Supporting Information

Part 1

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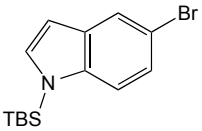
General Methods. All reactions were performed under nitrogen using oven-dried glassware and standard Schlenk or vacuum line techniques. Air- and moisture-sensitive solutions were handled under nitrogen and transferred via syringe. Anhydrous cyclopentyl methyl ether (CPME), dimethoxyethane (DME) and dioxane were purchased from Sigma-Aldrich and used as solvent without further purification. THF was dried over sodium benzophenone and triethylamine was distilled over calcium hydride and stored under nitrogen. Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were obtained from Sigma-Aldrich, Acros or Fisher Scientific, and solvents were purchased from Fisher Scientific. The progress of the reactions was monitored by thin-layer chromatography using WhatmanPartisil K6F 250 μmprecoated 60 Å silica gel plates and visualized by short- wave ultraviolet light as well as by treatment with ceric ammonium molybdate (CAM) stain. Silica gel (230–400 mesh, Silicycle) was used for flash chromatography. The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were obtained using a Brüker AM-500 Fourier-transform NMR spectrometer at 500 and 125 MHz, respectively. Chemical shifts are reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants are reported in hertz. The infrared spectra were obtained with KBr plates using a Perkin-Elmer Spectrum 100 Series FTIR spectrometer. High-resolution mass spectrometry (HRMS) data were obtained on a Waters LC-TOF mass spectrometer (model LCT-XE Premier) using chemical ionization (CI) or electrospray ionization (ESI) in positive or negative mode, depending on the analyte. Melting points were determined on a Unimelt Thomas-Hoover melting point apparatus and are uncorrected.

Preparation of Aryl Bromides:

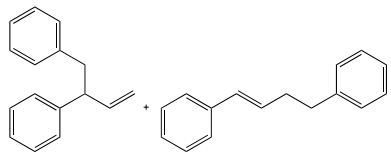


5-bromo-1-(*tert*-butyldimethylsilyl)-1*H*-indole (3j): Compound **3j** is prepared according to literature procedures.[1] The NMR spectral data match the previously published data.[1]

Procedure and Characterization for the Deprotonation/Benzylation of Allylbenzene.

General Procedure A: An oven-dried 10 mL reaction vial equipped with a stir bar was charged with $KN(SiMe_3)_2$ (0.3 mmol, 3 equiv) under a nitrogen atmosphere followed by 1 mL of dry CPME, and the reaction mixture was stirred for 5 min at 24 °C. Allylbenzene (0.3 mmol, 3 equiv) was added to the reaction mixture followed by benzyl chloride (0.1 mmol, 1 equiv). The reaction mixture was stirred for 12 h at room temperature. The reaction mixture was quenched with three drops of H_2O, diluted with 1 mL of ethyl acetate, and filtered over a pad of silica. The pad was rinsed with additional ethyl acetate, and the solution was concentrated in vacuo. The crude material

was loaded onto a silica gel column and purified by flash chromatography.



But-3-ene-1,2-diyldibenzene and (*E*)-but-1-ene-1,4-diyldibenzene: The reaction was performed following General Procedure A with allylbenzene (**1a**) (39.8μL, 0.3 mmol), $KN(SiMe_3)_2$ (59.8 mg, 0.30 mmol) and benzyl chloride (11.5 μL, 0.1 mmol) in 1 mL of CPME at room temperature. The crude material was purified by flash chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product (16.7 mg, α:γ = 5:1, 80% yield) as a colorless oil. The NMR spectral data match the previously published data.[2]

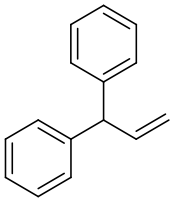
With NaHMDS: α:γ = 4:1, 71% yield.

With LiHMDS : α:γ = 1:1, 13% yield.

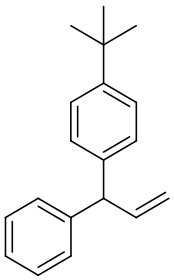
MO-*t*-Bu (M = K, Na, Li) = 0% (no reaction).

Procedure and Characterization for the Pd-Catalyzed DCCP of 1,1-diaryl-2-propenes.

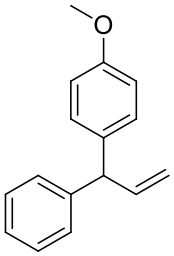
General Procedure B: An oven-dried 10 mL reaction vial equipped with a stir bar was charged with $LiN(SiMe_3)_2$ (4 equiv) under a nitrogen atmosphere. A solution (from a stock solution) of $Pd(OAc)_2$ (5 mol%) and PCy_3 (20 mol%) in 1 mL of dry CPME was taken up by syringe and added to the reaction vial. After stirring for 5 min at 24 °C, allylarene (4 equiv) was added to the reaction mixture followed by aryl bromide (1 equiv). The reaction mixture was stirred for 24–36 h at 80 °C, cooled, quenched with three drops of H_2O, diluted with 1 mL of ethyl acetate, and filtered over a pad of silica. The pad was rinsed with additional ethyl acetate, and the solution was concentrated in vacuo. The crude material was loaded onto a silica gel column and purified by flash chromatography.



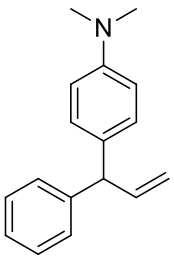
4a: Prop-2-ene-1,1-diyldibenzene. The reaction was performed following General Procedure B with allylbenzene (**1a**) (106μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (133.9 mg, 0.80 mmol, 4 equiv) and bromobenzene (**3a**) (21 μL, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (99% ^{1}H NMR yield with internal standard CH_2Br_2). The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4a** as a colorless oil (35.4 mg, 91% yield). The NMR spectral data match the previously published data.[3]



4b: 1-(*tert*-Butyl)-4-(1-phenylallyl)benzene. The reaction was performed following General Procedure B with allylbenzene (**1a**) (106 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (133.9 mg, 0.80 mmol, 4 equiv) and 1-bromo-4-*tert*-butylbenzene (**3b**) (34.7 μL, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (99% ^{1}H NMR yield with internal standard CH_2Br_2). The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4b** as a colorless oil (44.1 mg, 88% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.28 – 7.21 (m, 3H), 7.17 (dd, J = 9.5, 7.8 Hz, 2H), 6.41 – 6.27 (m, 1H), 5.32 – 5.19 (m, 1H), 5.04 (dt, J = 17.1, 1.5 Hz, 1H), 4.74 (d, J = 7.3 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.3, 143.7, 141.1, 140.4, 128.8, 128.6, 128.3, 126.5, 125.5, 116.3, 54.8, 34.6, 31.6. IR (neat) 3083, 3027, 2963, 2904, 2868, 1637, 1600, 1511, 1493, 918 cm^{-1}; HRMS *m/z* 235.1455 [(M)$^+$; calcd for $C_{19}H_{22}$: 235.1487].

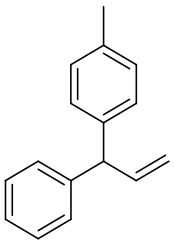


4c: 1-Methoxy-4-(1-phenylallyl)benzene. The reaction was performed following General Procedure B with allylbenzene (**1a**) (106 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (133.9 mg, 0.80 mmol, 4 equiv) and 4-bromoanisole (**3c**) (25.0 μL, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (99% ^{1}H NMR yield with internal standard CH_2Br_2). The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4c** as a colorless oil (43.5 mg, 97% yield). The NMR spectral data match the previously published data.[4]

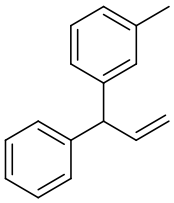


4d: N,N-dimethyl-4-(1-phenylallyl)aniline. The reaction was performed following General Procedure B with allylbenzene (**1a**) (106 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (200.8 mg, 1.2 mmol, 6 equiv) and 4-bromo-N,N-dimethylamine (**3d**) (40.0 mg, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction

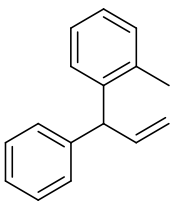
mixture was filtered through a short pad of silica to afford the product (86% ^{1}H NMR yield with internal standard CH_2Br_2). The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the product **4d** as a colorless oil (38.5 mg, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 2H), 7.23 – 7.13 (m, 3H), 7.04 (d, J = 8.7 Hz, 2H), 6.69 (d, J = 8.5 Hz, 2H), 6.33 – 6.22 (m, 1H), 5.17 (d, J = 10.1 Hz, 1H), 4.97 (d, J = 17.0 Hz, 1H), 4.64 (d, J = 7.2 Hz, 1H), 2.92 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 144.0, 141.2, 131.3, 129.1, 128.5, 128.2, 126.0, 115.6, 112.7, 54.1, 40.7. IR (neat) 3080, 3025, 2926, 2800, 1635, 1613, 1519, 1449, 1349cm^{-1}; HRMS *m/z* 238.1596 [$(M+H)^+$; calcd for $C_{17}H_{20}N^+$: 238.1596].



4e: 1-Methyl-4-(1-phenylallyl)benzene. The reaction was performed following General Procedure B with allylbenzene (**1a**) (106 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (133.9 mg, 0.80 mmol, 4 equiv) and 4-bromotoluene (**3e**) (24.7 μL, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (90% ^{1}H NMR yield with internal standard CH_2Br_2). The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4e** as a colorless oil (35.8 mg, 86% yield). The NMR spectral data match the previously published data.[4]

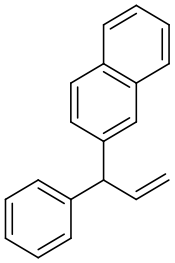


4f: 1-Methyl-3-(1-phenylallyl)benzene. The reaction was performed following General Procedure B with allylbenzene (**1a**) (106 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (133.9 mg, 0.80 mmol, 4 equiv) and 3-bromotoluene (**3f**) (24.3 μL, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (99% ^{1}H NMR yield with internal standard CH_2Br_2). The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4f** as a colorless oil (35.4 mg, 85% yield). The NMR spectral data match the previously published data.[4]

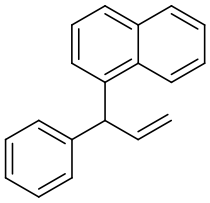


4g: 1-Methyl-2-(1-phenylallyl)benzene. The reaction was performed following General Procedure B with allylbenzene (**1a**) (159 μL, 1.2 mmol, 4 equiv), $LiN(SiMe_3)_2$ (300.0 mg, 1.8 mmol, 6 equiv) and 2-bromotoluene (**3g**) (37.0 μL, 0.3 mmol, 1 equiv) in 1 mL of CPME (0.3 M). The crude reaction mixture was filtered

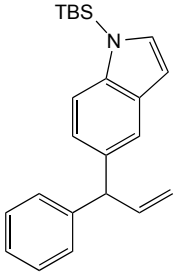
through a short pad of silica to afford the product (85% ^{1}H NMR yield with internal standard CH_2Br_2). The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4g** as a colorless oil (34.6 mg, 83% yield). The NMR spectral data match the previously published data.[4]



4h: 2-(1-Phenylallyl)naphthalene. The reaction was performed following General Procedure B with allylbenzene (**1a**) (106 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (133.9 mg, 0.80 mmol, 4 equiv) and 2-bromonaphthalene (**3h**) (41.4 mg, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (94% ^{1}H NMR yield with internal standard CH_2Br_2). The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4h** as a colorless oil (42.0 mg, 86% yield). The NMR spectral data match the previously published data.[4]

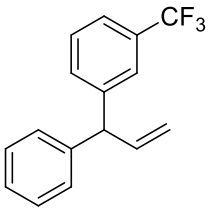


4i: 1-(1-Phenylallyl)naphthalene. The reaction was performed following General Procedure B with allylbenzene (**1a**) (106 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (133.9 mg, 0.80 mmol, 4 equiv) and 1-bromonaphthalene (41.5 mg, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (78% ^{1}H NMR yield with internal standard CH_2Br_2). The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4i** as a colorless oil (36.2 mg, 74% yield). The NMR spectral data match the previously published data.[5]

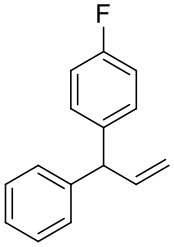


4j: 1-(*tert*-Butyldimethylsilyl)-6-(1-phenylallyl)-1H-indole. The reaction was performed following General Procedure B with allylbenzene (**1a**) (106 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (200.8 mg, 1.2 mmol, 6 equiv) and 5-bromo-1-(*tert*-butyldimethylsilyl)-1*H*-indole (**3j**) (62.1 mg, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product. The crude material was then purified by flash column chromatography on

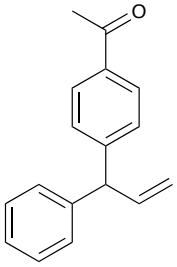
silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the product **4j** as a colorless oil (59.7mg, 86% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.39 (m, 2H), 7.35 – 7.23 (m, 4H), 7.21 (t, *J* = 7.1 Hz, 1H), 7.17 (d, *J* = 3.1 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 6.57 (d, *J* = 3.1 Hz, 1H), 6.40 (ddd, *J* = 17.1, 10.1, 7.3 Hz, 1H), 5.23 (d, *J* = 10.1 Hz, 1H), 5.03 (d, *J* = 17.1 Hz, 1H), 4.84 (d, *J* = 7.3 Hz, 1H), 0.93 (s, 9H), 0.60 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 145.6, 143.8, 138.8, 135.5, 135.3, 132.8, 132.4, 130.2, 126.6, 124.2, 119.8, 117.8, 108.9, 59.1, 30.4, 23.6, 0.06. IR (neat) 3080, 2954, 2929, 2884, 2858, 1636, 1600, 1520, 1470, 1446, 1290,1257, 1150cm^{-1}; HRMS *m/z* 348.2149 [$(M+H)^+$; calcd for $C_{23}H_{30}NSi^+$: 348.2148].



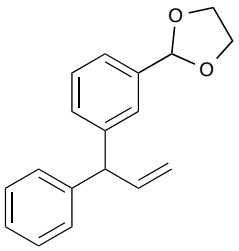
4k: 1-(1-Phenylallyl)-3-(trifluoromethyl)benzene. The reaction was performed following General Procedure B with allylbenzene (**1a**) (106 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (200.8 mg, 1.2 mmol, 6 equiv) and 3-bromo-benzotrifluoride (**3k**) (28 μL, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product. The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4k** as a colorless oil (34.6 mg, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (m, 2H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.36 – 7.29 (m, 3H), 7.26 – 7.21 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 6.37 – 6.16 (m, 1H), 5.27 (dd, *J* = 10.2, 0.9 Hz, 1H), 5.00 (dd, *J* = 17.1, 0.9 Hz, 1H), 4.75 (dd, *J* = 26.0, 7.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 142.2, 139.7, 132.0, 130.8 (q, *J* = 32 Hz), 128.8, 128.6, 128.5, 126.7, 125.2 (q, *J* = 3.8 Hz), 123.3 (q, *J* = 3.8 Hz), 117.1, 54.6. HRMS *m/z* 262.0956 [$(M)^+$; calcd for $C_{19}H_{22}$: 262.0969].



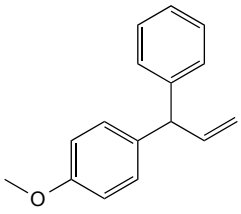
4l: 1-Fluoro-4-(1-phenylallyl)benzene. The reaction was performed following General Procedure B with allylbenzene (**1a**) (106 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (133.9 mg, 0.80 mmol, 4 equiv) and 1-bromo-4-fluorobenzene (**3r**) (22 μL, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product. The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4l** as a colorless oil (22.1 mg, 52% yield). The NMR spectral data match the previously published data.[6]



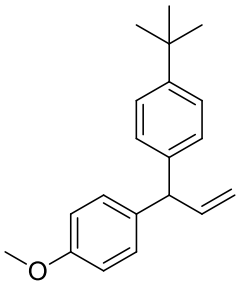
4m: **1-(4-(1-phenylallyl)phenyl)ethan-1-one**. The reaction was performed following General Procedure B with allylbenzene (**1a**) (106 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (200.8 mg, 1.2 mmol, 6 equiv) and *p*-bromo-acetophenone (**3m**) (28 μL, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product. The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4m** as a colorless oil (34.0 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, J = 6.6, 1.7 Hz, 2H), 7.34 – 7.23 (m, 4H), 7.21 (dd, J = 10.1, 4.1 Hz, 1H), 7.15 (dd, J = 13.7, 13.2 Hz, 2H), 6.28 (ddd, J = 17.2, 8.7, 5.5 Hz, 1H), 5.27 – 5.21 (m, 1H), 5.00 (dt, J = 17.1, 1.4 Hz, 1H), 4.77 (d, J = 7.1 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.8, 149.0, 142.6, 139.9, 135.6, 129.0, 128.7, 128.7, 128.7, 126.8, 117.2, 55.1, 26.7. IR (neat) 3082, 3028, 3004, 2979, 2922, 2869, 1683, 1636, 1606, 1570, 1494, 1451, 1410, 1358, 1268, 1182 cm^{-1}; HRMS *m/z* 236.1196 [$(M+H)^+$; calcd for $C_{17}H_{16}O^+$: 236.1201].



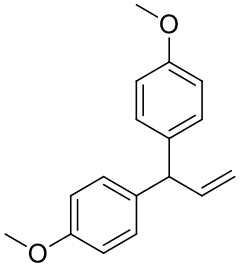
4n: **2-(3-(1-phenylallyl)phenyl)-1,3-dioxolane**. The reaction was performed following General Procedure B with allylbenzene (**1a**) (106 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (200.8 mg, 1.2 mmol, 6 equiv) and 2-(3-bromophenyl)-1,3-dioxolane (**3n**) (28 μL, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product. The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4n** as a colorless oil (46.3 mg, 87% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 5H), 7.24 – 7.07 (m, 4H), 6.29 (ddd, *J* = 17.2, 10.1, 7.3 Hz, 1H), 5.77 (s, 1H), 5.21 (d, *J* = 10.1 Hz, 1H), 4.98 (d, *J* = 17.1 Hz, 1H), 4.74 (d, *J* = 7.1 Hz, 1H), 4.11 – 4.08 (m, 2H), 4.00 – 3.99 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 143.3, 140.7, 138.2, 129.7, 128.8, 128.7, 128.6, 126.8, 126.6, 124.7, 116.7, 104.0, 65.5, 55.1. IR (neat) 3080, 3027, 2977, 2886, 1636, 1600, 1492, 1451, 1386, 1224, 1158, 1098, 1079, 1030 cm^{-1}; HRMS *m/z* 267.1384 [$(M+H)^+$; calcd for $C_{18}H_{18}O_2^+$: 267.1385].



4c: 1-Methoxy-4-(1-phenylallyl)benzene. The reaction was performed following General Procedure B with 4-allylanisole (**1b**) (122.3 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (133.9 mg, 0.80 mmol, 4 equiv) and bromobenzene (**3a**) (21 μL, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (99% ^{1}H NMR yield with internal standard CH_2Br_2). The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4c** as a colorless oil (39.5 mg, 88% yield). The NMR spectral data match the previously published data.[4]

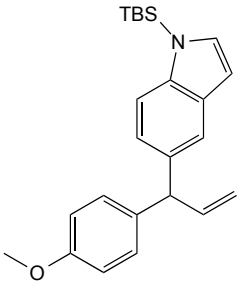


4o: 1-(*tert*-Butyl)-4-(1-(4-methoxyphenyl)allyl)benzene. The reaction was performed following General Procedure B with 4-allylanisole (**1b**) (122.3 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (133.9 mg, 0.80 mmol, 4 equiv) and 1-bromo-4-*tert*-butylbenzene (**3b**) (34.7 μL, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (86% ^{1}H NMR yield with internal standard CH_2Br_2). The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4o** as a colorless oil (45.4 mg, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.14 – 7.09 (m, 4H), 6.87 – 6.82 (m, 2H), 6.29 (ddd, J = 17.2, 10.1, 7.3 Hz, 1H), 5.19 (dt, J = 10.1, 1.4 Hz, 1H), 4.99 (dt, J = 17.0, 1.5 Hz, 1H), 4.66 (d, J = 7.4 Hz, 1H), 3.80 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.3, 149.3, 141.4, 140.8, 135.9, 129.7, 128.3, 125.5, 116.0, 114.0, 55.5, 54.0, 34.6, 31.6. IR (neat) 3080, 3024, 2962, 2858, 1637,1510, 1464, 1247, 1176cm^{-1}; HRMS *m/z* 281.1919 [$(M+H)^+$; calcd for $C_{20}H_{25}O^+$: 281.1905].

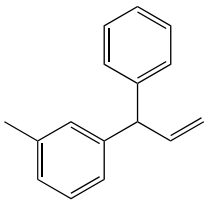


4p: 4,4'-(Prop-2-ene-1,1-diyl)bis(methoxybenzene). The reaction was performed following General Procedure B with 4-allylanisole (**1b**) (122.3 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (133.9 mg, 0.80 mmol, 4 equiv) and 4-bromoanisole (**3c**) (25 μL, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (76% ^{1}H NMR yield with internal standard CH_2Br_2). The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the

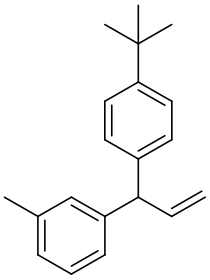
product **4p** as a colorless oil (36.6 mg, 72% yield). The NMR spectral data match the previously published data.[7]



4q: 1-(*tert*-Butyldimethylsilyl)-5-(1-(4-methoxyphenyl)allyl)-1*H*-indole. The reaction was performed following General Procedure B with 4-allylanisole (**1b**) (122.3 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (200.8 mg, 1.2 mmol, 6 equiv) and 5-bromo-1-(*tert*-butyldimethylsilyl)-1*H*-indole (**3j**) (62.1 mg, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product. The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the product **4q** as a colorless oil (49.8 mg, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.21 – 7.16 (m, 3H), 7.01 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.89 – 6.85 (m, 2H), 6.58 (d, *J* = 3.2 Hz, 1H), 6.39 (ddd, *J* = 17.2, 10.1, 7.3 Hz, 1H), 5.22 (d, *J* = 10.1 Hz, 1H), 5.04 (dt, *J* = 17.1, 1.5 Hz, 1H), 4.81 (d, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 0.96 (s, 9H), 0.61 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.0, 141.9, 139.8, 136.4, 135.1, 131.5, 131.2, 129.7, 122.6, 120.1, 115.5, 113.7, 113.7, 104.8, 55.3, 54.2, 26.34, 19.50, -3.97; HRMS *m/z* 378.2253 [$(M+H)^+$; calcd for $C_{19}H_{22}$: 378.2253].

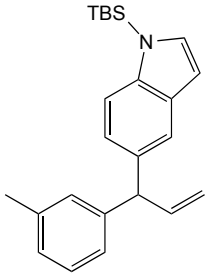


4f: 1-Methyl-3-(1-phenylallyl)benzene. The reaction was performed following General Procedure B with 1-allyl-3-methylbenzene (**1c**) (121.1 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (200.8 mg, 1.2 mmol, 6 equiv) and bromobenzene (**3a**) (21 μL, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product. The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4f** as a colorless oil (33.3 mg, 80% yield). The NMR spectral data match the previously published data.[4]

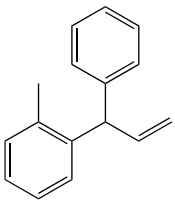


4r: 1-(1-(4-(*tert*-Butyl)phenyl)allyl)-3-methylbenzene. The reaction was performed following General Procedure B with 1-allyl-3-methylbenzene (**1c**) (121.1 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (133.9 mg, 0.80 mmol, 4 equiv) and 1-bromo-4-tert-butylbenzene (**3b**) (34.7 μL, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the

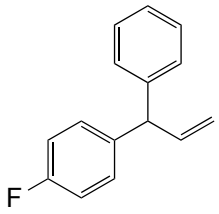
product. The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4r** as a colorless oil (48.1 mg, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 2H), 7.26 – 7.22 (m, 1H), 7.21 – 7.15 (m, 2H), 7.12 – 7.02 (m, 3H), 6.35 (ddd, *J* = 17.4, 10.1, 7.4 Hz, 1H), 5.25 (dt, *J* = 10.1, 1.3 Hz, 1H), 5.06 (dt, *J* = 17.0, 1.4 Hz, 1H), 4.71 (d, *J* = 7.4 Hz, 1H), 2.37 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 143.6, 141.1, 140.5, 138.1, 129.5, 128.5, 128.3, 127.3, 125.8, 125.5, 116.1, 54.8, 34.6, 31.6, 21.7. IR (neat) 3080, 3024, 2962, 2904, 2866, 1637, 1605, 1515, 1487, 918 cm^{-1}; HRMS *m/z* 264.1876 [$(M)^+$; calcd for $C_{20}H_{24}$: 264.1878].



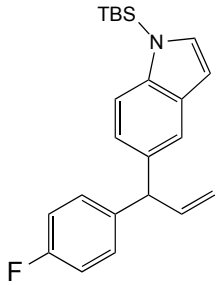
4s: 1-(*tert*-Butyldimethylsilyl)-6-(1-(m-tolyl)allyl)-1H-indole. The reaction was performed following General Procedure B with 1-allyl-3-methylbenzene (**1c**) (121.1 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (133.9 mg, 0.80 mmol, 4 equiv) and 5-bromo-1-(*tert*-butyldimethylsilyl)-1*H*-indole (**3j**) (62.1 mg, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product. The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the product **4s** as a colorless oil (59.3 mg, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 1.7 Hz, 1H), 7.45 (d, *J* = 8.6 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.18 (d, *J* = 3.2 Hz, 1H), 7.13 – 6.98 (m, 4H), 6.61 – 6.57 (m, 1H), 6.42 (ddd, *J* = 17.3, 10.1, 7.4 Hz, 1H), 5.26 – 5.20 (m, 1H), 5.05 (dt, *J* = 17.0, 1.6 Hz, 1H), 4.82 (d, *J* = 7.4 Hz, 1H), 2.34 (s, 3H), 0.96 (s, 9H), 0.60 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 145.4, 143.5, 141.6, 138.7, 135.2, 135.0, 133.2, 131.9, 130.7, 129.5, 126.3, 123.9, 119.4, 117.5, 108.6, 58.8, 30.1, 25.3, 23.3, -0.2. IR (neat) 3080, 3018, 2954, 2928, 2857, 1636, 1605, 1516, 1467, 1362, 1290,1257, 1148cm^{-1}; HRMS *m/z* 362.2312 [$(M+H)^+$; calcd for $C_{24}H_{32}NSi^+$: 362.2307].



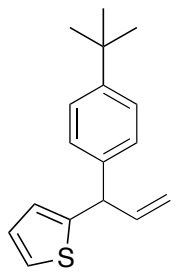
4g: 1-Methyl-2-(1-phenylallyl)benzene: The reaction was performed following General Procedure B with 1-allyl-2-methylbenzene (**1e**) (118.2 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (200.8 mg, 1.2 mmol, 6 equiv) and bromobenzene (**3a**) (21 μL, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product. The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4g** as a colorless oil (25.0 mg, 60% yield). The NMR spectral data match the previously published data. [4]



4l: 1-Fluoro-4-(1-phenylallyl)benzene. The reaction was performed following General Procedure B with 1-allyl-4-fluorobenzene (**1d**) (108 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (133.9 mg, 0.80 mmol, 4 equiv) and bromobenzene (**3a**) (21 μL, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product. The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 3:97) to give the product **4l** as a colorless oil (27.2 mg, 64% yield). The NMR spectral data match the previously published data.[6]



4t: 1-(*tert*-Butyldimethylsilyl)-6-(1-(4-fluorophenyl)allyl)-1H-indole. The reaction was performed following General Procedure B with 1-allyl-4-fluorobenzene (**1d**) (108 μL, 0.80 mmol, 4 equiv), $LiN(SiMe_3)_2$ (133.9 mg, 0.80 mmol, 4 equiv) and 5-bromo-1-(*tert*-butyldimethylsilyl)-1*H*-indole (**3j**) (62.1 mg, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product. The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes to EtOAc:hexanes = 5:95) to give the product **4t** as a colorless oil (48.3 mg, 66% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.19 – 7.14 (m, 3H), 6.98 – 6.91 (m, 3H), 6.54 (d, J = 3.1 Hz, 1H), 6.37 – 6.28 (m, 1H), 5.19 (d, J = 10.2 Hz, 1H), 5.00 – 4.95 (m, 1H), 4.79 (d, J = 7.2 Hz, 1H), 0.91 (s, 9H), 0.57 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3 (d, J = 250 Hz), 141.3, 139.8 (d, J = 3.8 Hz), 139.7, 134.4, 131.4 (d, J = 12.5 Hz), 130.1, 130.0, 122.3, 120.0, 115.8, 115.0 (d, J = 21 Hz), 113.7, 104.6, 54.1, 26.2, 19.4, -4.0; HRMS *m/z* 366.2062 [$(M)^+$; calcd for $C_{23}H_{29}NSiF^+$: 366.2053].



4u: **2-(1-(4-(*tert*-butyl)phenyl)allyl)thiophene**: The reaction was performed following General Procedure B with allylthiophene (**1u**) (124.0 mg, 1.0 mmol, 5 equiv), $LiN(SiMe_3)_2$ (100.4 mg, 0.6 mmol, 3 equiv) and 1-bromo-4-*tert*-butylbenzene (**3b**) (34.7 μL, 0.2 mmol, 1 equiv) in 1 mL of CPME (0.2 M). The crude reaction mixture was filtered through a short pad of silica to afford the product. The crude material was then purified by flash column chromatography on silica gel (eluted

with hexanes to EtOAc:hexanes = 3:97) to give the product **4n** as a colorless oil (26.0 mg, 51% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.21 – 7.14 (m, 3H), 6.94 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.82 – 6.75 (m, 1H), 6.36 – 6.20 (m, 1H), 5.19 (dd, *J* = 10.0, 1.0 Hz, 1H), 5.10 (dt, *J* = 16.9, 1.3 Hz, 1H), 4.88 (d, *J* = 7.5 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5, 147.4, 140.3, 139.8, 127.6, 126.6, 125.3, 124.8, 124.0, 115.9, 50.1, 34.4, 31.3. IR (neat) 3080, 2962, 2905, 2867, 1637, 1512, 1463, 1436, 1409, 1364, 1229, 1109 cm^{-1}; HRMS *m/z* 256.1290 [$(M+H)^+$; calcd for $C_{17}H_{20}S^+$: 256.1286].

Representative Microscale High-Throughput Experimentation for Base & Catalyst Identification.

General Experimental:

The experimental procedures in this work were similar to those reported.[8] Parallel synthesis was accomplished in an MBraun glovebox operating with a constant N_2-purge (oxygen typically <5 ppm). The experimental design was accomplished using Accelrys Library Studio. Screening reactions were carried out in 1 mL vials (30 mm height ×8 mm diameter) in a 96-well plate aluminum reactor block. Liquid chemicals were dosed using multi-channel or single-channel pipettors. Solid chemicals were dosed manually as solutions or slurries in appropriate solvents. Undesired additional solvent was removed using a GeneVac system located inside the glovebox. The reactions were heated and stirred on a heating block with a tumble-stirrer (V&P Scientific) using 1.98 mm diameter ×4.80 mm length parylene stir bars. The tumble stirring mechanism helped to insure uniform stirring throughout the 96-well plate. The reactions were sealed in the 96-well plate during reaction. Below each reactor vial in the aluminum 96-well plate was a 0.062 mm thick silicon-rubber gasket. Directly above the glass vial reactor tops was a Teflon perfluoroalkoxy copolymer resin sealing gasket and above that, two more 0.062 mm thick silicon-rubber gaskets. The entire assembly was compressed between an aluminum top and the reactor base with 9 evenly-placed screws.

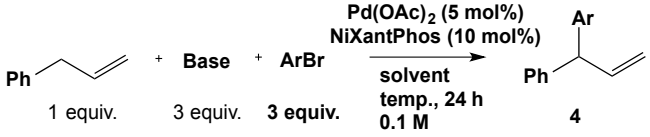
Set up:

Experiments were set up inside a glovebox under a nitrogen atmosphere. A 96-well aluminum block containing 1 mL glass vials was predosed manually with $Pd(OAc)_2$ (0.5 μmol) and PCy_3 (1 μmol) in THF. The solvent was evacuated to dryness using a GeneVac vacuum centrifuge, and $LiN(SiMe_3)_2$ (30 μmol) in THF was added to the ligand/catalyst mixture. The solvent was removed on the GeneVac, and a parylene stir bar was then added to each reaction vial. bromobenzene (30 μmol/reaction), allylbenzene (10 μmol/reaction) were then dosed together into each reaction vial as a solution in CPME (100 μL, 0.1 M). The 96-well plate was then sealed and stirred for 24 h at 110 °C.

Work up: Upon opening the plate to air, di-*t*ert-butylbenzene (used as an internal standard to measure HPLC yields) (1 μmol/reaction) in 500 μL of acetonitrile was syringed into each vial. The plate was then covered again and the vials stirred for 10 min to extract the product and to ensure good homogenization. Into a separate 96-well LC block was added 700 μL of acetonitrile, followed by 40 μL of the diluted reaction

mixtures. The LC block was then sealed with a silicon-rubber storage mat, and mounted on HPLC instrument modified with an autosampler for analysis.

(1) First Screening:



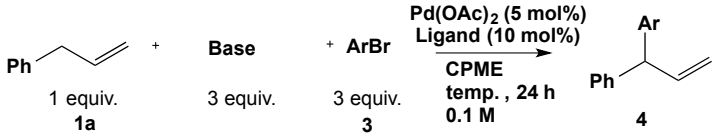
Bases: 3 bases [$KN(SiMe_3)_2$, $NaN(SiMe_3)_2$, $LiN(SiMe_3)_2$] were screened.

Solvents: 4 solvents [CPME, Dioxane, THF and DME] were screened.

Temperatures: 80 and 110 °C.

The lead hit from the first screen was the combination of $Pd(OAc)_2$ (5 mol%), NiXantPhos (10 mol%), $LiN(SiMe_3)_2$, CPME at 80 °C, which translated into 40% yield in a 2.6:1 ratio of α- and γ-arylated products on laboratory scale.

(2) Second Screening:



a) 3 bases [$KN(SiMe_3)_2$, $NaN(SiMe_3)_2$, $LiN(SiMe_3)_2$] were screened.

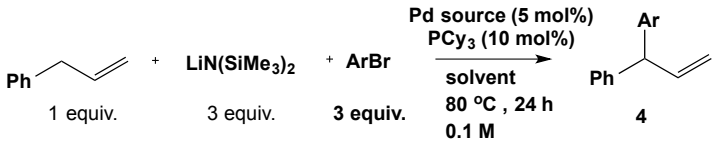
b) **Ligand** was used in a 4:1 ratio relative to Pd for monodentate ligands and 2:1 ratio for bidentate ligands.

$Pd(OAc)_2$ (5 mol %) was used to test 29 sterically and electronically diverse, mono- and bidentate phosphine ligands (ligands 1-29 from the Table below).

Temperatures: 80 and 110 °C.

The lead hit from the second screen was the combination of $Pd(OAc)_2$ (5 mol%), PCy_3 (10 mol%), $LiN(SiMe_3)_2$, CPME at 80 °C, which translated into 30% yield on laboratory scale.

(3) Third Screening:



b) **Pd sources:** 6 Pd sources [$Pd(OAc)_2$, $Pd(PCy_3)_2$, $Pd(PPh_3)_4$, $(\eta^3\text{-}C_3H_5)_2Pd_2Cl_2$, $Pd(cod)Cl_2$, and $Pd(dba)_2$] were screened.

c) **Solvents**: 4 solvents [CPME, Dioxane, THF and DME] were screened.

The lead hit from the third screen was the combination of $Pd(OAc)_2$ (5 mol %), PCy_3 (10 mol %), $LiN(SiMe_3)_2$ in CPME at 80°C, which translated into 30% yield on laboratory scale.

	Ligand libraries(1 – 17)	4a/IS	γ–selective Product/IS
1	2-Dicyclohexylphosphino-2',6'-di-i-propoxy-1,1'-biphenyl (RuPhos)	0.0	0.0
2	5-(Di-*t*-butylphosphino)-1', 3', 5'-triphenyl-1'H-[1,4']bipyrazole (BippyPhos)	0.17	0.0
3	2-Dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl (SPhos)	0.0	0.0
4	2-(Dicyclohexylphosphino)biphenyl (Cy-JohnPhos)	0.0	0.0
5	2-(Di-*t*-butylphosphino)-3-methoxy-6-methyl-2',4',6'-tri-i-propyl-1,1'-biphenyl (RockPhos)	0.42	0.55
6	2-(Dicyclohexylphosphino)-2'-methylbiphenyl (MePhos)	0.66	0.0
7	1-[2-[Bis(*t*-butyl)phosphino]phenyl]-3,5-diphenyl-1H-pyrazole (TrippyPhos)	0.0	0.0
8	Dicyclohexyl-[3,6-dimethoxy-2-(2,4,6-triisopropylphenyl)phenyl]phosphane (BrettPhos)	1.93	0.0
9	9,9-Dimethyl-4,5-bis(diphenylphosphino)xanthene (Xantphos)	0.57	0.0
10	4,6-Bis(diphenylphosphino)phenoxazine (NiXantphos)	0.78	0.71
11	Tri-*t*-butyl phosphonium tetrafluoroborate	0.1	0.0
12	Tricyclohexylphosphonium tetrafluoroborate	1.73	0.0
13	*N*-phenyl-2-(di-*t*-butylphosphino)pyrrole (cataCXium PtB)	0.0	0.0
14	1-(2,4,6-Trimethylphenyl)-2-(dicyclohexylphosphino)imidazole (cataCXium PICy)	0.3	0.0
15	Di-*t*-butyl-[1-(2-methoxyphenyl)pyrrol-2-yl]phosphane (cataCXium POMetB)	0.0	0.0
16	*N*-phenyl-2-(dicyclohexylphosphino)pyrrole (cataCXium PCy)	0.0	0.0
17	Di(1-adamantyl)-n-butylphosphine (CatCXium A)	0.0	0.0

	Ligand libraries(18 – 29)	4a/IS	γ–selective Product/IS
18	Di(1-adamantyl)-2-morpholinophenylphosphine (MorDalPhos)	0.0	0.0
19	2-(Di-*t*-butylphosphino)-2'-methylbiphenyl (*t*Bu-MePhos)	0.0	0.0
20	1,1'-Bis(diphenylphosphino)ferrocene (dppf)	0.0	0.4
21	1,1'-Bis(di-*t*-butylphosphino)ferrocene (dtbpf)	0.0	0.0
22	1,1'-Bis(diisopropylphosphino)ferrocene (dippf)	0.0	0.0
23	2-Dicyclohexylphosphino-2',4',6'-tri-i-propyl-1,1'-biphenyl (XPhos)	0.0	0.0
24	1,2,3,4,5-Pentaphenyl-1'-(di-*t*-butylphosphino)ferrocene (QPhos)	0.0	0.0
25	Tri-*o*-tolylphosphine	0.27	0.0
26	Triphenylphosphine (PPh_3)	0.0	0.0
27	(*S*)-(+)-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl ((*S*)-BINAP)	0.0	0.1
28	2-Dicyclohexylphosphino-2'-(*N,N*-dimethylamino)biphenyl (DavePhos)	0.0	0.0
29	2-(Di-*t*-butylphosphino)biphenyl (JohnPhos)	0.0	0.0

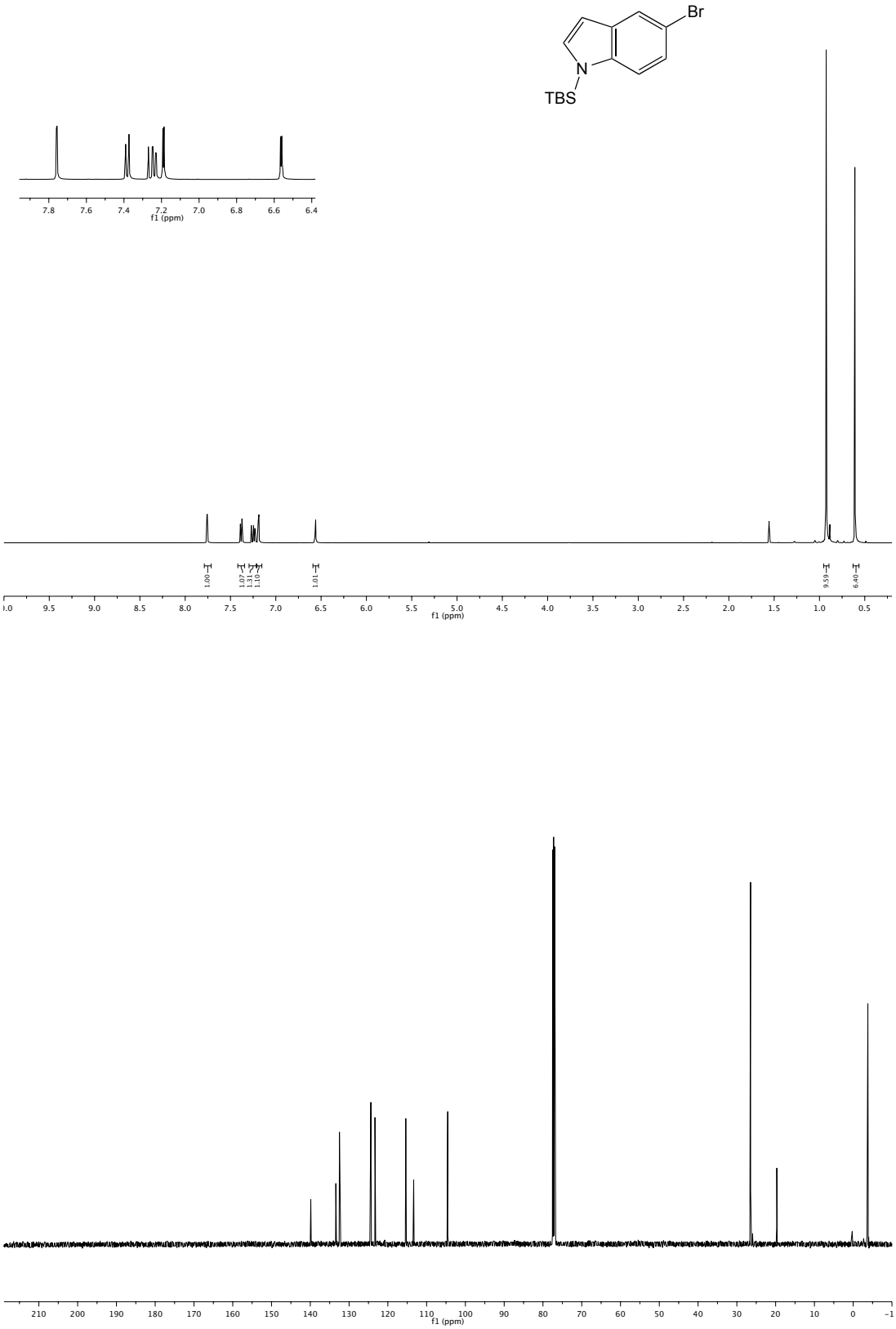


Figure S1 (**3j**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 5-bromo-1-(*tert*-butyldimethylsilyl)-1*H*-indole in $CDCl_3$.

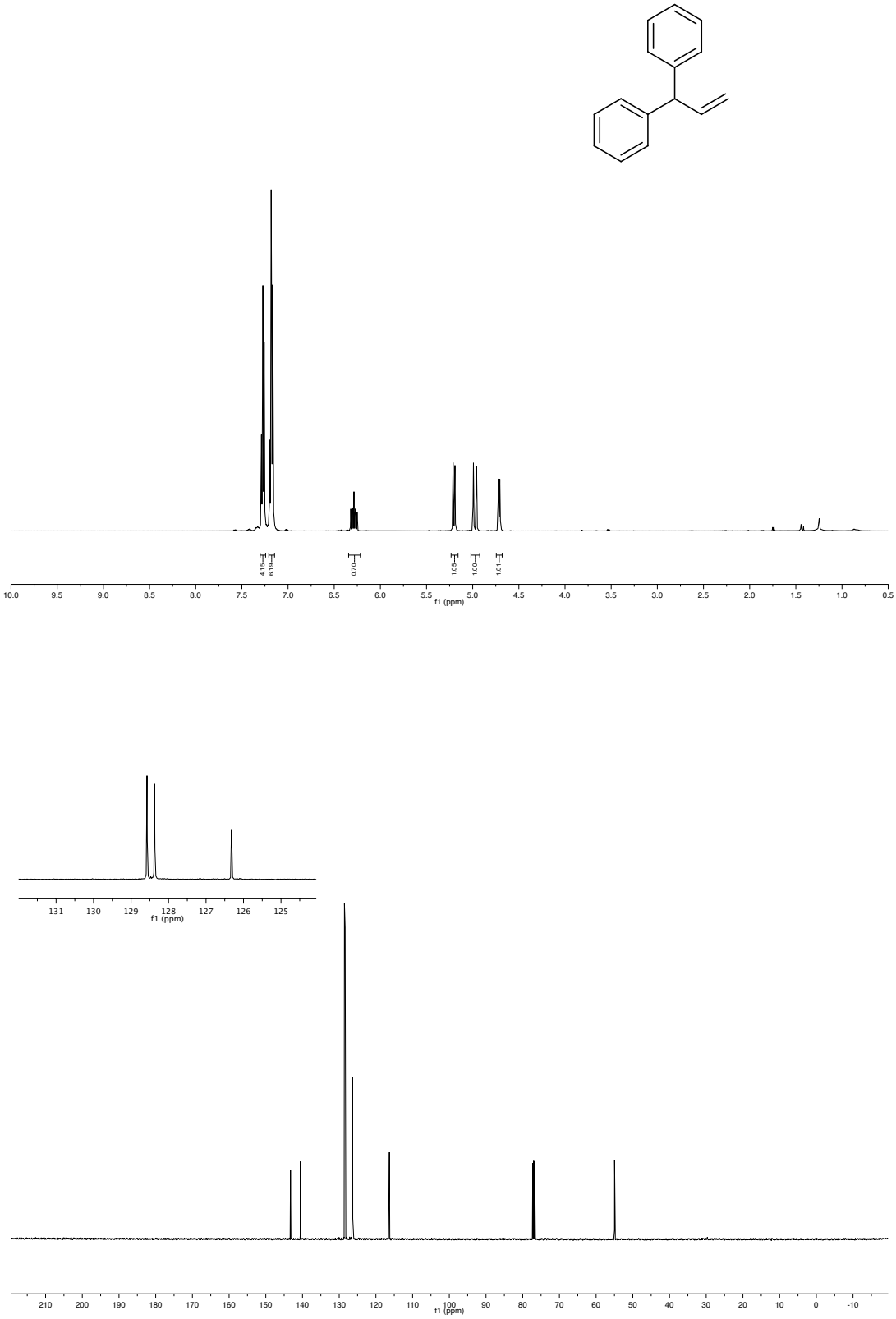


Figure S2 (**4a**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of prop-2ene-1,1-diyldibenzene in $CDCl_3$.

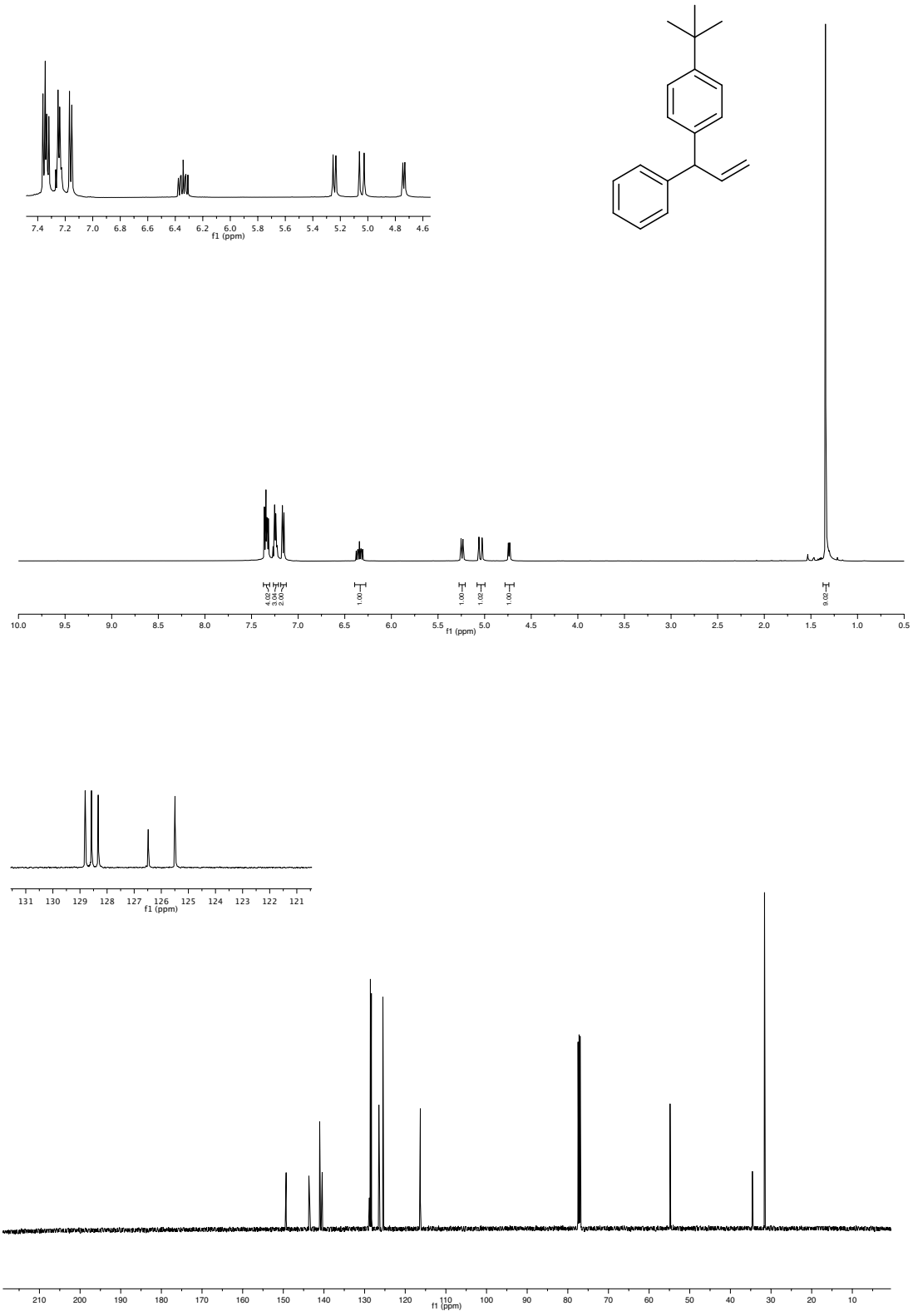


Figure S3 (**4b**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 1-(*tert*-butyl)-4-(1-phenylallyl)benzene in $CDCl_3$.

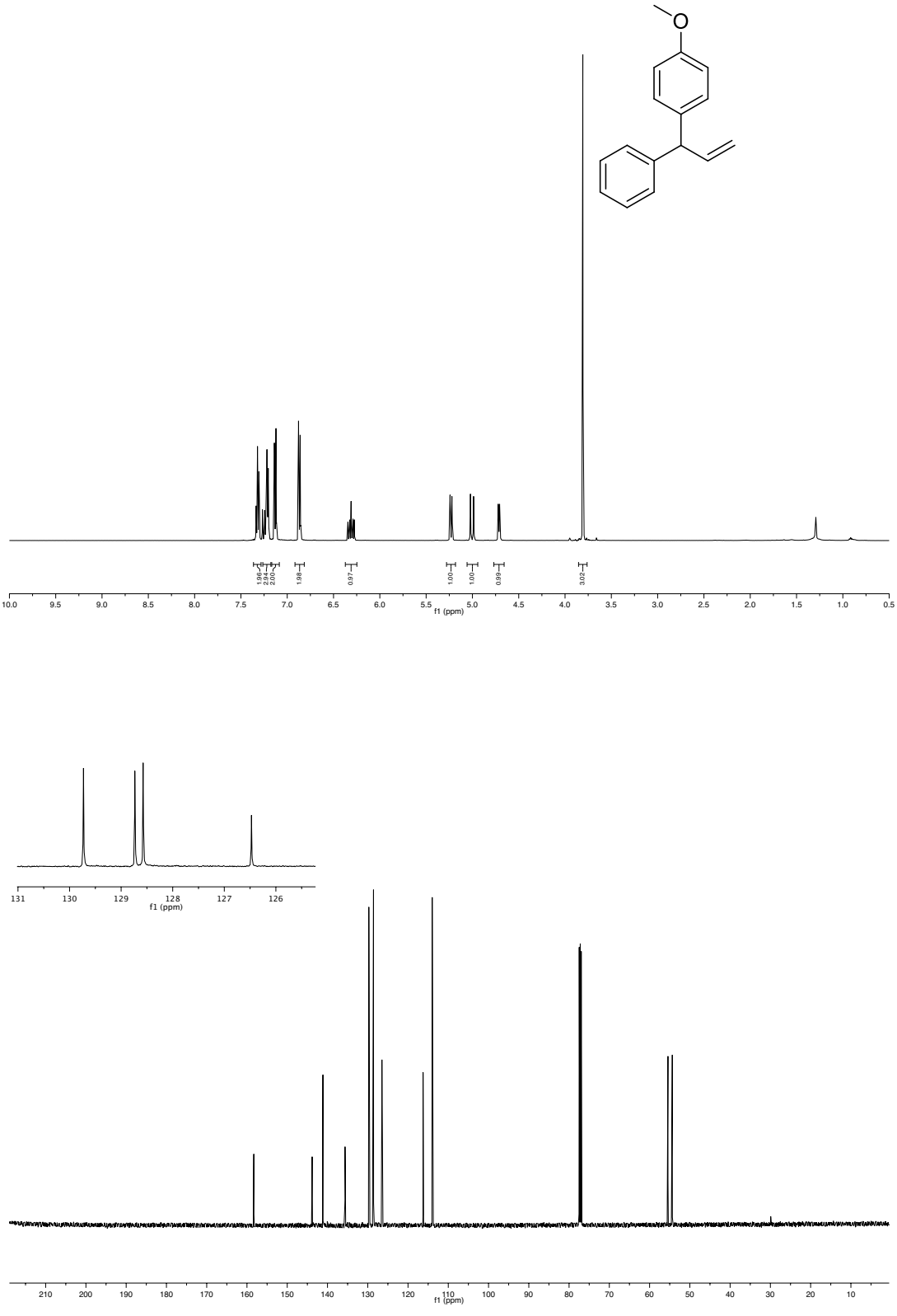


Figure S4 (**4c**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 1-methoxy-4-(1-phenylallyl)benzene in $CDCl_3$.

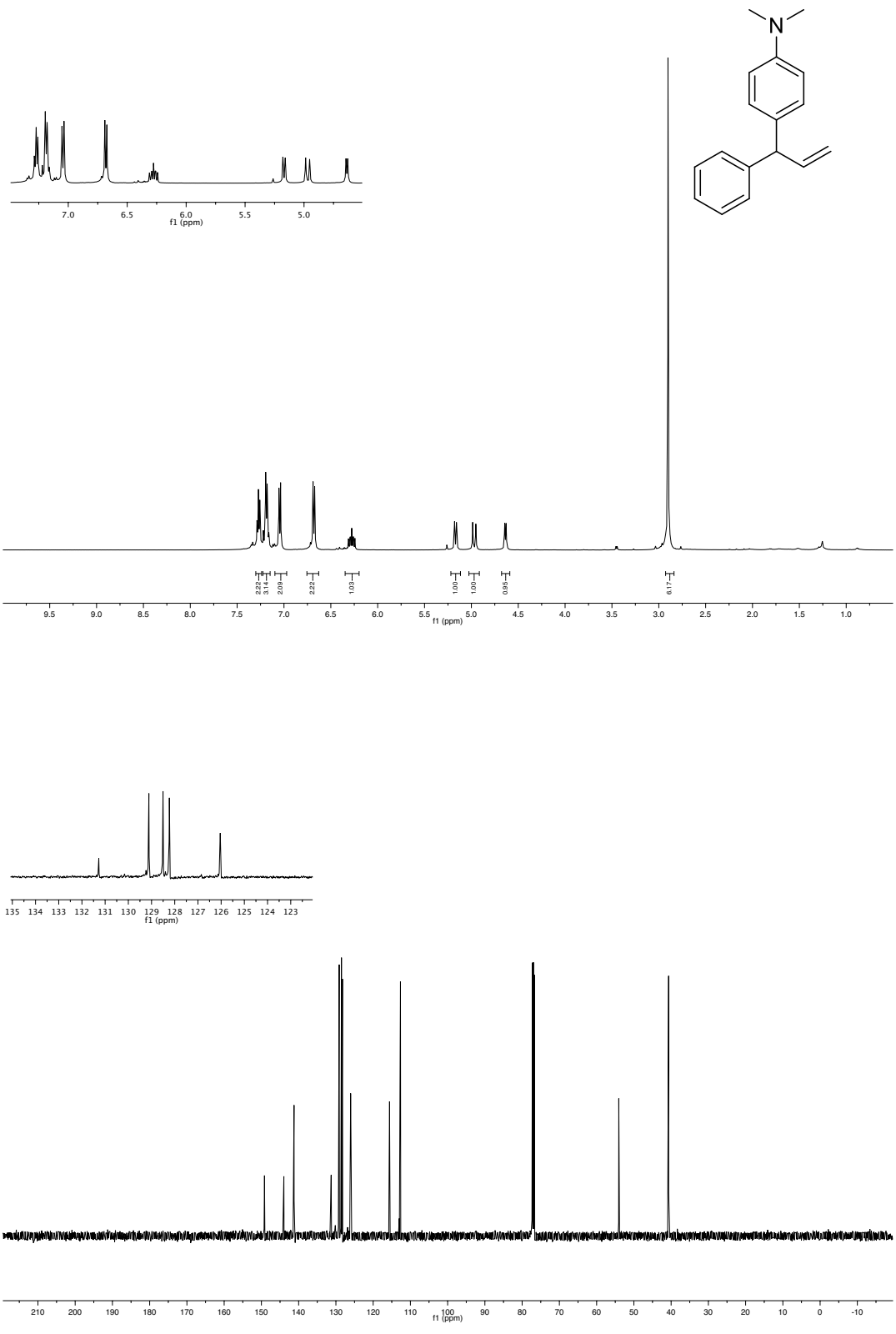


Figure S5 (**4d**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of N,N-dimethyl-4-(1-phenylallyl)aniline in $CDCl_3$.

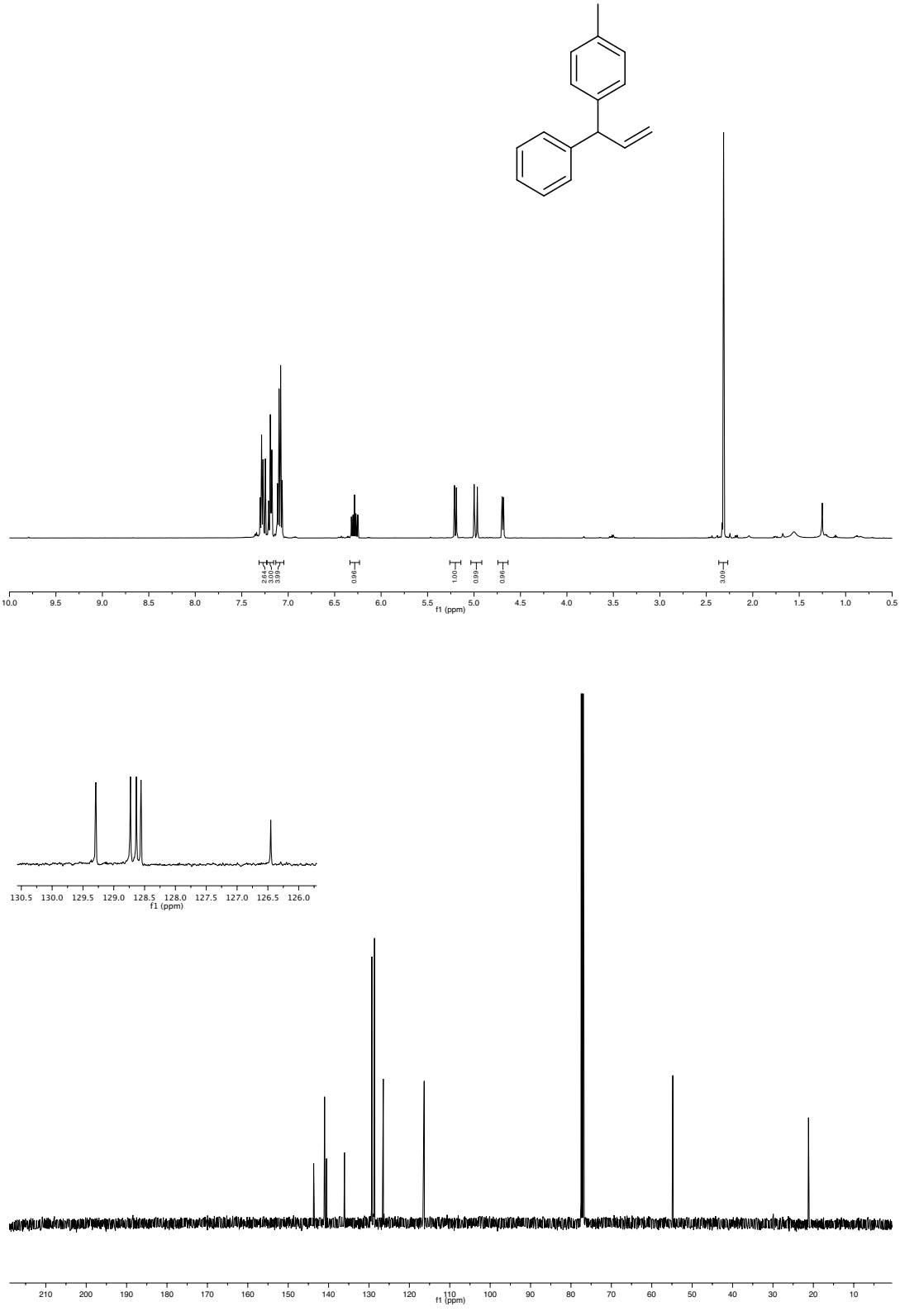


Figure S6 (**4e**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 1-methyl-4-(1-phenylallyl)benzene in $CDCl_3$.

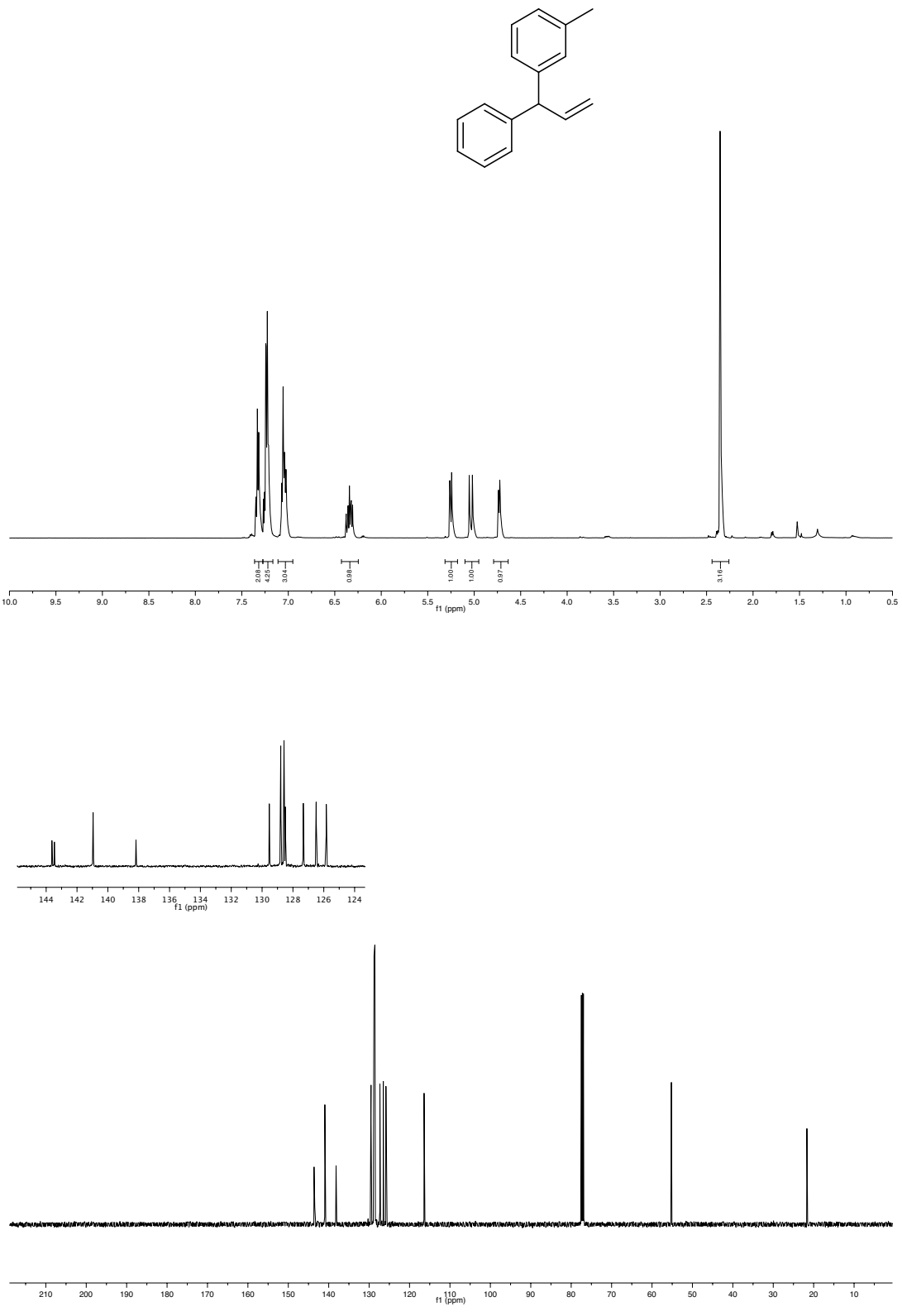


Figure S7 (**4f**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 1-methyl-3-(1-phenylallyl)benzene in $CDCl_3$.

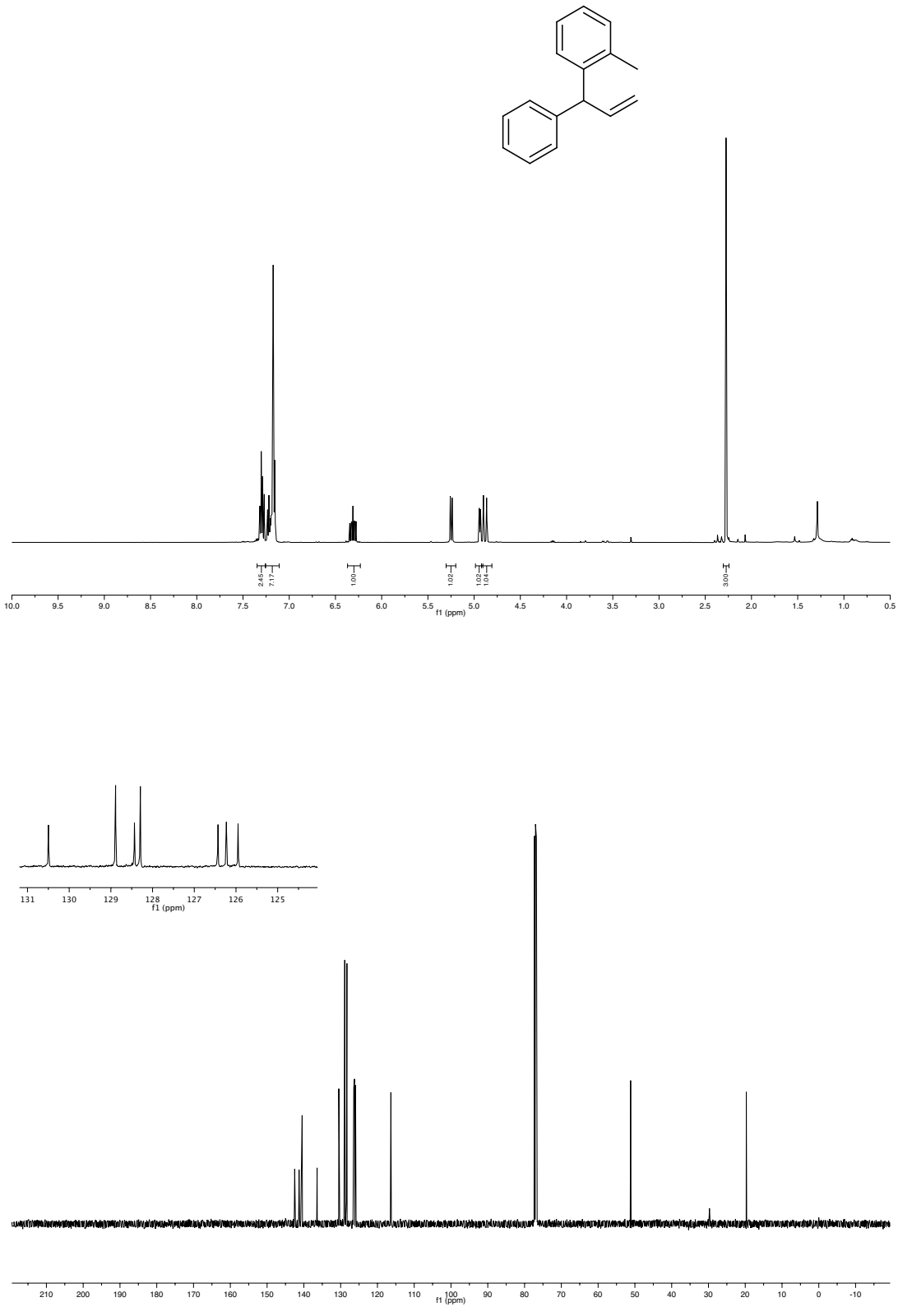


Figure S8 (**4g**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 1-methyl-2-(1-phenylallyl)benzene in $CDCl_3$.

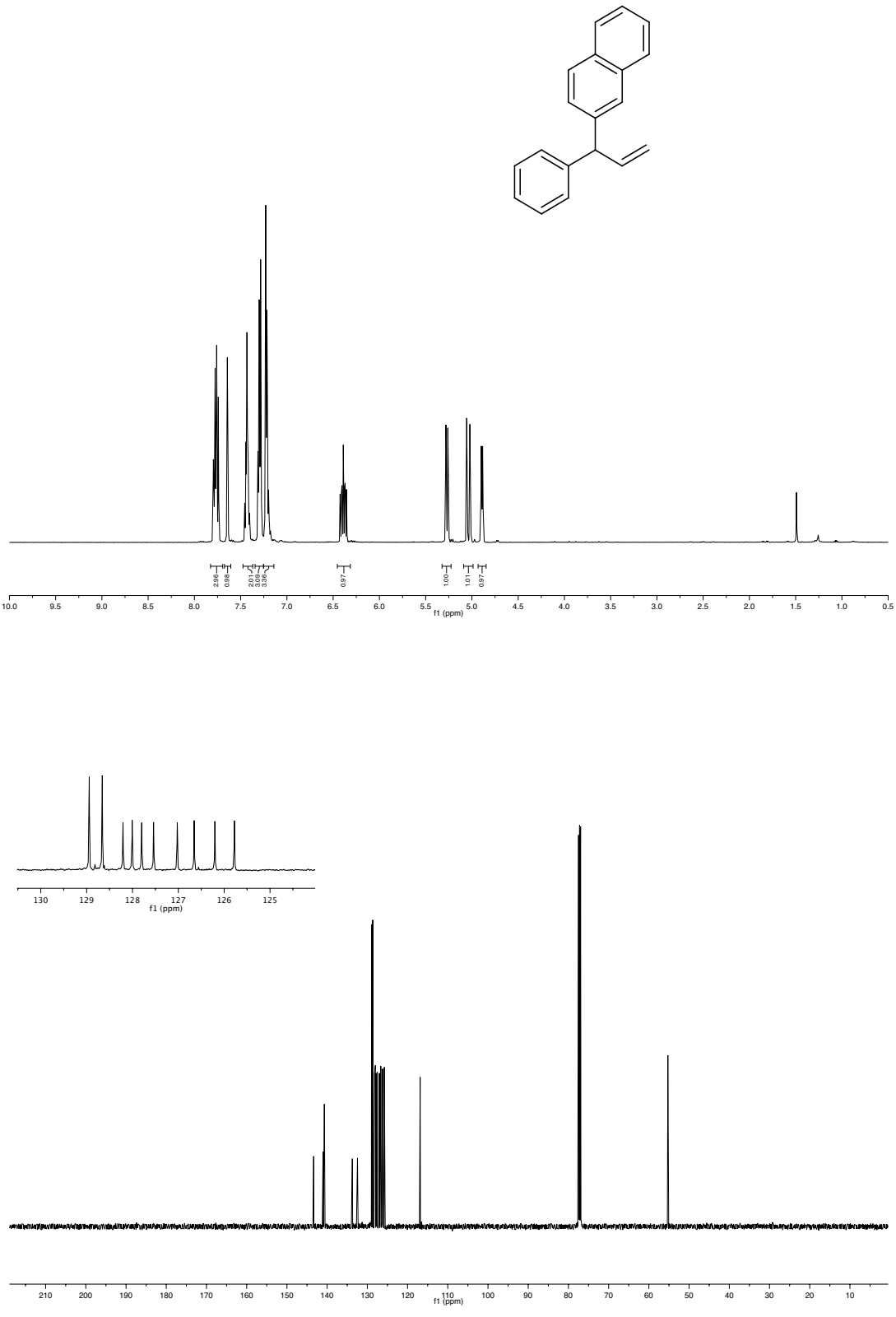


Figure S9 (**4h**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 2-(1-phenylallyl)naphthalene in $CDCl_3$.

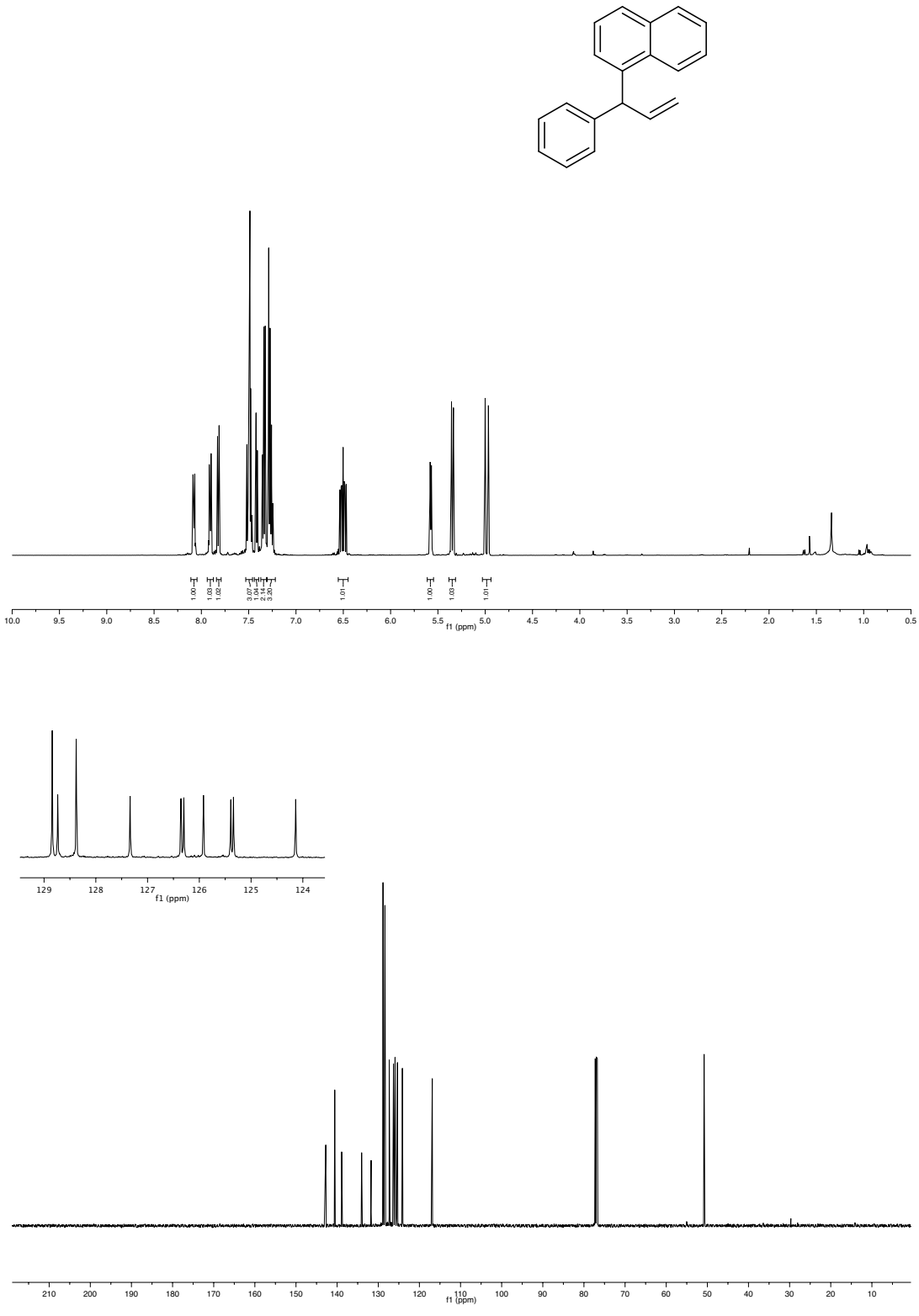


Figure S10 (**4i**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 1-(1-phenylallyl)naphthalene in $CDCl_3$.

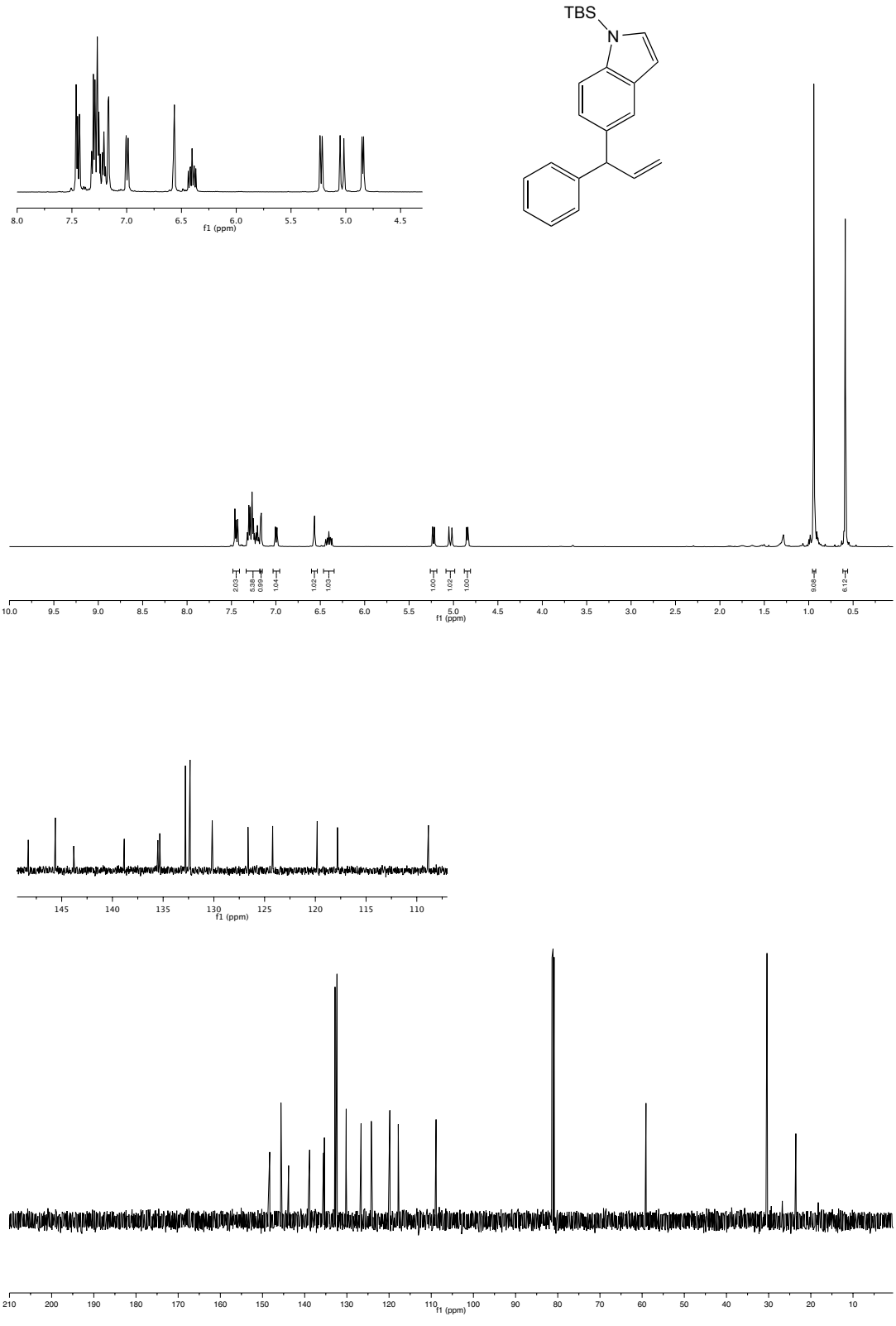


Figure S11 (**4j**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 1-(*tert*-butyldimethylsilyl)-6-(1-phenylallyl)-1H-indole in $CDCl_3$.

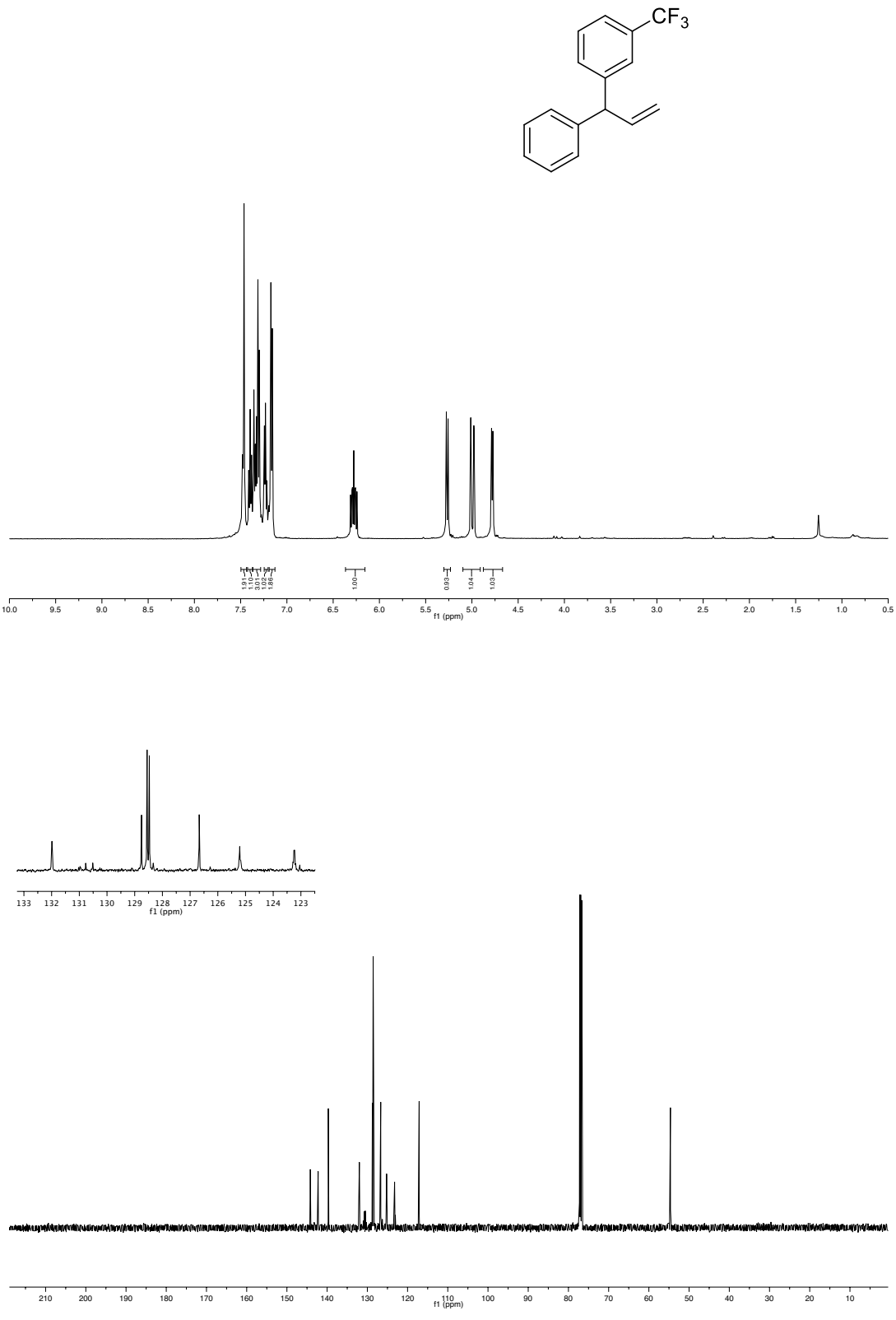


Figure S12 (**4k**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of1-(1-phenylallyl)-3-(trifluoromethyl)benzene in $CDCl_3$.

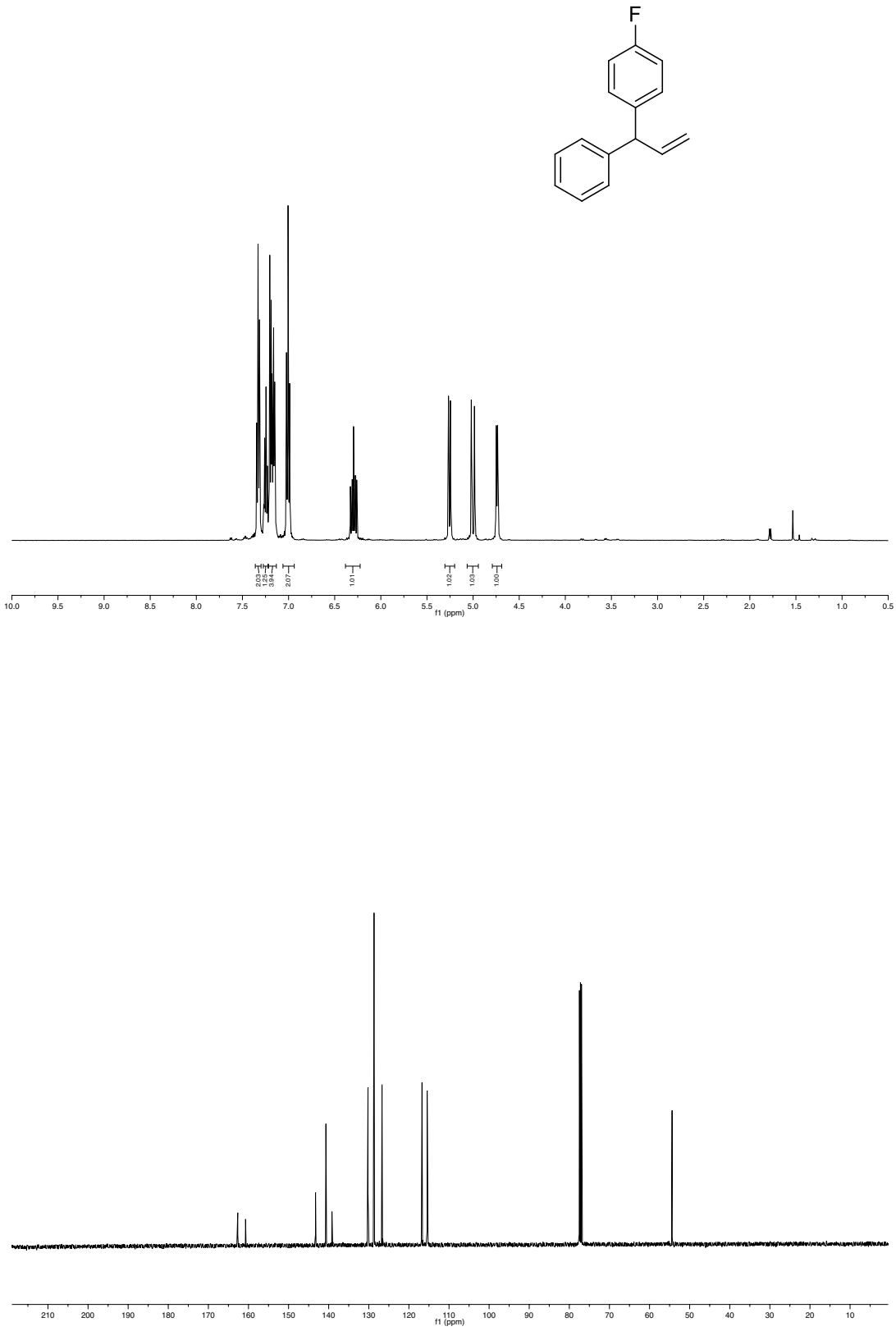


Figure S13 (**4l**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 1-fluoro-4-(1-phenylallyl)benzene in $CDCl_3$.

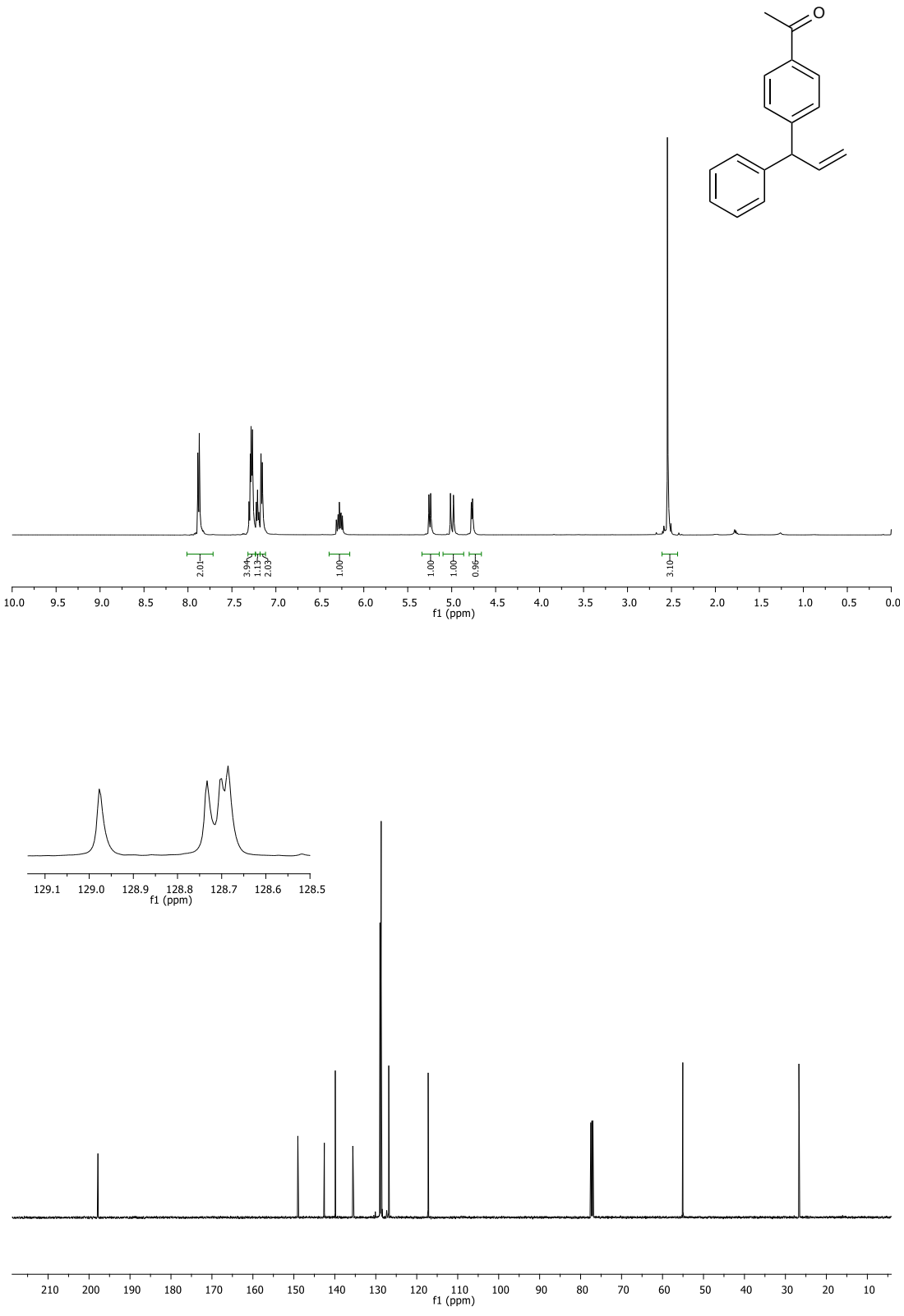


Figure S14 (**4m**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 1-(4-(1-phenylallyl)phenyl)ethan-1-one in $CDCl_3$.

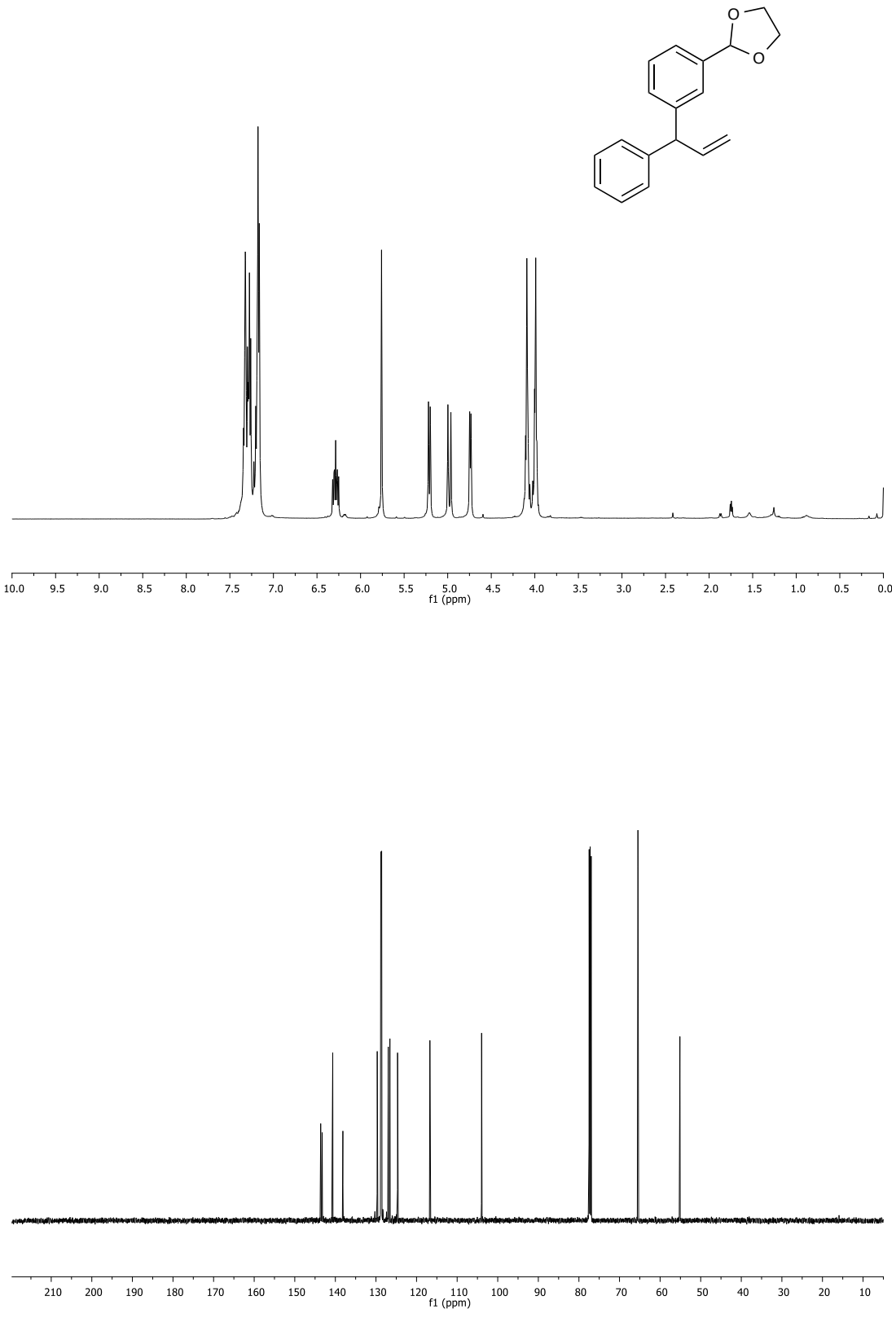


Figure S15 (**4n**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 2-(3-(1-phenylallyl)phenyl)-1,3-dioxolane in $CDCl_3$.

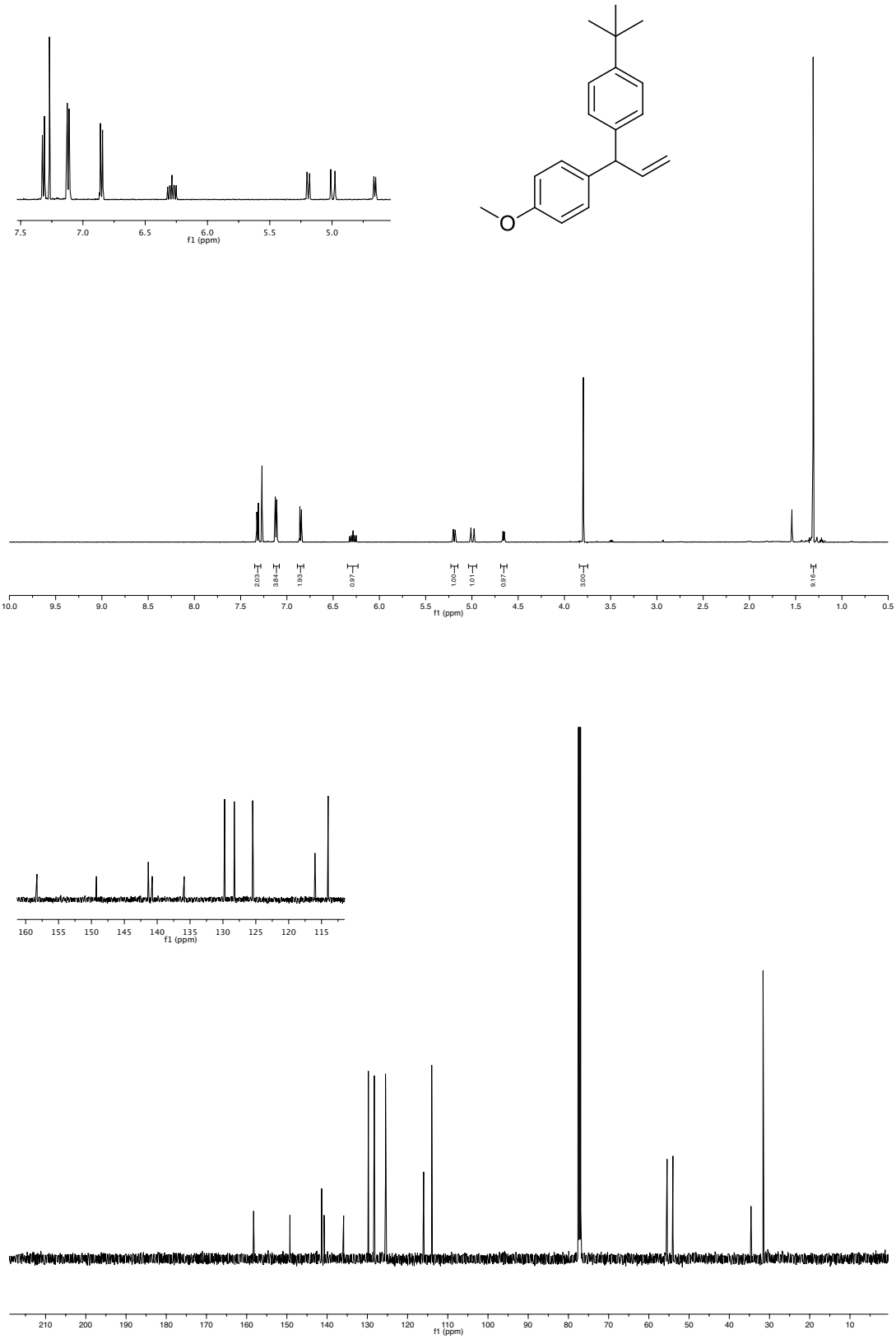


Figure S16 (**4o**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 1-(*tert*-butyl)-4-(1-(4-methoxyphenyl)allyl)benzene in $CDCl_3$.

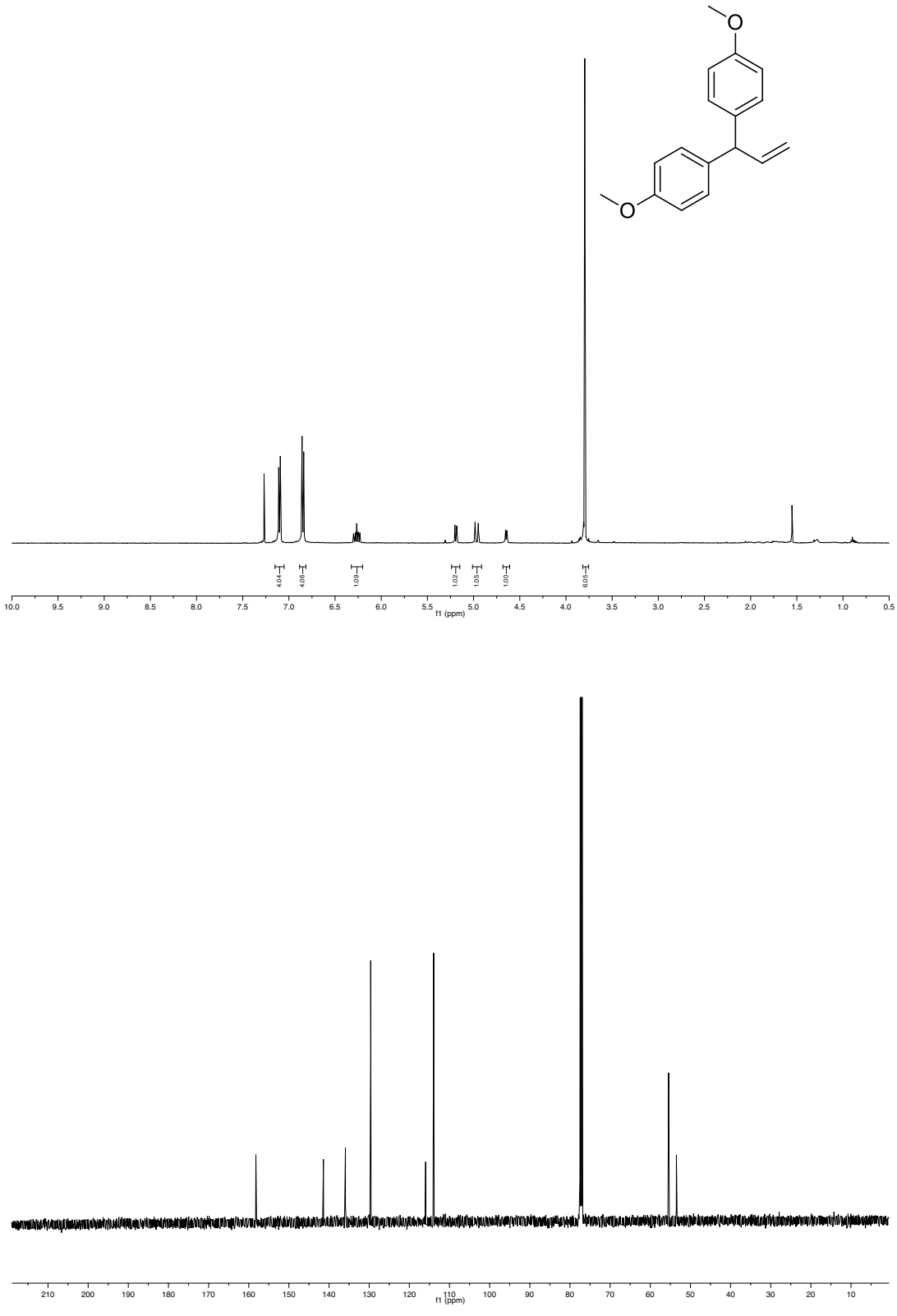


Figure S17 (**4p**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 4,4'-(prop-2-ene-1,1-diyl)bis-methoxybenzene in $CDCl_3$.

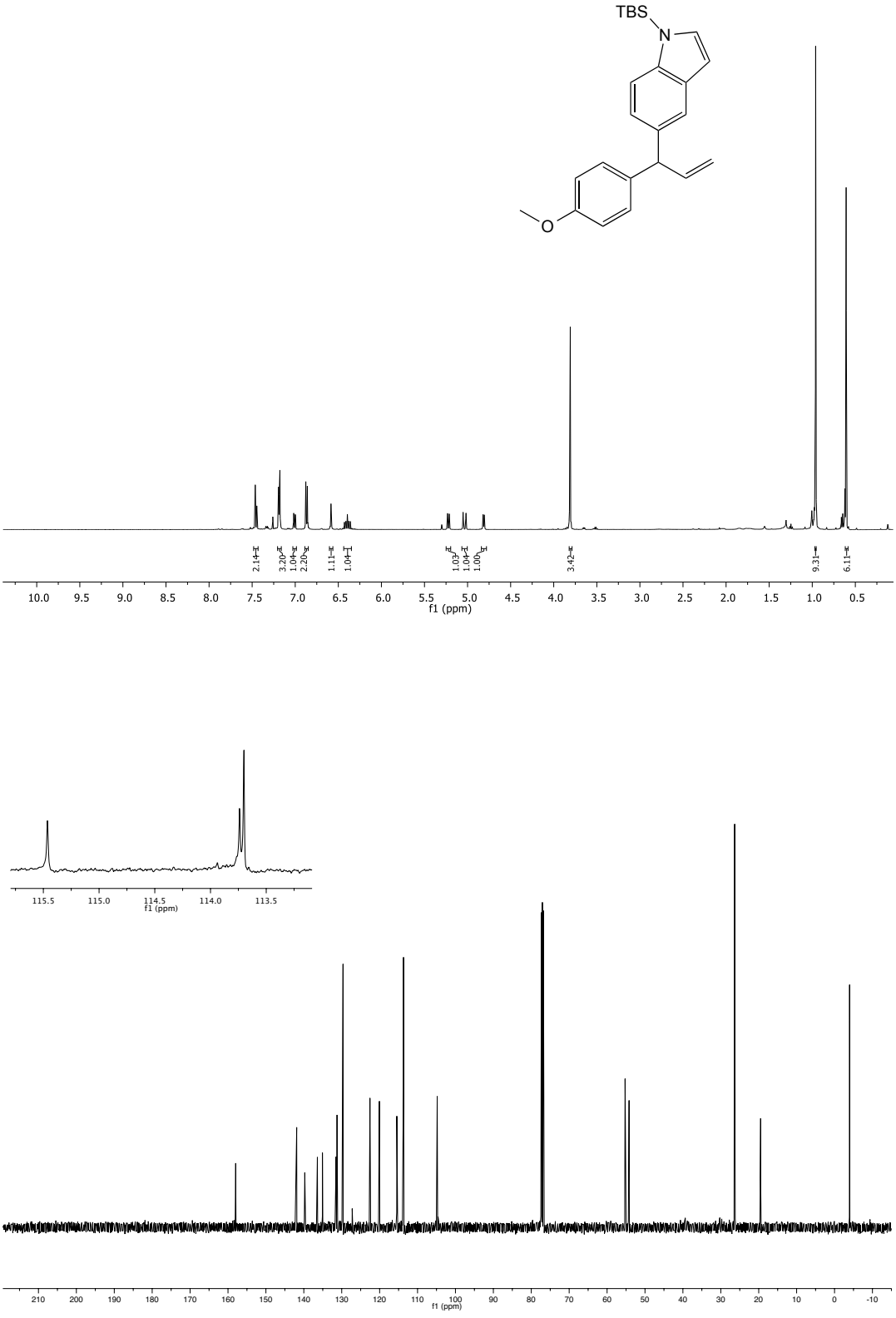


Figure S18 (**4q**) 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 1-(*tert*-butyldimethylsilyl)-5-(1-(4-methoxyphenyl)allyl)-1*H*-indole in $CDCl_3$.

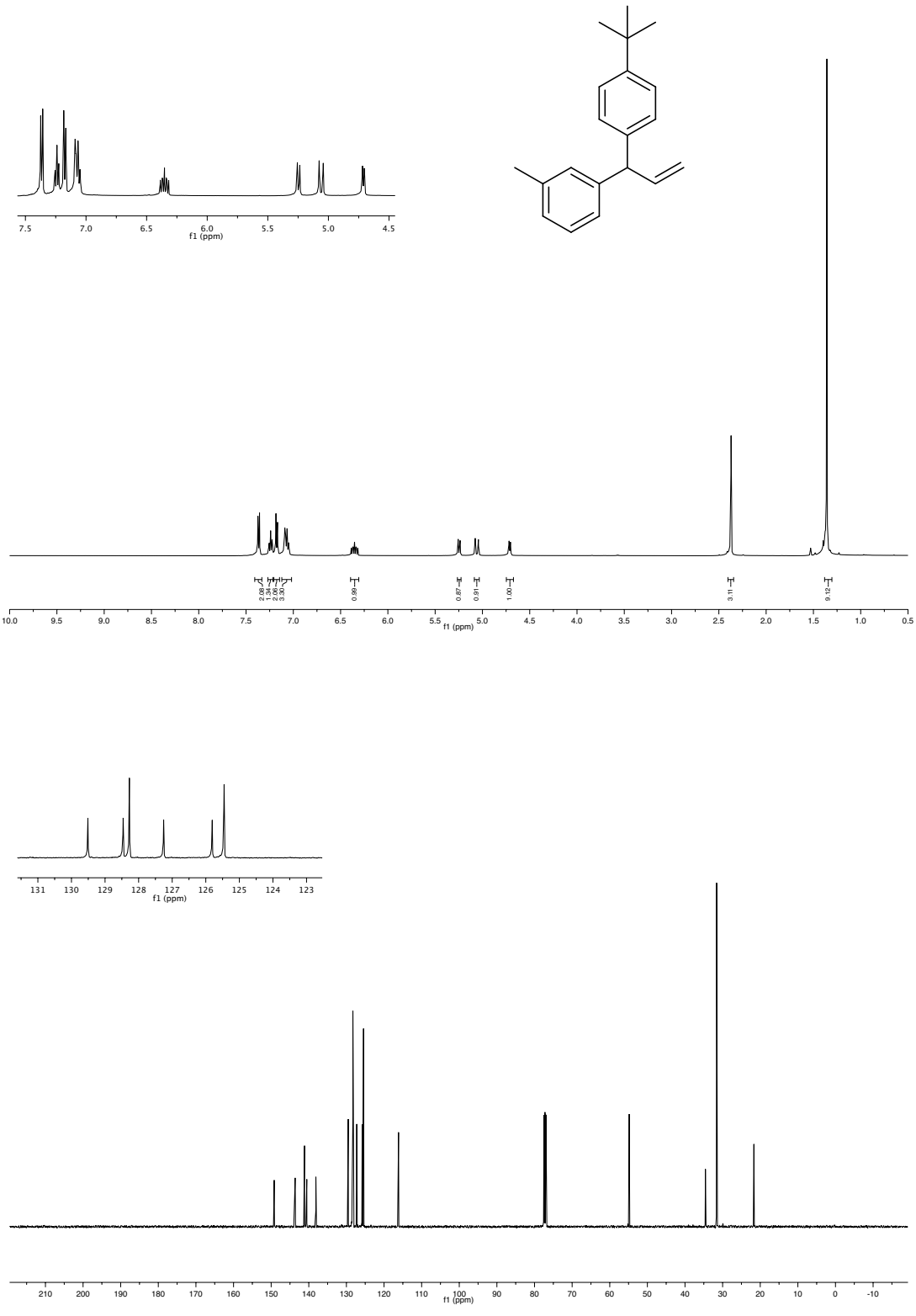


Figure S19 (**4r**) 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 1-(1-(4-(*tert*-butyl)phenyl)allyl)-3-methylbenzene in $CDCl_3$.

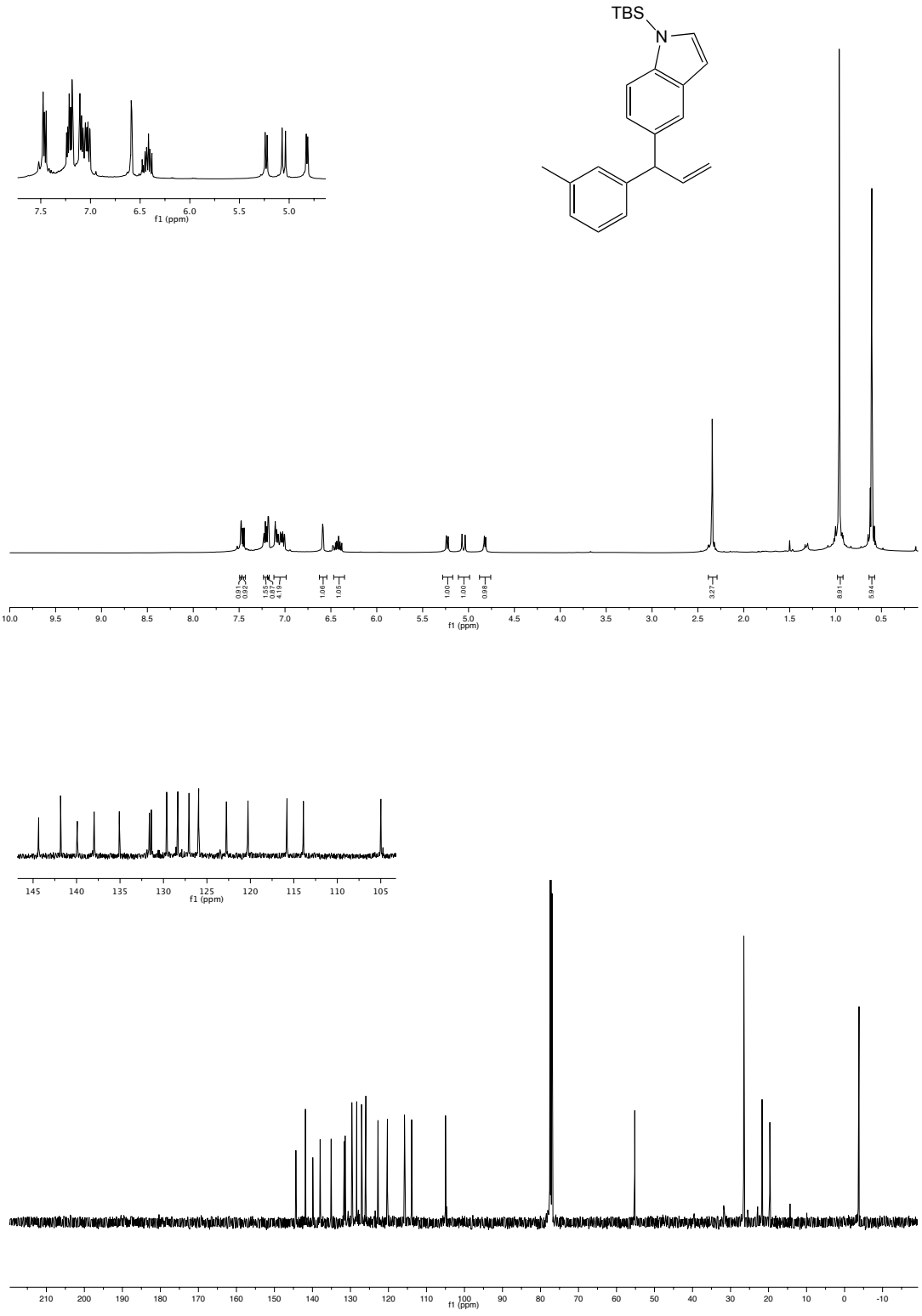


Figure S20 (**4s**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 1-(*tert*-butyldimethylsilyl)-6-(1-(m-tolyl)allyl)-1H-indole in $CDCl_3$.

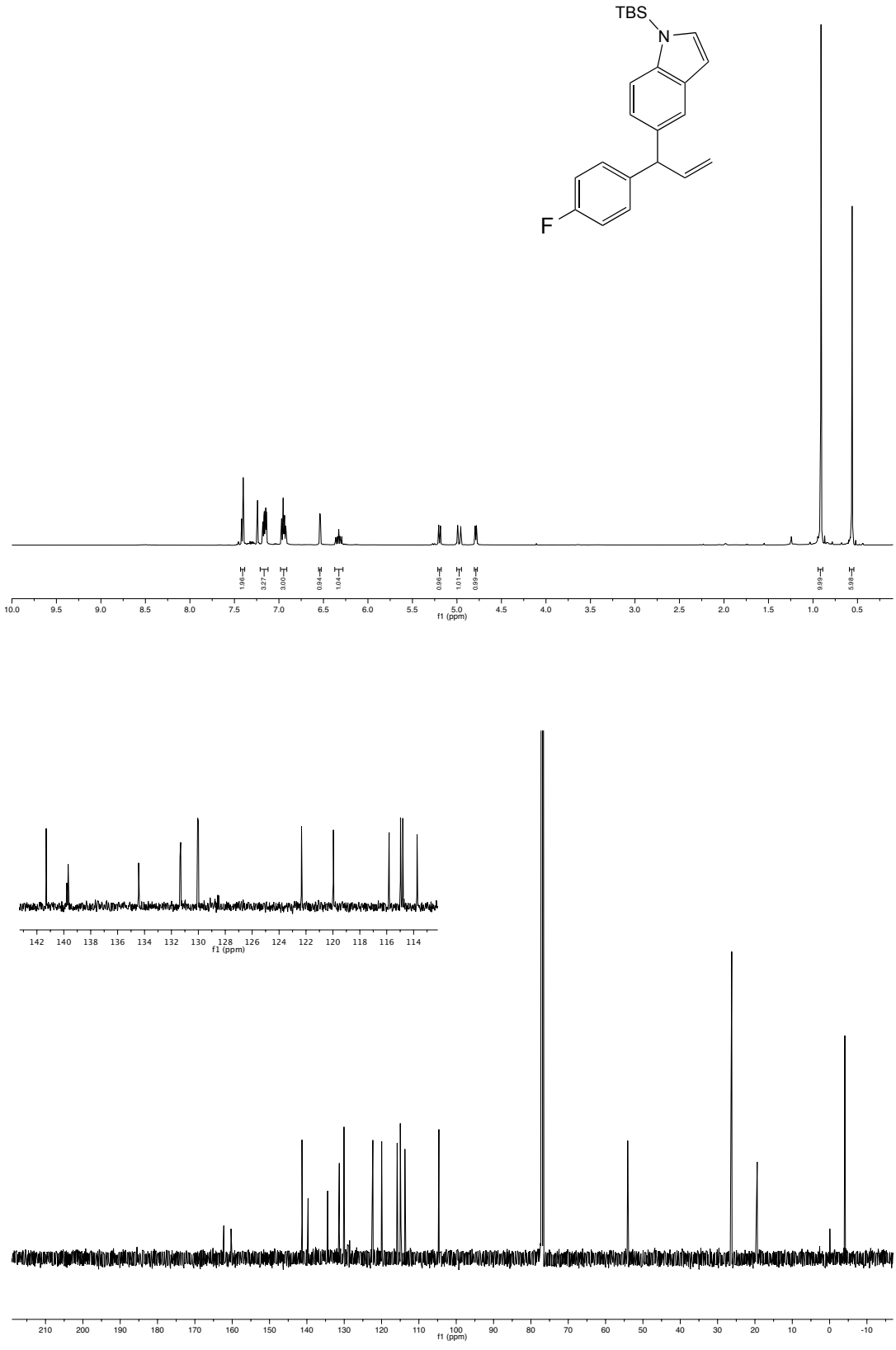


Figure S21 (**4t**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 1-(*tert*-butyldimethylsilyl)-6-(1-(4-fluorophenyl)allyl)-1H-indole in $CDCl_3$**.**

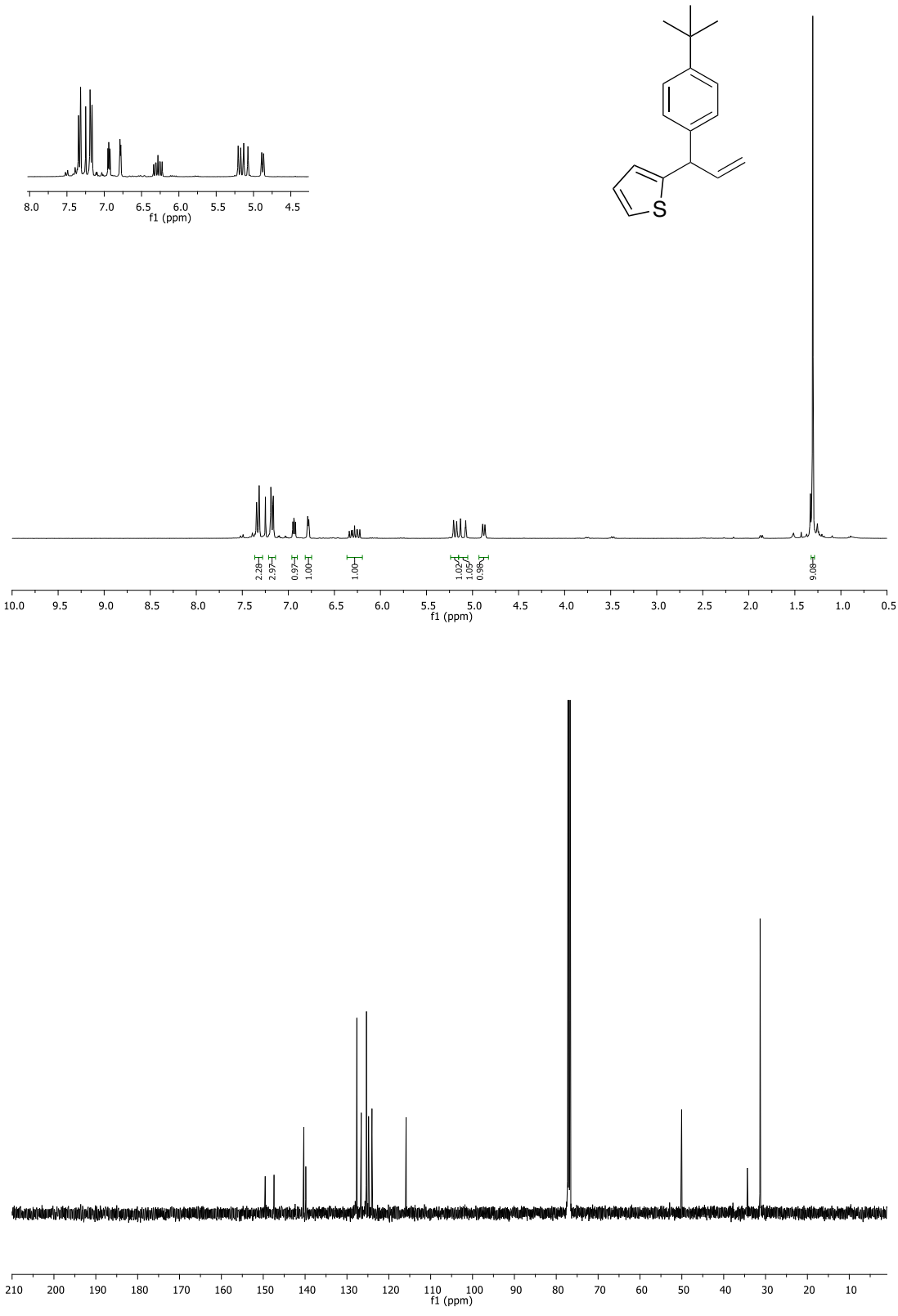


Figure S22 (**4u**). 300 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 2-(1-(4-(*tert*-butyl)phenyl)allyl)thiophene in $CDCl_3$**.**

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