Palladium-Catalyzed Direct α-Arylation of Benzyl Thioethers with Aryl Bromides

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Supporting Information

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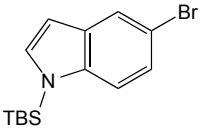
General Methods. All reactions were performed under nitrogen using oven-dried glassware and standard Schlenk or vacuum line techniques. Air- and moisture-sensitive solutions were handled under nitrogen and transferred via syringe. Anhydrous cyclopentyl methyl ether (CPME), dimethoxyethane (DME) and dioxane 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 Whatman Partisil K6F 250 μm precoated 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.

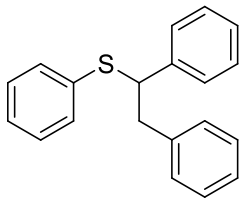
Preparation of Aryl Bromides.



5-Bromo-1-(*tert*-butyldimethylsilyl)-1*H*-indole (3k): Compound **3k** was prepared according to literature procedure.[1] The NMR spectral data match the previously published data.[1]

Procedure and Characterization for the Deprotonation/Benzylation of Benzyl phenyl sulfide.

An oven-dried 10 mL reaction vial equipped with a stir bar was charged with $KN(SiMe_3)_2$ (0.2 mmol, 2 equiv) under a nitrogen atmosphere followed by 1 mL of dry CPME, and the reaction mixture was stirred for 5 min at 24 °C. Benzyl phenyl sulfide (0.2 mmol, 2 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 under reduced pressure. The crude material was loaded onto a silica gel column and purified by flash chromatography.



(1,2-Diphenylethyl)(phenyl)sulfane. The reaction was performed with benzyl phenyl sulfide (**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 reaction mixture was stirred for 24h at 24 °C, quenched with three drops of H_2O, diluted with 1 mL of dichloromethane, and filtered over a pad of silica. The pad was rinsed with additional dichloromethane, and the solution was concentrated in vacuo. The crude material was purified by flash chromatography on silica gel (eluted with hexanes) to give the product (21.4 mg, 74% yield) as a colorless oil. The NMR spectral data match the previously published data.[2]

With NaHMDS: 45% yield.

With LiHMDS: 27% yield.

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

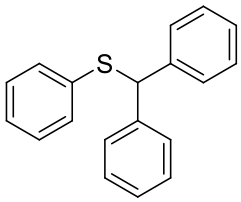
Procedures and Characterizations for the Pd-Catalyzed DCCP of Benzyl Phenyl Sulfides

General Procedure A: An oven-dried 10 mL reaction vial equipped with a stir bar was charged with $LiN(SiMe_3)_2$ (2 equiv) and the benzyl thioether (1 equiv) under a nitrogen atmosphere. A 1 mL solution (from a stock solution) of $[PdCl(allyl)]_2$ (5 mol %) and NiXantPhos (20 mol %) in dry THF was added to the vial via a syringe. After stirring for 5 min at 24 °C, aryl bromide (2 equiv) was added to the reaction mixture. The reaction mixture was stirred for 30 min at 24 °C, quenched with three drops of H_2O, diluted with 1 mL of dichloromethane, and filtered over a pad of silica. The pad was rinsed with additional dichloromethane, and the solution was concentrated under reduced pressure. The crude material was loaded onto a silica gel column and purified by flash chromatography.

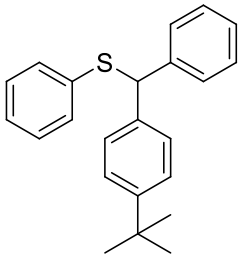
General Procedure B: An oven-dried 10 mL reaction vial equipped with a stir bar was charged with the benzyl thioether (1 equiv) under a nitrogen atmosphere. A 1 mL solution (from a stock solution) of $[PdCl(allyl)]_2$ (5 mol %) and NiXantPhos (20 mol %) in dry THF was added to the vial via a syringe. After stirring for 5 min at 24 °C, aryl bromide (2 equiv) was added to the reaction mixture followed by slow addition of a solution of $LiN(SiMe_3)_2$ (2 equiv) in 0.5 mL of THF for 40 min. The reaction mixture was stirred for 15 min at 24 °C, quenched with three drops of H_2O, diluted with 1 mL of dichloromethane, and filtered over a pad of silica. The pad was rinsed with additional dichloromethane, and the solution was concentrated under reduced pressure. The crude material was loaded onto a silica gel column and purified by flash chromatography.

General Procedure C: An oven-dried 10 mL reaction vial equipped with a stir bar was charged with KO-*t*Bu (2 equiv) and the benzyl thioether (1 equiv) under a nitrogen atmosphere. A 1 mL solution (from a stock solution) of $[PdCl(allyl)]_2$ (5 mol %) and

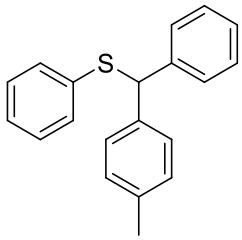
NiXantPhos (20 mol %) in dry THF was added to the vial via a syringe. After stirring for 5 min at 24 °C, aryl bromide (2 equiv) was added to the reaction mixture. The reaction mixture was stirred for 30 min at 50 °C, cooled to room temperature, quenched with three drops of H_2O, diluted with 1 mL of dichloromethane, and filtered over a pad of silica. The pad was rinsed with additional dichloromethane and the solution was concentrated under reduced pressure. The crude material was loaded onto a silica gel column and purified by flash chromatography.



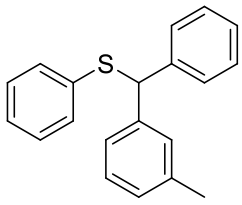
4a: Benzhydryl(phenyl)sulfane. The reaction was performed following General Procedure A with benzyl phenyl sulfide (**1a**) (20.0 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and bromobenzene (**3a**) (21 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (87% ^{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 give the product **4a** as a colorless solid (23.4 mg, 85% yield). The NMR spectral data match the previously published data.[3]



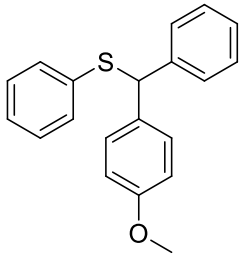
4b: ((4-(*tert*-Butyl)phenyl)(phenyl)methyl)(phenyl)sulfane. The reaction was performed following General Procedure B with benzyl phenyl sulfide (**1a**) (20.0 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and 4-*tert*-butyl bromobenzene (**3b**) (34.3 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (88% ^{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 give the product **4b** as a colorless solid (27.8 mg, 84% yield). Melting point: 65-68 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (d, J = 8.0 Hz, 2H), 7.39 – 7.08 (m, 12H), 5.51 (s, 1H), 1.26 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 150.0, 141.2, 137.8, 136.3, 130.3, 128.6, 128.4, 128.3, 127.9, 127.1, 126.4, 125.4, 57.0, 34.4, 31.2. IR (neat) 3058, 2962, 1583, 1480, 1363, 1268, 1025, 811, 737, 700, 611 cm^{-1}. HRMS *m/z* 331.1524 [$(M-H)^+$; calcd for $C_{23}H_{23}S$: 331.1520].



4c: Phenyl(phenyl(p-tolyl)methyl)sulfane. The reaction was performed following General Procedure B with benzyl phenyl sulfide (**1a**) (20.0 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and 4-bromotoluene (**3c**) (24 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 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 give the product **4c** as a colorless oil (23.8 mg, 82% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.33 – 7.26 (m, 4H), 7.26 – 7.20 (m, 3H), 7.20 – 7.15 (m, 2H), 7.15 – 7.05 (m, 3H), 5.53 (s, 1H), 2.31 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.2, 137.9, 136.8, 136.3, 130.3, 129.2, 128.6, 128.4, 128.3, 128.2, 127.1, 126.4, 57.0, 21.0. IR (neat) 3055, 3020, 2929, 2875, 1608, 1588, 1510, 1423, 1442, 1089, 1022, 735, 690 cm^{-1}. HRMS *m/z* 289.1049 [(M-H)$^+$; calcd for $C_{20}H_{17}S$: 289.1051].

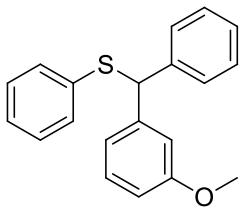


4d: Phenyl(phenyl(m-tolyl)methyl)sulfane. The reaction was performed following General Procedure A with benzyl phenyl sulfide (**1a**) (20.0 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and 3-bromotoluene (**3d**) (24.3 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (87% ^{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 give the product **4d** as a colorless oil (24.0 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.36 (m, 2H), 7.31 – 7.25 (m, 2H), 7.25 – 7.08 (m, 9H), 7.03 (d, *J* = 7.3 Hz, 1H), 5.48 (s, 1H), 2.27 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.1, 140.8, 138.1, 136.2, 130.3, 128.9, 128.6, 128.4, 128.4, 128.3, 128.0, 127.1, 126.4, 125.3, 57.3, 21.4. IR (neat) 3058, 3025, 2919, 2850, 1604, 1583, 1480, 1450, 1438, 1088, 1025, 737, 691 cm^{-1}. HRMS *m/z* 289.1055 [(M-H)$^+$; calcd for $C_{20}H_{17}S$: 289.1051].

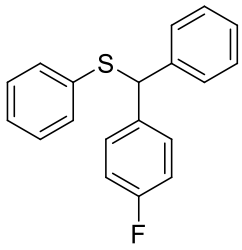


4e: ((4-Methoxyphenyl)(phenyl)methyl)(phenyl)sulfane. The reaction was performed following General Procedure B with benzyl phenyl sulfide (**1a**) (20.0 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and 4-bromoanisole (**3e**) (25.3 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M) at 0 °C. The

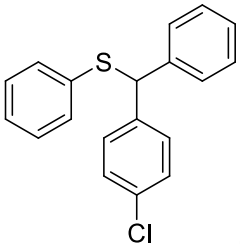
crude reaction mixture was filtered through a short pad of silica to afford the product (77% ^{1}H NMR yield with internal standard CH_2Br_2). The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes) to give the product **4e** as a colorless solid (22.3 mg, 73% yield). The NMR spectral data match the previously published data.[4]



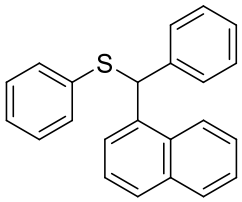
4f: ((3-Methoxyphenyl)(phenyl)methyl)(phenyl)sulfane. The reaction was performed following General Procedure A with benzyl phenyl sulfide (**1a**) (20.0 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and 3-bromoanisole (**3f**) (25.3 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (97% ^{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 give the product **4f** as a colorless oil (28.5 mg, 93% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 7.8 Hz, 2H), 7.31 – 7.10 (m, 9H), 7.03 – 6.97 (m, 2H), 6.76 (dd, J = 8.2, 2.6 Hz, 1H), 5.51 (s, 1H), 3.76 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.6, 142.5, 140.8, 136.1, 130.4, 129.5, 128.7, 128.5, 128.3, 127.2, 126.5, 120.7, 114.1, 112.6, 57.3, 55.1. IR (neat) 3058, 2933, 2834, 1597, 1583, 1488, 1451, 1437, 1263, 1142, 1049, 778, 738, 691 cm^{-1}. HRMS *m/z* 305.0996 [(M-H)$^+$; calcd for $C_{20}H_{17}OS$: 305.1000].



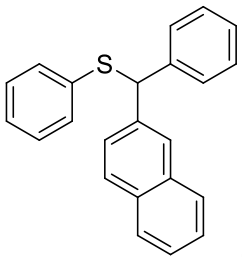
4g: ((4-Fluorophenyl)(phenyl)methyl)(phenyl)sulfane. The reaction was performed following General Procedure A with benzyl phenyl sulfide (**1a**) (20.0 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and 4-bromoflourobenzene (**3g**) (22 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (52% ^{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 give the product **4g** as a colorless oil (14.7 mg, 50% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 4H), 7.28 (dd, J = 16.6, 8.8 Hz, 3H), 7.26 – 7.20 (m, 3H), 7.20 – 7.14 (m, 2H), 6.96 (t, J = 8.6 Hz, 2H), 5.51 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.8 (d, J = 252 Hz), 140.7, 136.8, 135.7, 130.7, 129.9 (d, J = 9 Hz), 128.7, 128.5, 128.2, 127.0 , 126.7, 115.3 (d, J = 21 Hz), 56.7. IR (neat) 3060, 2919, 2850, 1603, 1583, 1505, 1480, 1452, 1438, 1225, 1157, 1095, 1025, 854, 814, 794, 737, 696, 610, 545 cm^{-1}. HRMS *m/z* 295.0962 [(M+H)$^+$; calcd for $C_{19}H_{16}FS$: 295.0956].



4h: ((4-Chlorophenyl)(phenyl)methyl)(phenyl)sulfane. The reaction was performed following General Procedure A with benzyl phenyl sulfide (**1a**) (20.0 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and 4-bromochlorobenzene (**3h**) (23 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (66% ^{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 give the product **4h** as a colorless oil (19.5 mg, 63% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.26 – 7.20 (m, 5H), 7.19 – 7.13 (m, 3H), 5.51 (s, 1H). 13C{1H} (126 MHz, $CDCl_3$) δ 140.4, 139.6, 135.5, 132.9, 130.7, 129.7, 128.7, 128.6, 128.6, 128.2, 127.4, 126.8, 56.8. IR (neat) 3027, 3058, 2957, 2922, 2850, 1582, 1488, 1480, 1451, 1438, 1372, 1265, 1088, 1014, 738, 694 cm^{-1}. HRMS *m/z* 311.0056 [$(M+H)^+$; calcd for $C_{19}H_{16}ClS$: 311.0661].

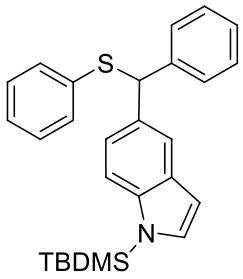


4i: (Naphthalen-1-yl(phenyl)methyl)(phenyl)sulfane. The reaction was performed following General Procedure B with benzyl phenyl sulfide (**1a**) (20.0 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and 1-bromonaphtalene (**3i**) (28 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (77% ^{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 give the product **4i** as a yellowish oil (23.5 mg, 72% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 – 8.06 (m, 1H), 7.92 – 7.83 (m, 1H), 7.79 (dd, *J* = 12.5, 7.7 Hz, 2H), 7.52 – 7.40 (m, 5H), 7.32 – 7.06 (m, 8H), 6.29 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 140.6, 136.8, 135.7, 134.0, 131.0, 129.3, 128.9, 128.7, 128.6, 128.5, 128.2, 127.2, 126.8, 126.2, 126.2, 125.6, 125.4, 123.5, 53.5. IR (neat) 3058, 2922, 2851, 1597, 1582, 1479, 1438, 1395, 1264, 1086, 1026, 777, 737, 695 cm^{-1}. HRMS *m/z* 325.1067 [$(M-H)^+$; calcd for $C_{23}H_{17}S$: 325.1051].

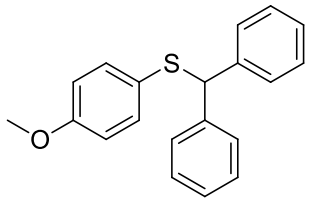


4j: (Naphthalen-2-yl(phenyl)methyl)(phenyl)sulfane. The reaction was performed following General Procedure B with benzyl phenylsulfide (**1a**) (20.0 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and 2-bromonaphtalene (**3j**) (41,4 mg, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude

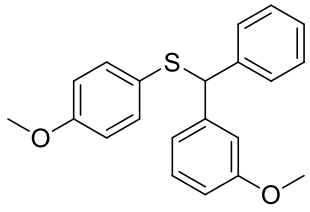
reaction mixture was filtered through a short pad of silica to afford the product (75% ^{1}H NMR yield with internal standard CH_2Br_2). The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes) to give the product **4j** as a yellowish solid (22.8mg, 70% yield). Melting point: 84-89 ^oC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.72 (m, 4H), 7.70 – 7.55 (m, 1H), 7.55 – 7.39 (m, 4H), 7.40 – 7.08 (m, 8H), 5.71 (s, 1H). 13C{1H} (126 MHz, $CDCl_3$) δ 140.8, 138.3, 136.0, 133.2, 132.6, 130.5, 128.7, 128.5, 128.5, 128.3, 127.9, 127.5, 127.3, 127.0, 126.6, 126.6, 126.1, 125.9, 57.6. IR (neat) 3057, 3026, 2957, 2922, 2850, 1655, 1598, 1582, 1492, 1479, 1450, 1438, 1287, 1265, 1025, 813, 739, 696 cm^{-1}. HRMS *m/z* 326.1121 [$(M)^+$; calcd for $C_{23}H_{18}S$: 326.1129].



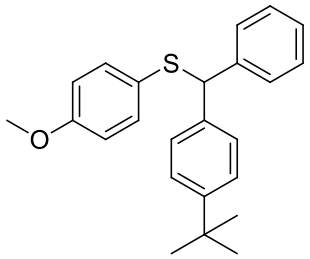
4k: 1-(*tert*-Butyldimethylsilyl)-5-(phenyl(phenylthio)methyl)-1H-indole. The reaction was performed following General Procedure A with benzyl phenyl sulfide (**1a**) (20.0 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and 5-bromo-1-(*tert*-butyldimethylsilyl)-1*H*-indole (**3k**) (62.1 mg, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (72% ^{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 give the product **4k** as a yellowish oil (16.3 mg, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 1.6 Hz, 1H), 7.49 (d, *J* = 7.3 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.31 – 7.05 (m, 10H), 6.57 (s, 1H), 5.68 (s, 1H), 0.91 (s, 9H), 0.58 (s, 6H). ^{13}C $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 145.9, 144.3, 141.0, 136.4, 135.5, 135.5, 134.1, 132.6, 132.5, 132.4, 130.9, 130.1, 126.2, 124.3, 117.9, 109.0, 61.7, 30.3, 23.4. IR (neat) 3059, 3026, 2954, 2929, 2857, 1583, 1468, 1290, 1147, 988, 839, 808, 735, 698, 581, 562 cm^{-1}. HRMS *m/z* 430.2030 [$(M+H)^+$; calcd for $C_{27}H_{31}NSSi$: 430.2024].



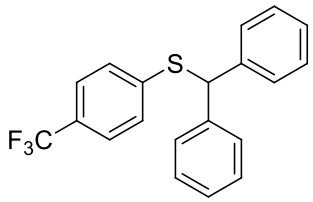
4l: Benzhydryl(4-methoxyphenyl)sulfane. The reaction was performed following General Procedure A with benzyl(4-methoxyphenyl)sulfane (**1b**) (23.0 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and bromobenzene (**3a**) (21 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (84% ^{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 give the product **4l** as a colorless solid (24.4 mg, 80% yield). The NMR spectral data match the previously published data.[5]



4m: (4-Methoxyphenyl)((3-methoxyphenyl)(phenyl)methyl)sulfane. The reaction was performed following General Procedure A with benzyl(4-methoxyphenyl)sulfane (**1b**) (23.0 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and 3-bromoanisole (**3f**) (25.3 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 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 give the product **4m** as a colorless oil (32.6 mg, 97% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 2H), 7.29 – 7.24 (m, 2H), 7.23 – 7.14 (m, 4H), 7.00 – 6.92 (m, 2H), 6.78 – 6.67 (m, 3H), 5.31 (s, 1H), 3.75 (s, 3H), 3.72 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.6, 159.3, 142.9, 141.2, 134.5, 129.3, 128.3, 128.3, 127.0, 126.0, 120.8, 114.3, 114.2, 112.5, 59.2, 55.2, 55.1. IR (neat) 3060, 3026, 3002, 2957, 2936, 2835, 1730, 1593, 1493, 1463, 1435, 1287, 1247, 1173, 1143, 1031, 827, 729, 701, 642 cm^{-1}. HRMS *m/z* 336.1175 [$(M)^+$; calcd for $C_{21}H_{20}O_2S$: 336.1184].

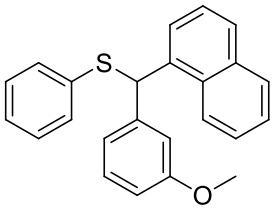


4n: ((4-(*tert*-Butyl)phenyl)(phenyl)methyl)(4-methoxyphenyl)sulfane. The reaction was performed following General Procedure B with benzyl(4-methoxyphenyl)sulfane (**1b**) (23.0 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and 4-*tert*-butyl bromobenzene (**3b**) (34.3 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (87% ^{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 give the product **4n** as a colorless oil (30.0 mg, 83% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, J = 7.7 Hz, 2H), 7.31 – 7.22 (m, 6H), 7.21 – 7.14 (m, 3H), 6.72 – 6.66 (m, 2H), 5.30 (s, 1H), 3.72 (s, 3H), 1.27 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.2, 149.9, 141.5, 138.1, 134.5, 128.4, 128.3, 127.9, 126.9, 126.2, 125.3, 114.2, 58.9, 55.2, 34.4, 31.2. IR (neat) 3057, 2961, 2925, 2866, 1597, 1582, 1509, 1479, 1438, 1266, 1025, 839, 797, 779, 737, 689, 562 cm^{-1}. HRMS *m/z* 331.1531 [$(M\text{-}C_3OH)^+$; calcd for $C_{23}H_{23}S$: 331.1520].

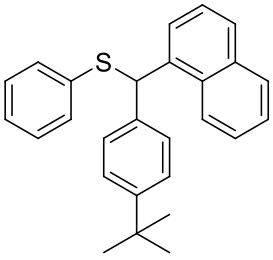


4o: Benzhydryl(4-(trifluoromethyl)phenyl)sulfane. The reaction was performed following General Procedure A with benzyl(4-(trifluoromethyl)phenyl)sulfane (**1c**) (26.8 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4

mg, 0.20 mmol, 2 equiv) and bromobenzene (**3a**) (21 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (64% ^{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 give the product **4o** as a colorless oil (20.6 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.38 (m, 6H), 7.32 (t, *J* = 7.6 Hz, 4H), 7.29 – 7.18 (m, 4H), 5.65 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.7 (d, *J* = 1 Hz), 140.1, 128.7, 128.7, 128.4, 128.3, 128.3, 127.5, 125.5 (q, *J* = 3 Hz), 56.2. IR (neat) 3062, 3028, 2922, 1605, 1493, 1450, 1400, 1337, 1165, 1121, 1094, 1063, 823, 748, 700 cm^{-1}. HRMS *m/z* 344.0851 [(M)$^+$; calcd for $C_{20}H_{15}F_3S$: 344.0847].

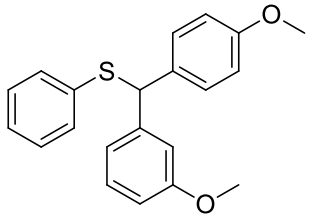


4p: ((3-Methoxyphenyl)(naphthalen-1-yl)methyl)(phenyl)sulfane. The reaction was performed following General Procedure A with (naphthalen-1-ylmethyl)(phenyl)sulfane (**1d**) (25.0 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and 3-bromoanisole (**3f**) (25.3 μL, 0.2 mmol, 2 equiv.) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (73% ^{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 give the product **4p** as a colorless oil (24.9 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.9 Hz, 1H), 7.91 – 7.83 (m, 1H), 7.83 – 7.75 (m, 2H), 7.54 – 7.40 (m, 3H), 7.27 – 7.02 (m, 8H), 6.80 – 6.72 (m, 1H), 6.30 (s, 1H), 3.74 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.7, 142.2, 136.9, 135.7, 134.0, 131.0, 129.5, 129.3, 128.9, 128.8, 128.2, 126.8, 126.3, 126.2, 125.6, 125.4, 123.5, 121.1, 114.5, 112.6, 55.1, 53.5. IR (neat) 3057, 2957, 2933, 2834, 1598, 1573, 1480, 1437, 1261, 1142, 1049, 782, 737, 691 cm^{-1}. HRMS *m/z* 355.1150 [(M-H)$^-$; calcd for $C_{24}H_{19}OS$: 355.1157].

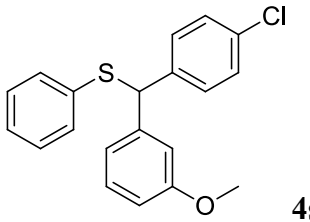


4q: ((4-(*tert*-Butyl)phenyl)(naphthalen-1-yl)methyl)(phenyl)sulfane. The reaction was performed following General Procedure A with (naphthalen-1-ylmethyl)(phenyl)sulfane (**1d**) (25.0 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and 4-*tert*-butyl bromobenzene (**3b**) (34.3 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (69% ^{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 give the product **4q** as a colorless oil (24.8 mg, 65% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.9 Hz, 1H), 7.91 – 7.82 (m, 2H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.50 – 7.41 (m, 3H), 7.40 – 7.33 (m, 2H), 7.33 – 7.26 (m, 2H), 7.26 – 7.17 (m, 3H), 7.16 – 7.07 (m, 2H), 6.32 (s, 1H), 1.29 (s, 9H). 13C{1H} (126 MHz, $CDCl_3$) δ 150.1, 137.4, 137.1, 135.9, 134.0, 131.1, 129.0, 128.8,

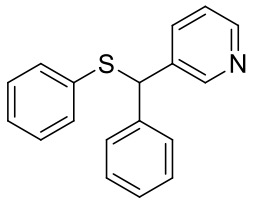
128.7, 128.2, 128.1, 126.7, 126.2, 125.9, 125.5, 125.4, 125.4, 123.5, 53.0, 34.4, 31.2. IR (neat) 3057, 2961, 2925, 2866, 1597, 1582, 158, 1479, 1438, 1394, 1363, 1266, 1108, 1088, 1025, 839, 824, 797, 779, 737, 689 cm^{-1}. HRMS *m/z* 381.1672 [$(M-H)^-$; calcd for $C_{27}H_{25}S$: 381.1677].



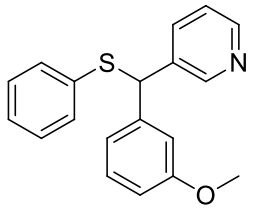
4r: ((3-Methoxyphenyl)(4-methoxyphenyl)methyl)(phenyl)sulfane. The reaction was performed following General Procedure B with (4-methoxybenzyl)(phenyl)sulfane (**1e**) (23.0 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and 3-bromoanisole (**3f**) (25.3 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (77% ^1H 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 give the product **4r** as a colorless oil (24.8 mg, 74% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, J = 8.6 Hz, 2H), 7.25 – 7.10 (m, 6H), 7.05 – 6.96 (m, 2H), 6.82 (d, J = 8.7 Hz, 2H), 6.75 (dd, J = 8.1, 2.3 Hz, 1H), 5.48 (s, 1H), 3.76 (s, 3H), 3.75 (s, 3H). $^{13C\{1H\}}$(126 MHz, $CDCl_3$) δ 159.6, 158.7, 142.8, 136.3, 132.9, 130.3, 129.4, 129.4, 128.6, 126.4, 120.7, 114.0, 113.8, 112.5, 56.6, 55.1, 55.1. IR (neat) 3060, 3026, 3002, 2957, 2936, 2835, 1730, 1593, 1493, 1463, 1454, 1435, 1287, 1247, 1173, 1143, 1031, 827, 778, 729, 701, 642 cm^{-1}. HRMS *m/z* 336.1123 [(M^+); calcd for $C_{21}H_{20}O_2S$: 336.1184].



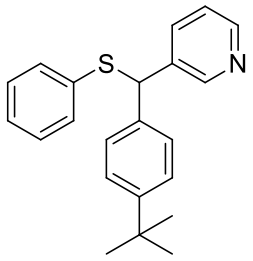
4s: ((4-Chlorophenyl)(3-methoxyphenyl)methyl)(phenyl)sulfane. The reaction was performed following General Procedure A with (4-chlorobenzyl)(phenyl)sulfane (**1f**) (23.4 mg, 0.10 mmol, 1 equiv), $LiN(SiMe_3)_2$ (33.4 mg, 0.20 mmol, 2 equiv) and 3-bromoanisole (**3f**) (25.3 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (79% ^1H 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 give the product **4s** as a colorless oil (235.1 mg, 74% yield). ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, J = 8.4 Hz, 2H), 7.32 – 7.10 (m, 8H), 7.02 – 6.90 (m, 2H), 6.83 – 6.73 (m, 1H), 5.39 (s, 1H), 3.77 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 159.7, 142.0, 139.5, 135.6, 132.9, 130.6, 129.7, 129.6, 128.8, 128.6, 126.8, 120.6, 114.1, 112.7, 56.7, 55.1. IR (neat) 3057, 2957, 2934, 2834, 1598, 1583, 1488, 1437, 1263, 1143, 1089, 1049, 1014, 828, 783, 753, 738, 691 cm^{-1}. HRMS *m/z* 339.0613 [$(M-H)^-$; calcd for $C_{20}H_{16}OSCl$: 339.0610].



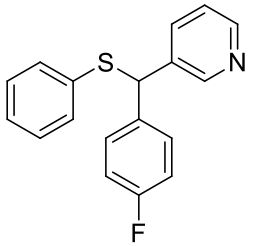
4t: 3-(Phenyl(phenylthio)methyl)pyridine. The reaction was performed following General Procedure C with 3-((phenylthio)methyl)pyridine (**1g**) (20,1 mg, 0.10 mmol, 1 equiv), KO*t*-Bu (22.4 mg, 0.20 mmol, 2 equiv) and bromobenzene (**3a**) (21 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (60% ^{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 give the product **4t** as a yellowish oil (15.5 mg, 56% yield). The NMR spectral data match the previously published data. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, J = 29.3 Hz, 1H), 8.44 (d, J = 3.9 Hz, 1H), 7.84 – 7.63 (m, 1H), 7.38 (dd, J = 15.3, 8.3 Hz, 2H), 7.35 – 7.00 (m, 9H), 5.52 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.7, 148.5, 139.8, 135.7, 134.9, 131.3, 129.2, 128.8, 128.7, 128.2, 127.6, 127.2, 123.3, 55.1. IR (neat) 3057, 3028, 2920, 2850, 1582, 1574, 1492, 179, 1451, 1438, 1421, 1025, 740, 713, 699 cm^{-1}. HRMS *m/z* 278.1016 [$(M+H)^+$; calcd for $C_{18}H_{16}NS$: 278.1003].



4u: 3-((3-Methoxyphenyl)(phenylthio)methyl)pyridine. The reaction was performed following General Procedure C with 3-((phenylthio)methyl)pyridine (**1g**) (20,1 mg, 0.10 mmol, 1 equiv), KO*t*-Bu (22.4 mg, 0.20 mmol, 2 equiv) and 3-bromoanisole (**3f**) (25.3 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (72% ^{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 give the product **4u** as a yellowish oil (21.4 mg, 70% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, J = 19.7 Hz, 1H), 8.44 (d, J = 4.3 Hz, 1H), 7.73 (dt, J = 18.2, 6.9 Hz, 1H), 7.27 – 7.14 (m, 9H), 7.10 – 6.99 (m, J = 13.1, 10.1 Hz, 1H), 5.46 (s, 1H), 2.30 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.7, 148.4, 139.7, 138.4, 136.9, 135.7, 135.0, 131.2, 128.8, 128.6, 128.4, 127.1, 125.2, 125.2, 123.3, 55.1, 21.4. IR (neat) 3413, 3054, 3030, 2920, 1605, 1583, 1574, 1479, 1438, 1421, 1265, 1025, 786, 739, 713, 701, 691 cm^{-1}. HRMS *m/z* 292.1169 [$(M-CH_3)^+$; calcd for $C_{24}H_{19}NOS$: 292.0796].



4v: 3-((4-(*tert*-Butyl)phenyl)(phenylthio)methyl)pyridine. The reaction was performed following General Procedure C with 3-((phenylthio)methyl)pyridine (**1g**) (20,1 mg, 0.10 mmol, 1 equiv), KO*t*-Bu (22.4 mg, 0.20 mmol, 2 equiv) and 4-*tert*-butyl bromobenzene (**3b**) (21 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (75% ^{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 give the product **4v** as a yellowish oil (23.6 mg, 71% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.43 (s, 1H), 7.76 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.34 – 7.27 (m, 4H), 7.25 – 7.14 (m, 6H), 5.48 (s, 1H), 1.28 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 150.6, 149.8, 148.4, 137.0, 136.7, 135.7, 135.1, 131.2, 128.8, 127.8, 127.1, 125.6, 123.3, 54.8, 34.4, 31.2. IR (neat) 3055, 3028, 2962, 2867, 1743, 1658, 1604, 1574, 1583, 1478, 1438, 1413, 1266, 1024, 740, 712, 702, 690 cm^{-1}. HRMS *m/z* 334.1629 [$(M+H)^+$; calcd for $C_{22}H_{24}NS$: 334.1629].

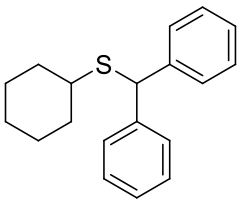


4x: 3-((4-Fluorophenyl)(phenylthio)methyl)pyridine. The reaction was performed following General Procedure C with 3-((phenylthio)methyl)pyridine (**1g**) (20,1 mg, 0.10 mmol, 1 equiv), KO*t*-Bu (22.4 mg, 0.20 mmol, 2 equiv) and 4-fluorobromobenzene (**3g**) (22 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (61% ^{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 give the product **4x** as a yellowish oil (16.8 mg, 57% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 21.6 Hz, 1H), 8.51 – 8.40 (m, 1H), 7.70 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.40 – 7.27 (m, 2H), 7.30 – 7.11 (m, 6H), 7.01 – 6.91 (m, 2H), 5.49 (s, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.8 (d, *J* = 241 Hz), 149.7, 148.6, 136.5, 135.6, 134.5, 131.5, 130.5 (d, *J* = 8 Hz), 129,8 (d, *J* = 9 Hz), 128.9, 127.4, 123.3, 115.6 (d, *J* = 22 Hz), 54.4. IR (neat) 3055, 2922, 1661, 1603, 1584, 1574, 1511, 1479, 1423, 1414, 1264, 1225, 1158, 1097, 1025, 1015, 855, 814, 740, 710, 691 cm^{-1}. HRMS *m/z* 296.0898 [$(M+H)^+$; calcd for $C_{18}H_{15}NFS$: 296.0909].

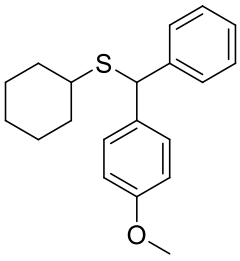
Procedure and Characterizations for the Pd-Catalyzed DCCP of Alkyl Benzyl Sulfides

General Procedure D: An oven-dried 10 mL reaction vial equipped with a stir bar was charged with $NaN(SiMe_3)_2$ (2 equiv) and the benzyl thioether (1 equiv) under a nitrogen atmosphere. A 1 mL solution (from a stock solution) of $[PdCl(allyl)]_2$ (5 mol %) and NiXantPhos (20 mol %) in dry THF was added to the vial via a syringe. After stirring

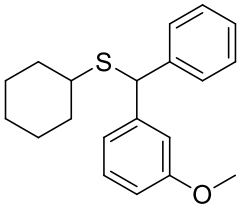
for 5 min at 24 °C, aryl bromide (2 equiv) was added to the reaction mixture. The reaction mixture was stirred for 1 hour at 50 °C, cooled to rt, quenched with three drops of H_2O, diluted with 1 mL of dichloromethane, and filtered over a pad of silica. The pad was rinsed with additional dichloromethane, and the solution was concentrated under reduced pressure. The crude material was loaded onto a silica gel column and purified by flash chromatography.



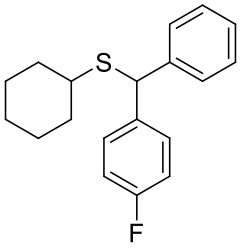
6a: Benzhydryl(cyclohexyl)sulfane. The reaction was performed following General Procedure D with benzyl(cyclohexyl)sulfane (**5a**) (20.6 mg, 0.10 mmol, 1 equiv), $NaN(SiMe_3)_2$ (36.6 mg, 0.20 mmol, 2 equiv) and bromobenzene (**3a**) (20 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (87% ^{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 give the product **6a** as a colorless solid (23.7 mg, 84% yield). The NMR spectral data match the previously published data.[6]



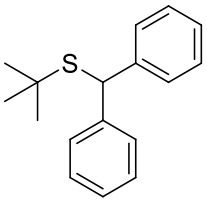
6b: Cyclohexyl((4-methoxyphenyl)(phenyl)methyl)sulfane. The reaction was performed following General Procedure D with benzyl(cyclohexyl)sulfane (**5a**) (20.6 mg, 0.10 mmol, 1 equiv), $NaN(SiMe_3)_2$ (36.6 mg, 0.20 mmol, 2 equiv) and 4-bromoanisole (**3e**) (25.3 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 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/ethyl acetate (95:5)) to give the product **6b** as a colorless oil (29.6 mg, 95% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, J = 14.2, 6.9 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.29 (dd, J = 10.4, 4.8 Hz, 2H), 7.20 (ddd, J = 8.5, 2.3, 1.1 Hz, 1H), 6.86 – 6.80 (m, 2H), 5.21 (s, 1H), 3.77 (s, 3H), 2.47 (tt, J = 10.4, 3.7 Hz, 1H), 1.90 (dd, J = 9.3, 4.0 Hz, 2H), 1.75 – 1.65 (m, 2H), 1.53 (dd, J = 5.7, 3.0 Hz, 1H), 1.42 – 1.33 (m, 2H), 1.23 (m, J = 14.8, 9.4, 3.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.5, 142.2, 134.0, 129.2, 128.4, 128.1, 126.8, 113.8, 55.2, 51.7, 43.5, 33.2, 25.8, 25.7. IR (neat) 3060, 3026, 3000, 2957, 2851, 1609, 1583, 1509, 1493, 1462, 1448, 1301, 1255, 1175, 1034, 910, 817, 734, 698, 611, 559, 529 cm^{-1}. HRMS *m/z* 311.1470 [$(M-H)^+$; calcd for $C_{20}H_{23}OS$: 311.1470].



6c: Cyclohexyl((3-methoxyphenyl)(phenyl)methyl)sulfane. The reaction was performed following General Procedure D with benzyl(cyclohexyl)sulfane (**5a**) (20.6 mg, 0.10 mmol, 1 equiv), $NaN(SiMe_3)_2$ (36.6 mg, 0.20 mmol, 2 equiv) and 3-bromoanisole (**3f**) (25.3 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (70% ^{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/ethyl acetate (95:5)) to give the product **6c** as a colorless oil (21.2 mg, 68% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (t, *J* = 9.0 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.20 (ddd, *J* = 7.4, 6.7, 3.9 Hz, 2H), 7.00 (dd, *J* = 11.6, 7.8 Hz, 2H), 6.79 – 6.71 (m, 1H), 5.19 (s, 1H), 3.75 (s, 3H), 2.53 – 2.44 (m, 1H), 1.90 (d, *J* = 12.9 Hz, 2H), 1.73 – 1.67 (m, 2H), 1.56 – 1.50 (m, 1H), 1.42 – 1.32 (m, 3H), 1.29 – 1.22 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.6, 143.5, 141.8, 129.4, 128.4, 128.2, 126.9, 120.6, 114.0, 112.2, 55.1, 52.4, 43.5, 33.2, 33.2, 25.8. IR (neat) 3059, 3025, 3000, 2954, 2851, 1597, 1488, 1449, 1313, 1262, 1142, 1049, 998, 778, 729, 701 cm^{-1}. HRMS *m/z* 311.1481 [(M-H)$^+$; calcd for $C_{20}H_{23}OS$: 311.1470].

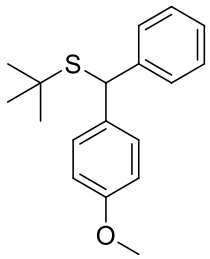


6d: Cyclohexyl((4-fluorophenyl)(phenyl)methyl)sulfane. The reaction was performed following General Procedure D with benzyl(cyclohexyl)sulfane (**5a**) (20.6 mg, 0.10 mmol, 1 equiv), $NaN(SiMe_3)_2$ (36.6 mg, 0.20 mmol, 2 equiv) and 4-fluorobenene (**3g**) (22 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (65% ^{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 give the product **6d** as a colorless oil (18.0 mg, 60% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (m, *J* = 7.9, 5.0 Hz, 4H), 7.29 (dd, *J* = 10.3, 4.9 Hz, 2H), 7.20 (dd, *J* = 10.5, 4.2 Hz, 1H), 7.00 – 6.94 (m, 2H), 5.20 (s, 1H), 2.44 (tt, *J* = 10.4, 3.6 Hz, 1H), 1.87 (d, *J* = 11.3 Hz, 2H), 1.73 – 1.67 (m, 2H), 1.52 (d, *J* = 10.4 Hz, 1H), 1.39 – 1.30 (m, 3H), 1.23 (d, *J* = 14.2 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.7 (d, *J* = 135 Hz), 141.7, 137.7, 129.7 (d, *J* = 7 Hz), 128.5, 128.1, 127.0, 115.2 (d, *J* = 21 Hz), 51.6, 43.6, 33.2, 33.1, 25.7. IR (neat) 3416, 3053, 2930, 2853, 1741, 1598, 1505, 1491, 1449, 1327, 1264, 1142, 1094, 1013, 739, 702 cm^{-1}. HRMS *m/z* 300.1340 [(M)$^+$; calcd for $C_{19}H_{21}FS$: 300.1348].

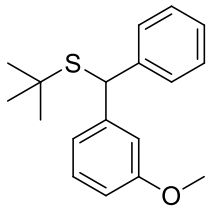


6e: Benzhydryl(tert-butyl)sulfane. The reaction was performed following General Procedure D with benzyl(*tert*-butyl)sulfane (**5b**) (18.0 mg, 0.10

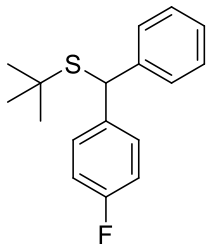
mmol, 1 equiv), $NaN(SiMe_3)_2$ (36.6 mg, 0.20 mmol, 2 equiv) and bromobenzene (**3a**) (20 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (91% ^{1}H NMR yield with internal standard CH_2Br_2). The crude material was then purified by flash column chromatography on silica gel (eluted with hexanes) to give the product **6e** as a colorless oil (22.3 mg, 87% yield). The NMR spectral data match the previously published data.[7]



6f: *tert*-Butyl((4-methoxyphenyl)(phenyl)methyl)sulfane. The reaction was performed following General Procedure D with benzyl(*tert*-butyl)sulfane (**5b**) (18.0 mg, 0.10 mmol, 1 equiv), $NaN(SiMe_3)_2$ (36.6 mg, 0.20 mmol, 2 equiv) and 4-bromoanisole (**3e**) (25.3 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 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/ethyl acetate (95:5)) to give the product **6f** as a colorless oil (25.5 mg, 89% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (dd, J = 12.5, 5.4 Hz, 2H), 7.39 – 7.32 (m, 2H), 7.32 – 7.25 (m, 2H), 7.18 (dt, J = 19.4, 6.5 Hz, 1H), 6.88 – 6.80 (m, 2H), 5.20 (s, 1H), 3.76 (s, 3H), 1.27 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.3, 143.5, 135.2, 129.3, 128.3, 128.2, 126.6, 113.7, 55.2, 51.5, 44.5, 31.3. IR (neat) 3060, 3026, 2958, 2898, 2860, 2835, 1609, 1583, 1513, 1493, 1459, 1363, 1301, 1247, 1175, 1108, 1034, 850, 805, 782, 733, 698, 617, 558, 527 cm^{-1}. HRMS *m/z* 285.1312 [(M-H)$^-$; calcd for $C_{18}H_{21}OS$: 285.1313].



6g: *tert*-Butyl((3-methoxyphenyl)(phenyl)methyl)sulfane. The reaction was performed following General Procedure D with benzyl(*tert*-butyl)sulfane (**5b**) (18.0 mg, 0.10 mmol, 1 equiv), $NaN(SiMe_3)_2$ (36.6 mg, 0.20 mmol, 2 equiv) and 3-bromoanisole (**3f**) (25.3 μL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 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/ethyl acetate (95:5)) to give the product **6g** as a colorless oil (21.4 mg, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (t, J = 9.7 Hz, 2H), 7.26 (dd, J = 12.3, 4.4 Hz, 2H), 7.20 – 7.13 (m, 2H), 7.01 (dd, J = 4.2, 2.1 Hz, 2H), 6.77 – 6.67 (m, 1H), 5.16 (d, J = 15.4 Hz, 1H), 3.75 (s, 3H), 1.25 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.5, 144.7, 143.0, 129.3, 128.3, 128.2, 126.7, 120.7, 114.2, 111.9, 55.1, 52.1, 44.5, 31.2. IR (neat) 3433, 2959, 1740, 1639, 1489, 1451, 1364, 1263, 1142, 1049, 735, 701 cm^{-1}. HRMS *m/z* 285.1346 [(M-H)$^+$; calcd for $C_{18}H_{21}OS$: 285.1313].



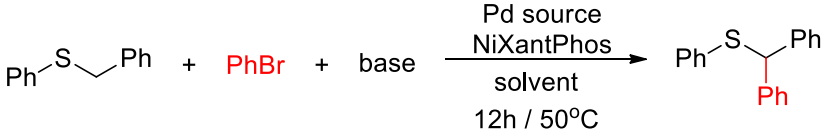
6h: *tert*-Butyl((4-fluorophenyl)(phenyl)methyl)sulfane. The reaction was performed following General Procedure D with benzyl(*tert*-butyl)sulfane (**5b**) (18.0 mg, 0.10 mmol, 1 equiv), $NaN(SiMe_3)_2$ (36.6 mg, 0.20 mmol, 2 equiv) and 4-fluorobenene (**3g**) (22 µL, 0.2 mmol, 2 equiv) in 1 mL of THF (0.1 M). The crude reaction mixture was filtered through a short pad of silica to afford the product (80% ^{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/ethyl acetate (95:5)) to give the product **6h** as a colorless oil (20.9 mg, 76% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 4H), 7.28 (dd, J = 10.4, 4.9 Hz, 2H), 7.19 (dd, J = 10.4, 4.3 Hz, 1H), 6.99 – 6.93 (m, 2H), 5.19 (s, 1H), 1.25 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.5 (d, J = 246 Hz), 142.9, 138.9 (d, J = 3 Hz), 129.8 (d, J = 7 Hz), 128.4, 128.2, 126.8, 115.1 (d, J = 21 Hz), 51.3, 44.6, 31.2. IR (neat) 3061, 3027, 2960, 2924, 2898, 2861, 1603, 1493, 1452, 1364, 1224, 1156, 1095, 856, 812, 795, 735, 697, 615, 542, 519 cm^{-1}. HRMS *m/z* 274.1203 [(M)$^+$; calcd for $C_{17}H_{19}FS$: 274.1192].

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 24- or 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 plate. The reactions were sealed in the plate during reaction. Below each reactor vial in the aluminum 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 evenly-placed screws.

(1) First Screening:



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 the different palladium sources (1.0 μmol of Pd) and NiXantPhos (2.0 μmol) in THF. The solvent was evacuated to dryness using a GeneVac vacuum centrifuge, and the respective base (20 μmol) solution 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 (20 μmol/reaction) and benzylphenyl sulfide (10 μmol/reaction) were then dosed together into each reaction vial as a solution in the respective solvent (100 μL, 0.1 M). The 96-well plate was then sealed and stirred for 12 h at 50 °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.

Pd source: 8 Pd sources [$Pd(OAc)_2$, $[PdCl(allyl)]_2$, $Pd(dba)_2$, $Pd(PPh_3)_4$, $PdCl_2(cod)$, $Pd(acac)_2$, $Pd(tfa)_2$ and $PdCl_2$]

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

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

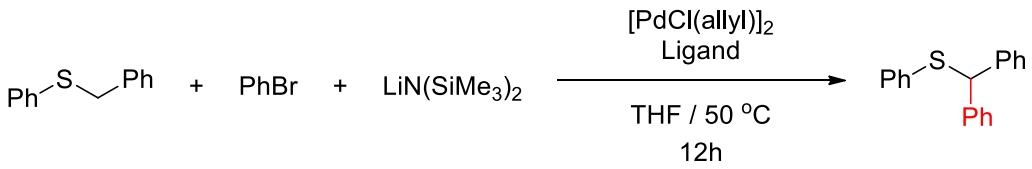
The lead hits from this screening were the combinations: a) $[PdCl(allyl)]_2$, $LiN(SiMe_3)_2$ and THF (Laboratory scale yield: 61%), b) $PdCl_2(cod)$, $LiN(SiMe_3)_2$ and DME (Laboratory scale yield: 57%), c) $PdCl_2(cod)$, $LiN(SiMe_3)_2$ and Toluene (Laboratory scale yield: 35%), d) $PdCl_2$, $LiN(SiMe_3)_2$ and Toluene (No reaction in laboratory scale), e) $Pd(OAc)_2$, $NaN(SiMe_3)_2$ and CPME (Laboratory scale yield: 56%), f) $PdCl_2(cod)$, $NaN(SiMe_3)_2$ and CPME (Laboratory scale yield: 58%), g) $[PdCl(allyl)]_2$, $NaN(SiMe_3)_2$ and Toluene (Laboratory scale yield: 45%).

Base	**Solvent**	**Pd source**	**Product / Internal Standard ratio**
$LiN(SiMe_3)_2$	CPME	$Pd(OAc)_2$	0.68
		$[PdCl(allyl)]_2$	4.20
		$PdCl_2(cod)$	3.03
		$PdCl_2$	0.50
	THF	$Pd(OAc)_2$	1.13
		$[PdCl(allyl)]_2$	5.02
		$PdCl_2(cod)$	2.43
		$PdCl_2$	0.06
	DME	$Pd(OAc)_2$	1.88
		$[PdCl(allyl)]_2$	2.76

		$PdCl_2(cod)$	3.89
		$PdCl_2$	0.13
	Toluene	$Pd(OAc)_2$	1.18
		$[PdCl(allyl)]_2$	2.68
		$PdCl_2(cod)$	4.41
		$PdCl_2$	0.41
$NaN(SiMe_3)_2$	CPME	$Pd(OAc)_2$	2.88
		$[PdCl(allyl)]_2$	1.49
		$PdCl_2(cod)$	4.41
		$PdCl_2$	0.03
	THF	$Pd(OAc)_2$	2.26
		$[PdCl(allyl)]_2$	2.87
		$PdCl_2(cod)$	3.73
		$PdCl_2$	0.06
	DME	$Pd(OAc)_2$	1.53
		$[PdCl(allyl)]_2$	1.61
		$PdCl_2(cod)$	2.04
		$PdCl_2$	0.33
	Toluene	$Pd(OAc)_2$	2.65
		$[PdCl(allyl)]_2$	3.23
		$PdCl_2(cod)$	1.24
		$PdCl_2$	0.16

Reactions using $KN(SiMe_3)_2$ as base and $Pd(dba)_2$, $Pd(PPh_3)_4$, $Pd(acac)_2$ and $Pd(tfa)_2$ as Palladium sources did not show relevant results.

(2) Second Screening:



Set up:

Experiments were set up inside a glovebox under a nitrogen atmosphere. A 24-well aluminum block containing 1 mL glass vials containing the different ligands was predosed manually with $[PdCl(allyl)]_2$ (0.5 µmol) in THF. The solvent was evacuated to dryness using a GeneVac vacuum centrifuge, and $LiN(SiMe_3)_2$ (20 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 (20

μmol/reaction) and benzylphenyl sulfide (10 μmol/reaction) were then dosed together into each reaction vial as a solution in CPME (100 μL, 0.1 M). The 24-well plate was then sealed and stirred for 12 h at 50 °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.

Ligand library	
1	4,6-Bis(diphenylphosphino)phenoxazine (NiXantPhos)
2	1,1'-Bis(diphenylphosphino)ferrocene (DPPF)
3	1,1'-Bis(di-*t*-butylphosphino)ferrocene (DTBPF)
4	1-[2-[Bis(*t*-butyl)phosphino]phenyl]-3,5-diphenyl-1H-pyrazole (TrippyPhos)
5	Tri-*o*-tolylphosphine
6	(*S*)-(+)-2,2'-Bis(diphenylphosphno)-1,1'-binaphthyl ((*S*)-BINAP)
7	di-*t*-butylneopentylphosphine
8	Triphenylphosphine
9	(R)-1-[(SP)-2-(Dicyclohexylphosphino)ferrocenyl]ethyldi-tert-butylphosphine
10	Di(1-adamantyl)-2-dimethylaminophenylphosphine (Me-DalPhos)
11	*N*,*N*-Dimethyl 4-(Di(*tert*-butyl)phosphino)aniline (A^{ta}-Phos)
12	9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene) (XantPhos)
13	2-dicyclohexyphosphino-2'-6'-dimethoxy-1,1'-biphenyl (SPhos)
14	5-(di-*t*-butylphosphino)-1',3',5'-triphenyl-1'H-[1,4']bipyrazole (BippyPhos)
15	Dicyclohexyl-[3,6-dimethoxy-2-(2,5,6-triisopropylphenyl)phenyl]phosphane (BrettPhos)
16	1-(2,4,6-Trimethylpheny)-2-(dicyclohexylphosphino)imidazole (cataCXium PICy)
17	Di(1-adamantyl)-n-butylphosphine (CatCXium A)
18	*N*-phenyl-2-(di-*t*-butylphosphino)pyrrole (CataCXium PtB)
19	1,1'-Bis(diisopropylphosphino)ferrocene (DIPPF)
20	*N*-phenyl-2-(dicyclohexylphosphino)pyrrole (CataXCium PCy)
21	2-(Di-*t*-butylphosphino)-3-methoxy-6-methyl-2',4',6'-tri-i-propyl-1,1'-biphenyl (RockPhos)
22	1,2,3,4,5-Pentaphenyl-1'-(di-*t*-butylphosphino)ferrocene (QPhos)
23	1-(dicyclohexylphosphino)-2-(o-tolyl)indoline
24	di-tert-butyl(2',4',6'-triisopropyl-3,4,5,6-tetramethyl-[1,1'-biphenyl]-2-yl)phosphine (Me_4*t*BuXPhos)

Only the reactions using NiXantPhos (Product / Internal Standard ratio: 5.23) and XantPhos (Product / I.S.: 0.72) led to the product. The reaction using NiXantPhos translated into 61% yield on laboratory scale.

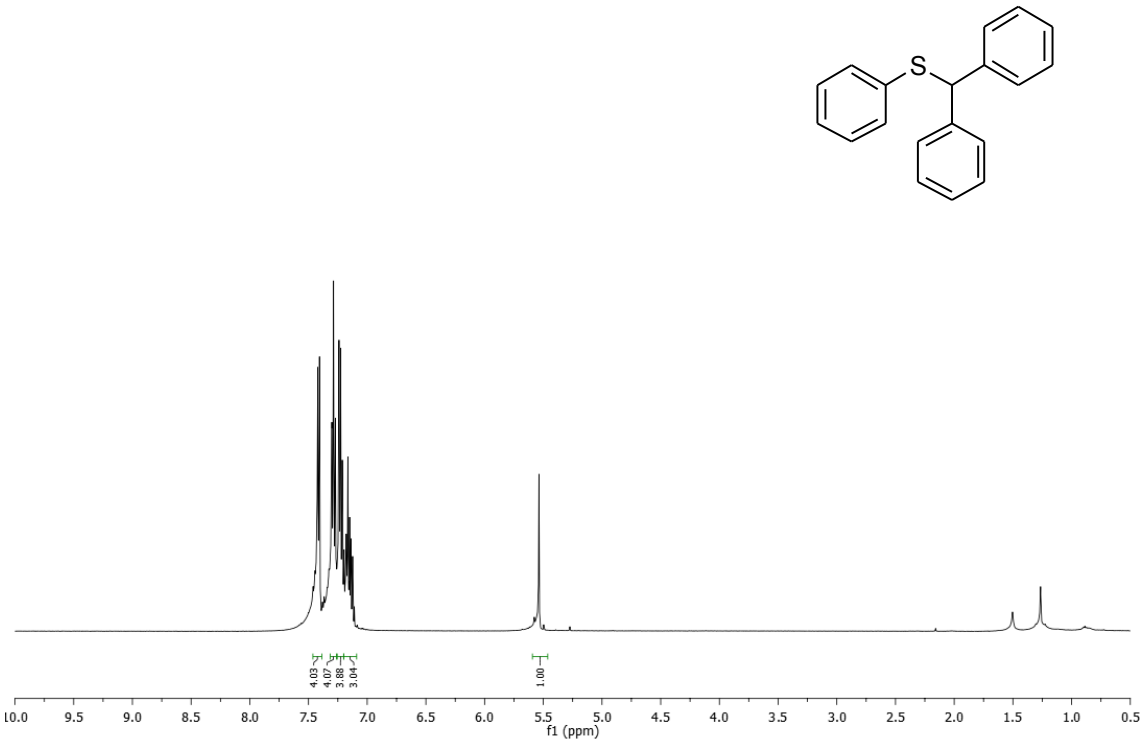
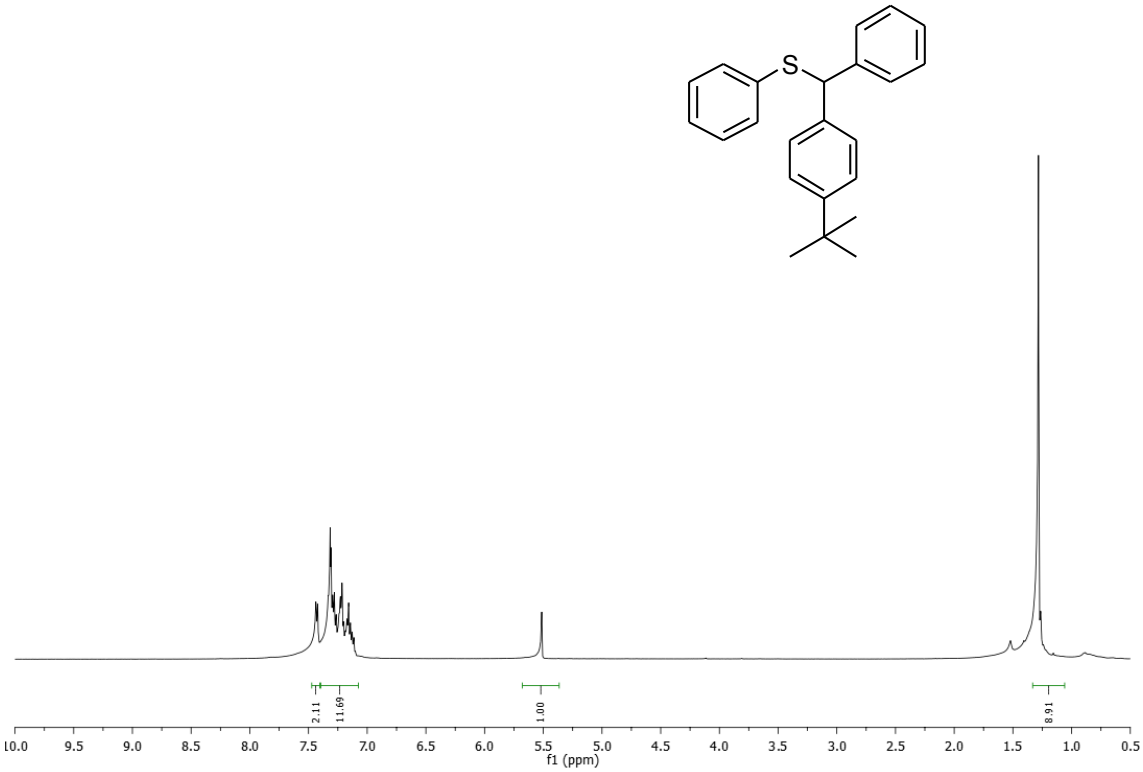


Figure S1 (**4a**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of benzhydryl(phenyl)sulfane in $CDCl_3$.



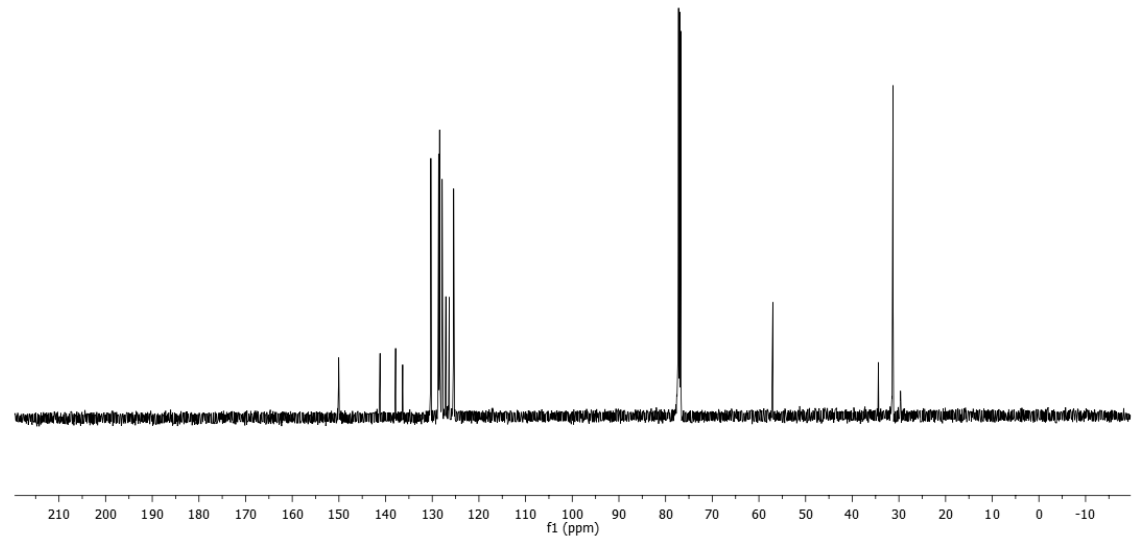


Figure S2 (**4b**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of ((4-(tert-butyl)phenyl)(phenyl)methyl)(phenyl)sulfane in $CDCl_3$.

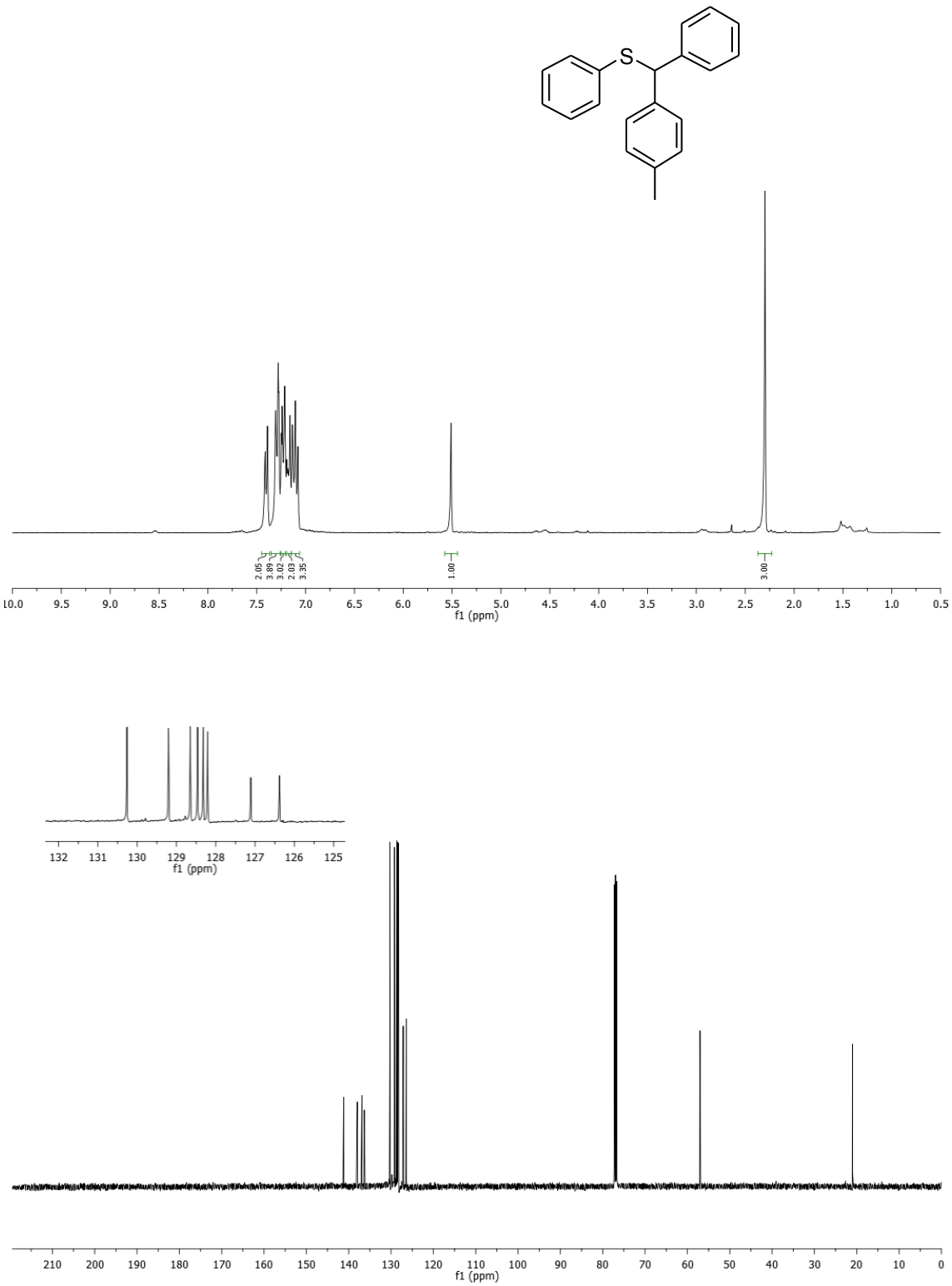


Figure S3 (**4c**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of phenyl(phenyl(p-tolyl)methyl)sulfane in $CDCl_3$.

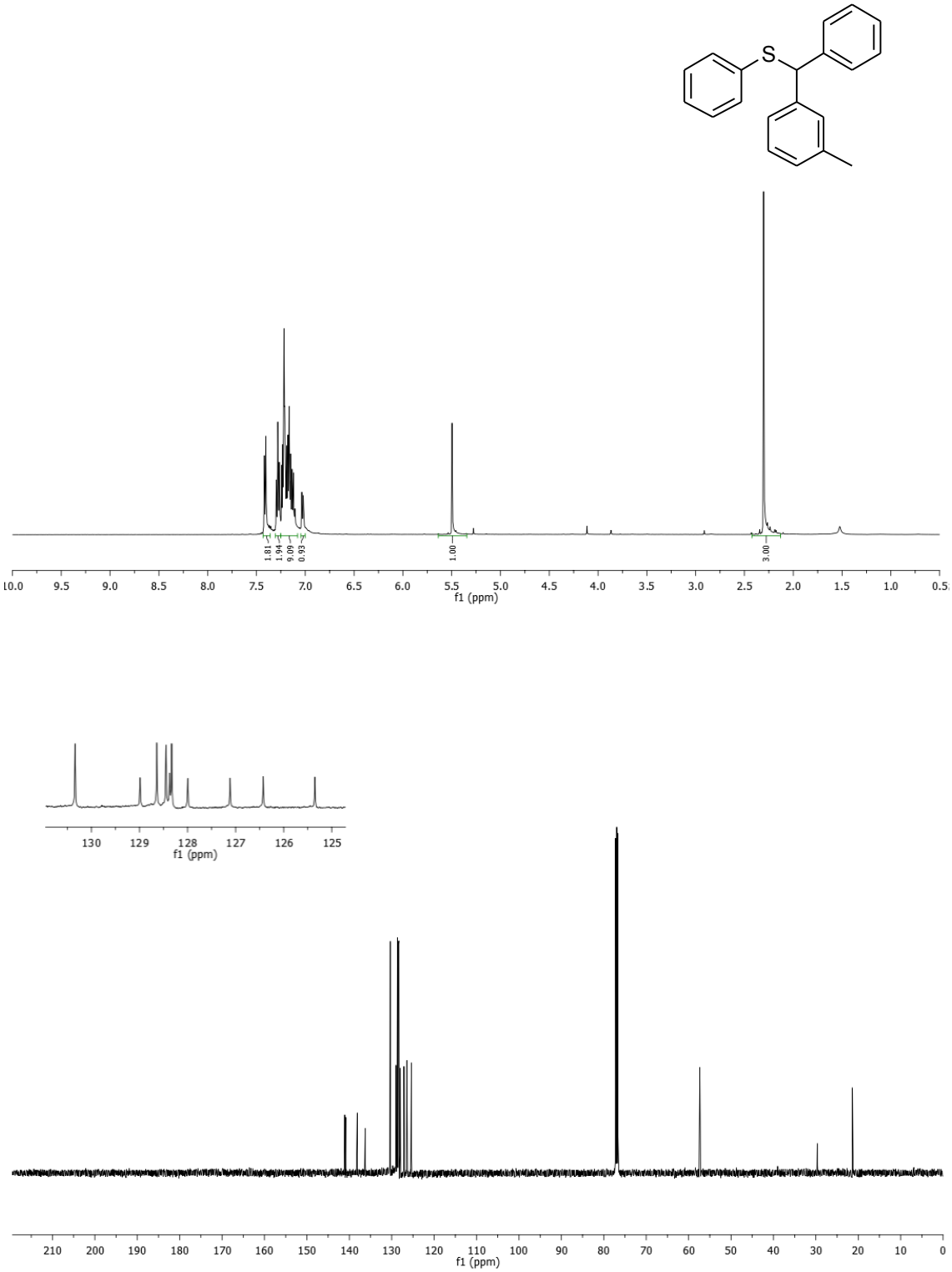


Figure S4 (**4d**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of phenyl(phenyl(m-tolyl)methyl)sulfane in $CDCl_3$.

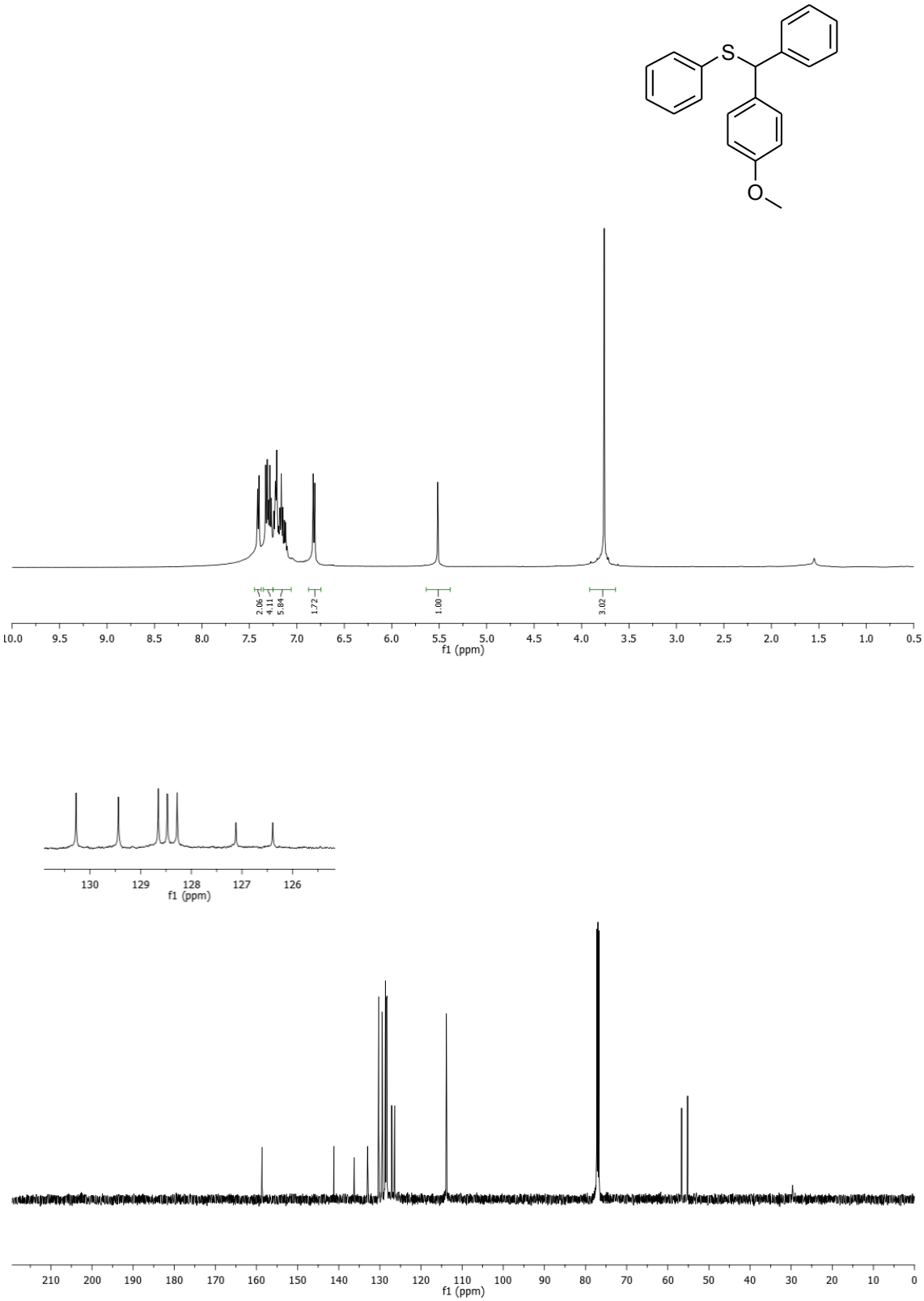
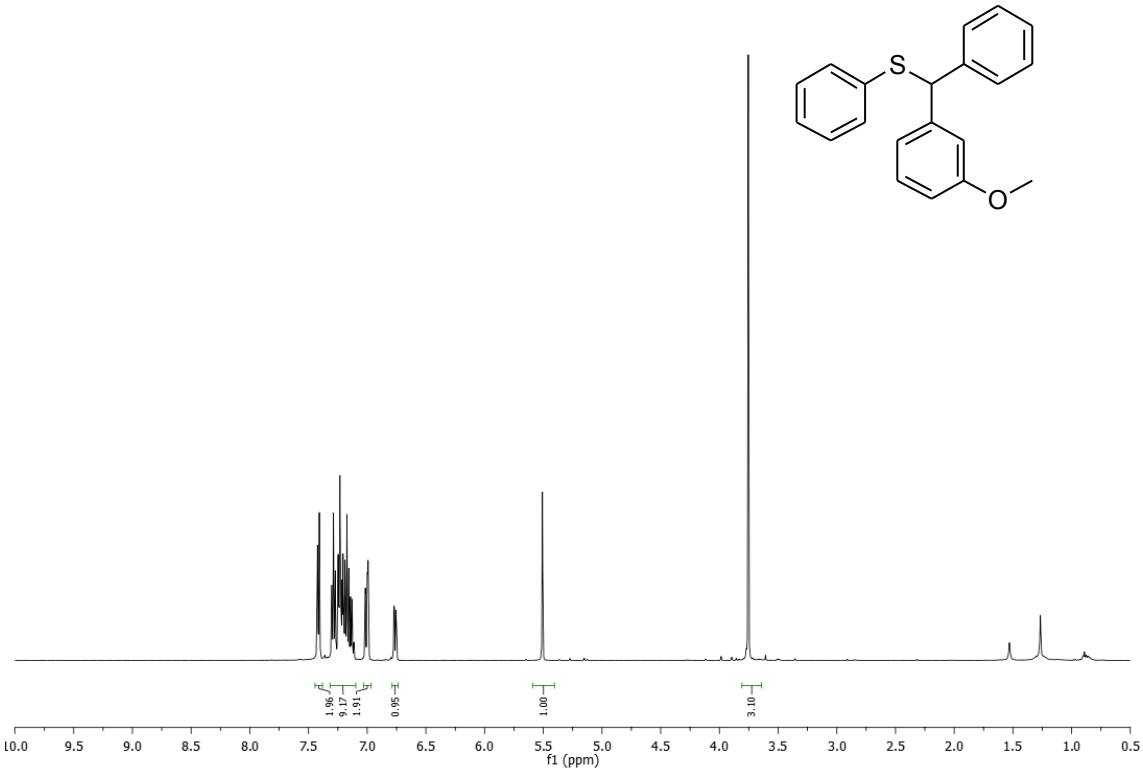


Figure S5 (**4e**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of ((4-methoxyphenyl)(phenyl)methyl)(phenyl)sulfane in $CDCl_3$.



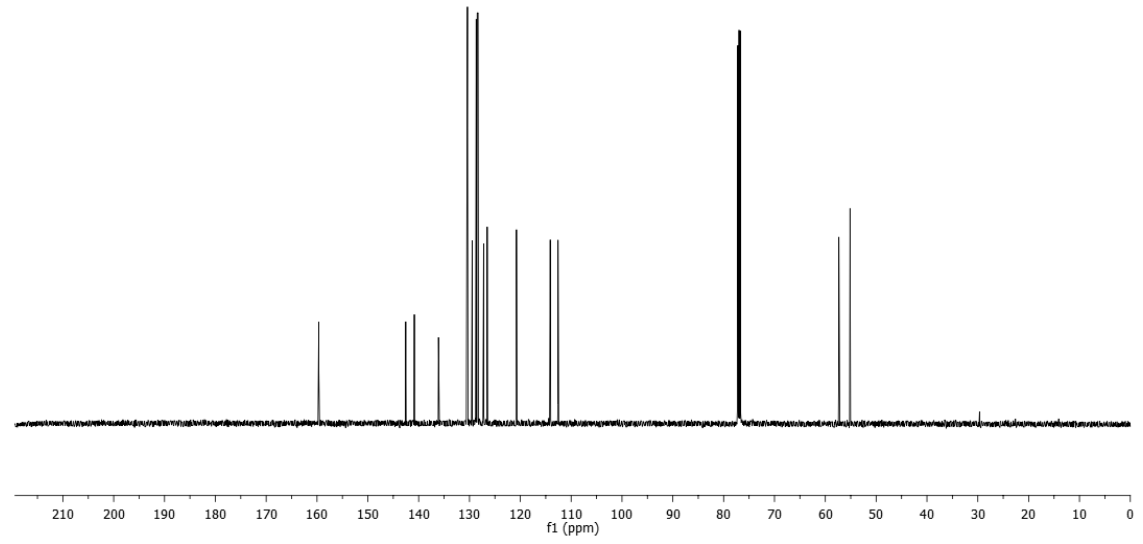
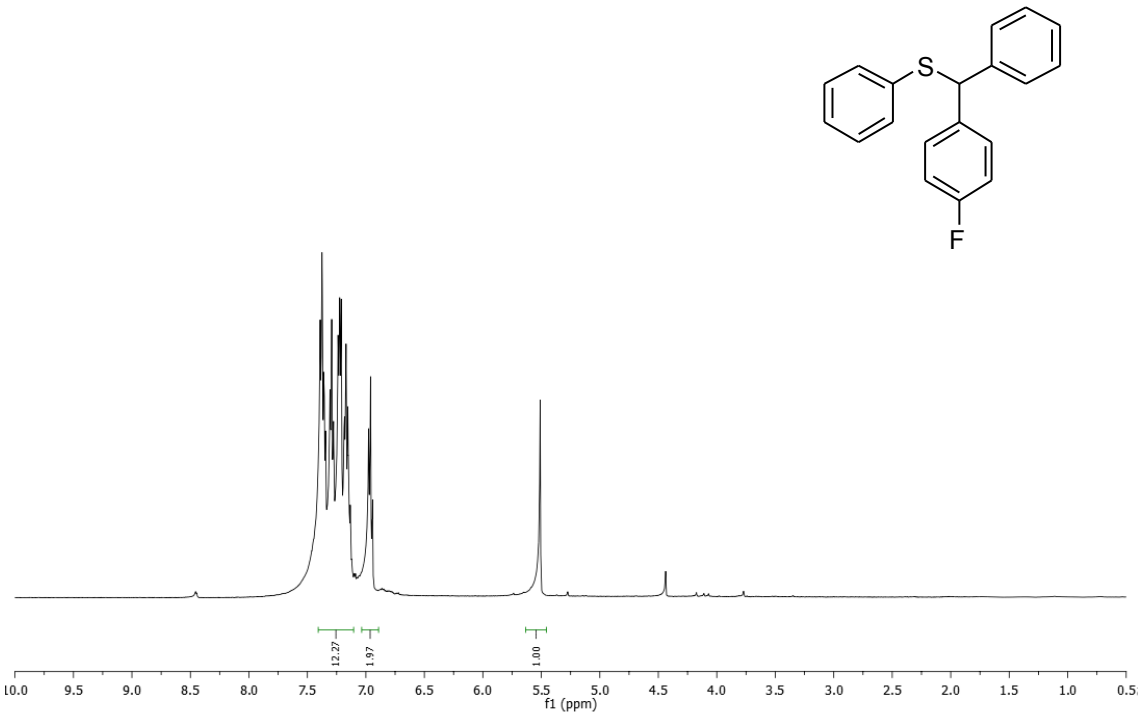


Figure S6 (**4f**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of ((3-methoxyphenyl)(phenyl)methyl)(phenyl)sulfane in $CDCl_3$.



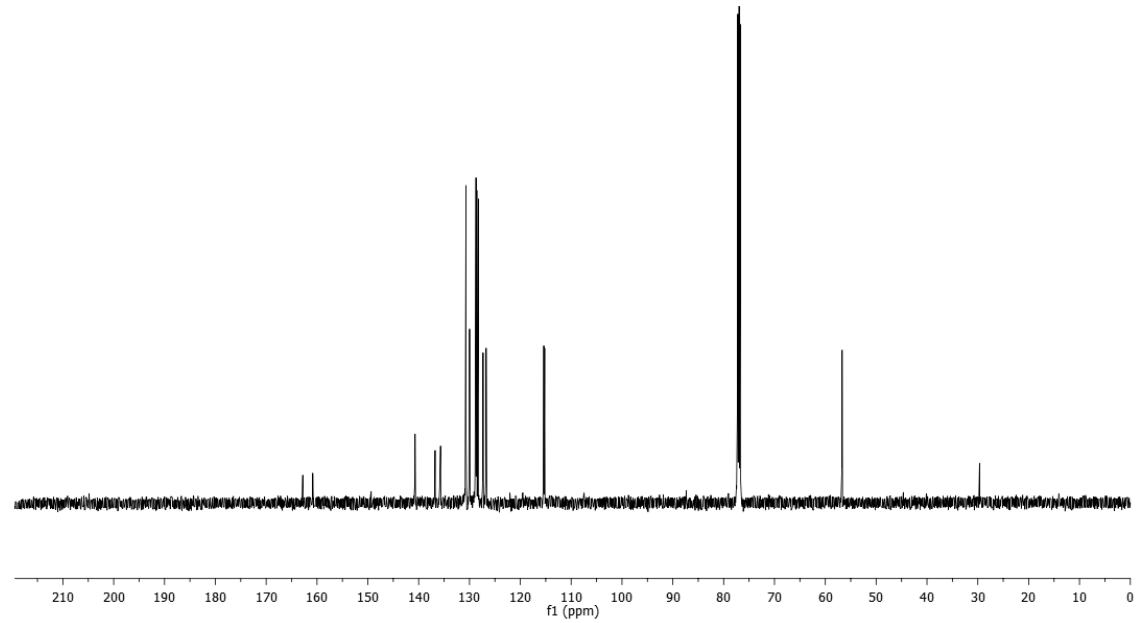


Figure S7 (**4g**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of ((4-fluorophenyl)(phenyl)methyl)(phenyl)sulfane in $CDCl_3$.

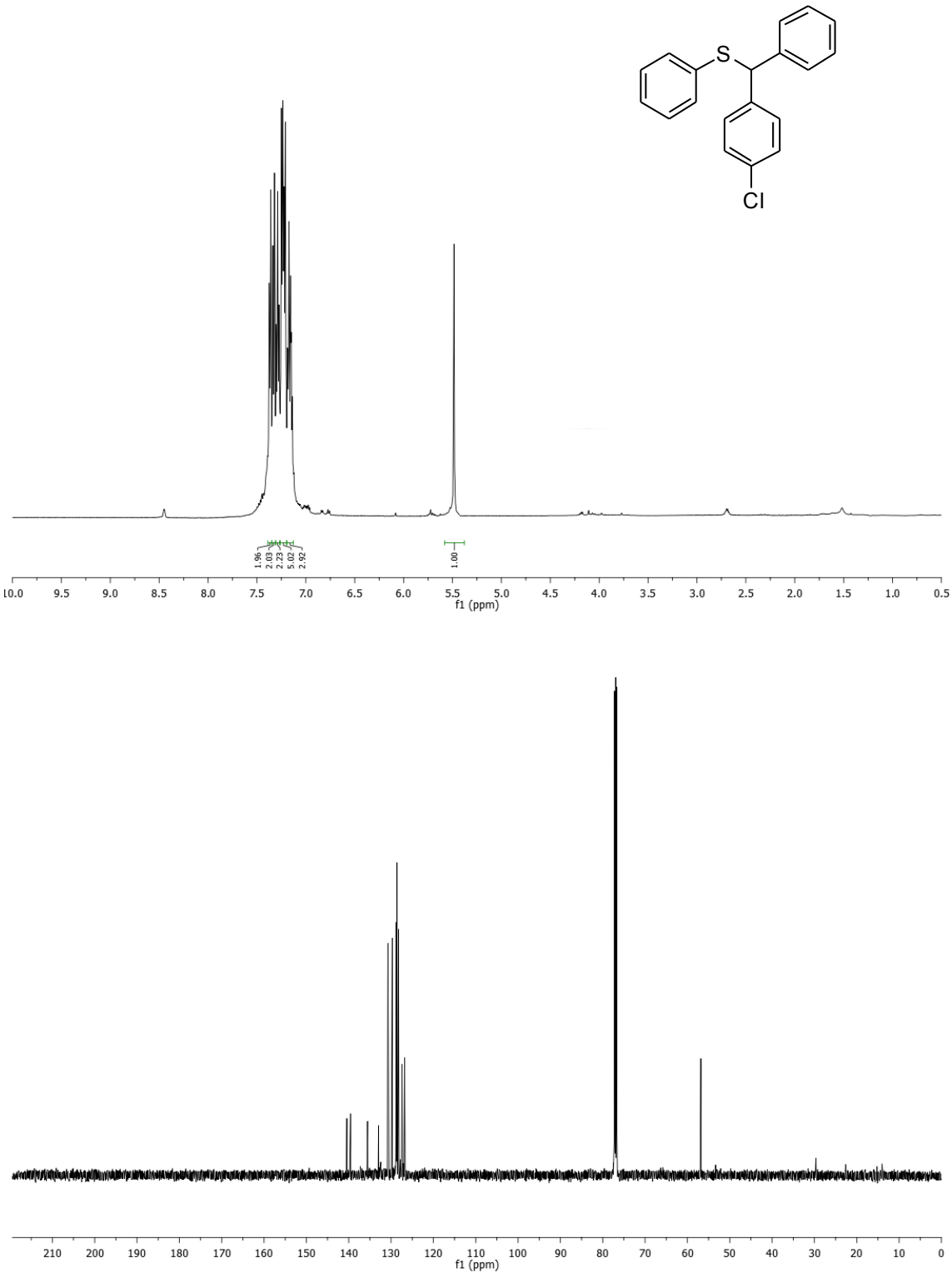


Figure S8 (**4h**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of ((4-chlorophenyl)(phenyl)methyl)(phenyl)sulfane in $CDCl_3$.

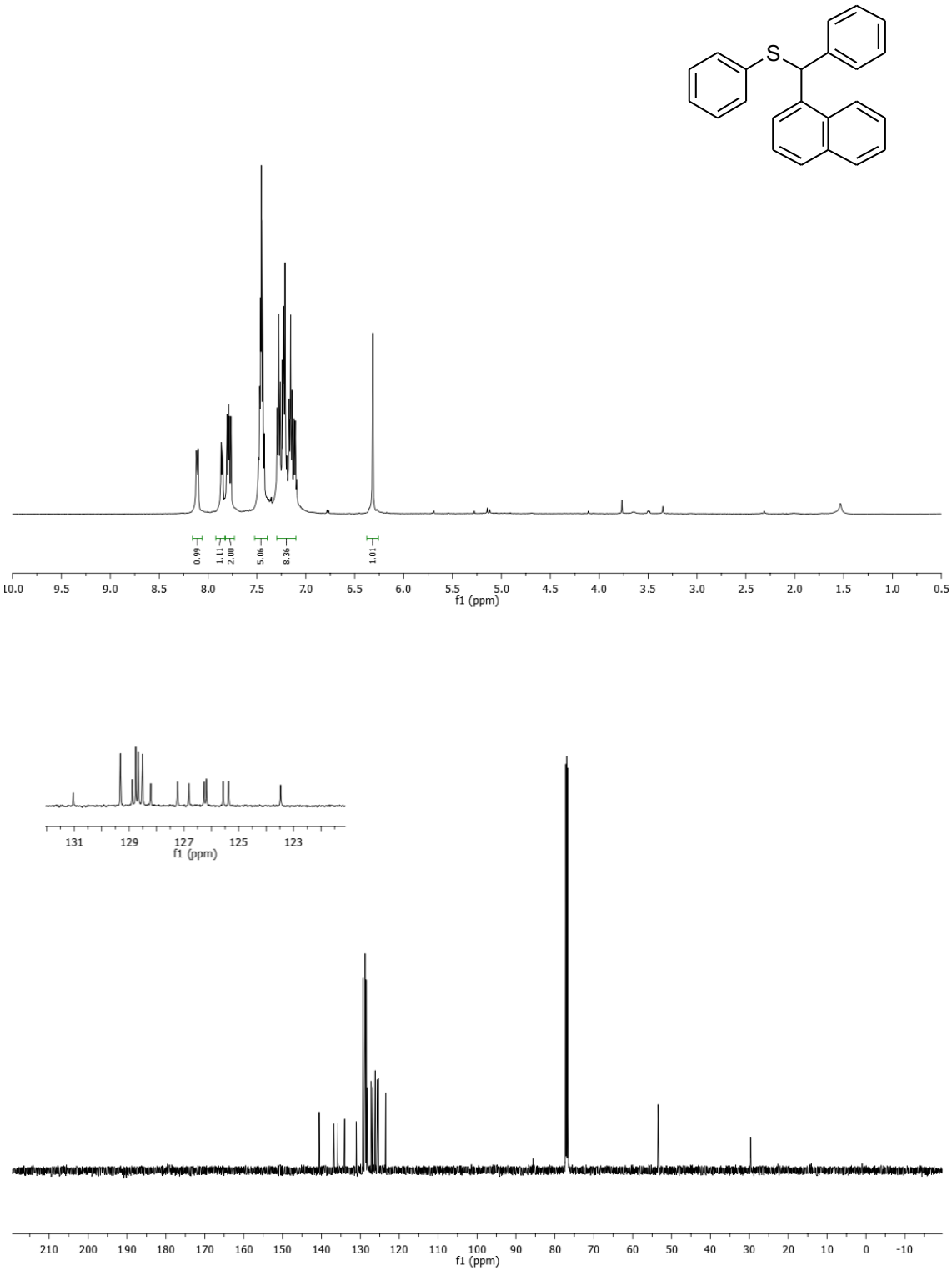


Figure S9 (**4i**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of (naphthalen-1-yl(phenyl)methyl)(phenyl)sulfane in $CDCl_3$.

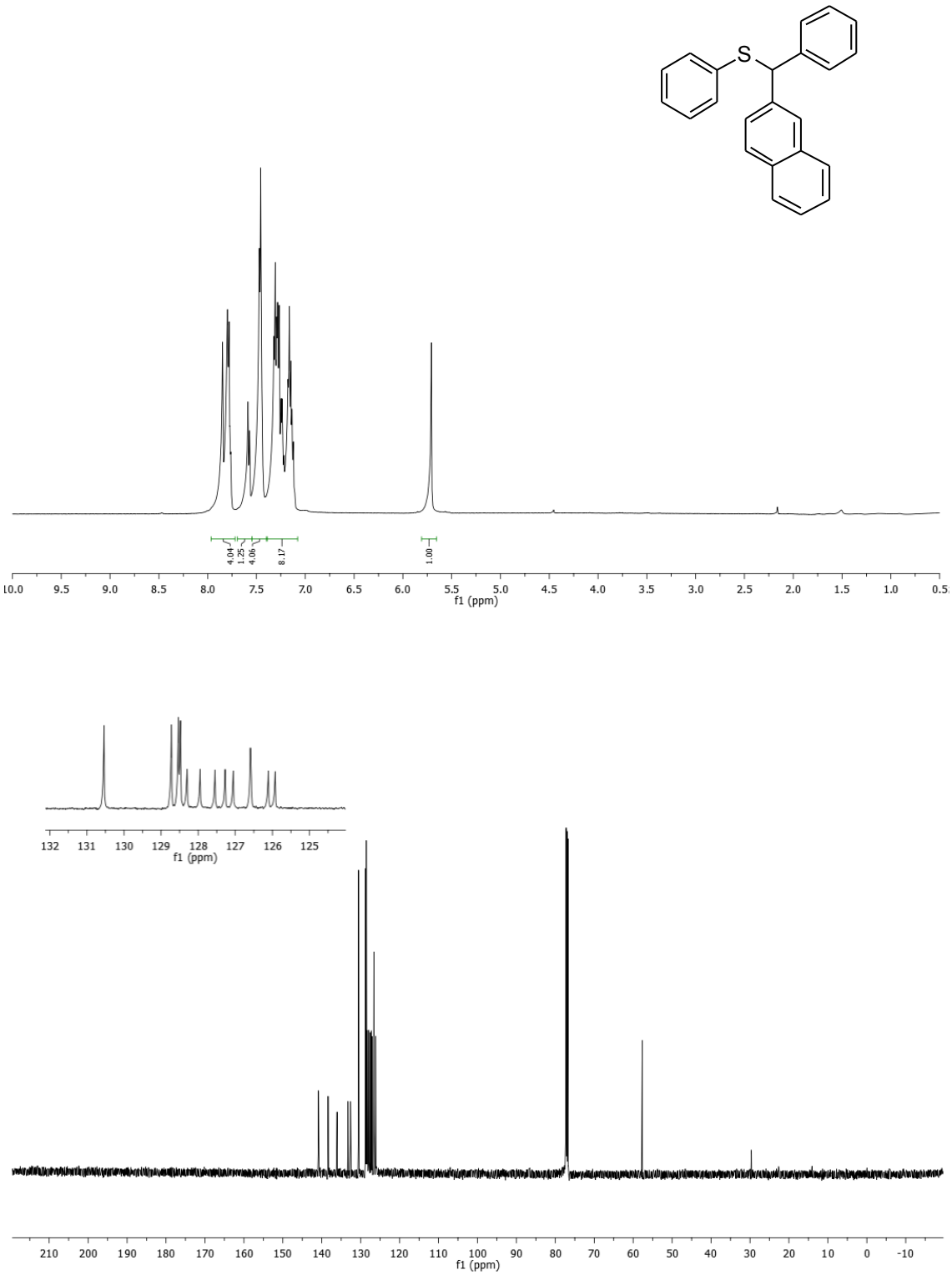


Figure S10 (**4j**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of (naphthalen-2-yl(phenyl)methyl)(phenyl)sulfane in $CDCl_3$.

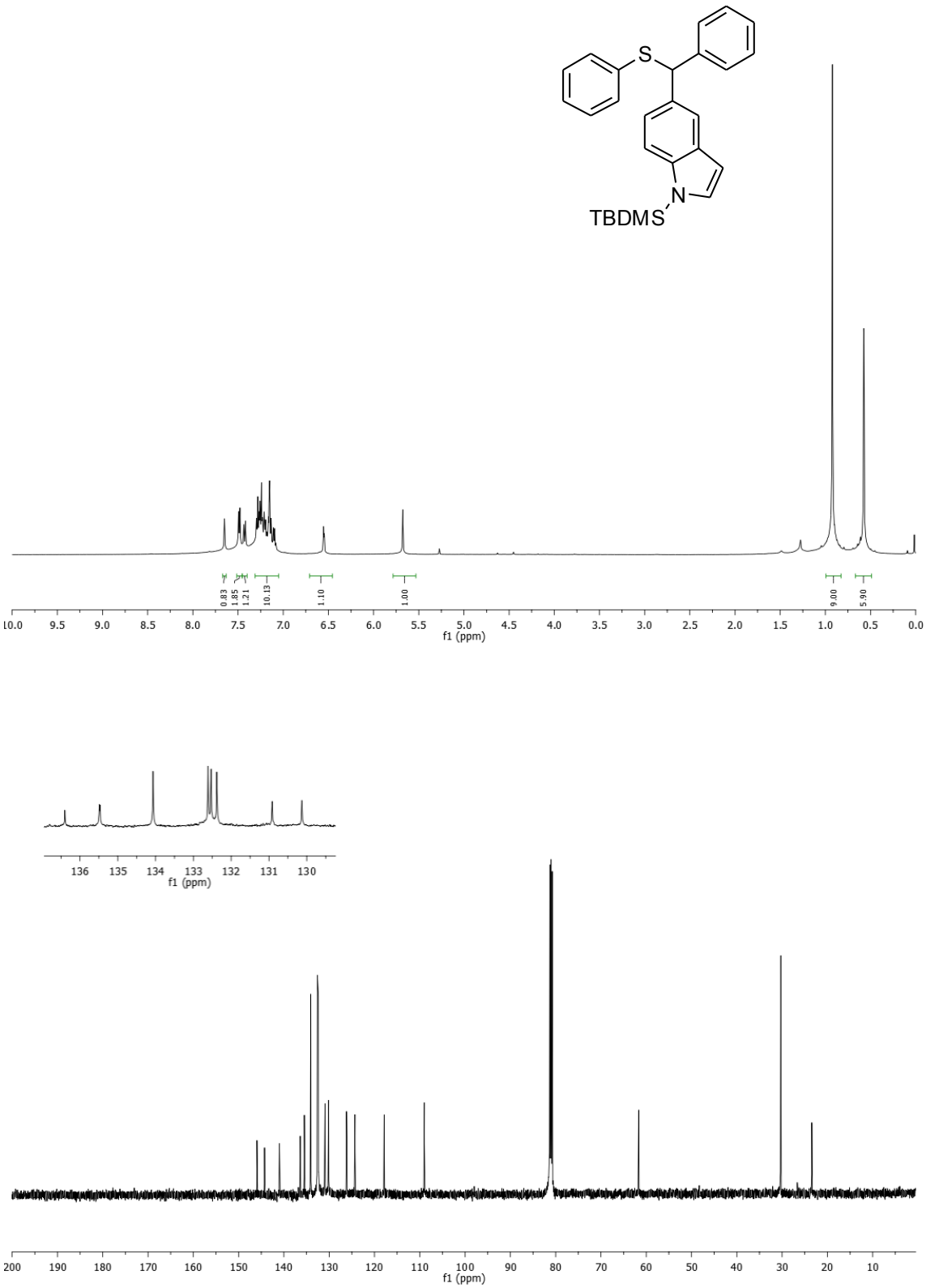


Figure S11 (**4k**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 1-(tert-butyldimethylsilyl)-5-(phenyl(phenylthio)methyl)-1H-indole in $CDCl_3$.

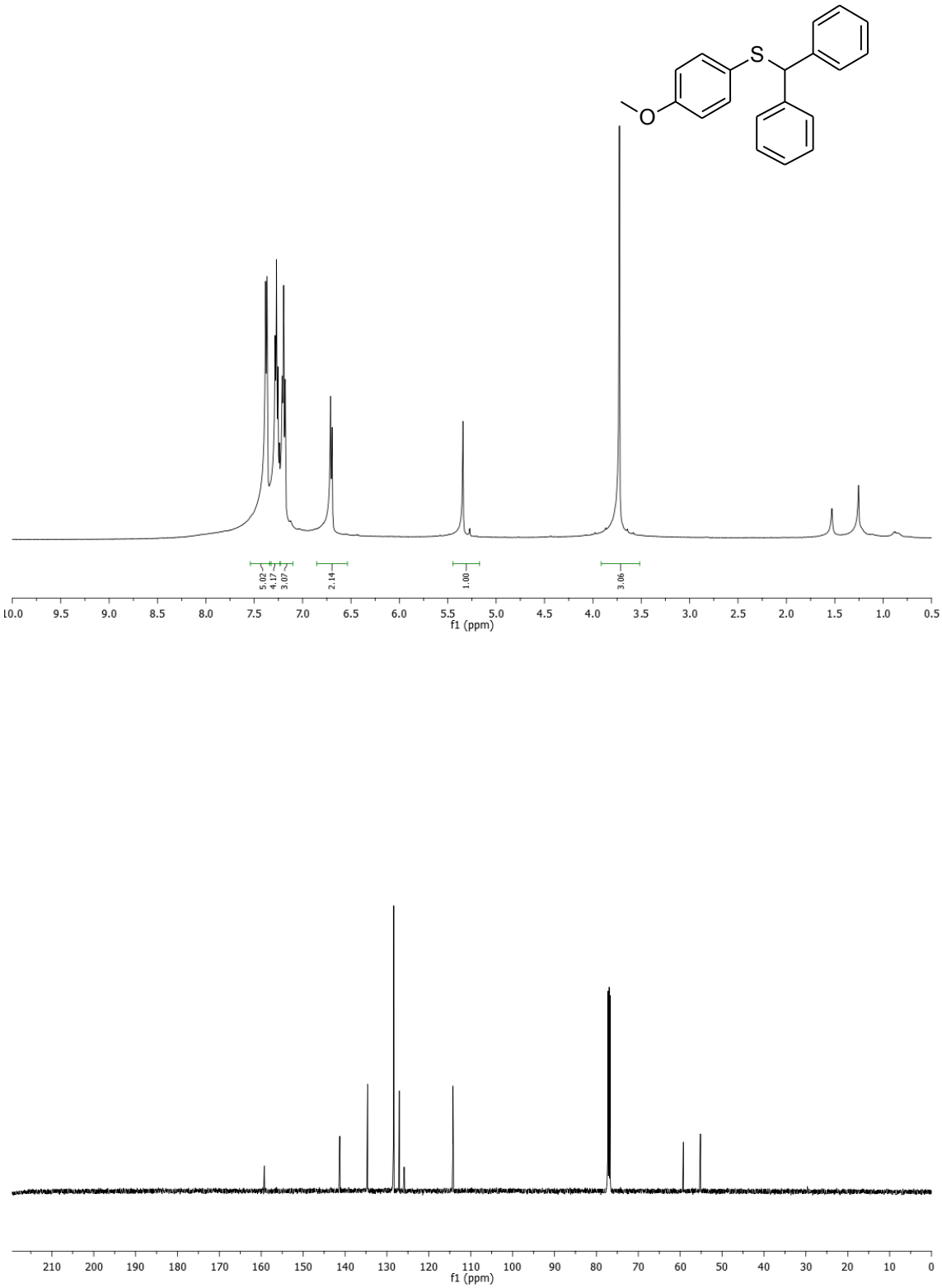


Figure S12 (**4l**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of benzhydryl(4-methoxyphenyl)sulfane in $CDCl_3$.

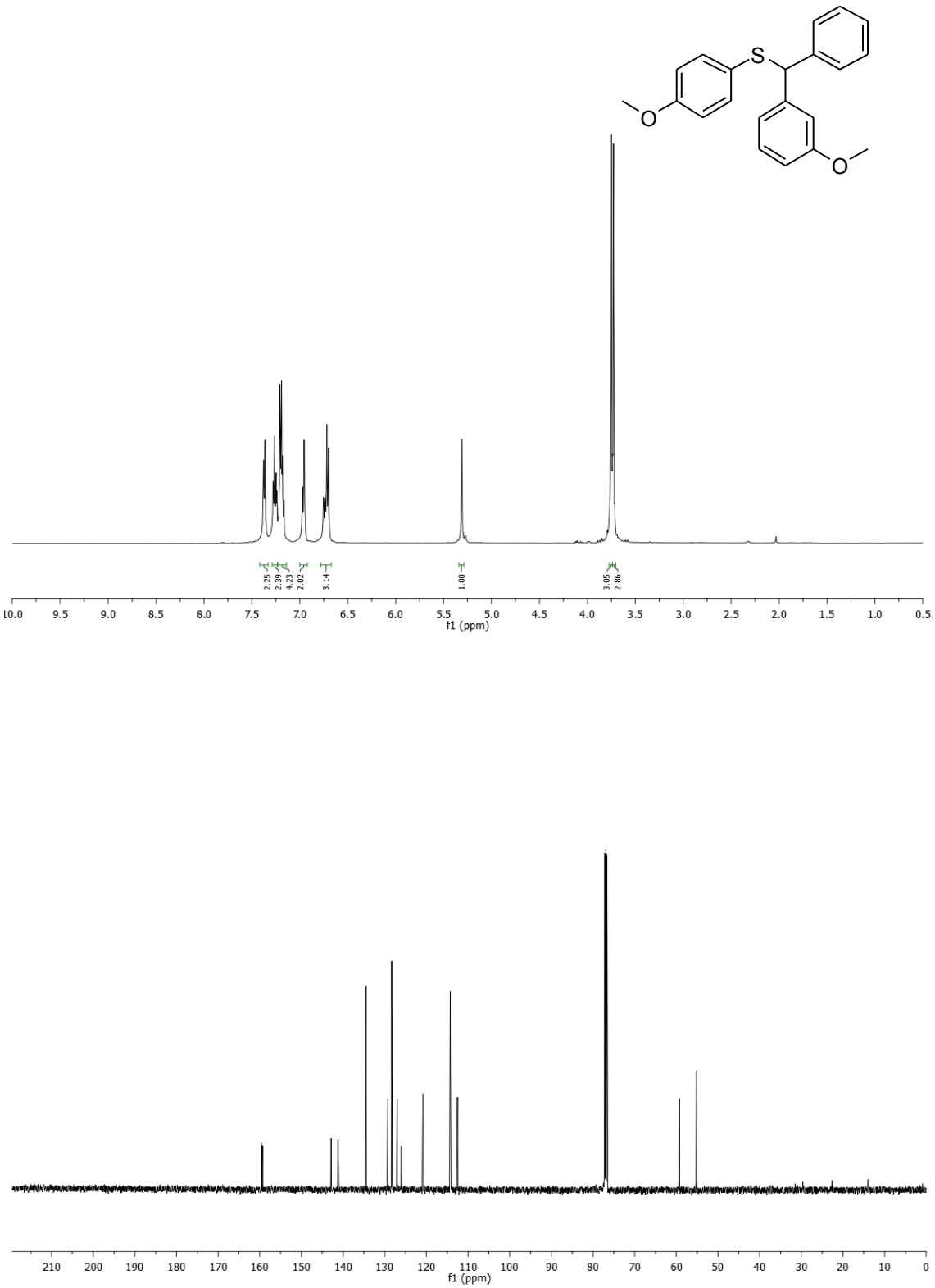


Figure S13 (**4m**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of (4-methoxyphenyl)((3-methoxyphenyl)(phenyl)methyl)sulfane in $CDCl_3$.

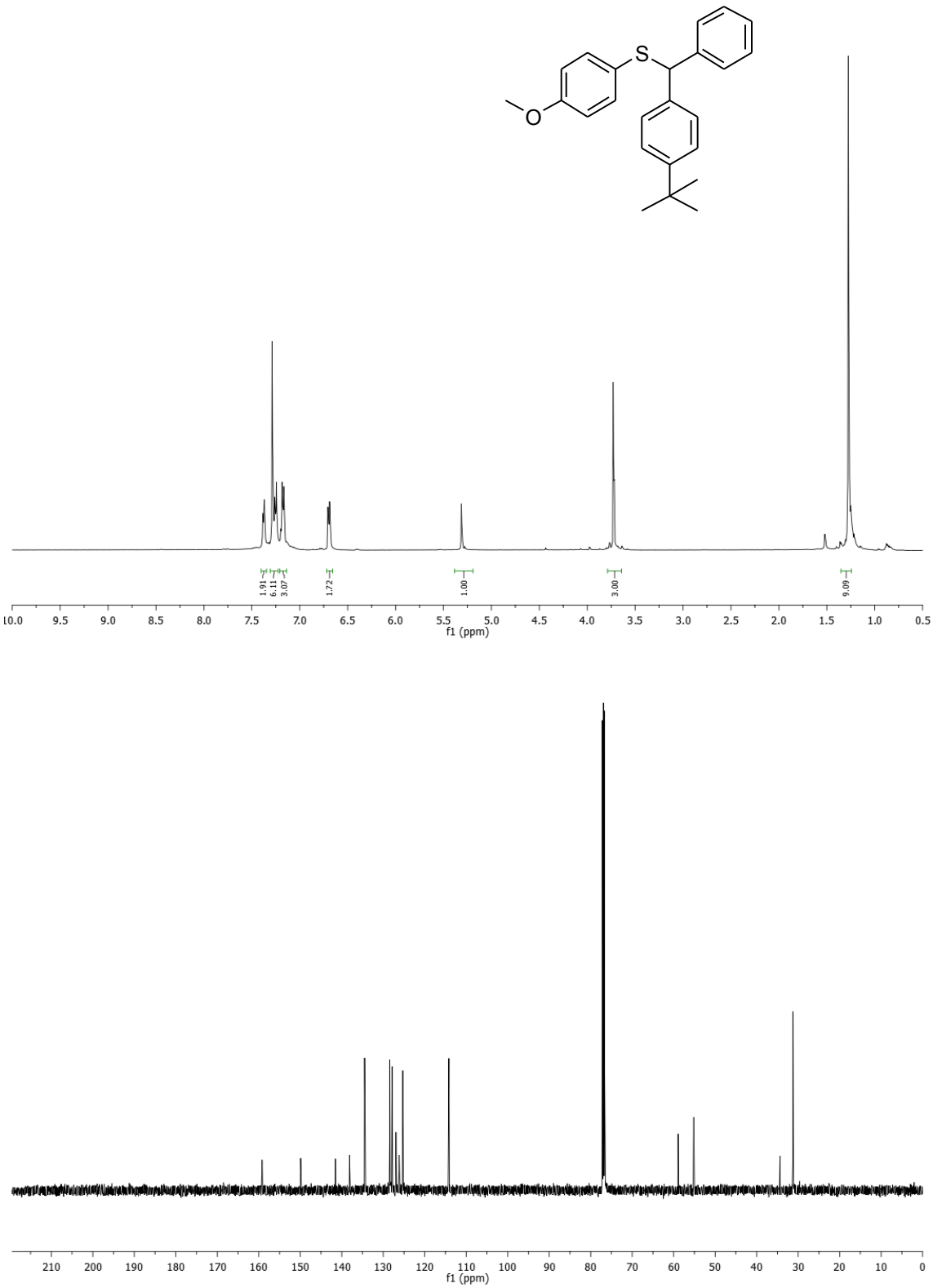


Figure S14 (**4n**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of ((4-(tert-butyl)phenyl)(phenyl)methyl)(4-methoxyphenyl)sulfane in $CDCl_3$.

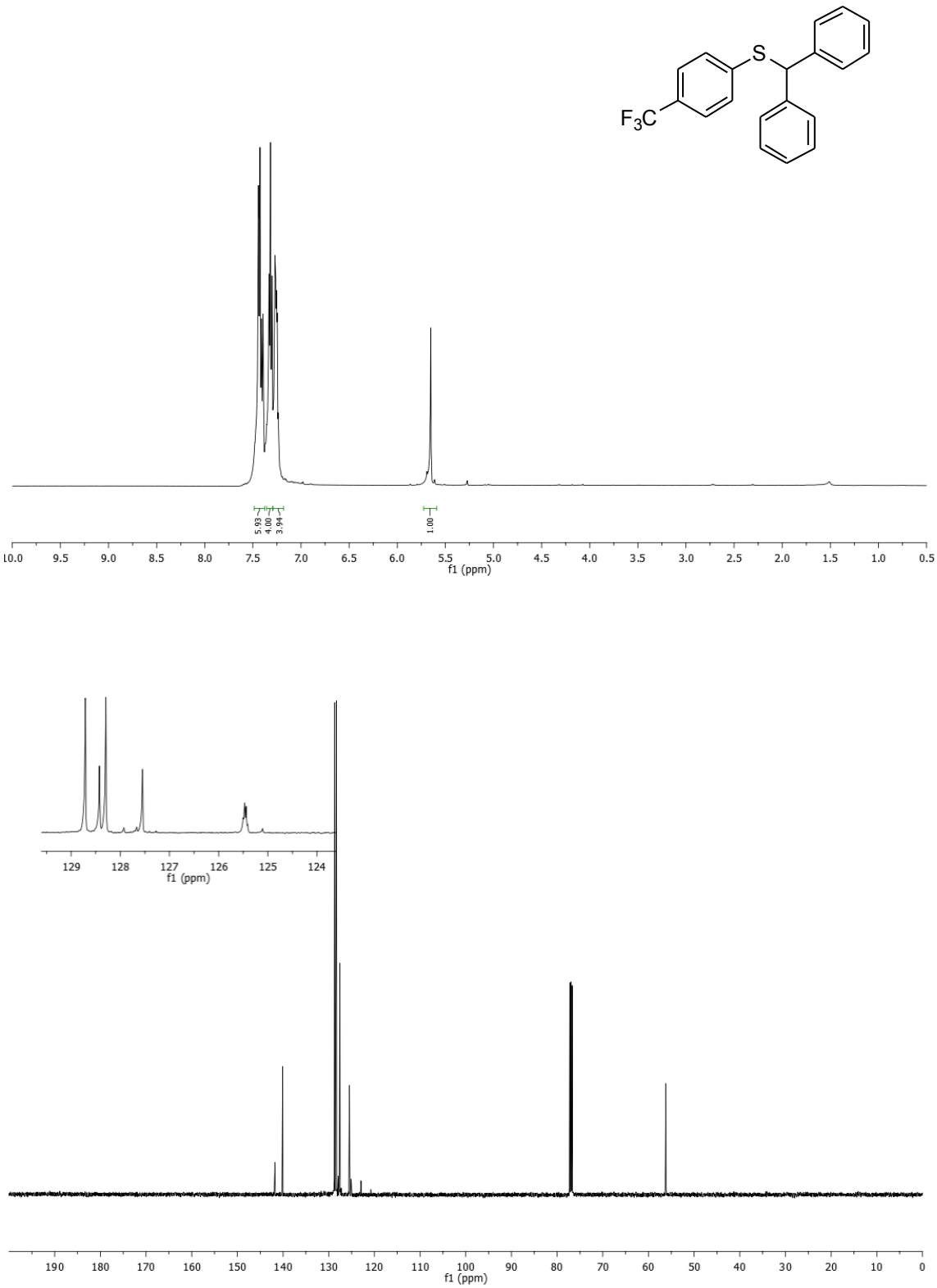


Figure S15 (**4o**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of benzhydryl(4-(trifluoromethyl)phenyl)sulfane in $CDCl_3$.

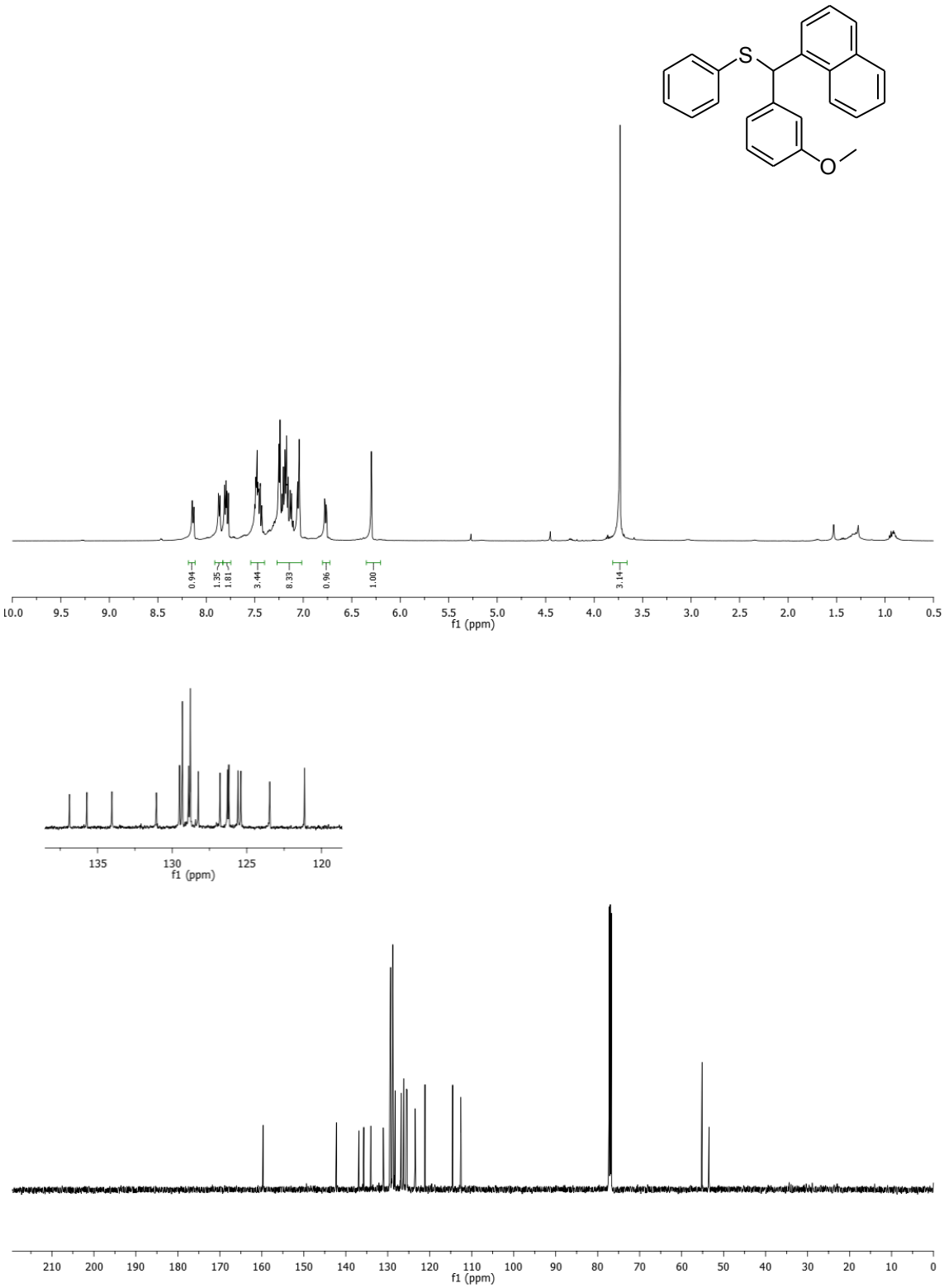


Figure S16 (**4p**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of ((3-methoxyphenyl)(naphthalen-1-yl)methyl)(phenyl)sulfane in $CDCl_3$.

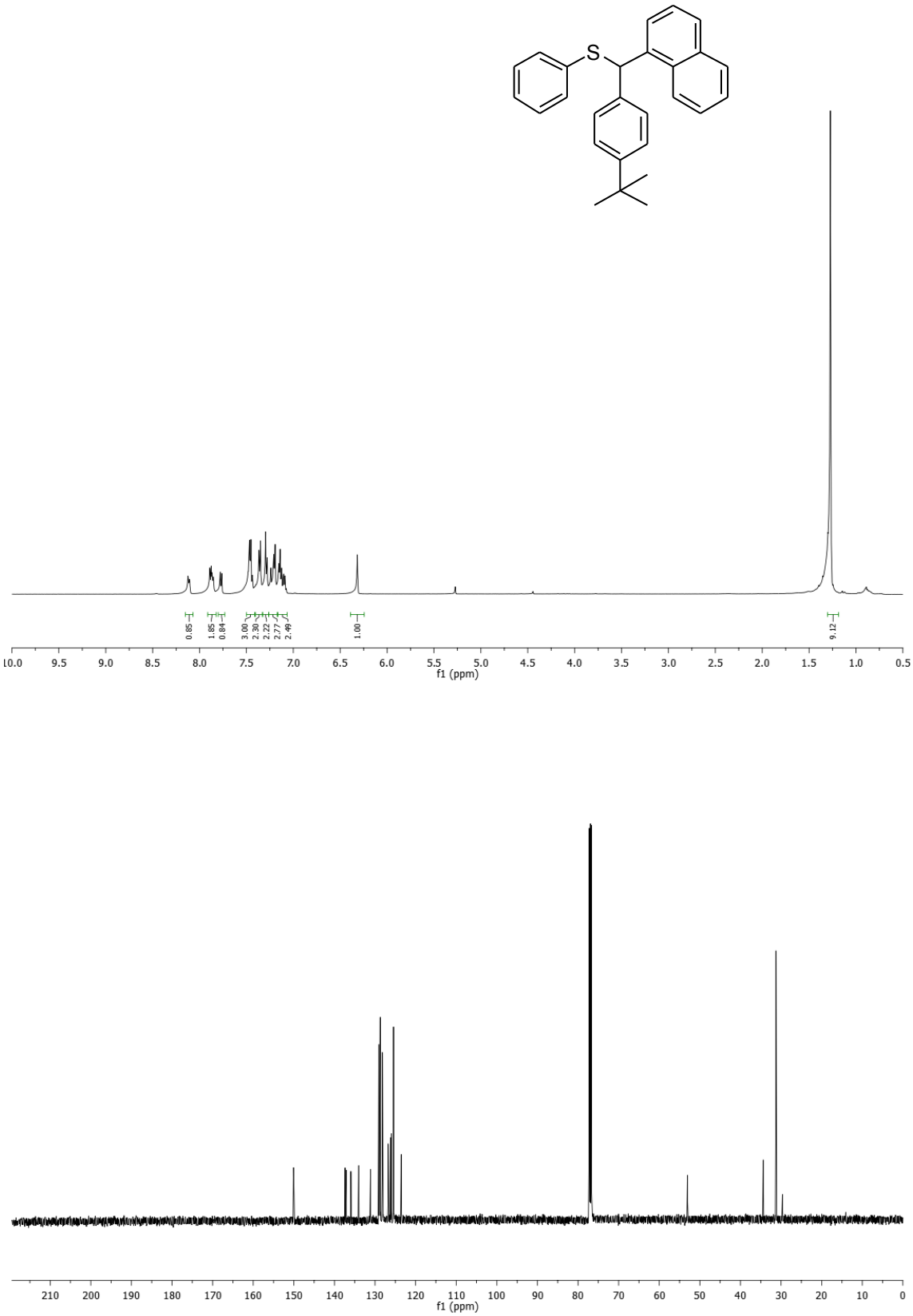


Figure S17 (**4q**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of ((4-(tert-butyl)phenyl)(naphthalen-1-yl)methyl)(phenyl)sulfane in $CDCl_3$.

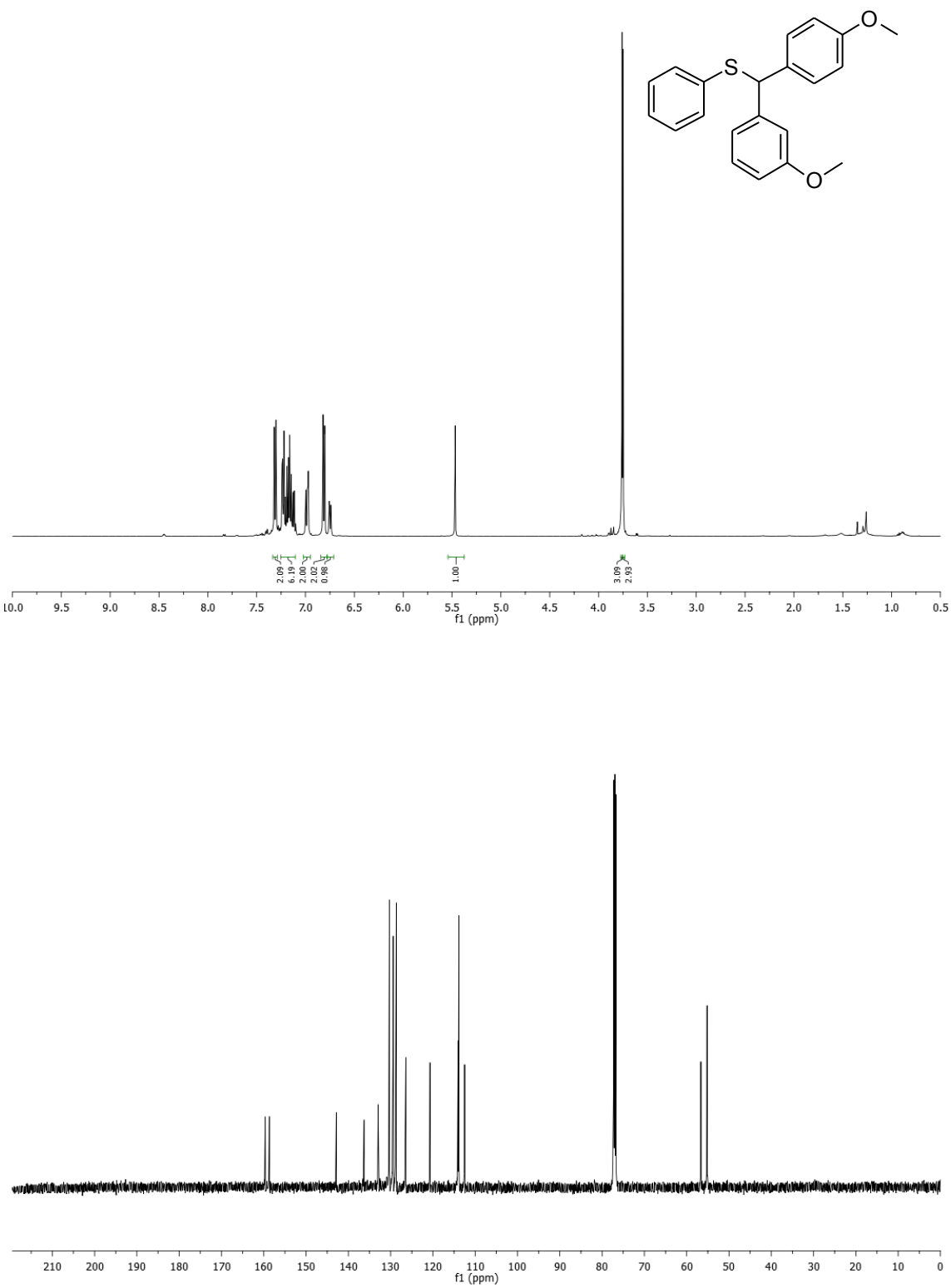
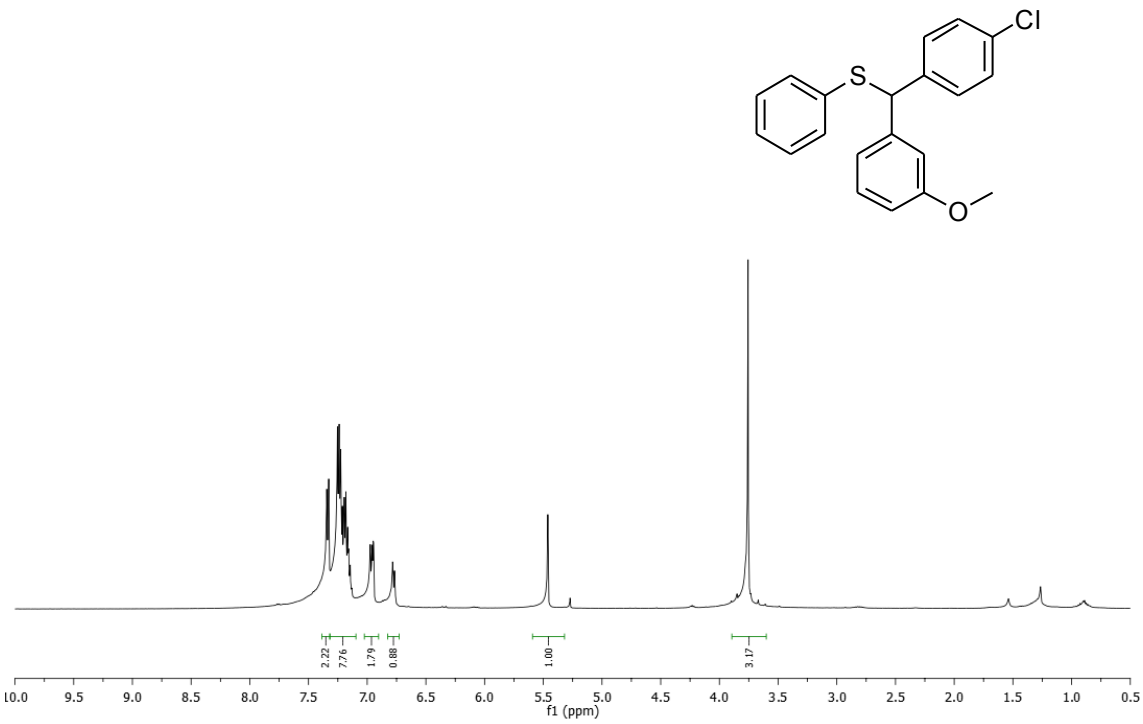


Figure S18 (**4r**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of ((3-methoxyphenyl)(4-methoxyphenyl)methyl)(phenyl)sulfane in $CDCl_3$.



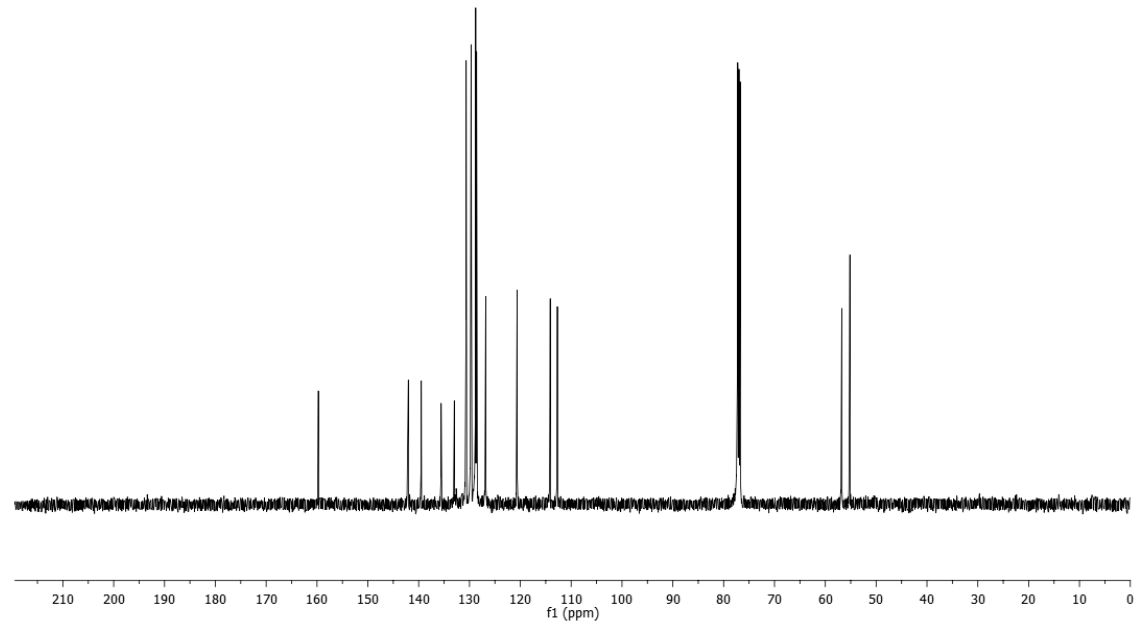
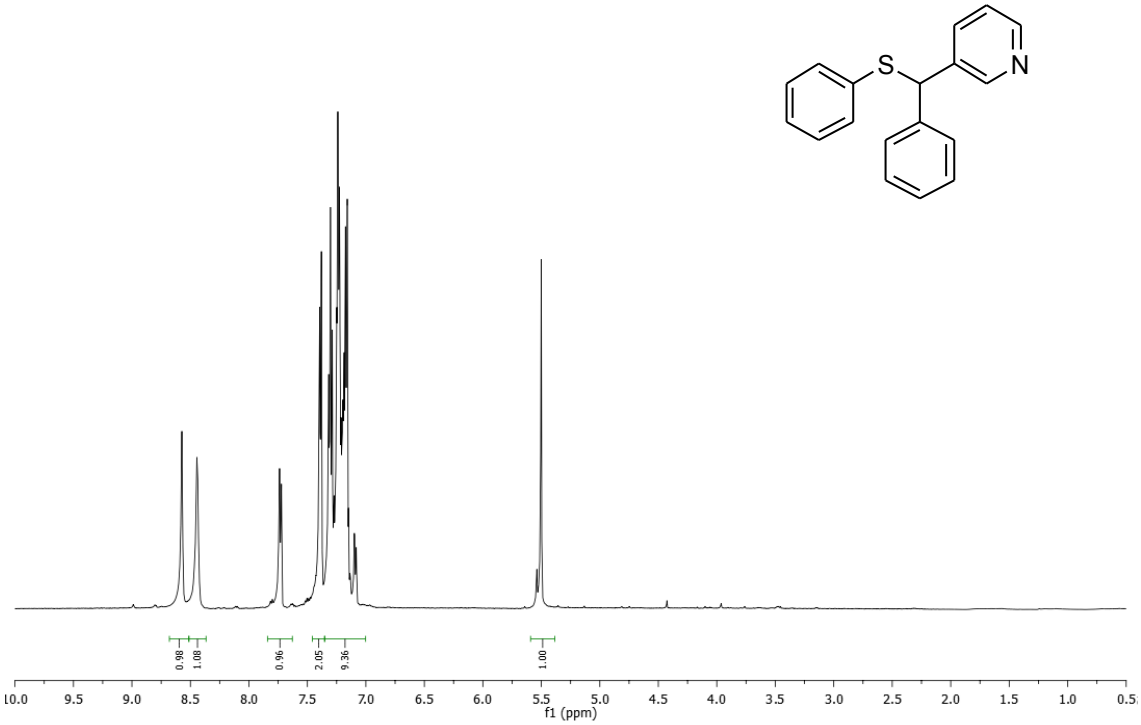


Figure S19 (**4s**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of ((4-chlorophenyl)(3-methoxyphenyl)methyl)(phenyl)sulfane in $CDCl_3$.



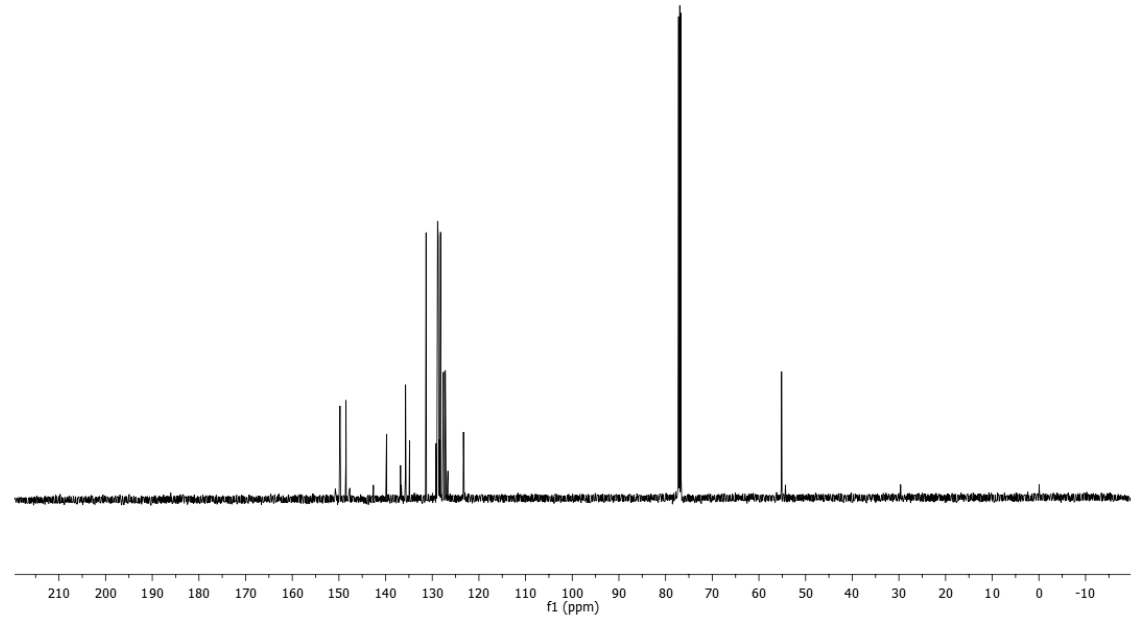


Figure S20 (**4t**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 3-(phenyl(phenylthio)methyl)pyridine in $CDCl_3$.

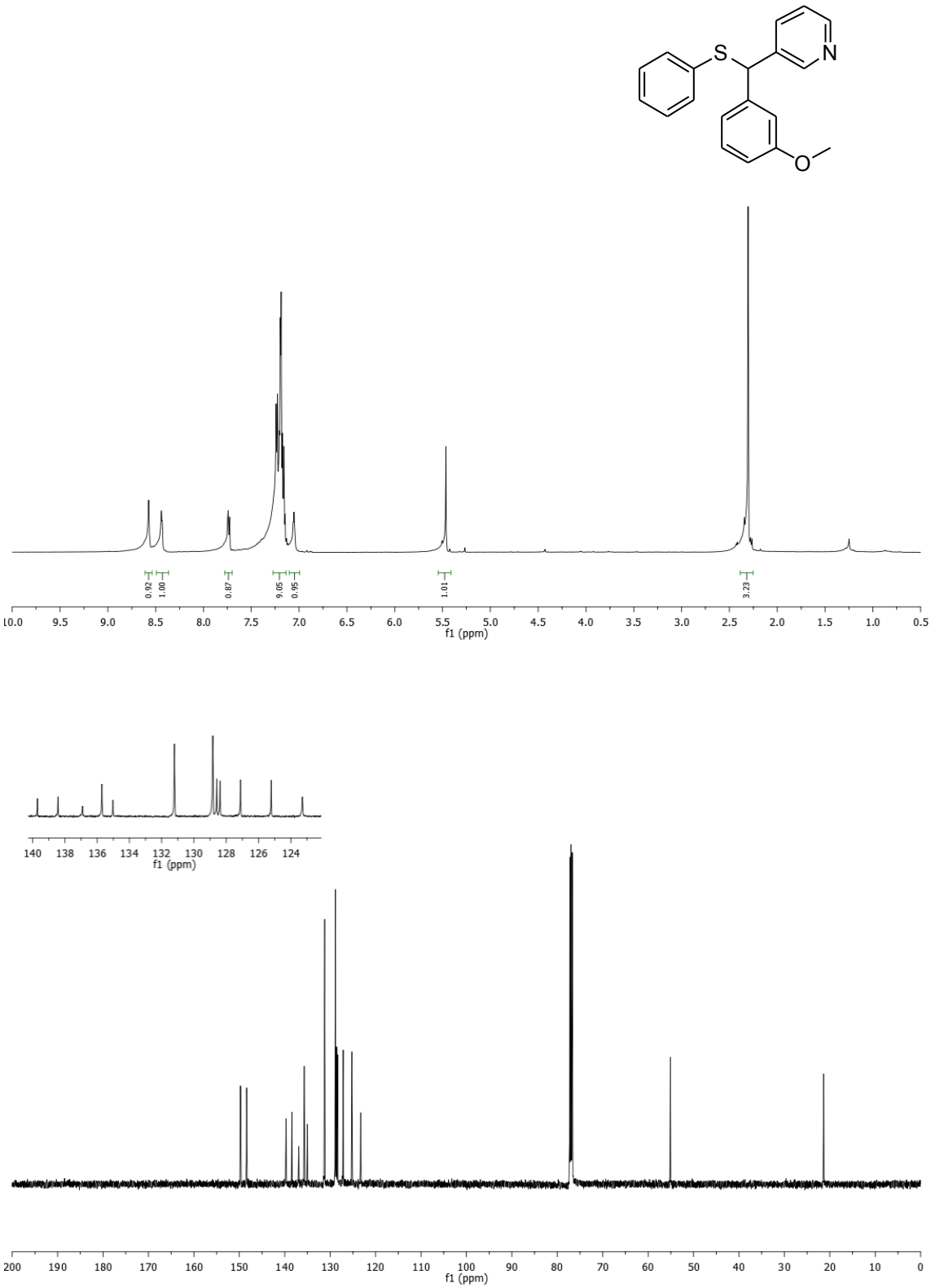


Figure S21 (**4u**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of ((4-(tert-butyl)phenyl)(phenyl)methyl)(phenyl)sulfane in $CDCl_3$.

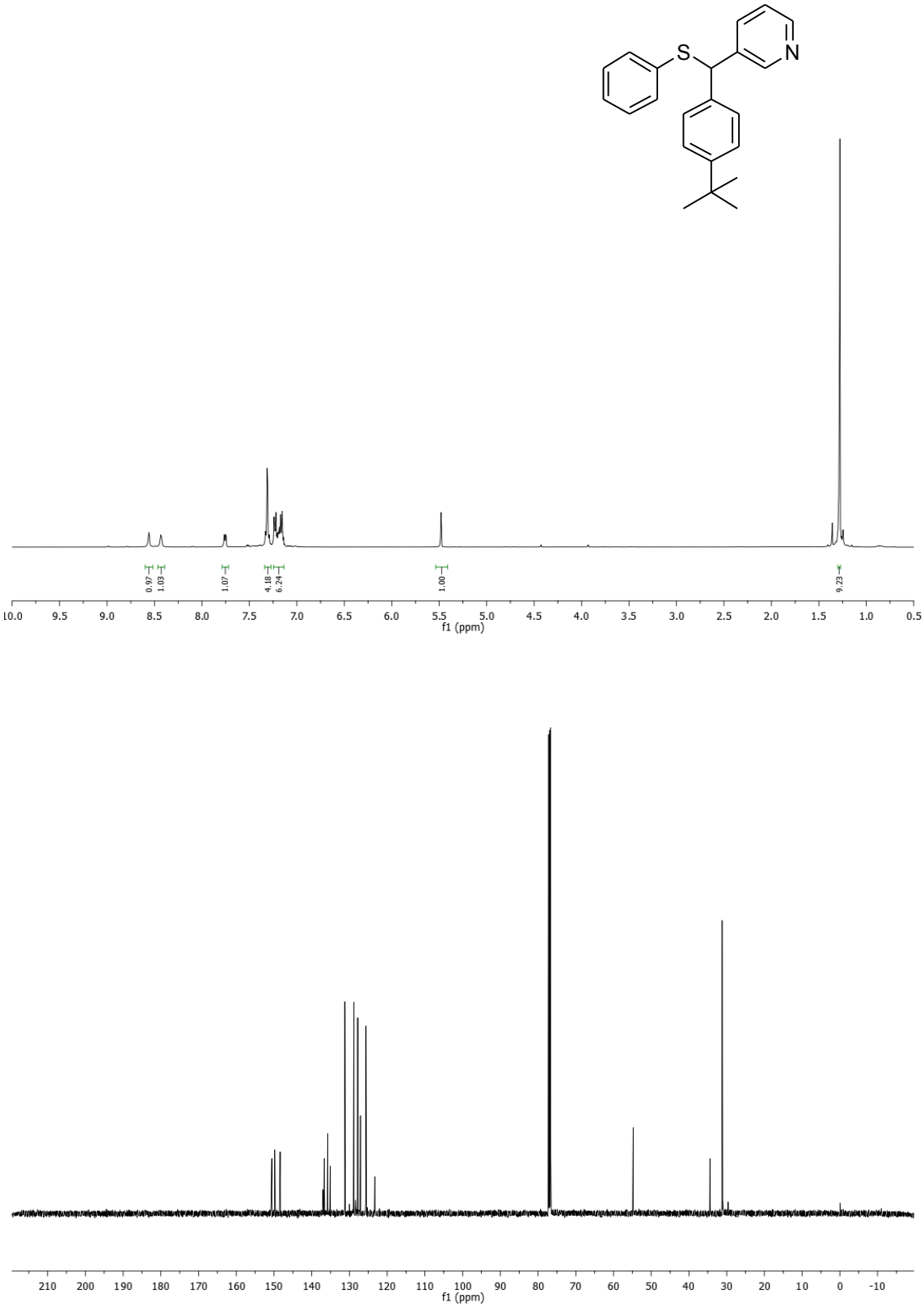
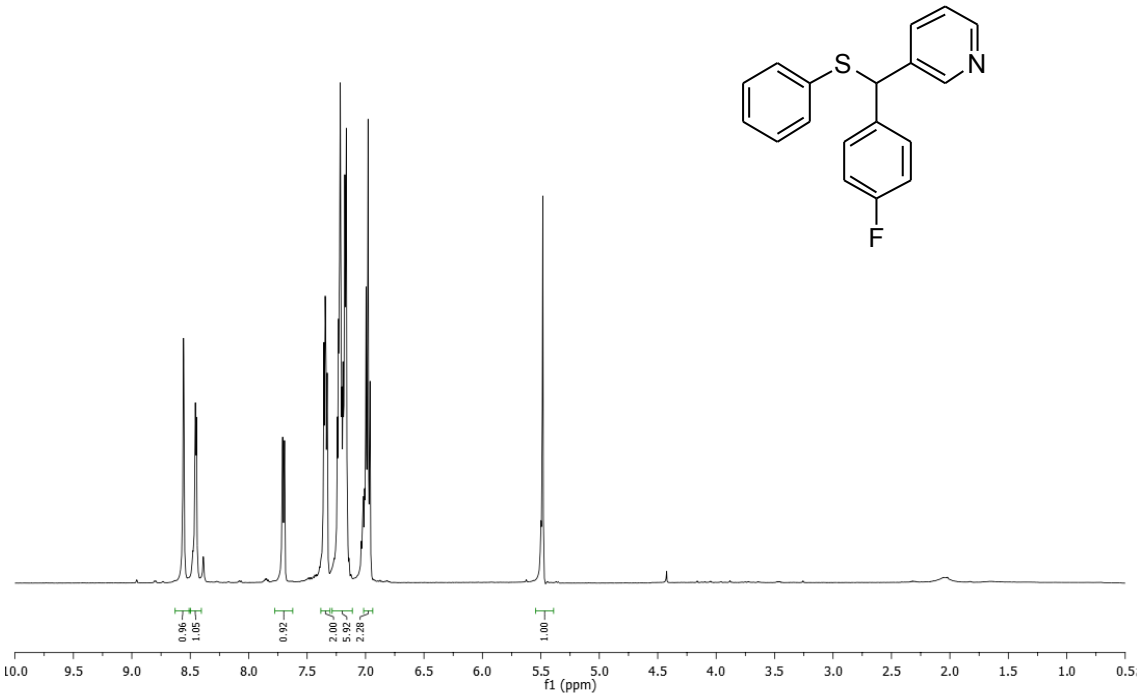


Figure S22 (**4v**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 3-((4-(tert-butyl)phenyl)(phenylthio)methyl)pyridine in $CDCl_3$.



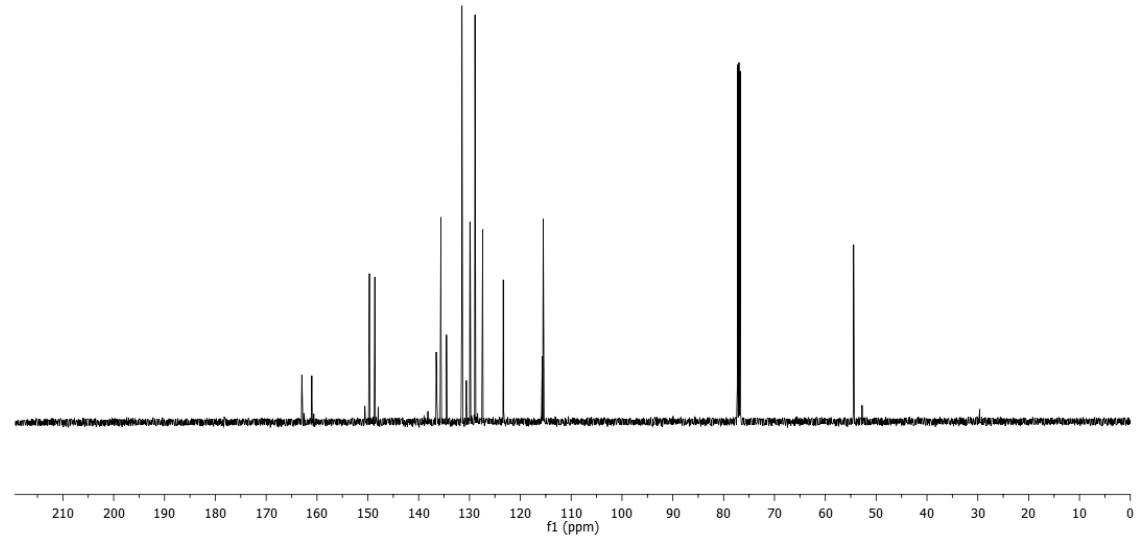


Figure S23 (**4x**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of 3-((4-fluorophenyl)(phenylthio)methyl)pyridine in $CDCl_3$.

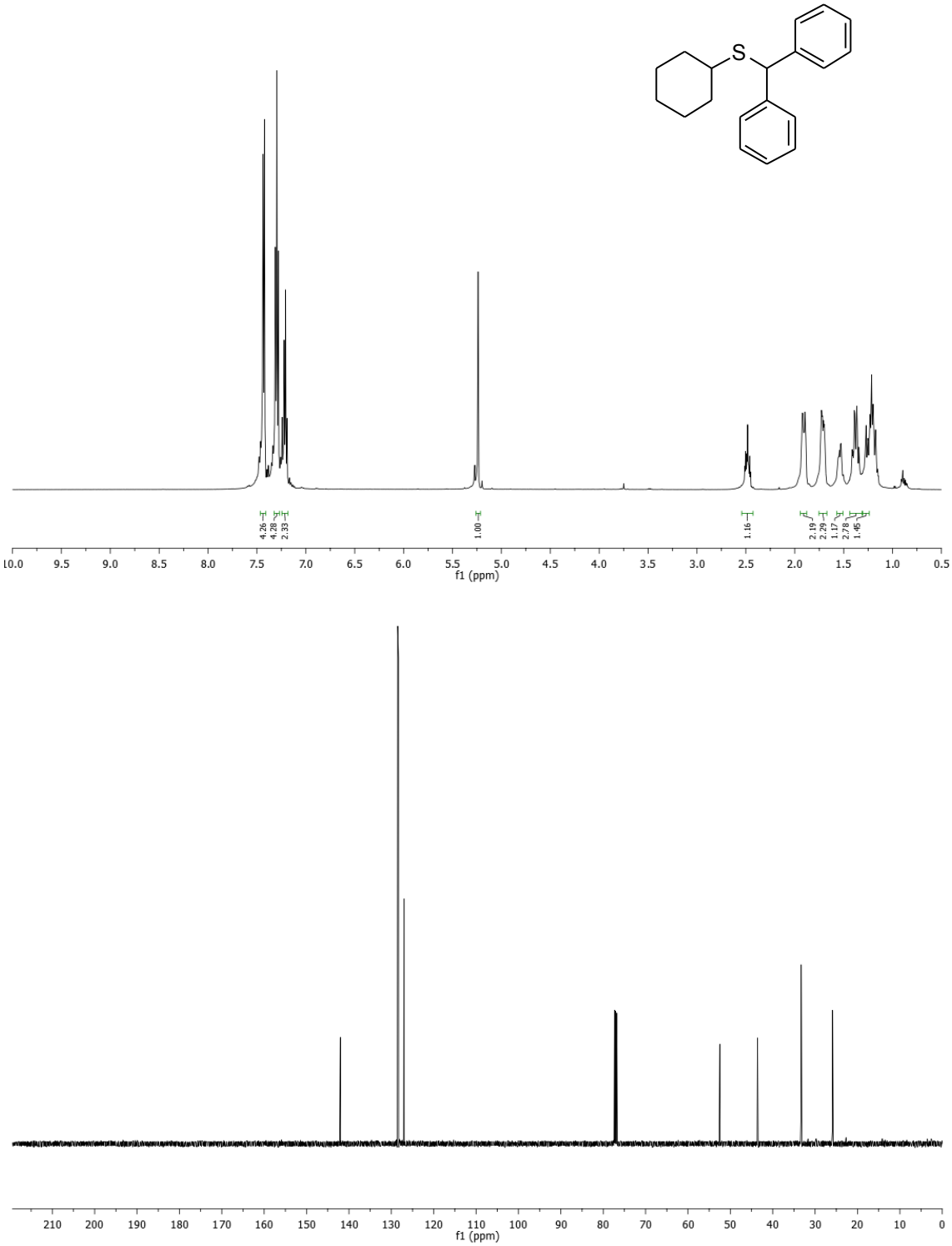
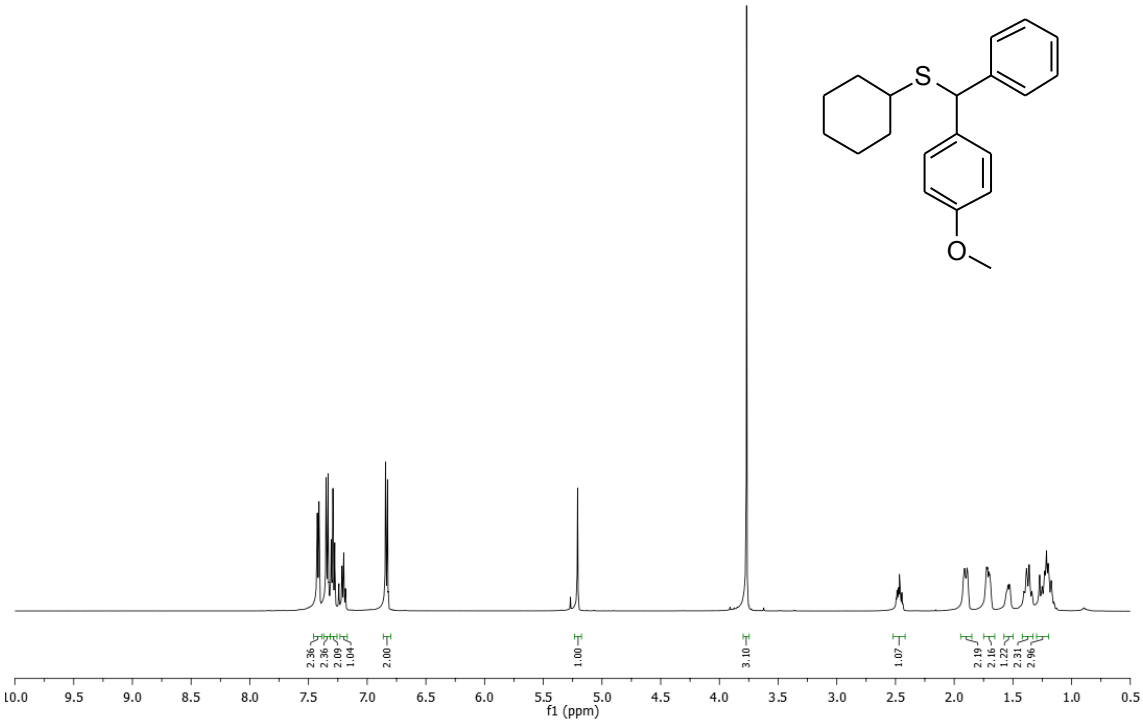


Figure S24 (**6a**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of benzhydryl(cyclohexyl)sulfane in $CDCl_3$.



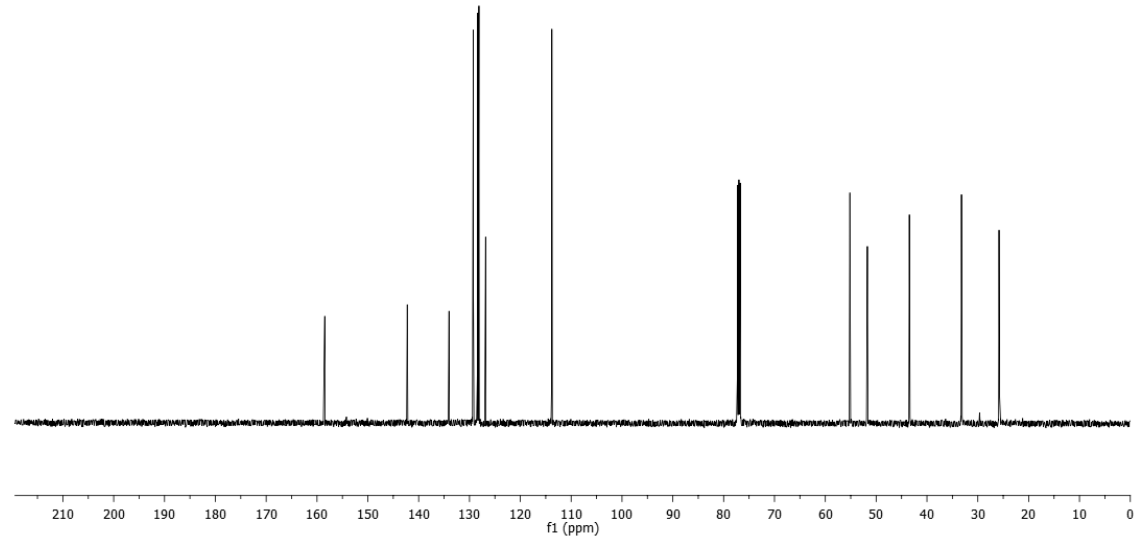
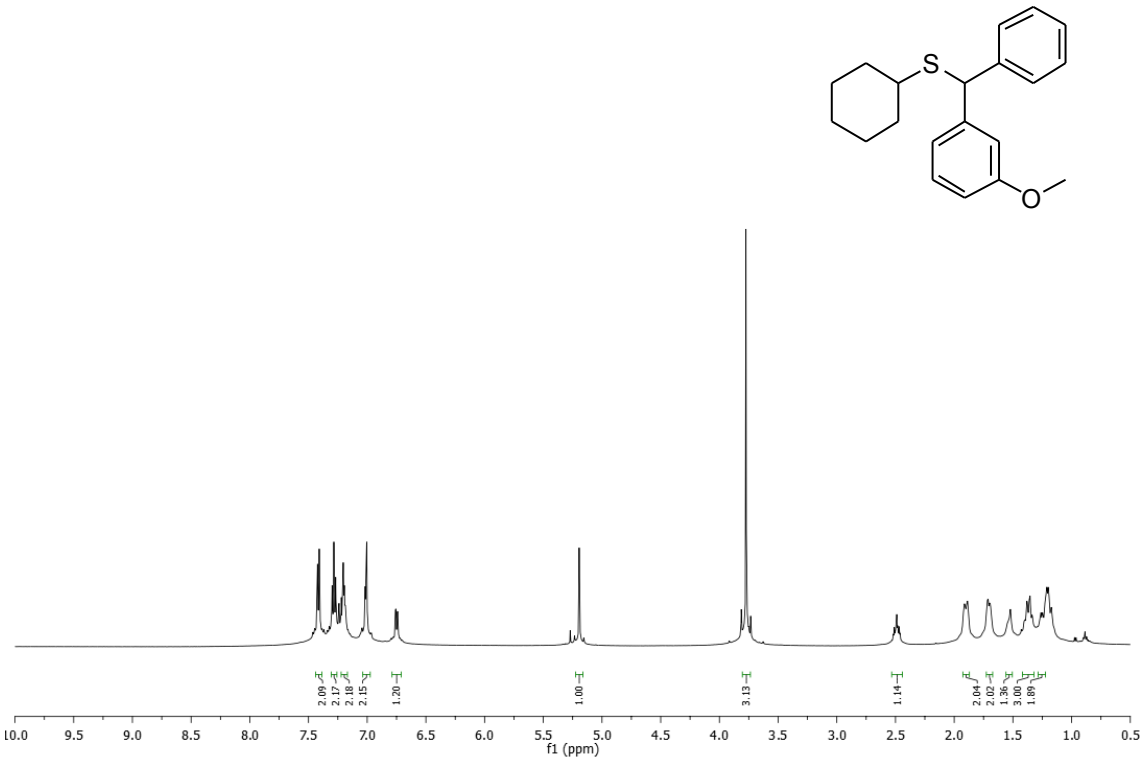


Figure S25 (**6b**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of cyclohexyl((4-methoxyphenyl)(phenyl)methyl)sulfane in $CDCl_3$.



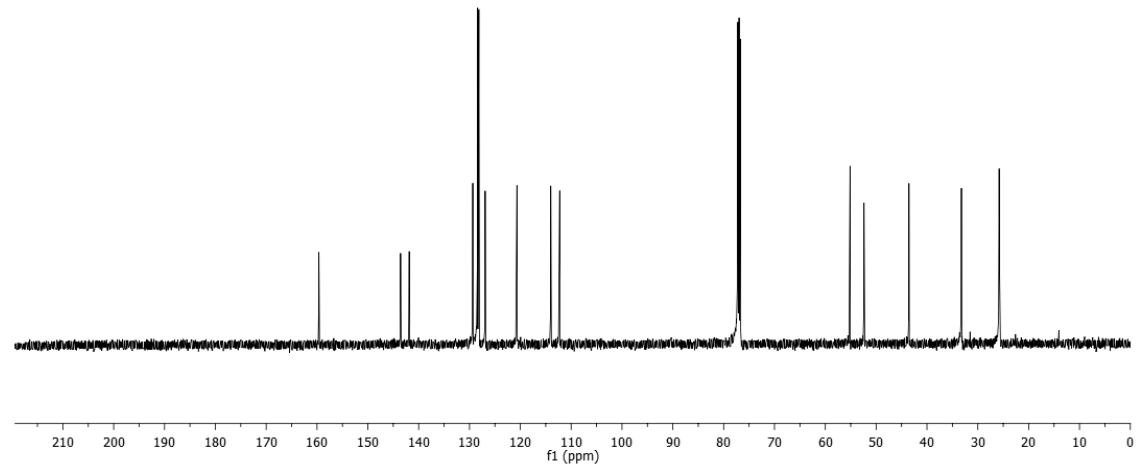


Figure S26 (**6c**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of cyclohexyl((3-methoxyphenyl)(phenyl)methyl)sulfane in $CDCl_3$.

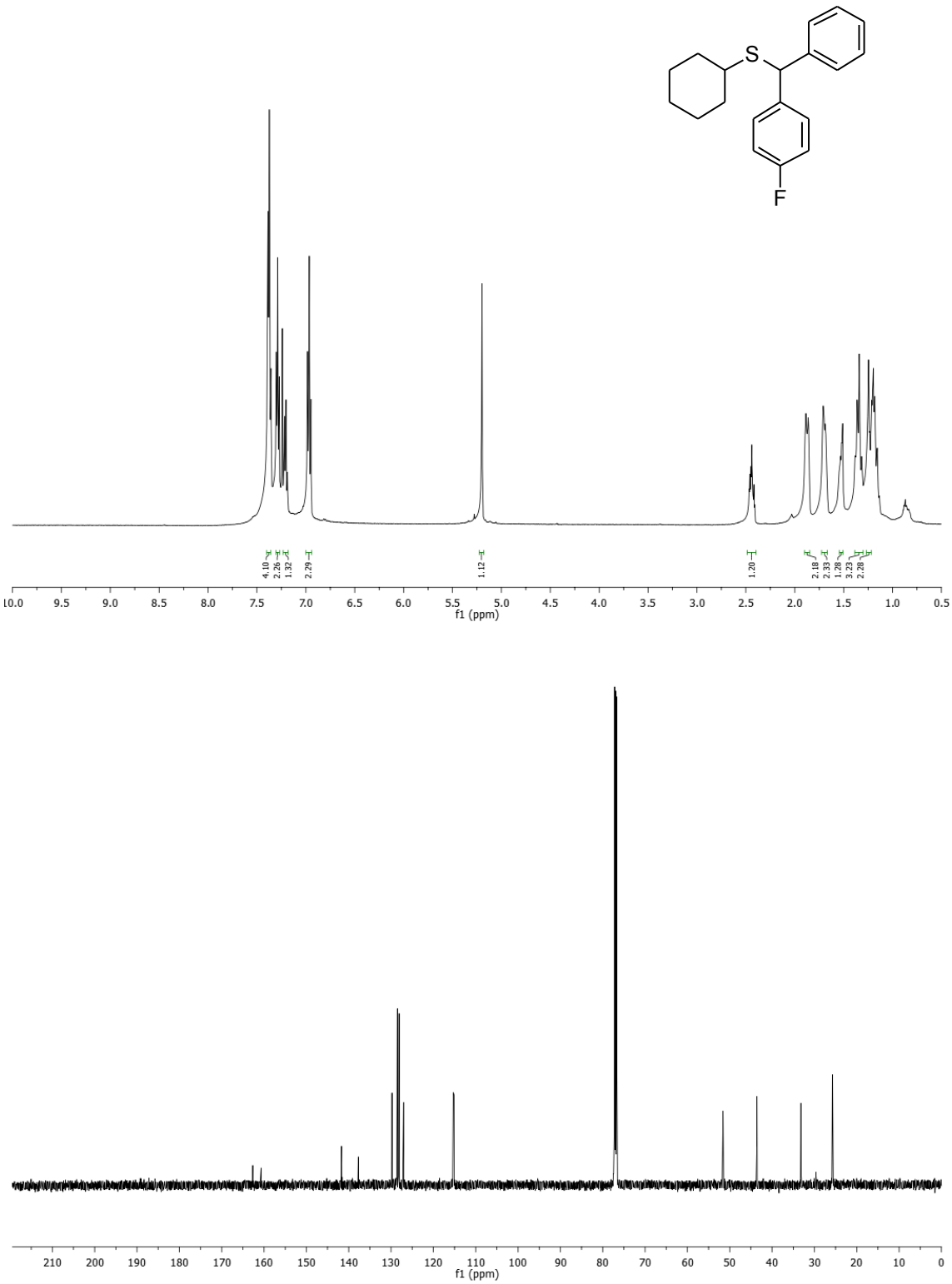


Figure S27 (**6d**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of cyclohexyl((4-fluorophenyl)(phenyl)methyl)sulfane in $CDCl_3$.

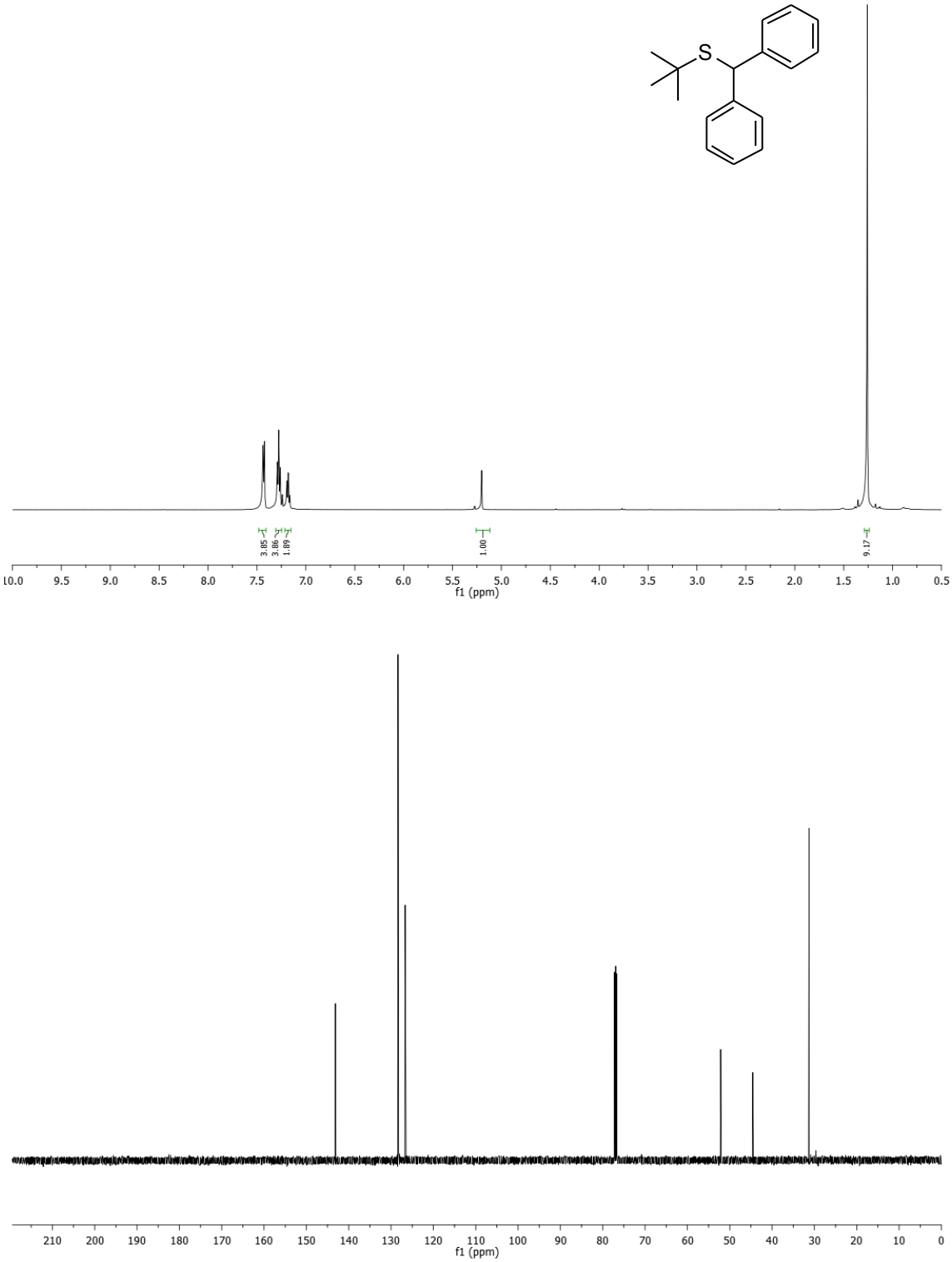
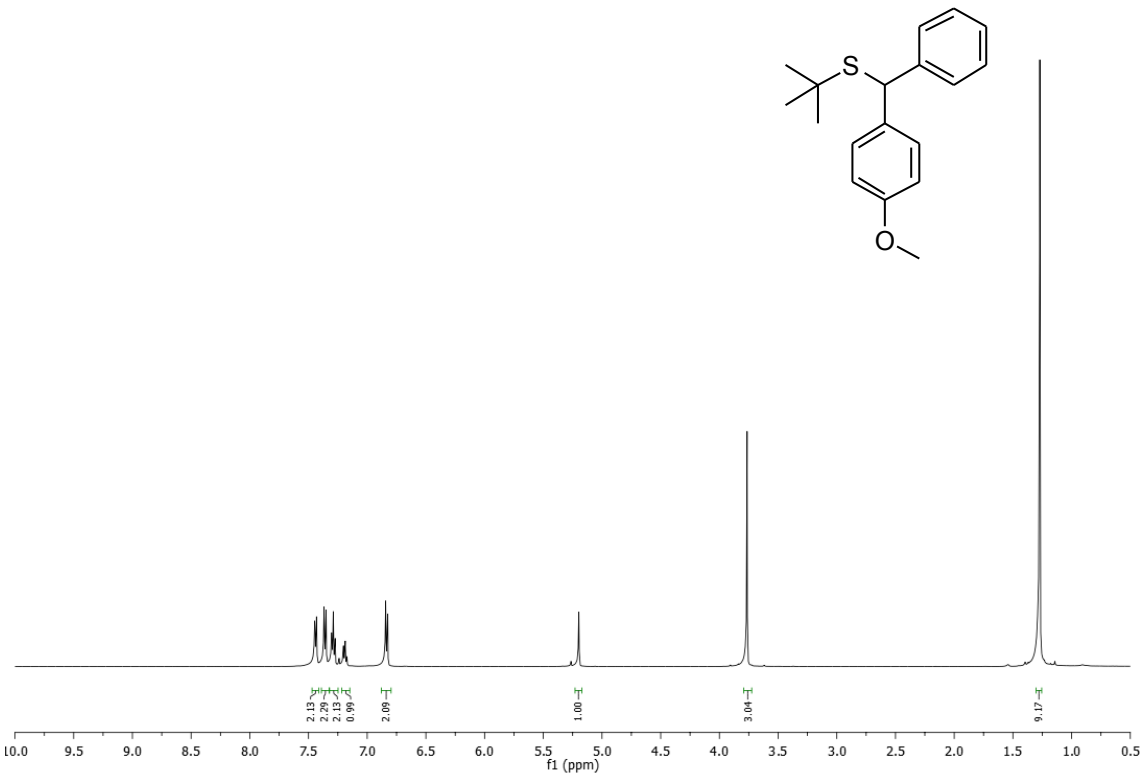


Figure S28 (**6e**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of benzhydryl(tert-butyl)sulfane in $CDCl_3$.



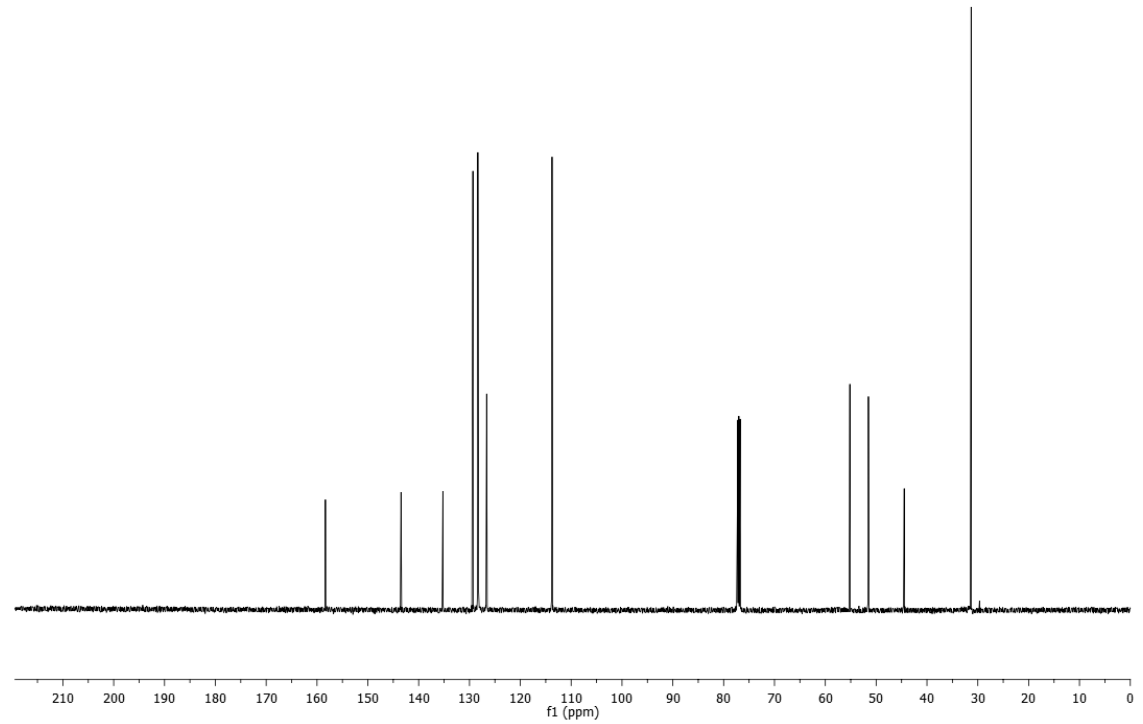


Figure S29 (**6f**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of tert-butyl((4-methoxyphenyl)(phenyl)methyl)sulfane in $CDCl_3$.

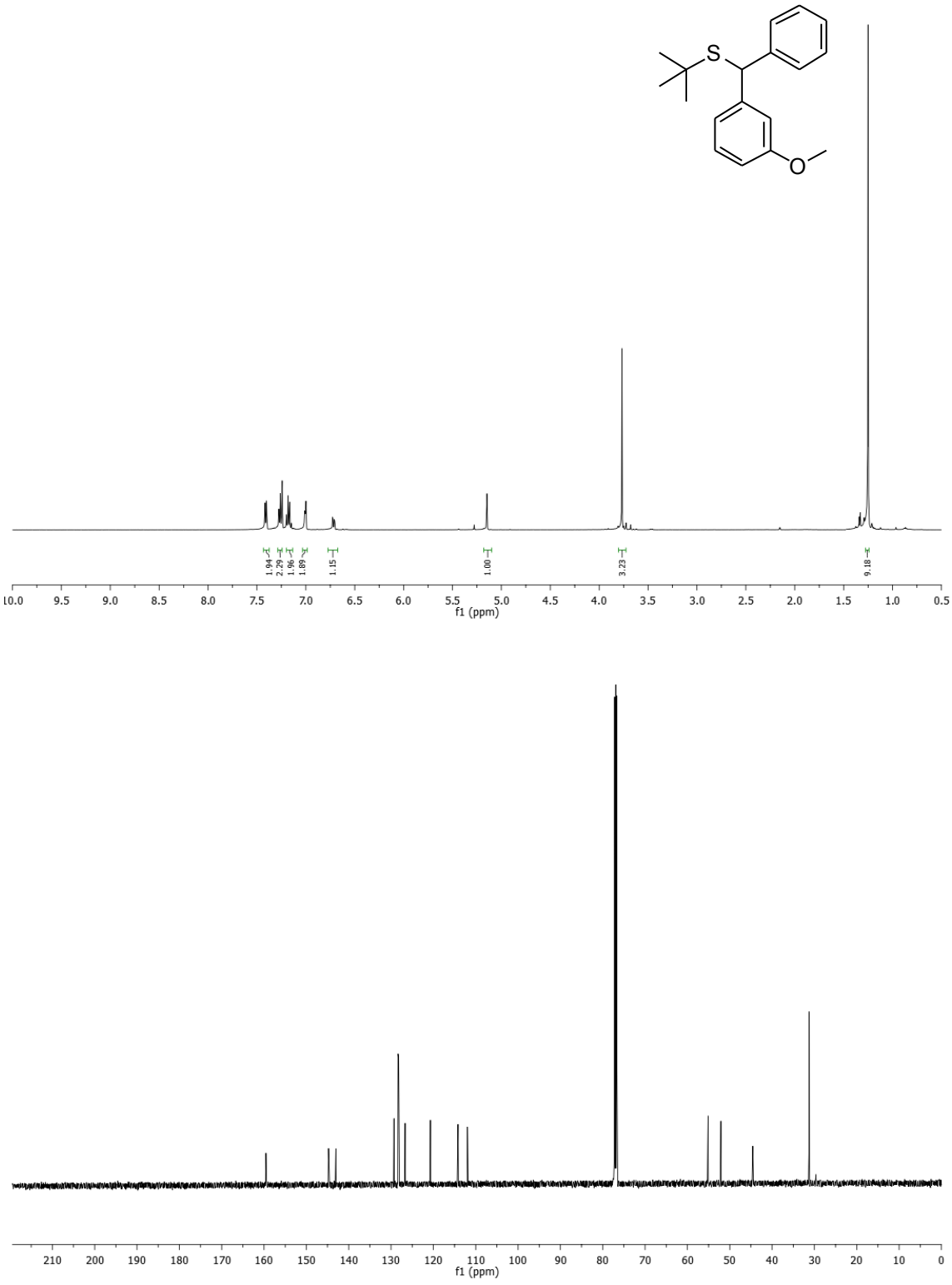
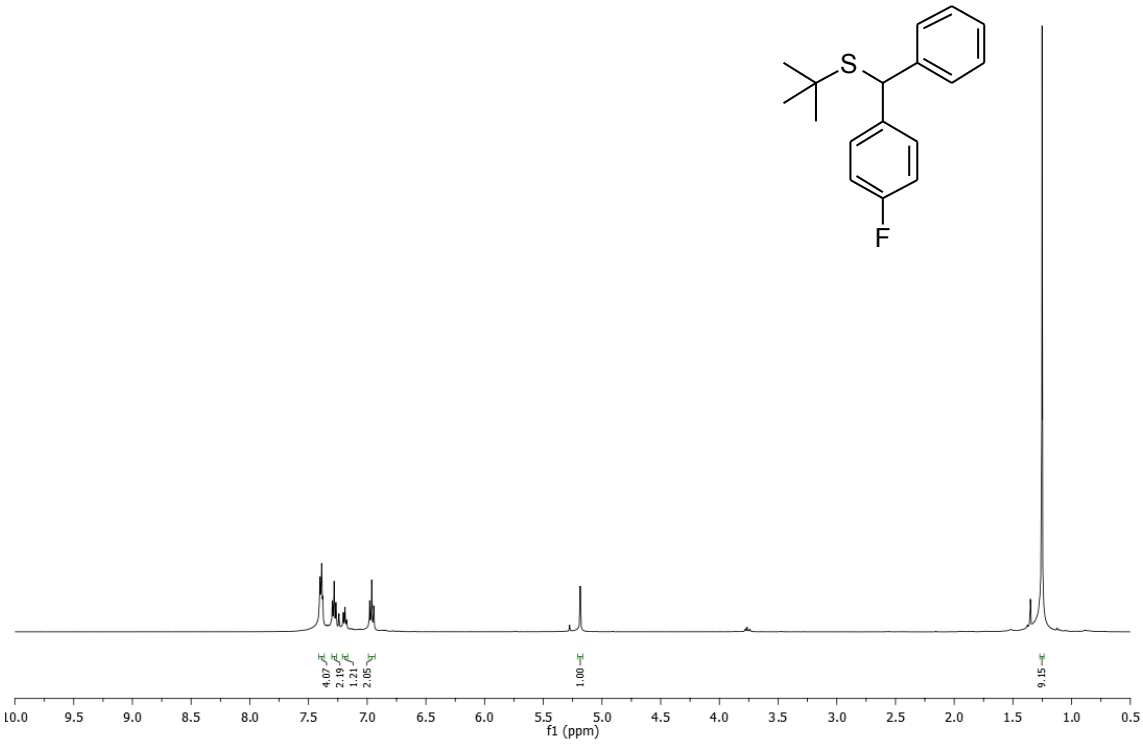


Figure S30 (**6g**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of tert-butyl((3-methoxyphenyl)(phenyl)methyl)sulfane in $CDCl_3$.



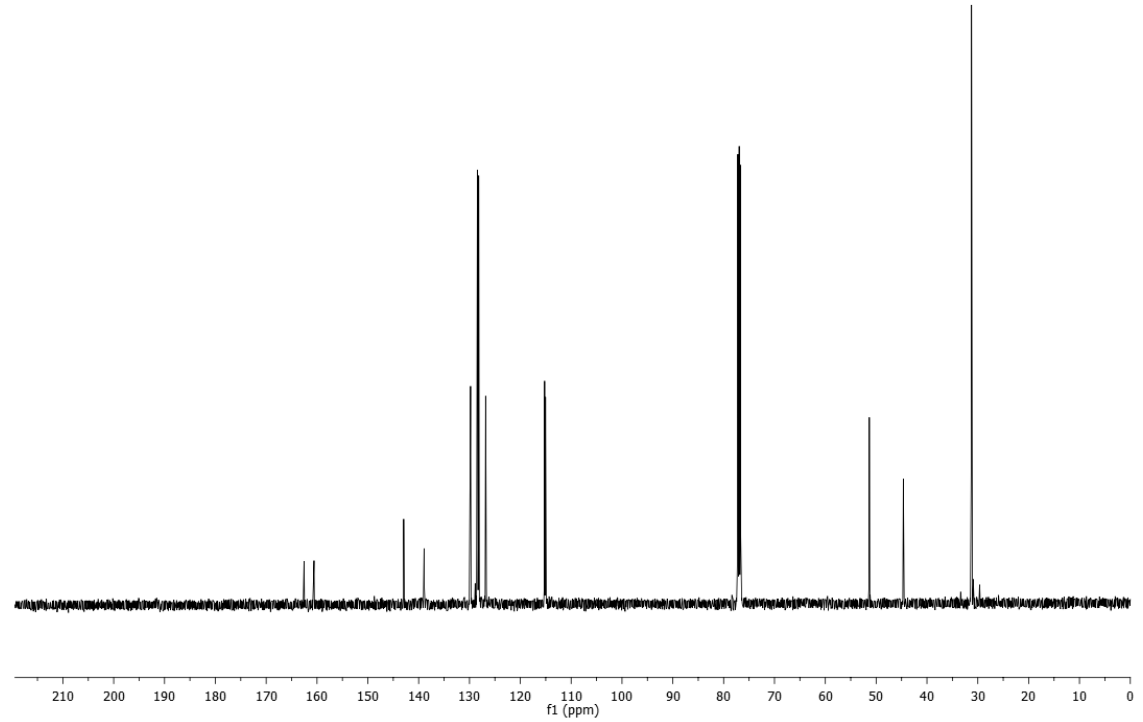


Figure S31 (**6h**). 500 MHz ^{1}H and 125 MHz $^{13}C\{^{1}H\}$ NMR of tert-butyl((4-fluorophenyl)(phenyl)methyl)sulfane in $CDCl_3$.

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