Supplementary Information

Selective functionalization of benzylic C-H bonds of two different benzylic ethers by bowl-shaped *N*-hydroxyimide derivatives as efficient organoradical catalysts

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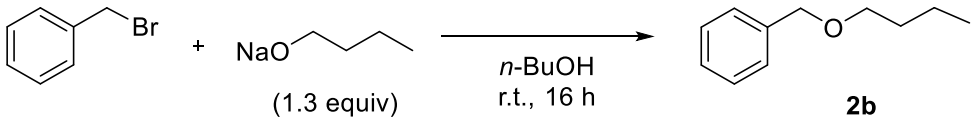
1. General information

^{1}H NMR spectra were measured on a JEOL JNM-FX400 (400 MHz) spectrometer. Data were reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent), coupling constants (Hz), and assignment. ^{13}C NMR spectra were recorded on a JEOL JNM-FX400 (100 MHz) spectrometer with complete proton decoupling. Chemical shift values in ^{1}H NMR spectra are relative to the internal tetramethylsilane (TMS) standard (0.0 ppm for ^{1}H). Chemical shifts are relative to the solvent peak of $CDCl_3$ (77.16 ppm for ^{13}C). High-resolution mass spectra (HRMS) were performed on Shimadzu ESI-IT-TOF mass spectrometer. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. The products were purified by flash column chromatography (silica gel 60, Kanto Chemical, 40–50 μm). All reactions were performed under an atmosphere of argon in dried glasswares using standard vacuum-line techniques. Tetrahydrofuran (THF), acetonitrile (MeCN), *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), dichloromethane (CH_2Cl_2) and 1,2-dichroloethane (DCE) were purchased from Fujifilm-Wako and Kanto Chemical as "Dehydrated". Commercially available reagents were purchased from Fujifilm-Wako, Sigma-Aldrich, and TCI and Nacalai Tesque, and used as received. Catalysts **1a**, **1b** and **1d**–**1f** were prepared according to the literature.[1]

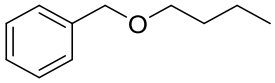
2. Synthesis and characterization of benzyl ethers

(a) Synthesis of 2b



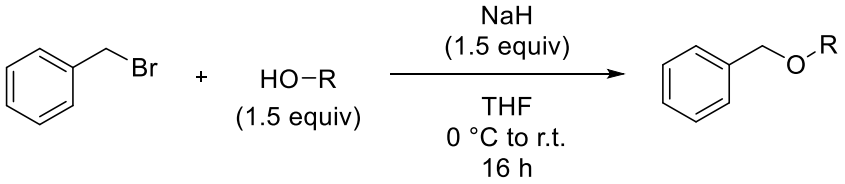
To a sodium *n*-butoxide solution prepared from sodium (0.30 g, 13 mmol) and *n*-butanol (10 mL) was added benzyl bromide (1.3 g, 10 mmol) and the reaction mixture was stirred at room temperature for 16 h. The reaction mixture was diluted with AcOEt and washed with H_2O. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluted with CH_2Cl_2/hexane) to afford benzyl butyl ether **2b** in 92% isolated yield (Colorless oil, 1.8 g, 9.2 mmol).

Benzyl butyl ether (2b)[2]



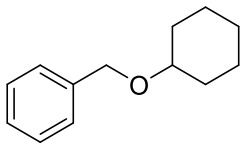
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.33 (m, 4H), 7.30–7.26 (m, 1H), 4.50 (s, 2H), 3.47 (t, J = 7.0 Hz, 2H), 1.64–1.57 (m, 2H), 1.45–1.35 (m, 2H), 0.92 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9, 128.4, 127.7, 127.6, 73.0, 70.3, 32.0, 19.5, 14.0.

(b) General procedure for the synthesis of alkyl benzyl ethers (2c, 3e)



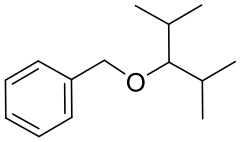
To a solution of alcohol (15 mmol) in anhydrous THF (20 mL) was added sodium hydride (0.40 g, 60% oil suspension, 15 mmol) at 0 °C. After stirring for 1 h, benzyl bromide (1.7 g, 10 mmol) was added at 0 °C and the reaction mixture was stirred at room temperature for 15 h. The reaction mixture was quenched with H_2O and extracted with CH_2Cl_2 three times. The combined organic layer was washed with H_2O, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluted with CH_2Cl_2/hexane) to afford the corresponding alkyl benzyl ether.

Benzyl cyclohexyl ether (2c)[3]



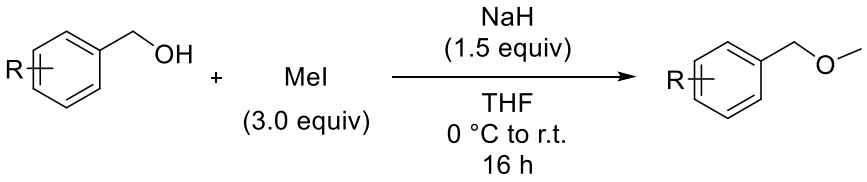
Colorless oil, 56% isolated yield (1.1 g, 5.6 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.31 (m, 4H), 7.28–7.24 (m, 1H), 4.55 (s, 2H), 3.39–3.32 (m, 1H), 1.97–1.94 (m, 2H), 1.78–1.74 (m, 2H), 1.55–1.51 (m, 1H), 1.40–1.20 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.6, 128.5, 127.7, 127.5, 77.6, 69.9, 32.5, 26.1, 24.4.

Benzyl 2,4-dimethyl-3-pentyl ether (3e)



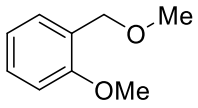
Colorless oil, 51% isolated yield (1.1 g, 5.1 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.24 (m, 5H), 4.60 (s, 2H), 2.89 (t, J = 5.2 Hz, 2H), 1.92–1.84 (s, 2H), 0.98–0.95 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.5, 128.4, 127.6, 127.4, 90.5, 75.6, 31.0, 20.5, 18.0; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{22}NaO$ 229.1563; Found 229.1576.

(c) General procedure for the synthesis of benzylic methyl ether (6a–6g, 10, 12)



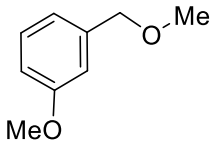
To a solution of benzylic alcohol (10 mmol) in anhydrous THF (15 mL) was added sodium hydride (0.4 g, 60% oil suspension, 15 mmol) at 0 °C. After stirring for 1 h, iodomethane (4.3 g, 30 mmol) was added at 0 °C and the reaction mixture was stirred for 15 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 and washed with $Na_2S_2O_3$ aq. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluted with CH_2Cl_2/hexane) to afford corresponding benzylic methyl ether.

2-Methoxybenzyl methyl ether (6a)[4]



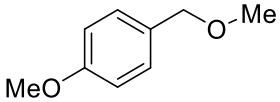
Colorless oil, 83% isolated yield (1.3 g, 8.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.5 Hz, 1H), 7.27 (t, J = 7.6 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.88 (d, J = 8.1 Hz, 1H), 4.50 (s, 2H), 3.84 (s, 3H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.3, 129.1, 128.8, 126.6, 120.4, 110.3, 69.6, 58.4, 55.4.

3-Methoxybenzyl methyl ether (6b)[5]



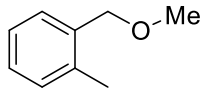
Colorless oil, 56% isolated yield (0.85 g, 5.6 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.24 (m, 1H), 6.92–6.90 (m, 2H), 6.84–6.82 (m, 1H), 4.44 (s, 2H), 3.82 (s, 3H), 3.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 139.9, 129.5, 120.0, 113.4, 112.9, 74.6, 58.2, 55.2.

4-Methoxybenzyl methyl ether (6c)[6]



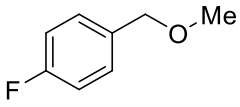
Colorless oil, 61% isolated yield (0.92 g, 6.1 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, J = 8.7 Hz, 2H), 6.88 (s, J = 6.1 Hz, 2H), 4.39 (s, 2H), 3.81 (s, 3H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 130.3, 129.4, 113.8, 74.4, 57.8, 55.3.

2-Methylbenzyl methyl ether (6d)[7]



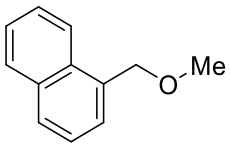
Colorless oil, 68% isolated yield (0.95 g, 6.8 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 7.6 Hz, 1H), 7.21–7.13 (m, 3H), 4.43 (s, 2H), 3.38 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 136.2, 130.3, 128.6, 127.9, 125.8, 73.1, 58.2, 18.7.

4-Fluorobenzyl methyl ether (6e)



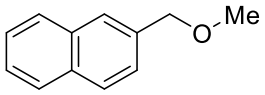
Colorless oil, 51% isolated yield (0.71 g, 5.1 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.29 (m, 2H), 7.02 (t, J = 8.7 Hz, 2H), 4.40 (s, 2H), 3.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, $J_{C\text{-}F}$ = 244.1 Hz), 134.0, 129.6 (d, $J_{C\text{-}F}$ = 7.6 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21.0 Hz), 74.0, 58.1; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for C_8H_9FNaO 163.0530; Found 163.0497.

Methyl 1-naphthalenemethyl ether (6f)[8]



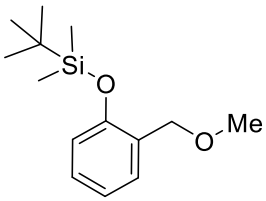
Colorless oil, 89% isolated yield (1.5 g, 8.9 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11(d, J = 8.1 Hz, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.56–7.42 (m, 4H), 4.91 (s, 2H), 3.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.0, 133.9, 132.0, 128.8, 128.7, 126.7, 126.4, 126.0, 125.4, 124.2, 73.4, 58.3.

Methyl 2-naphthalenemethyl ether (6g)[8]



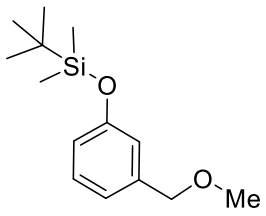
Colorless oil, 65% isolated yield (1.1 g, 6.5 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.78 (m, 4H), 7.50–7.45 (m, 3H), 4.63 (s, 2H), 3.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 133.4, 133.1, 128.2, 128.0, 127.8, 126.5, 126.2, 125.9, 125.8, 74.8, 58.2.

2-(*tert*-buthyldimethylsiloxy)benzyl methyl ether (10)



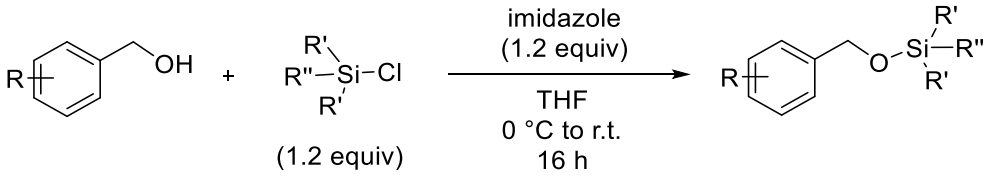
Prepared from 2-(*tert*-butyldimethylsiloxy)benzyl alcohol[9]. Colorless oil, 91% isolated yield (2.3 g, 9.1 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.0 Hz, 1H), 7.22 (t, J = 7.8 Hz, 1H), 6.93 (t, J = 7.8 Hz, 1H), 6.82 (d, J = 8.1 Hz, 1H), 4.76 (s, 2H), 3.82 (s, 3H), 0.96 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 130.0, 127.6, 126.8, 120.6, 109.6, 60.3, 55.2, 16.2, 18.6, -5.2; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{24}NaO_2Si$ 275.1438; Found 275.1428.

3-(*tert*-Buthyldimethylsiloxy)benzyl methyl ether (12)



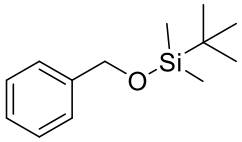
Prepared from 3-(*tert*-butyldimethylsiloxy)benzyl alcohol[10]. Colorless oil, 37% isolated yield (0.93 g, 3.7 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.21 (m, 1H), 6.96–6.88 (m, 2H), 6.80–6.77 (m, 1H), 4.73 (s, 2H), 3.81 (s, 3H), 0.95 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 143.3, 129.3, 118.3, 112.5, 111.6, 64.9, 55.3, 26.1, 18.6, -5.1; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{24}NaO_2Si$ 275.1438; Found 275.1403.

(d) General procedure for the synthesis of silyl ethers (3a–3d, 7a–7g)



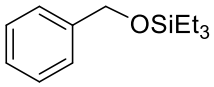
To a solution of benzylic alcohol (10 mmol) and imidazole (0.82 g, 12 mmol) in anhydrous THF (20 mL) was added trialkylsilyl chloride (12 mmol) at 0 °C and the reaction mixture was stirred at room temperature for 16 h. The mixture was quenched with H_2O and extracted with CH_2Cl_2 three times. The combined organic layer was washed with H_2O, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluted with CH_2Cl_2/hexane) to afford the corresponding benzylic silyl ether.

Benzyl *tert*-butyldimethylsilyl ether (3a)[11]



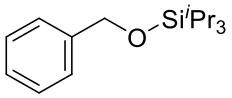
Colorless oil, 80% isolated yield. (1.8 g, 8.0 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.32 (m, 4H), 7.26–7.21 (m, 1H), 4,75 (s, 2H), 0.94 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6, 128.3, 127.0, 126.2, 65.1, 26.1, 18.6, -5.1.

Benzyl triethylsilyl ether (3b)[12]



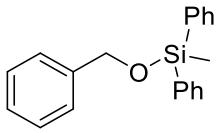
Colorless oil, 71% isolated yield (1.6 g, 7.1 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.29 (m, 4H), 7.24–7.21 (m, 1H), 4.73 (s, 2H), 0.97 (t, J = 7.5 Hz, 9H), 0.64 (q, J= 7.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 128.3, 127.1, 126.3, 64.9, 6.9, 4.7.

Benzyl triisopropylsilyl ether (3c)[13]



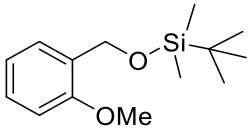
Colorless oil, 87% isolated yield (2.3 g, 8.7 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.31 (m, 4H), 7.24–7.21 (m, 1H), 4.84 (s, 2H), 1.24–1.14 (m, 3H), 1.09 (d, J = 6.8 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8, 128.3, 126.9, 125.8, 65.1, 18.2, 12.2.

Benzyl diphenylmethylsilyl ether (3d)[14]



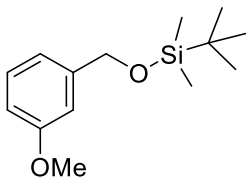
Colorless oil, 65% isolated yield (2.0 g, 6.5 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.41 (m, 4H), 7.44–7.22 (m, 11H), 4.80 (s, 2H), 0.66 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.8, 136.0, 134.5, 130.0, 128.4, 128.0, 127.2, 126.6, 65.4, -2.8.

***tert*-Butyldimethylsilyl 2-methoxybenzyl ether (7a)**



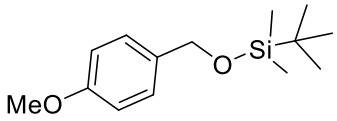
Colorless oil, 93% isolated yield (2.4 g, 9.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 6.7 Hz, 1H), 7.22 (t, J = 8.1 Hz, 1H), 6.97 (t, J = 7.6 Hz, 1H), 6.82 (d, J = 8.1 Hz, 1H), 4.76 (s, 2H), 3.82 (s, 3H), 0.96 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 130.0, 127.6, 126.8, 120.6, 109.6, 60.3, 56.2, 26.2, 18.6, -5.2; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{24}NaO_2Si$ 275.1438; Found 275.1442.

***tert*-Butyldimethylsilyl 3-methoxybenzyl ether (7b)**[15]



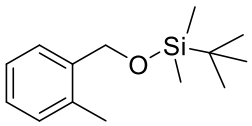
Colorless oil, 90% isolated yield (2.3 g, 9.0 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.21 (m, 1H), 6.91–6.88 (m, 2H), 6.82 (d, J = 8.1 Hz, 1H), 4.73 (s, 2H), 3.81 (s, 3H), 0.95 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 143.3, 129.3, 118.3, 112.5, 111.6, 112.5, 111.6, 64.9, 55.2, 26.1, 18.5, -5.1.

***tert*-Butyldimethylsilyl 4-methoxybenzyl ether (7c)**[16]



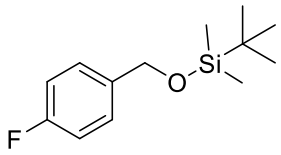
Colorless oil, 87% isolated yield (2.2 g, 8.7 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, J = 8.1 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 4.67 (s, 2H), 3.80 (s, 3H), 0.93 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 133.7, 127.6, 113.7, 64.8, 55.3, 26.1, 18.6, -5.1.

***tert*-Butyldimethylsilyl 2-metylbenzyl ether (7d)**



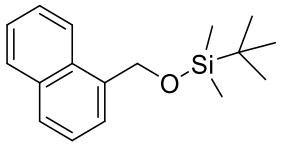
Colorless oil, 98% isolated yield (2.3 g, 9.8 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.0 Hz, 1H), 7.21–7.11 (m, 3H), 4.70 (s, 2H), 2.27 (s, 3H), 0.94 (s, 9H), 0.09 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 135.1, 129.9, 127.0, 126.5, 125.9, 63.4, 26.1, 18.7, 18.6, -5.2; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{24}NaOSi$ 259.1489; Found 259.1454.

***tert*-Butyldimethylsilyl 4-fluorobenzyl ether (7e)**



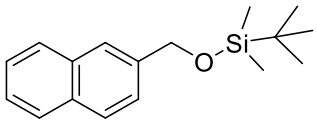
Colorless oil, 76% isolated yield (1.8 g, 7.6 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.27 (m, 2H), 7.01 (t, J = 8.4 Hz, 2H), 4.70 (s, 2H), 0.93 (s, 9H), 0.09, (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6 (d, $J_{C\text{-}F}$ = 242.2 Hz), 137.3, 127.8 (d, $J_{C\text{-}F}$ = 8.6 Hz), 115.1 (d, $J_{C\text{-}F}$ = 21.9 Hz), 64.5, 26.1, 18.5, -5.1; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{21}FNaOSi$ 263.1238; Found 263.1220.

***tert*-Butyldimethylsilyl 1-naphthalenemethyl ether (7f)**[17]



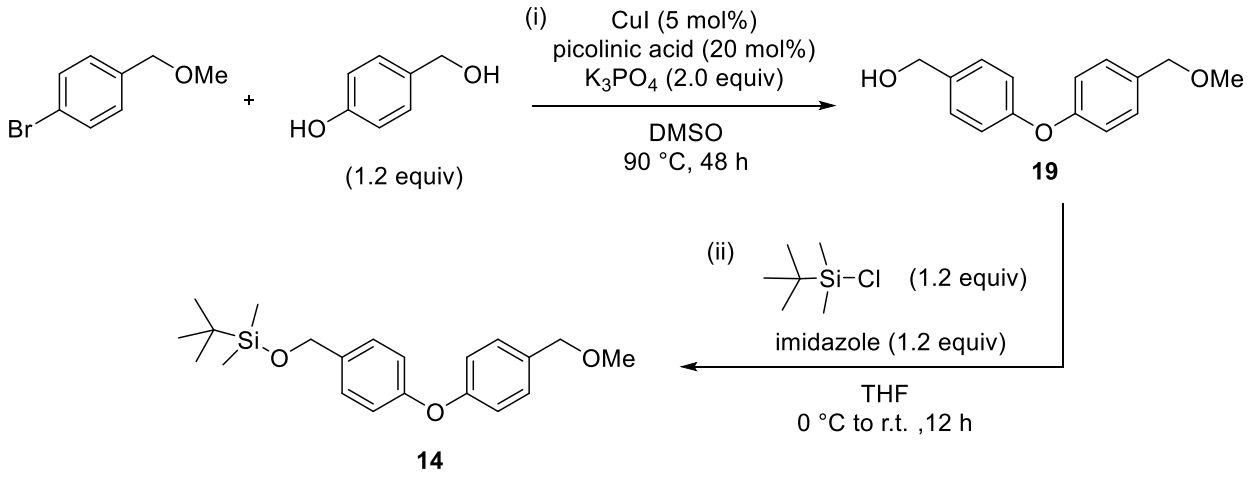
Colorless oil, 94% isolated yield (2.6 g, 9.4 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.7 Hz, 1H), 7.86 (d, J = 7.0 Hz, 1H), 7.76 (d, J = 8.1 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.52–7.44 (m, 3H), 5.21 (s, 2H), 0.96 (s, 9H), 0.13 (s, 6H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 133.7, 130.9, 128.7, 127.7, 125.9, 125.7, 125.6, 123.9, 123.4, 63.5, 26.1, 18.6, -5.1.

***tert*-Butyldimethylsilyl 2-naphthalenemethyl ether (7g)**



Colorless oil, 91% isolated yield (2.5 g, 9.1 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.77 (m, 4H), 7.48–7.42 (m, 3H), 4.90 (s, 2H), 0.97 (s, 9H), 0.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.1, 133.5, 132.9, 128.0, 127.8, 126.1, 125.6, 124.8, 124.5, 65.3, 26.2, 18.6, -5.0; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{24}NaOSi$ 295.1489; Found 295.1470.

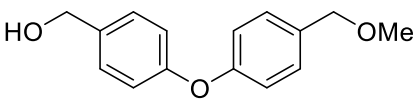
(e) Synthesis of 14



(i) The suspension of 4-bromobenzyl methyl ether (2.6 g, 13 mmol), 4-(hydroxymethyl)phenol (2.0 g, 16 mmol), copper iodide (0.12 g, 0.65 mmol), picolinic acid (0.27 g, 2.6 mmol), K_3PO_4 (5.5 g, 26 mmol) in anhydrous DMSO (30 mL) was stirred at 90 °C for 48 h. The reaction mixture was quenched with H_2O and then acidified with 1*N* HCl. The mixture was extracted by the mixture of AcOEt/Hexane (volume ratio = 1/3) three times and the combined organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluted with AcOEt/hexane = 1:2) to give product **19** in 31% yield.

(ii) To a solution of **19** (0.98 g, 4.0 mmol) and imidazole (0.32 g, 4.8 mmol) in anhydrous THF (10 mL) was added *tert*-butyldimethylchlorosilane (0.72 g, 4.8 mmol) at 0 °C and the reaction mixture was stirred at room temperature for 12 h. The mixture was quenched with H_2O and extracted with CH_2Cl_2 three times. The combined organic layer was washed with H_2O, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluted with CH_2Cl_2/hexane = 1:1) to give **14** in 83% yield.

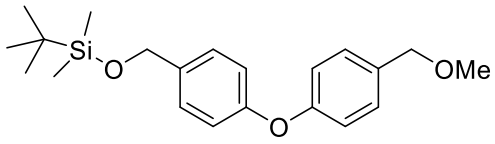
(4-(4-(Methoxymethyl)phenoxy)phenoxybenzene (19)



White solid, 31% isolated yield (0.99 g, 4.0 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (t, J = 9.4 Hz, 4H), 6.99–6.96 (m, 4H), 4.65 (s, 2H), 4.41 (s, 3H), 3.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)

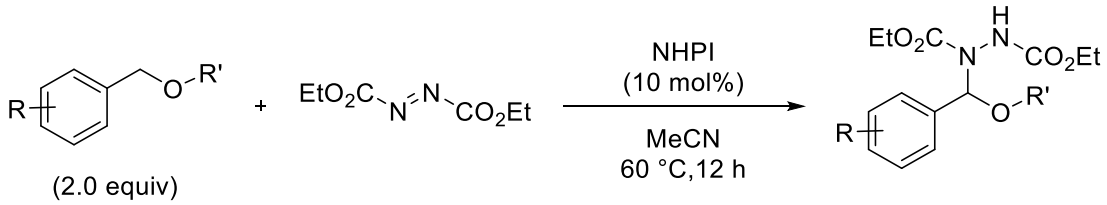
δ 156.9, 156.8, 135.9, 133.1, 129.6, 128.8, 119.0, 118.9, 74.3, 64.8, 58.1; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{16}NaO_3$ 267.0992; Found 267.0978.

(*tert*-butyldimethylsiloxy)methyl(4-(4-methoxymethyl))phenoxy benzene (14)



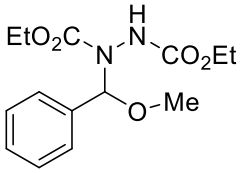
Colorless oil, 83% isolated yield (1.2 g, 3.3 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, J = 4.8 Hz, 4H), 6.99–6.94 (m, 4H), 4.71 (s, 2H), 4.42 (s, 2H), 3.39 (s, 3H), 0.94 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 156.2, 136.6, 133.0, 129.5, 127.7, 118.9, 118.7, 74.4, 64.7, 58.2, 26.1, 18.6, -5.1; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{30}NaO_3Si$ 381.1856; Found 381.1854.

3. Synthesis and characterization of aminated benzyl ethers



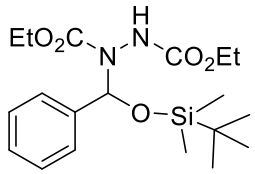
To a solution of benzylic ether (0.48 mmol), *N*-hydroxyphthalimide (NHPI, 3.3 mg, 0.02 mmol) in anhydrous MeCN (1mL) was added diethyl azodicarboxylate (DEAD, 42 mg, 0.24 mmol) and the reaction mixture was stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2. The solution was washed with sat $NaHCO_3$ aq, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluted with AcOEt/hexane= 1:3) to afford the corresponding product, which was used as an authentic ^{1}H NMR sample for selective amination of two different benzyl ethers (Tables 1–3 and Schemes 2–3).

Diethyl 1-(methoxy(phenyl)methyl)hydrazine-1,2-dicarboxylate (4a)



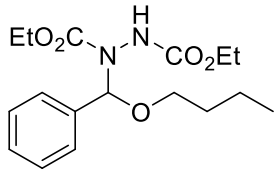
Colorless oil, 95% isolated yield (68 mg, 0.23 mmol). R_f = 0.3 (AcOEt/hexane = 1/3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.33 (m, 5H), 6.39-5.95 (br m, 2H), 4.30–4.07 (m, 4H), 3.63–3.42 (m, 3H), 1.32–0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 136.7, 128.5, 127.9, 127.2, 126.5, 87.7, 62.9, 61.8, 56.8, 14.5, 14.4; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{20}N_2NaO_5$ 319.1264; Found 319.1265.

Diethyl 1-((*tert*-butyldimethylsiloxy)(phenyl)methyl)hydrazine-1,2-dicarboxylate (5a)



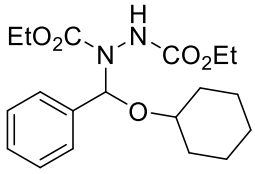
Colorless oil, 97% isolated yield (92 mg, 0.23 mmol). R_f = 0.6 (AcOEt/hexane = 1/3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 2H), 7.33–7.30 (m, 3H), 6.78–6.20 (br m, 2H), 4.27–3.56 (m, 4H), 1.31–0.85 (m, 6H), 0.92 (s, 9H), 0.15-0.10; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 138.6, 128.3, 127.8, 126.9, 81.0, 62.8, 61.7, 25.9, 18.3, 14.6, 14.5, 14.0, -4.8, -5.2; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{32}N_2NaO_5$ 419.1973; Found 419.1975.

Diethyl 1-(butoxy(phenyl)methyl)hydrazine-1,2-dicarboxylate (4b)



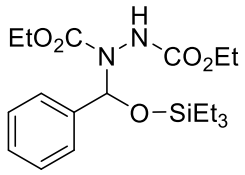
White solid, 99% isolated yield (81 mg, 0.24 mmol). R_f = 0.5 (AcOEt/hexane = 1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.30 (m, 5H), 6.47–6.13 (br m, 2H), 4.29–3.60 (m, 6H), 1.67–1.61 (m, 2H), 1.48–1.41 (m ,2H), 1.31–1.19 (m, 6H), 0.94 (t, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 137.0, 128.4, 127.8, 127.3, 126.5, 86.4, 68.7, 62.8, 61.8, 31.7, 19.5, 14.5, 14.4, 14.0; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{26}N_2NaO_5$ 361.1734; Found 361.1732.

Diethyl 1-((cyclohexyloxy)(phenyl)methyl)hydrazine-1,2-dicarboxylate (4c)



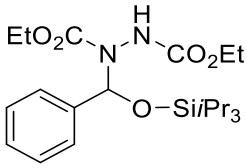
Colorless oil, 95% isolated yield (83 mg, 0.23 mmol). R_f = 0.4 (AcOEt/hexane = 1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.29 (m, 5H), 6.62–6.62 (m, 2H), 4.28–3.50 (m, 5H), 1.99–1.71 (m, 4H), 1.55–0.87 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 137.5, 128.3, 127.9, 127.3, 126.7, 83.8, 74.0, 62.8, 61.7, 32.8, 30.4, 25.9, 24.0, 23.8, 14.5, 14.4; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{28}N_2NaO_5$ 387.1890; Found 387.1858.

Diethyl 1-(phenyl(triethylsiloxy)methyl)hydrazine-1,2-dicarboxylate (5b)



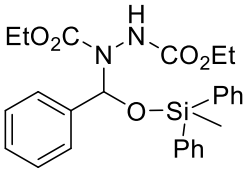
Colorless oil, 92% isolated yield (87 mg, 0.22 mmol). R_f = 0.6 (AcOEt/hexane = 1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 2H), 7.32–7.30 (m, 3H), 6.80 (br s, 1H), 6.24 (br s, 1H), 4.27–3.56 (m, 4H), 1.39–1.11 (m, 5H), 0.93–0.85 (m, 10 H), 0.68–0.66 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 138.6, 128.2, 127.8, 126.8, 80.8, 62.8, 61.6, 14.6, 14.4, 6.7, 4.6; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{32}N_2NaO_5Si$ 419.1973; Found 419.1948.

Diethyl 1-(phenyl(triisopropylsiloxy)methyl)hydrazine-1,2-dicarboxylate (5c)



Use of NHPI (20 mol%) for 120 h. Colorless oil, 39% isolated yield (41 mg, 0.094 mmol). R_f = 0.6 (AcOEt/hexane = 1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 2H), 7.34 (s, 3H), 6.89 (br s, 1H), 6.40–6.29 (m, 1H), 4.23–3.48 (m, 4H), 1.26–0.78 (m, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 138.9, 128.3, 127.8, 126.8, 80.6, 62.8, 62.6, 61.6, 17.9, 17.9, 14.6, 14.5, 13.9, 12.2; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{38}N_2NaO_5Si$ 461.2422; Found 461.2433.

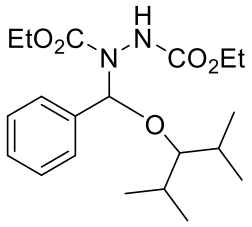
Diethyl 1-((methyldiphenylsiloxy)(phenyl)methyl)hydrazine-1,2-dicarboxylate (5d)



Colorless oil, 96% isolated yield (110 mg, 0.23 mmol). R_f = 0.4 (AcOEt/hexane = 1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.37 (m, 15H), 6.95–6.81 (m, 1H), 6.08–5.85 (m, 1H), 4.04–3.54 (m, 4H), 1.15–0.74 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 138.2, 135.4, 134.3, 130.1,

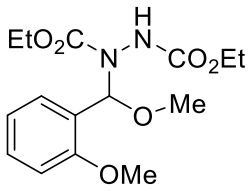
128.3, 128.0, 127.8, 127.8, 127.0, 126.8, 80.9, 62.8, 61.7, 14.4, 14.0, -2.9; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{30}N_2NaO_5Si$ 501.1816; Found 501.1817.

Diethyl 1-((2,4-dimethyl-3-pentanoxy)(phenyl)methyl)hydrazine-1,2-dicarboxylate (5e)



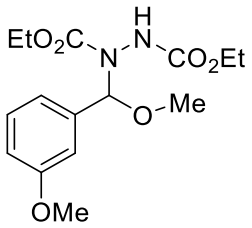
For 40 h. Colorless oil, 99% isolated yield (90 mg, 0.24 mmol), as a mixture of rotamer. R_f = 0.5 (AcOEt/hexane = 1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.47 (m, 2H), 7.31–7.28 (m, 3H), 6.70–6.50 (m, 1H), 6.24–6.15 (m, 1H), 4.25–3.31 (m, 5H), 1.90 (br s, 2H), 1.36–1.28 (m, 3H), 1.06 (br s, 2H), 0.97–0.88 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.6, 155.8, 154.7, 137.1, 128.1, 127.7, 90.1, 89.5, 88.1, 87.6, 62.8, 61.6, 31.1, 30.9, 30.1, 20.7, 20.1, 18.3, 18.2, 17.8, 14.6, 14.4, 14.0; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{32}N_2NaO_5$ 403.2203; Found 403. 2198.

Diethyl 1-(methoxy(2-methoxyphenyl)methyl)hydrazine-1,2-dicarboxylate (8a)



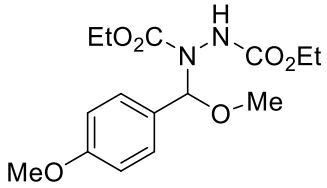
Colorless oil, 92% isolated yield (72 mg, 0.22 mmol). R_f = 0.3 (AcOEt/hexane = 1:2 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.47 (m, 1H), 7.29 (t, J = 7.6 Hz, 1H), 6.99–6.96 (m, 1H), 6.85 (d, J = 8.4 Hz, 1H), 6.45 (br s, 1H), 5.81-5.54 (br m, 1H), 4.29–4.10 (m, 4H), 3.79 (s, 3H), 3.62–3.41 (m, 3H), 1.31–0.84 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 129.6, 128.5, 124.7, 120.4, 110.2, 84.6, 83.9, 62.6, 61.7, 56.1, 55.5, 14.7, 14.4; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{22}N_2NaO_6$ 349.1379; Found 349.1379.

Diethyl 1-(methoxy(3-methoxyphenyl)methyl)hydrazine-1,2-dicarboxylate (8b)



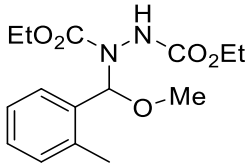
Colorless oil, 99% isolated yield (78 mg, 0.24 mmol). R_f = 0.3 (AcOEt/hexane = 1:2 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.24 (m, 1H), 6.99 (br s, 23.62H), 6.85 (d, J = 8.0 Hz, 1H), 6.35–5.64 (br m, 2H), 430–4.11 (m, 4H), 3.80 (s, 4H), 3.62–3.42 (m, 3H), 1.31–0.88 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 156.1, 138.4, 129.5, 118.7, 114.3, 112.0, 88.5, 87.6, 63.0, 61.9, 56.8, 55.3; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{22}N_2NaO_6$ 349.1370; Found 349.1379.

Diethyl 1-(methoxy(4-methoxyphenyl)methyl)hydrazine-1,2-dicarboxylate (8c)



Colorless oil, 95% isolated yield (74 mg, 0.23 mmol). R_f = 0.3 (AcOEt/hexane = 1:2 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 2H), 6.87 (d, J = 8.0 Hz, 2H), 6.33–5.58 (br m, 2H), 4.29–4.10 (m, 4H), 3.80 (s, 3H), 3.60–3.40 (m, 3H), 1.31–0.90 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 156.3, 128.4, 127.8, 113.8, 88.1, 62.9, 61.9, 56.8, 55.4, 14.6, 14.5; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{22}N_2NaO_6$ 349.1370; Found 349.1357.

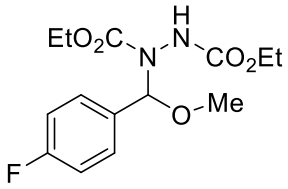
Diethyl 1-(methoxy(*o*-tolyl)methyl)hydrazine-1,2-dicarboxylate (8d)



For 48 h. Colorless oil, 93% isolated yield (69 mg, 0.22 mmol). R_f = 0.3 (AcOEt/hexane = 1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.53 (m, 1H), 7.20–7.12 (m, 3H), 6.50–6.16 (br m, 1H), 4.28–4.10 (m, 4H), 3.74–3.42 (m, 3H), 2.40–2.29 (m, 3H), 1.32–0.85 (m, 6H); ^{13}C NMR (100

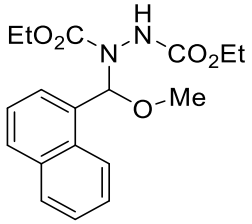
MHz, $CDCl_3$) δ 155.9, 130.3, 129.8, 128.4, 127.1, 125.6, 85.7, 62.9, 61.7, 56.1, 19.1, 14.6, 14.5, 13.8; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{22}N_2NaO_5$ 333.1421; Found 333.1428.

Diethyl 1-((4-fluorophenyl)(methoxy)methyl)hydrazine-1,2-dicarboxylate (8e)



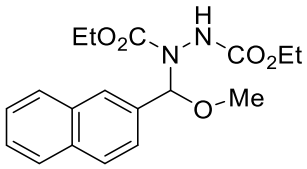
For 48 h. Colorless oil, 90% isolated yield (68 mg, 0.22 mmol). R_f = 0.3 (AcOEt/hexane = 1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 2H), 7.03 (t, J = 8.8 Hz, 2H), 6.34–5.63 (br m, 2H), 4.29–3.83 (m, 4H), 3.60–3.42 (m, 3H), 1.31–0.90 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, $J_{C\text{-}F}$ = 245.0 Hz), 156.2, 132.7, 129.0, 128.4, 115.6 (d, $J_{C\text{-}F}$ = 20.0 Hz), 87.3, 63.0, 61.9, 56.6, 14.5, 14.4; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{19}FN_2NaO_5$ 337.1170; Found 337.1149.

Diethyl 1-(methoxy(naphthalen-1-yl)methyl)hydrazine-1,2-dicarboxylate (8f)



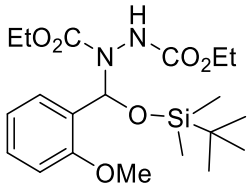
For 72 h. White solid, 99% isolated yield (83 mg, 0.24 mmol), as a mixture of rotamer. R_f = 0.3 (AcOEt/hexane = 1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.92–7.77 (m, 4H), 7.50–7.48 (m, 3H), 7.11–7.04 (m, 1H), 6.20–5.33 (br m, 1H), 4.33–2.86 (m, 4H), 1.29–1,21 (m, 5H) 0.11 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 133.5, 133.3, 131.4, 131.3, 129.9, 129.0, 128.9, 128.4, 126.6, 126.3, 125.6, 125.4, 125.2, 124.9, 123.6, 122.6, 85.2, 62.9, 62.1, 61.7, 61.1, 56.7, 55.9, 14.5, 14.4, 12.7; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{22}N_2NaO_5$ 369.1421; Found 369.1413.

Diethyl 1-(methoxy(naphthalen-2-yl)methyl)hydrazine-1,2-dicarboxylate (8g)



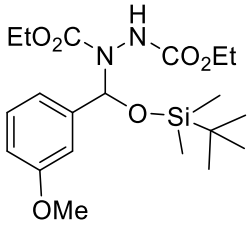
White solid, 95% isolated yield (79 mg, 0.23 mmol). R_f = 0.3 (AcOEt/hexane = 1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.86–7.81 (m, 3H), 7.50–7.48 (m, 3H), 6.56–5.93 (br m, 2H), 4.33–4.09 (m, 4H), 3.70–3.49 (m, 3H), 1.34–0.59 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 134.3, 133.3, 133.1, 128.4, 127.7, 126.4, 126.0, 124.0, 88.0, 63.0, 61.9, 56.8, 14.6, 14.4; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{22}N_2NaO_5$ 369.1421; Found 369.1402.

Diethyl 1-((*tert*-butyldimethylsiloxy)(2-methoxyphenyl)methyl)hydrazine-1,2-dicarboxylate (9a)



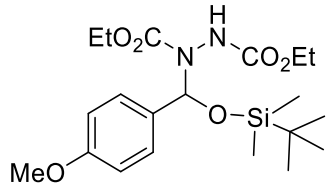
Colorless oil, 88% isolated yield (100 mg, 0.21 mmol). R_f = 0.5 (AcOEt/hexane = 1:2 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.05–6.92 (m, 2H), 6.83 (d, J = 8.0 Hz 1H), 6.19 (br s, 1H), 4.26–3.55 (m, 7H), 1.32–0.75 (m, 6H), 0.91 (s, 9H), 0.16–0.05 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5, 155.2, 129.4, 128.0, 126.9, 120.0, 10.3, 62.5, 61.5, 55.6, 25.9, 18.4, 14.7, 14.5, 14.0, -4.7, -5.2; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{34}N_2NaO_6Si$ 449.2078; Found 449.2092.

Diethyl 1-((*tert*-butyldimethylsiloxy)(3-methoxyphenyl)methyl)hydrazine-1,2-dicarboxylate (9b)



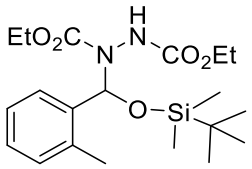
Colorless oil, 94% isolated yield (96 mg, 0.23 mmol). R_f = 0.6 (AcOEt/hexane = 1:2 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.22 (m, 1H), 7.04 (s, 2H), 6.82 (d, J = 8.8 Hz, 1H), 6.75 (br s, 1H), 6.18 (br s, 1H), 4.27–3.62 (m, 4H), 3.80 (s, 3H), 1,31–0.93 (m, 6H), 0.93 (s, 9H), 0.14 (br s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 155.3, 140.2, 128.8, 119.4, 114.1, 112.0, 80.8, 62.9, 61.7, 55.3, 25.8, 18.3, 14.6, 14.5, 14.0, -4.8, -5.2; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{34}N_2NaO_6Si$ 449.2078; Found 449.2077.

Diethyl 1-((*tert*-butyldimethylsiloxy)(4-methoxyphenyl)methyl)hydrazine-1,2-dicarboxylate (9c)



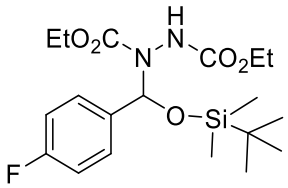
Colorless oil, 72% isolated yield (74 mg, 0.18 mmol). R_f = 0.6 (AcOEt/hexane = 1:2 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 5.2 Hz, 2H), 6.85 (d, J = 7.6 Hz, 2H), 6.73 (br s, 1H), 6.17 (br s, 1H), 4.26–3.64 (m, 4H), 3.80 (s, 3H), 1.31–0.91 (m, 6H), 0.91 (s, 9H), 0.13–0.11 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 155.4, 130.8, 128.2, 113.2, 81.0, 62.8, 61.7, 55.3, 25.9, 18.3, 14.6, 14.5, 14.1, -4.8, -5.2; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{34}N_2NaO_6Si$ 449.2078; Found 449.2082.

Diethyl 1-((*tert*-butyldimethylsiloxy)(o-tolyl)methyl)hydrazine-1,2-dicarboxylate (9d)



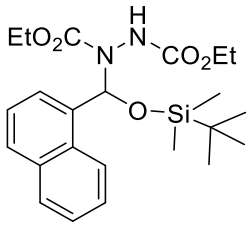
For 48 h. Colorless oil, 98% isolated yield (97 mg, 0.24 mmol). R_f = 0.5 (AcOEt/hexane = 1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.17–710 (m, 3H), 6.89 (br s, 1H), 6.34–6.20 (m, 2H), 4.26–3.50 (m, 4H), 2.38–2.34 (m, 3H), 1.30–0.84 (m, 6H), 0.91 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 136.2, 130.1, 129.7, 128.2, 127.2, 125.5, 78.8, 62.8, 61.6, 25.8, 19.0, 18.2, 14.6, 14.4, 13.8, -4.8, -5.2; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{34}N_2NaO_5Si$ 433.2129; Found 433.2119.

Diethyl 1-((*tert*-butyldimethylsiloxy)(4-fluorophenyl)methyl)hydrazine-1,2-dicarboxylate (9e)



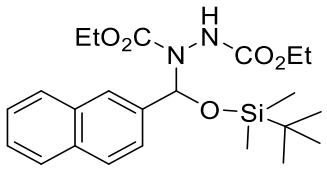
For 48 h. Colorless oil, 98% isolated yield (98 mg, 0.24 mmol). R_f = 0.5 (AcOEt/hexane = 1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 2H), 7.01 (t, J = 8.4 Hz, 2H), 6.76 (br s, 1H), 6.17 (br s, 1H), 4.26–3.66 (m, 4H), 1.31–0.92 (m, 6H), 0.92 (s, 9H), 0.13-0.11 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, $J_{C\text{-}F}$ = 245.0 Hz), 155.5, 134.6, 128.6, 114.7, 80.4, 62.9, 61.7, 25.8, 18.2, 14.6, 14.4, 14.1, -4.9, -5.3; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{31}FN_2NaO_5Si$ 437.1878; Found 437.1863.

Diethyl 1-((*tert*-butyldimethylsiloxy)(naphthalen-1-yl)methyl)hydrazine-1,2-dicarboxylate (9f)



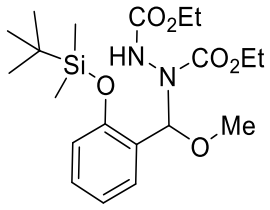
For 72 h. Colorless oil, 99% isolated yield (100 mg, 0.24 mmol), as a mixture of rotamer. R_f = 0.5 (AcOEt/hexane = 1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (br s, 1H), 7.89–7.78 (m, 3H), 7.55–7.45 (m, 4H), 6.26 (br s, 1H), 4.29–2.90 (br m, 4H), 1.29–0.94 (m, 5H), 0.94 (s, 9H), 0.21–0.10 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.1, 155.6, 133.7, 133.3, 131.0, 129.1, 128.9, 128.5, 126.3, 125.6, 125.5, 125.3, 125.0, 123.6, 78.1, 62.9, 61.5, 61.2, 25.9, 18.2, 14.7, 12.8, -4.7, -5.1; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{34}N_2NaO_5Si$ 469.2129; Found 469.2124.

Diethyl 1-((*tert*-butyldimethylsiloxy)(naphthalen-2-yl)methyl)hydrazine-1,2-dicarboxylate (9g)



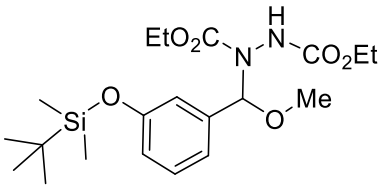
Colorless oil, 67% isolated yield (72 mg, 0.16 mmol). R_f = 0.5 (AcOEt/hexane = 1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (s, 1H), 7.83–7.80 (m, 3H), 7.56 (s, 1H), 7.48–7.46 (m, 2H), 6.94 (br s, 1H), 6.23 (br s, 1H), 4.29–3.36 (m, 4H), 1.33–0.70 (m, 6H), 0.95 (s, 9H), 1.84–1.51 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.6, 136.2, 133.4, 133.0, 128.4 127.8, 127.4, 126.2, 126.1, 125.9, 124.9, 81.2, 62.9, 61.7, 25.9, 18.4, 14.7, 14.4, 13.7, -4.7, -5.1; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{34}N_2NaO_5Si$ 469.2129; Found 469.2133.

Diethyl 1-((2-(*tert*-butyldimethylsiloxy)phenyl)(methoxy)methyl)hydrazine-1,2-dicarboxylate (11)



Colorless oil, 91% isolated yield (93 mg, 0.22 mmol). R_f = 0.4 (AcOEt/hexane = 1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.06–6.93 (m, 2H), 6.83 (d, J = 8.0 Hz, 1H), 6.19 (br s, 1H), 4.26–3.54 (m, 4H), 3.82 (s, 3H), 1.32–0.81 (m, 6H), 0.91 (s, 9H), 0.16–0.10 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 156.2, 155.2, 129.4, 128.1, 126.9, 120.0, 110.4, 109.9, 62.5, 61.5, 55.6, 25.8, 18.2, 14.7, 14.5, 14.0, -4.73, -5.22; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{34}N_2NaO_6Si$ 449.2078; Found 449.2112.

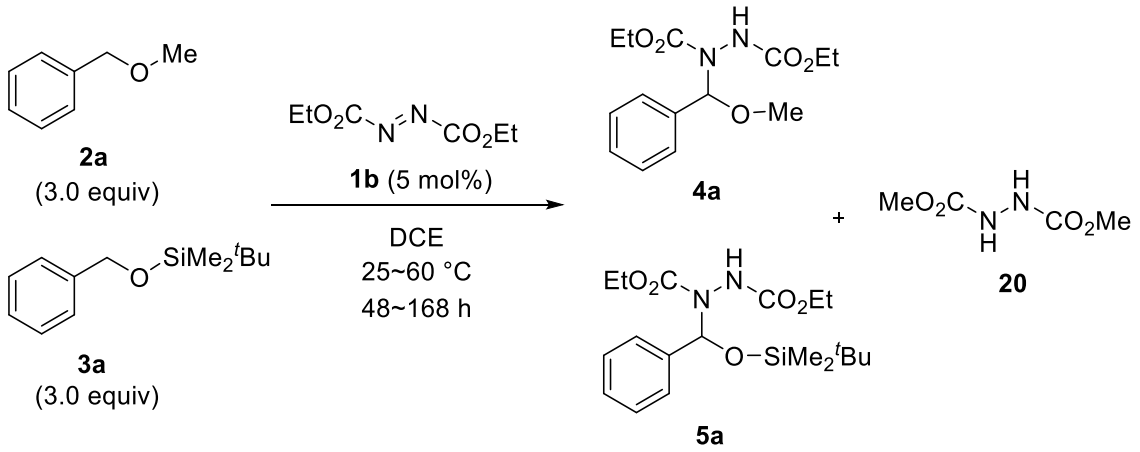
Diethyl 1-((3-(*tert*-butyldimethylsiloxy)phenyl)(methoxy)methyl)hydrazine-1,2-dicarboxylate (13)



Colorless oil, 52% isolated yield (53 mg, 0.12 mmol). R_f = 0.5 (AcOEt/hexane = 1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 7.05 (s, 2H), 6.51 (d, J = 7.6 Hz, 1H), 6.75 (br s, 1H), 6.18 (br s, 1H), 4.27–3.63 (m, 4H), 3.80 (s, 3H), 1.38–0.93 (m, 6H), 0.93 (s, 9H), 0.14–0.10 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 155.5, 140.3, 128.8, 119.3, 118.8, 114.1, 112.0, 62.8, 61.7, 25.8, 18.3, 14.6, 14.5, 14.0, -5.1, -5.2; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{34}N_2NaO_6Si$ 449.2078; Found 449.2102.

4. Reaction optimization for selective amination of benzyl ethers

Table S1. The effect of temperature and dark atmosphere[a]

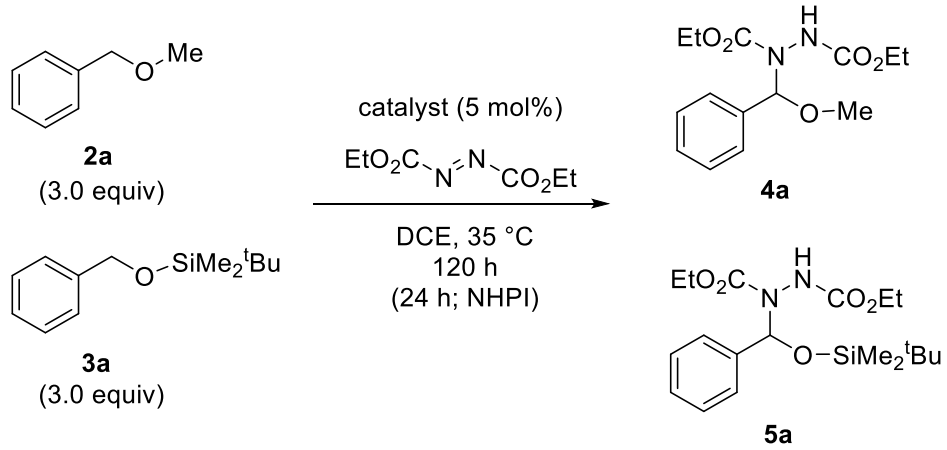


Entry	Temp (°C)	Time (h)	Dark atomosphere[b]	Conversion of DEAD[c] (%)	Yield[c] (%)		
					4a	**5a**	**20**
1	25	168	-	100	80	2	14
2	25	168	○	65	59	<1	0
3	35	120	○	100	86	4	<1
4	60	48	○	100	66	2	21

(a) The reactions were performed in the presence of **2a** (0.3 mmol), **3a** (0.3 mmol), **1b** (5 mol%), DEAD (0.1 mmol) in DCE (0.6 mL) at 25~60 °C for 48~168 h. (b) The vial was wrapped with aluminum foil. (c) The conversion and yield were determined by ^{1}H NMR spectroscopy using TCE as an internal standard.

5. Procedure for selective amination of benzyl ethers

(a) Typical procedure for selective amination of two different benzyl ethers (table 1)

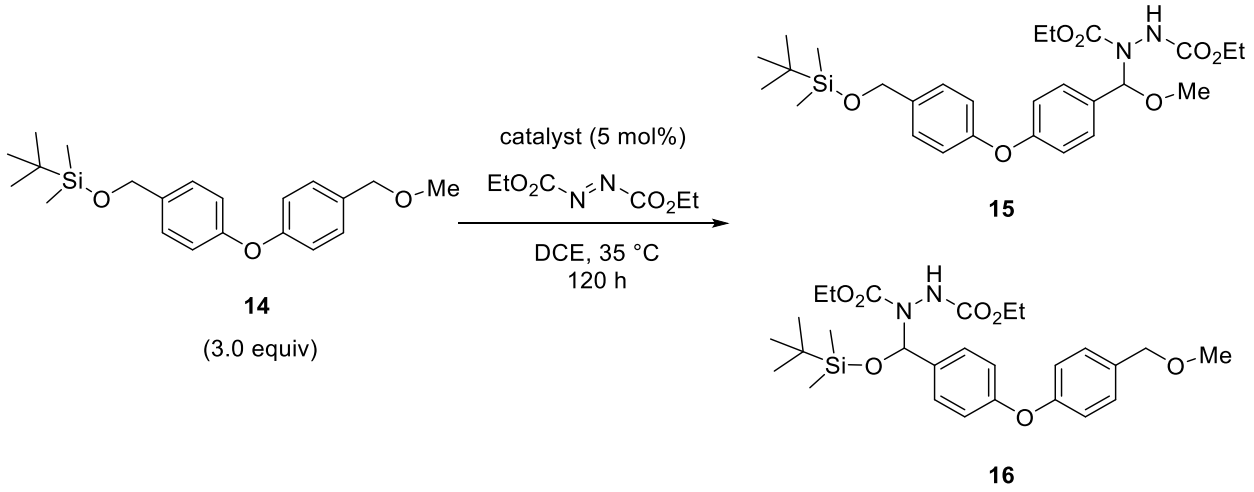


A screw vial with a magnetic stir bar was charged with benzyl methyl ether **2a** (37 mg, 0.30 mmol), benzyl *tert*-butyldimethylsilyl ehter **3a** (67 mg, 0.30 mmol) in anhydrous1,2-dichroloethane (DCE, 0.50 mL) under argon atmosphere. To the mixture was added the catalyst (5 mol%) and a solution of DEAD (17 mg, 0.10 mmol) in anhydrous DCE (0.10 mL) at room temperature. The vial was sealed and wrapped with aluminum foil and the mixture was stirred at 35 °C for 120 h. After the reaction, the yield and ratio were determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane (TEC) as an internal standard. In order to obtain more accurate data, the two products were roughly separated by column chromatography (eluted with AcOEt/hexane) and the NMR yields were measured again. It was confirmed that the yields in both cases were almost the same. As a result, the latter method was used for the subsequent measurement of the NMR yields.

For entry 1 (using NHIP as catalyst), the reaction mixture was stirred for 24 h.

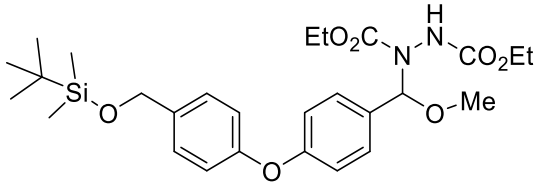
For entry 7, the residue was purified by flash column chromatography on silica gel (eluted with AcOEt/hexane = 1:3) to afford **4a** in 82% isolated yield (24 mg, 0.082 mmol).

(b) Intramolecular site-selective amination



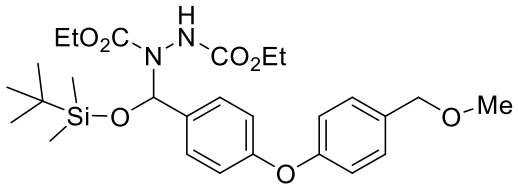
To a solution of **14** (120 mg, 0.30 mmol) and catalyst (5 mol%) in anhydrous DCE (0.50 mL) was added a solution of DEAD (17 mg, 0.10 mmol) in anhydrous DCE (0.10 mL) under argon atmosphere. The vial was sealed, wrapped with aluminum foil and the mixture was stirred at 35 °C for 120 h. The reaction mixture was concentrated under reduced pressure, and analyzed by ^{1}H NMR for the determination of NMR yield using TCE as internal standard. The products **15** and **16** were partially separated by flash column chromatography on silica gel (eluted with AcOEt/hexane = 1:3) for the spectra data in each product.

Diethyl 1-((4-(4-(((*tert*-butyldimethylsiloxy)methyl)phenoxy)phenyl)(methoxy)methyl)hydrazine-1,2-dicarboxylate (15)



Colorless oil. R_f = 0.3 (AcOEt/hexane =1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.25 (m, 4H), 6.97–6.95 (m, 4H), 6.38–5.64 (br m, 2H), 4.72 (s, 2H), 4.29–3.90 (m, 4H), 3.61–3.44 (m, 3H), 1.31–1.19 (m, 6H), 0.94 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 156.0, 136.8, 128.7, 128.0, 127.7, 119.2, 118.3, 87.7, 64.7, 63.0, 62.0, 56.9, 26.1, 18.6, 14.5, -5.1; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{40}N_2NaO_7Si$ 555.2477; Found 555.2476.

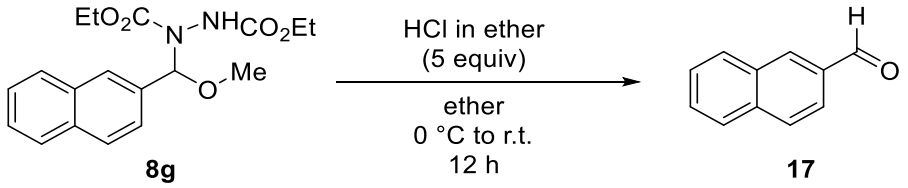
Diethyl 1-((*tert*-butyldimethylsiloxy)(4-(4-(methoxymethyl)phenoxy)phenyl)methyl)hydrazine-1,2-dicarboxylate (16)



Colorless oil. R_f = 0.3 (AcOEt/hexane = 1:3 as eluent). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.96 (t, J = 9.2 Hz, 4H), 6.76 (br s, 1H), 4.42 (s, 2H), 4.27–3.71 (br m, 4H), 3.39 (s, 3H), 1.31–0.92 (m, 6H), 0.92 (s, 9H), 0.14–0.10 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 129.5, 128.5, 128.1, 119.1, 118.3, 118.0, 117.9, 74.4, 62.9, 61.8, 58.2, 25.9, 18.4, 14.7, 0.14, -4.7, -5.1; HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{27}H_{40}N_2NaO_7Si$ 555.2497; Found 555.2476.

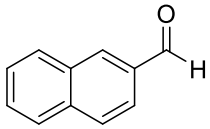
5. Subsequent transformation of amination product

(a)



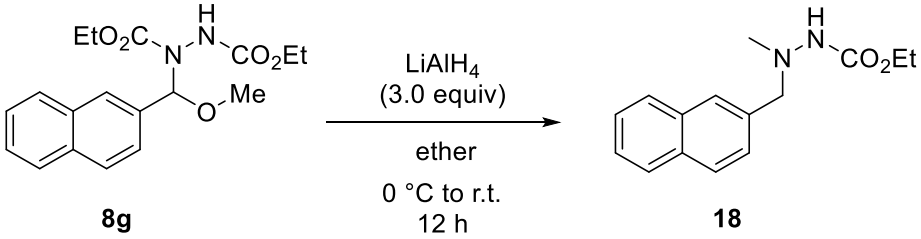
To a solution of **8g** (100 mg, 0.29 mmol) in Et_2O (5 mL) was added an ethereal solution of hydrogen chloride (1 M in Et_2O, 1.5 mL, 1.5 mmol) at 0 °C and the rection mixture was stirred at room temperature for 12 h. The mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel (eluted with CH_2Cl_2/hexane = 1:2) to afford 2-naphthaldehyde **17** in 96% yield.

2-Naphthaldehyde (17)[18]



White solid, 96% isolated yield (44 mg, 0.28 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H), 8.35 (s, 1H), 8.03–7.90 (m, 4H), 7.67–7.58 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 136.5, 134.6, 134.2, 132.7, 129.6, 129.2, 128.2 127.2, 122.8.

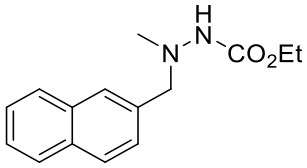
(b)



To a solution of **8g** (110 mg, 0.32 mmol) in Et_2O (5 mL) was added a suspension of lithium aluminium hydride (36 mg, 0.96 mmol) in Et_2O (2 mL) slowly at 0 °C. After stirring at room temperature for 12 h, the reaction was quenched with NH_4Cl aq. The reaction mixture was extracted with AcOEt three times, and the combined organic layer was dried over Na_2SO_4 and

concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluted with AcOEt/hexane = 1:2) to afford product **18** in 72% yield.

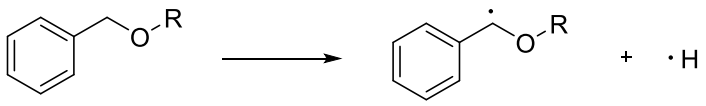
Ethyl 2-methyl-2-(naphthalen-2-ylmethyl)hydrazine-1-carboxylate (18)



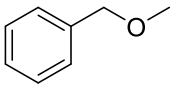
Colorless oil, 72% isolated yield (60 mg, 0.23 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.81 (m, 3H), 7.75 (s, 1H), 7.51–7.45 (m, 3H), 5.67 (br s, 1H), 4.18–4.07 (m, 4H), 2.69 (s, 3H), 1.17 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 133.9, 133.3, 133.0, 128.2, 128.1, 127.9, 127.7, 127.5, 126.1, 125.9, 63.2, 61.0, 45.1, 14.6; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2O_2$ 259.1441; Found 259.1438.

7. Computational Studies

The bond dissociation energy values at benzylic C–H bonds of **2a** and **3a** were calculated by the Gaussian 16 software package.[19] All DFT calculations such as geometry optimizations, frequency calculations and subsequent energy calculations were carried out using RB3LYP[20]/6-311++G(d,p)[21] and ROB3LYP/6-311++G(d,p) level of theory.



Cartesian coordinates of optimized structures

2a 

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C	2.61924300	-0.23739500	0.35023300
C	1.79261300	-1.31305200	0.02109000
C	0.47612200	-1.08967500	-0.37207200
C	-0.03686600	0.21110700	-0.43557400
H	0.40726300	2.29341900	-0.13462500
H	2.75187500	1.90134400	0.54874700
H	3.64524000	-0.41197800	0.65430800
H	2.17729000	-2.32600000	0.06763800
H	-0.16811500	-1.92523500	-0.62330100
C	-1.46381300	0.44623500	-0.89469400
H	-1.72623800	1.50576400	-0.75962600
H	-1.55775900	0.21451000	-1.95927800

C	-2.63744600	-0.06125100	1.11050800
H	-3.40701500	-0.74032500	1.47809000
H	-1.72799300	-0.19024500	1.70958300
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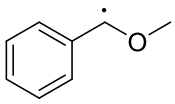
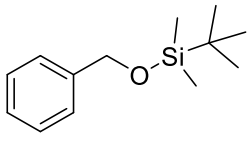
O	-2.42305000	-0.38424200	-0.25397700

2a_radical 

C	0.52016200	-1.08349800	-0.00006900
C	1.88192700	-1.34280000	0.00010300
C	2.81206800	-0.29849500	0.00016600
C	2.35601500	1.02503700	0.00006500
C	0.99971700	1.30251600	-0.00010800
C	0.04187200	0.25383700	-0.00017700
H	-0.19439000	-1.89672500	-0.00009800
H	2.22806700	-2.37101200	0.00017400
H	3.87463600	-0.51112700	0.00029400
H	3.06923600	1.84228200	0.00013200
H	0.65788700	2.33267100	-0.00018900
C	-1.33577800	0.56016500	-0.00034000
H	-1.70576700	1.57979900	-0.00057900
C	-3.61409700	-0.02788400	0.00078600
H	-4.21277900	-0.93718400	0.00084400
H	-3.84255200	0.56027000	0.89629900
H	-3.84424100	0.56124700	-0.89366300
O	-2.25017800	-0.43668500	-0.00072100

3a 

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C	-4.67302400	-0.92631100	0.18009900
C	-4.99251000	0.30901100	-0.38550700
C	-3.97194100	1.19972800	-0.70786800
C	-2.63844200	0.86334100	-0.46820000
C	-2.31369600	-0.36867000	0.09792600
H	-3.10357800	-2.22484600	0.85892300
H	-5.45992500	-1.62776400	0.43494600
H	-6.02773300	0.57175900	-0.57226900
H	-4.21126000	2.16146200	-1.14876300
H	-1.84029000	1.55027600	-0.71773600
O	0.02800700	0.24512000	-0.01428000
C	-0.87711400	-0.76853800	0.37268700
H	-0.65825000	-1.69631300	-0.17360500
H	-0.77072300	-0.99592400	1.44253700
Si	1.60655100	0.52186600	0.49518200
C	2.82988900	-0.48508100	-0.58745700
C	1.77514100	0.06453300	2.31850400
H	1.02932100	0.59581000	2.91793400
H	1.65226800	-1.00595100	2.50460800
H	2.76098200	0.35081800	2.69732800
C	1.85130200	2.37013100	0.26360300
H	1.64973400	2.67154000	-0.76759400
H	1.16462200	2.92352800	0.91063900

H	2.86960100	2.68194900	0.51349200
C	2.66020400	-0.08403700	-2.06836400
H	3.32970200	-0.67960200	-2.70198400
H	1.63720400	-0.24912600	-2.41824500
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C	2.55763800	-1.99799900	-0.44724500
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H	2.66326900	-2.34390300	0.58569700
H	1.55489900	-2.26599000	-0.79240300
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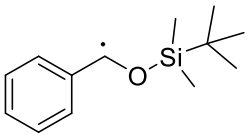
3a_radical 

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C	-2.22718500	-0.28496100	-0.18983500
H	-2.97433700	-1.17244300	-2.02186900
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H	-1.84868600	0.70701600	1.69310500
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C	2.53438600	0.87992800	-0.42900800
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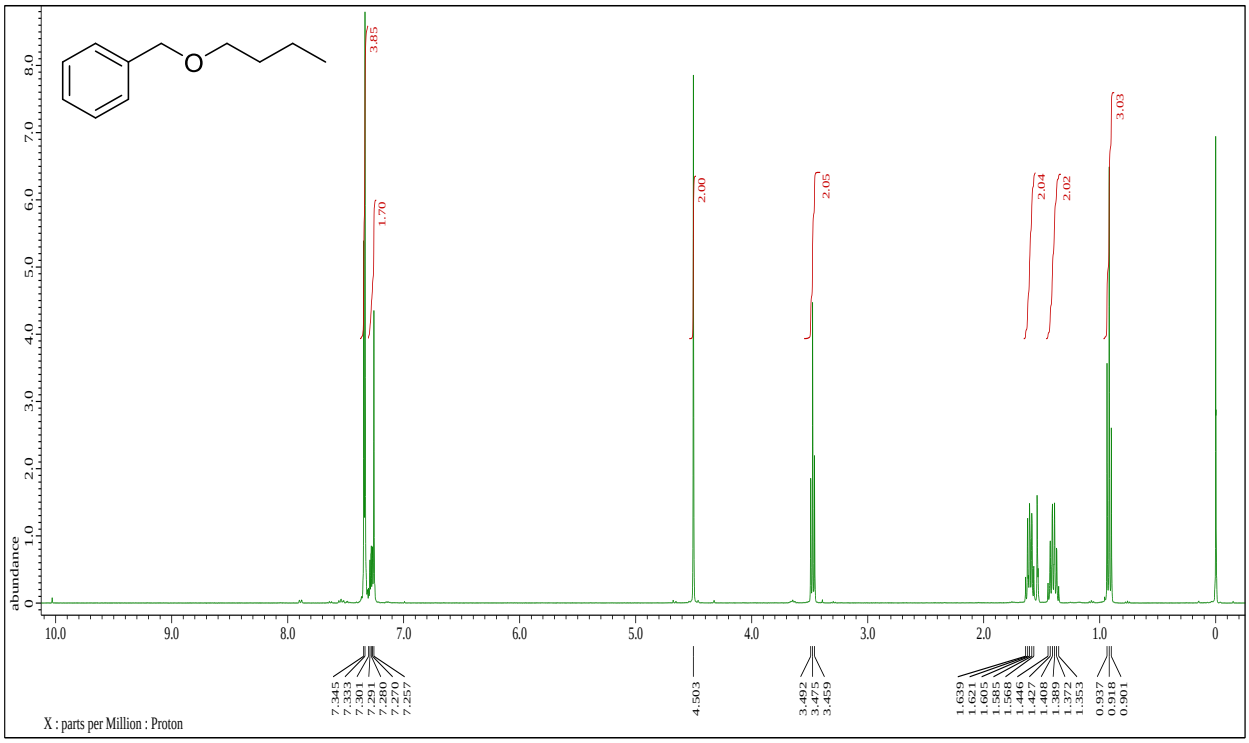
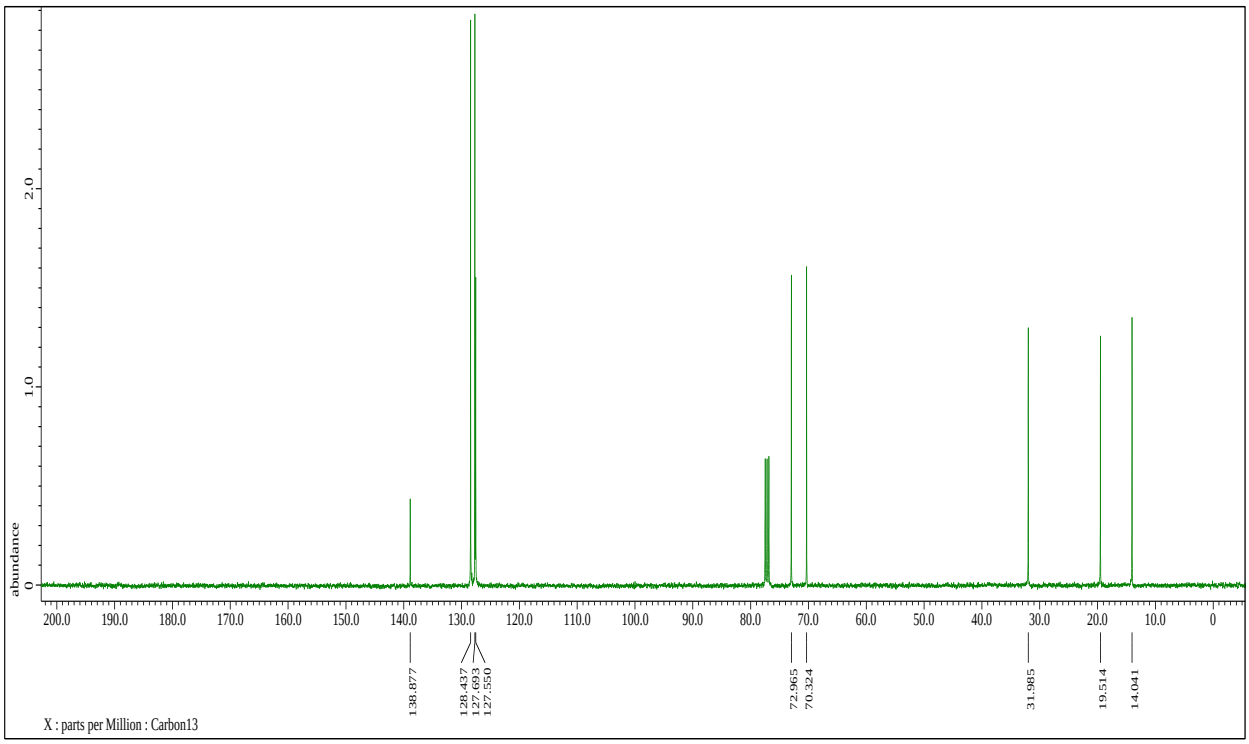
8. ^{1}H and ^{13}C NMR spectrua

Benzyl butyl ether (2b)

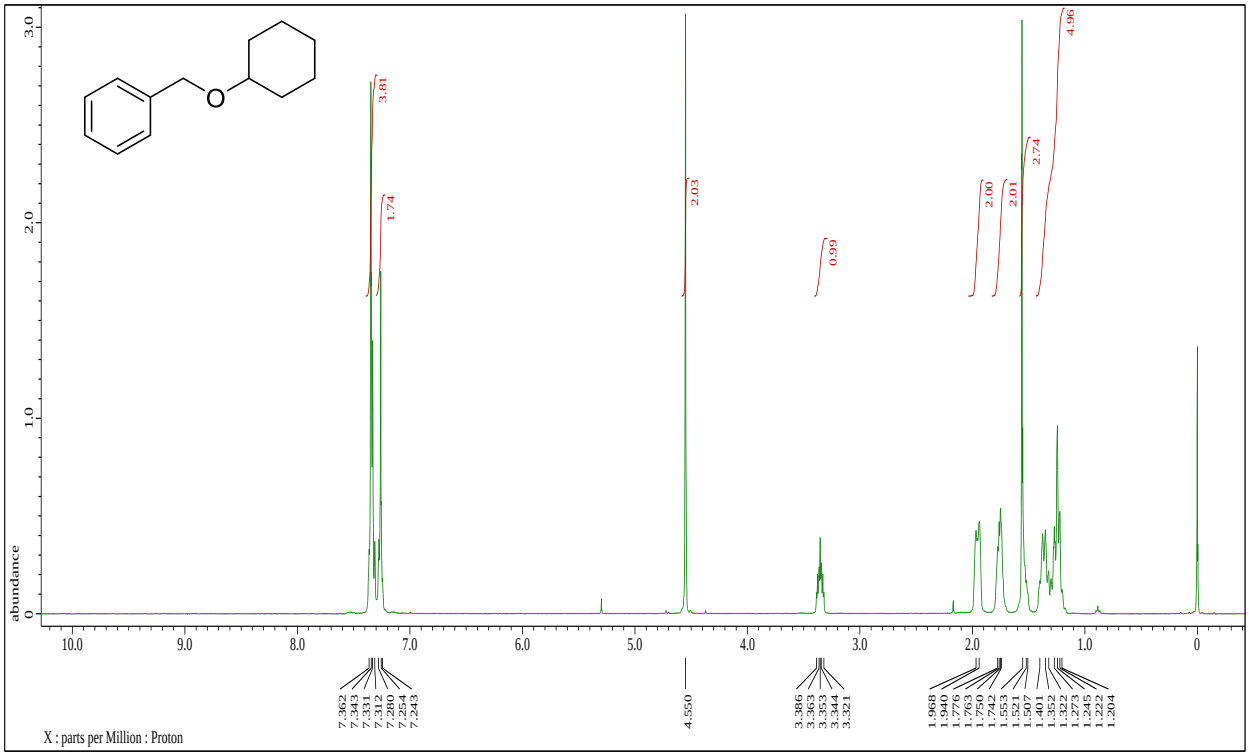


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2b**

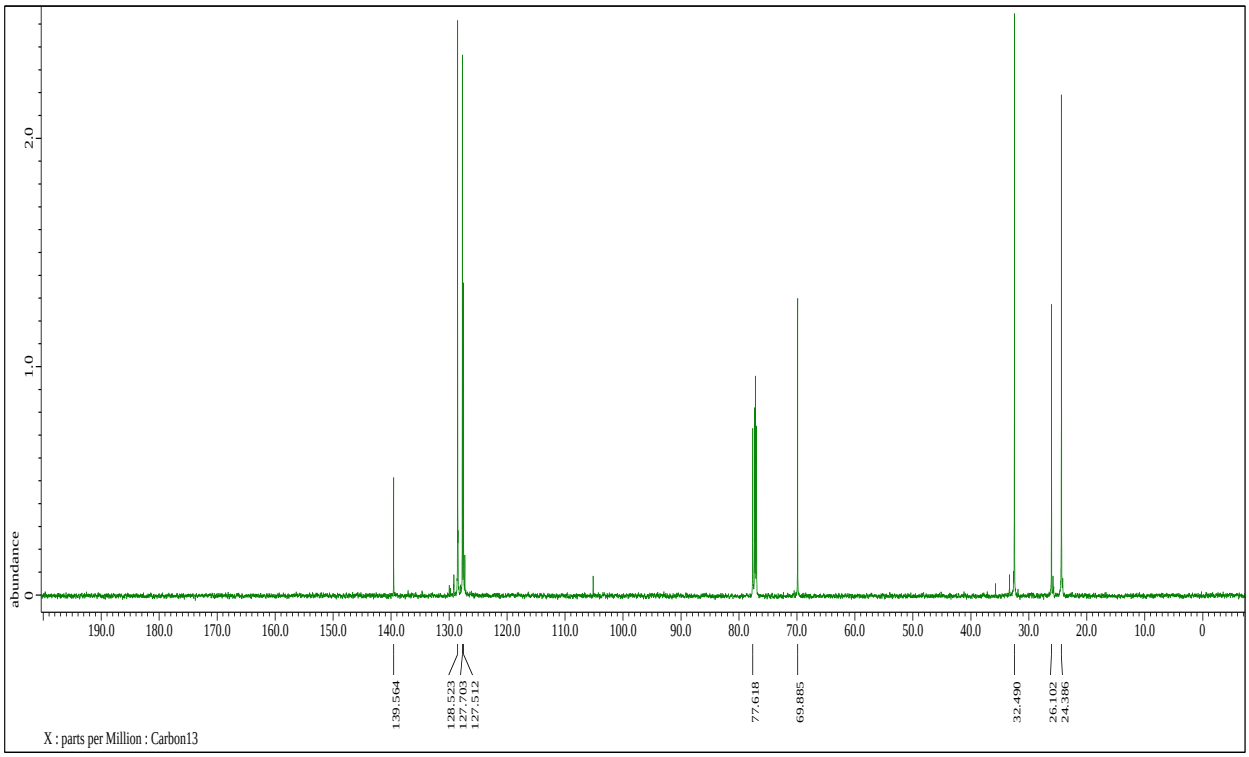


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2b**

Benzyl cyclohexyl ether (2c)

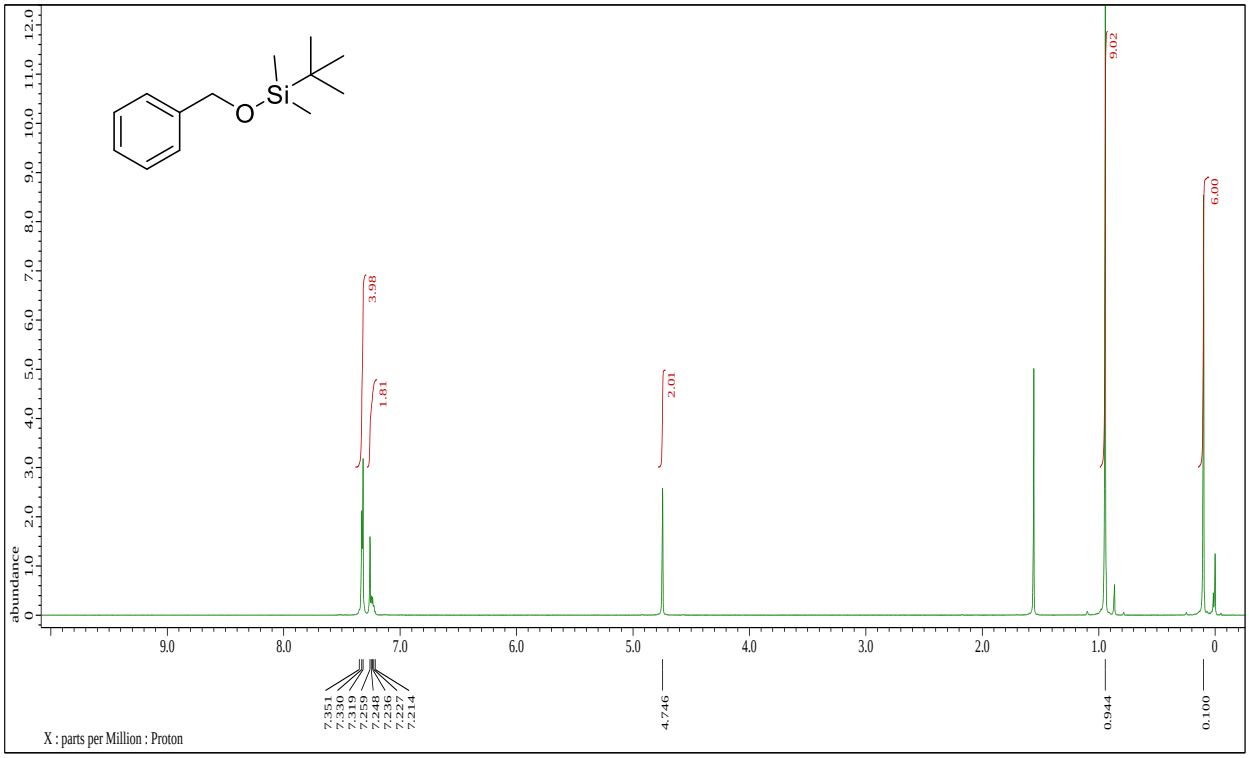


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2c**

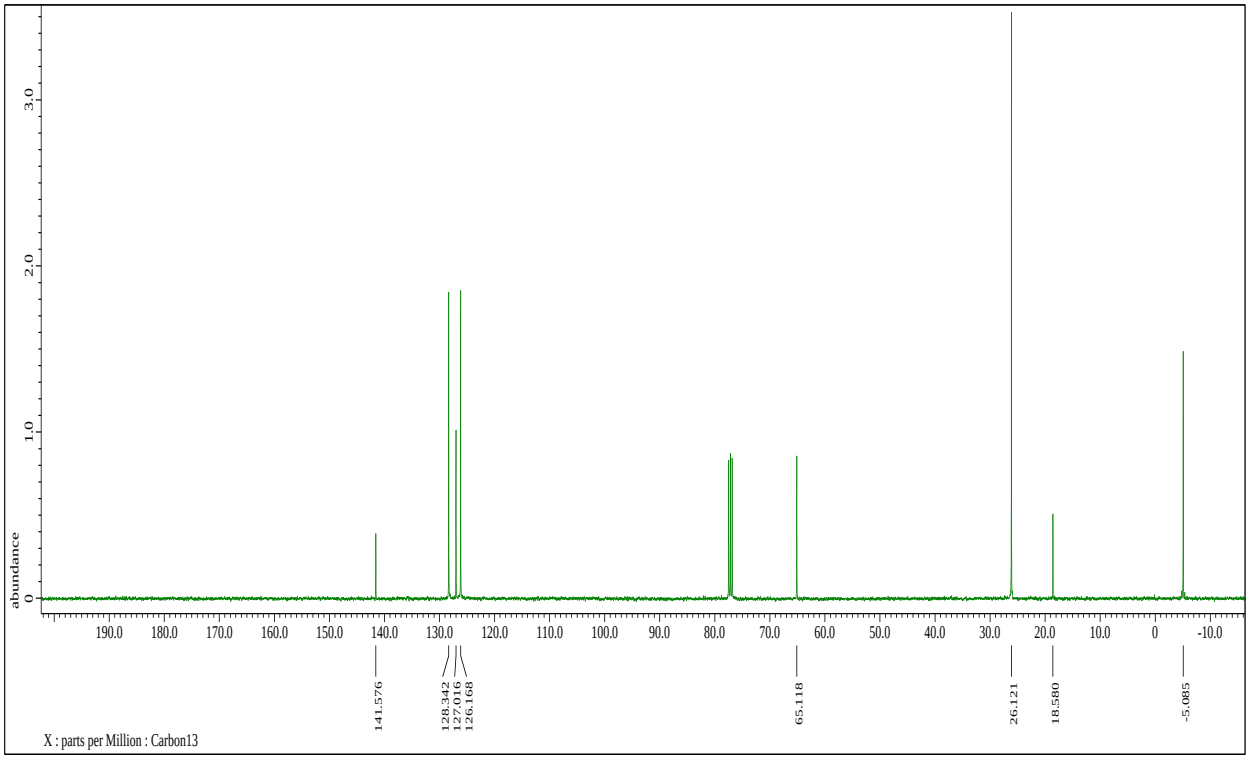


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2c**

Benzyl *tert*-butyldimethylsilyl ether (3a)

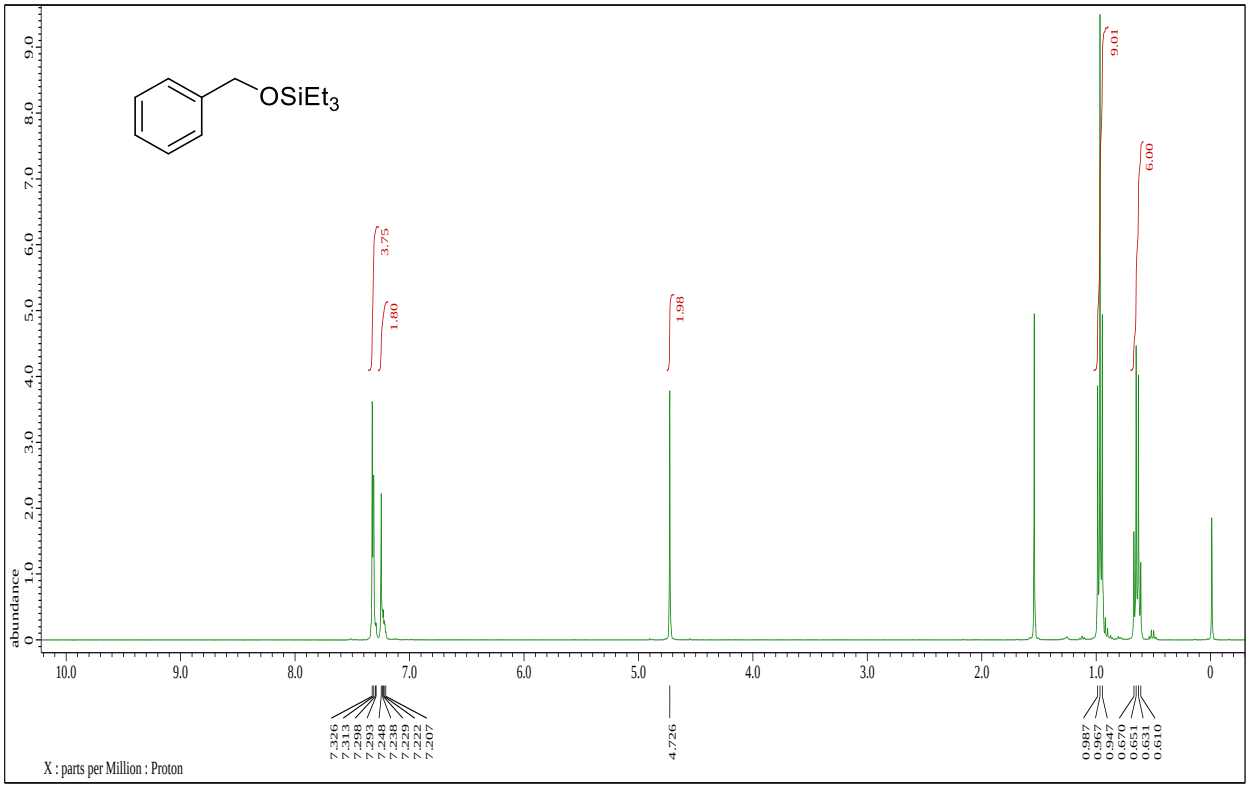


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3a**

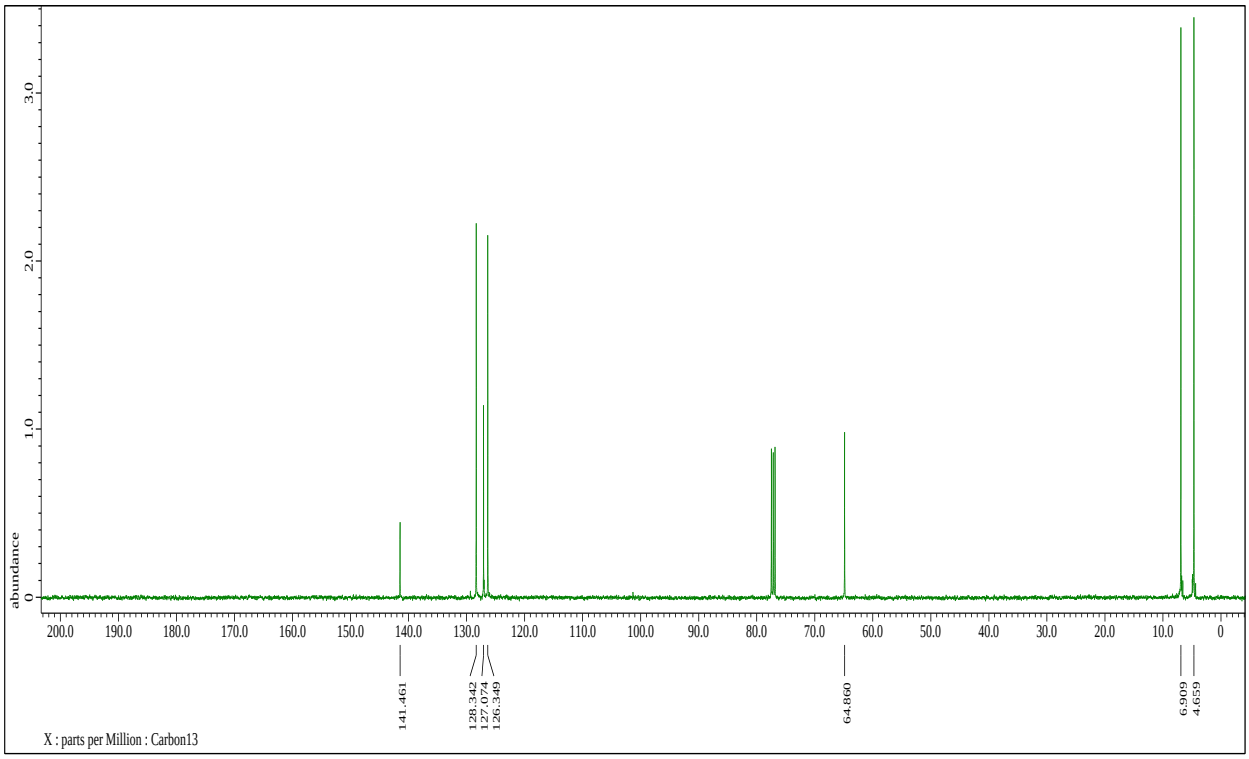


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3a**

Benzyl triethylsilyl ether (3b)

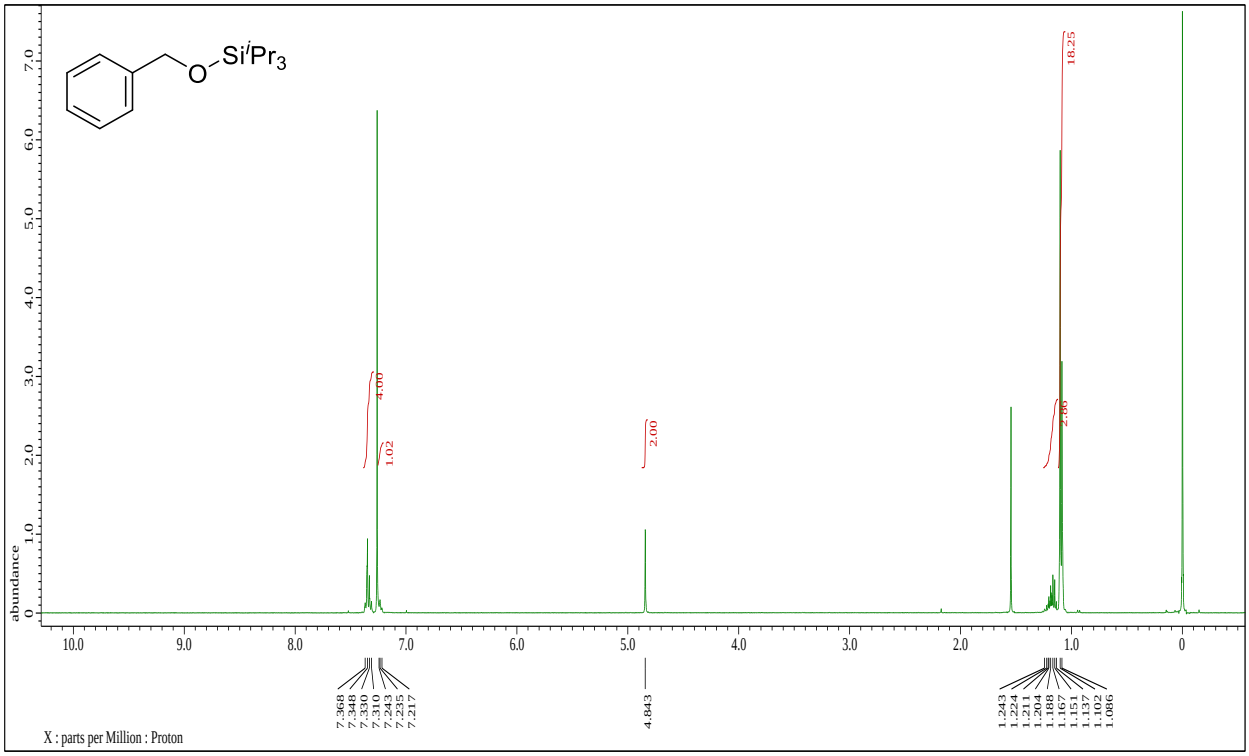


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3b**

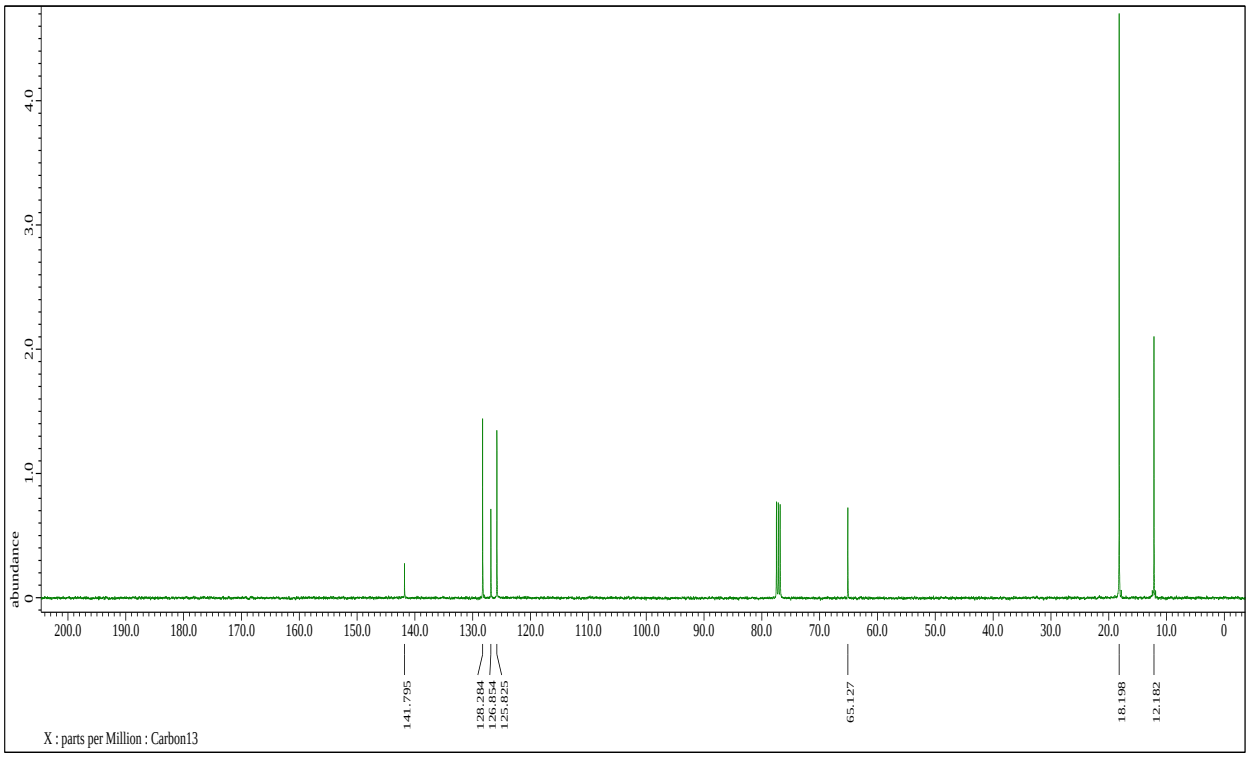


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3b**

Benzyl triisopropylsilyl ether (3c)

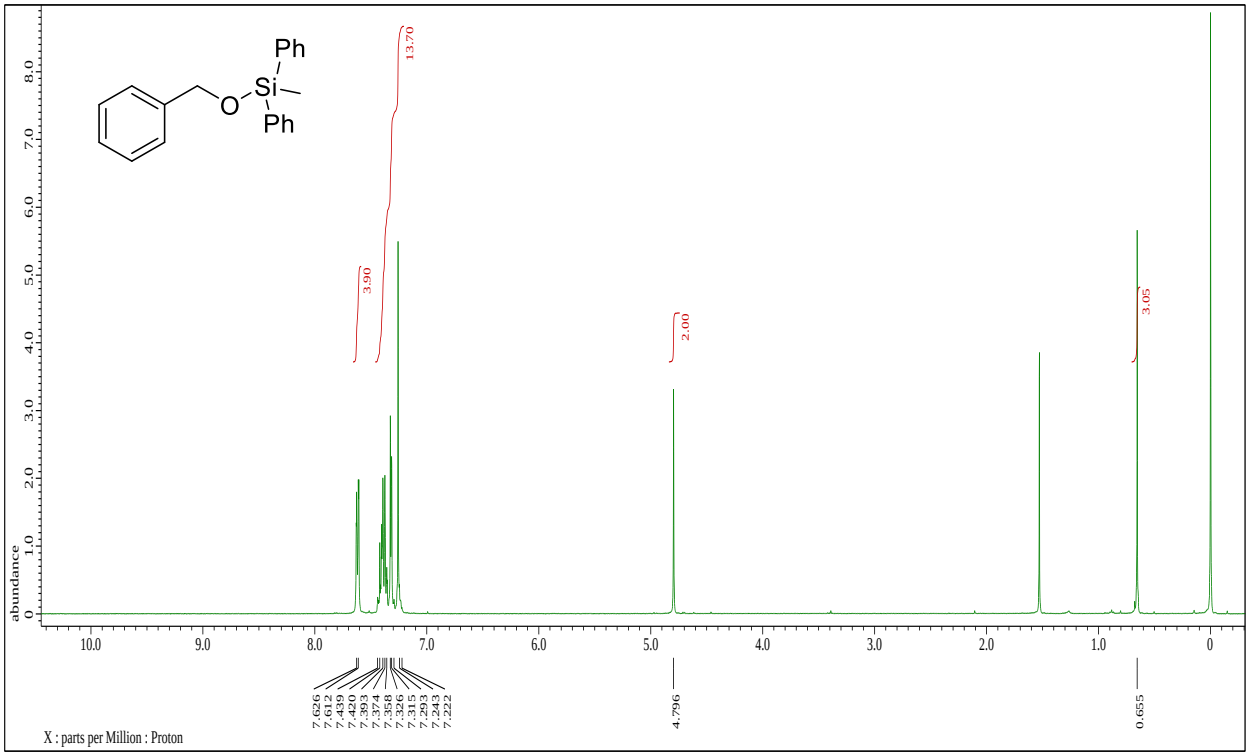


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3c**

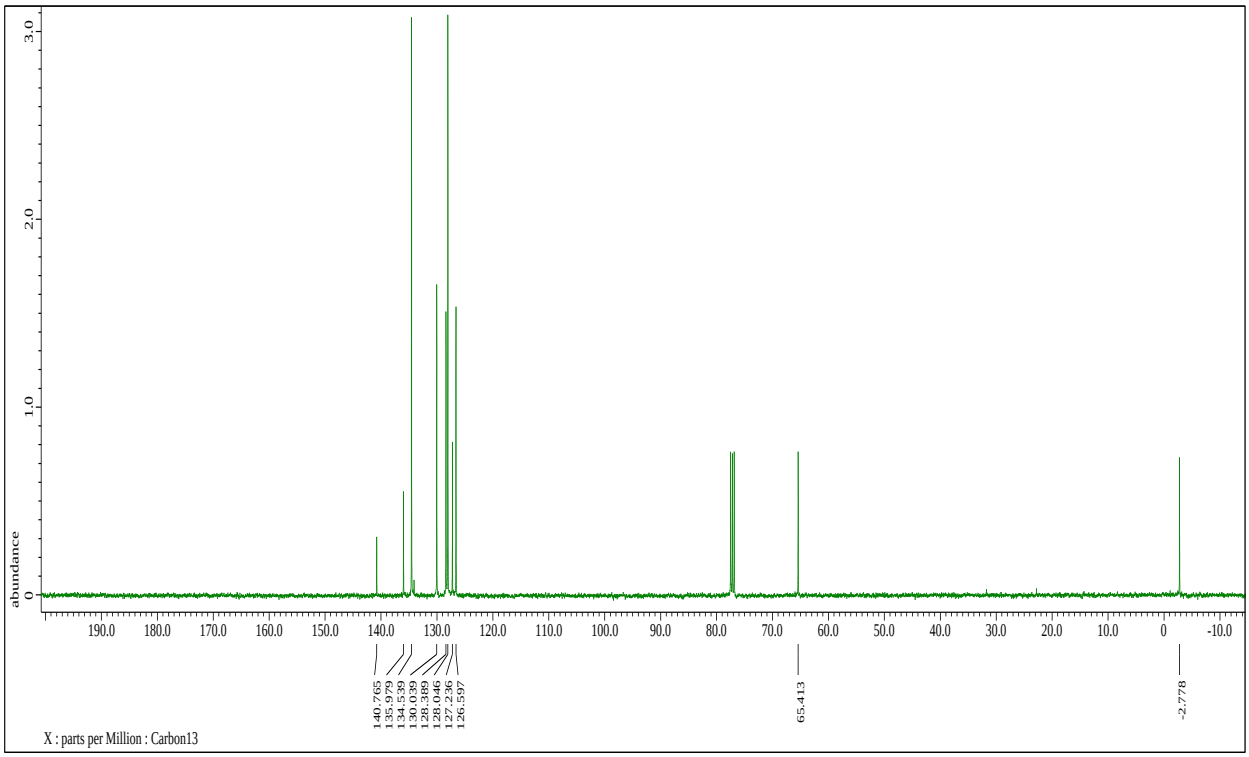


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3c**

Benzyl diphenylmethylsilyl ether (3d)

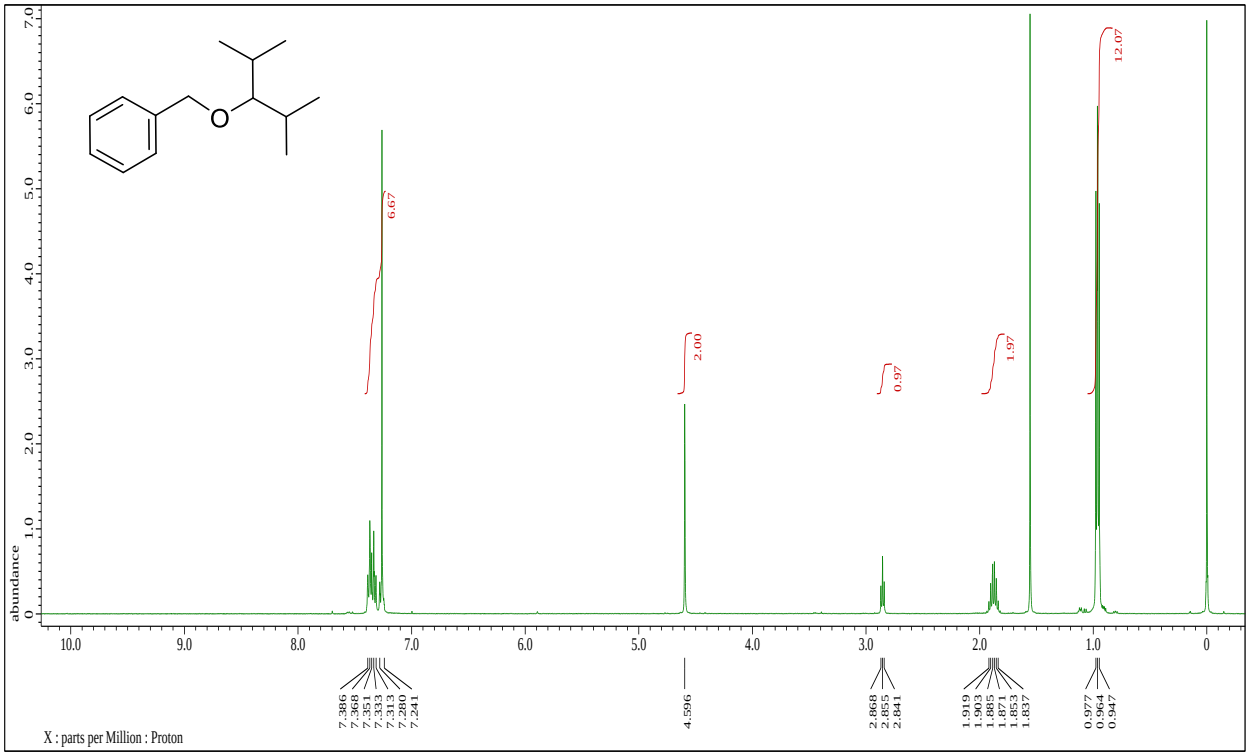


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3d**

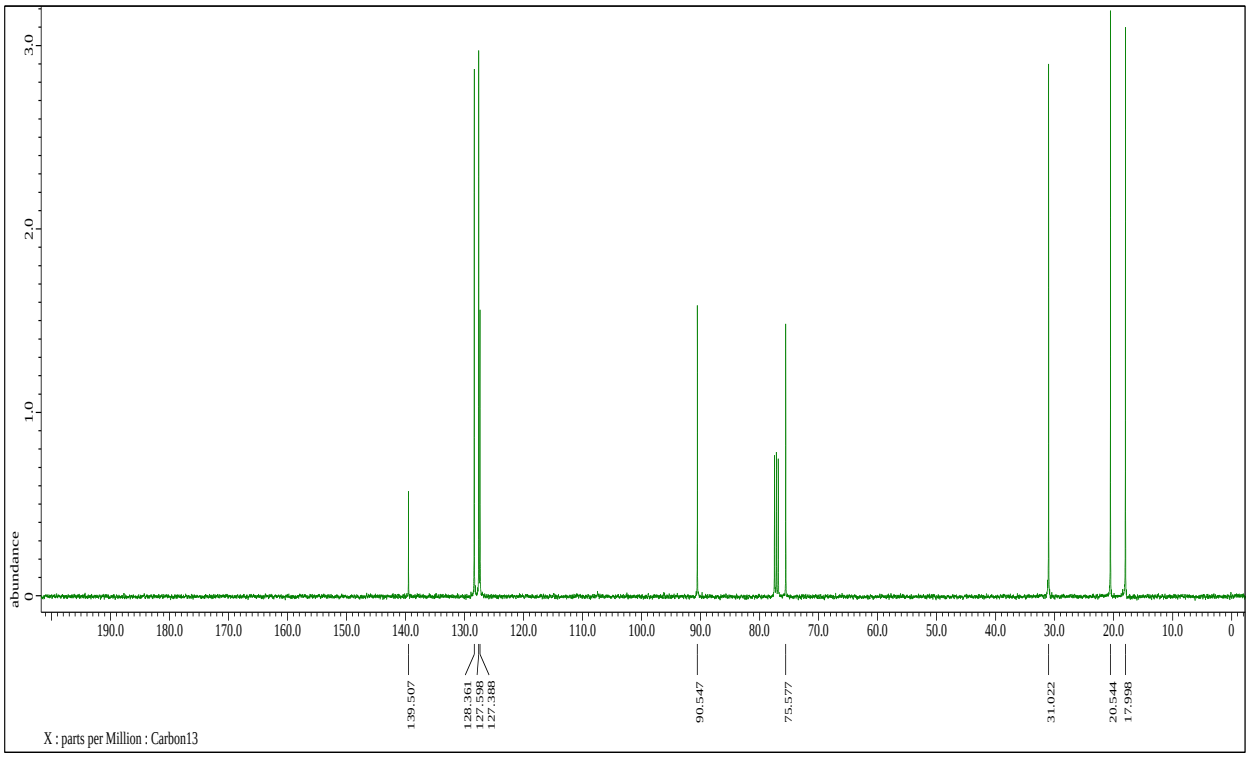


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3d**

Benzyl 2,4-dimethyl-3-pentyl ether (3e)

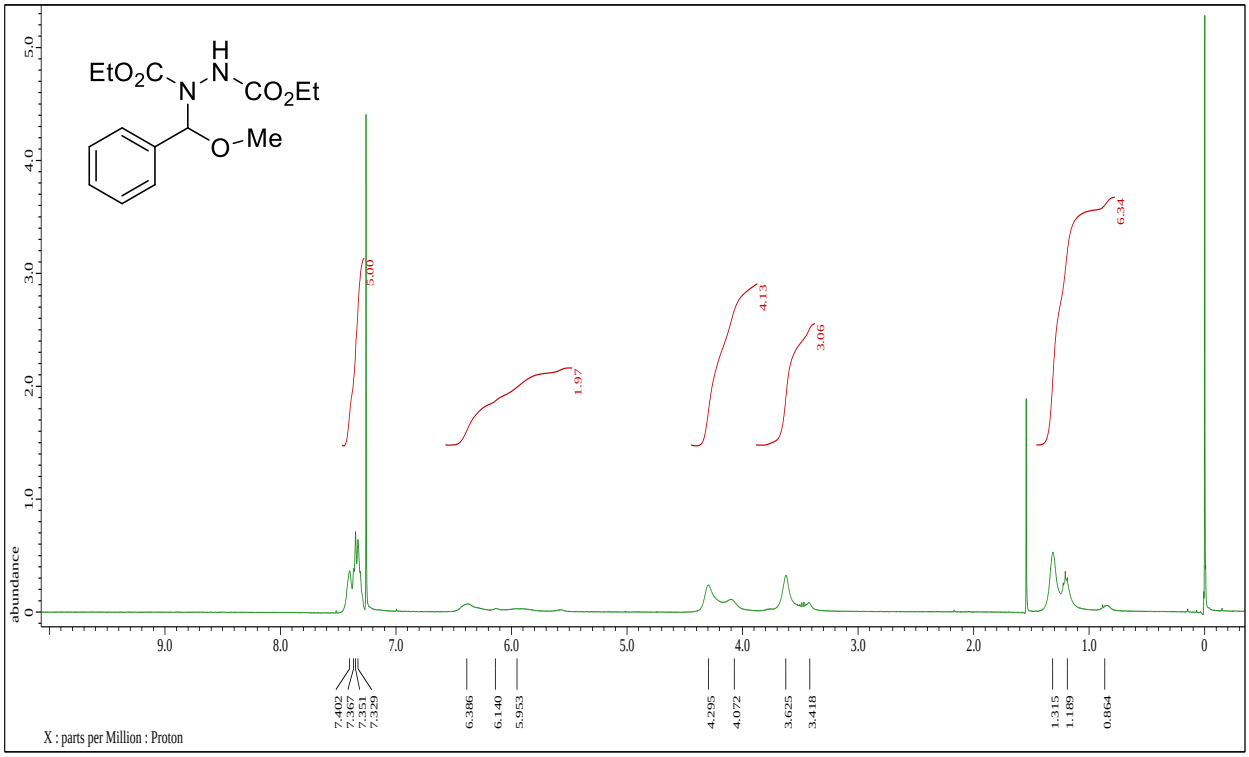


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3e**

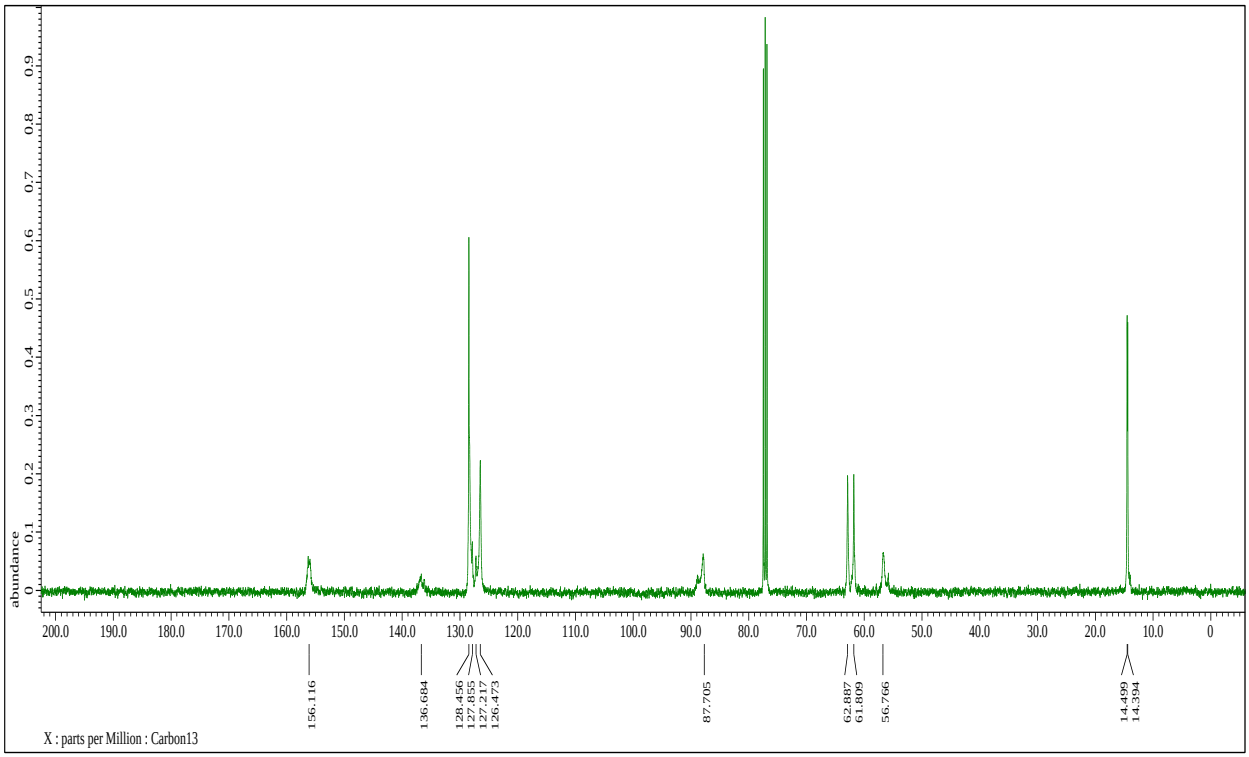


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3e**

Diethyl 1-(methoxy(phenyl)methyl)hydrazine-1,2-dicarboxylate (4a)

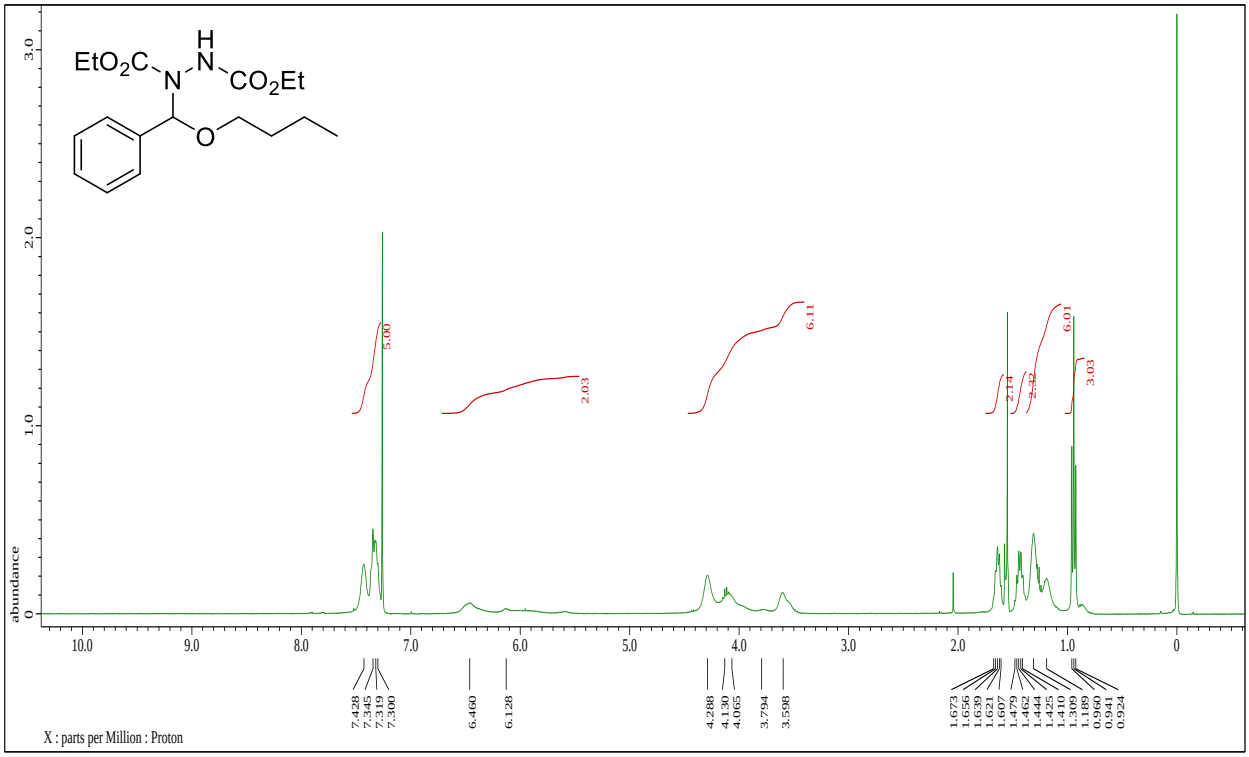


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4a**

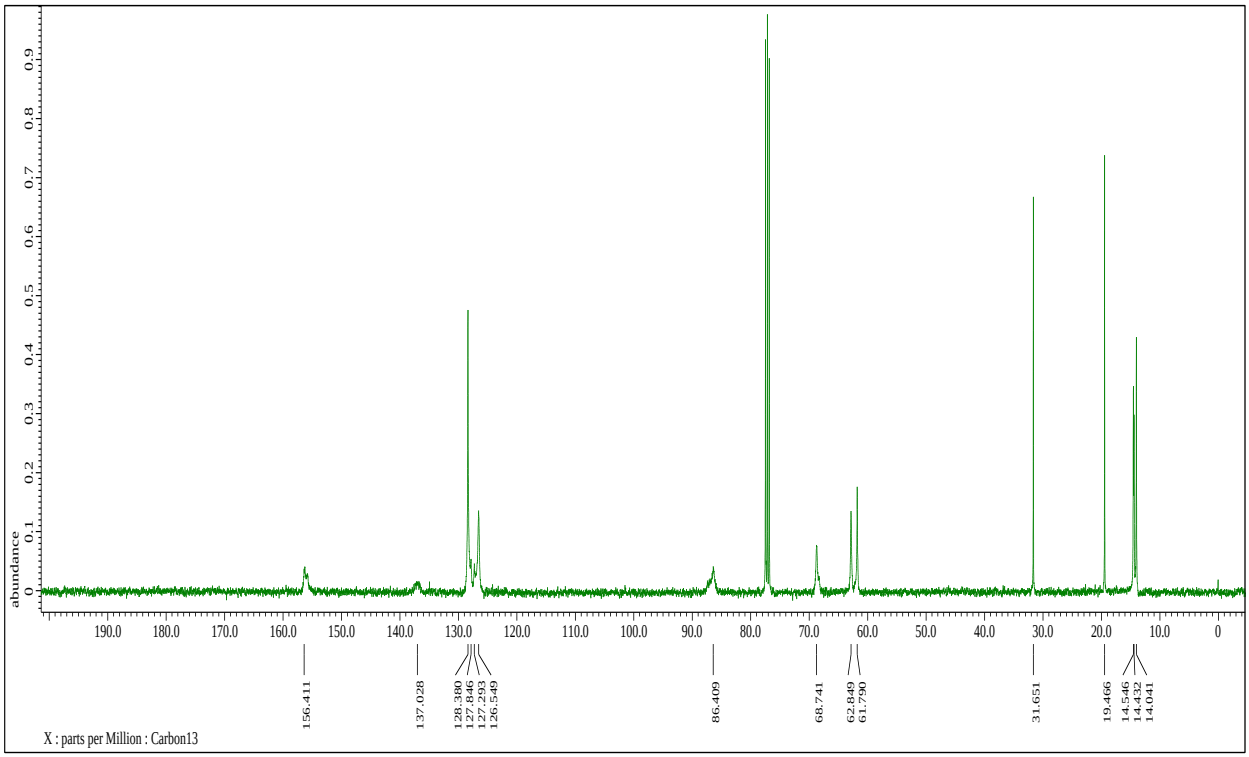


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4a**

Diethyl 1-(butoxy(phenyl)methyl)hydrazine-1,2-dicarboxylate (4b)

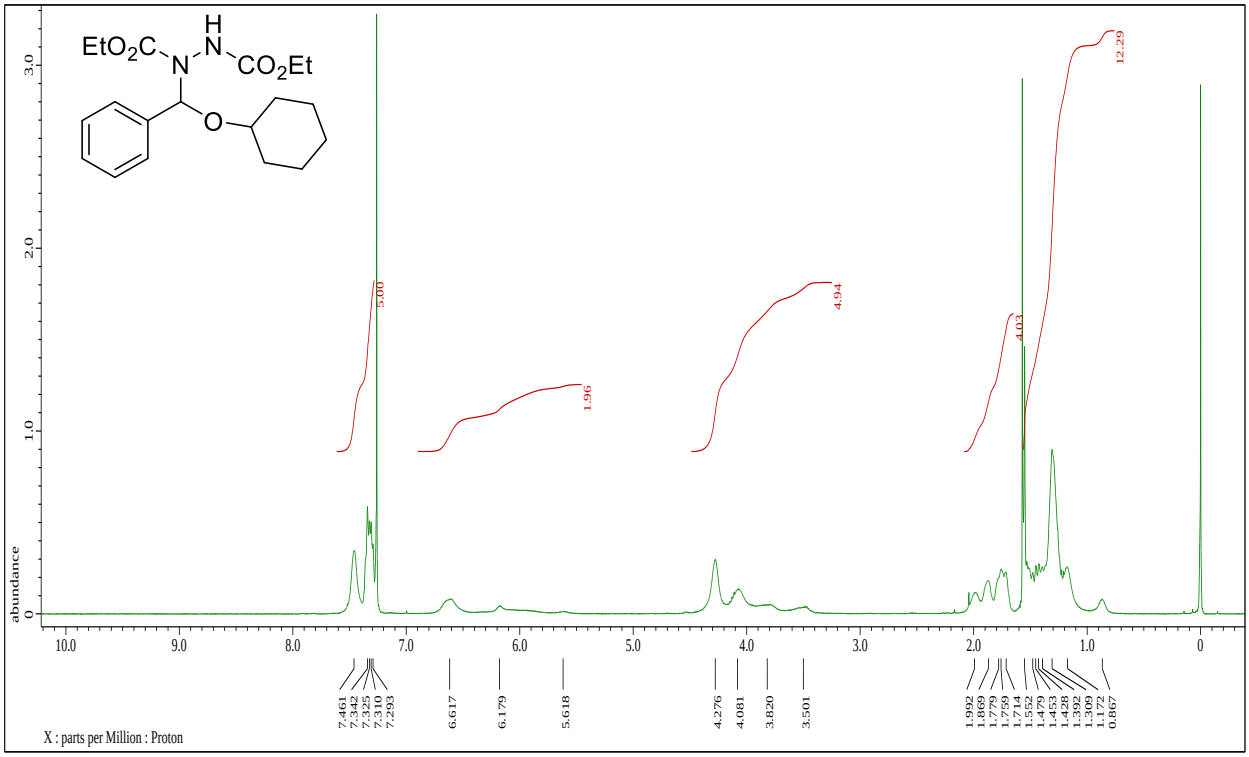


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4b**

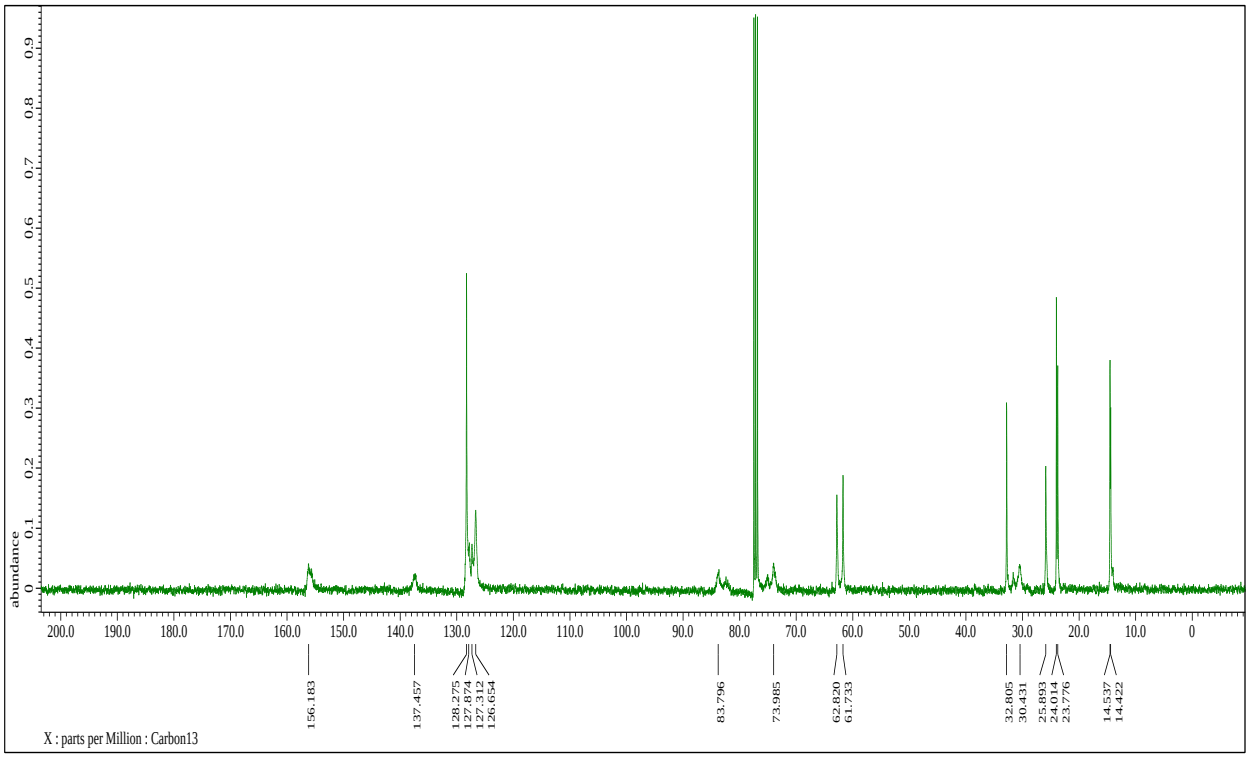


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4b**

Diethyl 1-((cyclohexyloxy)(phenyl)methyl)hydrazine-1,2-dicarboxylate (4c)

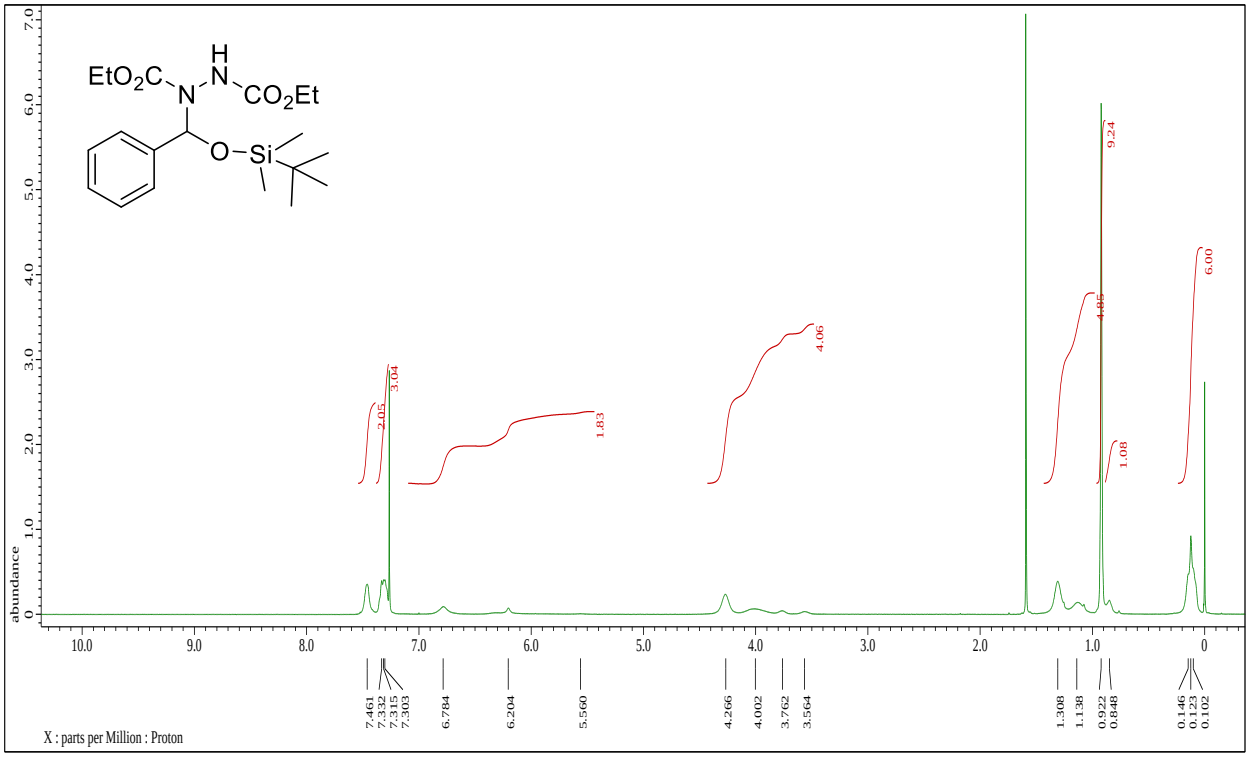


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4c**

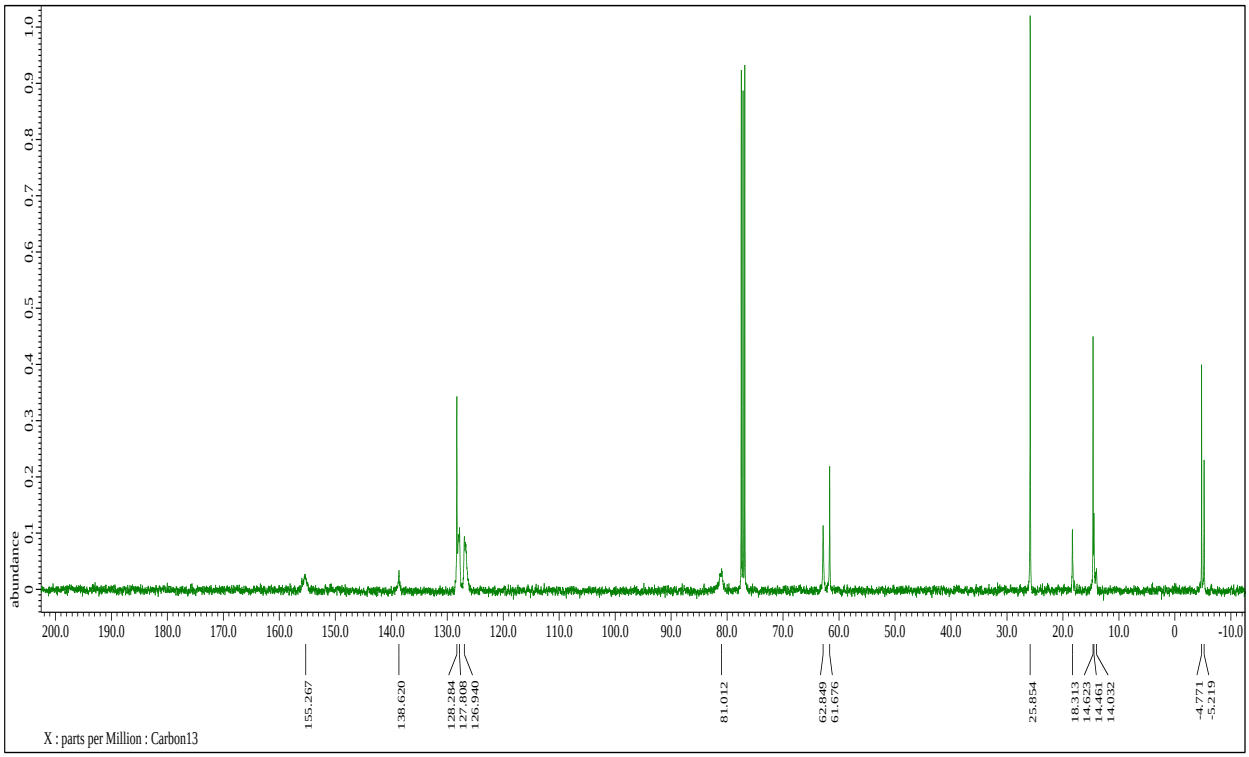


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **4c**

Diethyl 1-(((tert-butyldimethylsilyl)oxy)(phenyl)methyl)hydrazine-1,2-dicarboxylate (5a)

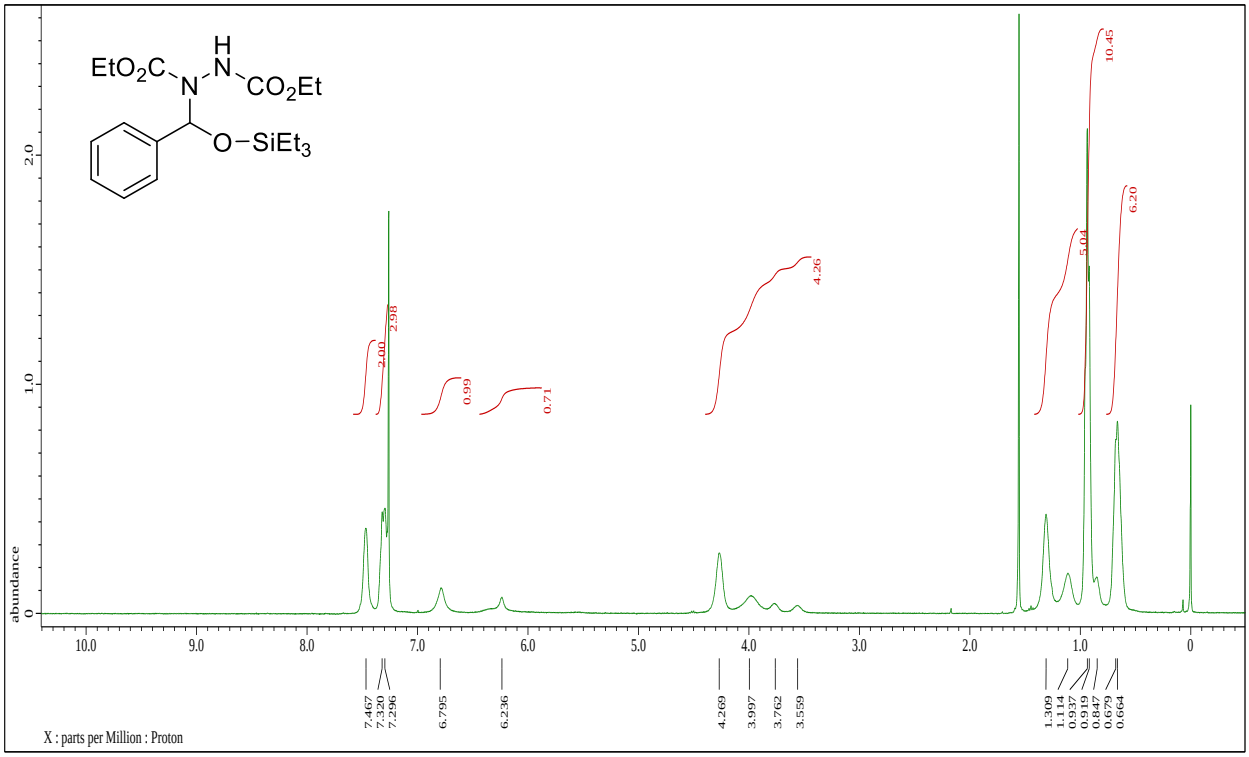


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5a**

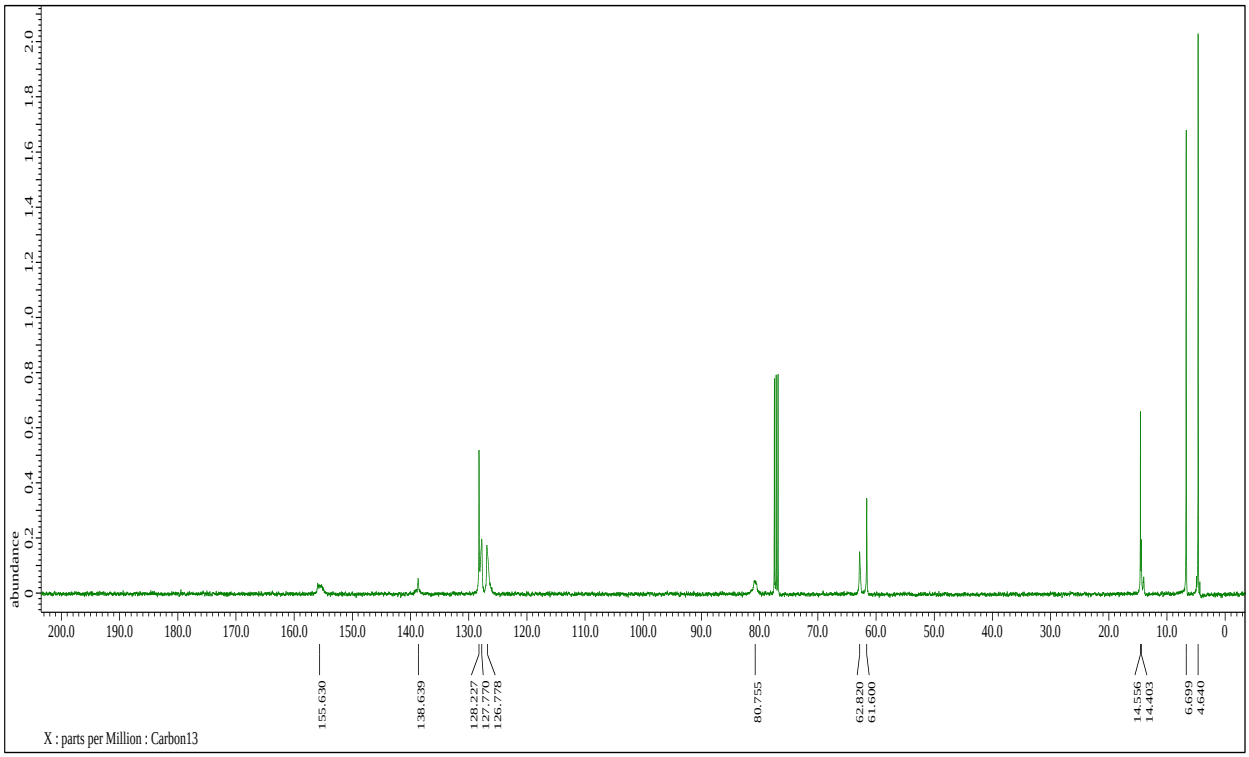


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5a**

Diethyl 1-(phenyl((triethylsilyl)oxy)methyl)hydrazine-1,2-dicarboxylate (5b)

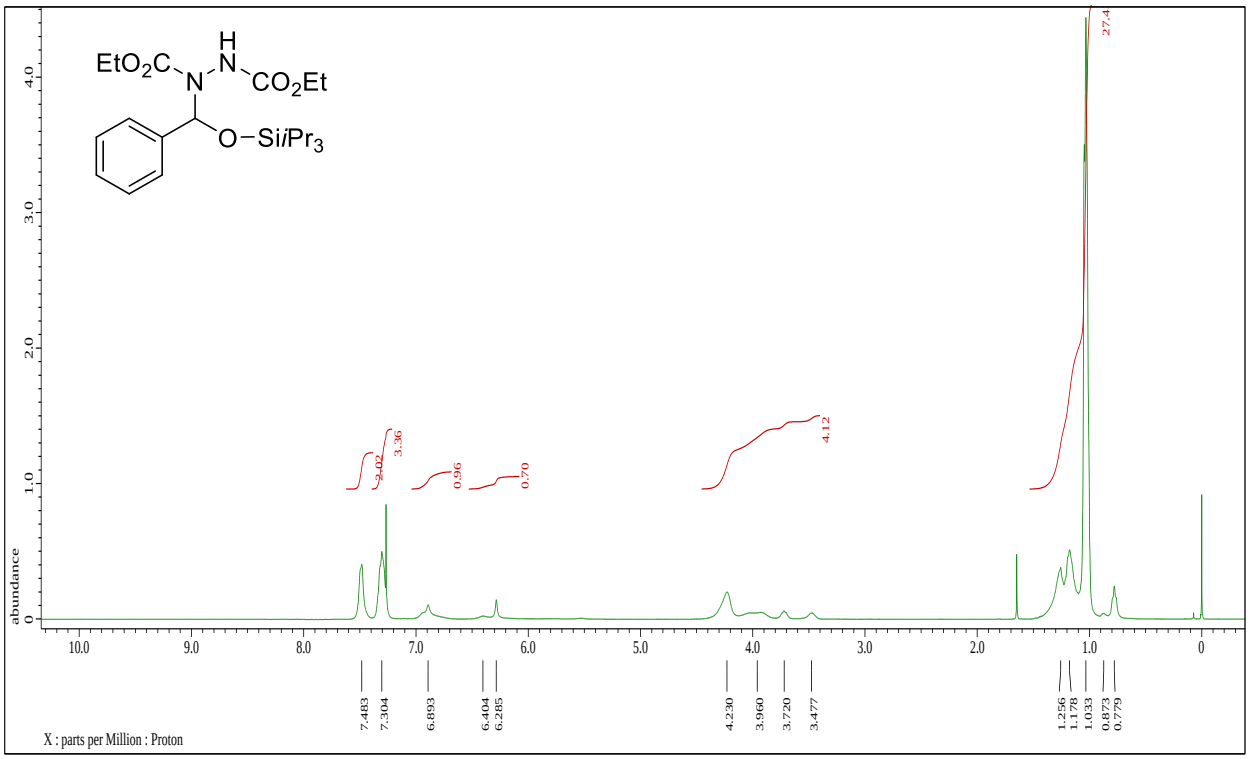


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5b**

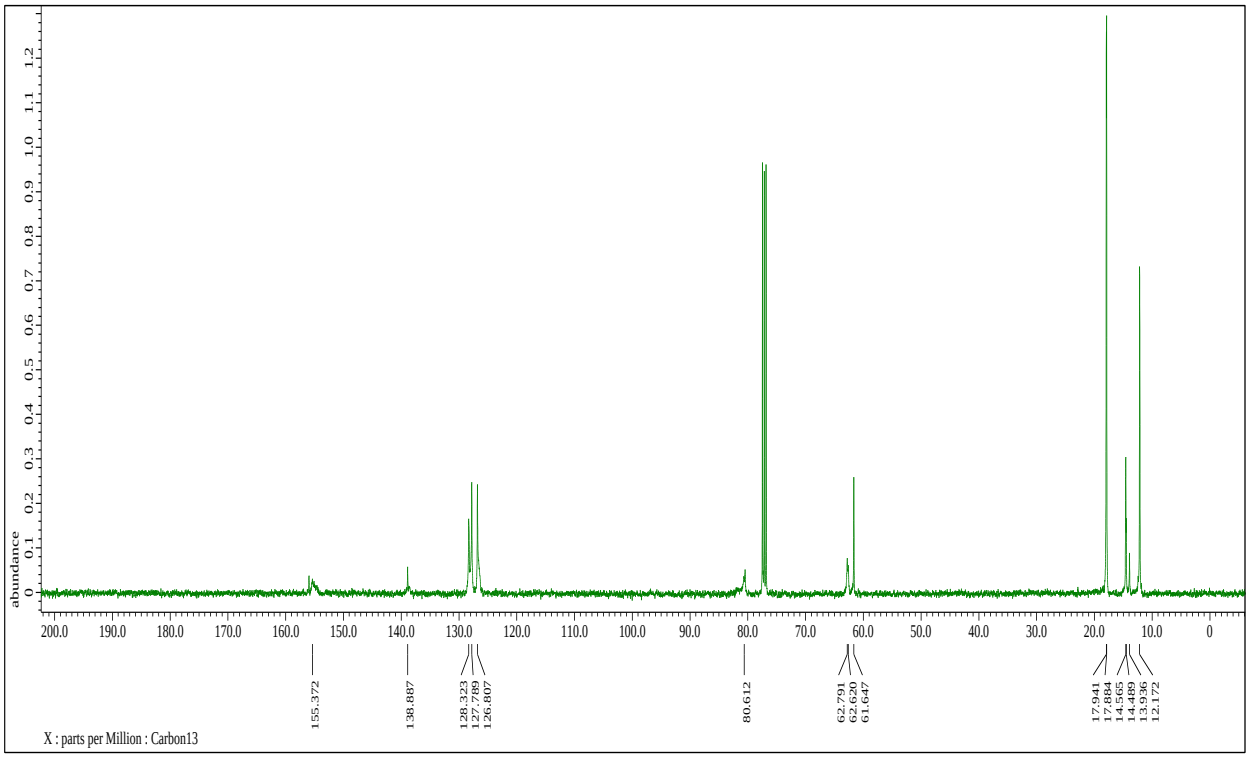


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5b**

Diethyl 1-(phenyl((triisopropylsilyl)oxy)methyl)hydrazine-1,2-dicarboxylate (5c)

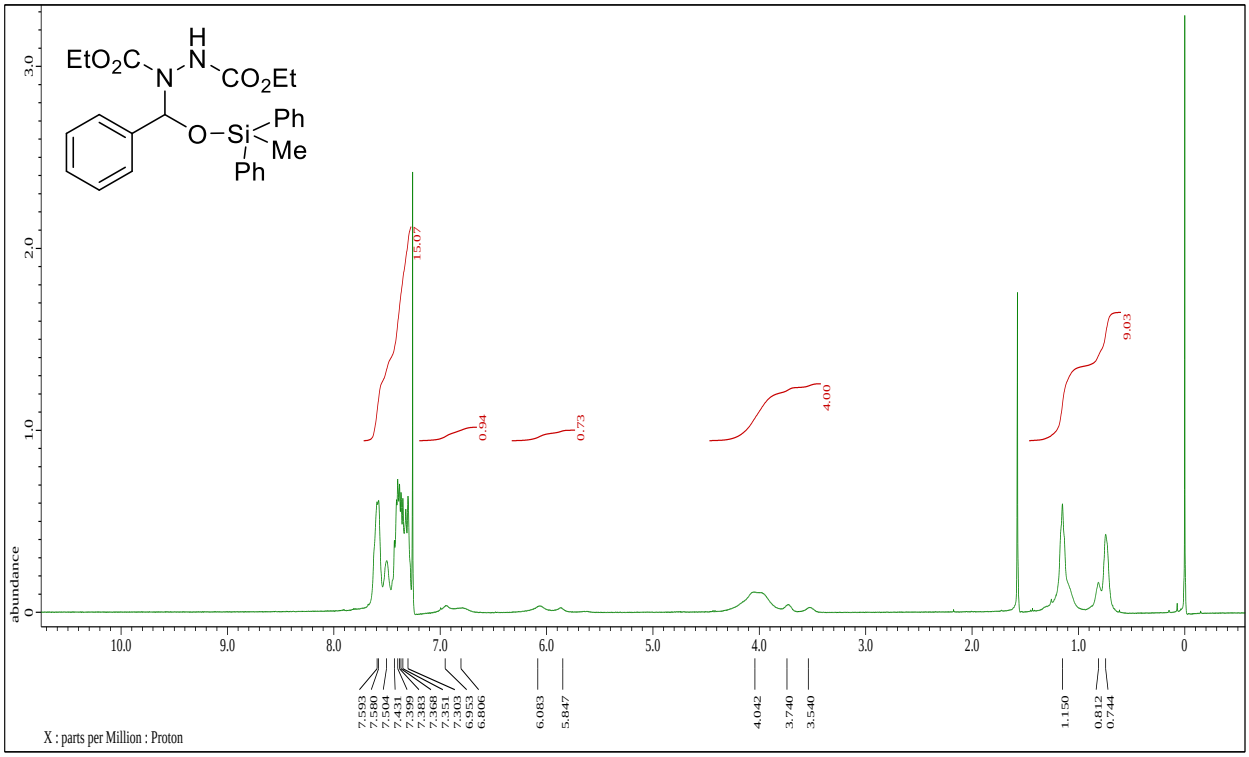


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5c**

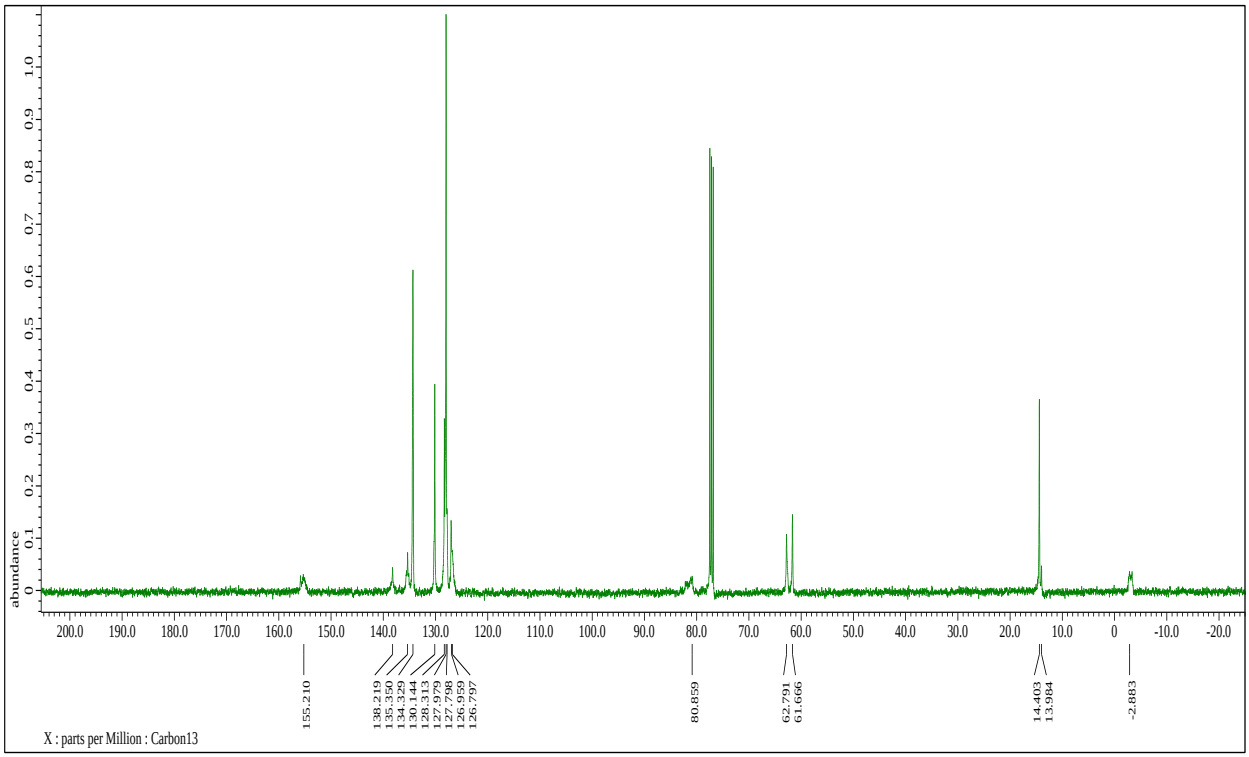


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5c**

Diethyl 1-(((methyldiphenylsilyl)oxy)(phenyl)methyl)hydrazine-1,2-dicarboxylate (5d)

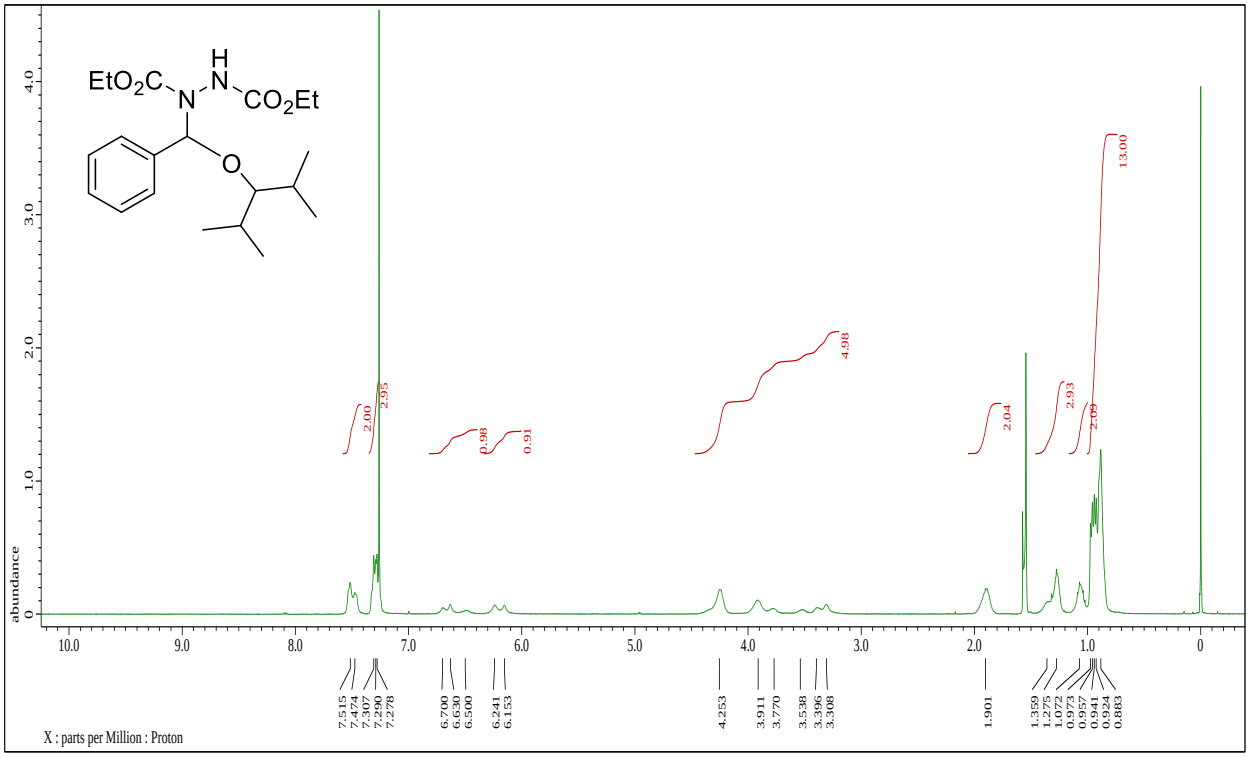


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5d**

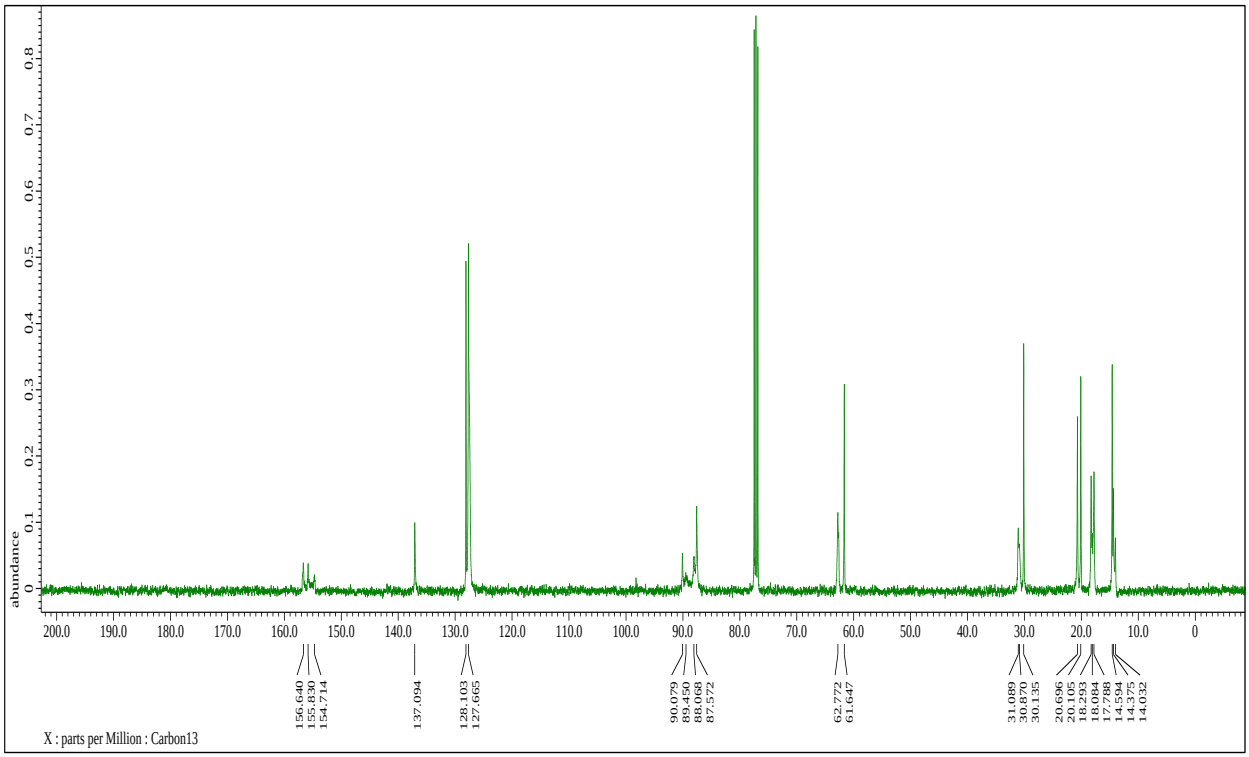


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5d**

Diethyl 1-(((2,4-dimethylpentan-3-yl)oxy)(phenyl)methyl)hydrazine-1,2-dicarboxylate (5e)

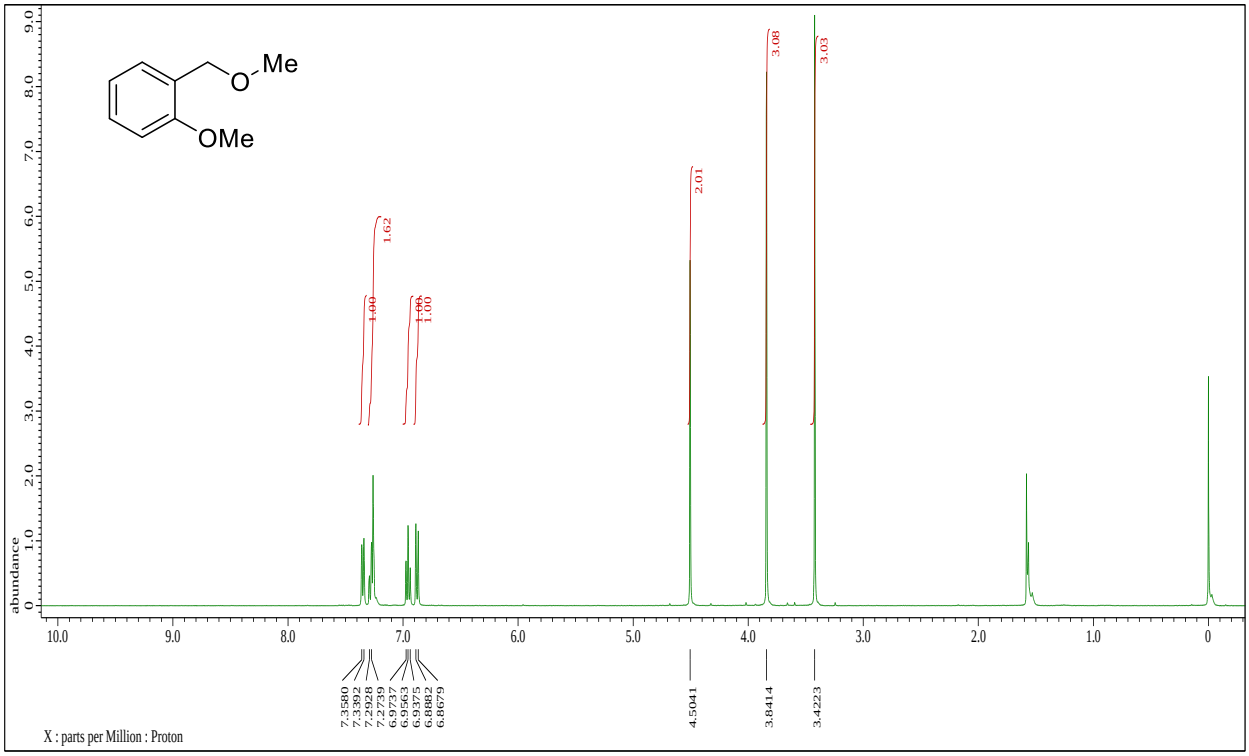


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5e**

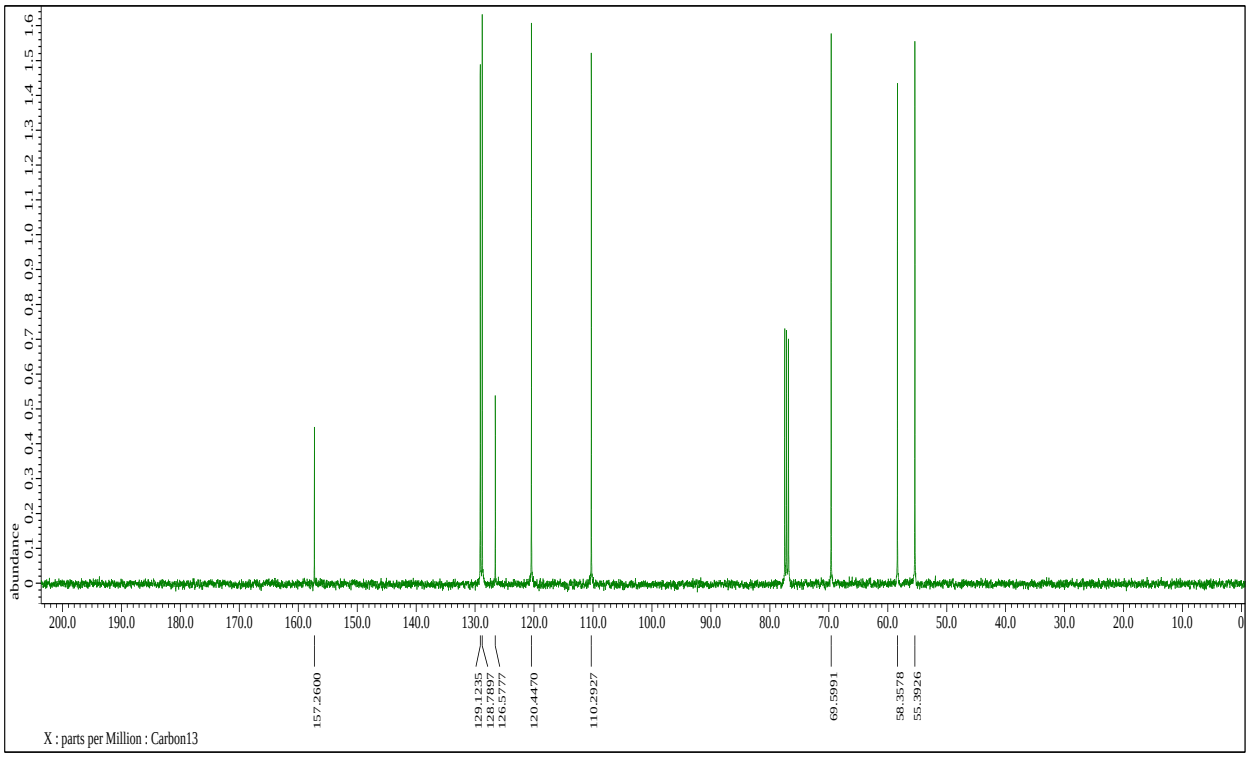


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5e**

2-Methoxybenzyl methyl ether (6a)

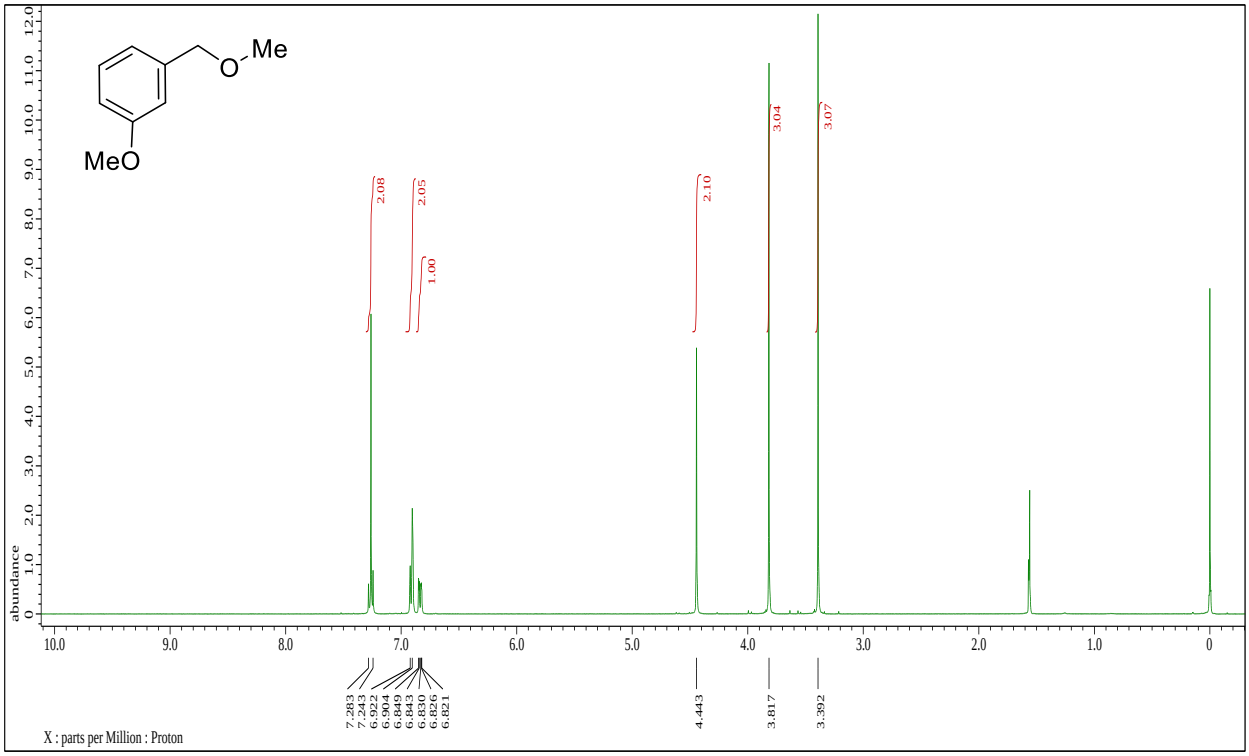


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6a**

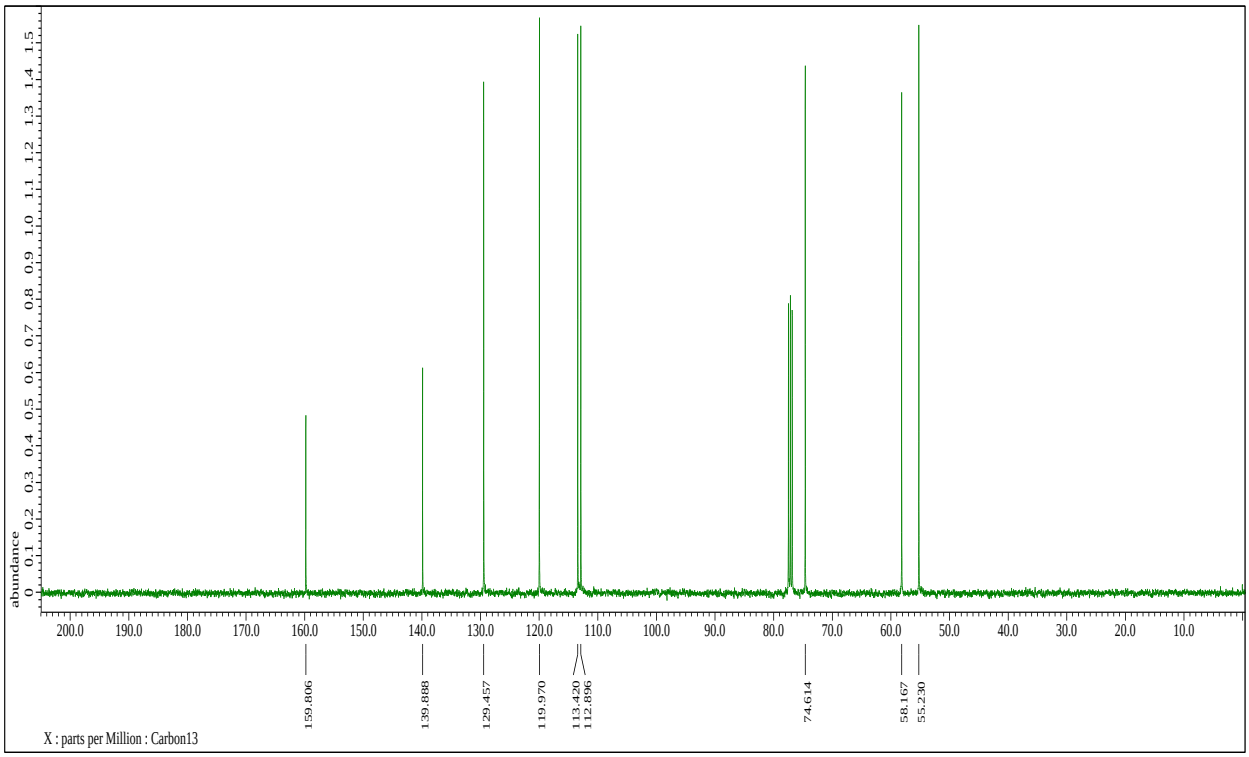


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6a**

3-Methoxybenzyl methyl ether (6b)

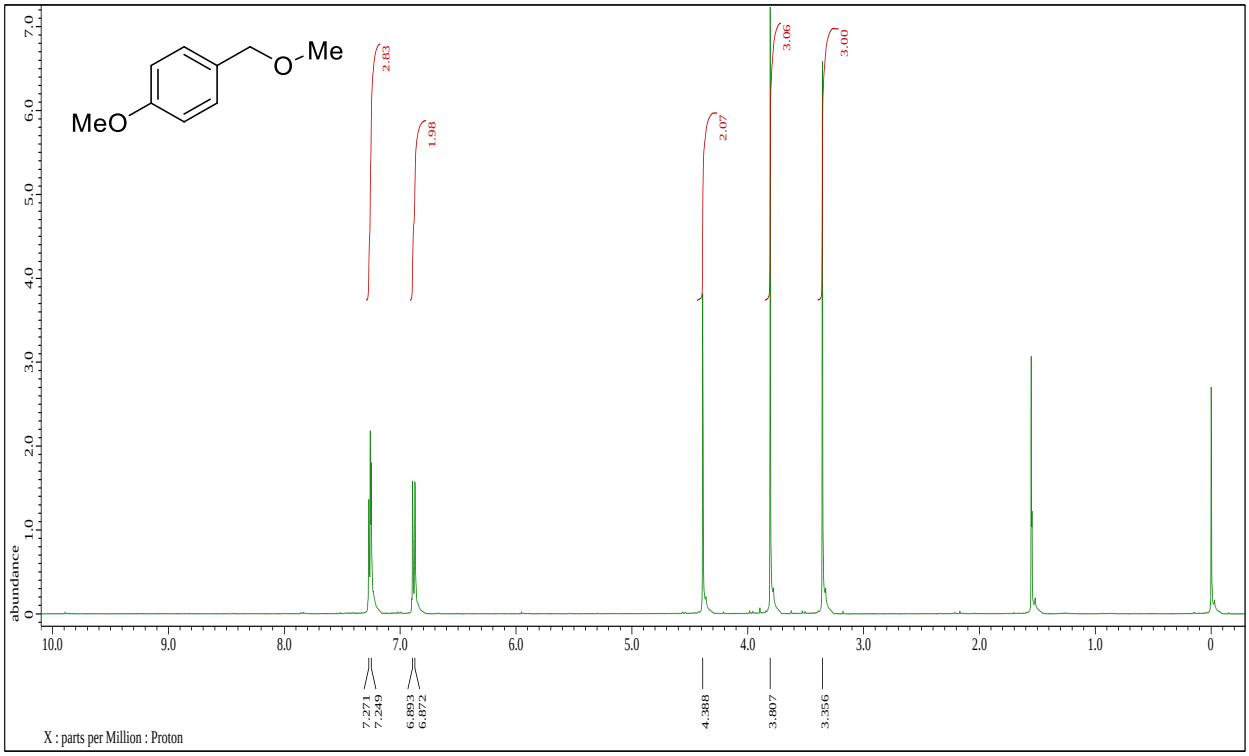


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6b**

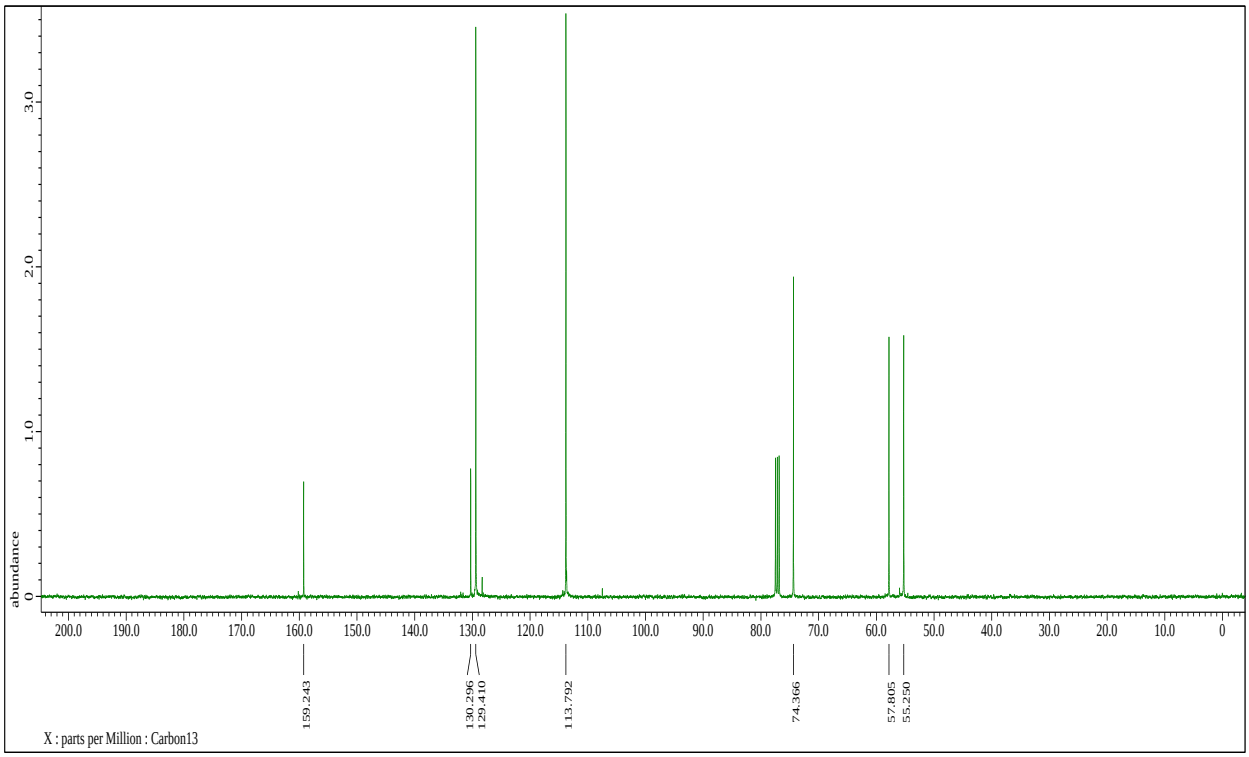


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6b**

4-Methoxybenzyl methyl ether (6c)

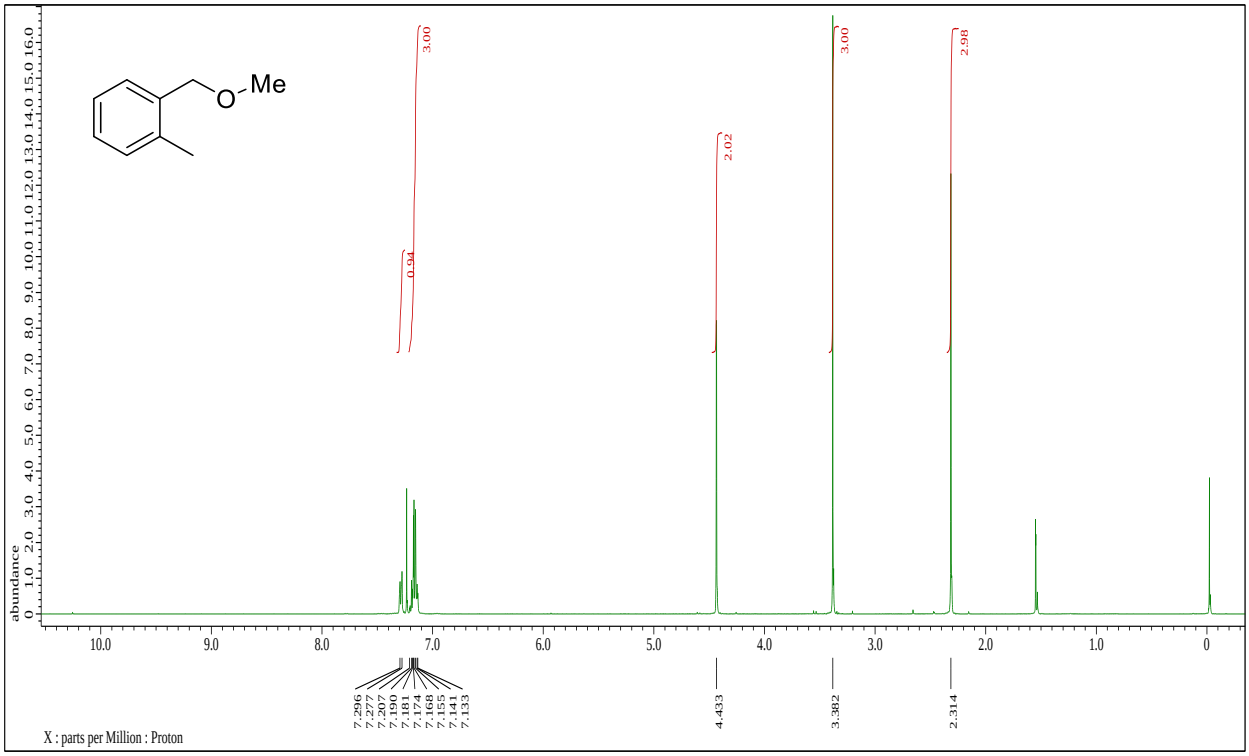


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6c**

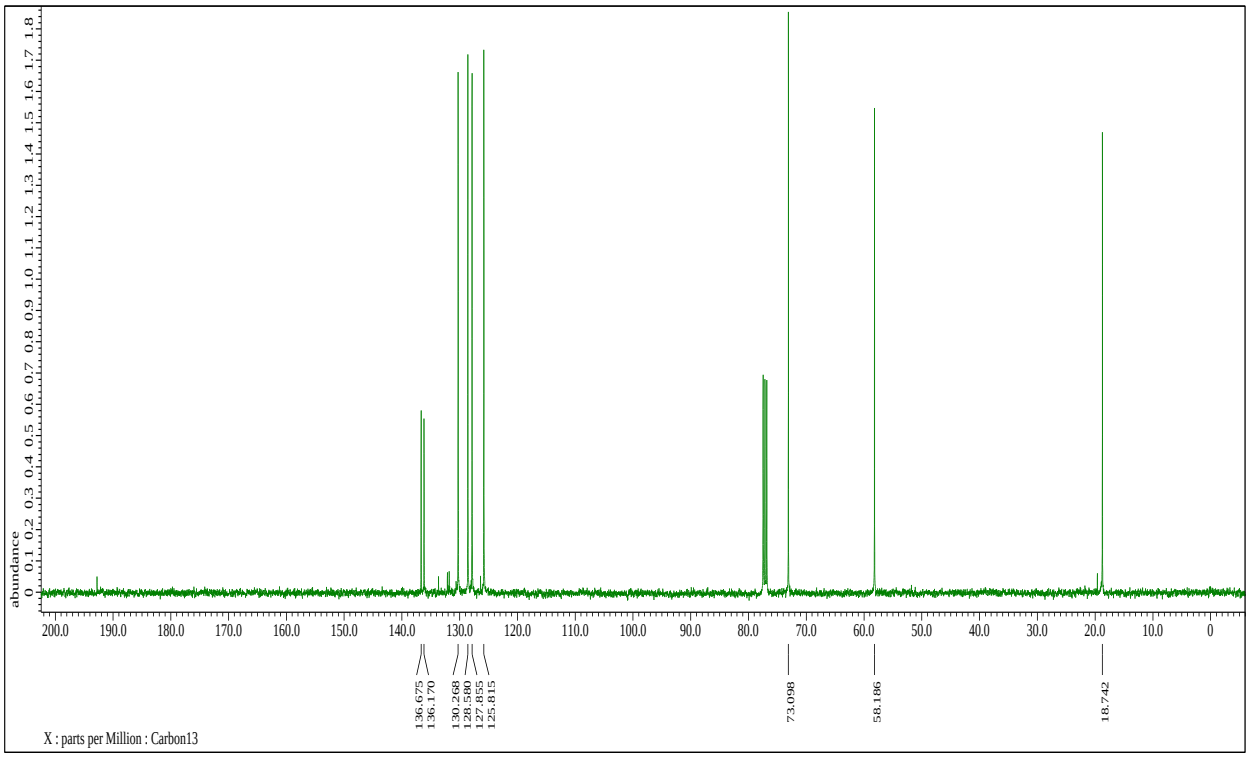


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6c**

2-Methylbenzyl methyl ether (6d)

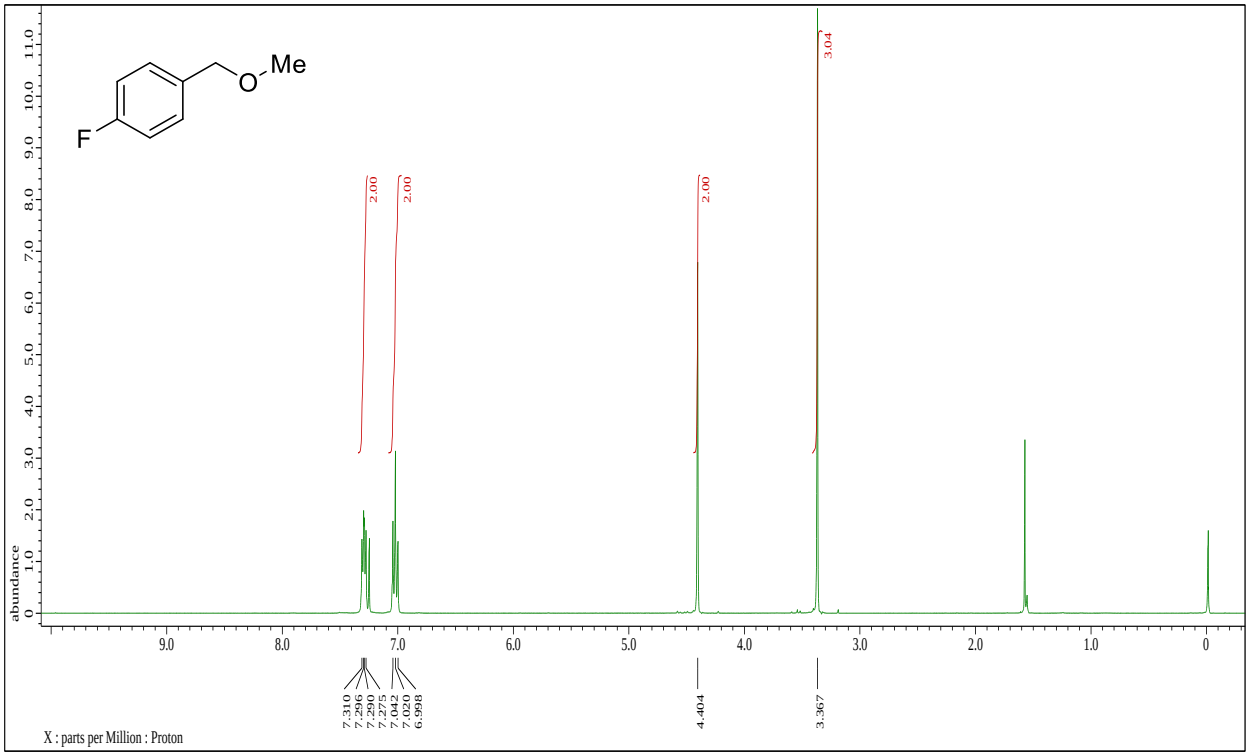


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6d**

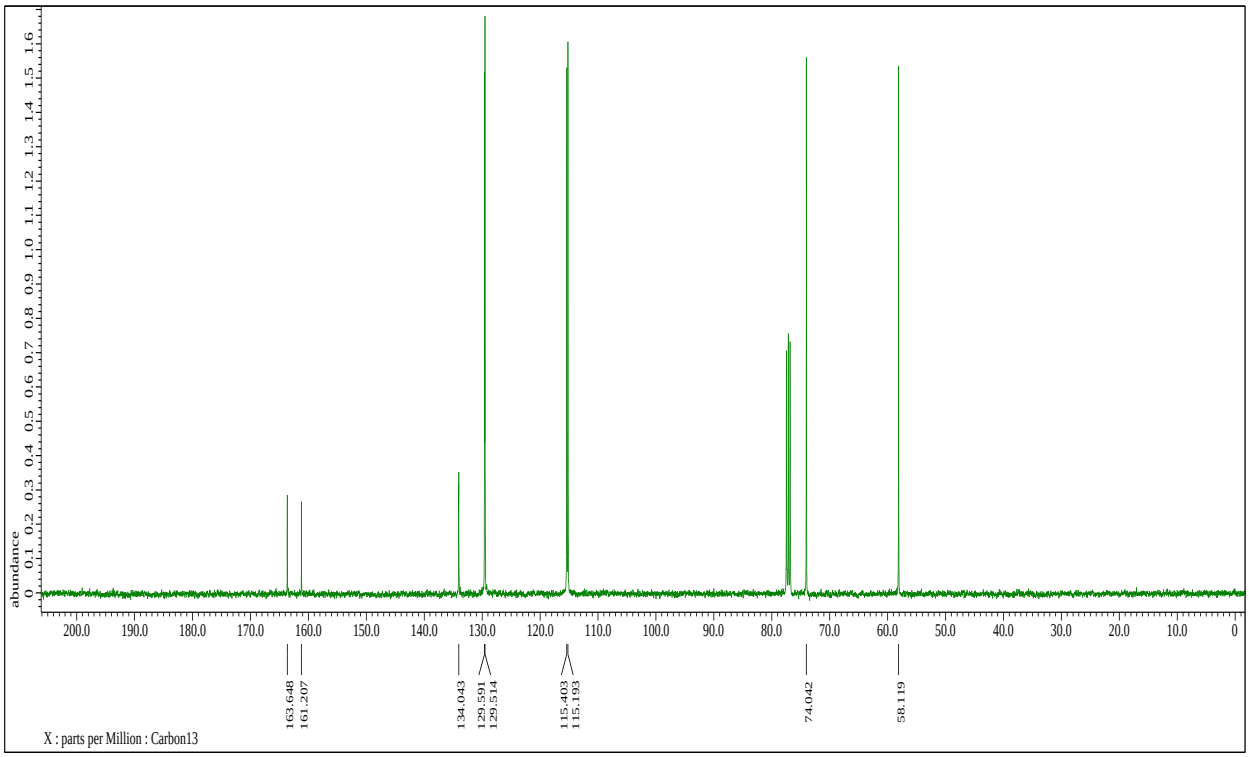


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6d**

4-Fluorobenzyl methyl ether (6e)

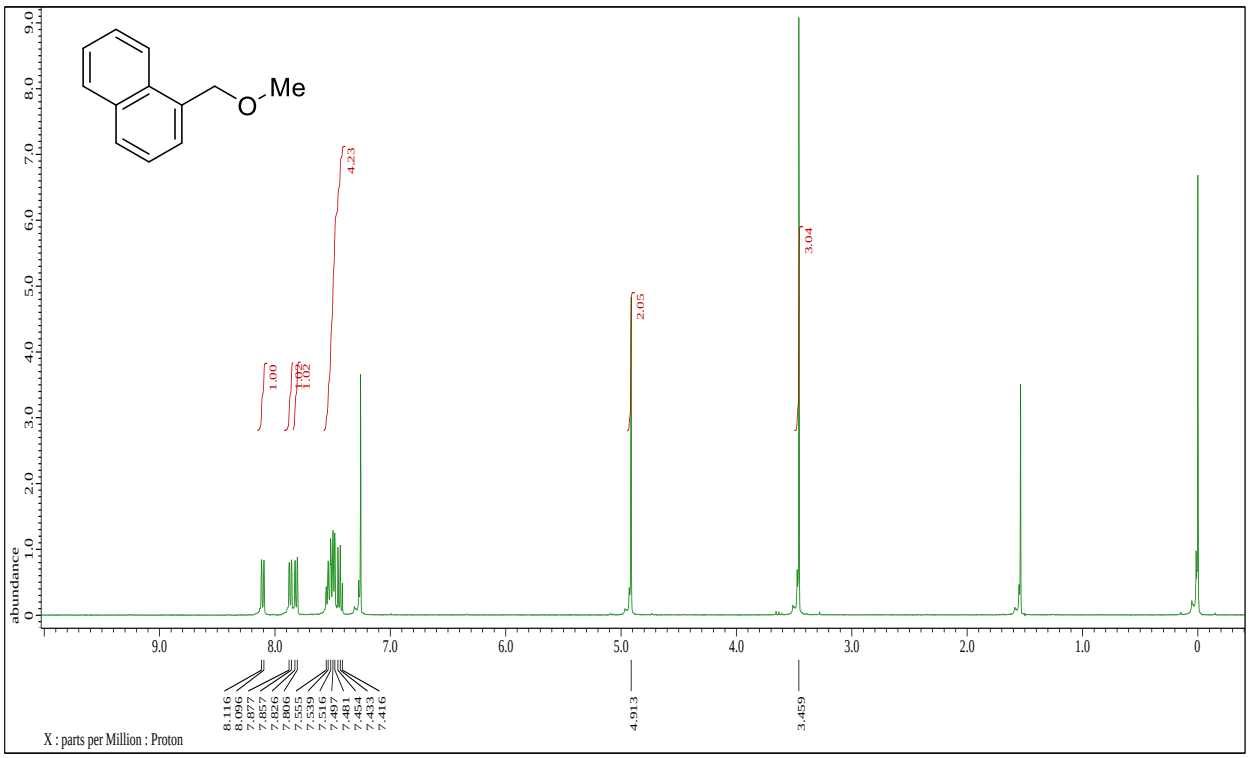


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6e**

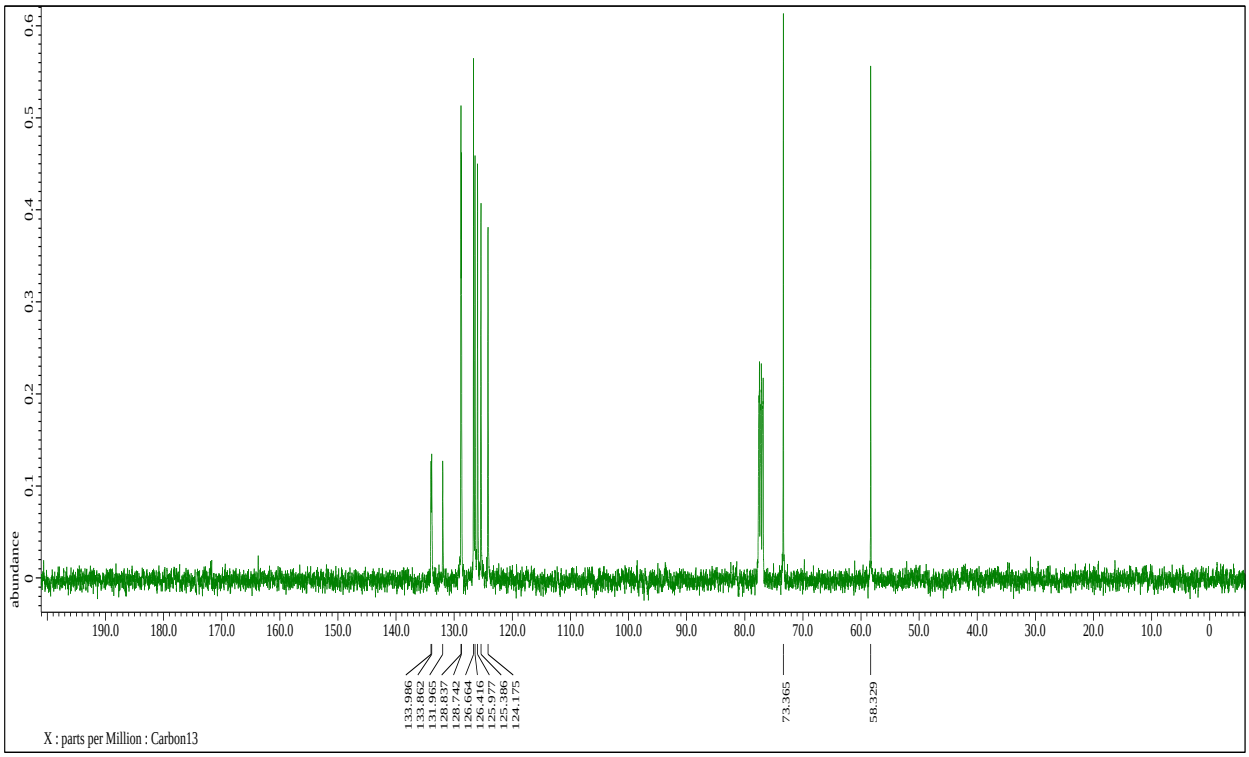


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6e**

Methyl 1-naphthalenemethyl ether (6f)

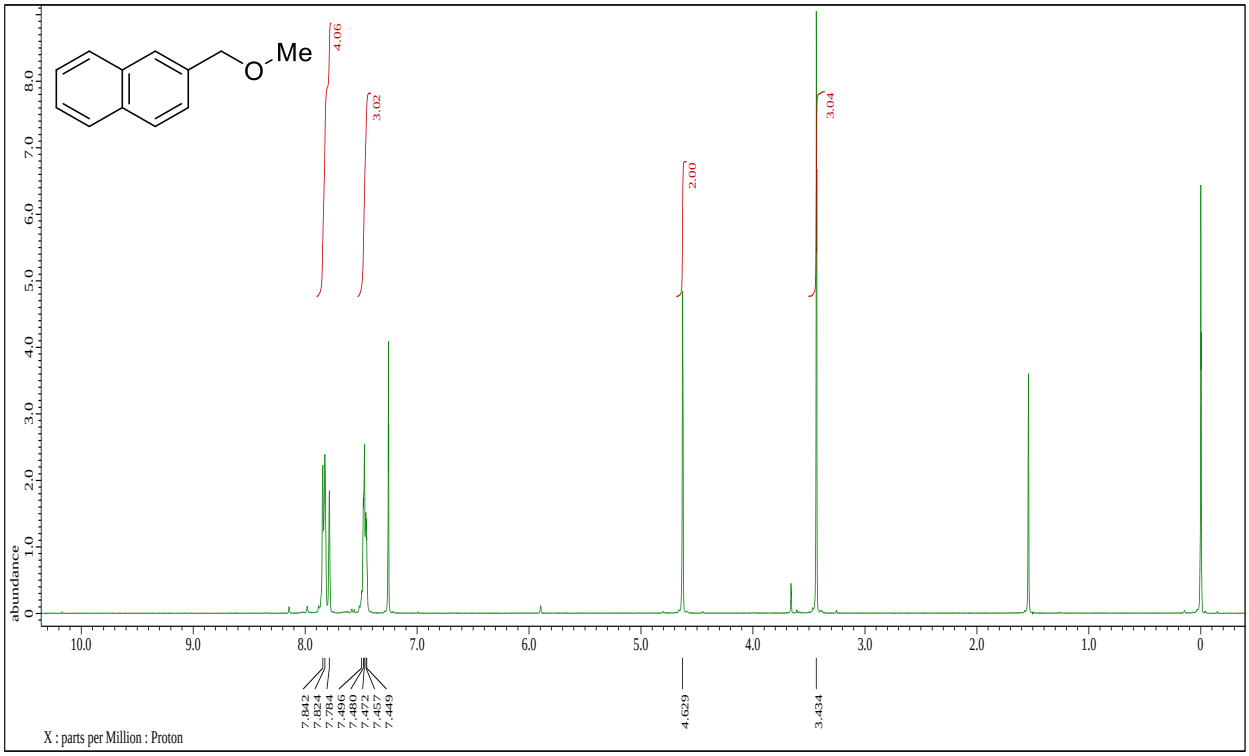


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6f**

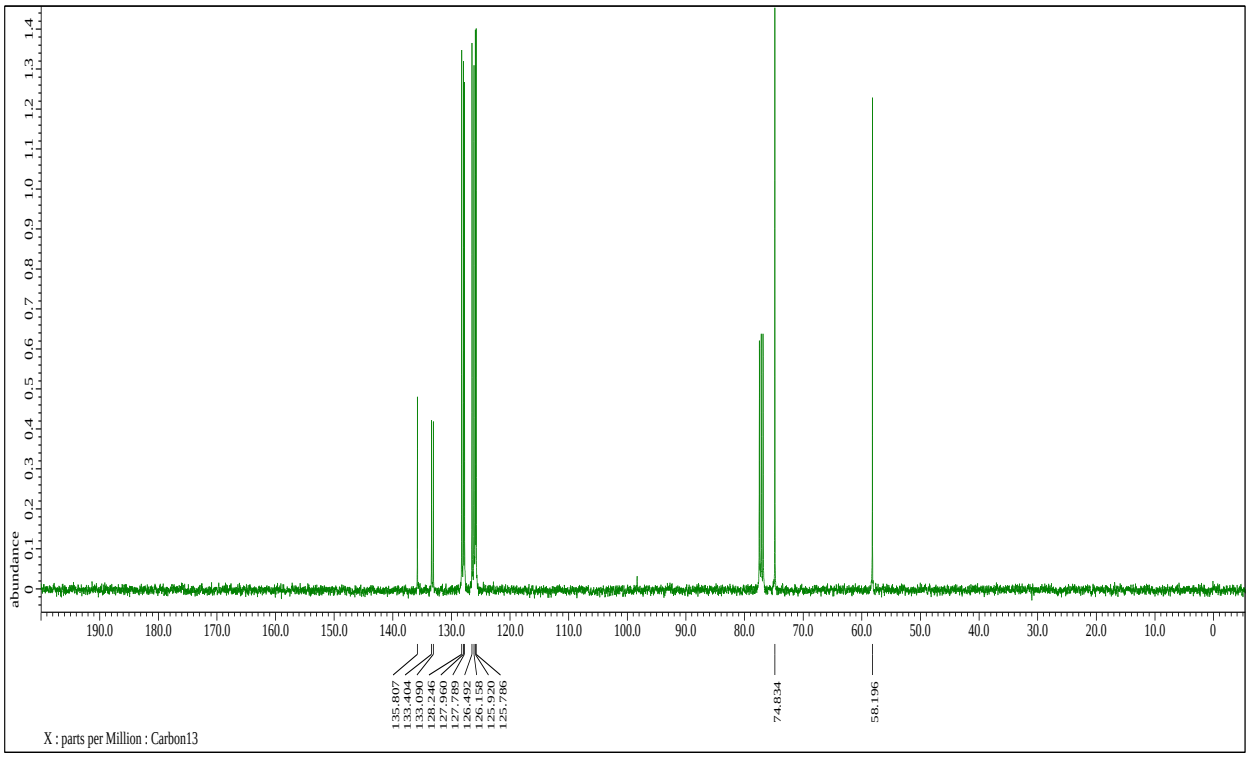


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6f**

Methyl 2-naphthalenemethyl ether (6g)

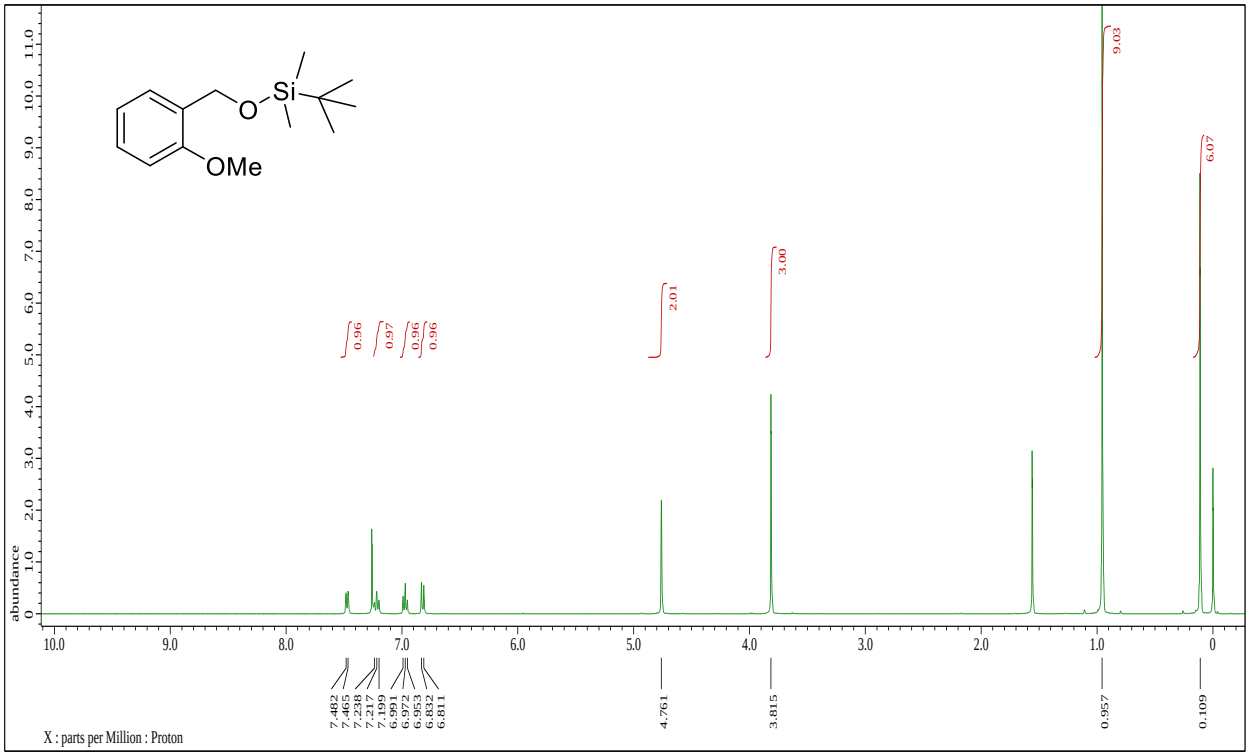


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6g**

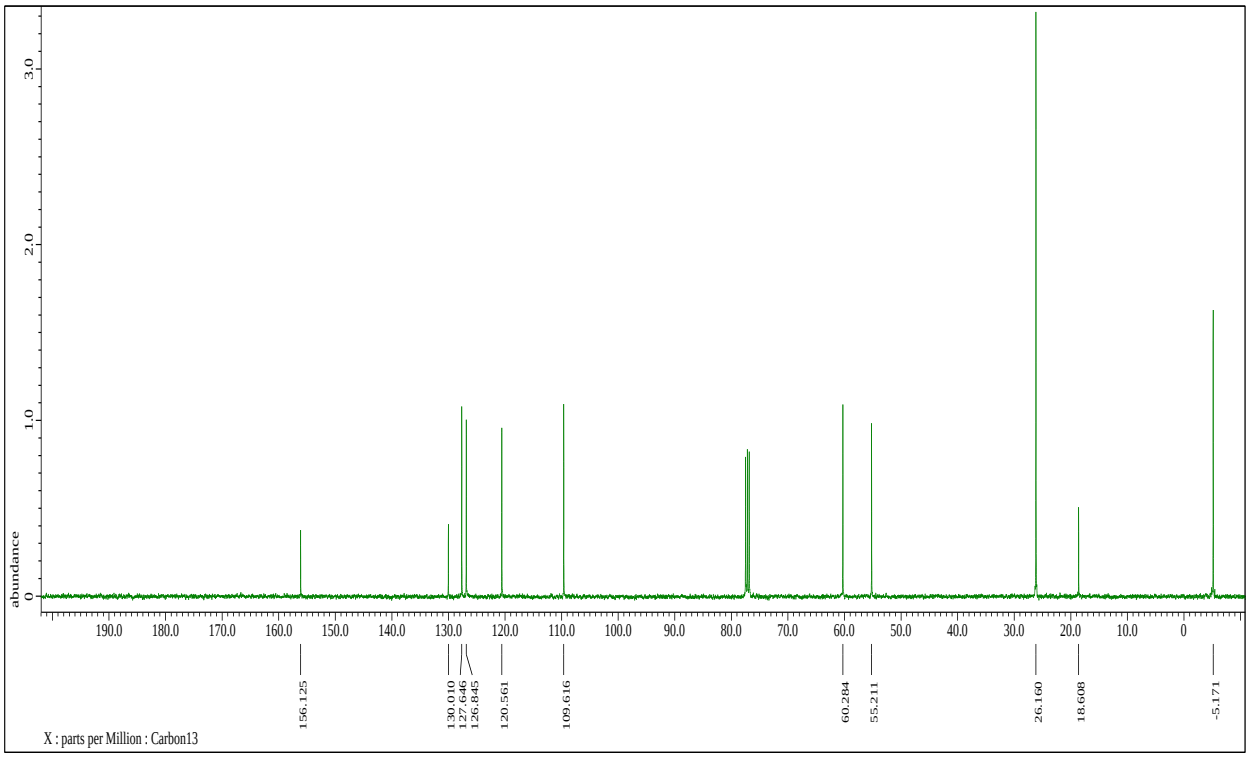


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6g**

tert-Butyldimethylsilyl 2-methoxybenzyl ether (7a)

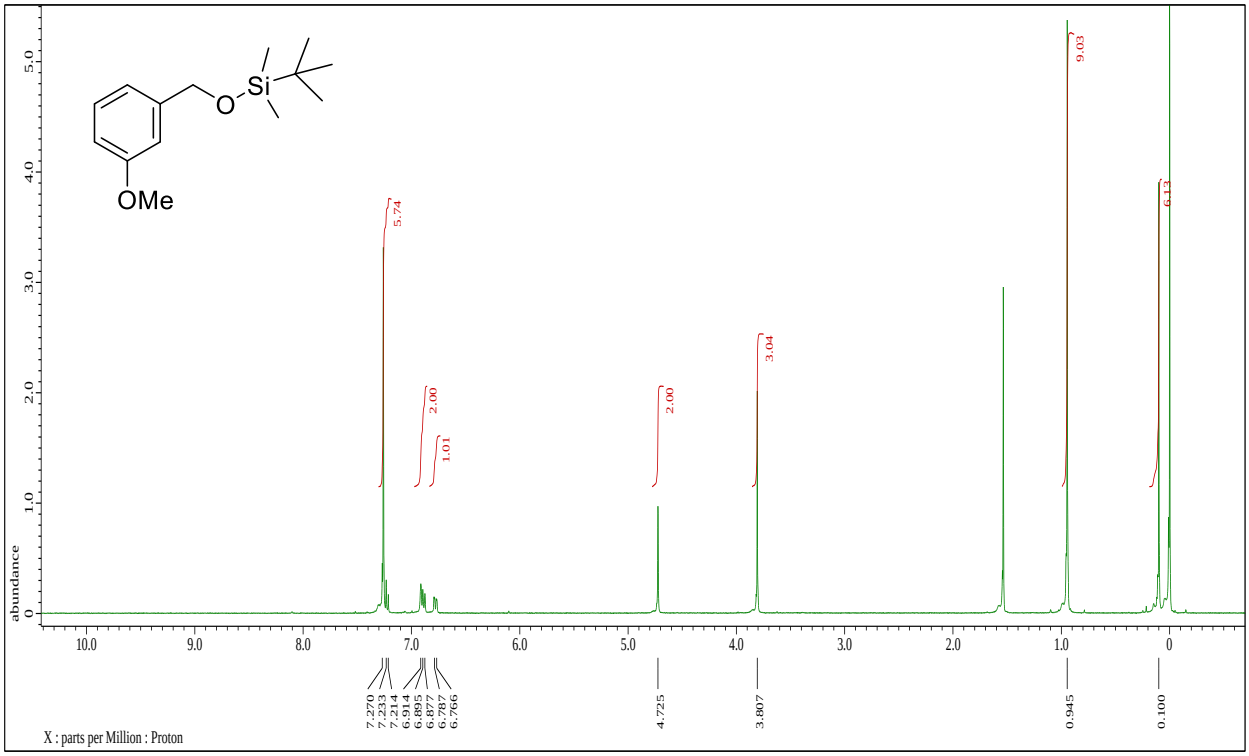


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7a**

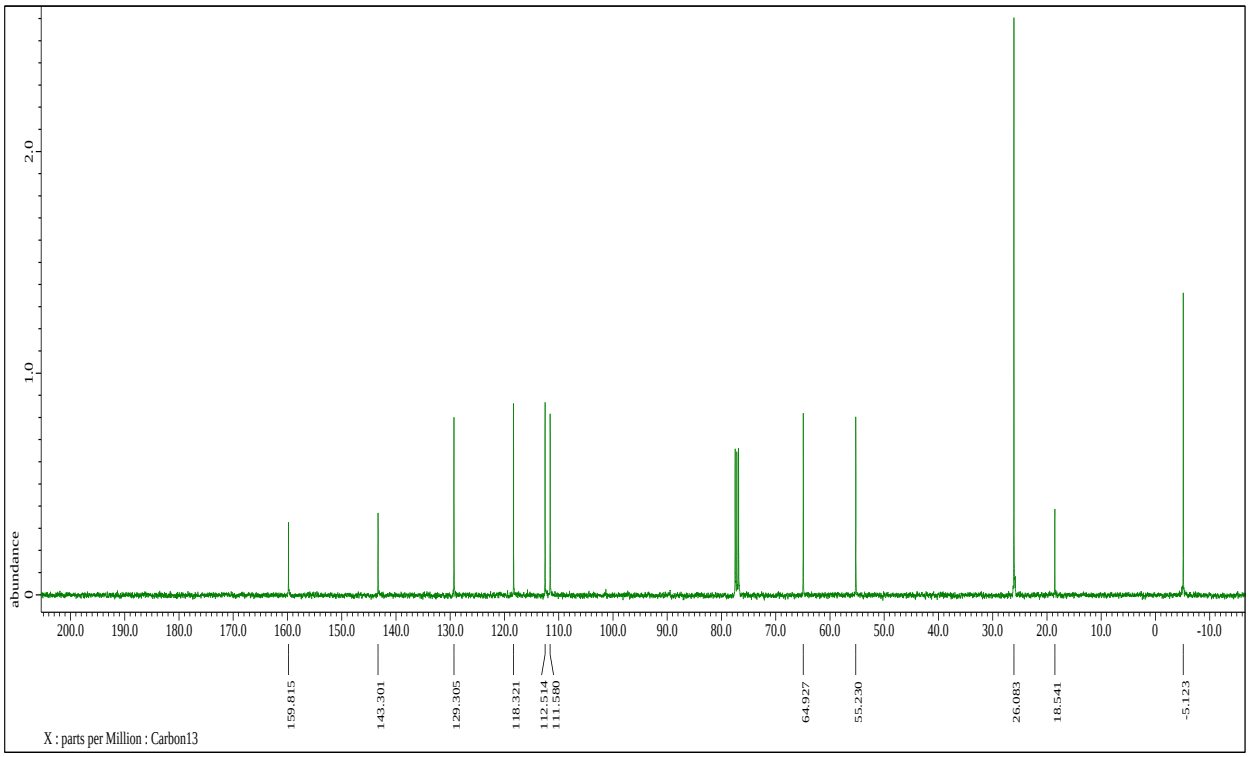


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **7a**

***tert*-Butyldimethylsilyl 3-methoxybenzyl ether (7b)**

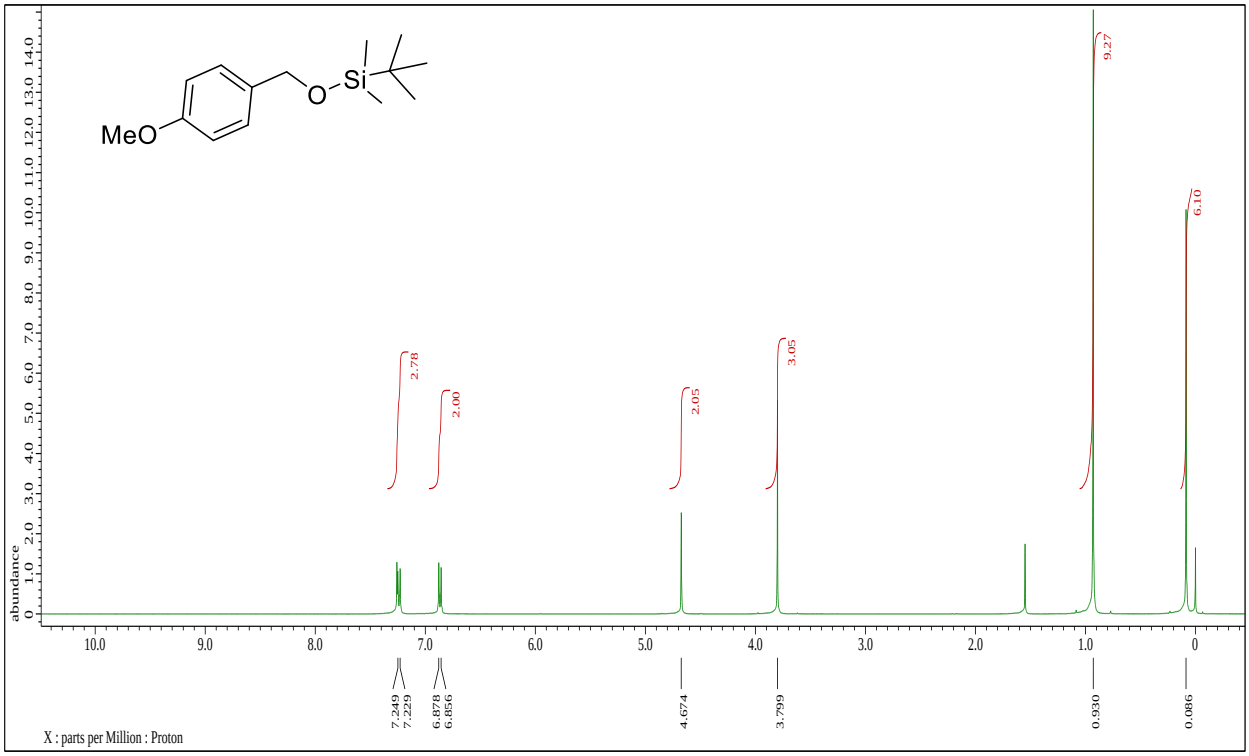


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7b**

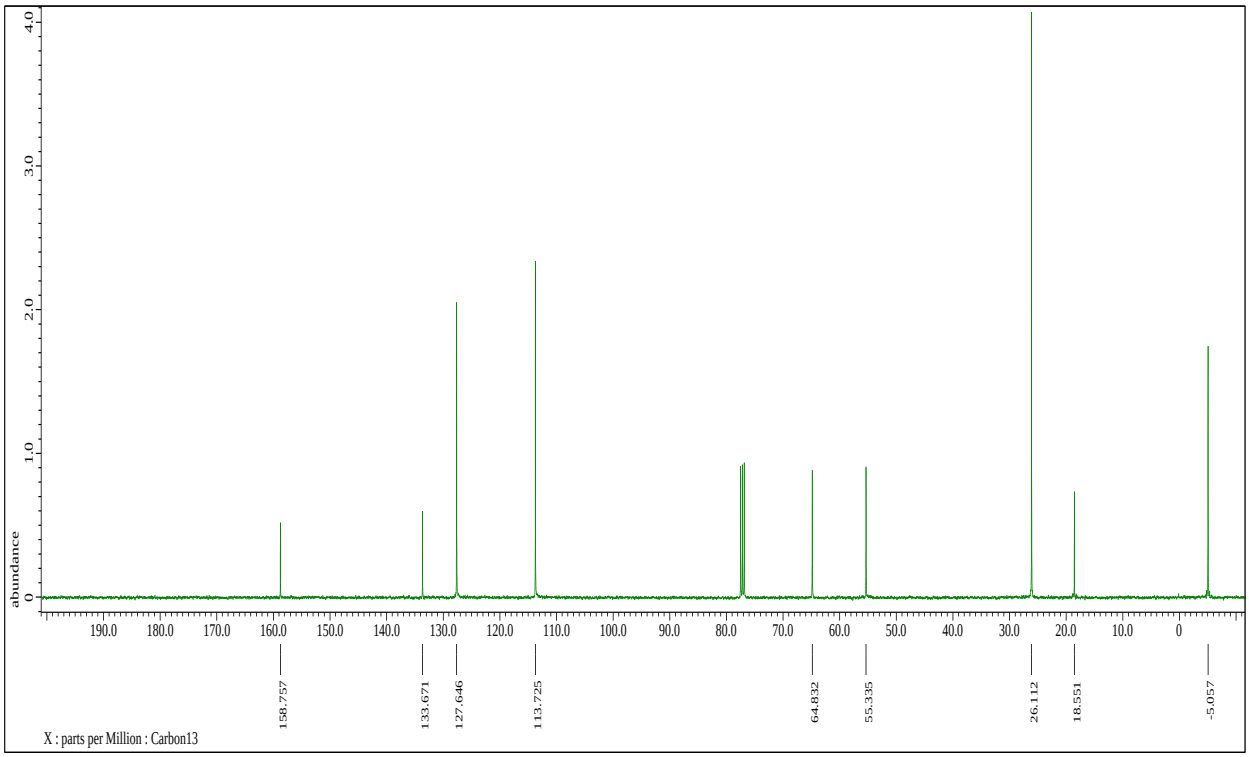


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **7b**

tert-Butyldimethylsilyl 4-methoxybenzyl ether (7c)

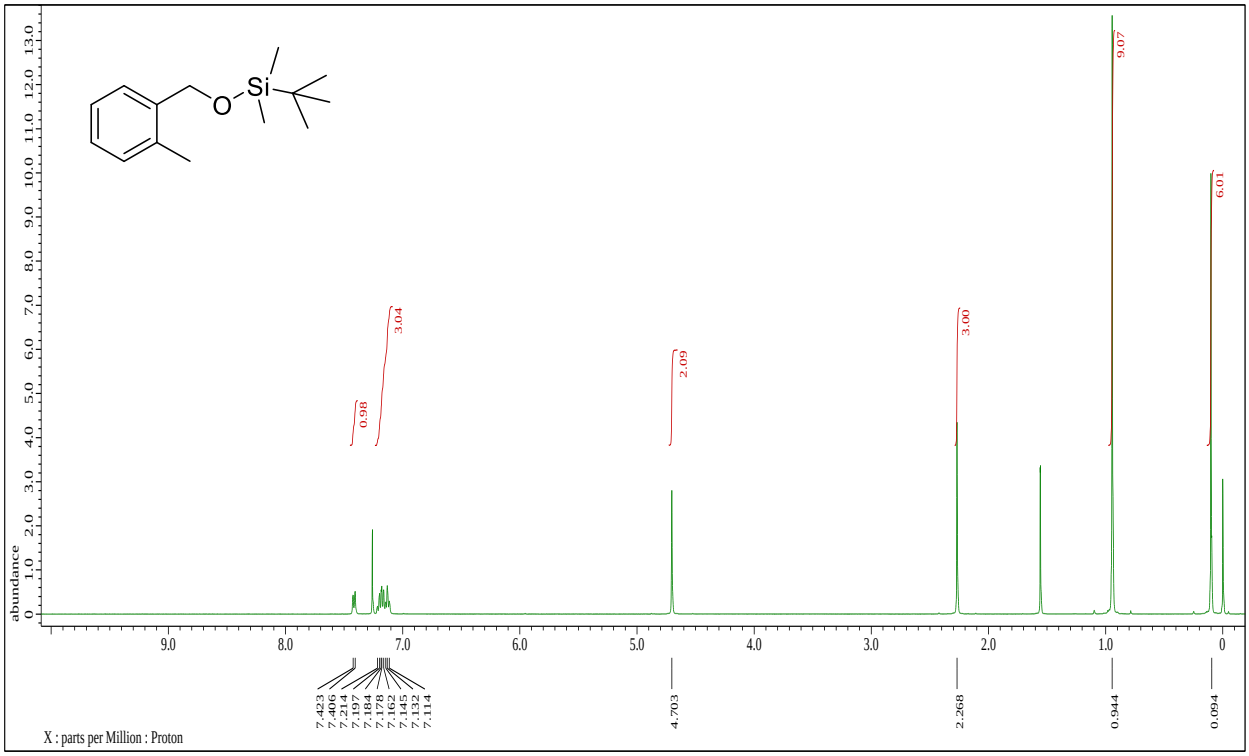


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7c**

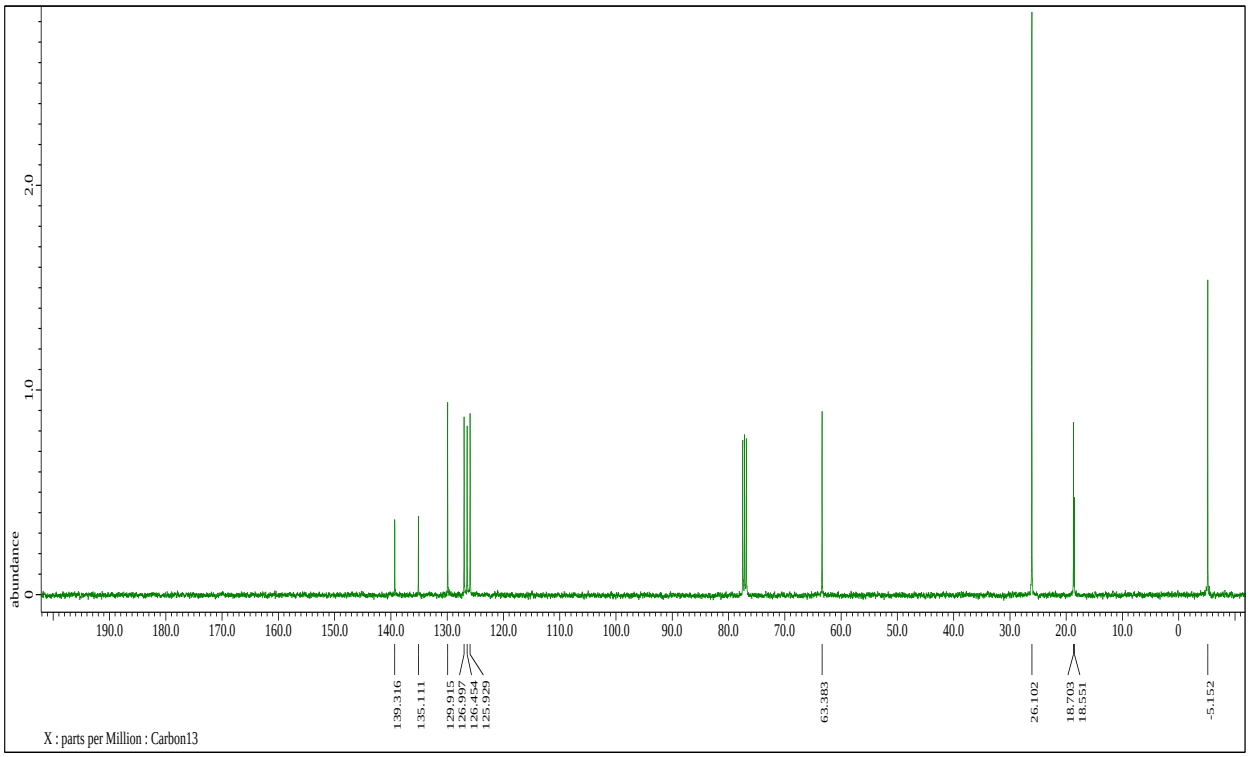


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **7c**

***tert*-Butyldimethylsilyl 2-methylbenzyl ether (7d)**

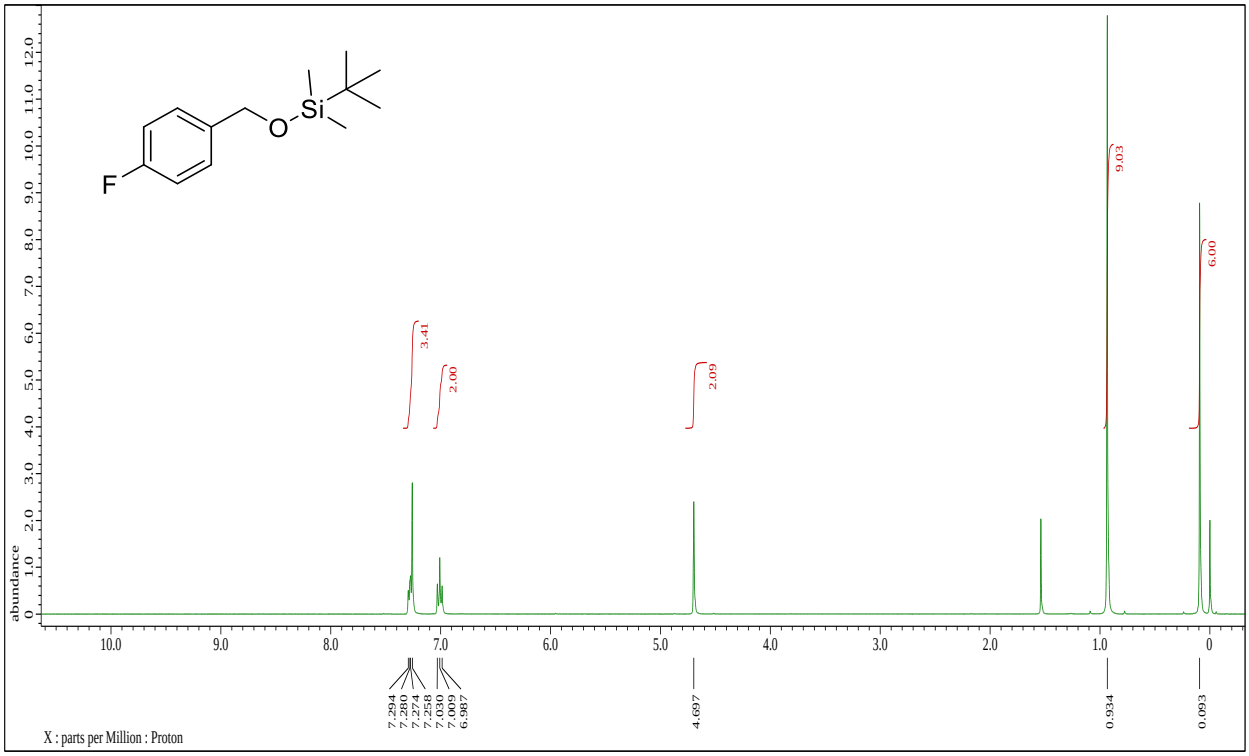


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7d**

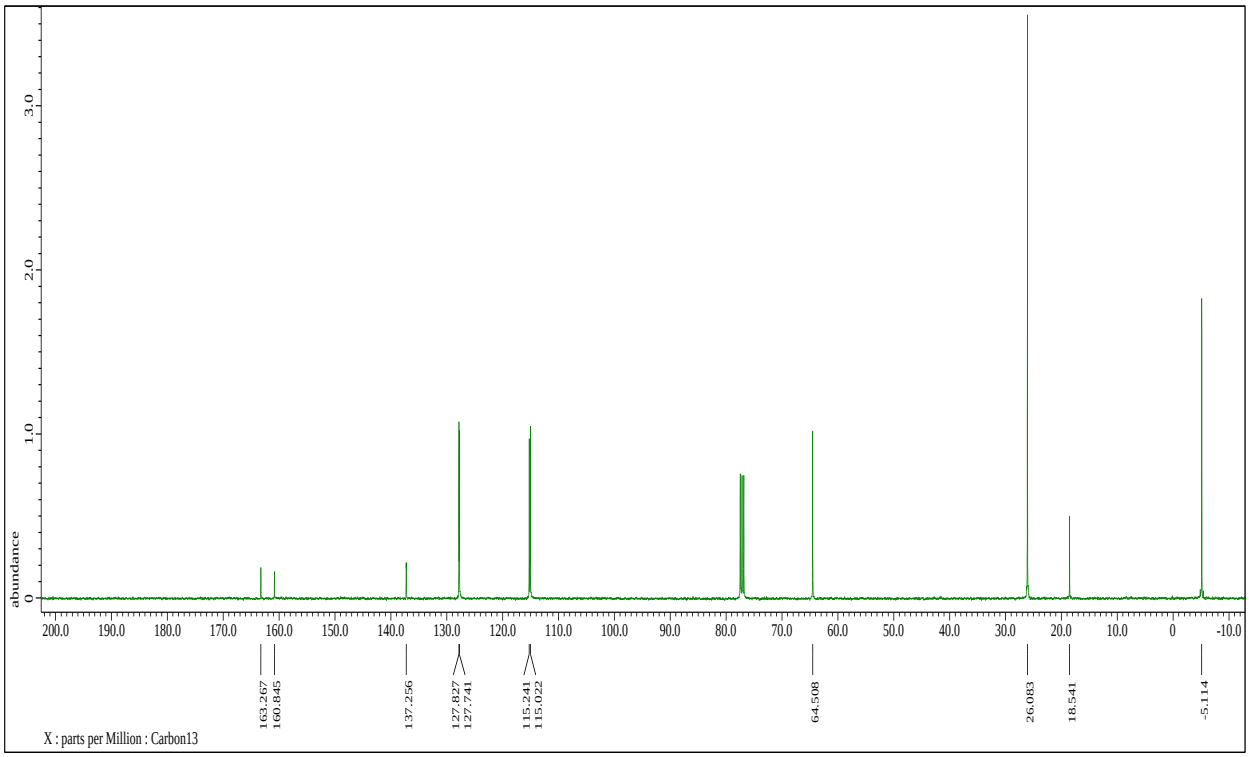


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **7d**

tert-Butyldimethylsilyl 4-fluorobenzyl ether (7e)

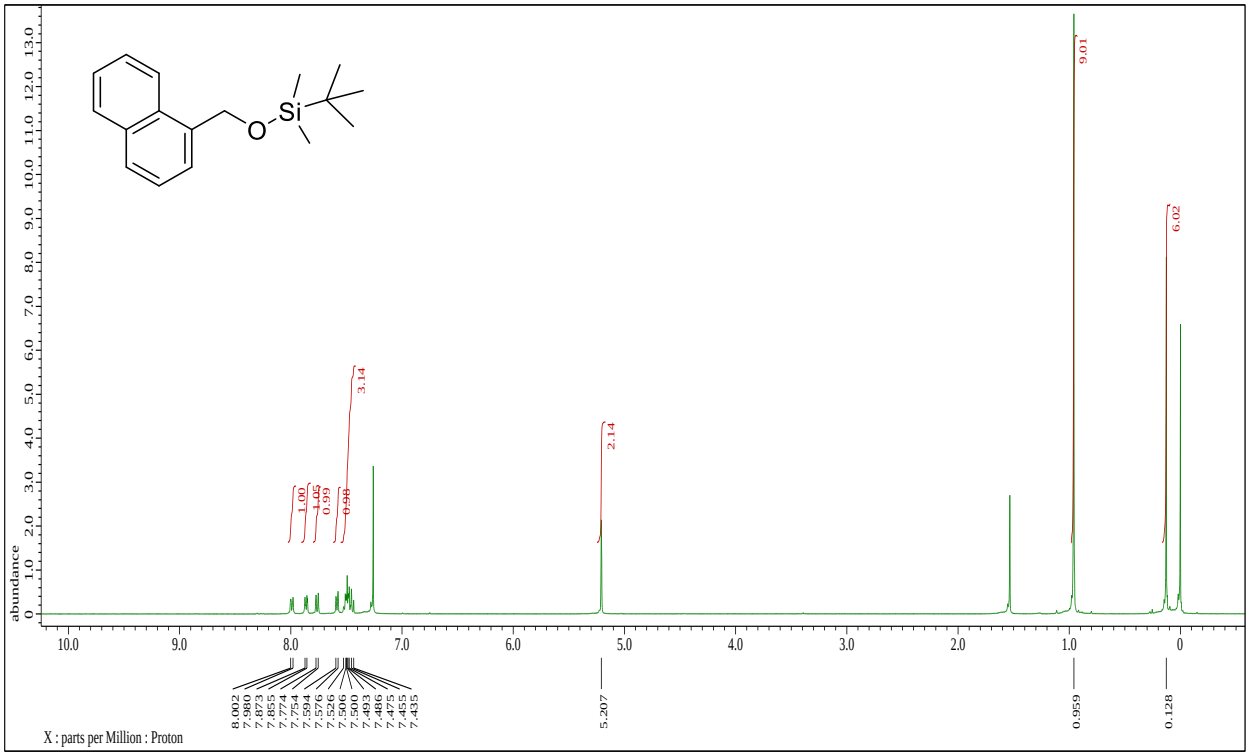


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7e**

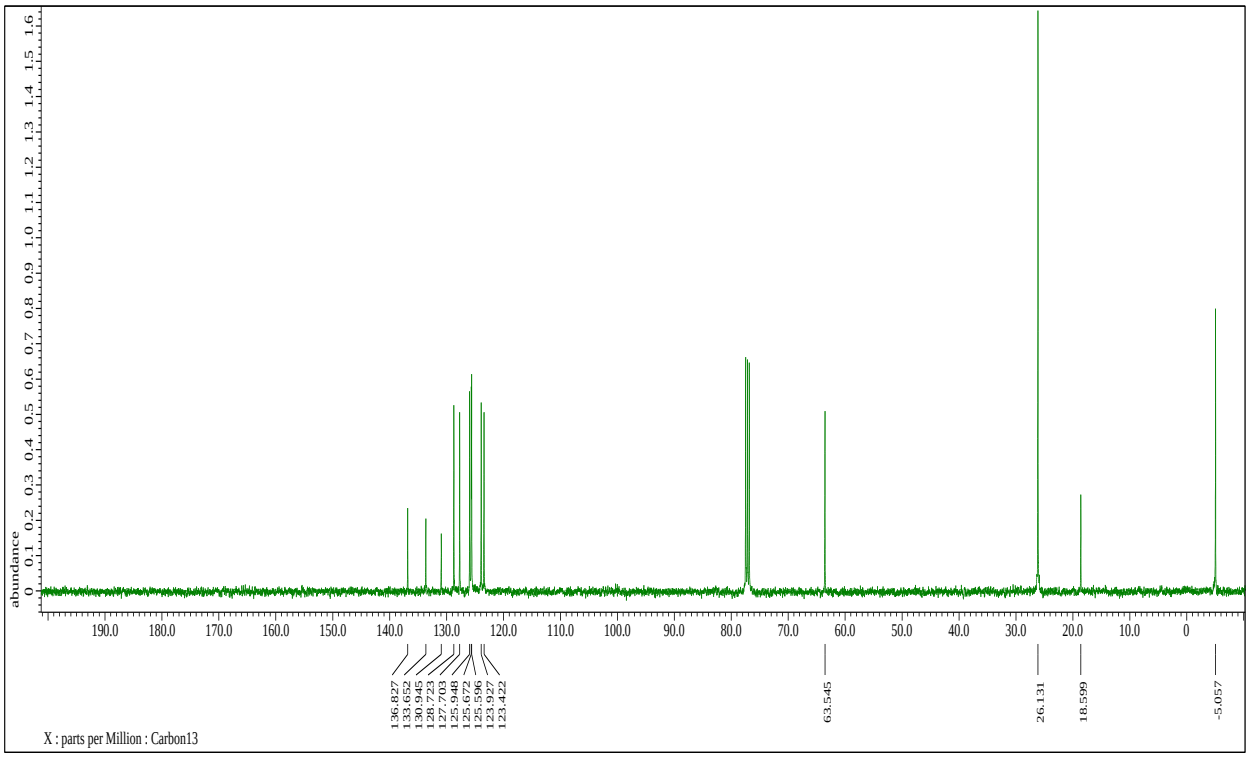


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **7e**

tert-Butyldimethylsilyl 1-naphthalenemethyl ether (7f)

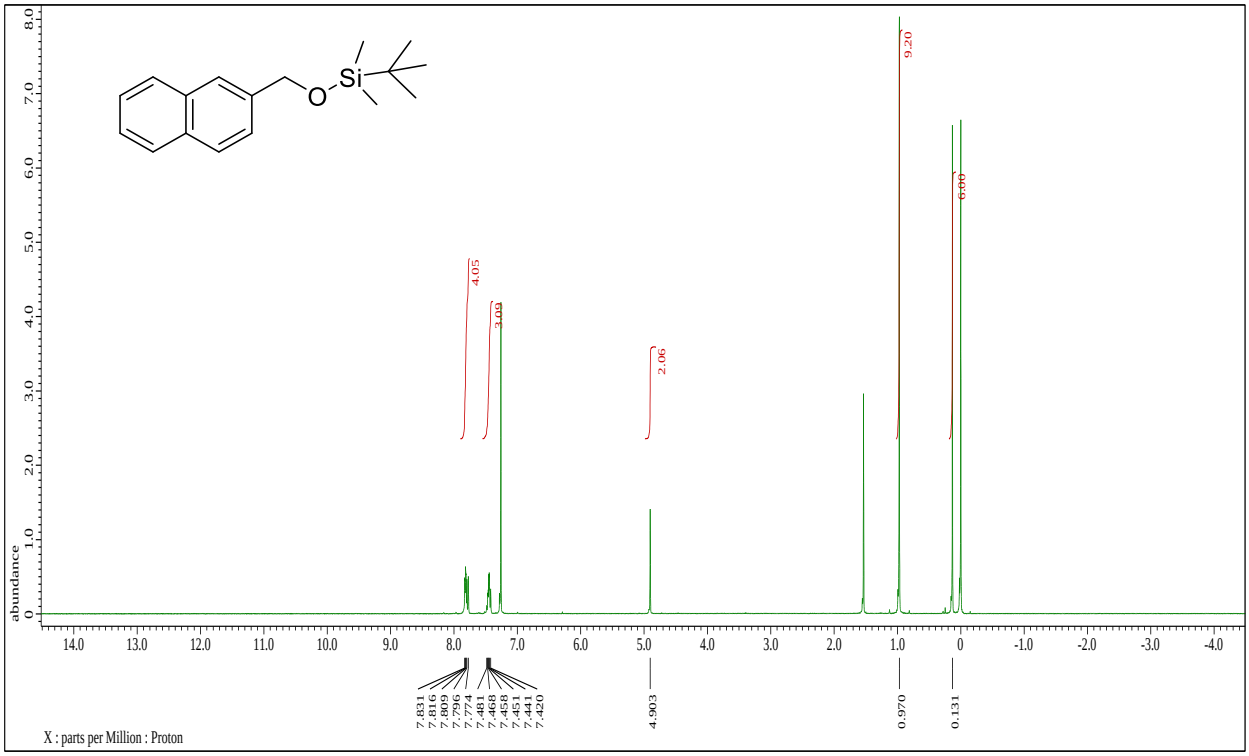


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7f**

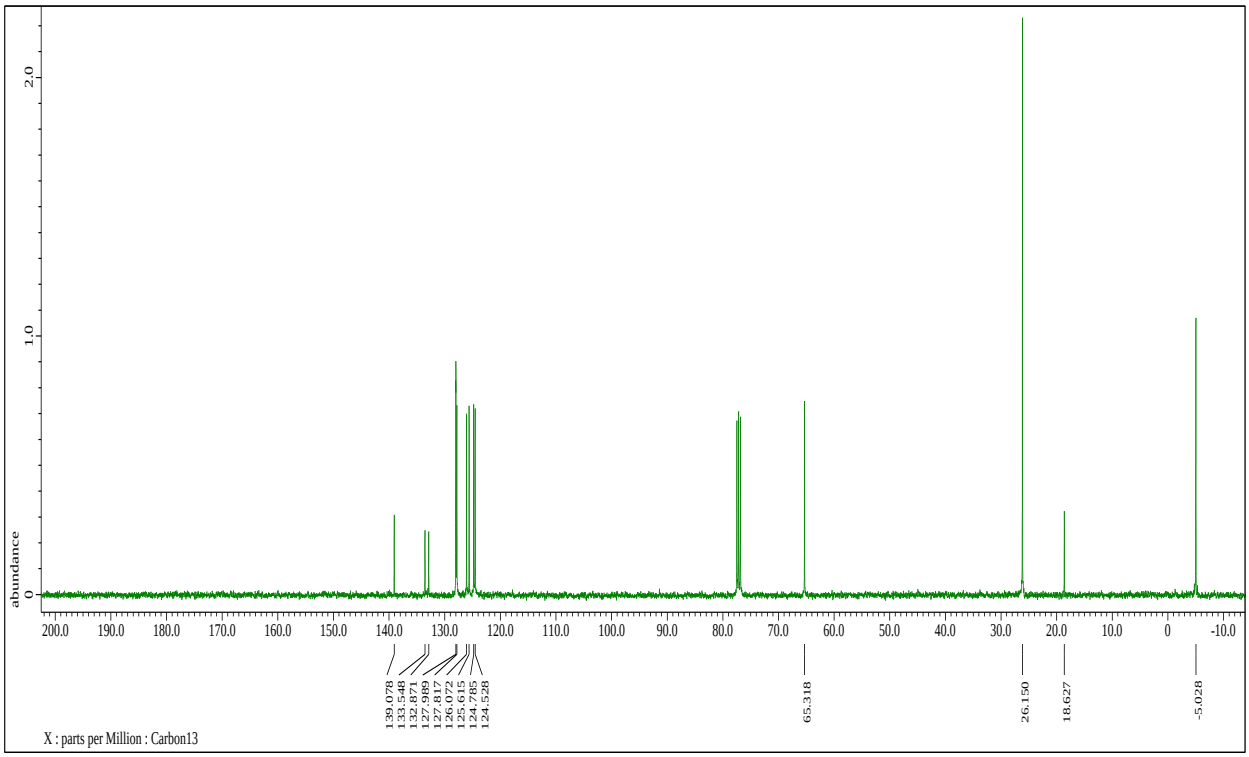


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **7f**

tert-Butyldimethylsilyl 2-naphthalenemethyl ether (7g)

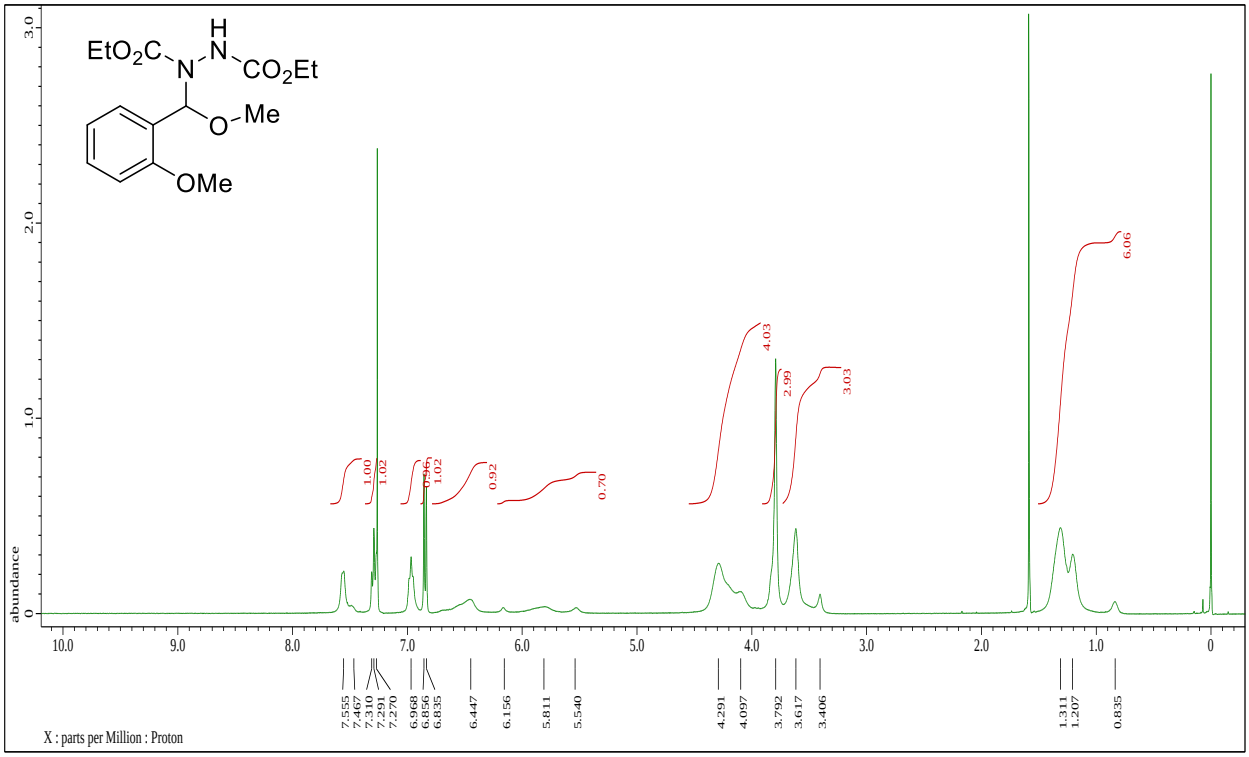


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7g**

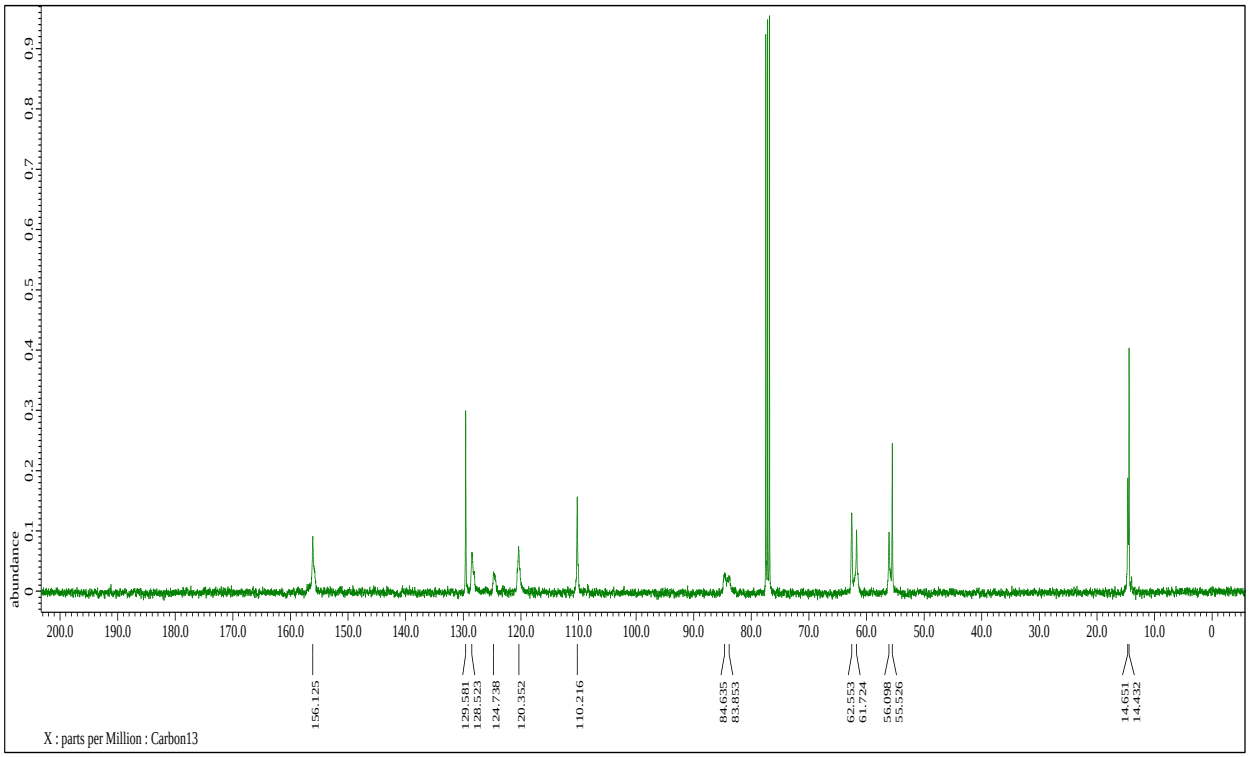


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **7g**

Diethyl 1-(methoxy(2-methoxyphenyl)methyl)hydrazine-1,2-dicarboxylate (8a)

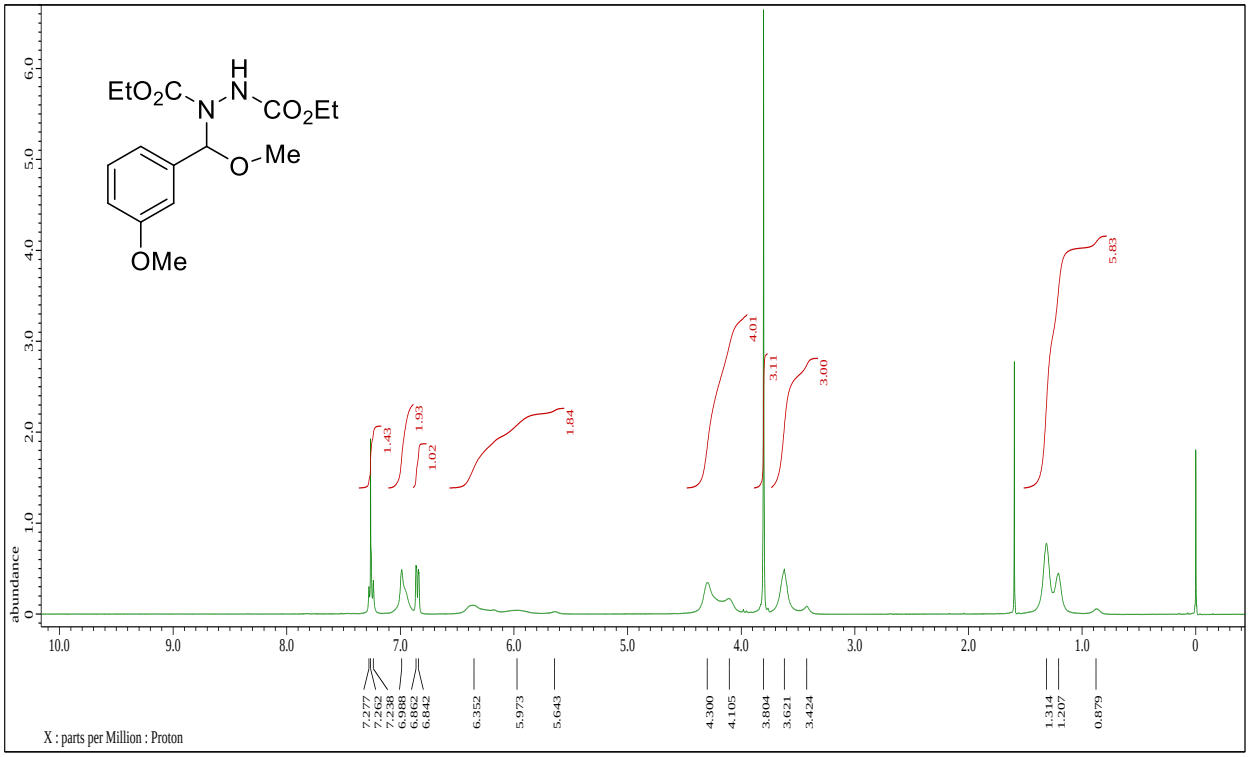


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8a**

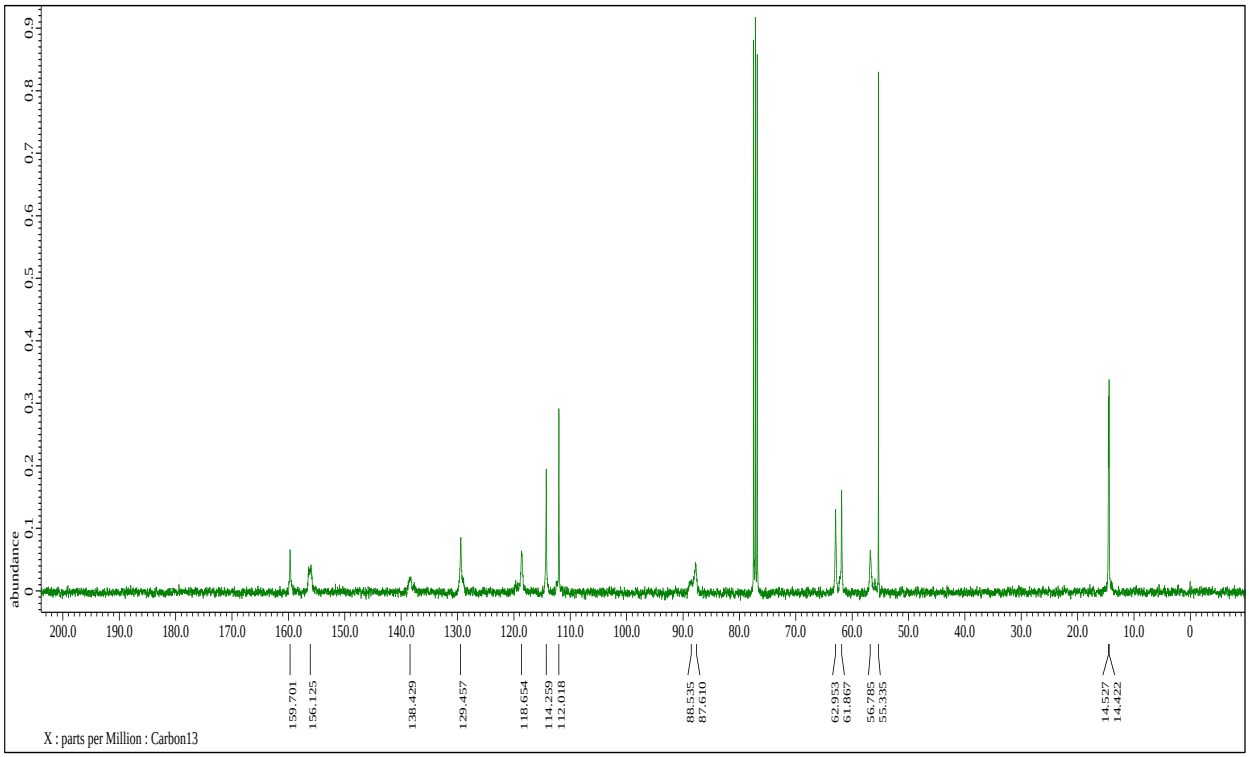


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **8a**

Diethyl 1-(methoxy(3-methoxyphenyl)methyl)hydrazine-1,2-dicarboxylate (8b)

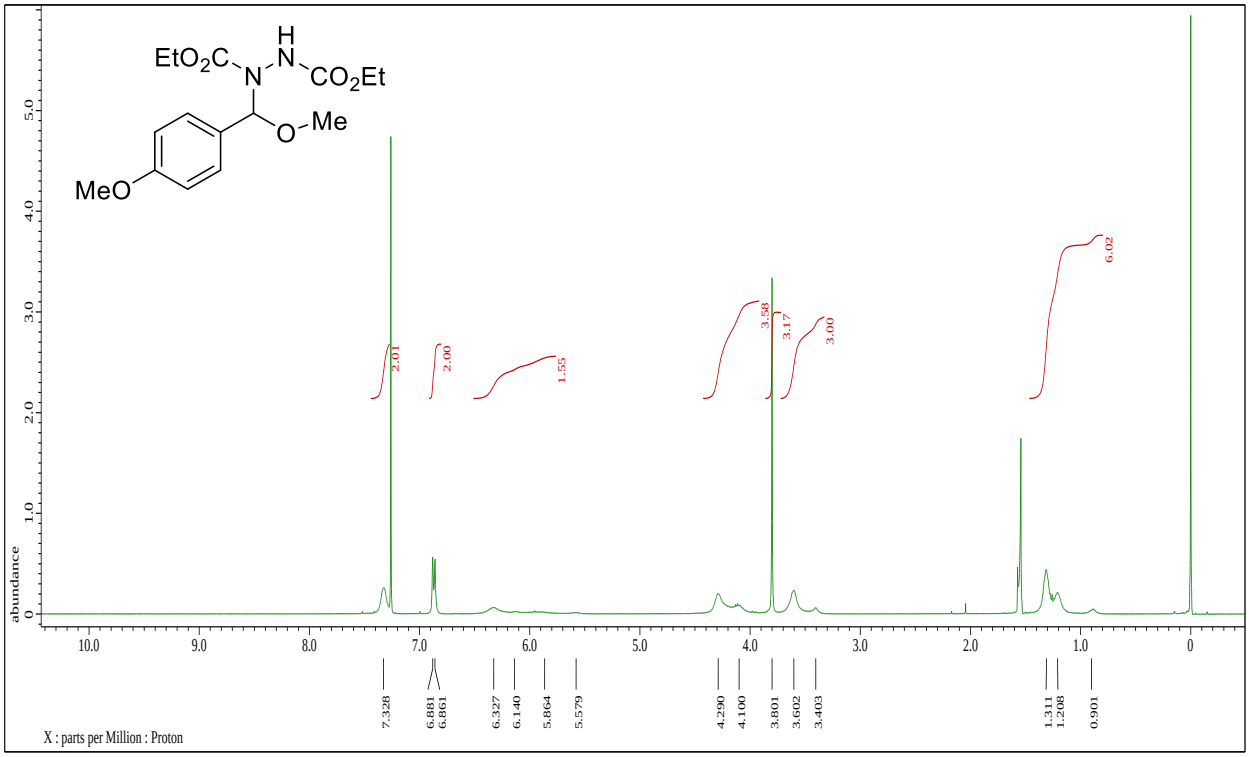


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8b**

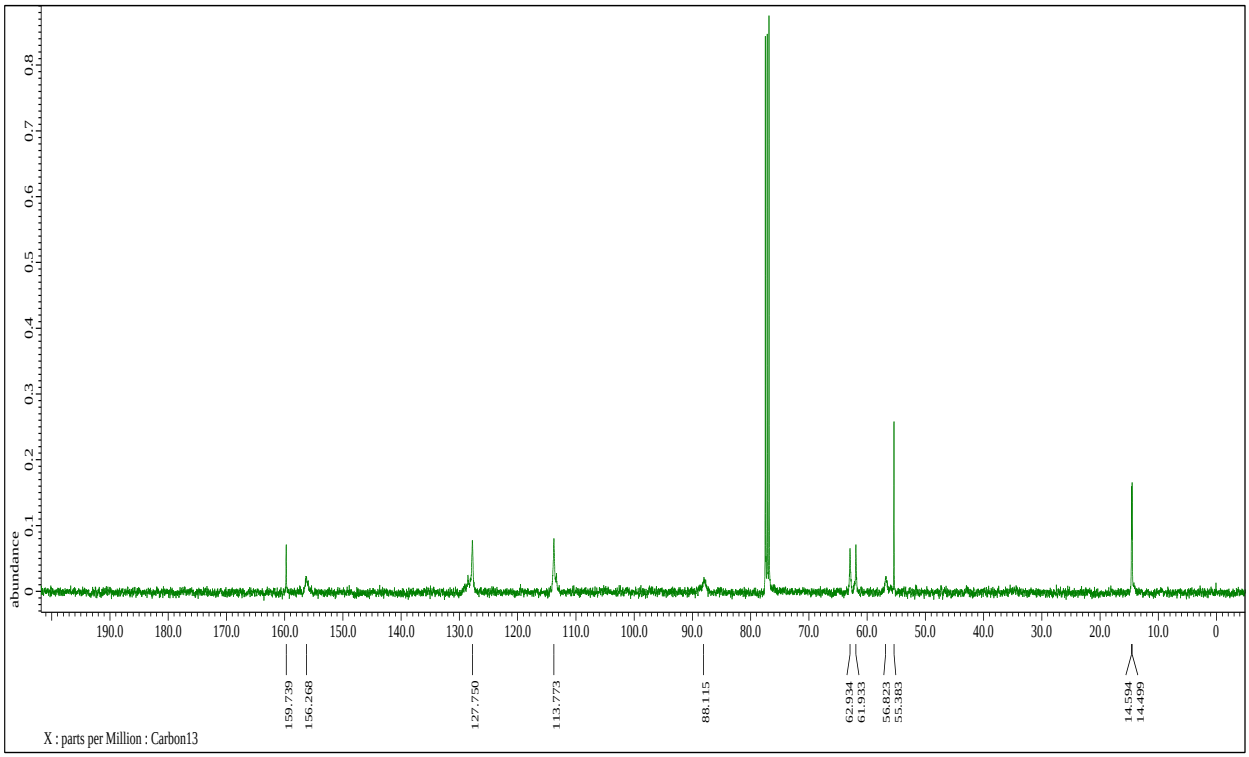


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **8b**

Diethyl 1-(methoxy(4-methoxyphenyl)methyl)hydrazine-1,2-dicarboxylate (8c)

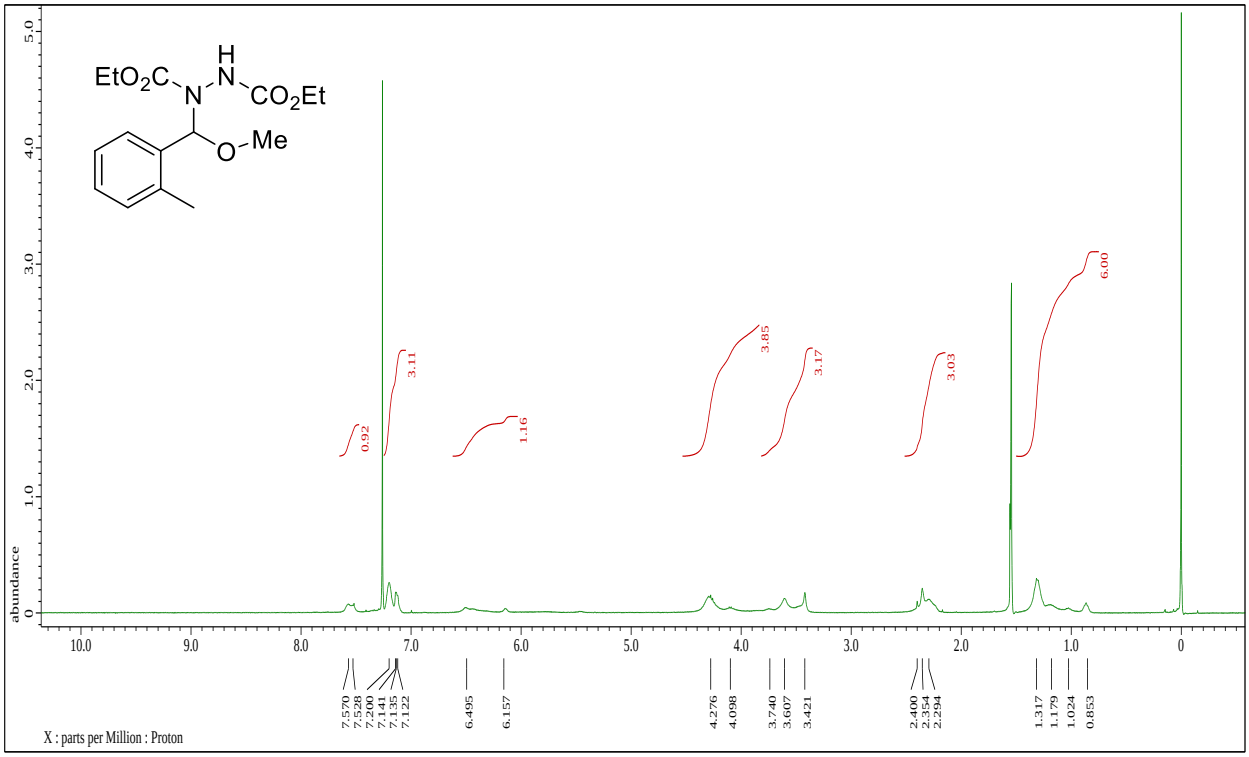


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8c**

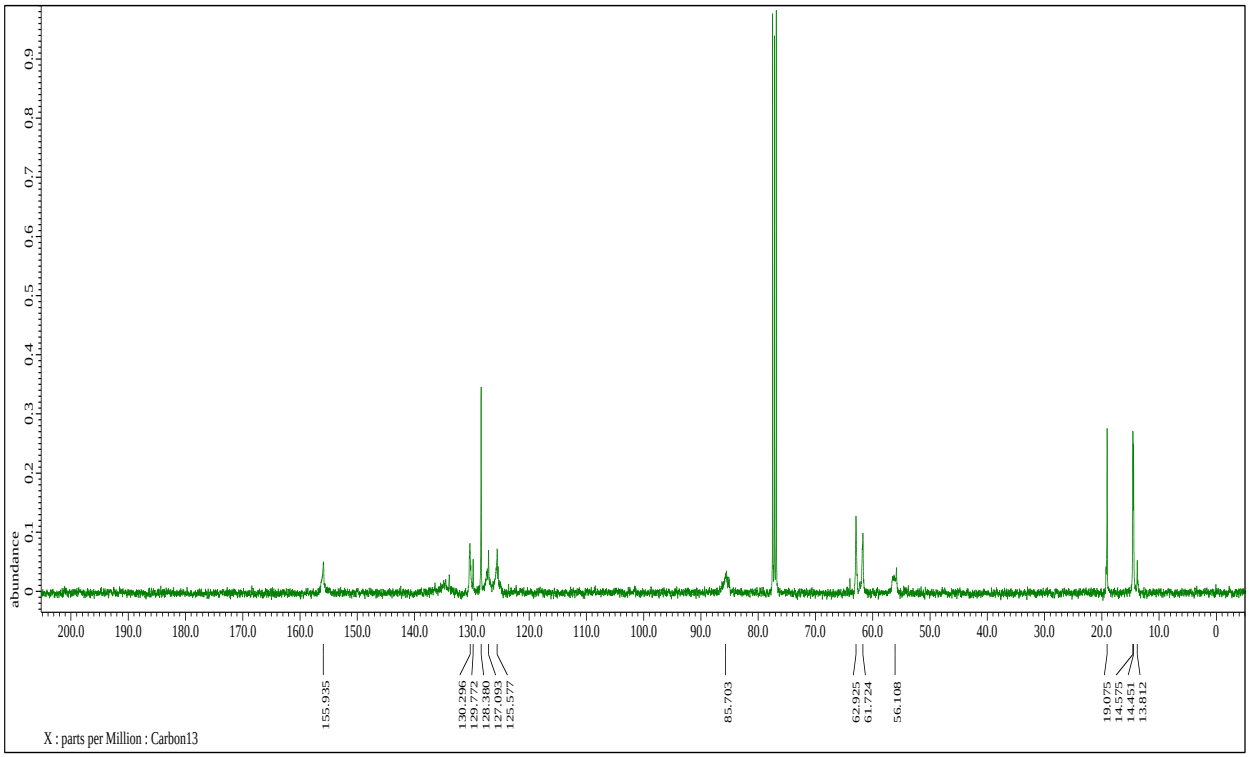


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **8c**

Diethyl 1-(methoxy(o-tolyl)methyl)hydrazine-1,2-dicarboxylate (8d)

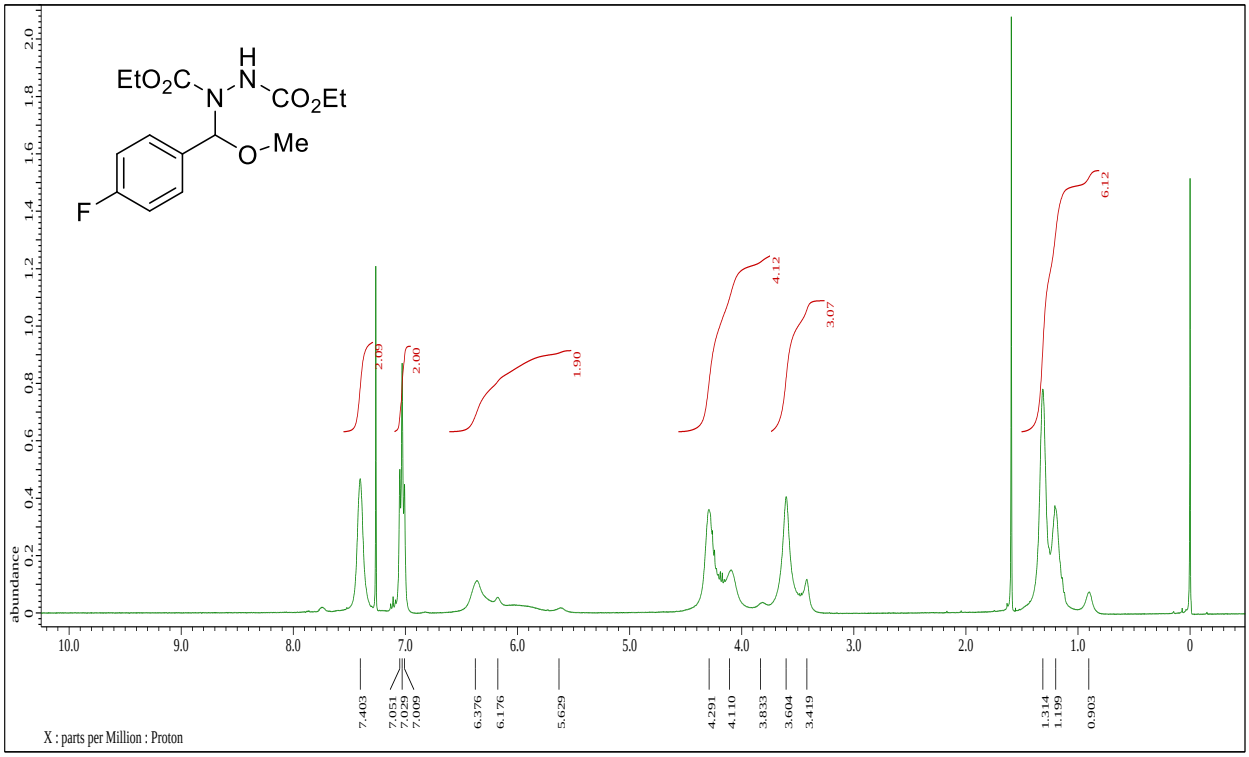


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8d**

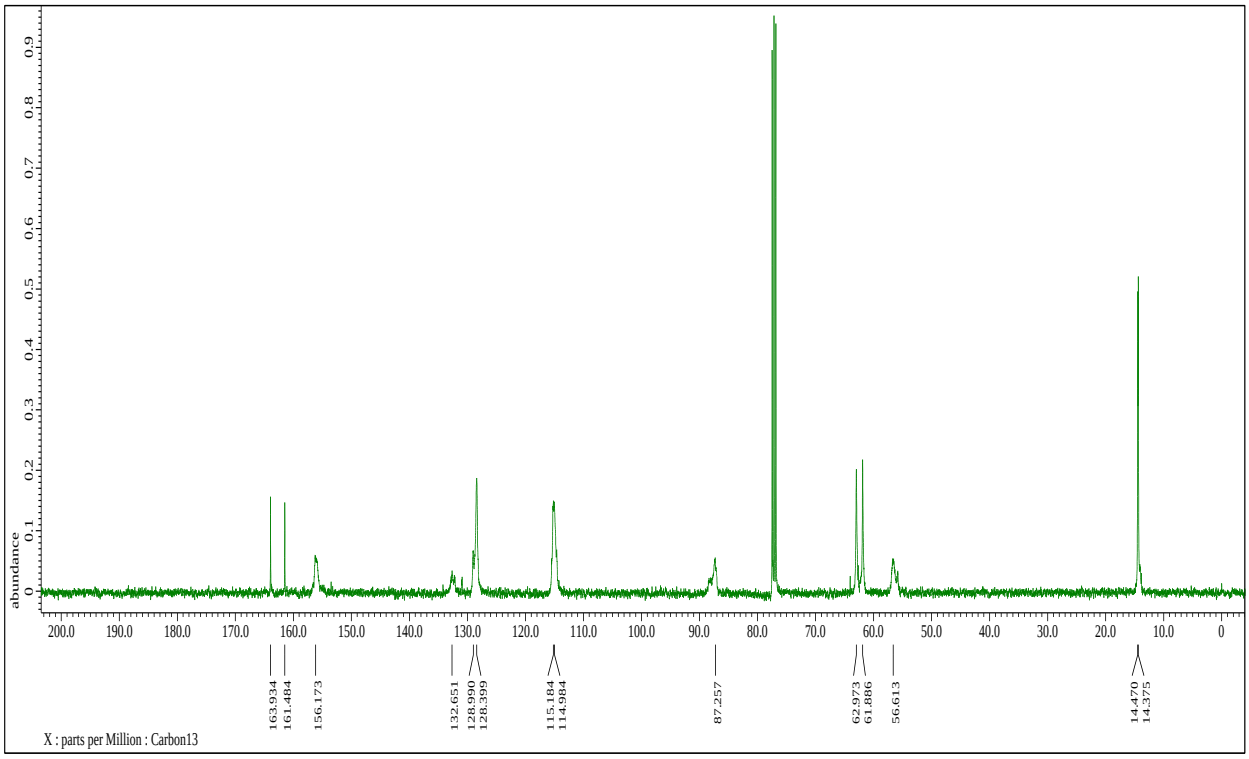


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **8d**

Diethyl 1-((4-fluorophenyl)(methoxy)methyl)hydrazine-1,2-dicarboxylate (8e)

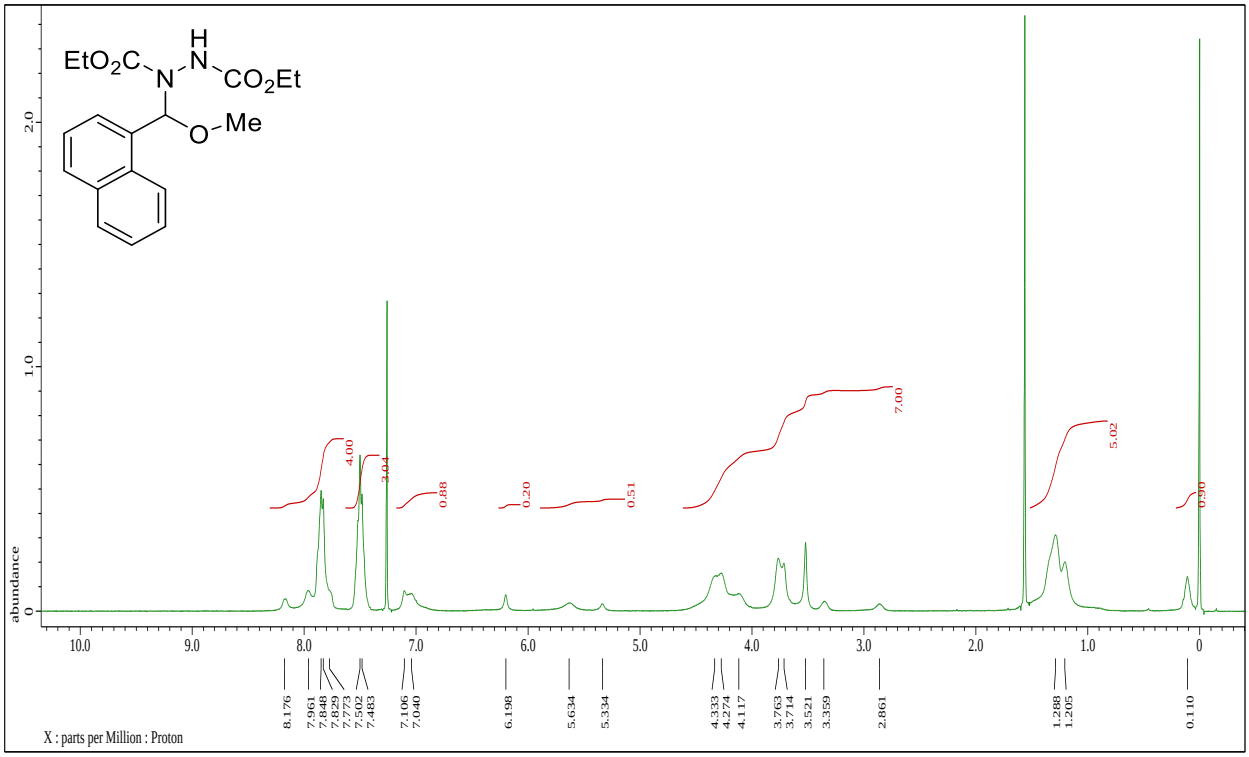


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8e**

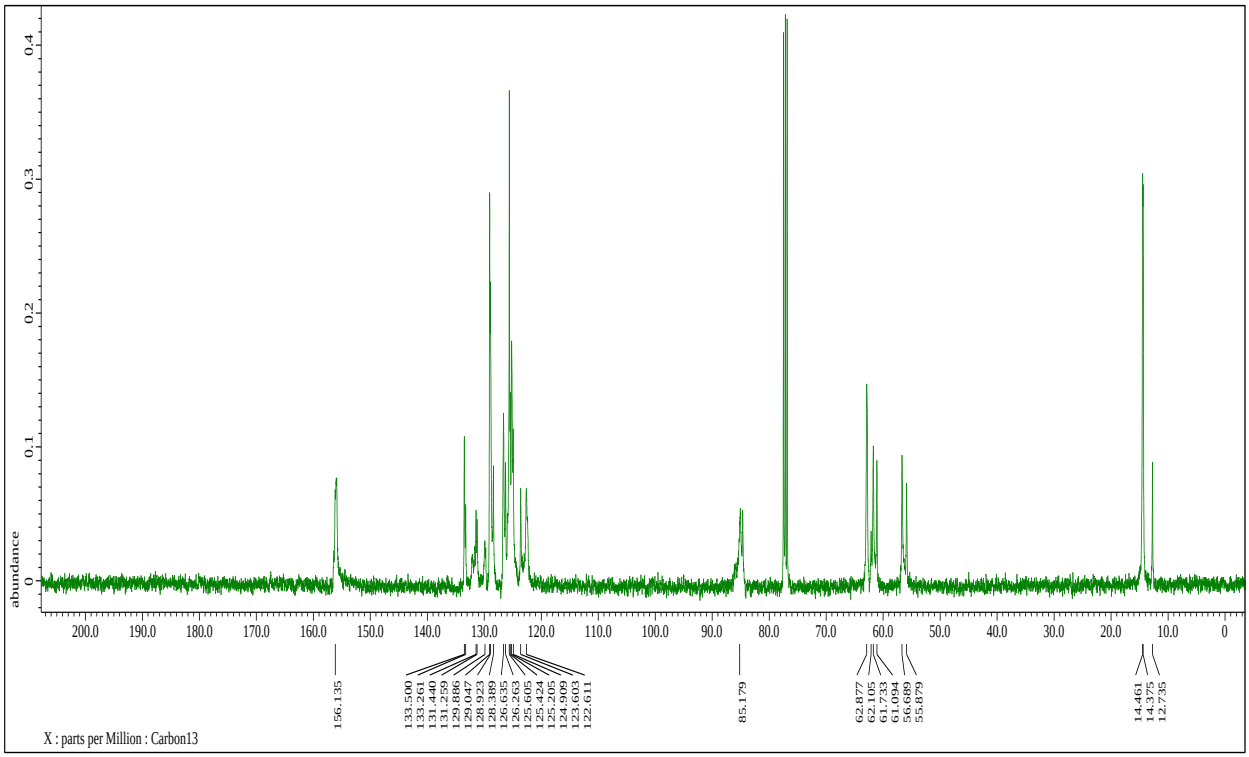


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **8e**

Diethyl 1-(methoxy(naphthalen-1-yl)methyl)hydrazine-1,2-dicarboxylate (8f)

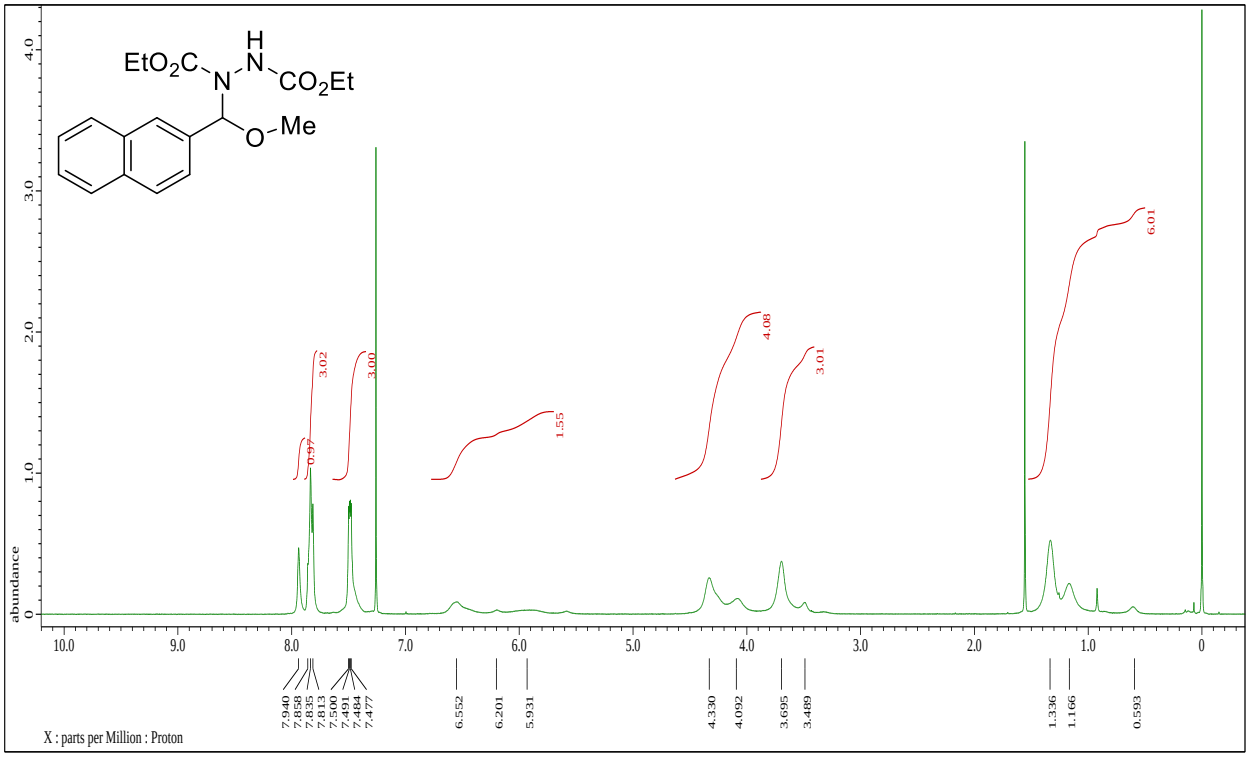


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8f**

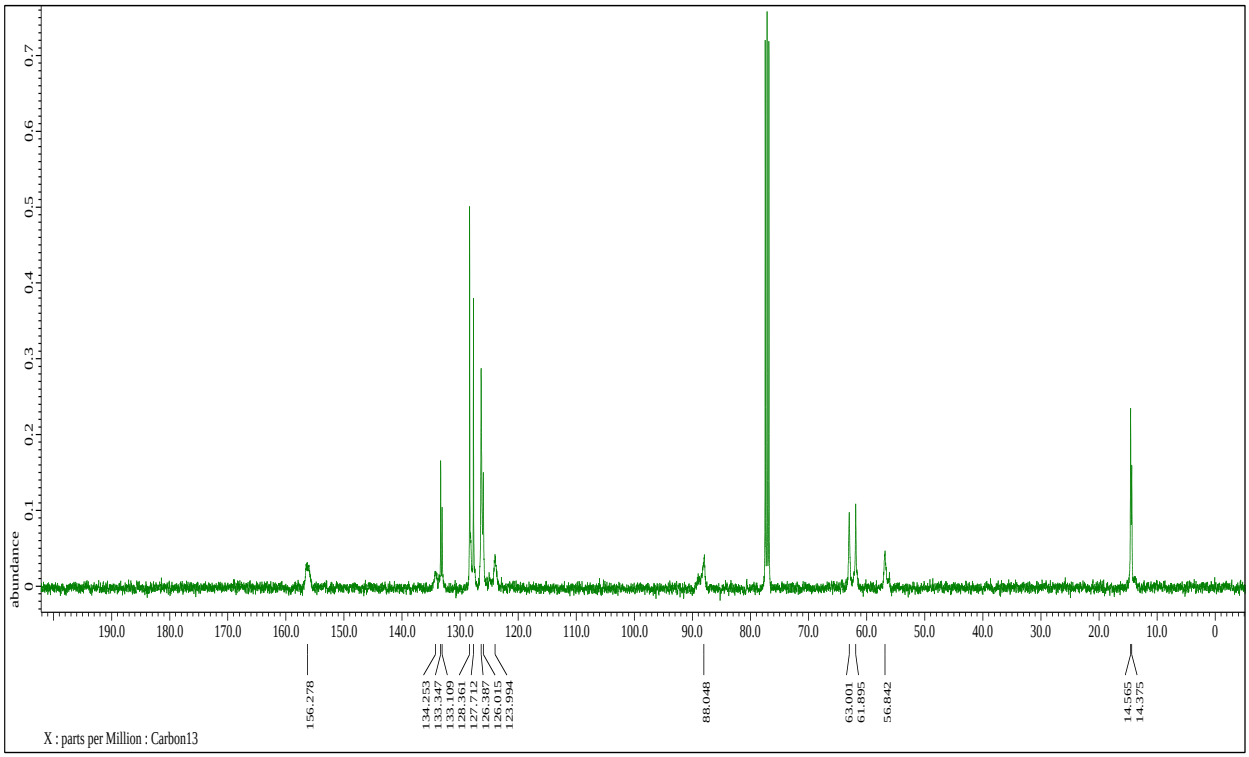


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **8f**

Diethyl 1-(methoxy(naphthalen-2-yl)methyl)hydrazine-1,2-dicarboxylate (8g)

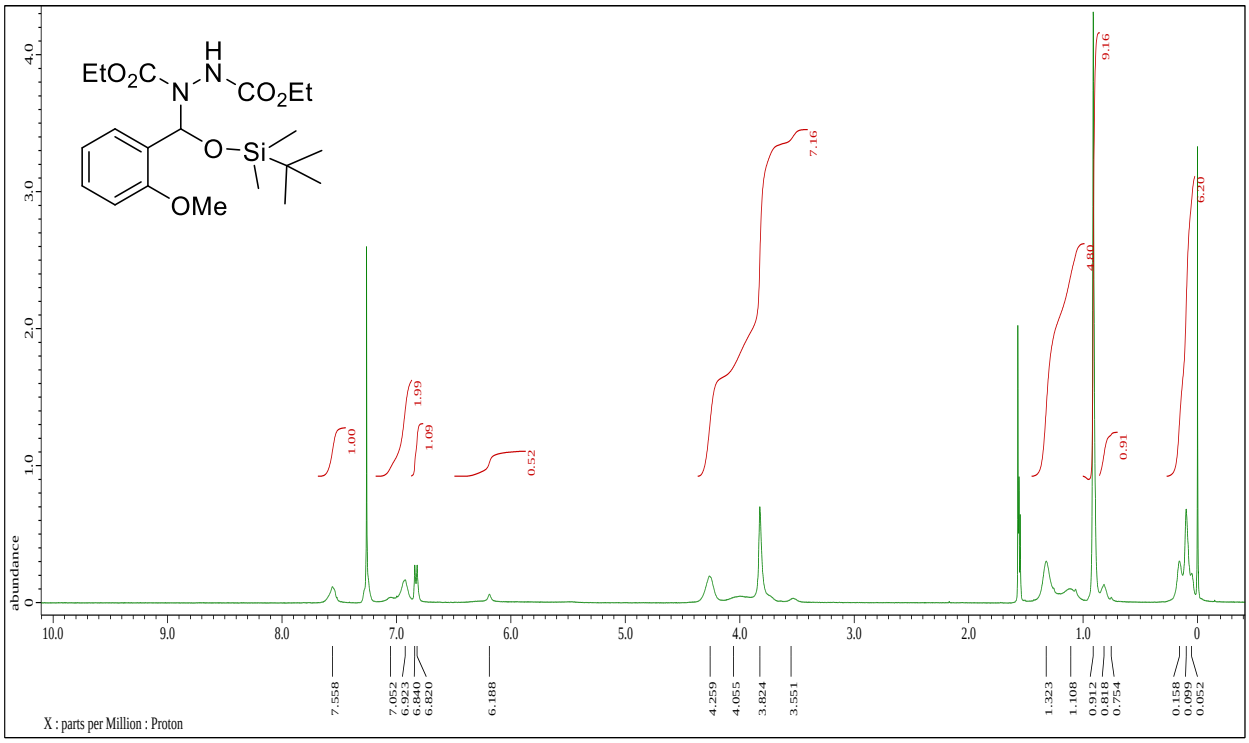


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8g**

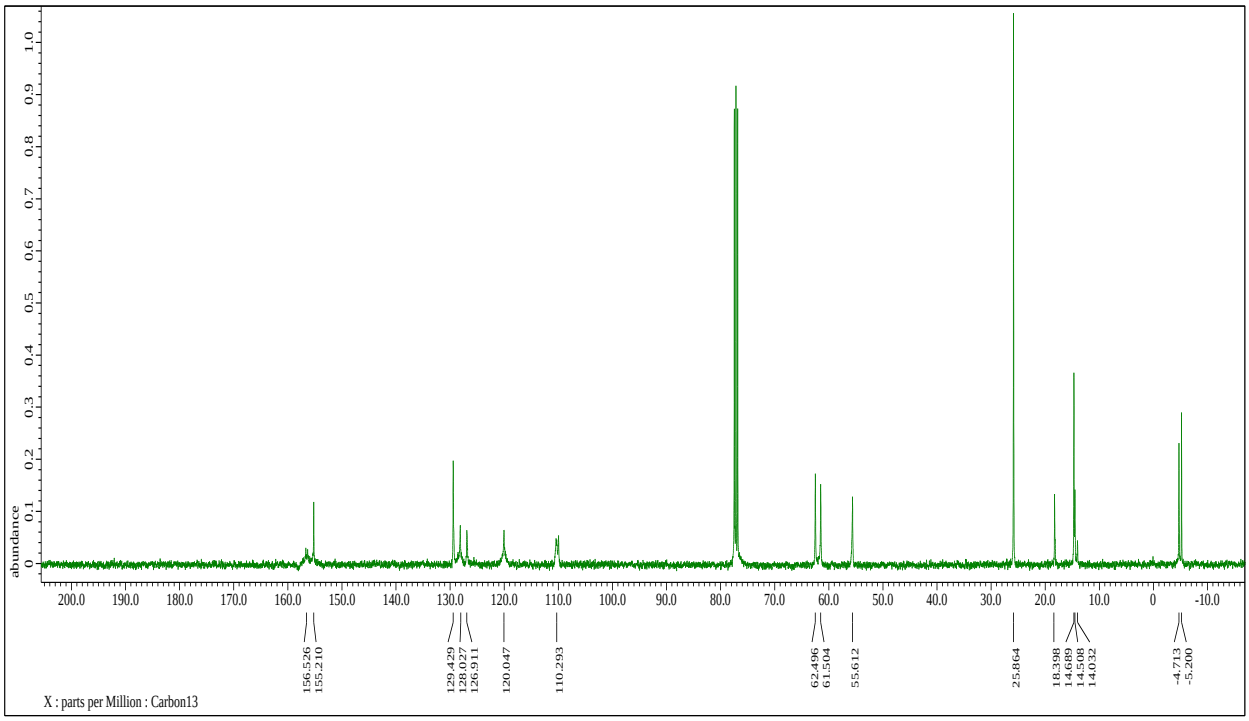


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **8g**

Diethyl 1-(((*tert*-butyldimethylsilyl)oxy)(2-methoxyphenyl)methyl)hydrazine-1,2-dicarboxylate (9a)

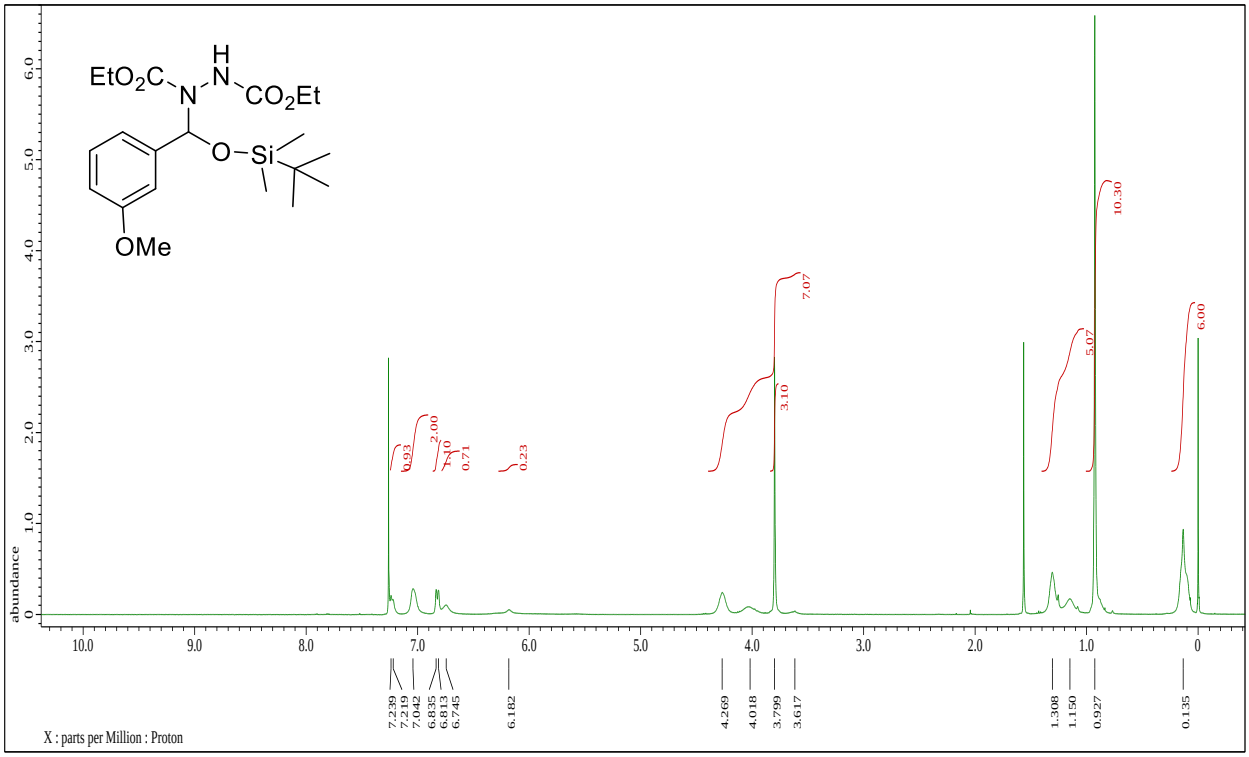


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9a**

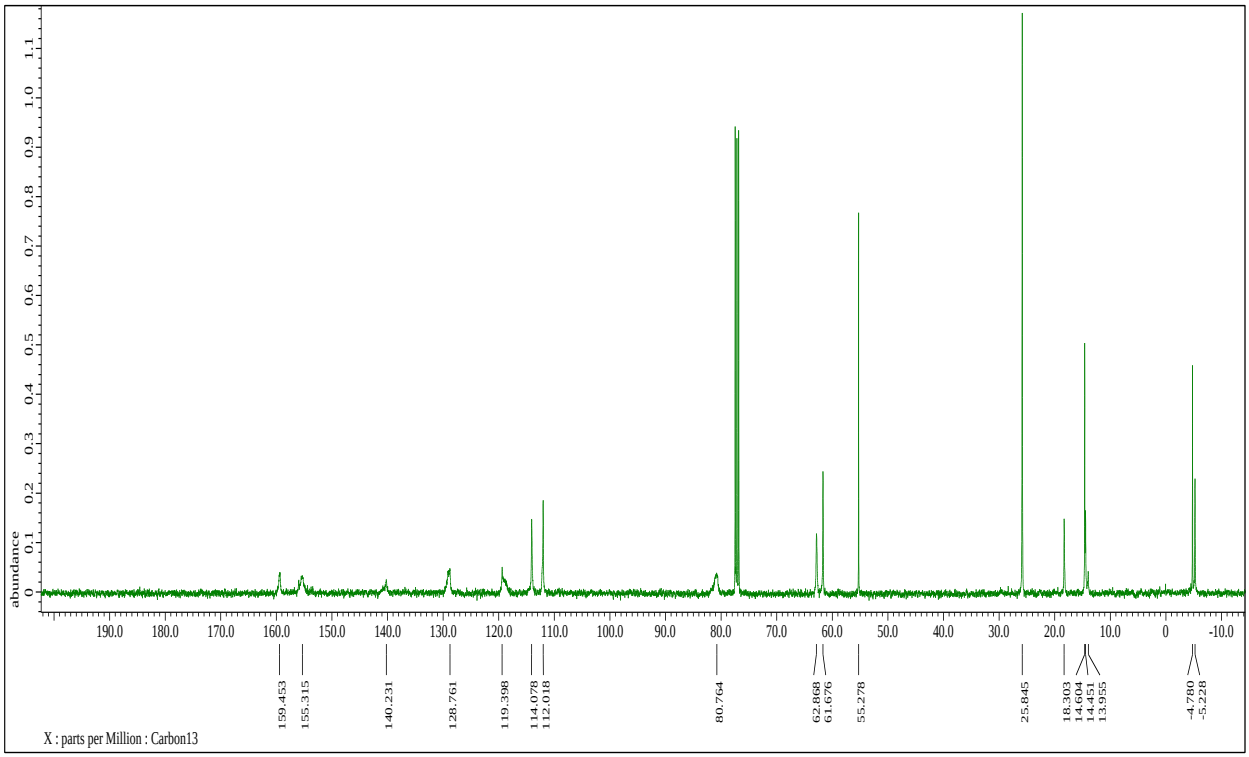


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **9a**

Diethyl 1-(((tert-butyldimethylsilyl)oxy)(3-methoxyphenyl)methyl)hydrazine-1,2-dicarboxylate (9b)

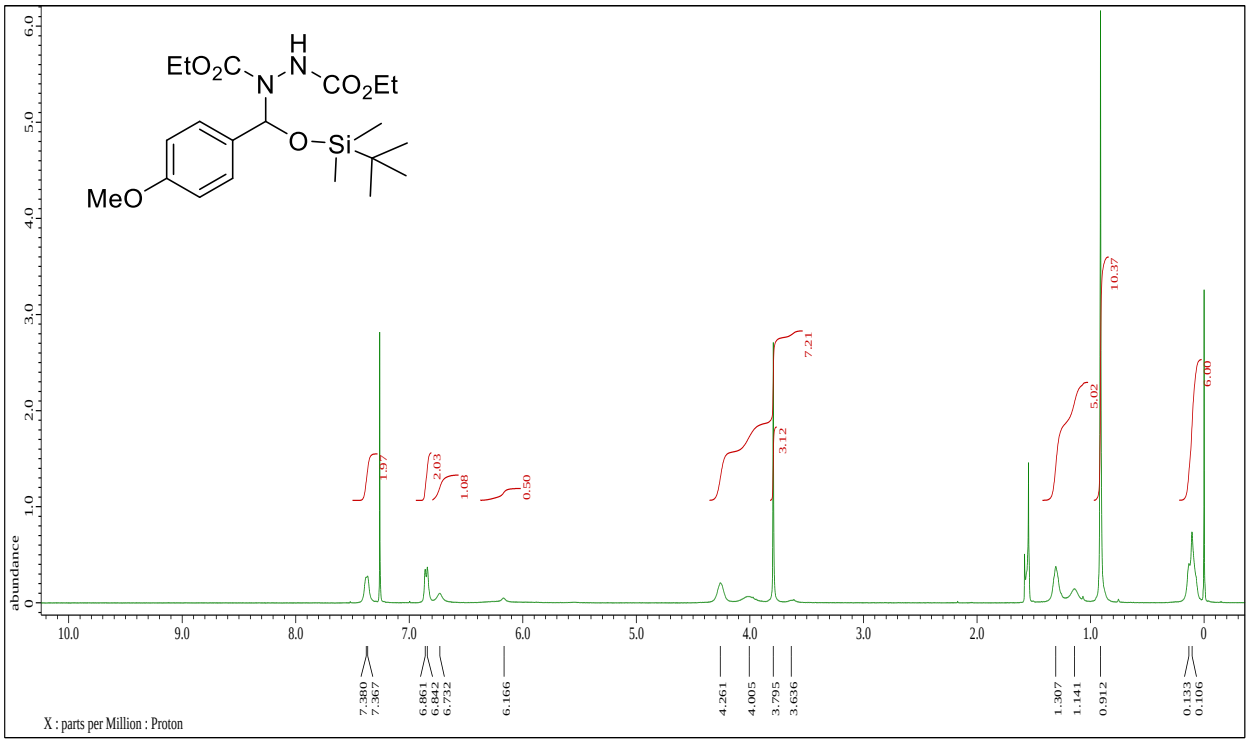


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9b**

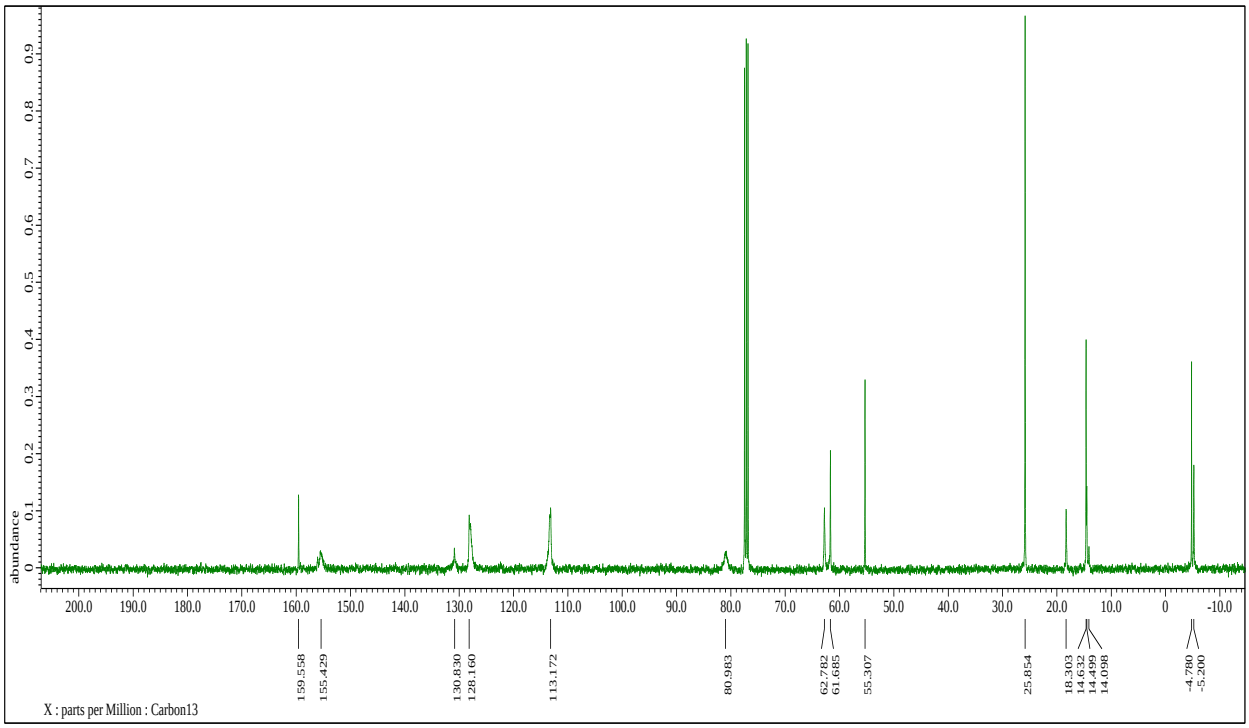


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **9b**

Diethyl 1-(((tert-butyldimethylsilyl)oxy)(4-methoxyphenyl)methyl)hydrazine-1,2-dicarboxylate (9c)

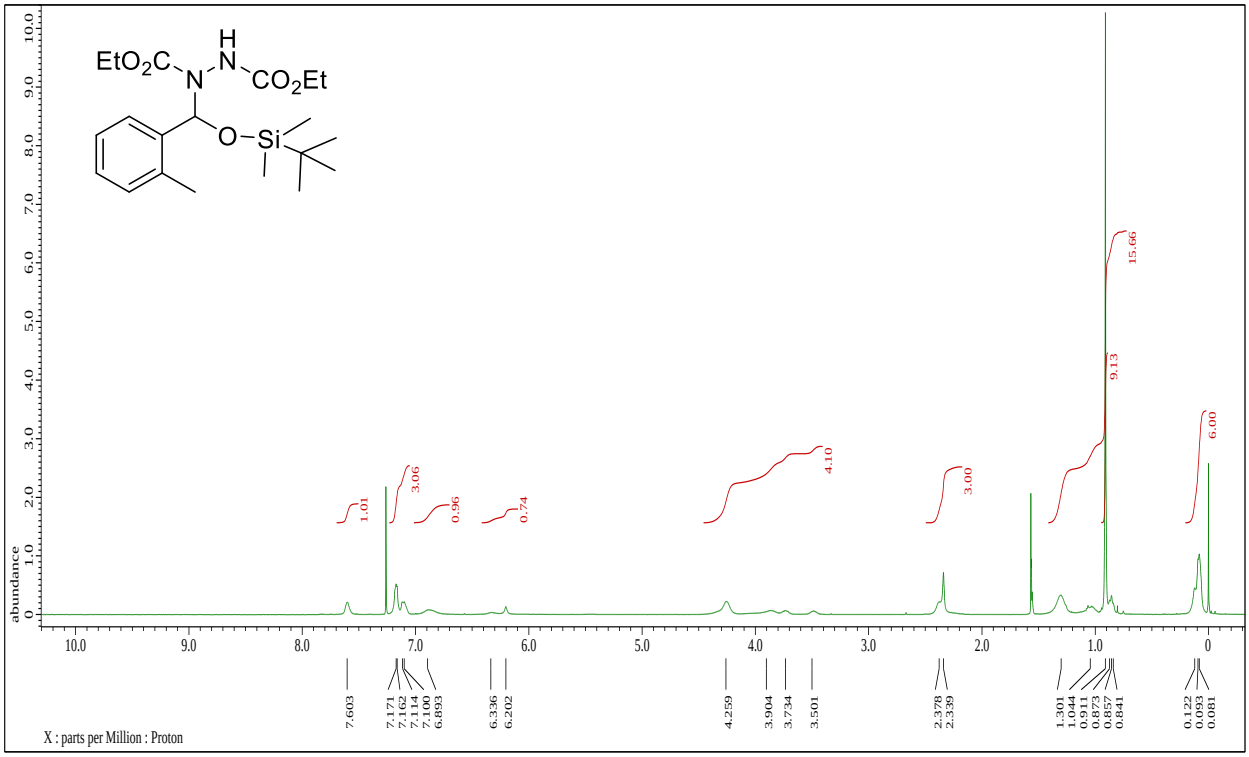


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9c**

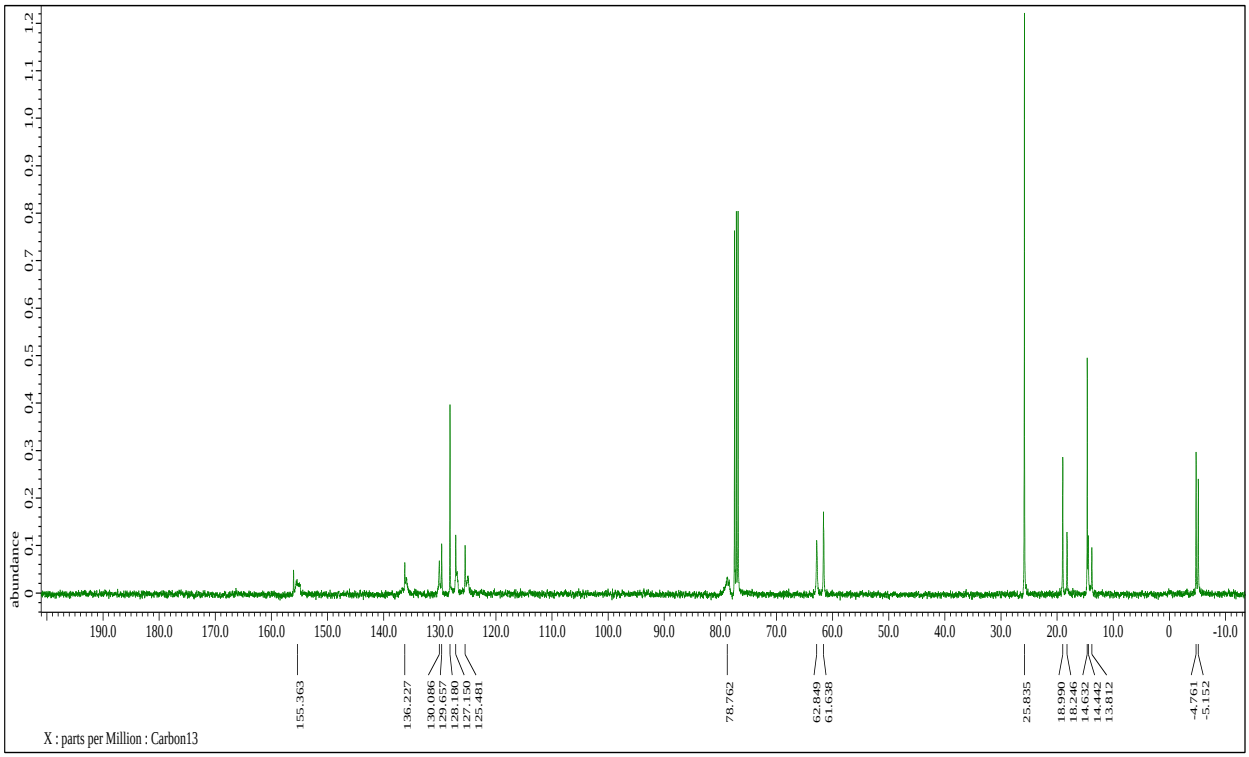


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **9c**

Diethyl 1-(((tert-butyldimethylsilyl)oxy)(o-tolyl)methyl)hydrazine-1,2-dicarboxylate (9d)

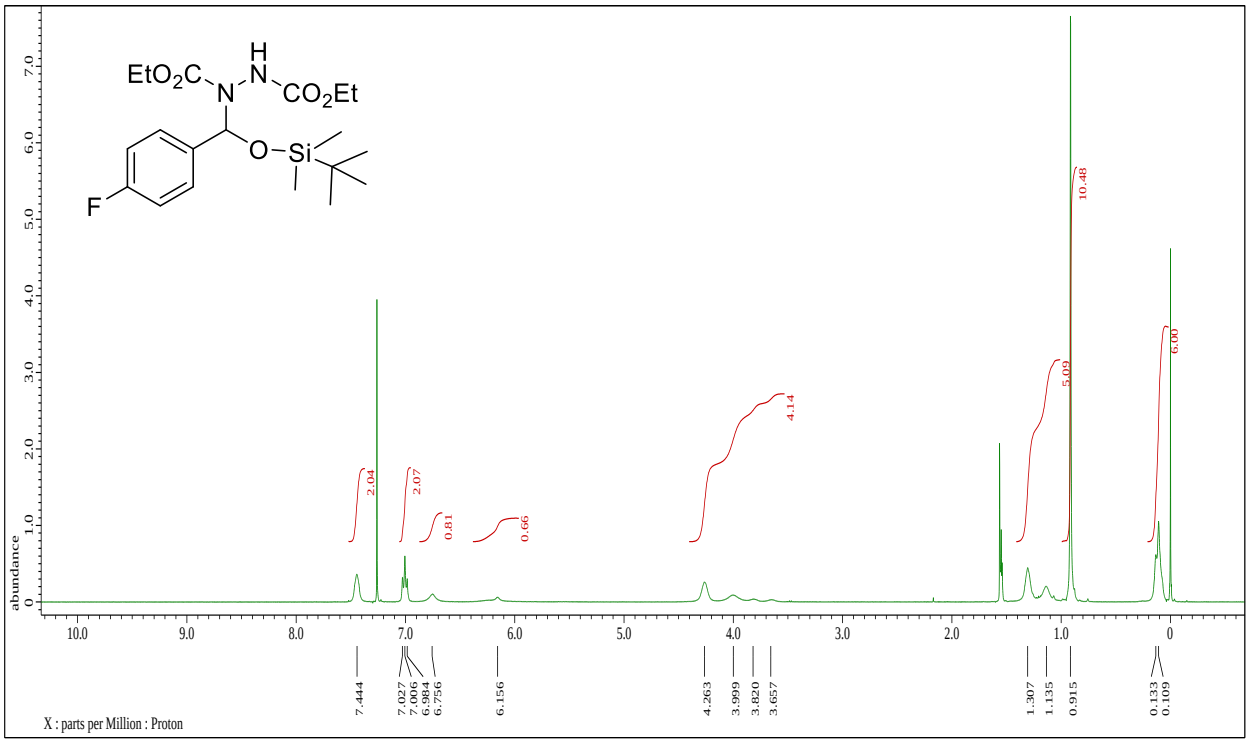


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9d**

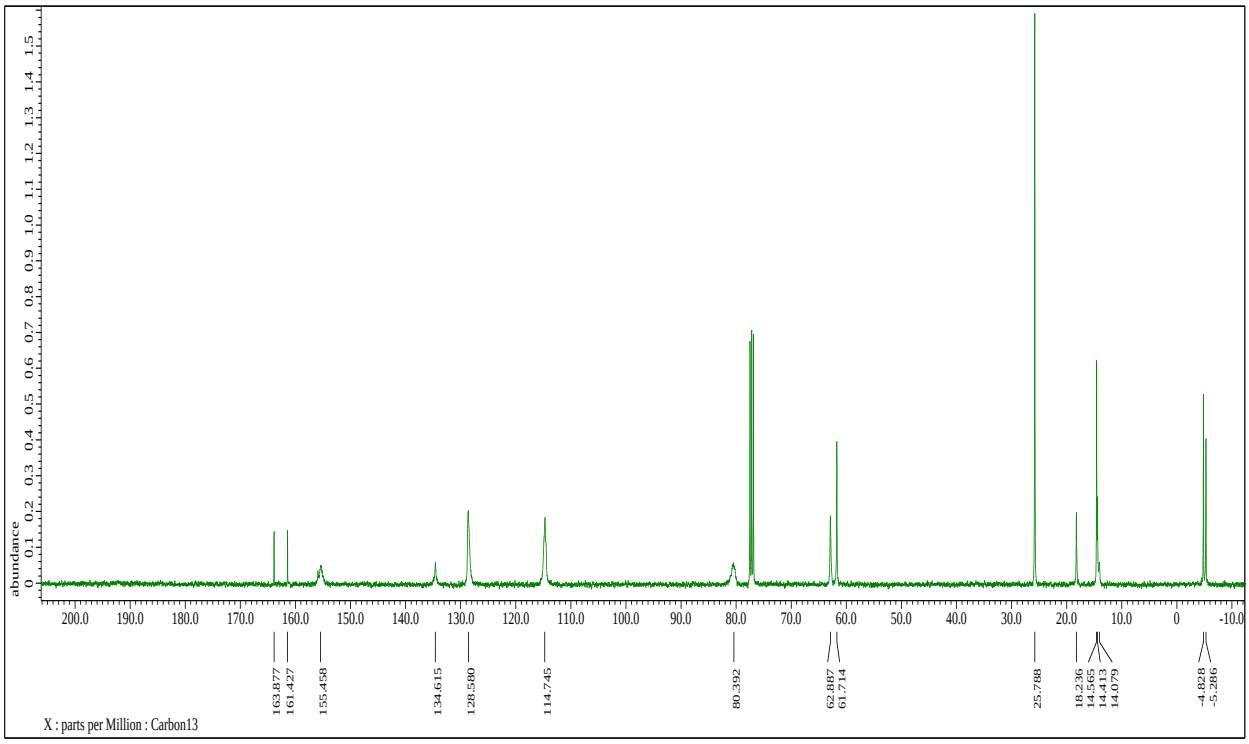


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **9d**

Diethyl 1-(((*tert*-butyldimethylsilyl)oxy)(4-fluorophenyl)methyl)hydrazine-1,2-dicarboxylate (9e)

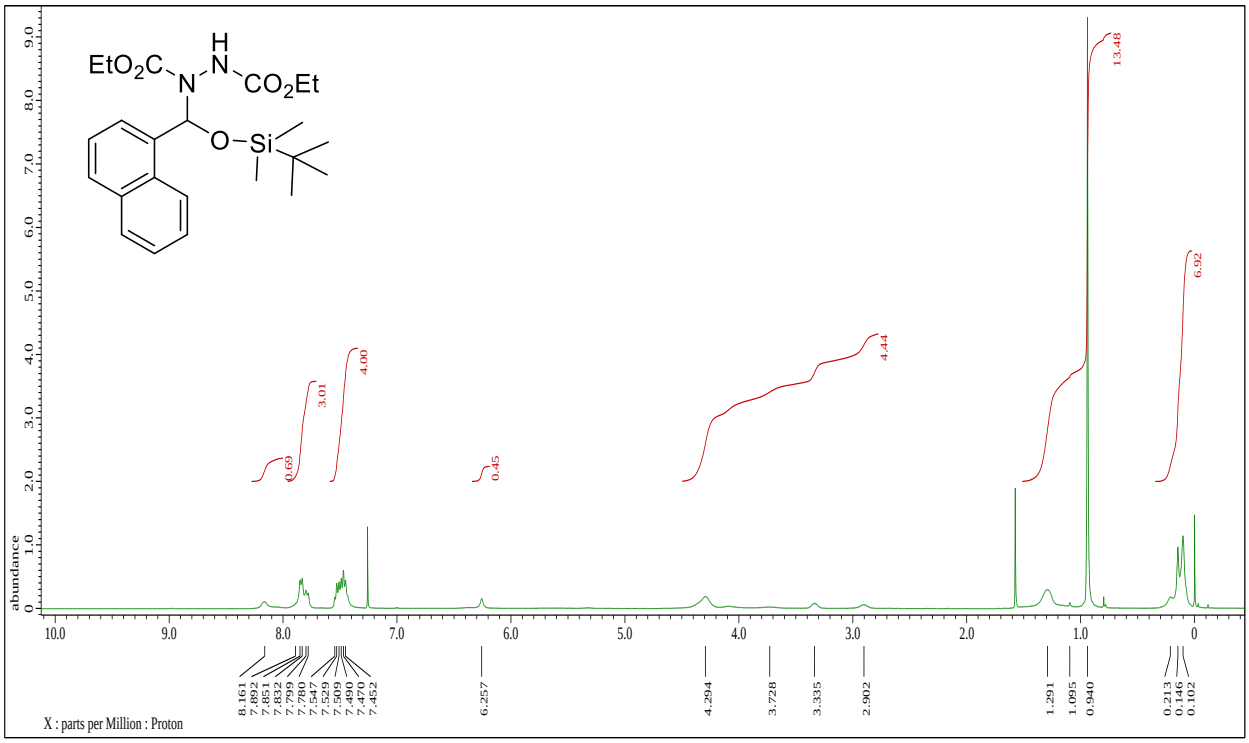


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9e**

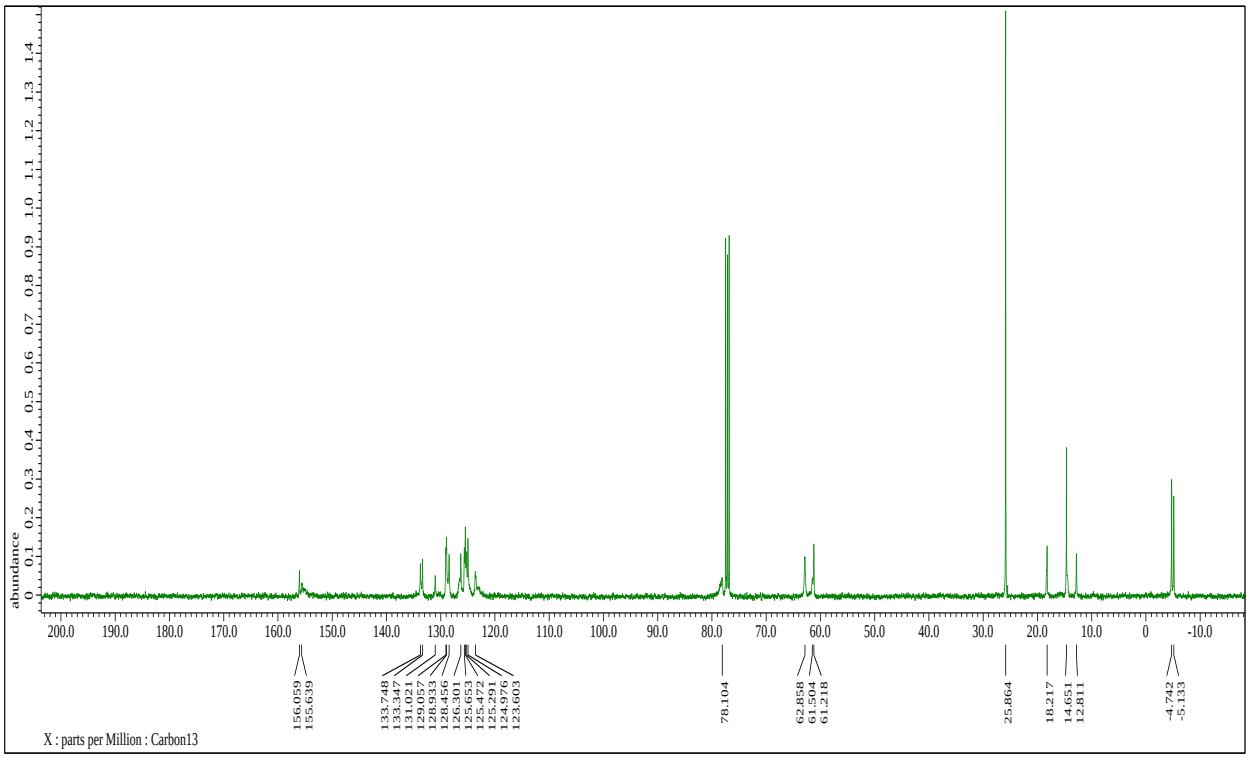


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **9e**

Diethyl 1-(((*tert*-butyldimethylsilyl)oxy)(naphthalen-1-yl)methyl)hydrazine-1,2-dicarboxylate (9f)

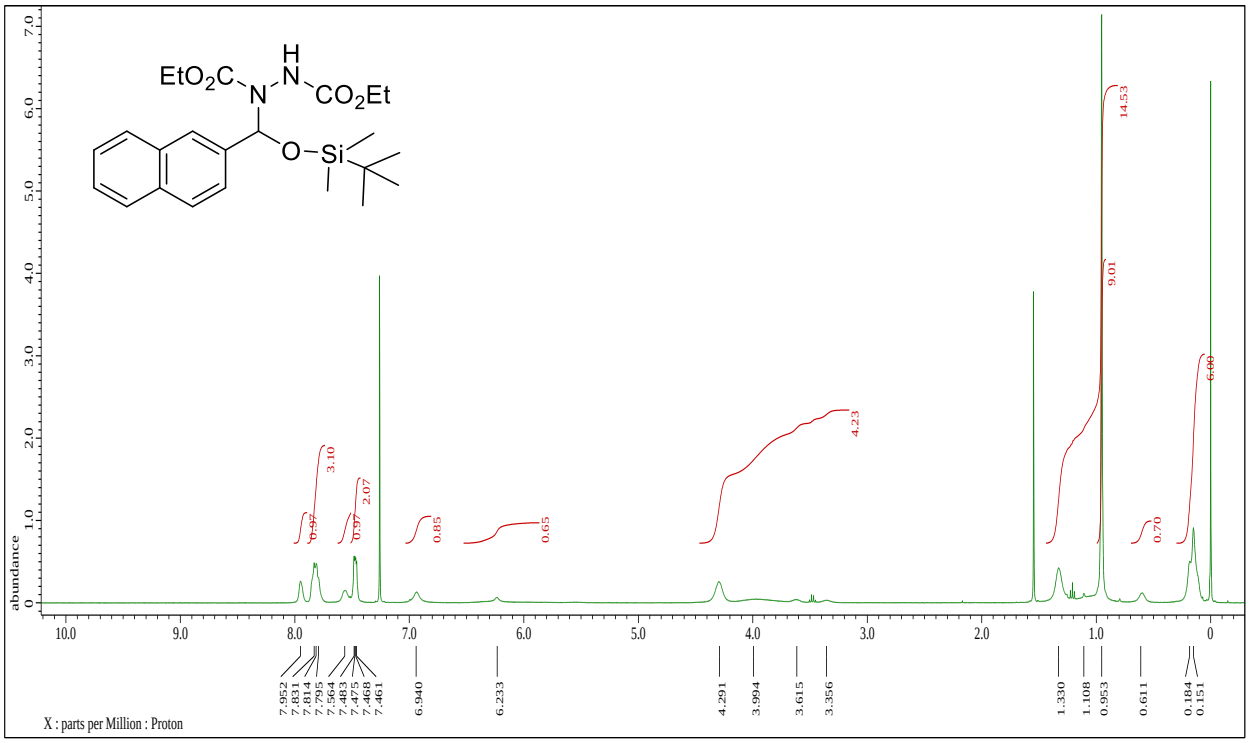


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9f**

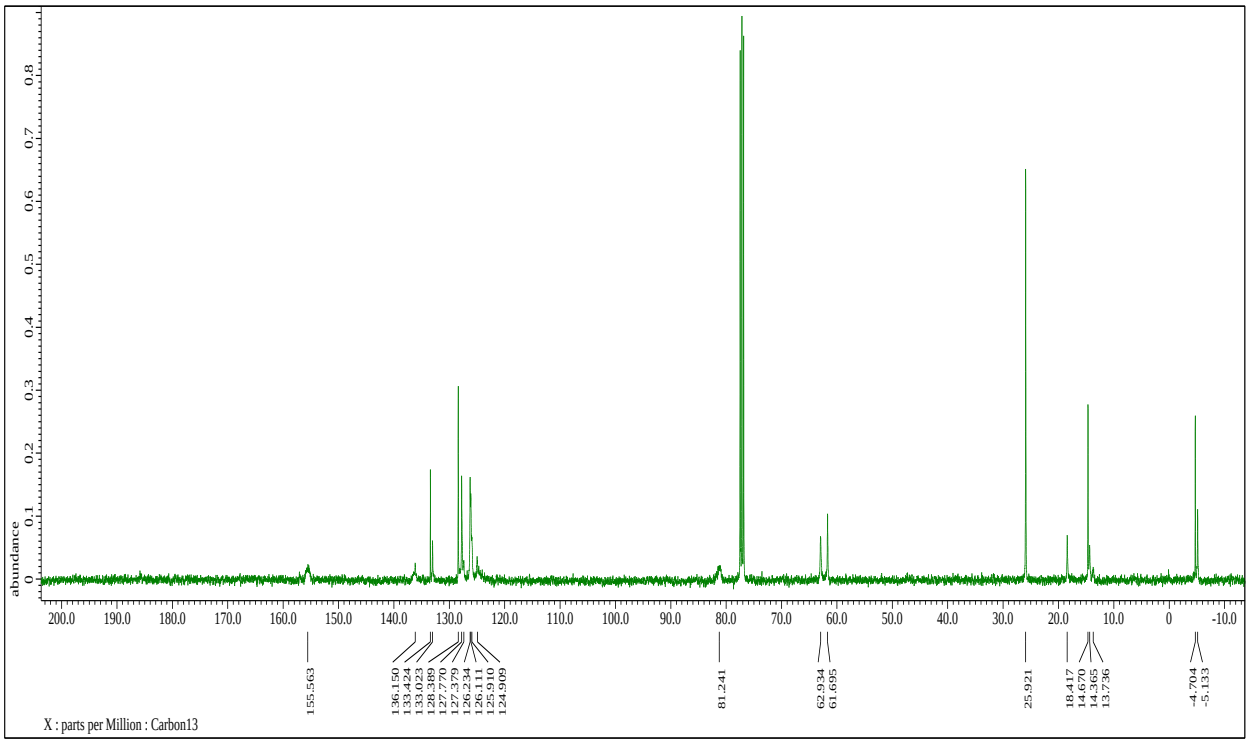


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **9f**

Diethyl 1-(((*tert*-butyldimethylsilyl)oxy)(naphthalen-2-yl)methyl)hydrazine-1,2-dicarboxylate (9g)

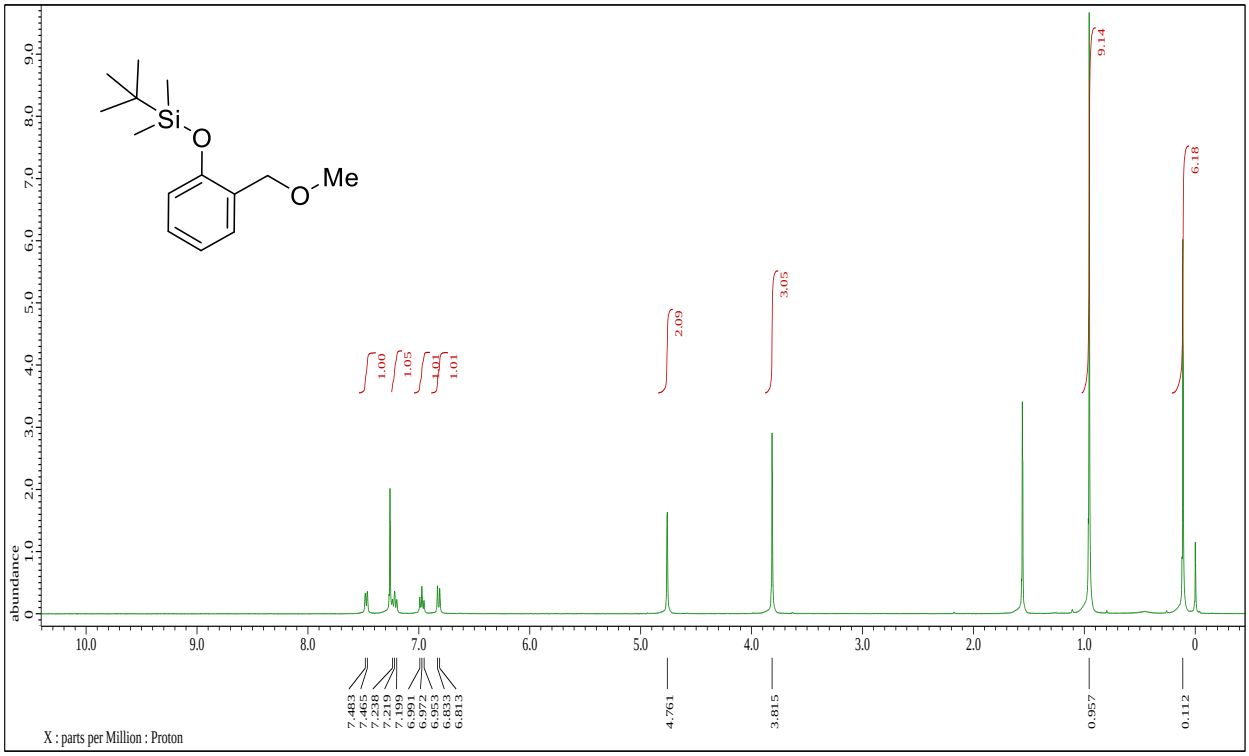


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **9g**

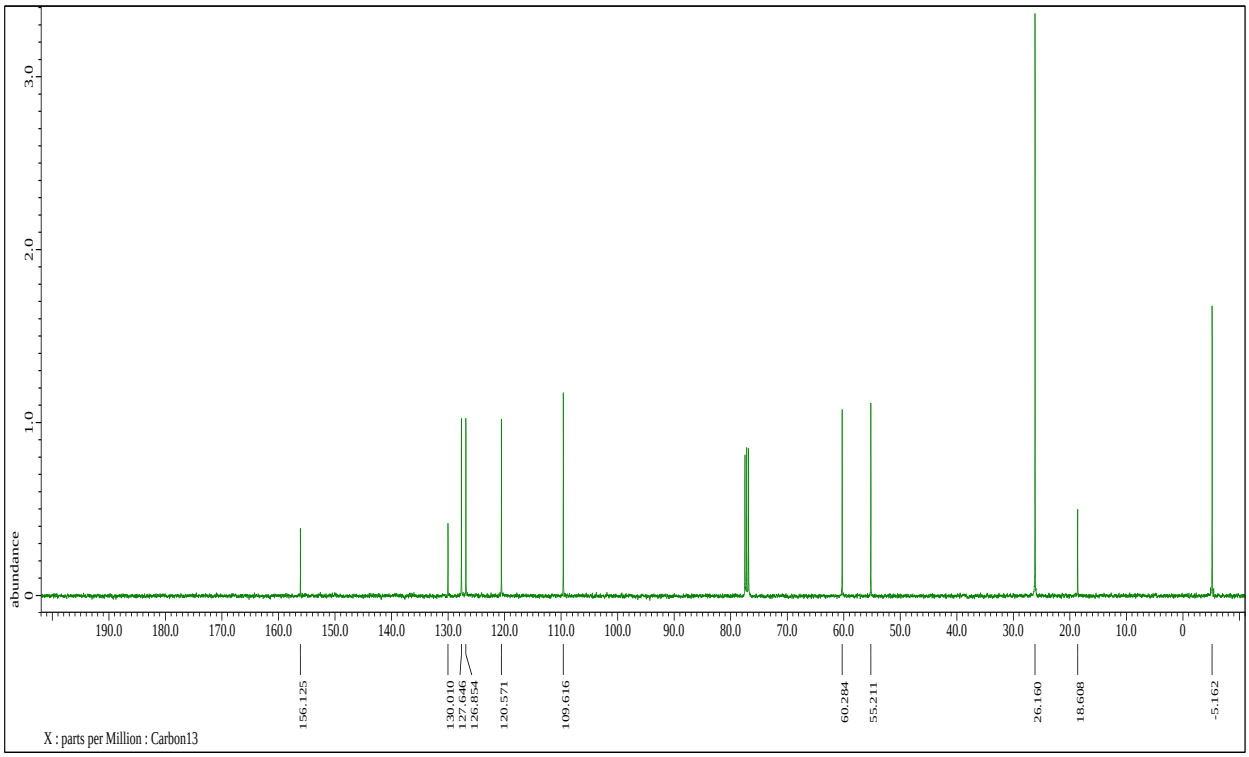


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **9g**

***tert*-Butyl(2-(methoxymethyl)phenoxy)dimethylsilane (10)**

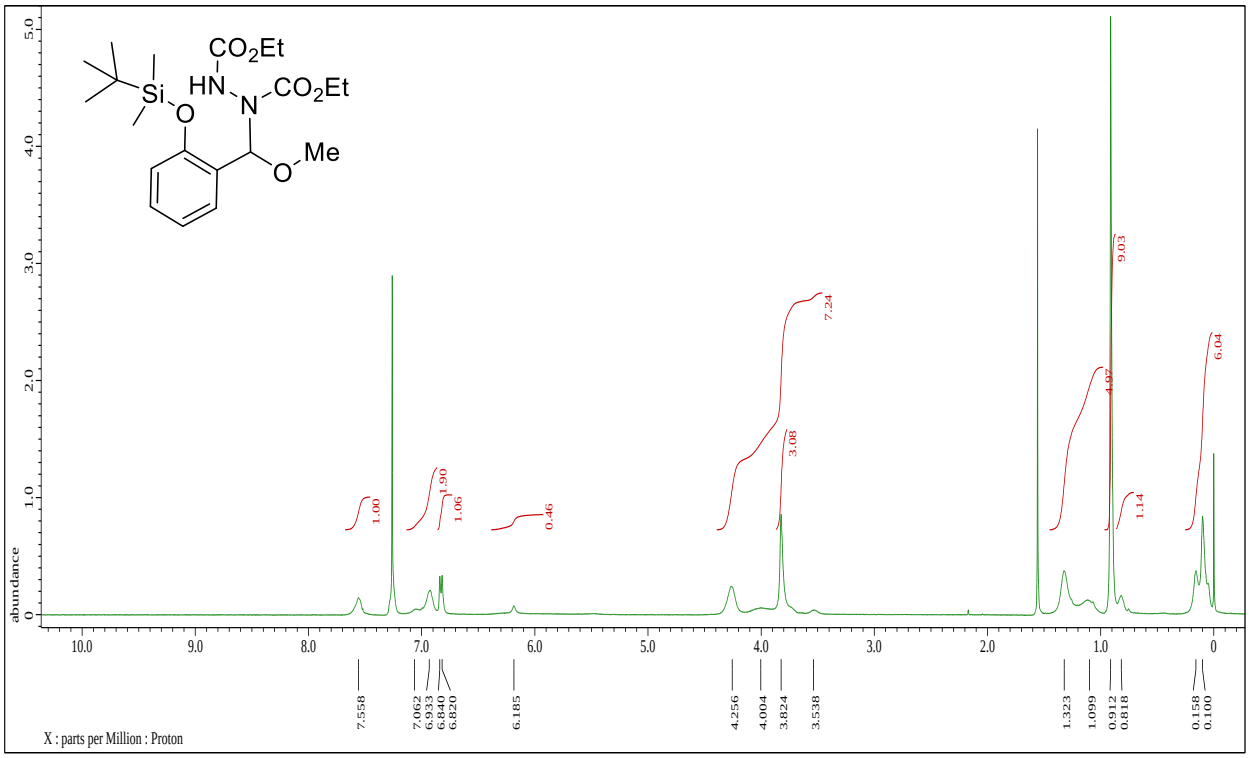


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10**

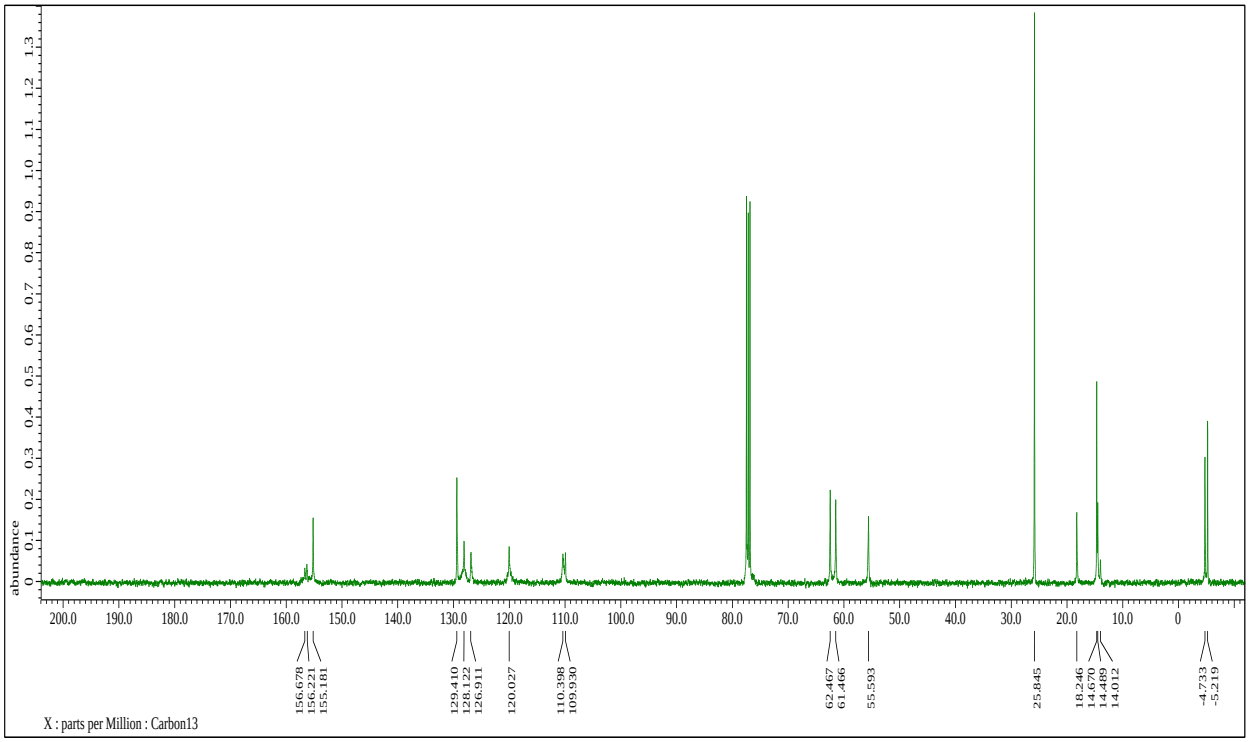


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10**

Diethyl 1-((2-((*tert*-butyldimethylsilyl)oxy)phenyl)(methoxy)methyl)hydrazine-1,2-dicarboxylate (11)

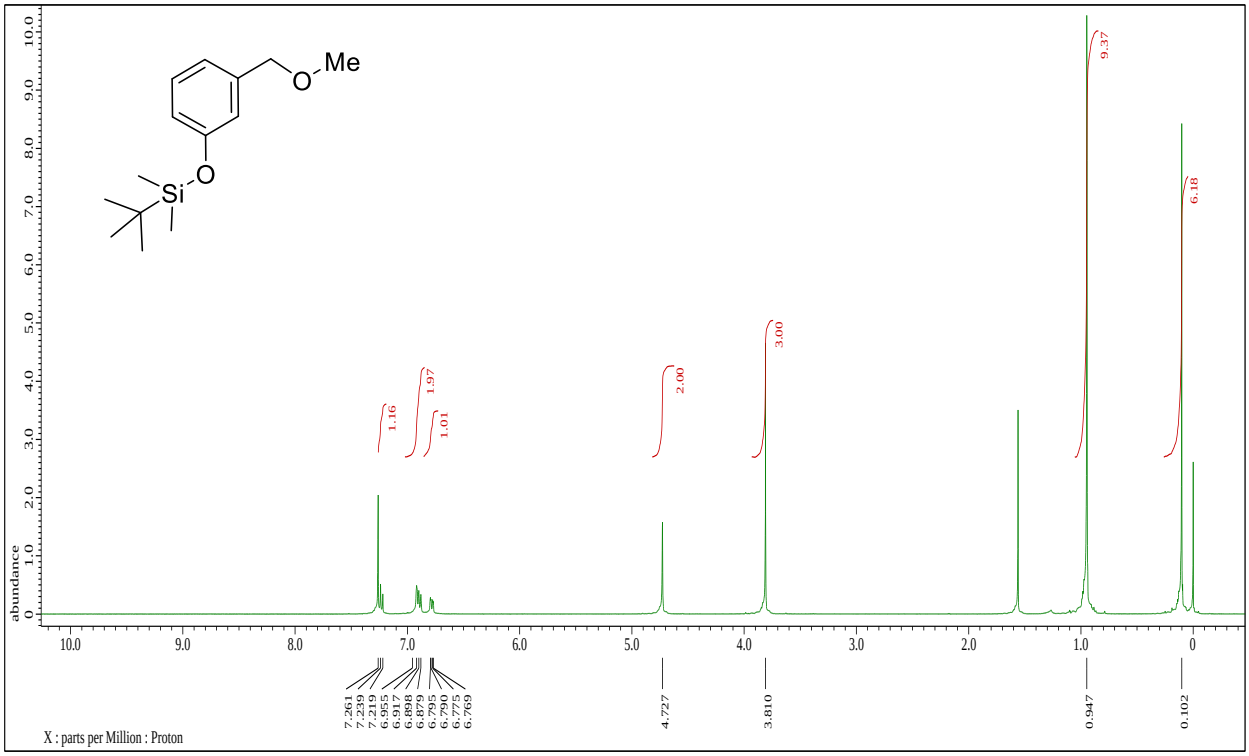


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11**

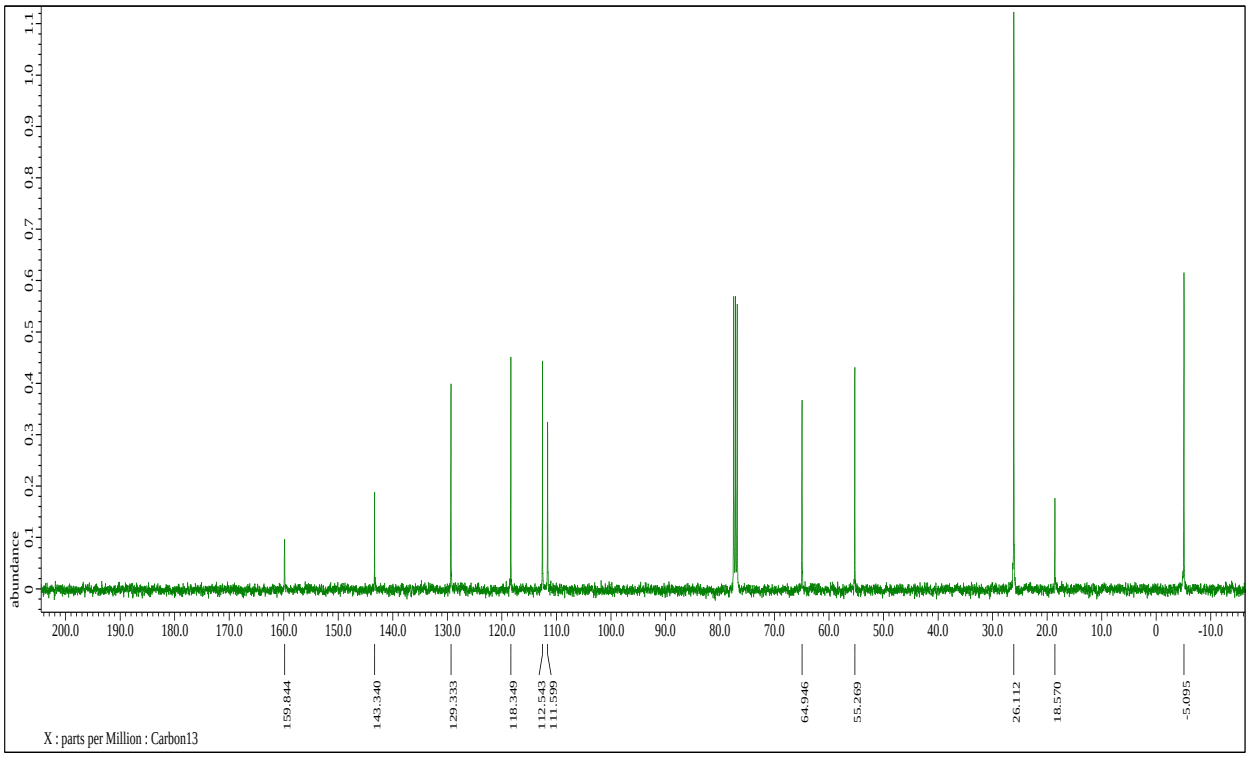


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **11**

***tert*-Butyl(3-(methoxymethyl)phenoxy)dimethylsilane (12)**

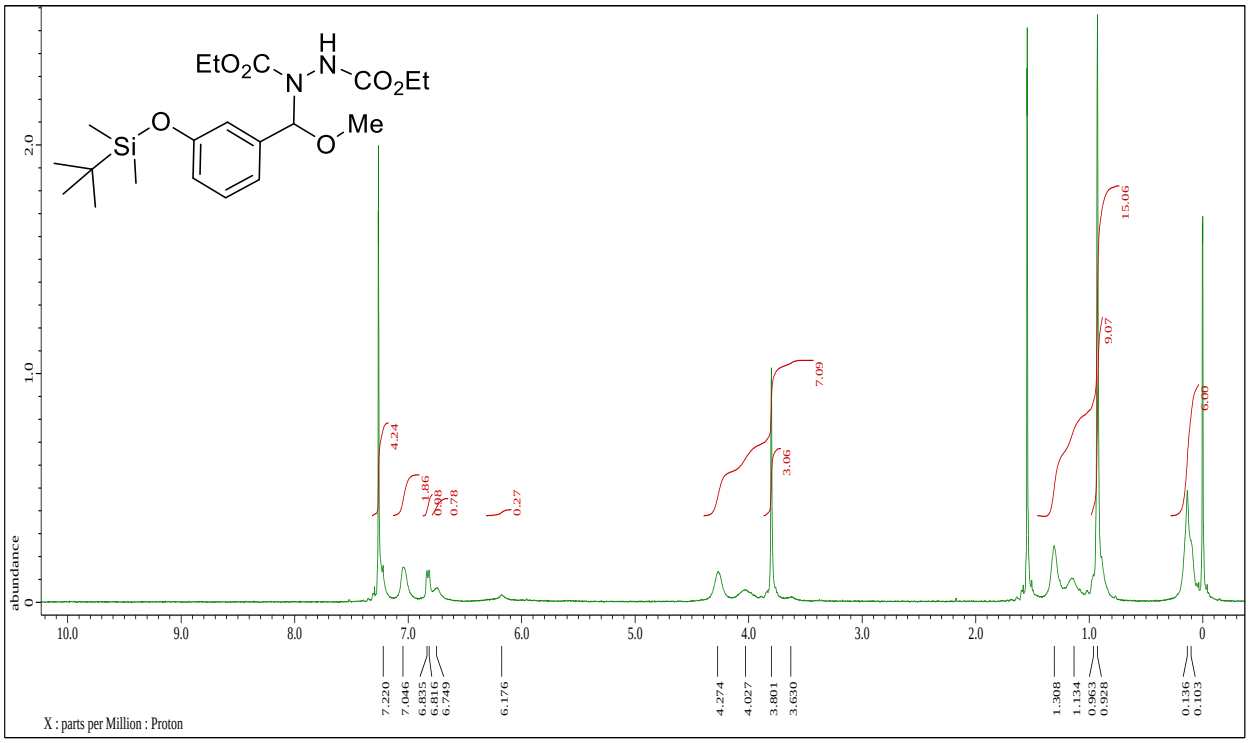


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **12**

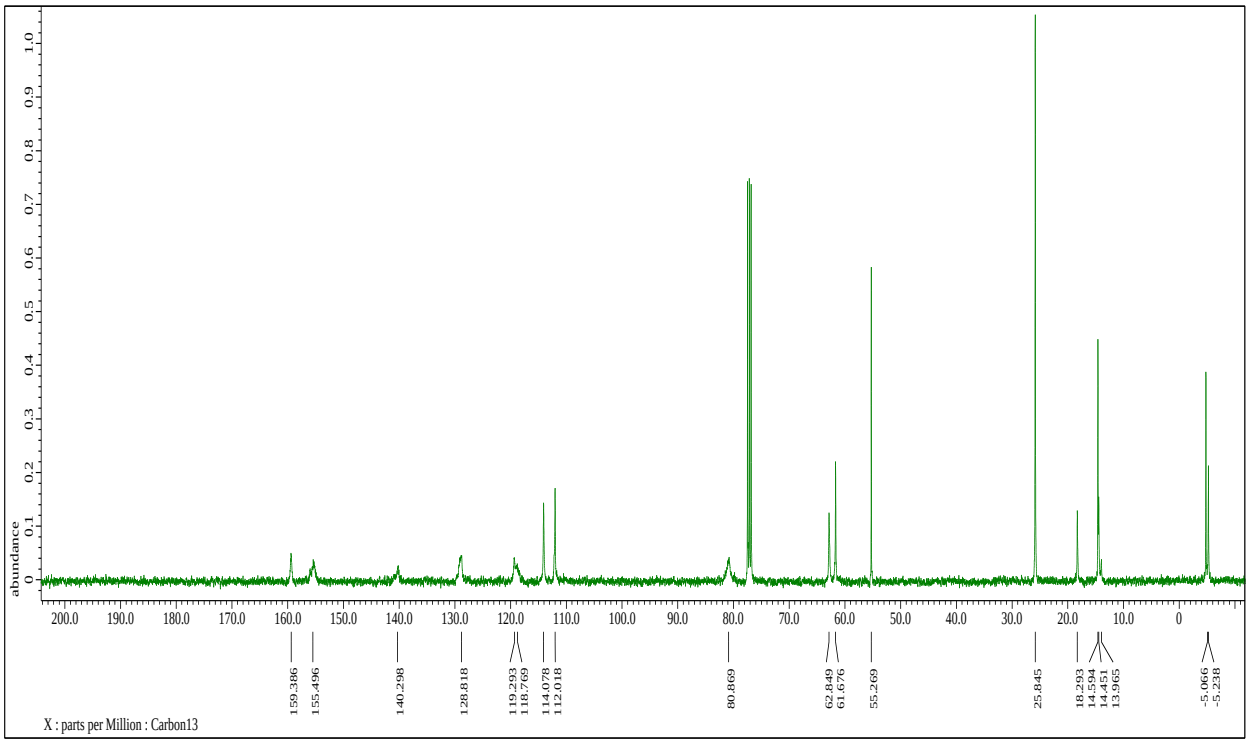


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **12**

Diethyl 1-((3-((*tert*-butyldimethylsilyl)oxy)phenyl)(methoxy)methyl)hydrazine-1,2-dicarboxylate (13)

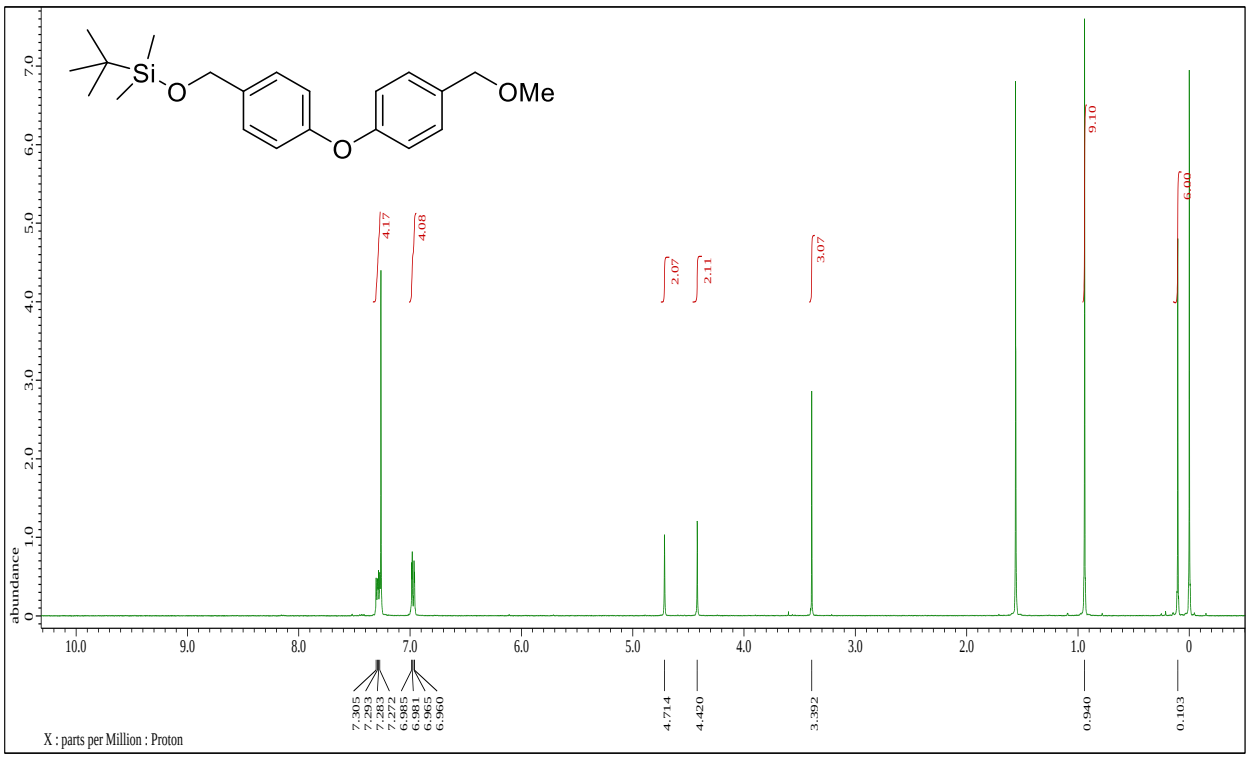


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **13**

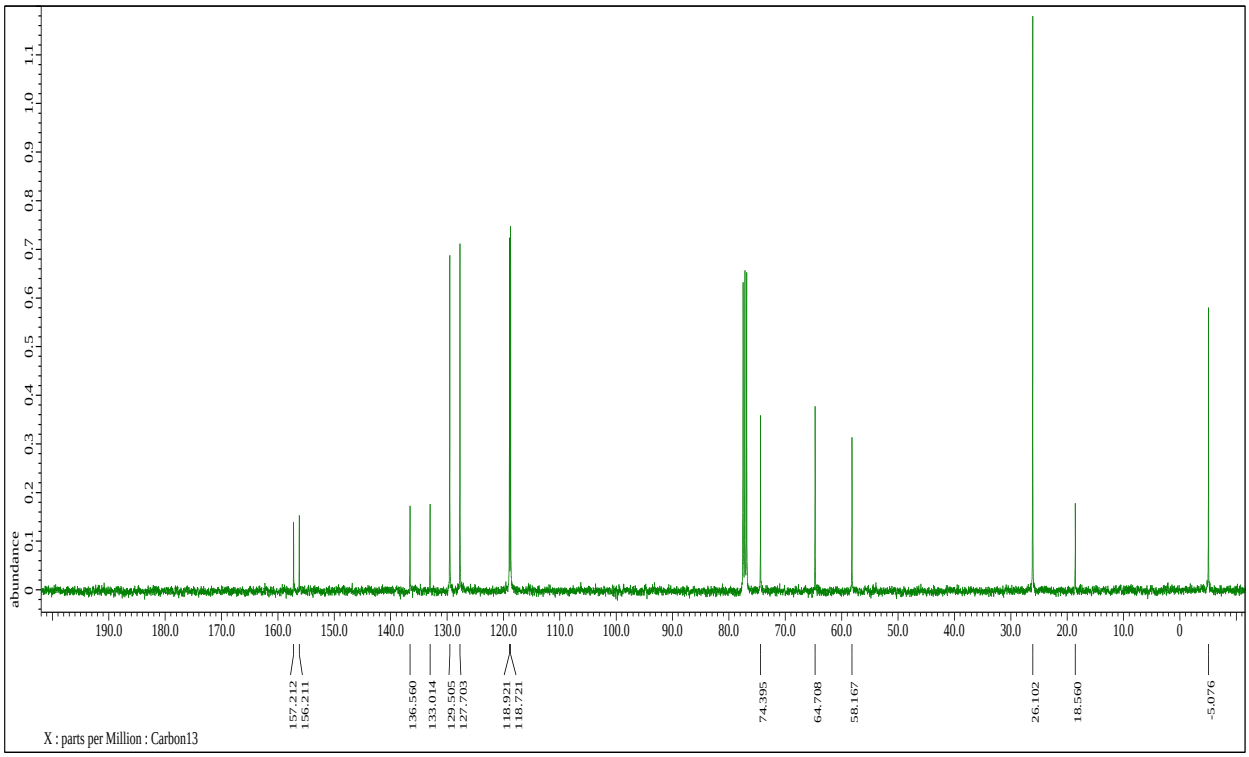


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **13**

(*tert*-butyldimethylsiloxy)methyl(4-(4-methoxymethyl)phenoxybenzene (14)

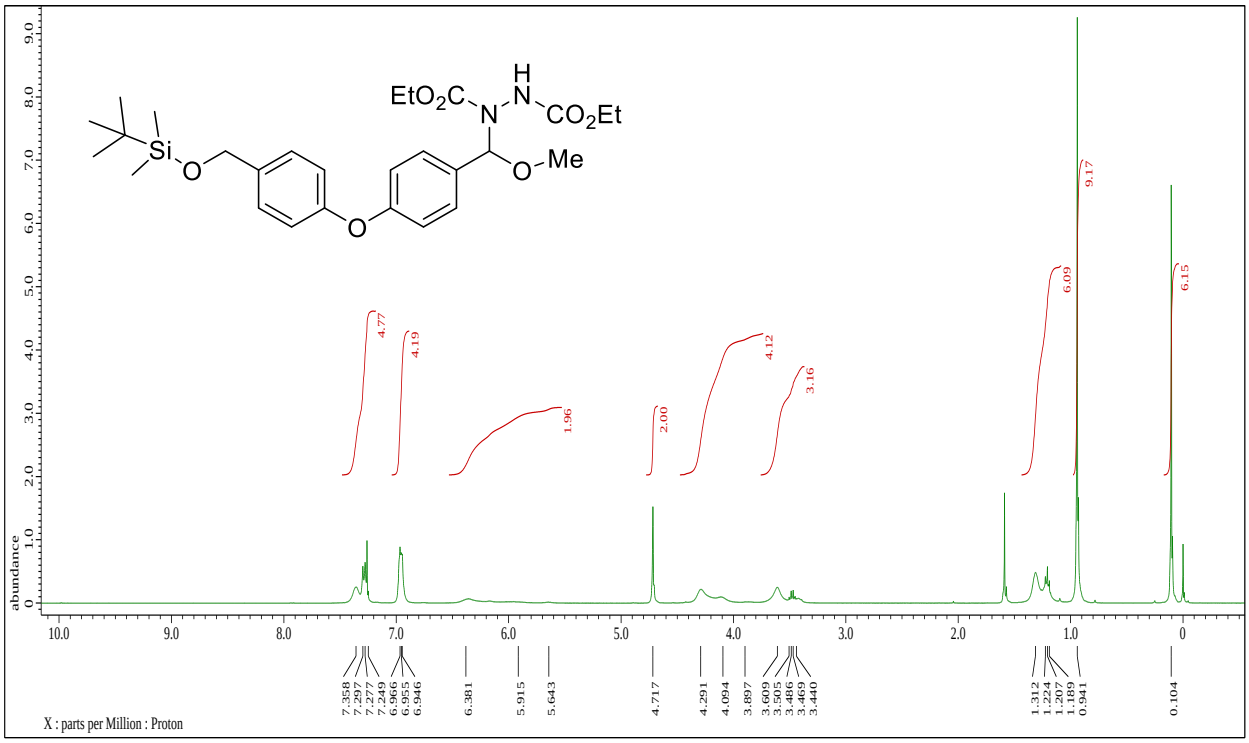


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **14**

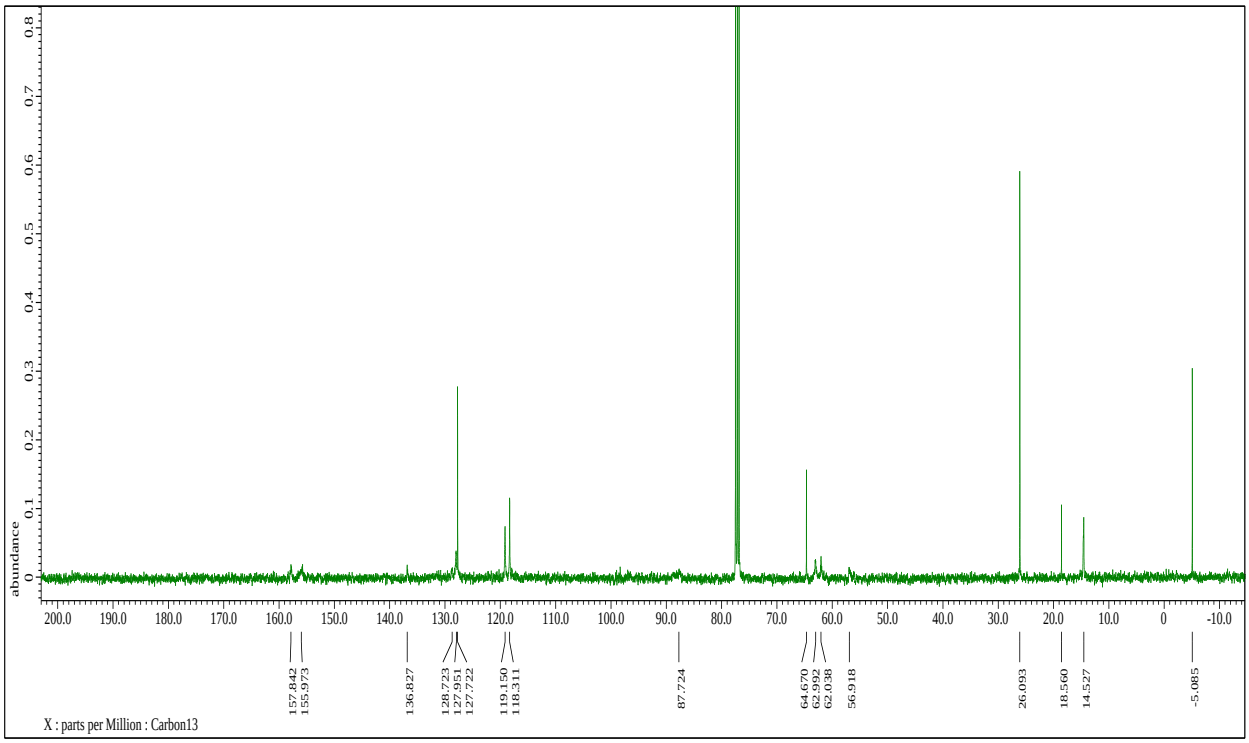


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **14**

Diethyl 1-((4-(4-(((tert-butyldimethylsilyl)oxy)methyl)phenoxy)phenyl)(methoxy)methyl)hydrazine-1,2-dicarboxylate (15)

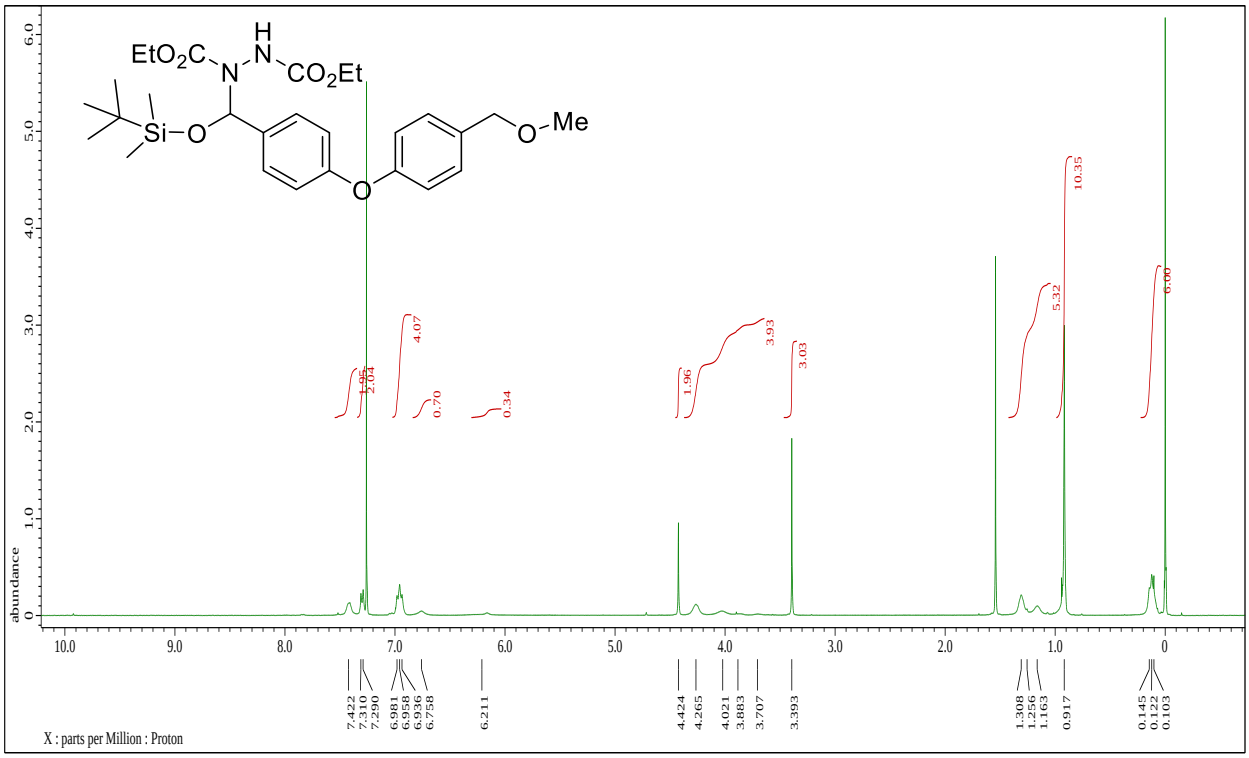


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **15**

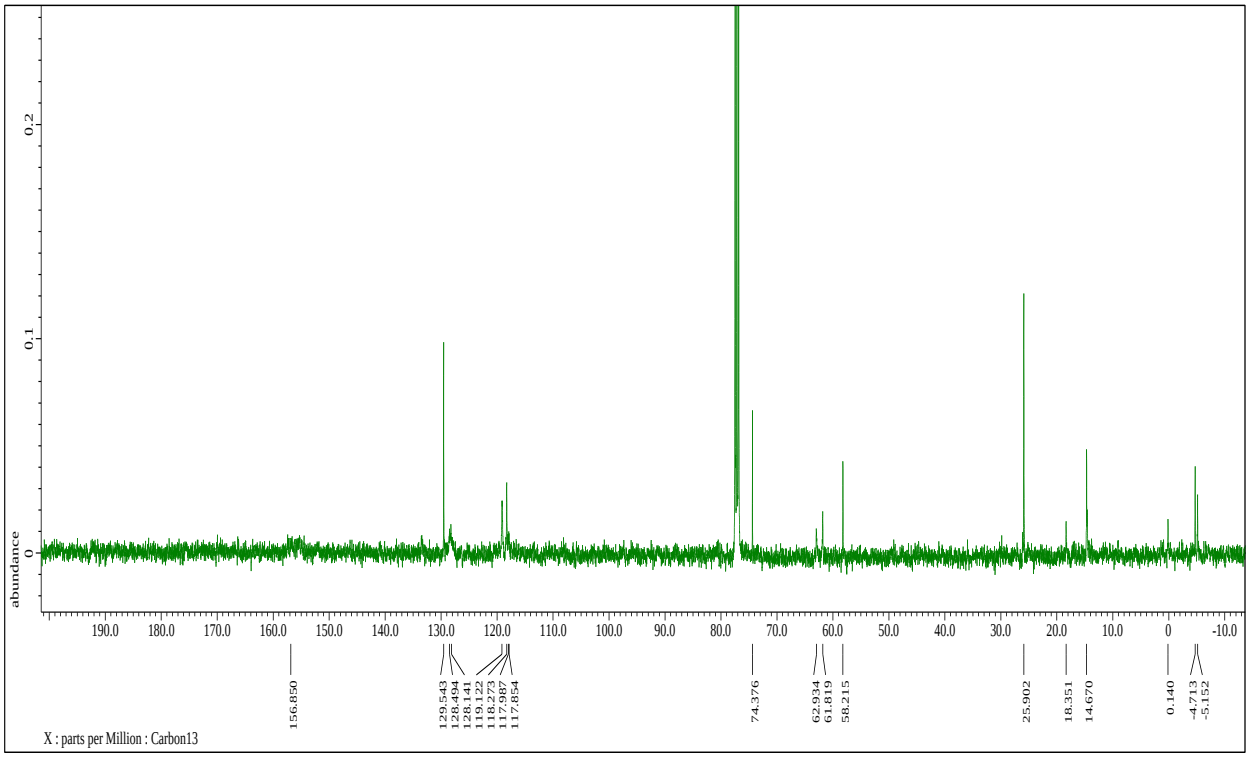


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **15**

Diethyl 1-(((tert-butyldimethylsilyl)oxy)(4-(4-(methoxymethyl)phenoxy)phenyl)methyl)hydrazine-1,2-dicarboxylate (16)

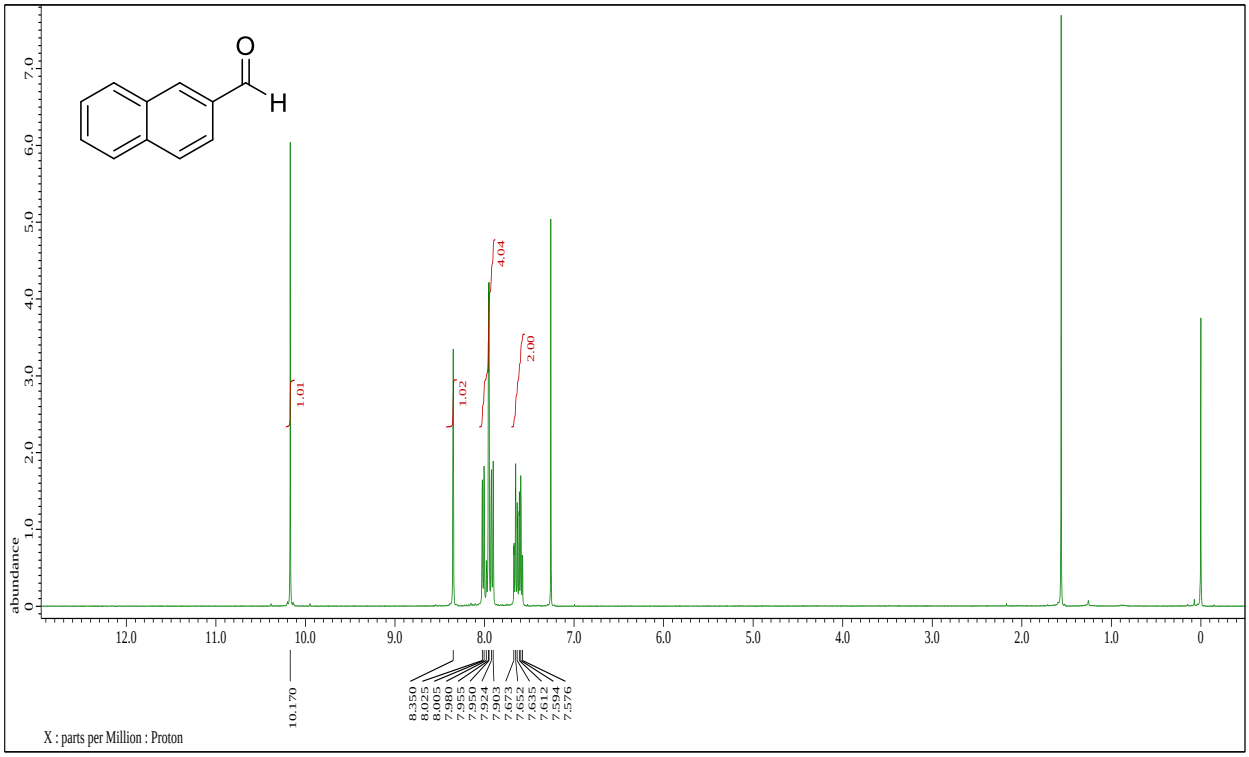


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **16**

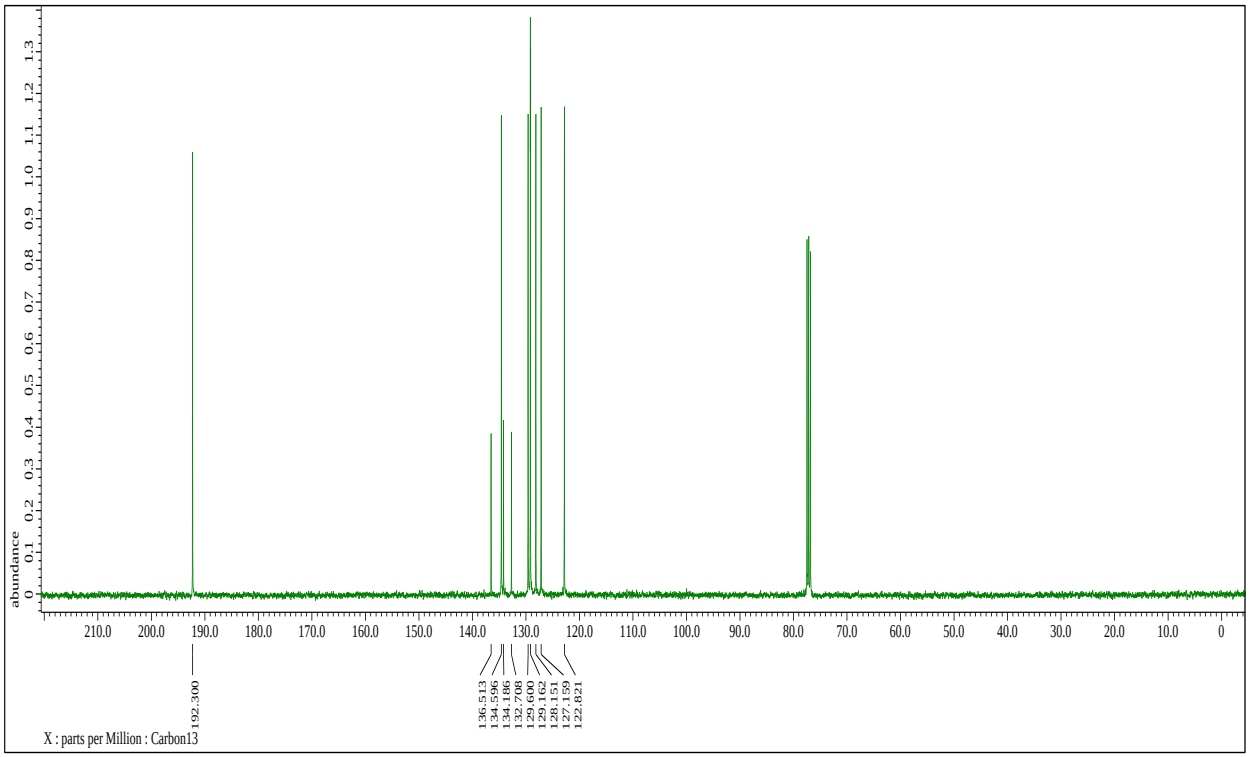


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **16**

2-Naphthaldehyde (17)

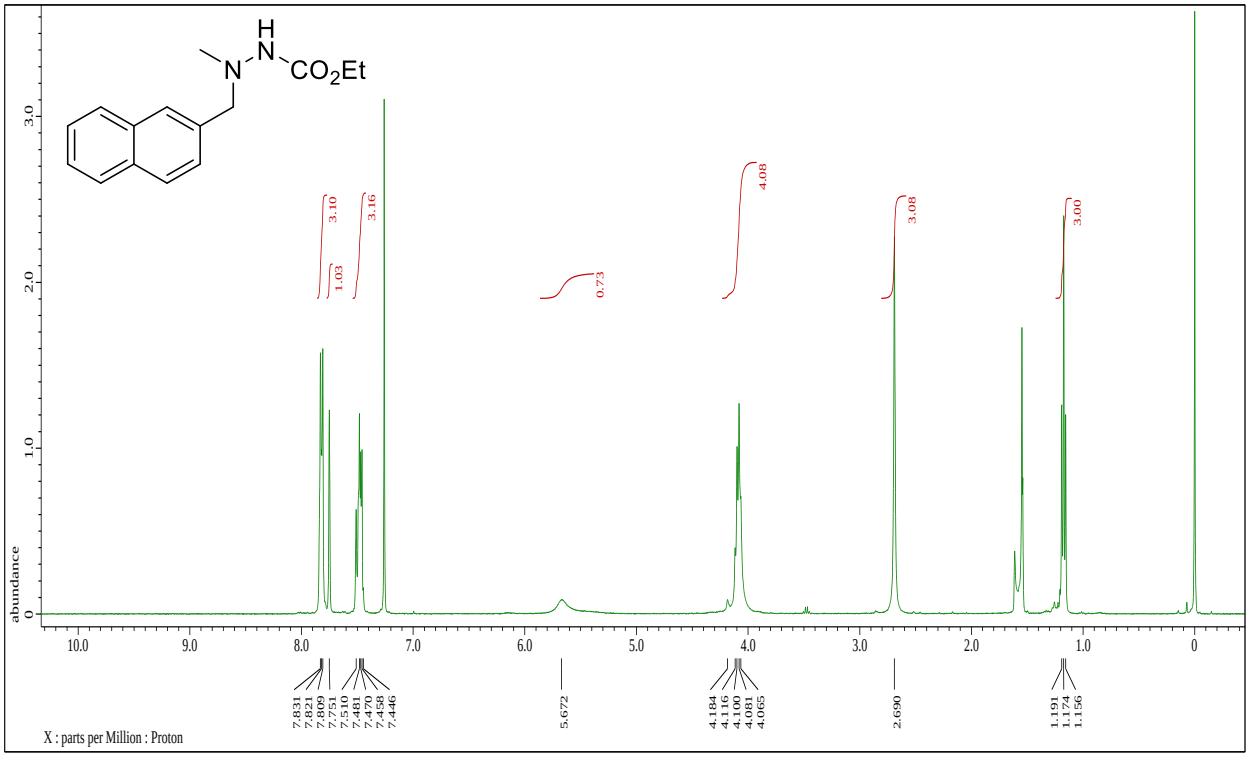


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **17**

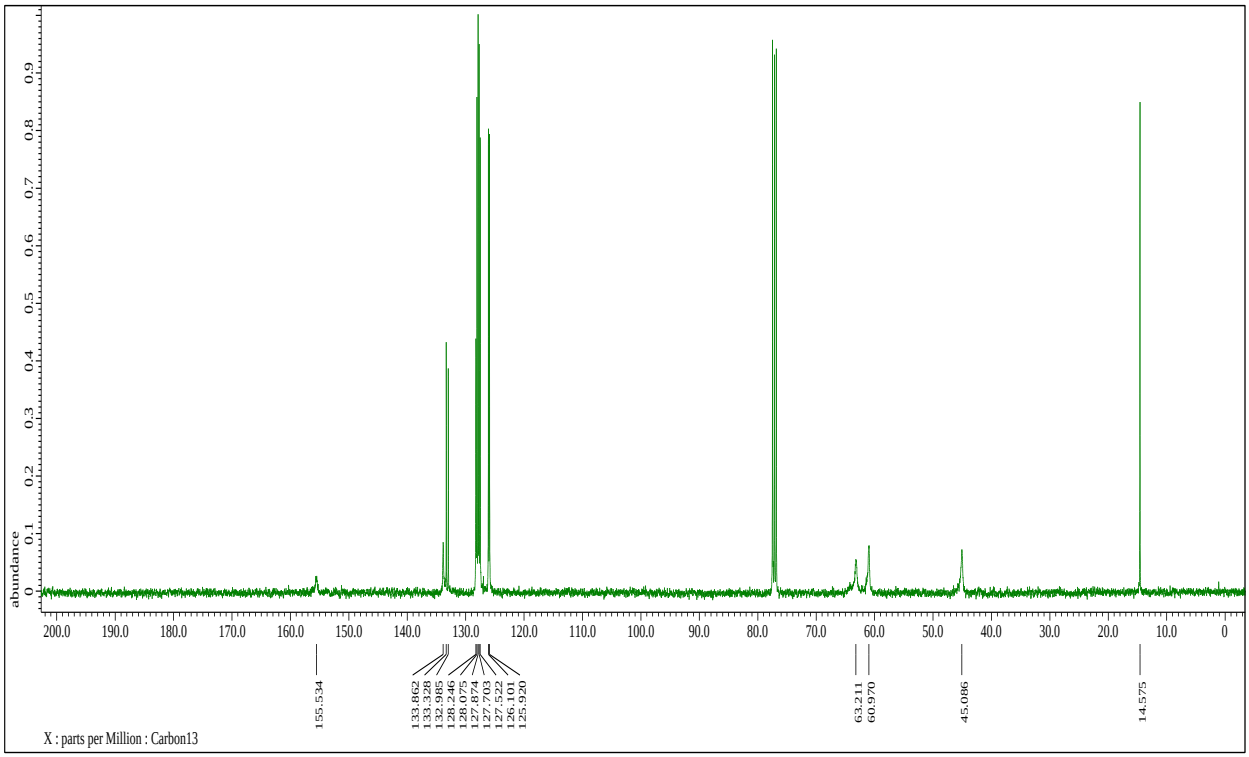


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **17**

Ethyl 2-methyl-2-(naphthalen-2-ylmethyl)hydrazine-1-carboxylate (18)

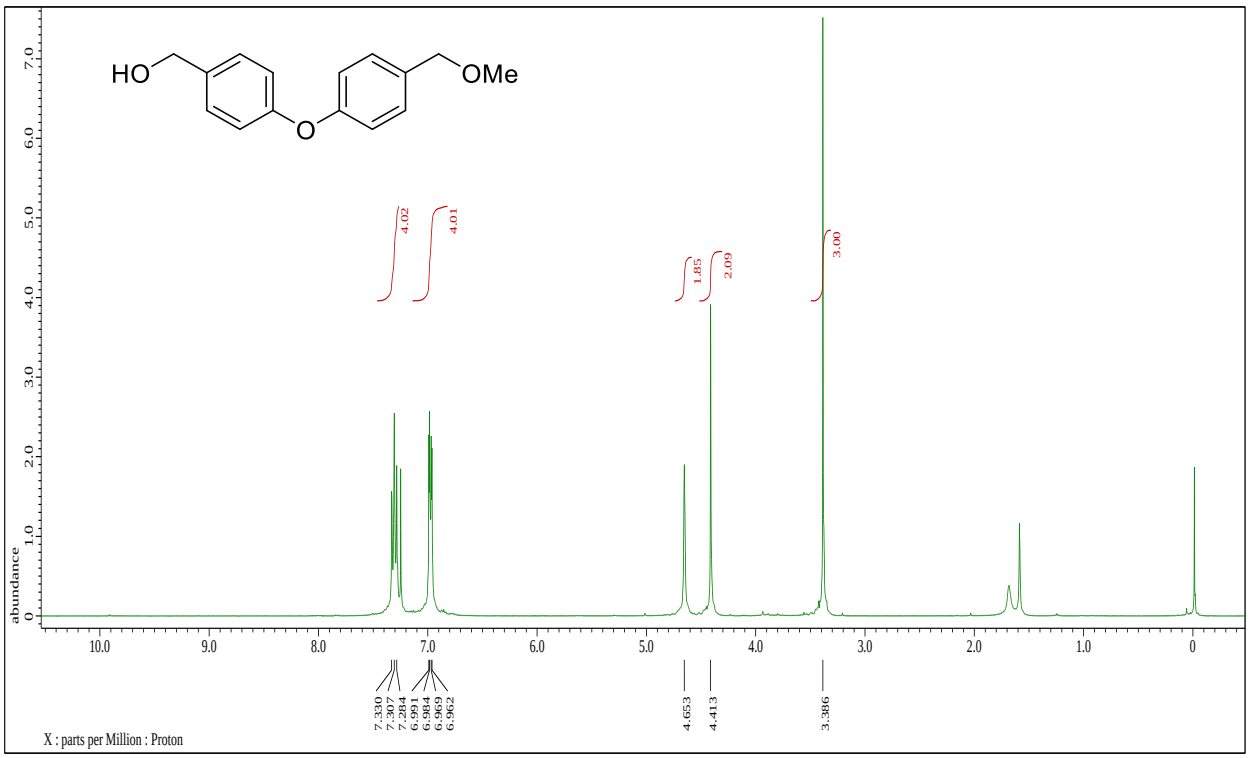


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **18**

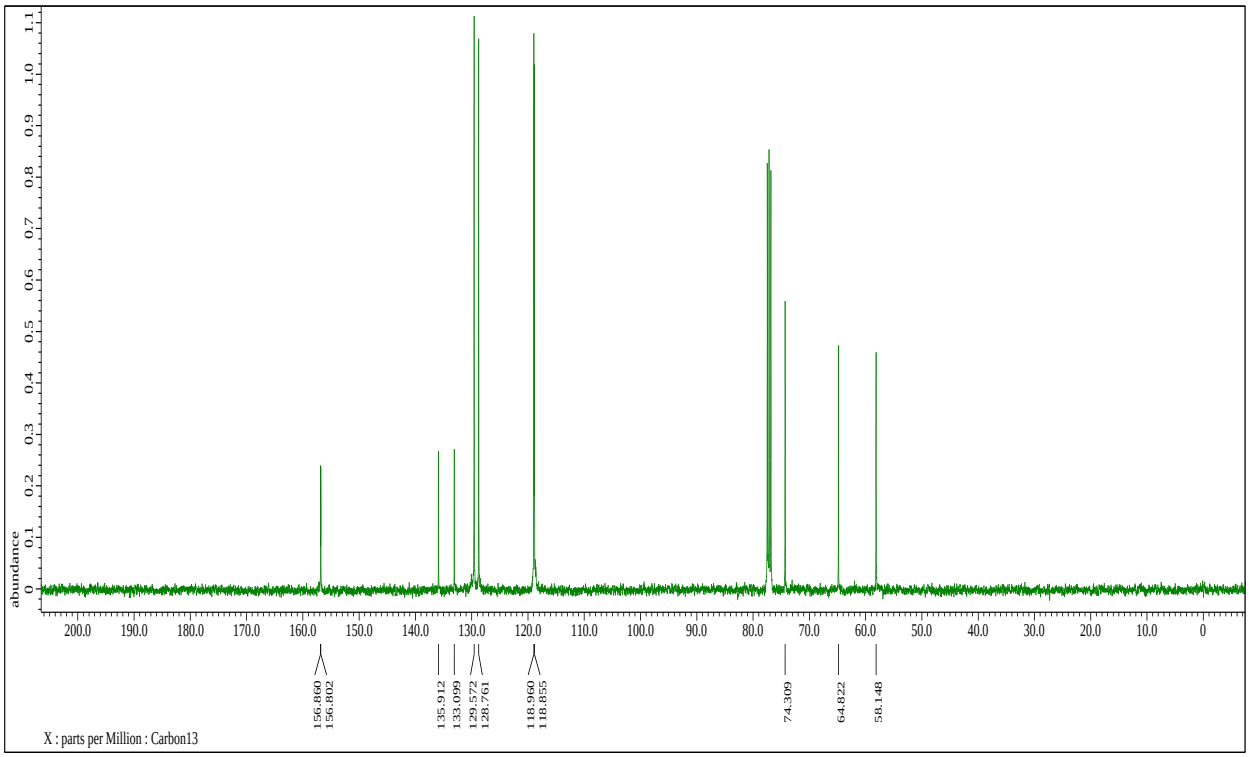


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **18**

(4-(4-(Methoxymethyl)phenoxy)phenyl)methanol (19)



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **19**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **19**