Supporting Information for

In situ generated cobalt(I) catalyst for the efficient synthesis of novel pyridines: Revisiting the mechanism of [2+2+2] cycloadditions

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1. Experimental details

The syntheses of the Co(III) complexes were carried out under an inert atmosphere using Schlenk techniques. The complexes were stored under an inert atmosphere in a Schlenk flask or in an MBraun dry box. The organic solvents were previously dried and distilled under argon or obtained from a solvent purification system (SPS) and collected under an inert atmosphere. All other starting materials were purchased from commercial suppliers and used without further purification. The complexes $[CoCp(CH_3CN)_2(PMePh_2)][BF_4]_2$[1] and $[CoCp^*(CH_3CN)(dppe)][BF_4]_2$ were synthesized from $[CoCp^*(CH_3CN)_3][BF_4]_2$[2] following procedures analogous to those described in the literature.

The NMR spectra were recorded at 298 K on Bruker Avance 300 MHz, Bruker ARX 300 MHz, and Bruker Avance 400 MHz spectrometers. Chemical shifts, expressed in ppm, were referenced to the residual peaks of the deuterated solvents (^1H and ^{13}C). Coupling constants (*J*) are expressed in Hz. Spectral assignments were achieved through a combination of ^1H-^1H COSY, $^{13}C\{^1H\}$ APT, ^1H-^{13}C HSQC, and ^1H-^{13}C HMBC experiments. High-resolution electrospray ionization mass spectra (HRMS) were acquired using a Bruker MicroTOF-Q quadrupole time-of-flight spectrometer.

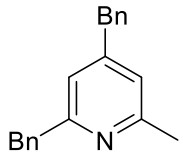
2. General procedure for [2+2+2] cycloaddition reaction

0.0075 mmol of cobalt precatalyst and 0.3 mL of C_6D_6 are introduced in an NMR tube. Then, 15 μL (0.015 mmol) of a $NaBEt_3H$ solution in THF (1 M) is added. After gently shaking the mixture, allowing the gases to escape under an argon flow, 0.15 mmol of alkyne and 0.45 mmol of nitrile are added (the optimized alkyne-nitrile stoichiometry is 1:3, but experiments were also conducted using 0.15 and 0.9 mmol of nitrile). The NMR tube was then sealed under argon and heated to the appropriate temperature. The reaction progress was monitored by ^1H NMR spectroscopy, and conversion was determined by integrating the representative signals of the products relative to an internal standard (1,3,5-triazine, 0.05 mmol).

The cycloaddition products were isolated using a puriFlash® 215 column with ethyl acetate and hexane as eluents. The mixture of 2,4-dibenzyl-6-(4-methoxyphenyl)pyridine (**py-7a**) and 3,6-dibenzyl-2-(4-methoxyphenyl)pyridine (**py-7b**) was isolated by distillation.

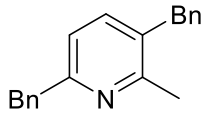
3. Characterization of pyridines

2,4-dibencyl-6-methylpyridine (py-1a). ^{1}H NMR, ^{1}H-^{1}H COSY (C_6D_6, 400 MHz): δ



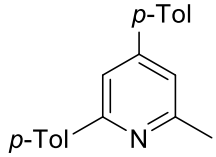
7.29-7.23 (m, 2H, CH_{Ar}), 7.14-7.00 (m, 6H, CH_{Ar}), 6.95-6.87 (m, 2H, CH_{Ar}), 6.64 (s, 1H, CH_{Py-3}), 6.50 (s, 1H, CH_{Py-5}), 4.07 (s, 2H, $C_{Py-2}CH_2$), 3.46 (s, 2H, $C_{Py-4}CH_2$), 2.36 (s, 3H, $C_{Py-6}CH_3$). ^{13}C{^{1}H} NMR APT, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC (C_6D_6, 101 MHz): δ 161.0 (s, C_{Py-2}), 158.4 (s, C_{Py-6}), 150.5 (s, C_{Py-4}), 140.6 (s, $C_{Py-2}CH_2C_{Ar}$), 139.9 (s, $C_{Py-4}CH_2C_{Ar}$), 129.5 (s, CH_{Ar}), 129.3 (s, CH_{Ar}), 128.8 (s, CH_{Ar}), 128.7 (s, CH_{Ar}), 126.4 (s, CH_{Ar}), 121.3 (s, CH_{Py-5}), 120.7 (s, CH_{Py-3}), 45.1 (s, $C_{Py-2}CH_2$), 41.3 (s, $C_{Py-4}CH_2$), 24.5 (s, $C_{Py-6}CH_3$). HRMS (ESI$^+$) *m/z* Calc. for $[C_{20}H_{20}N]^+$ 274.1596, found 274.1583.

3,6-dibencyl-2-methylpyridine (py-1b). ^{1}H NMR, ^{1}H-^{1}H COSY (C_6D_6, 400 MHz): δ



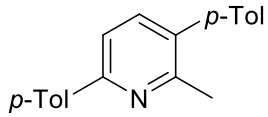
7.29-7.23 (m, 2H, CH_{Ar}), 7.14-7.00 (m, 6H, CH_{Ar}), 6.95-6.87 (m, 3H, CH_{Ar}+ CH_{Py-4}), 6.65 (d, $^{3}J_{H-H}$ = 7.4, 1H, CH_{Py-5}), 4.12 (s, 2H, $C_{Py-6}CH_2$), 3.55 (s, 2H, $C_{Py-3}CH_2$), 2.40 (s, 3H, $C_{Py-2}CH_3$). ^{13}C{^{1}H} NMR APT, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC (C_6D_6, 101 MHz): δ 158.7 (s, C_{Py-6}), 156.9 (s, C_{Py-2}), 140.6 (s, $C_{Py-6}CH_2C_{Ar}$), 139.9 (s, $C_{Py-3}CH_2C_{Ar}$), 137.6 (s, CH_{Py-4}), 131.3 (s, CH_{Py-3}), 129.6 (s, CH_{Ar}), 129.1 (s, CH_{Ar}), 128.8 (s, CH_{Ar}), 128.7 (s, CH_{Ar}), 126.7 (s, CH_{Ar}), 126.5 (s, CH_{Ar}), 120.5 (s, CH_{Py-5}), 44.8 (s, $C_{Py-6}CH_2$), 38.5 (s, $C_{Py-3}CH_2$), 22.7 (s, $C_{Py-2}CH_3$). HRMS (ESI$^+$) *m/z* Calc. for $[C_{20}H_{20}N]^+$ 274.1596, found 274.1583.

2-methyl-4,6-di(*p*-tolyl)pyridine (py-2a). ^{1}H NMR ($CDCl_3$, 300



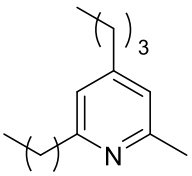
MHz): δ 8.00-7.92 (m, 2H, CH_{Ar}), 7.71 (s, 1H, CH_{Py}), 7.64-7.58 (m, 2H, CH_{Ar}), 7.34-7.29 (m, 5H, CH_{Ar}+ CH_{Py}), 2.70 (s, 3H, $C_{Py-6}CH_3$), 2.45 (s, 3H, CH_{3-Tol}), 2.44 (s, 3H, CH_{3-Tol}). HRMS (ESI$^+$) *m/z* Calc. for $[C_{20}H_{20}N]^+$ 274.1596, found 274.1586. The NMR data agree with those reported in the literature.[3]

2-methyl-3,6-di(*p*-tolyl)pyridine (py-2b). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.00-7.92



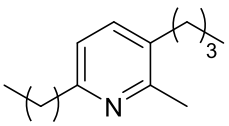
(m, 2H, CH_{Ar}), 7.64-7.58 (m, 4H, CH_{Ar}+ CH_{Py}), 7.34-7.29 (m, 4H, CH_{Ar}), 2.61 (s, 3H, $C_{Py-2}CH_3$), 2.45 (s, 3H, CH_{3-Tol}), 2.44 (s, 3H, CH_{3-Tol}). HRMS (ESI$^+$) *m/z* Calc. for $[C_{20}H_{20}N]^+$ 274.1596, found 274.1586. The NMR data agree with those reported in the literature.[4]

2,4-dibutyl-6-methylpyridine (py-3a). ^{1}H NMR, ^{1}H-^{1}H COSY (C_6D_6, 300 MHz): δ



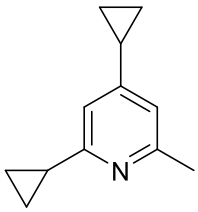
6.63 (s, 1H, C$H_{Py\text{-}5}$), 6.55 (s, 1H, C$H_{Py\text{-}3}$), 2.82 (t, $^{3}J_{H\text{-}H}$ = 7.6, 2H, $C_{Py\text{-}2}CH_2$), 2.50 (s, 3H, $C_{Py\text{-}6}CH_3$), 2.29 (t, $^{3}J_{H\text{-}H}$ = 7.6, 2H, $C_{Py\text{-}4}CH_2$), 1.89-1.78 (m, 2H, $C_{Py\text{-}2}CH_2CH_2$), 1.46-1.31 (m, 4H, $C_{Py\text{-}4}CH_2CH_2$+$C_{Py\text{-}2}(CH_2)_2CH_2$), 1.28-1.14 (m, 2H, $C_{Py\text{-}4}(CH_2)_2CH_2$), 0.90 (t, $^{3}J_{H\text{-}H}$ = 7.4, 3H, $C_{Py\text{-}2}(CH_2)_3CH_3$), 0.84 (t, $^{3}J_{H\text{-}H}$ = 7.4, 3H, $C_{Py\text{-}4}(CH_2)_3CH_3$). ^{13}C{^{1}H} NMR APT, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC (C_6D_6, 75 MHz): δ 162.1 (s, $C_{Py\text{-}2}$), 158.0 (s, $C_{Py\text{-}6}$), 151.6 (s, $C_{Py\text{-}4}$), 120.6 (s, $CH_{Py\text{-}5}$), 119.9 (s, $CH_{Py\text{-}3}$), 38.5 (s, $C_{Py\text{-}2}CH_2$), 35.2 (s, $C_{Py\text{-}4}CH_2$), 33.0 (s, $C_{Py\text{-}4}CH_2CH_2$), 32.5 (s, $C_{Py\text{-}2}CH_2CH_2$), 24.6 (s, $C_{Py\text{-}6}CH_3$), 23.0 (s, $C_{Py\text{-}2}(CH_2)_2CH_2$), 22.7 (s, $C_{Py\text{-}4}(CH_2)_2CH_2$), 14.2 (s, $C_{Py\text{-}2}(CH_2)_3CH_3$), 14.1 (s, $C_{Py\text{-}4}(CH_2)_3CH_3$). HRMS (ESI^{+}) *m/z* Calc. for $[C_{14}H_{24}N]^{+}$ 206.1909, found 206.1911.

3,6-dibutyl-2-methylpyridine (py-3b). ^{1}H NMR, ^{1}H-^{1}H COSY (C_6D_6, 400 MHz): δ



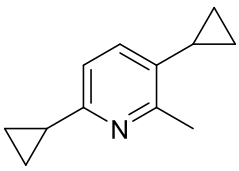
7.03 (d, $^{3}J_{H\text{-}H}$ = 7.7, 1H, C$H_{Py\text{-}4}$), 6.73 (d, $^{3}J_{H\text{-}H}$ = 7.7, 1H, C$H_{Py\text{-}5}$), 2.86-2.78 (m, 2H, $C_{Py\text{-}6}CH_2$), 2.51 (s, 3H, $C_{Py\text{-}2}CH_3$), 2.34-2.26 (m, 2H, $C_{Py\text{-}3}CH_2$), 1.88-1.77 (m, 2H, $C_{Py\text{-}6}CH_2CH_2$), 1.45-1.30 (m, 4H, $C_{Py\text{-}3}CH_2CH_2$+$C_{Py\text{-}6}(CH_2)_2CH_2$), 1.27-1.14 (m, 2H, $C_{Py\text{-}3}(CH_2)_2CH_2$), 0.90 (t, $^{3}J_{H\text{-}H}$ = 7.3, 3H, $C_{Py\text{-}6}(CH_2)_3CH_3$), 0.84 (t, $^{3}J_{H\text{-}H}$ = 7.3, 3H, $C_{Py\text{-}3}(CH_2)_3CH_3$). ^{13}C{^{1}H} NMR APT, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC (C_6D_6, 101 MHz): δ 159.1 (s, $C_{Py\text{-}6}$), 156.1 (s, $C_{Py\text{-}2}$), 132.7 (s, $C_{Py\text{-}3}$), 136.4 (s, $CH_{Py\text{-}4}$), 120.1 (s, $CH_{Py\text{-}5}$), 38.1 (s, $C_{Py\text{-}6}CH_2$), 32.9 (s, $C_{Py\text{-}3}CH_2$), 32.4 (s, $C_{Py}CH_2CH_2$), 32.3 (s, $C_{Py}CH_2CH_2$), 22.4 (s, $C_{Py}(CH_2)_2CH_2$), 22.8 (s, $C_{Py}(CH_2)_2CH_2$), 22.4 (s, $C_{Py\text{-}2}CH_3$), 14.2 (s, $C_{Py}(CH_2)_3CH_3$), 14.1 (s, $C_{Py}(CH_2)_3CH_3$). HRMS (ESI^{+}) *m/z* Calc. for $[C_{14}H_{24}N]^{+}$ 206.1909, found 206.1911.

2,4-dicyclopropyl-6-methylpyridine (py-4a). ^{1}H NMR, ^{1}H-^{1}H COSY (C_6D_6, 400

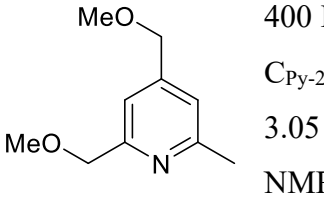


MHz): δ 6.54 (s, 1H, C$H_{Py\text{-}5}$), 6.34 (s, 1H, C$H_{Py\text{-}3}$), 2.36 (s, 3H, $C_{Py\text{-}6}CH_3$), 1.83-1.77 (m, 1H, $C_{Py\text{-}2}CH$), 1.47-1.40 (m, 1H, $C_{Py\text{-}4}CH$), 1.37-1.35 (m, 2H, $C_{Py\text{-}2}CH(CH_2)_2$), 0.84-0.77 (m, 2H, $C_{Py\text{-}2}CH(CH_2)_2$), 0.68-0.64 (m, 2H, $C_{Py\text{-}4}CH(CH_2)_2$), 0.57-0.52 (m, 2H, $C_{Py\text{-}4}CH(CH_2)_2$). ^{13}C{^{1}H} NMR APT, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC (C_6D_6, 101 MHz): δ 162.0 (s, $C_{Py\text{-}2}$), 157.9 (s, $C_{Py\text{-}6}$), 153.1 (s, $C_{Py\text{-}4}$), 117.1 (s, $CH_{Py\text{-}5}$), 116.3 (s, $CH_{Py\text{-}3}$), 24.6 (s, $C_{Py\text{-}6}CH_3$), 17.5 (s, $C_{Py\text{-}2}CH$), 15.0 (s, $C_{Py\text{-}4}CH$), 9.7 (bs, $C_{Py\text{-}2}(CH(CH_2)_2$+$C_{Py\text{-}4}(CH(CH_2)_2$). HRMS (ESI^{+}) *m/z* Calc. for $[C_{12}H_{16}N]^{+}$ 174.1283, found 174.1277.

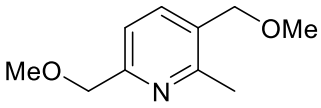
3,6-dicyclopropyl-2-methylpyridine (py-4b). ^{1}H NMR, ^{1}H-^{1}H COSY (C_6D_6, 400 MHz): δ 6.82 (d, $^{3}J_{H\text{-}H}$ = 7.8, 1H, C$H_{Py\text{-}4}$), 6.72 (d, $^{3}J_{H\text{-}H}$ = 7.8, 1H, C$H_{Py\text{-}5}$), 2.55 (s, 3H, $C_{Py\text{-}2}CH_3$), 1.89-1.83 (m, 1H, $C_{Py\text{-}6}CH$), 1.47-1.40 (m, 1H, $C_{Py\text{-}3}CH$), 1.33-1.30 (m, 2H, $C_{Py\text{-}6}CH(CH_2)_2$), 0.84-0.77 (m, 2H, $C_{Py\text{-}6}CH(CH_2)_2$), 0.57-0.52 (m, 2H, $C_{Py\text{-}3}CH(CH_2)_2$), 0.33-0.30 (m, 2H, $C_{Py\text{-}3}CH(CH_2)_2$). ^{13}C{^{1}H} NMR APT, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC (C_6D_6, 101 MHz): δ 159.2 (s, $C_{Py\text{-}2}$), 145.0 (s, $C_{Py\text{-}6}$), 133.2 (s, $CH_{Py\text{-}4}$), 132.8 (s, $C_{Py\text{-}3}$), 119.0 (s, $CH_{Py\text{-}5}$), 22.8 (s, $C_{Py\text{-}2}CH_3$), 17.1 (s, $C_{Py\text{-}6}CH$), 12.9 (s, $C_{Py\text{-}3}CH$), 9.8 (bs, $C_{Py\text{-}6}(CH(CH_2)_2$), 6.6 (bs, $C_{Py\text{-}3}(CH(CH_2)_2$). HRMS (ESI$^+$) *m/z* Calc. for $[C_{12}H_{16}N]^+$ 174.1283, found 174.1277.



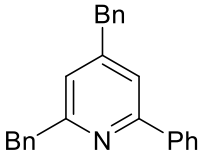
2,4-bis(methoxymethyl)-6-methylpyridine (py-5a). ^{1}H NMR, ^{1}H-^{1}H COSY (C_6D_6, 400 MHz): δ 7.37 (s, 1H, C$H_{Py\text{-}3}$), 6.80 (s, 1H, C$H_{Py\text{-}5}$), 4.62 (s, 2H, $C_{Py\text{-}2}CH_2$), 4.05 (s, 2H, $C_{Py\text{-}4}CH_2$), 3.19 (s, 3H, $C_{Py\text{-}2}CH_2OCH_3$), 3.05 (s, 3H, $C_{Py\text{-}4}CH_2OCH_3$), 2.44 (s, 3H, $C_{Py\text{-}6}CH_3$). ^{13}C{^{1}H} NMR APT, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC (C_6D_6, 101 MHz): δ 159.1 (s, $C_{Py\text{-}2}$), 158.0 (s, $C_{Py\text{-}6}$), 148.6 (s, $C_{Py\text{-}4}$), 119.7 (s, $CH_{Py\text{-}5}$), 116.2 (s, $CH_{Py\text{-}3}$), 76.0 (s, $C_{Py\text{-}2}CH_2$), 73.2 (s, $C_{Py\text{-}4}CH_2$), 58.4 (s, $C_{Py\text{-}2}CH_2OCH_3$), 58.1 (s, $C_{Py\text{-}4}CH_2OCH_3$), 24.4 (s, $C_{Py\text{-}6}CH_3$). HRMS (ESI$^+$) *m/z* Calc. for $[C_{10}H_{16}NO_2]^+$ 182.1181, found 182.1210.



3,6-bis(methoxymethyl)-2-methylpyridine (py-5b). ^{1}H NMR, ^{1}H-^{1}H COSY (C_6D_6, 400 MHz): δ 7.44 (d, $^{3}J_{H\text{-}H}$ = 7.8, 1H, C$H_{Py\text{-}4}$), 7.31 (d, $^{3}J_{H\text{-}H}$ = 7.8, 1H, C$H_{Py\text{-}5}$), 4.61 (s, 2H, $C_{Py\text{-}6}CH_2$), 4.02 (s, 2H, $C_{Py\text{-}3}CH_2$), 3.18 (s, 3H, $C_{Py\text{-}6}CH_2OCH_3$), 3.04 (s, 3H, $C_{Py\text{-}3}CH_2OCH_3$), 2.45 (s, 3H, $C_{Py\text{-}2}CH_3$). ^{13}C{^{1}H} NMR APT, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC (C_6D_6, 101 MHz): δ 156.7 (s, $C_{Py\text{-}6}$), 156.2 (s, $C_{Py\text{-}2}$), 136.1 (s, $CH_{Py\text{-}4}$), 130.1 (s, $C_{Py\text{-}3}$), 118.3 (s, $CH_{Py\text{-}5}$), 75.9 (s, $C_{Py\text{-}6}CH_2$), 71.9 (s, $C_{Py\text{-}3}CH_2$), 58.4 (s, $C_{Py\text{-}6}CH_2OCH_3$), 57.9 (s, $C_{Py\text{-}3}CH_2OCH_3$), 21.8 (s, $C_{Py\text{-}2}CH_3$). HRMS (ESI$^+$) *m/z* Calc. for $[C_{10}H_{16}NO_2]^+$ 182.1181, found 182.1210.

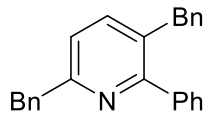


2,4-dibencyl-6-phenylpyridine (py-6a). ^{1}H NMR, ^{1}H-^{1}H COSY (C_6D_6, 400 MHz): δ 8.19-8.12 (m, 2H, CH_{Ar}), 7.30-7.22 (m, 6H, CH_{Ar}+ C$H_{Py\text{-}5}$), 7.15-6.99 (m, 6H, CH_{Ar}), 6.96-6.91 (m, 2H, CH_{Ar}), 6.73 (s, 1H, C$H_{Py\text{-}3}$), 4.12 (s, 2H, $C_{Py\text{-}2}CH_2$), 3.52 (s, 2H, $C_{Py\text{-}4}CH_2$). ^{13}C{^{1}H} NMR APT, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC (C_6D_6, 101 MHz): δ 161.4 (s, $C_{Py\text{-}2}$), 157.3 (s, $C_{Py\text{-}6}$), 151.2 (s,



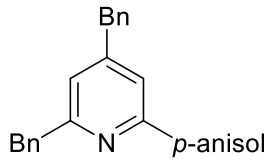
$C_{Py\text{-}4}$), 140.4 (s, $C_{Py\text{-}2}CH_2C_{Ar}$), 140.1 (s, $C_{Py\text{-}6}C_{Ar}$), 139.7 (s, $C_{Py\text{-}4}CH_2C_{Ar}$), 129.5 (s, CH_{Ar}), 129.3 (s, CH_{Ar}), 129.0 (s, CH_{Ar}), 128.9 (s, CH_{Ar}), 128.8 (s, CH_{Ar}), 128.8 (s, CH_{Ar}), 127.5 (s, CH_{Ar}), 126.8 (s, CH_{Ar}), 126.5 (s, CH_{Ar}), 122.3 (s, $CH_{Py\text{-}3}$), 118.5 (s, $CH_{Py\text{-}5}$), 45.2 (s, $C_{Py\text{-}2}CH_2$), 41.4 (s, $C_{Py\text{-}4}CH_2$). HRMS (ESI^+) *m/z* Calc. for $[C_{25}H_{22}N]^+$ 336.1752, found 336.1739.

3,6-dibencyl-2-phenylpyridine (py-6b). ^1H NMR, ^1H-^1H COSY (C_6D_6, 400 MHz): δ



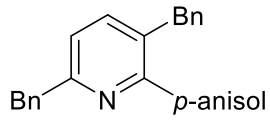
7.61 (d, $^3J_{H\text{-}H}$ = 6.8, 1H, $CH_{Py\text{-}5}$), 7.20-7.18 (m, 3H, CH_{Ar}), 7.15-6.99 (m, 12H, CH_{Ar}), 6.85 (d, $^3J_{H\text{-}H}$ = 6.8, 1H, $CH_{Py\text{-}4}$), 4.17 (s, 2H, $C_{Py\text{-}6}CH_2$), 3.83 (s, 2H, $C_{Py\text{-}3}CH_2$). $^{13}C\{^1H\}$ NMR APT, ^1H-^{13}C HSQC, ^1H-^{13}C HMBC (C_6D_6, 101 MHz): δ 159.1 (s, $C_{Py\text{-}6}$), 158.7 (s, $C_{Py\text{-}2}$), 141.4 (s, $C_{Py\text{-}2}C_{Ar}$), 141.0 (s, $C_{Py\text{-}3}CH_2C_{Ar}$), 140.3 (s, $C_{Py\text{-}6}CH_2C_{Ar}$), 139.1 (s, CH_{Ar}), 132.0 (s, CH_{Ar}), 132.0 (s, CH_{Ar}), 131.2 (s, $C_{Py\text{-}3}$), 129.8 (s, CH_{Ar}), 129.6 (s, $CH_{Py\text{-}5}$), 129.2 (s, $CH_{Py\text{-}4}$), 128.2 (s, CH_{Ar}), 126.5 (s, CH_{Ar}), 126.4 (s, CH_{Ar}), 121.6 (s, CH_{Ar}), 45.0 (s, $C_{Py\text{-}6}CH_2$), 38.5 (s, $C_{Py\text{-}3}CH_2$). HRMS (ESI^+) *m/z* Calc. for $[C_{25}H_{22}N]^+$ 336.1752, found 336.1739.

2,4-dibencyl-6-(4-methoxyphenyl)pyridine (py-7a). ^1H NMR, ^1H-^1H COSY (C_6D_6,



400 MHz): δ 8.18-8.13 (m, 2H, CH_{Ar}), 7.32-7.28 (m, 2H, CH_{Ar}), 7.26 (s, 1H, $CH_{Py\text{-}5}$), 7.15-7.01 (m, 6H, CH_{Ar}), 6.98-6.93 (m, 2H, CH_{Ar}), 6.87-6.84 (m, 2H, CH_{Ar}), 6.71 (s, 1H, $CH_{Py\text{-}3}$), 4.14 (s, 2H, $C_{Py\text{-}2}CH_2$), 3.55 (s, 2H, $C_{Py\text{-}4}CH_2$), 3.29 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR APT, ^1H-^{13}C HSQC, ^1H-^{13}C HMBC (C_6D_6, 101 MHz): δ 161.3 (s, $C_{Py\text{-}2}$), 161.0 (s, $C_{ipso}O$), 157.1 (s, $C_{Py\text{-}6}$), 151.1 (s, $C_{Py\text{-}4}$), 140.6 (s, $C_{Py\text{-}2}CH_2C_{Ar}$), 139.8 (s, $C_{Py\text{-}4}CH_2C_{Ar}$), 132.7 (s, $C_{Py\text{-}6}C_{Ar}$), 131.2 (s, CH_{Ar}), 129.6 (s, CH_{Ar}), 129.3 (s, CH_{Ar}), 128.9 (s, CH_{Ar}), 128.8 (s, CH_{Ar}), 126.7 (s, CH_{Ar}), 126.5 (s, CH_{Ar}), 121.6 (s, $CH_{Py\text{-}3}$), 117.8 (s, $CH_{Py\text{-}5}$), 114.3 (s, CH_{Ar}), 54.8 (s, OCH_3), 45.2 (s, $C_{Py\text{-}2}CH_2$), 41.5 (s, $C_{Py\text{-}4}CH_2$). HRMS (ESI^+) *m/z* Calc. for $[C_{26}H_{24}NO]^+$ 366.1858, found 366.1870.

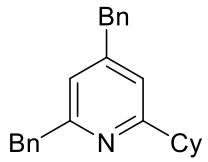
3,6-dibencyl-2-(4-methoxyphenyl)pyridine (py-7b). ^1H NMR, ^1H-^1H COSY (C_6D_6,



400 MHz): δ 7.63-7.58 (m, 2H, CH_{Ar}), 7.32-7.28 (m, 2H, CH_{Ar}), 7.15-7.01 (m, 7H, CH_{Ar}+$CH_{Py\text{-}4}$), 6.98-6.93 (m, 2H, CH_{Ar}), 6.82-6.78 (m, 2H, CH_{Ar}), 6.73 (d, $^3J_{H\text{-}H}$ = 7.9, 1H, $CH_{Py\text{-}5}$), 4.19 (s, 2H, $C_{Py\text{-}6}CH_2$), 3.90 (s, 2H, $C_{Py\text{-}3}CH_2$), 3.29 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR APT, ^1H-^{13}C HSQC, ^1H-^{13}C HMBC (C_6D_6, 101 MHz): δ 160.0 (s, $C_{ipso}O$), 159.1 (s, $C_{Py\text{-}6}$), 158.5 (s, $C_{Py\text{-}2}$), 141.3 (s, $C_{Py\text{-}3}CH_2C_{Ar}$), 140.5 (s, $C_{Py\text{-}6}CH_2C_{Ar}$), 139.2 (s, $CH_{Py\text{-}4}$), 133.8 (s, $C_{Py\text{-}2}C_{Ar}$), 131.1 (s, CH_{Ar}), 130.9 (s, $C_{Py\text{-}3}$), 129.6 (s, CH_{Ar}), 129.2 (s, CH_{Ar}), 128.8 (s, CH_{Ar}),

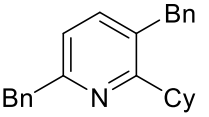
128.7 (s, CH_{Ar}), 126.5 (s, CH_{Ar}), 126.4 (s, CH_{Ar}), 121.2 (s, $CH_{Py\text{-}5}$), 113.8 (s, CH_{Ar}), 54.8 (s, OCH_3), 45.0 (s, $C_{Py\text{-}6}CH_2$), 38.7 (s, $C_{Py\text{-}3}CH_2$). HRMS (ESI^+) *m/z* Calc. for $[C_{26}H_{24}NO]^+$ 366.1858, found 366.1870.

2,4-dibencyl-6-ciclohexylpyridine (py-8a). ^1H NMR, ^1H-^1H COSY (C_6D_6, 400 MHz):

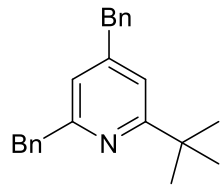


δ 7.31-7.25 (m, 2H, CH_{Ar}+ $CH_{Py\text{-}3}$), 7.14-7.08 (m, 4H, CH_{Ar}), 7.05-7.00 (m, 2H, CH_{Ar}), 6.89-6.94 (m, 2H, CH_{Ar}), 6.70-6.64 (m, 2H, CH_{Ar}+ $CH_{Py\text{-}5}$), 4.10 (s, 2H, $C_{Py\text{-}2}CH_2$), 3.53 (s, 2H, $C_{Py\text{-}4}CH_2$), 2.71-2.62 (m, 1H, CH_{Cy}), 2.01-1.94 (m, 2H, CH_{2Cy}), 1.78-1.66 (m, 4H, CH_{2Cy}), 1.33-1.19 (m, 4H, CH_{2Cy}). $^{13}C\{^1H\}$ NMR APT, ^1H-^{13}C HSQC, ^1H-^{13}C HMBC (C_6D_6, 101 MHz): δ 166.6 (s, $C_{Py\text{-}6}$), 160.9 (s, $C_{Py\text{-}2}$), 150.7 (s, $C_{Py\text{-}4}$), 140.7 (s, $C_{Py\text{-}2}CH_2C_{Ar}$), 139.9 (s, $C_{Py\text{-}4}CH_2C_{Ar}$), 129.5 (s, CH_{Ar}), 129.3 (s, $CH_{Py\text{-}3}$), 128.9 (s, CH_{Ar}), 128.7 (s, CH_{Ar}), 126.7 (s, CH_{Ar}), 126.4 (s, CH_{Ar}), 121.2 (s, CH_{Ar}), 119.3 (s, $CH_{Py\text{-}5}$), 46.8 (s, CH_{Cy}), 45.2 (s, $C_{Py\text{-}2}CH_2$), 41.5 (s, $C_{Py\text{-}4}CH_2$), 33.3 (s, CH_{2Cy}), 27.0 (s, CH_{2Cy}), 26.5 (s, CH_{2Cy}). HRMS (ESI^+) *m/z* Calc. for $[C_{25}H_{28}N]^+$ 342.2222, found 342.2209.

3,6-dibencyl-2-ciclohexylpyridine (py-8b). ^1H NMR, ^1H-^1H COSY (C_6D_6, 400 MHz):

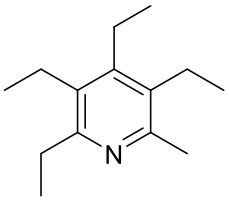


δ 7.29-7.24 (m, 2H, CH_{Ar}), 7.14-7.11 (m, 2H, CH_{Ar}), 7.09-7.07 (m, 2H, CH_{Ar}), 7.05-7.02 (m, 2H, CH_{Ar}), 6.99-6.96 (m, 2H, CH_{Ar}), 6.94 (d, $^3J_{H\text{-}H}$ = 7.8, 1H, $CH_{Py\text{-}4}$), 6.62 (d, $^3J_{H\text{-}H}$ = 7.8, 1H, $CH_{Py\text{-}5}$), 4.14 (s, 2H, $C_{Py\text{-}6}CH_2$), 3.75 (s, 2H, $C_{Py\text{-}3}CH_2$), 2.95-2.86 (m, 1H, CH_{Cy}), 2.16-2.01 (m, 2H, CH_{2Cy}), 1.82-1.70 (m, 4H, CH_{2Cy}), 1.34-1.22 (m, 4H, CH_{2Cy}). $^{13}C\{^1H\}$ NMR APT, ^1H-^{13}C HSQC, ^1H-^{13}C HMBC (C_6D_6, 101 MHz): δ 164.0 (s, $C_{Py\text{-}2}$), 158.9 (s, $C_{Py\text{-}6}$), 140.9 (s, $C_{Py\text{-}3}CH_2C_{Ar}$), 140.7 (s, $C_{Py\text{-}6}CH_2C_{Ar}$), 138.3 (s, $CH_{Py\text{-}4}$), 130.2 (s, $C_{Py\text{-}3}$), 129.6 (s, CH_{Ar}), 129.1 (s, CH_{Ar}), 128.8 (s, CH_{Ar}), 128.7 (s, CH_{Ar}), 126.5 (s, CH_{Ar}), 126.4 (s, CH_{Ar}), 120.2 (s, $CH_{Py\text{-}5}$), 45.0 (s, $C_{Py\text{-}6}CH_2$), 42.5 (s, CH_{Cy}), 38.1 (s, $C_{Py\text{-}3}CH_2$), 32.7 (s, CH_{2Cy}), 27.2 (s, CH_{2Cy}), 26.6 (s, CH_{2Cy}). HRMS (ESI^+) *m/z* Calc. for $[C_{25}H_{28}N]^+$ 342.2222, found 342.2209.

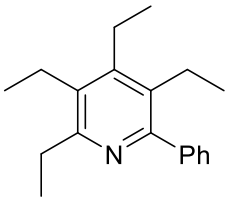


2,4-dibencyl-6-(*tert*-butyl)pyridine (py-9a). ^1H NMR, ^1H-^1H COSY (C_6D_6, 400 MHz): δ 7.31-7.24 (m, 2H, CH_{Ar}), 7.14-6.92 (m, 8H, CH_{Ar}), 6.94 (s, 1H, $CH_{Py\text{-}5}$), 6.65 (s, 1H, $CH_{Py\text{-}3}$), 4.06 (s, 2H, $C_{Py\text{-}2}CH_2$), 3.53 (s, 2H, $C_{Py\text{-}4}CH_2$), 1.41 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR APT, ^1H-^{13}C HSQC, ^1H-^{13}C HMBC (C_6D_6, 101 MHz): δ 169.2 (s, $C_{Py\text{-}6}$), 160.6 (s, $C_{Py\text{-}2}$), 151.0 (s, $C_{Py\text{-}4}$), 141.0 (s, $C_{Py\text{-}2}CH_2C_{Ar}$), 140.1 (s, $C_{Py\text{-}4}CH_2C_{Ar}$), 129.5 (s, CH_{Ar}), 129.2 (s, CH_{Ar}), 128.8 (s, CH_{Ar}), 128.7 (s, CH_{Ar}), 126.7 (s,

CH_{Ar}), 126.4 (s, CH_{Ar}), 120.7 (s, CH_{Py-3}), 117.0 (s, CH_{Py-5}), 45.2 (s, $C_{Py-2}CH_2$), 41.6 (s, $C_{Py-4}CH_2$), 37.8 (s, $C(CH_3)_3$), 30.4 (s, $C(CH_3)_3$). HRMS (ESI$^+$) *m/z* Calc. for $[C_{23}H_{26}N]^+$ 316.2065, found 316.2072.



2,3,4,5-tetraethyl-6-methylpyridine (py-10). ^{1}H NMR, ^{1}H-^{1}H COSY (C_6D_6, 300 MHz): δ 2.83 (q, $^3J_{H-H}$ = 7.5, 2H, $C_{Py-2}CH_2$), 2.56 (s, 3H, $C_{Py-6}CH_3$), 2.50-2.35 (m, 6H, $C_{Py-3}CH_2$+$C_{Py-4}CH_2$+$C_{Py-5}CH_2$), 1.45 (t, $^3J_{H-H}$ = 7.5, 3H, $C_{Py-2}CH_2CH_3$), 1.06-0.90 (m, 9H, $C_{Py-3}CH_2CH_3$+$C_{Py-4}CH_2CH_3$+$C_{Py-5}CH_2CH_3$). ^{13}C{^{1}H} NMR APT, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC (C_6D_6, 75 MHz): δ 157.9 (s, C_{Py-2}), 153.6 (s, C_{Py-6}), 147.8 (s, C_{Py-4}), 132.3 (s, CH_{Py-5}), 131.6 (s, CH_{Py-3}), 28.3 (s, $C_{Py-2}CH_2$), 22.7 (s, $C_{Py-6}CH_3$), 22.1 (s, $C_{Py-4}CH_2$), 21.8 (s, $C_{Py-m}CH_2$), 21.6 (s, $C_{Py-m}CH_2$), 15.6 (s, $C_{Py-m}CH_2CH_3$), 15.5 (s, $C_{Py-m}CH_2CH_3$), 14.5 (s, $C_{Py-4}CH_2CH_3$), 14.3 (s, $C_{Py-2}CH_2CH_3$). HRMS (ESI$^+$) *m/z* Calc. for $[C_{14}H_{24}N]^+$ 206.1909, found 206.1897.



2,3,4,5-tetraethyl-6-phenylpyridine (py-11). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.55-7.49 (m, 1H, CH_{Ar}), 7.48-7.40 (m, 4H, CH_{Ar}), 7.39-7.34 (m, 1H, CH_{Ar}), 2.85 (q, $^3J_{H-H}$ = 7.5, 2H, CH_2), 2.73 (q, $^3J_{H-H}$ = 7.5, 2H, CH_2), 2.72 (q, $^3J_{H-H}$ = 7.5, 2H, CH_2), 2.57 (q, $^3J_{H-H}$ = 7.5, 2H, CH_2), 1.29 (t, $^3J_{H-H}$ = 7.5, 3H, CH_3), 1.24 (t, $^3J_{H-H}$ = 7.5, 3H, CH_3), 1.22 (t, $^3J_{H-H}$ = 7.5, 3H, CH_3), 0.99 (t, $^3J_{H-H}$ = 7.5, 3H, CH_3). HRMS (ESI$^+$) *m/z* Calc. for $[C_{19}H_{26}N]^+$ 268.2065, found 268.2058. The NMR data agree with those reported in the literature.[5]

4. Crude ^{1}H-NMR spectra of [2+2+2] cycloaddition reactions

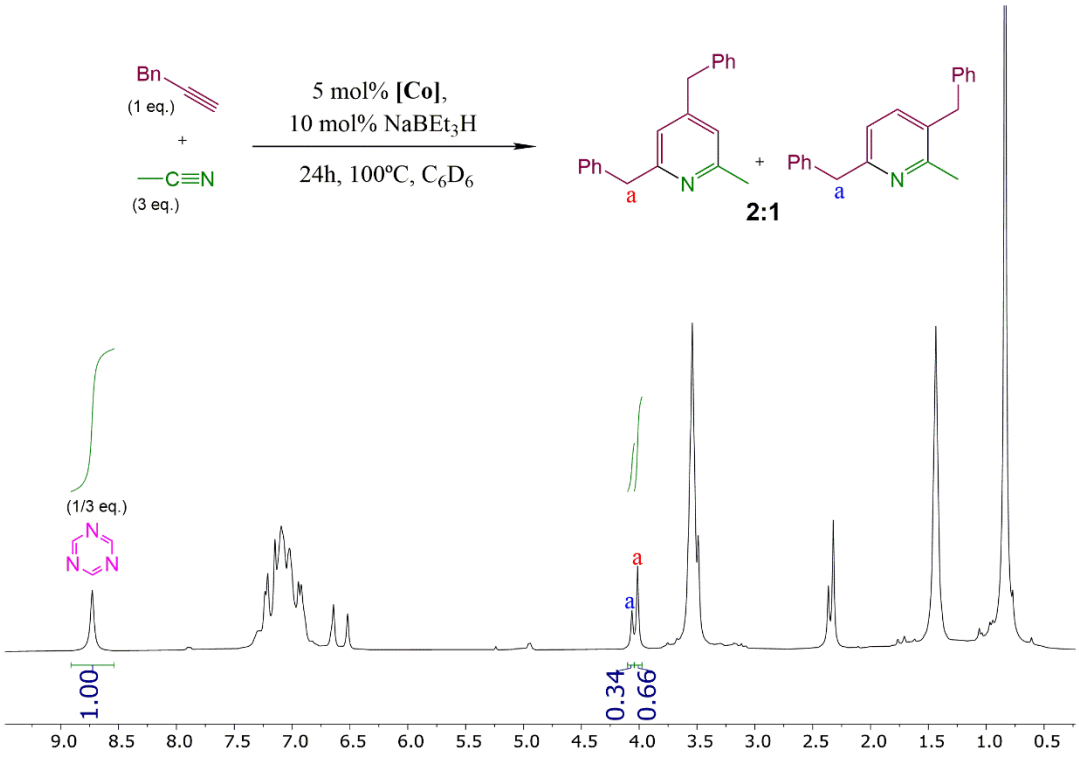


Figure S1. Crude ^{1}H NMR spectrum in C_6D_6 using s-triazine as internal standard (Table 4; Entry 1).

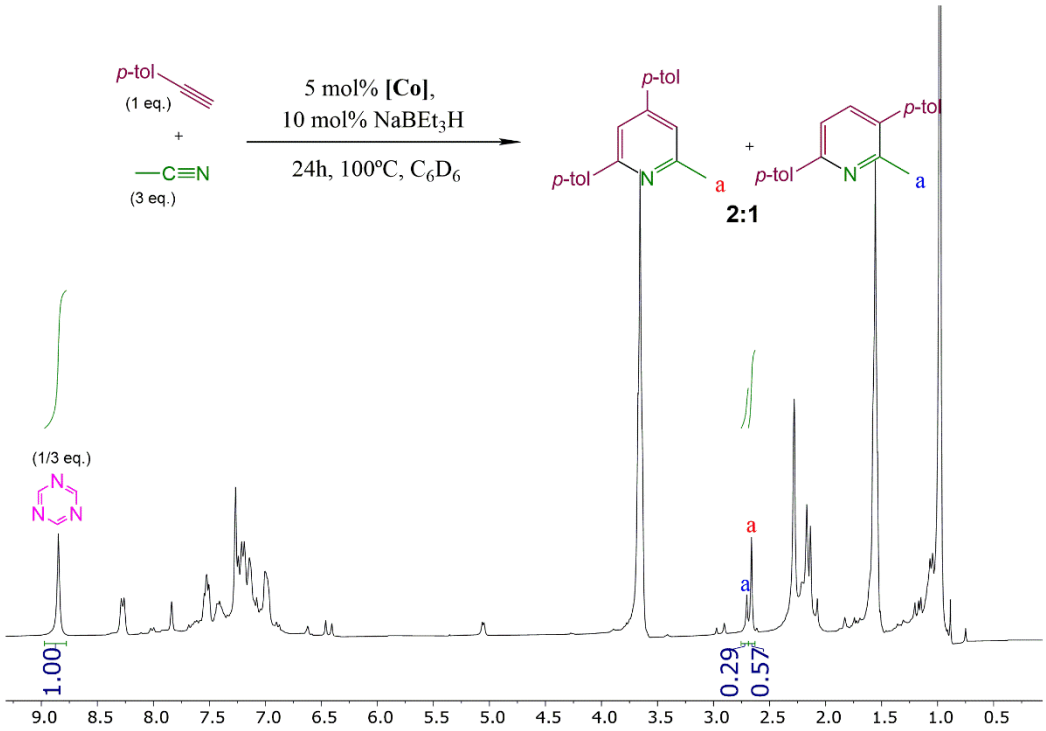


Figure S2. Crude ^{1}H NMR spectrum in C_6D_6 using s-triazine as internal standard (Table 4; Entry 2).

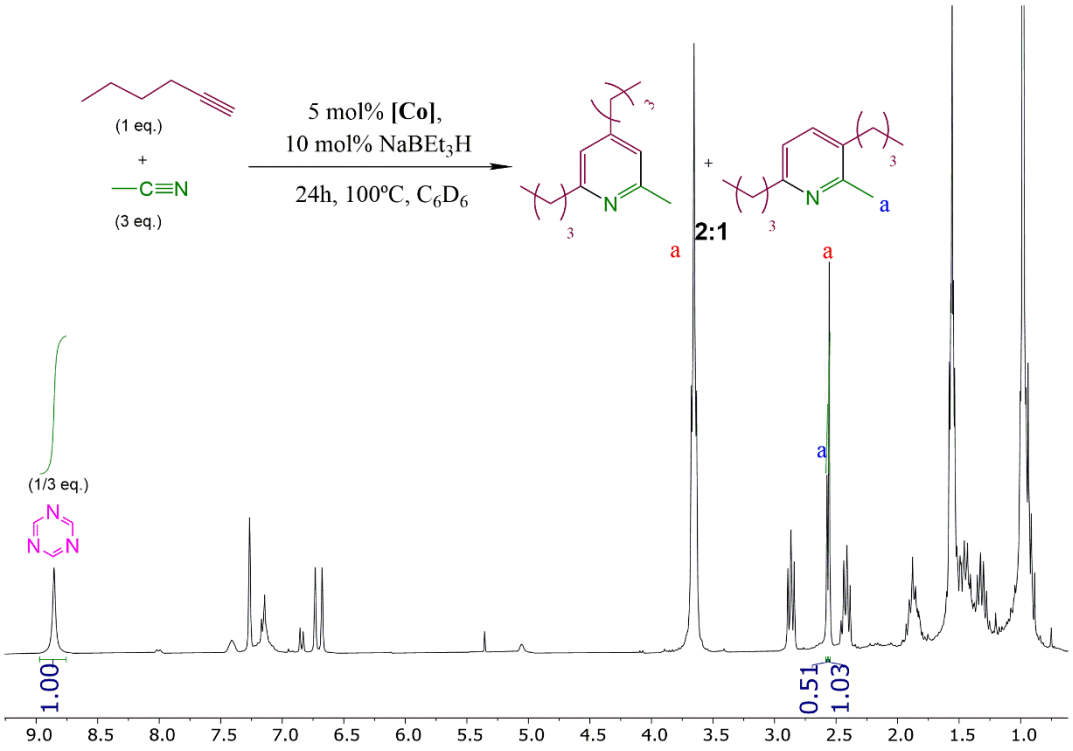


Figure S3. Crude ^{1}H NMR spectrum in C_6D_6 using s-triazine as internal standard (Table 4; Entry 3).

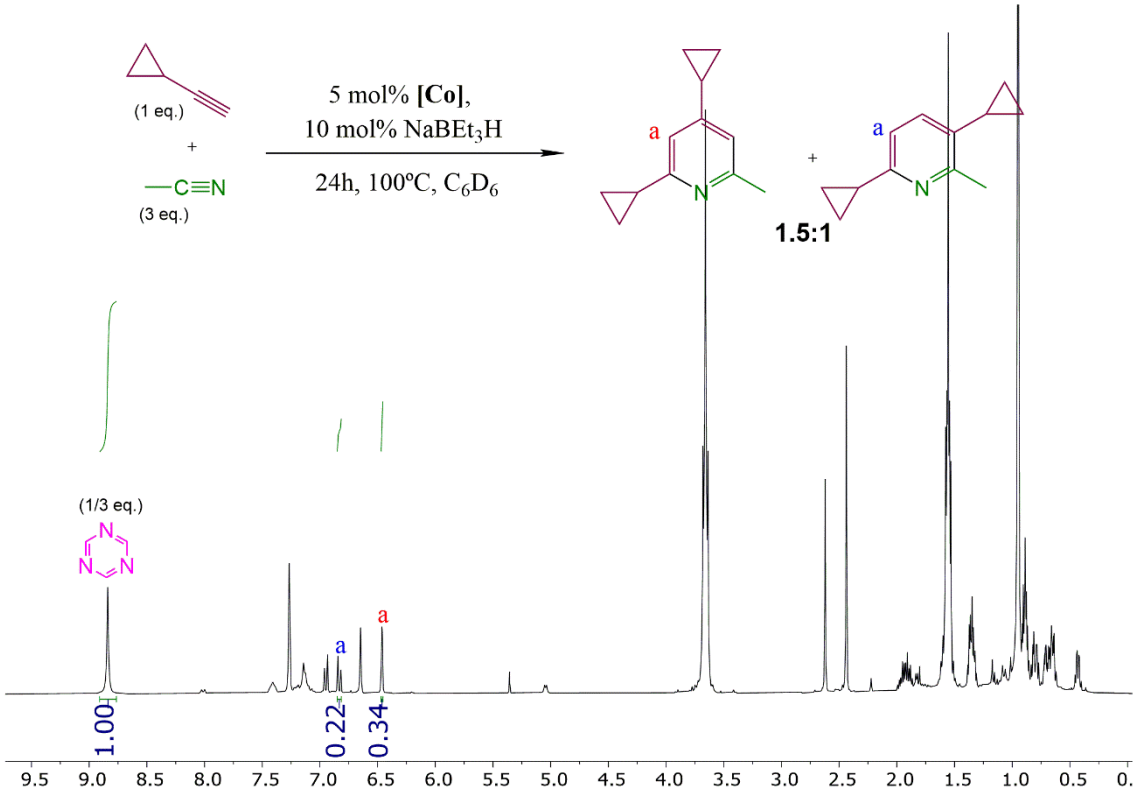


Figure S4. Crude ^{1}H NMR spectrum in C_6D_6 using s-triazine as internal standard (Table 4; Entry 4).

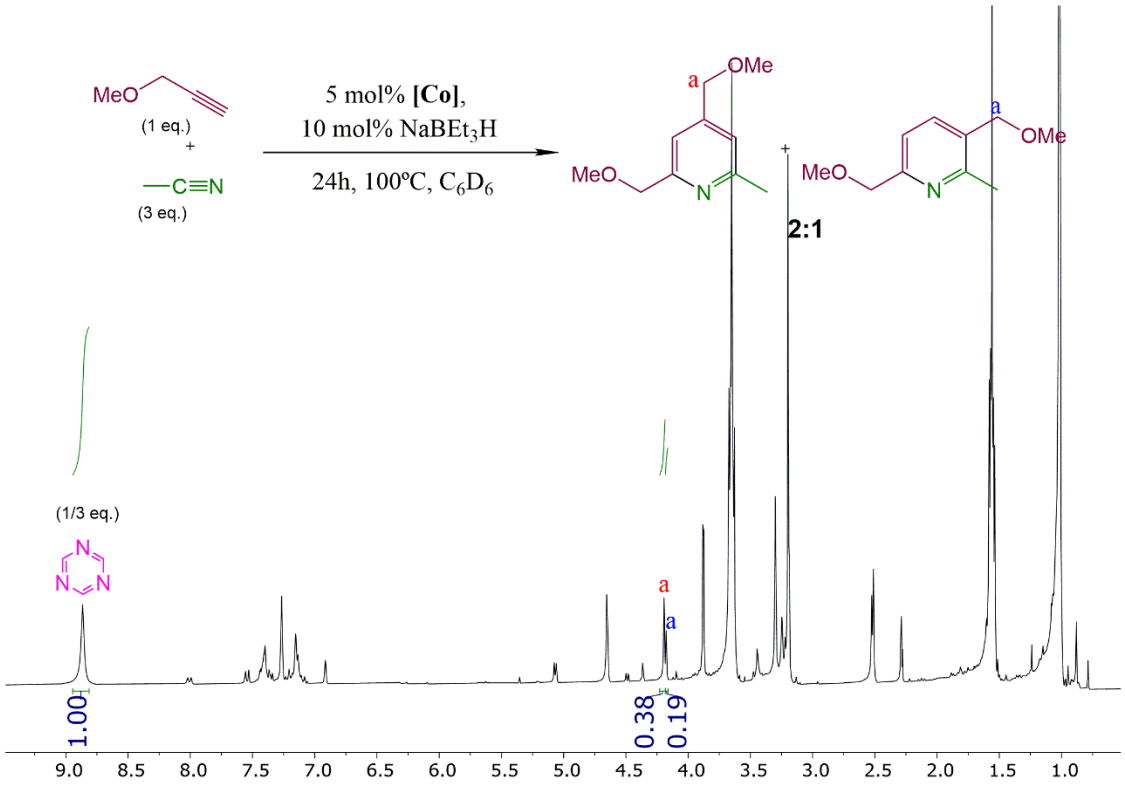


Figure S5. Crude ^{1}H NMR spectrum in C_6D_6 using s-triazine as internal standard (Table 4; Entry 5).

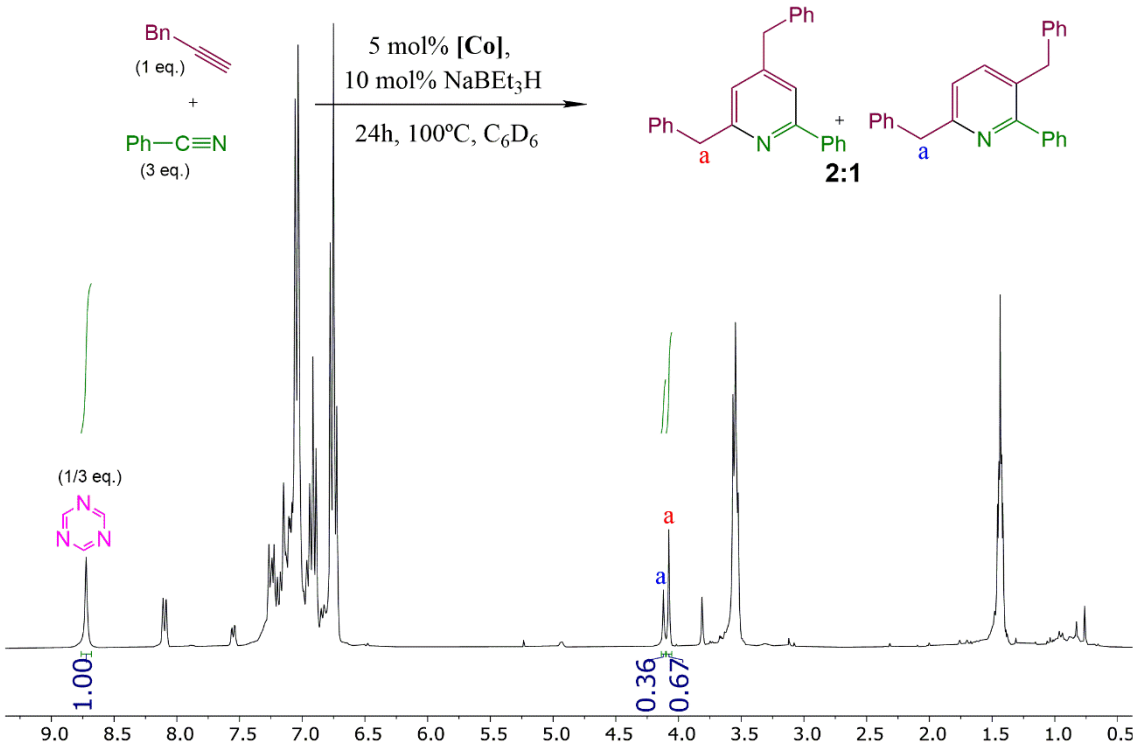


Figure S6. Crude ^{1}H NMR spectrum in C_6D_6 using s-triazine as internal standard (Table 5; Entry 1).

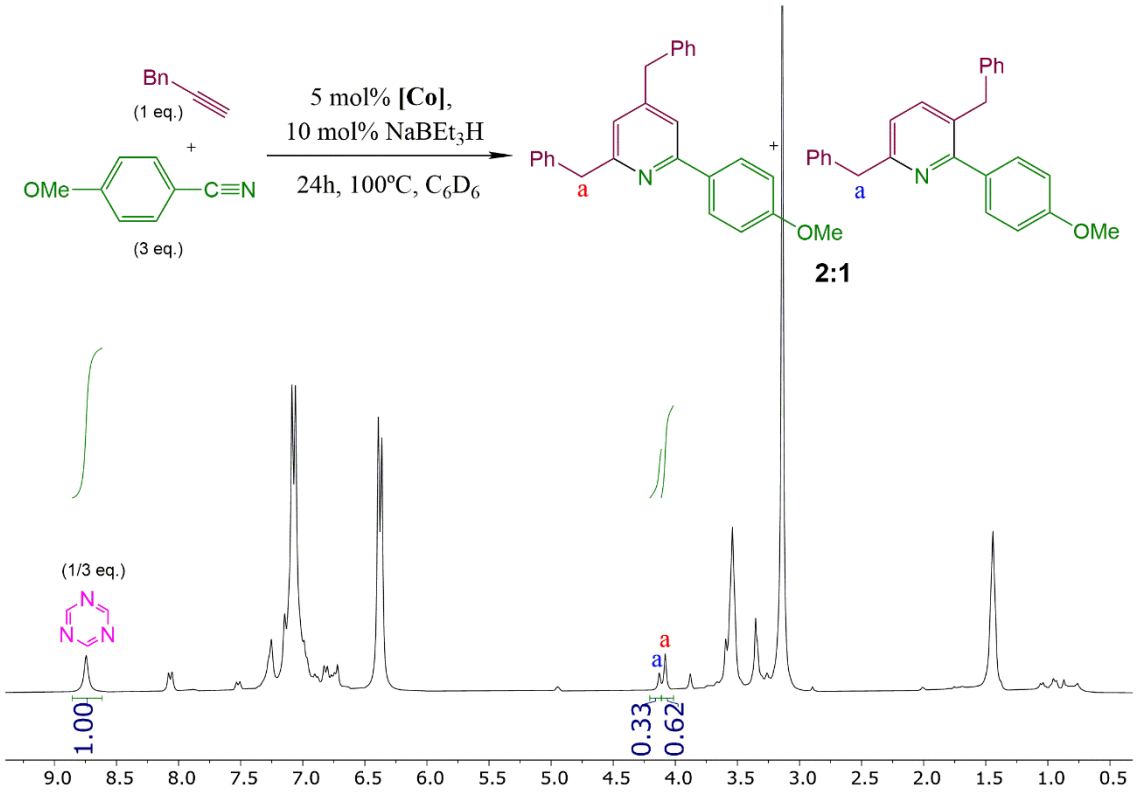


Figure S7. Crude ^{1}H NMR spectrum in C_6D_6 using s-triazine as internal standard (Table 5; Entry 2).

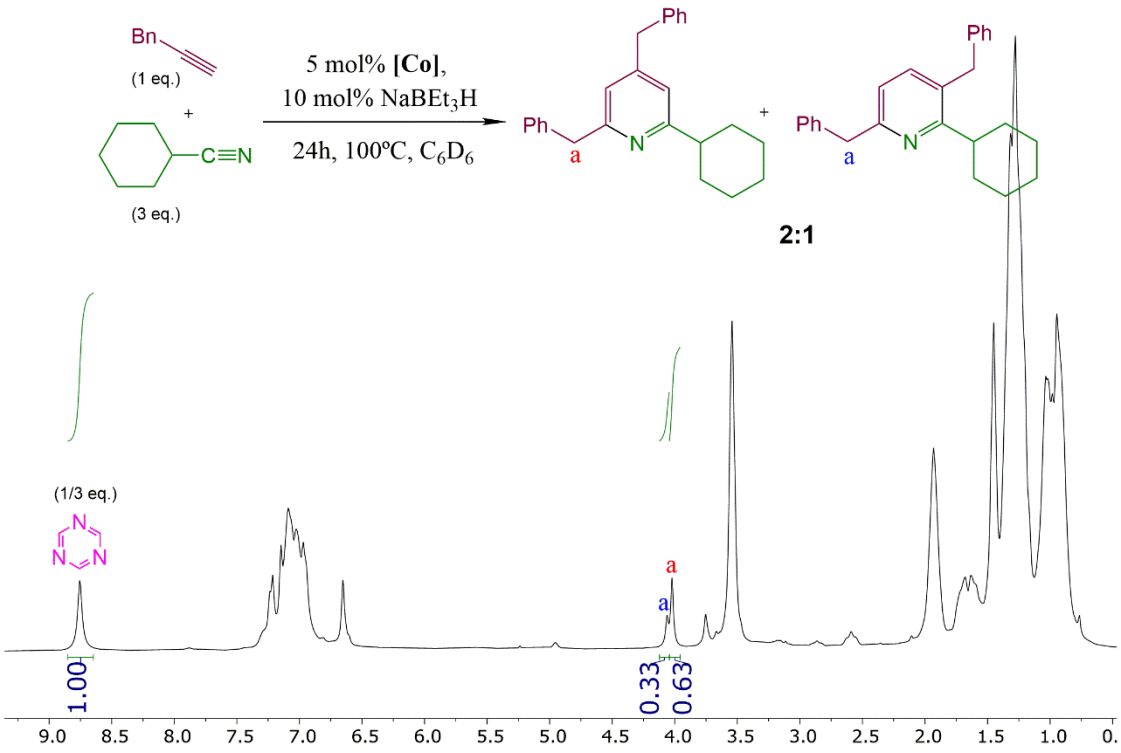


Figure S8. Crude ^{1}H NMR spectrum in C_6D_6 using s-triazine as internal standard (Table 5; Entry 5).

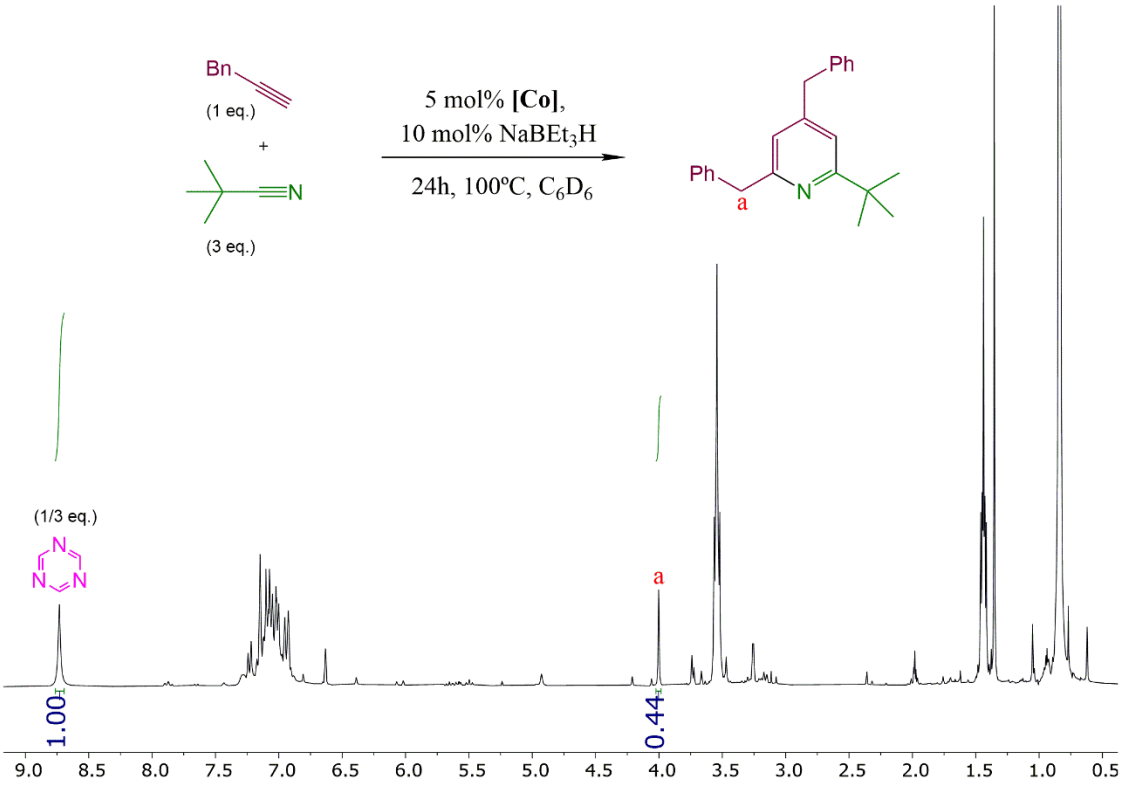


Figure S9. Crude ^{1}H NMR spectrum in C_6D_6 using s-triazine as internal standard (Table 5; Entry 6).

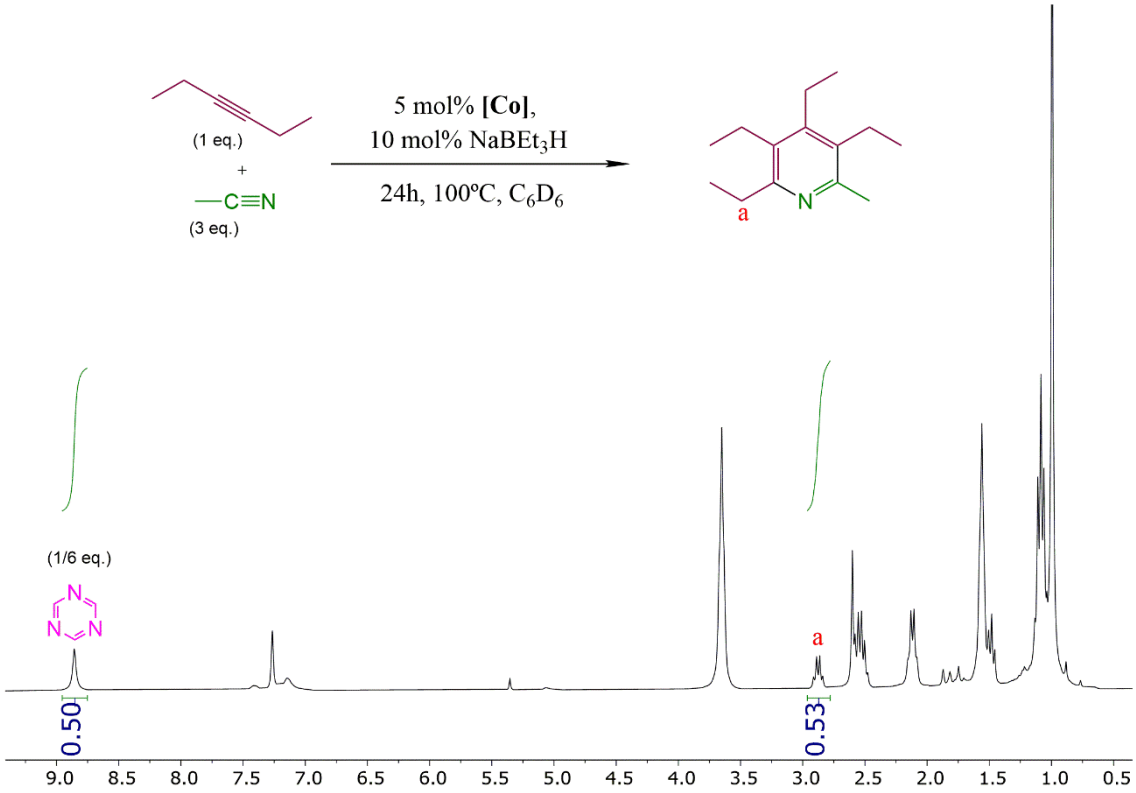


Figure S10. Crude ^{1}H NMR spectrum in C_6D_6 using s-triazine as internal standard (Table 6; Entry 1).

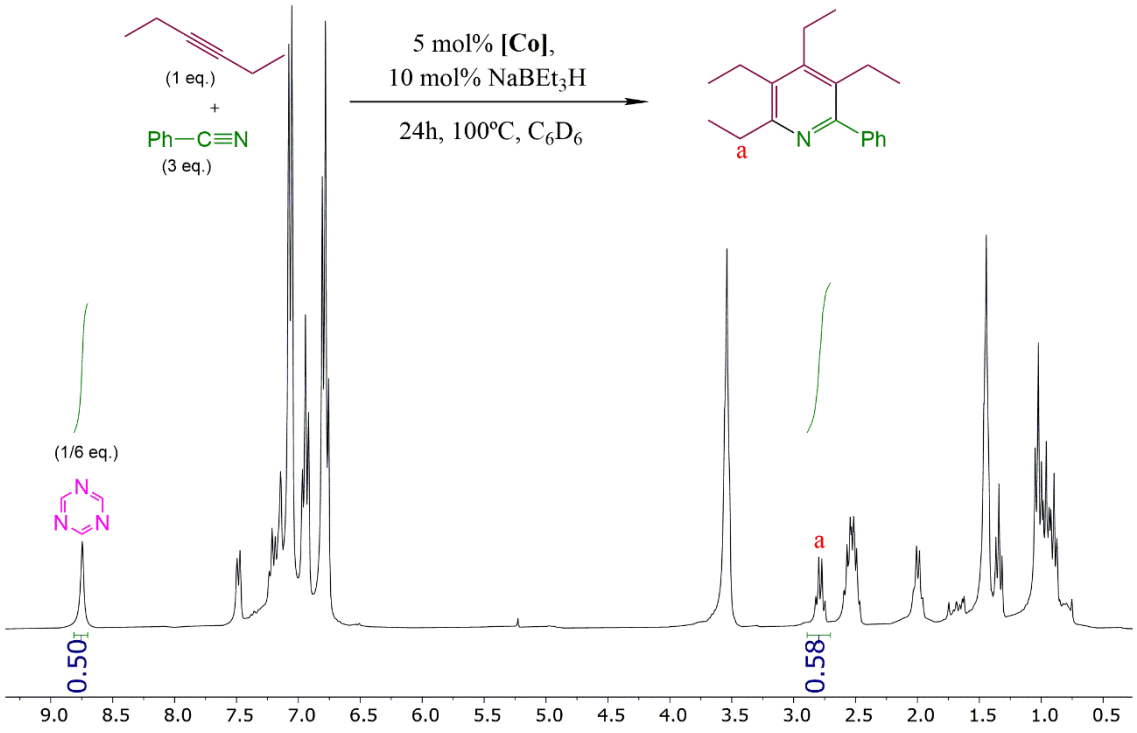


Figure S11. Crude ^{1}H NMR spectrum in C_6D_6 using s-triazine as internal standard (Table 4; Entry 2).

5. NMR spectra of isolated pyridines

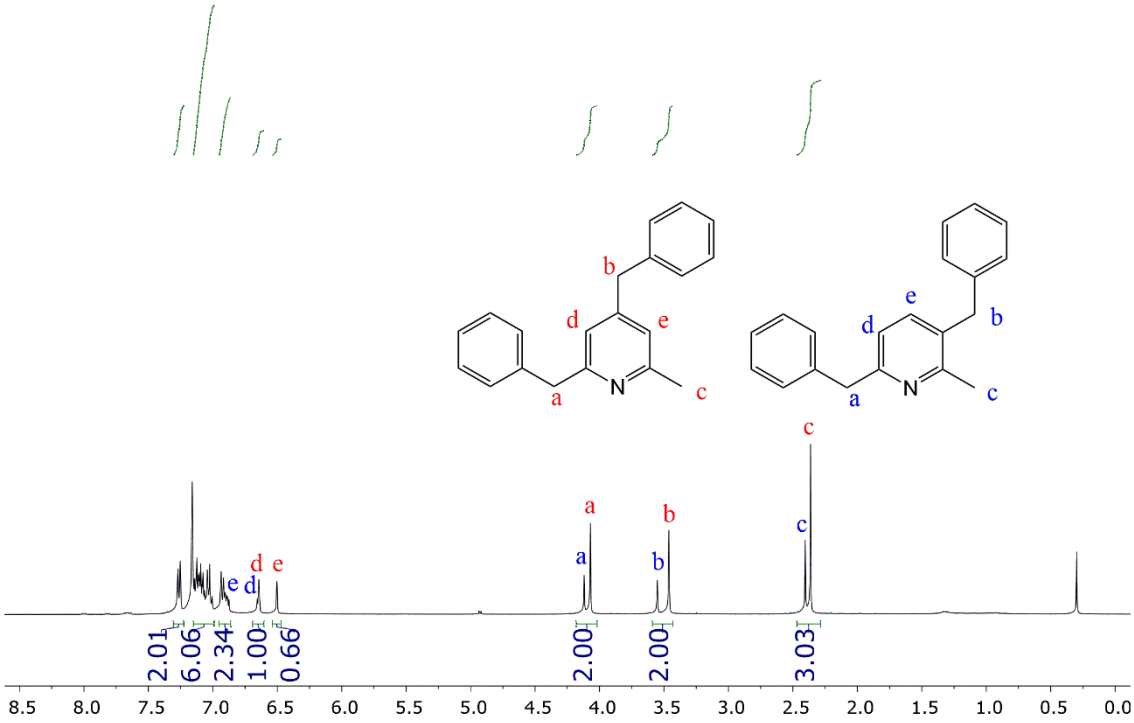


Figure S12. ^{1}H NMR spectrum of the mixture of 2,4-dibenzyl-6-methylpyridine and 3,6-dibenzyl-2-methylpyridine in C_6D_6.

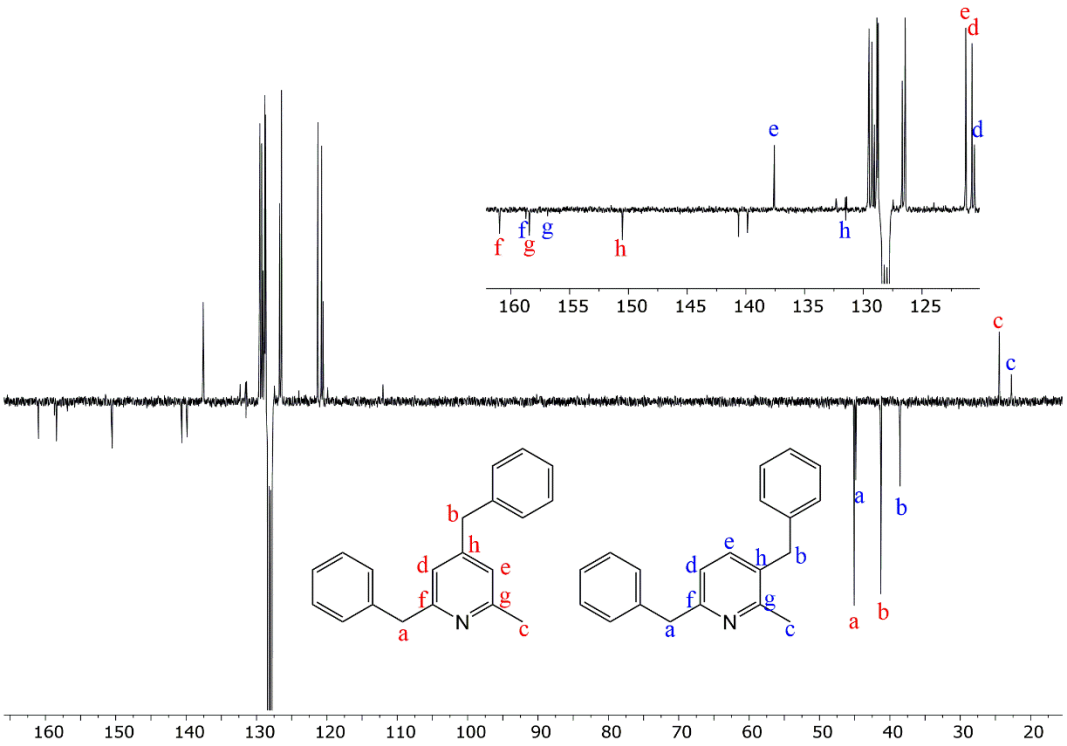


Figure S13. ^{13}C{^{1}H} NMR APT spectrum of the mixture of 2,4-dibenzyl-6-methylpyridine and 3,6-dibenzyl-2-methylpyridine in C_6D_6.

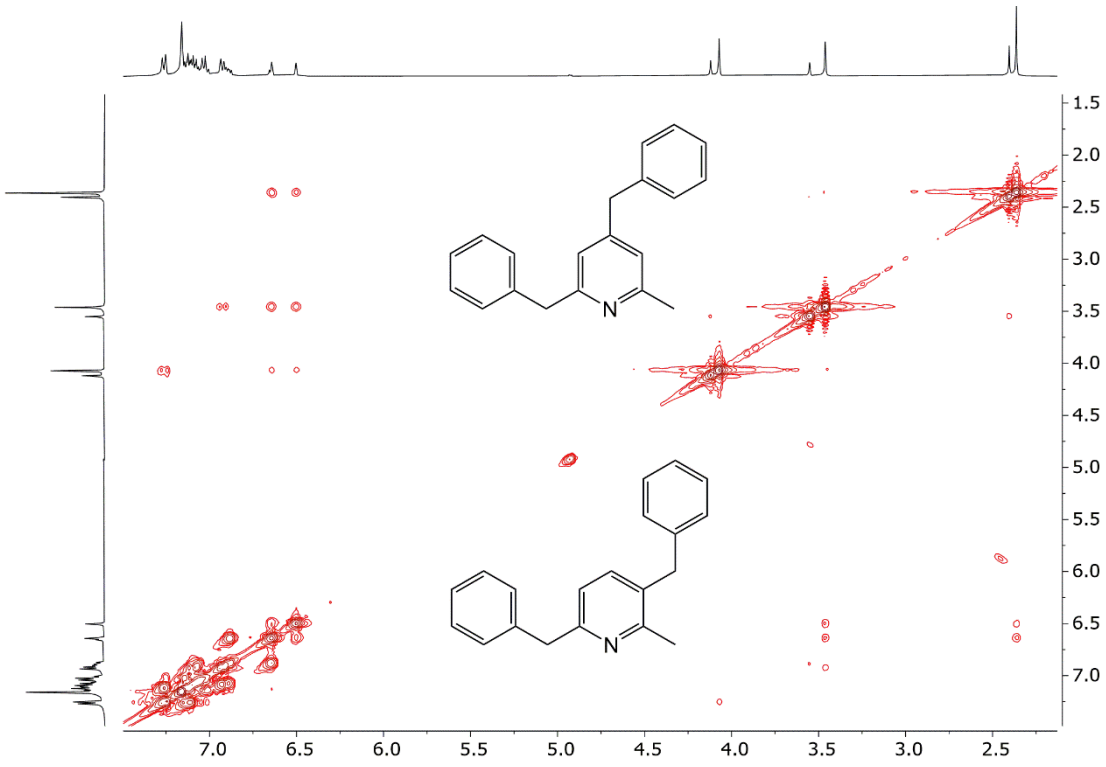


Figure S14. ^{1}H-^{1}H COSY spectrum of the mixture of 2,4-dibenzyl-6-methylpyridine and 3,6-dibenzyl-2-methylpyridine in C_6D_6.

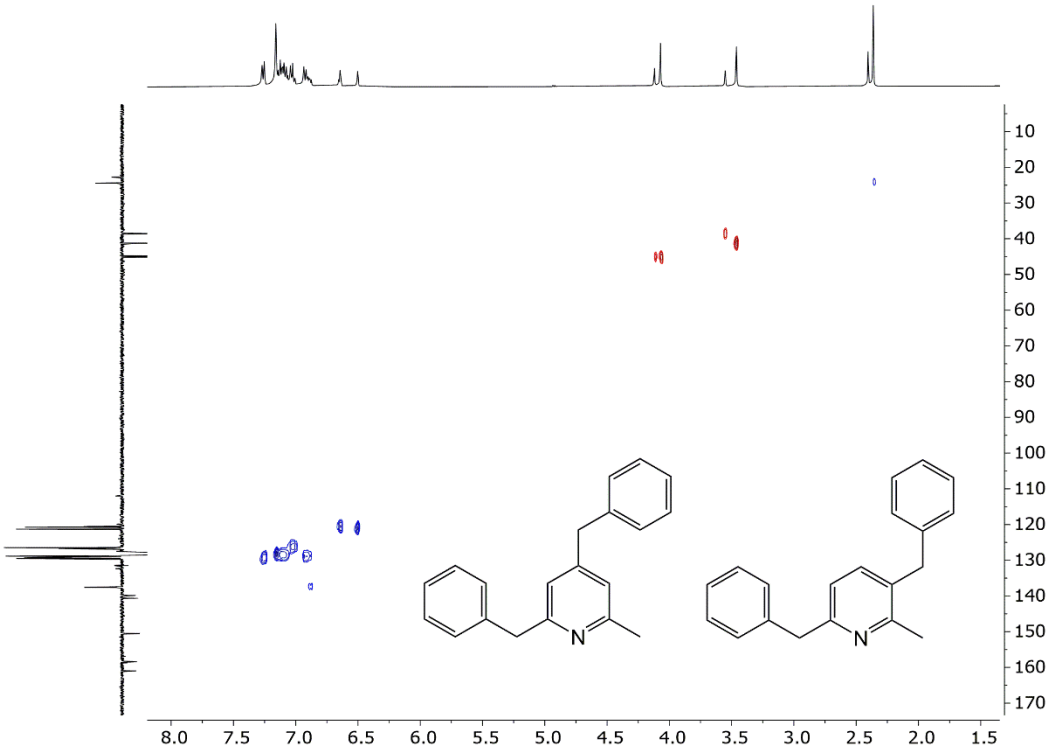


Figure S15. ^{1}H-^{13}C HSQC spectrum of the mixture of 2,4-dibenzyl-6-methylpyridine and 3,6-dibenzyl-2-methylpyridine in C_6D_6.

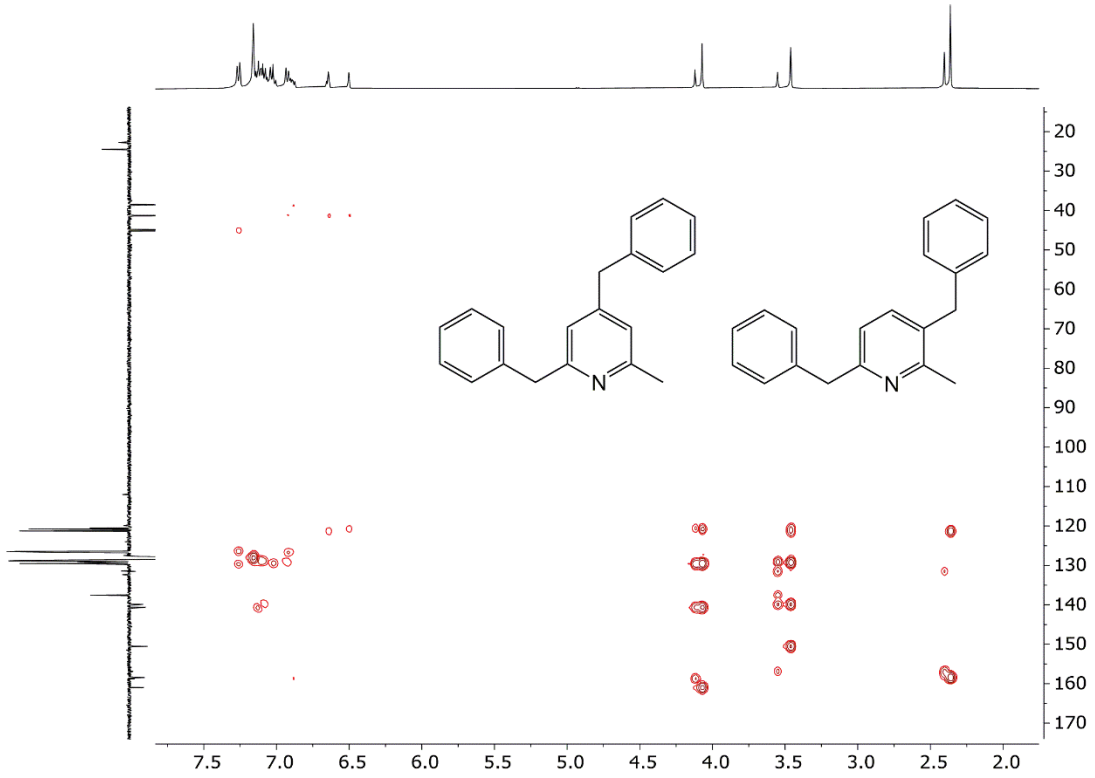


Figure S16. ^{1}H-^{13}C HMBC spectrum of the mixture of 2,4-dibenzyl-6-methylpyridine and 3,6-dibenzyl-2-methylpyridine in C_6D_6.

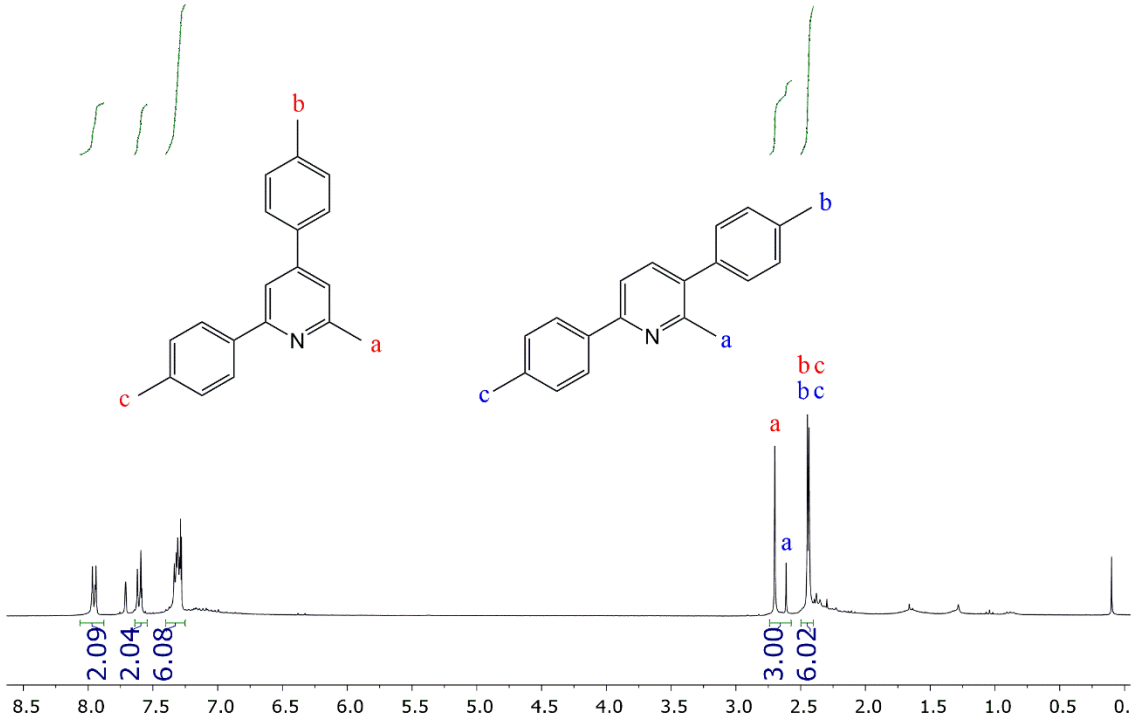


Figure S17. ^{1}H NMR spectrum of the mixture of 2-methyl-4,6-di(*p*-tolyl)pyridine and 2-methyl-3,6-di(*p*-tolyl)pyridine in $CDCl_3$.

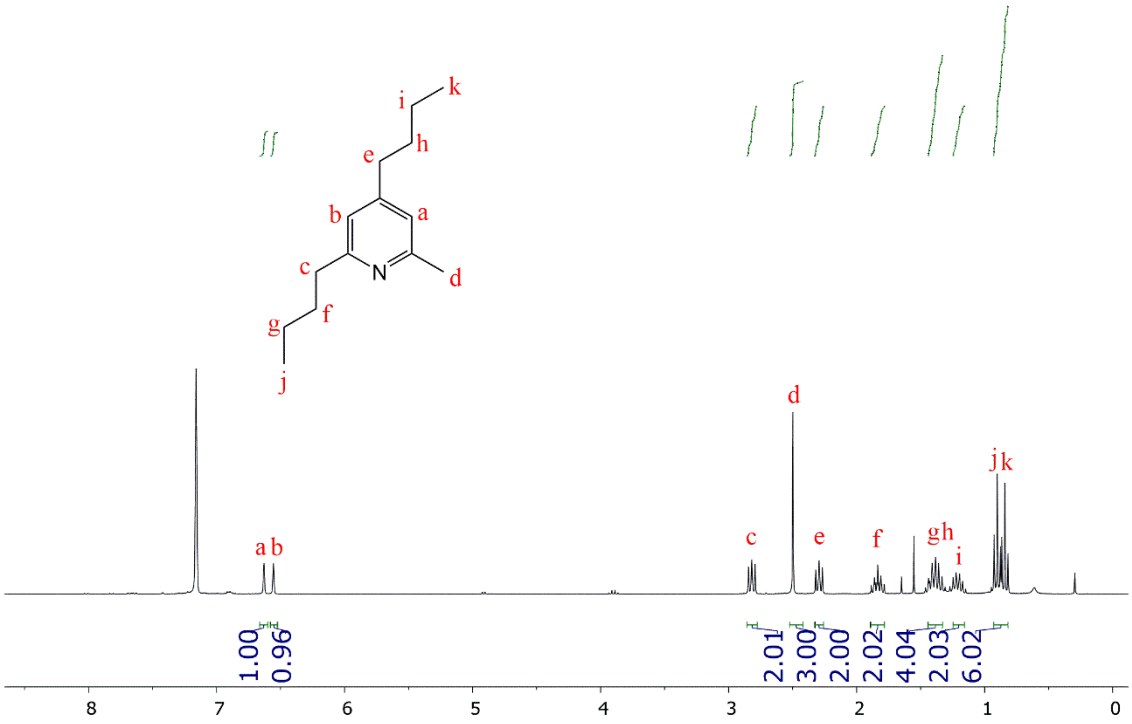


Figure S18. ^{1}H NMR spectrum of 2,4-dibutyl-6-methylpyridine in C_6D_6.

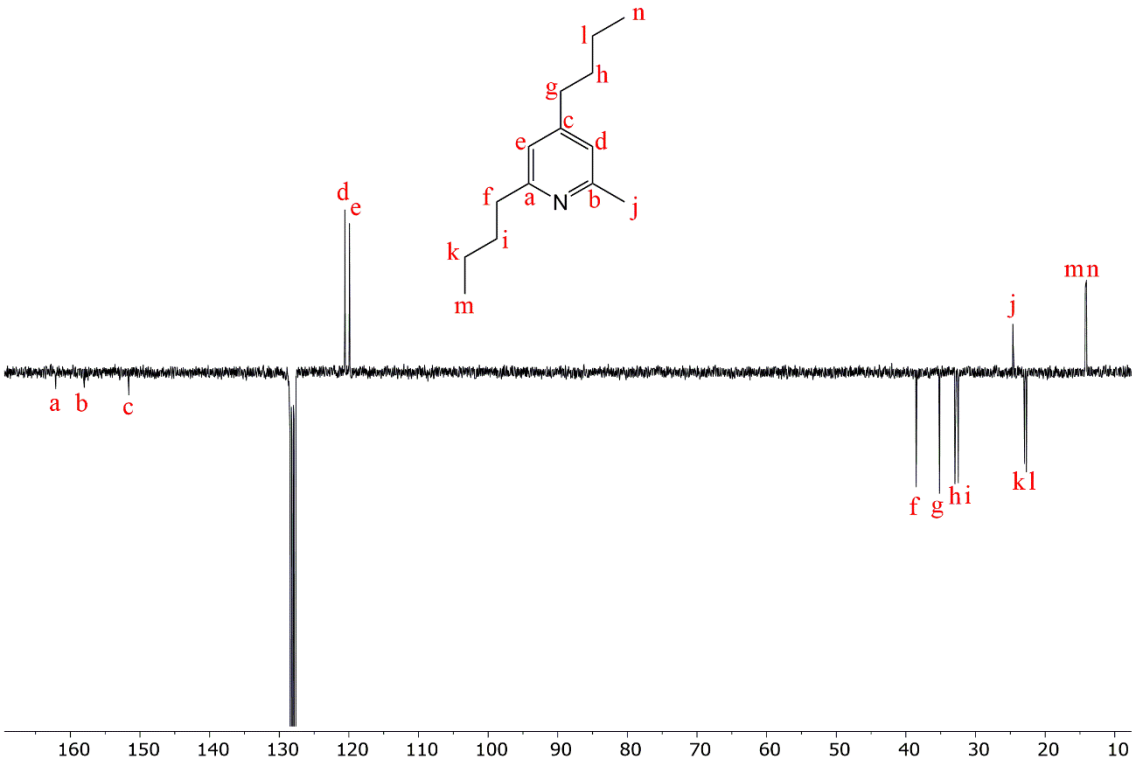


Figure S19. $^{13}C\{^{1}H\}$ NMR APT spectrum of 2,4-dibutyl-6-methylpyridine in C_6D_6.

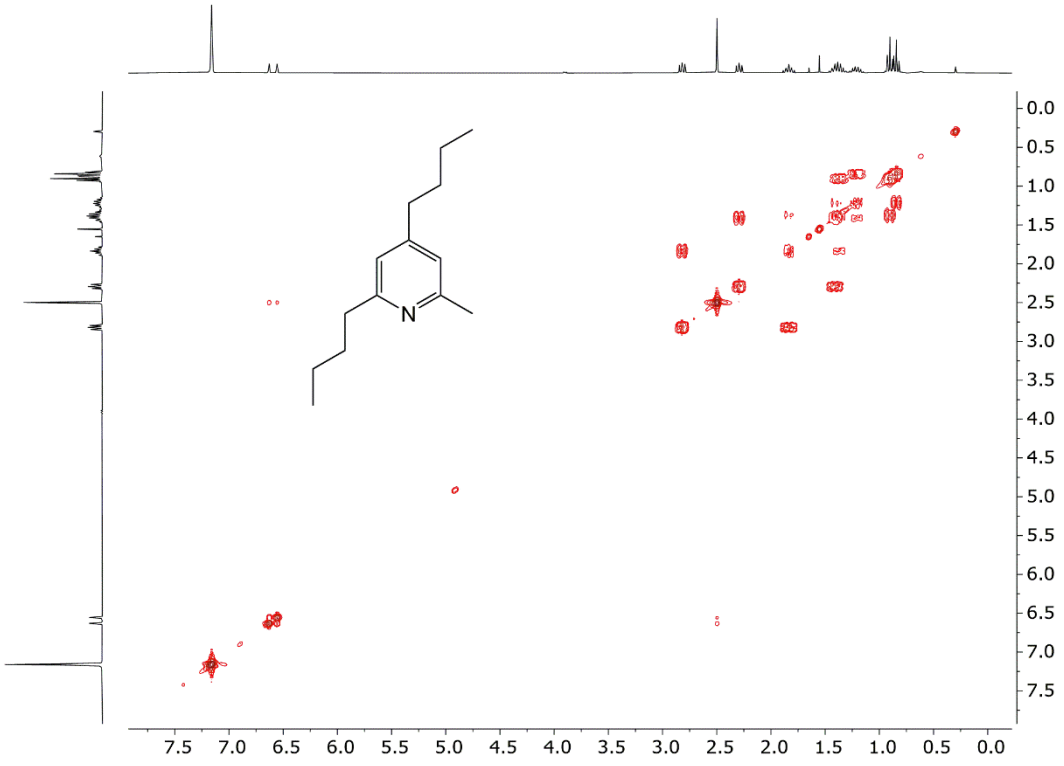


Figure S20. ^{1}H-^{1}H COSY spectrum of 2,4-dibutyl-6-methylpyridine in C_6D_6.

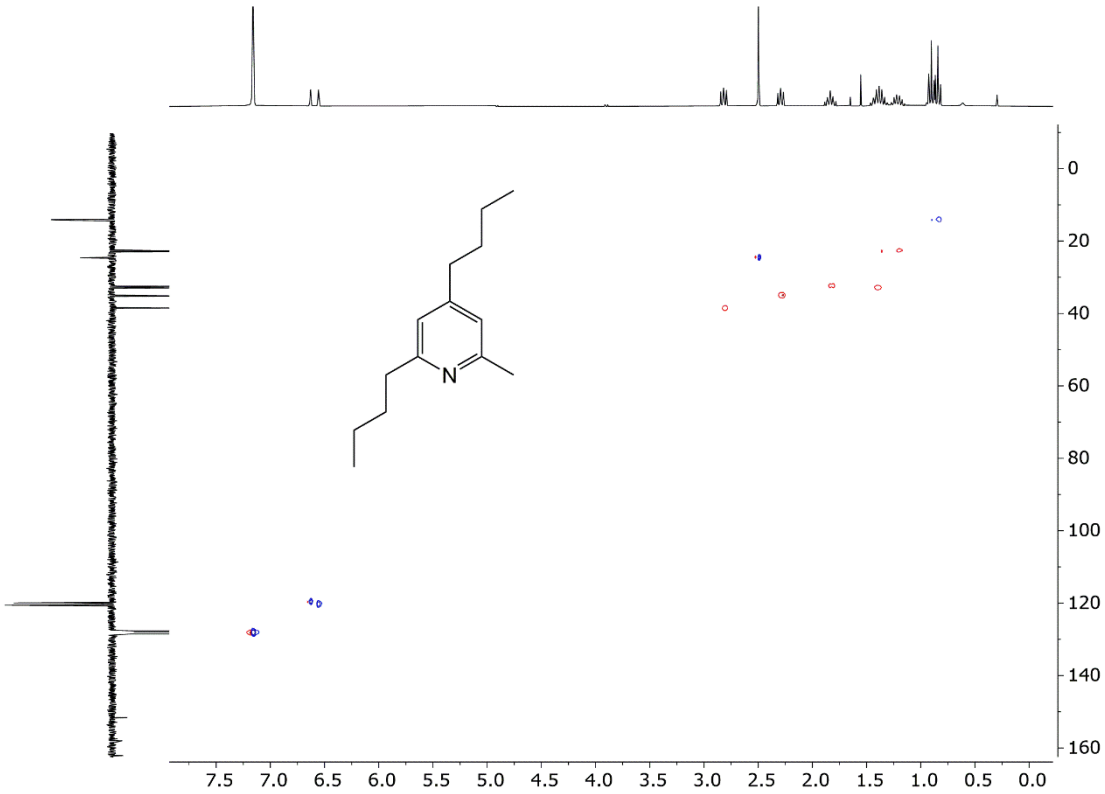


Figure S21. ^{1}H-^{13}C HSQC spectrum of 2,4-dibutyl-6-methylpyridine in C_6D_6.

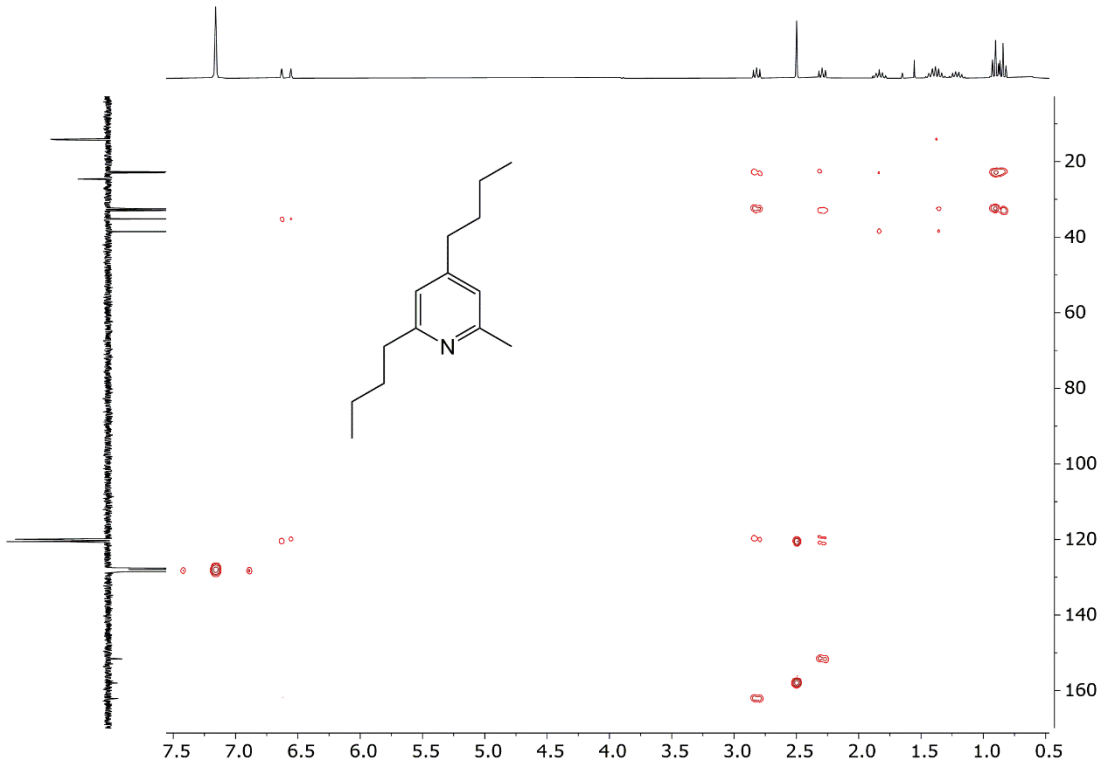


Figure S22. ^{1}H-^{13}C HMBC spectrum of 2,4-dibutyl-6-methylpyridine in C_6D_6.

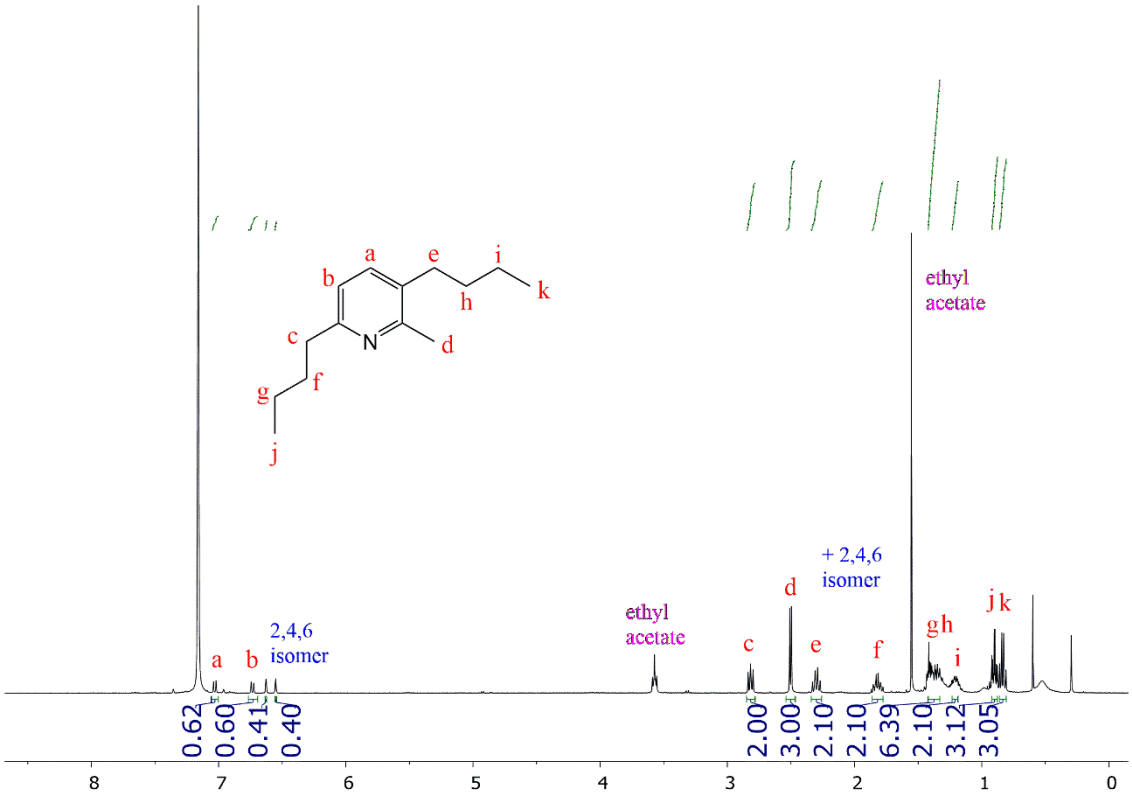


Figure S23. ^{1}H NMR spectrum of 3,6-dibutyl-2-methylpyridine in C_6D_6.

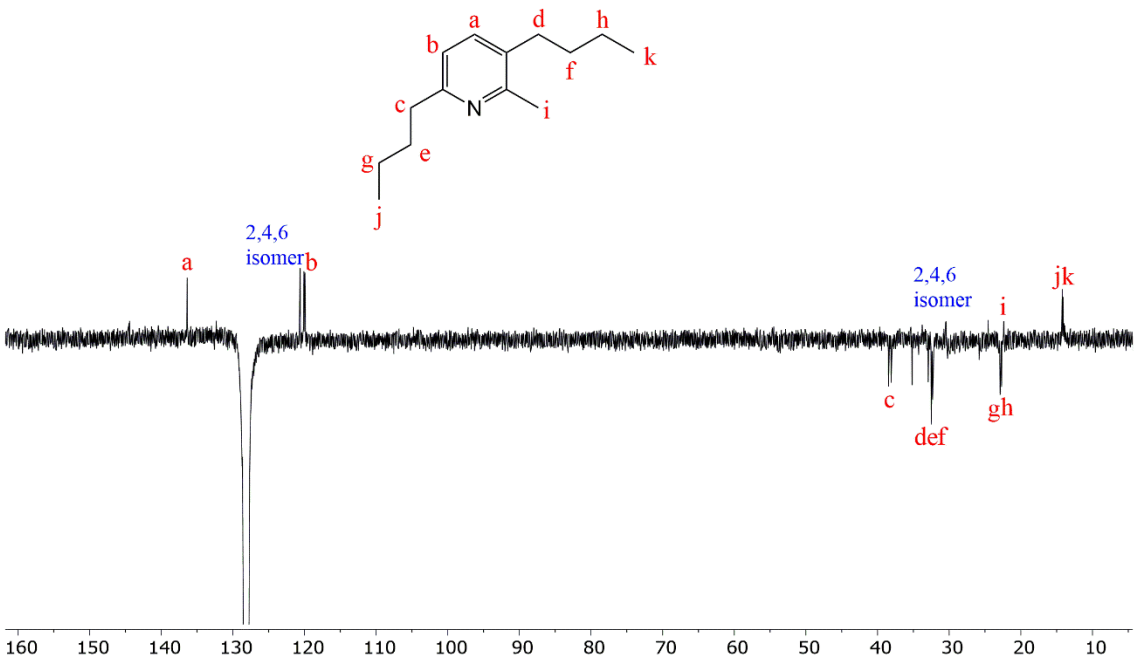


Figure S24. $^{13}C\{^{1}H\}$ NMR APT spectrum of 3,6-dibutyl-2-methylpyridine in C_6D_6.

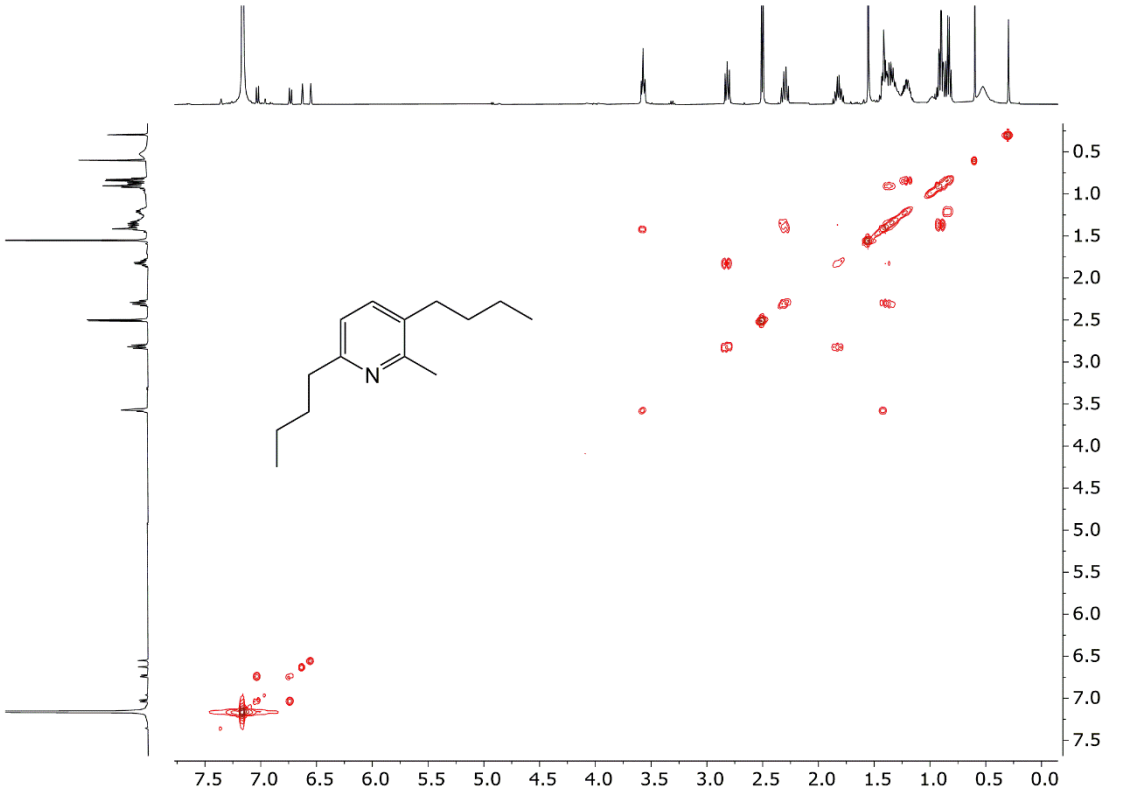


Figure S25. ^{1}H-^{1}H COSY spectrum of 3,6-dibutyl-2-methylpyridine in C_6D_6.

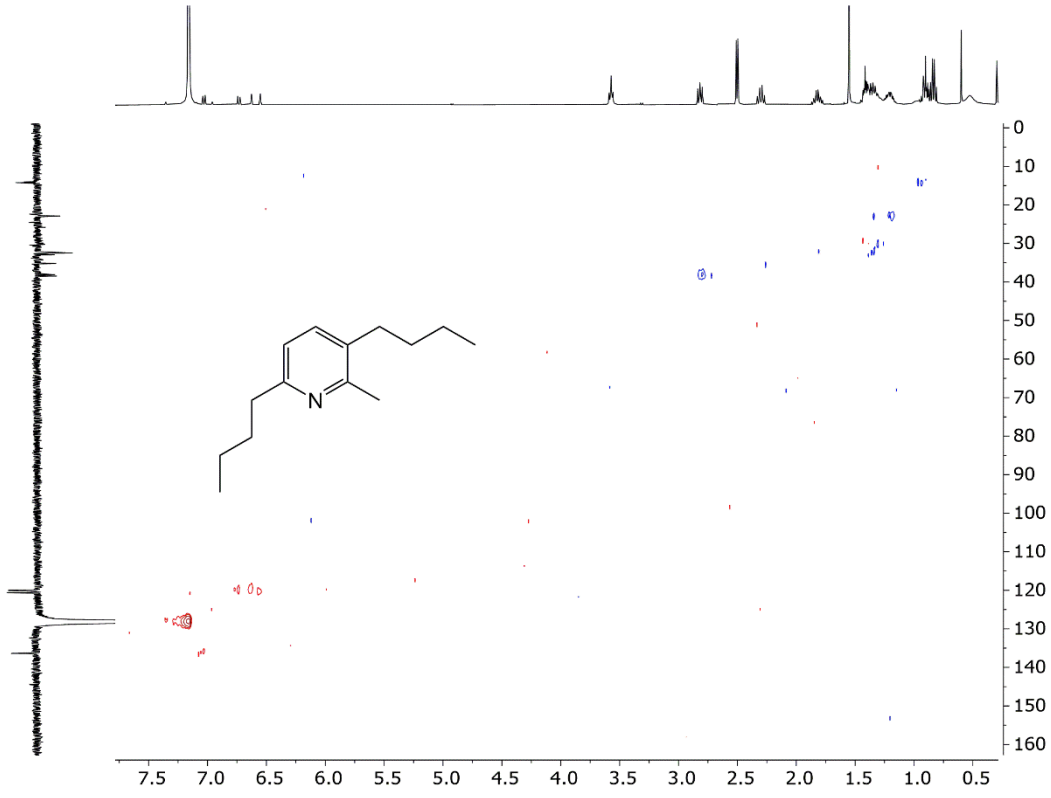


Figure S26. ^{1}H-^{13}C HSQC spectrum of 3,6-dibutyl-2-methylpyridine in C_6D_6.

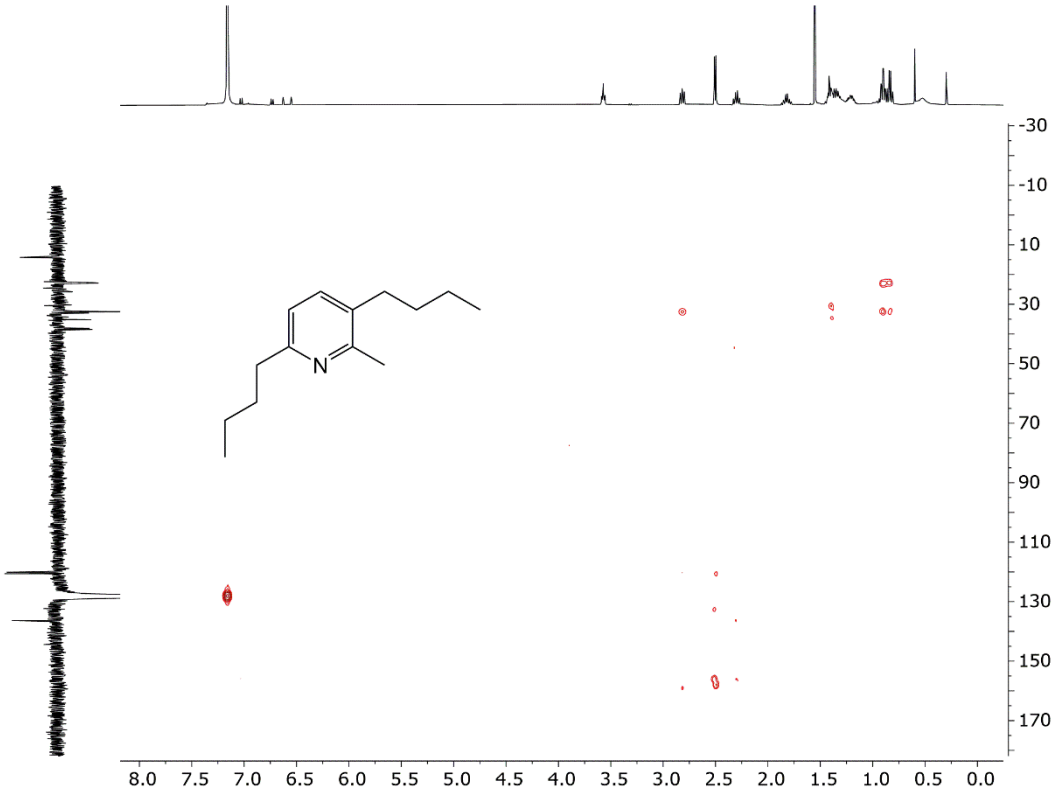


Figure S27. ^{1}H-^{13}C HMBC spectrum of 3,6-dibutyl-2-methylpyridine in C_6D_6.

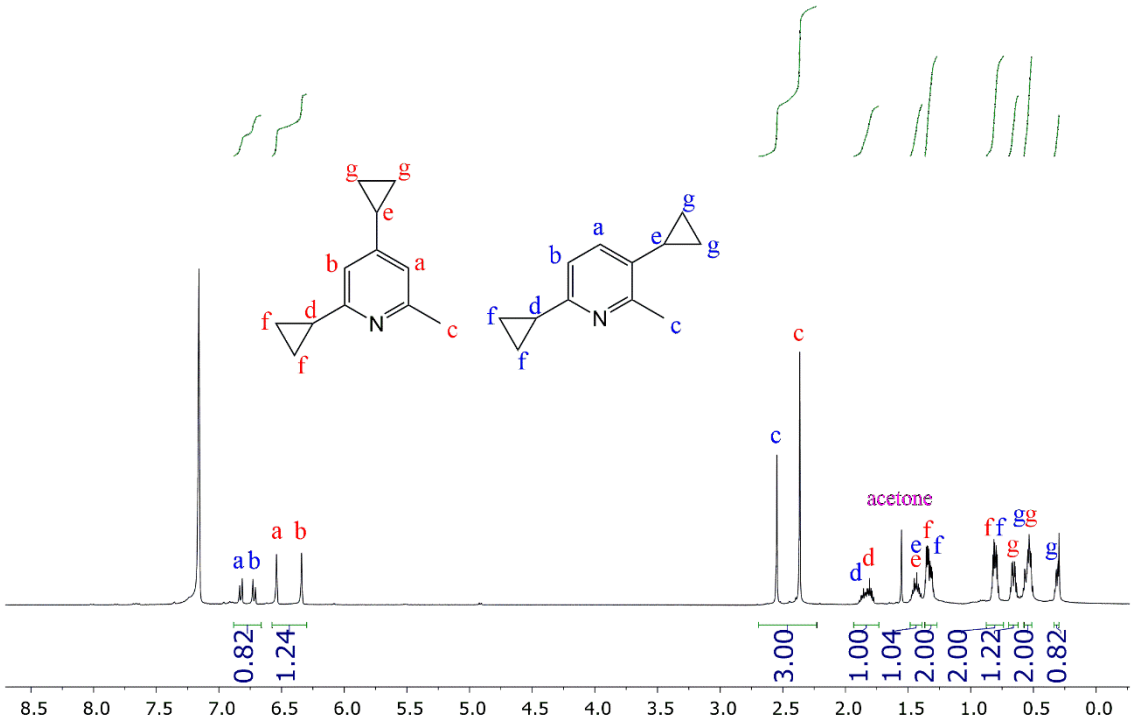


Figure S28. ^{1}H NMR spectrum of the mixture of 2,4-dicyclopropyl-6-methylpyridine and 3,6-dicyclopropyl-2-methylpyridine in C_6D_6.

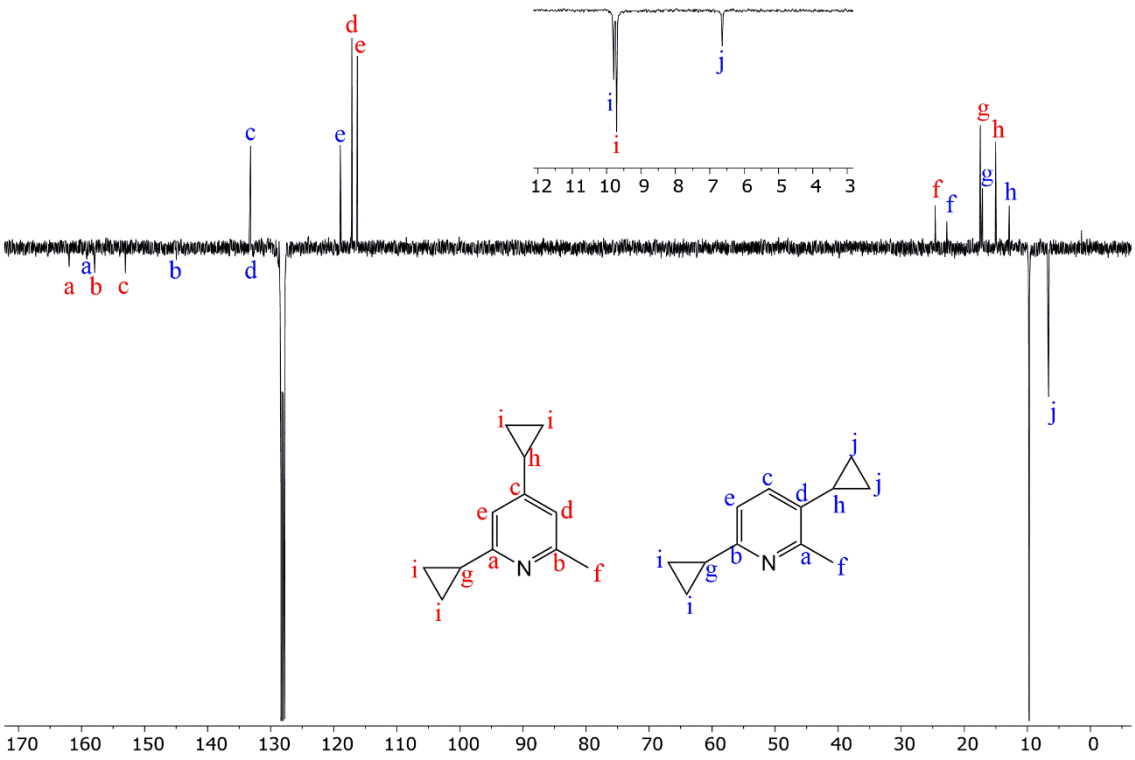


Figure S29. $^{13}C\{^{1}H\}$ NMR APT spectrum of the mixture of 2,4-dicyclopropyl-6-methylpyridine and 3,6-dicyclopropyl-2-methylpyridine in C_6D_6.

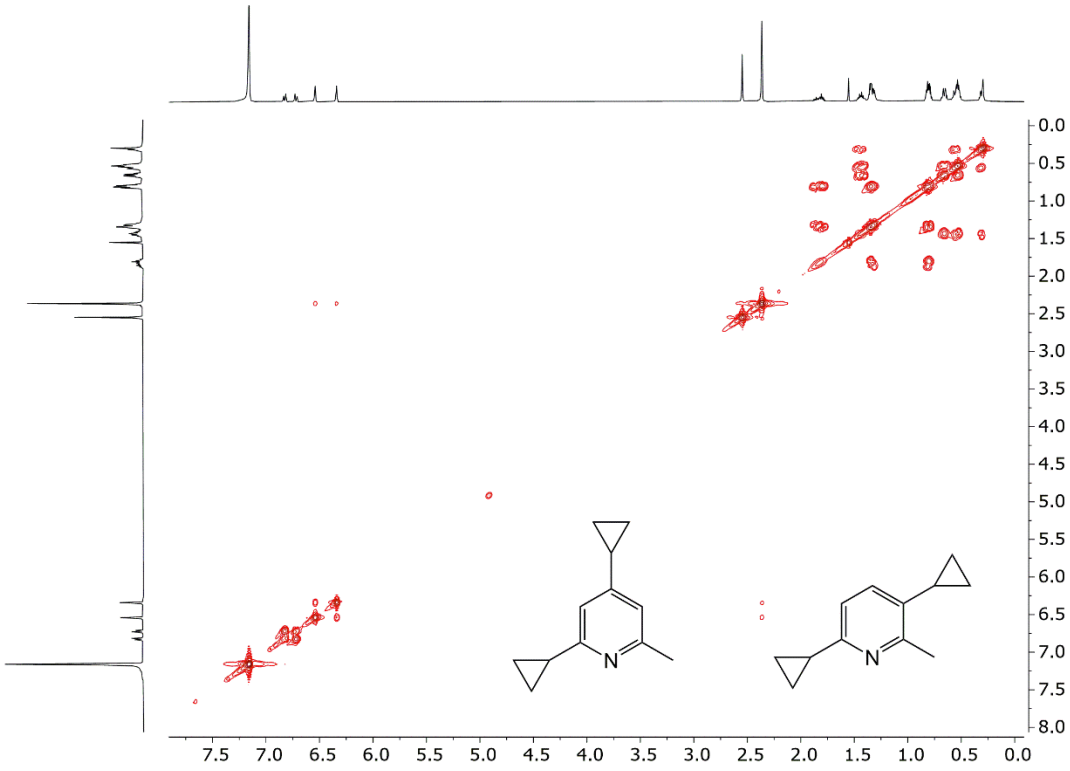


Figure S30. ^{1}H-^{1}H COSY spectrum of the mixture of 2,4-dicyclopropyl-6-methylpyridine and 3,6-dicyclopropyl-2-methylpyridine in C_6D_6.

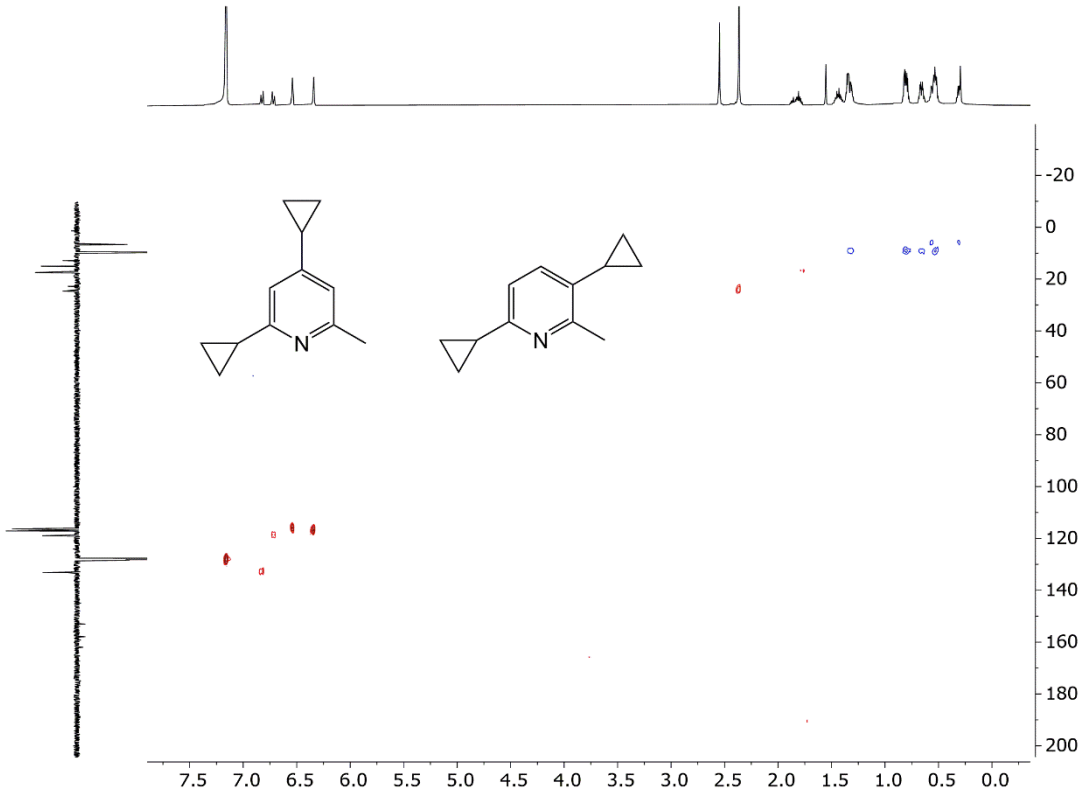


Figure S31. ^{1}H-^{13}C HSQC spectrum of the mixture of 2,4-dicyclopropyl-6-methylpyridine and 3,6-dicyclopropyl-2-methylpyridine in C_6D_6.

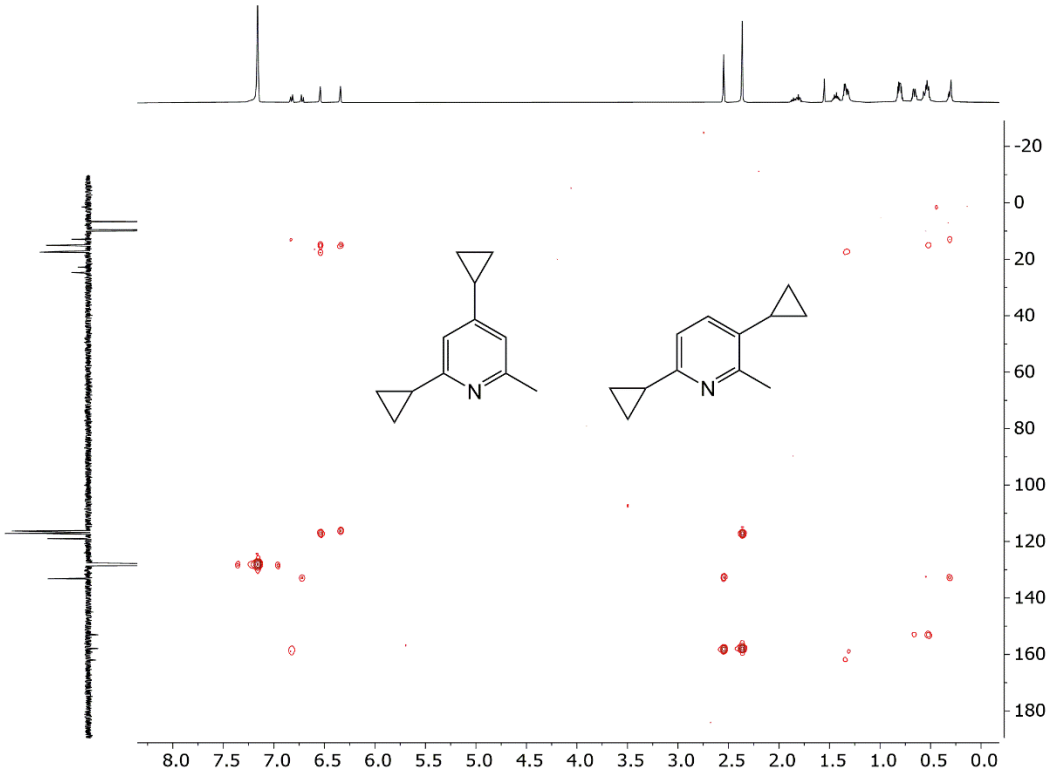


Figure S32. ^{1}H-^{13}C HMBC spectrum of the mixture of 2,4-dicyclopropyl-6-methylpyridine and 3,6-dicyclopropyl-2-methylpyridine in C_6D_6.

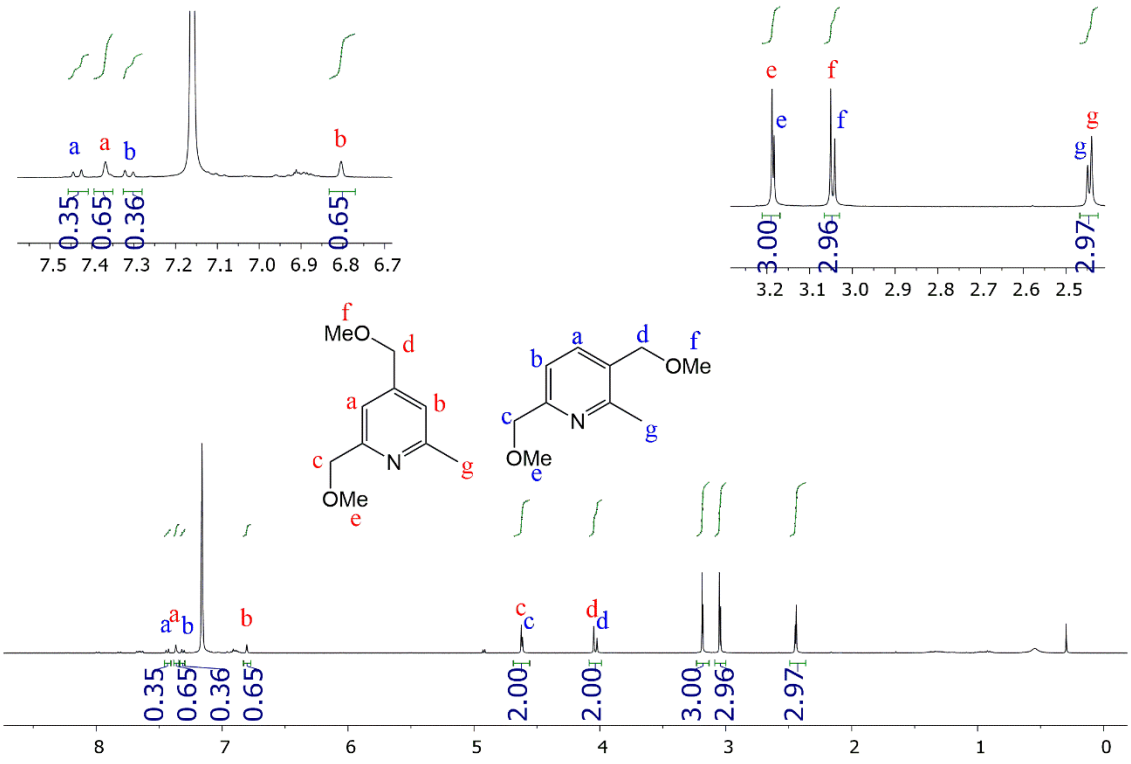


Figure S33. ^{1}H NMR spectrum of the mixture of 2,4-bis(methoxymethyl)-6-methylpyridine and 3,6-bis(methoxymethyl)-2-methylpyridine in C_6D_6.

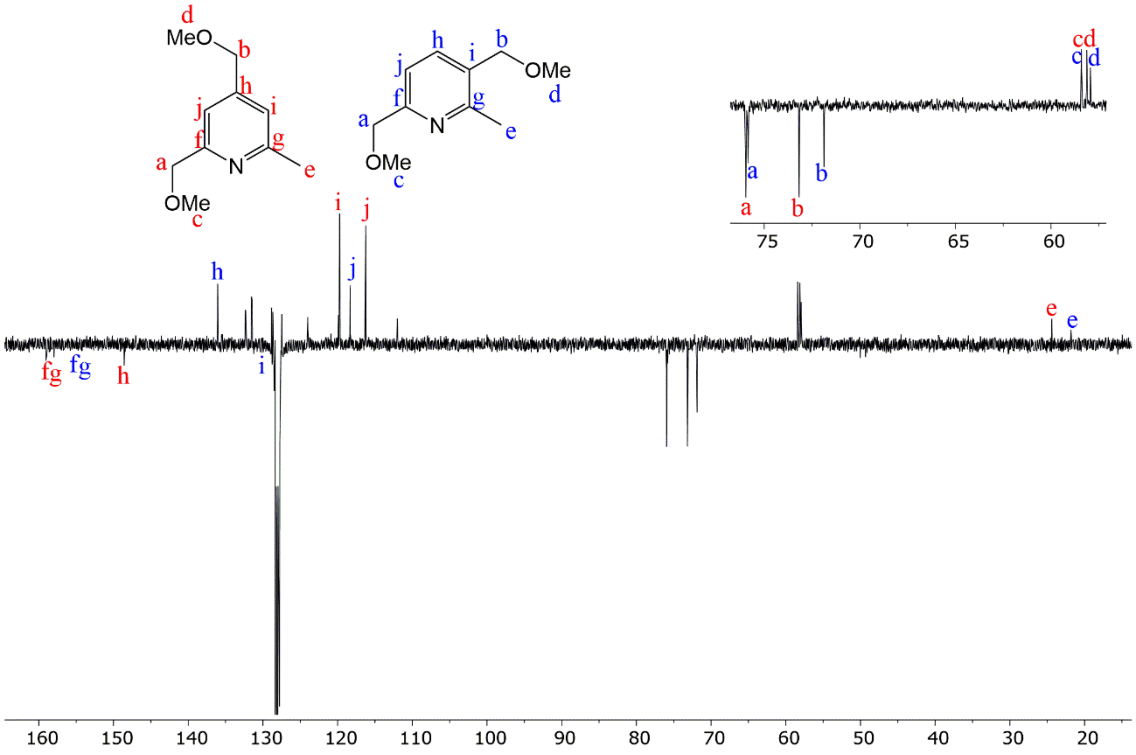


Figure S34. $^{13}C\{^{1}H\}$ NMR APT spectrum of the mixture of 2,4-bis(methoxymethyl)-6-methylpyridine and 3,6-bis(methoxymethyl)-2-methylpyridine in C_6D_6.

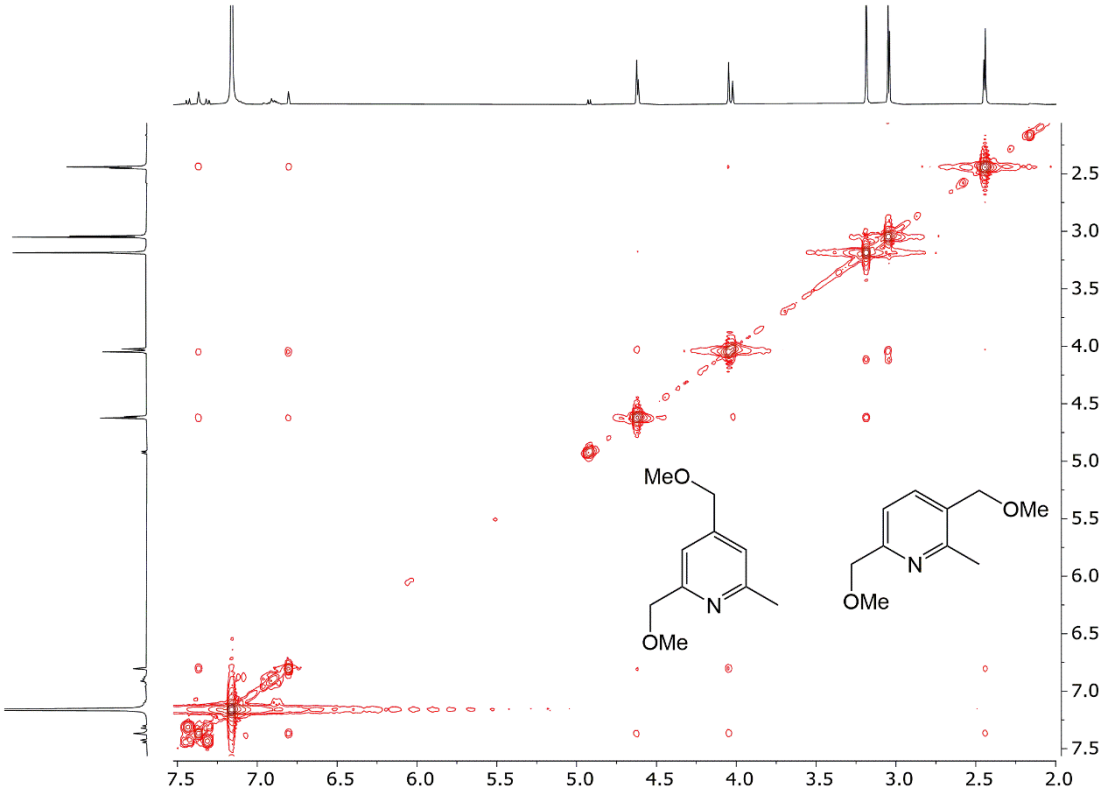


Figure S35. ^{1}H-^{1}H COSY spectrum of the mixture of 2,4-bis(methoxymethyl)-6-methylpyridine and 3,6-bis(methoxymethyl)-2-methylpyridine in C_6D_6.

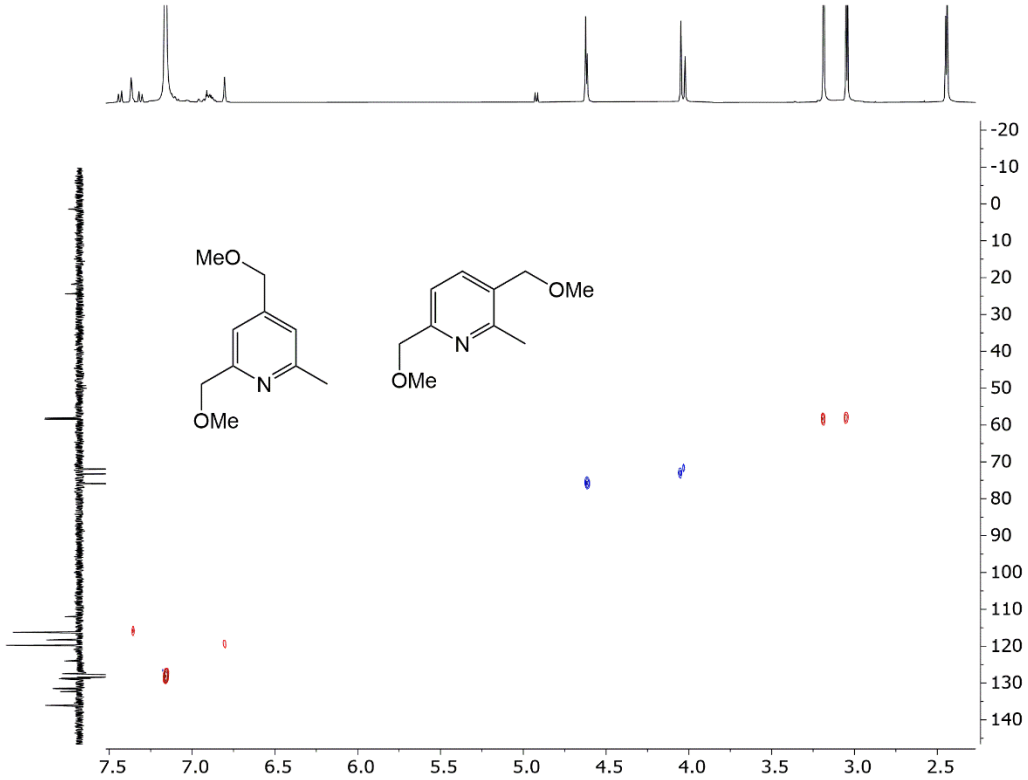


Figure S36. ^{1}H-^{13}C HSQC spectrum of the mixture of 2,4-bis(methoxymethyl)-6-methylpyridine and 3,6-bis(methoxymethyl)-2-methylpyridine in C_6D_6.

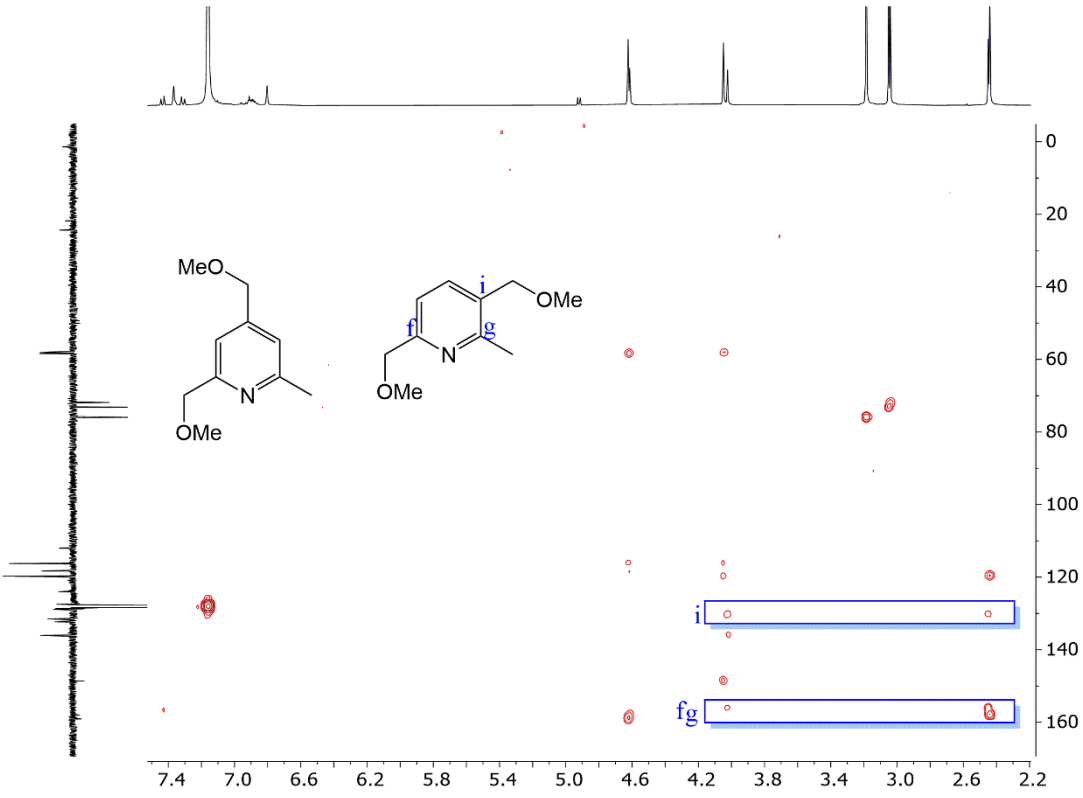


Figure S37. ^{1}H-^{13}C HMBC spectrum of the mixture of 2,4-bis(methoxymethyl)-6-methylpyridine and 3,6-bis(methoxymethyl)-2-methylpyridine in C_6D_6.

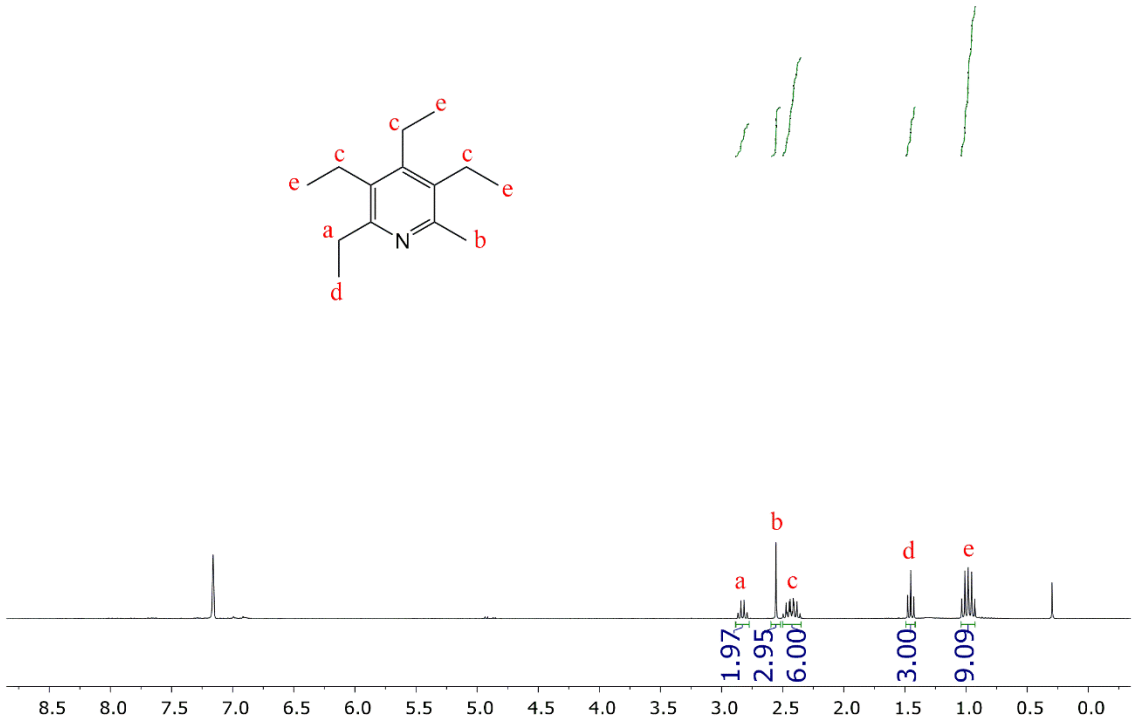


Figure S38. ^{1}H NMR spectrum of 2,3,4,5-tetraethyl-6-methylpyridine in C_6D_6.

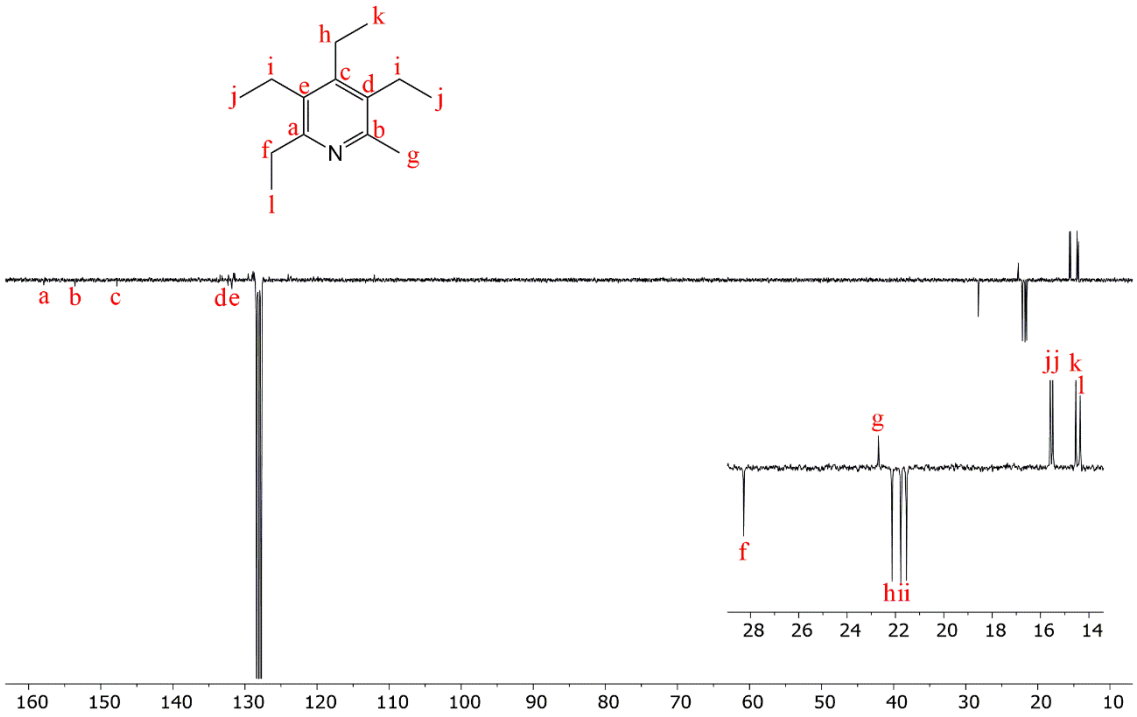


Figure S39. $^{13}C\{^{1}H\}$ NMR APT spectrum of 2,3,4,5-tetraethyl-6-methylpyridine in C_6D_6.

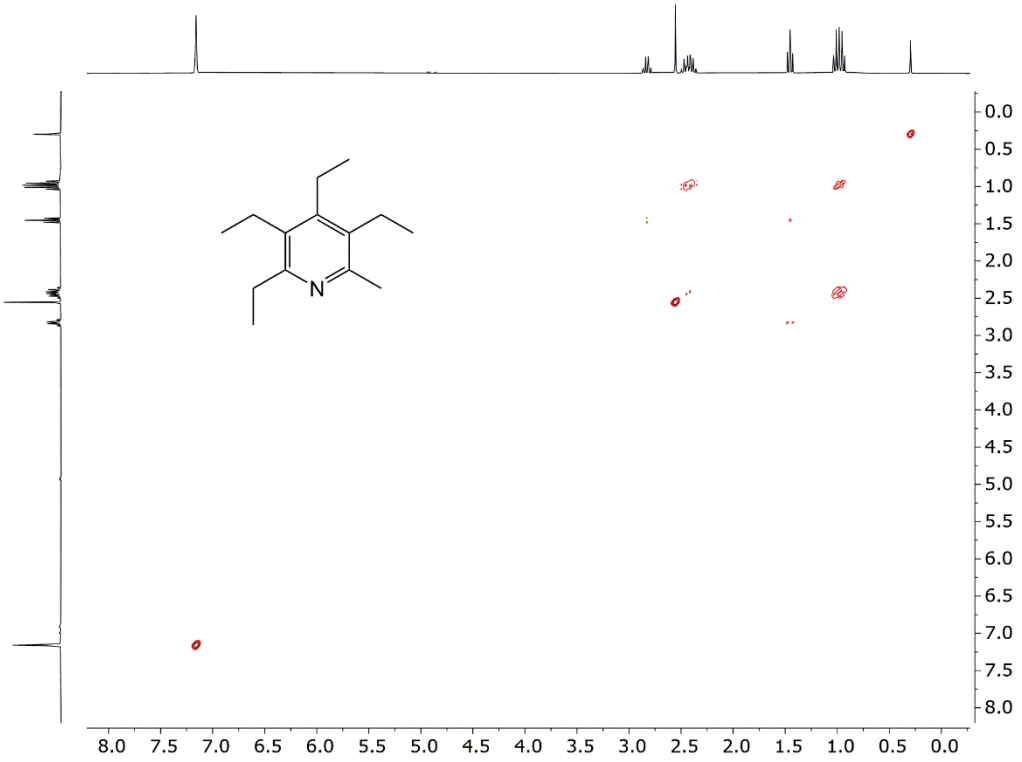


Figure S40. ^{1}H-^{1}H COSY spectrum of 2,3,4,5-tetraethyl-6-methylpyridine in C_6D_6.

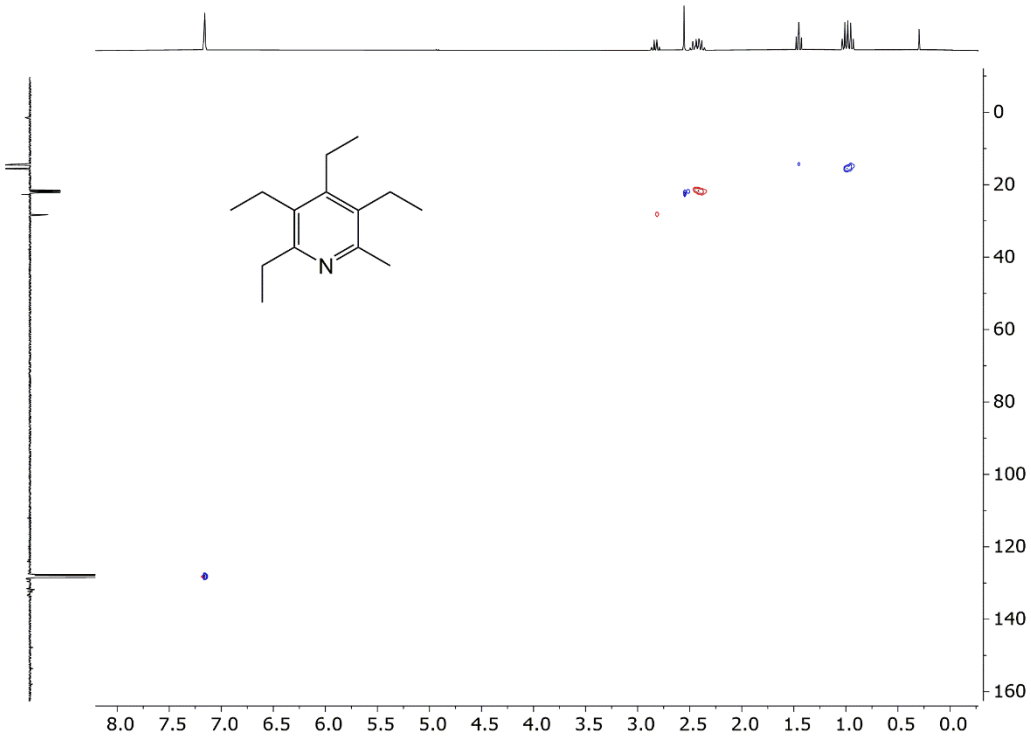


Figure S41. ^{1}H-^{13}C HSQC spectrum of 2,3,4,5-tetraethyl-6-methylpyridine in C_6D_6.

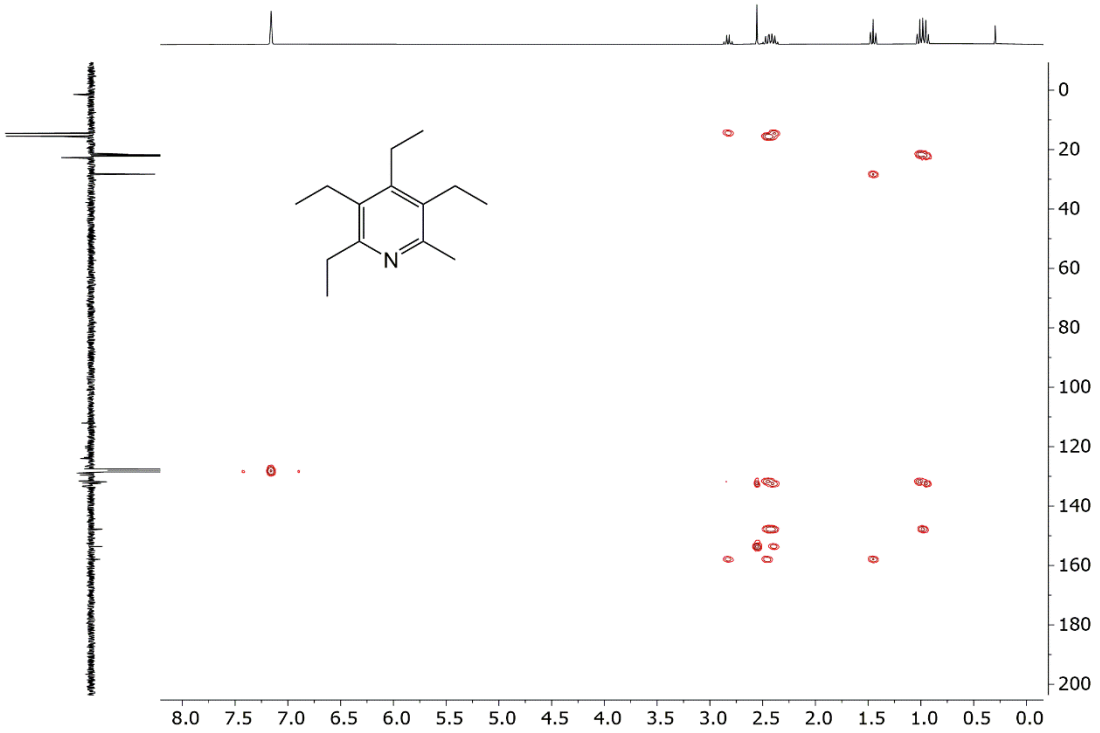


Figure S42. ^{1}H-^{13}C HMBC spectrum of 2,3,4,5-tetraethyl-6-methylpyridine in C_6D_6.

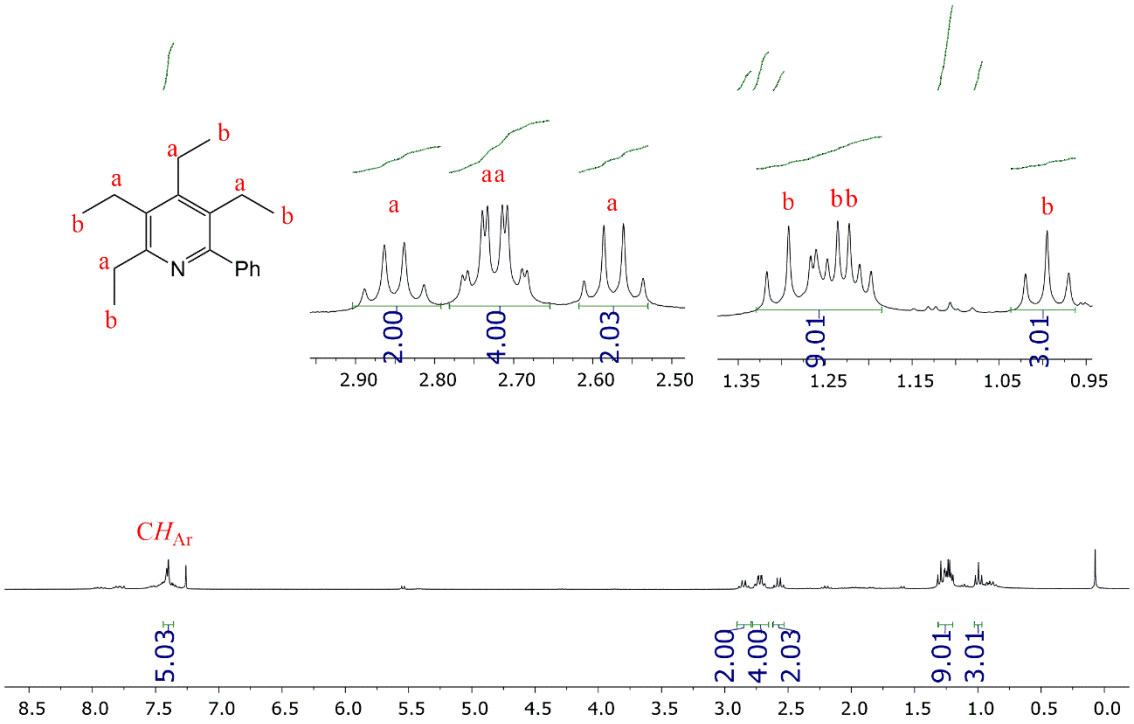


Figure S43. ^{1}H NMR spectrum of 2,3,4,5-tetraethyl-6-phenylpyridine in $CDCl_3$.

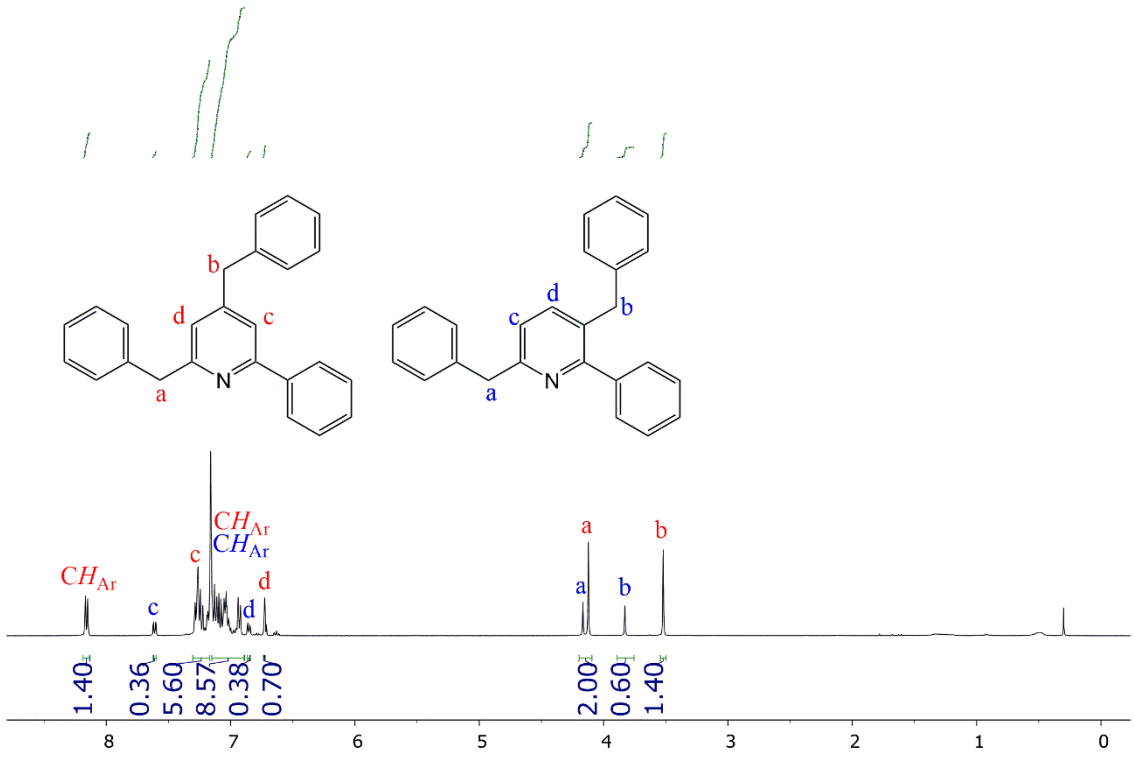


Figure S44. ^{1}H NMR spectrum of the mixture of 2,4-dibenzyl-6-phenylpyridine and 3,6-dibenzyl-2-phenylpyridine in C_6D_6.

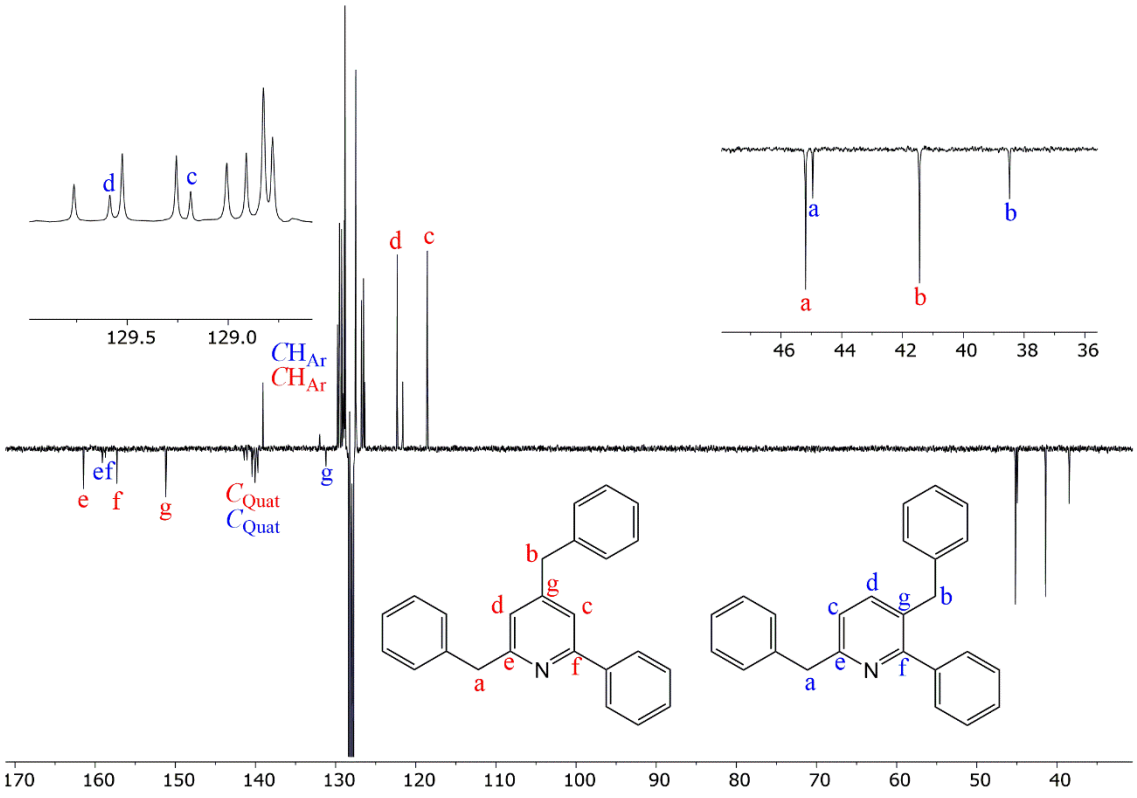


Figure S45. ^{13}C{^{1}H} NMR APT spectrum of the mixture of 2,4-dibenzyl-6-phenylpyridine and 3,6-dibenzyl-2-phenylpyridine in C_6D_6.

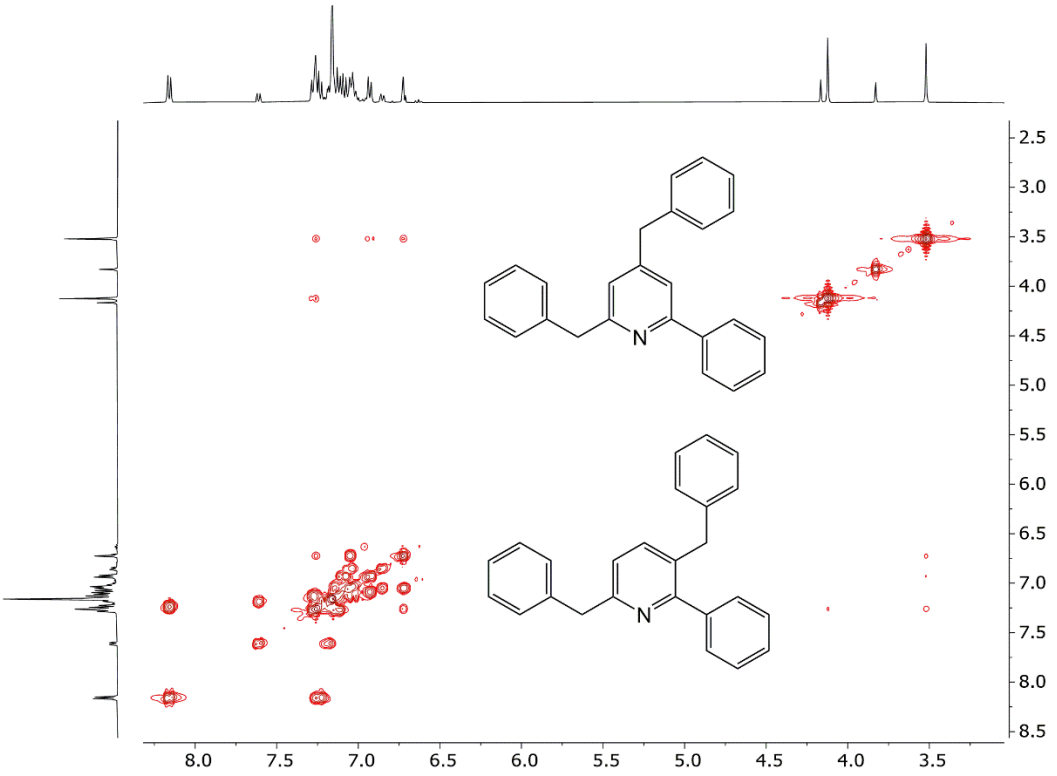


Figure S46. ^{1}H-^{1}H COSY spectrum of the mixture of 2,4-dibenzyl-6-phenylpyridine and 3,6-dibenzyl-2-phenylpyridine in C_6D_6.

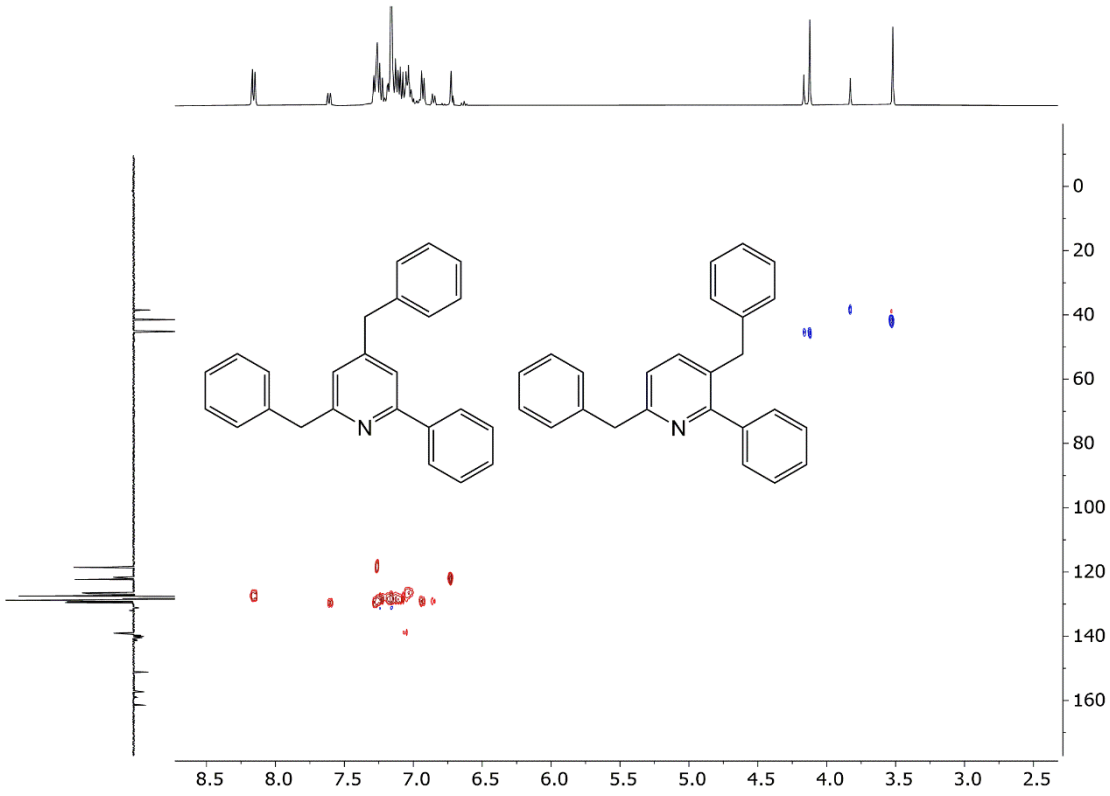


Figure S47. ^{1}H-^{13}C HSQC spectrum of the mixture of 2,4-dibenzyl-6-phenylpyridine and 3,6-dibenzyl-2-phenylpyridine in C_6D_6.

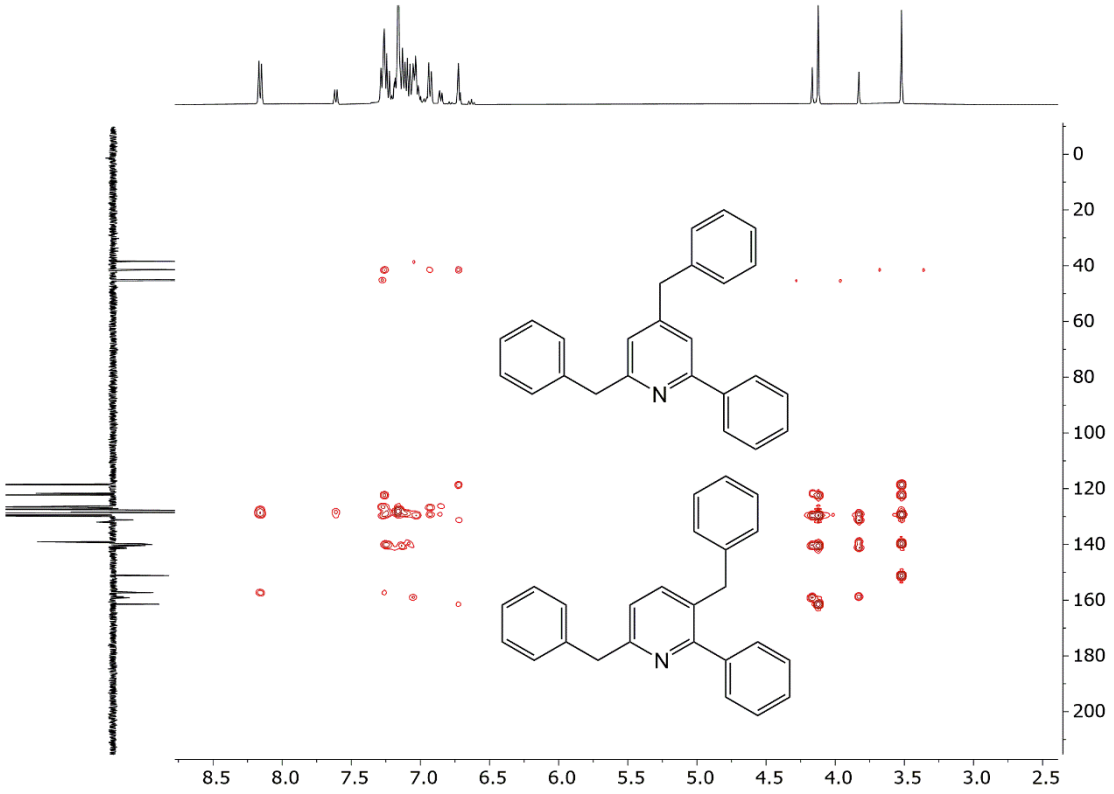


Figure S48. ^{1}H-^{13}C HMBC spectrum of the mixture of 2,4-dibenzyl-6-phenylpyridine and 3,6-dibenzyl-2-phenylpyridine in C_6D_6.

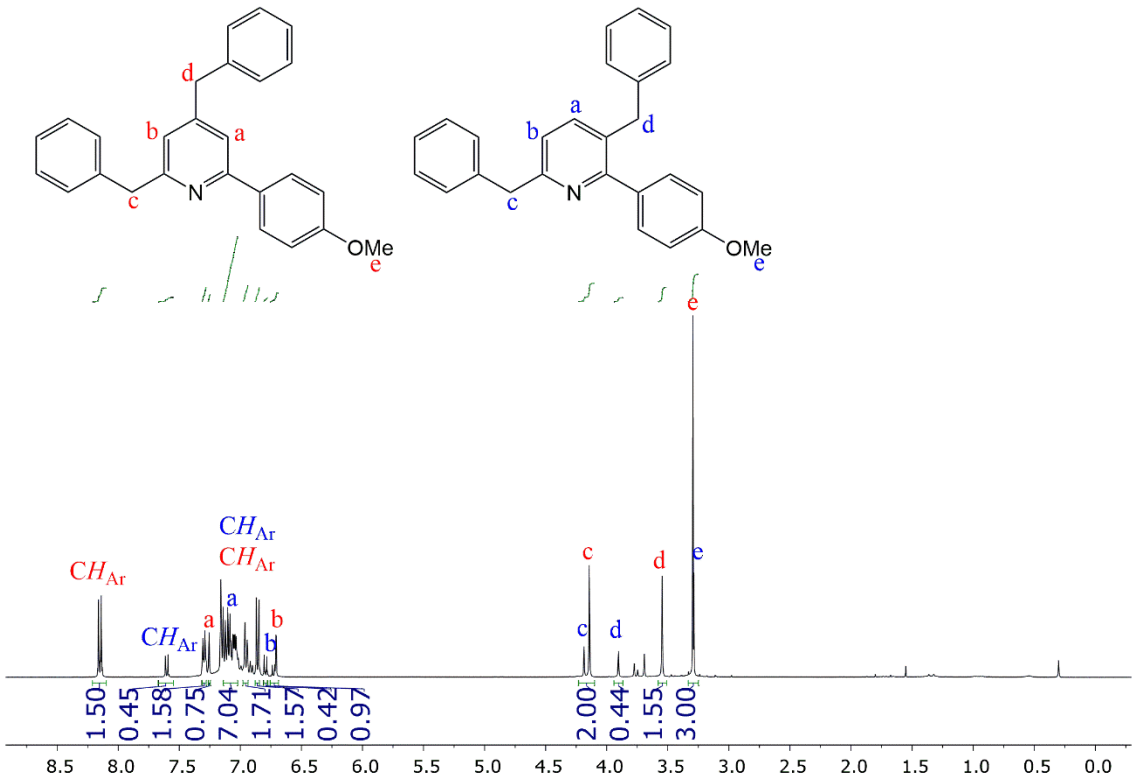


Figure S49. ^{1}H NMR spectrum of the mixture of 2,4-dibenzyl-6-(4-methoxyphenyl)pyridine and 3,6-dibenzyl-2-(4-methoxyphenyl)pyridine in C_6D_6.

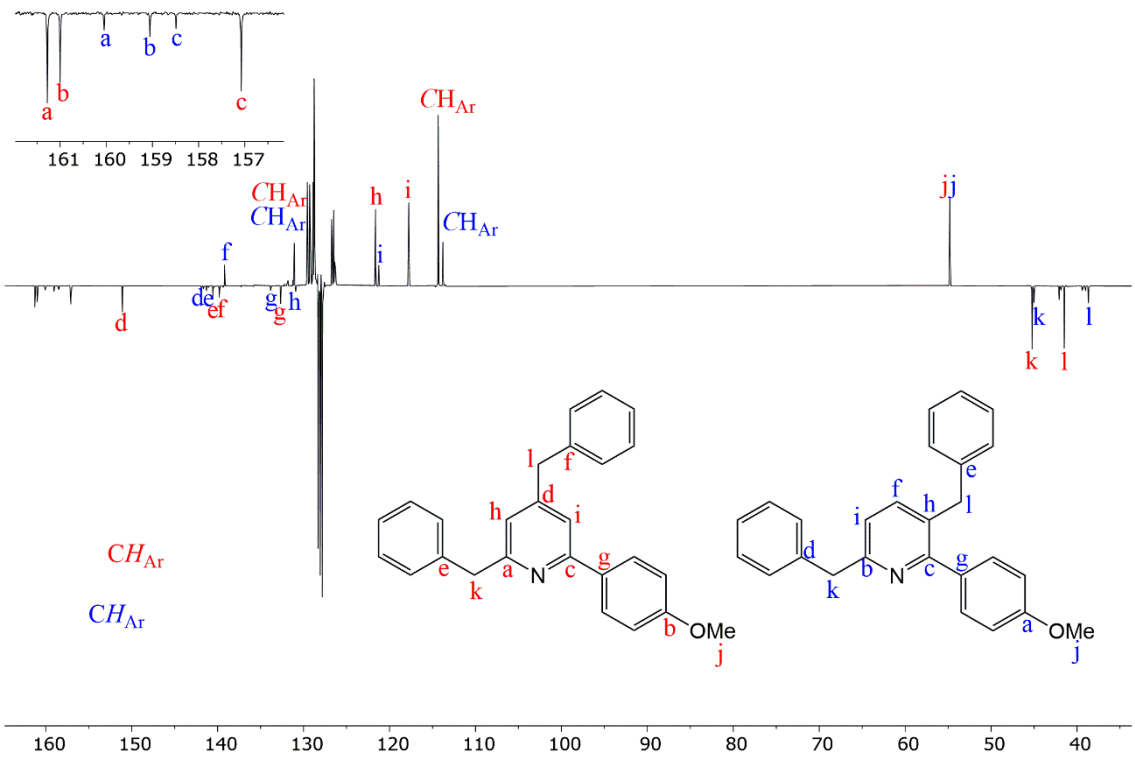


Figure S50. $^{13}C\{^{1}H\}$ NMR APT spectrum of the mixture of 2,4-dibenzyl-6-(4-methoxyphenyl)pyridine and 3,6-dibenzyl-2-(4-methoxyphenyl)pyridine in C_6D_6.

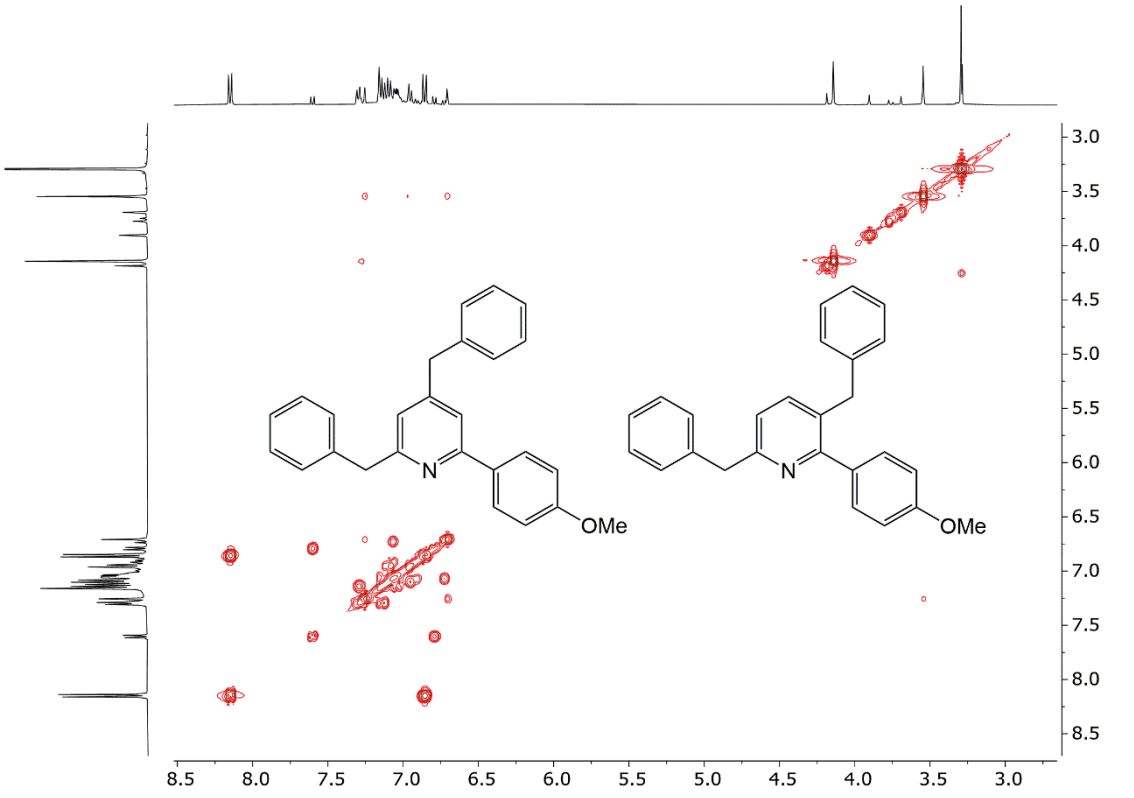


Figure S51. ^{1}H-^{1}H COSY spectrum of the mixture of 2,4-dibenzyl-6-(4-methoxyphenyl)pyridine and 3,6-dibenzyl-2-(4-methoxyphenyl)pyridine in C_6D_6.

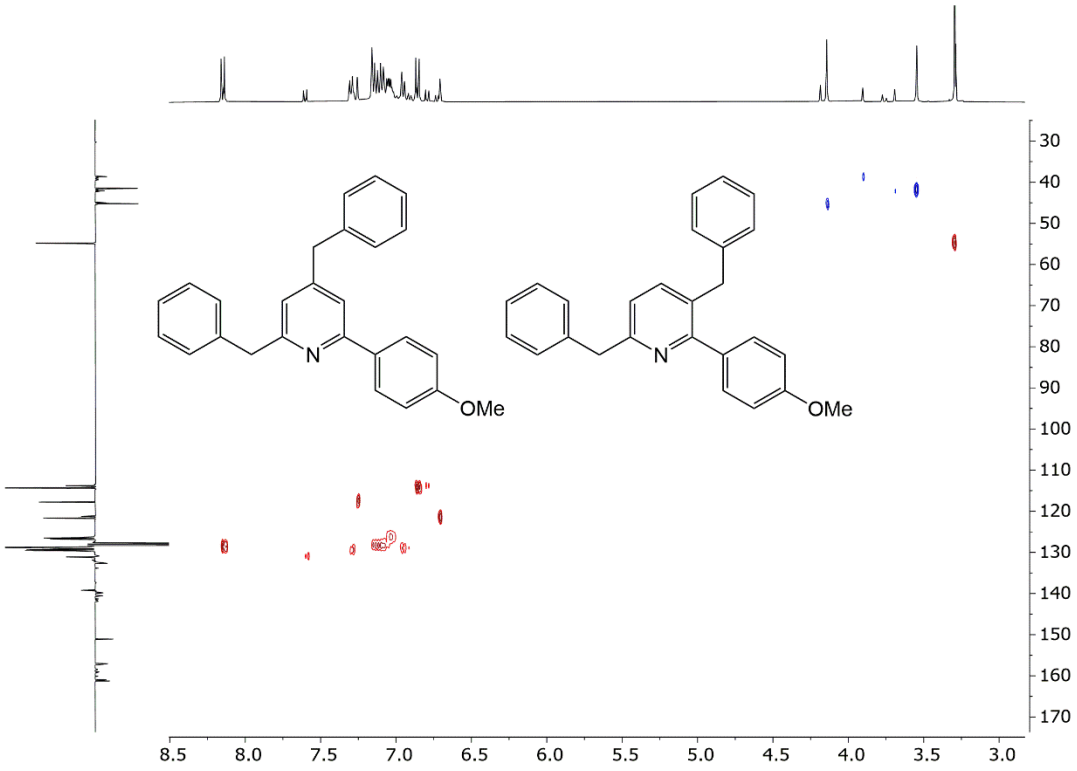


Figure S52. ^{1}H-^{13}C HSQC spectrum of the mixture of 2,4-dibenzyl-6-(4-methoxyphenyl)pyridine and 3,6-dibenzyl-2-(4-methoxyphenyl)pyridine in C_6D_6.

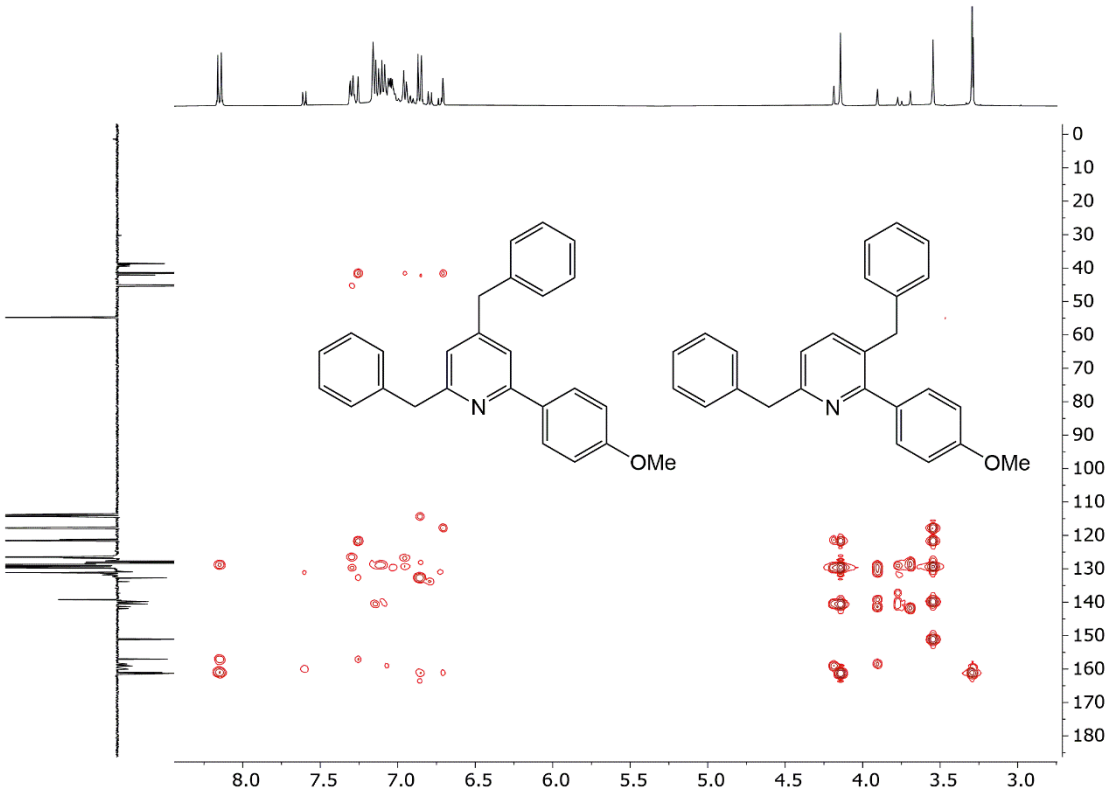


Figure S53. ^{1}H-^{13}C HMBC spectrum of the mixture of 2,4-dibenzyl-6-(4-methoxyphenyl)pyridine and 3,6-dibenzyl-2-(4-methoxyphenyl)pyridine in C_6D_6.

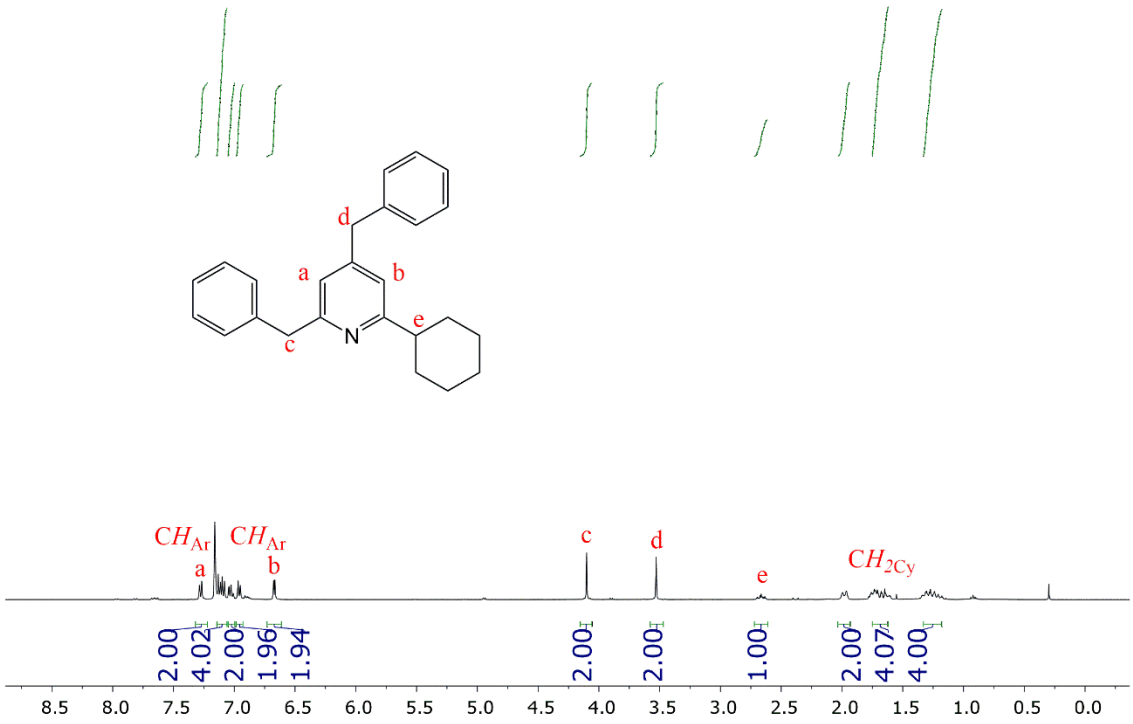


Figure S54. ^{1}H NMR spectrum of 2,4-dibenzyl-6-cyclohexylpyridine in C_6D_6.

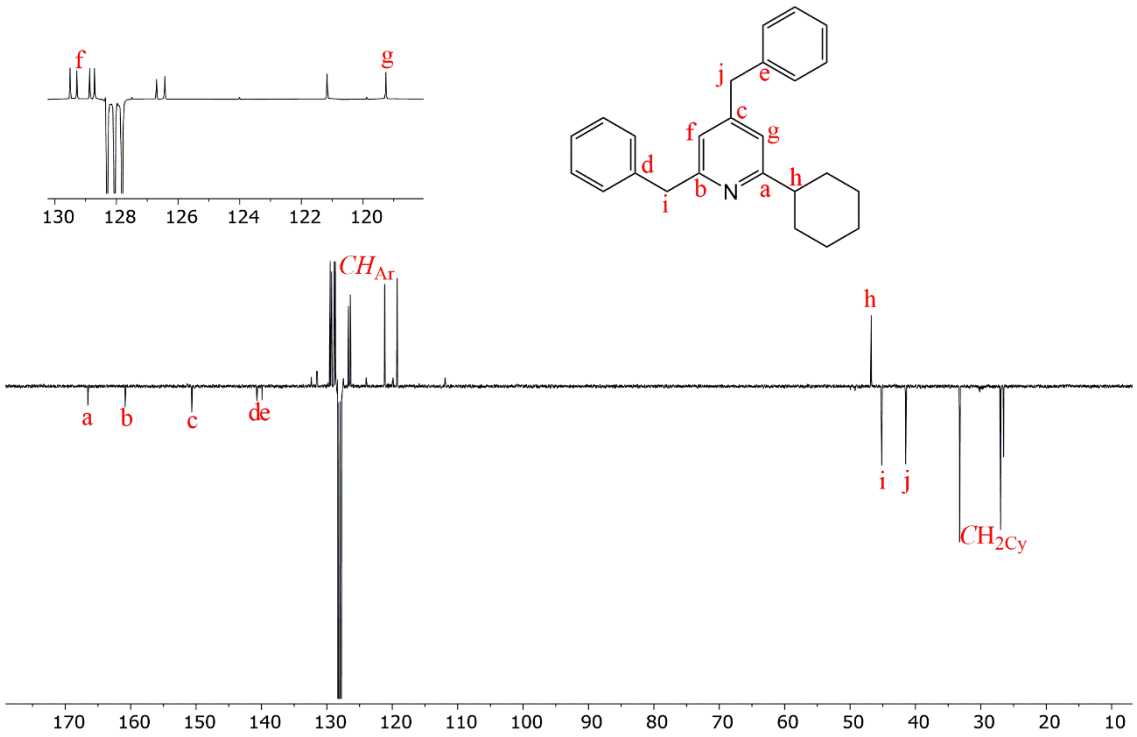


Figure S55. ^{13}C{^{1}H} NMR APT spectrum of 2,4-dibenzyl-6-cyclohexylpyridine in C_6D_6.

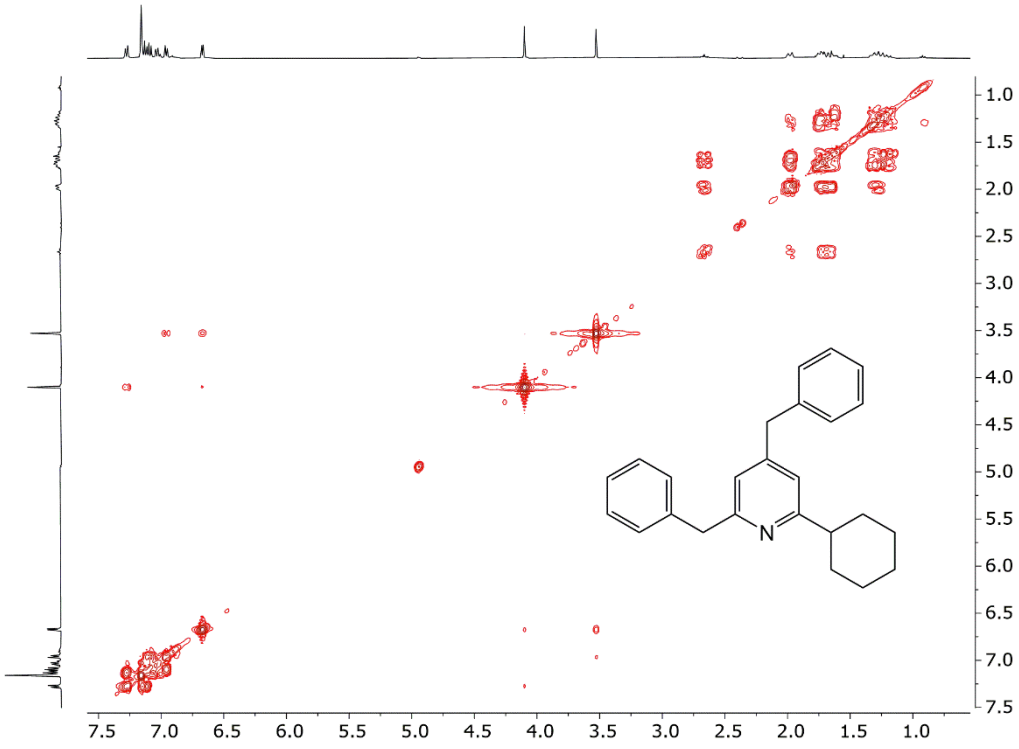


Figure S56. ^{1}H-^{1}H COSY spectrum of 2,4-dibenzyl-6-cyclohexylpyridine in C_6D_6.

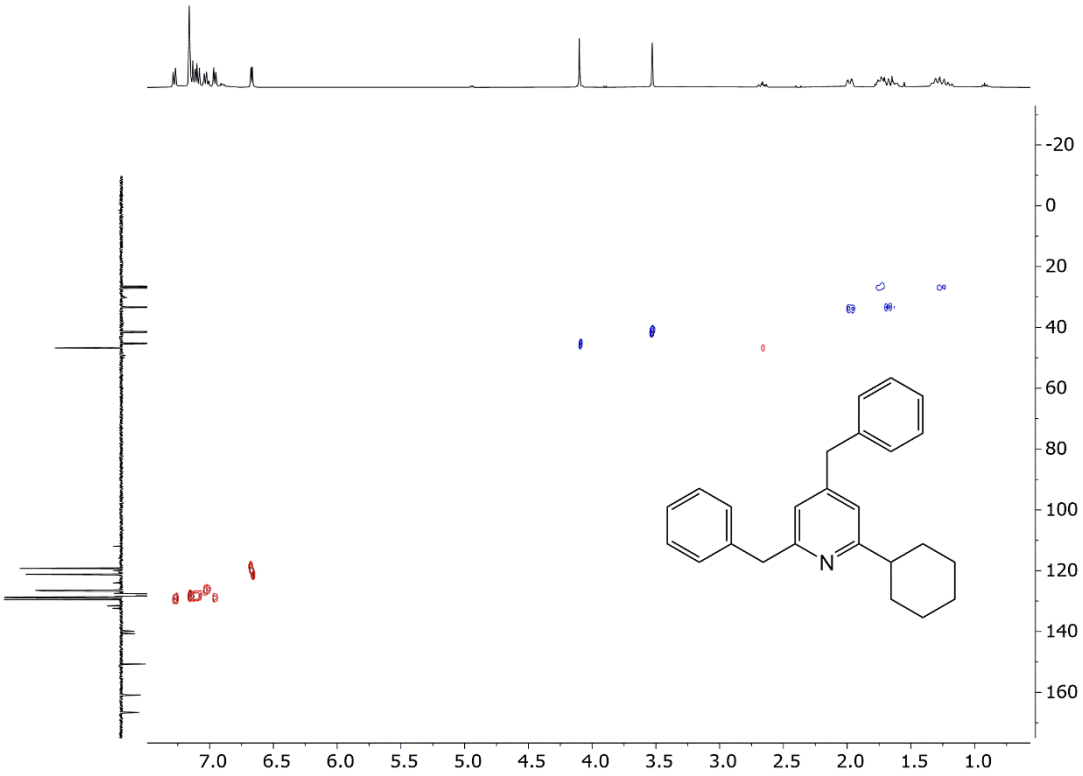


Figure S57. ^{1}H-^{13}C HSQC spectrum of 2,4-dibenzyl-6-cyclohexylpyridine in C_6D_6.

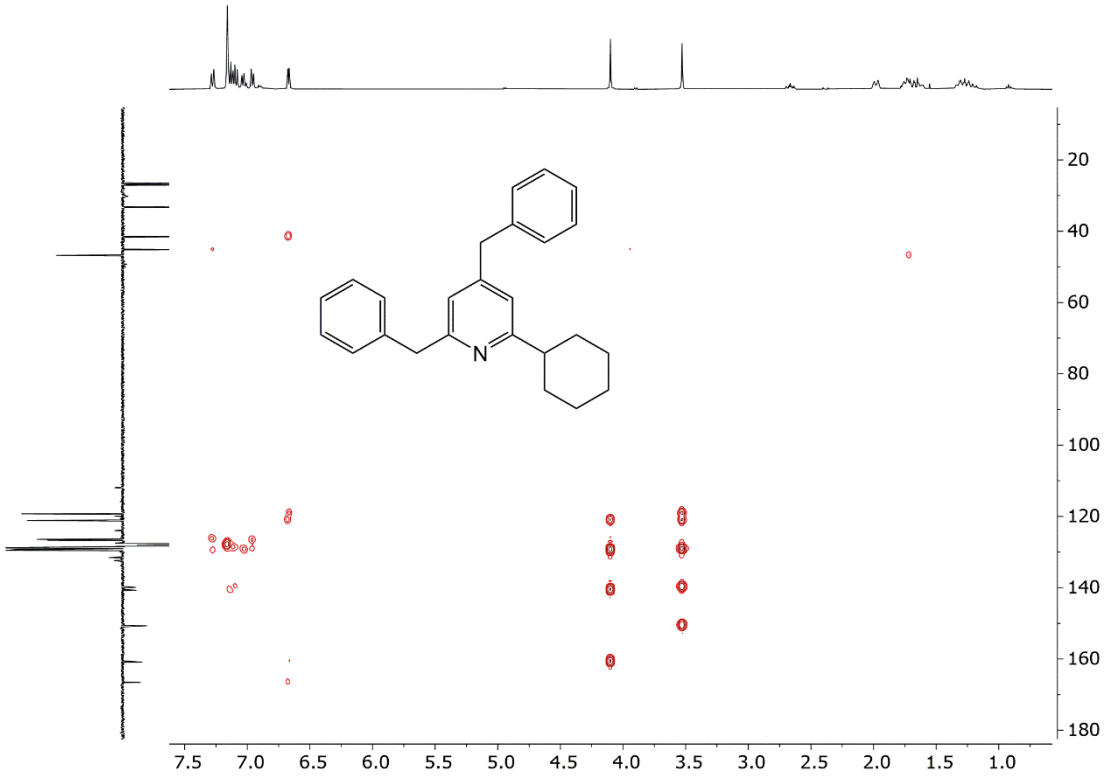


Figure S58. ^{1}H-^{13}C HMBC spectrum of 2,4-dibenzyl-6-cyclohexylpyridine in C_6D_6.

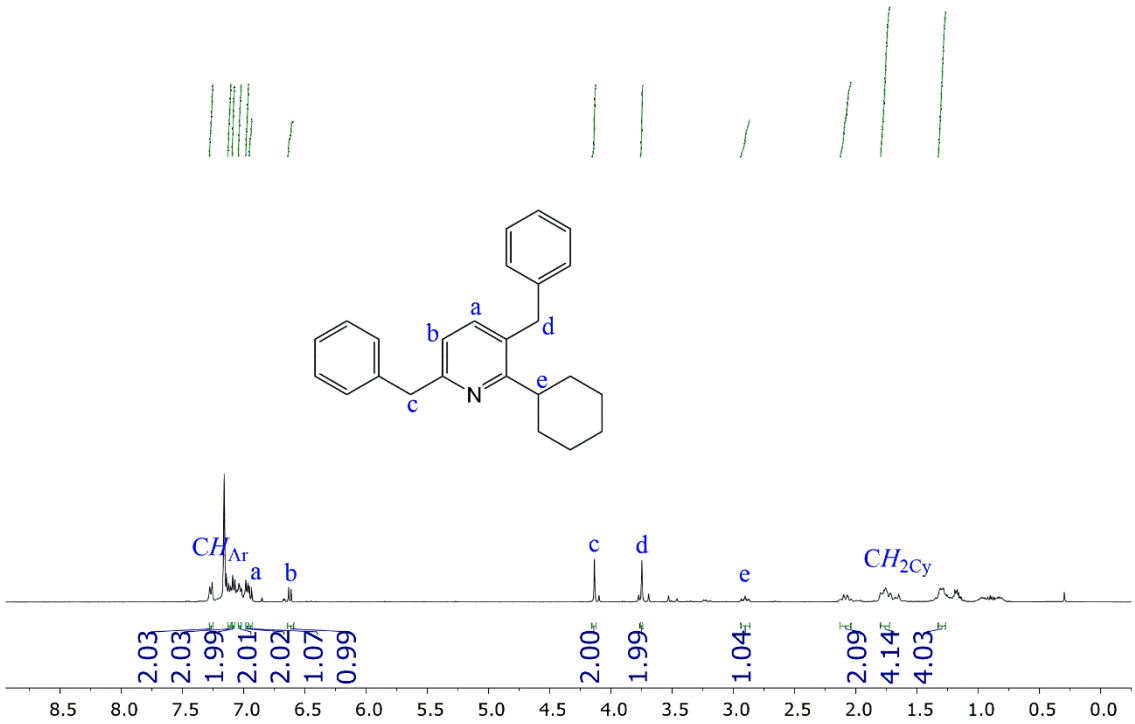


Figure S59. ^{1}H NMR spectrum of 3,6-dibenzyl-2-cyclohexylpyridine in C_6D_6.

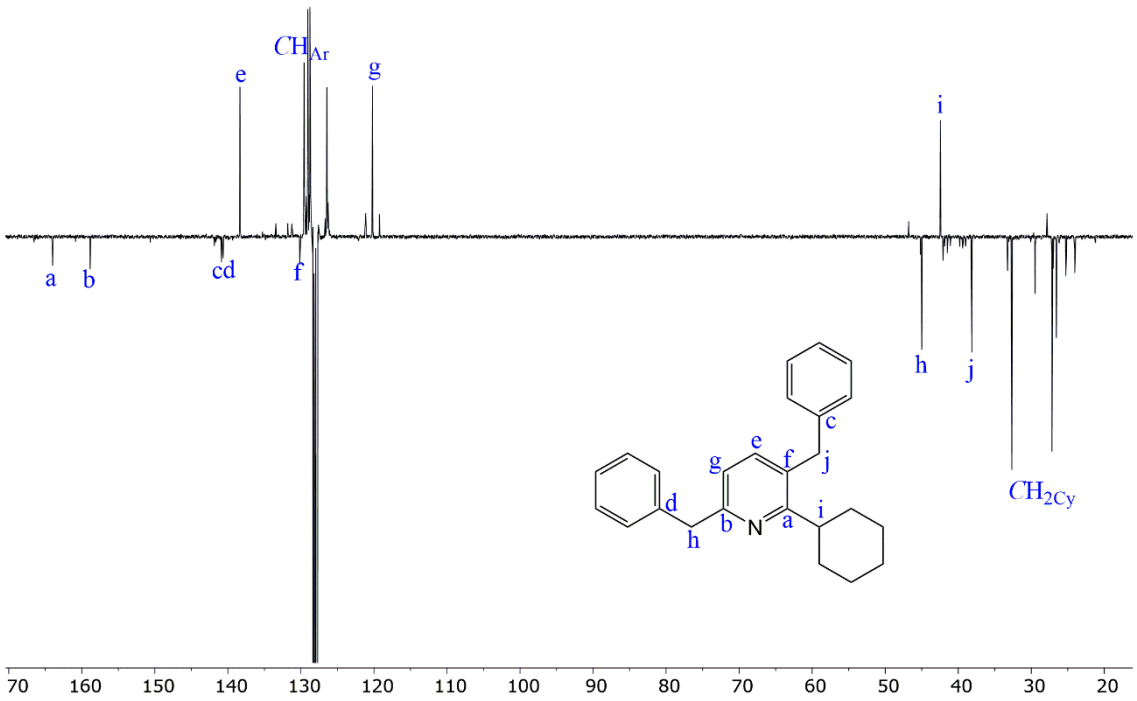


Figure S60. $^{13}C\{^{1}H\}$ NMR APT spectrum of 3,6-dibenzyl-2-cyclohexylpyridine in C_6D_6.

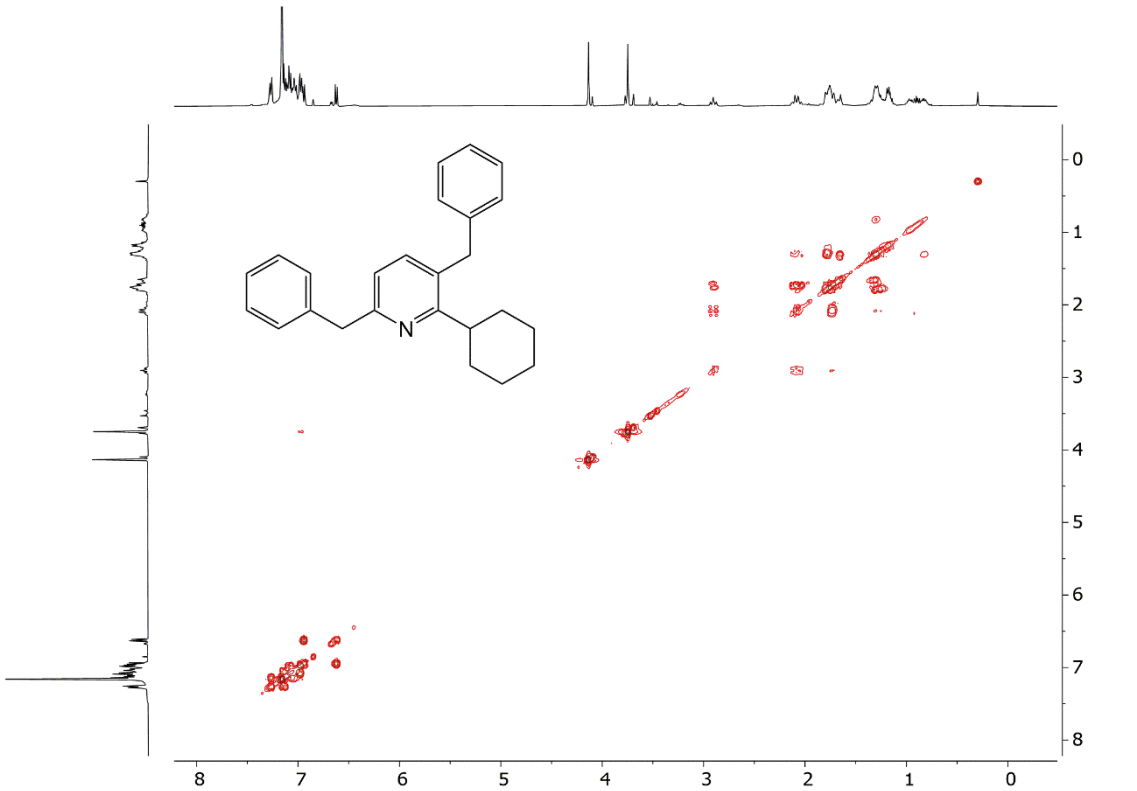


Figure S61. ^{1}H-^{1}H COSY spectrum of 3,6-dibenzyl-2-cyclohexylpyridine in C_6D_6.

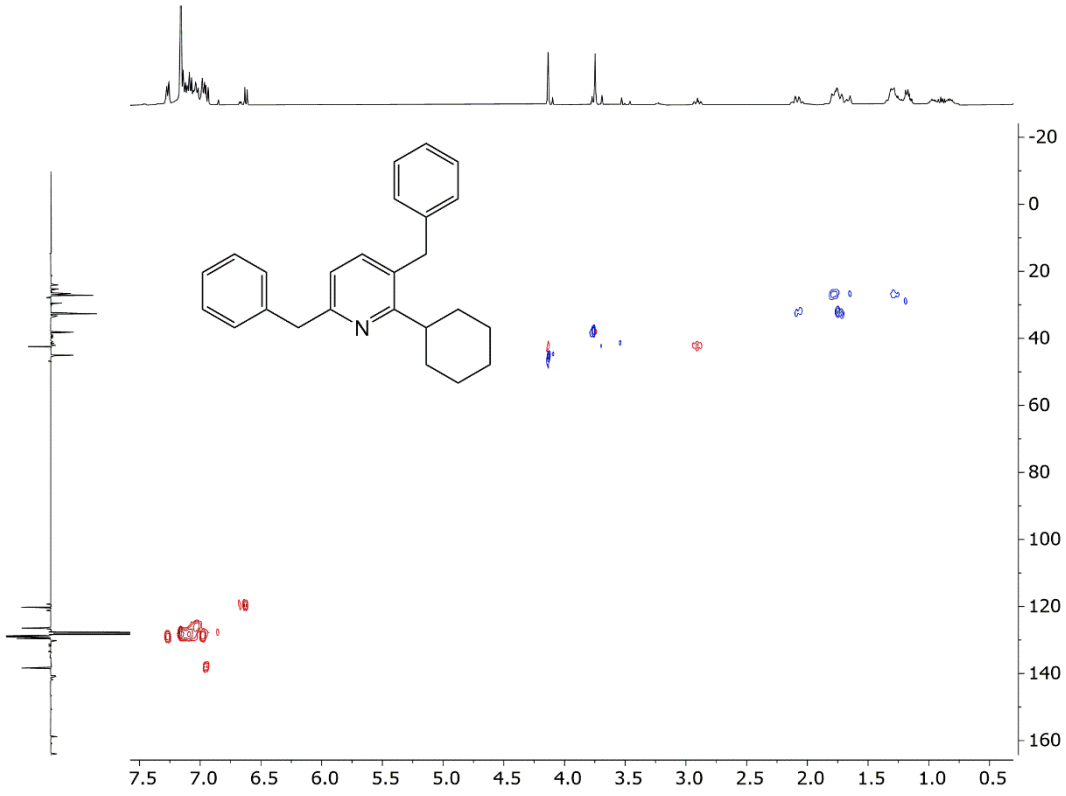


Figure S62. ^{1}H-^{13}C HSQC spectrum of 3,6-dibenzyl-2-cyclohexylpyridine in C_6D_6.

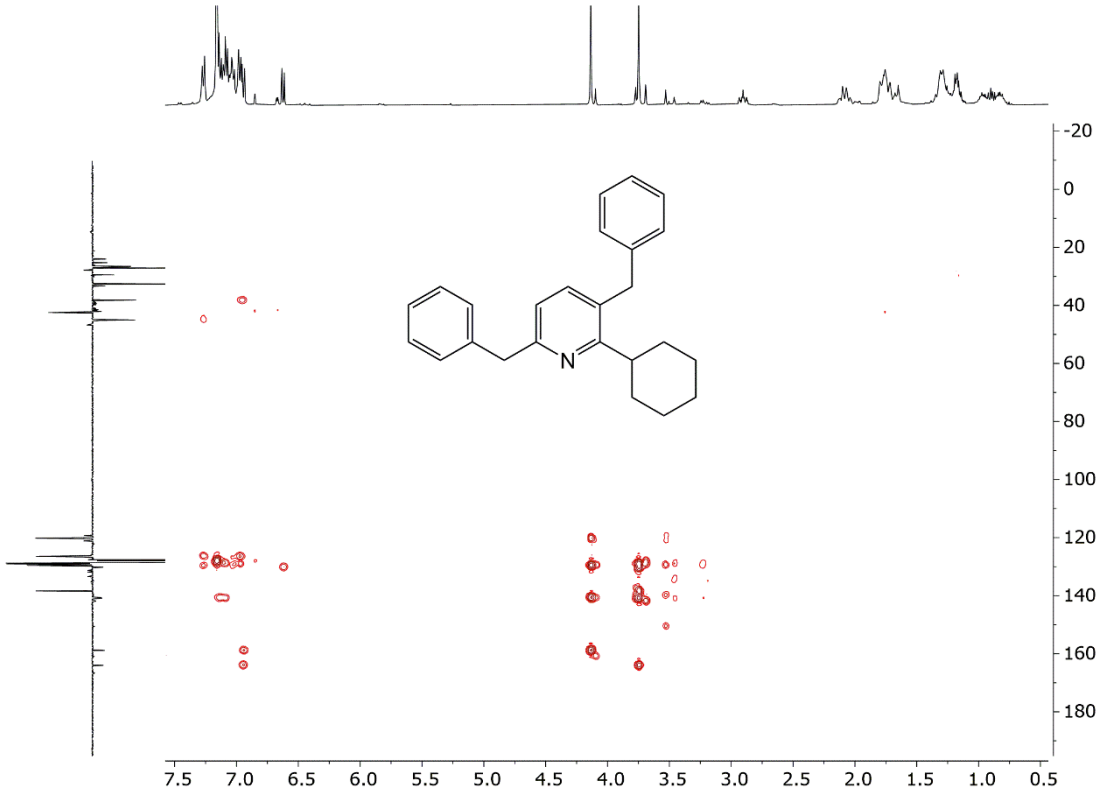


Figure S63. ^{1}H-^{13}C HMBC spectrum of 3,6-dibenzyl-2-cyclohexylpyridine in C_6D_6.

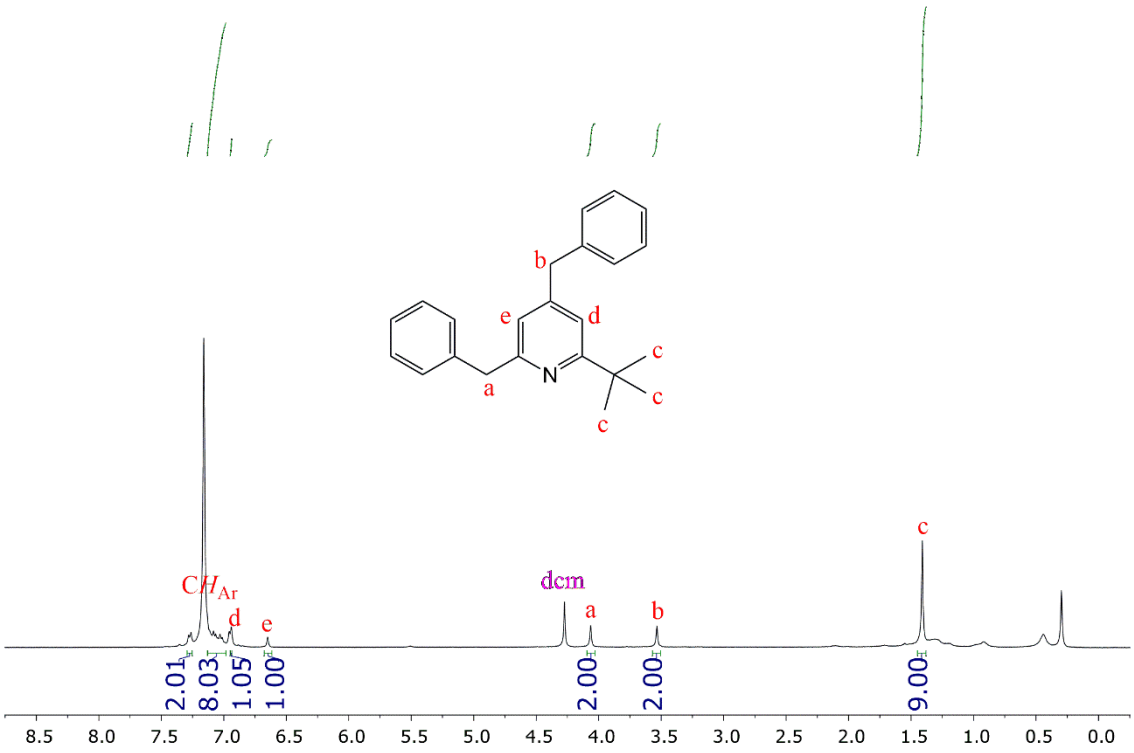


Figure S64. ^{1}H NMR spectrum of 2,4-dibenzyl-6-(*tert*-butyl)pyridine in C_6D_6.

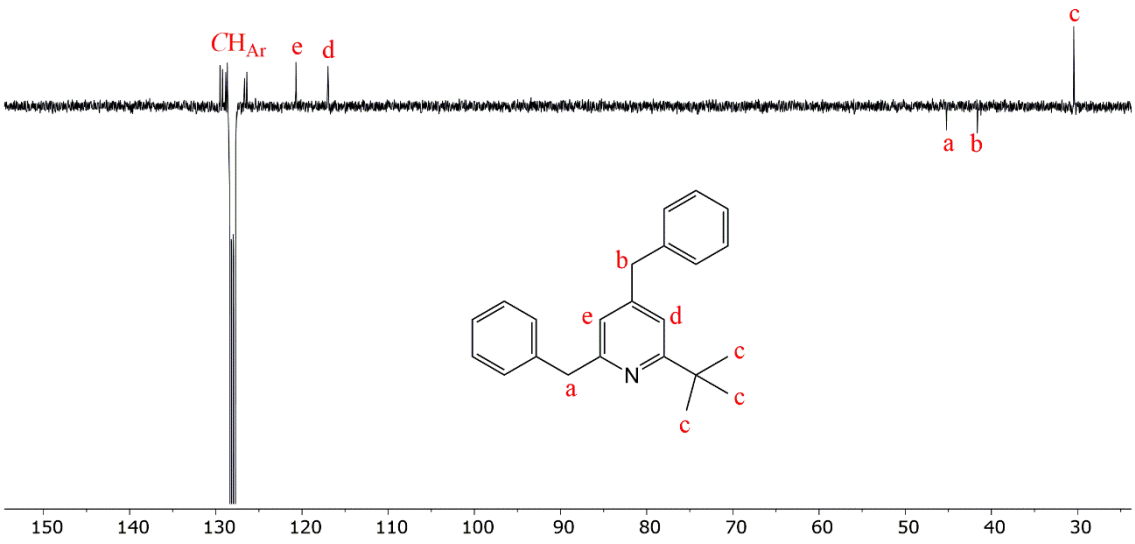


Figure S65. $^{13}C\{^{1}H\}$ NMR APT spectrum of 2,4-dibenzyl-6-(*tert*-butyl)pyridine in C_6D_6.

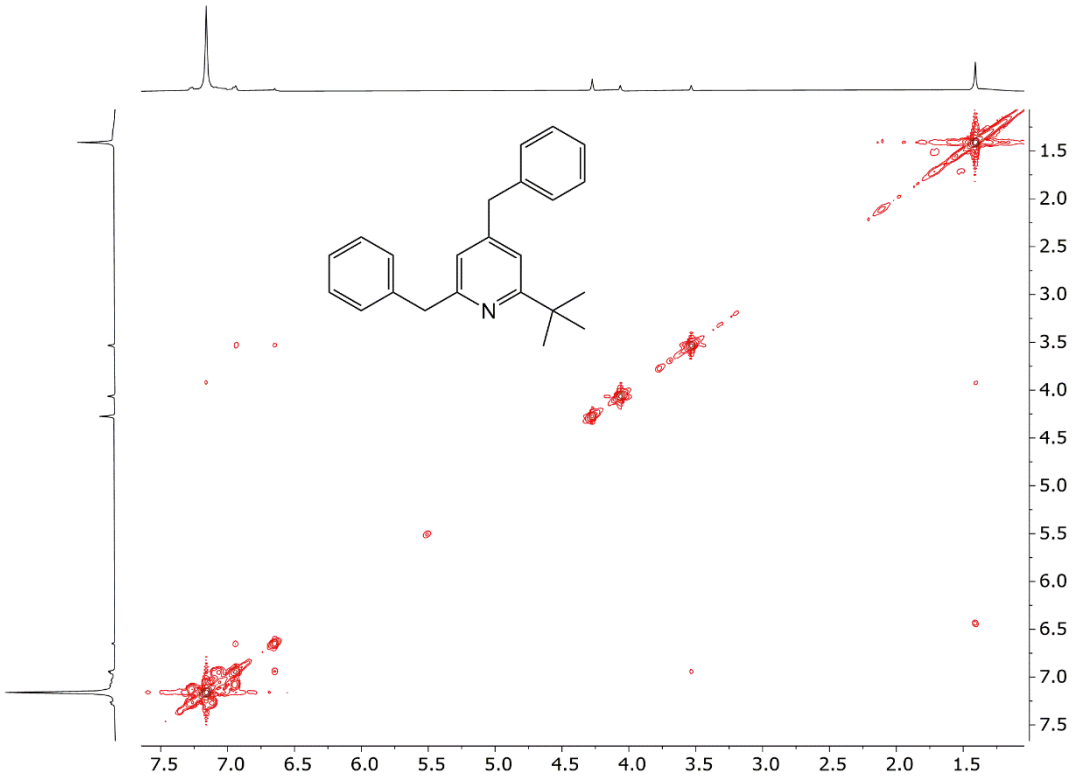


Figure S66. ^{1}H-^{1}H COSY spectrum of 2,4-dibenzyl-6-(*tert*-butyl)pyridine in C_6D_6.

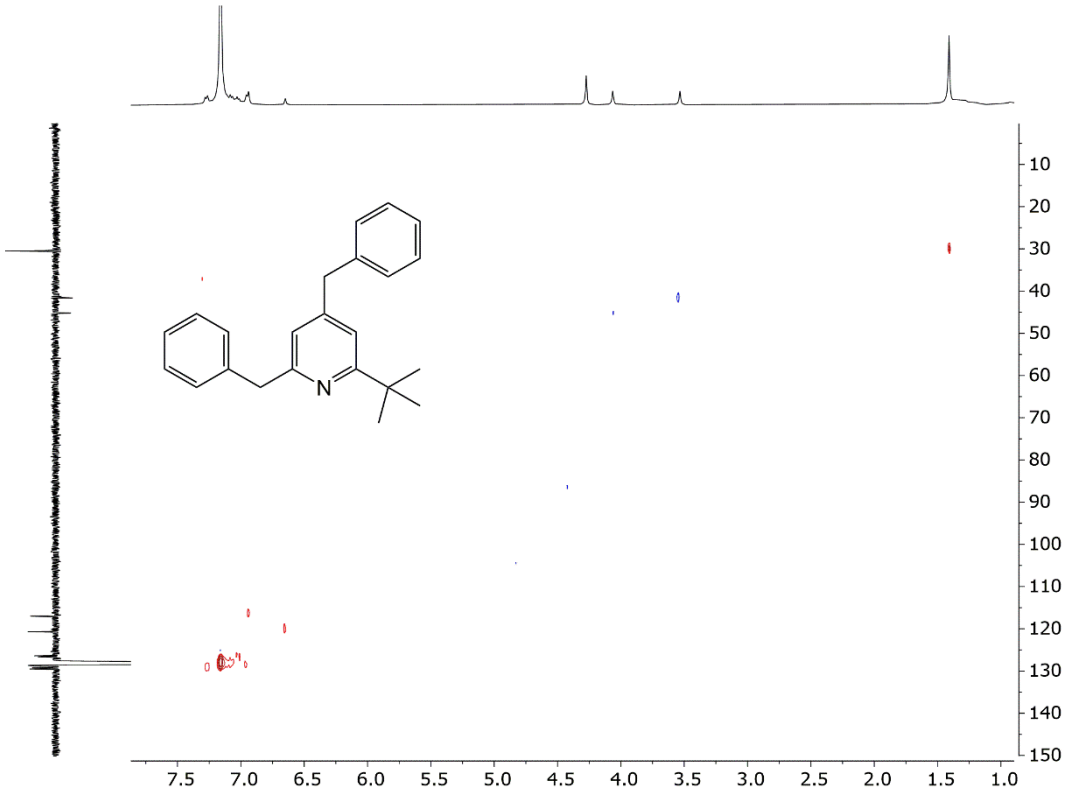


Figure S67. ^{1}H-^{13}C HSQC spectrum of 2,4-dibenzyl-6-(*tert*-butyl)pyridine in C_6D_6.

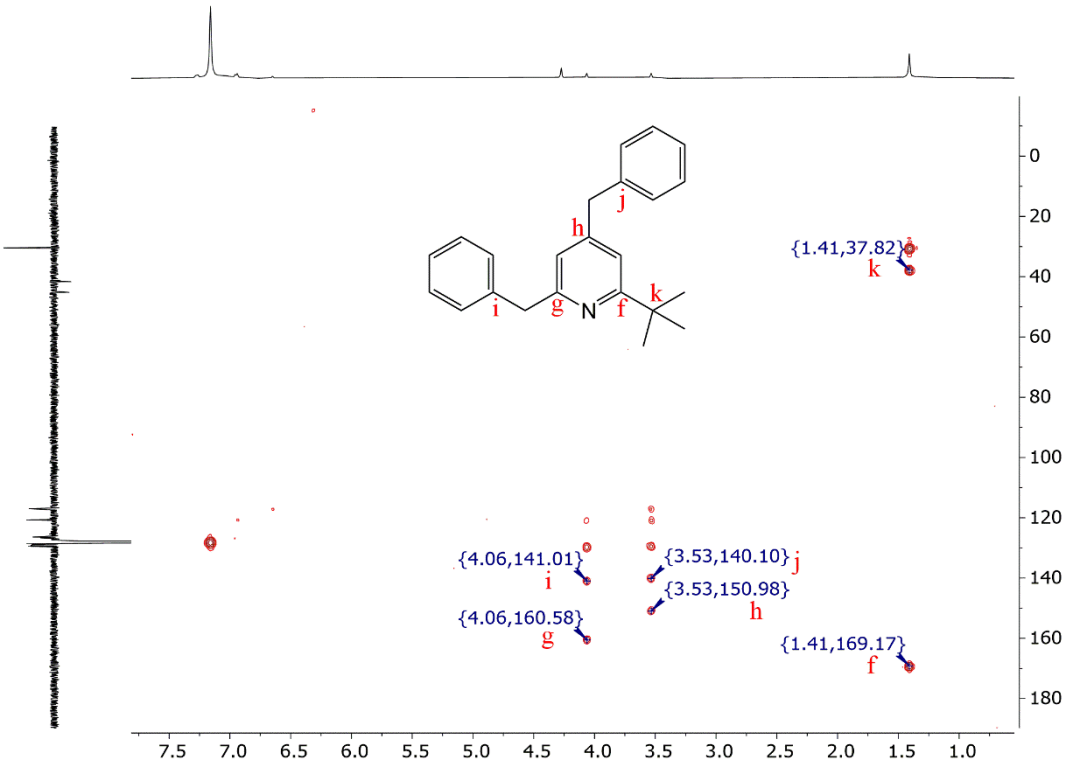


Figure S68. ^{1}H-^{13}C HMBC spectrum of 2,4-dibenzyl-6-(*tert*-butyl)pyridine in C_6D_6.

6. Stoichiometric study

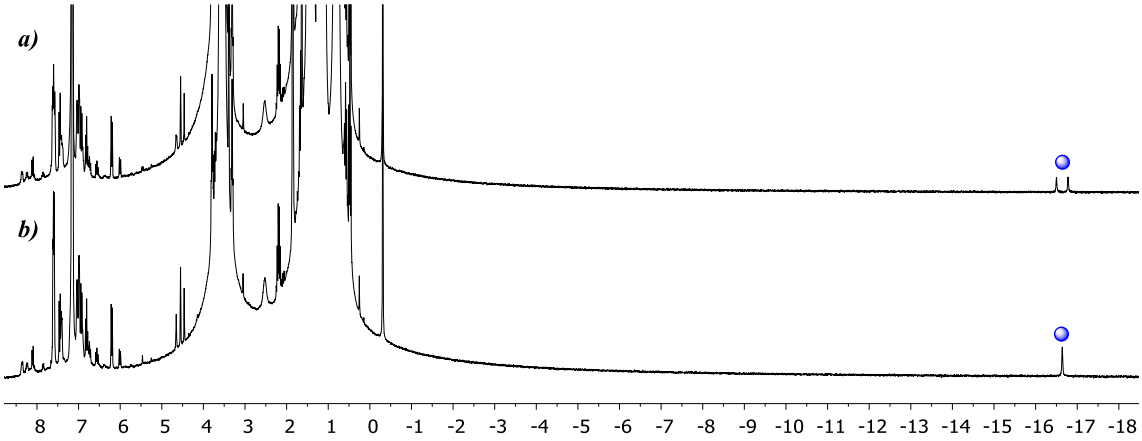


Figure S69. ^{1}H NMR (a) and $^{1}H\{^{31}P\}$ NMR (b) spectra of the *in situ* reduction of **1** with $NaBEt_3H$ in C_6D_6. Hydride resonances are marked with blue dots.

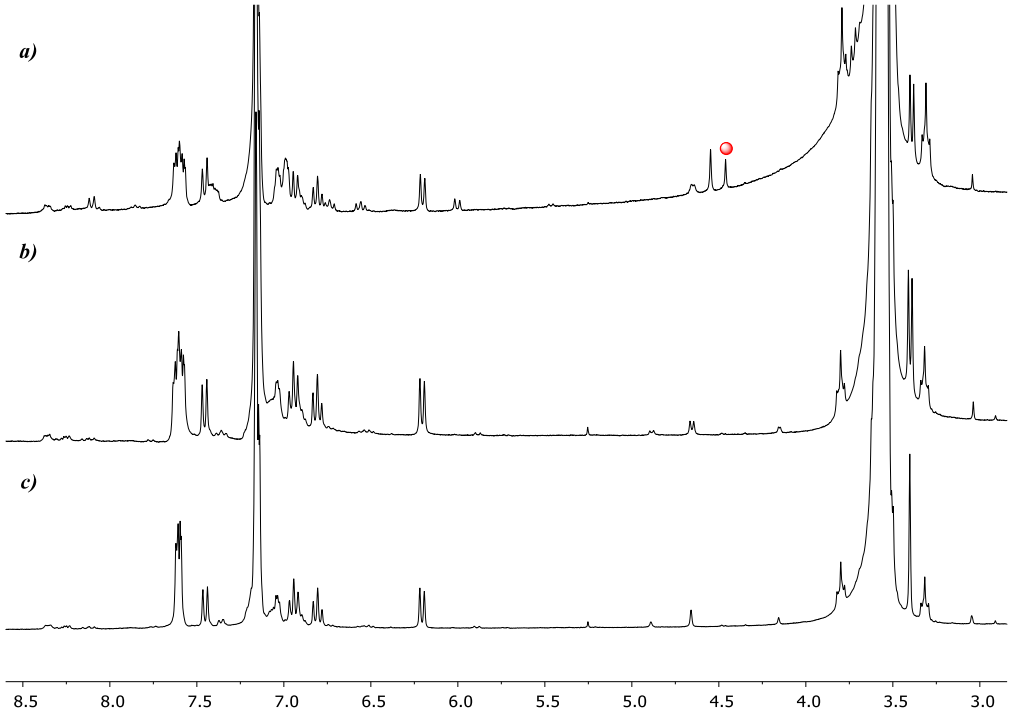


Figure S70. ^{1}H NMR spectra of the *in situ* reduction of **1** with $NaBEt_3H$ in C_6D_6. *(a)* ^{1}H NMR in a sealed tube; *(b)* ^{1}H NMR after gas release; *(c)* $^{1}H\{^{31}P\}$ NMR after gas release. The H_2 peak is marked with a red dot.

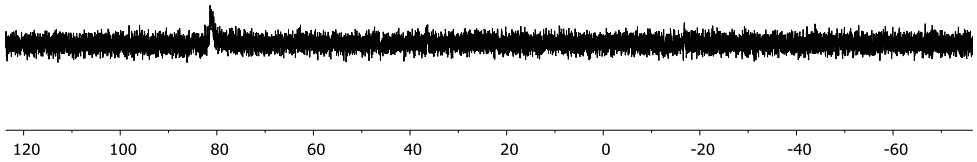


Figure S71. $^{31}P\{^{1}H\}$ NMR of the *in situ* reduction of **1** with $NaBEt_3H$ in C_6D_6 in a sealed tube.

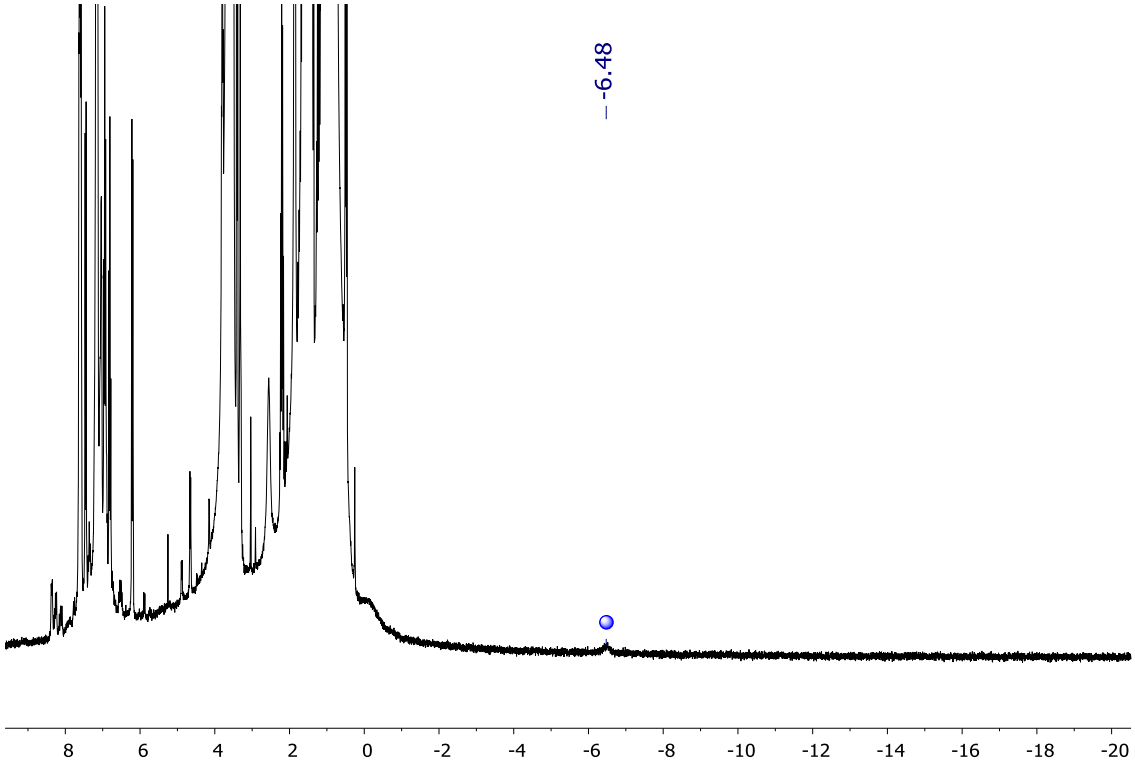


Figure S72. Full ^{1}H NMR of the *in situ* reduction of **1** with $NaBEt_3H$ in C_6D_6 after gas release. Peak of the postulated dihydrogen ligand marked with a blue dot at δ –6.46 ppm ($^{2}J_{P\text{-}H}$ = 21.6 Hz).

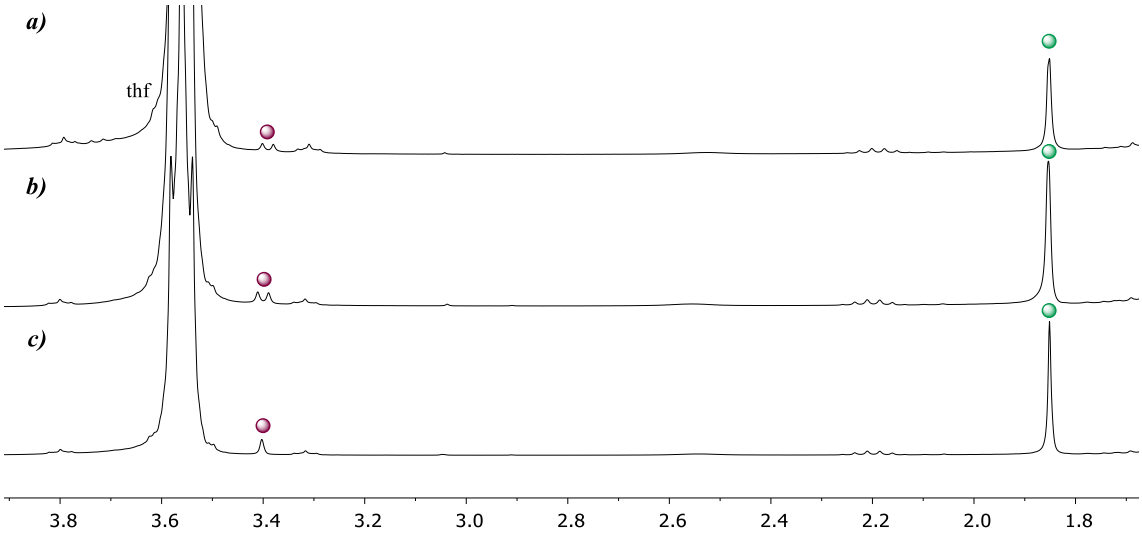


Figure 73. Expanded spectra of the *in situ* reduction of **2** with $NaBEt_3H$ in C_6D_6 (a) ^1H NMR in a sealed NMR tube; (b) ^1H NMR after gas release; (c) $^1H\{^{31}P\}$ NMR after gas release. Methylene and Cp* methyl signals marked with brown and green dots, respectively.

7. DFT calculations

Table S1. Energetic values for all DFT calculated structures. Geometrical optimizations and analytical frequencies were carried out using the M06L/def2-SVP method, E(M06L/DZ) energetic values. Energies were refined by single point calculations using MN15 exchange-correlation functional and including solvent corrections (SCRF=SMD) and a def2-TZVP basis set, E(MN15/TZ) values. Thermochemical corrections to the Gibbs free energy at 100 ºC and 1M standard state, and entropic quasi-harmonic corrections qh-Gcorr(1M,373) were calculated at the M06L/def2-SVP level using the Goodvibes program. All absolute energies in a.u. ΔG are the relative Gibbs free energies (to **A** and isolated molecules, in kcal/mol) were calculated considering the E(MN15/TZ) and Gibbs free energy corrections.

	E(M06L/DZ)	E(MN15/TZ)	qh-Gcorr(1M,373K)	ΔG
A	-3010.7964	-3011.1431	0.4528	0
B	-2467.2513	-2467.5588	0.4253	13.2
TSBC1	-2467.2365	-2467.5383	0.4289	28.3
TSBC2	-2467.2391	-2467.5366	0.4289	29.4
TSBC3	-2467.2267	-2467.5276	0.4282	34.6
C1	-2467.2736	-2467.5748	0.4305	6.4
C2	-2467.2776	-2467.5809	0.4330	4.2
C3	-2467.2753	-2467.5757	0.4308	6.1
CP(C1)	-2467.2684	-2467.5711	0.4308	8.9
CP(C2)	-2467.2649	-2467.5661	0.4287	10.8
CP(C3)	-2467.2693	-2467.5708	0.4316	9.6
^{3}C1	-2467.2773	-2467.5775	0.4275	2.9
^{3}C2	-2467.2799	-2467.5793	0.4289	2.6
^{3}C3	-2467.2814	-2467.5811	0.4277	0.7
TSCD1-N	-2599.9270	-2600.2295	0.4716	12.6
CP(D1-N)	-2599.9355	-2600.2379	0.4709	6.9
D1-N	-2599.9592	-2600.2645	0.4712	-9.6
TSDE1-N	-2599.9440	-2600.2484	0.4723	1.2
E1-N	-2599.9510	-2600.2527	0.4738	-0.6
TSEF1a-N	-2599.9487	-2600.2491	0.4739	1.8
F1a-N	-2600.0249	-2600.3322	0.4806	-46.2
TSEF1b-N	-2599.9403	-2600.2388	0.4755	9.3
F1b-N	-2600.0184	-2600.3263	0.4807	-42.4
TSCD1-A	-2814.6894	-2814.9740	0.5544	17.2
CP(D1-A)	-2814.6971	-2814.9847	0.5555	11.1
D1-A	-2814.7366	-2815.0189	0.5600	-7.5
TSDE1-A	-2814.7361	-2815.0191	0.5619	-6.4

E1-A	-2814.8606	-2815.1418	0.5681	-79.6
TSCD1-L	-3705.6771	-3705.9695	0.7138	12.2
CP(D1-L)	-3705.6888	-3705.9842	0.7106	0.9
D1-L	-3705.7343	-3706.0349	0.7165	-27.1
B-L	-3705.6589	-3705.9667	0.7082	10.4
TSBC1-L	-3705.5819	-3705.8810	0.7085	64.4
TSBC2-L	-3705.5761	-3705.8713	0.7082	70.3
TSBC3-L	-3705.5716	-3705.8676	0.7075	72.2
D1-L	-3705.7343	-3706.0349	0.7165	-27.1
D2-L	-3705.7214	-3706.0190	0.7181	-16.2
D3-L	-3705.7278	-3706.0287	0.7160	-23.6
TSCF1-N	-2599.9120	-2600.2083	0.4738	27.3
TSDG1-N	-2599.9418	-2600.2395	0.4747	8.3
G1-N	-2599.9649	-2600.2614	0.4750	-5.3
TSGF1-N	-2599.9587	-2600.2580	0.4766	-2.1
CP(F1a-N)	-2600.0074	-2600.3180	0.4780	-38.9
^{3}G1a-N	-2600.0319	-2600.3422	0.4724	-57.6
$HCCCH_2Ph$	-347.4053	-347.3911	0.0988	
NCMe	-132.6374	-132.6426	0.0192	
P-N	-1238.3758	-1238.3714	0.2509	
2,4,6-pyridine	-827.6446	-827.6035	0.2778	
1,3,5-benzyne	-1042.4718	-1042.4084	0.3626	

Figure S74. DFT calculated Gibbs free energy profile (in kcalmol^{-1}) for the oxidative coupling of bis(benzylacetylene) catalyzed by complex CoCp*(**P-N**) (**A**) without ligand dissociation.

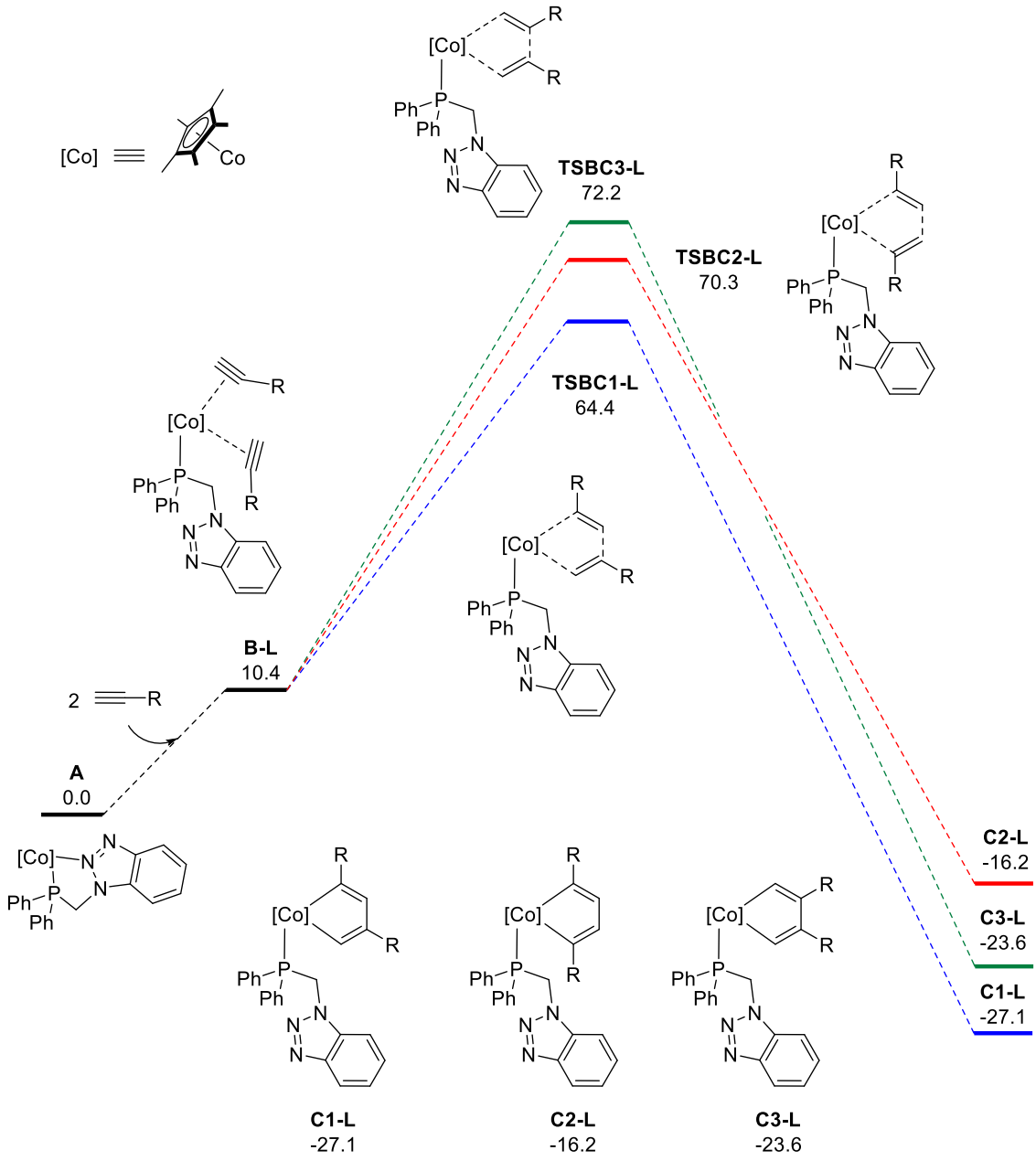


Figure S75. NCI plot of (a) **TSBC1**, (b) **TSBC2**, and (c) **TSBC3**. The plot corresponds to a reduced density gradient of 0.65 au, and is colored in the [–0.03, 0.03] au range of sign(λ2)·ρ.

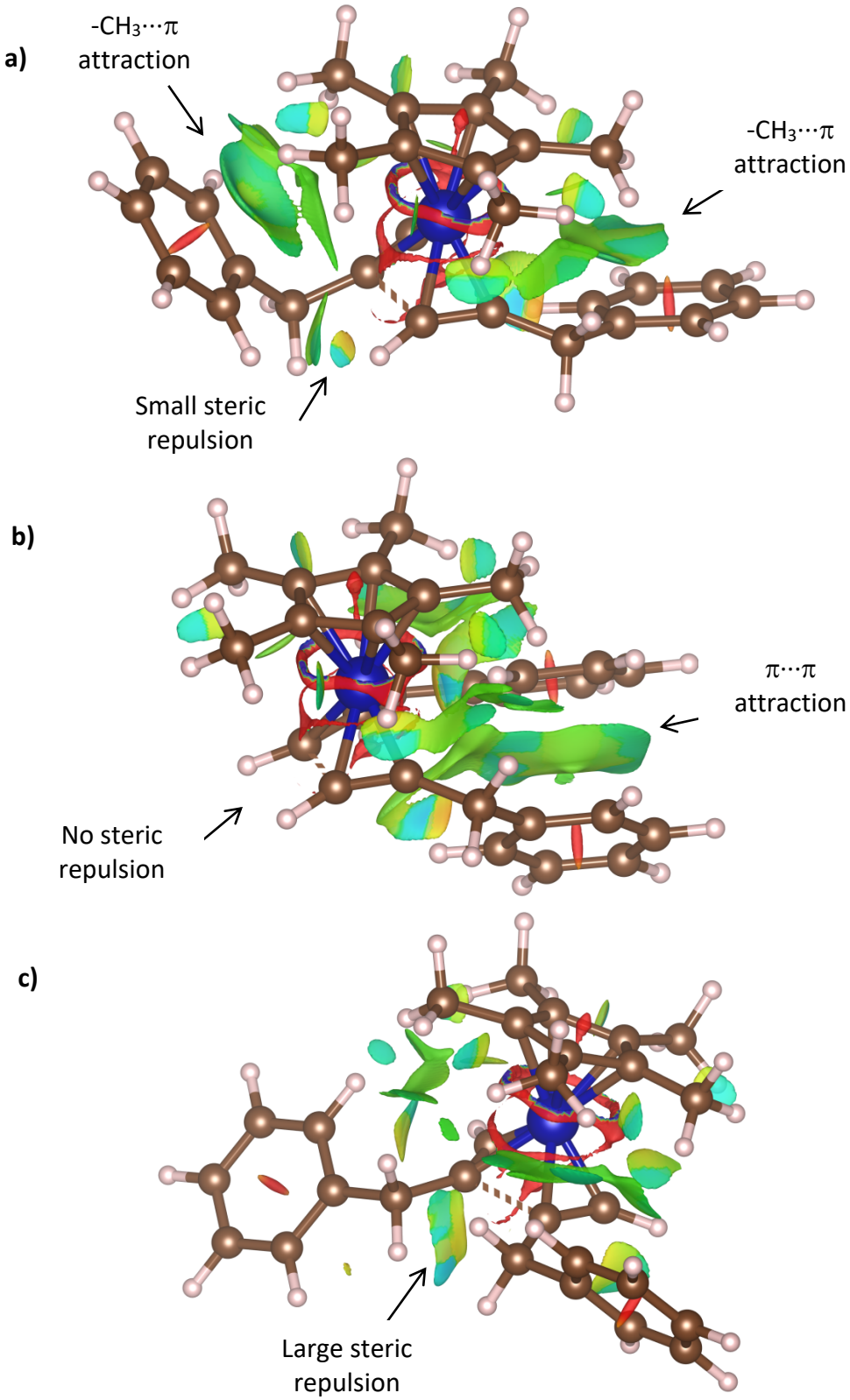


Figure S76. DFT calculated Gibbs energy profile (in kcalmol^{-1}, energies relative to **A** and isolated species) for possible reaction pathways of 1,3-cobaltacyclopentadiene **C1** and acetonitrile leading to 2,4,6-pyridyne.

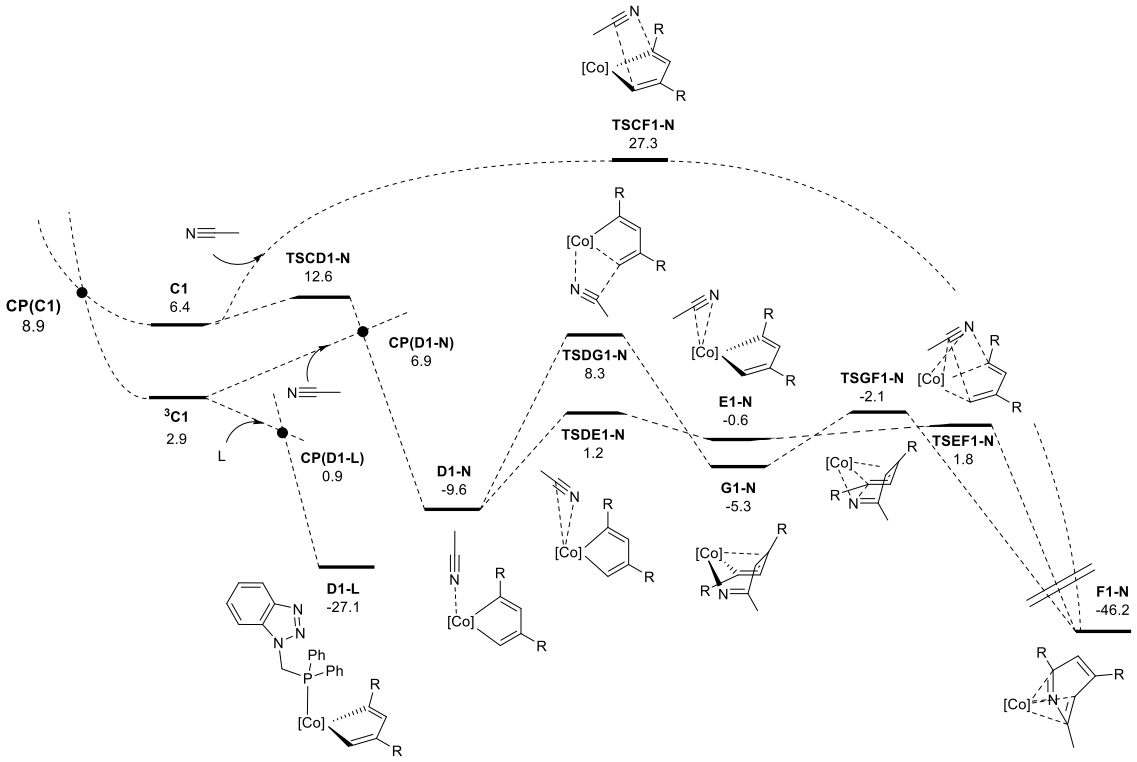


Figure S77. DFT calculated Gibbs energy profile (in kcalmol^{-1}, energies relative to **A** and isolated species) for η^4 (**F1a-N**) to η^6 (**^{3}G1a-N**) coordination of 2,4,6-pyridine to CoCp* via intersystem crossing point **CP(F1a-N)**.

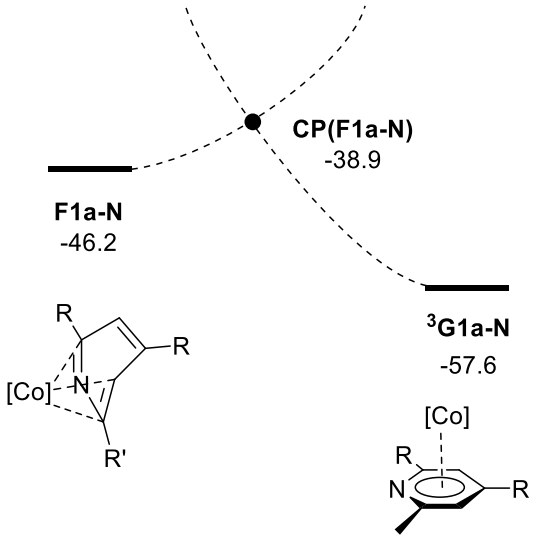
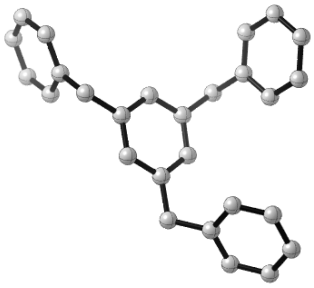
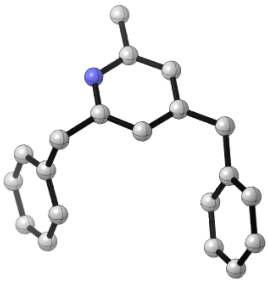


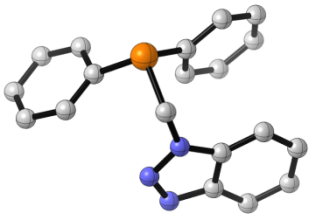
Figure S78. Geometrical representation for the DFT optimized structures. Hydrogen atoms are hidden. Key distances for TS are shown (in Å).



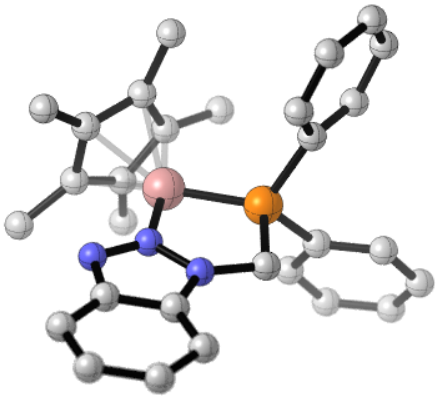
1,3,5-benzene



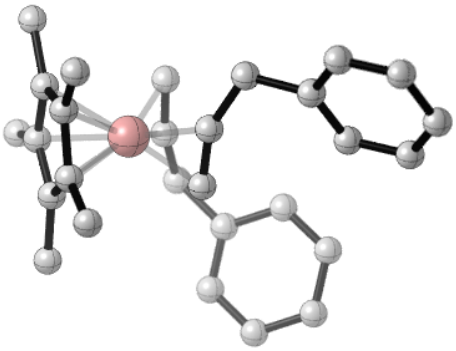
2,4,6-pyridine



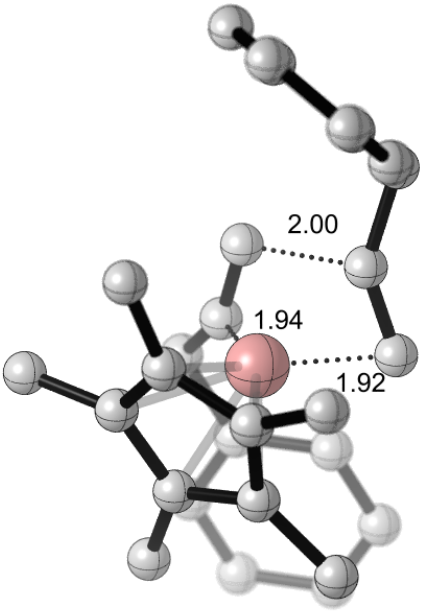
phosphine



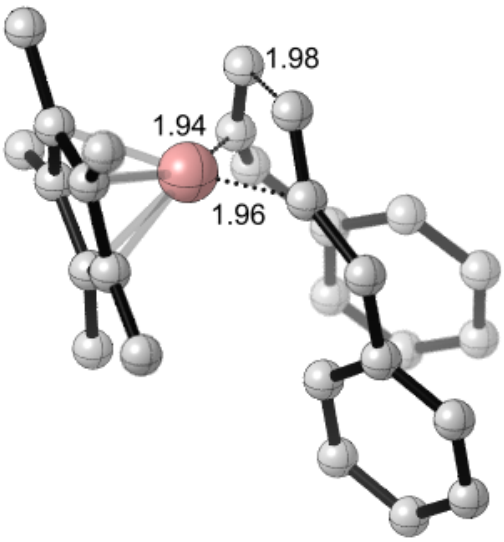
A



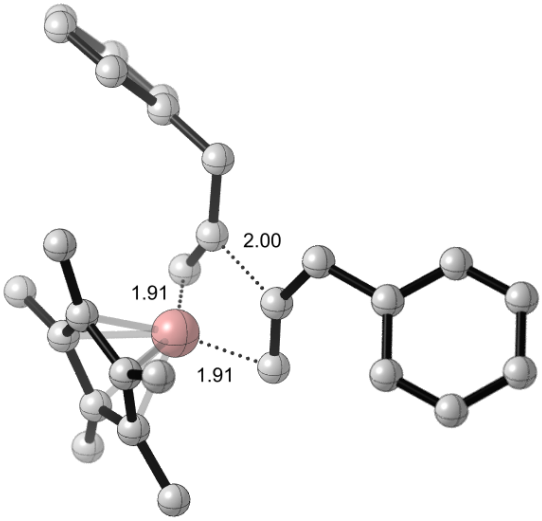
B



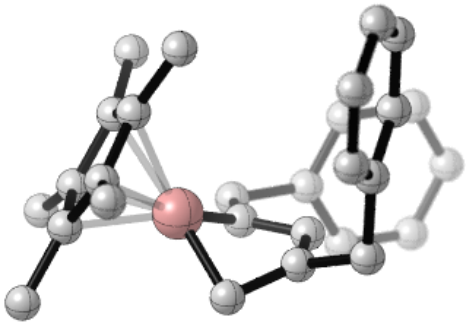
TSBC1



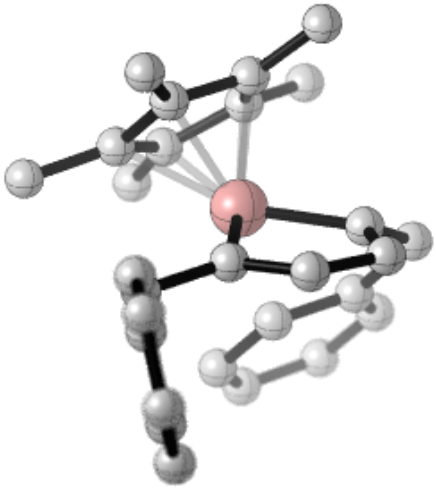
TSBC2



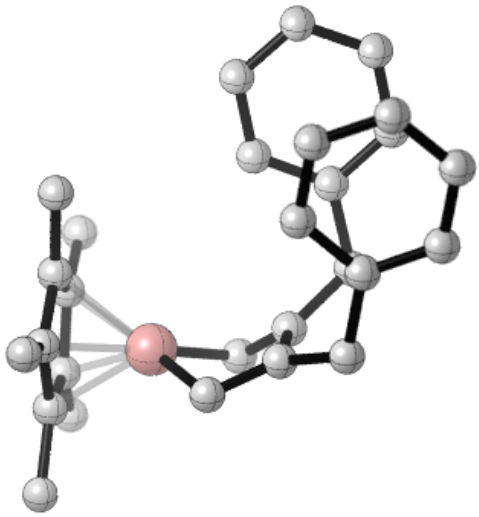
TSBC3



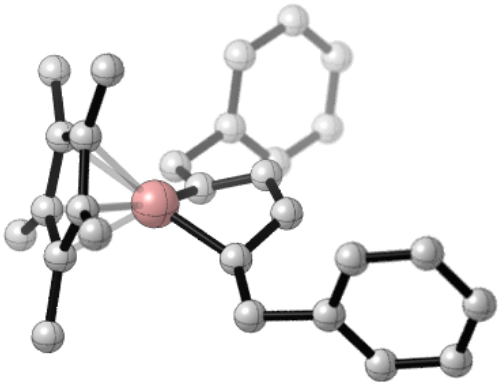
C1



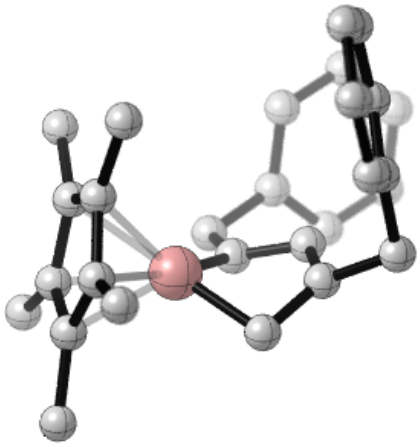
C2



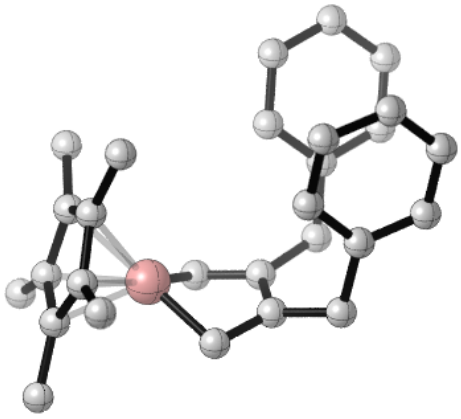
C3



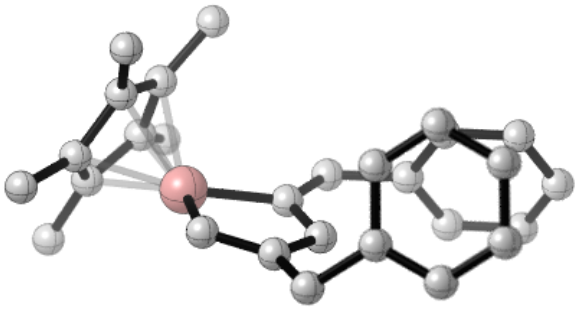
CP(C1)



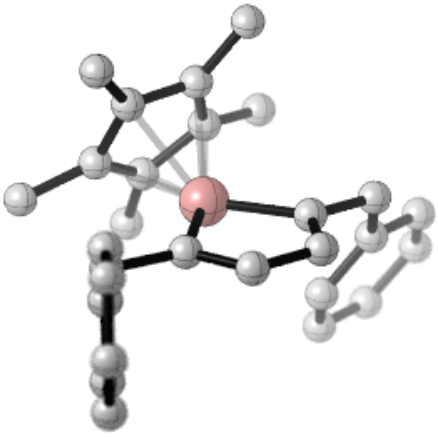
CP(C2)



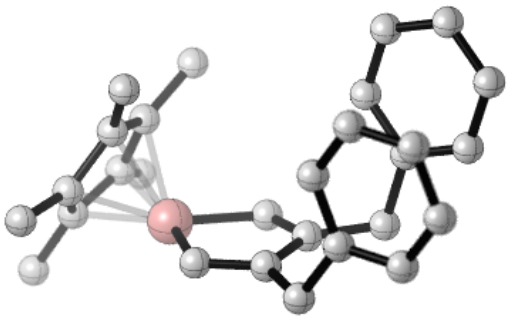
CP(C3)



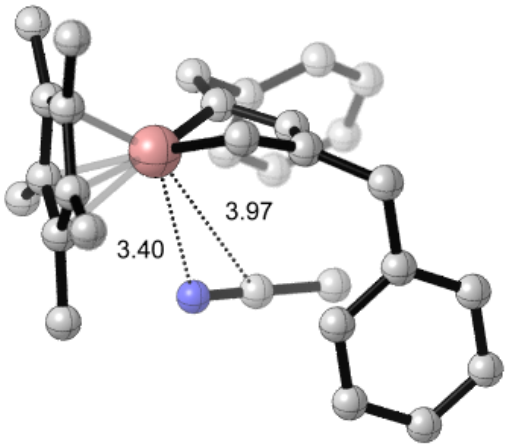
^{3}C1



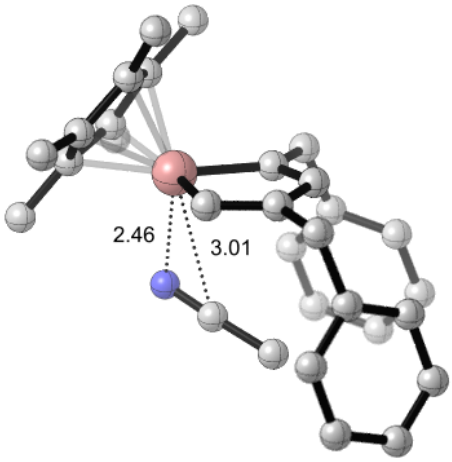
^{3}3C2



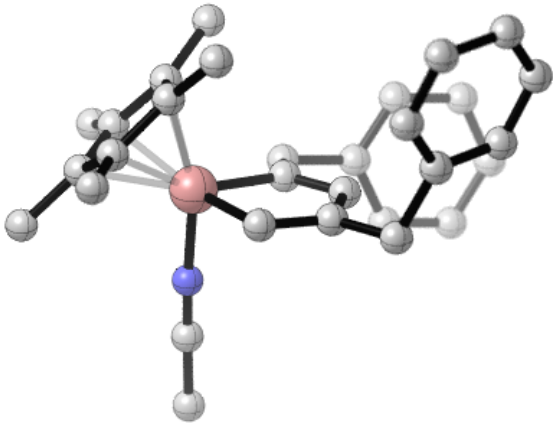
^{3}C3



TSCD1-N



CP(D1-N)



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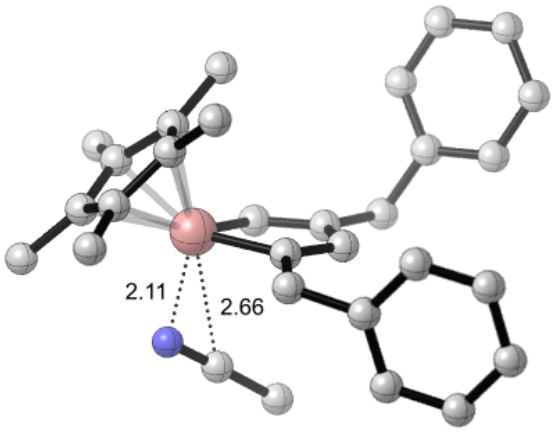

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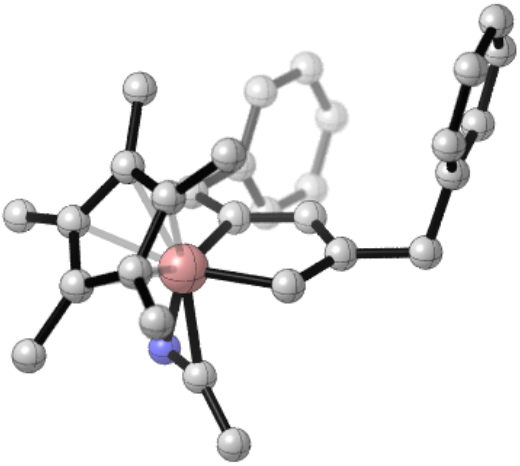

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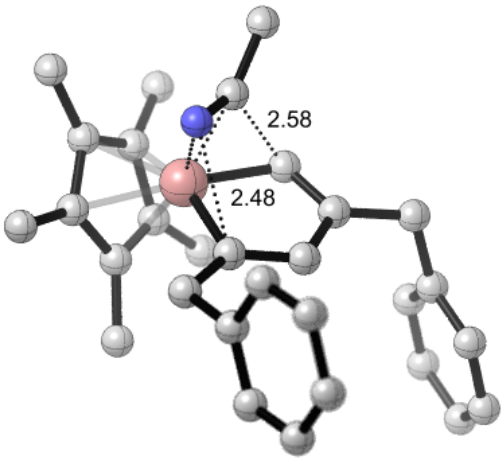

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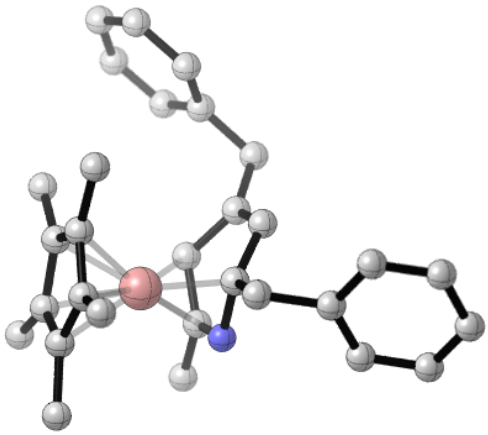

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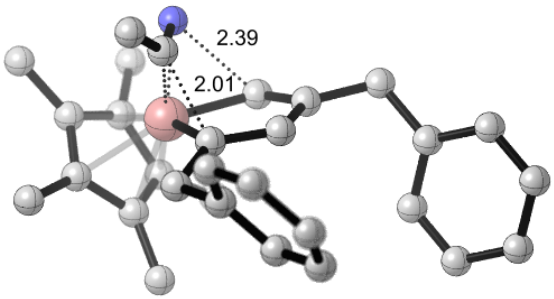

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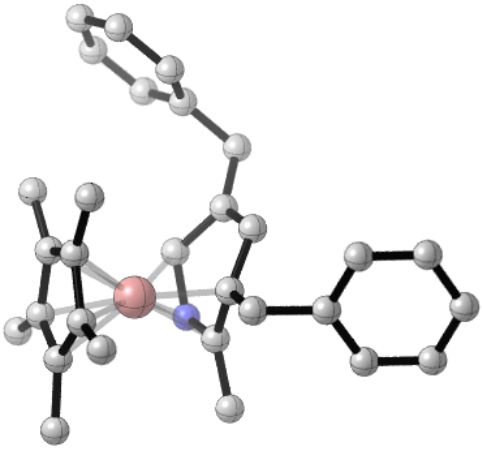

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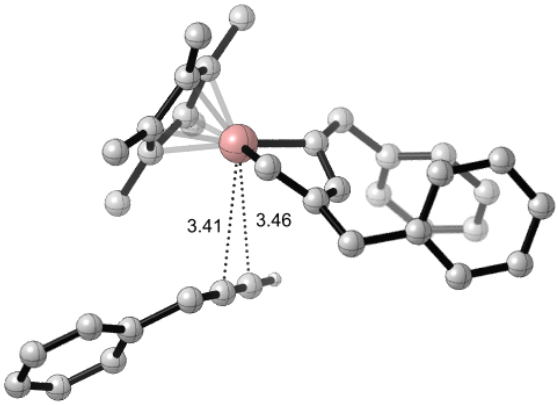

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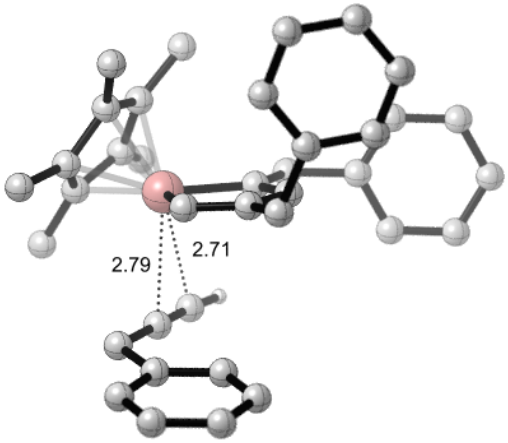

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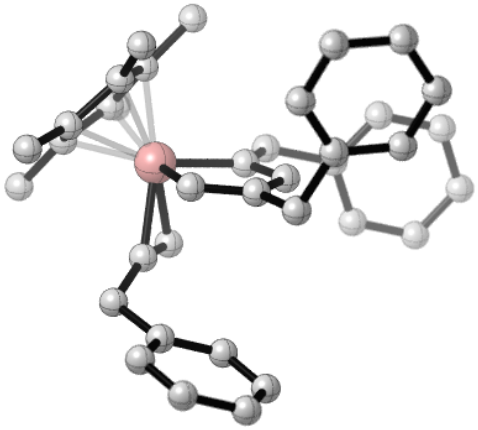

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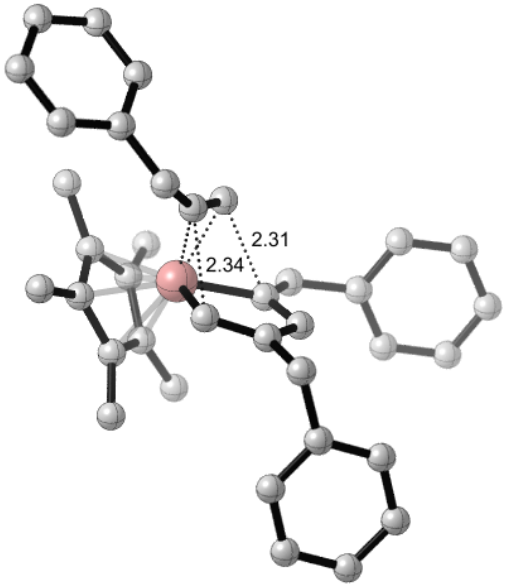

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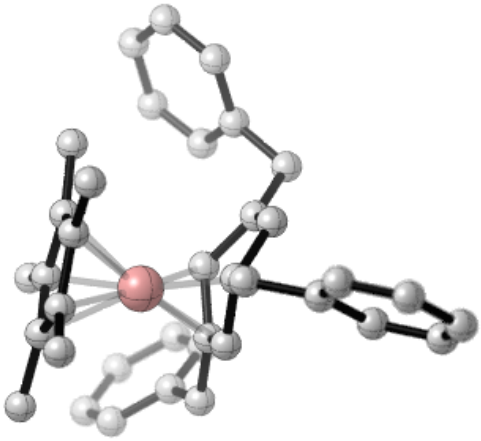

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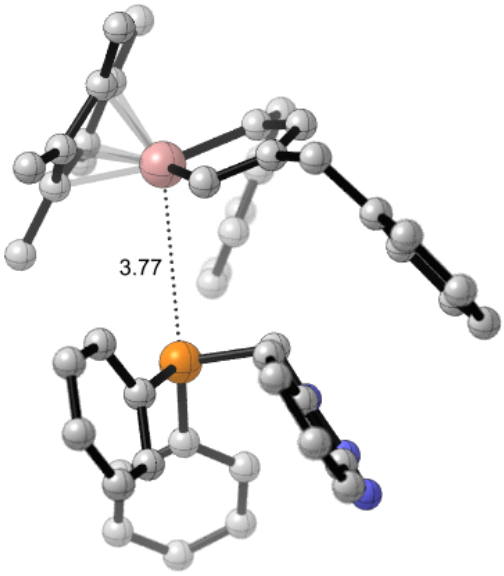

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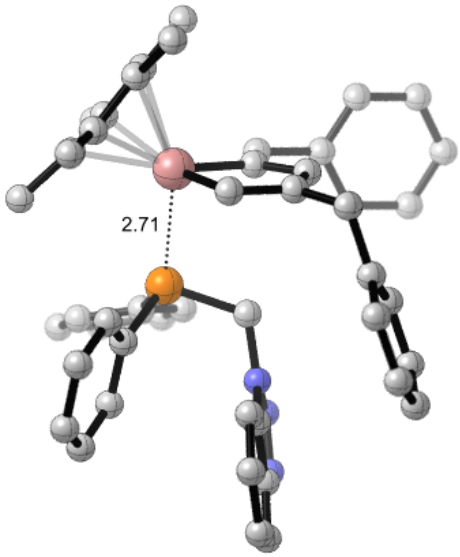

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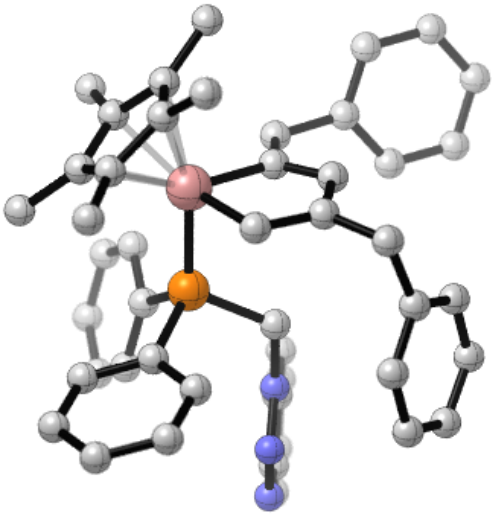

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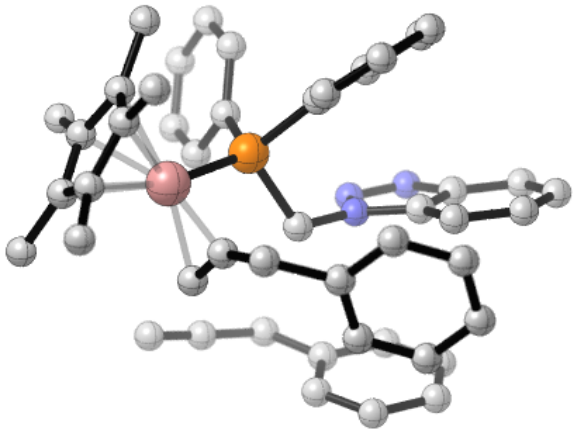

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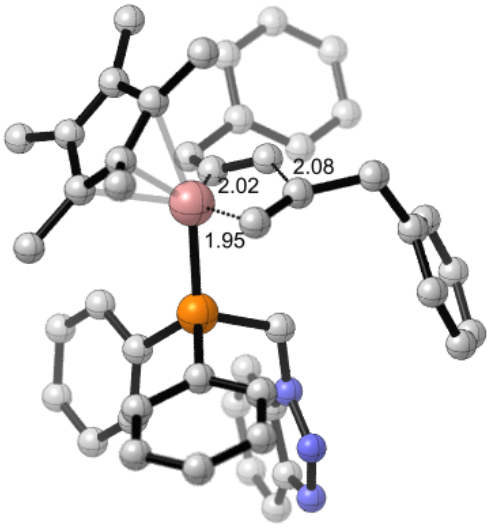

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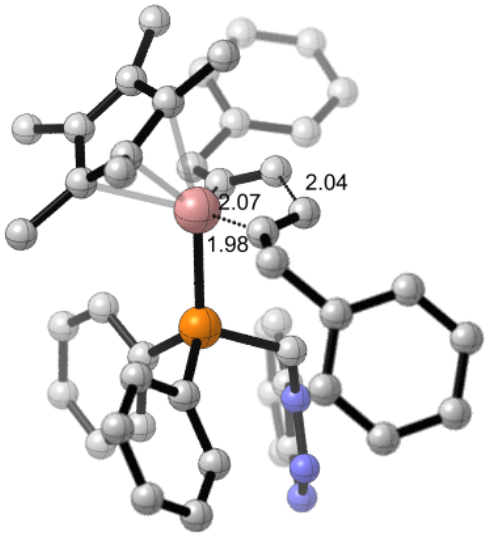

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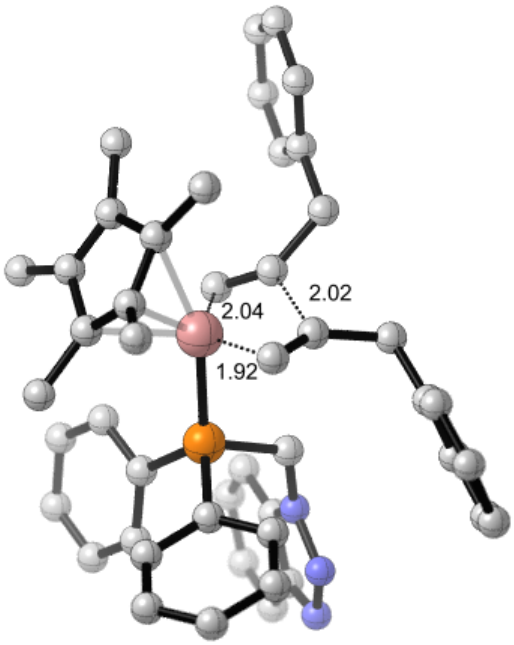

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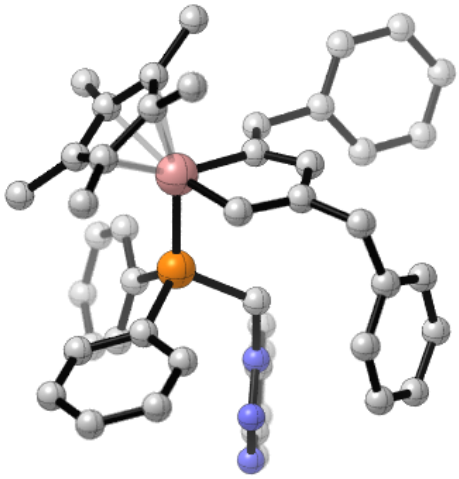

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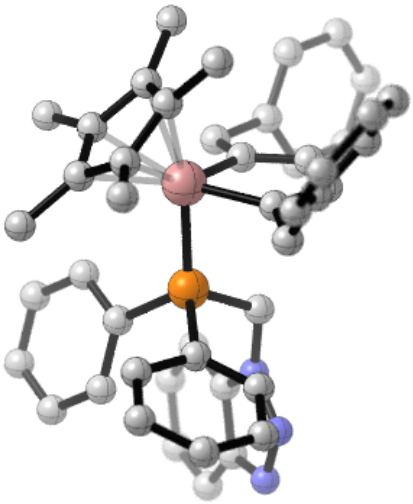

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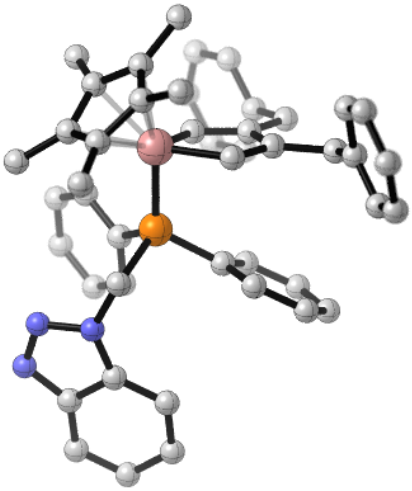
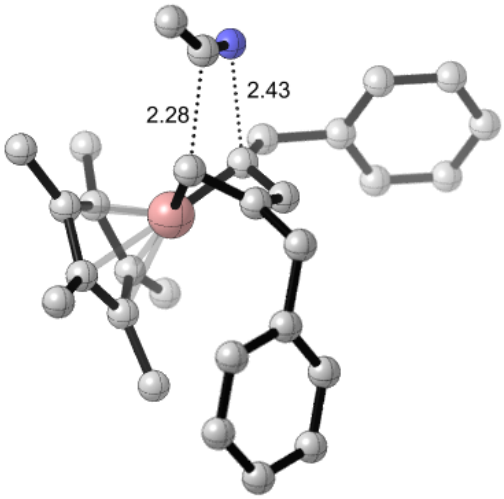


D3-L



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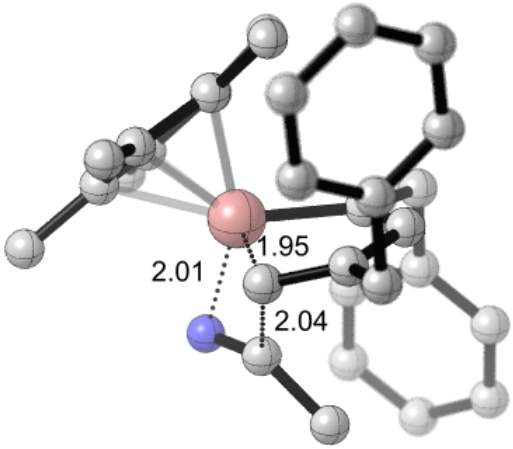

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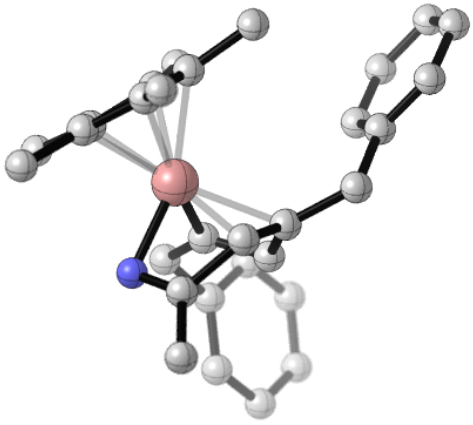

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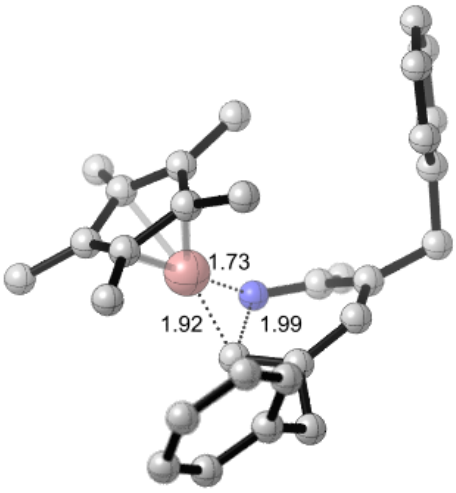

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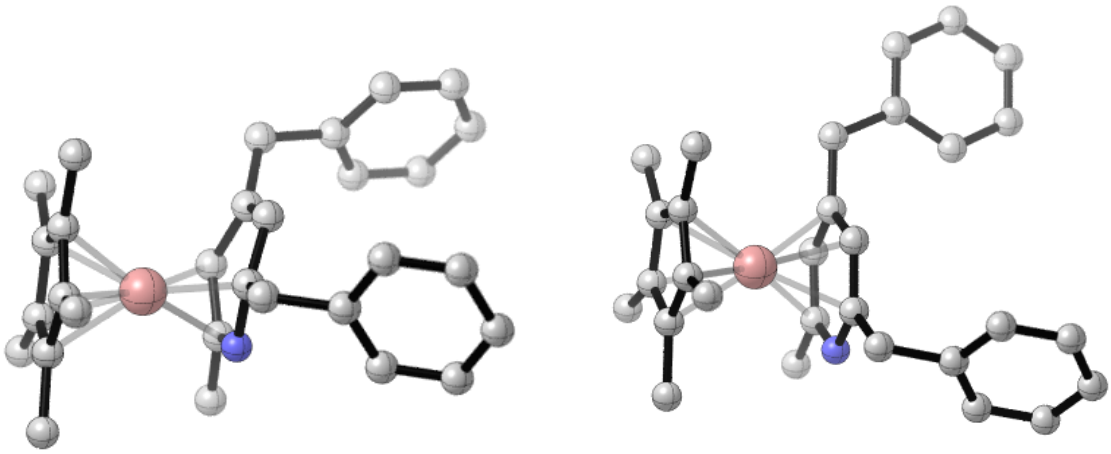

CP(F1a-N) **^{3}G1a-N**

8. References

[1] Fairhurst, G.; White, C. Syntheses of Pentamethylcyclopentadienylcobalt(III) Compounds and Reactions of $[Co(C_5Me_5)(Solvent)_3]X_2$ (Solvent = Acetonitrile or Acetone, X = BF_4 or PF_6). *J. Chem. Soc., Dalton Trans.* **1979**, 1524–1530.

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