Alkoxyhydrosilane–Facilitated Cross-Etherification Reaction of Secondary Benzyl Alcohol with Aliphatic Alcohol: Synthesis of Unsymmetrical Dialkyl Ethers

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Table of contents

General procedures.

The reactions were performed under Ar atmosphere using oven-dried glassware. Alcohols **1a**, **1e**, **1f**, **1i**, **1j**, **1k**, **1m**, **1p**, **1q**, and **1r** were purchased from Sigma-Aldrich Co. LLC or TCI Co., Ltd.. Alcohols **1b**, **1c**, **1d**, **1g**, **1h**, **1l**, **1n**, **1o**, **1s**, and **1t** were prepared by the reduction of the corresponding ketones using $NaBH_4$. Alcohols **1u** was prepared by the reaction of crotonaldehyde with PhMgBr.[1] Chiral alcohol (*S*)-**1j** was prepared by the Rh(pybox) catalyzed asymmetric hydrosilyation of the corresponding ketone.[2] The lignin model compound **1v** was prepared by the literature procedures.[3] $(EtO)_2MeSiH$, $(EtO)_2Me_2Si$, $(EtO)_2MePhSi$, $(EtO)_3SiH$, $(EtO)_4Si$, Me_2PhSiH, and $MePh_2SiH$ were purchased from TCI Co., Ltd. and Ph_3SiH, and *t*-$BuMe_2SiH$ were purchased from Sigma-Aldrich Co. LLC.. Orgnosilane compounds were distilled prior to use and stored at an Ar atmosphere. All other reagents employed in this study were obtained from common commercial suppliers and used without further purification.

Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR), spectra were recorded using a JEOL ECZ 400S spectrometer at ambient temperature. ^{1}H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) or the solvent resonance as the internal standard (TMS: 0.00 ppm or $CHCl_3$: 7.26 ppm). ^{13}C NMR chemical shifts are reported in ppm relative to the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). Data are presented in the following form: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet and/or multiplet resonances, br = broad), coupling constants (Hz), and signal area integration in natural numbers.

Analytical thin-layer chromatography (TLC) was performed on alumina plates (Merck Co., Inc., 1.05554.0001), which were visualized by exposure to ultraviolet light (254 nm) and/or by immersion in a phosphomolybdic acid ethanol solution followed by heating on a hot plate. Organic solutions were concentrated by rotary evaporation at *ca.* 30–400 mmHg. Purification of the products was performed by flash column chromatography on silica gel (Fuji Silysia Chemical LTD., spherical, neutral, CHROMATOREX PSQ 60B) or preparative thin-layer chromatography (PTLC) on silica gel (Merck Co., Inc. Silica gel 60 F254). IR spectra were recorded using a JASCO FT/IR-6700. Characteristic IR absorptions are reported in cm^{-1}. High-resolution mass spectra (HRMS) were recorded using the electrospray ionization (ESI) method on a bruker timsTOF mass spectrometer. High performance liquid chromatography (HPLC) was performed on JASCO PU-2080 and UV-2075 instruments using Daicel Chiralpak column (4.6 mm × 250 mm).

Experimental Procedures

Optimization of Reaction Conditions: Procedure for the Etherification Reaction of 1a with 2a Using Hydrosilane (Table 1 and S1).

A round-bottom flask equipped with a magnetic stir bar was charged with benzyl alcohol **1a** (0.50 mmol) ethanol (**2a**, 2.5 mL), and organosilane (2.0 mmol). The reaction mixture was stirred at 85 ºC for 24 h. Then, the resulting mixture was cool to room temperature and concentrated *in vacuo*. The crude residue was purified by flash column chromatography on silica gel to afford the corresponding product **3aa**.

Table S1. Optimization studies for organosilane

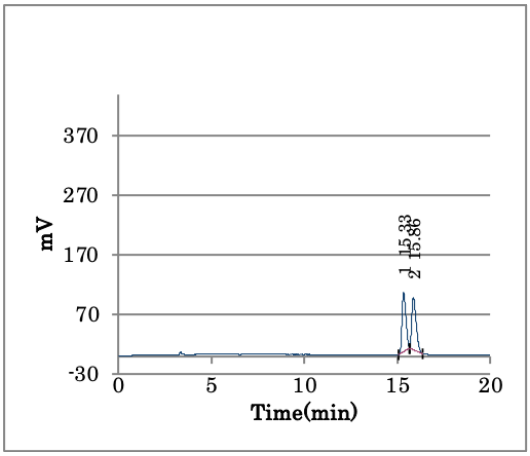
General Procedure for the Etherification Reaction of 1 with 2 Using $(EtO)_2MeSiH$ (Scheme 2–5 and Scheme 7).

A round-bottom flask equipped with a magnetic stir bar was charged with benzyl alcohol **1** (0.50 mmol) alcohol solvent (**2**, 2.5 mL), and $(EtO)_2MeSiH$ (2.0 mmol). The reaction mixture was stirred at 85–100 ºC for 24 h. Then, the resulting mixture was cool to room temperature and concentrated *in vacuo*. The crude residue was purified by flash column chromatography on silica gel to afford the corresponding product **3**.

The Etherification Reaction using (*S*)-1r (Scheme 6)

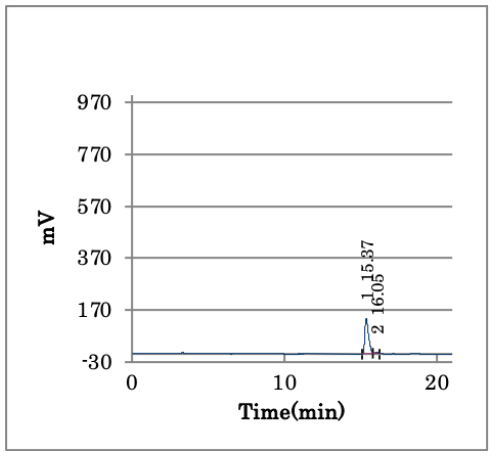
A round-bottom flask equipped with a magnetic stir bar was charged with chiral alcohol (*S*)-**1j** (97%ee, 86.3 mg, 0.50 mmol) ethanol (**2a**, 2.5 mL), and $(EtO)_2MeSiH$ (268.6 mg, 2.0 mmol). The reaction mixture was stirred at 85 ºC for 24 h. Then, the resulting mixture was cool to room temperature and concentrated in vacuo. The crude residue was purified by flash column chromatography on silica gel, eluting hexane/EtOAc (20/1), to afford the corresponding product **3ja** (83.5 mg, 84%, 14% ee).

(a) racemic **1j**



No.	Rt	Peak Name	Area	Area(%)
1	15.33		1427543	49.9996
2	15.86		1427565	50.0004

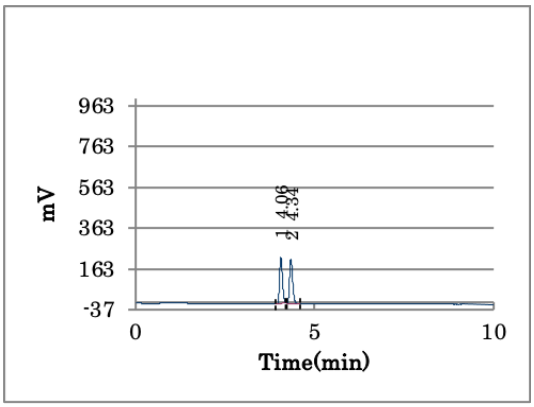
b) enantiomerically enriched (*S*)-**1j**



No.	Rt	Peak Name	Area	Area(%)
1	15.37		2244772	98.4343
2	16.05		35705	1.5657

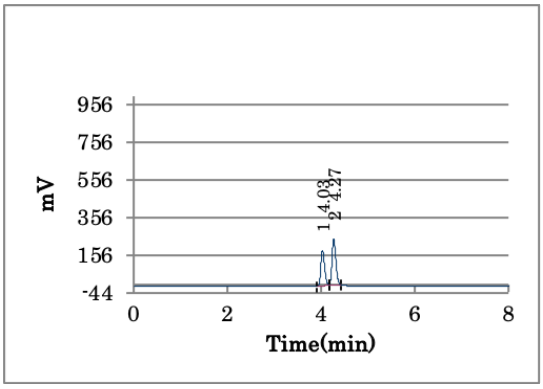
Figure S1 Chiral HPLC profiles of (a) racemic and (b) enantiomerically enriched (*S*)-**1j** using Daicel CHIRALPAK IE-3 (flow rate: 1.1 mL/min, *n*-hexane/ethyl acetate = 95/5 as an eluent monitored at 254 nm).

(a) racemic **3ja**



No.	Rt	Peak Name	Area	Area(%)
1	4.06		1258115	49.1953
2	4.34		1299272	50.8047

(b) the product **3ja**

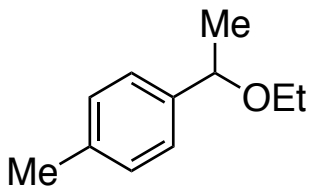


No.	Rt	Peak Name	Area	Area(%)
1	4.03		1046526	42.9947
2	4.27		1387553	57.0053

Figure S2 Chiral HPLC profiles of (a) racemic and (b) the product **3ja** using Daicel CHIRALPAK IC-3 (flow rate: 1.1 mL/min, *n*-hexane/ ethyl acetate = 99/1 as an eluent monitored at 254 nm).

Characterization Data of the Isolated Products

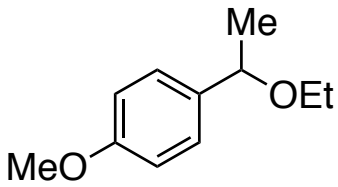
Synthesis of 1-(1-ethoxyethyl)-4-methylbenzene (3aa)



Compound **3aa** was prepared according to the general procedure using **1a** (68.8 mg, 0.51 mmol), and $(EtO)_2MeSiH$ (269.9 mg, 2.01 mmol) in ethanol (**2a**, 2.5 mL) at 85 ºC for 24 h. Product **3aa** was obtained in 95% yield (78.8 mg, 0.48 mmol) as a colorless oil.

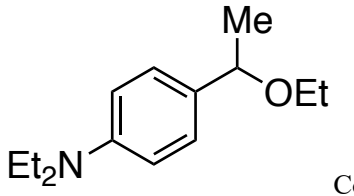
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (t, J = 7.2 Hz, 3H), 1.42 (d, J = 6.8 Hz, 3H), 2.34 (s, 3H), 3.34 (q, J = 7.2 Hz, 2H), 4.37 (q, J = 6.8 Hz, 1H), 7.14–7.16 (m, 2H), 7.20–7.22 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 21.1, 24.3, 63.8, 77.5, 126.1, 129.0, 136.9, 141.2 ppm. ^{1}H and ^{13}C NMR spectra have been attached. The product was characterized by comparison with previously reported ^{1}H and ^{13}C NMR data.[4]

Synthesis of 1-(1-ethoxyethyl)-4-methoxybenzene (3ba)



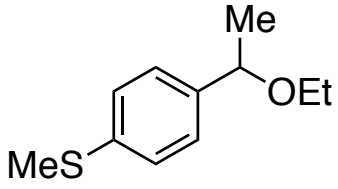
Compound **3ba** was prepared according to the general procedure using **1b** (76.8 mg, 0.50 mmol), and $(EtO)_2MeSiH$ (268.8 mg, 2.00 mmol) in ethanol (**2a**, 2.5 mL) at 85 ºC for 24 h. Product **3ba** was obtained in 94% yield (85.1mg, 0.47 mmol) as a colorless oil.
^1H NMR (400 MHz, $CDCl_3$) δ 1.17 (t, J = 7.2 Hz, 3H), 1.42 (d, J = 6.8 Hz, 3H), 3.33 (q, J = 7.2 Hz, 2H), 3.81 (s, 3H), 4.36 (q, J = 6.4 Hz, 1H), 6.86–6.90 (m, 2H), 7.22–7.26 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 24.2, 55.2, 63.6, 77.2, 113.7, 127.3, 136.2, 158.8 ppm. ^1H and ^{13}C NMR spectra have been attached. The product was characterized by comparison with previously reported ^1H and ^{13}C NMR data.[5]

Synthesis of 1-(1-ethoxyethyl)-4-diethylaminobenzene (3ca)



Compound **3ca** was prepared according to the general procedure using **1c** (96.7 mg, 0.50 mmol), and $(EtO)_2MeSiH$ (269.8 mg, 2.0 mmol) in ethanol (**2a**, 2.5 mL) at 85 ºC for 24 h. Product **3ca** was obtained in 84% yield (93.1 mg, 0.42 mmol) as a colorless oil.
^1H NMR (400 MHz, $CDCl_3$, 60 ºC) δ 1.15 (t, J = 6.8 Hz, 9H), 1.41 (d, J = 6.4 Hz, 3H), 3.30–3.38 (m, 6H), 4.30 (q, J = 6.4 Hz, 1H), 6.64–6.66 (m, 2H), 7.12–7.14 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$, 60 ºC) δ 12.7, 15.4, 23.8, 44.5, 63.4, 77.4, 112.1, 127.4, 131.2, 147.6 ppm. IR (Diamond-ATR, neat) 2970, 2928, 2868, 1739, 1613, 1519, 1372, 1353, 1262, 1198, 1189, 1093, 1011, 940, 813 cm^{-1}; HRMS (APCI): calcd for $C_{14}H_{24}N_1O_1$ $[M+H]^+$: 222.1852. found: 222.1853. ^1H and ^{13}C NMR spectra have been attached.

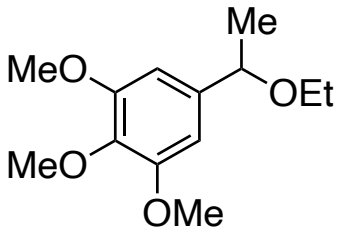
Synthesis of 1-(1-ethoxyethyl)-4-methylthiobenzene (3da)



Compound **3da** was prepared according to the general procedure using **1d** (84.2 mg, 0.50 mmol), and $(EtO)_2MeSiH$ (271.0 mg, 2.0 mmol) in ethanol (**2a**, 2.5 mL) at 85 ºC

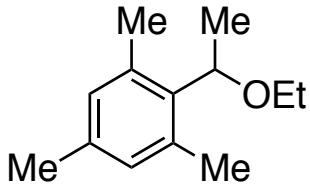
for 24 h. Product **3da** was obtained in 99% yield (96.8 mg, 0.49 mmol) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, *J* = 7.2 Hz, 3H), 1.42 (d, *J* = 6.4 Hz, 3H), 2.49 (s, 3H), 3.34 (q, *J* = 7.2 Hz, 2H), 4.37 (q, *J* = 6.8 Hz, 1H), 7.24 (s, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 15.9, 24.1, 63.8, 77.2, 126.59, 126.62, 137.1, 141.1 ppm. IR (Diamond-ATR, neat) 2972, 2925, 2865, 1738, 1599, 1489, 1439, 1368, 1216, 1209, 1095, 1007, 941, 818, 557 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{16}NaOS$ $[M+Na]^+$: 219.0814. found: 219.0816. ^{1}H and ^{13}C NMR spectra have been attached.

Synthesis of 1-(1-ethoxyethyl)-3,4,5-trimethoxybenzene (3ha)



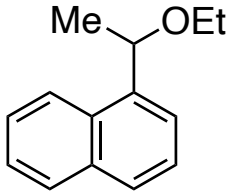
Compound **3ha** was prepared according to the general procedure using **1h** (106.8 mg, 0.50 mmol), and $(EtO)_2MeSiH$ (269.9 mg, 2.0 mmol) in ethanol (**2a**, 2.5 mL) at 85 ºC for 24 h. Product **3ha** was obtained in 93% yield (112.1 mg, 0.47 mmol) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, *J* = 7.2 Hz, 3H), 1.43 (d, *J* = 6.4 Hz, 3H), 3.34–3.42 (m, 2H), 3.84 (s, 3H), 3.87 (s, 6H), 4,33 (q, *J* = 6.4 Hz, 1H), 6.54 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 24.2, 55.9, 60.6, 63.8, 77.8, 102.5, 136.7, 140.0, 153.1 ppm. IR (Diamond-ATR, neat) 2972, 2932, 2870, 2839, 1590, 1507, 1457, 1418, 1339, 1326, 1231, 1122, 1100, 1008, 909, 837, 776, 690, 662, 611, 526 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{20}Na_1O_4$ $[M+Na]^+$: 263.1254. found: 263.1256. ^{1}H and ^{13}C NMR spectra have been attached.

Synthesis of 1-(1-ethoxyethyl)-2,4,6-trimethylbenzene (3ia)



Compound **3ia** was prepared according to the general procedure using **1i** (83.0 mg, 0.51 mmol), and $(EtO)_2MeSiH$ (269.2 mg, 2.0 mmol) in ethanol (**2a**, 2.5 mL) at 85 ºC for 24 h. Product **3ia** was obtained in 94% yield (91.2 mg, 0.47 mmol) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, *J* = 6.8 Hz, 3H), 1.47 (d, *J* = 6.8 Hz, 3H), 2.25 (s, 3H), 2.37 (s, 6H), 3.25–3.31 (m, 2H), 4.90 (q, *J* = 6.8 Hz, 1H), 6.81 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 20.3, 20.5, 20.7, 63.5, 74.2, 129.9, 135.6, 136.0, 136.1 ppm. IR (Diamond-ATR, neat) 2972, 2928, 2868, 1735, 1611, 1447, 1368, 1211, 1100, 850, 720, 582 cm^{-1}; HRMS (ESI): calcd for $C_{13}H_{20}Na_1O_1$ $[M+Na]^+$: 215.1406. found: 215.1398. ^{1}H and ^{13}C NMR spectra have been attached.

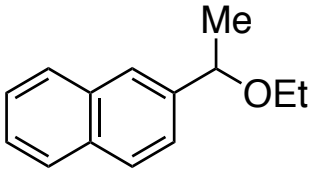
Synthesis of 1-(1-ethoxyethyl)-naphthalene (3ja)



Compound **3ja** was prepared according to the general procedure using **1j** (86.7 mg, 0.50 mmol), and $(EtO)_2MeSiH$ (269.8 mg, 0.20 mmol) in ethanol (**2a**, 2.5 mL) at 85 ºC for 24 h. Product **3ja** was obtained in 71% yield (72.1 mg, 0.36 mmol) as a colorless oil.

^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, J = 7.2 Hz, 3H), 1.61 (t, J = 6.8 Hz, 3H), 3.44 (q, J = 7.2 Hz, 2H), 5.16 (t, J = 6.4 Hz, 2H), 7.45–7.53 (m, 3H), 7.57–7.59 (m, 1H), 7.76–7.78 (m, 1H), 7.86–7.89 (m, 1H), 8.18–8.20 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.5, 23.6, 64.1, 75.4, 123.2, 123.3, 125.4, 125.5, 125.7, 127.6, 128.8, 130.8, 133.9, 139.7 ppm. IR (Diamond-ATR, neat) 3048, 2973, 2928, 2867, 1596, 1509, 1442, 1369, 1174, 1107, 1080, 798, 775, 625, 615, 474, 417 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{16}Na_1O_1$ $[M+Na]^+$: 223.1093. found: 223.1094. ^1H and ^{13}C NMR spectra have been attached.

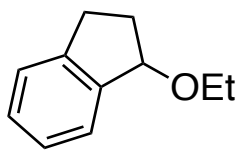
Synthesis of 2-(1-ethoxyethyl)-naphthalene (3ka)



Compound **3ka** was prepared according to the general procedure using **1k** (86.8mg, 0.50 mmol), and $(EtO)_2MeSiH$ (269.1 mg, 2.0 mmol) in ethanol (**2a**, 2.5 mL) at 85 ºC for 24 h. Product **3ka** was obtained in 80% yield (80.3 mg, 0.40 mmol) as a colorless oil.

^1H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, J = 6.8 Hz, 3H), 1.52 (d, J = 6.8 Hz, 3H), 3.34–3.44 (m, 2H), 4.57 (q, J = 6.4 Hz, 1H), 7.43–7.50 (m, 3H), 7.73 (s, 1H), 7.81–7.85 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 24.2, 64.0, 77.9, 124.2, 124.9, 125.6, 126.0, 127.7, 127.8, 128.3, 133.0, 133.3, 141.6 ppm. IR (Diamond-ATR, neat) 3055, 2972, 2927, 2865, 1738, 1508, 1455, 1441, 1369, 1309, 1217, 1097, 856, 819, 745, 478 cm^{-1}; HRMS (ESI): calcd for $C_{14}H_{16}Na_1O_1$ $[M+Na]^+$: 223.1093. found: 223.1093. ^1H and ^{13}C NMR spectra have been attached.

Synthesis of 1-ethoxy-2,3-dihydro-*1H*-indene (3la)

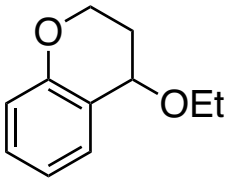


Compound **3la** was prepared according to the general procedure using **1l** (68.1 mg, 0.51 mmol), and $(EtO)_2MeSiH$ (268.9 mg, 2.00 mmol) in ethanol (**2a**, 2.5 mL) at 85 ºC for 24 h.

Product **3la** was obtained in 77% yield (63.8 mg, 0.39 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.2 Hz, 3H), 2.03–2.11 (m, 1H), 2.31–2.39 (m, 1H), 2.77–2.84 (m, 1H), 3.04–3.12 (m, 1H), 3.58–3.64 (m, 2H), 4.92 (dd, *J* = 6.8 and 4.4 Hz, 1H), 7.18–7.26 (m, 3H), 7.39–7.40 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 30.2, 32.5, 63.9, 83.0, 124.8, 125.0, 126.2, 128.2, 143.0, 143.9 ppm. IR (Diamond-ATR, neat) 3070, 3025, 2972, 2929, 2866, 1478, 1459, 1335, 1112, 1080, 1019, 970, 744, 601 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{14}Na_1O_1$ $[M+Na]^+$: 185.0937. found: 186.0932. ^{1}H and ^{13}C NMR spectra have been attached.

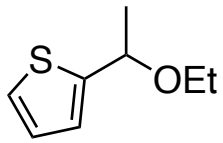
Synthesis of 4-ethoxy-3,4-dihydro-2H-1-benzopyran (3ma)



Compound **3ma** was prepared according to the general procedure using **1m** (75.9 mg, 0.51 mmol), and $(EtO)_2MeSiH$ (268.8 mg, 2.0 mmol) in ethanol (**2a**, 2.5 mL) at 85 ºC for 24 h. Product **3ma** was obtained in 93% yield (84.2 mg, 0.47 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.2 Hz, 3H), 2.00–2.16 (m, 2H), 3.57–3.70 (m, 2H), 4.22–4.34 (m, 2H), 4.37–4.39 (m, 1H), 6.82–6.84 (m, 1H), 6.87–6.91 (m, 1H), 7.17–7.21 (m, 1H), 7.24–7.26 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.6, 27.7, 62.2, 63.5, 70.1, 116.9, 119.9, 122.1, 129.5, 130.5, 154.8 ppm. IR (Diamond-ATR, neat) 2972, 2927, 2869, 1609, 1583, 1488, 1454, 1268, 1253, 1223, 1091, 1073, 1061, 1015, 752, 601 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{14}Na_1O_2$ $[M+Na]^+$: 201.0886. found: 201.0885. ^{1}H and ^{13}C NMR spectra have been attached.

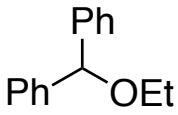
Synthesis of 2-(1-ethoxyethyl)-thiophene (3na)



Compound **3na** was prepared according to the general procedure using **1n** (64.6 mg, 0.50 mmol), and $(EtO)_2MeSiH$ (270.3 mg, 2.0 mmol) in ethanol (**2a**, 2.5 mL) at 85 ºC for 24 h. Product **3na** was obtained in 65% yield (51.5 mg, 0.33 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, *J* = 6.8 Hz, 3H), 1.55 (d, *J* = 6.4 Hz, 3H), 3.39–3.48 (m, 2H), 4.69 (q, *J* = 6.8 Hz, 1H), 6.95–6.97 (m, 2H), 7.24–7.25 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 24.3, 63.8, 73.1, 124.1, 124.4, 126.3, 148.2 ppm. IR (Diamond-ATR, neat) 2975, 2929, 2867, 2161, 1443, 1370, 1310, 1260, 1077, 906, 853, 804, 755, 696 cm^{-1}; HRMS (ESI): calcd for $C_8H_{12}Na_1O_1S_1$ $[M+Na]^+$: 179.0501. found: 179.0502. ^{1}H and ^{13}C NMR spectra have been attached.

Synthesis of (ethoxymethylene)dibenzene (3oa)



Compound **3oa** was prepared according to the general procedure using **1o** (92.4 mg, 0.50 mmol), and $(EtO)_2MeSiH$ (269.8 mg, 2.0 mmol) in ethanol (**2a**, 2.5 mL) at 85 ºC for 24 h. Product **3oa** was obtained in 82% yield (87.1 mg, 0.41 mmol) as a colorless oil.

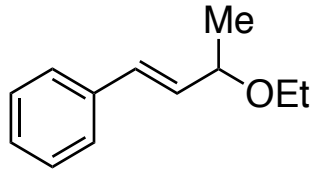
^1H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, *J* = 7.2 Hz, 3H), 3.52 (q, *J* = 7.2 Hz, 2H), 5.36 (s, 1H), 7.21–7.26 (m, 2H), 7.29–7.37 (m, 8H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 64.5, 83.5, 126.9, 127.3, 128.3, 142.5 ppm. ^1H and ^{13}C NMR spectra have been attached. The product was characterized by comparison with previously reported ^1H and ^{13}C NMR data.[4]

Synthesis of {4-[1-(Ethoxy)ethyl]phenyl}methanol (3sa)

Compound **3sa** was prepared according to the general procedure using **1s** (77.8 mg, 0.51 mmol), and $(EtO)_2MeSiH$ (269.2 mg, 2.0 mmol) in ethanol (**2a**, 2.5 mL) at 85 ºC for 24 h. Product **3sa** was obtained in 74% yield (68.2 mg, 0.38 mmol) as a colorless oil.

^1H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, *J* = 6.4 Hz, 3H), 1.43 (d, *J* = 6.4 Hz, 3H), 1.65 (br, 1H), 3.35 (q, *J* = 6.8 Hz, 2H), 4.41 (q, *J* = 6.4 Hz, 1H), 4.69 (d, *J* = 5.6 Hz, 2H), 7.31–7.37 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 24.2, 63.9, 65.1, 77.5, 126.3, 127.1, 139.9, 143.7 ppm. IR (Diamond-ATR, neat) 3376, 2974, 2928, 2867, 1444, 1420, 1397, 1369, 1211, 1095, 1064, 1007, 939, 845, 817, 719, 607, 554 cm^{-1}; HRMS (ESI): calcd for $C_{11}H_{16}Na_1O_2$ $[M+Na]^+$: 203.1043. found: 203.1043. ^1H and ^{13}C NMR spectra have been attached.

Synthesis of [(*1E*)-3-ethoxybut-1-en-1-yl]benzene (3ta)

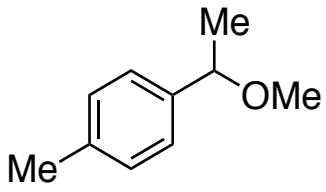


Compound **3ta** was prepared according to the general procedure using **1t** (75.3 mg, 0.51 mmol), and $(EtO)_2MeSiH$ (268.8 mg, 2.0 mmol) in ethanol (**2a**, 2.5 mL) at 85 ºC for 24 h. Product **3ta** was obtained in 90% yield (80.6 mg, 0.46 mmol) as a colorless oil.

^1H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, *J* = 6.8 Hz, 3H), 1.34 (d, *J* = 6.4 Hz, 3H), 3.38–3.45 (m, 1H), 3.53–3.61 (m, 1H), 3.97–4.04 (m, 1H), 6.12 (dd, *J* = 16.0 and 7.6 Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 7.22–7.26 (m, 1H), 7.30–7.34 (s, 2H), 7.38–7.41 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 21.8, 63.6, 76.3, 126.4, 127.5, 128.5, 130.8, 132.1, 136.7 ppm. ^1H and ^{13}C NMR spectra have been attached. The product was characterized by comparison with previously reported ^1H and ^{13}C NMR data.[6]

Compound **3ta** was prepared according to the general procedure using **1u** (74.6 mg, 0.50 mmol), and $(EtO)_2MeSiH$ (268.7 mg, 2.0 mmol) in ethanol (**2a**, 2.5 mL) at 85 ºC for 24 h. Product **3ta** was obtained in 96% yield (84.2 mg, 0.48 mmol) as a colorless oil.

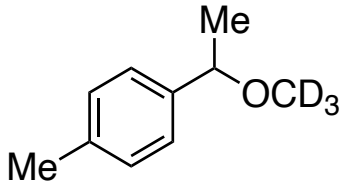
Synthesis of 1-(1-methoxyethyl)-4-methylbenzene (3ab)



Compound **3ab** was prepared according to the general procedure using **1a** (68.0 mg, 0.50 mmol), and $(EtO)_2MeSiH$ (269.4 mg, 2.0 mmol) in methanol (**2b**, 2.5 mL) at 85 ºC for 24 h. Product **3ab** was obtained in 78% yield (58.5 mg, 0.39 mmol) as a colorless oil.

^1H NMR (400 MHz, $CDCl_3$) δ 1.42 (d, J = 6.4 Hz, 3H), 2.35 (s, 3H), 3.21 (s, 3H), 4.26 (q, J = 6.4 Hz, 1H), 7.15–7.17 (m, 2H), 7.19–7.21 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 23.9, 56.3, 79.4, 126.1, 129.1, 137.1, 140.4 ppm. IR (Diamond-ATR, neat) 2976, 2927, 2819, 1738, 1514, 1448, 1370, 1219, 1210, 1106, 1085, 865, 816, 554 cm^{-1}; HRMS (APCI): calcd for $C_{10}H_{15}O$ $[M+Na]^+$: 151.1117. found: 151.1117. ^1H and ^{13}C NMR spectra have been attached.

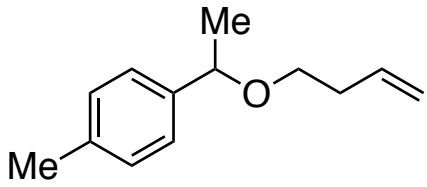
Synthesis of 1-(1-methoxyethyl)-4-methylbenzene-d_3 (3ab')



Compound **3ab** was prepared according to the general procedure using **1a** (69.3 mg, 0.51 mmol), and $(EtO)_2MeSiH$ (269.0 mg, 2.0 mmol) in methanol-d_4 (**2b'**, 2.5 mL) at 85 ºC for 24 h. Product **3ab'** was obtained in 77% yield (60.1 mg, 0.39 mmol) as a colorless oil.

^1H NMR (400 MHz, $CDCl_3$) δ 1.42 (d, J = 6.4 Hz, 3H), 2.35 (s, 3H), 4.26 (q, J = 6.4 Hz, 1H), 7.15–7.17 (m, 2H), 7.19–7.21 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 23.9, 55.4 (quin, J = 22.1 Hz), 79.3, 126.1, 129.1, 137.0, 140.4 ppm. IR (Diamond-ATR, neat) 2975, 2927, 2861, 2234, 2192, 2057, 1514, 1452, 1370, 1302, 1279, 1205, 1120, 1103, 1039, 816, 722, 548 cm^{-1}; HRMS (ESI): calcd for $C_{10}H_{11}D_3Na_1O_1$ $[M+Na]^+$: 176.1125. found: 176.1120. ^1H and ^{13}C NMR spectra have been attached.

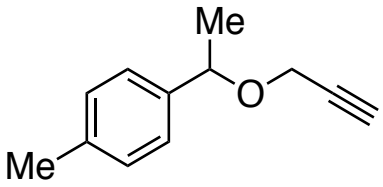
Synthesis of 1-[(But-3-en-1-yloxy)ethyl]-4-methylbenzene (3ac)



Compound **3ac** was prepared according to the general procedure using **1a** (68.5 mg, 0.50 mmol), and $(EtO)_2MeSiH$ (268.9 mg, 2.0 mmol) in 3-buten-1-ol (**2c**, 2.5 mL) at 85 ºC for 24 h. Product **3ac** was obtained in 92% yield (88.1 mg, 0.46 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (d, *J* = 6.4 Hz, 3H), 2.29–2.34 (m, 5H), 3.29–3.38 (m, 2H), 4.37 (q, *J* = 6.4 Hz, 1H), 4.99–5.08 (m, 2H), 5.74–5.85 (m, 1H), 7.14–7.16 (m, 2H), 7.19–7.22 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 24.2, 34.3, 67.8, 77.8, 116.1, 126.1, 129.0, 135.3, 136.9, 141.0 ppm. IR (Diamond-ATR, neat) 2976, 2927, 2858, 1738, 1642, 1514, 1443, 1368, 1204, 1097, 995, 911, 816, 722, 640, 552 cm^{-1}; HRMS (APCI): calcd for $C_{13}H_{19}O$ $[M+H]^+$: 191.1430. found: 191.1429. ^{1}H and ^{13}C NMR spectra have been attached.

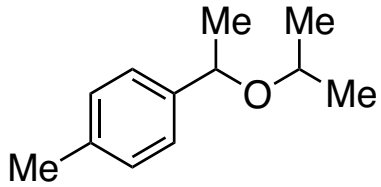
Synthesis of 1-methyl-4-[1-(prop-2-yn-1-yloxy)ethyl]benzene (3ad)



Compound **3ad** was prepared according to the general procedure using **1a** (69.1 mg, 0.51 mmol), and $(EtO)_2MeSiH$ (268.7 mg, 2.00 mmol) in 2-propyn-1-ol (**2d**, 2.5 mL) at 85 ºC for 24 h. Product **3ad** was obtained in 97% yield (85.7 mg, 0.49 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.47 (d, *J* = 6.4 Hz, 3H), 2.35 (s, 3H), 2.40 (t, *J* = 2.0 Hz, 1H), 3.86 (dd, *J* = 15.6 and 2.4 Hz, 1H), 4.07 (dd *J* = 15.6 and 2.4 Hz, 1H), 4.62 (q, *J* = 6.4 Hz, 1H), 7.15–7.18 (m, 2H), 7.21–7.23 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 23.7, 55.3, 73.9, 76.4, 80.0, 126.4, 129.2, 137.5, 139.3 ppm. ^{1}H and ^{13}C NMR spectra have been attached. The product was characterized by comparison with previously reported ^{1}H and ^{13}C NMR data.[4]

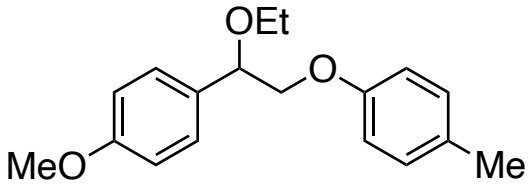
Synthesis of 1-methyl-4-[(1-methylethoxy)ethyl]benzene (3ae)



Compound **3ae** was prepared according to the general procedure using **1a** (68.5 mg, 0.50 mmol), and $(EtO)_2MeSiH$ (269.4 mg, 2.0 mmol) in 2-propanol (**2e**, 2.5 mL) at 100 ºC for 24 h. Product **3ae** was obtained in 22% yield (19.7 mg, 0.11 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (d, *J* = 6.4 Hz, 3H), 1.14 (d, *J* = 6.4 Hz, 3H), 1.39 (d, *J* = 6.4 Hz, 3H), 2.34 (s, 3H), 3.43–3.52 (m, 1H), 4.50 (q, *J* = 6.4 Hz, 1H), 7.14–7.17 (m, 2H), 7.21–7.23 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.3, 23.3, 24.8, 68.3, 74.3, 126.0, 129.0, 136.7, 141.8 ppm. IR (Diamond-ATR, neat) 2971, 2928, 2871, 1738, 1513, 1450, 1373, 1206, 1088, 1022, 971, 816, 553 cm^{-1}; HRMS (APCI): calcd for $C_{12}H_{19}O$ $[M+H]^+$: 179.1430. found:179.1430. ^{1}H and ^{13}C NMR spectra have been attached.

Synthesis of 1-[1-ethoxy-2-(4-methylphenoxy)ethyl]-4-methoxybenzene (3va)



Compound **3va** was prepared according to the general procedure using **1v** (129.3 mg, 0.50 mmol), and $(EtO)_2MeSiH$ (269.0 mg, 2.0 mmol) in ethanol (**2a**, 2.5 mL) at 85 ºC for 24 h. Product **3va** was obtained in 88% yield (125.6 mg, 0.44 mmol) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (d, *J* = 6.4 Hz, 3H), 2.27 (s, 3H), 3.45–3.50 (m, 2H), 3.82 (s, 3H), 3.94 (dd, *J* = 4.4 and 10 Hz, 1H), 4.14 (d, *J* = 8.0 and 10 Hz, 1H), 4.60–4.63 (m, 1H), 6.77–6.81 (m, 2H), 6.89–6.93 (m, 2H), 7.04–7.06 (m, 2H), 7.30–7.33 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 20.4, 55.2, 64.4, 72.5, 79.8, 113.8, 114.7, 128.1, 129.8, 130.0, 131.4, 156.7, 159.4 ppm. IR (Diamond-ATR, neat) 3031, 2973, 2926, 2868, 2836, 1611, 1508, 1454, 1301, 1292, 1238, 1173, 1099, 1033, 814, 586, 510 cm^{-1}; HRMS (ESI): calcd for $C_{18}H_{22}Na_1O_3$ $[M+Na]^+$: 309.1461. found: 309.1461. ^{1}H and ^{13}C NMR spectra have been attached.

Reference

[1] B. D. Stevens, C. J. Bungard, S. G. Nelson, *J. Org. Chem*. **2006**, *71*, 6397–6402.

[2] (a) H. Nishiyama, H. Sakaguchi, T. Nakamura, M. Horihata, K. Itoh, *Organometallics*, **1989**, *8*, 846–848. (b) H. Nishiyama, M. Kondo, T. Nakamura, K. Itoh, *Organometallics*, **1991**, *10*, 500–508.

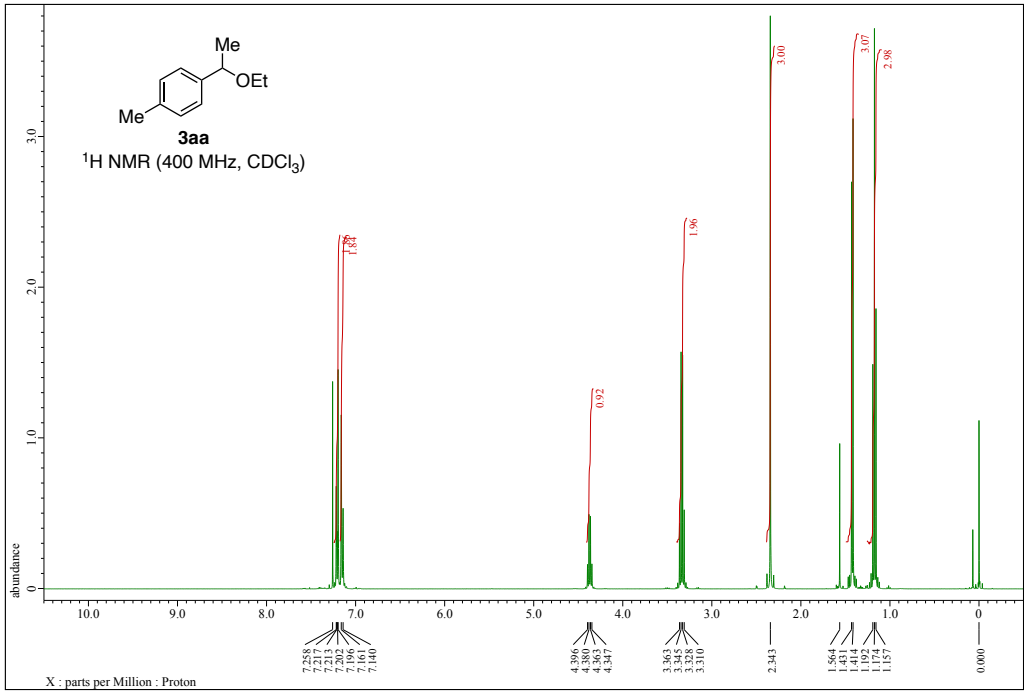
[3] K. Chen, J. Schwarz, T. A. Karl, A. Chatterjee, B. König, *Chem. Commun*. **2019**, *55*, 13144–11347.

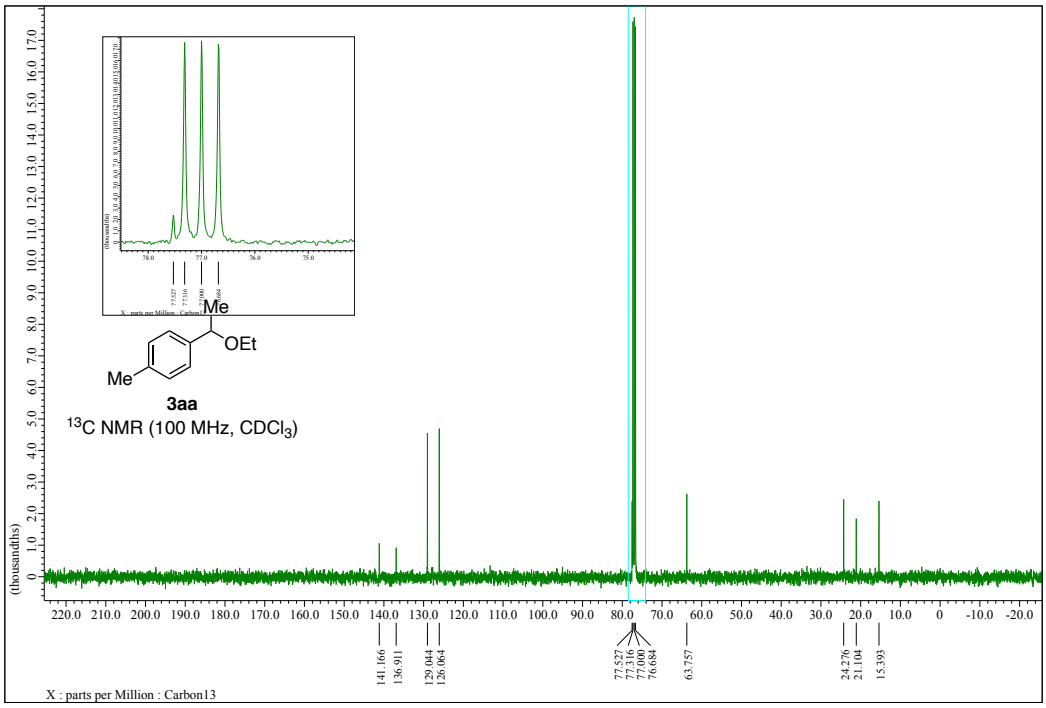
[4] L. Zhang, A. Gonzalez-de-Castro, C. Chen, F. Li, S. Xi, L. Xu, J. Xiao, *Molecular Catalysis*, **2017**, *433*, 62-67.

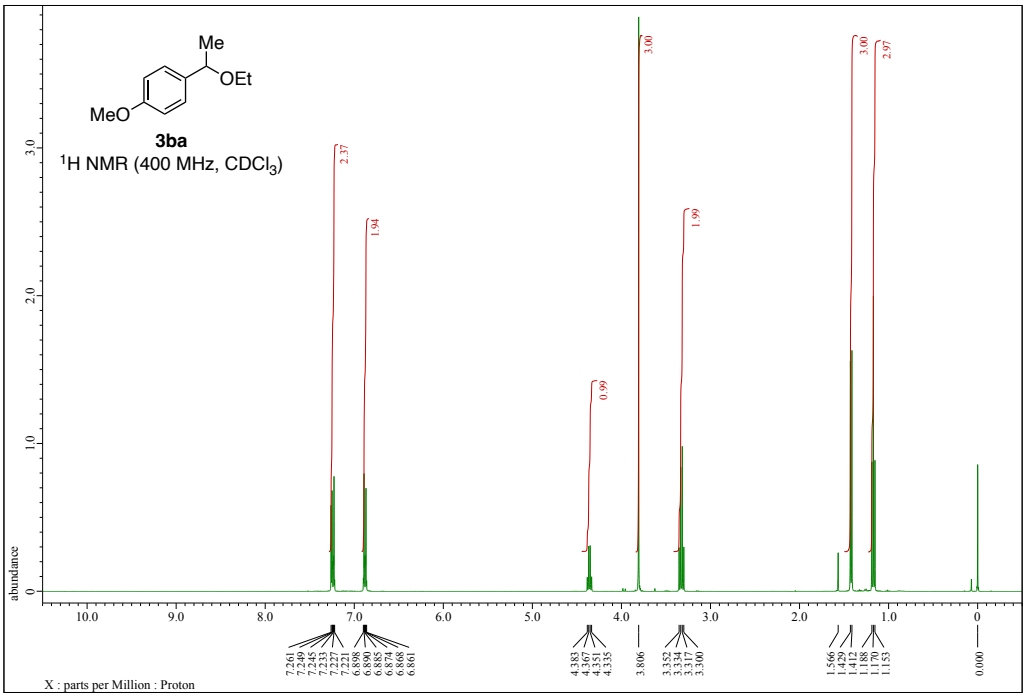
[5] J. Kim, D.-H. Lee, N. Kalutharage, C. S. Yi, *ACS Catal*. **2014**, *4*, 3881–3885.

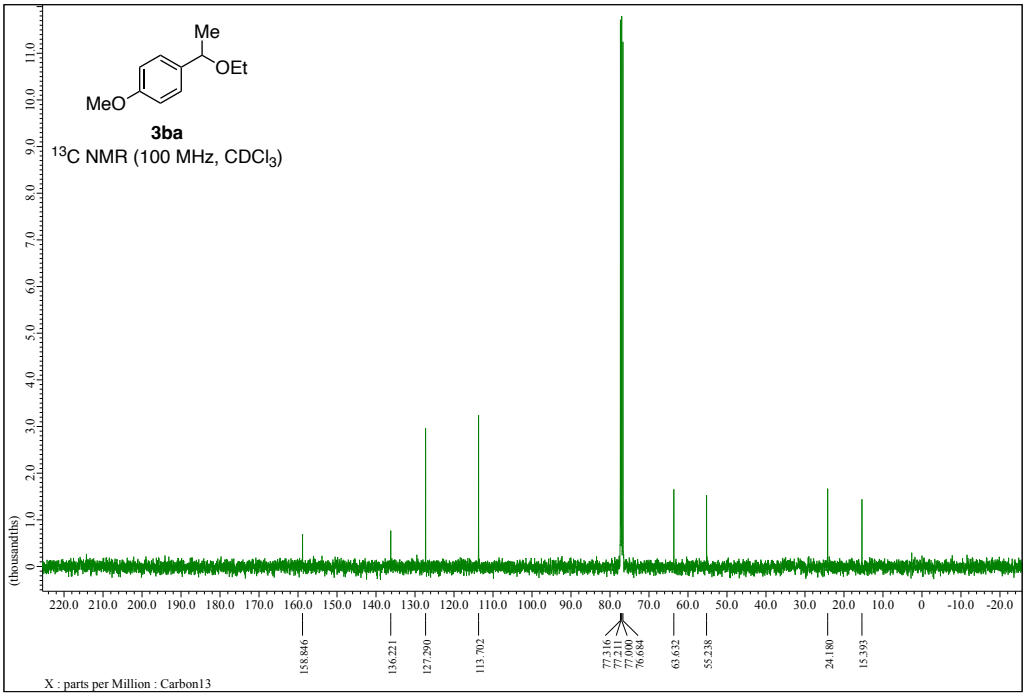
[6] L. Ouyang, Y. Xia, R. Miao, J. Liao, R. Luo, *Org. Biomol. Chem.*, **2022**, *20*, 2621–2625.

^{1}H NMR and ^{13}C NMR Spectra






Me
OEt
MeO
3ba
1H NMR (400 MHz, CDCl3)
abundance
X : parts per Million : Proton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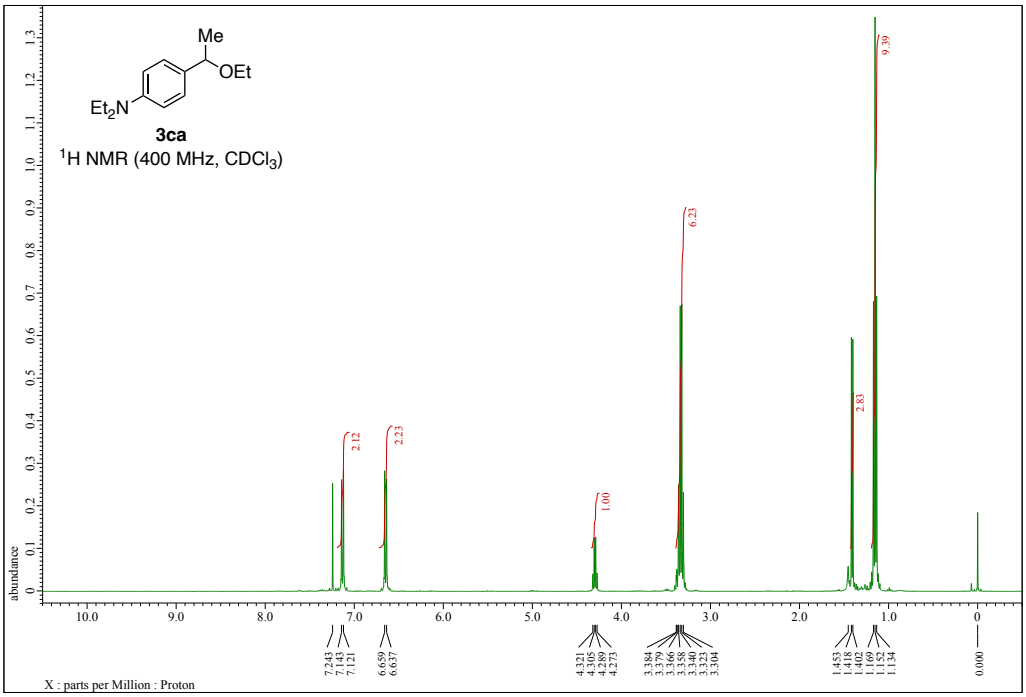
OEt
MeO
3ba
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13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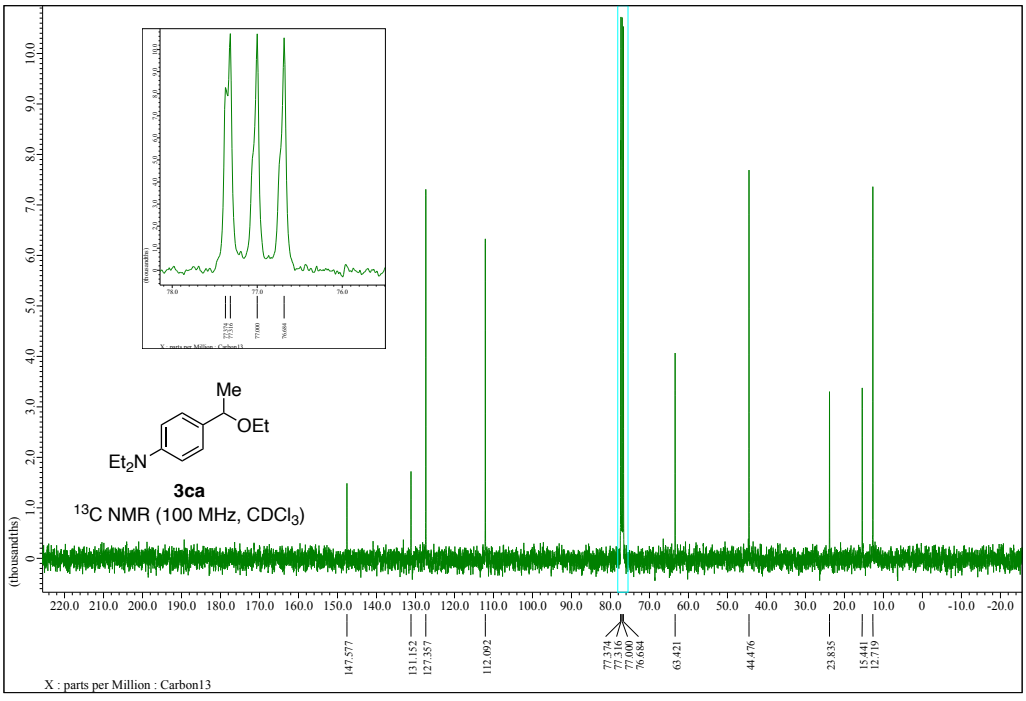
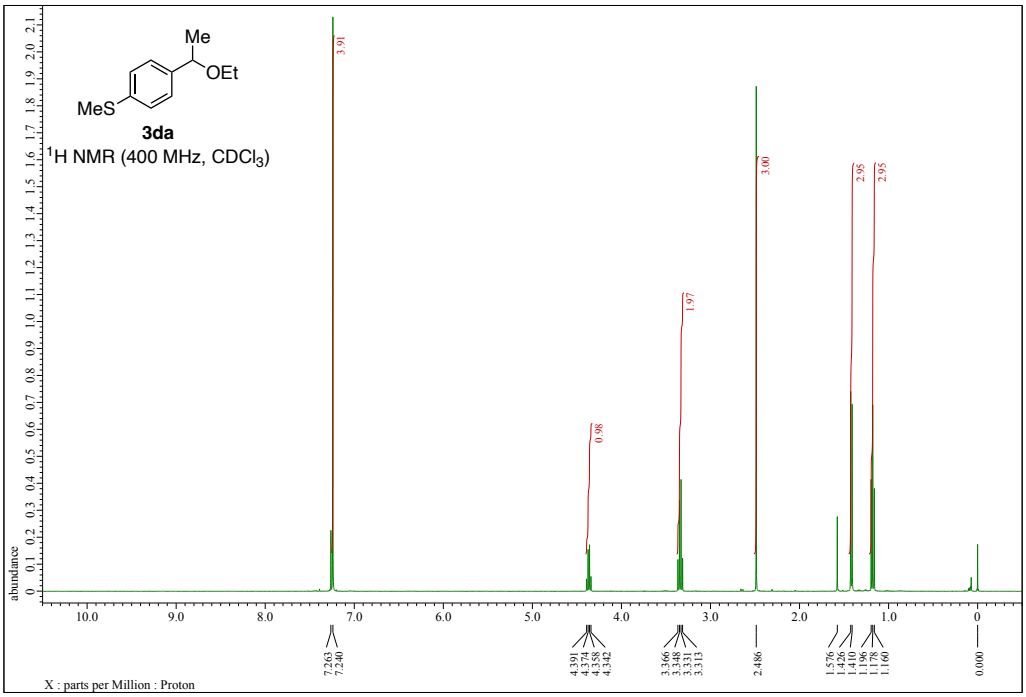
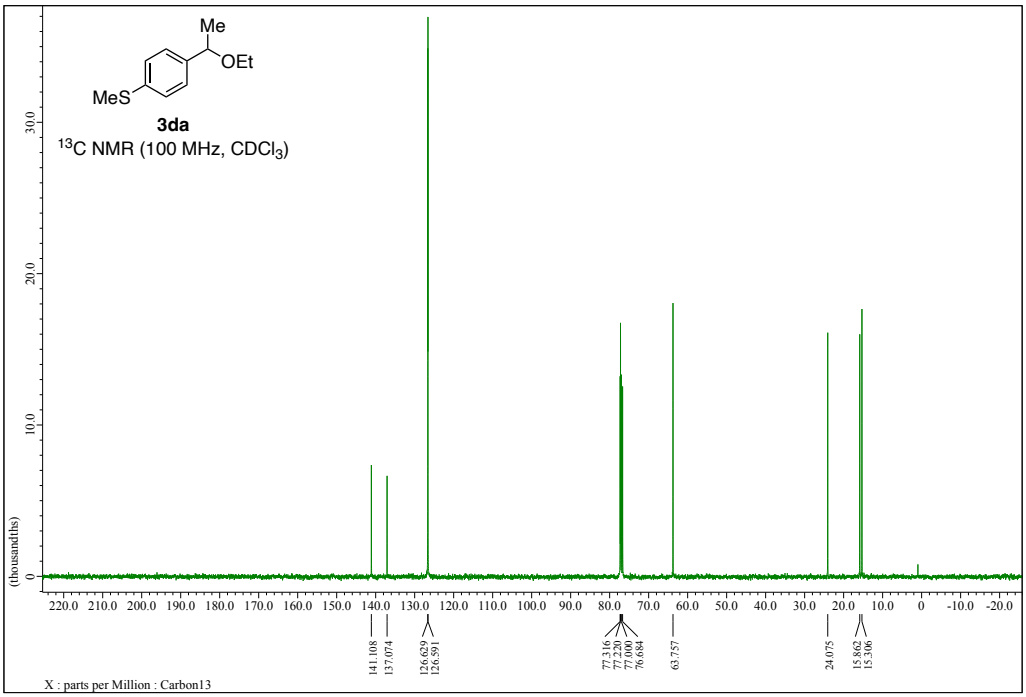
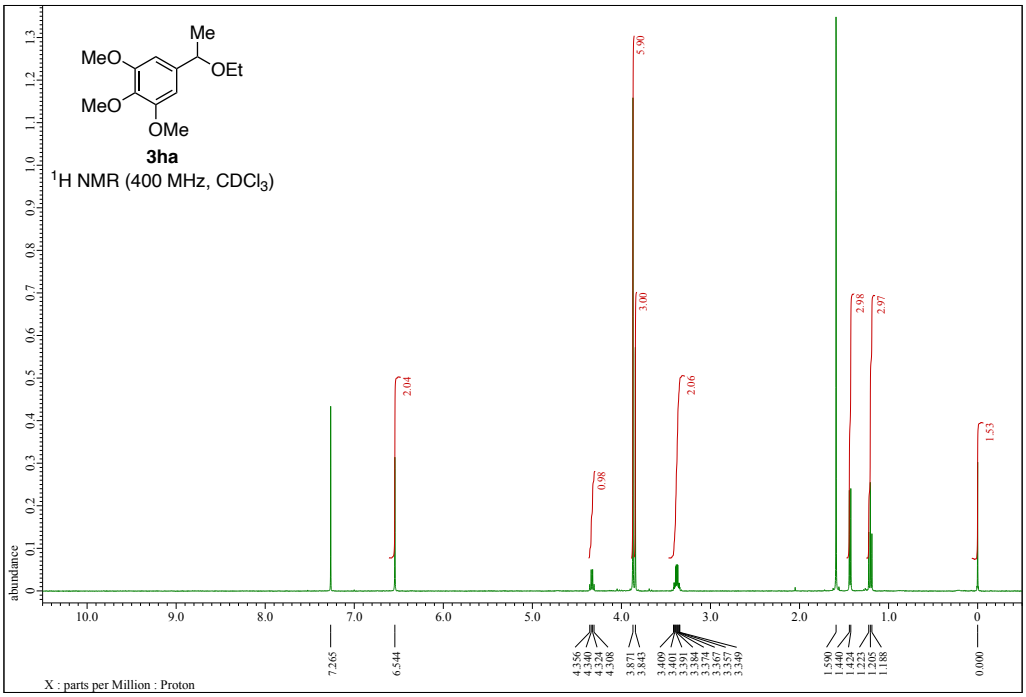
OEt
Et2N
3ca
1H NMR (400 MHz, CDCl3)
abundance
X : parts per Million : Proton


Me
OEt
Et2N
3ca
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13


Me
OEt
MeS
3da
1H NMR (400 MHz, CDCl3)
3.91
1.97
0.98
3.00
2.95
2.95
abundance
X : parts per Million : Proton


Me
OEt
MeS
3da
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13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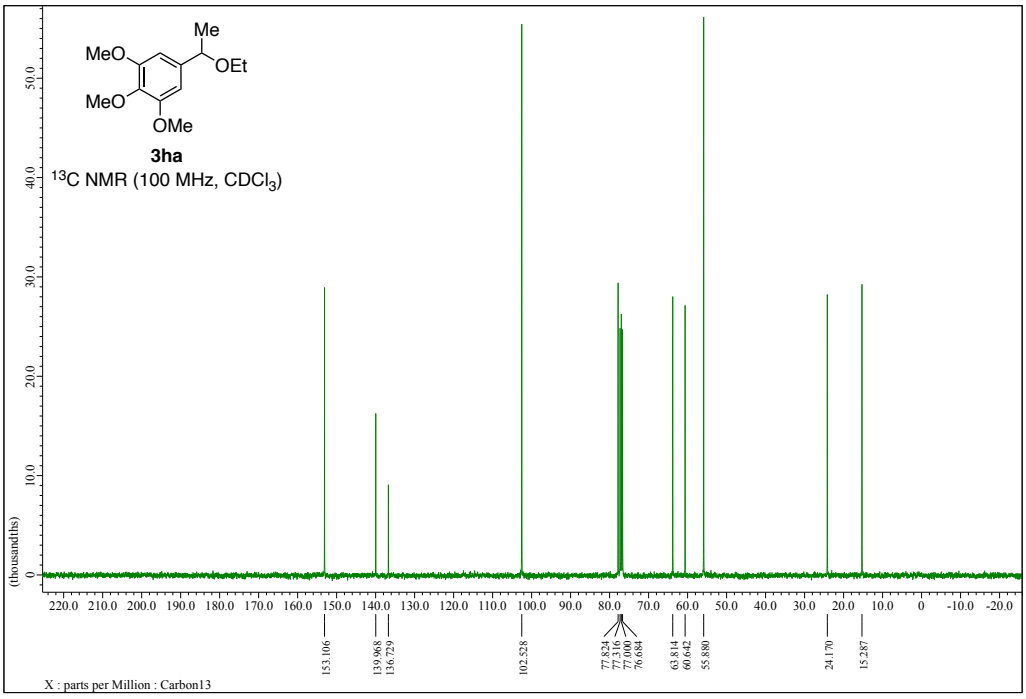
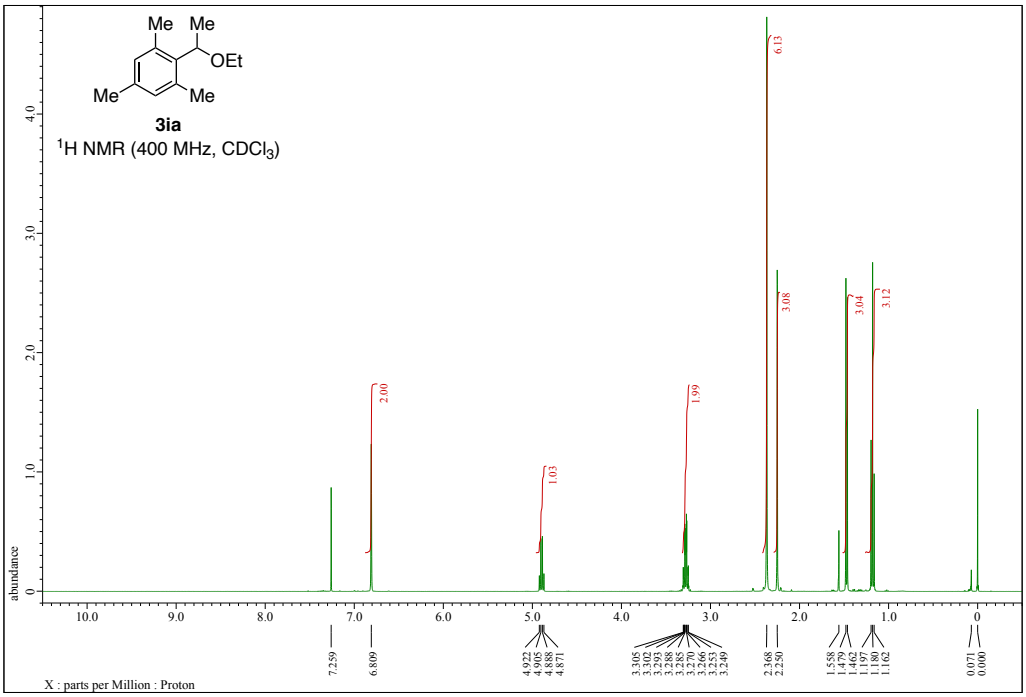
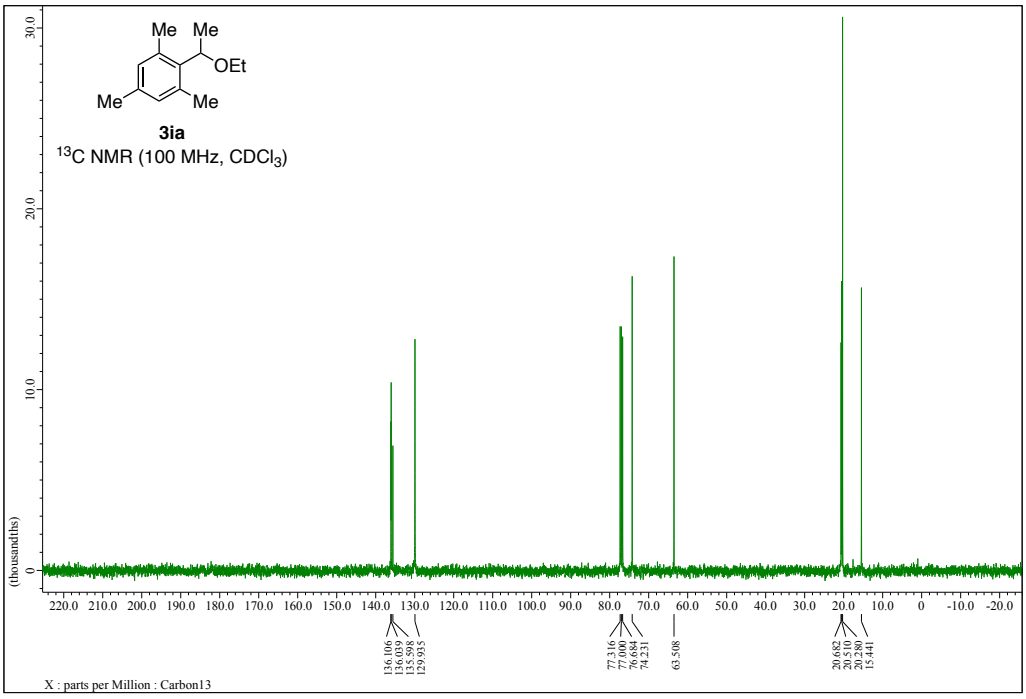
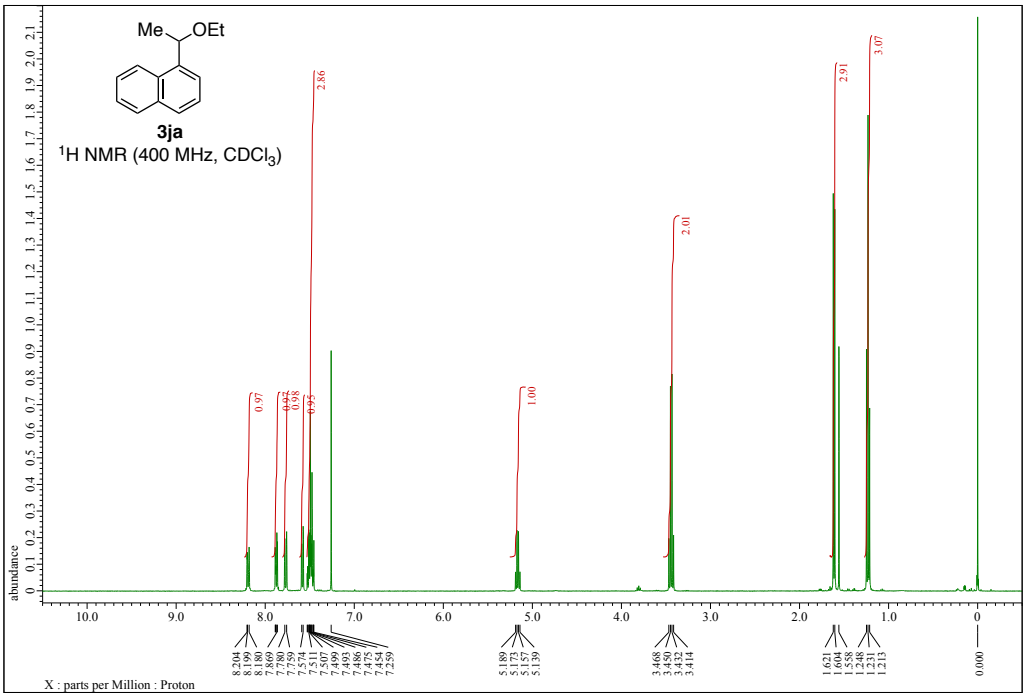
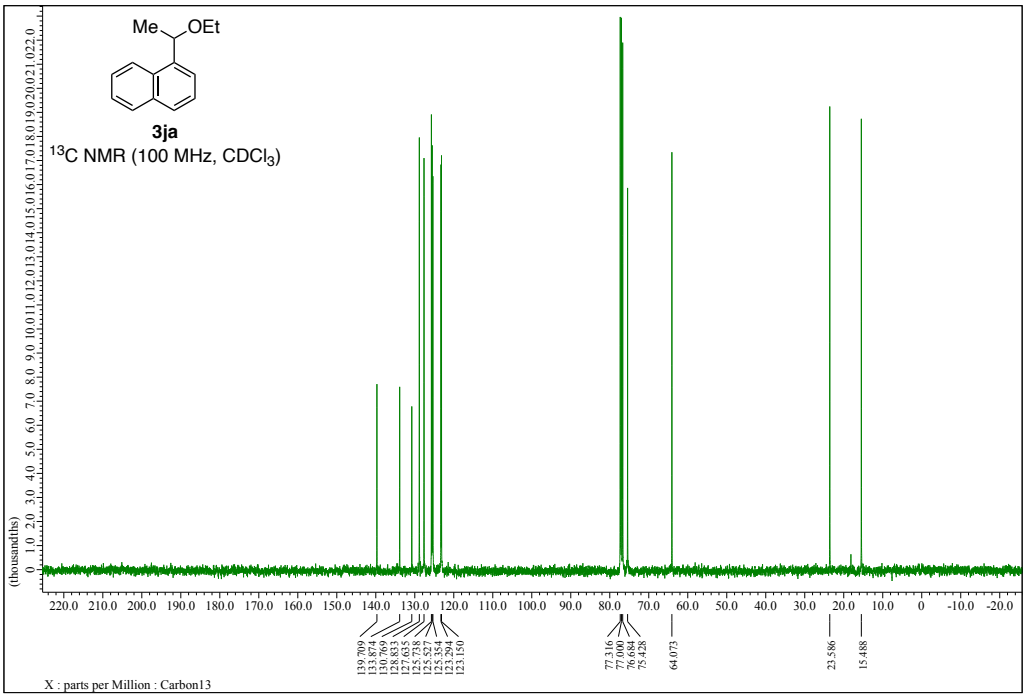
MeO
OEt
MeO
OMe
3ha
1H NMR (400 MHz, CDCl3)
abundance
X : parts per Million : Proton

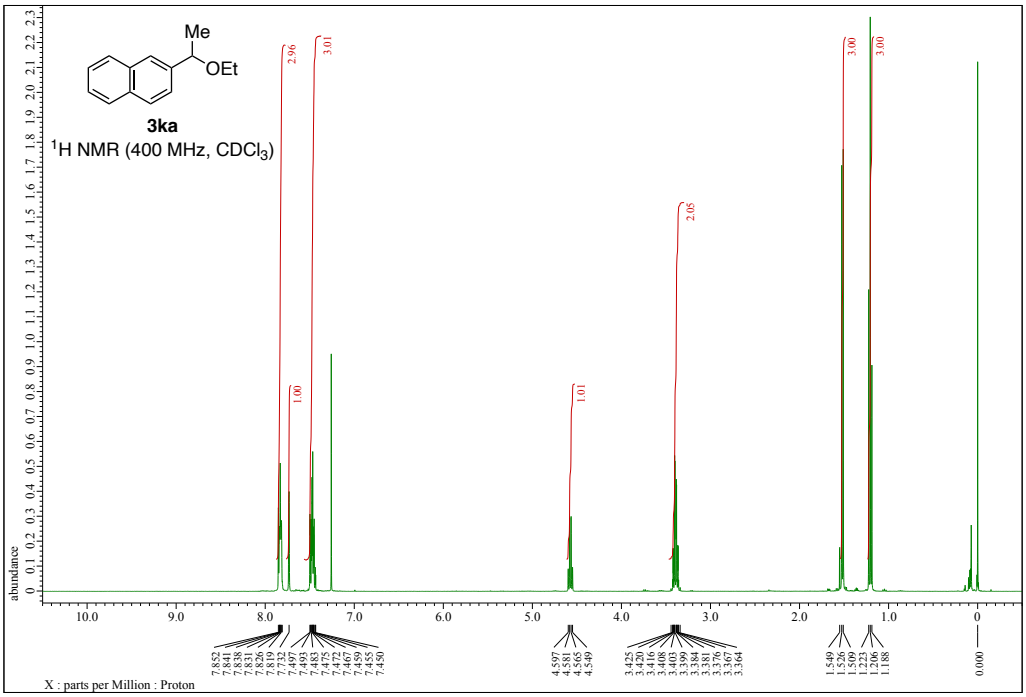

Me
MeO
OEt
MeO
OMe
3ha
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13

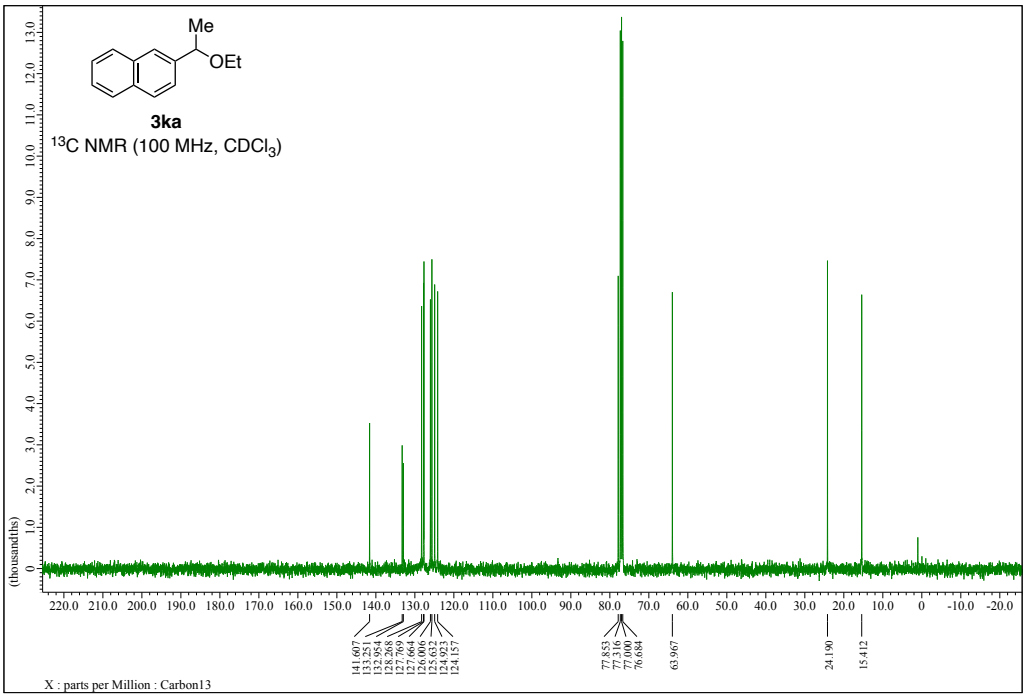

Me Me
OEt
Me
Me
3ia
1H NMR (400 MHz, CDCl3)
abundance
X : parts per Million : Proton

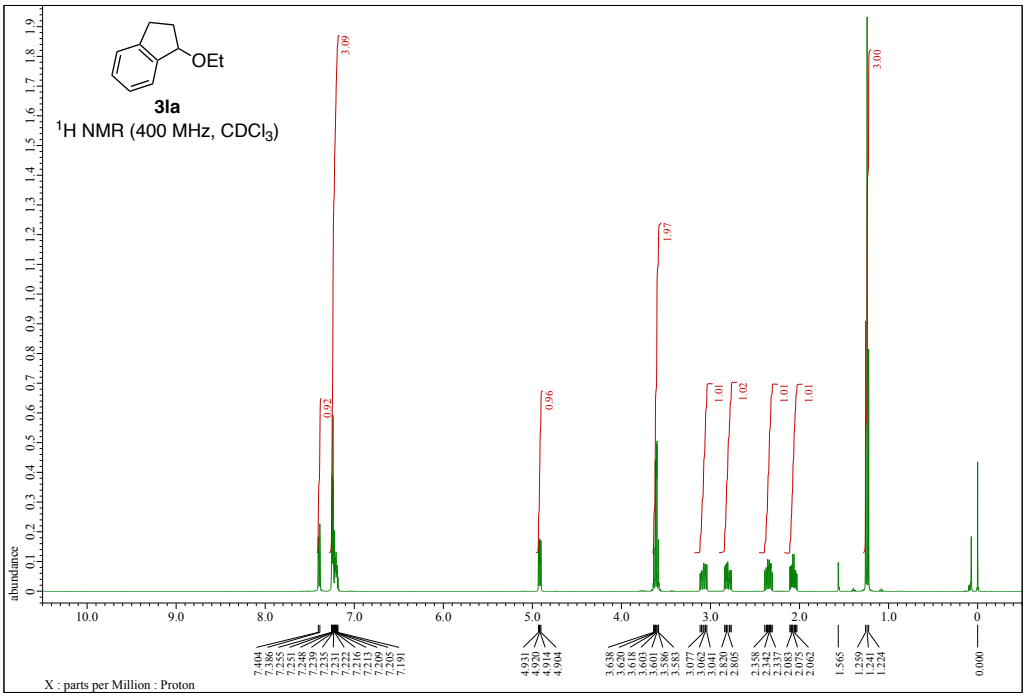

Me Me
OEt
Me
Me
3ia
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13

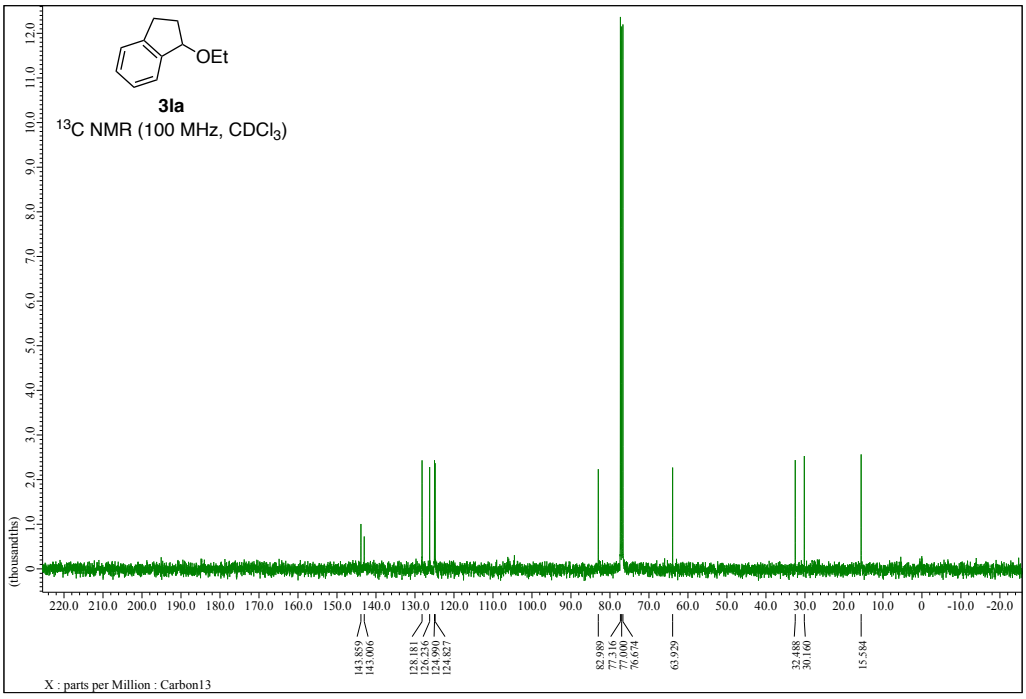

Me
OEt
3ja
1H NMR (400 MHz, CDCl3)
abundance
X : parts per Million : Proton

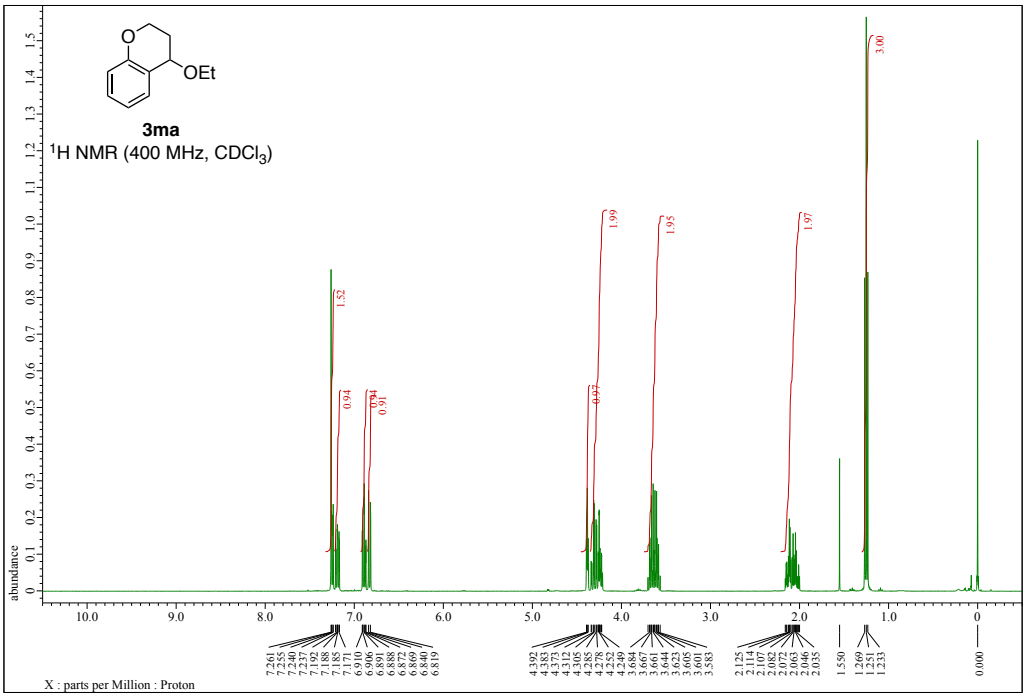

Me
OEt
3ja
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13

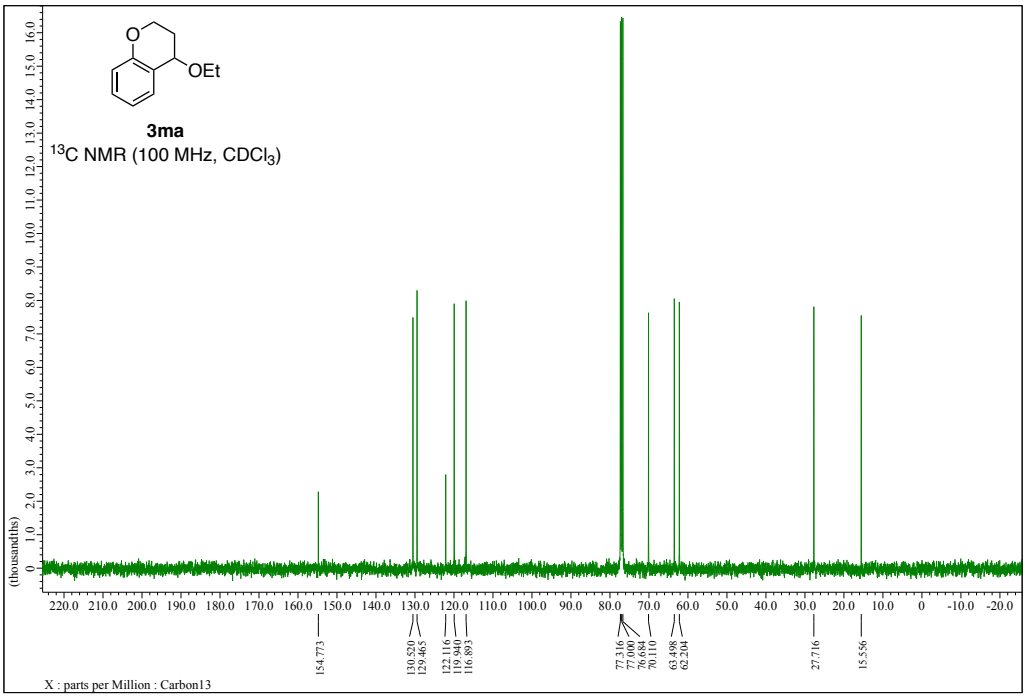

Me
OEt
3ka
1H NMR (400 MHz, CDCl3)
abundance
X : parts per Million : Proton

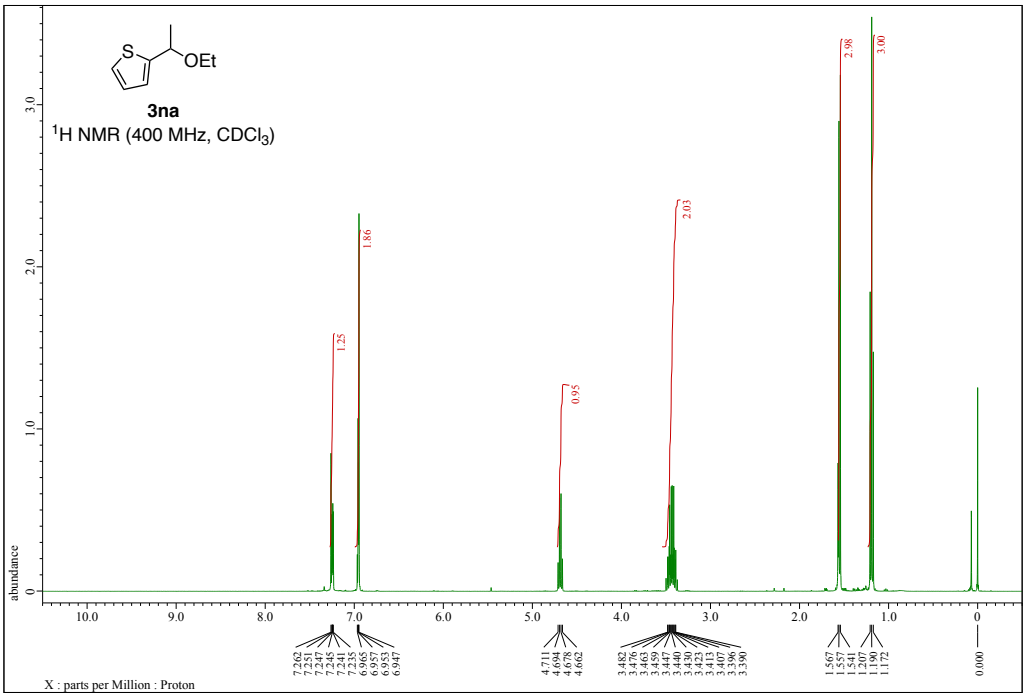

Me
OEt
3ka
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13

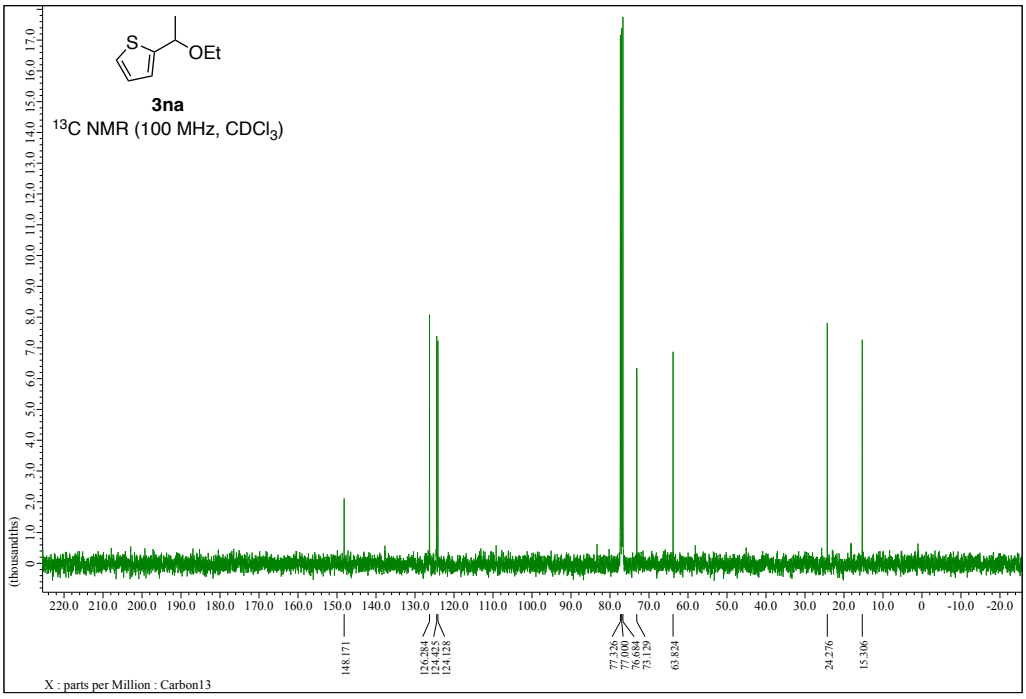

OEt
3la
1H NMR (400 MHz, CDCl3)
abundance
X : parts per Million : Proton

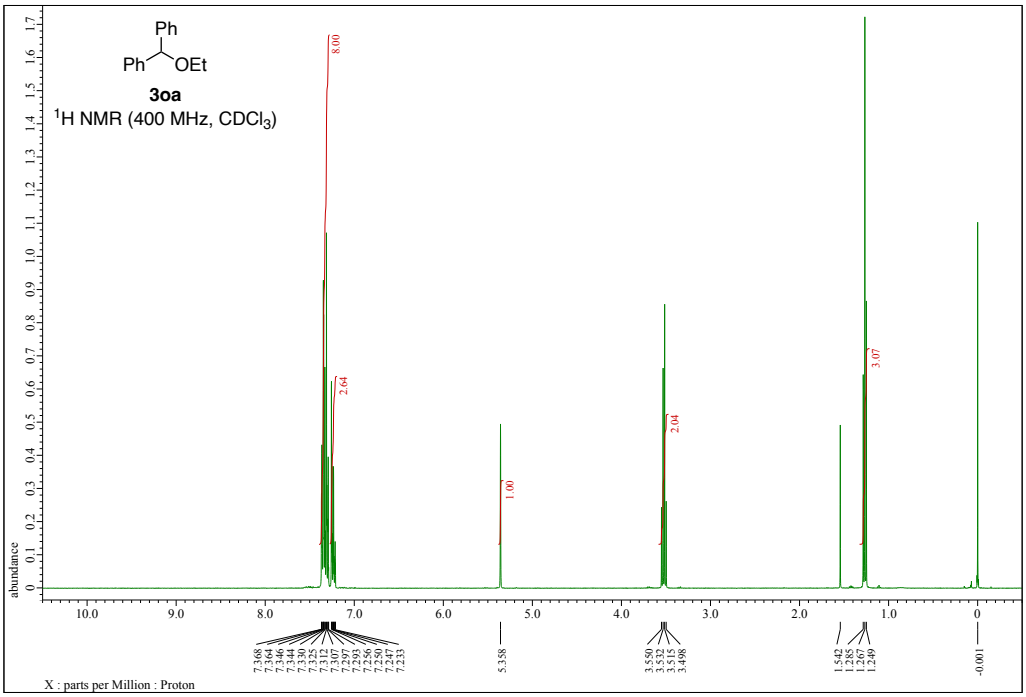

OEt
3la
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13

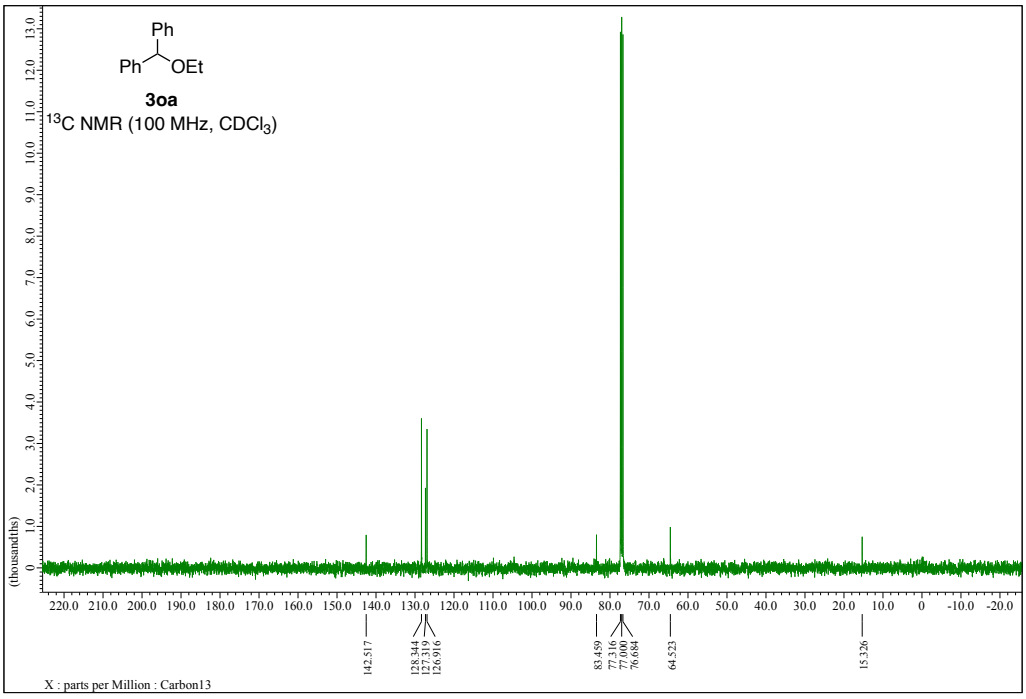

OEt
3ma
1H NMR (400 MHz, CDCl3)
abundance
X : parts per Million : Proton

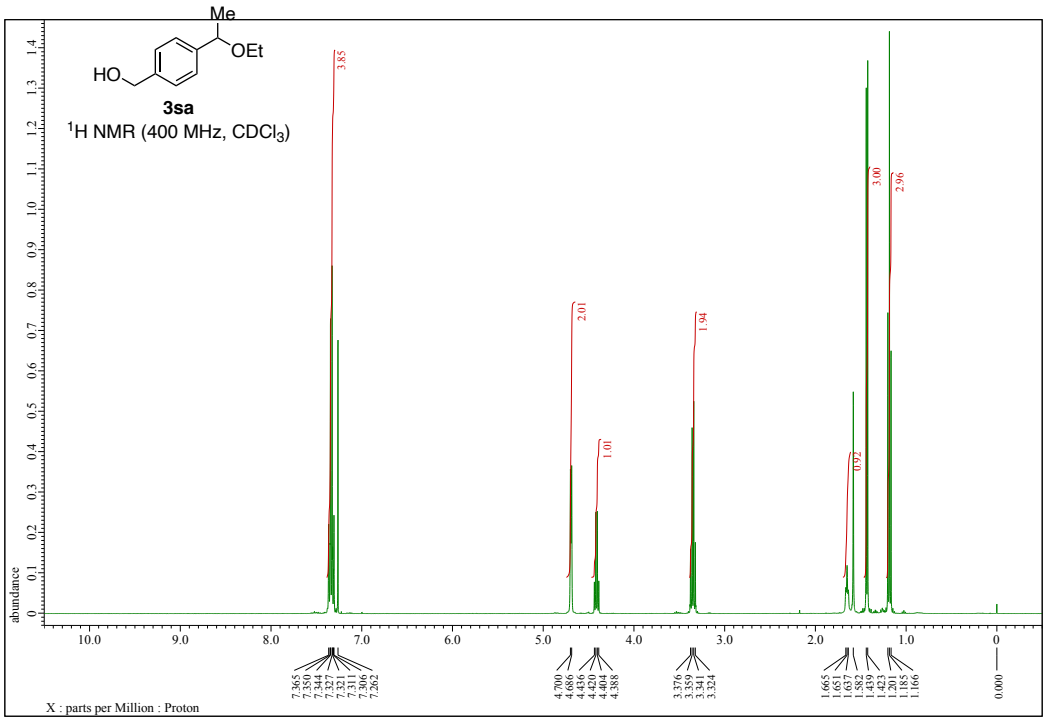

OEt
3ma
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13

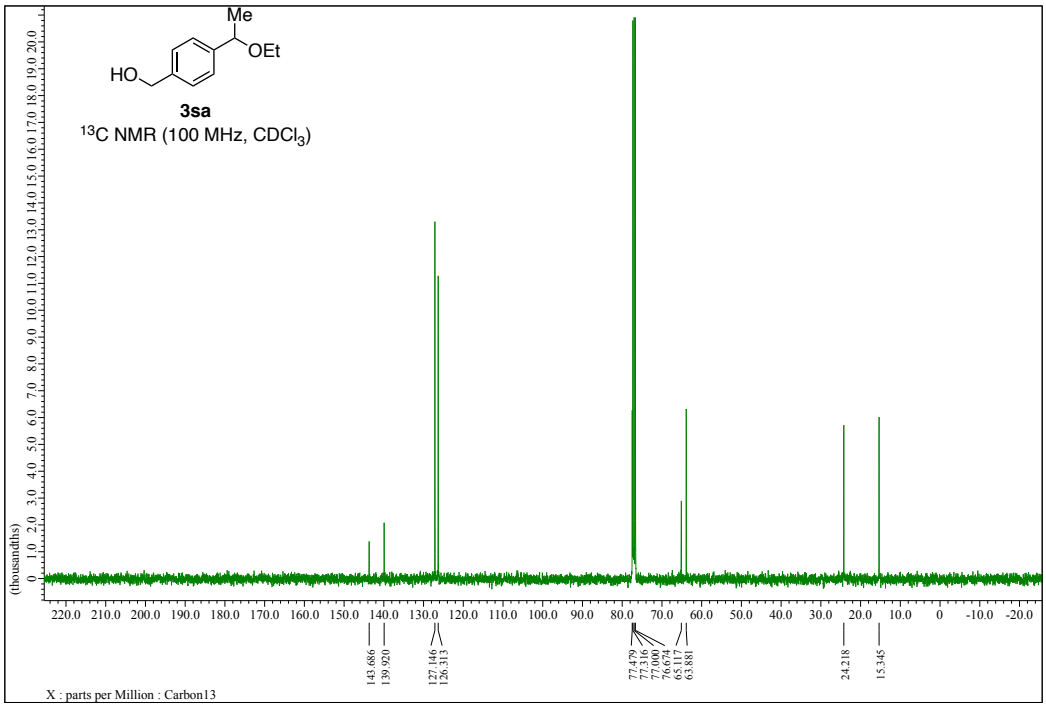

S
OEt
3na
1H NMR (400 MHz, CDCl3)
abundance
X : parts per Million : Proton

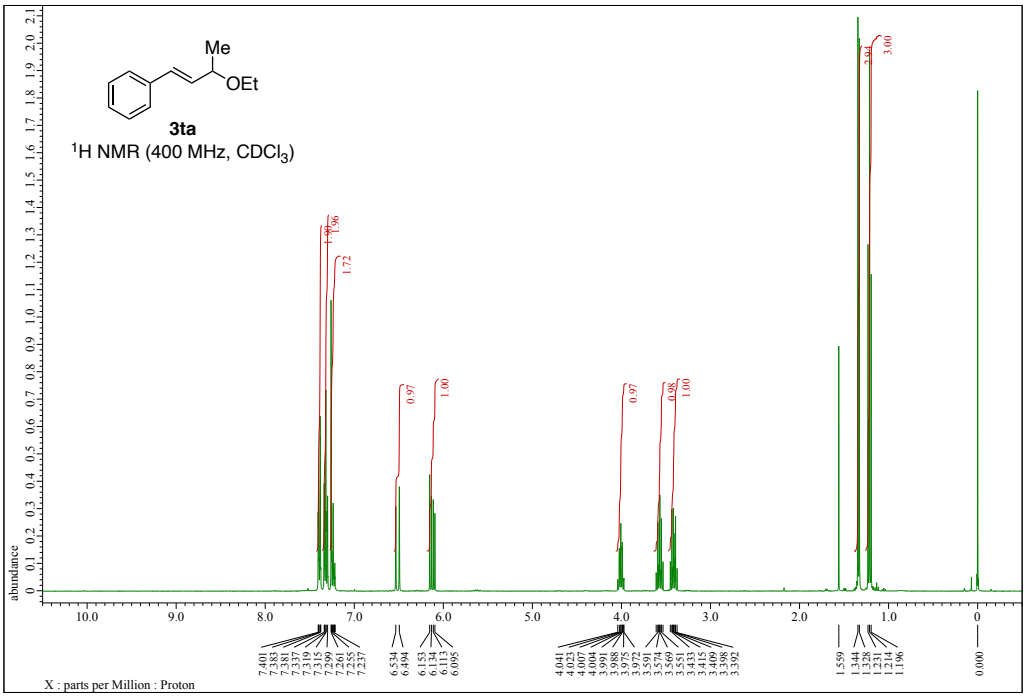

S
OEt
3na
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13

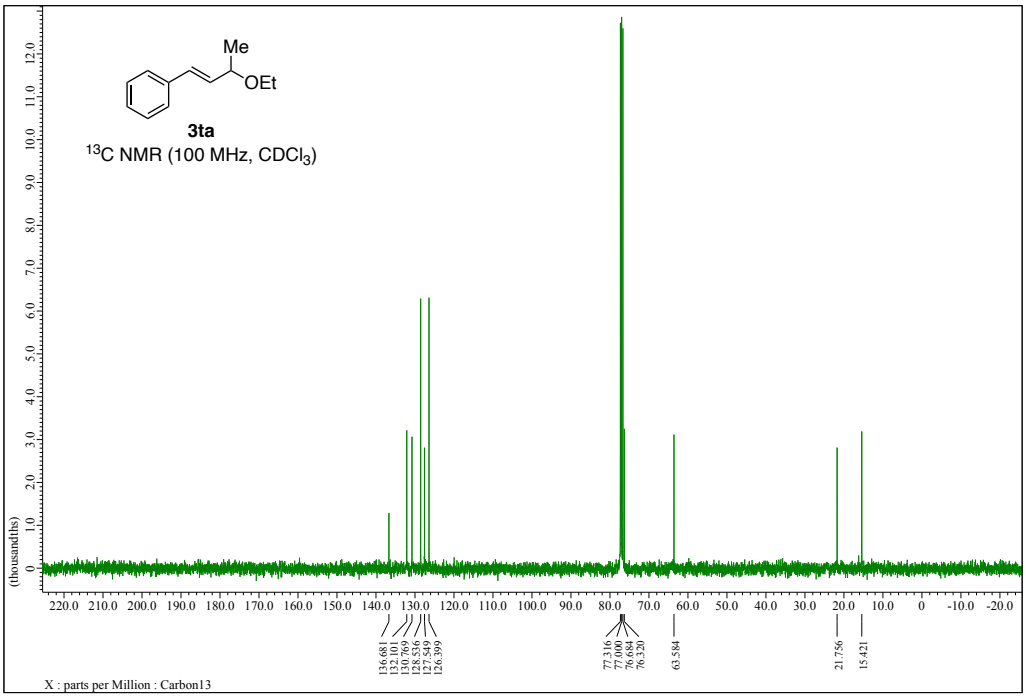

Ph
Ph
OEt
3oa
1H NMR (400 MHz, CDCl3)
abundance
X : parts per Million : Proton

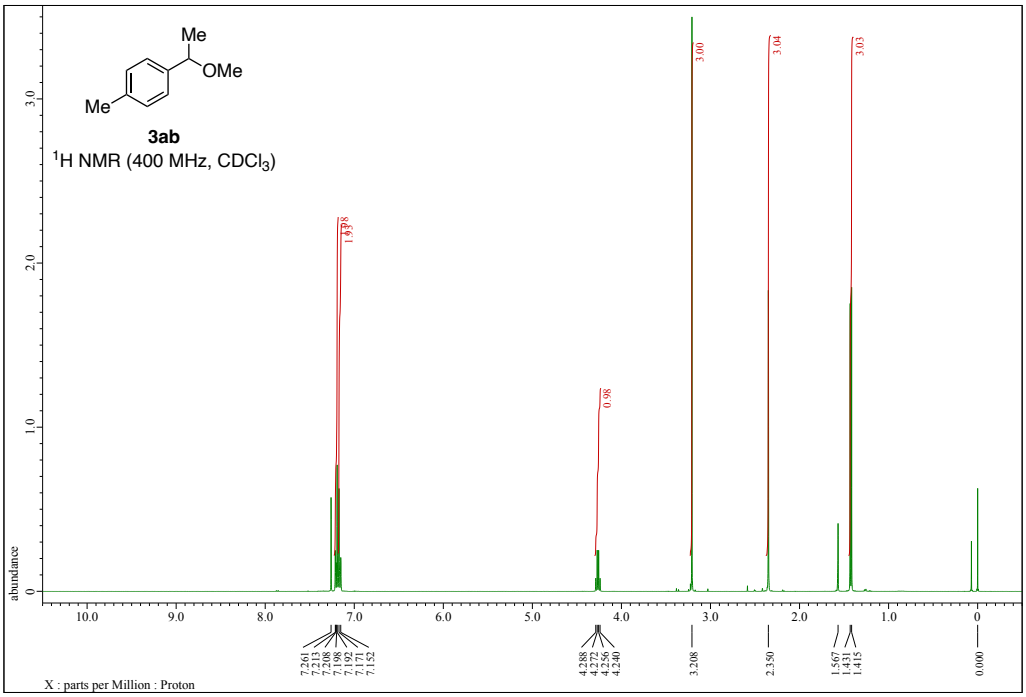

Ph
Ph
OEt
3oa
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13

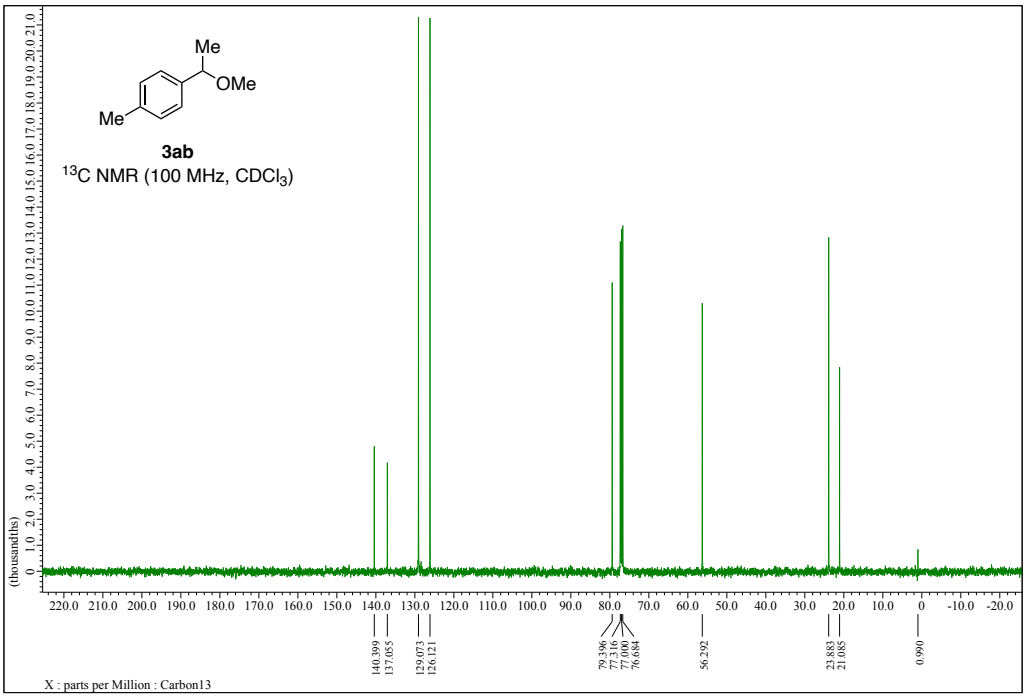

Me
OEt
HO
3sa
^{1}H NMR (400 MHz, CDCl$_3$)
abundance
X : parts per Million : Proton

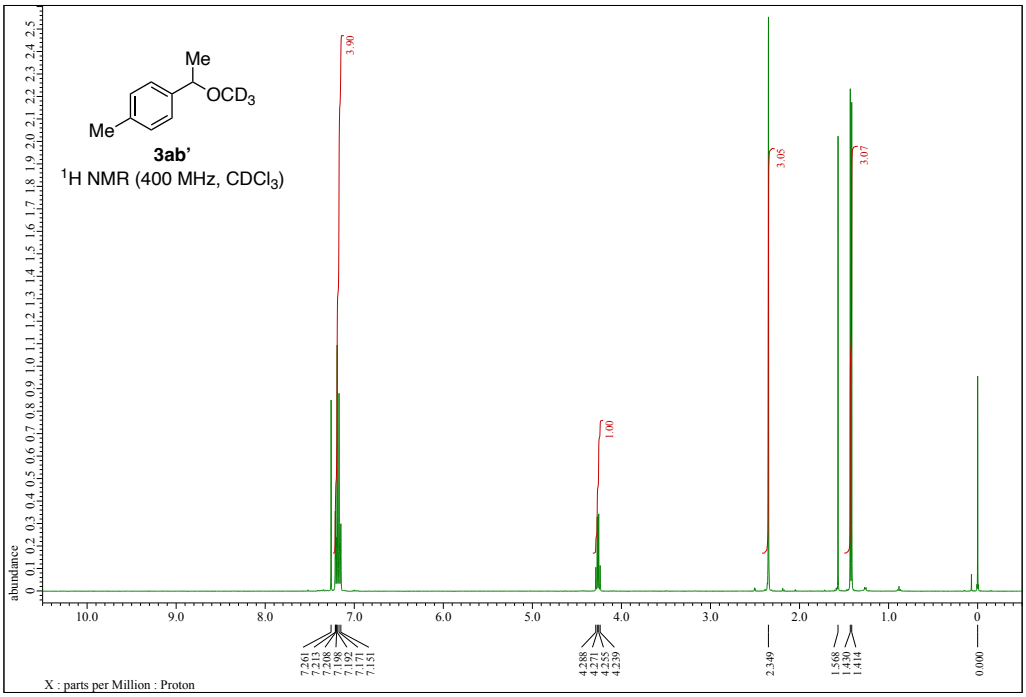

Me
OEt
HO
3sa
^{13}C NMR (100 MHz, CDCl$_3$)
(thousandths)
X : parts per Million : Carbon13

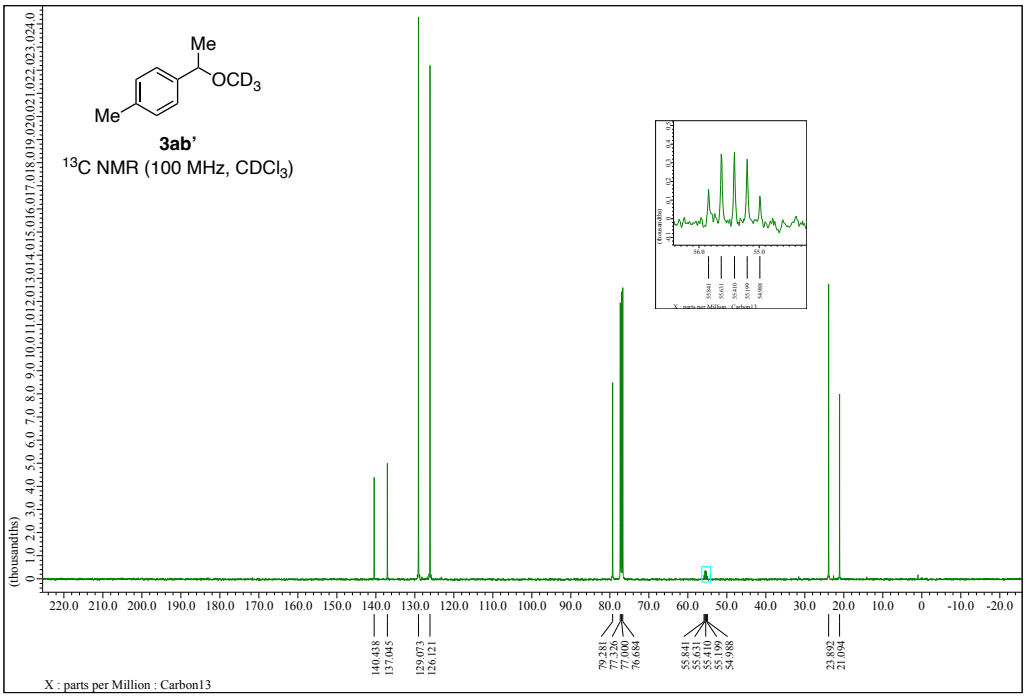

Me
OEt
3ta
1H NMR (400 MHz, CDCl3)
abundance
X : parts per Million : Proton

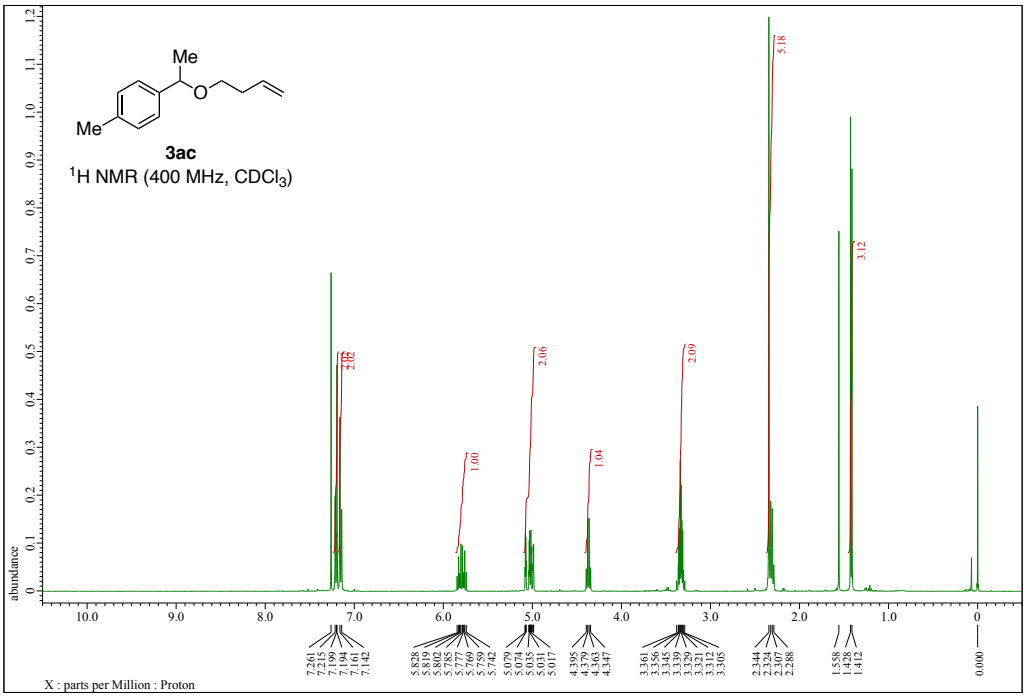

Me
OEt
3ta
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13

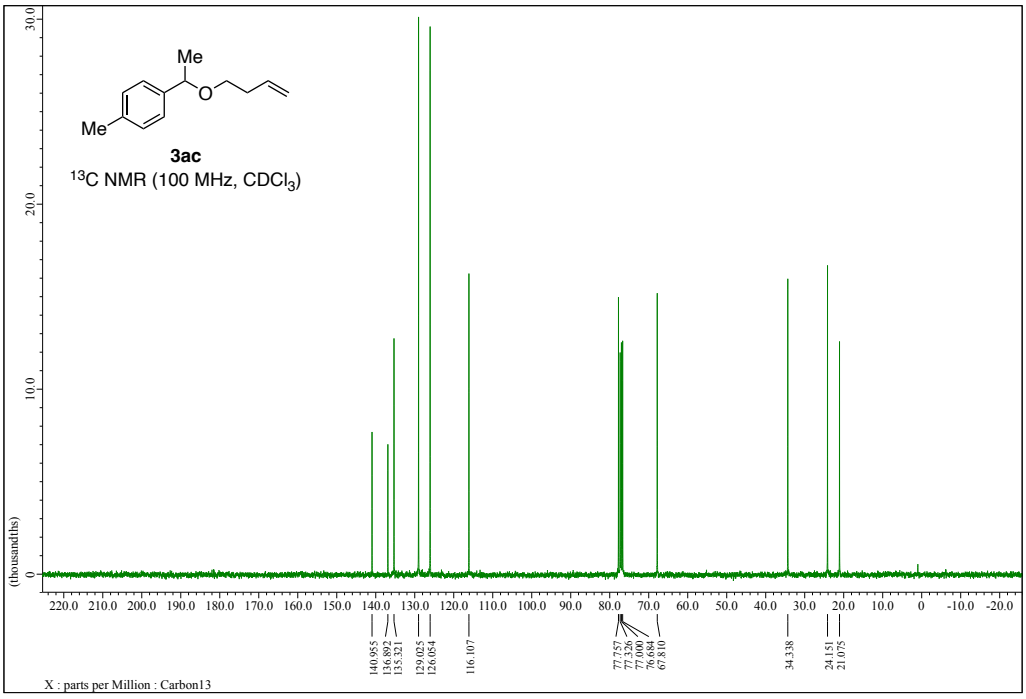

Me
OMe
Me
3ab
1H NMR (400 MHz, CDCl3)
abundance
X : parts per Million : Proton

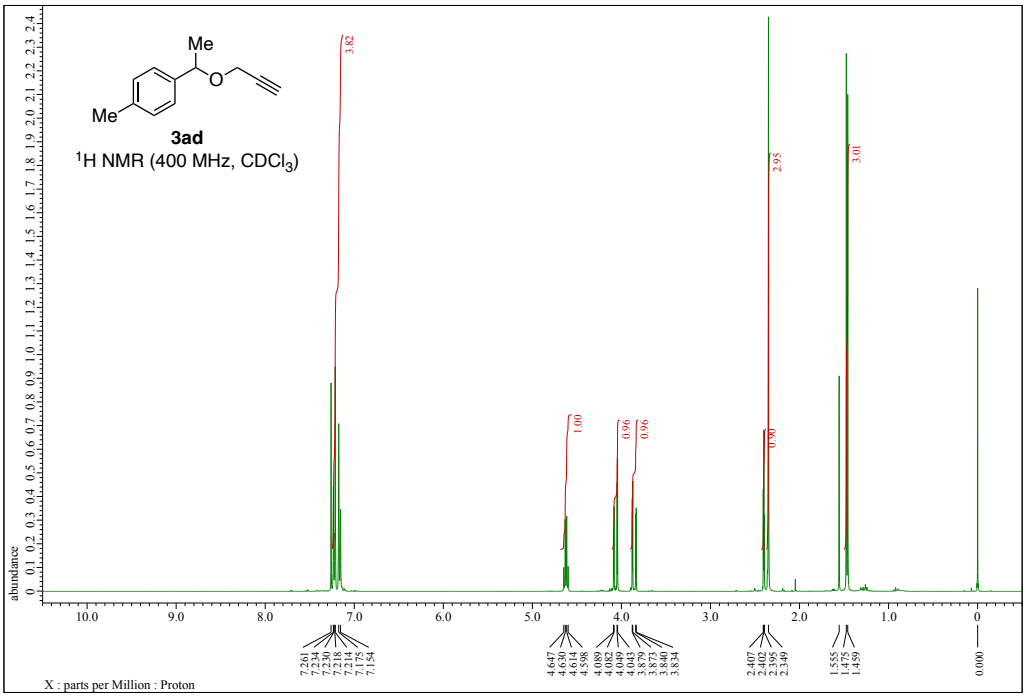

Me
OMe
Me
3ab
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13

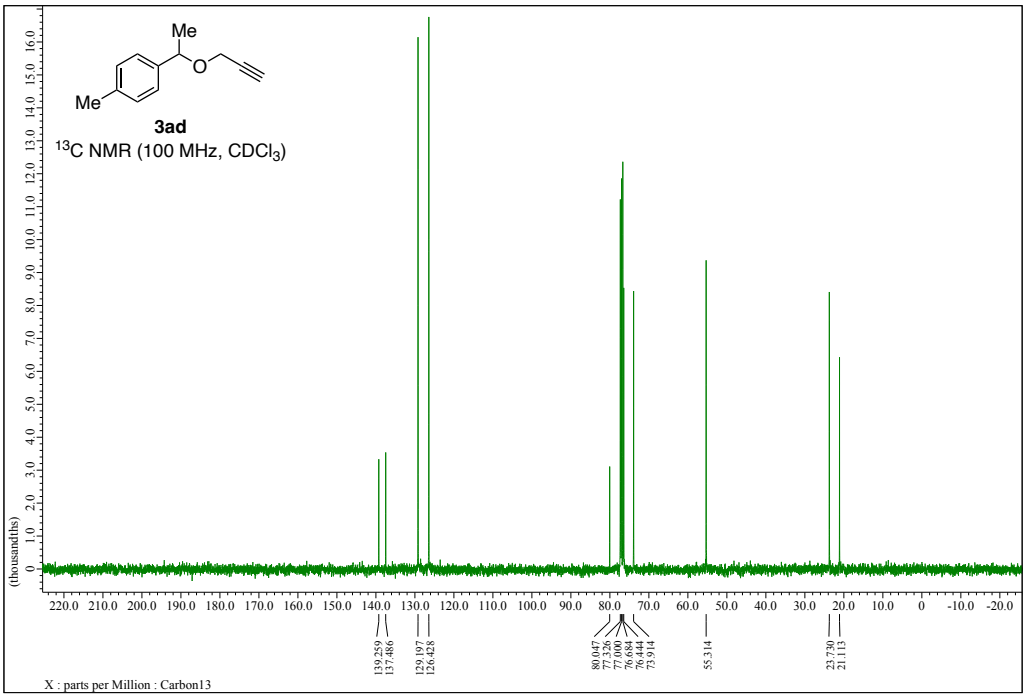

Me
OCD3
Me
3ab'
1H NMR (400 MHz, CDCl3)
abundance
X : parts per Million : Proton

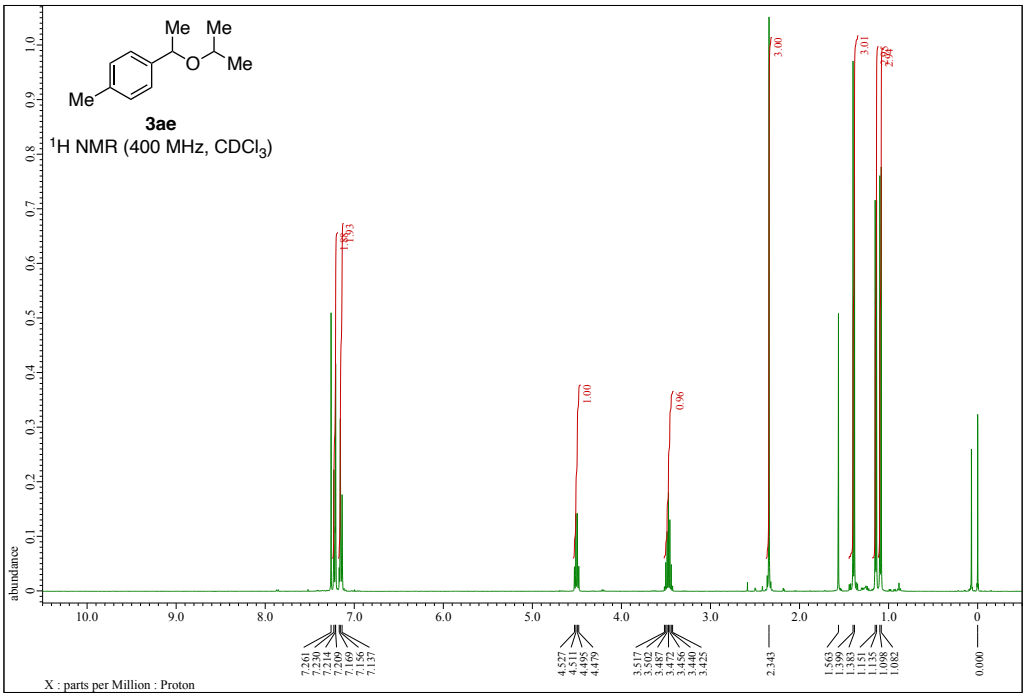

Me
OCD3
Me
3ab'
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13

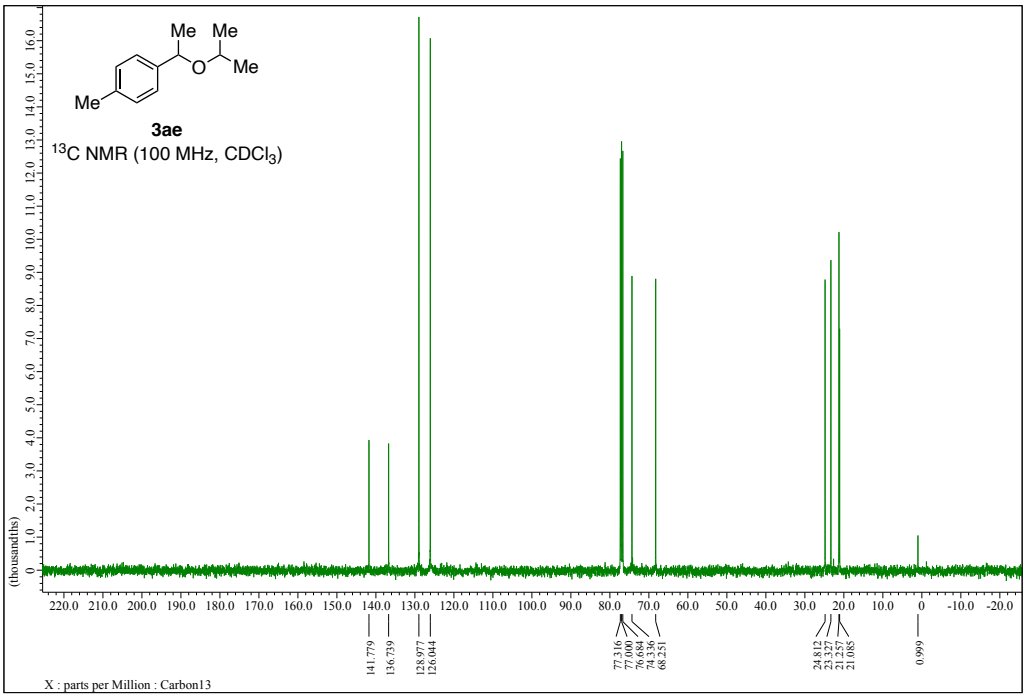

Me
O
Me
3ac
1H NMR (400 MHz, CDCl3)
abundance
X : parts per Million : Proton

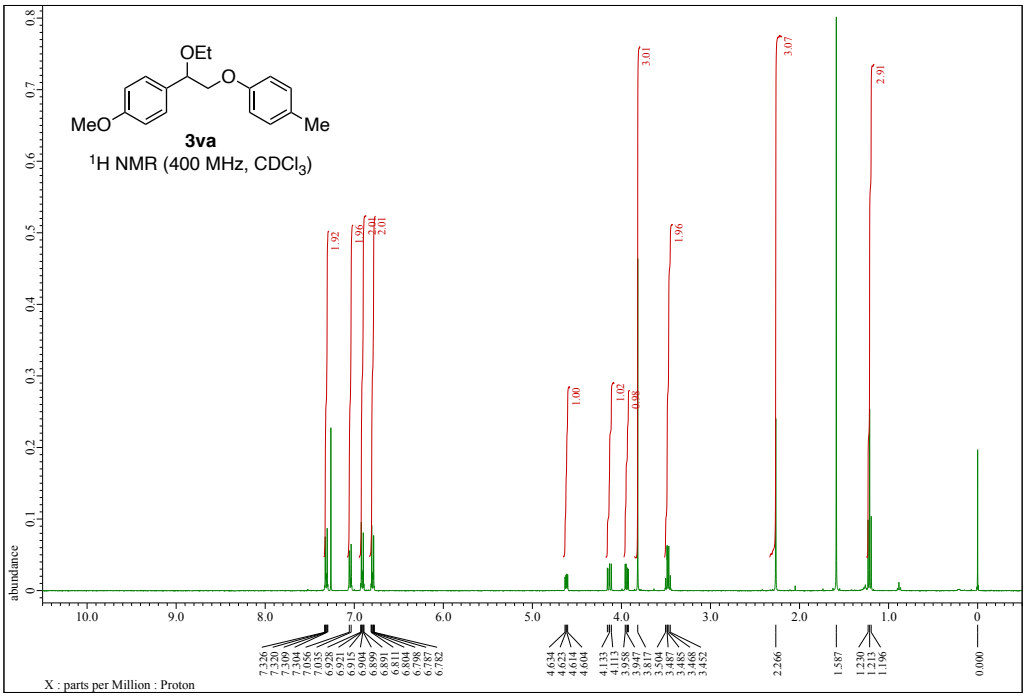

Me
O
Me
3ac
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13

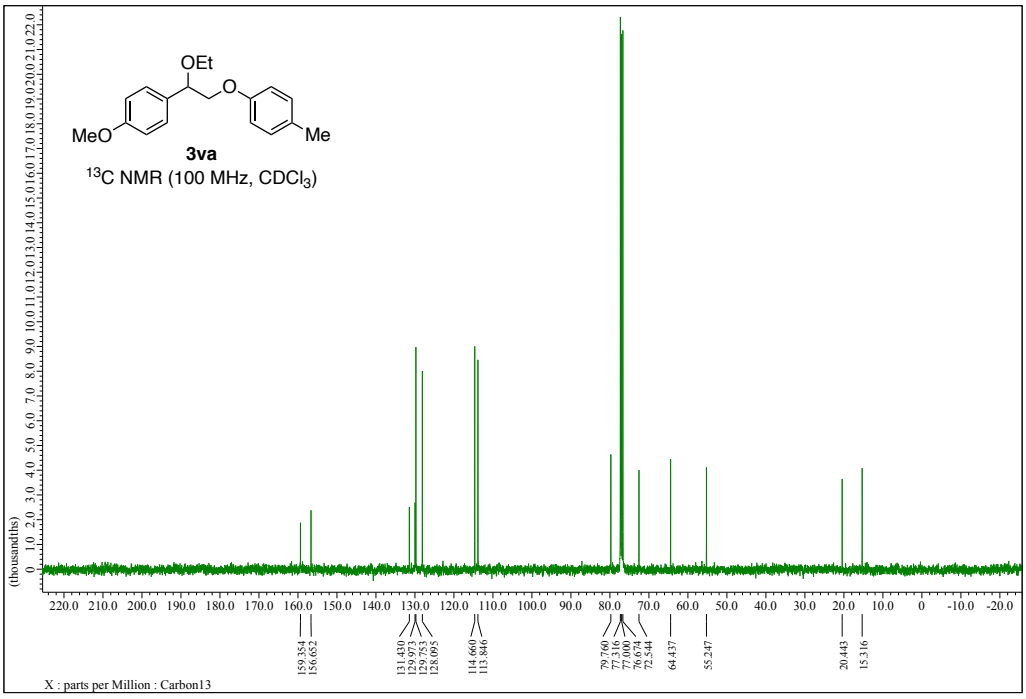

Me
O
Me
3ad
1H NMR (400 MHz, CDCl3)
abundance
X : parts per Million : Proton


Me
O
Me
3ad
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13


Me Me
O
Me
Me
3ae
1H NMR (400 MHz, CDCl3)
abundance
X : parts per Million : Proton


Me Me
O
Me
Me
3ae
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13


OEt
O
MeO
Me
3va
1H NMR (400 MHz, CDCl3)
abundance
X : parts per Million : Proton


OEt
O
MeO
Me
3va
13C NMR (100 MHz, CDCl3)
(thousandths)
X : parts per Million : Carbon13