.
	$\Delta E^{\ddagger}$	Δ	$\Delta E^{\ddagger}$	Δ	$\Delta E^{\ddagger}$	Δ	$\Delta E^{\ddagger}$	$\Delta H^{\ddagger}$
P-H_2	33.6	-0.7	36.3	2.0	32.5	-1.7	34.2	33.5
DA-H_2	26.7	-3.0	27.8	-1.9	25.3	-4.4	29.7	

UCAM-B3LYP-D3(BJ) and UPBE-D3(BJ) were also benchmarked against the experimental activation enthalpies reported by Gray *et al.* with excellent results (Figure S41).[22,29] There is an underestimation of the activation enthalpies by a few kcal/mol, consistent with the benchmark calculations in Table S7. For these particular compounds, UPBE-D3(BJ) performs even better than UCAM-B3LYP-D3(BJ), but the latter is still our method of choice as it can also be used to calculate accurate storage enthalpies. It can be noted in Figure S41 that both methods outperform the more complex CASPT2 calculations by Kuisma *et al.*[29] Finally we find that the solvent dependence is small as evidenced by the negligible effect of changing from the gas-phase to either toluene (ε = 2.4) or acetonitrile (ε = 35.7), as would be expected for a biradical mechanism (Table S8).

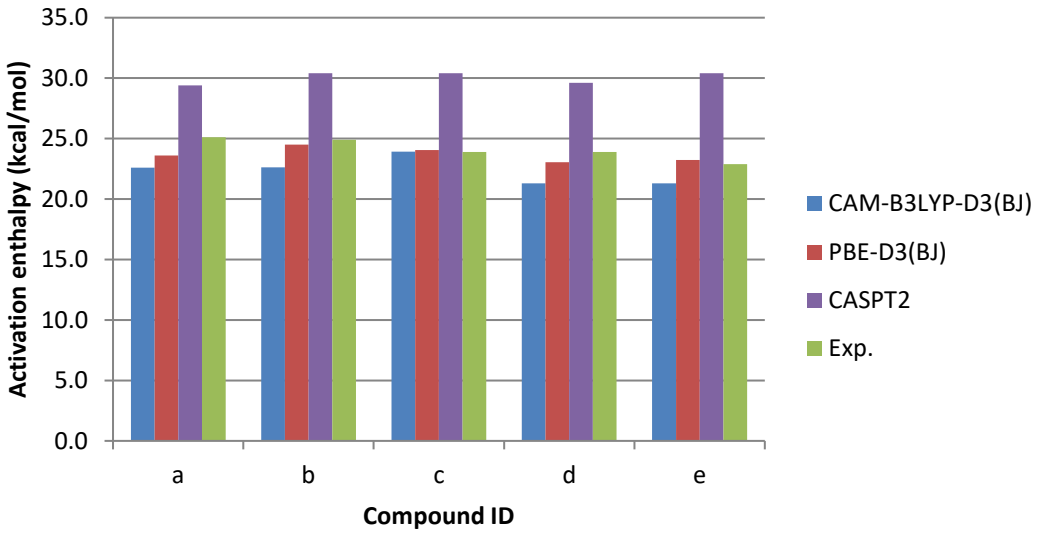


Figure S41. Calculated activation enthalpies for Gray compounds with various methods. The CASPT2 values neglect vibrational contributions as explained in the original reference.

Table S8. Calculated activation enthalpies for QC→NBD reaction with different solvents with CAM-B3LYP-D3(BJ)/6-311+G(d,p)//PBE-D3(BJ)/6-31+G(d,p) and the SMD solvent model.

	Gas-phase	Toluene	Acetonitrile
NBD-H_2	19.4	19.6	19.6
NBD-Me_2	19.1	18.9	19.0
NBD-*i*Pr_2	19.9	19.8	19.8

9.5 Character of S_1 homoaromatic minimum

9.5.1 Multicenter indices

The multicenter index (MCI) is a particular extension of the I_{ring} index[30] defined as:

$$I_{ring}(\mathcal{A}) = \sum_{i_1,i_2,\ldots i_N}^{NSO} n_{i_1} \ldots n_{i_N} S_{i_1 i_2}(A_1) S_{i_2 i_3}(A_2) \ldots S_{i_N i_1}(A_N) \qquad (1)$$

n_i being the occupancy of molecular orbital i. This expression is used both for closed-shell and open-shell species, and single-determinant and correlated wavefunctions. In this latter case, natural spin orbital (NSO) occupations and overlaps are used in eqn (1). $S_{ij}(A_1)$ are the elements of the atomic overlap matrix of the NSO integrated over the region of the atom A_1 defined in

the framework of the quantum theory of atoms in molecules (QTAIM).[31] Summing up all I_{ring} values resulting from the permutations of indices A_1, A_2... A_N, the mentioned MCI index[32] is obtained:

$$MCI(\mathcal{A}) = \frac{1}{2N} \sum_{P(\mathcal{A})} I_{ring}(\mathcal{A}) \qquad (2)$$

where $P(A)$ stands for a permutation operator which interchanges the atomic labels A_1, A_2, ..., A_N to generate the N! permutations of the elements in the string A. MCI is obtained with the ESI-3D program[33] MCI gives an idea of the electron sharing between all atoms in the ring. The more positive the MCI values for a given ring, the more aromatic the ring is. In this work, the NSO occupations are obtained from state-averaged CASSCF calculations.

9.5.2 NICS scans

We also performed NICS scans using Dalton2016.0. Here we used state-specific CASSCF with the 6-31G(d) and 6-31++G(d,p) basis sets. Although single-point NICS values[34] and ring-currents[35] have previously been used to characterize the aromaticity of excited states, the magnetic properties of aromatic molecules in the excited states are not well understood. We therefore believe that the results should only be taken as qualitative and it is highly recommended to also employ another type of aromaticity index besides NICS. That being said, the S_1 $NICS_{zz}$ scans of **P-H$_2$**, **DA-H$_2$** and **NBD-H$_2$** show the characteristic aromatic minima (Figure S42a). The $NICS(1)_{zz}$ values are -100.2 ppm for **P-H$_2$**, -132.8 ppm **DA-H$_2$** and -68.4 ppm for **NBD-H$_2$** with the 6-31G(d) basis set. The relative aromaticity given by NICS is therefore **DA-H$_2$** > **P-H$_2$** > **NBD-H$_2$**, which does not agree with MCI which gives **P-H$_2$** > **DA-H$_2$** > **NBD-H$_2$** As explained above, S_1 NICS should probably not be trusted for quantitative information and the relative order given by MCI is therefore more trustworthy.

The effect of increasing the basis set size from the rather small 6-31G(d) to 6-31++G(d,p) which includes diffuse functions is not large and does not change the qualitative results (Figure S42b). Unfortunately, **NBD-H2** was too big to calculate with the larger basis set. Increasing the active space size from 2in2 to 4in4 does have a significant effect on **P-H2** while **DA-H2** is less affected (Figure S43). It can be presumed that **NBD-H2** will behave similar as **DA-H2** as both are donor-acceptor NBDs. Importantly, the qualitative assessment of aromaticity is not changed as there is still a distinct minimum.

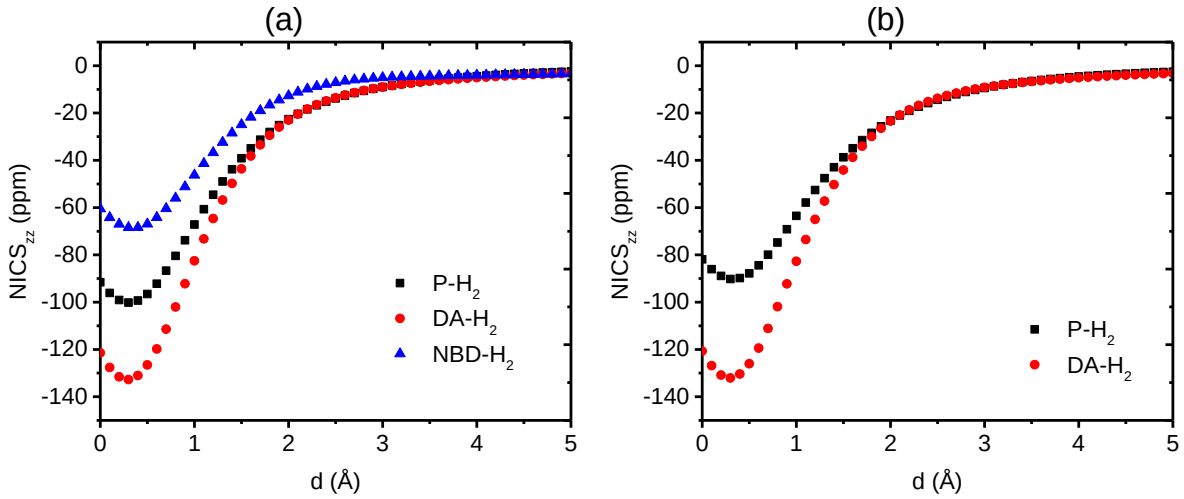


Figure S42. S_1 NICS scans with state-specific CASSCF(2in2) and the (a) 6-31G(d) and (b) 6-31++G(d,p) basis sets.

(a) (b)

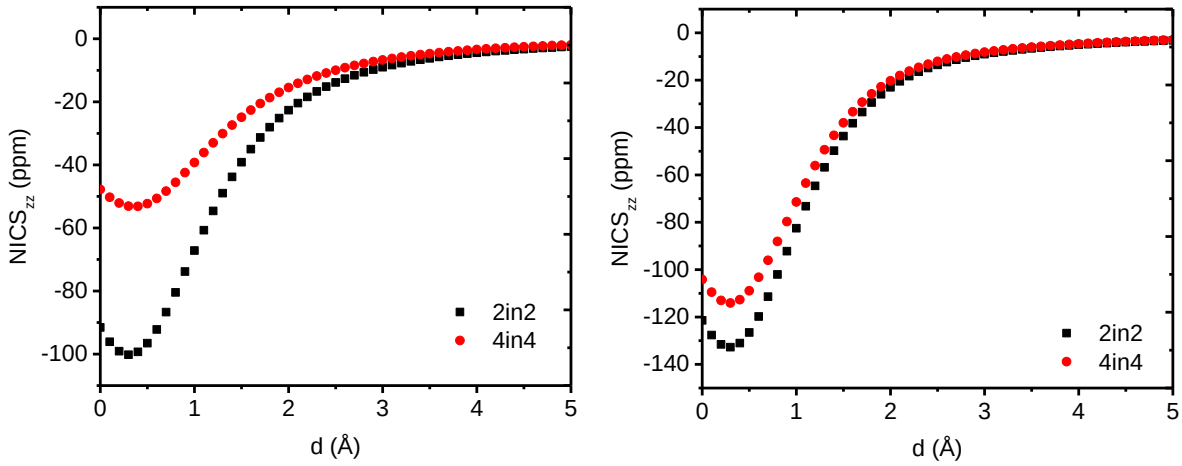


Figure S43. Dependance of active space size for S_1 NICS scans with CASSCF/6-31G(d) for (a) **P-H$_2$** and (b) **DA-H$_2$**.

9.6 MQ-R$_2$ compounds

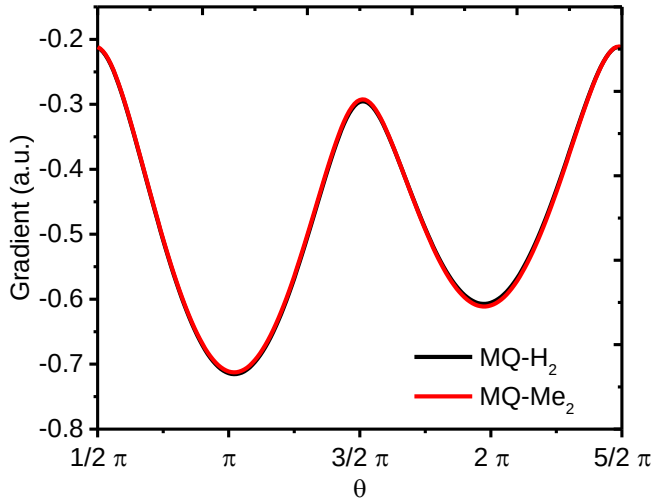


Figure S44. Gradient of the lower electronic state as a function of the angular coordinate θ for the CI of **MQ-R$_2$** with R = H and Me. Relaxation from minimum close to π leads to NBD and from minimum close to 2π to QC.

9.7 Coordinates and energies of the compounds

Below are coordinates and energies for minima and transition states optimized at the (U)PBE-D3(BJ)/6-31+G(d,p) level of theory. Conical intersection structures are given at the 2-SA-CASSCF(2in2)/6-31G(d) level.

P-H_2
NBD isomer
Symmetry: C_{2v}
Electronic energy: -271.152695918

C	1.24558	0.67398	-0.52114
C	0.00000	1.12671	0.27381
C	-0.00000	-1.12671	0.27381
C	1.24558	-0.67398	-0.52114
C	-0.00000	-0.00000	1.35626
H	-0.90844	-0.00000	1.98115
H	0.90844	0.00000	1.98115
C	-1.24558	0.67398	-0.52114
C	-1.24558	-0.67398	-0.52114
H	0.00000	2.16994	0.61950
H	-0.00000	-2.16994	0.61950
H	-1.93640	-1.34928	-1.02928
H	-1.93640	1.34928	-1.02928
H	1.93640	-1.34928	-1.02928
H	1.93640	1.34928	-1.02928

P-H_2
QC isomer
Symmetry: C_{2v}
Electronic energy: -271.127218008

C	0.76139	0.77602	-0.71189
C	0.00000	1.15396	0.55341
C	-0.00000	-1.15396	0.55341
C	0.76139	-0.77602	-0.71189
C	0.00000	0.00000	1.54316
H	-0.89909	0.00000	2.18475
H	0.89909	-0.00000	2.18475
C	-0.76139	0.77602	-0.71189
C	-0.76139	-0.77602	-0.71189
H	0.00000	2.19768	0.87945
H	-0.00000	-2.19768	0.87945
H	-1.45800	-1.43263	-1.23572
H	-1.45800	1.43263	-1.23572
H	1.45800	-1.43263	-1.23572
H	1.45800	1.43263	-1.23572

P-TS-H_2
Transition state
Symmetry: C_s
Electronic energy: -271.069414794
$<S^2> = 1.0093$

C	-0.59516	-0.62058	1.17226
C	0.20394	-1.19591	0.00000
C	0.64077	1.07188	0.00000
C	-0.59516	0.80553	0.83881
C	1.43870	-0.23905	0.00000
H	2.05857	-0.35476	-0.90465
H	2.05857	-0.35476	0.90465
C	-0.59516	-0.62058	-1.17226
C	-0.59516	0.80553	-0.83881
H	0.40769	-2.27365	0.00000
H	1.11870	2.05476	0.00000
H	-1.14205	1.59045	-1.36238
H	-1.38797	-1.14670	-1.70816
H	-1.14205	1.59045	1.36238
H	-1.38797	-1.14670	1.70816

P-CI-H_2
S_0/S_1 conical intersection
Symmetry: C_2

C	1.06889492	0.75413680	-0.56054614
C	-0.00556196	1.14397133	0.45025521
C	0.00544143	-1.14393524	0.45012659
C	0.87615472	-0.67411990	-0.63001586
C	0.00004656	-0.00001761	1.47016716
H	-0.88876773	-0.02025190	2.08975753
H	0.88891077	0.02016668	2.08970535
C	-0.87584203	0.67409749	-0.63014262
C	-1.07006106	-0.75423846	-0.55973981
H	-0.05616494	2.16762644	0.77915443
H	0.05626071	-2.16755983	0.77910925
H	-1.39529512	-1.36575387	-1.37483629
H	-1.28602153	1.32854706	-1.37458753
H	1.28641028	-1.32850408	-1.37448519
H	1.39559397	1.36583610	-1.37486309

P-H_2
S_1 minimum
Symmetry: C_{2v}

C	-1.056740	-0.692114	0.000292
C	-0.011887	-1.135106	-0.980055
C	0.012027	1.135085	-0.980200
C	-1.041929	0.714330	0.000199
C	-0.000088	-0.000076	-2.020195
C	1.042367	-0.714229	-0.000029
C	1.057178	0.692216	-0.000116
H	0.888902	-0.009482	-2.639697
H	-0.889267	0.009253	-2.639428
H	-0.022754	-2.161178	-1.310220
H	0.022793	2.161116	-1.310498
H	1.575086	1.333652	0.683064
H	1.546649	-1.366345	0.683233
H	-1.546005	1.366532	0.683531
H	-1.574438	-1.333465	0.683711

NICS scan:

bq	0.0	0.0	0.0

bq	0.0	0.0	0.1
bq	0.0	0.0	0.2
bq	0.0	0.0	0.3
bq	0.0	0.0	0.4
bq	0.0	0.0	0.5
bq	0.0	0.0	0.6
bq	0.0	0.0	0.7
bq	0.0	0.0	0.8
bq	0.0	0.0	0.9
bq	0.0	0.0	1.0
bq	0.0	0.0	1.1
bq	0.0	0.0	1.2
bq	0.0	0.0	1.3
bq	0.0	0.0	1.4
bq	0.0	0.0	1.5
bq	0.0	0.0	1.6
bq	0.0	0.0	1.7
bq	0.0	0.0	1.8
bq	0.0	0.0	1.9
bq	0.0	0.0	2.0
bq	0.0	0.0	2.1
bq	0.0	0.0	2.2
bq	0.0	0.0	2.3
bq	0.0	0.0	2.4
bq	0.0	0.0	2.5
bq	0.0	0.0	2.6
bq	0.0	0.0	2.7
bq	0.0	0.0	2.8
bq	0.0	0.0	2.9
bq	0.0	0.0	3.0
bq	0.0	0.0	3.1
bq	0.0	0.0	3.2
bq	0.0	0.0	3.3
bq	0.0	0.0	3.4
bq	0.0	0.0	3.5
bq	0.0	0.0	3.6
bq	0.0	0.0	3.7
bq	0.0	0.0	3.8
bq	0.0	0.0	3.9
bq	0.0	0.0	4.0
bq	0.0	0.0	4.1
bq	0.0	0.0	4.2
bq	0.0	0.0	4.3
bq	0.0	0.0	4.4
bq	0.0	0.0	4.5
bq	0.0	0.0	4.6
bq	0.0	0.0	4.7
bq	0.0	0.0	4.8
bq	0.0	0.0	4.9
bq	0.0	0.0	5.0

P-Me$_2$
NBD isomer
Symmetry: C_{2v}
Electronic energy: -349.679019193

C	1.23220	0.67379	-1.12689
C	0.00000	1.12472	-0.31921
C	-0.00000	-1.12472	-0.31921
C	1.23220	-0.67379	-1.12689
C	-0.00000	-0.00000	0.80633
C	-1.23220	0.67379	-1.12689
C	-1.23220	-0.67379	-1.12689
H	-0.00000	2.17053	0.02429
H	-0.00000	-2.17053	0.02429
H	-1.92978	-1.34941	-1.62505
H	-1.92978	1.34941	-1.62505
H	1.92978	-1.34941	-1.62505
H	1.92978	1.34941	-1.62505
C	-1.23501	0.00000	1.72090
H	-1.21741	-0.88800	2.37678
H	-1.21741	0.88800	2.37678
H	-2.18230	0.00000	1.16579
C	1.23501	-0.00000	1.72090
H	2.18230	-0.00000	1.16579
H	1.21741	0.88800	2.37678
H	1.21741	-0.88800	2.37678

P-Me$_2$
QC isomer
Symmetry: C_{2v}
Electronic energy: -349.658498758

C	-1.32763	-0.76202	-0.77660
C	-0.06531	-0.00004	-1.14998
C	-0.06530	0.00011	1.14997
C	-1.32755	-0.76198	0.77667
C	0.94344	0.00007	-0.00004
C	-1.32786	0.76195	-0.77655
C	-1.32782	0.76201	0.77656
H	0.27179	0.00000	-2.19104
H	0.27219	0.00017	2.19092
H	-1.85376	1.45675	1.43336
H	-1.85369	1.45669	-1.43344
H	-1.85381	-1.45689	1.43302
H	-1.85323	-1.45730	-1.43310
C	1.80721	1.27035	-0.00009
H	2.45774	1.30754	0.89099
H	2.45769	1.30749	-0.89120
H	1.17101	2.17104	-0.00010
C	1.80714	-1.27034	0.00009
H	1.17084	-2.17096	0.00016
H	2.45770	-1.30769	-0.89097
H	2.45760	-1.30748	0.89122

P-Me$_2$
Transition state
Symmetry: C_s
Electronic energy: -349.600835308
$\langle S^2 \rangle = 1.0086$

C	-1.07165	1.16870	0.74200
C	-0.17292	0.00000	1.14841
C	-0.18004	0.00000	-1.15391
C	-1.33660	0.84380	-0.65898
C	0.88239	0.00000	-0.02919
C	-1.07165	-1.16870	0.74200
C	-1.33660	-0.84380	-0.65898
H	0.23970	0.00000	2.16597
H	0.10663	0.00000	-2.21030
H	-2.02391	-1.36745	-1.32460
H	-1.74457	-1.71043	1.40923
H	-2.02391	1.36745	-1.32460

H	-1.74457	1.71043	1.40923
C	1.75259	-1.26062	-0.04948
H	2.38989	-1.27909	-0.95072
H	2.41768	-1.28842	0.83134
H	1.13341	-2.17243	-0.04028
C	1.75259	1.26062	-0.04948
H	1.13341	2.17243	-0.04028
H	2.41768	1.28842	0.83134
H	2.38989	1.27909	-0.95072

P-Me$_2$

S_0/S_1 conical intersection

Symmetry: C_2

C	-0.01183237	1.10531354	-1.24347162
C	-0.91093589	0.68509201	-0.16437569
C	0.91093848	-0.68508620	-0.16437950
C	1.24432598	0.40330076	-1.17969046
C	0.00000097	0.00000086	0.87945381
C	-1.24430410	-0.40327570	-1.17970894
C	0.01182720	-1.10532071	-1.24346513
H	-1.69954941	1.34164671	0.16447276
H	1.69954883	-1.34164415	0.16447116
H	0.29012179	-1.83128691	-1.98297227
H	-1.92832695	-0.29684722	-1.99510750
H	1.92831468	0.29683670	-1.99511441
H	-0.29013106	1.83127729	-1.98297934
C	0.74819891	1.00775180	1.75271633
H	1.44981907	0.50005609	2.40900932
H	1.30464897	1.71728159	1.15399436
H	0.05260393	1.55735406	2.38109231
C	-0.74819800	-1.00775245	1.75271246
H	-1.44982182	-0.50005934	2.40900420
H	-1.30464518	-1.71728496	1.15399009
H	-0.05260405	-1.55735377	2.38109004

P-*i*Pr$_2$

NBD isomer

Symmetry: C_2

Electronic energy: -506.716639767

C	1.22600	-0.66761	1.96983
C	-0.00000	-1.12313	1.15151
C	0.00000	1.12313	1.15151
C	1.22789	0.67920	1.96752
C	-0.00000	0.00000	0.00639
C	-1.22789	-0.67920	1.96752
C	-1.22600	0.66761	1.96983
H	0.01141	-2.17315	0.82500
H	-0.01141	2.17315	0.82500
H	-1.91827	1.34387	2.47499
H	-1.92199	-1.35657	2.46838
H	1.92199	1.35657	2.46838
H	1.91827	-1.34387	2.47499
C	-1.32228	0.04633	-0.83842
H	-2.10065	0.37496	-0.13265
C	1.32228	-0.04633	-0.83842
H	2.10065	-0.37496	-0.13265
C	-1.81510	-1.32007	-1.35160
H	-2.81348	-1.20026	-1.80715
H	-1.15897	-1.76371	-2.11458
H	-1.91670	-2.04524	-0.52738
C	-1.34152	1.09157	-1.96828
H	-0.69593	0.82146	-2.81929
H	-2.36999	1.18216	-2.35872
H	-1.03650	2.08915	-1.61112
C	1.81510	1.32007	-1.35160
H	2.81348	1.20026	-1.80715
H	1.15897	1.76371	-2.11458
H	1.91670	2.04524	-0.52738
C	1.34152	-1.09157	-1.96828
H	0.69593	-0.82146	-2.81929
H	2.36999	-1.18216	-2.35872
H	1.03650	-2.08915	-1.61112

P-*i*Pr$_2$

QC isomer

Symmetry: C_2

Electronic energy: -506.701018928

C	-0.76316	-0.77245	-2.18820
C	0.00000	-1.14784	-0.92819
C	0.00000	1.14784	-0.92819
C	-0.76161	0.77900	-2.18994
C	-0.00000	0.00000	0.09505
C	0.76161	-0.77900	-2.18994
C	0.76316	0.77245	-2.18820
H	-0.01454	-2.19368	-0.61132
H	0.01454	2.19368	-0.61132
H	1.46054	1.42999	-2.70967
H	1.45421	-1.43643	-2.71809
H	-1.45421	1.43643	-2.71809
H	-1.46054	-1.42999	-2.70967
C	1.35287	0.01597	0.88099
H	2.09984	0.22784	0.08999
C	-1.35287	-0.01597	0.88099
H	-2.09984	-0.22784	0.08999
C	1.77937	-1.32322	1.51175
H	2.81124	-1.23764	1.89459
H	1.14099	-1.61510	2.35991
H	1.76988	-2.14481	0.77799
C	1.47765	1.14248	1.92070
H	0.86788	0.93844	2.81689
H	2.52557	1.23232	2.25517
H	1.17060	2.12104	1.51679
C	-1.77937	1.32322	1.51175
H	-2.81124	1.23764	1.89459
H	-1.14099	1.61510	2.35991
H	-1.76988	2.14481	0.77799
C	-1.47765	-1.14248	1.92070
H	-0.86788	-0.93844	2.81689
H	-2.52557	-1.23232	2.25517
H	-1.17060	-2.12104	1.51679

P-*i*Pr$_2$

Transition state

Symmetry: C_1

Electronic energy: -506.642346250

$\langle S^2 \rangle = 1.0067$

C	2.16897	-0.97503	0.47407
C	1.00799	-0.24648	1.11616
C	1.04317	0.25249	-1.12675
C	1.93567	-0.97905	-0.96506

C	-0.05249	0.00083	0.00477
C	2.16743	0.68630	0.83735
C	1.93044	1.30339	-0.46239
H	0.72330	-0.46231	2.14917
H	0.66812	0.46551	-2.13488
H	2.60513	1.98520	-0.98299
H	2.84030	1.04933	1.61518
H	2.62171	-1.36142	-1.72304
H	2.84493	-1.63141	1.02359
C	-0.84937	1.30447	0.32379
H	-0.07701	1.99896	0.70743
C	-0.84731	-1.30691	-0.30130
H	-0.06984	-1.98732	-0.70650
C	-1.90005	1.15471	1.43723
H	-2.24277	2.15173	1.76349
H	-2.79048	0.60423	1.08962
H	-1.50201	0.63306	2.32316
C	-1.47153	2.02028	-0.89040
H	-2.30897	1.45869	-1.33101
H	-1.86578	3.00155	-0.57387
H	-0.72915	2.20941	-1.68238
C	-1.91656	-1.17027	-1.39781
H	-2.25310	-2.17127	-1.71794
H	-2.80727	-0.62908	-1.03647
H	-1.53738	-0.64497	-2.28959
C	-1.43871	-2.03512	0.92044
H	-2.27934	-1.48989	1.37681
H	-1.82265	-3.02163	0.60711
H	-0.68359	-2.21592	1.70256

P-*i*Pr$_2$

S_0/S_1 conical intersection

Symmetry: C_2

C	0.64744874	0.89389223	2.07908967
C	1.13743817	0.02666645	1.00037173
C	-1.13745592	-0.02672859	1.00035106
C	-0.78042874	1.05018721	2.01605617
C	-0.00000880	-0.00001289	-0.06309628
C	0.78045499	-1.05045367	2.01590480
C	-0.64744833	-0.89383355	2.07914159
H	2.16397545	0.11324602	0.69021939
H	-2.16400410	-0.11327697	0.69023038
H	-1.29714207	-1.32192020	2.81807566
H	1.40202159	-1.36987827	2.82564030
H	-1.40203962	1.36998825	2.82559781
H	1.29712653	1.32200009	2.81802782
C	0.00506479	1.34465826	-0.85700731
H	0.24694462	2.09699225	-0.11567700
C	-0.00508518	-1.34466762	-0.85704185
H	-0.24700218	-2.09700673	-0.11573503
C	1.35108941	-1.78338219	-1.43027183
H	1.26136322	-2.79092475	-1.82691547
H	1.69792373	-1.15177326	-2.23779952
H	2.11617457	-1.81179422	-0.66381349
C	-1.08671210	-1.45578685	-1.94012626
H	-0.86503395	-0.85031411	-2.81141548
H	-1.15524605	-2.48642769	-2.27631123
H	-2.06755496	-1.16985589	-1.57538682
C	1.08673662	1.45583157	-1.94004382
H	0.86511700	0.85035407	-2.81134395
H	1.15524596	2.48647662	-2.27622081
H	2.06757247	1.16993410	-1.57526209
C	-1.35108715	1.78336814	-1.43029990
H	-1.26138449	2.79096639	-1.82680753
H	-1.69780579	1.15184073	-2.23794071
H	-2.11626041	1.81163406	-0.66392197

P-*t*Bu$_2$

NBD isomer

Symmetry: C_1

Electronic energy: -585.201067093

C	-1.21958	2.06435	-0.63211
C	-0.02883	1.21572	-1.12179
C	0.02783	1.21575	1.12183
C	-1.20048	2.04564	0.71180
C	-0.00007	0.06623	0.00006
C	1.19893	2.04645	-0.71180
C	1.21800	2.06522	0.63211
H	-0.07199	0.89207	-2.17177
H	0.07122	0.89223	2.17184
H	1.91081	2.59039	1.29184
H	1.86430	2.55961	-1.40866
H	-1.86623	2.55831	1.40864
H	-1.91281	2.58904	-1.29180
C	1.34890	-0.85090	-0.01450
C	-1.34822	-0.85189	0.01452
C	1.68893	-1.25530	-1.47394
H	2.53405	-1.96596	-1.47388
H	0.86430	-1.71904	-2.02761
H	2.01146	-0.36533	-2.04037
C	1.26494	-2.10558	0.91192
H	0.39649	-2.75664	0.78389
H	2.15947	-2.72513	0.73104
H	1.29883	-1.79865	1.97164
C	-1.68734	-1.25769	1.47382
H	-2.53170	-1.96926	1.47349
H	-0.86210	-1.72082	2.02702
H	-2.01075	-0.36839	2.04082
C	-1.26351	-2.10559	-0.91319
H	-0.39453	-2.75616	-0.78617
H	-2.15752	-2.72601	-0.73277
H	-1.29796	-1.79749	-1.97256
C	-2.68041	-0.21959	-0.50648
H	-3.10396	0.53955	0.15966
H	-2.57601	0.22363	-1.50990
H	-3.41926	-1.03737	-0.58957
C	2.68024	-0.21784	0.50780
H	3.10370	0.54199	-0.15760
H	2.57472	0.22465	1.51145
H	3.41968	-1.03507	0.59102

P-*t*Bu$_2$

QC isomer

Symmetry: C_2

Electronic energy: -585.212822165

C	-0.65682	0.85914	-2.23085
C	-1.13188	0.16754	-0.96199
C	1.13188	-0.16754	-0.96199
C	0.87851	0.64104	-2.23115
C	-0.00000	-0.00000	0.06730

C	-0.87851	-0.64104	-2.23115
C	0.65682	-0.85914	-2.23085
H	-2.16560	0.33597	-0.64938
H	2.16560	-0.33597	-0.64938
H	1.20905	-1.64927	-2.74225
H	-1.62907	-1.23738	-2.75327
H	1.62907	1.23738	-2.75327
H	-1.20905	1.64927	-2.74225
C	-0.21690	-1.35319	0.91308
C	0.21690	1.35319	0.91308
C	-1.66189	-1.48273	1.45828
H	-1.75223	-2.42976	2.01869
H	-1.95501	-0.67284	2.13830
H	-2.39374	-1.52224	0.63490
C	0.77298	-1.51328	2.08934
H	0.63993	-0.76311	2.88153
H	0.62121	-2.50379	2.55316
H	1.81977	-1.47166	1.74465
C	1.66189	1.48273	1.45828
H	1.75223	2.42976	2.01869
H	1.95501	0.67284	2.13830
H	2.39374	1.52224	0.63490
C	-0.77298	1.51328	2.08934
H	-0.63993	0.76311	2.88153
H	-0.62121	2.50379	2.55316
H	-1.81977	1.47166	1.74465
C	-0.00000	2.61806	0.04003
H	0.67638	2.65331	-0.82681
H	-1.03601	2.70415	-0.32117
H	0.21122	3.50713	0.65926
C	-0.00000	-2.61806	0.04003
H	-0.67638	-2.65331	-0.82681
H	1.03601	-2.70415	-0.32117
H	-0.21122	-3.50713	0.65926

P-*t*Bu$_2$

Transition state

Symmetry: C_1

Electronic energy: -585.137652984

$\langle S^2 \rangle = 1.0000$

C	-2.03984	1.15811	0.72821
C	-1.10887	0.01845	1.14377
C	-1.06941	0.02975	-1.14264
C	-2.21758	0.90451	-0.67964
C	0.00405	0.01645	-0.00880
C	-2.00975	-1.14542	0.71756
C	-2.21019	-0.85661	-0.68602
H	-0.74739	0.02568	2.17930
H	-0.78096	0.02775	-2.19821
H	-2.87955	-1.37148	-1.37582
H	-2.71660	-1.65541	1.37510
H	-2.89814	1.41579	-1.36168
H	-2.74073	1.66700	1.39104
C	0.85937	-1.36651	0.00045
C	0.90234	1.35217	-0.01393
C	1.20012	-1.79077	1.45203
H	1.82101	-2.70330	1.42910
H	1.75479	-1.02704	2.01418
H	0.28453	-2.03549	2.01416
C	2.17825	-1.33283	-0.81854
H	2.89684	-0.56496	-0.50956
H	2.68068	-2.30762	-0.69547
H	1.98022	-1.21105	-1.89642
C	1.52526	1.62004	-1.41204
H	2.14873	2.52949	-1.35804
H	2.15707	0.81617	-1.80197
H	0.73206	1.81791	-2.15245
C	2.00368	1.32691	1.07669
H	2.74439	0.52476	0.96794
H	2.55597	2.28209	1.05069
H	1.55453	1.23949	2.08075
C	0.14123	2.67744	0.28616
H	-0.63756	2.90572	-0.45469
H	-0.31485	2.69624	1.28785
H	0.88289	3.49734	0.24827
C	0.11887	-2.58582	-0.62391
H	-0.75846	-2.89695	-0.03977
H	-0.20766	-2.39131	-1.65825
H	0.82295	-3.43602	-0.65213

P-*t*Bu$_2$

S_0/S_1 conical intersection

Symmetry: C_2

C	0.45086405	1.01611520	2.13264158
C	1.10713783	0.24304450	1.05769156
C	-1.10713706	-0.24304444	1.05769208
C	-0.96932001	0.86979701	2.08351796
C	0.00000008	0.00000009	-0.02041081
C	0.96932060	-0.86979602	2.08351871
C	-0.45086268	-1.01611516	2.13264209
H	2.09812941	0.53083084	0.75147737
H	-2.09812893	-0.53083118	0.75147814
H	-1.00815693	-1.57341761	2.86072174
H	1.64692431	-1.06316364	2.88803330
H	-1.64692382	1.06316315	2.88803258
H	1.00815846	1.57341780	2.86072045
C	-0.23791083	1.34432716	-0.88841351
C	0.23791072	-1.34432686	-0.88841382
C	1.70847221	-1.46955430	-1.34261212
H	1.82963936	-2.36922572	-1.93902200
H	2.05832148	-0.64218887	-1.93988907
H	2.36265055	-1.56510878	-0.48363238
C	-0.70254168	-1.46960772	-2.11301333
H	-0.62735573	-0.68186997	-2.84149955
H	-0.47306891	-2.39537851	-2.63032877
H	-1.73971405	-1.53400568	-1.80060975
C	0.70254214	1.46960911	-2.11301243
H	0.62735687	0.68187096	-2.84149784
H	0.47306905	2.39537987	-2.63032788
H	1.73971448	1.53400704	-1.80060821
C	-1.70847211	1.46955216	-1.34261204
H	-1.82964074	2.36922350	-1.93902253
H	-2.05832118	0.64218659	-1.93988885
H	-2.36265074	1.56510631	-0.48363252
C	0.04910832	2.67270979	-0.13151592
H	-0.61826940	2.83987567	0.69693371
H	1.07239622	2.73699671	0.22230117
H	-0.08715937	3.49155408	-0.83121761
C	-0.04910988	-2.67270943	-0.13151616
H	0.61826841	-2.83987540	0.69693313

H	-1.07239738	-2.73699404	0.22230211
H	0.08715689	-3.49155422	-0.83121759

DA-H₂
NBD isomer
Symmetry: C_s
Electronic energy: -534.001673929

C	0.24663	0.93017	0.68555
C	0.87316	-0.41733	1.12222
C	0.87316	-0.41733	-1.12222
C	0.24663	0.93017	-0.68555
C	1.94148	-0.54849	-0.00000
H	2.43798	-1.53095	-0.00000
H	2.68329	0.26737	0.00000
C	-0.11185	-1.52496	0.67741
C	-0.11185	-1.52496	-0.67741
H	1.20204	-0.45035	2.16953
H	1.20204	-0.45035	-2.16953
C	-0.93851	-2.29562	1.65246
H	-1.58683	-1.61918	2.24005
H	-1.58481	-3.03132	1.14930
H	-0.30529	-2.83615	2.37886
C	-0.27679	1.89652	1.57064
N	-0.69515	2.66879	2.35807
C	-0.27679	1.89652	-1.57064
N	-0.69515	2.66879	-2.35807
C	-0.93851	-2.29562	-1.65246
H	-1.58481	-3.03132	-1.14930
H	-1.58683	-1.61918	-2.24005
H	-0.30529	-2.83615	-2.37886

DA-H₂
QC isomer
Symmetry: C_s
Electronic energy: -533.972221642

C	-0.49085	0.23894	0.77792
C	0.70557	1.13293	1.15321
C	0.70557	1.13293	-1.15321
C	-0.49085	0.23894	-0.77792
C	1.02793	2.06497	-0.00000
H	2.09119	2.36240	-0.00000
H	0.40035	2.97163	-0.00000
C	0.95292	-0.31235	0.78087
C	0.95292	-0.31235	-0.78087
H	0.79432	1.43738	2.19928
H	0.79432	1.43738	-2.19928
C	1.53305	-1.37976	1.65760
H	1.21359	-1.23838	2.70245
H	1.20365	-2.38272	1.33957
H	2.63612	-1.35485	1.63121
C	-1.56288	-0.09836	1.64492
N	-2.42916	-0.40168	2.38323
C	-1.56288	-0.09836	-1.64492
N	-2.42916	-0.40168	-2.38323
C	1.53305	-1.37976	-1.65760
H	2.63612	-1.35485	-1.63121
H	1.20365	-2.38272	-1.33957
H	1.21359	-1.23838	-2.70245

DA-H₂
Transition state
Symmetry: C_1
Electronic energy: -533.927876020
$<S^2> = 0.9897$

C	0.19962	0.80643	0.31045
C	-0.92043	0.52592	1.33805
C	0.08283	-1.47568	0.78837
C	1.06596	-0.40349	0.30895
C	-0.54039	-0.78220	2.03078
H	-1.42652	-1.32408	2.40095
H	0.18463	-0.63954	2.84807
C	-1.28307	0.19709	-0.08866
C	-0.97949	-1.24689	-0.28123
H	-1.37908	1.37142	1.85641
H	0.48454	-2.48836	0.90720
C	-2.22291	1.00077	-0.93985
H	-2.18797	2.06909	-0.67651
H	-1.97483	0.90886	-2.00969
H	-3.25874	0.64745	-0.79445
C	0.57557	2.11137	-0.10063
N	0.83785	3.20348	-0.45876
C	2.31749	-0.57987	-0.24692
N	3.40203	-0.76803	-0.70194
C	-1.09096	-1.99042	-1.56280
H	-2.02623	-1.74216	-2.09130
H	-0.25593	-1.74863	-2.25601
H	-1.06436	-3.08033	-1.39883

DA-H₂
S_0/S_1 conical intersection
Symmetry: C_1

C	0.62492872	0.88527038	0.76734851
C	1.14442872	-0.51754350	1.13580009
C	1.17692394	-0.50882481	-1.13681100
C	0.30001665	0.56043201	-0.65424477
C	2.14158762	-0.80526884	0.00358396
H	2.49438244	-1.83067791	-0.02315405
H	2.97945332	-0.12269343	0.03454738
C	-0.09234934	-1.22985356	0.68338595
C	-0.18056939	-1.09843461	-0.71795555
H	1.45282975	-0.67823803	2.15574931
H	1.45253621	-0.57577231	-2.17319412
C	-1.12174423	-1.75963548	1.60422499
H	-1.51698637	-0.91765910	2.17107496
H	-1.93213265	-2.25697384	1.09166428
H	-0.66157818	-2.43509826	2.31849844
C	-0.34679663	1.48565856	1.59496068
N	-1.10977032	1.96712580	2.30329440
C	-0.43657125	1.40446041	-1.55941438
N	-1.01927054	2.04857826	-2.29096681
C	-1.23971385	-1.63492667	-1.64123080
H	-2.23568122	-1.48696858	-1.24018391
H	-1.20008119	-1.12602103	-2.59655027
H	-1.10013220	-2.69573646	-1.83042732

DA-H₂
S_1 minimum
Symmetry: C_s

C	-1.081078957	0.704686999	-0.000032382
C	0.023729515	1.128071310	-0.964957219

C	0.023840495	-1.127307689	-0.964924554
C	-1.081000000	-0.704000000	0.000000000
C	0.002323874	0.000363995	-2.004722454
C	1.081010854	0.708059855	0.000000000
C	1.081062846	-0.707160144	0.000034881
C	1.859298841	1.639750779	0.863557752
C	-1.754927273	1.600882400	0.852303863
C	-1.754742791	-1.600233597	0.852382845
C	1.859396666	-1.638751218	0.863659033
N	-2.275532196	2.363808303	1.525925029
N	-2.275238288	-2.363177691	1.526067013
H	0.877888045	0.000399335	-2.643937032
H	-0.898653427	0.000313484	-2.603082047
H	0.016194661	2.156430505	-1.286865373
H	0.016402278	-2.155679492	-1.286791440
H	1.219052421	2.436357523	1.228110437
H	2.304816518	1.142695690	1.714563592
H	2.655886564	2.105766228	0.285723841
H	2.304489811	-1.141706304	1.714894091
H	1.219304457	-2.435635487	1.227865324
H	2.656320784	-2.104388759	0.285981400

NICS scan:

bq	0.0	0.0	0.0
bq	0.0	0.0	0.1
bq	0.0	0.0	0.2
bq	0.0	0.0	0.3
bq	0.0	0.0	0.4
bq	0.0	0.0	0.5
bq	0.0	0.0	0.6
bq	0.0	0.0	0.7
bq	0.0	0.0	0.8
bq	0.0	0.0	0.9
bq	0.0	0.0	1.0
bq	0.0	0.0	1.1
bq	0.0	0.0	1.2
bq	0.0	0.0	1.3
bq	0.0	0.0	1.4
bq	0.0	0.0	1.5
bq	0.0	0.0	1.6
bq	0.0	0.0	1.7
bq	0.0	0.0	1.8
bq	0.0	0.0	1.9
bq	0.0	0.0	2.0
bq	0.0	0.0	2.1
bq	0.0	0.0	2.2
bq	0.0	0.0	2.3
bq	0.0	0.0	2.4
bq	0.0	0.0	2.5
bq	0.0	0.0	2.6
bq	0.0	0.0	2.7
bq	0.0	0.0	2.8
bq	0.0	0.0	2.9
bq	0.0	0.0	3.0
bq	0.0	0.0	3.1
bq	0.0	0.0	3.2
bq	0.0	0.0	3.3
bq	0.0	0.0	3.4
bq	0.0	0.0	3.5
bq	0.0	0.0	3.6
bq	0.0	0.0	3.7
bq	0.0	0.0	3.8
bq	0.0	0.0	3.9
bq	0.0	0.0	4.0
bq	0.0	0.0	4.1
bq	0.0	0.0	4.2
bq	0.0	0.0	4.3
bq	0.0	0.0	4.4
bq	0.0	0.0	4.5
bq	0.0	0.0	4.6
bq	0.0	0.0	4.7
bq	0.0	0.0	4.8
bq	0.0	0.0	4.9
bq	0.0	0.0	5.0

DA-Me$_2$

NBD isomer

Symmetry: C_s

Electronic energy: -612.530692568

C	-0.04588	1.04757	0.68578
C	0.34922	-0.37876	1.12019
C	0.34922	-0.37876	-1.12019
C	-0.04588	1.04757	-0.68578
C	1.41740	-0.70738	0.00000
C	-0.82074	-1.28377	0.67678
C	-0.82074	-1.28377	-0.67678
H	0.66534	-0.46910	2.16962
H	0.66534	-0.46910	-2.16962
C	-1.74870	-1.92380	1.65423
H	-2.26162	-1.16290	2.27140
H	-2.51980	-2.52875	1.15230
H	-1.20089	-2.58052	2.35475
C	-0.36802	2.09798	1.57025
N	-0.62293	2.93894	2.35749
C	-0.36802	2.09798	-1.57025
N	-0.62293	2.93894	-2.35749
C	-1.74870	-1.92380	-1.65423
H	-2.51980	-2.52875	-1.15230
H	-2.26162	-1.16290	-2.27140
H	-1.20089	-2.58052	-2.35475
C	2.65737	0.19929	-0.00000
H	3.27576	-0.01226	0.88908
H	3.27576	-0.01226	-0.88908
H	2.41824	1.27195	-0.00000
C	1.90151	-2.16384	0.00000
H	2.53008	-2.34976	-0.88716
H	2.53008	-2.34976	0.88716
H	1.07670	-2.88969	0.00000

DA-Me$_2$

QC isomer

Symmetry: C_s

Electronic energy: -612.504669968

C	-0.29129	-0.66798	0.77862
C	-0.19093	0.81923	1.14930
C	-0.19093	0.81923	-1.14930
C	-0.29129	-0.66798	-0.77862
C	-0.70192	1.68672	-0.00000
C	1.06763	0.07197	0.78112
C	1.06763	0.07197	-0.78112
H	-0.36848	1.09245	2.19355

H	-0.36848	1.09245	-2.19355
C	2.25518	-0.18359	1.65793
H	1.94095	-0.32027	2.70498
H	2.79516	-1.09382	1.34866
H	2.96069	0.66447	1.62198
C	-0.72844	-1.70333	1.64499
N	-1.06096	-2.56014	2.38200
C	-0.72844	-1.70333	-1.64499
N	-1.06096	-2.56014	-2.38200
C	2.25518	-0.18359	-1.65793
H	2.96069	0.66447	-1.62198
H	2.79516	-1.09382	-1.34866
H	1.94095	-0.32027	-2.70498
C	-0.02080	3.06563	-0.00000
H	1.07742	2.96518	-0.00000
H	-0.31287	3.64660	-0.89057
H	-0.31287	3.64660	0.89057
C	-2.23229	1.80563	-0.00000
H	-2.58281	2.35227	-0.89172
H	-2.70501	0.80989	-0.00000
H	-2.58281	2.35227	0.89172

DA-Me$_2$
Transition state
Symmetry: C_1
Electronic energy: -612.460904932
$\langle S^2 \rangle = 0.9925$

C	-0.79672	0.21572	-0.61002
C	0.62419	0.53246	-1.11708
C	0.80045	-0.83156	0.72557
C	-0.66020	-0.95882	0.29232
C	1.52850	-0.62484	-0.65273
C	0.21359	1.32931	0.09327
C	0.70318	0.58275	1.28026
H	0.73967	1.00829	-2.09539
H	1.18635	-1.61948	1.38400
C	-0.14665	2.78641	0.07915
H	-0.60557	3.07679	-0.87842
H	-0.85911	3.03173	0.88334
H	0.75968	3.40062	0.22248
C	-1.97773	0.63594	-1.27407
N	-2.94122	1.03591	-1.82366
C	-1.64347	-1.77303	0.81805
N	-2.46076	-2.50533	1.28146
C	0.45802	0.94916	2.69897
H	0.57219	2.03410	2.85901
H	-0.57105	0.68230	3.02501
H	1.15236	0.42415	3.37590
C	1.43444	-1.85004	-1.56673
H	1.85724	-1.62522	-2.56025
H	2.00212	-2.69546	-1.14267
H	0.39031	-2.17545	-1.70468
C	2.98243	-0.17213	-0.47775
H	3.42553	0.09467	-1.45201
H	3.05339	0.70454	0.18735
H	3.59056	-0.98363	-0.04339

DA-Me$_2$
S_0/S_1 conical intersection
Symmetry: C_1

C	-0.20144565	0.67736021	0.65807205
C	0.64579928	-0.42008904	1.13277162
C	0.61603351	-0.41056416	-1.13198402
C	0.11612548	0.99757963	-0.76199022
C	1.62448780	-0.75147294	-0.00208632
C	-0.72699999	-0.96922557	0.71366743
C	-0.63727267	-1.09898556	-0.68653938
H	0.91764968	-0.49802882	2.17073279
H	0.91982407	-0.57458636	-2.15405838
C	-1.79836992	-1.48572893	1.63411924
H	-1.76476321	-0.96402532	2.58284903
H	-2.78931841	-1.33628227	1.22138236
H	-1.66868681	-2.54492273	1.83935572
C	-0.90832170	1.53765771	1.57273990
N	-1.46630740	2.19488970	2.31187590
C	-0.83989761	1.62308610	-1.58638565
N	-1.59032039	2.12656739	-2.29328817
C	-1.66990832	-1.61278626	-1.61303226
H	-2.50034667	-2.08081339	-1.10495437
H	-2.03405957	-0.76909188	-2.19740926
H	-1.21859461	-2.31121870	-2.31092780
C	2.86273095	0.14402114	0.00436964
H	2.59476251	1.19014530	-0.01233253
H	3.46340232	-0.05318086	0.88786373
H	3.47996041	-0.06208064	-0.86492556
C	2.04270394	-2.22479542	-0.00167624
H	2.65468834	-2.45145758	0.86550382
H	1.19198210	-2.89985928	0.01202121
H	2.63052153	-2.45005348	-0.88573629

DA-Me$_2$
S_1 minimum
Symmetry: C_s

C	-0.160484	0.838648	0.698014
C	0.514441	-0.460518	1.125135
C	0.522997	-0.468022	-1.123543
C	-0.155128	0.833947	-0.710249
C	1.556520	-0.707939	0.005558
C	-0.685490	-1.240569	0.705716
C	-0.680112	-1.245283	-0.708071
H	0.821386	-0.527944	2.157088
H	0.837785	-0.542324	-2.152658
C	-1.717567	-1.781835	1.634745
H	-1.876830	-1.097100	2.460771
H	-2.666802	-1.952853	1.144652
H	-1.379753	-2.726311	2.058800
C	-0.811114	1.713774	1.590054
N	-1.328462	2.395355	2.347929
C	-0.798925	1.703079	-1.613040
N	-1.310472	2.379564	-2.379372
C	-1.705111	-1.792755	-1.641294
H	-2.658038	-1.960561	-1.157293
H	-1.858098	-1.113525	-2.473031
H	-1.364091	-2.740009	-2.056495
C	2.710958	0.292696	0.006610
H	2.366838	1.317452	0.001876
H	3.332007	0.148231	0.885457
H	3.338680	0.142377	-0.866495
C	2.116987	-2.132630	0.012443
H	2.734210	-2.293065	0.890907

H	1.338203	-2.887262	0.012007
H	2.740856	-2.298912	-0.860221

DA-*i*Pr$_2$
NBD isomer
Symmetry: C_1
Electronic energy: -769.569744611

C	1.47172	-0.26341	0.76636
C	0.14539	0.46449	1.07684
C	0.21080	0.18039	-1.14098
C	1.50916	-0.44121	-0.59231
C	-0.81092	-0.23642	0.01055
C	0.31527	1.86947	0.46163
C	0.35845	1.69648	-0.87976
H	-0.14674	0.43005	2.13555
H	-0.03305	-0.10293	-2.17423
C	0.46931	3.09737	1.29508
H	1.35082	3.01863	1.95825
H	0.59028	4.00012	0.67633
H	-0.40674	3.24977	1.95178
C	2.43583	-0.61679	1.73300
N	3.20040	-0.89258	2.58838
C	2.51809	-1.03001	-1.38204
N	3.32550	-1.51381	-2.09364
C	0.56733	2.67588	-1.98555
H	0.66856	3.70523	-1.60779
H	1.47797	2.43389	-2.56433
H	-0.27502	2.65545	-2.70186
C	-0.90239	-1.78551	0.24354
H	0.08043	-2.08672	0.64143
C	-2.18117	0.50574	-0.16844
H	-1.91978	1.49013	-0.58842
C	-1.07810	-2.62558	-1.03619
H	-0.98017	-3.69450	-0.78274
H	-2.05948	-2.49091	-1.51345
H	-0.30175	-2.39999	-1.78554
C	-1.90957	-2.21738	1.32356
H	-2.95581	-2.10766	0.99764
H	-1.75161	-3.28332	1.55793
H	-1.77929	-1.65193	2.26069
C	-3.13345	-0.13626	-1.19290
H	-3.58376	-1.07396	-0.83017
H	-3.96170	0.56200	-1.40091
H	-2.63072	-0.34663	-2.15101
C	-2.92915	0.82364	1.14085
H	-3.77406	1.49731	0.91770
H	-3.34486	-0.06756	1.63219
H	-2.28440	1.34304	1.86844

DA-*i*Pr$_2$
QC isomer
Symmetry: C_1
Electronic energy: -769.548148042

C	1.35275	-0.06545	0.85982
C	-0.04152	0.55645	1.02076
C	-0.02247	-0.21460	-1.13840
C	1.36632	-0.58786	-0.60517
C	-1.02397	-0.05307	0.01254
C	1.04408	1.36489	0.35545
C	1.05531	0.84059	-1.11438
H	-0.34200	0.81462	2.03875
H	-0.31209	-0.63414	-2.10458
C	1.62993	2.65915	0.83073
H	1.67478	2.68247	1.93130
H	2.65526	2.79981	0.45047
H	1.01775	3.51424	0.49561
C	2.20187	-0.45513	1.92786
N	2.91155	-0.74477	2.82258
C	2.23208	-1.55777	-1.17360
N	2.95338	-2.34328	-1.67436
C	1.64671	1.54773	-2.29526
H	1.03567	2.42308	-2.57592
H	2.67117	1.89641	-2.08404
H	1.69534	0.87382	-3.16549
C	-2.07801	1.03171	-0.40255
H	-1.46384	1.81091	-0.89787
C	-1.49881	-1.45417	0.52328
H	-0.57320	-1.90963	0.92797
C	-2.50542	-1.40032	1.68418
H	-3.50736	-1.09404	1.34047
H	-2.60788	-2.40172	2.13409
H	-2.19178	-0.70966	2.48381
C	-2.00086	-2.42288	-0.56375
H	-2.17194	-3.41507	-0.11356
H	-2.95247	-2.09931	-1.01207
H	-1.26649	-2.56087	-1.37322
C	-3.10702	0.55262	-1.43912
H	-3.85398	-0.11934	-0.98561
H	-3.65458	1.41758	-1.84966
H	-2.64090	0.02098	-2.28443
C	-2.79871	1.74023	0.76013
H	-3.38916	2.58321	0.36274
H	-3.49592	1.07446	1.29001
H	-2.09438	2.15578	1.49851

DA-*i*Pr$_2$
Transition state
Symmetry: C_1
Electronic energy: -769.504018791
$\langle S^2 \rangle = 1.0019$

C	-1.41990	0.09449	0.69701
C	-0.08193	-0.61230	0.98869
C	-0.02011	0.20283	-1.15544
C	-1.18849	0.93746	-0.50051
C	0.98074	0.02751	0.06126
C	-1.02514	-1.43532	0.15305
C	-0.68517	-1.16235	-1.26127
H	0.12697	-0.89045	2.02467
H	0.37319	0.64249	-2.07863
C	-1.78925	-2.62855	0.64785
H	-2.04890	-2.52457	1.71264
H	-2.72567	-2.76910	0.08408
H	-1.17824	-3.54126	0.53370
C	-2.43526	0.26722	1.67171
N	-3.27720	0.35562	2.49278
C	-1.94762	1.97216	-1.00881
N	-2.56590	2.87805	-1.47384
C	-1.41729	-1.67530	-2.44809
H	-1.68301	-2.73876	-2.32924
H	-2.36693	-1.12282	-2.62024

H	-0.81681	-1.56904	-3.36695
C	1.42510	1.41231	0.63020
H	0.48707	1.86327	1.01098
C	2.06944	-1.02943	-0.30932
H	1.49960	-1.79610	-0.87667
C	3.16297	-0.50995	-1.25553
H	3.86992	0.15538	-0.73350
H	3.74561	-1.35783	-1.65306
H	2.74727	0.04216	-2.11385
C	2.70296	-1.77729	0.87853
H	3.31730	-2.61079	0.49761
H	3.36161	-1.13456	1.48186
H	1.94410	-2.21180	1.54885
C	1.96734	2.41297	-0.40739
H	2.10306	3.39597	0.07373
H	2.94209	2.11124	-0.81864
H	1.26941	2.56116	-1.24656
C	2.37761	1.32287	1.83376
H	3.39611	1.03033	1.52898
H	2.45426	2.30913	2.32078
H	2.02769	0.60425	2.59276

DA-*i*Pr$_2$
S_0/S_1 conical intersection
Symmetry: C_1

C	1.34583882	-0.19002657	0.72195025
C	0.03321549	0.36497536	1.07431541
C	0.07352392	-0.15715592	-1.12432493
C	1.26364441	-0.94329182	-0.55575592
C	-0.98039874	-0.15829286	0.03211257
C	0.88327148	1.44557580	0.39417564
C	0.74257759	1.17858866	-0.98090313
H	-0.21970120	0.51583964	2.10719479
H	-0.25127061	-0.41274170	-2.11902281
C	1.49691418	2.64947143	1.05452520
H	1.73502285	2.43241165	2.08871403
H	2.41884041	2.94827719	0.56915556
H	0.81592821	3.49630722	1.04691781
C	2.40119689	-0.30268217	1.69639401
N	3.22120820	-0.37024829	2.47924022
C	2.40490174	-1.14805484	-1.35433763
N	3.30767286	-1.33328439	-2.03782887
C	1.33359654	1.92866650	-2.11153766
H	1.76283375	2.87404208	-1.81292728
H	2.11020157	1.30385091	-2.55015498
H	0.58241219	2.08748525	-2.87885728
C	-2.08328693	0.91214611	-0.25951658
H	-1.55189378	1.75365960	-0.70141721
C	-1.42085065	-1.60626414	0.41748794
H	-0.51949679	-2.07060109	0.79305155
C	-2.79198097	1.50443521	0.96900463
H	-3.39254906	2.35326916	0.65650527
H	-3.45680544	0.80175347	1.45138362
H	-2.09136036	1.86864931	1.71216477
C	-3.12612887	0.49565781	-1.30508185
H	-3.82779037	-0.23002286	-0.91320676
H	-3.69959773	1.36620954	-1.60811289
H	-2.67479242	0.07660946	-2.19733673
C	-1.85832212	-2.49372332	-0.75682899
H	-1.99701492	-3.50823625	-0.39636641
H	-2.79323922	-2.18278302	-1.20473107
H	-1.09986427	-2.53557864	-1.52834018
C	-2.45290262	-1.68769285	1.55063168
H	-3.44809177	-1.40199526	1.22976532
H	-2.51309391	-2.71291401	1.90130507
H	-2.18570531	-1.07322535	2.40440282

DA-*i*Pr$_2$
S_1 minimum
Symmetry: C_1

C	1.319616	-0.411196	0.844051
C	0.090760	0.469003	1.042679
C	0.105031	-0.100562	-1.128927
C	1.325046	-0.775506	-0.514625
C	-0.951577	-0.100502	0.023646
C	0.773025	1.585331	0.327164
C	0.786730	1.222767	-1.037140
H	-0.197956	0.640352	2.065908
H	-0.176949	-0.433341	-2.113511
C	1.399810	2.767358	0.984560
H	1.852386	2.479202	1.927259
H	2.160314	3.227554	0.367652
H	0.643249	3.518868	1.205409
C	2.299371	-0.618923	1.835429
N	3.070743	-0.758633	2.667221
C	2.312685	-1.448707	-1.260577
N	3.091181	-1.984217	-1.903815
C	1.435354	1.924598	-2.180971
H	2.199753	2.619640	-1.859669
H	1.887133	1.206737	-2.856708
H	0.690380	2.479535	-2.749503
C	-1.385518	-1.546109	0.421491
H	-0.490389	-2.003555	0.820744
C	-2.073273	0.946305	-0.281066
H	-1.555916	1.785242	-0.737238
C	-1.811468	-2.455482	-0.742324
H	-1.932871	-3.467614	-0.369441
H	-2.751956	-2.165160	-1.191382
H	-1.060717	-2.498275	-1.522812
C	-2.423837	-1.623915	1.549261
H	-3.419546	-1.351402	1.219531
H	-2.476062	-2.645281	1.912123
H	-2.163789	-0.996917	2.395365
C	-3.113245	0.498358	-1.316828
H	-3.804922	-0.231958	-0.915726
H	-3.699381	1.356662	-1.630493
H	-2.656776	0.076124	-2.205297
C	-2.788097	1.545396	0.941479
H	-3.394768	2.385810	0.617821
H	-3.448299	0.844645	1.432501
H	-2.092548	1.923796	1.682416

DA-*t*Bu$_2$
NBD isomer
Symmetry: C_1
Electronic energy: -848.056921218

C	1.63619	-0.04233	0.68576
C	0.21975	0.40798	1.10759
C	0.23171	0.35845	-1.12614
C	1.63413	-0.10307	-0.68149

C	-0.67811	-0.30910	0.00156
C	0.19613	1.87798	0.63889
C	0.23618	1.84789	-0.71127
H	-0.01498	0.22696	2.16530
H	-0.01018	0.15427	-2.17793
C	0.25400	3.02331	1.59266
H	1.15568	2.96568	2.23056
H	0.27138	3.99217	1.06945
H	-0.61531	3.02193	2.27678
C	2.70992	-0.24356	1.57688
N	3.57127	-0.39507	2.36904
C	2.68841	-0.42970	-1.55746
N	3.52746	-0.71023	-2.33881
C	0.40780	2.94803	-1.70362
H	0.37313	3.93973	-1.22627
H	1.38176	2.85609	-2.22038
H	-0.36962	2.91990	-2.48831
C	-0.59934	-1.93670	0.03290
C	-2.22063	0.22902	-0.00602
C	-0.75678	-2.49437	-1.40803
H	-0.84221	-3.59367	-1.36850
H	-1.62406	-2.11339	-1.95790
H	0.14320	-2.26539	-2.00343
C	-1.62879	-2.58114	1.00947
H	-2.67740	-2.30559	0.86856
H	-1.56938	-3.67648	0.89751
H	-1.35885	-2.35413	2.05516
C	-3.17729	-0.61826	-0.89849
H	-3.19291	-1.69554	-0.71450
H	-4.20533	-0.25236	-0.73960
H	-2.94643	-0.46267	-1.96613
C	-2.75165	0.30424	1.45101
H	-3.82591	0.55574	1.43529
H	-2.63503	-0.61793	2.03191
H	-2.24087	1.11168	2.00163
C	0.72109	-2.60394	0.53721
H	1.57784	-2.49873	-0.13926
H	1.02239	-2.26534	1.54178
H	0.52180	-3.68581	0.62069
C	-2.49137	1.65608	-0.57681
H	-2.11428	2.47252	0.04980
H	-2.09672	1.78628	-1.59652
H	-3.58687	1.77652	-0.64501

DA-*t*Bu$_2$
QC isomer
Symmetry: C_1
Electronic energy: -848.060822543

C	-1.50337	-0.24147	-0.77041
C	-0.06905	0.17124	-1.14620
C	-0.07116	0.22360	1.14042
C	-1.50629	-0.19284	0.78256
C	0.91021	-0.11722	0.00473
C	-1.08398	1.24005	-0.80986
C	-1.08170	1.28428	0.75052
H	0.21847	0.05178	-2.19364
H	0.20703	0.13032	2.19304
C	-1.61182	2.30702	-1.71933
H	-1.66624	1.93799	-2.75610
H	-2.62738	2.61638	-1.42158
H	-0.96307	3.19920	-1.70563
C	-2.41180	-0.92276	-1.62130
N	-3.16478	-1.46539	-2.34715
C	-2.41894	-0.82022	1.66974
N	-3.17754	-1.31115	2.42559
C	-1.60145	2.40083	1.60464
H	-0.93866	3.28255	1.56167
H	-2.60804	2.71427	1.28156
H	-1.67270	2.08020	2.65631
C	2.11247	0.95324	-0.00221
C	1.31937	-1.67409	0.01803
C	1.70160	-2.17480	-1.39732
H	2.51831	-1.61039	-1.86413
H	2.02488	-3.22745	-1.33153
H	0.83289	-2.14999	-2.07547
C	2.46772	-2.00185	1.00001
H	2.62909	-3.09322	0.99950
H	3.42712	-1.53539	0.73732
H	2.21145	-1.71541	2.03371
C	2.71785	1.15297	1.40984
H	3.10684	0.23201	1.86036
H	3.55612	1.86739	1.34444
H	1.97837	1.58789	2.10211
C	3.24654	0.60673	-0.99486
H	3.98258	1.42877	-0.98880
H	3.79001	-0.31474	-0.74524
H	2.86906	0.51772	-2.02706
C	1.62576	2.35951	-0.43941
H	1.29019	2.38124	-1.48773
H	0.81860	2.74761	0.19826
H	2.47174	3.06180	-0.35225
C	0.14859	-2.58785	0.46907
H	-0.15694	-2.40902	1.51110
H	-0.73616	-2.50911	-0.17831
H	0.48946	-3.63476	0.40707

DA-*t*Bu$_2$
Transition state
Symmetry: C_1
Electronic energy: -848.003211480
$\langle S^2 \rangle = 1.0156$

C	-1.54123	-0.27892	-0.68068
C	-0.16716	0.23841	-1.12609
C	-0.15999	0.14484	1.15215
C	-1.42919	-0.61461	0.74315
C	0.86406	-0.14664	-0.02873
C	-0.99441	1.39306	-0.61890
C	-0.72406	1.52086	0.81064
H	0.07124	0.18410	-2.19200
H	0.17847	-0.02536	2.18023
C	-1.66815	2.40604	-1.49073
H	-1.95389	1.97331	-2.46190
H	-2.57840	2.80717	-1.01694
H	-0.98347	3.25187	-1.68522
C	-2.57331	-0.64081	-1.57324
N	-3.42058	-0.90365	-2.35312
C	-2.39803	-1.12200	1.59145
N	-3.18864	-1.58191	2.35259
C	-1.39575	2.43334	1.77172
H	-1.65488	3.39671	1.30286

H	-2.33858	1.99562	2.16467
H	-0.75444	2.63743	2.64660
C	1.30013	-1.69117	-0.12459
C	2.09503	0.91361	0.01437
C	2.58697	1.11954	1.46952
H	2.88805	0.18868	1.96796
H	3.46152	1.79207	1.46652
H	1.81138	1.60219	2.08647
C	3.31114	0.53387	-0.87223
H	4.08378	1.31013	-0.74067
H	3.78072	-0.42623	-0.62859
H	3.04327	0.52912	-1.94138
C	2.39044	-2.06088	0.91219
H	2.61181	-3.13798	0.82582
H	3.34040	-1.52605	0.79221
H	2.02847	-1.88803	1.94006
C	1.75779	-2.06121	-1.56098
H	2.57418	-1.45104	-1.95933
H	2.09910	-3.11015	-1.56766
H	0.91027	-1.99817	-2.26383
C	1.73287	2.33436	-0.50658
H	1.36467	2.32191	-1.54506
H	0.99191	2.85065	0.12093
H	2.65059	2.94684	-0.49478
C	0.16759	-2.71817	0.16723
H	-0.20643	-2.67137	1.20100
H	-0.68184	-2.64949	-0.52727
H	0.59824	-3.72627	0.03498

DA-*t*Bu$_2$

S_0/S_1 conical intersection

Symmetry: C_1

C	1.41885083	-0.65243331	0.78299106
C	0.15591783	0.13747850	1.14791833
C	0.16064554	0.19778706	-1.10671062
C	1.49360801	-0.21292932	-0.61663161
C	-0.86560939	-0.18777225	-0.01124623
C	0.76359554	1.45871793	0.74649860
C	0.91913620	1.44211319	-0.64860526
H	-0.18300684	0.06949570	2.16817104
H	-0.05757905	0.11347023	-2.15540411
C	1.35617526	2.42915488	1.70023640
H	0.74677496	2.53037982	2.58898871
H	2.31977049	2.03031638	2.01422159
H	1.51532899	3.39938842	1.24937742
C	2.53708258	-0.66589064	1.63180941
N	3.42978095	-0.68912390	2.35220342
C	2.58450247	-0.46147429	-1.52173824
N	3.43283586	-0.64028930	-2.25581888
C	1.49738488	2.50771519	-1.53649165
H	2.35845258	2.98384684	-1.08218075
H	1.82364116	2.08405755	-2.47864121
H	0.76359588	3.27781321	-1.76302706
C	-2.12926965	0.81301647	0.02896278
C	-1.23857581	-1.76853883	-0.09411689
C	-0.16746658	-2.64221567	-0.80542598
H	0.01734806	-2.31872512	-1.82478651
H	0.76630954	-2.68393036	-0.27361894
H	-0.55149012	-3.65461747	-0.87009219
C	-1.39973980	-2.36496290	1.32069773
H	-2.14990391	-1.86455803	1.91745028
H	-1.69718356	-3.40560832	1.24013497
H	-0.46205053	-2.34118369	1.85972632
C	-2.50937116	-2.09986797	-0.91741177
H	-2.66361228	-3.17160907	-0.87032410
H	-3.42250928	-1.64488269	-0.57477521
H	-2.37942894	-1.85251584	-1.96508312
C	-3.17108851	0.39835691	1.09427442
H	-3.98526400	1.11552325	1.09010646
H	-3.60866533	-0.57283741	0.94895092
H	-2.73685346	0.41718138	2.08871770
C	-2.80147301	0.97030067	-1.35477269
H	-3.18686302	0.05951559	-1.77584795
H	-3.63546402	1.65970217	-1.27062548
H	-2.10995680	1.40056396	-2.07242546
C	-1.80081196	2.27655524	0.43261424
H	-1.37042911	2.35939033	1.42390691
H	-1.17224694	2.79666502	-0.27611289
H	-2.73364354	2.82804150	0.47089608

NBD-H$_2$

NBD isomer

Symmetry: C_1

Electronic energy: -1188.05047714

C	1.79977	0.31136	0.77719
C	0.68752	0.87787	1.69056
C	0.37166	-1.33523	1.59292
C	1.59901	-1.03527	0.71697
C	0.59883	-0.28415	2.71341
H	-0.26033	-0.18888	3.39612
H	1.53270	-0.44727	3.27661
C	-0.64404	0.66448	0.92249
C	-0.85321	-0.68767	0.89260
H	0.87040	1.89677	2.05448
H	0.25434	-2.38854	1.87430
C	-1.33552	1.76675	0.24293
C	-1.86470	1.60362	-1.05947
C	-1.44373	3.03804	0.85189
C	-2.49246	2.66697	-1.71685
H	-1.76728	0.63436	-1.55583
C	-2.07739	4.10094	0.19471
H	-1.03866	3.19031	1.85728
C	-2.60627	3.92078	-1.09267
H	-2.88715	2.51933	-2.72692
H	-2.15746	5.07345	0.69023
H	-3.09730	4.75134	-1.60846
C	-1.93580	-1.49236	0.32500
C	-1.66950	-2.79065	-0.17431
C	-3.26932	-1.01643	0.28703
C	-2.69854	-3.56967	-0.72081
H	-0.64810	-3.18415	-0.14487
C	-4.29298	-1.80091	-0.25272
H	-3.49461	-0.02729	0.69494
C	-4.01267	-3.07990	-0.76514
H	-2.47037	-4.56678	-1.10964
H	-5.31792	-1.41738	-0.26617
H	-4.81566	-3.69255	-1.18578
C	2.79703	1.17458	0.10238
O	4.00251	0.97558	0.02873
C	2.21992	-2.09436	-0.09810

O	1.95235	-3.29119	0.03422
O	2.17495	2.28707	-0.39043
O	3.09131	-1.61660	-1.02065
C	3.74779	-2.62469	-1.81910
H	3.00949	-3.19167	-2.40799
H	4.43048	-2.06988	-2.47499
H	4.30478	-3.32199	-1.17426
C	3.04696	3.22267	-1.06343
H	2.38873	4.02614	-1.41746
H	3.80349	3.61260	-0.36441
H	3.55737	2.73262	-1.90706

NBD-H_2
QC isomer
Symmetry: C_1
Electronic energy: -1188.02089872

C	0.93484	-1.13560	0.67536
C	1.21224	-0.42258	2.02045
C	-1.02957	-0.94778	2.06553
C	-0.56546	-1.47649	0.72867
C	0.13969	-0.81014	3.02177
H	-0.03016	-0.01983	3.77350
H	0.37208	-1.75684	3.53843
C	0.65407	0.37083	0.87077
C	-0.87973	0.04134	0.90450
H	2.26254	-0.29030	2.29077
H	-2.04355	-1.18986	2.39309
C	1.30908	1.50557	0.17897
C	1.12565	1.68517	-1.20778
C	2.10694	2.42381	0.88648
C	1.72509	2.76352	-1.86887
H	0.50741	0.97120	-1.76108
C	2.71109	3.50293	0.22403
H	2.24880	2.28996	1.96372
C	2.51989	3.67662	-1.15511
H	1.57416	2.89238	-2.94498
H	3.32907	4.20957	0.78645
H	2.98856	4.51871	-1.67316
C	-1.97981	0.85873	0.34888
C	-3.20412	0.27202	-0.04367
C	-1.84439	2.26099	0.25461
C	-4.25404	1.06587	-0.52189
H	-3.34214	-0.81008	0.03197
C	-2.89839	3.05086	-0.22657
H	-0.91080	2.73850	0.56056
C	-4.10700	2.45889	-0.62046
H	-5.19329	0.59000	-0.82035
H	-2.76973	4.13569	-0.29173
H	-4.92790	3.07572	-0.99797
C	1.98833	-1.85313	-0.06250
O	1.90424	-3.00739	-0.46858
C	-1.32453	-2.40876	-0.13625
O	-2.31347	-3.05251	0.20794
O	3.10335	-1.07433	-0.20766
O	-0.82627	-2.40246	-1.39964
C	-1.47781	-3.30682	-2.31768
H	-2.53896	-3.03729	-2.43675
H	-0.93652	-3.19437	-3.26560
H	-1.40453	-4.34140	-1.94866
C	4.20767	-1.72229	-0.87563
H	5.00153	-0.96561	-0.91996
H	4.53947	-2.60602	-0.30796
H	3.91283	-2.03791	-1.88843

NBD-H_2
Transition state
Symmetry: C_1
Electronic energy: -1187.98670998
$\langle S^2 \rangle = 0.9808$

C	1.38450	-0.17300	0.67300
C	0.84536	0.29394	2.03351
C	-0.11998	-1.73049	1.49760
C	1.07132	-1.60831	0.57070
C	0.38368	-0.96879	2.76125
H	-0.42936	-0.76696	3.47850
H	1.20932	-1.49752	3.26523
C	-0.12489	0.51580	0.89172
C	-1.01233	-0.68431	0.83818
H	1.32811	1.13823	2.52953
H	-0.52009	-2.73845	1.63939
C	-0.37190	1.83489	0.26139
C	-0.53118	1.93003	-1.13861
C	-0.43139	3.00929	1.03744
C	-0.74926	3.17313	-1.74381
H	-0.46986	1.02160	-1.74468
C	-0.65548	4.25324	0.43095
H	-0.30589	2.94202	2.12246
C	-0.81385	4.33864	-0.96128
H	-0.86425	3.23353	-2.83013
H	-0.70531	5.15688	1.04600
H	-0.98509	5.30959	-1.43571
C	-2.29342	-0.88234	0.25556
C	-2.78086	-2.21071	0.02807
C	-3.15793	0.20440	-0.09713
C	-4.04266	-2.42964	-0.52098
H	-2.13395	-3.06336	0.24995
C	-4.42159	-0.03244	-0.63668
H	-2.83275	1.23012	0.08375
C	-4.87710	-1.34608	-0.85709
H	-4.38017	-3.45546	-0.69793
H	-5.06496	0.81741	-0.88512
H	-5.86799	-1.52333	-1.28473
C	2.28196	0.62145	-0.19437
O	2.50230	0.40273	-1.38004
C	1.59090	-2.69985	-0.21924
O	0.99686	-3.78036	-0.36306
O	2.77486	1.70738	0.48025
O	2.81472	-2.43308	-0.76418
C	3.34298	-3.48104	-1.59949
H	4.30508	-3.10008	-1.96573
H	3.48223	-4.40891	-1.02127
H	2.65999	-3.68429	-2.43960
C	3.47283	2.65873	-0.35318
H	3.82268	3.44244	0.33111
H	4.31982	2.17694	-0.86498
H	2.78427	3.07709	-1.10471

NBD-H_2
S_0/S_1 conical intersection
Symmetry: C_1

C	1.41711470	0.61171462	1.69431860
C	1.26695846	-0.08749700	3.01902117
C	0.69969529	-1.66408176	1.48643706
C	0.66543475	-0.34971659	0.85758104
C	1.61346105	-1.55233779	2.69603432
H	1.34726991	-2.25557914	3.47885247
H	2.66086749	-1.65819181	2.44380569
C	-0.24074742	-0.09130913	2.97577656
C	-0.60781697	-0.92345604	1.87837943
H	1.72333962	0.36663803	3.87963922
H	0.60642251	-2.55642617	0.89616815
C	-1.06681659	0.71623310	3.85190785
C	-2.35393745	0.30358075	4.21794687
C	-0.54439693	1.90374030	4.38566495
C	-3.09090614	1.04813400	5.11674335
H	-2.75925738	-0.60718555	3.82497653
C	-1.30925519	2.66344088	5.24902020
H	0.42725258	2.24925051	4.08335264
C	-2.57332828	2.23188646	5.62326148
H	-4.06755326	0.71322142	5.41445698
H	-0.91630662	3.58589726	5.63479540
H	-3.15687448	2.81839703	6.31019570
C	-1.96013146	-1.28591771	1.37799775
C	-2.87828128	-0.31327575	0.97995262
C	-2.33618430	-2.62374818	1.29249267
C	-4.13443935	-0.67170318	0.52583212
H	-2.59953856	0.72265653	1.01877900
C	-3.59108468	-2.98385950	0.82686571
H	-1.64561562	-3.39005092	1.59627208
C	-4.49554766	-2.00859244	0.44503174
H	-4.82890186	0.09261286	0.22540319
H	-3.85931772	-4.02353993	0.76741084
H	-5.47024663	-2.28503114	0.08469679
C	1.76233450	1.95326646	1.53094044
O	2.09355979	2.71510465	2.42510641
C	0.30845087	-0.19293303	-0.59271567
O	0.73821258	-0.91623340	-1.43104456
O	1.74639609	2.37008991	0.24530970
O	-0.51360618	0.80460273	-0.81631217
C	-0.83486125	1.07893536	-2.16844440
H	-1.33581538	0.23340496	-2.61702337
H	-1.49014630	1.93511012	-2.14503078
H	0.06134293	1.30717278	-2.72601287
C	2.11918718	3.70535871	0.01227444
H	2.05173655	3.85154655	-1.05708382
H	1.45477850	4.39244898	0.51883631
H	3.13086058	3.89243220	0.34440018

NBD-H_2

S_1 minimum

Symmetry: C_1

C	-1.118000000	0.725768390	0.000000000
C	0.043462581	1.135579887	-0.899191911
C	-0.005801996	-1.102841371	-0.958384749
C	-1.118000000	-0.677000000	0.000000000
C	0.024265367	0.037437116	-1.972837560
C	1.157972073	0.685917575	0.000000000
C	1.077115546	-0.734866403	0.022374594
C	2.106679604	1.580366313	0.643194686
C	3.430383281	1.182675009	0.885926759
C	1.735926025	2.898094158	0.952419080
C	4.345169119	2.069085450	1.418242810
C	2.653518994	3.768900126	1.507219387
C	3.959368181	3.362341077	1.738557389
C	1.707445452	-1.682917422	0.929291093
C	2.023062461	-1.341953935	2.252617813
C	1.971684109	-2.988934347	0.499179043
C	2.596905860	-2.267449068	3.100216763
C	2.560751606	-3.907223408	1.345248657
C	2.874806781	-3.549531955	2.647474708
C	-1.914993535	1.756320410	0.629617773
C	-1.707652332	-1.707878833	0.836487843
C	-3.060302645	-2.232691337	2.659519647
C	-3.919589543	2.323416306	1.676659079
O	-1.563085721	2.909630808	0.712195124
O	-1.528384135	-2.883420274	0.644017380
O	-3.102902289	1.354710387	1.057930334
O	-2.443770084	-1.260613890	1.845158203
H	0.908957981	0.034523546	-2.600733644
H	-0.867590670	0.074559261	-2.585508958
H	0.063266322	2.165444980	-1.208272260
H	-0.055550959	-2.123376284	-1.290784723
H	3.747677806	0.191480713	0.627458849
H	0.723844512	3.217583546	0.793822295
H	5.359490212	1.751768503	1.580618598
H	2.347861624	4.768689154	1.757281747
H	4.671809509	4.048252814	2.160575537
H	1.790835741	-0.361103148	2.618432251
H	1.724480825	-3.279724590	-0.503605679
H	2.820347645	-1.993372546	4.115310882
H	2.765094912	-4.902102720	0.993938446
H	3.324569148	-4.267903327	3.309064811
H	-2.320914554	-2.857309261	3.141146966
H	-3.621977635	-1.682771168	3.399754384
H	-3.723900713	-2.857731834	2.078462997
H	-4.822160483	1.805473971	1.964099269
H	-3.433964252	2.736506172	2.549830739
H	-4.153565562	3.126007169	0.991280208

NICS scan:

bq	0.0	0.0	0.0
bq	0.0	0.0	0.1
bq	0.0	0.0	0.2
bq	0.0	0.0	0.3
bq	0.0	0.0	0.4
bq	0.0	0.0	0.5
bq	0.0	0.0	0.6
bq	0.0	0.0	0.7
bq	0.0	0.0	0.8
bq	0.0	0.0	0.9
bq	0.0	0.0	1.0
bq	0.0	0.0	1.1
bq	0.0	0.0	1.2
bq	0.0	0.0	1.3
bq	0.0	0.0	1.4
bq	0.0	0.0	1.5
bq	0.0	0.0	1.6
bq	0.0	0.0	1.7
bq	0.0	0.0	1.8
bq	0.0	0.0	1.9
bq	0.0	0.0	2.0

bq	0.0	0.0	2.1
bq	0.0	0.0	2.2
bq	0.0	0.0	2.3
bq	0.0	0.0	2.4
bq	0.0	0.0	2.5
bq	0.0	0.0	2.6
bq	0.0	0.0	2.7
bq	0.0	0.0	2.8
bq	0.0	0.0	2.9
bq	0.0	0.0	3.0
bq	0.0	0.0	3.1
bq	0.0	0.0	3.2
bq	0.0	0.0	3.3
bq	0.0	0.0	3.4
bq	0.0	0.0	3.5
bq	0.0	0.0	3.6
bq	0.0	0.0	3.7
bq	0.0	0.0	3.8
bq	0.0	0.0	3.9
bq	0.0	0.0	4.0
bq	0.0	0.0	4.1
bq	0.0	0.0	4.2
bq	0.0	0.0	4.3
bq	0.0	0.0	4.4
bq	0.0	0.0	4.5
bq	0.0	0.0	4.6
bq	0.0	0.0	4.7
bq	0.0	0.0	4.8
bq	0.0	0.0	4.9
bq	0.0	0.0	5.0

NBD-Me$_2$
NBD isomer
Symmetry: C_1
Electronic energy: -1266.58037886

C	1.73897	0.40234	0.34377
C	0.67278	0.93733	1.31873
C	0.41798	-1.28182	1.25033
C	1.57271	-0.94931	0.29884
C	0.67438	-0.21848	2.39110
C	-0.67874	0.67822	0.61245
C	-0.84710	-0.67958	0.59432
H	0.84294	1.96499	1.66664
H	0.35125	-2.33729	1.54644
C	-1.45854	1.75560	-0.00528
C	-2.03307	1.59622	-1.28885
C	-1.61935	2.99865	0.64914
C	-2.75724	2.63478	-1.88364
H	-1.89425	0.64969	-1.81852
C	-2.35130	4.03539	0.05523
H	-1.17817	3.14634	1.63989
C	-2.92520	3.85844	-1.21328
H	-3.18636	2.49217	-2.88029
H	-2.47224	4.98541	0.58488
H	-3.49212	4.66950	-1.67988
C	-1.93794	-1.52003	0.09999
C	-1.66973	-2.82775	-0.37225
C	-3.28292	-1.07551	0.11259
C	-2.70424	-3.64742	-0.84277
H	-0.64027	-3.19979	-0.37993
C	-4.31321	-1.89899	-0.35132
H	-3.51219	-0.07864	0.49870
C	-4.02982	-3.18759	-0.83690
H	-2.47244	-4.65156	-1.21072
H	-5.34598	-1.53779	-0.32619
H	-4.83820	-3.83052	-1.19752
C	2.73176	1.24675	-0.34992
O	3.85108	0.90624	-0.71689
C	2.25363	-2.00279	-0.47646
O	2.40977	-3.14997	-0.05495
O	2.24032	2.51598	-0.50012
O	2.64518	-1.58532	-1.70460
C	3.38065	-2.56249	-2.47354
H	2.77089	-3.46523	-2.63576
H	3.60905	-2.06613	-3.42501
H	4.30668	-2.84097	-1.94716
C	3.13165	3.43112	-1.17334
H	2.59166	4.38579	-1.21107
H	4.07428	3.53276	-0.61284
H	3.35739	3.06955	-2.18878
C	2.00187	-0.40264	3.14086
H	2.17675	0.45540	3.81259
H	1.95589	-1.30917	3.76764
H	2.86969	-0.49711	2.47279
C	-0.44766	-0.11444	3.43262
H	-0.47909	-1.03064	4.04661
H	-0.24836	0.73073	4.11374
H	-1.43942	0.03103	2.98183

NBD-Me$_2$
QC isomer
Symmetry: C_1
Electronic energy: -1266.55414216

C	1.11414	-0.90034	0.22384
C	1.29593	-0.30223	1.63537
C	-0.79993	-1.23697	1.65011
C	-0.29383	-1.52421	0.25932
C	0.35523	-0.99571	2.61871
C	0.56524	0.49568	0.59443
C	-0.87974	-0.11871	0.61230
H	2.31078	-0.00729	1.91615
H	-1.73769	-1.70150	1.96758
C	0.97321	1.80412	0.03204
C	0.73920	2.09118	-1.32871
C	1.57964	2.78276	0.84166
C	1.10011	3.33308	-1.86432
H	0.27135	1.33067	-1.96184
C	1.94555	4.02620	0.30473
H	1.75981	2.56451	1.89928
C	1.70426	4.30530	-1.04908
H	0.91160	3.54402	-2.92135
H	2.41652	4.77824	0.94521
H	1.98661	5.27550	-1.46879
C	-2.13126	0.53083	0.16771
C	-3.24325	-0.23210	-0.25530
C	-2.25892	1.93604	0.21860
C	-4.44031	0.39549	-0.62164
H	-3.17760	-1.32310	-0.29005
C	-3.45949	2.55921	-0.15121
H	-1.41637	2.54632	0.55165

C	-4.55517	1.79430	-0.57623
H	-5.28866	-0.21532	-0.94563
H	-3.53466	3.65002	-0.10477
H	-5.49071	2.28159	-0.86644
C	2.25790	-1.33021	-0.59802
O	2.38769	-2.44451	-1.09457
C	-0.89548	-2.48202	-0.69483
O	-1.75273	-3.31838	-0.41648
O	3.19021	-0.33544	-0.70655
O	-0.42694	-2.26745	-1.95169
C	-0.92841	-3.17847	-2.95349
H	-2.02083	-3.07978	-3.05226
H	-0.42345	-2.88991	-3.88407
H	-0.68049	-4.21617	-2.68209
C	4.37640	-0.70047	-1.44487
H	5.00490	0.19940	-1.44382
H	4.89393	-1.54104	-0.95607
H	4.11450	-0.99191	-2.47387
C	0.94710	-2.31330	3.13989
H	1.84426	-2.12612	3.75457
H	0.21497	-2.85120	3.76496
H	1.23228	-2.97134	2.30257
C	-0.05242	-0.05350	3.76196
H	-0.80758	-0.52892	4.41022
H	0.81769	0.20211	4.39039
H	-0.48124	0.88174	3.36494

NBD-Me$_2$
Transition state
Symmetry: C_1
Electronic energy: -1266.52062081
$\langle S^2 \rangle$ = 0.9887

C	1.30243	0.37352	0.32304
C	0.70700	0.44927	1.73569
C	0.50626	-1.70507	0.94825
C	1.52385	-1.05421	0.04058
C	0.77801	-0.97198	2.32366
C	-0.33532	0.43550	0.63963
C	-0.73722	-0.98810	0.44274
H	0.88034	1.34614	2.33604
H	0.50755	-2.79966	0.97249
C	-1.07804	1.63671	0.18560
C	-1.32614	1.83208	-1.19055
C	-1.53212	2.60127	1.10613
C	-2.01785	2.96629	-1.63165
H	-0.96242	1.09104	-1.90821
C	-2.23000	3.73431	0.66400
H	-1.34030	2.45566	2.17369
C	-2.47375	3.92030	-0.70588
H	-2.19821	3.10861	-2.70133
H	-2.58268	4.47313	1.39003
H	-3.01534	4.80585	-1.05174
C	-1.91418	-1.56547	-0.10445
C	-1.93444	-2.95391	-0.45944
C	-3.12432	-0.82193	-0.29566
C	-3.08350	-3.54856	-0.97641
H	-1.02053	-3.54469	-0.35774
C	-4.26815	-1.43443	-0.80593
H	-3.15778	0.23191	-0.01508
C	-4.26207	-2.79836	-1.15440
H	-3.06245	-4.60742	-1.25208
H	-5.18074	-0.84317	-0.93068
H	-5.16227	-3.27021	-1.55827
C	1.81743	1.53375	-0.43766
O	2.05880	1.54628	-1.63919
C	2.41966	-1.77963	-0.82775
O	2.29062	-2.98590	-1.09037
O	1.90718	2.64069	0.36446
O	3.44470	-1.00971	-1.30342
C	4.33408	-1.68719	-2.21151
H	5.07391	-0.93219	-2.50744
H	4.82211	-2.54224	-1.71597
H	3.78040	-2.05423	-3.09038
C	2.18776	3.86732	-0.34509
H	2.23336	4.64584	0.42737
H	3.14462	3.79245	-0.88408
H	1.38144	4.07947	-1.06523
C	2.15874	-1.30149	2.89834
H	2.36264	-0.68874	3.79311
H	2.21371	-2.36257	3.19505
H	2.95906	-1.10926	2.16468
C	-0.32828	-1.22701	3.35155
H	-0.32317	-2.28194	3.67425
H	-0.17849	-0.60003	4.24737
H	-1.32406	-1.00241	2.93519

NBD-Me$_2$
S_0/S_1 conical intersection
Symmetry: C_1

C	1.27213419	0.54109262	0.54965639
C	0.65335458	0.87954070	1.82623184
C	0.49088096	-1.35037883	1.49226733
C	1.52997482	-0.91062873	0.49727593
C	0.65467506	-0.38084651	2.69576321
C	-0.44777985	0.67297900	0.75395582
C	-0.64840458	-0.73593708	0.71758733
H	0.76380566	1.86633497	2.23911521
H	0.41544357	-2.40286776	1.70359718
C	-1.26335788	1.76731361	0.16567968
C	-1.54859193	1.81751526	-1.19975010
C	-1.75376826	2.78521154	0.97949505
C	-2.31036496	2.84482920	-1.72528752
H	-1.15996981	1.05520917	-1.84791544
C	-2.50739165	3.82185508	0.45105487
H	-1.54912046	2.76646965	2.03499400
C	-2.79097051	3.85346988	-0.90279456
H	-2.51961968	2.86497935	-2.78009047
H	-2.87311157	4.59853132	1.09878090
H	-3.37580577	4.65598088	-1.31545271
C	-1.64960906	-1.51647934	0.01230057
C	-1.32734026	-2.80468607	-0.43870512
C	-2.94676473	-1.02590676	-0.17706439
C	-2.28247361	-3.56674027	-1.08252071
H	-0.32729556	-3.18106557	-0.32915982
C	-3.90531466	-1.81369283	-0.78301325
H	-3.20832157	-0.04729190	0.17232932
C	-3.57071208	-3.07819096	-1.24494375
H	-2.02402674	-4.54263083	-1.45003947
H	-4.90569165	-1.44025196	-0.90352391
H	-4.31474620	-3.68282696	-1.73198342

C	1.93100085	1.59185237	-0.29771747
O	2.70329868	2.36985619	0.15952743
C	2.15541040	-1.73662378	-0.43621359
O	2.07930286	-2.92043099	-0.48819885
O	1.56814521	1.55099757	-1.55709593
O	2.92758166	-1.05084547	-1.31239250
C	3.63198406	-1.82392463	-2.24948754
H	2.95779695	-2.40089672	-2.86834210
H	4.18461866	-1.12560334	-2.86285207
H	4.31828806	-2.50278012	-1.76141219
C	2.21996600	2.44756494	-2.43914670
H	1.80437067	2.25163022	-3.41476472
H	2.03039013	3.47033132	-2.14762254
H	3.28381524	2.26197578	-2.43966172
C	1.97392988	-0.57521543	3.44154116
H	2.10679940	0.20718490	4.18368475
H	1.97832971	-1.52844149	3.96232652
H	2.81665148	-0.55472282	2.76495363
C	-0.51756472	-0.43096182	3.67899186
H	-0.54993912	-1.39323659	4.18066041
H	-0.41421039	0.33363630	4.44330614
H	-1.47616949	-0.28129531	3.19167002

NBD-Me$_2$

S_1 minimum

Symmetry: C_1

C	1.560103	0.367549	0.244726
C	0.716855	0.832555	1.428946
C	0.416052	-1.376356	1.280920
C	1.408977	-1.025184	0.180760
C	0.756879	-0.359570	2.403728
C	-0.554493	0.637200	0.645585
C	-0.780925	-0.767369	0.614545
H	0.937128	1.822826	1.786860
H	0.342995	-2.418951	1.539285
C	-1.237963	1.703224	-0.075713
C	-1.801045	1.492975	-1.342026
C	-1.305109	2.987548	0.475931
C	-2.421122	2.525095	-2.016842
H	-1.726686	0.527167	-1.802507
C	-1.939495	4.014125	-0.195614
H	-0.868728	3.177372	1.437886
C	-2.499016	3.786304	-1.443349
H	-2.836947	2.349404	-2.992455
H	-1.989420	4.991534	0.248593
H	-2.984822	4.588009	-1.969977
C	-1.920765	-1.522511	0.114170
C	-1.757242	-2.848265	-0.313950
C	-3.214208	-0.979991	0.130385
C	-2.847723	-3.587071	-0.730732
H	-0.774695	-3.277449	-0.354562
C	-4.299924	-1.735185	-0.266960
H	-3.371447	0.020563	0.482688
C	-4.121235	-3.038353	-0.706176
H	-2.701623	-4.595281	-1.074003
H	-5.285586	-1.307174	-0.231096
H	-4.967345	-3.621728	-1.022343
C	2.091403	1.385909	-0.647498
O	2.116678	2.554304	-0.359982
C	1.975304	-2.083622	-0.629185
O	1.507271	-3.195075	-0.692830
O	2.523062	0.934299	-1.817208
O	3.098636	-1.759458	-1.253088
C	3.692609	-2.754380	-2.057225
H	3.018205	-3.069415	-2.841253
H	4.572600	-2.298516	-2.485299
H	3.970078	-3.614738	-1.464484
C	3.073733	1.886412	-2.700114
H	3.382266	1.332863	-3.574256
H	2.338210	2.631011	-2.970742
H	3.925374	2.379337	-2.252536
C	2.127695	-0.586267	3.041443
H	2.363471	0.226565	3.722455
H	2.126523	-1.507037	3.617655
H	2.919058	-0.648140	2.307757
C	-0.300765	-0.287066	3.508820
H	-0.316747	-1.210268	4.080249
H	-0.073723	0.520837	4.198435
H	-1.300349	-0.121278	3.123396

NBD-*i*Pr$_2$

NBD isomer

Symmetry: C_1

Electronic energy: -1423.62153148

C	1.55788	0.47618	-0.46264
C	0.68450	0.89998	0.73071
C	0.38061	-1.29737	0.47668
C	1.35699	-0.86079	-0.62176
C	0.85191	-0.36426	1.68063
C	-0.76831	0.71388	0.23641
C	-0.96472	-0.63385	0.10783
H	0.91872	1.89158	1.13680
H	0.35196	-2.38043	0.65219
C	-1.62702	1.85048	-0.10791
C	-2.43306	1.83482	-1.27120
C	-1.64212	3.01083	0.70071
C	-3.23629	2.93172	-1.60015
H	-2.41294	0.95393	-1.91878
C	-2.45271	4.10571	0.37336
H	-1.02332	3.04633	1.60303
C	-3.25450	4.07147	-0.77785
H	-3.84610	2.90148	-2.50843
H	-2.45627	4.98931	1.01906
H	-3.88295	4.92848	-1.03763
C	-2.14583	-1.41682	-0.25585
C	-2.00095	-2.67084	-0.89675
C	-3.45386	-0.97522	0.06136
C	-3.12246	-3.43926	-1.23581
H	-0.99970	-3.03973	-1.14085
C	-4.57055	-1.74723	-0.27270
H	-3.58340	-0.02336	0.58339
C	-4.41247	-2.98129	-0.92768
H	-2.98631	-4.40142	-1.73890
H	-5.57154	-1.38957	-0.01226
H	-5.28810	-3.58412	-1.18593
C	2.46502	1.35829	-1.21690
O	3.40435	1.00250	-1.92253
C	1.93407	-1.82807	-1.57543
O	2.35570	-2.93098	-1.22613
O	2.14116	2.67244	-1.00099

O	1.90776	-1.38852	-2.85510
C	2.54498	-2.26497	-3.81233
H	2.08806	-3.26649	-3.78536
H	2.38970	-1.78712	-4.78764
H	3.61940	-2.34872	-3.58687
C	2.97954	3.61781	-1.69912
H	2.59281	4.60730	-1.42369
H	4.02985	3.50418	-1.38744
H	2.91158	3.46050	-2.78698
C	2.34138	-0.65601	2.07484
H	2.84624	-0.94297	1.13777
C	-0.17482	-0.32737	2.86414
H	-1.06986	0.17176	2.45585
C	3.12515	0.56898	2.58356
H	2.78233	0.92935	3.56441
H	4.19037	0.30039	2.68542
H	3.06831	1.41166	1.87468
C	2.53803	-1.86267	3.00828
H	3.61392	-2.09707	3.07330
H	2.18141	-1.67302	4.03317
H	2.02966	-2.76217	2.62515
C	0.25372	0.53514	4.06506
H	-0.60446	0.65497	4.74801
H	1.07222	0.08153	4.64635
H	0.57314	1.54448	3.75583
C	-0.67580	-1.70771	3.33157
H	0.10620	-2.31454	3.81068
H	-1.48395	-1.56865	4.07009
H	-1.09854	-2.29084	2.49721

NBD-*i*Pr$_2$
QC isomer
Symmetry: C_1
Electronic energy: -1423.59883886

C	-0.64239	0.73219	0.87461
C	-1.12381	1.03633	-0.55979
C	-1.13323	-1.24756	-0.39873
C	-0.66127	-0.80458	0.96042
C	-1.93364	-0.14772	-1.10452
C	0.32372	0.71231	-0.33303
C	0.33314	-0.85248	-0.24425
H	-1.40191	2.07457	-0.75314
H	-1.33769	-2.31045	-0.54456
C	1.48801	1.59777	-0.56520
C	2.60456	1.53073	0.29380
C	1.51024	2.50115	-1.64401
C	3.71929	2.34835	0.07384
H	2.58894	0.82987	1.13437
C	2.62540	3.32368	-1.86308
H	0.64885	2.55112	-2.31743
C	3.73341	3.24801	-1.00572
H	4.57973	2.28617	0.74699
H	2.62953	4.02141	-2.70614
H	4.60476	3.88744	-1.17617
C	1.47617	-1.75350	-0.50088
C	1.54966	-3.03341	0.09344
C	2.49257	-1.36959	-1.40257
C	2.61229	-3.89630	-0.20245
H	0.76786	-3.36073	0.78451
C	3.55573	-2.23644	-1.69297
H	2.45108	-0.38820	-1.88082
C	3.62387	-3.50226	-1.09321
H	2.64934	-4.88329	0.26895
H	4.33322	-1.91675	-2.39367
H	4.45491	-4.17708	-1.31873
C	-0.82183	1.68736	1.97978
O	-1.36099	1.42975	3.05160
C	-0.59466	-1.66093	2.16509
O	-1.12071	-2.76707	2.27742
O	-0.34462	2.92472	1.64575
O	0.18935	-1.09477	3.11856
C	0.27967	-1.83741	4.35382
H	0.73234	-2.82574	4.17756
H	0.91272	-1.22803	5.01115
H	-0.72184	-1.96937	4.79146
C	-0.54372	3.93915	2.65413
H	-0.09417	4.85041	2.23908
H	-1.61791	4.08590	2.84941
H	-0.04597	3.65133	3.59314
C	-3.38539	-0.09236	-0.52123
H	-3.23041	0.21343	0.53257
C	-1.70969	-0.26968	-2.64861
H	-0.61999	-0.45495	-2.73483
C	-1.98969	1.00413	-3.46867
H	-1.59928	0.87332	-4.49234
H	-3.06500	1.22165	-3.55481
H	-1.49856	1.89417	-3.04319
C	-2.41748	-1.46995	-3.29808
H	-3.50508	-1.30490	-3.37168
H	-2.03875	-1.61890	-4.32343
H	-2.25218	-2.40664	-2.74199
C	-4.29056	0.97240	-1.16209
H	-4.61903	0.67205	-2.17099
H	-5.19851	1.10660	-0.55040
H	-3.79518	1.95403	-1.24335
C	-4.12057	-1.44431	-0.45448
H	-5.07258	-1.31348	0.08765
H	-4.36414	-1.84432	-1.45089
H	-3.53811	-2.20210	0.09285

NBD-*i*Pr$_2$
Transitions state
Symmetry: C_1
Electronic energy: -1423.56527269
$\langle S^2 \rangle = 1.0041$

C	-0.55988	-1.17359	-0.17221
C	-0.48199	-0.61851	1.25526
C	-1.18693	1.04690	-0.16171
C	-1.38553	-0.23295	-0.93867
C	-1.46976	0.57123	1.33413
C	0.68908	-0.19583	0.39903
C	0.33285	1.11463	-0.20479
H	-0.33994	-1.32977	2.07103
H	-1.74544	1.91629	-0.51799
C	2.04061	-0.79890	0.48871
C	2.77335	-1.06473	-0.68863
C	2.60651	-1.13049	1.73541
C	4.04656	-1.64168	-0.61592
H	2.32880	-0.82432	-1.65872
C	3.88387	-1.70399	1.80783

H	2.04226	-0.92881	2.65121
C	4.60698	-1.96149	0.63255
H	4.60140	-1.84725	-1.53616
H	4.31441	-1.95075	2.78306
H	5.60276	-2.41143	0.68842
C	1.13930	2.15308	-0.74603
C	0.54345	3.18645	-1.54001
C	2.54770	2.24529	-0.50022
C	1.30912	4.22964	-2.05729
H	-0.52338	3.13416	-1.77236
C	3.29836	3.29936	-1.01893
H	3.03517	1.49263	0.12133
C	2.69247	4.29931	-1.80321
H	0.82677	4.99592	-2.67193
H	4.37075	3.34798	-0.80531
H	3.28877	5.12117	-2.20947
C	-0.12454	-2.52966	-0.57036
O	0.06896	-2.90562	-1.72093
C	-2.23786	-0.35413	-2.09651
O	-2.72471	0.62072	-2.69223
O	0.13206	-3.30261	0.53203
O	-2.48578	-1.65181	-2.44812
C	-3.30067	-1.81046	-3.62519
H	-3.38956	-2.89494	-3.77011
H	-4.29168	-1.35071	-3.47946
H	-2.81556	-1.34082	-4.49580
C	0.78680	-4.55630	0.23912
H	0.91536	-5.05079	1.21065
H	0.16833	-5.16903	-0.43451
H	1.76350	-4.36829	-0.23475
C	-2.93207	0.04339	1.47406
H	-2.96447	-0.84497	0.81215
C	-0.94595	1.64078	2.34053
H	0.01610	1.96853	1.89782
C	-0.59068	1.12104	3.74724
H	-0.03429	1.90210	4.29308
H	-1.47965	0.87371	4.34690
H	0.05378	0.22748	3.71264
C	-1.82079	2.89998	2.44762
H	-2.74829	2.70545	3.01119
H	-1.27152	3.69172	2.98434
H	-2.09907	3.29972	1.45921
C	-3.28941	-0.45654	2.88367
H	-3.43573	0.38145	3.58517
H	-4.23613	-1.02160	2.84936
H	-2.51835	-1.12373	3.30245
C	-4.03168	0.98818	0.95216
H	-5.00063	0.46064	0.97114
H	-4.13918	1.89097	1.57202
H	-3.85505	1.30189	-0.08865

NBD-*t*Bu$_2$
NBD isomer
Symmetry: C_1
Electronic energy: -1502.10991524

C	1.33812	0.78948	-0.46520
C	0.72860	0.58466	0.93409
C	0.43565	-1.33230	-0.16062
C	1.12343	-0.37191	-1.14222
C	1.11351	-0.92936	1.22038
C	-0.78218	0.50019	0.60011
C	-0.97138	-0.70559	-0.01862
H	1.00855	1.34485	1.67327
H	0.46724	-2.38686	-0.45978
C	-1.66434	1.66262	0.73993
C	-2.61785	1.96923	-0.26185
C	-1.53766	2.55786	1.82801
C	-3.42768	3.10465	-0.16235
H	-2.70375	1.31243	-1.13142
C	-2.35342	3.69197	1.93039
H	-0.79418	2.36169	2.60654
C	-3.30580	3.97037	0.93806
H	-4.15066	3.32271	-0.95452
H	-2.24126	4.36273	2.78785
H	-3.93946	4.85889	1.01502
C	-2.16683	-1.35948	-0.54715
C	-2.06317	-2.27627	-1.62352
C	-3.44864	-1.13568	0.01629
C	-3.20009	-2.91803	-2.13187
H	-1.08692	-2.47280	-2.07761
C	-4.57886	-1.78469	-0.48913
H	-3.54972	-0.44501	0.85774
C	-4.46277	-2.67717	-1.56923
H	-3.09600	-3.61223	-2.97135
H	-5.55654	-1.59851	-0.03389
H	-5.34869	-3.18403	-1.96309
C	2.00496	2.03043	-0.90021
O	2.92267	2.11615	-1.71056
C	1.32503	-0.74798	-2.55162
O	1.44403	-1.91635	-2.93001
O	1.49590	3.10248	-0.21890
O	1.31996	0.31831	-3.38838
C	1.56695	0.00351	-4.77590
H	0.78700	-0.67070	-5.16369
H	1.54557	0.96885	-5.29711
H	2.55003	-0.47939	-4.88842
C	2.08732	4.37349	-0.56474
H	1.54793	5.11618	0.03687
H	3.16214	4.37623	-0.32356
H	1.96203	4.57500	-1.64002
C	2.72594	-1.19444	1.25268
C	0.36000	-1.56020	2.51619
C	3.41488	-0.09196	2.10041
H	2.99755	0.04246	3.10535
H	4.48652	-0.33128	2.21123
H	3.35597	0.87977	1.58172
C	3.11609	-2.61434	1.76503
H	4.21331	-2.64845	1.87238
H	2.69259	-2.92250	2.72458
H	2.84584	-3.37775	1.01589
C	1.13622	-1.34169	3.84950
H	0.61114	-1.89350	4.64733
H	2.17883	-1.66999	3.86852
H	1.11489	-0.27497	4.13265
C	0.07232	-3.06527	2.26712
H	0.94206	-3.65394	1.95465
H	-0.32684	-3.52030	3.19007
H	-0.70222	-3.17530	1.48976
C	-1.03875	-0.98199	2.90042
H	-1.03647	0.11172	3.02261

H	-1.84001	-1.25401	2.20473
H	-1.30780	-1.41205	3.88149
C	3.49765	-1.16278	-0.10718
H	3.06379	-1.84486	-0.85587
H	3.60323	-0.16735	-0.55547
H	4.52041	-1.52633	0.09512

NBD-*t*Bu$_2$
QC isomer
Symmetry: C_1
Electronic energy: -1502.11242371

C	-0.42673	0.80735	0.91374
C	-1.04807	1.03388	-0.47930
C	-1.05251	-1.23188	-0.19277
C	-0.44571	-0.72179	1.08899
C	-1.91963	-0.16923	-0.88494
C	0.41954	0.70549	-0.37304
C	0.43284	-0.84845	-0.18292
H	-1.33342	2.06477	-0.70038
H	-1.27091	-2.29984	-0.26319
C	1.56119	1.58191	-0.72600
C	2.74506	1.52608	0.04013
C	1.49126	2.48294	-1.80458
C	3.83398	2.34772	-0.27256
H	2.80222	0.82999	0.88305
C	2.58121	3.30933	-2.11689
H	0.57598	2.53489	-2.40226
C	3.75617	3.24266	-1.35357
H	4.74576	2.29305	0.32998
H	2.51163	4.00442	-2.95922
H	4.60723	3.88570	-1.59711
C	1.53635	-1.79588	-0.44441
C	1.54899	-3.06976	0.16937
C	2.57407	-1.47755	-1.34672
C	2.56871	-3.98797	-0.10703
H	0.75354	-3.35017	0.86613
C	3.59629	-2.39874	-1.61730
H	2.58201	-0.50555	-1.84379
C	3.60188	-3.65701	-0.99896
H	2.55595	-4.96770	0.38044
H	4.39021	-2.12715	-2.31983
H	4.40032	-4.37430	-1.21057
C	-0.40716	1.81898	1.98014
O	-0.62408	1.59987	3.16811
C	-0.27886	-1.50755	2.33554
O	-0.93158	-2.50564	2.63524
O	-0.13297	3.06094	1.47515
O	0.74434	-1.01910	3.07997
C	0.95568	-1.68898	4.34182
H	1.19122	-2.75215	4.17818
H	1.80123	-1.16721	4.80749
H	0.05515	-1.60741	4.96991
C	-0.09967	4.11644	2.45976
H	0.13670	5.02859	1.89684
H	-1.07489	4.20755	2.96351
H	0.67566	3.91316	3.21483
C	-3.37210	-0.11885	-0.18424
C	-1.88981	-0.35863	-2.47974
C	-2.23339	0.95184	-3.23163
H	-2.17223	0.76969	-4.31837
H	-3.23723	1.33668	-3.01900
H	-1.50673	1.74700	-2.99709
C	-2.82572	-1.48507	-2.97375
H	-3.89138	-1.27976	-2.80290
H	-2.68738	-1.61129	-4.06145
H	-2.57922	-2.44998	-2.50044
C	-4.41875	0.71091	-0.96332
H	-4.68445	0.28856	-1.94259
H	-5.34709	0.75012	-0.36794
H	-4.08414	1.75150	-1.10992
C	-3.93228	-1.54316	0.05762
H	-4.94526	-1.46141	0.48779
H	-4.01320	-2.14834	-0.85498
H	-3.31364	-2.09213	0.78576
C	-3.32146	0.54244	1.21802
H	-2.65552	0.02601	1.92277
H	-3.03211	1.60405	1.17046
H	-4.33442	0.50151	1.65359
C	-0.47998	-0.75927	-2.98510
H	0.29008	-0.01590	-2.73274
H	-0.15286	-1.73898	-2.60709
H	-0.51299	-0.82572	-4.08578

NBD-*t*Bu$_2$
Transition state
Symmetry: C_1
Electronic energy: -1502.06536876
$\langle S^2 \rangle = 1.0117$

C	0.42368	-1.13284	0.51923
C	0.58306	-0.89724	-0.98503
C	1.11943	1.03508	0.09219
C	1.06154	-0.00712	1.19245
C	1.65106	0.21155	-1.16183
C	-0.71119	-0.24941	-0.54843
C	-0.39475	1.10759	-0.09144
H	0.54481	-1.77915	-1.62810
H	1.62752	1.97056	0.34294
C	-2.03950	-0.86137	-0.73455
C	-2.99679	-0.82330	0.30508
C	-2.36529	-1.52388	-1.93703
C	-4.24865	-1.42497	0.13805
H	-2.73915	-0.33418	1.24838
C	-3.62260	-2.11913	-2.10533
H	-1.62710	-1.56500	-2.74408
C	-4.56786	-2.07208	-1.06824
H	-4.97562	-1.39643	0.95513
H	-3.86387	-2.62244	-3.04645
H	-5.54781	-2.54131	-1.19713
C	-1.24646	2.18376	0.31533
C	-0.76122	3.18529	1.21027
C	-2.57034	2.33528	-0.19688
C	-1.56614	4.26491	1.57819
H	0.23200	3.07197	1.65467
C	-3.35989	3.42536	0.17250
H	-2.95823	1.60411	-0.90924
C	-2.86873	4.39731	1.06344
H	-1.17742	5.00764	2.28171
H	-4.36704	3.52410	-0.24446
H	-3.49339	5.24774	1.35170
C	-0.18008	-2.33807	1.10443

O	-0.61576	-2.44912	2.24717
C	1.43707	0.27833	2.55910
O	1.69959	1.42199	2.96896
O	-0.27281	-3.33642	0.16254
O	1.53161	-0.83779	3.33808
C	1.87330	-0.58643	4.71515
H	1.89589	-1.57549	5.19055
H	2.85483	-0.09099	4.79013
H	1.11313	0.05487	5.18889
C	-1.04615	-4.47939	0.58395
H	-1.02984	-5.17136	-0.26821
H	-0.59769	-4.94489	1.47531
H	-2.07895	-4.17373	0.81665
C	3.15326	-0.34385	-0.88876
C	1.45833	0.99747	-2.55073
C	1.38753	0.01578	-3.75235
H	1.31608	0.59828	-4.68695
H	2.24295	-0.65934	-3.85133
H	0.47535	-0.60188	-3.69097
C	2.55488	2.06641	-2.77873
H	3.57342	1.66782	-2.85670
H	2.34184	2.60338	-3.71889
H	2.54237	2.81405	-1.96790
C	3.89147	-0.85934	-2.15262
H	4.00465	-0.12255	-2.95660
H	4.90860	-1.16223	-1.85190
H	3.40157	-1.75577	-2.56782
C	4.02999	0.74377	-0.21617
H	5.05048	0.34762	-0.07598
H	4.11477	1.66665	-0.80590
H	3.64808	1.01161	0.78176
C	3.21844	-1.58060	0.05755
H	2.94431	-1.36530	1.09899
H	2.59505	-2.41691	-0.29681
H	4.26371	-1.93466	0.07488
C	0.13692	1.80895	-2.67211
H	-0.77005	1.19220	-2.58437
H	0.06886	2.63890	-1.95404
H	0.11877	2.25593	-3.68215

MQ-H$_2$
NBD isomer
Symmetry: C_1
Electronic energy: -803.990649210

C	-5.26672	-0.56102	1.12292
C	-5.09502	0.20867	-0.19930
C	-3.65342	-1.52243	-0.24910
C	-4.40216	-1.59578	1.09288
C	-4.80569	-0.99029	-1.15163
H	-4.46838	-0.67669	-2.15304
H	-5.64964	-1.69509	-1.22257
C	-3.67061	0.82080	-0.17658
C	-2.77952	-0.23533	-0.20118
H	-5.89395	0.91012	-0.47209
H	-3.11289	-2.42380	-0.56546
H	-4.18188	-2.31567	1.88278
H	-5.91363	-0.24546	1.94324
C	-3.38565	2.19294	-0.06396
N	-3.18098	3.35398	0.02423
C	-1.38963	-0.22698	-0.14648
C	-0.15366	-0.24418	-0.10949
C	1.25579	-0.19276	-0.06160
C	1.93187	1.05268	0.04600
C	2.05030	-1.36796	-0.12377
C	3.31952	1.12165	0.09270
H	1.34119	1.97164	0.09114
C	3.43929	-1.30783	-0.07912
H	1.55523	-2.33894	-0.21251
C	4.11684	-0.05899	0.03730
H	3.79069	2.10262	0.17320
H	4.00584	-2.23878	-0.13601
N	5.49394	0.00512	0.09681
C	6.28676	-1.20737	-0.03892
H	7.35058	-0.95487	0.06162
H	6.03687	-1.94120	0.74918
H	6.13821	-1.69368	-1.02317
C	6.16175	1.29765	0.13856
H	7.24666	1.14004	0.19953
H	5.95051	1.90398	-0.76393
H	5.85366	1.88125	1.02540

MQ-H$_2$
QC isomer
Symmetry: C_1
Electronic energy: -803.952230522

C	-4.75318	0.15044	1.03499
C	-5.16570	0.11035	-0.42087
C	-3.75614	-1.70117	-0.15710
C	-3.81621	-1.06130	1.21656
C	-4.94319	-1.27461	-1.00332
H	-4.70039	-1.24123	-2.07872
H	-5.82080	-1.92717	-0.85013
C	-3.81469	0.73033	-0.03763
C	-2.85354	-0.49871	0.14610
H	-5.95019	0.78192	-0.77780
H	-3.27117	-2.67270	-0.27454
H	-3.54822	-1.54740	2.15456
H	-5.26776	0.70817	1.81758
C	-3.43143	2.07891	-0.26097
N	-3.11034	3.19928	-0.43326
C	-1.44010	-0.45863	0.09614
C	-0.21296	-0.37822	0.05583
C	1.20305	-0.26728	0.01412
C	1.83791	0.99417	0.13395
C	2.03352	-1.40451	-0.13839
C	3.22548	1.11580	0.09507
H	1.22127	1.88826	0.26089
C	3.42265	-1.29225	-0.17171
H	1.57252	-2.39257	-0.22417
C	4.06060	-0.02437	-0.07122
H	3.66189	2.11077	0.19715
H	4.01550	-2.20224	-0.27862
N	5.44172	0.09633	-0.14106
C	6.26563	-1.10185	-0.10287
H	7.32191	-0.81387	-0.19462
H	6.13993	-1.67685	0.83820
H	6.02844	-1.77111	-0.94830
C	6.06397	1.37275	0.17552
H	7.15051	1.28572	0.03789
H	5.70515	2.16596	-0.50321

H	5.86780	1.69612	1.21888

MQ-H$_2$
Transition state
Symmetry: C_1
Electronic energy: -803.920460301
$<S^2> = 1.0150$

C	-5.04411	0.07671	0.81893
C	-5.03138	0.13979	-0.69234
C	-3.72138	-1.63185	0.00584
C	-4.56714	-1.24123	1.20801
C	-4.67957	-1.27132	-1.17261
H	-4.16621	-1.27342	-2.14759
H	-5.56680	-1.92574	-1.20758
C	-3.74857	0.69169	-0.06321
C	-2.76088	-0.42540	-0.04205
H	-5.69728	0.81120	-1.23906
H	-3.25324	-2.62218	-0.00443
H	-4.39753	-1.57746	2.23211
H	-5.59522	0.78149	1.44172
C	-3.43673	2.07429	-0.00394
N	-3.19117	3.22638	0.05558
C	-1.40944	-0.37766	-0.01612
C	-0.15686	-0.33333	0.00287
C	1.23887	-0.24270	0.01658
C	1.89462	1.02502	-0.00957
C	2.06915	-1.40218	0.04819
C	3.27990	1.12585	-0.00039
H	1.28501	1.93201	-0.04218
C	3.45531	-1.30371	0.05789
H	1.59831	-2.38894	0.06005
C	4.10614	-0.03542	0.04376
H	3.72769	2.12078	-0.02925
H	4.04247	-2.22362	0.07446
N	5.48638	0.06484	0.07743
C	6.30113	-1.13617	-0.02419
H	7.36081	-0.85964	0.05829
H	6.07332	-1.84044	0.79550
H	6.15301	-1.66687	-0.98662
C	6.12158	1.36223	-0.09800
H	7.21019	1.24349	-0.01353
H	5.89530	1.81180	-1.08589
H	5.79981	2.07138	0.68506

MQ-H$_2$
S_0/S_1 conical intersection

C	-4.615880	-1.228306	0.693955
C	-5.074952	0.123294	0.294083
C	-3.715594	-0.654792	-1.370882
C	-3.729486	-1.714969	-0.276546
C	-5.052677	0.070897	-1.240018
H	-5.037354	1.062996	-1.671816
H	-5.866039	-0.509354	-1.662181
C	-3.697570	0.693184	0.635729
C	-2.862237	-0.146155	-0.289016
H	-5.926346	0.546439	0.798747
H	-3.288478	-0.902249	-2.325379
H	-3.144864	-2.607773	-0.238036
H	-4.786294	-1.662909	1.660741
C	-3.289511	1.052942	1.927952
N	-2.963990	1.388400	2.975617
C	-1.447801	-0.202759	-0.279866
C	-0.254540	-0.214925	-0.232581
C	1.173851	-0.210680	-0.144993
C	1.812584	0.293259	0.987117
C	1.970094	-0.707510	-1.173845
C	3.185233	0.304368	1.088821
H	1.220028	0.678836	1.796598
C	3.344149	-0.704265	-1.083648
H	1.504322	-1.105211	-2.057362
C	3.994154	-0.188274	0.050476
H	3.623934	0.699815	1.982035
H	3.908199	-1.103048	-1.902047
N	5.368810	-0.157004	0.136488
C	6.159517	-0.868285	-0.844832
H	7.207054	-0.730660	-0.621712
H	5.952174	-1.937026	-0.855200
H	5.988087	-0.477503	-1.840928
C	5.995481	0.179225	1.397451
H	7.068183	0.160604	1.274614
H	5.724133	1.179743	1.712240
H	5.732379	-0.514465	2.193996

MQ-Me$_2$
NBD isomer
Symmetry: C_1
Electronic energy: -882.518660159

C	4.64112	-0.03526	-1.62242
C	4.52728	0.55868	-0.21089
C	3.14616	-1.21454	-0.29542
C	3.81141	-1.09659	-1.67245
C	4.34216	-0.76511	0.64166
C	3.08970	1.11827	-0.11276
C	2.23425	0.03437	-0.16666
H	5.31835	1.25469	0.10201
H	2.64798	-2.16603	-0.06185
H	3.57982	-1.73455	-2.52685
H	5.24239	0.39122	-2.42709
C	2.75887	2.48092	-0.02161
N	2.51648	3.63520	0.06269
C	0.84470	-0.00641	-0.13034
C	-0.38947	-0.07870	-0.09528
C	-1.79975	-0.10292	-0.05215
C	-2.54576	1.10080	0.06650
C	-2.52652	-1.32031	-0.13083
C	-3.93539	1.09026	0.10942
H	-2.00854	2.05147	0.12208
C	-3.91672	-1.33968	-0.08871
H	-1.97693	-2.26037	-0.23083
C	-4.66429	-0.13293	0.04131
H	-4.46223	2.04182	0.19701
H	-4.42893	-2.30061	-0.16021
N	-6.04338	-0.14763	0.10189
C	-6.76641	-1.39960	-0.06189
H	-7.84180	-1.21187	0.05712
H	-6.60177	-1.85073	-1.06062
H	-6.46623	-2.13768	0.70377
C	-6.78381	1.10546	0.12582
H	-7.85805	0.88682	0.18838
H	-6.51133	1.71593	1.00588

H	-6.60582	1.71208	-0.78386
C	3.95521	-0.53539	2.11007
H	3.71642	-1.49999	2.59007
H	4.80629	-0.09688	2.65883
H	3.08988	0.13051	2.23328
C	5.55354	-1.70901	0.62154
H	6.38697	-1.26039	1.18915
H	5.29667	-2.66144	1.11639
H	5.90745	-1.93106	-0.39416

MQ-Me$_2$
QC isomer
Symmetry: C_1
Electronic energy: -882.484116525

C	4.13071	1.04725	-1.08264
C	4.59480	0.47053	0.23393
C	3.23157	-1.15235	-0.66397
C	3.21925	-0.04086	-1.69040
C	4.44588	-1.05062	0.25873
C	3.21814	1.13690	0.15474
C	2.28240	0.03120	-0.46186
H	5.37796	0.97714	0.80476
H	2.78427	-2.11914	-0.90910
H	2.92645	-0.14109	-2.73548
H	4.59699	1.88253	-1.60530
C	2.81221	2.28628	0.88215
N	2.47572	3.24711	1.47541
C	0.87187	-0.02570	-0.36981
C	-0.35529	-0.04674	-0.27680
C	-1.77257	-0.07340	-0.17240
C	-2.55354	1.06727	-0.48422
C	-2.46063	-1.24059	0.24202
C	-3.94296	1.04924	-0.38096
H	-2.04951	1.98063	-0.81194
C	-3.85023	-1.27083	0.34258
H	-1.88442	-2.13834	0.48322
C	-4.63324	-0.11941	0.04759
H	-4.49546	1.95500	-0.63645
H	-4.33032	-2.19905	0.65710
N	-6.01311	-0.13370	0.18085
C	-6.69512	-1.39016	0.44813
H	-7.77210	-1.19938	0.55106
H	-6.54841	-2.13492	-0.36129
H	-6.34345	-1.83783	1.39445
C	-6.79335	0.99470	-0.30268
H	-7.85499	0.81736	-0.08276
H	-6.49842	1.92813	0.20821
H	-6.68454	1.15037	-1.39585
C	4.13658	-1.57296	1.66947
H	3.94214	-2.65856	1.65039
H	4.98544	-1.39446	2.35096
H	3.24762	-1.07172	2.08569
C	5.67797	-1.73952	-0.34910
H	6.57242	-1.56985	0.27408
H	5.52032	-2.82890	-0.42132
H	5.88298	-1.35325	-1.36131

MQ-Me$_2$
Transition state
Symmetry: C_1
Electronic energy: -882.452616419
$\langle S^2 \rangle = 1.0151$

C	4.41174	0.74873	-1.17700
C	4.51570	0.53499	0.31476
C	3.25781	-1.16401	-0.60458
C	3.97076	-0.50225	-1.77113
C	4.30112	-0.97284	0.56820
C	3.15701	1.09903	-0.09939
C	2.23709	-0.06007	-0.27588
H	5.18742	1.13873	0.93163
H	2.85243	-2.17367	-0.74187
H	3.74260	-0.66116	-2.82590
H	4.86775	1.59256	-1.69531
C	2.76226	2.44251	0.12743
N	2.44729	3.56501	0.30697
C	0.88545	-0.09816	-0.22475
C	-0.36612	-0.13584	-0.17201
C	-1.76337	-0.14005	-0.10236
C	-2.49131	1.05704	0.17060
C	-2.52396	-1.32951	-0.30535
C	-3.87860	1.06272	0.24146
H	-1.93678	1.98713	0.32147
C	-3.91201	-1.32618	-0.23445
H	-1.99737	-2.26203	-0.52603
C	-4.63449	-0.13115	0.05174
H	-4.38400	2.00801	0.44657
H	-4.44358	-2.26390	-0.40569
N	-6.01575	-0.13036	0.14834
C	-6.76483	-1.33012	-0.19178
H	-7.83383	-1.14756	-0.01765
H	-6.62987	-1.62702	-1.25181
H	-6.46201	-2.18040	0.44471
C	-6.73024	1.13092	0.27640
H	-7.80582	0.92695	0.36511
H	-6.41612	1.67548	1.18443
H	-6.57185	1.79543	-0.59691
C	3.70907	-1.25486	1.95256
H	3.46345	-2.32554	2.05706
H	4.43536	-0.99828	2.74268
H	2.78893	-0.67485	2.12698
C	5.58702	-1.77842	0.34869
H	6.33998	-1.52485	1.11453
H	5.38187	-2.85995	0.42558
H	6.02011	-1.58248	-0.64568

MQ-Me$_2$
S_0/S_1 conical intersection

C	3.96857332	0.07754992	-1.43607783
C	4.44047431	0.53734040	-0.10802792
C	3.14709045	-1.30624298	0.23297734
C	3.11858959	-1.02219630	-1.26184942
C	4.49284121	-0.75871385	0.74068776
C	3.05105939	1.10802179	0.17378259
C	2.25251818	-0.15327042	0.05571303
H	5.27385174	1.21930454	-0.06973304
H	2.75221589	-2.24153637	0.58892911
H	2.53141156	-1.51885571	-2.00287591
H	4.11243100	0.62164223	-2.35038643
C	2.59796971	2.36187752	-0.25463452
N	2.23540910	3.40440915	-0.56814233

C	0.83854276	-0.22246778	0.04286321
C	-0.35578777	-0.22877641	0.03995327
C	-1.78653224	-0.20067576	0.03335851
C	-2.47078821	0.99274997	-0.19314084
C	-2.54046219	-1.35201523	0.24678679
C	-3.84643411	1.03794183	-0.20403894
H	-1.91154944	1.89443148	-0.36424035
C	-3.91706089	-1.32094070	0.23633814
H	-2.03916114	-2.28690924	0.42106283
C	-4.61249212	-0.11926434	0.01833080
H	-4.32122946	1.98034232	-0.38619327
H	-4.44764830	-2.23650781	0.40133858
N	-5.98896630	-0.07549336	0.03197566
C	-6.74118379	-1.31142109	0.05249291
H	-7.79652356	-1.08300503	0.06081238
H	-6.53707195	-1.94004531	-0.81253683
H	-6.52764061	-1.88324932	0.94806319
C	-6.66814995	1.12800461	-0.39905903
H	-7.73469557	0.98043968	-0.31686432
H	-6.40880676	1.96923572	0.23273911
H	-6.44009866	1.39041692	-1.43048550
C	4.48599958	-0.49387961	2.24602748
H	4.39360505	-1.42751081	2.79377327
H	5.41607684	-0.02420392	2.55259965
H	3.67086636	0.15684540	2.53165284
C	5.67042152	-1.66236245	0.36804613
H	6.61003479	-1.18849339	0.63537567
H	5.61515365	-2.60543720	0.90344735
H	5.69712600	-1.88423213	-0.69288313

10 NMR spectra

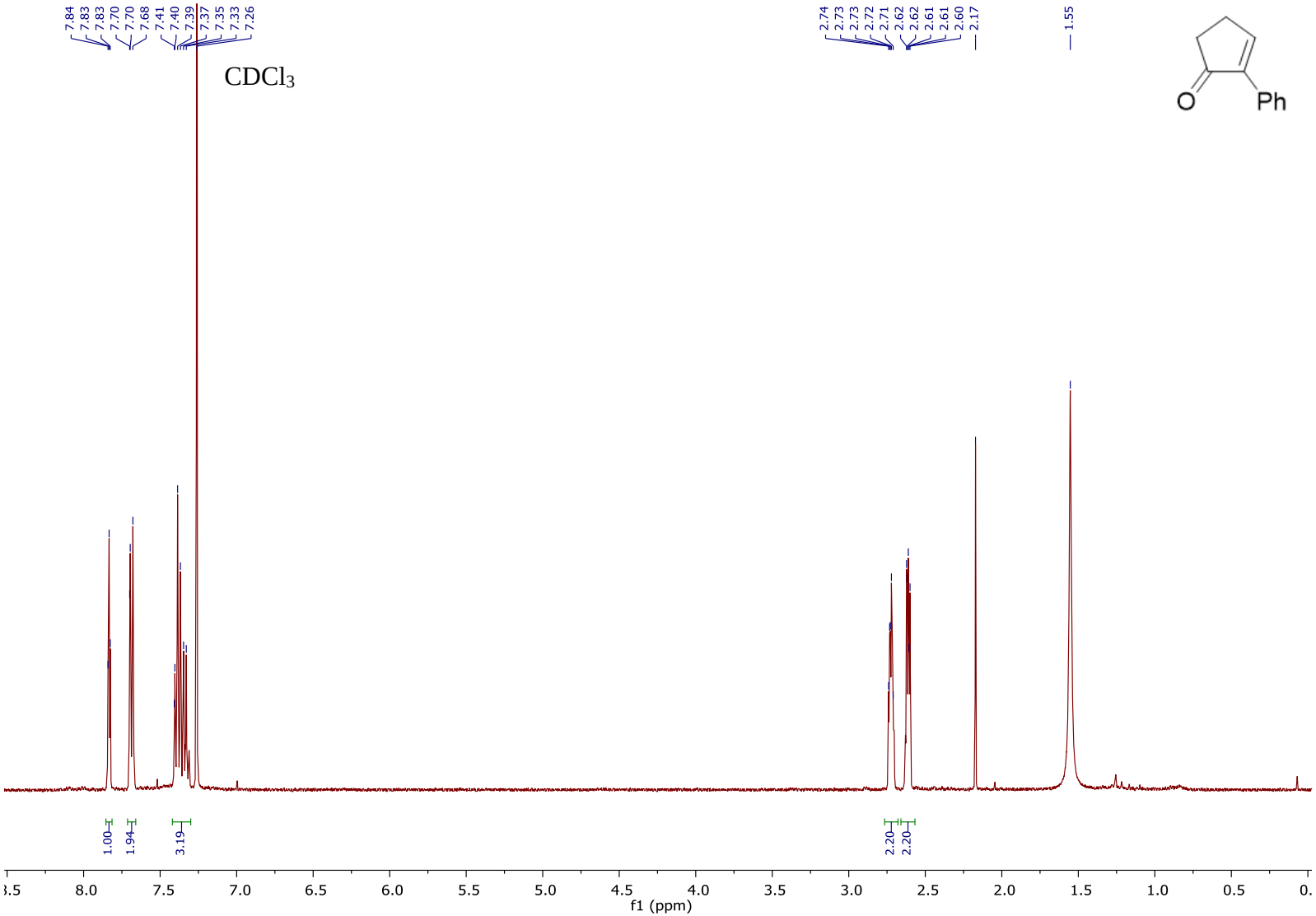


Figure S45. 400 MHz ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

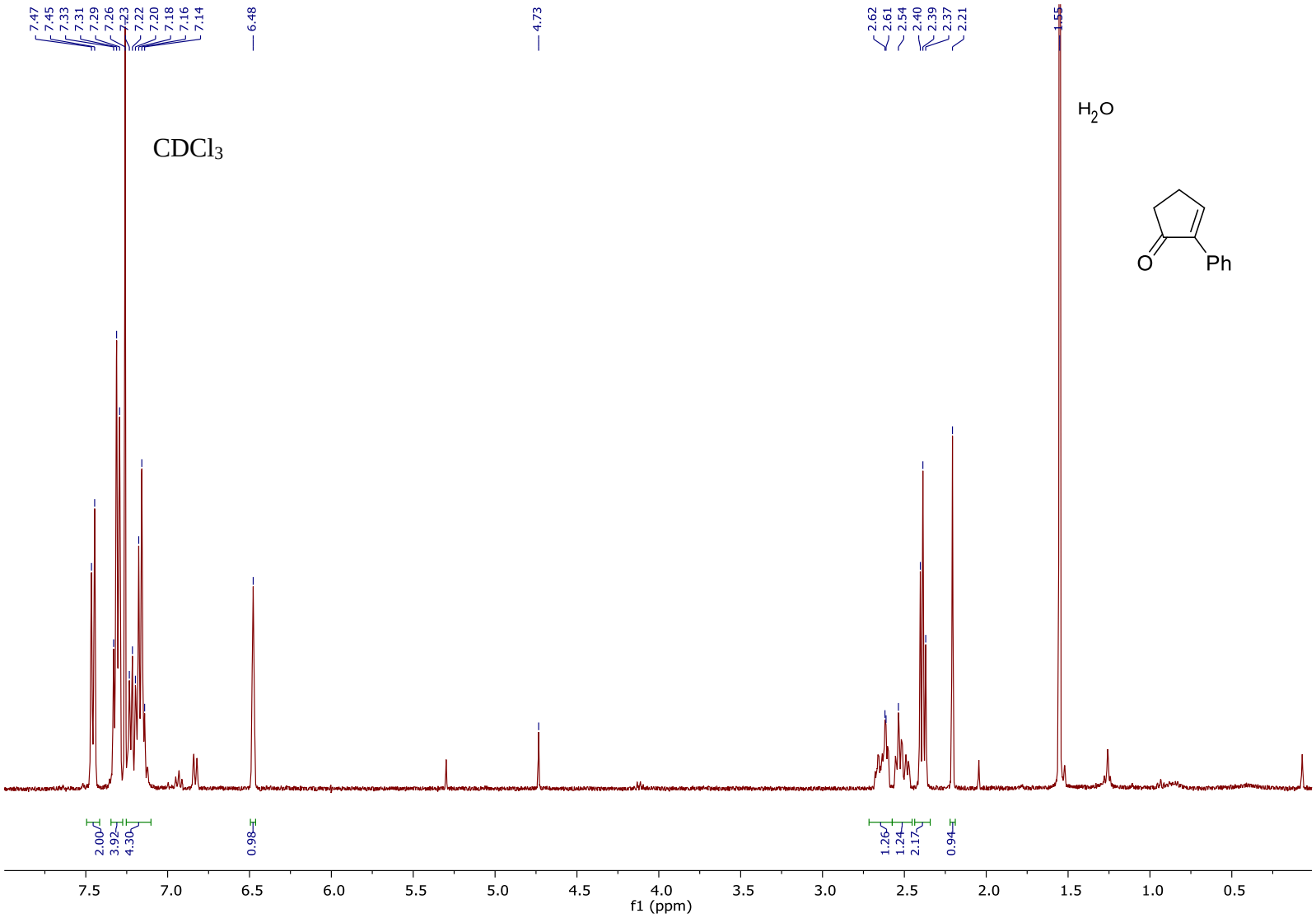


Figure S46. 400 MHz ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

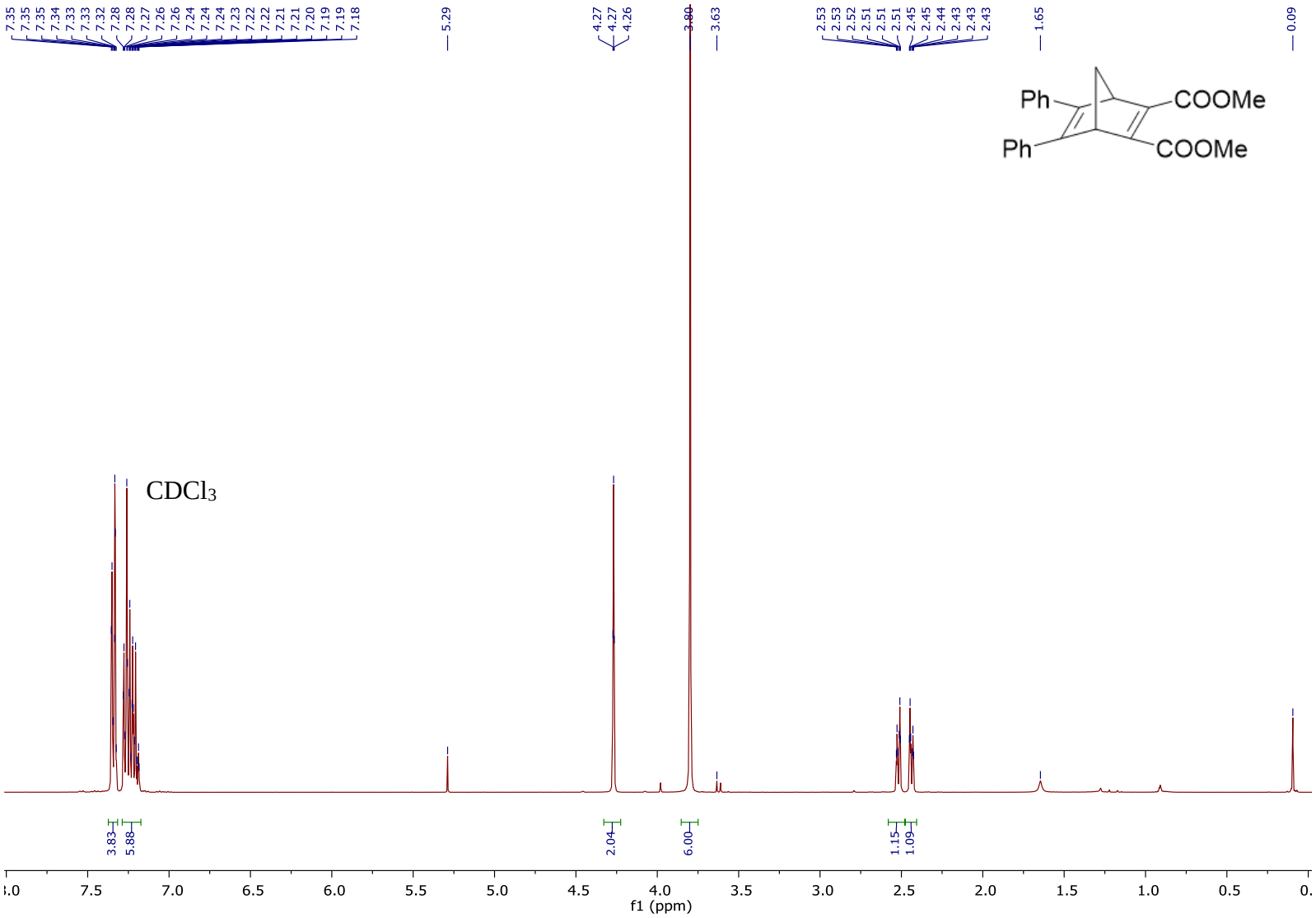


Figure S47. 400 MHz ^{1}H NMR spectrum of compound **NBD-H2** in $CDCl_3$.

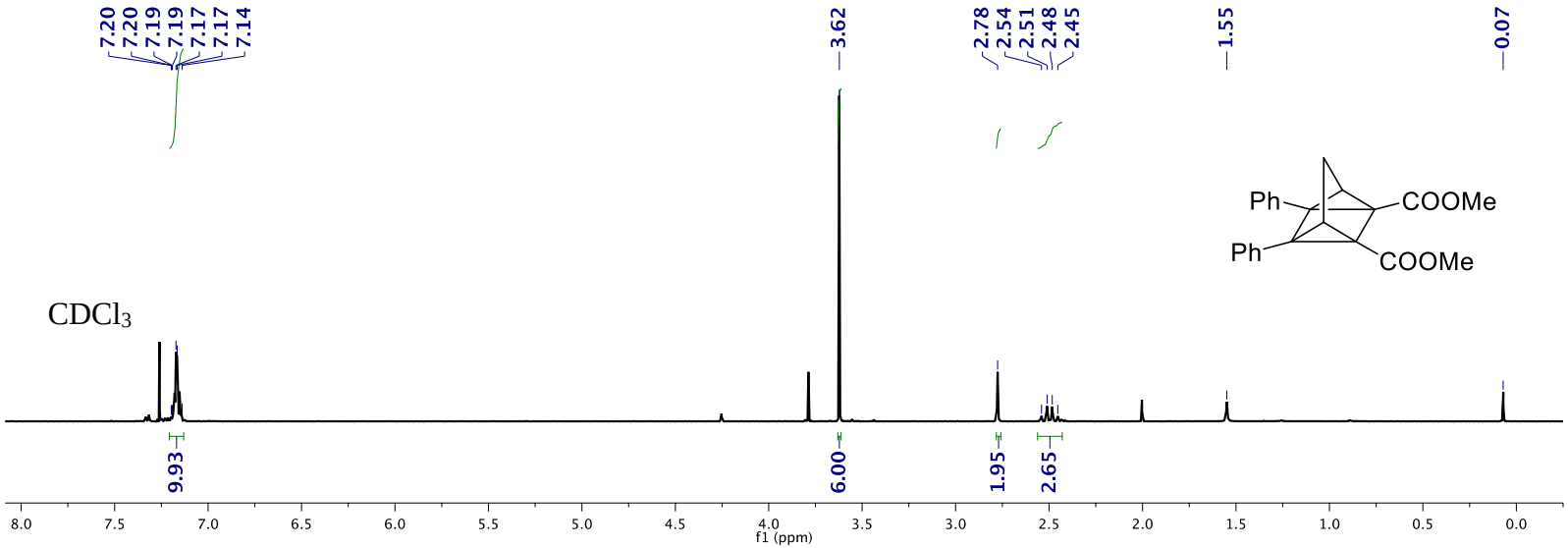


Figure S48. 400 MHz ^{1}H NMR spectrum of compound **QC-H$_2$** in $CDCl_3$.

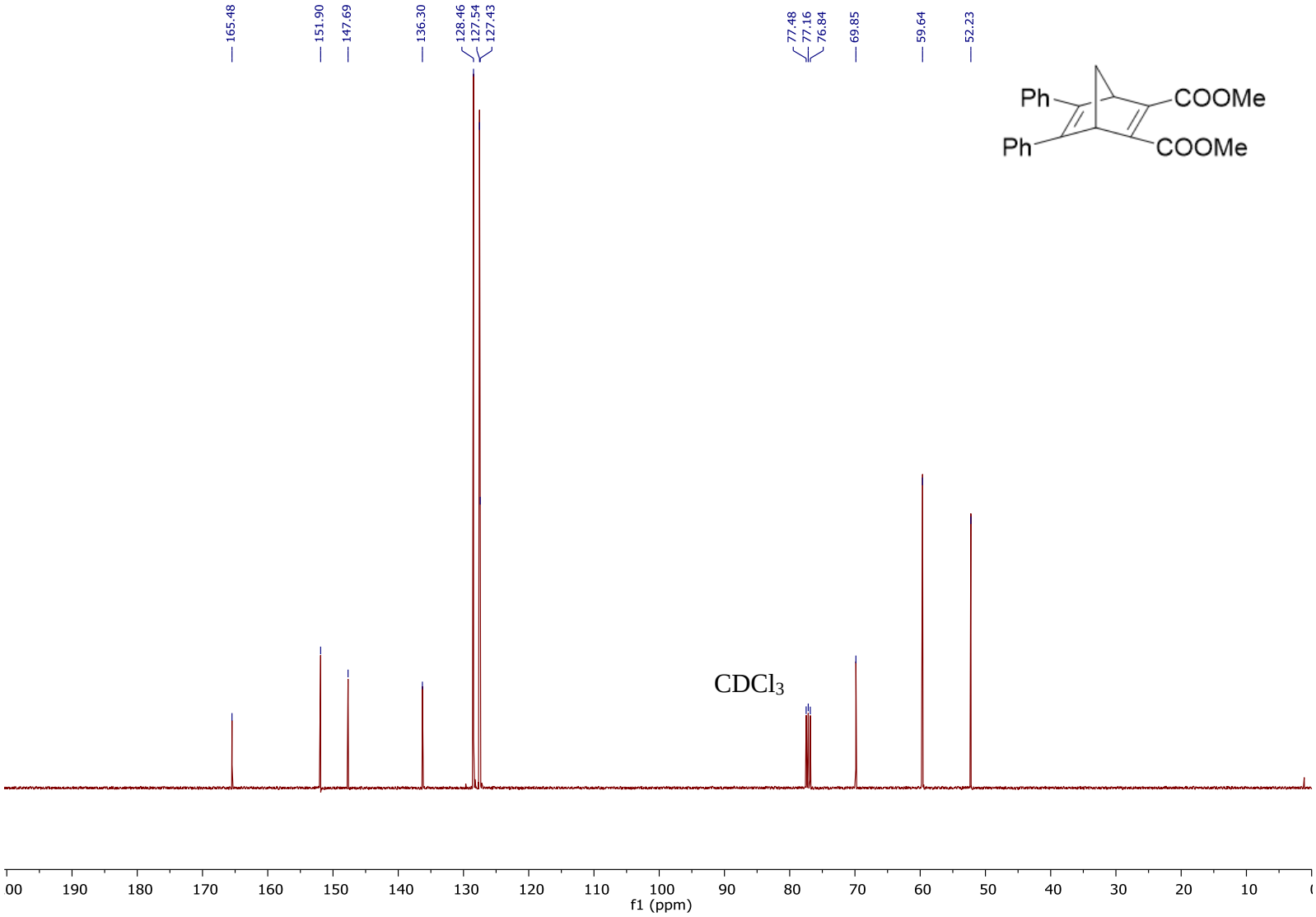


Figure S49. 100 MHz ^{13}C NMR spectrum of compound **NBD-H$_2$** in $CDCl_3$.

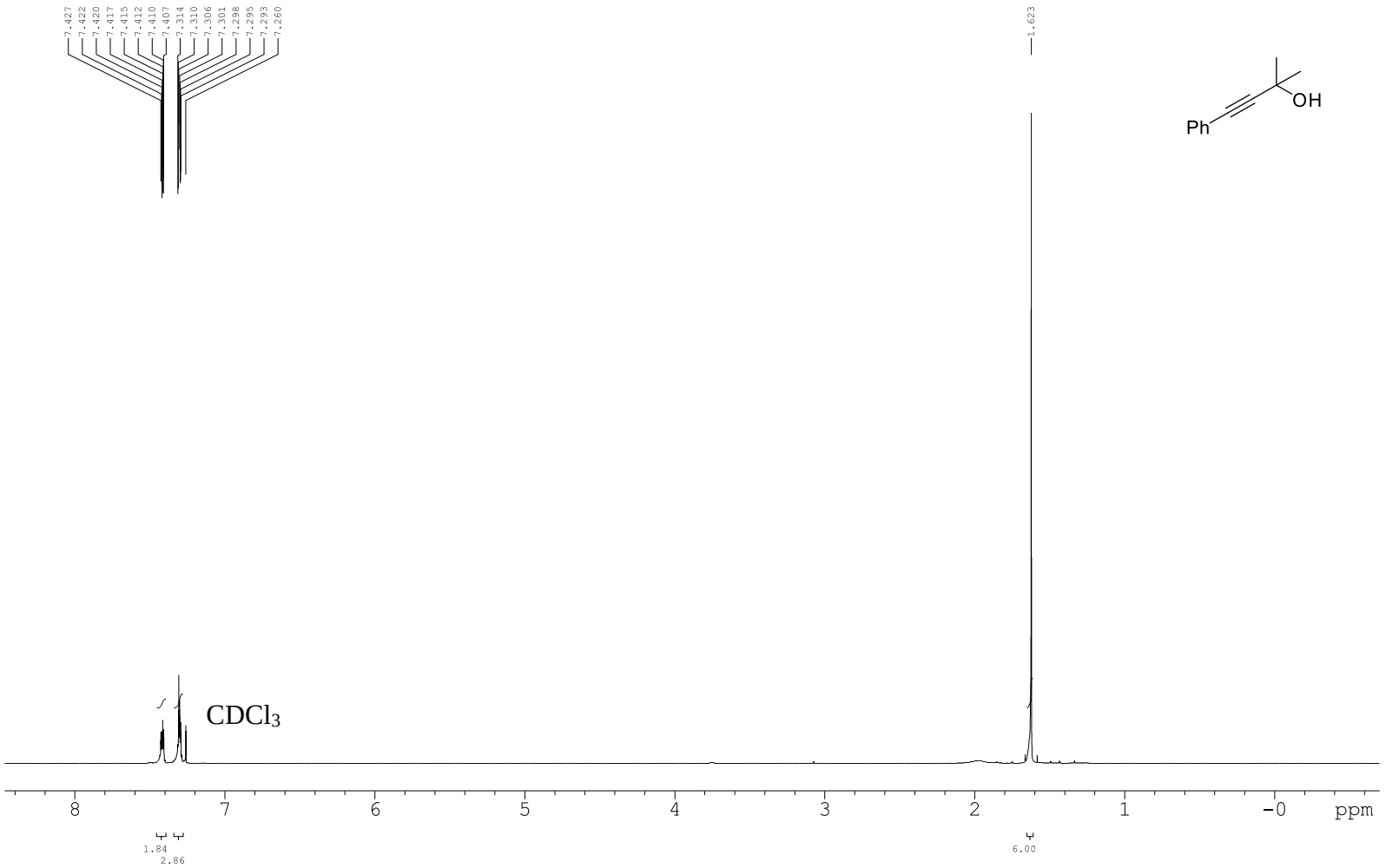


Figure S50. 500 MHz ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

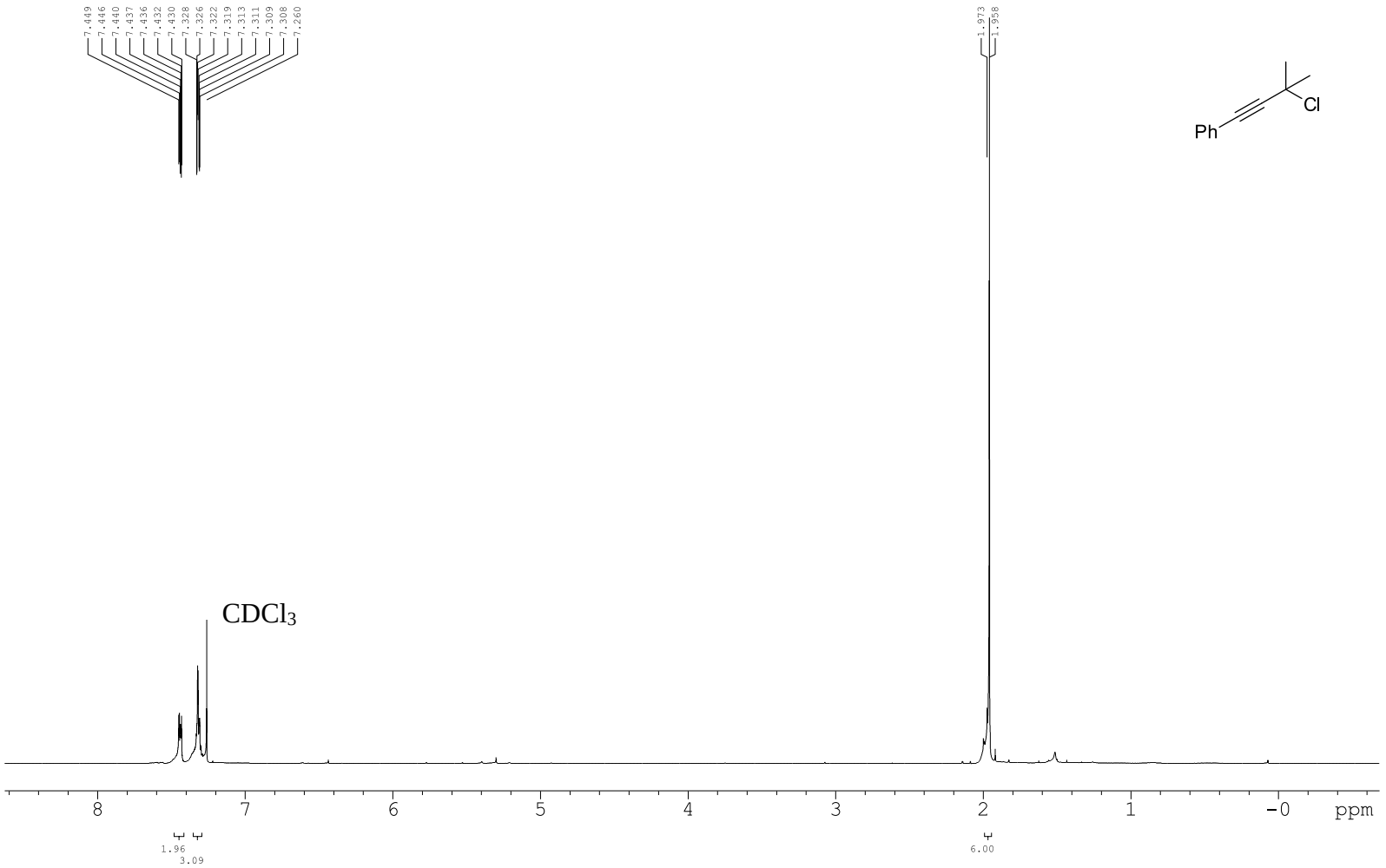


Figure S51. 500 MHz ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

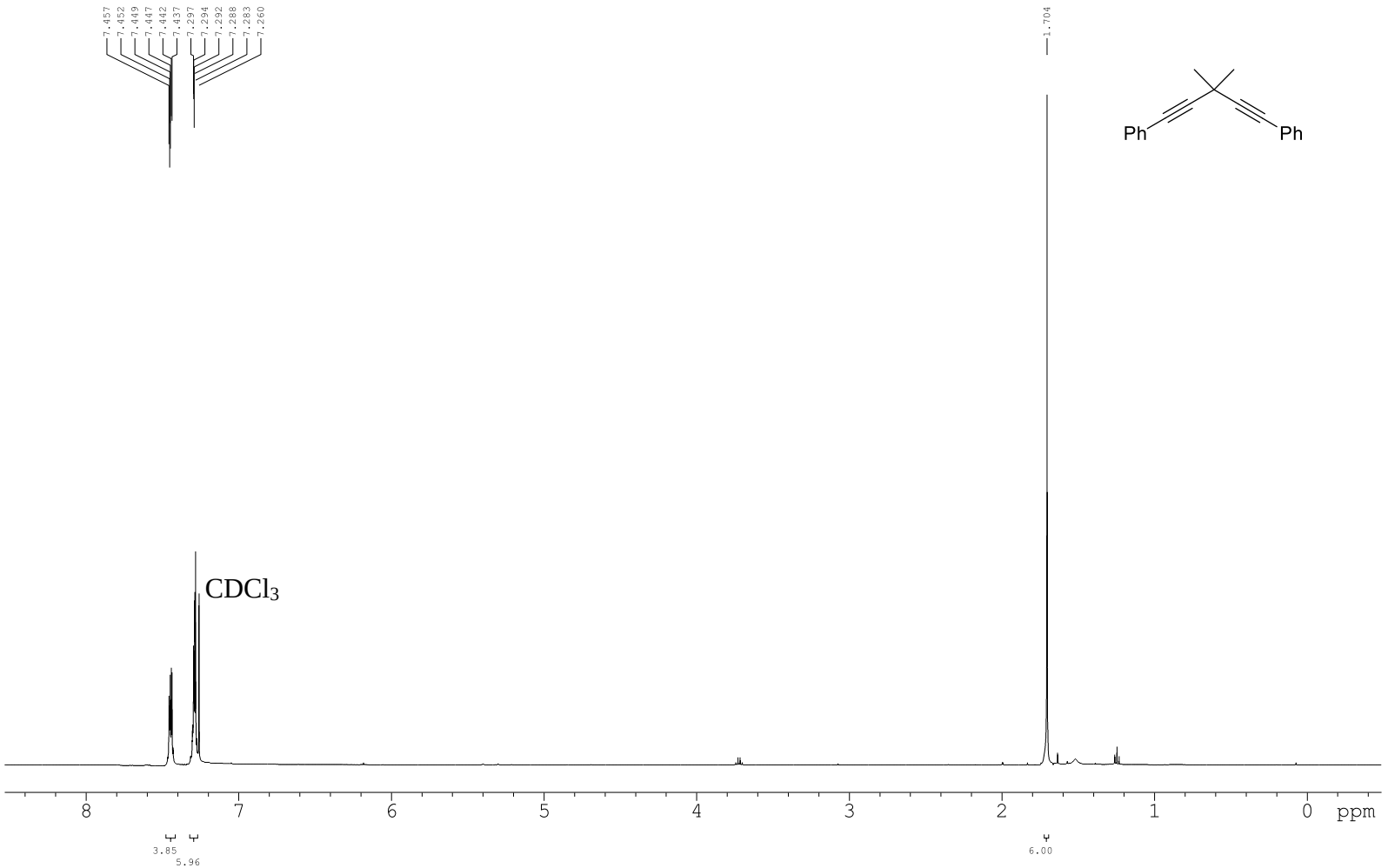


Figure S52. 500 MHz ^{1}H NMR spectrum of compound **5** in $CDCl_3$.

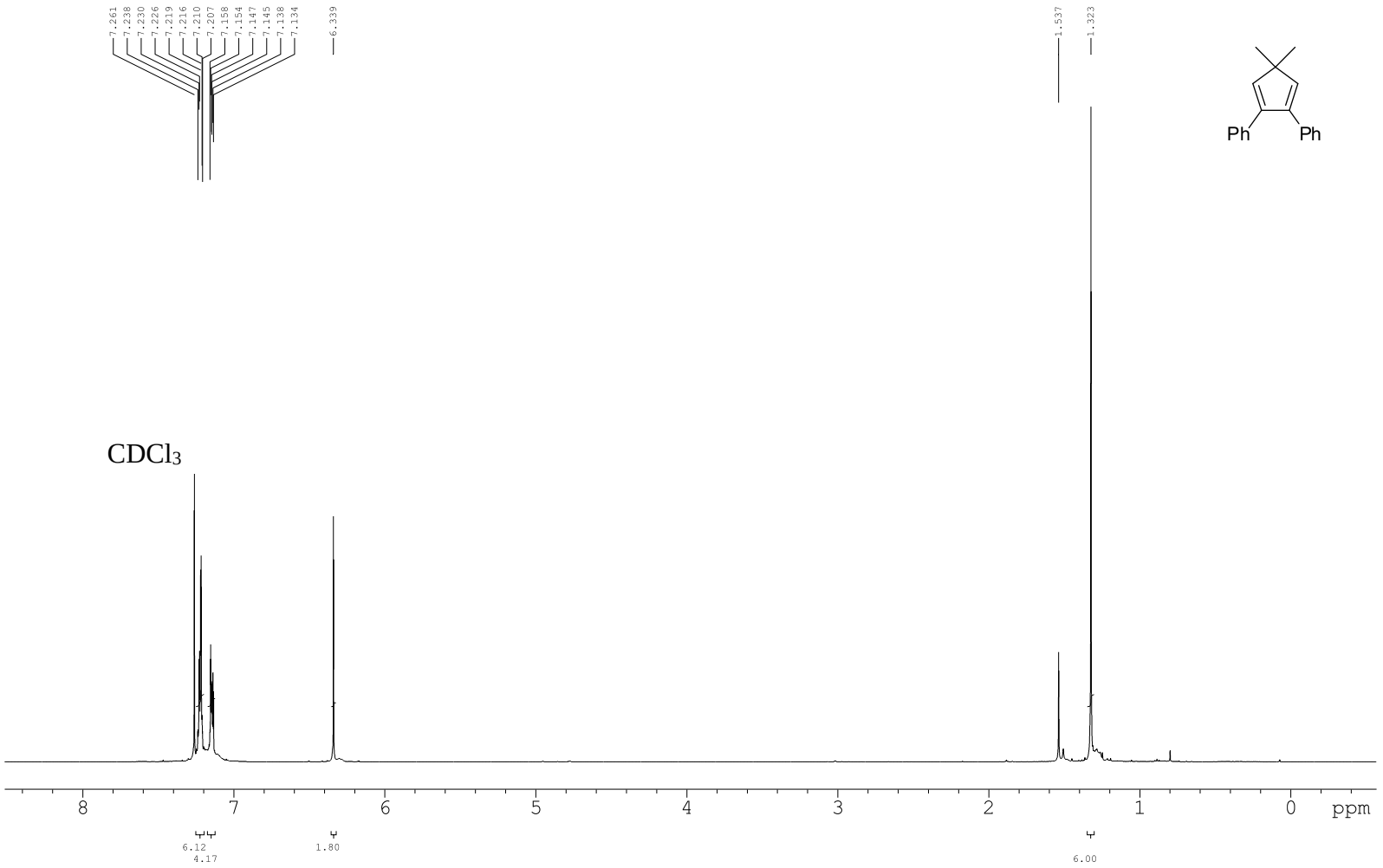


Figure S53. 500 MHz ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

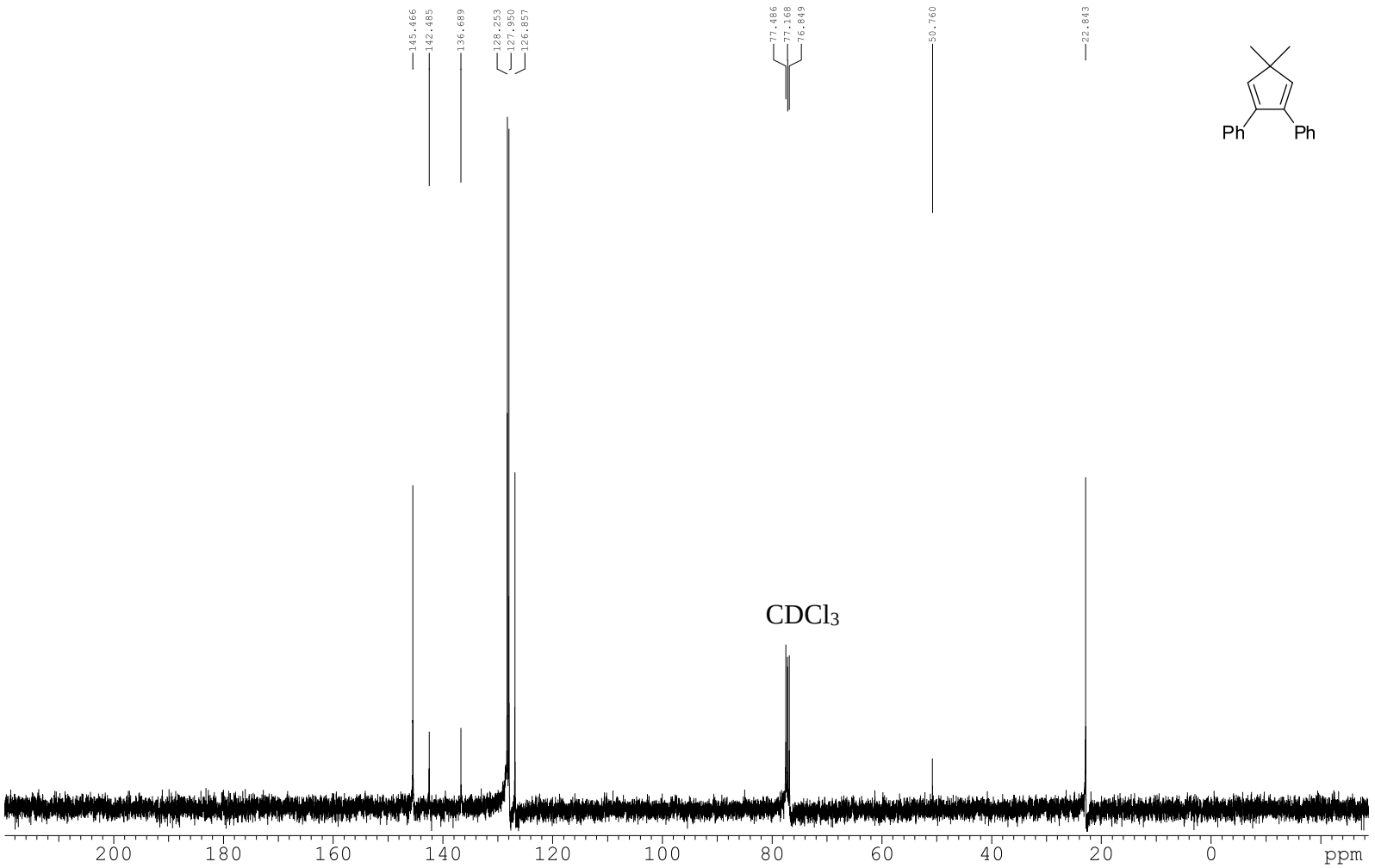


Figure S54. 100 MHz ^{13}C spectrum of compound **6** in $CDCl_3$.

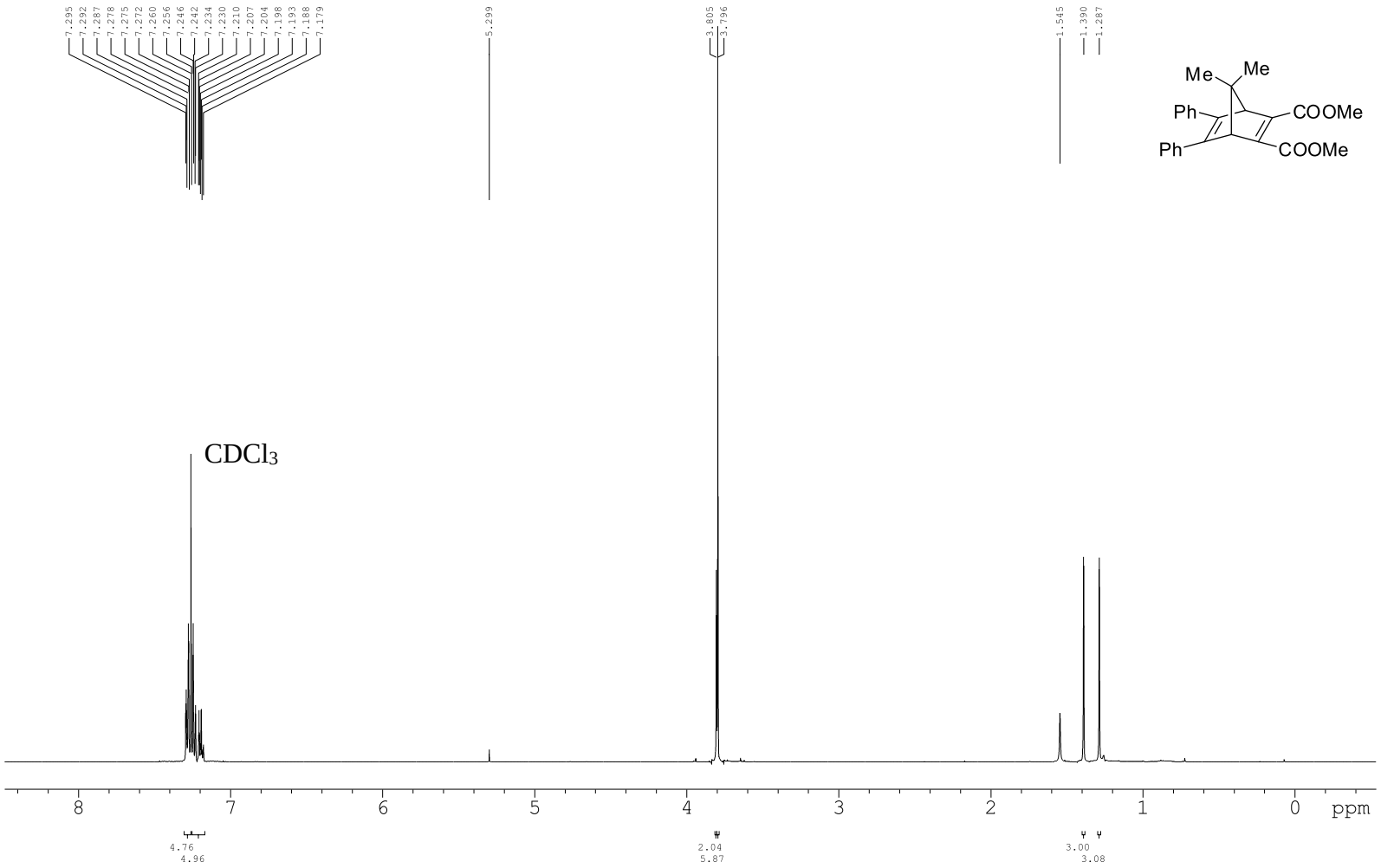


Figure S55. 500 MHz ^{1}H NMR spectrum of compound **NBD-Me$_2$** in $CDCl_3$.

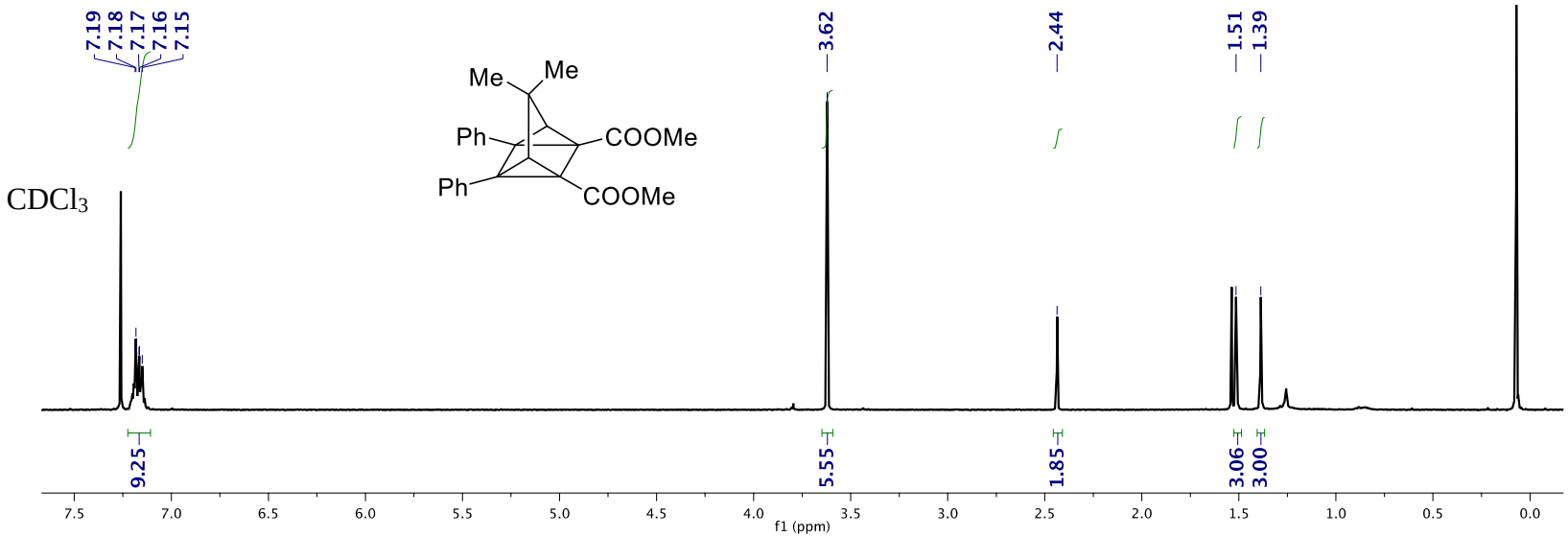


Figure S56. 400 MHz ^{1}H NMR spectrum of compound **QC-Me$_2$** in $CDCl_3$.

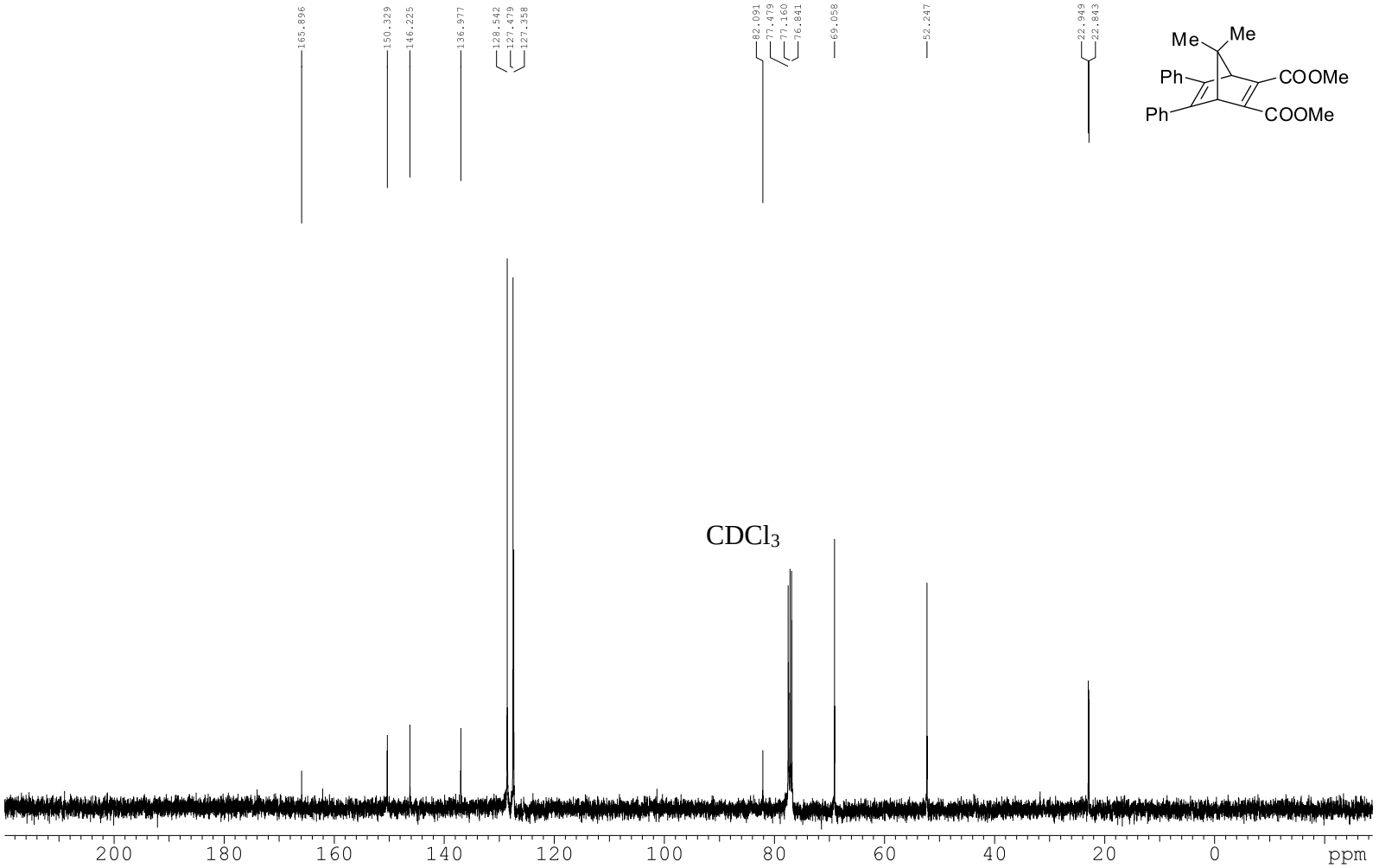


Figure S57. 100 MHz ^{13}C NMR spectrum of **NBD-Me$_2$** in $CDCl_3$.

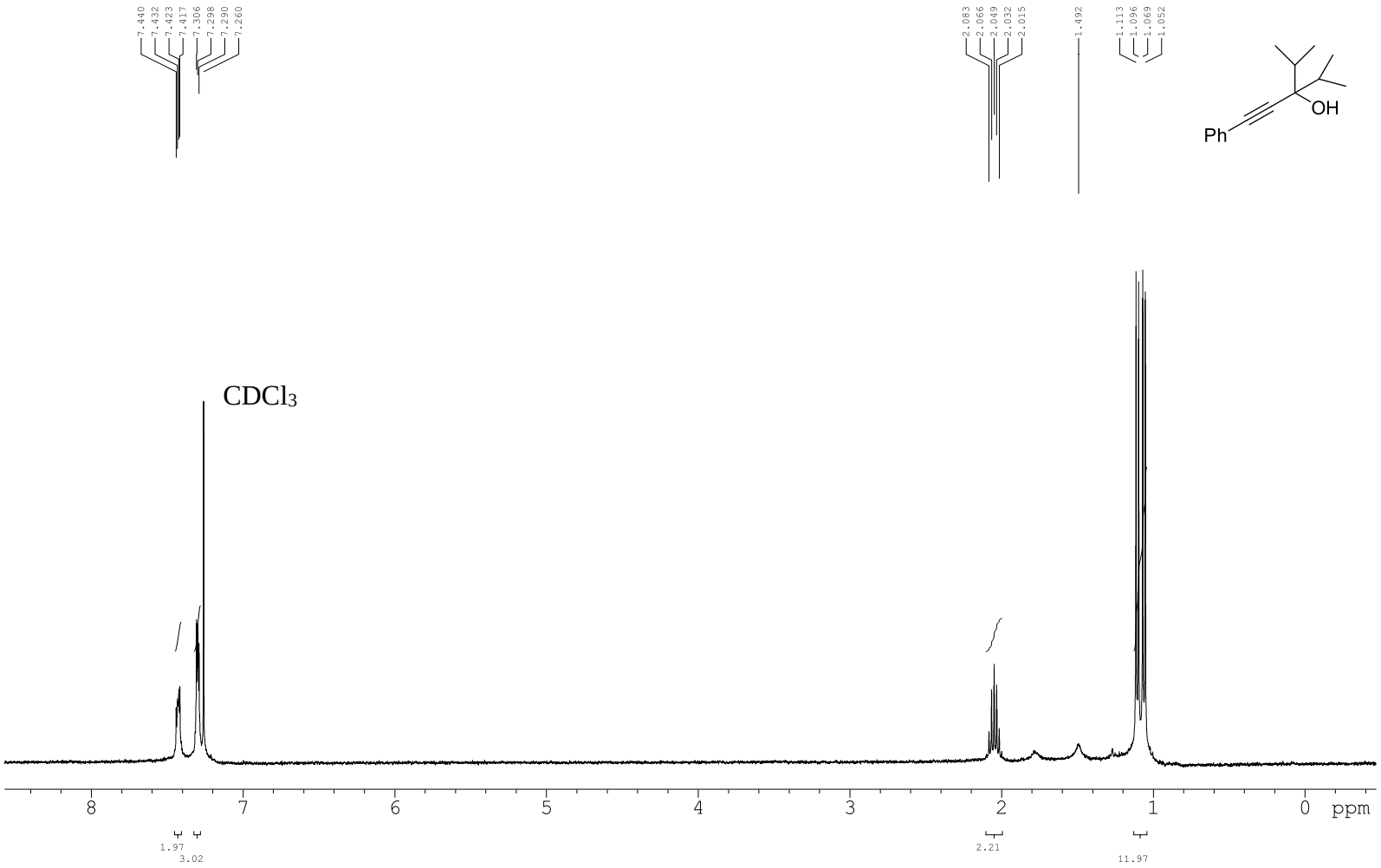


Figure S58. 400 MHz ^{1}H NMR spectrum of compound **8** in $CDCl_3$.

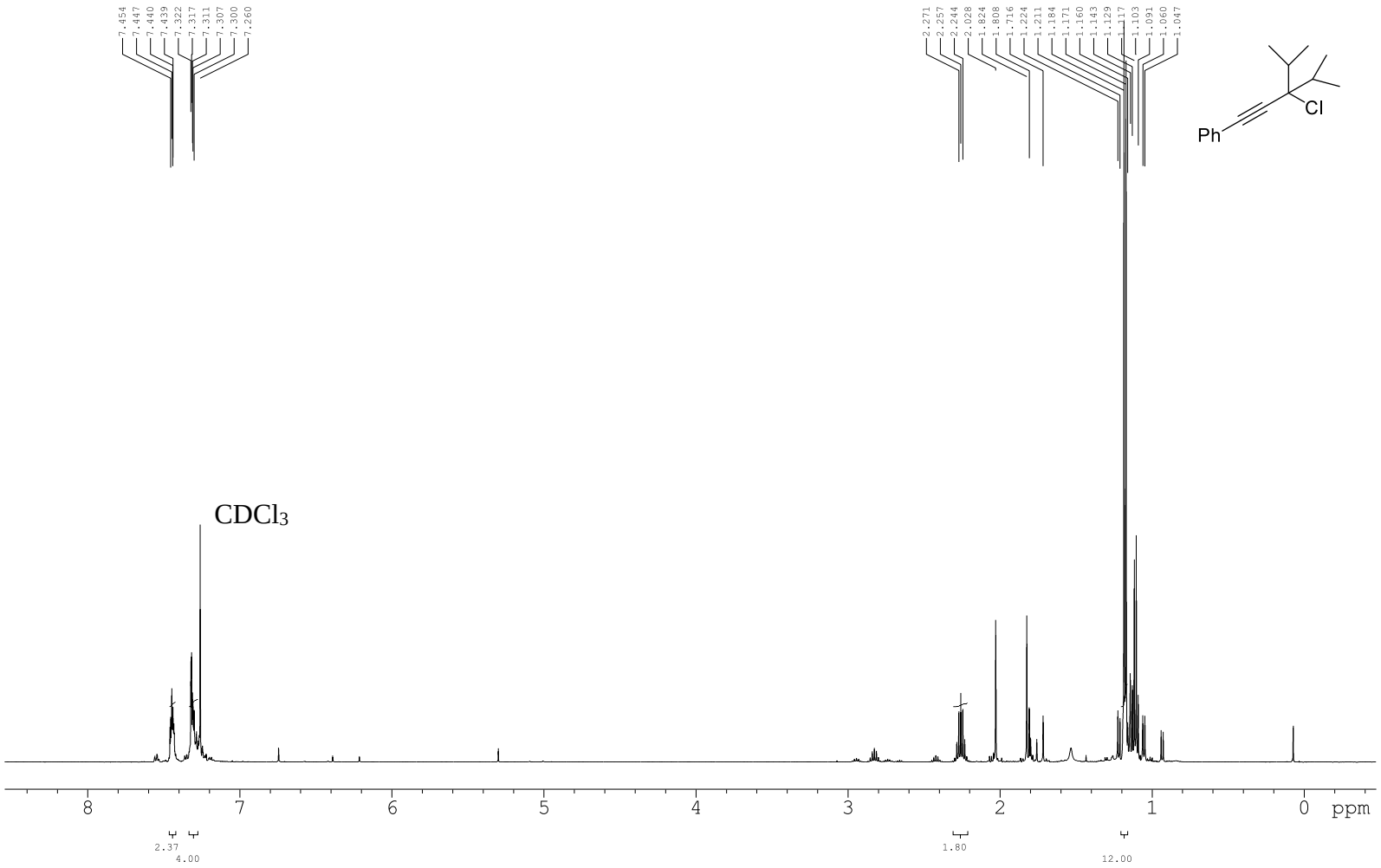


Figure S59. 500 MHz ^{1}H NMR spectrum of crude product containing compound **9** in $CDCl_3$.

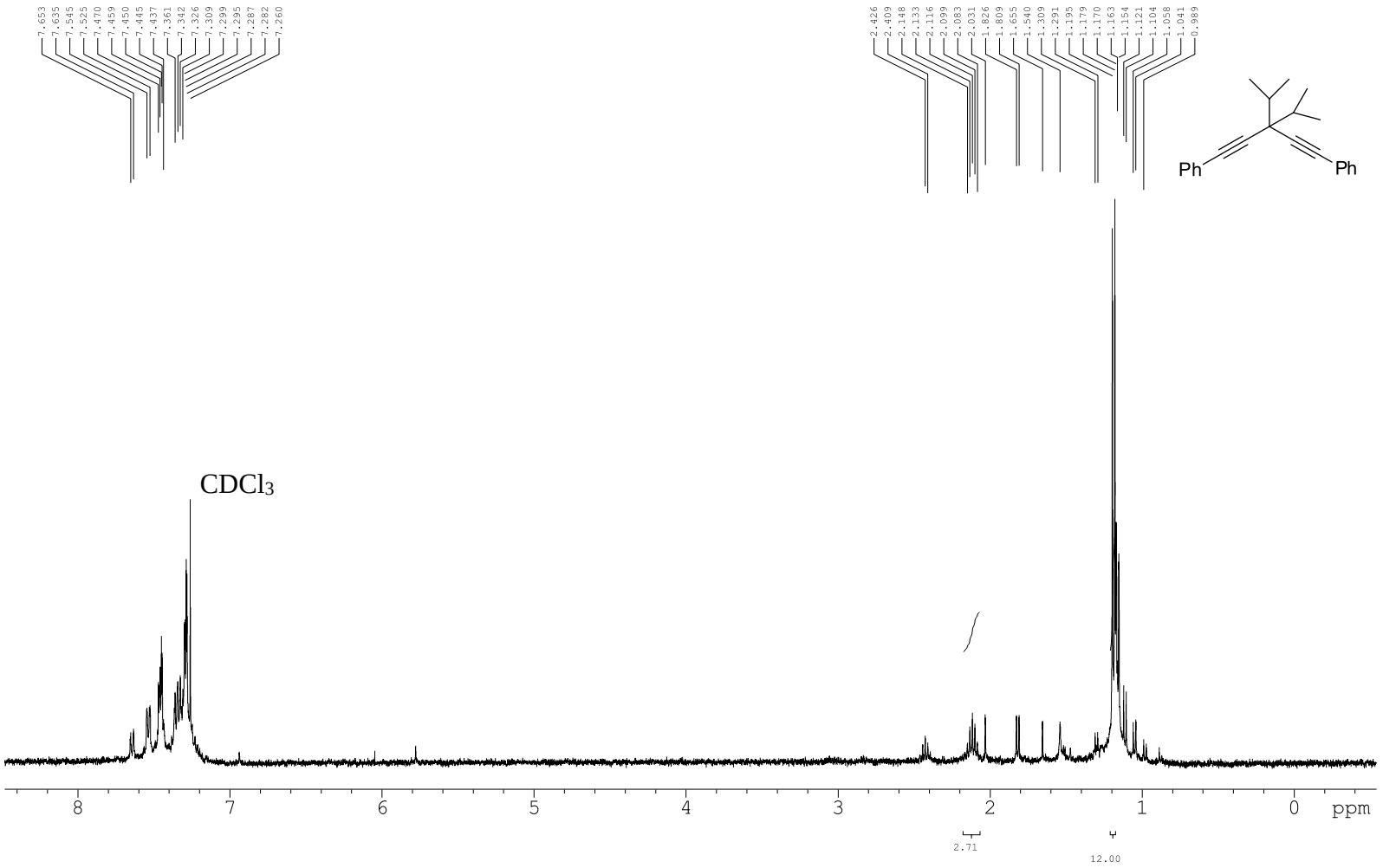


Figure S60. 500 MHz ^{1}H NMR spectrum of crude product containing compound **10** in $CDCl_3$.

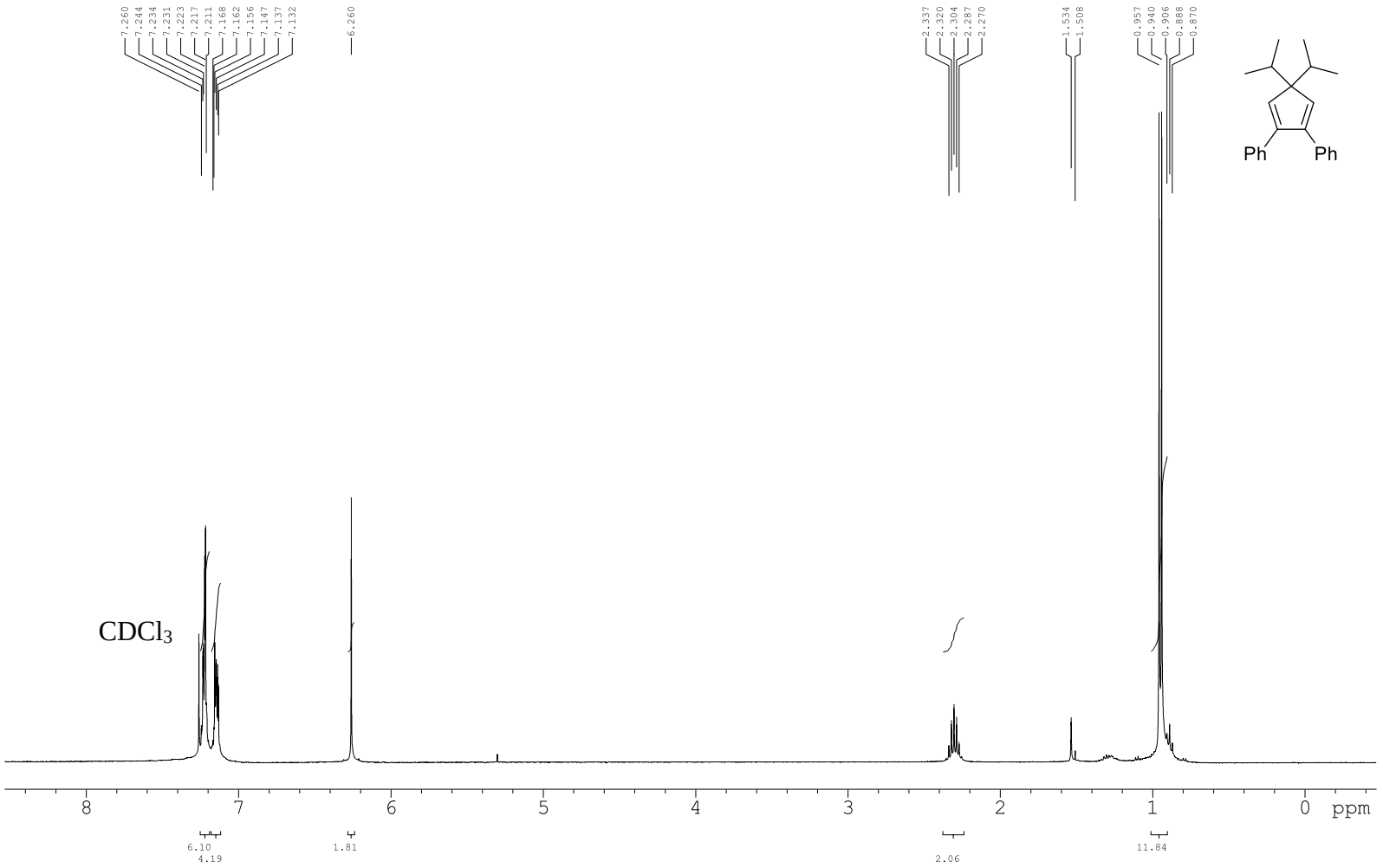


Figure S61. 400 MHz ^{1}H NMR spectrum of compound **11** in $CDCl_3$.

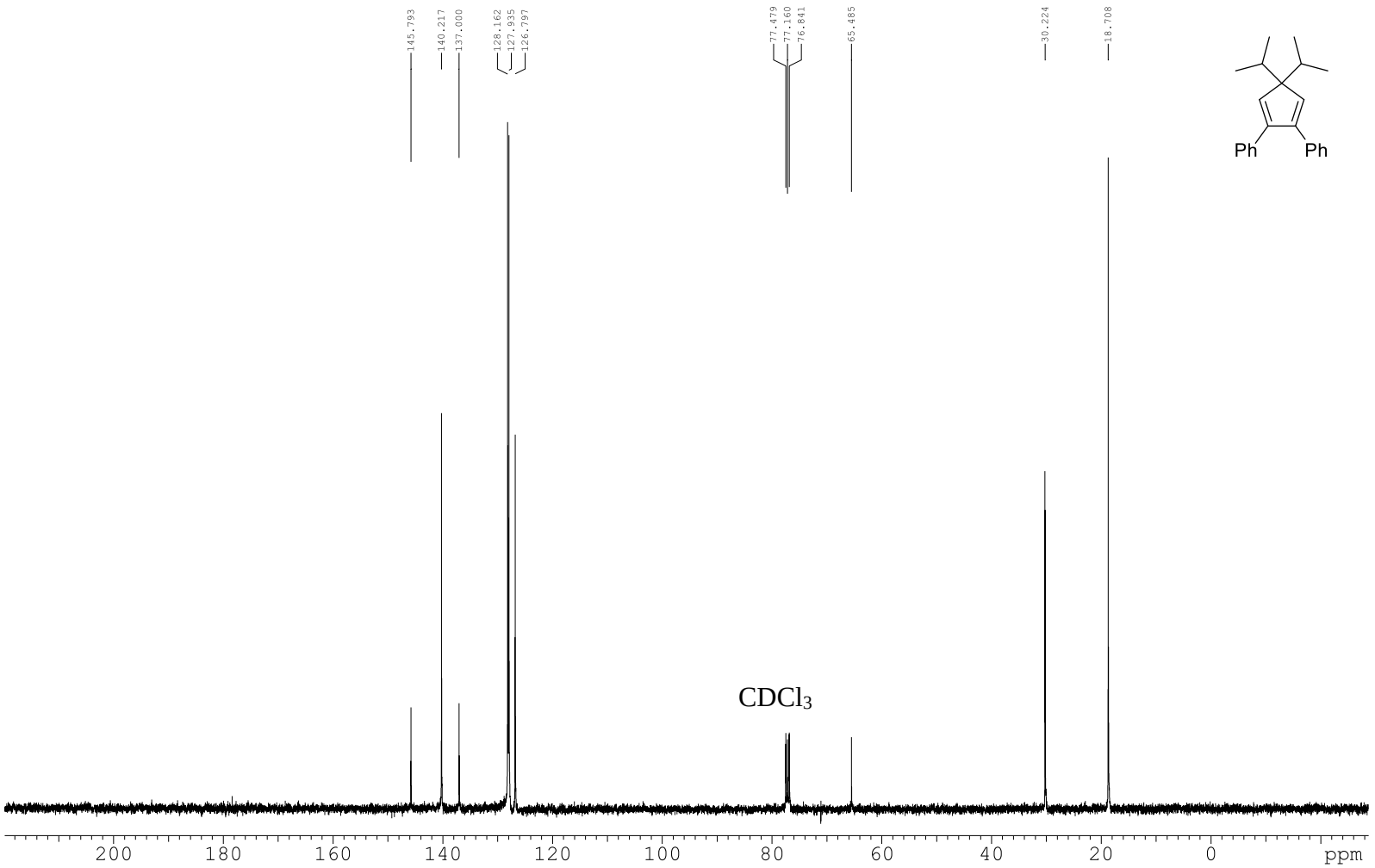


Figure S62. 100 MHz ^{13}C spectrum of compound **11** in $CDCl_3$.

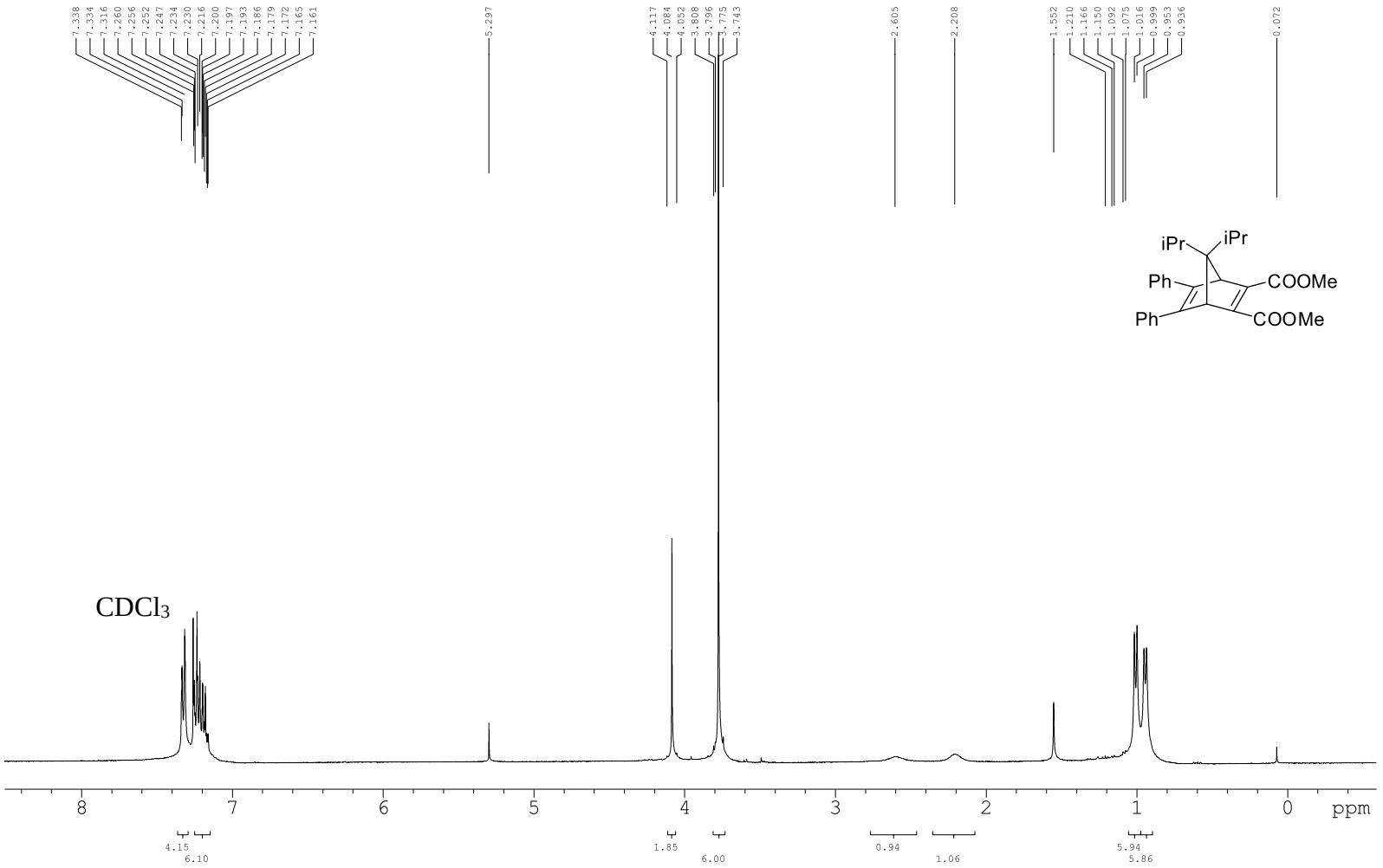


Figure S63. 400 MHz ^{1}H NMR spectrum of compound **NBD-*i*Pr$_2$** in $CDCl_3$.

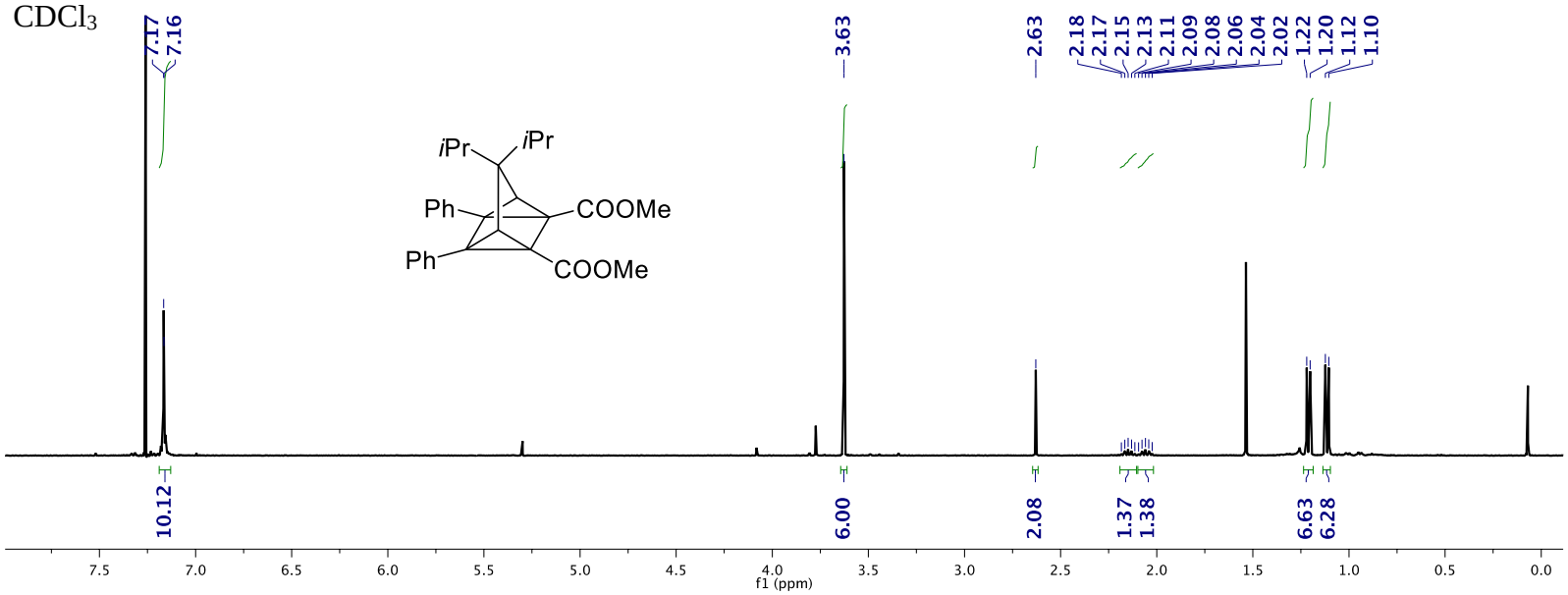


Figure S64. 400 MHz ^{1}H NMR spectrum of compound **QC-*i*Pr$_2$** in $CDCl_3$.

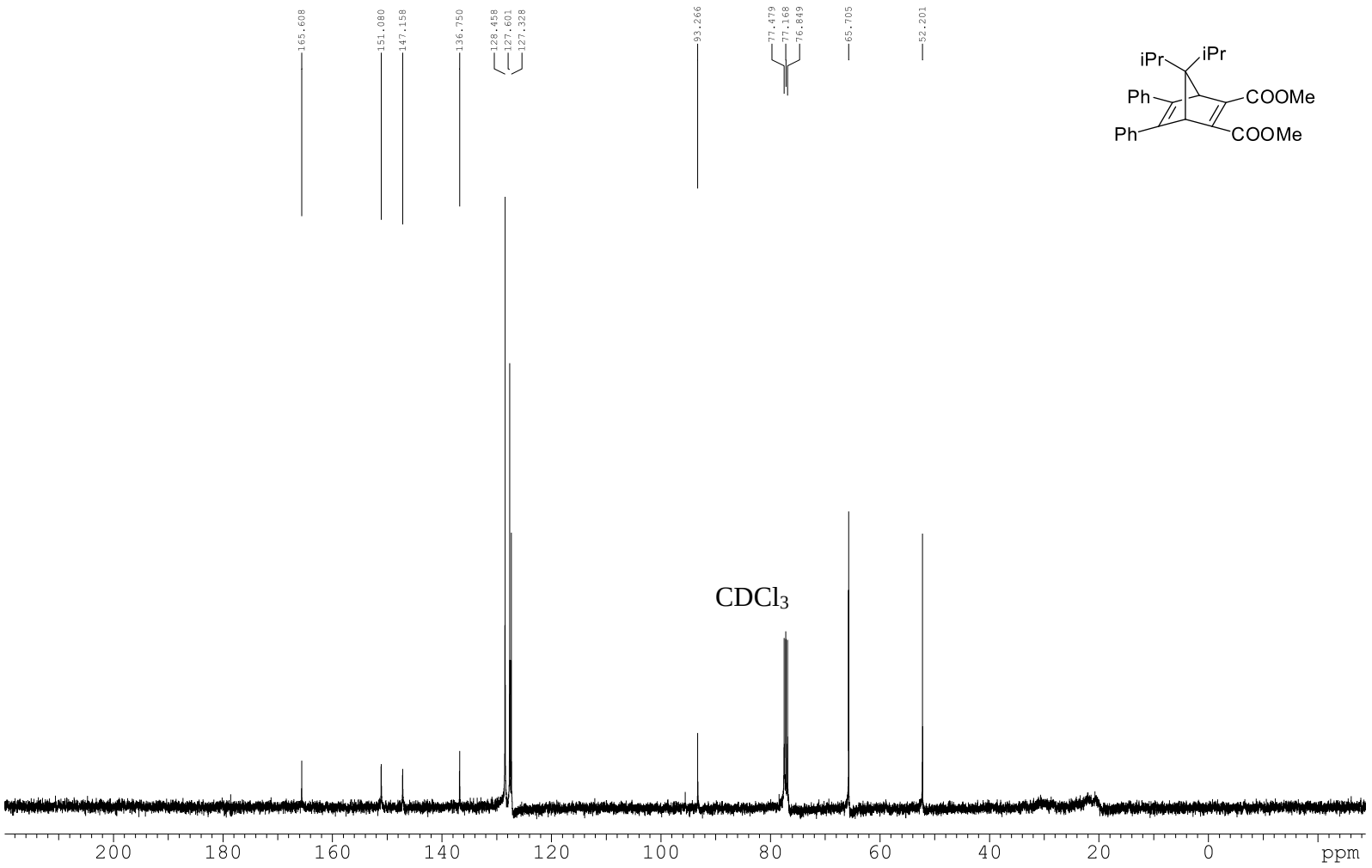


Figure S65. 100 MHz ^{13}C spectrum of compound **NBD-*i*Pr$_2$** in $CDCl_3$.

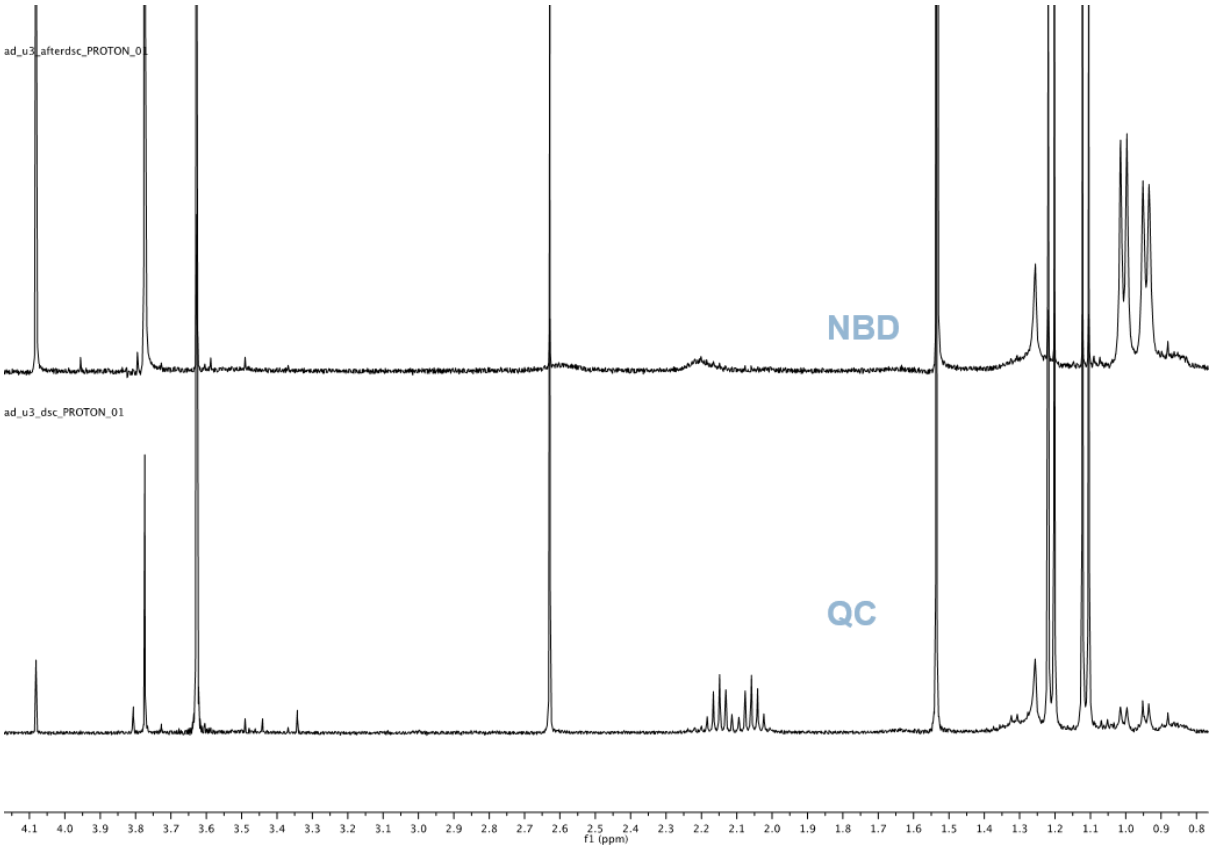


Figure S66. Room-temperature 400 MHz ^{1}H NMR spectra of **NBD-*i*Pr$_2$** and **QC-*i*Pr$_2$** in toluene-d$_6$, highlighting the methine protons of the *i*Pr groups.

11 References

Full Gaussian09 reference

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