Electronic Supplementary Material (ESI) for Dalton Transactions.

Increasing Steric Demand through Flexible Bulk – Primary Phosphanes with 2,6-Bis(benzhydryl)phenyl Backbones

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1. Experimental

General Information. If not stated otherwise, experiments were carried out without using predried solvents under standard working conditions (exposure to air). Whenever anhydrous solvents were used, Schlenk or drybox techniques were employed and glassware was prepared by heating three times with a heat gun (650 °C) *in vacuo* (10^{-3} mbar) and subsequent flushing with argon. Solvents and reactants were obtained from commercial sources or synthesized. Anhydrous solvents were dried and distilled under argon atmosphere and handled with syringes, which were purged three times with argon prior to use. Dichloromethane (CH_2Cl_2) was purified according to a literature procedure, dried over P_4O_{10}, distilled, stored over CaH_2, distilled again and degassed.[1] Tetrahydrofuran (THF) was dried over Na/benzophenone and distilled. *n*-Pentane was dried over Na/benzophenone/tetraglyme (= $Me(OCH_2CH_2)_4OMe$) and distilled. Deuterated dichloromethane (CD_2Cl_2) was dried over P_4O_{10}, stored over CaH_2, distilled and degassed. Deuterated benzene (C_6D_6) and tetrahydrofuran (THF-d_8) were dried over Na and distilled. THF-d_8 was consecutively stored over molecular sieves (4 Å) in the refrigerator.

The following starting materials and reactants were used as purchased without further purification: diphenylmethanol (Tokyo Chemical Industry), zinc chloride (Riedel-de Haën), hydrochloric acid (ChemSolute, 37.0 %), potassium carbonate (Grüssing GmbH), sodium sulfate (Riedel-de Haën), benzyltriethylammonium chloride (Sigma-Aldrich, 99 %), acetic acid (ChemSolute, 99.5 %), sodium nitrite (KMF Laborchemie), magnesium sulfate (Grüssing GmbH), hydrobromic acid (Riedel-de Haën, 33 wt. % in acetic acid), sodium sulfite (VWR), potassium iodide (VK Labor- und Feinchemikalien), tetrafluoroboric acid (Merck, 35 wt. % in water), *n*-butyllithium (Sigma-Aldrich, 2.5 M in hexanes), *tert*-butyllithium (Sigma-Aldrich, 1.7 M in pentane), di(*iso*-butyl)aluminium hydride (Sigma-Aldrich, 1.0 M in hexanes), 1,4-diazabicyclo[2.2.2]octane (Merck), lithium aluminium hydride (abcr GmbH), sodium borohydride (abcr GmbH) and potassium *tert*-butoxide (Merck).

4-Methylaniline (J&K, 99 %) was sublimed twice, 4-*tert*-butylaniline (abcr GmbH) was distilled, phosphorus trichloride (Merck) was dried over P_4O_{10}, distilled and degassed, antimony trichloride (Merck) was sublimed.

NMR spectra were obtained on a Bruker AVANCE 250, 300, 400 or 500 MHz spectrometer and were referenced internally to the deuterated solvent (^{13}C: CD_2Cl_2 δ_{ref} = 54.0 ppm, C_6D_6 δ_{ref} = 128.4 ppm, THF-d_8 $\delta_{ref,1}$ = 25.4 ppm, $\delta_{ref,2}$ = 67.6 ppm), to protic impurities in the deuterated solvent (^{1}H: $CHDCl_2$ 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. NMR signals were assigned on the basis of experimental data (chemical shifts, coupling constants, integrals).

IR spectra of crystalline samples were recorded on a Nicolet 380 FT-IR spectrometer, equipped with a Smart Orbit ATR unit or on a Bruker Alpha IR spectrometer, equipped with a platinum ATR unit at ambient temperature.

Raman spectra of crystalline samples were recorded using a LabRAM HR 800 Horiba Jobin YVON spectrometer, equipped with an Olympus BX41 microscope with variable lenses (Olympus MPlan 10x/0.25, 50x/0.75, 100x/0.90 and LMPlanFL N 50x/0.50). The samples were excited by a red laser (633 nm, 17 mW). All measurements were carried out at ambient temperature.

Elemental analyses were obtained using an Elementar vario Micro cube CHNS analyzer.

Melting points (uncorrected) were determined using a Stanford Research Systems EZ Melt at a heating rate of 5, 10 or 20 °C/min.

DSC analyses were carried out at a heating rate of 5 °C/min, using a Mettler-Toledo DSC 823e.

2. Structural Data

Structure Determination. X-ray quality single-crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. The samples were cooled to 123(2) K or 150(2) K during measurements. Data was collected on a Bruker Kappa Apex II CCD, a Bruker D8 Quest CMOS or an Agilent SuperNova Dual Atlas diffractometer, using monochromatic Mo K_α radiation (λ = 0.71073 Å) or Cu K_α radiation (λ = 1.54184 Å). The structures were solved by direct methods (SHELXS97 or SHELXTL) and refined by full-matrix least squares procedures (SHELXL2013 or SHELXL-2014/7).[2–5] Semi-empirical absorption corrections were applied (SADABS).[6] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to phosphorus atoms were refined freely. Other hydrogen atoms were refined at calculated positions, using a riding model. Disordered molecular groups were split in parts, with their occupancy being refined freely.

5Me was refined as a 2-component inversion twin.

Table S1. Crystallographic Details of **2Me**, **3Me** and **4Me**.

Compound	^{Me}Bhp−Cl (**2Me**)	^{Me}Bhp−Br (**3Me**)	^{Me}Bhp−I (**4Me**)
Chem. Formula	$C_{33}H_{27}Cl$	$C_{33}H_{27}Br$	$C_{33}H_{27}I$
Formula weight / g/mol	458.99	503.45	550.44
Color	colorless	colorless	colorless
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	*Pnma*	$P2_1/n$	$P2_1/n$
a / Å	17.070(2)	9.595(1)	9.598(1)
b / Å	24.879(2)	11.547(1)	11.694(1)
c / Å	5.8722(6)	22.342(3)	22.470(2)
α / degrees	90	90	90
β / degrees	90	94.331(4)	94.856(4)
γ / degrees	90	90	90
V / Å³	2493.8(4)	2468.3(5)	2512.9(4)
Z	4	4	4
$\rho_{calcd.}$ / g/cm³	1.223	1.355	1.455
μ / mm^{-1}	0.172	1.685	1.294
T / K	123(2)	123(2)	123(2)
Measured reflections	67901	76496	118940
Independent reflections	4399	7533	7992
Reflections with $I > 2\sigma(I)$	3691	5740	7091
R_{int}	0.0600	0.0758	0.0426
F(000)	968	1040	1112
$R_1(R[F^2>2\sigma(F^2)])$	0.0467	0.0409	0.0366
w$R_2(F^2)$	0.1144	0.0936	0.0994
GooF	1.081	1.055	1.104
No. of Parameters	161	308	308
CCDC #	1894110	1894109	1894112

Table S2. Crystallographic Details of **4*t*Bu**, **5Me** and **6Me**.

Compound	$^{t\mathrm{Bu}}$Bhp−I (**4*t*Bu**)	[$^{\mathrm{Me}}$Bhp−N_2][BF_4] (**5Me**)	$^{\mathrm{Me}}$Bhp−F (**6Me**)
Chem. Formula	$C_{36}H_{33}I$	$[C_{33}H_{27}N_2][BF_4]\cdot CH_2Cl_2$	$C_{33}H_{27}F$
Formula weight / g/mol	592.52	623.30	442.54
Color	colorless	colorless	colorless
Crystal system	orthorhombic	orthorhombic	orthorhombic
Space group	*Pnma*	$P2_12_12_1$	*Pnma*
a / Å	19.007(2)	14.616(4)	17.169(1)
b / Å	24.840(2)	16.962(4)	24.765(2)
c / Å	5.9476(6)	24.922(6)	5.5609(4)
α / degrees	90	90	90
β / degrees	90	90	90
γ / degrees	90	90	90
V / Å³	2808.1(5)	6178(3)	2364.5(3)
Z	4	8	4
$\rho_{\mathrm{calcd.}}$ / g/cm³	1.402	1.340	1.243
μ / mm^{-1}	1.163	0.261	0.076
T / K	123(2)	123(2)	123(2)
Measured reflections	62311	63096	21181
Independent reflections	5162	10865	3831
Reflections with $I > 2\sigma(I)$	4899	7054	2695
R_{int}	0.0380	0.1127	0.0676
F(000)	1208	2576	936
$R_1(R[F^2>2\sigma(F^2)])$	0.0470	0.0573	0.0482
w$R_2(F^2)$	0.0982	0.1207	0.1261
GooF	1.303	1.026	1.027
No. of Parameters	176	798	161
CCDC #	1894114	1894108	1894111

Table S3. Crystallographic Details of **7Me**, **7*t*Bu** and **8Me**.

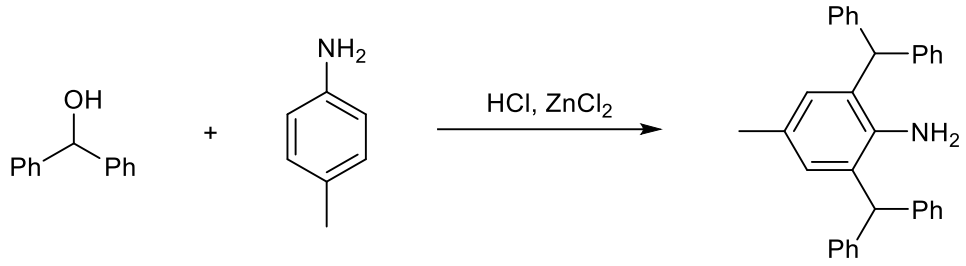
Compound	^{Me}Bhp–PX_2 (**7Me**)	^{tBu}Bhp–PX_2 (**7*t*Bu**)	^{Me}Bhp–PH_2 (**8Me**)
Chem. Formula	$C_{33}H_{27}Cl_{1.52}I_{0.48}P$	$C_{36}H_{33}Cl_{1.63}I_{0.37}P$	$C_{33}H_{29}P$
Formula weight / g/mol	569.31	600.87	456.53
Color	colorless	colorless	colorless
Crystal system	triclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	*Pbcn*
a / Å	10.4208(5)	11.2059(5)	34.494(1)
b / Å	14.0280(7)	19.1823(9)	8.2825(2)
c / Å	20.090(1)	14.8511(6)	17.2074(5)
α / degrees	71.795(5)	90	90
β / degrees	81.683(4)	105.670(2)	90
γ / degrees	77.745(4)	90	90
V / Å³	2716.5(3)	3073.7(2)	4916.1(2)
Z	4	4	8
$\rho_{calcd.}$ / g/cm³	1.392	1.298	1.234
μ / mm^{-1}	6.698	0.621	1.117
T / K	150.0(1)	123(2)	150(2)
Measured reflections	28346	67030	16224
Independent reflections	11218	8147	5118
Reflections with $I > 2\sigma(I)$	8677	6650	4099
R_{int}	0.0543	0.0712	0.0335
F(000)	1165	1245	1936
$R_1(R[F^2>2\sigma(F^2)])$	0.0498	0.0712	0.0337
w$R_2(F^2)$	0.1280	0.1540	0.0829
GooF	1.049	1.266	1.032
No. of Parameters	690	504	317
CCDC #	1894117	1894116	1894118

Table S4. Crystallographic Details of **8*t*Bu** and **10Me**.

Compound	^{tBu}Bhp–PH_2 (**8b**)	^{Me}Bhp–SbX_2 (**10a**)
Chem. Formula	$C_{36}H_{35}P$	$0.885(C_{33}H_{27}Cl_2Sb)\cdot0.115(C_{33}H_{27}I_2Sb)$
Formula weight / g/mol	498.61	636.85
Color	colorless	colorless
Crystal system	orthorhombic	triclinic
Space group	*Pnma*	$P\bar{1}$
a / Å	18.868(4)	9.5535(9)
b / Å	24.821(5)	12.482(1)
c / Å	5.947(1)	13.531(1)
α / degrees	90	104.561(4)
β / degrees	90	106.008(4)
γ / degrees	90	109.385(4)
V / Å³	2785(1)	1354.4(2)
Z	4	2
$\rho_{calcd.}$ / g/cm³	1.189	1.562
μ / mm^{-1}	0.121	1.471
T / K	123(2)	123(2)
Measured reflections	38890	82814
Independent reflections	3777	9811
Reflections with $I > 2\sigma(I)$	3273	8009
R_{int}	0.0545	0.0765
F(000)	1064	636
$R_1(R[F^2>2\sigma(F^2)])$	0.0532	0.0363
w$R_2(F^2)$	0.1424	0.0765
GooF	1.134	1.058
No. of Parameters	185	340
CCDC #	1894115	1894113

3. Syntheses of Compounds

2,6-Bis(benzhydryl)-4-methyl-aniline (^{Me}Bhp−NH_2, **1Me**)



^{Me}Bhp−NH_2 was prepared according to a modified protocol by Berthon-Gelloz *et al*.[7]

Diphenylmethanol (114.79 g, 623.1 mmol), 4-methylaniline (33.25 g, 310.3 mmol) and zinc chloride (21.66 g, 158.9 mmol) are placed together in a 1 L round-bottom flask with a large stir bar. After adding concentrated hydrochloric acid (37.0 %, 35 mL), the flask is equipped with a condenser and the mixture is heated to 150 °C for 2 hours in an oil bath. After cooling to ambient temperature, the product is extracted with dichloromethane (600 mL). Residual acid is neutralized *via* slow addition of an aqueous potassium carbonate solution (55 g in 400 mL). Layers are separated and the organic layer is washed twice with water. After drying over sodium sulfate, the solution is decanted and volatiles are removed at the rotary evaporator. The crude product is crushed into a fine powder and washed with cold ethyl acetate, leaving a white solid, which is eventually dried *in vacuo*. Yield: 102.98 g (234.3 mmol, 75.5 %).

Mp.: 178-184 °C. CHN calcd. (exptl.) in %: C 90.16 (90.32), H 6.65 (6.81). ^{1}H NMR (CD_2Cl_2, 500.1 MHz): δ = 2.03 (s, 3 H, *p*-C*H*$_3$), 3.35 (s, 2 H, N*H*$_2$), 5.46 (s, 2 H, C*H*Ph$_2$), 6.43 (s, 2 H, *m*-H), 7.13 (m, 8 H, Ph), 7.25 (tt, 4 H, ^3J(^{1}H,^{1}H) = 7.25 Hz, ^4J(^{1}H,^{1}H) = 1.22 Hz, *p*-H (Ph)), 7.31 (m, 8 H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ = 21.2 (s, *p*-*C*H$_3$), 52.9 (s, *C*HPh$_2$), 126.9 (s, *o*-C), 127.1 (s, *p*-C (Ph)), 129.0 (s, *o*-C (Ph)), 129.4 (s, *m*-C), 129.7 (s, *C*−CH$_3$), 130.0 (s, *m*-C (Ph)), 140.3 (s, *C*−NH$_2$), 143.5 (s, *ipso*-C (Ph)). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3443 (w), 3377 (w), 3083 (vw), 3052 (w), 3023 (w), 3000 (w), 2941 (vw), 2914 (w), 2864 (w), 1951 (vw), 1939 (vw), 1881 (vw), 1811 (vw), 1791 (vw), 1770 (vw), 1624 (w), 1599 (w), 1583 (w), 1550 (vw), 1492 (m), 1463 (m), 1442 (m), 1319 (w), 1292 (w), 1271 (w), 1253 (w), 1236 (w), 1177 (w), 1156 (w), 1133 (w), 1115 (w), 1076 (w), 1030 (w), 1001 (w), 966 (vw), 942 (vw), 921 (w), 911 (w), 882 (w), 863 (w), 830 (w), 752 (s), 696 (vs), 637 (m), 620 (m), 602 (s), 554 (s), 499 (m), 488 (m), 480 (m), 472 (m). Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3066 (1), 3051 (2), 3039 (1), 2922 (1), 2870 (1), 1627 (1), 1600

(2), 1585 (1), 1385 (1), 1293 (1), 1276 (1), 1256 (1), 1192 (1), 1174 (1), 1155 (1), 1031 (2), 1003 (6), 985 (2), 865 (1), 833 (1), 819 (1), 769 (1), 749 (1), 638 (1), 620 (1), 604 (1), 500 (1), 466 (1), 278 (1), 250 (1), 240 (2), 220 (1), 207 (1), 159 (2).

Figure S1. NMR, IR and Raman spectra of **1Me** (solvent signals marked by asterisk).

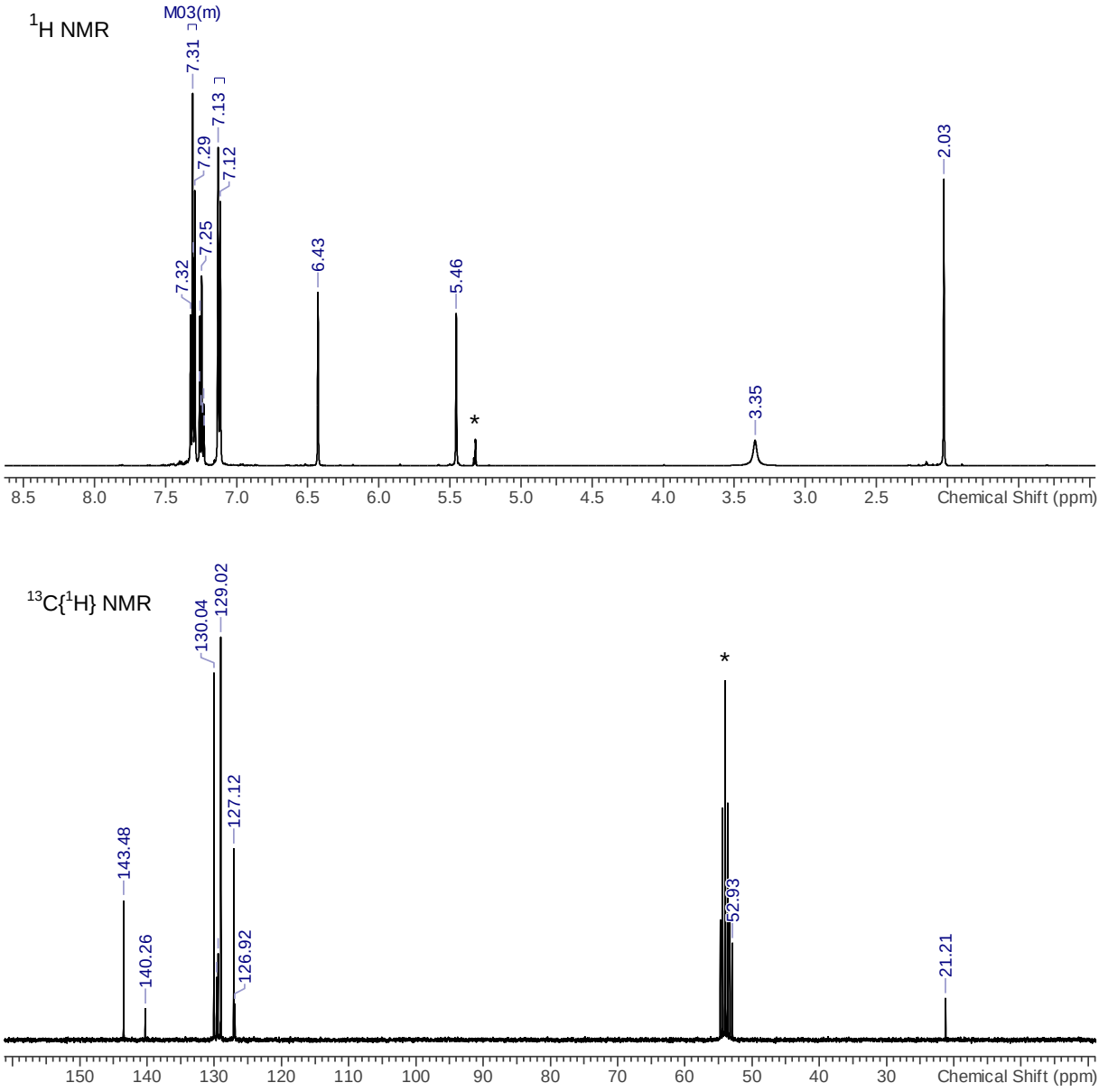
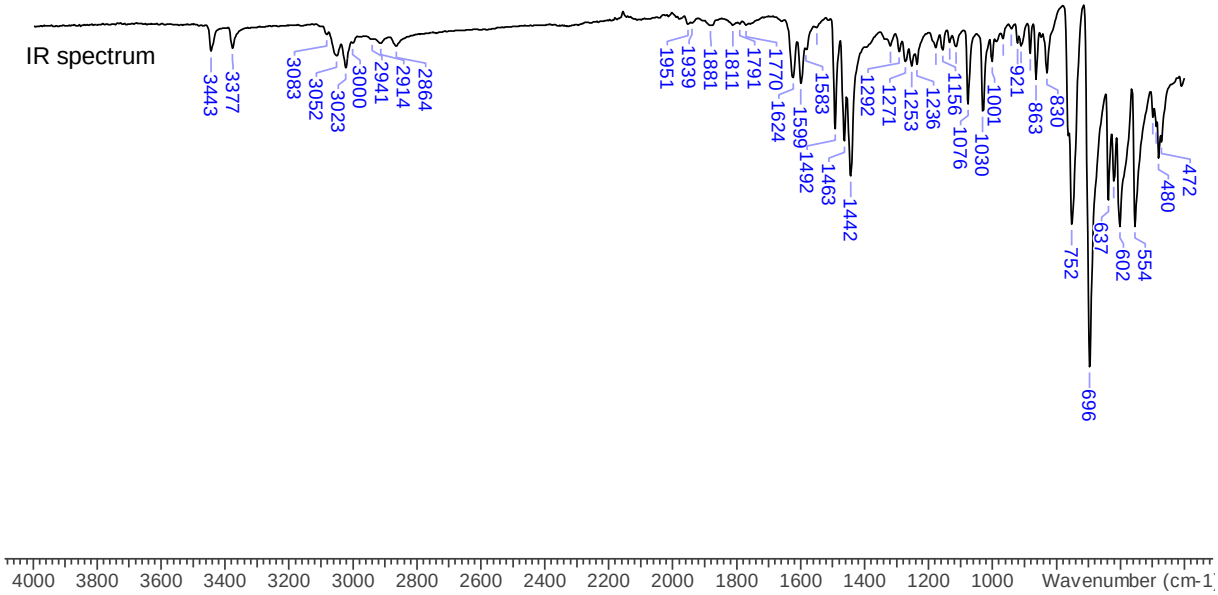
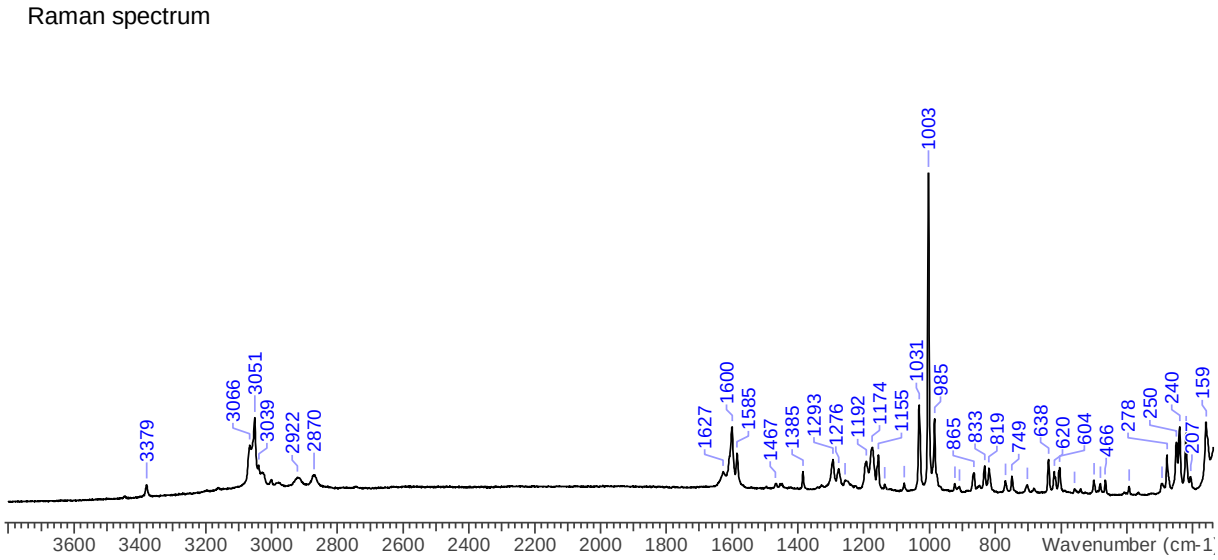
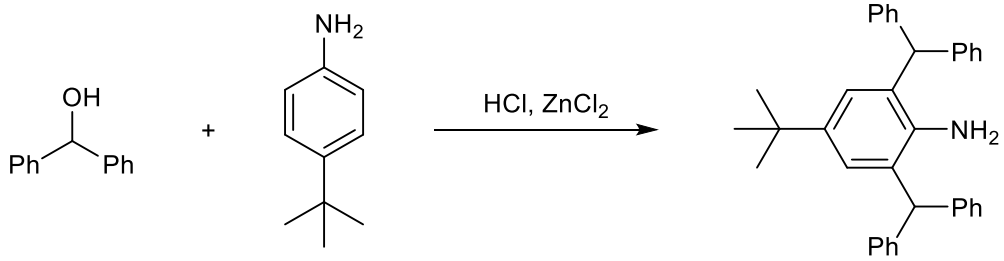


Figure S1 (continued).





2,6-Bis(benzhydryl)-4-*tert*-butyl-aniline ($^{t\text{Bu}}$Bhp−NH_2, **1*t*Bu**)



$^{t\text{Bu}}$Bhp−NH_2 was prepared according to a modified protocol by Fortier *et al.*[8]

Diphenylmethanol (48.75 g, 264.6 mmol), 4-*tert*-butylaniline (19.73 g, 132.2 mmol) and zinc chloride (9.83 g, 72.1 mmol) are placed together in a 1 L round-bottom flask with a large stir bar. After adding concentrated hydrochloric acid (37.0 %, 15 mL), the flask is equipped with a condenser and the mixture is heated to 150 °C for 2 hours in an oil bath. After cooling to ambient temperature, the product is extracted with dichloromethane (300 mL). Residual acid is neutralized *via* slow addition of an aqueous potassium carbonate solution (25 g in 200 mL). Layers are separated and the organic layer is washed twice with water. After drying over sodium sulfate, the solution is decanted and volatiles are removed at the rotary evaporator. The crude product is crushed into a fine powder and washed with cold methanol, leaving a white solid, which is recrystallized from hot benzene and eventually dried *in vacuo*. Yield: 37.39 g (77.6 mmol, 58.7 %).

Mp.: 211-214 °C. CHN calcd. (exptl.) in %: C 89.77 (90.13), H 7.32 (7.45). ^{1}H NMR (CD_2Cl_2, 500.1 MHz): δ = 0.99 (s, 9 H, *p*-*t*Bu), 3.33 (s, 2 H, NH_2), 5.47 (s, 2 H, CHPh$_2$), 6.63 (s, 2 H, *m*-H), 7.13 (dd, 8 H, $^{3}J(^{1}H,^{1}H)$ = 7.37 Hz, $^{4}J(^{1}H,^{1}H)$ = 1.51 Hz, *o*-H (Ph)), 7.24 (tt, 4 H, $^{3}J(^{1}H,^{1}H)$ = 7.32 Hz, $^{4}J(^{1}H,^{1}H)$ = 1.32 Hz, *p*-H (Ph)), 7.31 (m, 8 H, Ph). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 125.8 MHz): δ = 31.6 (s, CCH$_3$), 34.4 (s, CCH$_3$), 53.2 (s, CHPh$_2$), 126.0 (s, *o*-C), 127.1 (s, *p*-C (Ph)), 129.0 (s, *o*-C (Ph)), 129.0 (s, *m*-C), 130.0 (s, *C*–*t*Bu), 140.1 (s, *m*-C (Ph)), 140.4 (s, *C*–NH$_2$), 143.6 (s, *ipso*-C (Ph)). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3423 (w), 3357 (vw), 3081 (vw), 3058 (w), 3027 (w), 2959 (w), 2899 (vw), 2864 (vw), 1951 (vw), 1892 (vw), 1817 (vw), 1799 (vw), 1628 (w), 1599 (w), 1492 (m), 1471 (m), 1447 (m), 1424 (w), 1391 (vw), 1362 (w), 1339 (vw), 1319 (vw), 1294 (w), 1271 (w), 1243 (w), 1189 (vw), 1156 (vw), 1137 (vw), 1117 (vw), 1078 (w), 1030 (w), 1004 (vw), 948 (vw), 925 (vw), 911 (w), 892 (w), 865 (w), 835 (w), 814 (vw), 760 (s), 736 (s), 696 (vs), 659 (m), 643 (m), 624 (s), 608 (s), 585 (m), 521 (w), 509 (w), 486 (w), 472 (w), 439 (w). Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3360 (1), 3056 (3), 3039 (1), 3003 (1), 2964 (1), 2862 (1), 1628 (1), 1601 (2), 1586 (1), 1466 (1), 1298 (1), 1274 (1), 1257 (1), 1246 (1), 1196 (1), 1171 (2), 1158 (1), 1120 (1), 1076 (1), 1031 (3), 1003 (9), 992 (1), 984 (1), 950 (1), 910 (1), 867 (1), 836 (2), 751 (1), 738 (1), 645 (1), 634 (1), 620 (1), 613 (1), 607 (1), 589 (1), 523 (1), 252 (1), 242 (3), 220 (3), 156 (3).

Figure S2. NMR, IR and Raman spectra of **1*t*Bu** (solvent signals marked by asterisk).

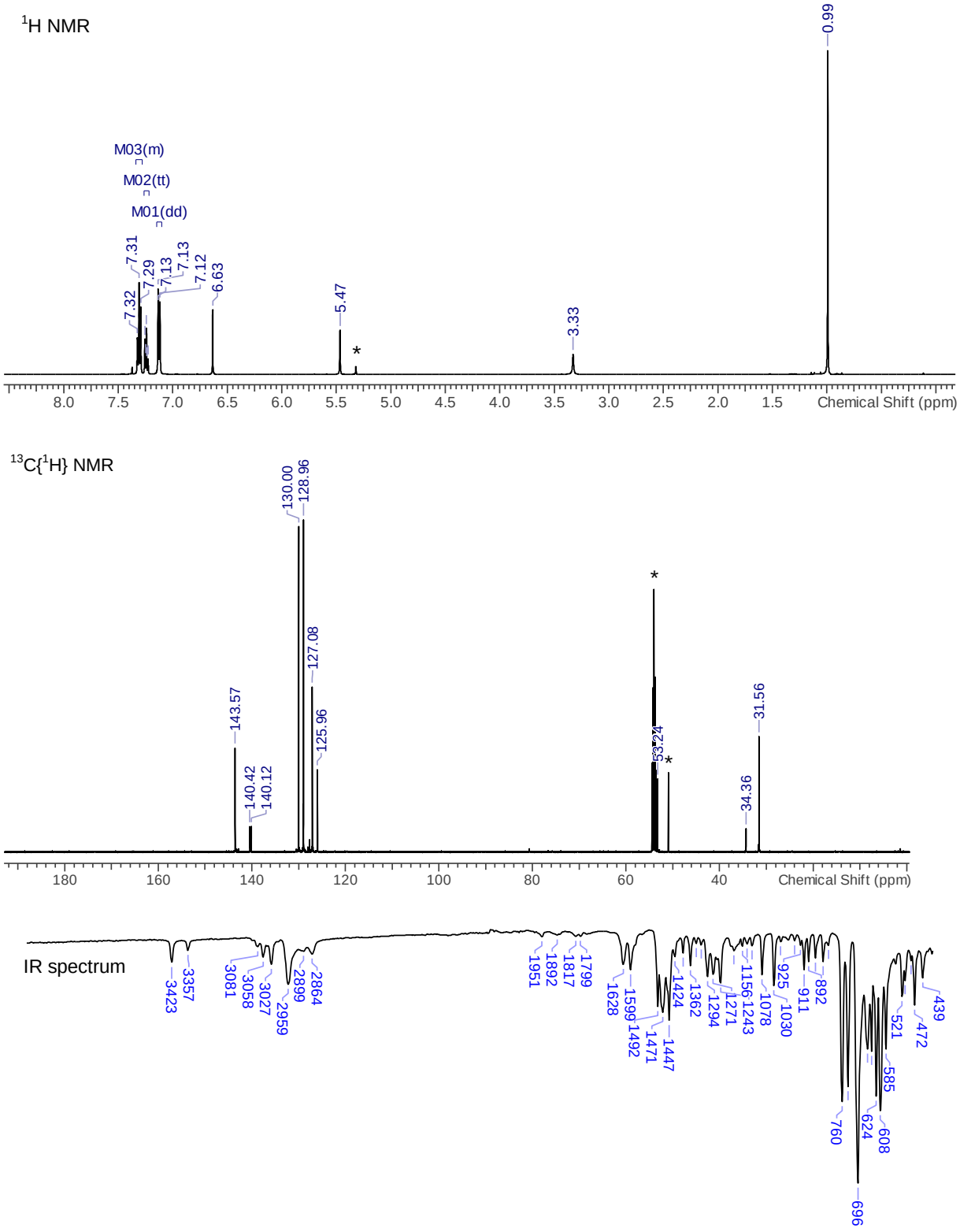
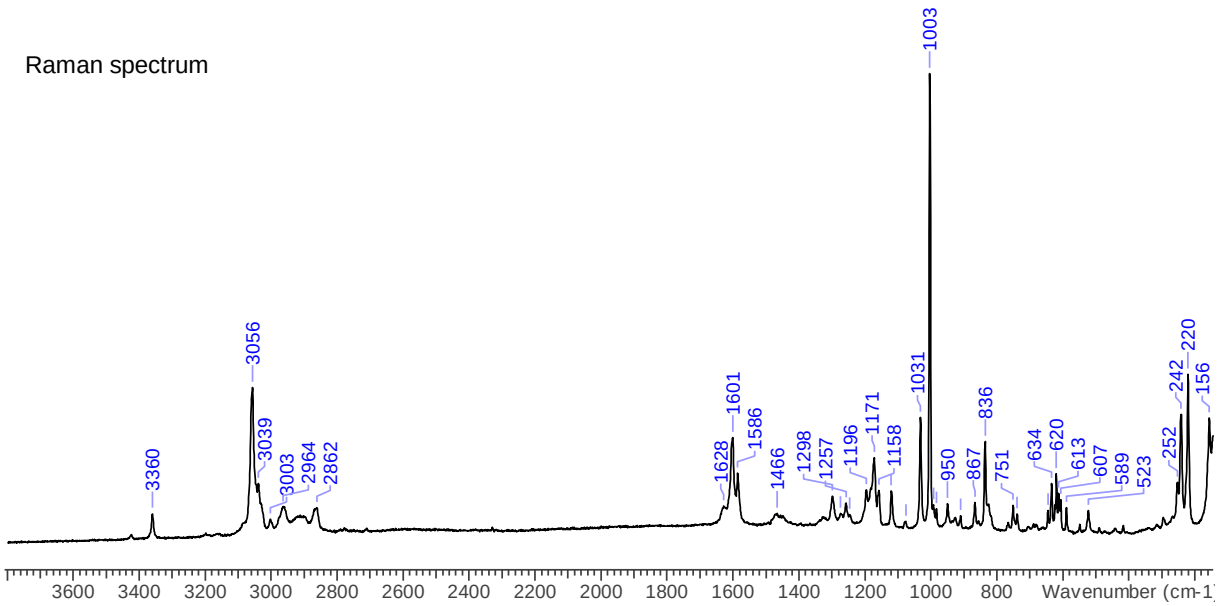
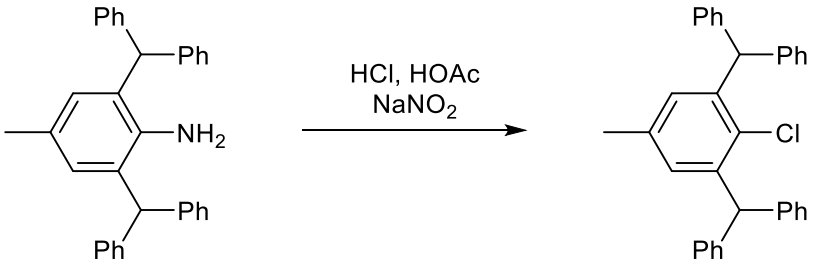


Figure S2 (continued).



2,6-Bis(benzhydryl)-4-methyl-phenylchloride (^{Me}Bhp−Cl, **2Me**)



2,6-Bis(benzhydryl)-4-methyl-aniline (3.84 g, 8.7 mmol) and benzyltriethylammonium chloride (0.10 g, 0.4 mmol) are placed together in a 100 mL two-neck round-bottom flask with a large stir bar and dissolved in dichloromethane (20 mL). After cooling the mixture to 0 °C, concentrated hydrochloric acid (37.0 %, 10 mL) and glacial acetic acid (99.5 %, 10 mL) are added. An aqueous solution (18 mL) of sodium nitrite (0.69 g, 10.0 mmol) is subsequently added dropwise, resulting in a bright red mixture. The flask is equipped with a condenser and heated to reflux for 90 min with visible gas formation and a color change to brown. After cooling to ambient temperature, the layers are separated and the aqueous layer is washed twice with dichloromethane. The combined organic phases are washed with water to pH neutrality, dried over magnesium sulfate and decanted. Volatiles are removed at the rotary evaporator and the product is crystallized from a mixture of toluene and *n*-pentane (3:1). Yield: 1.82 g (4.0 mmol, 46.0 %).

Mp.: 203 °C. CHN calcd. (exptl.) in %: C 86.35 (85.77), H 5.93 (5.28). ^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ = 2.11 (s, 3 H, *p*-C*H*$_3$), 5.98 (s, 2 H, C*H*Ph$_2$), 6.67 (s, 2 H, *m*-H), 7.08 (m, 8 H, Ph), 7.27 (m, 12 H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ = 21.6 (s, *p*-*C*H$_3$), 54.5 (s, *C*HPh$_2$), 127.0 (s, *p*-C (Ph)), 128.9 (s, *o*-C (Ph)), 130.1 (s, *m*-C (Ph)), 130.7 (s, *m*-C), 132.4 (s, *C*–Cl), 136.2 (s, *C*–CH$_3$), 142.3 (s, *o*-C), 143.6 (s, *ipso*-C (Ph)). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3084 (vw), 3059 (w), 3022 (w), 1595 (w), 1493 (m), 1450 (m), 1435 (m), 1423 (m), 1335 (w), 1321 (w), 1248 (w), 1180 (w), 1157 (w), 1076 (w), 1043 (m), 1030 (m), 1003 (w), 987 (w), 964 (w), 920 (w), 908 (w), 881 (w), 858 (w), 827 (w), 787 (m), 764 (m), 742 (s), 696 (vs), 638 (m), 621 (m), 604 (s), 598 (s), 548 (m), 532 (m). Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3060 (2), 3042 (1), 3002 (1), 2897 (1), 1597 (2), 1593 (1), 1241 (2), 1192 (2), 1179 (1), 1158 (1), 1044 (2), 1033 (1), 1004 (9), 992 (1), 984 (1), 979 (1), 788 (1), 703 (1), 632 (1), 618 (1), 597 (1), 393 (1), 267 (1), 261 (1), 244 (1), 214 (1), 198 (1), 163 (3). MS (EI, 70 eV, m/z): 458 ([M]$^{+}$, 100 %), 423 ([M −Cl]$^{+}$, 73 %), 291 ([M −CHPh$_2$]$^{+}$, 67 %), 167 ([CHPh$_2$]$^{+}$, 99 %).

Figure S3. NMR, IR and Raman spectra of **2Me** (solvent signals marked by asterisk).

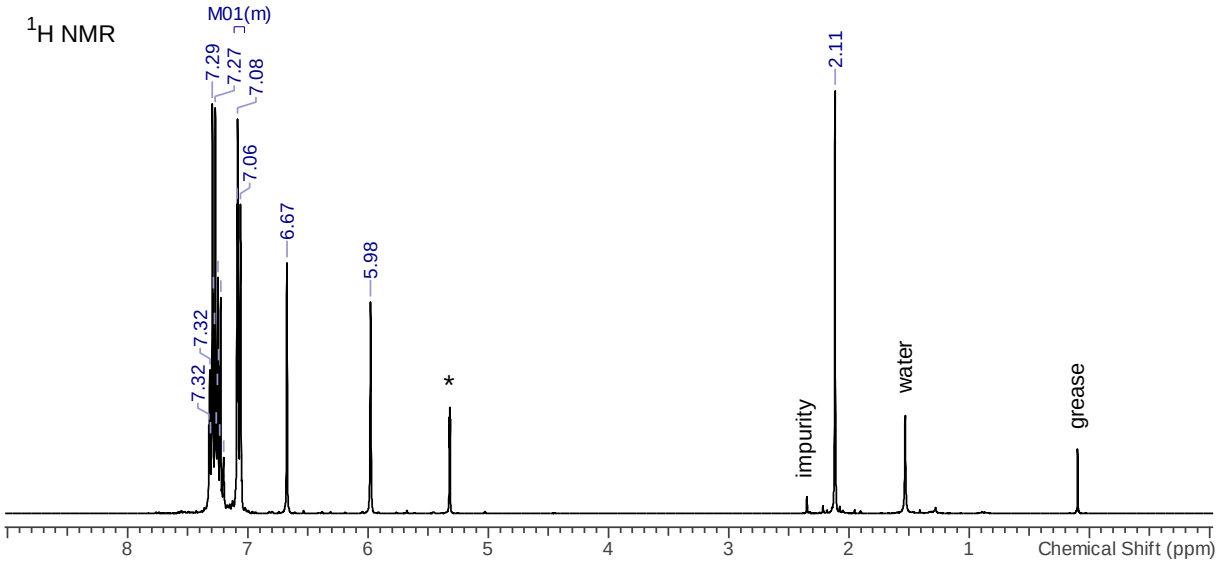
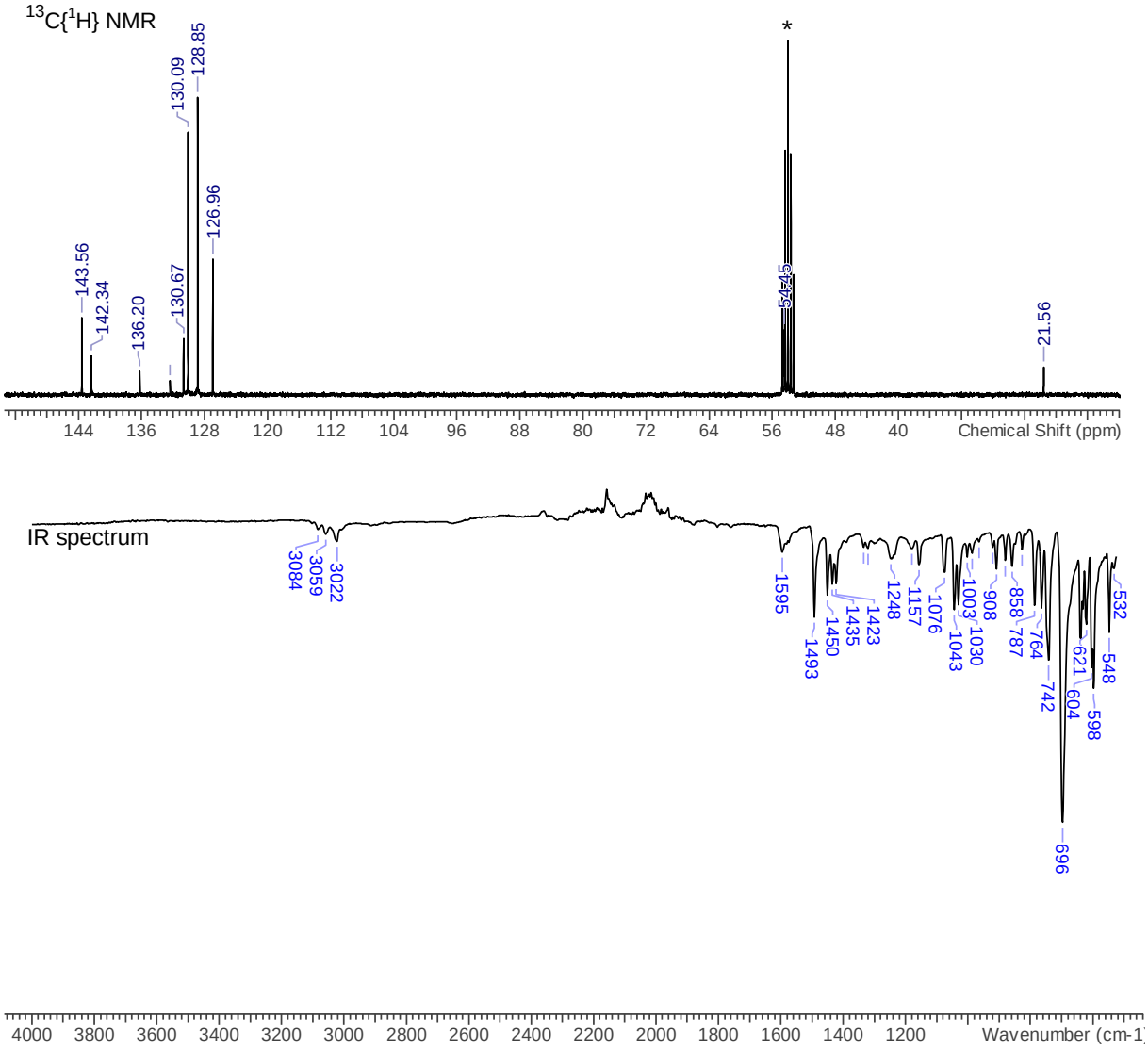
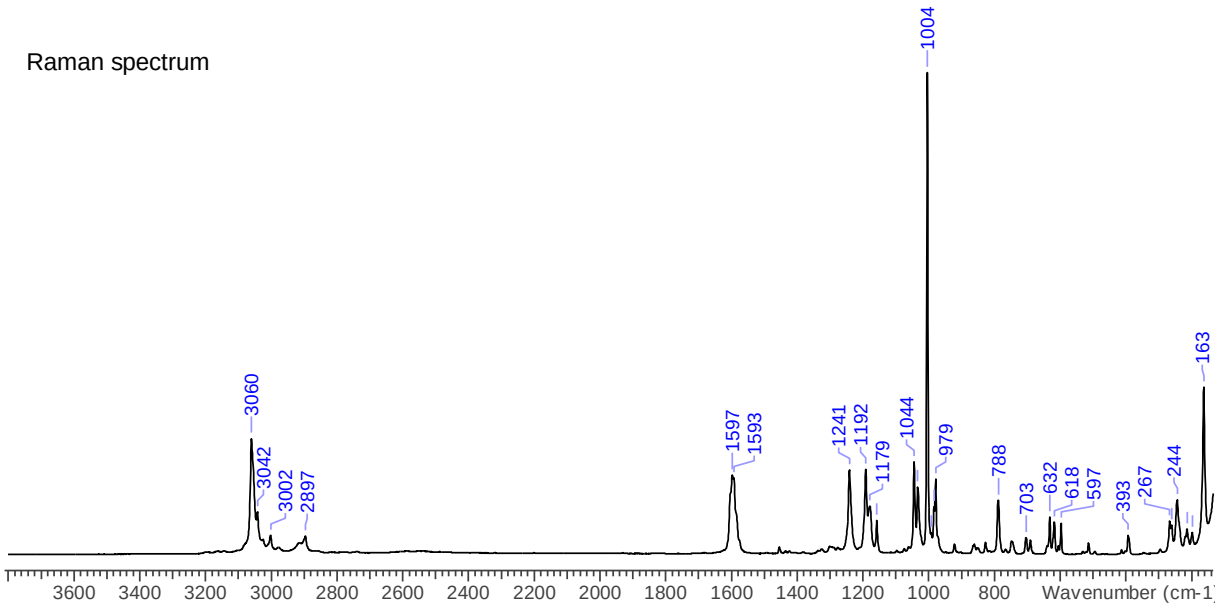
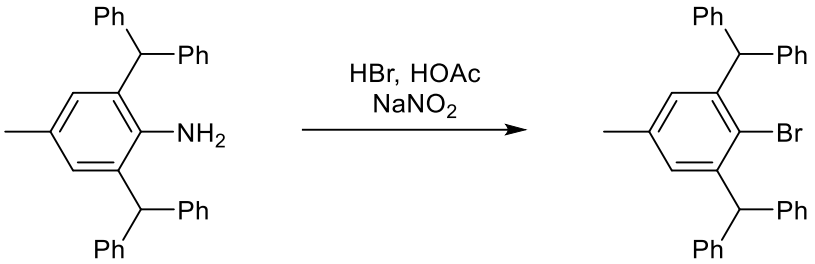


Figure S3 (continued).





2,6-Bis(benzhydryl)-4-methyl-phenylbromide (^{Me}Bhp−Br, **3Me**)



2,6-Bis(benzhydryl)-4-methyl-aniline (0.86 g, 2.0 mmol) and benzyltriethylammonium chloride (0.03 g, 0.1 mmol) are placed together in a 100 mL two-neck round-bottom flask with a large stir bar and dissolved in dichloromethane (10 mL). After cooling the mixture to 0 °C, hydrobromic acid in acetic acid (33 wt. %, 7 mL) and water (4 mL) are added. An aqueous solution (4 mL) of sodium nitrite (0.15 g, 2.1 mmol) is subsequently added dropwise, resulting in an orange mixture. The flask is equipped with a condenser and heated to reflux for 90 min with visible gas formation. After cooling to ambient temperature, unreacted bromine components are reduced by careful addition of an aqueous sodium sulfite solution. The layers are separated and the aqueous layer is washed twice with dichloromethane. The combined organic phases are washed with water to pH neutrality, dried over magnesium sulfate and decanted. Volatiles are removed at the rotary evaporator and the product is crystallized from a mixture of toluene and *n*-pentane (1:1). Yield: 0.47 g (0.9 mmol, 45.0 %).

Mp.: 171 °C. CHN calcd. (exptl.) in %: C 78.72 (78.88), H 5.41 (5.00). ^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ = 2.10 (s, 3 H, *p*-C*H*$_3$), 6.03 (s, 2 H, *m*-H), 6.68 (s, 2 H, C*H*Ph$_2$), 7.07 (m, 8 H, Ph) 7.28 (m, 12 H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ = 21.5 (s, *p*-*C*H$_3$), 57.3 (s, *C*HPh$_2$), 126.0 (s, *C*−Br), 127.0 (s, *p*-C (Ph)), 128.9 (s, *o*-C (Ph)), 130.2 (s, *m*-C (Ph)), 131.0 (s, *m*-C), 136.9 (s, *C*−CH$_3$), 143.7 (s, *o*-C), 144.2 (s, *ipso*-C (Ph)). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3084 (vw), 3055 (w), 3024 (w), 2919 (w), 2855 (vw), 1948 (vw), 1874 (vw), 1599 (w), 1583 (w), 1552 (vw), 1492 (m), 1447 (m), 1430 (w), 1416 (m), 1334 (vw), 1319 (vw), 1247 (w), 1177 (w), 1156 (w), 1109 (vw), 1076 (w), 1031 (w), 1020 (m), 1002 (w), 965 (vw), 911 (w), 882 (w), 857 (w), 843 (w), 829 (w), 785 (w), 761 (m), 746 (s), 695 (vs), 637 (m), 620 (m), 606 (m), 585 (m), 542 (m), 507 (w), 491 (w), 474 (m). Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3067 (1), 3056 (2), 3050 (1), 2923 (1), 2901 (1), 1601 (1), 1586 (1), 1241 (1), 1179 (1), 1154 (1), 1032 (1), 1022 (1), 1004 (8), 983 (1), 831 (1), 788 (1), 748 (1), 639 (1), 620 (1), 613 (1), 608 (1), 356 (1), 322 (1), 292 (1), 264 (1), 255

(1), 246 (1), 239 (1), 207 (1), 153 (2). MS (EI, 70 eV, m/z): 502 ([M]$^+$, 86 %), 423 ([M −Br]$^+$, 90 %), 335 ([M −$CHPh_2$]$^+$, 24 %), 167 ([$CHPh_2$]$^+$, 100 %).

Figure S4. NMR, IR and Raman spectra of **3Me** (solvent signals marked by asterisk).

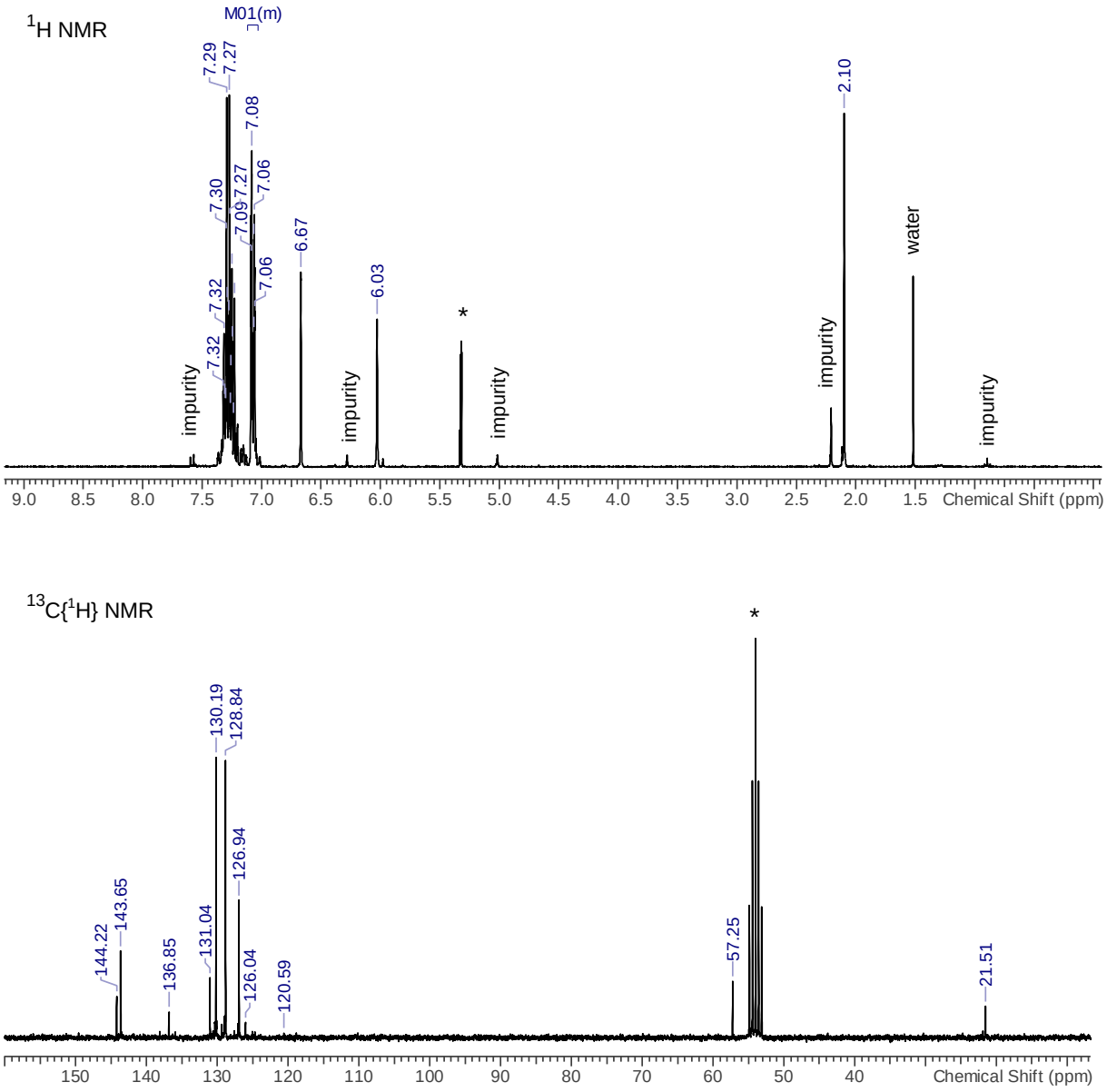
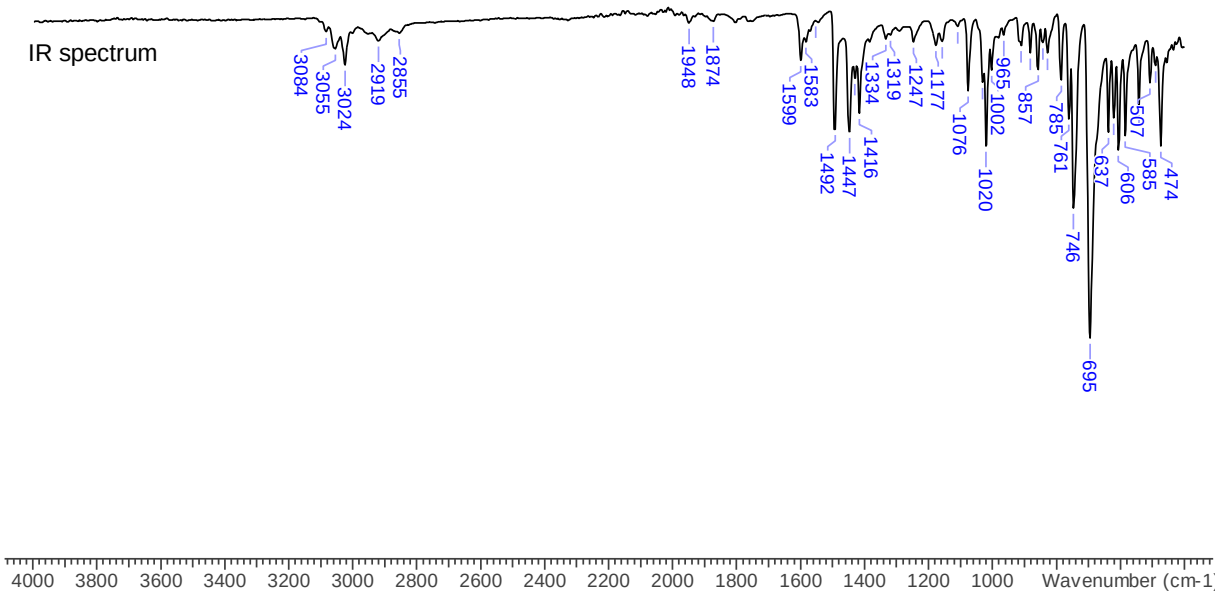
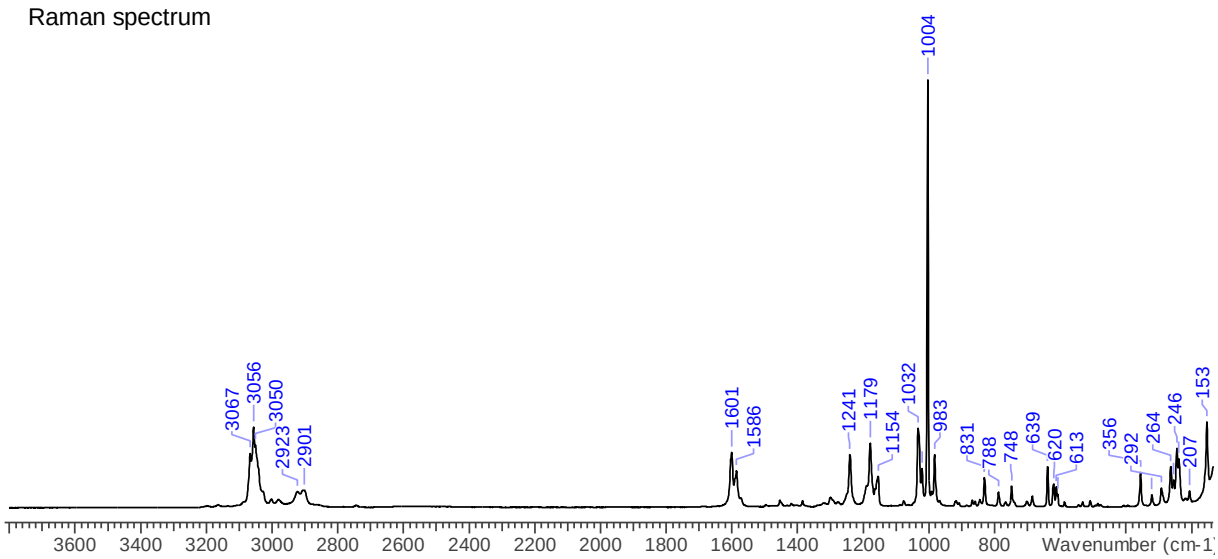
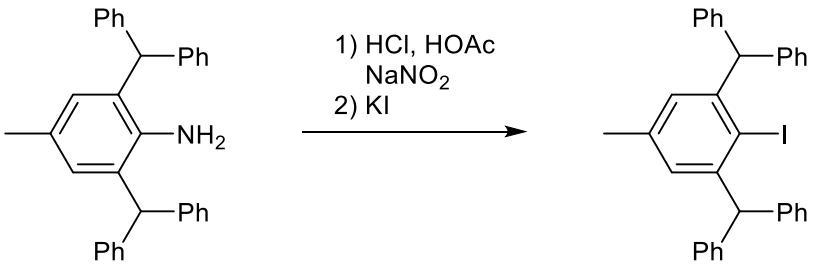


Figure S4 (continued).





2,6-Bis(benzhydryl)-4-methyl-phenyliodide (^{Me}Bhp–I, **4Me**)



In a 2 L two-neck round-bottom flask, equipped with a big stir bar, a dropping funnel and a condenser, 2,6-bis(benzhydryl)-4-methyl-aniline (66.50 g, 151.3 mmol) is dissolved in

dichloromethane (500 mL). After cooling to 0 °C, concentrated hydrochloric acid (37.0 %, 90 mL) and glacial acetic acid (99.5 %, 90 mL) are added. Afterwards, an aqueous solution (40 mL) of sodium nitrite (12.00 g, 173.9 mmol) is added dropwise, resulting in a bright red mixture, which is stirred for 30 min. An aqueous solution (400 mL) of potassium iodide (253.00 g, 1524.1 mmol) is subsequently added dropwise, resulting in visible gas formation. The mixture is then warmed to ambient temperature and stirred for another 30 min. Remaining iodine/triiodide is reduced by adding an aqueous solution (500 mL) of sodium sulfite (120.00 g, 952.1 mmol), resulting in a colorless aqueous and orange organic layer. Phases are separated, the aqueous layer is washed twice with dichloromethane and the organic layer is washed with water to pH neutrality. Organic phases are combined, dried over magnesium sulfate and decanted. Volatiles are removed at the rotary evaporator and the product is crystallized from a mixture of toluene and *n*-pentane (3:2). Yield: 44.00 g (79.9 mmol, 52.8 %).

Mp.: 168-170 °C. CHN calcd. (exptl.) in %: C 72.00 (71.78), H 4.94 (4.51). ^{1}H NMR (CD_2Cl_2, 500.1 MHz): δ = 2.12 (s, 3 H, *p*-C*H*$_3$), 6.06 (s, 2 H, C*H*Ph$_2$), 6.69 (s, 2 H, *m*-H), 7.11 (m, 8 H, Ph) 7.30 (m, 12 H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ = 21.4 (s, *p*-*C*H$_3$), 62.6 (s, *C*HPh$_2$), 108.3 (s, *C*–I), 126.9 (s, *p*-C (Ph)), 128.9 (s, *o*-C (Ph)), 130.4 (s, *m*-C (Ph)), 130.8 (s, *m*-C), 137.8 (s, *C*–CH$_3$), 143.8 (s, *ipso*-C (Ph)), 147.7 (s, *o*-C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3083 (vw), 3058 (w), 3023 (w), 1947 (vw), 1879 (vw), 1597 (w), 1581 (w), 1556 (vw), 1492 (m), 1447 (m), 1409 (w), 1321 (w), 1288 (vw), 1243 (w), 1177 (w), 1154 (w), 1078 (w), 1030 (w), 1001 (m), 968 (vw), 909 (w), 882 (w), 857 (w), 826 (w), 783 (w), 764 (m), 750 (m), 736 (m), 696 (vs), 639 (m), 620 (m), 604 (s), 571 (w), 538 (m), 505 (m), 497 (w), 474 (m), 451 (w). Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3066 (2), 3042 (1), 2896 (1), 1600 (2), 1587 (1), 1240 (1), 1178 (1), 1158 (1), 1031 (2), 1005 (10), 992 (1), 980 (1), 870 (1), 828 (1), 784 (1), 643 (1), 636 (1), 621 (1), 619 (1), 609 (1), 606 (1), 297 (1), 265 (1), 253 (2), 242 (1), 233 (1), 192 (1), 153 (1), 141 (2). MS (EI, 70 eV, m/z): 550 ([M]$^+$, 100 %), 423 ([M −I]$^+$, 59 %), 167 ([CHPh$_2$]$^+$, 81 %).

Figure S5. NMR, IR and Raman spectra of **4Me** (solvent signals marked by asterisk).

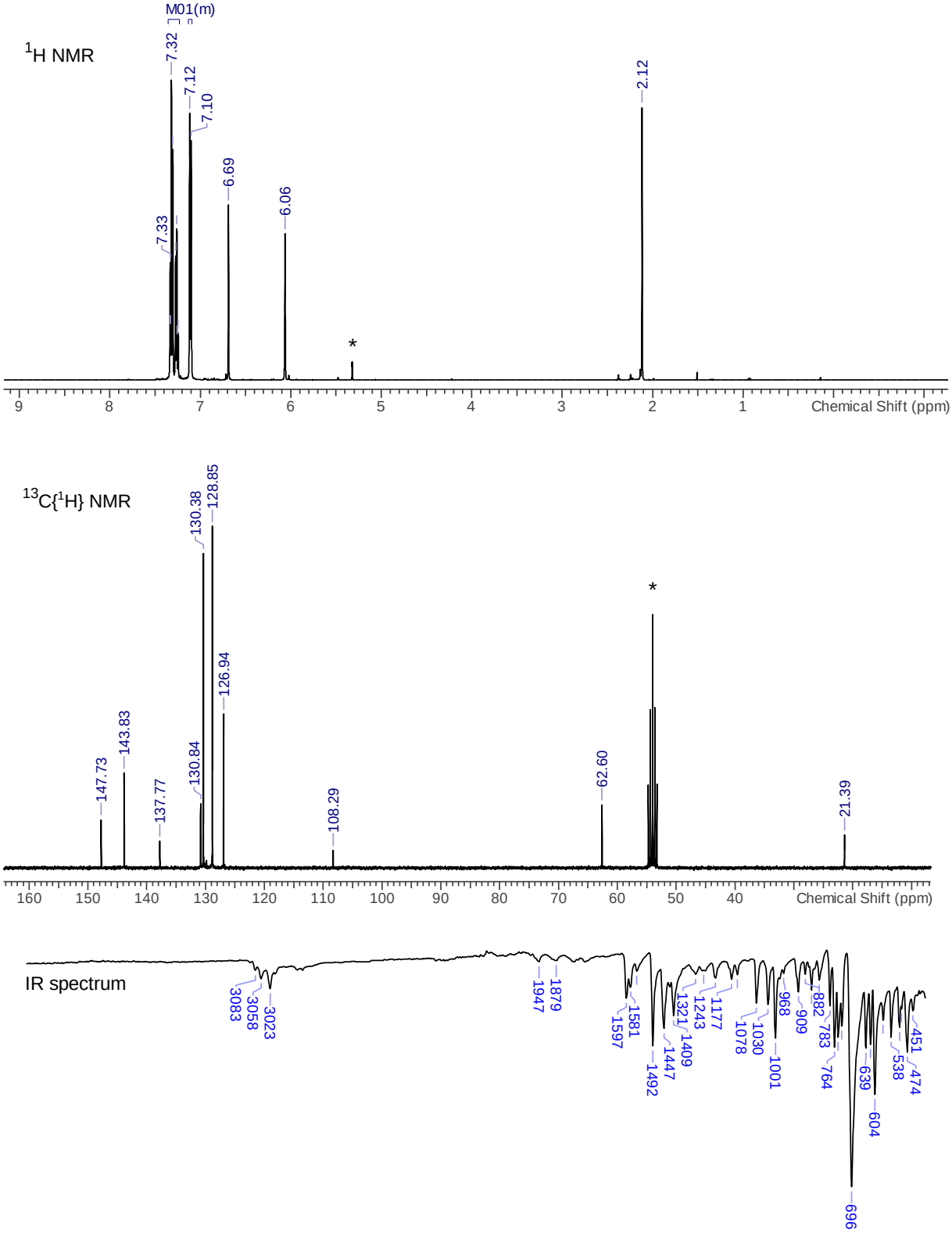
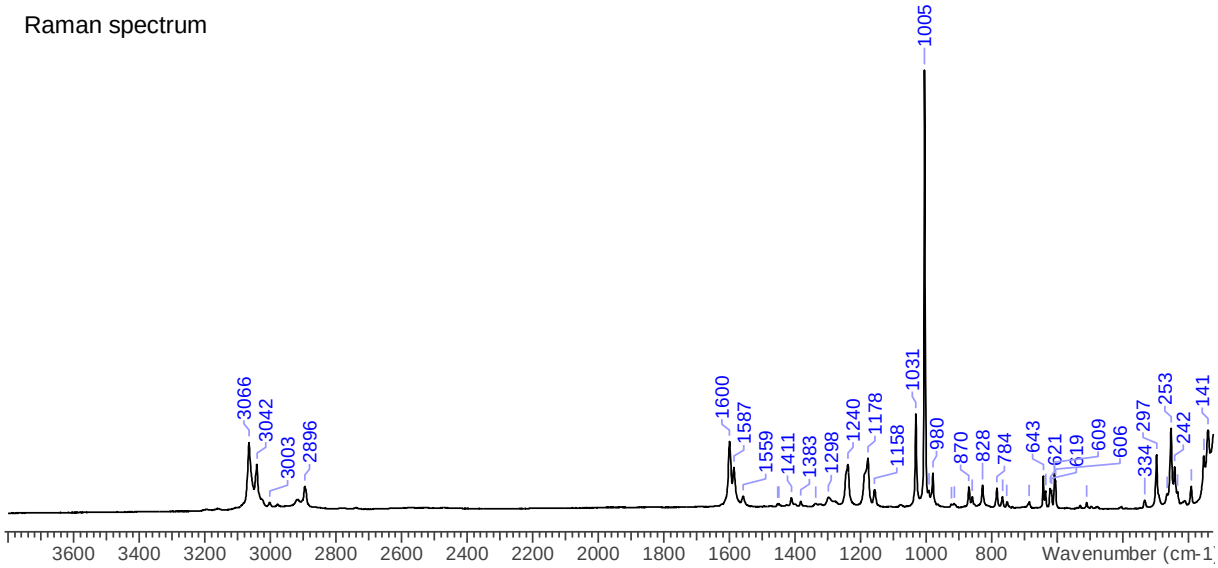
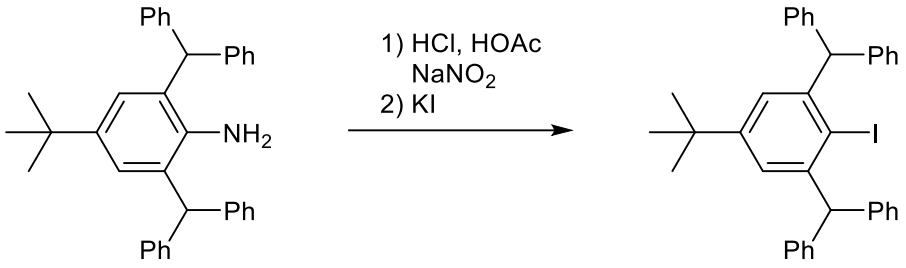


Figure S5 (continued).



2,6-Bis(benzhydryl)-4-*tert*-butyl-phenyliodide ($^{t\mathrm{Bu}}$Bhp–I, **4*t*Bu**)



In a 1 L two-neck round-bottom flask, equipped with a big stir bar, a dropping funnel and a condenser, 2,6-bis(benzhydryl)-4-*tert*-butyl-aniline (15.52 g, 32.2 mmol) is dissolved in dichloromethane (150 mL). After cooling to 0 °C, concentrated hydrochloric acid (37.0 %, 25 mL) and glacial acetic acid (99.5 %, 25 mL) are added. Afterwards, an aqueous solution (40 mL) of sodium nitrite (2.83 g, 41.0 mmol) is added dropwise, resulting in a bright red mixture, which is stirred for 30 min. An aqueous solution (100 mL) of potassium iodide (53.66 g, 323.3 mmol) is subsequently added dropwise, resulting in visible gas formation. The mixture is then warmed to ambient temperature and stirred for another 30 min. Remaining iodine/triiodide is reduced by adding an aqueous solution (150 mL) of sodium sulfite (31.69 g, 251.4 mmol), resulting in a colorless aqueous and yellow organic layer. Phases are separated, the aqueous layer is washed twice with dichloromethane and the organic layer is washed with water to pH neutrality. Organic phases are combined, dried over magnesium sulfate and decanted.

Volatiles are removed at the rotary evaporator and the product is crystallized from a mixture of toluene and *n*-pentane (3:1). Yield: 10.67 g (18.0 mmol, 55.9 %).

Mp.: 187-190 °C. CHN calcd. (exptl.) in %: C 72.97 (73.99), H 5.61 (5.69). ^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ = 1.05 (s, 9 H, *p*-*t*Bu), 6.06 (s, 2 H, C*H*Ph$_2$), 6.89 (s, 2 H, *m*-H), 7.11 (m, 8 H, *o*-H (Ph)), 7.30 (m, 12 H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ = 31.2 (s, C(CH_3)), 34.8 (s, *C*(CH_3)), 62.8 (s, *C*HPh$_2$), 108.2 (s, *C*–I), 126.9 (s, *p*-C (Ph)), 127.5 (s, *o*-C (Ph)), 128.8 (s, *m*-C (Ph)), 130.4 (s, *m*-C), 144.0 (s, *C*–*t*Bu), 147.3 (s, *ipso*-C (Ph)), 150.7 (s, *o*-C). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3081 (vw), 3058 (vw), 3025 (w), 3000 (vw), 2959 (w), 2864 (w), 1953 (vw), 1883 (vw), 1599 (w), 1581 (w), 1556 (vw), 1492 (m), 1475 (w), 1449 (m), 1416 (w), 1399 (w), 1362 (w), 1335 (w), 1251 (w), 1205 (w), 1175 (w), 1144 (w), 1076 (w), 1030 (w), 1004 (m), 913 (w), 892 (w), 859 (w), 832 (vw), 810 (vw), 767 (m), 746 (m), 699 (vs), 639 (m), 620 (m), 604 (m), 581 (m), 556 (w), 507 (w), 495 (w), 474 (m). Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3055 (5), 3030 (1), 3003 (1), 2974 (1), 2962 (1), 2923 (1), 2905 (1), 2886 (1), 1603 (2), 1584 (1), 1455 (1), 1451 (1), 1322 (1), 1298 (1), 1274 (1), 1244 (1), 1176 (3), 1157 (1), 1078 (1), 1032 (2), 1004 (9), 994 (1), 986 (1), 946 (1), 836 (2), 769 (1), 751 (1), 643 (2), 634 (1), 620 (2), 513 (1), 259 (1), 248 (1), 239 (2), 225 (1), 188 (1), 156 (3), 136 (4). MS (EI, 70 eV, m/z): 592 ([M]$^+$, 95 %), 577 ([M −Me]$^+$, 17 %), 535 ([M −*t*Bu]$^+$, 4 %), 465 ([M −I]$^+$, 70 %), 167 ([CHPh$_2$]$^+$, 100 %).

Figure S6. NMR, IR and Raman spectra of **4*t*Bu** (solvent signals marked by asterisk).

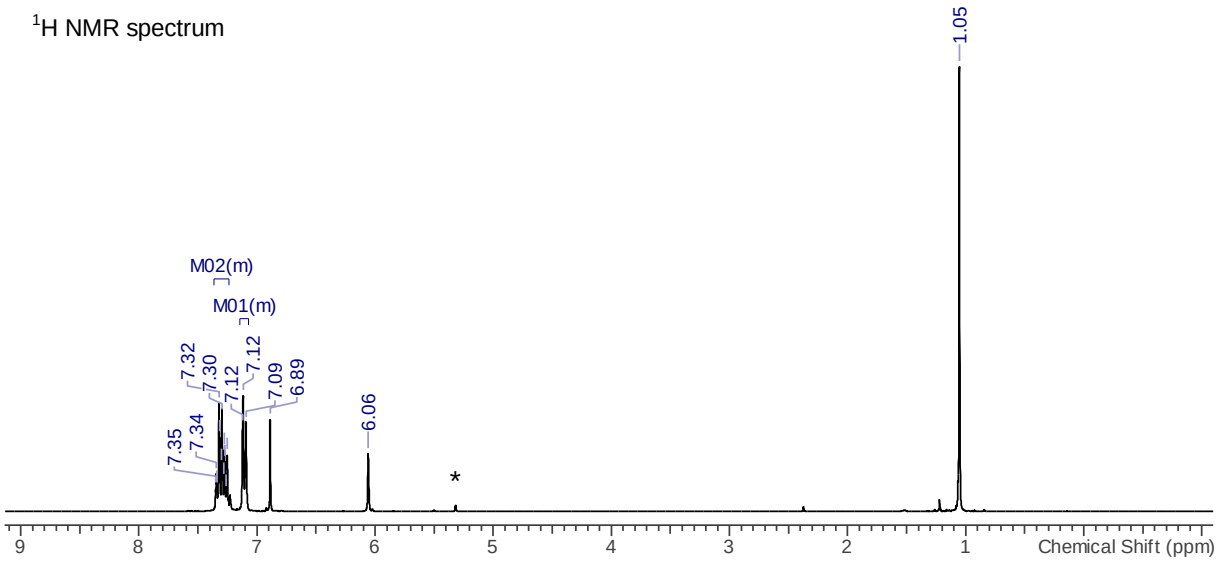
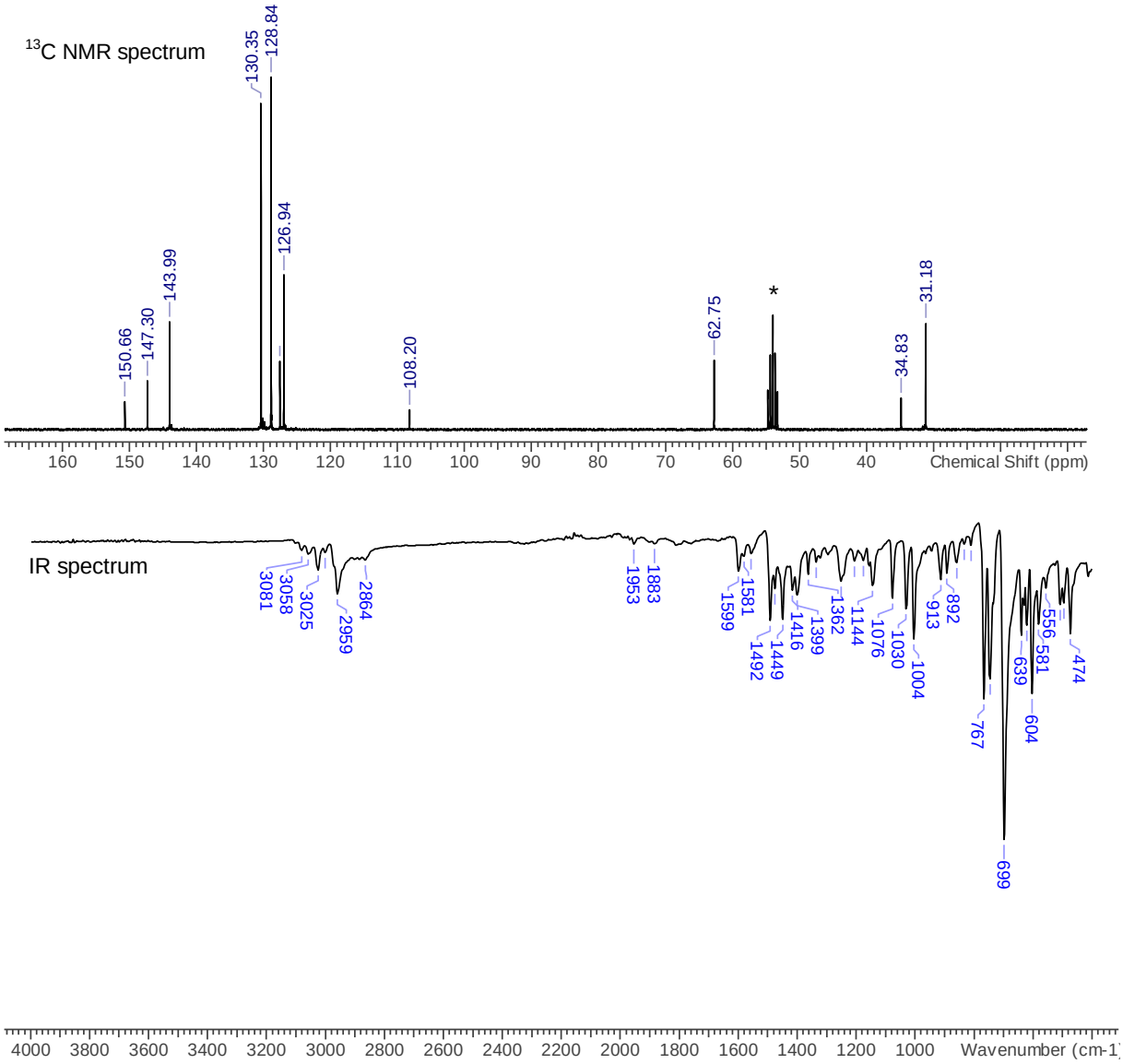
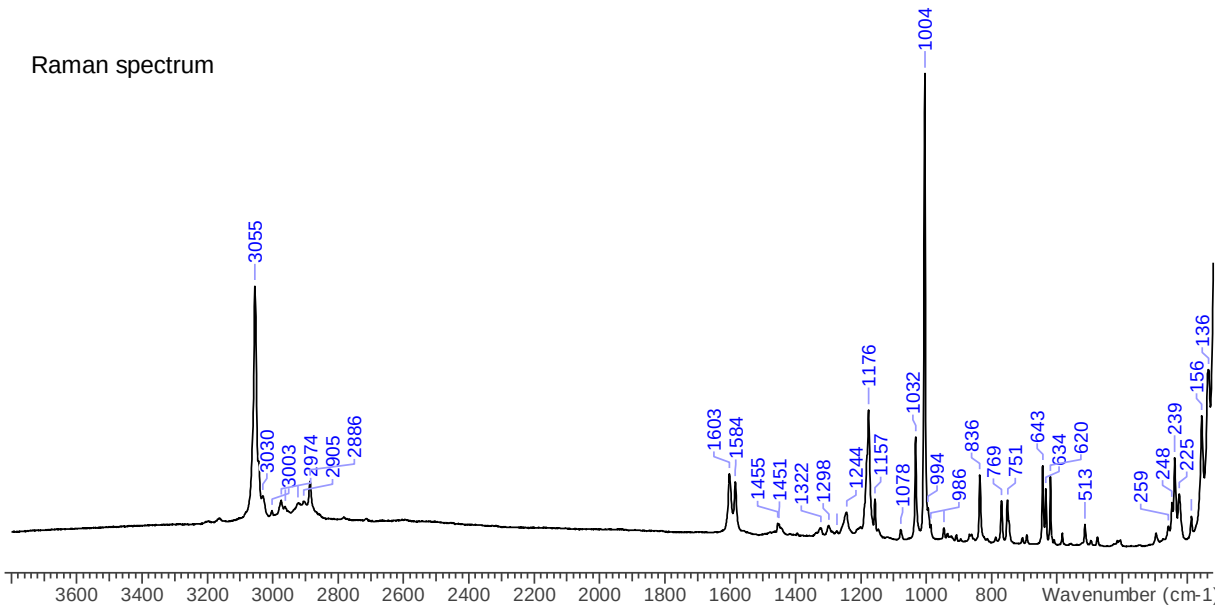
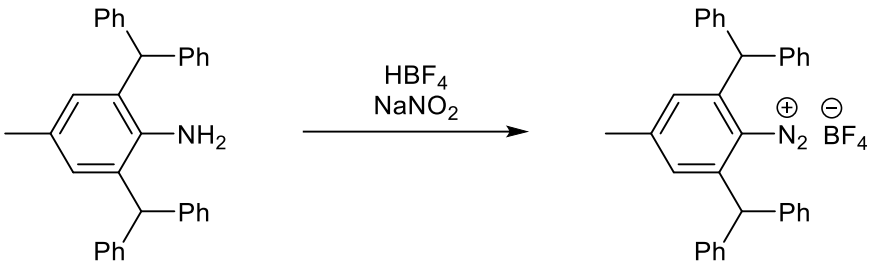


Figure S6 (continued).





2,6-Bis(benzhydryl)-4-methyl-phenyldiazonium tetrafluoroborate ([^{Me}Bhp−N_2][BF_4], **5Me**)



[^{Me}Bhp−N_2][BF_4] was prepared according to a modified protocol by Colleville, Horan and Tomkinson.[9]

In a 100 mL round-bottom flask, equipped with a big stir bar, 2,6-bis(benzhydryl)-4-methyl-aniline (0.82 g, 1.9 mmol) is dissolved in dichloromethane (40 mL). After adding an aqueous solution of tetrafluoroboric acid (35 wt. %, 1 mL) dropwise, the mixture is cooled to 0 °C. An aqueous solution (5 mL) of sodium nitrite (0.15 g, 2.2 mmol) is then added dropwise and the mixture is subsequently stirred for 30 min. The resulting brown mixture is stirred at ambient temperature for another 30 min. Afterwards, phases are separated and the organic layer is washed once with water. After drying over magnesium sulfate and decantation, the solution is concentrated under reduced pressure. Addition of small amounts of *n*-pentane led to crystallization of orange needles, which were eventually dried at ambient temperature and stored at −40 °C. Yield: 0.34 g (0.6 mmol, 31.6 %).

(Apart from the diazonium salt **5Me**, a small amount of single-crystals of 2,6-bis(benzhydryl)-4-methyl-phenylfluoride (**6Me**) were isolated. Analytical data for both compounds are presented separately.)

2,6-Bis(benzhydryl)-4-methyl-phenyldiazonium tetrafluoroborate dichloromethane solvate (**5Me·CH_2Cl_2**):

Mp.: 119 °C (decomp.). CHN calcd. (exptl.) in %: C 65.52 (66.51), H 4.69 (4.89), N 4.49 (4.28). ^{1}H NMR (THF-d_8, 500.1 MHz): δ = 2.37 (s, 3 H, *p*-CH_3), 5.50 (s, 2 H, CH_2Cl_2), 6.31 (s, 2 H, C*H*Ph_2), 6.98 (s, 2 H, *m*-H), 7.27 (m, 20 H, Ph). ^{13}C{^{1}H} NMR (THF-d_8, 75.5 MHz): δ = 23.3 (s, *p*-*C*H_3), 53.3 (s, *C*HPh_2), 112.3 (s, *C*–N_2), 128.7 (s, *p*-C (Ph)), 129.9 (s, *o*-C (Ph)), 130.6 (s, *m*-C (Ph)), 132.5 (s, *m*-C), 140.3 (s, *ipso*-C (Ph)), 152.4 (s, *o*-C). ^{11}B NMR (THF-d_8, 160.5 MHz): δ = −0.9 (s, *B*F_4). ^{19}F NMR (THF-d_8, 282.4 MHz): δ = −154.4 (s, 3 F, B*F*$_3$·THF), −153.3 (s, 4 F, B*F*$_4$). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3061 (vw), 3028 (vw), 2230 (w), 1585 (m), 1494 (w), 1451 (m), 1329 (w), 1317 (w),

1286 (w), 1270 (w), 1245 (w), 1156 (w), 1078 (s), 1064 (s), 1043 (s), 1024 (s), 919 (w), 882 (w), 860 (w), 827 (w), 769 (m), 754 (m), 736 (s), 715 (s), 699 (vs), 653 (w), 635 (w), 620 (w), 602 (m), 585 (m), 559 (w), 519 (m), 488 (m), 472 (w), 416 (w). DSC (Al_2O_3 crucible, 25-250 °C, 5 K/min, Ar atmosphere): 93 °C (endothermic, Δm = −19 %, loss of N_2 and DCM). MS (LCMS, MeOH/HCOOH (99.9:0.1)): 423 ($[M-N_2]^+$), 167 ($[CHPh_2]^+$).

Figure S7. NMR, IR and Raman spectra of **5Me** (solvent signals marked by asterisk).

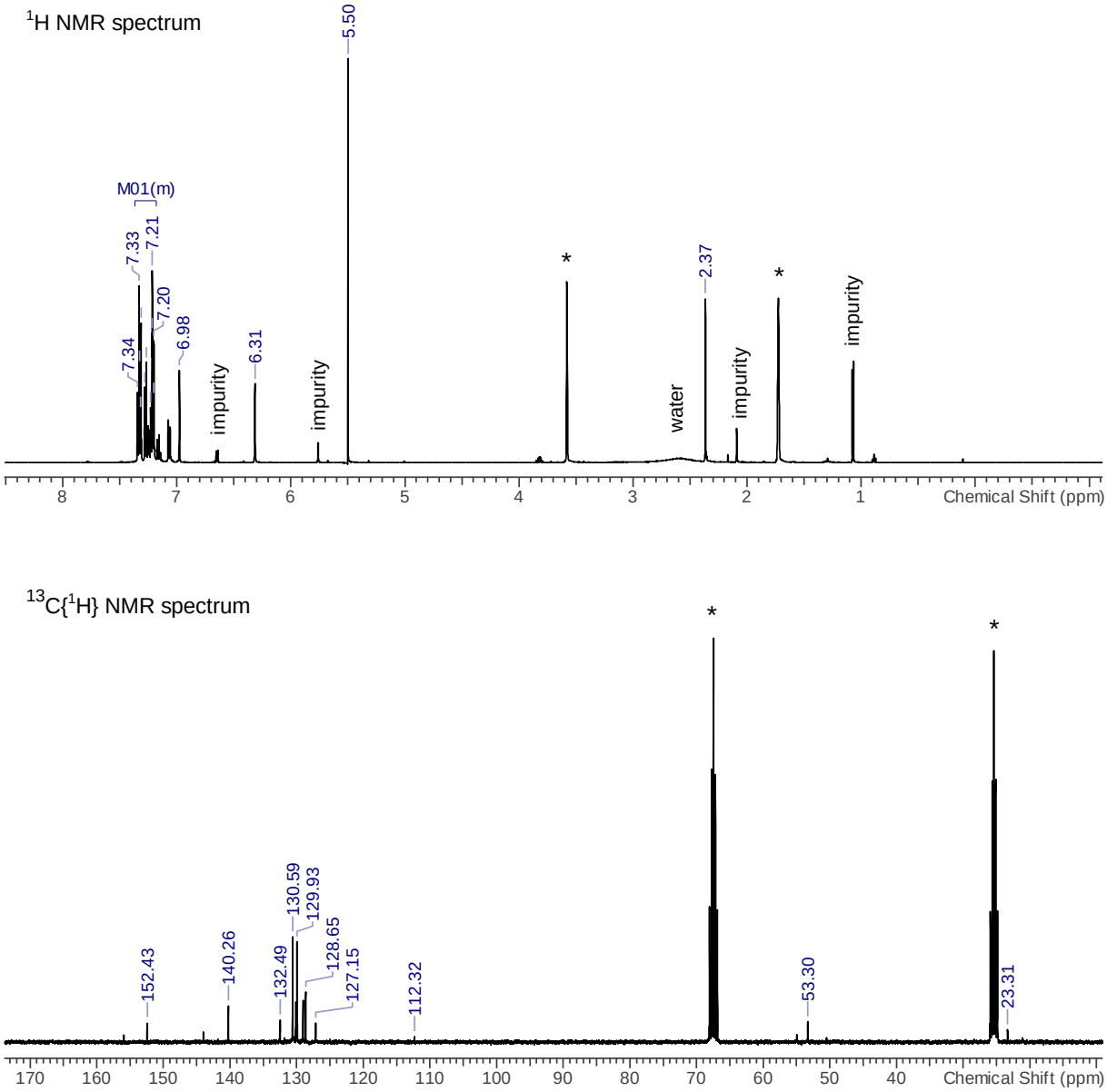
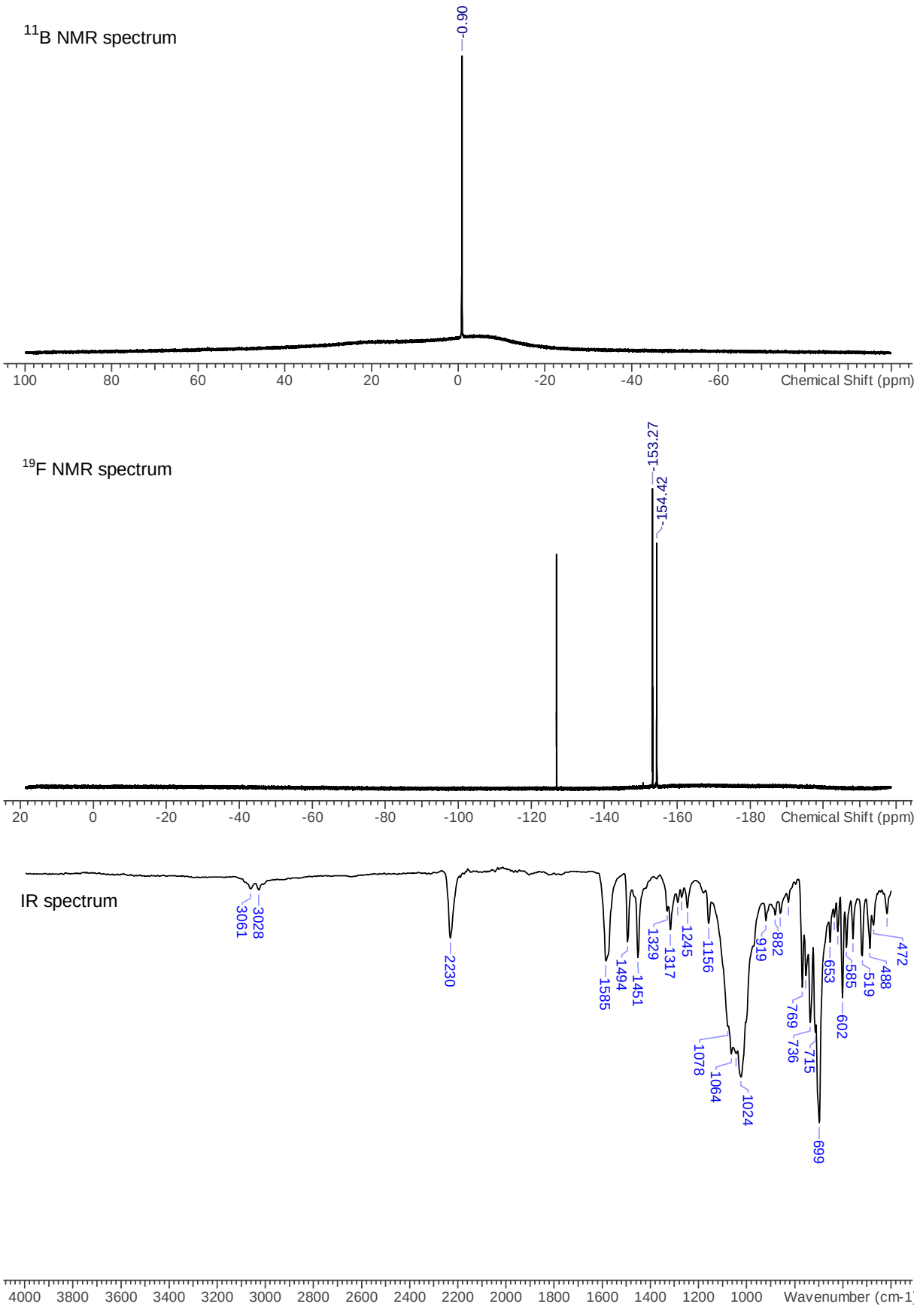


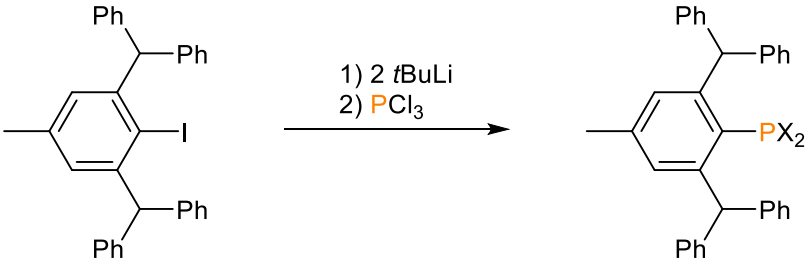
Figure S7 (continued).



2,6-Bis(benzhydryl)-4-methyl-phenylfluoride (**6Me**):

^{1}H NMR (THF-d_8, 300.1 MHz): δ = 2.10 (s, 3 H, *p*-C*H*$_3$), 5.76 (s, 2 H, C*H*Ph$_2$), 6.65 (d, 2 H, ^{4}J(^{1}H,^{19}F) = 7.00 Hz, *m*-H), 7.12 (m, 20 H, Ph). ^{13}C{^{1}H} NMR (THF-d_8, 125.8 MHz): δ = 21.2 (s, *p*-*C*H$_3$), 50.6 (s, *C*HPh$_2$), 127.3 (s, *p*-C (Ph)), 129.2 (s, *o*-C (Ph)), 130.3 (s, *m*-C (Ph)), 130.5 (s, *m*-C), 131.8 (d, ^{2}J(^{13}C,^{19}F) = 16 Hz, *o*-C), 133.6 (d, ^{4}J(^{13}C,^{19}F) = 5 Hz, *p*-C), 144.1 (s, *ipso*-C (Ph)), 158.0 (d, ^{1}J(^{13}C,^{19}F) = 246 Hz, *C*–F). ^{11}B NMR (THF-d_8, 160.5 MHz): δ = –0.8 (s, *B*F$_3$·THF). ^{19}F NMR (THF-d_8, 282.4 MHz): δ = –127.0 (t, 1 F, ^{4}J(^{19}F,^{1}H) = 7 Hz, C–F). MS (EI, 70 eV, m/z): 442 ([M]$^+$, 100 %), 275 ([M –CHPh$_2$]$^+$, 97 %), 167 ([CHPh$_2$]$^+$, 60 %).

2,6-Bis(benzhydryl)-4-methyl-phenyldihalophosphane (^{Me}Bhp–PX$_2$, X = Cl, I, **7Me**)



A 250 mL Schlenk flask containing 2,6-bis(benzhydryl)-4-methyl-phenyliodide (5.70 g, 10.4 mmol) and a stir bar is degassed and flushed with argon three times. After adding anhydrous tetrahydrofuran (50 mL), the colorless solution is cooled to and kept at –80 °C, whereupon a 1.7 M solution of *tert*-butyllithium in pentane (12.2 mL, 20.7 mmol) is added dropwise. The resulting red mixture is then stirred for 30 min. Afterwards, phosphorus trichloride (2.3 mL, 26.3 mmol) is quickly added *via* syringe, turning the mixture instantly yellow. Stirring at low temperature is continued for two hours and concluded by removing volatiles *in vacuo*. The red solid is then dissolved in anhydrous dichloromethane and the resulting suspension is filtered over a celite-packed frit. Volatiles are removed *in vacuo*, leaving a mixture of dihalophosphanes (percentage by ^{31}P NMR: ^{Me}Bhp–PCl$_2$ 62.1 %, ^{Me}Bhp–PClI 31.1 %, ^{Me}Bhp–PI$_2$ 3.7 %). Single-crystals were obtained from a mixture of dichloromethane and *n*-pentane. Yield: 5.08 g (9.1 mmol, 87.5 %).

Mp.: 175-180 °C. CHN calcd. (exptl.) in %: C 68.94 (65.21), H 4.73 (4.77). ^{1}H NMR (CD$_2$Cl$_2$, 300.1 MHz): δ = 2.17 (s, 3 H, *p*-C*H*$_3$), 6.76 (m, 4 H, C*H*Ph$_2$ + *m*-H), 7.22 (m, 20 H, Ph). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 75.5 MHz): δ = 22.0-22.2 (s, *p*-*C*H$_3$), 53.9-54.6 (s, *C*HPh$_2$), 127.0-127.1 (s, *p*-C (Ph)), 128.8-128.9 (s, *o*-C (Ph)), 130.5-130.7 (s, *m*-C (Ph)), 131.9 (s, *m*-C), 143.1-143.9 (s, *ipso*-C (Ph)

+ *C*–CH_3), 149.4-149.7 (s, *o*-C), *C*–P not observed. ^{31}P NMR (CD_2Cl_2, 121.5 MHz): δ = 76.7 (s, 1 P, ^{Me}Bhp–*P*I_2), 128.9 (s, 1 P, ^{Me}Bhp–*P*ClI), 157.6 (s, 1P, ^{Me}Bhp–*P*Cl_2). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3083 (vw), 3056 (w), 3025 (w), 1947 (vw), 1877 (vw), 1803 (vw), 1597 (w), 1583 (w), 1552 (w), 1494 (m), 1449 (w), 1409 (w), 1337 (w), 1276 (w), 1241 (w), 1201 (w), 1179 (w), 1156 (w), 1076 (w), 1045 (w), 1030 (w), 1001 (w), 911 (w), 882 (w), 855 (w), 847 (w), 822 (w), 781 (vw), 762 (m), 744 (m), 694 (vs), 645 (m), 633 (m), 620 (m), 604 (m), 544 (m), 525 (m), 484 (s), 468 (vs), 449 (s). Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3060 (1), 2918 (1), 1599 (3), 1376 (1), 1239 (1), 1163 (1), 1044 (2), 1033 (1), 1005 (3), 989 (1), 635 (1), 527 (1), 486 (1), 450 (1), 395 (1), 337 (1), 308 (1), 246 (1), 227 (2), 218 (1), 206 (1), 148 (1), 138 (2). MS (EI, 70 eV, m/z): 524 ([^{Me}Bhp–PCl_2]$^+$, 28 %), 489 ([^{Me}Bhp–PCl]$^+$, 54 %), 454 ([^{Me}Bhp–P]$^+$, 46 %).

Figure S8. NMR, IR and Raman spectra of **7Me** (solvent signals marked by asterisk).

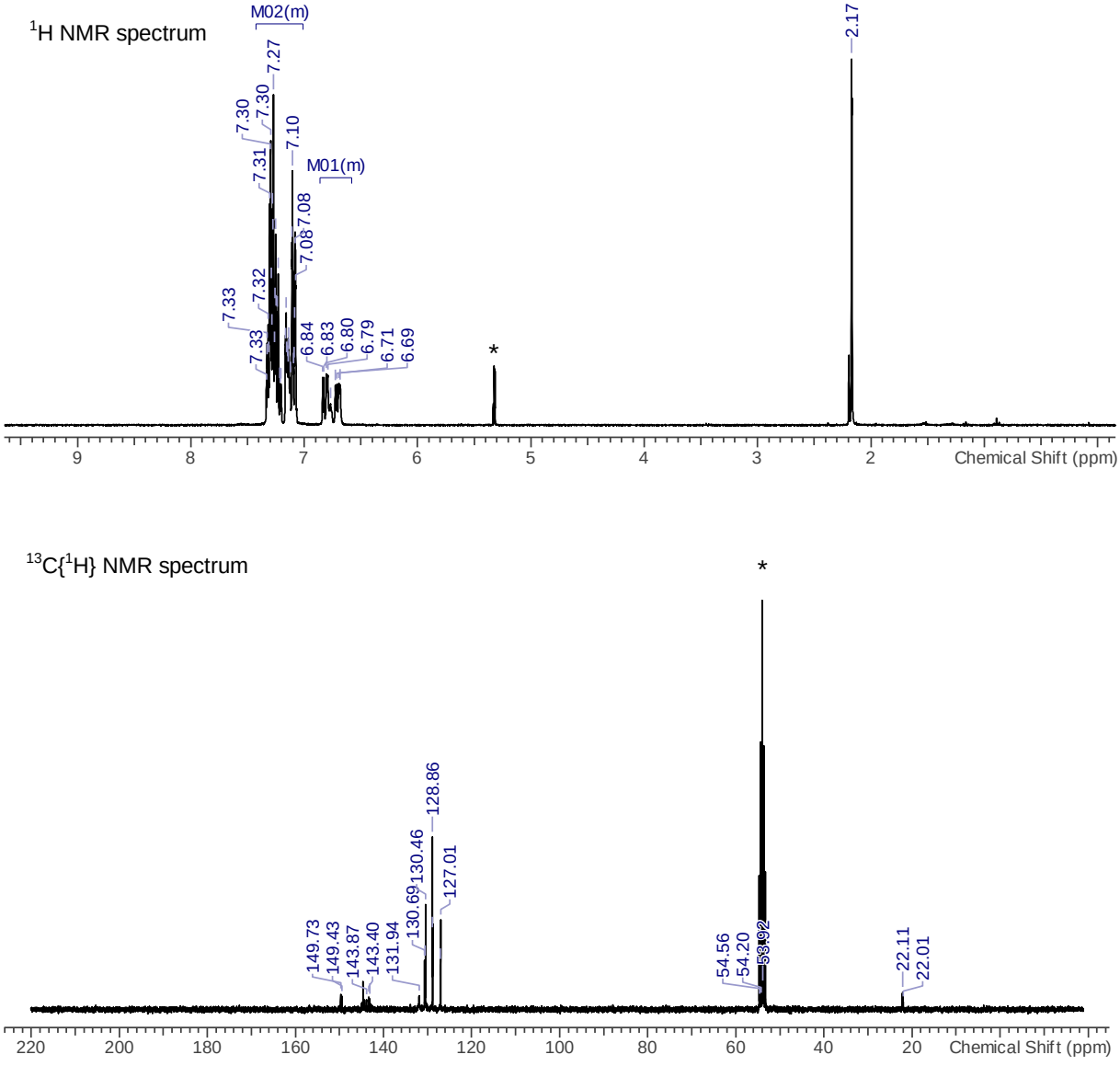
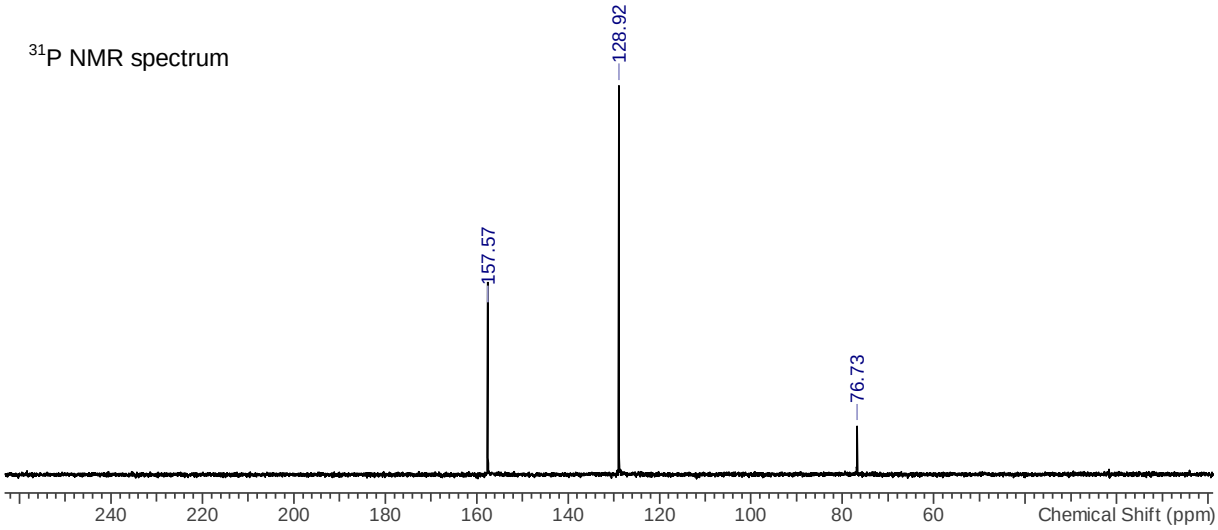
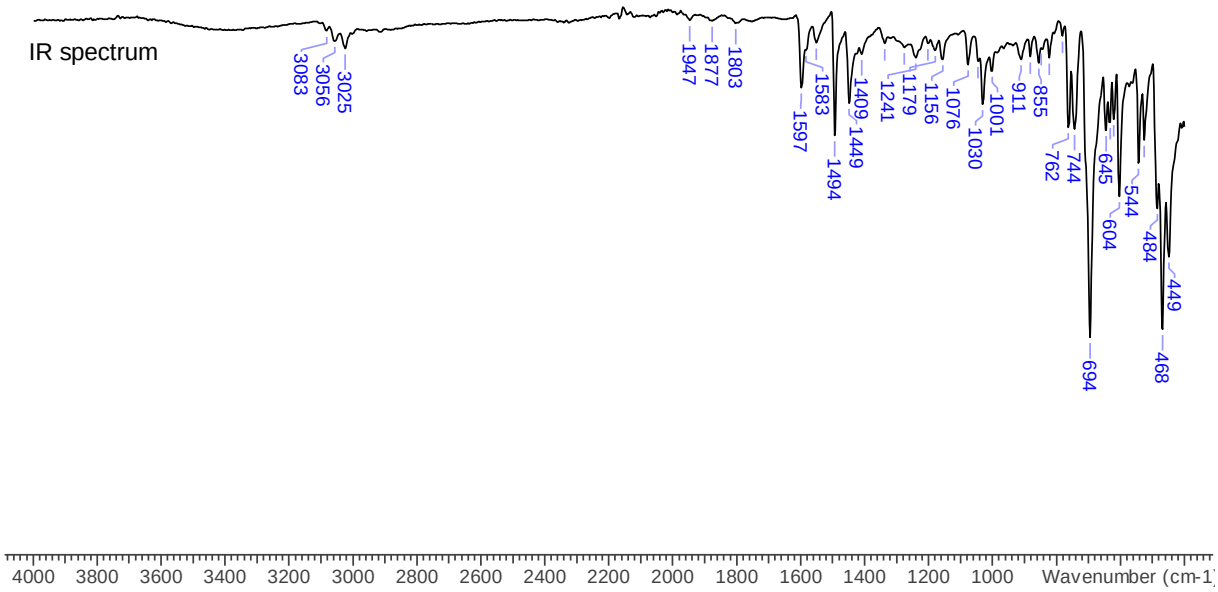
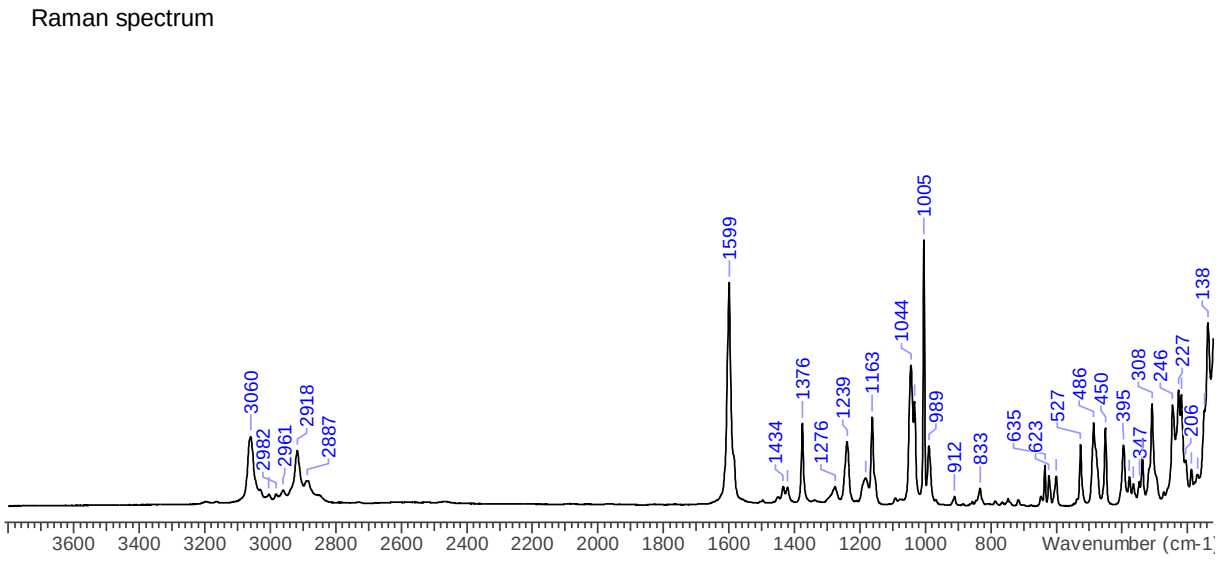


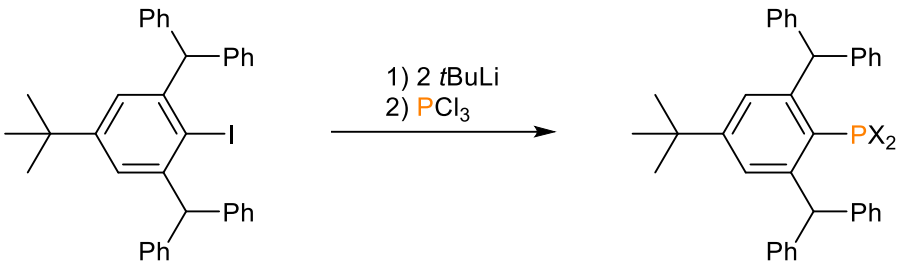
Figure S8 (continued).







2,6-Bis(benzhydryl)-4-*tert*-butyl-phenyldihalophosphane ($^{t\text{Bu}}$Bhp−PX_2, X = Cl, I, **7*t*Bu**)



A 100 mL Schlenk flask containing 2,6-bis(benzhydryl)-4-*tert*-butyl-phenyliodide (5.38 g, 9.1 mmol) and a stir bar is degassed and flushed with argon three times. After adding anhydrous tetrahydrofuran (50 mL), the colorless solution is cooled to and kept at −80 °C, whereupon a 1.7 M solution of *tert*-butyllithium in pentane (10.7 mL, 18.2 mmol) is added dropwise. The resulting red mixture is then stirred for 30 min. Afterwards, phosphorus trichloride (2.3 mL, 26.3 mmol) is quickly added *via* syringe, turning the mixture instantly yellow. Stirring at low temperature is continued for two hours and concluded by removing volatiles *in vacuo*. The red solid is then dissolved in anhydrous dichloromethane and the resulting suspension is filtered over a celite-packed frit. Volatiles are removed *in vacuo*, leaving a mixture of dihalophosphanes (percentage by ^{31}P NMR: $^{t\text{Bu}}$Bhp−PCl_2 55.4 %, $^{t\text{Bu}}$Bhp−PClI 44.6 %, $^{t\text{Bu}}$Bhp−PI_2 not observed). Single-crystals were obtained from a mixture of dichloromethane and *n*-pentane. Yield: 4.93 g (8.1 mmol, 89.3 %).

CHN calcd. (exptl.) in %: C 71.08 (67.75), H 5.47 (5.73). ^{1}H NMR (CD_2Cl_2, 500.1 MHz): δ = 1.03-1.05 (s, 9 H, *p*-*t*Bu), 6.74 (d, 2 H, $^4J(^1H,^{31}P)$ = 3.4 Hz, C*H*Ph_2), 7.21 (m, 22 H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ = 30.8-31.6 (s, C(*C*H_3)$_3$), 34.6-35.4 (s, *C*$(CH_3)_3$), 57.6 (s, *C*HPh_2), 126.7-127.3 (s, *p*-C (Ph)), 128.5-128.9 (s, *o*-C (Ph)), 129.8-130.1 (s, *m*-C (Ph)), 130.4-130.7 (s, *m*-C), 144.8 (s, *C*–*t*Bu), 149.1-149.4 (s, *ipso*-C (Ph)), 155.5-155.8 (s, *o*-C), *C*–P not observed. ^{31}P NMR (CD_2Cl_2, 202.5 MHz): δ = 128.8 (s, 1 P, $^{t\text{Bu}}$Bhp−*P*ClI), 157.4 (s, 1P, $^{t\text{Bu}}$Bhp−*P*Cl_2). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3083 (vw), 3056 (w), 3025 (w), 2965 (w), 2866 (w), 1945 (vw), 1875 (vw), 1801 (vw), 1597 (m), 1583 (w), 1541 (w), 1492 (m), 1449 (m), 1409 (w), 1362 (w), 1249 (w), 1195 (w), 1183 (w), 1078 (w), 1030 (m), 946 (w), 911 (w), 894 (w), 826 (w), 764 (m), 742 (m), 696 (vs), 643 (m), 628 (w), 620 (m), 604 (m), 585 (m), 532 (m), 509 (w), 472 (vs), 443 (m). Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3055 (2), 2968 (1), 2952 (1), 2907 (1), 2891 (1), 1599 (5), 1583 (1), 1429 (1), 1203 (1), 1194 (1), 1170 (2), 1154 (1), 1041 (3), 1030 (2), 1001 (5), 832 (1), 620 (1), 531 (1), 480 (3), 466 (1), 415 (1), 379 (1), 329 (1), 248 (1), 230 (1), 219 (1), 212 (2), 186 (1),

157 (1), 146 (2), 123 (3). MS (EI, 70 eV, m/z): 566 ([$^{t\mathrm{Bu}}$Bhp−PCl_2]$^+$, 74 %), 531 ([$^{t\mathrm{Bu}}$Bhp−PCl]$^+$, 98 %), 496 ([$^{t\mathrm{Bu}}$Bhp−P]$^+$, 40 %), 466 ([$^{t\mathrm{Bu}}$Bhp]$^+$, 42 %), 167 ([$CHPh_2$]$^+$, 100 %).

Figure S9. NMR, IR and Raman spectra of **7*t*Bu** (solvent signals marked by asterisk).

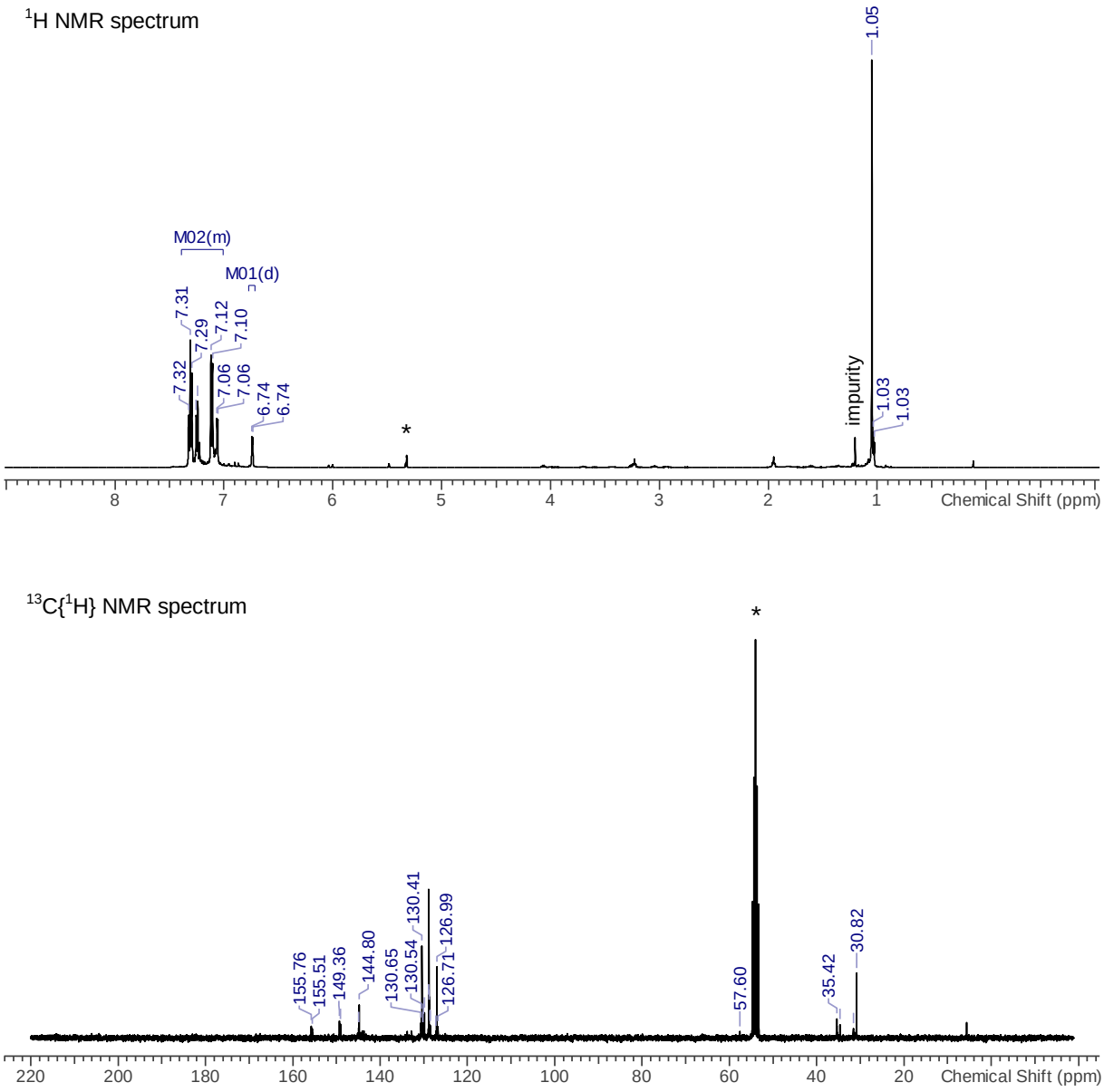
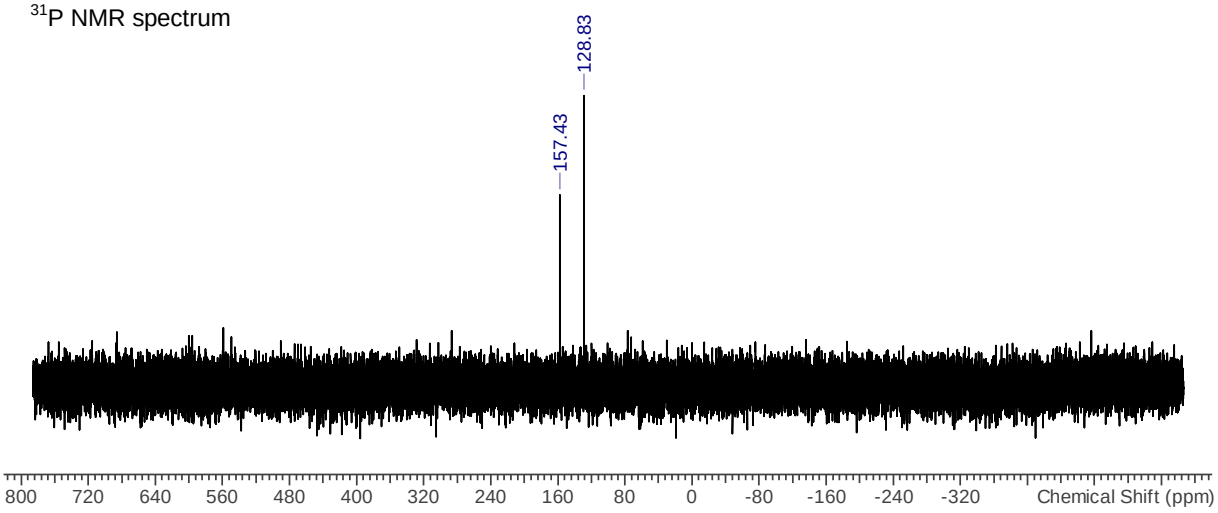
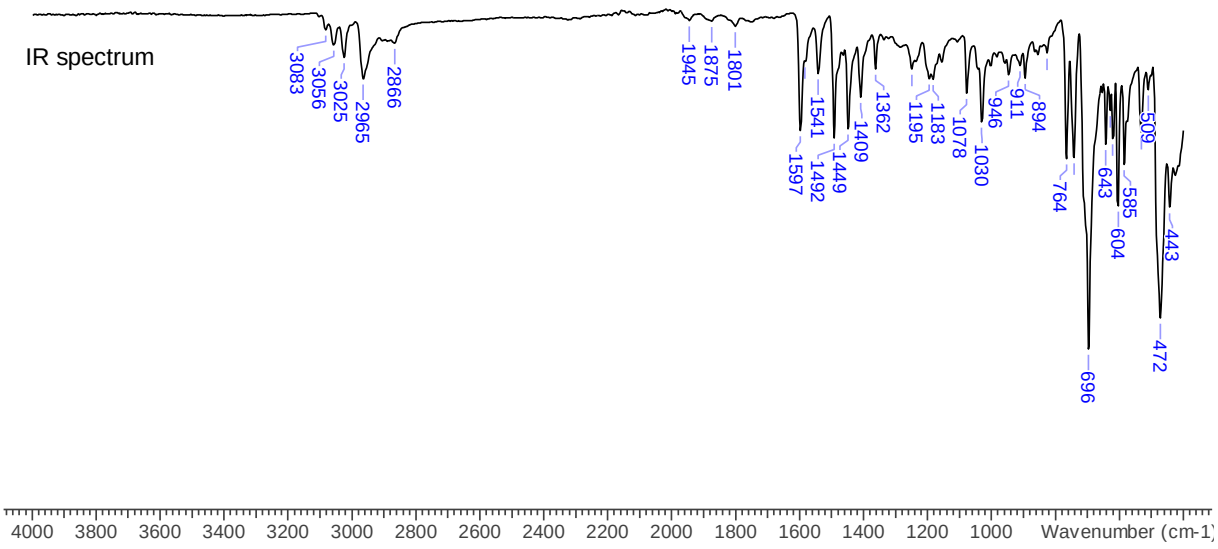


Figure S9 (continued).

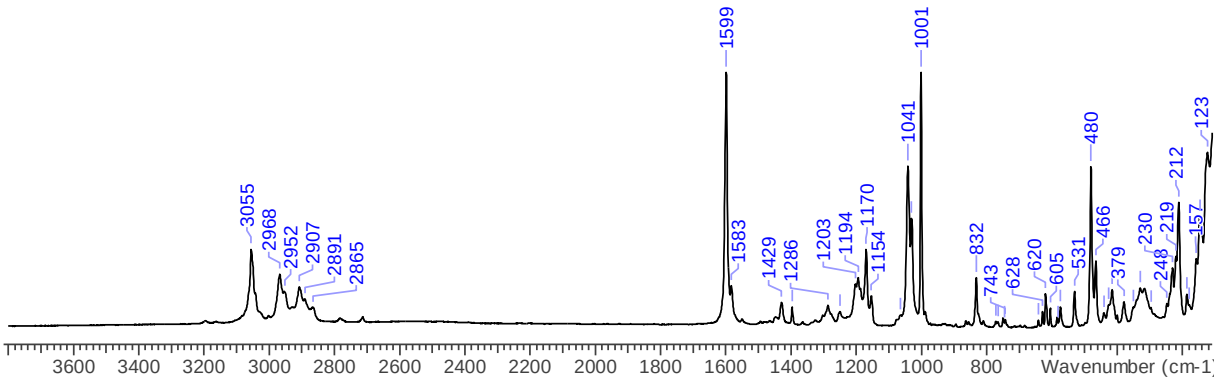
^{31}P NMR spectrum



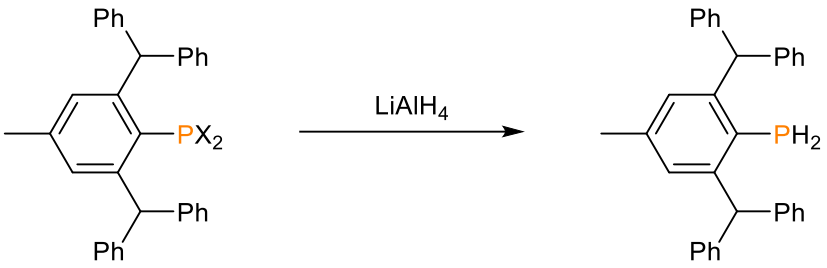
IR spectrum



Raman spectrum



2,6-Bis(benzhydryl)-4-methyl-phenylphosphane (^{Me}Bhp−PH_2, **8Me**)



In a 500 mL Schlenk flask, a solution of 2,6-bis(benzhydryl)-4-methyl-phenyldihalophosphane (2.34 g, 4.2 mmol) in anhydrous tetrahydrofuran (20 mL) is added to a suspension of lithium aluminium hydride (0.35 g, 9.2 mmol) in anhydrous tetrahydrofuran (20 mL) at 0 °C and left stirring at ambient temperature overnight. Afterwards, the mixture is carefully quenched with water (100 mL) and dried *in vacuo*. The residue is dissolved in dichloromethane (100 mL) and filtered. The filtrate is washed twice with water, dried over magnesium sulfate and decanted. The work-up should be carried out without delays to circumvent formation of phosphane oxides. Volatiles are removed at the rotary evaporator, leaving a colorless solid, which is eventually dried at 10^{-3} mbar. Single-crystals were obtained from a mixture of dichloromethane and *n*-pentane. Yield: 1.32 g (2.9 mmol, 69.0 %).

Mp.: 156-158 °C. CHN calcd. (exptl.) in %: C 86.81 (86.55), H 6.40 (6.14). ^{1}H NMR (CD_2Cl_2, 500.1 MHz): δ = 2.10 (s, 3 H, *p*-CH_3), 3.58 (d, 2 H, $^1J(^1H,^{31}P)$ = −210 Hz, PH_2), 5.98 (d, 2 H, $^4J(^1H,^{31}P)$ = 3.1 Hz, CHPh$_2$), 6.65 (s, 2 H, *m*-H), 7.20 (m, 20 H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ = 21.8 (s, *p*-CH$_3$), 55.8 (d, $^3J(^{13}C,^{31}P)$ = 11 Hz, CHPh$_2$), 126.5 (s, *p*-C (Ph)), 128.3 (s, *o*-C (Ph)), 128.5 (d, $^3J(^{13}C,^{31}P)$ = 4 Hz, *m*-C), 130.2 (s, *m*-C (Ph)), 138.5 (s, C−CH$_3$), 144.2 (s, *ipso*-C (Ph)), 148.8 (d, $^2J(^{13}C,^{31}P)$ = 11 Hz, *o*-C), C−P not observed. ^{31}P NMR (CD_2Cl_2, 202.5 MHz): δ = −155.2 (t, 1 P, $^1J(^{31}P,^1H)$ = −212 Hz, PH$_2$). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3083 (vw), 3058 (vw), 3023 (vw), 2916 (vw), 2320 (vw), 2310 (w), 1597 (w), 1583 (vw), 1552 (vw), 1492 (w), 1449 (w), 1436 (w), 1179 (vw), 1154 (vw), 1094 (w), 1076 (w), 1030 (w), 1004 (w), 968 (w), 911 (w), 882 (vw), 851 (w), 837 (w), 818 (w), 783 (w), 762 (w), 744 (m), 736 (w), 696 (vs), 643 (w), 620 (m), 604 (m), 536 (w), 509 (w), 476 (w), 445 (w). Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3058 (3), 3001 (1), 2978 (1), 2920 (1), 2302 (1), 1600 (2), 1584 (1), 1556 (1), 1495 (1), 1453 (1), 1379 (1), 1297 (1), 1244 (1), 1180 (2), 1164 (1), 1157 (1), 1077 (1), 1053 (1), 1031 (3), 1004 (10), 985 (2), 918 (1), 866 (1), 833 (1), 786 (1), 748 (1), 637 (1), 620 (1), 608 (1), 598 (1), 539 (1), 495 (1), 372 (1), 293

(1), 269 (1), 242 (1), 163 (2). MS (EI, 70 eV, m/z): 456 ([M]$^+$, 57 %), 455 ([M –H]$^+$, 100 %), 422 ([M –PH_3]$^+$, 18 %), 167 ([$CHPh_2$]$^+$, 31 %).

Figure S10. NMR, IR and Raman spectra of **8Me** (solvent signals marked by asterisk).

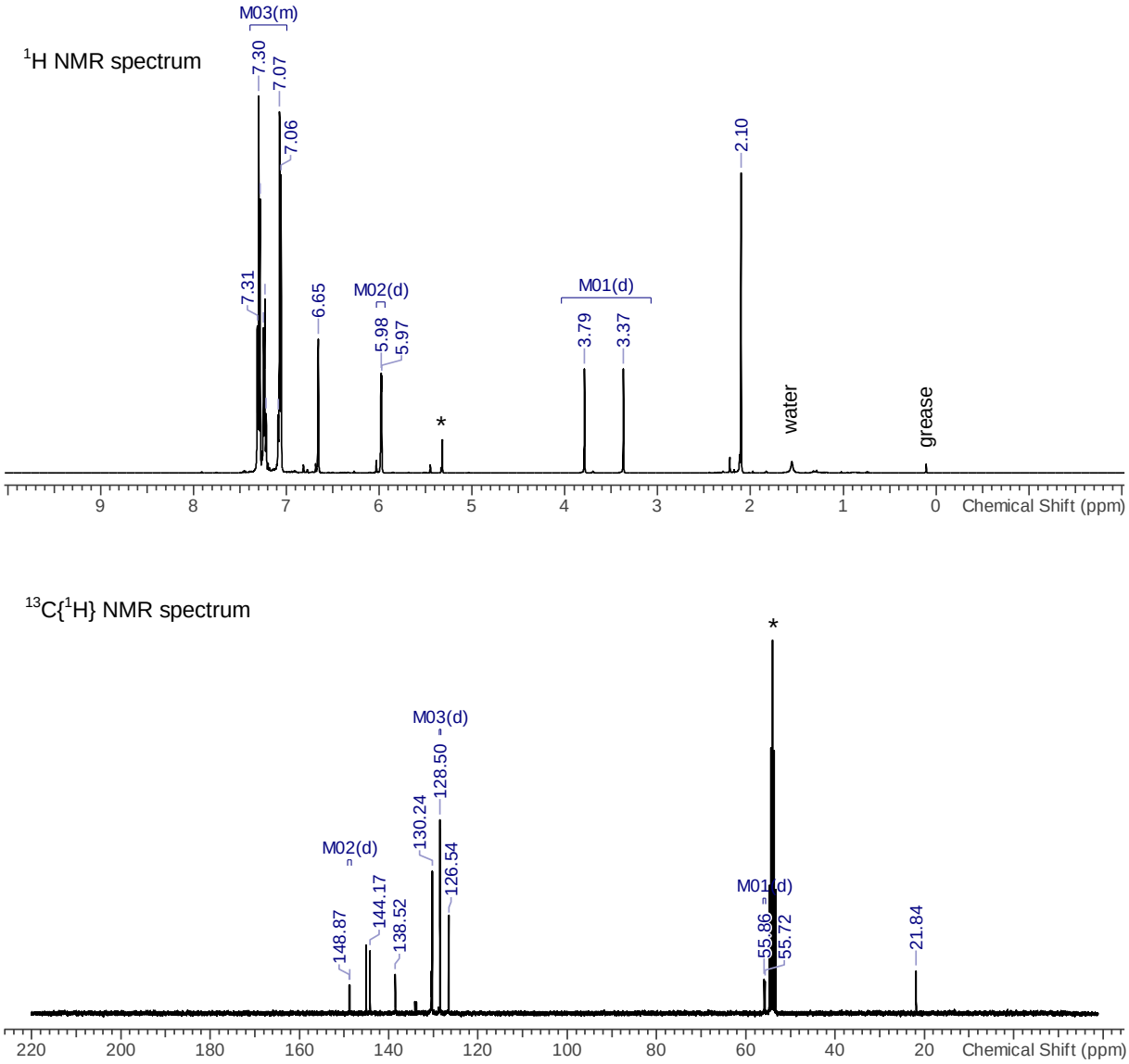
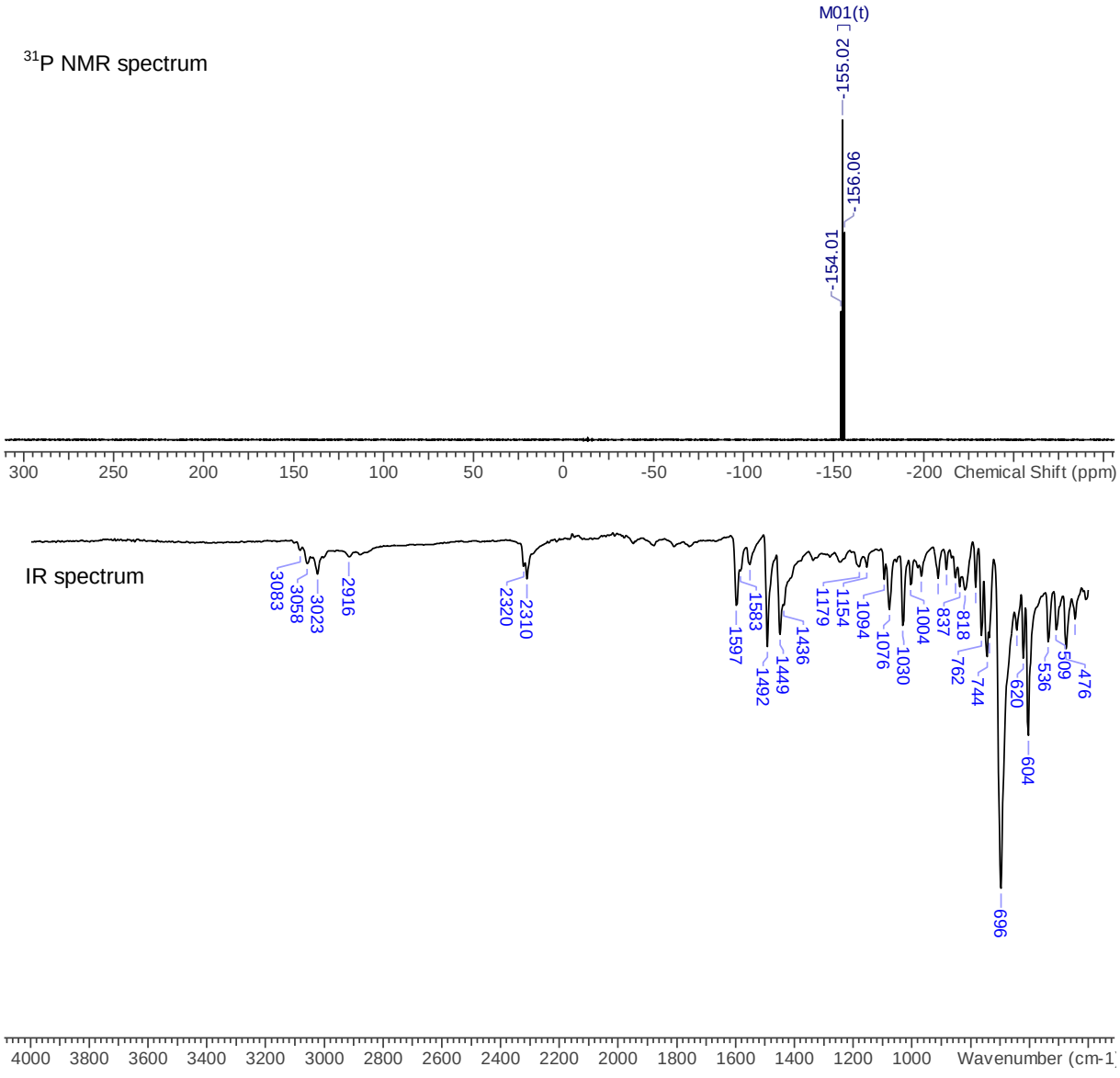
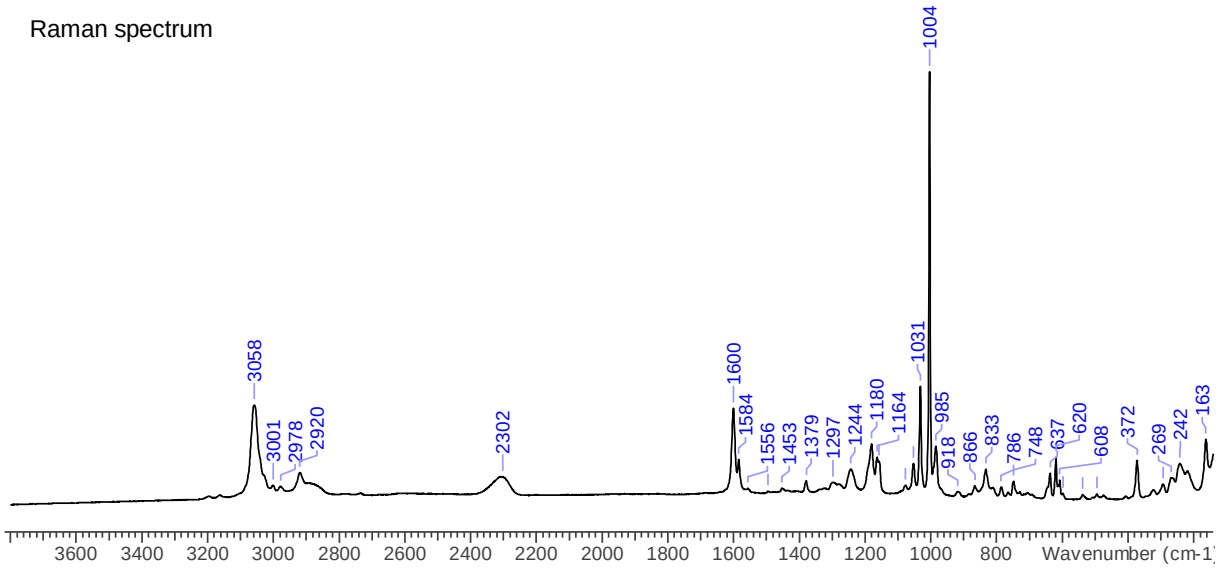
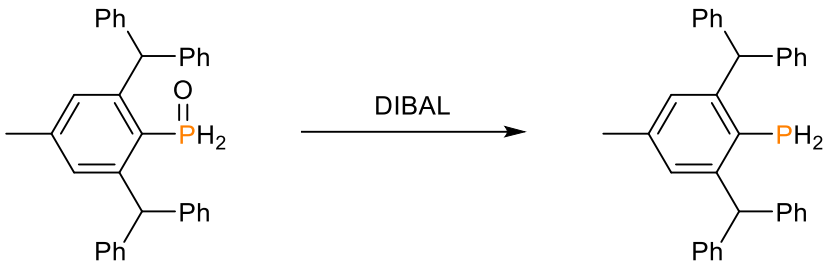


Figure S10 (continued).





Reduction of 2,6-bis(benzhydryl)-4-methyl-phenylphosphane oxide (^{Me}Bhp–P(O)H$_2$)



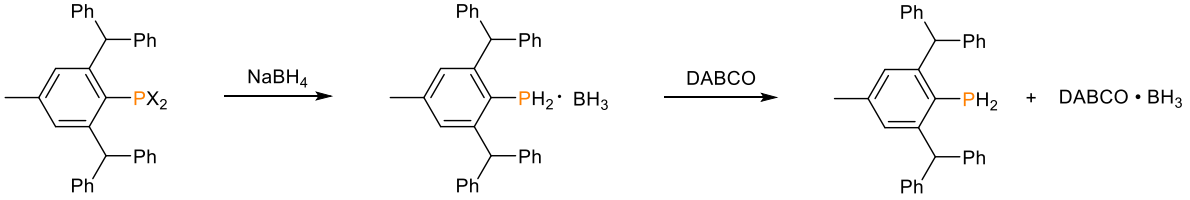
The reduction was carried out according to a modified protocol by Busacca *et al*.[10]

A mixture of 2,6-bis(benzhydryl)-4-methyl-phenylphosphane oxide and 2,6-bis(benzhydryl)-4-methyl-phenylphosphane (3.00 g, 81 % ^{Me}Bhp–PH$_2$ and 19 % ^{Me}Bhp–P(O)H$_2$) is placed in a Schlenk tube, equipped with a stir bar and pressure release valve. After degassing the tube and flushing with argon three times, anhydrous tetrahydrofuran (30 mL) is added, resulting in a white suspension. Afterwards, a 1.0 M solution of diisobutylaluminium hydride in hexane (5.5 mL, 5.5 mmol) is added dropwise at 0 °C with visible gas formation. The mixture is subsequently stirred at ambient temperature for 2 days. Afterwards, the mixture is carefully quenched with water and dried *in vacuo*. The residue is dissolved in dichloromethane and filtered. The filtrate is washed twice with water, dried over magnesium sulfate and decanted. Volatiles are removed at the rotary evaporator. The crude product is eventually recrystallized from dichloromethane/*n*-pentane. Yield: 2.16 g.

(The following NMR data relates to the starting material.)

^{31}P NMR (THF-d$_8$, 121.5): δ = −13.3 (t, 1 P, $^1J(^{31}P,^1H)$ = −486 Hz, *P*(O)H$_2$).

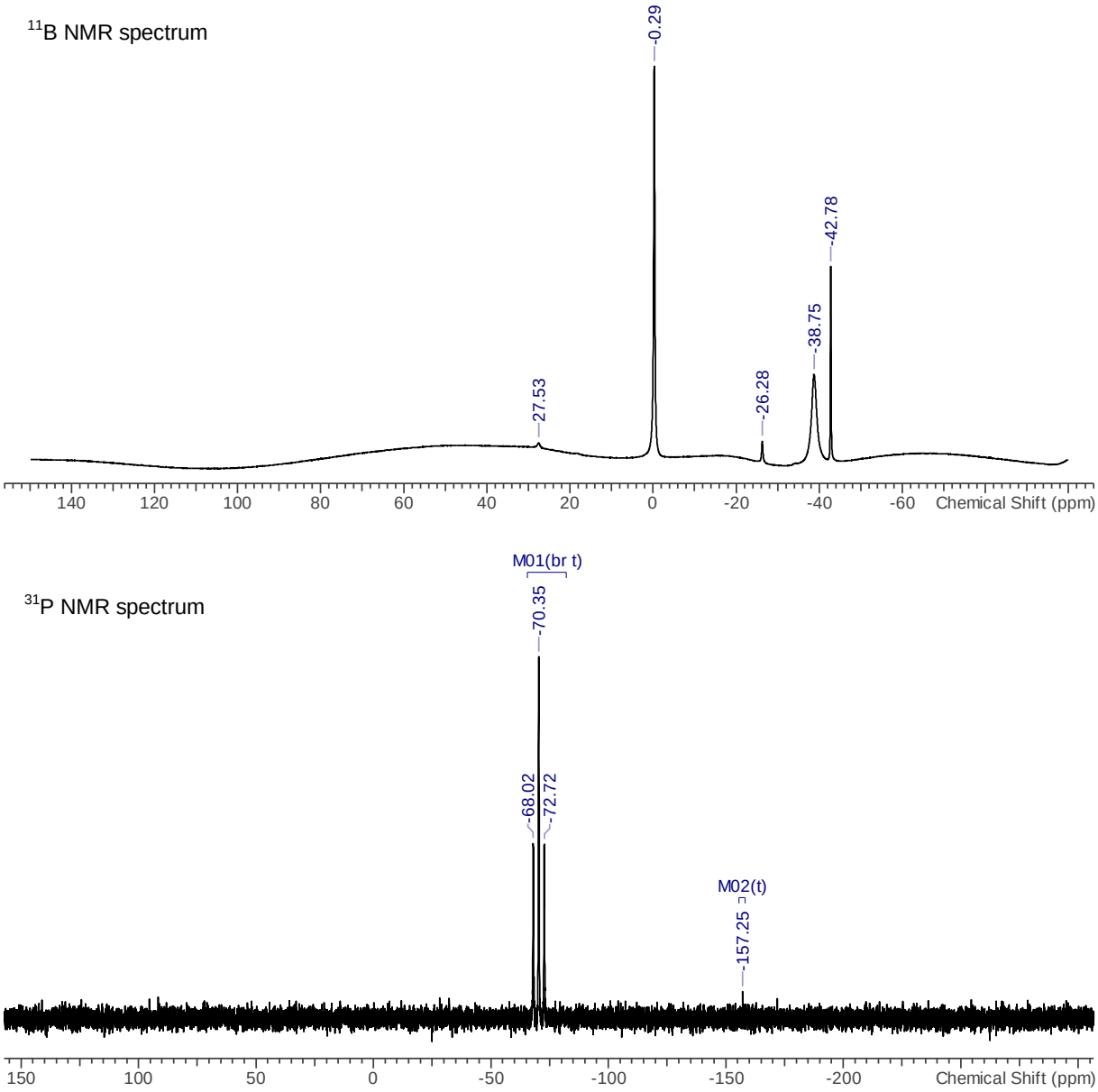
2,6-Bis(benzhydryl)-4-methyl-phenylphosphane monoborane adduct (^{Me}Bhp–PH$_2$·BH$_3$)



In a glovebox, 2,6-bis(benzhydryl)-4-methyl-phenyldihalophosphane (23 mg, 0.04 mmol) and sodium borohydride (3 mg, 0.08 mmol) are placed in an NMR tube. After adding deuterated tetrahydrofuran (0.5 mL), the tube is sealed and sonicated for 10 min, whereupon the solution turns colorless and a white precipitate is formed. The product was not isolated and the product mixture was used for NMR measurements.

$^{11}B\{^{1}H\}$ NMR (THF-d_8, 128.4): δ = −42.8 (s, Na*B*H_4), −38.8 (s, PH_2·*B*H_3), −26.3 (s), −0.3 (s, THF·*B*H_3), 27.5 (s). ^{31}P NMR (THF-d_8, 162.0): δ = −157.3 (t, 1 P, $^{1}J(^{31}P,^{1}H)$ = −213 Hz, *P*H_2), −70.4 (t, 1 P, $^{1}J(^{31}P,^{1}H)$ = −381 Hz, *P*H_2·BH_3).

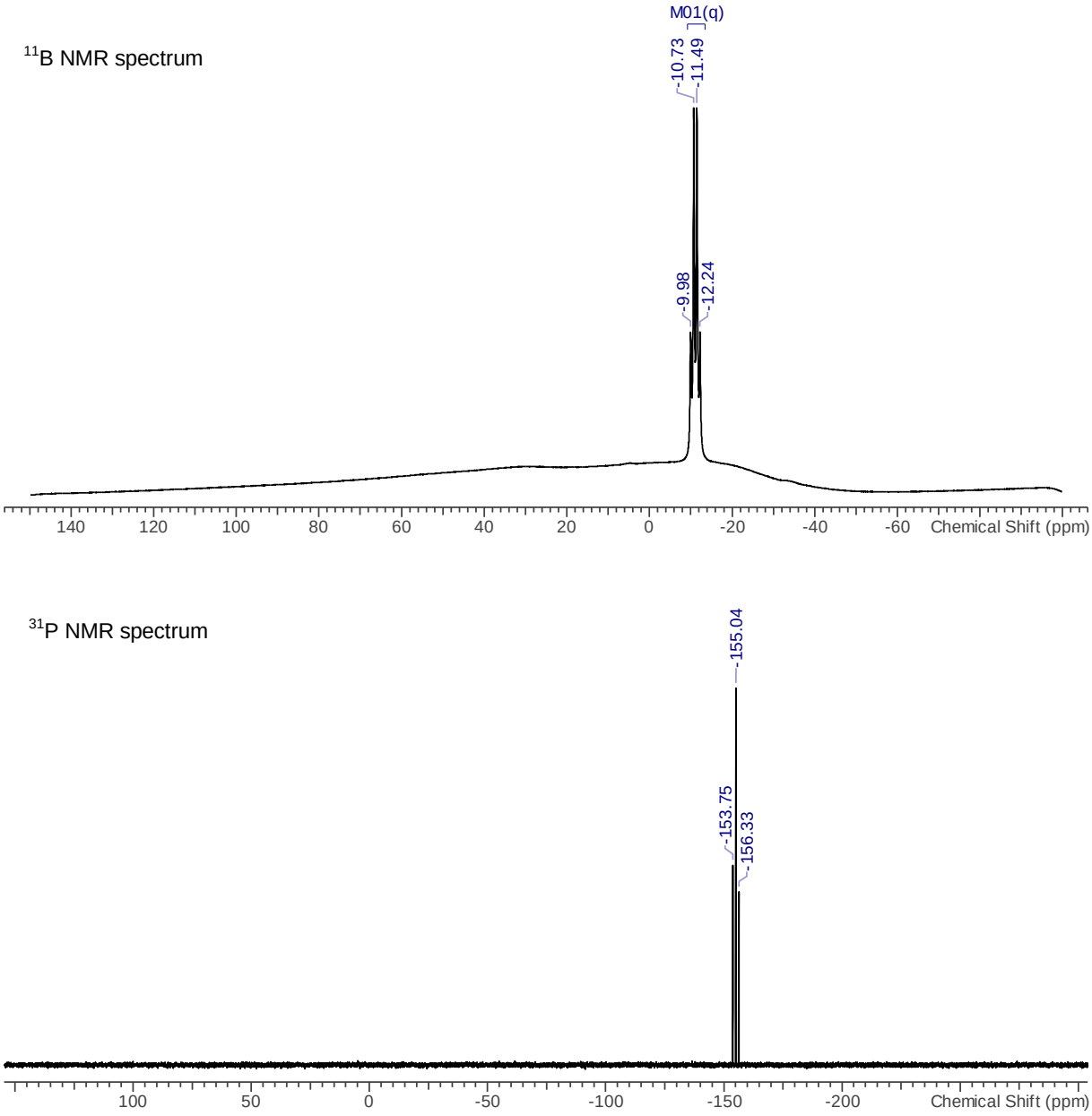
Figure S11. NMR spectra of ^{Me}Bhp−PH_2·BH_3.



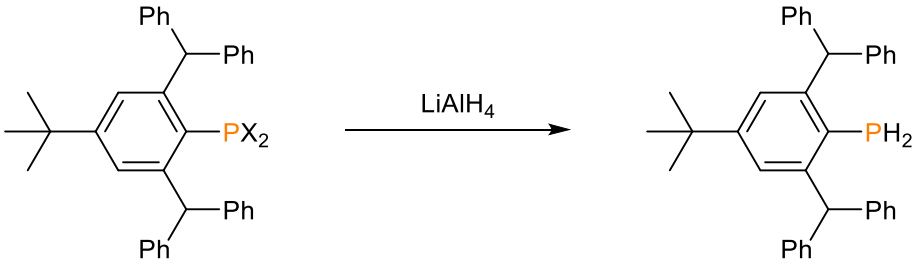
After measuring NMR spectra, a small spatula of 1,4-diazabicyclo[2.2.2]octane was added. The tube was sealed again, sonicated for 30 min and another set of measurements was carried out.

^{11}B NMR (THF-d_8, 128.4): δ = −11.1 (q, $^{1}J(^{11}B,^{1}H)$ = 97 Hz, DABCO·*B*H_3). ^{31}P NMR (THF-d_8, 162.0): δ = −155.0 (t, 1 P, $^{1}J(^{31}P,^{1}H)$ = −209 Hz, *P*H_2).

Figure S12. NMR spectra of ^{Me}Bhp−PH_2·BH_3 + DABCO.



2,6-Bis(benzhydryl)-4-*tert*-butyl-phenylphosphane ($^{t\text{Bu}}$Bhp−PH_2, **8*t*Bu**)



In a 250 mL Schlenk flask, a solution of 2,6-bis(benzhydryl)-4-*tert*-butyl-phenyldihalophosphane (4.28 g, 7.0 mmol) in anhydrous tetrahydrofuran (40 mL) is added to

a suspension of lithium aluminium hydride (0.80 g, 21.0 mmol) in anhydrous tetrahydrofuran (40 mL) at 0 °C and left stirring at ambient temperature overnight. Afterwards, the mixture is carefully quenched with water (150 mL) and dried *in vacuo*. The residue is dissolved in dichloromethane (100 mL) and filtered. The filtrate is washed twice with water, dried over magnesium sulfate and decanted. The work-up should be carried out without delays to circumvent formation of phosphane oxides. Volatiles are removed at the rotary evaporator, leaving a colorless solid, which is eventually dried at 10^{-3} mbar. Single-crystals were obtained from a mixture of toluene and *n*-pentane. Yield: 2.35 g (4.7 mmol, 67.0 %).

Mp.: 228-234 °C. CHN calcd. (exptl.) in %: C 86.71 (85.75), H 7.08 (6.89). ^{1}H NMR (CD_2Cl_2, 250.1 MHz): δ = 1.01 (s, 9 H, *p*-*t*Bu), 3.57 (d, 2 H, $^{1}J(^{1}H,^{31}P)$ = −210 Hz, PH_2), 5.98 (d, 2 H, $^{4}J(^{1}H,^{31}P)$ = 3.0 Hz, C*H*Ph_2), 6.86 (d, 2 H, $^{4}J(^{1}H,^{1}H)$ = 2.1 Hz, *m*-H), 7.07 (m, 8 H, Ph), 7.28 (m, 12 H, Ph). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 125.8 MHz): δ = 31.2 (s, C(CH_3)$_3$), 34.9 (s, *C*(CH_3)$_3$), 57.2 (d, $^{3}J(^{13}C,^{31}P)$ = 10 Hz, *C*HPh_2), 126.3 (s, *p*-C (Ph)), 126.9 (s, *o*-C (Ph)), 128.9 (s, *m*-C (Ph)), 130.3 (s, *m*-C), 144.3 (s, *C*–*t*Bu), 147.8 (d, $^{4}J(^{13}C,^{31}P)$ = 9 Hz, *ipso*-C (Ph)), 150.5 (s, *o*-C), *C*–P not observed. ^{31}P NMR (CD_2Cl_2, 101.3 MHz): δ = −155.5 (t, 1 P, $^{1}J(^{31}P,^{1}H)$ = −210 Hz, *P*H_2). IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3081 (vw), 3058 (vw), 3025 (w), 3000 (vw), 2961 (w), 2901 (vw), 2862 (vw), 2326 (vw), 1807 (vw), 1595 (w), 1541 (vw), 1490 (w), 1475 (w), 1449 (w), 1405 (w), 1362 (w), 1337 (vw), 1247 (w), 1203 (vw), 1156 (w), 1096 (vw), 1076 (w), 1030 (w), 1004 (w), 944 (vw), 915 (w), 892 (w), 828 (vw), 808 (vw), 764 (m), 746 (m), 732 (w), 699 (vs), 639 (w), 620 (m), 604 (m), 583 (w), 507 (w), 474 (w), 414 (w). Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3054 (4), 3002 (1), 2972 (1), 2923 (1), 2908 (1), 2864 (1), 2329 (2), 1598 (3), 1583 (2), 1450 (1), 1322 (1), 1297 (1), 1247 (2), 1188 (2), 1181 (2), 1174 (3), 1156 (2), 1075 (1), 1050 (2), 1031 (3), 1003 (10), 944 (1), 869 (1), 837 (1), 772 (1), 748 (1), 647 (1), 640 (1), 632 (1), 618 (2), 246 (2), 238 (2). MS (EI, 70 eV, m/z): 498 ($[M]^+$, 92 %), 497 ($[M-H]^+$, 100 %), 167 ($[CHPh_2]^+$, 10 %).

Figure S13. NMR, IR and Raman spectra of **8*t*Bu** (solvent signals marked by asterisk).

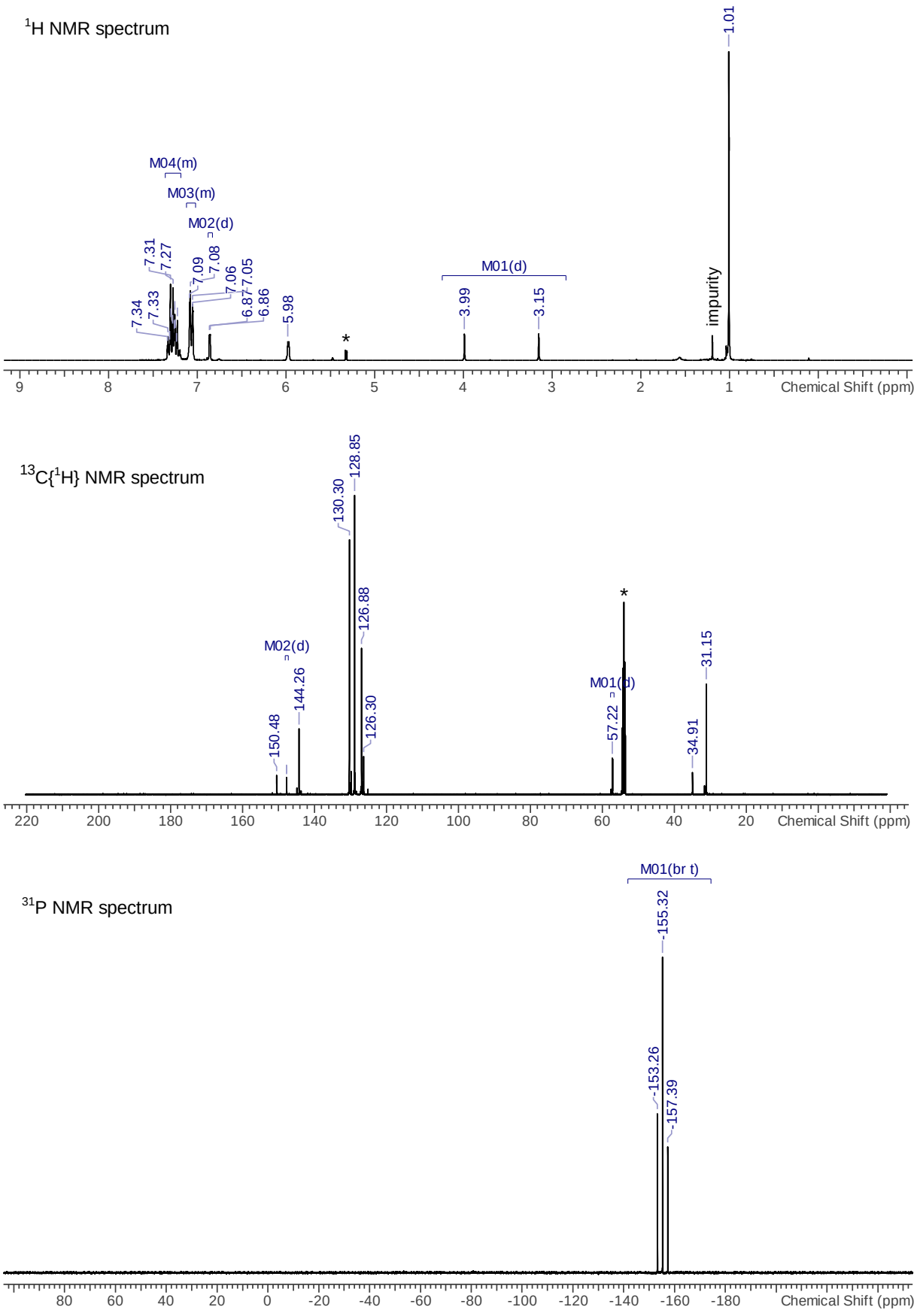
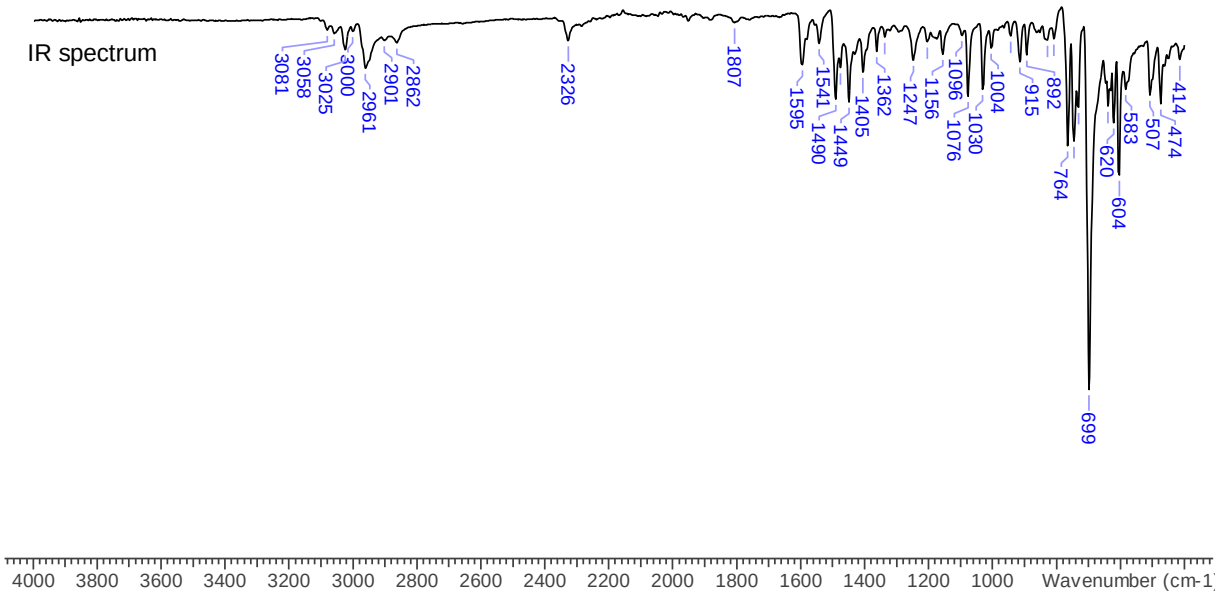
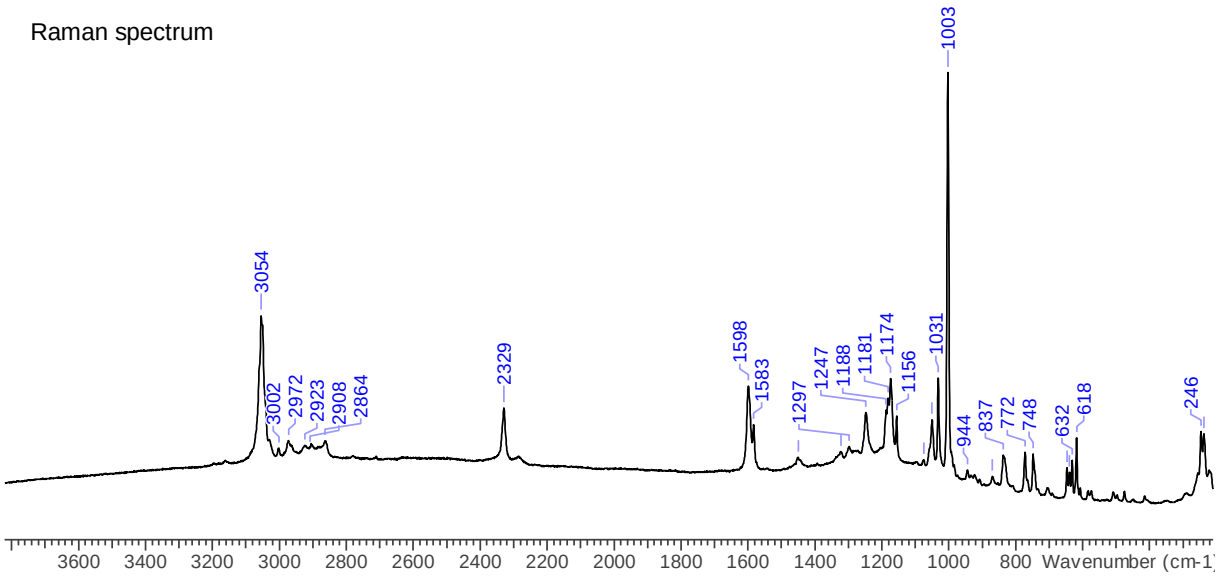
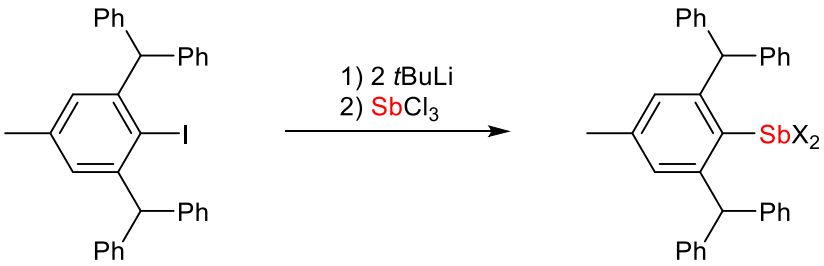


Figure S13 (continued).





2,6-Bis(benzhydryl)-4-methyl-phenyldihalostibane (^{Me}Bhp−SbX_2, X = Cl, I, **10Me**)



A 50 mL Schlenk flask containing 2,6-bis(benzhydryl)-4-methyl-phenyliodide (0.18 g, 0.3 mmol) and a stir bar is degassed and flushed with argon three times. After adding anhydrous

tetrahydrofuran (3 mL), the colorless solution is cooled to and kept at −80 °C, whereupon a 1.7 M solution of *tert*-butyllithium in pentane (0.4 mL, 0.7 mmol) is added dropwise. The resulting red mixture is then stirred for 30 min. Afterwards, a solution of antimony trichloride (0.19 g, 0.8 mmol) in anhydrous tetrahydrofuran (2 mL) is quickly added *via* syringe, turning the mixture instantly brown/dark yellow. Stirring at low temperature is continued for two hours and concluded by removing volatiles *in vacuo*. The dark solid is then dissolved in anhydrous dichloromethane and the resulting suspension is filtered over a celite-packed frit. Filtration is repeated whenever non-crystalline solids are formed. Single-crystals were obtained from a mixture of dichloromethane and *n*-pentane. Yield: undetermined.

Mp.: 232 °C. ^{1}H NMR (CD_2Cl_2, 300.1 MHz): δ = 2.12 (s, 3 H, *p*-C*H*$_3$), 6.45 (s, 2 H, C*H*Ph$_2$), 6.76 (s, 2 H, *m*-H) 7.24 (m, 20 H, Ph). ^{13}C{^{1}H} NMR (CD_2Cl_2, 100.6 MHz): δ = 22.0 (s, *p*-*C*H$_3$), 56.4 (s, *C*HPh$_2$), 127.5 (s, *p*-C (Ph)), 129.2 (s, *m*-C (Ph)), 131.0 (s, *o*-C (Ph)), 131.7 (s, *m*-C), 141.4 (s, *C*−CH$_3$), 144.4 (s, *ipso*-C (Ph)), 151.3 (s, *o*-C), *C*−Sb not observed. IR (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3084 (w), 3061 (w), 3048 (w), 3024 (w), 2999 (w), 2947 (w), 2879 (w), 1948 (vw), 1880 (vw), 1810 (vw), 1754 (vw), 1593 (w), 1492 (m), 1447 (m), 1402 (w), 1261 (w), 1181 (w), 1154 (w), 1076 (w), 1031 (m), 1002 (w), 913 (w), 884 (w), 855 (w), 783 (w), 765 (m), 742 (m), 717 (m), 697 (vs), 637 (w), 627 (m), 620 (m), 604 (m), 569 (w), 536 (m), 507 (w), 495 (w), 470 (m), 449 (w). Raman (633 nm, 20 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3193 (1), 3158 (1), 3064 (3), 3056 (3), 3029 (1), 3003 (1), 2982 (1), 2949 (1), 2922 (1), 2878 (1), 1594 (2), 1582 (1), 1451 (1), 1410 (1), 1384 (1), 1340 (1), 1325 (1), 1299 (1), 1264 (1), 1245 (1), 1237 (1), 1228 (1), 1191 (1), 1178 (1), 1161 (2), 1034 (2), 1004 (9), 993 (1), 987 (2), 919 (1), 887 (1), 856 (1), 835 (1), 786 (1), 748 (1), 722 (1), 638 (1), 621 (1), 618 (1), 612 (1), 607 (1), 571 (1), 510 (1), 484 (1), 473 (1), 349 (1), 338 (2), 326 (2), 307 (2), 295 (1), 288 (2), 266 (1), 256 (3), 244 (2), 235 (2), 187 (2), 153 (1). MS (EI, 70 eV, m/z): 579 ([^{Me}Bhp−SbCl]$^+$, 23 %), 544 ([^{Me}Bhp−Sb]$^+$, 27 %), 423 ([^{Me}Bhp]$^+$, 19 %) 167 ([CHPh$_2$]$^+$, 81 %).

Figure S14. NMR, IR and Raman spectra of **10Me** (solvent signals marked by asterisk).

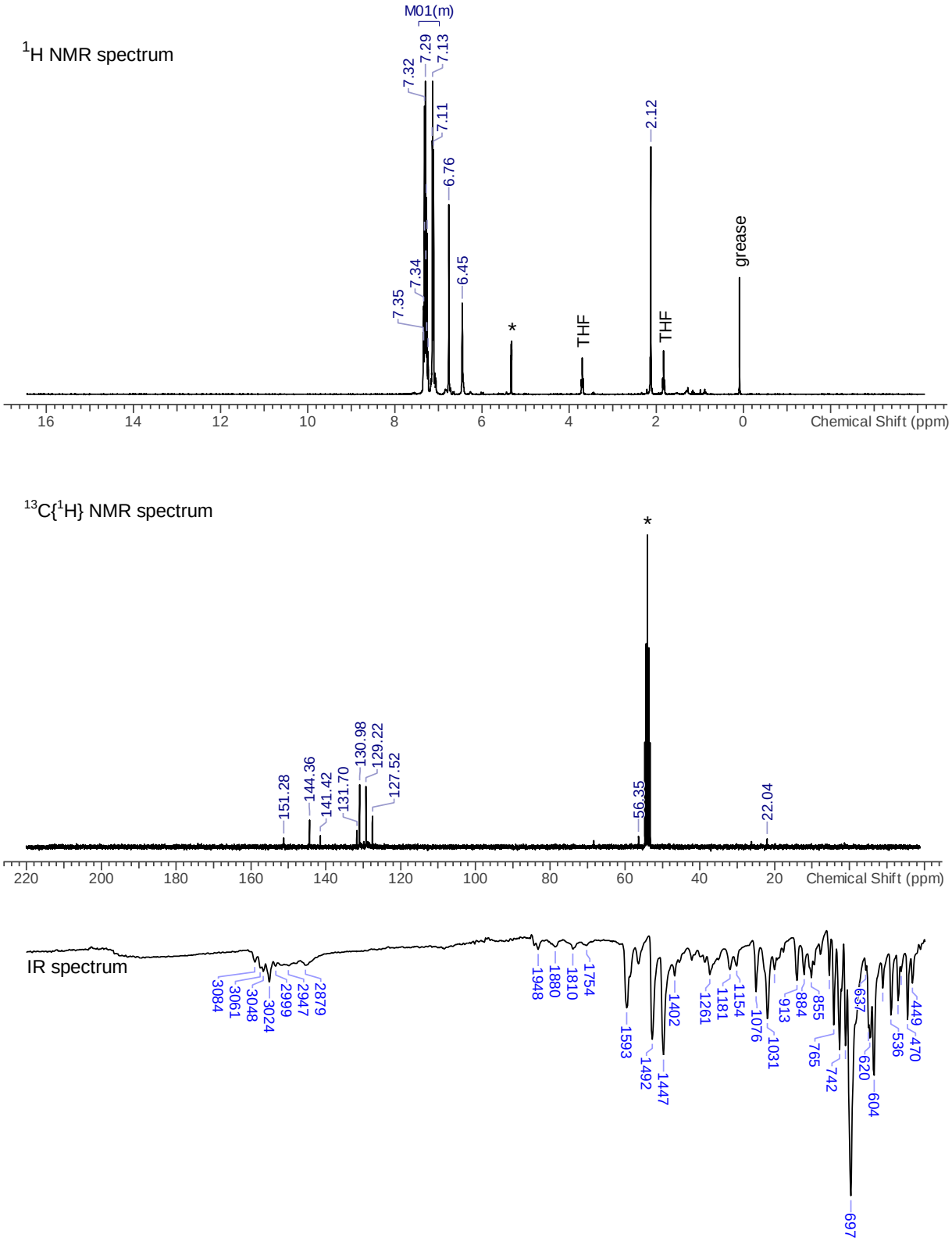
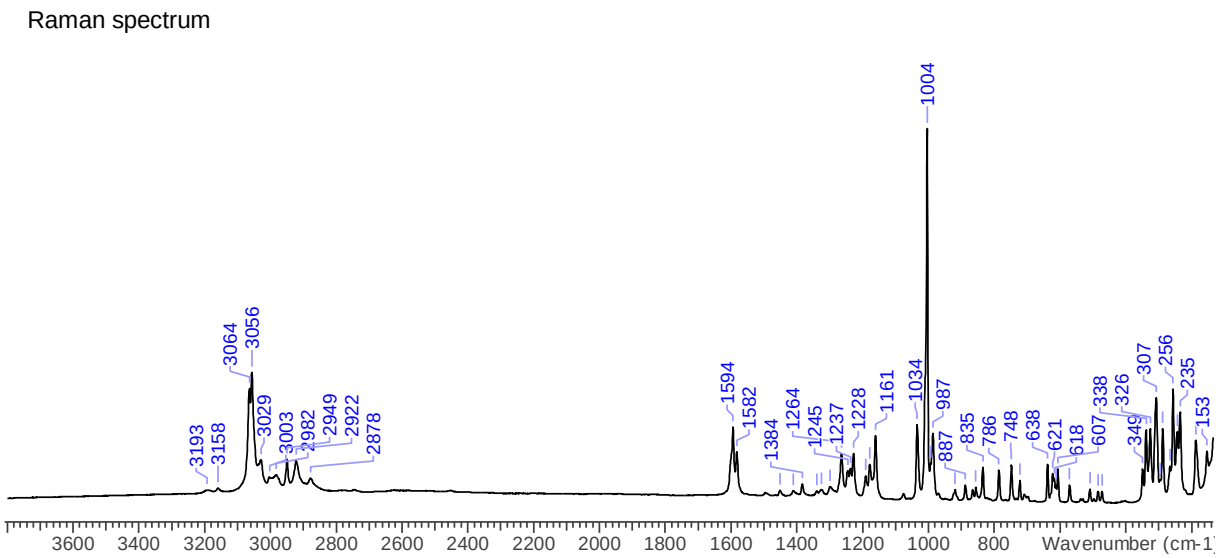


Figure S14 (continued).



4. Computational Details

All computations were carried out using ORCA 4.0.1.2 (an *ab initio*, DFT and semiempirical electronic structure package) with the CBLAS interface (fast vector & matrix operations), the LAPACKE interface (fast linear algebra routines) and the SCALAPACK package (parallel linear algebra routines).[11] Structures were fully optimized using the hybrid DFT functional PBE0 and the def2-TZVP basis set with additional atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ).[12–17] The calculations used the libint2 library for the computation of 2-el integrals.[18]

All structures were confirmed as minima by frequency analyses.

For the computation of gas-phase acidities, the structures of the phosphanes and their conjugate bases were optimized and confirmed as minima by frequency analyses. The gas-phase Gibbs free enthalpies of dissociation reactions were calculated as

$$\Delta G^{\circ}_{diss} = G^{\circ}(H^{+}) + G^{\circ}(A^{-}) - G^{\circ}(HA)$$

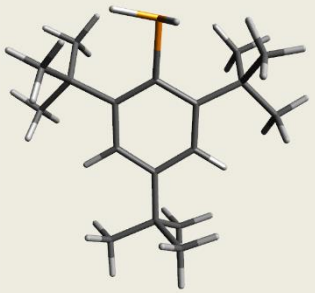
with the Gibbs free enthalpy of the proton at 1 atm $G^{\circ}(H^{+}) = -26.3101$ kJ/mol.[19] The gas-phase pK_a values were then calculated as

$$pK_a = \frac{\Delta G^{\circ}_{diss}}{RT} \log(e)$$

Cartesian coordinates of the optimized structures are presented below.

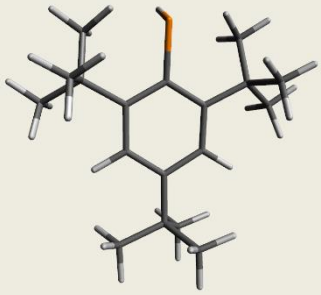
a) Mes*−PH_2

Atom	x	y	z
C	-4.92429	1.04442	-0.31100
C	-4.39591	-0.20977	-0.00360
C	-5.17869	-1.32636	0.20887
C	-6.55293	-1.13859	0.21585
C	-7.15814	0.07936	-0.06041
C	-6.32481	1.16628	-0.44598
C	-3.91778	2.20498	-0.44649
C	-2.56722	1.86157	0.19967
C	-3.60361	2.50016	-1.91975
C	-4.39539	3.44653	0.31928
C	-8.68613	0.17731	0.15857
C	-9.25915	-1.12103	0.73697
C	-8.98250	1.26477	1.20050
C	-9.47782	0.44692	-1.12925
C	-4.59824	-2.70808	0.48066
C	-3.07396	-2.71503	0.43027
C	-5.03400	-3.18409	1.87019
C	-5.12003	-3.68716	-0.57615
P	-7.15577	2.65119	-1.17134
H	-3.32580	-0.31424	0.06432
H	-7.17519	-1.98574	0.45920
H	-1.94137	2.75669	0.19190
H	-2.68406	1.54197	1.23749
H	-2.02268	1.08771	-0.34430
H	-2.89845	3.33302	-1.99256
H	-4.47935	2.74908	-2.51516
H	-3.13892	1.62379	-2.37758
H	-5.35852	3.84149	0.00510
H	-4.47231	3.21476	1.38429
H	-3.66527	4.25181	0.20251
H	-10.31825	-0.96383	0.95085
H	-9.18981	-1.95649	0.03583
H	-8.77265	-1.40589	1.67210
H	-10.06034	1.32194	1.37634
H	-8.64540	2.25086	0.88331
H	-8.49504	1.02496	2.14829
H	-9.13178	-0.19064	-1.94639
H	-10.53405	0.22611	-0.95450
H	-9.42207	1.48348	-1.45468
H	-2.70730	-3.72715	0.61669
H	-2.70062	-2.40067	-0.54743
H	-2.63970	-2.06143	1.19061
H	-4.62942	-4.17966	2.07264
H	-6.12069	-3.24144	1.95587
H	-4.67240	-2.50324	2.64432
H	-4.81541	-3.37574	-1.57804
H	-4.72290	-4.68943	-0.39322
H	-6.20970	-3.74975	-0.56248
H	-6.06005	3.25950	-1.80548
H	-7.56199	2.02480	-2.37672



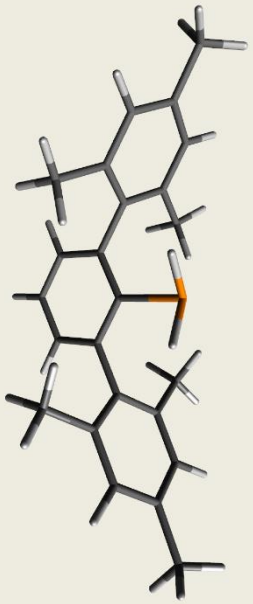
b) [Mes*−PH]⁻

Atom	x	y	z
C	8.33569	-9.01986	-3.37641
C	7.69413	-9.19303	-2.15721
C	7.87750	-10.31814	-1.36846
C	8.74183	-11.29732	-1.84769
C	9.41133	-11.18646	-3.05172
C	9.19393	-10.03410	-3.83659
P	10.16669	-9.77838	-5.34336
C	8.15439	-7.70875	-4.12764
C	10.41113	-12.26262	-3.44978
C	7.18825	-10.50973	-0.02686
C	6.72432	-7.16895	-4.02031
C	9.13969	-6.67912	-3.56473
C	8.42568	-7.91626	-5.59823
C	9.95192	-13.66377	-3.03520
C	10.56816	-12.28758	-4.95120
C	11.76196	-11.94692	-2.79924
C	6.26386	-9.34779	0.31833
C	6.35912	-11.79833	-0.06531
C	8.25862	-10.62668	1.06486
H	7.02672	-8.41573	-1.81521
H	8.89767	-12.18733	-1.25338
H	9.34255	-10.33218	-6.35146
H	6.60396	-6.30019	-4.67088
H	5.98874	-7.92186	-4.30927
H	6.50023	-6.83790	-3.00628
H	9.02883	-5.71947	-4.07519
H	10.17563	-7.01101	-3.67730
H	8.95776	-6.52235	-2.50098
H	9.53453	-8.17674	-5.76658
H	7.77276	-8.64153	-6.07945
H	8.42309	-6.98410	-6.17147
H	10.63466	-14.41429	-3.43869
H	9.95928	-13.77939	-1.95144
H	8.94581	-13.88044	-3.39890
H	11.35100	-12.97351	-5.28857
H	11.06418	-11.31584	-5.31495
H	9.64846	-12.48739	-5.49754
H	11.66613	-11.93219	-1.71297
H	12.50524	-12.70187	-3.06603
H	12.13905	-10.96846	-3.11050
H	5.78871	-9.53759	1.28219
H	6.80798	-8.40392	0.40468
H	5.46720	-9.22670	-0.42013
H	5.86522	-11.94701	0.89711
H	6.97746	-12.67710	-0.25743
H	5.58859	-11.74959	-0.83809
H	8.86231	-9.71829	1.12370
H	7.78199	-10.78118	2.03516
H	8.93048	-11.46919	0.88952



c) Ter–PH_2

Atom	x	y	z
C	-13.92079	-6.95833	3.21648
C	-12.90188	-7.86985	3.47508
C	-13.18442	-9.20025	3.73178
C	-14.49962	-9.63301	3.72082
C	-15.53837	-8.74634	3.46180
C	-15.25329	-7.39306	3.22896
P	-16.61589	-6.24610	2.79543
C	-13.56750	-5.54304	2.93596
C	-16.93539	-9.24859	3.42013
C	-13.34333	-4.66264	4.00080
C	-12.99912	-3.34572	3.72812
C	-12.86733	-2.87952	2.42580
C	-13.10503	-3.76729	1.38571
C	-13.45378	-5.09328	1.61664
C	-17.49852	-9.62709	2.19575
C	-18.80604	-10.09500	2.17330
C	-19.56780	-10.19620	3.33083
C	-18.99000	-9.80836	4.53246
C	-17.68397	-9.33794	4.59773
C	-13.71573	-6.01198	0.46112
C	-12.44674	-1.46750	2.15490
C	-13.49293	-5.12892	5.41709
C	-17.09265	-8.92208	5.91054
C	-16.70384	-9.53836	0.92774
C	-20.96461	-10.73637	3.28446
H	-11.87550	-7.51934	3.47062
H	-12.38115	-9.89977	3.93203
H	-14.73613	-10.67487	3.90819
H	-16.12703	-5.10000	3.46842
H	-17.52077	-6.61496	3.82040
H	-12.82731	-2.66507	4.55687
H	-13.01597	-3.42040	0.36043
H	-19.24188	-10.38825	1.22271
H	-19.57243	-9.87080	5.44701
H	-13.37615	-5.56524	-0.47395
H	-13.21398	-6.97309	0.59024
H	-14.78548	-6.22131	0.36150
H	-12.81929	-0.78656	2.92245
H	-11.35556	-1.38271	2.14565
H	-12.80980	-1.12257	1.18521
H	-12.77284	-5.91479	5.65846
H	-13.34772	-4.30476	6.11617
H	-14.48541	-5.55585	5.58751
H	-17.83695	-8.97109	6.70606
H	-16.25222	-9.56328	6.18935
H	-16.70192	-7.90166	5.86531
H	-15.82030	-10.18066	0.96954
H	-17.30705	-9.83896	0.07062
H	-16.34607	-8.52038	0.75223
H	-21.49521	-10.39153	2.39457
H	-20.95799	-11.83032	3.25609
H	-21.53745	-10.43409	4.16257



d) [Ter–PH]$^-$

Atom	x	y	z
C	9.20142	-11.56696	-6.07045
C	9.27323	-11.78740	-4.69947
C	10.10836	-12.79607	-4.23850
C	10.87604	-13.55564	-5.11387
C	10.82516	-13.34329	-6.49303
C	9.97908	-12.34320	-6.94176
P	9.72836	-11.91347	-8.69938
C	8.42468	-10.60134	-6.83355
C	11.60238	-14.12206	-7.48561
C	7.99495	-11.12158	-8.13440
C	7.54815	-10.16085	-9.11521
C	7.48777	-8.82469	-8.84698
C	7.83216	-8.41028	-7.54123
C	8.28039	-9.24775	-6.52677
C	12.69881	-13.54318	-8.13666
C	13.34847	-14.27316	-9.12812
C	12.94316	-15.54860	-9.48591
C	11.85235	-16.10261	-8.81883
C	11.17617	-15.41735	-7.82397
C	8.66953	-8.67891	-5.19913
C	7.04697	-7.81655	-9.85794
C	7.07532	-12.35903	-8.07432
C	10.00234	-16.05344	-7.14127
C	13.23843	-12.19112	-7.76806
C	13.66433	-16.32403	-10.54273
H	8.67226	-11.21729	-4.00341
H	10.16456	-12.99373	-3.17493
H	11.53669	-14.32102	-4.72313
H	10.42221	-10.67063	-8.66259
H	7.21979	-10.54211	-10.07729
H	7.77626	-7.34672	-7.32305
H	14.19933	-13.82556	-9.63248
H	11.51337	-17.09691	-9.09231
H	8.71865	-7.59162	-5.24209
H	7.94080	-8.94665	-4.43032
H	9.64111	-9.05653	-4.87483
H	6.78296	-8.29091	-10.80231
H	6.17881	-7.25794	-9.50097
H	7.84146	-7.09142	-10.05159
H	7.49273	-13.12080	-7.41689
H	6.09697	-12.06402	-7.69231
H	6.95162	-12.77964	-9.07204
H	9.69489	-16.95701	-7.66681
H	10.24022	-16.33536	-6.11193
H	9.14370	-15.37888	-7.09356
H	12.56973	-11.62970	-7.11628
H	14.18895	-12.29619	-7.23782
H	13.43700	-11.59268	-8.65967
H	14.26492	-15.67199	-11.17747
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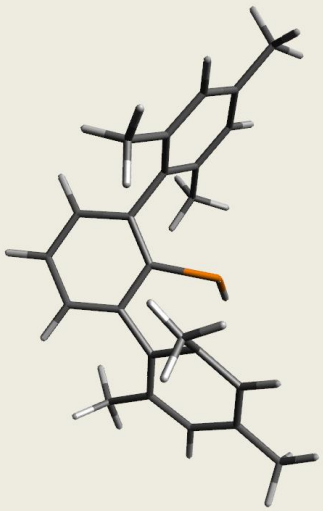
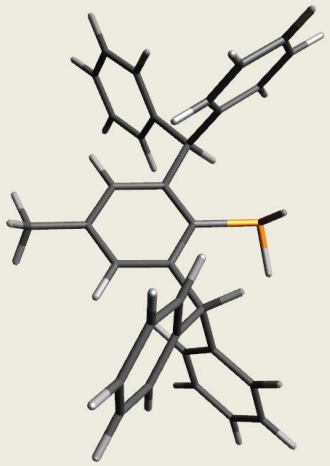
H	12.96674	-16.87487	-11.17623



e) ^{Me}Bhp–PH_2

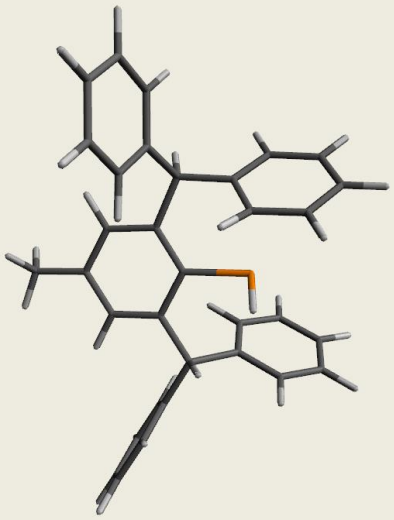
Atom	x	y	z
C	-3.57403	0.34043	-0.08731
C	-3.08990	-0.88314	0.35563
C	-3.92605	-1.83507	0.92116
C	-5.28230	-1.55199	0.99566
C	-5.80545	-0.34372	0.55468
C	-4.94263	0.63620	0.03622
C	-3.39245	-3.14397	1.41494
C	-2.64656	1.32615	-0.77874
C	-1.18171	1.03492	-0.53469
C	-2.98071	1.45193	-2.25188
C	-7.30352	-0.12196	0.62901
C	-8.06865	-1.41176	0.40198
C	-7.74474	0.60942	1.87918
C	-2.71328	2.64640	-2.91477
C	-2.99660	2.79014	-4.26254
C	-3.55342	1.73516	-4.97302
C	-3.81975	0.53993	-4.32409
C	-3.53670	0.40068	-2.97255
C	-0.62225	1.37679	0.69429
C	0.70214	1.08960	0.97846
C	1.49385	0.45328	0.03174
C	0.94947	0.11611	-1.19709
C	-0.37861	0.40707	-1.47871
C	-9.00009	1.21462	1.89341
C	-9.45826	1.87764	3.01813
C	-8.66311	1.94901	4.15484
C	-7.41201	1.35443	4.15016
C	-6.95611	0.68827	3.01945
C	-8.08618	-1.95644	-0.88024
C	-8.74116	-3.14767	-1.13846
C	-9.39213	-3.81972	-0.11165
C	-9.38224	-3.28592	1.16645
C	-8.72594	-2.08839	1.42132
P	-5.49155	2.32336	-0.45457
H	-2.03238	-1.09851	0.25691
H	-5.95867	-2.30131	1.39303
H	-2.30538	-3.18394	1.33823
H	-3.66583	-3.30848	2.46029
H	-3.80483	-3.97753	0.83976
H	-2.84693	2.30995	-0.33837
H	-7.56142	0.52822	-0.21339
H	-2.28565	3.47477	-2.35964
H	-2.78974	3.73089	-4.75967
H	-3.78276	1.84747	-6.02632
H	-4.25546	-0.28952	-4.86958
H	-3.76106	-0.53193	-2.46758
H	-1.24177	1.86595	1.43927
H	1.11988	1.36449	1.94028
H	2.53136	0.22864	0.25018
H	1.56088	-0.37464	-1.94582
H	-0.79504	0.14566	-2.44440
H	-9.62508	1.15546	1.00810
H	-10.43720	2.34302	3.00819
H	-9.01767	2.47030	5.03640
H	-6.78147	1.41023	5.03023
H	-5.97390	0.23057	3.02155



H	-7.56841	-1.43780	-1.68121
H	-8.74592	-3.55390	-2.14351
H	-9.90714	-4.75235	-0.31034
H	-9.88985	-3.80130	1.97402
H	-8.72879	-1.67427	2.42274
H	-6.62326	2.42111	0.39078
H	-6.25245	1.98700	-1.60649

f) $[^{Me}Bhp–PH]^-$

Atom	x	y	z
C	-15.59468	4.08665	2.93058
C	-15.16931	3.02401	3.70419
C	-16.03428	2.35913	4.57184
C	-17.34462	2.80367	4.65639
C	-17.80425	3.87460	3.89991
C	-16.93249	4.51673	3.01925
C	-15.56471	1.20168	5.39410
C	-14.66055	4.82653	1.99380
C	-13.28004	4.21927	1.87486
C	-15.31396	5.04048	0.64408
C	-19.24975	4.29421	4.09177
C	-19.59063	4.64240	5.53210
C	-19.63155	5.44753	3.21456
C	-15.09988	6.23193	-0.06029
C	-15.63197	6.41425	-1.32276
C	-16.37059	5.39891	-1.91965
C	-16.57867	4.20449	-1.24733
C	-16.05956	4.02626	0.02387
C	-12.23103	4.77741	2.59608
C	-10.95780	4.23084	2.53496
C	-10.72092	3.11442	1.74853
C	-11.76169	2.55189	1.02310
C	-13.03196	3.10237	1.08369
C	-20.64658	5.35476	2.26864
C	-20.98603	6.44916	1.49266
C	-20.32306	7.66910	1.63341
C	-19.31401	7.78970	2.56036
C	-18.92529	6.67185	3.33027
C	-20.89404	4.45592	5.97920
C	-21.25753	4.82165	7.26552
C	-20.31931	5.38498	8.11752
C	-19.01643	5.57104	7.67937
C	-18.65272	5.20011	6.39394
P	-17.49369	5.79840	1.84457
H	-14.13867	2.69861	3.62555
H	-18.03072	2.31909	5.34407
H	-14.50095	1.01585	5.24913
H	-15.73882	1.38170	6.45745
H	-16.10771	0.29079	5.12964
H	-14.51523	5.82374	2.43127
H	-19.87661	3.44453	3.80332
H	-14.50916	7.01767	0.39929
H	-15.46358	7.34523	-1.85037
H	-16.78298	5.54173	-2.91130
H	-17.15139	3.41086	-1.71153
H	-16.24128	3.10026	0.55793
H	-12.41291	5.64955	3.21597



H	-10.15044	4.68079	3.10036
H	-9.72753	2.68550	1.69658
H	-11.58201	1.68279	0.40144
H	-13.83205	2.65629	0.50419
H	-21.17200	4.41551	2.14313
H	-21.78026	6.35603	0.76104
H	-20.61059	8.51662	1.02437
H	-18.79389	8.73077	2.69401
H	-18.25707	6.81084	4.17244
H	-21.63259	4.01634	5.31634
H	-22.27439	4.66291	7.60387
H	-20.60050	5.67009	9.12401
H	-18.27609	5.99924	8.34461
H	-17.62439	5.32209	6.07112
H	-16.59736	6.81912	2.27032

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