ELECTRONIC SUPPLEMENTARY INFORMATION

Reversible switching between housane and cyclopentanediyl isomers: An isonitrile-catalysed thermal reverse reaction

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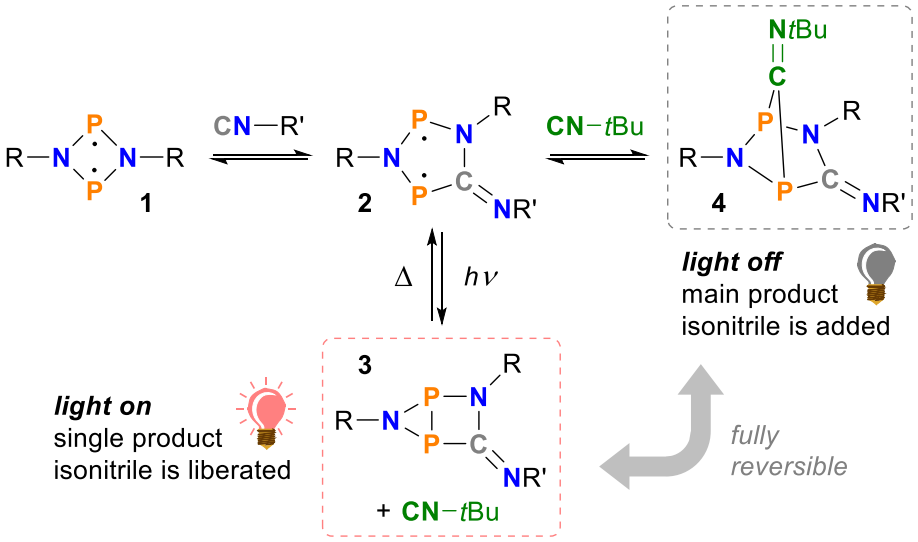

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1 Experimental

General Information. If not stated otherwise, all manipulations were carried out under oxygen- and moisture-free conditions under an inert atmosphere of argon using standard Schlenk or Drybox techniques.

Table S1. Origin and purification of solvents and reactants.

Substance	Origin	Purification
CH_2Cl_2	local trade	purified according to literature procedure[1] dried over P_4O_{10}, stored over CaH_2 freshly distilled and degassed (freeze-pump-thaw)
C_6H_6	local trade	dried over Na freshly distilled prior to use
CD_2Cl_2	euriso-top	dried over P_4O_{10} and CaH_2 freshly distilled prior to use
C_6D_6	euriso-top	dried over Na freshly distilled prior to use
THF-d_8	euriso-top	dried over Na distilled and stored over molecular sieves (4 Å)
$NaHCO_3$	J. T. Baker	used as recieved
HCOOH	old stock	used as recieved
NEt_3	Sigma Aldrich, 99%	dried over Na freshly distilled prior to use
$POCl_3$	old stock	dried over P_4O_{10} freshly distilled and degassed (freeze-pump-thaw)
$DmpNH_2$	Arcos Organics, 99%	freshly distilled
*t*BuNC	TCI, 95%	freshly distilled
$[P(\mu\text{-NTer})]_2$	synthesized[2]	Re-crystallized as described in the literature[2]

NMR spectra were obtained on Bruker spectrometers AVANCE 250, 300 or 500 and were referenced internally to the signals of deuterated solvents (^{13}C: CD_2Cl_2 δ_{ref} = 54.0 ppm, C_6D_6 δ_{ref} = 128.4 ppm), to the signals of protic species in the deuterated solvents (^1H: $CHDCl_2$ δ_{ref} = 5.32 ppm, C_6HD_5 δ_{ref} = 7.16 ppm, THF-d_7 $\delta_{ref,1}$ = 1.73 ppm, $\delta_{ref,2}$ = 3.58 ppm) or externally (^{31}P: 85% H_3PO_4 δ_{ref} = 0 ppm). All

measurements were carried out at ambient temperature (293(2) K) unless denoted otherwise.

NMR spectra under irradiation were recorded by means of an adopted setup previously published by the Gschwind group,[3] who used a fibre-coupled light emitting diode (LED) to direct light into the NMR spectrometer. Instead of an LED, a laser diode (Oclaro HL63193MG, 638 nm, 700 mW) was used. To ensure inert conditions, all samples were prepared in a glovebox and the tubes were sealed with custom-made PTFE caps as well as 2–3 layers of PTFE tape.[2]

IR spectra of crystalline samples were recorded on a Bruker Alpha II FT-IR spectrometer with an ATR unit at ambient temperature.

Raman spectra of crystalline samples were recorded using a LabRAM HR 800 Horiba Jobin YVON Raman spectrometer equipped with an Olympus BX41 microscope with variable lenses. The samples were excited by a red laser (633 nm, 17 mW, air-cooled HeNe laser). All measurements were carried out at ambient temperature unless stated otherwise.

Elemental analyses were obtained using an Elementar vario Micro cube CHNS analyser or a LECO TruSpec Micro CHNS analyser.

Melting points (uncorrected) were determined using a Stanford Research Systems EZ Melt at a heating rate of 20 °C/min.

Mass spectra were recorded on a Thermo Electron MAT 95-XP sector field mass spectrometer using crystalline samples.

UV-Vis spectra were acquired on a Perkin-Elmer Lambda 19 UV-Vis spectrometer.

2 Structure Elucidation

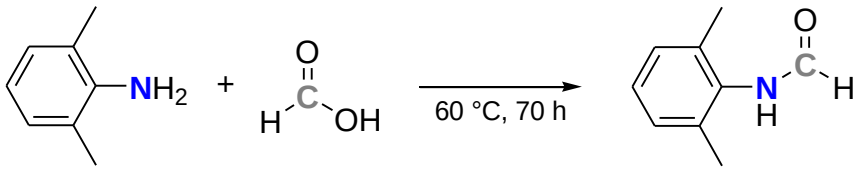
X-Ray Structure Determination: X-Ray quality crystals were selected in Fomblin YR-1800 perfluoro-ether (Alfa Aesar) at ambient temperature. The sample was cooled to 123(2) K during measurement. Data was collected on a Bruker D8 Quest diffractometer using Mo K_α radiation (λ = 0.71073 Å). The structure was solved by iterative methods (SHELXT)[4] and refined by full matrix least squares procedures (SHELXL-2013).[5] Semi-empirical absorption corrections were applied (SADABS).[6] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

Table S2. Crystallographic details.

Compound	**4a**
Chem. Formula	$C_{63}H_{66}N_4P_2$
Formula weight [g/mol]	941.09
Colour	colourless
Crystal system	monoclinic
Space group	$C2/_c$
a [Å]	18.465(2)
b [Å]	12.035(2)
c [Å]	47.112(2)
α [°]	90
β [°]	95.726(2)
γ [°]	90
V [Å^3]	10416.9(2)
Z	8
$\rho_{calcd.}$ [g/cm^3]	1.157
μ [mm^{-1}]	0.13
T [K]	123
Measured reflections	114341
Independent reflections	15205
Reflections with $I > 2\sigma(I)$	11086
R_{int}	0.067
$F(000)$	3984
$R_1(R[F^2>2\sigma(F^2)])$	0.45
$wR_2(F^2)$	0.116
GooF	1.02
No. of Parameters	630
CCDC #	2013704

3 Syntheses of Starting Materials

3.1 DmpN(H)COH



DmpN(H)COH was synthesized according to a modified literature procedure.[7] *The synthesis was carried out under non-inert conditions.*

2,6-Dimethylaniline (5.030 g, 41.51 mmol) was dissolved in formic acid (5.040 g, 109.5 mmol). The solution was degassed by several freeze-pump-thaw cycles. Afterwards the reaction mixture was stored at 60 °C for 70 hours (drying oven) resulting in white needles. The crude product was washed three times with water (25 mL) and dried *in vacuo* at 100 °C (10^{-3} mbar, oil bath). Yield: 5.423 g (36.34 mmol, 88%).

$C_9H_{11}NO$ (149.19 g/mol). **Mp.** 169 °C. **CHN** calcd. (found) in %: C 72.46 (72.22), H 7.43 (7.33), N 9.39 (9.33). **^{1}H NMR** (CD_2Cl_2, 250.1 MHz): δ = 2.22 (s, 6 H, *trans-o-C*H_3), 2.30 (s, 6 H, *cis-o-C*H_3), 7.08-7.09 (m, 3 H, *cis/trans-m/p-CH*), 7.09 (s, 2 H, *trans-m-CH*), 7.12-13 (m, 3 H, *cis/trans-m/p-CH*), 8.06 (d, $^3J(^1H,^1H)$ = 12 Hz, 1 H, N*H*), 8.30 (d, $^3J(^1H,^1H)$ = 12 Hz, 1 H, *CHO*). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 62.9 MHz): δ = 18.7 (CH_3), 18.9 (CH_3), 127.9 (*C*H), 127.09 (*C*H), 128.5 (*C*H), 129.0 (*C*H), 133.3 (*C*), 133.8 (*C*), 135.8 (*C*), 135.9 (*C*),159.7 (*C*), 165.0 (*C*). **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3231 (m), 3182 (w), 2881 (m), 2753 (w), 2741 (w), 1960 (w), 1873 (w), 1787 (w), 1653 (s), 1593 (m), 1519 (m), 1494 (m), 1471 (m), 1436 (m), 1383 (s), 1300 (w), 1284 (w), 1259 (m), 1226 (m), 1175 (w), 1152 (m), 1090 (w), 1045 (w), 1034 (w), 983 (w), 927 (w), 898 (w), 876 (m), 800 (w), 779 (vs), 729 (m), 709 (s), 643 (m), 565 (w), 521 (m), 482 (m). **Raman** (633 nm, 20 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3235 (1), 3183 (1), 3074 (1), 3044 (2), 3015 (1), 2987 (1), 2951 (2), 2922 (5), 2884 (2), 2743 (1), 2582 (1), 2565 (1), 2046 (1), 1960 (1), 1655 (3), 1600 (2), 1592 (2), 1523 (1), 1475 (1), 1444 (1), 1384 (7), 1381 (6), 1301 (1), 1286 (1), 1259 (4), 1228 (1), 1174 (1), 1154 (1), 1091 (3),

1046 (1), 1025 (1), 995 (2), 981 (1), 929 (1), 891 (1), 876 (1), 799 (1), 778 (1), 737 (1), 711 (2), 645 (10), 565 (1), 523 (2), 514 (1), 492 (2), 484 (2), 383 (1), 326 (1), 298 (2), 282 (4), 238 (4), 202 (2). **MS** (GC-MS) m/z (%): 119 (13) $[C_7H_5NO]^+$, 134 (100) $[C_8H_8NO]^+$, 149 (36) $[M]^+$.

Figure S1. NMR, Raman und IR spectra of DmpN(H)COH in CD_2Cl_2 (solvent signals indicated by asterisks).

^{1}H NMR spectrum

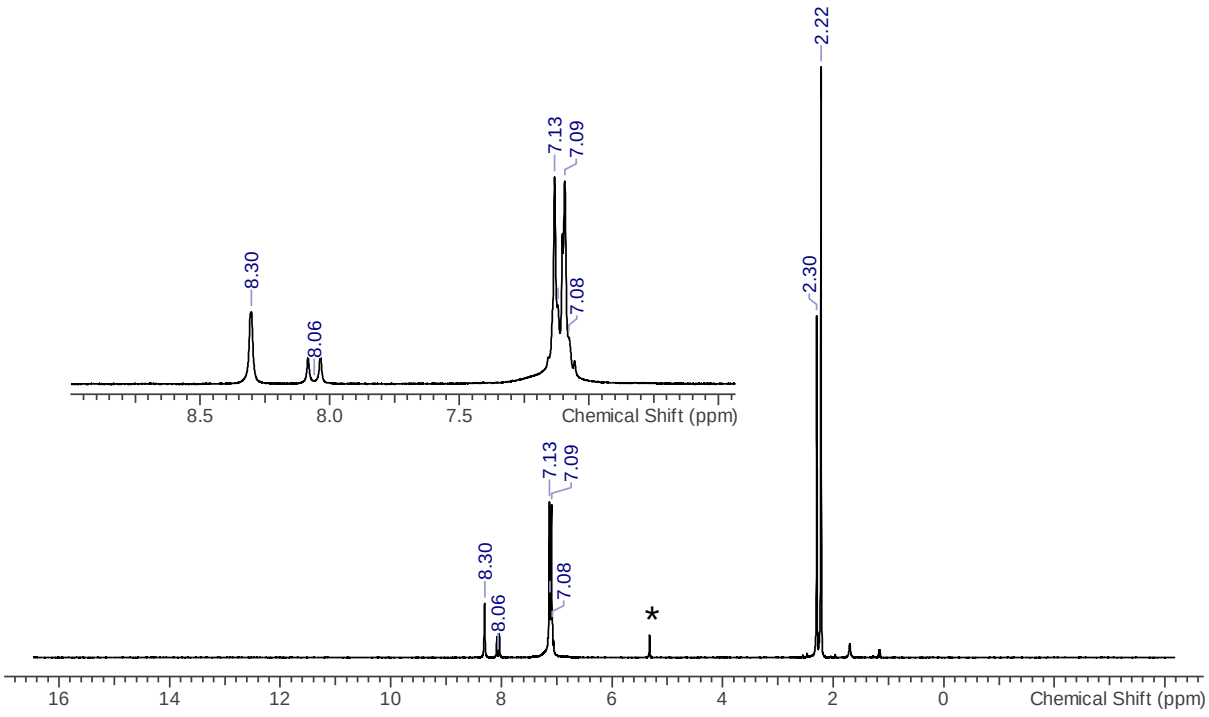
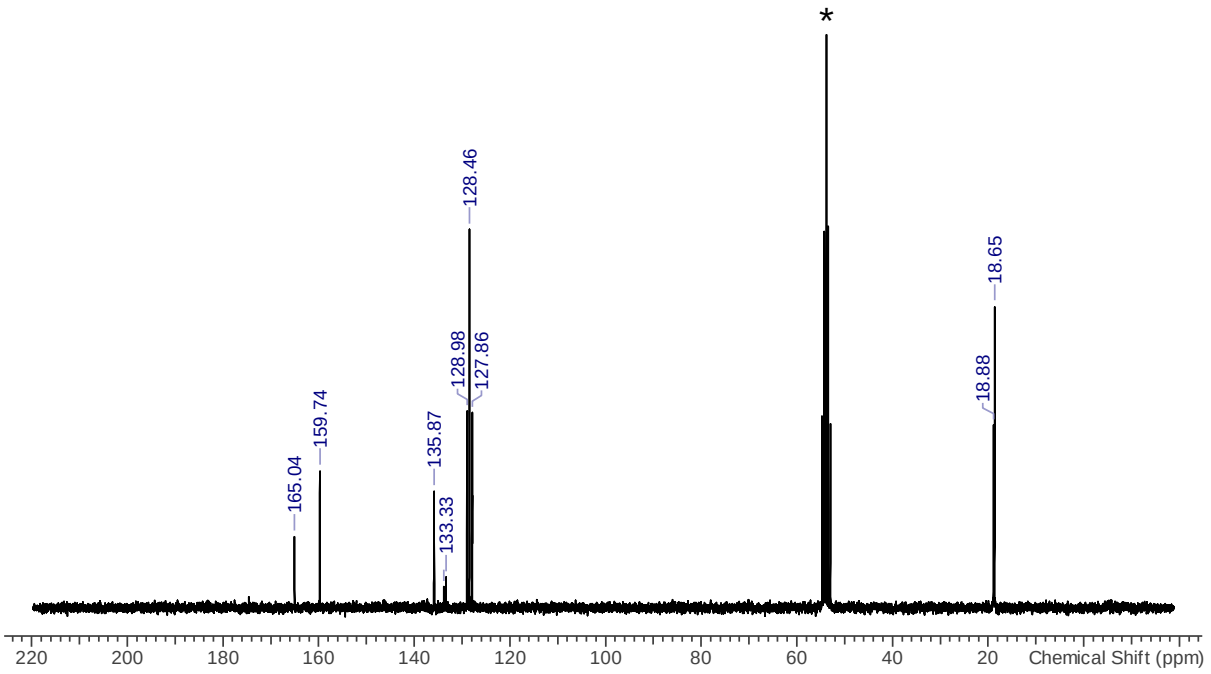
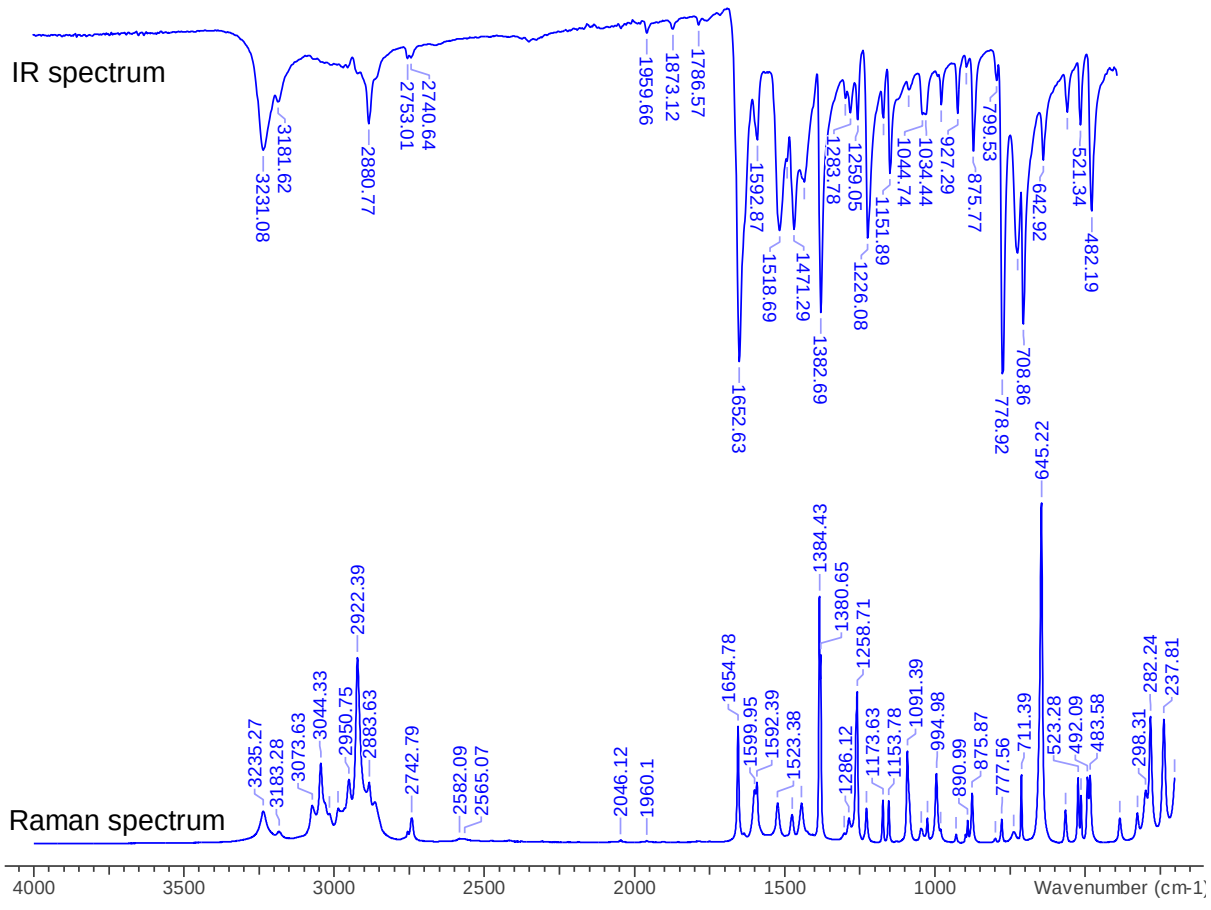


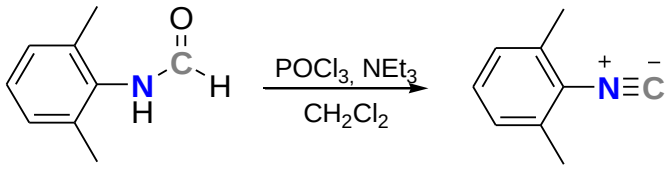
Figure S1 continued.

$^{13}C\{^{1}H\}$ NMR spectrum





3.2 DmpNC



DmpNC was synthesized according to a modified literature procedure.[7] *The synthesis was carried out under non-inert conditions.*

N-(2,6-dimethylphenyl)formamide (5.423 g, 36.34 mmol) was dissolved in CH_2Cl_2 (50 mL). Two equivalents of phosphoryl trichloride (11.16 g, 72.75 mmol) were added at 0 °C followed by the dropwise addition of 10 equivalents of NEt_3 (30.55 g, 363.4 mmol). The reaction mixture was stirred for 16 h, whereupon it turned orange and became cloudy.

Afterwards, the orange suspension was diluted in ice water (100 mL). The aqueous phase was extracted three times with CH_2Cl_2 (40 mL). The combined organic layers were extracted two times with water (50 mL) and two times with a saturated $NaHCO_3$ solution (50 mL).

The solvent was removed in *vacuo* and the crude product was purified by distillation of the melt (80 °C, 10^{-3} mbar, oil bath). Afterwards, the pale yellow product was sublimed *in vacuo* at 60 °C (10^{-3} mbar, oil bath) yielding large colorless crystals of 2,6-dimethylphenyl isocyanide. Yield: 3.271 g (24.94 mmol, 69%).

C_9H_9N (131.18 g/mol). **Mp.** 76 °C. **CHN** calcd. (found) in %: C 82.41 (82.46), H 6.92 (6.92), N 10.68 (10.66). **^{1}H NMR** (CD_2Cl_2, 300.1 MHz): δ = 2.41 (s, 6 H, *o*-C*H*$_3$), 7.00-7.20 (m, 3H, *m*,*p*-CH). **^{13}C{^{1}H} NMR** (CD_2Cl_2, 75.5 MHz): δ = 19.1 (*o*-CH_3), 128.1 (*p*-CH), 129.0 (*m*-CH), 135.3 (*o*-*C*), 168.7 (*i*-*C*), N*C* not observed. **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3233 (w), 3184 (w), 2984 (w), 2947 (w), 2920 (w), 2881 (w), 2739 (w), 2120 (m), 2085 (w), 1949 (w), 1879 (w), 1811 (w), 1655 (m), 1591 (w), 1525 (w), 1490 (w), 1471 (m), 1440 (m), 1379 (m), 1302 (w), 1282 (w), 1228 (w), 1170 (m), 1084 (m), 1036 (m), 991 (w), 977 (w), 923 (w), 800 (w), 775 (vs), 721 (m), 637 (w), 548 (w). **Raman** (633 nm, 20 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3071 (3), 3043 (3), 2985 (3), 2947 (4), 2919 (10), 2911 (9), 2885 (3), 2882 (3), 2873 (3), 2863 (4),

2740 (3), 2735 (3), 2119 (7), 1600 (1), 1590 (2), 1471 (1), 1464 (1), 1437 (1), 1423 (1), 1408 (1), 1383 (1), 1373 (1), 1264 (1), 1254 (2), 1171 (2), 1092 (1), 1078 (2), 990 (1), 796 (1), 779 (1), 727 (1), 719 (1), 636 (8), 565 (1), 542 (1), 518 (1), 505 (1), 491 (1), 458 (1), 361 (4), 284 (1), 240 (2). **MS** (GC-MS) m/z (%): 103 (30) $[C_7H_4N]^+$, 116 (62) $[C_8H_8N]^+$, 130 (100) $[C_9H_8N]^+$, 131 (68) $[M]^+$.

Figure S2. NMR, Raman und IR spectra of DmpNC in CD_2Cl_2 (solvent signals indicated by asterisks).

^{1}H NMR spectrum

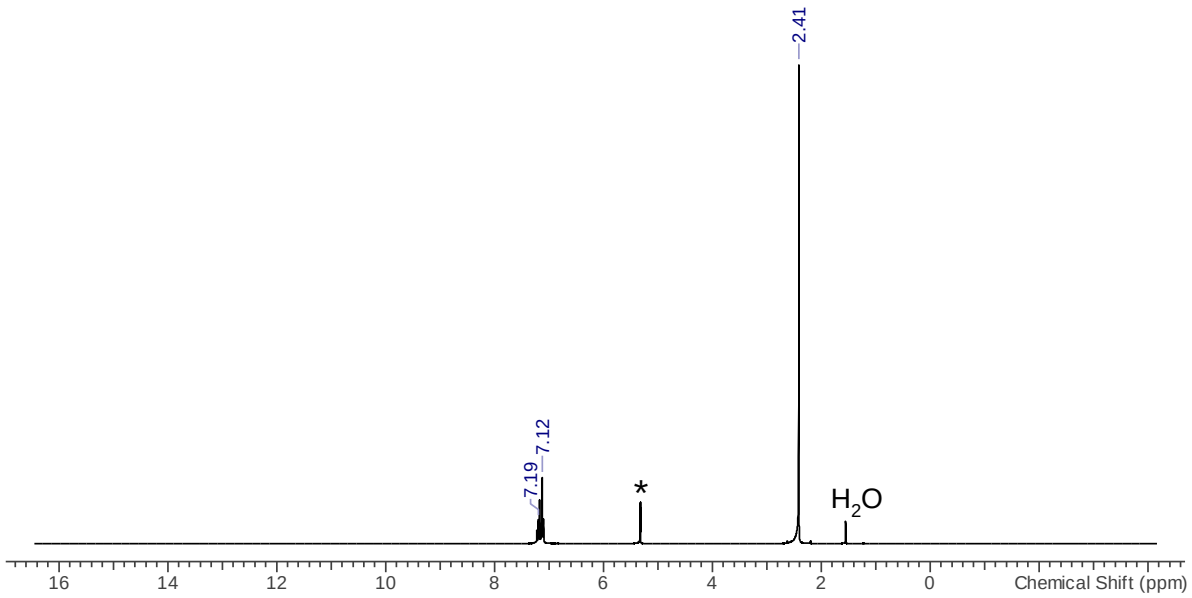
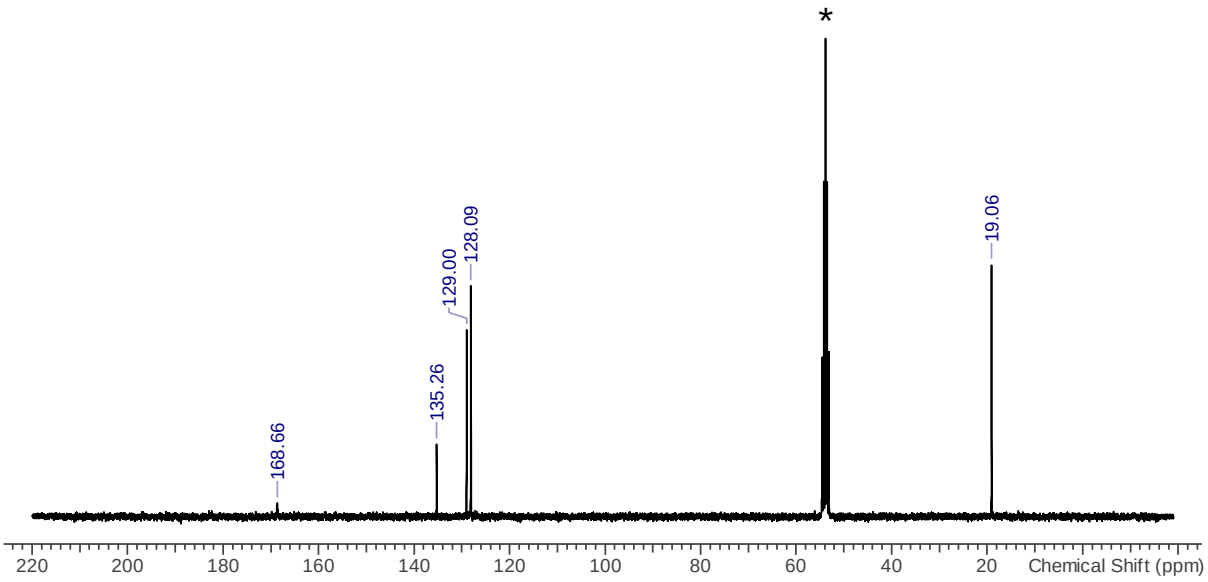


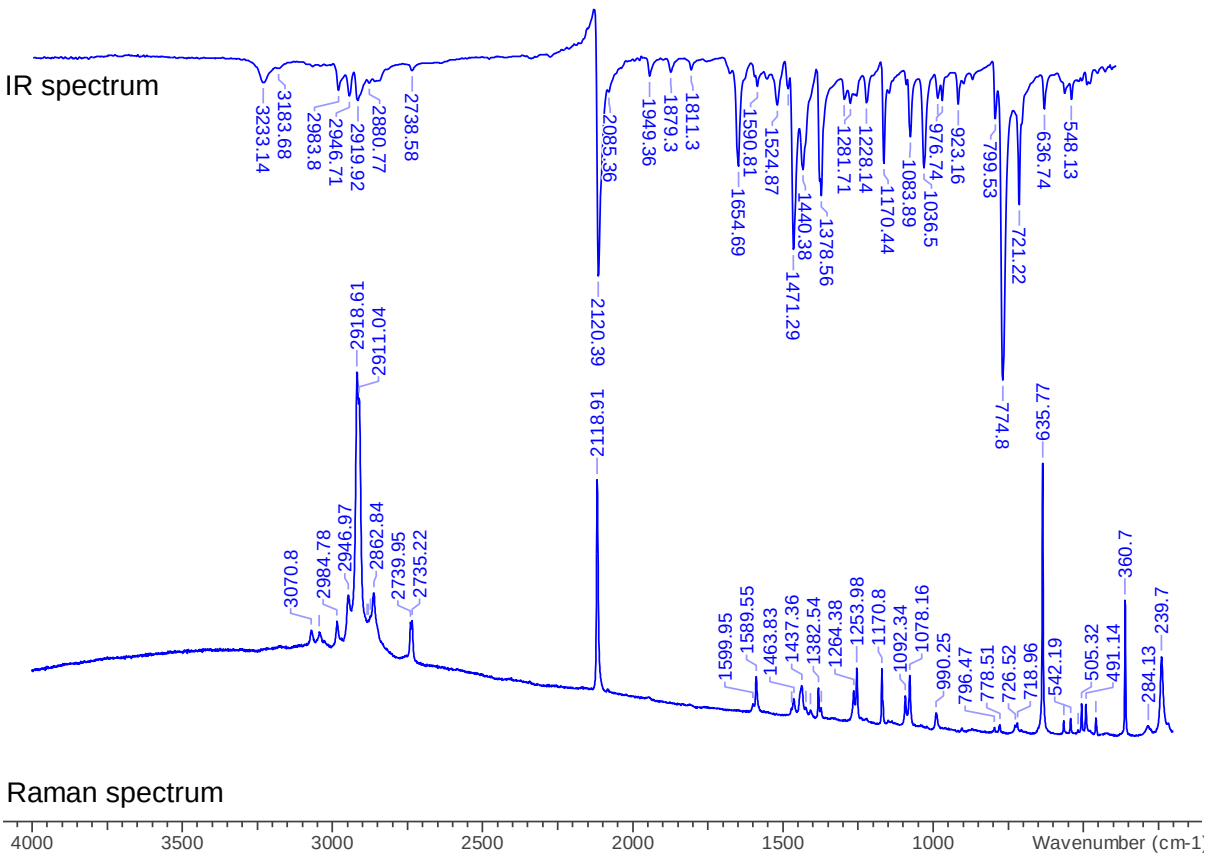
Figure S2 continued.

$^{13}C\{^{1}H\}$ NMR spectrum

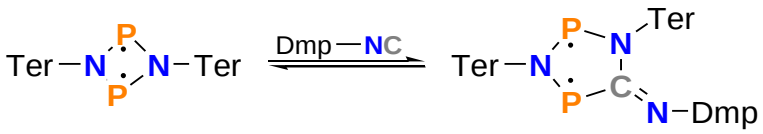


IR spectrum

Raman spectrum



3.3 [TerNP]$_2$DmpNC (2a)



[TerNP]$_2$DmpNC *was synthesized according to a modified literature procedure.*[2]

To a solution of [P(μ-NTer)]$_2$ (459 mg, 0.640 mmol) in benzene (10 mL), DmpNC (82 mg, 0.64 mmol) was added. An immediate colour change from red to deep blue was observed. After two hours the solvent was removed and the blue residue was dried *in vacuo* (10^{-3} mbar). The product was crystallized from a minimal amount of fresh benzene at ambient temperature. The supernatant was removed by syringe and the crystals were dried *in vacuo* (10^{-3} mbar). Yield: 480 mg (0.560 mmol, 88%).

$C_{57}H_{59}N_3P_2$ (848.07 g/mol). **Mp.** 207 °C. **CHN** calcd. (found) in %: C 80.73 (80.36), H 7.01 (6.54), N 4.95 (4.81). **^{1}H NMR** (C_6D_6, 500.1 MHz): δ = 1.68 (s, 6 H, C*H*$_3$), 1.72 (s, 6 H, C*H*$_3$), 1.94 (br s, 12 H, *o*-C*H*$_3$), 2.27 (s, 6 H, C*H*$_3$), 2.27 (s, 6 H, C*H*$_3$), 2.28 (s, 6 H, C*H*$_3$), 6.72-6.99 (m, 17 H, C*H*). **^{13}C{^{1}H} NMR** (C_6D_6, 75.5 MHz): δ = 18.5 (s, *C*H$_3$), 18.6 (s, *C*H$_3$), 20.6 (s, *C*H$_3$), 20.7 (s, *C*H$_3$), 21.0 (s, *C*H$_3$), 21.0 (s, *C*H$_3$), 21.1 (s, *C*H$_3$), 121.4 (*arom. C*), 127.4 (*arom. C*), 127.6 (*arom. C*), 127.8 (*arom. C*), 128.0 (arom. C), 128.2 (*arom. C*), 128.3 (*arom. C*), 128.4 (*arom. C*), 128.9 (*arom. C*), 129.6 (*arom. C*), 130.8 (*arom. C),* 131.9 (*arom. C*), 135.3 (*arom. C*), 135.9 (*arom. C*), 136.5 (*arom. C*), 136.5 (*arom. C*), 136.6 (*arom. C*), 137.1 (*arom. C*), 137.5 (*arom. C*), 138.9 (*arom. C*), 140.1 (*arom. C*), 142.8 (*arom. C*), 145.6 (*arom. C*), 150.0 (*arom. C*). **^{14}N NMR** No signals observed. **^{31}P{^{1}H} NMR** (C_6D_6, 202.5 MHz): δ = 221.7 (d, $^2J(^{31}P,^{31}P)$ = 136 Hz, 1 P, N*P*C), 258.3 (d, $^2J(^{31}P,^{31}P)$ = 136 Hz, 1 P, N*P*N). **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3444 (w), 3350 (w), 3030 (w), 2937 (m), 2912 (m), 2852 (w), 2727 (w), 2324 (w), 1815 (w), 1740 (w), 1724 (w), 1641 (w), 1610 (m), 1591 (w), 1572 (w), 1537 (m), 1477 (m), 1450 (m), 1406 (m), 1377 (m), 1342 (w), 1329 (w), 1298 (w), 1284 (w), 1271 (m), 1238 (m), 1223 (m), 1192 (m), 1165 (m), 1142 (m), 1092 (m), 1082 (m), 1030 (m), 1016 (m), 982 (m), 960 (m), 951 (m), 887 (m), 877 (m), 845 (s), 837 (s), 800 (s), 771 (m), 760 (s), 750 (s), 710 (m), 687 (m), 677 (vs), 658 (m), 652 (m), 619 (m), 600 (m),

580 (m), 573 (m), 559 (m), 548 (m), 530 (m). **Raman** (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3048 (1), 3014 (1), 2920 (2), 2860 (1), 2733 (1), 1692 (1), 1643 (1), 1613 (2), 1591 (3), 1581 (2), 1483 (1), 1438 (1), 1405 (1), 1380 (1), 1305 (3), 1285 (1), 1271 (1), 1259 (1), 1216 (1), 1206 (1), 1188 (1), 1166 (1), 1096 (1), 1083 (1), 1033 (1), 1008 (1), 948 (1), 881 (1), 851 (1), 806 (1), 797 (1), 744 (1), 700 (1), 687 (1), 653 (1), 616 (1), 600 (1), 579 (3), 557 (2), 525 (1), 504 (1), 445 (1), 419 (1), 395 (1), 355 (1), 337 (1), 317 (1), 265 (1), 242 (2), 151 (2), 80 (10). **MS** (CI^+, iso-butane, m/z (%)): 330 (22) $[TerNH_3]^+$, 687 (10) $(\mu\text{-NTer})_2PH^+$, 716 (100) $[P(\mu\text{-NTer})]_2^+$, 748 $[M]^+$ (2).

Figure S3. NMR, Raman und IR spectra of $[P(\mu\text{-NTer})]_2$DmpNC in C_6D_6 (solvent signals indicated by asterisks).

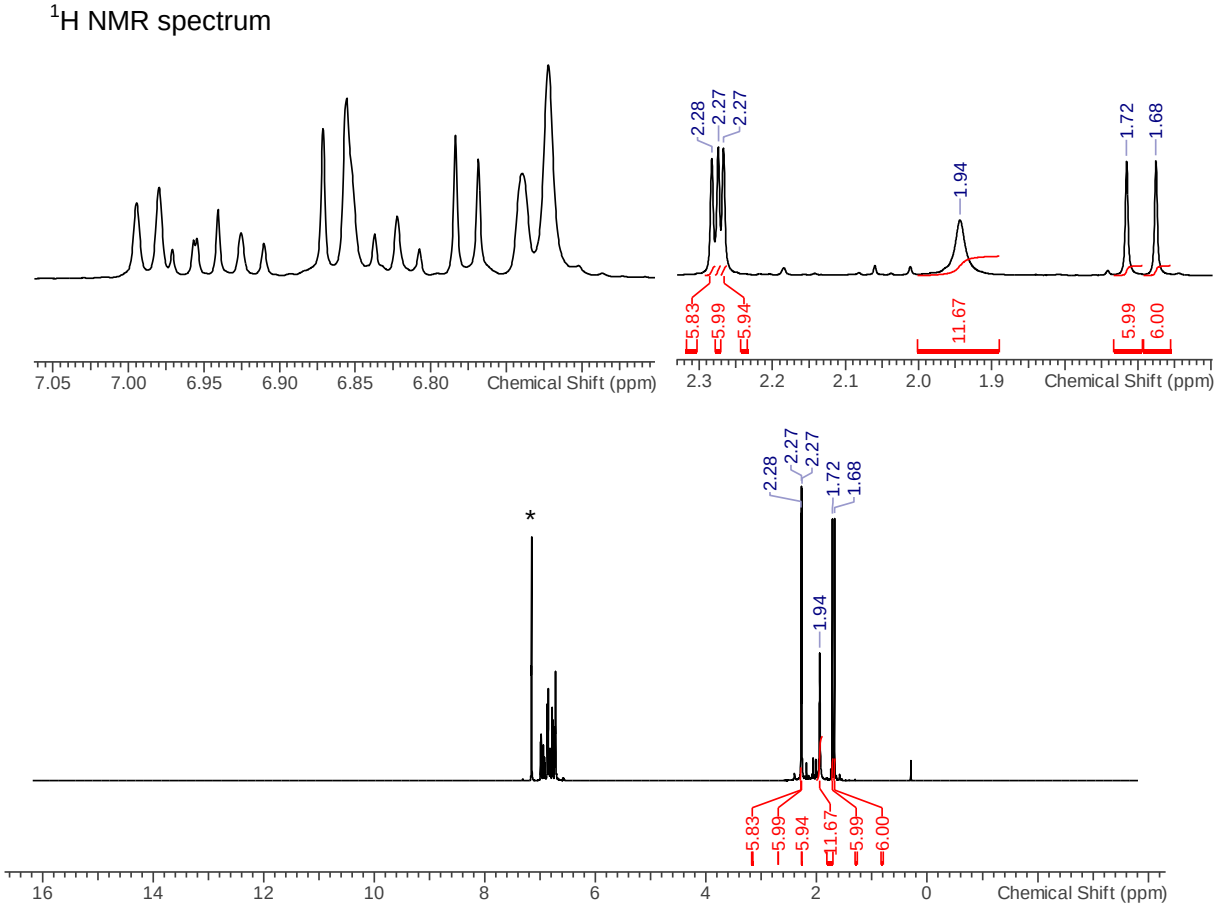


Figure S3 continued.

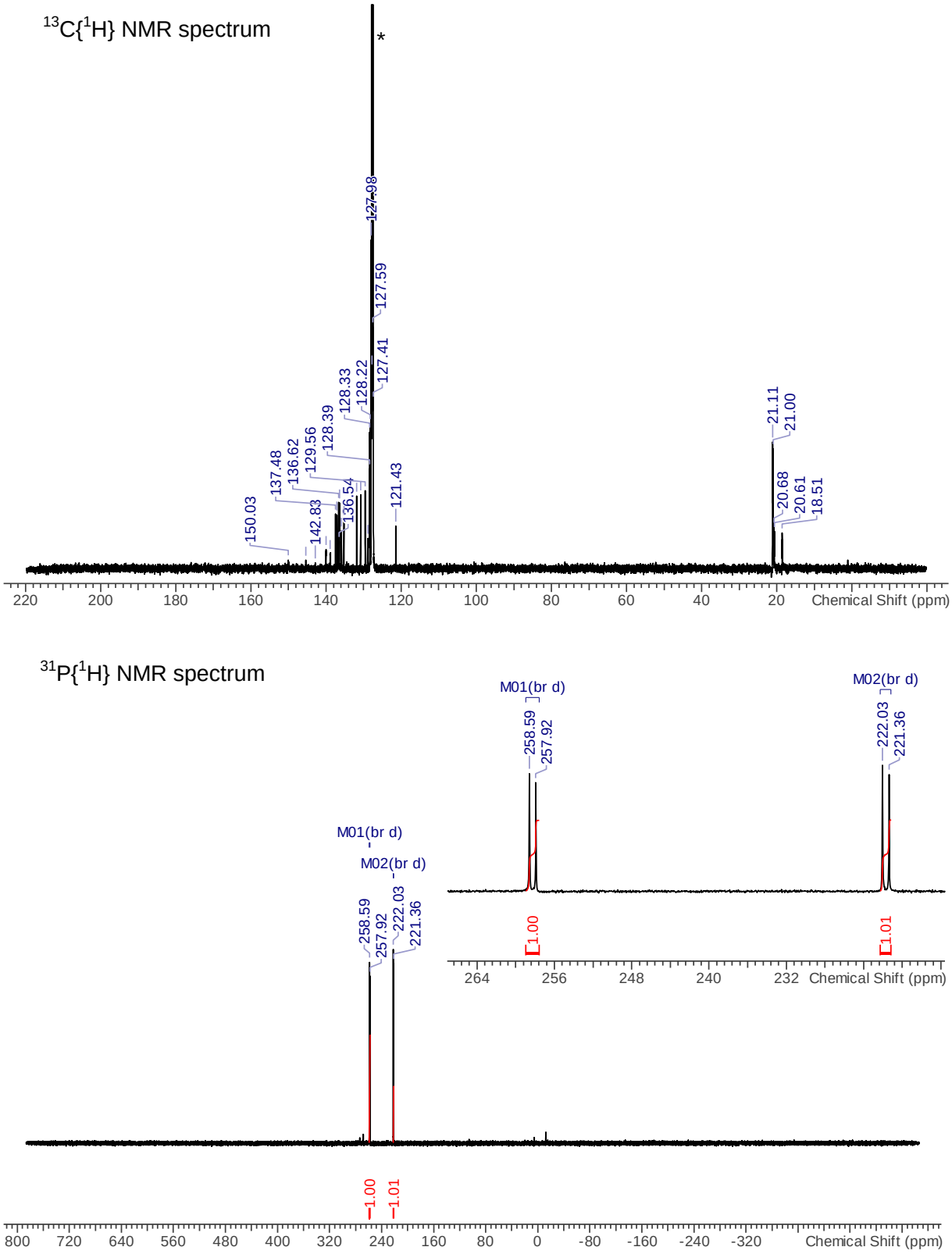
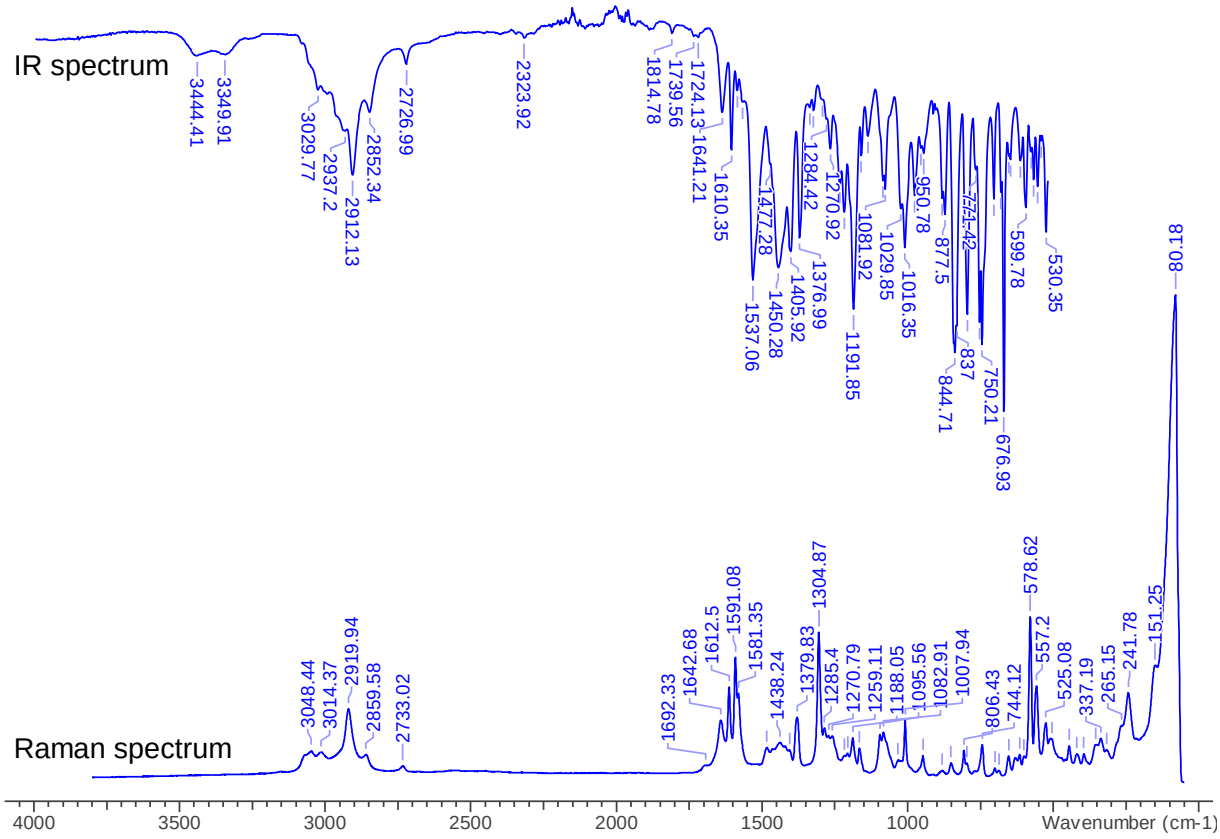
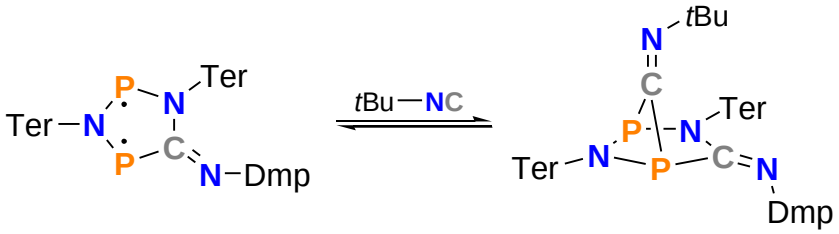


Figure S3 continued.



4 Syntheses of Compounds

4.1 [TerNP]$_2$DmpNC*t*BuNC (4a)



[TerNP]$_2$DmpNC (**2a**, 60 mg, 0.07 mmol) was dissolved in *t*BuNC (1.849 mg, 2.5 mL, 22.1 mmol). The light blue solution was stored at −20 °C. Some colorless crystals suitable for X-ray structure determination were obtained.

Because of the equilibrium between the starting material **2a** and the product **4a**, it was not possible to obtain a full set of analytical data of the pure compound **4a**. When washing colourless crystals of **4a**, small amounts of the substance were re-dissolved, which partly fragmented into *t*BuNC and the biradical **2a**. Thus, adduct **4a** and biradical **2a** could never be fully separated and a small amount of the blue solution always adhered to the colourless crystals.

$C_{62}H_{68}N_4P_2$ (931.20 g/mol). **Mp.** 148 °C. **CHN** calcd. (found) in %: C 79.97 (79.05), H 7.36 (7.18), N 6.02 (5.87). Deviations due to adhering impurities described above. **^{1}H NMR** (243 K, THF-d_8, 250.1 MHz): δ = 1.67 (s, 6 H, CH_3), 1.72 (s, 6 H, CH_3), 1.93 (s, 6 H, CH_3), 1.96 (s, 6 H, CH_3), 1.98 (s, 9 H, *t*Bu), 2.01 (s, 12 H, *o*-CH_3), 2.09 (s, 6 H, CH_3), 6.56-6.94 (m, 17 H, C*H*). **^{31}P{^{1}H} NMR** (243 K, THF-d_8, 101.5 MHz): δ = 188.2 (d, $^2J(^{31}P,^{31}P)$ = 33 Hz, 1P, N*P*C), 222.7 (d, $^2J(^{31}P,^{31}P)$ = 33 Hz, 1P, N*P*N). **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3029 (w), 3000 (w), 2965 (m), 2957 (m), 2914 (m), 2854 (w), 1659 (w), 1611 (s), 1578 (m), 1442 (m), 1416 (m), 1397 (s), 1374 (m), 1360 (m), 1243 (m), 1228 (m), 1216 (m), 1195 (s), 1162 (m), 1113 (m), 1096 (m), 1067 (m), 1028 (m), 1006 (m), 979 (s), 968

(m), 921 (m), 890 (m), 861 (m), 841 (s), 810 (m), 795 (s), 762 (vs), 752 (s), 742 (s), 723 (m), 688 (m), 647 (m), 614 (s), 596 (m), 571 (m), 558 (m), 550 (m), 525 (m), 511 (m), 499 (s), 490 (s), 470 (m), 460 (m), 451 (m), 439 (m), 416 (m), **Raman** (633 nm, 8 mW, 20 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3083 (1), 3079 (1), 3048 (3), 3037 (2), 3013 (3), 2991 (2), 2987 (2), 2977 (4), 2966 (3), 2954 (3), 2940 (4), 2916 (7), 2858 (2), 2819 (1), 2731 (1), 2724 (1), 2704 (1), 1618 (3), 1614 (3), 1586 (5), 1576 (3), 1561 (1), 1485 (1), 1455 (2), 1441 (2), 1416 (2), 1400 (2), 1383 (2), 1378 (3), 1304 (6), 1287 (2), 1277 (2), 1255 (3), 1244 (1), 1226 (1), 1194 (2), 1188 (2), 1164 (2), 1095 (2), 1067 (3), 1027 (1), 1003 (2), 985 (1), 968 (1), 947 (1), 919 (1), 890 (1), 863 (1), 848 (1), 812 (1), 799 (1), 796 (1), 784 (1), 773 (1), 741 (3), 723 (1), 688 (1), 654 (1), 621 (2), 614 (2), 597 (1), 577 (10), 572 (7), 557 (4), 550 (3), 545 (3), 532 (4), 526 (3), 511 (2), 499 (2), 490 (1), 469 (1), 459 (2), 451 (1), 417 (2), 399 (1), 381 (1), 366 (1), 353 (1), 331 (1), 315 (1), 291 (1), 270 (2), 263 (3), 251 (4), 237 (4), 202 (1).

Figure S4. Raman, IR and NMR spectra of [P(μ-NTer)]$_2$[DmpNC][*t*BuNC] in THF-d_8 at −30 °C (solvent signals indicated by asterisks).

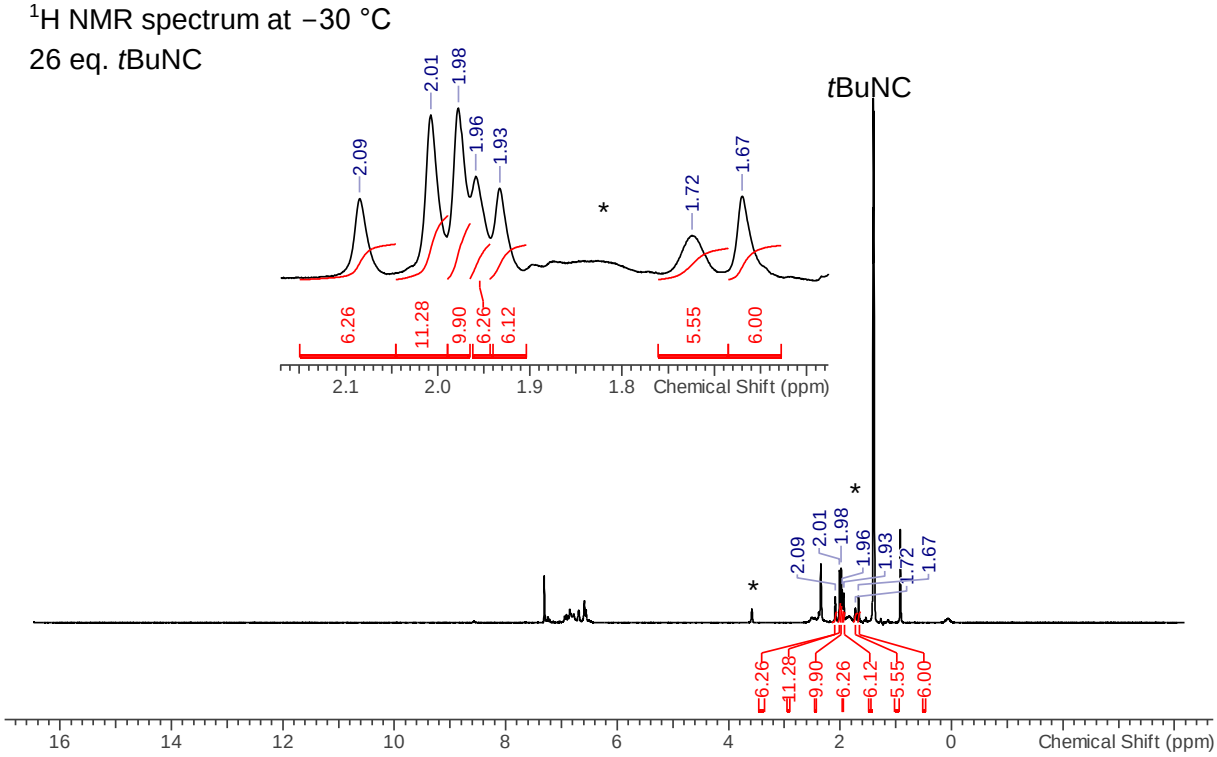


Figure S4 continued.

$^{31}P\{^{1}H\}$ NMR spectrum at −30 °C
26 eq. *t*BuNC

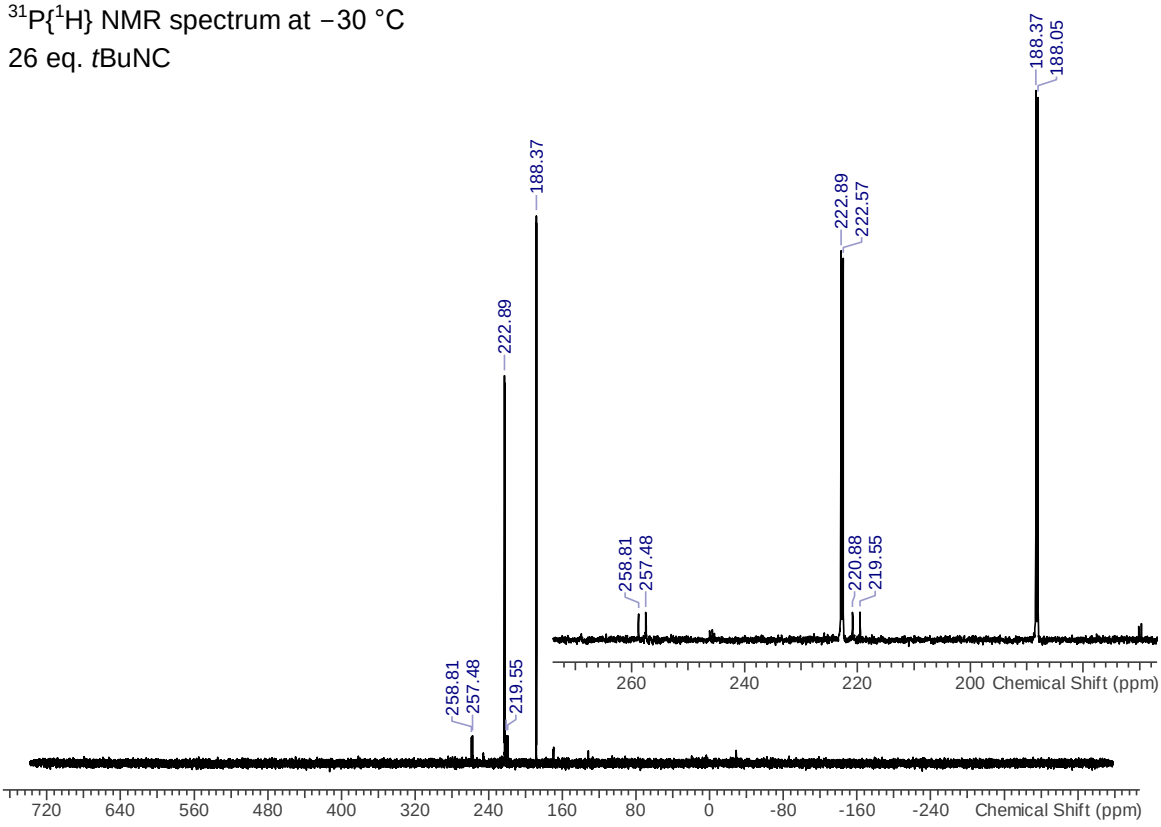
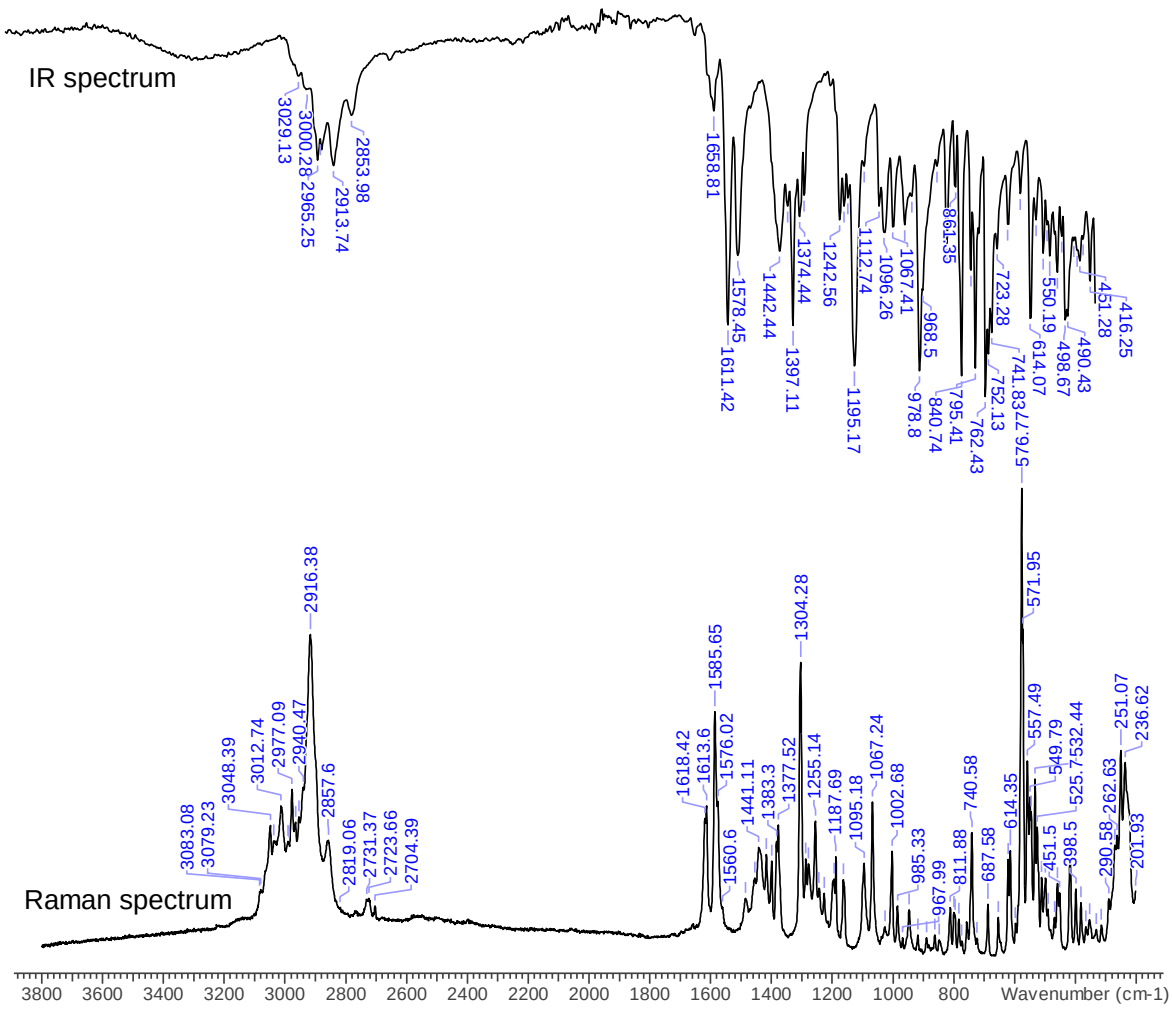


Figure S4 continued.

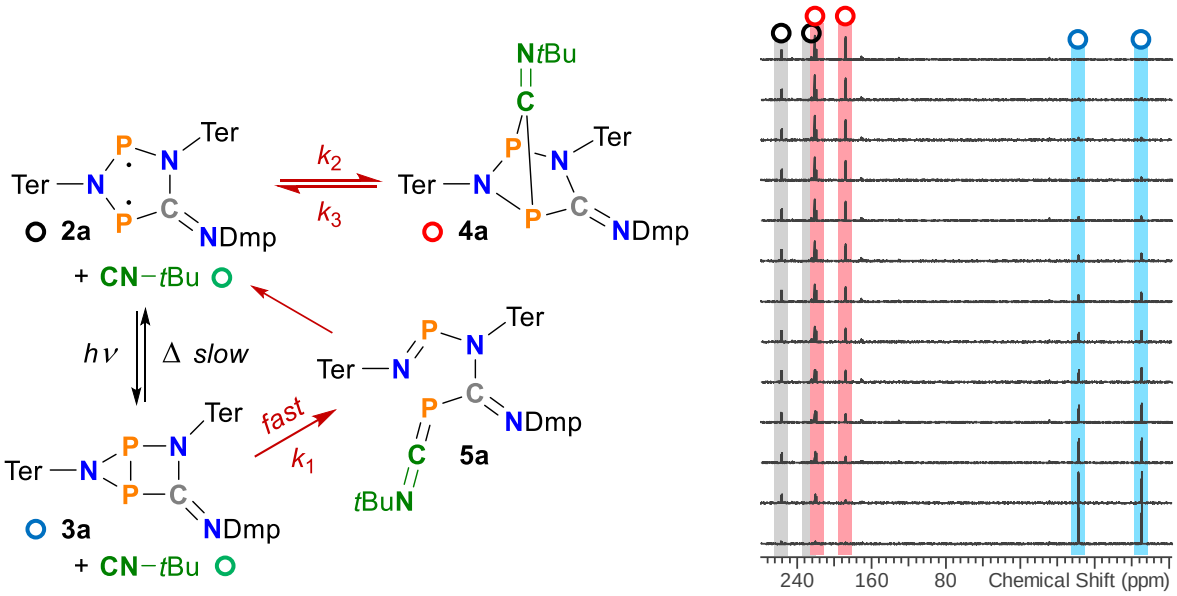


5 Additional Spectroscopic Data

5.1 Reaction kinetics of thermal equilibration

To investigate the thermal reverse reaction **3a** → **2a** (housane → biradical) in the presence of *t*BuNC, solutions of the biradical **2a** with different concentrations of *t*BuNC were irradiated in the NMR spectrometer (diode current: 500 mA). When a dynamic steady-state between photoconversion of the biradical **2a** to the housane **3a** and thermal reverse reaction was reached, the laser diode was turned off and the thermal equilibration (Figure S5) was traced by *in-situ* ^{31}P NMR spectroscopy (broadband decoupled, 30° pulse, 75 transients, 2 s delay).

Figure S5. Left: Thermal equilibration highlighted in red. Right: ^{31}P NMR spectra recorded at −20 °C (1 equiv. *t*BuNC).



The concentrations of all species were inferred from the NMR spectra. The ^{31}P NMR signals were integrated and normalized with respect to the sum of all integrals (which must be constant for every reaction that involves only dissolved, diamagnetic species).

Stock solutions of *t*BuNC and the biradical **2a** were prepared in order to easily calculate the concentrations of P-containing species from the relative integrals:

$$c_i = c_0 \cdot x_i$$

where x_i is the area of the normalized integrals and c_0 is the initial concentration, which is given by the relation

$$c_0 = c_{\text{stock}} \cdot \frac{V}{V_{\text{tot}}}$$

V being the volume of the stock solution and V_{tot} being the volume of the sample solution. The concentration of *t*BuNC was then calculated from its initial concentration (as defined above) and the concentration of the adduct **4a**:

$$c_{t\text{BuNC}} = c_{0,t\text{BuNC}} - c_{\mathbf{4a}}$$

Using the approximations explained in the manuscript, the following differential rate equations were obtained:

$$\frac{d[\mathbf{2a}]}{dt} = +k_1[\mathbf{3a}][t\text{BuNC}] - k_2[\mathbf{2a}][t\text{BuNC}] + k_3[\mathbf{4a}]$$

$$\frac{d[\mathbf{3a}]}{dt} = -k_1[\mathbf{3a}][t\text{BuNC}]$$

$$\frac{d[\mathbf{4a}]}{dt} = +k_2[\mathbf{2a}][t\text{BuNC}] - k_3[\mathbf{4a}]$$

$$\frac{d[t\text{BuNC}]}{dt} = -k_2[\mathbf{2a}][t\text{BuNC}] + k_3[\mathbf{4a}]$$

The terms in square brackets indicate the concentration of the respective species, and t is the reaction time. The differential equations were used in a non-linear fitting procedure against the experimental concentration data. Therefore, the facility to fit Ordinary Differential Equations (ODE) in the program *Origin* was used. The fitting functions were defined in *Origin C* code as follows:[8]

```
#pragma numlittype(push, TRUE)
#pragma warning(error : 15618)
#include <origin.h>

// Add your special include files here.
// For example, if you want to fit with functions from the NAG library,
// add the header file for the NAG functions here.

#include <oc_nag.h>
#include <ONLSF.H>

// Add code here for other Origin C functions that you want to define
// in this file, and access in your fitting function.

// ============================================================================

struct user   // parameters in the ODE
{
    double k1, k2, k3;
};

// Define the differential equations
static void NAG_CALL f(Integer neq, double t, double y[], double yp[],
  Nag_User *comm)
{
    neq; // Number of ordinary differential equations
    t;   // Independent variable
    y;   // Dependent variables y1, y2, ..., yneq
    yp;  // First derivatives (y')

    // Retrieve the original object's address
    struct user *sp = (struct user *)(comm->p);

    // Parameters in the ODE (local copy of the ones defined above)
    double k1, k2, k3;

    k1 = sp->k1;
    k2 = sp->k2;
    k3 = sp->k3;

    // Differential equations
    // H = y[0]   (Housane)
    // B = y[1]   (Biradical)
    // N = y[2]   (isoNitrile)
    // A = y[3]   (Adduct)

    // H' = -k1*H*N
    yp[0] = -k1*y[0]*y[2];

    // B' = +k1*H*N -k2*B*N +k3*A
    yp[1] = +k1*y[0]*y[2] -k2*y[1]*y[2] +k3*y[3];

    // N' = -k2*B*N +k3*A
    yp[2] = -k2*y[1]*y[2] +k3*y[3];

    // A' = +k2*B*N -k3*A
    yp[3] = +k2*y[1]*y[2] -k3*y[3];

}

```

```
61
62   // Use Runge-Kutta ODE23 to solve ODE
63   static bool nag_ode_fit( const double k1, const double k2,
64     const double k3, const double H0, const double B0, const double N0,
65     const double A0, const double tstart, const double tend, const int nout,
66     vector &vH, vector &vB, vector &vN, vector &vA )
67   {
68       // nout: Number of points to output
69       if( nout < 2 ) return false;
70
71       // The y values are stored as vectors
72       // Set the first value to the resp. y0 value
73       vH.SetSize( nout );
74       vB.SetSize( nout );
75       vN.SetSize( nout );
76       vA.SetSize( nout );
77       vH[0] = H0;
78       vB[0] = B0;
79       vN[0] = N0;
80       vA[0] = A0;
81
82       int neq = 4; // Number of ordinary differential equations
83       Nag_RK_method method;
84
85       double hstart, tgot, tinc;
86
87       double tol, twant;
88       int i, j;
89
90       vector thres(neq), ygot(neq), ymax(neq), ypgot(neq), ystart(neq);
91
92       Nag_ErrorAssess errass;
93       Nag_ODE_RK opt;
94       Nag_User comm;
95
96       // Retrieve parameters
97       struct user s;
98       s.k1 = k1;
99       s.k2 = k2;
100      s.k3 = k3;
101      comm.p = (Pointer)&s;
102
103      ystart[0] = H0;
104      ystart[1] = B0;
105      ystart[2] = N0;
106      ystart[3] = A0;
107
108      for (i=0; i<neq; i++) thres[i] = 1.0e-8;
109
110      errass = Nag_ErrorAssess_off;
111
112      hstart = 0;
113      method = Nag_RK_2_3;
114
115      tinc = (tend-tstart)/(nout-1);
116
117      tol = 1.0e-3;
118
119      NagError nagErr1;
120      // Setup ODE
```

```
121     d02pvc(neq, tstart, ystart, tend, tol, thres, method, Nag_RK_range,
        errass, hstart, &opt, &nagErr1);
122
123     if( nagErr1.code != NE_NOERROR ) return false;
124
125     for (j=1; j<nout; j++)
126     {
127         twant = tstart + j*tinc;
128
129         NagError nagErr2;
130         // Solve ODE
131         d02pcc(neq, f, twant, &tgot, ygot, ypgot, ymax, &opt, &comm,
            &nagErr2);
132
133         if( nagErr2.code != NE_NOERROR ) return false;
134
135         vH[j] = ygot[0];
136         vB[j] = ygot[1];
137         vN[j] = ygot[2];
138         vA[j] = ygot[3];
139     }
140
141     // Free functions for Runge-Kutta suite
142
143     d02ppc(&opt);
144
145     return true;
146 }
147
148 // ====================================================================
149
150 // You can access C functions defined in other files, if those files are
151 // loaded and compiled in your workspace, and the functions have been
152 // prototyped in a header file that you have included above.
153
154 // You can access NLSF object methods and properties directly in your
155 // function code.
156
157 // You should follow C-language syntax in defining your function.
158 // For instance, if your parameter name is P1, you cannot use p1 in your
159 // function code. When using fractions, remember that integer division
160 // such as 1/2 is equal to 0, and not 0.5
161 // Use 0.5 or 1/2.0 to get the correct value.
162
163 // For more information and examples, please refer to the "User-Defined
164 // Fitting Function" section of the Origin Help file.
165
166 //--------------------------------------------------------------
167 //
168 void _nlsfhm_b_001_005(
169 // Fit Parameter(s):
170 double H0, double B0, double N0, double A0, double k1, double k2,
171 double k3, double tmax, double npoints,
172 // Independent Variable(s):
173 double t,
174 // Dependent Variable(s):
175 double& H, double& B, double& N, double& A)
176 {
177     // Beginning of editable part
178
```

```
    NLFitContext *pCtxt = Project.GetNLFitContext();
    if ( pCtxt )
    {
        static vector vT, vH, vB, vN, vA;
        static int nSize;

        BOOL bIsNewParamValues = pCtxt->IsNewParamValues();
        // If parameters were updated, we will recalculate the ODE result.
        if ( bIsNewParamValues )
        {
            // Initial and final values of the independent variable
            double tstart = 0.01, tend = tmax, tinc;
            int nout = npoints; // Number of points

            tinc = (tend-tstart)/(nout-1);
            vT.Data( tstart, tend, tinc );
            nSize = vT.GetSize();

            if( !nag_ode_fit(k1, k2, k3, H0, B0, N0, A0, tstart, tend, nout,
            vH, vB, vN, vA) ) return;
        }

        // Interpolate y values from fitting data's x on the ODE result.
        ocmath_interpolate( &t, &H, 1, vT, vH, nSize );
        ocmath_interpolate( &t, &B, 1, vT, vB, nSize );
        ocmath_interpolate( &t, &N, 1, vT, vN, nSize );
        ocmath_interpolate( &t, &A, 1, vT, vA, nSize );
    }
    // End of editable part
}
```

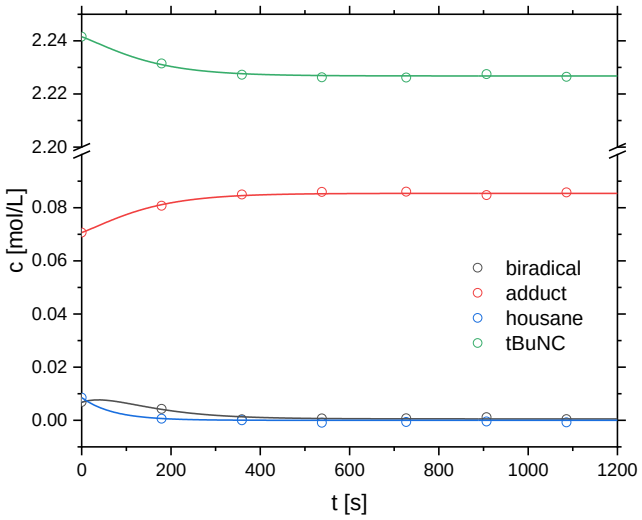
The reaction kinetics were studied at different temperatures (Figure S6 - Figure S10) to determine the temperature dependence of the rate constant and thus the enthalpy and entropy of activation, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, according to the Eyring theory (Figure S11).

$$k = \kappa \frac{k_B T}{h} \exp\left(\frac{\Delta G^{\ddagger}}{RT}\right)$$

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\ddagger}}{R} \cdot \frac{1}{T} + \frac{\Delta S^{\ddagger}}{R} + \ln\left(\frac{k_B}{T}\right)$$

The transmission coefficient κ is assumed to be unity in the second equation.

Figure S6. Thermal reverse reaction at −30 °C. Ratio of **2a** to *t*BuNC is 1:27.



B_0 = 0.0068(4) mol/L

H_0 = 0.0085(4) mol/L

A_0 = 0.0707(3) mol/L

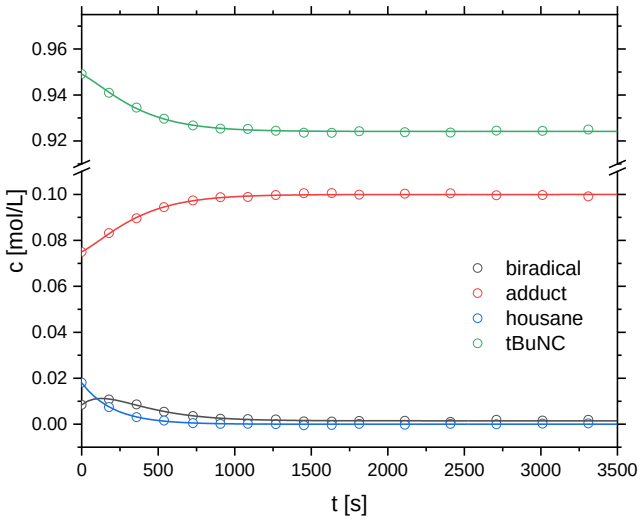
N_0 = 2.2416 mol/L

$k_1 = 6(2)\times10^{-3}$ L/(mol·s)

$k_2 = 4.4(5)\times10^{-3}$ L/(mol·s)

$k_3 = 6(3)\times10^{-5}$ 1/s

Figure S7. Thermal reverse reaction at −30 °C. Ratio of **2a** to *t*BuNC is 1:10.



B_0 = 0.0084(3) mol/L

H_0 = 0.0189(3) mol/L

A_0 = 0.0750(2) mol/L

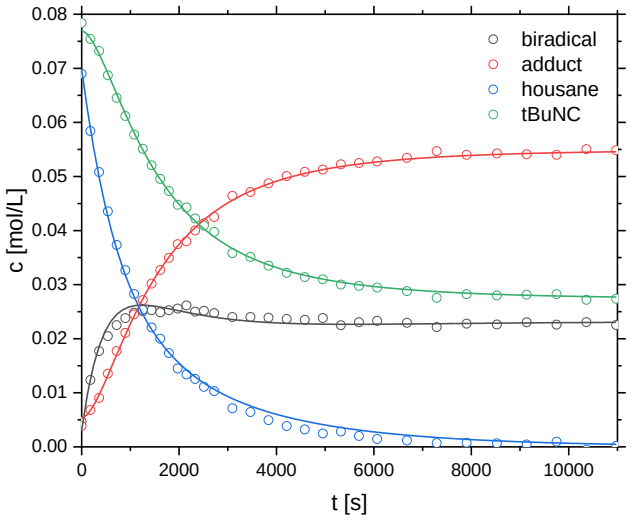
N_0 = 0.9491(2) mol/L

$k_1 = 5.1(2)\times10^{-3}$ L/(mol s)

$k_2 = 5.0(1)\times10^{-3}$ L/(mol s)

$k_3 = 6.8(6)\times10^{-5}$ 1/s

Figure S8. Thermal reverse reaction at −20 °C. Ratio of **2a** to *t*BuNC is 1:1.



B_0 = 0.0031(5) mol/L

H_0 = 0.0698(4) mol/L

A_0 = 0.0052(3) mol/L

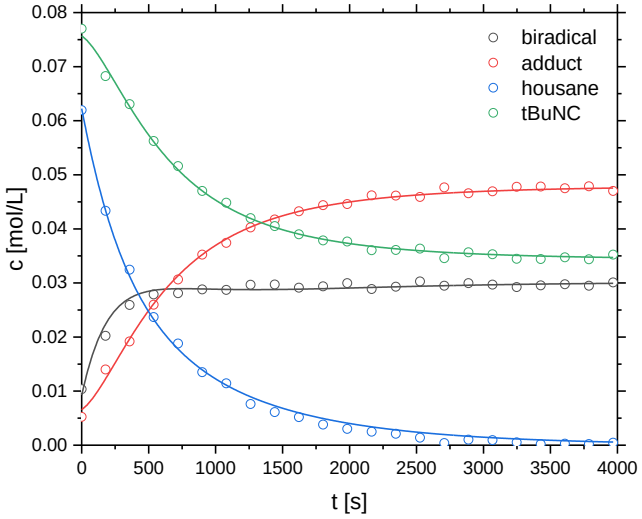
N_0 = 0.0771(3) mol/L

$k_1 = 1.25(1)\times10^{-2}$ L/(mol s)

$k_2 = 1.51(2)\times10^{-2}$ L/(mol s)

$k_3 = 1.74(4)\times10^{-4}$ 1/s

Figure S9. Thermal reverse reaction at −10 °C. Ratio of **2a** to *t*BuNC is 1:1.



B_0 = 0.0093(5) mol/L

H_0 = 0.0623(5) mol/L

A_0 = 0.0064(4) mol/L

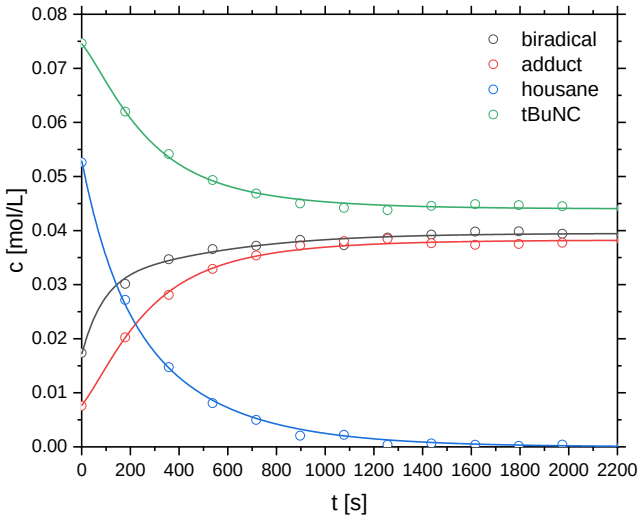
N_0 = 0.0757(4) mol/L

$k_1 = 2.76(3)\times10^{-2}$ L/(mol s)

$k_2 = 3.11(8)\times10^{-2}$ L/(mol s)

$k_3 = 6.7(2)\times10^{-4}$ 1/s

Figure S10. Thermal reverse reaction at 0 °C. Ratio of **2a** to *t*BuNC is 1:1.



B_0 = 0.0171(4) mol/L

H_0 = 0.0530(4) mol/L

A_0 = 0.0076(4) mol/L

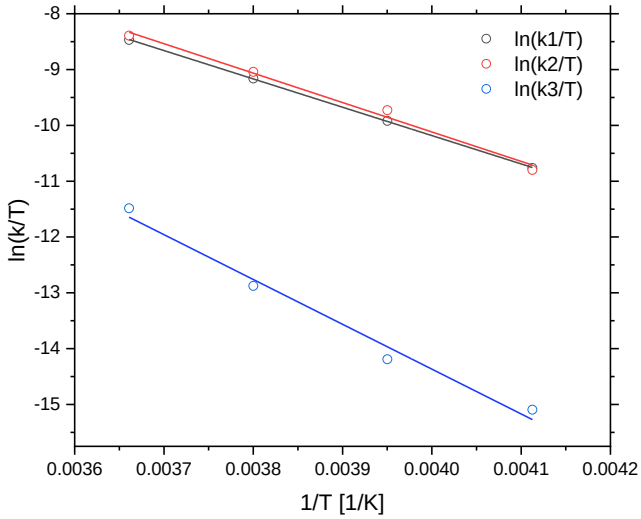
N_0 = 0.0746(4) mol/L

$k_1 = 5.72(9)\times10^{-2}$ L/(mol s)

$k_2 = 6.2(2)\times10^{-2}$ L/(mol s)

$k_3 = 2.8(1)\times10^{-3}$ 1/s

Figure S11. Eyring plot of the thermal reverse reaction with following conditions: −30 °C (1:10), −20 °C (1:1), −10 °C (1:1), 0 °C (1:1).



k_1
H_{act} = 42.2±0.3 kJ/mol
S_{act} = −113±1 J/(mol K)

k_2
H_{act} = 43±3 kJ/mol
S_{act} = −106±11 J/(mol K)

k_3
H_{act} = 67±6 kJ/mol
S_{act} = −50±23 J/(mol K)

6 Computational Details

6.1 General Remarks

Computations were carried out using ORCA 4.2.1[9] and Gaussian 09.[10]

Structure optimizations were performed using the PBE exchange-correlation functional[11,12] in conjunction with Grimme's dispersion correction D3(BJ)[13,14] and Ahlrichs's def2 basis set family[15] (notation: (U)PBE-D3/def2-SVP or (U)PBE-D3/def2-TZVP). The resolution of identity (RI) approximation was employed, using the appropriate Coulomb fitting basis of the Ahlrichs group.[16] The stability of all Kohn-Sham wavefunctions was checked, and the broken-symmetry solution was used if it was lower in energy (indicating a substantial amount of multi-reference character of the wavefunction). All structures were then fully optimized and confirmed as minima or transition states by frequency analyses. Chemical shifts and coupling constants were derived by the GIAO method.[17–21] The calculated absolute shifts ($\sigma_{calc,X}$) were referenced to the experimental absolute shift of 85 % H_3PO_4 in the gas phase ($\sigma_{ref,1}$ = 328.35 ppm),[22] using PH_3 ($\sigma_{ref,2}$ = 594.45 ppm) as a secondary standard:[23]

$$\begin{aligned} \delta_{calc,X} &= (\sigma_{ref,1} - \sigma_{ref,2}) - (\sigma_{calc,X} - \sigma_{calc,PH_3}) \\ &= \sigma_{calc,PH_3} - \sigma_{calc,X} - 266.1 \text{ ppm} \end{aligned}$$

At the PBE-D3/def2-SVP level of theory, σ_{calc,PH_3} amounts to + 617.22 ppm.

More accurate electronic energies for optimized structures were computed by single-point DLPNO-CCSD(T)[24–27] calculations employing the def2-TZVP basis set[15] and def2-TZVP/C correlation fitting basis[28] (notation: DLPNO-CCSD(T)/def2-TZVP//PBE-D3/def2-SVP). Thermodynamic quantities at this level of theory were calculated using the DLPNO-CCSD(T) single point energy and the thermal corrections at the PBE-D3/def2-SVP level of theory. The T_1 diagnostic was evaluated to ensure reliable results

(empirically, CCSD(T) results are considered reliable if T_1 < 0.02).[29] Nonetheless, it should be noted that many of the species discussed here possess at least a small amount of multi-reference character (biradical character), so the use of single-reference methods always entails some loss of accuracy and should be regarded as an approximation!

6.2 Reaction mechanism

The reaction mechanism of the catalysed reverse reaction was first investigated using a simple model system, where all Ter, Dmp, and *t*Bu substituents were replaced by Me groups. Several transition states were located on the PES using the Nudged Elastic Band (NEB) algorithm[30–34] implemented in ORCA[35] at the PBE-D3/def2-TZVP level of theory. All transition state (TS) structures were verified to be connected to the corresponding minima using Intrinsic Reaction Coordinate (IRC)[36,37] scans.

The two simplest reaction paths (i.e. via **TS0** as well as via **TS1**, **INT1**, **TS2**) were then also calculated at the DLPNO-CCSD(T)/def2-TZVP//PBE-D3/def2-SVP level of theory using the complete molecular structures of **2a**/**3a** and *t*BuNC. To this end, the minima and TS structures were optimized at the PBE-D3/def2-SVP level of theory and confirmed as minima or transitions states by frequency analyses. The optimized structures were subjected to single-point energy evaluations at the DLPNO-CCSD(T)/def2-TZVP level of theory as described above.

6.3 Summary of calculated data

Table S3. Summary of calculated data, including point group information, electronic energies, thermal corrections, and T_1 diagnostic. All energies given in a.u.

Compd.	**Opt/Freq**	**PG**	E_{tot}[a]	ΔH[b]	ΔG[c]	$E_{CCSD(T)}$[d]	T_1
*t*BuNC	PBE-D3/def2-SVP	C_{3v}	−250.1523	0.1343	0.0966	−250.1971	0.011
biradical **2a**	PBE-D3/def2-SVP	C_1	−3049.5828	1.0422	0.8914	−3049.2274	0.011
housane **3a**	PBE-D3/def2-SVP	C_1	−3049.5729	1.0419	0.8919	−3049.2186	0.011
TS0	UPBE-D3/def2-SVP	C_1	−3049.5422	1.0399	0.8898	−3049.1717	0.014
TS1	PBE-D3/def2-SVP	C_1	−3299.7346	1.1769	1.0101	−3299.4008	0.011
INT1=**5a**	PBE-D3/def2-SVP	C_1	−3299.7608	1.1781	1.0116	−3299.4257	0.011
TS2	PBE-D3/def2-SVP	C_1	−3299.7433	1.1767	1.0118	−3299.4103	0.012
A1=**4a**	PBE-D3/def2-SVP	C_1	−3299.7871	1.1793	1.0166	−3299.4529	0.011
A1′	PBE-D3/def2-SVP	C_1	−3299.7835	1.1793	1.0173	−3299.4487	0.011
A2	PBE-D3/def2-SVP	C_1	−3299.7614	1.1787	1.0178	−3299.4286	0.011
A3	PBE-D3/def2-SVP	C_1	−3299.7421	1.1776	1.0173	−3299.4077	0.011
model system (all R=Me)							
MeNC	PBE-D3/def2-TZVP	C_{3v}	-132.5985	0.1461	0.0978	—	—
biradical **2c**	PBE-D3/def2-TZVP	C_s	-1004.2530	0.1471	0.0991	—	—
housane **3c**	PBE-D3/def2-TZVP	C_1	-1004.2334	0.0486	0.0206	—	—
TS0_Me	UPBE-D3/def2-TZVP	C_1	-1004.1999	0.1447	0.0963	—	—
TS1_Me	PBE-D3/def2-TZVP	C_1	-1136.8230	0.1950	0.1352	—	—
INT1=**5c**	PBE-D3/def2-TZVP	C_1	-1136.8521	0.1972	0.1383	—	—
TS2_Me	PBE-D3/def2-TZVP	C_1	-1136.8451	0.1958	0.1390	—	—
TS3	PBE-D3/def2-TZVP	C_1	-1136.8447	0.1961	0.1380	—	—
INT2	PBE-D3/def2-TZVP	C_1	-1136.8509	0.1972	0.1381	—	—
TS4	PBE-D3/def2-TZVP	C_1	-1136.8439	0.1958	0.1387	—	—
A3_Me	PBE-D3/def2-TZVP	C_1	-1136.8708	0.1976	0.1423	—	—
TS5	PBE-D3/def2-TZVP	C_1	-1136.8530	0.1965	0.1388	—	—

[a] Total SCF energy; [b] sum of thermal corrections to enthalpy (298 K); [c] sum of thermal corrections to Gibbs energy (298 K); [d] single-point DLPNO-CCSD(T)/def2-TZVP energy

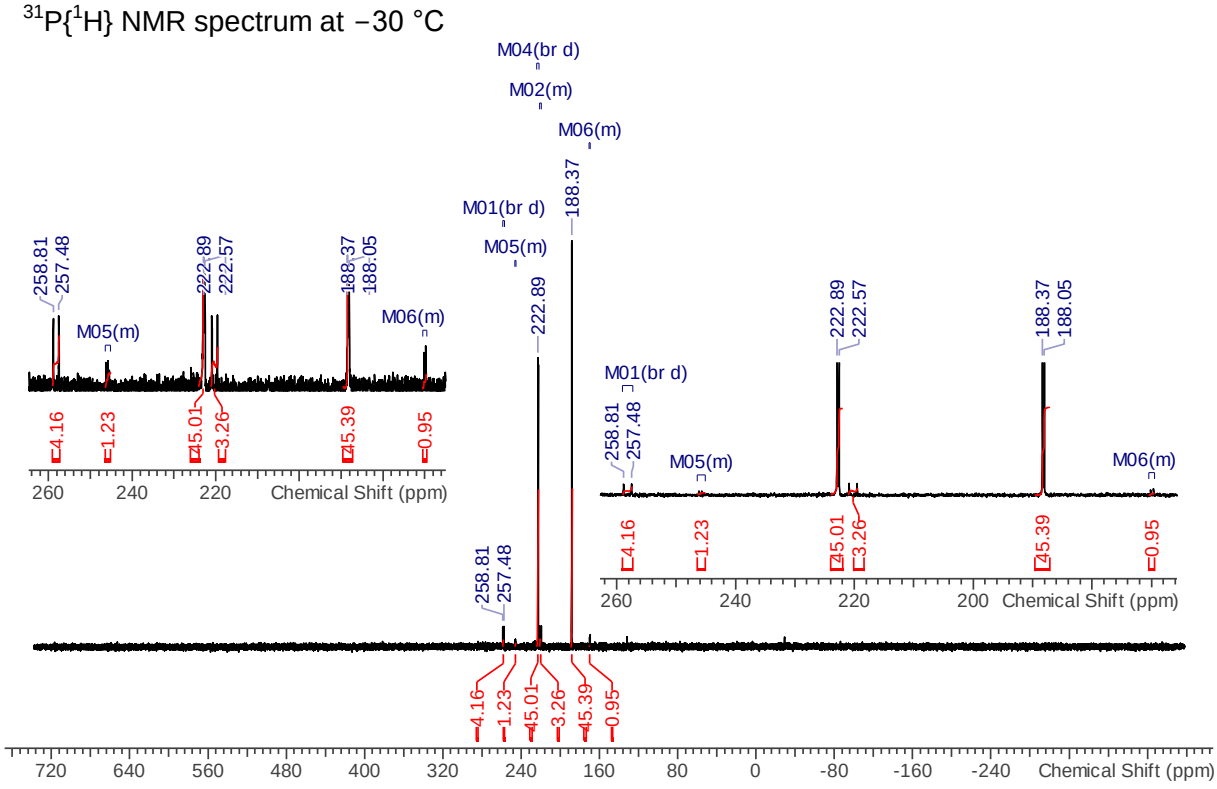
6.4 Calculated NMR data

Table S4. Summary of calculated ^{31}P NMR data (PBE-D3/def2-SVP). Experimentally observed data given in brackets.

isomer	**δ** [ppm]		**J** [Hz]
	P_A	**P_X**	
biradical **2a**	+240.3 (+221.7)	+259.1 (+258.3)	+163 (136)
housane **3a**[a]	−125.1 (−129.9)	−45.7 (−63.4)	−19 (65)
A1=**4a**	+163.0 (+188.2)	+201.8 (+222.7)	−33 (33)
A1′	+151.4 (+170.0)	+206.5 (+245.8)	−31 (47)
A2	+125.3 (—)	+142.0 (—)	−24 (—)
A3	+82.3 (—)	+125.0 (—)	−22 (—)

[a] Calculated values taken from ref. 2.

Figure S12. At −30 °C, an AX spin system (M05, M06) of very low intensity could be detected in the ^{31}P NMR spectrum, which was assigned to a second isomer (**A1'**) of adduct **A1** (=**4a**). Due to the low concentration of **A1'**, the integrals of both **A1** and **A1'**were added for the evaluation of the reaction kinetics and they were approximately treated as a single isomer.



6.5 Optimized structures (.xyz files)

6.5.1 PH_3 (NMR standard)

```
4
PH3, C3v, PBE-D3/def2-SVP
P           0.00000        0.00000        0.13355
H           0.00000        1.19789       -0.66776
H           1.03740       -0.59894       -0.66776
H          -1.03740       -0.59894       -0.66776
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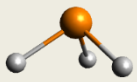

6.5.2 *t*BuNC

```
15
tBuNC, C3v, PBE-D3/def2-SVP
C           0.00000       -0.34713        0.00000
C           0.73174       -0.82892        1.26742
C           0.73174       -0.82892       -1.26742
N          -0.00000        1.09289       -0.00000
C          -1.46349       -0.82892        0.00000
H           1.77630       -0.46144        1.28026
H           0.74670       -1.93632        1.29332
H           0.22059       -0.46144        2.17845
H          -1.49340       -1.93632        0.00000
H          -1.99689       -0.46144       -0.89819
H          -1.99689       -0.46144        0.89819
H           1.77630       -0.46144       -1.28026
H           0.22059       -0.46144       -2.17845
H           0.74670       -1.93632       -1.29332
C           0.00000        2.27923       -0.00000
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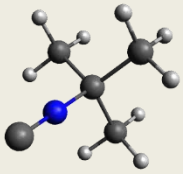

6.5.3 Biradical 2a

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121
Biradical 2a, C1, PBE-D3/def2-SVP
C           6.05817       -0.53163       -2.82021
C           4.60099       -0.91362       -2.73260
C           4.19502       -2.01896       -1.95934
C           3.62054       -0.21932       -3.45699
C           6.16377        0.01831        1.26757
C           2.85609       -2.43667       -1.90716
C           4.51795        1.40847       -0.05638
C           2.26128       -0.59517       -3.42877
C           4.95635        0.91748        1.18641
C           2.46338       -3.69071       -1.16958
C           2.93442        2.70829       -1.53195
C           1.87708       -1.69558       -2.62769
C           1.27937        0.14633       -4.30534
C           3.36281        2.19683       -0.17847
C           0.17634       -3.17884       -3.64650
C           3.09850       -2.13764        1.83157
C           4.22536        1.27303        2.33190
C           0.48472       -2.24238       -2.63809
C          -1.05253       -3.84506       -3.66619
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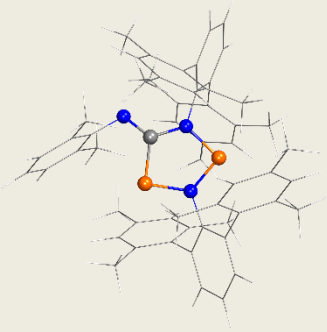

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C          2.62297        2.51208        0.99007
C          2.41362       -2.04288        4.25760
C          2.04380       -2.14273        2.90380
C          3.07360        2.07929        2.26227
C         -0.48912       -1.95819       -1.64303
C          1.45325       -2.03600        5.27744
C          1.39854        3.35889        0.85588
C          1.49692        4.74124        1.10165
C          0.66032       -2.24544        2.56840
C         -1.98836       -3.58340       -2.66080
C         -1.68962        3.95855       -2.62719
C          0.07563       -1.13222        0.68449
C          2.35327        2.47844        3.52575
C         -1.73552       -2.63792       -1.64545
C          0.09691       -2.12436        4.94182
C          0.40158        5.59166        0.90722
C          0.15202        2.83089        0.41575
C         -0.32166       -2.22132        3.60111
C         -3.48682       -0.27010       -1.91099
C         -0.80877        5.06180        0.44942
C         -0.96133        3.68085        0.19689
C         -1.78626       -2.30229        3.26887
C         -2.68899        3.44858       -1.61789
C         -2.83392       -2.39567       -0.66131
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C         -2.30937        3.22491       -0.26838
C         -4.01708        3.19097       -2.00360
C         -2.20629       -4.57810        0.48745
C         -3.10675       -3.37948        0.32746
C         -4.77628       -1.13003        0.07323
C         -3.25638        2.73690        0.66887
C         -4.97801        2.72052       -1.09158
C         -2.87582        2.51109        2.10947
C         -4.21488       -3.19937        1.17081
C         -4.57224        2.49443        0.23582
C         -5.05257       -2.07186        1.07562
C         -6.38811        2.41940       -1.53115
C         -6.20102       -1.88223        2.03465
H          6.60390       -1.20097       -3.51954
H          6.19095        0.50509       -3.18766
H          6.56206       -0.61673       -1.83646
H          7.02905        0.44582        0.72017
H          4.95085       -2.59374       -1.39912
H          3.92009        0.63521       -4.08601
H          6.47435       -0.16082        2.31517
H          5.08965        1.16958       -0.96417
H          5.94737       -0.97018        0.80837
H          3.72974        2.55509       -2.28494
H          1.31470        1.23911       -4.11557
H          2.02255       -4.43223       -1.86794
H          3.34008       -4.15950       -0.68363
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H          4.08950       -1.89685        2.26001
H          2.67682        3.78611       -1.50205
H          1.52590       -0.00225       -5.37809
H          3.16798       -3.12761        1.33998
H          2.03238        2.16952       -1.89467
H          1.69169       -3.48968       -0.39656
H          0.23756       -0.19219       -4.15406
H          4.55397        0.90717        3.31809
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H           3.48416       -1.96356        4.50678
H          -1.27948       -4.57068       -4.46180
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H           1.76126       -1.95540        6.33104
H          -1.28893        4.95354       -2.34509
H          -0.81124        3.28301       -2.70305
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H          -2.96221       -4.09597       -2.65877
H           2.53565        3.54575        3.77376
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H          -2.06065       -3.32133        2.93236
H           1.25649        2.35333        3.42902
H          -4.45531        0.09965       -2.29886
H          -2.40862       -2.05884        4.15175
H          -1.67860        5.71667        0.28870
H          -4.30817        3.36580       -3.05222
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H          -2.42141        3.41927        2.55651
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H          -5.30782        2.12960        0.97089
H          -7.11777        2.59992       -0.71700
H          -6.88832       -1.08178        1.69727
H          -5.83262       -1.60188        3.04498
H          -6.79044       -2.81391        2.15683
N           0.27518       -2.31469        1.20066
N          -0.24013       -0.90375       -0.67922
N           0.02668        1.40220        0.24437
P           0.22447        0.39294        1.66377
P          -0.24940        0.71649       -1.27991
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6.5.4 Housane 3a

```
121
Housane 3a, C1, PBE-D3/def2-SVP
C           3.39675       -2.78278       -4.70461
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C           2.71752       -3.74452       -2.45862
C           1.11398       -2.40700       -3.66073
C           6.14020        2.91295        1.08934
C           1.82351       -3.90280       -1.38423
C           4.28243        2.84618       -0.64133
C           0.18291       -2.54529       -2.61506
C           4.71236        3.13769        0.66451
C           2.23468       -4.71669       -0.18284
C           2.52045        2.73320       -2.46090
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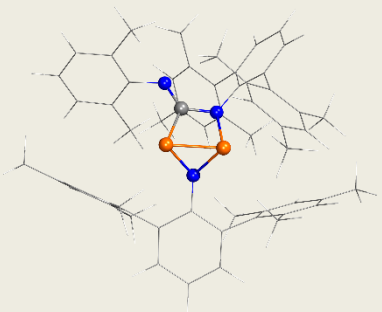

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C         -0.98236       -4.81084       -0.24650
C          3.26917       -0.43483       -1.16980
C          3.76144        3.62866        1.57873
C         -0.47296       -3.50357       -0.39317
C         -2.01474       -5.10681        0.64933
C          1.99712        3.47492       -0.09110
C          5.24365       -0.51738        0.41922
C          3.88145       -0.75939        0.16626
C          2.41563        3.81393        1.22456
C         -1.02300       -2.46793        0.41345
C          5.83726       -0.87405        1.63807
C          0.59383        3.73693       -0.53806
C          0.28324        5.06416       -0.89393
C          3.10828       -1.38423        1.18736
C         -2.57648       -4.07374        1.40806
C         -1.34092        1.37193       -3.57348
C          0.85567       -0.87442        0.73216
C          1.42253        4.32430        2.23631
C         -2.09635       -2.75564        1.30311
C          5.06475       -1.49540        2.62969
C         -0.96952        5.41854       -1.40499
C         -0.39649        2.71648       -0.68747
C          3.70208       -1.76778        2.42139
C         -4.66882       -1.72382        0.43104
C         -1.92458        4.41282       -1.58499
C         -1.66298        3.07173       -1.24278
C          2.86336       -2.43617        3.47712
C         -2.59773        1.29129       -2.74405
C         -2.74987       -1.67382        2.09745
C         -4.00269       -1.16354        1.66122
C         -2.72861        2.07738       -1.56854
C         -3.66914        0.46867       -3.13416
C         -0.85558       -1.76127        3.78783
C         -2.13526       -1.15940        3.26877
C         -4.58831       -0.10551        2.37518
C         -3.93108        2.03894       -0.81454
C         -4.87092        0.41403       -2.40436
C         -4.07819        2.85841        0.44212
C         -2.75267       -0.08912        3.94244
C         -4.97994        1.21073       -1.25098
C         -3.96973        0.46309        3.50492
C         -5.99418       -0.49483       -2.83511
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H          4.05867       -1.91951       -4.47401
H          6.81528        2.80643        0.21770
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H          0.82334       -1.83349       -4.55630
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H          5.01538        2.48419       -1.38040
H          6.22279        1.98107        1.68834
H          3.36146        2.33999       -3.06318
H         -1.38227       -1.61342       -3.78598
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H         -4.03403       -1.57066       -0.46637
H         -3.39956       -4.27744        2.11005
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H         -3.91659        3.93862        0.25612
H         -5.78582       -1.54851       -2.54854
H         -6.13136       -0.48244       -3.93516
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H         -5.07965        2.72576        0.89407
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H         -6.95525       -0.20997       -2.36402
H         -5.69209        1.54732        4.27317
H         -4.38097        2.58549        3.65622
H         -4.19105        1.76693        5.23407
N          1.77382       -1.73765        0.94423
N         -0.46963       -1.15198        0.40151
N         -0.12385        1.35805       -0.36017
P          0.83085        0.98687        1.15581
P         -1.27696        0.45317        0.71288
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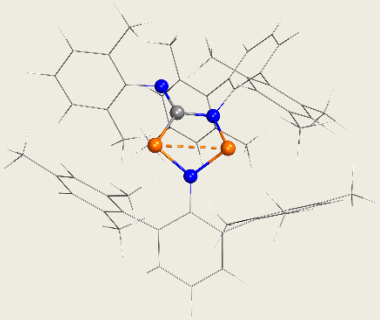
6.5.6 TS0



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121
TS0, C1, UPBE-D3/def2-SVP
C           3.17940       -2.38502       -4.83868
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C           2.62550       -3.41644       -2.58886
C           0.93114       -2.11011       -3.69393
C           5.84058        2.80076        1.78528
C           1.78101       -3.63123       -1.48382
C           4.13760        3.10836       -0.06504
C           0.04916       -2.30231       -2.61514
C           4.46993        3.19603        1.30048
C           2.26493       -4.48834       -0.34055
C           2.50477        3.28492       -1.99768
C           0.48827       -3.04315       -1.48625
C          -1.36247       -1.78246       -2.69408
C           2.84387        3.39300       -0.53207
C          -0.95372       -4.62905       -0.24166
C           3.22297       -0.31522       -1.29069
C           3.47830        3.63288        2.19780
C          -0.48099       -3.30842       -0.38134
C          -1.94745       -4.96451        0.68434
C           1.84141        3.75867        0.40666
C           5.23771       -0.68794        0.17083
C           3.84571       -0.80578       -0.00881
C           2.16850        3.92053        1.77738
C          -1.02032       -2.29887        0.46797
C           5.87485       -1.14677        1.33048
C           0.44876        4.00031       -0.07578
C           0.10182        5.32256       -0.40420
C           3.08118       -1.41568        1.03354
C          -2.50662       -3.95735        1.47684
C          -1.34665        1.66299       -3.19729
C           0.85776       -0.72035        0.69551
C           1.10404        4.29954        2.77471
C          -2.05856       -2.62540        1.38368
C           5.11534       -1.75979        2.33958
C          -1.16041        5.65185       -0.91131
C          -0.50271        2.94106       -0.25486
C           3.72824       -1.91589        2.20489
C          -4.72698       -1.71625        0.66487
C          -2.07881        4.61790       -1.12112
C          -1.77796        3.27645       -0.81723
C           2.90392       -2.57407        3.27715
C          -2.63559        1.54712       -2.42450
C          -2.71980       -1.58786        2.23183
C          -4.03109       -1.15452        1.87896
C          -2.81271        2.27187       -1.21491
C          -3.68074        0.72567       -2.88224
C          -0.67020       -1.44393        3.74749
C          -2.06934       -1.03863        3.36598
C          -4.64788       -0.16030        2.65260
C          -4.04002        2.17971       -0.50077
C          -4.89723        0.60795       -2.18645
C          -4.22926        2.91833        0.79887
C          -2.73210       -0.04481        4.11335
C          -5.05506        1.34848       -1.00007
C          -4.01201        0.41721        3.77007
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C          -5.98717       -0.30917       -2.67957
C          -4.69060        1.51102        4.55485
H           3.88854       -3.22378       -4.98517
H           2.64000       -2.21533       -5.79164
H           3.78857       -1.47528       -4.64310
H           6.63256        3.11930        1.07797
H           3.63612       -3.85638       -2.57193
H           0.58247       -1.53359       -4.56670
H           6.06574        3.23396        2.77928
H           4.90842        2.79492       -0.78771
H           5.91026        1.69505        1.87481
H           3.38508        2.97989       -2.59480
H          -1.58618       -1.39581       -3.70576
H           2.02206       -5.55963       -0.50773
H           3.36440       -4.41128       -0.23169
H          -0.53431       -5.39992       -0.90515
H           3.92645       -0.44259       -2.13722
H           2.12828        4.25018       -2.39427
H          -2.09892       -2.57731       -2.45717
H           2.28955       -0.85121       -1.53921
H           1.69548        2.54590       -2.17330
H           1.80045       -4.17742        0.61240
H          -1.54882       -0.96182       -1.97324
H           3.72652        3.72784        3.26740
H           5.83233       -0.22851       -0.63512
H          -2.29549       -6.00424        0.77545
H           2.97769        0.76351       -1.22383
H           0.86347        6.10325       -0.25270
H           6.96494       -1.04368        1.44193
H          -1.08514        2.72388       -3.38724
H          -0.50077        1.22911       -2.62195
H          -1.40594        1.13493       -4.16767
H          -4.89001       -2.80924        0.74896
H           1.53378        4.46538        3.78115
H          -1.41652        6.69228       -1.15845
H          -4.11603       -1.55772       -0.24800
H          -3.29938       -4.19183        2.20348
H           0.55576        5.21231        2.46724
H           5.60733       -2.13512        3.25096
H           2.20972       -3.32062        2.83857
H           0.34376        3.49242        2.85809
H          -5.70706       -1.22882        0.50641
H           3.54402       -3.07185        4.03071
H          -3.06521        4.83310       -1.56068
H          -3.54528        0.16863       -3.82318
H           0.05564       -0.68567        3.37929
H          -0.37750       -2.41500        3.30771
H           2.26311       -1.83732        3.80593
H          -5.65533        0.18382        2.36753
H          -0.55353       -1.49866        4.84807
H          -3.49922        2.56018        1.55718
H          -4.06107        4.00797        0.69040
H          -6.99199        0.05218       -2.38375
H          -5.86961       -1.32898       -2.25229
H          -2.22115        0.38747        4.98914
H          -5.24492        2.75665        1.20794
H          -6.00323        1.27706       -0.44255
H          -5.96645       -0.41509       -3.78219
H          -5.72518        1.22702        4.83708
H          -4.76725        2.44130        3.95211
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H          -4.13613        1.75685        5.48096
N           1.71261       -1.66603        0.90357
N          -0.49606       -0.96638        0.44722
N          -0.20311        1.60404        0.07476
P           1.22260        1.06385        1.02434
P          -1.47160        0.51518        0.71844
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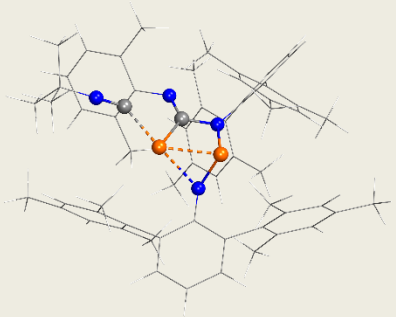
6.5.7 TS1



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136
TS1, C1, PBE-D3/def2-SVP
C           3.43193       -2.14043       -4.85949
C           2.33860       -2.53722       -3.90031
C           2.58520       -3.44341       -2.85402
C           1.05316       -1.97568       -3.99553
C           5.83890        2.92616        0.06168
C           1.60677       -3.76503       -1.89535
C           3.83158        2.66718       -1.47023
C           0.03736       -2.27891       -3.07065
C           4.37309        3.09659       -0.24812
C           1.93966       -4.73326       -0.78711
C           1.90777        2.20773       -3.04666
C           0.32699       -3.15655       -1.99302
C          -1.34003       -1.69743       -3.25318
C           2.45313        2.74178       -1.74762
C          -1.26082       -4.82187       -1.03408
C           3.14643       -0.53811       -0.99703
C           3.49165        3.64656        0.70147
C          -0.76166       -3.50392       -1.03368
C          -2.34265       -5.19705       -0.22941
C           1.58317        3.29662       -0.77475
C           4.90615       -1.10746        0.73245
C           3.56401       -1.14375        0.31184
C           2.11256        3.76299        0.46048
C          -1.37192       -2.54623       -0.17587
C           5.31923       -1.71725        1.92598
C           0.15074        3.55108       -1.12058
C          -0.16678        4.89808       -1.39745
C           2.60725       -1.80811        1.13882
C          -2.96536       -4.23550        0.57407
C          -1.93502        1.51973       -4.19382
C           0.45965       -1.01781        0.46170
C           1.20795        4.32748        1.52654
C          -2.49901       -2.90713        0.61203
C           4.37674       -2.39641        2.71449
C          -1.44314        5.29505       -1.80451
C          -0.86217        2.54260       -1.24152
C           3.02553       -2.46366        2.33588
C          -5.08290       -1.95764       -0.30846
C          -2.42369        4.31022       -1.96896
C          -2.15792        2.95458       -1.70508
C           2.01535       -3.19215        3.17787
C          -3.13897        1.30696       -3.31208
C          -3.22967       -1.89893        1.43843
C          -4.49107       -1.43151        0.97446
C          -3.23574        1.98387       -2.06603
C          -4.20268        0.48890       -3.72907
C          -1.38517       -1.91427        3.20053
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C          -2.69397       -1.40787        2.65463
C          -5.16526       -0.44808        1.71446
C          -4.41486        1.86996       -1.28484
C          -5.37871        0.35412       -2.96765
C          -4.54176        2.59204        0.03202
C          -3.40200       -0.41248        3.35645
C          -5.46567        1.06245       -1.75644
C          -4.62986        0.09206        2.89974
C          -6.49997       -0.54086       -3.43175
C          -5.34842        1.19338        3.63708
H           3.97696       -1.24637       -4.48419
H           4.18018       -2.94763       -4.98709
H           3.02850       -1.87846       -5.85787
H           6.45160        2.88435       -0.86039
H           3.58465       -3.89906       -2.76117
H           0.82445       -1.28539       -4.82426
H           6.22493        3.74880        0.69676
H           4.50098        2.23856       -2.23390
H           6.01357        1.97704        0.61507
H           2.72126        1.93654       -3.74691
H          -1.49040       -1.35071       -4.29247
H           1.60974       -5.76581       -1.02986
H           3.03204       -4.76667       -0.60912
H          -0.79051       -5.55576       -1.70532
H           4.02446       -0.33888       -1.64020
H           1.23933        2.93954       -3.54350
H          -2.13310       -2.43225       -3.01261
H           2.44991       -1.20107       -1.54197
H           1.29681        1.29894       -2.85607
H           1.44265       -4.43390        0.15444
H          -1.49480       -0.82295       -2.59008
H           3.89391        4.01484        1.66030
H           5.64402       -0.60194        0.08899
H          -2.71072       -6.23397       -0.24190
H           2.62274        0.42497       -0.85057
H           0.63855        5.64344       -1.30434
H           6.37709       -1.68592        2.22831
H          -1.81536        2.59474       -4.44198
H          -1.00046        1.21268       -3.68256
H          -2.02081        0.95116       -5.13944
H          -5.22007       -3.05661       -0.28186
H           1.78678        4.65315        2.41312
H          -1.66203        6.35099       -2.02135
H          -4.41696       -1.74246       -1.16972
H          -3.82660       -4.50637        1.20376
H           0.61532        5.19055        1.16482
H           4.69523       -2.90595        3.63854
H           1.34616       -3.81119        2.54581
H           0.46888        3.56174        1.84986
H          -6.06237       -1.48975       -0.51608
H           2.50686       -3.83996        3.92936
H          -3.42551        4.57859       -2.33963
H          -4.12123       -0.03737       -4.69442
H          -1.09071       -2.87750        2.74595
H          -1.43526       -2.04120        4.30070
H           1.35317       -2.48363        3.71935
H          -6.13772       -0.08332        1.34633
H          -0.56318       -1.19591        2.99358
H          -3.81198        2.18836        0.76699
H          -4.32898        3.67480       -0.06495
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H          -6.28344       -1.60568       -3.19649
H          -6.64683       -0.47753       -4.52875
H          -2.97728       -0.02472        4.29720
H          -5.55419        2.46815        0.46163
H          -6.38550        0.98776       -1.15384
H          -7.45880       -0.28504       -2.93947
H          -6.44520        1.03186        3.64602
H          -5.17184        2.17566        3.14739
H          -5.00244        1.28021        4.68558
N           1.28788       -1.95867        0.72612
N          -0.81681       -1.23848       -0.04082
N          -0.58509        1.18437       -0.98198
P           0.49257        0.83934        0.90882
P          -1.64046        0.36440        0.09243
C           1.48699        0.38227        2.62475
N           2.14986        0.80192        3.51199
C           3.09577        1.22257        4.50805
C           2.58033        2.53082        5.13670
C           4.44662        1.43897        3.79623
C           3.20442        0.10019        5.55856
H           4.35065        2.20359        3.00175
H           4.79365        0.49614        3.33077
H           5.19780        1.77936        4.53564
H           2.47013        3.31784        4.36559
H           3.30068        2.88237        5.90056
H           1.59796        2.37566        5.62420
H           2.22656       -0.08143        6.04599
H           3.93730        0.39230        6.33567
H           3.54650       -0.83812        5.08024
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6.5.8 INT1 (5a)

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136
INT1 (=5a), C1, PBE-D3/def2-SVP
C           3.80656       -2.07394       -4.04085
C           2.69250       -2.41409       -3.08418
C           2.92742       -3.20694       -1.94849
C           1.38791       -1.92895       -3.28625
C           5.76976        3.51401        1.33067
C           1.92855       -3.46201       -0.99010
C           3.97031        3.08033       -0.39310
C           0.35420       -2.16834       -2.36241
C           4.34125        3.61047        0.85542
C           2.24216       -4.37124        0.17148
C           2.28648        2.51416       -2.19073
C           0.64529       -2.88063       -1.16811
C          -1.05446       -1.74931       -2.69312
C           2.65128        3.15072       -0.87396
C          -0.97474       -4.38030        0.00148
C           3.59882       -0.31453       -0.23091
C           3.34275        4.22416        1.63184
C          -0.43233       -3.08866       -0.15287
C          -2.00711       -4.63553        0.91231
C           1.66952        3.80324       -0.08554
C           5.28475       -1.49633        1.23708
C           3.94715       -1.16526        0.95520
C           2.01511        4.34011        1.18022
C          -0.95546       -2.03622        0.64820
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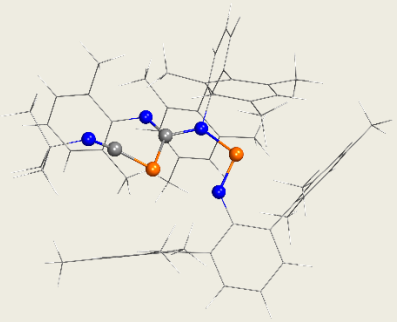

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C           5.63112       -2.29595        2.33589
C           0.31208        4.05005       -0.65781
C           0.07372        5.35474       -1.13453
C           2.92292       -1.66911        1.81707
C          -2.54506       -3.58277        1.65995
C          -1.63478        1.66118       -3.77899
C           0.87127       -0.51063        1.25247
C           0.96220        4.96559        2.06030
C          -2.04446       -2.27108        1.53249
C           4.61859       -2.77885        3.17825
C          -1.12456        5.70235       -1.76669
C          -0.70282        3.04732       -0.79400
C           3.26593       -2.48493        2.93566
C          -4.61675       -1.33450        0.56362
C          -2.10526        4.71813       -1.94497
C          -1.91261        3.40826       -1.47616
C           2.18271       -3.00364        3.83908
C          -2.85943        1.57419       -2.90380
C          -2.72271       -1.15270        2.26054
C          -3.97402       -0.68986        1.76488
C          -2.97996        2.40794       -1.76108
C          -3.89825        0.67467       -3.19846
C          -0.93393       -1.15292        4.06910
C          -2.15938       -0.56636        3.42089
C          -4.59757        0.39588        2.40206
C          -4.13761        2.34643       -0.94515
C          -5.06014        0.59745       -2.40777
C          -4.25016        3.21872        0.27947
C          -2.80819        0.53546        4.00978
C          -5.16243        1.44960       -1.29315
C          -4.01897        1.04315        3.50987
C          -6.14724       -0.39679       -2.72705
C          -4.67437        2.25470        4.12333
H           4.57994       -2.86688       -4.06943
H           3.43102       -1.91598       -5.07143
H           4.31478       -1.13424       -3.73153
H           6.11176        2.45830        1.36495
H           3.93250       -3.62812       -1.78371
H           1.15789       -1.36134       -4.20308
H           6.45903        4.05255        0.64669
H           4.73435        2.58755       -1.01611
H           5.89597        3.94360        2.34346
H           3.18803        2.21041       -2.75685
H          -1.13285       -1.39852       -3.73937
H           2.02392       -5.42975       -0.08814
H           3.31260       -4.30948        0.44592
H          -0.56717       -5.19441       -0.61616
H           4.46254       -0.21324       -0.91642
H           1.68169        3.19302       -2.82537
H          -1.76952       -2.58401       -2.54599
H           2.74887       -0.73611       -0.80178
H           1.67089        1.60514       -2.01839
H           1.64219       -4.11311        1.06138
H          -1.42482       -0.92226       -2.04572
H           3.60451        4.63180        2.62255
H           6.07039       -1.11698        0.56396
H          -2.40398       -5.65561        1.02681
H           3.29686        0.70331        0.09019
H           0.87344        6.10189       -1.01540
H           6.68451       -2.54584        2.53196
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H          -1.48069        2.69361       -4.15378
H          -0.71674        1.39751       -3.21280
H          -1.70950        0.98029       -4.64804
H          -4.74994       -2.42564        0.70027
H           1.38839        5.28803        3.02997
H          -1.28520        6.72611       -2.13650
H          -3.98558       -1.20017       -0.34007
H          -3.37332       -3.76261        2.36209
H           0.48302        5.84409        1.58297
H           4.87572       -3.41438        4.04089
H           1.33221       -3.40821        3.25200
H           0.15030        4.23581        2.26527
H          -5.60503       -0.88620        0.35355
H           2.56232       -3.79488        4.51390
H          -3.04534        4.95398       -2.46759
H          -3.80404        0.02476       -4.08389
H          -0.23366       -1.58131        3.33227
H          -1.22348       -1.98520        4.74751
H           1.76525       -2.18968        4.46942
H          -5.56310        0.75418        2.01014
H          -0.38729       -0.40303        4.67199
H          -3.45006        2.97442        1.01005
H          -4.13285        4.29234        0.03004
H          -5.93226       -1.38100       -2.25650
H          -6.23656       -0.57125       -3.81760
H          -2.35095        1.00385        4.89648
H          -5.22339        3.07982        0.78707
H          -6.07031        1.41401       -0.66951
H          -7.13255       -0.06296       -2.34631
H          -5.77648        2.14314        4.17140
H          -4.46940        3.16448        3.51803
H          -4.30084        2.44948        5.14748
N           1.59140       -1.55768        1.44817
N          -0.38387       -0.70152        0.61128
N          -0.45410        1.77124       -0.29463
P           1.16745        1.23405        1.89331
P          -1.43084        0.50317       -0.12732
C           1.97026        0.75860        3.32039
N           2.41614        0.72835        4.45171
C           3.73311        0.90849        5.08117
C           3.96699       -0.28241        6.02351
C           3.64078        2.22101        5.88264
C           4.82934        0.99937        4.01156
H           2.81907        2.17479        6.62397
H           3.45391        3.07788        5.20472
H           4.59355        2.39957        6.41955
H           3.14372       -0.36752        6.75972
H           4.92016       -0.14537        6.57138
H           4.03045       -1.22478        5.44666
H           4.89875        0.05878        3.43320
H           5.81193        1.19250        4.48681
H           4.61077        1.82441        3.30592
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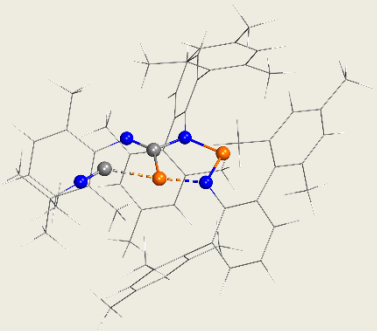
6.5.10 TS2



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136
TS2, C1, PBE-D3/def2-SVP
C           5.20231       -1.22804       -2.49546
C           3.87106       -1.73896       -2.00747
C           3.78634       -2.60682       -0.90590
C           2.67120       -1.33095       -2.61569
C           6.07070        2.61335       -0.75818
C           2.55294       -3.02101       -0.37034
C           3.66228        2.47747       -1.54172
C           1.41419       -1.72587       -2.12208
C           4.60400        2.92294       -0.60084
C           2.53278       -3.99665        0.77893
C           1.32468        2.21666       -2.44315
C           1.35419       -2.52792       -0.95118
C           0.16407       -1.36686       -2.88267
C           2.28304        2.71348       -1.39147
C          -0.33757       -4.31698       -0.65196
C           3.37254        0.14246        0.79469
C           4.12691        3.61684        0.52616
C           0.03069       -2.97721       -0.41728
C          -1.56699       -4.82606       -0.21903
C           1.82472        3.42617       -0.25264
C           4.78428       -0.90556        2.58157
C           3.51259       -0.72559        2.00578
C           2.76006        3.88006        0.71799
C          -0.87998       -2.13764        0.28363
C           4.98005       -1.68999        3.72634
C           0.40308        3.89886       -0.20986
C           0.22486        5.27012       -0.49276
C           2.37928       -1.36831        2.60616
C          -2.45858       -3.98643        0.45362
C          -3.05861        2.59992       -2.79643
C           0.44589       -0.39371        1.50454
C           2.29791        4.58990        1.96515
C          -2.13838       -2.63664        0.71362
C           3.86915       -2.31892        4.31052
C          -1.04386        5.83717       -0.63857
C          -0.75312        3.07453       -0.05054
C           2.58186       -2.18005        3.76909
C          -4.52427       -1.69012       -0.71816
C          -2.16684        5.00964       -0.54472
C          -2.04341        3.63341       -0.26871
C           1.40822       -2.86508        4.40882
C          -3.87282        2.47507       -1.53198
C          -3.16774       -1.82660        1.43945
C          -4.35579       -1.44840        0.76216
C          -3.32585        2.86321       -0.27923
C          -5.19077        1.99090       -1.57565
C          -1.84411       -2.09512        3.59299
C          -3.03884       -1.58997        2.83363
C          -5.39639       -0.85236        1.49695
C          -4.08319        2.72140        0.90912
C          -5.98877        1.91274       -0.41957
C          -3.47338        3.06707        2.24312
C          -4.08816       -0.95026        3.51546
C          -5.40888        2.26506        0.81151
C          -5.28261       -0.58502        2.87085
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C          -7.42407        1.45742       -0.50906
C          -6.39574        0.08756        3.63441
H           6.01804       -1.95233       -2.30152
H           5.18563       -1.00389       -3.58076
H           5.47253       -0.28468       -1.97152
H           6.34126        2.43721       -1.81805
H           4.71204       -2.95937       -0.42316
H           2.71005       -0.69716       -3.51678
H           6.70914        3.43104       -0.36783
H           4.00843        1.92779       -2.43207
H           6.34277        1.69401       -0.19365
H           1.85906        1.93104       -3.36930
H           0.40552       -0.87779       -3.84576
H           2.44952       -5.04178        0.41011
H           3.46097       -3.92227        1.37661
H           0.36847       -4.96104       -1.19716
H           4.34242        0.25368        0.27637
H           0.55790        2.97563       -2.69840
H          -0.45384       -2.26466       -3.08889
H           2.63832       -0.25579        0.07021
H           0.78442        1.31661       -2.08464
H           1.67417       -3.80619        1.44774
H          -0.49046       -0.66869       -2.31318
H           4.84467        3.96388        1.28788
H           5.64610       -0.41674        2.09725
H          -1.83095       -5.87705       -0.41111
H           3.01191        1.15919        1.06338
H           1.12560        5.88724       -0.63114
H           5.98672       -1.82078        4.15142
H          -2.81660        3.65876       -3.02361
H          -2.08364        2.07482       -2.70600
H          -3.59636        2.17356       -3.66480
H          -4.63962       -2.76875       -0.95288
H           3.15570        4.85058        2.61512
H          -1.15536        6.91004       -0.85549
H          -3.63991       -1.33868       -1.28784
H          -3.43031       -4.36768        0.80225
H           1.73904        5.52083        1.74408
H           3.99935       -2.94740        5.20664
H           0.82959       -3.44849        3.66323
H           1.60393        3.93550        2.53603
H          -5.41070       -1.15412       -1.10754
H           1.73246       -3.54369        5.22148
H          -3.17774        5.41814       -0.69531
H          -5.61493        1.69211       -2.54846
H          -0.88597       -1.85855        3.09490
H          -1.87732       -3.20296        3.67680
H           0.69771       -2.12715        4.83634
H          -6.32565       -0.58650        0.97274
H          -1.81736       -1.68140        4.61943
H          -2.56115        2.46154        2.43005
H          -3.15648        4.13008        2.28258
H          -7.50528        0.45266       -0.97504
H          -8.02625        2.14667       -1.13759
H          -3.97581       -0.76379        4.59628
H          -4.18291        2.88195        3.07217
H          -6.00934        2.18630        1.73042
H          -7.90163        1.40818        0.48868
H          -7.33488        0.11839        3.04798
H          -6.12902        1.13551        3.89330
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H          -6.60587        -0.43088         4.59218
N           1.13023        -1.37749         2.00963
N          -0.56407        -0.75018         0.55078
N          -0.59501         1.71585         0.34992
P           0.46166         1.40495         1.87470
P          -1.43166         0.43442        -0.33487
C           1.54929         0.94380         3.76853
N           2.28388         1.44448         4.55159
C           3.29086         1.97377         5.42892
C           2.71891         3.22844         6.11476
C           4.52009         2.32477         4.56691
C           3.64399         0.88437         6.45989
H           4.26049         3.08855         3.80815
H           4.89169         1.42098         4.04596
H           5.32352         2.72583         5.21565
H           2.44728         3.99583         5.36344
H           3.47622         3.65718         6.79985
H           1.81461         2.97560         6.70242
H           2.75573         0.61326         7.06349
H           4.43243         1.26109         7.14077
H           4.01218        -0.02454         5.94490
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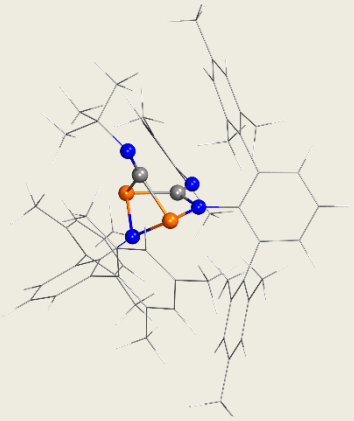
6.5.11 A1 (4a)



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136
Adduct A1 (=4a), C1, PBE-D3/def2-SVP
C           5.52345         1.68524         3.81157
C           4.41228        -0.47047         3.05936
C           3.44728        -2.66852         2.25972
C           4.68695         1.18050         0.18398
C           5.60976        -3.69622        -0.80680
C           4.30139         0.84980         3.52788
C           5.12691        -1.24244        -0.38902
C           3.28395        -1.25636         2.76266
C           4.48473        -0.03166        -0.68654
C           4.96706        -2.38829        -1.19254
C           3.01141         1.38568         3.68990
C           0.68979        -2.42386         4.11535
C           1.99288        -0.70131         2.96239
C          -0.37022        -3.31772         4.27968
C           1.85459         0.63111         3.42791
C           4.18864        -2.27435        -2.35431
C           3.65639         0.04381        -1.84190
C           0.80444        -1.61073         2.96512
C           3.69541         2.28281        -2.93746
C           1.50059         3.40702         1.17566
C           3.54929        -1.06977        -2.70975
C           3.00077         1.35281        -2.13911
C           3.20716         3.57637        -3.15304
C          -1.32192        -3.43307         3.26171
C           0.48696         1.19969         3.69143
C          -0.18702        -1.70479         1.95548
C          -0.40935        -4.10379        -0.36718
C           1.75725         1.72638        -1.55238
C           2.02258         3.96400        -2.51509
C          -1.24241        -2.65371         2.09256
C           0.23280         3.78241         0.45697
C           1.29423         3.07345        -1.70473
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C          2.75851       -1.00931       -3.98806
C         -0.84945        4.33175        1.16761
C          0.11627        3.60320       -0.94750
C         -1.84115       -3.68727       -0.12204
C         -2.24283       -2.95399        1.02544
C         -1.20167        0.00351        0.47383
C         -0.20539       -0.96030       -1.84264
C         -2.04207        4.71722        0.53173
C         -2.82516       -4.09546       -1.04142
C         -1.07154        4.01040       -1.61541
C         -3.17253        5.34416        1.30593
C         -3.61885       -2.66614        1.24243
C         -4.09422       -1.97018        2.49433
C         -2.12997        4.54338       -0.86186
C         -1.22195        3.82625       -3.10342
C         -4.18414       -3.78278       -0.87543
C         -4.55799       -3.07023        0.27756
C         -1.12402       -1.49567       -4.07407
C         -0.41459       -2.19060       -5.25303
C         -1.34920       -0.01491       -4.42315
C         -5.19965       -4.16455       -1.92236
C         -2.46492       -2.20898       -3.82922
H          6.43381        1.06151        3.90566
H          5.41394       -0.91077        2.92663
H          4.51510       -2.95161        2.19819
H          5.52855        1.03073        0.88385
H          6.58376       -3.54026       -0.30134
H          5.77833       -1.29204        0.49720
H          5.40915        2.27378        4.74428
H          5.70450        2.41453        2.99219
H          2.92887       -3.40199        2.90929
H          5.77455       -4.34933       -1.68612
H          4.88346        2.08656       -0.42238
H          3.78517        1.39281        0.79442
H          3.00892       -2.77133        1.24438
H          4.96390       -4.25749       -0.09711
H          1.46100       -2.32557        4.89451
H         -0.44523       -3.93393        5.18820
H          2.89793        2.41777        4.05972
H          4.65053        1.96491       -3.38332
H          1.50101        3.78544        2.21485
H          2.39544        3.80385        0.65539
H          4.08405       -3.14556       -3.02180
H          3.76232        4.28691       -3.78298
H          1.62385        2.30554        1.21616
H         -0.06177        0.58988        4.43872
H          0.26824       -3.80983        0.45565
H         -0.33960       -5.20618       -0.47541
H         -2.14173       -4.16195        3.34594
H          0.54343        2.23863        4.06763
H         -0.02759       -3.66324       -1.31205
H          3.32994       -1.44700       -4.83149
H         -0.74718        4.47787        2.25552
H         -0.13924        1.19357        2.77849
H          1.65322        4.99658       -2.61075
H          1.82539       -1.59674       -3.87432
H          2.47468        0.02640       -4.25409
H         -3.14900        5.04663        2.37229
H         -4.33397       -2.70421        3.29341
H         -2.51254       -4.69140       -1.91404
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H          -3.32377       -1.28193        2.88584
H          -4.15622        5.04834        0.89302
H          -0.53554        4.48168       -3.67723
H          -0.97668        2.78478       -3.39827
H          -3.11140        6.45365        1.26778
H           0.51224       -1.65870       -5.54048
H          -0.38164        0.52223       -4.49733
H          -5.01197       -1.38387        2.29414
H          -3.06057        4.82616       -1.38009
H          -1.97303        0.50581       -3.67261
H          -0.14791       -3.23036       -4.98020
H          -2.25653        4.04473       -3.43105
H          -2.30746       -3.29377       -3.68345
H          -5.61963       -2.81993        0.43690
H          -4.95864       -5.13908       -2.39234
H          -2.97489       -1.81840       -2.93172
H          -6.22234       -4.22508       -1.50123
H          -1.08203       -2.21585       -6.13741
H          -1.86390        0.06618       -5.40134
H          -5.22470       -3.41066       -2.73998
H          -3.12663       -2.06962       -4.70743
N           0.94214        0.82396       -0.83248
N          -0.14737       -0.85962        0.79586
N          -0.26486       -1.67598       -2.87805
P           1.13612       -0.92323       -0.45571
P          -0.82664        0.77936       -1.21357
C          -4.16254        0.82500       -0.09613
C          -3.77241        1.81280        2.13147
C          -5.37544        1.53902       -0.16028
C          -4.98828        2.50110        2.02008
C          -5.79221        2.37886        0.87696
H          -6.01193        1.41052       -1.05058
H          -5.31131        3.14257        2.85521
H          -6.74843        2.91894        0.80666
C          -3.33171        0.97781        1.05547
N          -2.17400        0.23989        1.27815
C          -2.92617        1.94772        3.36528
H          -2.58954        0.95491        3.72681
H          -2.00319        2.52602        3.15372
H          -3.47679        2.46352        4.17542
C          -3.81288       -0.09802       -1.23126
H          -3.29912        0.44728       -2.05360
H          -3.15984       -0.93151       -0.91050
H          -4.72546       -0.54690       -1.67103
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6.5.12 A1’

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 136
Adduct A1’, C1, PBE-D3/def2-SVP
C          -4.12014       -3.62903        3.67089
C          -3.37996       -1.20470        3.74866
C          -2.81007        1.26303        3.72133
C          -5.02806        0.20413        1.25874
C          -5.82800        4.26509       -1.64966
C          -3.05086       -2.56695        3.64394
C          -5.35129        2.21356       -0.22875
C          -2.41177       -0.18872        3.63246
C          -4.78836        0.93919       -0.02889
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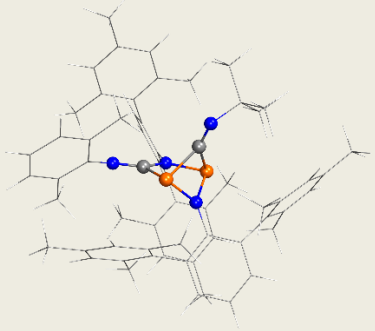

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C          -5.24294        2.88997       -1.45441
C          -1.69554       -2.90731        3.48451
C           0.38805        0.85554        4.80394
C          -1.06065       -0.55859        3.42326
C           1.50901        1.65111        5.04647
C          -0.69039       -1.92897        3.39625
C          -4.54135        2.25194       -2.49344
C          -4.03264        0.33787       -1.06746
C           0.03826        0.45082        3.49765
C          -4.53550       -2.08600       -1.04436
C          -0.17815       -4.14952        0.62535
C          -3.92056        1.00214       -2.32267
C          -3.55206       -1.07989       -0.96886
C          -4.19757       -3.42900       -1.24673
C           2.29178        2.05418        3.96103
C           0.76579       -2.31316        3.34761
C           0.81085        0.89676        2.38988
C           1.07830        4.12731        1.37686
C          -2.17217       -1.45337       -1.00938
C          -2.85221       -3.75967       -1.44913
C           1.96148        1.70782        2.63530
C           0.35276       -3.92330       -0.76276
C          -1.82970       -2.79586       -1.35726
C          -3.17826        0.37057       -3.47067
C           1.61205       -4.41782       -1.14654
C          -0.44141       -3.23502       -1.71287
C           2.39842        3.52168        0.97221
C           2.83497        2.32123        1.58836
C           1.29997       -0.12950        0.17185
C          -0.16028        1.51587       -1.31733
C           2.10514       -4.26128       -2.45281
C           3.25383        4.17985        0.07110
C           0.02180       -3.09863       -3.05117
C           3.46325       -4.77656       -2.85084
C           4.15793        1.85572        1.37635
C           4.72902        0.70521        2.16488
C           1.28718       -3.60418       -3.38953
C          -0.80808       -2.39915       -4.09447
C           4.53668        3.68512       -0.22708
C           4.97260        2.53440        0.45096
C          -0.72090        3.73832       -2.23083
C          -1.73580        3.98155       -1.10532
C          -1.42480        3.75250       -3.60319
C           5.40805        4.35799       -1.25685
C           0.37927        4.81426       -2.23297
H          -5.01326       -3.29946        4.23785
H          -4.42938       -0.91956        3.92494
H          -3.86475        1.37335        4.03759
H          -5.33009        0.89472        2.06879
H          -6.61727        4.48628       -0.90488
H          -5.91290        2.67941        0.59750
H          -3.75181       -4.57353        4.11852
H          -4.45624       -3.86697        2.63780
H          -2.17199        1.82447        4.43198
H          -6.26247        4.38454       -2.66258
H          -5.83547       -0.55076        1.14736
H          -4.12853       -0.35083        1.58110
H          -2.69417        1.75807        2.73294
H          -5.04376        5.04601       -1.54140
H          -0.22762        0.48916        5.63968
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H          1.77780        1.94540        6.07204
H         -1.40694       -3.97039        3.45197
H         -5.59317       -1.78344       -1.00435
H          0.59357       -4.57764        1.29234
H         -1.04514       -4.84300        0.61646
H         -4.47561        2.74578       -3.47624
H         -4.97989       -4.19968       -1.31078
H         -0.55108       -3.20813        1.07090
H          1.31090       -1.88519        4.21466
H          1.06391        4.34483        2.46479
H          0.87279        5.07022        0.83653
H          3.18221        2.68093        4.12133
H          0.89596       -3.41106        3.36757
H          0.23318        3.43290        1.19653
H         -3.38048        0.89980       -4.42136
H          2.22366       -4.95181       -0.40231
H          1.27309       -1.91470        2.44674
H         -2.56475       -4.79216       -1.70136
H         -2.08194        0.39868       -3.29881
H         -3.44997       -0.69616       -3.59410
H          3.91348       -5.40026       -2.05483
H          5.24590        1.07680        3.07609
H          2.91972        5.11936       -0.39713
H          3.93666        0.00530        2.48282
H          4.15833       -3.93239       -3.03939
H         -1.87424       -2.69609       -4.04603
H         -0.77498       -1.29758       -3.94514
H          3.41082       -5.38046       -3.78017
H         -2.52078        3.20105       -1.09455
H         -2.19592        2.96339       -3.65439
H          5.47033        0.14214        1.56506
H          1.64512       -3.48346       -4.42504
H         -0.68954        3.57587       -4.41205
H         -1.24707        4.00117       -0.11317
H         -0.42749       -2.60317       -5.11353
H          0.93541        4.81097       -1.27962
H          5.98650        2.14701        0.25954
H          5.18440        5.44000       -1.34129
H          1.10326        4.62147       -3.04854
H          6.48486        4.24194       -1.02270
H         -2.23834        4.95922       -1.25023
H         -1.91457        4.73273       -3.77099
H          5.24482        3.91249       -2.26273
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N         -1.17885       -0.48941       -0.77272
N          0.43357        0.52236        1.05185
N         -0.03784        2.43930       -2.15765
P         -1.15727        0.94256        0.26330
P          0.44414       -0.29332       -1.52205
C          3.86642       -0.31993       -1.50763
C          4.17310       -2.19478        0.07838
C          4.97206       -0.80879       -2.23320
C          5.26289       -2.64006       -0.68168
C          5.66792       -1.95610       -1.83898
H          5.29887       -0.25067       -3.12526
H          5.80867       -3.53850       -0.35207
H          6.53356       -2.30883       -2.41982
C          3.44875       -1.03501       -0.34155
N          2.45667       -0.56975        0.51616
C          3.76241       -2.91030        1.33467
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H          3.76004       -2.21931        2.20299
H          2.73025       -3.30490        1.25594
H          4.44220       -3.75567        1.55554
C          3.21014        0.95812       -1.96424
H          2.36800        0.78082       -2.67243
H          2.81245        1.55604       -1.12280
H          3.93478        1.59479       -2.50835
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6.5.13 A2

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 136
Adduct A2, C1, PBE-D3/def2-SVP
C         -4.74407        1.57674        3.97998
C         -2.28087        2.10671        3.63827
C          0.15412        2.77096        3.40054
C         -0.75615        4.51890        0.55285
C          4.27988        4.97412        0.76855
C         -3.30180        1.16027        3.83455
C          1.75799        4.77333        0.56855
C         -0.93177        1.72849        3.49835
C          0.59810        4.31549       -0.07156
C          3.03834        4.57366        0.01436
C         -2.94009       -0.19664        3.91504
C          1.52901       -0.10051        4.67883
C         -0.60578        0.34993        3.52113
C          2.87734       -0.46511        4.73423
C         -1.60697       -0.62141        3.77666
C          3.12558        3.97463       -1.25286
C          0.71911        3.62329       -1.31297
C          0.82407       -0.07581        3.45783
C         -1.06229        3.96473       -2.99685
C         -3.78538        2.25011        0.38723
C          1.98723        3.52291       -1.94639
C         -0.52532        3.14157       -1.98689
C         -2.27192        3.66011       -3.62597
C          3.52823       -0.83651        3.55459
C         -1.23513       -2.07377        3.95173
C          1.49207       -0.44875        2.25995
C          4.44962        1.02749        0.66587
C         -1.21706        1.95429       -1.59401
C         -2.99369        2.55026       -3.17612
C          2.85508       -0.84664        2.31562
C         -4.20342        1.05895       -0.43156
C         -2.51159        1.70849       -2.15259
C          2.11855        3.02039       -3.36023
C         -5.29070        0.27063       -0.02300
C         -3.50558        0.71563       -1.62565
C          4.39024       -0.44374        0.34304
C          3.63155       -1.33597        1.13698
C          0.11241       -1.32497        0.33045
C         -5.70787       -0.86050       -0.74872
C          5.17253       -0.96982       -0.70332
C         -3.92166       -0.40987       -2.38147
C         -6.83515       -1.72848       -0.25139
C          3.72913       -2.73834        0.93730
C          3.06274       -3.68793        1.90042
C         -5.00630       -1.18150       -1.92044
C         -3.22419       -0.83370       -3.64918
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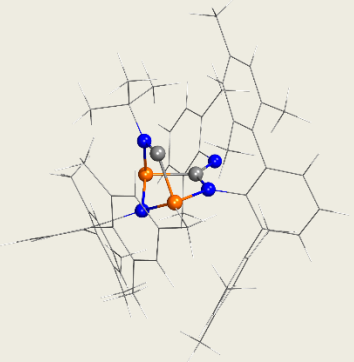

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C          5.22593       -2.34749       -0.97482
C          4.50746       -3.21704       -0.13144
C          6.00725       -2.87992       -2.14937
H         -4.86139        2.67642        3.92641
H         -2.53803        3.17831        3.61008
H         -0.26487        3.79322        3.45273
H         -0.69797        5.19272        1.42810
H          4.08675        5.81671        1.46135
H          1.66352        5.28761        1.53853
H         -5.16883        1.23541        4.94697
H         -5.37188        1.12881        3.18114
H          0.88666        2.65598        4.22579
H          5.10121        5.26462        0.08399
H         -1.47900        4.94127       -0.17375
H         -1.18749        3.55569        0.89597
H          0.73297        2.67902        2.45774
H          4.65255        4.12451        1.38140
H          0.99006        0.18651        5.59486
H          3.41690       -0.46423        5.69338
H         -3.71963       -0.95402        4.09922
H         -0.49998        4.86887       -3.27605
H         -4.53329        2.48322        1.16766
H         -3.63565        3.15073       -0.24082
H          4.11328        3.85635       -1.72694
H         -2.66972        4.30338       -4.42460
H         -2.82239        2.04720        0.90067
H         -0.60036       -2.20980        4.85248
H          3.46248        1.44177        0.95190
H          5.13051        1.20946        1.52613
H          4.58643       -1.13946        3.57207
H         -2.13473       -2.70819        4.06754
H          4.81193        1.61295       -0.19939
H          1.94475        3.84934       -4.08066
H         -5.83151        0.55155        0.89564
H         -0.64553       -2.45314        3.09152
H         -3.98868        2.32981       -3.59185
H          3.13183        2.61793       -3.54633
H          1.37687        2.23479       -3.59173
H         -7.60381       -1.13716        0.28506
H          3.44834       -3.53774        2.92965
H          5.76006       -0.27333       -1.32327
H          1.96848       -3.51047        1.93826
H         -6.45826       -2.49313        0.46377
H         -2.50874       -0.07268       -4.01013
H         -2.66019       -1.77481       -3.47403
H         -7.33016       -2.27397       -1.07881
H          3.24493       -4.74132        1.61698
H         -5.31222       -2.06302       -2.50744
H         -3.95412       -1.03661       -4.45914
H          4.57194       -4.30529       -0.29521
H          6.84136       -2.20570       -2.42714
H          6.42589       -3.88501       -1.94309
H          5.35470       -2.97673       -3.04487
N         -0.65502        0.99772       -0.68180
N          0.81230       -0.32537        0.98628
P         -0.64786       -0.65461       -1.26585
C         -0.37810       -4.60821       -0.55461
C         -2.29676       -3.18910        0.06981
C         -1.26478       -5.46093       -1.23664
C         -3.14525       -4.08260       -0.61052
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C          -2.64107       -5.20306       -1.28045
H          -0.85566       -6.35415       -1.73554
H          -4.22836       -3.88253       -0.60238
H          -3.31857       -5.88479       -1.81659
C          -0.88891       -3.42848        0.06272
N          -0.00794       -2.54973        0.73386
C          -2.88688       -2.01705        0.80032
H          -2.30300       -1.74796        1.69419
H          -2.92243       -1.10746        0.16659
H          -3.92801       -2.22657        1.10992
C           1.07841       -4.97412       -0.45871
H           1.38484       -5.61946       -1.30538
H           1.73245       -4.08647       -0.43649
H           1.27464       -5.53878        0.47701
P           0.93993        1.24835        0.13971
N           1.24727       -0.28429       -1.97935
C           1.94868        0.56170       -1.32990
C           1.65478       -1.08284       -3.17890
C           3.06382       -0.67571       -3.61838
H           3.37459       -1.30636       -4.47563
H           3.09367        0.38446       -3.92933
H           3.77924       -0.80762       -2.78720
C           1.62935       -2.56114       -2.77632
H           2.37525       -2.75355       -1.98136
H           0.62939       -2.86850       -2.40598
H           1.87048       -3.19770       -3.65073
C           0.63991       -0.80294       -4.29854
H           0.92912       -1.36176       -5.21045
H          -0.38034       -1.12055       -4.01077
H           0.61035        0.27686       -4.54689
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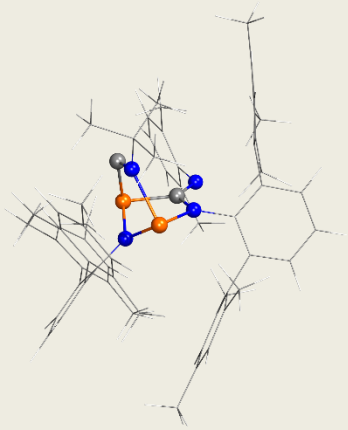
6.5.15 A3



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 136
Adduct A3, C1, PBE-D3/def2-SVP
C          -4.91431        1.14302        4.21876
C          -2.56318        1.99370        3.79454
C          -0.28812        2.99734        3.34119
C          -2.76815        3.84801        1.03615
C          -0.79309        6.64214       -2.69169
C          -3.44317        0.91473        3.98442
C          -1.74930        5.17183       -0.85529
C          -1.20074        1.80657        3.49380
C          -2.29101        3.96271       -0.38300
C          -1.39579        5.35005       -2.20376
C          -2.90976       -0.38459        3.92823
C           1.41521        0.18779        4.53590
C          -0.70310        0.48272        3.37383
C           2.79862        0.04919        4.64842
C          -1.55280       -0.61814        3.64539
C          -1.59068        4.26823       -3.08162
C          -2.42703        2.86472       -1.27127
C           0.77580        0.26839        3.27840
C          -4.60269        1.82001       -0.85505
C          -3.46861       -2.60292        1.41512
C          -2.08292        3.02586       -2.64316
C          -3.20430        1.63780       -0.88980
C          -5.48606        0.73877       -0.80270
C           3.56656        0.09345        3.48318
C          -0.98173       -2.00913        3.67515
C           1.55370        0.20346        2.08705
C           3.32540        2.99319        1.65004
C          -2.66171        0.32010       -0.77307
C          -4.95241       -0.55251       -0.86307
C           2.97720        0.21168        2.20731
C          -3.11039       -3.10397        0.04445
C          -3.56373       -0.78935       -0.86878
C          -2.28001        1.89888       -3.62217
C          -2.75754       -4.44997       -0.16594
C          -3.15058       -2.21865       -1.05814
C           4.15423        1.96941        0.91250
C           3.95613        0.57662        1.13429
C           0.93610       -1.16686        0.12276
C          -2.47223       -4.95007       -1.44736
C           5.19572        2.38724        0.06798
C          -2.92347       -2.71574       -2.37066
C          -2.05582       -6.38233       -1.66216
C           4.86678       -0.36140        0.58721
C           4.83755       -1.81024        1.00354
C          -2.58411       -4.06702       -2.53737
C          -2.96905       -1.80176       -3.56661
C           6.05025        1.46689       -0.56691
C           5.87352        0.10259       -0.28369
C           7.10273        1.93346       -1.53949
H          -5.10538        2.11129        4.72259
H          -2.94701        3.02157        3.89478
H          -0.78854        3.92989        3.66437
H          -2.31433        4.62341        1.68244
H          -1.07172        7.49666       -2.04438
H          -1.62536        6.00892       -0.14892
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H         -5.36367        0.33636        4.83128
H         -5.46275        1.16311        3.25164
H          0.64341        2.87614        3.92925
H         -1.10638        6.87388       -3.72919
H         -3.87145        3.96194        1.09944
H         -2.53709        2.85274        1.45746
H          0.01913        3.12976        2.28164
H          0.31717        6.58044       -2.69525
H          0.78394        0.23416        5.43644
H          3.27712       -0.04315        5.63493
H         -3.56743       -1.24585        4.12746
H         -4.99009        2.84761       -0.93238
H         -3.26090       -3.36088        2.19378
H         -4.54503       -2.33691        1.47639
H         -1.35799        4.39839       -4.15100
H         -6.57392        0.89972       -0.78068
H         -2.91587       -1.67742        1.66250
H         -0.18448       -2.09739        4.44131
H          3.53547        2.95604        2.74001
H          3.53927        4.01830        1.29227
H          4.66555        0.08677        3.54322
H         -1.75549       -2.76753        3.89455
H          2.23725        2.81023        1.55202
H         -2.08429        2.22627       -4.66084
H         -2.71287       -5.13007        0.70028
H         -0.50443       -2.26495        2.71131
H         -5.61793       -1.42769       -0.92021
H         -1.59304        1.05624       -3.40003
H         -3.30875        1.48999       -3.56553
H         -2.16634       -6.98400       -0.73906
H          5.39555       -1.94488        1.95553
H          5.34063        3.46663       -0.10289
H          3.80052       -2.15787        1.16991
H         -0.99040       -6.43363       -1.96963
H         -3.81715       -1.09089       -3.51974
H         -2.04089       -1.18963       -3.62441
H         -2.65355       -6.86395       -2.46320
H          5.31877       -2.45972        0.24682
H         -2.38684       -4.44141       -3.55517
H         -3.03628       -2.37664       -4.51007
H          6.55768       -0.63426       -0.73549
H          7.52123        2.91806       -1.24972
H          7.93792        1.21028       -1.62013
H          6.67223        2.05066       -2.55817
N         -1.27015        0.11235       -0.55130
N          0.90411        0.06218        0.79554
P         -0.32707       -1.23411       -1.29984
C          2.47225       -3.41153       -1.52199
C          1.20361       -4.53406        0.27665
C          2.56802       -4.65400       -2.17913
C          1.32951       -5.74927       -0.41571
C          1.99864       -5.81598       -1.64535
H          3.12213       -4.70136       -3.13011
H          0.89738       -6.65913        0.03025
H          2.09501       -6.77582       -2.17530
C          1.75216       -3.35009       -0.29227
N          1.69382       -2.15229        0.44791
C          0.49087       -4.46837        1.59633
H          1.06958       -3.87471        2.33286
H         -0.49540       -3.97204        1.48562
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H           0.31111        -5.48008         2.00852
C           3.14129        -2.19995        -2.11588
H           2.42244        -1.56926        -2.68679
H           3.56778        -1.53806        -1.33914
H           3.95251        -2.49975        -2.80786
P          -0.15237         1.29704         0.04365
C           0.74679        -0.09210        -2.32191
N           0.84222         1.07580        -1.81461
C           1.74887         2.12614        -2.40752
C           1.66951         3.39029        -1.55218
H           2.30831         4.18037        -1.99472
H           0.63304         3.77439        -1.49744
H           2.03251         3.20303        -0.52589
C           1.29934         2.41382        -3.84737
H           0.29818         2.87635        -3.87087
H           2.01614         3.11411        -4.32148
H           1.28026         1.47217        -4.42878
C           3.16784         1.53938        -2.43430
H           3.89961         2.32202        -2.71675
H           3.45001         1.13988        -1.44594
H           3.22156         0.71505        -3.17022
```

6.5.16 MeNC

```
6
MeNC, C3v, PBE-D3/def2-SVP
C           0.00000        -1.37412         0.00000
N           0.00000        -0.19699        -0.00000
C          -0.00000         1.22001        -0.00000
H          -0.51630         1.59463         0.89425
H          -0.51630         1.59463        -0.89425
H           1.03259         1.59463         0.00000
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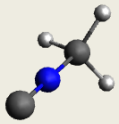

6.5.17 Biradical 2c

```
18
Biradical 2c, Cs, PBE-D3/def2-SVP
C           0.05338        -0.71808        -0.79268
N          -0.97602        -0.88465        -1.54950
N           0.88921        -1.83527        -0.51946
N           1.98965        -0.04221         0.73149
P           0.64754         0.79567         0.03110
P           2.24056        -1.66908         0.46147
C           2.93863         0.68287         1.58395
C          -1.77314         0.30225        -1.77683
C           0.53073        -3.11842        -1.11675
H          -2.62619         0.06604        -2.42705
H          -1.18808         1.10991        -2.26449
H          -2.17371         0.72279        -0.83066
H           3.71649        -0.00492         1.94498
H           2.41532         1.11432         2.44810
H           3.41487         1.49269         1.01456
H          -0.47538        -3.41101        -0.78712
H           1.26489        -3.87799        -0.81763
H           0.50658        -3.02243        -2.21069
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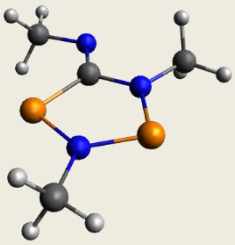

6.5.18 Housane 3c

```
18
Housane 3c, C1, PBE-D3/def2-SVP
C           0.45088       -0.06340       -0.99901
N          -0.60849       -0.45447       -1.57975
N           1.74707       -0.35507       -1.41275
N           1.82752       -0.45226        1.17152
P           0.80391        0.94818        0.59315
P           2.74763        0.30704       -0.14850
C           2.36571       -0.27668        2.53040
C          -1.89567       -0.05686       -1.05727
C           2.06230       -1.43679       -2.33409
H          -2.49109        0.41211       -1.85564
H          -1.82962        0.64609       -0.20278
H          -2.45191       -0.94645       -0.72238
H           3.17196       -1.00990        2.67952
H           1.56784       -0.48309        3.25794
H           2.76992        0.73010        2.74894
H           1.50690       -1.29624       -3.27067
H           1.79326       -2.41944       -1.91446
H           3.13903       -1.41666       -2.54735
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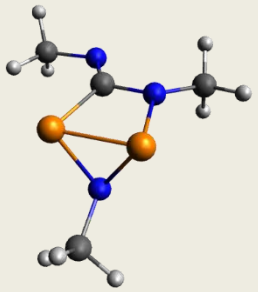
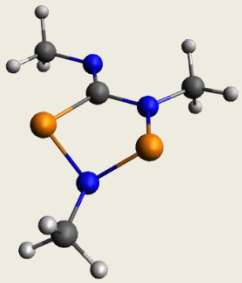


6.5.19 TS0_Me

```
18
TS0_Me, C1, UPBE-D3/def2-SVP
C           0.13302       -1.07323       -0.86585
N          -0.99786       -1.45209       -1.33578
N           1.25910       -1.88685       -0.95203
N           1.89181       -0.23667        0.84692
P           0.62016        0.56065       -0.09299
P           2.69671       -1.09899       -0.43580
C           2.71156        0.61743        1.70541
C          -2.12892       -0.55604       -1.26099
C           1.20562       -3.21125       -1.55140
H          -2.53836       -0.39951       -2.27125
H          -1.90089        0.43000       -0.81038
H          -2.92821       -1.02365       -0.66362
H           3.46286       -0.00373        2.21474
H           2.06588        1.07798        2.46671
H           3.23548        1.42776        1.16446
H           0.63600       -3.17631       -2.49008
H           0.71447       -3.92964       -0.87701
H           2.23009       -3.55374       -1.74801
```



6.5.20 TS1_Me

```
24
TS1_Me, C1, PBE-D3/def2-SVP
C          -0.02519       -0.83337       -1.12045
N          -1.15963       -1.38584       -1.26368
N           1.19021       -1.40817       -1.44574
N           1.93049       -0.36919        0.80284
P           0.50932        0.85845       -0.41668
P           2.39899       -0.32396       -0.80768
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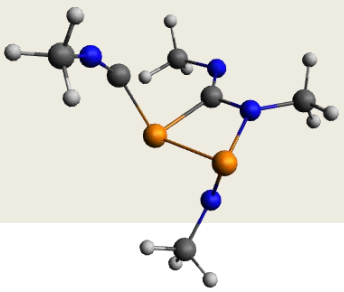

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C           2.66341        0.49731        1.72113
C          -2.36084       -0.66688       -0.90914
C           1.34692       -2.83012       -1.70551
C          -0.07461        1.80912       -2.00009
N           0.20193        2.64863       -2.79714
C           1.08553        3.57491       -3.41691
H          -3.00672       -0.55464       -1.79465
H          -2.16746        0.33908       -0.48740
H          -2.93051       -1.24612       -0.16535
H           1.19712        3.32659       -4.48104
H           2.07154        3.54063       -2.92595
H           0.67288        4.58996       -3.33949
H           3.70613        0.15599        1.84853
H           2.17491        0.47221        2.70593
H           2.70759        1.55957        1.40210
H           0.67159       -3.13557       -2.51591
H           1.11515       -3.43340       -0.81294
H           2.38611       -3.01859       -2.00840
```

6.5.22 INT1_Me (5c)

```
24
INT1_Me, C1, PBE-D3/def2-SVP
C           0.19312       -0.55617       -0.90490
N          -0.86369       -1.04169       -1.43961
N           1.33201       -1.39660       -0.89240
N           2.24110       -0.23661        1.21898
P           0.42856        1.18178       -0.17285
P           2.69169       -1.28042        0.12362
C           3.13868        0.31562        2.20783
C          -2.09627       -0.30220       -1.54185
C           1.26830       -2.60519       -1.72173
C          -0.06904        1.92749       -1.60411
N          -0.41184        2.58859       -2.56367
C           0.35147        3.16330       -3.65142
H          -2.16555        0.19677       -2.52384
H          -2.20582        0.48101       -0.77078
H          -2.93622       -1.00890       -1.47647
H           0.00355        2.72825       -4.59888
H           1.43217        2.98558       -3.53763
H           0.15575        4.24371       -3.69211
H           4.17495       -0.06981        2.16856
H           2.73333        0.12212        3.21398
H           3.17745        1.41161        2.09067
H           0.48191       -3.28366       -1.36437
H           2.24368       -3.11032       -1.66981
H           1.04023       -2.33749       -2.76164
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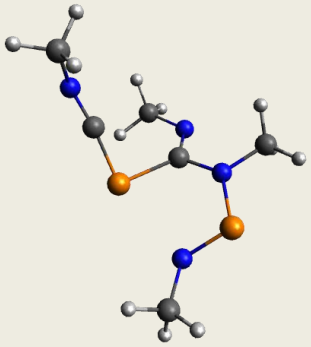
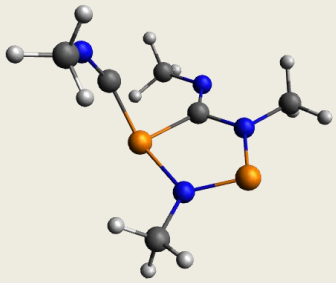


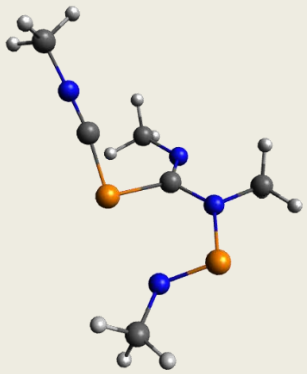
6.5.23 TS2_Me

```
24
TS2_Me, C1, PBE-D3/def2-SVP
C          -0.70977       -1.06584        0.12018
N          -1.75860       -1.64305       -0.33387
N           0.50292       -1.79915        0.04636
N           1.23873        0.07285        1.45974
P          -0.51998        0.61978        0.88914
P           1.91365       -1.24603        0.77149
C           2.02786        1.01357        2.24694
C          -3.06102       -1.02407       -0.23195
C           0.50264       -3.07360       -0.66832
C          -1.14057        1.48075       -0.57032
N          -0.95413        2.39671       -1.35899
C           0.22533        3.19169       -1.61842
H          -3.32844       -0.51391       -1.16983
H          -3.12228       -0.26757        0.57334
H          -3.80945       -1.81350       -0.06180
H           0.55857        3.03272       -2.65427
H           1.04070        2.92313       -0.92127
H          -0.01978        4.25757       -1.50785
H           3.10871        0.83437        2.14342
H           1.75480        0.93738        3.31016
H           1.81432        2.03968        1.91283
H          -0.17271       -3.78467       -0.17435
H           1.52647       -3.47251       -0.67981
H           0.14395       -2.92676       -1.69527
```



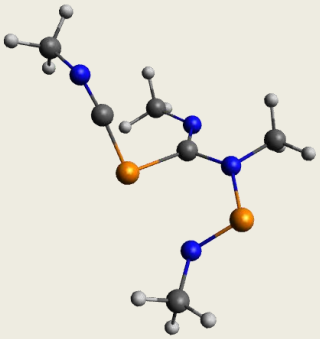
6.5.24 TS3

```
24
TS3, C1, PBE-D3/def2-SVP
C          -0.26633       -0.75190        0.13097
N          -1.34094       -1.13543       -0.45926
N           0.70985       -1.76445        0.33254
N           1.58589       -0.54142        2.41110
P           0.22458        0.96386        0.73487
P           1.95270       -1.77048        1.48855
C           2.45678       -0.02928        3.44300
C          -2.44890       -0.24918       -0.69532
C           0.51889       -3.02312       -0.39448
C          -0.31006        1.73525       -0.71189
N          -0.55119        2.43168       -1.64349
C          -0.86208        3.28110       -2.71735
H          -2.39849        0.19167       -1.70698
H          -2.49801        0.58651        0.02848
H          -3.38161       -0.83153       -0.65022
H          -1.19640        2.68040       -3.57668
H           0.02264        3.86096       -3.02651
H          -1.66981        3.98107       -2.44870
H           3.40763       -0.58063        3.57031
H           1.92175       -0.03252        4.40644
H           2.70043        1.02367        3.22239
H           0.44906       -2.82953       -1.47288
H          -0.40691       -3.52239       -0.07819
H           1.38051       -3.67430       -0.18668
```



6.5.25 INT2

```
24
INT2, C1, PBE-D3/def2-SVP
C           0.36590       -0.32033       -0.14088
N          -0.76371       -0.36210       -0.74168
N           1.38029       -1.15620       -0.66634
N           2.45167       -1.44159        1.66038
P           0.89102        0.75638        1.33563
P           2.75484       -1.75252        0.14284
C           3.42770       -1.61193        2.71258
C          -1.89410        0.44067       -0.35494
C           1.13984       -1.72920       -1.99558
C           0.33178        2.18621        0.62799
N           0.12211        3.30575        0.20802
C          -1.04748        4.15538        0.27069
H          -1.96146        1.33621       -0.99605
H          -1.85839        0.78039        0.69649
H          -2.81302       -0.14049       -0.52327
H          -1.35579        4.41467       -0.75183
H          -0.77703        5.09073        0.78020
H          -1.88507        3.67766        0.80176
H           4.40269       -2.02219        2.38818
H           3.01166       -2.27447        3.48850
H           3.61158       -0.63822        3.19706
H           0.28115       -2.41392       -1.97814
H           2.04241       -2.27770       -2.30190
H           0.92563       -0.92988       -2.71683
```



6.5.26 TS4

```
24
TS4, C1, PBE-D3/def2-SVP
C           0.05292       -0.62513       -0.15832
N          -1.05828       -0.67420       -0.78978
N           1.19448       -1.13892       -0.80781
N           2.12091       -0.91100        1.46842
P           0.39205        0.09942        1.54325
P           2.67989       -1.27462       -0.01613
C           3.01993       -0.77335        2.60870
C          -2.28180       -0.19901       -0.18460
C           1.08350       -1.53092       -2.21115
C           0.21226        1.73029        0.96068
N           0.75538        2.81777        0.74254
C           0.06088        4.03937        0.36230
H          -2.54843        0.79029       -0.58697
H          -2.21751       -0.09798        0.91517
H          -3.09677       -0.88909       -0.45293
H           0.44933        4.38022       -0.60839
H           0.29018        4.82275        1.09915
H          -1.03142        3.90718        0.29543
H           4.08001       -0.72592        2.31417
H           2.87991       -1.61887        3.29942
H           2.77556        0.15183        3.15145
H           0.39739       -2.38195       -2.31764
H           2.08106       -1.80901       -2.57861
H           0.68434       -0.69742       -2.80364
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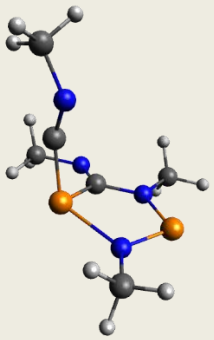

6.5.27 A3_Me

```
24
A3_Me, C1, PBE-D3/def2-SVP
C          -0.27831       -0.60626       -0.09373
N          -1.33793       -0.92599       -0.72956
N           0.94876       -0.47546       -0.74679
N           1.66641       -0.41483        1.61775
P          -0.08026       -0.11452        1.72083
P           2.20551        0.25137        0.16159
C           2.43392       -0.12611        2.83653
C          -2.59185       -1.05426       -0.02380
C           0.99476       -0.58139       -2.20054
C          -0.04258        1.68470        1.12844
N           1.06702        1.89288        0.51940
C           1.44448        3.14084       -0.13312
H          -3.29155       -0.27688       -0.36794
H          -2.49274       -0.96441        1.07637
H          -3.05025       -2.02734       -0.26004
H           1.56298        2.96914       -1.21423
H           2.40865        3.49241        0.26221
H           0.66715        3.89500        0.03921
H           2.33017        0.91871        3.17774
H           3.49825       -0.33080        2.65373
H           2.09044       -0.78859        3.64217
H           0.62359       -1.56750       -2.50974
H           2.03342       -0.46067       -2.53353
H           0.35721        0.18012       -2.67636
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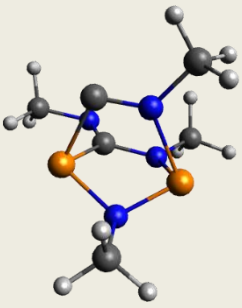

6.5.28 TS5

```
24
TS5, C1, PBE-D3/def2-SVP
C          -0.28350       -0.68451       -0.08847
N          -1.34366       -0.94220       -0.76952
N           0.94448       -0.49431       -0.75227
N           1.59317       -0.27565        1.61226
P          -0.10212       -0.45754        1.71939
P           2.31275       -0.02788        0.11795
C           2.34917        0.08769        2.81466
C          -2.56383       -1.14777       -0.01285
C           0.95688       -0.57486       -2.20808
C          -0.27322        2.06963        1.08603
N           0.75183        2.37314        0.54054
C           1.52157        3.38496       -0.11928
H          -2.94700       -0.20043        0.40937
H          -2.42362       -1.85286        0.83295
H          -3.34367       -1.55858       -0.66857
H           1.69986        3.08987       -1.16179
H           2.49713        3.49128        0.37226
H           0.98951        4.34808       -0.09685
H           2.04012        1.07803        3.18064
H           3.42386        0.10869        2.58407
H           2.17433       -0.65692        3.60241
H           0.58149       -1.55748       -2.52475
H           1.98243       -0.42949       -2.57228
H           0.28876        0.18743       -2.63430
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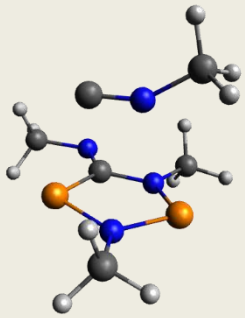

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