

[4+2] Cycloaddition of *o*-Xylylenes with Imines Using Palladium Catalyst

Satoshi Ueno, Masakazu Ohtsubo, and Ryoichi Kuwano*

*Department of Chemistry, Graduate School of Sciences, Kyushu University, 6-10-1 Hakozaki, Higashi-ku,
Fukuoka 812-8581, Japan*

Supporting Information

Table of Contents

| | |
|---|---------|
| General and Materials | S2 |
| Preparations of 2-[(Trimethylsilyl)methyl]benzyl Carbonates 1 | S2–S5 |
| Preparations of <i>N</i> -Tosylbenzimidines 2 | S6–S8 |
| Palladium-Catalyzed [4+2] Cycloaddition of 2-[(Trimethylsilyl)methyl]benzyl Carbonates 1 with <i>N</i> -Tosylbenzimidines 2 | |
| Optimization of Reaction Conditions for the [4+2] Cycloaddition of 1a with 2a | S8–S10 |
| Experimental Details of Scheme 1 | S10–S11 |
| Experimental Details of all entries in Table 1 | S11–S14 |
| Experimental Details of all entries in Table 2 | S14–S19 |
| References | S19 |
| ¹ H and ¹³ C { ¹ H} NMR spectra of 1 | S20–S25 |
| ¹ H and ¹³ C { ¹ H} NMR spectra of 2 | S26–S27 |
| ¹ H and ¹³ C { ¹ H} NMR spectra of 3 | S28–S38 |
| ¹ H and ¹³ C { ¹ H} NMR spectra of 4 , 5 , and related spectra to Table 2 | S38–S47 |

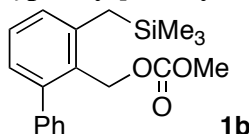
General and Materials. All NMR spectra were measured with Bruker AVANCE 400 (9.4 T magnet) spectrometer. In ^1H NMR spectra, chemical shifts (ppm) referenced to internal tetramethylsilane (0.00 ppm, in CDCl_3). In ^{13}C NMR spectra, chemical shifts (ppm) referenced to the carbon signal of the deuterated solvents (77.0 ppm in CDCl_3 , 29.3 ppm in acetone- d_6 , 66.5 ppm in 1,4-dioxane- d_8). IR spectra and melting points were measured with JASCO FT/IR-4100 and Büchi Melting Point B-545, respectively. Elemental and high resolution mass (HRMS) analyses were performed by Service Centre of Elementary Analysis of Organic Compounds and Institute for Materials Chemistry and Engineering (IMCE) in Kyushu University, respectively. All reactions were conducted under nitrogen atmosphere. Flash column chromatographies were performed with silica gel 60 (230–400 mesh, Merck).

Diethyl ether (Et_2O) was dried with sodium-benzophenone ketyl. Dichloromethane (CH_2Cl_2) was dried with phosphorus(V) oxide. Pyridine was dried with calcium hydride. These dry solvents were distilled under nitrogen atmosphere before use. Tetrahydrofuran (THF) (HPLC grade, without inhibitor) was deoxidized by purging with nitrogen for 30 min and was dried with an alumina and copper column system (GlassContour Co.). Methyl [2-((trimethylsilyl)methyl)phenyl]methyl carbonate (**1a**),¹ 2-methyl-6-phenylbenzoic acid,² methyl [3-phenyl-2-((trimethylsilyl)methyl)phenyl]methyl carbonate (**1c**),¹ (2,6-dimethylphenyl)methanol,³ [2,4-dimethyl-6-((trimethylsilyl)methyl)phenyl]methyl carbonate (**1f**),¹ *N*-phenylmethyldene-4-methylbenzenesulfonamide (**2a**),⁴ and $\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cp}$,^{5,6} were prepared according to literature procedures.

Potassium fluoride (spray dried), 1,5-bis(diphenylphosphino)pentane (DPPPent), dry *N,N*-dimethylformamide ($\text{H}_2\text{O} < 50$ ppm), lithium aluminum hydride, butyllithium solution in hexane, chlorotrimethylsilane, methyl chloroformate, 4-dimethylaminopyridine, 2,3-dimethylbenzoic acid, *p*-toluenesulfonamide, 2-methylbenzaldehyde, 2,6-dimethylbenzaldehyde, 4-methoxybenzaldehyde, 4-(trifluoromethyl)benzaldehyde, 3-(trifluoromethyl)benzaldehyde, 1-naphthaldehyde, 2-naphthaldehyde, (2-methyl-3-phenylphenyl)methanol, sodium bromate, sodium hydrogensulfate, acetonitrile, and lithium aluminium deuteride were purchased and used without further purification.

Preparations of 2-[(Trimethylsilyl)methyl]benzyl Carbonates 1.

Methyl [6-Phenyl-2-((trimethylsilyl)methyl)phenyl]methyl Carbonate (1b**).**



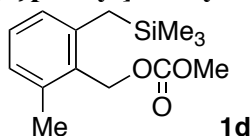
A mixture (1.33 g) of 2-methyl-6-phenylbenzoic acid (5.9 mmol estimated by ^1H NMR) and 2-methylbenzoic acid (0.70 mmol estimated by ^1H NMR), which was prepared according to the procedure of J. Q. Yu *et al.*,² was dissolved in dry THF (10 mL). The solution was added dropwise to a mixture of lithium aluminum hydride (254 mg, 6.7 mmol) in dry THF (15 mL) at 0 °C for 45 min. After hydrogen evolution ceased, the reaction mixture was stirred under reflux for 20 h. After the reaction vessel was cooled with ice bath, H_2O was carefully added to the resulting mixture at 0 °C. The mixture was filtered

through a Celite pad. The filter cake was washed with methanol. The combined filtrate was extracted three times with EtOAc. The combined organic layer was washed with saturated Na_2CO_3 aq., with brine, dried with Na_2SO_4 , and then evaporated under reduced pressure. The ^1H NMR spectrum of the residue indicated that it contains (2-methylphenyl)methanol (89.4 mg, 0.73 mmol) as well as (2-methyl-6-phenylphenyl)methanol (580 mg, 2.9 mmol, 49%). We used the mixture for the next reaction without further purification. ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.54 (s, 3H), 4.60 (d, J = 2.8 Hz, 2H), 7.16–7.43 (m, 8H).

The above mixture (670 mg) containing (2-methyl-6-phenylphenyl)methanol (2.9 mmol) was dissolved in dry Et_2O (7.3 mL). A solution of butyllithium in hexane (1.7 M, 5.1 mL, 8.5 mmol) was added dropwise to the solution of (2-methyl-6-phenylphenyl)methanol at 0 °C for 30 min. After stirred under reflux for 24 h, the reaction mixture was cooled to –78 °C. Chlorotrimethylsilane (1.2 mL, d 0.856 g/mL, 9.5 mmol) was added dropwise to the resulting solution for 45 min. The mixture was stirred at room temperature for 3 h, and then 10% H_2SO_4 aq. (4.0 mL) was carefully added to it. After stirred at room temperature for 14 h, the mixture was extracted three times with EtOAc. The combined organic layer was washed with brine, dried with Na_2SO_4 , and then evaporated under reduced pressure. The residue was purified with a flash column chromatography (EtOAc/hexane = 1/30) to give [2-phenyl-6-((trimethylsilyl)methyl)phenyl]methanol (574 mg, 73%) as colorless oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 0.05 (s, 9H), 2.38 (s, 2H), 4.51 (s, 2H), 7.01 (d, J = 7.5 Hz, 1H), 7.05 (d, J = 7.1 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.32–7.45 (m, 5H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ –1.4, 23.5, 59.9, 126.4, 126.9, 127.4, 128.0, 128.7, 129.2, 134.1, 140.7, 141.8, 143.4; IR (neat) 3566 w, 3330 brm, 3058 m, 3023 w, 2953 m, 2897 m, 1582 m, 1494 w, 1459 m, 1418 m, 1249 s, 1192 m, 1156 m, 1069 w, 1001 m, 909 m, 846 s, 802 m, 762 s, 734 s, 702 s cm^{-1} ; Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{OSi}$: C, 75.50; H, 8.20. Found: C, 75.65; H, 8.32.

Methyl chloroformate (223 mg, 2.4 mmol) was added dropwise to a solution of [2-phenyl-6-((trimethylsilyl)methyl)phenyl]methanol (389 mg, 1.4 mmol), dry pyridine (0.24 mL, d 0.978 g/mL, 3.0 mmol), and 4-dimethylaminopyridine (3.0 mg, 25 μmol) in dry CH_2Cl_2 (1.5 mL) at 0 °C for 10 min. The mixture was stirred at room temperature for 22 h. After 1 N HCl aq. (3.0 mL) was added, the resulting mixture was extracted three times with EtOAc. The combined organic layer was washed with brine, dried with Na_2SO_4 , and then evaporated under reduced pressure. The residue was purified with a flash column chromatography (EtOAc/hexane = 1/30) to give **1b** (399 mg, 84%) as colorless oil: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 0.04 (s, 9H), 2.26 (s, 2H), 3.76 (s, 3H), 5.01 (s, 2H), 7.03 (d, J = 7.6 Hz, 1H), 7.06 (d, J = 7.7 Hz, 1H), 7.26 (t, J = 7.6 Hz, 1H), 7.30–7.42 (m, 5H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ –1.5, 23.5, 54.5, 65.3, 126.3, 127.0, 127.9, 128.28, 128.36, 128.42, 129.1, 141.2, 141.8, 144.7, 155.4; IR (neat) 3740 w, 3059 m, 3023 m, 2954 s, 2898 m, 1947 w, 1747 s, 1584 m, 1443 s, 1376 m, 1264 s, 1201 m, 1176 m, 1154 m, 1073 w, 1029 w, 941 s, 848 s, 792 m, 764 s, 703 s, 631 w, 608 w, 587 w, 540 m cm^{-1} ; Anal. Calcd for $\text{C}_{19}\text{H}_{24}\text{O}_3\text{Si}$: C, 69.47; H, 7.36. Found: C, 69.53; H, 7.33.

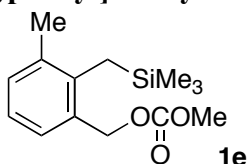
Methyl [2-Methyl-6-((trimethylsilyl)methyl)phenyl]methyl Carbonate (1d).



A solution of butyllithium in hexane (1.7 M, 7.0 mL, 12 mmol) was added dropwise to a solution of (2,6-dimethylphenyl)methanol³ (680 mg, 5.0 mmol) in dry Et₂O (10 mL) at 0 °C for 30 min. After stirred under reflux for 20 h, the reaction mixture was cooled to -78 °C. Chlorotrimethylsilane (1.6 mL, *d* 0.856 g/mL, 13 mmol) was added dropwise to the resulting solution for 15 min. The mixture was stirred at room temperature for 3 h, and then 10% H₂SO₄ aq. (5.0 mL) was carefully added to it. After stirred at room temperature for 16 h, the mixture was extracted three times with EtOAc. The combined organic layer was washed with brine, dried with Na₂SO₄, and then evaporated under reduced pressure. The residue was purified with a flash column chromatography (EtOAc/hexane = 1/10) to give [2-methyl-6-((trimethylsilyl)methyl)phenyl]methanol (476 mg, 46%) as colorless oil: ¹H NMR (400 MHz, CDCl₃, TMS) δ 0.00 (s, 9H), 2.26 (s, 2H), 2.43 (s, 3H), 4.67 (s, 2H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ -1.5, 19.7, 23.7, 59.4, 126.8, 127.5, 127.8, 135.0, 137.8, 139.8; IR (neat) 3309 brm, 3064 w, 3021 w, 2954 m, 2898 m, 1587 w, 1466 m, 1417 m, 1295 w, 1248 m, 1195 w, 1248 m, 1195 w, 1155 m, 1078 w, 1034 w, 1001 m, 850 s, 792 m, 762 m, 694 m, 653 w cm⁻¹; Anal. Calcd for C₁₂H₂₀OSi: C, 69.17; H, 9.67. Found: C, 68.93; H, 9.61.

Methyl chloroformate (199 mg, 2.1 mmol) was added dropwise to a solution of [2-methyl-6-((trimethylsilyl)methyl)phenyl]methanol (321 mg, 1.5 mmol), dry pyridine (0.19 mL, *d* 0.978 g/mL, 2.4 mmol), and 4-dimethylaminopyridine (1.9 mg, 16 μmol) in dry CH₂Cl₂ (1.5 mL) at 0 °C for 10 min. The mixture was stirred at room temperature for 13 h. After 1 N HCl aq. (1.5 mL) was added, the resulting mixture was extracted three times with EtOAc. The combined organic layer was washed with brine, dried with Na₂SO₄, and then evaporated under reduced pressure. The residue was purified with a flash column chromatography (EtOAc/hexane = 1/20) to give **1d** (325 mg, 79%) as colorless oil: ¹H NMR (400 MHz, CDCl₃, TMS) δ -0.01 (s, 9H), 2.25 (s, 2H), 2.39 (s, 3H), 3.79 (s, 3H), 5.20 (s, 2H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ -1.7, 19.7, 23.6, 54.5, 64.4, 126.5, 127.2, 128.4, 129.5, 138.7, 140.8, 155.8; IR (neat) 3066 w, 3021 m, 2955 m, 2899 m, 1747 s, 1589 m, 1443 m, 1373 m, 1270 s, 1155 m, 1081 w, 1035 w, 943 s, 852 s, 792 m, 763 m, 694 m cm⁻¹; Anal. Calcd for C₁₄H₂₂O₃Si: C, 63.12; H, 8.32. Found: C, 63.30; H, 8.35.

Methyl [3-Methyl-2-((trimethylsilyl)methyl)phenyl]methyl Carbonate (1e).



A solution of 2,3-dimethyl-6-phenylbenzoic acid (2.25 g, 15 mmol) in dry THF (24 mL) was added dropwise to a mixture of lithium aluminum hydride (569 mg, 15 mmol) in dry THF (36 mL) at 0 °C for 30 min. After hydrogen evolution ceased, the reaction mixture was stirred under reflux for 21 h. After the reaction vessel was cooled with ice bath, H₂O was carefully added to the resulting mixture at 0 °C. The mixture was filtered through a Celite pad. The filter cake was washed with methanol. The combined filtrate was extracted three times with EtOAc. The combined organic layer was washed with saturated Na₂CO₃ *aq.*, with brine, dried with Na₂SO₄, and then evaporated under reduced pressure. The residue was purified with a flash column chromatography (hexane/EtOAc = 5/1) to give (2,3-dimethylphenyl)methanol⁷ (1.25 g, 61%) as a colorless solid: ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.16 (s, 3H), 2.24 (s, 3H), 4.53 (s, 2H), 7.01–7.15 (m, 3H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 14.3, 20.1, 63.6, 125.3, 125.5, 129.3, 134.6, 136.8, 138.5.

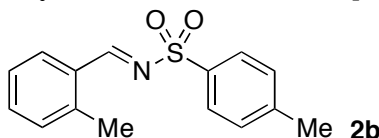
A solution of butyllithium in hexane (1.6 M, 7.0 mL, 11 mmol) was added dropwise to a solution of (2,3-dimethylphenyl)methanol (679 mg, 5.0 mmol) in dry Et₂O (10 mL) at 0 °C for 30 min. After stirred under reflux for 24 h, the reaction mixture was cooled to –78 °C. Chlorotrimethylsilane (1.6 mL, *d* 0.856 g/mL, 13 mmol) was added dropwise to the resulting solution for 45 min. The mixture was stirred at room temperature for 2 h, and then 10% H₂SO₄ *aq.* (5.0 mL) was carefully added to it. After stirred at room temperature for 17 h, the mixture was extracted three times with EtOAc. The combined organic layer was washed with brine, dried with Na₂SO₄, and then evaporated under reduced pressure. The residue was purified with a flash column chromatography (EtOAc/hexane = 1/10) to give [3-methyl-2-((trimethylsilyl)methyl)phenyl]methanol (722 mg, 70%) as colorless oil: ¹H NMR (400 MHz, CDCl₃, TMS) δ 0.04 (s, 9H), 2.26 (s, 2H), 2.27 (s, 3H), 4.62 (s, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 7.4 Hz, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ –0.3, 19.1, 20.9, 63.9, 123.9, 125.8, 129.7, 135.2, 137.2, 137.6; IR (neat) 3327 brm, 2953 s, 2899 m, 1462 m, 1417 m, 1249 s, 1188 m, 1154 w, 1054 w, 1011 m, 897 m, 843 s, 770 s, 740 w, 691 m cm^{–1}; Anal. Calcd for C₁₂H₂₀OSi: C, 69.17; H, 9.67. Found: C, 69.18; H, 9.68.

Methyl chloroformate (292 mg, 3.1 mmol) was added dropwise to a solution of [2-methyl-2-((trimethylsilyl)methyl)phenyl]methanol (516 mg, 2.5 mmol), dry pyridine (0.28 mL, *d* 0.978 g/mL, 3.5 mmol), and 4-dimethylaminopyridine (3.3 mg, 27 μmol) in dry CH₂Cl₂ (2.5 mL) at 0 °C for 15 min. The mixture was stirred at room temperature for 15 h. After 1 N HCl *aq.* (2.5 mL) was added, the resulting mixture was extracted three times with EtOAc. The combined organic layer was washed with brine, dried with Na₂SO₄, and then evaporated under reduced pressure. The residue was purified with a flash column chromatography (EtOAc/hexane = 1/20) to give **1e** (461 mg, 69%) as colorless oil: ¹H NMR (400 MHz, CDCl₃, TMS) δ 0.02 (s, 9H), 2.24 (s, 2H), 2.25 (s, 3H), 3.79 (s, 3H), 5.15 (s, 2H), 7.00 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ –0.5, 19.4, 20.9, 54.6, 68.5, 123.9, 127.5, 130.6, 131.6, 135.3, 138.6, 155.7; IR (neat) 2955 m, 1749 s, 1596 w, 1443 m, 1376 m, 1264 s, 1191 w, 1156 w, 1097 w, 947 m, 903 w, 846 s, 791 m, 772 m, 743 w, 691 w cm^{–1}; Anal. Calcd for C₁₄H₂₂O₃Si: C, 63.12; H, 8.32. Found: C, 62.90; H, 8.21.

Preparations of *N*-Tosylbenzimidines 2.

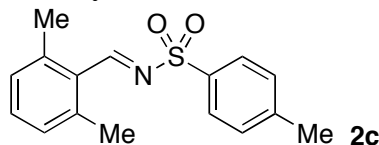
General Procedure.⁴ *p*-Toluenesulfonamide (856 mg, 5.0 mmol) was placed in a 50 mL two-neck round-bottom flask equipped with a magnetic stirring bar, Teflon stopper, and Dean-Stark trap. A Dimroth condenser equipped with a three-way cock was placed on the Dean-Stark trap. After the reaction vessel was evacuated and charged with nitrogen, toluene (14 mL) and then an aldehyde (6.0 mmol) was added to the sulfonamide. The reaction mixture was refluxed for 2–4 days with azeotropic removal of water. The resulting mixture was filtered, and then evaporated under reduced pressure. The residue was recrystallized from EtOAc–hexane to give the desired *N*-tosylimines **2**.

***N*-(2-Methylphenyl)methylidene-4-methylbenzenesulfonamide [343598-64-1] (**2b**).⁸**



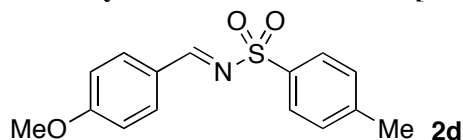
The general procedure was followed with use of *p*-toluenesulfonamide (856 mg, 5.0 mmol) and 2-methylbenzaldehyde (758 mg, 6.3 mmol). The reaction was conducted for 3 days. The crude product was recrystallized from EtOAc–hexane to give **2b** (612 mg, 45%) as colorless crystals: ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.42 (s, 3H), 2.59 (s, 3H), 7.23–7.29 (m, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 2H), 7.99 (d, *J* = 7.6 Hz, 1H), 9.33 (s, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 19.6, 21.6, 126.6, 128.0, 129.7, 130.4, 130.7, 131.5, 134.5, 135.5, 142.2, 144.4, 168.6.

***N*-(2,6-Dimethylphenyl)methylidene-4-methylbenzenesulfonamide [1010721-72-8] (**2c**).**



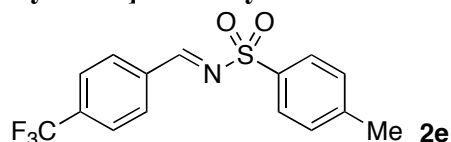
The general procedure was followed with use of *p*-toluenesulfonamide (855 mg, 5.0 mmol) and 2,6-dimethylbenzaldehyde (822 mg, 6.1 mmol). The reaction was conducted for 4 days. The crude product was recrystallized from EtOAc–hexane to give **2c** (747 mg, 52%) as colorless crystals: mp 122.4–122.5 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.42 (s, 3H), 2.53 (s, 6H), 7.07 (d, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 8.2 Hz, 2H), 9.47 (s, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 21.54, 21.57, 127.8, 128.8, 129.6, 129.7, 133.3, 135.6, 142.3, 144.3, 169.3; IR (thin film) 3357 w, 3261 w, 3060 w, 2964 m, 2923 m, 1587 m, 1458 m, 1380 m, 1307 m, 1149 s, 1087 m, 1033 m, 929 m, 799 s, 716 s, 655 m, 568 s, 513 m, 459 s cm⁻¹; Anal. Calcd for C₁₆H₁₇NO₂S: C, 66.87; H, 5.96; N, 4.87. Found: C, 66.62; H, 5.96; N, 4.84.

***N*-(4-Methoxyphenyl)methylidene-4-methylbenzenesulfonamide [14674-38-5] (2d).⁹**



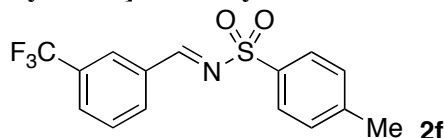
The general procedure was followed with use of *p*-toluenesulfonamide (859 mg, 5.0 mmol) and 4-methoxybenzaldehyde (847 mg, 6.2 mmol). The reaction was conducted for 3 days. The crude product was recrystallized from EtOAc–hexane to give **2d** (1.16 g, 80%) as colorless crystals: ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.40 (s, 3H), 3.85 (s, 3H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.85–7.88 (m, 4H), 8.93 (s, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 21.6, 55.6, 114.6, 125.2, 127.8, 129.7, 133.6, 135.7, 144.2, 165.2, 169.1.

***N*-[4-(Trifluoromethyl)phenyl]methylidene-4-methylbenzenesulfonamide [198012-02-1] (2e).⁸**



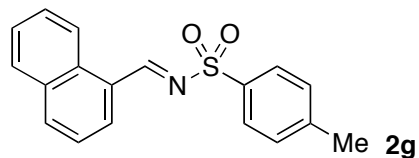
The general procedure was followed with use of *p*-toluenesulfonamide (858 mg, 5.0 mmol) and 4-(trifluoromethyl)benzaldehyde (1.06 g, 6.1 mmol). The reaction was conducted for 3 days. The crude product was recrystallized from EtOAc–hexane to give **2e** (1.34 g, 82%) as colorless crystals: ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.44 (s, 3H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 8.05 (d, *J* = 8.1 Hz, 2H), 9.09 (s, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 21.6, 123.3 (q, *J* = 273 Hz), 126.0 (q, *J* = 4 Hz), 128.2, 129.9, 131.3, 134.5, 135.4, 135.8 (q, *J* = 33 Hz), 145.0, 168.4.

***N*-[3-(Trifluoromethyl)phenyl]methylidene-4-methylbenzenesulfonamide [442157-30-4] (2f).**



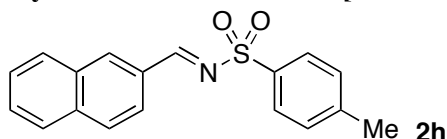
The general procedure was followed with use of *p*-toluenesulfonamide (858 mg, 5.0 mmol) and 2-methylbenzaldehyde (1.06 g, 6.1 mmol). The reaction was conducted for 2 days. The crude product was recrystallized from EtOAc–hexane to give **2f** (543 mg, 33%) as colorless crystals: mp 103.8–103.9 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.45 (s, 3H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 2H), 8.10 (d, *J* = 7.8 Hz, 1H), 8.20 (s, 1H), 9.08 (s, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 21.5, 123.3 (q, *J* = 273 Hz), 127.3 (q, *J* = 4 Hz), 128.2, 129.77, 129.85, 130.9 (q, *J* = 4 Hz), 131.7 (q, *J* = 33 Hz), 133.0, 134.4, 134.5, 145.0, 168.4; IR (thin film) 3076 w, 3052 w, 1605 s, 1484 m, 1361 m, 1316 s, 1209 m, 1161 s, 1131 s, 1092 s, 1067 s, 1003 m, 913 m, 806 s, 753 m, 734 m, 686 s, 658 m, 618 m, 550 s cm⁻¹; Anal. Calcd for C₁₅H₁₂NO₂F₃S: C, 55.04; H, 3.70; N, 4.28. Found: C, 54.99; H, 3.77; N, 4.29.

***N*-[(1-Naphthyl)methylidene]-4-methylbenzenesulfonamide [36216-15-6] (**2g**).⁹**



The general procedure was followed with use of *p*-toluenesulfonamide (858 mg, 5.0 mmol) and 1-naphthaldehyde (956 mg, 6.1 mmol). The reaction was conducted for 3 days. The crude product was recrystallized from EtOAc–hexane to give **2g** (1.10 g, 71%) as colorless crystals: ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.42 (s, 3H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.52–7.59 (m, 2H), 7.65 (t, *J* = 7.2 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 8.08 (d, *J* = 8.2 Hz, 1H), 8.13 (d, *J* = 7.2 Hz, 1H), 8.97 (d, *J* = 8.6 Hz, 1H), 9.59 (s, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 21.6, 124.2, 125.0, 126.9, 127.6, 128.0, 128.8, 129.0, 129.8, 131.8, 133.7, 135.0, 135.5, 136.0, 144.4, 169.7.

***N*-[(2-Naphthyl)methylidene]-4-methylbenzenesulfonamide [17692-84-1] (**2h**).⁸**



The general procedure was followed with use of *p*-toluenesulfonamide (856 mg, 5.0 mmol) and 2-naphthaldehyde (781 mg, 5.0 mmol). The reaction was conducted for 3 days. The crude product was recrystallized from EtOAc–hexane to give **2h** (1.20 g, 78%) as colorless crystals: ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.40 (s, 3H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.98 (d, *J* = 8.6 Hz, 1H), 8.26 (s, 1H), 9.14 (s, 1H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 21.6, 124.1, 127.2, 128.02, 128.08, 129.1, 129.42, 129.46, 129.8, 130.1, 132.6, 135.3, 136.0, 136.5, 144.5, 170.0.

Palladium-Catalyzed [4+2] Cycloaddition of 2-[(Trimethylsilyl)methyl]benzyl Carbonates **1 with *N*-Tosylbenzimidines **2****

Optimization of Reaction Conditions for the [4+2] Cycloaddition of **1a with **2a****

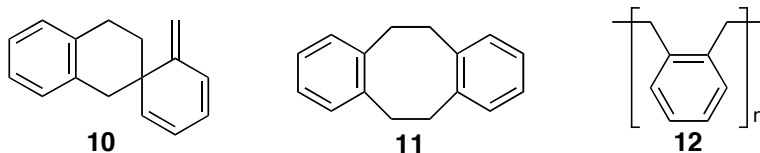
The reactions for the optimization were conducted as follows: In a nitrogen-filled drybox, a palladium source (4.5 μmol), a ligand (5.0 or 9.9 μmol), **2a** (46.7 mg, 0.18 mmol), a fluoride source (0.23 mmol), and naphthalene (15 mg, as an internal standard for GC analysis) were placed in a 5 mL screw-capped vial equipped with a stirring bar. After dry solvent (1.0 mL) was added, the vial was sealed with a screw cap containing a PTFE/silicone septum and removed from the drybox. Substrate **1a** (37.9 mg, 0.15 mmol) was added into the vial through the septum by using a micro-syringe at room temperature. When TBAF (1.0 M solution in THF, 0.23 mL, 0.23 mmol) was used as a fluoride source, the solution was added into the mixture in a similar manner. The solution was stirred at 120 or 100 °C. The reaction was monitored by GC

analysis with J&W capillary column DB-1 (0.53 mm $\phi \times 15$ m, d_f 1.5 μ m). The selected results of the above reactions were summarized in Table S-1.

Table S-1. Optimization of reaction conditions for the [4+2] cycloaddition of **1a** with **2a**.^a

| entry | ligand ^b | [F ⁻] | temp, °C | time, h | yield (3a), % ^c |
|-----------------|---------------------|-------------------|----------|---------|-------------------------------------|
| 1 | DPPE (3.3) | — | 120 | 24 | 10 |
| 2 | DPPP (3.3) | — | 120 | 24 | 25 |
| 3 | DPPB (3.3) | — | 120 | 24 | 51 (61) |
| 4 | DPPPent (3.3) | — | 120 | 24 | 48 (54) |
| 5 | DPPF (3.3) | — | 120 | 24 | 34 |
| 6 | DPEphos (3.3) | — | 120 | 24 | 27 |
| 7 | DPPB (6.6) | — | 120 | 24 | 87 (87) |
| 8 | DPPPent (6.6) | — | 120 | 24 | 73 (96) |
| 9 | DPPPent (6.6) | KF | 100 | 3 | 89 |
| 10 | DPPPent (6.6) | TBAF ^d | 100 | 3 | 0 |
| 11 | DPPPent (6.6) | CsF | 100 | 3 | 12 |
| 12 ^e | — | KF | 100 | 3 | 2 ^f |

^a Reactions were conducted on a 0.15 mmol scale in DMF (1.0 mL). The ratio of **1a**:**2a**: $[F^-]$:Pd(η^3 -C₃H₅)Cp:ligand was 100:120:150:3.0:3.3 or 6.6. ^b Amounts of ligand in mol% to **1a** were given in parentheses. ^c Yields were determined by GC analysis (average of two runs). GC yields at 48 h were given in parentheses. ^d 1.0 M solution in THF was used. ^e The reaction was conducted in the absence of Pd(η^3 -C₃H₅)Cp. ^f *o*-Xylylene dimer **10** and [2,2]orthocyclophane **11** were formed in 44% and 32% yield, respectively.



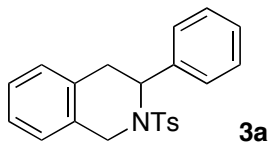
As seen in entry 12 of Table S-1, compound **1a** failed to react with **2a** in the absence of the palladium catalyst. The substrate would be converted with KF into free *o*-xylylene. The resulting *o*-xylylene rapidly dimerized before reacting with **2a**, giving the undesirable products **10** and **11** in 44% and 32% yields, respectively. The observation indicates that the formation of the cycloaddition product **3a** requires the palladium catalysis. No side products **10** and **11** were detected in GC analyses to monitor the reactions in entries 1–9 of Table S-1, Scheme 1, and Table 1. Furthermore, treatment of **1a** with the palladium catalyst in the absence of **2a** and KF yielded poly(*o*-xylylene) **12** and a small amount of **11**, which would be formed

through Hiyama coupling. Therefore, we believe that the present palladium-catalyzed reaction does not involve free *o*-xylylene.

General Procedure A. In a nitrogen-filled drybox, Pd(η^3 -C₃H₅)Cp (1.0 mg, 4.7 μ mol), DPPent (4.4 mg, 10.0 μ mol), and an imine **2** (0.18 mmol) were placed in a 5 mL screw-capped vial equipped with a stirring bar. After dry DMF (1.0 mL) was added, the vial was sealed with a screw cap containing a PTFE/silicone septum and removed from the drybox. A 2-[(trimethylsilyl)methyl]benzyl carbonate **1** (0.15 mmol) was added into the vial through the septum by using a micro-syringe at room temperature. The solution was stirred at 120 °C until **1** was consumed completely (monitored by GC), and then evaporated under reduced pressure. The residue was purified with a flash column chromatography (EtOAc/hexane) to give the desired cycloadduct **3**. Alternatively, it was purified with MPLC (EtOAc/hexane) after passed through a short silica gel column.

General Procedure B. In a nitrogen-filled drybox, Pd(η^3 -C₃H₅)Cp (1.0 mg, 4.7 μ mol), DPPent (4.4 mg, 10.0 μ mol), an imine **2** (0.18 mmol), and spray dried potassium fluoride (13.1 mg, 0.23 mmol) were placed in a 5 mL screw-capped vial equipped with a stirring bar. After dry DMF (1.0 mL) was added, the vial was sealed with a screw cap containing a PTFE/silicone septum and removed from the drybox. A 2-[(trimethylsilyl)methyl]benzyl carbonate **1** (0.15 mmol) was added into the vial through the septum by using a micro-syringe at room temperature. The solution was stirred at 100 °C until **1** was consumed completely (monitored by GC), and then evaporated under reduced pressure. The residue was purified with a flash column chromatography (EtOAc/hexane) to give the desired cycloadduct **3**. Alternatively, it was purified with MPLC (EtOAc/hexane) after passed through a short silica gel column.

2-(4-Methylbenzenesulfonyl)-3-phenyl-1,2,3,4-tetrahydroisoquinoline (**3a**) (Scheme 1).

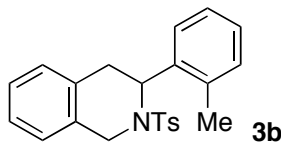


The general procedure A was followed with use of **1a** (36.8 mg, 0.15 mmol) and **2a** (46.6 mg, 0.18 mmol). The reaction was conducted for 48 h. The crude product was purified with a flash column chromatography (EtOAc/hexane = 1/10) to give **3a** (48.6 mg, 92%) as a colorless solid: mp 105.7–105.9 °C; ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.34 (s, 3H), 3.00–3.11 (m 2H), 4.18 (d, *J* = 16.5 Hz, 1H), 4.69 (d, *J* = 16.5 Hz, 1H), 5.38 (t, *J* = 4.5 Hz, 1H), 6.95–7.05 (m, 2H), 7.08–7.25 (m, 9H), 7.62 (d, *J* = 8.2 Hz, 2H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 21.4, 32.2, 44.0, 54.6, 125.8, 126.3, 127.02, 127.07, 127.3, 128.3, 128.5, 129.4, 132.3, 132.5, 137.1, 139.8, 143.1; ¹³C {¹H} NMR (100 MHz, acetone-*d*₆) δ 20.8, 32.9, 44.5, 55.4, 126.2, 126.6, 127.25, 127.31, 127.40, 127.45, 128.5, 128.7, 129.9, 133.1, 133.3, 137.8, 141.3, 143.6; IR (thin film) 3062 m, 3029 m, 2922 w, 2855 w, 1599 m, 1495 m, 1451 m, 1335 s, 1266 w, 1214 w, 1159 s, 1119 m, 1092 s, 1051 s,

953 m, 912 s, 860 w, 815 m, 778 m, 735 s, 702 s, 684 s, 645 m, 609 w, 586 m, 557 s cm^{-1} ; Anal. Calcd for $\text{C}_{22}\text{H}_{21}\text{NO}_2\text{S}$: C, 72.70; H, 5.82; N, 3.85. Found: C, 72.61; H, 5.66; N, 3.93.

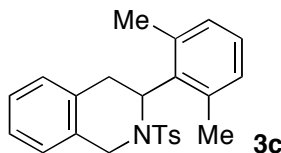
Alternatively, the title compound **3a** was obtained from the reaction of **1a** (37.7 mg, 0.15 mmol) and **2a** (47.0 mg, 0.18 mmol) with the general procedure B. The reaction was conducted for 3 h and afforded **3a** (46.2 mg) in 85% yield.

3-(2-Methylphenyl)-2-(4-methylbenzenesulfonyl)-1,2,3,4-tetrahydroisoquinoline (3b) (Table 1, entry 1).



The general procedure A was followed with use of **1a** (37.6 mg, 0.15 mmol) and **2b** (49.3 mg, 0.18 mmol). The reaction was conducted for 24 h. The crude product was purified with MPLC (EtOAc/hexane = 1/3) to give **3b** (47.3 mg, 84%) as a colorless solid: mp 110.9–111.2 °C; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.30 (s, 3H), 2.52 (s, 3H), 2.84 (dd, J = 3.8, 16.3 Hz, 1H), 3.06 (dd, J = 16.3, 6.6 Hz, 1H), 4.26 (d, J = 16.3 Hz, 1H), 4.64 (d, J = 16.3 Hz, 1H), 5.45 (dd, J = 3.8, 6.6 Hz, 1H), 6.86–6.94 (m, 3H), 7.00–7.16 (m, 7H), 7.53 (d, J = 8.2 Hz, 2H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 19.5, 21.4, 32.6, 45.2, 52.8, 125.7, 126.36, 126.45, 127.2, 127.3, 127.4, 128.1, 129.1, 130.7, 133.1, 133.3, 135.8, 136.4, 139.1, 143.0; ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, acetone- d_6) δ 19.0, 20.8, 33.5, 45.8, 53.7, 126.0, 126.2, 126.6, 126.8, 127.40, 127.48, 127.7, 128.1, 129.6, 130.7, 134.16, 134.19, 135.5, 137.1, 140.9, 143.4; IR (thin film) 3064 w, 3026 w, 2955 w, 2922 m, 2860 w, 1598 m, 1493 m, 1458 m, 1400 w, 1342 s, 1292 m, 1159 s, 1119 m, 1090 m, 1039 m, 1000 w, 971 m, 910 s, 863 w, 813 m, 758 s, 732 s, 680 s, 644 m, 614 m, 593 m, 567 m, 547 m, 519 m, 492 m, 462 m, 418 cm^{-1} ; Anal. Calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_2\text{S}$: C, 73.18; H, 6.14; N, 3.71. Found: C, 73.10; H, 6.13; N, 3.67.

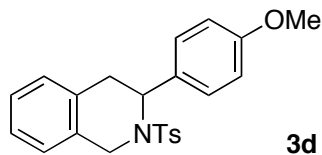
3-(2,6-Dimethylphenyl)-2-(4-methylbenzenesulfonyl)-1,2,3,4-tetrahydroisoquinoline (3c) (Table 1, entry 2).



The general procedure A was followed with use of **1a** (38.1 mg, 0.15 mmol) and **2c** (51.7 mg, 0.18 mmol). The reaction was conducted for 24 h. The crude product was purified with a flash column chromatography (EtOAc/hexane = 1/5) to give **3c** (46.1 mg, 78%) as a colorless solid: mp 170.6–170.7 °C; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.29 (s, 3H), 2.40 (s, 6H), 2.79 (dd, J = 5.2, 15.2 Hz, 1H), 3.00 (t, J = 12.7, 15.2 Hz, 1H), 4.41 (d, J = 15.7 Hz, 1H), 4.86 (d, J = 15.7 Hz, 1H), 5.04 (dd, J = 5.2, 12.7 Hz, 1H), 6.95–7.21 (m, 9H), 7.34 (d, J = 8.2 Hz, 2H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 21.1, 21.3, 33.7, 46.8, 55.5, 125.7, 126.6, 126.9, 127.1, 127.6, 129.0, 129.6, 135.1, 135.7, 136.0, 136.5, 138.2, 142.7; ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, 1,4-dioxane- d_8) δ 21.1, 34.1, 47.1, 56.2, 126.4, 127.0, 127.14, 127.21, 127.9, 128.0, 129.5, 130.1, 136.2,

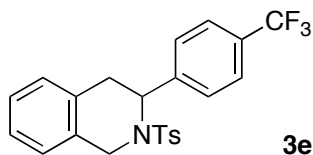
136.6, 137.3, 137.9, 139.6, 143.1; IR (thin film) 3027 w, 2960 w, 2923 w, 2866 w, 1597 s, 1471 m, 1336 s, 1159 s, 1091 s, 1065 m, 996 s, 905 m, 767 m, 750 m, 733 s, 716 m, 658 m, 549 m cm^{-1} ; Anal. Calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_2\text{S}$: C, 73.62; H, 6.44; N, 3.58. Found: C, 73.41; H, 6.46; N, 3.60.

3-(4-Methoxyphenyl)-2-(4-methylbenzenesulfonyl)-1,2,3,4-tetrahydroisoquinoline (3d) (Table 1, entry 3).



The general procedure A was followed with use of **1a** (38.1 mg, 0.15 mmol) and **2d** (52.1 mg, 0.18 mmol). The reaction was conducted for 24 h. The crude product was purified with a flash column chromatography (EtOAc/hexane = 1/4) to give **3d** (51.8 mg) containing a small amount of impurities. The impurities were removed by MPLC (EtOAc/hexane = 1/3), which gave pure **3d** (47.7 mg, 81%) as a colorless solid: mp 132.2–133.3 °C; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.35 (s, 3H), 2.98–3.10 (m, 2H), 3.73 (s, 3H), 4.14 (d, J = 16.6 Hz, 1H), 4.68 (d, J = 16.6 Hz, 1H), 5.36 (dd, J = 3.6, 6.1 Hz, 1H), 6.72 (d, J = 8.7 Hz, 2H), 6.96–7.06 (m, 2H), 7.08–7.19 (m, 6H), 7.63 (d, J = 8.2 Hz, 2H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 21.4, 32.1, 43.7, 53.9, 55.2, 113.7, 125.8, 126.3, 127.00, 127.05, 128.4, 128.6, 129.5, 131.6, 132.3, 132.6, 137.3, 143.1, 158.8; IR (thin film) 3028 w, 2916 w, 2837 w, 1918 m, 1610 w, 1512 m, 1456 m, 1373 w, 1333 m, 1305 m, 1252 s, 1179 m, 1159 s, 1117 m, 1091 m, 1036 m, 953 w, 924 m, 889 w, 836 m, 812 m, 751 m, 734 m, 675 m, 645 m, 604 w, 577 m, 555 s, 502 s cm^{-1} ; Anal. Calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_3\text{S}$: C, 70.20; H, 5.89; N, 3.56. Found: C, 70.06; H, 5.89; N, 3.56.

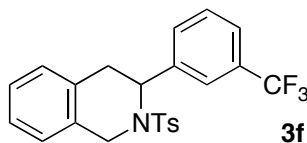
2-(4-Methylbenzenesulfonyl)-3-[4-(trifluoromethyl)phenyl]-1,2,3,4-tetrahydroisoquinoline (3e) (Table 1, entry 5).



The general procedure B was followed with use of **1a** (37.4 mg, 0.15 mmol) and **2e** (58.9 mg, 0.18 mmol). The reaction was conducted for 3 h. The crude product was purified with a flash column chromatography (EtOAc/hexane = 1/10) to give **3e** (42.8 mg, 67%) as a colorless solid: mp 110.2–110.3 °C; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.36 (s, 3H), 3.00 (dd, J = 3.24, 16.1 Hz, 1H), 3.09 (dd, J = 16.1, 5.7 Hz, 1H), 4.27 (d, J = 16.2 Hz, 1H), 4.67 (d, J = 16.2 Hz, 1H), 5.37 (dd, J = 3.3, 5.7 Hz, 1H), 7.00–7.04 (m, 2H), 7.12–7.16 (m, 2H), 7.17 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 21.4, 33.0, 44.5, 54.8, 124.0 (q, J = 272 Hz), 125.3 (q, J = 4 Hz), 125.9, 126.7, 127.1, 127.33, 127.36, 128.4, 129.5 (q, J = 32 Hz), 129.6, 132.1, 132.3, 136.5, 143.5, 144.4; IR (thin film) 3030 w, 2925 w, 2858 w, 1619 w, 1598 w, 1495 w, 1454 w, 1415 w, 1326 s, 1267 w, 1215 w, 1162 s,

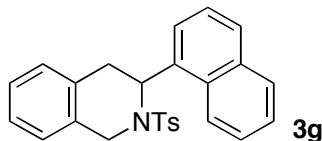
1120 s, 1092 m, 1067 m, 1017 m, 954 w, 910 m, 841 w, 814 m, 735 m, 685 m, 651 m, 602 w, 555 m cm^{-1} ; Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{NO}_2\text{F}_3\text{S}$: C, 64.02; H, 4.67; N, 3.25. Found: C, 63.95; H, 4.68; N, 3.21.

2-(4-Methylbenzenesulfonyl)-3-[3-(trifluoromethyl)phenyl]-1,2,3,4-tetrahydroisoquinoline (3f) (Table 1, entry 6).



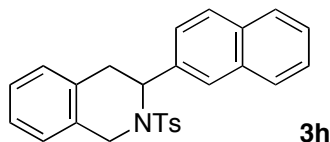
The general procedure B was followed with use of **1a** (37.7 mg, 0.15 mmol) and **2f** (58.9 mg, 0.18 mmol). The reaction was conducted for 3 h. The crude product was purified with a flash column chromatography (EtOAc/hexane = 1/10) to give **3f** (48.7 mg, 76%) as a colorless solid: mp 102.1–102.2 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.35 (s, 3H), 3.00 (dd, $J = 3.3, 16.0$ Hz, 1H), 3.12 (dd, $J = 5.7, 16.0$ Hz, 1H), 4.26 (d, $J = 16.1$ Hz, 1H), 4.71 (d, $J = 16.1$ Hz, 1H), 5.37 (dd, $J = 3.3, 5.7$ Hz, 1H), 7.00–7.06 (m, 2H), 7.10–7.20 (m, 4H), 7.27–7.44 (m, 4H), 7.62 (d, $J = 8.1$ Hz, 2H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 21.4, 33.3, 44.6, 54.9, 123.8 (q, $J = 4$ Hz), 123.9 (q, $J = 272$ Hz), 124.2 (q, $J = 4$ Hz), 125.9, 126.7, 127.0, 127.4, 128.4, 128.8, 129.6, 130.2, 130.6 ($J = 32$ Hz), 132.1, 132.4, 136.5, 141.5, 143.5; IR (thin film) 3031 w, 2924 w, 2856 w, 1598 w, 1495 w, 1451 m, 1331 s, 1161 s, 1123 s, 1092 m, 1076 m, 1051 m, 909 m, 802 m, 749 m, 704 m, 689 m, 660 m, 555 m cm^{-1} ; Anal. Calcd for $\text{C}_{23}\text{H}_{20}\text{NO}_2\text{F}_3\text{S}$: C, 64.02; H, 4.67; N, 3.25. Found: C, 63.91; H, 4.65; N, 3.27.

2-(4-Methylbenzenesulfonyl)-3-(1-naphthyl)-1,2,3,4-tetrahydroisoquinoline (3g) (Table 1, entry 7).



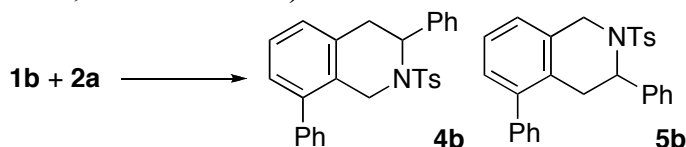
The general procedure B was followed with use of **1a** (37.5 mg, 0.15 mmol) and **2g** (55.7 mg, 0.18 mmol). The reaction was conducted for 3 h. The crude product was purified with a flash column chromatography (EtOAc/hexane = 1/10) to give **3g** (52.5 mg, 85%) as a colorless solid: mp 154.7–154.8 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.31 (s, 3H), 3.07 (dd, $J = 2.4, 16.6$ Hz, 1H), 3.26 (dd, $J = 6.6, 16.6$ Hz, 1H), 4.17 (d, $J = 16.7$ Hz, 1H), 4.60 (d, $J = 16.7$ Hz, 1H), 6.15 (dd, $J = 2.4, 6.6$ Hz, 1H), 6.93 (d, $J = 6.6$ Hz, 1H), 7.01 (d, $J = 6.6$ Hz, 1H), 7.05–7.19 (m, 6H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.59–7.64 (m, 3H), 7.71 (d, $J = 7.8$ Hz, 1H), 7.84 (d, $J = 8.0$ Hz, 1H), 8.50 (d, $J = 8.5$ Hz, 1H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 21.4, 32.1, 44.7, 51.9, 123.6, 124.6, 124.8, 125.6, 125.8, 126.4, 126.5, 127.1, 127.4, 128.2, 128.5, 128.7, 129.2, 130.9, 132.5, 133.1, 133.8, 135.5, 136.4, 143.2; IR (thin film) 3050 w, 2924 w, 2855 w, 1598 w, 1495 w, 1442 w, 1399 w, 1337 s, 1262 w, 1204 w, 1159 s, 1119 m, 1090 m, 1041 m, 911 s, 796 m, 776 m, 733 s, 677 s, 647 m, 608 m, 571 m, 544 m cm^{-1} ; Anal. Calcd for $\text{C}_{26}\text{H}_{23}\text{NO}_2\text{S}$: C, 75.52; H, 5.61; N, 3.39. Found: C, 75.25; H, 5.61; N, 3.32.

2-(4-Methylbenzenesulfonyl)-3-(2-naphthyl)-1,2,3,4-tetrahydroisoquinoline (**3h**) (Table 1, entry 8).



The general procedure B was followed with use of **1a** (38.1 mg, 0.15 mmol) and **2h** (55.6 mg, 0.18 mmol). The reaction was conducted for 3 h. The crude product was purified with a flash column chromatography (EtOAc/hexane = 1/10) to give **3h** (50.4 mg, 81%) as a colorless solid: mp 158.5–158.6 °C; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.31 (s, 3H), 3.06–3.22 (m, 2H), 4.22 (d, J = 16.5 Hz, 1H), 4.74 (d, J = 16.5 Hz, 1H), 5.50–5.57 (m, 1H), 6.93–7.22 (m, 6H), 7.34–7.47 (m, 3H), 7.52 (s, 1H), 7.57–7.77 (m, 5H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 21.4, 32.1, 44.2, 54.8, 125.3, 125.8, 125.89, 125.91, 126.4, 127.03, 127.08, 127.4, 128.0, 128.2, 128.5, 129.4, 132.3, 132.47, 132.54, 132.9, 137.12, 137.14, 143.1; IR (thin film) 3056 w, 2920 w, 2854 w, 1599 w, 1496 w, 1450 w, 1335 s, 1159 s, 1118 m, 1092 m, 1051 m, 910 m, 862 w, 813 m, 731 s, 674 m, 554 cm^{-1} ; Anal. Calcd for $\text{C}_{26}\text{H}_{23}\text{NO}_2\text{S}$: C, 75.52; H, 5.61; N, 3.39. Found: C, 75.40; H, 5.57; N, 3.34.

Reaction of **1b** with **2a** (Table 2, entries 1 and 2).

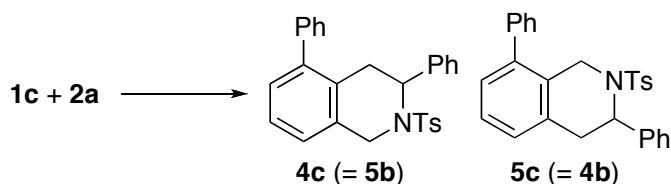


The general procedure B was followed with use of **1b** (50.2 mg, 0.15 mmol) and **2a** (46.7 mg, 0.18 mmol) (Table 2, entry 1). The reaction was conducted for 3 h. The crude product contained the cycloadducts **4b** and **5b** in the ratio 89:11, which was determined with the ^1H NMR spectrum (see Figure S-32). The crude product was purified with a flash column chromatography (EtOAc/hexane = 1/10) to give a mixture of 2-(4-methylbenzenesulfonyl)-3,8-diphenyl-1,2,3,4-tetrahydroisoquinoline (**4b**) and 2-(4-methylbenzenesulfonyl)-3,5-diphenyl-1,2,3,4-tetrahydroisoquinoline (**5b**) (54.2 mg, **4b:5b** = 89:11, 81%) as a colorless solid.

Alternatively, the cycloadducts were obtained from the reaction of **1b** (49.0 mg, 0.15 mmol) and **2a** (47.3 mg, 0.18 mmol) with the general procedure A (Table 2, entry 2). The reaction was conducted for 72 h. The crude product contains the cycloadducts **4b** and **5b** in the ratio 89:11, which was determined with the ^1H NMR spectrum (see Figure S-33). The reaction afforded a mixture of **4b** and **5b** (47.5 mg, **4b:5b** = 88:12) in 72% yield.

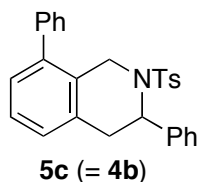
The spectrum data of pure **4b** were given in the following section.

Reaction of **1c** with **2a** (Table 2, entries 3 and 4).



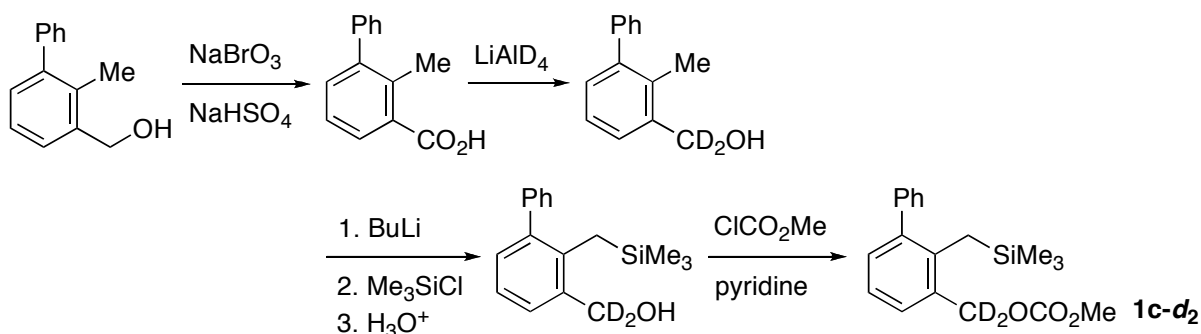
The general procedure B was followed with use of **1c** (51.3 mg, 0.16 mmol) and **2a** (46.7 mg, 0.18 mmol) (Table 2, entry 3). The reaction was conducted for 4 h. The crude product contained the cycloadducts **4c** and **5c** in the ratio 10:90, which was determined with the ^1H NMR spectrum (see Figure S-34). The crude product was purified with a flash column chromatography (EtOAc/hexane = 1/10) to give a mixture of **4c** and **5c** (51.9 mg, **4c:5c** = 12:88, 76%) as a colorless solid. Compounds **4c** and **5c** are identical with **5b** and **4b**, respectively.

Alternatively, the cycloadducts were obtained from the reaction of **1c** (39.1 mg, 0.12 mmol) and **2a** (46.7 mg, 0.18 mmol) with the general procedure A (Table 2, entry 4). The reaction was conducted for 24 h. The crude product contains the cycloadducts **4c** and **5c** in the ratio 11:89, which was determined with the ^1H NMR spectrum (see Figure S-35). The reaction afforded a mixture of **4c** and **5c** (37.6 mg, **4c:5c** = 10:90) in 72% yield.



The major product **5c** can be separated from **4c** by recrystallization. The crude product, which resulted from the reaction using **1c** (49.4 mg, 0.15 mmol) and **2a** (47.0 mg, 0.18 mmol) for 24 h with the general procedure A, was recrystallized from EtOAc–hexane after passed through a short silica gel column (EtOAc/hexane = 1/3) to give **5c** (44.2 mg, 67%) as colorless crystals: mp 143.6–143.7 °C; ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.35 (s, 3H), 3.07 (dd, J = 4.4, 16.1 Hz, 1H), 3.19 (dd, J = 6.46, 16.1 Hz, 1H), 4.15 (d, J = 16.6 Hz, 1H), 4.60 (d, J = 16.6 Hz, 1H), 5.28 (dd, J = 4.4, 6.4 Hz, 1H), 7.02 (d, J = 7.5 Hz, 1H), 7.07 (d, J = 7.7 Hz, 1H), 7.09 (d, J = 7.9 Hz, 1H), 7.15–7.27 (m, 8H), 7.34–7.44 (m, 5H); ^{13}C $\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 21.4, 33.9, 42.9, 55.3, 126.9, 127.1, 127.37, 127.45, 127.9, 128.39, 128.45, 129.0, 129.3, 130.9, 133.7, 136.9, 139.7, 139.9, 140.8, 142.9; IR (thin film) 3059 w, 3029 w, 2919 w, 2851 w, 1597 w, 1494 m, 1453 m, 1335 s, 1267 w, 1216 w, 1158 s, 1117 m, 1090 m, 1049 m, 936 w, 813 m, 796 m, 761 m, 737 m, 702 s, 665 m, 610 w, 549 m, 490 m, 475 s, 432 s, 409 m cm^{-1} ; Anal. Calcd for $\text{C}_{28}\text{H}_{25}\text{NO}_2\text{S}$: C, 76.51; H, 5.73; N, 3.19. Found: C, 76.51; H, 5.81; N, 3.19.

The major product was assigned to **5c** through the reaction of methyl 1,1-dideuterio-1-[3-phenyl-2- $\{(\text{trimethylsilyl})\text{methyl}\}$ phenyl]methyl carbonate (**1c- d_2**) with **2a**. The labelled substrate **1c- d_2** was prepared as follows.



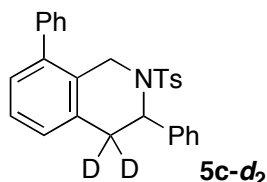
A suspension of (2-methyl-3-phenylphenyl)methanol (3.97 g, 20 mmol), sodium bromate (9.05 g, 60 mmol), and sodium hydrogensulfate monohydrate (2.79 g, 20 mmol) in acetonitrile (100 mL) was stirred under reflux for 1.5 h. After cooled to room temperature, the mixture was filtered through a Celite pad. After the filtrate was evaporated under reduced pressure, the residue was dissolved in 0.5 *N* NaOH *aq.* (100 mL), washed three times with EtOAc, acidified with 2 *N* HCl, and then extracted three times with EtOAc. The combined organic layer was washed with brine, dried with Na₂SO₄, and then evaporated under reduced pressure to give crude 2-methyl-3-phenylbenzoic acid (3.28 g).¹⁰

A solution of the crude carboxylic acid (3.28 g) in THF (36 mL) was added dropwise to a mixture of lithium aluminum deuteride (681 mg, 16 mmol) in THF (24 mL) at 0 °C for 30 min. After hydrogen evolution ceased, the reaction mixture was stirred under reflux for 11 h. After the reaction vessel was cooled with ice bath, H₂O was carefully added to the resulting mixture at 0 °C. The mixture was filtered through a Celite pad. The filter cake was washed with methanol. The combined filtrate was extracted three times with EtOAc. The combined organic layer was washed with saturated Na₂CO₃ *aq.*, with brine, dried with Na₂SO₄, and then evaporated under reduced pressure. The residue was purified with a flash column chromatography (EtOAc/hexane = 1/3) to give 1,1-dideuterio-1-(2-methyl-3-phenylphenyl)methanol (1.79 g, 45%) as a colorless solid: ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.22 (s, 3H), 1.82–2.52 (br, 1H), 7.10–7.48 (m, 8H).

A solution of butyllithium in hexane (1.6 *M*, 7.0 mL, 11 mmol) was added dropwise to a solution of the benzylic alcohol (1.01 g, 5.0 mmol) in dry Et₂O (10 mL) at 0 °C for 30 min. After stirred under reflux for 24 h, the reaction mixture was cooled to –78 °C. Chlorotrimethylsilane (1.6 mL, *d* 0.856 g/mL, 13 mmol) was added dropwise to the resulting solution for 30 min. The mixture was stirred at room temperature for 3 h, and then 10% H₂SO₄ *aq.* (5.0 mL) was carefully added to it. After stirred at room temperature for 12 h, the mixture was extracted three times with EtOAc. The combined organic layer was washed with brine, dried with Na₂SO₄, and then evaporated under reduced pressure. The residue was purified with a flash column chromatography (EtOAc/hexane = 1/5) to give 1,1-dideuterio-1-[3-phenyl-2-{(trimethylsilyl)methyl}phenyl]methanol (948 mg, 69%) as a colorless solid: ¹H NMR (400 MHz, CDCl₃, TMS) δ –0.29 (s, 9H), 1.94 (s, 1H), 2.37 (s, 2H), 7.09–7.15 (m, 2H), 7.26–7.40 (m, 6H).

The silylated compound (665 mg, 2.4 mmol) and 4-dimethylaminopyridine (4.6 mg, 38 μmol) was dissolved in dry CH₂Cl₂ (2.5 mL). After dry pyridine (0.32 mL, *d* 0.978 g/mL, 4.0 mmol) was added,

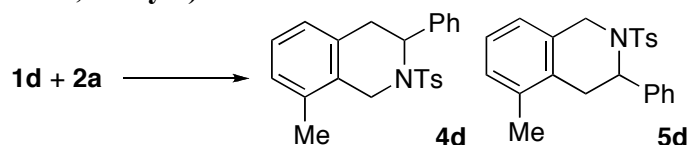
methyl chloroformate (335 mg, 3.5 mmol) was added dropwise to the solution at 0 °C for 15 min. The mixture was stirred at room temperature for 19 h. After 1 *N* HCl *aq.* was added, the resulting mixture was extracted three times with EtOAc. The combined organic layer was washed with brine, dried with Na₂SO₄, and then evaporated under reduced pressure. The residue was purified with a flash column chromatography (EtOAc/hexane = 1/20) to give **1c-d₂** (606 mg, 75%) as a colorless solid: ¹H NMR (400 MHz, CDCl₃, TMS) δ -0.29 (s, 9H), 2.37 (s, 2H), 3.80 (s, 3H), 7.09–7.17 (m, 2H), 7.28–7.41 (m, 6H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ -0.8, 19.3, 54.7, 68.1 (quintet, *J* = 23 Hz), 123.9, 126.8, 128.1, 128.9, 129.7, 130.9, 132.0, 138.2, 141.4, 142.4, 155.8; IR (neat) 3059 w, 3026 w, 2955 m, 2898 w, 2853 w, 2254 w, 2139 w, 1748 s, 1587 w, 1494 w, 1442 s, 1281 s, 1249 s, 1194 m, 1155 m, 1062 m, 1040 m, 1002 w, 926 m, 846 s, 790 m, 763 m, 734 m, 706 m cm⁻¹.



The general procedure A was followed with use of **1c-d₂** (50.4 mg, 0.15 mmol) and **2a** (46.6 mg, 0.18 mmol). The reaction was conducted for 29 h. The crude product was purified with a flash column chromatography (EtOAc/hexane = 1/10) to give a mixture of **4c-d₂** and **5c-d₂** (57.3 mg, **4c-d₂**:**5c-d₂** = 12:88, 85%) as a colorless solid. **5c-d₂**: ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.31 (s, 3H), 4.16 (d, *J* = 16.6 Hz, 1H), 4.61 (d, *J* = 16.6 Hz, 1H), 5.26 (s, 1H), 6.98–7.44 (m, 17H); ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 21.4, 33.1 (br), 42.9, 55.2, 126.85, 126.88, 127.0, 127.35, 127.42, 127.44, 127.9, 128.38, 128.44, 128.9, 129.3, 130.8, 133.5, 136.9, 139.7, 139.9, 140.8, 142.9; IR (thin film) 3060 w, 3029 w, 2254 w, 1597 w, 1495 m, 1452 m, 1342 s, 1160 s, 1091 m, 1032 m, 956 m, 911 m, 865 m, 813 m, 783 m, 760 m, 733 s, 703 s, 679 m cm⁻¹.

The resonances at 3.07 and 3.19 ppm, which is assigned to the 4-position of tetrahydroisoquinoline, disappeared from the ¹H NMR of the major product in the reaction of **1c** with **2a** (Figure S-34 or S-35 vs S-41). The observation indicates that the benzylic ester moiety of **1c** reacted with the imino carbon of **2a**. Therefore, the major product is assigned to **5c**.

Reaction of **1d** with **2a** (Table 2, entry 5).

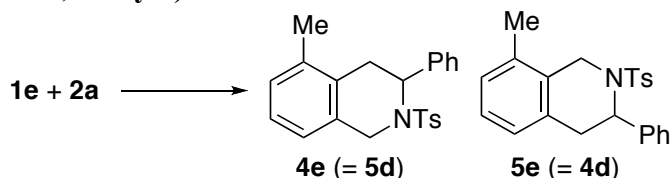


The general procedure B was followed with use of **1d** (40.8 mg, 0.15 mmol) and **2a** (46.7 mg, 0.18 mmol). The reaction was conducted for 4 h. The crude product contained the cycloadducts **4d** and **5d** in the ratio 56:44, which was determined with the ¹H NMR spectrum (see Figure S-43). The crude product was purified with a flash column chromatography (EtOAc/hexane = 1/20) to give a mixture of **4d** and **5d** (42.4 mg, **4d**:**5d** = 58:42, 73%) as colorless liquid: ¹H NMR (400 MHz, CDCl₃, TMS) δ 2.14 (s, 1.2 H), 2.15 (s,

1.8H), 2.347 (s, 1.2H), 2.35 (s, 1.8H), 2.84 (dd, $J = 6.7, 16.9$ Hz, 0.4H), 3.03 ($J = 1.3, 16.9$ Hz, 0.4H), 3.07–3.11 (m, 1.2H), 3.99 (d, $J = 17.0$ Hz, 0.6H), 4.13 (d, $J = 16.6$ Hz, 0.4H), 4.64 (d, $J = 16.6$ Hz, 0.4H), 4.69 (d, $J = 17.0$ Hz, 0.6H), 5.40–5.46 (m, 1H), 6.84 (d, $J = 7.1$ Hz, 0.4H), 6.91 (d, $J = 7.5$ Hz, 0.6H), 6.94–7.07 (m, 2H), 7.12–7.24 (m, 7H), 7.61–7.65 (m, 2H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 18.5, (19.1), (21.41), 21.43, (28.7), 32.1, 41.8, (43.9), 53.9, (54.4), (123.6), (125.9), 126.4, 126.6, 126.9, (127.11), (127.15), 127.23, 127.3, (127.4), 128.0, 128.36, (128.39), (129.4), 129.5, 130.5, (131.0), (132.15), 132.19, 134.0, (135.9), (137.2), 137.4, 139.4, (139.8), (143.08), 143.11 (Chemical shifts in parentheses might be assigned to the minor regioisomer **5d**.); Anal. Calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_2\text{S}$: C, 73.18; H, 6.14; N, 3.71. Found: C, 72.93; H, 6.22; N, 3.57.

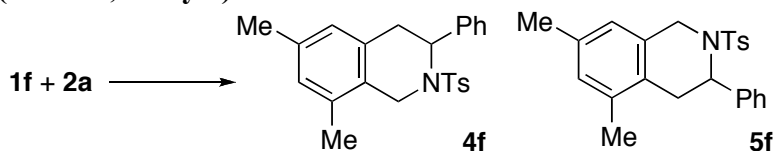
The above reaction would proceed with the similar regioselectivity to the reaction of **1f** with **2a**. The major product was assigned to **4d** by comparing the mixture of **4d** and **5d** to that of **4f** and **5f** in their ^1H and ^{13}C NMR spectra (Figure S-44 vs S-48 or S-45 vs S-49).

Reaction of **1e** with **2a** (Table 2, entry 6).



The general procedure A was followed with use of **1e** (40.6 mg, 0.15 mmol) and **2a** (47.2 mg, 0.18 mmol). The reaction was conducted for 48 h. The crude product contained the cycloadducts **4e** and **5e** in the ratio 43:57, which was determined with the ^1H NMR spectrum (see Figure S-46). The crude product was purified with a flash column chromatography (EtOAc/hexane = 1/10) to give a mixture of **4e** and **5e** (44.8 mg, **4e:5e** = 43:57, 78%) as colorless liquid. Compounds **4e** and **5e** are identical with **5d** and **4d**, respectively.

Reaction of **1f** with **2a** (Table 2, entry 7).



The general procedure B was followed with use of **1f** (42.9 mg, 0.15 mmol) and **2a** (46.8 mg, 0.18 mmol). The reaction was conducted for 3 h. The crude product contained the cycloadducts **4f** and **5f** in the ratio 87:13, which was determined with the ^1H NMR spectrum (see Figure S-47). The crude product was purified with a flash column chromatography (EtOAc/hexane = 1/10) to give a mixture of **4f** and **5f** (45.4 mg, **4f:5f** = 86:14, 76%) as colorless liquid: ^1H NMR (400 MHz, CDCl_3 , TMS) δ 2.10 (s, 3H), 2.22 (s, 3H), 2.35 (s, 3H), 3.00–3.11 (m, 2H), 3.96 (d, $J = 16.9$ Hz, 1H), 4.64 (d, $J = 16.9$ Hz, 1H), 5.41 (dd, $J = 3.4, 5.1$ Hz, 1H), 6.73 (s, 1H), 6.78 (s, 1H), 7.13–7.24 (m, 7H), 7.63 (d, $J = 8.2$ Hz, 1H); ^{13}C { ^1H } NMR (100 MHz, CDCl_3) δ 18.4, 20.9, 21.4, 32.1, 41.7, 53.9, 126.93, 126.96, 127.25, 127.26, 127.4, 128.3, 128.9, 129.5, 132.0, 133.8, 136.1, 137.4, 139.4, 143.0; IR (thin film) 3061 w, 3029 w, 2919 w, 2855 w, 1598 w, 1493 w, 1450 m,

1334 s, 1268 w, 1217 w, 1159 s, 1095 s, 1068 w, 1023 w, 947 m, 912 m, 849 w, 814 m, 771 m, 735 m, 703 m, 681 m, 648 m, 586 m, 559 m cm^{-1} ; Anal. Calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_2\text{S}$: C, 73.62; H, 6.44; N, 3.58. Found: C, 73.53; H, 6.35; N, 3.68.

The major product was assigned with the NOE experiments. The $^1\text{H}\{^1\text{H}\}$ -NOE experiment was summarized in Figure S-1, indicating that the reaction afforded **4f** preferentially.

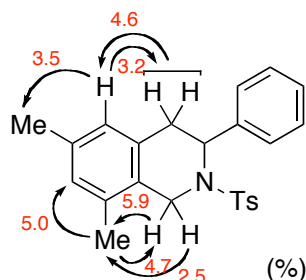


Figure S-1. Summary of the $^1\text{H}\{^1\text{H}\}$ -NOE experiment of **4f**.

References

1. Kuwano, R.; Shige, T. *J. Am. Chem. Soc.* **2007**, *129*, 3802–3803.
2. Giri, R.; Mangel, N.; Li, J.-J.; Wang, D.-H.; Breazzano, S. P.; Saunders, L. B.; Yu, J.-Q. *J. Am. Chem. Soc.* **2007**, *129*, 3510–3511.
3. Soloshonok, V. A.; Tang, X.; Hruby, V. J. *Tetrahedron* **2001**, *57*, 6375–6382.
4. Wynnea, J. H.; Pricea, S. E.; Rorera, J. R.; Stalick, W. M. *Synth. Commun.* **2003**, *33*, 341–352.
5. Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 220–223.
6. Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1990**, *28*, 342–345.
7. Neudeck, H. K. *Monatsh. Chem.* **1996**, *127*, 185–200.
8. Nishimura, T.; Yasuhara, Y.; Hayashi, T. *Org. Lett.* **2006**, *8*, 979–981.
9. Tokunaga, N.; Otomaru, Y.; Okamoto, K.; Ueyama, K.; Shintani, R.; Hayashi, T. *J. Am. Chem. Soc.* **2004**, *126*, 13584–13585.
10. Alder, K.; Haydn, J.; Heimbach, K.; Neufang, K.; Hansen, G.; Gerhard, W. *Liebigs Ann. Chem.* **1954**, *586*, 110–137.

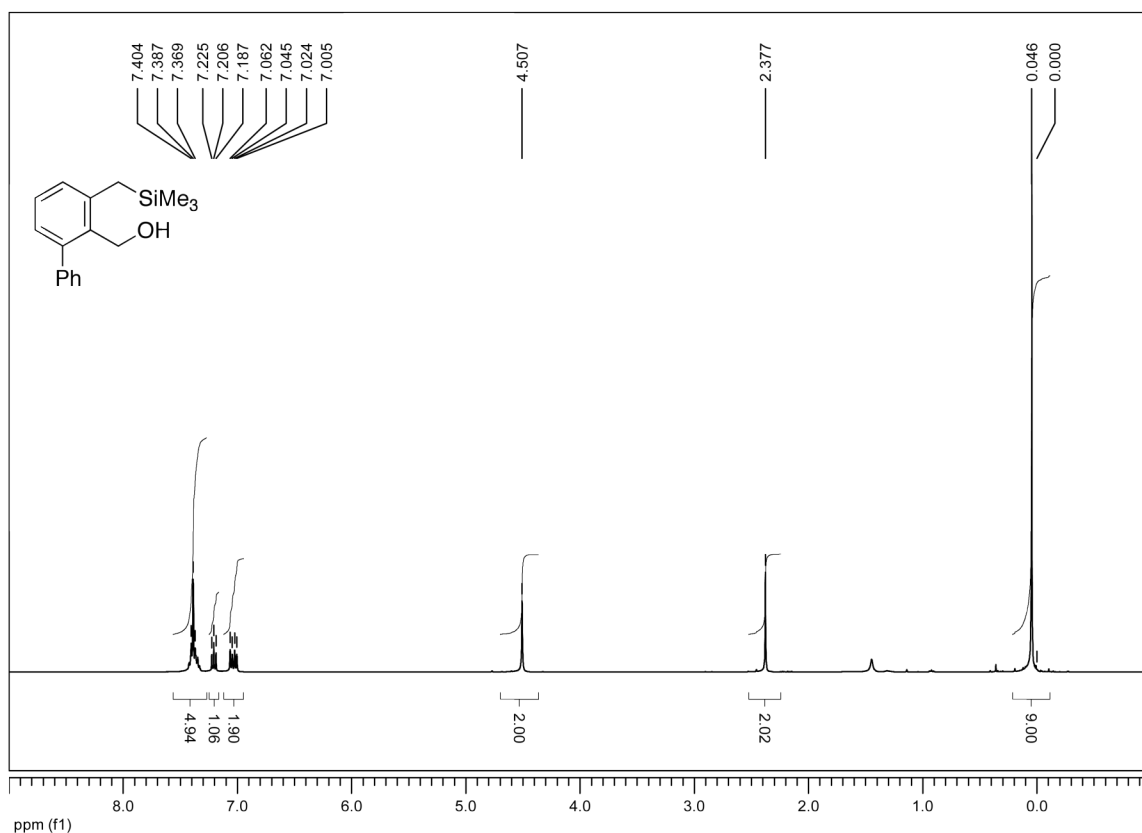


Figure S-2. ¹H NMR spectrum (CDCl₃) of [2-phenyl-6-((trimethylsilyl)methyl)phenyl]methanol.

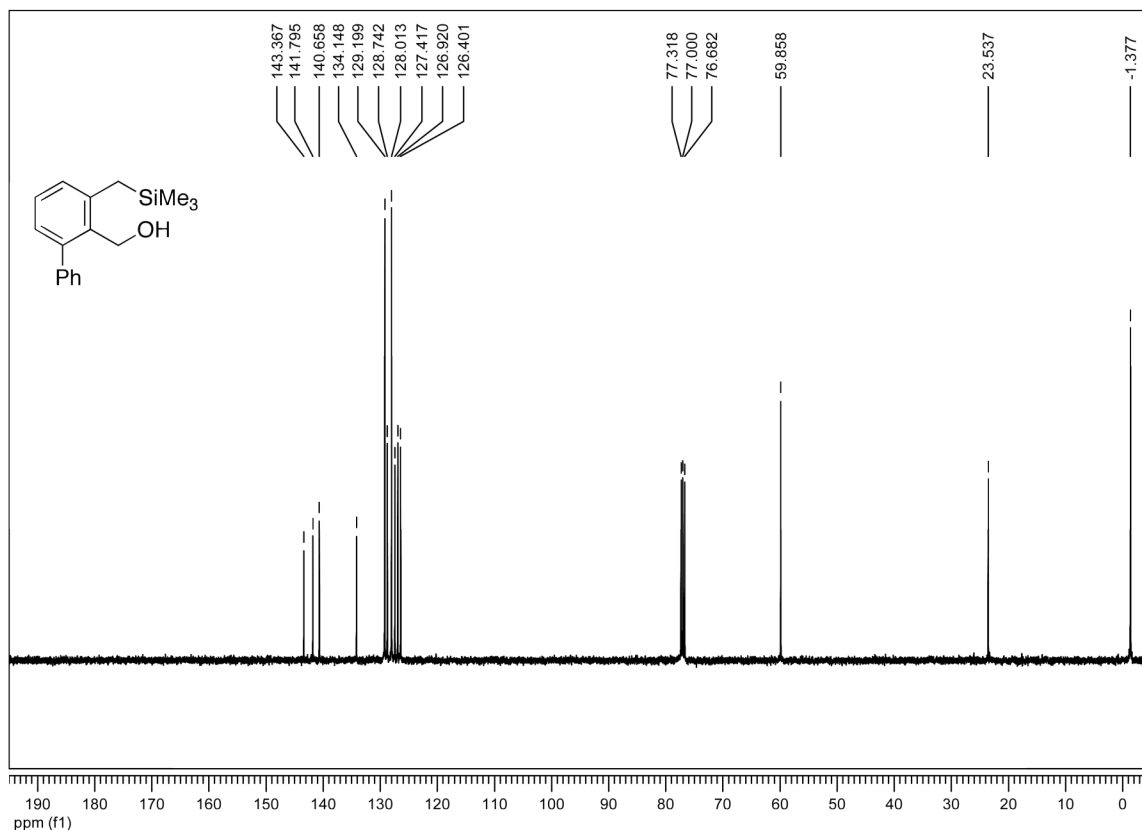


Figure S-3. ¹³C {¹H} NMR spectrum (CDCl₃) of [2-phenyl-6-((trimethylsilyl)methyl)phenyl]methanol.

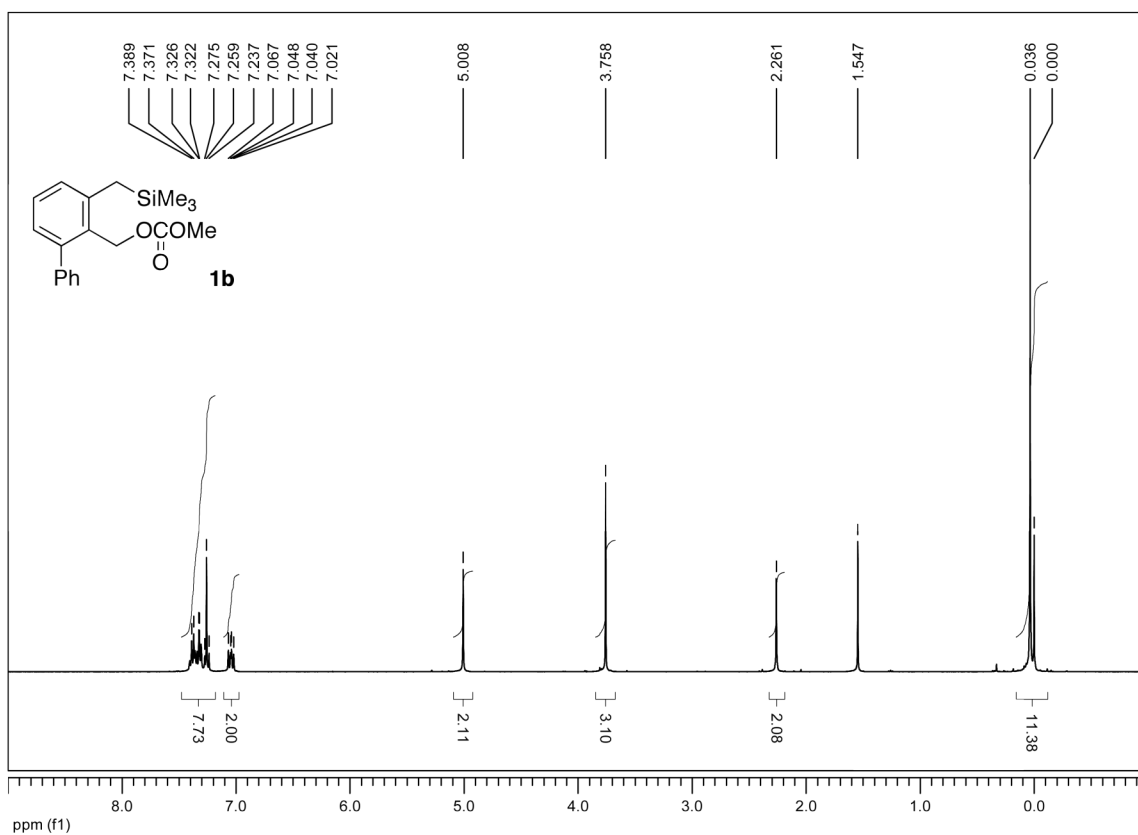


Figure S-4. ¹H NMR spectrum (CDCl₃) of **1b**.

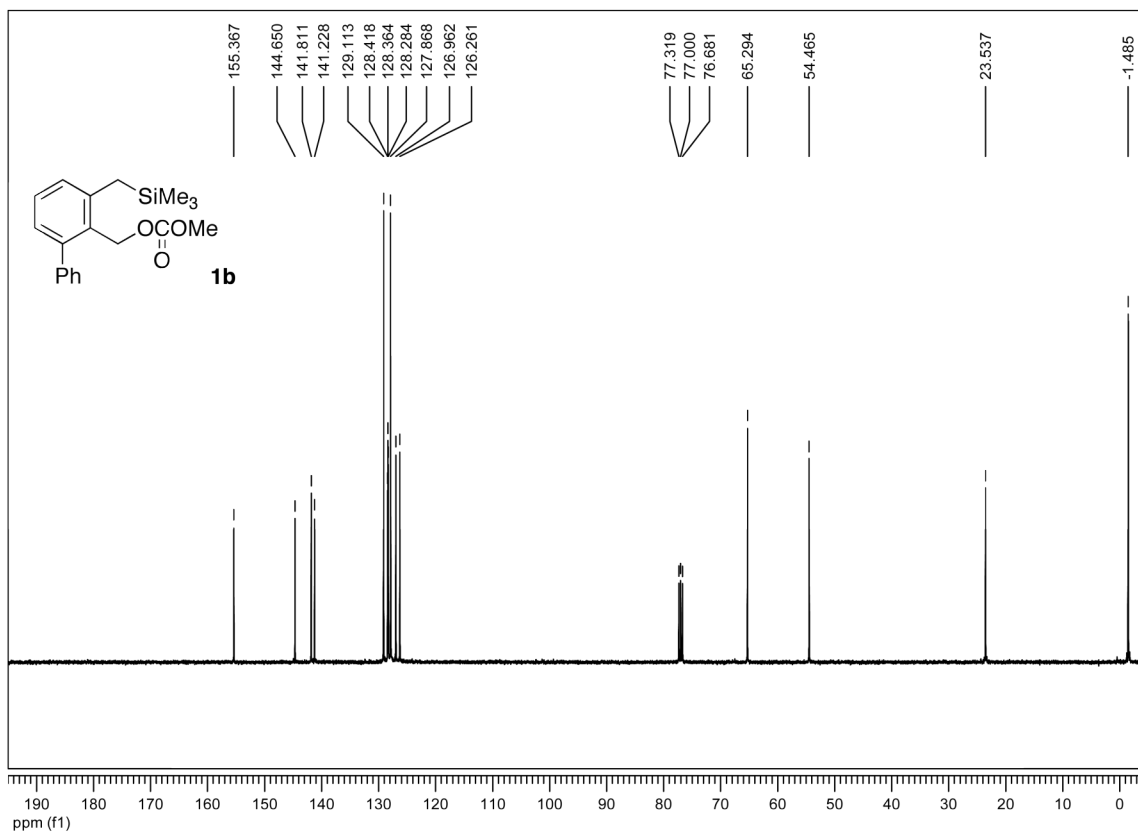


Figure S-5. ¹³C {¹H} NMR spectrum (CDCl₃) of **1b**.

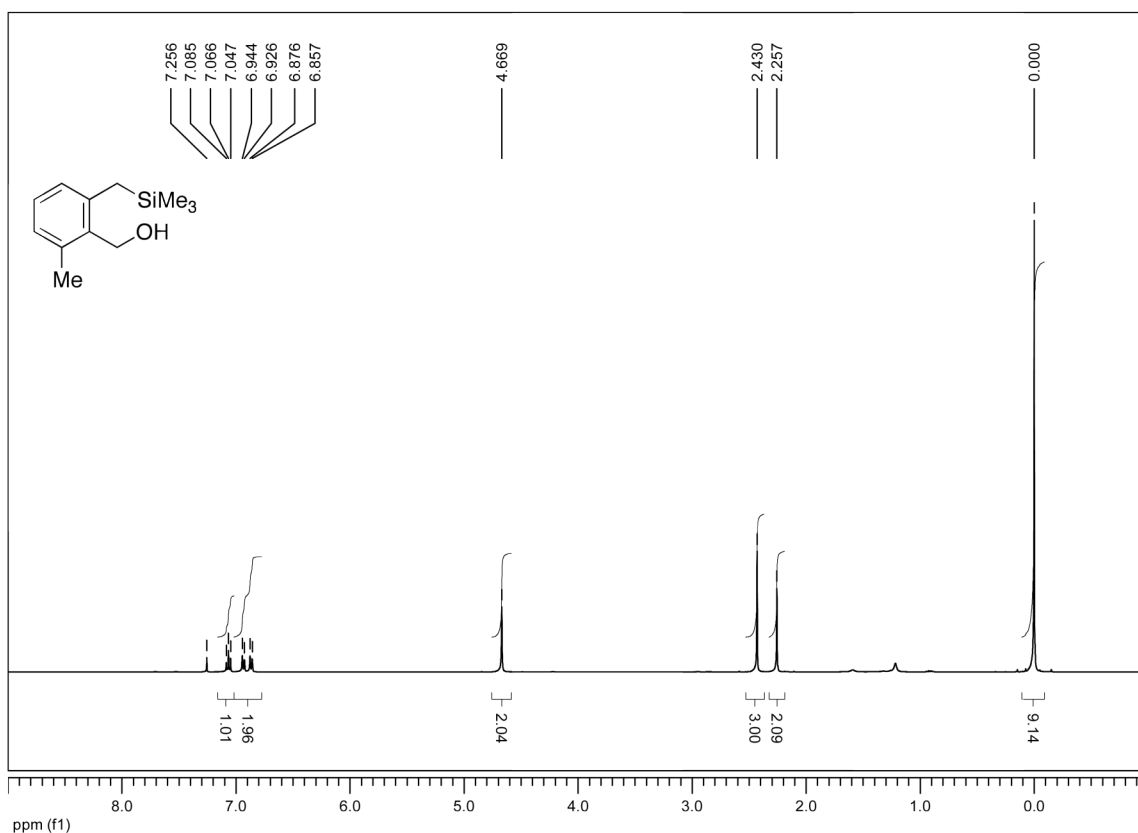


Figure S-6. ¹H NMR spectrum (CDCl₃) of [2-methyl-6-((trimethylsilyl)methyl)phenyl]methanol.

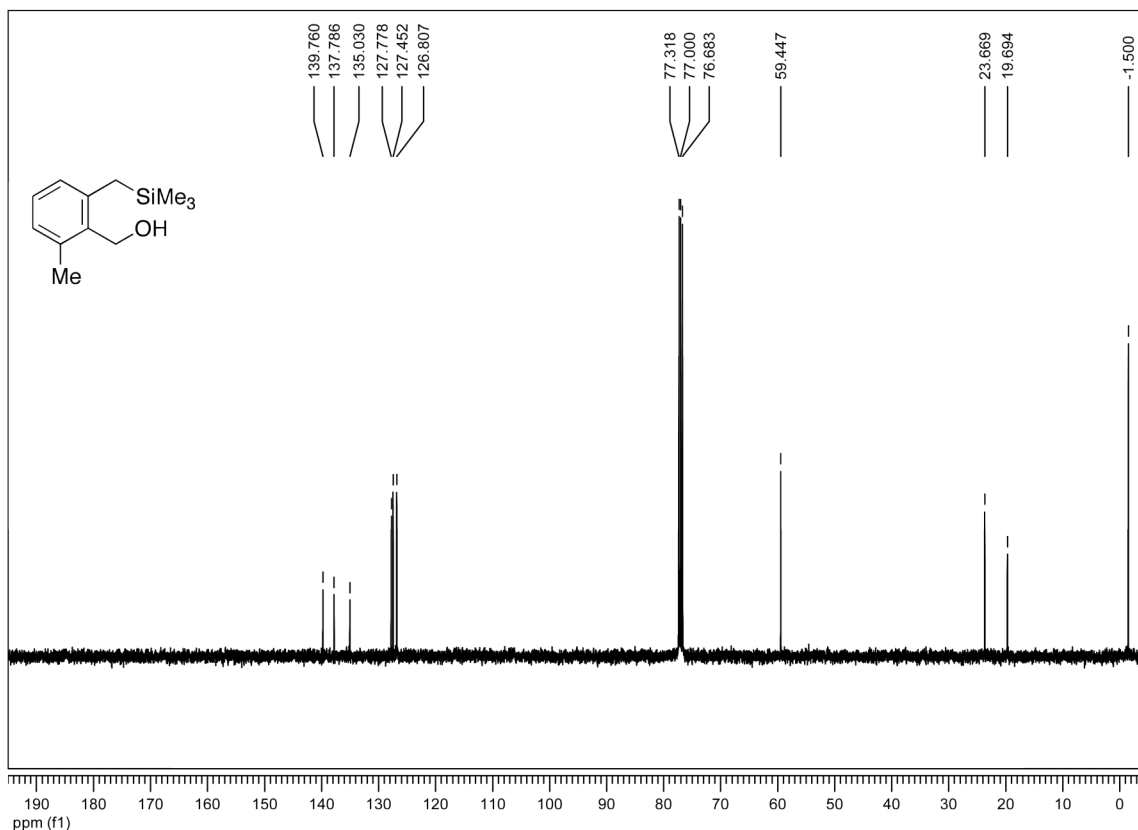


Figure S-7. ¹³C {¹H} NMR spectrum (CDCl₃) of [2-methyl-6-((trimethylsilyl)methyl)phenyl]methanol.

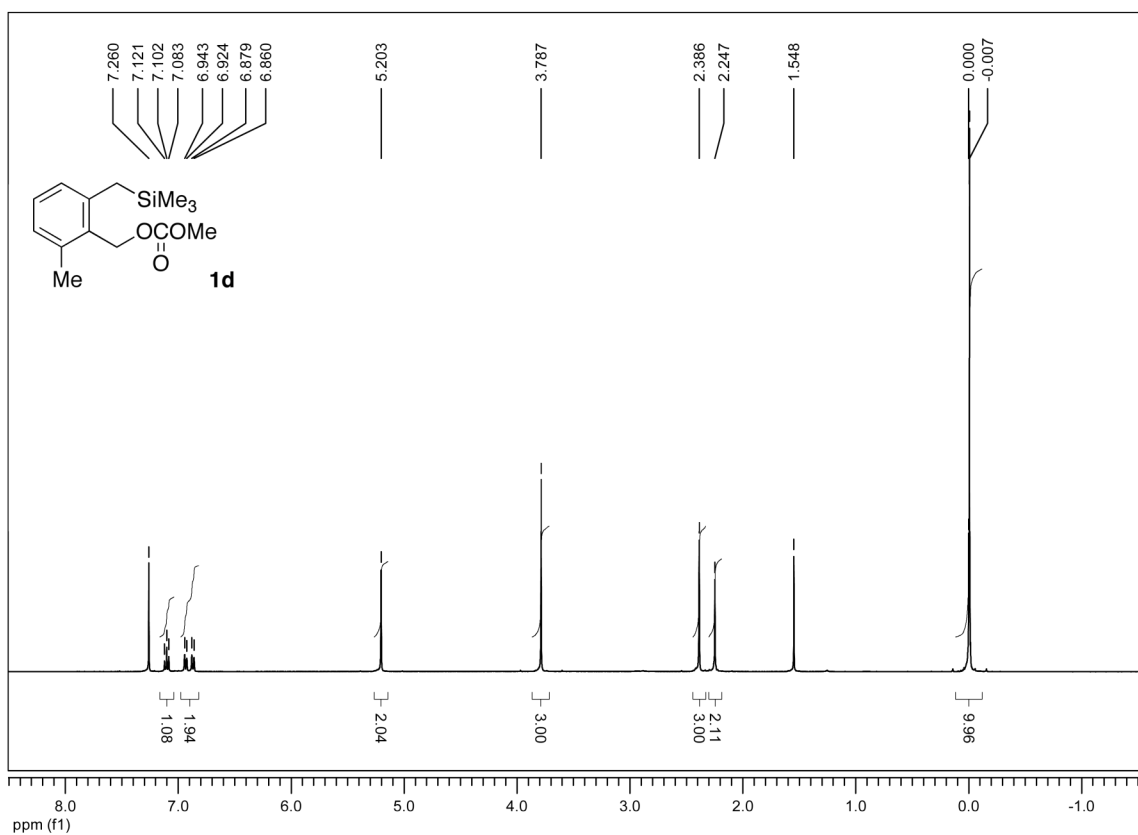


Figure S-4. ¹H NMR spectrum (CDCl₃) of **1d**.

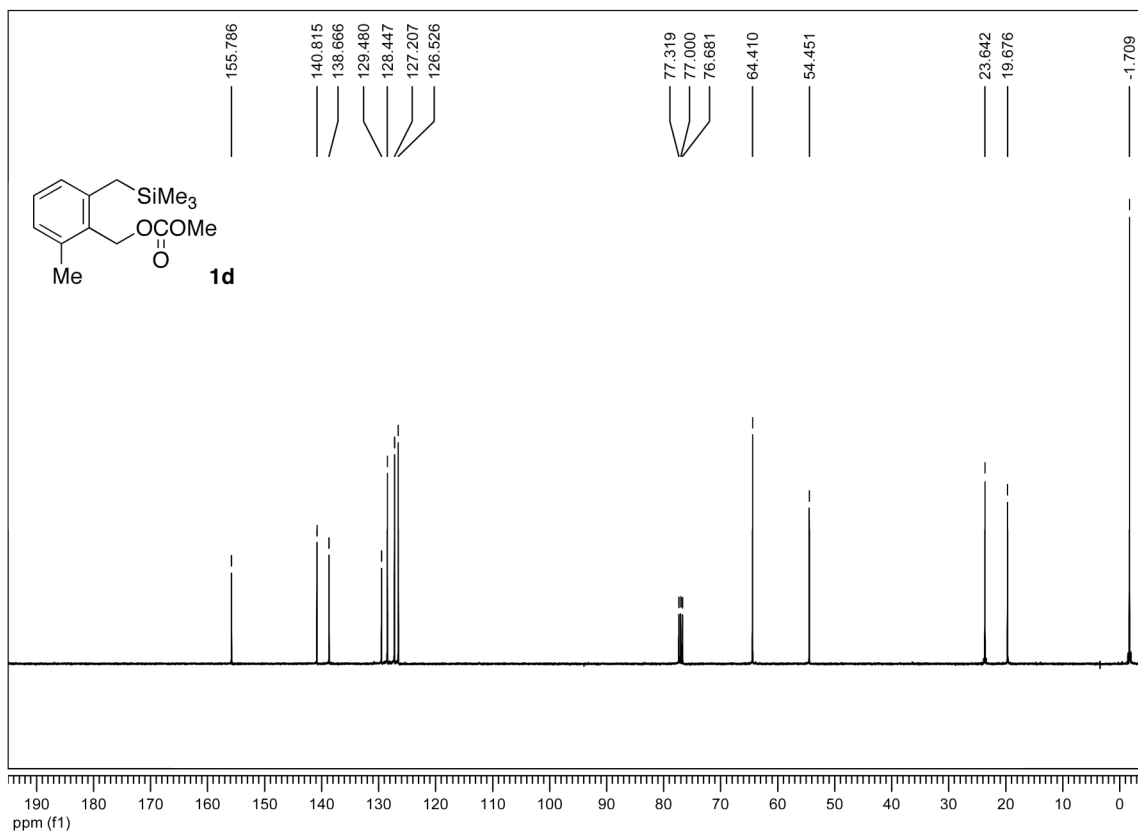


Figure S-5. ¹³C {¹H} NMR spectrum (CDCl₃) of **1d**.

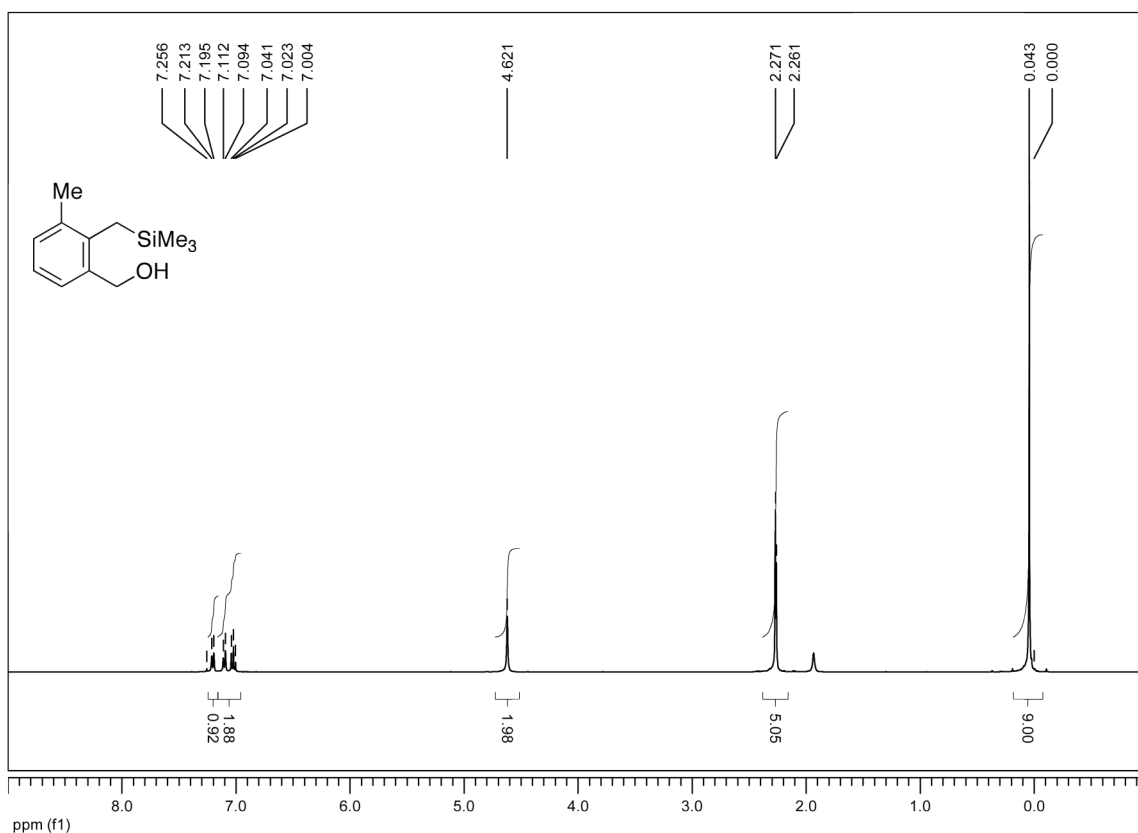


Figure S-6. ^1H NMR spectrum (CDCl_3) of [3-methyl-2-((trimethylsilyl)methyl)phenyl]methanol.

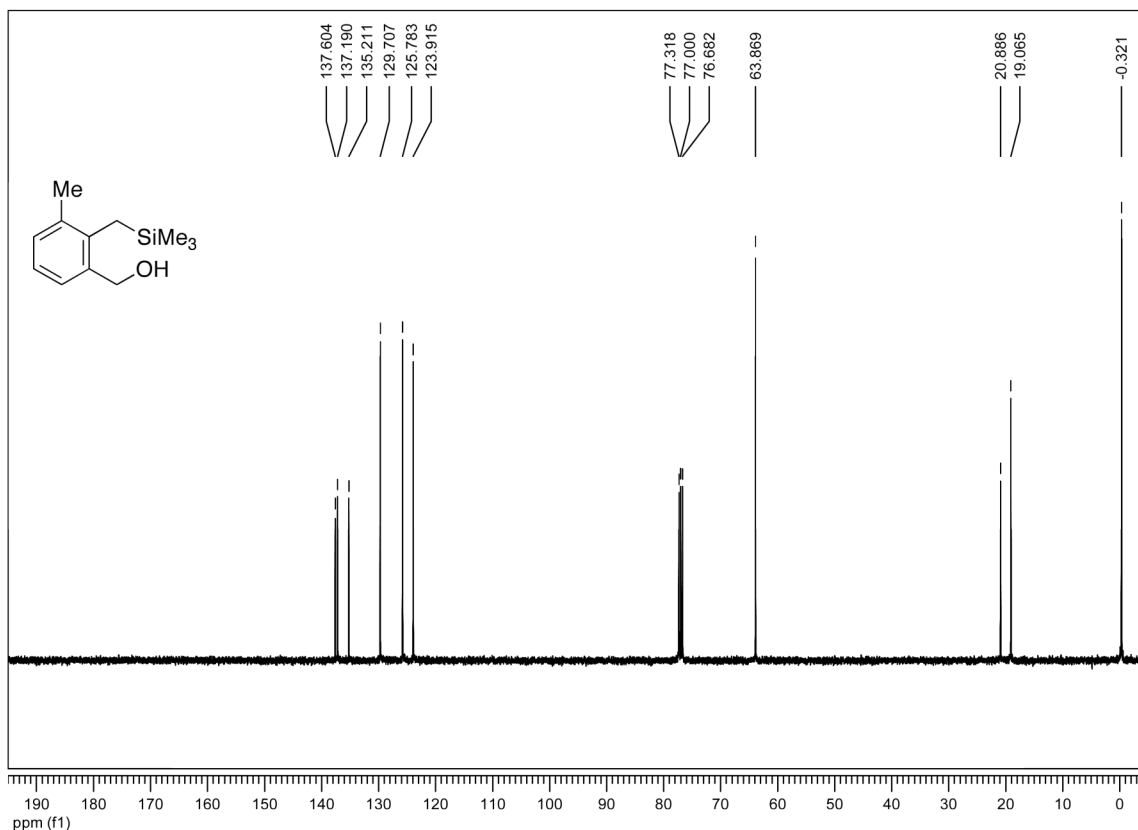


Figure S-7. ^{13}C $\{^1\text{H}\}$ NMR spectrum (CDCl_3) of [3-methyl-2-((trimethylsilyl)methyl)phenyl]methanol.

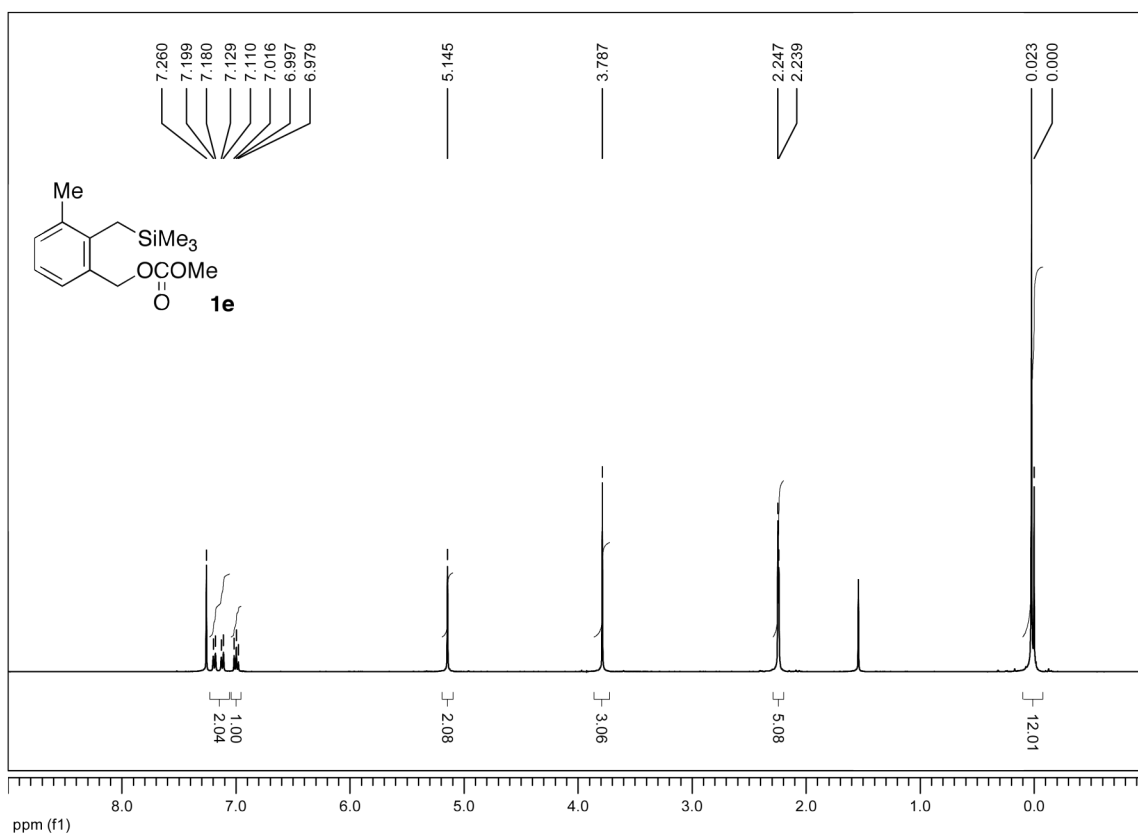


Figure S-8. ¹H NMR spectrum (CDCl₃) of **1e**.

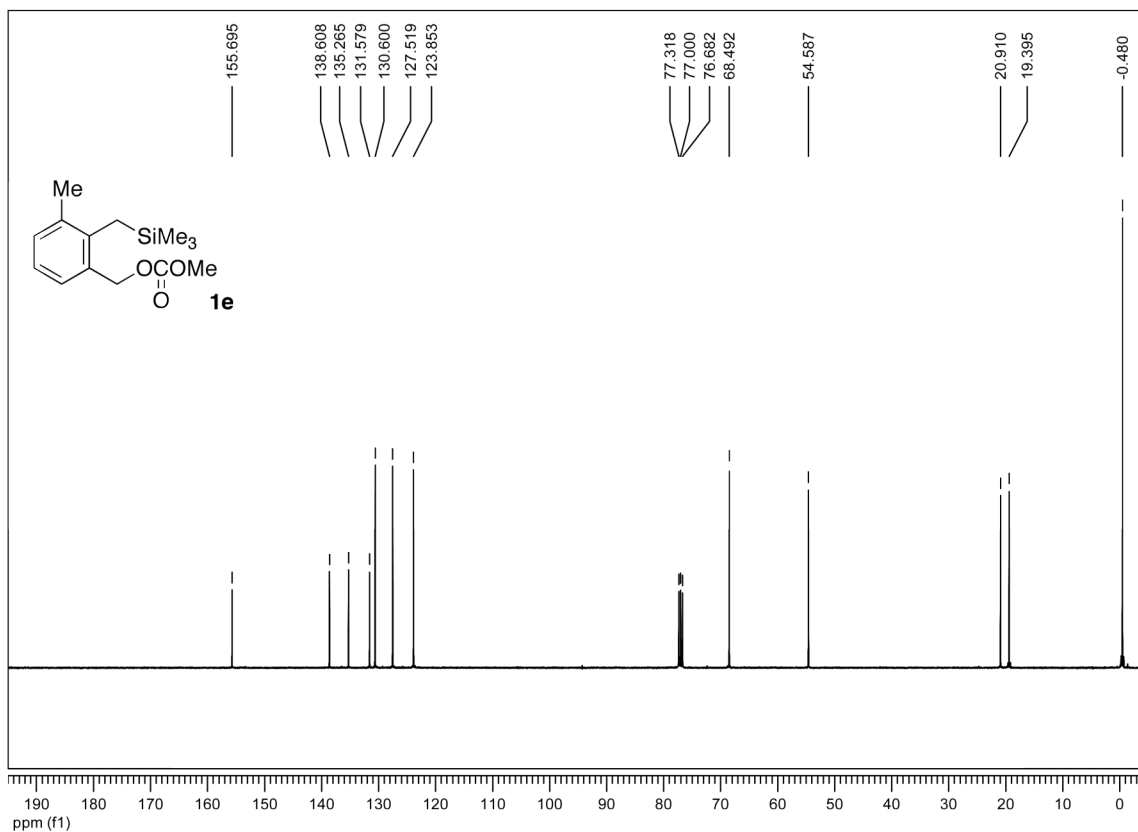


Figure S-9. ¹³C {¹H} NMR spectrum (CDCl₃) of **1e**.

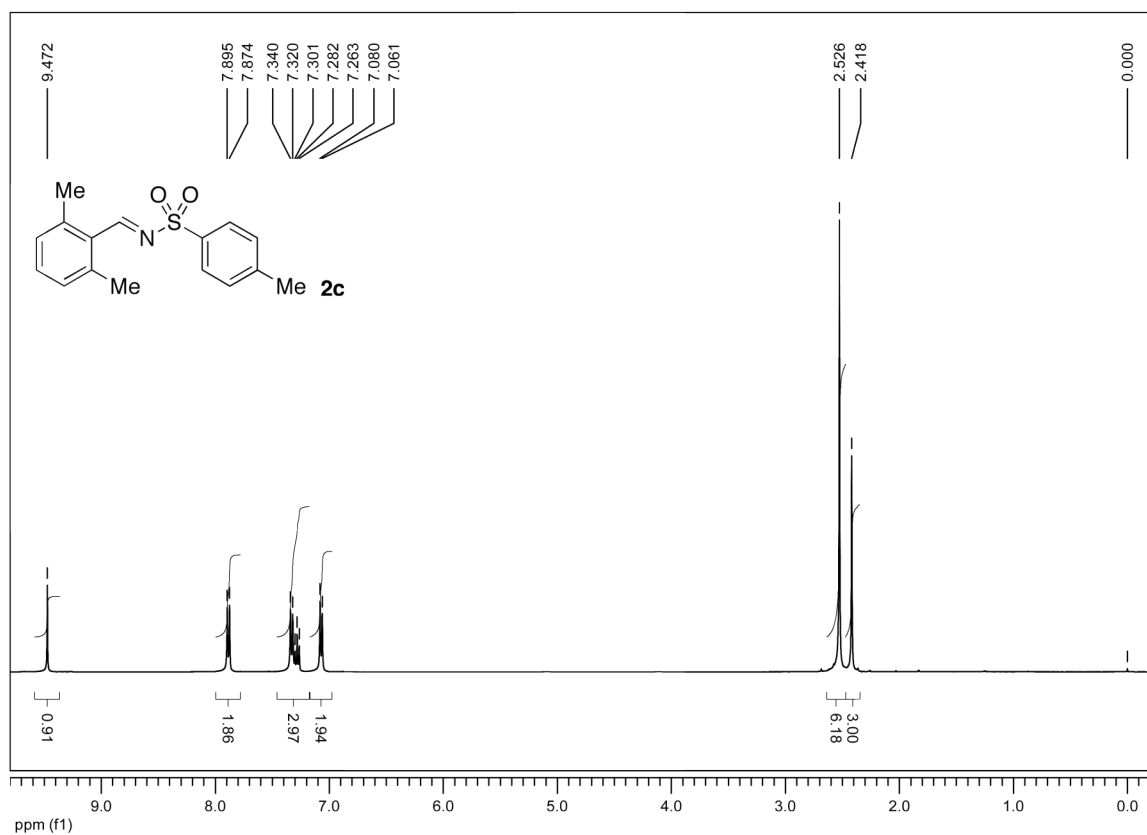


Figure S-10. ¹H NMR spectrum (CDCl₃) of **2c**.

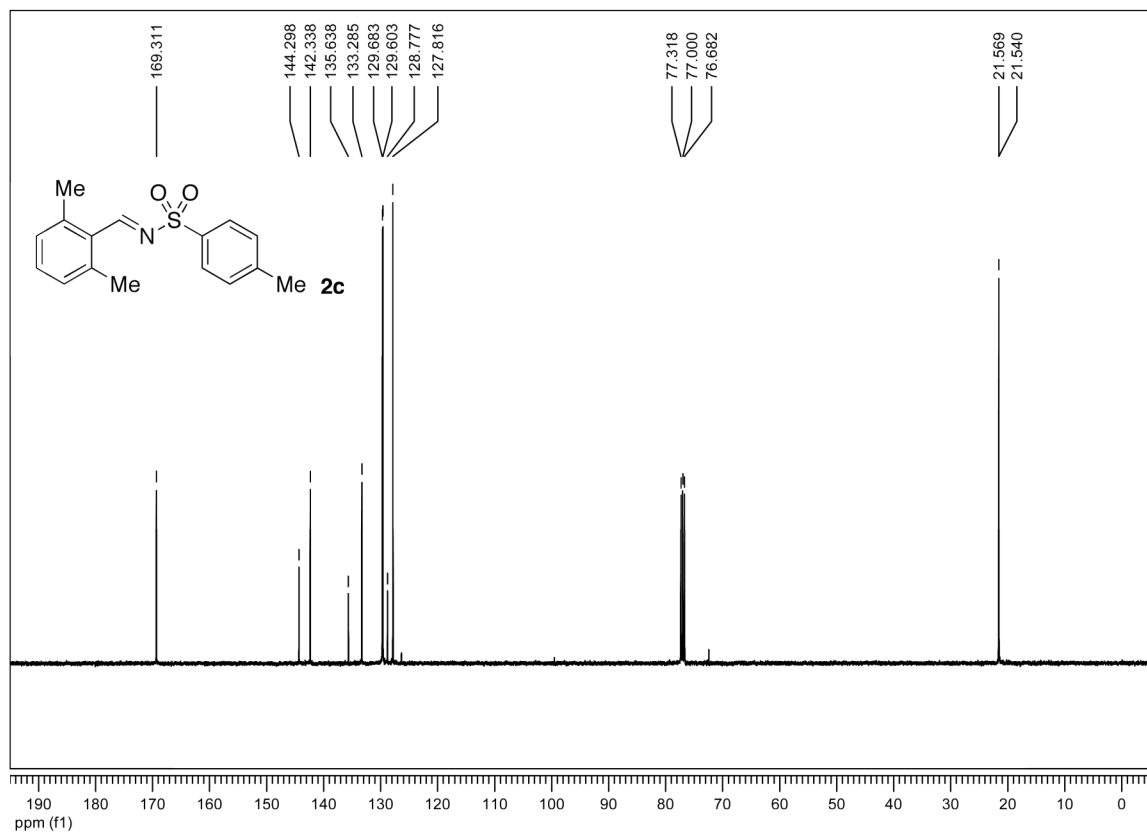


Figure S-11. ¹³C {¹H} NMR spectrum (CDCl₃) of **2c**.

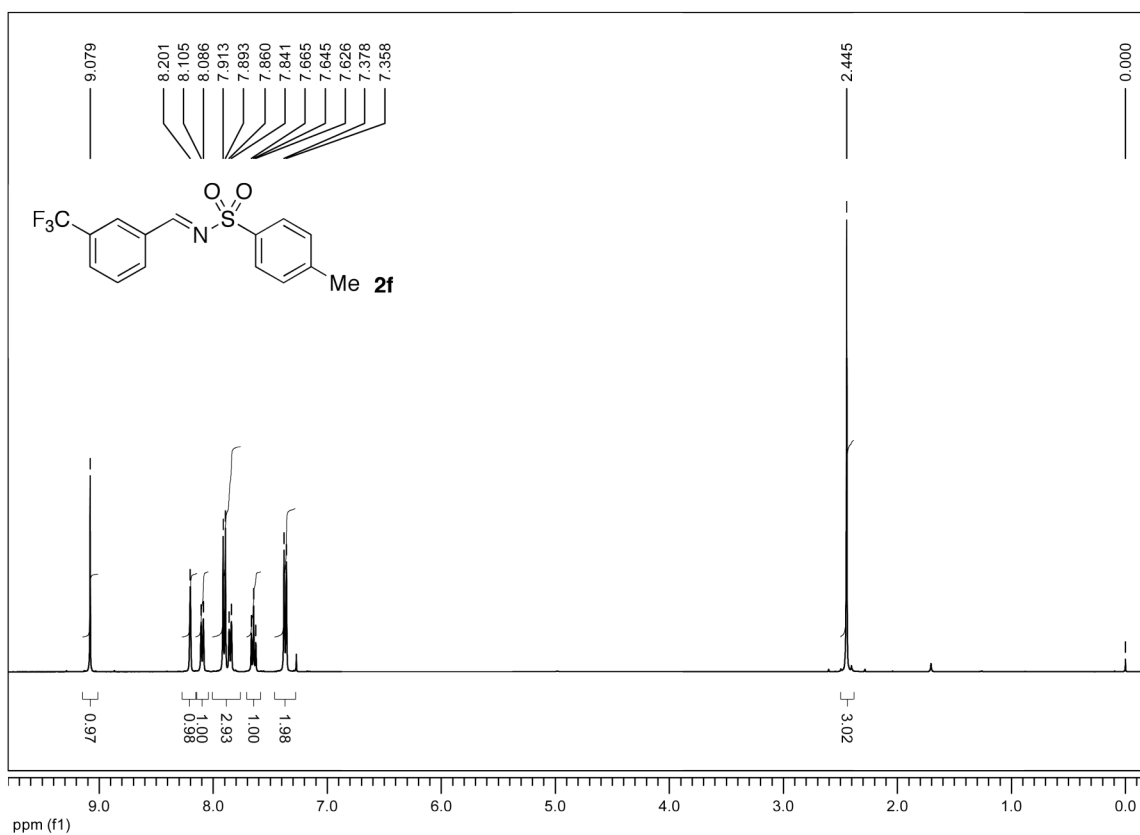


Figure S-12. ¹H NMR spectrum (CDCl₃) of **2f**.

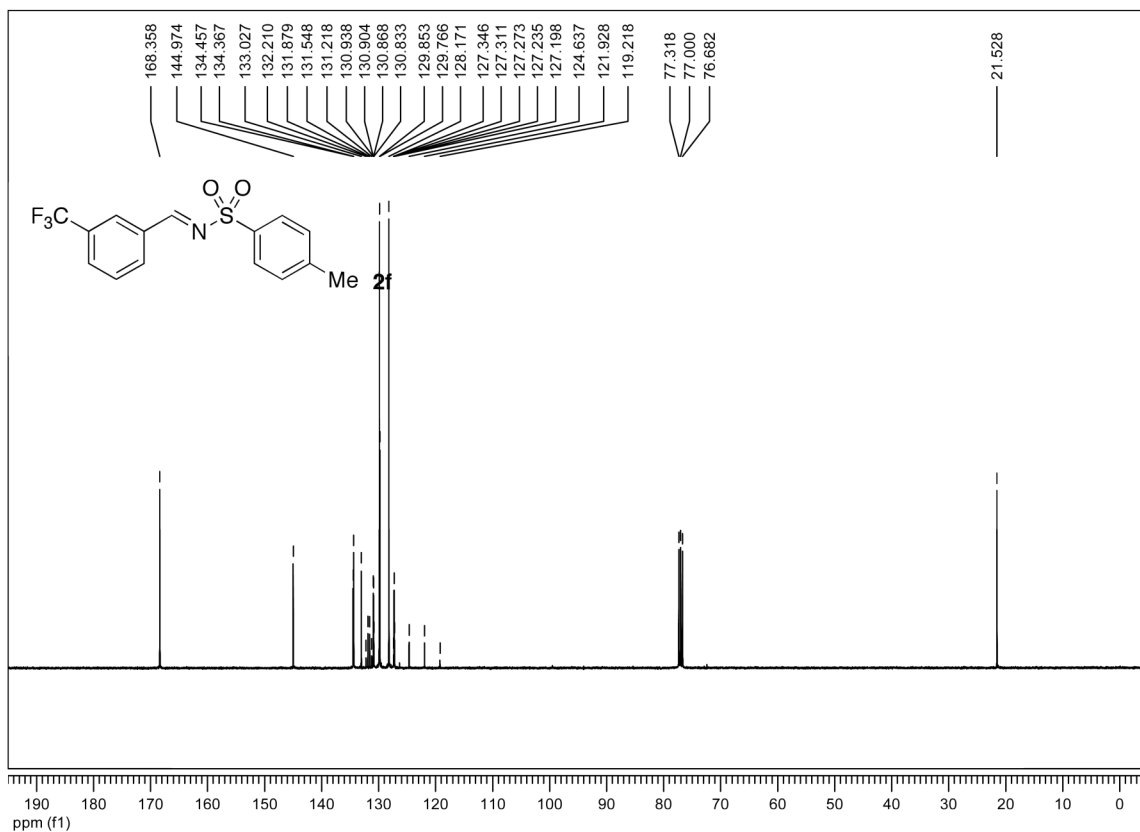


Figure S-13. ¹³C {¹H} NMR spectrum (CDCl₃) of **2f**.

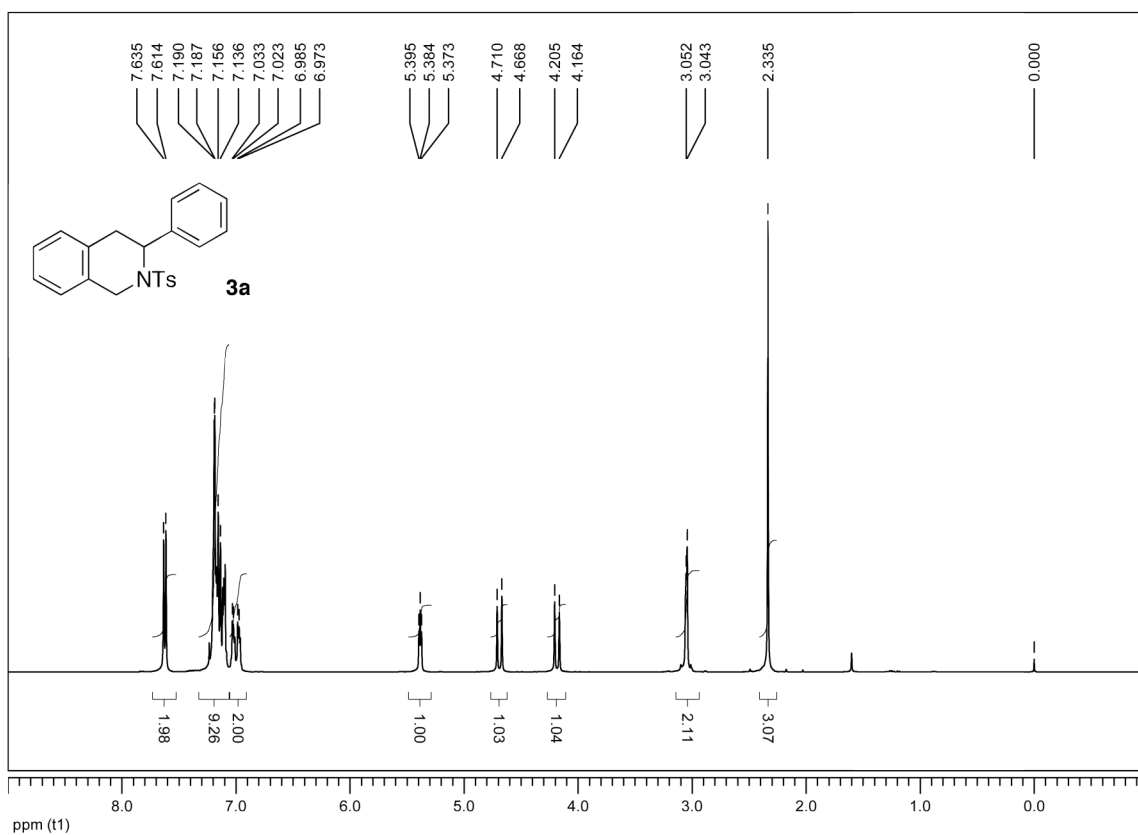


Figure S-14. ¹H NMR spectrum (CDCl₃) of **3a**.

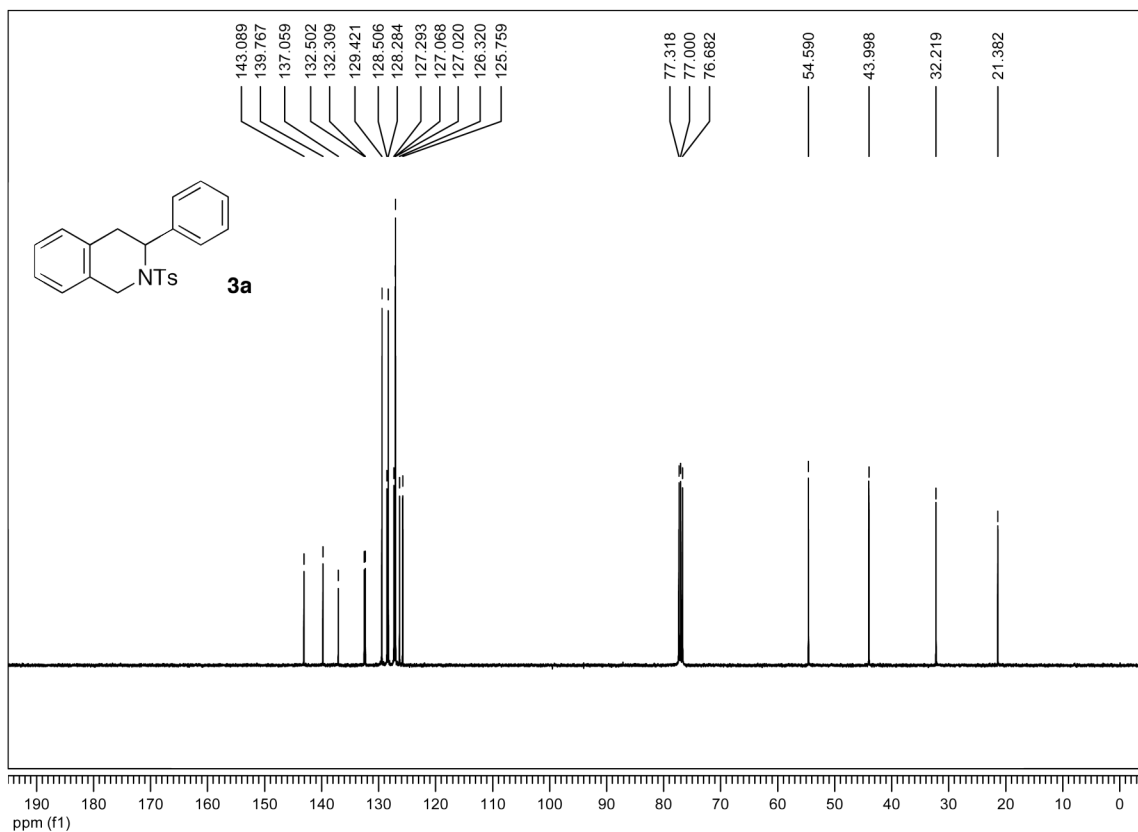


Figure S-15. ¹³C {¹H} NMR spectrum (CDCl₃) of **3a**.

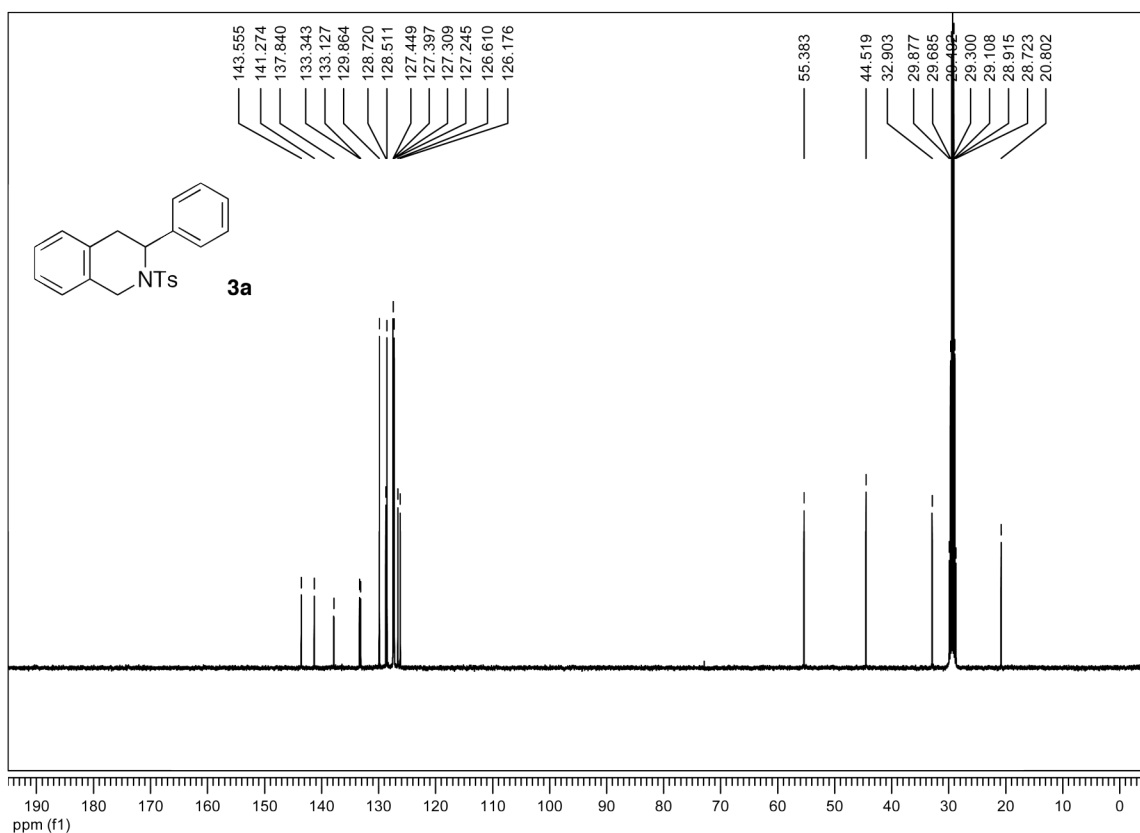


Figure S-16. ¹³C {¹H} NMR spectrum (acetone-*d*₆) of **3a**.

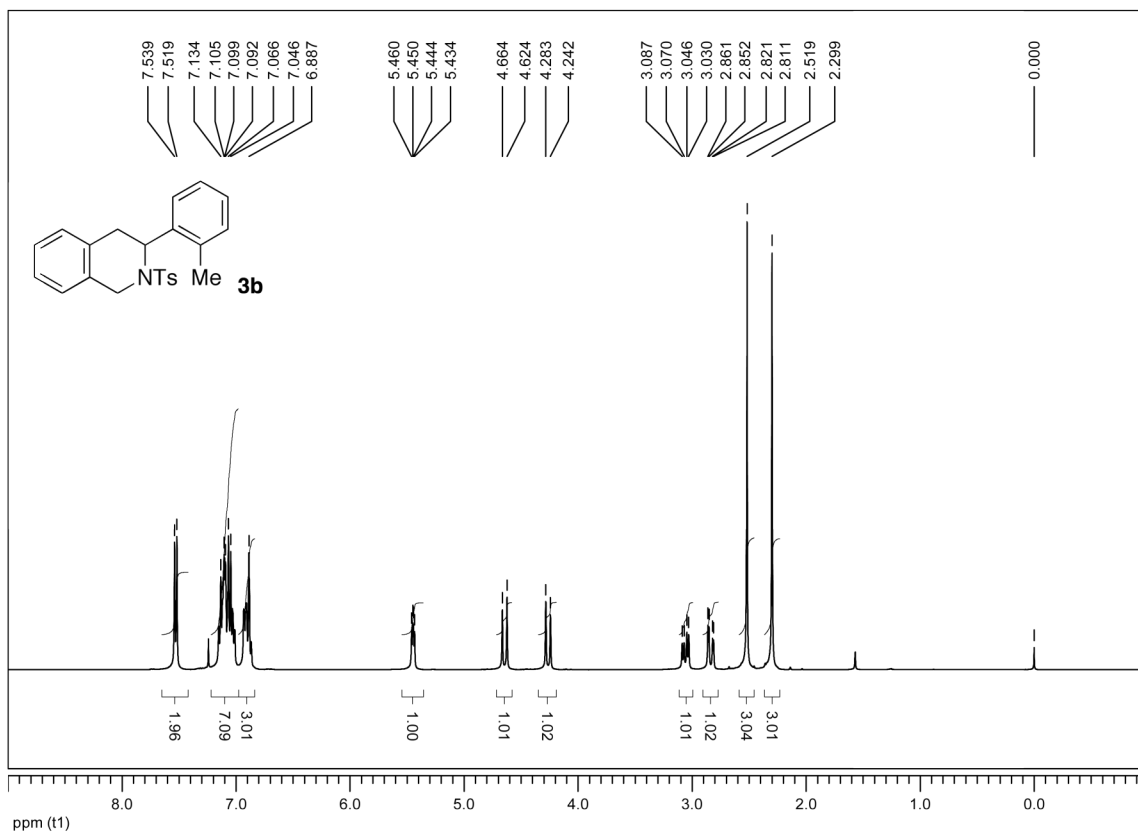


Figure S-17. ¹H NMR spectrum (CDCl₃) of **3b**.

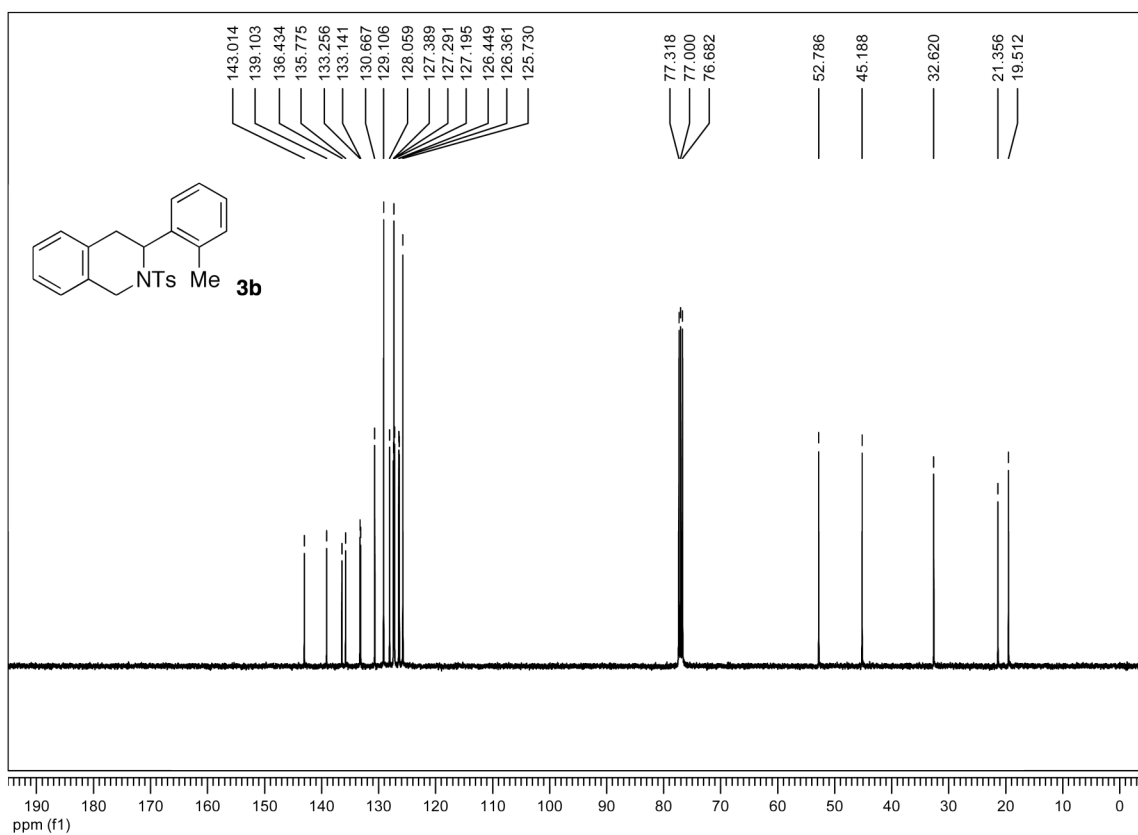


Figure S-18. ¹³C {¹H} NMR spectrum (CDCl₃) of **3b**.

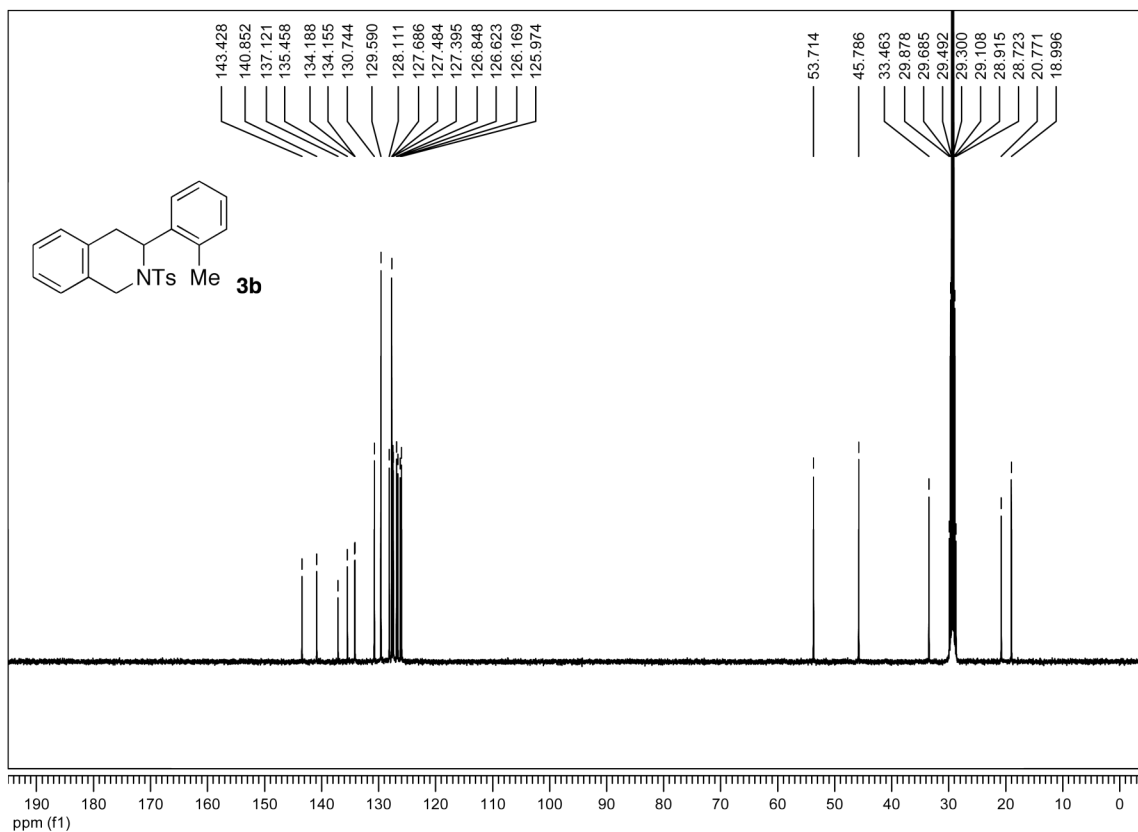


Figure S-19. ¹³C {¹H} NMR spectrum (acetone-*d*₆) of **3b**.

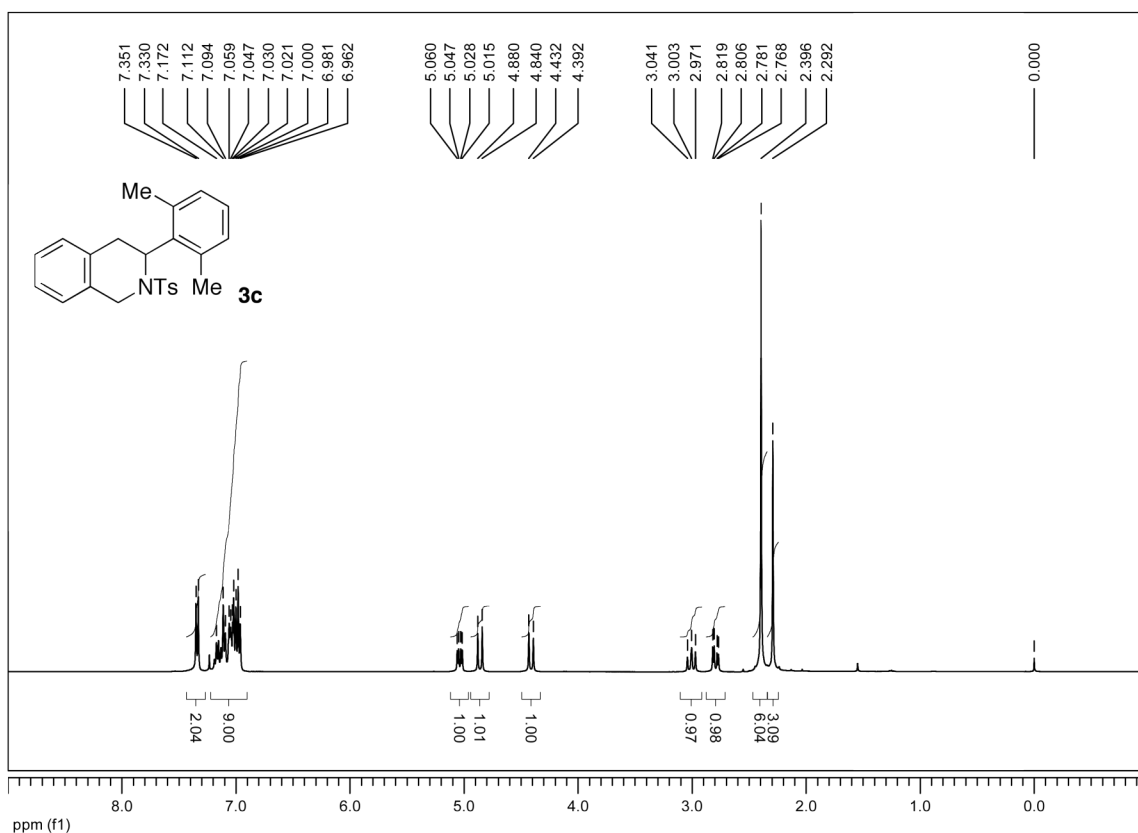


Figure S-20. ¹H NMR spectrum (CDCl₃) of **3c**.

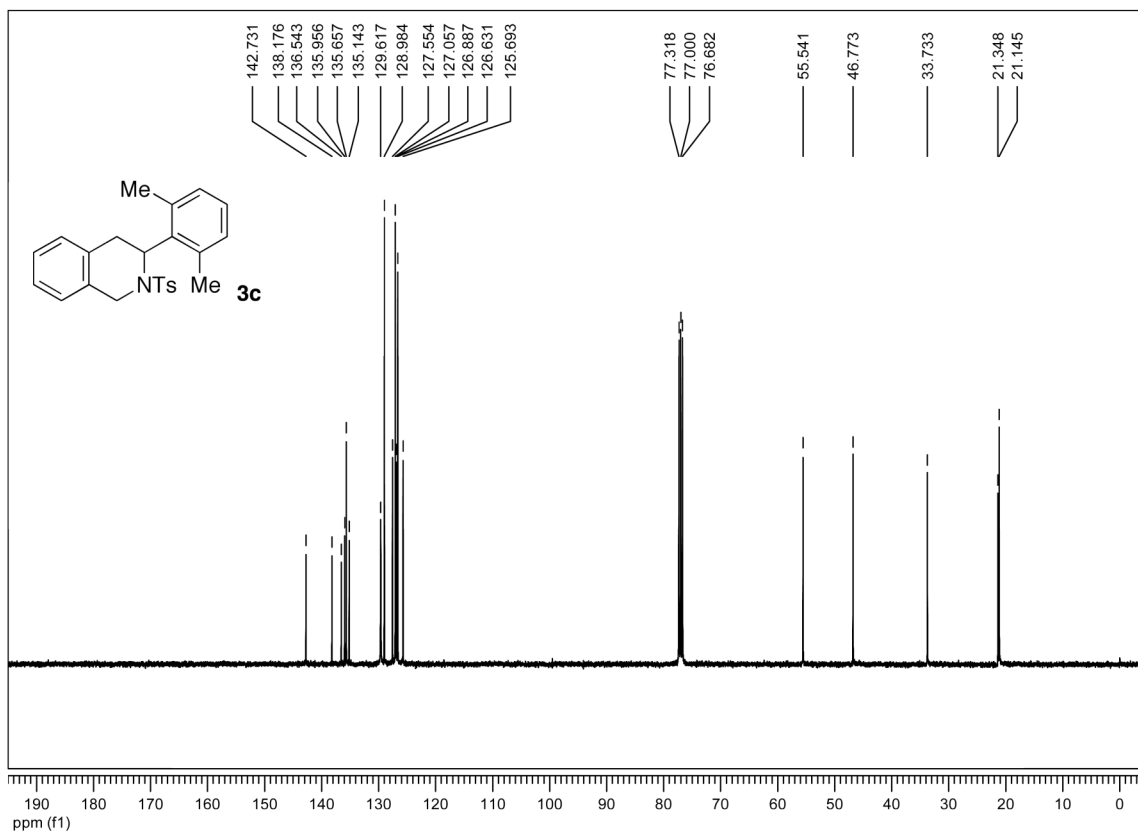


Figure S-21. ¹³C {¹H} NMR spectrum (CDCl₃) of **3c**.

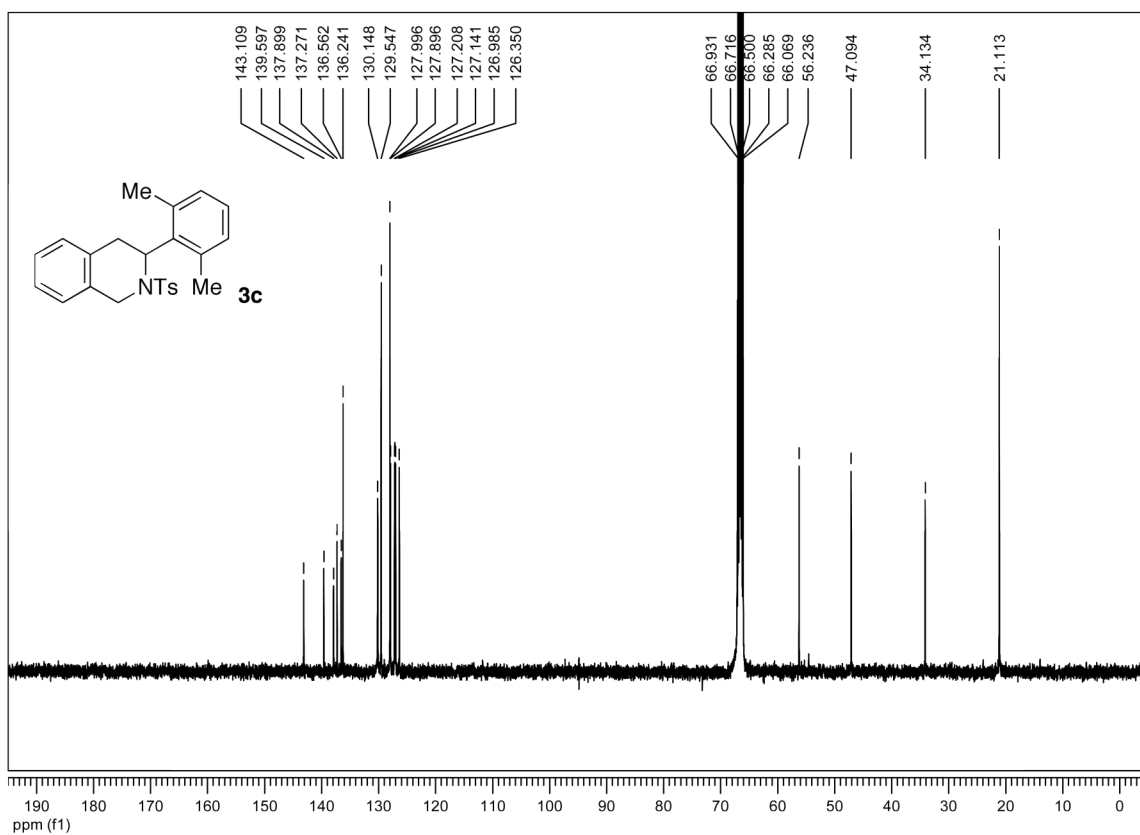


Figure S-22. ¹³C {¹H} NMR spectrum (dioxane-*d*₈) of **3c**.

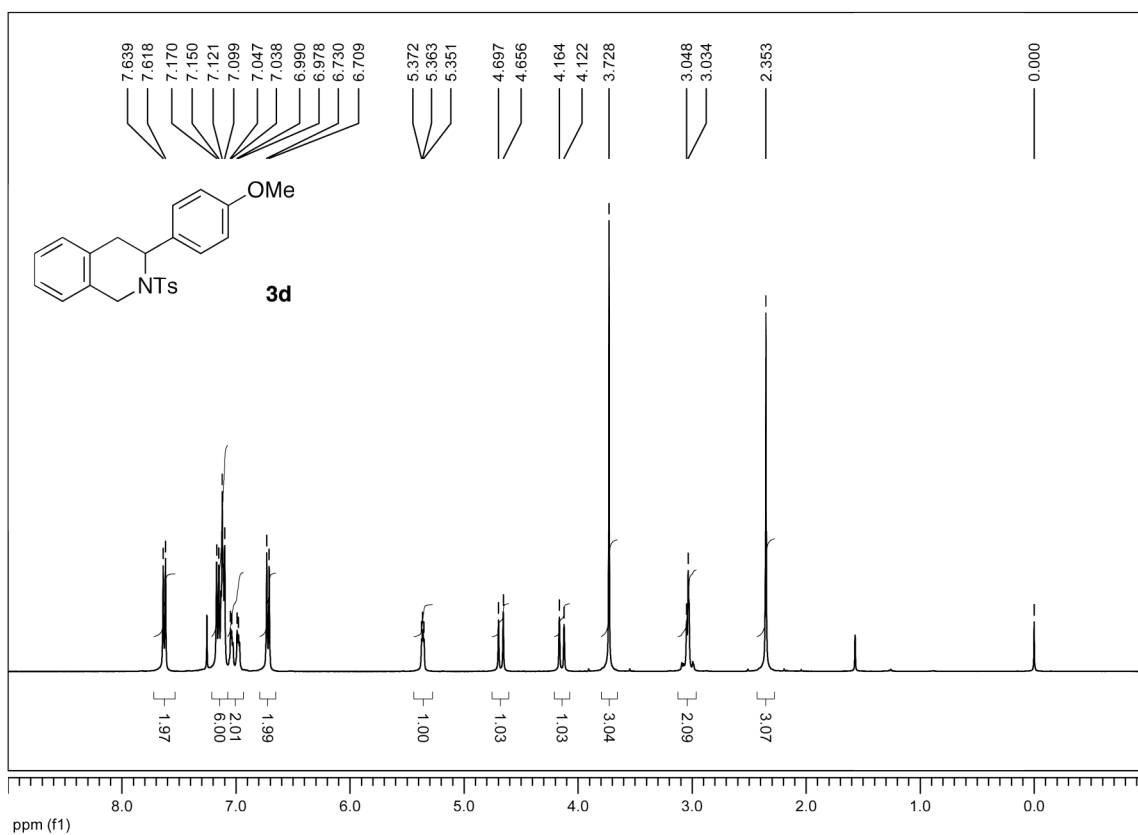


Figure S-23. ¹H NMR spectrum (CDCl₃) of **3d**.

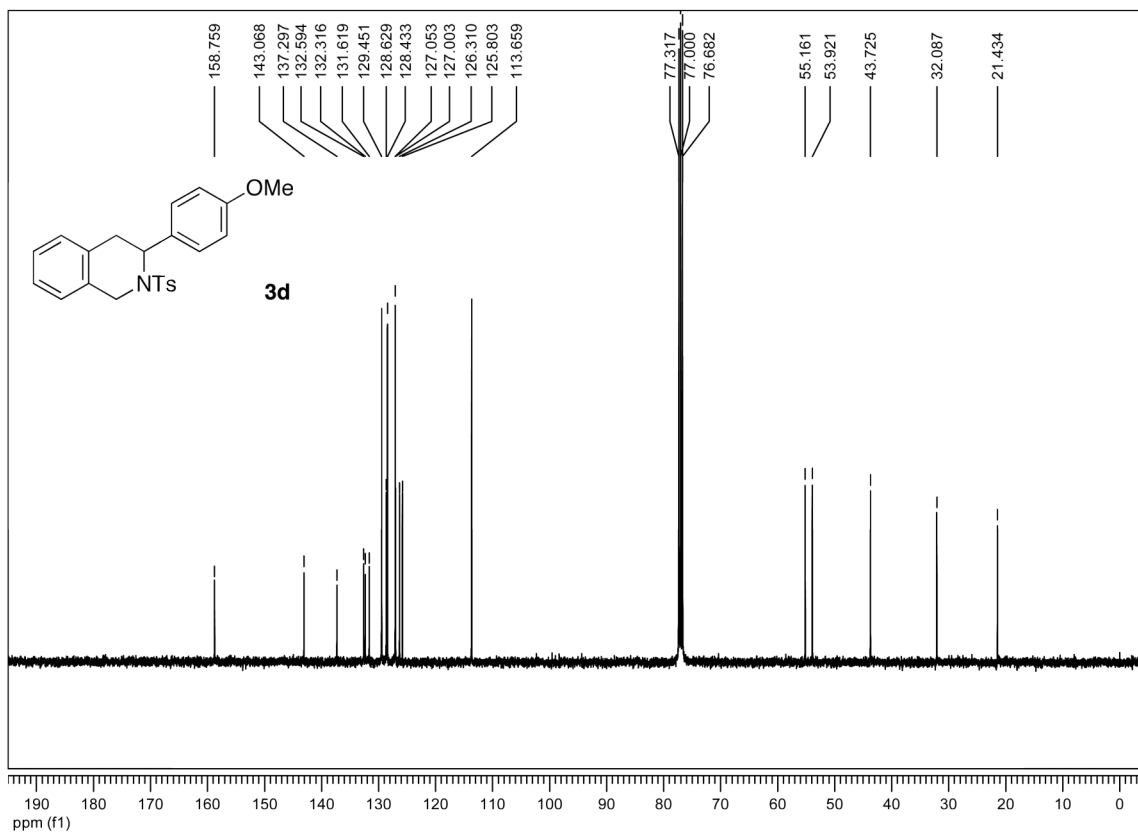


Figure S-24. ¹³C {¹H} NMR spectrum (CDCl₃) of **3d**.

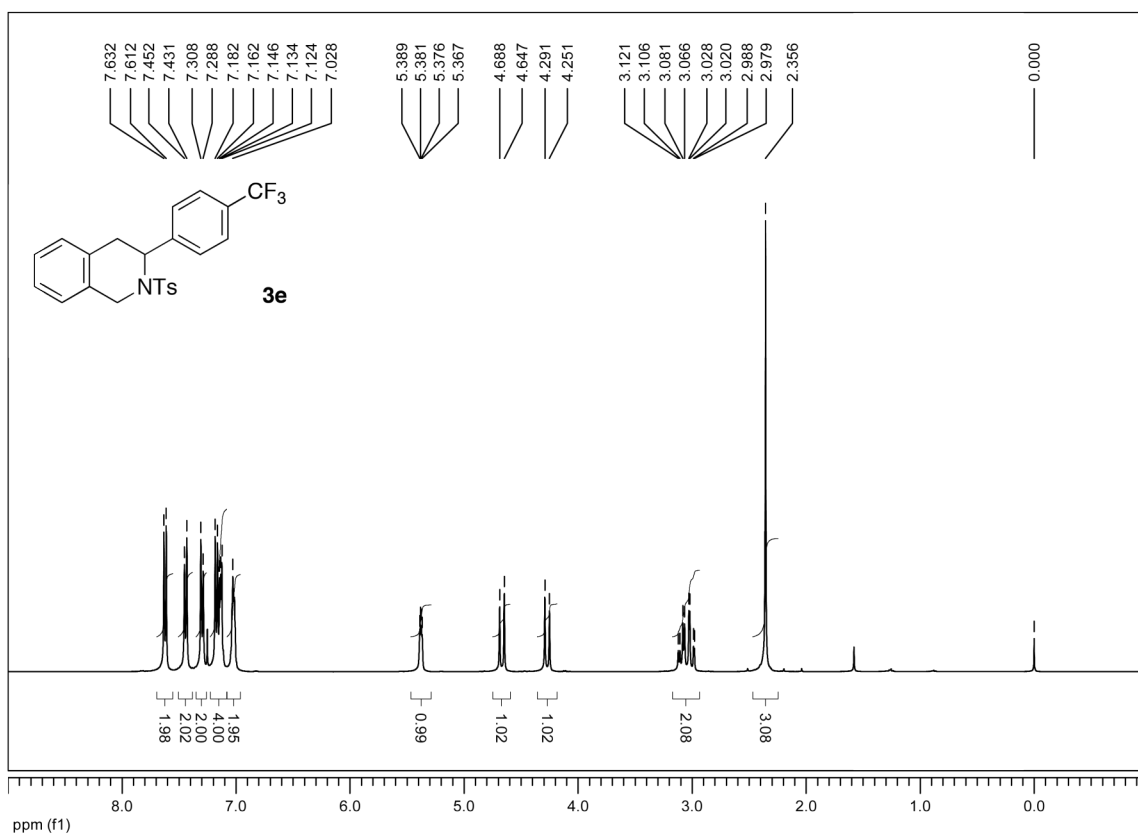


Figure S-25. ¹H NMR spectrum (CDCl₃) of **3e**.

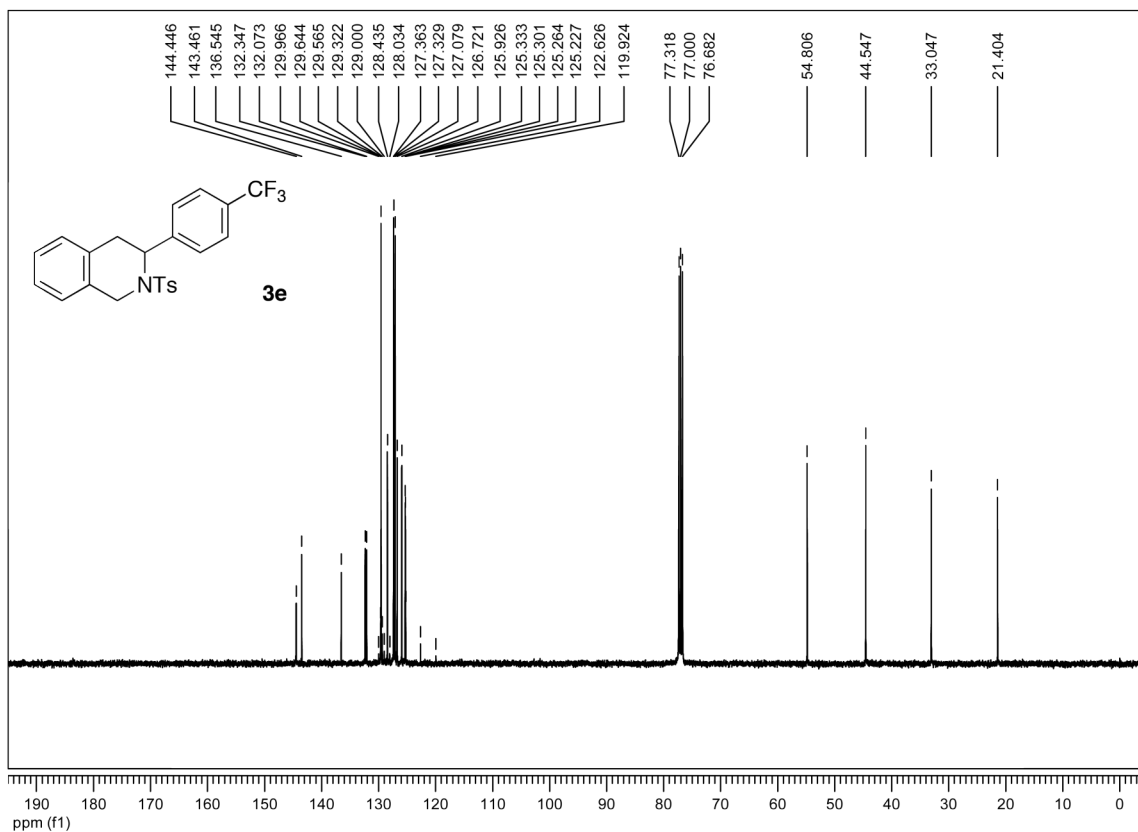


Figure S-26. ¹³C {¹H} NMR spectrum (CDCl₃) of **3e**.

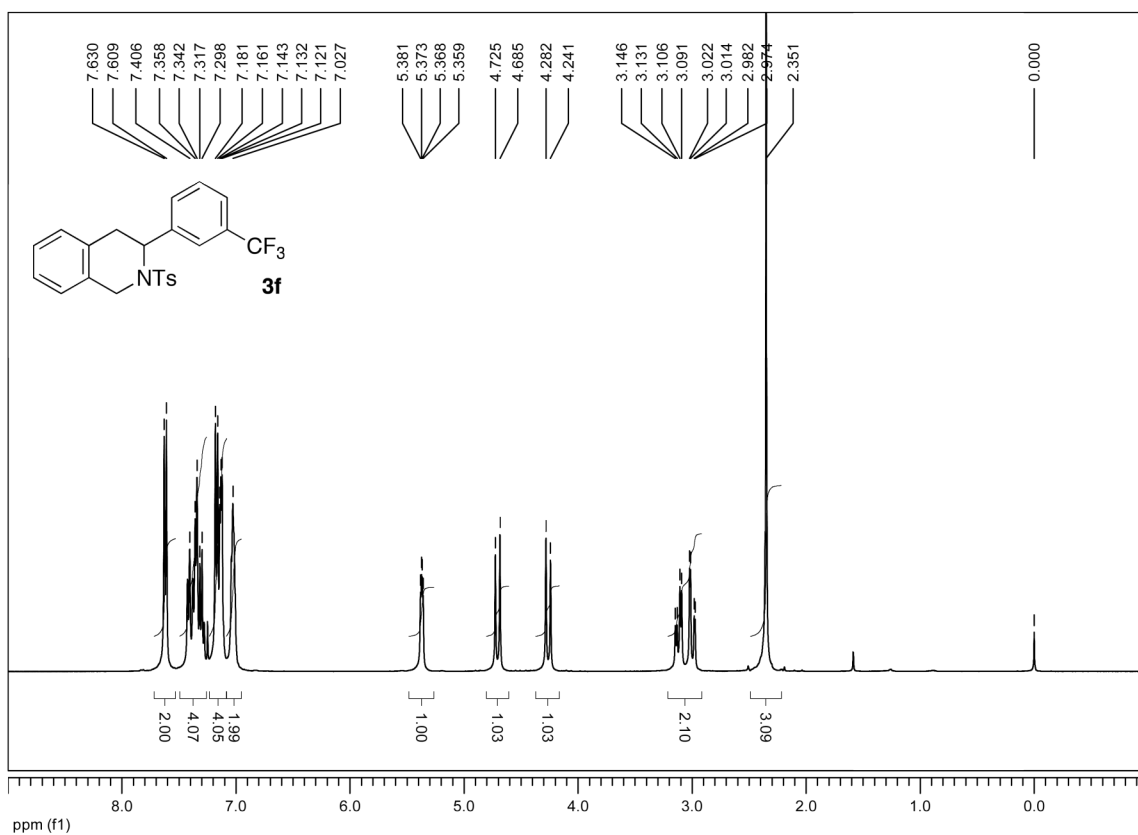


Figure S-27. ¹H NMR spectrum (CDCl₃) of **3f**.

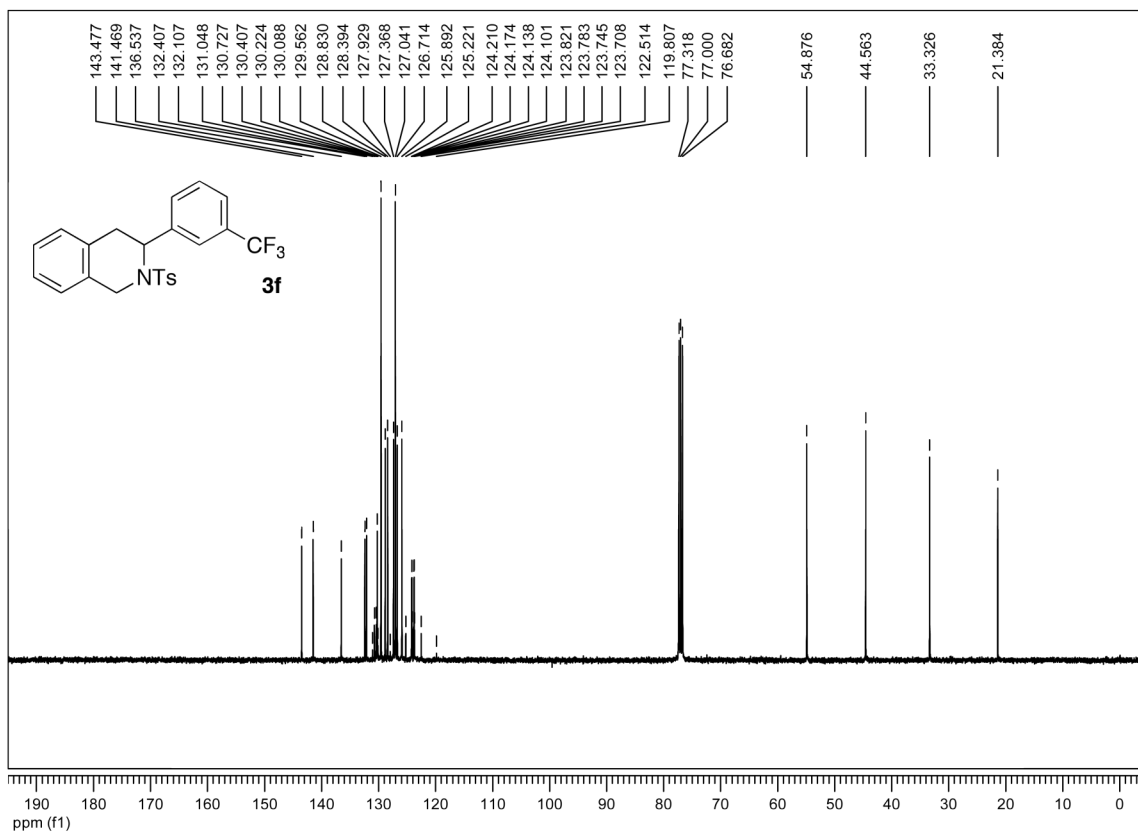


Figure S-28. ¹³C {¹H} NMR spectrum (CDCl₃) of **3f**.

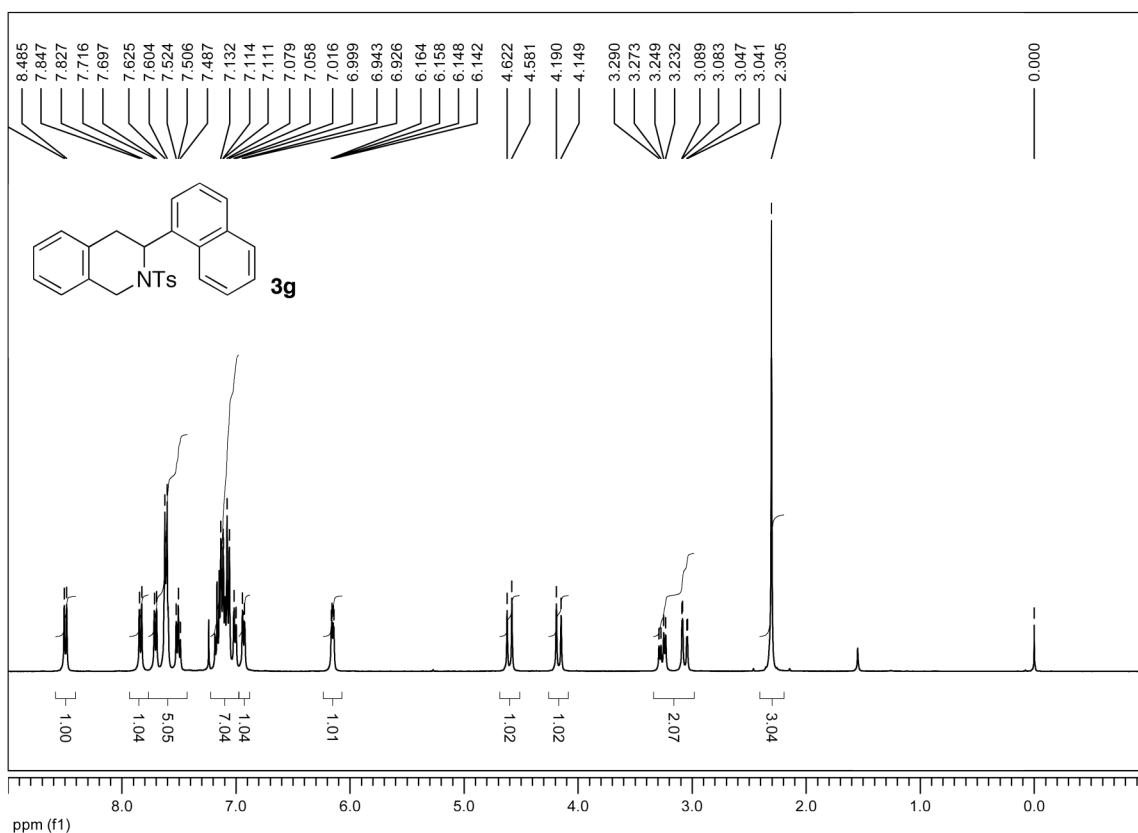


Figure S-29. ¹H NMR spectrum (CDCl₃) of **3g**.

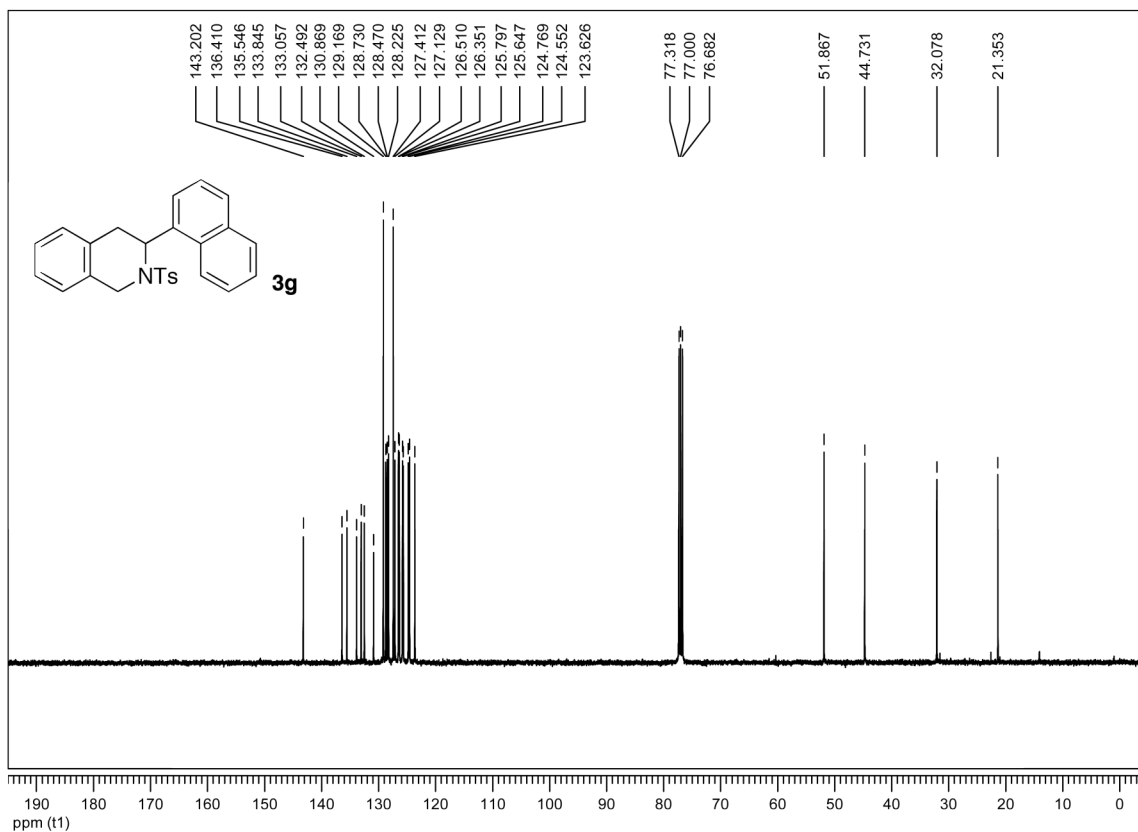


Figure S-29. ¹³C {¹H} NMR spectrum (CDCl₃) of **3g**.

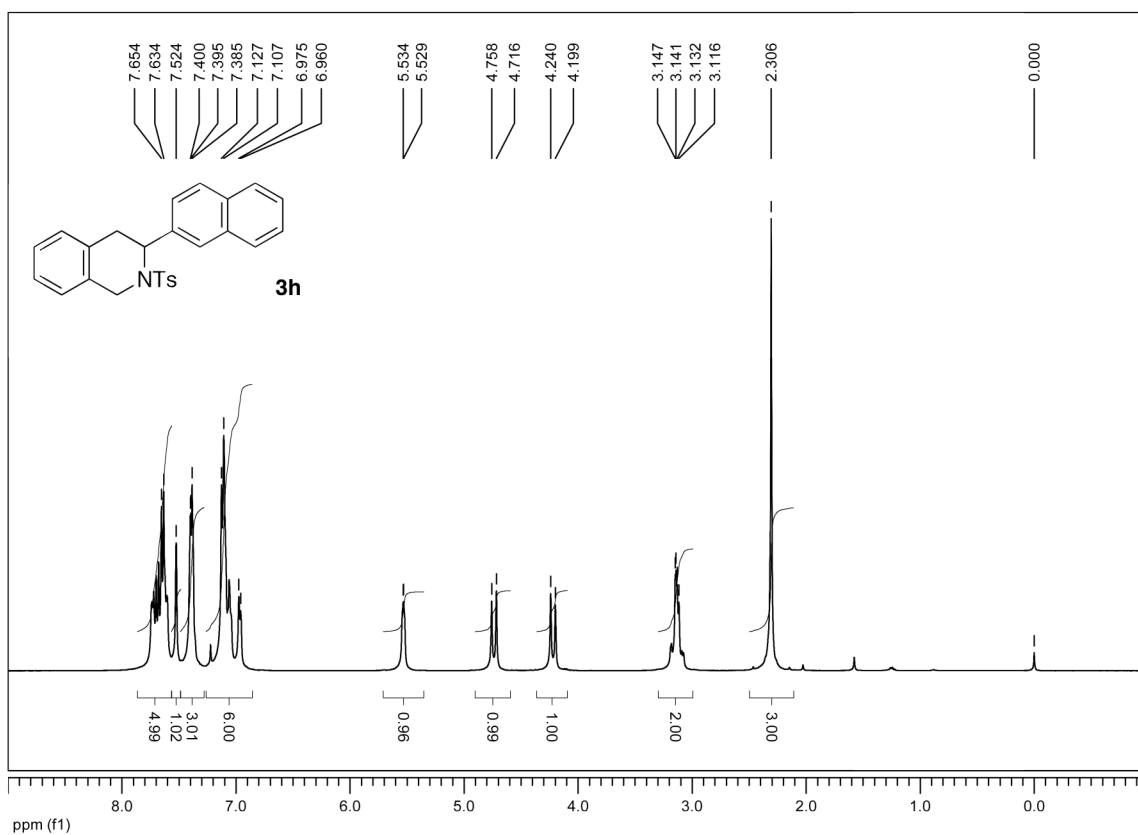


Figure S-30. ¹H NMR spectrum (CDCl₃) of **3h**.

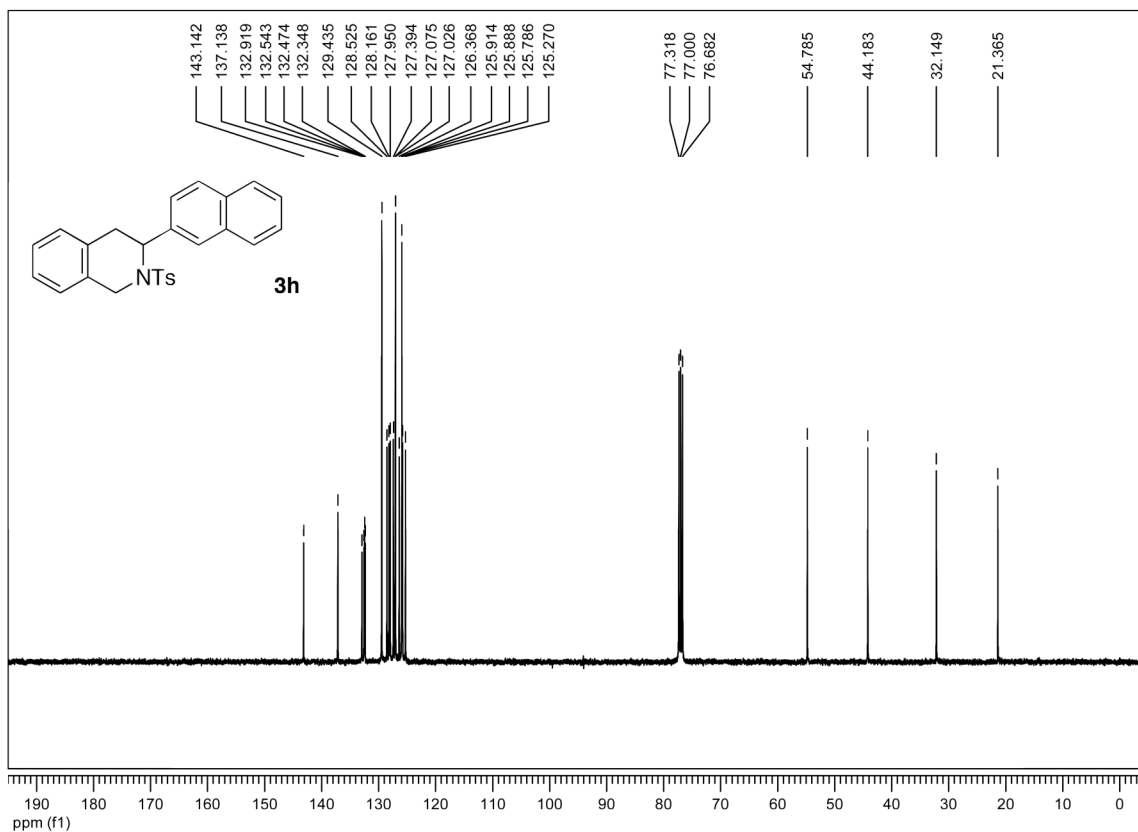


Figure S-31. ¹³C {¹H} NMR spectrum (CDCl₃) of **3h**.

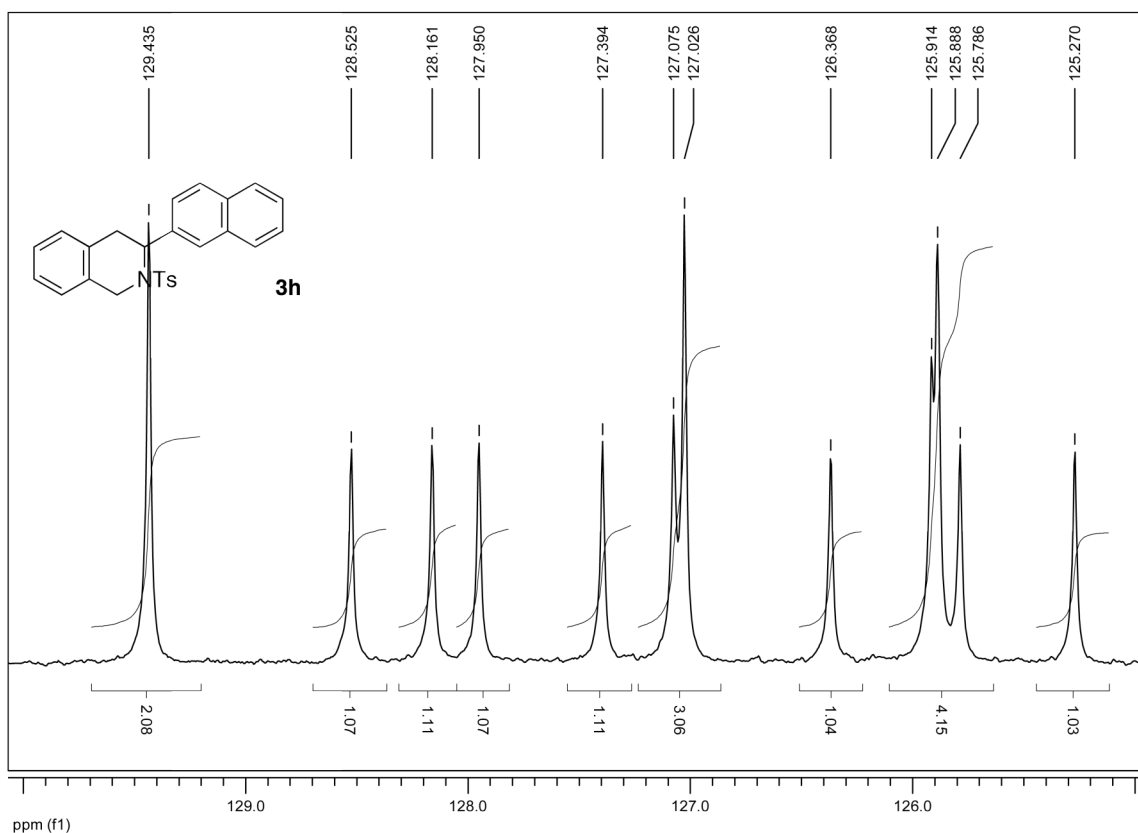


Figure S-31. ^{13}C { ^1H } NMR spectrum (CDCl₃) of **3h** (125–130 ppm).

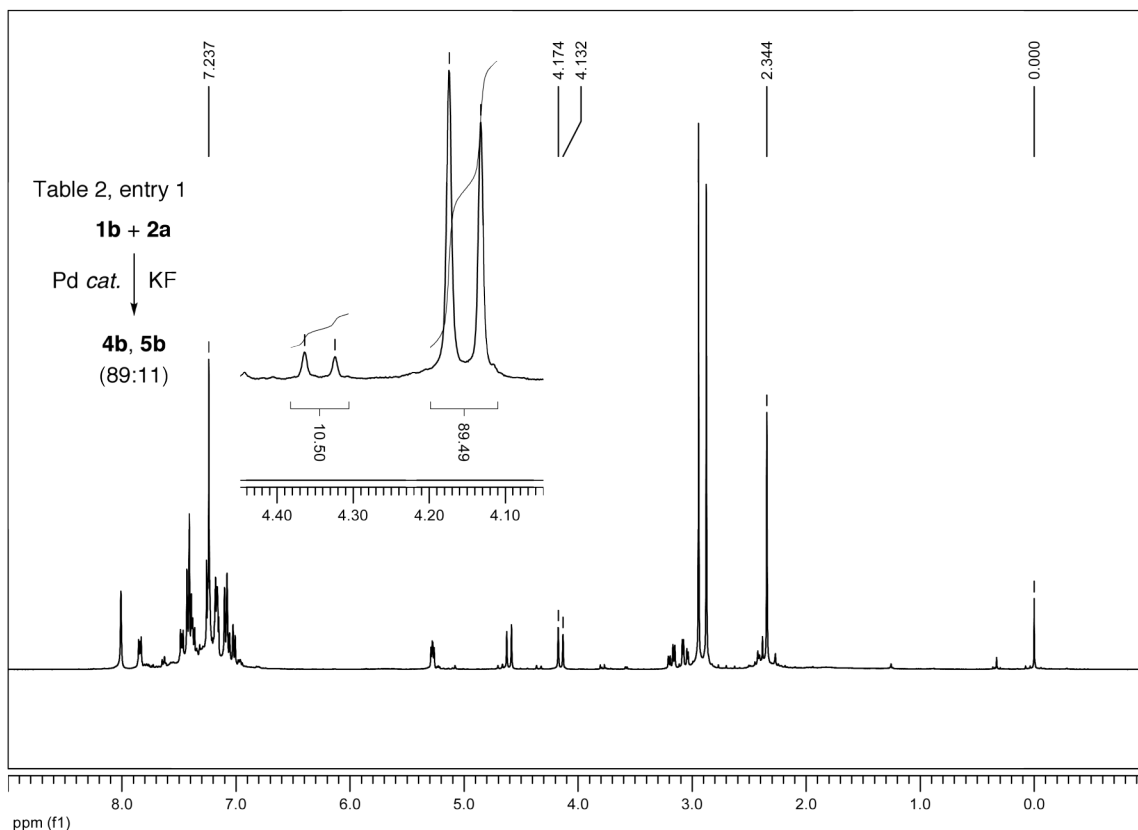


Figure S-32. ^1H NMR spectrum (CDCl₃) of the crude product of the reaction in Table 2, entry 1.

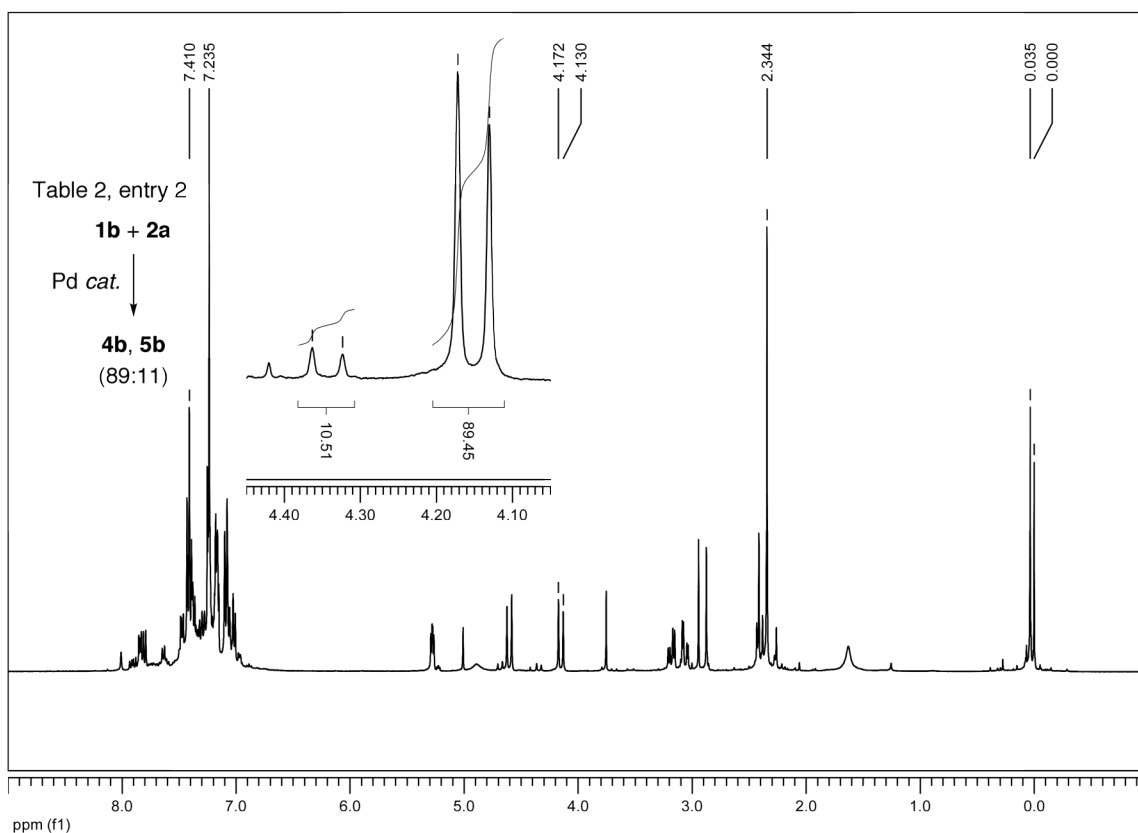


Figure S-33. ^1H NMR spectrum (CDCl_3) of the crude product of the reaction in Table 2, entry 2.

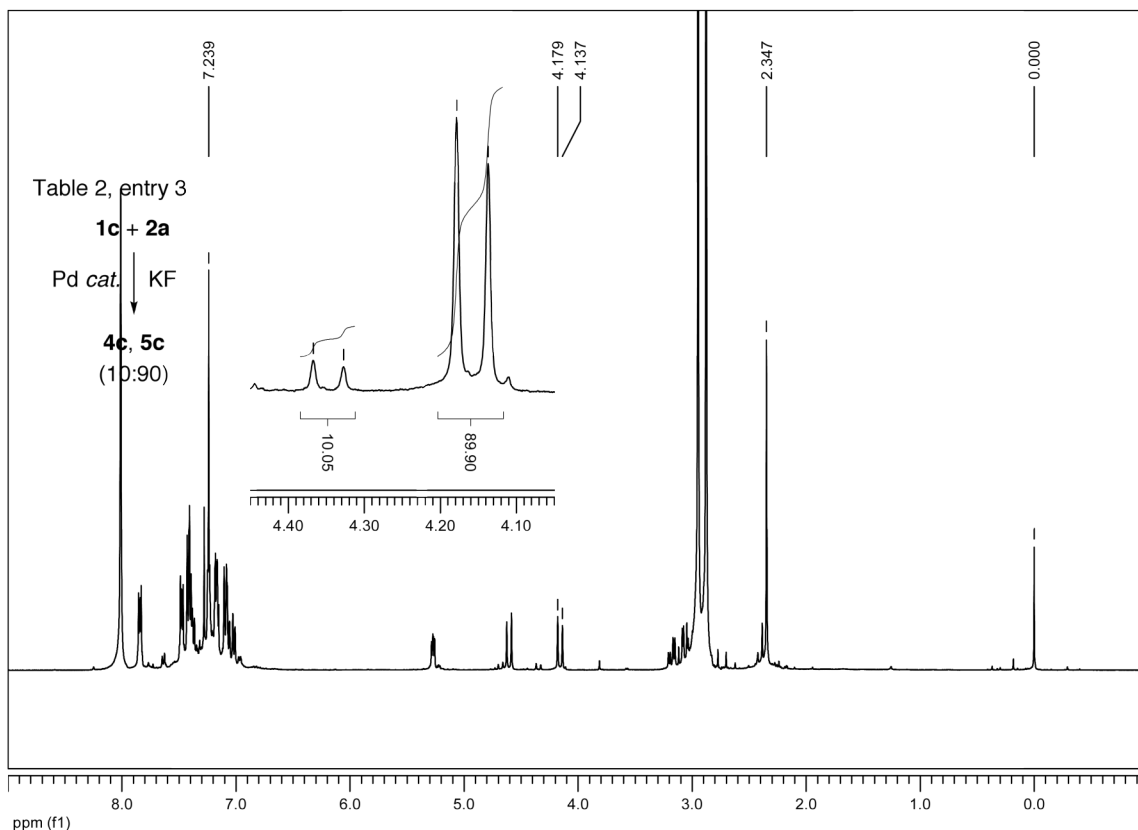


Figure S-34. ^1H NMR spectrum (CDCl_3) of the crude product of the reaction in Table 2, entry 3.

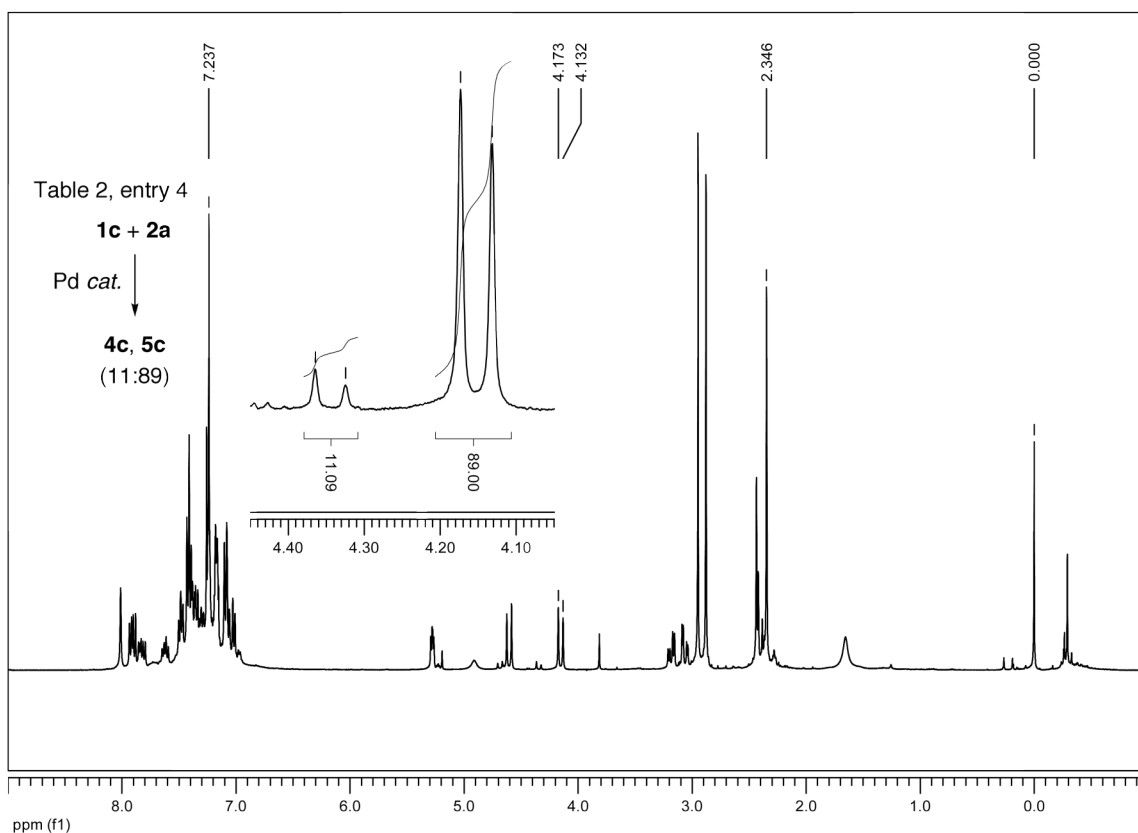


Figure S-35. ^1H NMR spectrum (CDCl_3) of the crude product of the reaction in Table 2, entry 4.

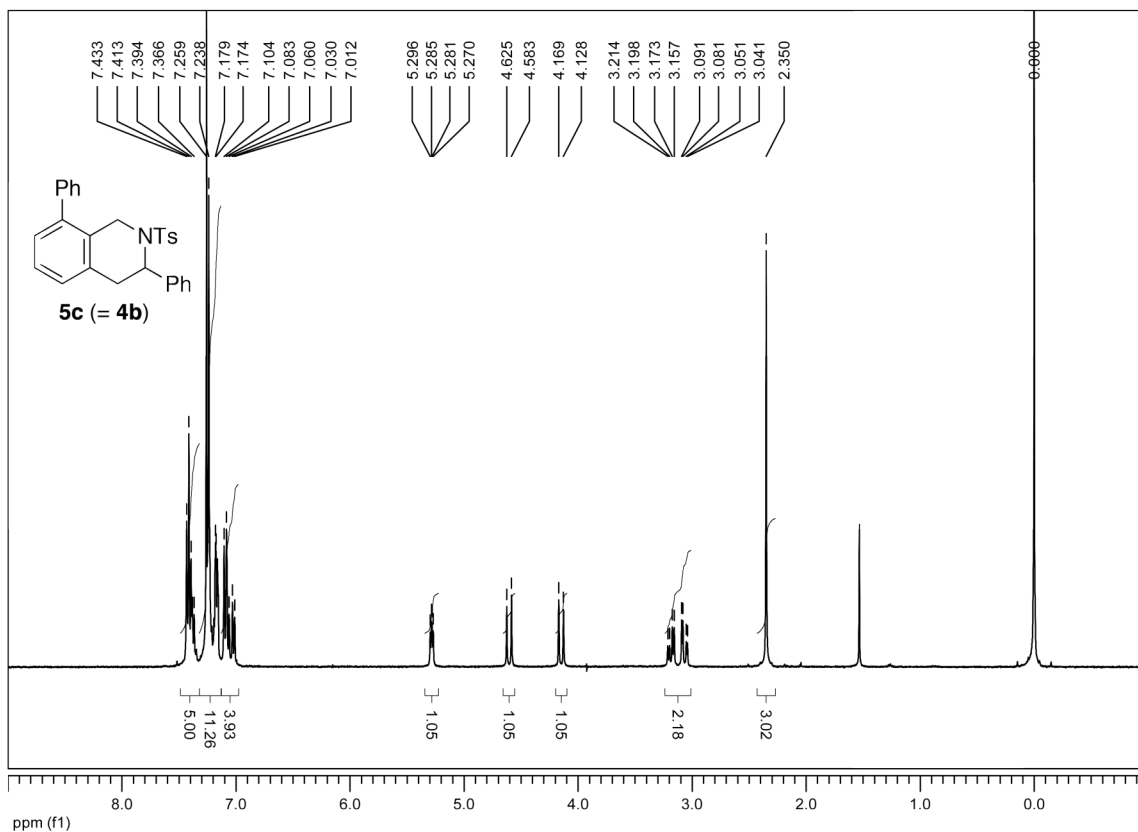


Figure S-36. ^1H NMR spectrum (CDCl_3) of **5c (= 4b)**.

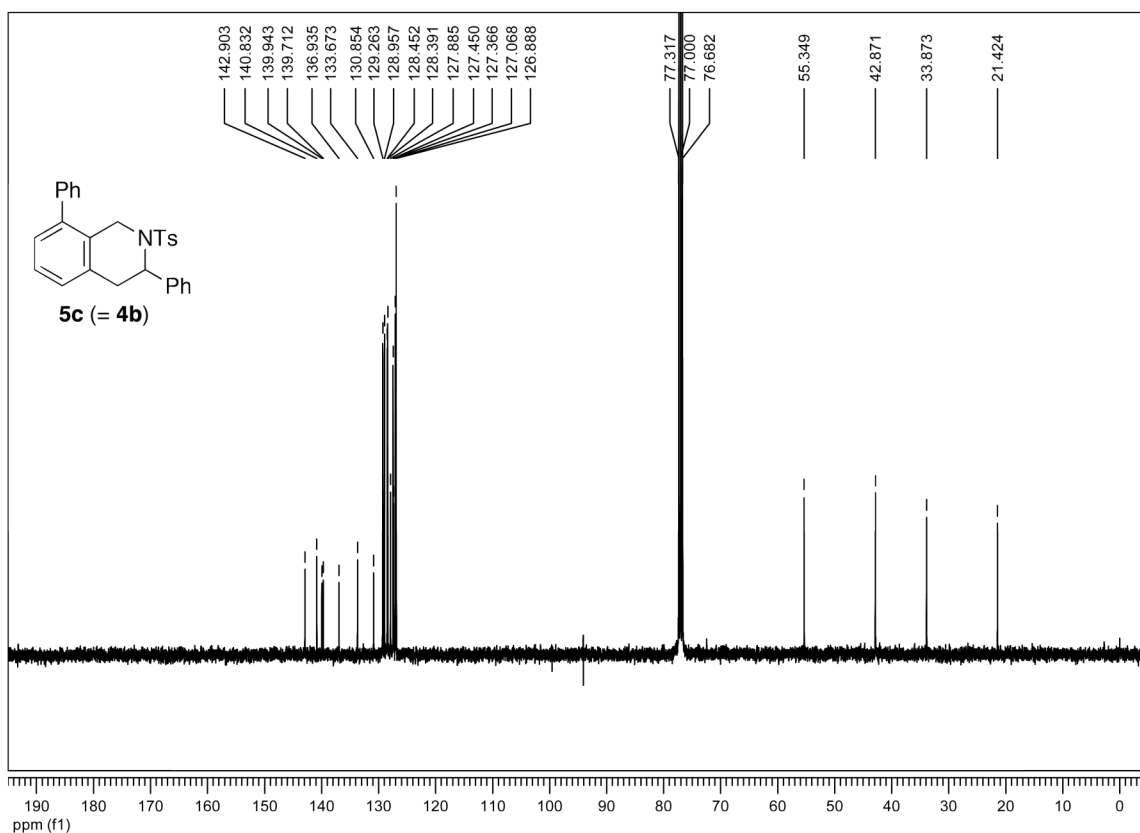


Figure S-37. ¹³C {¹H} NMR spectrum (CDCl₃) of **5c (= 4b)**.

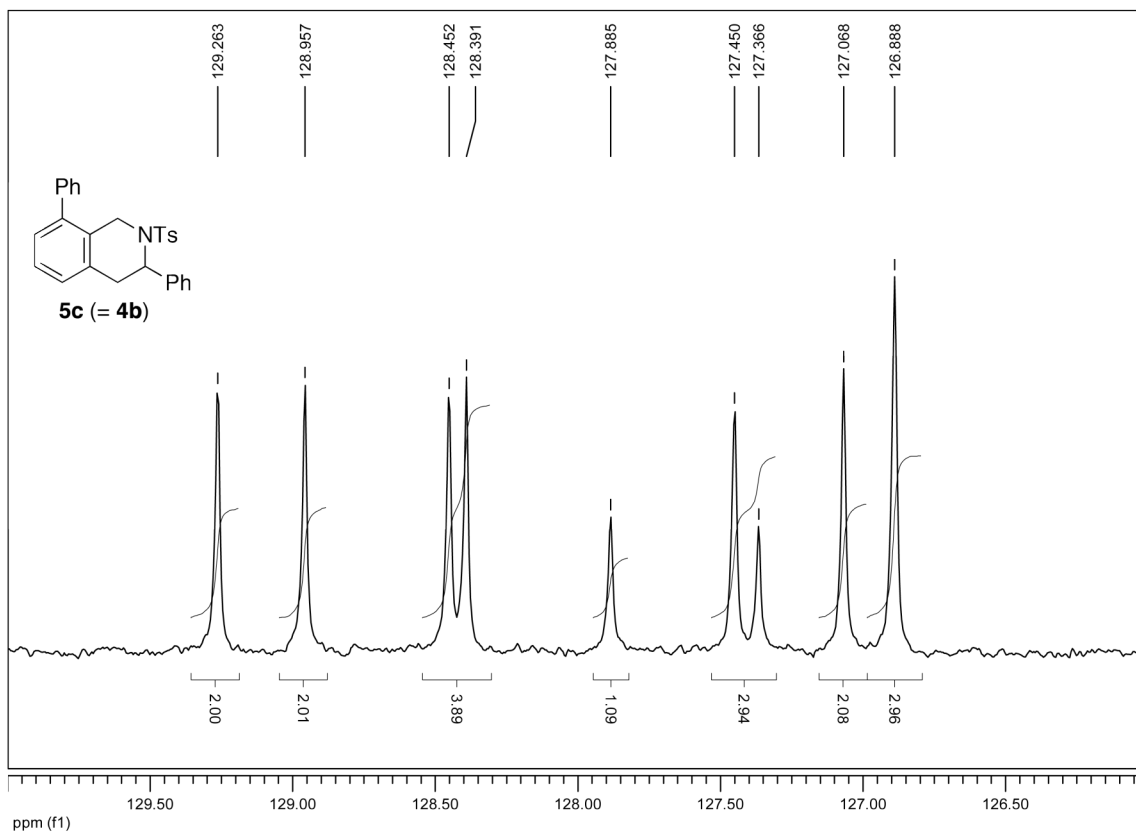


Figure S-38. ¹³C {¹H} NMR spectrum (CDCl₃) of **5c (= 4b)** (126–130 ppm).

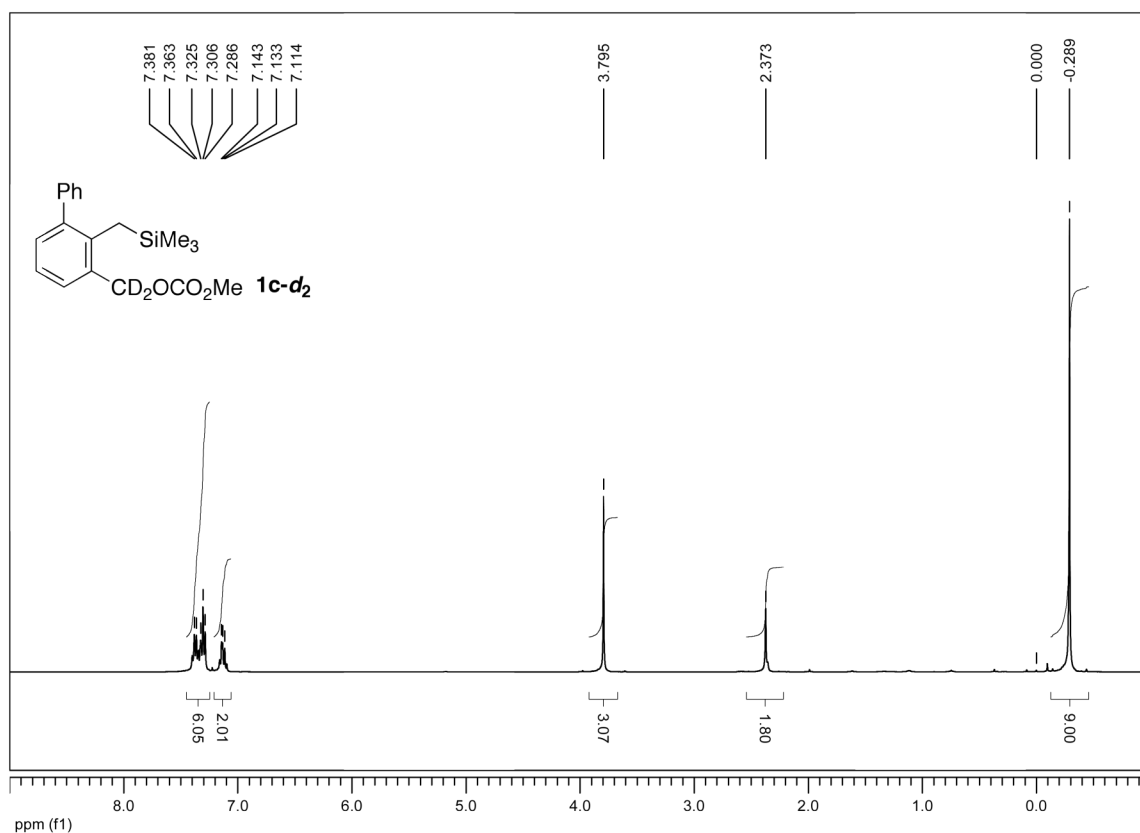


Figure S-39. ¹H NMR spectrum (CDCl₃) of **1c-d₂**.

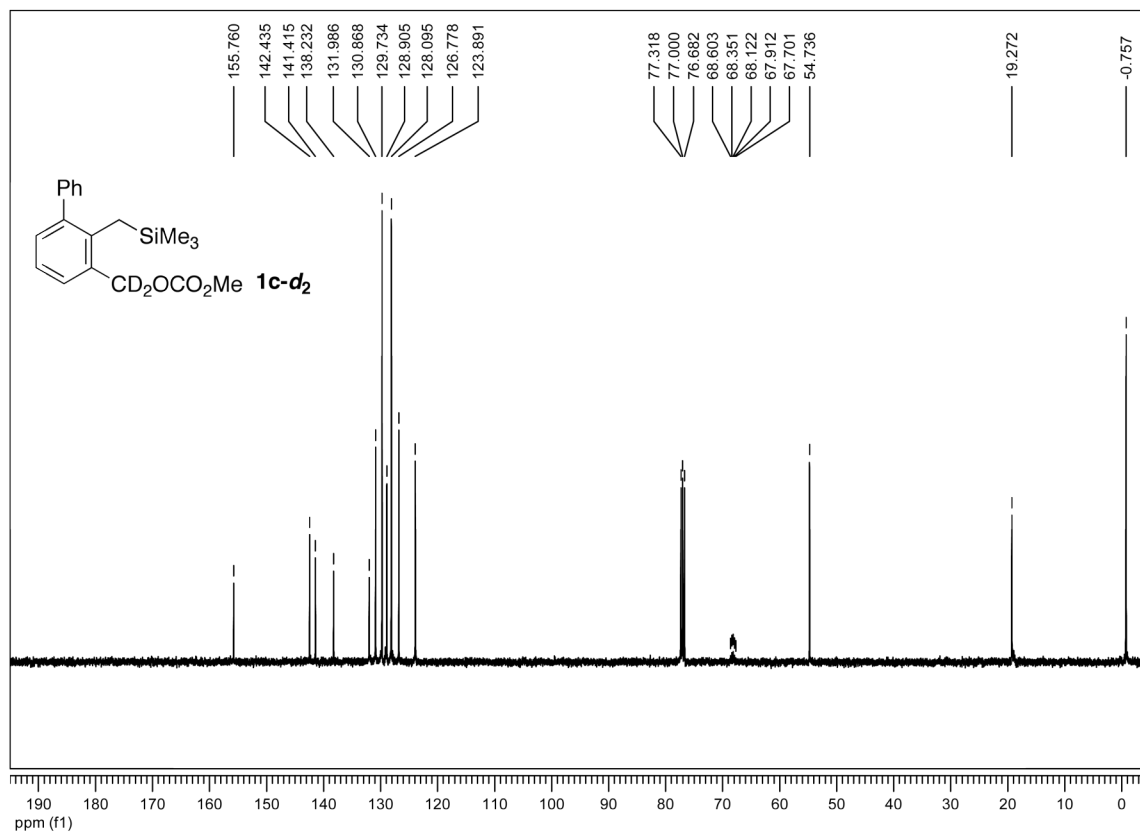


Figure S-40. ¹³C {¹H} NMR spectrum (CDCl₃) of **1c-d₂**.

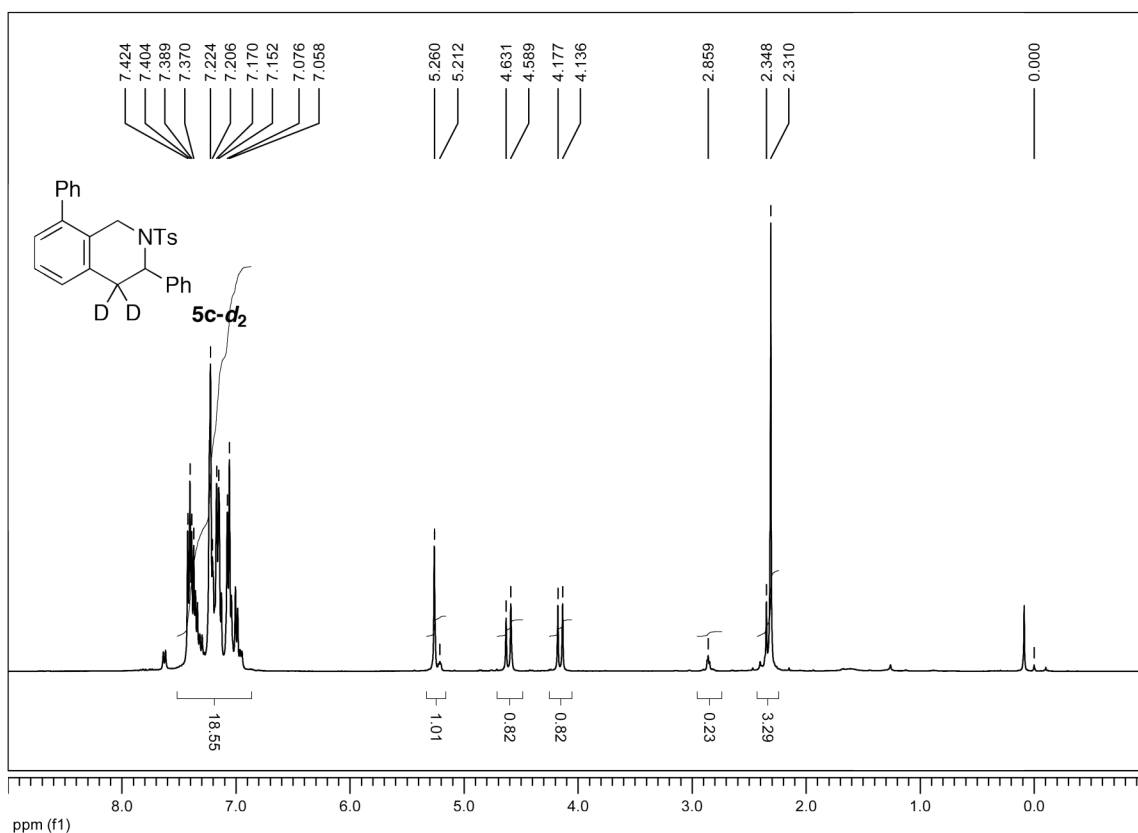


Figure S-41. ¹H NMR spectrum (CDCl₃) of **5c-d₂** (containing a small amount of **4c-d₂**).

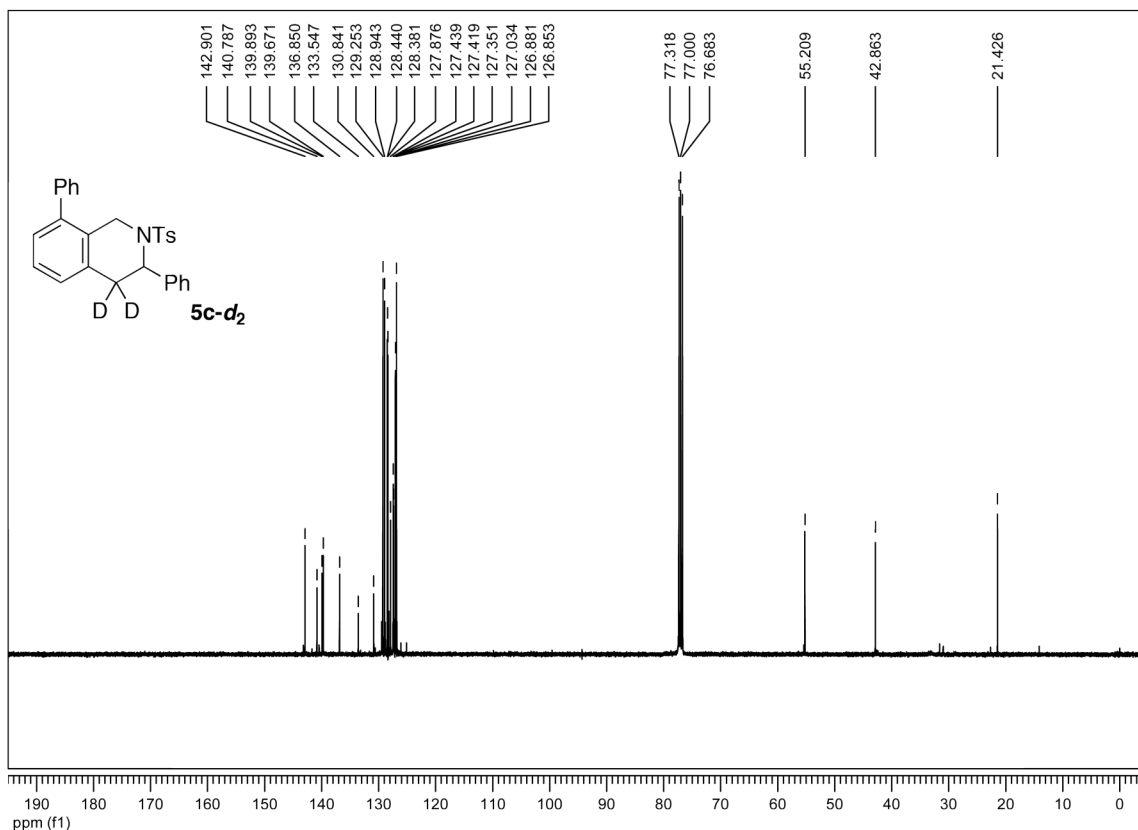


Figure S-42. ¹³C {¹H} NMR spectrum (CDCl₃) of **5c-d₂** (containing a small amount of **4c-d₂**).

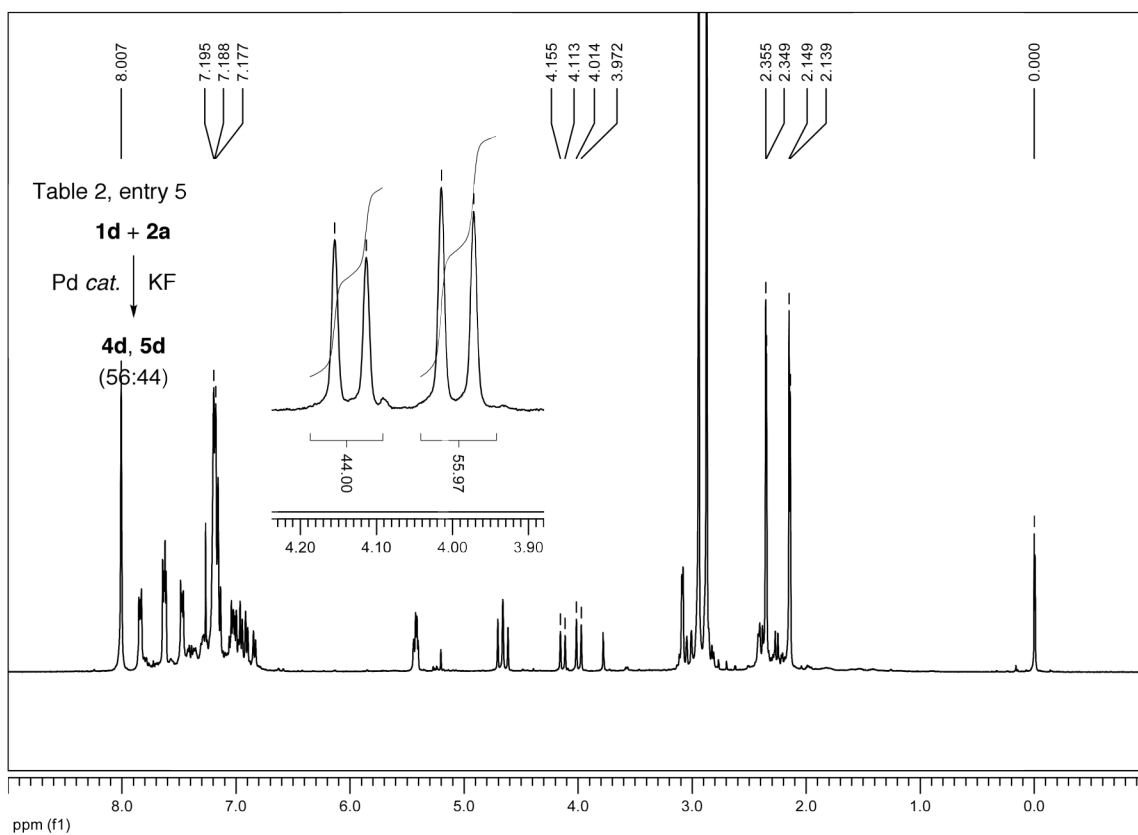


Figure S-43. ^1H NMR spectrum (CDCl_3) of the crude product of the reaction in Table 2, entry 5.

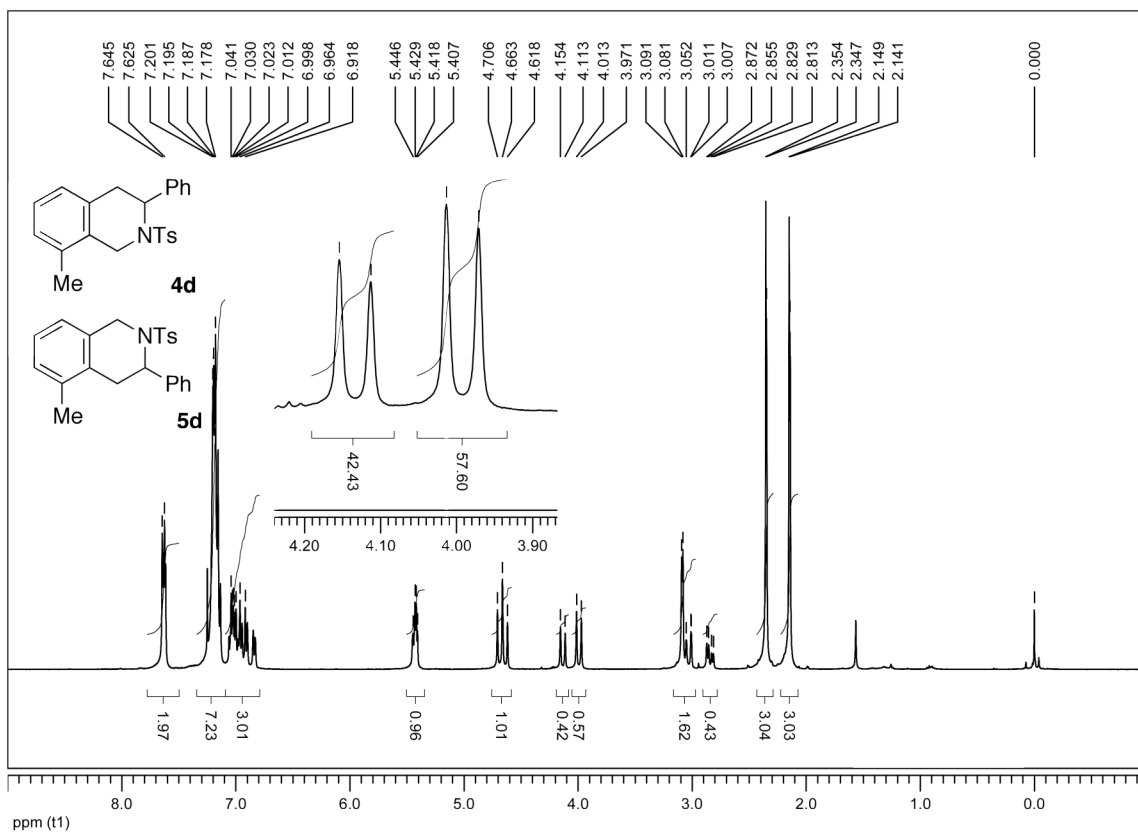


Figure S-44. ^1H NMR spectrum (CDCl_3) of the mixture of **4d** and **5d**.

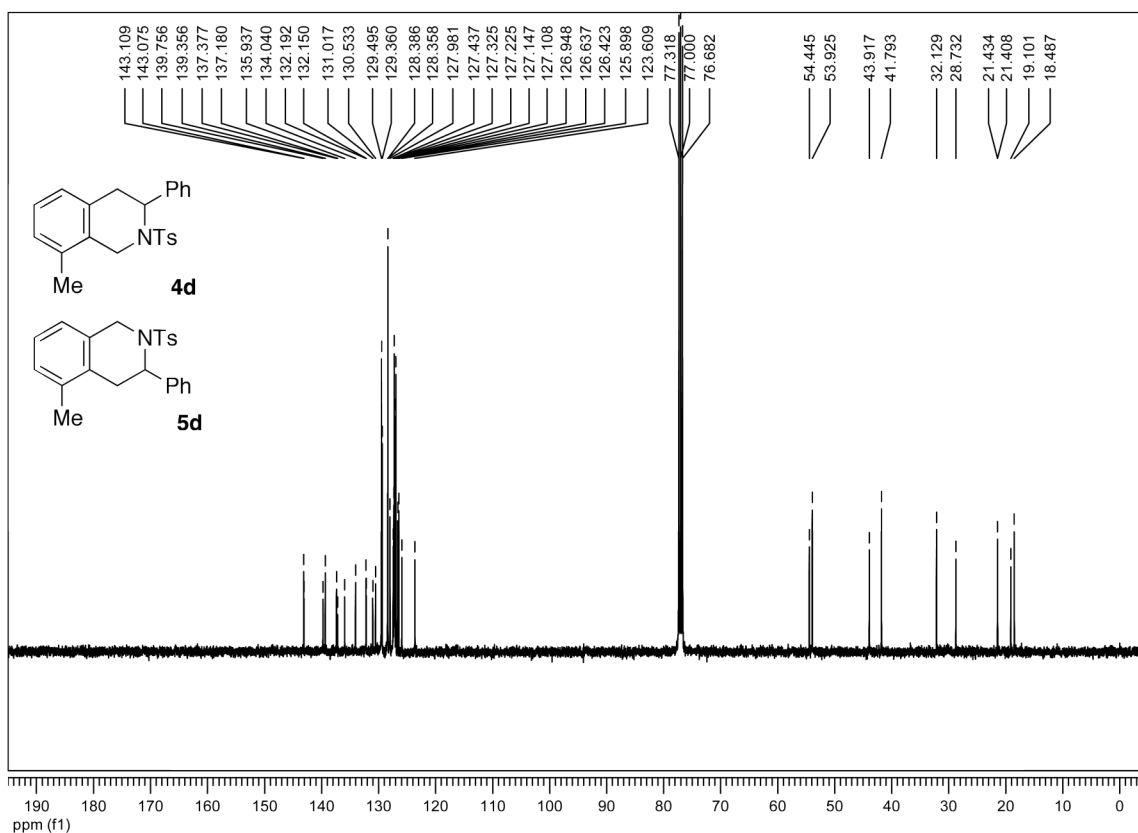


Figure S-45. ¹³C {¹H} NMR spectrum (CDCl₃) of the mixture of **4d** and **5d**.

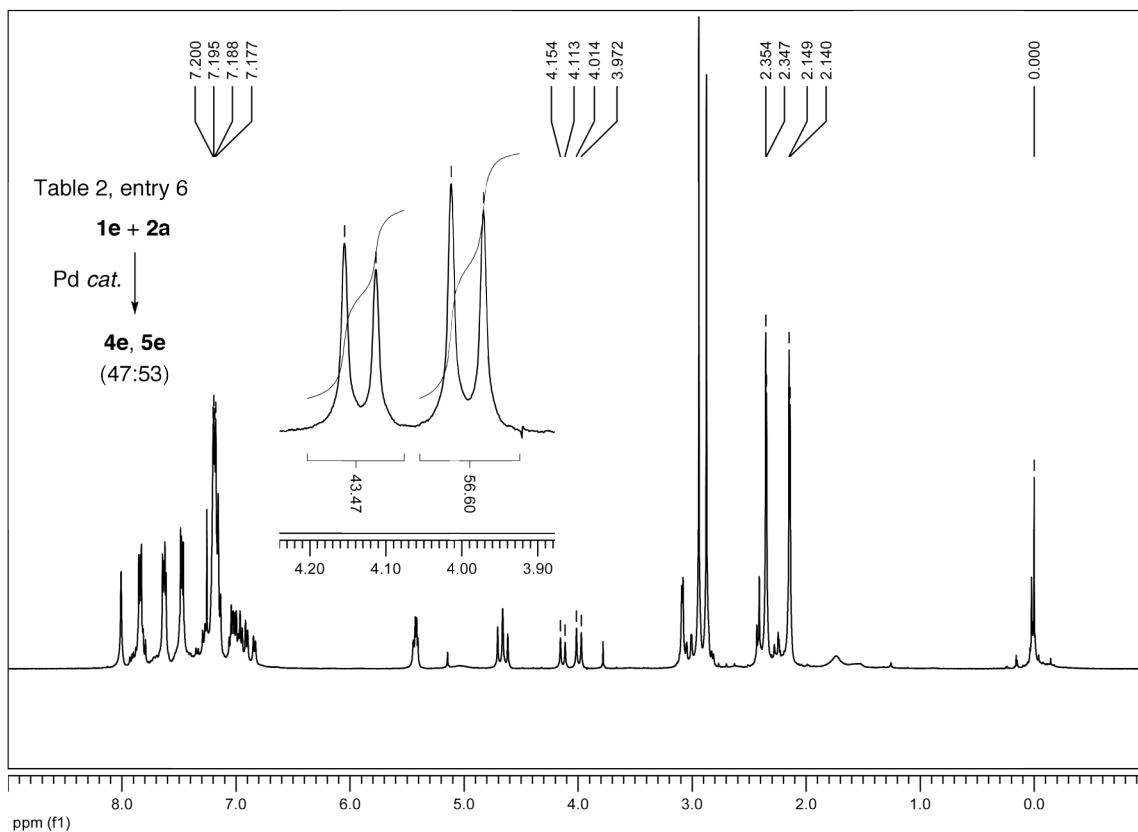


Figure S-46. ¹H NMR spectrum (CDCl₃) of the crude product of the reaction in Table 2, entry 6.

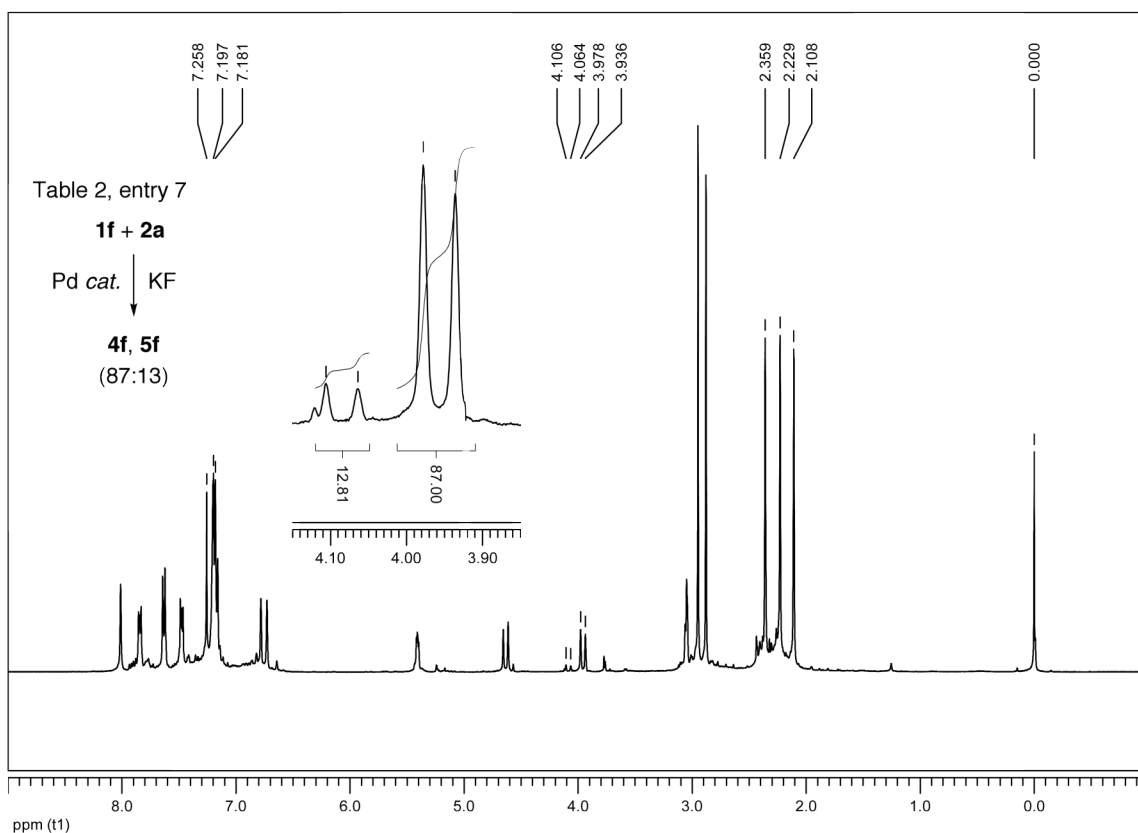


Figure S-47. ^1H NMR spectrum (CDCl_3) of the crude product of the reaction in Table 2, entry 7.

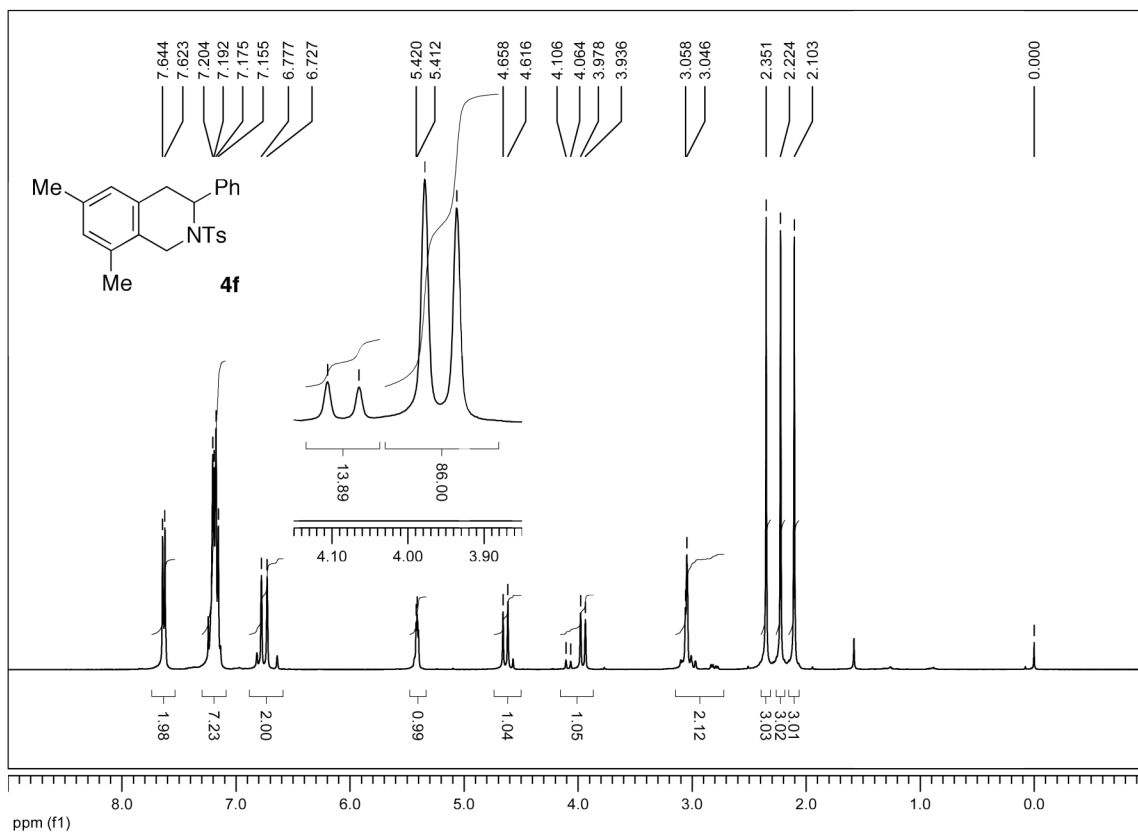


Figure S-48. ^1H NMR spectrum (CDCl_3) of **4f** (containing a small amount of **5f**).

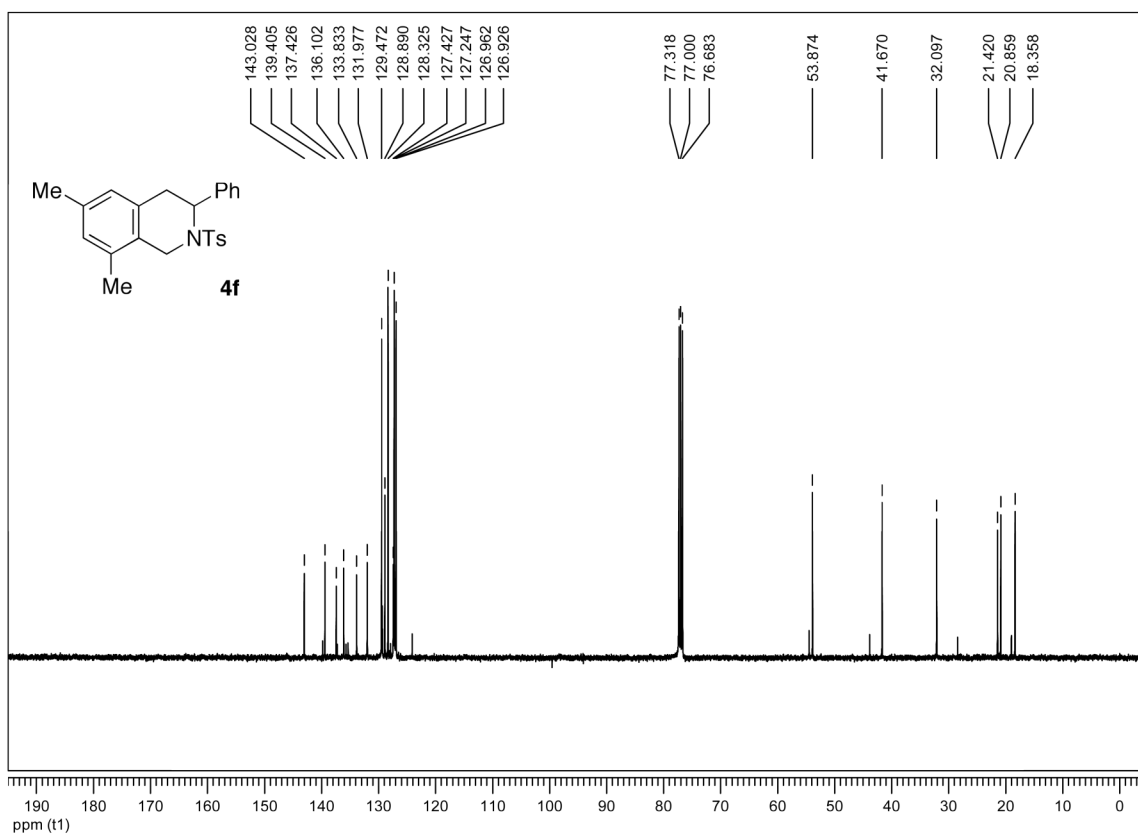


Figure S-49. ^{13}C $\{^1\text{H}\}$ NMR spectrum (CDCl_3) of **4f** (containing a small amount of **5f**).