Supplementary Materials for:

Synthesis of Indoles by Palladium-Catalyzed Reductive Cyclization of β-Nitrostyrenes with Phenyl Formate as a CO Surrogate

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1. Apparatus employed

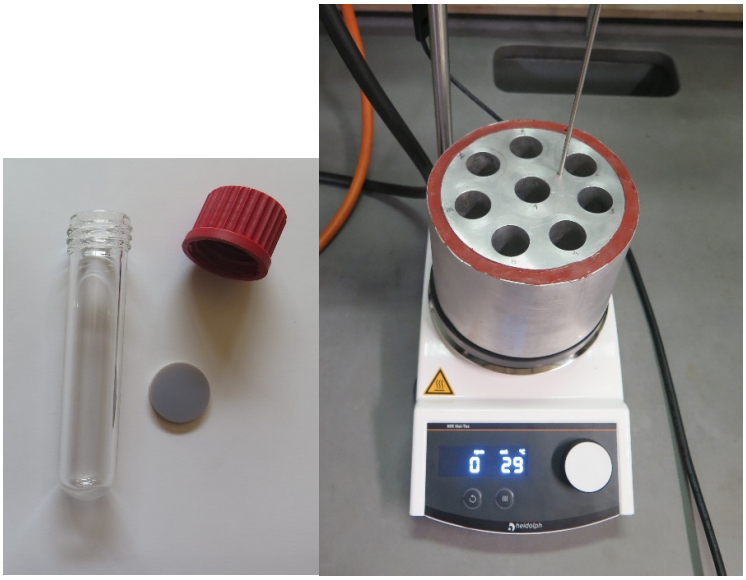
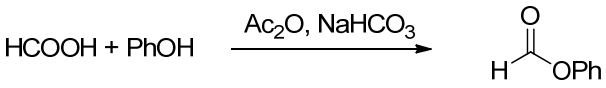


Figure S1. Left: Pressure tube employed during the present study (tube by Duran and caps by Schott, both commercialized by Fisher Scientific). Right: Heating block. In order to improve the temperature uniformity, the central aluminum block was thermally insulated by placing it into a larger aluminum pot and the *ca*. 1 cm wide gap on the sides, not on the bottom, was filled with vermiculite and sealed with a silicone sealant for high-temperatures.

2. Phenyl formate synthesis



The procedure was adapted from a previously reported one.[1] In a dry 250 mL round bottom Schlenk flask, formic acid (35 mL, 0.93 mol) and acetic anhydride (70 mL, 0.74 mol) were stirred at 60 ºC for 1 hour. The mixture was then allowed to cool to room temperature and transferred using a cannula into an ice-cooled 500 mL Schlenk containing phenol (17.4 g, 0.19 mol) and sodium bicarbonate (15.5 g, 0.19 mol). After the addition, the reaction temperature let to reach to room temperature and stirred overnight under a dinitrogen atmosphere. A mixture of CH_2Cl_2 (80 mL) and water (100 mL) was then added and the biphasic system was stirred vigorously. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3×50 mL). The combined organic layers were washed with water (7×50 mL) and brine (3×25 mL), to get rid of residual acid, dried over Na_2SO_4 and filtered. The solvent was evaporated to give the final product as pale-yellow liquid (16.5 mL, 0.15 mol, 82%). The so obtained formate is analytically (NMR) pure and can be used without further purification.

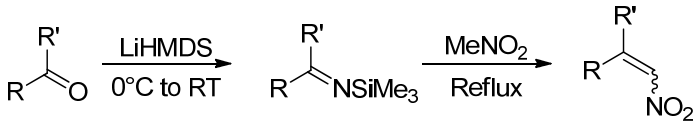
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.30 (t, J = 7.4 Hz, 1H, overlapped with $CDCl_3$ signal), 7.17 (d, J = 7.7 Hz, 2H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3 (H*C*O), 149.9 (*C*), 129.6 (*C*H), 126.3 (*C*H), 121.1 (*C*H) ppm.

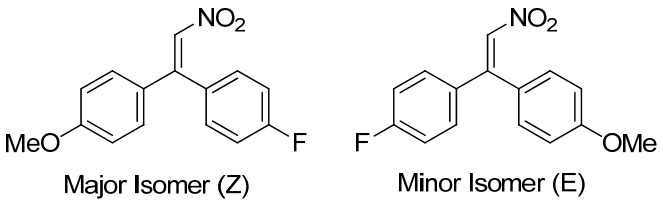
3. Preparation of β-nitrostyrenes

Nitroolefins **1a**,[2] **1b**,[3] **1c**,[4] **1k**,[3a] were prepared as previously reported in the literature. **1e** was synthesized from commercial auramine hydrochloride following a previously reported procedure.[5] Analytical data were in agreement to previous reports.[6] The other substrates were synthesized following the modified procedure herein reported.

3.1. General synthetic procedure for the synthesis of α-aryl-β-nitrostyrenes – Method A

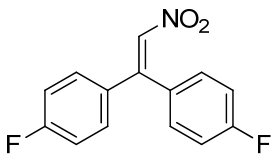


The method was adapted from a procedure previously reported in the literature.[4] In an oven dried Schlenk flask, the substituted benzophenone (4 mmol.) was dissolved in dry THF (20 mL) and the flask cooled in an ice-bath. Lithium hexamethyldisilazane (LiHMDS) (9 mL, 1 M solution in THF) was added dropwise and then the mixture stirred for 24 h at room temperature. THF was then evaporated under vacuum and ethyl acetate (20 mL) was added in the air. The organic layer was washed with brine (3×15 mL), dried over anhydrous Na_2SO_4, and filtered. The solvent was evaporated and nitromethane (15 mL) was added to the residue. The mixture was refluxed under a dinitrogen atmosphere for 48 h. Nitromethane was then evaporated to give the residue, which was purified by either crystallization or column chromatography. Substrates **1d**, **1e** and **1g** were prepared using this method.

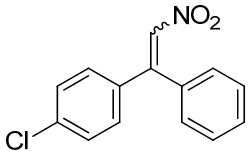


1-fluoro-4-(1-(4-methoxyphenyl)-2-nitrovinyl)benzene (1d). Obtained as yellow solid (361 mg, 1.32 mmol, isomeric mixture *Z:E* = 1.7:1) after column chromatography (CH_2Cl_2/hexane 1:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (s, 1H, major isomer), 7.32 (s, 1H, minor isomer), 7.29 (dd, *J* = 8.8, 5.3 Hz, 2H, minor isomer), 7.23 – 7.20 (m, 4H, major isomer), 7.18 – 7.06 (m, 2H, major isomer and 4H, minor isomer), 6.94 (d, *J* = 8.8 Hz, 2H major isomer), 6.90 (d, *J* = 8.9 Hz, 2H, minor isomer), 3.86 (s, 3H), 3.84 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4 (d, *J* = 252.6 Hz, *C*F, minor isomer), 163.2 (d, *J* = 249.8 Hz *C*F, major isomer), 162.2 (*C*OCH_3, major isomer), 160.9 (*C*OCH_3, minor isomer), 149.7 (*C*, major isomer), 149.52 (*C*, minor isomer), 133.8 (d, *J* = 3.2 Hz, *C*, minor isomer), 133.5 (*C*H olefin, minor isomer), 133.05 (*C*H olefin, minor isomer), 131.6 (d, *J* = 3.4 Hz, *C*, major isomer), 131.3 (d, *J* = 8.6 Hz, *C*H, minor isomer), 131.0 (*C*H, minor isomer) overlapped with 130.9 (d, *C*H, major isomer), 130.7 (*C*H, major isomer), 116.0 (d, *J* = 21.9 Hz, *C*H, minor isomer), 115.7 (d, *J* = 21.9 Hz, *C*H, major isomer), 114.4 (*C*H, major isomer), 114.0(*C*H,

minor isomer), 55.5 (*C*H_3, major isomer), 55.35 (*C*H_3, minor isomer) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.96, -111.36 ppm. Elemental Analysis for $C_{15}H_{12}FNO_3$ Calc.: C, 65.93; H, 4.43; N, 5.13. Found: C,65.53; H,4.63; N,5.14.

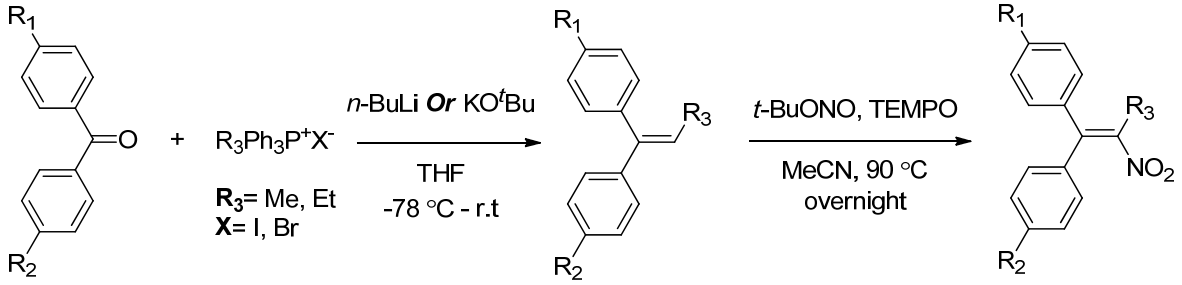


4,4'-(2-nitroethene-1,1-diyl)bis(fluorobenzene) (1e). Obtained as a yellow solid (439 mg, 1.7 mmol, 42% yield) after recrystallization from hexane:isopropanol = 8:2;. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.30 - 7.25 (m, 2H), 7.24 – 7.18 (m, 2H), 7.18 – 7.05 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6 (d, *J* = 253.2 Hz, *C*F), 163.5 (d, *J* = 250.2 Hz, *C*F), 148.5 (*C*), 133.2 (d, *J* = 3.1 Hz, *C*) 131.3 (d, *J* = 3.4 Hz, *C*), 131.2 (*C*H), 131.1 (d, $J_{C\text{-}F}$ = 1.4 Hz, *C*H), 116.4 (d, $J_{C\text{-}F}$ = 21.9 Hz, *C*H), 116.0 (d, $J_{C\text{-}F}$ = 21.9 Hz, *C*H) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -108.58, -110.90 ppm. Elemental Analysis for $C_{14}H_9F_2NO_2$ Calc.: C, 64.37; H, 3.47; N, 5.36. Found: C, 64.84; H, 4.08; N, 5.46



1-chloro-4-(2-nitro-1-phenylvinyl)benzene (1g). Obtained as a yellow solid (582 mg, 2.2 mmol, 56% yield, mixture of two isomers) after recrystallization from (hexane:isopropanol = 8:2);. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.33 (m, 6H), 7.28-7.16 (m, 4H, overlapped with $CDCl_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4 (*C*), 149.3 (*C*), 137.4 (*C*), 136.8 (*C*), 135.71 (*C*), 135.68 (*C*), 135.2 (*C*), 134.8 (*C*H), 134.6 (*C*H), 134.0 (*C*), 131.3 (*C*H), 130.4 (*C*H), 130.3 (*C*H), 129.7 (*C*H), 129.4 (*C*H), 129.2 (*C*H), 129.02 (*C*H), 129.00 (*C*H), 128.9 (*C*H), 128.8 (*C*H) ppm. Elemental Analysis for $C_{14}H_{10}ClNO_2$ Calc.: C, 64.75; H, 3.88; N, 5.39. Found: C, 64.84; H, 4.08; N, 5.46.

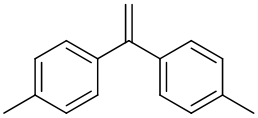
3.2. General synthetic procedure for the synthesis of α-aryl-β-nitrostyrenes – Method B



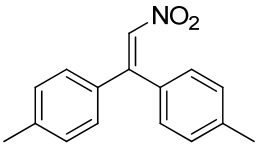
General procedure for the synthesis of the olefins by Wittig reaction. [7] In an oven dried Schlenk flask, the phosphonium salt (2 eq.) was added and dissolved in dry THF then cooled to -78 °C. *n*-BuLi (2 eq., 2.5 M solution in hexane) or KO^{t}Bu was slowly added (dark yellow color was immediately observed) then the mixture allowed to warm up to room temperature and stirred for 1 h. After that, the mixture was cooled again to -78 °C and a solution of benzophenone (1 eq.) in THF was added gradually. After stirring for another 0.5 h, the resulting solution was allowed to warm up to room temperature and left with stirring under nitrogen atmosphere overnight. The reaction was quenched by addition of a saturated aqueous ammonium chloride solution and was extracted with hexane several times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated. The residue was purified by column chromatography on silica-gel using hexane as the eluent to give the olefin.

General procedure for the synthesis of the nitroalkenes by nitration of the corresponding olefins.[8] In an oven dried pressure tube equipped with a stirring bar, the olefin (1 eq.), TEMPO (1 eq.), *tert*-butyl nitrite (2 eq.) and acetonitrile were added. The reaction was closed under an oxygen atmosphere and left at 90 °C overnight. After reaction completion the solvent was evaporated and the reaction mixture was purified by column chromatography on silica-gel using hexane:AcOEt (95:5) as the eluent to give the nitroalkene.

Synthesis of 4,4'-(2-nitroethene-1,1-diyl)bis(methylbenzene) (1h)

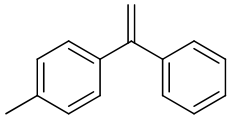


4,4'-(ethene-1,1-diyl)bis(methylbenzene). Prepared by Wittig reaction performed under inert atmosphere. Methyl triphenylphosphonium iodide (2.20 g, 5.4 mmol) was suspended in dry THF (30 mL) and KO^{t}Bu (640 mg, 5.7 mmol) was added. The mixture was stirred at room temperature for 1h and then 4,4'-dimethylbenzophenone (954 mg, 4.5 mmol) in dry THF (10 mL) was added gradually. The reaction was stirred overnight and then quenched with saturated aqueous ammonium chloride solution (25 mL) then extracted with hexane (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and the solvent was evaporated. The residue was purified by column chromatography on silica-gel using hexane as the eluent to give the olefin as white solid (510 mg, 2.4 mmol, 53% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.1 Hz, 4H), 7.17 (d, *J* = 8.1 Hz, 4H), 5.41 (s, 2H), 2.40 (s, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.9 (*C*), 138.9 (*C*), 137.6(*C*), 129.0 (*C*H), 128.3 (*C*H), 113.1 (CH_2), 21.3 ppm (CH_3) ppm. Elemental Analysis for $C_{16}H_{16}$ Calcd.: C, 92.26; H, 7.74. Found: C,92.25; H,7.75.

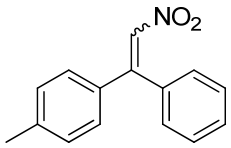


4,4'-(2-nitroethene-1,1-diyl)bis(methylbenzene) (1h). Prepared according to the general synthetic procedure for the nitration of olefins from 4,4'-(ethene-1,1-diyl)bis(methylbenzene) (312 mg, 1.5 mmol), TEMPO (234 mg, 1.5 mmol), *tert*-butyl nitrite (360 μL, 3.0 mmol) and acetonitrile (6 mL). The product was obtained as yellow crystals (220 mg, 0.87 mmol, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.18 (s, 4H), 7.11 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H), 2.39 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0 (*C*), 141.6 (*C*), 139.6 (*C*), 134.7 (*C*), 133.6 , 132.8 (*C*), 129.7 (*C*H), 129.3 (*C*H), 129.15 (*C*H), 129.10 (*C*H), 21.6 (CH_3), 21.5 (CH_3) ppm. Elemental Analysis for $C_{16}H_{15}NO_2$ Calcd.: C, 75.87; H, 5.97; N, 5.53. Found: C,75.75; H,6.07; N,5.49.

Synthesis of 1-methyl-4-(2-nitro-1-phenylvinyl)benzene (1i).

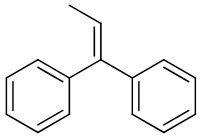


1-methyl-4-(1-phenylvinyl)benzene. Prepared by Wittig reaction performed under inert atmosphere from methyl triphenylphosphonium iodide (1.62 g, 4.0 mmol) dissolved in dry THF (25 mL), *n*-BuLi (1.6 mL, 4.0 mmol, 2.5 M solution in hexane) and 4-methylbenzophenone (392 mg, 2 mmol) dissolved in dry THF (5 mL). The reaction was quenched with 30 mL of saturated aqueous ammonium chloride solution then extracted with hexane (3 × 15 mL). Column chromatography purification was performed using hexane as the eluent. The product was isolated as colorless oil (300 mg, 1.5 mmol, 77% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.43 (m, 5H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.57 (d, *J* = 1.0 Hz, 1H), 5.55 (d, *J* = 1.0 Hz, 1H), 2.50 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0 (*C*), 141.8 (*C*), 138.7 (*C*), 137.6 (*C*), 129.0, 128.4 (*C*H), 128.3 (*C*H), 128.2 (*C*H), 127.8 (*C*H), 113.7 (CH_2), 21.3 (CH_3) ppm. Elemental Analysis for $C_{15}H_{14}$ Calc.: C, 92.74; H, 7.26. Found: C, 92.62; H, 7.19.

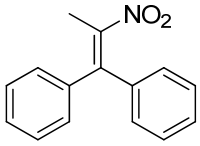


1-methyl-4-(2-nitro-1-phenylvinyl)benzene (1i). Prepared according to the general synthetic procedure for the nitration of olefins from 1-methyl-4-(1-phenylvinyl)benzene (220 mg, 1.1 mmol), TEMPO (177 mg, 1.1 mmol), *tert*-butyl nitrite (270 μL, 2.3 mmol) and acetonitrile (4.5 mL). The product was obtained as yellow crystals (172 mg, 0.72 mmol, 63% yield, mixture of two isomers ca. 1:1 ratio). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.34 (m, 8H), 7.32 – 7.26 (m, 2H), 7.26 – 7.15 (m, 6H, overlapped with the olefinic CH signal), 7.18 (s, 2H, olefinic CH), 7.12 (d, *J* = 8.1 Hz, 2H), 2.42 (s, 3H), 2.39 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8 (*C*), 141.7 (*C*), 139.7 (*C*), 137.6 (*C*), 135.9 (*C*), 134.3 (*C*), 134.3 (olefinic *C*H), 133.9 (olefinic *C*H), 132.7 (*C*), 130.9 (*C*H), 129.8, 129.3 (*C*H), 129.2 (*C*H), 129.1 (*C*H), 129.0 (*C*H), 128.9 (*C*H), 128.9 (*C*H), 128.6 (*C*H), 21.6 (CH_3), 21.51 (CH_3) ppm. Elemental Analysis for $C_{15}H_{13}NO_2$ Calc.: C, 75.30; H, 5.48; N, 5.85. Found: C,75.42; H,5.50; N,5.70.

Synthesis of 1-methyl-4-(2-nitro-1-phenylvinyl)benzene (1i).

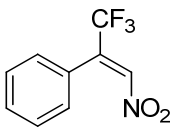


Prop-1-ene-1,1-diyldibenzene. Prepared by Wittig reaction according to the general synthetic procedure from ethyl triphenylphosphonium bromide (6.00 g, 16.4 mmol) dissolved in dry THF (50 mL), *n*-BuLi (6.4 mL, 16.4 mmol, 2.5 M solution in hexane) and benzophenone (1.50 g, 8.2 mmol) in dry THF (10 mL). Reaction was quenched with saturated aqueous ammonium chloride solution (30 mL) then extracted with hexane (3 × 20 mL). The solvent was evaporated and the residue was purified by column chromatography on silica-gel using hexane as the eluent to give the product as white solid (1.47 g, 7.6 mmol, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 7.2 Hz, 2H), 7.39 – 7.21 (m, 8H), 6.24 (q, *J* = 7.0 Hz, 1H), 1.83 (d, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1 (*C*), 142.6 (*C*), 140.2 (*C*), 130.2 (*C*H), 128.3 (*C*H), 128.2 (*C*H), 127.3 (*C*H), 127.0 (*C*H), 126.9 (*C*H), 124.3 (*C*H), 15.8 (*C*H_3) ppm. Elemental Analysis for $C_{16}H_{16}$ Calc.: C, 92.74; H, 7.26. Found: C,92.49; H,7.25.



(2-nitroprop-1-ene-1,1-diyl)dibenzene (2j). Prepared according to the general synthetic procedure for the nitration of olefins from prop-1-ene-1,1-diyldibenzene (291 mg, 1.5 mmol), TEMPO (234 mg, 1.5 mmol), *tert*-butyl nitrite (360 mL, 3 mmol) and acetonitrile (6 mL). The product was obtained as pale-yellow crystals (200 mg, 0.84 mmol, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 3H), 7.33 – 7.28 (m, 3H), 7.21 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.17-7.15 (m, 2H), 2.35 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5 (*C*), 140.0 (*C*), 138.4 (*C*), 138.3 (*C*), 129.5 (*C*H), 128.9 (*C*H), 128.7 (*C*H), 128.7 (*C*H), 128.7 (*C*H), 128.3, 18.3 (*C*H_3) ppm. Elemental Analysis for $C_{15}H_{13}NO_2$ Calc.: C, 75.30; H, 5.48; N, 5.85. Found: C,75.38; H,5.65; N,5.79.

Synthesis of (*E*)-(3,3,3-trifluoro-1-nitroprop-1-en-2-yl)benzene (1l)



The compound was prepared following a procedure previously reported in the literature.[9] In a two neck round bottomed flask, NEt_3 (1.2 mL, 8.6 mmol) was added, under N_2, to a solution of 2,2,2-trifluoroacetophenone (900 mg, 6.1 mmol) in nitromethane (8 mL). The mixture was stirred overnight at room temperature and then ethyl acetate (20 mL) was added. The mixture was washed with 1M HCl (10 mL), water (10 mL), and brine (10 mL) and then dried over Na_2SO_4. Filtration and evaporation of the solvent afforded the crude nitro alcohol that was used in the subsequent step without further purification. The crude was dissolved in toluene (8 mL) and $SOCl_2$ (0.70 mL, 9.6 mmol) and pyridine (1.5 mL, 18.6 mmol) were slowly added at 0 °C while stirring. The mixture was stirred at room temperature for 4h and then ethyl acetate (20 mL) was added. The organic phase was washed with water (3×10 mL) and brine (10 mL), dried over Na_2SO_4 and filtered. The solvent was removed under vacuum and the residue was purified by flash column chromatography on silica gel using hexane: CH_2Cl_2 (95:5). The product was obtained as yellow oil (638 mg, 2.9 mmol, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 1.1 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.32 (d, J = 7.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1 (*C*H), 136.1 (q, J= 31.9 Hz, *C*-CF_3), 130.7 (*C*H), 129.0 (*C*H), 128.3 (*C*H), 127.0 (*C*), 122.0 (q, J = 274 Hz, *C*F_3) ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -67.11 ppm.

4. NMR spectra

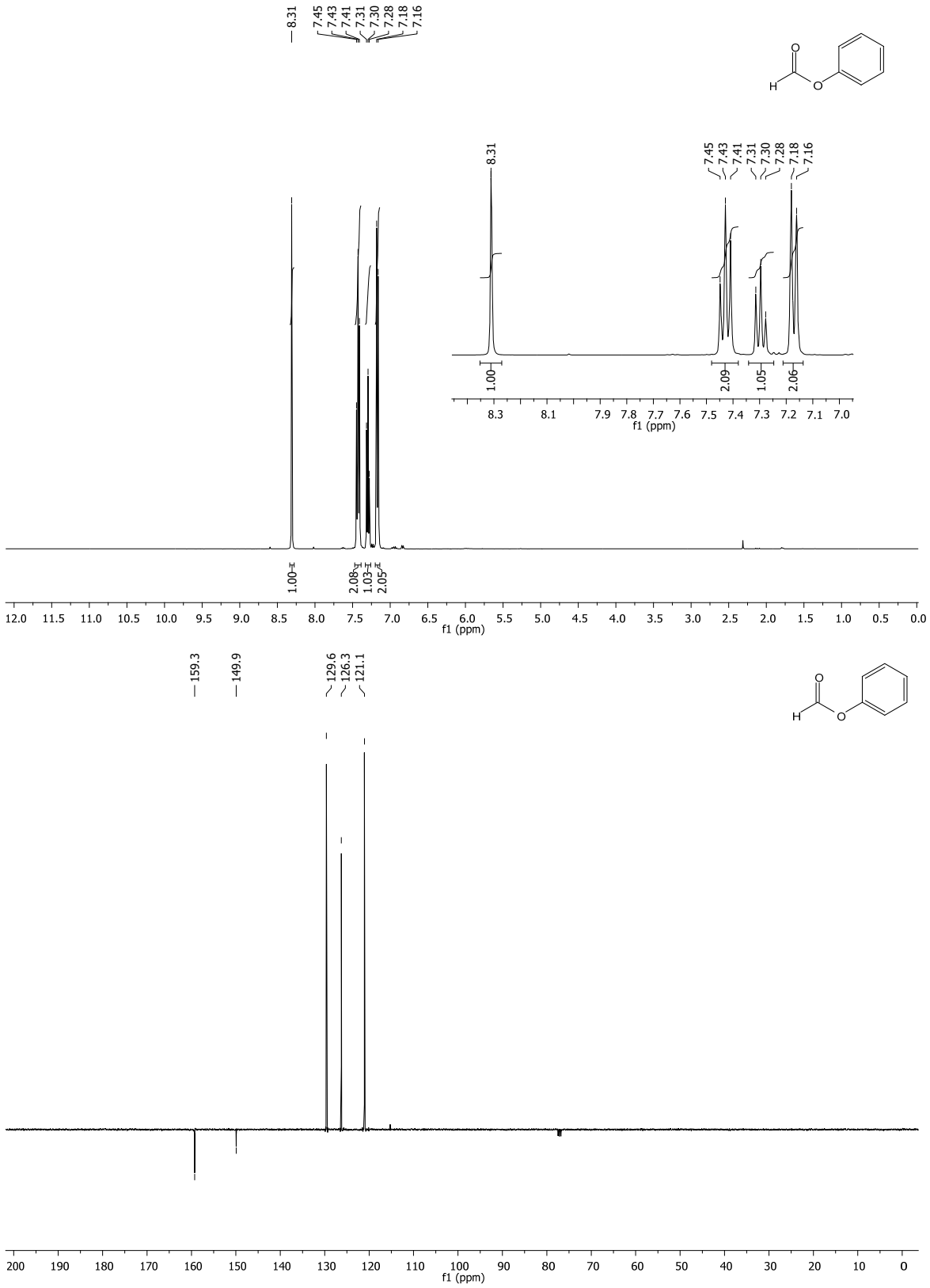


Figure S2. ^{1}H NMR and ^{13}C APT NMR of phenyl formate.

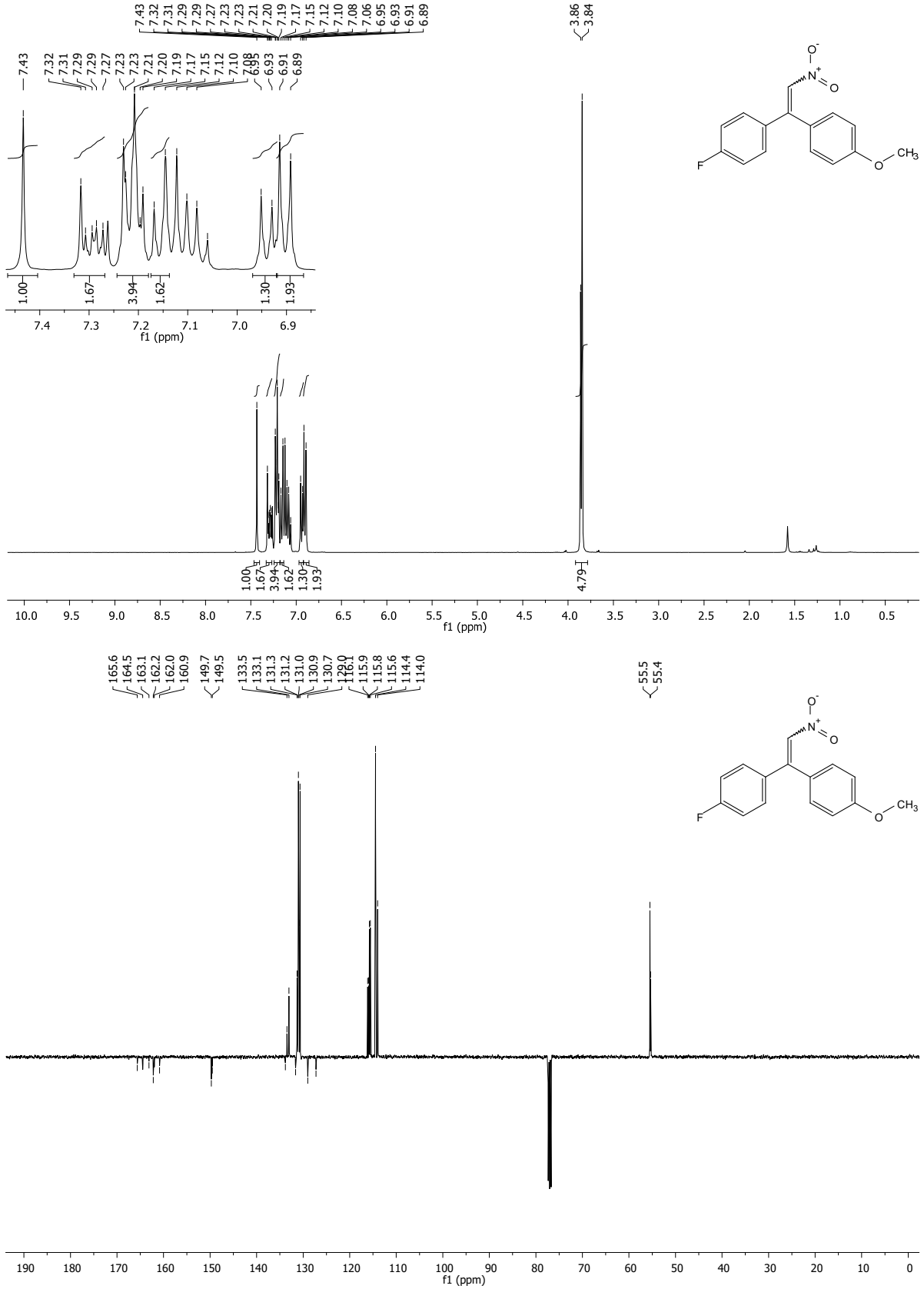


Figure S3. ^{1}H NMR and ^{13}C APT NMR of 1-fluoro-4-(1-(4-methoxyphenyl)-2-nitrovinyl)benzene (**1d**).

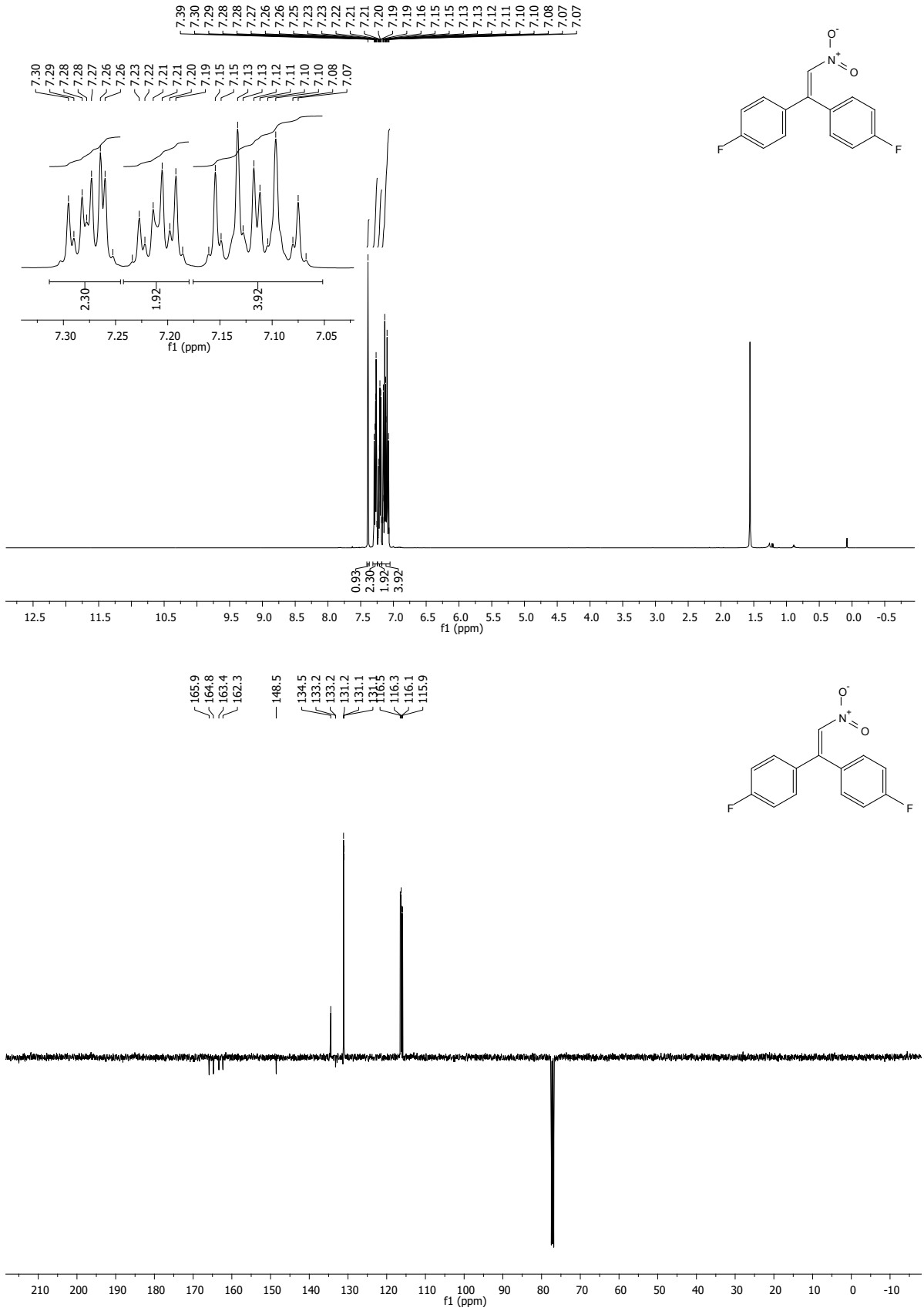


Figure S4. ^{1}H NMR and ^{13}C APT NMR of 4,4'-(2-nitroethene-1,1-diyl)bis(fluorobenzene) (**1e**).

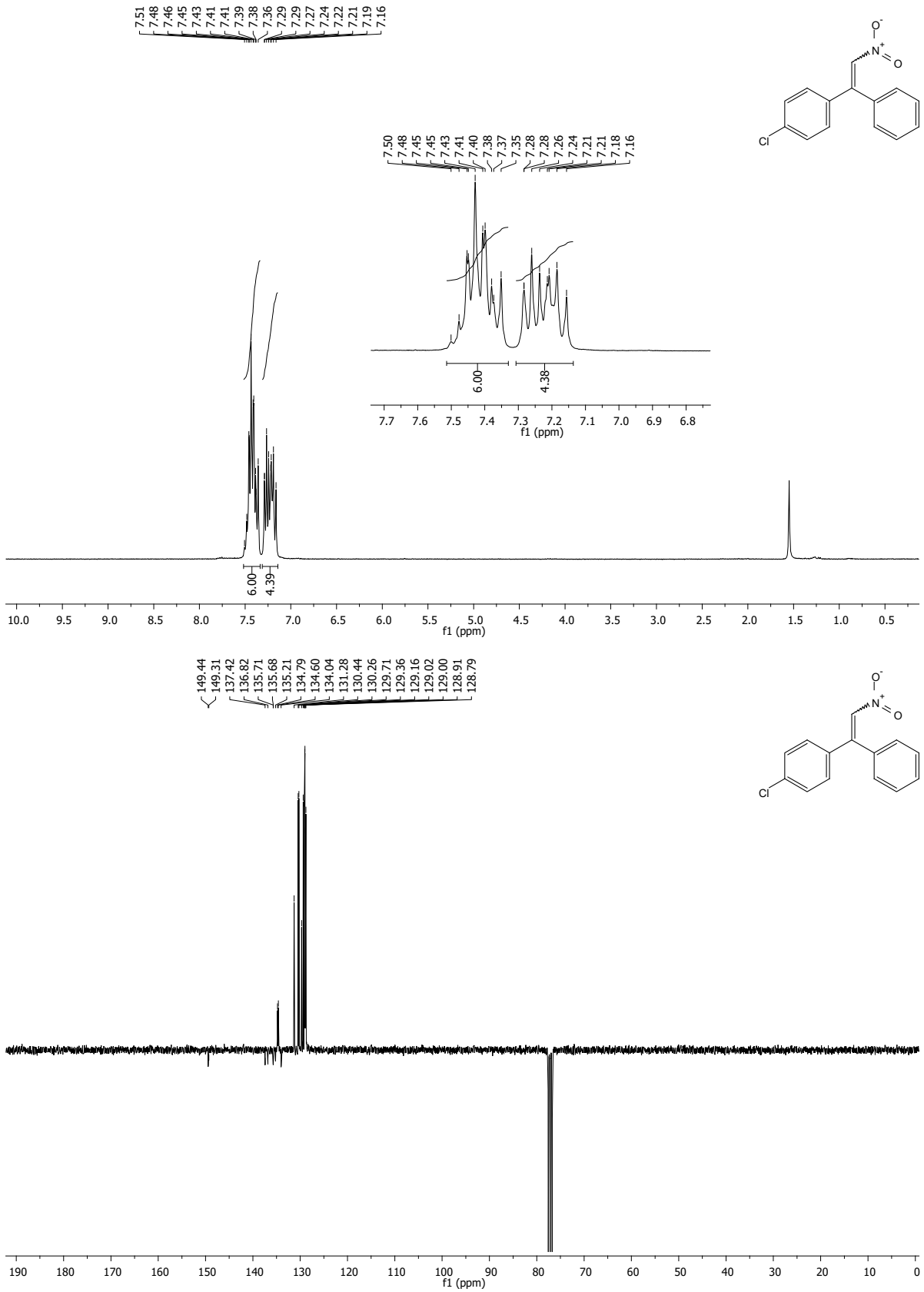


Figure S5. ^{1}H NMR and ^{13}C APT NMR of 1-chloro-4-(2-nitro-1-phenylvinyl)benzene (**1g**).

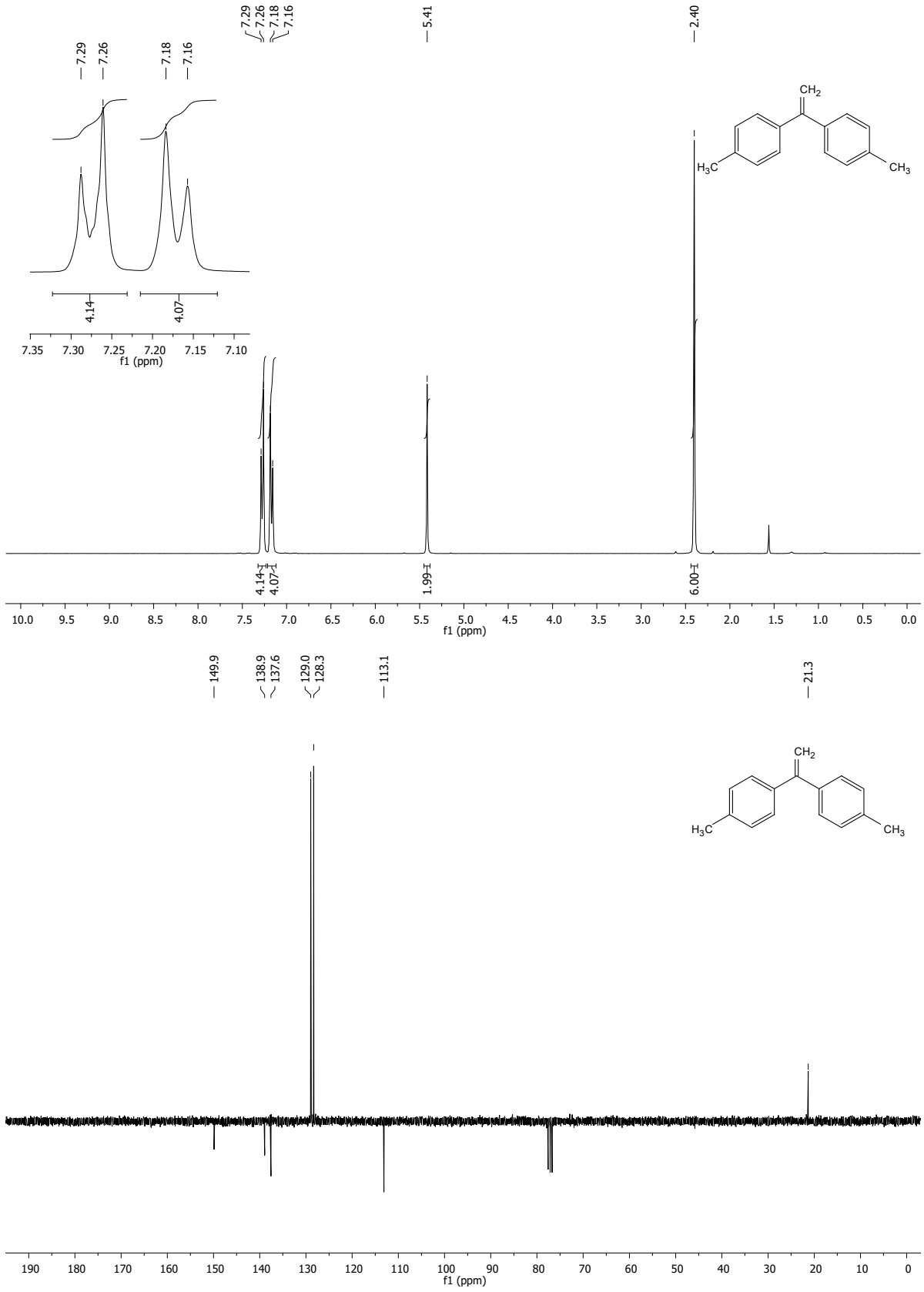


Figure S6. ^{1}H NMR and ^{13}C NMR of 4,4'-(ethene-1,1-diyl)bis(methylbenzene).

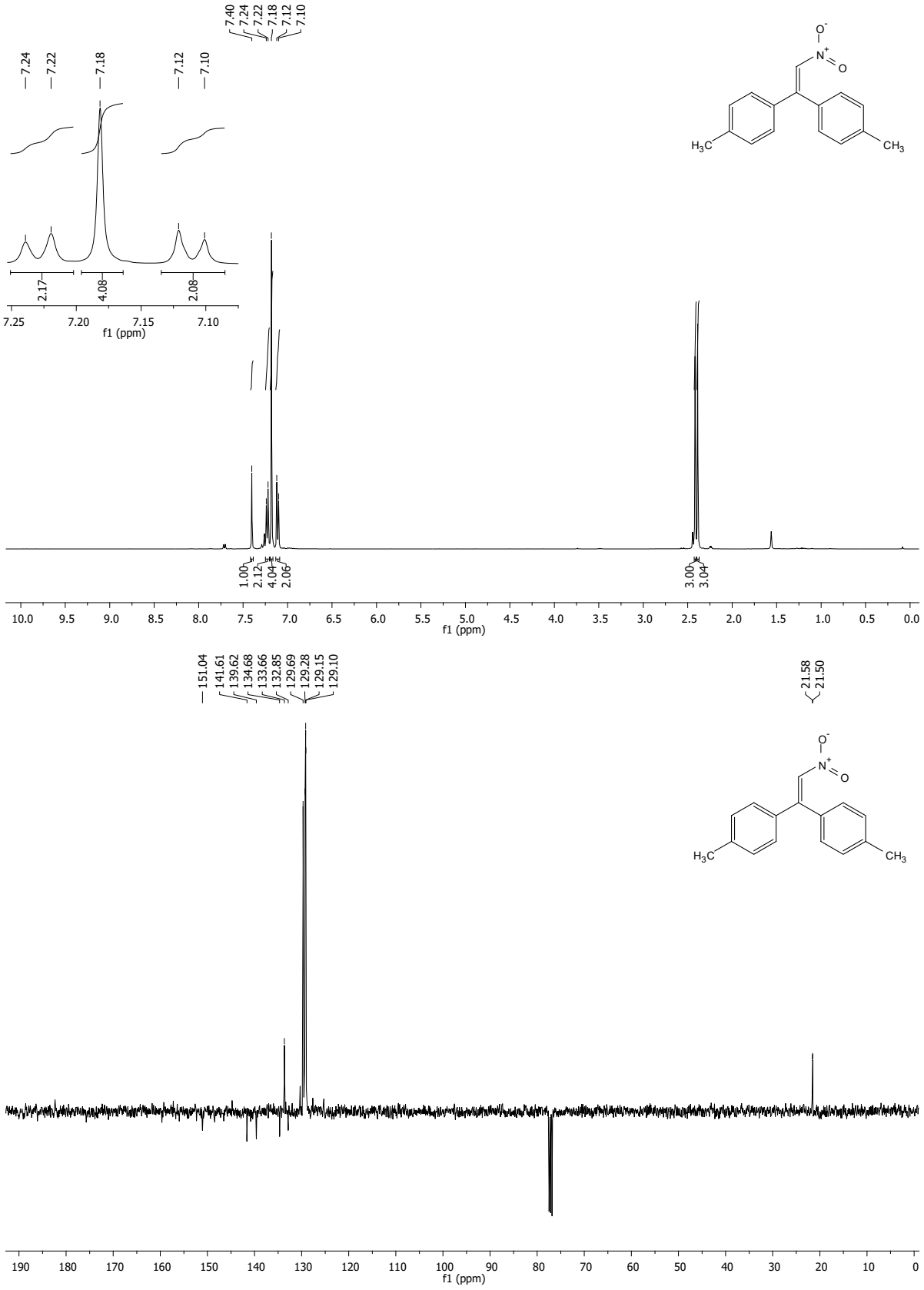


Figure S7. ^{1}H NMR and ^{13}C APT NMR of 4,4'-(2-nitroethene-1,1-diyl)bis(methylbenzene) (**1h**).

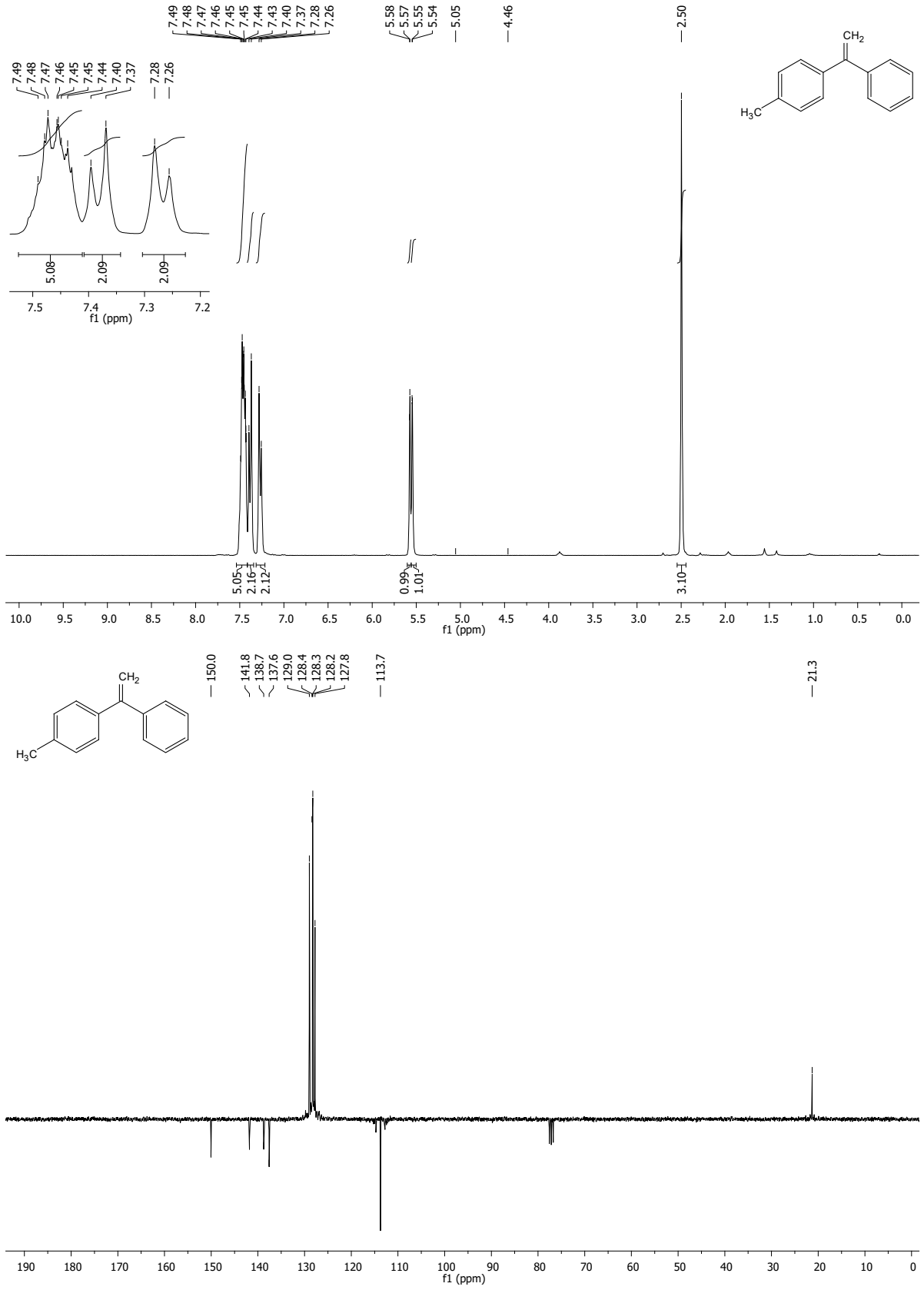


Figure S8. ^{1}H NMR and ^{13}C APT NMR of 1-methyl-4-(1-phenylvinyl)benzene.

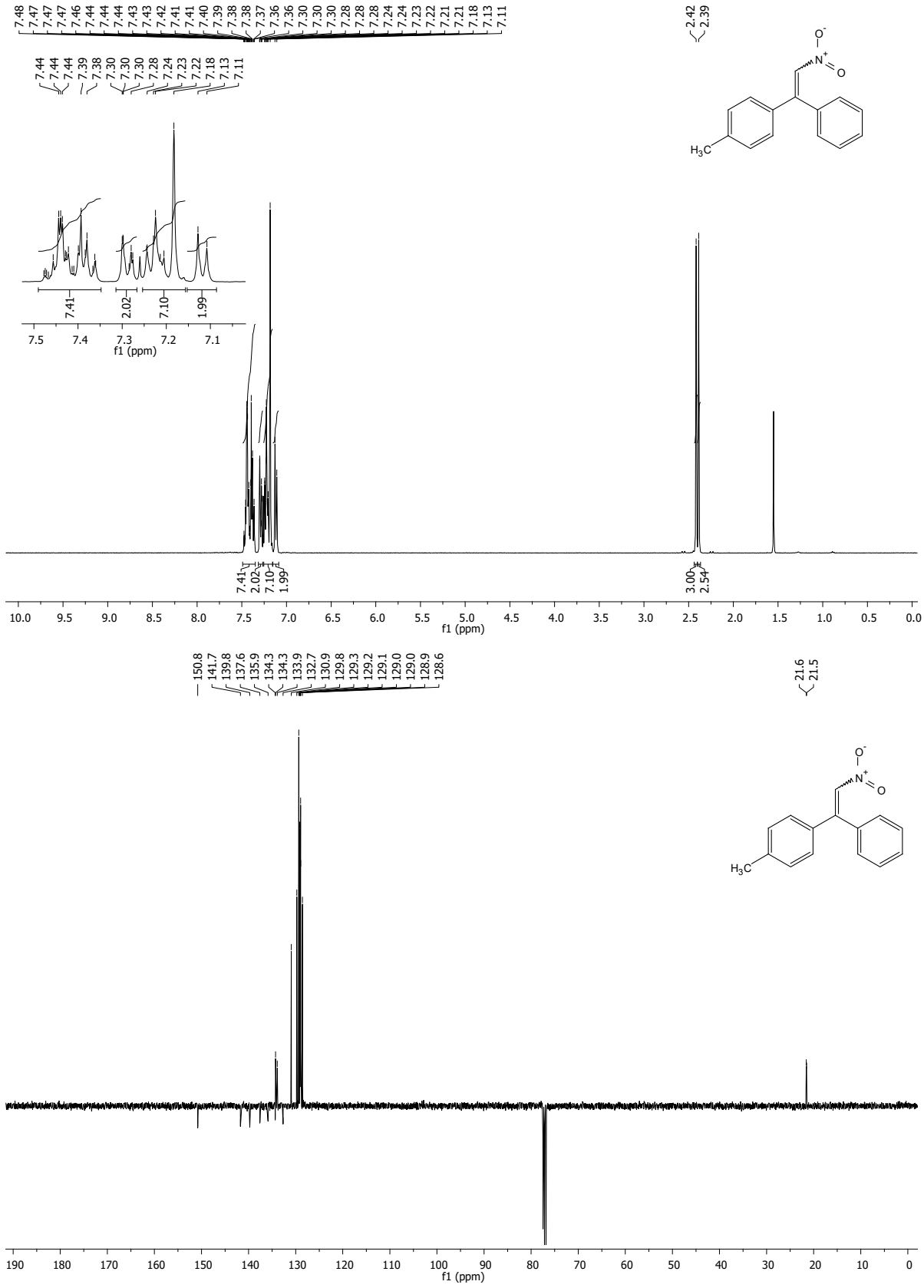


Figure S9. ^{1}H NMR and ^{13}CAPT NMR of 1-methyl-4-(2-nitro-1-phenylvinyl)benzene (**1i**).

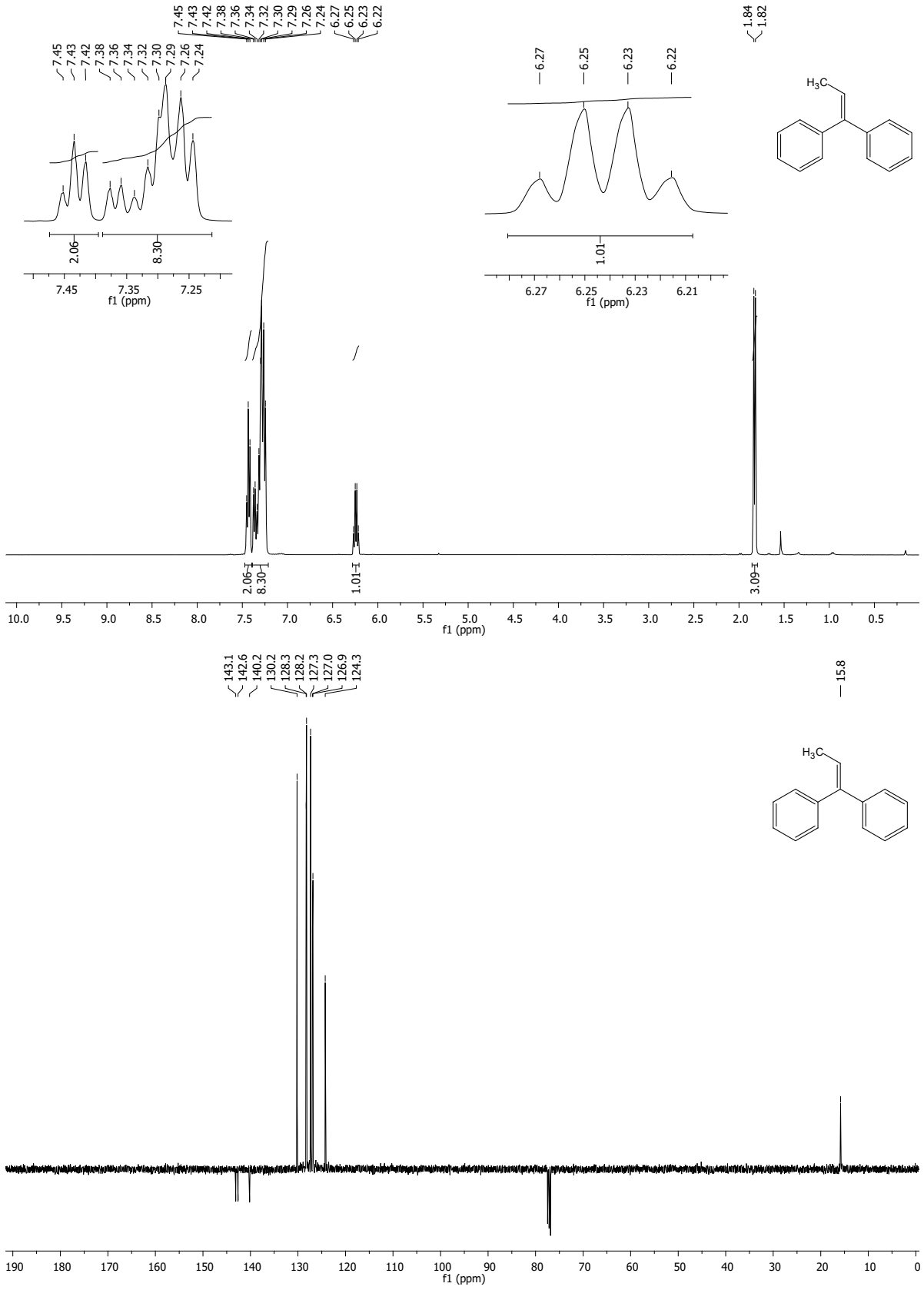


Figure S10. ^{1}H NMR and ^{13}CAPT NMR of prop-1-ene-1,1-diyldibenzene.

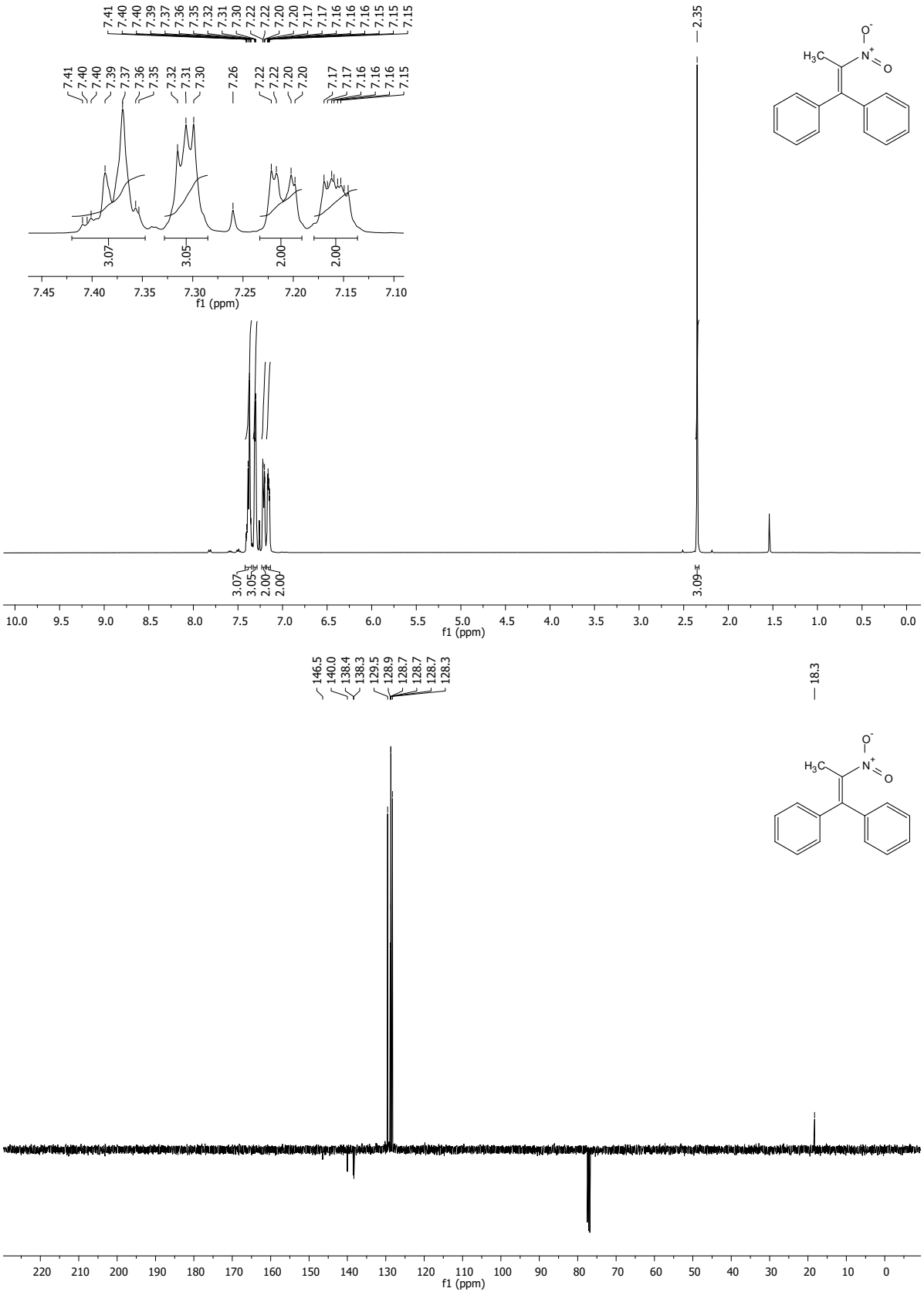


Figure S11. ^{1}H NMR and ^{13}C NMR of (2-nitroprop-1-ene-1,1-diyl)dibenzene (**2j**).

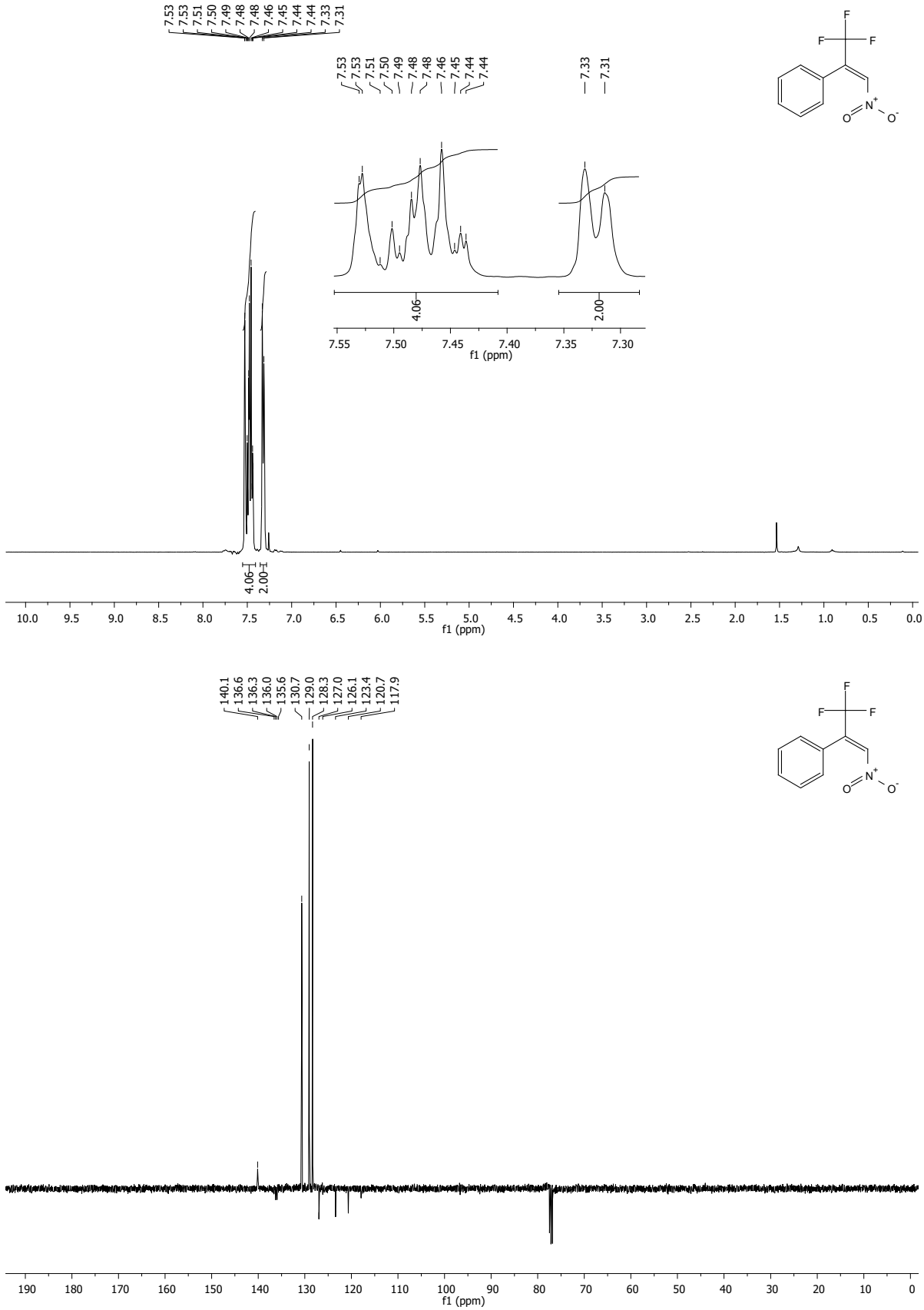


Figure S12. ^{1}H NMR and ^{13}C APT NMR of (*E*)-(3,3,3-trifluoro-1-nitroprop-1-en-2-yl)benzene (**1l**).

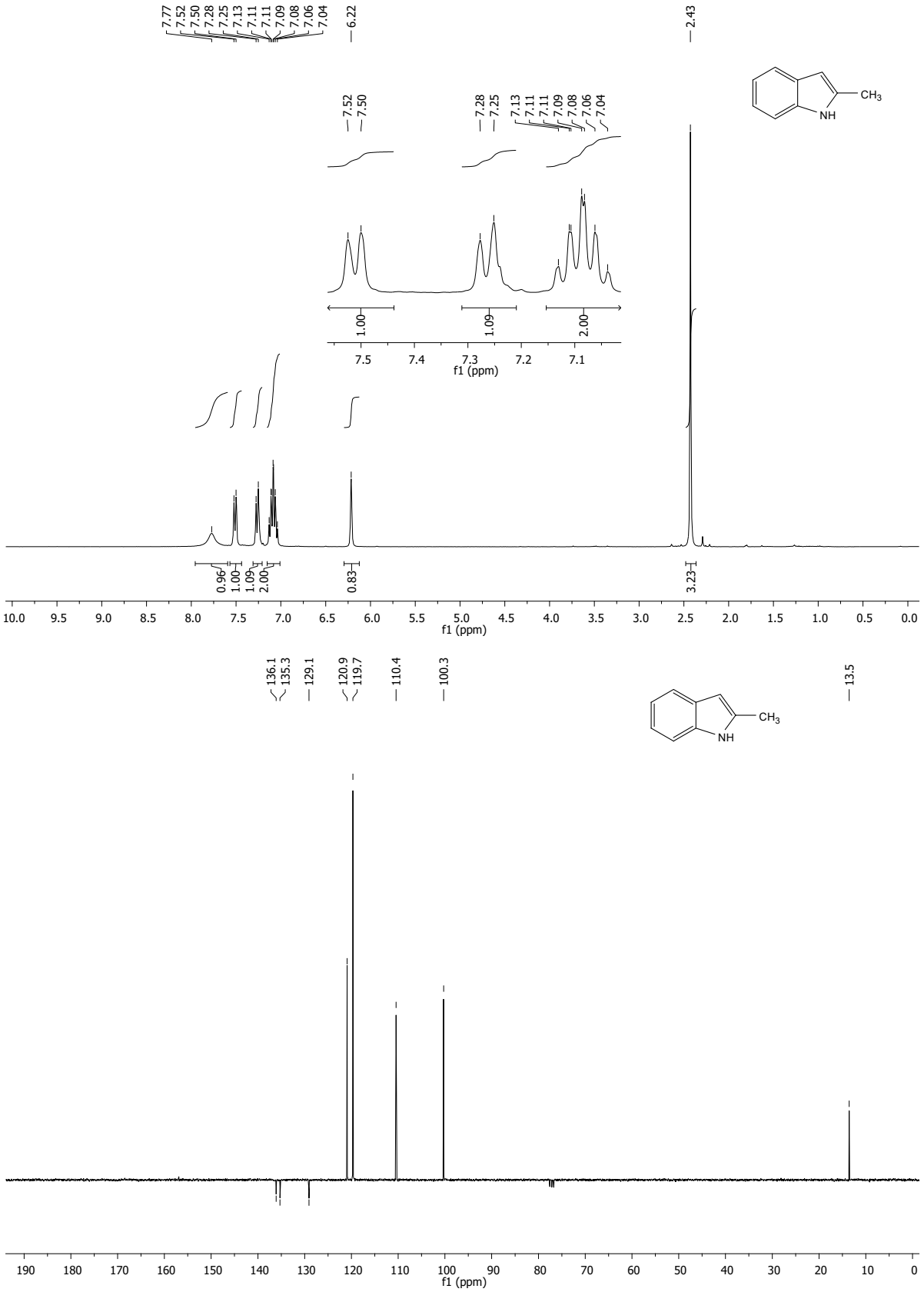


Figure S13. ^{1}H NMR and ^{13}C APT NMR of 2-methyl-1*H*-indole (**2a**)

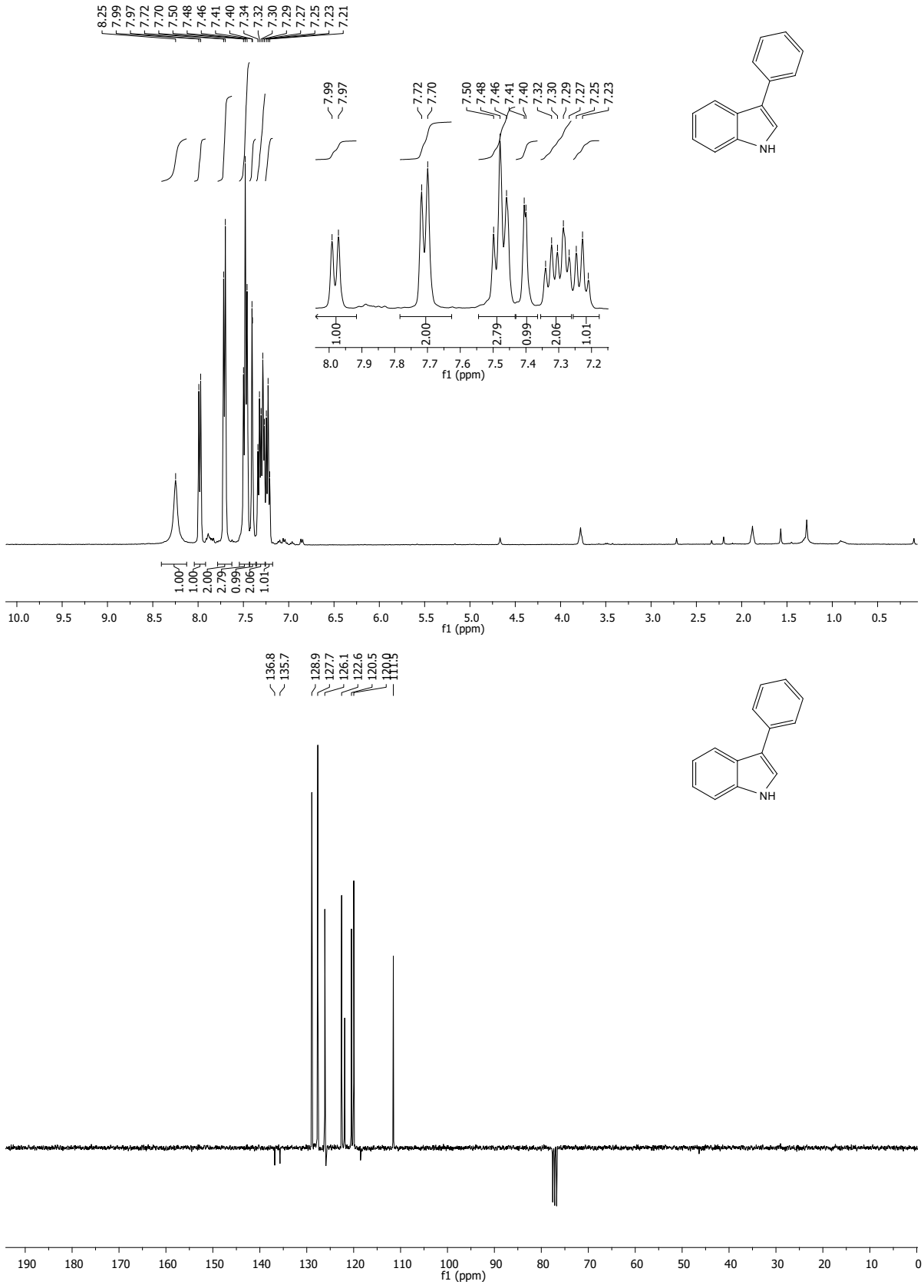


Figure S14. ^{1}H NMR and ^{13}C APT NMR of 3-phenyl-1*H*-indole (**2b**)

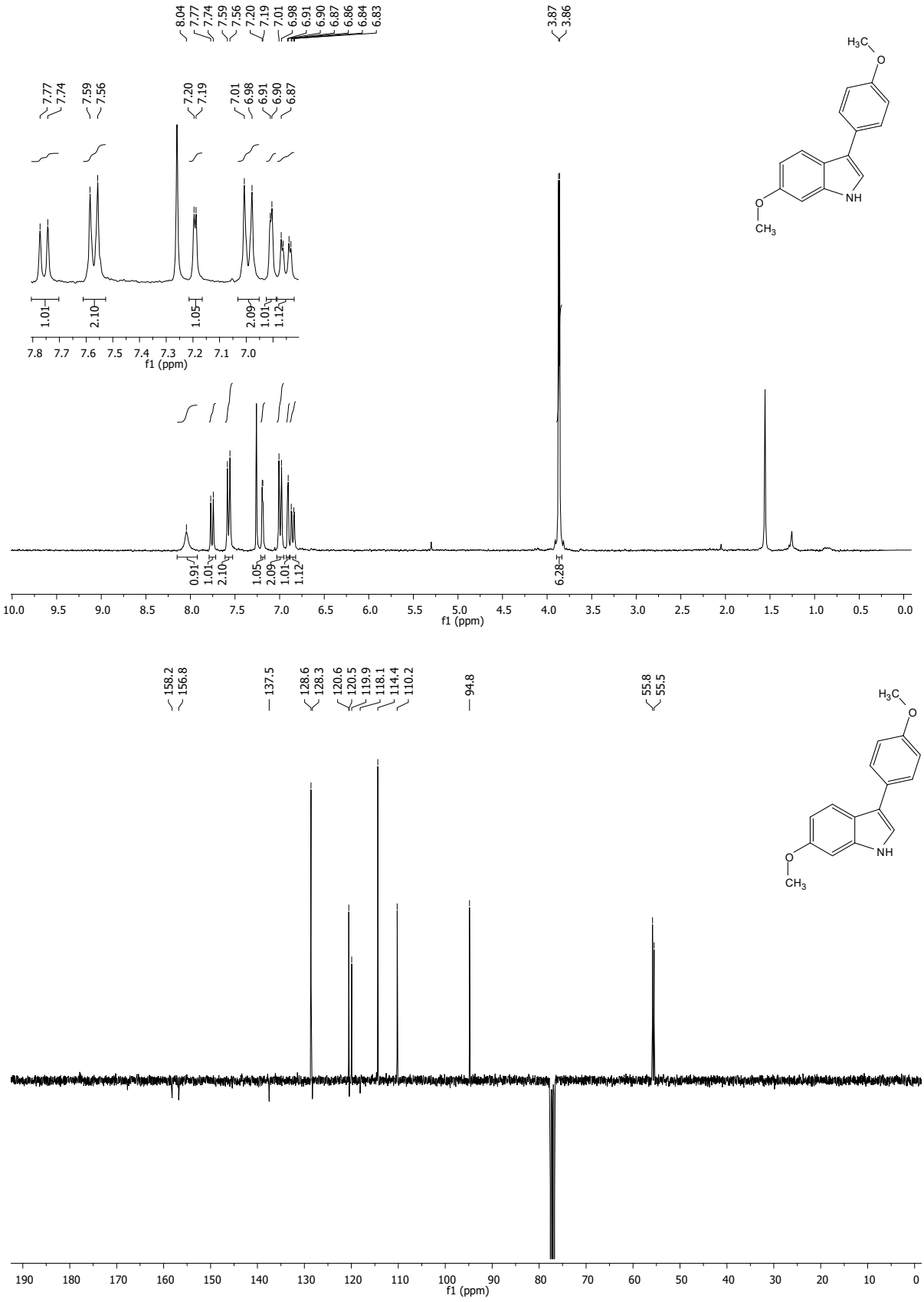


Figure S15. ^{1}H NMR and ^{13}C APT NMR of 6-methoxy-3-(4-methoxyphenyl)-1*H*-indole (**2c**).

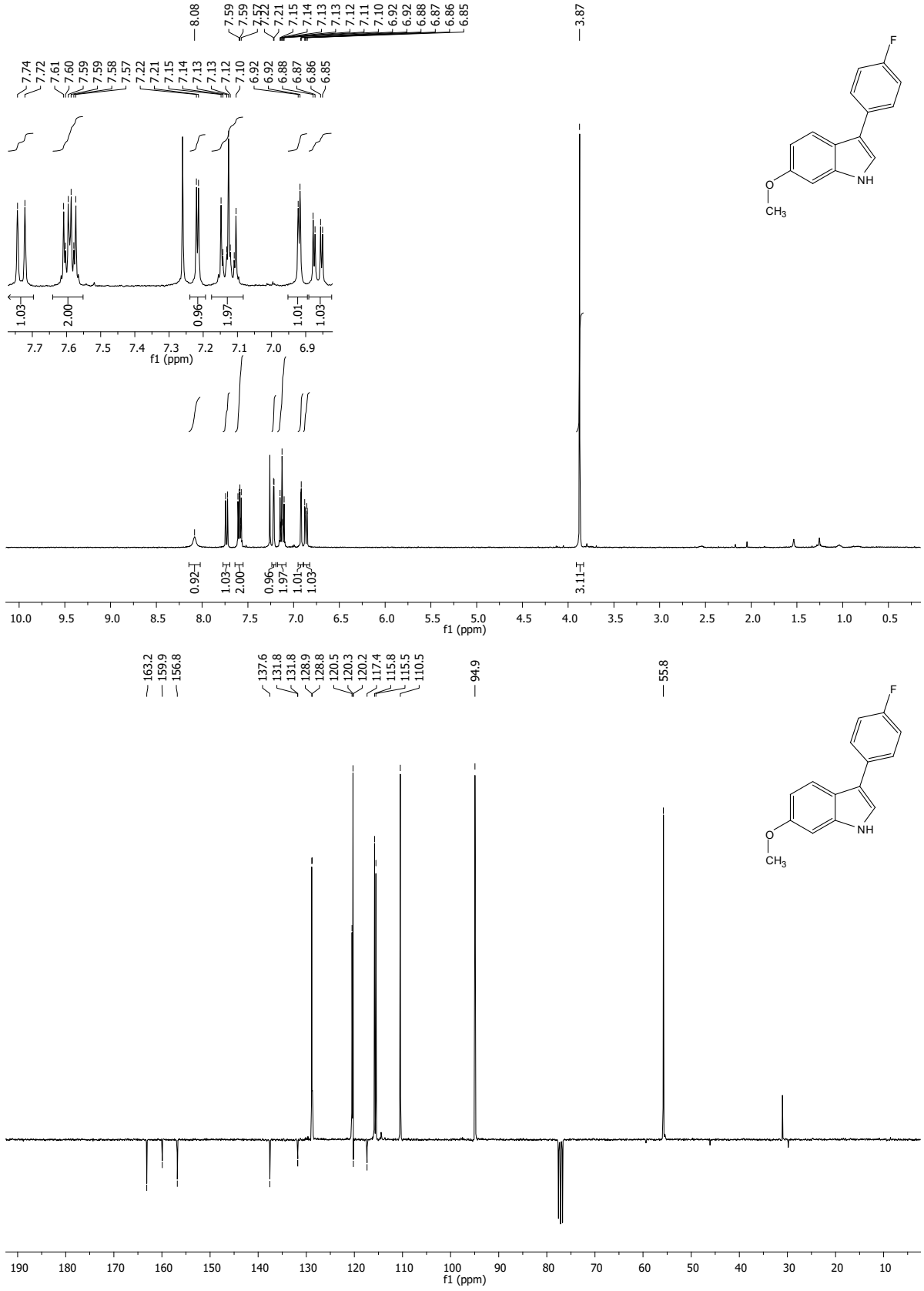


Figure S16. ^{1}H NMR and ^{13}C APT NMR of 3-(4-fluorophenyl)-6-methoxy-1*H*-indole (**2d'**).

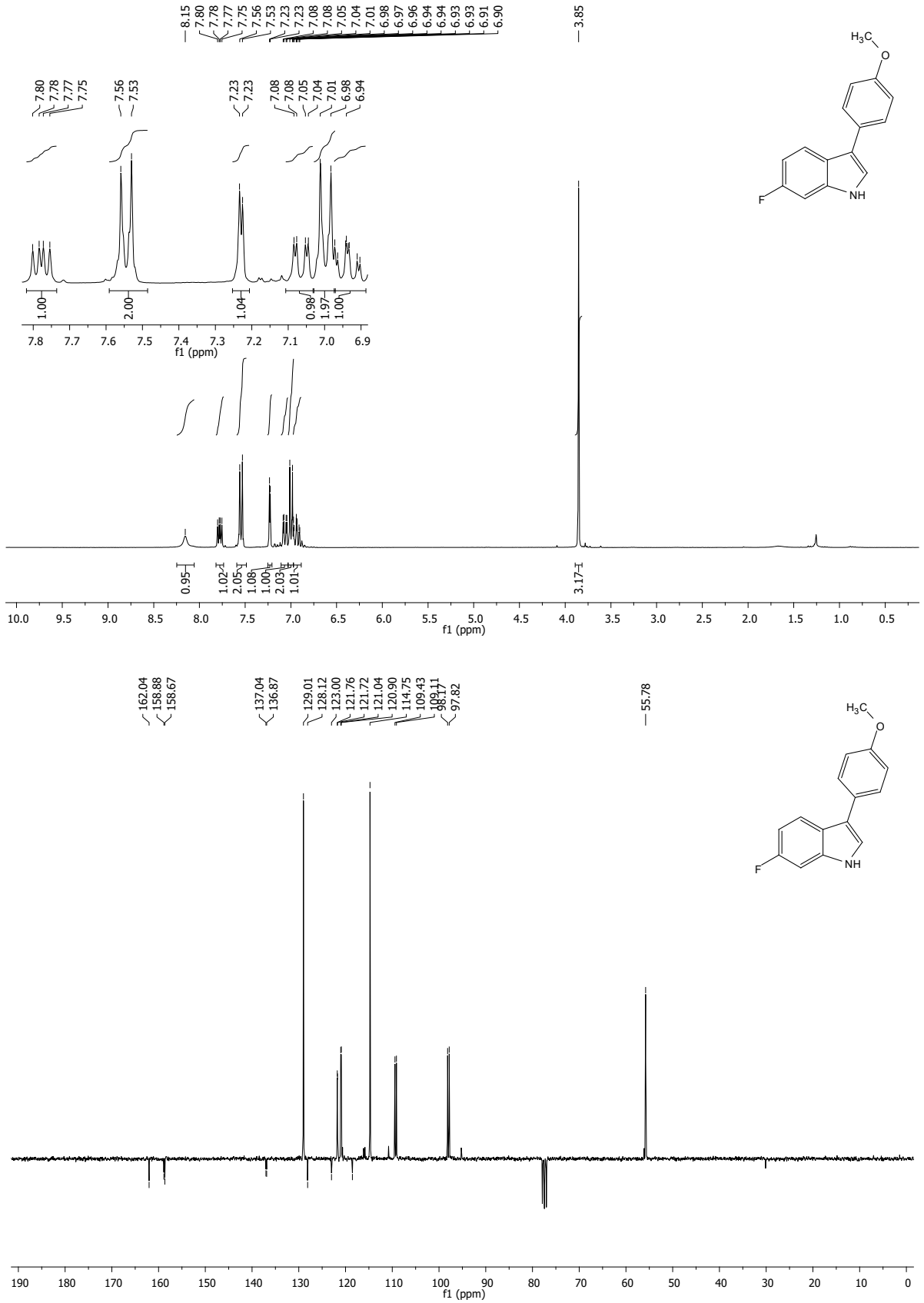


Figure S17. ^{1}H NMR and ^{13}C APT NMR of 6-fluoro-3-(4-methoxyphenyl)-1*H*-indole (**2d''**).

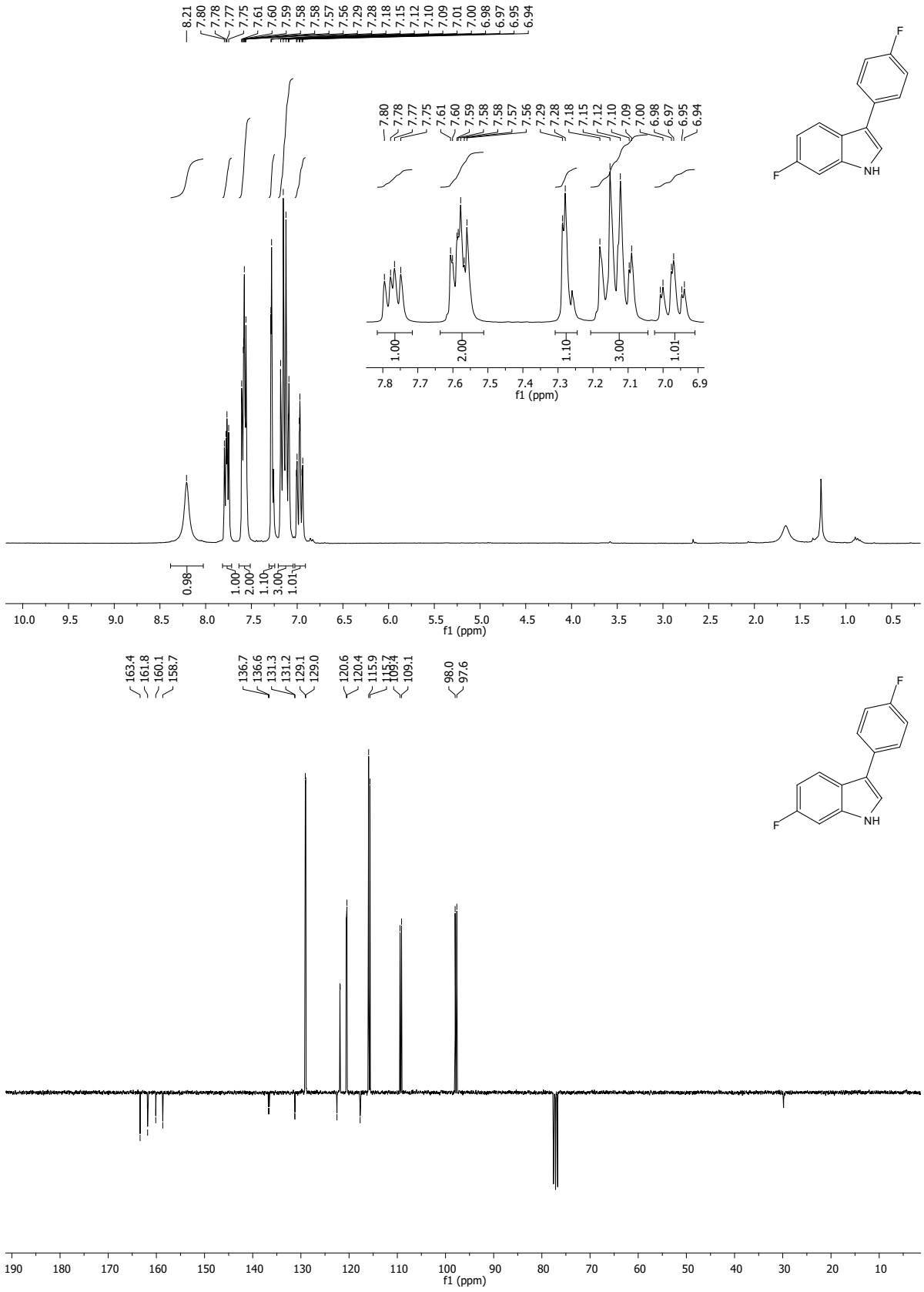


Figure S18. ^{1}H NMR and ^{13}C APT NMR 6-fluoro-3-(4-fluorophenyl)-1*H*-indole (**2e**).

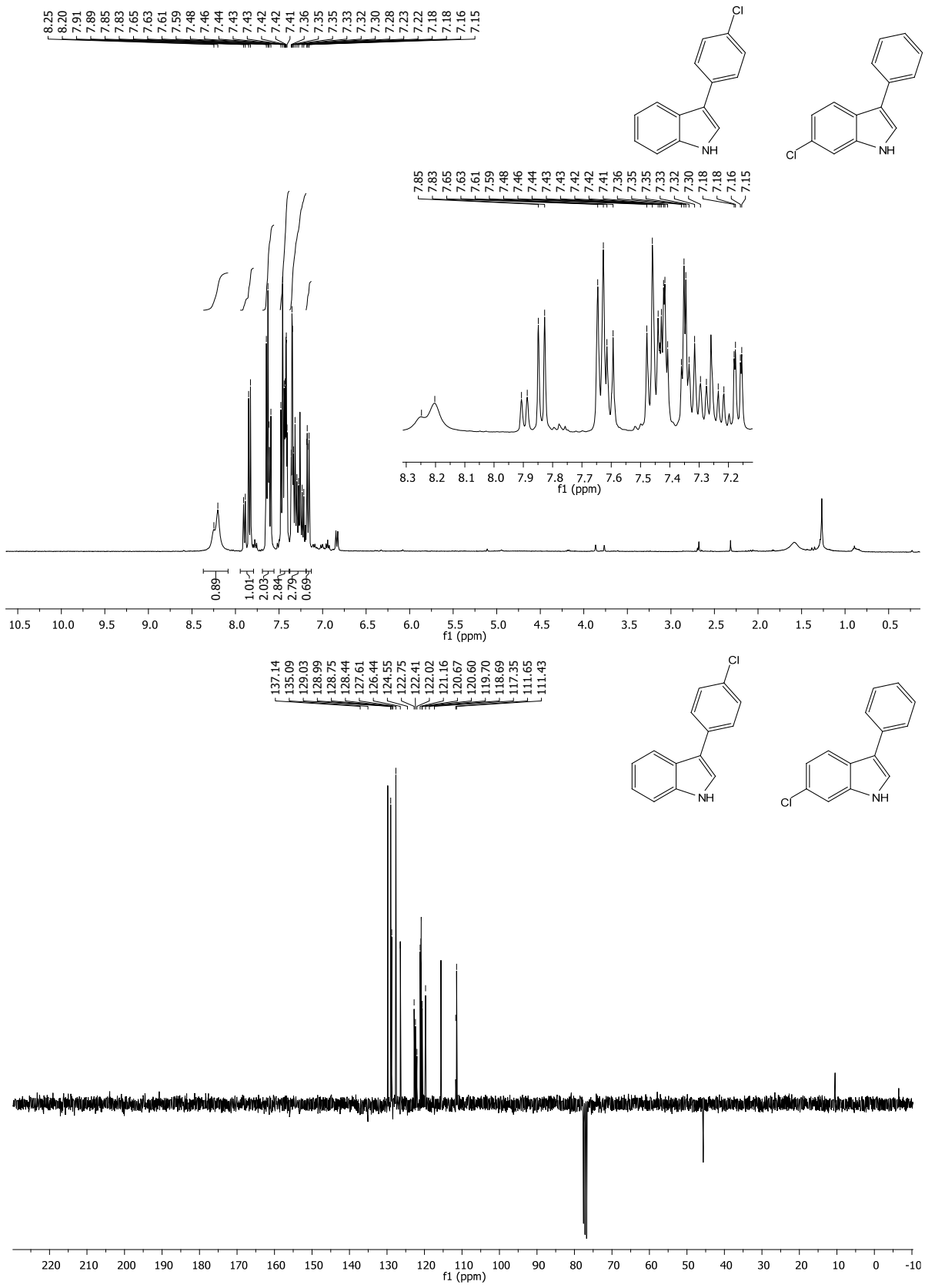


Figure S19. ^{1}H NMR and ^{13}C APT NMR 3-(4-chlorophenyl)-1*H*-indole (**2g'**) and 6-chloro-3-phenyl-1*H*-indole (**2g''**).

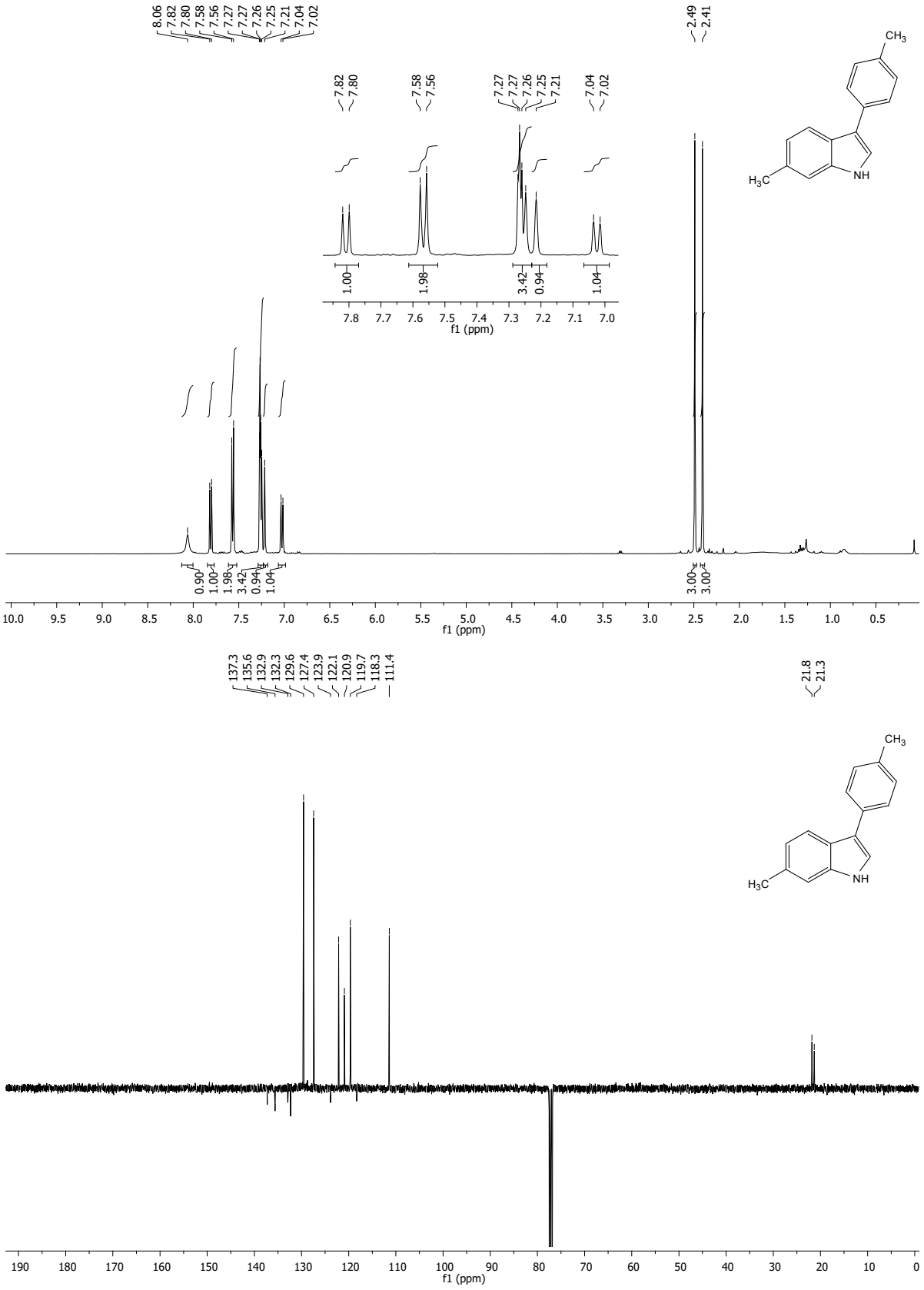


Figure S20. ^{1}H NMR and ^{13}C APT NMR of 6-methyl-3-(4-methylphenyl)-1*H*-indole (**2h**).

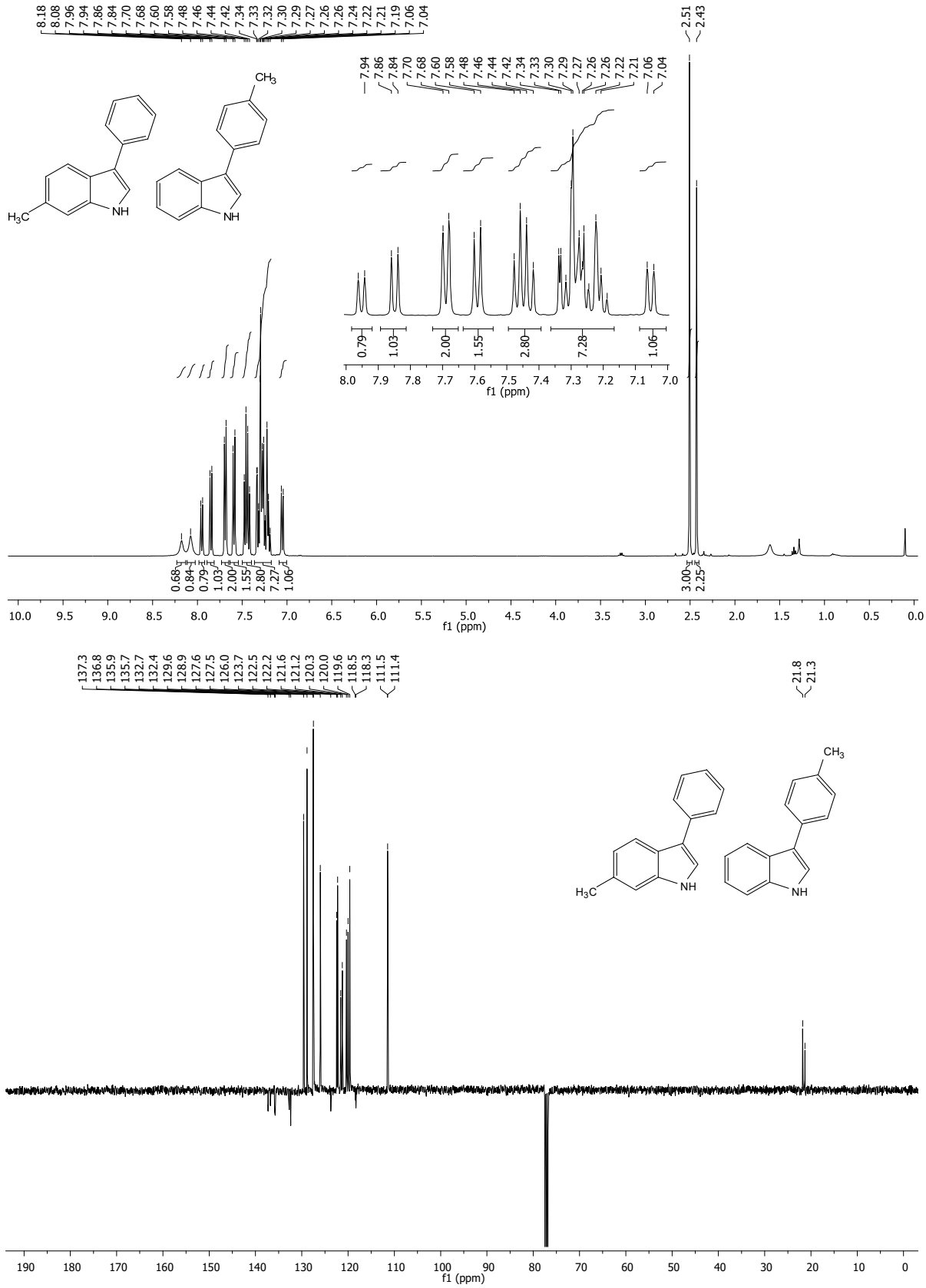


Figure S21. ^{1}H NMR and ^{13}C APT NMR of 6-methyl-3-phenyl-1*H*-indole (**2i'**) and 3-(4-methylphenyl)-1*H*-indole(**2i''**).

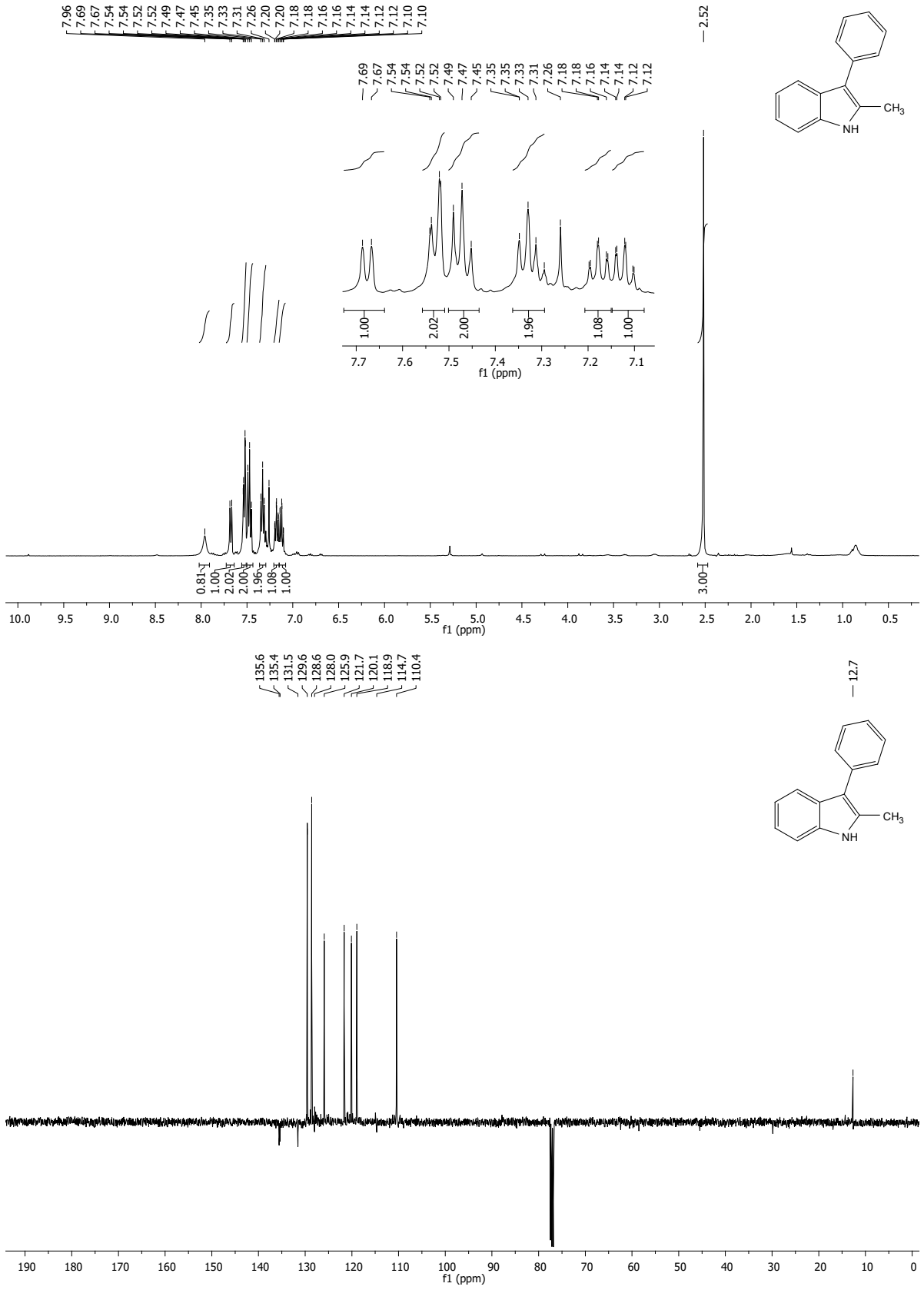


Figure S22. ^{1}H NMR and ^{13}C APTNMR of 2-methyl-3-phenyl-1*H*-indole (**2j**).

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