

Supporting information

Guerbet-Type β -alkylation of Secondary Alcohols Catalyzed by Chromium Chloride and its Corresponding NNN Pincer Complex

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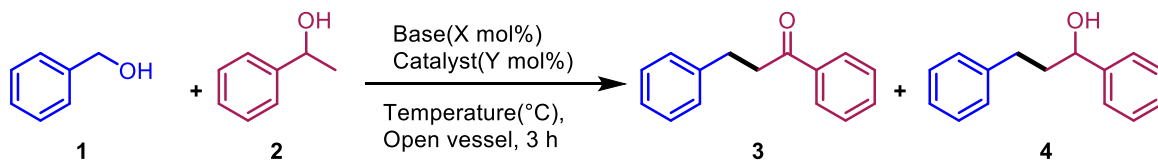
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1. Optimization:

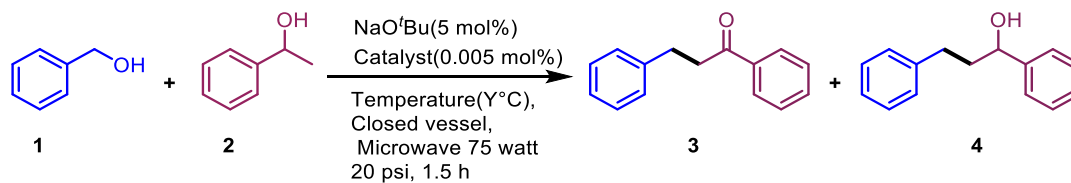
Table S1. Optimization of the chromium catalyzed solvent-free β -alkylation of 1-phenylethanol with benzyl alcohol under conventional heating^a



Entry	Base (X mol%) ^b	Catalyst(Y mol%) ^b	Yield(%) ^c and [TON] ^f		Selectivity of 4=((Yield of 4/Total yield 4+3)*100)
			4	3	
1	Na ₂ CO ₃ (5)	5(0.005)	0[0]	0[0]	0
2	NaHCO ₃ (5)	5(0.005)	0[0]	0[0]	0
3	K ₂ CO ₃ (5)	5(0.005)	0[0]	0[0]	0
4	KO ^t Bu (5)	5(0.005)	5[1000]	2[400]	71
5	KOH (5)	5(0.005)	5±2[1000]	4±0[800]	56
6	NaOH (5)	5(0.005)	45±0.3[9000]	4[800]	92
7	NaOH (2.5)	5(0.005)	11±2[2200]	5±1[1000]	69
8	NaOH (1.25)	5(0.005)	3±1[600]	2±1[400]	60
9	NaO ^t Bu (5)	5(0.005)	84±0.3[16800]	8±1[1600]	91
10	NaO ^t Bu (2.5)	5(0.005)	9±2[1800]	3±1[600]	75
11	NaO ^t Bu (1.25)	5(0.005)	2±0.3[400]	1±1[200]	67
12	NaO ^t Bu (5)	5(0.01)	70[7000]	6[600]	92
13	NaO ^t Bu (5)	5(0.0075)	70±2[9333]	6±1[800]	92
14	NaO ^t Bu (5)	5(0.0025)	71±0.1[14200]	5±1[1000]	93
15	NaO ^t Bu (5)	5(0.00125)	61±2[12200]	3±1[600]	95
16 ^d	NaO ^t Bu (5)	5 (0.005)	12±2[2400]	3±1[600]	80
17 ^e	NaO ^t Bu (5)	5(0.005)	5±0.5[1000]	2±1[400]	71
18	NaO ^t Bu (5)	CrCl ₃ .6H ₂ O(0.005)	79±2[15800]	12±1[2400]	87
19	NaO ^t Bu (5)	–	8	2	80
20	–	CrCl ₃ .6H ₂ O(0.005)	0	0	0
21	–	5 (0.005)	0	0	0

^aConditions: Benzyl alcohol (4 mmol), 1-phenylethanol (4 mmol), base (X mol%), and Cr catalyst (Y mol%) were heated together at 140 °C for 3 hours. ^bMol% of base is with respect to total alcohol content (1+2). ^cYield determined from ¹H NMR analysis using toluene as an internal standard. Yields reported are the average of two runs. ^dReaction performed at 120 °C. ^eReaction performed at 100 °C. ^fTON are written in the parenthesis.

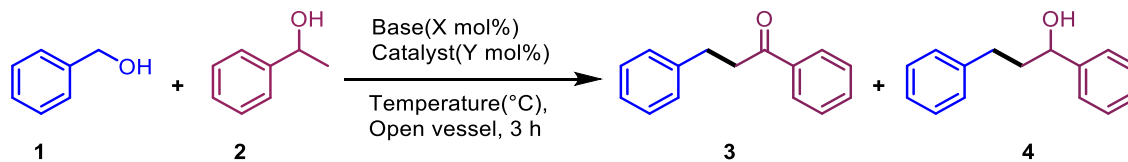
Table S2. Chromium catalyzed solvent-free β -alkylation of 1-phenyl ethanol with benzyl alcohol under microwave conditions^a



Entry	Temperature	Catalyst (0.005 mol %) ^b	Yield (%) ^c and [TON] ^f		Selectivity of 4 = (Yield of 4 /Total yield 4+3)*100)
	(T °C)		4	3	
1	140	5	90[18000]	7[1400]	93
2	120	5	26[5200]	2[400]	93
3	100	5	8[1600]	2[400]	80
4	140	CrCl ₃ ·6H ₂ O	76[15200]	3[600]	96
5	120	CrCl ₃ ·6H ₂ O	31[6200]	3[600]	91

^aConditions: Benzyl alcohol (2 mmol), 1-phenyl ethanol (2 mmol), NaO^tBu (5 mol%), and Cr catalyst (0.005 mol%) were heated together in air at 140 °C for 1.5 hours under 75 W microwave irradiation. ^bMol% of base and catalyst is with respect to total alcohol content (**1+2**). ^cYield determined from ¹H NMR analysis using toluene as an internal standard. Yields reported are the average of two runs. ^fTON are written in the parenthesis.

Table S3. Effect of hot filtration and mercury drop test in the chromium catalyzed solvent-free β -alkylation of 1-phenyl ethanol with benzyl alcohol under conventional heating ^a



Entry	Base (5 mol%) ^b	Catalyst (Y mol %) ^b	Yield(%) ^c and [TON] ^f		Selectivity of 4 = ((Yield of 4 /Total yield 4+3)*100)
			4	3	
1	NaO ^t Bu	5	84±0.3[16800]	8±1[1600]	91
2 ^d	NaO ^t Bu	5	82[16400]	11[2200]	88
3 ^e	NaO ^t Bu	5	81[16200]	6[1200]	93
4	NaO ^t Bu	CrCl ₃ ·6H ₂ O	79±2[15800]	12±1[2400]	86
5 ^d	NaO ^t Bu	CrCl ₃ ·6H ₂ O	83[16600]	9[1800]	90
6 ^e	NaO ^t Bu	CrCl ₃ ·6H ₂ O	80[16000]	6[1200]	93

^aConditions: Benzyl alcohol (2 mmol), 1-phenyl ethanol (2 mmol), base (5 mol%), and Cr catalyst (Y mol%) were heated together in air at 140 °C for 3 hours. ^bMol% of base and catalyst is with respect to total alcohol content (**1+2**). ^cYield determined from ¹H NMR analysis using toluene as an internal standard. Yields reported are the average of two runs. ^dResult obtained from heating the filtrate for 2.5 h post hot-filtration after 30 minutes of reaction. ^eReaction performed in the presence of excess mercury. ^fTON are written in the parenthesis.

2. HRMS analysis:

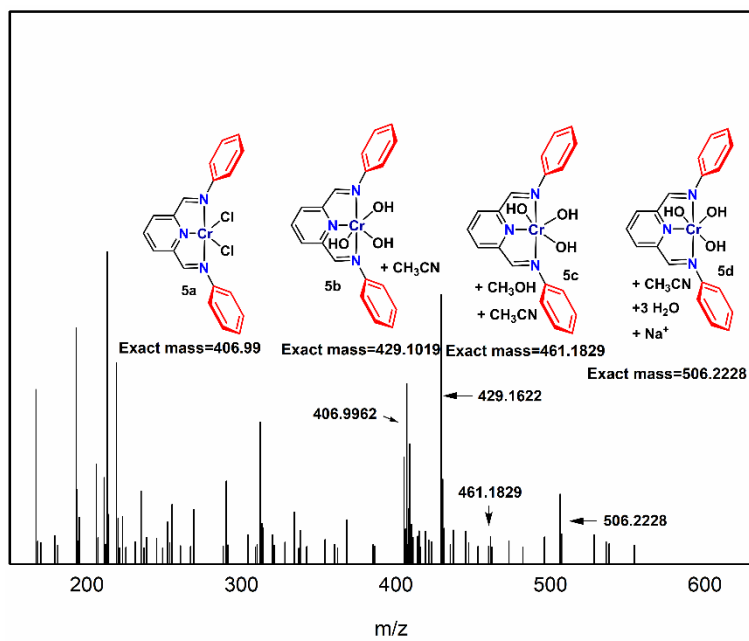


Figure S1. HRMS (ESI) plot of complex 5.

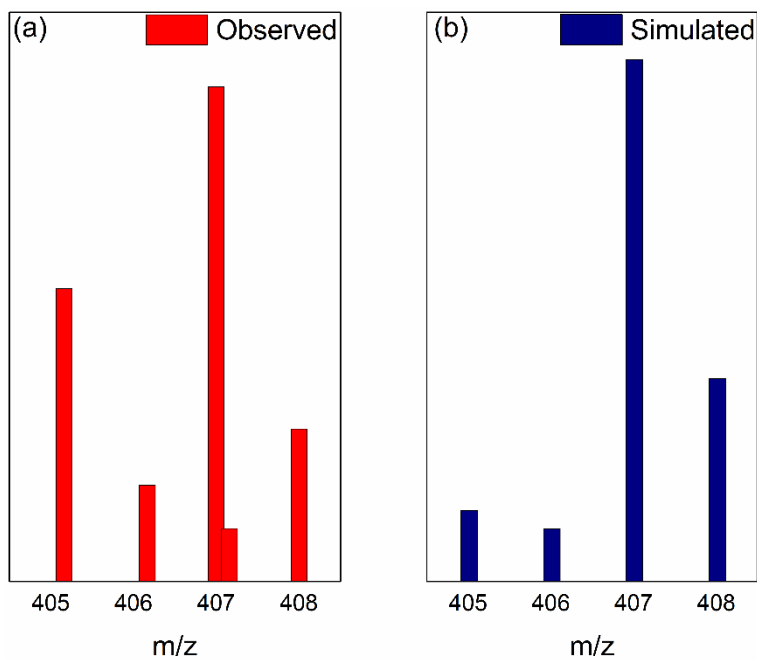


Figure S2. HRMS (ESI) expanded spectra of m/z 406.9962 (a) Observed (b) Simulated.

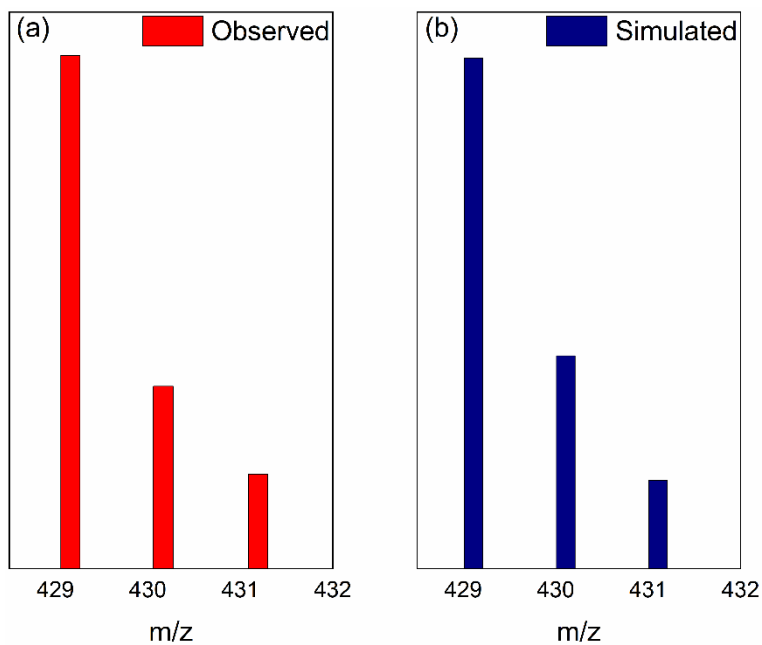


Figure S3. HRMS (ESI) expanded spectra of m/z 429.1622 (a) Observed (b) Simulated.

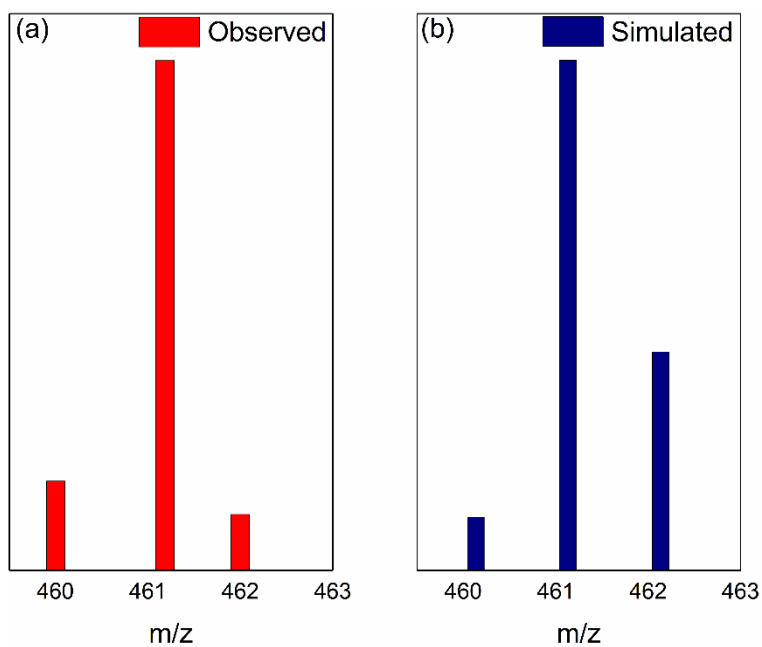


Figure S4. HRMS (ESI) expanded spectra of m/z 461.1829 (a) Observed (b) Simulated.

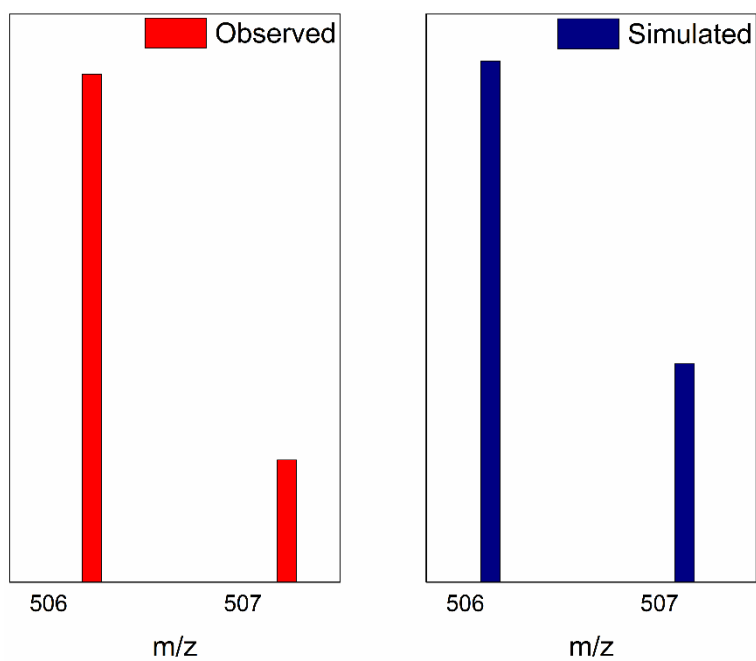


Figure S5. HRMS (ESI) expanded spectra of m/z 506.2228 (a) Observed (b) Simulated.

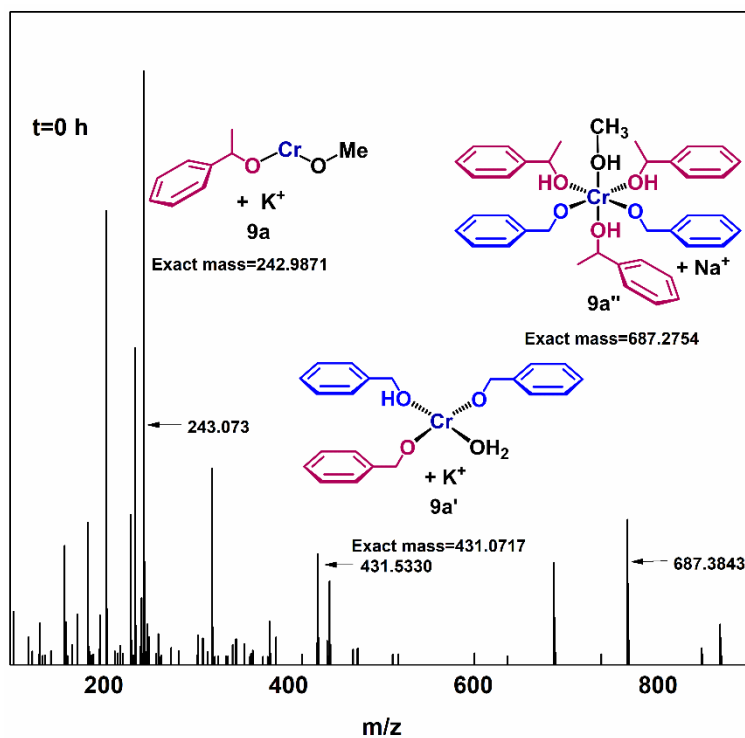


Figure S6. HRMS (ESI) plot of the reaction mixture containing **1** (4 mmol) and **2** (4 mmol) in the presence of 5 mol% $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ and 5 mol% NaO^tBu at $t = 0$ h at 140°C .

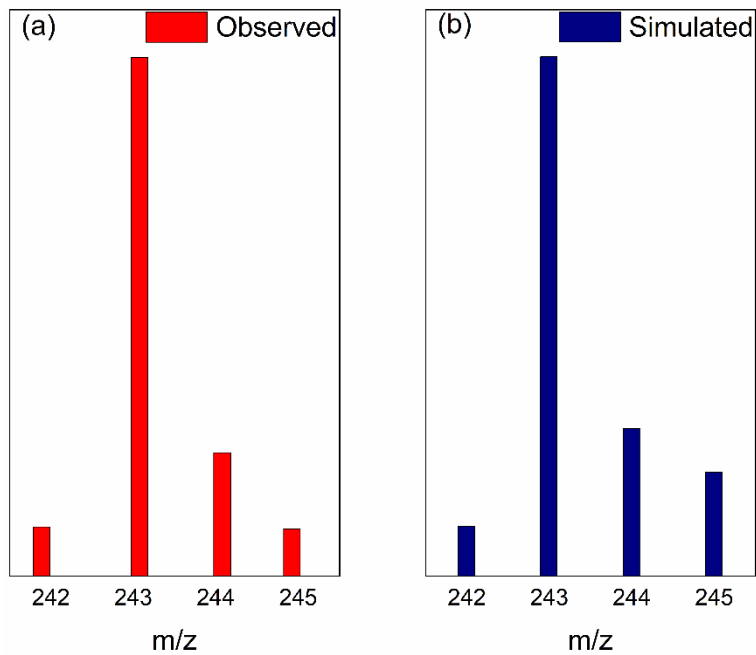


Figure S7. HRMS (ESI) expanded spectra of m/z 243.073 (a) Observed (b) Simulated.

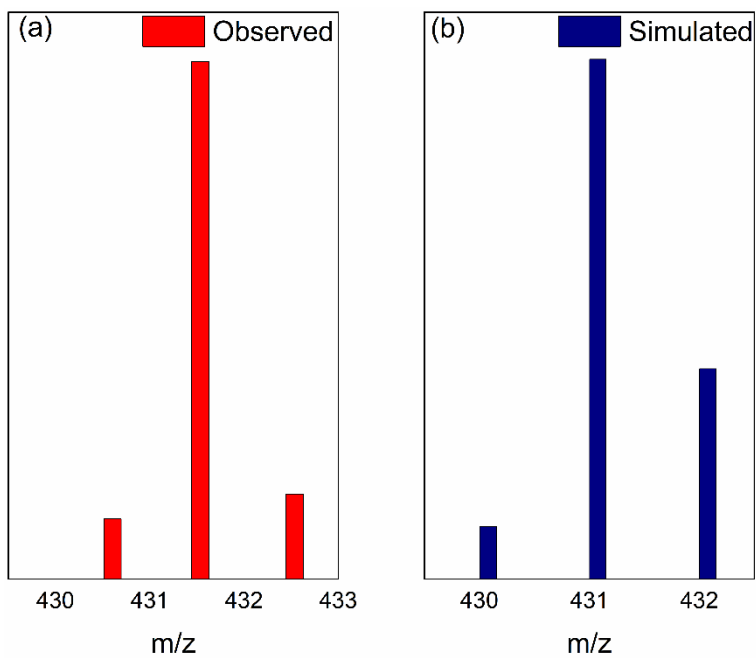


Figure S8. HRMS (ESI) expanded spectra of m/z 431.5330 (a) Observed (b) Simulated.

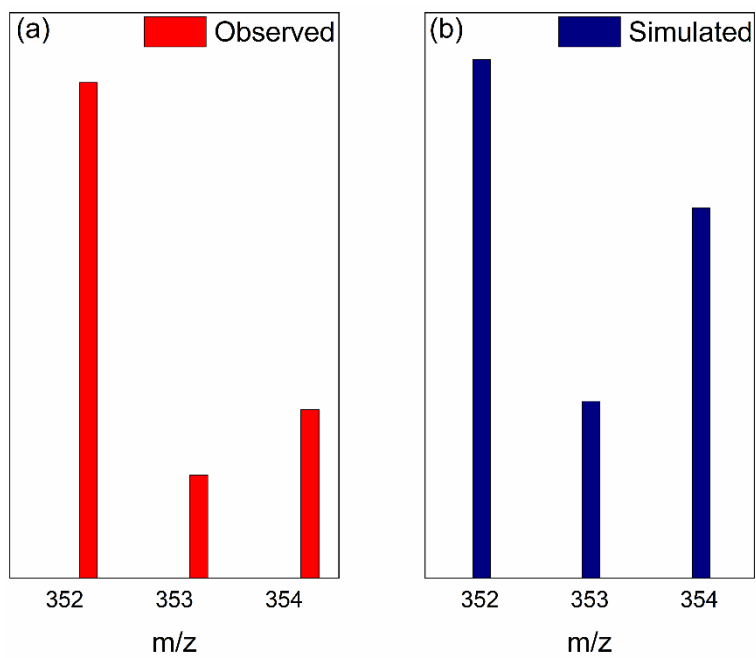


Figure S11. HRMS (ESI) expanded spectra of m/z 352.2153 (a) Observed (b) Simulated.

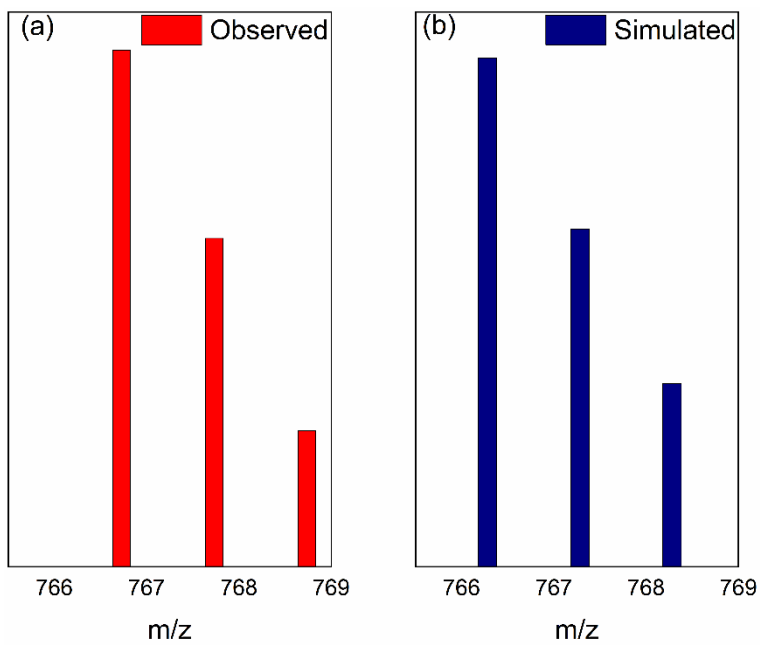


Figure S12. HRMS (ESI) expanded spectra of m/z 766.2749 (a) Observed (b) Simulated.

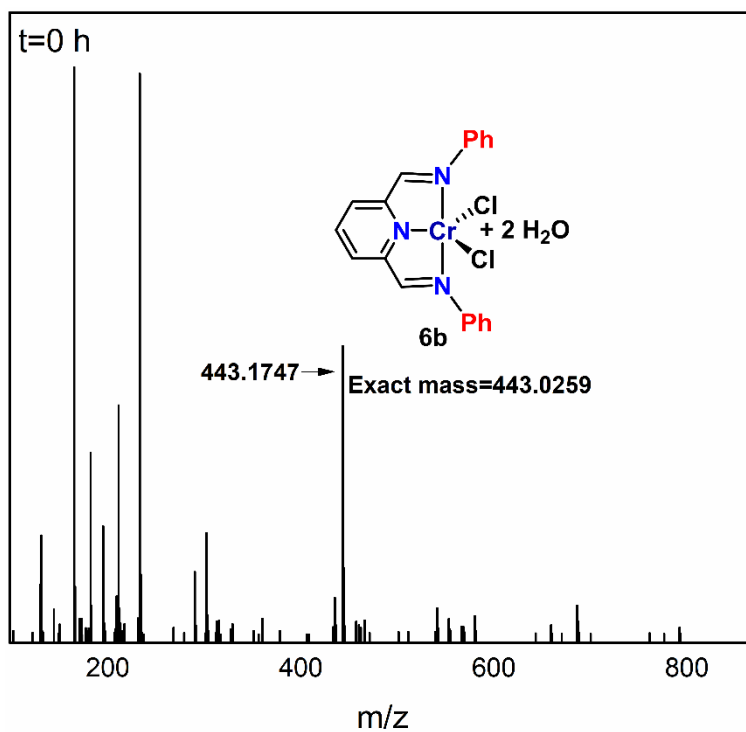


Figure S13. HRMS (ESI) plot of the reaction mixture containing **1** (4 mmol) and **2** (4 mmol) in the presence of 5 mol% **5** and 5 mol% NaO^tBu at t = 0 h at 140 °C.

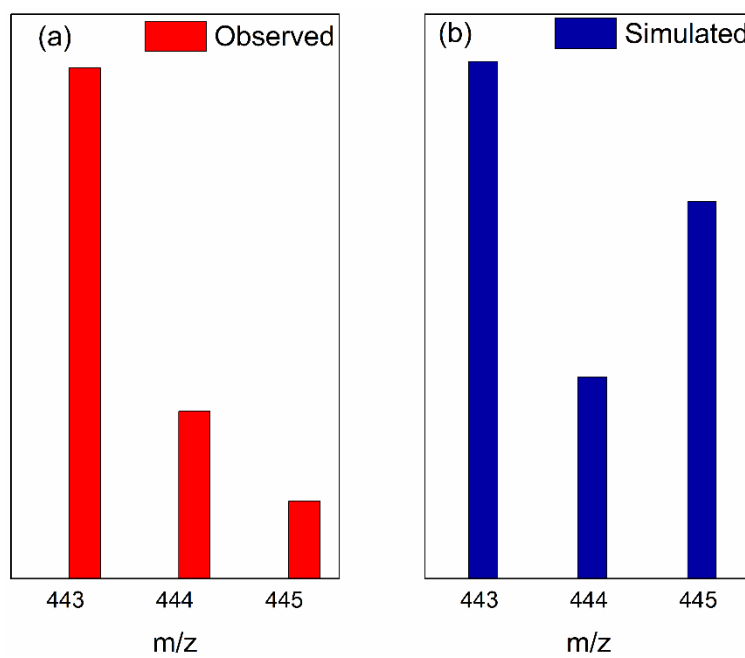


Figure S14. HRMS (ESI) expanded spectra of m/z 443.1747 (a) Observed (b) Simulated.

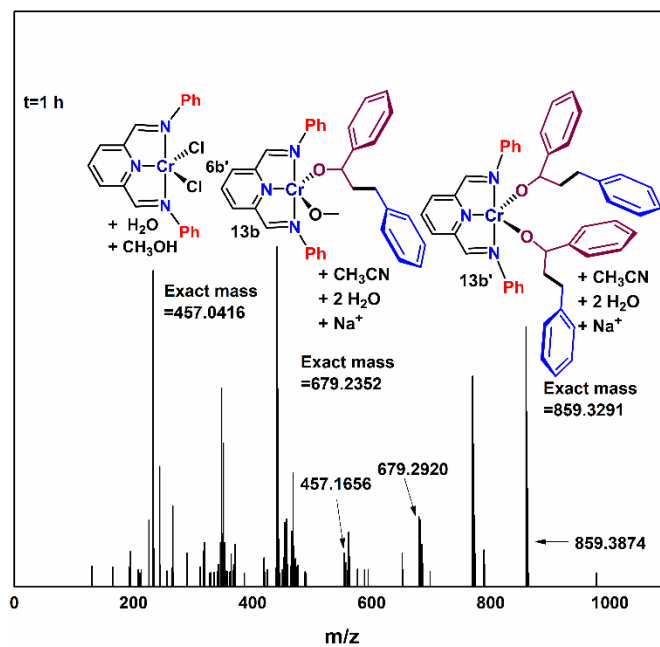


Figure S15. HRMS (ESI) plot of the reaction mixture containing **1** (4 mmol) and **2** (4 mmol) in the presence of 5 mol% **5** and 5 mol% NaO^tBu at t = 1 h at 140 °C.

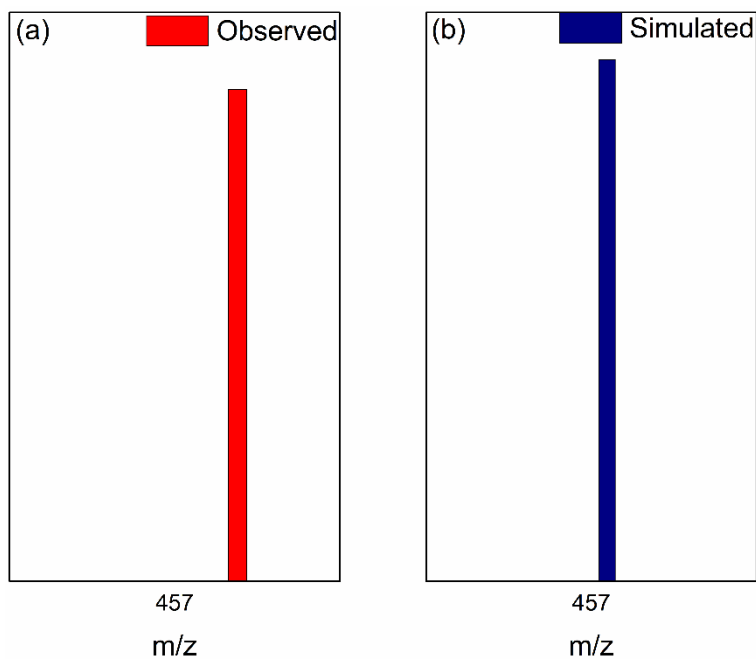


Figure S16. HRMS (ESI) expanded spectra of m/z 457.1656 (a) Observed (b) Simulated.

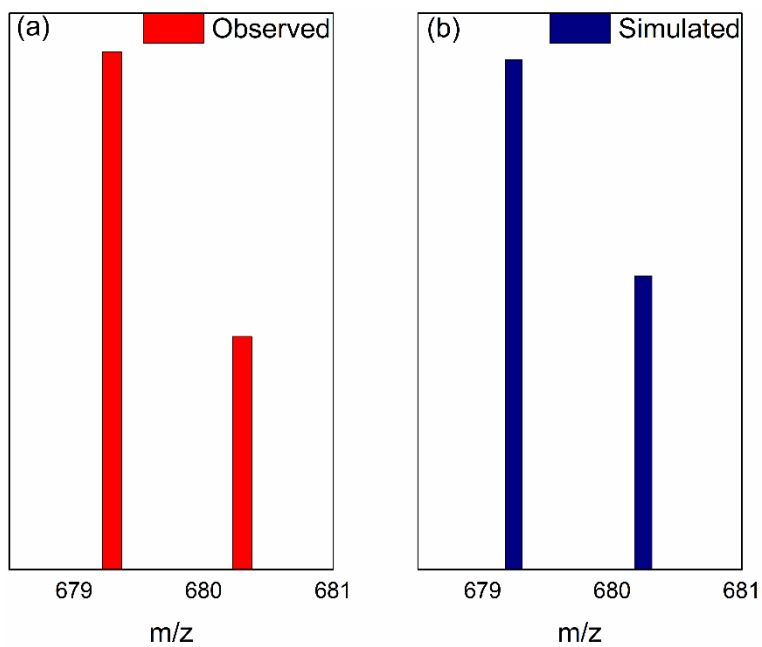


Figure S17. HRMS (ESI) expanded spectra of m/z 679.2920 (a) Observed (b) Simulated.

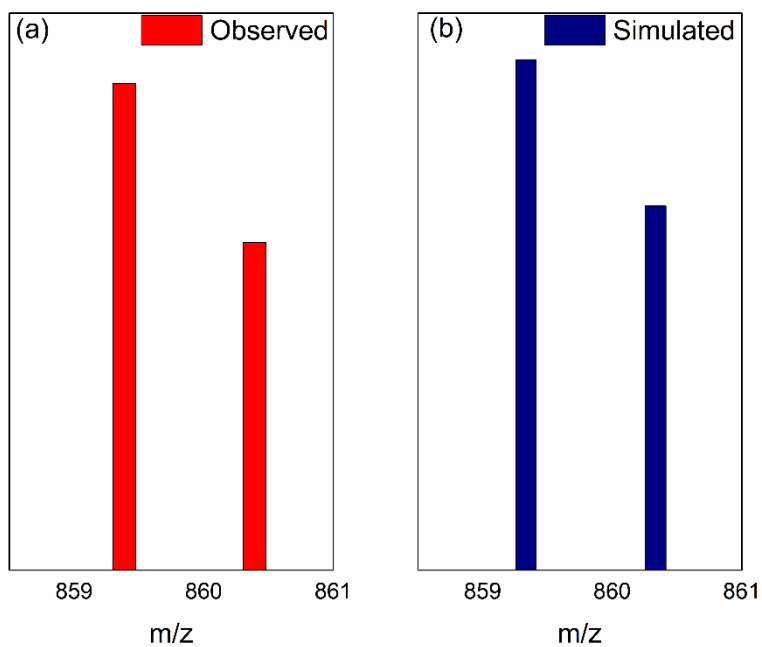


Figure S18. HRMS (ESI) expanded spectra of m/z 859.3874 (a) Observed (b) Simulated.

3. Gas Chromatography Analysis:

GC analysis (TCD detection) was performed on an Agilent 7820-GC instrument fitted with Agilent Front SSZ Inlet N2 HP-PLOT Q column (30 m length x 530 μm x 40 μm) using the following method:

Agilent 7820-GC back detector TCD

Oven temperature: 50 $^{\circ}\text{C}$

Time at starting temp: 0 min

Hold time = 10 min

Inlet temperature: 100 $^{\circ}\text{C}$

Detector temperature (TCD): 250 $^{\circ}\text{C}$

Detector temperature (FID): 300 $^{\circ}\text{C}$

Flow rate (carrier): 5 mL/min (N₂)

Split ratio: 10

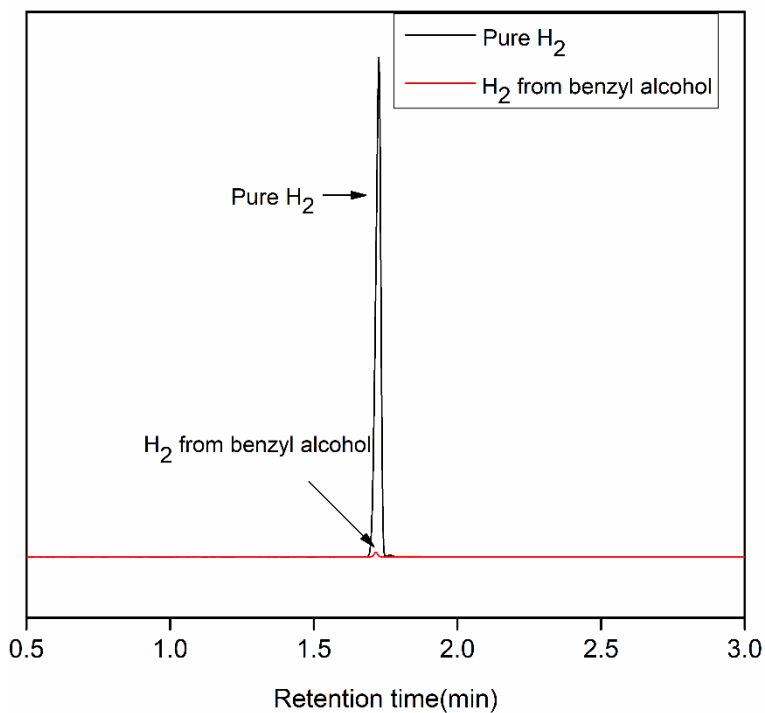


Figure S19: Evidence for H₂ evolution in the dehydrogenation of benzyl alcohol (**1**) catalyzed by **5** (0.01 mol %) and NaO^tBu (10 mol%) at 140 $^{\circ}\text{C}$ via GC analysis.

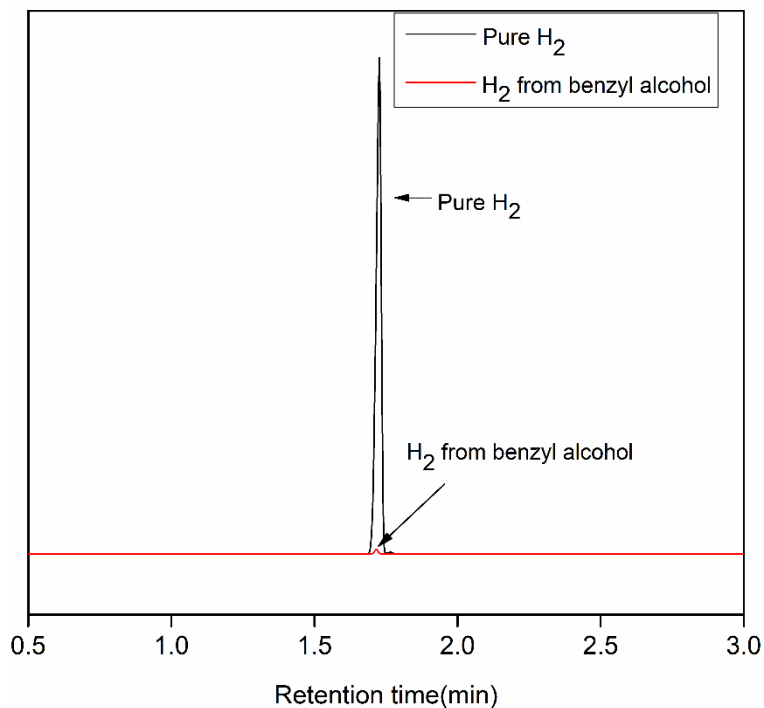


Figure S20: Evidence for H₂ evolution in the dehydrogenation of benzyl alcohol (**1**) catalyzed by CrCl₃·6H₂O (0.01 mol %) and NaO^tBu (10 mol%) at 140 °C via GC analysis.

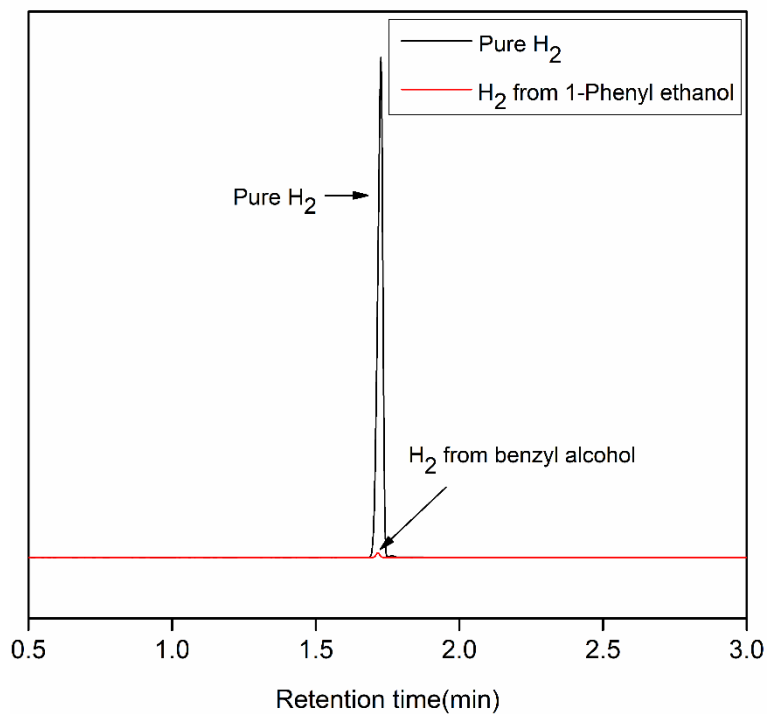


Figure S21: Evidence for H₂ evolution in the dehydrogenation of 1-Phenyl ethanol (**2**) catalyzed by **5** (0.01 mol %) and NaO^tBu (10 mol%) at 140 °C via GC analysis.

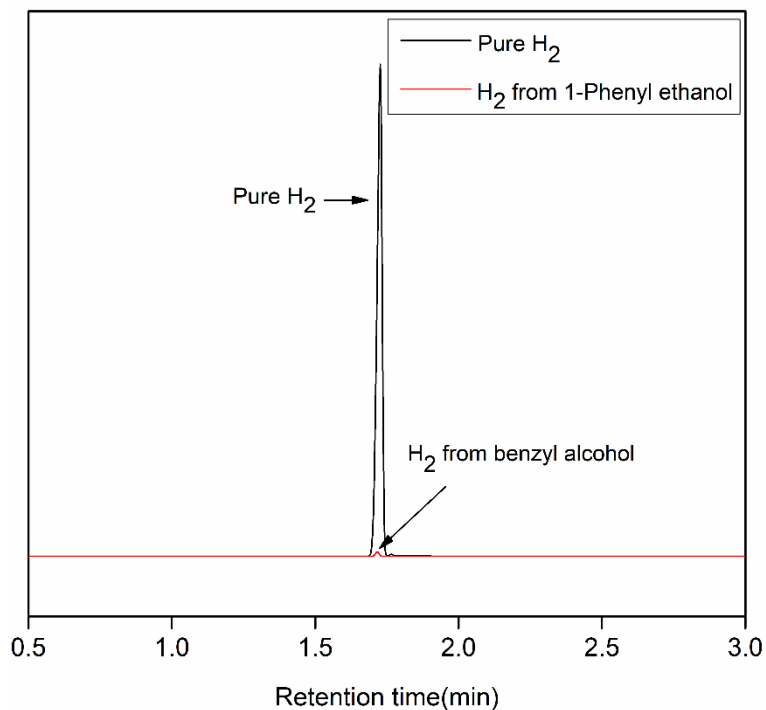


Figure S22: Evidence for H₂ evolution in the dehydrogenation of 1-Phenyl ethanol (**2**) catalyzed by CrCl₃·6H₂O (0.01 mol %) and NaO^tBu (10 mol%) at 140 °C via GC analysis.

4. EPR analysis:

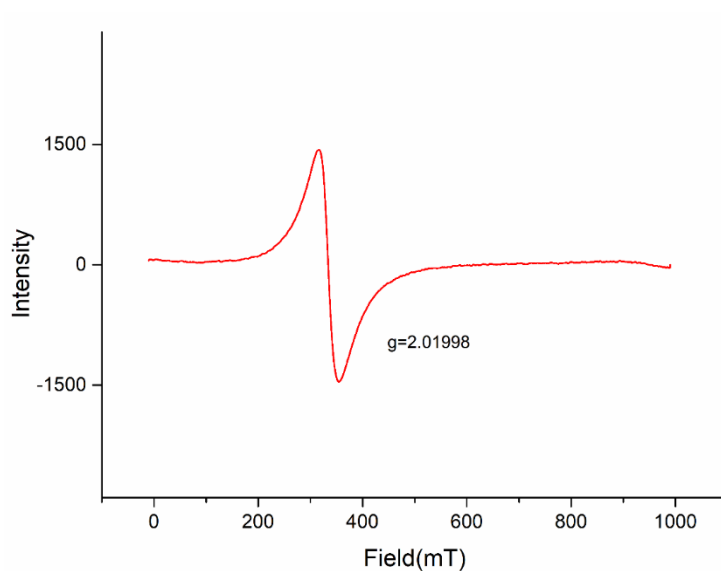


Figure S23. The X-band EPR spectra of the complex **5** recorded on a JES-FA200 ESR spectrometer at room temperature with microwave power of 0.998 mW and microwave frequency of 9.14 GHz.

5. NMR Data and Spectra:

1,3-diphenylpropan-1-ol (4a):

^1H NMR (500 MHz, CDCl_3): δ 7.26 (d, $J = 4.3$ Hz, 4H), 7.18 (q, $J = 6.0$ Hz, 3H), 7.10 (d, $J = 7.5$ Hz, 3H), 4.60 (t, $J = 6.4$ Hz, 1H), 2.62-2.55 (m, 2H), 2.10 – 1.89 (m, 2H), 1.80 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 144.70, 141.92, 128.66, 127.79, 126.00, 74.04, 40.60, 32.20.

1-(3-methoxyphenyl)-3-phenylpropan-1-ol(4b):

^1H NMR (500 MHz, CDCl_3): δ 7.33 – 7.18 (m, 6H), 6.94 (d, $J = 6.5$ Hz, 2H), 6.84 (d, $J = 8.0$ Hz, 1H), 4.69 (s, 1H), 3.83 (s, 3H), 2.80-2.66 (m, 2H), 2.19 – 2.00 (m, 2H), 1.92 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 146.43, 141.89, 129.68, 128.52, 125.99, 118.36, 113.22, 111.52, 73.95, 55.37, 40.53, 32.17.

1-(4-(tert-butyl)phenyl)-3-phenylpropan-1-ol(4d):

^1H NMR (500 MHz, CDCl_3): δ 7.37 (d, $J = 8.2$ Hz, 2H), 7.26 (dd, $J = 15.2, 7.2$ Hz, 4H), 7.18 (dd, $J = 13.2, 7.2$ Hz, 3H), 4.66 (t, $J = 7.8$ Hz, 1H), 2.80 – 2.63 (m, 2H), 2.18 – 1.99 (m, 2H), 1.85 (d, $J = 2.9$ Hz, 1H), 1.32 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 150.76, 142.01, 141.68, 128.57, 128.49, 125.94, 125.81, 125.55, 73.82, 40.39, 34.66, 32.27, 31.49.

3-phenyl-1-(thiophen-2-yl)propan-1-ol(4f):

^1H NMR (600 MHz, CDCl_3): δ 7.34 – 7.30 (m, 2H), 7.30 – 7.28 (m, 1H), 7.24 (d, $J = 7.9$ Hz, 3H), 7.02 – 6.99 (m, 2H), 4.99 – 4.93 (m, 1H), 2.84 – 2.71 (m, 2H), 2.30 – 2.15 (m, 2H), 2.05 (d, $J = 4.2$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 148.62, 141.57, 128.57, 126.09, 124.83, 124.07, 69.65, 40.82, 32.14.

1-(4-chlorophenyl)-3-phenylpropan-1-ol (4g):

^1H NMR (500 MHz, CDCl_3): δ 7.32 (d, $J = 8.6$ Hz, 2H), 7.30 – 7.25 (m, 4H), 7.21 – 7.17 (m, 3H), 4.67 (ddd, $J = 8.3, 5.1, 3.3$ Hz, 1H), 2.76-2.63 (m, 2H), 2.14 – 1.95 (m, 2H), 1.88 (d, $J = 3.5$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 143.16, 141.62, 133.40, 128.78, 128.59, 128.55, 127.44, 126.10, 73.30, 40.64, 32.06.

1-(3-chlorophenyl)-3-phenylpropan-1-ol(4i):

^1H NMR (600 MHz, CDCl_3): δ 7.38 (s, 1H), 7.34 – 7.26 (m, 4H), 7.23 (dd, $J = 13.4, 8.0$ Hz, 4H), 4.69 (dt, $J = 8.0, 4.1$ Hz, 1H), 2.80-2.68 (m, 2H), 2.16 – 2.00 (m, 2H), 1.98 (d, $J = 3.3$ Hz, 1H).

1-(3-bromophenyl)-3-phenylpropan-1-ol(4j):

^1H NMR (600 MHz, CDCl_3): δ 7.54 (s, 1H), 7.43 (d, $J = 7.8$ Hz, 1H), 7.34 – 7.27 (m, 3H), 7.26 – 7.20 (m, 4H), 4.68 (dt, $J = 8.2, 4.4$ Hz, 1H), 2.81 – 2.67 (m, 2H), 2.16 – 1.97 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 147.07, 141.55, 130.77, 130.22, 129.15, 128.59, 128.55, 126.11, 124.63, 122.77, 73.26, 40.61, 32.03.

3-phenyl-1-(p-tolyl)propan-1-ol(4l):

^1H NMR (600 MHz, CDCl_3): δ 7.31 (t, $J = 7.6$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.21 (dd, $J = 16.2, 7.7$ Hz, 5H), 4.68 (t, $J = 5.2$ Hz, 1H), 2.80 – 2.66 (m, 2H), 2.39 (s, 3H), 2.20 – 2.02 (m, 2H), 1.91 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 141.97, 141.69, 137.45, 129.31, 128.56, 128.49, 126.02, 125.94, 73.85, 40.47, 32.21, 21.24.

3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-ol(4m):

^1H NMR (600 MHz, CDCl_3): δ 7.61 (d, $J = 8.1$ Hz, 2H), 7.46 (d, $J = 8.2$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.20 (t, $J = 8.1$ Hz, 3H), 4.76 (dt, $J = 8.1, 4.3$ Hz, 1H), 2.79 – 2.67 (m, 2H), 2.15 – 2.00 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 148.65, 141.45, 128.63, 128.54, 126.29, 126.17, 125.61, 125.58, 125.56, 125.53, 73.29, 40.69, 31.97.

1-(naphthalen-2-yl)-3-phenylpropan-1-ol(4p):

^1H NMR (600 MHz, CDCl_3): δ 7.88 – 7.77 (m, 4H), 7.59 – 7.48 (m, 3H), 7.39 – 7.21 (m, 5H), 4.89 (dt, $J = 7.9, 3.1$ Hz, 1H), 2.82 – 2.70 (m, 2H), 2.30 – 2.15 (m, 2H), 2.03 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 142.01, 141.86, 133.41, 133.15, 128.59, 128.54, 128.52, 128.06, 127.83, 126.32, 126.01, 124.82, 124.17, 74.12, 40.46, 32.18.

1-(4-methoxyphenyl)-3-phenylpropan-1-ol(4q):

^1H NMR (600 MHz, CDCl_3): δ 7.32 – 7.28 (m, 4H), 7.21 (d, $J = 7.1$ Hz, 3H), 6.92 (d, $J = 8.7$ Hz, 2H), 4.66 (t, $J = 6.6$ Hz, 1H), 3.83 (s, 3H), 2.76 – 2.64 (m, 2H), 2.20 – 2.00 (m, 2H), 1.86 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 159.24, 141.95, 136.80, 128.56, 127.34, 125.96, 114.02, 73.63, 55.42, 40.46, 32.25.

3-(3-methoxyphenyl)-1-phenylpropan-1-ol (4r):

^1H NMR (500 MHz, CDCl_3): δ 7.25 – 7.06 (m, 6H), 6.70 – 6.61 (m, 3H), 4.57 – 4.51 (m, 1H), 3.66 (s, 3H), 2.65 – 2.48 (m, 2H), 2.14 (s, 1H), 1.95 (dtd, $J = 49.6, 14.1, 7.3$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ 159.68, 143.52, 129.38, 128.52, 127.63, 125.97, 120.93, 114.26, 111.24, 77.09, 76.90, 73.82, 55.16, 40.37, 32.14.

1-phenyl-3-(m-tolyl)propan-1-ol (4s):

^1H NMR (600 MHz, CDCl_3): δ 7.36 (d, $J = 4.3$ Hz, 4H), 7.32 – 7.27 (m, 1H), 7.17 (t, $J = 7.4$ Hz, 1H), 7.03 – 6.98 (m, 3H), 4.72 – 4.68 (m, 1H), 2.75–2.61 (m, 2H), 2.32 (s, 3H), 2.16 – 2.00 (m, 3H), 1.85 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 144.71, 141.83, 138.08, 129.39, 128.65, 128.42, 127.77, 126.73, 126.06, 125.56, 74.10, 40.63, 32.12, 21.53.

1-phenyl-3-(pyridin-3-yl)propan-1-ol(4t):

^1H NMR (600 MHz, CDCl_3): δ 8.43 – 8.38 (m, 2H), 7.52 (dt, $J = 7.9, 2.0$ Hz, 1H), 7.37 (d, $J = 4.5$ Hz, 4H), 7.32 – 7.28 (m, 1H), 7.21 (dd, $J = 7.8, 4.8$ Hz, 1H), 4.70 (dd, $J = 8.0, 5.2$ Hz, 1H), 2.80–2.68 (m, 3H), 2.17–1.99 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 147.44, 144.72, 137.43, 136.21, 128.79, 127.94, 126.10, 73.59, 40.33, 29.39.

3-(naphthalen-1-yl)-1-phenylpropan-1-ol(4u):

^1H NMR (600 MHz, CDCl_3) : δ 8.02 – 7.99 (m, 1H), 7.89 – 7.85 (m, 1H), 7.74 (d, $J = 8.1$ Hz, 1H), 7.53 – 7.47 (m, 3H), 7.43 – 7.35 (m, 6H), 7.34 – 7.30 (m, 1H), 4.83 (dt, $J = 8.0, 4.2$ Hz, 1H), 3.31 – 3.10 (m, 2H), 2.32 – 2.15 (m, 2H), 1.96 (d, $J = 3.3$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 144.65, 138.12, 134.04, 131.96, 128.89, 128.69, 127.85, 126.82, 126.09, 125.93, 125.68, 125.59, 123.91, 74.35, 39.98, 29.26.

3-(3-chlorophenyl)-1-phenylpropan-1-ol(4z):

^1H NMR (600 MHz, CDCl_3): δ 7.36 (d, $J = 6.5$ Hz, 4H), 7.29 (ddd, $J = 8.5, 5.8, 2.1$ Hz, 1H), 7.22 – 7.15 (m, 3H), 7.07 (dt, $J = 7.4, 1.5$ Hz, 1H), 4.68 (t, $J = 6.4$ Hz, 1H), 2.77 – 2.62 (m, 2H), 2.15 – 1.97 (m, 2H), 1.89 (s, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 144.49, 143.99, 134.25, 129.75, 128.72, 127.91, 126.19, 126.00, 73.84, 40.30, 31.85.

3-(4-chlorophenyl)-1-phenylpropan-1-ol(4zb):

^1H NMR (600 MHz, CDCl_3): δ 7.41 – 7.35 (m, 4H), 7.32 (t, $J = 7.6$ Hz, 1H), 7.29 – 7.25 (m, 2H), 7.14 (d, $J = 8.3$ Hz, 2H), 4.70 (ddd, $J = 8.2, 5.2, 3.4$ Hz, 1H), 2.78 – 2.63 (m, 2H), 2.17 – 1.98 (m, 2H), 1.90 (d, $J = 3.3$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 144.53, 140.34, 131.69, 129.92, 128.71, 128.60, 127.89, 126.01, 73.85, 40.44, 31.51.

1-phenyl-3-(p-tolyl)propan-1-ol(4ze):

^1H NMR (600 MHz, CDCl_3): δ 7.40 – 7.35 (m, 4H), 7.30 (tt, J = 6.5, 3.0 Hz, 1H), 7.12 (s, 4H), 4.71 – 4.67 (m, 1H), 2.76 – 2.62 (m, 2H), 2.35 (s, 3H), 2.17 – 2.00 (m, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 144.71, 135.38, 129.18, 128.60, 128.42, 127.70, 126.05, 73.98, 40.65, 21.10.

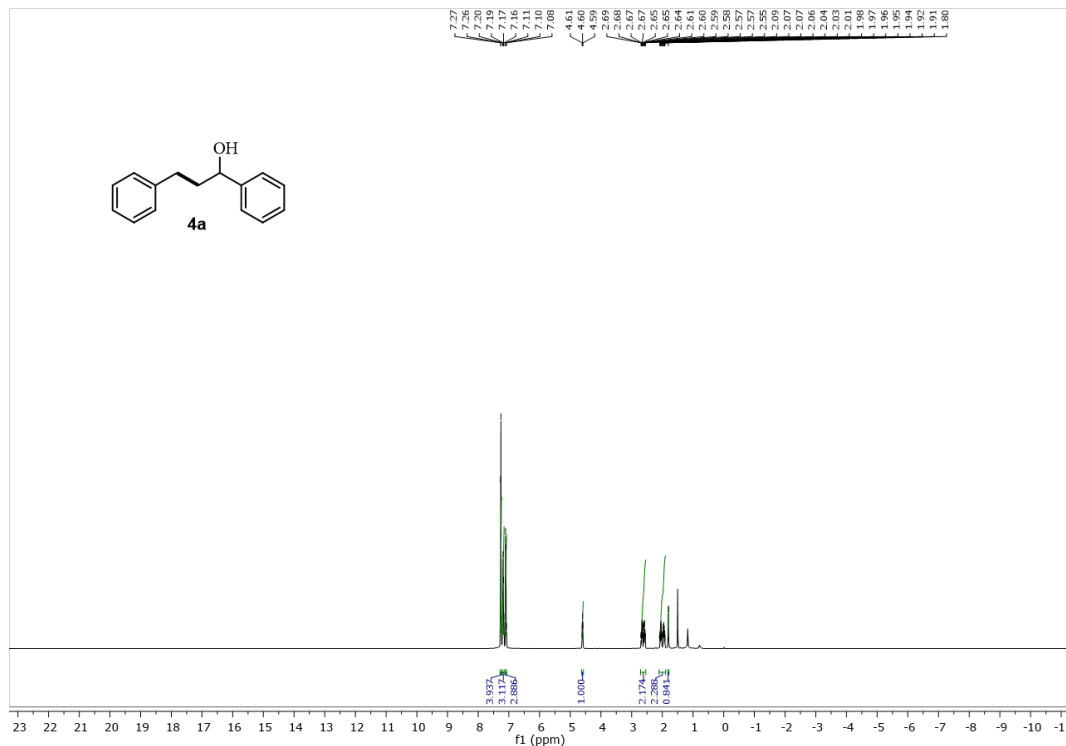


Figure S24. ^1H NMR spectra of 1,3-diphenylpropan-1-ol (4a) recorded in CDCl_3 .

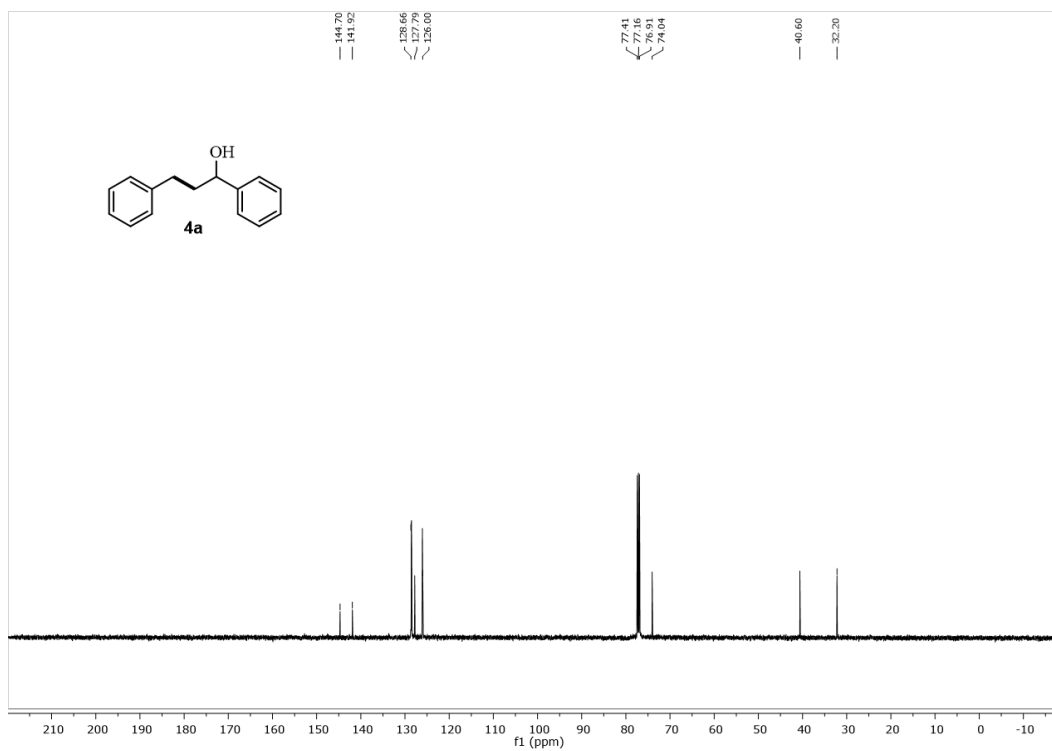


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 1,3-diphenylpropan-1-ol(**4a**) recorded in CDCl_3 .

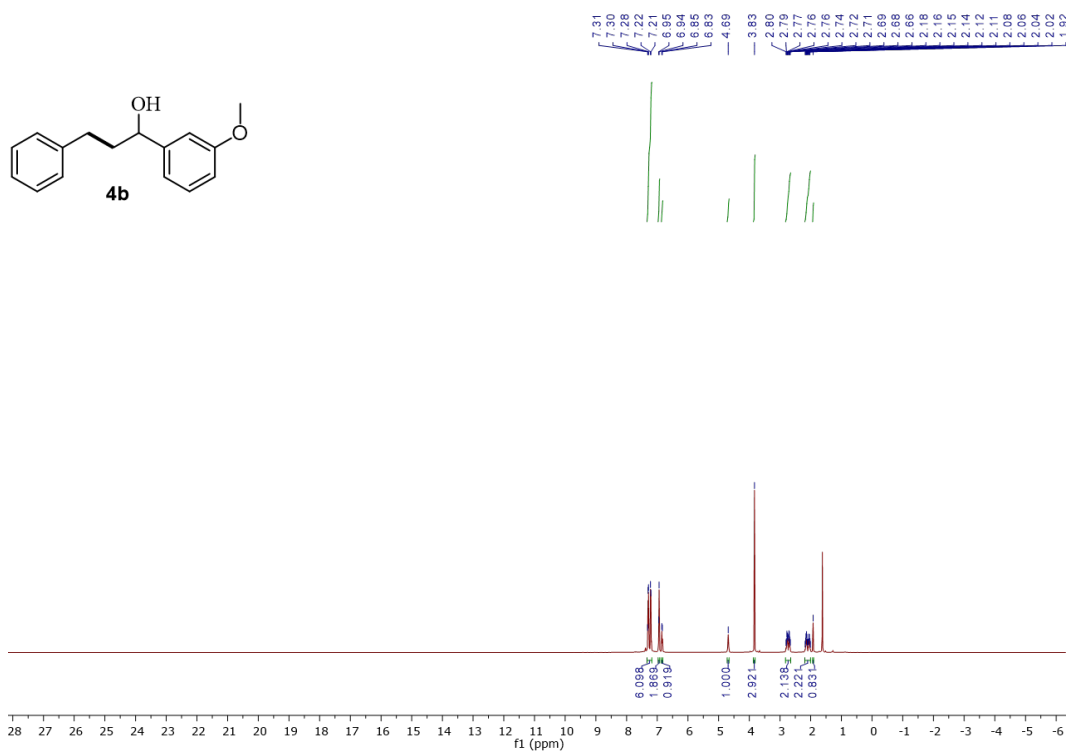


Figure S26: ^1H NMR spectra of 1-(3-methoxyphenyl)-3-phenylpropan-1-ol(**4b**) recorded in CDCl_3 .

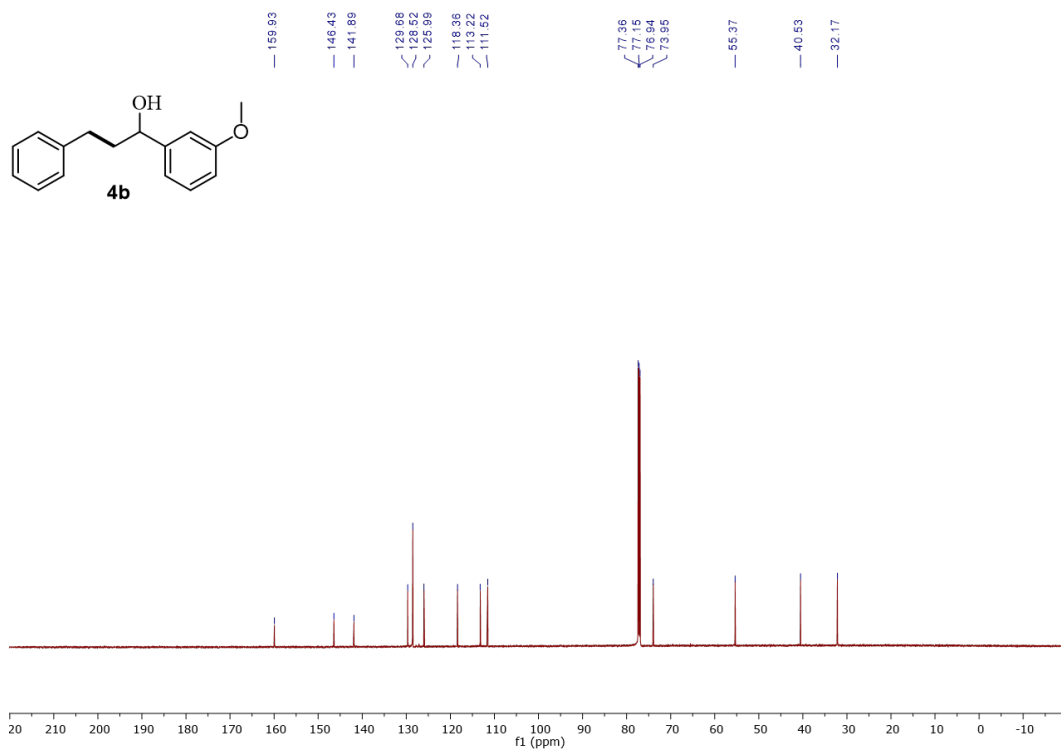


Figure S27: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 1-(3-methoxyphenyl)-3-phenylpropan-1-ol(**4b**) recorded in CDCl_3 .

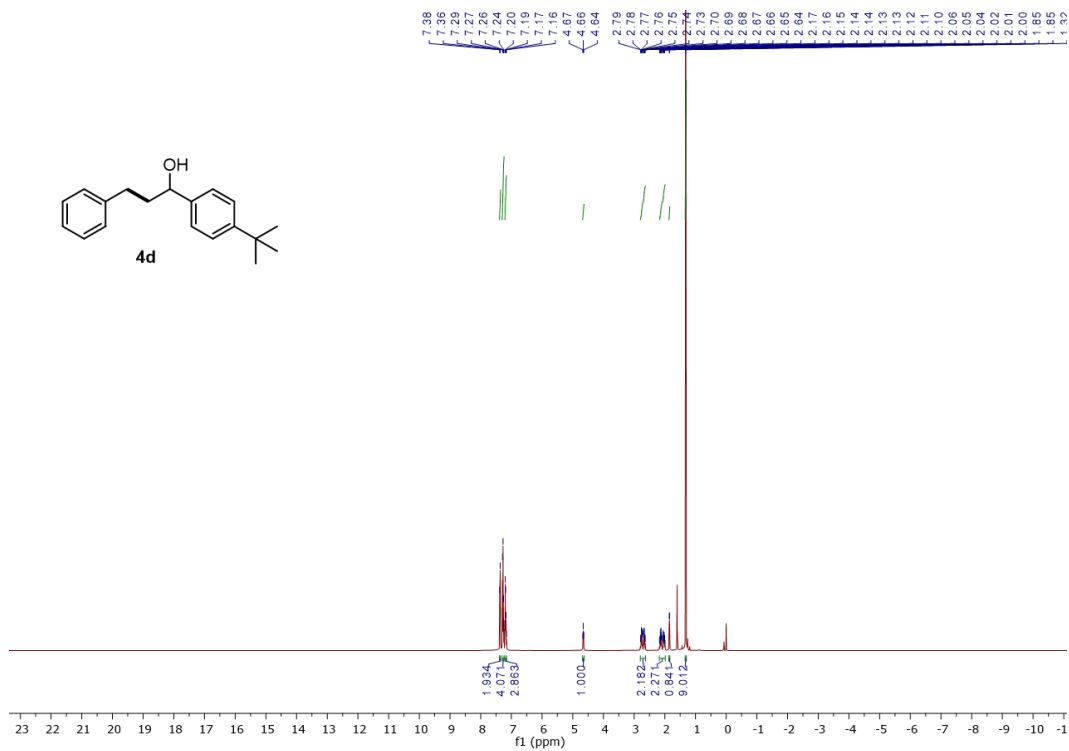


Figure S28: ^1H NMR spectra of 1-(4-(tert-butyl)phenyl)-3-phenylpropan-1-ol(**4d**) recorded in CDCl_3 .

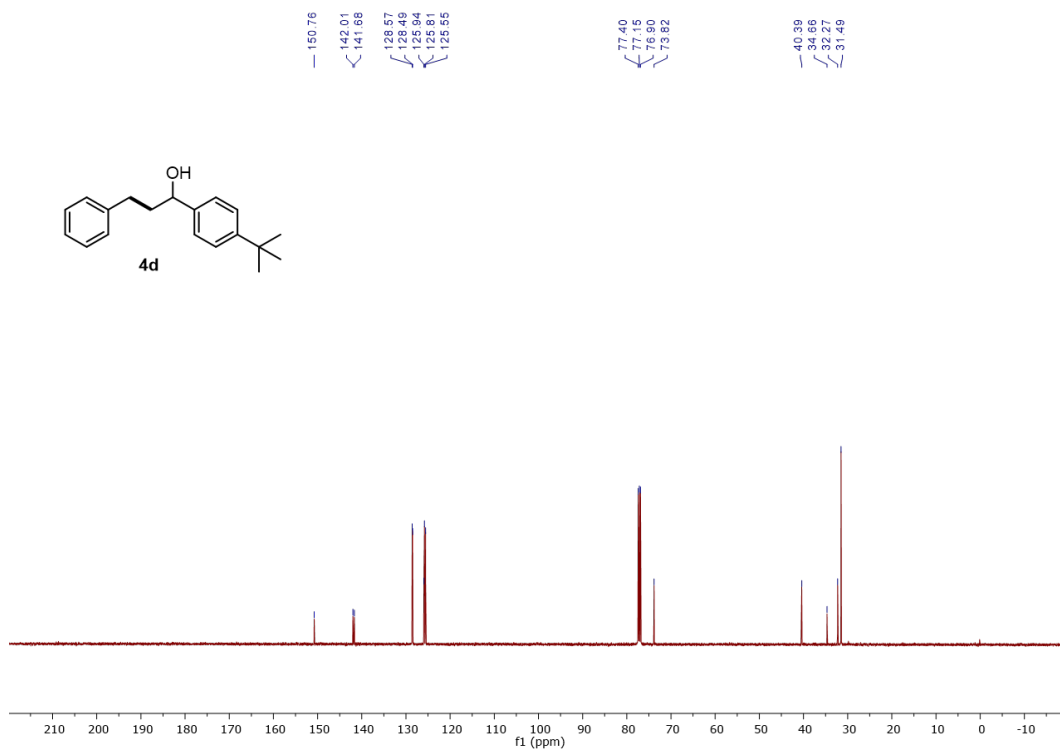


Figure S29: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 1-(4-(tert-butyl)phenyl)-3-phenylpropan-1-ol(**4d**) recorded in CDCl_3 .

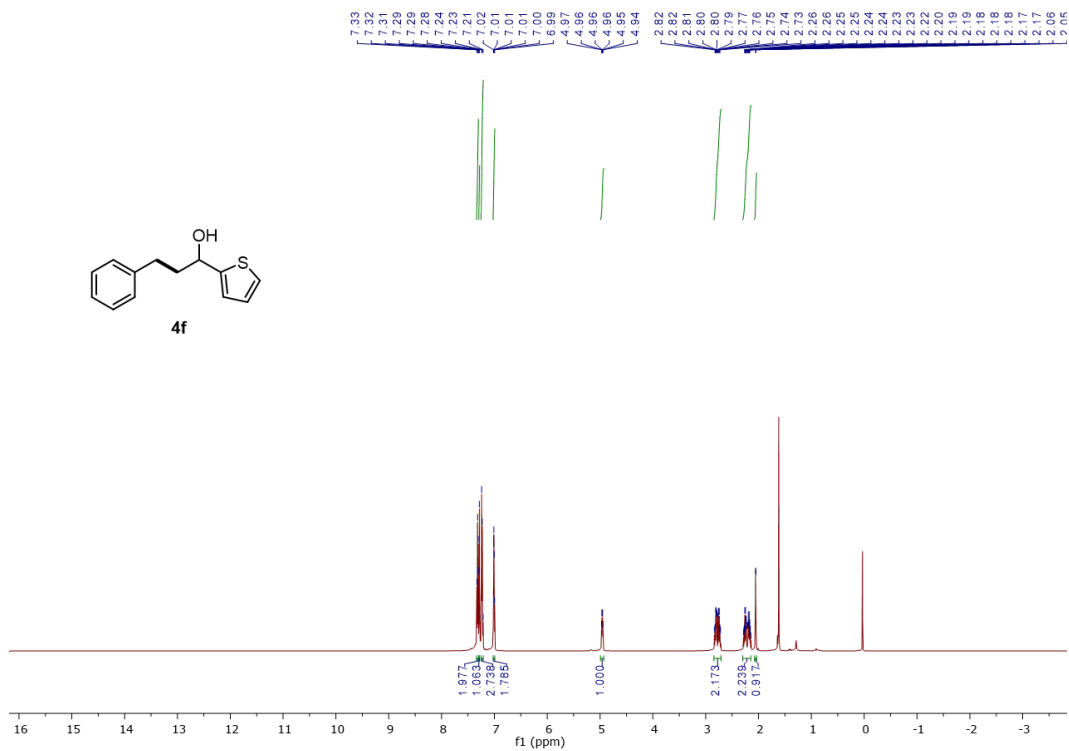


Figure S30: ^1H NMR spectra of 3-phenyl-1-(thiophen-2-yl)propan-1-ol(**4f**) recorded in CDCl_3 .

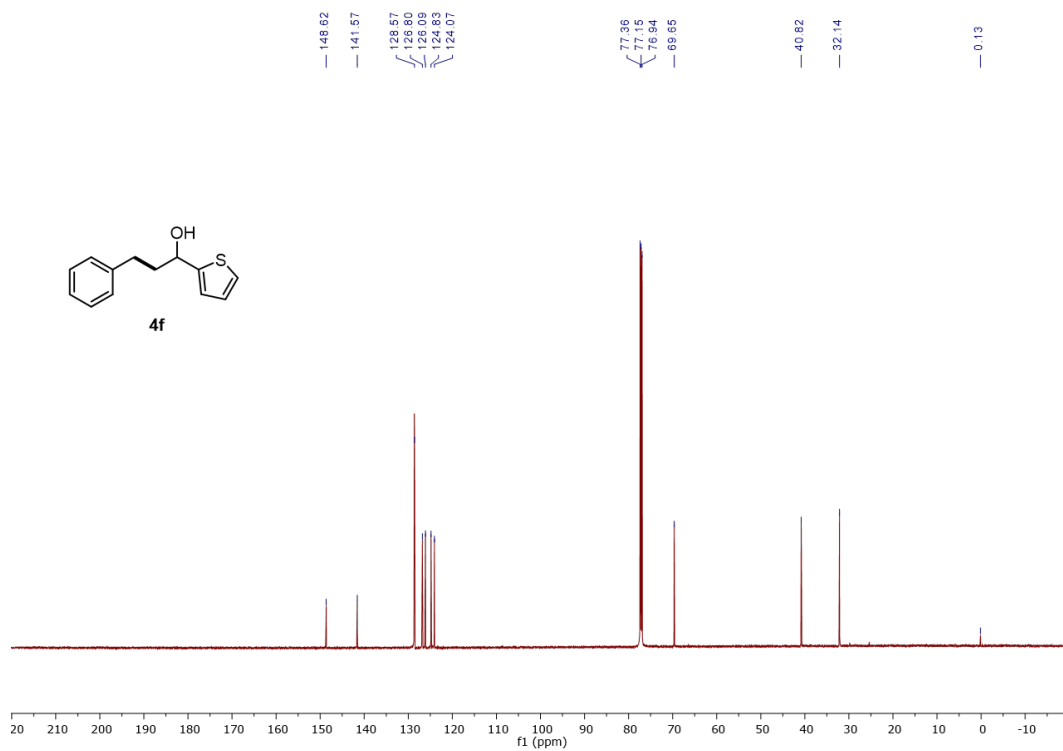


Figure S31: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 3-phenyl-1-(thiophen-2-yl)propan-1-ol(**4f**) recorded in CDCl_3 .

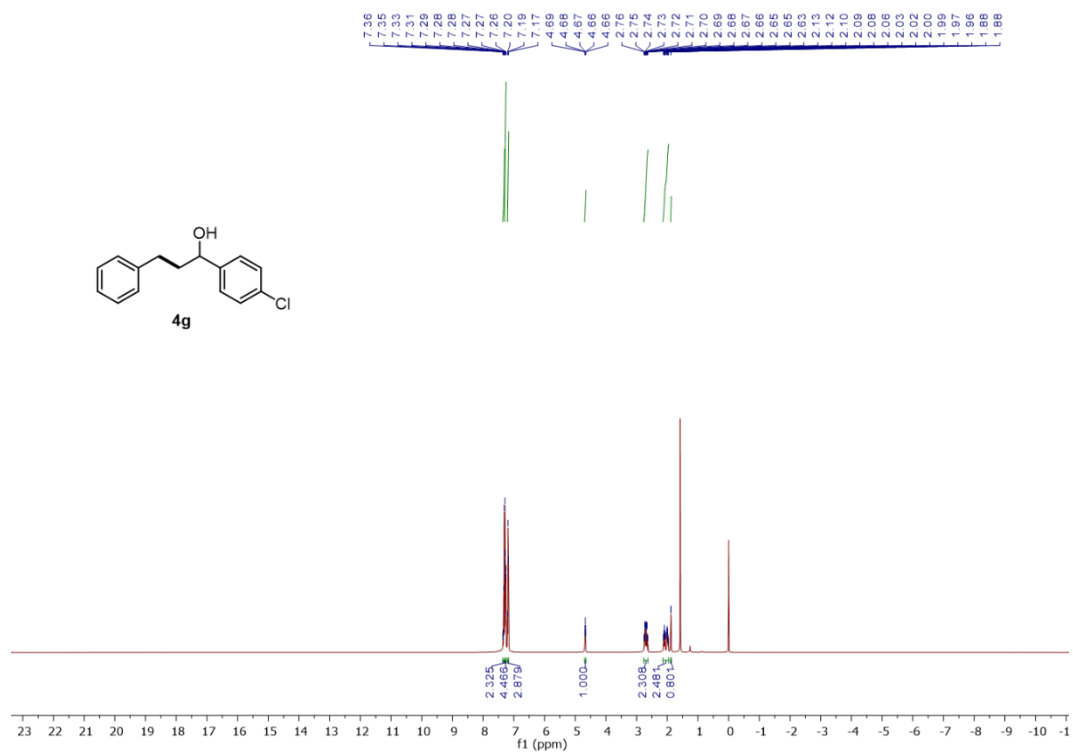


Figure S32: ^1H NMR spectra of 1-(4-chlorophenyl)-3-phenylpropan-1-ol(**4g**) recorded in CDCl_3 .

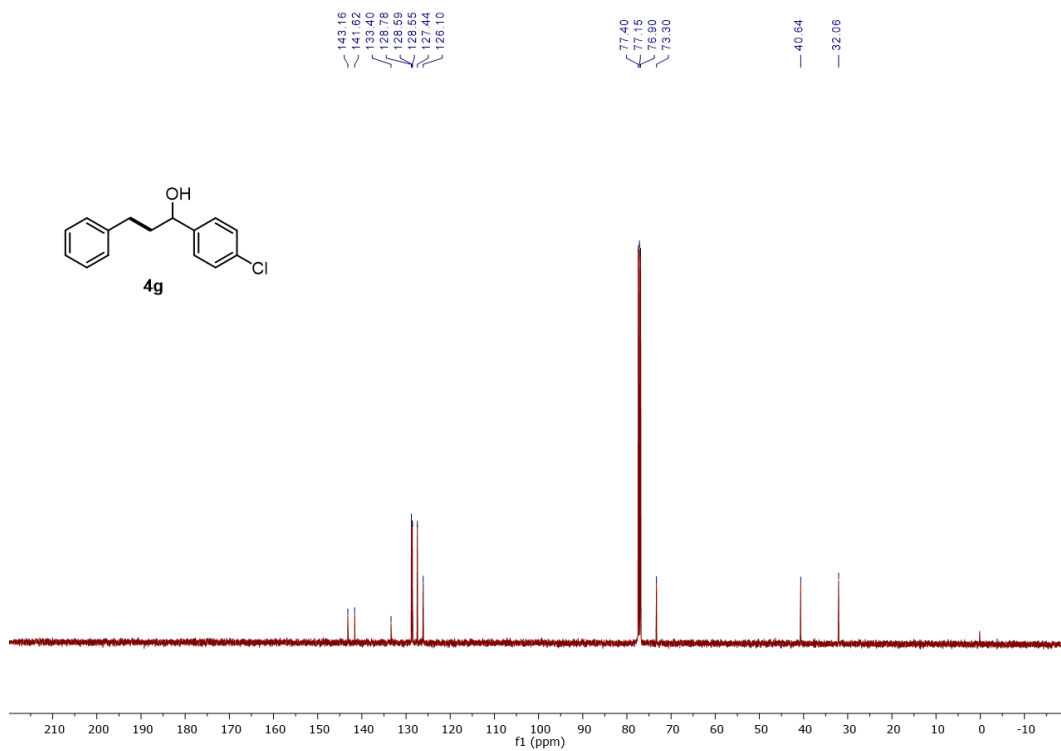


Figure S33: ^{13}C $\{^1\text{H}\}$ NMR spectra of 1-(4-chlorophenyl)-3-phenylpropan-1-ol (**4g**) recorded in CDCl_3 .

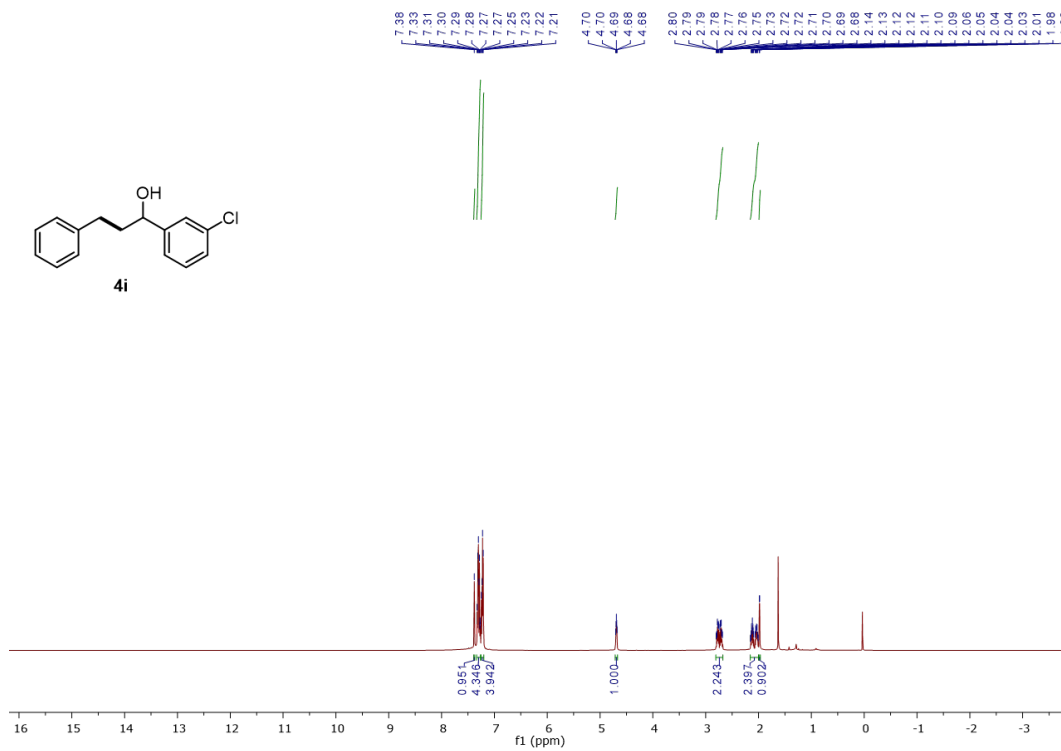


Figure S34: ^1H NMR spectra of 1-(3-chlorophenyl)-3-phenylpropan-1-ol (**4i**) recorded in CDCl_3 .

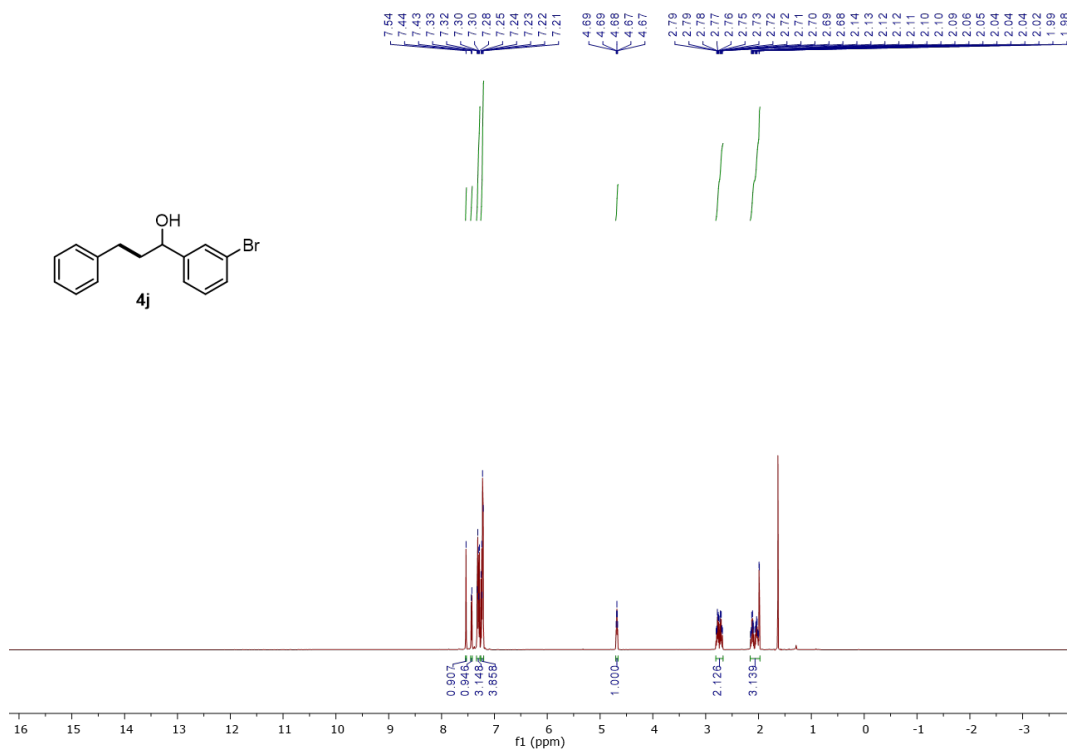


Figure S35: ^1H NMR spectra of 1-(3-bromophenyl)-3-phenylpropan-1-ol(**4j**) recorded in CDCl₃.

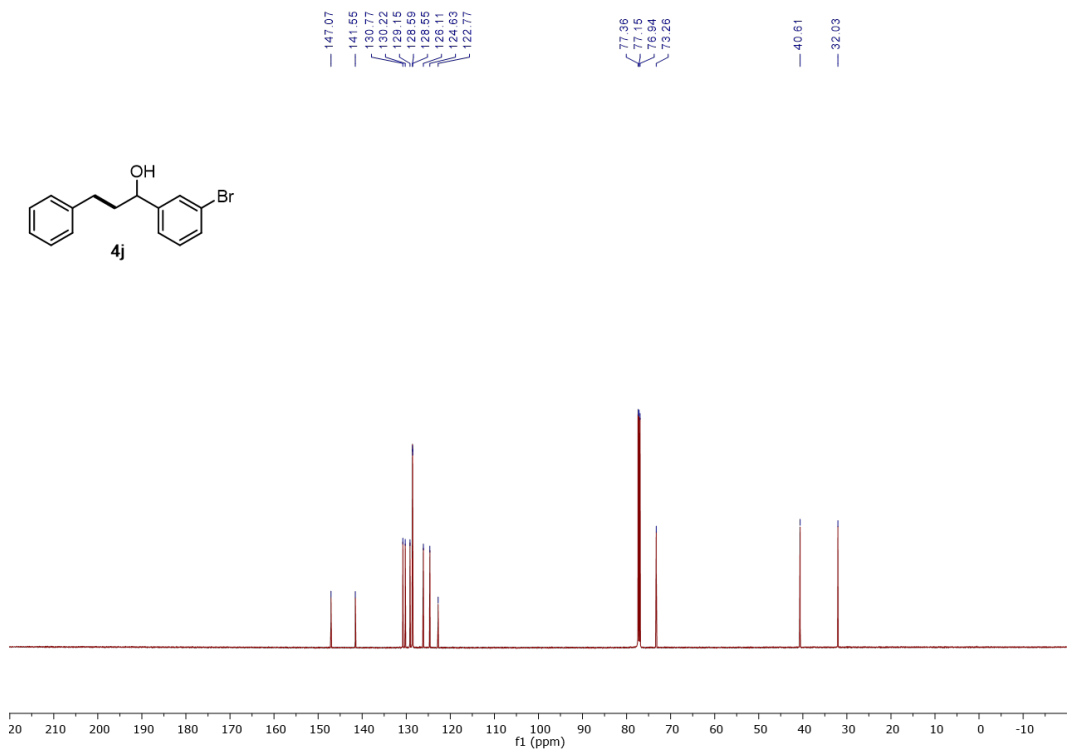


Figure S36: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 1-(3-bromophenyl)-3-phenylpropan-1-ol(**4j**) recorded in CDCl₃.

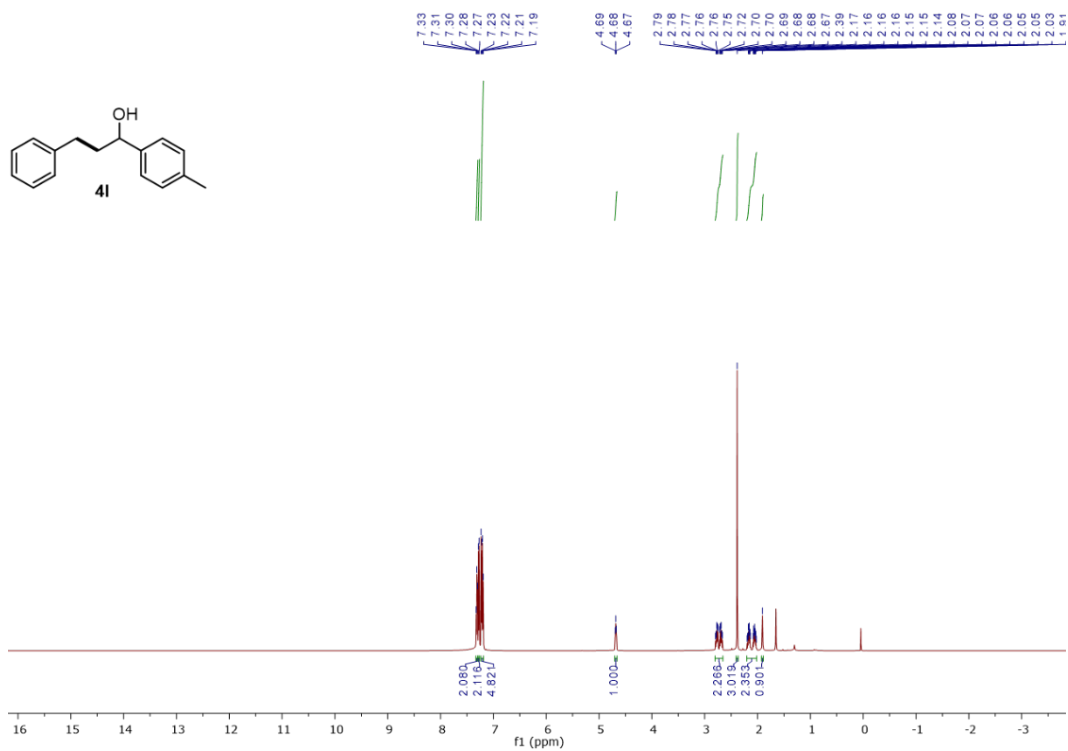


Figure S37: ^1H NMR spectra of 3-phenyl-1-(p-tolyl)propan-1-ol (**4I**) recorded in CDCl₃.

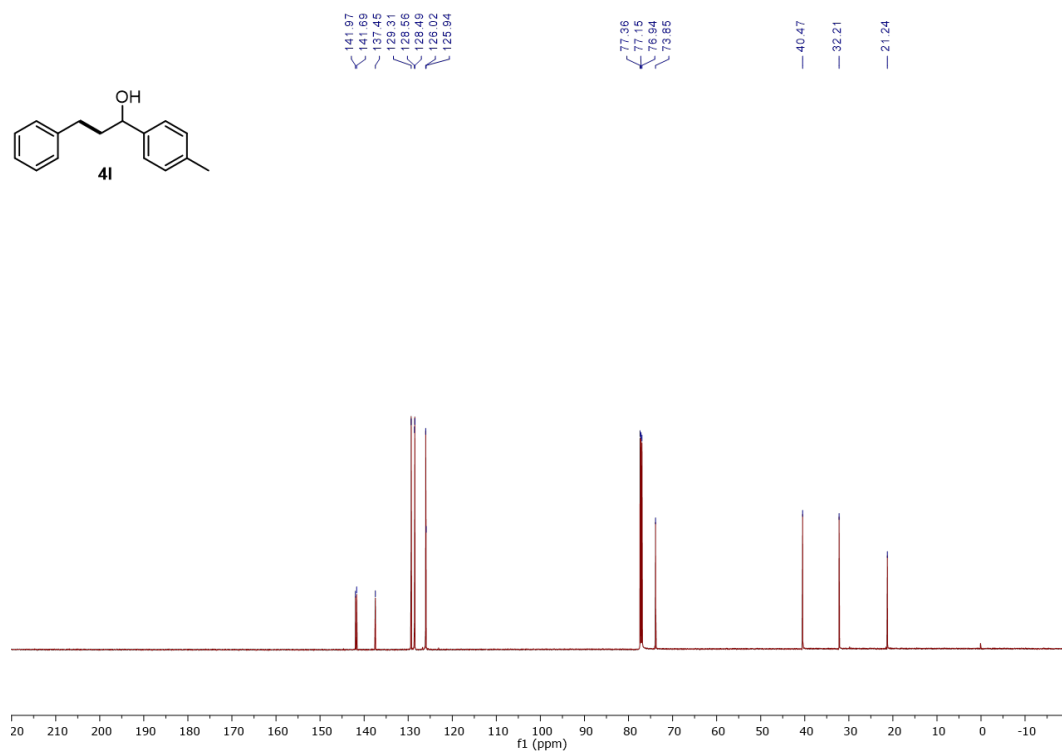


Figure S38: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 3-phenyl-1-(p-tolyl)propan-1-ol (**4I**) recorded in CDCl₃.

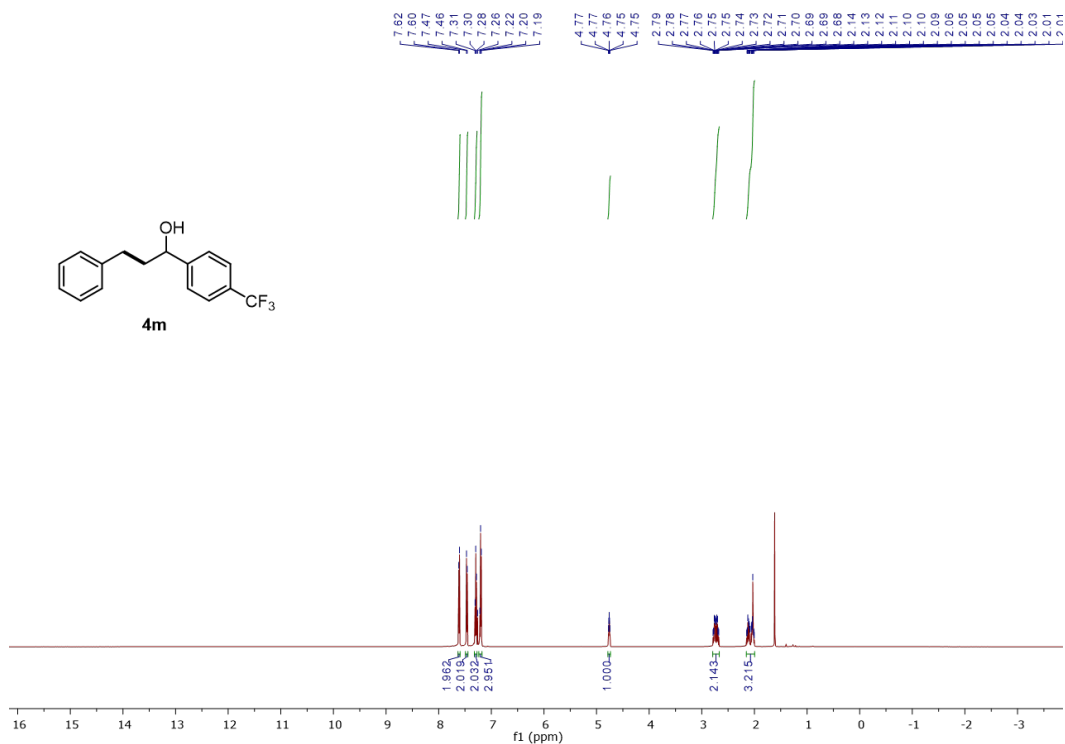


Figure S39: ¹H NMR spectra of 3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-ol(4m) recorded in CDCl₃.

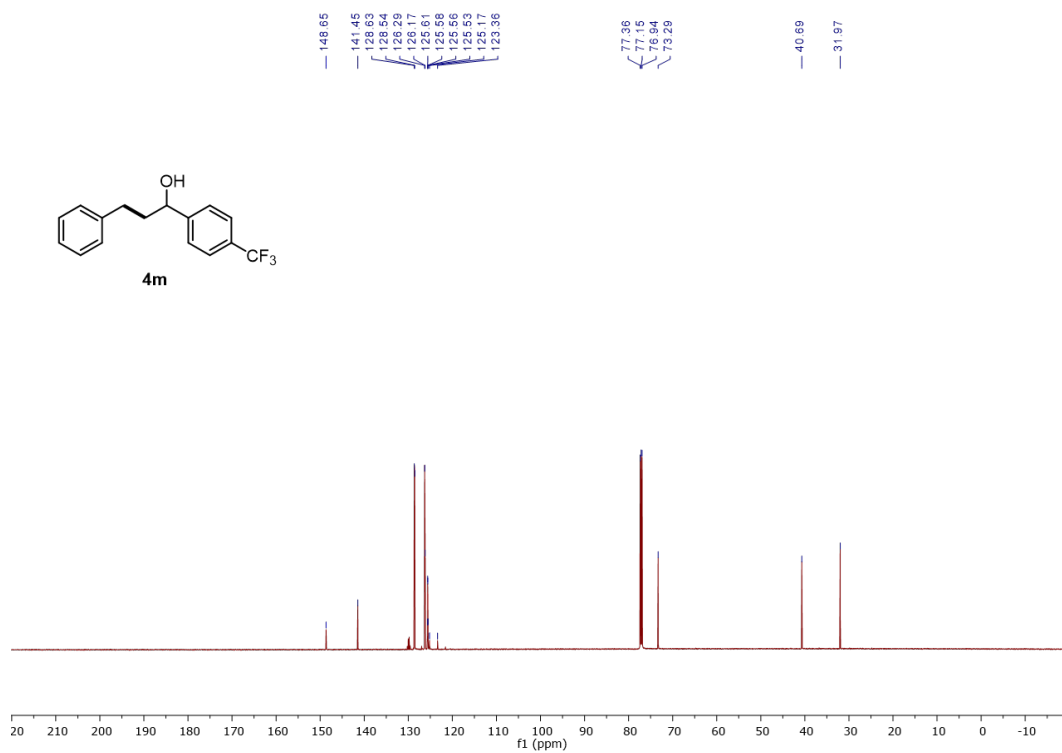


Figure S40: ¹³C{¹H} NMR spectra of 3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-ol(4m) recorded in CDCl₃.

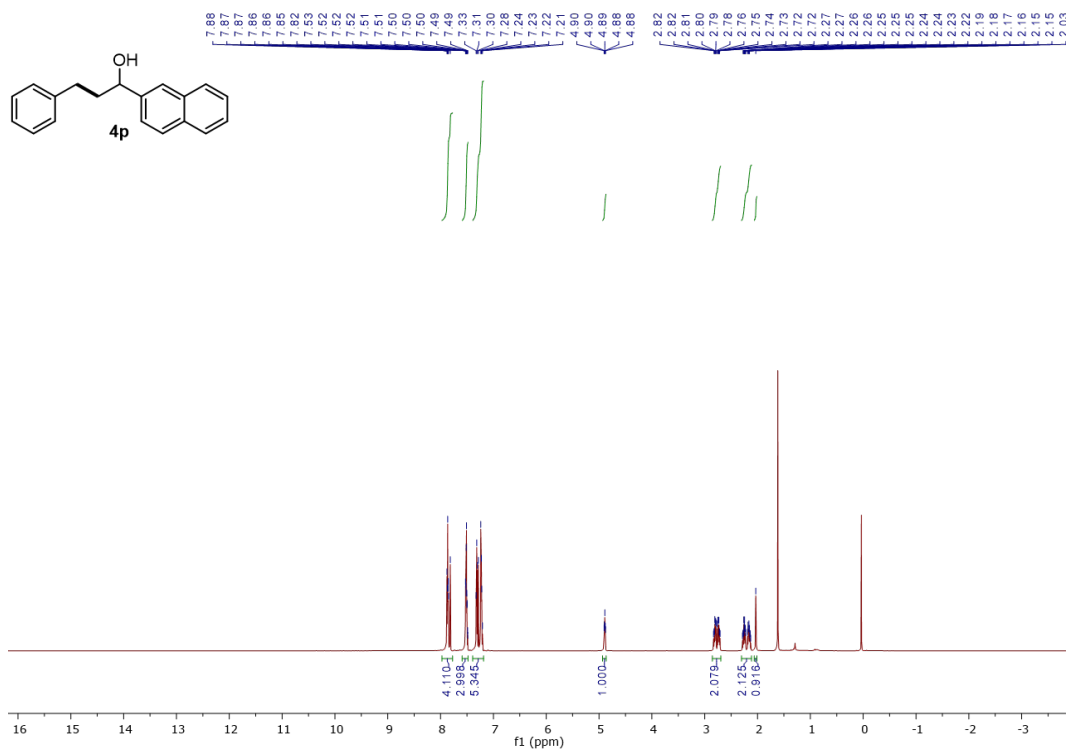


Figure S41: $^1\text{H NMR}$ spectra of 1-(naphthalen-2-yl)-3-phenylpropan-1-ol(**4p**) recorded in CDCl₃.

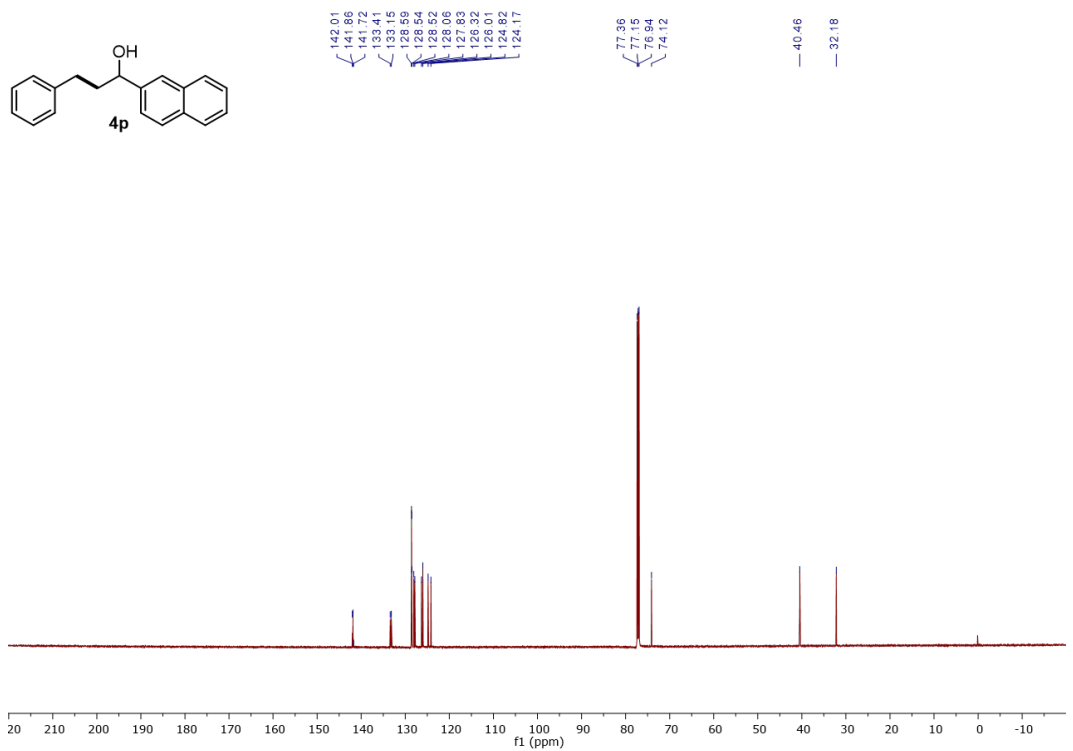


Figure S42: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 1-(naphthalen-2-yl)-3-phenylpropan-1-ol(**4p**) recorded in CDCl₃.

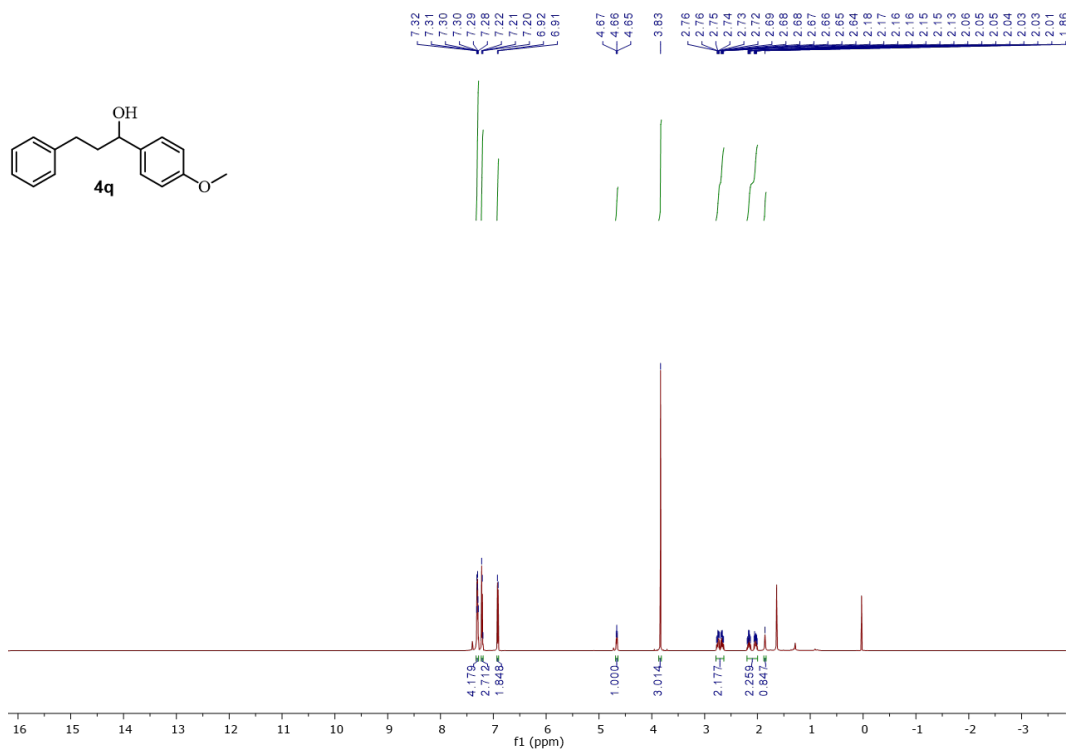


Figure S43: ¹H NMR spectra of 1-(4-methoxyphenyl)-3-phenylpropan-1-ol(**4q**) recorded in CDCl₃.

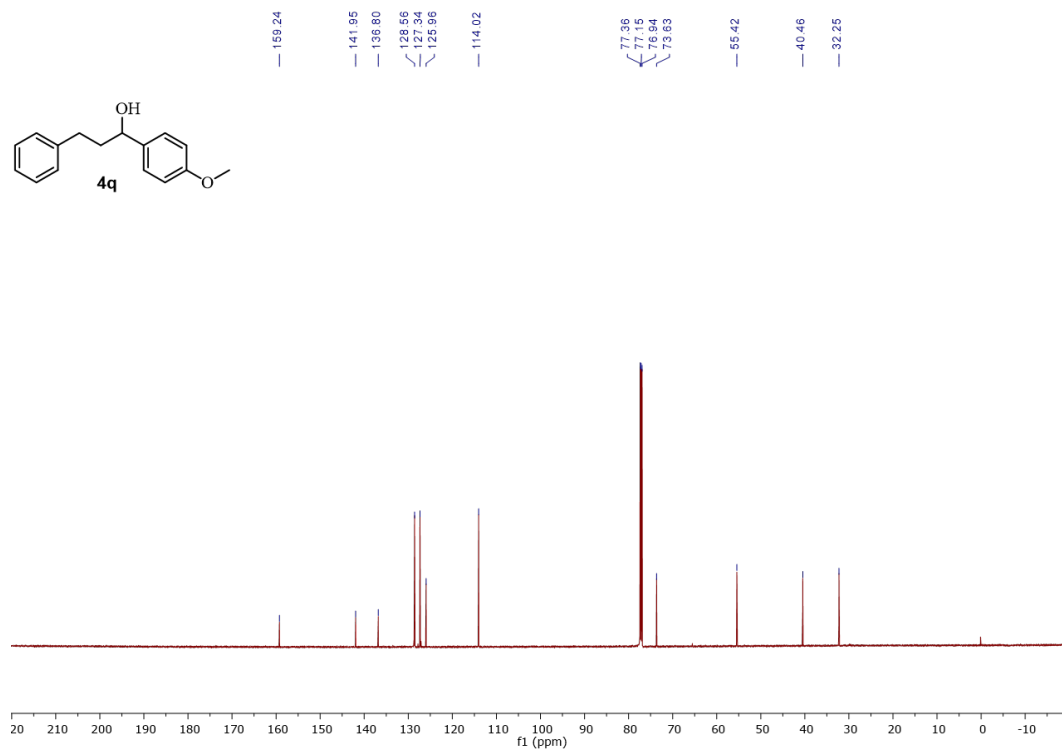


Figure S44: ¹³C{¹H} NMR spectra of 1-(4-methoxyphenyl)-3-phenylpropan-1-ol(**4q**) recorded in CDCl₃.

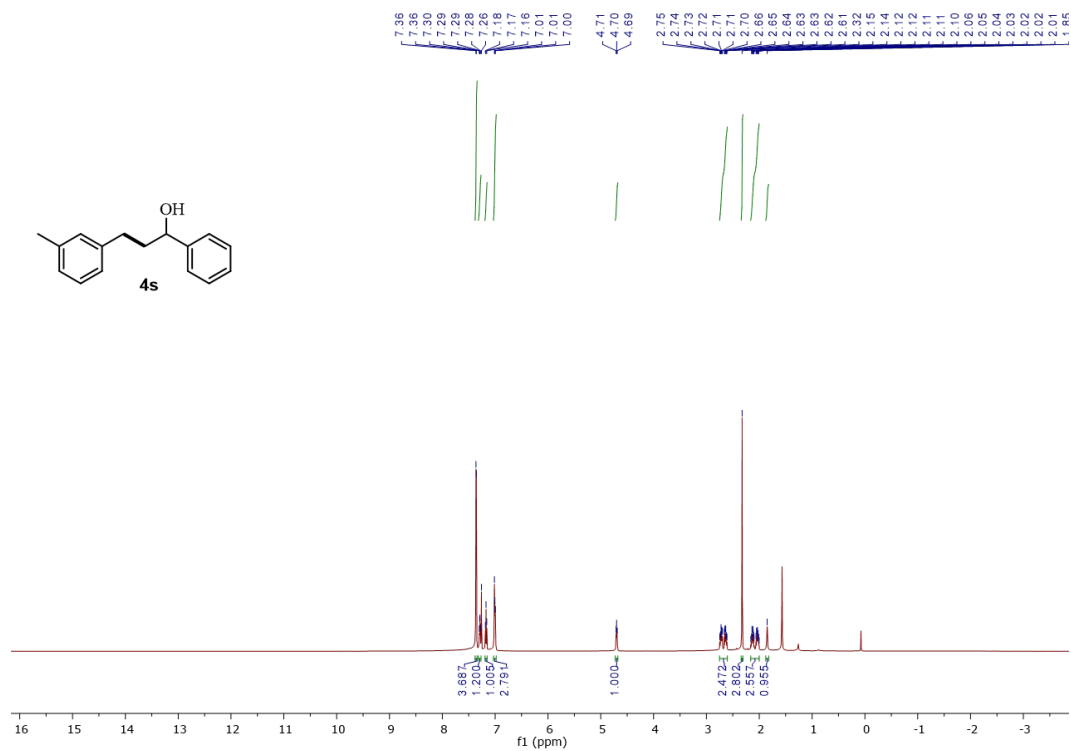


Figure S47: ¹H NMR spectra of 1-phenyl-3-(m-tolyl)propan-1-ol (**4s**) recorded in CDCl₃.

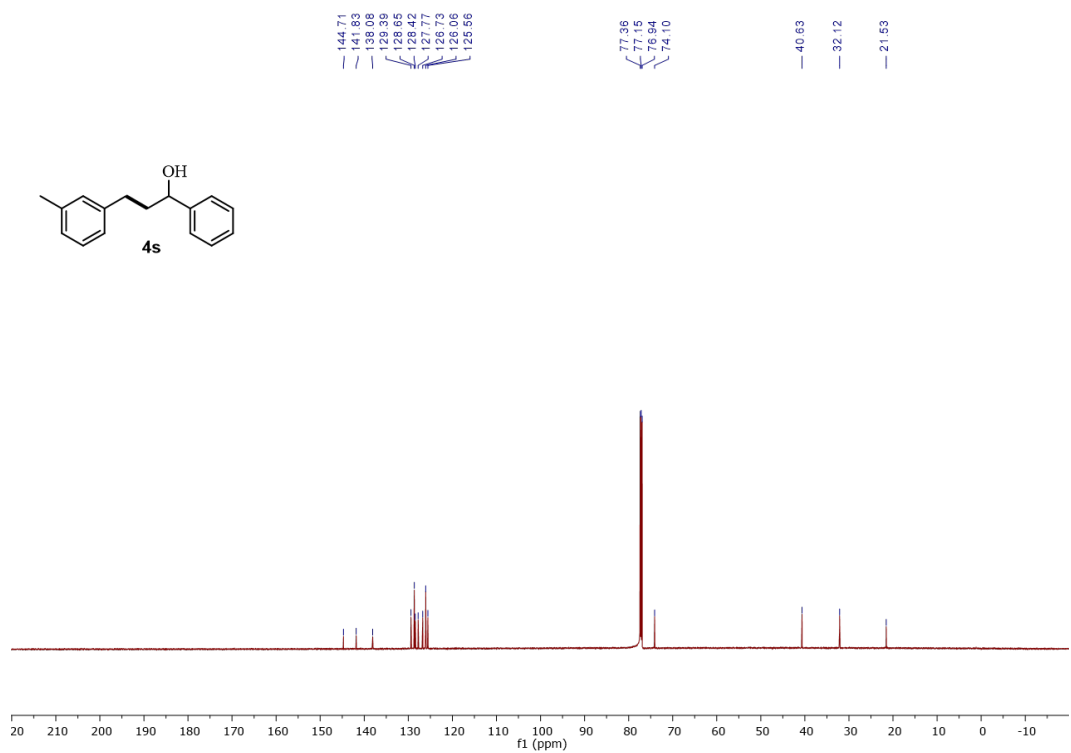


Figure S48: ¹³C{¹H} NMR spectra of 1-phenyl-3-(m-tolyl)propan-1-ol (**4s**) recorded in CDCl₃.

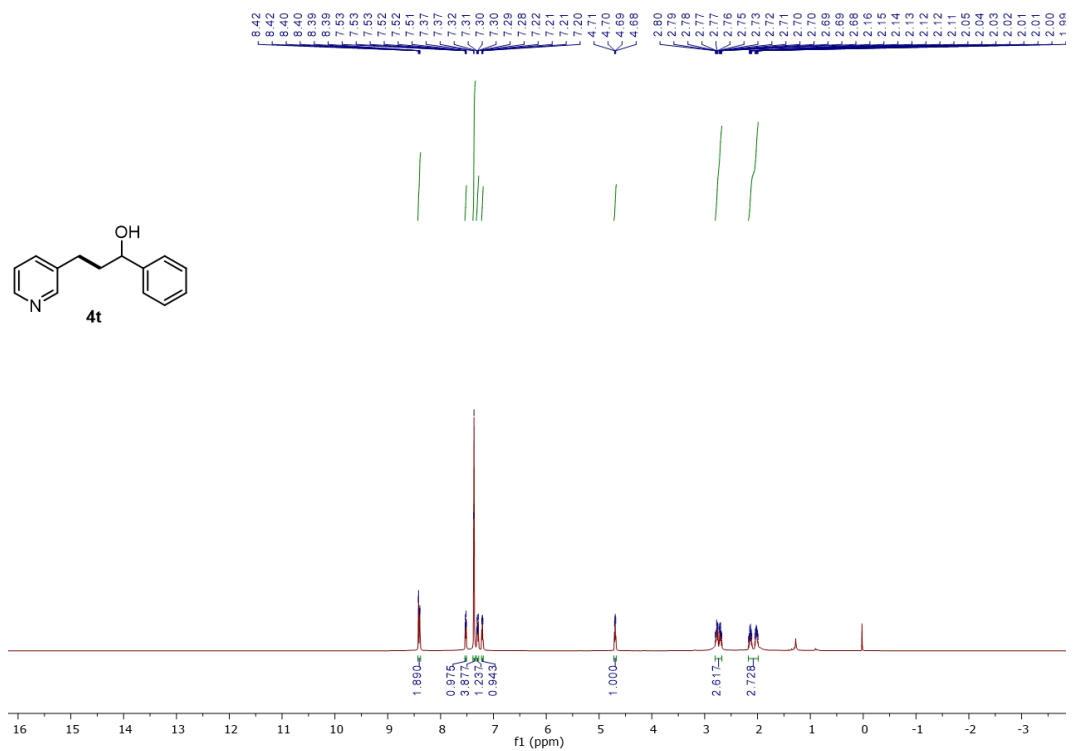


Figure S49: ^1H NMR spectra of 1-phenyl-3-(pyridin-3-yl)propan-1-ol(**4t**) recorded in CDCl₃.

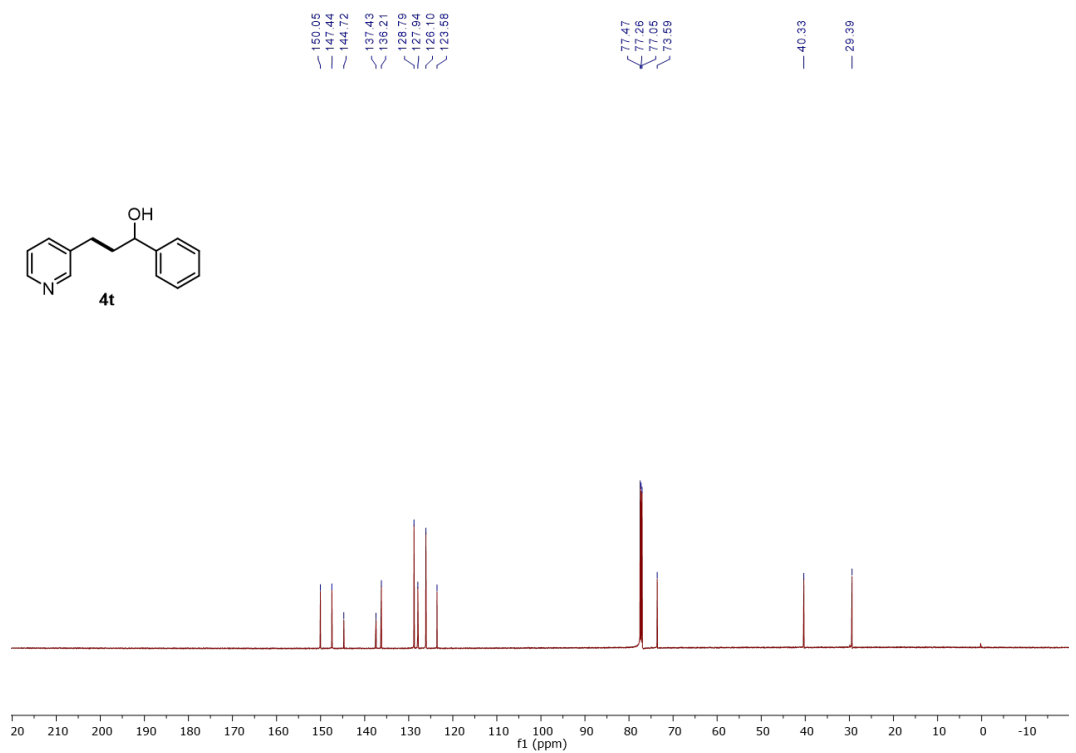


Figure S50: $^{13}\text{C}\{^1\text{H}\}$ NMR of 1-phenyl-3-(pyridin-3-yl)propan-1-ol(**4t**) recorded in CDCl₃.

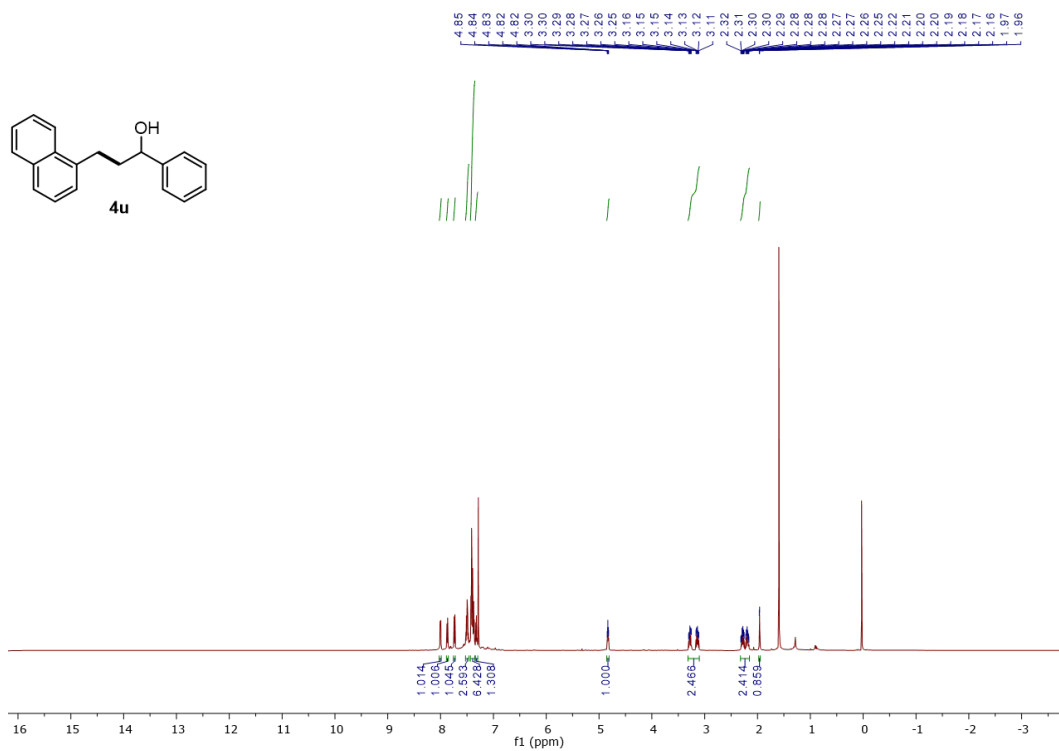


Figure S51: ^1H NMR spectra of 3-(naphthalen-1-yl)-1-phenylpropan-1-ol(**4u**) recorded in CDCl_3 .

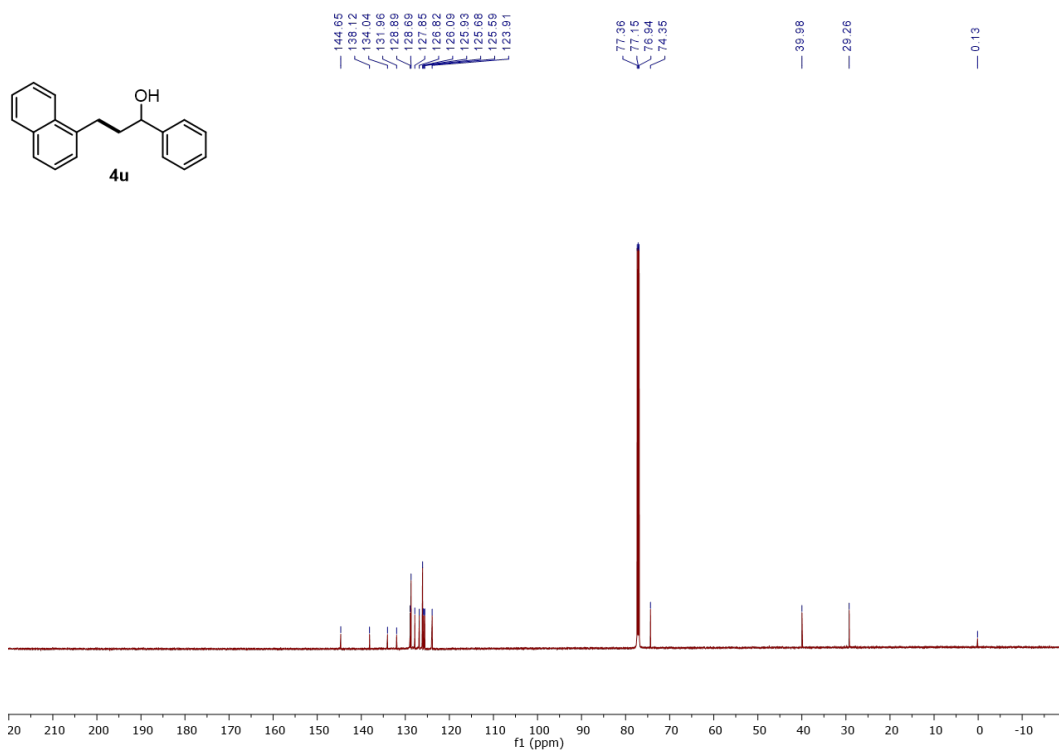


Figure S52: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 3-(naphthalen-1-yl)-1-phenylpropan-1-ol(**4u**) recorded in CDCl_3 .

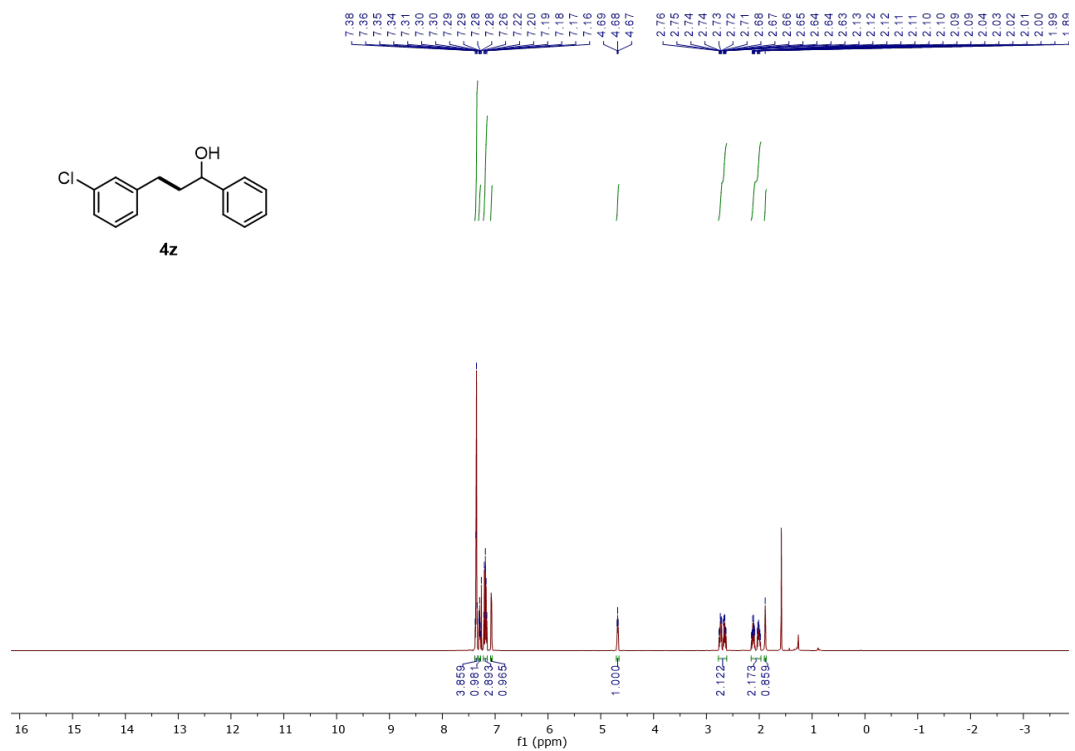


Figure S53: ^1H NMR spectra of 3-(3-chlorophenyl)-1-phenylpropan-1-ol(**4z**) recorded in CDCl₃.

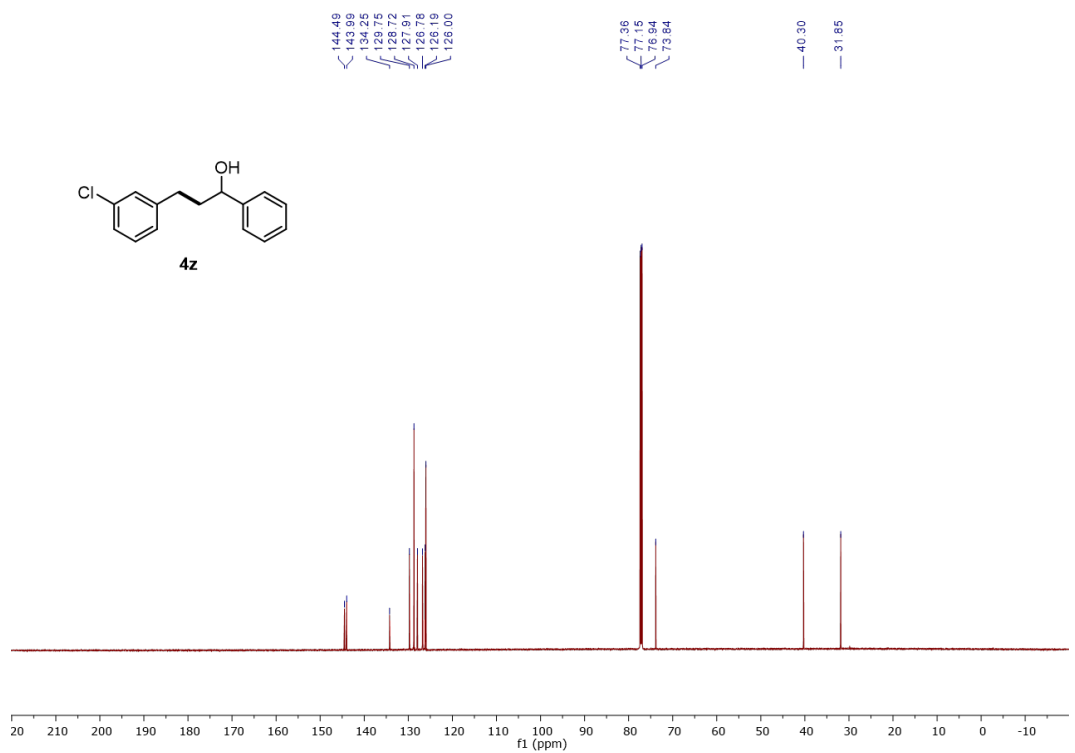


Figure S54: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 3-(3-chlorophenyl)-1-phenylpropan-1-ol(**4z**) recorded in CDCl₃.

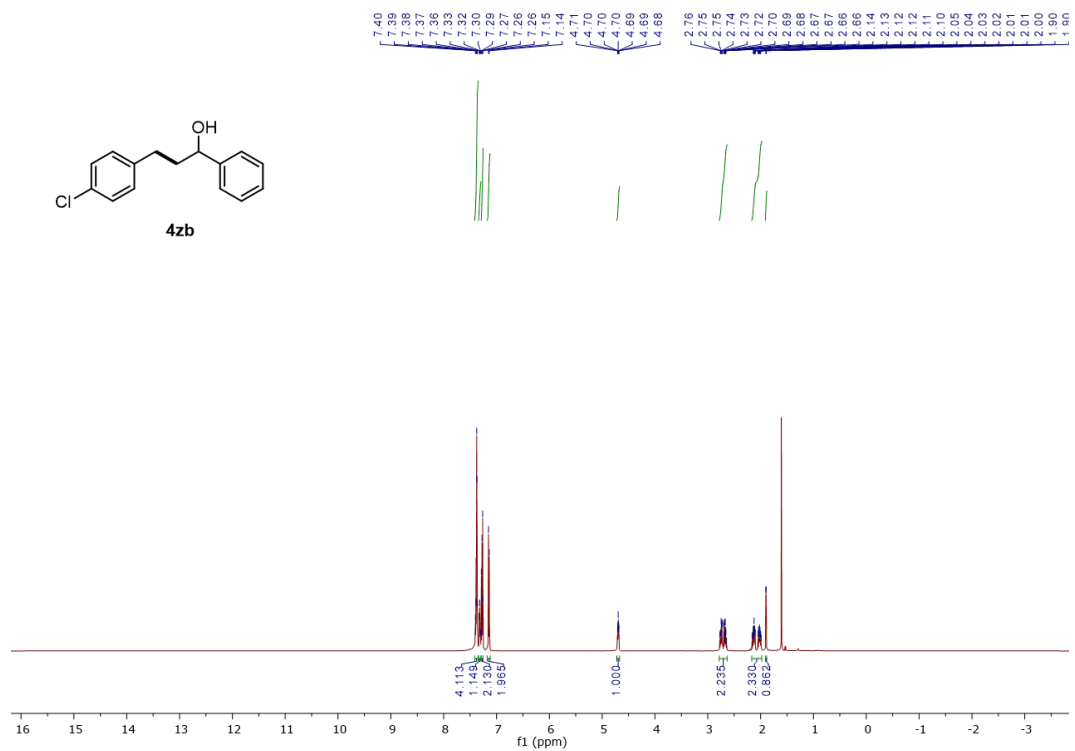


Figure S55: ^1H NMR spectra of 3-(4-chlorophenyl)-1-phenylpropan-1-ol (**4zb**) recorded in CDCl₃.

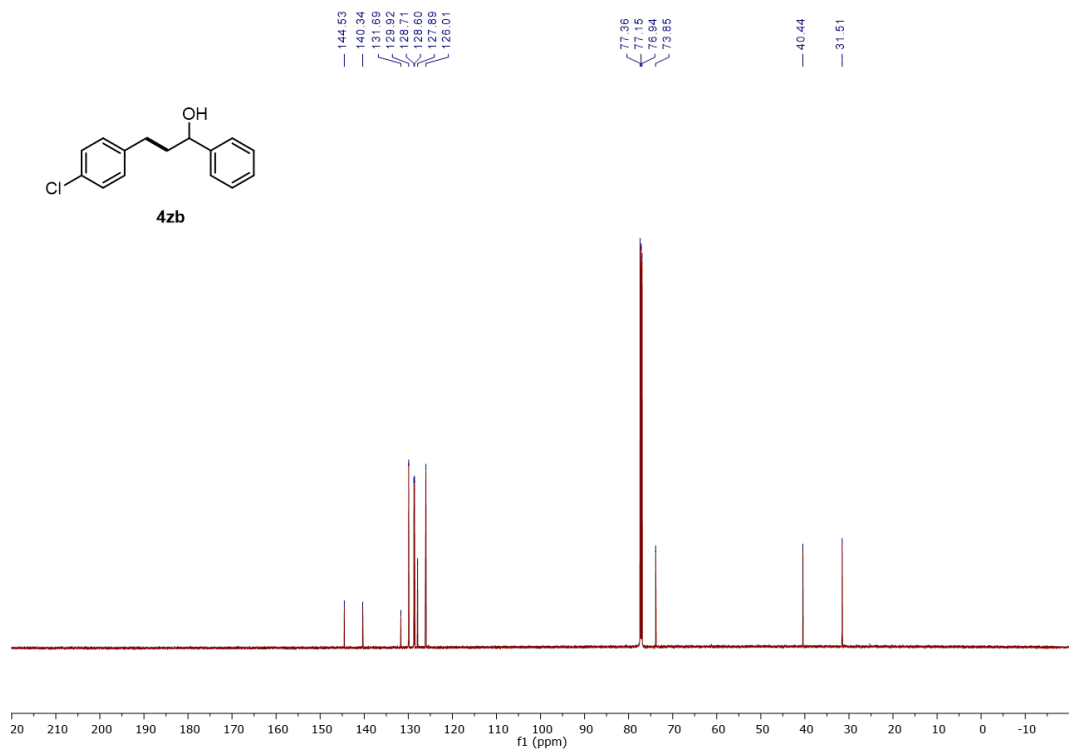


Figure S56: $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of 3-(4-chlorophenyl)-1-phenylpropan-1-ol (**4zb**) recorded in CDCl₃.

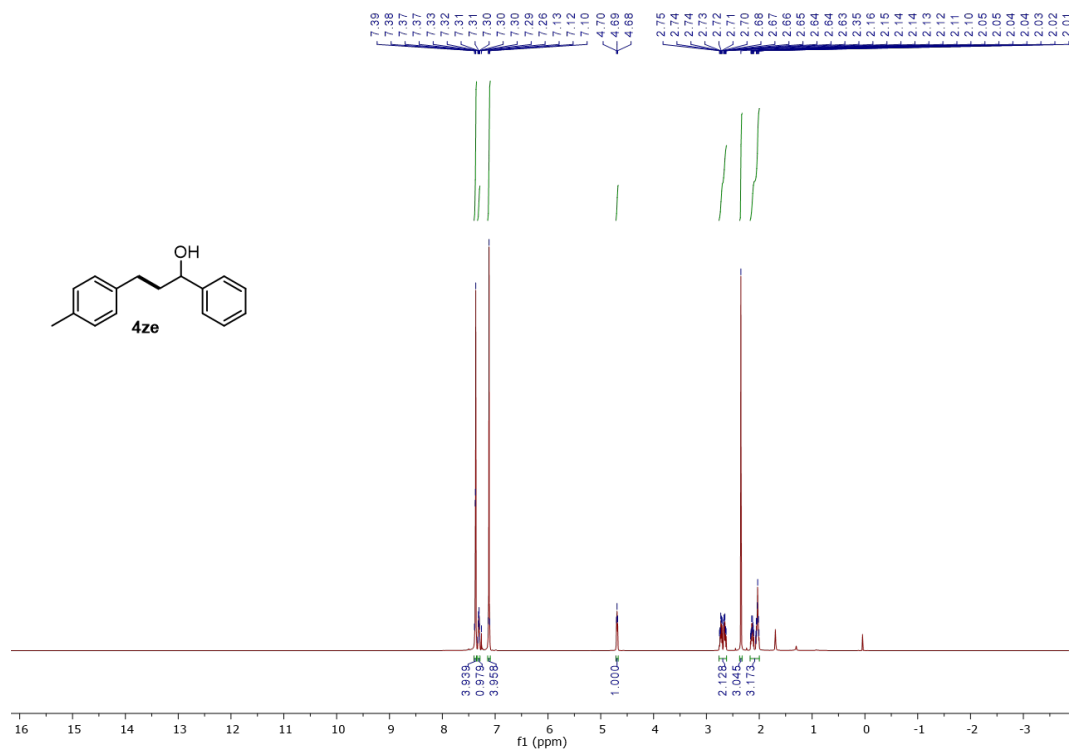


Figure S57: ¹H NMR spectra of 1-phenyl-3-(p-tolyl)propan-1-ol(4ze) recorded in CDCl₃.

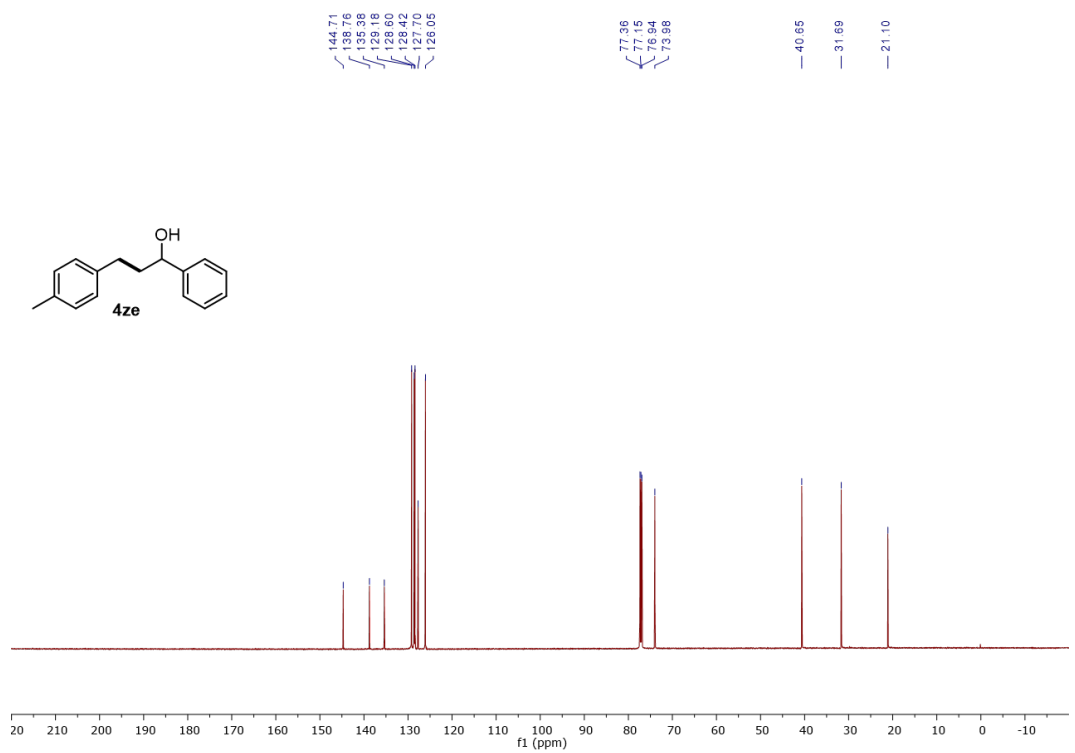


Figure S58: ¹³C{¹H} NMR spectra of 1-phenyl-3-(p-tolyl)propan-1-ol(4ze) recorded in CDCl₃.

6. Calculation of Kinetic Isotopic Effect (KIE):

$$\frac{k_{\text{Ha}}}{k_{\text{D}}} = \text{KIE}$$

Where, k_{Ha} and k_{D} are the proton content and deuterium content at C_a of the product **4a** as determined by $^1\text{H-NMR}$

$$k_{\text{Ha}} = \frac{\text{Integral value}}{\text{Number of protons}} * 100 = A * 100$$

$$k_{\text{D}} = (1-A)*100$$

7. Magnetic moment of **5** in solution (Evan's method):

Magnetic moment in solution was measured by following the Evan's NMR method.¹⁻³ A solution of ($^{\text{Ph}_2}\text{NNN}$)CrCl₃ (0.00055 g, 0.00125 mmol) in a 0.5 mL mixture of MeOH- d_4 / t -BuOH (98:2) was prepared. To the same NMR tube a capillary containing the 2% t -BuOH in MeOH- d_4 solution was inserted. NMR spectrum was recorded on a Bruker ASCEND 600 operating at 600 MHz. A chemical shift difference of 30 Hz was observed for the t -BuOH peak for the samples in the inner and outer tubes. Based on the equation² $\mu_{\text{B}} = 798(\chi_{\text{M}}T)^{0.5}$ [T= temperature of measurement and $\chi_{\text{M}} = 3\Delta f/1000fc$, where Δf is the paramagnetic shift of the solvent in Hz, f is the frequency of the NMR instrument in Hz, and c is the molar concentration of the metal complex], we have observed the magnetic moment $\mu_{\text{eff}} = 3.4 \mu_{\text{B}}$ which is in agreement with a octahedral Cr(III) species.⁴

Subsequently, NaOH (0.044g, 1.1 mmol) was added to a stock solution of ($^{\text{Ph}_2}\text{NNN}$)CrCl₃ (0.0006 g, 0.00145 mmol) in a 0.5 mL mixture of MeOH- d_4 / t -BuOH (98:2). To the same NMR tube a capillary containing the 2% t -BuOH in MeOH- d_4 solution was inserted. NMR spectrum was recorded on a Bruker ASCEND 600 operating at 600 MHz. A chemical shift difference of 72 Hz was observed for the t -BuOH peak for the samples in the inner and outer tubes which gave a magnetic moment of $4.8 \mu_{\text{B}}$ which is in agreement with a octahedral Cr(II) species.⁴

8. References:

1. D. F. Evans, *J Chem Soc.*, 1959, DOI: 10.1039/JR9590002003, 2003-2005.
2. T. Inagaki, A. Ito, J.-i. Ito and H. Nishiyama, *Angew. Chem. Int. Ed.*, 2010, **49**, 9384-9387.
3. G. J. P. Britovsek, V. C. Gibson, S. K. Spitzmesser, K. P. Tellmann, A. J. P. White and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 2002, DOI: 10.1039/B106614P, 1159-1171.
4. J. E. Huheey, E. A. Keiter, R. L. Keiter, O. K. Medhi, *Inorganic Chemistry: Principles of Structure and Reactivity*. Pearson Education: **2006**.