Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Chemo-, Regio-, and Stereoselective Heck-Matsuda Arylation of Allylic Alcohols under Mild Conditions

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Table of Contents

General Information: All manipulations with air-sensitive reagents were carried out under a dry nitrogen atmosphere. Unless otherwise stated, all commercial reagents were used without additional purification. Solvents were dried using standard methods and distilled before use. TLC was performed on silica gel plates (Merck silica gel 60, f_{254}), and the spots were visualized with UV light (254 and 365 nm) or by charring the plate dipped in $KMnO_4$ or vanillin charring solution. ^1H NMR was recorded at 300 MHz (Bruker-DPX) and 600 MHz (Bruker-Avance) frequency and ^{13}C NMR spectra were recorded at 75 MHz (Bruker-DPX) and 150 MHz (Bruker-Avance) frequency in $CDCl_3$ solvent using TMS as the internal standard. Chemical shifts were measured in parts per million (ppm) referenced to 0.0 ppm for tetramethylsilane. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br. = broad. Coupling constants, *J* were reported in Hertz unit (Hz). HRMS (m/z) were measured using EI and ESI techniques (JEOL-JMS 700 and Q-Tof Micro mass spectrometer respectively). Infrared (IR) spectra were recorded on Fourier Transform Infrared Spectroscopy (Bruker Tensor 27), only intense peaks were reported.

General Experimental Procedure for the Preparation of Diazonium salt: [1]

The aniline substrates (4.85 mmol) were dissolved in a minimum amount of water and 48% tetrafluoroboric acid (21.8 mmol, 2.68 mL) was added to it. In a separate flask, sodium nitrite (0.670 g) was dissolved in a minimum amount of water. The sodium nitrite solution was dropwise added into the aniline/acid solution cooled in an ice/salt bath (0 to -5 ^oC). The resulting precipitate was washed with cold water (2x5 mL) and purified by re-precipitation from acetonitrile/ether. The pure salt was dried under vacuum and analyzed by IR as a KBr pellet.

General Experimental Procedure for the Reaction with Allyl Alcohols:

To a solution of allyl alcohol (0.6 mmol) in a 25 ml two neck round bottom flask equipped with magnetic stir bar under argon atmosphere was added the corresponding arenediazonium salt (0.2 mmol) followed by $Pd_2(dba)_3$ (9.15 mg, 5 mol%) in NMP (3 ml) at 20 ^oC. The solution was stirred for 30 min at ambient temperature. After completing the reaction, the reaction mixture was diluted with ethyl acetate (10 mL) and transferred to separating funnel. To this distilled water (10 mL) was added and aqueous layer extracted with ethyl acetate (2× 20 ml). Combined organic layer was washed with distilled water (2×10 mL) and brine solution (10 mL).Then

organic layer was dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was removed under reduced pressure. This crude material was purified by silica gel column chromatography using hexane-ethyl acetate (80:20) as eluent to furnish the desired product.

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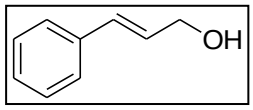
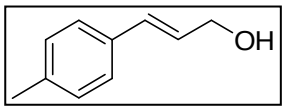


(*E*)-3-phenylprop-2-en-1-ol, 2a [2], Table 1

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a colorless oil, (10 mg, 38%).

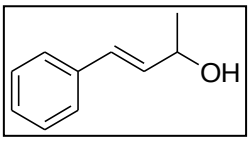
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.41 (m, 2H), 7.30-7.34 (m, 2H), 7.22-7.27 (m, 1H), 6.62 (d, J = 15.9 Hz, 1H), 6.37 (dt, J_1 = 15.6 Hz, J_2 = 6.0 Hz, 1H), 4.33 (dd, J_1 = 5.4 Hz, J_2 = 1.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.5, 130.7, 128.44, 128.38, 127.5, 126.3, 63.2.



(*E*)-3-p-tolylprop-2-en-1-ol, 2b [3], Table 1

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a colorless solid, (11 mg, 37%), m.p. 50-52 ^{o}C.

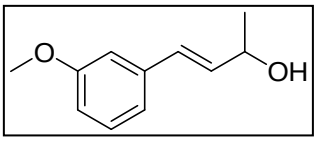
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 7.8 Hz, 2H), 6.59 (d, J = 15.6 Hz, 1H), 6.32 (dt, J_1 = 15.9 Hz, J_2 = 6.0 Hz, 1H), 4.31 (d, J = 5.4 Hz, 2H), 2.34 (s, 3H), 1.45 (br. s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.6, 133.8, 131.2, 129.3, 127.4, 126.4, 63.8, 21.2.



(*E*)-4-phenylbut-3-en-2-ol, 2c [4], Table 1

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a white solid, (20 mg, 68%), m.p. 50-52 ^oC.

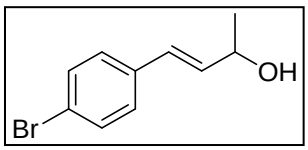
^1H NMR (300 MHz, $CDCl_3$): δ 7.22-7.40 (m, 5H), 6.57 (d, J = 15.9 Hz, 1H), 6.27 (dd, J_1 = 15.9 Hz, J_2 = 6.6 Hz, 1H), 4.46-4.54 (m, 1H), 1.38 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 136.7, 133.6, 129.4, 128.6, 127.6, 126.5, 68.9, 23.4.



(*E*)-4-(3-methoxyphenyl)but-3-en-2-ol, 2d[4], Table 1

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a colorless oil, (27 mg, 75%).

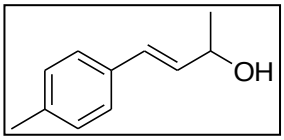
^1H NMR (300 MHz, $CDCl_3$): δ 7.23 (d, J = 8.1 Hz, 1H), 6.97 (d, J = 7.5 Hz, 1H), 6.91 (s, 1H), 6.80 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H), 6.53 (d, J = 15.6 Hz, 1H), 6.25 (dd, J_1 = 16.2 Hz, J_2 = 6.3 Hz, 1H), 4.44-4.52 (m, 1H), 3.81 (s, 3H), 1.89 (br. s, 1H), 1.37 (d, J = 6.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 159.7, 138.1, 133.8, 129.5, 129.2, 119.1, 113.3, 111.7, 68.8, 55.2, 23.3.



(*E*)-4-(4-bromophenyl)but-3-en-2-ol, 2e[4], Table 1

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a white solid, (26 mg, 57%), m.p. 60-62 ^oC.

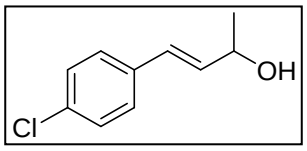
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.26 (dd, J_1 = 15.9 Hz, J_2 = 6.0 Hz, 1H), 4.44-4.52 (m, 1H), 1.36 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.6, 134.3, 131.6, 128.1, 128.0, 121.3, 68.7, 23.4.



(E)-4-p-tolylbut-3-en-2-ol, 2f [5], Table 1

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a colorless gummy liquid, (21 mg, 66%).

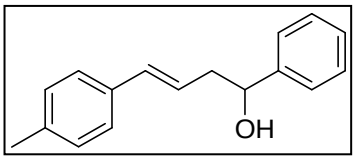
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28 (d, *J* = 9.3 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 6.54 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, J_1 = 15.9 Hz, J_2 = 6.3 Hz, 1H), 4.46-4.50 (m, 1H), 2.34 (s, 3H), 1.37 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.4, 133.8, 132.5, 129.3, 129.2, 126.3, 69.0, 23.4, 21.2.



(*E*)-4-(4-chlorophenyl)but-3-en-2-ol, 2g[4], Table 1

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a white solid, (22 mg, 60%), m.p. 54-56 ^{o}C.

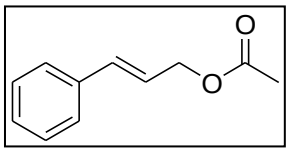
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29-7.30 (m, 4H), 6.53 (dd, J_1 = 15.9 Hz, J_2 = 1.2 Hz, 1H), 6.24 (dd, J_1 = 15.9 Hz, J_2 = 6.0 Hz, 1H), 4.47-4.51 (m, 1H), 1.38 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 135.2, 134.2, 133.2, 128.7, 128.1, 127.6, 68.8, 23.4.



(*E*)-1-phenyl-4-p-tolylbut-3-en-1-ol, 2h, Table 1

The same general procedure was followed using homo allyl alcohol instead of allyl alcohol. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a white solid, (20 mg, 42%), m.p. 56-58 ^oC.

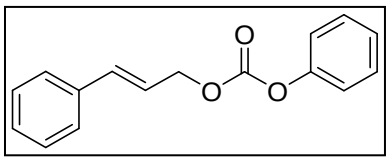
^1H NMR (300 MHz, $CDCl_3$): δ 7.33-7.40 (m, 4H), 7.27-7.33 (m, 1H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.47 (d, *J* = 15.6 Hz, 1H), 6.09-6.19 (m, 1H), 4.78-4.82 (m, 1H), 2.62-2.67 (m, 2H), 2.32 (s, 3H), 2.11 (br. s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.9, 137.2, 134.4, 133.4, 129.2, 128.5, 127.6, 126.1, 125.8, 124.8, 73.7, 43.2, 21.2; IR (neat): υ_{max} 3383, 3026, 1512, 1451, 1044, 968, 700 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{17}H_{18}ONa$ $[M + Na]^+$: 261.1255; found: 261.1268.



cinnamyl acetate, 2i[6], Table 1

The same general procedure was followed using allyl acetate instead of allyl alcohol. Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a colorless oil, (29 mg, 82%).

^1H NMR (300 MHz, $CDCl_3$): δ 7.24-7.41 (m, 5H), 6.66 (d, *J* = 15.6 Hz, 1H), 6.29 (dt, J_1 = 15.6 Hz, J_2 = 6.6 Hz, 1H), 4.73 (dd, J_1 = 5.7 Hz, J_2 = 0.6 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.8, 136.1, 134.2, 128.6, 128.0, 126.6, 123.1, 65.0, 21.0.



cinnamyl phenyl carbonate, 2j[7], Table 1

The same general procedure was followed using allyl carbonate instead of allyl alcohol. Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a colorless oil, (34 mg, 67%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18-7.44 (m, 10H), 6.75 (d, J = 15.9 Hz, 1H), 6.36 (dt, J_1 = 15.9 Hz, J_2 = 6.9 Hz, 1H), 4.90 (dd, J_1 = 6.9 Hz, J_2 = 1.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.6, 151.1, 135.9, 135.5, 129.5, 128.7, 128.4, 126.8, 126.1, 121.9, 121.1, 69.2; IR (neat): υ_{max} 2923, 1763, 1594, 1455, 1234, 691 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{16}H_{14}O_3Na$ $[M + Na]^+$: 277.0841; found: 277.0853.

General Experimental Procedure for the Reaction with Cinnamyl Alcohols:

To the solution of cinnamyl alcohol (0.2 mmol) in a 25 ml two neck round bottom flask equipped with magnetic stir bar under argon atmosphere was added the corresponding arenediazonium salt (0.3mmol) followed by $Pd_2(dba)_3$ (0.01 mmol) in DMA (2 mL) at 25 ^{o}C. The solution was stirred for 3 hr at ambient temperature. After completing the reaction as indicated by TLC, the reaction mixture was diluted with 10 ml of ethyl acetate and transferred to the separating funnel. To this 10 ml of distilled water was added and aqueous layer was extracted with ethyl acetate (2× 20 mL). Combined organic layer was washed with distilled water (2×10 mL) and brine solution (10 mL). Then the organic layer was dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was removed under reduced pressure. The crude material was purified by silica gel column chromatography using hexane-ethyl acetate (80:20) eluent to furnish the desired product.

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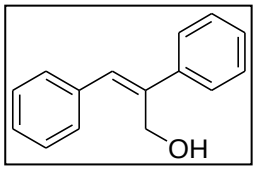
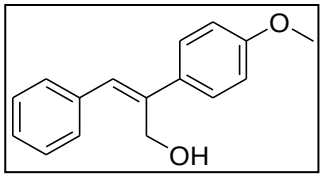


(*Z*)-2,3-diphenylprop-2-en-1-ol, 3a[8], Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a pale yellow solid, (26 mg, 62%), m.p. 72-74 ^{o}C.

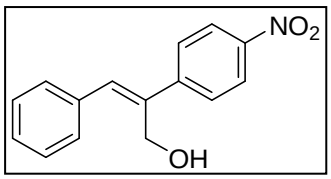
^{1}H NMR (300 $MH_{Z,}$ $CDCl_3$): δ 7.58-7.61 (m, 2H), 7.30-7.44 (m, 8H), 6.98 (s, 1H), 4.72 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.5, 140.1, 136.9, 131.3, 128.9, 128.7, 128.4, 127.7, 127.4, 126.6, 60.3.



(*Z*)-2-(4-methoxyphenyl)-3-phenylprop-2-en-1-ol, 3b, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a yellow solid, (31 mg, 65%), m.p. 74-76 ^{o}C.

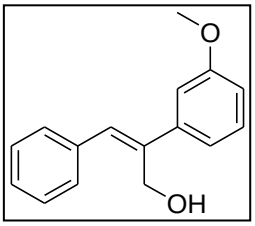
^{1}H NMR (600 $MH_{Z,}$ $CDCl_3$): δ 7.54 (d, *J* = 9.0 Hz, 2H), 7.38-7.42 (m, 4H), 7.28-7.31 (m, 1H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.92 (s, 1H), 4.70 (s , 2H), 3.85 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.3, 139.5, 137.1, 132.8, 129.8, 128.9, 128.4, 127.7, 127.2, 114.1, 60.3, 56.3; IR (neat): υ_{max} 3281, 1602, 1511, 1248, 1179, 1020, 828 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{16}H_{16}O_2$ $[M]^+$: 240.1150; found: 240.1143.



(*Z*)-2-(4-nitrophenyl)-3-phenylprop-2-en-1-ol, 3c, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a yellow solid, (36 mg, 71%), m.p. 54-56 ^{o}C.

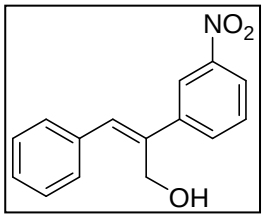
^{1}H NMR (300 $MHz_{,}$ $CDCl_3$): δ 8.26 (d, *J* = 9.0 Hz, 2H), 7.78 (d, *J* = 8.7 Hz, 2H), 7.35-7.44 (m, 5H), 7.14 (s, 1H) 4.74 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.5, 147.0, 138.2, 135.9, 134.5, 129.0, 128.6, 128.2, 127.3, 123.8, 60.0; IR (neat): υ_{max} 3262, 1592, 1513, 1341, 698 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{15}H_{13}NO_3Na$ $[M + Na]^+$: 278.0795; found: 278.0859.



(*Z*)-2-(3-methoxyphenyl)-3-phenylprop-2-en-1-ol, 3d, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as an orange oil, (31 mg, 64%).

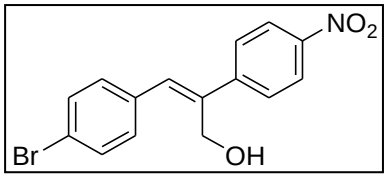
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.27-7.42 (m, 6H), 7.13-7.18 (m, 2H), 6.97 (s, 1H), 6.88 (dd, J_1 = 7.8 Hz, J_2 = 2.1 Hz, 1H), 4.69 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.9, 142.2, 140.1, 136.8, 131.5, 129.7, 129.0, 128.4, 127.4, 119.0, 113.1, 112.5, 60.4, 55.3; IR (neat): υ_{max} 3414, 2930, 1599, 1488, 1286, 1172, 1038, 698 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{16}H_{16}O_2$ $[M]^+$: 240.1150; found: 240.1152.



(*Z*)-2-(3-nitrophenyl)-3-phenylprop-2-en-1-ol, 3e, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a yellow oil, (33 mg, 64%).

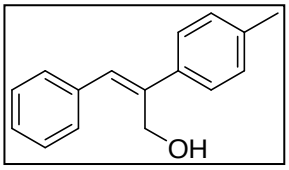
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.47-8.48 (m, 1H), 8.15-8.19 (m, 1H), 7.93-7.97 (m, 1H), 7.57 (t, J = 9.0 Hz, 1H), 7.32-7.43 (m, 5H), 7.10 (s, 1H), 4.75 (s, 2H), 1.74 (br. s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.5, 142.6, 137.9, 136.0, 133.5, 132.6, 129.4, 128.9, 128.5, 128.0, 122.2, 121.4, 60.0; IR (neat): υ_{max} 3436, 1527, 1347, 1001, 743, 698 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{15}H_{13}NO_3Na$ $[M + Na]^+$: 278.0793; found: 247.0801.



(*Z*)-3-(4-bromophenyl)-2-(4-nitrophenyl)prop-2-en-1-ol, 3f, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a yellow solid, (51 mg, 76%), m.p. 106-108 ^oC.

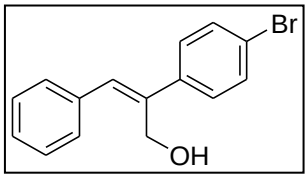
^1H NMR (300 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.7 Hz, 2H), 7.75 (d, *J* = 9.0 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.03 (s, 1H), 4.69 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.3, 147.1, 138.7, 134.8, 133.4, 131.7, 130.6, 127.3, 123.9, 122.3, 59.9; IR (neat): υ_{max} 3542, 1586, 1510, 1341, 1000, 820 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{15}H_{12}BrNO_3$ $[M]^+$: 333.0001; found: 333.0003.



(*Z*)-3-phenyl-2-p-tolylprop-2-en-1-ol, 3g, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a white solid, (29 mg, 64%), m.p. 78-80 ^oC.

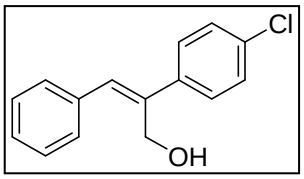
^1H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.8 Hz, 2H), 7.35-7.42 (m, 4H), 7.26-7.31 (m, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 6.94 (s, 1H), 4.69 (s, 2H), 2.38 (s, 3H), 1.60 (br. s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.0, 137.6, 137.5, 137.0, 130.5, 129.4, 128.9, 128.4, 127.2, 126.4, 60.3, 21.1; IR (neat): υ_{max} 3376, 2916, 1509, 1015, 816, 698 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{16}H_{16}O$ $[M]^+$: 224.1201; found: 224.1197.



(*Z*)-2-(4-bromophenyl)-3-phenylprop-2-en-1-ol, 3h, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a white solid, (34 mg, 58%), m.p. 100-102 ^{o}C.

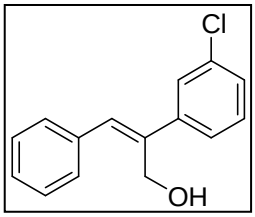
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.53 (m, 5H), 7.40-7.39 (m, 4H), 6.97 (s, 1H), 4.67 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.6, 138.9, 136.5, 131.8, 131.7, 128.9, 128.4, 128.2, 127.6, 121.6, 60.1; IR (neat): υ_{max} 3367, 1486, 1012, 822, 702 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{15}H_{13}BrO$ $[M]^+$: 288.0150; found: 288.0154.



(*Z*)-2-(4-chlorophenyl)-3-phenylprop-2-en-1-ol, 3i [9], Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a white solid, (26 mg, 52%), m.p. 76-78 ^{o}C.

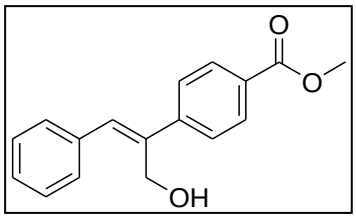
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.7 Hz, 2H), 7.28-7.41 (m, 7H), 6.97 (s, 1H), 4.69 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 139.1, 139.0, 136.6, 133.5, 131.7, 128.9, 128.8, 128.5, 127.9, 127.6, 60.3; IR (neat): υ_{max} 3289, 1491, 1095, 1009, 826, 702 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{15}H_{13}ClO$ $[M]^+$: 244.0655; found: 244.0652.



(*Z*)-2-(3-chlorophenyl)-3-phenylprop-2-en-1-ol, 3j, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a white gummy liquid, (25 mg, 50%).

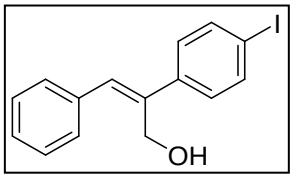
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (s, 1H), 7.48 (dt, J_1 = 7.2 Hz, J_2 = 1.8 Hz, 1H), 7.28-7.42 (m, 7H), 6.99 (s, 1H), 4.68 (s, 2H); ^{13}C-NMR (75 MHz, $CDCl_3$): 142.7, 138.9, 136.5, 134.6, 132.4, 129.9, 129.0, 128.5, 127.7, 126.8, 124.8, 60.2; IR (neat): υ_{max} 3363, 1496, 1065, 1016, 746 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{15}H_{13}ClO$ $[M]^+$: 244.0655; found: 244.0656.



methyl 4-((*Z*)-3-hydroxy-1-phenylprop-1-en-2-yl)benzoate, 3k, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 7:3 hexane/ethyl acetate) afforded the desired product as a light brown solid, (39 mg, 73%), m.p. 90-92 ^{o}C.

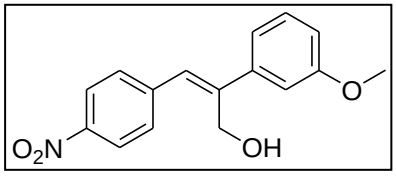
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.07 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.30-7.45 (m, 5H), 7.08 (s, 1H), 4.73 (s, 2H), 3.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 166.9, 145.4, 139.2, 136.4, 133.0, 129.9, 129.1, 129.0, 128.5, 127.7, 126.5, 60.1, 52.1; IR (neat): υ_{max} 3459, 1702, 1600, 1439, 1294, 1114, 774, 702 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{17}H_{16}O_3$ $[M]^+$: 268.1099; found: 268.1105.



(*Z*)-2-(4-iodophenyl)-3-phenylprop-2-en-1-ol, 3l, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a gray solid, (27 mg, 40%), m.p. 88-90 ^{o}C.

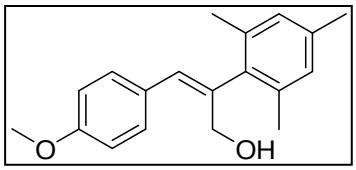
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.30-7.41 (m, 7H), 6.98 (s, 1H), 4.68 (s, 2H), 1.65 (br. s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): 140.2, 139.1, 137.7, 136.5, 131.8, 128.9, 128.4, 127.6, 93.2, 60.1; IR (neat): υ_{max} 3288, 1484, 1001, 816, 700 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{15}H_{13}IO$ $[M]^+$: 336.0011; found: 336.0012.



(*Z*)-2-(3-methoxyphenyl)-3-(4-nitrophenyl)prop-2-en-1-ol, 3m, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 7:3 hexane/ethyl acetate) afforded the desired product as an orange oil, (37 mg, 65%).

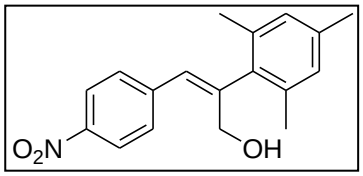
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.7 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.12-7.18 (m, 2H), 6.97 (s, 1H), 6.93 (dd, J_1 = 8.1 Hz, J_2 = 2.1 Hz, 1H), 4.65 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.0, 146.8, 143.5, 143.2, 141.4, 129.9, 129.8, 129.2, 123.7, 119.0, 113.7, 112.7, 60.2, 55.3; IR (neat): υ_{max} 3488, 1592, 1509, 1339, 1004, 880, 696 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{16}H_{15}NO_4$ $[M]^+$: 285.1001; found: 285.0988.



(*Z*)-2-mesityl-3-(4-methoxyphenyl)prop-2-en-1-ol, 3n, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a pale yellow solid, (48 mg, 85%), m.p. 72-74 ^oC.

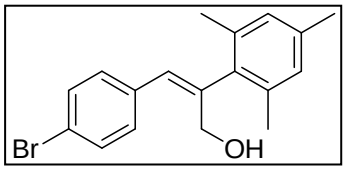
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.7 Hz, 2H), 6.92-6.94 (m, 4H), 6.37 (s, 1H), 4.56 (d, *J* = 3.3 Hz, 2H), 3.84 (s, 3H), 2.30 (s, 3H), 2.29 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.8, 138.9, 137.6, 136.7, 136.5, 131.1, 130.2, 129.5, 128.3, 113.8, 62.2, 55.3, 21.0, 20.3; IR (neat): υ_{max} 3207, 1606, 1507, 1247, 1034 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{19}H_{22}O_2$ $[M]^+$: 282.1620; found: 282.1622.



(*Z*)-2-mesityl-3-(4-nitrophenyl)prop-2-en-1-ol, 3o, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a pale yellow oil, (55 mg, 92%).

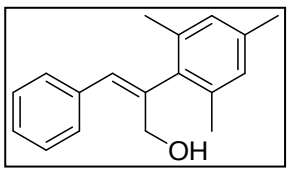
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.7 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 6.94 (s, 2H), 6.49 (s, 1H), 4.52 (s, 2H), 2.31 (s, 3H), 2.29 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 146.6, 144.4, 143.3, 137.2, 136.6, 136.0, 129.7, 129.5, 128.4, 123.6, 61.9, 20.9, 20.2; IR (neat): υ_{max} 3440, 1593, 1517, 1340, 1008, 852 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{18}H_{19}NO_3$ $[M]^+$: 297.1365; found: 297.1366.



(*Z*)-3-(4-bromophenyl)-2-mesitylprop-2-en-1-ol, 3p, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a pale yellow solid, (60 mg, 90%), m.p. 68-70 ^{o}C.

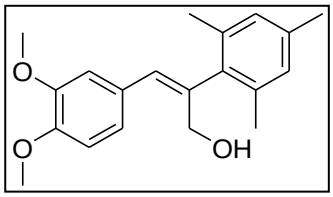
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 6.3 Hz, 2H), 6.92 (s, 2H), 6.36 (s, 1H), 4.49 (s, 2H), 2.30 (s, 3H), 2.27 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.3, 137.0, 136.9, 136.2, 135.6, 131.5, 130.4, 128.4, 121.1, 62.0, 21.0, 20.2; IR (neat): υ_{max} 3258, 2917, 1482, 1048, 813 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{18}H_{19}BrO$ $[M]^+$: 330.0619; found: 330.0621.



(*Z*)-2-mesityl-3-phenylprop-2-en-1-ol, 3q, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a pale yellow solid, (35 mg, 70%), m.p. 78-80 ^oC.

^1H NMR (300 MHz, $CDCl_3$): δ 7.38-7.43 (m, 5H), 6.93 (s, 2H), 6.44 (s, 1H), 4.57 (d, 2H), 2.30 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): 140.6, 137.3, 136.9, 136.8, 136.4, 131.5, 128.9, 128.4, 128.4, 127.2, 62.1, 21.0, 20.3; IR (neat): υ_{max} 3278, 2919, 1444, 1032, 859, 764, 704 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{18}H_{20}O$ $[M]^+$: 252.1514; found: 252.1518. For NOESY see the Spectra.

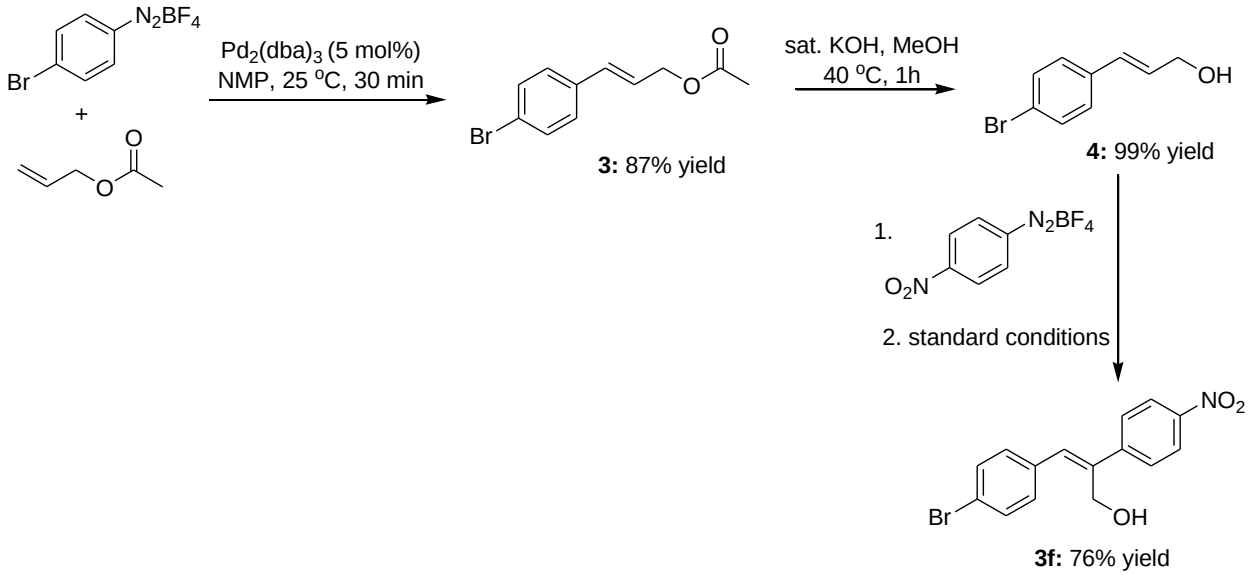


(*Z*)-2-mesityl-3-(3,4-dimethoxyphenyl)prop-2-en-1-ol, 3r, Table 2

The same general procedure was followed. Column chromatography (SiO_2, eluting with 7:3 hexane/ethyl acetate) afforded the desired product as a pale yellow oil, (56 mg, 90%).

^1H NMR (300 MHz, $CDCl_3$): 6.88-6.96 (m, 5H), 6.38 (s, 1H), 4.56 (s, 2H), 3.92 (s, 3H), 3.91 (s, 3H), 2.30 (s, 3H), 2.29 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 148.7, 148.2, 139.0, 137.6, 136.7, 136.4, 131.4, 129.7, 128.3, 121.4, 112.0, 110.9, 62.3, 55.9, 55.8, 20.9, 20.3; IR (neat): υ_{max} 3523, 2925, 1513, 1460, 1265, 1143, 1027, 852 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{20}H_{24}O_3$ $[M]^+$: 312.1725; found: 312.1711.

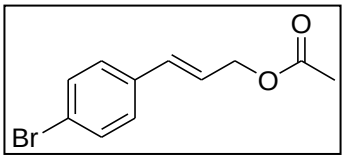
Sequential Diarylation:



Preparation of 4-bromocinnamyl acetate(3):

To a solution of allyl acetate (0.6 mmol) in a 25 ml two neck round bottom flask equipped with magnetic stir bar under argon atmosphere was added the 4-bromoarenediazonium salt (0.2 mmol) followed by $Pd_2(dba)_3$ (9.15 mg, 5 mol%) in NMP (3 ml) at 25 ^oC. The solution was stirred for 30 min at ambient temperature. After completing the reaction, the reaction mixture was diluted with ethyl acetate (10 mL) and transferred to separating funnel. To this distilled water (10 mL) was added and aqueous layer extracted with ethyl acetate (2× 20 ml). Combined organic layer was washed with distilled water (2×10 mL) and brine solution (10 mL).Then organic layer was dried over anhydrous Na_2SO_4. The mixture was filtered and the solvent was removed under reduced pressure. This crude material was purified by silica gel column chromatography using hexane-acetone (98:2) as eluent to furnish the desired product.

SPECTRAL DATA:



4-bromocinnamyl acetate, 3[10]

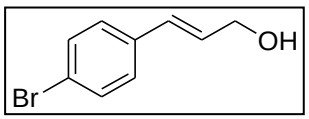
Column chromatography (SiO_2, eluting with 98:2 hexane/acetone) afforded the desired product as a yellowish oil, (44 mg, 87%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.28 (dt, J_1 =15.9 Hz, J_2 = 6.3 Hz, 1H), 4.71 (dd, J_1 = 6.3 Hz, J_2 = 1.2 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.6, 135.0, 132.6, 131.6, 128.0, 123.9, 121.8, 64.7, 20.8.

Preparation of (*E*)-3-(4-bromophenyl)prop-2-en-1-ol(4):

A solution of 4-bromocinnamyl acetate (51 mg, 0.2 mmol) in 3:1 MeOH/sat. aq. KOH (3 mL) was taken in a 10 ml round bottom flask and stirred at 40 ^{o}C for 1 h. After completion the reaction mixture was diluted with saturated NH_4Cl solution (10 mL) and was extracted with ethyl acetate (20×2 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified by column chromatography to provide the desire product.

SPECTRAL DATA:

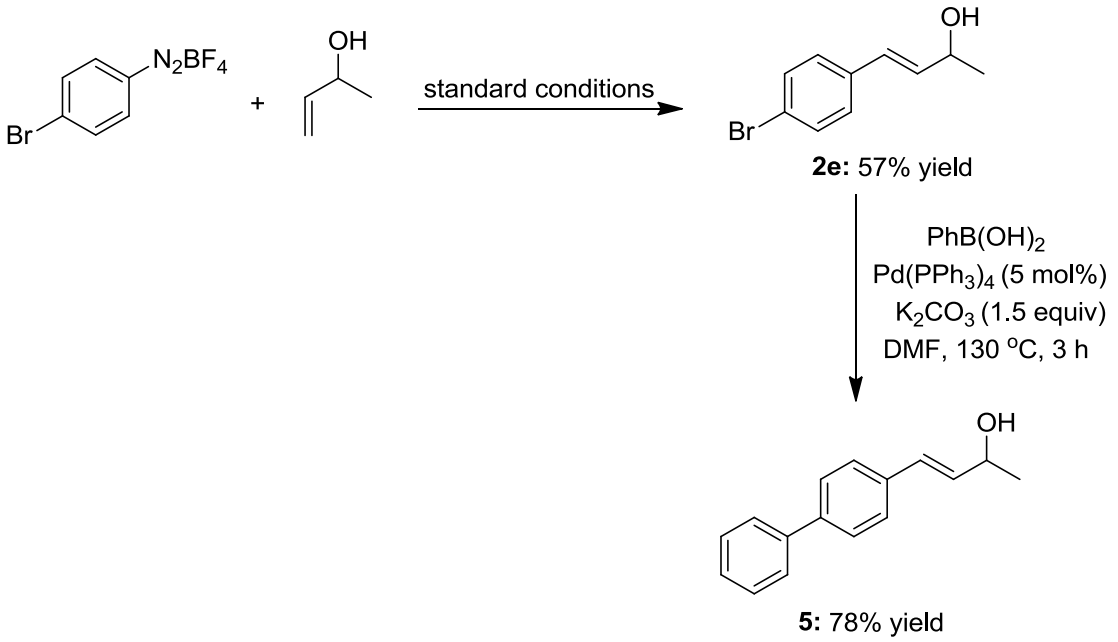


(*E*)-3-(4-bromophenyl)prop-2-en-1-ol, 4[11]

Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a white solid, (42 mg, 99%), m.p. 64-66 ^{o}C.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.35 (dt, J_1 = 15.6 Hz, J_2 = 5.7 Hz, 1H), 4.32 (dd, J_1 = 5.4 Hz, J_2 = 1.2 Hz, 2H), 1.66 (br. s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.6, 131.7, 129.7, 129.3, 127.9, 121.4, 63.5.

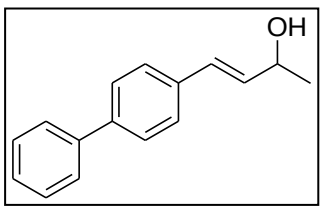
Orthogonal Heck/Suzuki Coupling Reaction:



Preparation of (*E*)-4-biphenylbut-3-en-2-ol(5) from (*E*)-4-(4-bromophenyl)but-3-en-2-ol(2e) by Suzuki Coupling Reaction:

A mixture of (*E*)-4-(4-bromophenyl)but-3-en-2-ol (0.20 mmol), phenylboronic acid (0.30 mmol), potassium carbonate (0.30 mmol), and $Pd(PPh_3)_4$ (0.01 mmol) was placed in a reaction tube under argon and was diluted with DMF (3 mL). The sealed reaction tube was heated at 130 ^oC for 3 h. After consumption of the starting material indicated by TLC, the reaction mixture was diluted with ethyl acetate (25 mL) and washed with water (20 mL), brine (5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure left the crude product which was purified by flash column chromatography on silica gel using ethyl acetate/hexane (2:8) eluent. The pure product was isolated as a white solid in 78% yield.

SPECTRAL DATA:



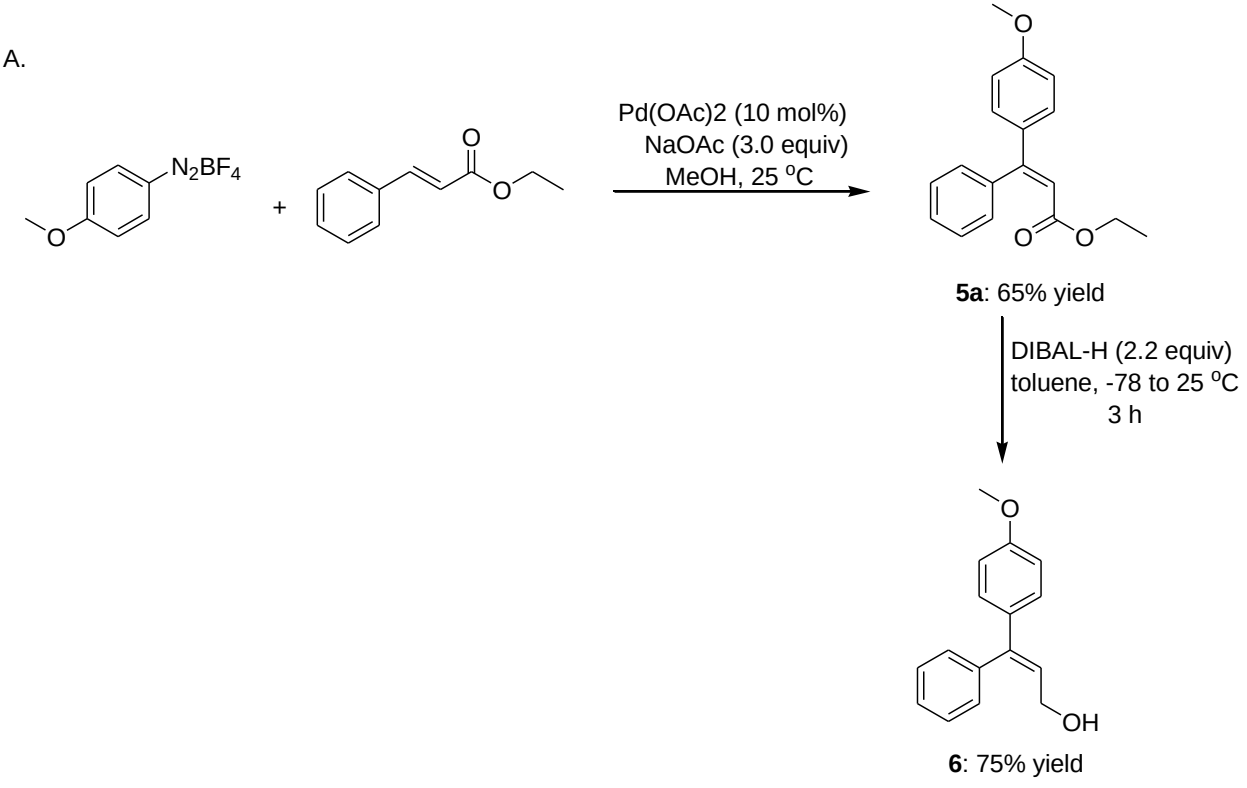
(*E*)-4-biphenylbut-3-en-2-ol, 5[4]

Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a white solid, (35 mg, 78%), m.p. 145-147 ^oC.

^1H NMR (300 MHz, $CDCl_3$): δ 7.55-7.61 (m, 4H), 7.41-7.47 (m, 4H), 7.32-7.36 (m, 1H), 6.61 (d, J = 15.9 Hz, 1H), 6.31 (dd, J_1 = 16.2 Hz, J_2 = 6.6 Hz, 1H), 4.48-4.56 (m, 1H), 1.66 (br. s, 1H), 1.39 (d, J = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.6, 140.4, 135.7, 133.6, 129.0, 128.8, 127.31, 127.27, 126.92, 126.89, 69.0, 23.4; IR (neat): υ_{max} 3420, 2924, 1640, 1458, 1064, 758 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{16}H_{16}ONa$ $[M + Na]^+$: 247.1099; found: 247.1100.

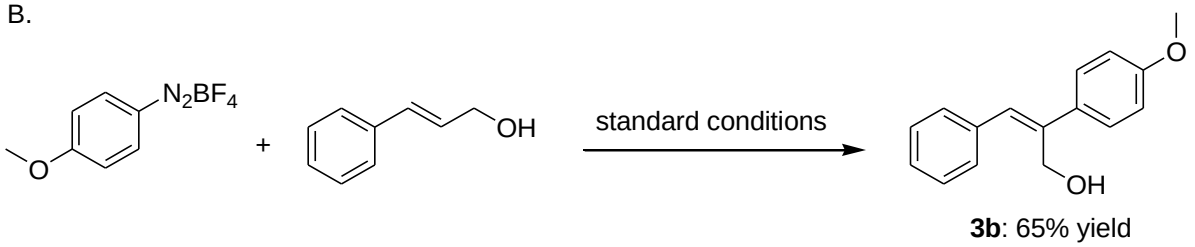
Preparation of β,β- vs β,α diaryl allylic alcohols:

A.



Selective β-arylation

B.



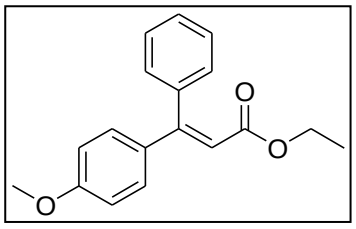
3b: 65% yield

Selective α-arylation

Preparation of (*E*)-ethyl 3-(4-methoxyphenyl)-3-phenylacrylate(5a)[12]:

To a solution of (*E*)-ethyl cinnamate (352 mg, 2.0 mmol) in 12 mL of methanol was added, at once, a mixture of the 4-methoxyarenediazonium salt (2.4 mmol, 1.2 equiv.), sodium acetate and palladium(II)acetate(48 mg, 10 mol%). The reaction mixture was allowed to stir at room temperature for 14 h. After cooling, the mixture was filtered through a pad of celite and the reaction mixture was diluted with ethyl acetate (25 mL) and washed with water (20 mL), brine (5 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure left the crude product which was purified by flash column chromatography on silica gel using ethyl acetate/hexane (3:7) eluent. The pure product was isolated as colorless oil in 65% yield.

SPECTRAL DATA:



(*Z*)-ethyl 3-(4-methoxyphenyl)-3-phenylacrylate, 5a[13]

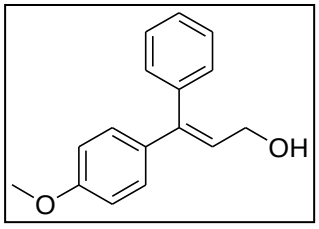
Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a colorless oil, (367 mg, 65%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37-7.40 (m, 3H), 7.18-7.26 (m, 4H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.31 (s, 1H), 4.03 (q, *J* = 6.9 Hz, 2H), 3.81 (s, 3H), 1.10 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR (75 MHz, $CDCl_3$): δ 166.2, 160.7, 156.3, 139.2, 133.0, 129.7, 129.0, 127.9, 127.8, 115.3, 113.7, 59.8, 55.3, 14.0.

Preparation of (*E*)-3-(4-methoxyphenyl)-3-phenylprop-2-en-1-ol(6):

A 1M solution of DIBAL-H in toluene (1.2 mL, 1.1 mmol) was added dropwise at -78 ^{o}C to a stirred solution of crude (*E*)-ethyl 3-(4-methoxyphenyl)-3-phenylacrylate (141 mg, 0.5 mmol) in dry THF (4 mL) and the mixture was stirred for 40 min at -78 ^{0}C then the reaction mixture was allowed to stir at room temperature for 2 h. The reaction mixture was poured into 0.1 N HCl (20 mL). The reaction mixture was diluted with ethyl acetate (60 mL) and washed with water (20 mL), brine (10 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure left the crude product which was purified by flash column chromatography on silica gel using ethyl acetate/hexane (2:8) eluent. The pure product was isolated as pale yellow oil in 75% yield.

SPECTRAL DATA:



(*E*)-3-(4-methoxyphenyl)-3-phenylprop-2-en-1-ol, 6

Column chromatography (SiO_2, eluting with 8:2 hexane/ethyl acetate) afforded the desired product as a pale yellow oil, (90 mg, 75%).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33-7.40 (m, 3H), 7.15-7.20 (m, 4H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.17 (t, *J* = 6.9 Hz, 1H), 4.19 (d, *J* = 6.9 Hz, 2H), 3.80 (s, 3H), 1.64 (br. s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2, 143.7, 139.2, 134.4, 129.7, 128.7, 128.1, 127.5, 125.7, 113.5, 60.7, 55.2; IR (neat): υ_{max} 3355, 2929, 1605, 1510, 1248, 1180, 1032, 828, 705 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{16}H_{16}O_2Na$ $[M + Na]^+$: 263.1048; found: 263.1139.

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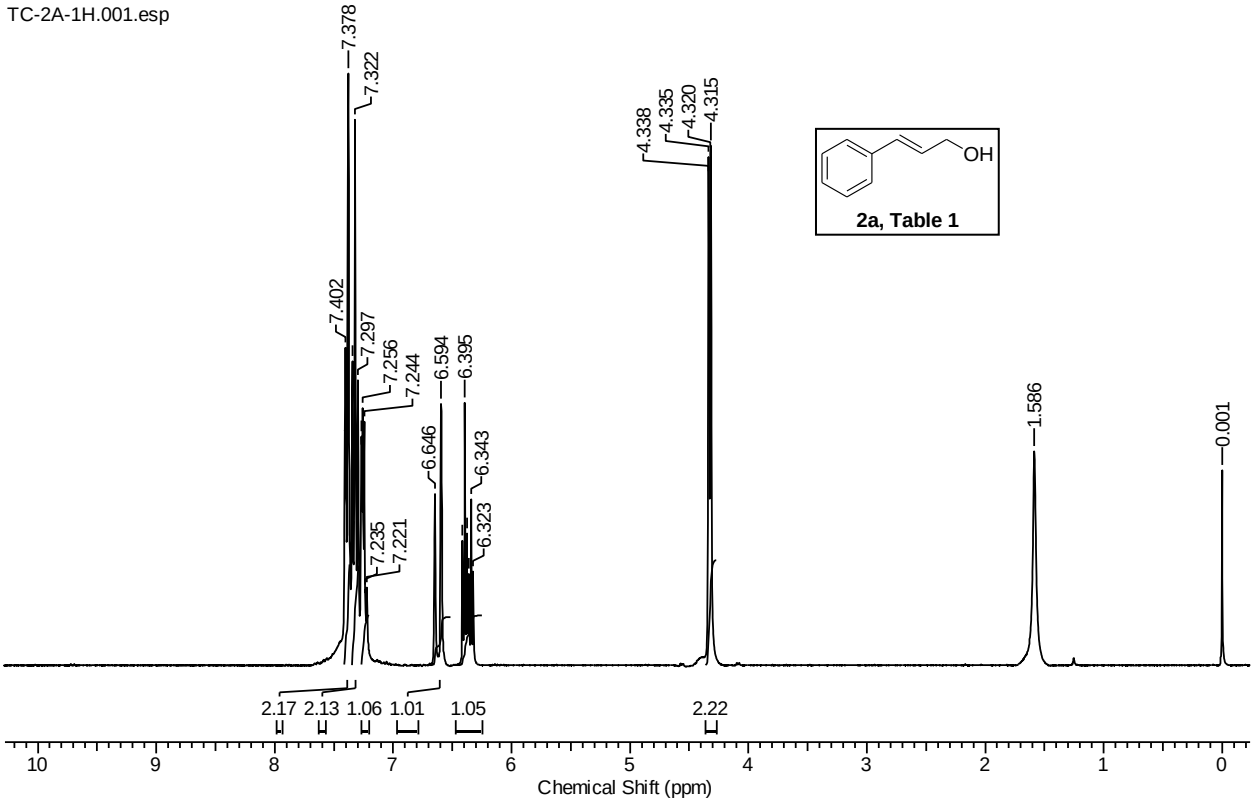
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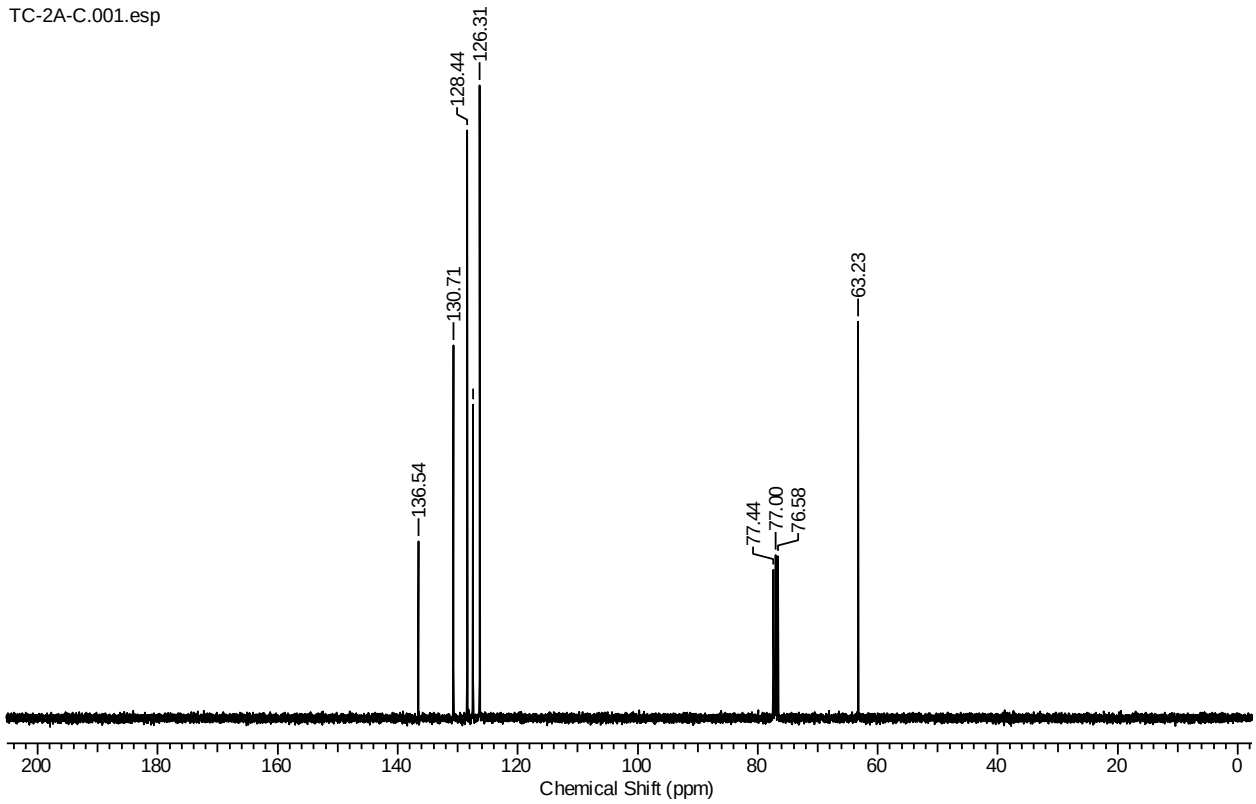
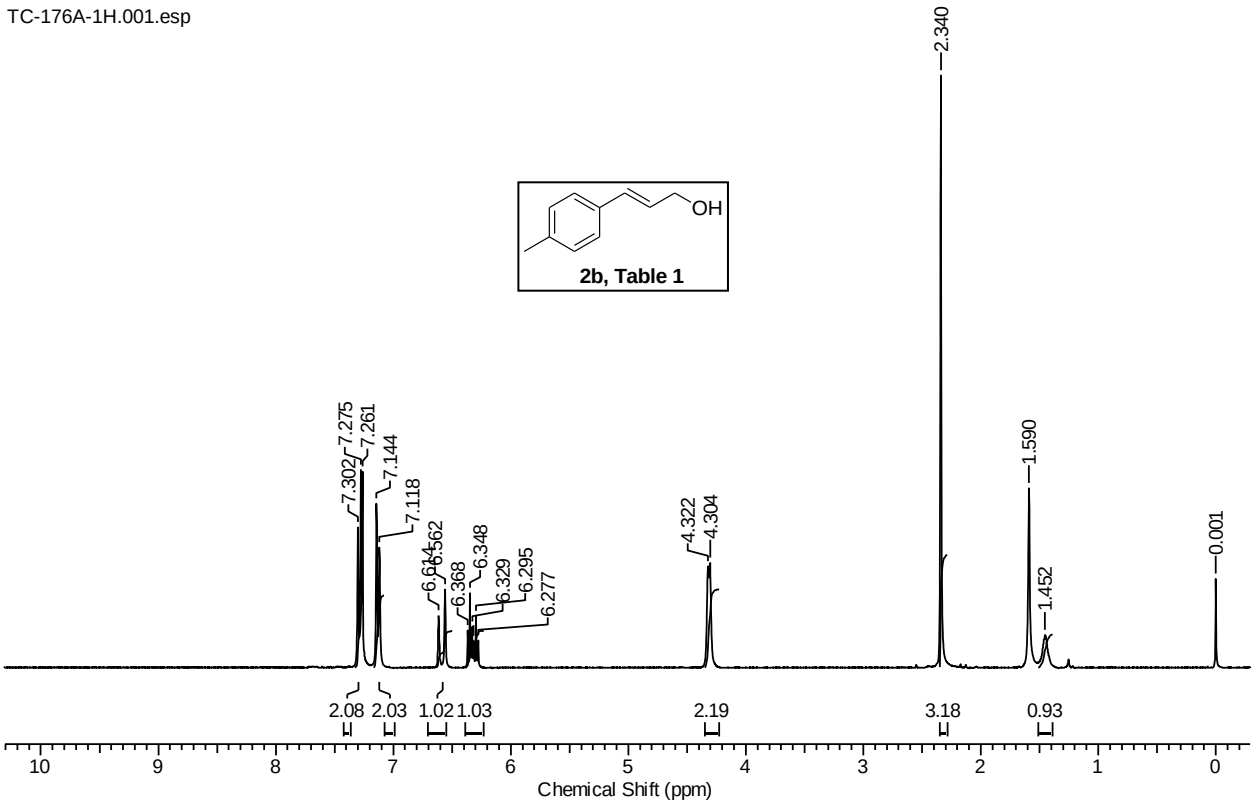
7.378
7.322
4.338
4.335
4.320
4.315
OH
2a, Table 1
7.402
7.297
7.256
7.244
6.594
6.395
6.646
6.343
6.323
7.235
7.221
1.586
0.001
2.17 2.13 1.06 1.01 1.05 2.22
Chemical Shift (ppm)


TC-2A-C.001.esp
128.44
126.31
130.71
63.23
136.54
77.44
77.00
76.58
Chemical Shift (ppm)

TC-176A-1H.001.esp



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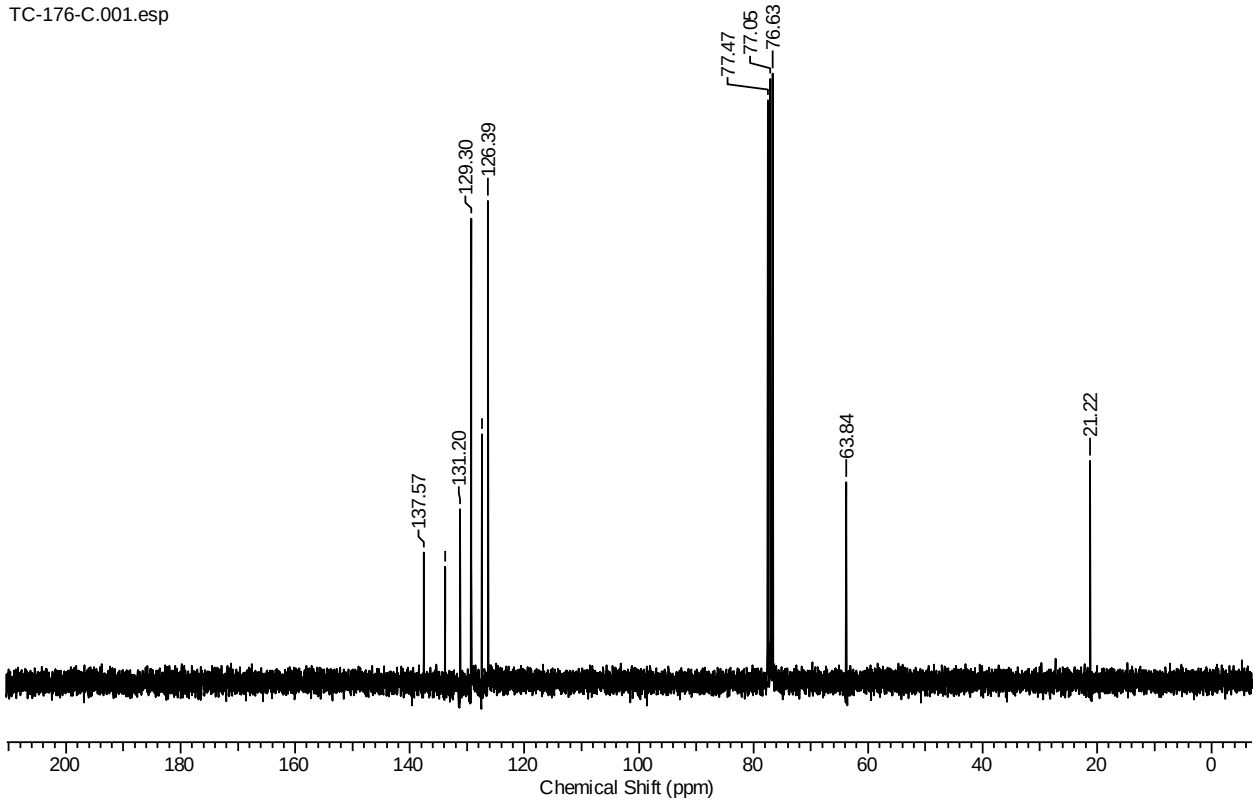

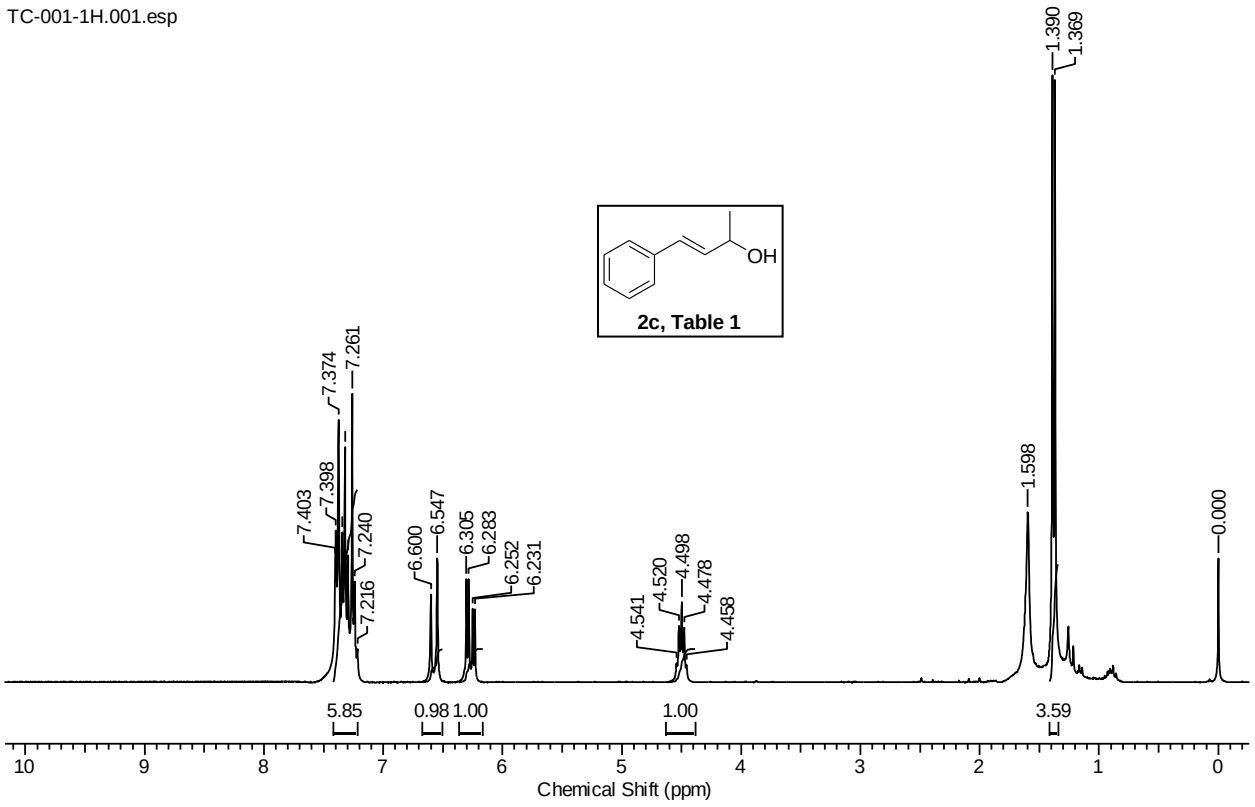
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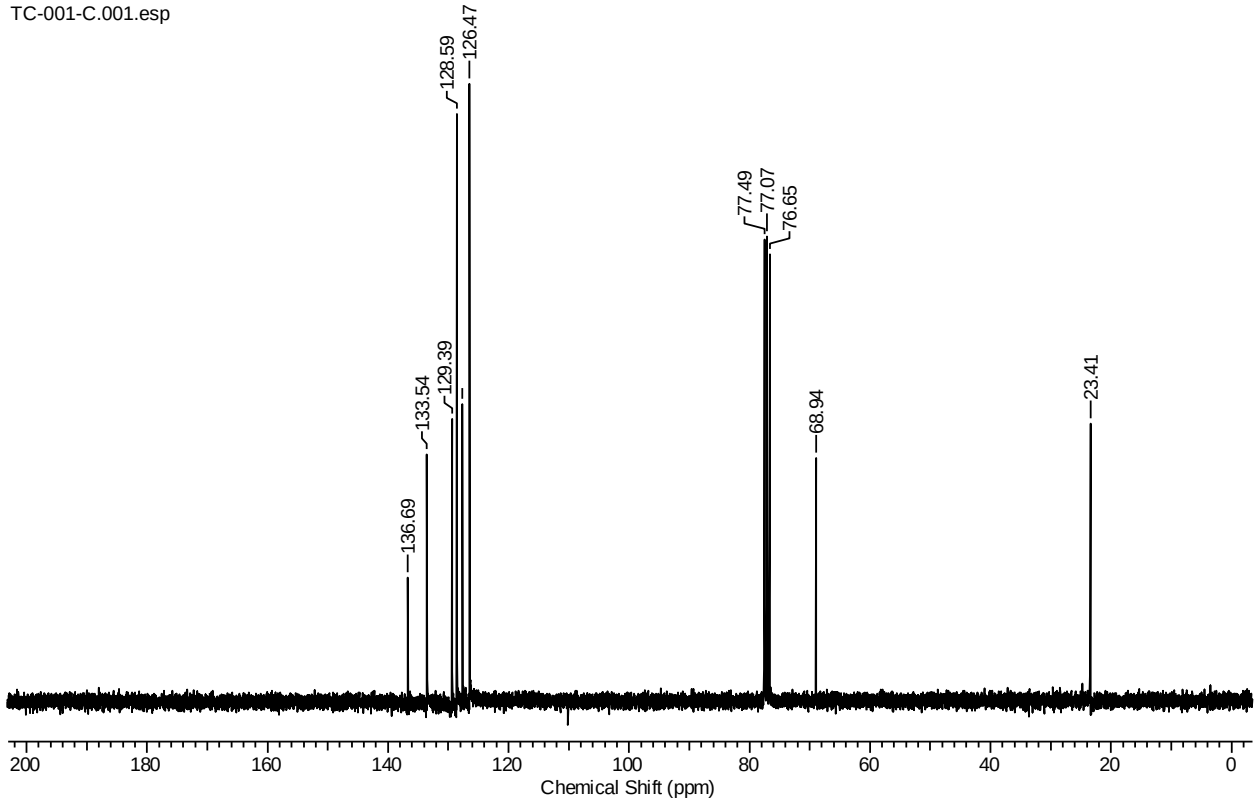
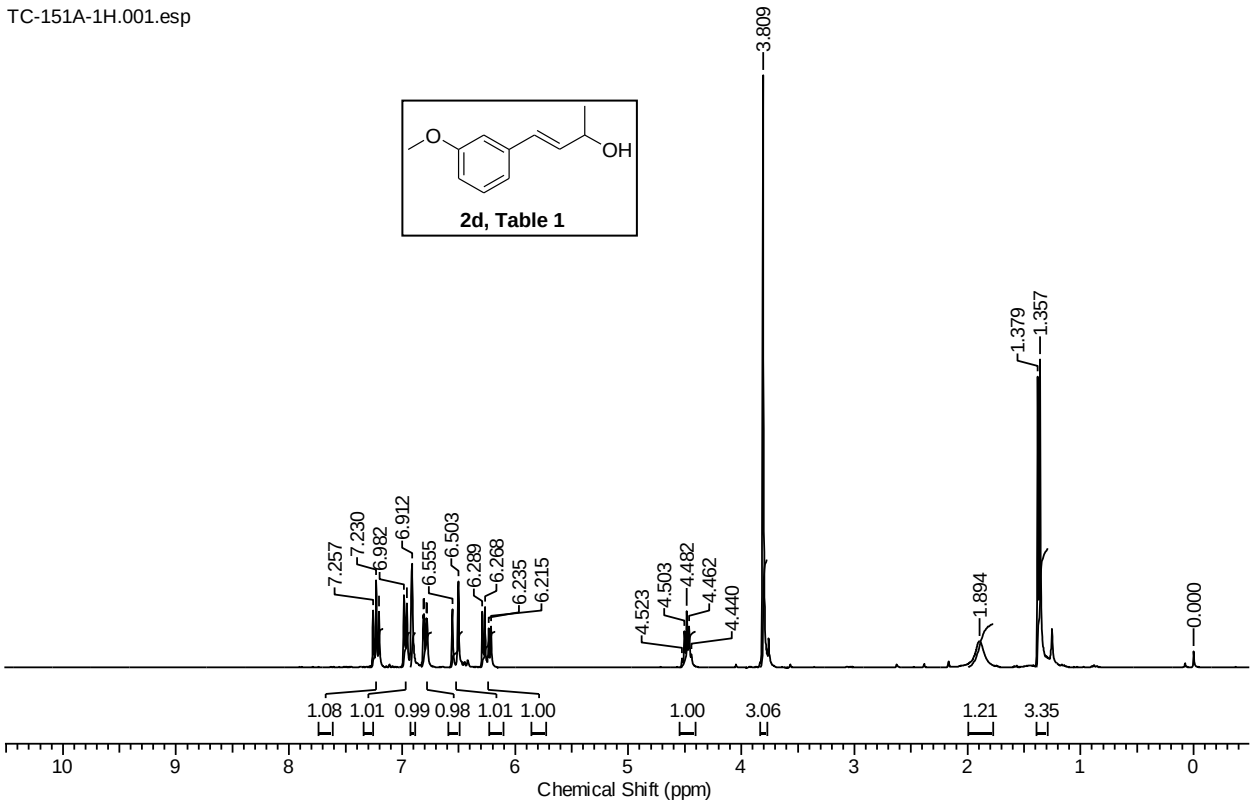
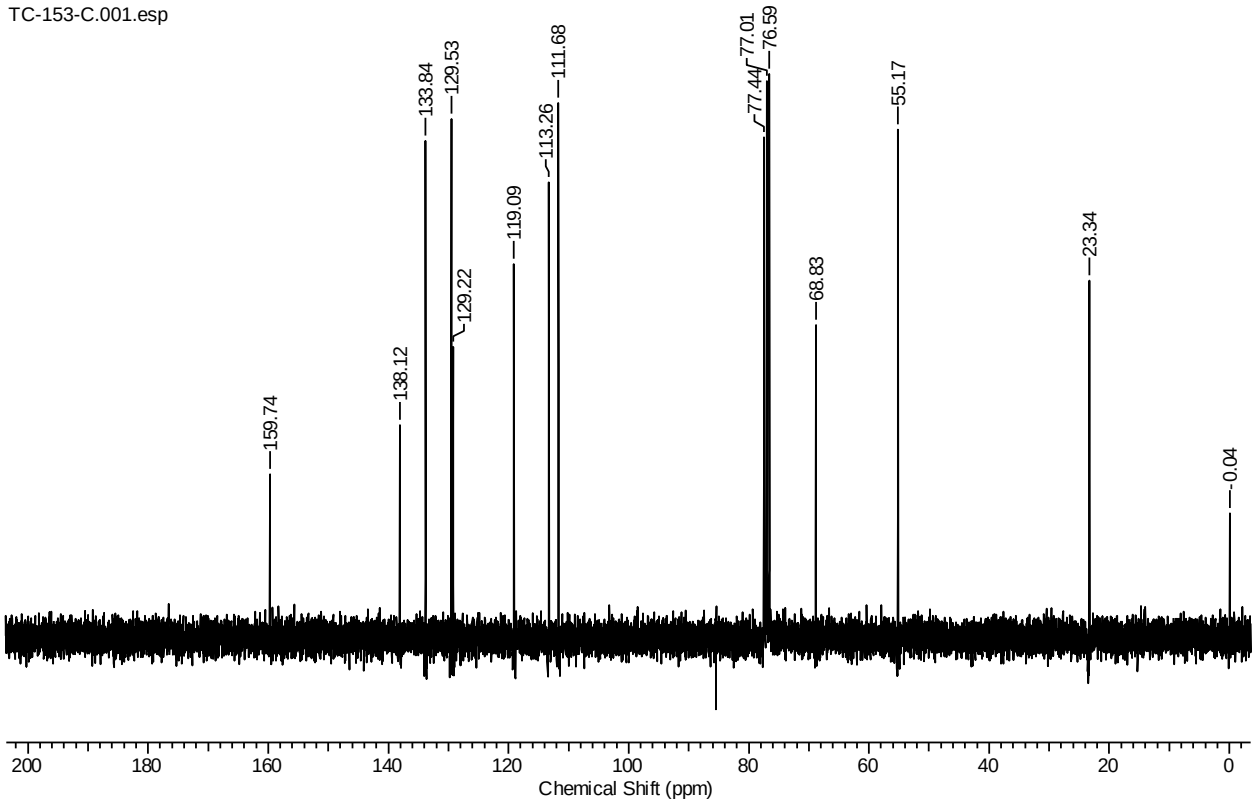
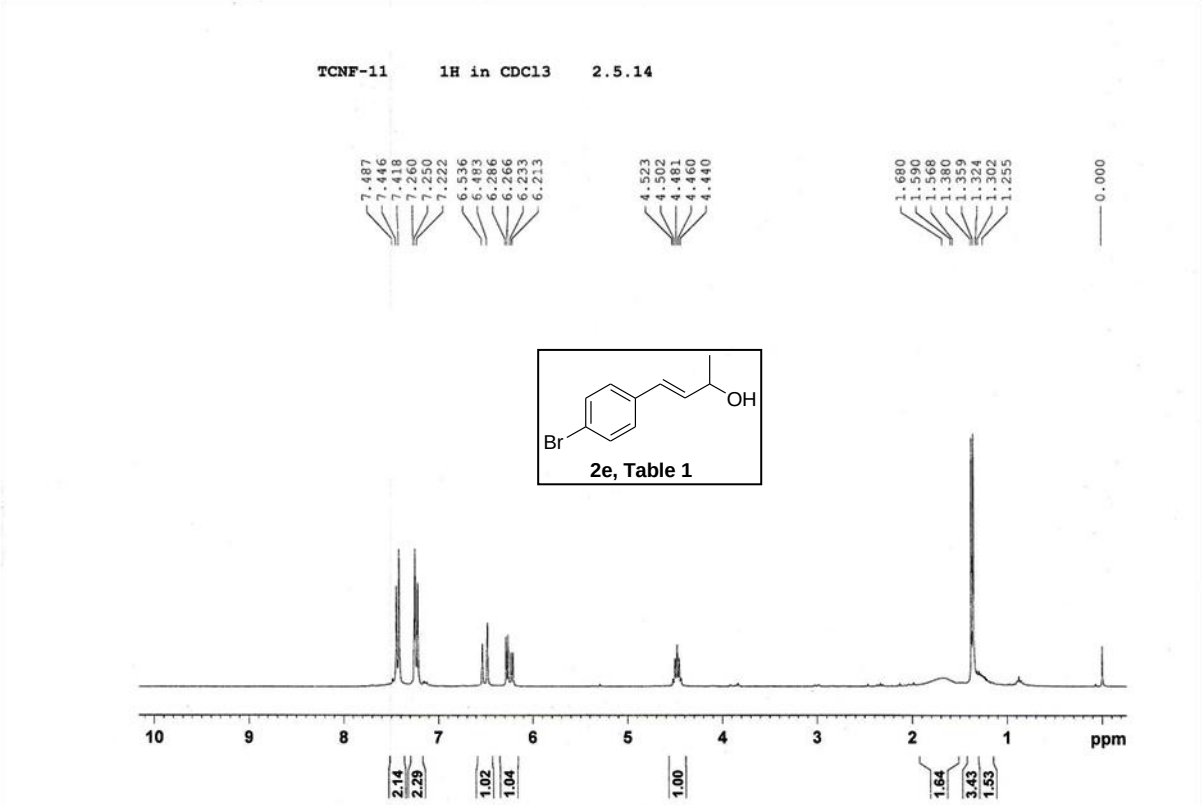
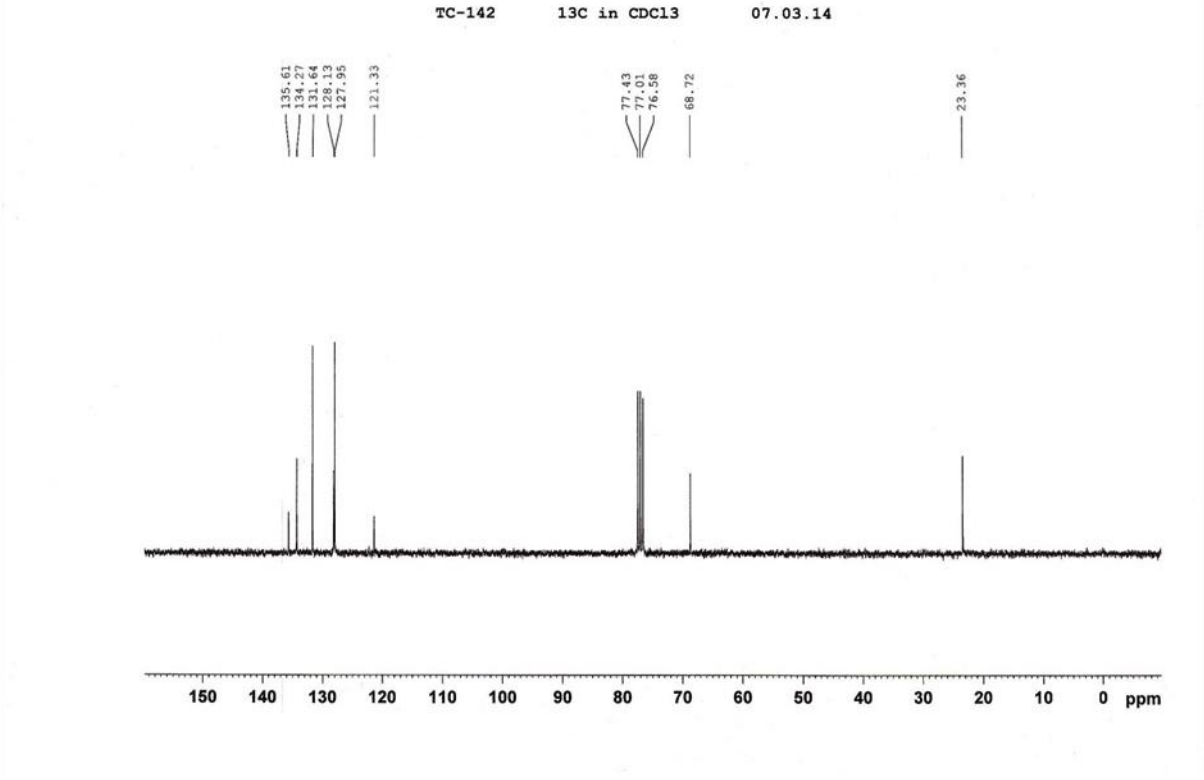
OH
2c, Table 1
7.403
7.398
7.374
7.261
7.240
7.216
6.600
6.547
6.305
6.283
6.252
6.231
4.541
4.520
4.498
4.478
4.458
1.598
1.390
1.369
0.000
5.85
0.98
1.00
1.00
3.59
Chemical Shift (ppm)

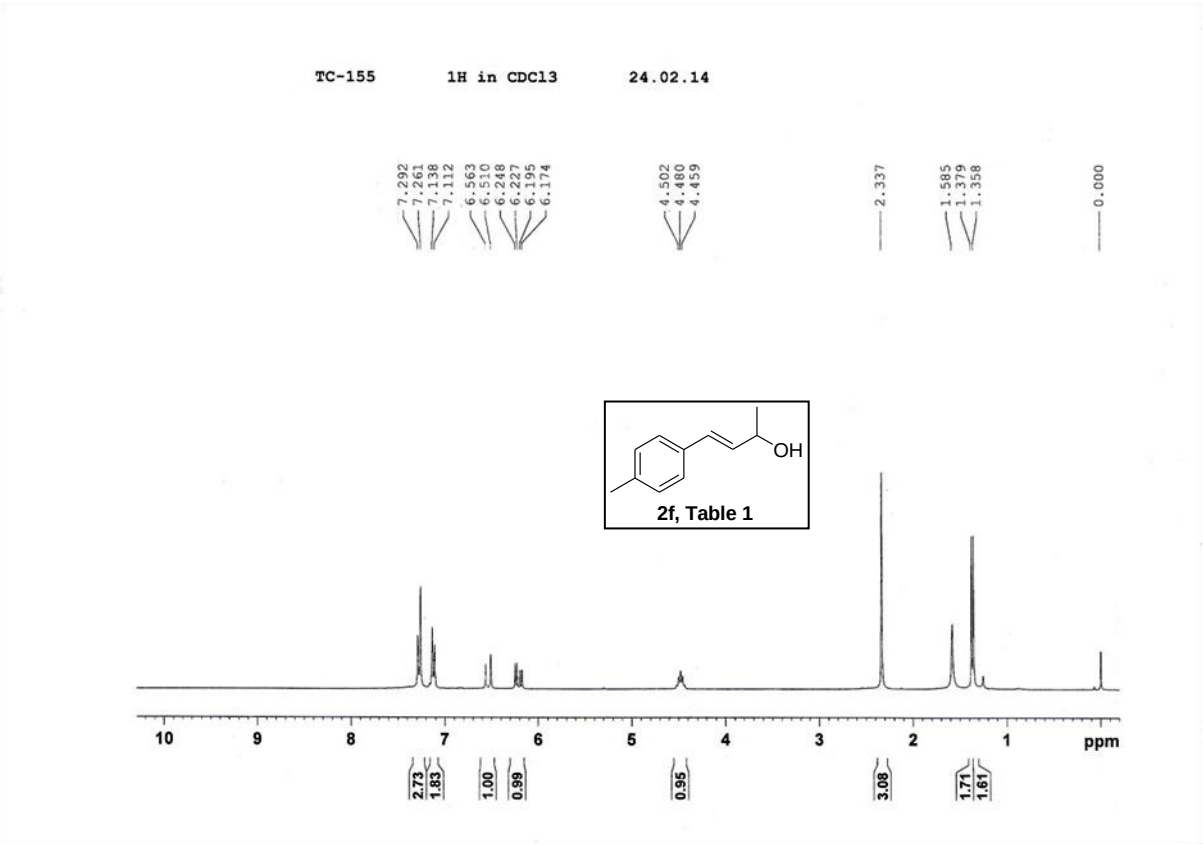

TC-001-C.001.esp
136.69
133.54
129.39
128.59
126.47
77.49
77.07
76.65
68.94
23.41
Chemical Shift (ppm)

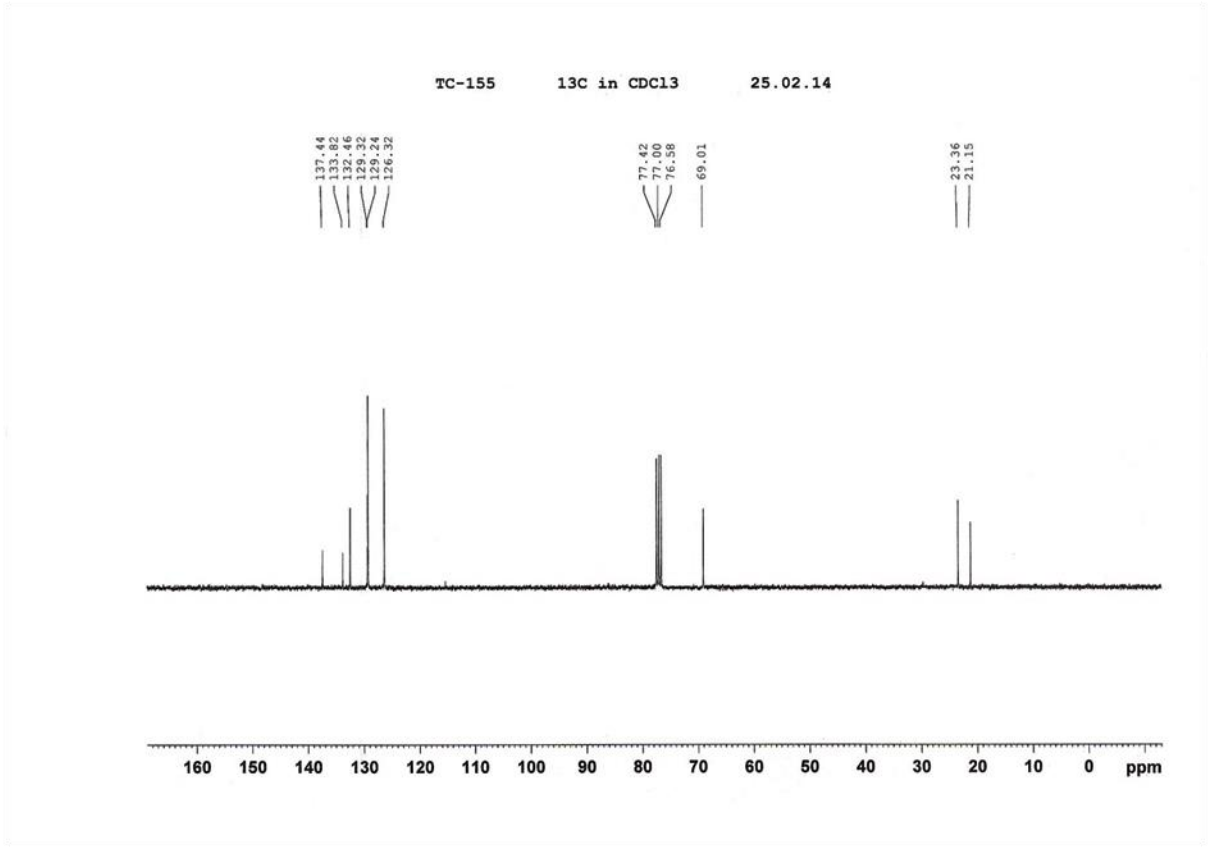

TC-151A-1H.001.esp
O
OH
2d, Table 1
3.809
1.379
1.357
7.257
7.230
6.982
6.912
6.555
6.503
6.289
6.268
6.235
6.215
4.523
4.503
4.482
4.462
4.440
1.894
0.000
1.08 1.01 0.99 0.98 1.01 1.00 1.00 3.06 1.21 3.35
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

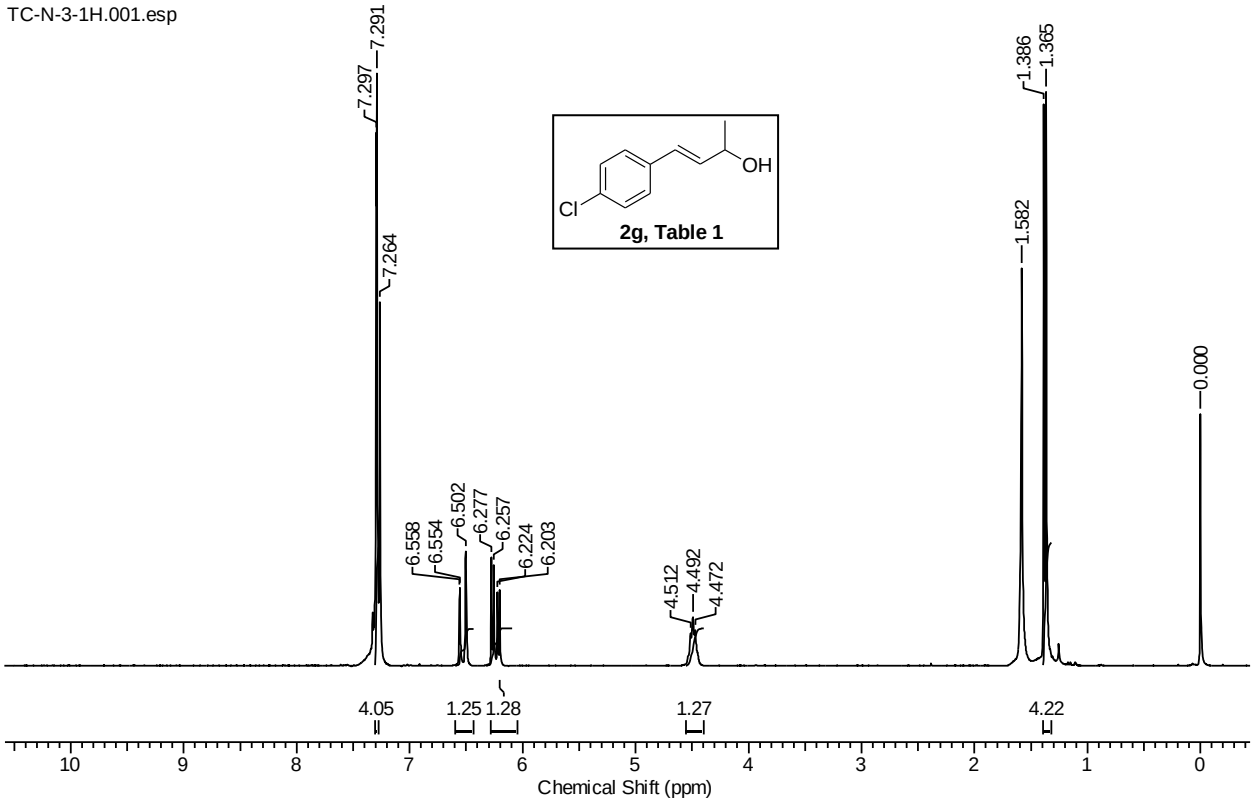

TC-153-C.001.esp
159.74
138.12
133.84
129.53
129.22
119.09
113.26
111.68
77.44
77.01
76.59
68.83
55.17
23.34
0.04
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)

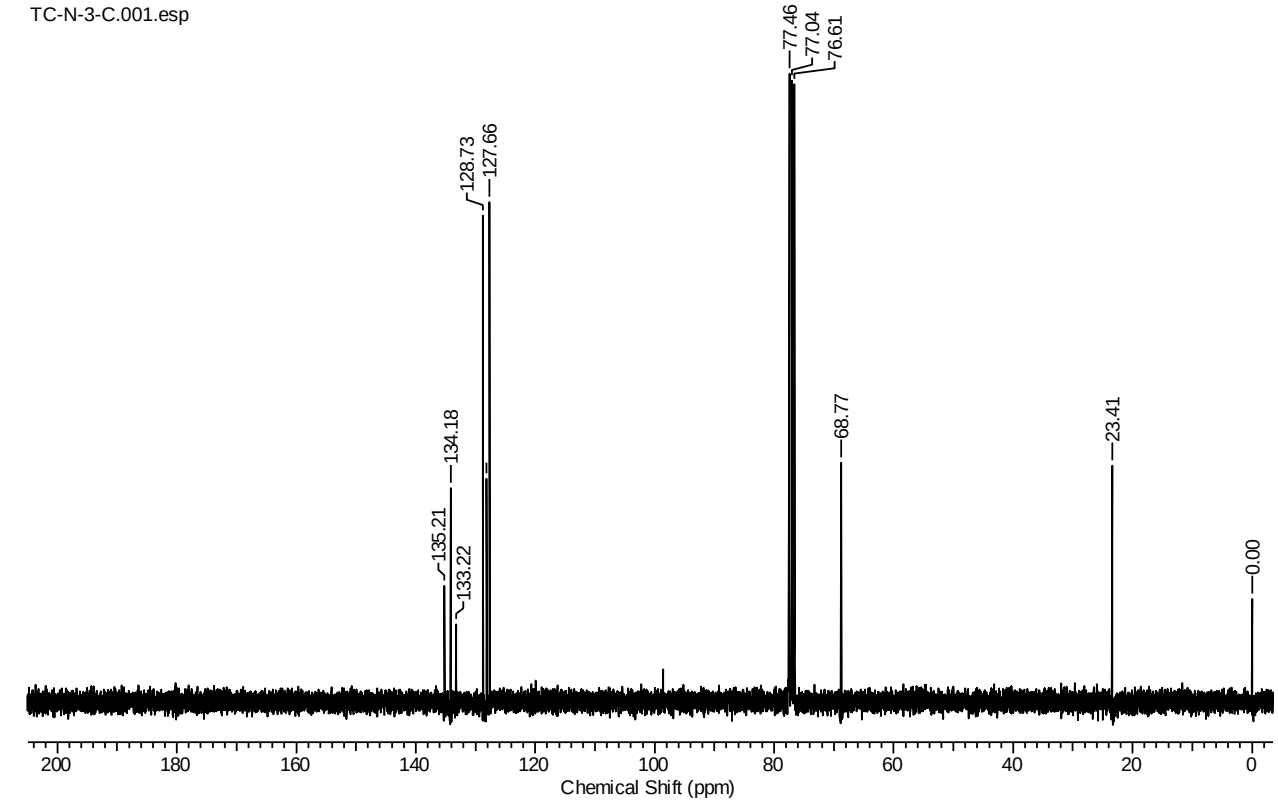

TCNF-11 1H in CDCl3 2.5.14
7.487
7.446
7.418
7.260
7.250
7.222
6.536
6.483
6.286
6.266
6.233
6.213
4.523
4.502
4.481
4.460
4.440
1.680
1.590
1.568
1.380
1.359
1.324
1.302
1.255
0.000
OH
Br
2e, Table 1
10
9
8
7
6
5
4
3
2
1
ppm
2.14
2.29
1.02
1.04
1.00
1.64
3.43
1.53


TC-142 13C in CDCl3 07.03.14
135.61
134.27
131.64
128.13
127.95
121.33
77.43
77.01
76.58
68.72
23.36
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

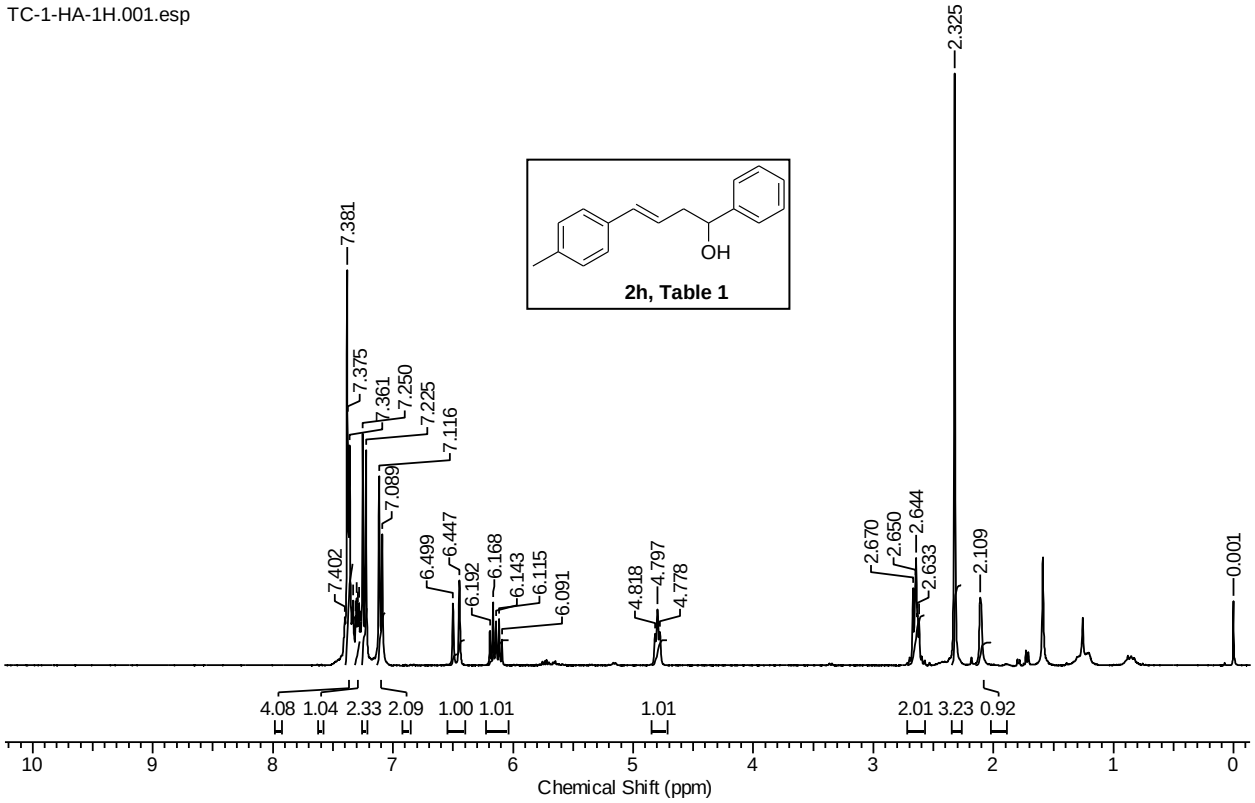

TC-155 1H in CDCl3 24.02.14
7.292
7.261
7.138
7.112
6.563
6.510
6.248
6.227
6.195
6.174
4.502
4.480
4.459
2.337
1.585
1.379
1.358
0.000
OH
2f, Table 1
10 9 8 7 6 5 4 3 2 1 ppm
2.73
1.83
1.00
0.99
0.95
3.08
1.71
1.61


TC-155 13C in CDCl3 25.02.14
137.44
133.82
132.46
129.32
129.24
126.32
77.42
77.00
76.58
69.01
23.36
21.15
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


TC-N-3-1H.001.esp
7.297
7.291
7.264
6.558
6.554
6.502
6.277
6.257
6.224
6.203
4.512
4.492
4.472
1.386
1.365
1.582
0.000
OH
Cl
2g, Table 1
4.05
1.25
1.28
1.27
4.22
Chemical Shift (ppm)


TC-N-3-C.001.esp
77.46
77.04
76.61
128.73
127.66
134.18
135.21
133.22
68.77
23.41
0.00
Chemical Shift (ppm)

TC-1-HA-1H.001.esp



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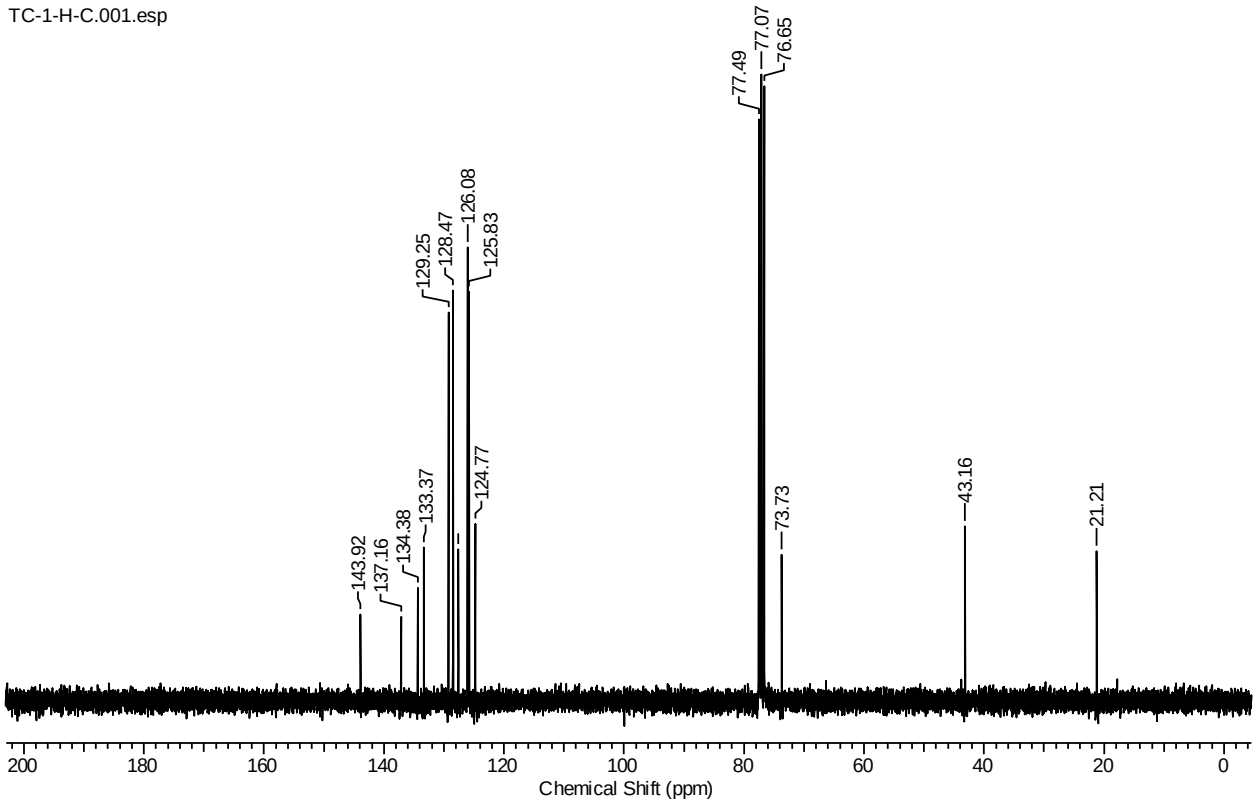
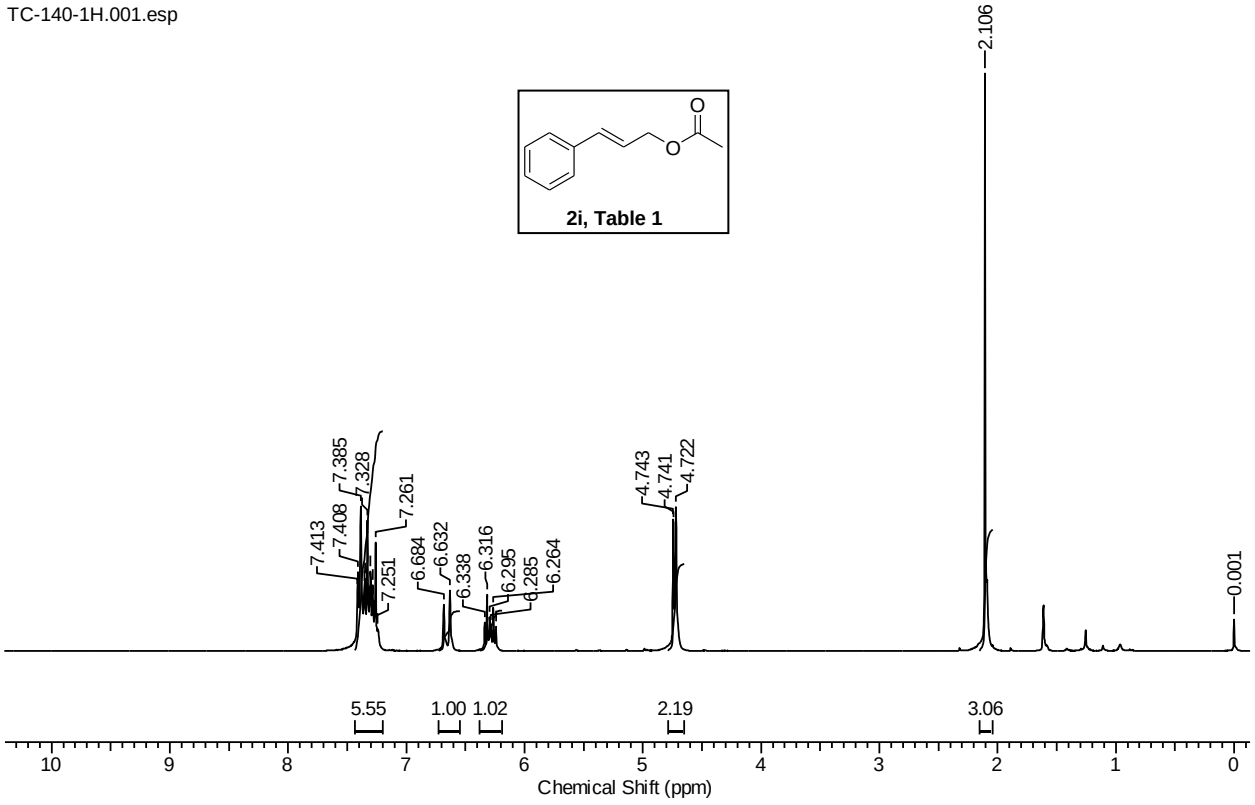
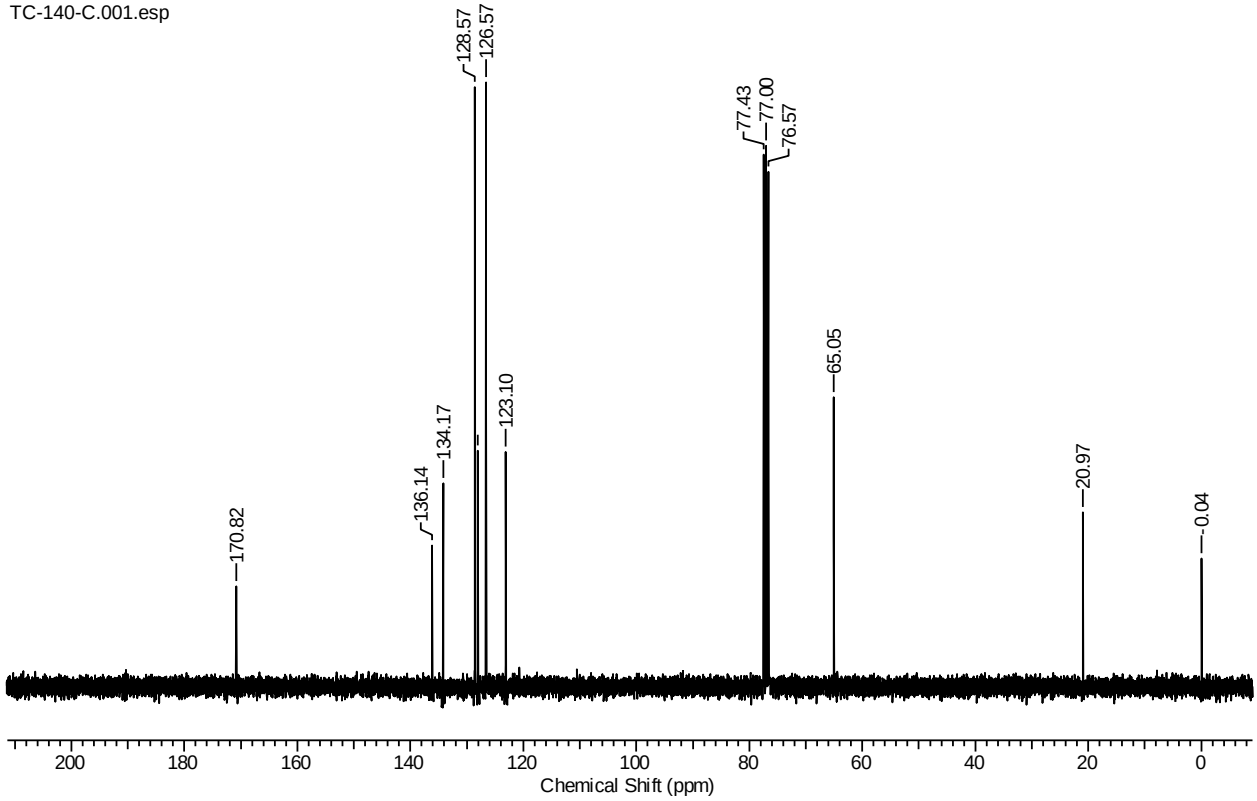


TC-140-1H.001.esp



2i, Table 1

TC-140-C.001.esp



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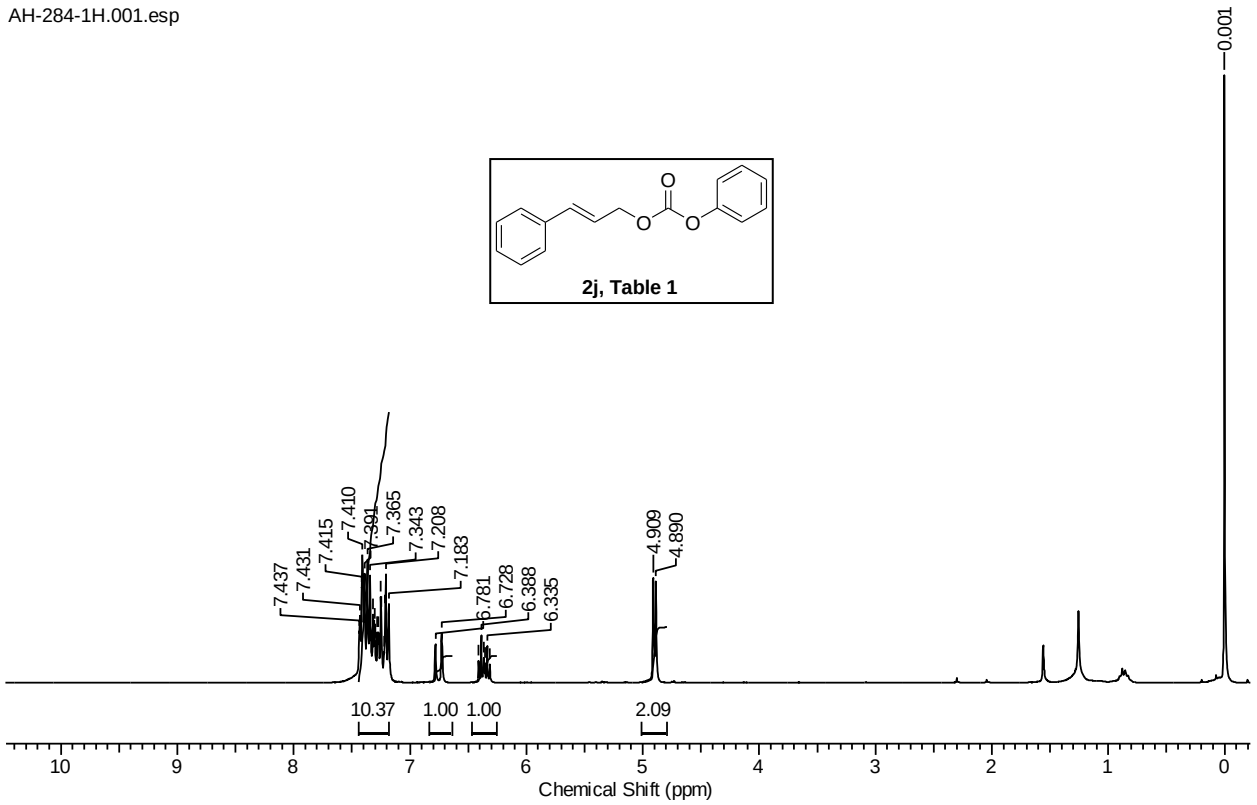

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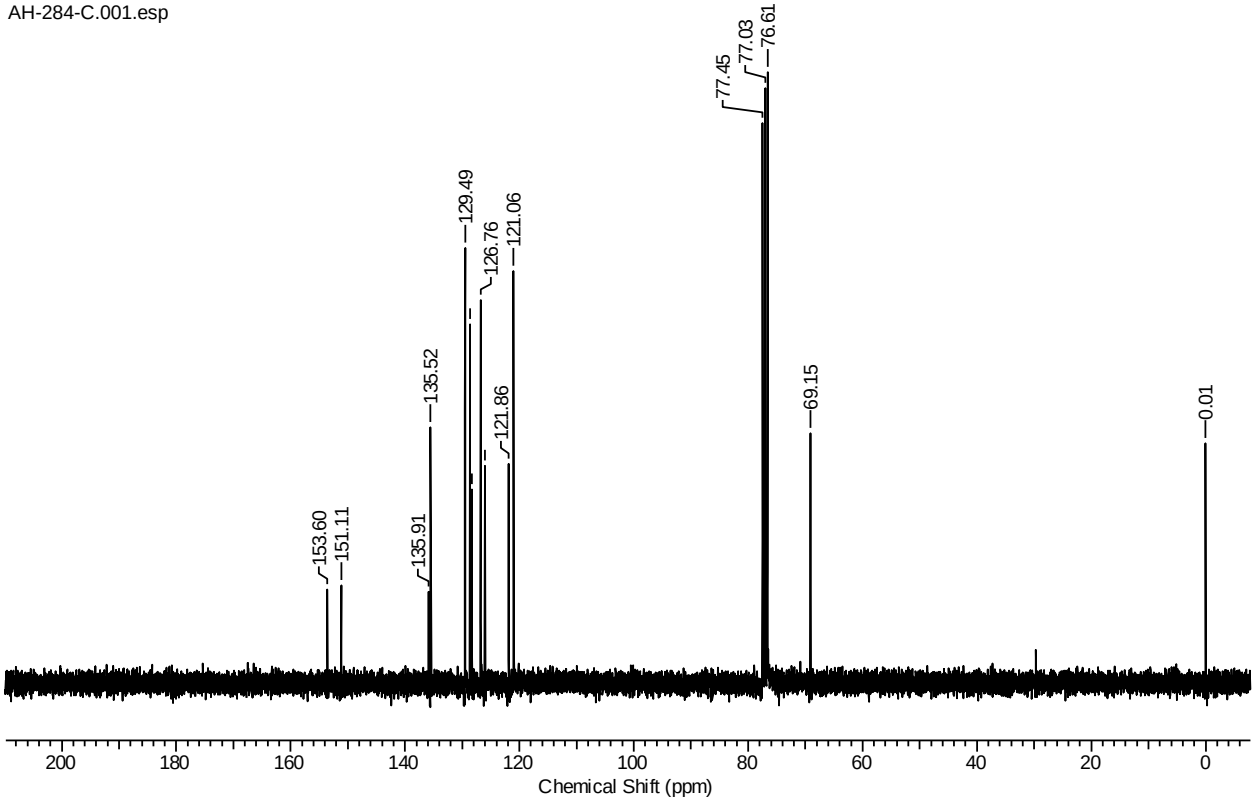
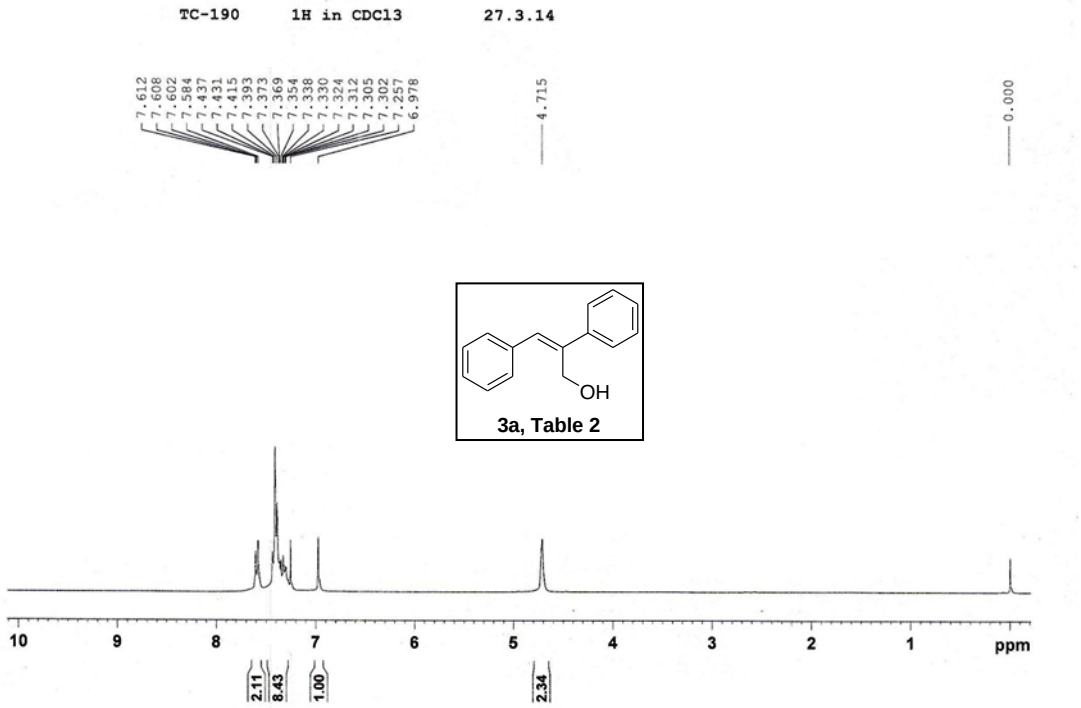
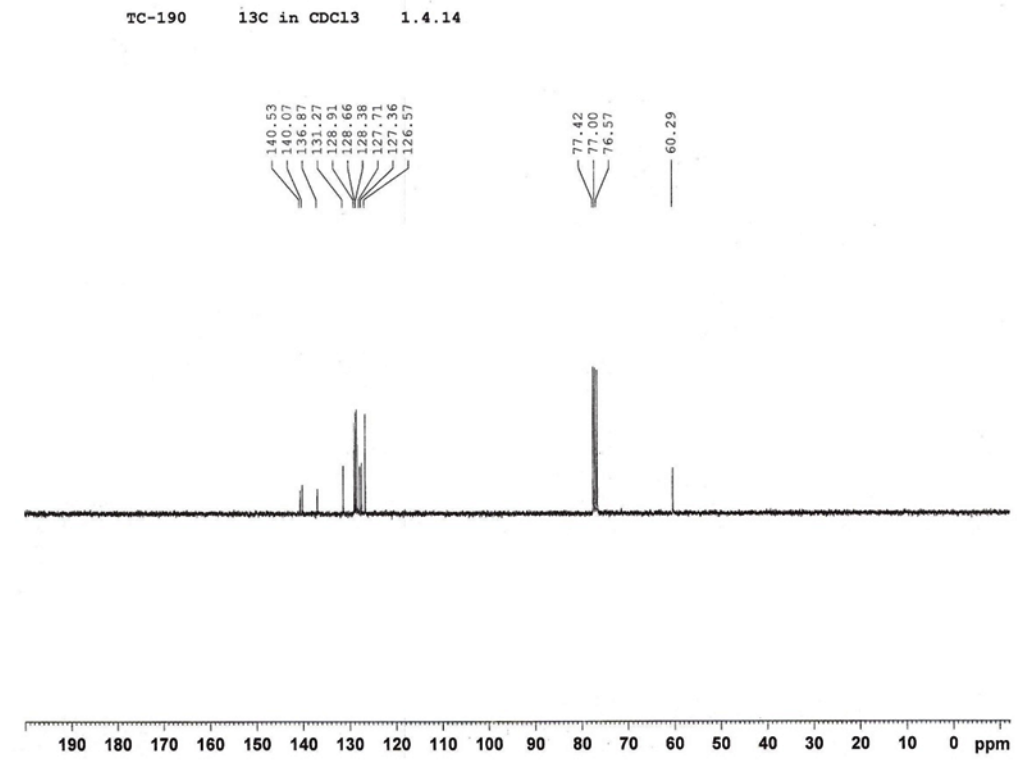
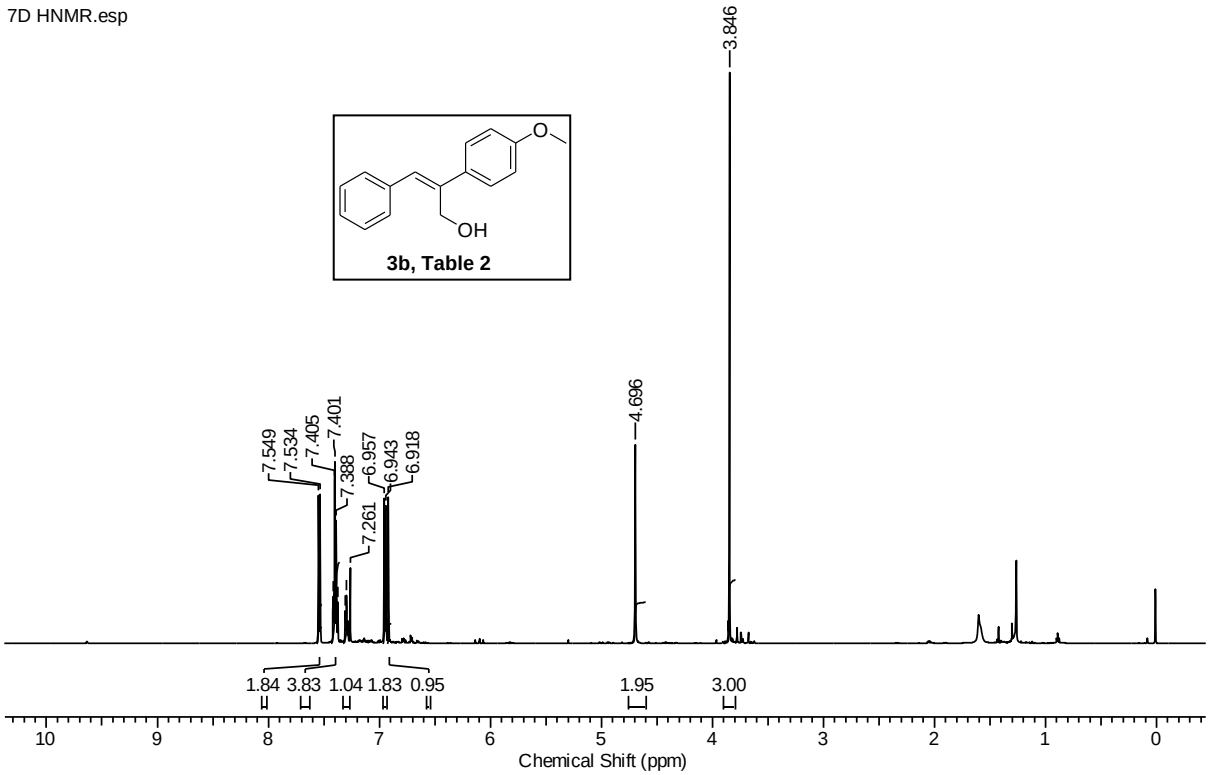



TC-190 1H in CDCl3 27.3.14
7.612
7.608
7.602
7.584
7.437
7.431
7.415
7.393
7.373
7.369
7.354
7.338
7.330
7.324
7.312
7.305
7.302
7.257
6.978
4.715
0.000
OH
3a, Table 2
10
9
8
7
6
5
4
3
2
1
ppm
2.11
8.43
1.00
2.34

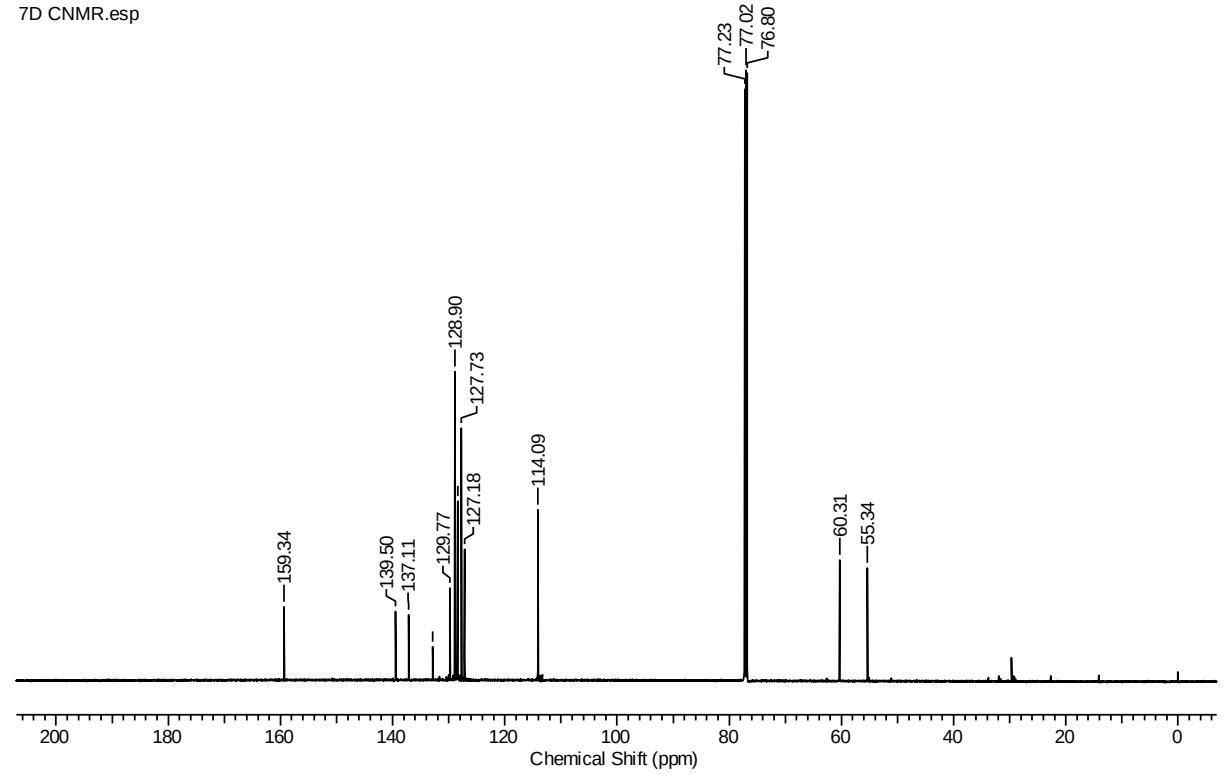

TC-190 13C in CDCl3 1.4.14
140.53
140.07
136.87
131.27
128.91
128.66
128.38
127.71
127.36
126.57
77.42
77.00
76.57
60.29
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

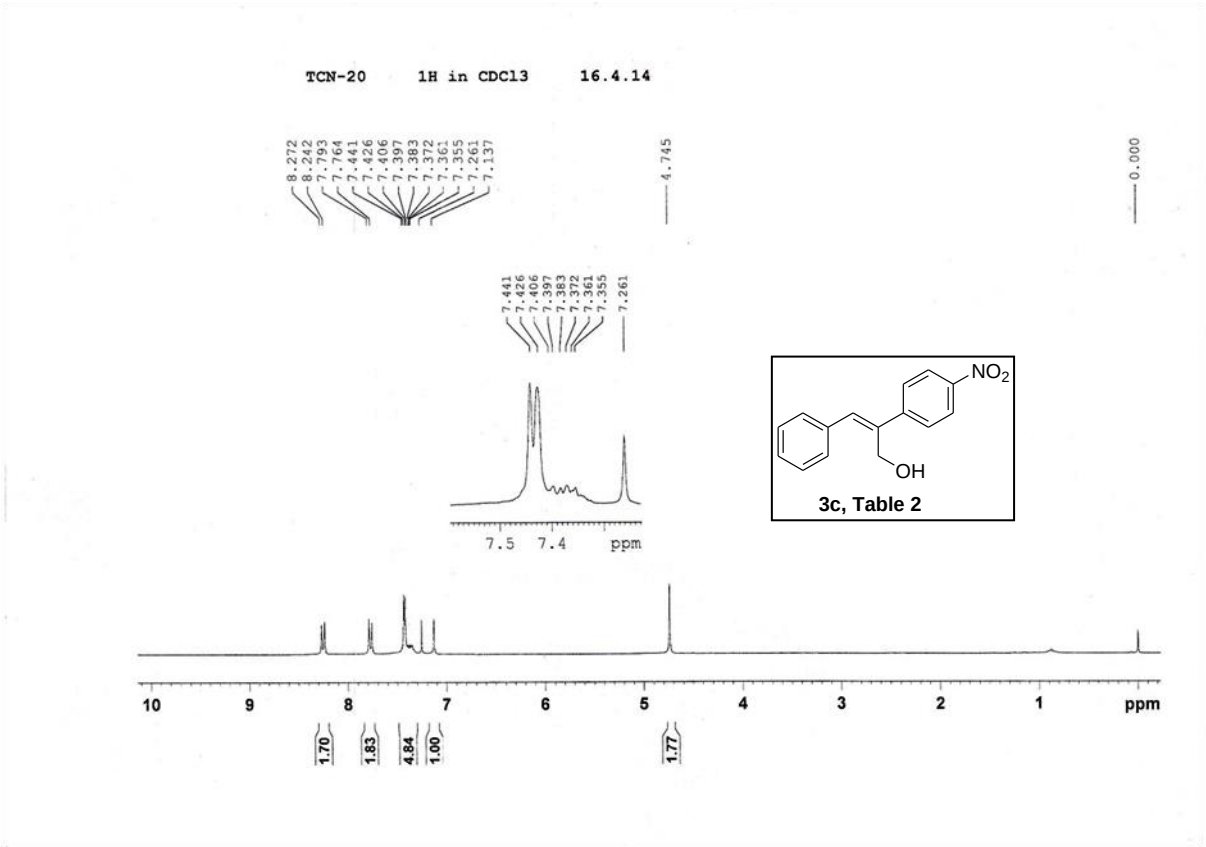
7D HNMR.esp

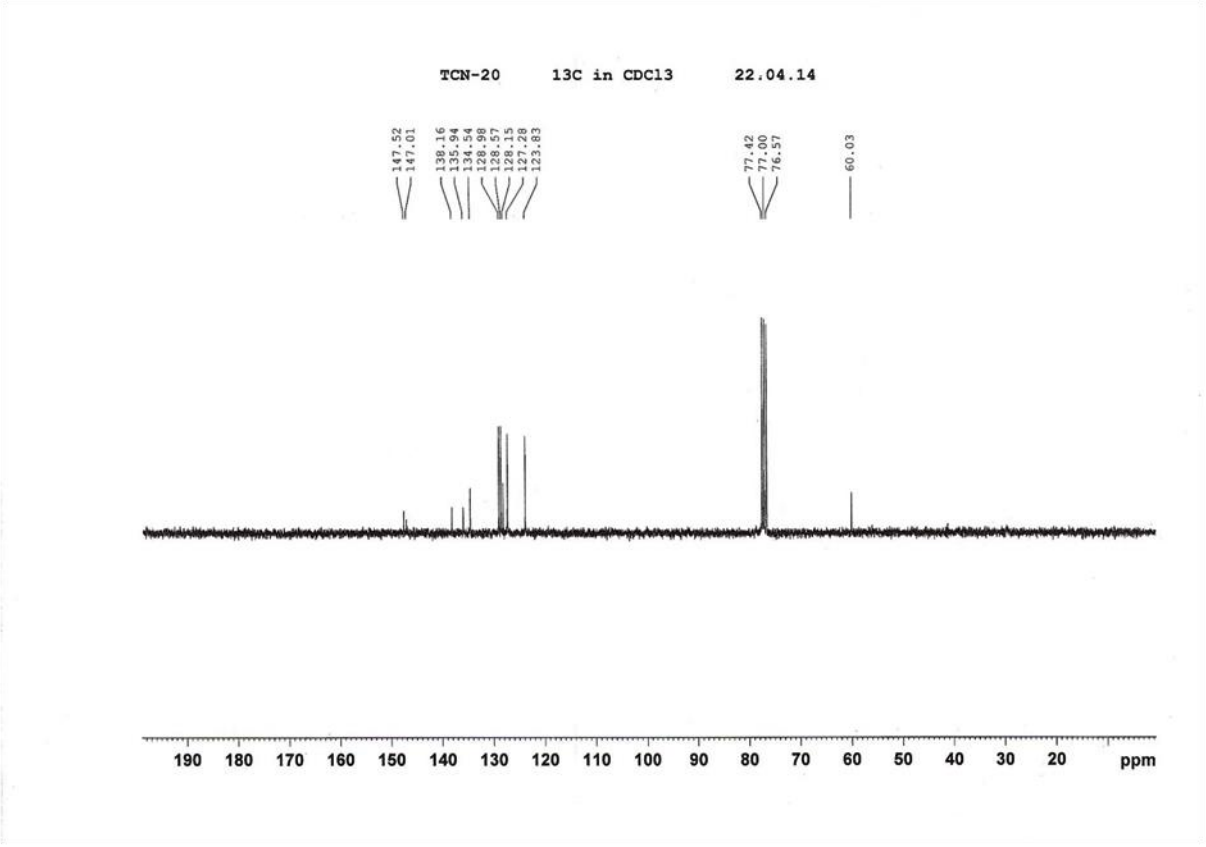


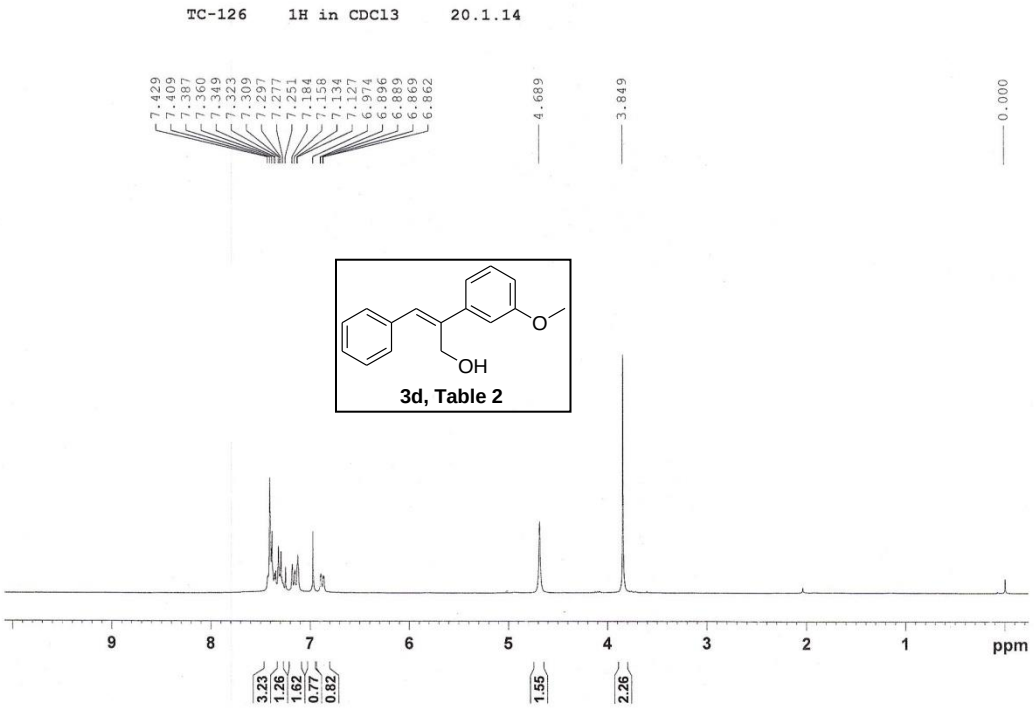
3b, Table 2

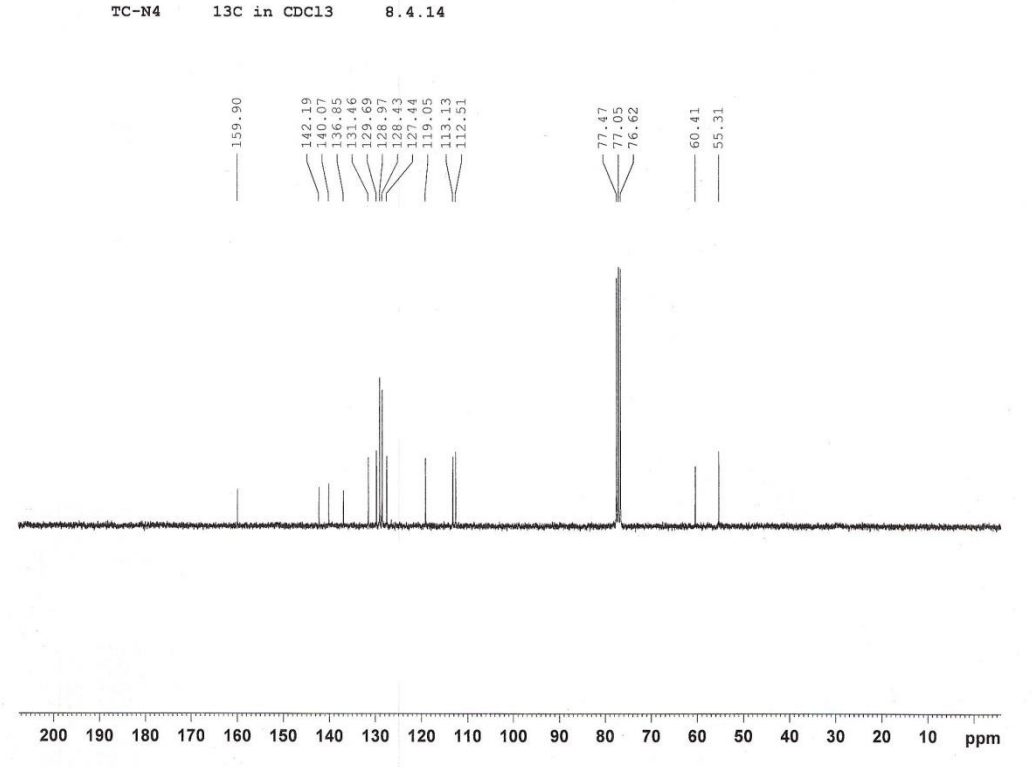
7D CNMR.esp

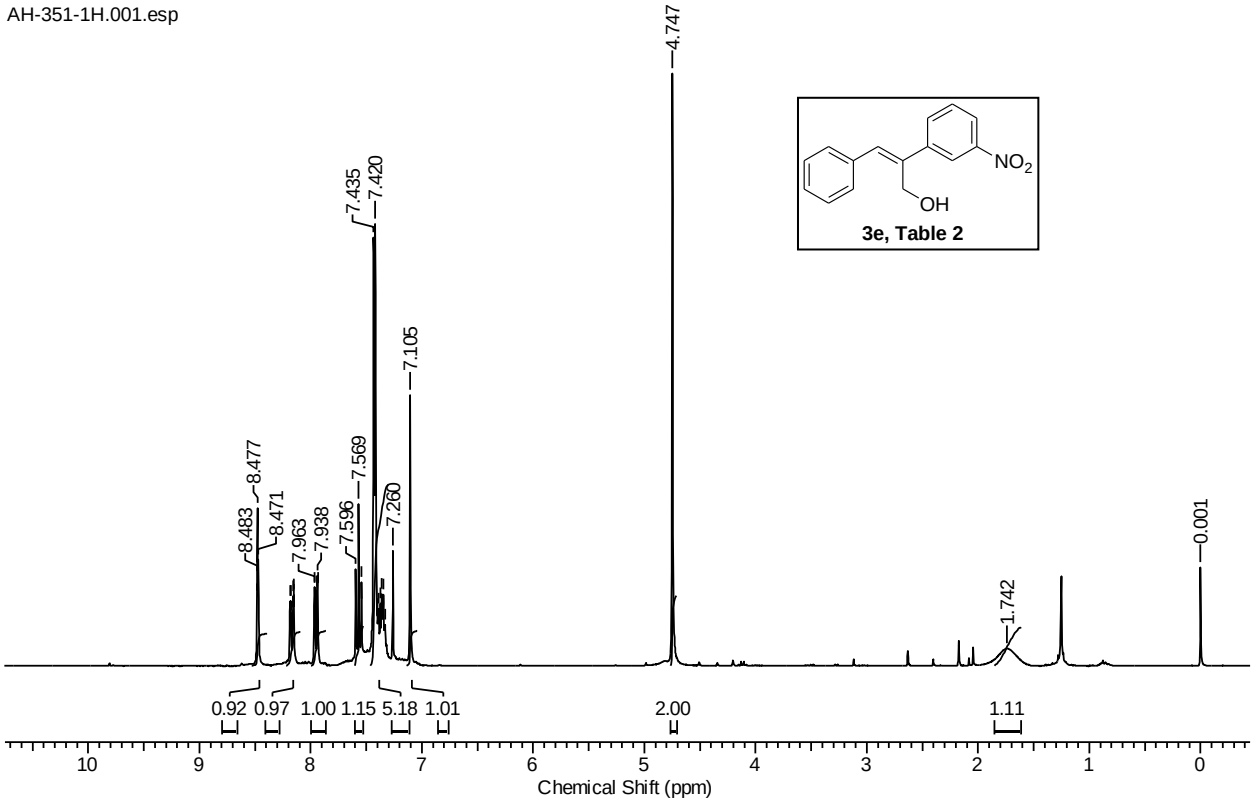


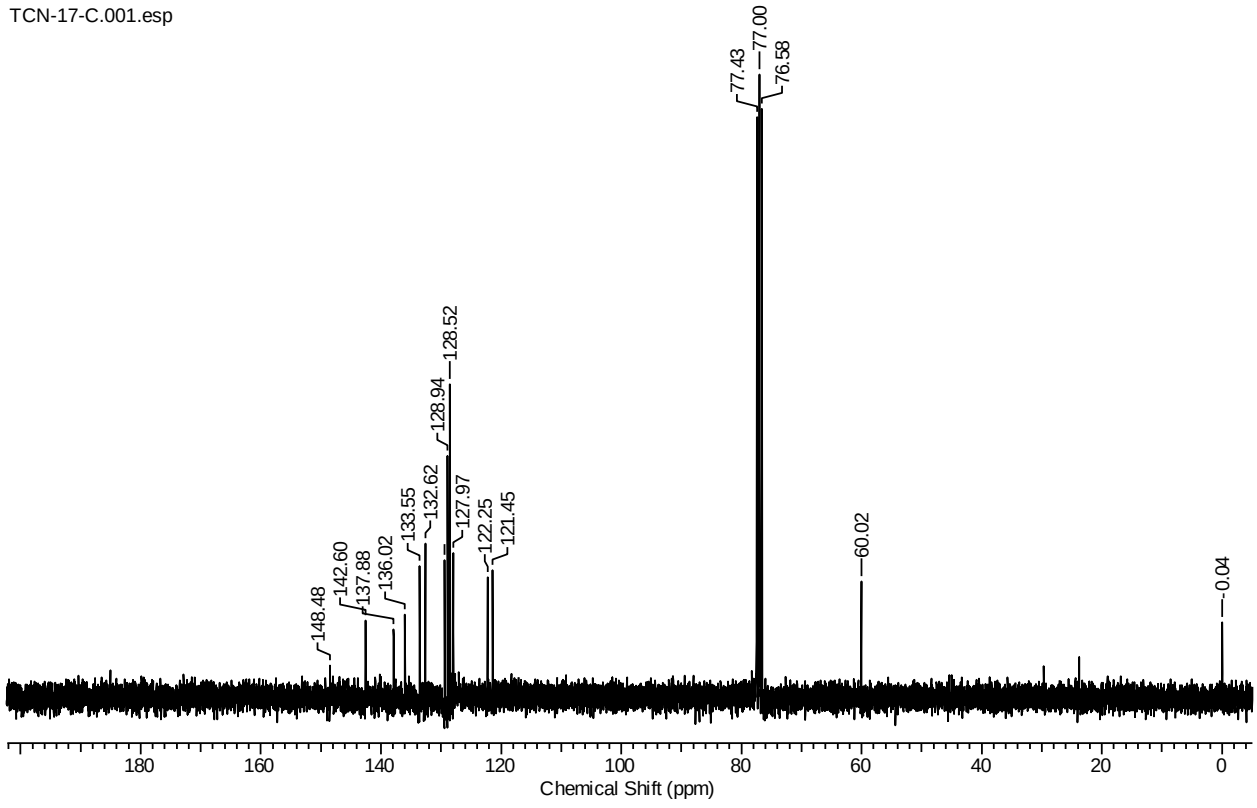

TCN-20 1H in CDCl3 16.4.14
8.272
8.242
7.793
7.764
7.441
7.426
7.406
7.397
7.383
7.372
7.361
7.355
7.261
7.137
4.745
0.000
7.5 7.4 ppm
NO2
OH
3c, Table 2
10 9 8 7 6 5 4 3 2 1 ppm
1.70
1.83
4.84
1.00
1.77


TCN-20 13C in CDCl3 22.04.14
147.52
147.01
138.16
135.94
134.54
128.98
128.57
128.15
127.28
123.83
77.42
77.00
76.57
60.03
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

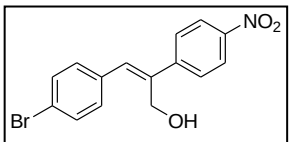

TC-126 1H in CDCl3 20.1.14
7.429
7.409
7.387
7.360
7.349
7.323
7.309
7.297
7.277
7.251
7.184
7.158
7.134
7.127
6.974
6.896
6.889
6.869
6.862
4.689
3.849
0.000
O
OH
3d, Table 2
9
8
7
6
5
4
3
2
1
ppm
3.23
1.26
1.62
0.77
0.82
1.55
2.26


TC-N4 13C in CDCl3 8.4.14
159.90
142.19
140.07
136.85
131.46
129.69
128.97
128.43
127.44
119.05
113.13
112.51
77.47
77.05
76.62
60.41
55.31
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

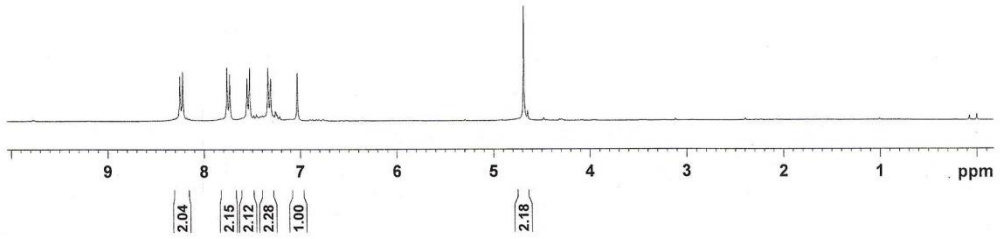

AH-351-1H.001.esp
4.747
7.435
7.420
7.105
8.483
8.477
8.471
7.963
7.938
7.596
7.569
7.260
1.742
0.001
NO2
OH
3e, Table 2
0.92 0.97 1.00 1.15 5.18 1.01 2.00 1.11
Chemical Shift (ppm)


TCN-17-C.001.esp
77.43
77.00
76.58
128.52
128.94
132.62
133.55
127.97
122.25
121.45
148.48
142.60
137.88
136.02
60.02
0.04
Chemical Shift (ppm)

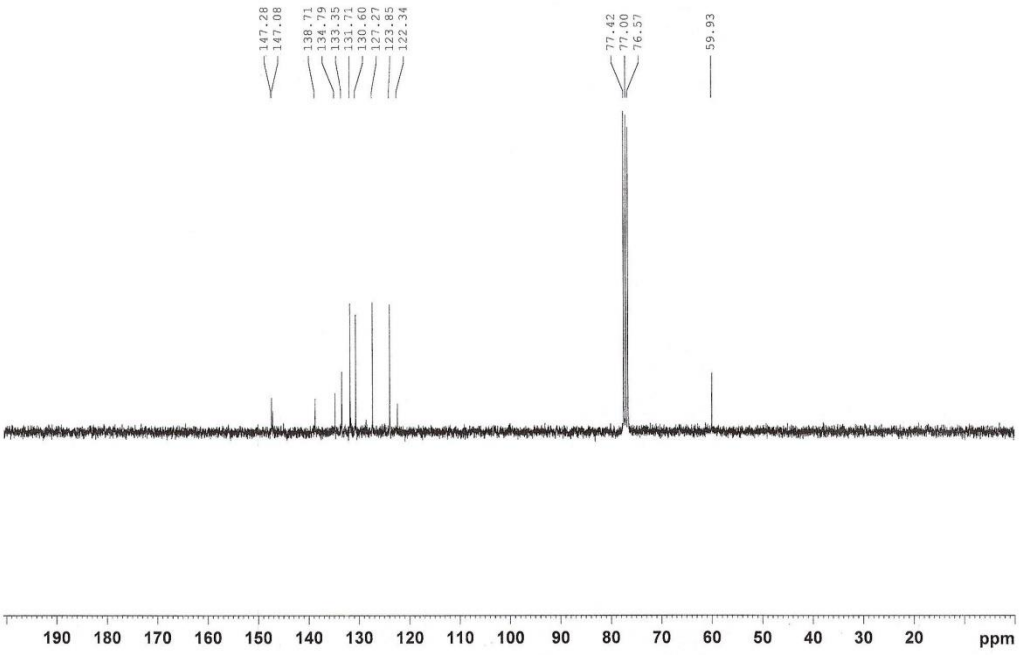
TCNF-20 1H in CDCl3 19.05.14

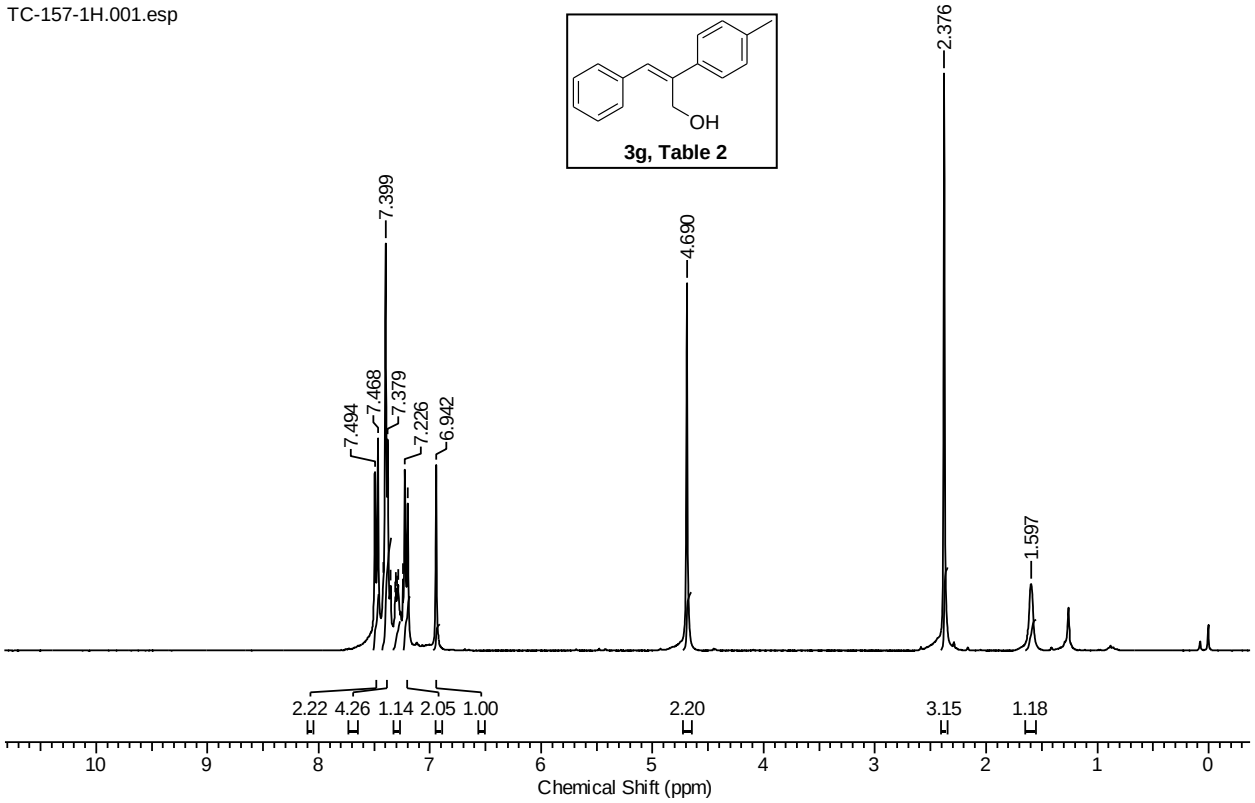


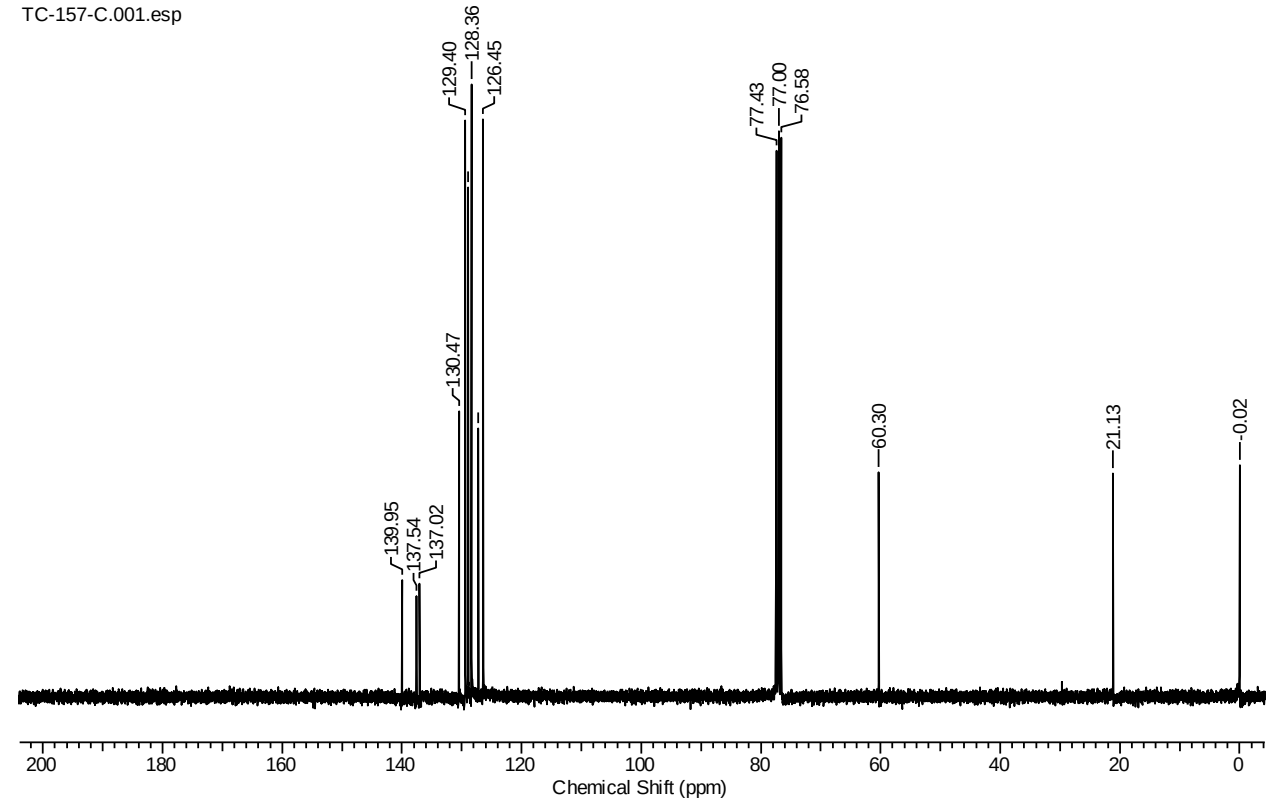
3f, Table 2



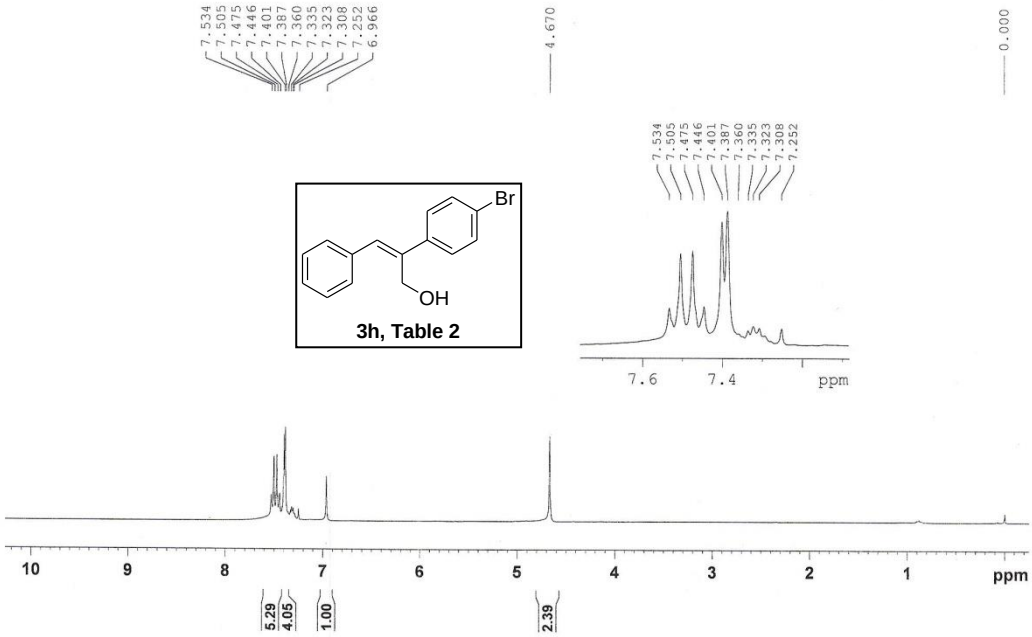
TCNF-20 13C in CDCl3 20.5.14



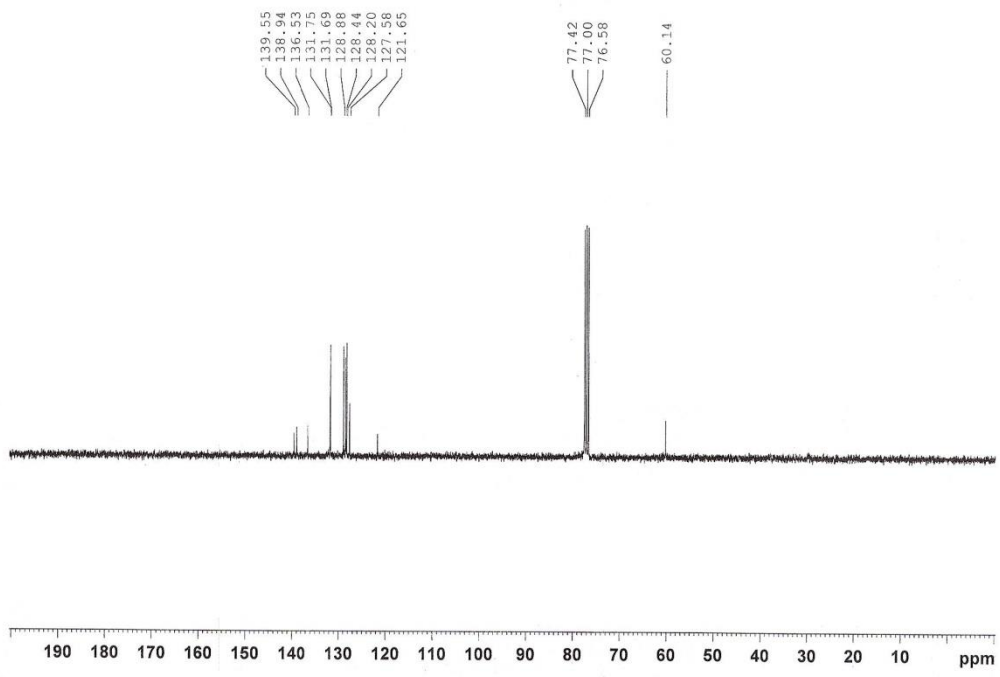

TC-157-1H.001.esp
OH
3g, Table 2
2.376
7.399
4.690
7.494
7.468
7.379
7.226
6.942
1.597
2.22 4.26 1.14 2.05 1.00
2.20
3.15
1.18
10 9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)

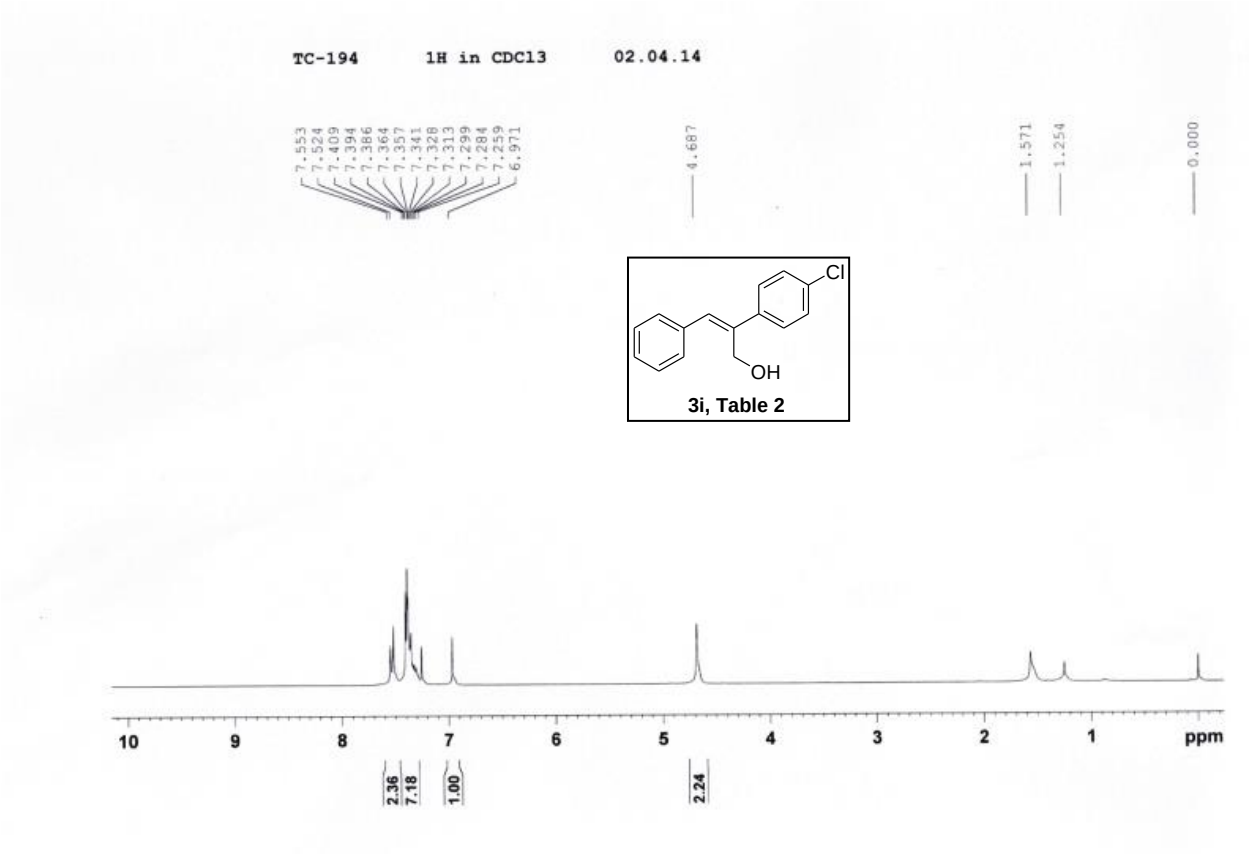

TC-157-C.001.esp
129.40
128.36
126.45
77.43
77.00
76.58
130.47
60.30
21.13
-0.02
139.95
137.54
137.02
200 180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)

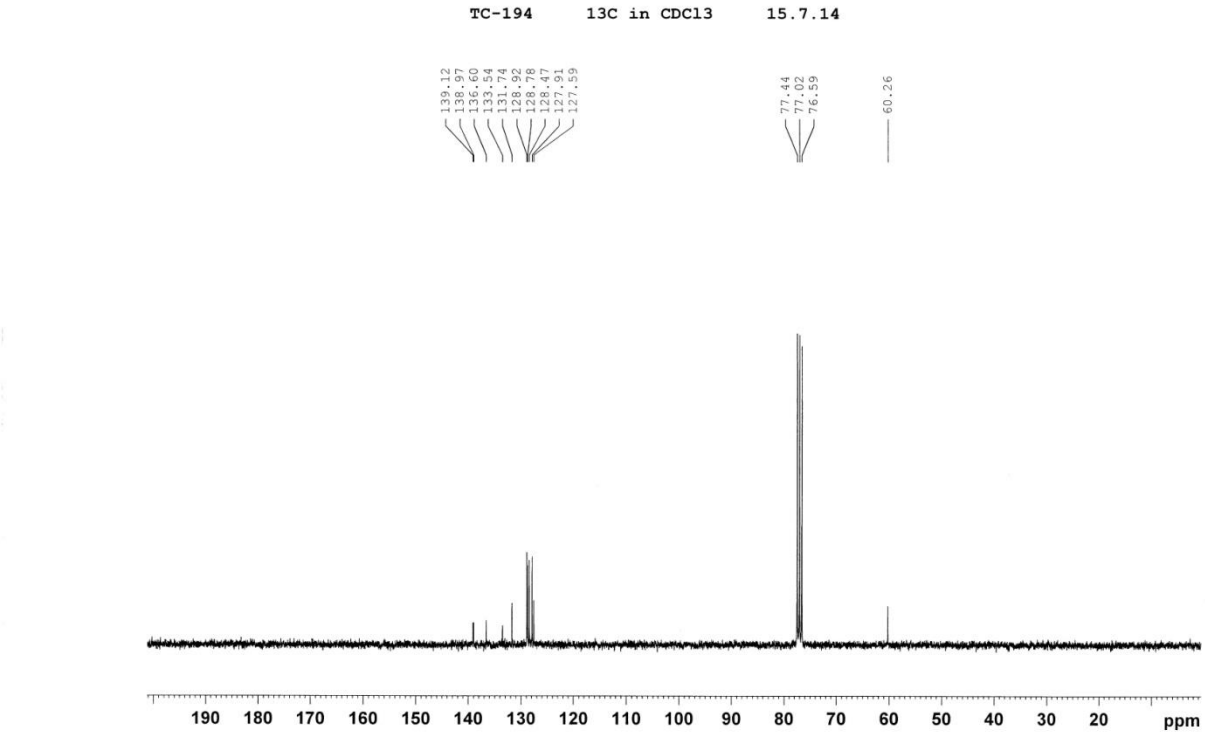
TC-192 1H in CDCl3 5.5.14

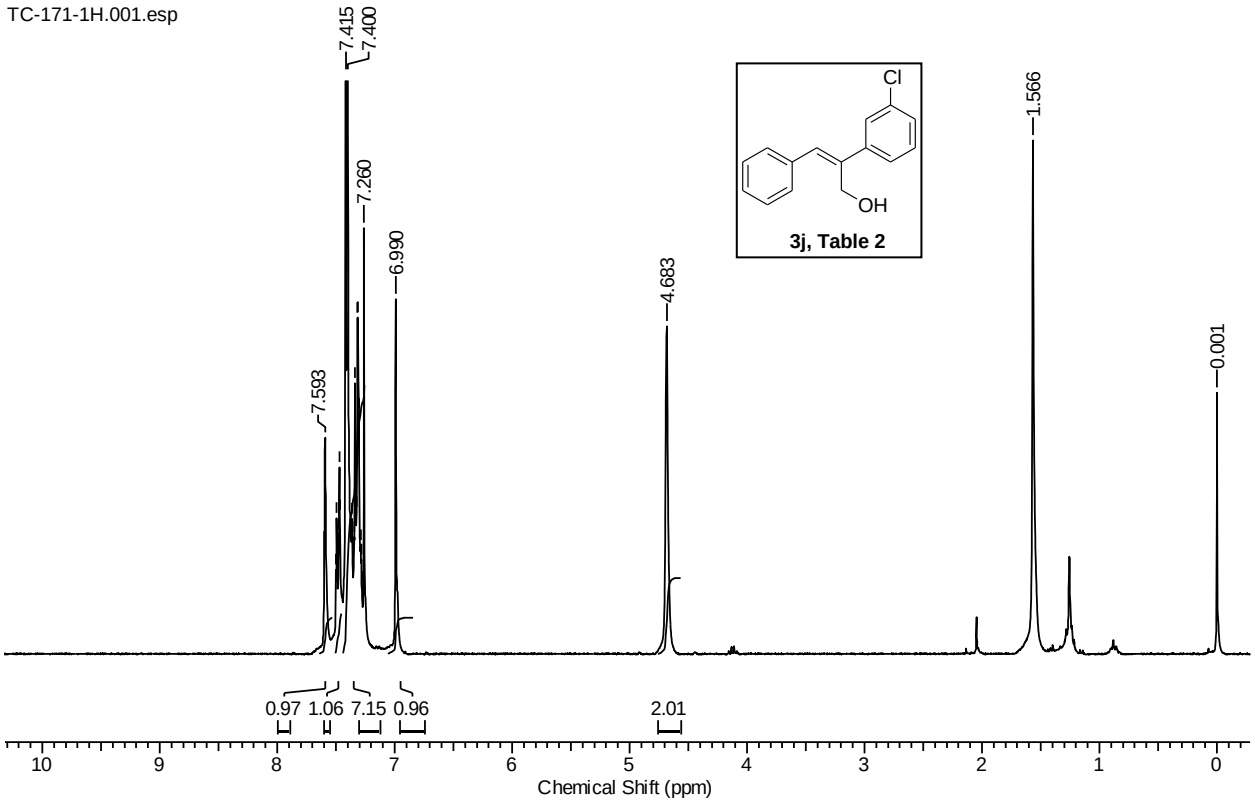


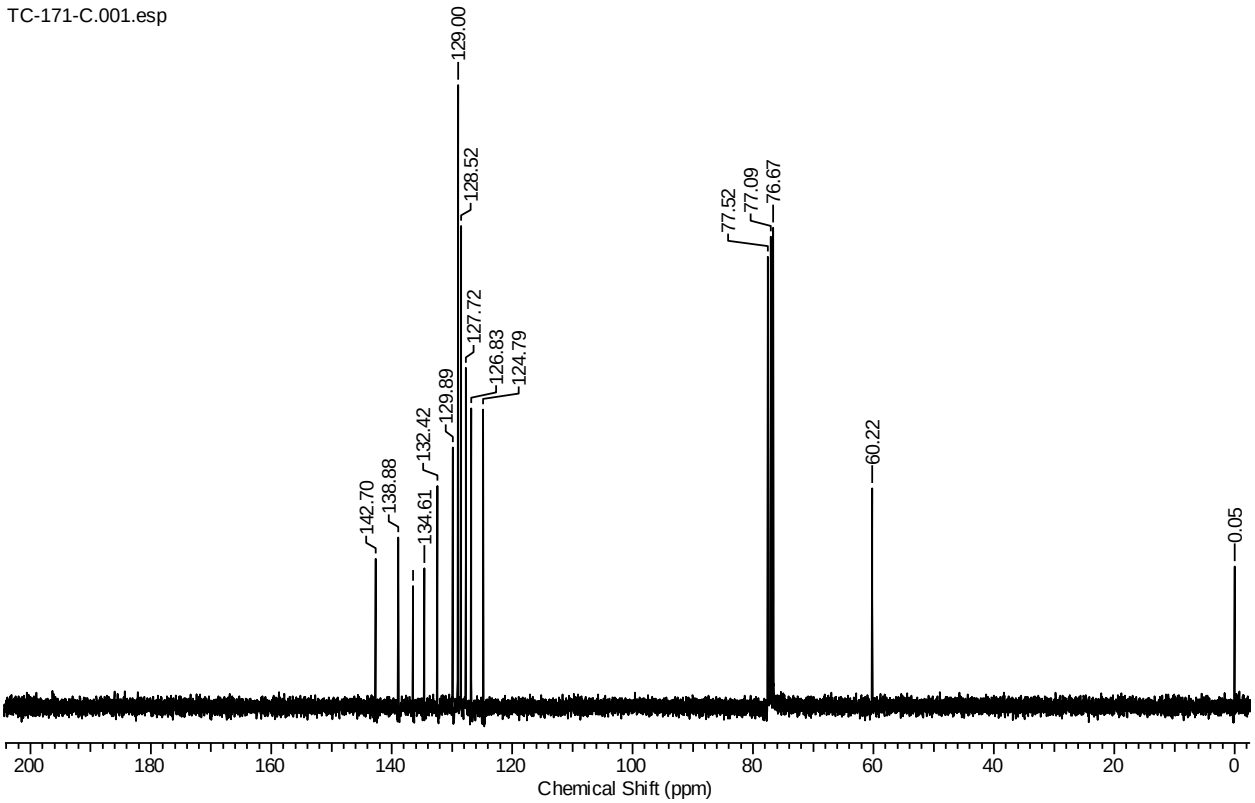
TC-192 13C in CDCl3 1.4.14

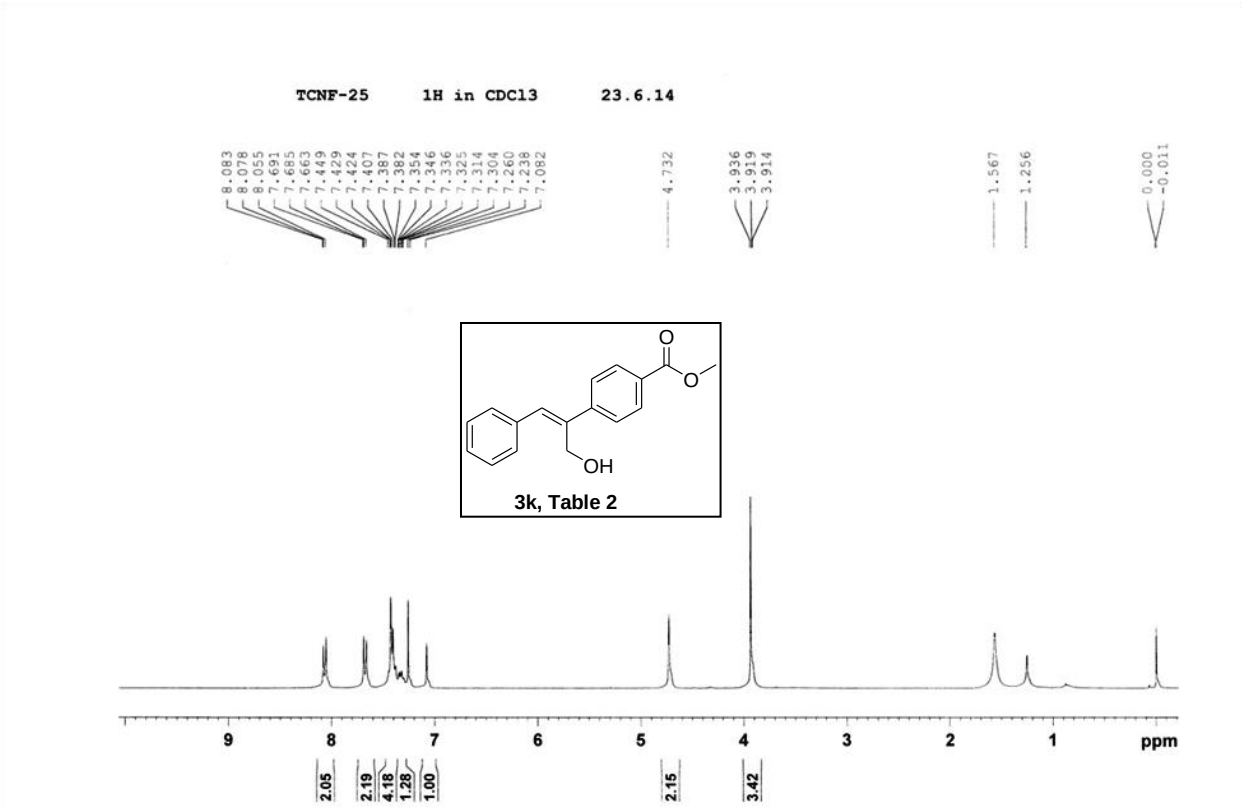


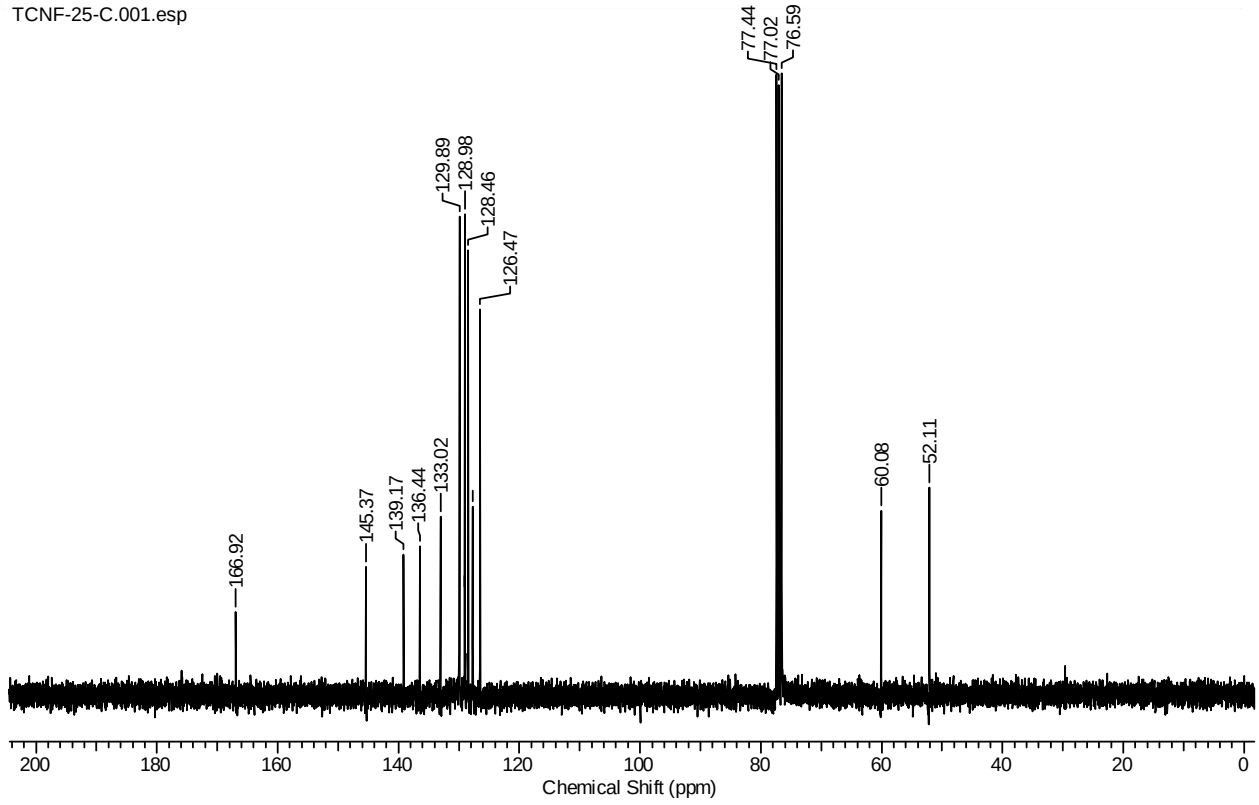

TC-194 1H in CDCl3 02.04.14
7.553
7.524
7.409
7.394
7.386
7.364
7.357
7.341
7.328
7.313
7.299
7.284
7.259
6.971
4.687
1.571
1.254
0.000
Cl
OH
3i, Table 2
10
9
8
7
6
5
4
3
2
1
ppm
2.36
7.18
1.00
2.24

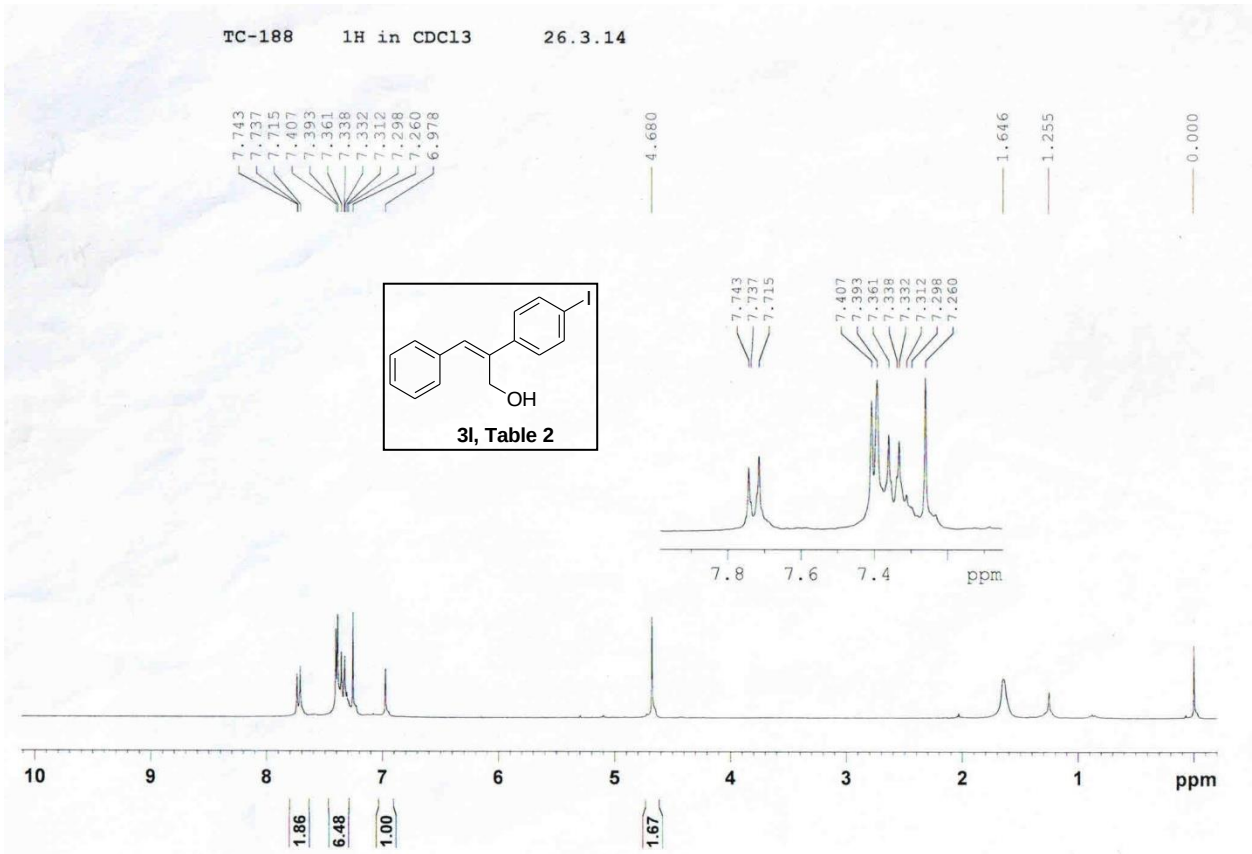

TC-194 13C in CDCl3 15.7.14
139.12
138.97
136.60
133.54
131.74
128.92
128.78
128.47
127.91
127.59
77.44
77.02
76.59
60.26
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

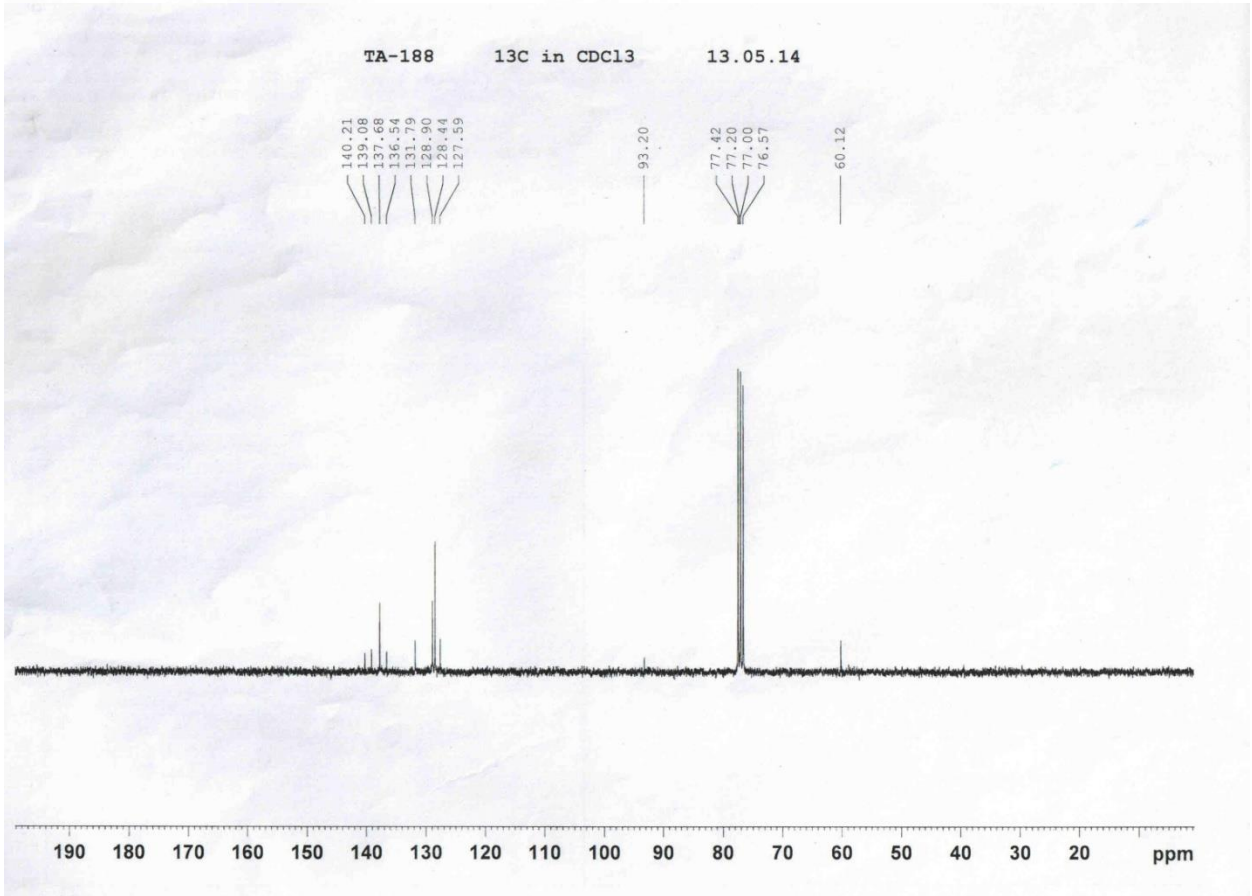

TC-171-1H.001.esp
7.415
7.400
7.260
6.990
7.593
4.683
1.566
0.001
Cl
OH
3j, Table 2
0.97
1.06
7.15
0.96
2.01
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

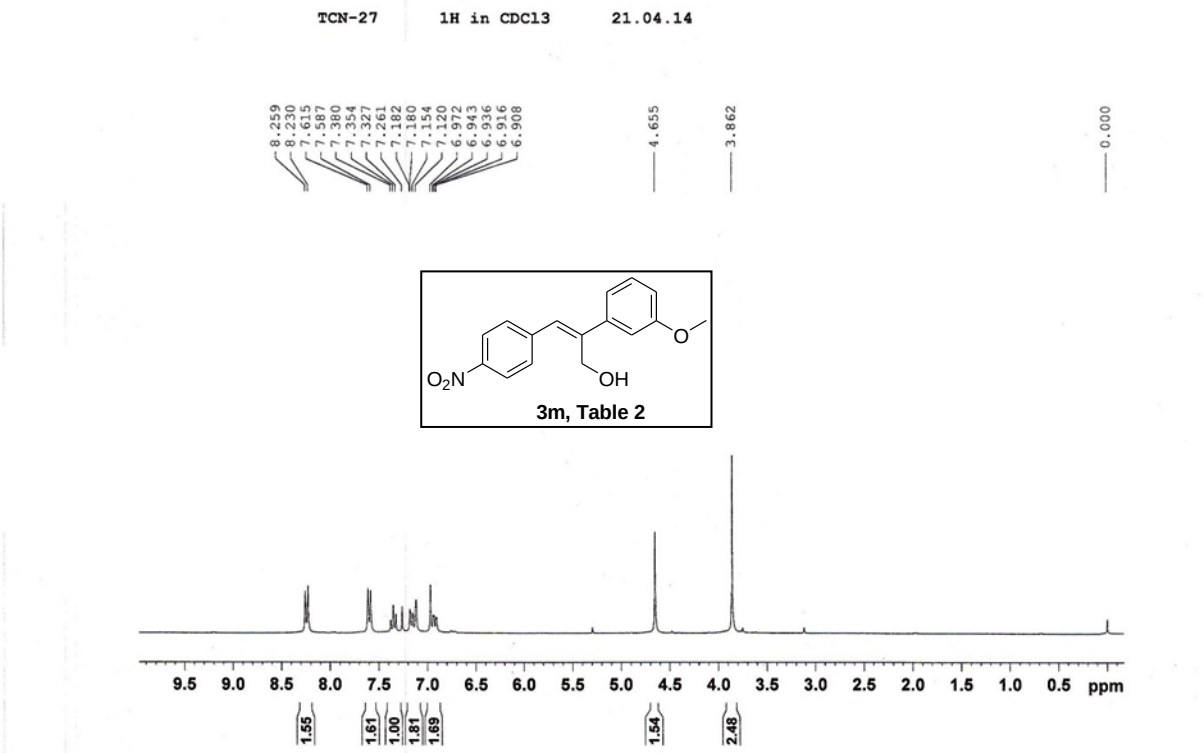

TC-171-C.001.esp
129.00
128.52
127.72
126.83
124.79
129.89
132.42
134.61
138.88
142.70
77.52
77.09
76.67
60.22
0.05
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

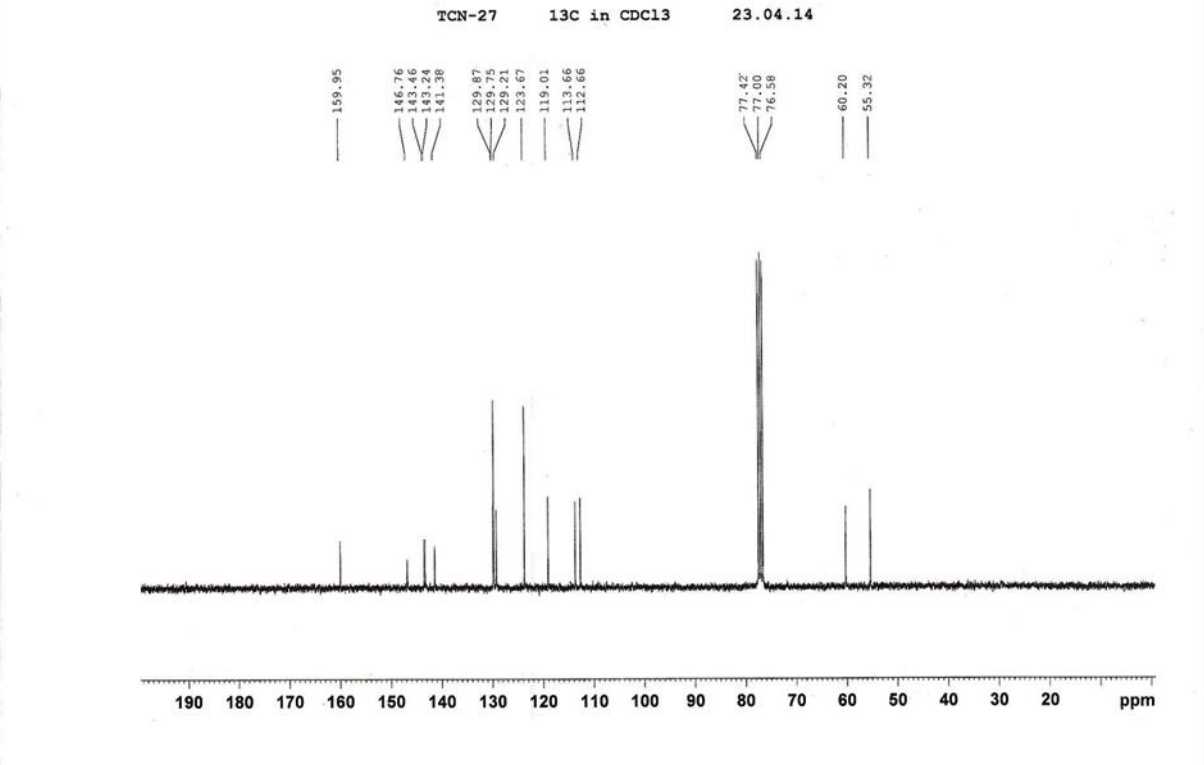

TCNF-25 1H in CDCl3 23.6.14
8.083
8.078
8.055
7.691
7.685
7.663
7.449
7.429
7.424
7.407
7.387
7.382
7.354
7.346
7.336
7.325
7.314
7.304
7.260
7.238
7.082
4.732
3.936
3.919
3.914
1.567
1.256
0.000
-0.011
O
O
OH
3k, Table 2
9
8
7
6
5
4
3
2
1
ppm
2.05
2.19
4.18
1.28
1.00
2.15
3.42

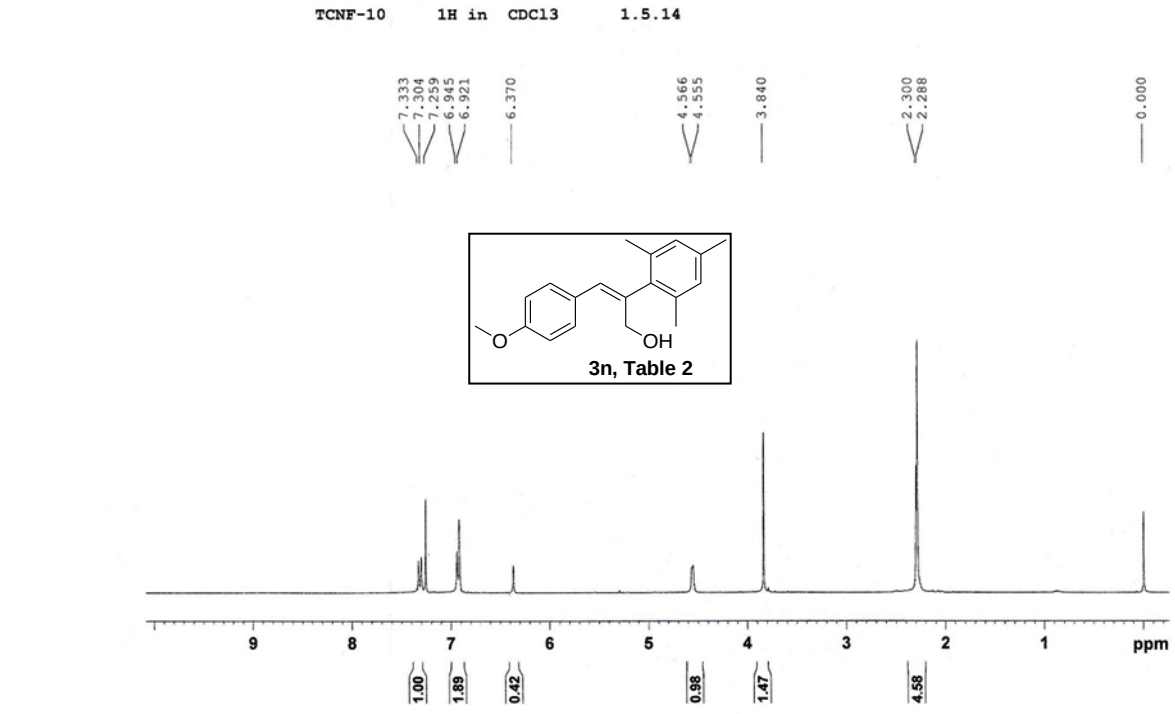

TCNF-25-C.001.esp
77.44
77.02
76.59
129.89
128.98
128.46
126.47
166.92
145.37
139.17
136.44
133.02
60.08
52.11
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

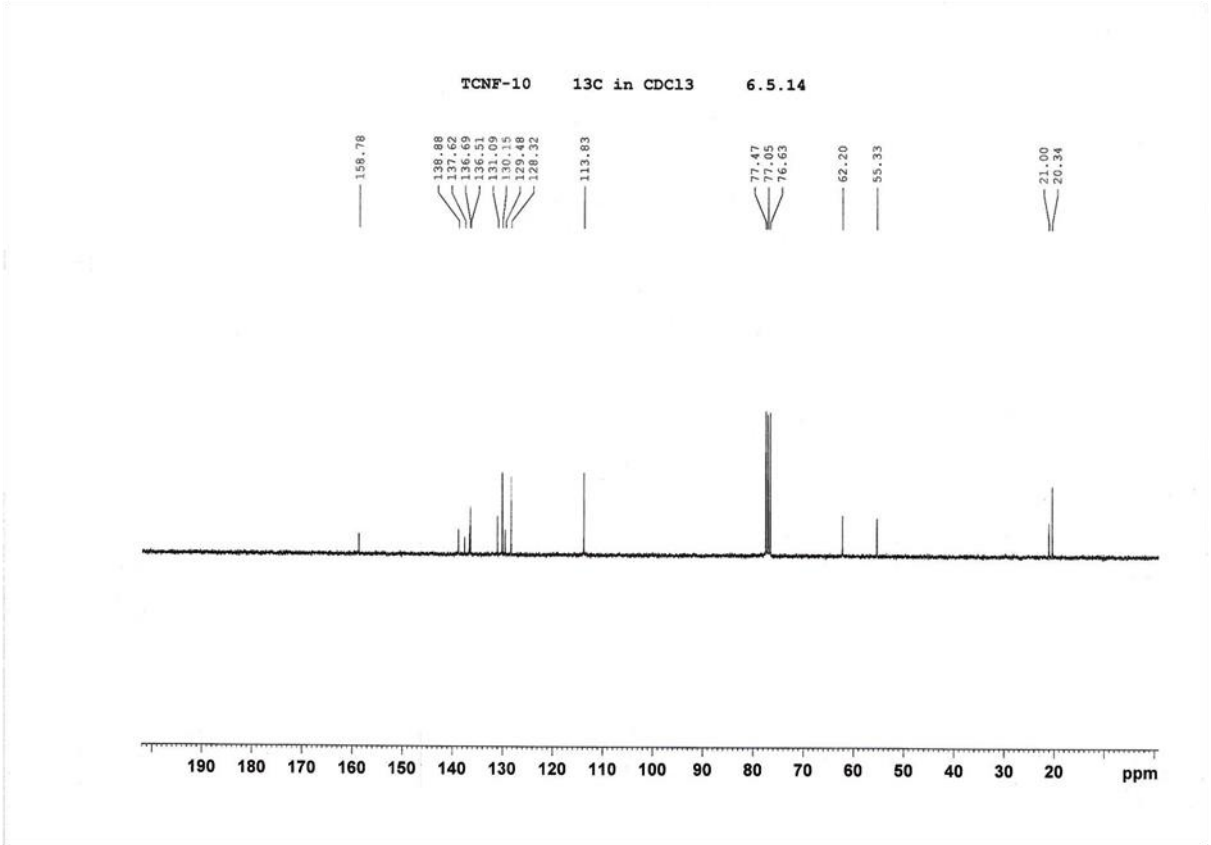

TC-188 1H in CDCl3 26.3.14
7.743
7.737
7.715
7.407
7.393
7.361
7.338
7.332
7.312
7.298
7.260
6.978
4.680
1.646
1.255
0.000
OH
3l, Table 2
7.8
7.6
7.4
ppm
10
9
8
7
6
5
4
3
2
1
ppm
1.86
6.48
1.00
1.67

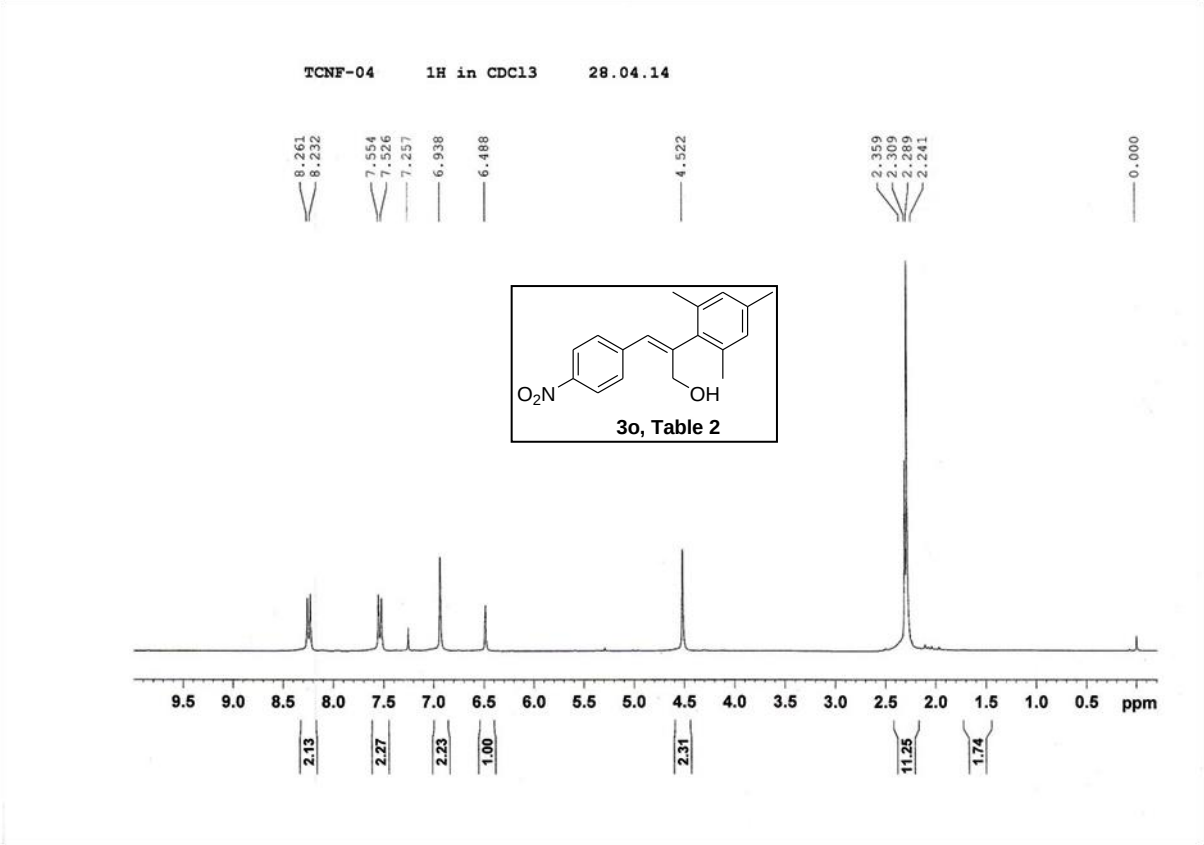

TA-188 13C in CDCl3 13.05.14
140.21
139.08
137.68
136.54
131.79
128.90
128.44
127.59
93.20
77.42
77.20
77.00
76.57
60.12
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

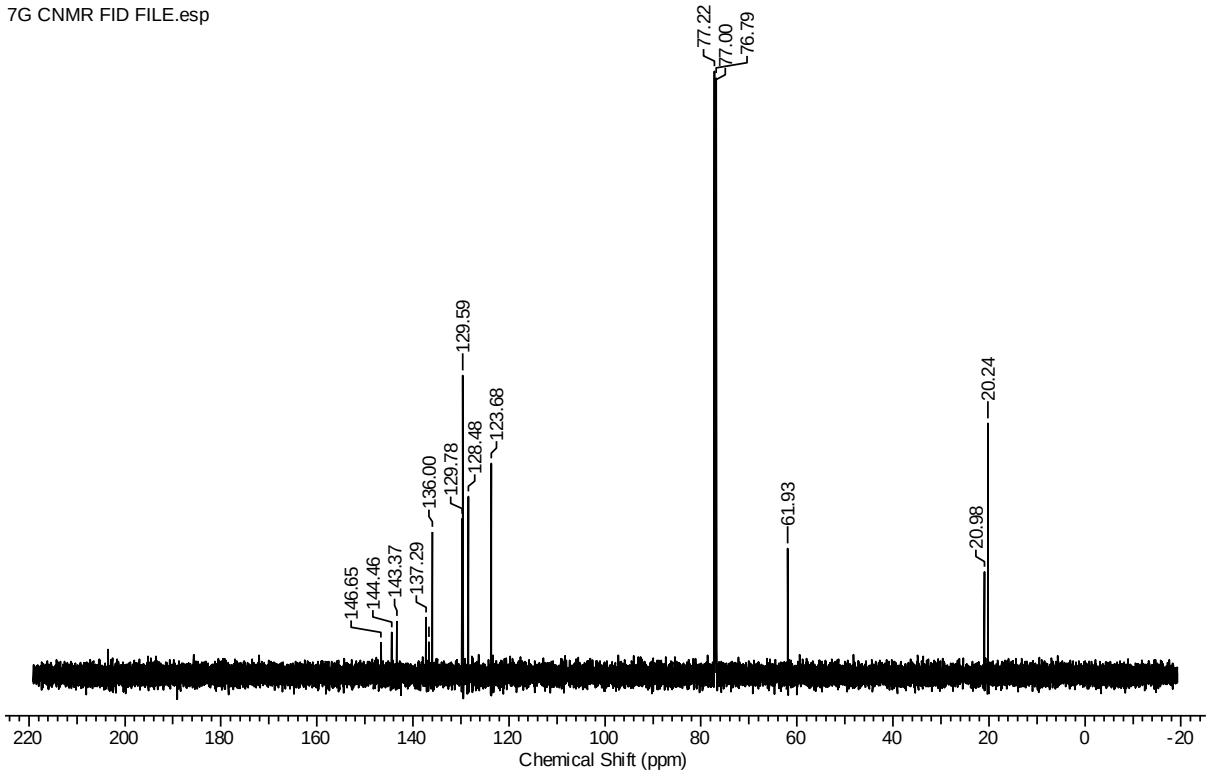

TCN-27 1H in CDCl3 21.04.14
8.259
8.230
7.615
7.587
7.380
7.354
7.327
7.261
7.182
7.180
7.154
7.120
6.972
6.943
6.936
6.916
6.908
4.655
3.862
0.000
O2N
OH
O
3m, Table 2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.55
1.61
1.00
1.81
1.69
1.54
2.48

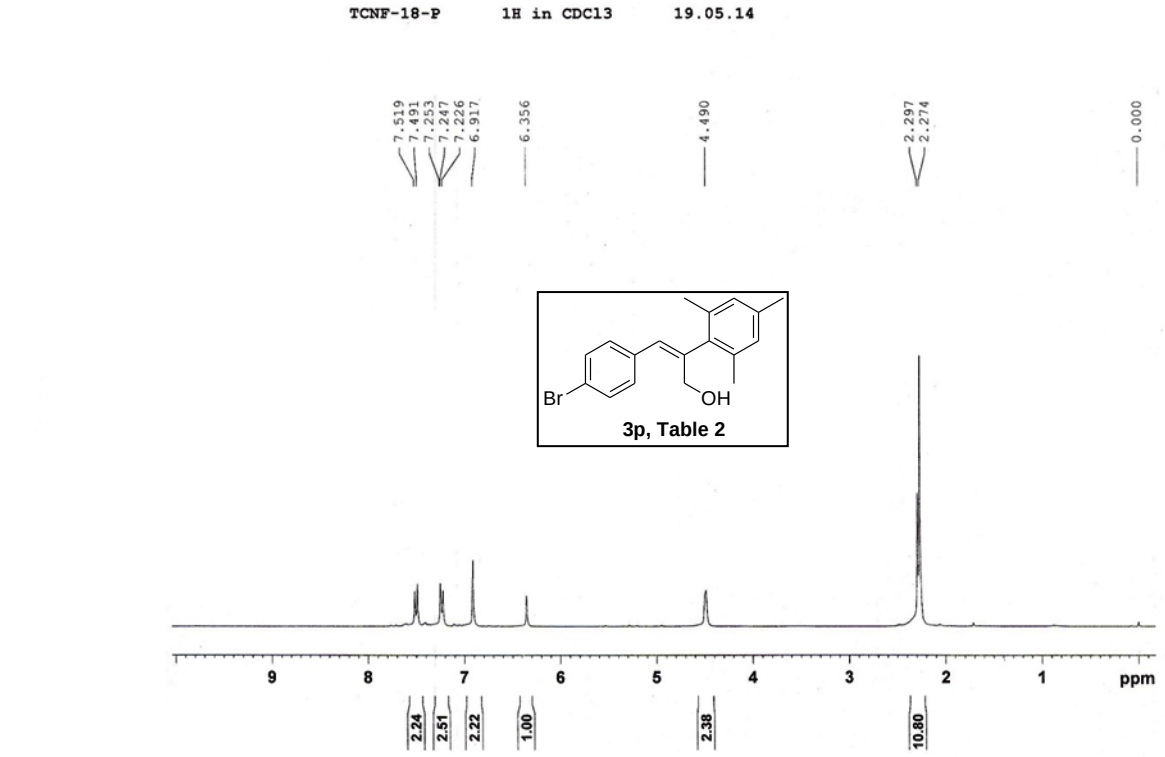

TCN-27 13C in CDCl3 23.04.14
159.95
146.76
143.46
143.24
141.38
129.87
129.75
129.21
123.67
119.01
113.66
112.66
77.42
77.00
76.58
60.20
55.32
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

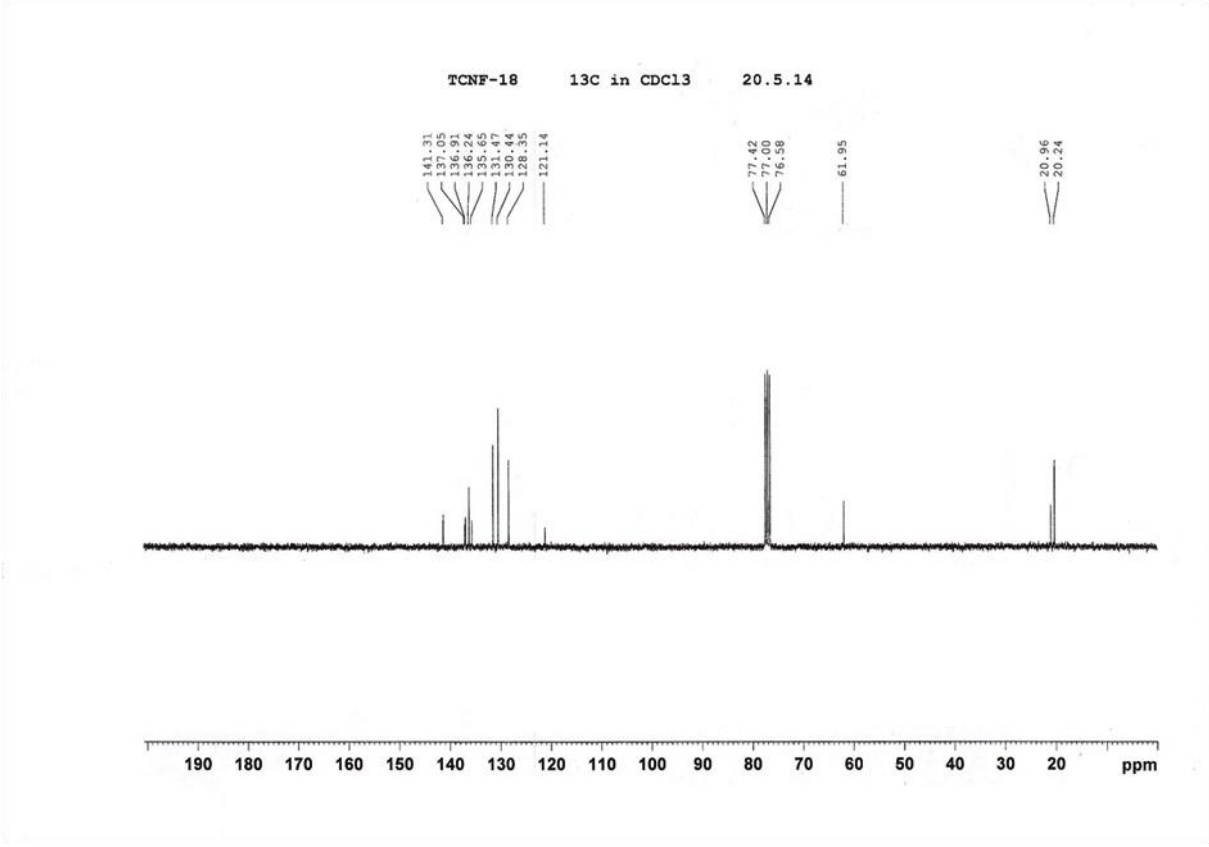

TCNF-10 1H in CDCl3 1.5.14
7.333
7.304
7.259
6.945
6.921
6.370
4.566
4.555
3.840
2.300
2.288
0.000
O
OH
3n, Table 2
9
8
7
6
5
4
3
2
1
ppm
1.00
1.89
0.42
0.98
1.47
4.58

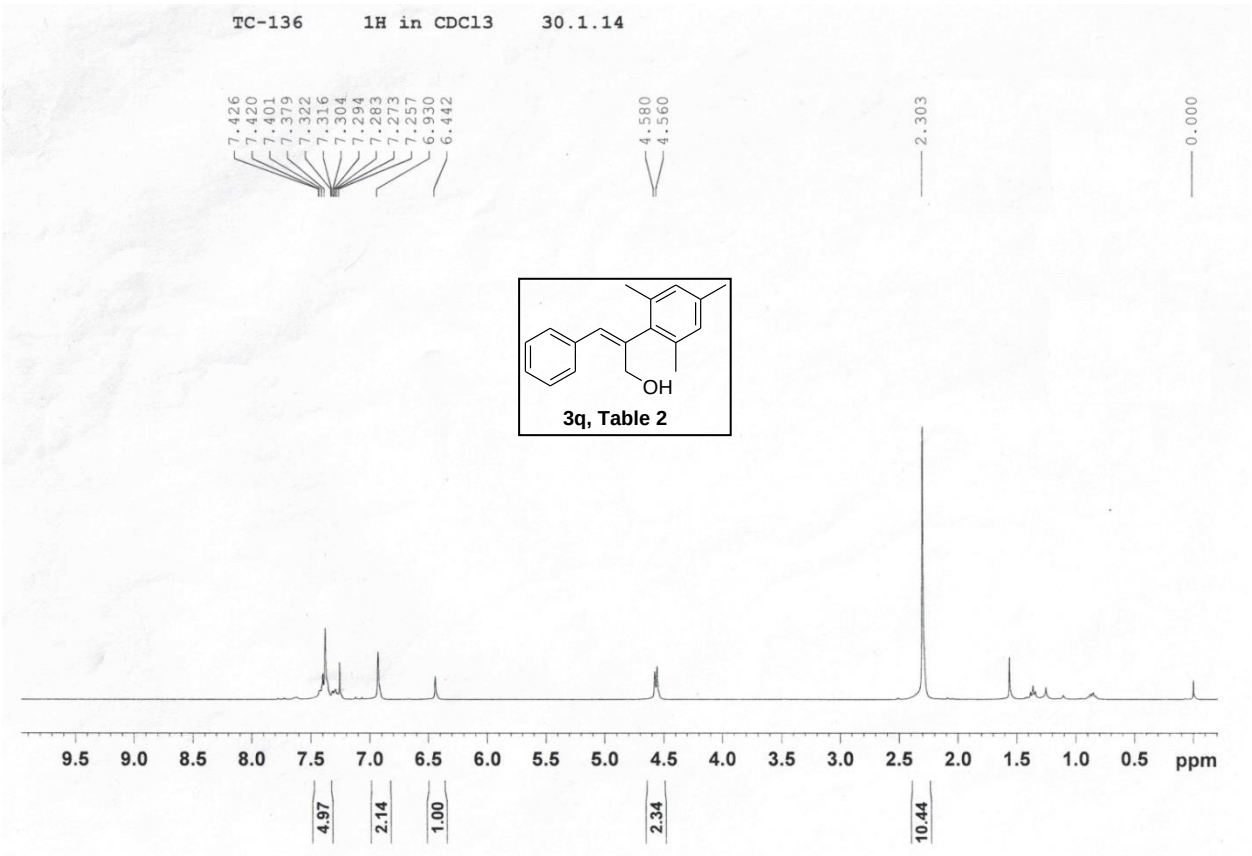

TCNF-10 13C in CDCl3 6.5.14
158.78
138.88
137.62
136.69
136.51
131.09
130.15
129.48
128.32
113.83
77.47
77.05
76.63
62.20
55.33
21.00
20.34
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

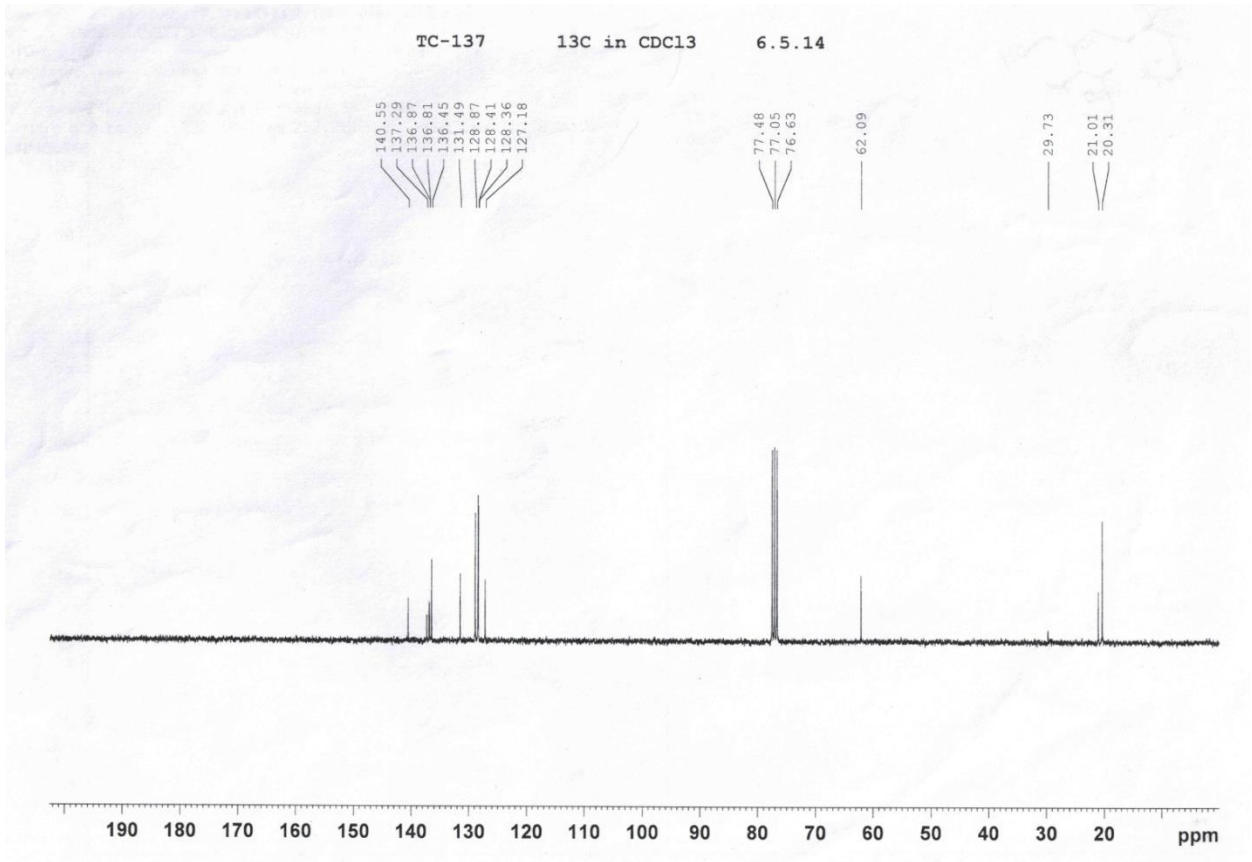

TCNF-04 1H in CDCl3 28.04.14
8.261
8.232
7.554
7.526
7.257
6.938
6.488
4.522
2.359
2.309
2.289
2.241
0.000
O2N
OH
3o, Table 2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.13
2.27
2.23
1.00
2.31
11.25
1.74


7G CNMR FID FILE.esp
77.22
77.00
76.79
146.65
144.46
143.37
137.29
136.00
129.78
129.59
128.48
123.68
61.93
20.98
20.24
220 200 180 160 140 120 100 80 60 40 20 0 -20
Chemical Shift (ppm)

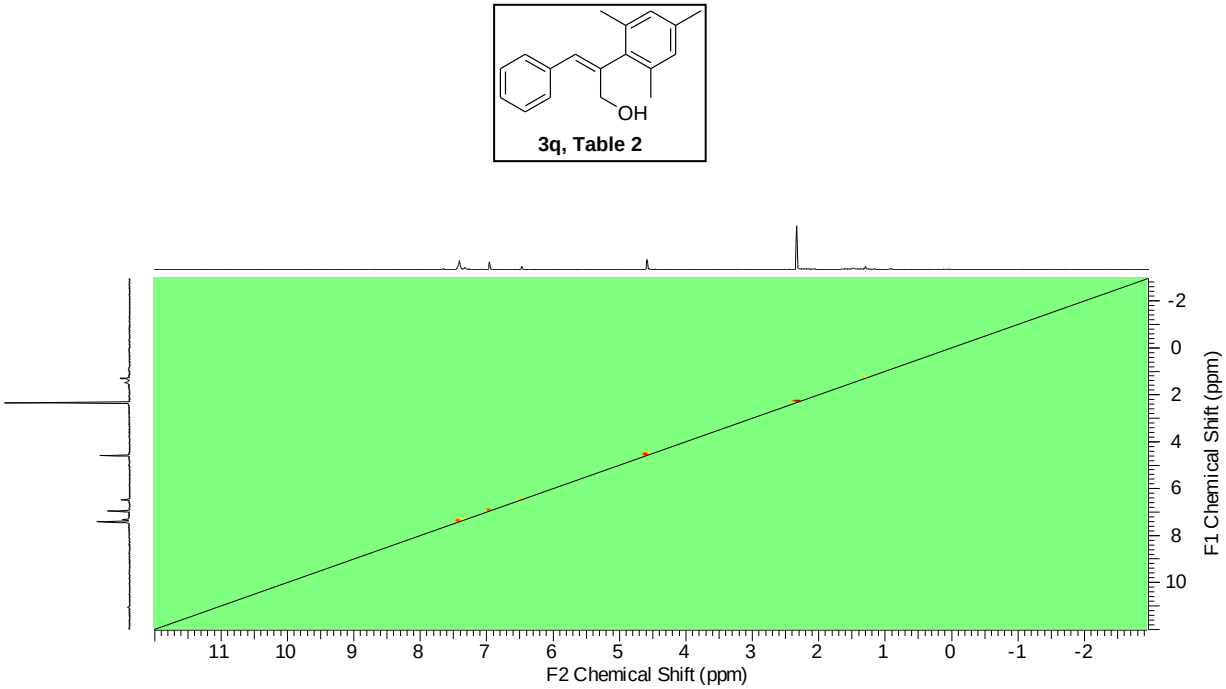

TCNF-18-P 1H in CDCl3 19.05.14
7.519
7.491
7.253
7.247
7.226
6.917
6.356
4.490
2.297
2.274
0.000
Br
OH
3p, Table 2
9
8
7
6
5
4
3
2
1
ppm
2.24
2.51
2.22
1.00
2.38
10.80

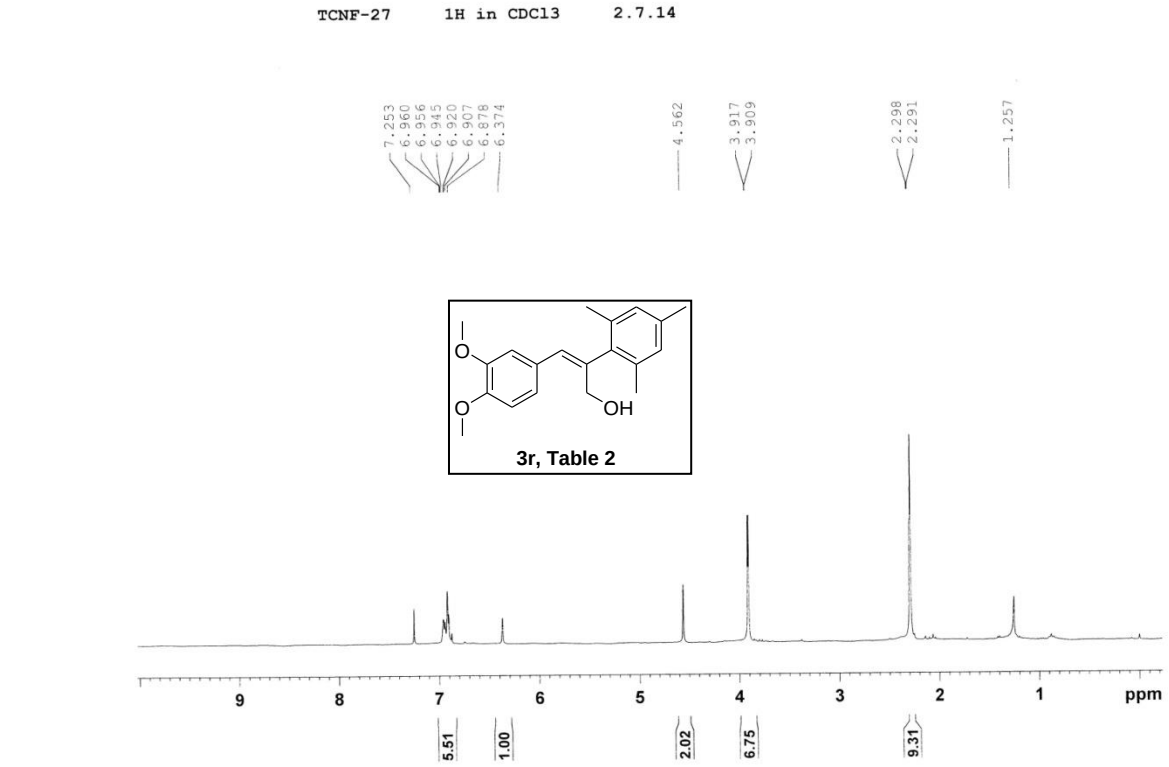

TCNF-18 13C in CDCl3 20.5.14
141.31
137.05
136.91
136.24
135.65
131.47
130.44
128.35
121.14
77.42
77.00
76.58
61.95
20.96
20.24
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

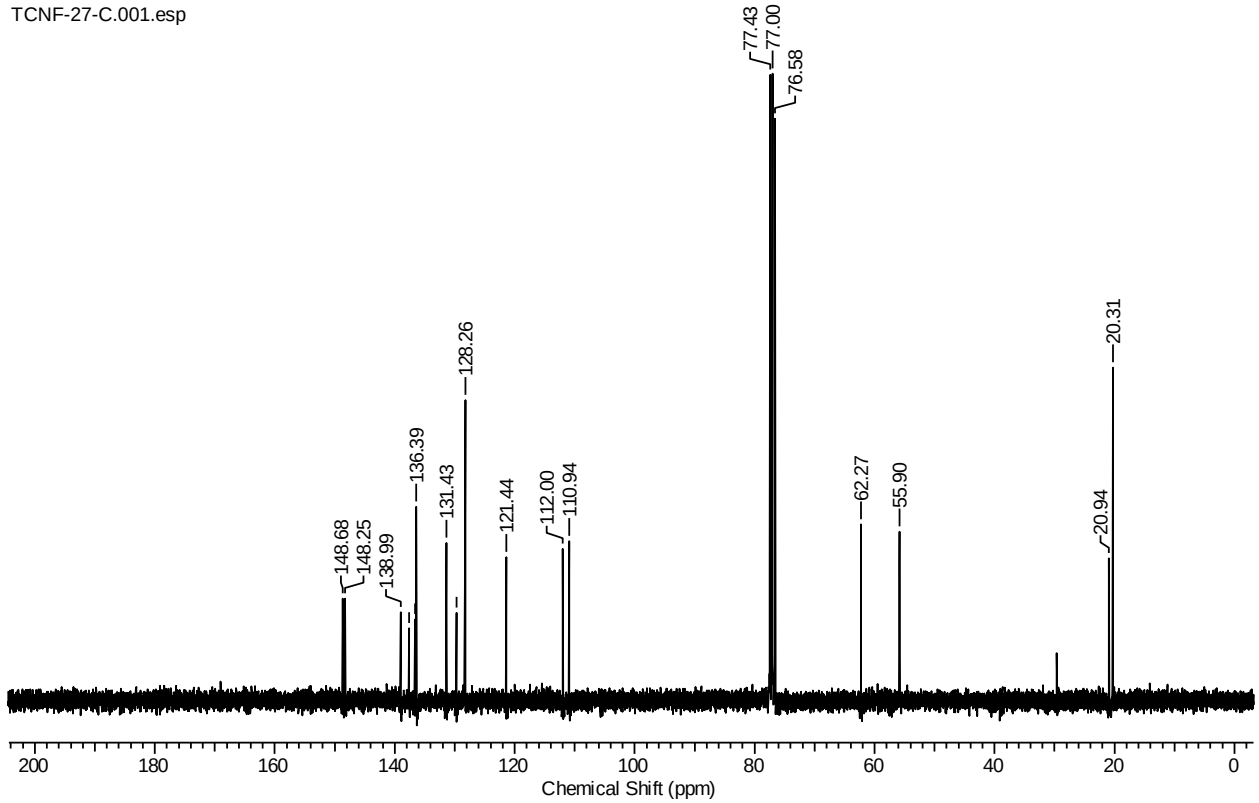

TC-136 1H in CDCl3 30.1.14
7.426
7.420
7.401
7.379
7.322
7.316
7.304
7.294
7.283
7.273
7.257
6.930
6.442
4.580
4.560
2.303
0.000
OH
3q, Table 2
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
4.97
2.14
1.00
2.34
10.44


TC-137 13C in CDCl3 6.5.14
140.55
137.29
136.87
136.81
136.45
131.49
128.87
128.41
128.36
127.18
77.48
77.05
76.63
62.09
29.73
21.01
20.31
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

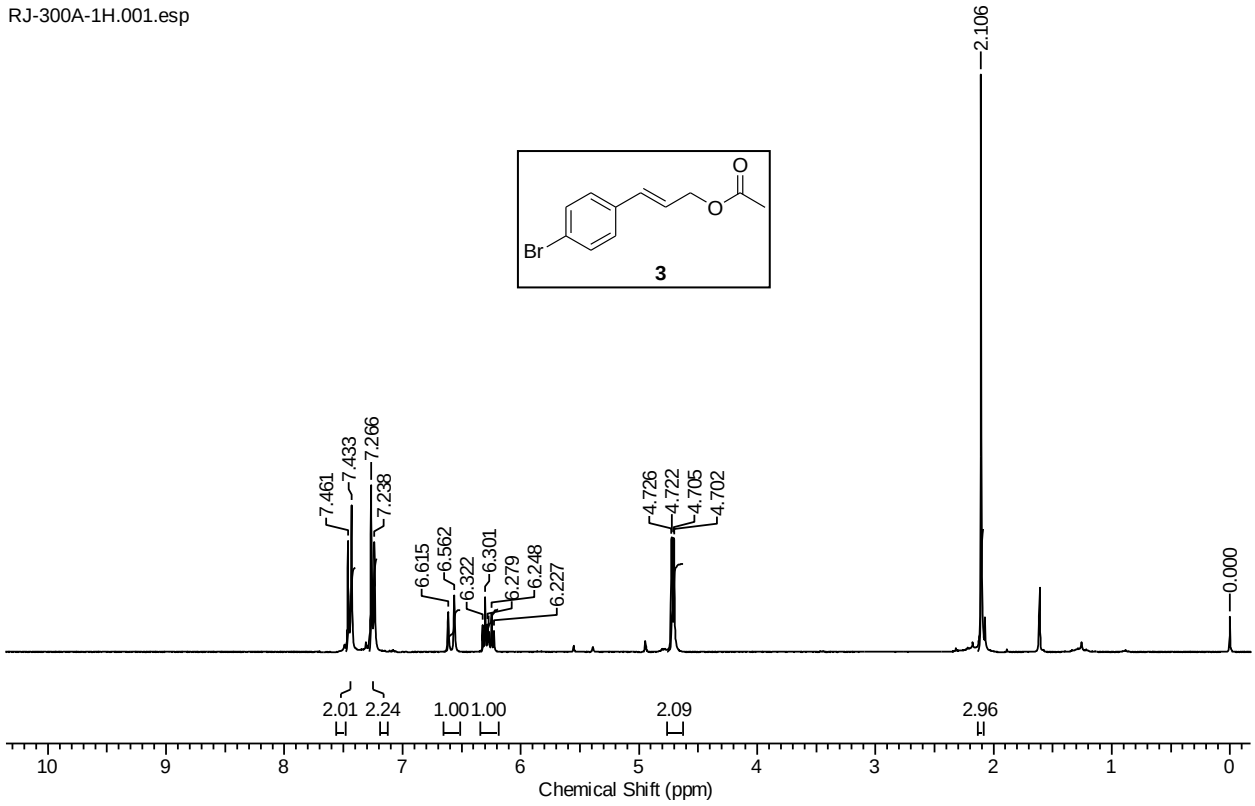
NOESY Spectra of Compound 3q, Table 2



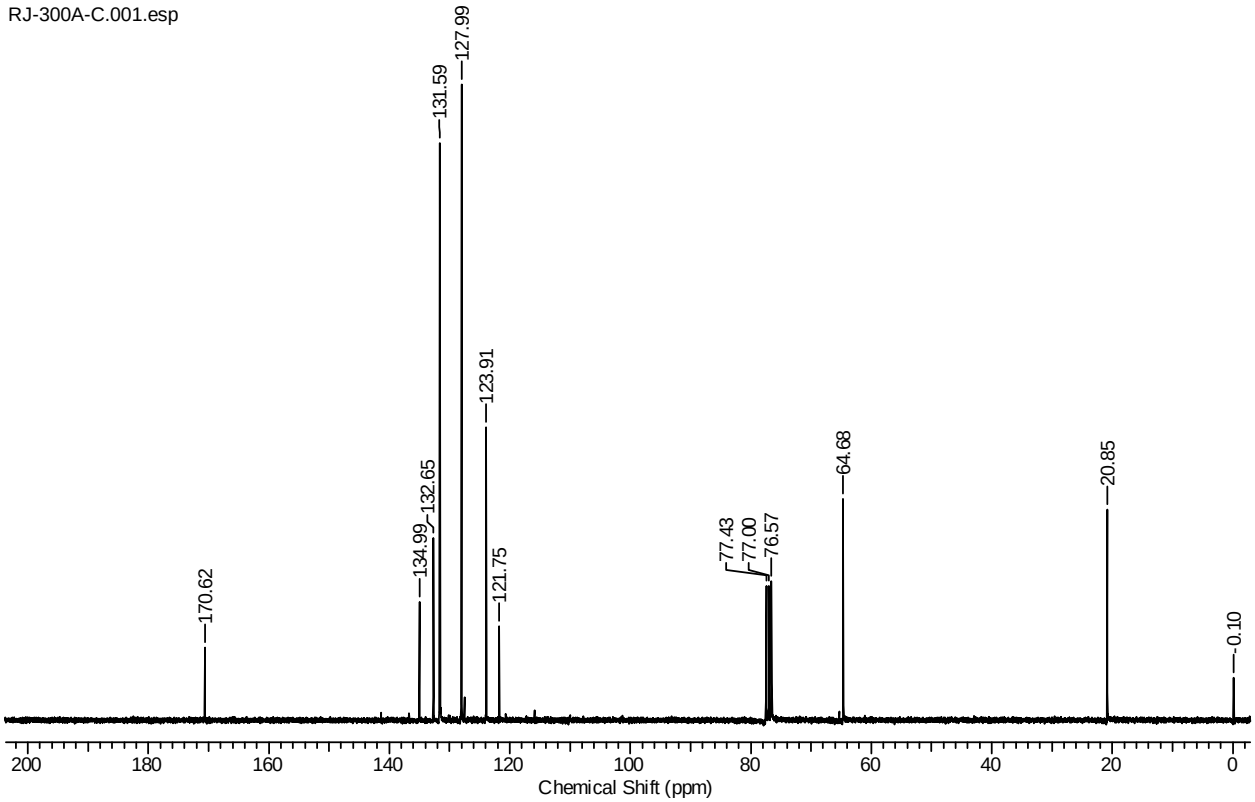

TCNF-27 1H in CDCl3 2.7.14
7.253
6.960
6.956
6.945
6.920
6.907
6.878
6.374
4.562
3.917
3.909
2.298
2.291
1.257
O
O
OH
3r, Table 2
9
8
7
6
5
4
3
2
1
ppm
5.51
1.00
2.02
6.75
9.31

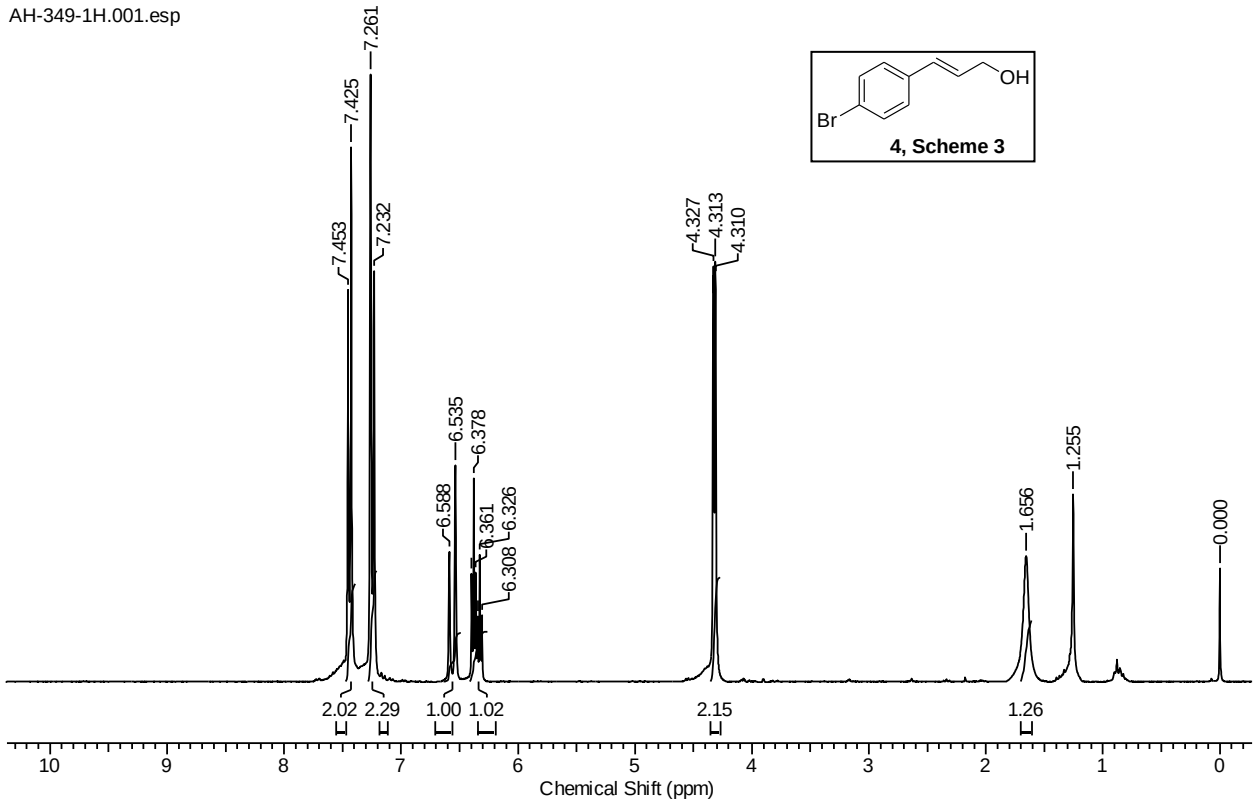

TCNF-27-C.001.esp
77.43
77.00
76.58
148.68
148.25
138.99
136.39
131.43
128.26
121.44
112.00
110.94
62.27
55.90
20.94
20.31
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

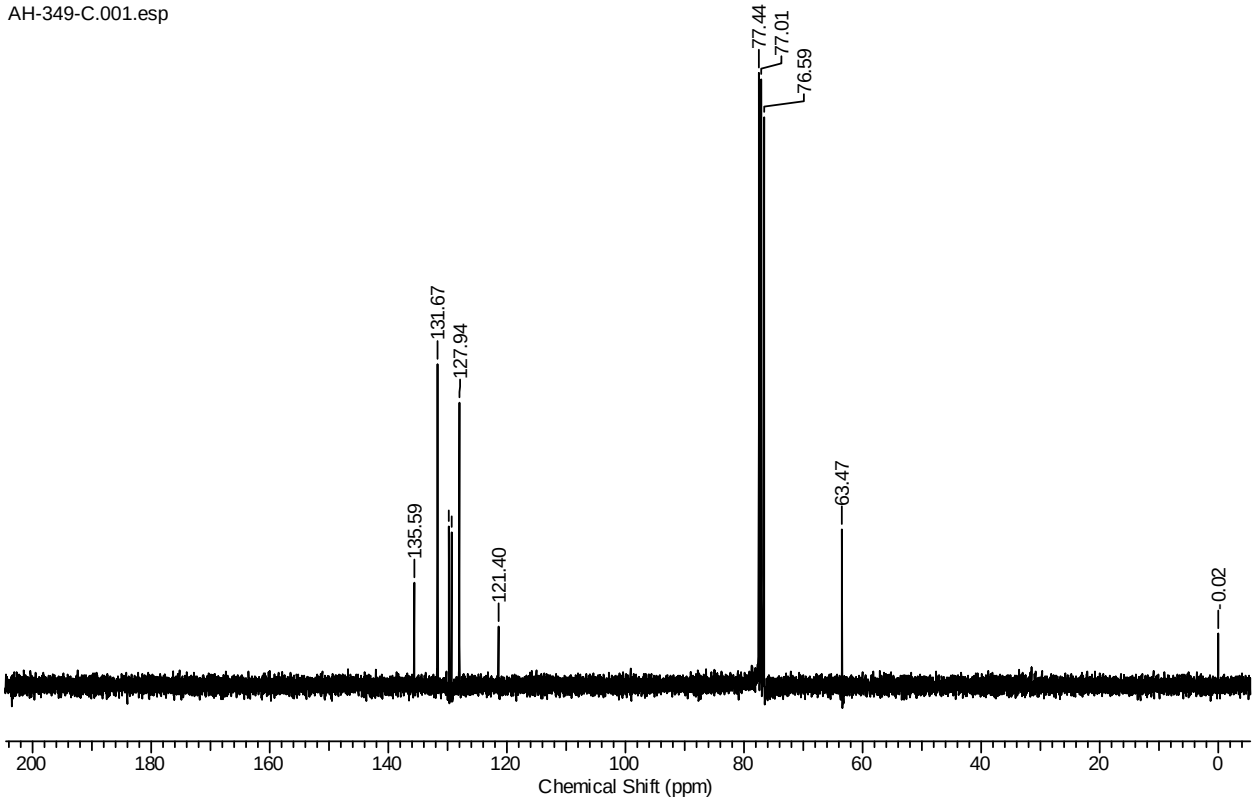
RJ-300A-1H.001.esp

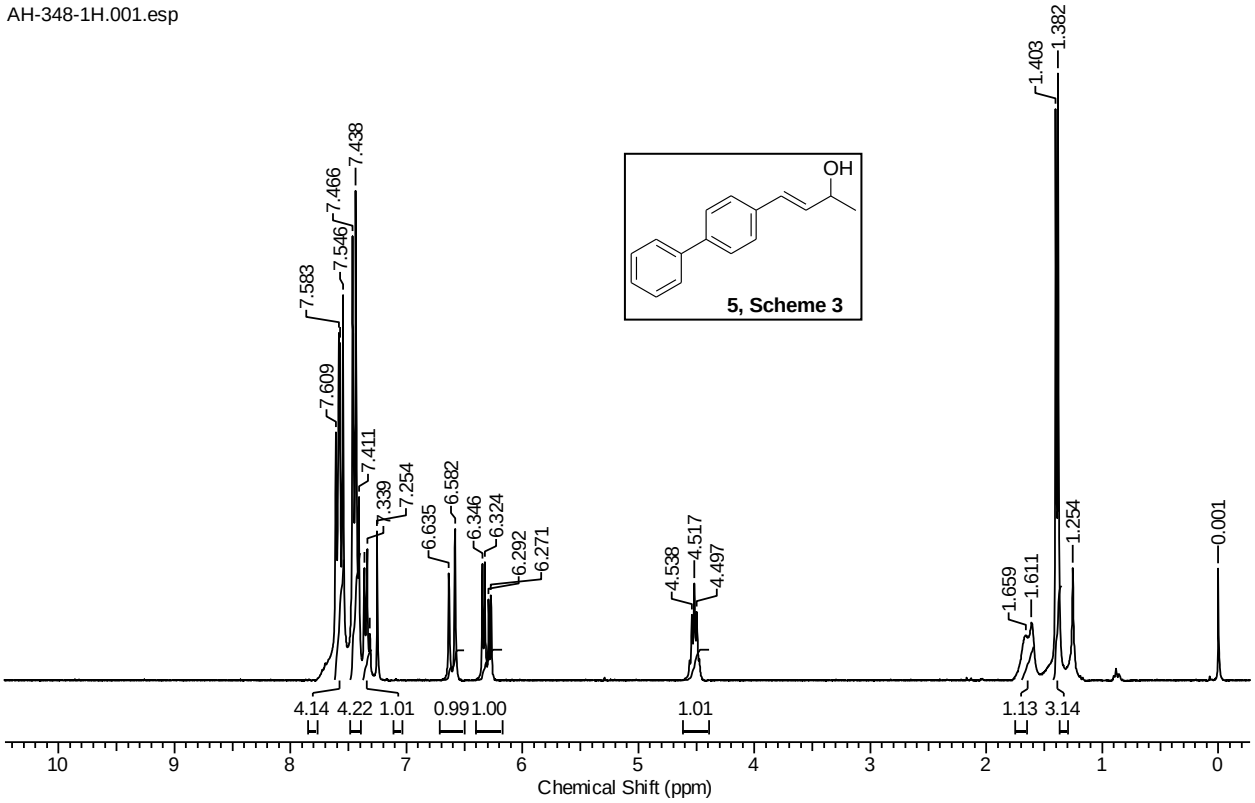


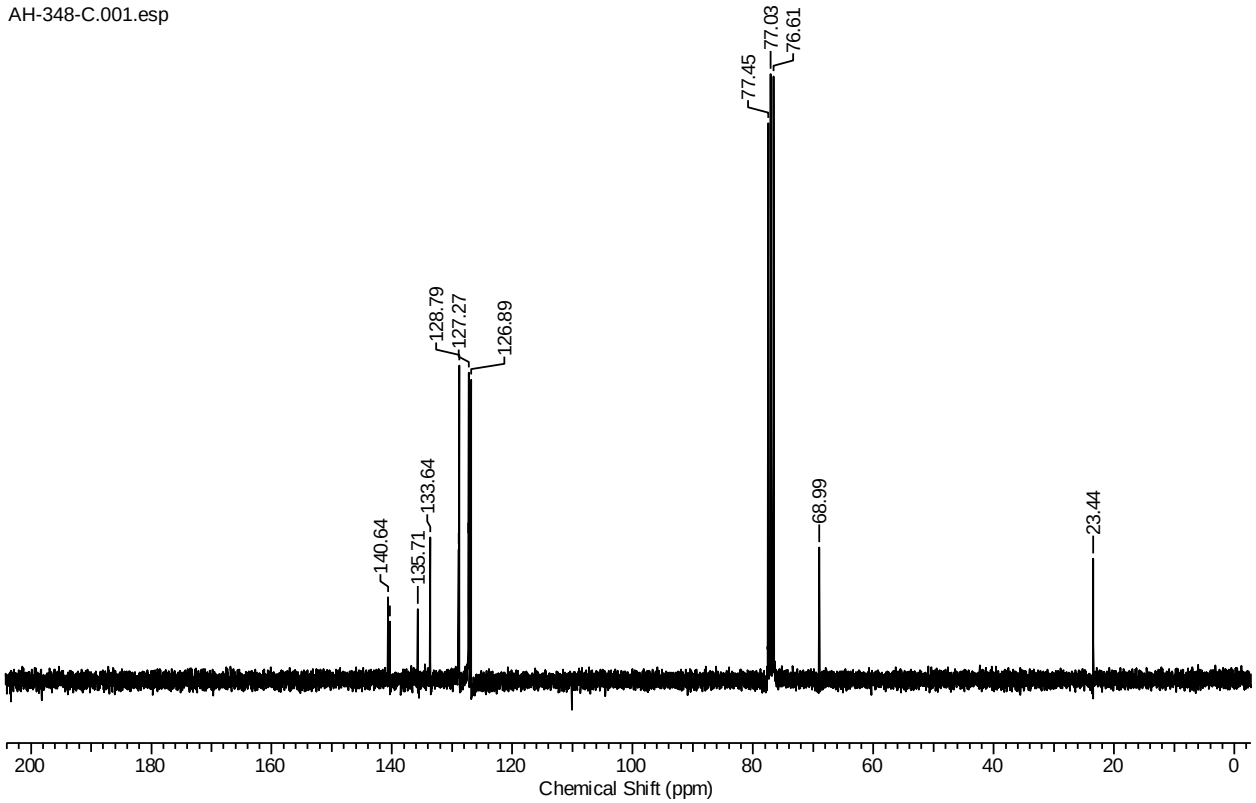
RJ-300A-C.001.esp



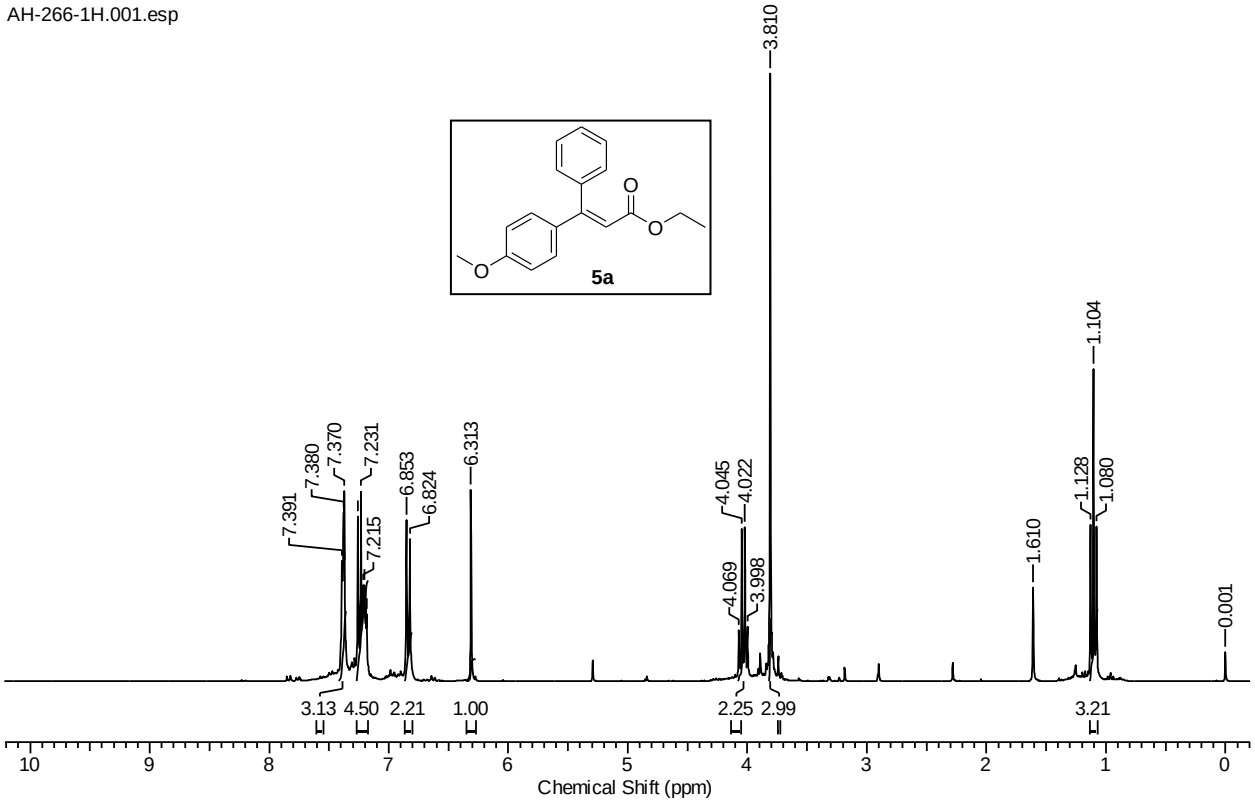

AH-349-1H.001.esp
7.261
7.425
7.453
7.232
6.535
6.378
6.588
6.361
6.326
6.308
4.327
4.313
4.310
1.656
1.255
0.000
OH
Br
4, Scheme 3
2.02
2.29
1.00
1.02
2.15
1.26
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


AH-349-C.001.esp
77.44
77.01
76.59
131.67
127.94
135.59
121.40
63.47
0.02
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)


AH-348-1H.001.esp
OH
5, Scheme 3
7.583
7.609
7.546
7.466
7.438
7.411
7.339
7.254
6.635
6.582
6.346
6.324
6.292
6.271
4.538
4.517
4.497
1.659
1.611
1.403
1.382
1.254
0.001
4.14
4.22
1.01
0.99
1.00
1.01
1.13
3.14
Chemical Shift (ppm)

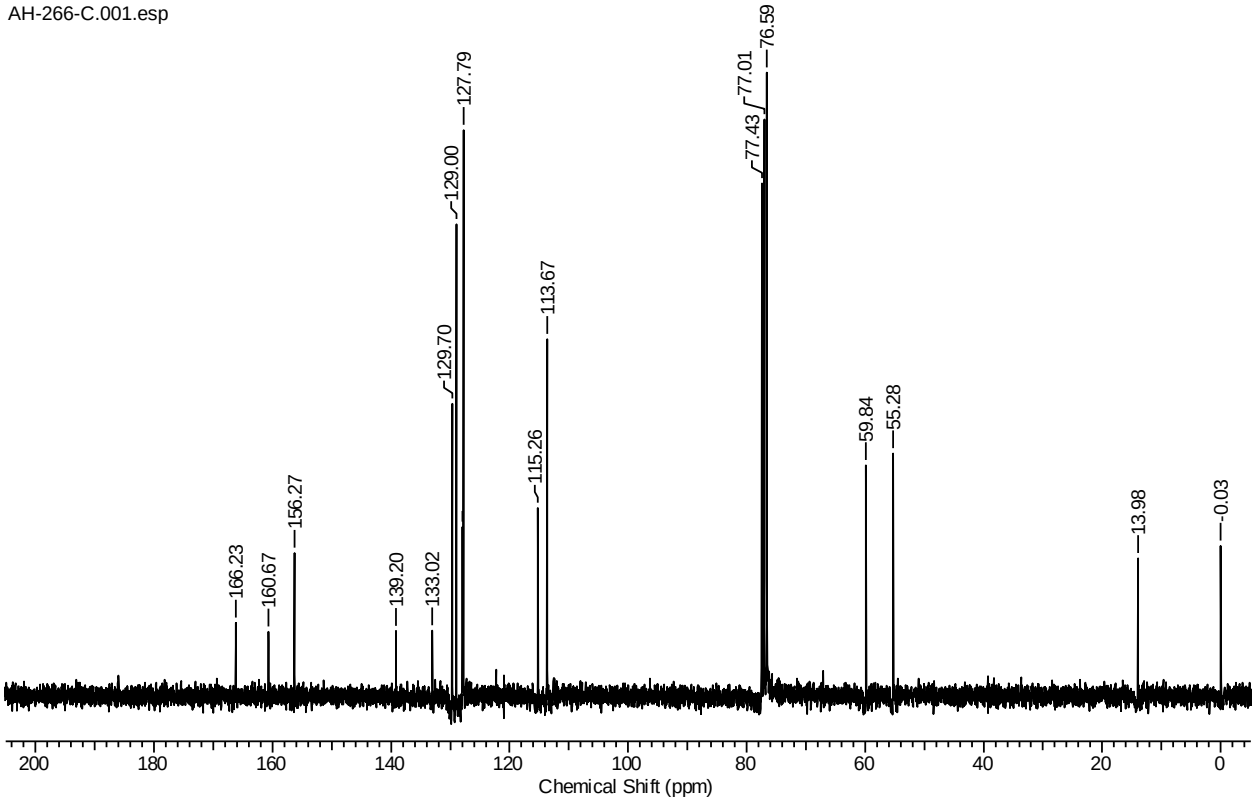

AH-348-C.001.esp
77.45
77.03
76.61
128.79
127.27
126.89
140.64
135.71
133.64
68.99
23.44
Chemical Shift (ppm)

AH-266-1H.001.esp

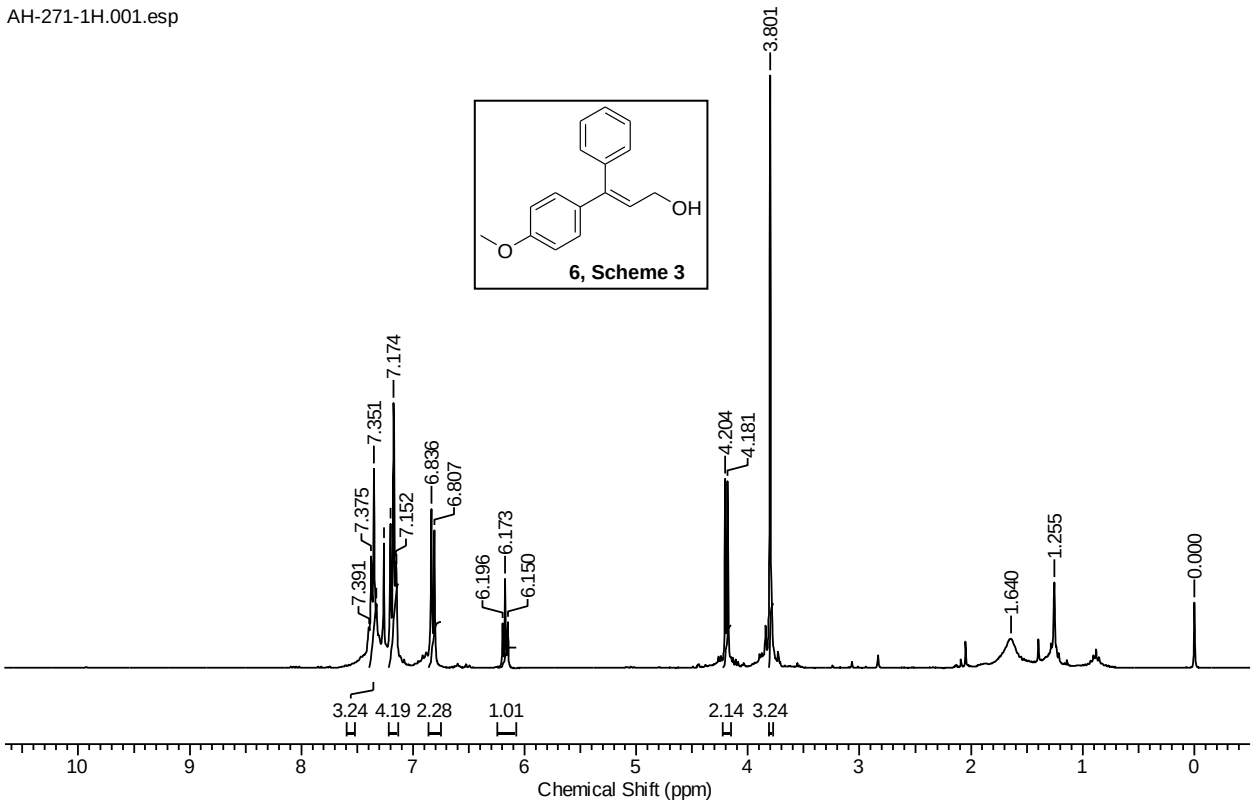


5a

AH-266-C.001.esp



AH-271-1H.001.esp



AH-271-C.001.esp