Nickel-Catalyzed, Ligand-Free, Diastereoselective Synthesis of 3-Methyleneindan-1-ols

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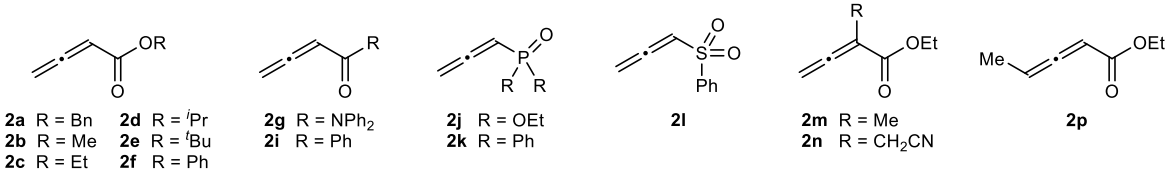
General Considerations

All air-sensitive reactions were carried out under an inert atmosphere using oven-dried apparatus. All commercially available reagents were used as received unless otherwise stated. Petroleum ether refers to Sigma-Aldrich product 24587 (petroleum ether boiling point 40-60 °C). Thin layer chromatography (TLC) was performed on Merck DF-Alufoilien 60F254 0.2 mm precoated plates. Compounds were visualized by exposure to UV light or by dipping the plates into solutions of potassium permanganate or vanillin followed by gentle heating. Flash column chromatography was carried out using silica gel (Fisher Scientific 60 Å particle size 35-70 micron or Fluorochem 60 Å particle size 40-63 micron). Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. The solvent of recrystallization is reported in parentheses. Infrared (IR) spectra were recorded on Bruker platinum alpha FTIR spectrometer on the neat compound using the attenuated total reflection technique. NMR spectra were acquired on Bruker Ascend 400 or Ascend 500 spectrometers. ^{1}H and ^{13}C NMR spectra were referenced to external tetramethylsilane *via* the residual protonated solvent (^{1}H) or the solvent itself (^{13}C). All spectra were obtained at 298 K unless otherwise stated. All chemical shifts are reported in parts per million (ppm). For $CDCl_3$, the shifts are referenced to 7.26 ppm for ^{1}H NMR spectroscopy and 77.16 ppm for ^{13}C NMR spectroscopy. For $(CD_3)_2SO$, the shifts are referenced to 2.50 ppm for ^{1}H NMR spectroscopy and 39.52 ppm for ^{13}C NMR spectroscopy. For CD_3CN, the shifts are referenced to 1.94 ppm for ^{1}H NMR spectroscopy and 118.26 ppm for ^{13}C NMR spectroscopy. Coupling constants (*J*) are quoted to the nearest 0.1 Hz. Assignments were made using the DEPT sequence with secondary pulses at 90° and 135°. ^{19}F NMR spectra and ^{31}P NMR spectra were referenced through the solvent lock (^{2}H) signal according to IUPAC-recommended secondary referencing method according to Bruker protocols. High-resolution mass spectra were recorded using electrospray ionization (ESI) or gas chromatography mass spectrometry (GC/MS) techniques. X-ray diffraction data were collected at 120 K on an Agilent SuperNova diffractometer using CuKα radiation.

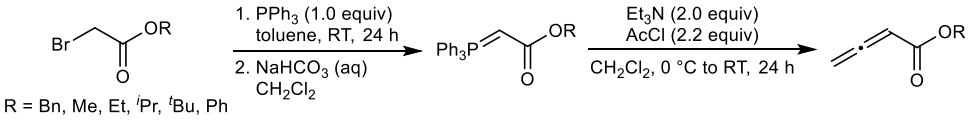
Preparation of Allenes



2a R = Bn **2d** R = ^{i}Pr **2g** R = NPh_2 **2j** R = OEt **2l** **2m** R = Me **2p**
2b R = Me **2e** R = ^{t}Bu **2i** R = Ph **2k** R = Ph **2n** R = CH_2CN
2c R = Et **2f** R = Ph

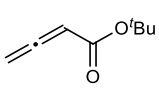
Allenes **2a**,[1] **2b**,[2] **2c**,[1] **2d**,[3] **2f**,[2] **2g**,[4] **2i**,[5,6] **2m**,[7] **2n**[8] and allene **2p**[9] were prepared according to a modified literature procedure (General Procedure A). Allenes **2j**,[10] **2k**,[11] and **2l**[7,12] were prepared according to literature procedures.

General Procedure A: Synthesis of Allenoates



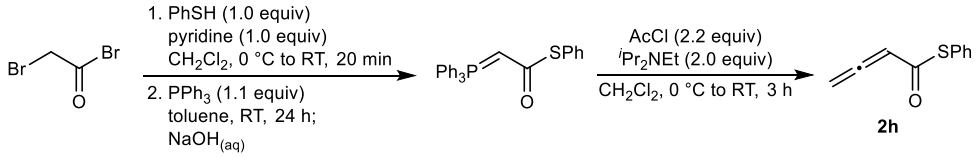
R = Bn, Me, Et, ^{i}Pr, ^{t}Bu, Ph

To a solution of PPh_3 (1.0 equiv) in toluene (0.5 M) at room temperature was added the relevant bromoacetate (1.0 equiv). The resulting suspension was stirred overnight and filtered to leave the phosphonium salt. The salt was dissolved in CH_2Cl_2 and washed with saturated aqueous Na_2CO_3 solution (×3) and brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo* to leave the ylide. To a solution of the ylide in CH_2Cl_2 (0.1 M) at 0 °C was added Et_3N (1.0 equiv) and a solution of acetyl chloride (1.1 equiv) in CH_2Cl_2 (10 mL) and the solution was stirred at room temperature overnight. The mixture was cooled to 0 °C and further Et_3N (1.0 equiv) and acetyl chloride (1.1 equiv) were added. The solution was stirred at room temperature for 1 h and concentrated *in vacuo*. The residue was suspended in 10% EtOAc/petroleum ether (250 mL) and silica gel was added. The mixture was stirred vigorously at room temperature for 40 min and then filtered. The filtrate was concentrated onto silica then purified by column chromatography to give the allene.



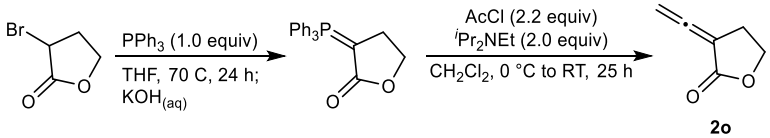
***tert*-Butyl buta-2,3-dienoate (2e).** The title compound was prepared following General Procedure A from PPh_3 (26.2 g, 100 mmol), *tert*-butyl 2-bromoacetate (19.5 g, 100 mmol), acetyl chloride (2 × 7.82 mL, 220 mmol), and Et_3N (2 × 13.94 mL, 200 mmol) in CH_2Cl_2 (100 mL). Purification by column chromatography (5% EtOAc/petroleum ether) gave **2e** as a pale yellow oil (2.60 g, 19%). R_f = 0.45 (10% EtOAc/petroleum ether); IR 2979, 1703 (C=O), 1368, 1276, 1140, 961, 845 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.54 (1H, t, *J* = 6.5 Hz, =C**H**), 5.16 (2H, d, *J* = 6.5 Hz, C$\mathbf{H}_2$), 1.48 (9H, s, 3 × C$\mathbf{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.5 (C), 165.2 (C), 89.7 (CH), 81.2 (C), 79.1 (CH_2), 28.2 (3 × CH_3); HRMS (ESI) Exact mass calculated for $[C_8H_{12}O_2Na]^+$ $[M+Na]^+$: 163.0730, found: 163.0728.

_S_-Phenyl buta-2,3-dienethioate (2h)



To a solution of pyridine (2.80 mL, 34.0 mmol) in CH_2Cl_2 (60 mL) at 0 °C was added thiophenol (3.49 mL, 34.0 mmol) followed by the dropwise addition of bromoacetyl bromide (3.00 mL, 34.0 mmol). The resulting suspension was stirred at 0 °C for 10 min and then room temperature for 10 min. The reaction was diluted with CH_2Cl_2 (60 mL), washed with brine (100 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo* to leave *S*-phenyl 2-bromoethanethioate (7.82 g, 99%). To a solution of *S*-phenyl 2-bromoethanethioate (7.82 g, 33.8 mmol) in toluene (34 mL) was added PPh_3 (9.76 g, 37.2 mmol) and the resulting suspension was stirred at room temperature for 24 h. The reaction was filtered and the collected solid was washed with toluene. The resulting phosphonium salt was dissolved in CH_2Cl_2 (200 mL) and washed with 2 M aqueous NaOH solution (3 × 150 mL), brine (150 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resulting phosphonium ylide was in CH_2Cl_2 (30 mL) and the solution was cooled to 0 °C. $^{i}Pr_2NEt$ (4.94 mL, 28.3 mmol) was added followed by acetyl chloride (2.22 mL, 31.2 mmol), and the resulting solution was warmed to room temperature over 2 h. The solution was then cooled to 0 °C and further $^{i}Pr_2NEt$ (4.94 mL, 28.3 mmol) and acetyl chloride (2.22 mL, 31.2 mmol) were added. The solution was warmed to room temperature and stirred for 1 h, then concentrated *in vacuo*. *n*-Pentane/Et_2O (1:1, 600 mL) was added and the suspension was stirred vigorously for 40 min, filtered and concentrated *in vacuo*. Purification of the residue by column chromatography (0-5% EtOAc/petroleum ether) gave **2h** as a yellow oil (1.49 g, 30%). R_f = 0.41 (10% EtOAc/petroleum ether); IR 3061, 1967, 1670 (C=O), 1439, 1132, 1023, 850, 745, 687, 594 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.50-7.38 (5H, m, Ar**H**), 5.97 (1H, t, *J* = 6.5 Hz, =C**H**), 5.43 (2H, d, *J* = 6.5 Hz, =C**H**$_2$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 214.9 (C), 187.6 (C), 135.0 (2 × CH), 129.6 (CH), 129.3 (2 × CH), 127.6 (C), 95.6 (CH), 82.1 (CH_2); HRMS (ESI) Exact mass calculated for $[C_{10}H_8NaOS]^+$ $[M+Na]^+$: 199.0188, found: 199.0211.

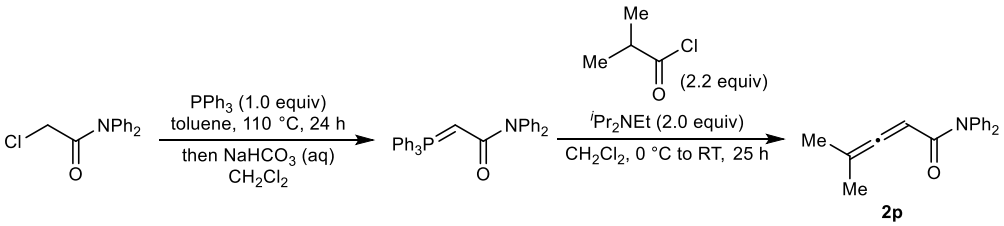
3-Vinylidenedihydrofuran-2(3*H*)-one (2o)



To a solution of PPh_3 (15.9 g, 60.6 mmol) in THF (25 mL) was added α-bromo-γ-butyrolactone (10.0 g, 60.6 mmol) and the mixture was stirred at 70 °C for 24 h, cooled to room temperature, and filtered to leave the phosphonium salt (22.8 g, 88%). A portion of the phosphonium salt (5.00 g,

11.7 mmol) was suspended in CH_2Cl_2 (50 mL) and washed with 1 M aqueous KOH solution (3 × 50 mL) and brine (50 mL). The solution was dried (Na_2SO_4), filtered, and concentrated *in vacuo.* The resulting phosphonium ylide was dissolved in CH_2Cl_2 (12 mL) and the solution was cooled to 0 °C. $^{i}Pr_2NEt$ (2.00 mL, 11.7 mmol) was added followed by acetyl chloride (0.92 mL, 12.9 mmol) and the resulting solution was stirred at room temperature for 24 h. The solution was then cooled to 0 °C and further $^{i}Pr_2NEt$ (2.00 mL, 11.7 mmol) and acetyl chloride (0.92 mL, 12.9 mmol) were added. The solution was warmed to room temperature and stirred for 1 h. H_2O was added (10 mL) and the suspension was stirred for 15 min and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine (20 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (5-15% EtOAc/petroleum ether) gave **2o** as a pale yellow oil (589 mg, 46%). R_f = 0.36 (20% EtOAc/petroleum ether); IR 2989, 2935, 1730 (C=O), 1653, 1378, 1280, 1193, 1157, 1091, 1066, 751, 699, 446 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.37 (2H, t, *J* = 5.1 Hz, =C**H**$_2$), 4.39 (2H, t, *J* = 7.5 Hz, OC**H**$_2$), 3.07 (2H, tt, *J* = 7.5, 5.1 Hz, C**H**$_2$$CH_2O$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.4 (C), 170.4 (C), 93.4 (C), 82.5 (CH_2), 66.2 (CH_2), 26.4 (CH_2); HRMS (ESI) Exact mass calculated for $[C_6H_7O]^+$ $[M+H]^+$: 111.0441, found: 111.0443.

4-Methyl-*N*,*N*-diphenylpenta-2,3-dienamide (2p)

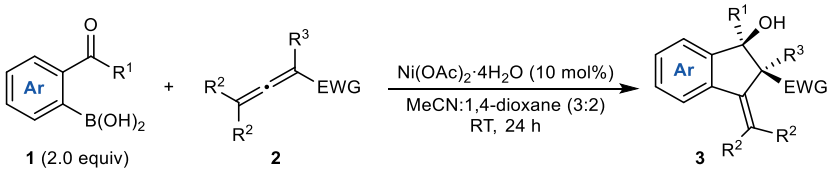


To a solution of 2-chloro-*N*,*N*-diphenylacetamide[13] (20.9 g, 84.9 mmol) in toluene (85 mL) was added PPh_3 (22.3 g, 84.9 mmol). The resulting suspension was stirred at reflux for 24 h, cooled to room temperature, and filtered under vacuum to give the phosphonium salt as a white solid (39.53 g, 92%). The phosphonium salt (5.00 g, 9.84 mmol) was dissolved in CH_2Cl_2 (80 mL) and washed with saturated aqueous $NaHCO_3$ solution (3 × 80 mL), brine (80 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo* to give the phosphonium ylide. This ylide was dissolved in CH_2Cl_2 (10 mL), the solution was cooled to 0 °C, and $^{i}Pr_2NEt$ (1.71 mL, 9.84 mmol) was added followed by isobutyryl chloride (1.04 mL, 10.83 mmol). The solution was warmed to room temperature and stirred for 24 h. The solution was then cooled to 0 °C and further $^{i}Pr_2NEt$ (1.71 mL, 9.84 mmol) and isobutyryl chloride (1.04 mL, 10.83 mmol) were added. The mixture was stirred at room temperature for 1 h then concentrated *in vacuo*. 20% EtOAc/petroleum (200 mL) was added to the residue followed by silica gel and the resulting suspension was stirred vigorously for 40 min, filtered under vacuum, and concentrated *in vacuo*. Purification of the residue by column

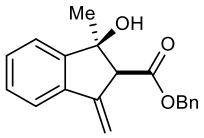
chromatography (10-30% EtOAc/petroleum ether) gave **2p** as an off-white solid (1.18 g, 54% from the phosphonium salt). R_f = 0.45 (20% EtOAc/petroleum ether); m.p 110-112 °C ($Et_2O/CHCl_3$); IR 2978, 1755, 1654, 1592, 1399, 1290, 1221, 1176, 1072, 813, 752, 690 cm^{-1}; ^1H NMR (500 MHz, $(CD_3)_2SO$) δ 7.45-7.34 (4H, m, Ar**H**), 7.34-7.20 (6H, m, Ar**H**), 5.45 (1H, sept, *J* = 2.9 Hz, =C**H**), 1.61 (3H, s, C**H**$_3$), 1.60 (3H, s, C**H**$_3$); ^{13}C NMR (126 MHz, $(CD_3)_2SO$, 343 K) δ 207.8 (C), 163.9 (C), 142.8 (C), 128.8 (4 × CH), 127.3 (4 × CH), 126.3 (2 × CH), 98.9 (C), 87.6 (CH), 18.6 (2 × CH_3); HRMS (ESI) Exact mass calculated for $[C_{18}H_{17}NO]^+$ $[M+H]^+$: 264.1383, found: 264.1383.

Nickel-Catalyzed Synthesis of 3-Methyleneindan-1-ols

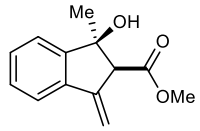
General Procedure B



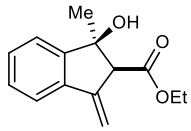
A flask was charged with the relevant allene (0.30 mmol, 1.0 equiv), $Ni(OAc)_2 \cdot 4H_2O$ (7.5 mg, 0.03 mmol) and the relevant boronic acid (0.60 mmol, 2.0 equiv). The flask was sealed with a rubber septum and purged with argon. Degassed MeCN (1.8 mL) and degassed 1,4-dioxane (1.2 mL) were added and the resulting solution was stirred at room temperature for 24 h, diluted with Et_2O (*ca.* 3 mL), filtered through a plug of silica gel using Et_2O as the eluent, and concentrated in *vacuo*. Purification of the residue by column chromatography gave the 3-methyleneindan-1-ol.



(±)-Benzyl (1*S*,2*S*)-1-hydroxy-1-methyl-3-methylene-2,3-dihydro-1*H*-indene-2-carboxylate (3aa). The title compound was prepared following General Procedure B from allene **2a** (52.3 mg, 0.30 mmol) and 2-acetylphenylboronic acid (**1a**) (98.4 mg, 0.60 mmol). Purification by column chromatography (10% EtOAc/petroleum ether) gave **3aa** as a pale yellow oil (74.2 mg, 84%). R_f = 0.27 (20% EtOAc/petroleum ether); IR 3485 (br, OH), 1717 (C=O), 1643, 1315, 1153, 1009, 845, 757, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51-7.44 (2H, m, Ar**H**), 7.40-7.30 (7H, m, Ar**H**), 5.66 (1H, d, *J* = 1.8 Hz, =C**H**$_a$H$_b$), 5.27 (1H, d, *J* = 1.8 Hz, =CH$_a$**H**$_b$), 5.22-5.17 (2H, m, C**H**$_2$Ph), 3.86 (1H, t, *J* = 1.8 Hz, C**H**C=O), 3.54 (1H, s, O**H**), 1.60 (3H, s, C**H**$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0 (C), 149.6 (C), 144.4 (C), 137.9 (C), 135.7 (C), 129.8 (CH), 129.0 (CH), 128.8 (2 × CH), 128.5 (CH), 128.3 (2 × CH), 123.2 (CH), 120.9 (CH), 107.7 (CH_2), 79.9 (C), 67.0 (CH_2), 61.3 (CH), 28.9 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{19}H_{18}NaO_3]^+$ $[M+Na]^+$: 317.1148, found: 317.1140.

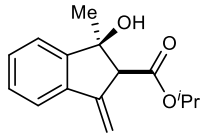


(±)-Methyl (1*S*,2*S*)-1-hydroxy-1-methyl-3-methylene-2,3-dihydro-1*H*-indene-2-carboxylate (3ab). The title compound was prepared following General Procedure B from allene **2b** (29.4 mg, 0.30 mmol) and 2-acetylphenylboronic acid (**1a**) (98.4 mg, 0.60 mmol). Purification by column chromatography (10-30% EtOAc/petroleum ether) gave **3ab** as a yellow oil (26.2 mg, 40%). R_f = 0.18 (20% EtOAc/petroleum ether); IR 3426 (br, OH), 1724 (C=O), 1435, 1367, 1337, 1297, 1257, 1195, 1137, 951, 903, 761, 610, 563 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50-7.44 (2H, m, Ar**H**), 7.39-7.27 (2H, m, Ar**H**), 5.67 (1H, d, *J* = 1.8 Hz, =C**H**$_a$CH$_b$), 5.27 (1H, d, *J* = 1.8 Hz, =CH$_a$C**H**$_b$), 3.82 (1H, t, *J* = 1.8 Hz, C**H**C=O), 3.75 (3H, s, OC**H**$_3$), 3.54 (1H, d, *J* = 0.9 Hz, O**H**), 1.60 (3H, d, *J* = 0.9 Hz, CC**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6 (C), 149.6 (C), 144.5 (C), 137.9 (C), 129.8 (CH), 129.0 (CH), 123.3 (CH), 120.9 (CH), 107.5 (CH_2), 79.7 (C), 61.2 (CH), 52.4 (CH_3), 28.9 (CH_3); GCMS (EI) 218.0 ($[M]^+$).



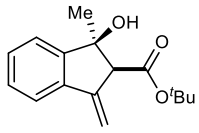
(±)-Ethyl (1*S*,2*S*)-1-hydroxy-1-methyl-3-methylene-2,3-dihydro-1*H*-indene-2-carboxylate (3ac). The title compound was prepared following General Procedure B from allene **2c** (33.6 mg, 0.30 mmol) and 2-acetylphenylboronic acid (**1a**) (98.4 mg, 0.60 mmol). Purification by column chromatography (10% EtOAc/petroleum ether) gave **3ac** as a yellow oil (60.0 mg, 86%). R_f = 0.23 (20% EtOAc/petroleum ether); IR 3441 (br, OH), 2978, 1718 (C=O), 1643, 1369, 1317, 1179, 1087, 1032, 927, 759 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.51-7.42 (2H, m, Ar**H**), 7.37-7.29 (2H, m, Ar**H**), 5.66 (1H, d, *J* = 1.8 Hz, =C**H**$_a$CH$_b$), 5.28 (1H, d, *J* = 1.8 Hz, =CH$_a$C**H**$_b$), 4.21 (2H, q, *J* = 7.1 Hz, OC**H**$_2$), 3.81-3.76 (1H, m, C**H**C=O), 3.68 (1H, s, O**H**), 1.59 (3H, s, CC**H**$_3$), 1.30 (3H, t, *J* = 7.1 Hz, CH$_2$C**H**$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3 (C), 149.8 (C), 144.7 (C), 137.9 (C), 129.8 (CH), 129.0 (CH), 123.2 (CH), 120.9 (CH), 107.4 (CH_2), 79.7 (C), 61.3 (CH_2), 61.1 (CH), 28.9 (CH_3), 14.3 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{14}H_{16}NaO_3]^+$ $[M+Na]^+$: 255.0992, found: 255.0993.

These data are consistent with those reported previously,[14] although the relative configuration of the product in that previous paper[14] was not determined.

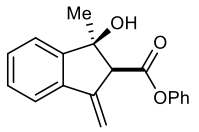


(±)-Isopropyl (1*S*,2*S*)-1-hydroxy-1-methyl-3-methylene-2,3-dihydro-1*H*-indene-2-carboxylate (3ad). The title compound was prepared following General Procedure B from allene **2d** (37.8 mg, 0.30 mmol) and 2-acetylphenylboronic acid (**1a**) (98.4 mg, 0.60 mmol). Purification by column chromatography (30% petroleum ether/CH_2Cl_2) gave **3ad** as an off-white solid (65.0 mg, 88%). R_f = 0.33 (20% EtOAc/petroleum ether); m.p. 58-60 °C (Et_2O/*n*-pentane); IR 3428 (br, OH), 1717 (C=O), 1369, 1339, 1325, 1254, 1207, 1104, 884, 772 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51-7.43 (2H, m, Ar**H**), 7.37-7.28 (2H, m, Ar**H**), 5.65 (1H, d, *J* = 1.9 Hz, =C**H**$_a$H$_b$), 5.28 (1H, d, *J* = 1.9 Hz, =CH$_a$**H**$_b$), 5.08 (1H, sept, *J* = 6.3 Hz,

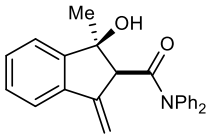
C**H**$(CH_3)_2$), 3.81 (1H, d, *J* = 0.9 Hz, O**H**), 3.74 (1H, t, *J* = 1.9 Hz, C**H**C=O), 1.58 (3H, d, *J* = 0.9 Hz, CC**H**$_3$), 1.29 (3H, d, *J* = 6.2 Hz, CH(C**H**$_3)_2$), 1.25 (3H, d, *J* = 6.2 Hz, CH(C**H**$_3)_2$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.9 (C), 149.9 (C), 144.8 (C), 137.8 (C), 129.8 (CH), 128.9 (CH), 123.2 (CH), 120.9 (CH), 107.2 (CH_2), 79.6 (C), 68.8 (CH), 61.0 (CH), 28.9 (CH_3), 22.0 (CH_3), 21.8 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{15}H_{18}NaO_3]^+$ $[M+Na]^+$: 269.1148, found: 269.1148.



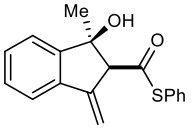
(±)-*tert*-Butyl (1*S*,2*S*)-1-hydroxy-1-methyl-3-methylene-2,3-dihydro-1*H*-indene-2-carboxylate (3ae). The title compound was prepared following General Procedure B from allene **2e** (42.1 mg, 0.30 mmol) and 2-acetylphenylboronic acid (**1a**) (98.4 mg, 0.60 mmol). Purification by preparative TLC (30% petroleum ether/CH_2Cl_2) gave **3ae** as a white solid (53.1 mg, 68%). R_f = 0.33 (20% EtOAc/petroleum ether); m.p. 75-77 °C (Et_2O/*n*-pentane); IR 3432 (br, OH), 1718 (C=O), 1392, 1155, 1094, 1038, 937, 757, 563 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.43 (2H, m, Ar**H**), 7.36-7.28 (2H, m, Ar**H**), 5.65 (1H, d, *J* = 1.8 Hz, =C**H**$_a$H$_b$), 5.27 (1H, d, *J* = 1.8 Hz, =CH$_a$**H**$_b$), 3.92 (1H, d, *J* = 1.0 Hz, O**H**), 3.68 (1H, t, *J* = 1.8 Hz, C**H**C=O), 1.56 (3H, d, *J* = 1.0 Hz, ArCC**H**$_3$), 1.47 (9H, s, C(C**H**$_3)_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.8 (C), 150.1 (C), 145.1 (C), 137.9 (C), 129.7 (CH), 128.8 (CH), 123.2 (CH), 120.8 (CH), 106.9 (CH_2), 82.1 (C), 79.5 (C), 61.7 (CH), 29.0 (CH_3), 28.2 (3 × CH_3); HRMS (ESI) Exact mass calculated for $C_{16}H_{20}NaO_3$ $[M+Na]^+$: 283.1305, found: 283.1301.



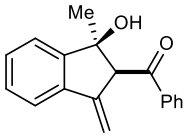
(±)-Phenyl (1*S*,2*S*)-1-hydroxy-1-methyl-3-methylene-2,3-dihydro-1*H*-indene-2-carboxylate (3af). The title compound was prepared following General Procedure B from allene **2f** (48.1 mg, 0.30 mmol) and 2-acetylphenylboronic acid (**1a**) (98.4 mg, 0.60 mmol). Purification by column chromatography (10% EtOAc/petroleum ether) gave **3af** as a yellow oil (69.8 mg, 83%). R_f = 0.27 (20% EtOAc/petroleum ether); IR 3501 (br, OH), 3070, 3042, 2971, 2928, 1740 (C=O), 1592, 1491, 1191, 1161, 1122, 1047, 950, 784, 728 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (1H, dd, *J* = 6.7, 1.8 Hz, Ar**H**), 7.50-7.47 (1H, m, Ar**H**), 7.40-7.33 (4H, m, Ar**H**), 7.26-7.21 (1H, m, Ar**H**), 7.16-7.10 (2H, m, Ar**H**), 5.79 (1H, d, *J* = 1.8 Hz, =C**H**$_a$H$_b$), 5.45 (1H, d, *J* = 1.8 Hz, =CH$_a$**H**$_b$), 4.07 (1H, s, C**H**C=O), 3.52-3.25 (1H, m, O**H**), 1.71 (3H, s, C**H**$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6 (C), 150.7 (C), 149.3 (C), 144.2 (C), 137.9 (C), 129.9 (CH), 129.6 (2 × CH), 129.2 (CH), 126.2 (CH), 123.3 (CH), 121.6 (2 × CH), 121.0 (CH), 108.2 (CH_2), 80.2 (C), 61.3 (CH), 29.0 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{18}H_{16}NaO_3]^+$ $[M+Na]^+$: 303.0992, found: 303.0990.



(±)-(1*S*,2*S*)-1-Hydroxy-1-methyl-3-methylene-*N*,*N*-diphenyl-2,3-dihydro-1*H*-indene-2-carboxamide (3ag). The title compound was prepared following General Procedure B from allene **2g** (70.1 mg, 0.30 mmol) and 2-acetylphenylboronic acid (**1a**) (98.4 mg, 0.60 mmol). Purification by column chromatography (10-30% EtOAc/petroleum ether) gave **3ag** as a pale yellow solid (96.0 mg, 90%). R_f = 0.15 (20% EtOAc/petroleum ether); m.p. 120-122 °C (Et_2O/*n*-pentane); IR 3493 (br, OH), 1650 (C=O), 1633, 1585, 1488, 1370, 1291, 1119, 703, 694, 569, 506 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.52-7.37 (7H, m, Ar**H**), 7.35-7.27 (4H, m, Ar**H**), 7.24 (2H, d, *J* = 8.1 Hz, Ar**H**), 7.19 (1H, t, *J* = 7.4 Hz, Ar**H**), 5.60 (1H, d, *J* = 1.9 Hz, =C**H**$_a$H$_b$), 5.11 (1H, d, *J* = 1.9 Hz, =CH$_a$**H**$_b$), 4.28-4.24 (1H, m, C**H**C=O), 4.06 (1H, d, *J* = 1.8 Hz, O**H**), 1.46 (3H, s, C**H**$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3 (C), 150.8 (C), 147.5 (C), 142.9 (C), 142.3 (C), 138.4 (C), 130.2 (CH), 129.7 (CH), 129.11 (2 × CH), 129.05 (CH), 128.7 (2 × CH), 128.3 (CH), 126.69 (CH), 126.65 (2 × CH), 123.1 (CH), 120.8 (2 × CH), 105.7 (CH_2), 80.2 (C), 59.0 (CH), 28.5 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{24}H_{21}NNaO_2]^+$ $[M+Na]^+$: 378.1464, found: 378.1460.



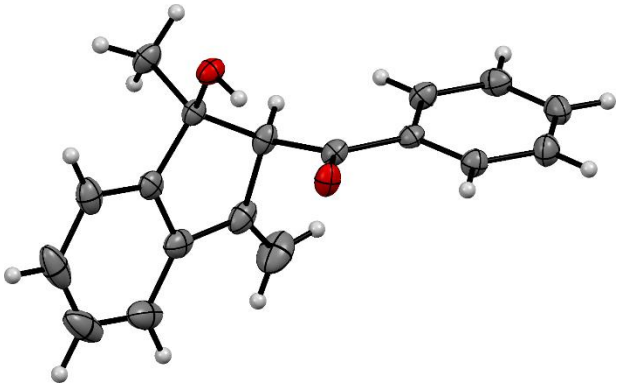
(±)-*S*-Phenyl (1*S*,2*S*)-1-hydroxy-1-methyl-3-methylene-2,3-dihydro-1*H*-indene-2-carbothioate (3ah). The title compound was prepared following General Procedure B from allene **2h** (52.9 mg, 0.30 mmol) and 2-acetylphenylboronic acid (**1a**) (98.4 mg, 0.60 mmol). Purification by column chromatography (5-20% EtOAc/petroleum ether) gave **3ah** as an orange oil (77.4 mg, 87%). R_f = 0.33 (20% EtOAc/petroleum ether); IR 3423 (br, OH), 1682 (C=O), 1477, 1440, 1250, 1013, 908, 839, 728, 688 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51-7.46 (1H, m, Ar**H**), 7.46-7.37 (6H, m, Ar**H**), 7.32 (2H, m, Ar**H**), 5.75 (1H, d, *J* = 1.6 Hz, =C**H**$_a$H$_b$), 5.45 (1H, d, *J* = 1.6 Hz, =CH$_a$**H**$_b$), 4.11 (1H, t, *J* = 1.6 Hz, C**H**C=O), 3.23 (1H, br s, O**H**), 1.62 (3H, s, C**H**$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.4 (C), 150.0 (C), 144.6 (C), 137.5 (C), 134.6 (2 × CH), 129.9 (CH), 129.7 (CH), 129.3 (2 × CH), 129.0 (CH), 127.4 (C), 123.0 (CH), 121.0 (CH), 108.3 (CH_2), 80.9 (C), 69.6 (CH), 29.5 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{18}H_{16}NaO_2S]^+$ $[M+Na]^+$: 319.0763, found: 319.0768.

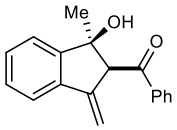


(±)-[(1*S*,2*S*)-1-Hydroxy-1-methyl-3-methylene-2,3-dihydro-1*H*-inden-2-yl](phenyl)methanone (3ai). The title compound was prepared following General Procedure B from allene **2i** (43.2 mg, 0.30 mmol) and 2-acetylphenylboronic acid (**1a**) (98.4 mg, 0.60 mmol). Purification by column chromatography (10% EtOAc/petroleum ether) gave **3ai** as a yellow solid (44.4 mg, 56%). R_f = 0.30 (20% EtOAc/petroleum ether); m.p. 102-103 °C (Et_2O/*n*-pentane); IR 3491 (br, OH), 1782 (C=O), 1660, 1461, 1373, 1258, 888, 759, 708, 678, 608, 583, 563, 519 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08-8.02 (2H, m, Ar**H**),

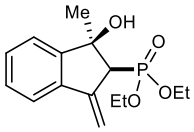
7.66-7.60 (1H, m, Ar**H**), 7.57-7.49 (3H, m, Ar**H**), 7.44 (1H, app dt, *J* = 7.6, 1.0 Hz, Ar**H**), 7.38 (1H, td, *J* = 7.4, 1.2 Hz, Ar**H**), 7.31 (1H, td, *J* = 7.4, 1.2 Hz, Ar**H**), 5.60 (1H, d, *J* = 1.6 Hz, =C**H**$_a$H$_b$), 4.98 (1H, d, *J* = 1.6 Hz, =CH$_a$**H**$_b$), 4.88 (1H, t, *J* = 1.6 Hz, C**H**C=O), 4.17 (1H, d, *J* = 1.0 Hz, O**H**), 1.63 (3H, d, *J* = 1.0 Hz, C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1 (C), 150.9 (C), 145.4 (C), 137.7 (C), 137.0 (C), 133.8 (CH), 129.9 (CH), 129.3 (2 × CH), 128.9 (2 × CH), 128.7 (CH), 122.9 (CH), 121.0 (CH), 108.0 (CH_2), 80.7 (C), 61.8 (CH), 29.4 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{18}H_{16}NaO_3]^+$ $[M+Na]^+$: 265.1223, found: 265.1213.

Slow evaporation of a solution of **3ai** in Et_2O/*n*-pentane gave crystals that were suitable for X-ray crystallography:

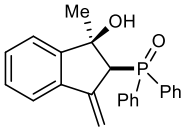




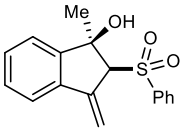
3ai
CCDC 1858962



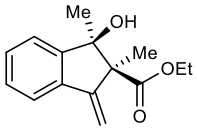
(±)-Diethyl [(1*R*,2*S*)-1-hydroxy-1-methyl-3-methylene-2,3-dihydro-1*H*-inden-2-yl]phosphonate (3aj). The title compound was prepared following General Procedure B from allene **2j** (52.8 mg, 0.30 mmol) and 2-acetylphenylboronic acid (**1a**) (98.4 mg, 0.60 mmol). Purification by column chromatography (80% EtOAc/petroleum ether) gave **3aj** as a yellow oil (57 mg, 64%). R_f = 0.11 (80% EtOAc/petroleum ether); IR 3336 (br, OH), 2976, 2927, 1229, 1162, 1021, 952, 757, 537 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.45 (1H, m, Ar**H**), 7.46-7.41 (1H, m, Ar**H**), 7.35-7.26 (2H, m, Ar**H**), 5.70 (1H, dd, *J* = 5.7, 2.2 Hz, =C**H**$_a$H$_b$), 5.36 (1H, dd, *J* = 4.8, 2.1 Hz, =CH$_a$**H**$_b$), 4.25-4.11 (2H, m, OC**H**$_2$), 4.13-3.94 (2H, m, OC**H**$_2$), 3.93 (1H, s, O**H**), 3.41 (1H, dt, *J* = 24.7, 2.1 Hz, C**H**P), 1.65 (3H, d, *J* = 1.8 Hz, CC**H**$_3$), 1.34 (3H, t, *J* = 7.1 Hz, CH$_2$C**H**$_3$), 1.19 (3H, t, *J* = 7.0 Hz, CH$_2$C**H**$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.4 (d, *J* = 2.8 Hz, C), 142.5 (d, *J* = 8.1 Hz, C), 138.3 (d, *J* = 6.9 Hz, C), 129.6 (CH), 128.9 (CH), 123.3 (CH), 120.5 (CH), 107.8 (d, *J* = 7.3 Hz, CH_2), 79.9 (d, *J* = 4.7 Hz, C), 62.8 (d, *J* = 7.0 Hz, CH_2), 62.3 (d, *J* = 7.1 Hz, CH_2), 54.7 (d, *J* = 138.0 Hz, CH), 30.7 (d, *J* = 5.5 Hz, CH_3), 16.5 (d, *J* = 6.3 Hz, CH_3), 16.4 (d, *J* = 5.8 Hz, CH_3); ^{31}P NMR (202 MHz, $CDCl_3$) δ 25.5 (dt, *J* = 23.9, 7.8 Hz); HRMS (ESI) Exact mass calculated for $[C_{15}H_{24}PNaO_4]^+$ $[M+Na]^+$: 319.1070, found: 319.1067.



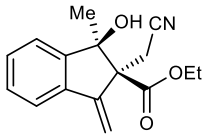
(±)-[(1*R*,2*S*)-1-Hydroxy-1-methyl-3-methylene-2,3-dihydro-1*H*-inden-2-yl]diphenylphosphine oxide (3ak). The title compound was prepared following General Procedure B from allene **2k** (72.1 mg, 0.30 mmol) and 2-acetylphenylboronic acid (**1a**) (98.4 mg, 0.60 mmol). Purification by column chromatography (80% EtOAc/petroleum ether) gave **3ak** as a pale yellow solid (76 mg, 70%). R_f = 0.19 (80% EtOAc/petroleum ether); m.p. 143-145 °C ($CHCl_3$/Et_2O); IR 3428 (br, OH), 2919, 1475, 1262, 1162, 1119, 782, 691, 500, 465 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (2H, ddt, *J* = 11.5, 6.5, 1.7 Hz, Ar**H**), 7.72-7.64 (2H, m, Ar**H**), 7.58-7.50 (3H, m, Ar**H**), 7.48-7.43 (1H, m, Ar**H**), 7.42-7.38 (4H, m, Ar**H**), 7.32-7.24 (2H, m, Ar**H**), 5.38 (1H, dd, *J* = 5.5, 1.7 Hz, =C**H**$_a$H$_b$), 4.64 (1H, br s, O**H**), 4.15 (1H, dd, *J* = 4.7, 1.7 Hz, =CH$_a$**H**$_b$), 3.97 (1H, dt, *J* = 10.3, 1.7 Hz, C**H**P), 1.62 (3H, d, *J* = 1.7 Hz, C**H**$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.3 (C), 142.6 (d, *J* = 7.2 Hz, C), 138.3 (d, *J* = 3.6 Hz, C), 134.1 (d, *J* = 99.0 Hz, C), 132.0 (d, *J* = 8.9 Hz, 2 × CH), 131.8 (d, *J* = 3.3 Hz, 2 × CH), 131.2 (d, *J* = 8.4 Hz, 2 × CH), 131.0 (d, *J* = 101.1 Hz, C), 129.7 (CH), 128.9-128.6 (m, 3 × CH), 128.2 (d, *J* = 12.5 Hz, 2 × CH), 123.1 (CH), 120.2 (CH), 108.5 (d, *J* = 7.3 Hz, CH_2), 81.9 (d, *J* = 4.6 Hz, C), 56.6 (d, *J* = 67.1 Hz, CH), 31.7 (d, *J* = 4.8 Hz, CH_3); ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.2; HRMS (ESI) Exact mass calculated for $[C_{23}H_{21}PNaO_2]^+$ $[M+Na]^+$: 383.1171, found: 383.1169.



(±)-(1*R*,2*S*)-1-Methyl-3-methylene-2-(phenylsulfonyl)-2,3-dihydro-1*H*-inden-1-ol (3al). The title compound was prepared following General Procedure B from allene **2l** (54.1 mg, 0.30 mmol) and 2-acetylphenylboronic acid (**1a**) (98.4 mg, 0.60 mmol). Purification by column chromatography (0-30% EtOAc/*n*-pentane) gave a mixture of **3al** and a small quantity of an unidentified, inseparable impurity (38.1 mg). By using 1,3,5-trimethoxybenzene as the internal standard, the yield of **3al** was determined by ^1H NMR analysis to be 36%. R_f = 0.10 (20% EtOAc/petroleum ether); IR 3469 (br, OH), 1447, 1305, 1153, 1133, 1083, 757, 729, 687, 521 cm^{-1}; ^1H NMR (400 MHz, CD_3CN) δ 7.90-7.85 (2H, m, Ar**H**), 7.67-7.61 (1H, m, Ar**H**), 7.56-7.47 (3H, m, Ar**H**), 7.37-7.26 (3H, m, Ar**H**), 5.83 (1H, d, *J* = 1.6 Hz, =C**H**$_a$H$_b$), 5.21 (1H, d, *J* = 1.6 Hz, =CH$_a$**H**$_b$), 4.57 (1H, t, *J* = 1.6 Hz, C**H**SO$_2$Ph), 3.83 (1H, s, O**H**), 1.42 (3H, s, C**H**$_3$); ^{13}C NMR (101 MHz, CD_3CN) δ 149.8 (C), 140.9 (C), 140.6 (C), 138.2 (C), 134.4 (CH), 130.5 (CH), 130.1 (2 × CH), 129.8 (CH), 129.5 (2 × CH), 123.8 (CH), 121.2 (CH), 113.3 (CH_2), 80.7 (C), 78.0 (CH), 31.5 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{17}H_{26}SNaO_3]^+$ $[M+Na]^+$: 323.0712, found: 323.0713.

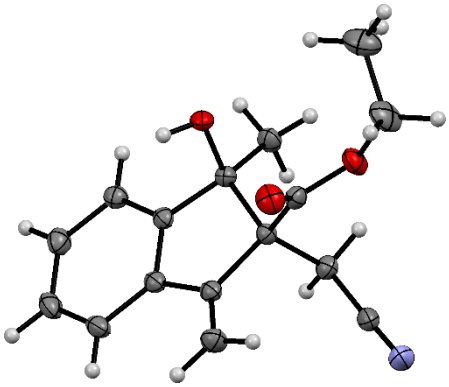


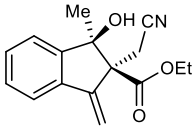
(±)-Ethyl (1*R*,2*S*)-1-hydroxy-1,2-dimethyl-3-methylene-2,3-dihydro-1*H*-indene-2-carboxylate (3am). The title compound was prepared following General Procedure B from allene **2m** (37.8 mg, 0.30 mmol) and 2-acetylphenylboronic acid (**1a**) (98.4 mg, 0.60 mmol). Purification by column chromatography (0-10% EtOAc/petroleum ether) gave **3am** as a colorless oil (37.9 mg, 51%). R_f = 0.33 (20% EtOAc/petroleum ether); IR 3423 (br, OH), 2981, 1702 (C=O), 1442, 1377, 1243, 1129, 1077, 882, 762 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.48-7.40 (2H, m, Ar**H**), 7.33 (1H, app td, *J* = 7.4, 1.3 Hz, Ar**H**), 7.32-7.23 (1H, m, Ar**H**), 5.63 (1H, s, =C**H**$_a$H$_b$), 5.20 (1H, s, =CH$_a$**H**$_b$), 4.16-4.02 (2H, m, OC**H**$_2$), 3.98 (1H, d, *J* = 0.9 Hz, O**H**), 1.54 (3H, s, CC**H**$_3$), 1.36 (3H, d, *J* = 0.8 Hz, CC**H**$_3$), 1.18 (3H, t, *J* = 7.1 Hz, CH$_2$C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8 (C), 150.01 (C), 149.96 (C), 137.3 (C), 129.6 (CH), 128.4 (CH), 122.6 (CH), 120.9 (CH), 106.4 (CH_2), 82.6 (C), 62.4 (C), 61.3 (CH_2), 25.7 (CH_3), 17.6 (CH_3), 14.0 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{15}H_{18}NaO_3]^+$ $[M+Na]^+$: 269.1148, found: 269.1151.



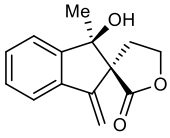
(±)-Ethyl (1*R*,2*S*)-2-(cyanomethyl)-1-hydroxy-1-methyl-3-methylene-2,3-dihydro-1*H*-indene-2-carboxylate (3an). The title compound was prepared following General Procedure B from **2n** (45.3 mg, 0.30 mmol) and 2-acetylphenylboronic acid (**1a**) (98.4 mg, 0.60 mmol). Purification by column chromatography (5-30% EtOAc/petroleum ether) gave **3an** as a white solid (49.7 mg, 61%). R_f = 0.14 (20% EtOAc/petroleum ether); m.p. 121-123 °C (Et_2O/*n*-pentane); IR 3430 (br, OH), 2252 (C≡N), 1724 (C=O), 1370, 1288, 1021, 898, 791, 772 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51-7.45 (1H, m, Ar**H**), 7.47-7.41 (1H, m, Ar**H**), 7.41-7.30 (2H, m, Ar**H**), 5.81 (1H, d, *J* = 1.2 Hz, =C**H**$_a$H$_b$), 5.31 (1H, d, *J* = 1.2 Hz, =CH$_a$**H**$_b$), 4.30-4.15 (2H, m, OC**H**$_2$), 3.31 (1H, br s, O**H**), 2.97 (1H, d, *J* = 16.7 Hz, C**H**$_a$H$_b$CN), 2.93 (1H, d, *J* = 16.7 Hz, CH$_a$**H**$_b$CN), 1.57 (3H, s, CC**H**$_3$), 1.24 (3H, t, *J* = 7.1 Hz, CH$_2$C**H**$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6 (C), 148.0 (C), 146.2 (C), 136.6 (C), 130.3 (CH), 129.3 (CH), 122.8 (CH), 121.2 (CH), 117.5 (C), 108.8 (CH_2), 82.7 (C), 63.3 (C), 62.4 (CH_2), 24.6 (CH_3), 21.9 (CH_2), 14.0 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{16}H_{17}NNaO_3]^+$ $[M+Na]^+$: 294.1101, found: 294.1102.

Slow evaporation of a solution of **3an** from Et_2O gave crystals that were suitable for X-ray crystallography:



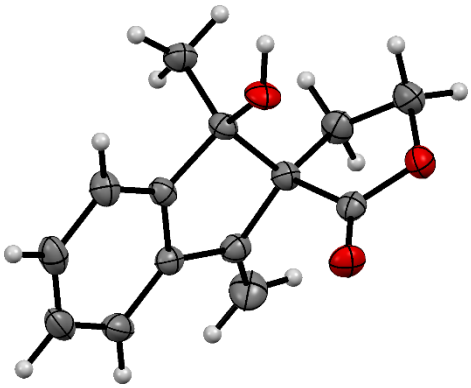


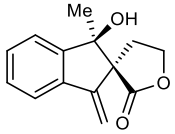
3an
CCDC 1858963



(±)-(1'*R*,3*S*)-1'-Hydroxy-1'-methyl-3'-methylene-1',3',4,5-tetrahydro-2*H*-spiro[furan-3,2'-inden]-2-one (3ao). The title compound was prepared following General Procedure B from allene **2o** (33.0 mg, 0.30 mmol) and 2-acetylphenylboronic acid (**1a**) (98.4 mg, 0.60 mmol). Purification by column chromatography (20-30% EtOAc/petroleum ether) gave **3ao** as a white solid (49.0 mg, 71%). R_f = 0.10 (20% EtOAc/petroleum ether); m.p. 110-111 °C ($CHCl_3$/Et_2O); IR 3410 (br, OH), 2969, 1738 (C=O), 1643, 1489, 1464, 1253, 1221, 1201, 1144, 1016, 931, 619, 503, 420 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.51-7.45 (2H, m, Ar**H**), 7.39 (1H, app t, *J* = 7.4 Hz, Ar**H**), 7.35-7.30 (1H, m, Ar**H**), 5.61 (1H, s, =C**H**$_a$H$_b$), 5.21 (1H, s, =CH$_a$**H**$_b$), 4.54-4.49 (2H, m, C**H**$_2$O), 3.26 (1H, s, O**H**), 2.81 (1H, app dt, *J* = 13.3, 9.5 Hz, C**H**$_a$H$_b$CH$_2$O), 2.53 (1H, ddd, *J* = 13.3, 5.7, 3.8 Hz, CH$_a$**H**$_b$CH$_2$O), 1.37 (3H, s, C**H**$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.2 (C), 149.1 (C), 148.1 (C), 136.9 (C), 130.3 (CH), 129.0 (CH), 122.9 (CH), 121.1 (CH), 104.9 (CH_2), 81.4 (C), 66.5 (CH_2), 63.4 (C), 28.9 (CH_2), 26.2 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{14}H_{14}NaO_3]^+$ $[M+Na]^+$: 352.0835, found: 352.0832.

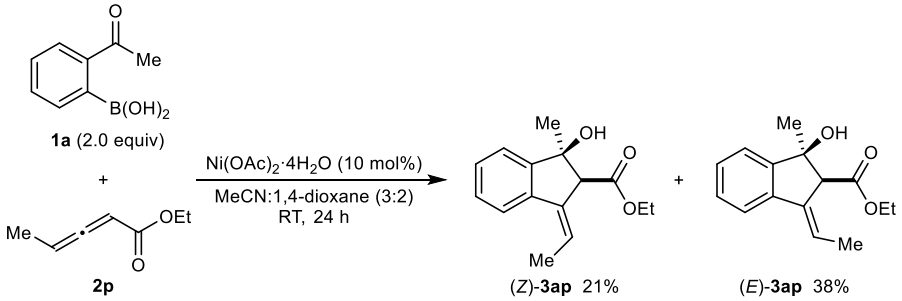
Slow evaporation of a solution of **3ao** in Et_2O/*n*-pentane gave crystals that were suitable for X-ray crystallography:





3ao
CCDC 1858964

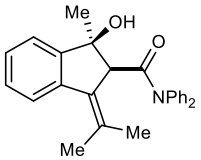
(±) Ethyl (1*S*,2*S*,*E*)-3-ethylidene-1-hydroxy-1-methyl-2,3-dihydro-1*H*-indene-2-carboxylate [(*E*)-3ap] and ethyl (1*S*,2*S*,*Z*)-3-ethylidene-1-hydroxy-1-methyl-2,3-dihydro-1*H*-indene-2-carboxylate [(*Z*)-3ap]



General Procedure B was followed using from allene **2p** (37.8 mg, 0.30 mmol) and 2-acetylphenylboronic acid (98.4 mg, 0.60 mmol). Purification by column chromatography (0-5% EtOAc/*n*-pentane) gave (*Z*)-**3ap** as a colorless oil (15.7 mg, 21%), followed by (*E*)-**3ap** as a colorless oil (28.3 mg, 38%).

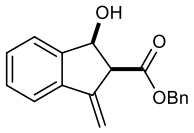
Data for (Z)-**3ap**: R_f = 0.15 (10% EtOAc/petroleum ether); IR 3057 (br, OH), 2975, 1713 (C=O), 1367, 1321, 1177, 1085, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59-7.54 (1H, m, Ar**H**), 7.49-7.45 (1H, m, Ar**H**), 7.33-7.29 (2H, m, Ar**H**), 5.88 (1H, qd, *J* = 7.3, 1.5 Hz, =C**H**), 4.17 (2H, qd, *J* = 7.2, 1.5 Hz, OC**H**$_2$CH$_3$), 3.77 (1H, d, *J* = 1.0 Hz, O**H**), 3.68 (1H, t, *J* = 1.4 Hz, C**H**C=O), 2.04 (3H, dd, *J* = 7.3, 1.3 Hz, =CC**H**$_3$), 1.54 (3H, s, C**H**$_3$COH), 1.27 (3H, t, *J* = 7.2 Hz, OCH$_2$C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0 (C), 151.3 (C), 137.6 (C), 136.5 (C), 128.6 (CH), 128.5 (CH), 124.8 (CH), 123.0 (CH), 121.9 (CH), 79.1 (C), 63.0 (CH), 61.1 (CH_2), 28.8 (CH_3), 14.9 (CH_3), 14.3 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{15}H_{18}NaO_3]^+$ $[M+Na]^+$: 269.1148, found: 269.1145.

Data for (E)-**3ap**: R_f = 0.14 (10% EtOAc/petroleum ether); IR 3493 (br, OH), 2926, 1715 (C=O), 1445, 1311, 1153, 1034, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46-7.33 (2H, m, Ar**H**), 7.28-7.22 (2H, m, Ar**H**), 6.18 (1H, qd, *J* = 7.1, 1.9 Hz, =C**H**), 4.24-4.12 (2H, m, OC**H**$_2$CH$_3$), 3.93-3.86 (1H, m, C**H**C=O), 3.32 (1H, br s, O**H**), 1.87 (3H, dd, *J* = 7.1, 1.0 Hz, =CC**H**$_3$), 1.55 (3H, s, C**H**$_3$COH), 1.27 (3H, t, *J* = 7.1 Hz, OCH$_2$C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.2 (C), 148.9 (C), 138.8 (C), 137.4 (C), 128.8 (CH), 128.6 (CH), 123.1 (CH), 120.0 (CH), 119.1 (CH), 80.4 (C), 61.1 (CH_2), 59.6 (CH), 29.6 (CH_2), 15.2 (CH_3), 14.3 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{15}H_{18}NaO_3]^+$ $[M+Na]^+$: 269.1148, found: 269.1150.

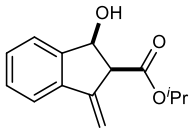


(±)-(1*S*,2*S*)-1-Hydroxy-1-methyl-*N*,*N*-diphenyl-3-(propan-2-ylidene)-2,3-dihydro-1*H*-indene-2-carboxamide (3aq). The title compound was prepared following General Procedure B from allene **2q** (79.0 mg, 0.30 mmol) and 2-

acetylphenylboronic acid (**1a**) (98.4 mg, 0.60 mmol). Purification by column chromatography (0-20% EtOAc/petroleum ether) gave **3aq** as a white solid (35.8 mg, 31%). R_f = 0.18 (20% EtOAc/petroleum ether); m.p. 120-122 °C (Et_2O/*n*-pentane); IR 3433 (br, OH), 2921, 1676, 1658, 1490, 1348, 1295, 1236, 1091, 947, 753, 703, 691, 603 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.62-7.52 (2H, m, Ar**H**), 7.52-7.45 (2H, m, Ar**H**), 7.44-7.35 (2H, m, Ar**H**), 7.35-7.23 (4H, m, Ar**H**), 7.23-7.13 (4H, m, Ar**H**), 4.04 (1H, s, C**H**C=O), 3.01 (1H, s, O**H**), 2.11 (3H, s, =C(C**H**$_3$)$_2$), 1.88 (3H, s, =C(C**H**$_3$)$_2$), 1.43 (3H, s, HOCC**H**$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3 (C), 151.3 (C), 143.0 (C), 142.8 (C), 140.2 (C), 133.8 (C), 129.7 (CH), 129.3 (CH), 128.9 (CH), 128.3 (2 × CH), 128.0 (CH), 127.2 (2 × CH), 126.9 (CH), 126.4 (CH), 124.4 (2 × CH), 122.6 (2 × CH), 80.5 (C), 61.2 (CH), 28.8 (CH_3), 24.6 (CH_3), 22.0 (CH_3); HRMS (ESI) Exact mass calculated for $[C_{26}H_{25}NNaO_2]^+$ $[M+Na]^+$: 406.1777, found: 406.1782.

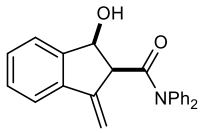


(±)-Benzyl (1*S*,2*S*)-1-hydroxy-3-methylene-2,3-dihydro-1*H*-indene-2-carboxylate (3ba). The title compound was prepared following General Procedure B from **2a** (52.3 mg, 0.30 mmol) and 2-formylphenylboronic acid (**1b**) (90.0 mg, 0.60 mmol). Purification by column chromatography (20% EtOAc/petroleum ether) gave **3ba** as a yellow oil (71.9 mg, 86%). R_f = 0.33 (20% EtOAc/petroleum ether); IR 3448 (br, OH), 3032, 2956, 1716, 1643, 1319, 1242, 1153, 739, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56-7.47 (2H, m, Ar**H**), 7.42-7.30 (7H, m, Ar**H**), 5.67 (1H, d, *J* = 1.9 Hz, =C**H**$_a$H$_b$), 5.44 (1H, dd, *J* = 9.9, 7.1 Hz, C**H**OH), 5.30 (1H, d, *J* = 1.9 Hz, =CH$_a$**H**$_b$), 5.20 (2H, s, OC**H**$_2$Ph), 4.14 (1H, dt, *J* = 7.1, 1.9 Hz, C**H**C=O), 3.31 (1H, d, *J* = 9.9 Hz, O**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5 (C), 145.7 (C), 144.6 (C), 138.9 (C), 135.6 (C), 129.7 (CH), 129.2 (CH), 128.8 (2 × CH), 128.5 (CH), 128.3 (2 × CH), 125.1 (CH), 121.0 (CH), 107.5 (CH_2), 74.4 (CH), 67.1 (CH_2), 54.6 (CH); HRMS (ESI) Exact mass calculated for $[C_{18}H_{16}O_3Na]^+$ $[M+Na]^+$: 303.0992, found: 303.0992.

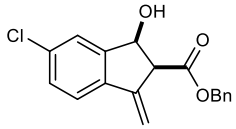


(±)-Isopropyl (1*S*,2*S*)-1-hydroxy-3-methylene-2,3-dihydro-1*H*-indene-2-carboxylate (3bd). The title compound was prepared following General Procedure B from allene **2d** (37.9 mg, 0.30 mmol) and 2-formylphenylboronic acid (**1b**) (90.0 mg, 0.60 mmol). Purification by column chromatography (0-20% EtOAc/petroleum ether) gave **3bd** as a yellow oil (62.1 mg, 89%). R_f = 0.30 (20% EtOAc/petroleum ether); IR 3449 (br, OH), 2980, 1706 (C=O), 1464, 1373, 1254, 1174, 1062, 910, 760, 731 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.53-7.48 (2H, m, Ar**H**), 7.36-7.30 (2H, m, Ar**H**), 5.66 (1H, d, *J* = 2.0 Hz, =C**H**$_a$H$_b$), 5.38 (1H, dd, *J* = 10.0, 7.0 Hz, C**H**OH), 5.30 (1H, d, *J* = 2.0 Hz, =CH$_a$**H**$_b$), 5.08 (1H, sept, *J* = 6.2 Hz, C**H**(CH_3)$_2$), 4.01 (1H, dt, *J* = 7.0, 2.0 Hz, C**H**C=O), 3.64 (1H, d, *J* = 10.0 Hz, O**H**), 1.29 (3H, d, *J* = 6.3 Hz, CH(C**H**$_3$)$_2$), 1.26 (3H, d, *J* = 6.3 Hz, CH(C**H**$_3$)$_2$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4 (C),

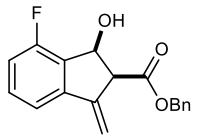
146.0 (C), 145.0 (C), 138.8 (C), 129.5 (CH), 129.0 (CH), 125.0 (CH), 120.8 (CH), 106.9 (CH_2), 74.2 (CH), 68.8 (CH), 54.3 (CH), 21.9 (CH_3), 21.8 (CH_3); HRMS (ESI) Exact mass calculated for $C_{14}H_{16}NO_3$ $[M+Na]^+$: 255.0992, found: 255.0998.



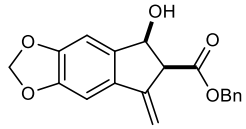
(±)-(1*S*,2*S*)-1-Hydroxy-3-methylene-*N*,*N*-diphenyl-2,3-dihydro-1*H*-indene-2-carboxamide (3bg). The title compound was prepared following General Procedure B using allene **2g** (71.0 mg, 0.30 mmol) and 2-formylphenylboronic acid (**1b**) (90.0 mg, 0.60 mmol). Purification by column chromatography (0-30% EtOAc/petroleum ether) gave **3bg** as a white solid (77.2 mg, 75%). R_f = 0.15 (20% EtOAc/petroleum ether); m.p. 167-170 °C ($CHCl_3$/Et_2O); IR 3470 (br, OH), 2981, 1707 (C=O), 1465, 1374, 1175, 1102, 910, 729 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) 7.52-7.46 (6H, m, Ar**H**), 7.47-7.37 (1H, m, Ar**H**), 7.37-7.29 (5H, m, Ar**H**), 7.20 (1H, t, *J* = 7.4 Hz, Ar**H**), 5.65 (1H, d, *J* = 2.0 Hz, =C**H**$_a$H$_b$), 5.25 (1H, t, *J* = 7.9 Hz, C**H**OH), 5.14 (1H, d, *J* = 2.0 Hz, =CH$_a$**H**$_b$), 4.36-4.31 (1H, m, C**H**C=O), 3.68-3.62 (1H, m, O**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.2 (C), 147.6 (C), 146.6 (C), 142.9 (C), 142.4 (C), 139.4 (C), 130.2 (2 × CH), 129.5 (CH), 129.1 (2 × CH), 128.9 (2 × CH), 128.8 (2 × CH), 128.3 (CH), 126.6 (CH), 125.1 (CH), 120.8 (CH), 106.0 (CH_2), 74.9 (CH), 52.6 (CH); HRMS (ESI) Exact mass calculated for $[C_{23}H_{20}NO_2]^+$ $[M+H]^+$: 342.1489, found: 342.1488.



(±)-Benzyl (1*S*,2*S*)-5-chloro-3-hydroxy-1-methylene-2,3-dihydro-1*H*-indene-2-carboxylate (3ca). The title compound was prepared following General Procedure B from allene **2a** (52.3 mg, 0.30 mmol) and 4-chloro-2-formylphenylboronic acid (**1c**) (110.6 mg, 0.60 mmol). Purification by column chromatography (20% EtOAc/petroleum ether) gave **3ca** as a yellow oil (28 mg, 30%). R_f = 0.38 (20% EtOAc/petroleum ether); IR 3334 (br, OH), 1712 (C=O), 1386, 1312, 1238, 1130, 913, 732, 697 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.49-7.47 (1H, m, Ar**H**), 7.41 (1H, d, *J* = 8.2 Hz, Ar**H**), 7.39-7.32 (5H, m, Ar**H**), 7.29 (1H, dd, *J* = 8.2, 2.0 Hz, Ar**H**), 5.63 (1H, d, *J* = 1.8 Hz, =C**H**$_a$H$_b$), 5.38 (1H, dd, *J* = 10.3, 7.1 Hz, C**H**OH), 5.30 (1H, d, *J* = 1.8 Hz, =CH$_a$**H**$_b$), 5.18 (2H, s, C**H**$_2$Ph), 4.13 (1H, dt, *J* = 7.1, 2.0 Hz, C**H**C=O), 3.43 (1H, d, *J* = 10.3 Hz, O**H**); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3 (C), 147.5 (C), 143.5 (C), 137.3 (C), 135.41 (C), 135.44 (C), 129.6 (CH), 128.8 (CH), 128.6 (CH), 128.36 (CH), 125.3 (CH), 122.2 (CH), 108.1 (CH_2), 73.9 (CH), 67.2 (CH_2), 54.7 (CH); HRMS (ESI) Exact mass calculated for $[C_{18}H_{15}ClNaO_3]^+$ $[M+Na]^+$: 337.0602, found: 337.0600.



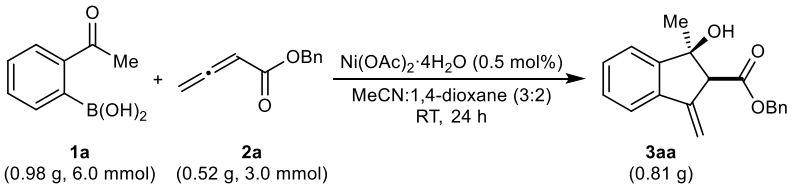
(±)-Benzyl (1*S*,2*S*)-4-fluoro-3-hydroxy-1-methylene-2,3-dihydro-1*H*-indene-2-carboxylate (3da). The title compound was prepared following General Procedure B from allene **2a** (52.3 mg, 0.30 mmol) and (3-fluoro-2-formylphenyl)boronic acid (**1d**) (100.8 mg, 0.60 mmol). Purification by column chromatography (20% EtOAc/petroleum ether) gave **3da** as a yellow oil (52 mg, 58%). R_f = 0.28 (20% EtOAc/petroleum ether); IR 3426 (br, OH), 2920, 1713 (C=O), 1498, 1256, 1163, 997, 746, 699, 594 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42-7.30 (7H, m, Ar**H**), 7.08-6.96 (1H, m, Ar**H**), 5.76 (1H, d, *J* = 2.4 Hz, =C**H**$_a$H$_b$), 5.67 (1H, app t, *J* = 7.4 Hz, C**H**OH), 5.38 (1H, d, *J* = 2.4 Hz, =CH$_a$**H**$_b$), 5.27-5.22 (2H, m, C**H**$_2$Ph), 4.10 (1H, dt, *J* = 6.9, 2.4 Hz, C**H**C=O), 3.23 (1H, d, *J* = 8.0 Hz, O**H**); ^{13}C NMR (126 MHz, $CDCl_3$) 170.9 (C), 160.2 (d, *J* = 251.5 Hz, CF), 143.8 (d, *J* = 3.5 Hz, C), 142.7 (d, *J* = 4.6 Hz, C), 135.6 (C), 131.4 (d, *J* = 7.3 Hz, CH), 131.0 (d, *J* = 16.4 Hz, C), 128.8 (2 × CH), 128.6 (CH), 128.5 (2 × CH), 116.9 (d, *J* = 3.6 Hz, CH), 116.0 (d, *J* = 20.0 Hz, CH), 109.3 (CH_2), 71.6 (CH), 67.2 (CH_2), 54.2 (CH); ^{19}F NMR (376 MHz, $CDCl_3$) δ −119.41; HRMS (ESI) Exact mass calculated for $[C_{18}H_{15}O_3FNa]^+$ $[M+Na]^+$: 321.0897, found: 321.0893.



(±)-Benzyl (1*S*,2*S*)-5-hydroxy-7-methylene-6,7-dihydro-5*H*-indeno[5,6-d][1,3]dioxole-6-carboxylate (3ea). The title compound was prepared following General Procedure B from allene **2a** (52.3 mg, 0.30 mmol) and (6-formylbenzo[*d*][1,3]dioxol-5-yl)boronic acid (**1e**) (116.4 mg, 0.60 mmol). Purification by column chromatography (20% EtOAc/petroleum ether) gave **3ea** as a yellow oil (46 mg, 48%). R_f = 0.20 (20% EtOAc/petroleum ether); IR 3492 (br, OH), 3339, 2922, 1721 (C=O), 1499, 1382, 1161, 1067, 863, 729 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.32 (5H, m, Ar**H**), 6.96-6.83 (2H, m, Ar**H**), 6.00 (2H, s, OC**H**$_2$O), 5.42 (1H, d, *J* = 1.8 Hz, =C**H**$_a$H$_b$), 5.35-5.26 (1H, m, C**H**OH), 5.20 (2H, s, C**H**$_2$Ph), 5.14 (1H, d, *J* = 1.8 Hz, =CH$_a$**H**$_b$), 4.18-4.02 (1H, m, C**H**C=O), 3.27 (1H, d, *J* = 10.4 Hz, O**H**); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6 (C), 149.7 (C), 149.4 (C), 144.2 (C), 140.4 (C), 135.6 (C), 133.3 (C), 128.8 (2 × CH), 128.5 (CH), 128.4 (2 × CH), 110.1 (C), 105.0 (CH_2), 104.9 (CH), 101.8 (CH_2), 100.7 (CH), 73.9 (CH), 67.1 (CH_2), 54.9 (CH); HRMS (ESI) Exact mass calculated for $[C_{19}H_{16}O_5Na]^+$ $[M+Na]^+$: 347.0890, found: 347.0889.

Preparation of 3aa on a 3.00 mmol Scale

(±)-(1*S*,2*S*)-Benzyl 1-hydroxy-1-methyl-3-methylene-2,3-dihydro-1*H*-indene-2-carboxylate (*ent*-3aa)

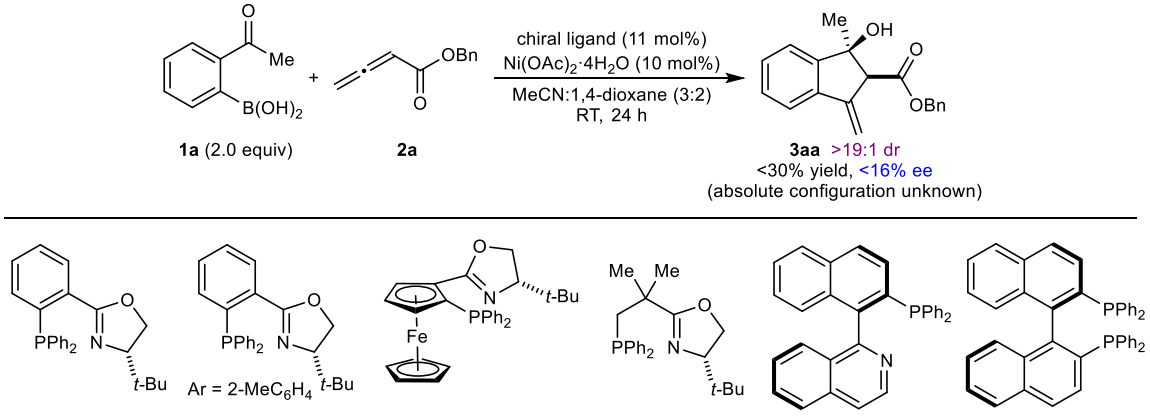


A flask was charged with allene **2a** (523 mg, 3.00 mmol), 2-acetylphenylboronic acid (**1a**) (984 mg, 6.00 mmol), and $Ni(OAc)_2·4H_2O$ (3.8 mg, 0.015 mmol). The flask was sealed with a rubber septum and purged with argon. Degassed MeCN (18 mL) and degassed 1,4-dioxane (12 mL) were added and the resulting solution was stirred at room temperature for 24 h, diluted with Et_2O (*ca.* 30 mL), filtered through a plug of silica gel using Et_2O as the eluent, and concentrated in *vacuo*. Purification of the residue by column chromatography (10% EtOAc/petroleum ether) gave **3aa** as a pale yellow oil (810 mg, 92%). For the characterization data of **3aa**, see page 6.

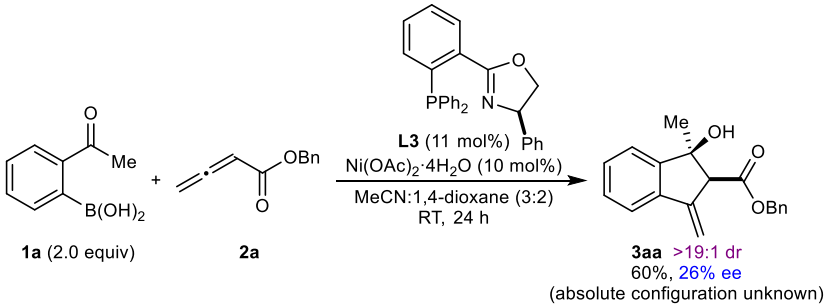
Investigations into Developing an Enantioselective Reaction

First, a range of chiral ligands were evaluated in the reaction between **1a** and **2a** under our standard reaction conditions (Table S1). Unfortunately, all gave low yields (< *ca.* 30% by ^{1}H NMR analysis) and enantioselectivities (0–16% ee).

Table S1

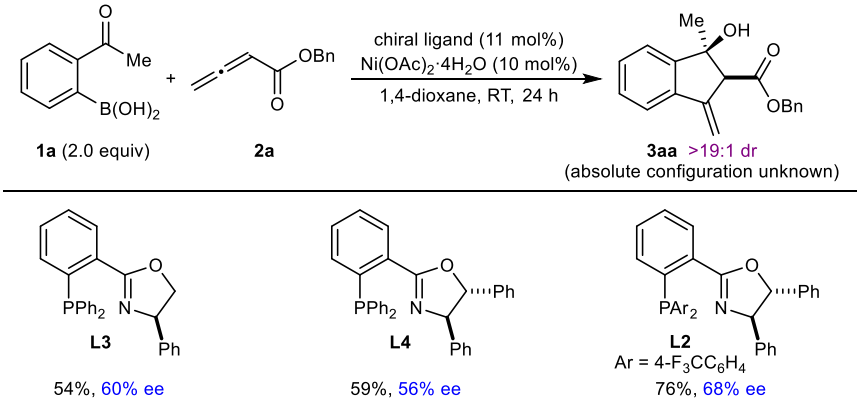


However, (*R*)-Ph-Phox (**L3**) gave **3aa** in 60% NMR yield and 26% ee:



Furthermore, replacing the mixed solvent system with 1,4-dioxane led to improved results (Table S2). Evaluation of derivatives of **L3** (ligands **L4** and **L2**) led to the finding that **L2** gives **3aa** in 68% ee .

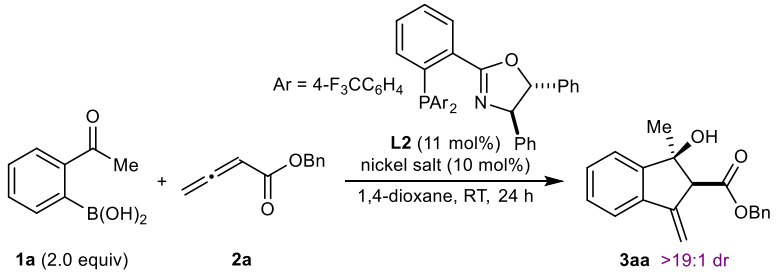
Table S2



(All yields determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard)

Finally, the nickel salt was varied and nickel trifluoroacetate was found to give the best results (Table S3).

Table S3

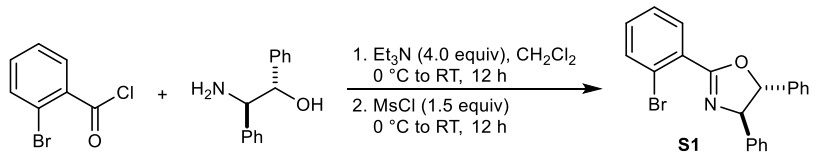


$Ni(OAc)_2·4H_2O$	$Ni(OTf)_2$	$Ni(O_2CCF_3)_2·4H_2O$	$Ni(acac)_2$	$NiCl_2·6H_2O$	$Ni(NO_3)_2·6H_2O$	$NiBr_2·DME$
76%, 68% ee	80%, 64% ee	73%, 74% ee	79%, 10% ee	71%, 22% ee	83%, 66% ee	62%, 70% ee

(All yields determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard)

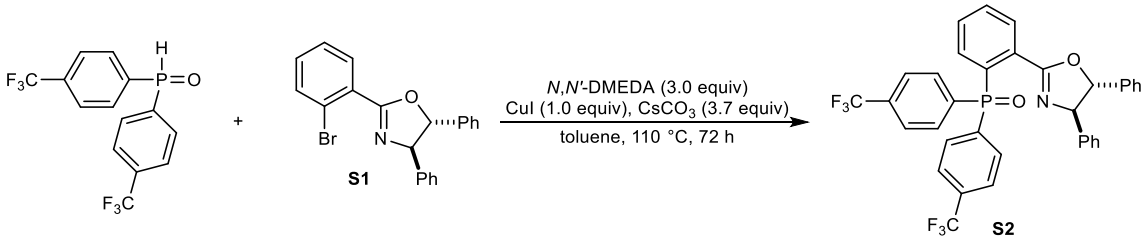
Preparation of Ligand L2

(4*R*,5*R*)-2-(2-Bromophenyl)-4,5-diphenyl-4,5-dihydrooxazole (S1)



To a solution of (1*S*,2*R*)-2-amino-1,2-diphenylethanol (1.66 g, 7.78 mmol) and Et_3N (4.34 mL, 31.1 mmol) in CH_2Cl_2 (40 mL) at 0 °C was added 2-bromobenzoyl chloride (1.12 mL, 8.56 mmol) dropwise, and the resulting solution was warmed to room temperature and stirred overnight. The suspension was then cooled to 0 °C and MsCl (0.88 mL, 11.7 mmol) was added dropwise. The solution was warmed to room temperature and stirred overnight, quenched with saturated aqueous NH_4Cl solution (50 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (20% EtOAc/petroleum ether) gave the title compound as a pale yellow oil (1.36 g, 47%). R_f = 0.27 (20% EtOAc/petroleum ether); $[\alpha]_D^{22}$ +16.0 (*c* 1.00, $CHCl_3$); IR 1647, 1493, 1321, 1259, 1025, 957, 913, 759, 733, 693, 542 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (1H, dt, *J* = 7.6, 1.3 Hz, Ar**H**), 7.72 (1H, dd, *J* = 7.9, 1.3 Hz, Ar**H**), 7.45-7.32 (12H, m, Ar**H**), 5.43 (1H, dd, *J* = 8.0, 1.1 Hz, C**H**Ph), 5.31 (1H, dd, *J* = 8.0, 1.4 Hz, C**H**Ph); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7 (C), 141.8 (C), 140.2 (C), 134.2 (CH), 132.1 (CH), 131.8 (CH), 129.7 (CH), 129.1 (2 × CH), 129.0 (2 × CH), 128.7 (CH), 128.0 (CH), 127.4 (CH), 126.9 (2 × CH), 126.1 (2 × CH), 122.2 (C), 89.6 (CH), 79.3 (CH); HRMS (ESI) Exact mass calculated for $[C_{21}H_{17}NOBr]^+$ $[M+H]^+$: 378.0488, found: 378.0484.

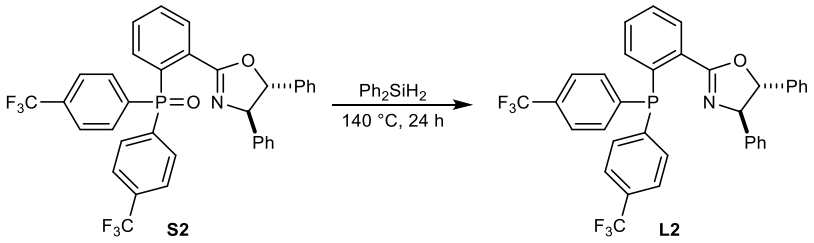
{2-[(4*R*,5*R*)-4,5-diphenyl-4,5-dihydrooxazol-2-yl]phenyl}bis[4-(trifluoromethyl)phenyl] phosphine oxide (S2)



A schlenk flask was evacuated and back filled with argon (3 cycles). Under a flow of argon, CuI (389 mg, 2.04 mmol) and bis[4-(trifluoromethyl)phenyl]phosphine oxide[15] (900 mg, 2.65 mmol) were added followed by toluene (7 mL) and *N*,*N*′-dimethylethylenediamine (0.66 mL, 6.13 mmol). A solution of aryl bromide **S1** (773 mg, 2.04 mmol) in toluene (2 mL) was added followed by Cs_2CO_3 (2.46 g, 7.56 mmol). The schlenk flask was then sealed with a rubber septum and PTFE

tape, and the resulting suspension was stirred at 110 °C for 72 h, filtered over celite, concentrated *in vacuo* and absorbed onto silica gel. Purification by column chromatography (20-60% EtOAc/petroleum ether) gave the title compound as a pale yellow solid (456 mg, 35%). R_f = 0.18 (50% EtOAc/petroleum ether); $[\alpha]_D^{23}$ −4.0 (*c* 1.00, $CHCl_3$); m.p. 78-80 °C ($CHCl_3$); IR 1658, 1398, 1319, 1166, 1124, 1105, 1060, 1016, 833, 710, 697, 565, 548 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.18 (1H, ddd, *J* = 7.8, 4.1, 1.3 Hz, Ar**H**), 7.86-7.70 (7H, m, Ar**H**), 7.67-7.60 (5H, m, Ar**H**), 7.31-7.27 (5H, m, Ar**H**), 7.08 (2H, dd, *J* = 7.4, 2.2 Hz, Ar**H**), 6.99-6.96 (2H, m, Ar**H**), 5.13 (1H, d, *J* = 10.0 Hz, C**H**Ph), 4.82 (1H, d, *J* = 10.0 Hz, C**H**Ph); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.5 (d, $J_{C\text{-}P}$ = 2.7 Hz, C), 140.5 (2 × C), 138.6 (d, $J_{C\text{-}P}$ = 108.6 Hz, C), 138.5 (2 × C), 137.2 (d, $J_{C\text{-}P}$ = 107.2 Hz, C), 135.3 (d, $J_{C\text{-}P}$ = 10.2 Hz, CH), 133.8-133.1 (m, C), 132.9 (d, $J_{C\text{-}P}$ = 2.7 Hz, CH), 132.6 (d, $J_{C\text{-}P}$ = 10.1 Hz, 2 × CH), 131.7 (d, $J_{C\text{-}P}$ = 10.7 Hz, 2 × CH), 131.6 (d, $J_{C\text{-}P}$ = 8.9 H, CH), 131.2 (d, $J_{C\text{-}P}$ = 12.3 Hz, CH), 131.0 (d, $J_{C\text{-}P}$ = 100.9 Hz, C), 128.8 (4 × CH), 128.7 (CH), 127.9 (CH), 127.0 (2 × CH), 126.2 (2 × CH), 125.3 (dq, *J* = 12.2, *J* = 3.8 Hz, 4 × CH), 127.0-119.6 (m, 2 × C), 89.6 (CH), 78.2 (CH); ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.3 (d, *J* = 12.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.08, –63.14; HRMS (ESI) Exact mass calculated for $[C_{35}H_{24}O_2F_6NPNa]^+$ $[M+Na]^+$: 658.1341, found: 658.1317.

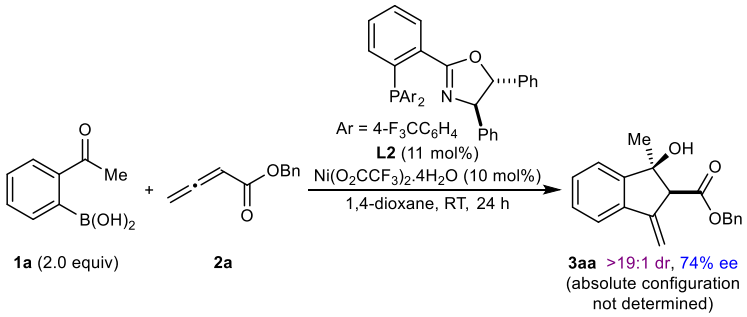
(4*R*,5*R*)-2-(2-{bis[4-(trifluoromethyl)phenyl]phosphanyl}phenyl)-4,5-diphenyl-4,5-dihydrooxazole (L2)



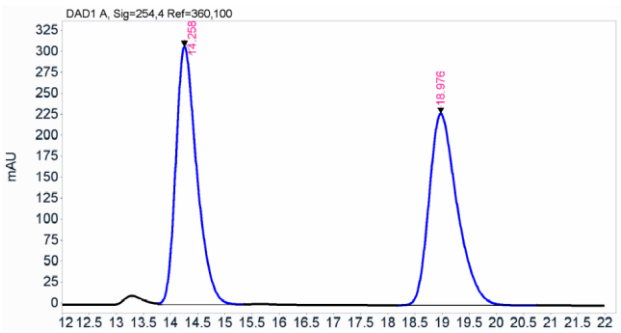
In a schlenk flask, a solution of phosphine oxide **S2** (450 mg, 0.71 mmol) and Ph_2SiH_2 (0.92 mL, 4.96 mmol) under argon was stirred at 140 °C for 24 h and cooled to room temperature. The mixture was absorbed onto silica gel and purified by column chromatography (0-10% EtOAc/petroleum ether) to give the title compound as a white solid (411 mg, 93%). R_f = 0.45 (20% EtOAc/petroleum ether); $[\alpha]_D^{22}$ −8.0 (*c* 1.00, $CHCl_3$); m.p 168-170 °C (*n*-hexane); IR 3069, 2130, 1428, 1323, 1167, 1115, 1059, 1016, 997, 816, 732, 696, 494 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.17 (1H, ddd, *J* = 7.8, 3.9, 1.4 Hz, Ar**H**), 7.59 (2H, d, *J* = 7.9 Hz, 2 × Ar**H**), 7.57-7.46 (3H, m, Ar**H**), 7.45-7.32 (9H, m, Ar**H**), 7.25-7.15 (4H, m, Ar**H**), 6.92 (1H, ddd, *J* = 7.8, 3.9, 1.2 Hz, Ar**H**), 6.84-6.80 (2H, m, Ar**H**), 5.18 (2H, s, 2 × C**H**Ph); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.8 (d, $J_{C\text{-}P}$ = 3.7 Hz, C), 143.2 (d, $J_{C\text{-}P}$ = 4.5 Hz, C), 143.1 (C), 141.4 (C), 139.8 (C), 137.8 (d, $J_{C\text{-}P}$ = 25.9 Hz, C), 134.8 (d, $J_{C\text{-}P}$ = 21.6 Hz, 2 × CH), 134.3 (CH), 133.9 (d, $J_{C\text{-}P}$ = 20.1 Hz, 2 × CH), 131.4 (CH),

131.32-130.84 (m, 2 × C), 130.7 (d, $J_{C\text{-}P}$ = 3.4 Hz, CH), 129.1 (CH), 129.0 (2 × CH), 128.7 (CH), 128.6 (2 × CH), 127.6 (CH), 126.5 (2 × CH), 126.3 (2 × CH), 125.5 (app ddd, J = 10.6, 7.1, 3.7 Hz, 4 × CH), 127.6-120.8 (m, 2 × C), 89.0 (CH), 79.1 (CH); ^{31}P NMR (162 MHz, $CDCl_3$) δ −7.29; ^{19}F NMR (376 MHz, $CDCl_3$) δ −62.6, −62.8; HRMS (ESI) Exact mass calculated for $[C_{35}H_{25}OF_6NP]^+$ $[M+H]^+$: 620.1572, found: 620.1579.

Enantioselective Reaction



A flask was charged with $Ni(O_2CCF_3)_2{\cdot}4H_2O$ (10.7 mg, 0.03 mmol) and **L2** (20.4 mg, 0.032 mmol). The flask was sealed with a rubber septum and purged with argon. Degassed 1,4-dioxane (0.60 mL) was added and the resulting suspension was stirred at 80 °C for 30 min before being cooled to room temperature. A solution of allene **2a** (52.3 mg, 0.30 mmol) and 2-acetylphenylboronic acid (**1a**) (98.4 mg, 0.60 mmol) in 1,4-dioxane (2.4 mL) was added and the resulting solution was stirred at room temperature for 24 h. The reaction was diluted with Et_2O (*ca.* 3 mL), filtered through a plug of silica gel using as Et_2O as the eluent, and concentrated *in vacuo*. Purification of the residue by column chromatography (10% EtOAc/*n*-pentane) gave the title compound as a pale yellow oil (67.5 mg, 76%). For the characterization data of **3aa**, see page 6 $[\alpha]_D^{21}$ −20.0 (*c* 1.00, $CHCl_3$). Enantiomeric excess was determined by HPLC with Chiralpak AD-H column (90:10 *iso*-hexane:EtOH, 1.0 mL/min, 254 nm, 25 °C); t_r (major) = 14.2 min, t_r (minor) = 18.9 min, 74% ee.



Signal: DAD1 A, Sig=254,4 Ref=360,100

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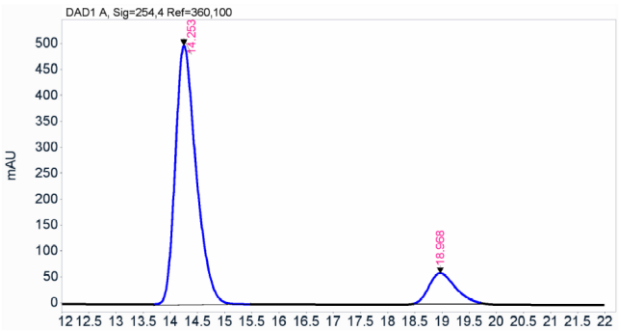
18.976	BB	0.5418	8215.963	228.3300	49.95



Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
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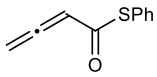
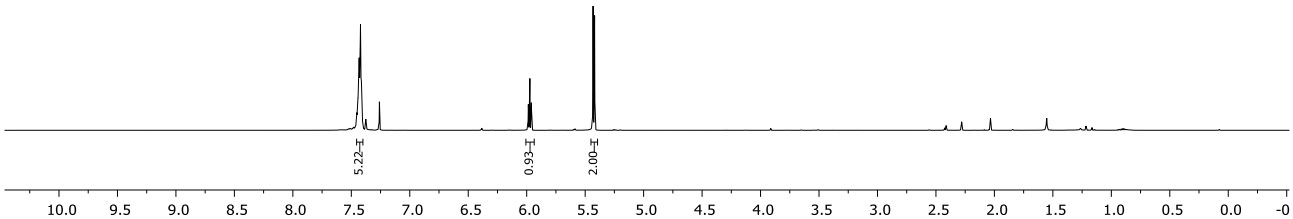
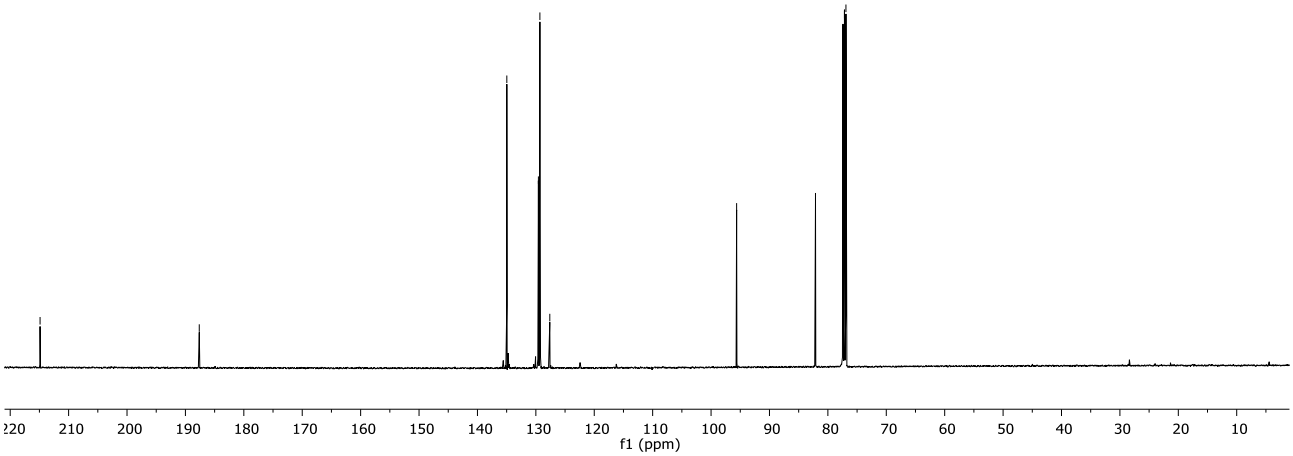
18.968	MM	0.5699	2037.808	59.5966	13.23

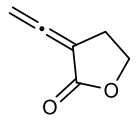
NMR Spectra



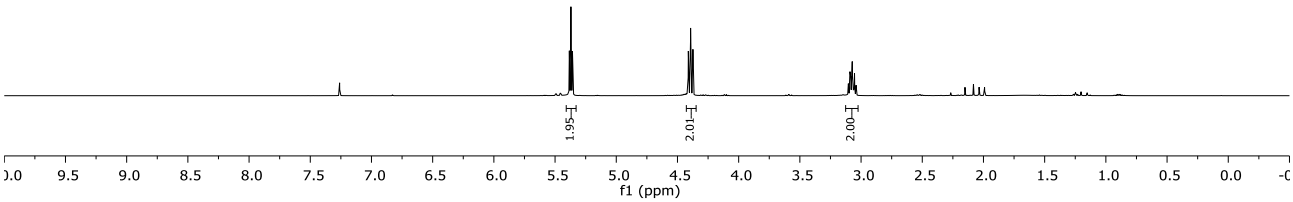
2h

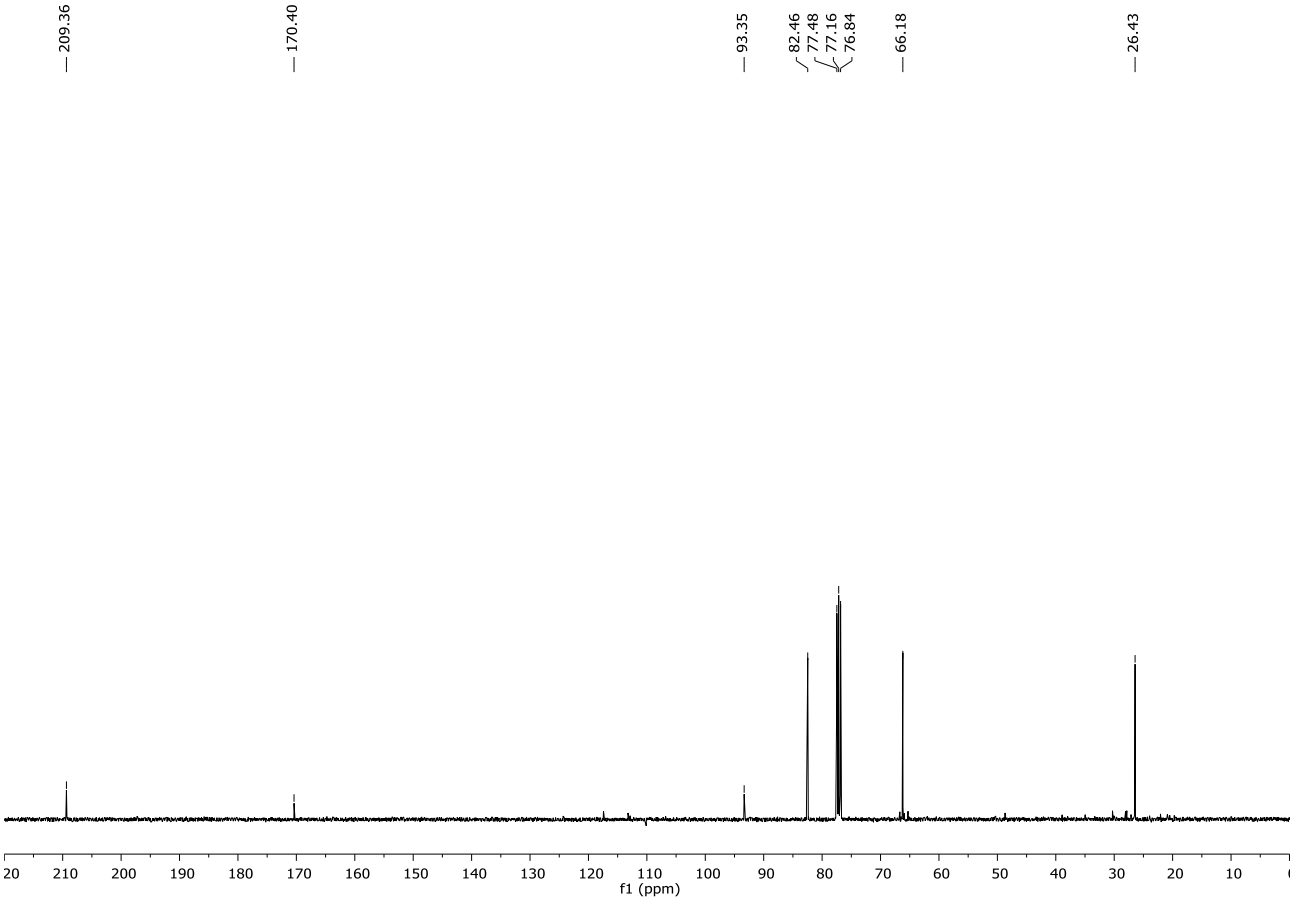


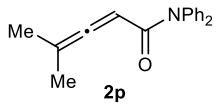




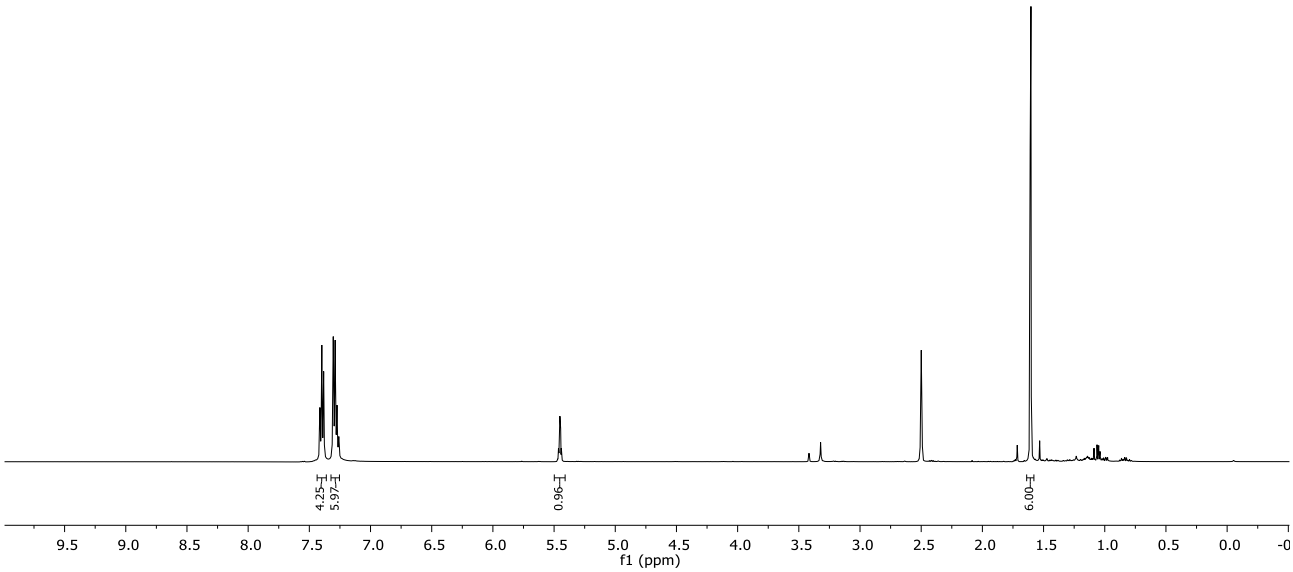
2o

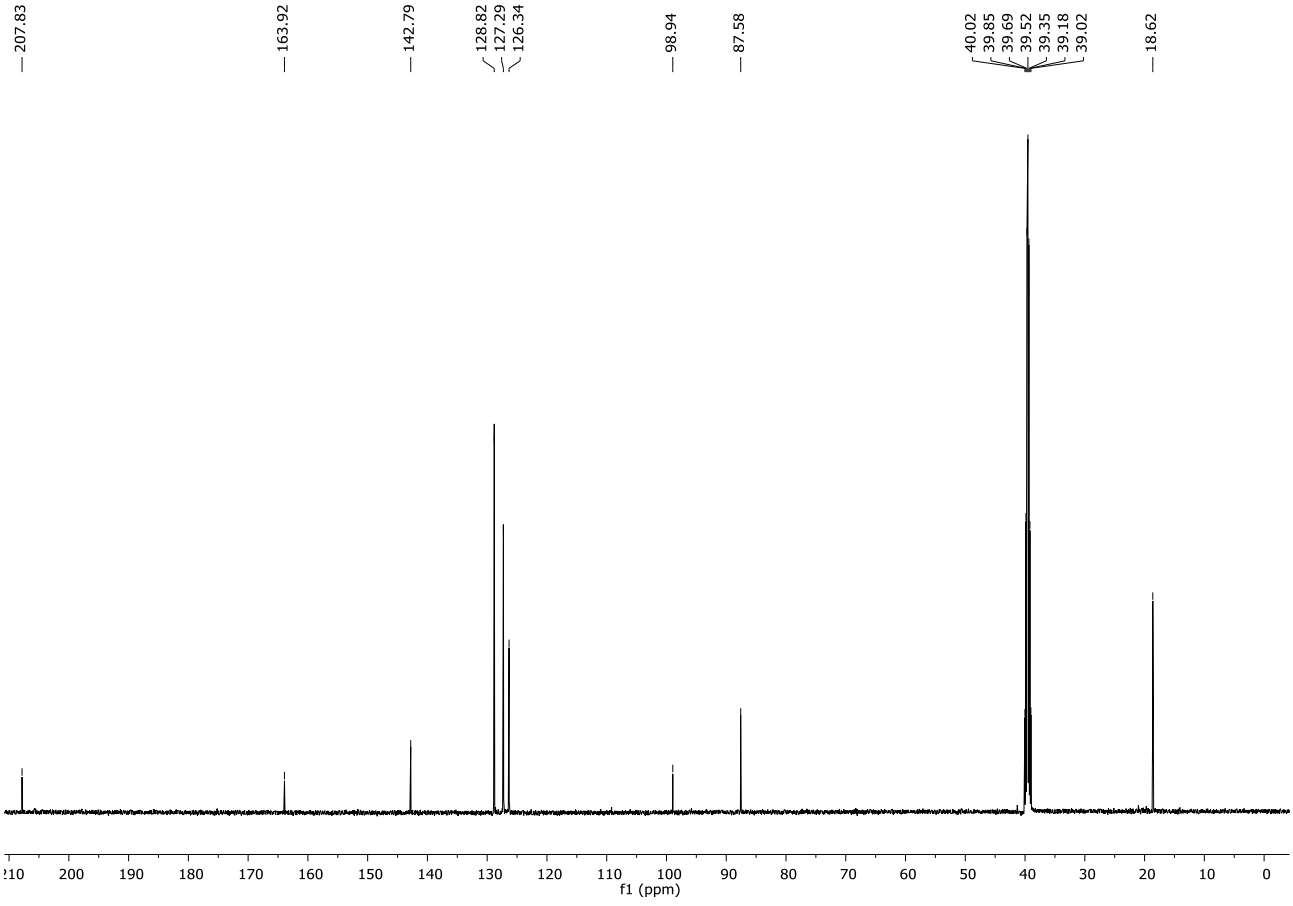

1.95
2.01
2.00
f1 (ppm)

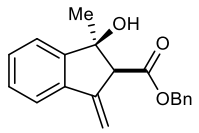

209.36
170.40
93.35
82.46
77.48
77.16
76.84
66.18
26.43
f1 (ppm)


Me
NPh2
O
Me

2p

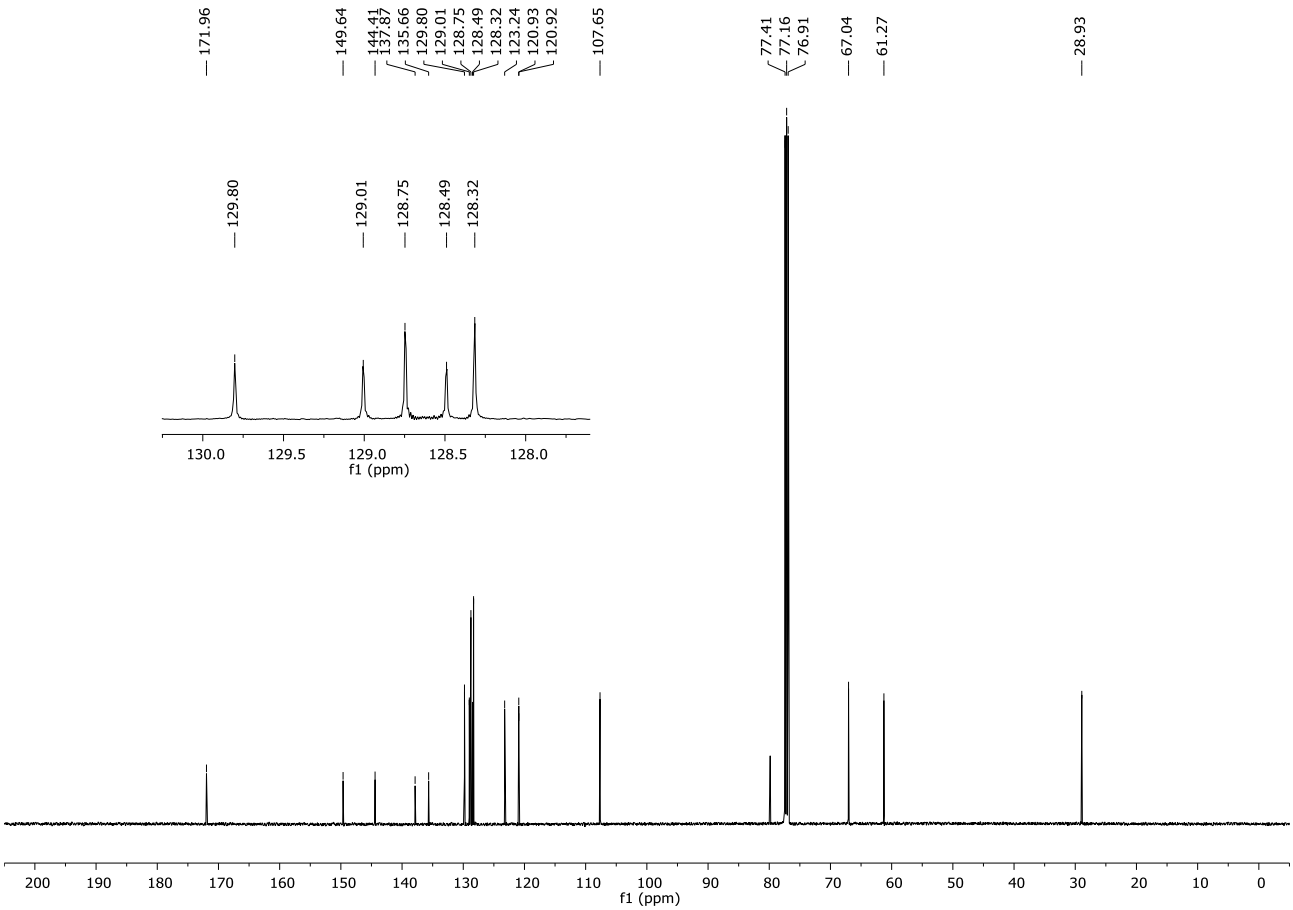

4.25
5.97
0.96
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

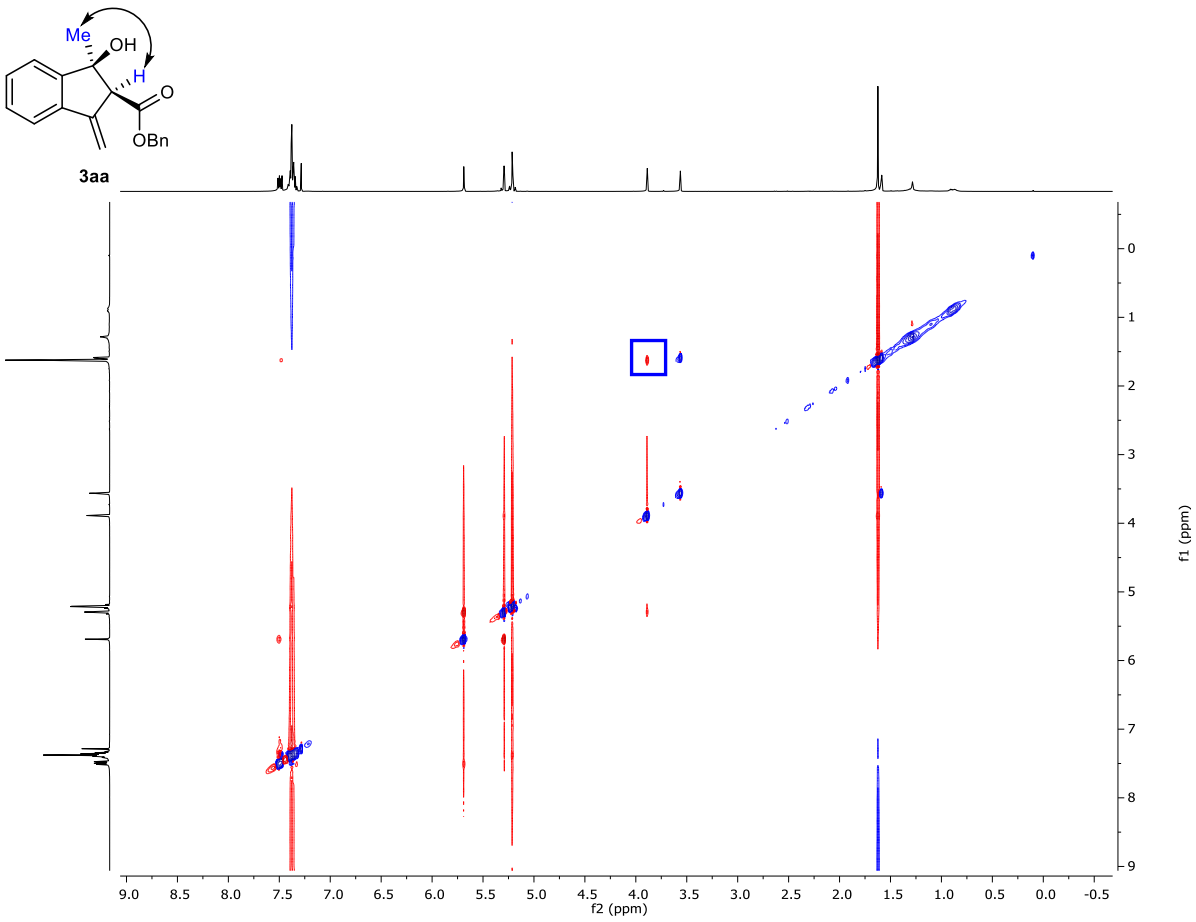

207.83
163.92
142.79
128.82
127.29
126.34
98.94
87.58
40.02
39.85
39.69
39.52
39.35
39.18
39.02
18.62
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

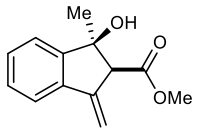

Me
OH
O
OBn

3aa

2.04
6.98
1.00
1.00
2.05
0.99
0.90
3.14
f1 (ppm)

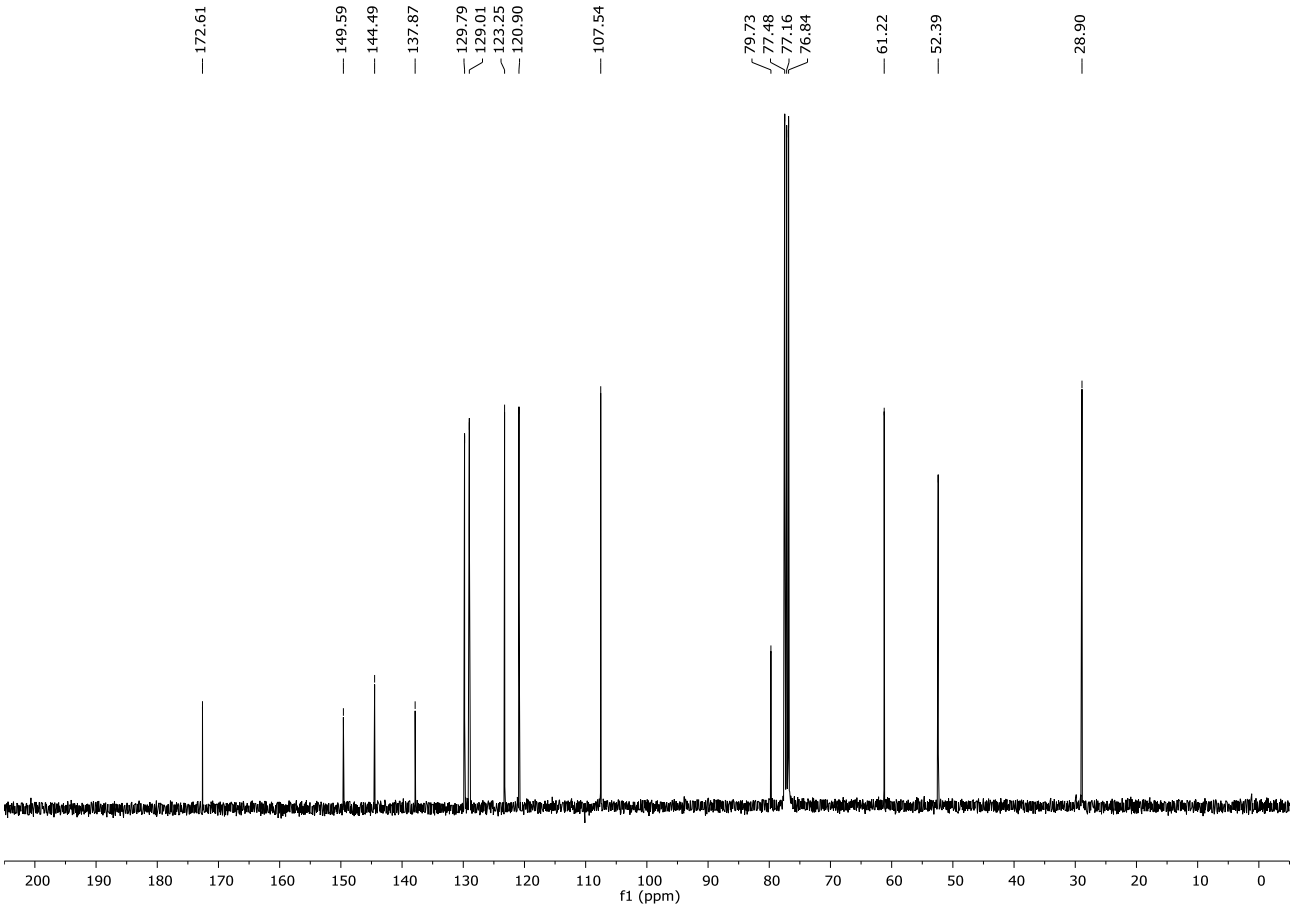

171.96
149.64
144.41
137.87
135.66
129.80
129.01
128.75
128.49
128.32
123.24
120.93
120.92
107.65
77.41
77.16
76.91
67.04
61.27
28.93
129.80
129.01
128.75
128.49
128.32
f1 (ppm)

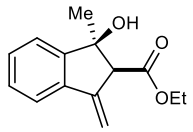

Me
OH
H
O
OBn
3aa
f2 (ppm)
f1 (ppm)


Me
OH
O
OMe

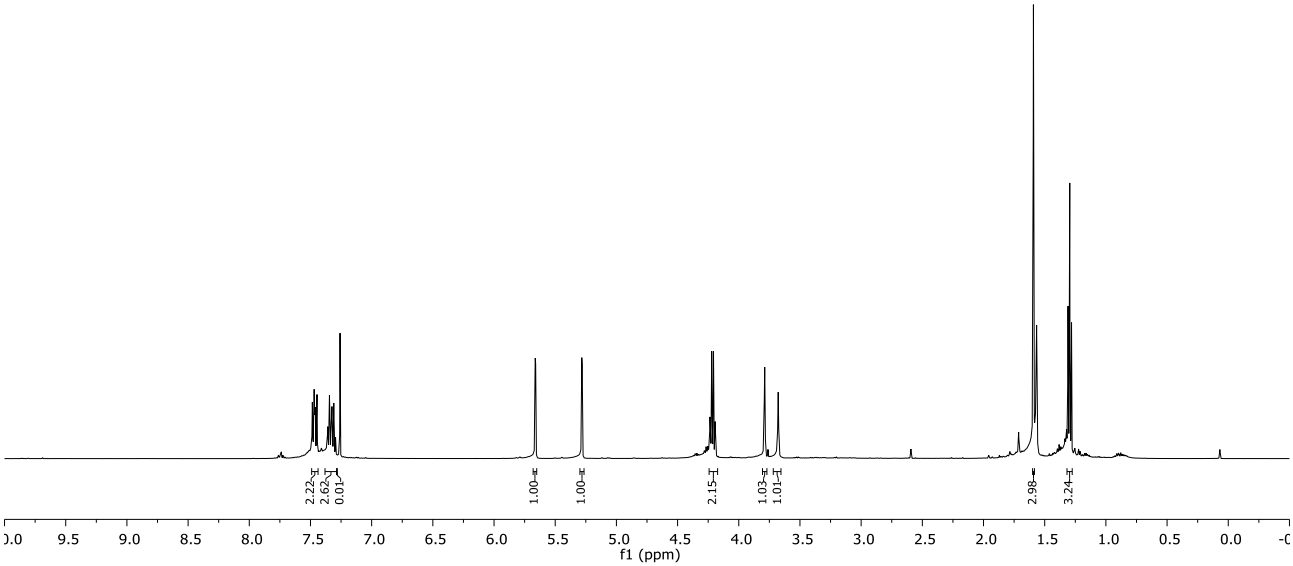
3ab

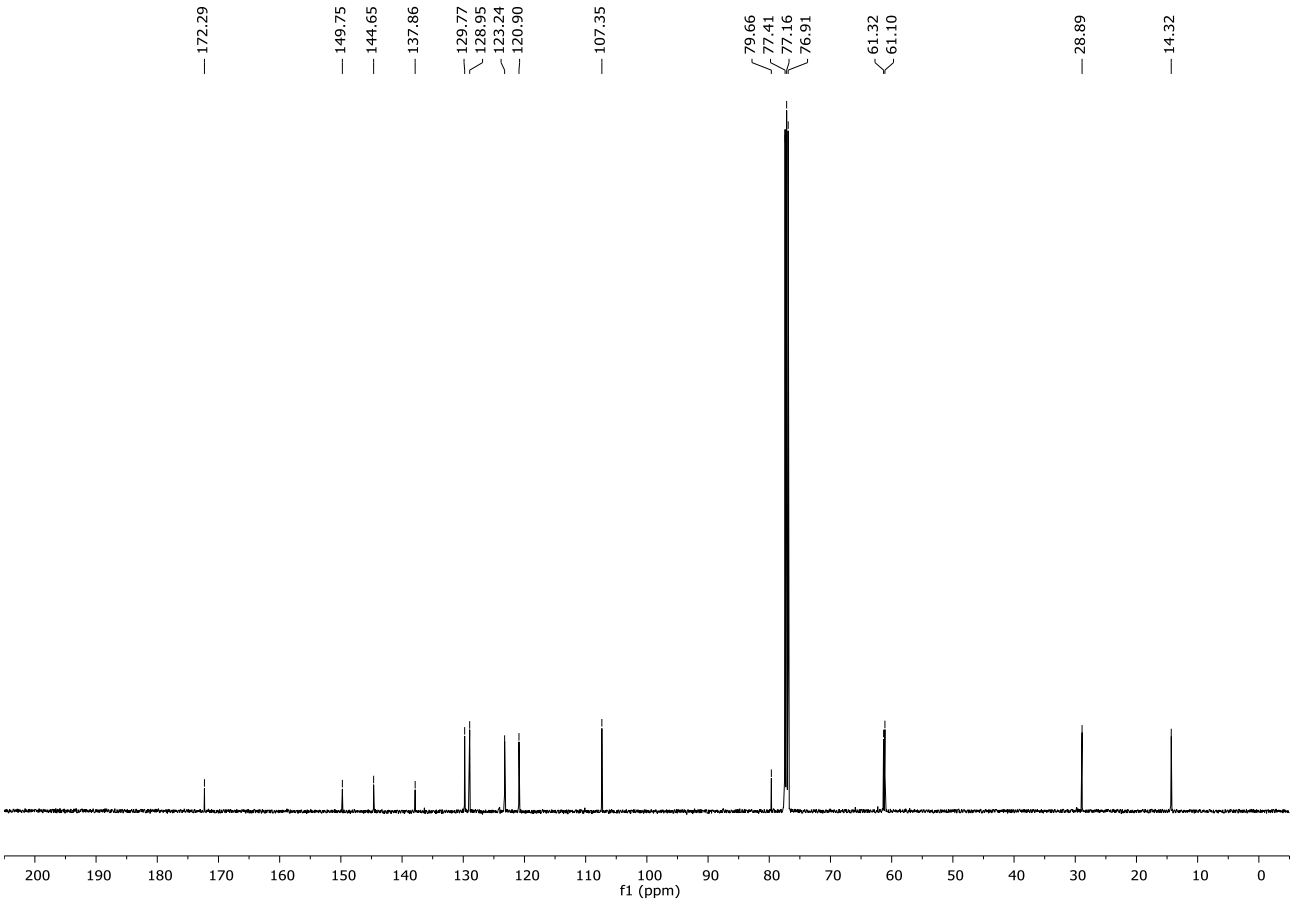
2.01
2.01
1.00
1.00
1.03
3.00
0.96
3.13
f1 (ppm)

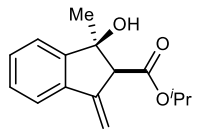

172.61
149.59
144.49
137.87
129.79
129.01
123.25
120.90
107.54
79.73
77.48
77.16
76.84
61.22
52.39
28.90
f1 (ppm)


Me
OH
O
OEt

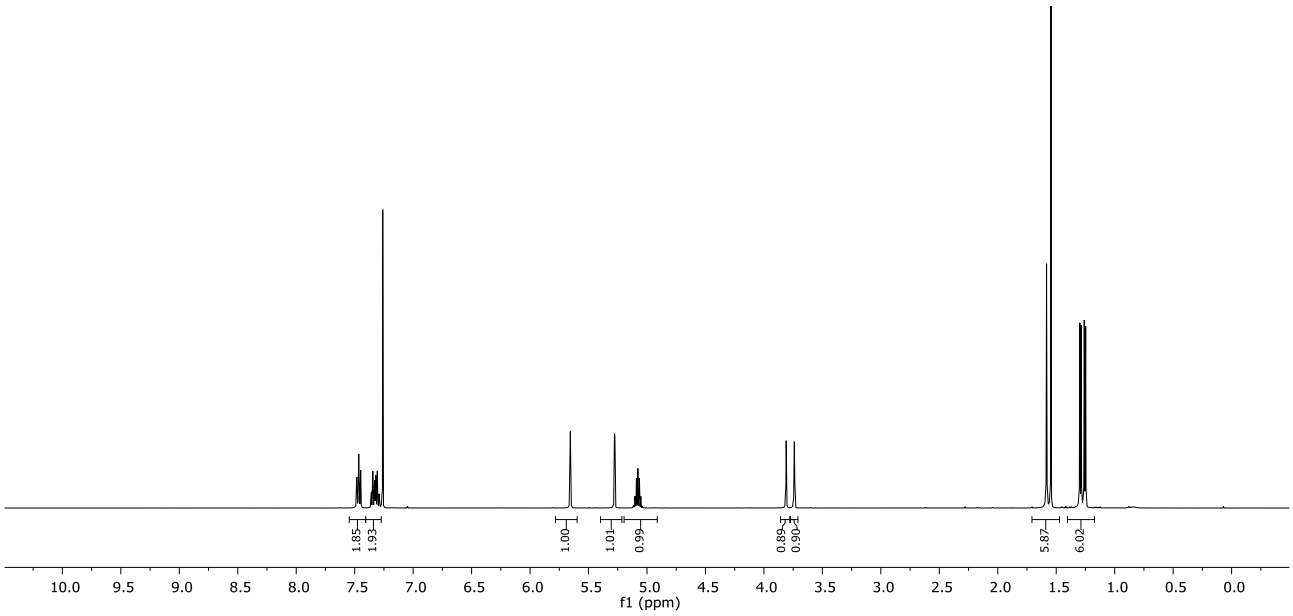
3ac

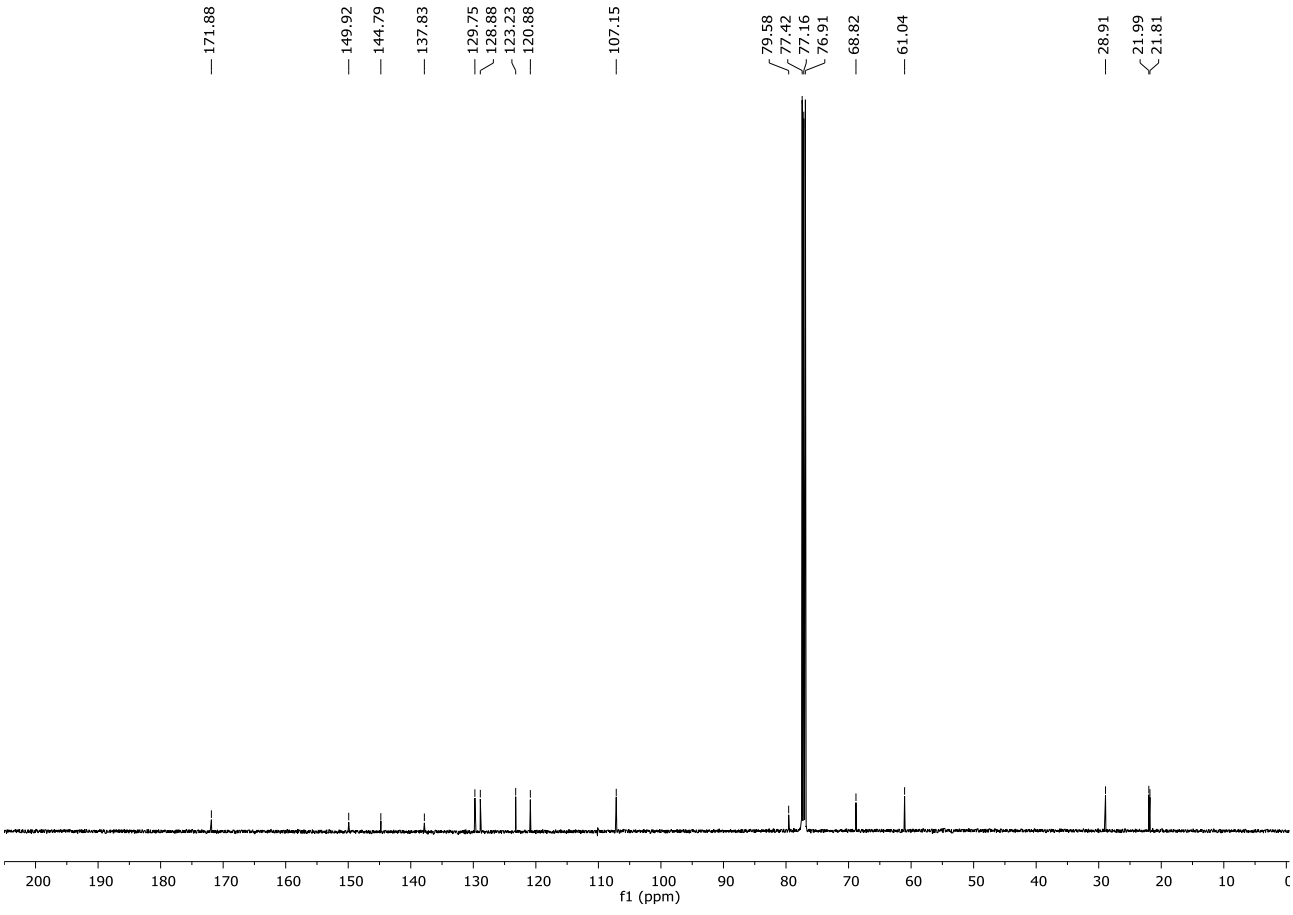

2.22
2.62
0.01
1.00
1.00
2.15
1.03
1.01
2.98
3.24
f1 (ppm)

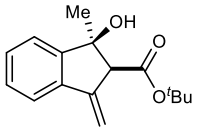

172.29
149.75
144.65
137.86
129.77
128.95
123.24
120.90
107.35
79.66
77.41
77.16
76.91
61.32
61.10
28.89
14.32
f1 (ppm)


Me
OH
O
O^{i}Pr

3ad

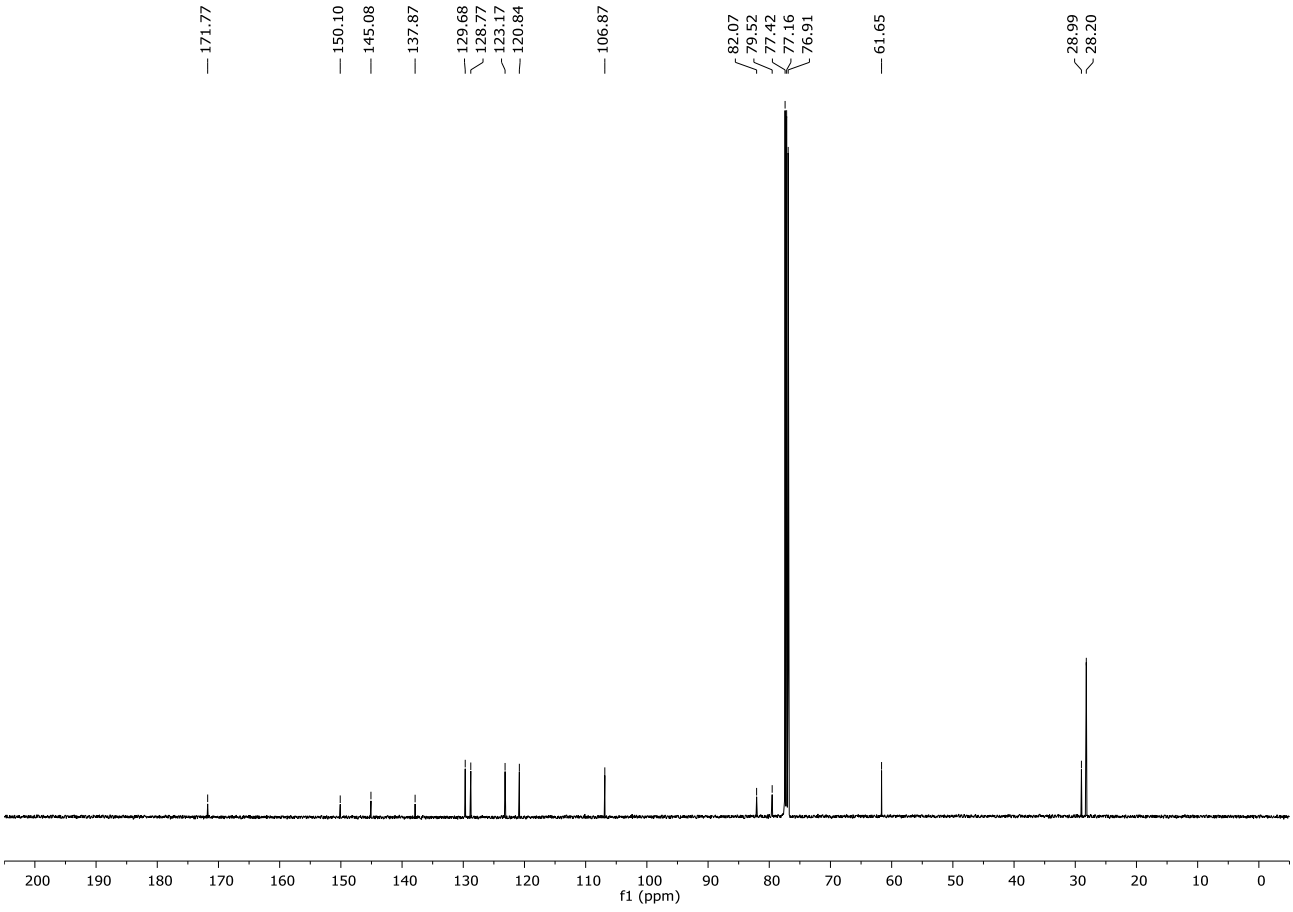

1.85
1.93
1.00
1.01
0.99
0.89
0.90
5.87
6.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

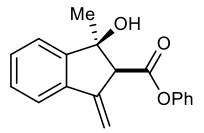

171.88
149.92
144.79
137.83
129.75
128.88
123.23
120.88
107.15
79.58
77.42
77.16
76.91
68.82
61.04
28.91
21.99
21.81
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Me
OH
O
O^{t}Bu

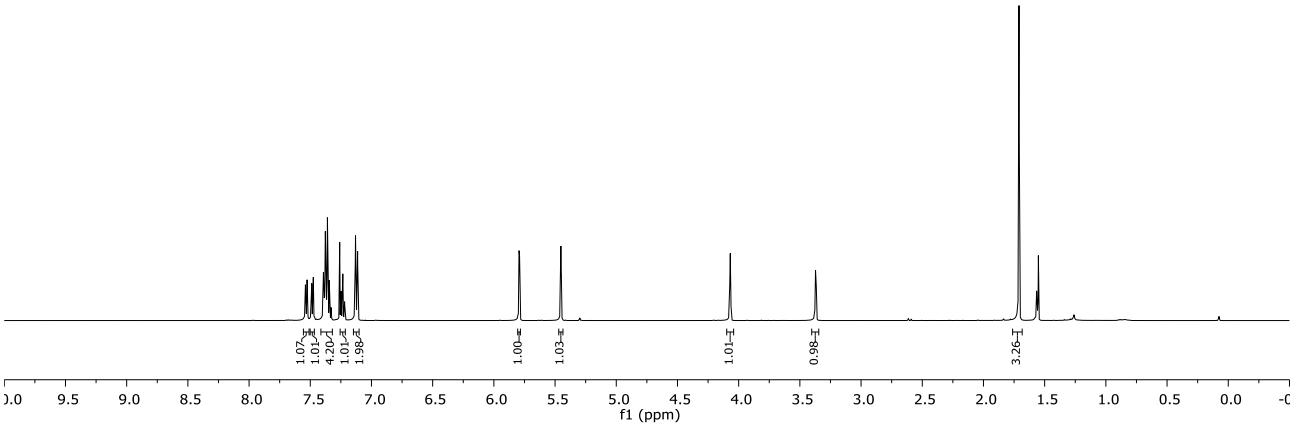
3ae

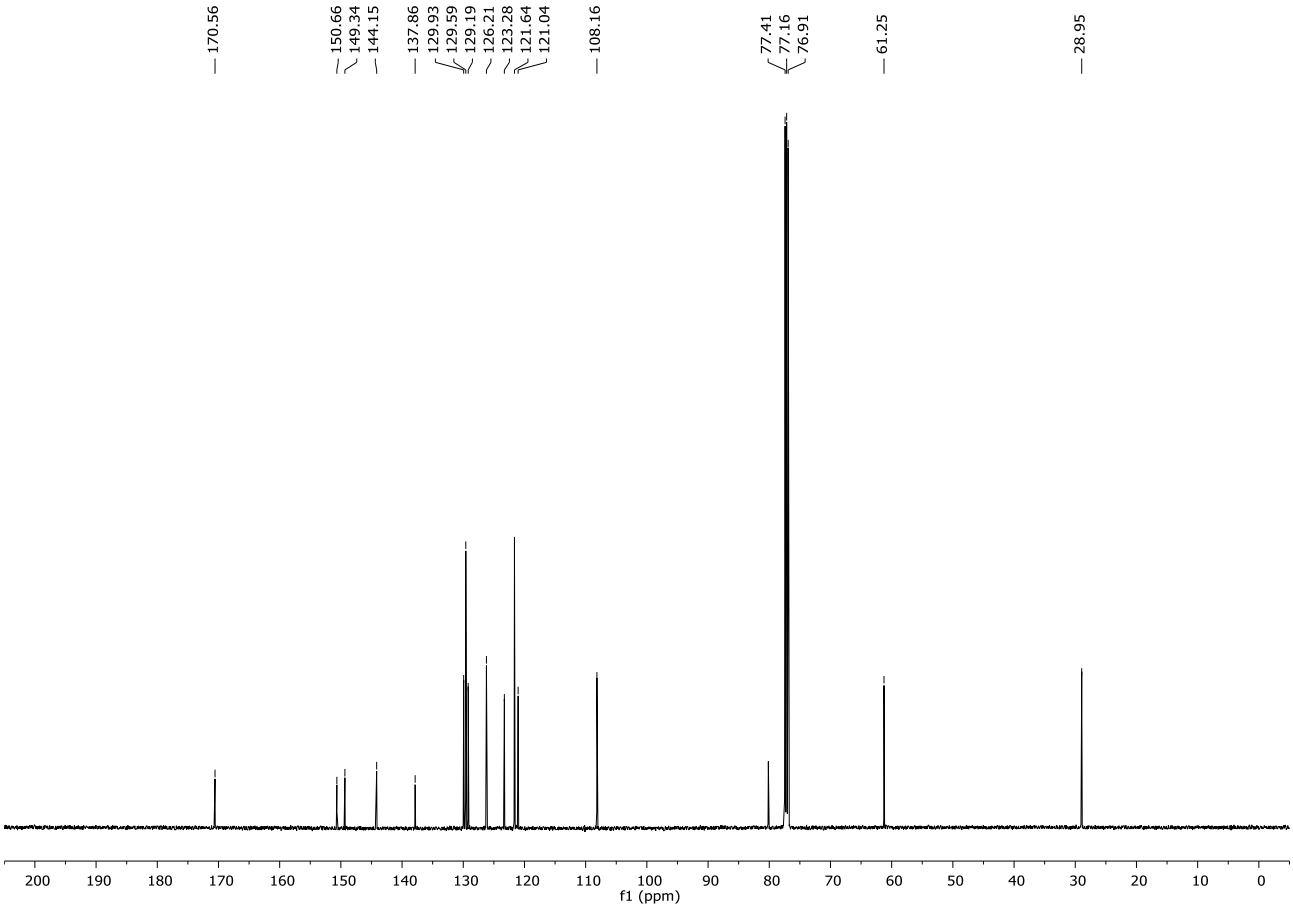
2.00
2.06
1.00
1.00
0.97
0.94
3.00
9.19
f1 (ppm)

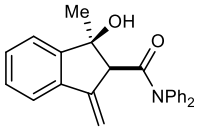

171.77
150.10
145.08
137.87
129.68
128.77
123.17
120.84
106.87
82.07
79.52
77.42
77.16
76.91
61.65
28.99
28.20
f1 (ppm)


Me
OH
O
OPh

3af

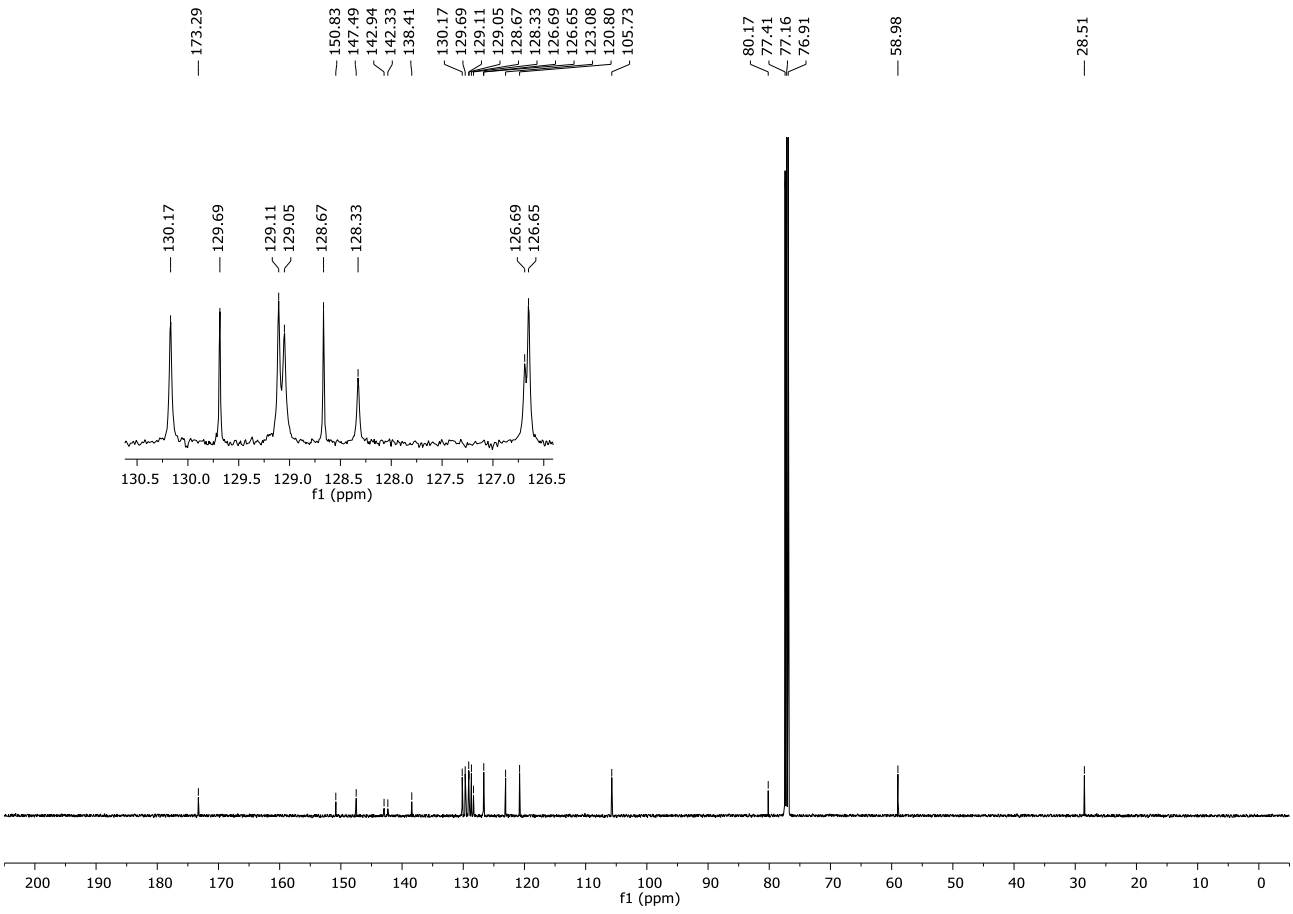

1.07
1.01
4.20
1.01
1.98
1.00
1.03
1.01
0.98
3.26
f1 (ppm)

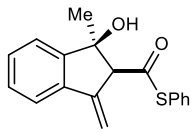

170.56
150.66
149.34
144.15
137.86
129.93
129.59
129.19
126.21
123.28
121.64
121.04
108.16
77.41
77.16
76.91
61.25
28.95
f1 (ppm)


Me
OH
O
NPh2

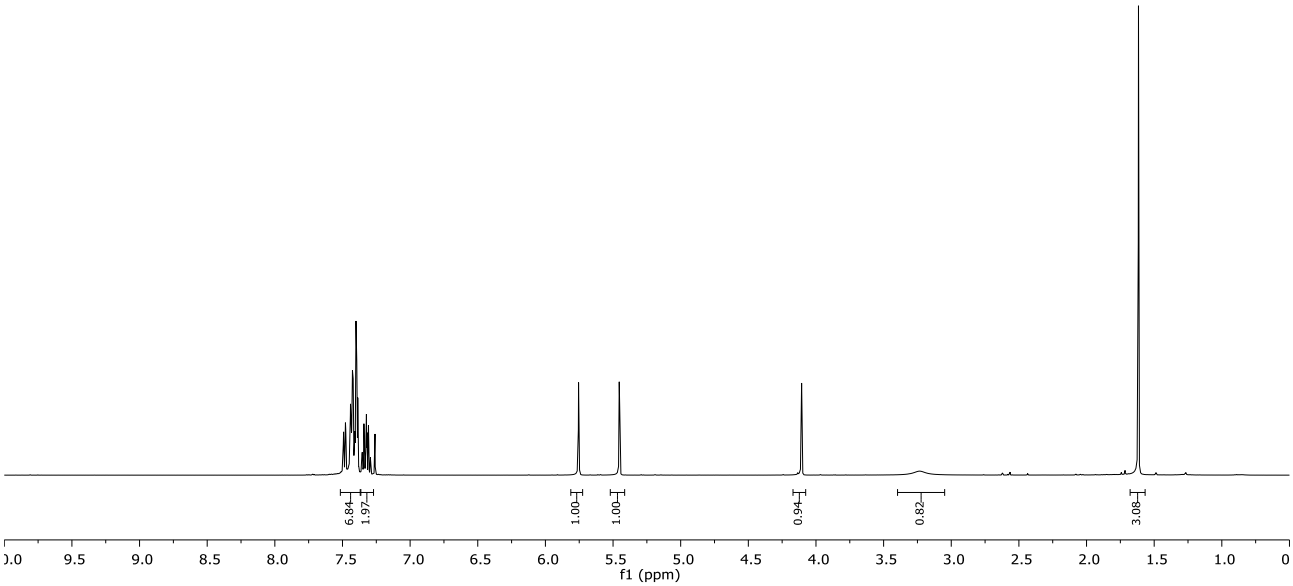
3ag

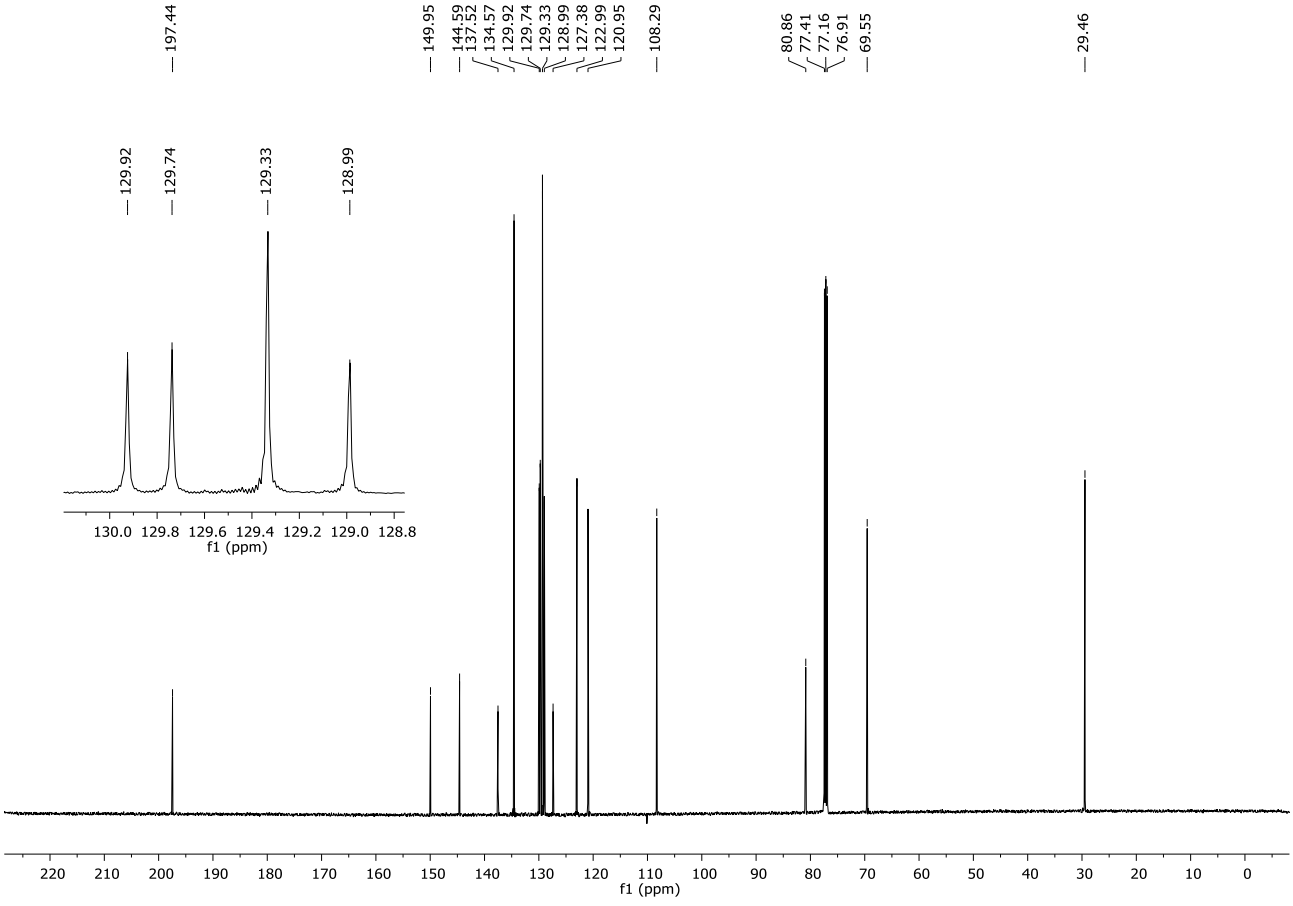
7.13
4.17
1.88
1.02
1.00
1.00
0.92
0.99
2.99
f1 (ppm)

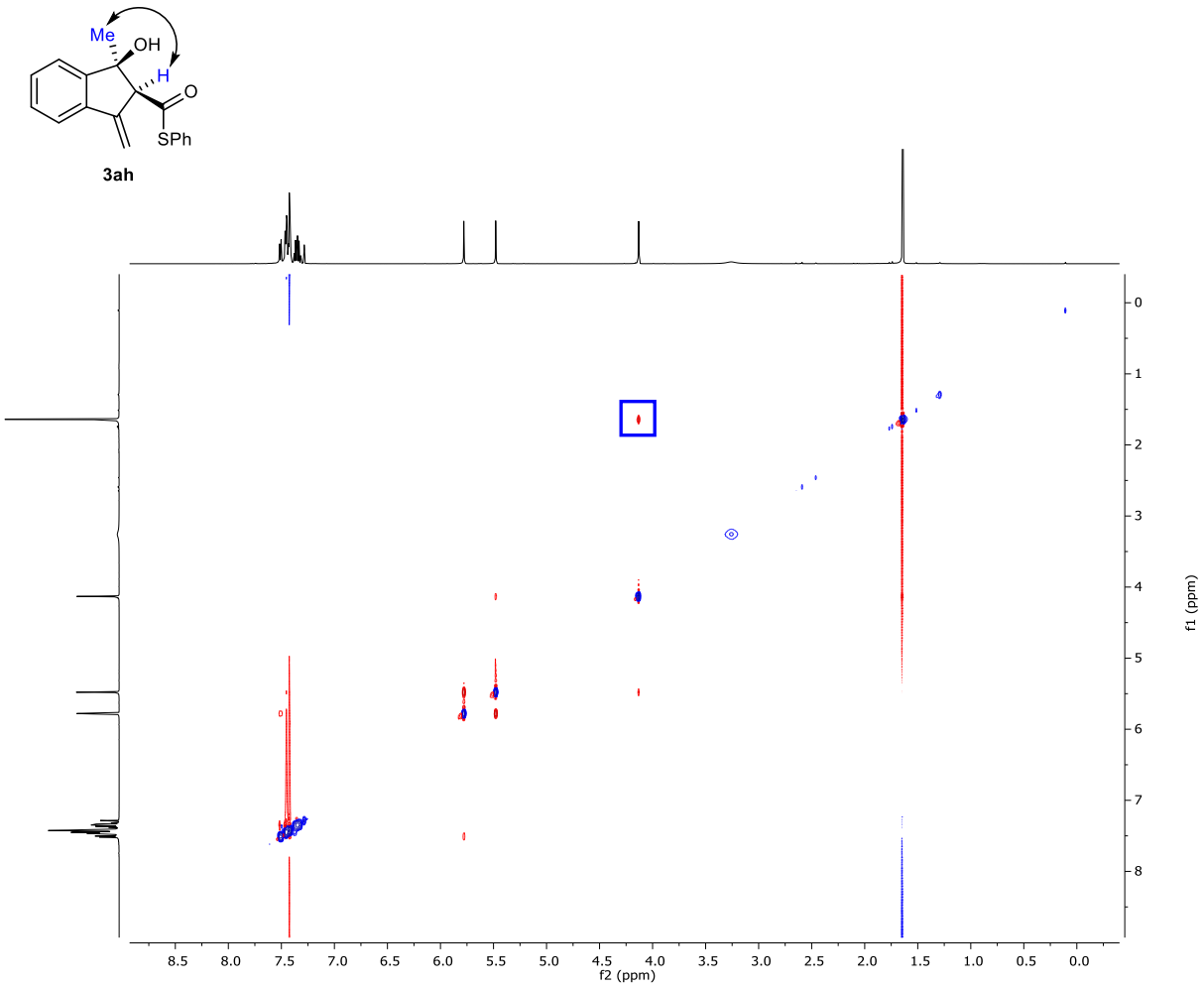

173.29
150.83
147.49
142.94
142.33
138.41
130.17
129.69
129.11
129.05
128.67
128.33
126.69
126.65
123.08
120.80
105.73
80.17
77.41
77.16
76.91
58.98
28.51
f1 (ppm)

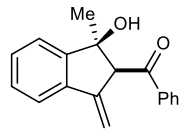

Me
OH
O
SPh

3ah

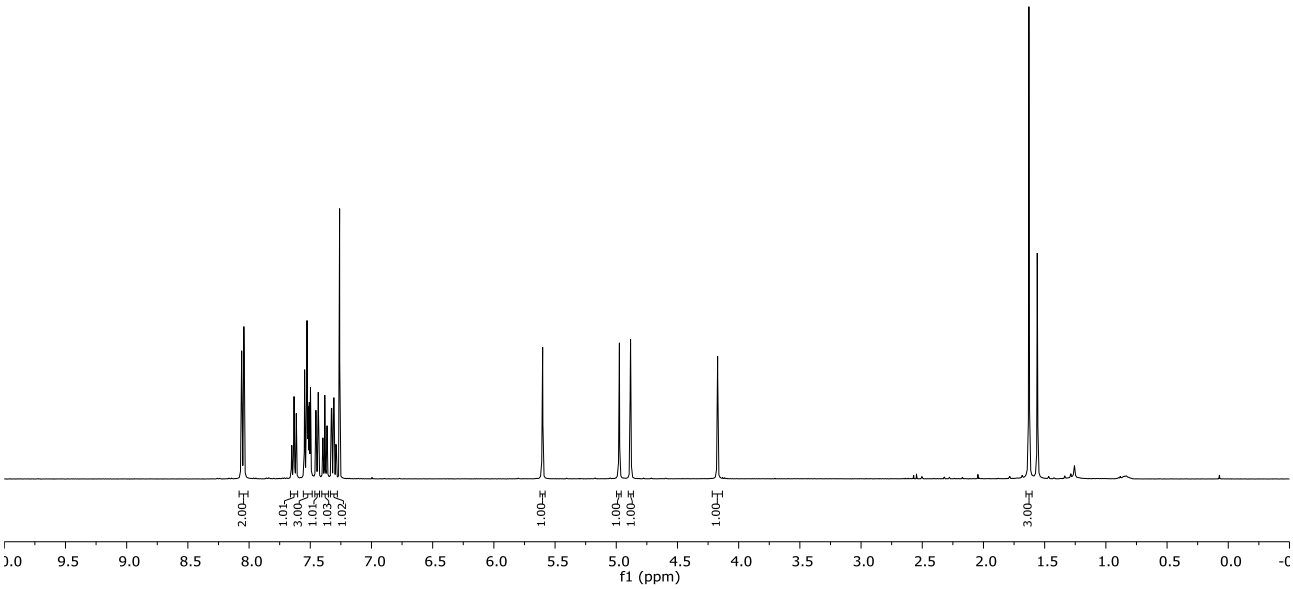

6.84
1.97
1.00
1.00
0.94
0.82
3.08
f1 (ppm)

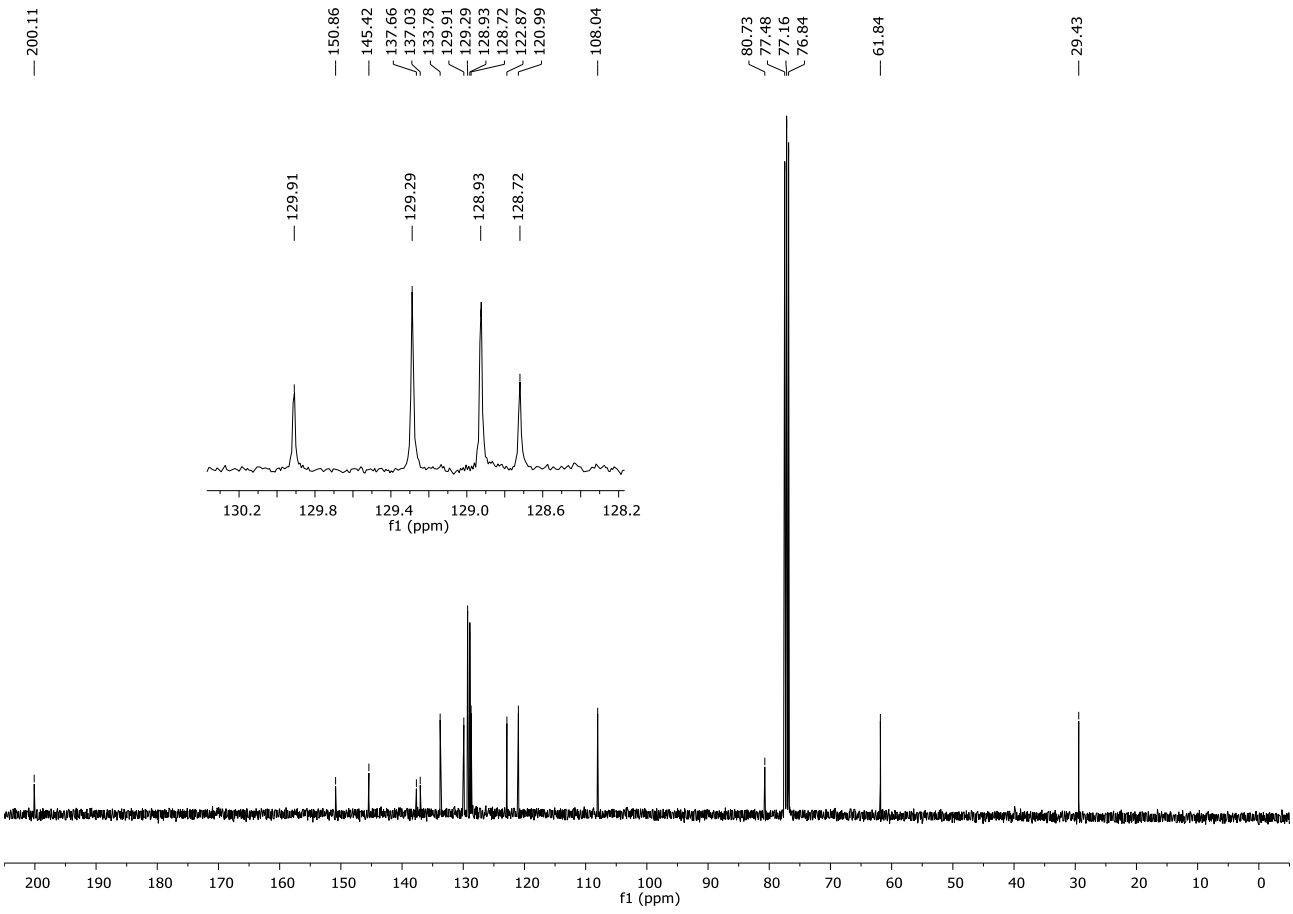

197.44
149.95
144.59
137.52
134.57
129.92
129.74
129.33
128.99
127.38
122.99
120.95
108.29
80.86
77.41
77.16
76.91
69.55
29.46
129.92
129.74
129.33
128.99
130.0 129.8 129.6 129.4 129.2 129.0 128.8
f1 (ppm)
f1 (ppm)

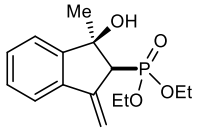

Me
OH
H
O
SPh
3ah
f2 (ppm)
f1 (ppm)


Me
OH
O
Ph

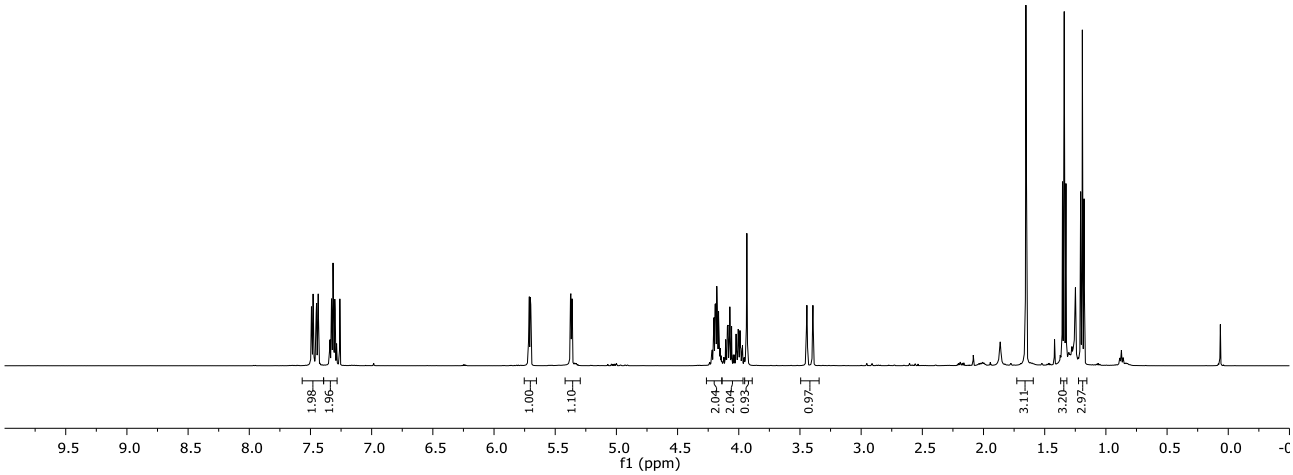
3ai

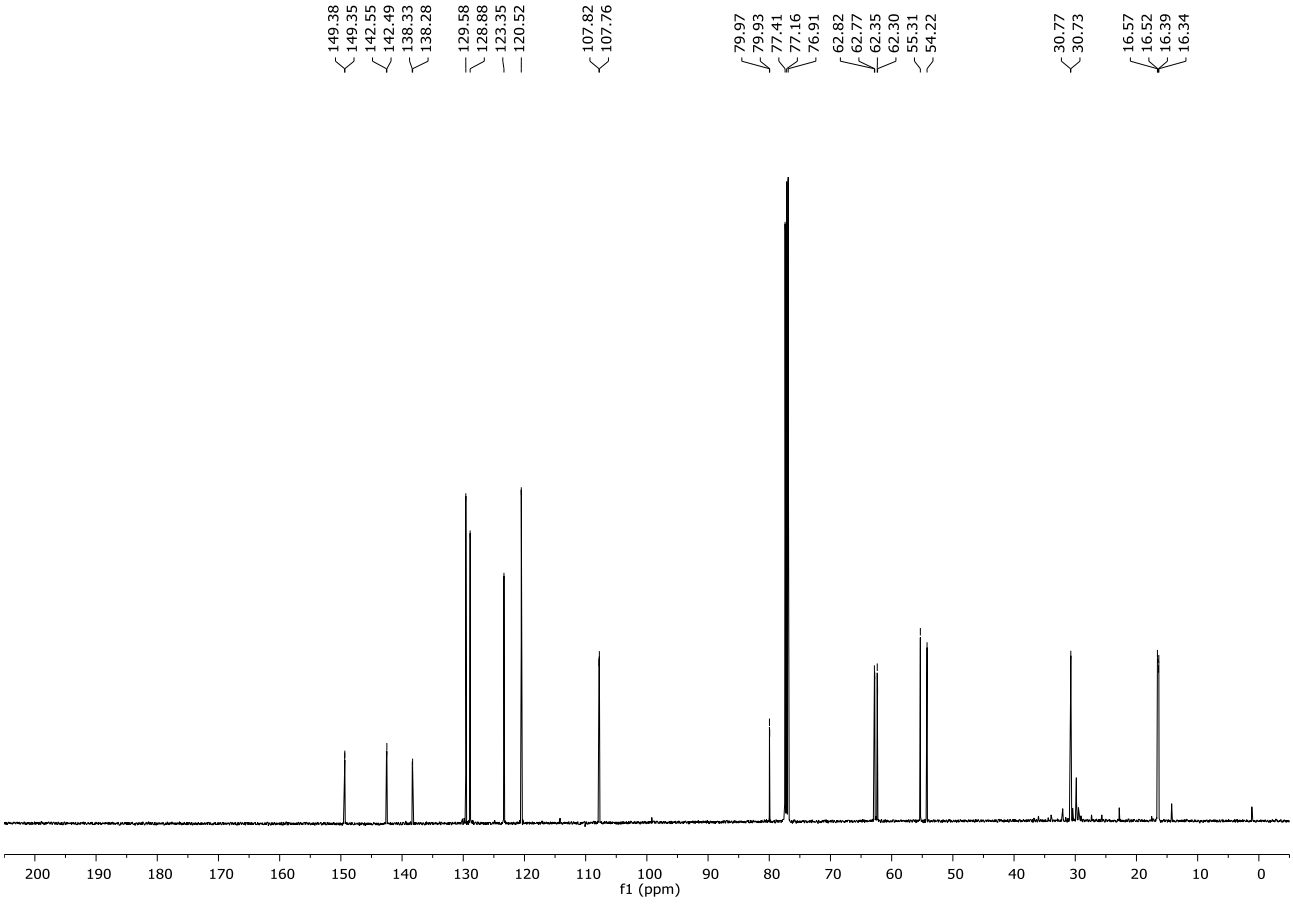

2.00
1.01
3.00
1.01
1.03
1.02
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

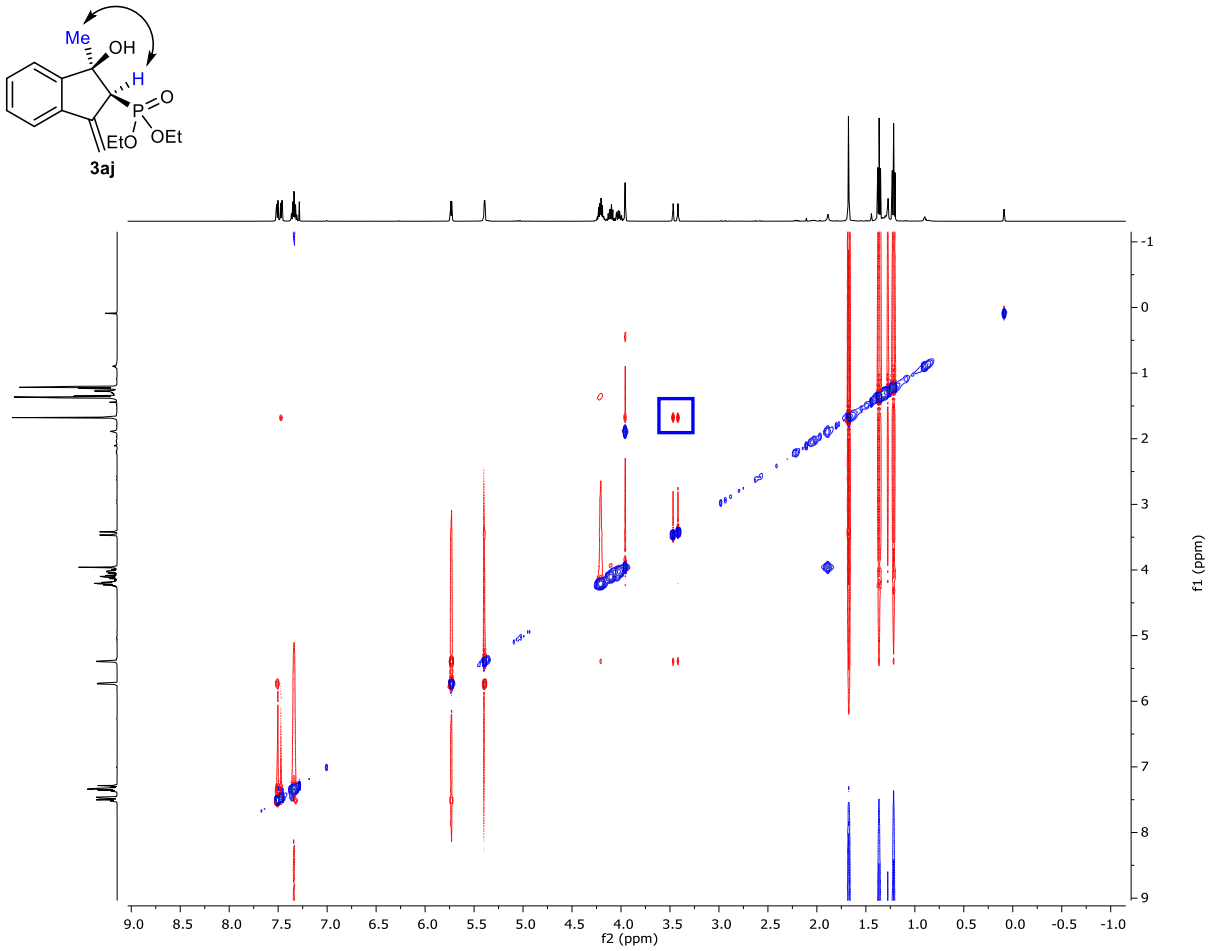

200.11
150.86
145.42
137.66
137.03
133.78
129.91
129.29
128.93
128.72
122.87
120.99
108.04
80.73
77.48
77.16
76.84
61.84
29.43
129.91
129.29
128.93
128.72
130.2
129.8
129.4
129.0
128.6
128.2
f1 (ppm)
f1 (ppm)

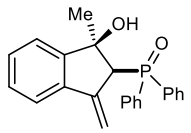

Me
OH
O
P
EtO
OEt

3aj

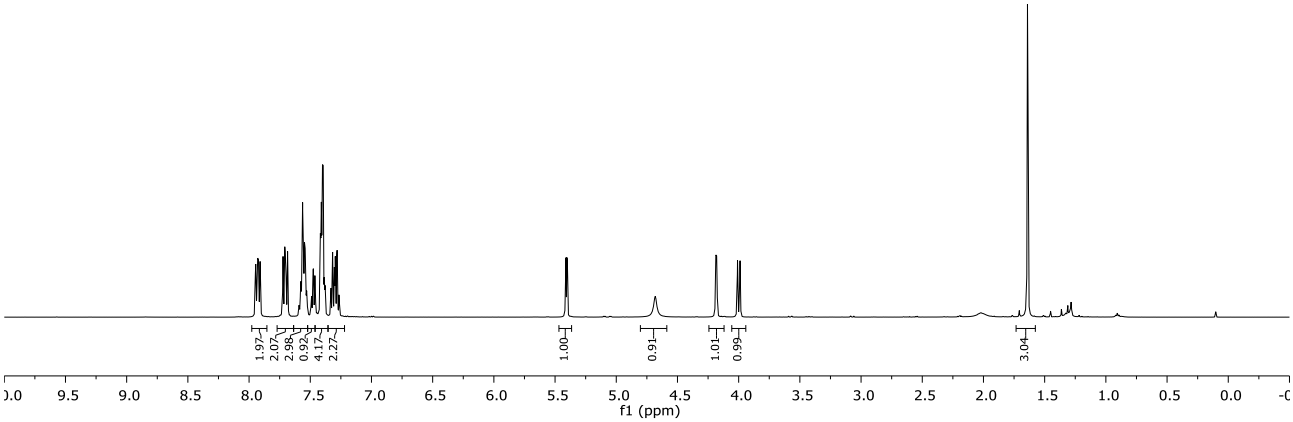

1.98
1.96
1.00
1.10
2.04
2.04
0.93
0.97
3.11
3.20
2.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

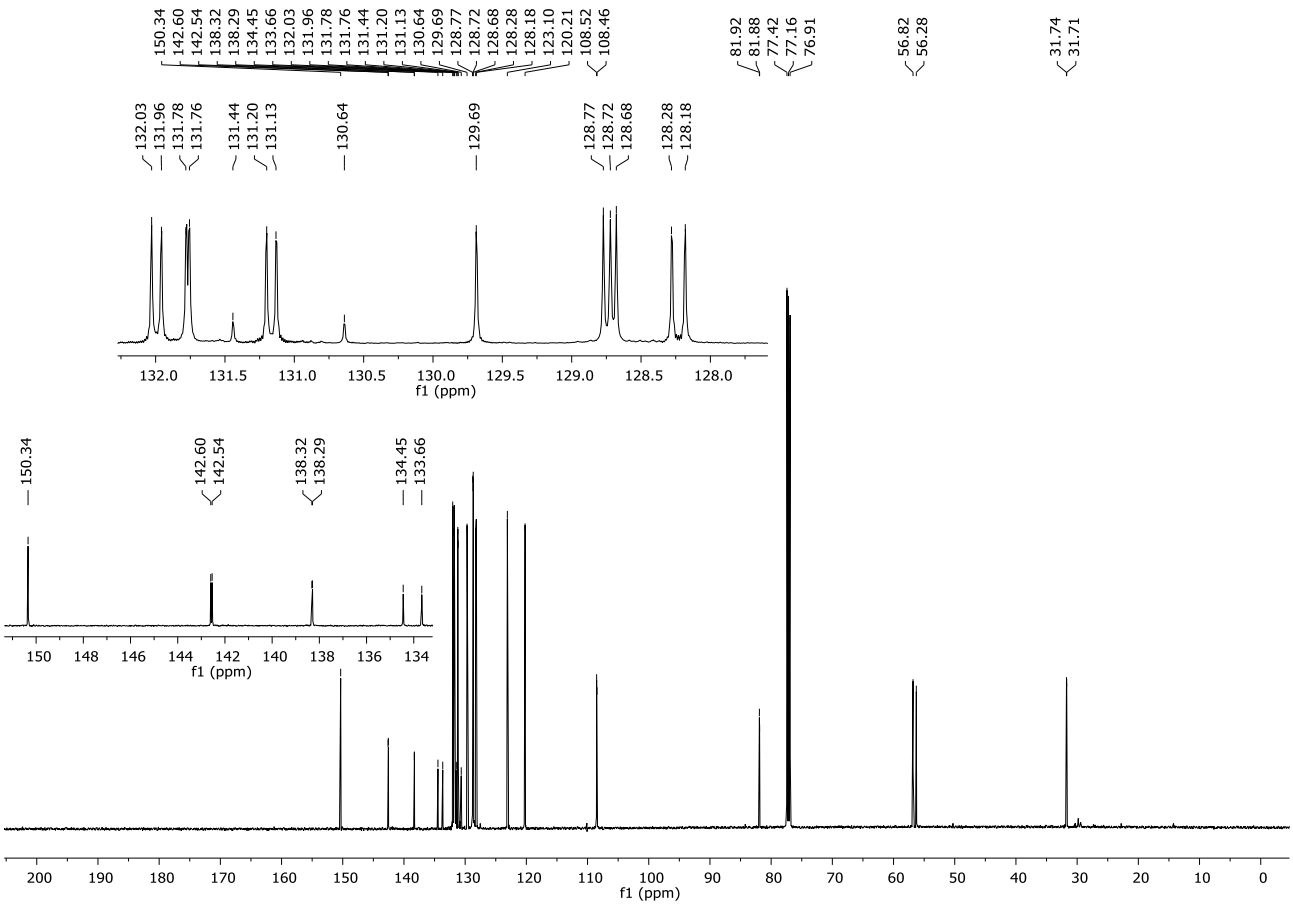

149.38
149.35
142.55
142.49
138.33
138.28
129.58
128.88
123.35
120.52
107.82
107.76
79.97
79.93
77.41
77.16
76.91
62.82
62.77
62.35
62.30
55.31
54.22
30.77
30.73
16.57
16.52
16.39
16.34
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

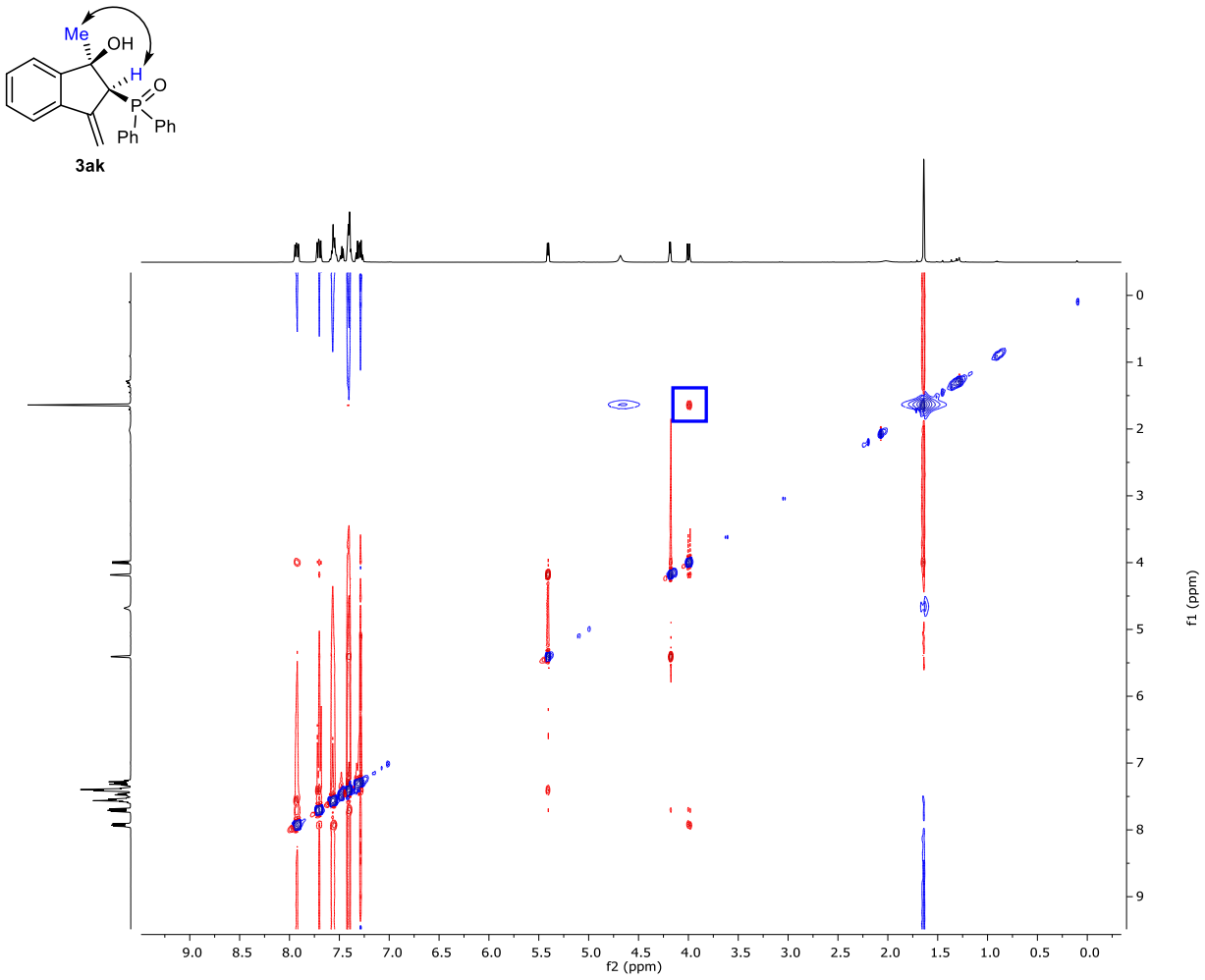

Me
OH
H
O
P
EtO
OEt
3aj
f2 (ppm)
f1 (ppm)

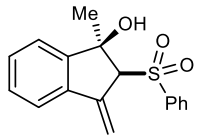

Me
OH
O
P
Ph
Ph

3ak

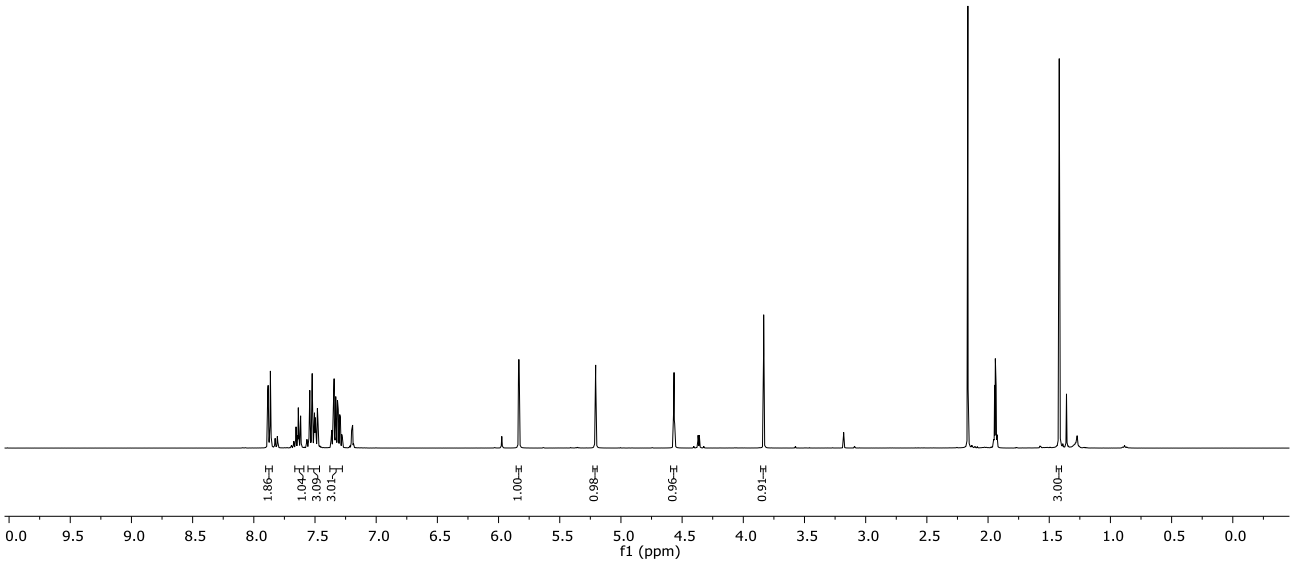

1.97
2.07
2.96
0.92
4.17
2.27
1.00
0.91
1.01
0.99
3.04
f1 (ppm)

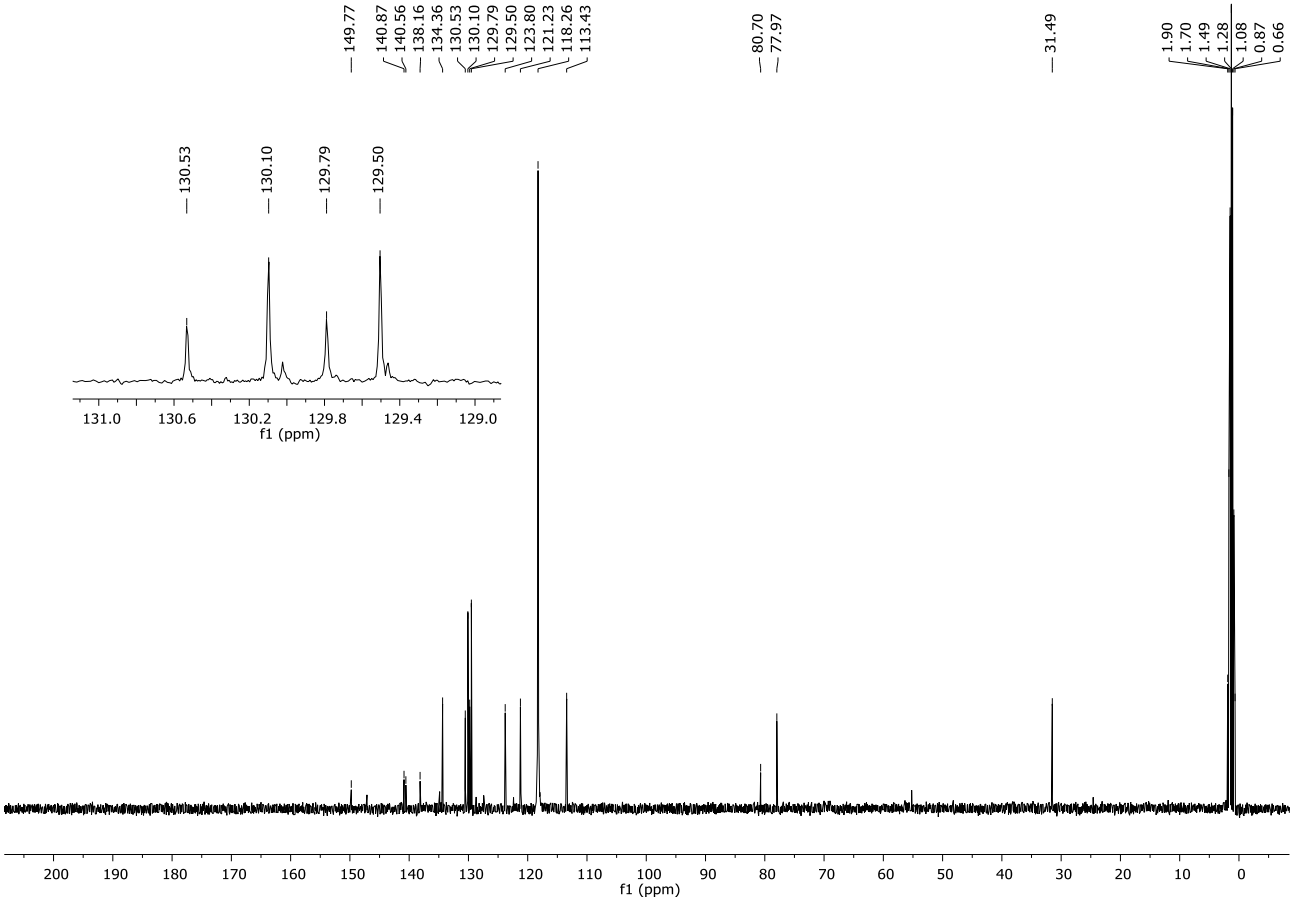

150.34
142.60
142.54
138.32
138.29
134.45
133.66
132.03
131.96
131.78
131.76
131.44
131.44
131.20
131.13
130.64
129.69
128.77
128.72
128.68
128.28
128.18
123.10
120.21
108.52
108.46
81.92
81.88
77.42
77.16
76.91
56.82
56.28
31.74
31.71
f1 (ppm)

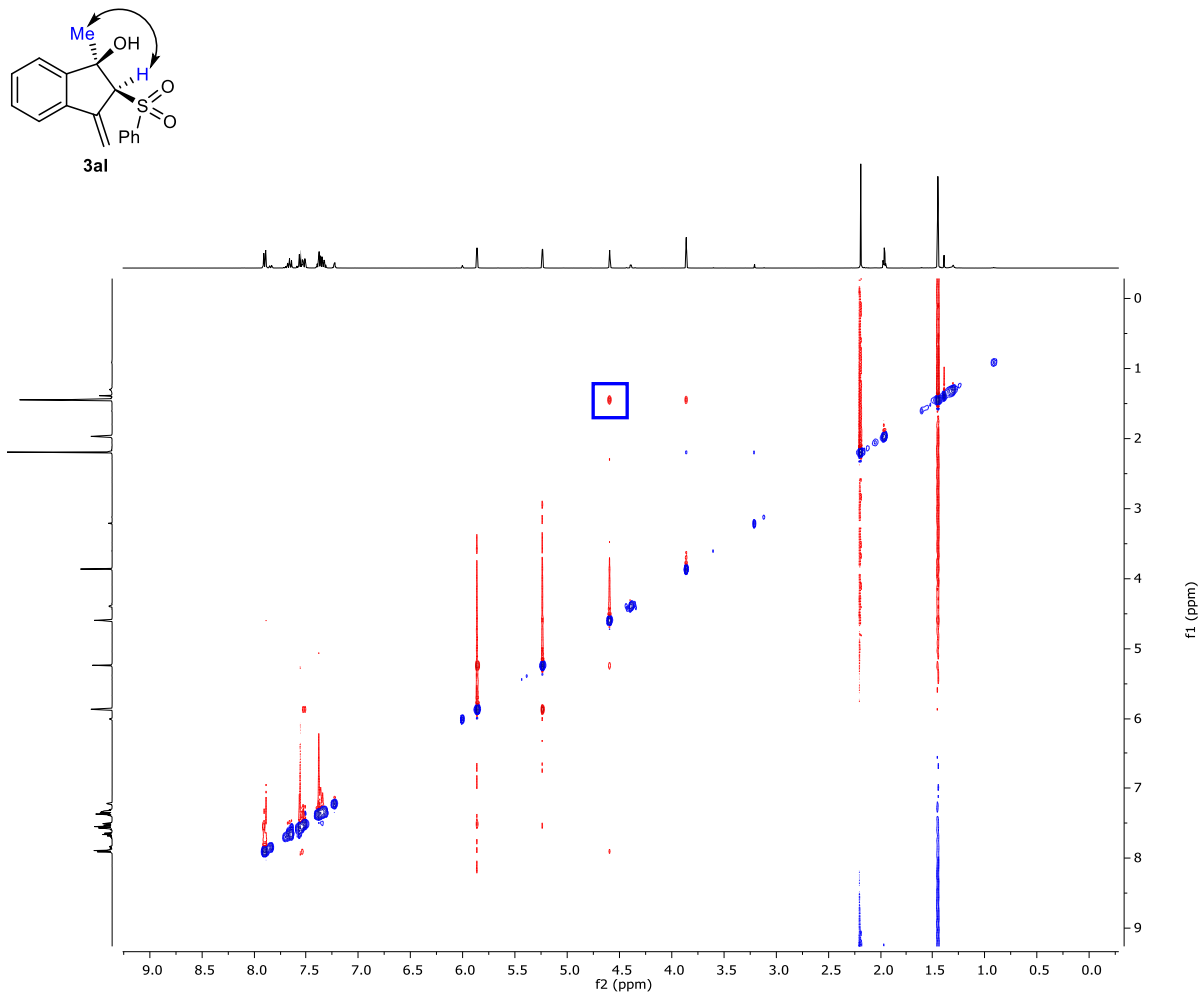

Me
OH
H
O
P
Ph
Ph
3ak
f2 (ppm)
f1 (ppm)

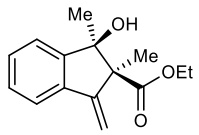


3al
(contains a minor, unidentified impurity)

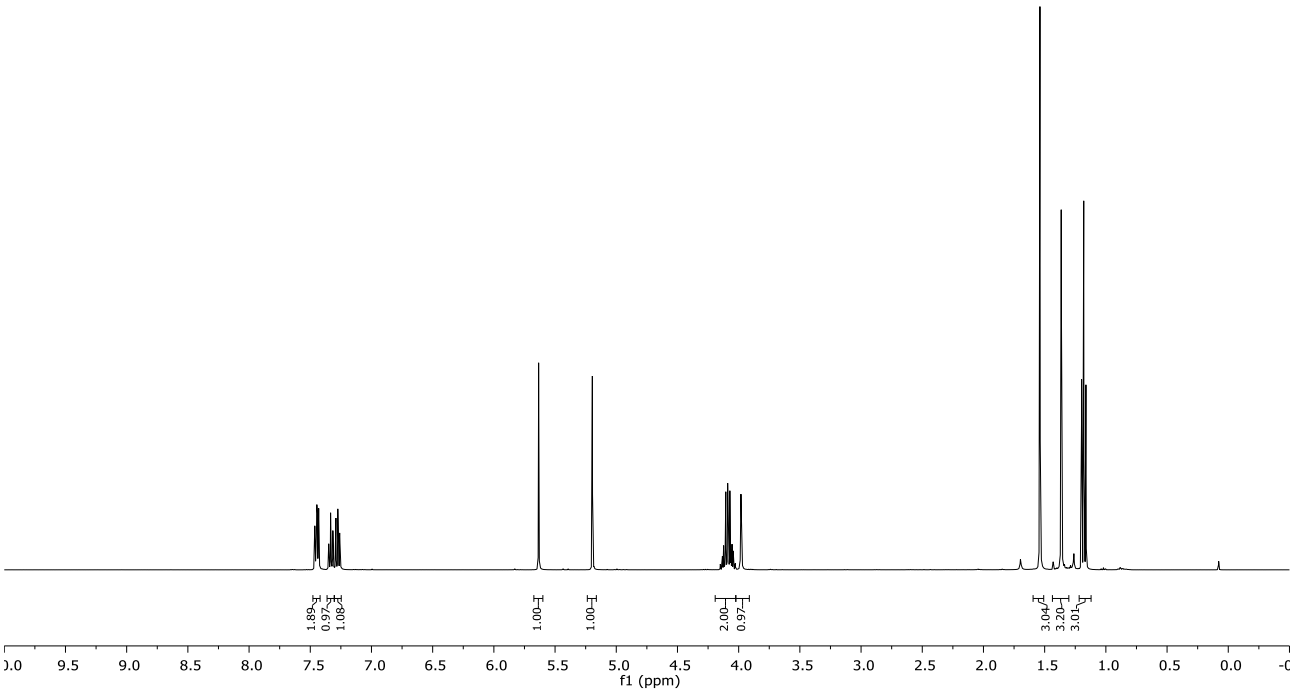


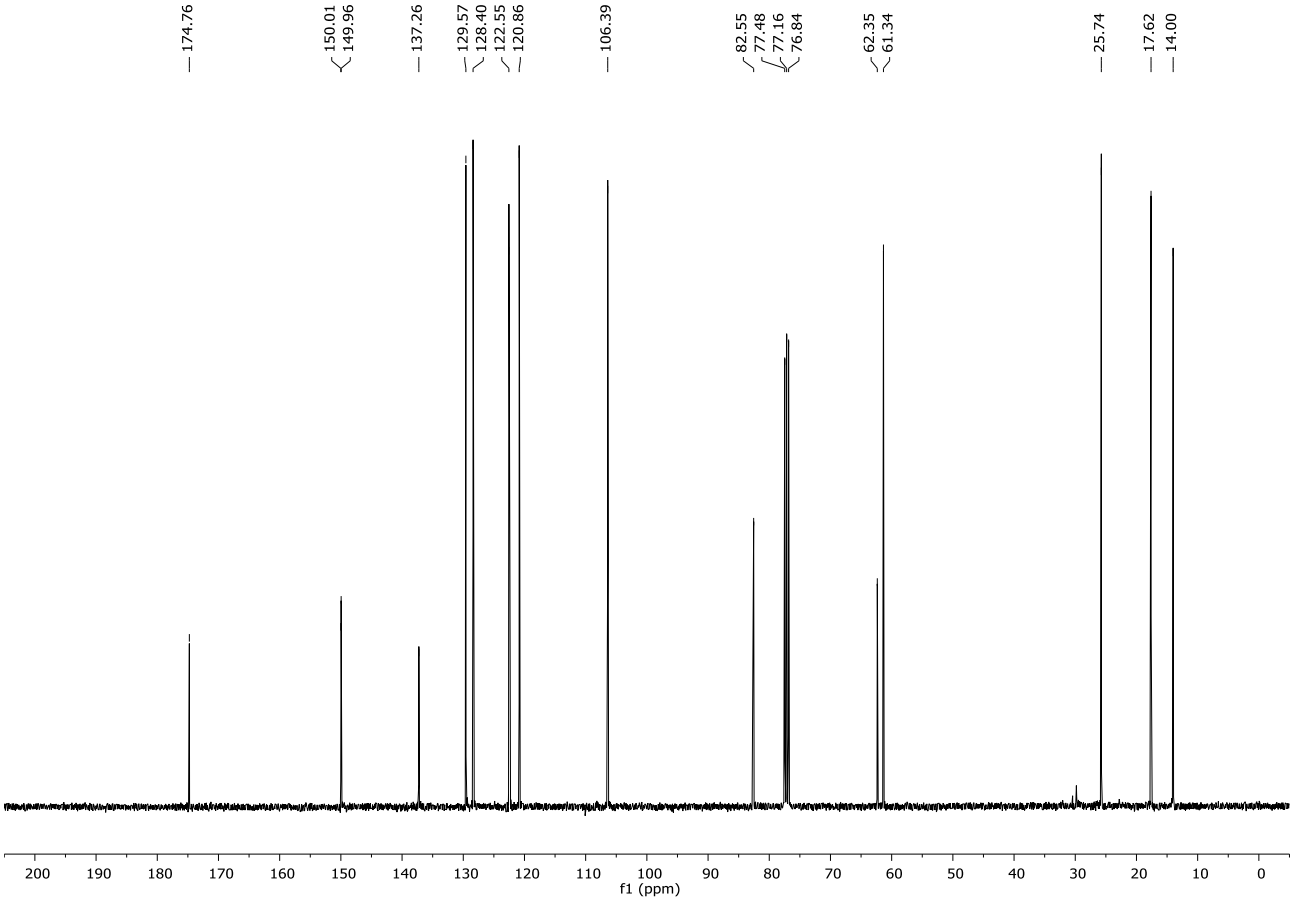


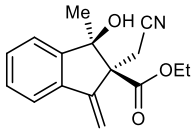

Me
OH
H
O
S
O
Ph
3al
f2 (ppm)
f1 (ppm)


Me
OH
Me
OEt
O

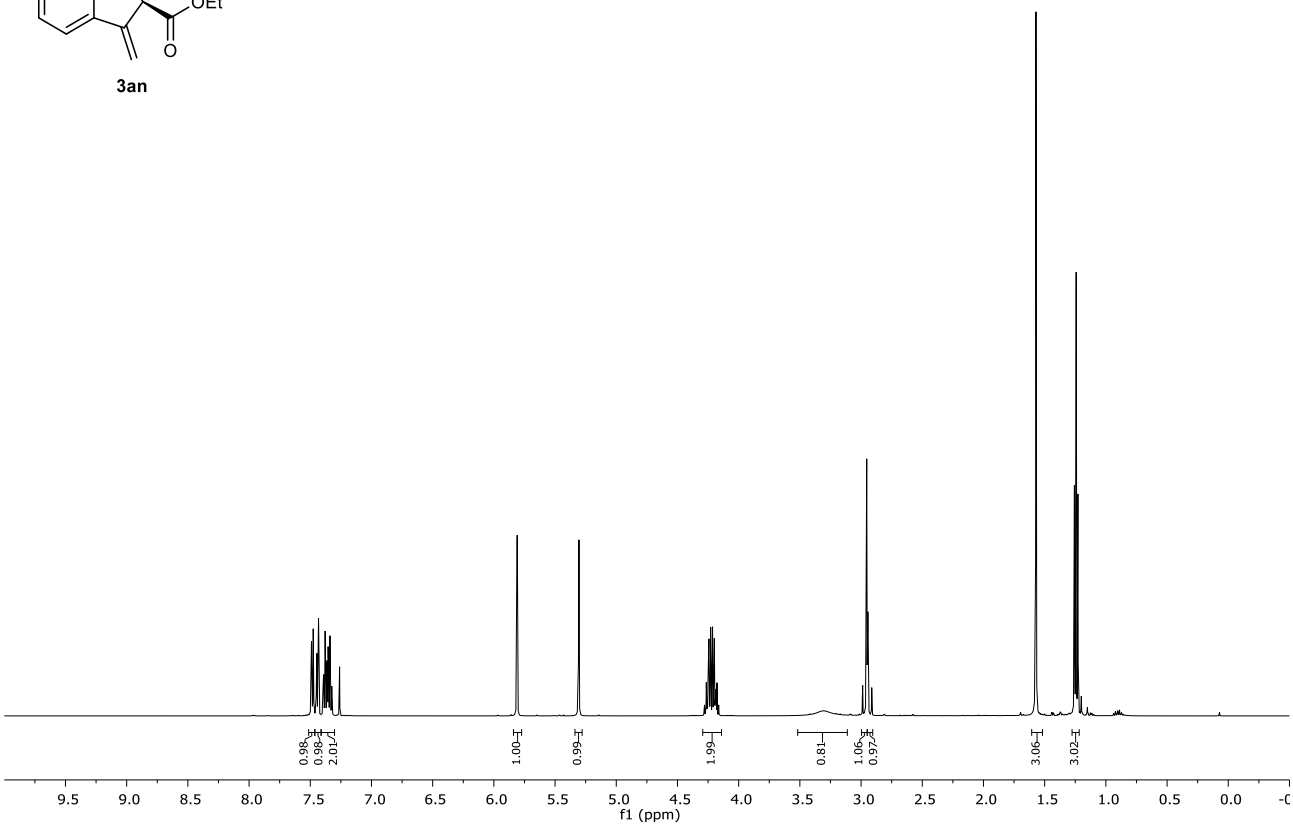
3am

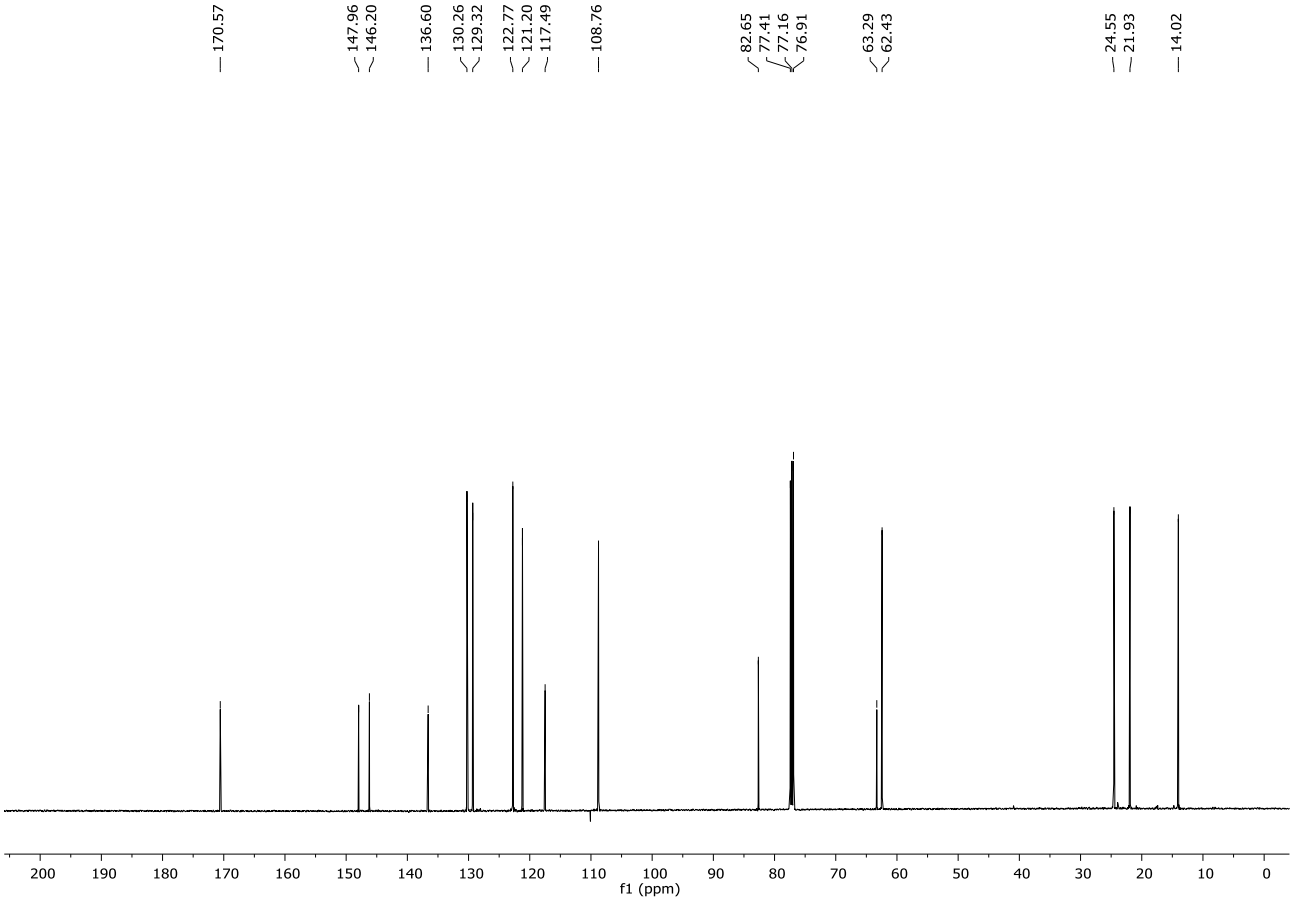

1.89
0.97
1.08
1.00
1.00
2.00
0.97
3.04
3.20
3.01
f1 (ppm)

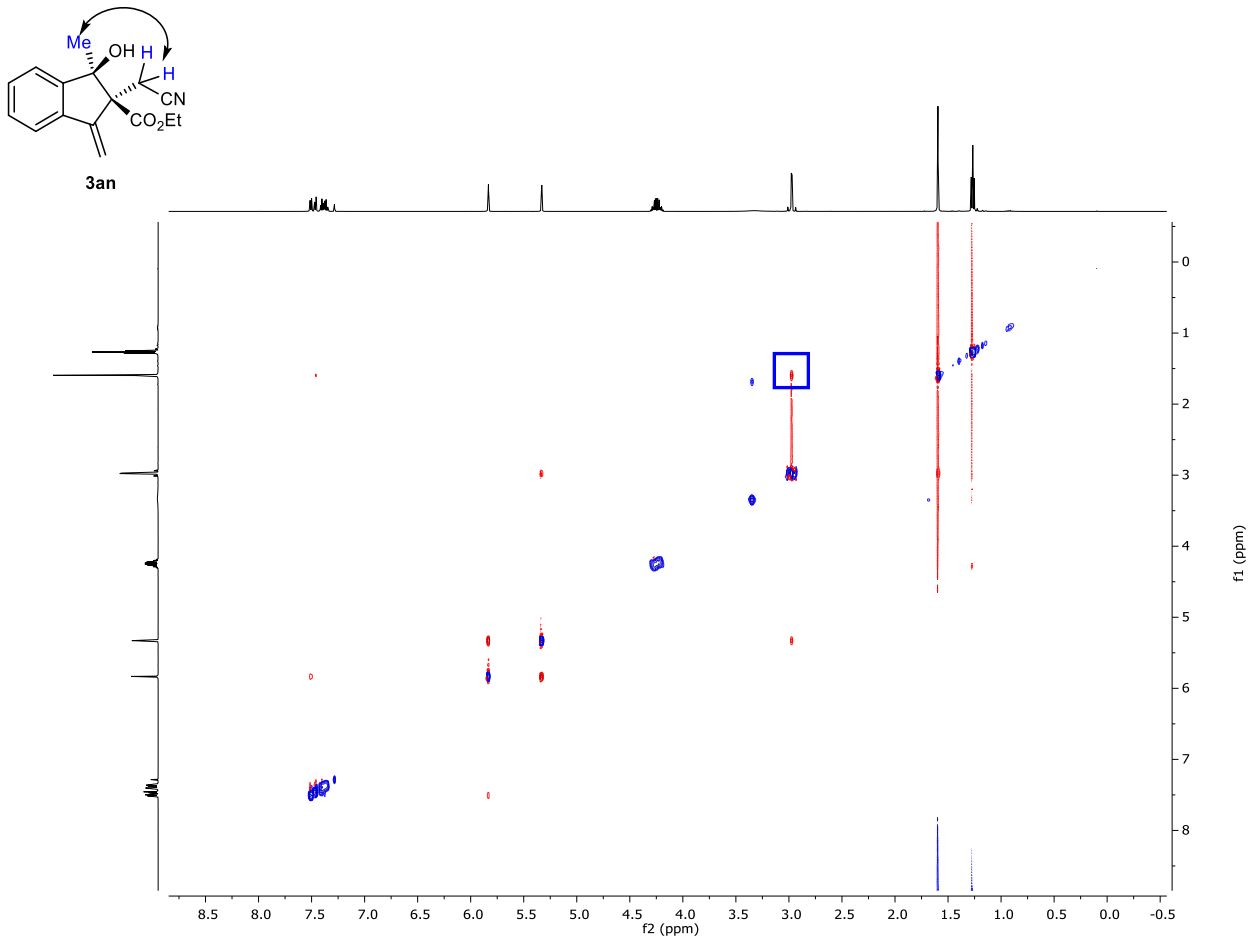

174.76
150.01
149.96
137.26
129.57
128.40
122.55
120.86
106.39
82.55
77.48
77.16
76.84
62.35
61.34
25.74
17.62
14.00
f1 (ppm)

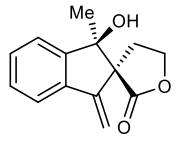

Me
OH CN
OEt
O

3an

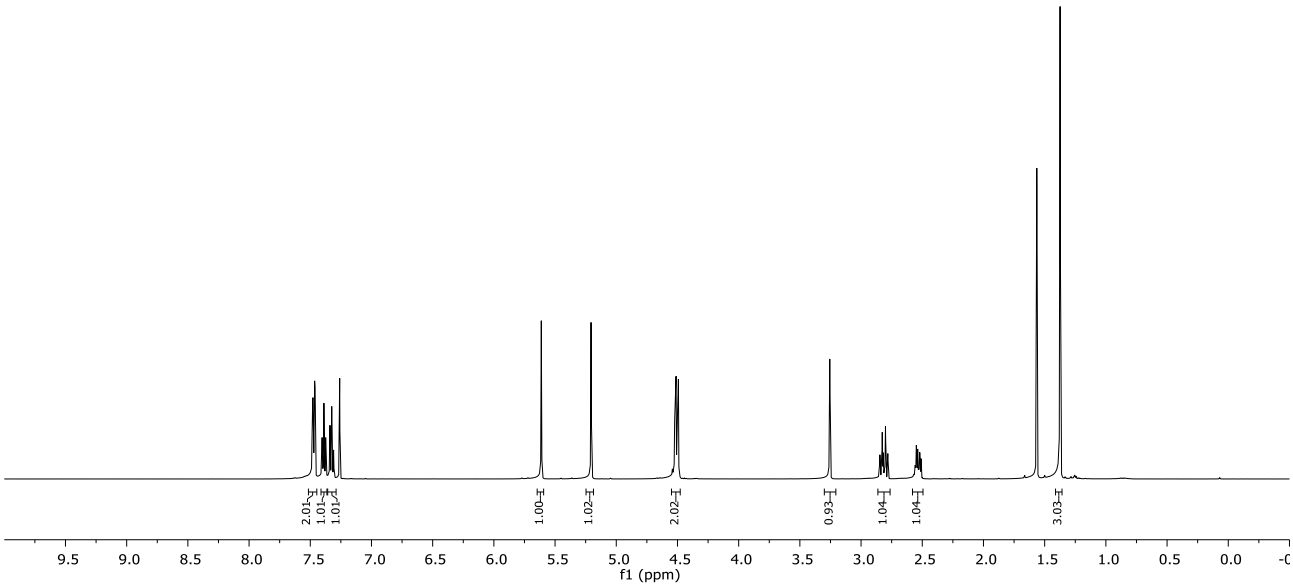

0.98
0.98
2.01
1.00
0.99
1.99
0.81
1.06
0.97
3.06
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

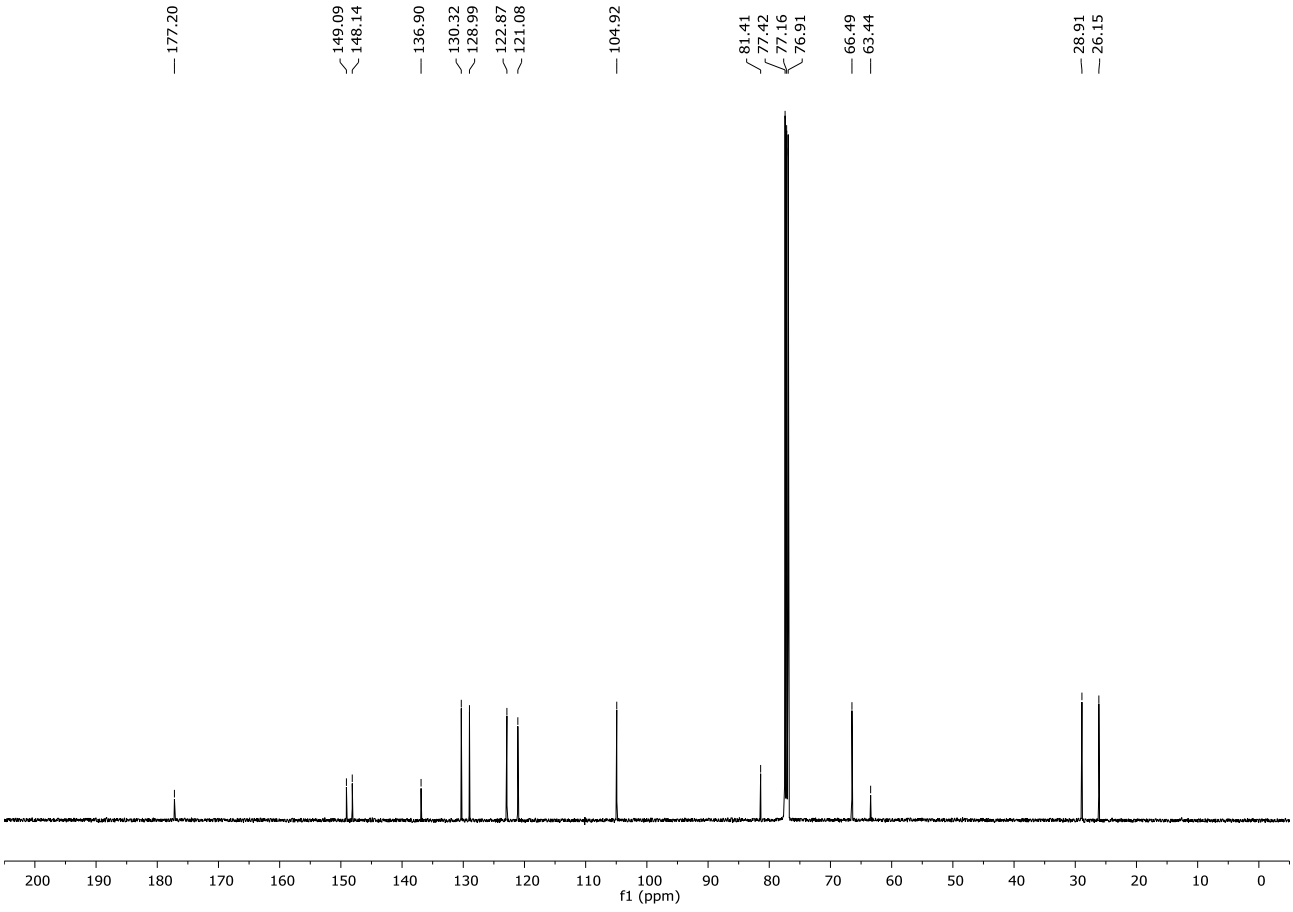

170.57
147.96
146.20
136.60
130.26
129.32
122.77
121.20
117.49
108.76
82.65
77.41
77.16
76.91
63.29
62.43
24.55
21.93
14.02
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

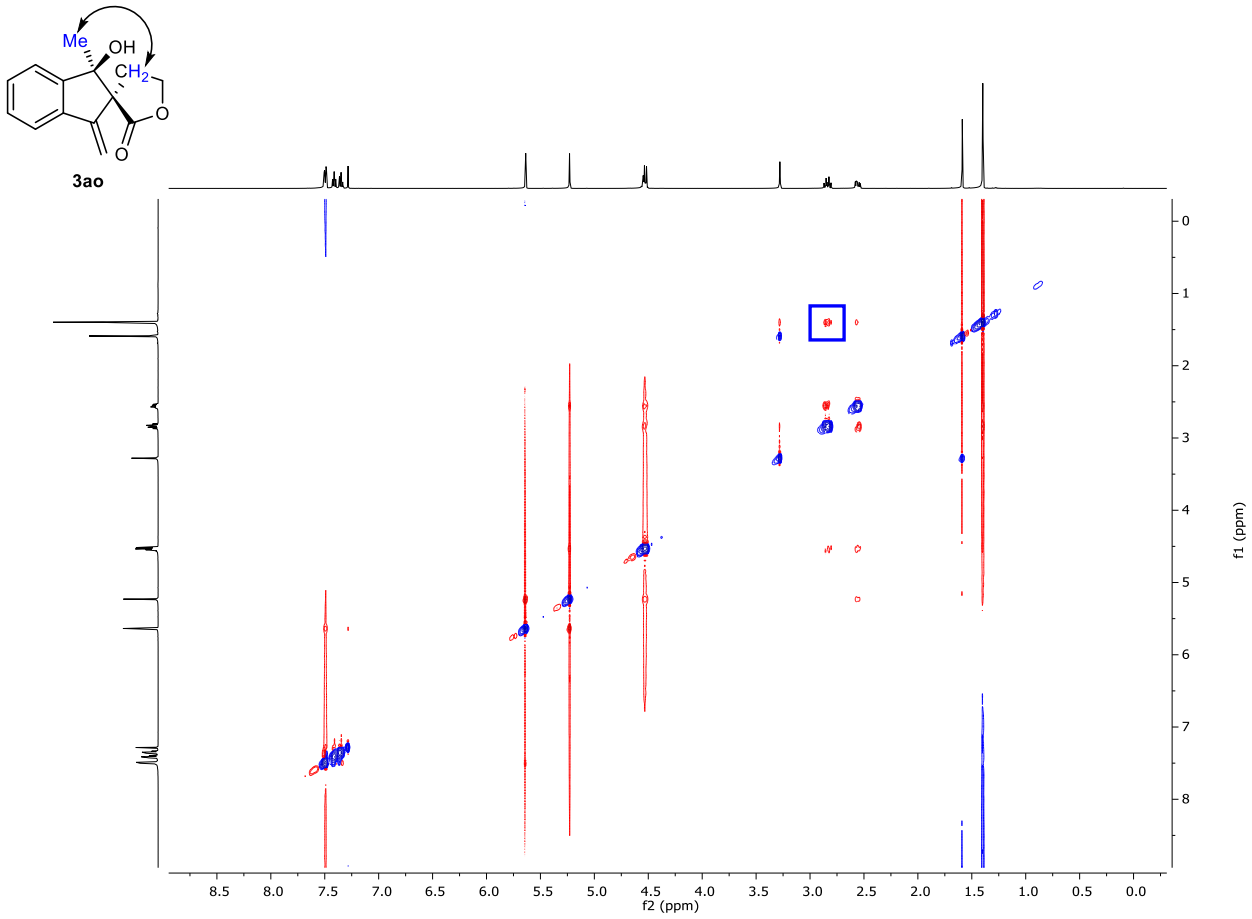

Me
OH H
H
CN
CO2Et
3an
f2 (ppm)
f1 (ppm)

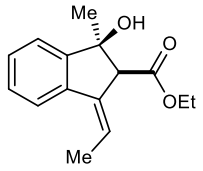

Me
OH
O
O

3ao

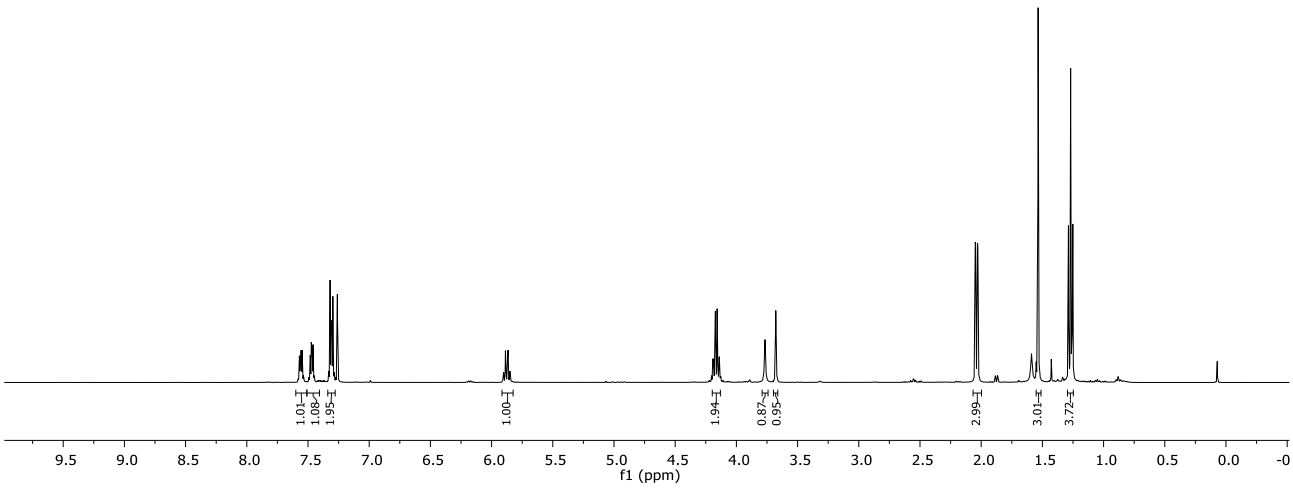

2.01
1.01
1.01
1.00
1.02
2.02
0.93
1.04
1.04
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

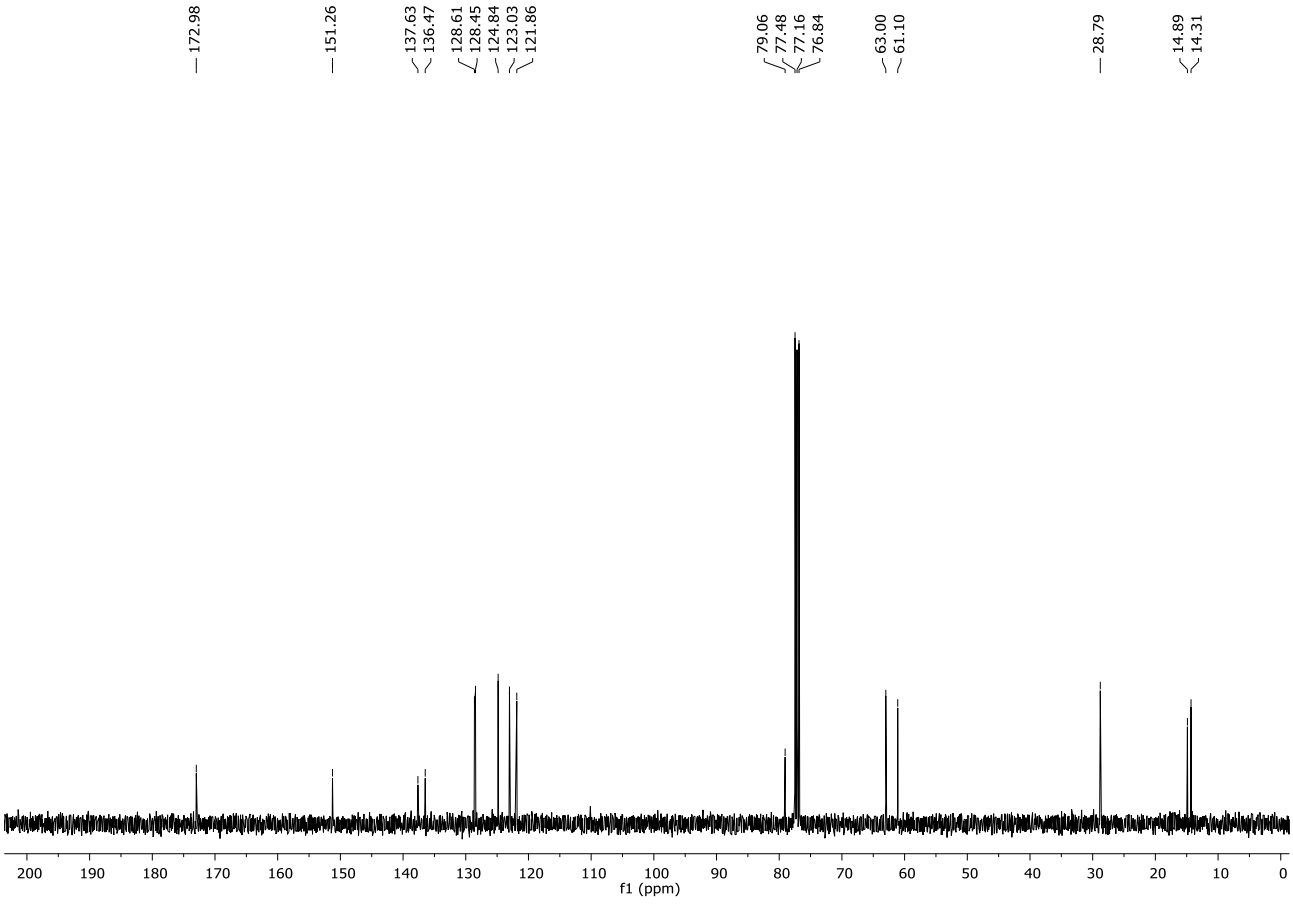

177.20
149.09
148.14
136.90
130.32
128.99
122.87
121.08
104.92
81.41
77.42
77.16
76.91
66.49
63.44
28.91
26.15
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

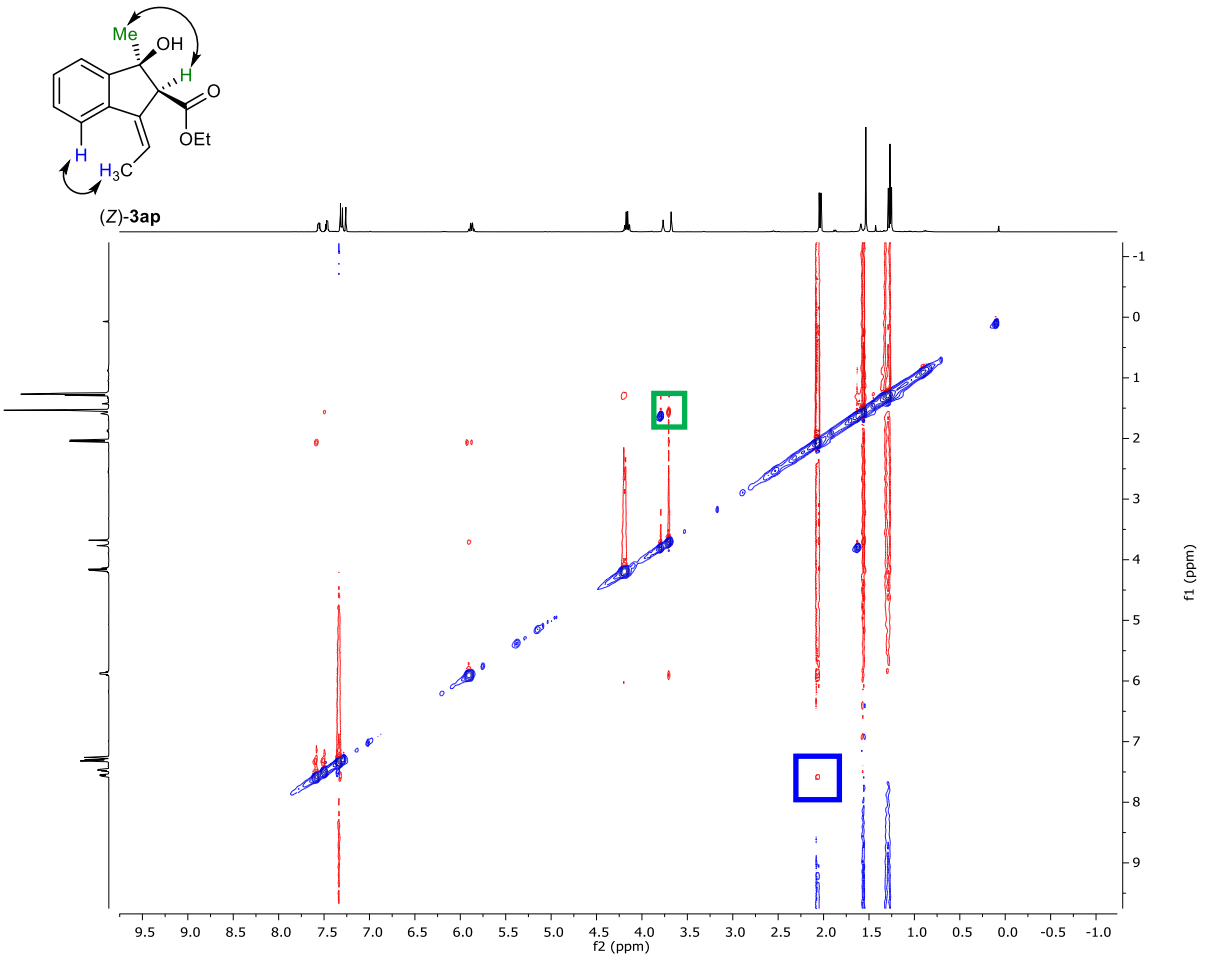

Me
OH
CH2
O
O
3ao
f2 (ppm)
f1 (ppm)

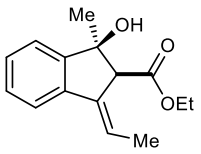

Me
OH
O
OEt
Me

(*Z*)-**3ap**

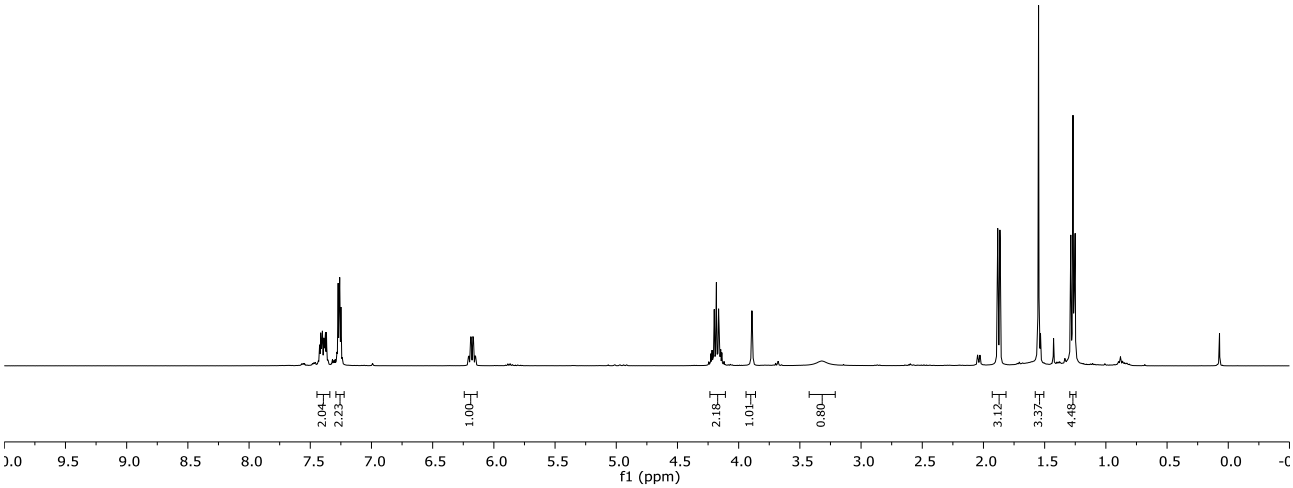

1.01
1.08
1.95
1.00
1.94
0.87
0.95
2.99
3.01
3.72
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

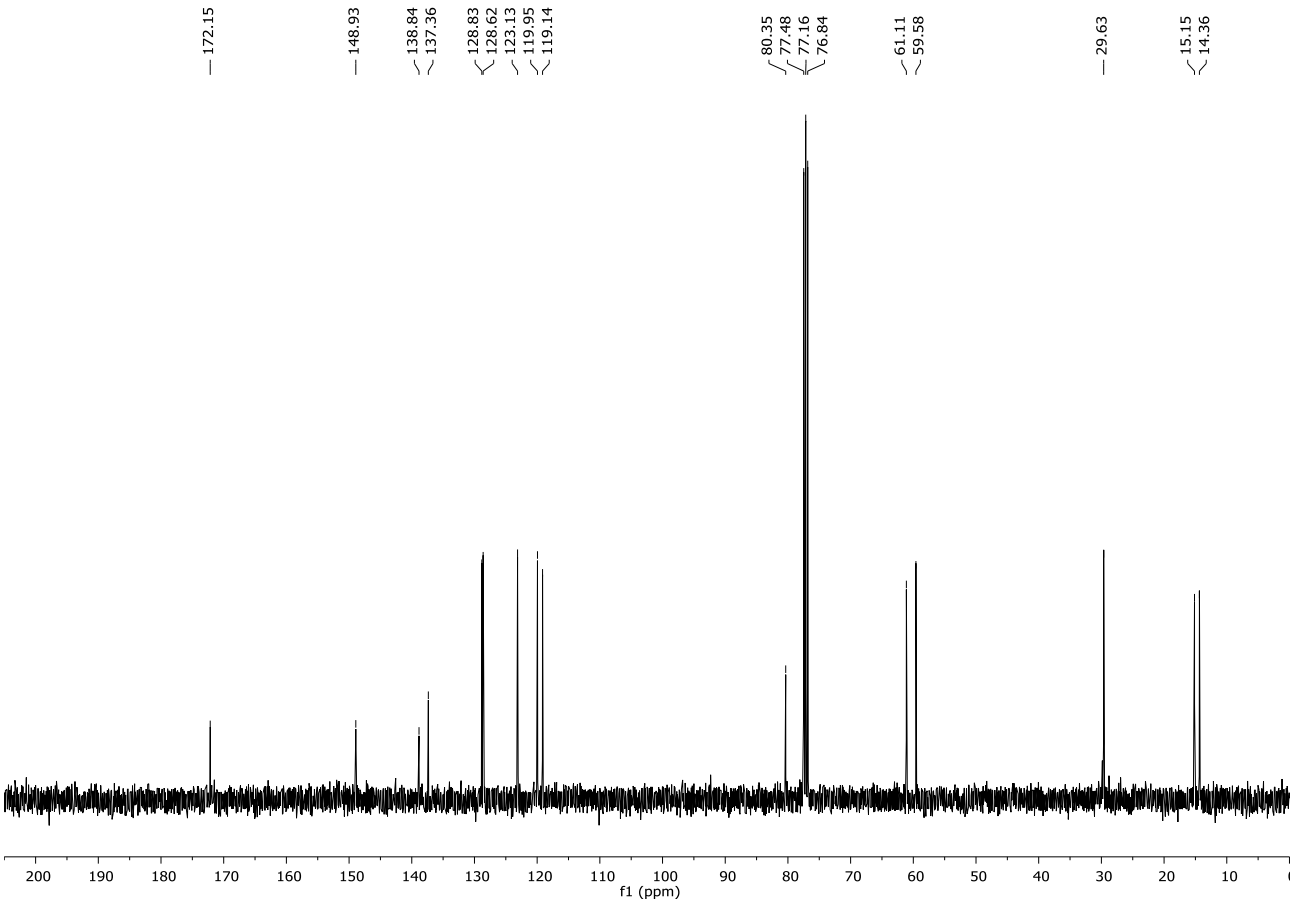

172.98
151.26
137.63
136.47
128.61
128.45
124.84
123.03
121.86
79.06
77.48
77.16
76.84
63.00
61.10
28.79
14.89
14.31
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

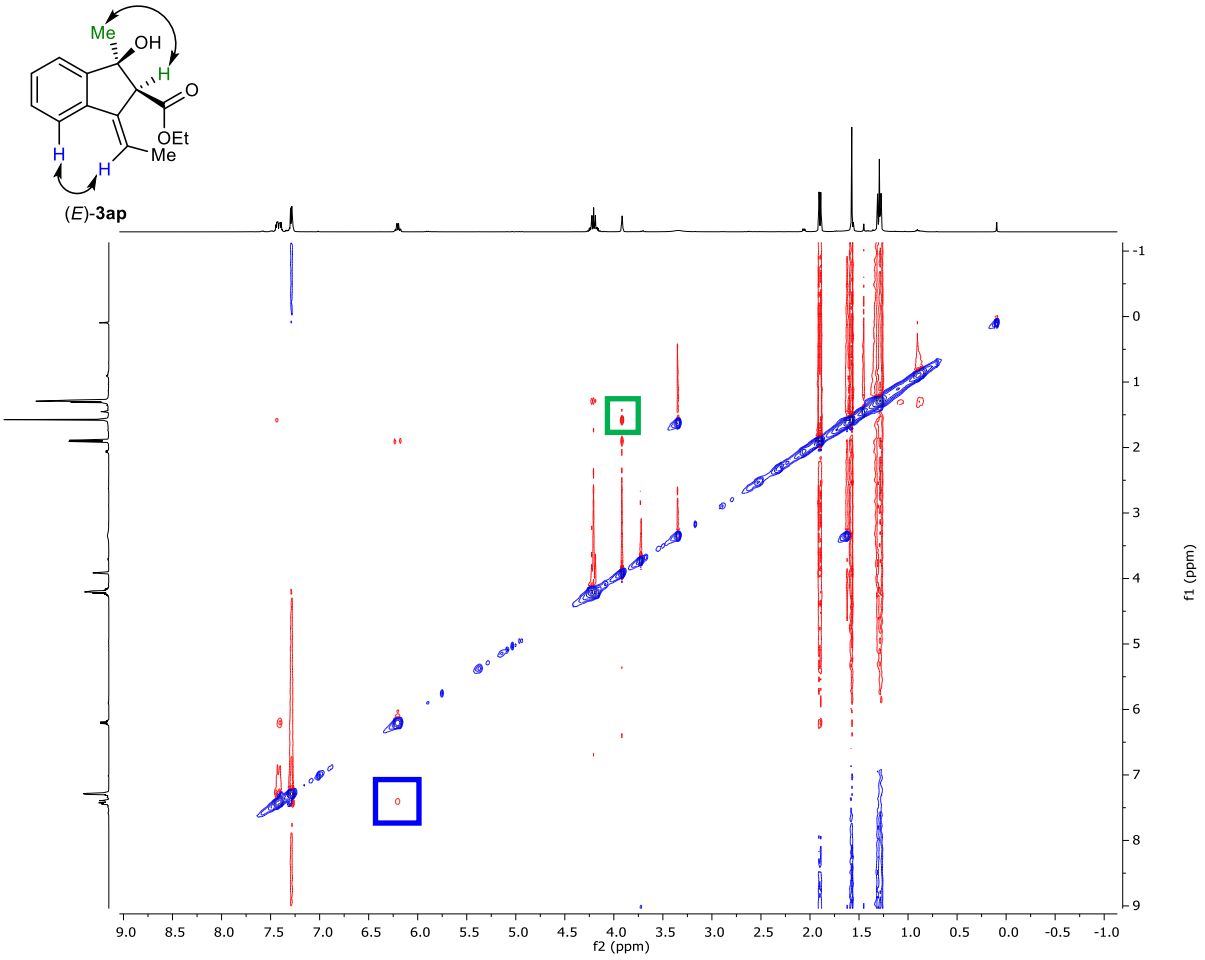

Me
OH
H
O
OEt
H
H3C
(Z)-3ap
f2 (ppm)
f1 (ppm)

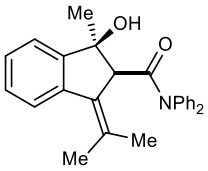

Me
OH
O
OEt
Me

(*E*)-**3ap**

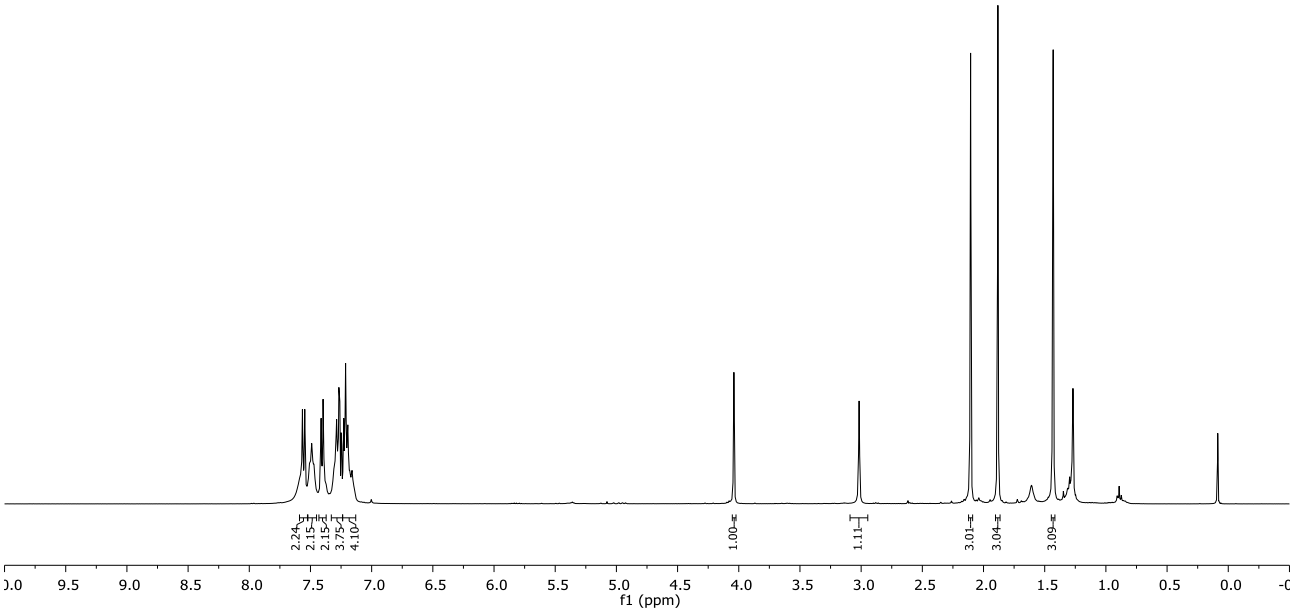

2.04
2.23
1.00
2.18
1.01
0.80
3.12
3.37
4.48
f1 (ppm)

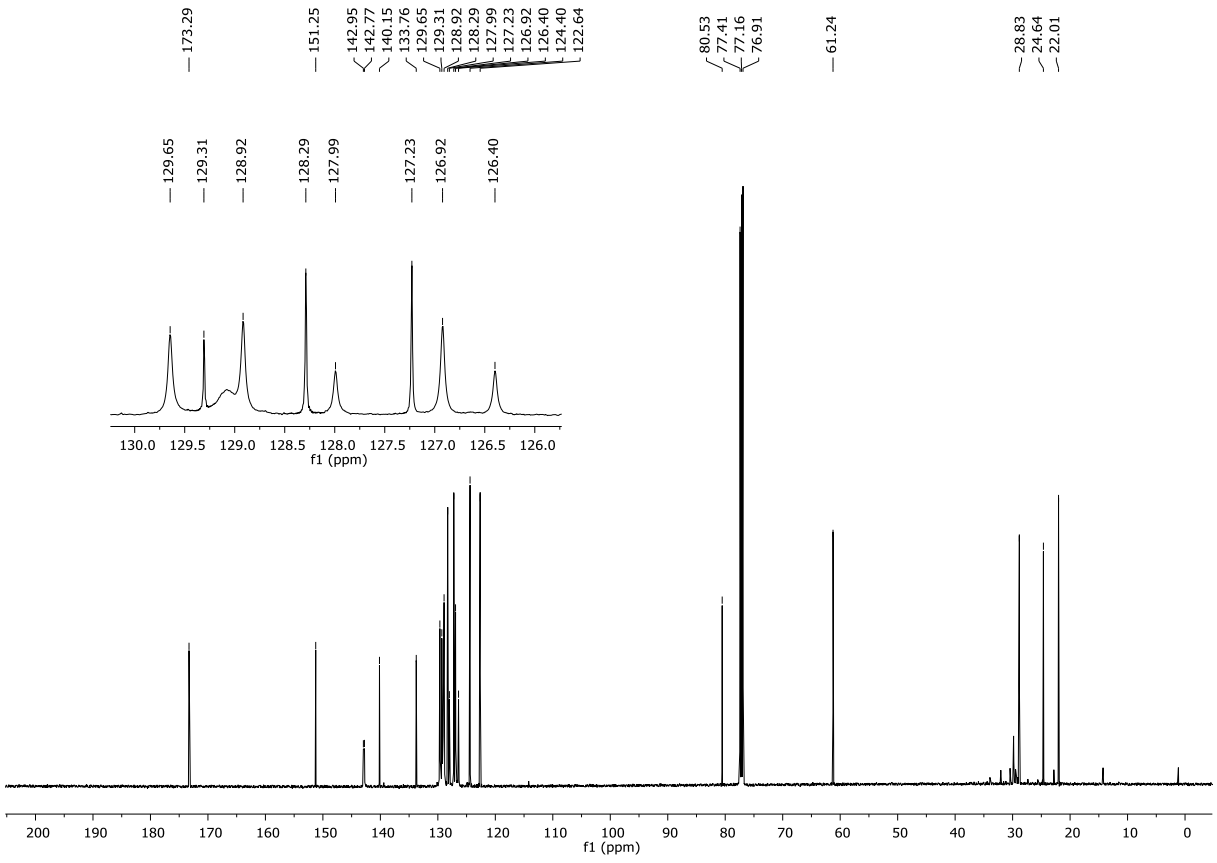

172.15
148.93
138.84
137.36
128.83
128.62
123.13
119.95
119.14
80.35
77.48
77.16
76.84
61.11
59.58
29.63
15.15
14.36
f1 (ppm)

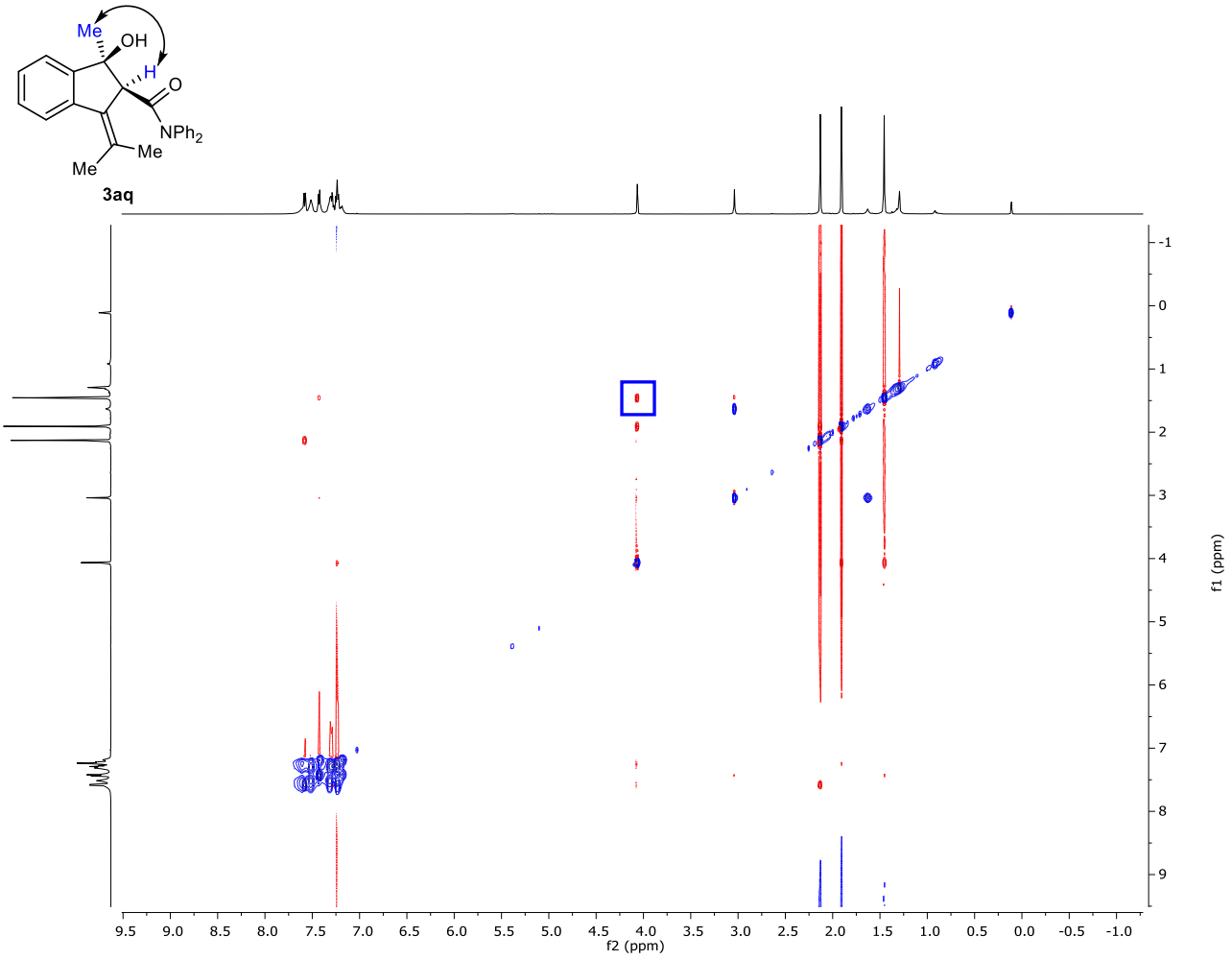

Me
OH
H
O
OEt
Me
H
H
(E)-3ap
f2 (ppm)
f1 (ppm)

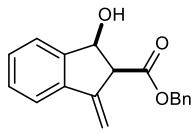

Me
OH
O
NPh2
Me
Me

3aq

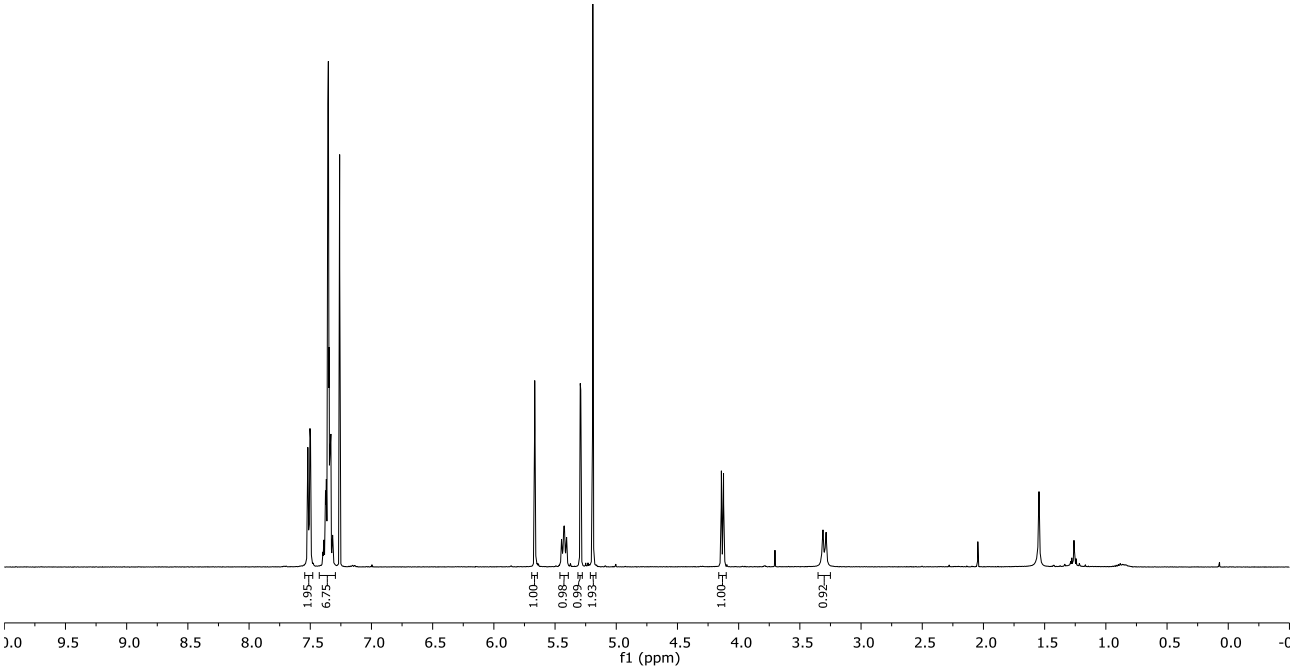

2.24
2.15
2.15
3.75
4.10
1.00
1.11
3.01
3.04
3.09
f1 (ppm)

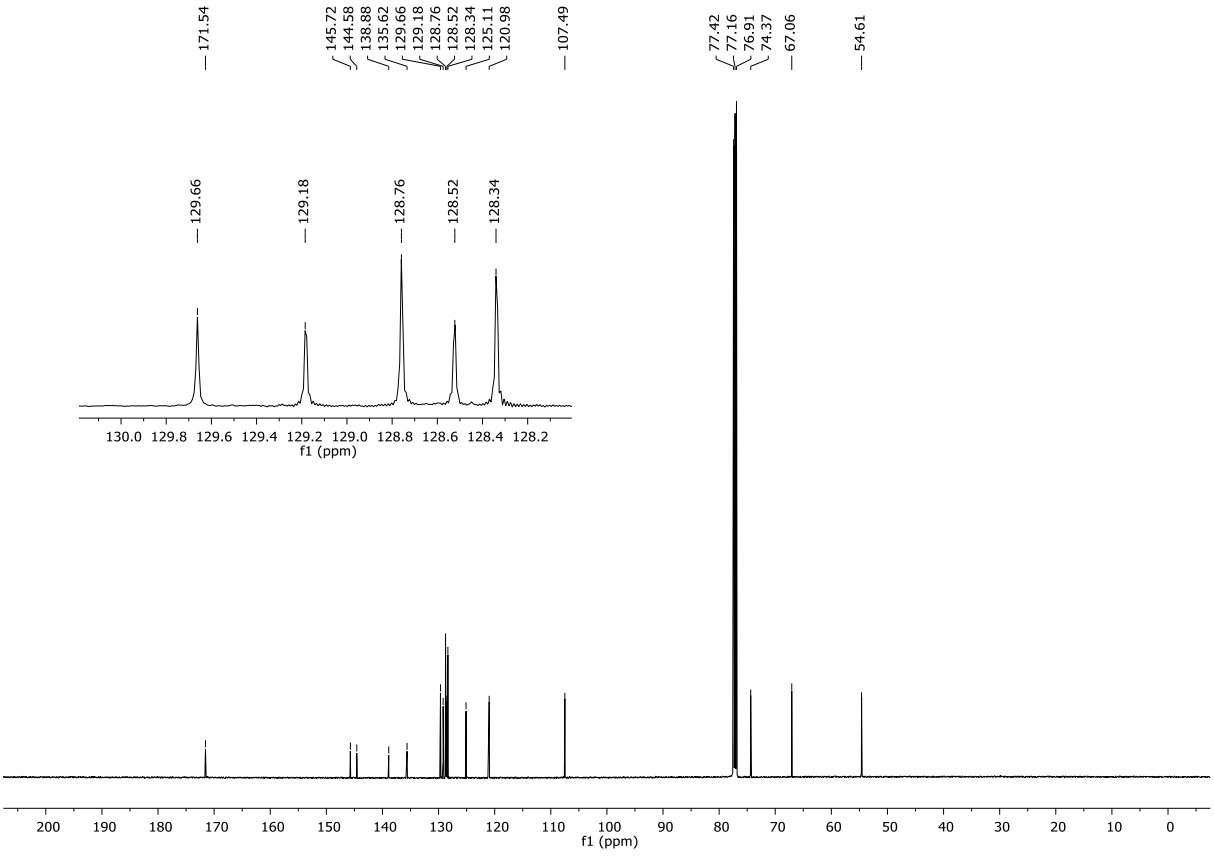

173.29
151.25
142.95
142.77
140.15
133.76
129.65
129.31
128.92
128.29
127.99
127.23
126.92
126.40
124.40
122.64
80.53
77.41
77.16
76.91
61.24
28.83
24.64
22.01
f1 (ppm)

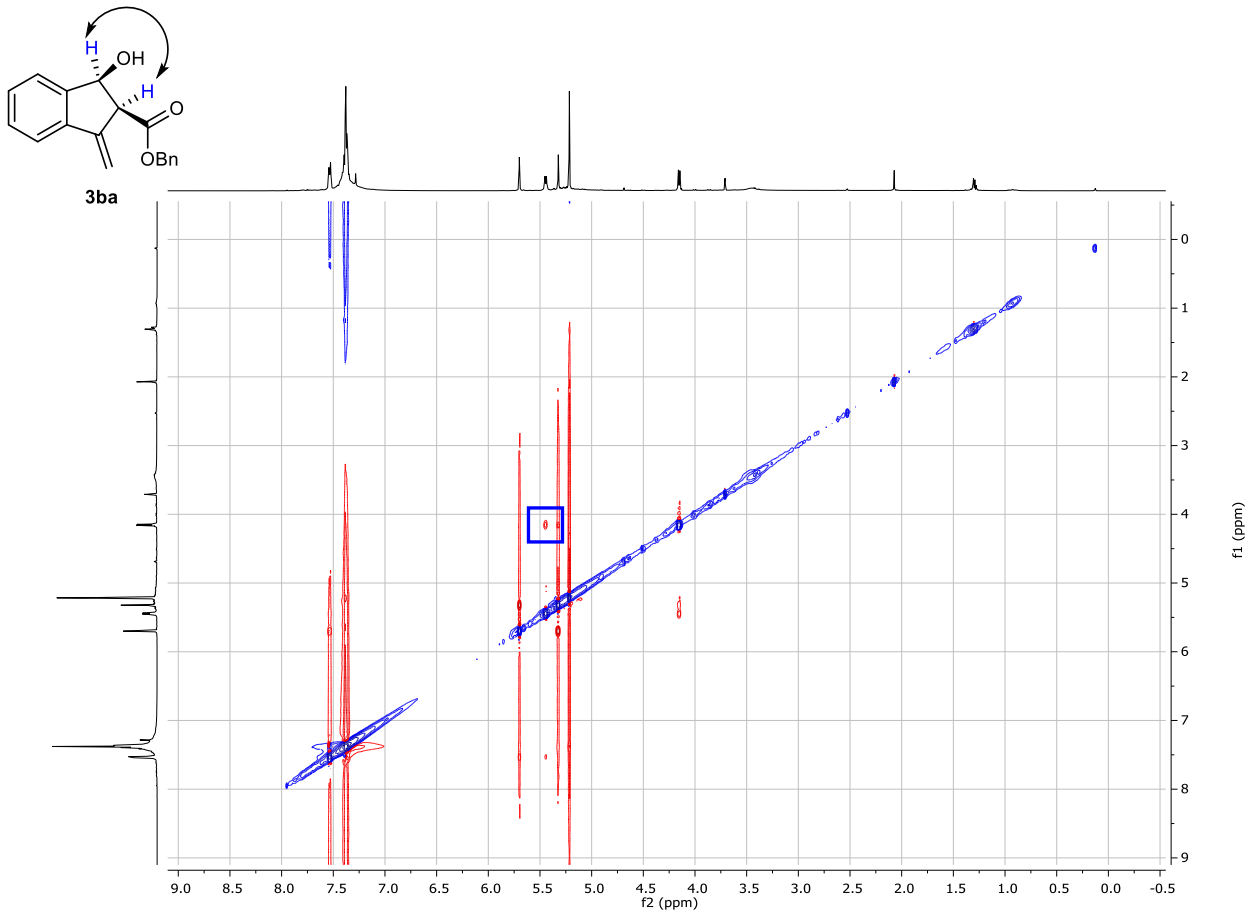

Me
OH
H
O
NPh2
Me
Me
3aq
f2 (ppm)
f1 (ppm)

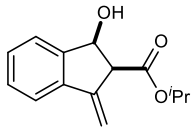

OH
O
OBn

3ba

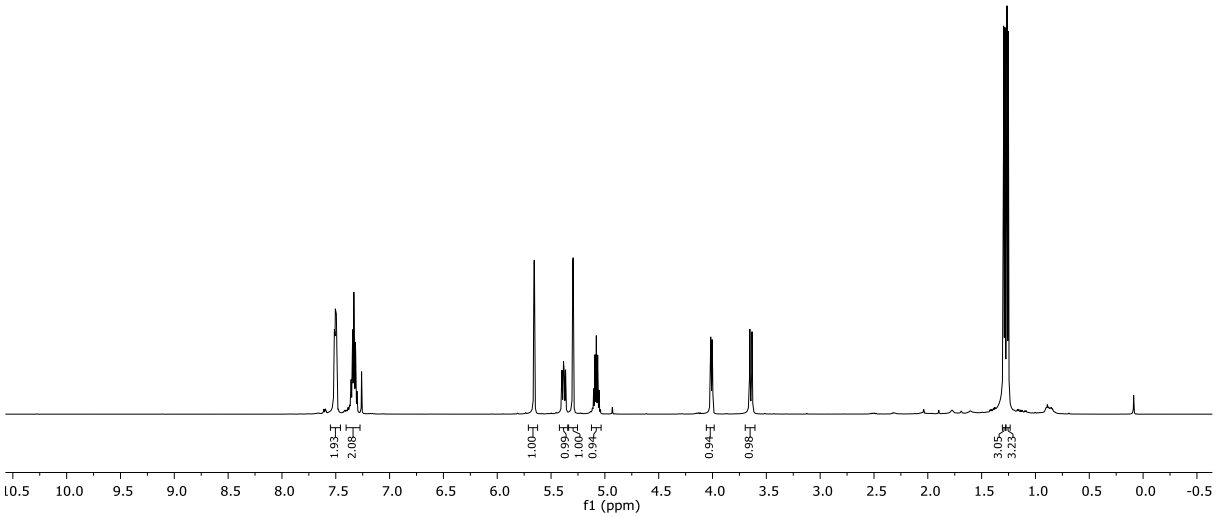

1.95
6.75
1.00
0.98
0.99
1.93
1.00
0.92
f1 (ppm)

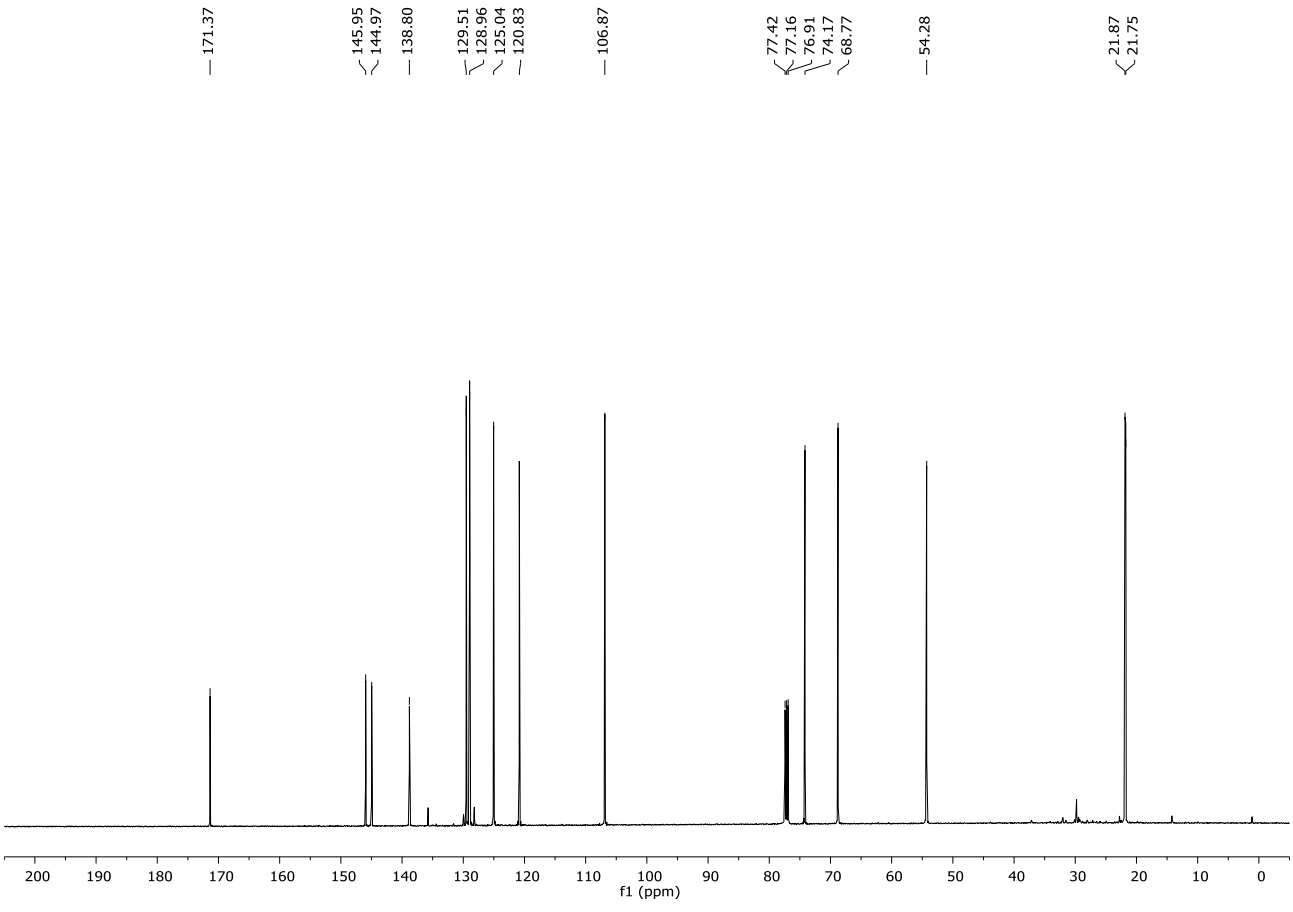

171.54
145.72
144.58
138.88
135.62
129.66
129.18
128.76
128.52
128.34
125.11
120.98
107.49
77.42
77.16
76.91
74.37
67.06
54.61
129.66
129.18
128.76
128.52
128.34
f1 (ppm)

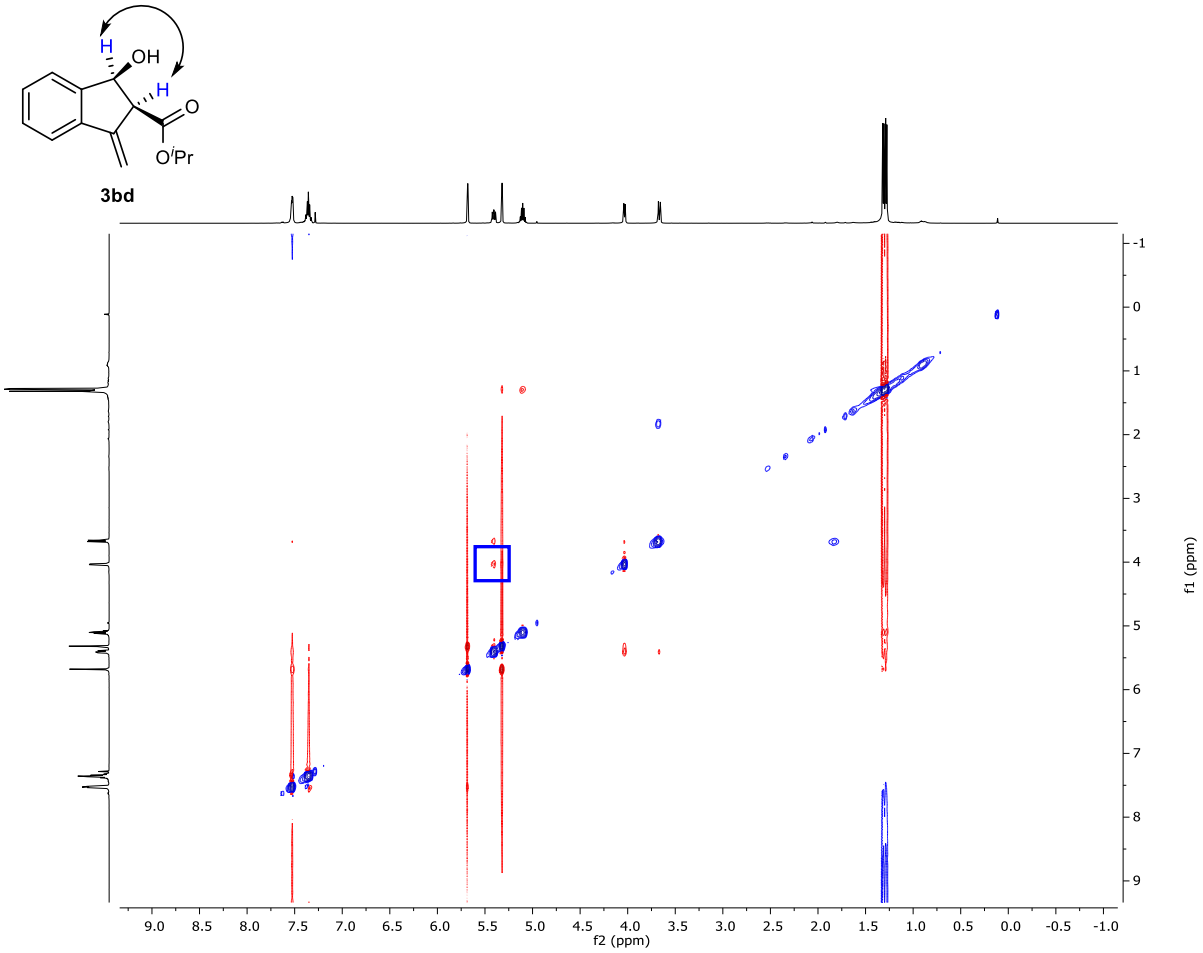

H
OH
H
O
OBn
3ba
f2 (ppm)
f1 (ppm)

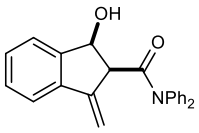

OH
O
O'Pr

3bd

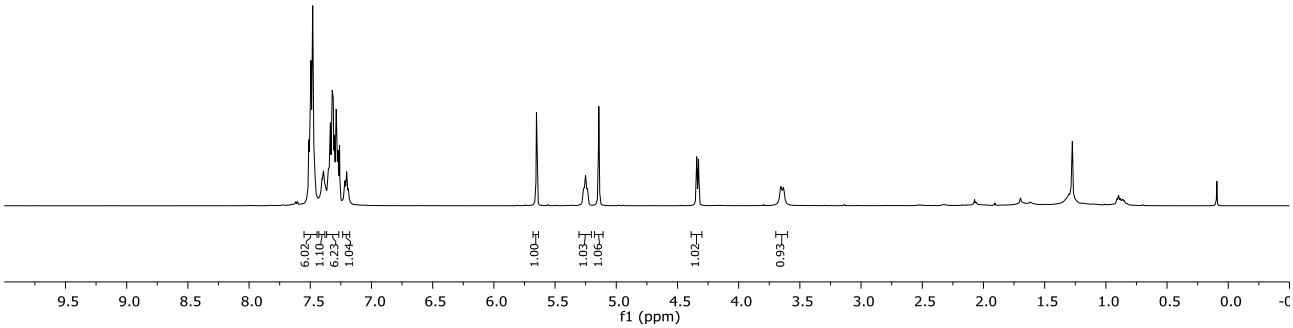

1.93
2.08
1.00
0.99
1.00
0.94
0.94
0.98
3.05
3.23
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

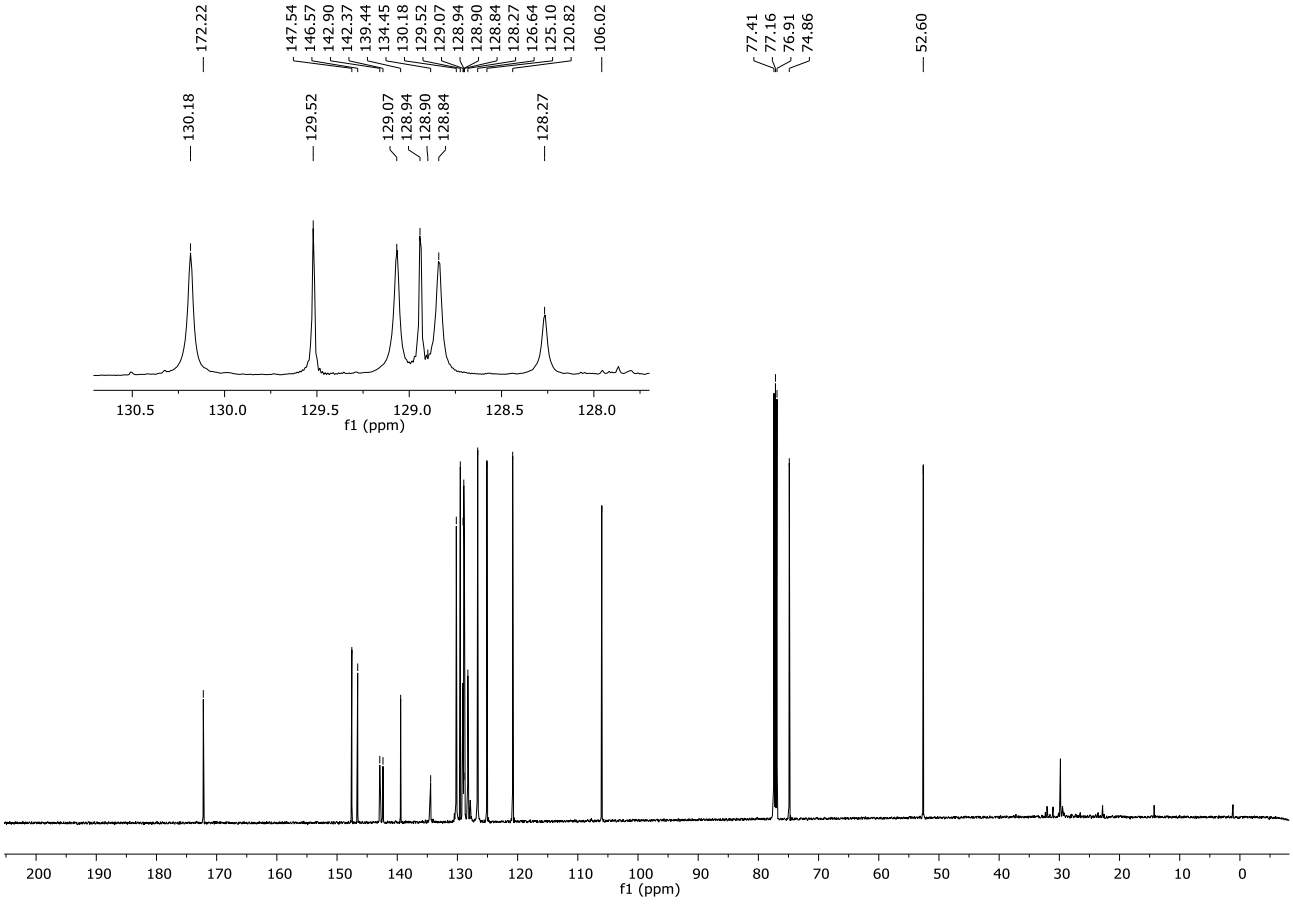

171.37
145.95
144.97
138.80
129.51
128.96
125.04
120.83
106.87
77.42
77.16
76.91
74.17
68.77
54.28
21.87
21.75
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

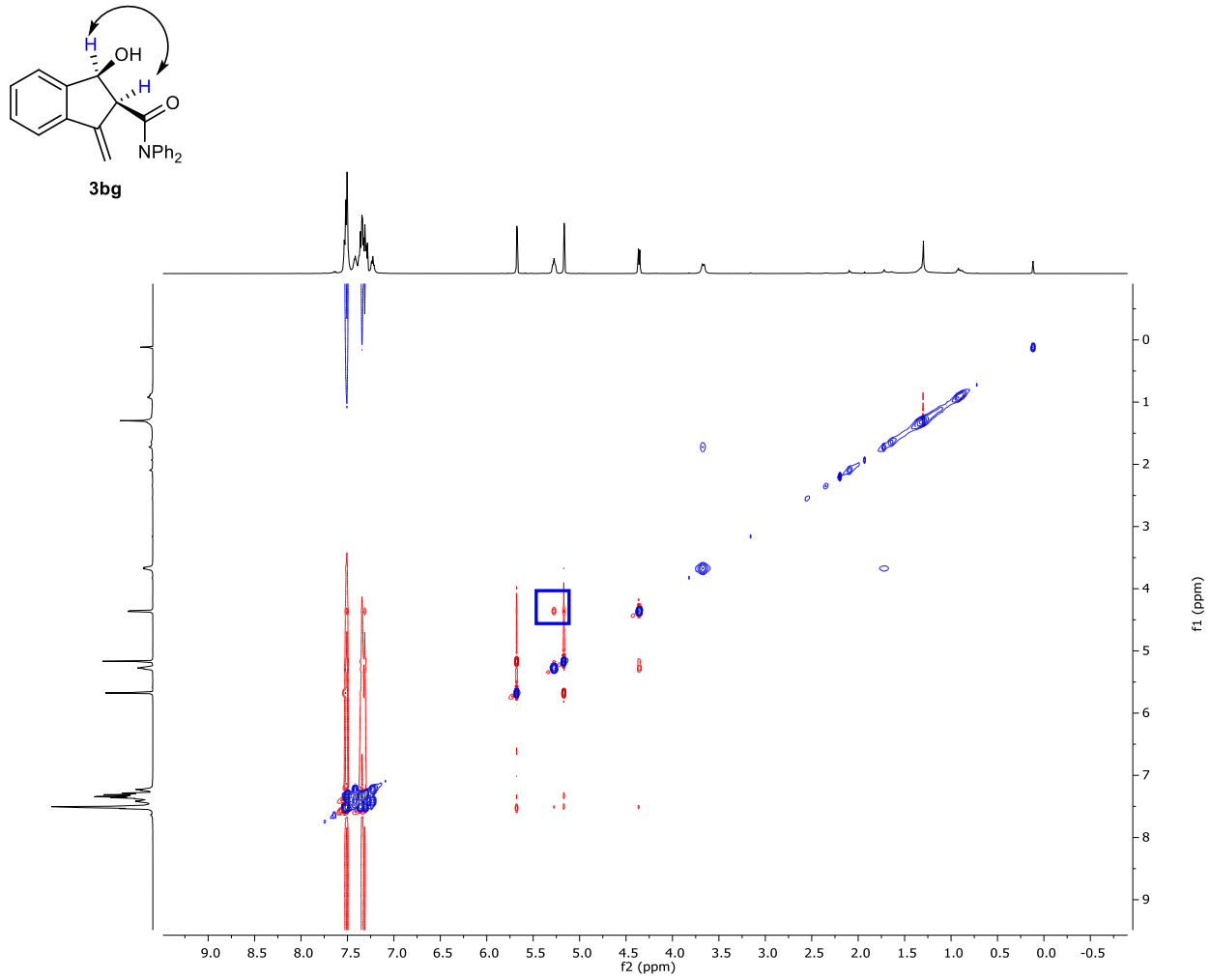

H
OH
H
O
O^{i}Pr
3bd
f2 (ppm)
f1 (ppm)

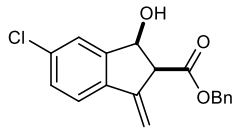

OH
O
NPh2

3bg

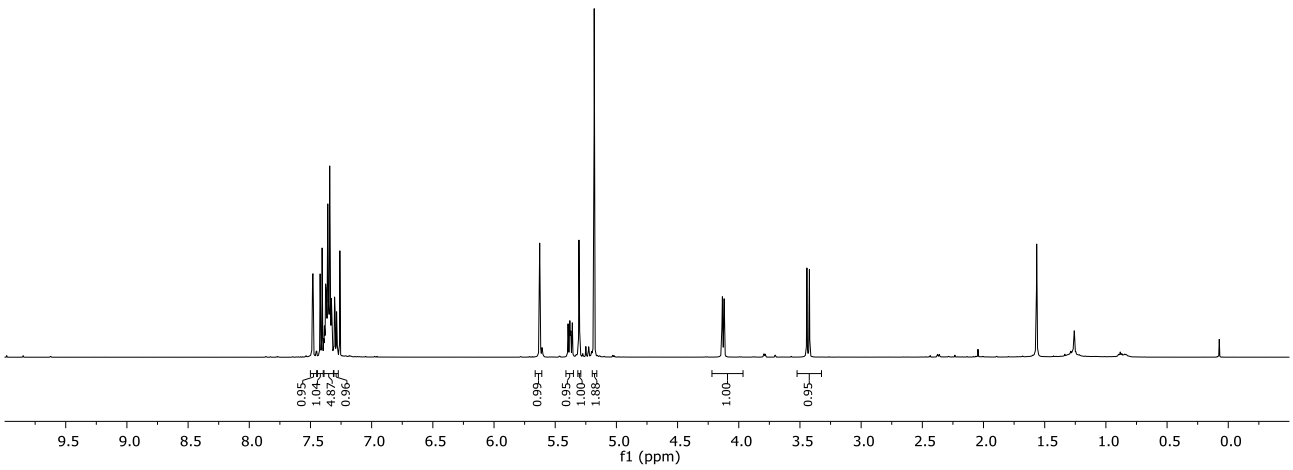

6.02
1.10
6.23
1.04
1.00
1.03
1.06
1.02
0.93
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

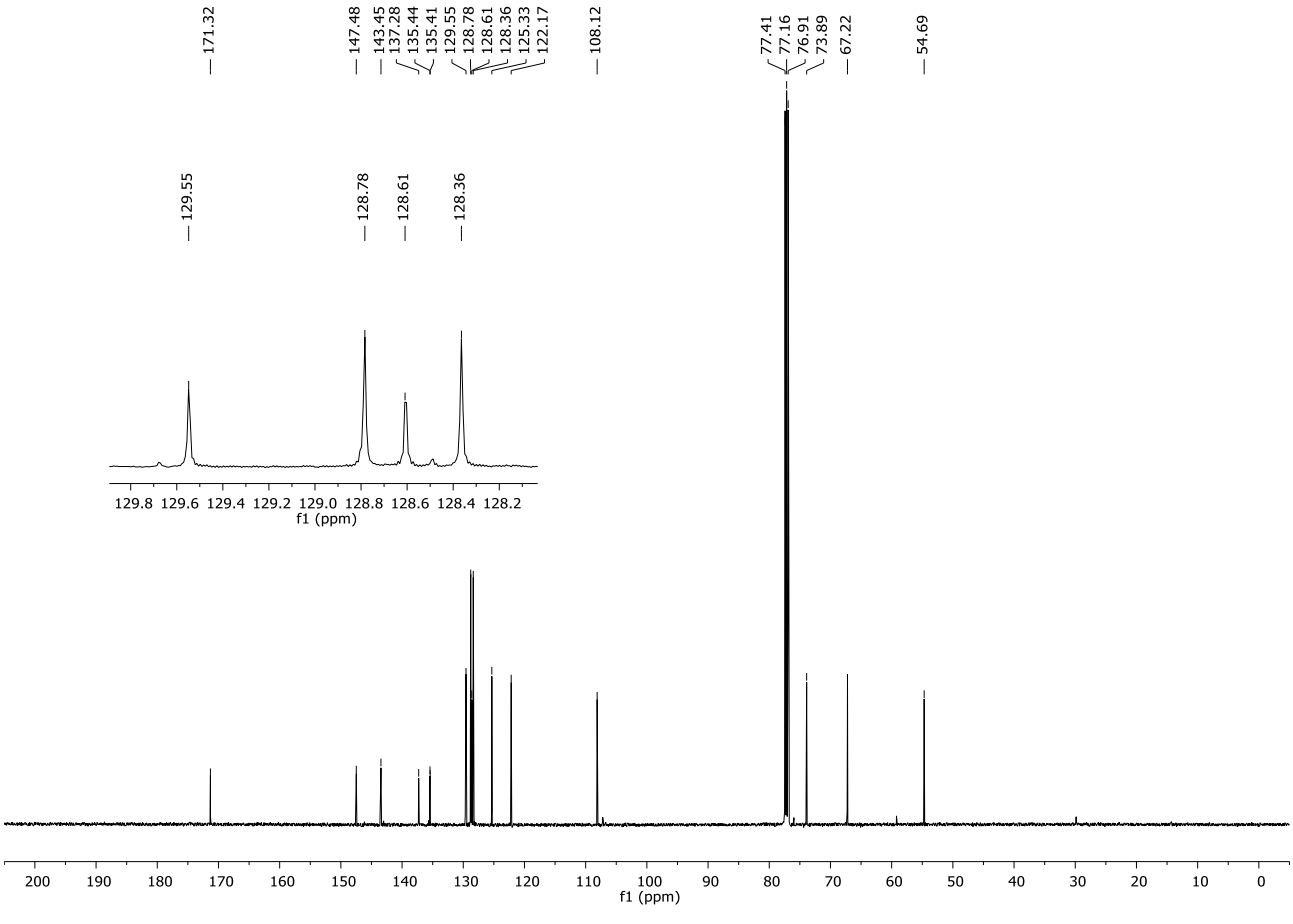

172.22
147.54
146.57
142.90
142.37
139.44
134.45
130.18
129.52
129.07
128.94
128.90
128.84
128.27
126.64
125.10
120.82
106.02
77.41
77.16
76.91
74.86
52.60
130.18
129.52
129.07
128.94
128.90
128.84
128.27
130.5 130.0 129.5 129.0 128.5 128.0
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

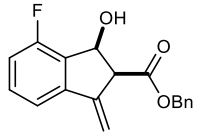

H
OH
H
O
NPh2
3bg
f2 (ppm)
f1 (ppm)


OH
Cl
O
OBn

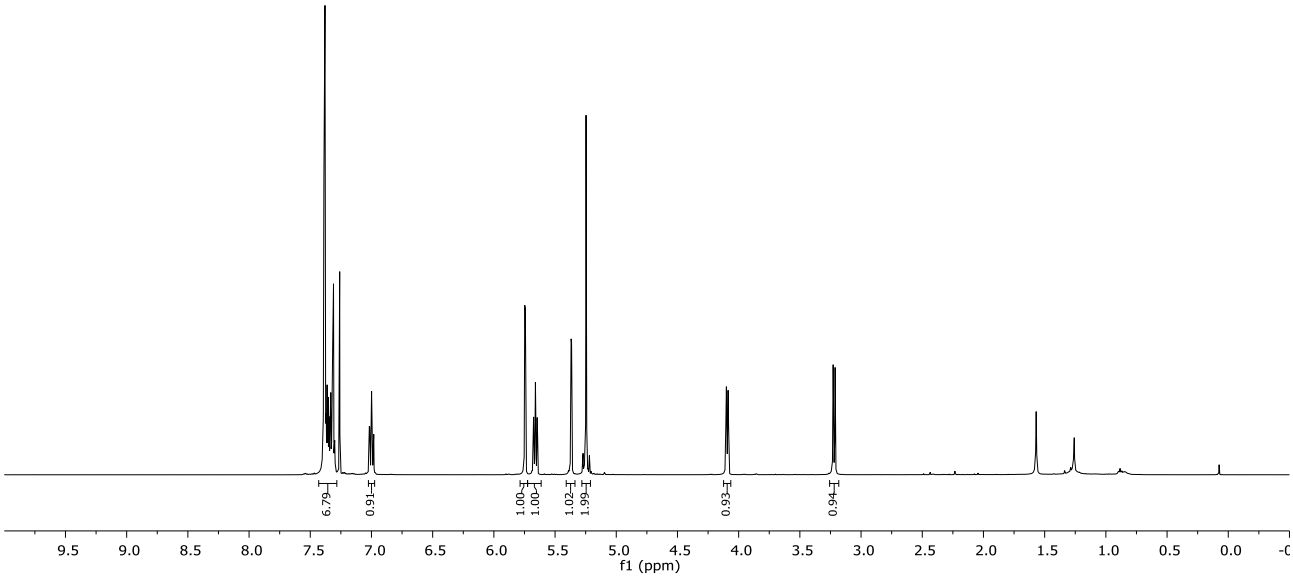
3ca

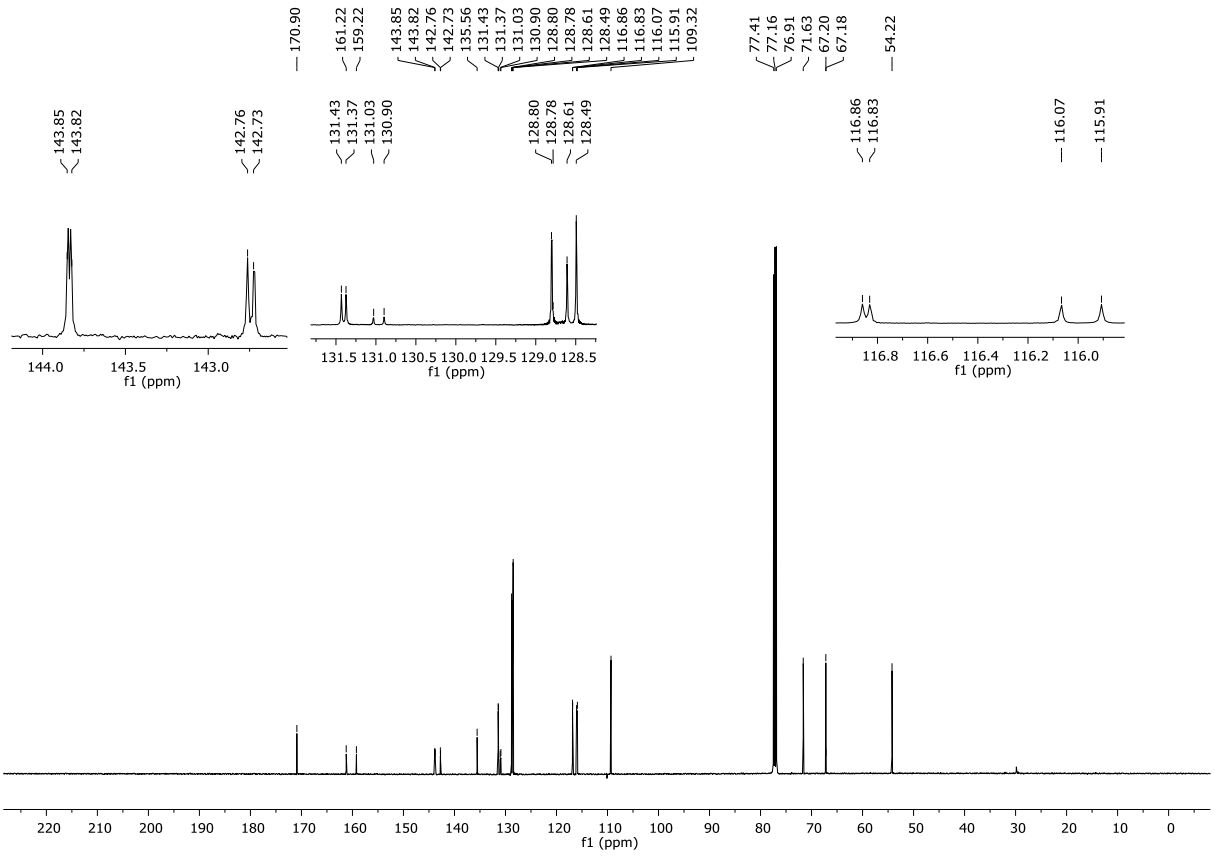

0.95
1.04
4.87
0.96
0.99
0.95
1.00
1.88
1.00
0.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

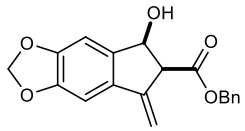

171.32
147.48
143.45
137.28
135.44
135.41
129.55
128.78
128.61
128.36
125.33
122.17
108.12
77.41
77.16
76.91
73.89
67.22
54.69
129.55
128.78
128.61
128.36
129.8 129.6 129.4 129.2 129.0 128.8 128.6 128.4 128.2
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


F
OH
O
OBn

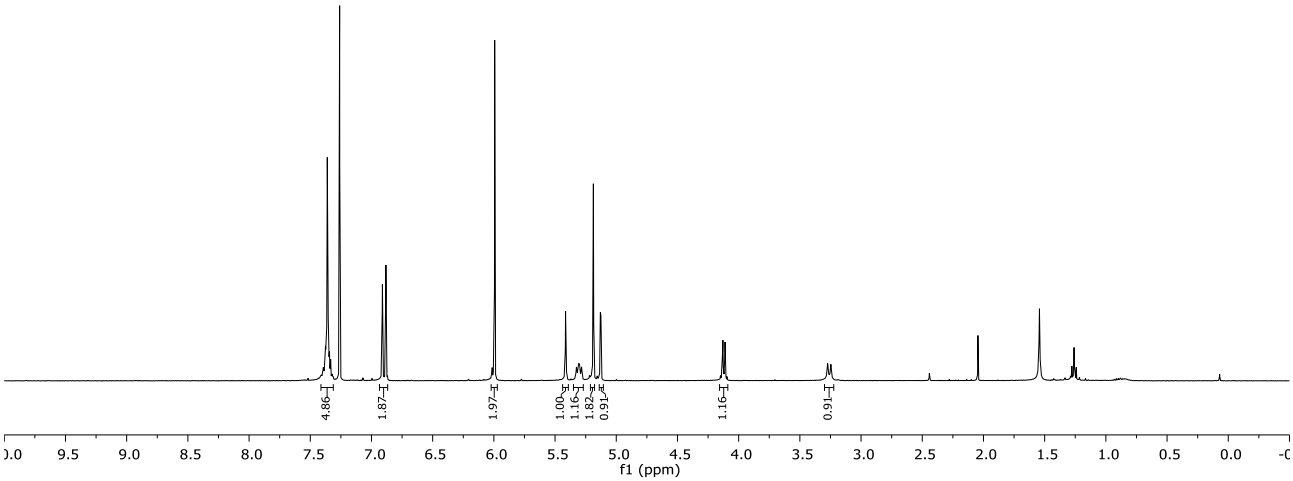
3da

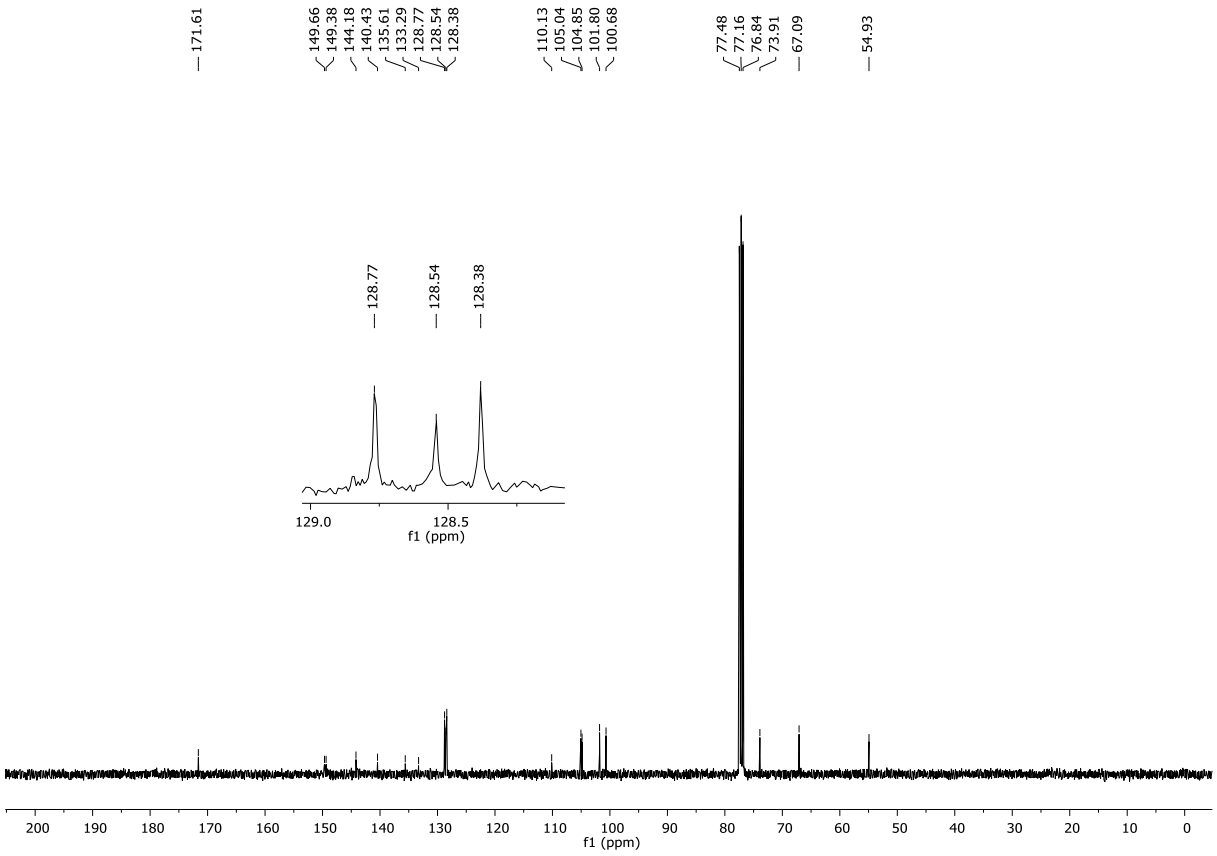

6.79
0.91
1.00
1.00
1.02
1.99
0.93
0.94
f1 (ppm)

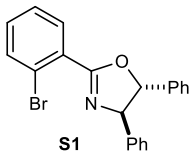

170.90
161.22
159.22
143.85
143.82
142.76
142.73
135.56
131.43
131.37
131.03
130.90
128.80
128.78
128.61
128.49
116.86
116.83
116.07
115.91
109.32
77.41
77.16
76.91
71.63
67.20
67.18
54.22
f1 (ppm)


OH
O
O
O
OBn

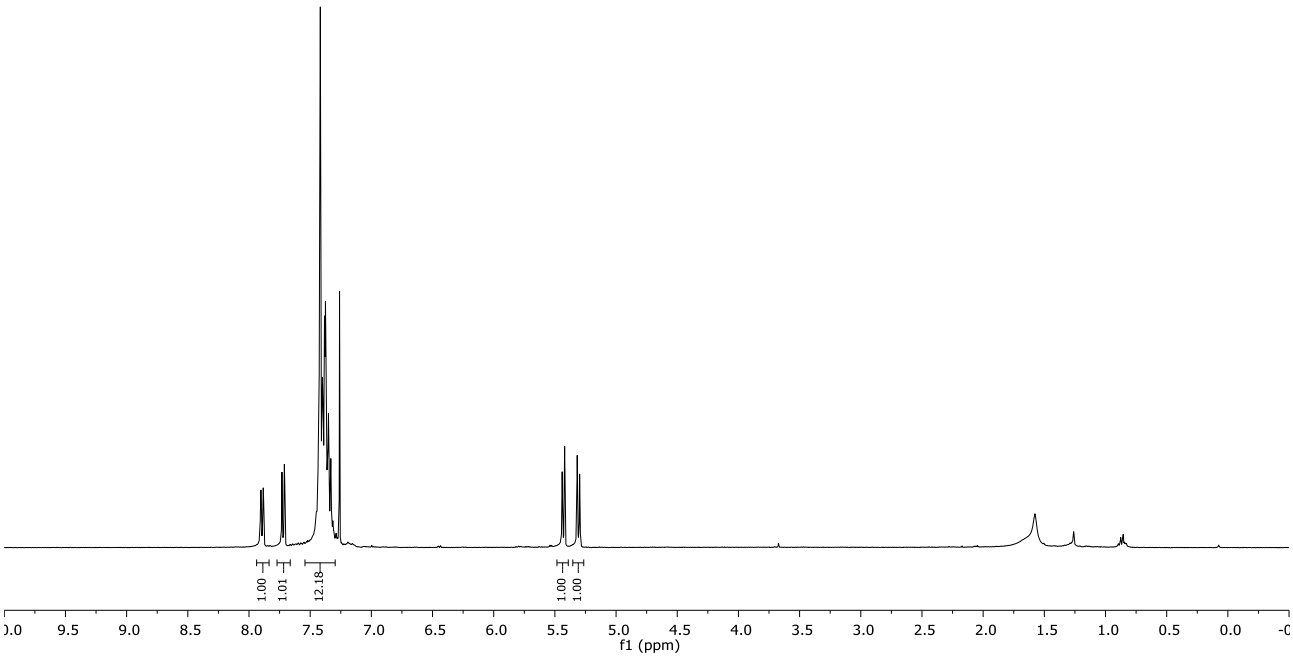
3ea

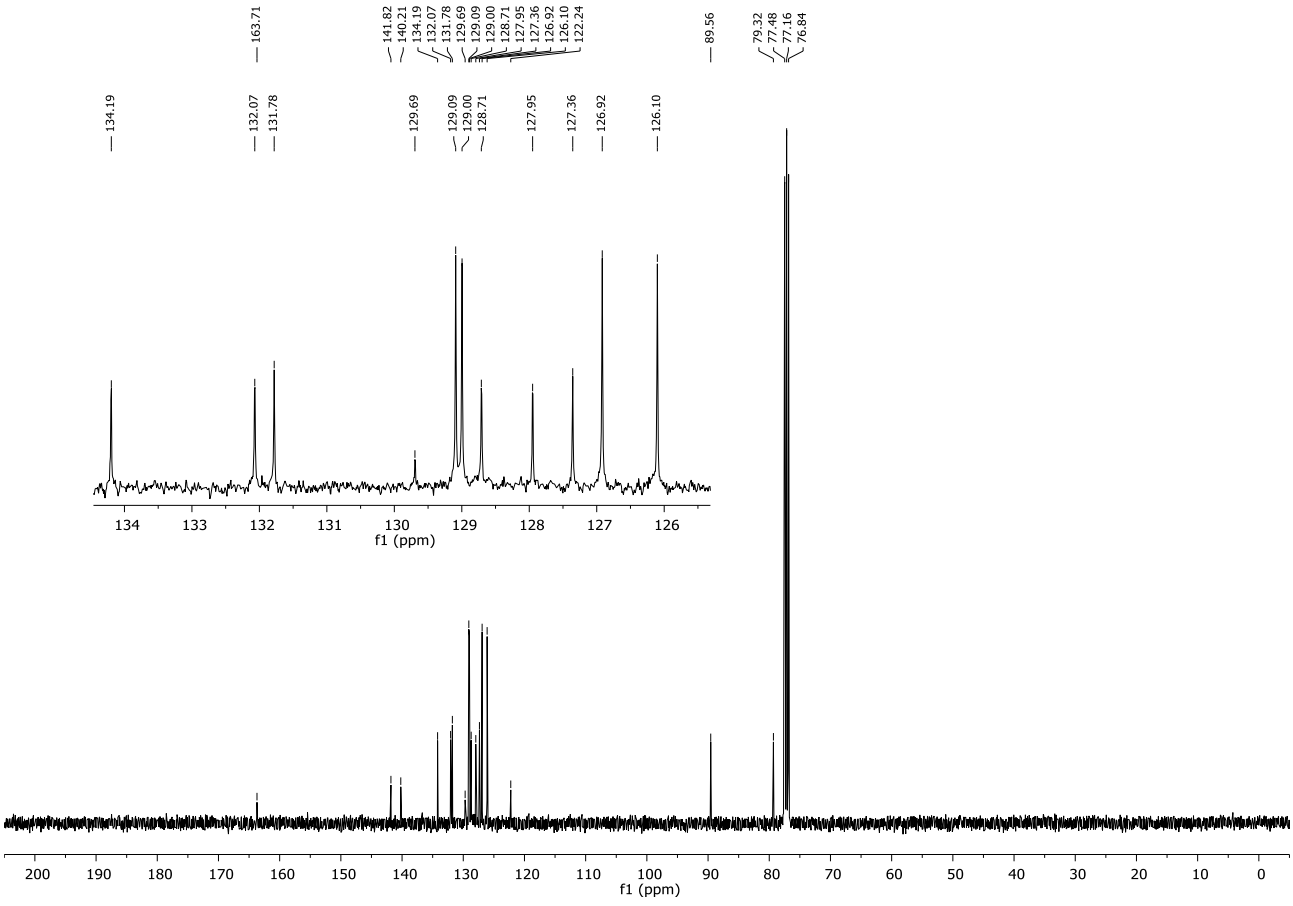

4.86
1.87
1.97
1.00
1.16
1.82
0.91
1.16
0.91
f1 (ppm)

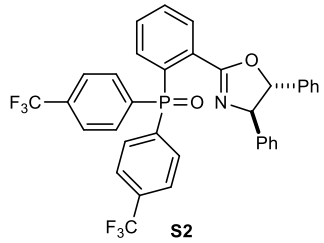

171.61
149.66
149.38
144.18
140.43
135.61
133.29
128.77
128.54
128.38
110.13
105.04
104.85
101.80
100.68
77.48
77.16
76.84
73.91
67.09
54.93
128.77
128.54
128.38
129.0
128.5
f1 (ppm)
f1 (ppm)


Br
N
O
Ph
Ph

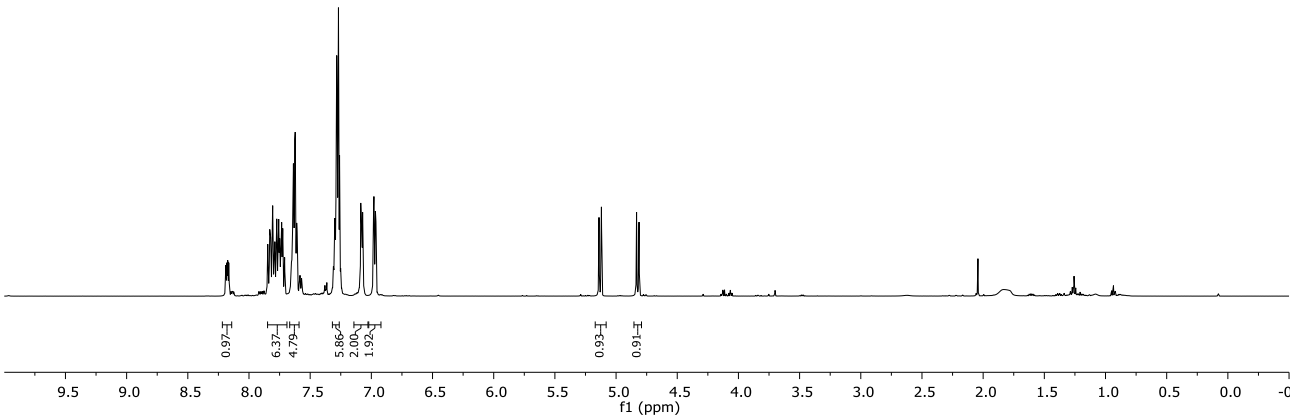
S1

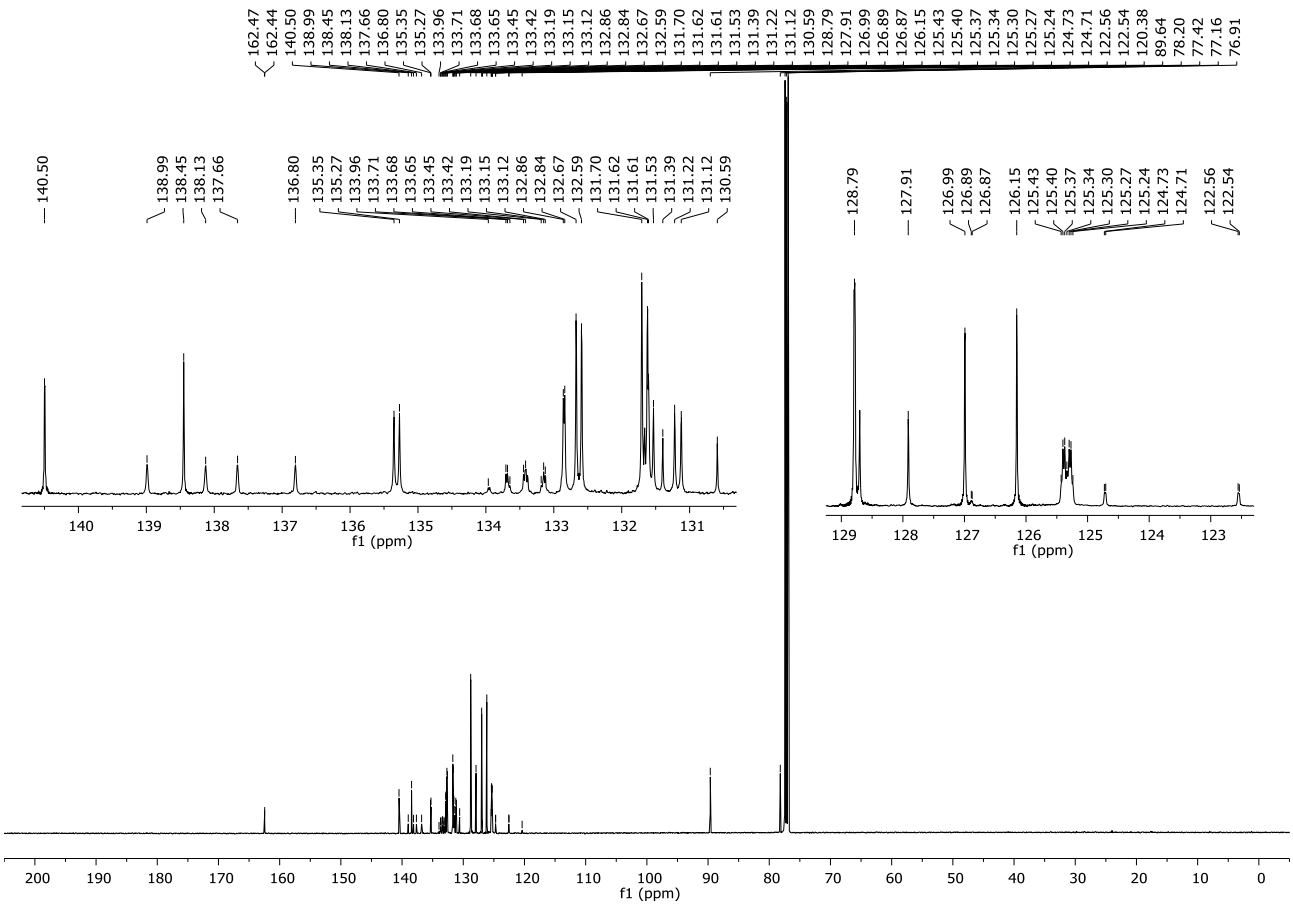

1.00
1.01
12.18
1.00
1.00
f1 (ppm)

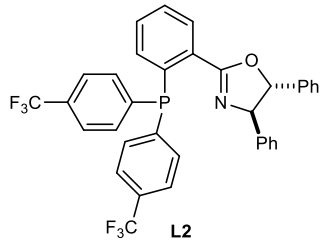

163.71
141.82
140.21
134.19
132.07
131.78
129.69
129.09
129.00
128.71
127.95
127.36
126.92
126.10
122.24
89.56
79.32
77.48
77.16
76.84
134.19
132.07
131.78
129.69
129.09
129.00
128.71
127.95
127.36
126.92
126.10
f1 (ppm)
f1 (ppm)


F3C
P=O
O
N
Ph
Ph
F3C

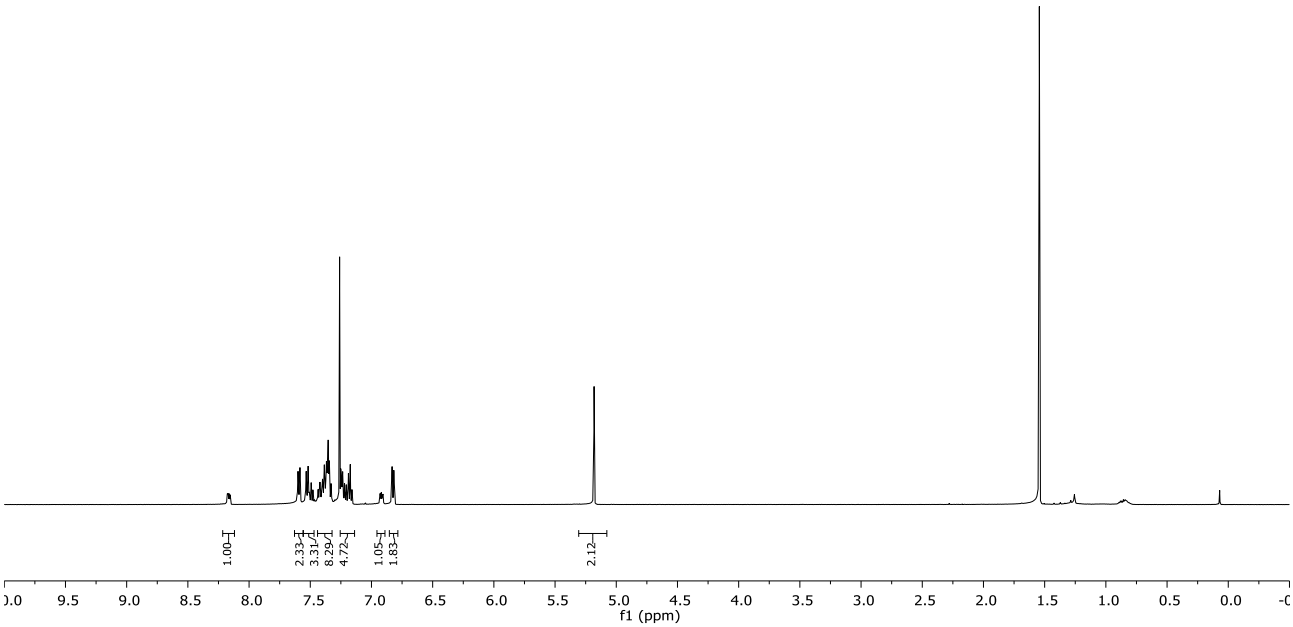
S2

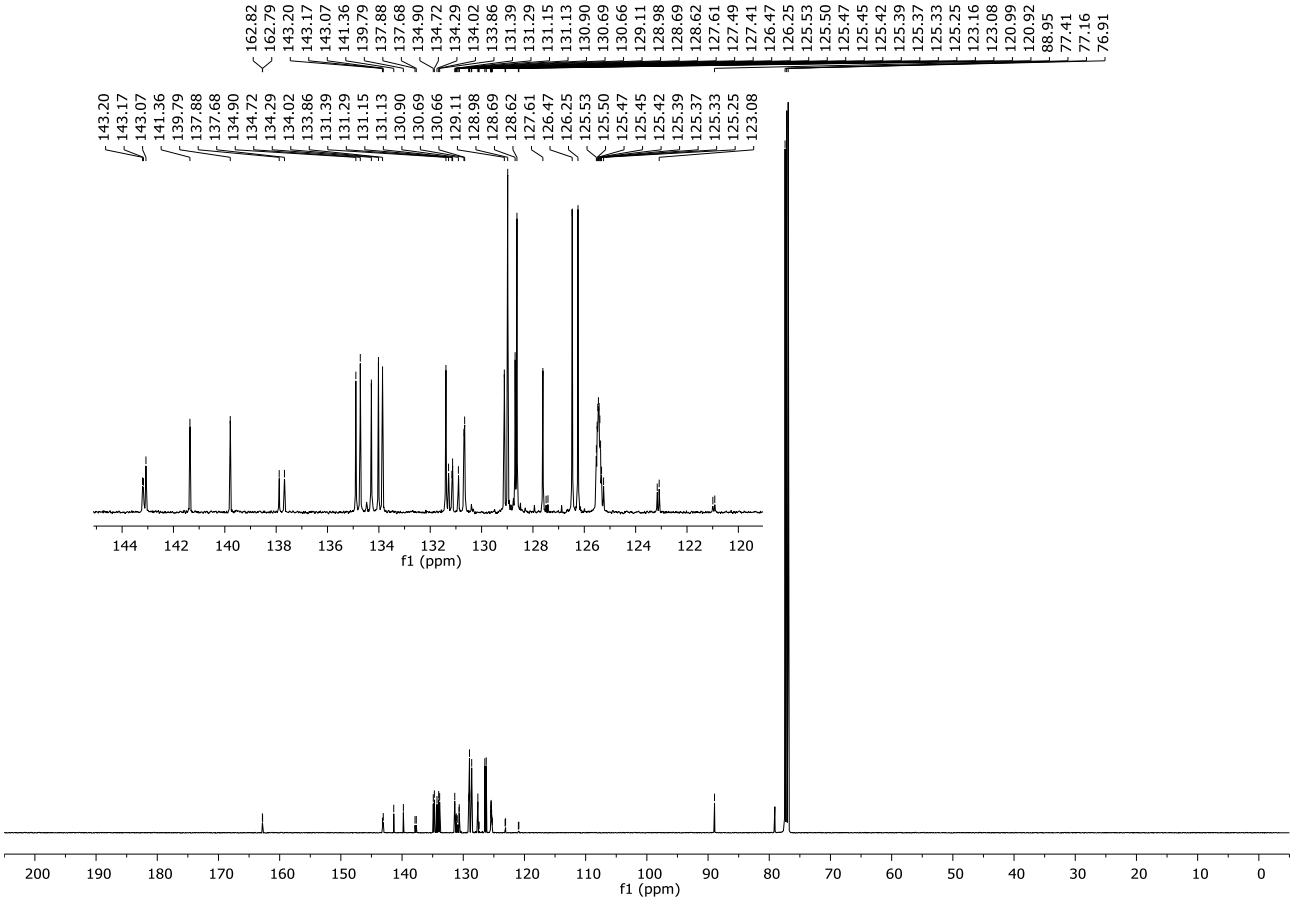

0.97
6.37
4.79
5.86
2.00
1.92
0.93
0.91
f1 (ppm)


162.47
162.44
140.50
138.99
138.45
138.13
137.66
136.80
135.35
135.27
133.96
133.71
133.68
133.65
133.45
133.42
133.19
133.15
133.12
132.86
132.84
132.67
132.59
131.70
131.62
131.61
131.53
131.39
131.22
131.12
130.59
128.79
127.91
126.99
126.89
126.87
126.15
125.43
125.40
125.37
125.34
125.30
125.27
125.24
124.73
124.71
122.56
122.54
120.38
89.64
78.20
77.42
77.16
76.91
f1 (ppm)


F3C
P
O
N
Ph
Ph
F3C

L2


1.00
2.33
3.31
8.29
4.72
1.05
1.83
2.12
f1 (ppm)


162.82
162.79
143.20
143.17
143.07
141.36
139.79
137.88
137.68
134.90
134.72
134.29
134.02
133.86
131.39
131.29
131.15
131.13
130.90
130.69
130.66
129.11
128.98
128.69
128.62
127.61
126.47
126.25
125.53
125.50
125.47
125.45
125.42
125.39
125.37
125.33
125.25
123.08
f1 (ppm)

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