

Supplementary Materials: Transformation of Tertiary Benzyl Alcohols into the Vicinal Halo-Substituted Derivatives Using *N*-Halosuccinimides

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S1. General Information

All alcohol substrates were commercially available and were used without further purification. Reactions were carried out in 10 mL round-bottom flasks. All reactions were monitored by thin layer chromatography (TLC) (using silica gel/TLC cards, DC-Alufohlen-Kieselgel (Fluka, Sigma-Aldrich, St. Louis, MO, USA), (mobile phase: hexane/ethyl acetate) and visualized by UV lamp (254 nm) and KI (0.1 M) test. Column chromatography (CC) was performed using silica gel Kieselgel 60 (Fluka, Sigma-Aldrich) (particle size: 0.063–0.200 mm). Spectroscopic methods: nuclear magnetic resonance (Varian INOVA 300 NMR instrument, recorded at National Institute of Chemistry, Ljubljana, Slovenia, ^1H : at 303.0 MHz, ^{13}C : at 76.2 MHz) using CDCl_3 as the solvent with SiMe_4 (TMS) as an internal reference and melting points (open capillary tube methodology; uncorrected, by Buchi 535 equipment at the Jožef Stefan Institute, Ljubljana, Slovenia) were used for identification and structure elucidation.

S2. General Procedure for Vicinal Halo-Substituted Derivatives using NXS on mmol Scale

A solvent (5 mL) was placed in a 10 mL round bottom-flask equipped with a magnetic stirrer under reflux, NXS (1.1 mmol) was then added and, after being dissolved, the substrate (1 mmol) was added and the solution was stirred for 4–24 h. The progress of the reaction mixture was monitored by TLC, whilst the consumption of NXS was tested by KI (0.1 M). Upon completion of the reaction, the crude reaction mixture was cooled down at room temperature, diluted with EtOAc (15 mL), washed with aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (6 mL), NaHCO_3 (6 mL), and water (10 mL), and dried over anhydrous Na_2SO_4 . The solvent was evaporated under reduced pressure and the crude product obtained was analyzed by ^1H -NMR. The pure final products were obtained after flash chromatography, column chromatography or preparative thin layer chromatography.

S3. Characterization Data of Isolated Final Products

Table S1. 2-Chloro-1,1-diphenylethanol (**2a**) [1].

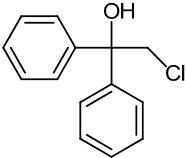
		$\text{C}_{14}\text{H}_{13}\text{ClO}$ (Mr = 232.71)
Reaction conditions	1 mmol 1,1-diphenylethanol 1 (198.1 mg), 1.1 mmol NCS (146.8 mg), 0.008 M SDS (11.5 mg), H_2O (5 mL), 95–100 °C, 7 h stirring 1000 rpm	
Purification	CC (SiO_2 , EtOAc/hexane 9:1)	
Yield	186 mg (80%), colourless oil	
^1H -NMR (300 MHz, CDCl_3)	δ = 7.45–7.25 (m, 10H), 4.18 (s, 2H), 3.16 (s, 1H)	
^{13}C -NMR (76 MHz, CDCl_3)	δ = 143.4, 128.5, 127.8, 126.5, 78.0, 53.3	

Table S2. 2-Bromo-1,1-diphenylethanol (**2b**) [2].

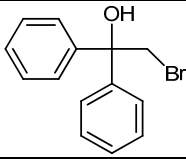
		$\text{C}_{14}\text{H}_{13}\text{BrO}$ (Mr = 277.16)
Reaction conditions	1 mmol 1,1-diphenylethanol 1 (198.1 mg), 1.1 mmol NBS (195.6 mg), 0.05M SDS (72 mg), H_2O (5 mL), 95–100 °C, 7 h stirring 1000 rpm	
Purification	TLC-preparative (EtOAc/hexane 9:1)	
Yield	164 mg (59%), yellow oil	
^1H -NMR (300 MHz, CDCl_3)	δ = 7.54–7.20 (m, 10H), 4.11 (s, 2H), 3.10 (s, 1H)	
^{13}C -NMR (76 MHz, CDCl_3)	δ = 143.4, 128.5, 127.8, 126.4, 77.3, 44.1	

Table S3. (2-Chloroethene-1,1-diyl)dibenzene (**3a**) [3].

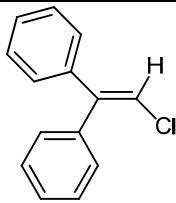
	C₁₄H₁₁Cl (Mr = 214.69)
Reaction conditions	1 mmol 1,1-diphenylethanol 1 (198.1 mg), 1.1 mmol NCS (146.8 mg), CH ₃ COOH (5 mL), 115–117 °C, 4 h stirring 400 rpm
Purification	Crystallization (hexane)
Yield	173 mg (80%), white crystals
Mp.	39–40 °C, (lit.[3] 39–40 °C)
¹ H-NMR (300 MHz, CDCl ₃)	δ = 7.41–7.18 (m, 10H), 6.58 (s, 1H)
¹³ C-NMR (76 MHz, CDCl ₃)	δ = 144.0, 140.3, 137.7, 130.0, 128.6, 128.3, 128.2, 128.1, 127.9, 116.0

Table S4. (2-Bromoethene-1,1-diyl)dibenzene (**3b**) [4].

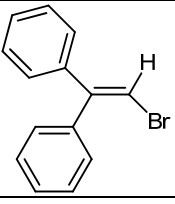
	C₁₄H₁₁Br (Mr = 259.14)
Reaction conditions	1 mmol 1,1-diphenylethanol 1 (198.1 mg), 1.1 mmol NBS (195.6 mg), CH ₃ COOH (5 mL), 115–117 °C, 4 h stirring 400 rpm
Purification	FCH (SiO ₂ , EtOAc); white crystals
Yield	250 mg (97%), white crystals
Mp.	47–49 °C, (Ref. [4] 48–50 °C)
¹ H-NMR (300 MHz, CDCl ₃)	δ = 7.42–7.18 (m, 10H), 6.77 (s, 1H)
¹³ C-NMR (76 MHz, CDCl ₃)	δ = 147.0, 140.9, 139.2, 129.8, 128.6, 128.4, 128.3, 128.1, 127.8, 105.3

Table S5. (2-chloro-1-methoxyethane-1,1-diyl)dibenzene (**5a**) [5].

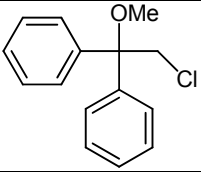
	C₁₅H₁₅ClO (Mr = 246.73)
Reaction conditions	1 mmol 1,1-diphenylethanol 1 (198.1 mg), 1.1 mmol NCS (146.8 mg), CH ₃ OH (5 mL), 60–70 °C, 22 h stirring 400 rpm
Purification	CC (SiO ₂ , EtOAc/hexane 9:1)
Yield	160 mg (65%), white solid
Mp.	46–48 °C, (Ref. [5] 47–49 °C)
¹ H-NMR (300 MHz, CDCl ₃)	δ = 7.38–7.25 (m, 10H), 4.34 (s, 2H), 3.18 (s, 3H)
¹³ C-NMR (76 MHz, CDCl ₃)	δ = 142.6, 128.2, 127.6, 127.3, 82.0, 50.9, 48.8

Table S6. (2-bromo-1-methoxyethane-1,1-diyl)dibenzene (**5b**) [6].

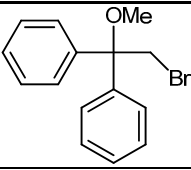
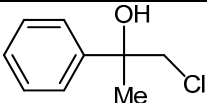
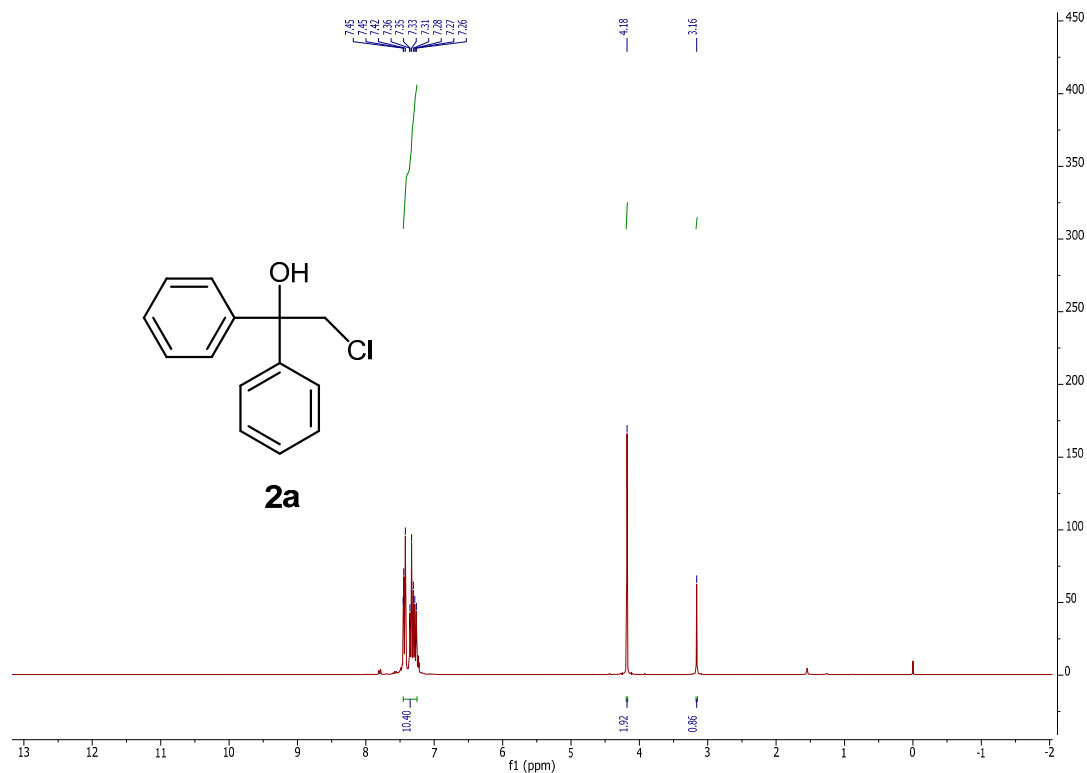
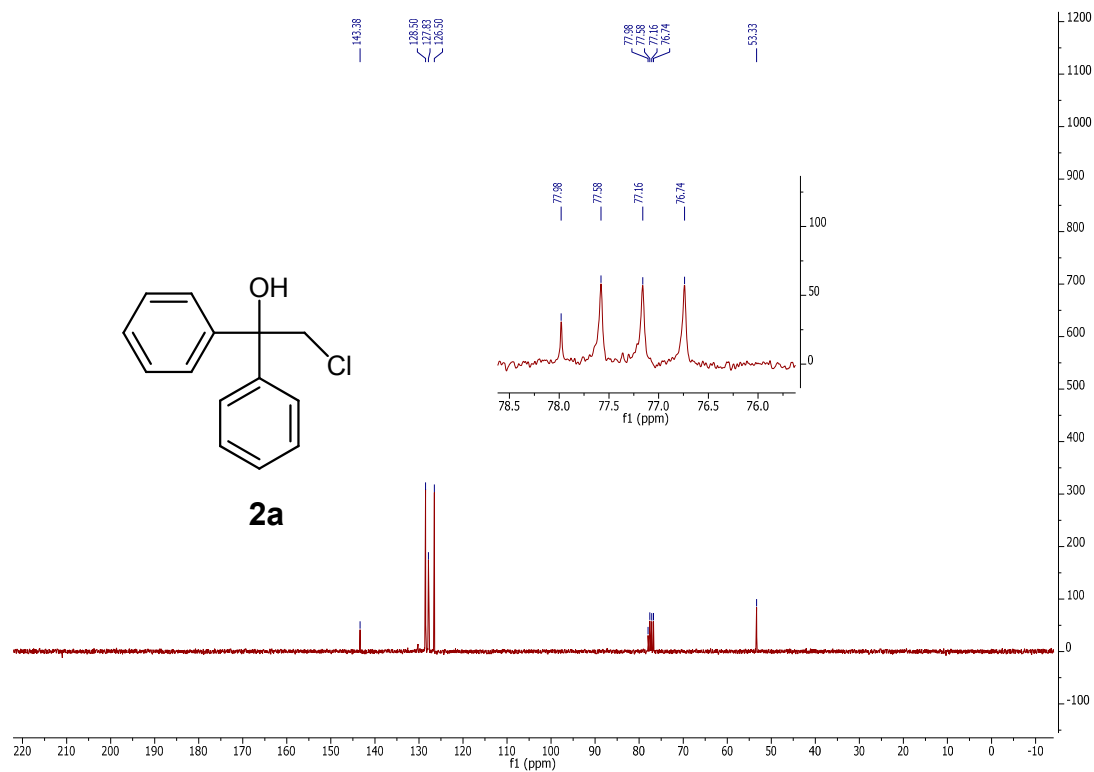
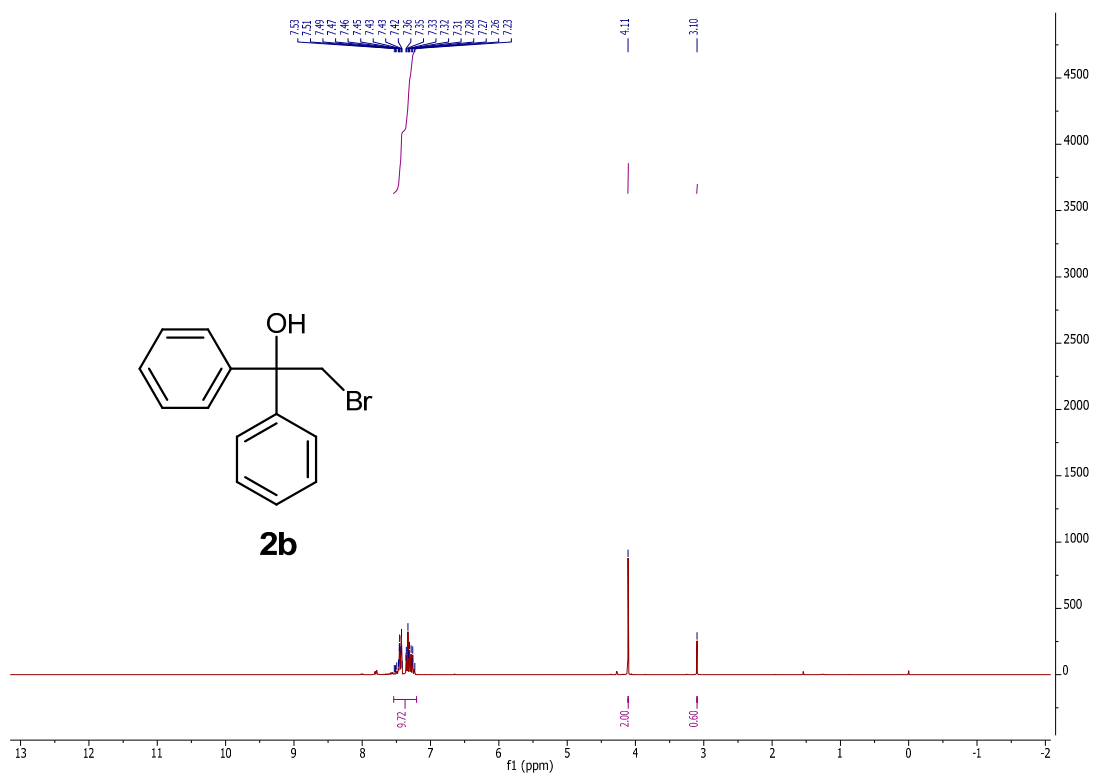
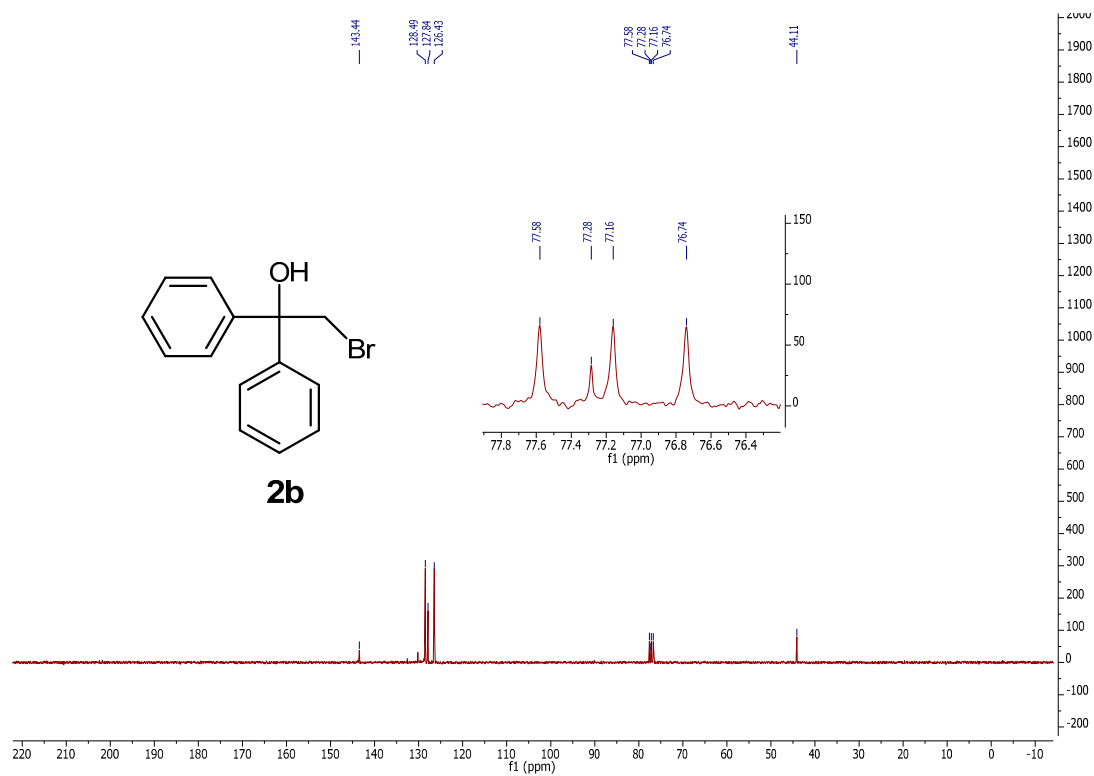
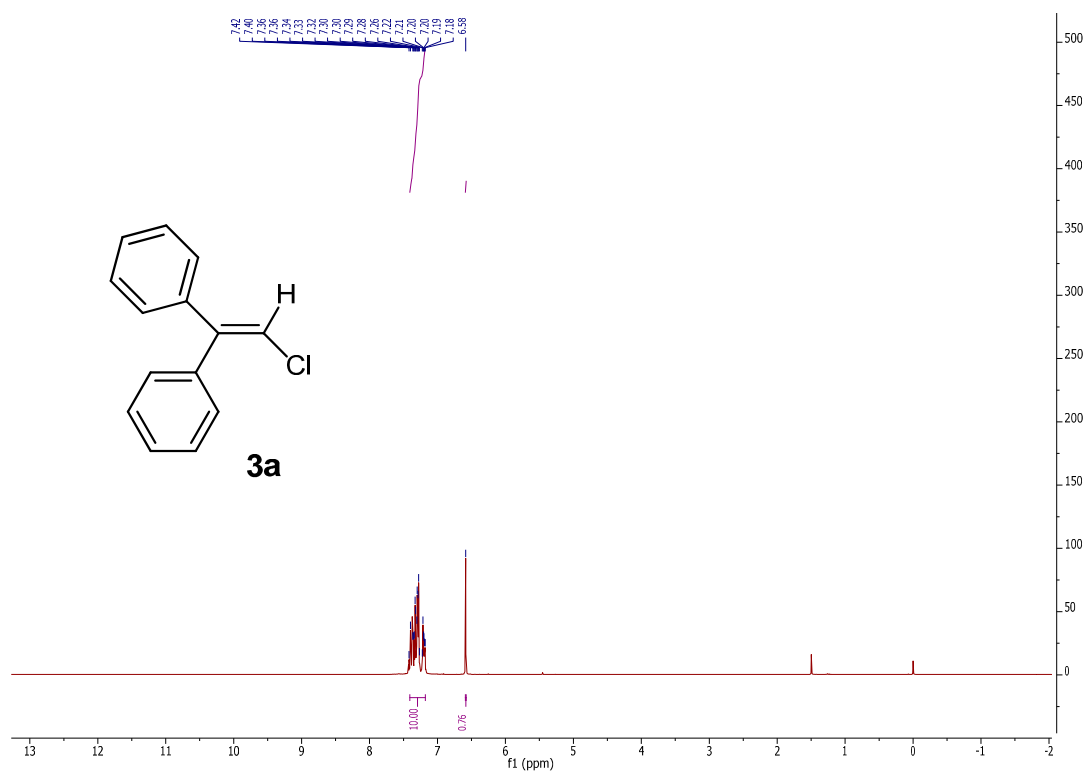
	C₁₅H₁₅BrO (Mr = 291.18)
Reaction conditions	1 mmol 1,1-diphenylethanol 1 (198.1 mg), 1.1 mmol NBS (195.6 mg), CH ₃ OH (5 mL), 60–70 °C, 22 h stirring 400
Purification	CC (SiO ₂ , EtOAc/hexane 9:1)
Yield	102 mg (35%), colourless oil
¹ H-NMR (300 MHz, CDCl ₃)	δ = 7.38–7.22 (m, 10H), 4.23 (s, 2H), 3.16 (s, 3H) rpm
¹³ C-NMR (76 MHz, CDCl ₃)	δ = 142.8, 128.2, 127.5, 127.2, 81.3, 50.7, 38.8

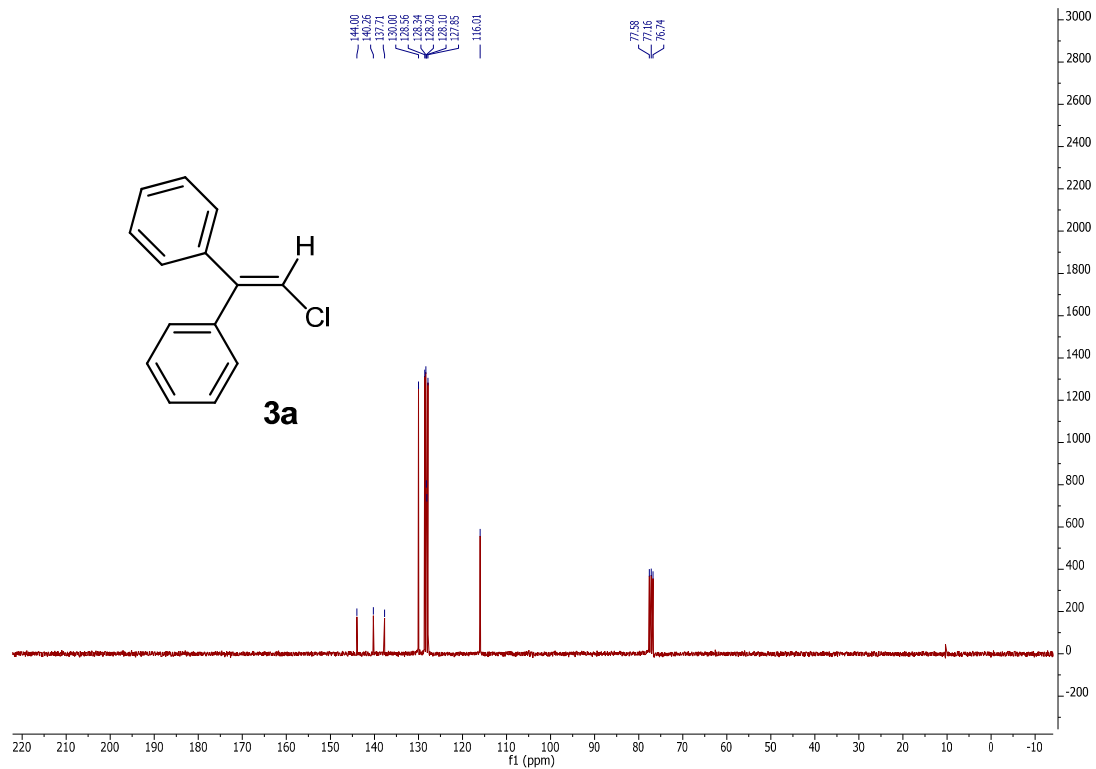
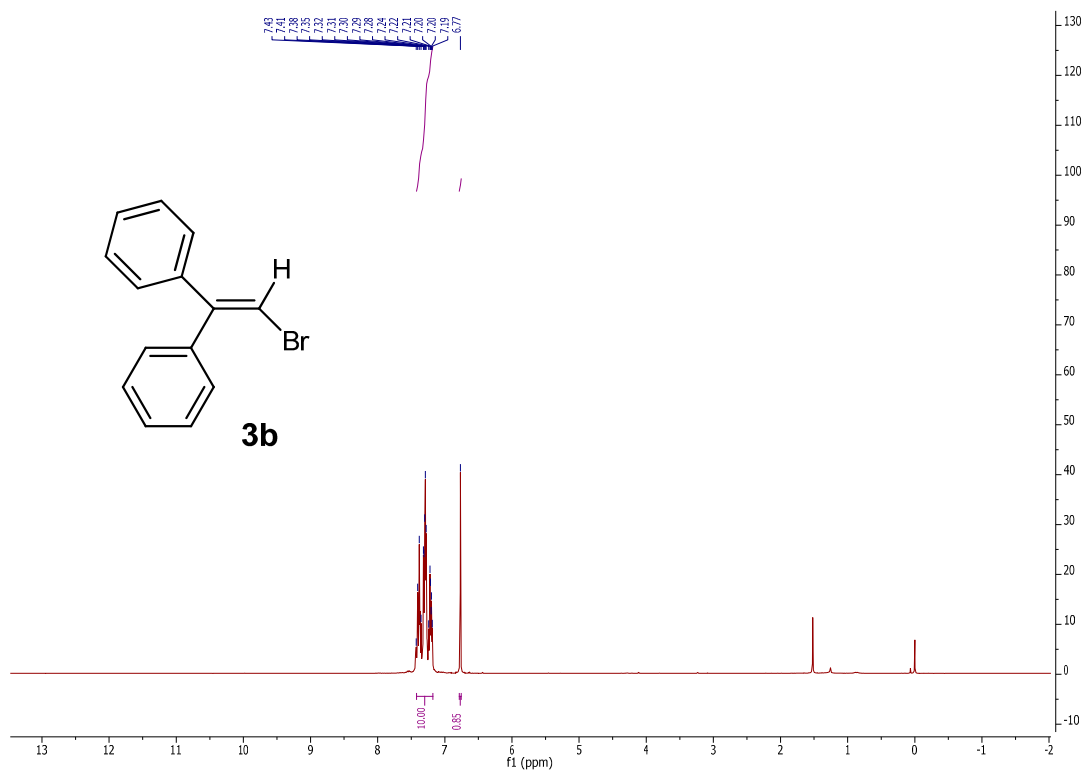
Table S7. 1-chloro-2-phenylpropan-2-ol (**7a**) [1].

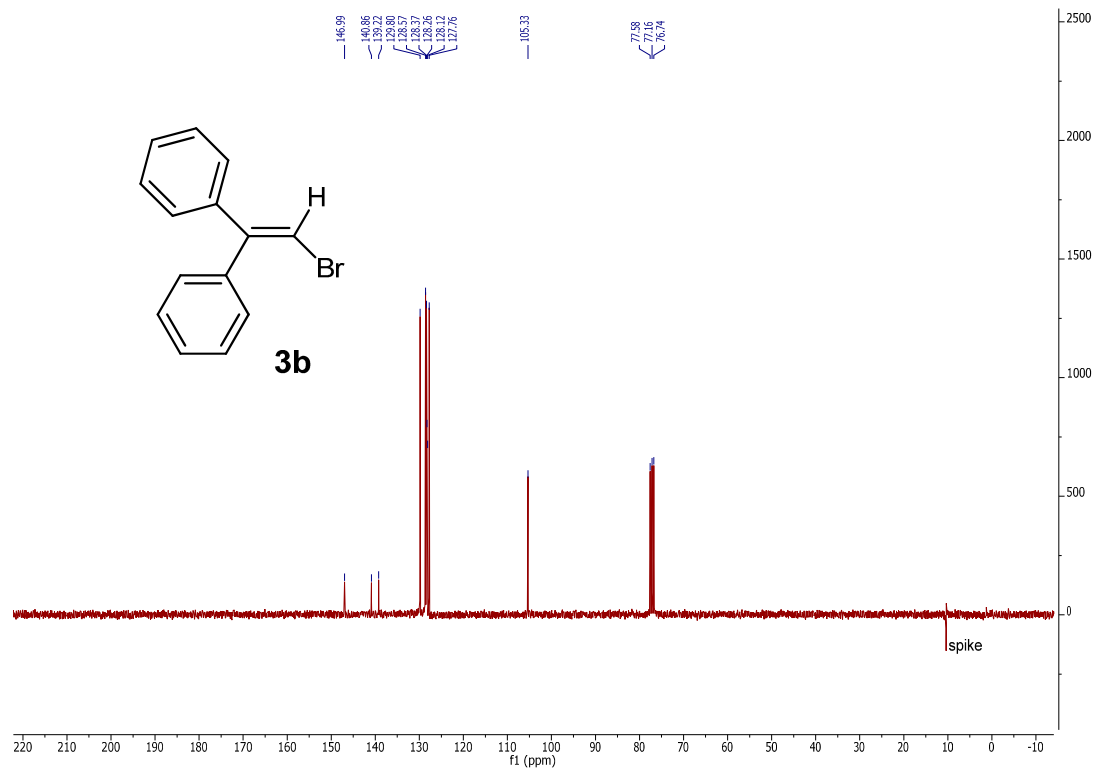
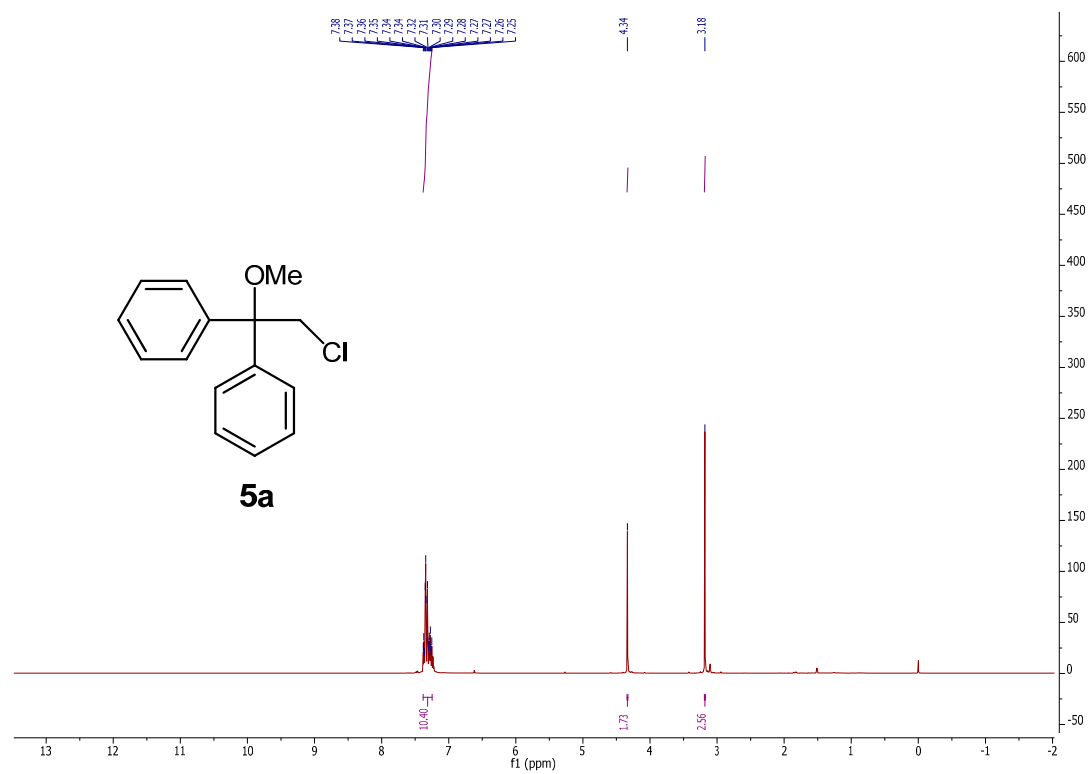
	C₉H₁₁ClO (Mr = 170.64)
Reaction conditions	1 mmol 2-phenylpropan-2-ol 6 (136.1 mg), 1.1 mmol NCS (146.8 mg), CH ₃ COOH (5 mL), 115–117 °C, 4 h stirring 400 rpm
Purification	FCH (SiO ₂ , EtOAc)
Yield	159 mg (93%), colourless oil
¹ H-NMR (300 MHz, CDCl ₃)	δ = 7.50–7.25 (m, 5H), 3.86–3.73 (m, 2H), 2.60 (s, 1H), 1.64 (s, 3H)
¹³ C-NMR (76 MHz, CDCl ₃)	δ = 144.3, 128.5, 127.6, 125.1, 73.9, 55.5, 27.4

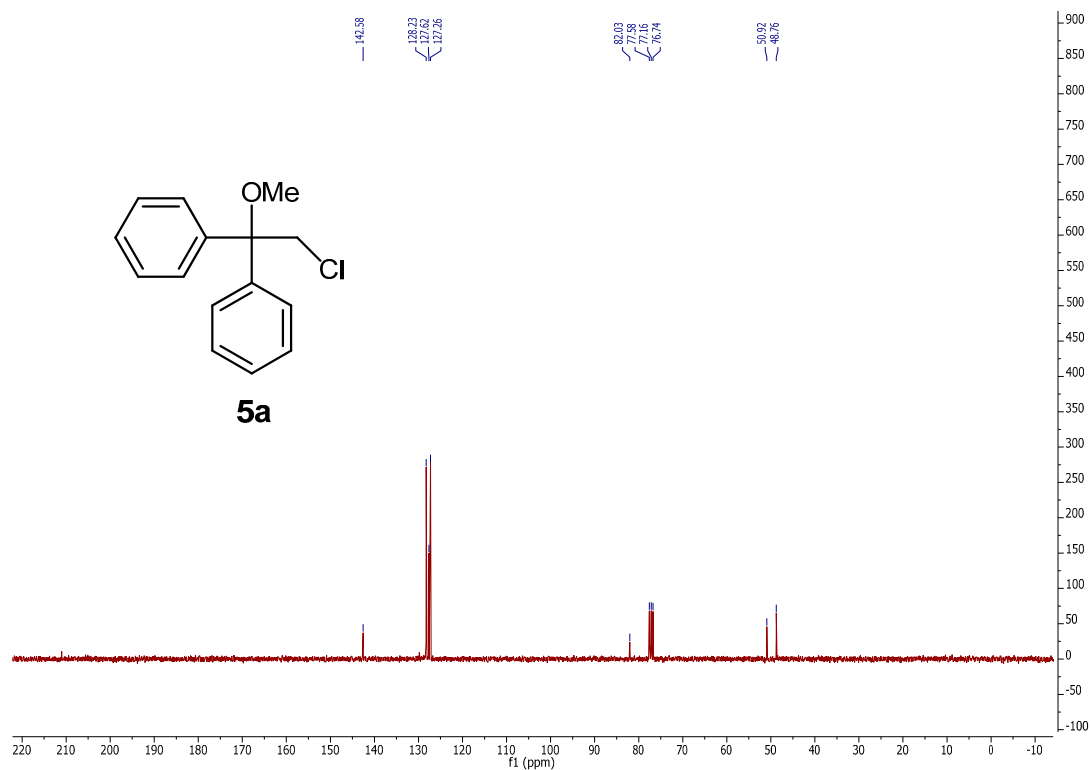
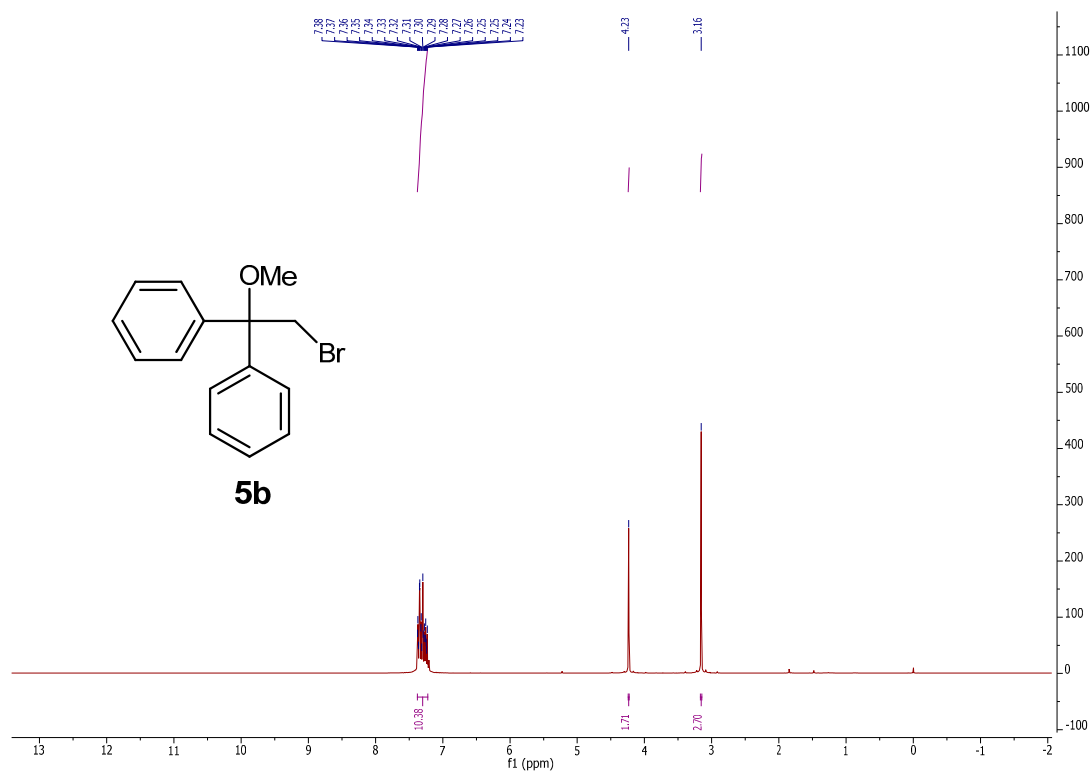
S4. ¹H-NMR and ¹³C-NMR Spectra of Isolated Final Products**Figure S1.** ¹H-NMR spectrum of compound **2a**.

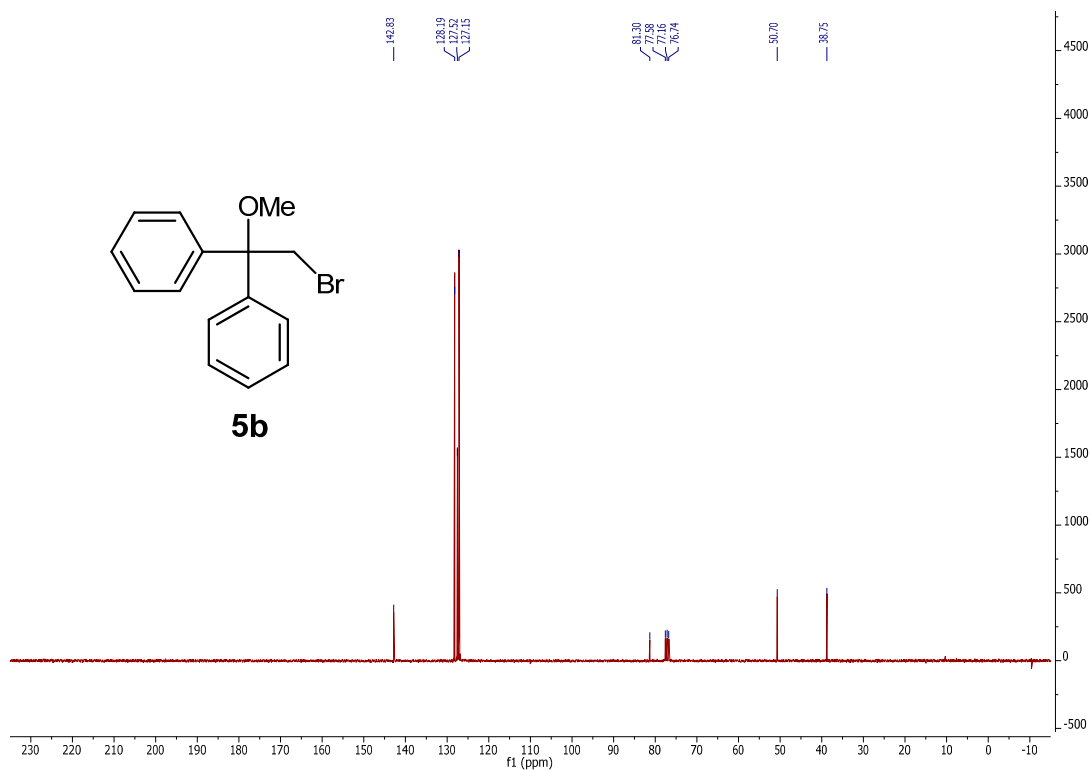
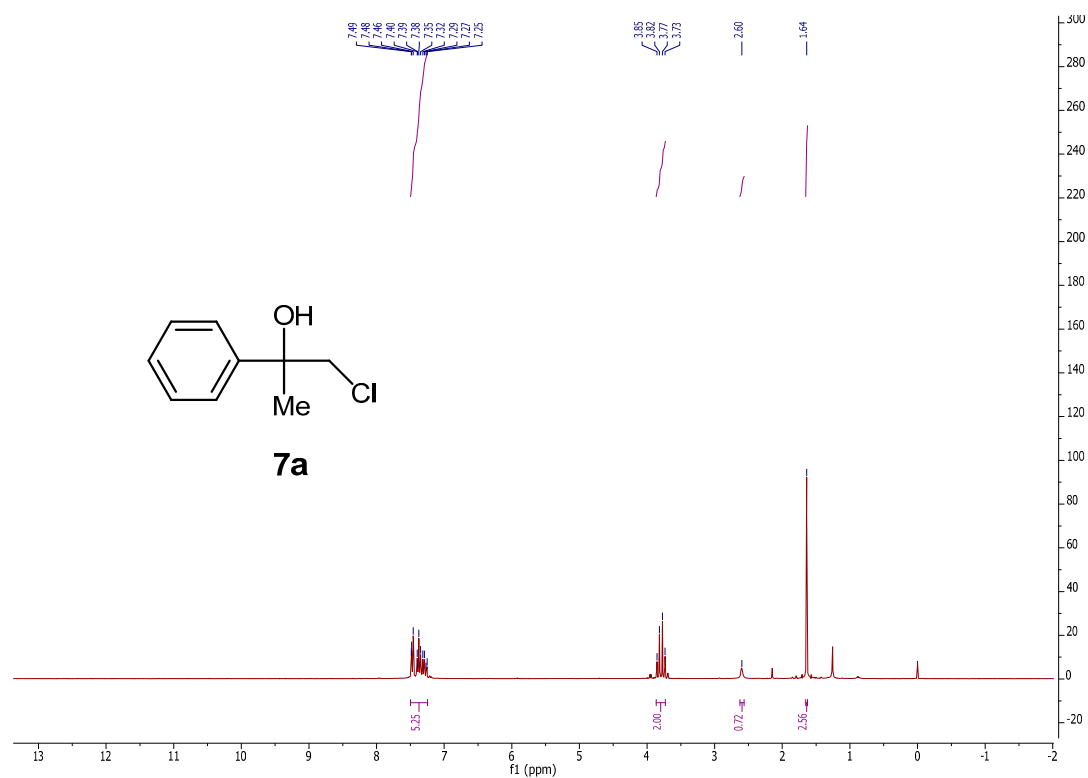
Figure S2. ¹³C-NMR spectrum of compound **2a**.Figure S3. ¹H-NMR spectrum of compound **2b**.

Figure S4. ^{13}C -NMR spectrum of compound **2b**.Figure S5. ^1H -NMR spectrum of compound **3a**.

Figure S6. ¹³C-NMR spectrum of compound 3a.Figure S7. ¹H-NMR spectrum of compound 3b.

Figure S8. ¹³C-NMR spectrum of compound **3b**.Figure S9. ¹H-NMR spectrum of compound **5a**.

Figure S10. ¹³C-NMR spectrum of compound 5a.Figure S11. ¹H-NMR spectrum of compound 5b.

Figure S12. ¹³C-NMR spectrum of compound **5b**.Figure S13. ¹H-NMR spectrum of compound **7a**.

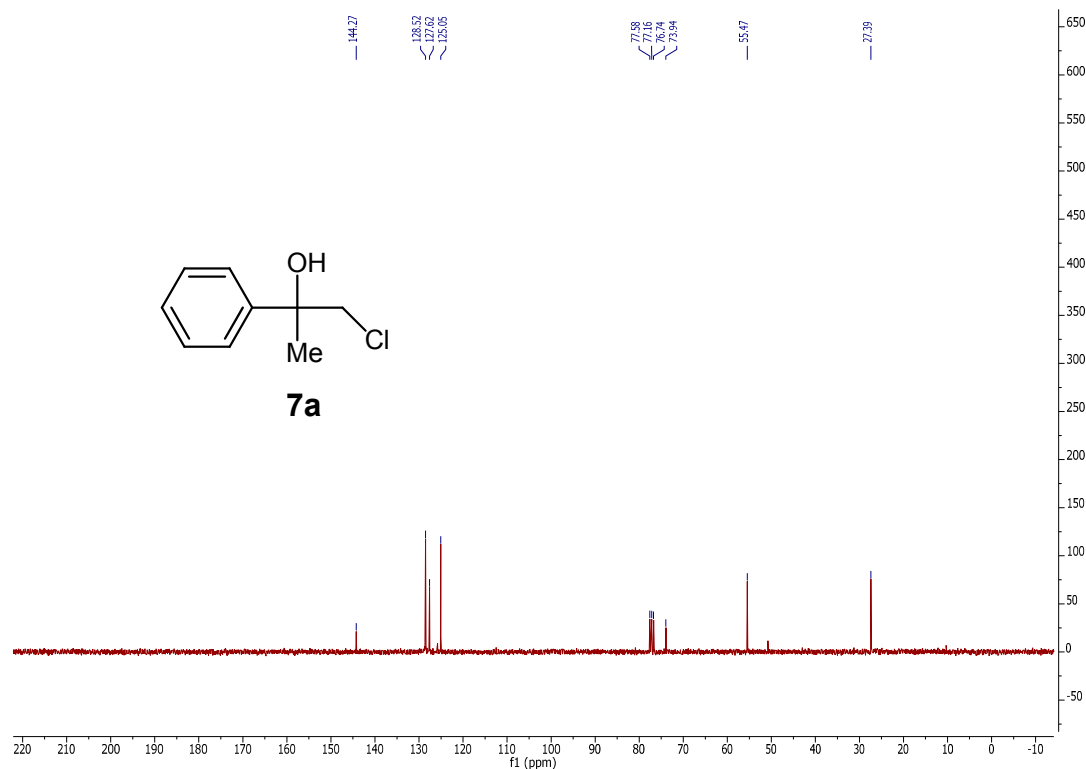


Figure S14. ¹³C-NMR spectrum of compound 7a.

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