Electronic Supplementary Information

Platinum thiolate complexes supported by PBP and POCOP pincer ligands as efficient catalysts for hydrosilylation of carbonyl compounds

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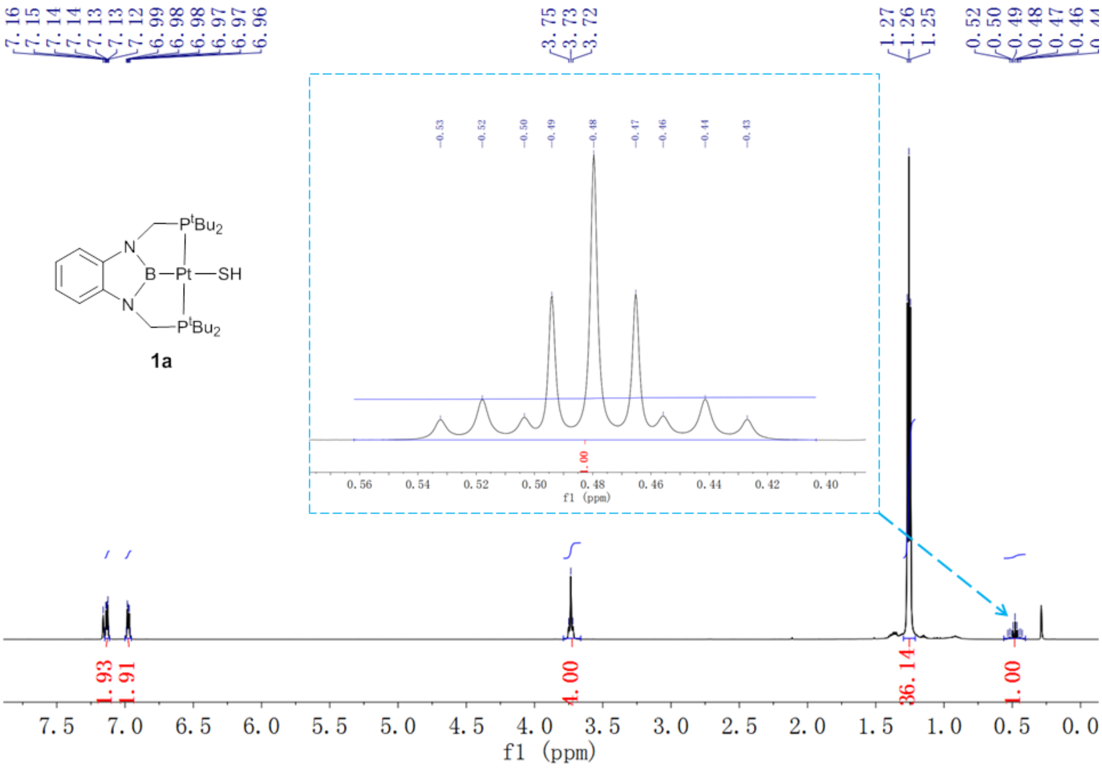

Fig. S1 ^{1}H NMR spectrum of complex **1a** (600 MHz, C_6D_6)

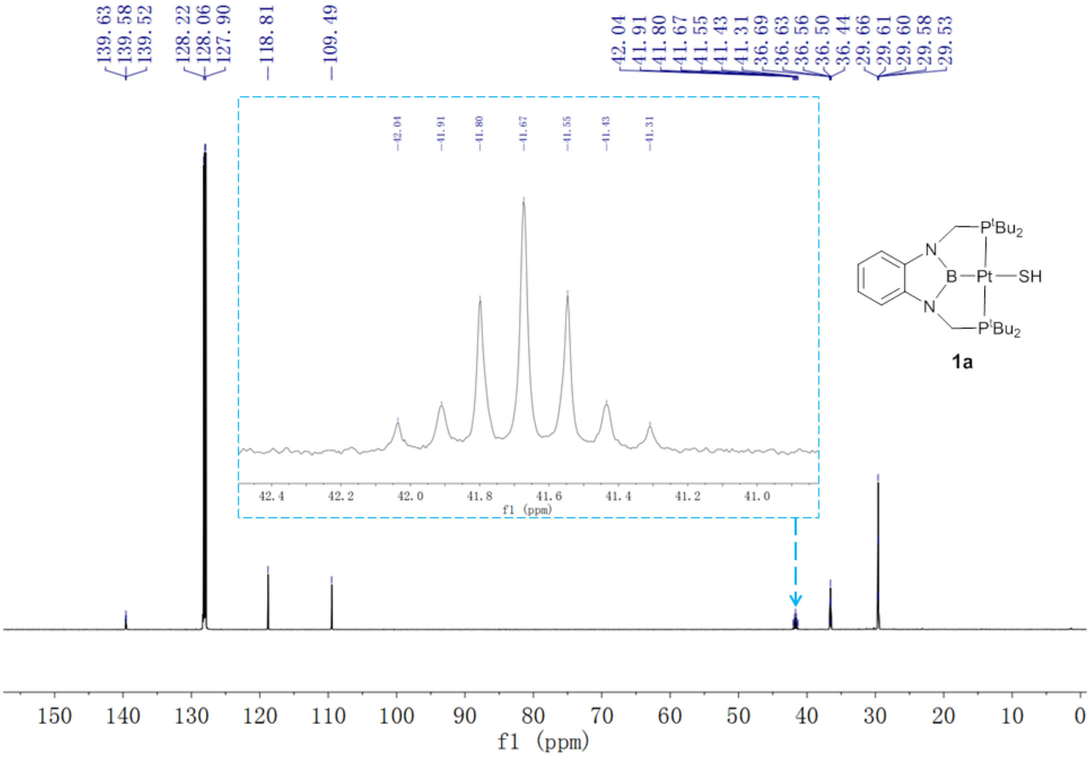

Fig. S2 ^{13}C{^{1}H} NMR spectrum of complex **1a** (151 MHz, C_6D_6)

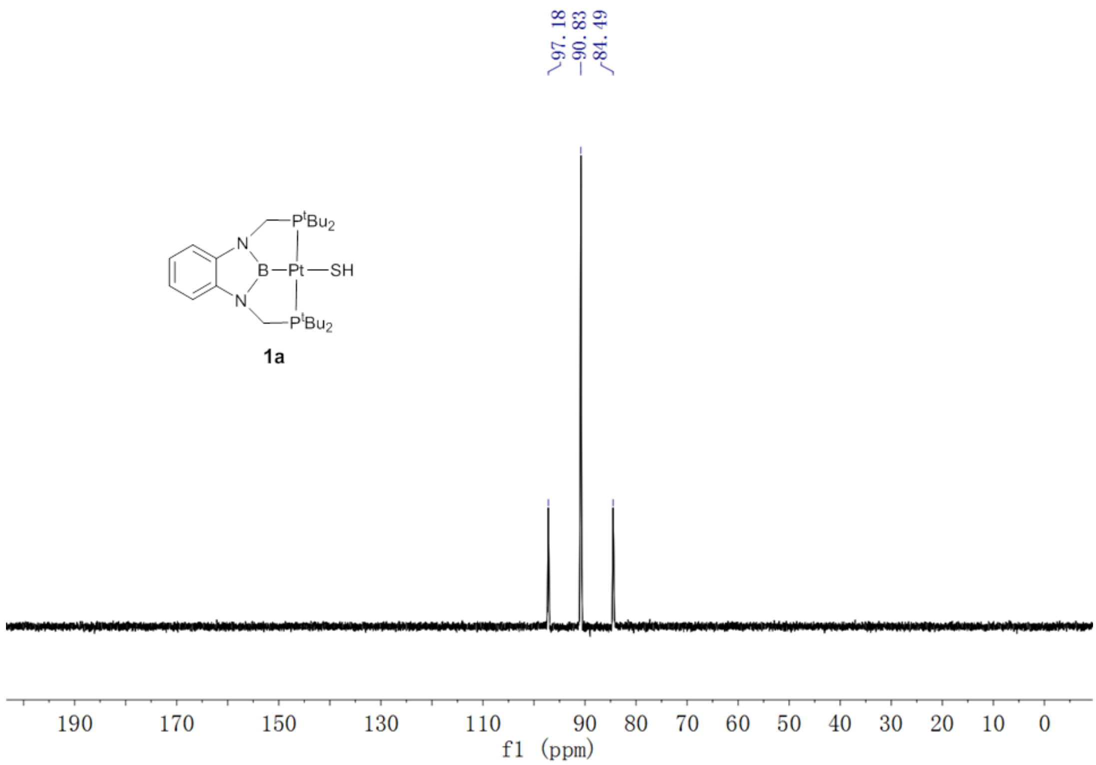

Fig. S3 $^{31}P\{^1H\}$ NMR spectrum of complex **1a** (243 Hz, C_6D_6)

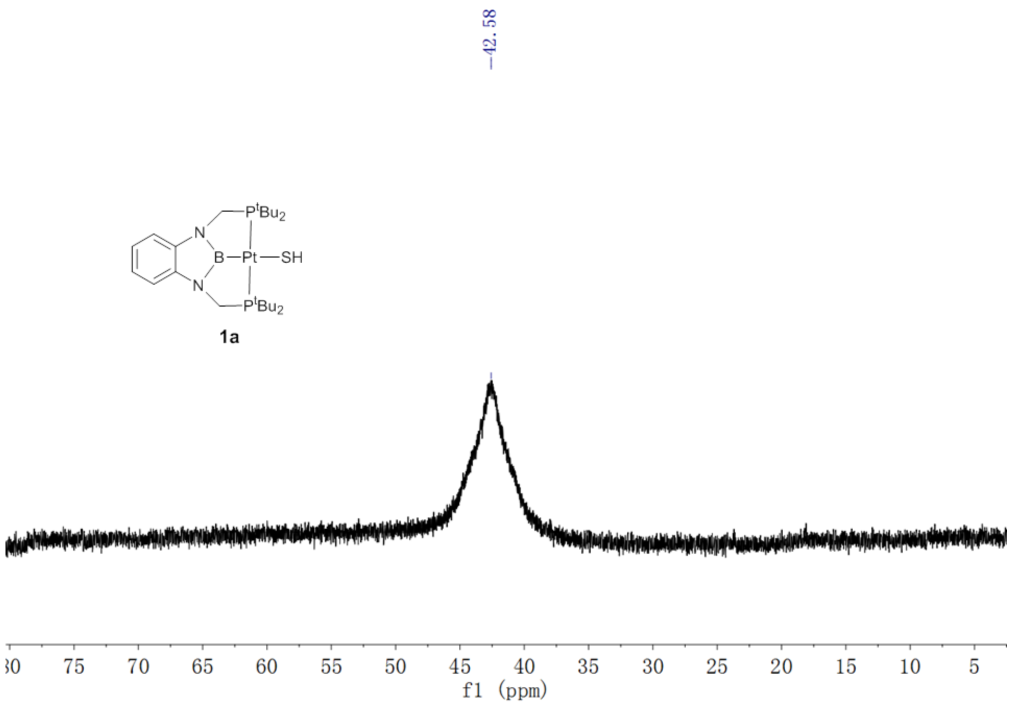

Fig. S4 ^{11}B NMR spectrum of complex **1a** (193 Hz, C_6D_6)

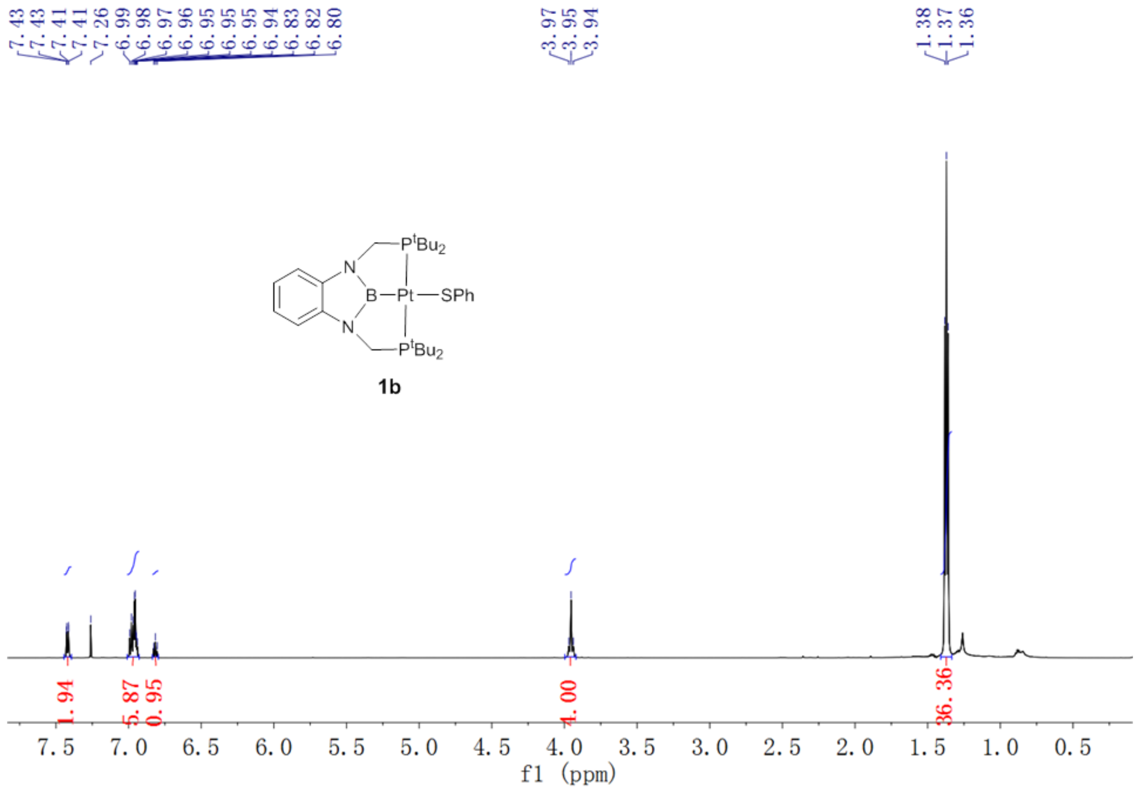

Fig. S5 ^{1}H NMR spectrum of complex **1b** (600 MHz, $CDCl_3$)

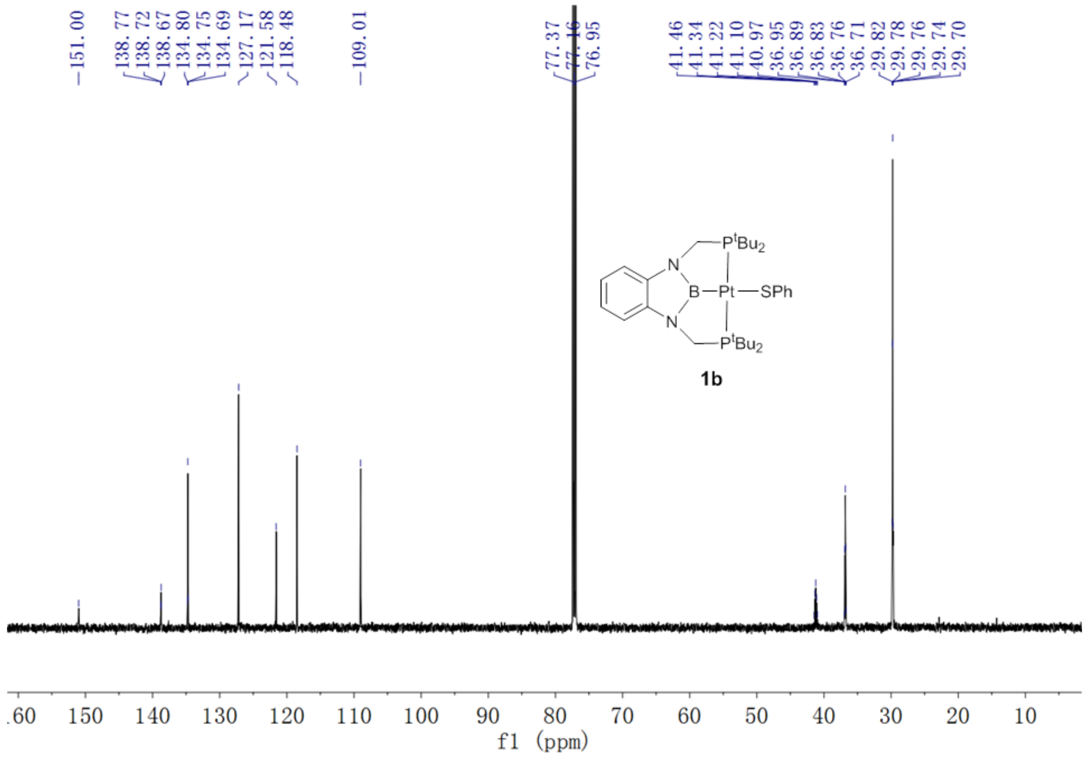

Fig. S6 $^{13}C\{^{1}H\}$ NMR spectrum of complex **1b** (151 MHz, $CDCl_3$)

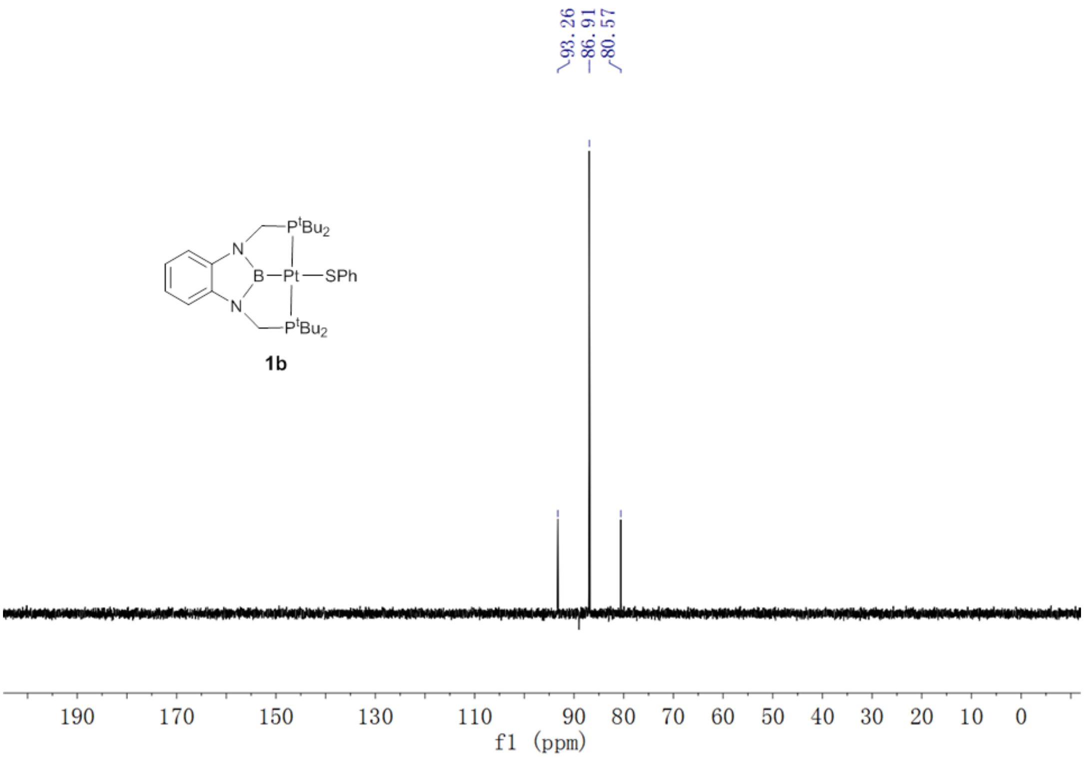

Fig. S7 $^{31}P\{^1H\}$ NMR spectrum of complex **1b** (243 MHz, $CDCl_3$)

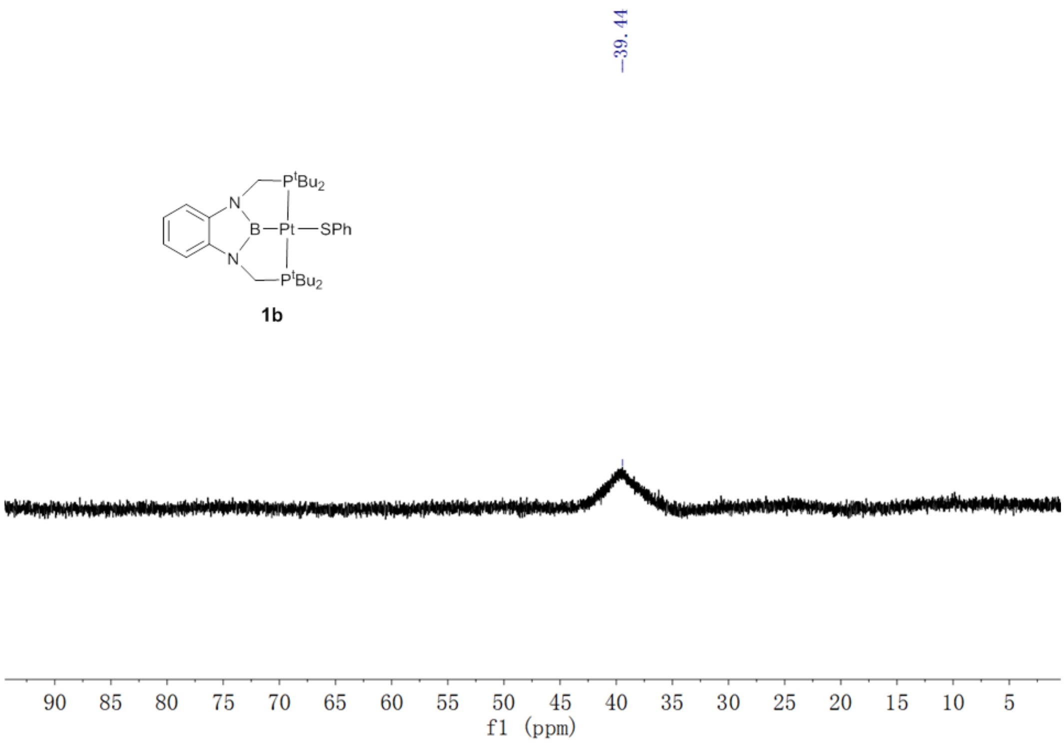

Fig. S8 ^{11}B NMR spectrum of complex **1b** (193 MHz, $CDCl_3$)

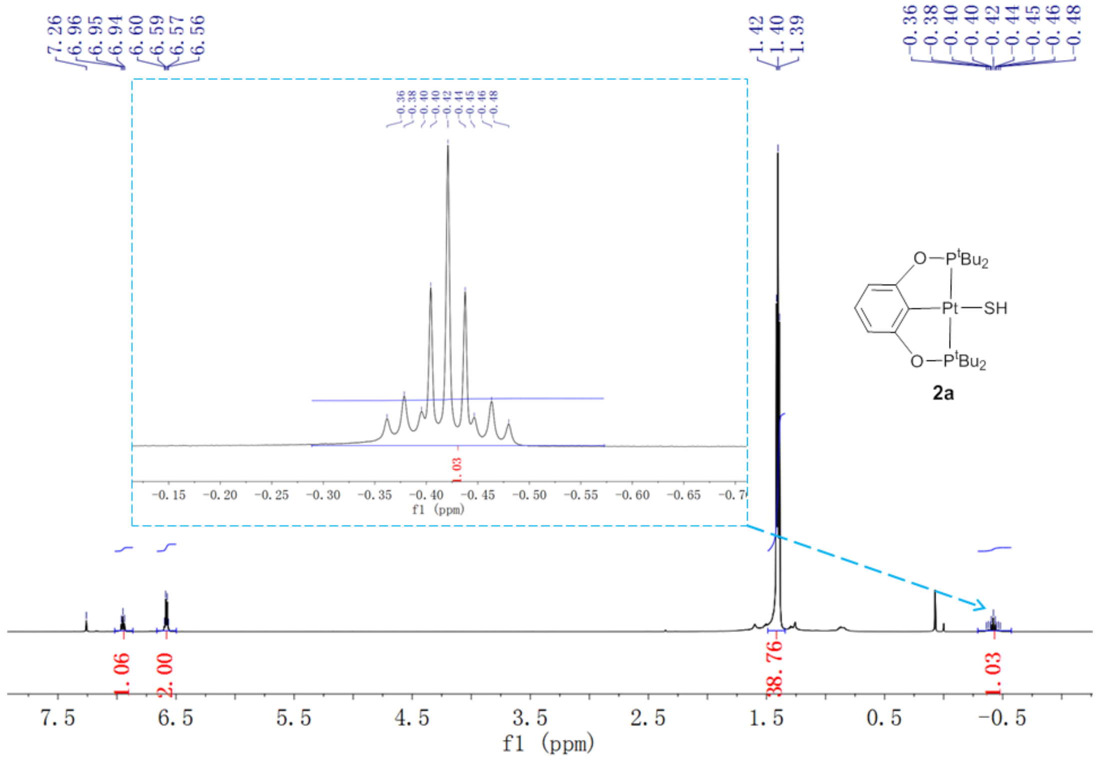

Fig. S9 ^{1}H NMR spectrum of complex **2a** (600 MHz, $CDCl_3$)

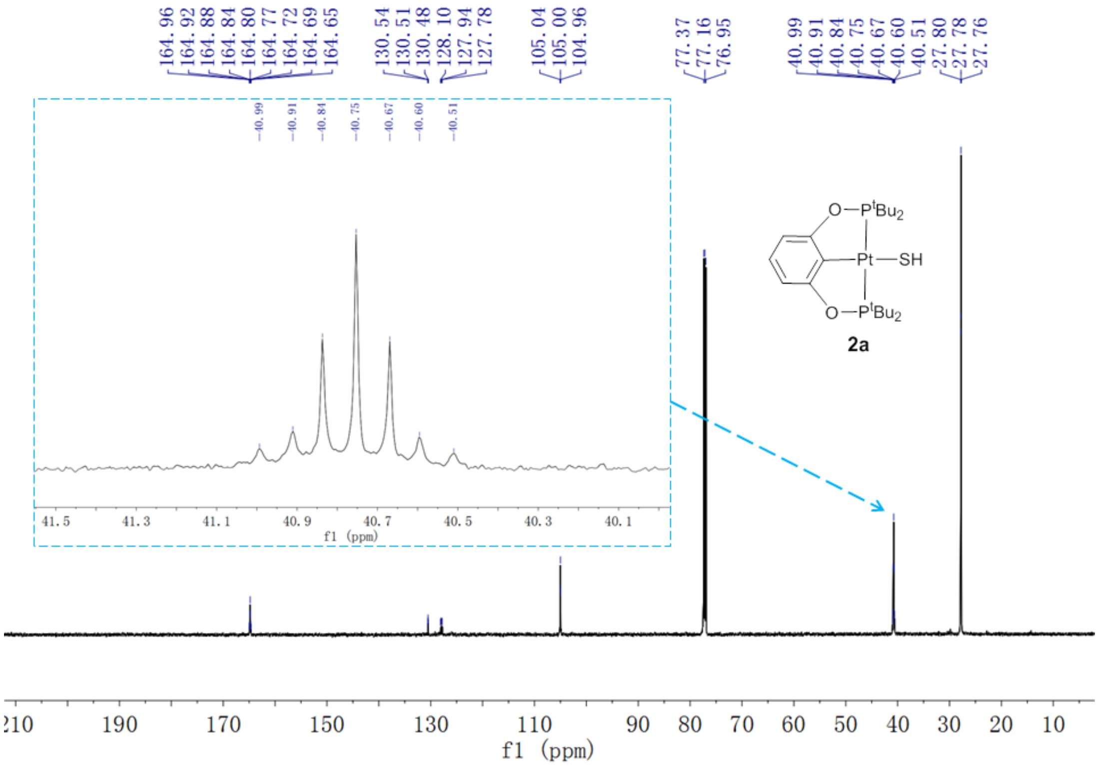

Fig. S10 $^{13}C\{^{1}H\}$ NMR spectrum of complex **2a** (151 MHz, $CDCl_3$)

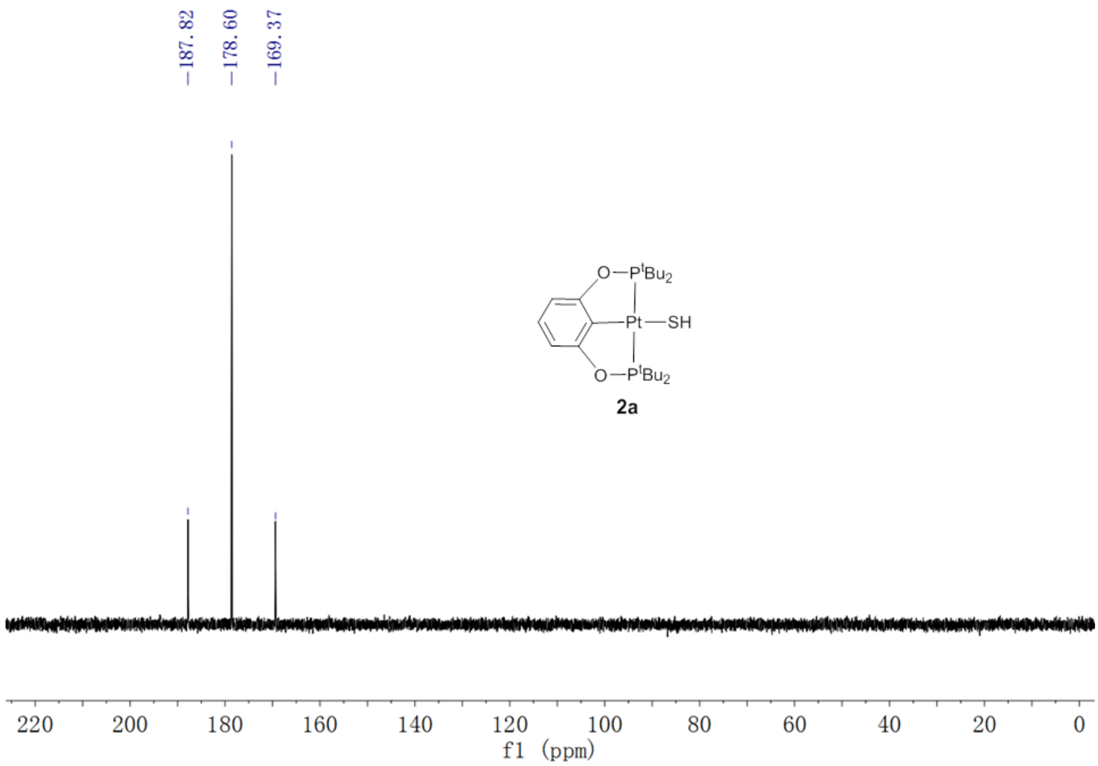

Fig. S11 $^{31}P\{^1H\}$ NMR spectrum of complex **2a** (162 MHz, C_6D_6)

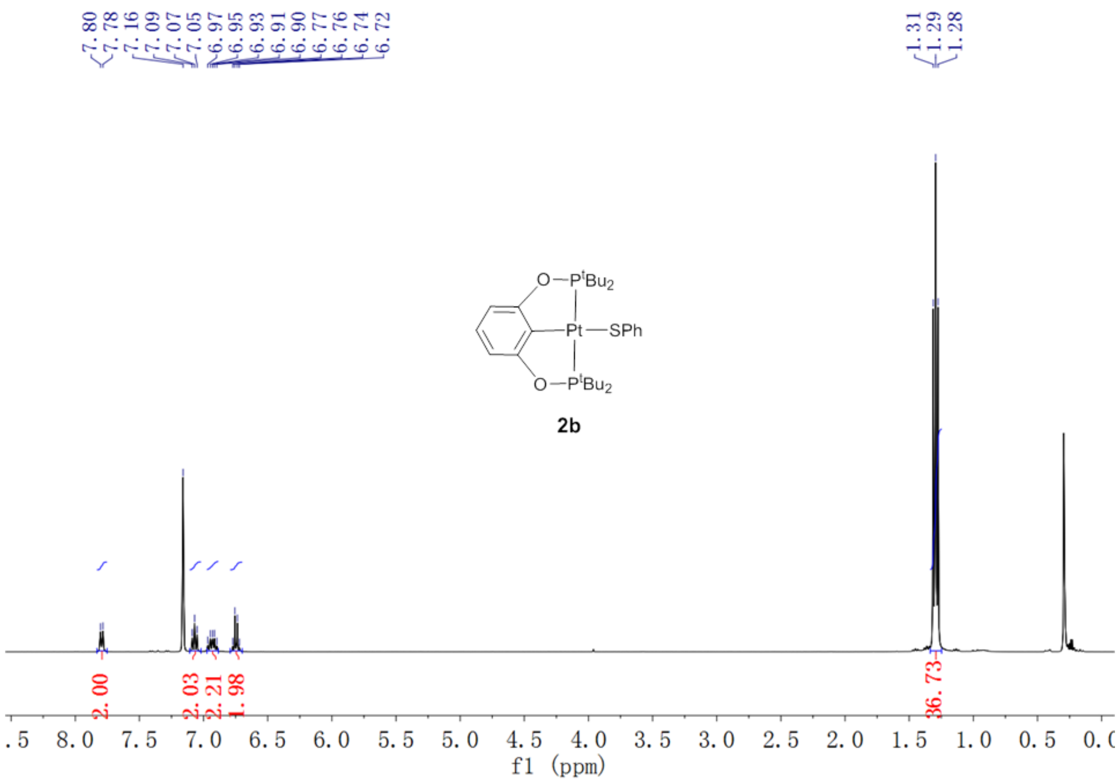

Fig. S12 ^1H NMR spectrum of complex **2b** (400 MHz, C_6D_6)

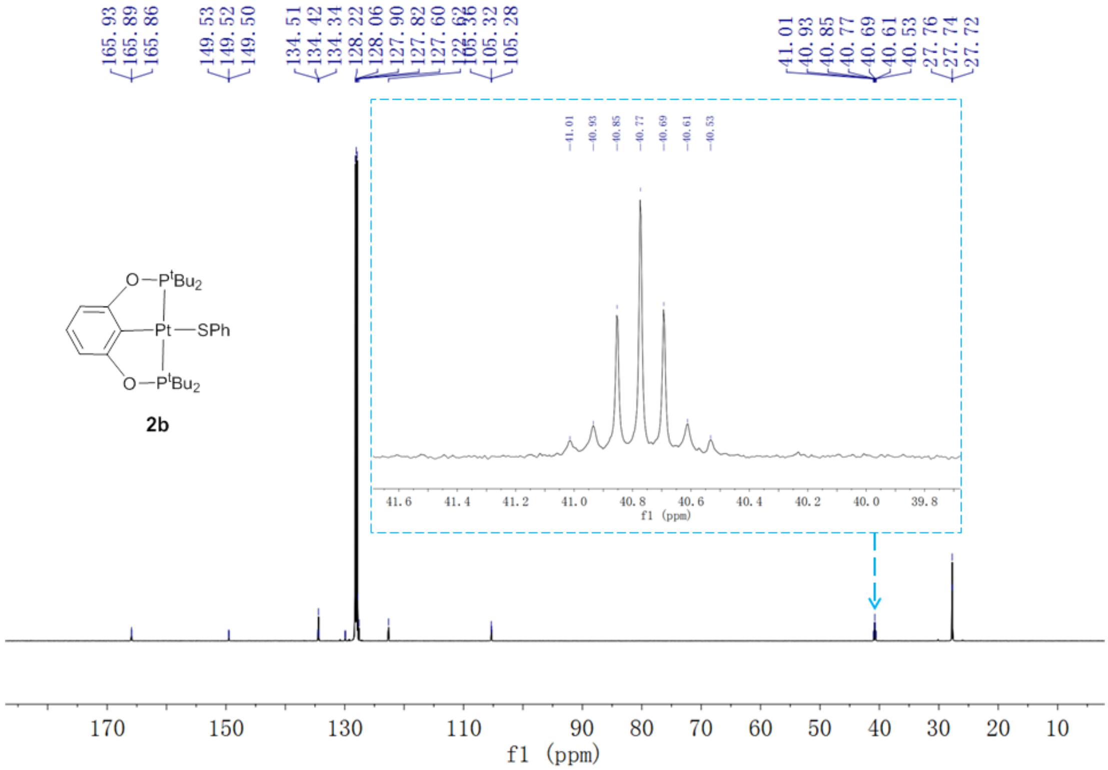

Fig. S13 $^{13}C\{^{1}H\}$ NMR spectrum of complex **2b** (151 MHz, C_6D_6)

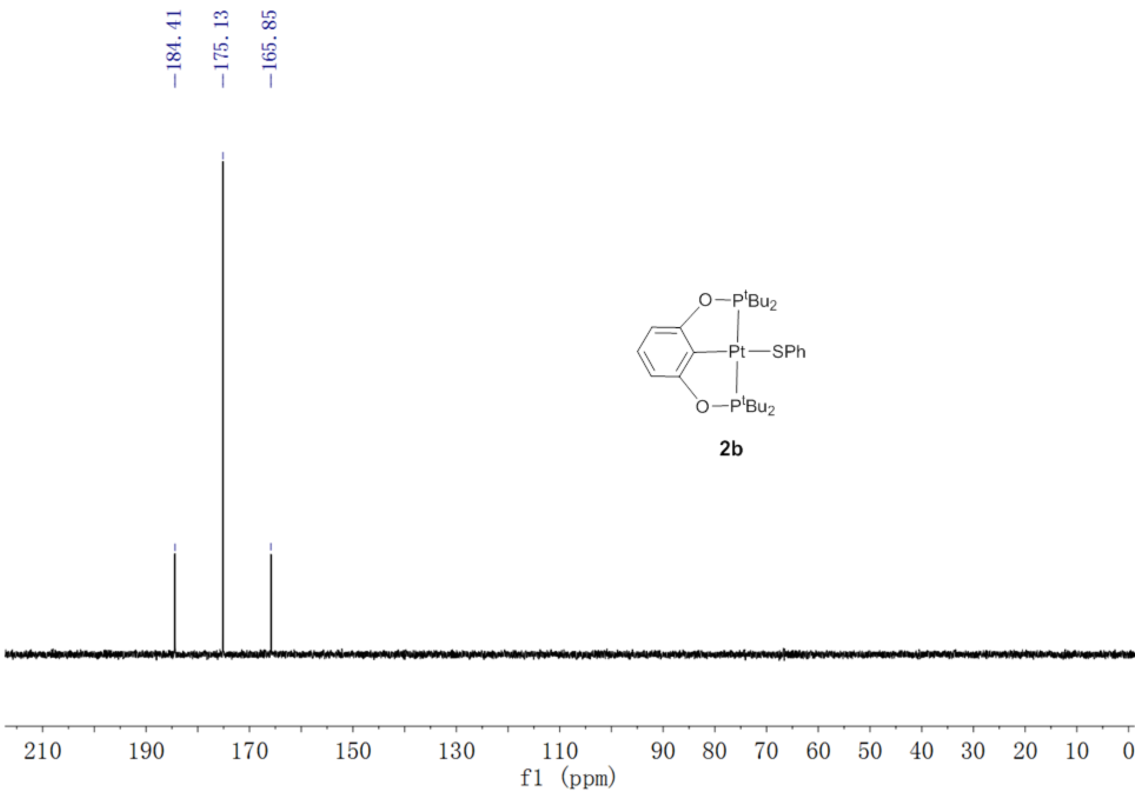

Fig. S14 $^{31}P\{^{1}H\}$ NMR spectrum of complex **2b** (162 MHz, C_6D_6)

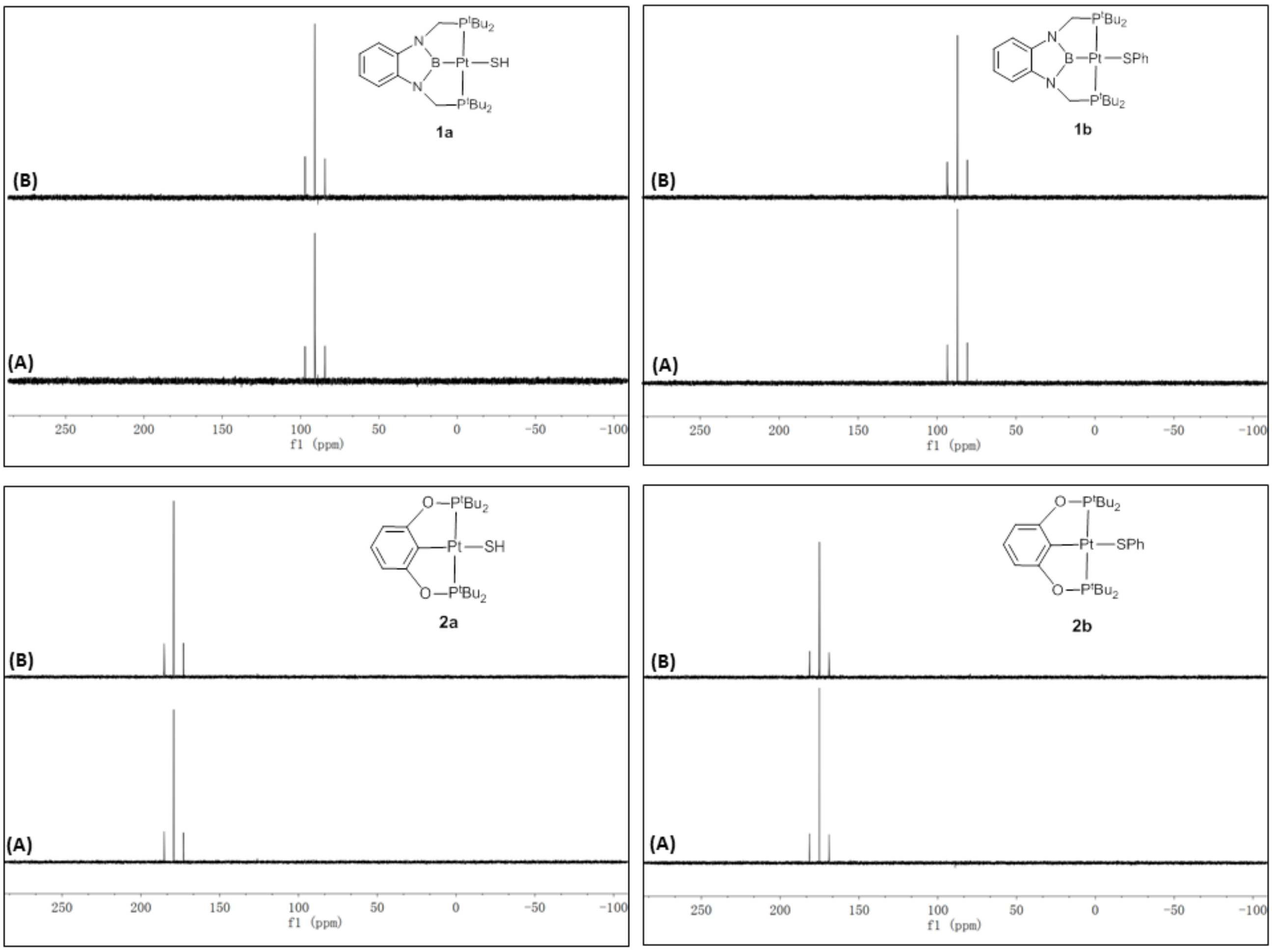

Fig. S15 $^{31}P\{^{1}H\}$ NMR spectra of complexes **1a**,**b** and **2a**,**b** recorded at room temperature under an air atmosphere (162 MHz, C_6D_6). (A) spectra recorded immediately after making the solutions under an air atmosphere; (B) spectra recorded after the NMR tubes were exposed in air for 6 h.

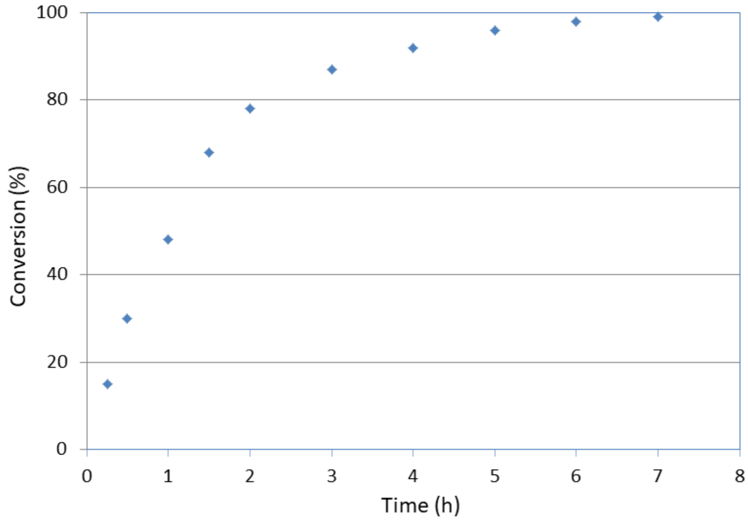

Fig. S16 The profile of conversion *vs* time for hydrosilylation of benzaldehyde with $PhSiH_3$ catalysed by **1a** at 25 ˚C (see Table 2 entry 9 in the main text for detailed reaction conditions).

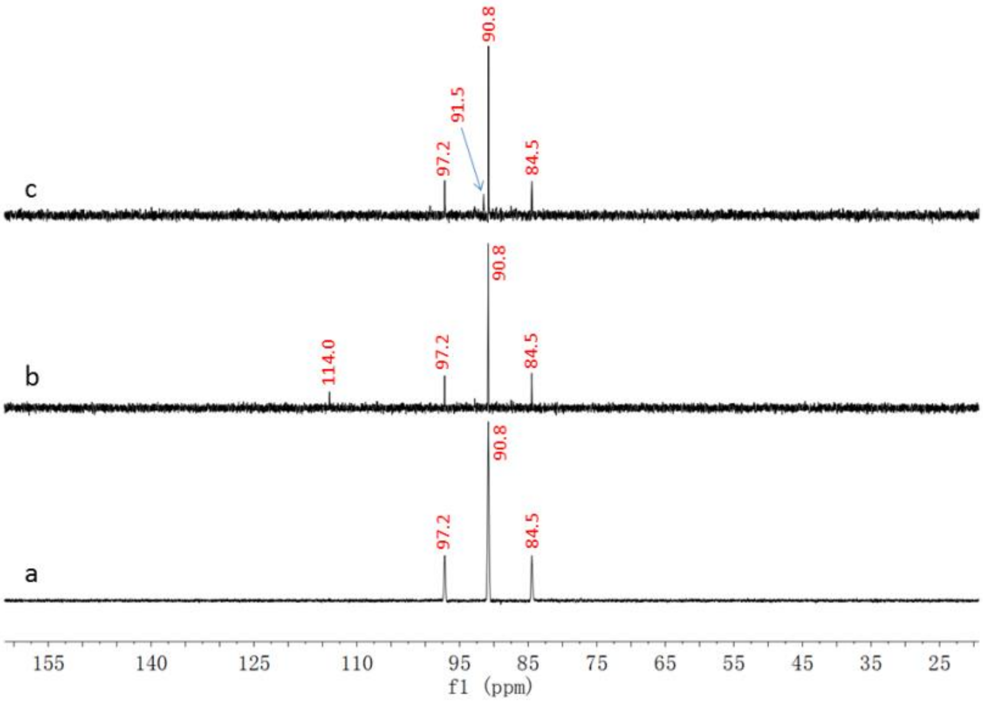

Fig. S17 $^{31}P\{^{1}H\}$ NMR spectra of the reaction mixture of **1a** (0.1 mmol), PhCHO (0.1 mmol) and $PhSiH_3$ (0.1 mmol) in C_6D_6 at room temperature. (a) **1a** in C_6D_6 before adding PhCHO and $PhSiH_3$; (b) spectrum recorded 5 h after adding PhCHO and $PhSiH_3$; (c) spectrum recorded 23 h after adding PhCHO and $PhSiH_3$.

Table S1. The highest turnover frequency values (TOF/h^{-1}) of the reported platinum catalyst systems for the hydrosilylation of carbonyl compounds

Entry	Catalyst	Temp. (˚C)	TOF for aldehyde	TOF for ketone	Ref
1[a]	$[Pt(PPh_3)_3]$	45	0.1		S1
2[a]	$[\{Pt(PMe_3)\}_3(\mu\text{-}SiPh_2)_3]$	25	0.7		S1,S2
3[a]	$[Pt(C_2H_4)(PPh_3)_2]$	80	9		S3
4[a]	$[PtCl_2\{(S,R)Fe(C_5H_5)(C_5H_3(CHMeNMe_2)PPh_2\text{-}1,2)\}]$	20		2	S4
5	$[PtH(^tBu_2PO)_2\text{-}1,3\text{-}C_6H_3]$	60	3,200	200	S5
6	$[Pt(SH)\{B(NCH_2P^tBu_2)_2\text{-}1,2\text{-}C_6H_4\}]$	65	67,000	3,300	This work

[a] The TOF values were calculated based on the experimental data reported in the literature

Table S2. Summary of crystal data and structure refinement for complexes **1a** and **1b**

Complex	**1a**	**1b**
CCDC number	2124656	2124657
Empirical formula	$C_{24}H_{45}BN_2P_2PtS$	$C_{30}H_{45}BN_2P_2PtS$
Formula weight	661.52	733.58
Temp, K	150.0(3)	293(2)
Crystal system	orthorhombic	Monoclinic
Space group	Pbca	$P2_1/n$
a, Å	12.01270(10)	12.87340(10)
b, Å	14.4319(2)	17.4918(2)
c, Å	32.1440(5)	14.8878(2)
α (°)	90	90
β (°)	90	103.5780(10)
γ (°)	90	90
Volume, Å^3	5572.68(13)	3258.72(6)
Z	8	4
d_{calc}, g cm^{-3}	1.577	1.495
λ, Å	1.54184	1.54184
μ, mm^{-1}	11.299	9.727
No. of data collected	15153	13424
No. of unique data	5223	6216
R_{int}	0.0413	0.0423
Goodness-of-fit on F^2	1.088	1.158
R_1, wR_2 ($I > 2\sigma(I)$)	0.0416, 0.1080	0.0567, 0.1682
R_1, wR_2 (all data)	0.0597, 0.1174	0.0632, 0.1732

Table S3. Summary of crystal data and structure refinement for complexes **2a** and **2b**

Complex	**2a**	**2b**
CCDC number	2124658	2124659
Empirical formula	$C_{22}H_{40}O_2P_2PtS$	$C_{28}H_{44}O_2P_2PtS$
Formula weight	625.63	701.72
Temp, K	169.99(10)	169.99(10)
Crystal system	triclinic	monoclinic
Space group	P-1	$P2_1/n$
a, Å	8.3204(3)	12.79010(10)
b, Å	12.0711(4)	12.6583(2)
c, Å	13.4168(4)	20.8480(2)
α (°)	100.588(3)	90
β (°)	95.692(3)	106.5180(10)
γ (°)	104.316(3)	90
Volume, Å^3	1268.58(8)	3236.01(7)
Z	2	4
d_{calc}, g cm^{-3}	1.638	1.440
λ, Å	1.54184	1.54184
μ, mm^{-1}	12.414	9.800
No. of data collected	8829	15296
No. of unique data	4809	6160
R_{int}	0.0220	0.0338
Goodness-of-fit on F^2	1.049	1.074
R_1, wR_2 ($I > 2\sigma(I)$)	0.0204, 0.0484	0.0327, 0.0887
R_1, wR_2 (all data)	0.0224, 0.0491	0.0354, 0.0902

Characterization of the isolated products

Benzyl alcohol

Clear colorless liquid, 0.102 g, 95% yield, purity: >99% based on ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.31–7.39 (m, Ar*H*, 5H), 4.60 (s, CH_2, 2H), 3.33 (s, O*H*, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 140.89, 128.44, 127.46, 126.98, 64.84. HRMS (ESI): *m/z* calculated for C_7H_9O $[M + H]^+$ 109.0648, found 109.0647. These spectral data correspond to previously reported data.[S6-S8]

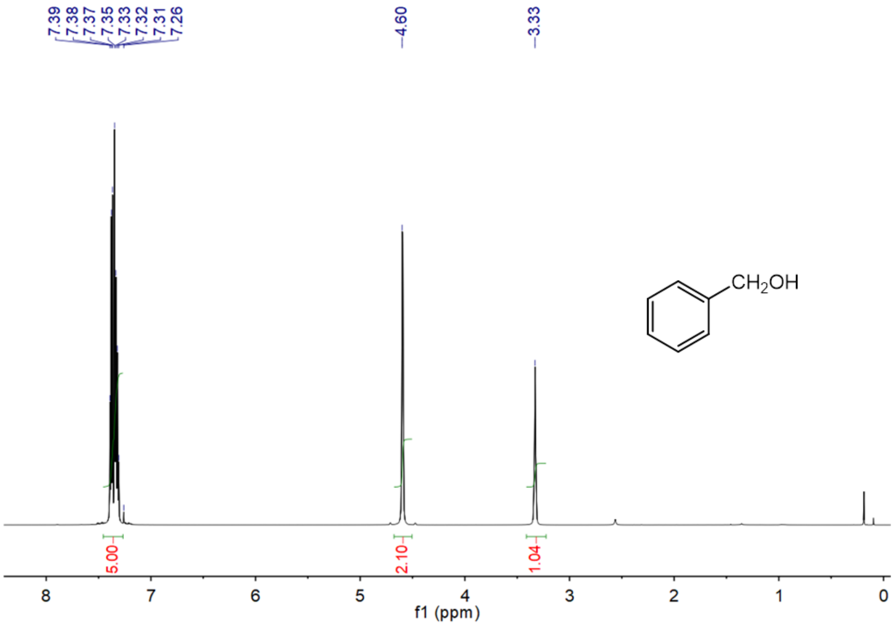

Fig. S18 ^{1}H NMR spectrum of the isolated benzyl alcohol (600 MHz, $CDCl_3$)

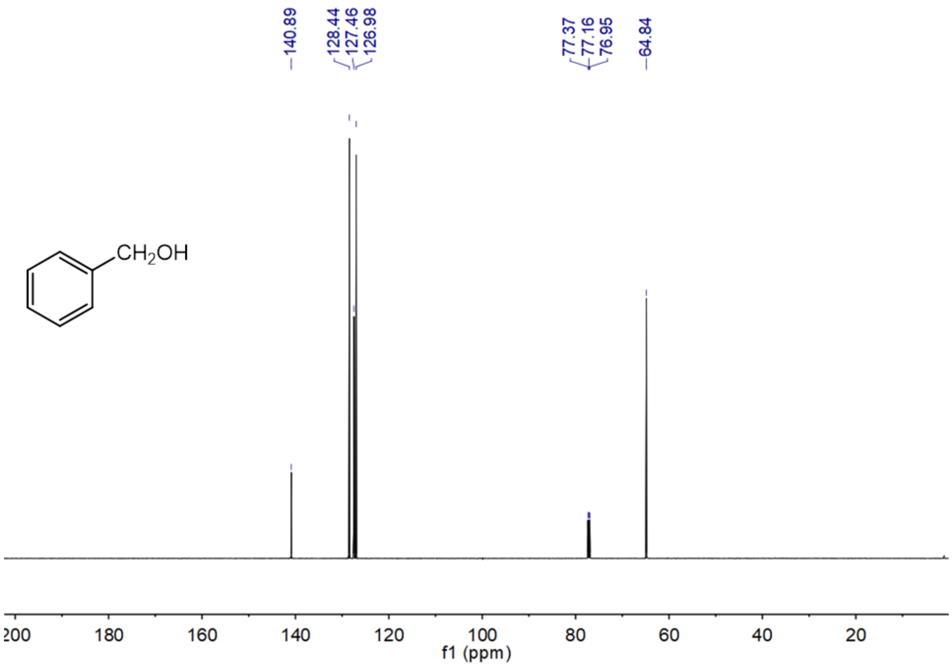

Fig. S19 ^{13}C{^{1}H} NMR spectrum of the isolated benzyl alcohol (151 MHz, $CDCl_3$)

4-Methoxyphenylmethanol

Light yellow liquid, 0.134 g, 97% yield, purity: >99% based on ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.27 (d, J = 8.6 Hz, ArH, 2H), 6.89 (d, J = 8.6 Hz, ArH, 2H), 4.56 (s, CH_2, 2H), 3.80 (s, CH_3, 3H), 2.53 (s, br., OH, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 159.12, 133.22, 128.66, 113.93, 64.80, 55.30. HRMS (ESI): m/z calculated for $C_8H_{11}O_2$ [M + H]$^+$ 139.0754, found 139.0756. These spectral data correspond to previously reported data.[S6-S9]

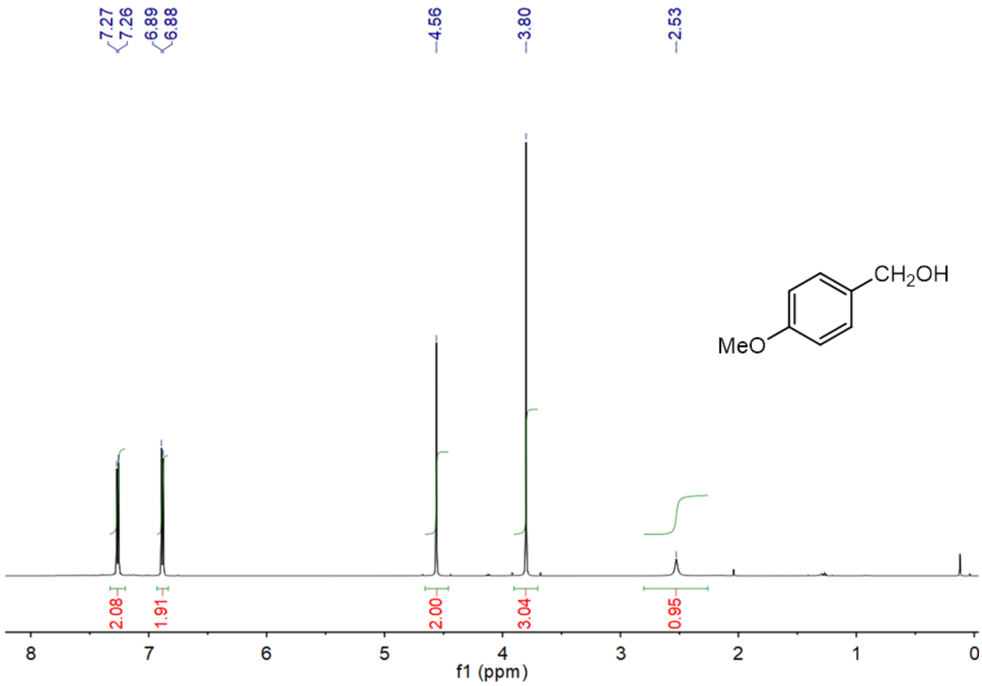

Fig. S20 ^{1}H NMR spectrum of the isolated 4-methoxyphenylmethanol (600 MHz, $CDCl_3$)

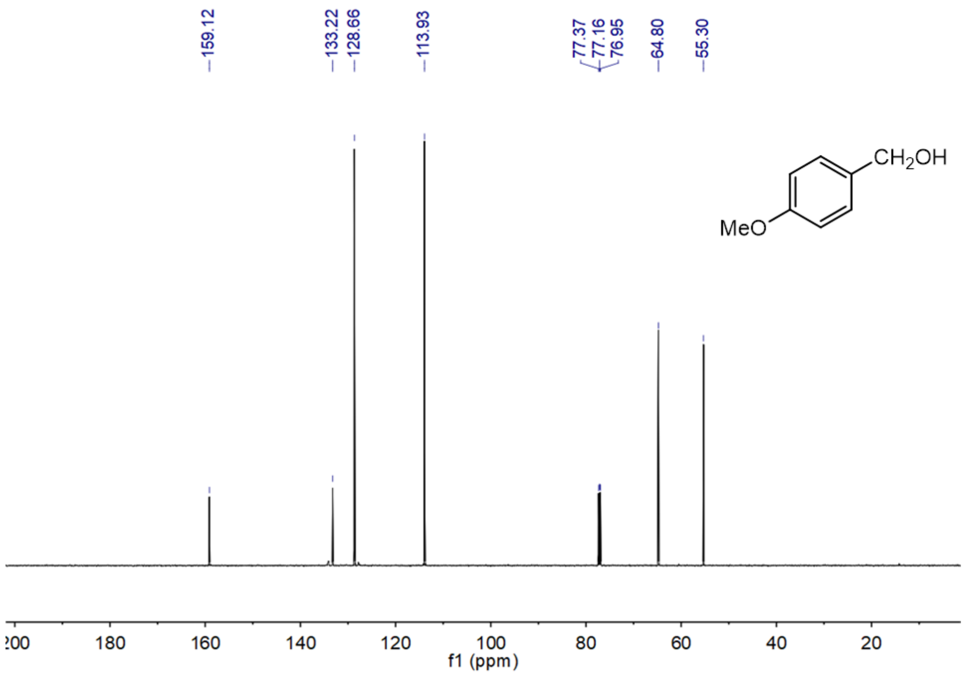

Fig. S21 ^{13}C{^{1}H} NMR spectrum of the isolated 4-methoxyphenylmethanol (151 MHz, $CDCl_3$)

3-Methoxyphenylmethanol

Clear colorless liquid, 0.133 g, 96% yield, purity: >99% based on ^1H NMR spectra. ^1H NMR (600 MHz, $CDCl_3$, δ): 7.17 (t, $J_{H\text{-}H}$ = 7.8Hz, Ar*H*, 1H), 6.81–6.83 (m, Ar*H*, 2H), 6.73–6.75 (m, Ar*H*, 1H), 4.51 (s, C*H*$_2$, 2H), 3.70 (s, C*H*$_3$, 3H), 2.72 (br., O*H*, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, δ): 159.77, 142.64, 129.55, 119.16, 113.18, 112.27, 64.98, 55.21. HRMS (ESI): *m/z* calculated for $C_8H_{11}O_2$ [M + H]$^+$ 139.0754, found 139.0753. These spectral data correspond to previously reported data.[S10]

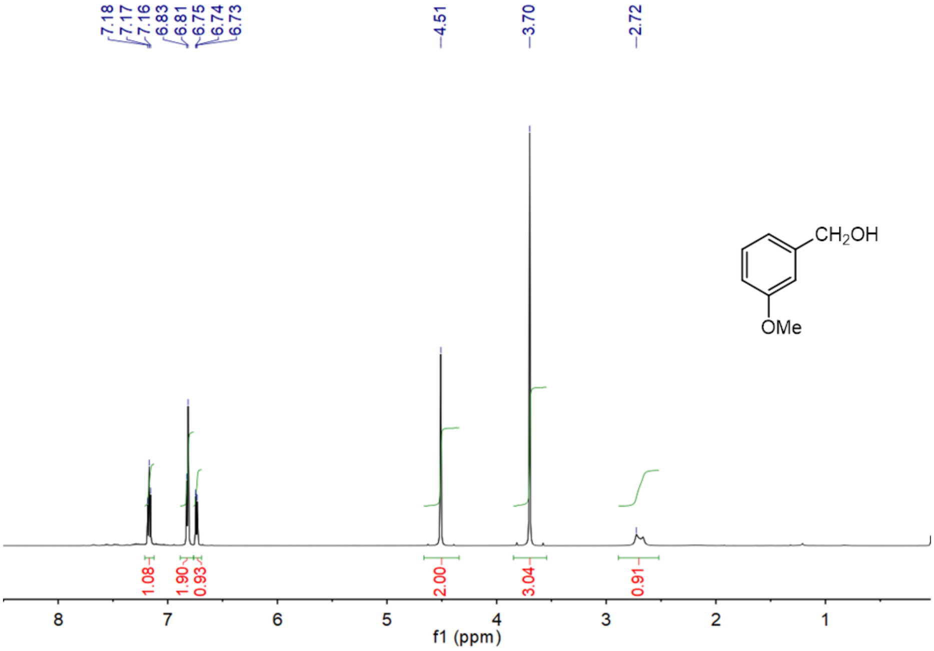

Fig. S22 ^1H NMR spectrum of the isolated 3-methoxyphenylmethanol (600 MHz, $CDCl_3$)

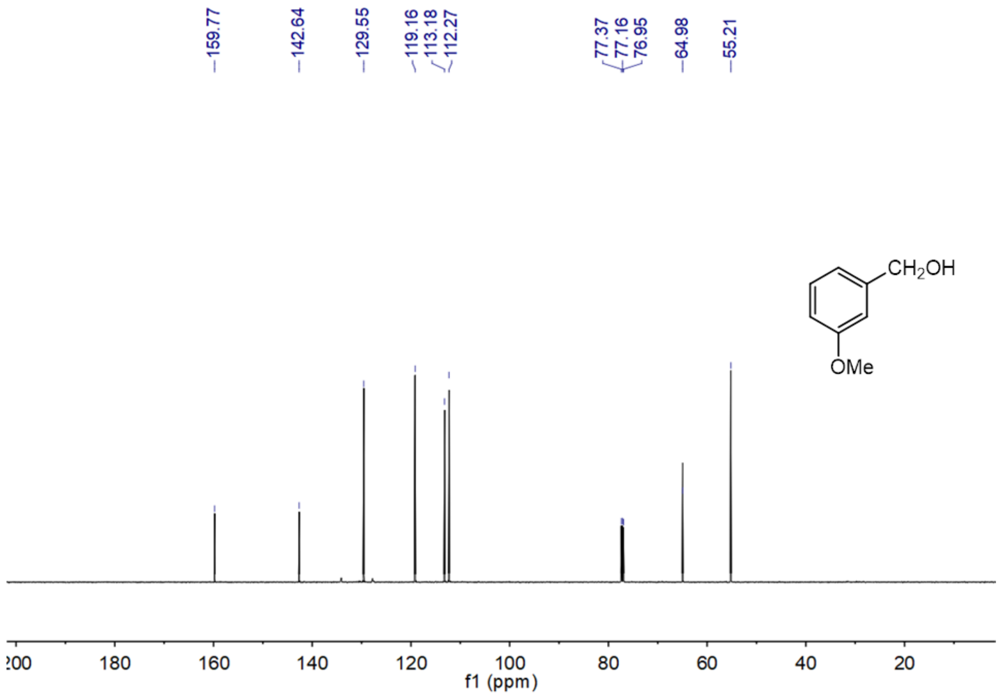

Fig. S23 $^{13}C\{^1H\}$ NMR spectrum of the isolated 3-methoxyphenylmethanol (151 MHz, $CDCl_3$)

2-Methoxyphenylmethanol

Colorless liquid, 0.126 g, 91% yield, purity: >99% based on ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.27–7.30 (m, Ar*H*, 2H), 6.94–6.97 (m, Ar*H*, 1H), 6.88–6.90 (m, Ar*H*, 1H), 4.69 (s, C*H*$_2$, 2H), 3.86 (s, C*H*$_3$, 3H), 2.52 (s, br, O*H*, 1H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, δ): 157.43, 129.13, 128.93, 128.71, 120.67, 110.22, 61.95, 55.27. HRMS (ESI): *m/z* calculated for $C_8H_{11}O_2$ $[M + H]^+$ 139.0754, found 139.0755. These spectral data correspond to previously reported data.[S11]

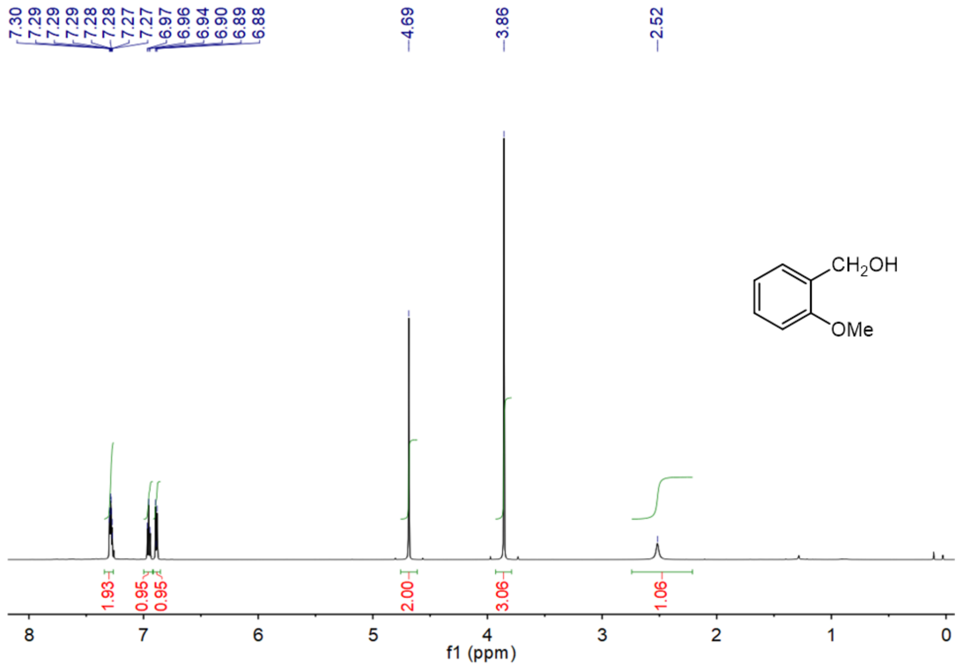

Fig. S24 ^{1}H NMR spectrum of the isolated 2-methoxyphenylmethanol (600 MHz, $CDCl_3$)

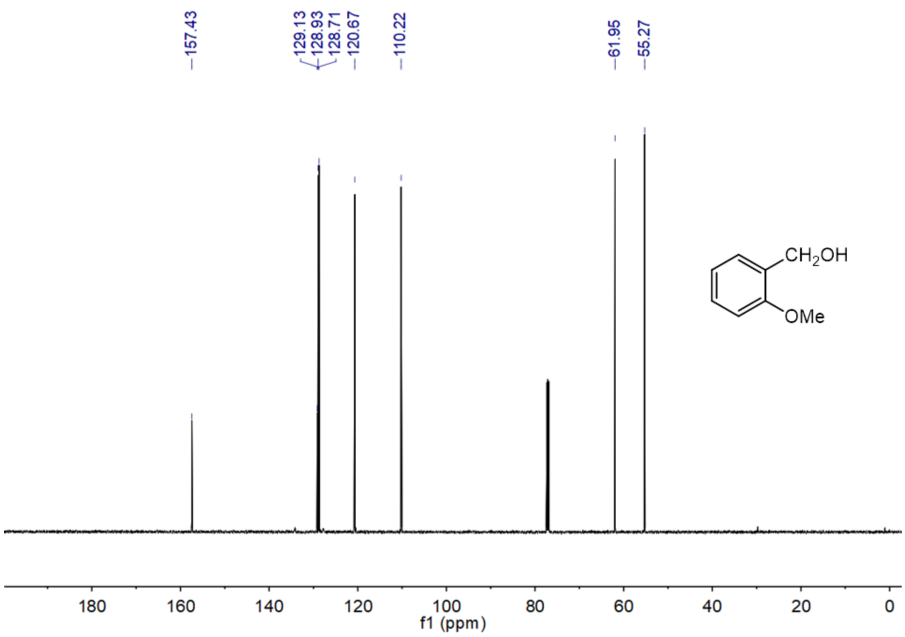

Fig. S25 $^{13}C\{^{1}H\}$ NMR spectrum of the isolated 2-methoxyphenylmethanol (151 MHz, $CDCl_3$)

4-Tolyl-methanol

Colorless crystalline solid, 0.112 g, 92% yield, purity: >99% based on ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.07 (d, J_{H-H} = 8.0 Hz, Ar*H*, 2H), 6.99 (d, J_{H-H} = 8.0 Hz, Ar*H*, 2H), 4.46 (s, C*H*$_2$, 2H), 2.17 (s, C*H*$_3$, 3H), 1.44 (s, br., O*H*, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 138.05, 137.56, 129.39, 127.26, 65.43, 21.29. HRMS (ESI): *m/z* calculated for $C_8H_{11}O$ $[M + H]^+$ 123.0804, found 123.0808. These spectral data correspond to previously reported data.[S7,S9]

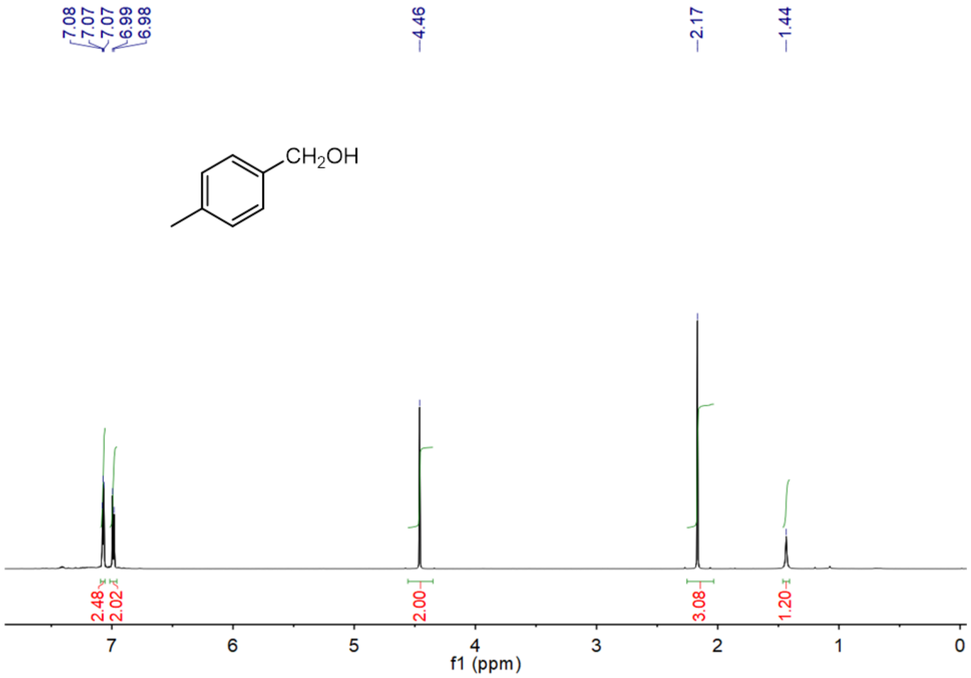

Fig. S26 ^{1}H NMR spectrum of the isolated 4-tolyl-methanol (600 MHz, $CDCl_3$)

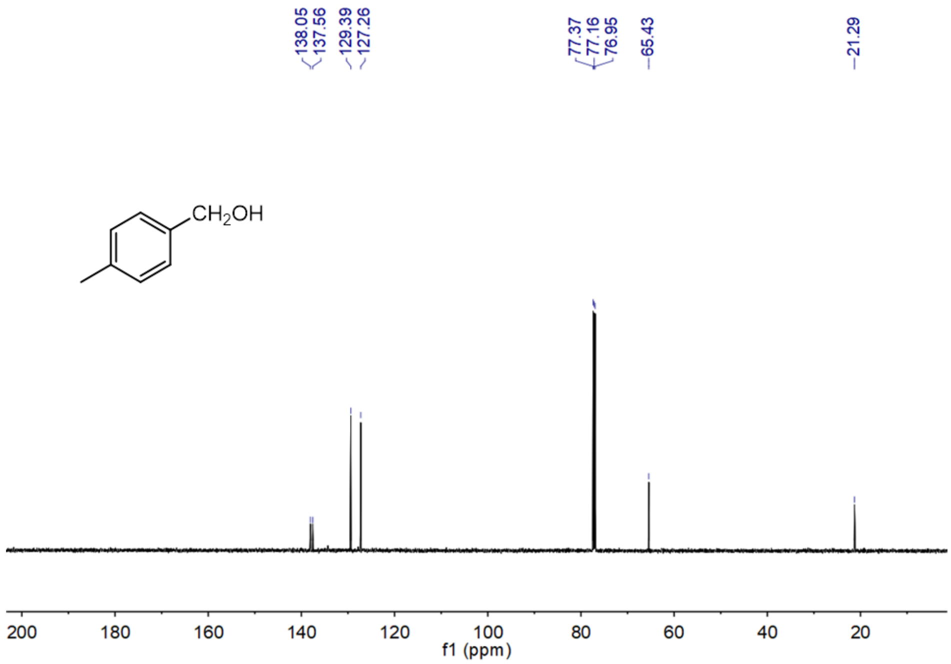

Fig. S27 ^{13}C{^{1}H} NMR spectrum of the isolated 4-tolyl-methanol (151 MHz, $CDCl_3$)

4-Nitrophenyl-methanol

Yellow crystalline solid, 0.145 g, 95% yield, purity: >99% based on ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.21 (d, $J_{H\text{-}H}$ = 8.7 Hz, Ar*H*, 2H), 7.53 (d, $J_{H\text{-}H}$ = 8.7 Hz, Ar*H*, 2H), 4.83 (s, C*H*$_2$, 2H), 2.10 (s, br., O*H*, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 148.31, 147.42, 127.13, 123.86, 64.12. HRMS (ESI): *m/z* calculated for $C_7H_8NO_3$ [M + H]$^+$ 154.0499, found 154.0498. These spectral data correspond to previously reported data.[S6]

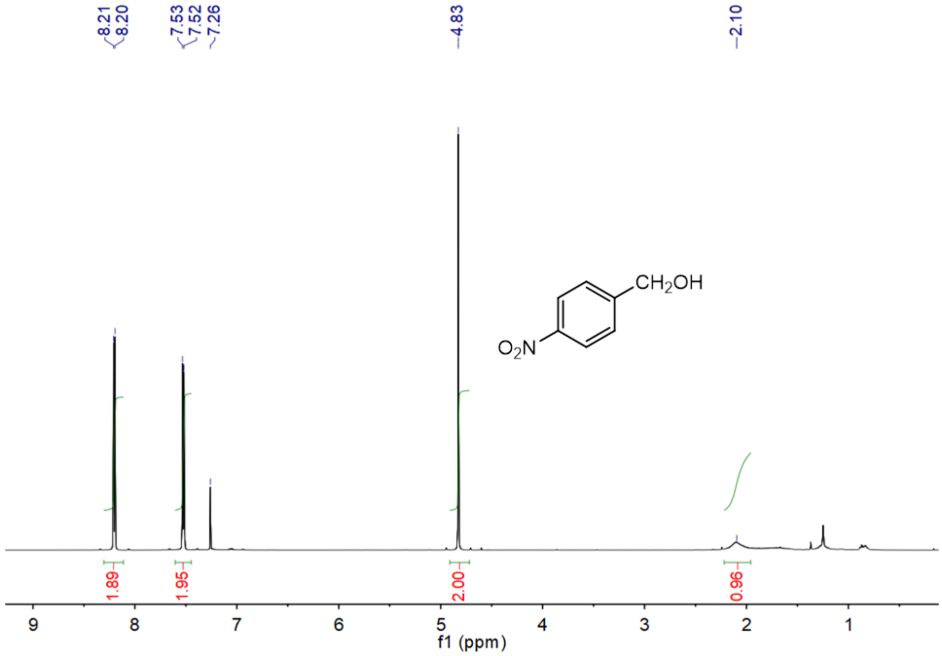

Fig. S28 ^{1}H NMR spectrum of the isolated 4-nitrophenyl-methanol (600 MHz, $CDCl_3$)

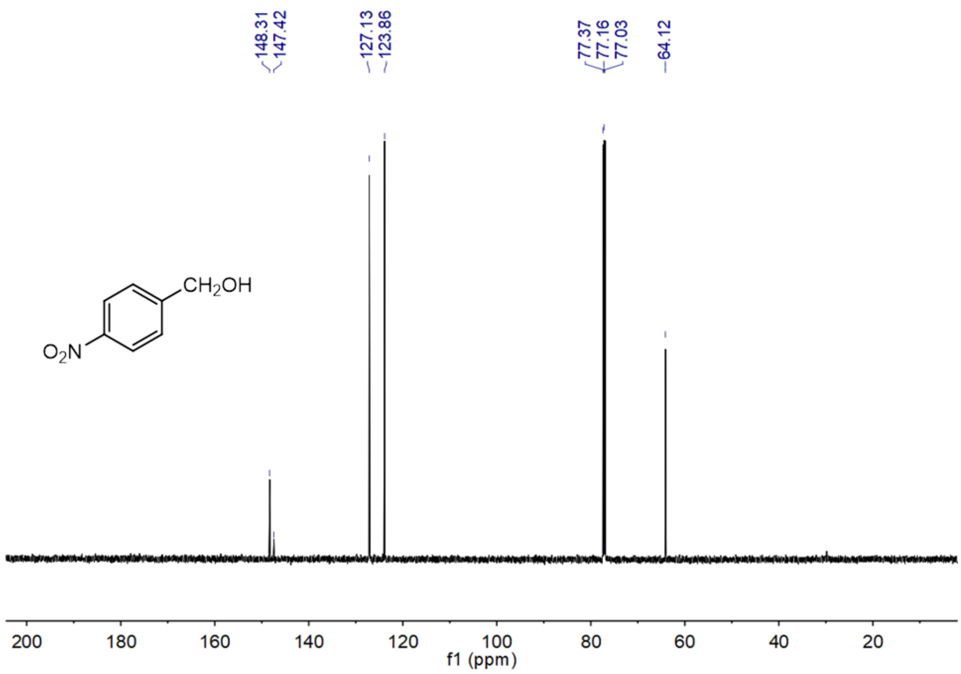

Fig. S29 ^{13}C{^{1}H} NMR spectrum of the isolated 4-nitrophenyl-methanol (151 MHz, $CDCl_3$)

4-Cyanobenzenemethanol

Colorless liquid, 0.109 g, 82% yield, purity: >98% based on ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.47–7.49 (m, Ar*H*, 2H), 7.34–7.35 (m, Ar*H*, 2H), 4.61 (s, C*H*$_2$, 2H), 3.98 (br., O*H*, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 146.61, 132.26, 127.03, 118.94, 110.74, 63.92. HRMS (ESI): *m/z* calculated for C_8H_8NO [M + H]$^+$ 134.0600, found 134.0601. These spectral data correspond to previously reported data.[S8]

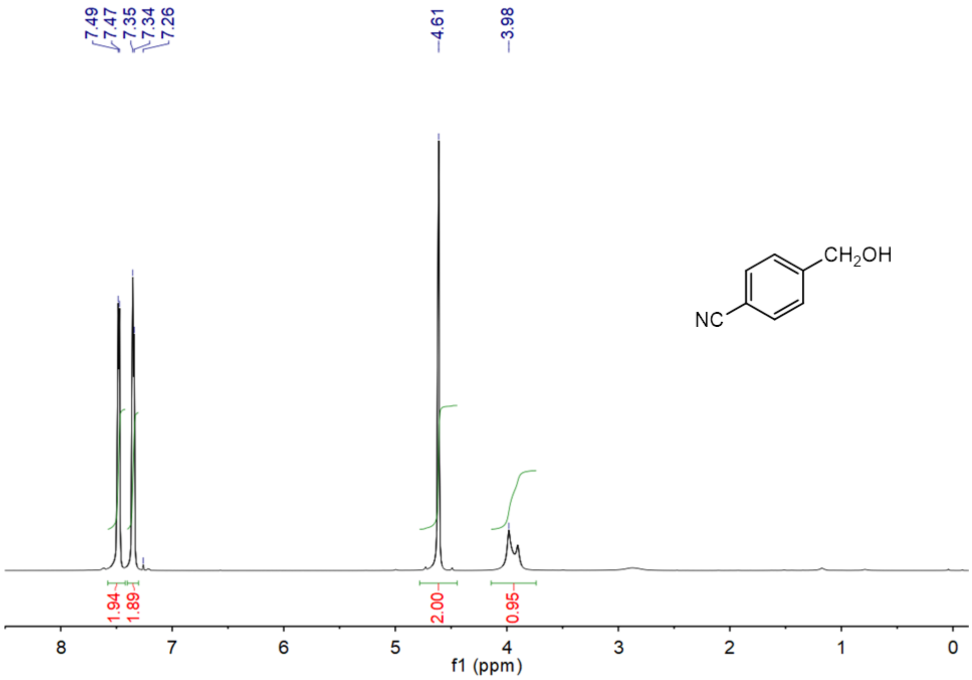

Fig. S30 ^{1}H NMR spectrum of the isolated 4-cyanobenzenemethanol (600 MHz, $CDCl_3$)

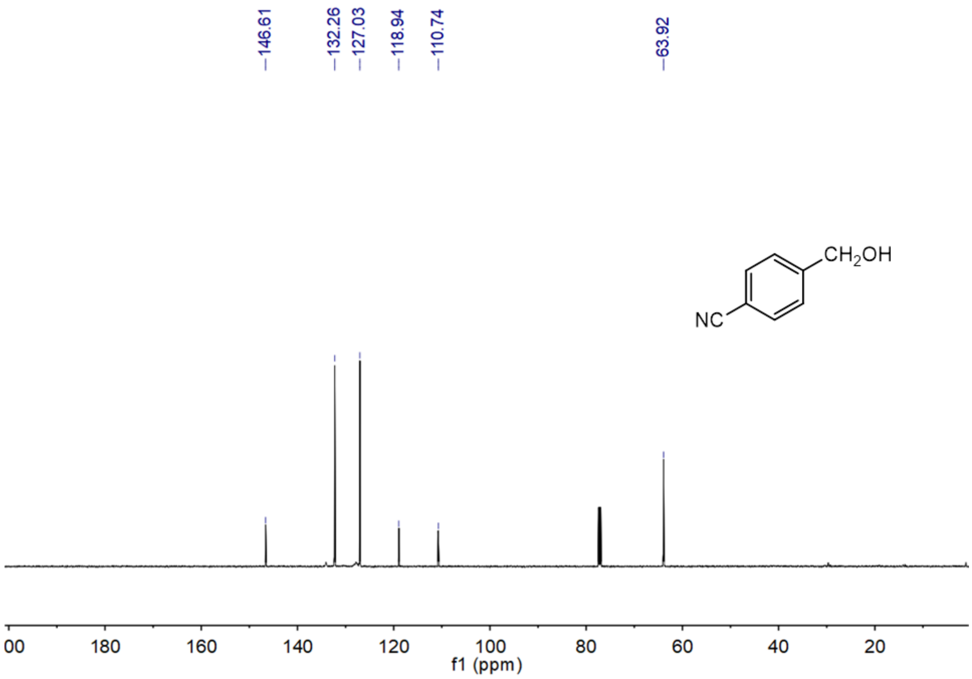

Fig. S31 ^{13}C{^{1}H} NMR spectrum of the isolated 4-cyanobenzenemethanol (151 MHz, $CDCl_3$)

4-Fluorophenyl-methanol

Clear colorless liquid, 0.115 g, 91% yield, purity: >97% based on ^1H NMR spectrum. ^1H NMR (600 MHz, $CDCl_3$, δ): 7.30–7.33 (m, Ar*H*, 2H), 7.02–7.05 (m, Ar*H*, 2H), 4.63 (s, CH_2, 2H), 1.97 (s, br., O*H*, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$, δ): 162.44 (d, $^1J_{C\text{-}F}$ = 246 Hz, Ar*C*), 136.67 (s, Ar*C*), 128.88 (d, $^3J_{C\text{-}F}$ = 8 Hz, Ar*C*), 115.50 (d, $^2J_{C\text{-}F}$ = 21 Hz, Ar*C*), 64.72 (*C*H_2). HRMS (ESI): *m/z* calculated for C_7H_8FO [M + H]$^+$ 127.0554, found 127.0551. These spectral data correspond to previously reported data.[S7]

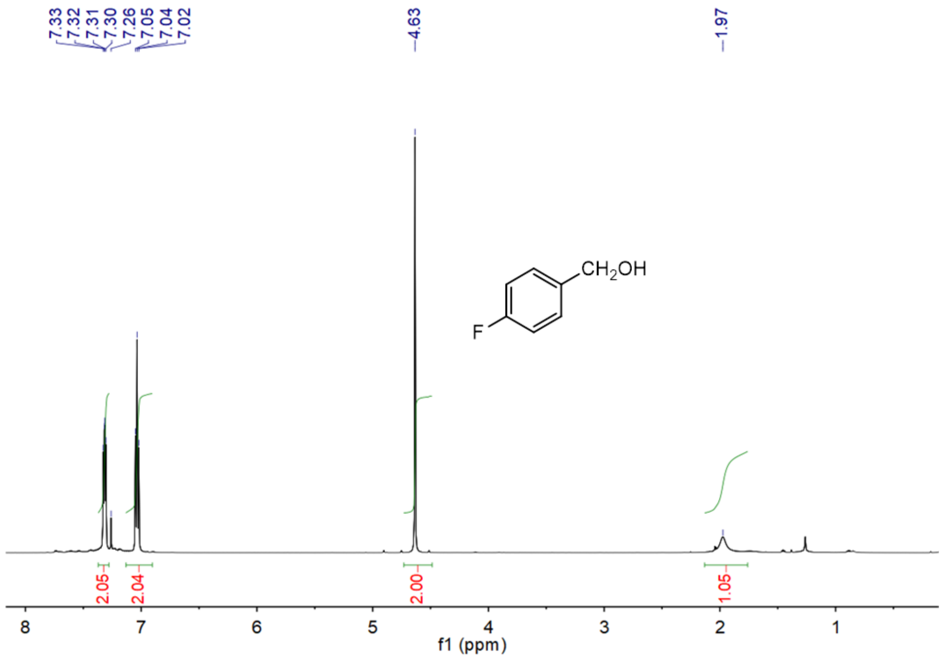

Fig. S32 ^1H NMR spectrum of the isolated 4-fluorophenyl-methanol (600 MHz, $CDCl_3$)

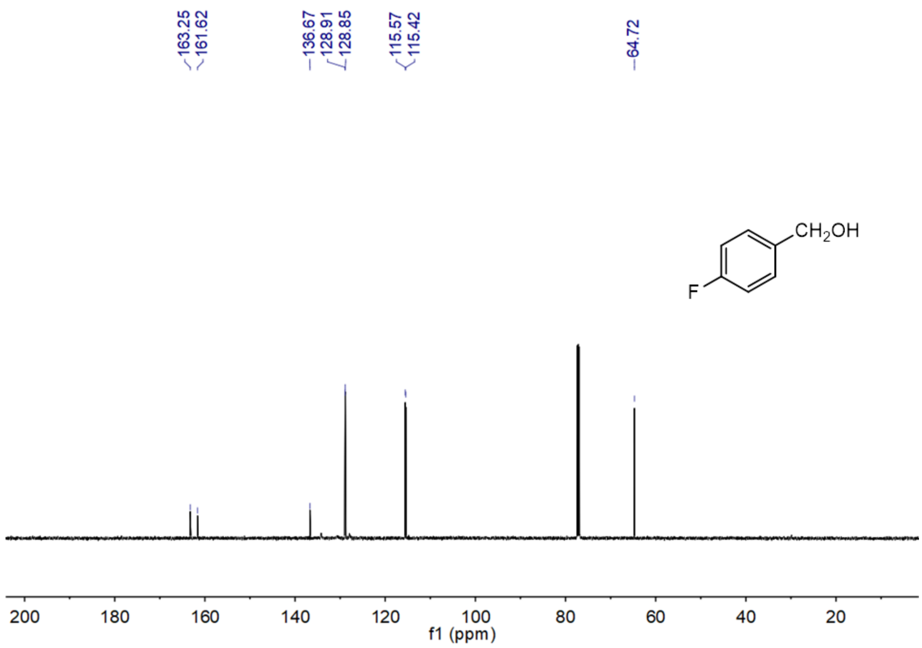

Fig. S33 $^{13}C\{^1H\}$ NMR spectrum of the isolated 4-fluorophenyl-methanol (151 MHz, $CDCl_3$)

4-Chlorophenyl-methanol

Colorless crystalline solid, 0.111 g, 78% yield, purity: >97% based on ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.20 (d, $J_{H\text{-}H}$ = 8.3 Hz, Ar*H*, 2H), 7.15 (d, $J_{H\text{-}H}$ = 8.3 Hz, Ar*H*, 2H), 4.51 (s, C*H*$_2$, 2H), 1.95 (s, br., O*H*, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 139.35, 133.44, 128.77, 128.39, 64.60. HRMS (ESI): *m/z* calculated for C_7H_8ClO $[M + H]^+$ 143.0258, found 143.0261. These spectral data correspond to previously reported data.[S6,S10]

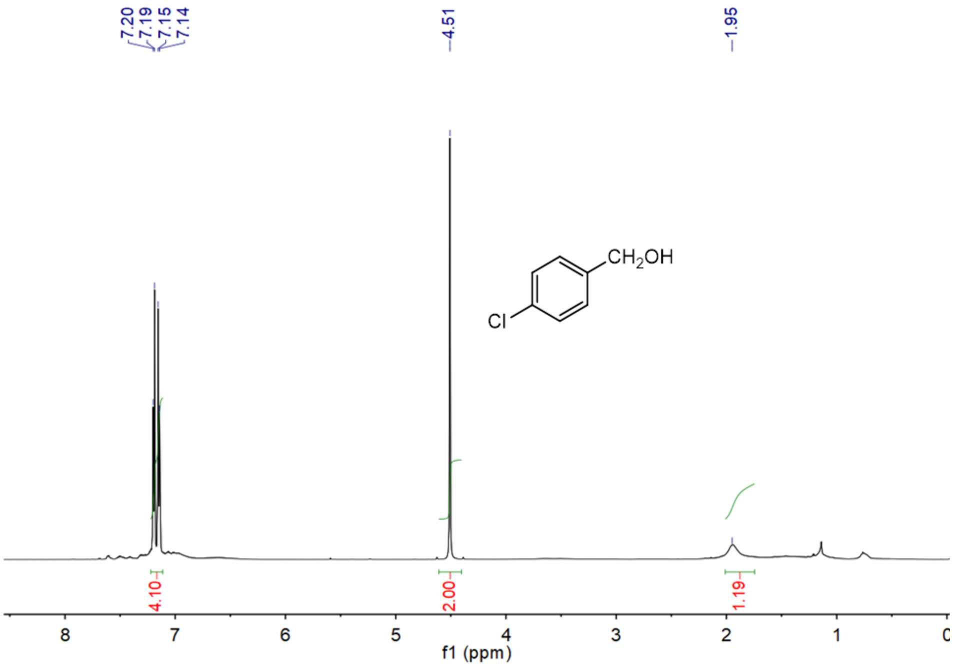

Fig. S34 ^{1}H NMR spectrum of the isolated 4-chlorophenyl-methanol (600 MHz, $CDCl_3$)

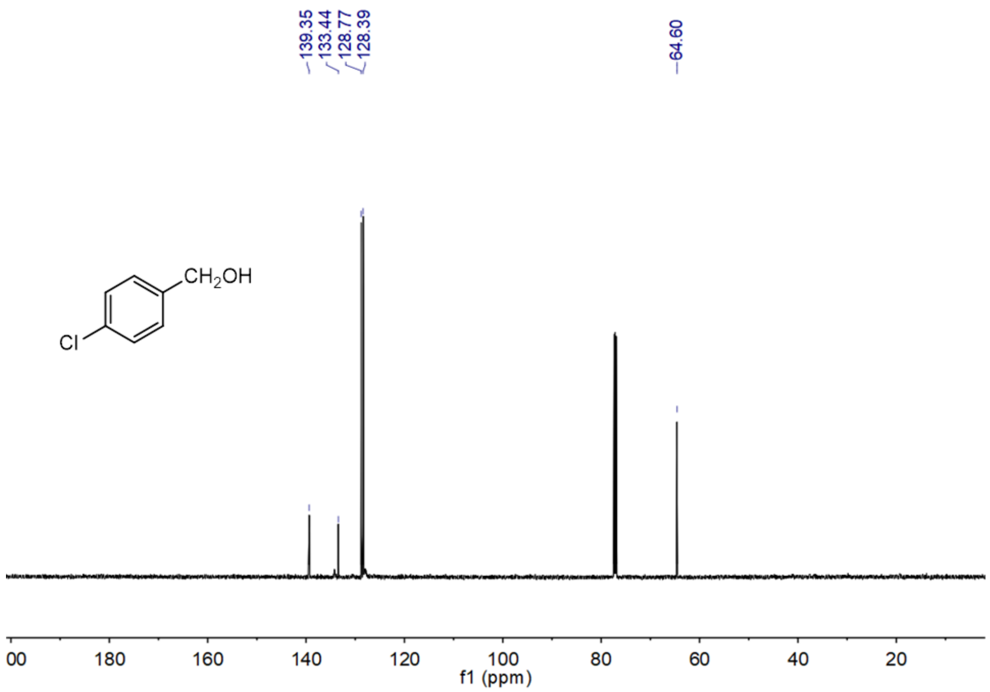

Fig. S35 ^{13}C{^{1}H} NMR spectrum of the isolated 4-chlorophenyl-methanol (151 MHz, $CDCl_3$)

4-Bromophenyl-methanol

Colorless crystalline solid, 0.155 g, 84% yield, purity: >97% based on ^{1}H NMR spectra. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.47 (d, $J_{H\text{-}H}$ = 8.3 Hz, Ar*H*, 2H), 7.22 (d, $J_{H\text{-}H}$ = 8.3 Hz, Ar*H*, 2H), 4.62 (s, C*H*$_2$, 2H), 2.02 (s, br., O*H*, 1H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, δ): 139.86, 131.73, 128.70, 121.55, 64.63. HRMS (ESI): *m/z* calculated for C_7H_7BrONa $[M + Na]^+$ 208.9572, found 208.9570. These spectral data correspond to previously reported data.[S9]

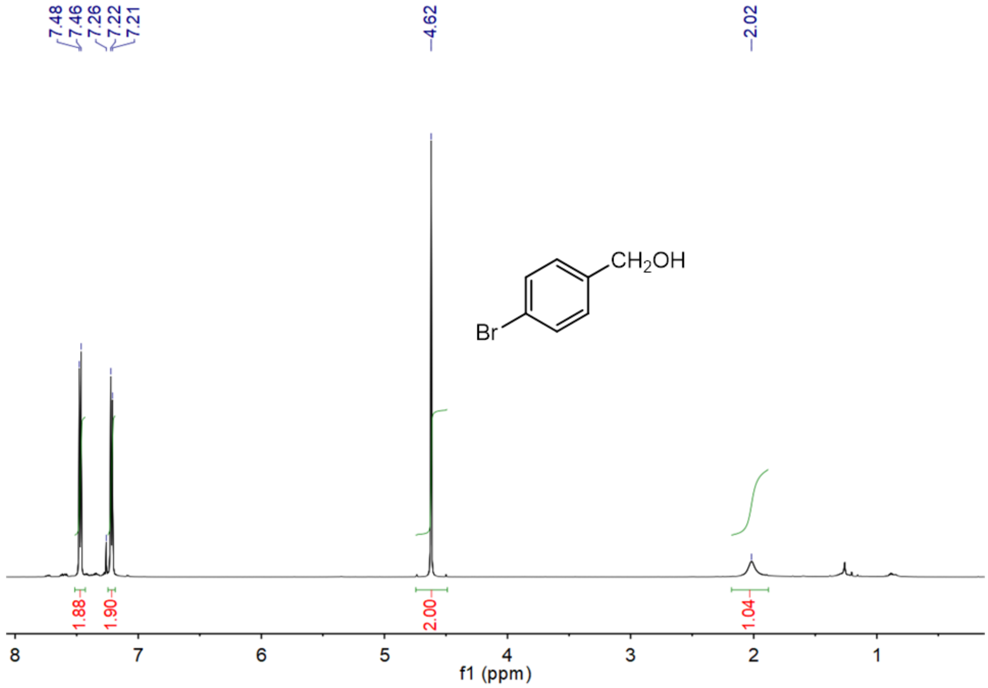

Fig. S36 ^{1}H NMR spectrum of the isolated 4-bromophenyl-methanol (600 MHz, $CDCl_3$)

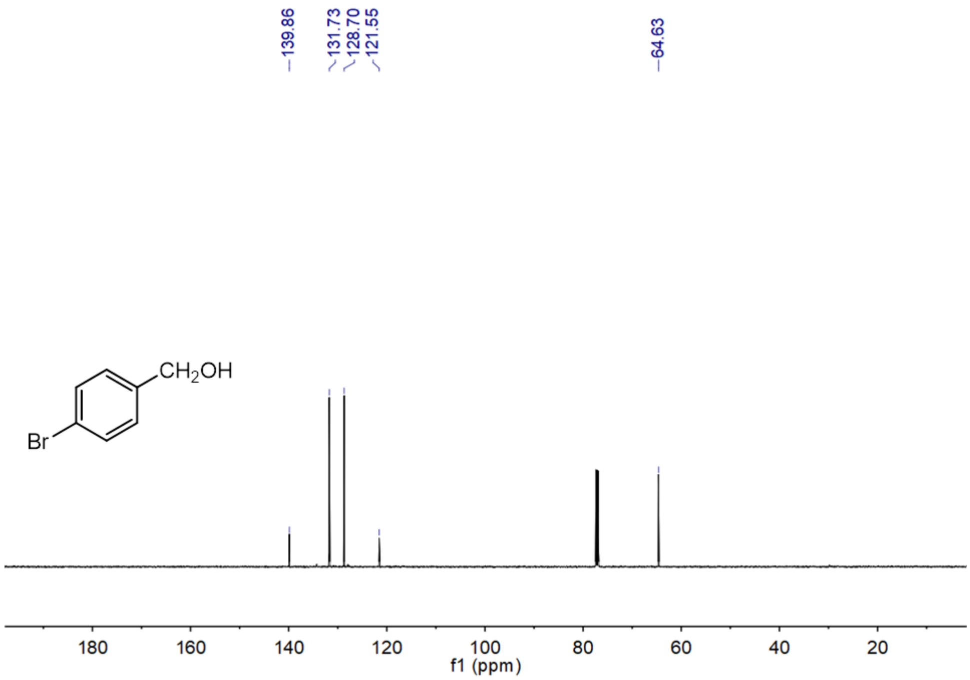

Fig. S37 $^{13}C\{^{1}H\}$ NMR spectrum of the isolated 4-bromophenyl-methanol (151 MHz, $CDCl_3$)

2-Naphthalenemethanol

Colorless crystalline solid, 0.119 g, 75% yield, purity: >99% based on ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.81–7.85 (m, Ar*H*, 4H), 7.47–7.51 (m, Ar*H*, 3H), 4.86 (s, CH_2, 2H), 1.84 (s, O*H*, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 138.44, 133.51, 133.08, 128.48, 128.02, 127.85, 126.33, 126.04, 125.58, 125.30, 65.63. HRMS (ESI): *m/z* calculated for $C_{11}H_{11}O$ $[M + H]^+$ 159.0804, found 159.0805. These spectral data correspond to previously reported data.[S6,S7,S12]

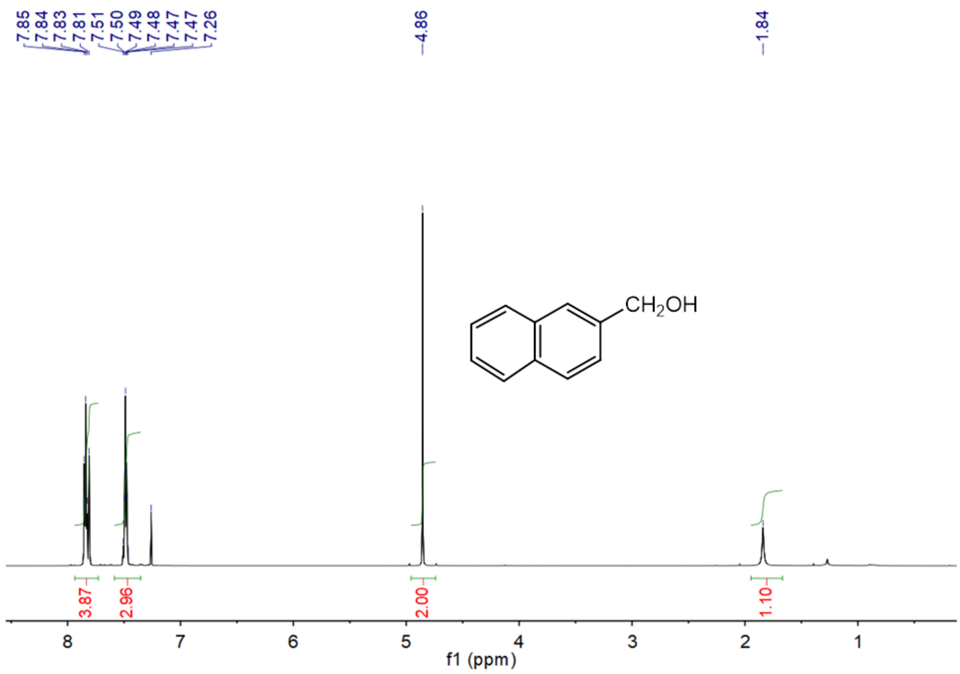

Fig. S38 ^{1}H NMR spectrum of the isolated 2-naphthalenemethanol (600 MHz, $CDCl_3$)

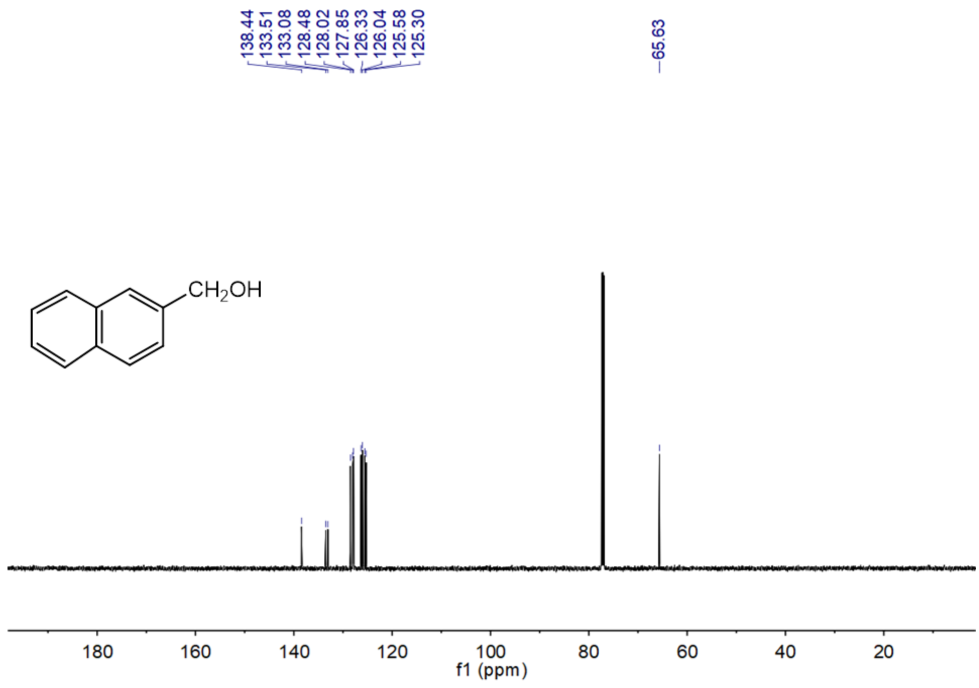

Fig. S39 ^{13}C{^{1}H} NMR spectrum of the isolated 2-naphthalenemethanol (151 MHz, $CDCl_3$)

4-Phenylbenzyl alcohol

White solid, 0.164 g, 89% yield, purity: >97% based on ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.59–7.61 (m, Ar*H*, 4H), 7.44–7.46 (m, Ar*H*, 4H), 7.34–7.37 (m, Ar*H*, 1H), 4.75 (s, C*H*$_2$, 2H), 1.73 (s, br., O*H*, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 140.97, 140.81, 140.01, 128.93, 127.61, 127.48, 127.47, 127.24, 65.28. HRMS (ESI): *m/z* calculated for $C_{13}H_{13}O$ $[M + H]^+$ 185.0961, found 185.0960. These spectral data correspond to previously reported data.[S13]

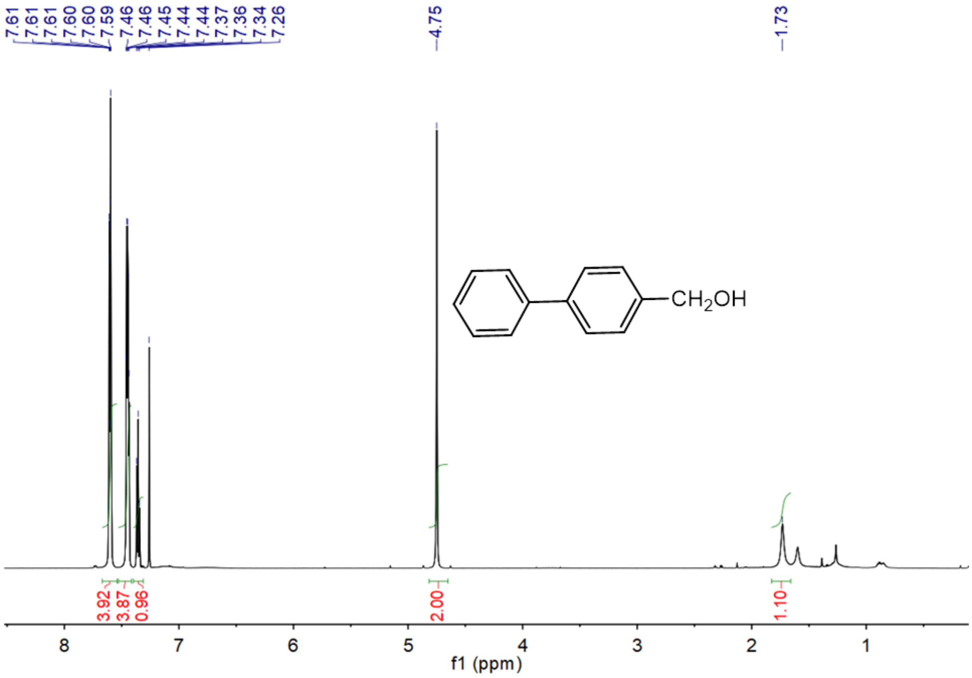

Fig. S40 ^{1}H NMR spectrum of the isolated 4-phenylbenzyl alcohol (600 MHz, $CDCl_3$)

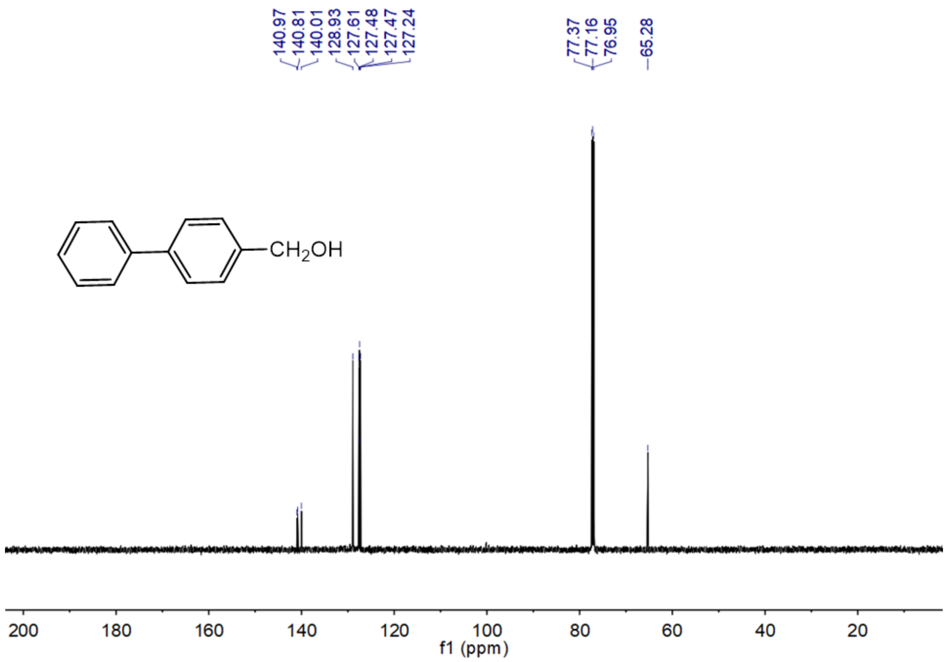

Fig. S41 ^{13}C{^{1}H} NMR spectrum of the isolated 4-phenylbenzyl alcohol (151 MHz, $CDCl_3$)

2-Pyridinylmethanol

Clear colorless liquid, 0.087 g, 80% yield, purity: >97% based on ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 8.55 (d, $J_{H\text{-}H}$ = 4.7 Hz, Ar*H*, 1H), 7.68 (t, $J_{H\text{-}H}$ = 7.7 Hz, Ar*H*, 1H), 7.26 (d, $J_{H\text{-}H}$ = 7.2 Hz, Ar*H*, 1H), 7.20 (t, $J_{H\text{-}H}$ = 7.7 Hz, Ar*H*, 1H), 4.76 (s, CH_2, 2H), 3.49 (s, br, O*H*, 1H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, δ): 159.19, 148.63, 136.84, 122.48, 120.68, 64.27. HRMS (ESI): *m/z* calculated for C_6H_8NO $[M + H]^+$ 110.0600, found 110.0601. These spectral data correspond to previously reported data.[S14,S15]

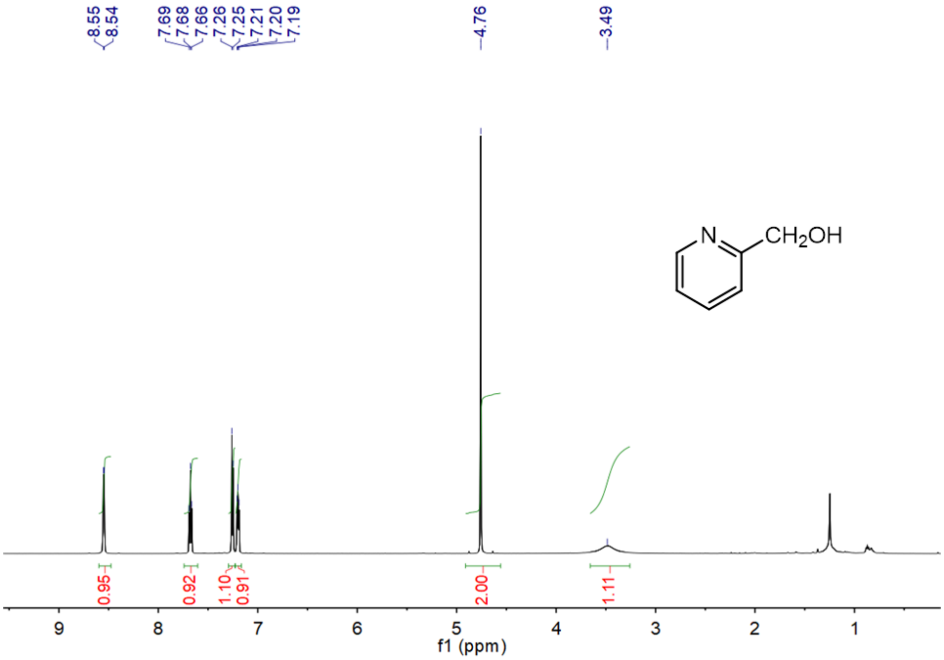

Fig. S42 ^{1}H NMR spectrum of the isolated 2-pyridinylmethanol (600 MHz, $CDCl_3$)

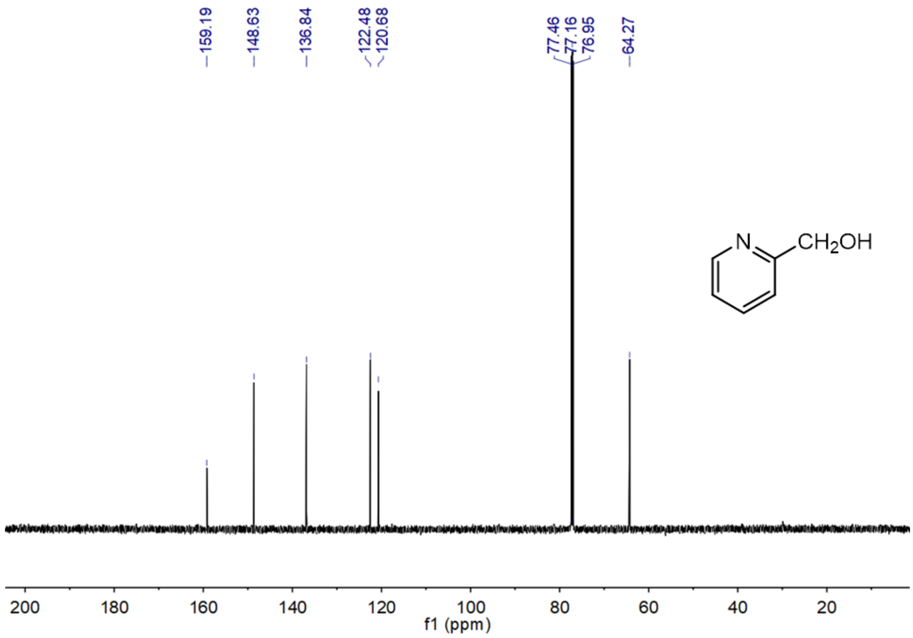

Fig. S43 $^{13}C\{^{1}H\}$ NMR spectrum of the isolated 2-pyridinylmethanol (151 MHz, $CDCl_3$)

2-Furanmethanol

Clear colorless liquid, 0.091 g, 93% yield, purity: >98% based on ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.40 (s, Ar*H*, 1H), 6.33–6.34 (m, Ar*H*, 1H), 6.28–6.29 (m, Ar*H*, 1H), 4.60 (s, C*H*$_2$, 2H), 2.01 (s, br., O*H*, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 154.11, 142.70, 110.48, 107.89, 57.57. HRMS (ESI): *m/z* calculated for $C_5H_7O_2$ $[M + H]^+$ 99.0441, found 99.0440. These spectral data correspond to previously reported data.[S6–S9]

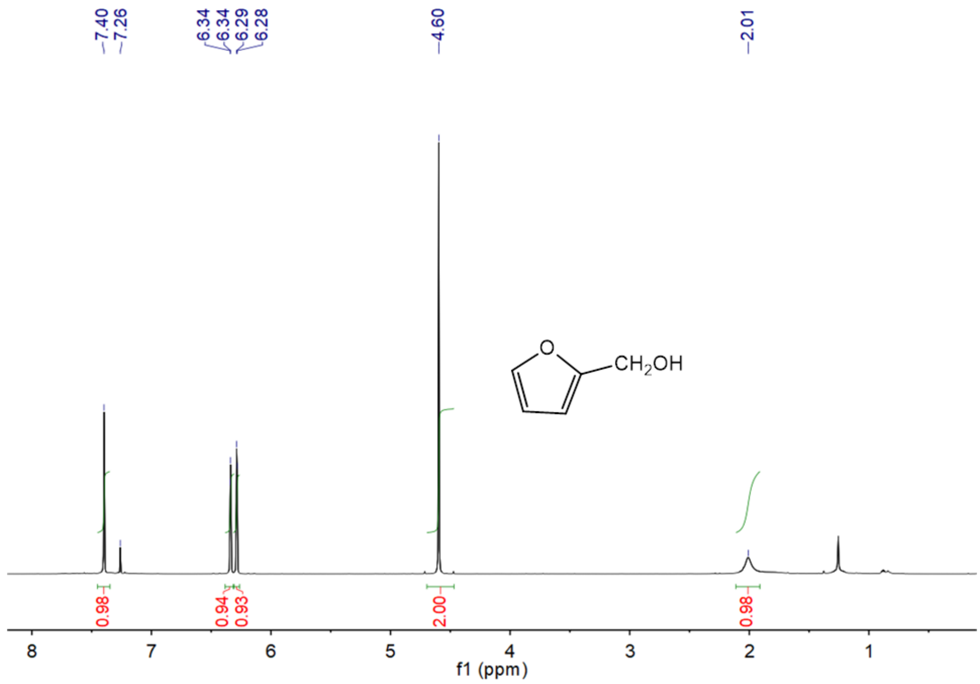

Fig. S44 ^{1}H NMR spectrum of the isolated 2-furanmethanol (600 MHz, $CDCl_3$)

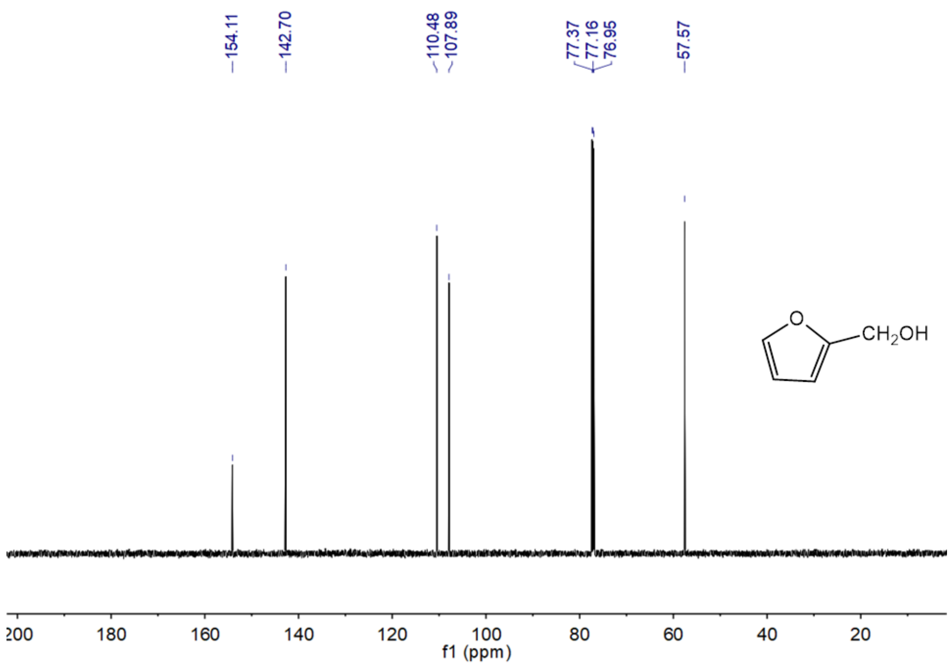

Fig. S45 ^{13}C{^{1}H} NMR spectrum of the isolated 2-furanmethanol (151 MHz, $CDCl_3$)

3-Cyclohexene-1-methanol

Clear colorless liquid, 0.097 g, 87% yield, purity: >99% based on ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 5.65–5.59 (m, 2H), 3.50–3.56 (m, 2H), 2.05–2.12 (m, 3H), 1.73–1.82 (m, 3H), 1.55 (s, br., O*H*, 1H), 1.24–1.31 (m, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 127.28, 126.01, 67.98, 36.44, 28.20, 25.33, 24.75. HRMS (ESI): *m/z* calculated for $C_7H_{13}O$ $[M + H]^+$ 113.0961, found 113.0962. These spectral data correspond to previously reported data.[S14]

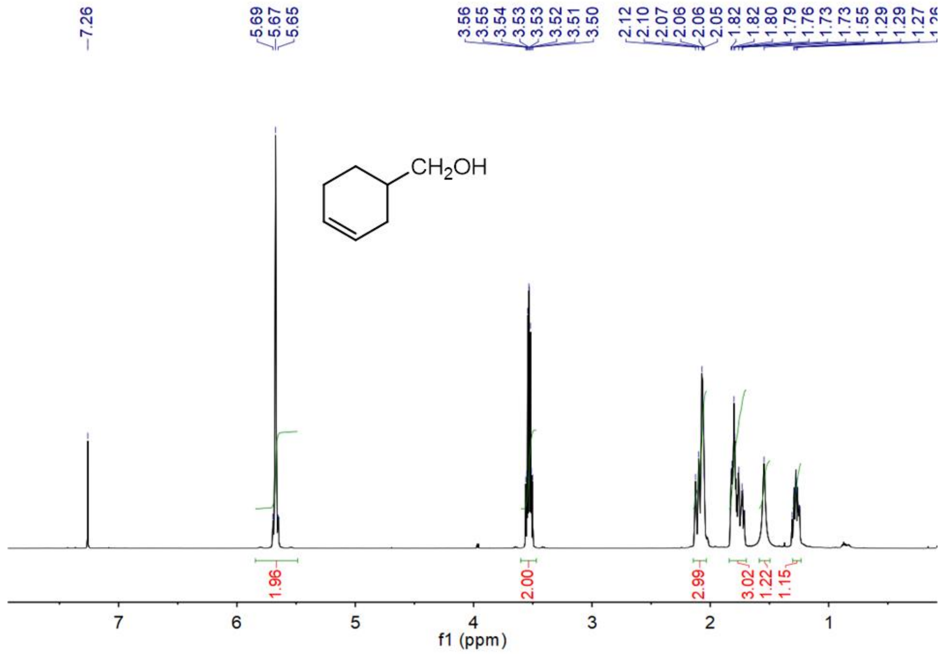

Fig. S46 ^{1}H NMR spectrum of the isolated 3-cyclohexene-1-methanol (600 MHz, $CDCl_3$)

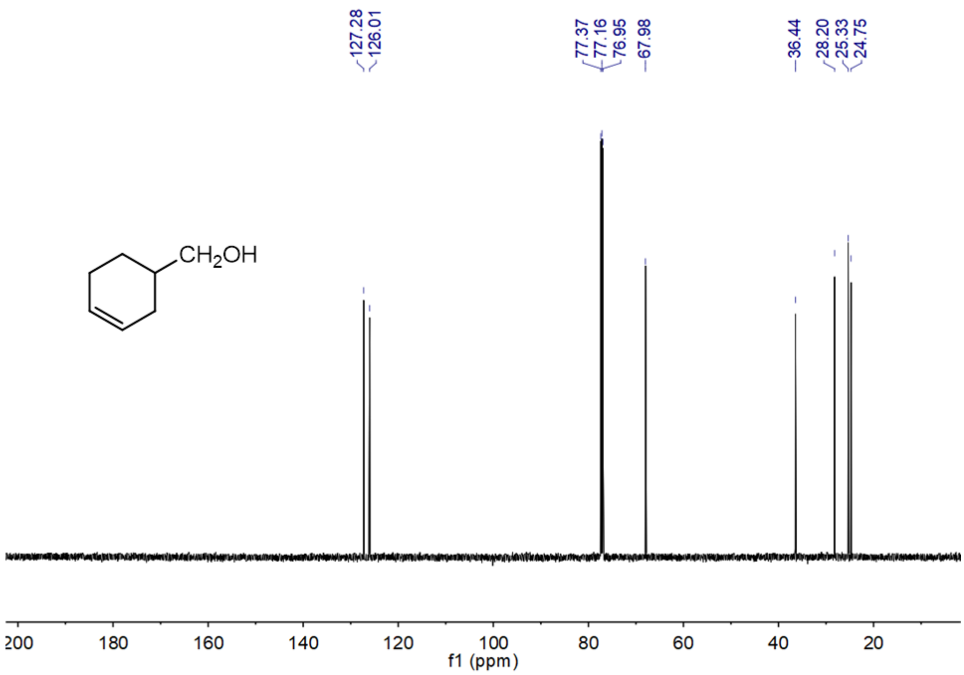

Fig. S47 ^{13}C{^{1}H} NMR spectrum of the isolated 3-cyclohexene-1-methanol (151 MHz, $CDCl_3$)

3-Phenylallyl alcohol

Colorless liquid, 0.110 g, 82% yield, purity: >95% based on ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.30 (d, $J_{H\text{-}H}$= 7.4 Hz, Ar*H*, 2H), 7.23 (t, $J_{H\text{-}H}$= 7.5 Hz, Ar*H*, 2H), 7.16 (t, $J_{H\text{-}H}$= 7.1 Hz, Ar*H*, 1H), 6.52 (d, $J_{H\text{-}H}$= 15.9 Hz, C*H*, 1H), 6.25–6.29 (m, C*H*, 1H), 4.23 (d, $J_{H\text{-}H}$= 5.3 Hz, CH_2, 2H), 1.88 (s, br., O*H*, 1H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, δ): 136.78, 131.21, 128.69, 128.59, 127.78, 126.57, 63.76. HRMS (ESI): *m/z* calculated for $C_9H_{11}O$ $[M + H]^+$ 135.0804, found 135.0803. These spectral data correspond to previously reported data.[S8,S16,S17]

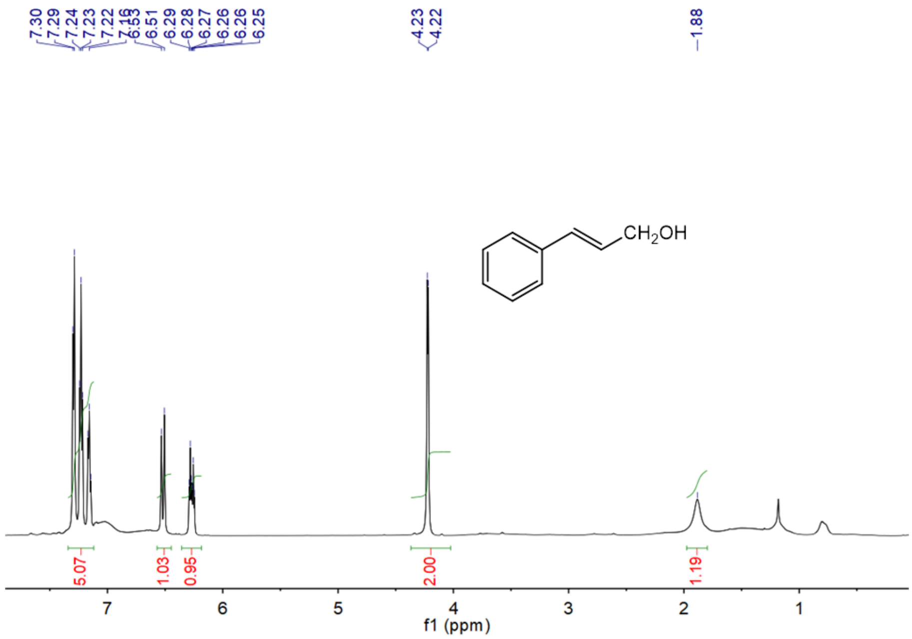

Fig. S48 ^{1}H NMR spectrum of the isolated 3-phenylallyl alcohol (600 MHz, $CDCl_3$)

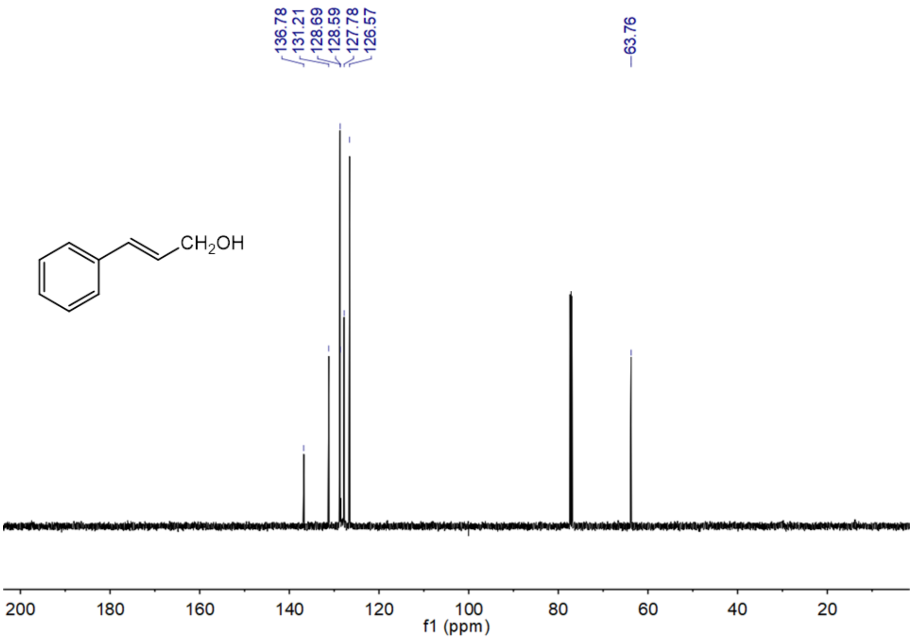

Fig. S49 $^{13}C\{^{1}H\}$ NMR spectrum of the isolated 3-phenylallyl alcohol (151 MHz, $CDCl_3$)

3-Phenyl-2-propynyl alcohol

Light yellow liquid, 0.121 g, 92% yield, purity: >96% based on ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.44–7.45 (m, Ar*H*, 2H), 7.30–7.32 (m, Ar*H*, 3H), 4.50 (s, CH_2, 2H), 1.98 (s, br., O*H*, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 131.81, 128.62, 128.44, 122.66, 87.34, 85.81, 51.75. HRMS (ESI): *m/z* calculated for C_9H_9O $[M + H]^+$ 133.0648, found 133.0645. These spectral data correspond to previously reported data.[S16]

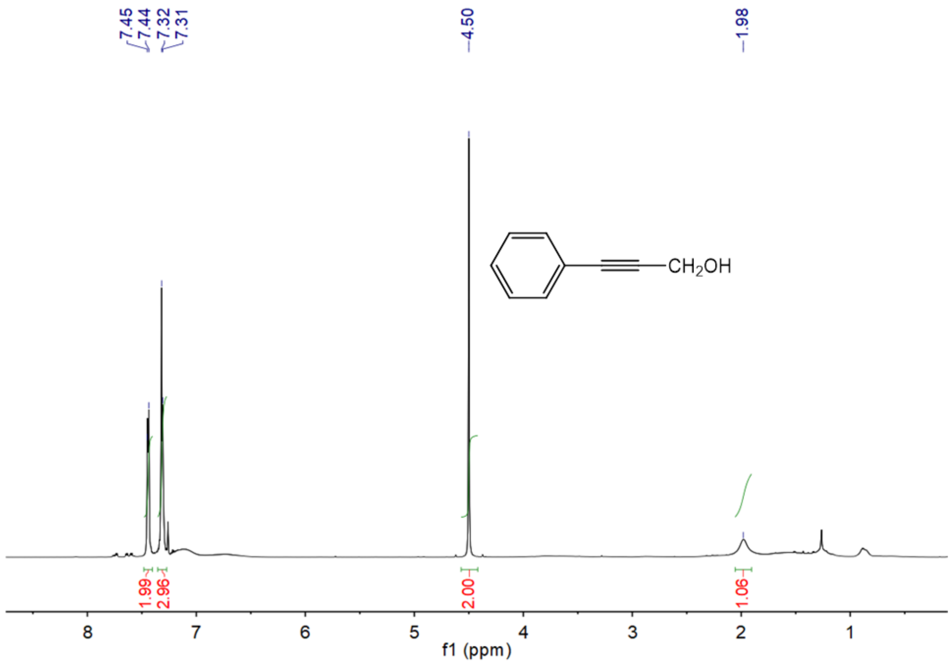

Fig. S50 ^{1}H NMR spectrum of the isolated 3-phenyl-2-propynyl alcohol (600 MHz, $CDCl_3$)

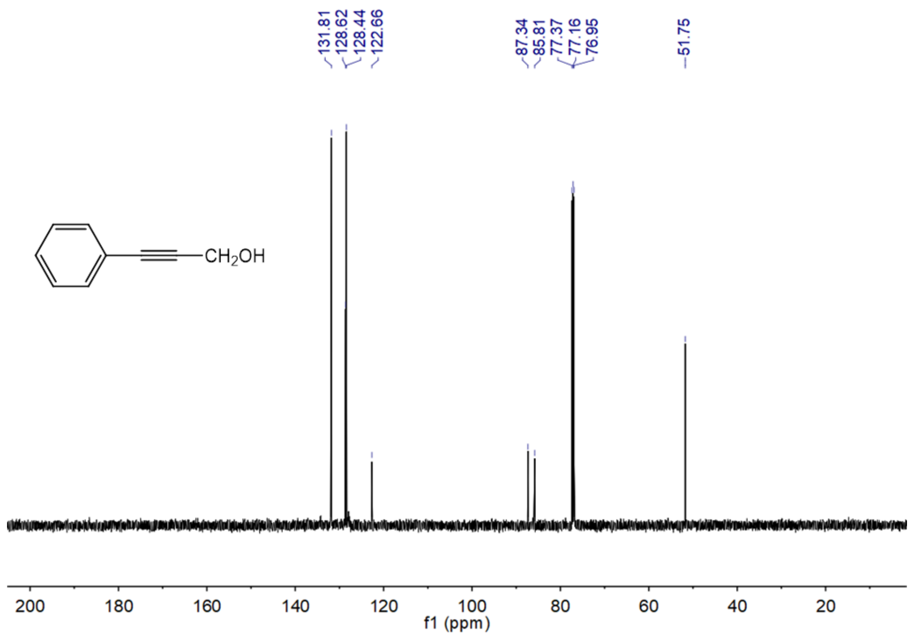

Fig. S51 ^{13}C{^{1}H} NMR spectrum of the isolated 3-phenyl-2-propynyl alcohol (151 MHz, $CDCl_3$)

3,7-Dimethyl-trans-2,6-octadien-1-ol

Light yellow liquid, 0.112 g, 73% yield, purity: >98% based on ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 5.40–5.43 (m, 1H), 5.08–5.11 (m, 1H), 4.16 (d, $J_{H\text{-}H}$= 6.9 Hz, CH_2, 2H), 2.08–2.12 (m, 2H), 2.02–2.04 (m, 2H), 1.68 (s, CH_3, 6H), 1.60 (s, CH_3, 3H), 1.25 (s, br., O*H*, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 139.97, 131.90, 124.03, 123.45, 59.57, 39.68, 26.53, 25.82, 17.83, 16.41. HRMS (ESI): *m/z* calculated for $C_{10}H_{19}O$ $[M + H]^+$ 155.1430, found 155.1432. These spectral data correspond to previously reported data.[S17,S18]

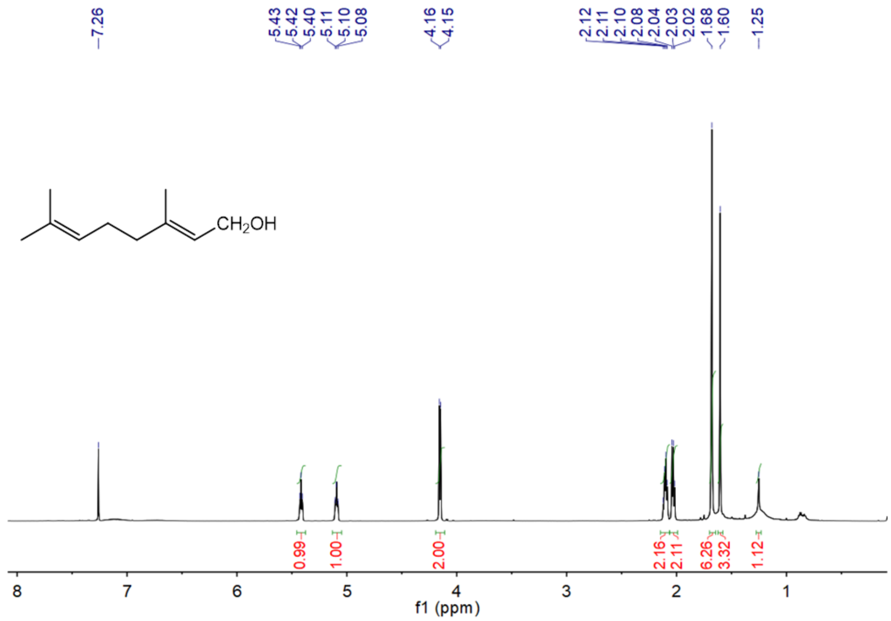

Fig. S52 ^{1}H NMR spectrum of the isolated 3,7-dimethyl-trans-2,6-octadien-1-ol (600 MHz, $CDCl_3$)

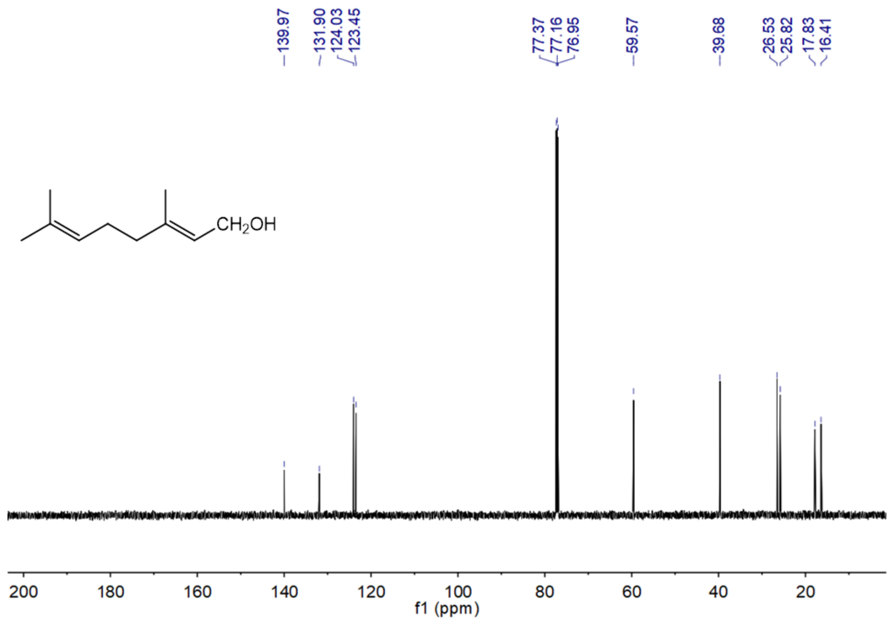

Fig. S53 ^{13}C{^{1}H} NMR spectrum of the isolated 3,7-dimethyl-trans-2,6-octadien-1-ol (151 MHz, $CDCl_3$)

1-Phenylethanol

Clear colorless liquid, 0.110 g, 90% yield, purity: >98% based on ^{1}H NMR spectra. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.34–7.39 (m, Ar*H*, 4H), 7.26–7.29 (m, Ar*H*, 1H), 4.91 (quart, $J_{H\text{-}H}$=6.5 Hz, C*H*(OH)CH_3, 1H), 1.90 (s, br., O*H*, 1H), 1.51 (d, $J_{H\text{-}H}$ = 6.5 Hz, CH_3, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 145.94, 128.62, 127.59, 125.51, 70.53, 25.27. HRMS (ESI): *m/z* calculated for $C_8H_{11}O$ $[M + H]^+$ 123.0804, found 123.0803. These spectral data correspond to previously reported data.[S7,S8]

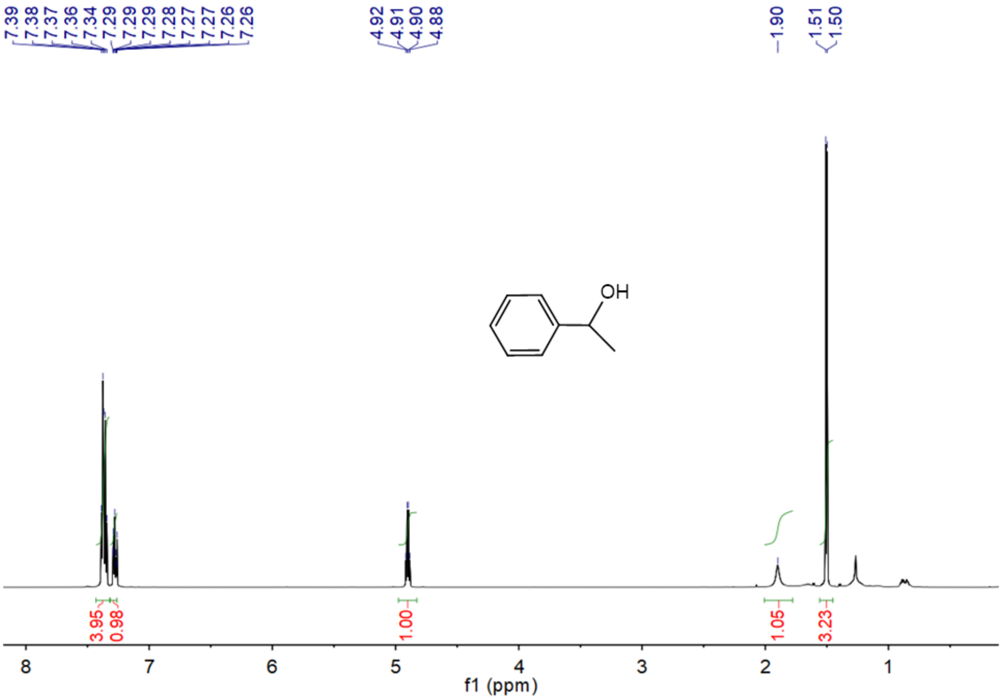

Fig. S54 ^{1}H NMR spectrum of the isolated 1-phenylethanol (600 MHz, $CDCl_3$)

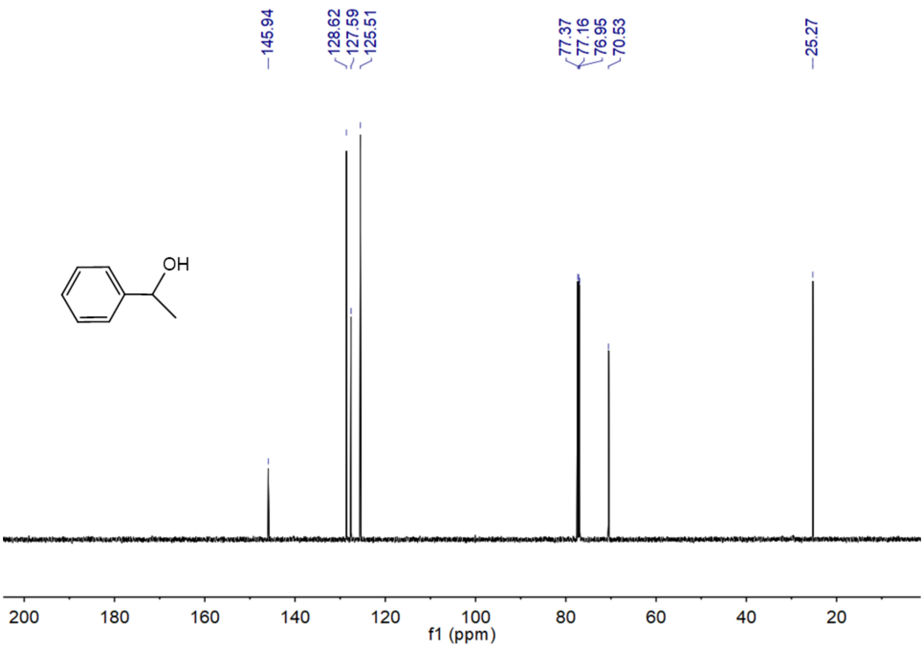

Fig. S55 ^{13}C{^{1}H} NMR spectrum of the isolated 1-phenylethanol (151 MHz, $CDCl_3$)

1-(p-Tolyl)ethanol

Clear colorless liquid, 0.117g, 86% yield, purity: >97% based on ^{1}H NMR spectra. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.27 (d, J_{H-H} = 8.0 Hz, Ar*H*, 2H), 7.17 (d, J_{H-H} = 7.9 Hz, Ar*H*, 2H), 4.88 (quart, J_{H-H} = 6.4 Hz, C*H*(OH)CH_3, 1H), 2.35 (s, ArCH_3, 3H), 1.73 (s, br, O*H*, 1H), 1.49 (d, J_{H-H} = 6.5 Hz, CH(OH)CH_3, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 142.99, 137.27, 129.29, 125.48, 70.38, 25.20, 21.21. HRMS (ESI): *m/z* calculated for $C_9H_{13}O$ $[M + H]^+$ 137.0961, found 137.0960. These spectral data correspond to previously reported data.[S19,S20]

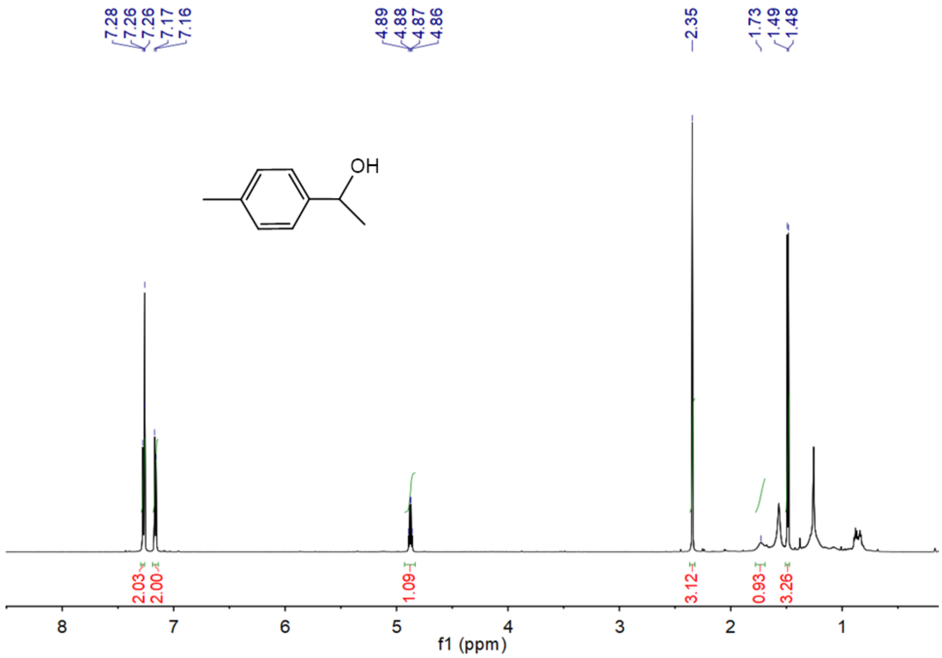

Fig. S56 ^{1}H NMR spectrum of the isolated 1-(p-tolyl)ethanol (600 MHz, $CDCl_3$)

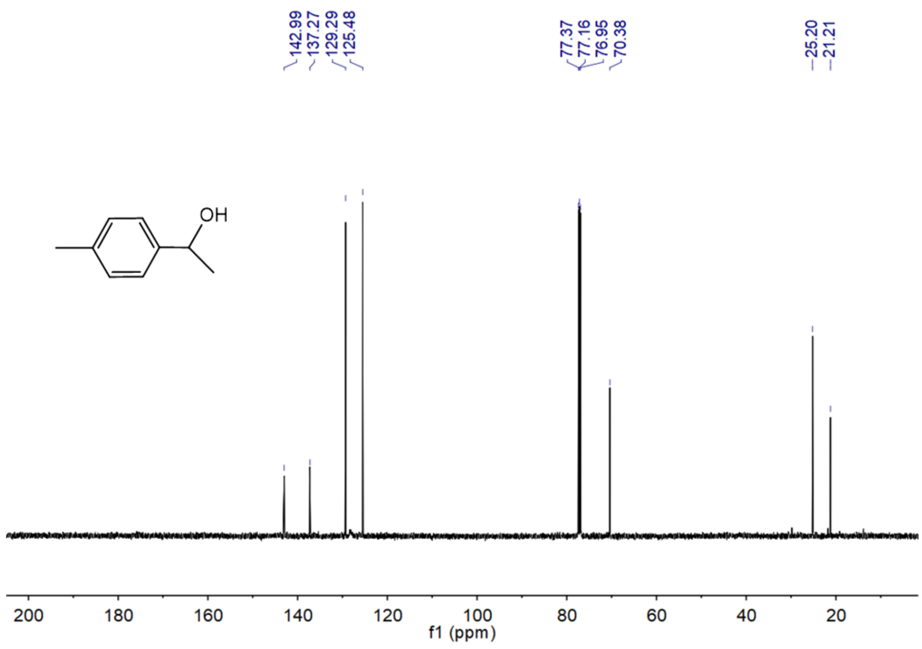

Fig. S57 ^{13}C{^{1}H} NMR spectrum of the isolated 1-(p-tolyl)ethanol (151 MHz, $CDCl_3$)

4-Methoxy-α-methylbenzyl alcohol

Clear colorless liquid, 0.135 g, 89% yield, purity: >99% based on ^{1}H NMR spectra. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.30 (d, $J_{H\text{-}H}$ = 8.6 Hz, Ar*H*, 2H), 6.88 (d, $J_{H\text{-}H}$ = 8.6 Hz, Ar*H*, 2H), 4.85 (quart, $J_{H\text{-}H}$ = 6.4 Hz, C*H*(OH)CH_3, 1H), 3.80 (s, OCH_3, 3H), 1.88 (s, br, O*H*, 1H), 1.48 (d, $J_{H\text{-}H}$ = 6.4 Hz, CH(OH)CH_3, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 159.10, 138.14, 126.79, 113.97, 70.10, 55.42, 25.14. HRMS (ESI): *m/z* calculated for $C_9H_{13}O_2$ $[M + H]^+$ 153.0910, found 153.0913. These spectral data correspond to previously reported data.[S16,S19]

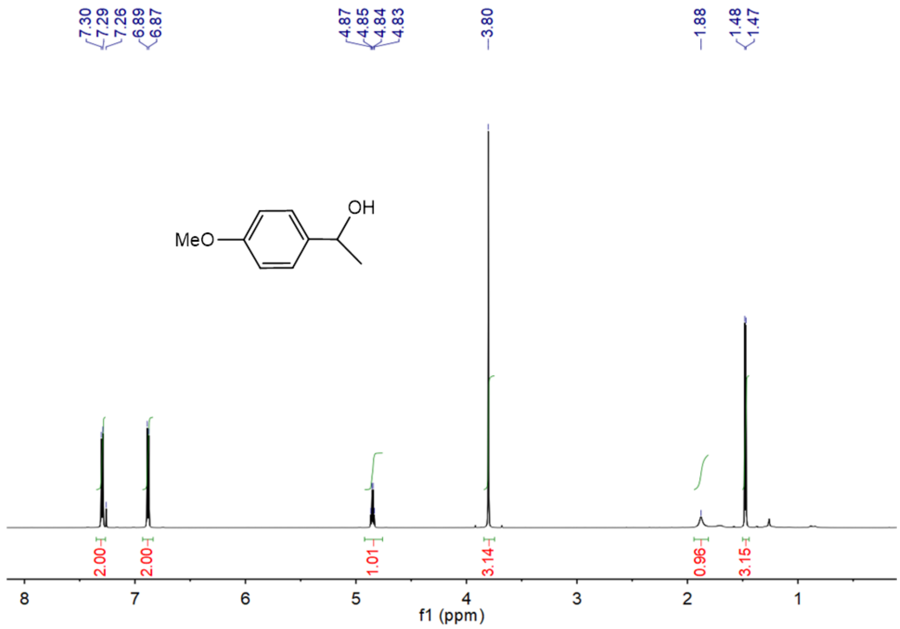

Fig. S58 ^{1}H NMR spectrum of the isolated 4-methoxy-α-methylbenzyl alcohol (600 MHz, $CDCl_3$)

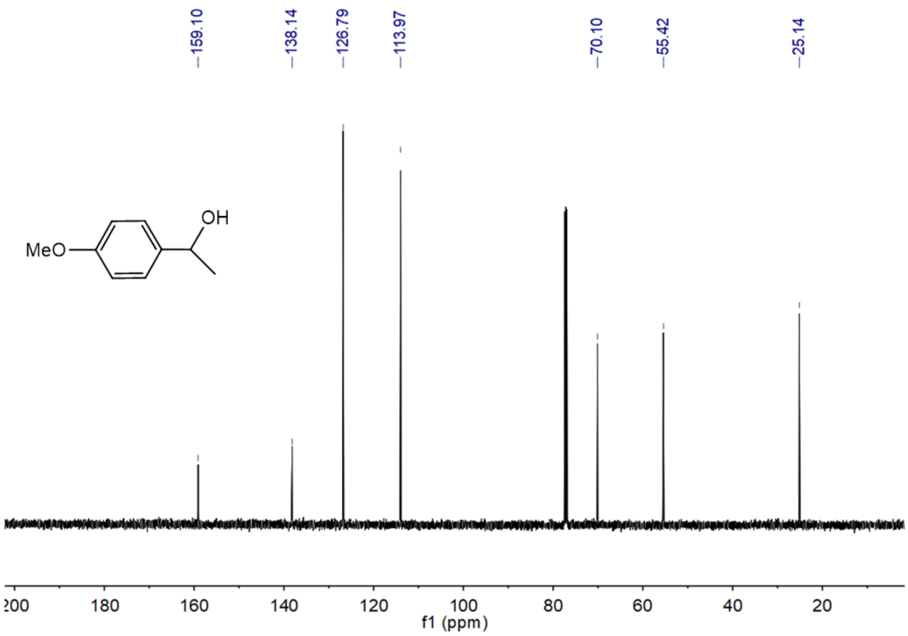

Fig. S59 ^{13}C{^{1}H} NMR spectrum of the isolated 4-methoxy-α-methylbenzyl alcohol (151 MHz, $CDCl_3$)

1-(4-Bromophenyl)ethanol

Clear colorless liquid, 0.141 g, 71% yield, purity: >99% based on ^{1}H NMR spectra. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.47 (d, J_{H-H} = 8.4 Hz, *Ar*, 2H), 7.25 (d, J_{H-H} = 8.4 Hz, *Ar*, 2H), 4.87 (quart, J_{H-H} = 6.5 Hz, C*H*(OH)CH_3, 1H), 1.87 (s, br, O*H*, 1H), 1.47 (d, J_{H-H} = 6.5 Hz, CH(OH)CH_3, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 144.90, 131.70, 127.29, 121.30, 69.93, 25.39. HRMS (ESI): *m/z* calculated for C_8H_9BrONa $[M + Na]^+$ 222.9729, found 222.9731. These spectral data correspond to previously reported data.[S19]

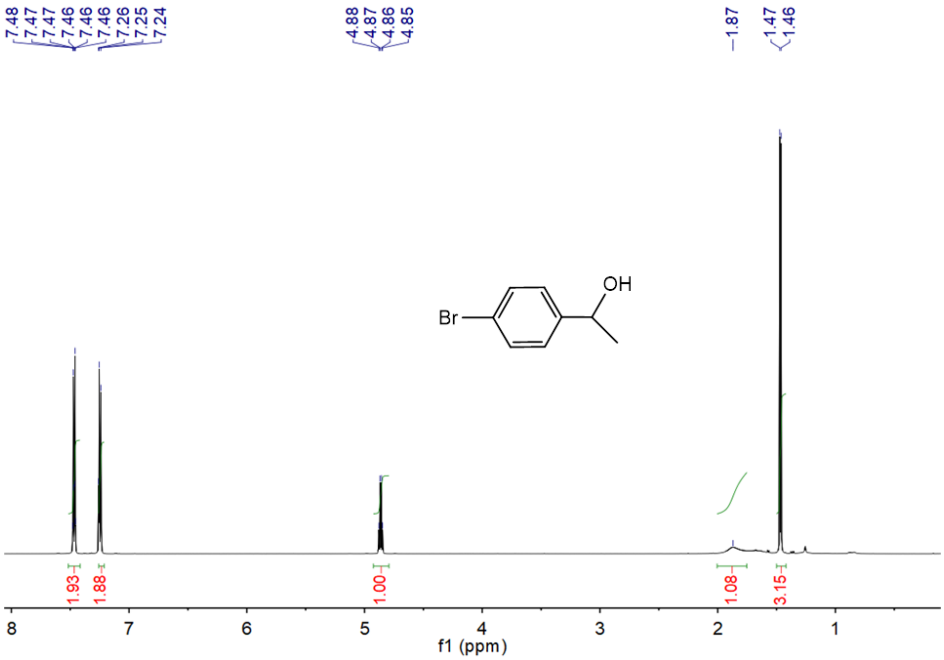

Fig. S60 ^{1}H NMR spectrum of the isolated 1-(4-bromophenyl)ethanol (600 MHz, $CDCl_3$)

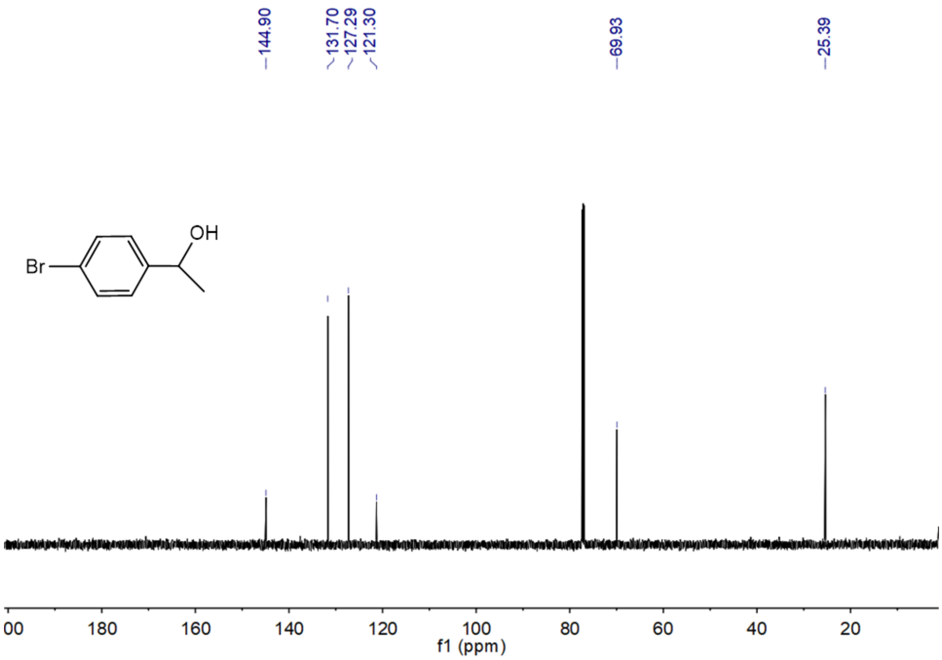

Fig. S61 ^{13}C{^{1}H} NMR spectrum of the isolated 1-(4-bromophenyl)ethanol (151 MHz, $CDCl_3$)

1-(4-Chlorophenyl)ethanol

Clear colorless liquid, 0.120 g, 77% yield, purity: >99% based on ^{1}H NMR spectra. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.30–7.33 (m, Ar*H*, 4H), 4.89 (quart, $J_{H\text{-}H}$ = 6.5 Hz, C*H*(OH)CH_3, 1H), 1.82 (br., O*H*, 1H), 1.48 (d, $J_{H\text{-}H}$ = 6.5 Hz, CH(OH)CH_3, 3H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, δ): 144.39, 133.19, 128.73, 126.93, 69.87, 25.41. HRMS (ESI): *m/z* calculated for $C_8H_{10}ClO$ $[M + H]^+$ 157.0415, found 157.0415. These spectral data correspond to previously reported data.[S8,S19]

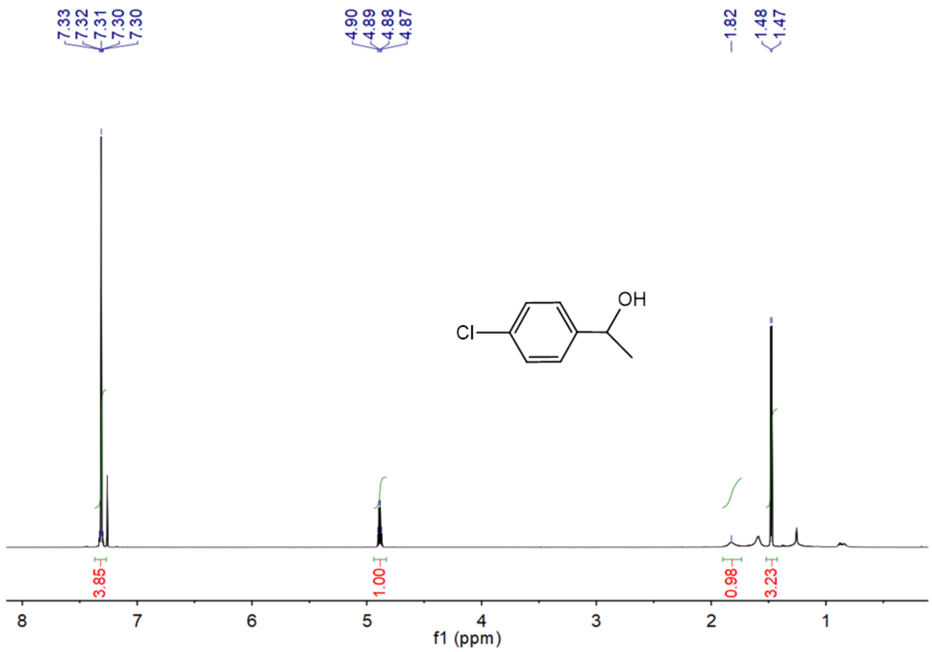

Fig. S62 ^{1}H NMR spectrum of the isolated 1-(4-chlorophenyl)ethanol (600 MHz, $CDCl_3$)

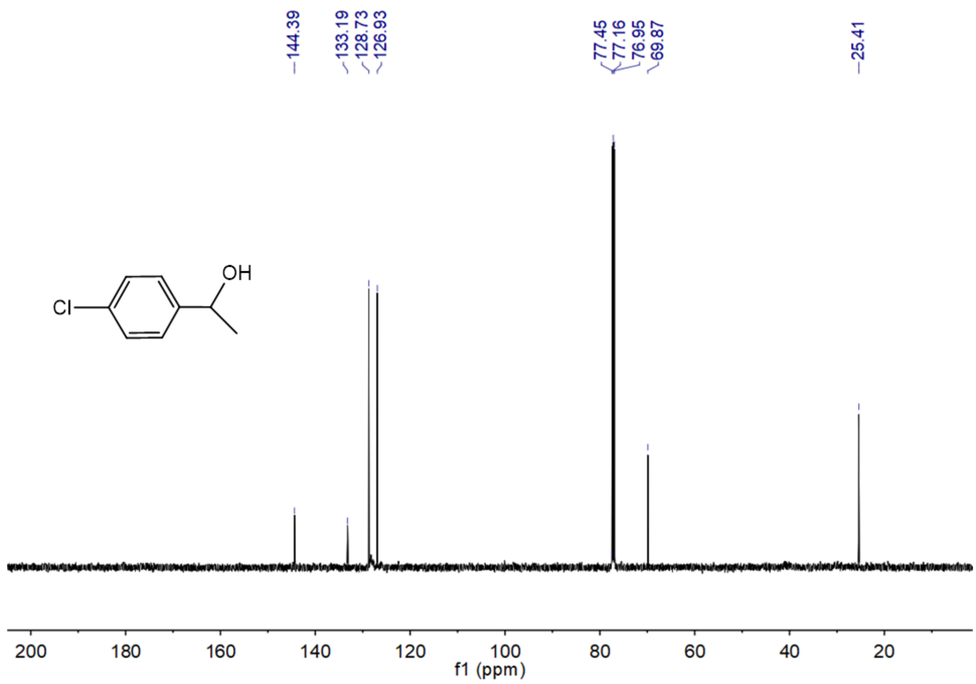

Fig. S63 $^{13}C\{^{1}H\}$ NMR spectrum of the isolated 1-(4-chlorophenyl)ethanol (151 MHz, $CDCl_3$)

1,2,3,4-Tetrahydro-1-naphthalenol

Clear colorless liquid, 0.129 g, 87% yield, purity: >97% based on ^{1}H NMR spectra. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.43–7.44 (m, Ar*H*, 1H), 7.19–7.22 (m, Ar*H*, 2H), 7.10–7.12 (m, Ar*H*, 1H), 4.78 (t, $J_{H\text{-}H}$ = 4.8 Hz, C*H*(OH), 1H), 2.81–2.86 (m, CH_2, 1H), 2.71–2.76 (m, CH_2, 1H), 1.95–2.03 (m, CH_2, O*H*, 3H), 1.89–1.93 (m, CH_2, 1H), 1.76–1.81 (m, CH_2, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 138.88, 137.20, 129.08, 128.76, 127.64, 126.25, 68.21, 32.34, 29.33, 18.90. HRMS (ESI): *m/z* calculated for $C_{10}H_{13}O$ $[M + H]^+$ 149.0961, found 149.0962. These spectral data correspond to previously reported data.[S7,S19]

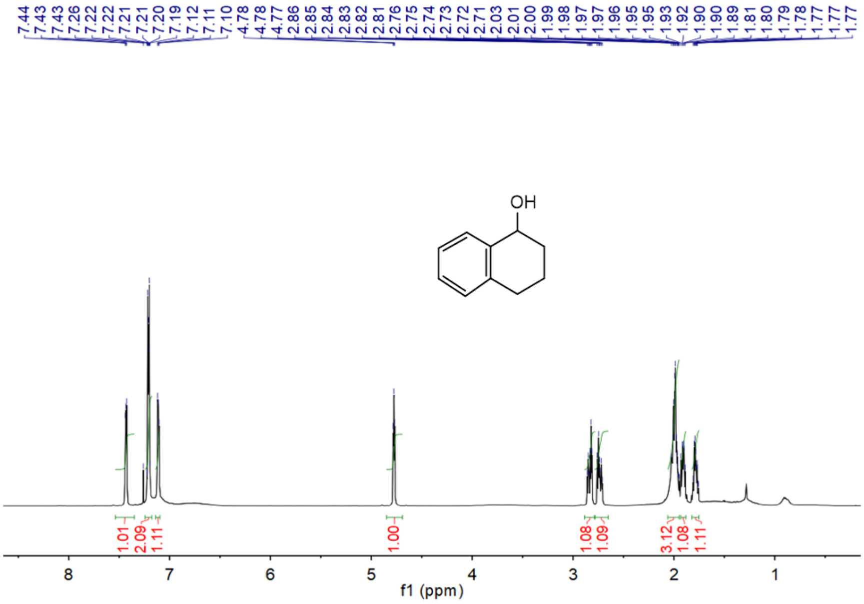

Fig. S64 ^{1}H NMR spectrum of the isolated 1,2,3,4-tetrahydro-1-naphthalenol (600 MHz, $CDCl_3$)

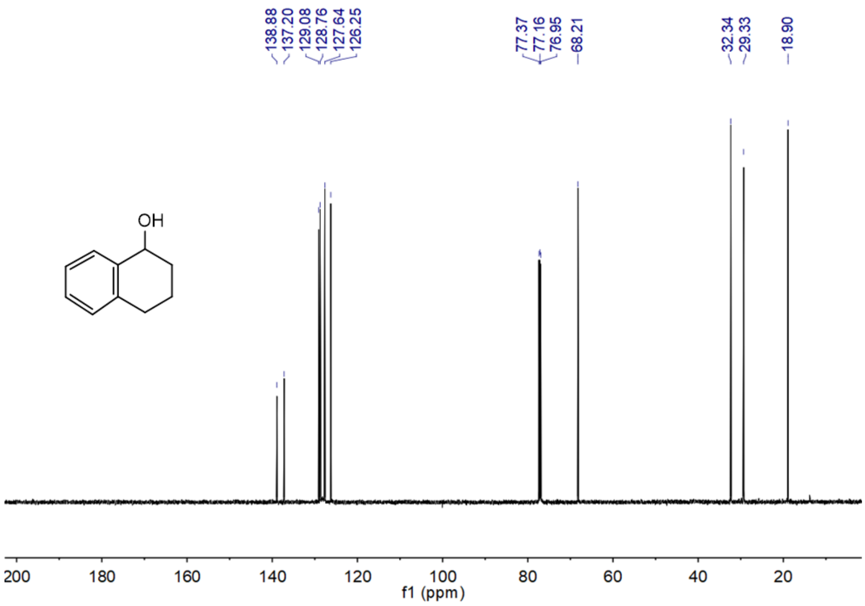

Fig. S65 ^{13}C{^{1}H} NMR spectrum of the isolated 1,2,3,4-tetrahydro-1-naphthalenol (151 MHz, $CDCl_3$)

α-Methyl-4-(trifluoromethyl)benzyl alcohol

Light yellow liquid, 0.143 g, 75% yield, purity: >97% based on ^{1}H NMR spectra. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.60 (d, $J_{H\text{-}H}$ = 8.1 Hz, Ar*H*, 2H), 7.48 (d, $J_{H\text{-}H}$ = 8.1 Hz, Ar*H*, 2H), 4.95 (quart, $J_{H\text{-}H}$ = 6.5 Hz, C*H*(OH)CH_3, 1H), 2.20 (s, br, O*H*, 1H), 1.50 (d, $J_{H\text{-}H}$ = 6.5 Hz, CH_3, 3H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, δ): 149.83, 129.73 (q, $^{2}J_{C\text{-}F}$ = 32 Hz), 125.78, 125.65 (q, $^{3}J_{C\text{-}F}$ = 4 Hz), 124.30 (q, $^{1}J_{C\text{-}F}$ = 272 Hz), 69.93, 25.49. HRMS (ESI): *m/z* calculated for $C_9H_{10}F_3O$ $[M + H]^+$ 191.0678, found 191.0679. These spectral data correspond to previously reported data.[S7,S20]

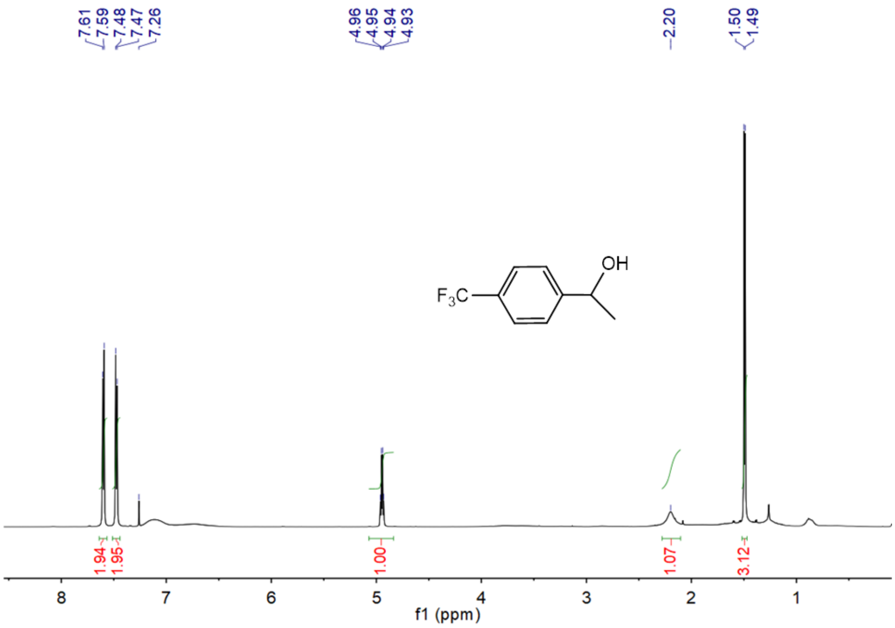

Fig. S66 ^{1}H NMR spectrum of the isolated α-methyl-4-(trifluoromethyl)benzyl alcohol (600 MHz, $CDCl_3$)

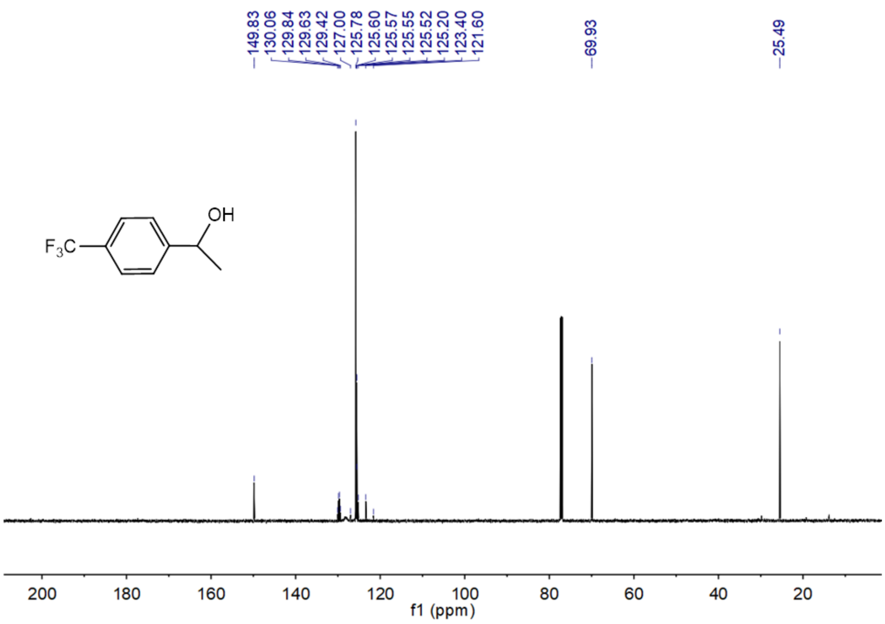

Fig. S67 $^{13}C\{^{1}H\}$ NMR spectrum of the isolated α-methyl-4-(trifluoromethyl)benzyl alcohol (151 MHz, $CDCl_3$)

4,4'-Difluorobenzhydryl alcohol

Colorless crystalline solid, 0.154 g, 70% yield, purity: >96% based on ^{1}H NMR spectra. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.30–7.33 (m, Ar*H*, 4H), 7.01–7.04 (m, Ar*H*, 4H), 5.80 (s, C*H*(OH), 1H), 2.42 (s, br., O*H*, 1H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, δ): 162.35 (d, $^{1}J_{C\text{-}F}$ = 246 Hz), 139.55 (d, $^{4}J_{C\text{-}F}$ = 3 Hz), 128.30 (d, $^{3}J_{C\text{-}F}$ = 8 Hz), 115.52 (d, $^{2}J_{C\text{-}F}$ = 22 Hz), 75.05. HRMS (ESI): *m/z* calculated for $C_{13}H_{10}F_2ONa$ $[M + Na]^+$ 243.0592, found 243.0591. These spectral data correspond to previously reported data.[S12]

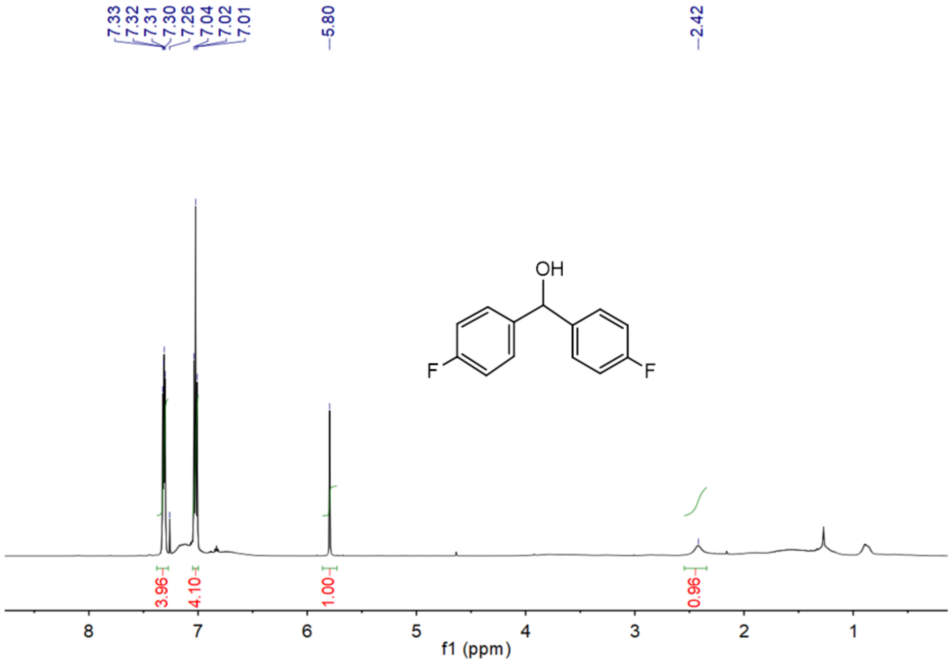

Fig. S68 ^{1}H NMR spectrum of the isolated 4,4'-difluorobenzhydryl alcohol (600 MHz, $CDCl_3$)

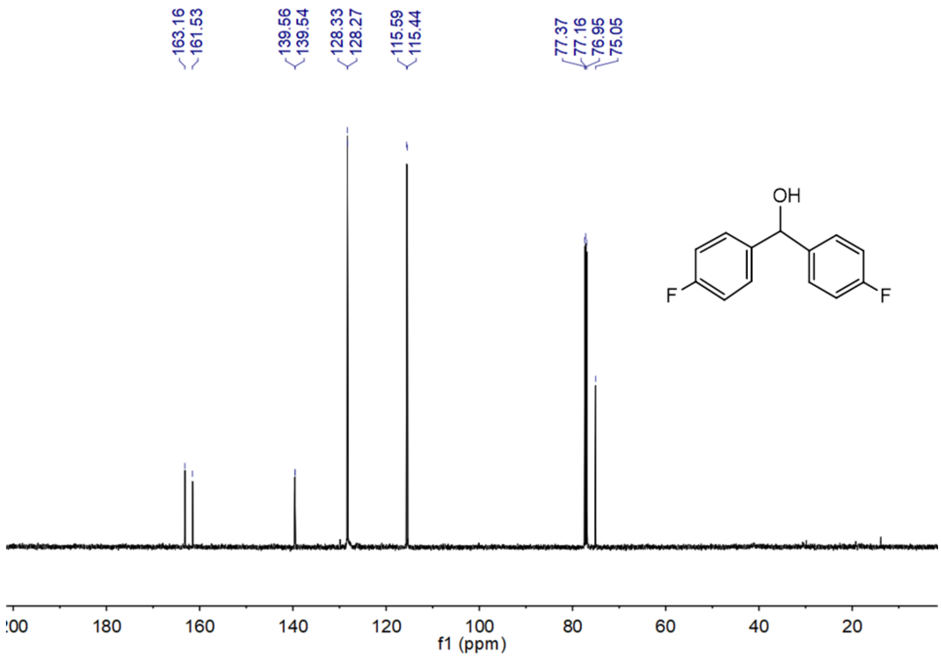

Fig. S69 $^{13}C\{^{1}H\}$ NMR spectrum of the isolated 4,4'-difluorobenzhydryl alcohol (151 MHz, $CDCl_3$)

4-Bromo-α-phenylbenzenemethanol

Colorless crystalline solid, 0.183 g, 70% yield, purity: >97% based on ^{1}H NMR spectra. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.45–7.47 (m, Ar*H*, 2H), 7.33–7.36 (m, Ar*H*, 4H), 7.28–7.31 (m, Ar*H*, 1H), 7.24–7.26 (m, Ar*H*, 2H), 5.76 (s, C*H*(OH), 1H), 2.46 (s, br., O*H*, 1H). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, δ): 143.44, 142.82, 131.64, 128.76, 128.33, 127.98, 126.64, 121.51, 75.73. HRMS (ESI): *m/z* calculated for $C_{13}H_{11}BrONa$ $[M + Na]^+$ 284.9885, found 284.9884. These spectral data correspond to previously reported data.[S20]

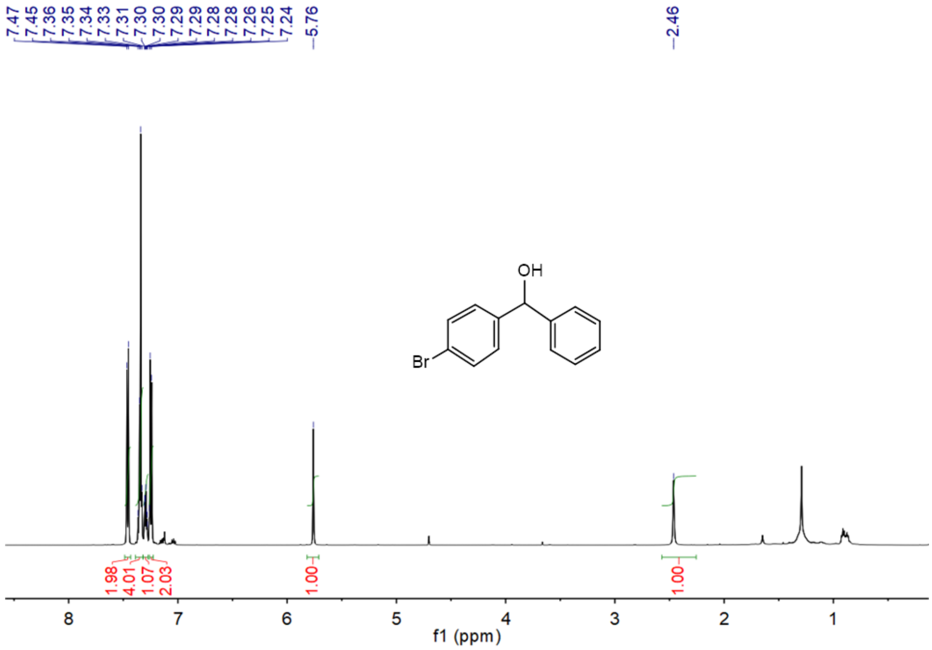

Fig. S70 ^{1}H NMR spectrum of the isolated 4-bromo-α-phenylbenzenemethanol (600 MHz, $CDCl_3$)

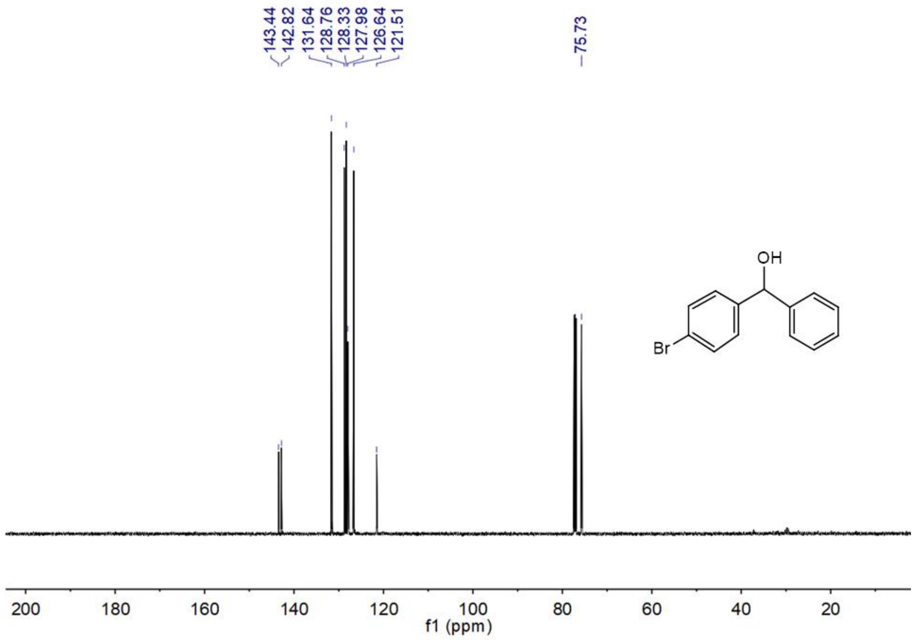

Fig. S71 $^{13}C\{^{1}H\}$ NMR spectrum of the isolated 4-bromo-α-phenylbenzenemethanol (151 MHz, $CDCl_3$)

4-Phenyl-3-buten-2-ol

Colorless crystalline solid, 0.121 g, 82% yield, purity: >96% based on ^{1}H NMR spectrum. ^{1}H NMR (600 MHz, $CDCl_3$, δ): 7.42 (d, $J_{H\text{-}H}$ = 7.6 Hz, Ar*H*, 2H), 7.35 (t, $J_{H\text{-}H}$ = 7.6 Hz, Ar*H*, 2H), 7.28 (d, $J_{H\text{-}H}$ = 7.5 Hz, Ar*H*, 1H), 6.60 (d, $J_{H\text{-}H}$ = 15.9 Hz, C*H*, 1H), 6.26 (dd, $J_{H\text{-}H}$ = 15.9 and 6.4 Hz, C*H*, 1H), 4.52 (quint, $J_{H\text{-}H}$ = 6.3 Hz, C*H*(OH), 1H), 1.86 (s, br, O*H*, 1H), 1.41 (d, $J_{H\text{-}H}$ = 6.4 Hz, CH_3, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, δ): 136.81, 133.66, 129.52, 128.70, 127.75, 126.57, 69.17, 23.53. HRMS (ESI): *m/z* calculated for $C_{10}H_{13}O$ [M + H]$^{+}$ 149.0961, found 149.0960. These spectral data correspond to previously reported data.[S21]

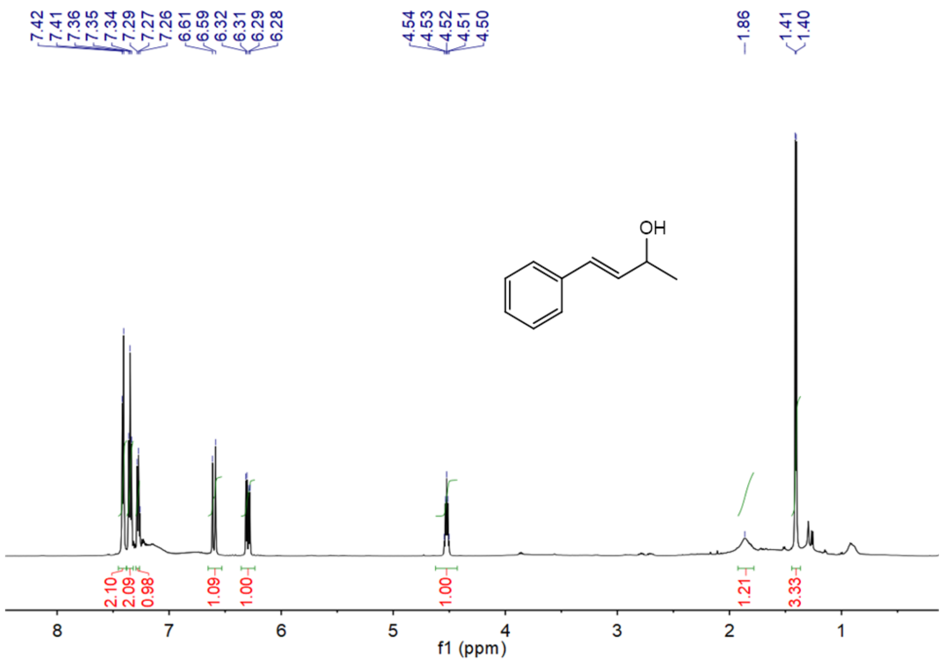

Fig. S72 ^{1}H NMR spectrum of the isolated 4-phenyl-3-buten-2-ol (600 MHz, $CDCl_3$)

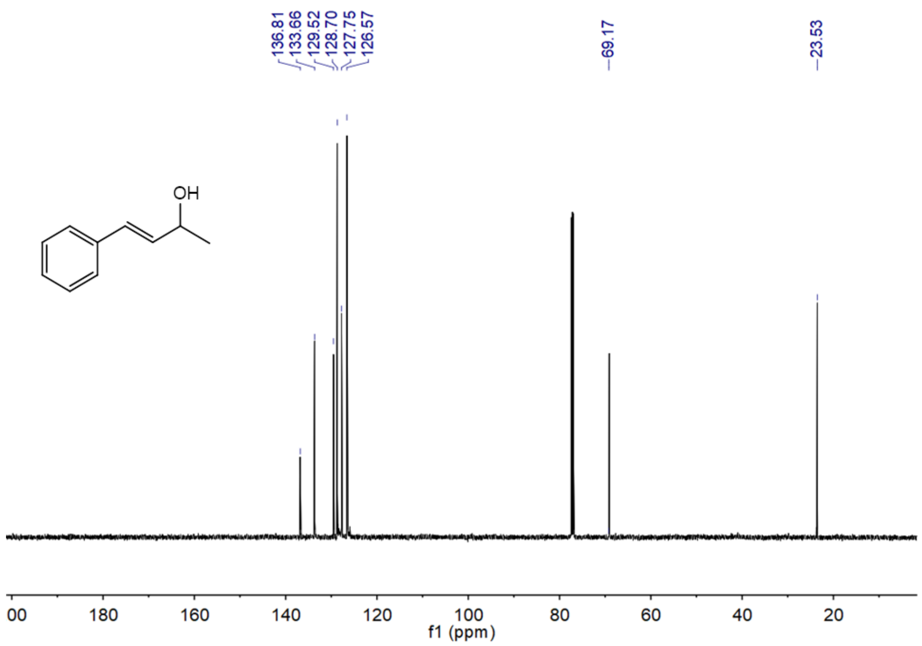

Fig. S73 ^{13}C{^{1}H} NMR spectrum of the isolated 4-phenyl-3-buten-2-ol (151 MHz, $CDCl_3$)

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