Cobalt-catalyzed reduction of esters to alkanes

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Supporting Information

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General experimental

All reactions were performed in nitrogen atmosphere MBRAUN glove box. All chemicals were purchased from Acros, Sigma Aldrich, Alfa-aesar, Himedia. Chemicals are used without further purification. Dry solvents were prepared according to standard procedures. Infrared (IR) spectra were recorded in Perkin-Elmer FT-IR and Thermo-Nicolet FT-IR spectrophotometers. High-resolution mass spectra (HRMS) were obtained on Water Spectrometer and are reported as m/z (relative intensity). Accurate masses are reported for the molecular ion $[M+Na]^+$, $[M+H]^+$, and $[M]^+$. Nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded at Bruker AV-400 (^{1}H at 400 MHz, ^{13}C at 101 MHz) and Jeol (^{1}H at 400 MHz, ^{13}C at 101 MHz). ^{1}H NMR chemical shifts are referenced in parts per million (ppm) with respect to tetramethyl silane (TMS, δ 0.00 ppm) and ^{13}C {^{1}H} NMR chemical shifts are referenced in parts per million (ppm) with respect to $CDCl_3$ (δ 77.160 ppm). Coupling constants are reported in Hertz (Hz). ^{1}H NMR spectroscopy abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplets; dq, doublet of quartets; td, triplet of doublets; qd, quartets of doublets; ddd, doublets of doublets of doublets; m, multiplet; br, broad.

GC method

Gas chromatography data were obtained using a gas chromatograph equipped with a SH-Rtx-1 capillary column (30μm×250μm). The instrument was set to an injection volume of 1 μL, an inlet split ratio of 10:1, and inlet and detector temperatures of 300 and 330 °C, respectively. The temperature program used for all of the analysis is as follows:50 °C, 1 min; S3 12 °C/min to 320 °C, 7 min. Response factors for all of the necessary compounds with respect to standard dodecane were calculated from the average of three independent GC runs.

Experimental procedure for the synthesis of starting materials

(a) General procedure for the synthesis of methyl esters:[1] An oven dried round bottom flask (25 mL) charged with carboxylic acids (5 mmol) in MeOH (15 mL) was added $SOCl_2$ (10 mmol). This mixture was heated to reflux and completion of the reaction was monitored by TCL. Upon completion, solvent was evaporated under vacuum and the residue was dissolved in DCM (15 mL), washed with aqueous $NaHCO_3$, water and brine, dried over anhydrous Na_2SO_4, and concentrated to give 100% yield of crude methyl esters. It was further purified by column chromatography for liquid substrates and recrystallized for solid substrates prior to use.

(b) General procedure for the synthesis of alkyl esters: Alkyl esters were synthesized following the slightly modified literature method.[1] An oven dried round bottom flask (25 mL) charged with carboxylic acids (5 mmol) and an alcohol (to be condensed as alkyl part of the ester) as solvent (10 mL) was added $SOCl_2$ (10 mmol). This mixture was heated to reflux and completion of reaction monitored by TLC. Upon completion, solvent was evaporated under vacuum and the residue was dissolved in DCM (15 mL), washed with aqueous $NaHCO_3$, water and brine, dried over anhydrous Na_2SO_4, and concentrated to obtain quantitative yield of crude methyl esters. It was further purified by column chromatography for liquid substrates and recrystallized for solid substrates prior to use.

(c) General procedure for the synthesis of aryl esters: An oven dried 25 mL round bottom flask charged with carboxylic acids (5 mmol) in DMF (10 mL) was stirred in room temperature for 30 min. Then substituted aryl bromide (5 mmol) was added dropwise and stirred at room temperature. After completion of reaction, solvent was evaporated under vacuum and the residue was dissolved in DCM (15 mL), washed with water and brine, dried over anhydrous Na_2SO_4, and concentrated to give crude product. It was further purified by column chromatography for liquid substrates and recrystallized for solid substrates prior to use.

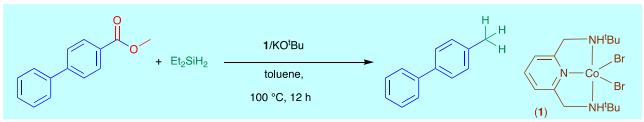
(d) General procedure for the synthesis 6-substituted methyl-2-naphthoate:[2] To an oven dried sealed tube (25 mL), methyl 6-bromo-2-naphthoate (1 mmol, 265 mg), $Pd(OAc)_2$ (1 mol %, 2.24 mg), BINAP (1.5 mol %, 18.8 mg,) and Cs_2CO_3 (1.5 mmol, 488 mg) were added under nitrogen atmosphere inside the glove box. Toluene (6 mL), and amine (2 mmol) were then added in succession. The sealed tube taken out of the glove box, and reaction mixture was allowed to stir at 120 °C in a preheated oil bath for 16 h. After completion, the reaction mixture was filtered by silica gel. This solution was concentrated under reduced pressure to evaporate the solvent. The residue was purified by column chromatography on neutral alumina using hexane/EtOAc =96:4).

General optimization for reduction of esters:

Investigation for the exhaustive reduction of esters to alkanes was emanated from optimizing the reaction conditions using methyl [1,1'-biphenyl]-4-carboxylate as a model substrate. Reaction tested using cobalt catalyst **1** (3 mol %), KO^{t}Bu base (30 mol %), methyl [1,1'-biphenyl]-4-carboxylate and 4 equiv of diethylsilane provided the desired product in 80% yield (entry 1, Table S1). A similar reaction using 40 mol % of base delivered the desired methyl arene in 84% yield (entry 2, Table S1). Increasing

the silane equivalents (to 4.5 equiv) diminished the yield of the product (entry 3, Table S1). Upon employing increased catalyst load (**1**, 5 mol %), the desired product was obtained in 87% yield (entry 4, Table S1). Lowering silane equivalents (3 equiv) provided 54% of expected product (entry 5, Table S1). Next, different bases such as KOH, NaO^{t}Bu, LiO^{t}Bu, and K_2CO_3 were employed in the reaction, which provided product in 13-82% yields; while KOH provided the comparable yield, use of NaO^{t}Bu and LiO^{t}Bu bases resulted poor yields of the product, whereas K_2CO_3 failed to produce the desired product (entry 6-9, Table S1). Experiments carried out employing [Co(dppe)Br_2] and $CoBr_2$ as catalyst delivered the product in lower yields (entries 10-11, Table S1). Control reactions without catalyst and base were performed where no desired product was obtained, which confirmed the necessity of the catalyst and base for the exhaustive reduction of esters to methyl arenes (entries 12-13, Table S1). From these studies, the use of 5 mol % catalyst **1**, 4 equiv of diethylsilane, and 40 mol % of KO^{t}Bu, which delivered the desired methyl arene product in 87% yield (entry 4, Table S1) emerged as the optimized condition.

Table S1. Optimization of reaction conditions for cobalt catalyzed reduction of esters to alkanes[a]



entry	1 (mol %)	silane (equiv)	base (mol %)	conv. (%)[b]	yield (%)[c]
1	3	4	30	99	80
2	3	4	40	99	84
3	3	4.5	40	99	78
4	5	4	40	99	87
5	5	3	40	99	54
6[d]	5	4	40	99	82
7[e]	5	4	40	70	24
8[f]	5	4	40	50	13
9[g]	5	4	40	-	-
10[h]	5	4	40	99	50
11[i]	5	4	40	99	20
12	-	4	40	-	-
13	5	4	-	-	-

[a]Reaction conditions: catalyst **1** (0.03-0.05 mmol), KO^{t}Bu (0.3-0.4 mmol), and toluene (1 mL) were taken in a vial and stirred at room temperature for one min. Then methyl [1,1'-biphenyl]-4-carboxylate (1 mmol), and diethylsilane (4-4.5 mmol) were added and heated at 100 °C under closed condition. [b]Conversion was determined by GC using dodecane as an

internal standard. [c]Isolated yields after column chromatography. [d]Reaction performed using KOH as a base. [e]Reaction performed using NaO^{t}Bu. [f]Reaction performed using LiO^{t}Bu. [g]Reaction performed using K_2CO_3. [h]Reaction performed using [Co(dppe)Br_2] as a catalyst. [i]Reaction performed using $CoBr_2$ as a catalyst.

General optimization procedure for reduction of esters

To an oven dried Teflon sealed vial, catalyst, KO^{t}Bu, and toluene (1 mL) were added under nitrogen atmosphere inside the glove box and stirred for one min in room temperature. Methyl 4-biphenylcarboxylate (1 mmol) and diethylsilane were added, and the reaction mixture was allowed to stir at 100 °C in a preheated oil bath for 12 h. After cooling the reaction mixture to room temperature, the solvent was evaporated under vacuum. The conversion was calculated by GC using dodecane as an internal standard, and the products were isolated by column chromatography on silica gel (100-200 mesh, hexane/EtOAc =100:0).

General procedure for reduction of esters

To an oven dried Teflon sealed vial, catalyst **1** (5 mol %, 0.025 mmol), KO^{t}Bu (40 mol %, 0.20 mmol), and toluene (1 mL) were added under nitrogen atmosphere inside the glove box and stirred for one min in room temperature. Ester (0.5 mmol, 1 equiv.), and diethylsilane (2 mmol, 4 equiv.) were added, and the reaction mixture was allowed to stir at 100 °C in a preheated oil bath for 12 hours. After cooling the reaction mixture to room temperature, the solvent was evaporated under vacuum. The conversion was calculated by GC using dodecane as an internal standard, and the products were isolated by column chromatography on silica gel (100-200 mesh, hexane/EtOAc =100:0).

Procedure for large scale synthesis of 4-methyl-1,1'-biphenyl (7)

To an oven dried sealed tube (50 mL), catalyst **1** (5 mol %, 0.25 mmol), KO^{t}Bu (40 mol %, 2 mmol), and toluene (10 mL) were added under nitrogen atmosphere inside the glove box and stirred for one min in room temperature. methyl [1,1'-biphenyl]-4-carboxylate (5 mmol, 1 equiv.), and diethylsilane (20 mmol, 4 equiv.) were added, and the reaction mixture was allowed to stir at 100 °C in a preheated oil bath for 12 hours. After cooling the reaction mixture to room temperature, the solvent was evaporated under vacuum. The conversion was calculated by GC using dodecane as an internal standard, and the products were isolated by column chromatography on silica gel (100-200 mesh, hexane/EtOAc =100:0).

Mechanistic studies

EPR studies: To an oven dried Teflon sealed vial, catalyst **1** (0.025 mmol, 5 mol %), KO^{t}Bu (0.2 mmol, 40 mol %), and toluene (1 mL) were taken in a vial and stirred at room temperature for one min. Then methyl 4-biphenylcarboxylate (0.5 mmol, 1 equiv.), and diethylsilane (2 mmol, 4 equiv.) were added and heated at 100 °C under closed conditions. After given time, the reaction mixture was cooled to room temperature and transferred to an EPR tube, sealed, and EPR spectrum was recorded. Spectra were recorded at room temperature in toluene solution under microwave frequency (9.85GHz).

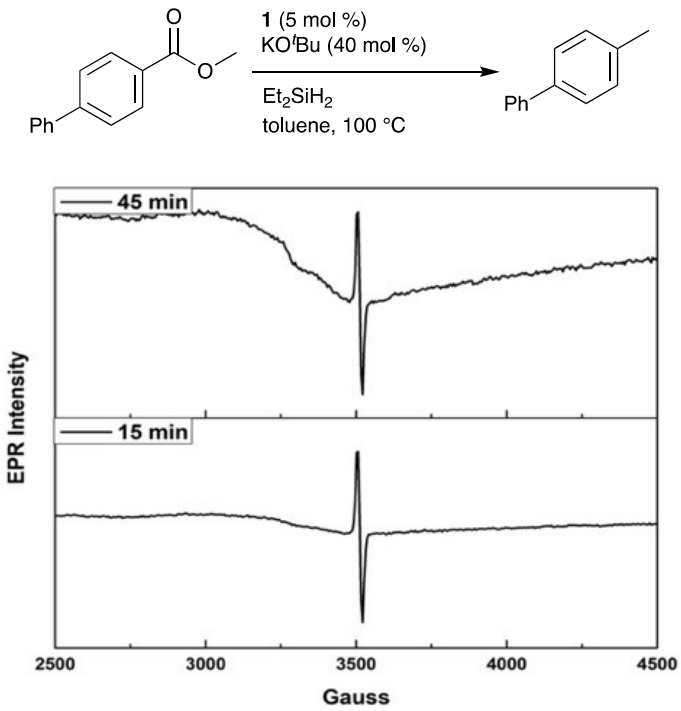


Figure S1. X-band EPR spectra of the reaction mixture: catalyst **1** (0.025 mmol, 5 mol %), KO^{t}Bu (0.2 mmol, 40 mol %) and toluene (1 mL) were taken in a vial and stirred at room temperature for one min. Then the substrate (0.5 mmol, 1 equiv), and diethylsilane (2 mmol, 4 equiv) were added, and heated at 100 °C under the closed condition. Spectra were recorded at room temperature in toluene solution under microwave frequency (9.85 GHz) after 15 and 45 minutes.

Mercury poisoning experiment in the reduction of esters to alkanes (Scheme 4a): To an oven-dried Teflon sealed vial, catalyst **1** (5 mol %, 11.7 mg), KO^{t}Bu (40 mol %, 22 mg), methyl 4-biphenylcarboxylate (1 equiv., 0.5 mmol, 106 mg), diethylsilane (4 equiv., 2 mmol, 259 µL), and Hg (Condition A: 50 mol %, 50 mg and Condition B: 250 mol %, 250 mg) in toluene (1 mL) were charged under the nitrogen atmosphere. The reaction mixture was heated at 100 °C for 12 h. After cooling to room temperature, the reaction mixture was decanted from mercury

and washed with DCM (3 × 2 mL). Solvents were removed under the reduced pressure and the resulted residue was purified by column chromatography using silica gel (100-200 mesh, hexane).

Experiment to verify involvement of radical in reduction of esters with TEMPO (Scheme 4b):

To an oven-dried Teflon sealed vial, catalyst **1** (5 mol %, 11.7 mg), KO^{t}Bu (40 mol %, 22 mg), methyl 4-biphenylcarboxylate (1 equiv., 0.5 mmol, 106 mg), diethylsilane (4 equiv., 2 mmol, 259 µL), and TEMPO (2 equiv., 1 mmol, 156 mg), in toluene (1 mL) were charged under the nitrogen atmosphere. The reaction mixture was heated at 100 °C for 12 h. After cooling the reaction mixture to room temperature, the reaction mixture was subjected to GC analysis, which confirmed no formation of the anticipated reduced alkane product.

Experiment to verify involvement of radical in reduction of esters with galvinoxyl radicals (Scheme 4b):

To an oven-dried Teflon sealed vial, catalyst **1** (5 mol %, 11.7 mg), KO^{t}Bu (40 mol %, 22 mg), methyl 4-biphenylcarboxylate (1 equiv., 0.5 mmol, 106 mg), diethylsilane (4 equiv., 2 mmol, 259 µL), and galvinoxyl radical (2 equiv., 1 mmol, 421 mg) in toluene (1 mL) were charged under the nitrogen atmosphere. The reaction mixture was heated at 100 °C for 12 h. After cooling the reaction mixture to room temperature, the reaction mixture was subjected to GC analysis, which confirmed no formation of the anticipated reduced alkane product.

Mass spectrometric analysis of reaction mixture for trapping the radical intermediate using TEMPO (Scheme 4c): To an oven-dried Teflon sealed vial, catalyst **1** (5 mol %, 11.7 mg), KO^{t}Bu (40 mol %, 22 mg), methyl 4-biphenylcarboxylate (1 equiv., 0.5 mmol, 106 mg), diethylsilane (4 equiv., 2 mmol, 259 µL), and TEMPO (2 equiv., 1 mmol, 156 mg), in toluene (1 mL) were charged under the nitrogen atmosphere. The reaction mixture was heated at 100 °C for 2 h. After cooling the reaction mixture to room temperature, solvent was evaporated under reduced pressure, and the resulted solid was analyzed by mass spectrometry, and obtained the TEMPO trapped benzylic radical **26**.

Experiment to verify involvement of silyl ether intermediate in reduction of ester (Scheme 4d-4e):

To an oven-dried Teflon sealed vial, catalyst **1** (2 mol %, 4.6 mg), KO^{t}Bu (20 mol %, 11.2 mg), methyl 4-biphenylcarboxylate (1 equiv., 0.5 mmol, 106 mg), diethylsilane (2.5 equiv., 1.25

mmol, 200 µL), and toluene (1 mL) were charged under the nitrogen atmosphere, and the reaction mixture allowed to stir at room temperature for 12 h. Upon completion, the solvent was evaporated under reduced pressure, and resulted residue was purified by column chromatography using silica gel (100-200 mesh, hexane/EtOAc = 97:3).

Then again to an oven-dried Teflon sealed vial, catalyst **1** (3 mol %, 7 mg), KO^{t}Bu (20 mol %, 11.22 mg), bis([1,1'-biphenyl]-4-ylmethoxy) diethylsilane (**27**, 1 equiv, 0.25 mmol, 113 mg), diethylsilane (3 equiv., 0.75 mmol, 97 µL), and toluene (1 mL) were charged under the nitrogen atmosphere and the reaction mixture allowed to stir at 100 °C in a pre-heated oil bath for 12 h. Upon completion, the solvent was evaporated under reduced pressure, and the reduced product was purified by column chromatography using silica gel (100-200 mesh, hexane/EtOAc = 100:0).

Experiment to verify involvement of silyl acetal intermediate in reduction of ester (Scheme 4f):

To an oven dried Teflon sealed vial, catalyst **1** (3 mol %, 0.015 mmol), KO^{t}Bu (20 mol %, 0.1 mmol), and toluene (1 mL) were added under nitrogen atmosphere inside the glove box and stirred for one min in room temperature. Methyl 4-biphenylcarboxylate (0.5 mmol, 1 equiv.), and diethylsilane (1 mmol, 2 equiv.) were added, and the reaction mixture was allowed to stir at 60 °C in a preheated oil bath for 2 hours. After cooling the reaction mixture to room temperature, the solvent was evaporated under vacuum. The reaction mixture was then subjected to NMR analysis and mass spectrometric analysis.

Experiment to verify alkyl part of the carboxylate esters (Scheme 4g):

To an oven-dried Teflon sealed vial, catalyst **1** (5 mol %, 11.7 mg), KO^{t}Bu (40 mol %, 22 mg), nonyl [1,1'-biphenyl]-4-carboxylate (1 equiv., 0.5 mmol, 162 mg), diethylsilane (4 equiv., 2 mmol, 259 µL), in toluene (1 mL) were charged under the nitrogen atmosphere. The reaction mixture was heated at 100 °C for 12 h. Upon completion, solvents were removed under the reduced pressure and the resulted residue was purified by column chromatography using silica gel (100-200 mesh, hexane).

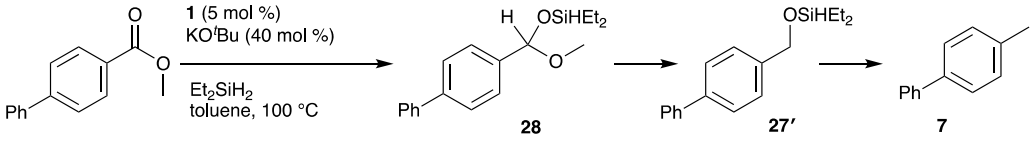
Experiment to test stability of the catalyst (Scheme 4h)

To an oven dried Teflon sealed vial, catalyst **1** (5 mol %, 0.025 mmol), KO^{t}Bu (40 mol %, 0.20 mmol), and toluene (1 mL) were added under nitrogen atmosphere inside the glove box and stirred for one min in room temperature. Methyl [1,1'-biphenyl]-4-carboxylate (0.5 mmol, 1

equiv.), and diethylsilane (2 mmol, 4 equiv.) were added, and the reaction mixture was allowed to stir at 100 °C in a preheated oil bath for 12 hours. After cooling the reaction mixture to room temperature, another batch of methyl [1,1'-biphenyl]-4-carboxylate (0.5 mmol, 1 equiv.), and diethylsilane (2 mmol, 4 equiv.) were added, and the reaction mixture was allowed to stir at 100 °C in a preheated oil bath for another 12 hours. Then, the reaction mixture was cooled to room temperature, and the solvent was evaporated under vacuum. The conversion was calculated by GC using dodecane as an internal standard, and the products were isolated by column chromatography on silica gel (100-200 mesh, hexane/EtOAc =100:0)

Kinetics studies

Eight separate oven-dried Teflon sealed vials (8 mL) have been taken and each charged with catalyst **1** (0.025 mmol, 5 mol %), KO^{t}Bu (0. 2 mmol, 40 mol %) and toluene (1 mL) were stirred at room temperature for one minute. Then methyl [1,1'-biphenyl]-4-carboxylate (0.5 mmol, 1 equiv), and diethylsilane (2 mmol, 4 equiv) were added in each vial, and heated at 100 °C under closed condition at variable duration of time: 5 min., 15 min., 30 min., 45 min., 90 min., 2 h, 4 h, 6 h, 8 h, 10 h, and 12 h. To each vial dodecane (1 equiv, 0.5 mmol, 113.5 µL) was added as an internal standard. Aliquots were taken and yields were calculated from GC analysis.



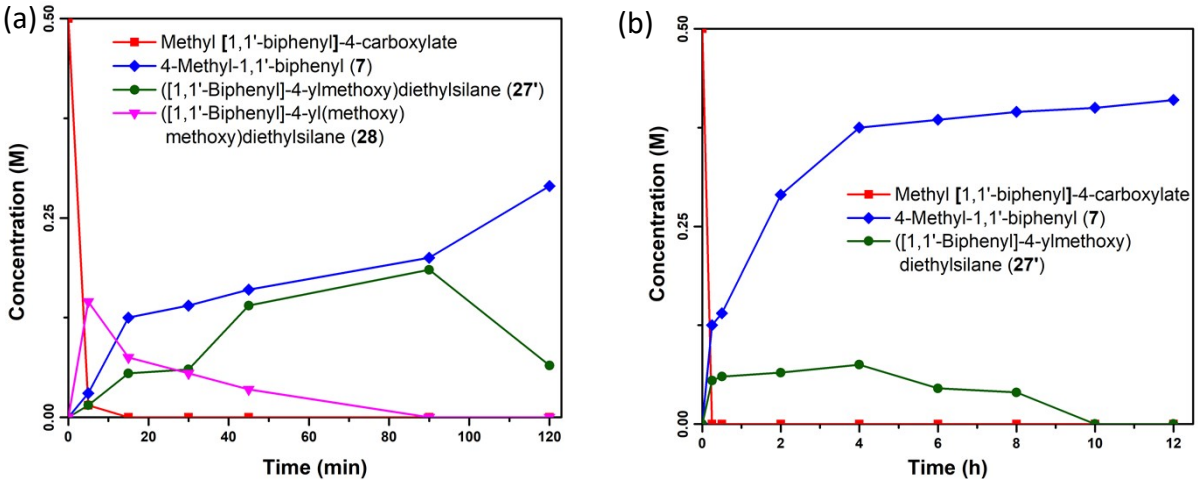


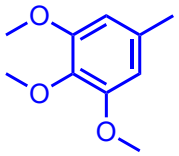
Figure S2. Kinetic studies of cobalt-catalyzed reduction of esters to methyl arenes. (a) Kinetics plot for initial 120 min. (b) Kinetics plot for 12h.

Mass spectrometric analysis of reaction mixture:

For detection of intermediates I: To a screw cap scintillation vial, catalyst **1** (1 equiv, 23 mg) and KO^{t}Bu (2 equiv, 11.2 mg) in toluene (0.5 mL) were added under nitrogen atmosphere and the reaction mixture was allowed to stir at room-temperature for 15 min. Diethylsilane (10 equiv., 64.77 μL) was added, and further stirred at room-temperature for 30 min. Solvent was evaporated under reduced pressure, and the resulted solid was analyzed by mass spectrometry, which revealed the presence of intermediates **I**.

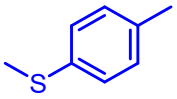
For detection of intermediates III: To a screw cap scintillation vial, catalyst **1** (1 equiv, 23.4 mg) and KO^{t}Bu (2 equiv, 11.2 mg) in toluene (0.5 mL) were added under nitrogen atmosphere and the reaction mixture was allowed to stir at room-temperature for 15 min. Diethylsilane (2 equiv.,12.95 μL) and methyl 4-biphenylcarboxylate (1 equiv., 10.6 mg) were added, and further stirred at room-temperature for 30 min. Solvent was evaporated under reduced pressure, and the resulted solid was analyzed by mass spectrometry, which revealed the presence of intermediates **III**.

Spectral data of alkanes



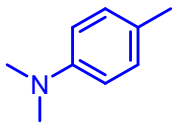
1,2,3-Trimethoxy-5-methylbenzene (3):[3a] Purified by silica-gel column chromatography using EtOAc:hexane (2:98) as an eluent. Isolated as a colourless liquid. Yield: 65 mg, 70%. IR (DCM): 3054, 2936, 1590, 1508, 1455, 1332, 1238, 813cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (d, J = 0.8 Hz, 2H), 3.76 (s, 6H), 3.74 (s, 3H), 2.23 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$): δ 153.10, 135.89, 133.67, 106.04, 60.94, 56.09, 21.91

1-Methyl-4-phenoxybenzene (4):[3b] Purified by silica-gel column chromatography using EtOAc:hexane (1:99) as an eluent. Isolated as a colourless liquid. Yield: 62 mg, 68%. IR (DCM): 3443, 2103,1655, 1644, 1634, 1239, 691, 667 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.28 (m, 2H), 7.14-7.12 (m, 2H), 7.08-7.04 (m, 1H), 6.99-6.96 (m, 2H), 6.92-6.90 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 157.95, 154.83, 133.05, 130.38, 129.79, 122.93, 119.27, 118.47, 20.85.

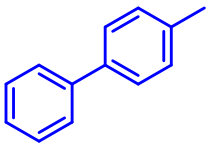


Methyl(*p*-tolyl)sulfane (5):[4] Purified by silica-gel column chromatography using hexane as an eluent. Isolated as white solid. Yield: 45 mg, 65%. IR (DCM): 3018, 2922, 2866, 1438, 1264, 1212, 802, 738 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 7.13-7.10 (m, 2H), 7.05-7.01 (m, 2H), 2.39 (s, 3H), 2.24 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): 135.19, 134.79, 129.74, 127.38, 21.06, 16.65.

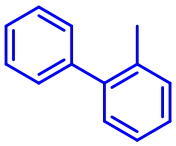
***N,N*,4-Trimethylaniline (6):**[3] Purified by silica-gel column chromatography using hexane as an eluent. Isolated as colorless Liquid. Yield: 54 mg, 79%. IR (DCM): 2925, 2854, 1675, 1515, 1465, 1353, 1264, 817, 738 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (dd, J_1 = 8.6, J_2 = 2.5 Hz, 2H), 6.76 (dt, J_1 = 8.6, J_2 = 1.8 Hz, 2H), 2.96 (s, 6H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 148.98, 129.70, 126.19, 113.34, 41.16, 20.35.



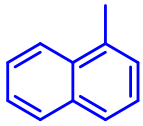
4-Methyl-1,1'-biphenyl (7):[3] Purified by silica-gel column chromatography using hexane as an eluent. Isolated as white solid. Yield: 75 mg, 87%. IR (DCM): 3079, 3026, 1600, 1547, 1486, 1145, 1276, 824, 763 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 - 7.50 (m, 2H), 7.43-7.41 (m, 2H), 7.36-7.33 (m, 2H), 7.26-7.23 (m, 1H), 7.18-7.16 (m, 2H), 2.32 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 141.31, 138.50, 137.16, 129.62, 128.85, 127.14, 21.25.



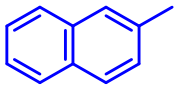
2-Methyl-1,1'-biphenyl (8):[3b] Purified by silica-gel column chromatography using hexane as an eluent. Isolated as white solid. Yield: 71 mg, 84%. IR (DCM): 3060, 3022, 2962, 2876, 1478, 1255, 748, 716 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 7.36-7.31 (m, 2H), 7.28-7.24 (m, 3H), 7.20-7.15 (m, 4H), 2.20 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 142.12, 135.49, 130.44, 129.94, 129.34, 128.20, 127.39, 126.90, 125.90, 20.60.



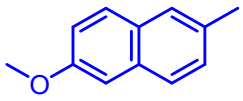
1-Methylnaphthalene (9):[5] Purified by silica-gel column chromatography using hexane as an eluent. Isolated as white solid. Yield: 57 mg, 80%. IR (DCM): 3048, 2968,1630, 1600, 1508, 1429, 1355, 1264, 812, 738 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.1 Hz, 1H), 7.76 (dd, J_1 = 7.5, J_2 = 1.8 Hz, 1H), 7.62 (d, J = 8.1 Hz, 1H), 7.46-7.38 (m, 2H), 7.31-7.22 (m, 2H), 2.61 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 134.40, 133.69, 132.76, 128.66, 126.69, 126.51, 125.85, 125.71, 125.67, 124.24, 19.51.



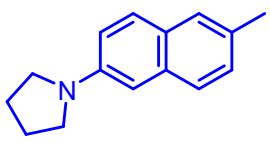
2-Methylnaphthalene (10):[6] Purified by silica-gel column chromatography using hexane as an eluent. Isolated as white solid. Yield: 63 mg, 88%. IR (DCM): 3157, 3069, 2921, 2851, 1642, 1264, 726 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ7.84-7.75 (m, 3H), 7.64-7.63 (m, 1H), 7.50-7.40 (m, 2H), 7.36-7.33 (m, 1H), 2.55 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 135.57, 133.79, 131.82, 128.25, 127.82, 127.73, 127.36, 126.97, 125.99, 125.08, 21.85.



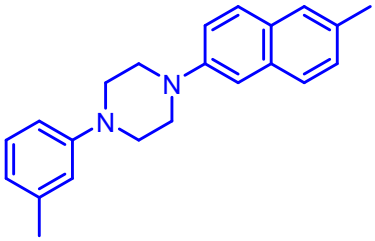
2-Methoxy-6-methylnaphthalene (11):[3b] Purified by silica-gel column chromatography using hexane as an eluent. Isolated as white solid. Yield: 74 mg, 86%. IR (DCM): 3089, 2882, 1789, 1482, 1389, 1228, 1034, 852, 764 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (dd, J_1 = 9.1, J_2 = 3.6 Hz, 2H), 7.47 (s, 1H), 7.22-7.18 (m, 2H), 7.05-7.03 (m, 2H), 3.84 (s, 3H), 2.40 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 157.16, 133.17, 132.78, 129.29, 128.85, 128.73, 126.85, 126.71, 118.76, 105.80, 55.42, 21.60.



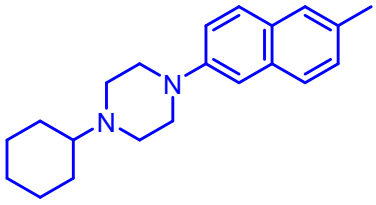
1-(6-Methylnaphthalen-2-yl)pyrrolidine (12):[7] Purified by neutral alumina column chromatography using hexane/EtOAc (98:2) mixture as an eluent. Isolated as a white solid. Yield: 71 mg, 67%. IR (DCM): 2961, 2909, 2840, 1602, 1391, 1170, 807, 653 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ



7.53 (d, J = 8.9 Hz, 1H), 7.47 (d, J = 8.4 Hz, 1H), 7.37 (s, 1H), 7.11 (dd, J_1 = 8.4, J_2 = 1.8 Hz, 1H), 6.89 (dd, J_1 = 8.9, J_2 = 2.5 Hz, 1H), 6.66 (s, 1H), 3.31 (t, J = 6.6 Hz, 4H), 2.36 (s, 3H), 2.01-1.92 (m, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 145.51, 133.48, 128.54, 128.25, 126.69, 125.83, 115.88, 104.87, 48.02, 25.61, 21.54.

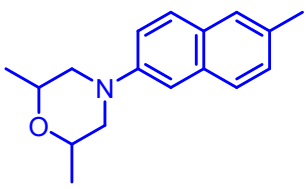


1-(6-Methylnaphthalen-2-yl)-4-(m-tolyl)piperazine (13): Purified by neutral alumina column chromatography using hexane/EtOAc (98:2) mixture as an eluent. Isolated as a white solid. Yield: 117 mg, 74%. IR (DCM): 3749, 3647, 2922, 2848, 2821, 1601, 1263, 1225, 846, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.57 (dd, J_1 =18.7, J_2 = 8.7 Hz, 2H), 7.43 (s, 1H), 7.22-7.17 (m, 2H), 7.14-7.07 (m, 2H), 6.76-6.73 (m, 2H), 6.66 (d, J = 7.4 Hz, 1H), 3.35-3.28 (m, 8H), 2.40 (s, 3H), 2.27 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 151.46, 148.63, 139.05, 133.17, 132.79, 129.18, 129.08, 128.68, 128.27, 126.80, 126.63, 121.14, 119.89, 117.36, 113.63, 110.78, 50.14, 49.68, 21.94, 21.64. HRMS (ESI) calcd for $C_{22}H_{25}N_2$ $[M+H]^+$: 317.2018 found: 317.1961.



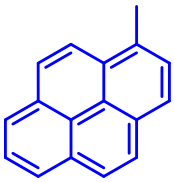
1-Cyclohexyl-4-(6-methylnaphthalen-2-yl)piperazine (14): Purified by neutral alumina column chromatography using hexane/EtOAc (98:2) mixture as an eluent. Isolated as a white solid. Yield: 120 mg, 78%. IR (DCM): 3749, 2921, 2848, 2819, 2358, 1599, 1447, 1261, 1148, 806 cm^{-1}. ^1H NMR (700 MHz, $CDCl_3$): δ7.56 (d, J = 8.9 Hz, 1H), 7.52 (d, J = 8.3 Hz, 1H), 7.41 (s, 1H), 7.18-7.15 (m, 2H), 7.02 (d, J = 2.4 Hz, 1H), 3.22-3.20 (m, 4H), 2.71 (t, J = 5.0 Hz, 4H), 2.39 (s, 3H), 2.27-2.23 (m, 1H), 1.88-1.87 (m, 2H), 1.77-1.75 (m, 2H), 1.58 (dd, J_1 = 14.0, J_2 = 3.5 Hz, 1H), 1.22-1.16 (m, 4H), 1.10-1.04 (m, 1H).. $^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$): δ 148.85, 132.89, 132.86, 128.87, 128.55, 128.08, 126.77, 126.58, 119.67, 110.39, 63.69, 50.35, 49.21, 29.17, 26.48, 26.04, 21.62. HRMS (ESI) calcd for $C_{21}H_{29}N_2$ $[M+H]^+$: 309.2331 found: 309.2251

2,6-Dimethyl-4-(6-methylnaphthalen-2-yl)morpholine (15): Purified by neutral alumina column chromatography using hexane/EtOAc (98:2) mixture as an eluent. Isolated as a white solid. Yield: 100 mg, 78%. IR (DCM): 3749, 2973, 2870, 2359, 1602, 1262, 1083, 733 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (dd, J_1 = 17.3, J_2 =8.7 Hz, 2H), 7.44-7.41 (m,

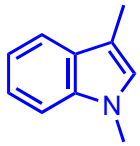


1H), 7.18-7.13 (m, 2H), 6.99 (d, J = 2.4 Hz, 1H), 3.83-3.75 (m, 2H), 3.46 (dt, J_1 = 10.9, J_2 = 2.1 Hz, 2H), 2.43-2.37 (m, 5H), 1.22 (s, 3H), 1.20 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 148.34, 133.04, 132.82, 128.94, 128.67, 128.25, 126.73, 126.60, 119.36, 110.29, 71.85, 55.61, 21.62, 19.24. HRMS (ESI) calcd for $C_{17}H_{21}NO$ $[M]^+$: 255.1623 found: 255.1633.

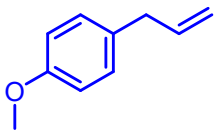
1-Methylpyrene (16):[6] Purified by silica-gel column chromatography using hexane as an eluent. Isolated as off white solid. Yield: 81 mg, 75%. IR (DCM): 3039, 2958, 2881, 1605, 1510, 1460, 1240, 1085, 841cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 9.2 Hz, 1H), 8.18-8.14 (m, 2H), 8.12-8.07 (m, 2H), 8.04-7.97 (m, 3H), 7.86 (dd, J_1 = 7.7, J_2 = 0.8 Hz, 1H), 2.98 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 132.38, 131.60, 131.14, 129.88, 129.35, 128.00, 127.68, 127.25, 126.56, 125.92, 125.01, 124.95, 124.88, 124.81, 123.84, 19.94.



1,3-Dimethyl-1*H*-indole (17):[8] Purified by silica-gel column chromatography using hexane/EtOAc (96:4) mixture as an eluent. Isolated as a pale yellow solid. Yield: 39 mg, 54%. IR (DCM): 3942, 3052, 2925, 2953, 1726, 1264, 1025, 737 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (dt, J_1 = 7.8, J_2 =1.0 Hz, 1H), 7.29 (dt, J_1 = 8.3, J_2 = 1.0 Hz, 1H), 7.25-7.21 (m, 1H), 7.14-7.10 (m, 1H), 6.83 (q, J = 1.1 Hz, 1H), 3.74 (s, 3H), 2.34 (q, J = 1.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 137.12, 128.77, 126.64, 121.53, 119.06, 118.61, 110.24, 109.11, 32.61, 9.66.



1,5-Dimethyl-1*H*-indole (18):[8] Purified by silica-gel column chromatography using hexane/EtOAc (96:4) mixture as an eluent. Isolated as a pale yellow solid. Yield: 52 mg, 82%. IR (DCM): 3052, 2971, 2918, 1595, 1264, 740cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.33 (m, 1H), 7.16-7.12 (m, 1H), 6.98-6.96 (m, 1H), 6.92 (d, J = 3.1 Hz, 1H), 6.32 (dd, J_1 = 3.1, J_2 = 0.9 Hz, 1H), 3.68 (s, 3H), 2.37 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 135.26, 128.94, 128.85, 128.55, 123.23, 120.61, 108.98, 100.39, 32.96, 21.53.



1-Allyl-4-methoxybenzene (19):[9] Purified by silica-gel column chromatography using hexane as an eluent. Isolated as a colorless liquid. Yield: 63 mg, 85%. IR (DCM): 3168, 2914, 2862, 1642, 1254, 853, 737 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.14-7.11 (m, 2H), 6.87-6.85 (m, 2H), 6.03-5.92 (m, 1H), 5.10-5.05 (m, 2H), 3.80 (s, 3H), 3.35 (dd, J_1 = 6.8, J_2 = 1.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 158.13, 138.02, 132.22, 129.62, 115.53, 113.97, 55.37, 39.46.

1-Allyl-4-fluorobenzene (20):[9] Purified by silica-gel column chromatography using hexane as an eluent. Isolated as a colorless liquid. Yield: 53 mg, 79%. IR (DCM): 3059, 2914, 2851, 1588, 1109, 840, 726 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.16-7.11 (m, 2H), 7.00-6.94 (m, 2H), 5.99-5.89 (m, 1H), 5.08-5.03 (m, 2H), 3.35 (d, J = 6.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 162.74, 160.32, 137.38, 135.71, 130.07, 129.99, 116.02, 115.32, 115.11, 39.43.

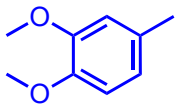
Mesitylene (21): Purified by silica-gel column chromatography using hexane as an eluent. Isolated as a colorless liquid. Yield: 53 mg, 78%. IR (DCM): 3131, 3081, 2928, 1264, 726 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.82 (s, 3H), 2.29 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 136.88, 126.06, 20.34.

1-Methylnaphthalene (9) and 2-Methylnaphthalene (10):[10] Purified by silica-gel column chromatography using hexane as an eluent. Isolated as white solid. Yield: 118 mg, 83%. IR (DCM): 3174, 3133, 3082, 3066, 2944, 2928, 2867, 2841, 1621, 1434, 1277, 1226, 894, 854, 746, 709 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.05 - 8.03 (m, 1H), 7.90-7.87 (m, 1H), 7.84-7.74 (m, 4H), 7.65 (s, 1H), 7.58-7.34 (m, 7H), 2.74 (s, 3H), 2.55 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 135.57, 134.40, 133.81, 133.70, 132.76, 131.85, 128.66, 128.25, 127.83, 127.74, 127.37, 126.97, 126.70, 126.51, 126.00, 125.85, 125.71, 125.67, 125.09, 124.25, 21.84, 19.50.

1-Methoxy-4-methylbenzene (22):[11] Purified by silica-gel column chromatography using hexane as an eluent. Isolated as colorless liquid. Yield: 85 mg, 69%. IR (DCM): 3301, 2953, 1494, 1456, 1240, 1033, 745 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ7.12 - 7.05 (m, 2H), 6.8-6.74 (m, 2H), 3.75 (s, 3H), 2.15 (s, 3H).. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 157.83, 130.73, 126.92, 126.71, 120.38, 110.00, 55.36, 16.35

1-Methoxy-4-methylbenzene (23):[3b] Purified by silica-gel column chromatography using hexane as an eluent. Isolated as colorless liquid. Yield: 37 mg, 61%. IR (DCM): 2952, 2833, 1620, 1585, 1512, 1464, 1294, 1037, 738 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ ^1H NMR (400 MHz, $CDCl_3$) δ 7.03-6.99 (m, 2H), 6.74-6.71 (m, 2H), 3.70 (s, 3H), 2.21 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 157.62, 130.02, 129.96, 113.84, 55.40, 20.57.

3,4-Dimethoxy-3-methylbenzene (24):[3b] Purified by silica-gel column chromatography using

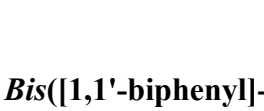


EtOAc:hexane (2:98) as an eluent. Isolated as a colourless liquid. Yield: (53 mg, 70%). IR (DCM): 3445, 3046, 2934, 1332, 1147, 796, 735 cm-1 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.71-6.69 (m, 1H), 6.65-6.62 (m, 2H), 3.79 (s, 3H), 3.78 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.80, 146.94, 130.51, 120.86, 112.51, 111.31, 56.06, 55.87, 21.11.

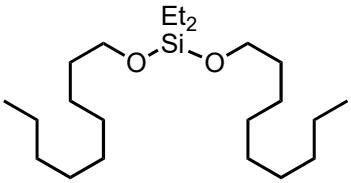
3-Methylpyridine (25): Purified by silica-gel column chromatography using diethyl ether : pentane (2:98) as an eluent. Isolated as a colourless liquid. Yield: 34 mg, 36%. IR (DCM): 3348,1692, 1480, 788, 707 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41-8.37 (m, 2H), 7.45-7.43 (m, 1H), 7.14 (dd, J_1 = 7.8, J_2 = 4.8 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.34, 147.01, 136.54, 133.20, 123.22, 18.53.

Spectral data of silyl ether intermediates:

***Bis*([1,1'-biphenyl]-4-ylmethoxy) diethylsilane (27):** Purified by silica-gel column chromatography using hexane/EtOAc = 97:3 as an eluent. Isolated as colourless liquid. Yield: 75 mg, 66%. IR (DCM): 3029, 2956, 2911, 2878, 1486, 1459, 1044, 736 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 7.51-7.47 (m, 8H), 7.37-7.31 (m, 8H), 7.26 (t, J = 7.3 Hz, 2H), 4.77 (s, 4H), 0.98 (t, J = 7.9 Hz, 6H), 0.69 (q, J = 8.0 Hz, 4H).^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ δ 141.15, 140.22, 139.96, 128.88, 127.31, 127.22, 127.19, 127.00, 64.41, 6.70, 4.11. ^{29}Si NMR (80 MHz, $CDCl_3$) δ -2.23.



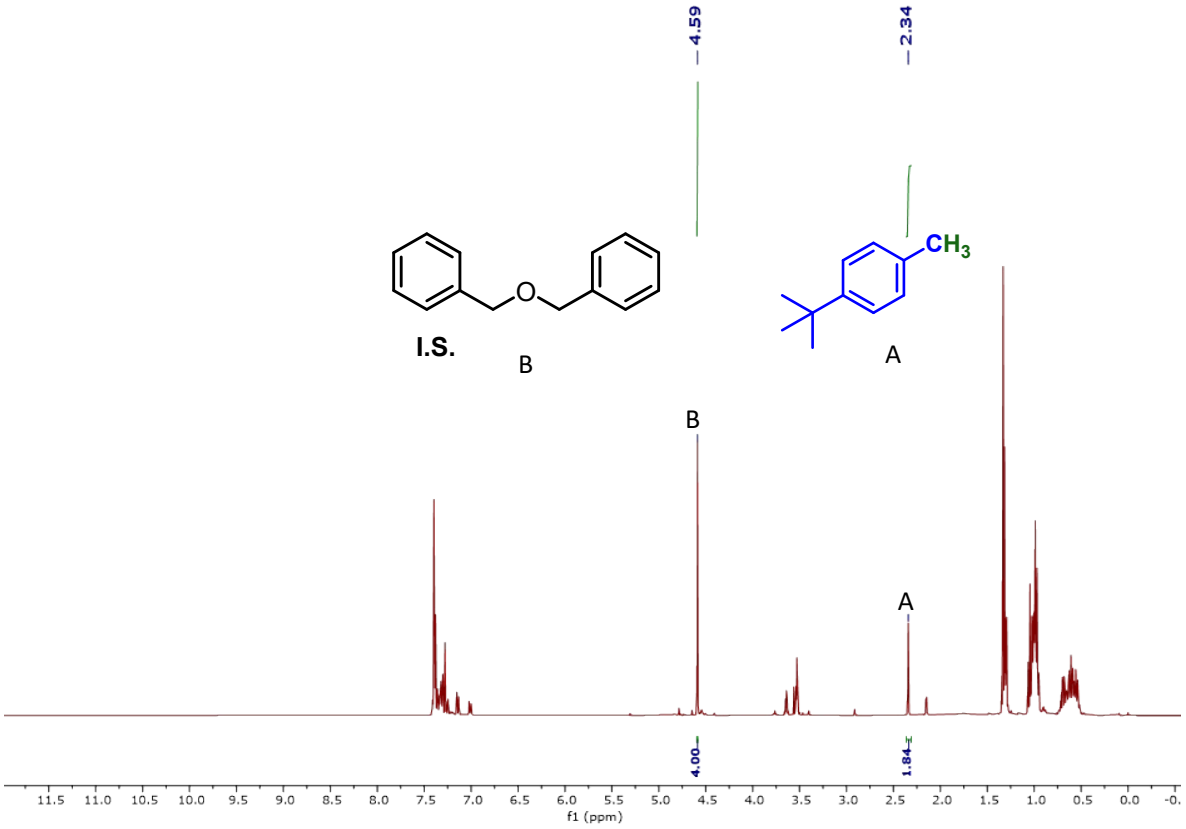
([1,1'-Biphenyl]-4-ylmethoxy)diethylsilane (27'):[10] Purified by silica-gel column chromatography using hexane/EtOAc = 97:3 as an eluent. Isolated as colourless liquid. Yield: 11 mg, 8%. IR (DCM): 3029, 2956, 2911, 2878, 1486, 1459, 1044, 736 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): 7.51 (dd, J = 12.3, 7.8 Hz, 4H), 7.38 – 7.33 (m, 4H), 7.26 (t, J = 7.3 Hz, 1H), 4.77 (s, 2H), 4.45 (dq, J = 7.7, 2.6 Hz, 1H), 0.95 – 0.88 (m, 6H), 0.50 – 0.42 (m, 4H).^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 141.30, 140.37, 140.21, 128.86, 127.23, 127.11, 126.86, 126.83, 63.95, 63.91, 6.73, 5.91.



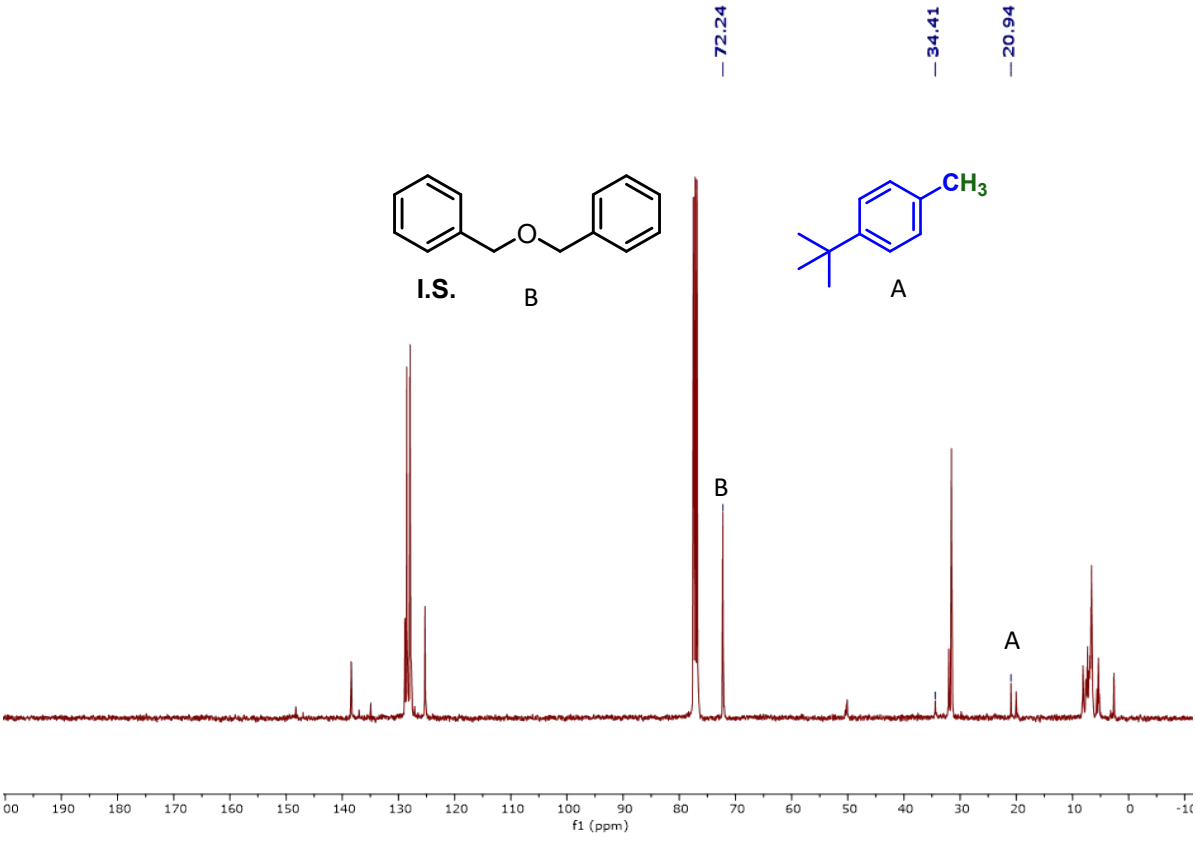
Diethylbis(nonyloxy)silane (29): Purified by silica-gel column chromatography using hexane/EtOAc = 98:2 as an eluent. Isolated as colorless liquid. Yield: 40 mg, 43%. IR (DCM): 2956, 2916,1264, 1049, 1006, 736 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.61 (t, *J* = 6.8 Hz, 4H), 1.48 (p, *J* = 6.8 Hz, 4H), 1.25 – 1.20 (m, 24H), 0.90 (t, *J* = 7.9 Hz, 6H), 0.83 – 0.79 (m, 6H), 0.54 (q, *J* = 8.0 Hz, 4H). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ 62.81, 32.91, 32.06, 29.77, 29.63, 29.45, 25.97, 22.83, 14.25, 6.68, 3.91. 29Si NMR (80 MHz, $CDCl_3$) δ -4.74.

Reaction mixture NMR spectra of methyl arenes 2:

^{1}H NMR spectrum of 1-(*tert*-butyl)-4-methylbenzene (**2**, 400 MHz, $CDCl_3$):

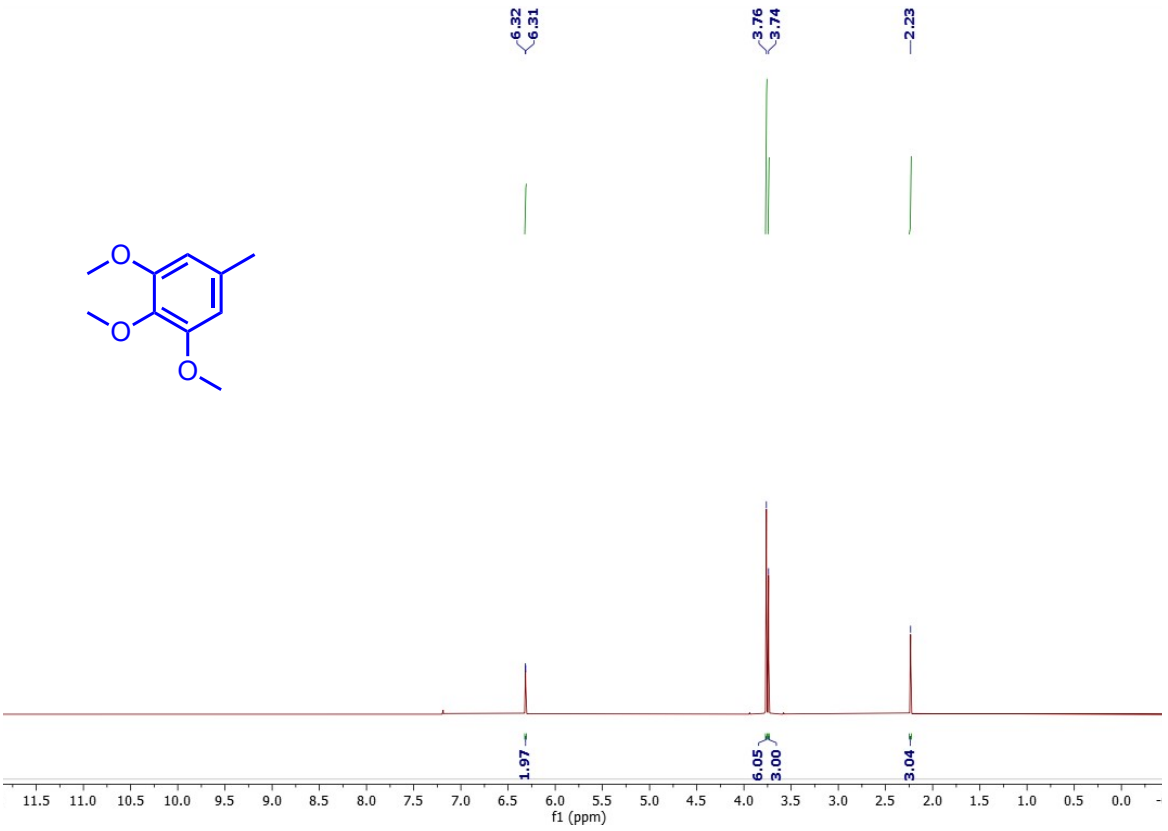


^{13}C{^{1}H} NMR spectrum of 1-(*tert*-butyl)-4-methylbenzene (**2**, 101 MHz, $CDCl_3$):s

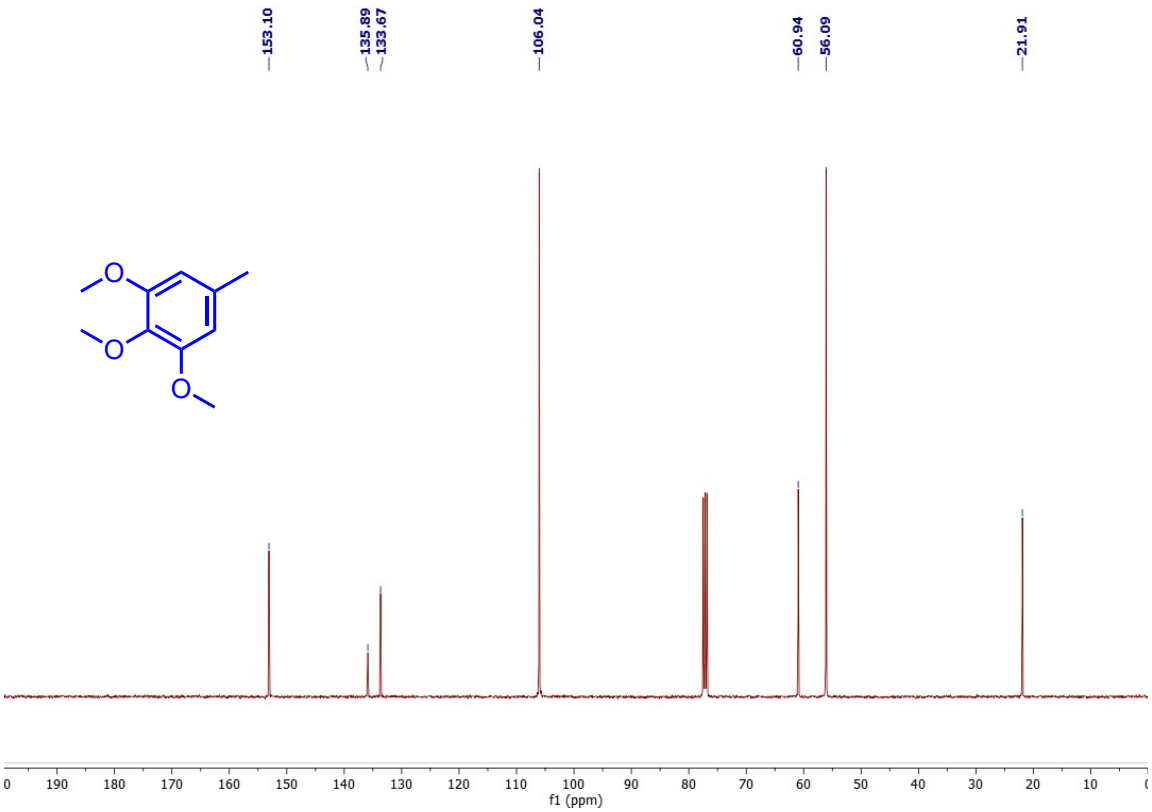


NMR spectra of alkanes from deoxygenation of esters:

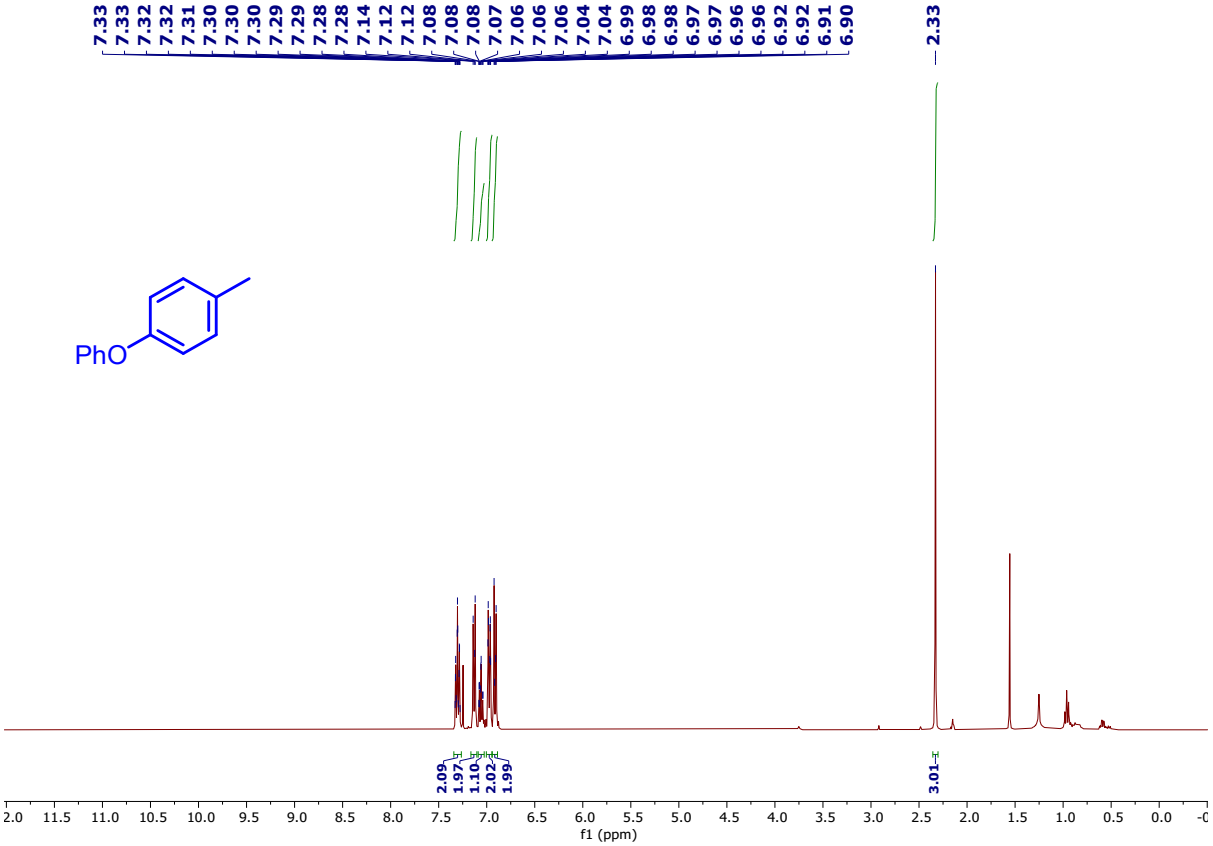
^{1}H NMR spectrum of 1,2,3-trimethoxy-5-methylbenzene (**3**, 400 MHz, $CDCl_3$):



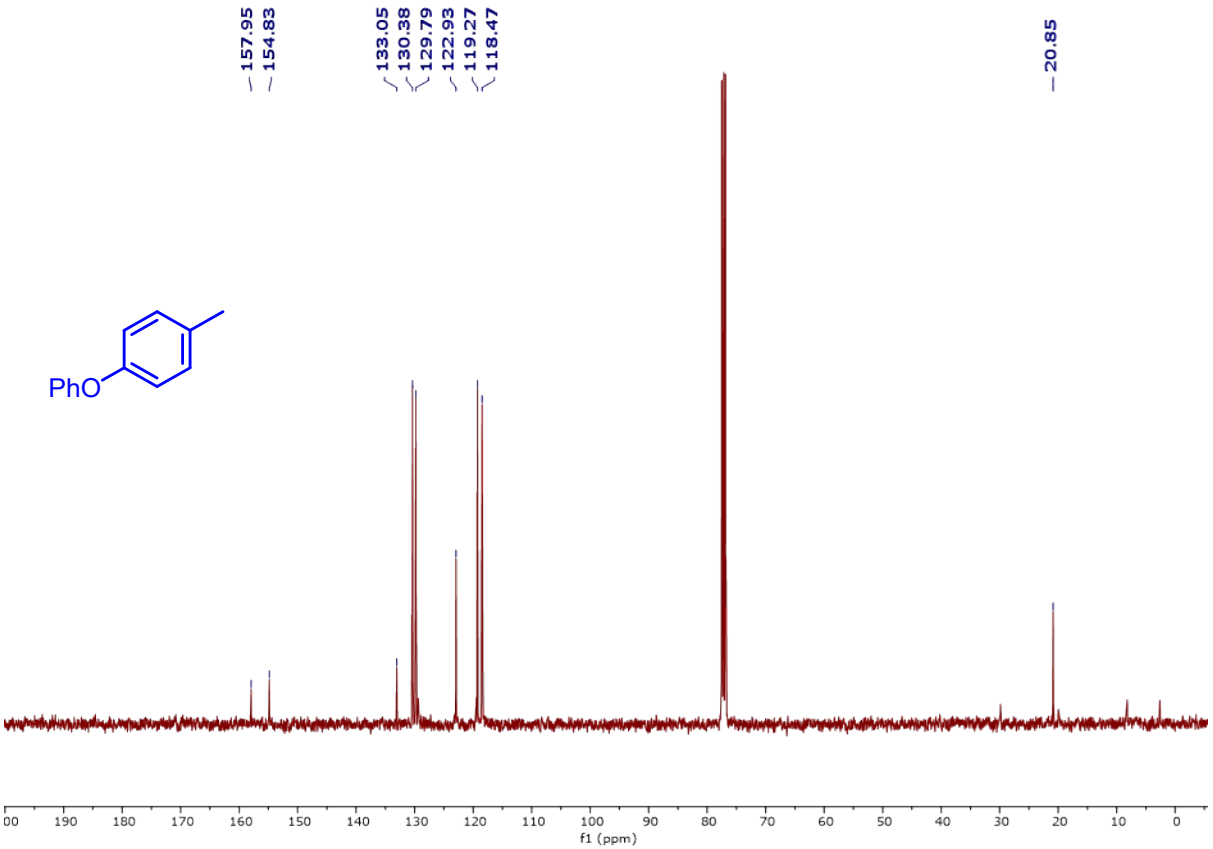
^{13}C{^{1}H} NMR spectrum of 1,2,3-trimethoxy-5-methylbenzene (**3**, 101 MHz, $CDCl_3$):



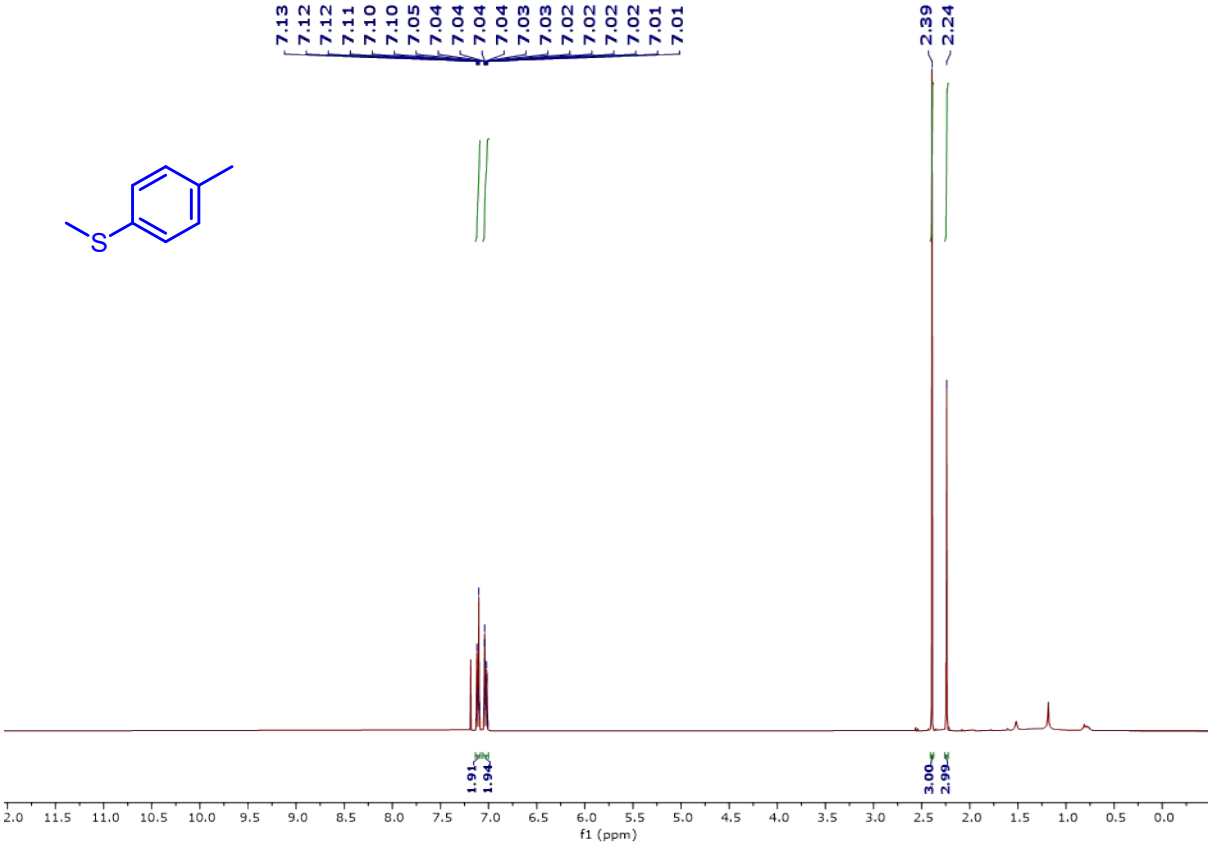
^{1}H NMR spectrum of 1-methyl-4-phenoxybenzene (**4**, 400 MHz, $CDCl_3$):



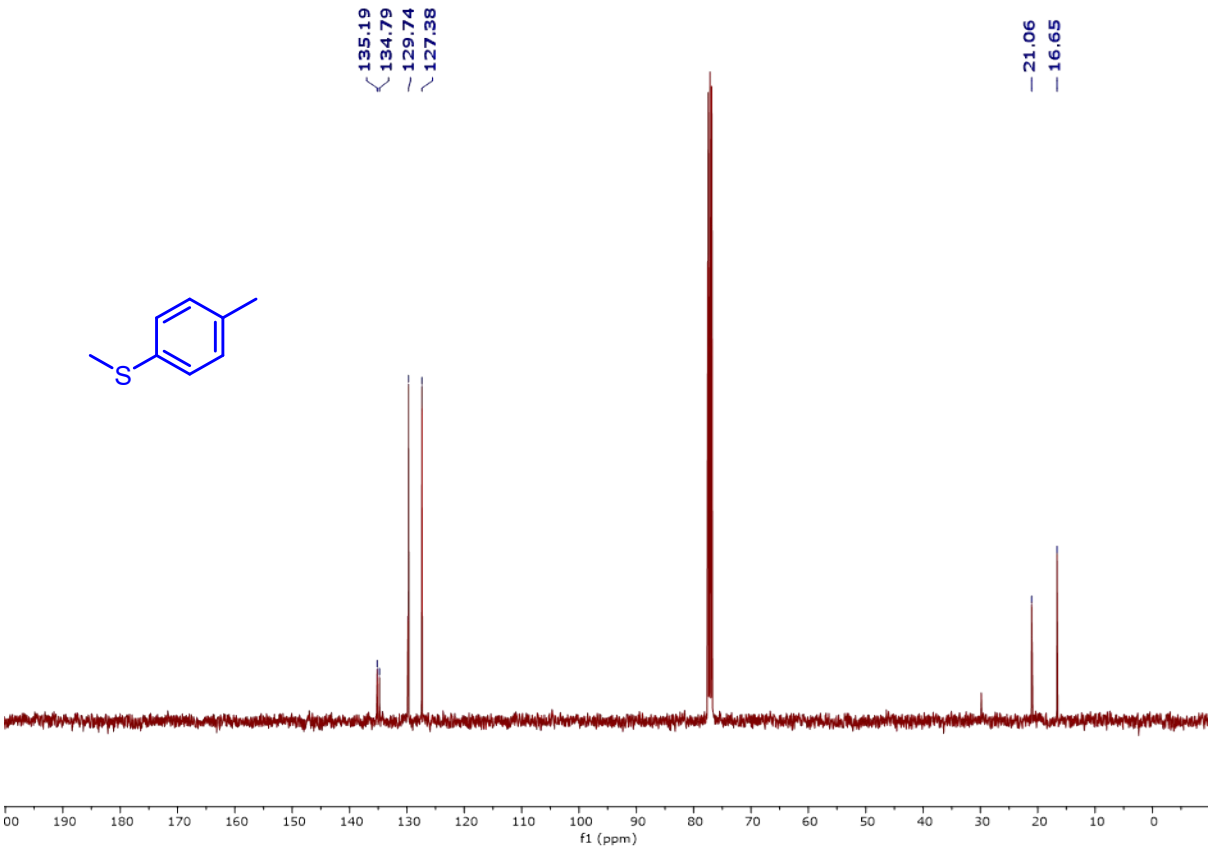
^{13}C{^{1}H} NMR spectrum of 1-methyl-4-phenoxybenzene (**4**, 101 MHz, $CDCl_3$):



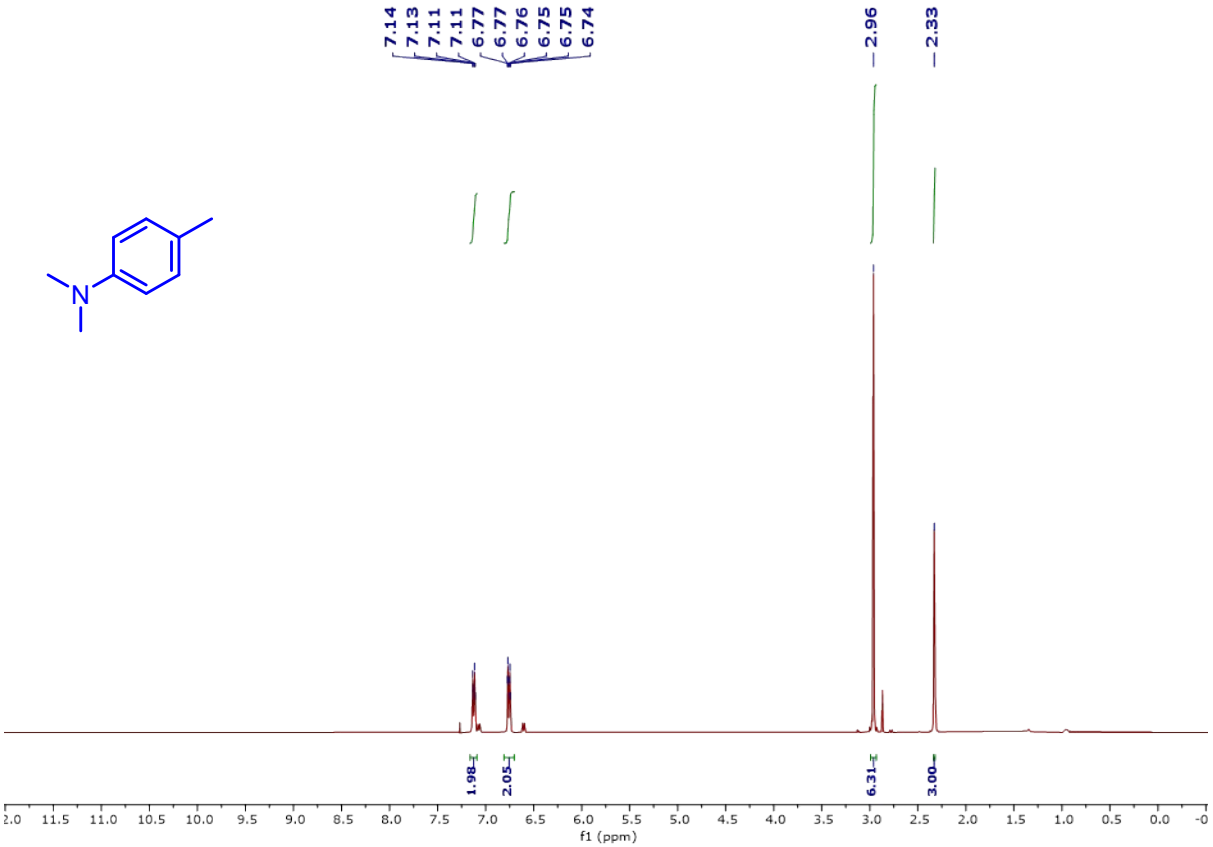
^{1}H NMR spectrum of methyl(*p*-tolyl)sulfane (**5**, 400 MHz, CDCl3):



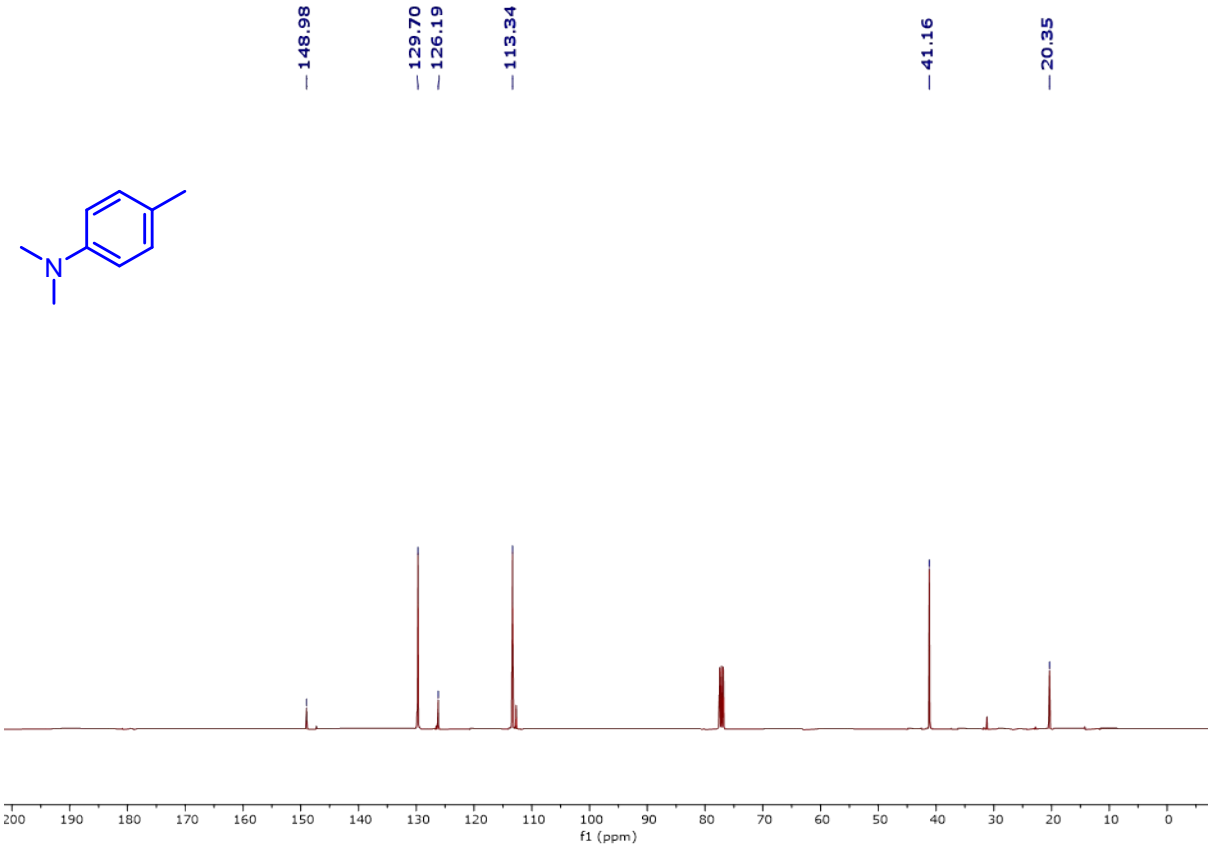
^{13}C{^{1}H} NMR spectrum of methyl(*p*-tolyl)sulfane (**5**, 101 MHz, CDCl3):



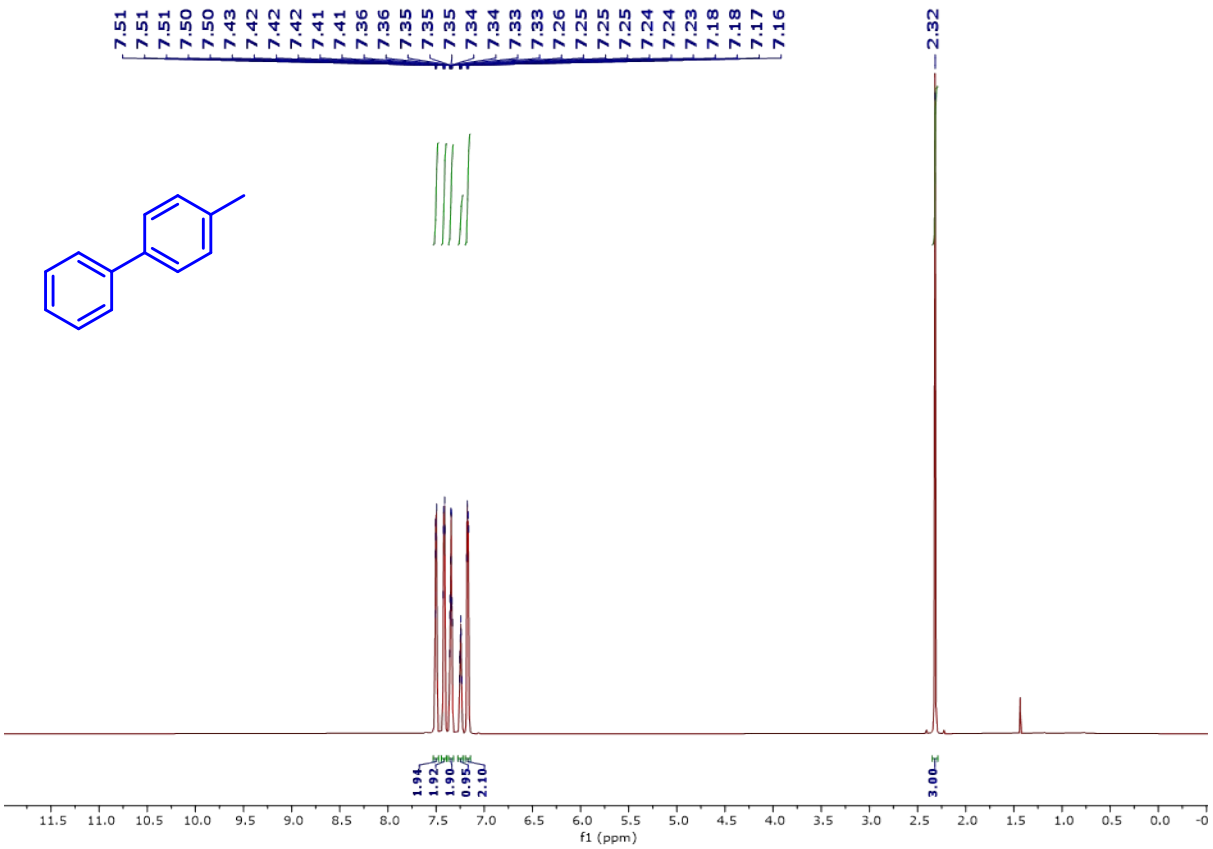
^{1}H NMR spectrum of *N,N*,4-trimethylaniline (**6**, 400 MHz, $CDCl_3$):



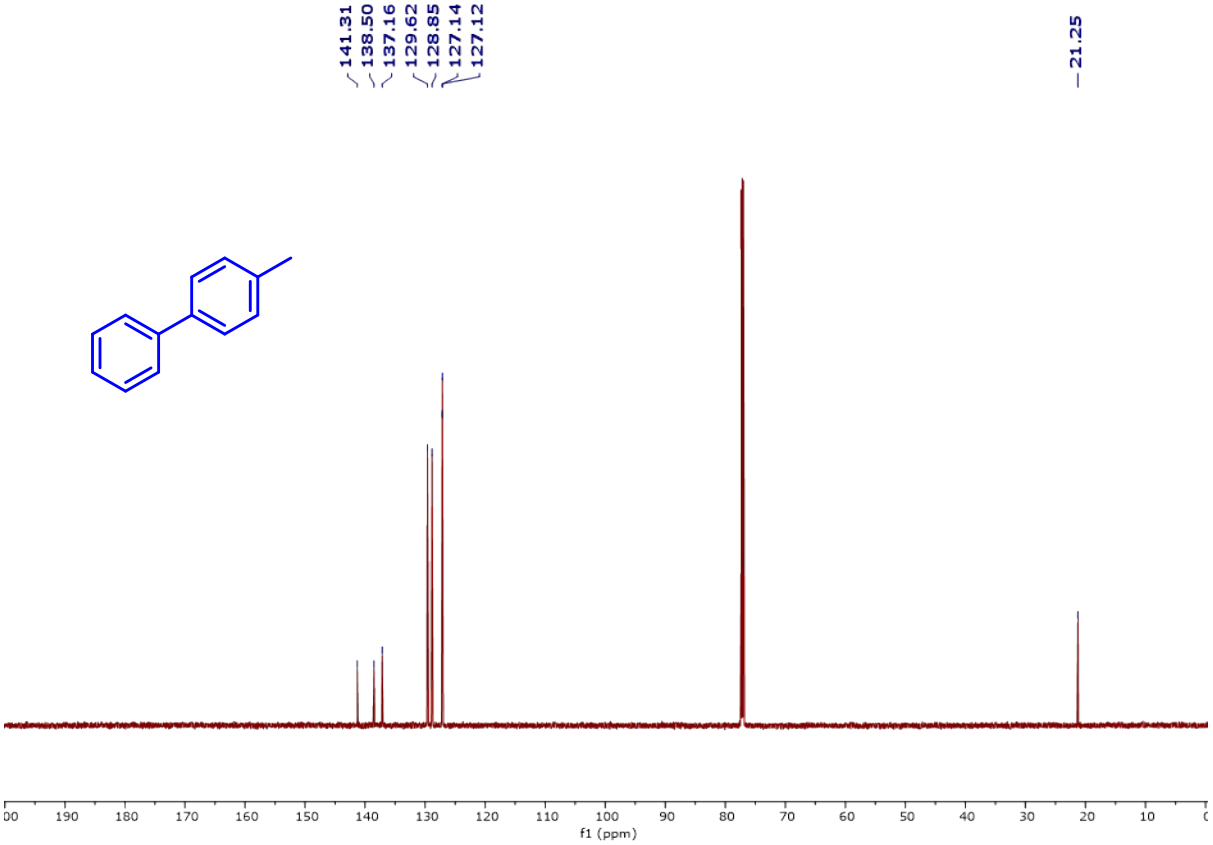
^{13}C{^{1}H} NMR spectrum of *N,N*,4-trimethylaniline (**6**, 101 MHz, $CDCl_3$):



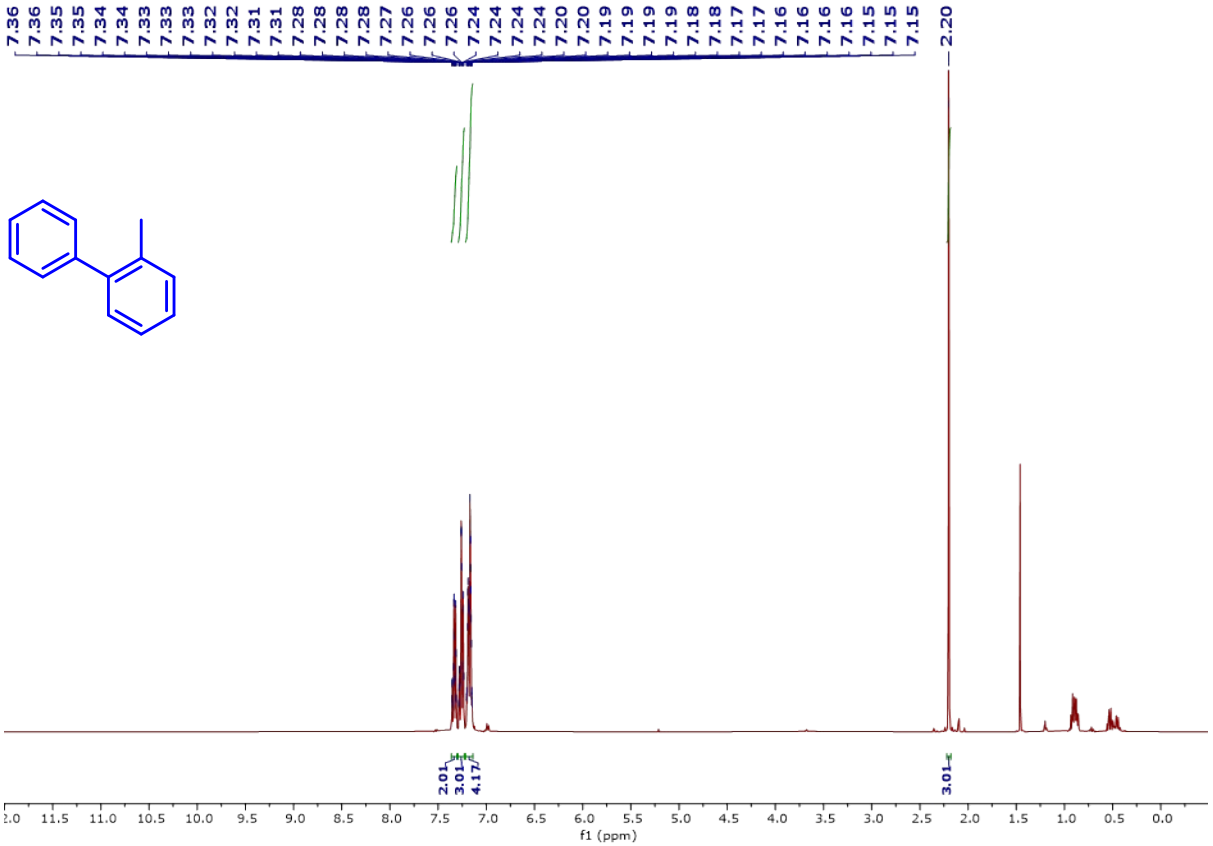
^{1}H NMR spectrum of 4-methyl-1,1'-biphenyl (**7**, 400 MHz, $CDCl_3$):



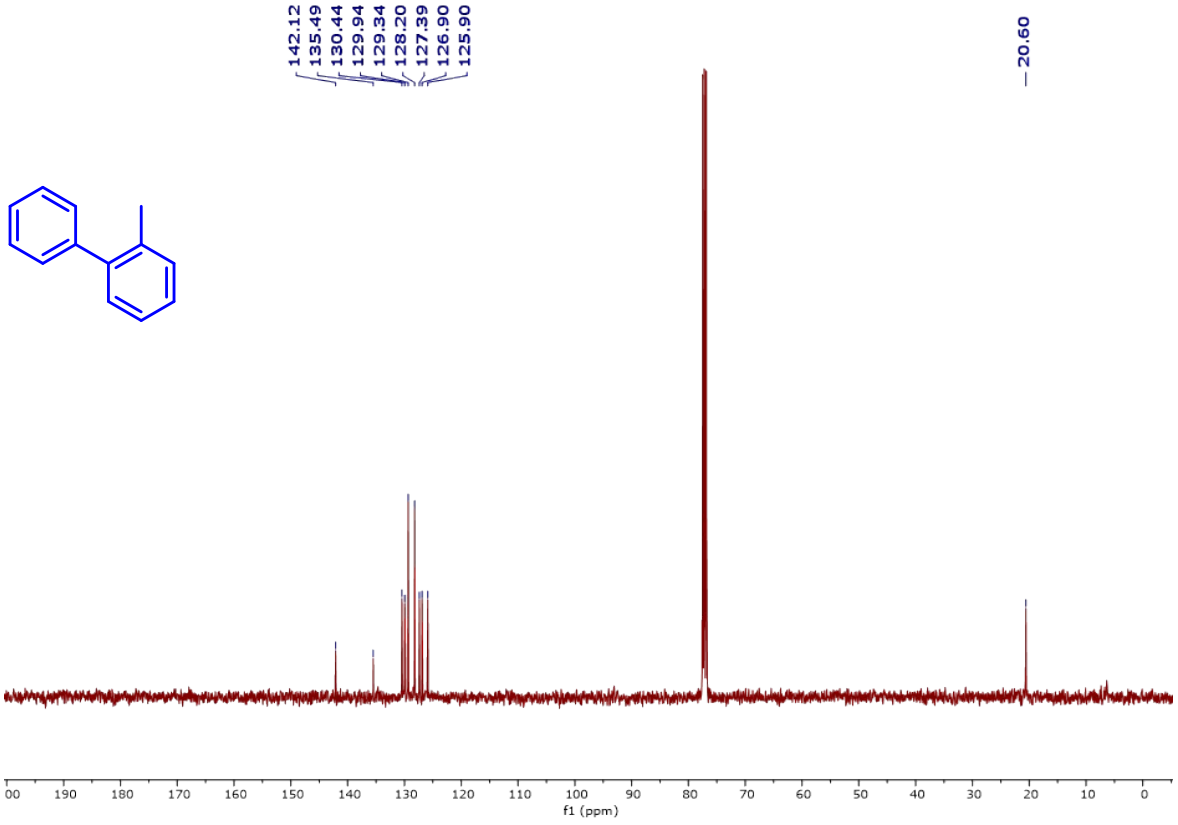
^{13}C{^{1}H} NMR spectrum of 4-methyl-1,1'-biphenyl (**7**, 101 MHz, $CDCl_3$):



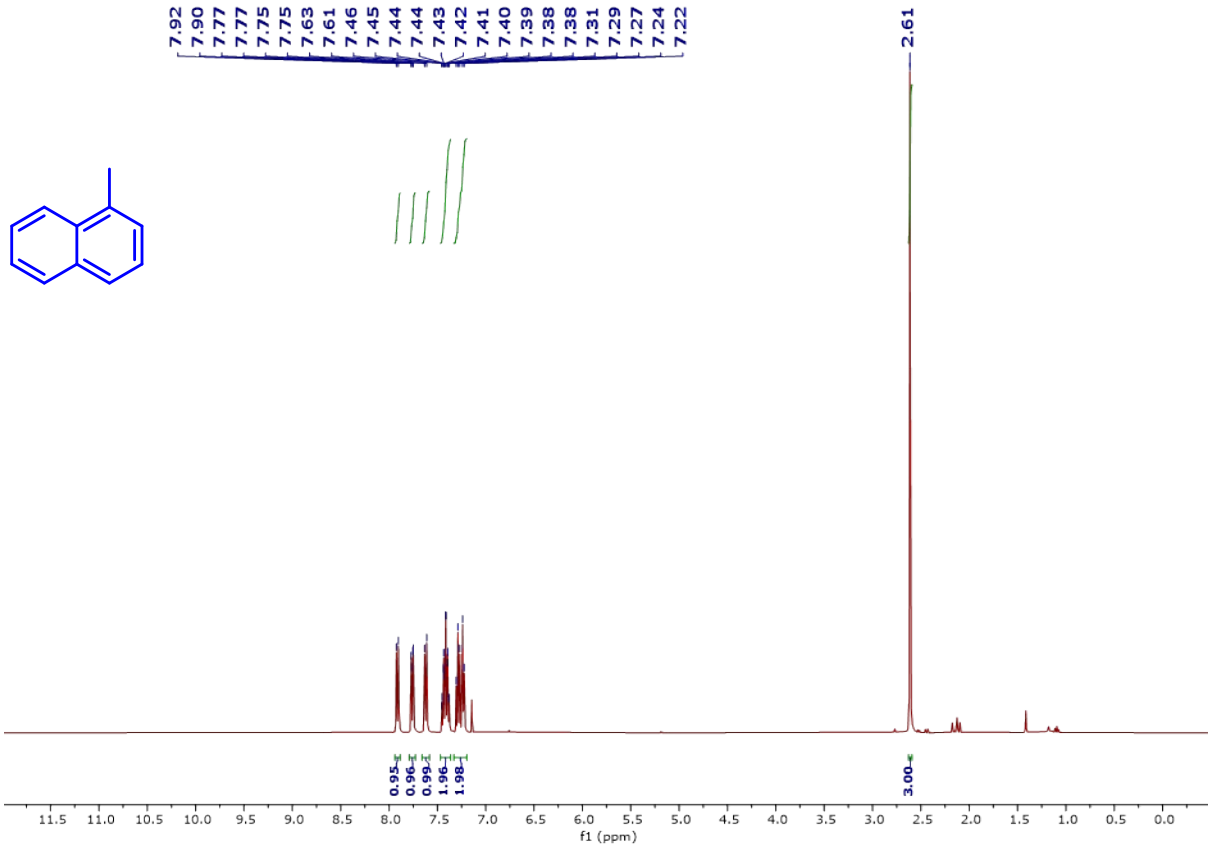
^{1}H NMR spectrum of 2-methyl-1,1'-biphenyl (**8**, 400 MHz, $CDCl_3$):



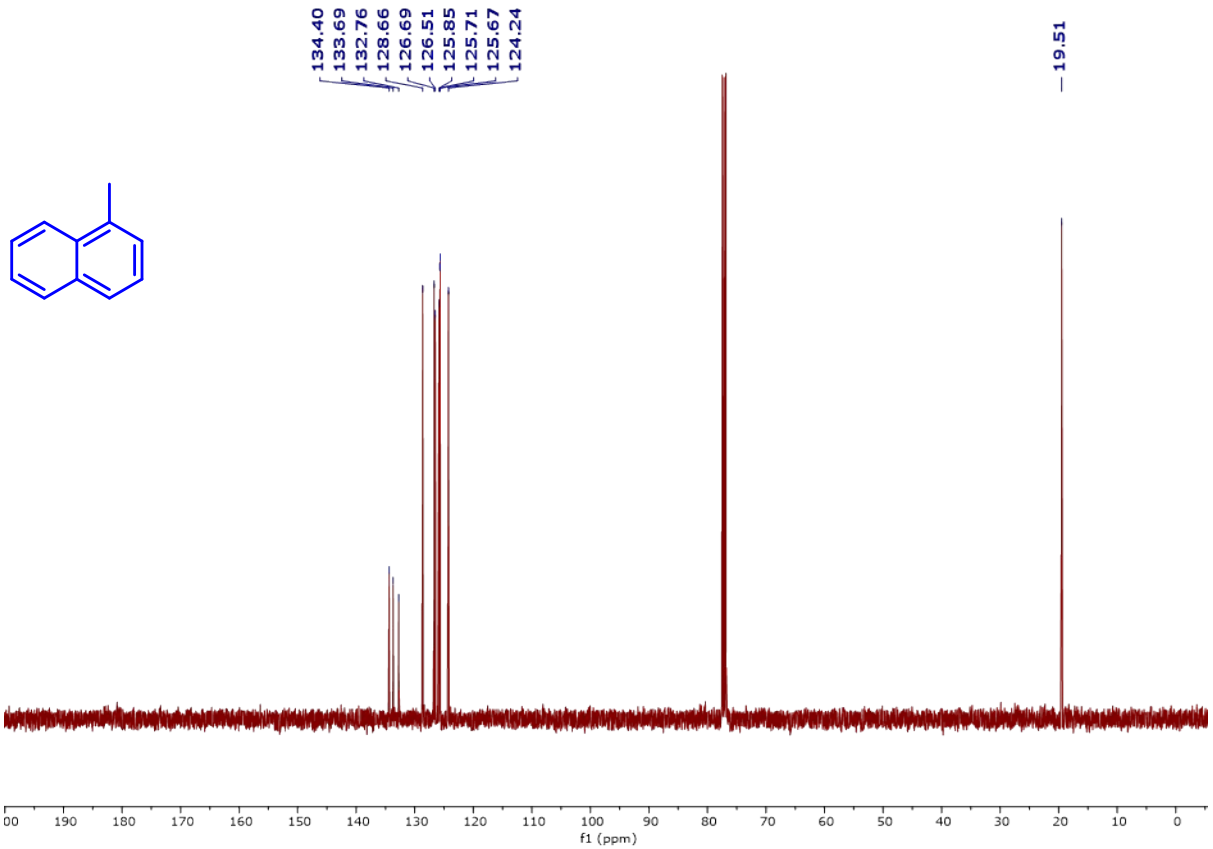
^{13}C{^{1}H} NMR spectrum of 2-methyl-1,1'-biphenyl (**8**, 101 MHz, $CDCl_3$):



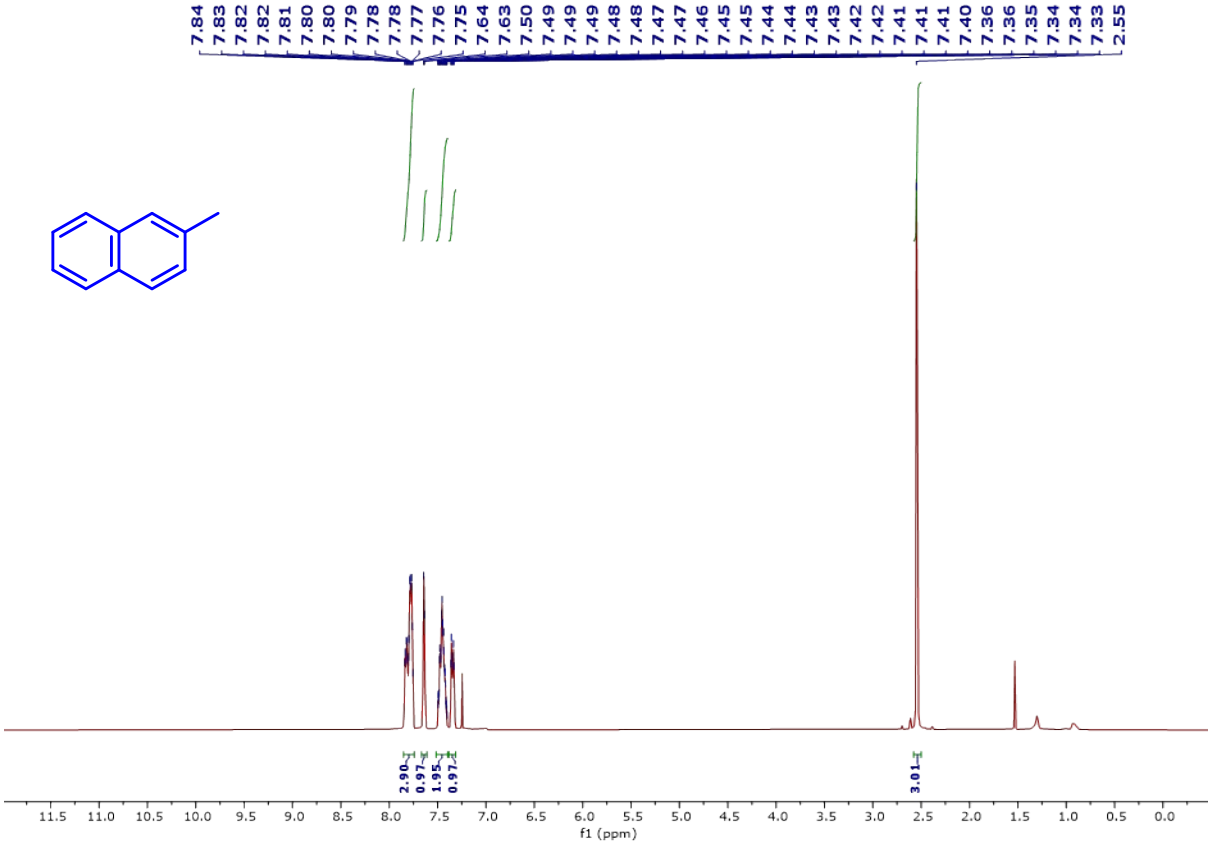
^{1}H NMR spectrum of 1-methylnaphthalene (**9**, 400 MHz, $CDCl_3$):



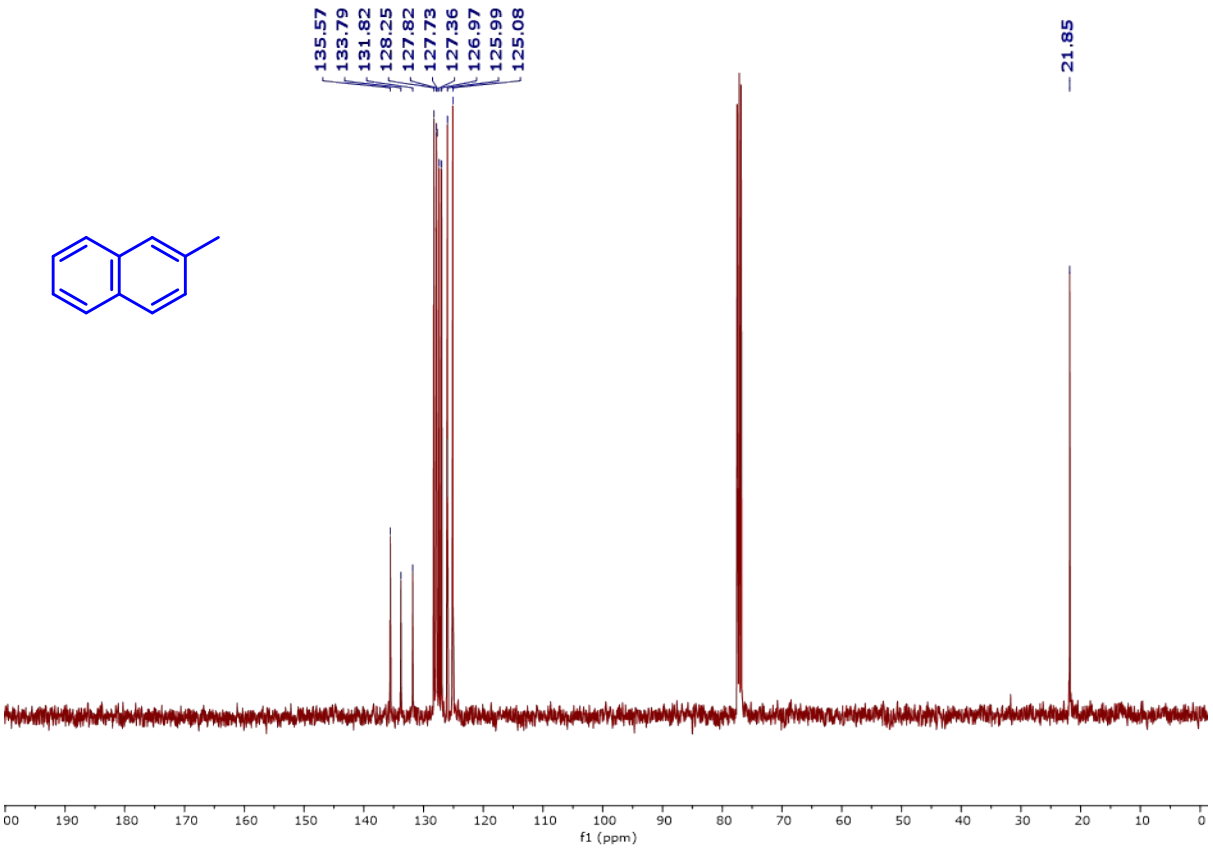
^{13}C{^{1}H} NMR spectrum of 1-methylnaphthalene (**9**, 101 MHz, $CDCl_3$):



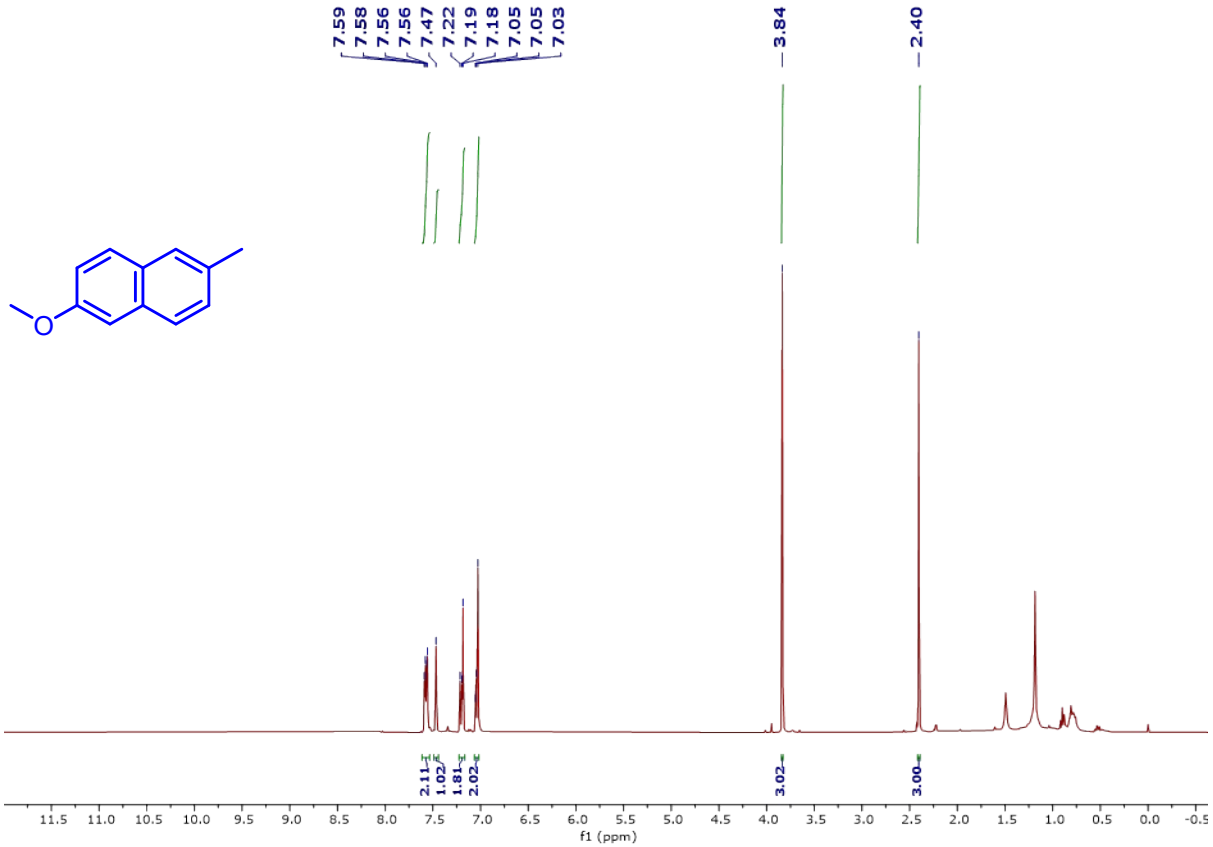
^{1}H NMR spectrum of 2-methylnaphthalene (**10**, 400 MHz, $CDCl_3$):



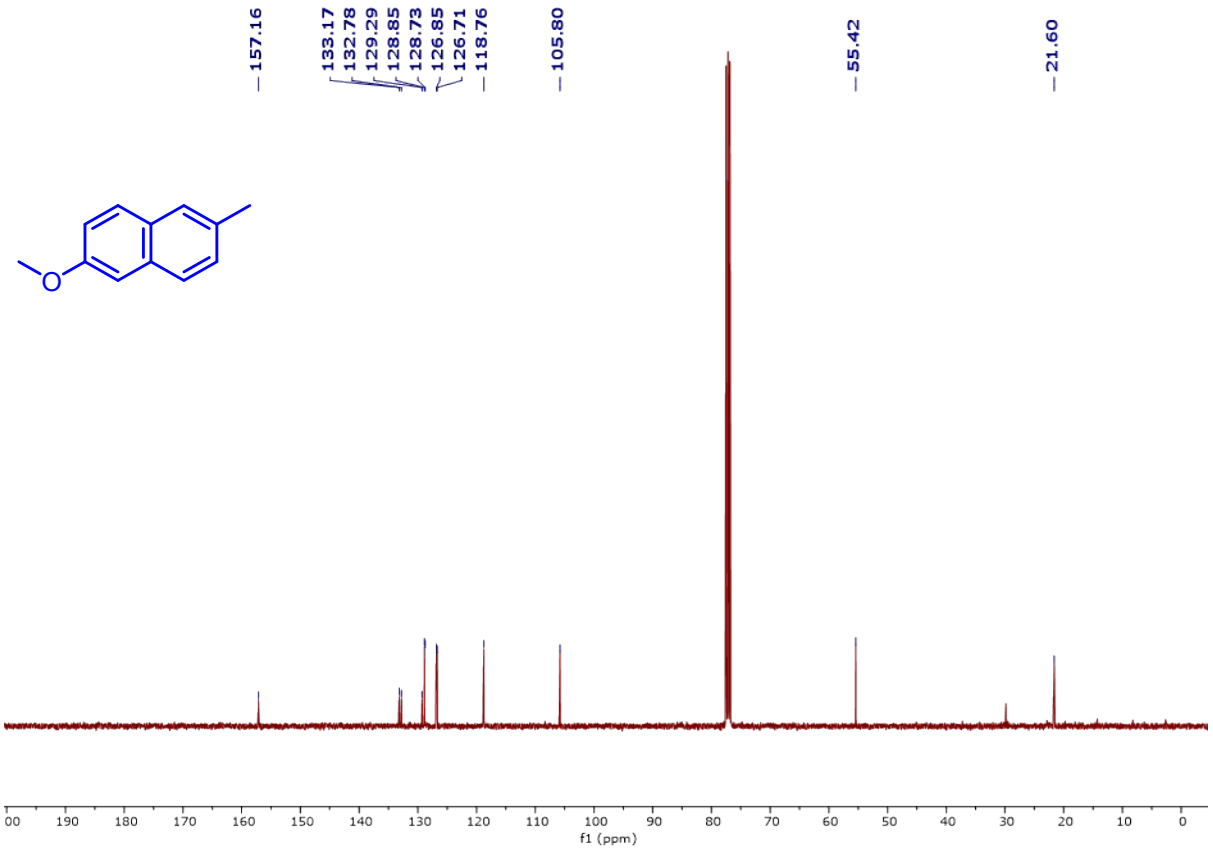
^{13}C{^{1}H} NMR spectrum of 2-methylnaphthalene (**10**, 101 MHz, $CDCl_3$):



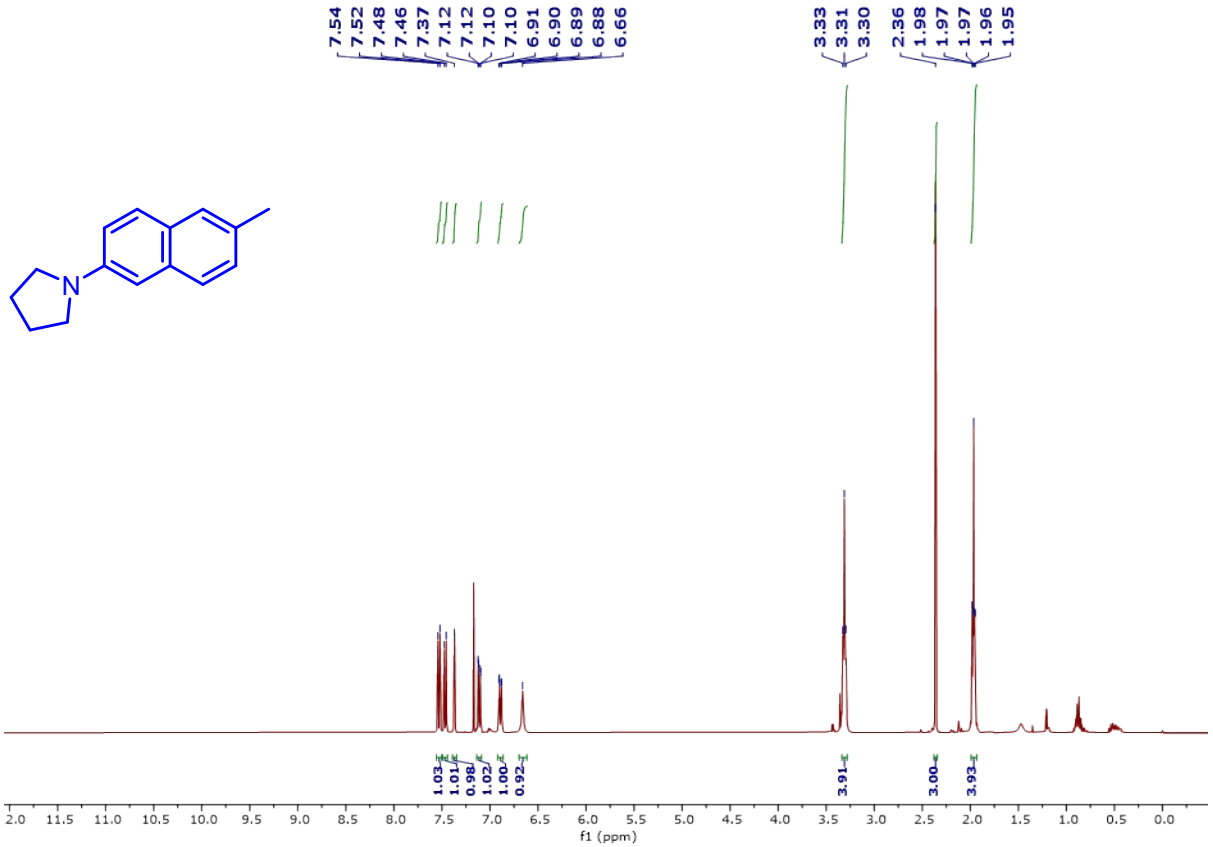
^{1}H NMR spectrum of 2-methoxy-6-methylnaphthalene (**11**, 400 MHz, $CDCl_3$):



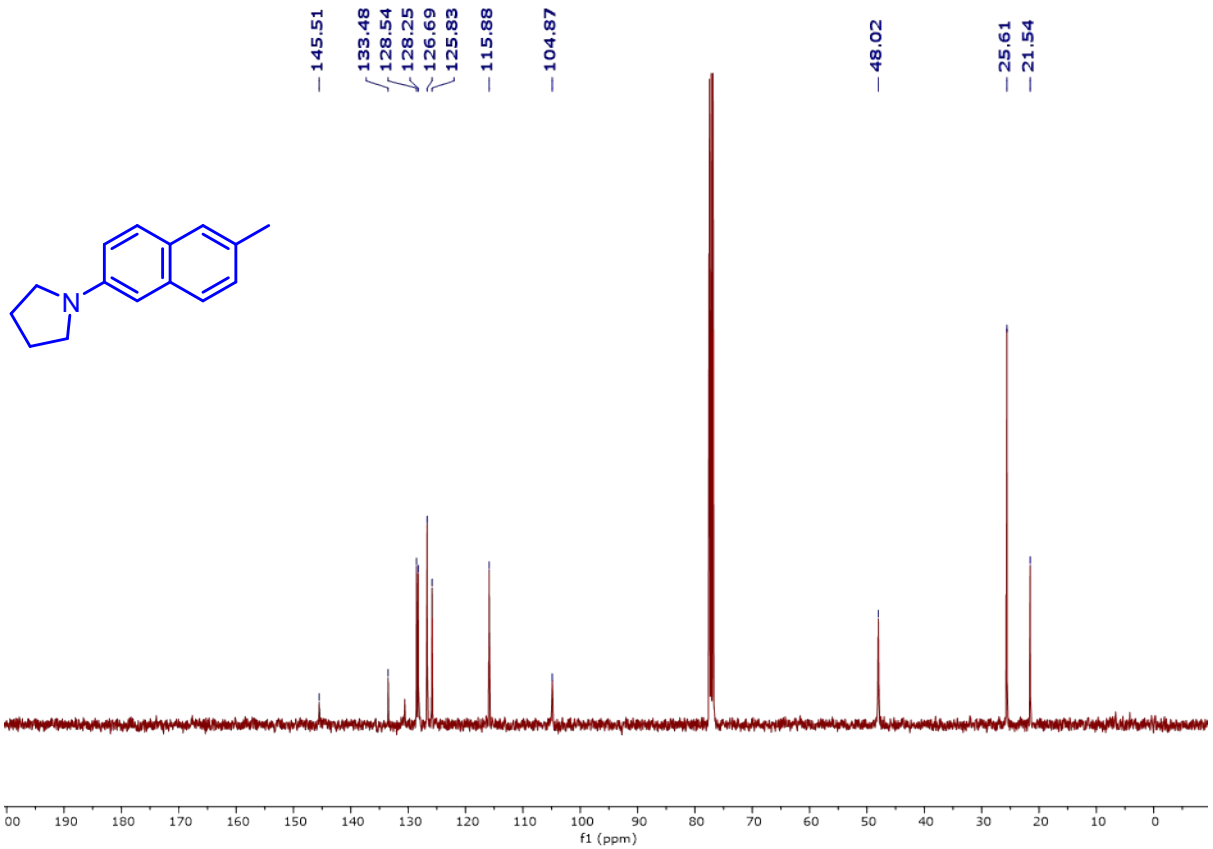
^{13}C{^{1}H} NMR spectrum of 2-methoxy-6-methylnaphthalene (**11**, 101 MHz, $CDCl_3$):



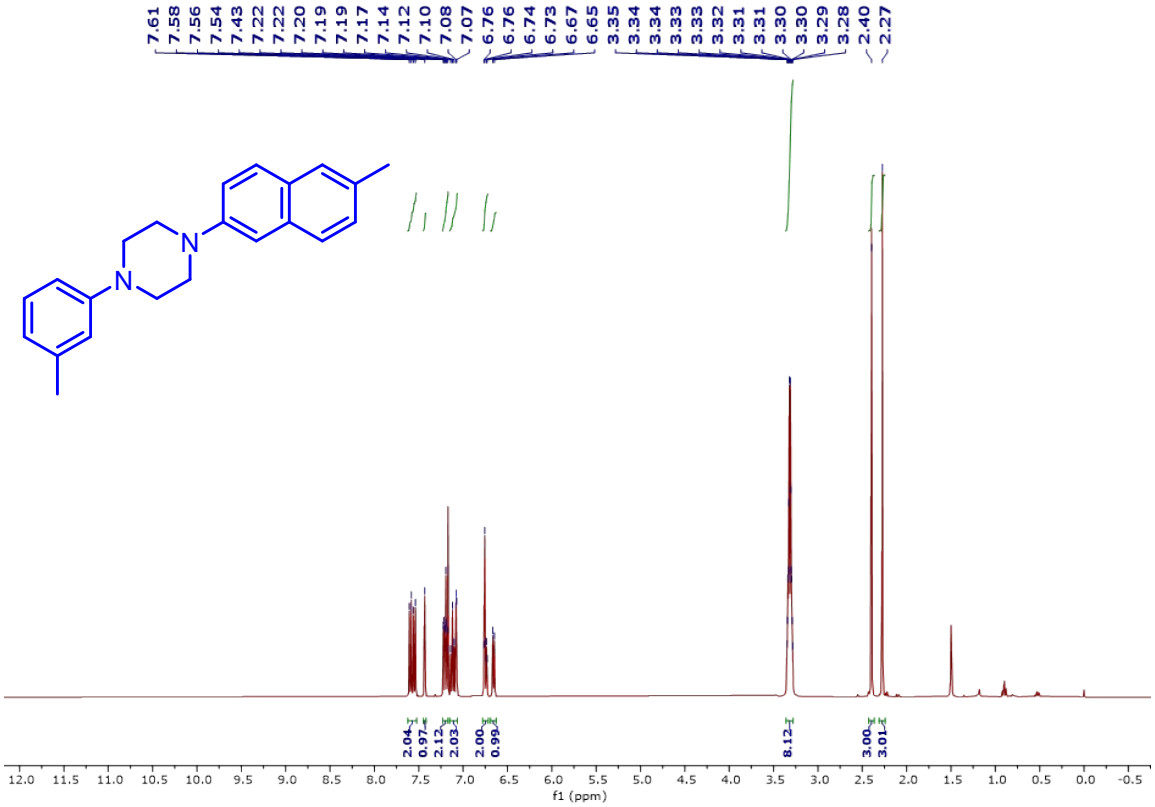
^{1}H NMR spectrum of 1-(6-methylnaphthalen-2-yl)pyrrolidine (**12**, 400 MHz, $CDCl_3$):



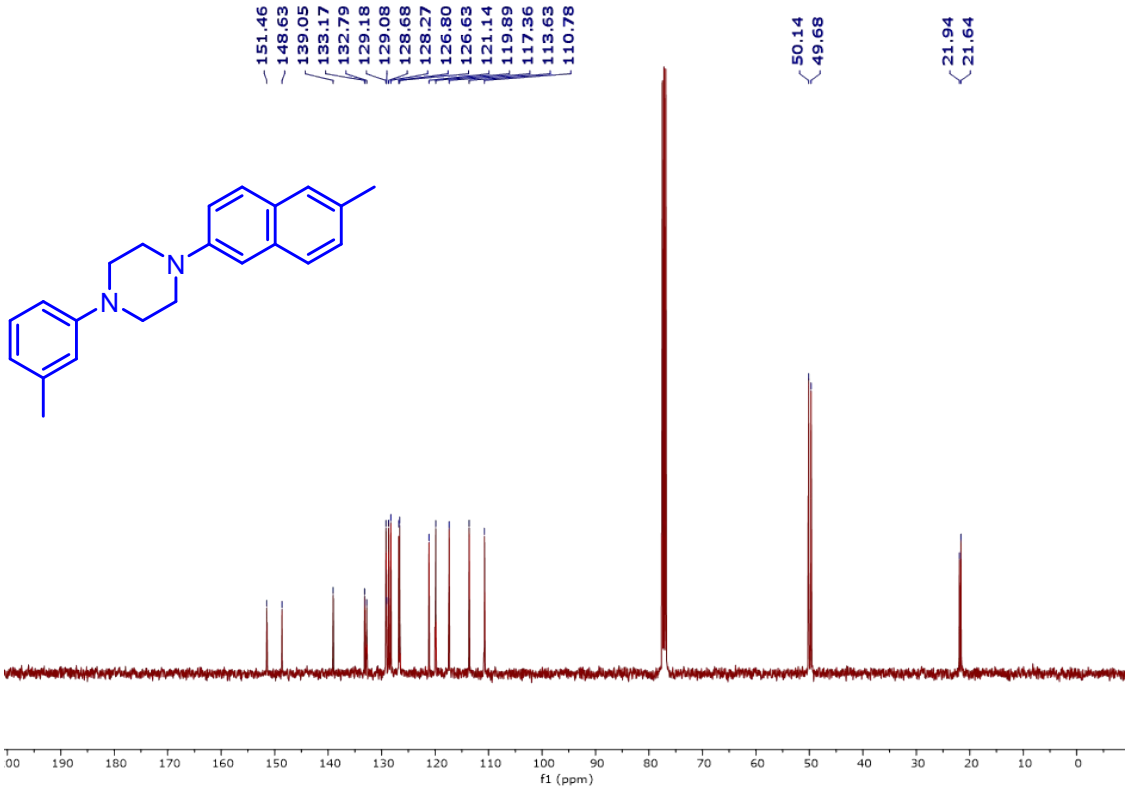
^{13}C{^{1}H} NMR spectrum of of 1-(6-methylnaphthalen-2-yl)pyrrolidine (**12**,101 MHz, $CDCl_3$):



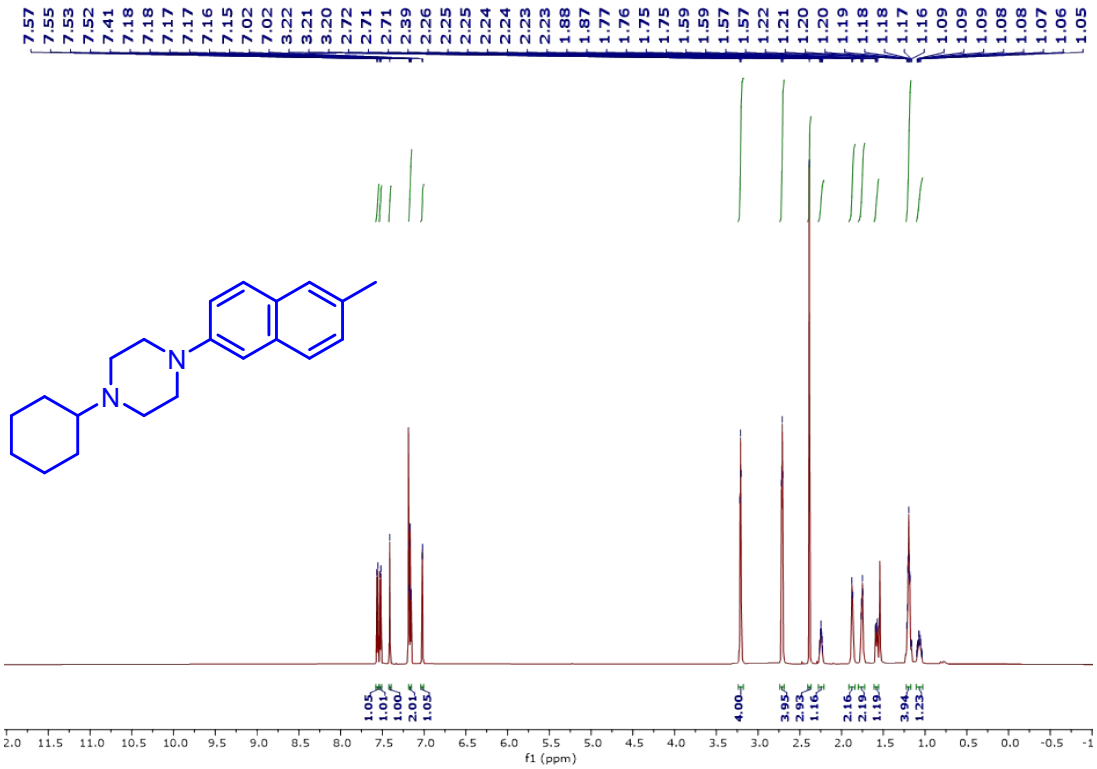
^{1}H NMR spectrum of 1-(6-methylnaphthalen-2-yl)-4-(m-tolyl)piperazine (**13**, 400 MHz, $CDCl_3$):



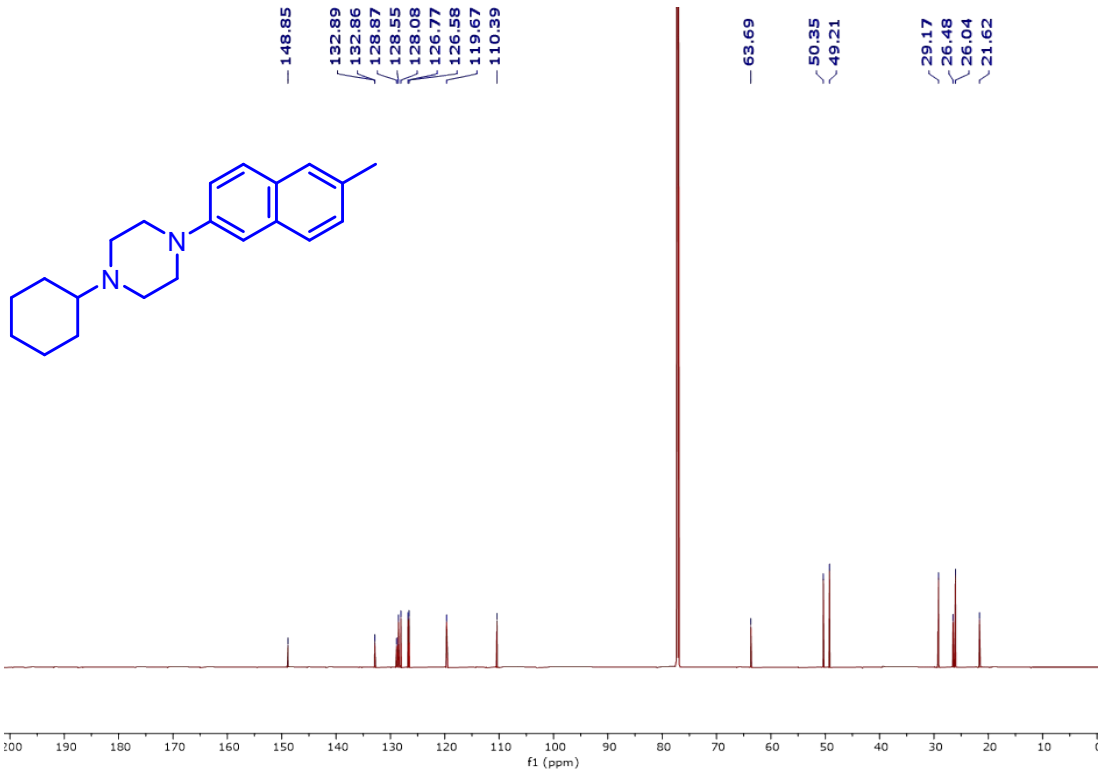
^{13}C{^{1}H} NMR spectrum of 1-(6-methylnaphthalen-2-yl)-4-(m-tolyl)piperazine (**13**, 101 MHz, $CDCl_3$):



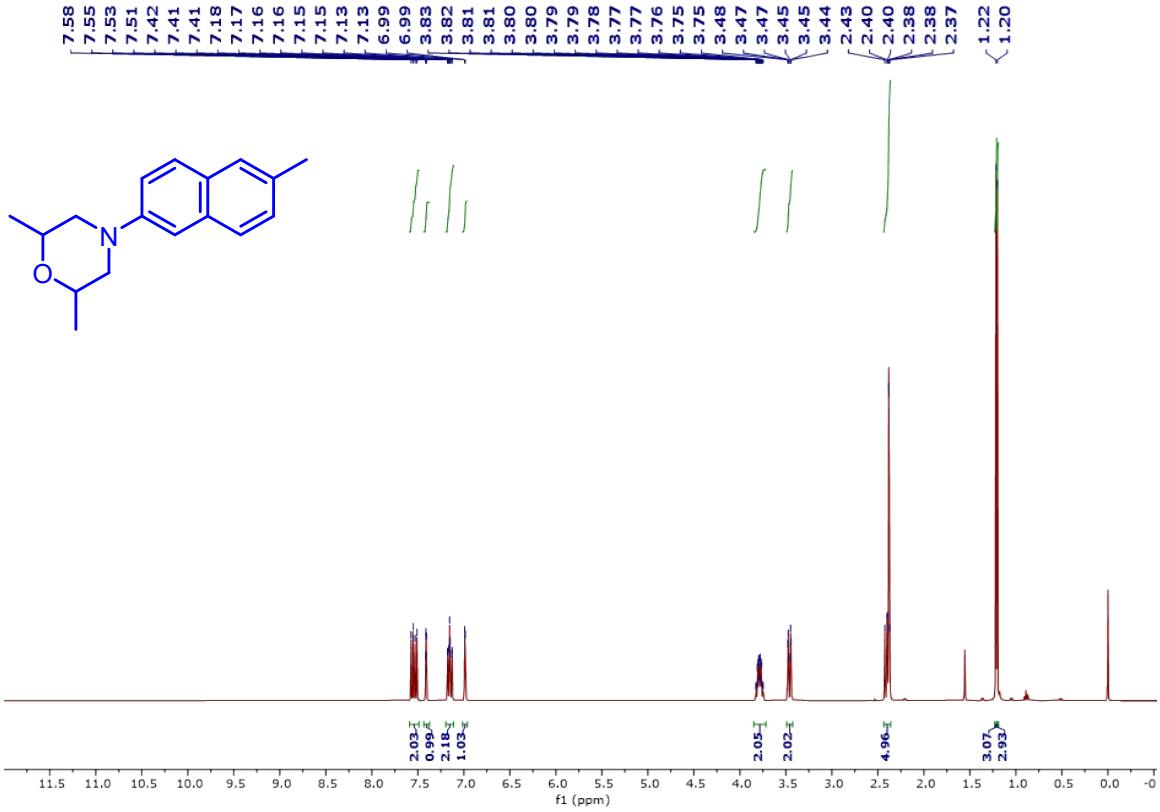
^{1}H NMR spectrum of 1-cyclohexyl-4-(6-methylnaphthalen-2-yl)piperazine (**14**, 700 MHz, $CDCl_3$):



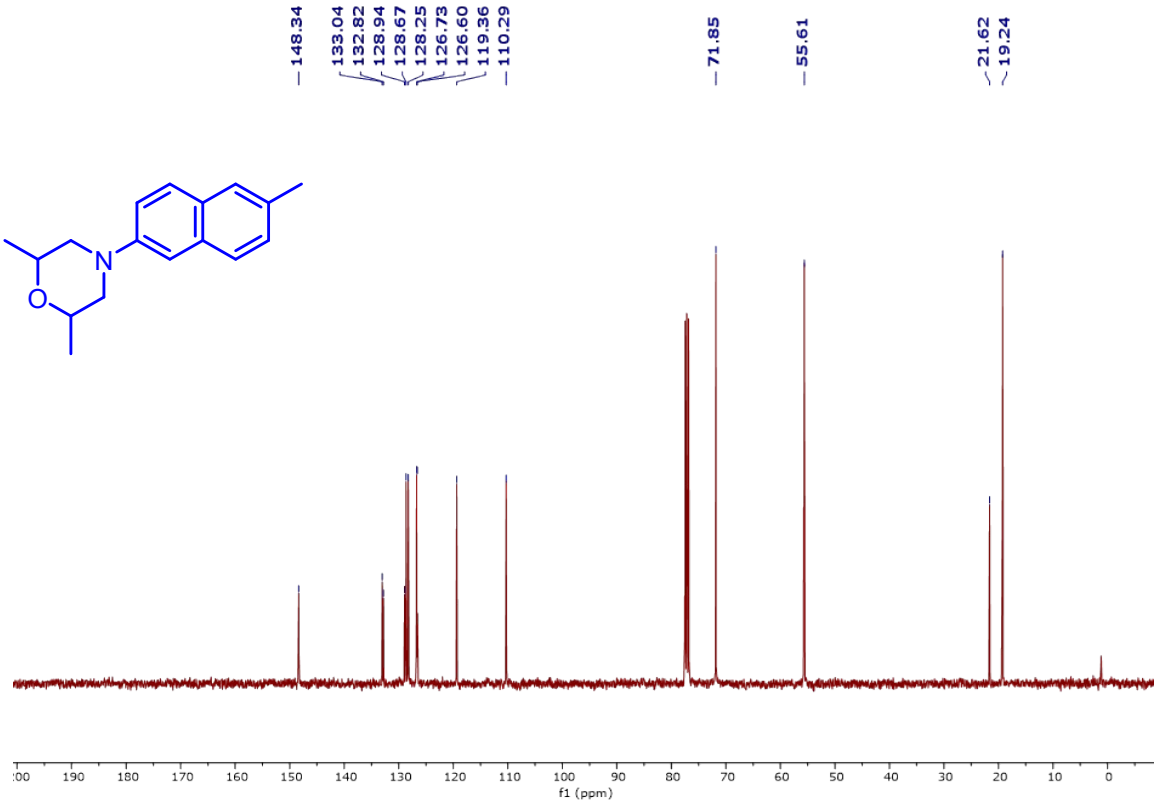
^{13}C{^{1}H} NMR spectrum of 1-cyclohexyl-4-(6-methylnaphthalen-2-yl)piperazine (**14**, 176 MHz, $CDCl_3$):



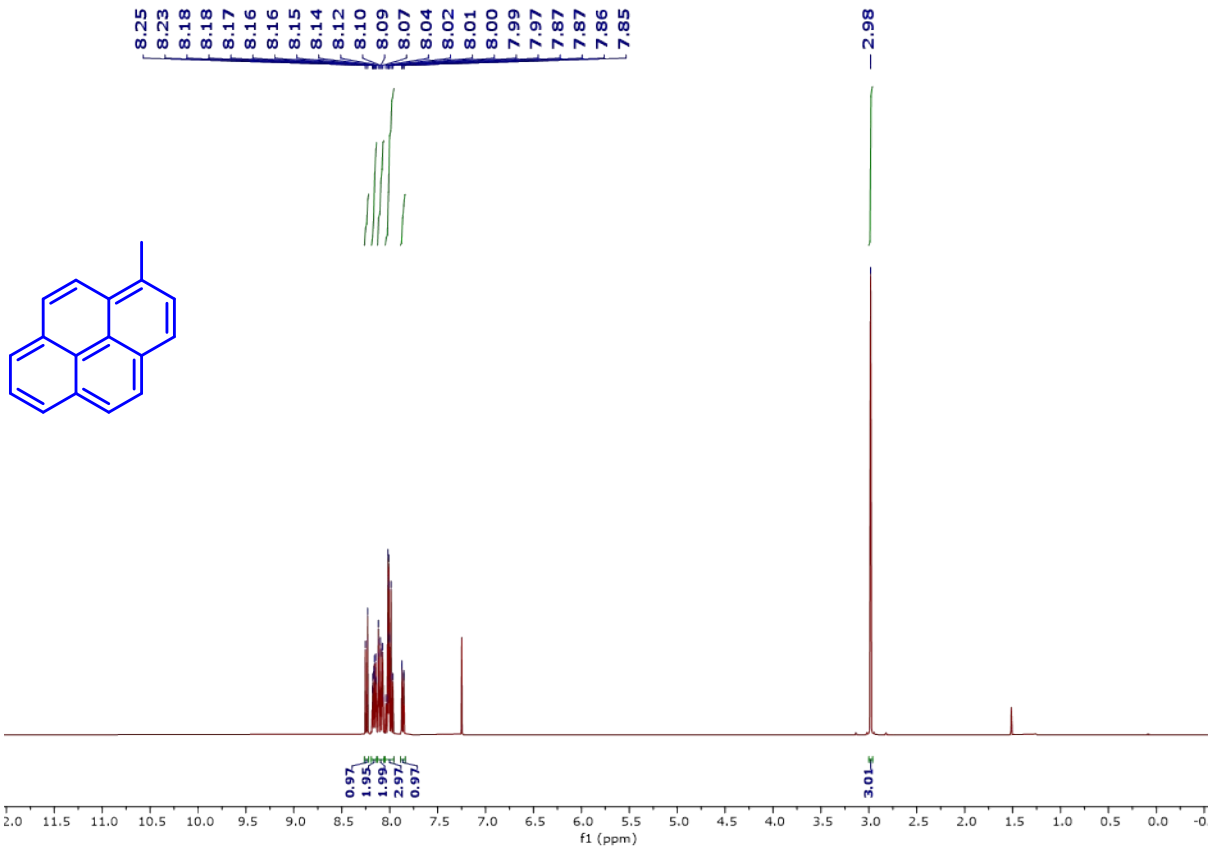
^{1}H NMR spectrum of 2,6-dimethyl-4-(6-methylnaphthalen-2-yl)morpholine (**15**, 400 MHz, $CDCl_3$):



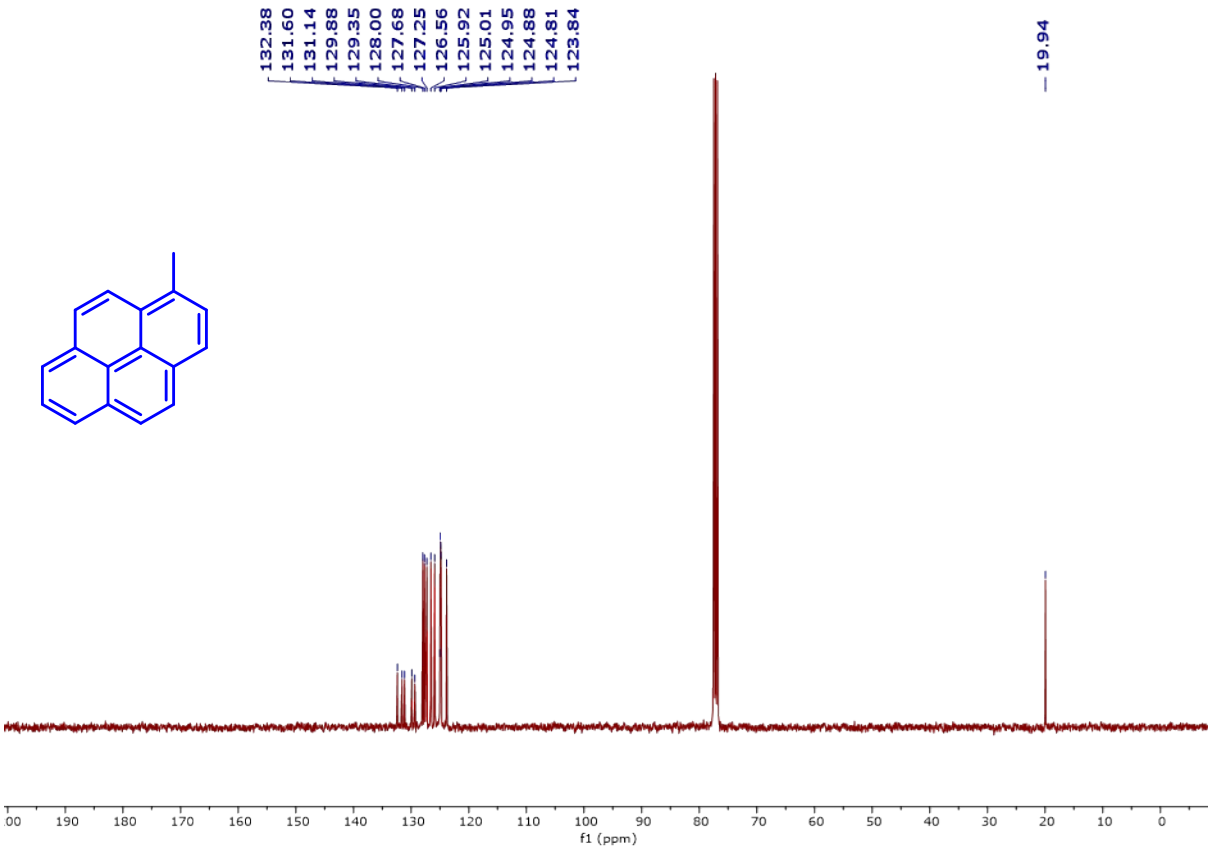
^{13}C{^{1}H} NMR spectrum of 2,6-dimethyl-4-(6-methylnaphthalen-2-yl)morpholine (**15**, 101 MHz, $CDCl_3$):



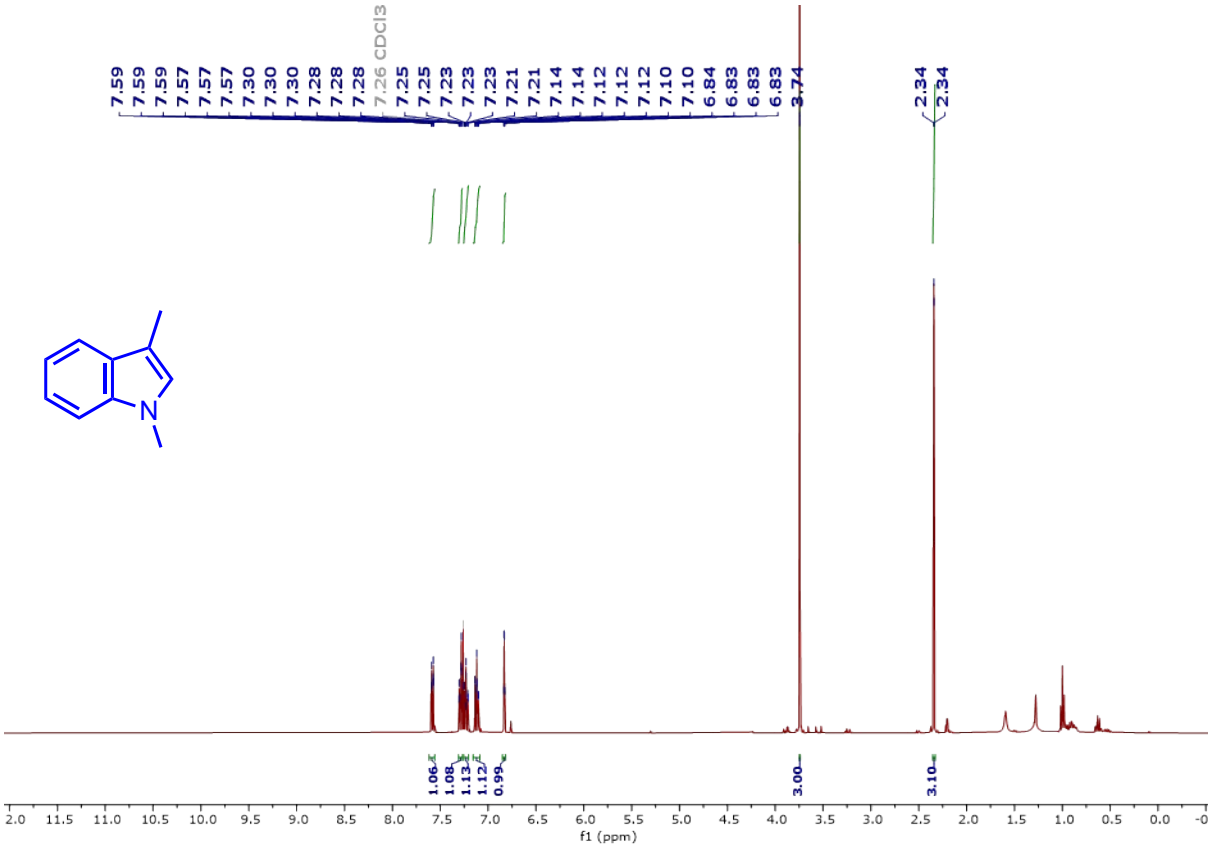
^{1}H NMR spectrum of 1-methylpyrene (**16**, 400 MHz, $CDCl_3$):



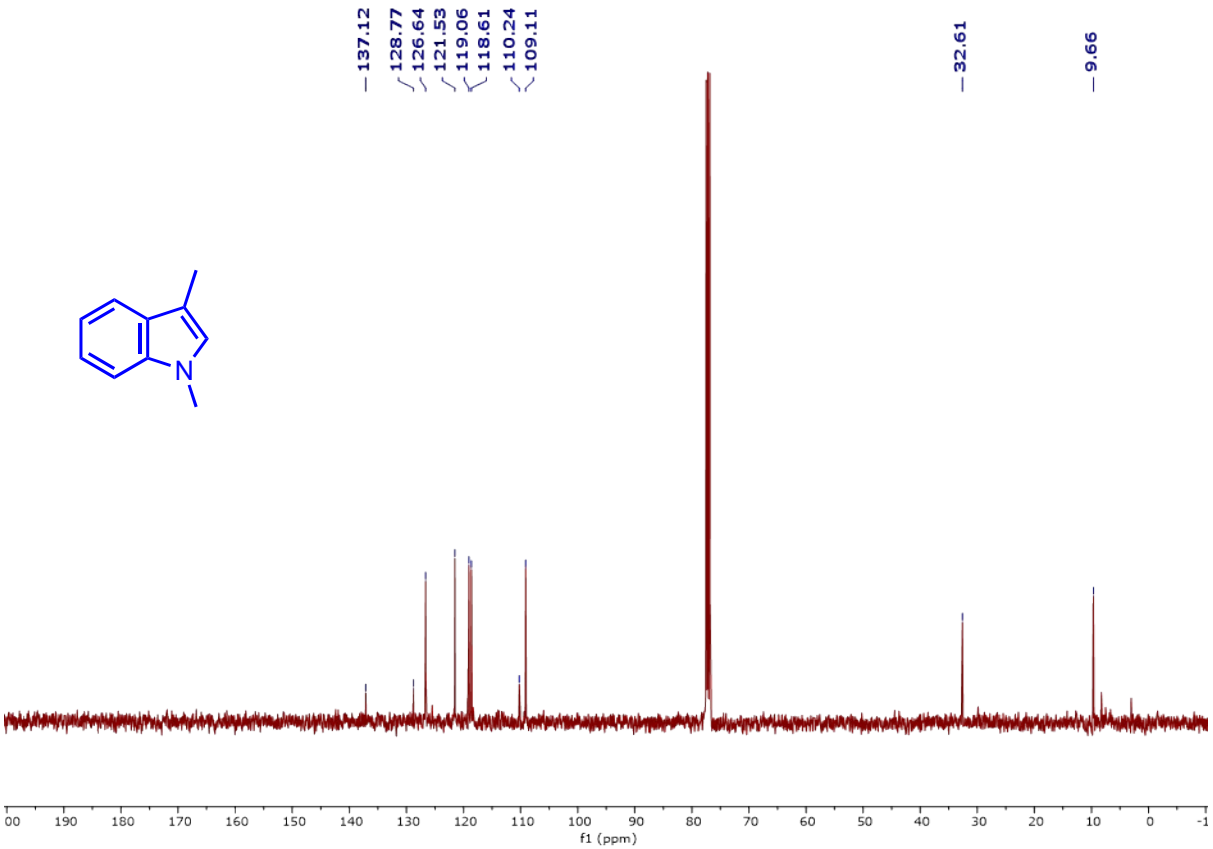
^{13}C{^{1}H} NMR spectrum of 1-methylpyrene (**16**, 101 MHz, $CDCl_3$):



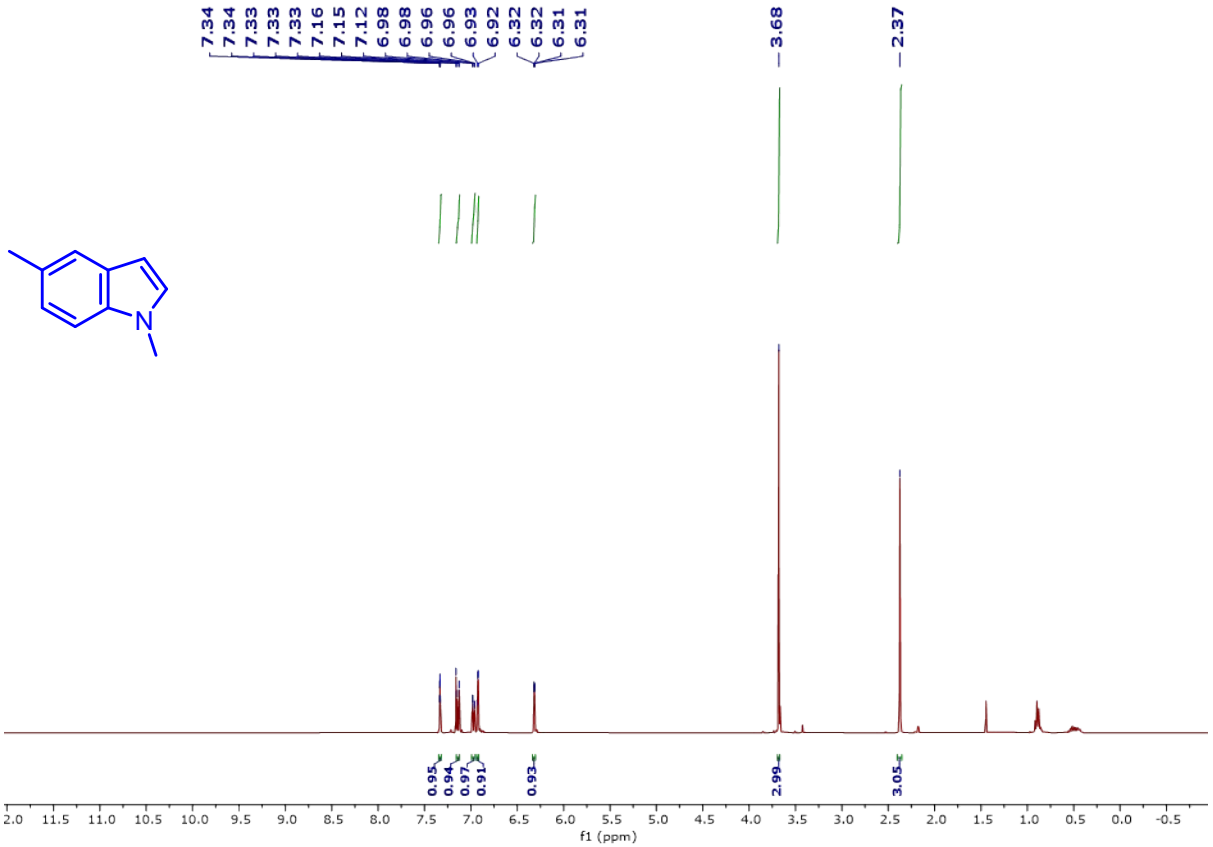
^{1}H NMR spectrum of 1,3-dimethyl-1H-indole (**17**, 400 MHz, $CDCl_3$):



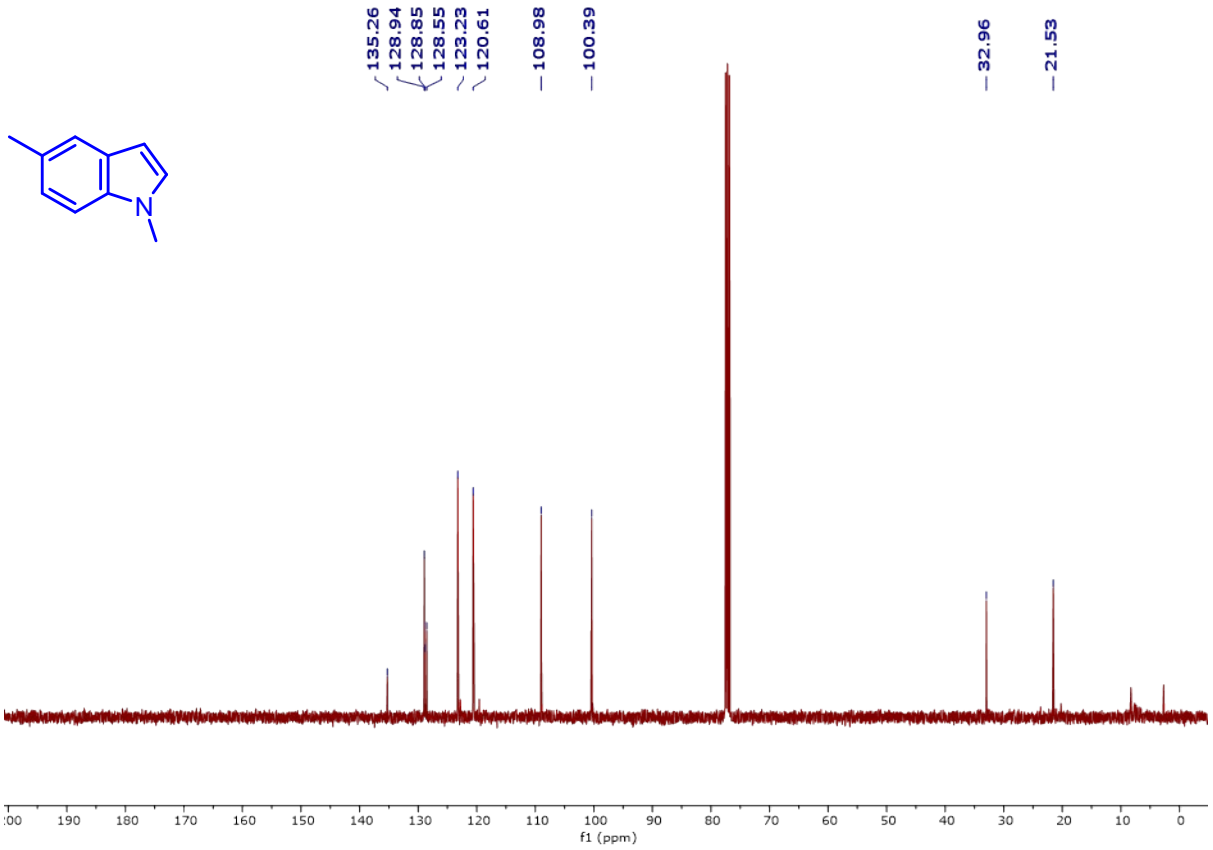
^{13}C{^{1}H} NMR spectrum of 1,3-dimethyl-1*H*-indole (**17**, 101 MHz, $CDCl_3$):



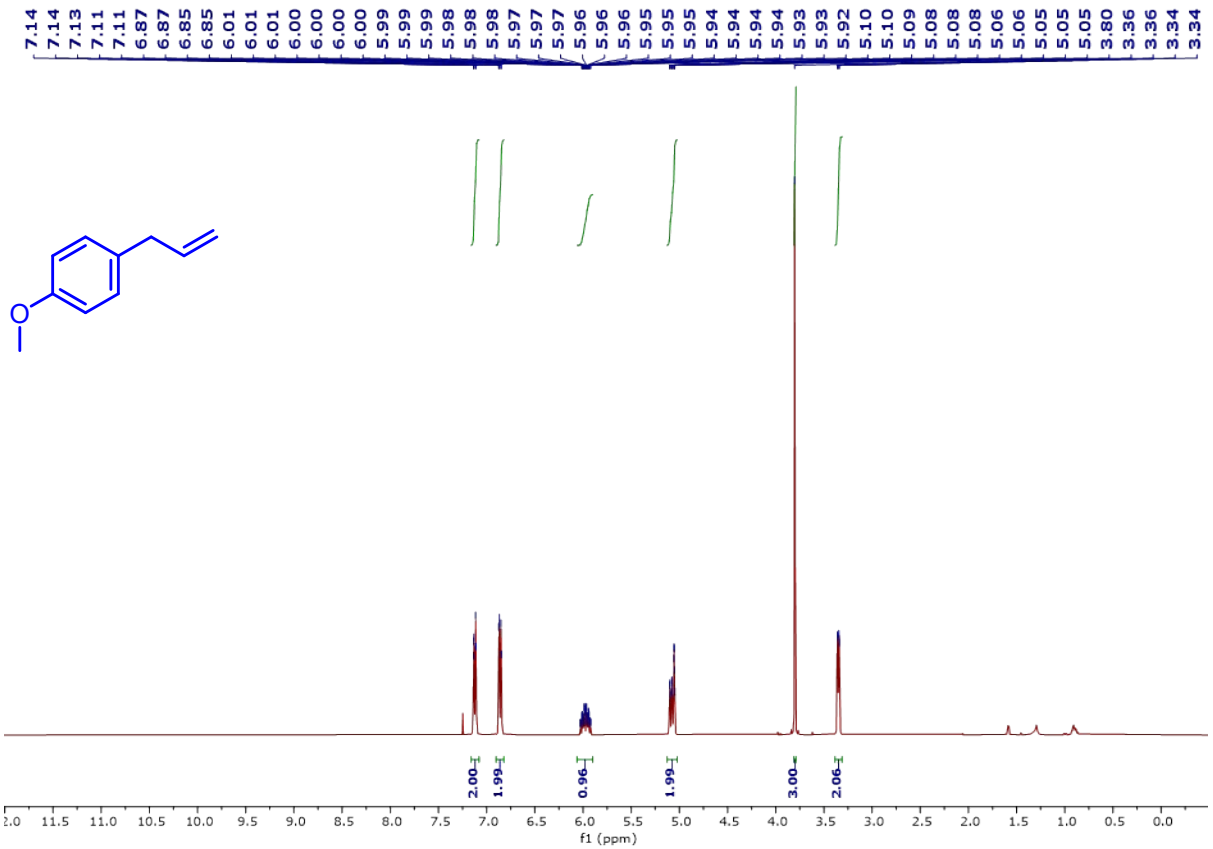
^{1}H NMR spectrum of 1,5-dimethyl-1*H*-indole (**18)**, 400 MHz, $CDCl_3$):



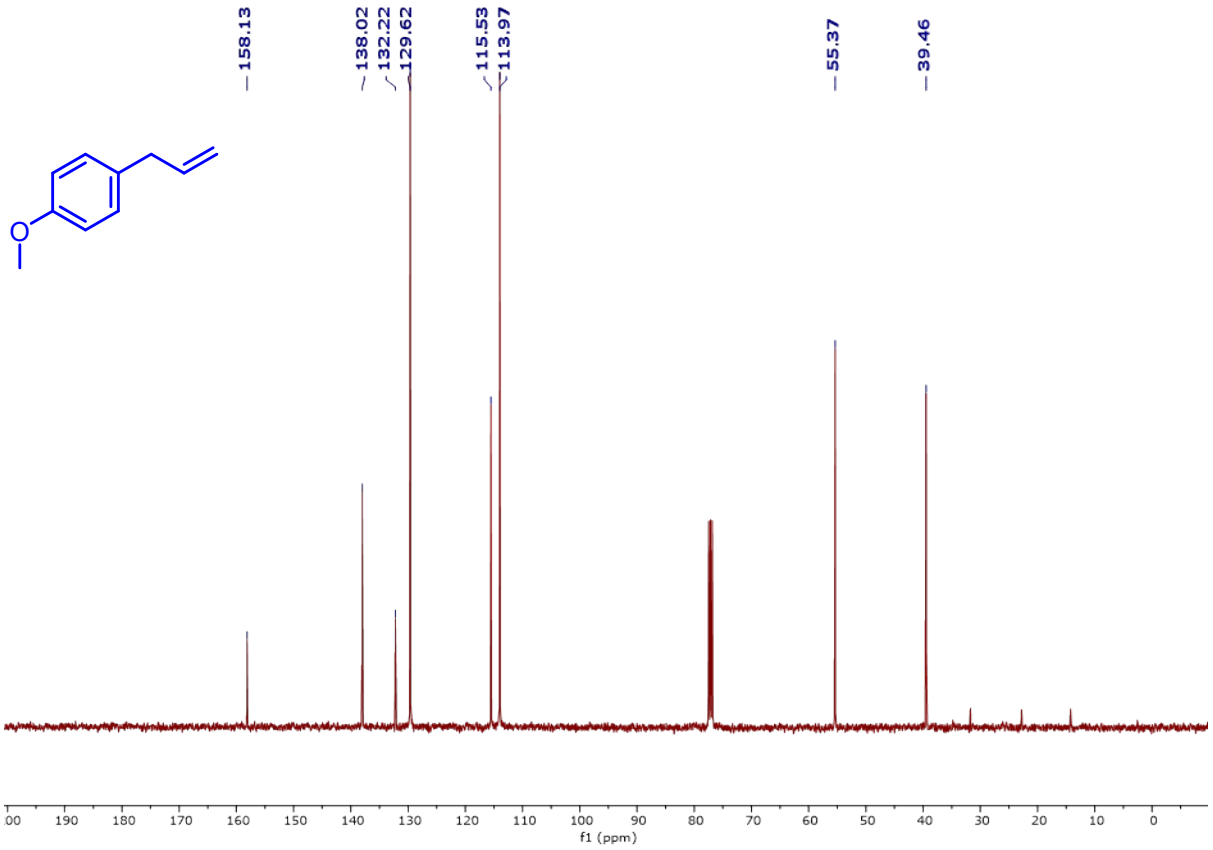
^{13}C{^{1}H} NMR spectrum of 1,5-dimethyl-1*H*-indole (**18**, 101 MHz, $CDCl_3$):



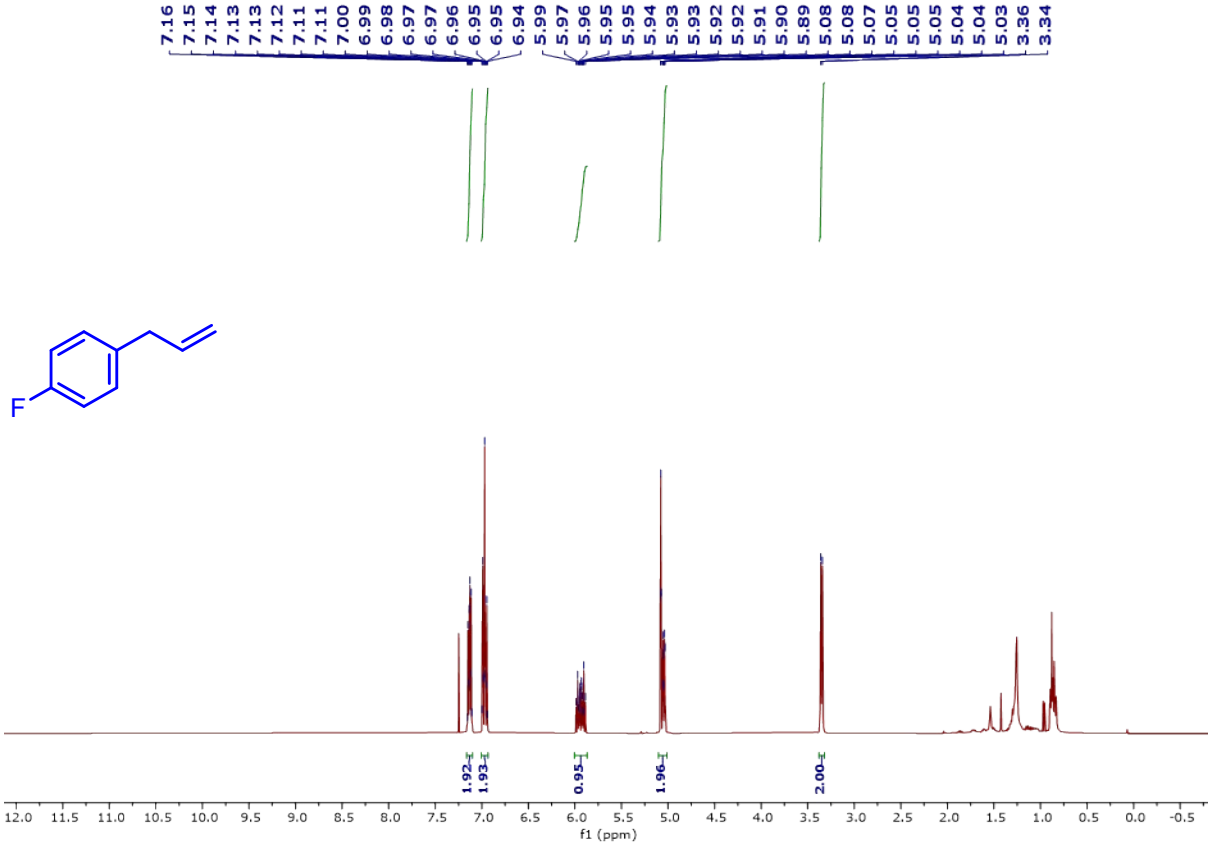
^{1}H NMR spectrum of 1-allyl-4-methoxybenzene (**19**, 400 MHz, $CDCl_3$):



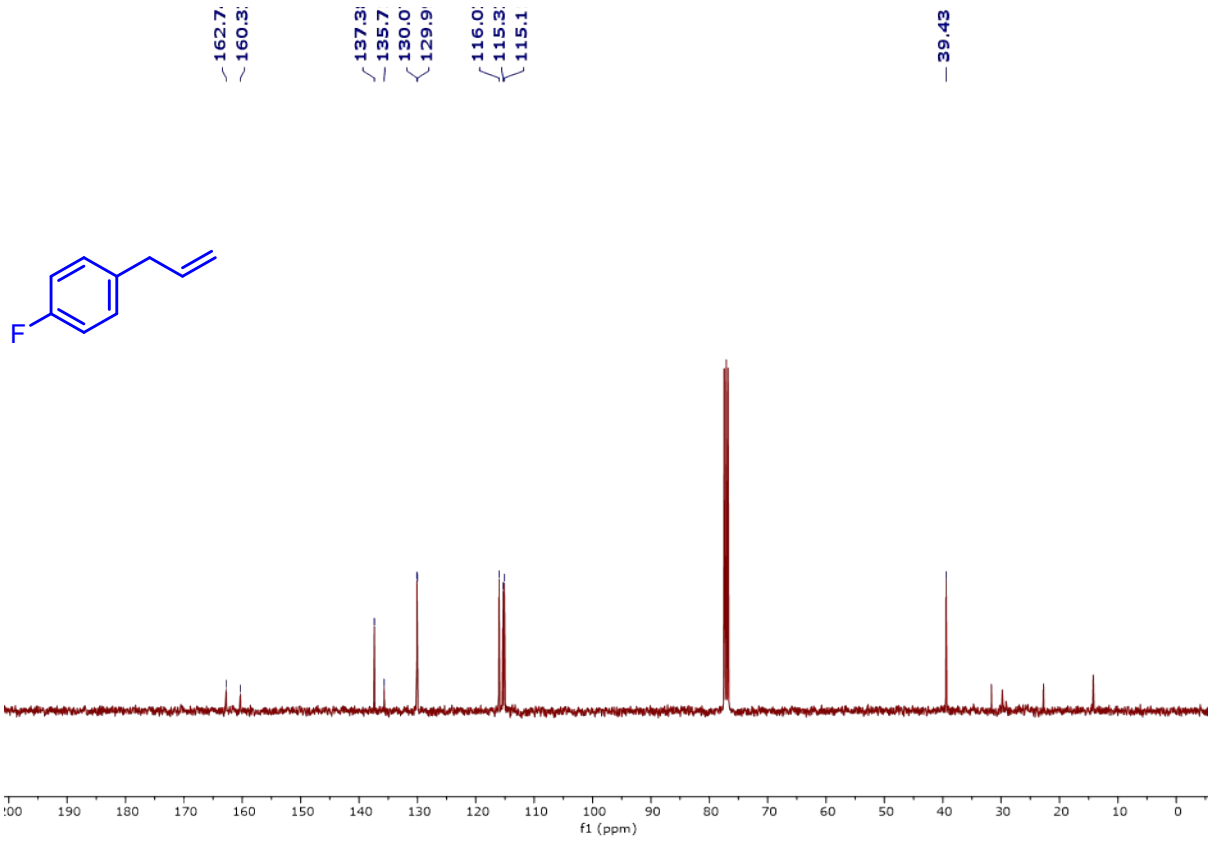
^{13}C{^{1}H} NMR spectrum of 1-allyl-4-methoxybenzene (**19**, 101 MHz, $CDCl_3$):



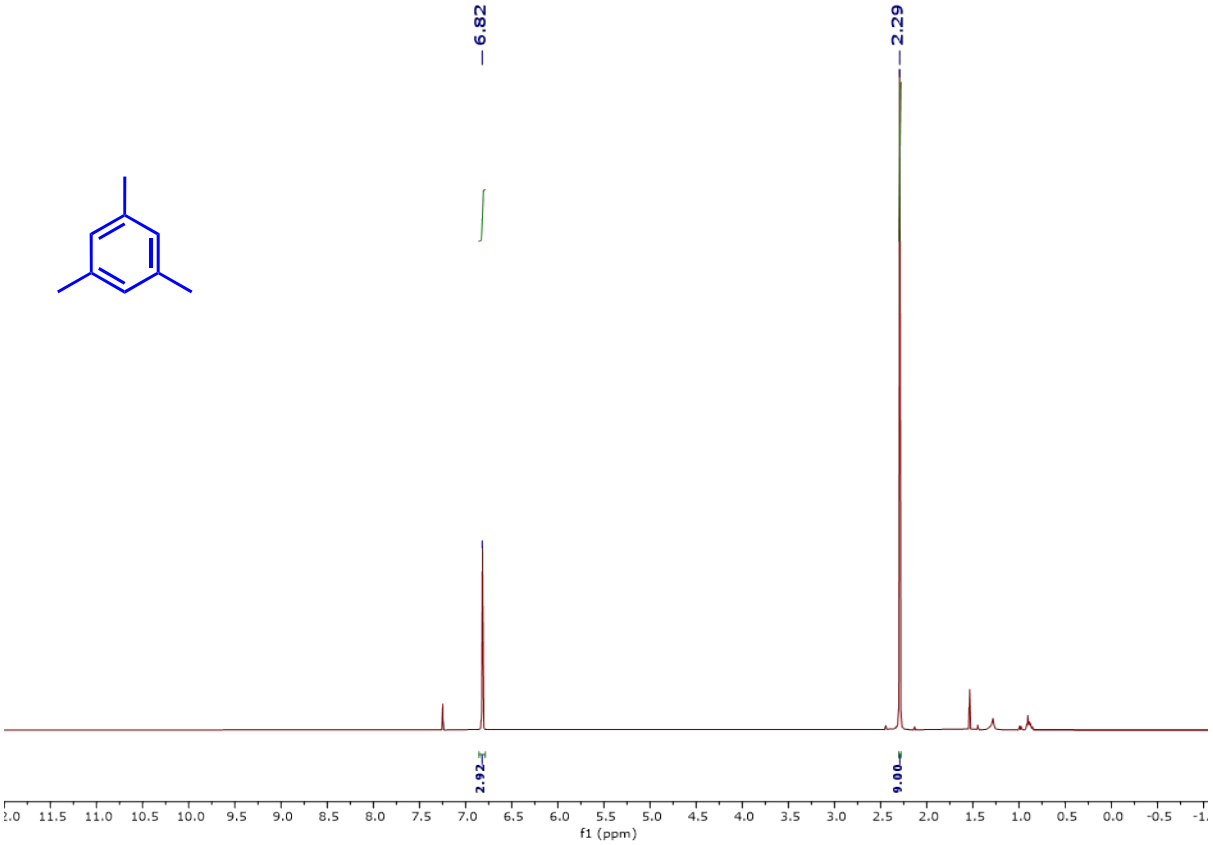
^{1}H NMR spectrum of 1-allyl-4-fluorobenzene (**20**, 400 MHz, $CDCl_3$):



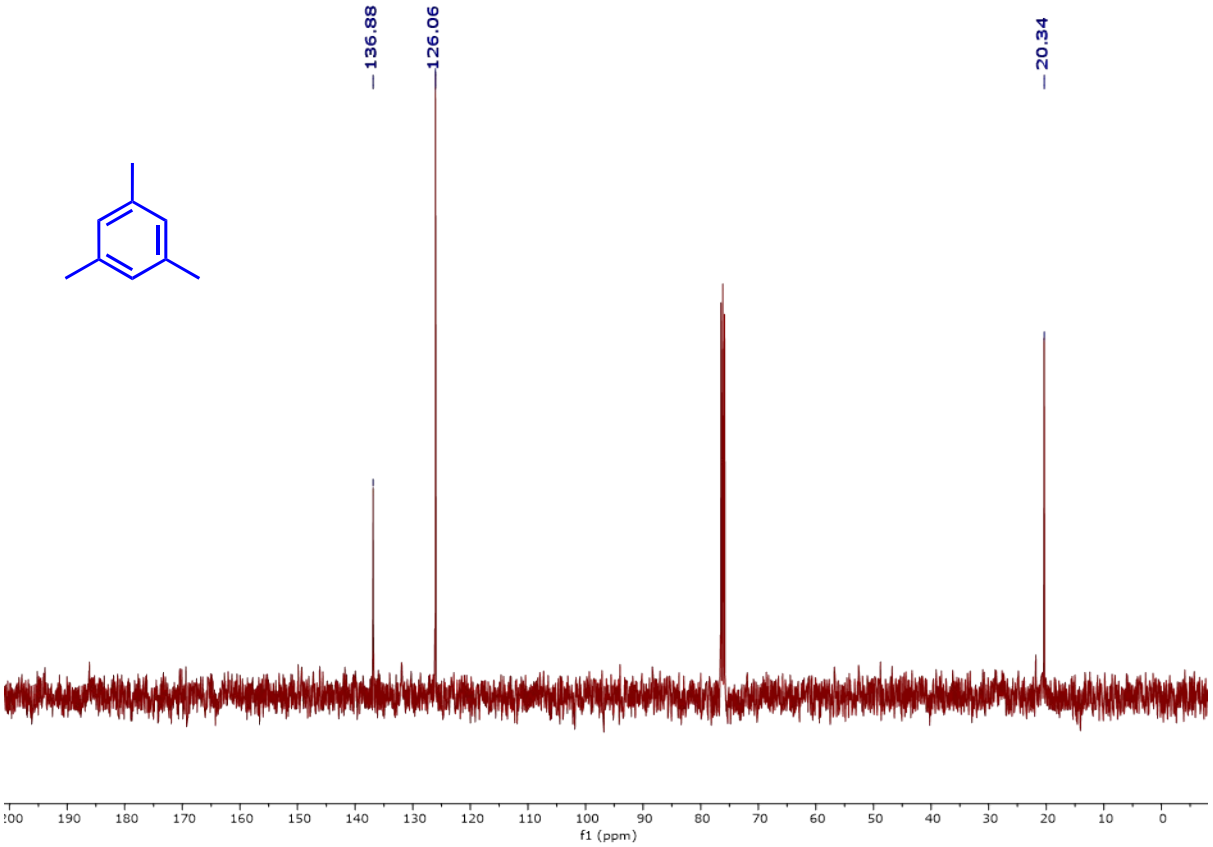
^{13}C{^{1}H} NMR spectrum of 1-allyl-4-fluorobenzene (**20**, 101 MHz, $CDCl_3$):



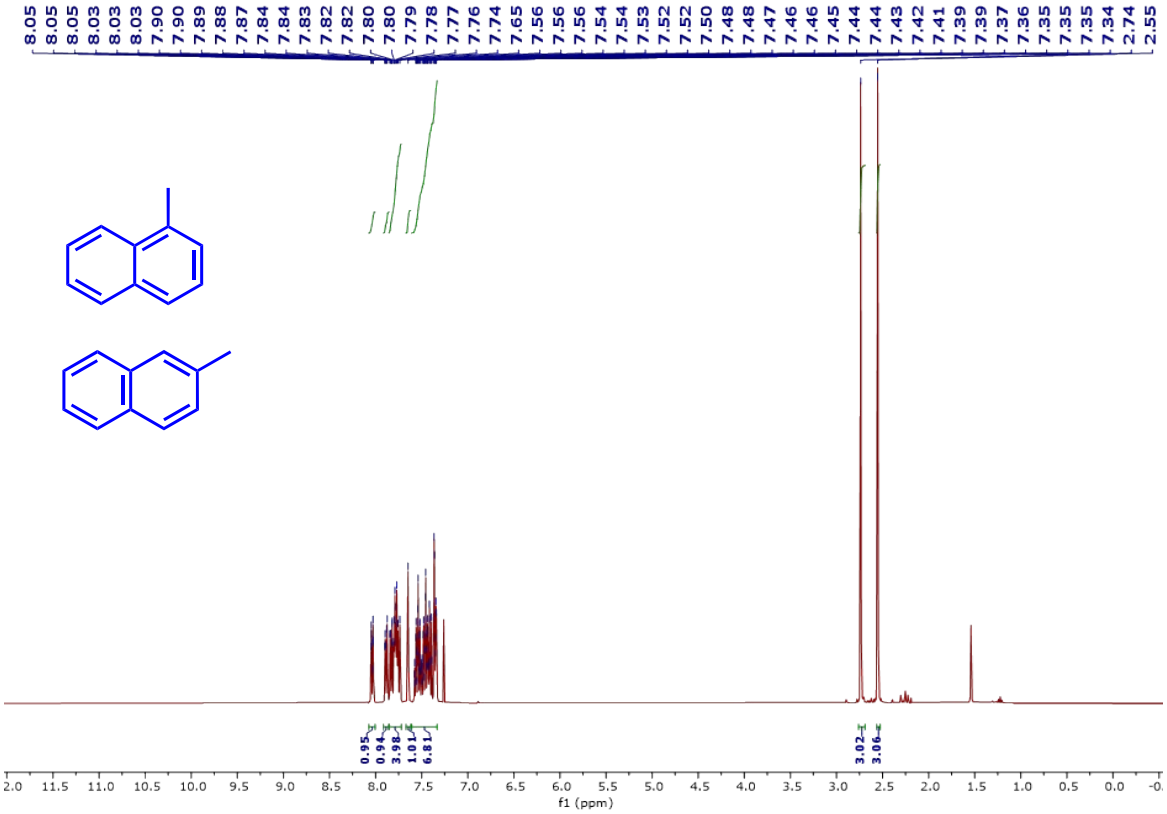
^{1}H NMR spectrum of mesitylene (**21**, 400 MHz, $CDCl_3$):



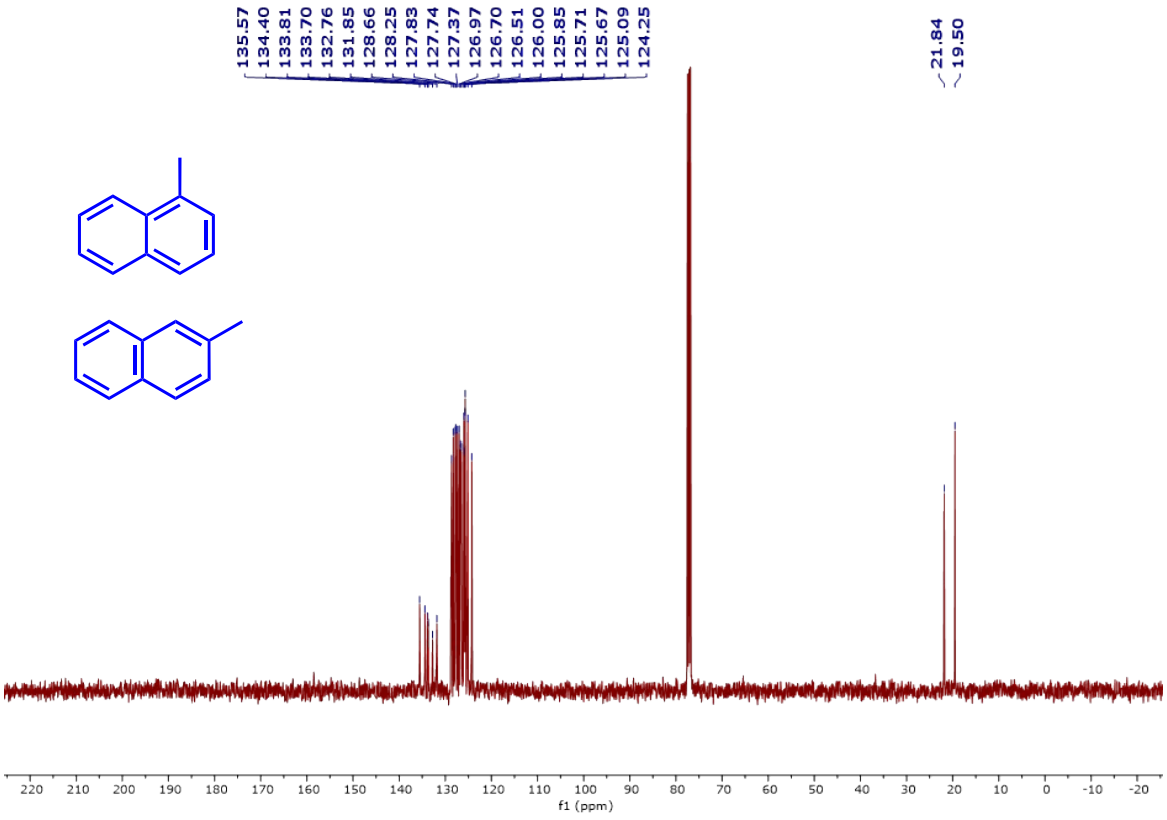
^{13}C{^{1}H} NMR spectrum of mesitylene (**21**, 101 MHz, $CDCl_3$):



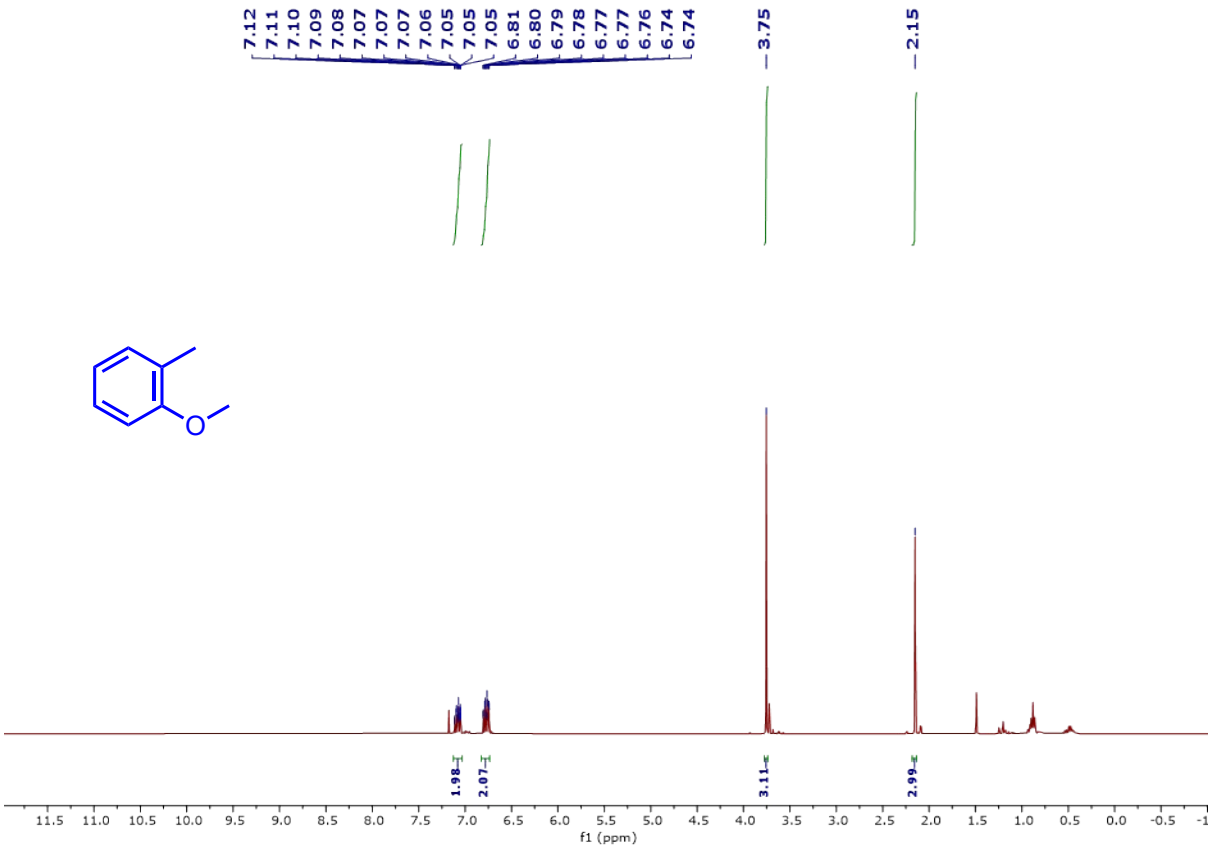
^{1}H NMR spectrum of 1-methylnaphthalene and 2-methylnaphthalene (**9** and **10**, 400 MHz, $CDCl_3$):



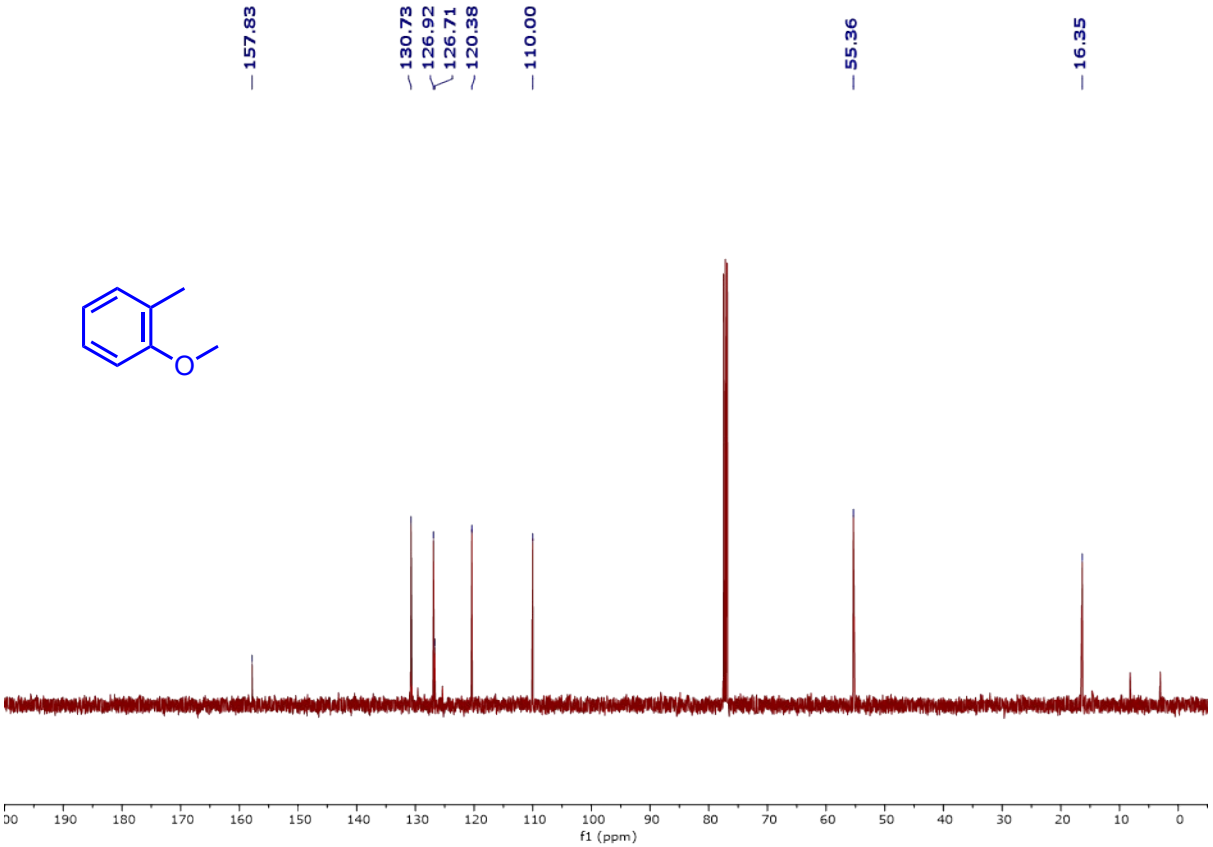
^{13}C{^{1}H} NMR spectrum of 1-methylnaphthalene and 2-methylnaphthalene (**9** and **10**, 101 MHz, $CDCl_3$):



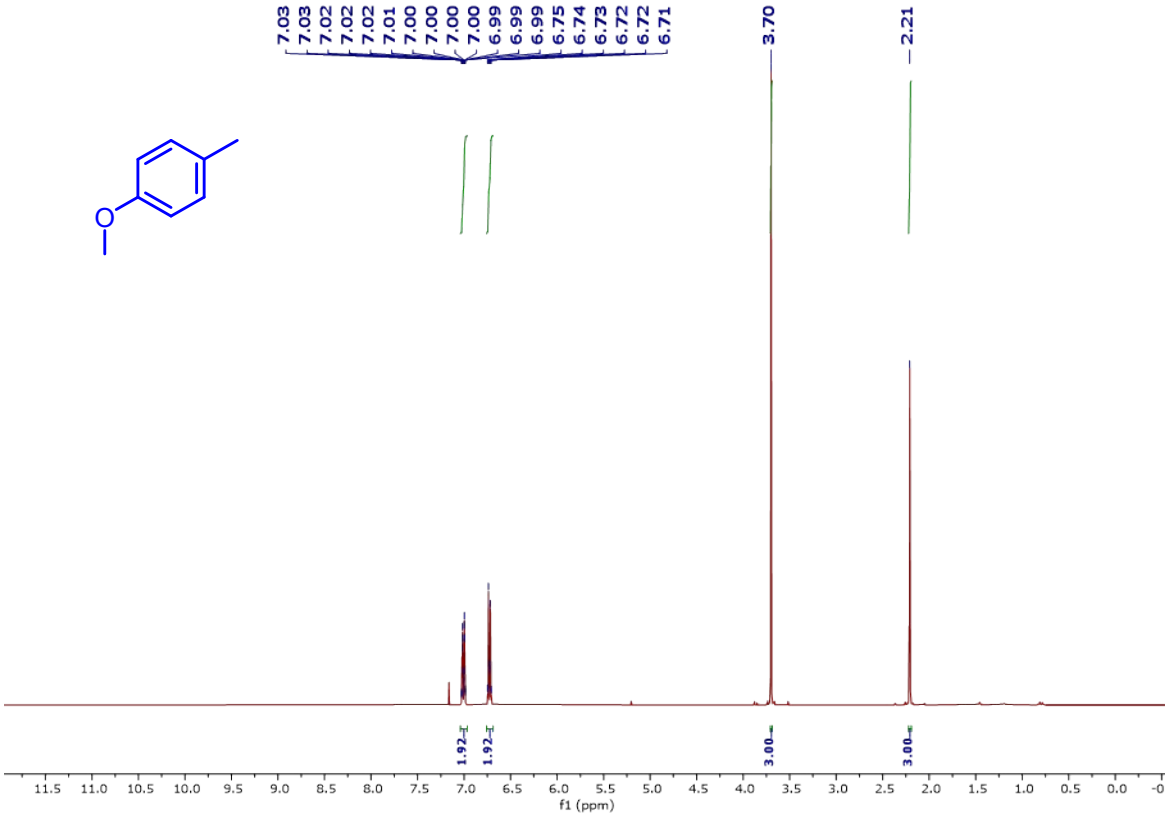
^{1}H NMR spectrum of 1-methoxy-2-methylbenzene (**22**, 400 MHz, $CDCl_3$):



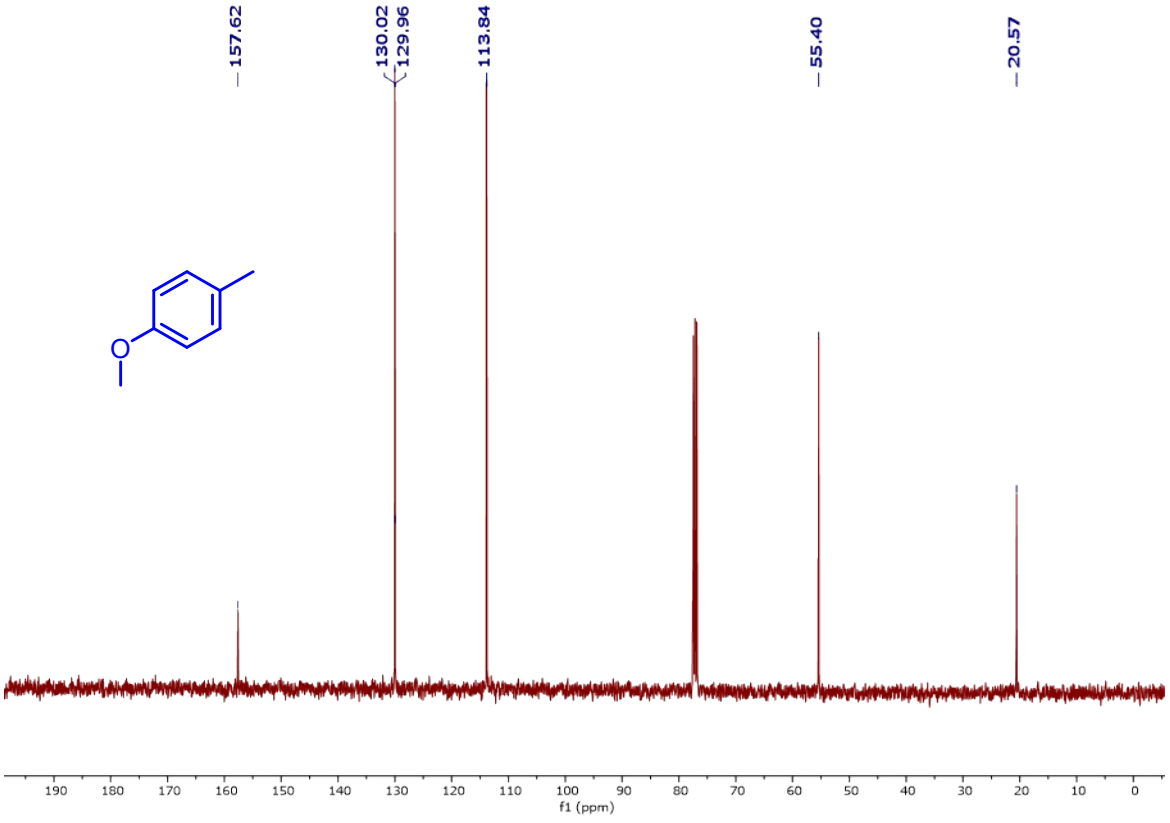
^{13}C{^{1}H} NMR spectrum of 1-methoxy-2-methylbenzene (**22**, 101 MHz, $CDCl_3$):



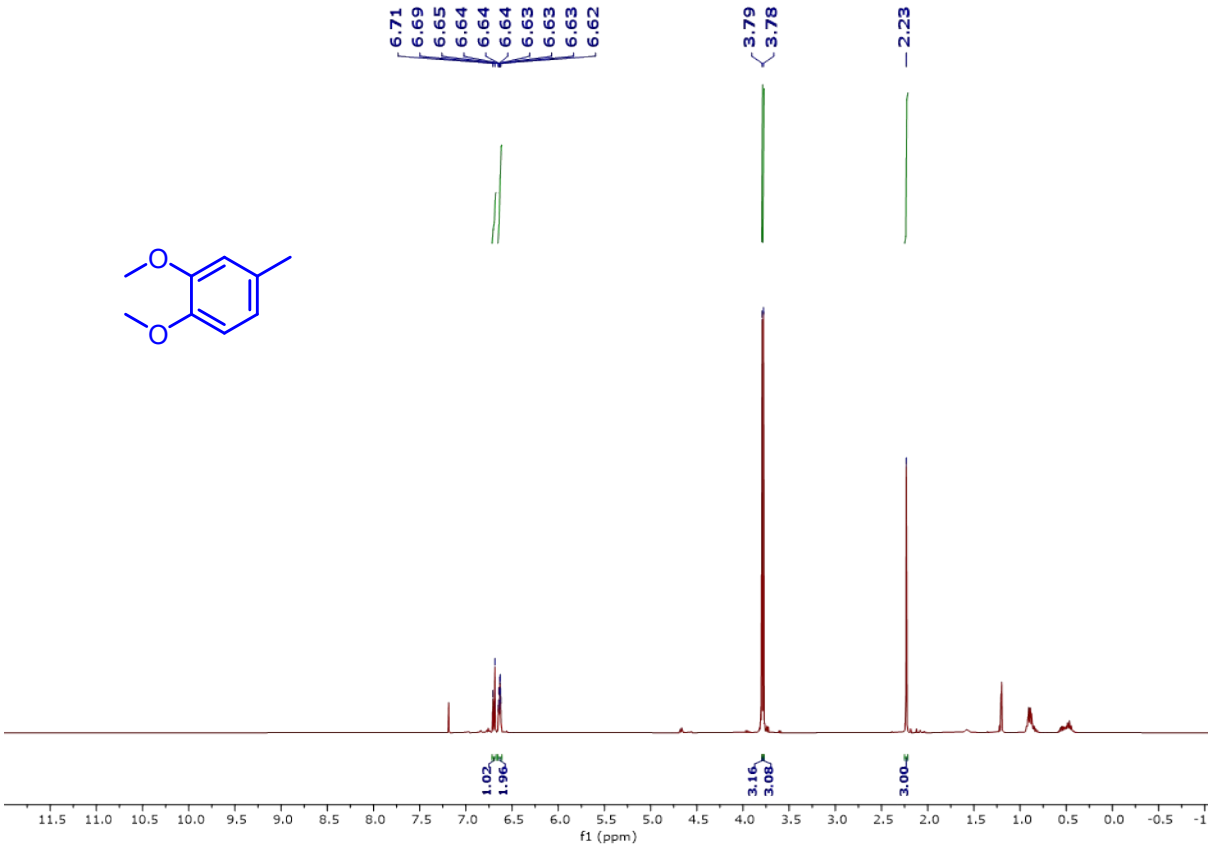
^{1}H NMR spectrum of 1-methoxy-4-methylbenzene (**23**, 400 MHz, $CDCl_3$):



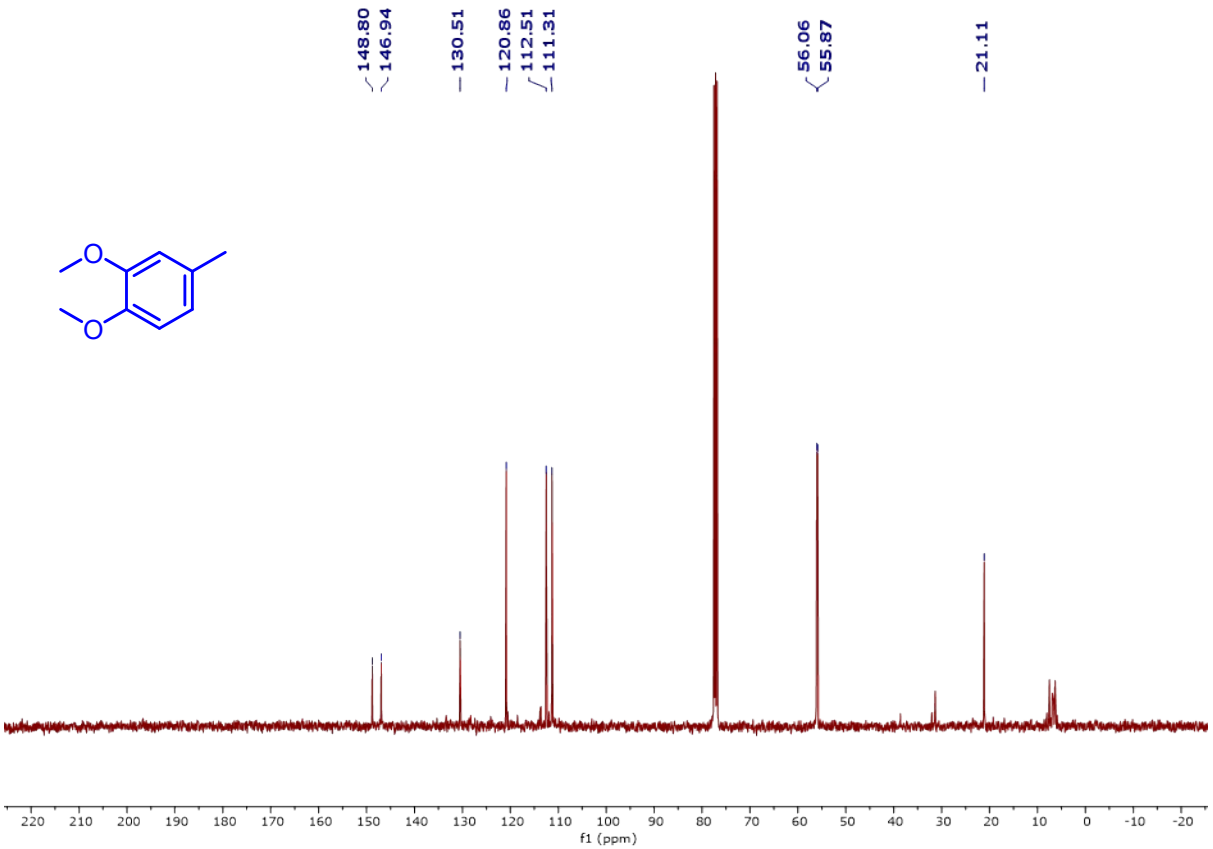
^{13}C{^{1}H} NMR spectrum of 1-methoxy-4-methylbenzene (**23**, 101 MHz, $CDCl_3$):



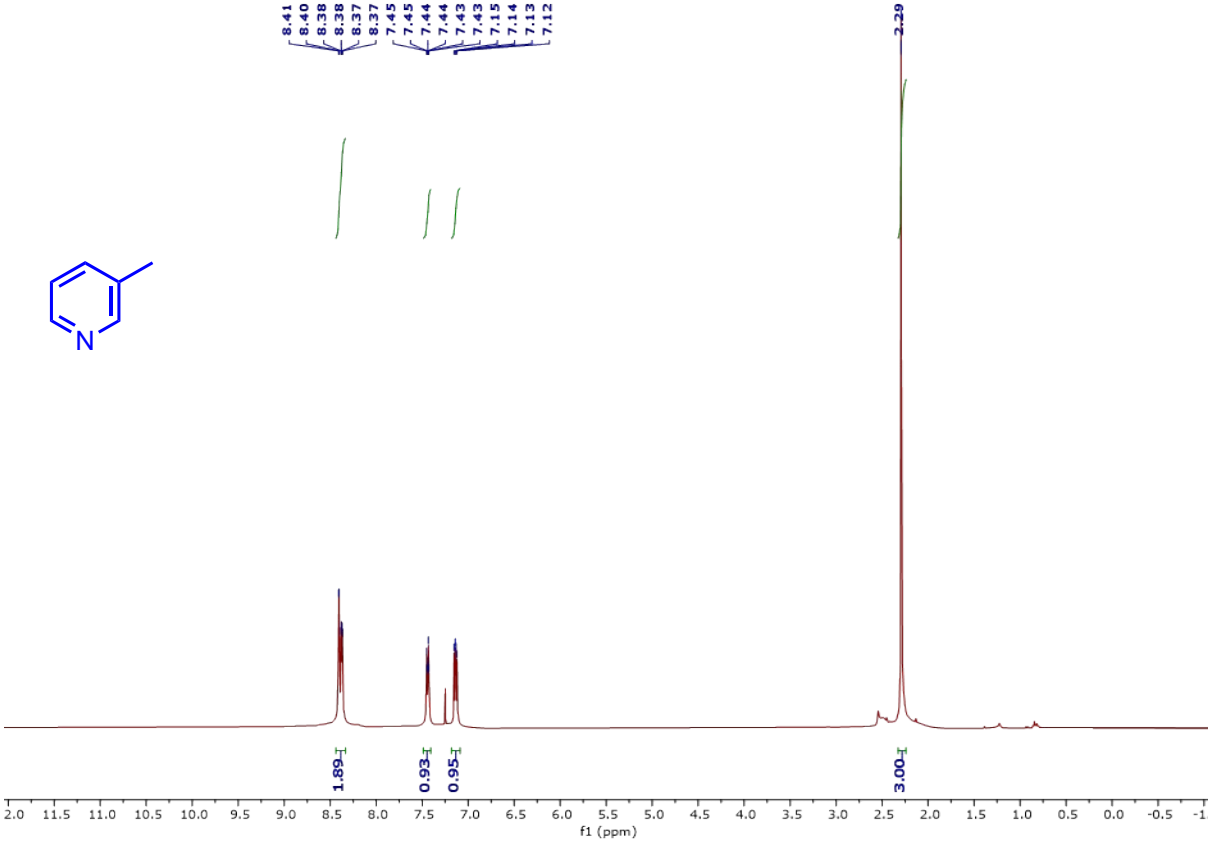
^{1}H NMR spectrum of 1,2-dimethoxy-3-methylbenzene (**24**, 400 MHz, $CDCl_3$):



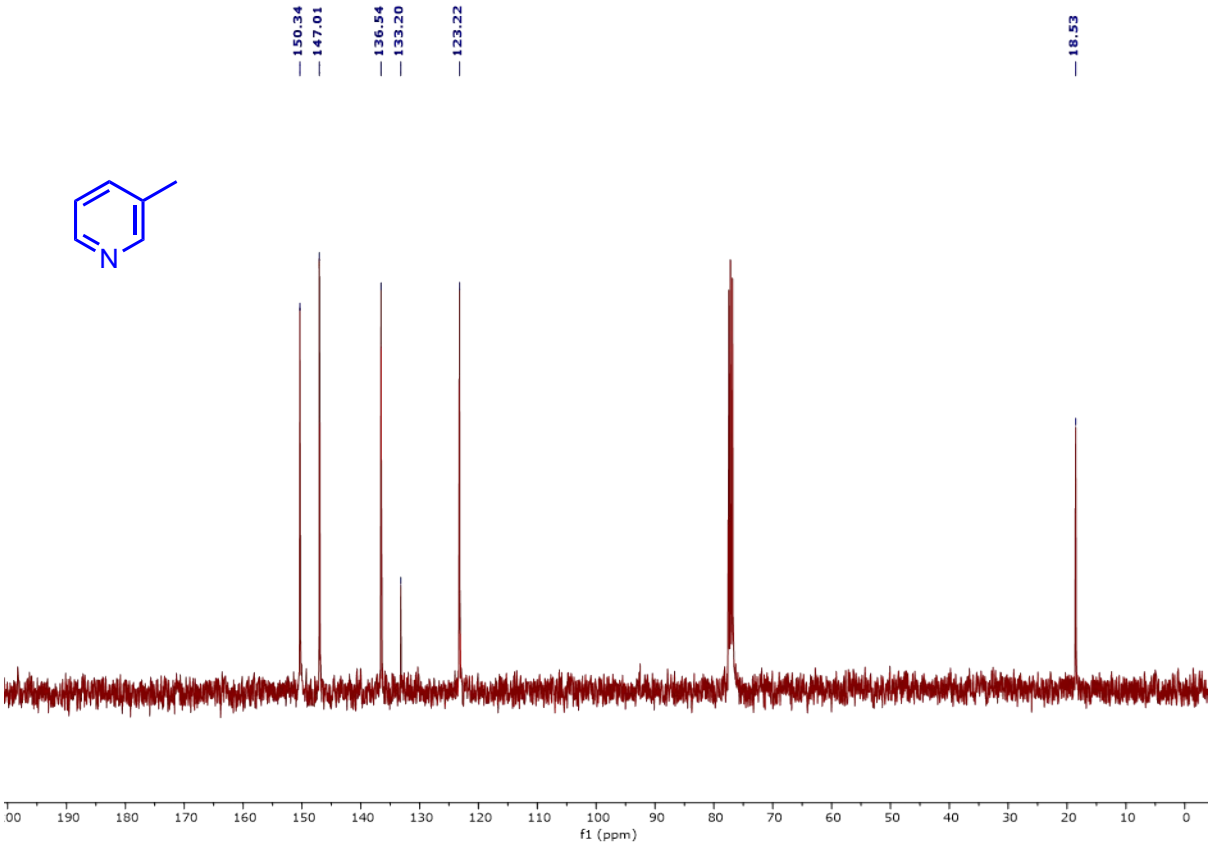
^{13}C{^{1}H} NMR spectrum of 1,2-dimethoxy-3-methylbenzene (**24**, 101 MHz, $CDCl_3$):



^{1}H NMR spectrum of 3-methylpyridine (**25**, 400 MHz, $CDCl_3$):

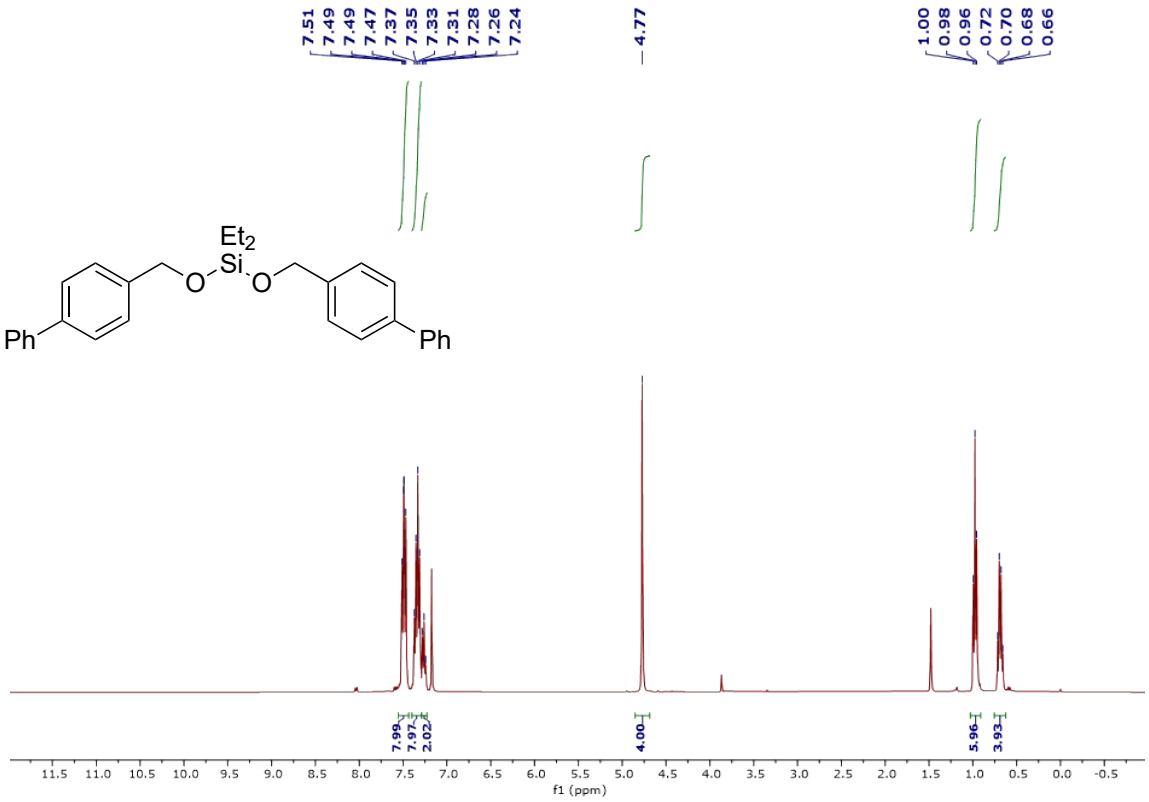


^{13}C{^{1}H} NMR spectrum of 3-methylpyridine (**25**, 101 MHz, $CDCl_3$):

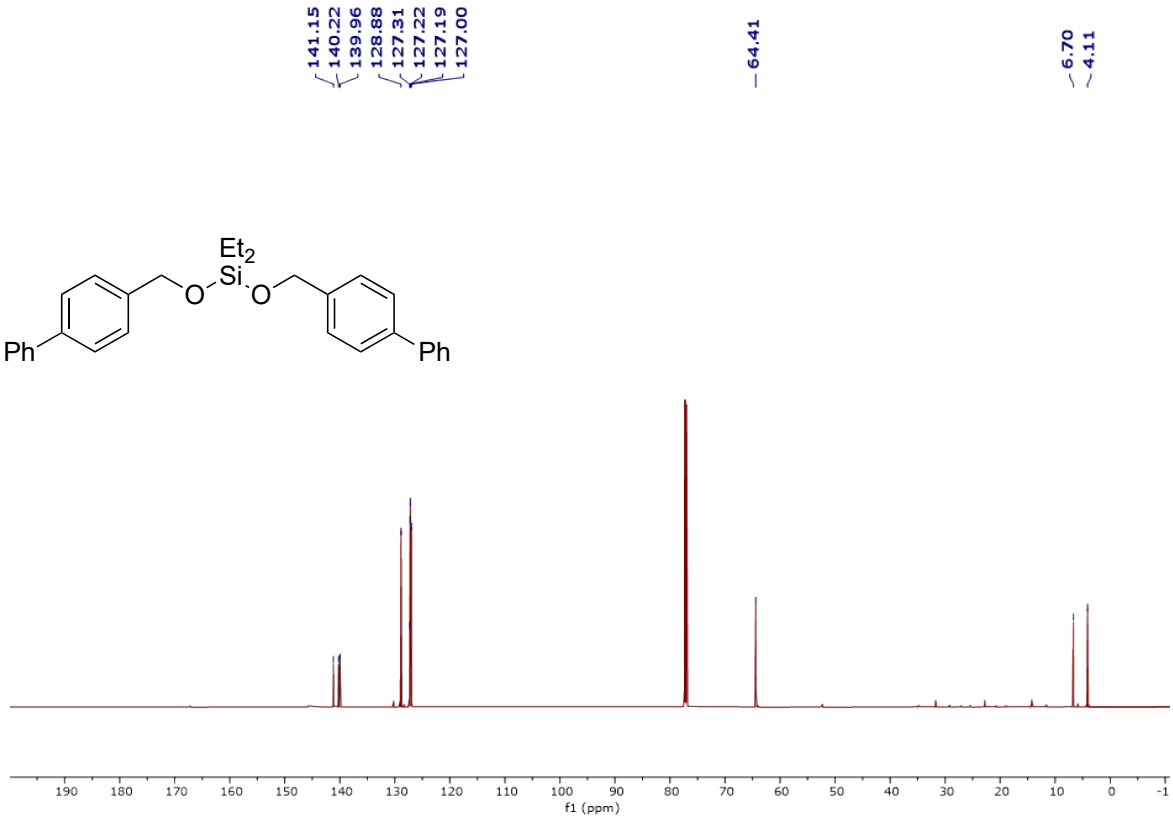


NMR spectra of silyl ether intermediates

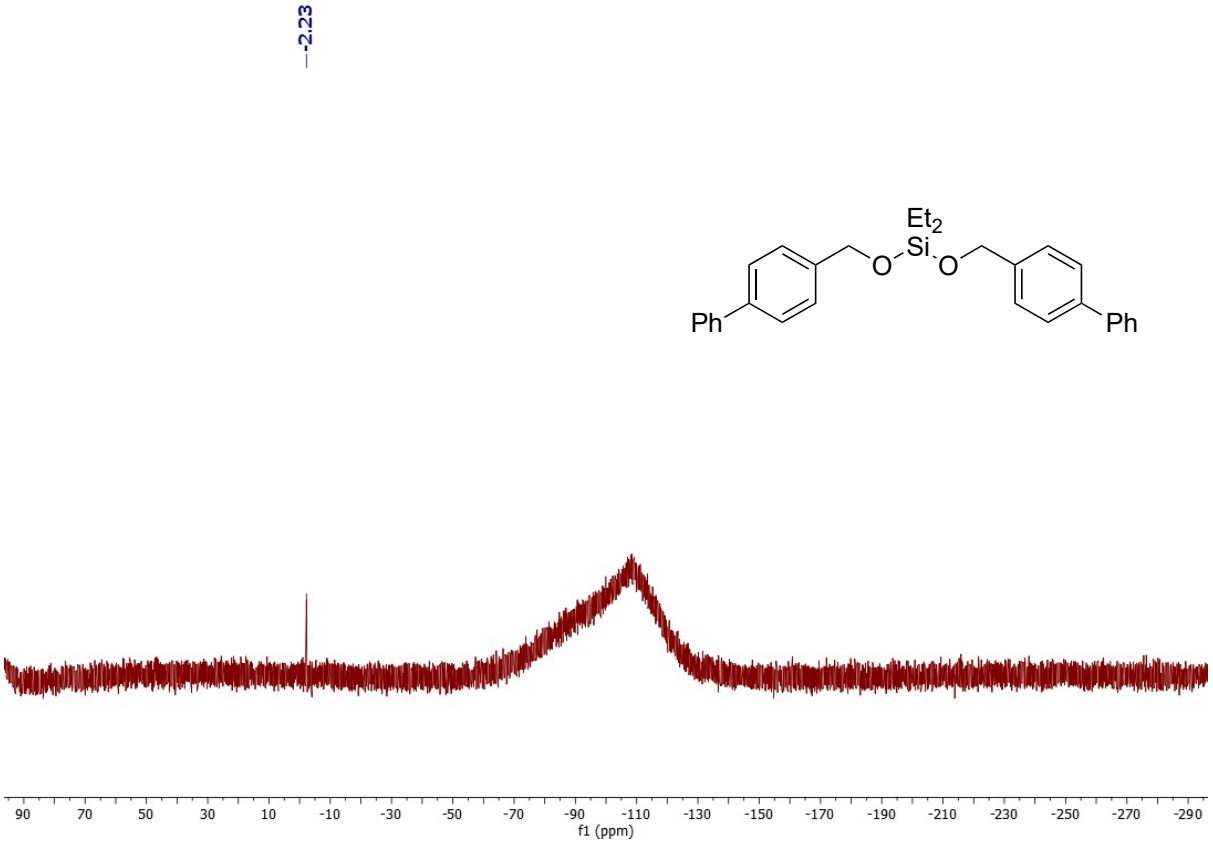
^{1}H NMR spectrum of bis([1,1'-biphenyl]-4-ylmethoxy) diethylsilane (**27**, 400 MHz, $CDCl_3$):



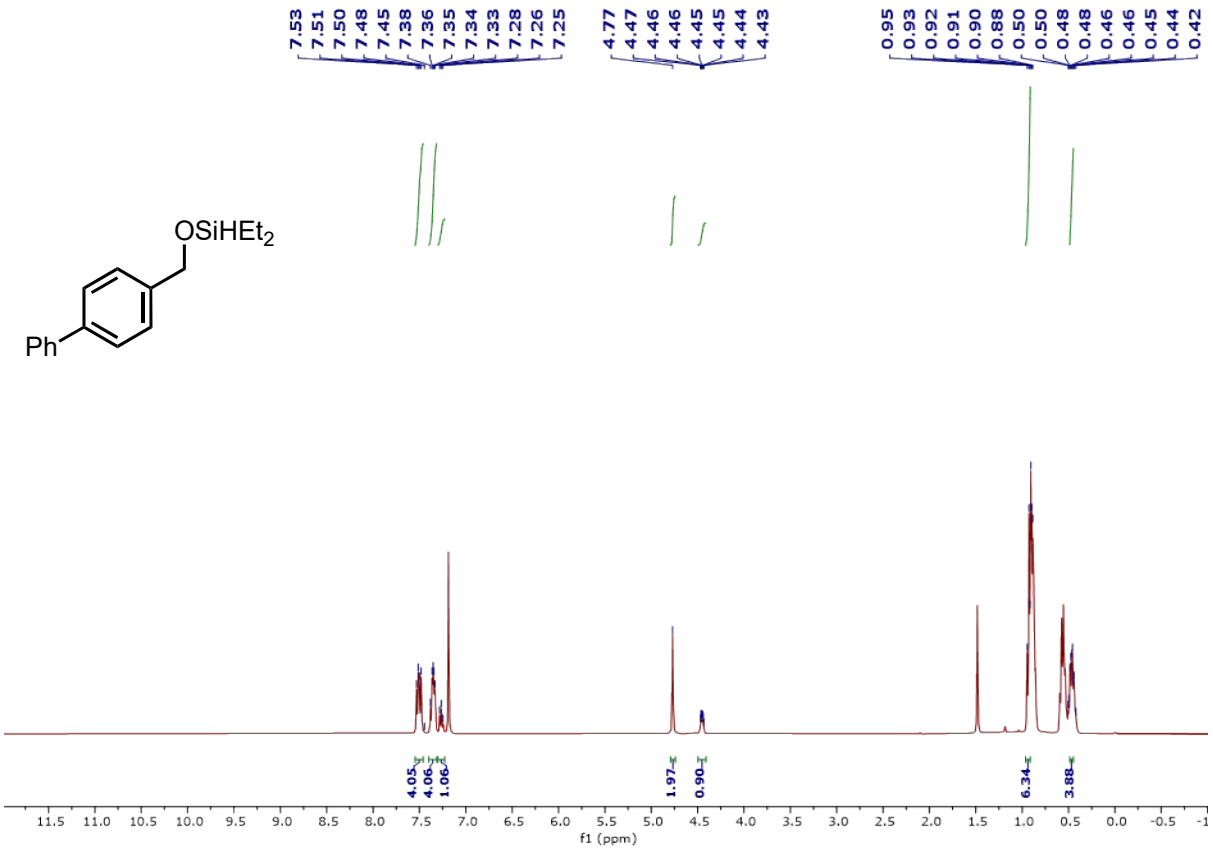
^{13}C{^{1}H} NMR spectrum of bis([1,1'-biphenyl]-4-ylmethoxy) diethylsilane (**27**, 101 MHz, $CDCl_3$):



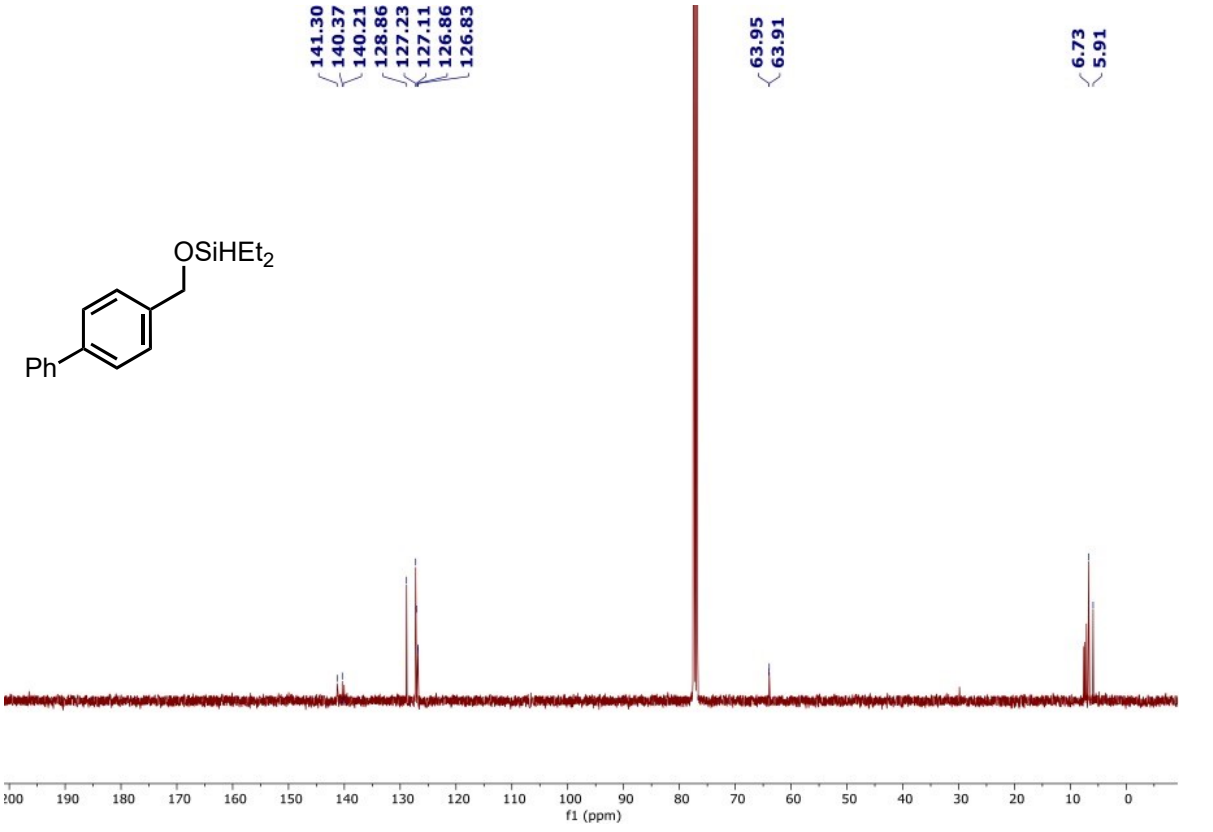
^{29}Si NMR spectrum of bis([1,1'-biphenyl]-4-ylmethoxy) diethylsilane (**27**, 80 MHz, $CDCl_3$):



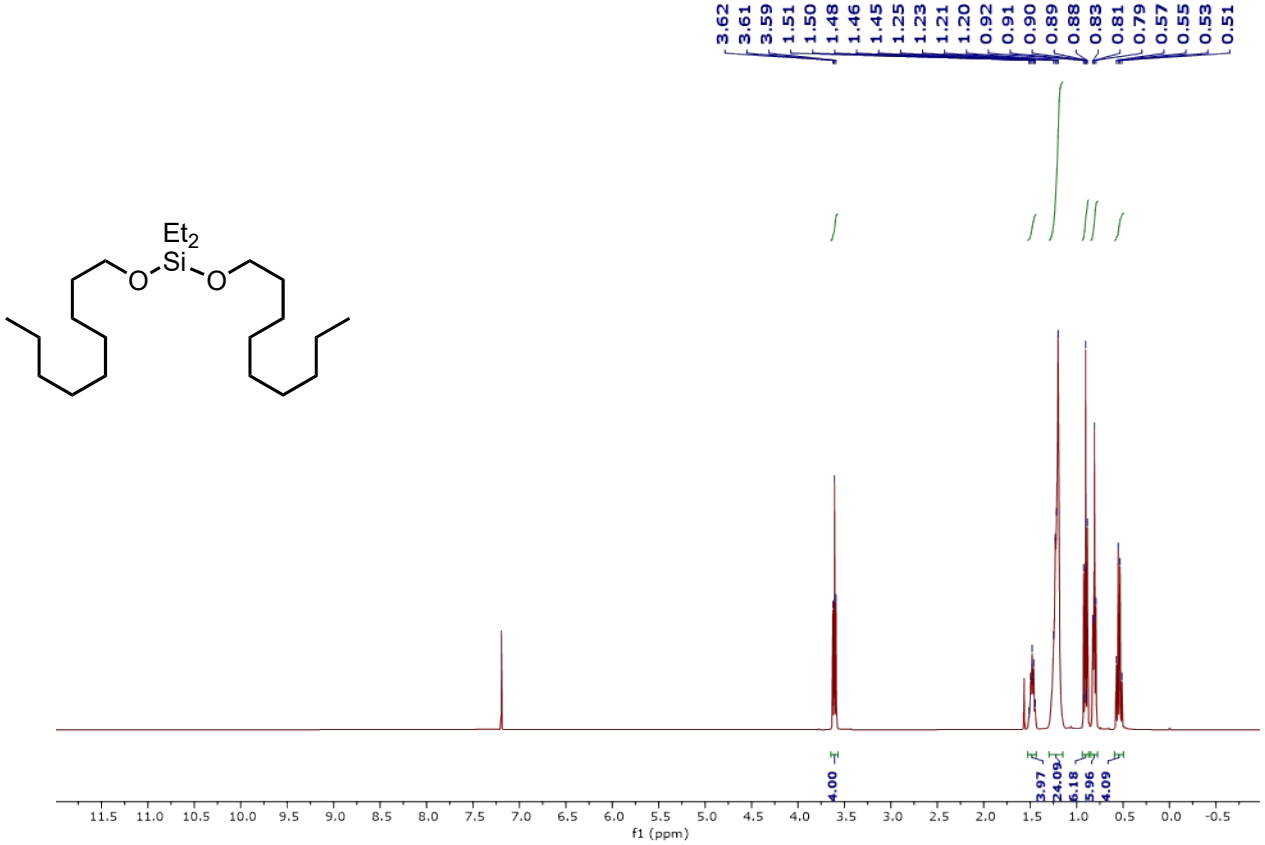
^{1}H NMR spectrum of [1,1'-biphenyl]-4-ylmethoxy)diethylsilane (**27'**, 400 MHz, $CDCl_3$):



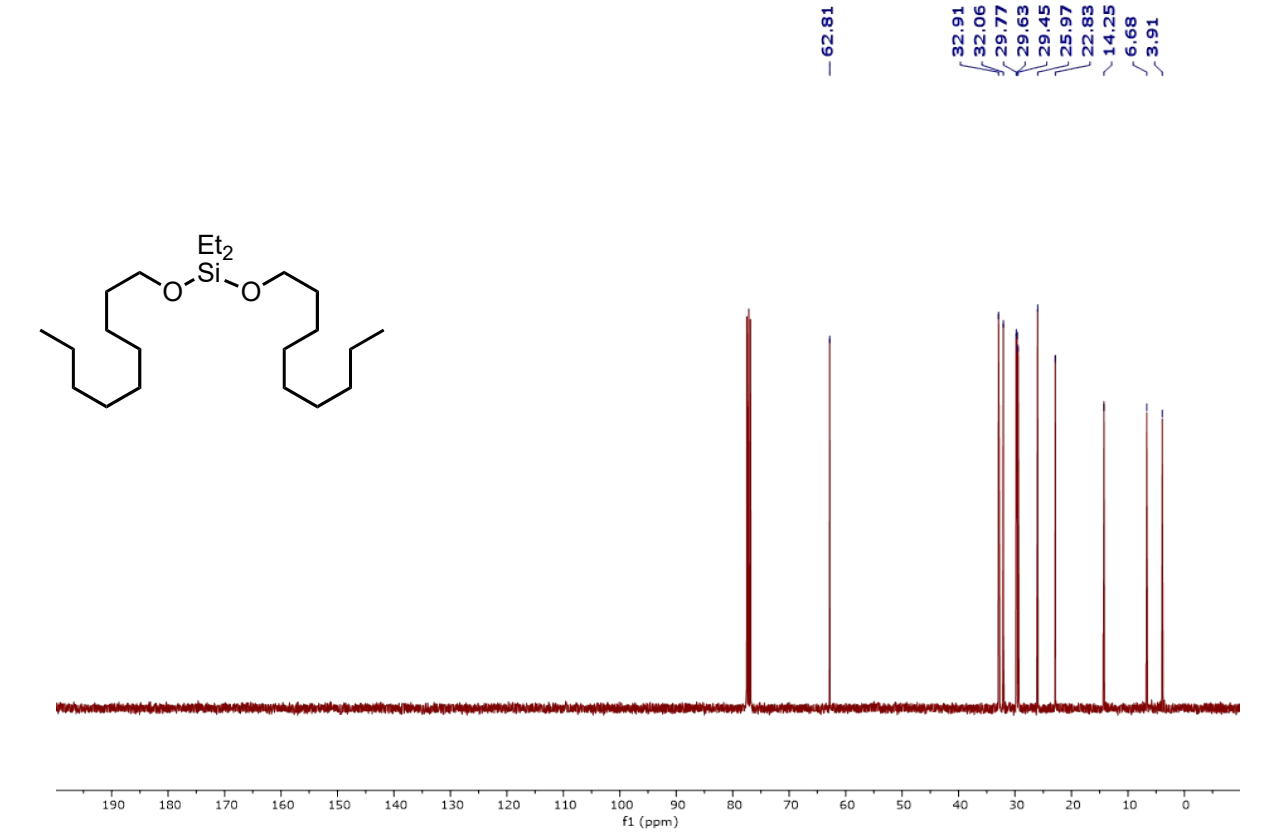
^{13}C{^{1}H} NMR spectrum of [1,1'-biphenyl]-4-ylmethoxy)diethylsilane (**27'**, 101 MHz, $CDCl_3$):



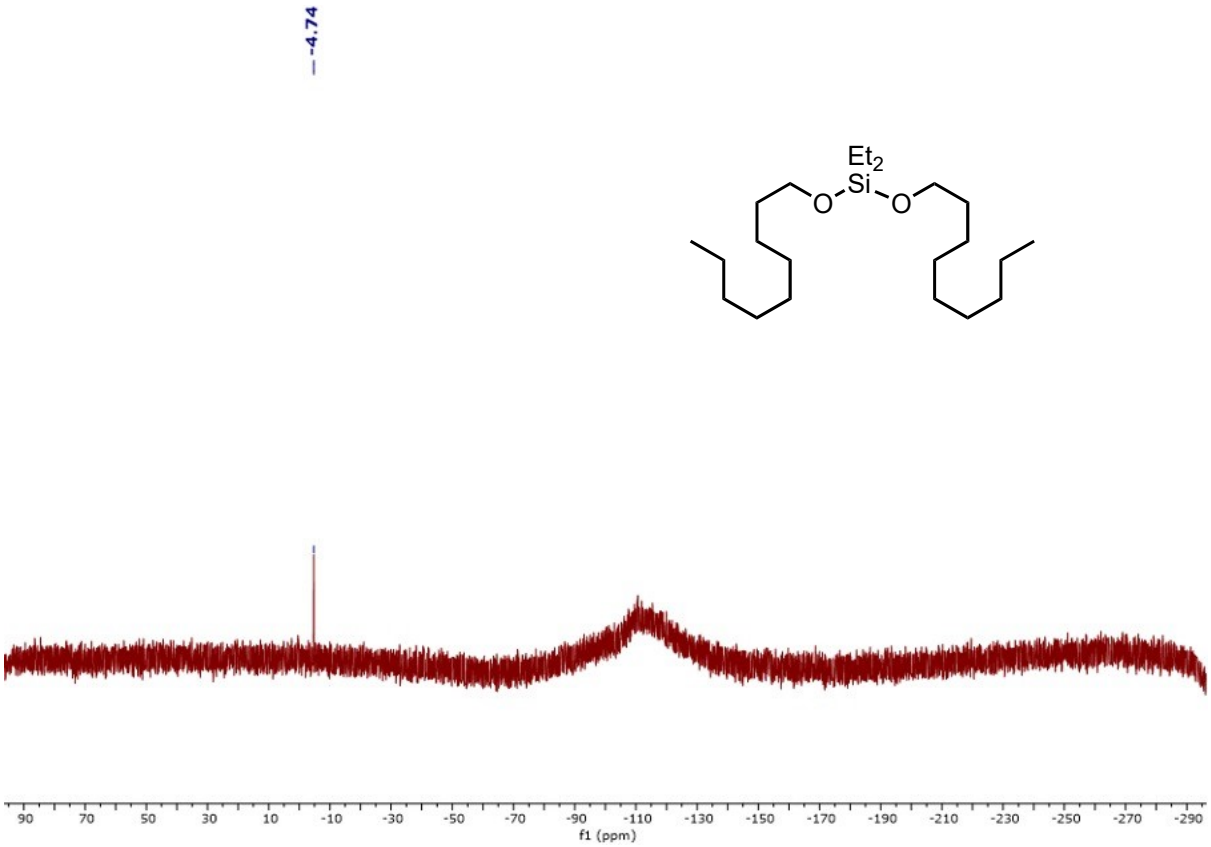
^{1}H NMR spectrum of diethylbis(nonyloxy)silane (**29**, 400 MHz, $CDCl_3$):



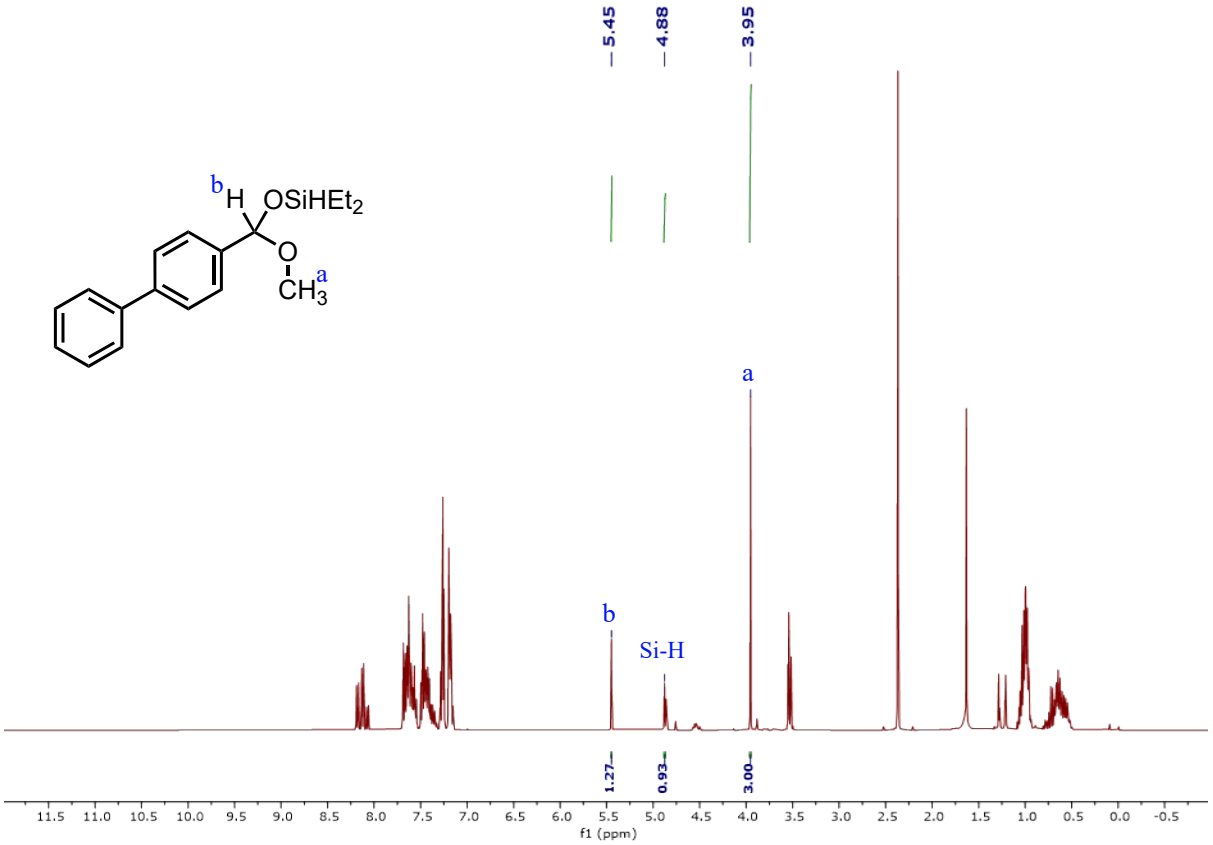
^{13}C{^{1}H} NMR spectrum of diethylbis(nonyloxy)silane (**29**, 101 MHz, $CDCl_3$):



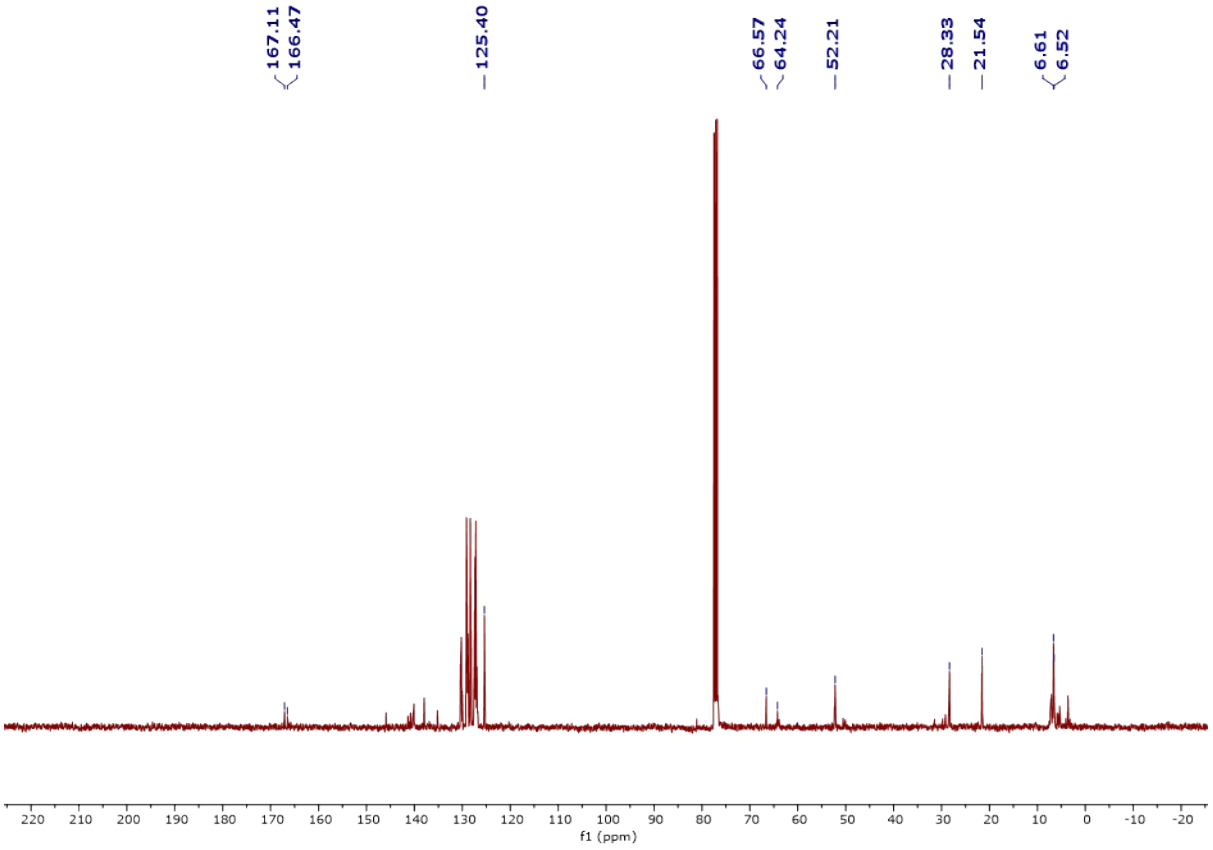
^{29}Si NMR spectrum of diethyl(nonyloxy)silane (**29**, 80 MHz, $CDCl_3$):



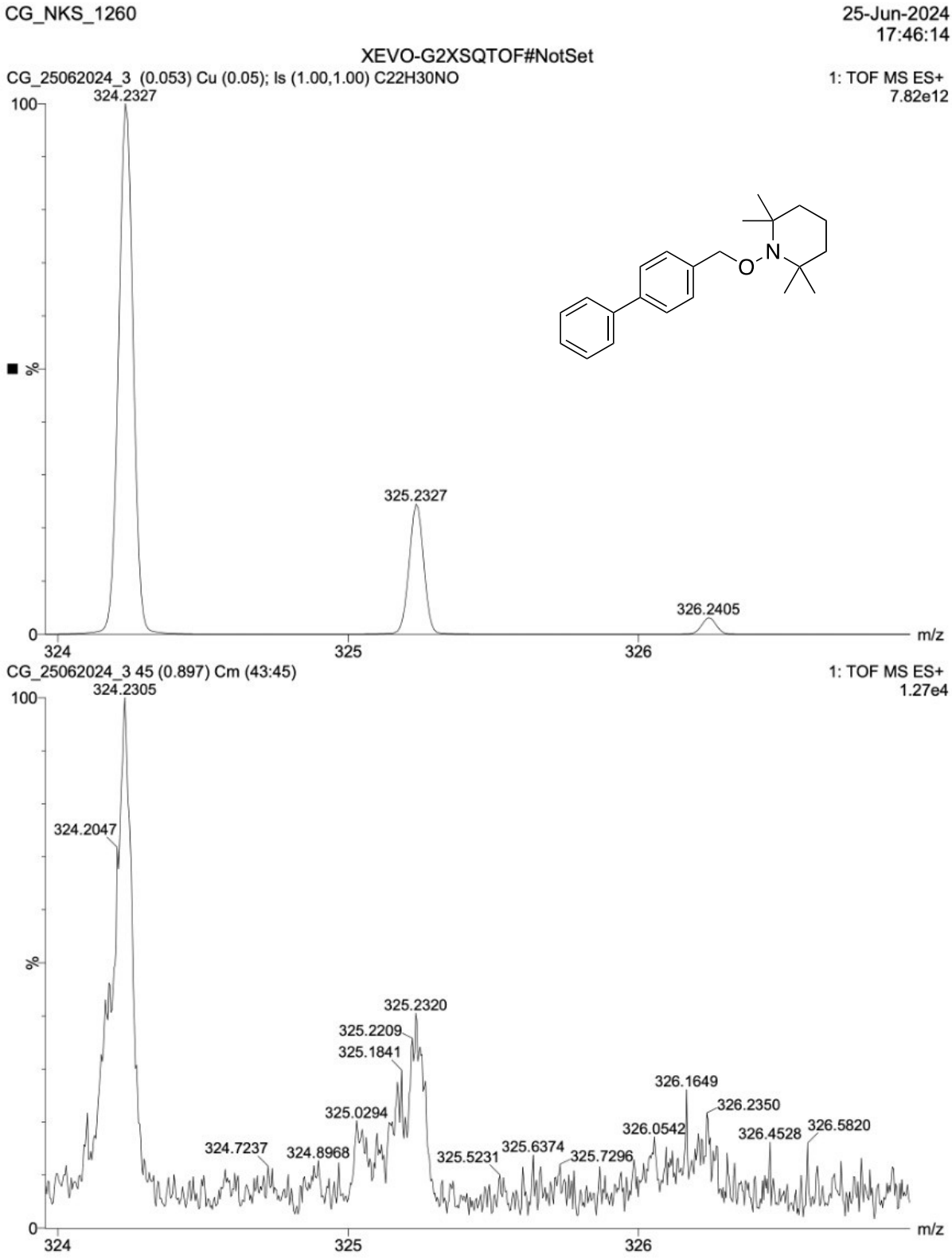
^{1}H NMR spectrum of reaction mixture (Scheme 4f, 400 MHz, $CDCl_3$):



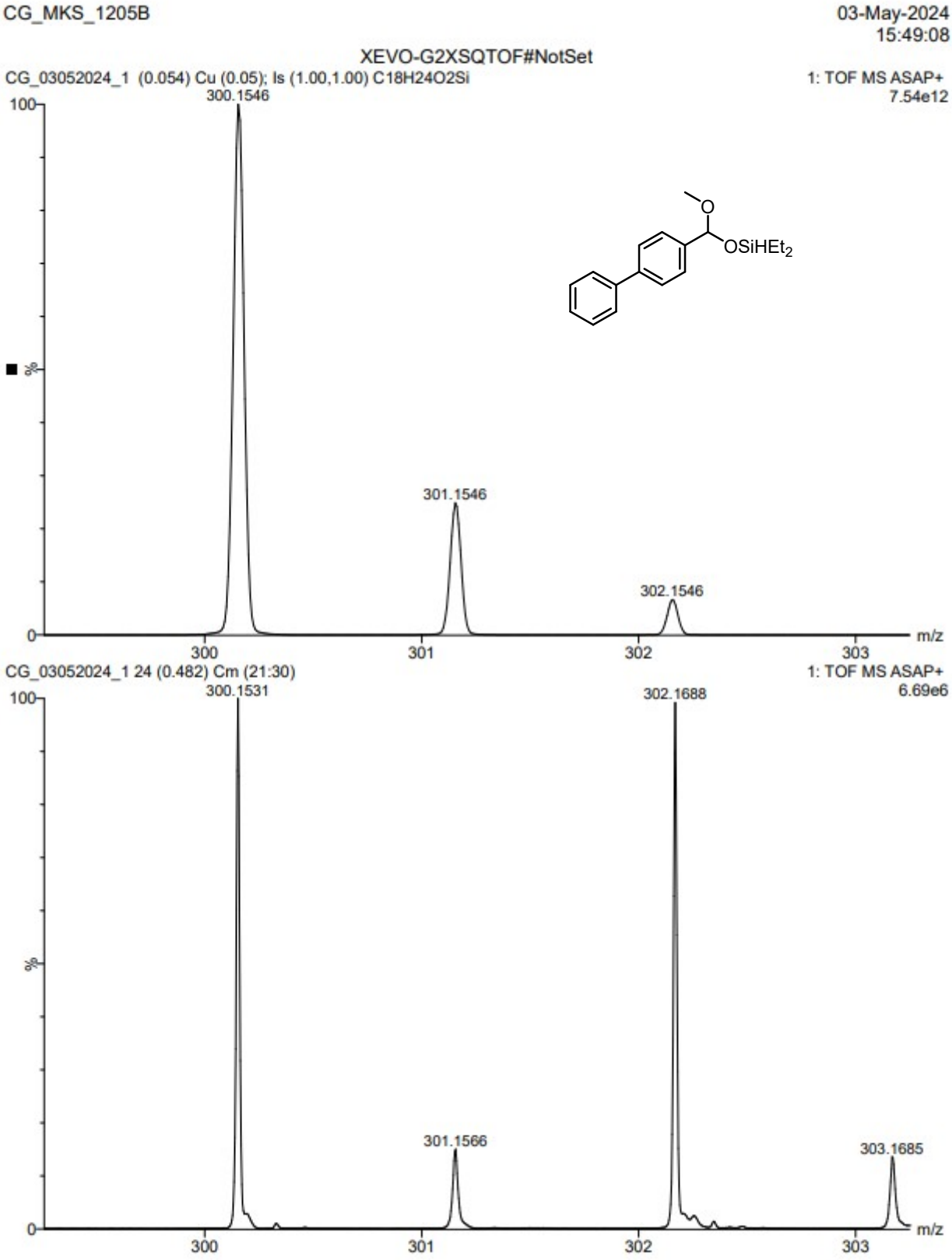
^{13}C NMR spectrum of reaction mixture (Scheme 4f, 106 MHz, $CDCl_3$):



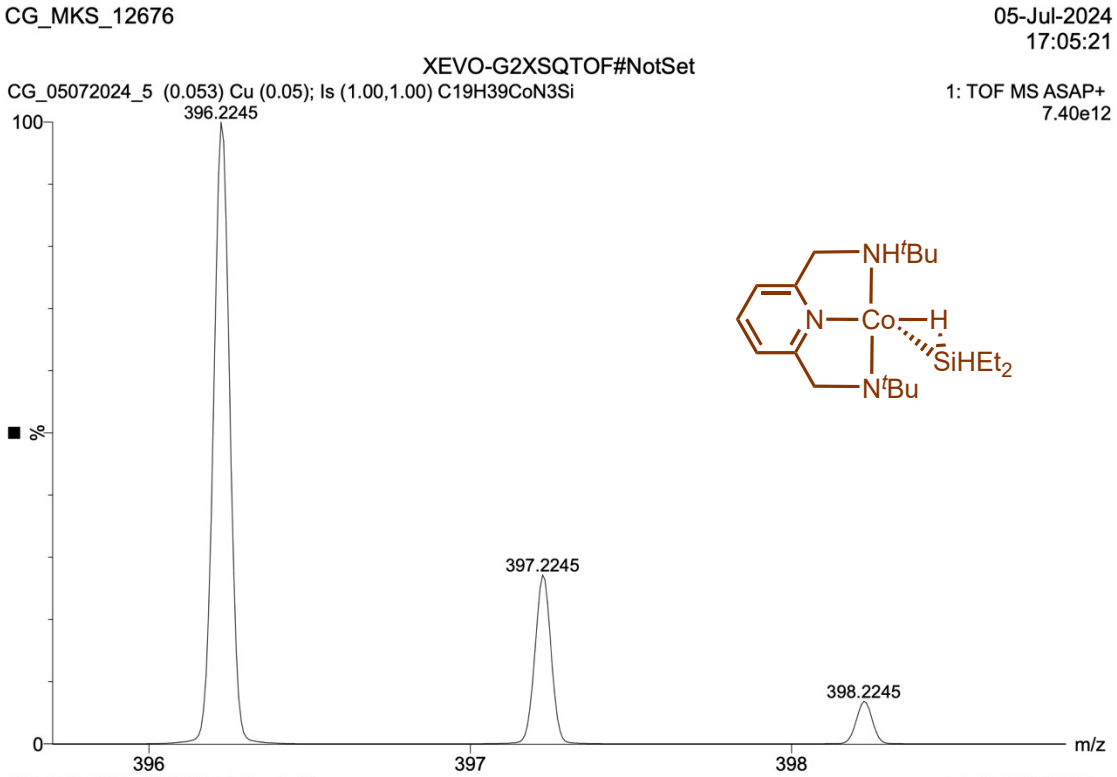
HRMS spectrum for TEMPO trapped benzylic radical:

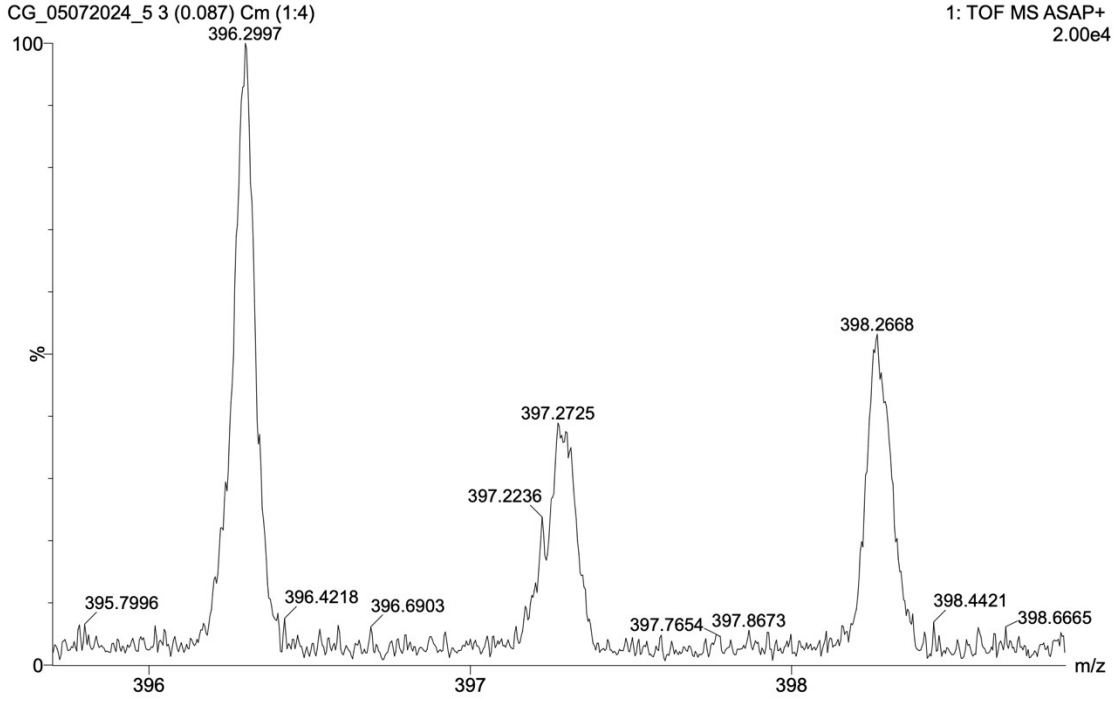


ESI mass data in support of intermediate 23:

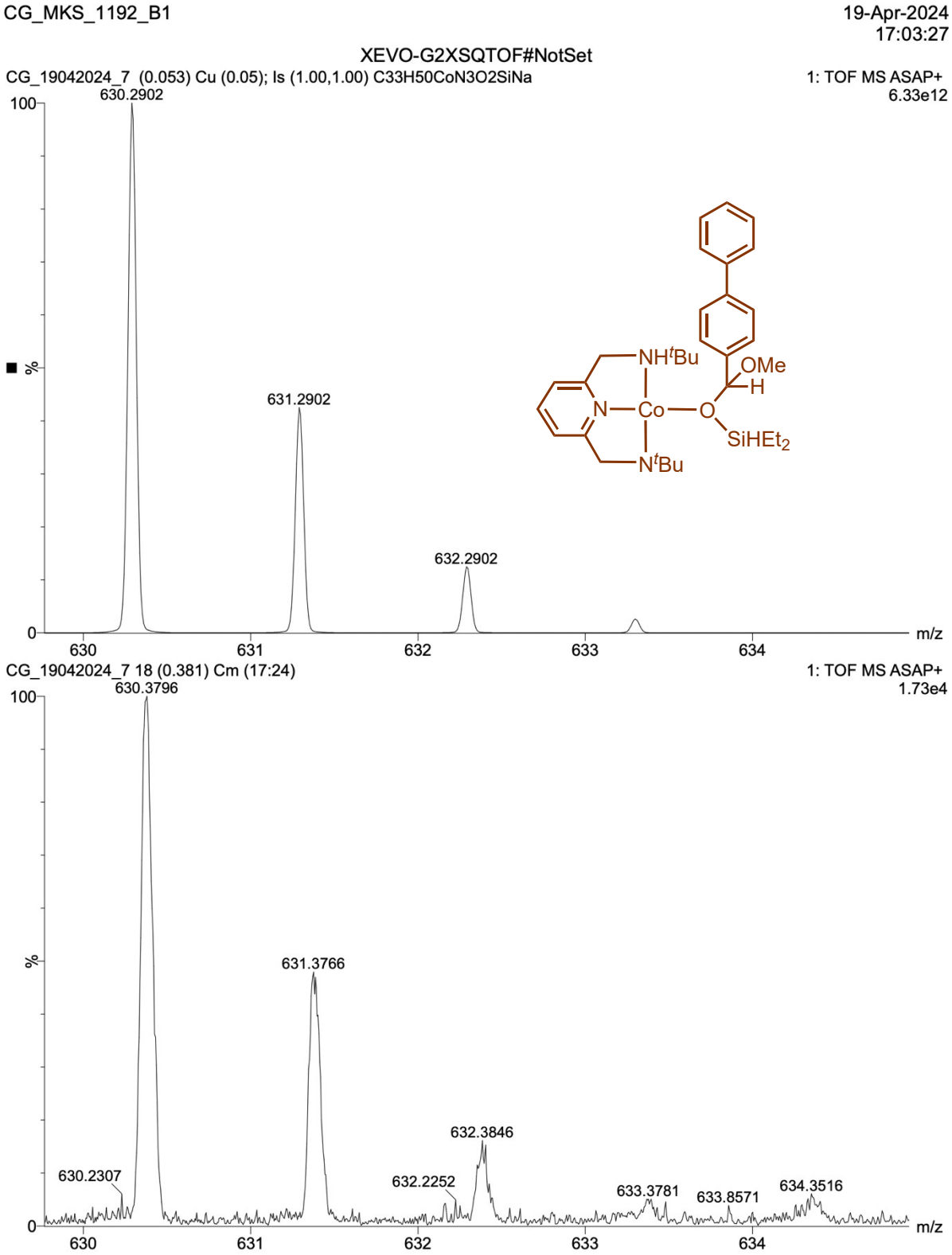


ESI mass data in support of intermediate I:





ESI mass data in support of intermediate III:



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