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Copper-Catalyzed Hiyama Cross-Coupling Using Vinylsilanes and Benzylic Electrophiles

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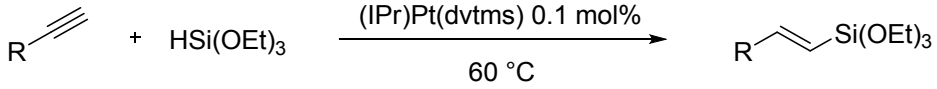
I. Instrumentation and chemicals

Unless otherwise noted, all manipulations were performed under an argon atmosphere using flame dried flasks. Diethyl ether and THF were distilled on sodium/benzophenone under an argon atmosphere. Dichloromethane and acetonitrile were distilled on CaH_2 under an argon atmosphere. Solvents used for work-up were of technical grade. Commercial reagents were purchased from Acros, Sigma-Adrich, ABCR or TCI and used as received unless stated otherwise. All ^{1}H and ^{13}C NMR spectra were recorded in deuteriochloroform ($CDCl_3$) with tetramethylsilane (TMS) as an internal standard, at ambient temperature on a Bruker DPX 300 MHz Fourier Transform Spectrometer operating at 300 MHz for ^{1}H and at 75 MHz for ^{13}C. All the spectra were calibrated at δ 0.00 ppm for ^{1}H and δ 77.00 ppm for ^{13}C. Spectral features were designed as follows: s = singulet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad. IR absorption spectra were recorded as a liquid deposition on a ZnSe crystal on a Shimadzu FTIR 8400 Spectrophotometer from 4000 cm^{-1} to 400 cm^{-1}. High resolution Mass Spectra were obtained from a Thermo Scientific QExactive, with accurate mass reported for the molecular ion or suitable fragment ions. Column chromatography was carried out on silica gel (ROCC 60, 40-63 µm). TLC analyses were performed on commercial aluminum plates bearing a 0.25 mm layer of Merck Silica gel $60F_{254}$.

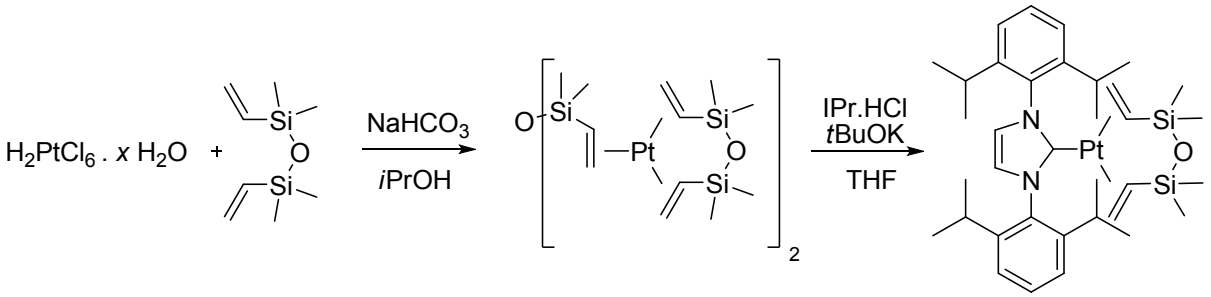
II. Vinylsilane synthesis : hydrosilylations

Hydrosilylation: general procedure [1-3]



(IPr)Pt(dvtms) (0.001 eq.) was added to neat triethoxysilane (1.05 equiv.). The solution was stirred at 60°C during 60 minutes. To the resulting mixture was added the alkyne (1 equiv.) dropwise and the alkyne-containing flask was rinsed with a minimum amount of toluene. The solution was stirred at 60°C during 2 hours prior to be filtrated trough a short pad of silica gel/Celite/$MgSO_4$ (1:1:1) and eluted with diethyl ether. The solution was evaporated *in vacuo* to afford the desired β(*E*)-vinylsilane. No further purification was required.

- **(IPr)Pt(dvtms)** [1-3]

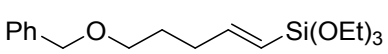


A solution of hexachloroplatinic acid hydrate (40%wt, 300 mg, 0.615 mmol) in isopropanol (4.4 mL) was heated at 70°C during 30 minutes. The heating bath was removed to allow the solution to cool down to room temperature. $NaHCO_3$ (413 mg, 4.92 mmol) was added over 5 minutes and the solution was stirred during 10 minutes. 1,3-Divinyltetramethyldisiloxane (1.1 mL, 4.90 mmol) was added and the resulting solution was stirred at 70°C during 1 hour. The mixture is cooled down to room temperature, is filtrated trough a pad of silica gel/Celite/$MgSO_4$ (1:1:1) and eluted with Diethyl ether (50 mL). The resulting filtrate was concentrated *in vacuo* to reach a volume of approximately 5 mL, affording the intermediate Karstedt's catalyst.

To the above solution was added THF (6.2 mL), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr.HCl) (314 mg, 0.738 mmol) and potassium *tert*-butoxyde (75 mg, 0.74 mmol). The mixture was stirred at room temperature during 1 hour then diluted with water (10 mL). The aqueous phase was extracted with dichloromethane (3 x 10 mL). The combined organic phases were dried over $MgSO_4$ and evaporated *in vacuo*. The resulting crude product was recrystallized from isopropanol overnight to afford **(IPr)Pt(dvtms)** (255 mg, 54% yield) as pale yellow crystals. R_f (10% Et_2O in petroleum ether)

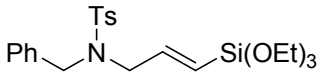
0.35; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.8 Hz, 1H), 7.21 – 7.16 (m, 6H), 3.05 – 2.89 (m, 4H), 1.83 – 1.18 (m, 6H), 1.24 (d, *J* = 6.8 Hz, 12H), 1.13 (d, *J* = 6.8 Hz, 12H), 0.13 (s, 6H), -0.76 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.1 ($^{1}J_{Pt\text{-}C}$ = 1412.3 Hz), 145.9, 136.8 ($^{4}J_{Pt\text{-}C}$ = 9.8 Hz), 129.5, 124.0 ($^{3}J_{Pt\text{-}C}$ = 42.0 Hz), 123.7, 41.9 ($^{1}J_{Pt\text{-}C}$ = 165.0 Hz), 35.6 ($^{1}J_{Pt\text{-}C}$ = 119.3 Hz), 28.5, 26.0, 22.6, 1.7, -2.2.

- **(E)-(5-(Benzyloxy)pent-1-enyl)triethoxysilane (1a)**



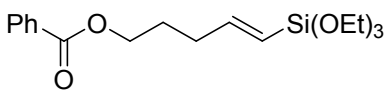
General procedure was used. No further purification was required to furnish (**1a**) (91 % yield) as a colorless oil. R_f (5% EtOAc in petroleum ether) 0.30; IR (thin film) : 1738, 1628, 1454, 1366, 1165, 1088, 1072, 957, 816,775, 734, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.29 (m, 5H), 6.46 (dt, *J* = 18.8, 6.2 Hz, 1H), 5.46 (dt, *J* = 18.8, 1.6 Hz, 1H), 4.52 (s, 2H), 3.83 (q, *J* = 7.0 Hz, 6H), 3.50 (t, *J* = 6.5 Hz, 2H), 2.33 – 2.23 (m, 2H), 1.83 – 1.72 (m, 2H), 1.24 (t, *J* = 7.0 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.03, 138.52, 128.34, 127.59, 127.50, 119.42, 72.89, 69.66, 58.42, 33.08, 28.34, 18.22; HRMS (ESI): calcd for $C_{18}H_{31}O_4\,^{28}Si_1$ [MH^+] 339.1989, found 339.1986.

- **(E)-N-benzyl-4-methyl-N-(3-(triethoxysilyl)allyl)benzenesulfonamide (1b)**



General procedure was used. No further purification was required to furnish (**1b**) (98 % yield) as a colorless oil. R_f (10% EtOAc in petroleum ether) 0.36; IR (thin film): 2974, 1620, 1599, 1495, 1456, 1441, 1391, 1344, 1159, 1068, 957, 928, 814, 783, 756, 727, 698, 652 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 2H), 7.39 – 7.20 (m, 7H), 6.01 (dt, *J* = 18.8, 5.9 Hz, 1H), 5.40 (dt, *J* = 18.7, 1.5 Hz, 1H), 4.33 (s, 2H), 3.82 (dd, *J* = 5.8, 1.4 Hz, 2H), 3.71 (q, *J* = 7.0 Hz, 6H), 2.44 (s, 3H), 1.17 (t, *J* = 7.0 Hz, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.78, 143.25, 137.46, 135.77, 129.73, 128.52, 128.40, 127.74, 127.18, 124.21, 58.45, 51.50, 50.68, 21.49, 18.18; HRMS (ESI): calcd for $C_{23}H_{34}O_5N_1\,^{32}S_1\,^{28}Si_1$ [MH^+] 464.1923, found 464.1921.

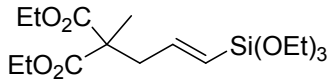
- **(E)-5-(Triethoxysilyl)pent-4-enyl benzoate (1c)**



General procedure was used. No further purification was required to furnish (**1c**) (95 % yield) as a colorless oil. R_f (5% EtOAc in petroleum ether) 0.29; IR (thin film) : 1720, 1273, 1167, 1099, 1076, 959, 783, 712 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 2H), 7.61 – 7.52 (m, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 6.47 (dt, *J* = 18.7, 6.1

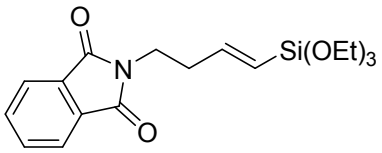
Hz, 1H), 5.50 (d, *J* = 18.8 Hz, 1H), 4.34 (t, *J* = 6.5 Hz, 2H), 3.82 (q, *J* = 7.0 Hz, 6H), 2.40 – 2.27 (m, 2H), 1.99 – 1.85 (m, 2H), 1.23 (t, *J* = 7.0 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 152.0, 132.9, 130.4, 129.5, 128.4, 120.2, 64.3, 58.5, 32.9, 27.4, 18.3; HRMS (ESI): calcd for $C_{18}H_{29}O_5\,^{28}Si_1$ [MH^+] 353.1779, found 353.1781.

- **(E)-Diethyl 2-methyl-2-(3-(triethoxysilyl)allyl)malonate (1d)**



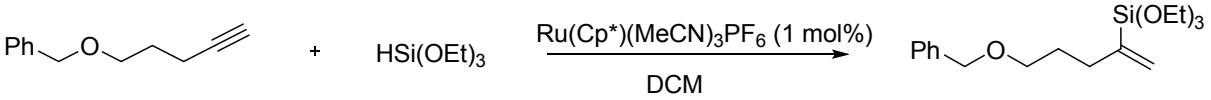
General procedure was used. No further purification was required to furnish (**1d**) (99 % yield) as a colorless oil. R_f (5% EtOAc in petroleum ether) 0.30; IR (thin film): 2976, 1732, 1622, 1446, 1391, 1296, 1249, 1182, 1167, 1097, 1074, 1022, 959, 779 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.27 (dt, *J* = 18.6, 7.0 Hz, 1H), 5.53 (dt, *J* = 18.5, 1.2 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 4H), 3.80 (q, *J* = 7.0 Hz, 6H), 2.72 (dd, *J* = 7.0, 1.3 Hz, 2H), 1.40 (s, 3H), 1.30 – 1.17 (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.69, 146.92, 124.82, 61.27, 58.43, 53.25, 42.81, 19.82, 18.18, 14.01; HRMS (ESI): calcd for $C_{17}H_{33}O_7\,^{28}Si_1$ [MH^+] 377.1990, found 377.1984.

- **(E)-2-(4-(triethoxysilyl)but-3-enyl)isoindoline-1,3-dione (1e)**



General procedure was used. No further purification was required to furnish (**1e**) (92 % yield) as a colorless oil. R_f (10% EtOAc in petroleum ether) 0.32; IR (thin film): 1713, 1393, 1167, 1101, 1074, 959, 818, 779, 719 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.71 (dd, *J* = 5.5, 3.1 Hz, 2H), 6.39 (dt, *J* = 18.7, 6.5 Hz, 1H), 5.50 (dt, *J* = 18.7, 1.4 Hz, 1H), 3.83 (t, *J* = 7.1 Hz, 2H), 3.75 (q, *J* = 7.0 Hz, 6H), 2.63 – 2.51 (m, 2H), 1.17 (t, *J* = 7.0 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.17, 148.65, 133.88, 132.06, 123.15, 122.91, 58.41, 36.73, 35.38, 18.16; HRMS (ESI): calcd for $C_{18}H_{26}O_5N_1\,^{28}Si_1$ [MH^+] 364.1574, found 364.1571.

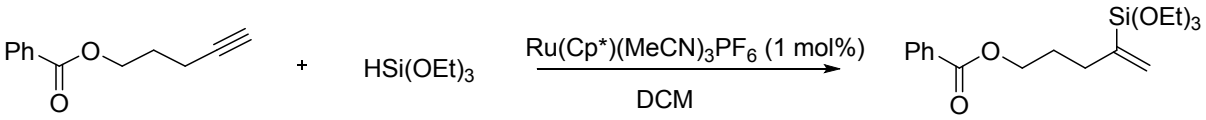
- **(5-(Benzyloxy)pent-1-en-2-yl)triethoxysilane (1f)[4]**



To a solution of the corresponding alkyne (0.174 g, 1.00 mmol) in DCM (2 mL) was added Triethoxysilane (203 µL, 1.20 mmol). The solution was cooled down to 0°C, and $Ru(Cp^*)(MeCN)_3PF_6$ (5.0 mg, 0.01 mmol) was added. The resulting solution was stirred for 1 hour at room temperature, filtrated through a short pad of silica, and eluted with diethyl ether. The solvents were removed *in vacuo* to afford (**1f**) (0.332 g, 98% yield as a 92:8 mixture of α and β isomers) as a pale yellow oil. R_f

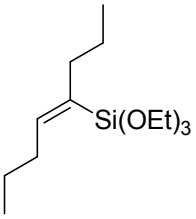
(5% EtOAc in petroleum ether) 0.45; IR (thin film): 2974, 2926, 2881, 1738, 1610, 1454, 1389, 1364, 1165, 1099, 1078, 959, 781, 733, 696 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, major + minor isomer) δ 7.42 – 7.28 (m, major 5H + minor 5H), 6.55 (dt, *J* = 14.8, 7.5 Hz, minor 1H), 5.76 (dt, *J* = 3.0, 1.4 Hz, major 1H), 5.66 (d, *J* = 3.1 Hz, major 1H), 5.34 (dt, *J* = 14.1, 1.2 Hz, minor 1H), 4.52 (s, major 2H + minor 2H), 3.84 (q, *J* = 7.0 Hz, major 6H + minor 6H), 3.51 (t, *J* = 6.5 Hz, major 2H + minor 2H), 2.46 – 2.33 (m, minor 2H), 2.33 – 2.22 (t, *J* = 7.5 Hz, major 2H), 1.91 – 1.76 (m, major 2H + minor 2H), 1.24 (t, *J* = 7.0 Hz, major 9H + minor 9H); ^{13}C NMR (75 MHz, $CDCl_3$, major isomer only) δ 143.05, 138.69, 129.44, 128.29, 127.58, 127.42, 72.75, 69.98, 58.47, 32.38, 28.70, 18.20.HRMS (ESI): calcd for $C_{18}H_{31}O_4\,^{28}Si_1$ [MH^+] 339.1986, found 339.1985.

- **<u>4-(Triethoxysilyl)pent-4-enyl benzoate (1g)</u>[4]**



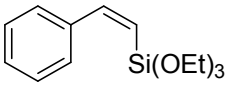
To a solution of the corresponding alkyne (0.188 g, 1.00 mmol) in DCM (2 mL) was added Triethoxysilane (203 µL, 1.20 mmol). The solution was cooled down to 0°C, and $Ru(Cp^*)(MeCN)_3PF_6$ (5.0 mg, 0.01 mmol) was added. The resulting solution was stirred for 1 hour at room temperature, filtrated through a short pad of silica, and eluted with diethyl ether. The solvents were removed *in vacuo* to afford (**1g**) (0.364 g, 99% yield as a 90:10 mixture of α and β isomers) as a pale yellow oil. R_f (5% EtOAc in petroleum ether) 0.35; IR (thin film): 2970, 2922, 2879,1720, 1273, 1167, 1101, 1078, 1028, 959, 783, 712 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, major + minor isomer) δ 8.05 (d, *J* = 7.1 Hz, major 2H + minor 2H), 7.63 – 7.37 (m, major 3H + minor 3H), 6.47 (dt, *J* = 18.8, 6.2 Hz, minor 1H), 5.78 (dt, *J* = 2.8, 1.2 Hz, major 1H), 5.69 (d, *J* = 3.0 Hz, major 1H), 5.50 (dt, *J* = 18.8, 1.5 Hz, minor 1H), 4.33 (t, *J* = 6.5 Hz, major 2H + minor 2H), 3.84 (q, *J* = 7.0 Hz, major 6H + minor 6H), 2.39 – 2.28 (m, major 2H + minor 2H), 2.04 – 1.87 (m, major 2H + minor 2H), 1.23 (t, *J* = 7.0 Hz, major 9H + minor 9H); ^{13}C NMR (75 MHz, $CDCl_3$, major isomer only) δ 166.60, 142.53, 132.77, 130.47, 129.89, 129.51, 128.28, 64.56, 58.53, 32.36, 27.80, 18.19; HRMS (ESI): calcd for $C_{18}H_{29}O_5\,^{28}Si_1$ [MH^+] 353.1779, found 353.1782.

- **(Z)-triethoxy(oct-4-en-4-yl)silane (1h)[5]**



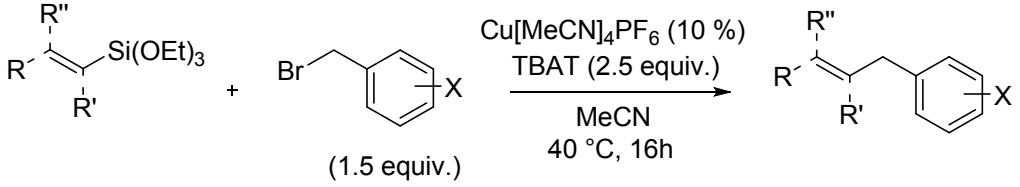
Compound (**1h**) was obtained according to the literature. The data were consistent with those already published.

- **(Z)-triethoxy(styryl)silane *Z*-(4)[6]**



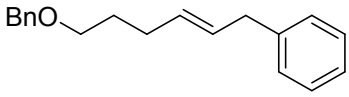
Compound *Z*-(**4**) was obtained according to the literature. The data were consistent with those already published.

III. Vinylsilane cross-couplings : general procedure



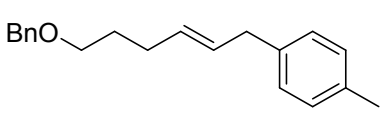
To a solution of the vinylsilane (0.20 mmol, 1.0 equiv.) in MeCN (1 mL) was added the benzylic bromide (0.30 mmol, 1.5 equiv.). The mixture was transferred to a Shlenck flask containing $Cu(MeCN)_4PF_6$ (0.02 mmol, 0.1 equiv.) and tetrabutylammonium difluorotriphenylsilicate (TBAT) (0.5 mmol, 2.5 eq.) under argon. The resulting mixture was stirred at 40 °C in an oil bath for 16 hours. The solution was diluted with diethyl ether (5 mL), filtrated trough a short pad of silica and eluted with diethyl ether (25 mL). The ethereal solution was evaporated under reduced pressure to afford the crude product. The crude product was purified by flash chromatography using DCM in petroleum ether to afford the desired olefin.

- **(E)-(6-(benzyloxy)hex-2-enyl)benzene (2a)**



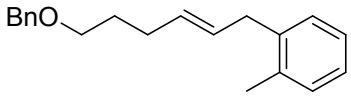
General procedure was used. The crude product was purified by flash chromatography using 30% DCM in petroleum ether to afford (**2a**) (91 % yield) as a colorless oil. R_f (30% DCM in petroleum ether) 0.54; IR (thin film): 1495, 1452, 1364, 1099, 1074, 1028, 966, 735, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 7H), 7.21 – 7.11 (m, 3H), 5.66 – 5.41 (m, 2H), 4.48 (s, 1H), 3.47 (t, *J* = 6.5 Hz, 2H), 3.31 (d, *J* = 6.1 Hz, 2H), 2.20 – 2.04 (m, 2H), 1.83 – 1.62 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.92, 138.60, 131.13, 129.34, 128.43, 128.30, 127.59, 127.45, 125.85, 72.84, 69.70, 39.00, 29.47, 29.03; HRMS (ESI): calcd for $C_{19}H_{23}O_1$ [MH^+] 267.1743, found 267.1737.

- **(E)-1-(6-(benzyloxy)hex-2-enyl)-4-methylbenzene (2b)**



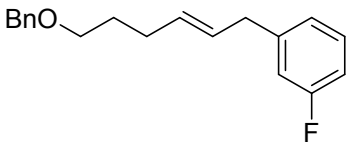
General procedure was used. The crude product was purified by flash chromatography using 40% DCM in petroleum ether to afford (**2b**) (97 % yield) as a colorless oil. R_f (40% DCM in petroleum ether) 0.58; IR (thin film): 1718, 1514, 1452, 1364, 1275, 1203, 1099, 968, 804, 744, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.17 (m, 5H), 7.09 – 6.93 (m, 4H), 5.59 – 5.32 (m, 2H), 4.41 (s, 2H), 3.40 (t, *J* = 6.5 Hz, 2H), 3.20 (d, *J* = 6.1 Hz, 2H), 2.24 (s, 3H), 2.15 – 1.95 (m, 2H), 1.72 – 1.54 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.62, 137.85, 135.30, 130.87, 129.63, 129.01, 128.32, 127.61, 127.46, 72.84, 69.73, 38.57, 29.47, 29.03, 20.97; HRMS (ESI): calcd for $C_{20}H_{25}O_1$ [MH^+] 281.1900, found 281.1901.

- **(E)-1-(6-(benzyloxy)hex-2-enyl)-2-methylbenzene (2c)**



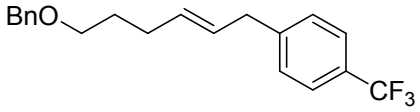
General procedure was used. The crude product was purified by flash chromatography using 40% DCM in petroleum ether to afford (**2c**) (95 % yield) as a colorless oil. R_f (40% DCM in petroleum ether) 0.58; IR (thin film): 1718, 1452, 1275, 1099, 1072, 1028, 970, 748, 714, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.26 (m, 5H), 7.22 – 7.00 (m, 4H), 5.58 (dt, *J* = 13.9, 6.2 Hz, 1H), 5.43 (dt, *J* = 13.8, 6.5 Hz, 1H), 4.50 (s, 2H), 3.48 (t, *J* = 6.5 Hz, 2H), 3.32 (dd, *J* = 6.2, 1.0 Hz, 2H), 2.29 (s, 3H), 2.23 – 2.05 (m, 2H), 1.82 – 1.61 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.96, 138.60, 136.21, 130.96, 130.05, 128.91, 128.47, 128.32, 127.61, 127.47, 126.07, 125.93, 72.84, 69.71, 36.50, 29.48, 29.06, 19.31; HRMS (ESI): calcd for $C_{20}H_{25}O_1$ [MH^+] 281.1900, found 281.1901.

- **(E)-1-(6-(benzyloxy)hex-2-enyl)-3-fluorobenzene (2d)**



General procedure was used. The crude product was purified by flash chromatography using 40% DCM in petroleum ether to afford (**2d**) (99 % yield) as a colorless oil. R_f (40% DCM in petroleum ether) 0.61; IR (thin film): 1614, 1589, 1487, 1246, 1136, 1101, 1076, 968, 779, 735, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.26 (m, 5H), 7.24 – 7.16 (m, 1H), 6.98 – 6.83 (m, 3H), 5.61 – 5.45 (m, 2H), 4.49 (s, 2H), 3.48 (t, *J* = 6.5 Hz, 2H), 3.31 (d, *J* = 4.9 Hz, 2H), 2.18 – 2.08 (m, 2H), 1.78 – 1.64 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.91 (d, *J* = 245.1 Hz), 143.55 (d, *J* = 7.3 Hz), 138.58, 131.85, 129.65 (d, *J* = 8.3 Hz), 128.51, 128.33, 127.62, 127.49, 124.04 (d, *J* = 2.4 Hz), 115.26 (d, *J* = 21.1 Hz), 112.73 (d, *J* = 21.1 Hz) , 72.88, 69.66, 38.68, 29.43, 29.04; ^{19}F NMR (282 MHz, $CDCl_3$) δ -115.20 ; HRMS (ESI): calcd for $C_{19}H_{22}O_1F_1$ $[MH^+]$ 285.1649, found 285.1647.

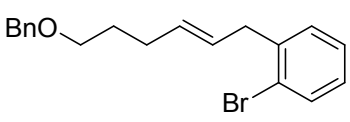
- **(E)-1-(6-(benzyloxy)hex-2-enyl)-4-(trifluoromethyl)benzene (2e)**



General procedure was used. The crude product was purified by flash chromatography using 40% DCM in petroleum ether to afford (**2e**) (88 % yield) as a colorless oil. R_f (40% DCM in petroleum ether) 0.55; IR (thin film): 1718, 1618, 1418, 1323, 1161, 1119, 1067, 1018, 968, 820, 737, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.21 (m, 7H), 5.63 – 5.43 (m, 2H), 4.49 (s, 2H), 3.47 (t, *J* = 6.5 Hz, 2H), 3.36 (d, *J* = 4.4 Hz, 2H), 2.22 – 2.09 (m, 2H), 1.78 – 1.65 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.06, 138.56, 132.16, 128.74, 128.34, 128.24, 127.60, 127.51, 125.23 (q, *J* = 3.7 Hz)., 72.88, 69.62, 38.77, 29.40, 29.05; ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.64 ; HRMS (ESI): calcd for $C_{20}H_{22}O_1F_3$ $[MH^+]$ 335.1617, found 335.1618.

Note: The two quaternary quartets carbons signals were not identified because of both their inherent very low intensity and the overlapping with other signals.

- **(E)-1-(6-(benzyloxy)hex-2-enyl)-2-bromobenzene (2f)**

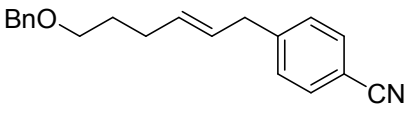


General procedure was used. The crude product was purified by flash chromatography using 40% DCM in petroleum ether to afford (**2f**) (88 % yield) as a colorless oil. R_f (40% DCM in petroleum ether) 0.62; IR (thin film): 1738, 1470, 1439, 1364, 1101, 1078, 1024, 968, 748, 735, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.15 (m, 7H), 7.10 – 7.01 (m, 1H), 5.63 – 5.42 (m, 2H), 4.48 (s, 2H), 3.47 (t, *J* = 6.5 Hz, 2H), 3.43 (d, *J* = 5.8 Hz, 2H), 2.18 – 2.06 (m, 2H), 1.78 – 1.62 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.23, 138.60, 132.66, 132.02, 130.28, 128.32, 127.61 (br, signal overlap), 127.47,

127.40 (br, signal overlap), 124.50, 72.86, 69.65, 39.06, 29.38, 29.07; HRMS (ESI): calcd for $C_{19}H_{22}O_1{}^{79}Br_1$ [MH^+] 345.0848, found 345.0846.

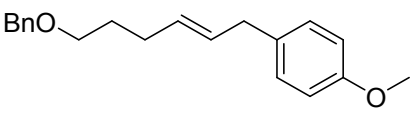
Note: Only 15 of the 17 ^{13}C NMR signals are observed because of an overlap of carbon with very similar shifts.

- **(E)-4-(6-(benzyloxy)hex-2-enyl)benzonitrile (2g)**



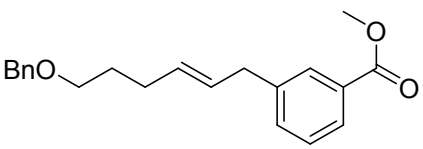
General procedure was used. The crude product was purified by flash chromatography using 100% DCM to afford (**2g**) (83 % yield) as a white solid. The isolated product contains a certain amount of 4-(fluoromethyl)benzonitrile. R_f (100% DCM) 0.56; IR (thin film): 2226, 1607, 1504, 1454, 1101, 1028, 970, 833, 818, 737, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.65 – 7.47 (m, 2H), 7.44 – 7.14 (m, 7H), 5.63 – 5.39 (m, 2H), 4.49 (s, 2H), 3.47 (t, *J* = 6.4 Hz, 2H), 3.36 (d, *J* = 3.6 Hz, 2H), 2.20 – 2.05 (m, 2H), 1.81 – 1.63 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 146.57, 138.51, 132.72, 132.13, 129.20, 128.31, 127.56, 127.53, 127.49, 119.07, 109.74, 72.85, 69.55, 38.99, 29.34, 29.04; HRMS (ESI): calcd for $C_{20}H_{22}O_1N_1$ [MH^+] 292.1696, found 292.1695.

- **(E)-1-(6-(benzyloxy)hex-2-enyl)-4-methoxybenzene (2h)**



General procedure was used. The crude product was purified by flash chromatography using 100% DCM to afford (**2h**) (87 % yield) as a colorless oil. R_f (75 % DCM in petroleum ether) 0.58; IR (thin film): 1610, 1510, 1454, 1364, 1300, 1242, 1175, 1105, 1035, 968, 818, 735, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.25 (m, 5H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.63 – 5.40 (m, 2H), 4.49 (s, 2H), 3.78 (s, 2H), 3.47 (t, *J* = 6.5 Hz, 2H), 3.25 (d, *J* = 6.1 Hz, 2H), 2.20 – 2.04 (m, 2H), 1.79 – 1.59 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.81, 138.61, 132.99, 130.79, 129.77, 129.33, 128.32, 127.60, 127.46, 113.74, 72.85, 69.73, 55.25, 38.09, 29.50, 29.03; HRMS (ESI): calcd for $C_{20}H_{25}O_2$ [MH^+] 297.1849, found 297.1848.

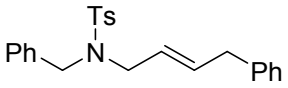
- **(E)-methyl 3-(6-(benzyloxy)hex-2-enyl)benzoate (2i)**



General procedure was used. The crude product was purified by flash chromatography using 100% DCM to afford (**2i**) (88 % yield) as a colorless oil. R_f (100 % DCM) 0.49; IR (thin film): 1720, 1587, 1445, 1433, 1279, 1198, 1103, 1082, 970, 739, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.78 (m, 2H), 7.44 – 7.26 (m, 7H), 5.66 – 5.41 (m, 2H), 4.48 (s, 2H), 3.90 (s, 3H), 3.47 (t, *J* = 6.5 Hz, 2H), 3.36 (d, *J* = 5.4 Hz, 2H), 2.24 – 2.03 (m, 2H), 1.82 – 1.64 (m,

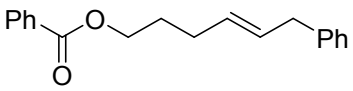
2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.20, 141.26, 138.57, 133.09, 131.77, 130.16, 129.56, 128.69, 128.34, 128.30, 127.59, 127.45, 127.20, 72.84, 69.63, 52.03, 38.74, 29.39, 29.02; HRMS (ESI): calcd for $C_{21}H_{25}O_3$ [MH^+] 325.1798, found 325.1795.

- **(E)-N-benzyl-4-methyl-N-(4-phenylbut-2-enyl)benzenesulfonamide (3b)**



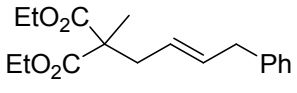
General procedure was used. The crude product was purified by flash chromatography using 80% DCM in petroleum ether to afford (**3b**) (92 % yield) as a white solid. R_f (80% DCM in petroleum ether) 0.67; IR (thin film): 1599, 1495, 1454, 1339, 1157, 1092, 928, 814, 748, 729, 698, 656 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.15 (m, 10H), 7.01 (d, *J* = 7.2 Hz, 2H), 5.53 (dt, *J* = 13.7, 6.7 Hz, 1H), 5.27 – 5.08 (m, 1H), 4.31 (s, 2H), 3.72 (d, *J* = 6.8 Hz, 2H), 3.20 (d, *J* = 6.6 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.15, 139.50, 137.43, 136.09, 134.60, 129.65, 128.44 (br), 128.39, 128.32, 127.57, 127.18, 126.11, 124.95, 50.19, 48.77, 38.51, 21.53; HRMS (ESI): calcd for $C_{24}H_{26}O_2N_1{}^{32}S_1$ [MH^+] 392.1679, found 392.1688.

- **(E)-6-phenylhex-4-enyl benzoate (3c)**



General procedure was used. The crude product was purified by flash chromatography using 50% DCM in petroleum ether to afford (**3c**) (86 % yield) as a colorless oil. R_f (50% DCM in petroleum ether) 0.66; IR (thin film): 1717, 1601, 1450, 1313, 1271, 1175, 1113, 1070, 1026, 968, 710, 698 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 – 7.96 (m, 2H), 7.59 – 7.51 (m, 1H), 7.47 – 7.39 (m, 2H), 7.34 – 7.25 (m, 2H), 7.18 (t, *J* = 6.7 Hz, 3H), 5.73 – 5.46 (m, 2H), 4.33 (td, *J* = 6.5, 1.2 Hz, 2H), 3.34 (d, *J* = 6.3 Hz, 2H), 2.28 – 2.15 (m, 2H), 1.93 – 1.79 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.58, 140.72, 132.80, 130.41, 130.35, 129.99, 129.51, 128.44, 128.35, 128.30, 125.92, 64.41, 38.97, 28.93, 28.46; HRMS (ESI): calcd for $C_{19}H_{21}O_2$ [MH^+] 281.1536, found 281.1533.

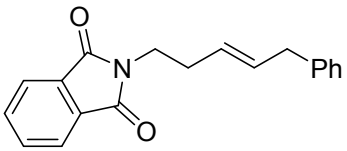
- **(E)-diethyl 2-methyl-2-(4-phenylbut-2-enyl)malonate (3d)**



General procedure was used. The crude product was purified by flash chromatography using 70% DCM in petroleum ether to afford (**3d**) (79 % yield) as a colorless oil. R_f (70% DCM in petroleum ether) 0.68; IR (thin film): 1730, 1454, 1238, 1107, 1022, 972, 860, 746, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 2H), 7.20 – 7.07 (m, 3H), 5.66 (dt, *J* = 15.0, 6.9 Hz, 1H), 5.42 (dt, *J* = 15.0, 7.4 Hz, 1H), 4.15 (q, *J* =

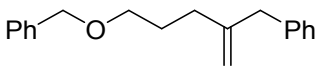
7.1 Hz, 4H), 3.33 (d, *J* = 6.8 Hz, 2H), 2.66 – 2.52 (m, 2H), 1.39 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.98, 140.32, 133.73, 128.44, 128.34, 125.97, 125.40, 61.15, 53.71, 39.06, 38.75, 19.80, 14.03; HRMS (ESI): calcd for $C_{18}H_{25}O_4$ [MH^+] 305.1747, found 305.1751.

- **(E)-2-(5-phenylpent-3-enyl)isoindoline-1,3-dione (3e)**



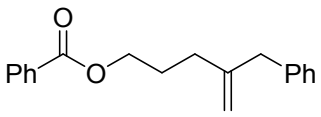
General procedure was used. The crude product was purified by flash chromatography using 95% DCM in petroleum ether to afford (**3e**) (87 % yield) as a colorless oil. R_f (95% DCM in petroleum ether) 0.64; IR (thin film): 1771, 1699, 1493, 1466, 1393, 1360, 1070, 1049, 968, 746, 717, 696 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.20 – 7.10 (m, 3H), 7.07 – 7.00 (m, 2H), 5.61 (dt, *J* = 14.3, 6.5 Hz, 1H), 5.48 (dt, *J* = 15.2, 6.8 Hz, 1H), 3.75 (t, *J* = 7.0 Hz, 2H), 3.27 (d, *J* = 6.5 Hz, 2H), 2.52 – 2.30 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.31, 140.30, 133.80, 132.26, 132.05, 128.34, 128.24, 127.24, 125.84, 123.15, 38.94, 37.60, 31.60; HRMS (ESI): calcd for $C_{19}H_{18}O_2N_1$ [MH^+] 292.1332, found 292.1337.

- **(5-(benzyloxy)-2-methylenepentyl)benzene (3f)**



General procedure was used. The crude product was purified by flash chromatography using 30% DCM in petroleum ether to afford (**3f**) (70 % yield as a 89:11 mixture of α and β isomers) as a colorless oil. R_f (30% DCM in petroleum ether) 0.55; IR (thin film): 2941, 2854, 1643, 1495, 1452, 1362, 1101, 1074, 1028, 893, 733, 696 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, major + minor isomer) δ 7.44 – 7.28 (m, major 7H + minor 7H), 7.22 – 7.09 (m, major 3H + minor 3H), 5.69 – 5.42 (m, minor 2H), 4.83 (d, *J* = 0.7 Hz, major 1H), 4.75 (br s, major 1H), 4.50 (s, minor 2H), 4.47 (s, major 2H), 3.50 (t, *J* = 6.5 Hz, minor 2H), 3.45 (t, *J* = 6.6 Hz, major 2H), 3.40 (d, *J* = 6.8 Hz, minor 2H), 3.34 (s, major 2H), 2.33 – 2.21 (m, minor 2H), 2.12 – 2.00 (m, major 2H), 1.85 – 1.70 (m, major 2H + minor 2H); ^{13}C NMR (75 MHz, $CDCl_3$, major isomer) δ 148.42, 139.68, 138.56, 128.98, 128.33, 128.26, 127.62, 127.48, 126.04, 111.28, 72.85, 69.92, 43.06, 31.83, 27.69; HRMS (ESI): calcd for $C_{19}H_{23}O_1$ [MH^+] 267.1743, found 267.1736.

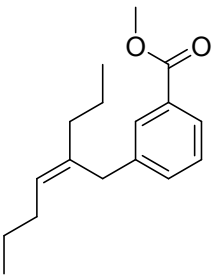
- **4-benzylpent-4-enyl benzoate (3g)**



General procedure was used. The crude product was purified by flash chromatography using 40% DCM in petroleum ether to afford (**3g**) (58 % yield as a 89:11 mixture of α and β isomers) as a colorless oil. R_f (40%

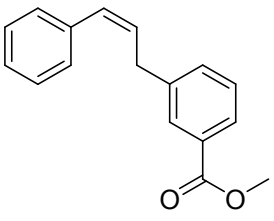
DCM in petroleum ether) 0.58; IR (thin film): 1717, 1450, 1271, 1113, 1070, 1026, 912, 742, 710 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, major + minor isomer) δ 8.13 – 7.98 (m, major 2H + minor 2H), 7.63 – 7.54 (m, major 1H + minor 1H), 7.50 – 7.42 (m, major 2H + minor 2H), 7.34 – 7.17 (m, major 5H + minor 5H), 5.76 – 5.48 (m, minor 2H), 4.91 (br s, major 1H), 4.85 (s, major 1H), 4.39 (t, *J* = 6.4 Hz, minor 2H), 4.32 (t, *J* = 6.5 Hz, major 2H), 3.44 (d, *J* = 6.9 Hz, minor 2H), 3.40 (s, major 2H), 2.43 – 2.28 (m, 1H), 2.23 – 2.10 (m, major 2H), 2.03 – 1.87 (m, major 2H + minor 2H); ^{13}C NMR (75 MHz, $CDCl_3$, major isomer) δ 166.56, 147.66, 139.46, 132.81, 130.37, 129.51, 128.94 (br), 128.30, 126.12, 111.81, 64.48, 43.05, 31.56, 26.66; HRMS (ESI): calcd for $C_{19}H_{21}O_2$ [MH^+] 281.1536, found 281.1532.

- **(Z)-methyl 3-(2-propylhex-2-enyl)benzoate (3h)**



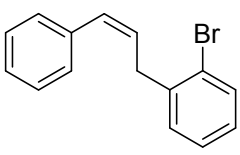
General procedure was used. The crude product was purified by flash chromatography using 30% DCM in petroleum ether to afford (**3h**) (51 % yield) as a colorless oil. R_f (30% DCM in petroleum ether) 0.40; IR (thin film): 1724, 1587, 1433, 1281, 1196, 1105, 993, 744, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.92 – 7.79 (m, 2H), 7.42 – 7.30 (m, 2H), 5.36 (t, *J* = 7.2 Hz, 1H), 3.91 (s, 3H), 3.42 (s, 2H), 2.21 – 2.05 (m, 2H), 1.86 (t, *J* = 7.3 Hz, 2H), 1.50 – 1.29 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 2H), 0.83 (t, *J* = 7.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.31, 140.94, 136.92, 133.06, 130.08, 129.69, 128.26, 127.08, 127.05, 52.05, 38.70, 35.66, 30.23, 23.18, 21.05, 13.90, 13.76; HRMS (ESI): calcd for $C_{17}H_{25}O_2$ [MH^+] 261.1849, found 261.1848.

- **(Z)-methyl 3-(3-phenylallyl)benzoate *Z*-(5a)**



General procedure was used. The crude product was purified by flash chromatography using 60% DCM in petroleum ether to afford *Z*-(**5a**) (92 % yield) as a pale yellow oil. R_f (60% DCM in petroleum ether) 0.63; IR (thin film): 1720, 1445, 1431, 1284, 1219, 1200, 1105, 1080, 989, 959, 789, 748, 717, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.96 – 7.80 (m, 2H), 7.48 – 7.25 (m, 7H), 6.63 (d, *J* = 11.5 Hz, 1H), 5.85 (dt, *J* = 11.5, 7.4 Hz, 1H), 3.91 (s, 3H), 3.72 (dd, *J* = 7.4, 1.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.16, 141.13, 136.99, 132.95, 130.54, 130.34, 129.84, 129.42, 128.66, 128.53, 128.27, 127.39, 126.93, 52.08, 34.36; HRMS (ESI): calcd for $C_{17}H_{17}O_2$ [MH^+] 253.1223, found 253.1220.

- **(Z)-1-bromo-2-(3-phenylallyl)benzene Z-(5b)**



General procedure was used. The crude product was purified by flash chromatography using 1% EtOAc in petroleum ether to afford *Z*-(**5b**) (75 % yield) as a pale yellow oil. R_f (1% EtOAc in petroleum ether) 0.56; IR (thin

film): 1599, 1566, 1495, 1470, 1439, 1024, 770, 748, 733, 700, 663 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.18 (m, 7H), 7.14 – 7.05 (m, 1H), 6.65 (d, *J* = 11.5 Hz, 1H), 5.81 (dt, *J* = 11.5, 7.4 Hz, 1H), 3.77 (dd, *J* = 7.4, 1.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.00, 137.04, 132.73, 130.81, 129.92, 129.00, 128.64, 128.27, 127.81, 127.52, 126.89, 124.60, 35.09; HRMS (APCI): calcd for $C_{15}H_{13}{}^{19}Br$ [MH^+] 272.0195, found 272.0193.

IV. References

[1] G. Berthon-Gelloz, J.-M. Schumers; G. De Bo, I. E. Markó, *J. Org. Chem.* **2008**, *73*, 4190-4197.

[2] G. De Bo, G. Berthon-Gelloz, B. Tinant, I. E. Markó, *Organometallics* **2006**, *25*, 1881-1890.

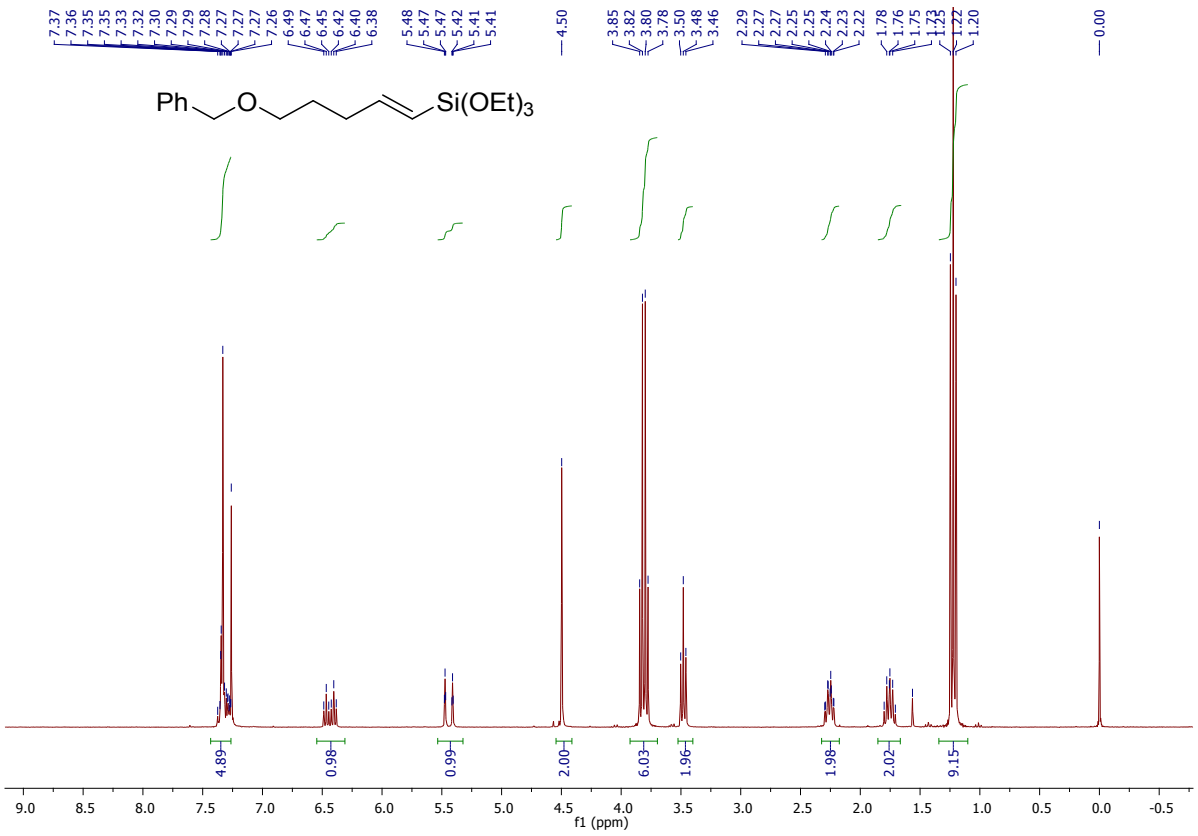
[3] S. Dierick, I. E. Markó, personal communications.

[4] B. M. Trost, Z. T. Ball *J. Am. Chem. Soc.* **2005**, *127*, 17644-17655.

[5] B. M. Trost, Z. T. Ball *J. Am. Chem. Soc.* **2001**, *123*, 12726–12

[6] J. W. Faller, D. G. D'Alliessi *Organometallics*, **2002**, *21*, 1743.

V. Spectra of the new compounds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5.41
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1.75
1.73
1.22
1.20
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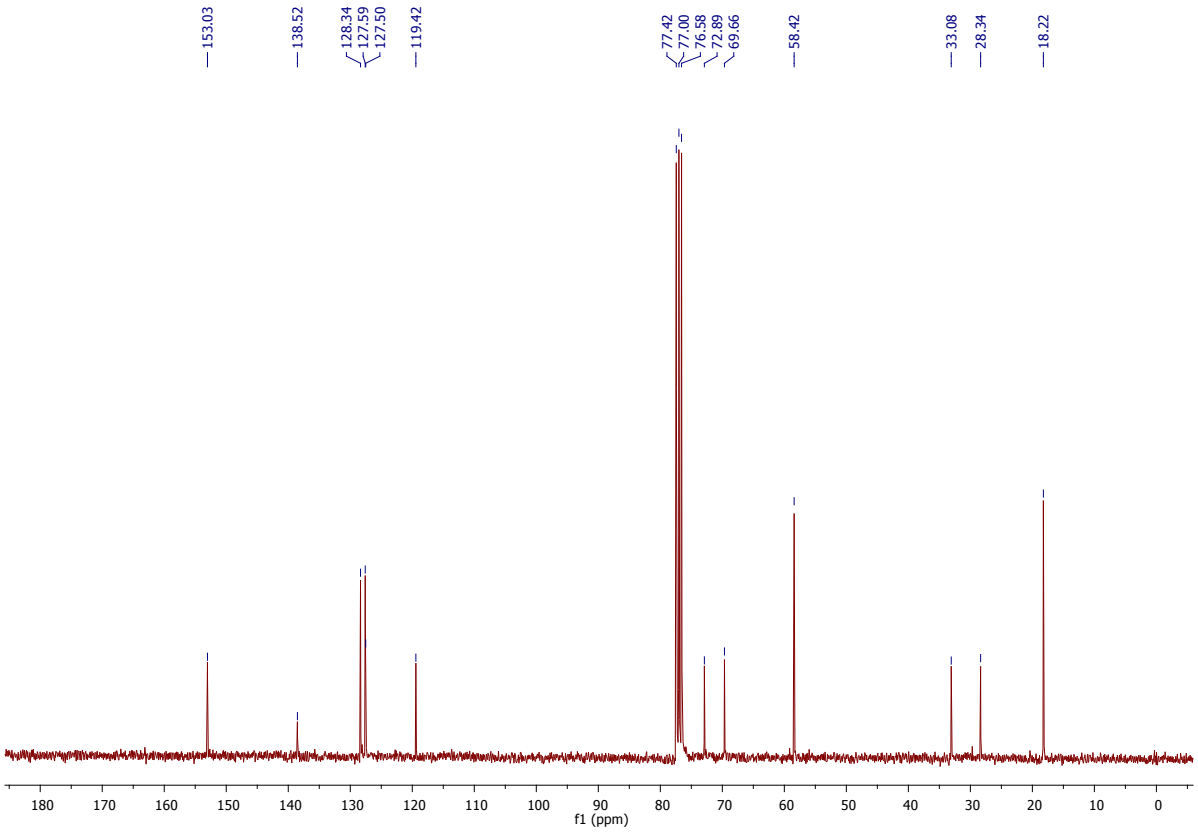
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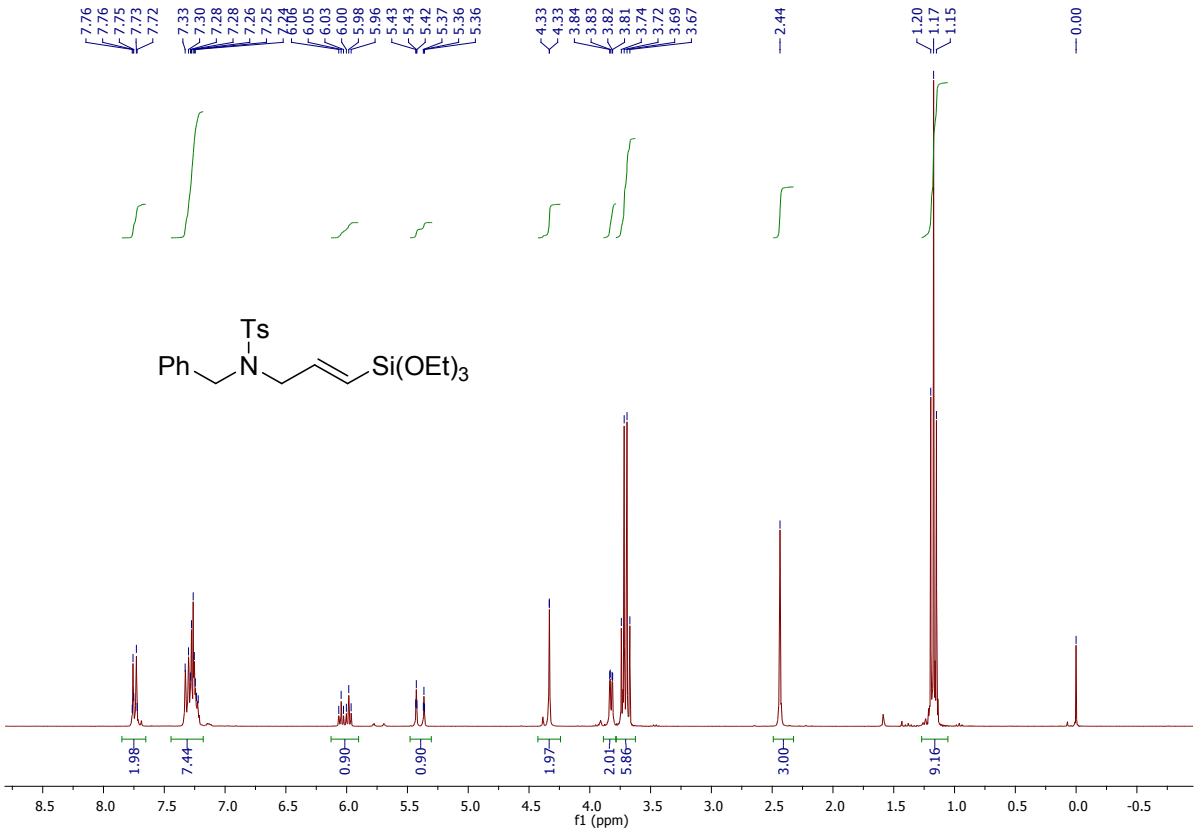
f1 (ppm)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6.00
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5.43
5.42
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5.36
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4.33
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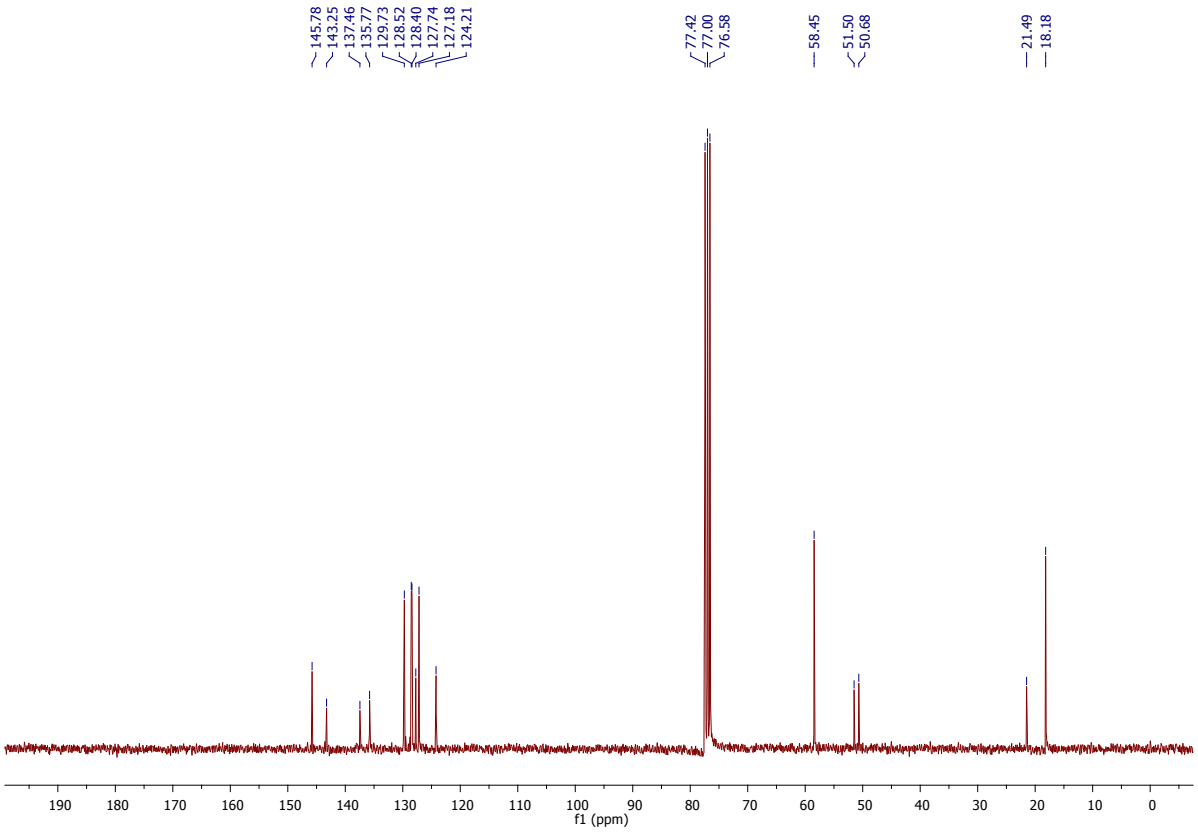
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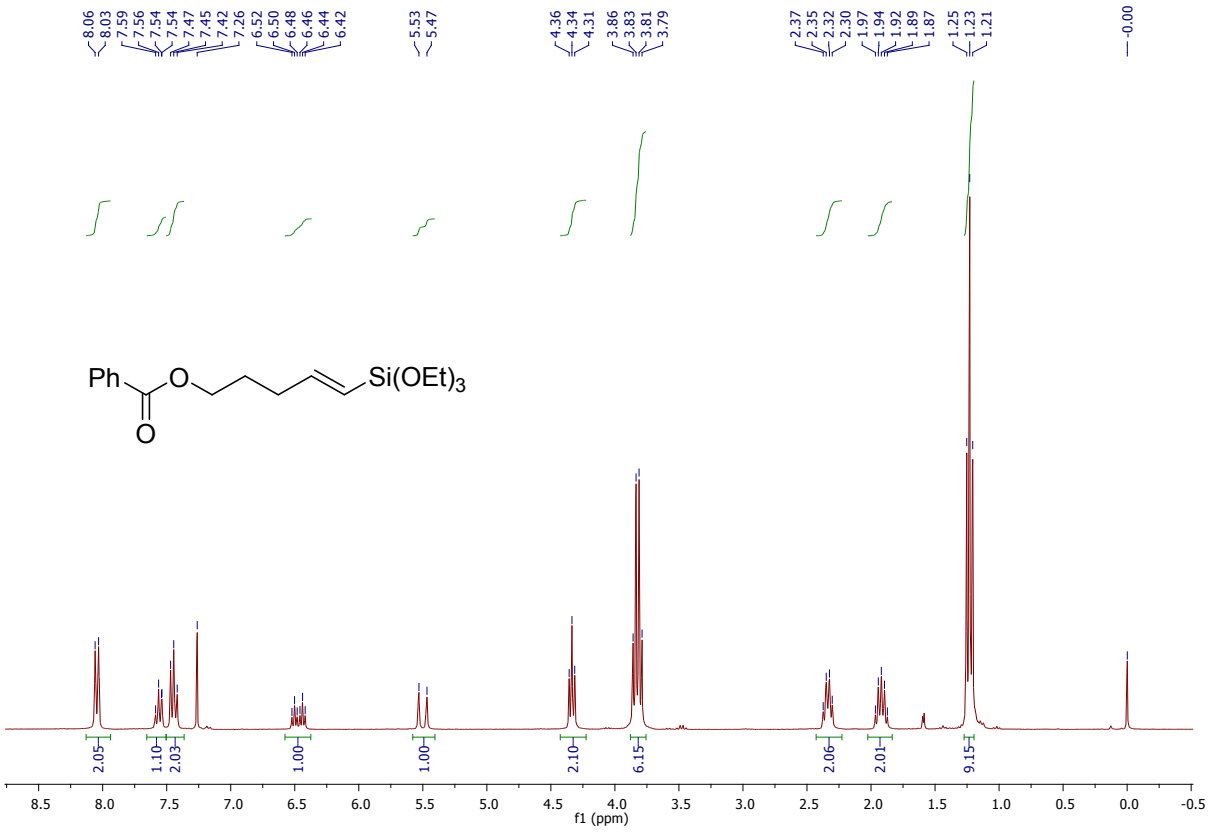
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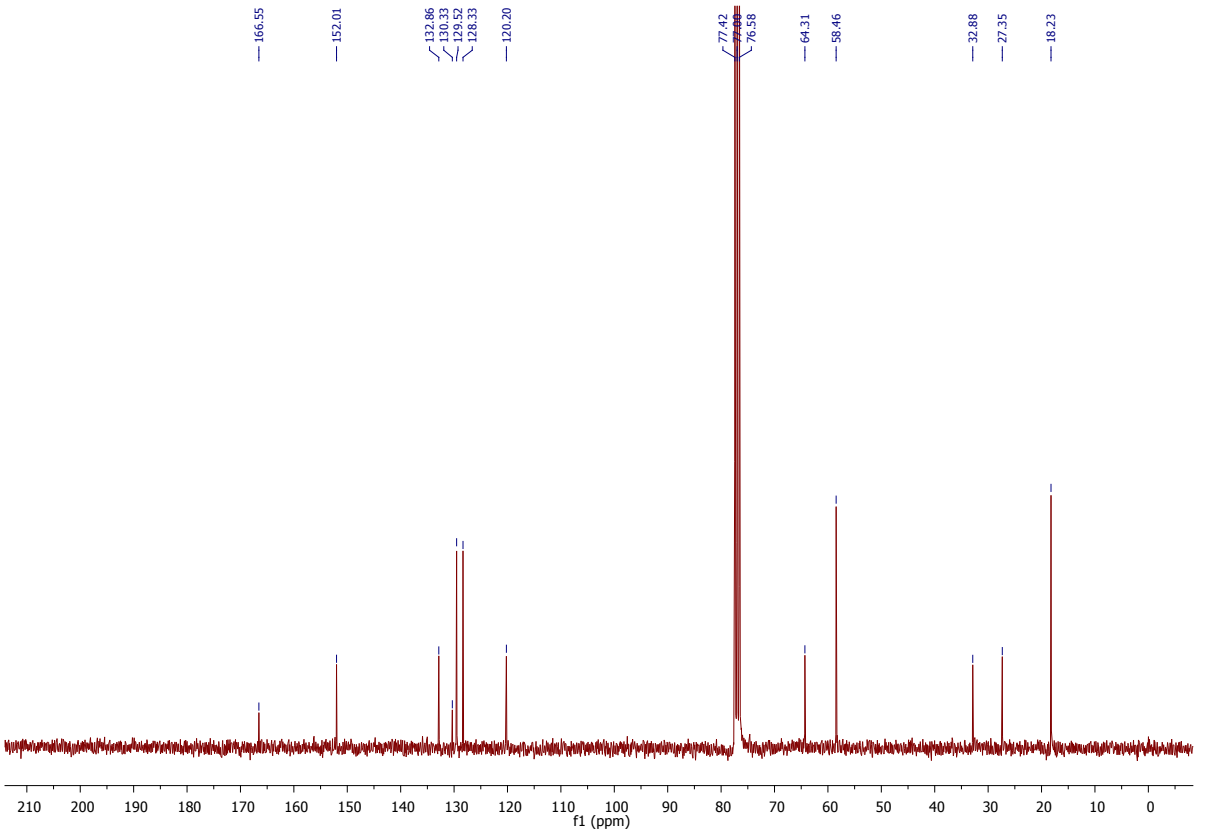
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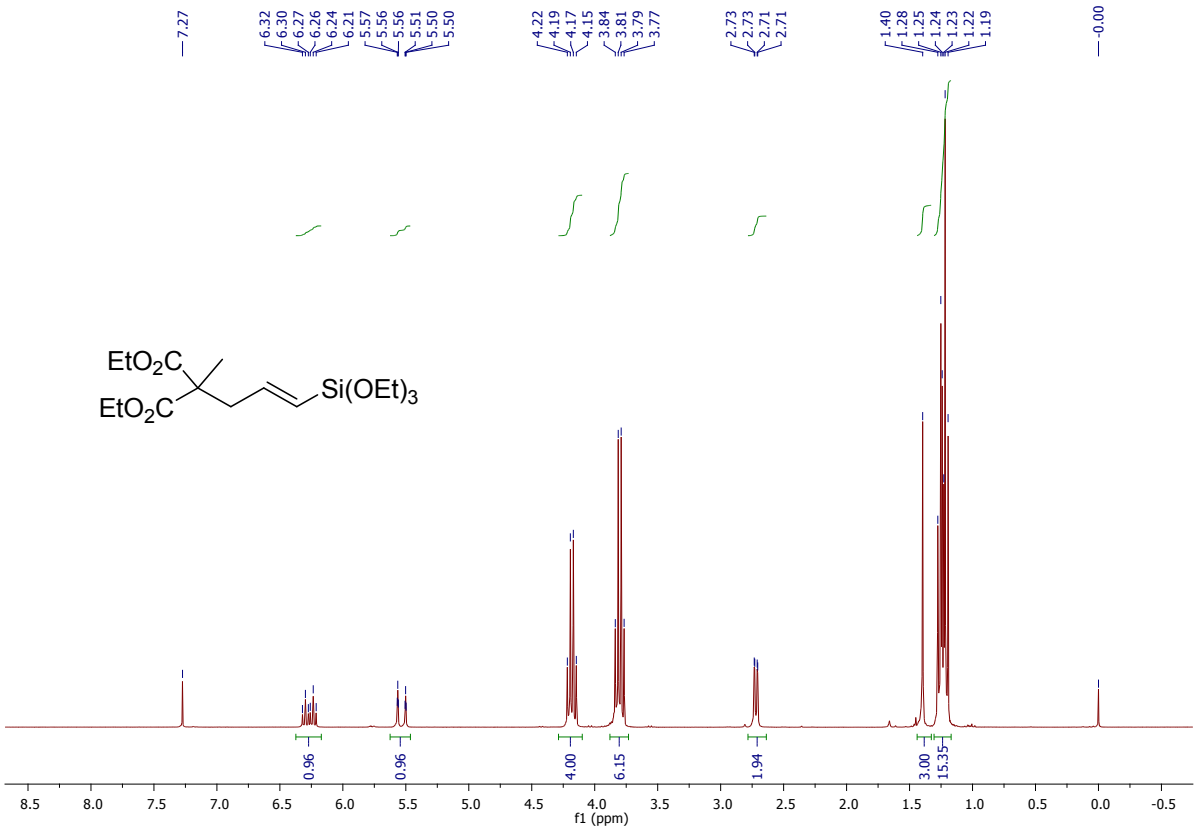
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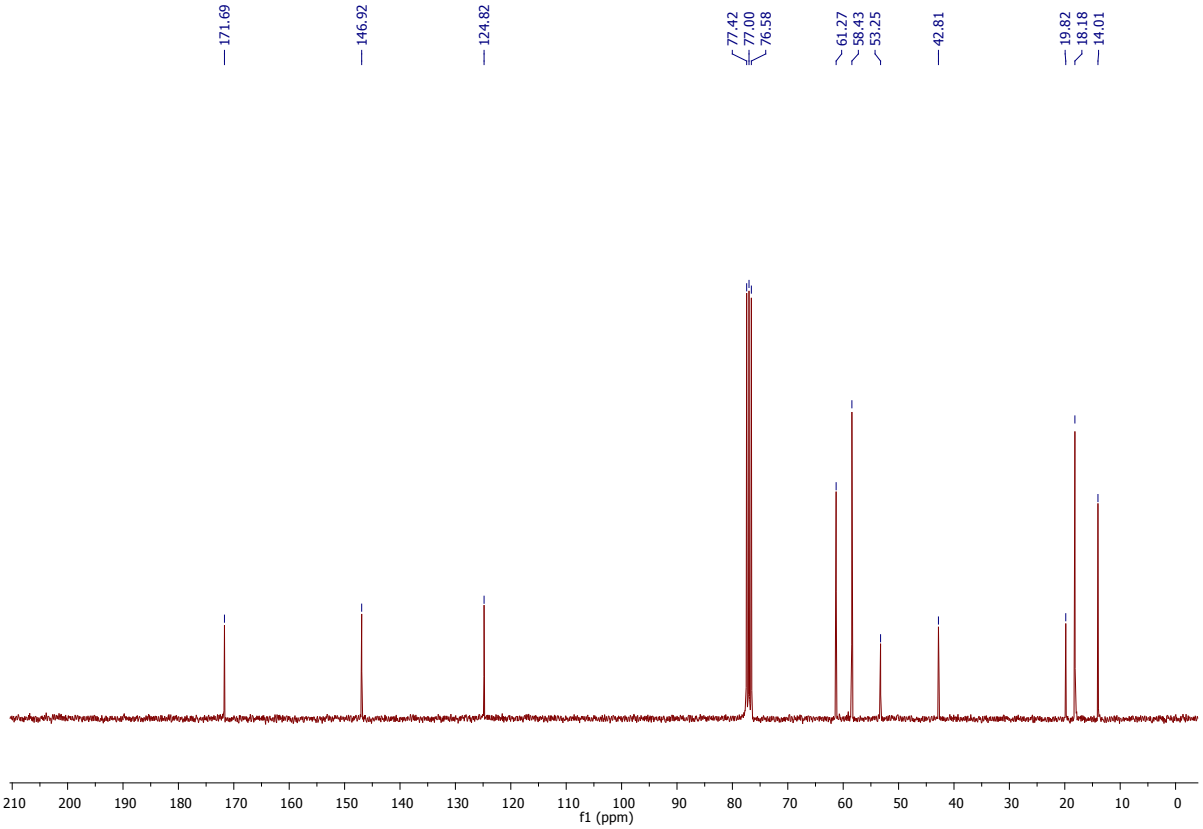
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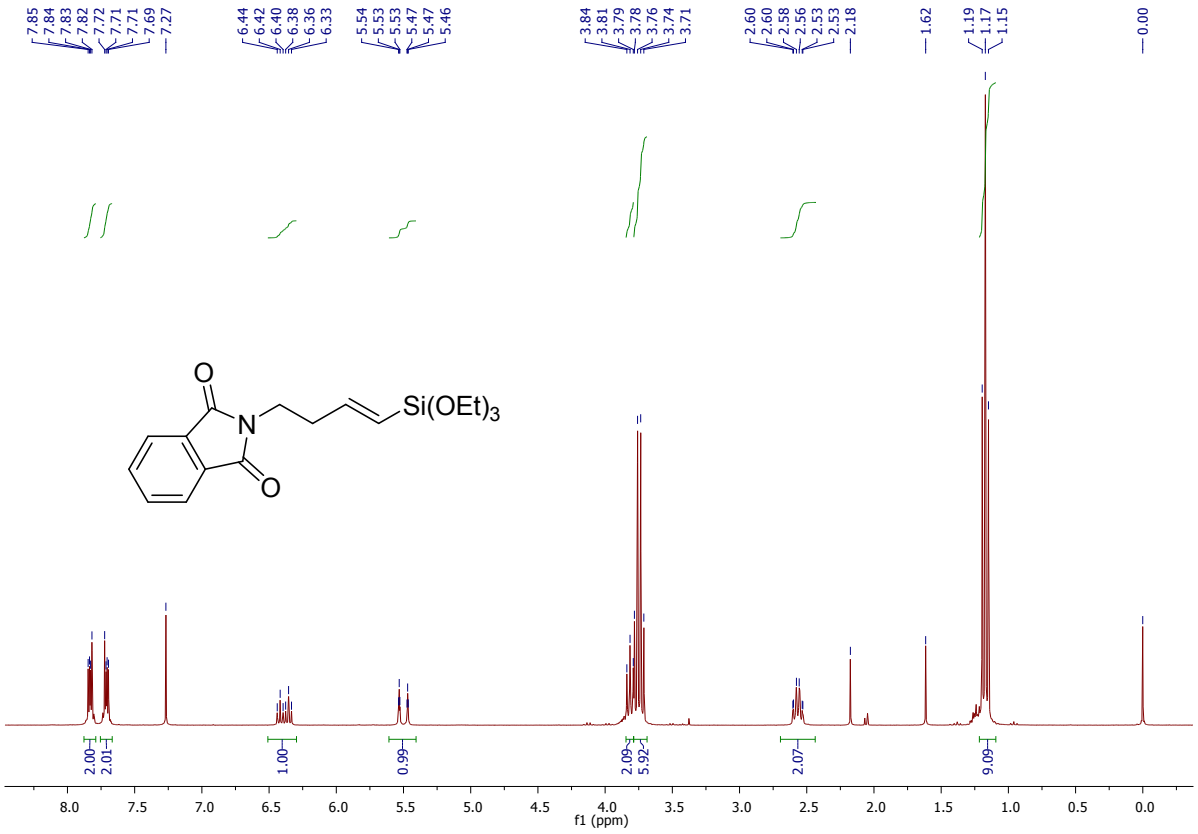
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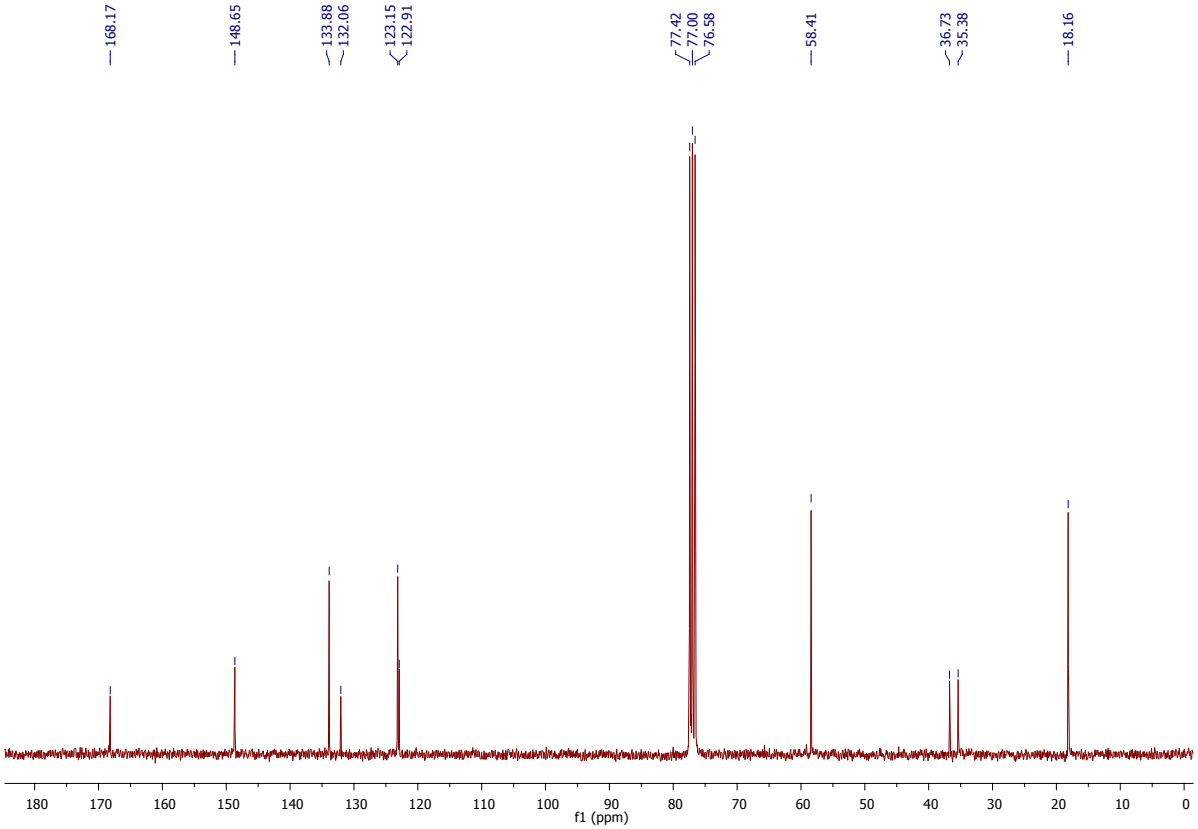
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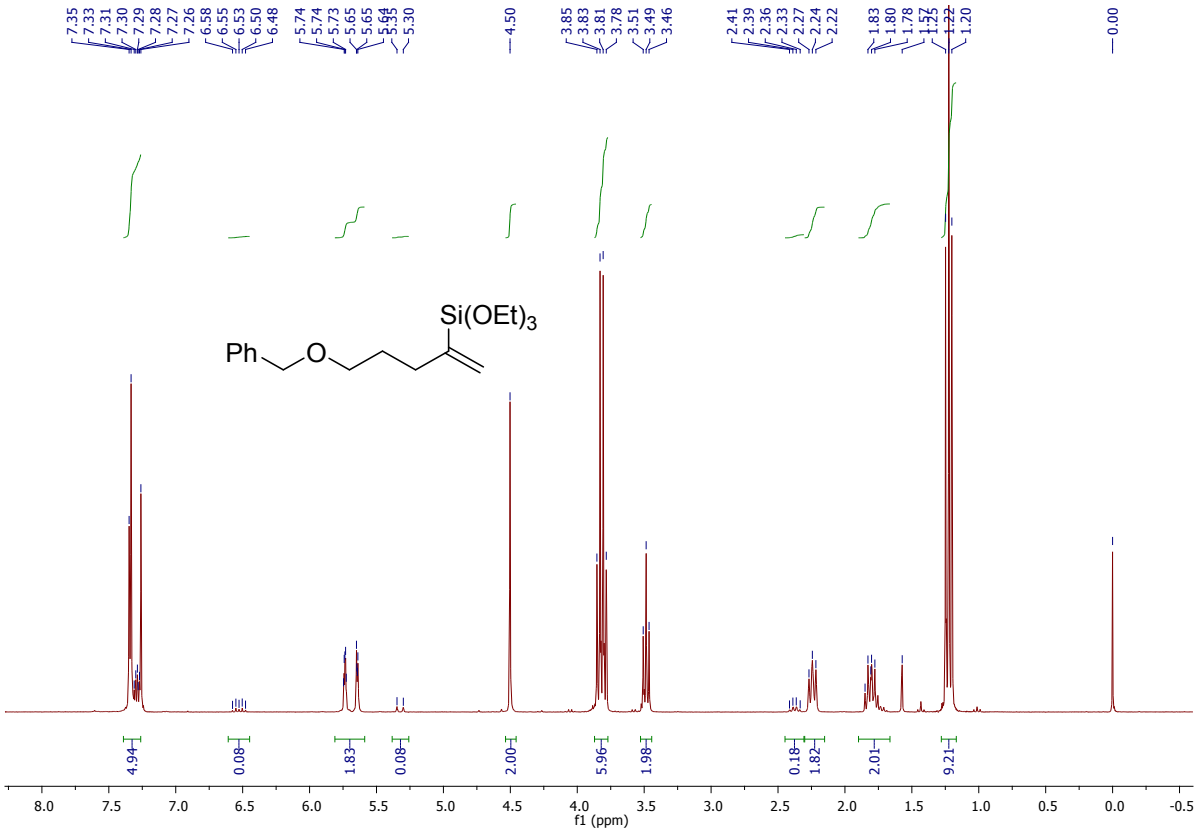
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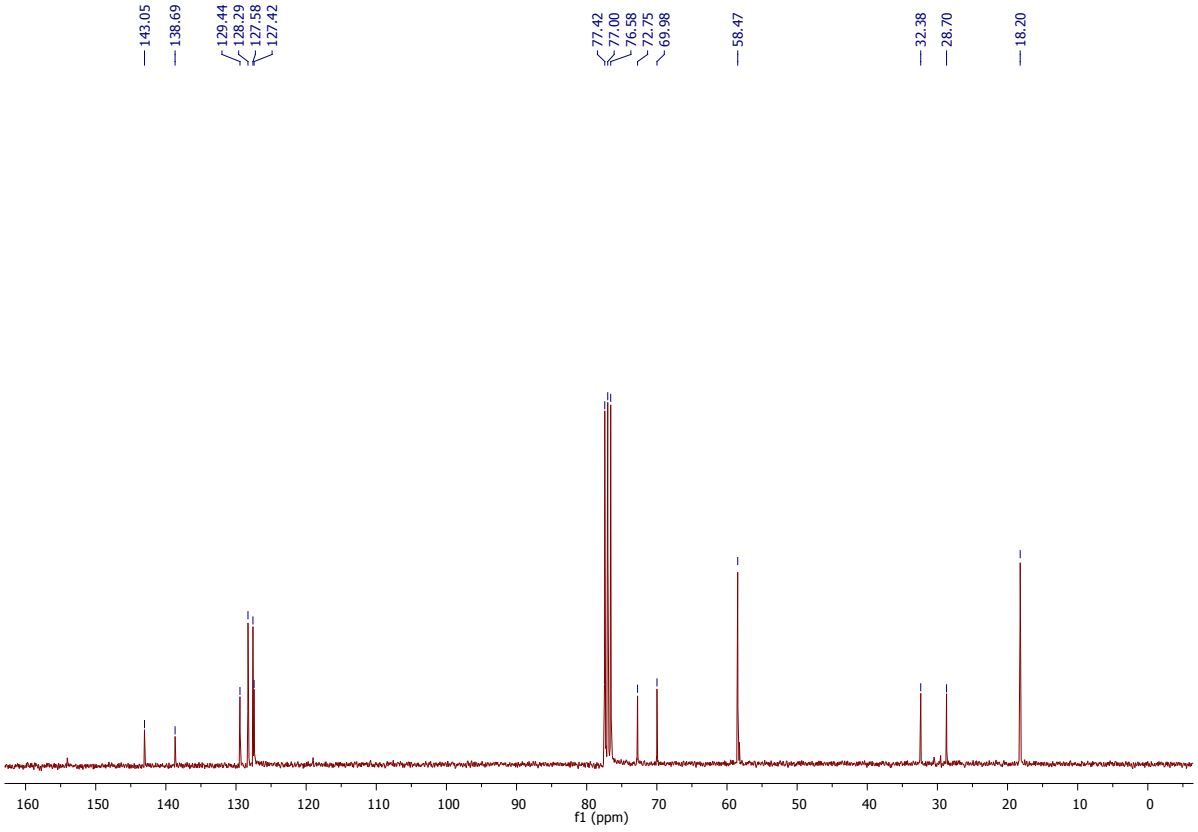
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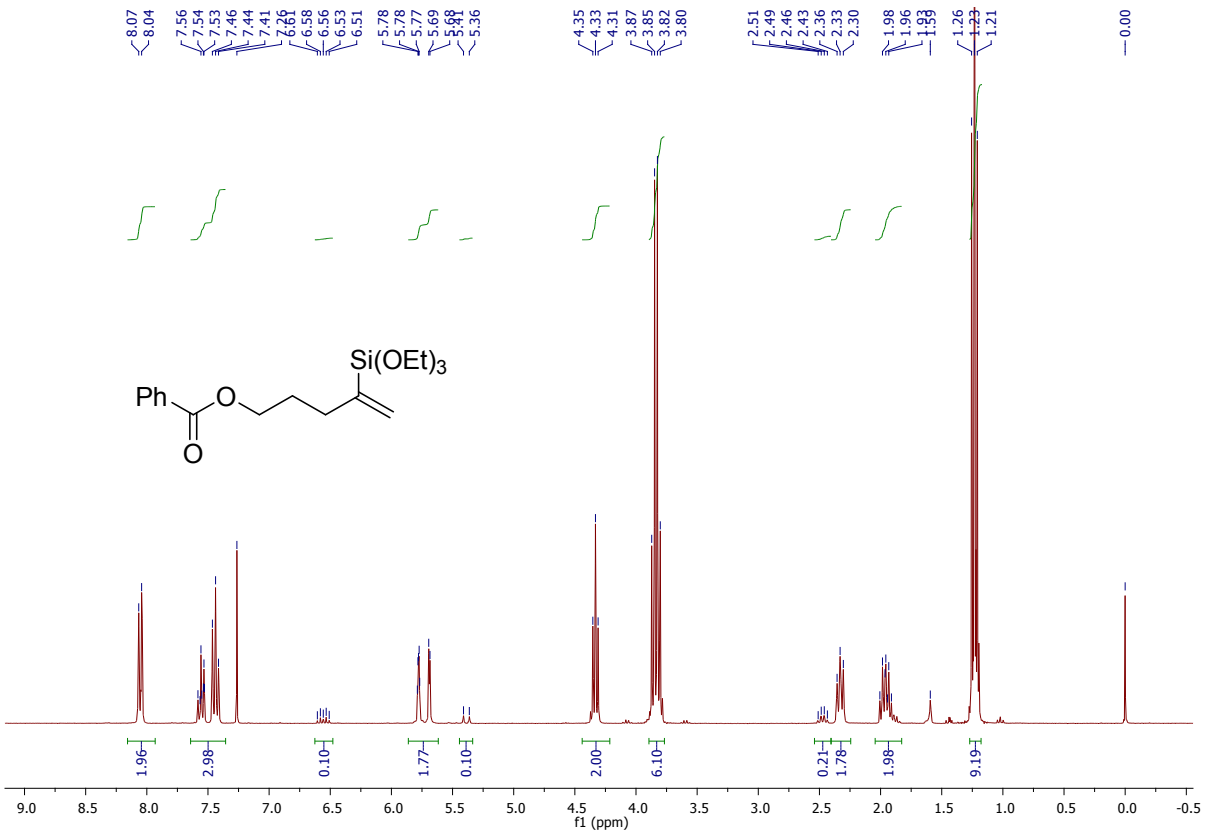
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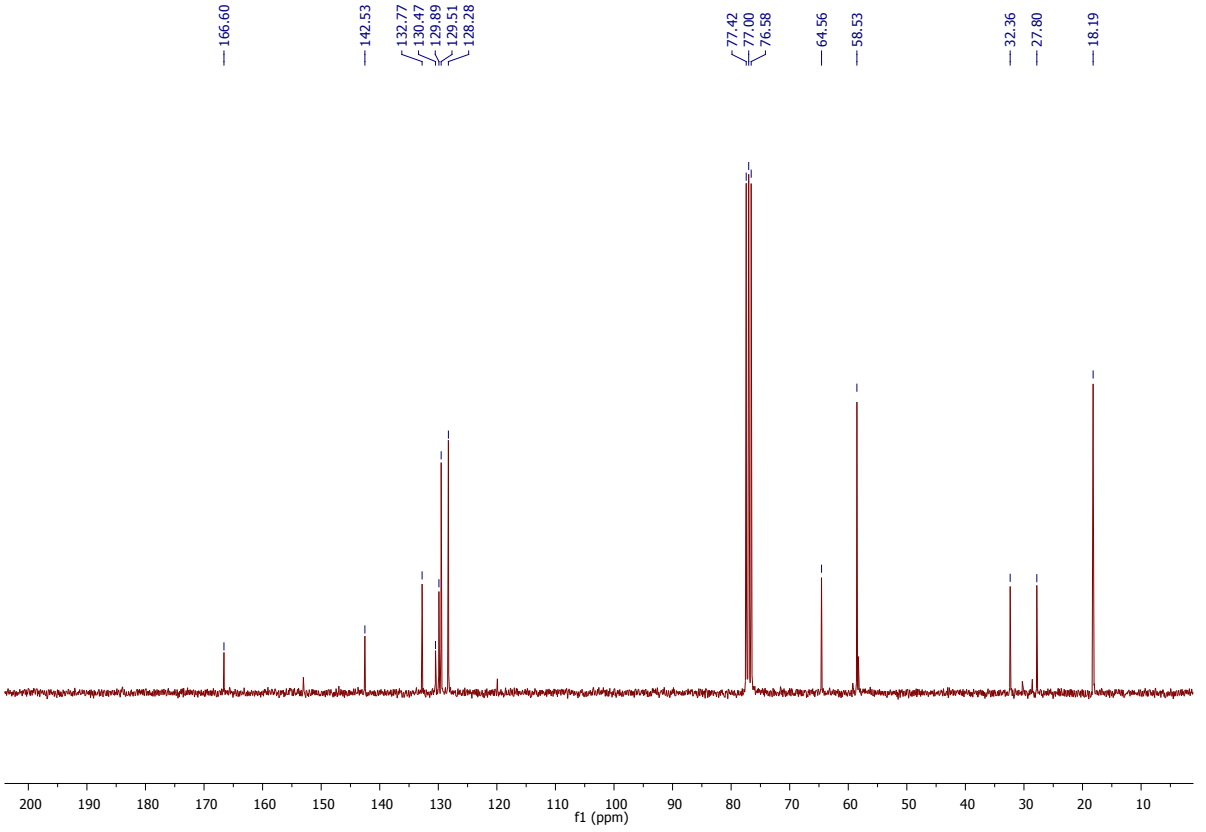
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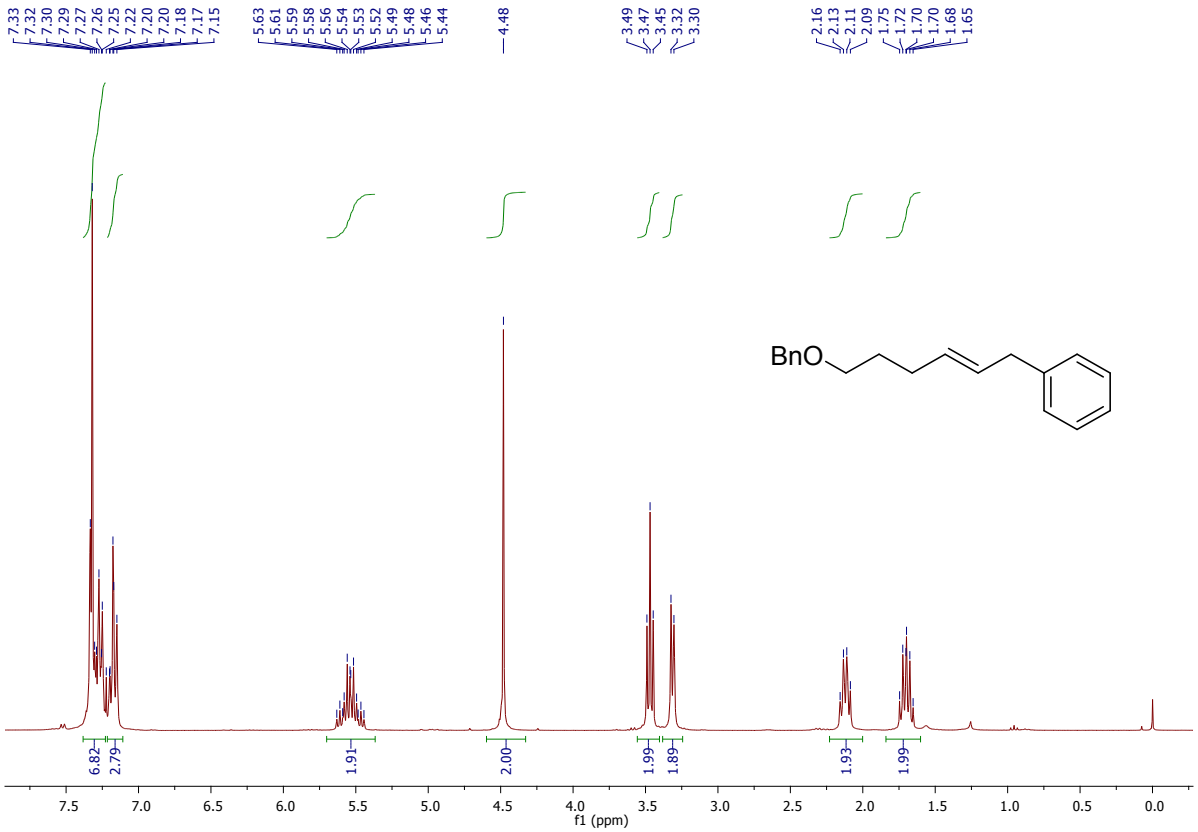
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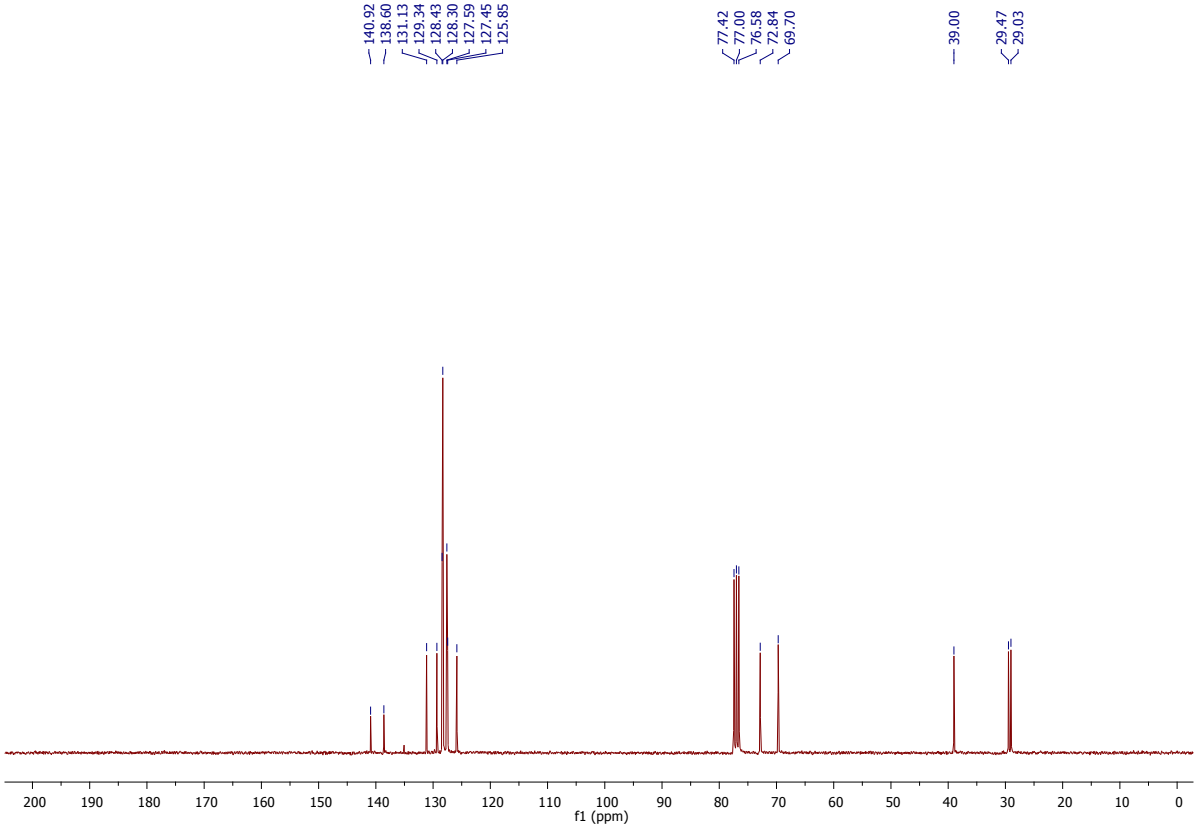
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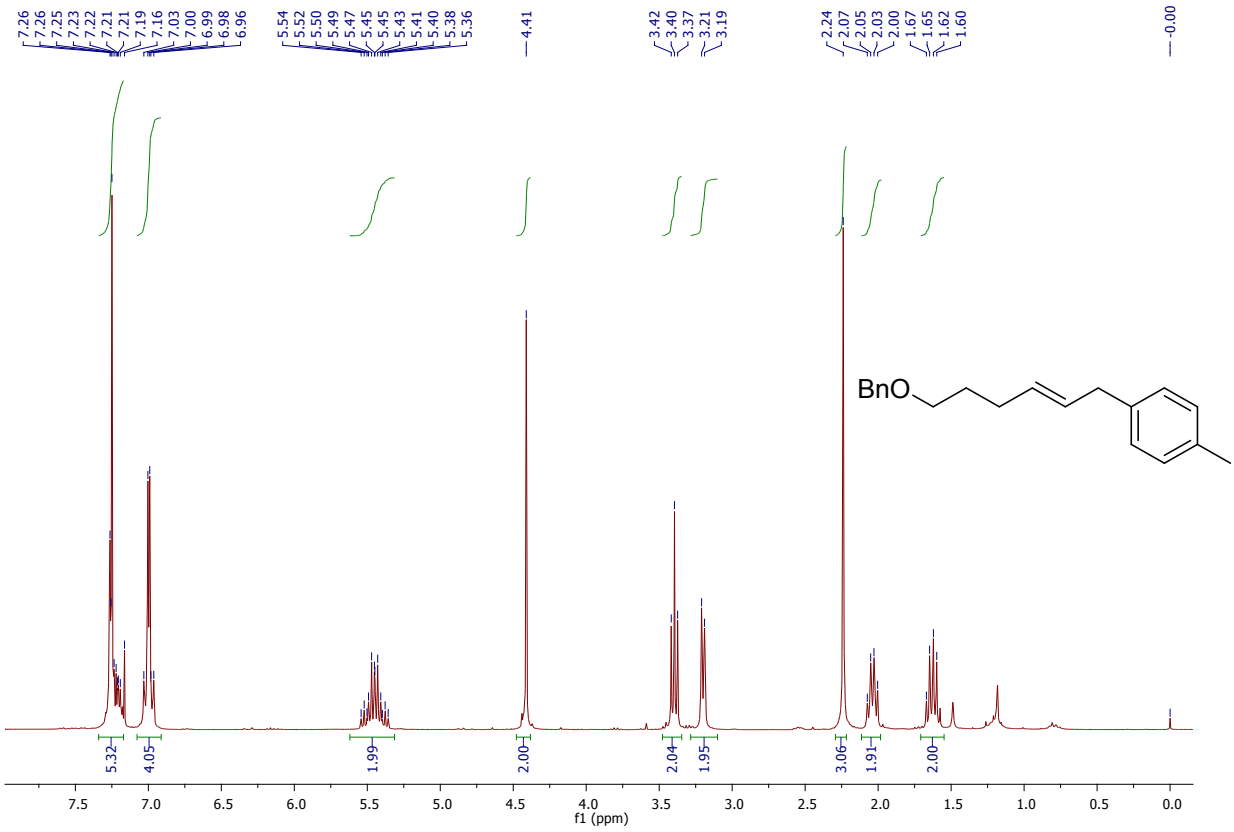
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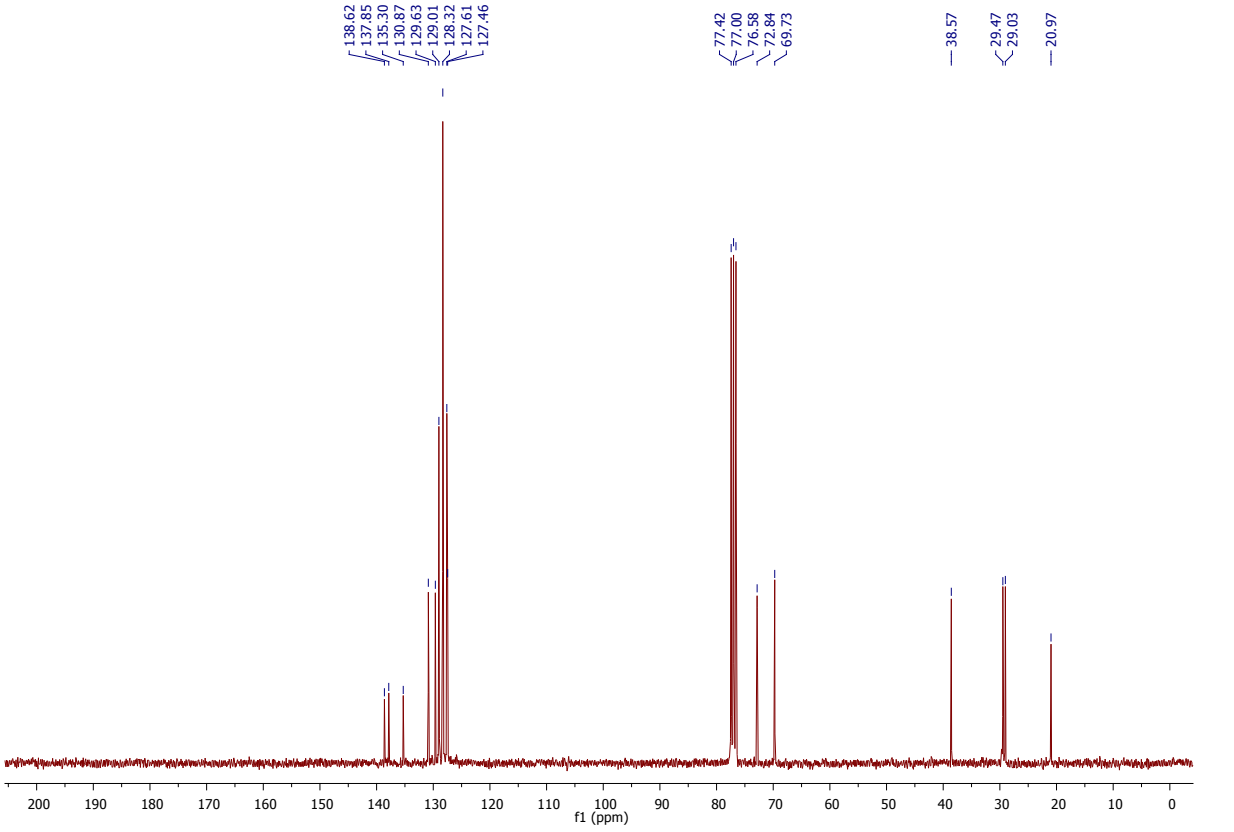
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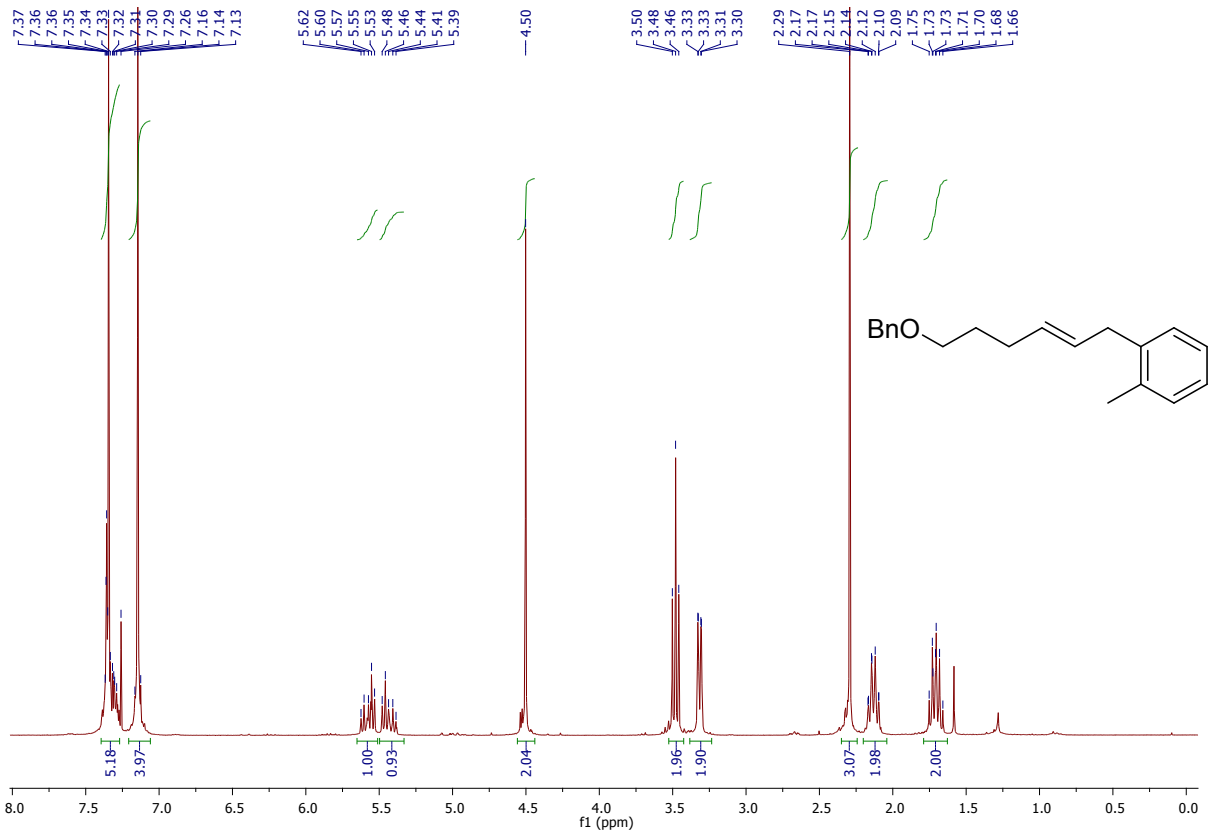
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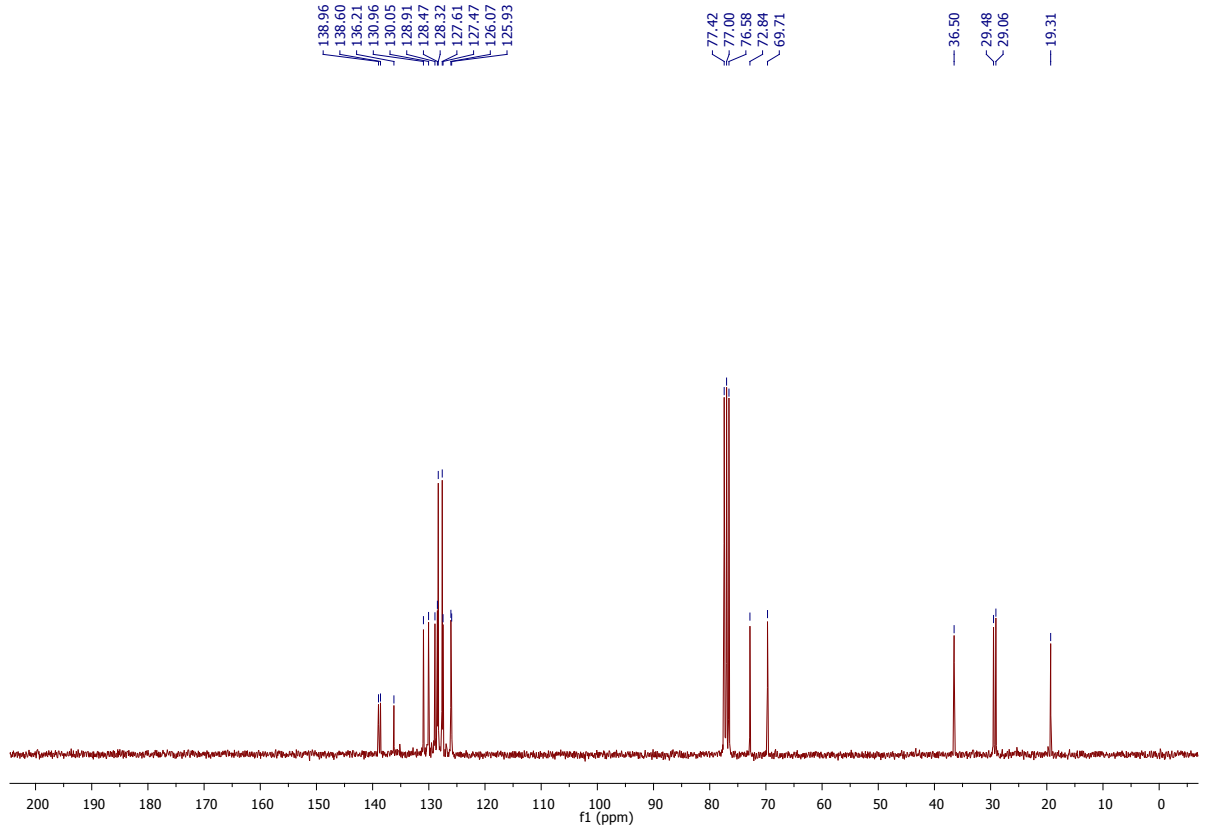
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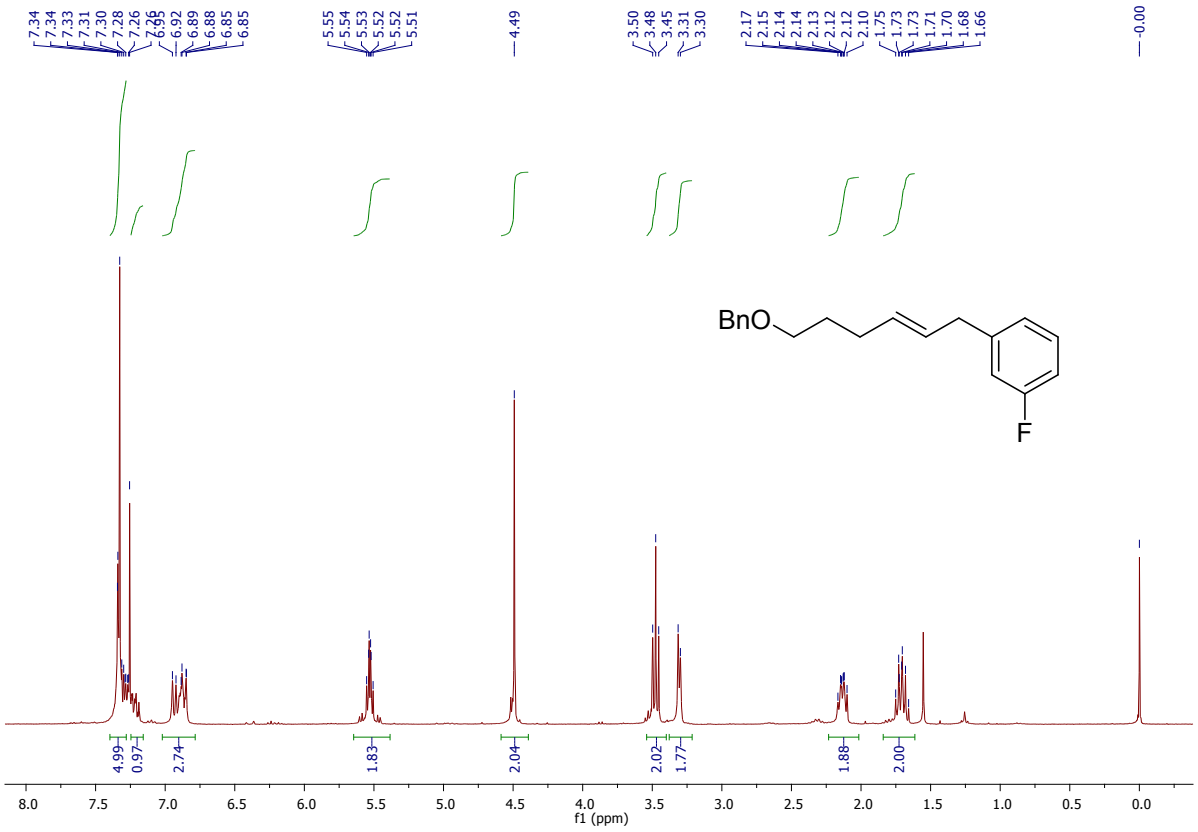
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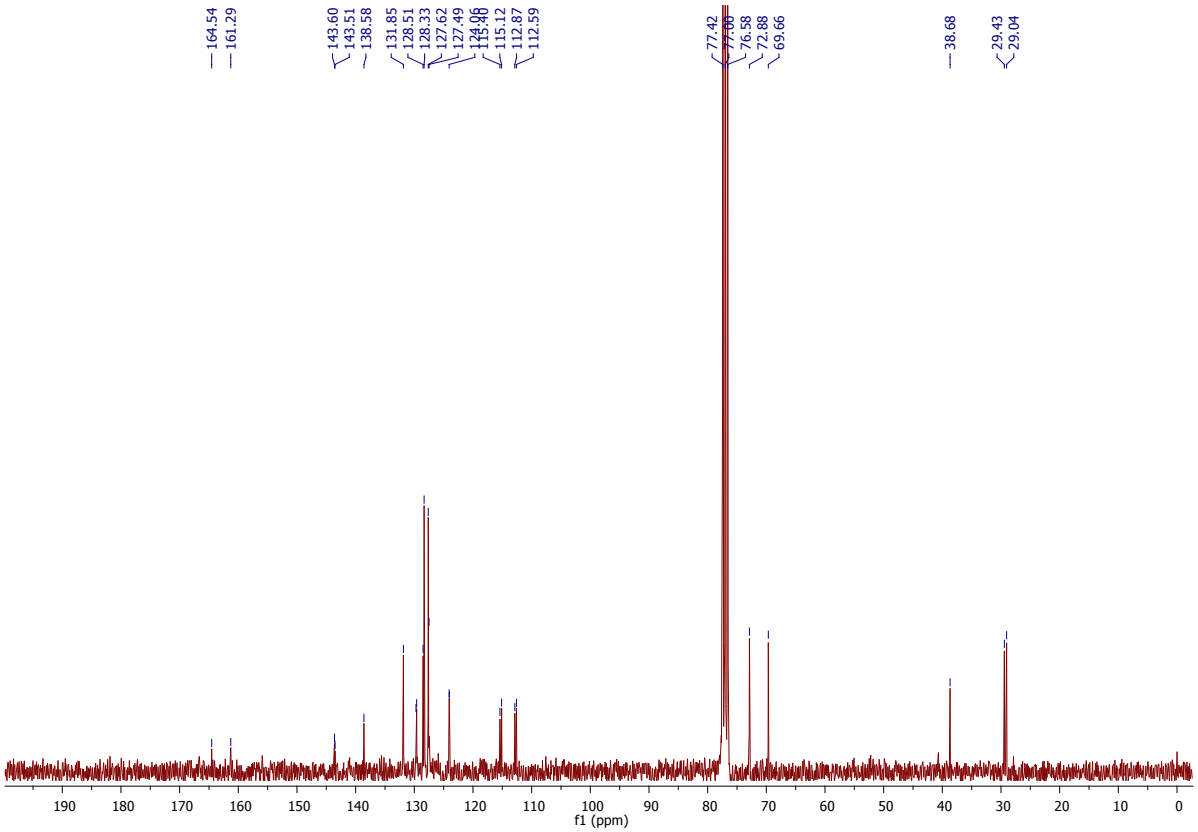
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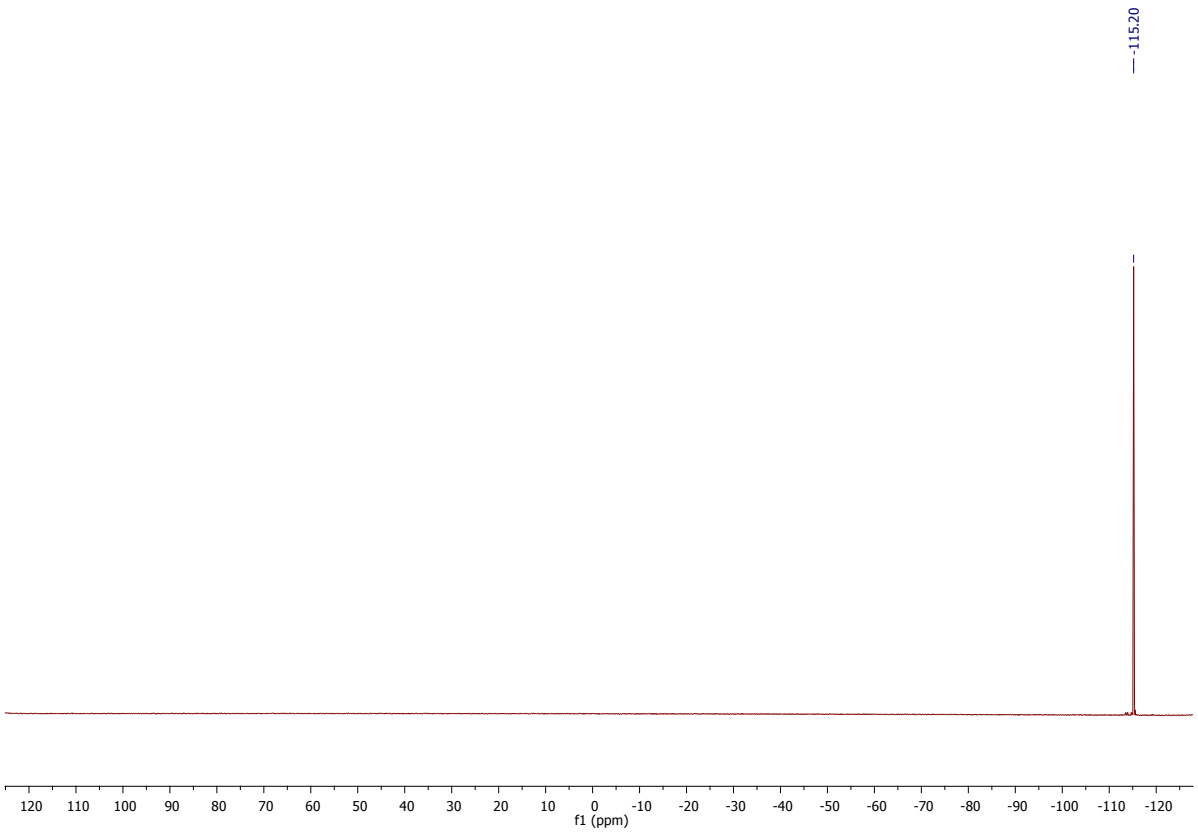
f1 (ppm)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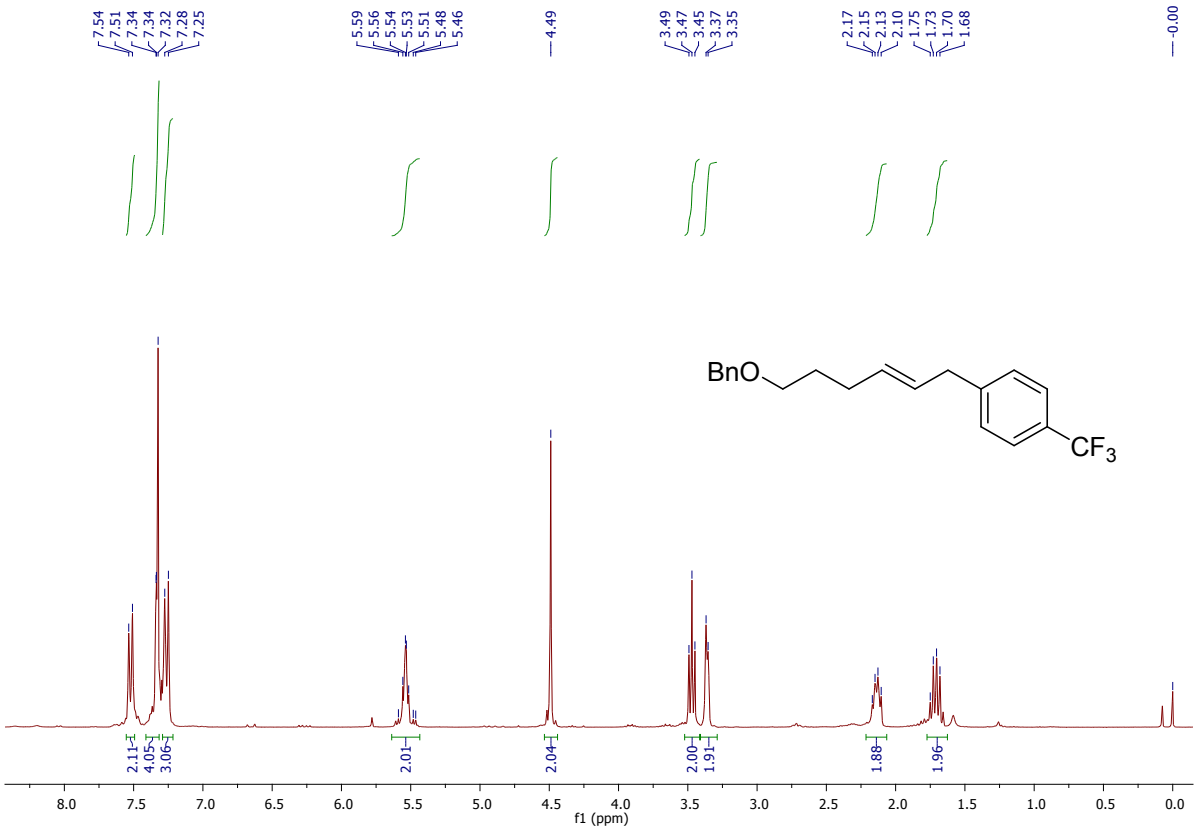
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2.15
2.13
2.10
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1.73
1.70
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-0.00
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2.04
2.00
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1.96
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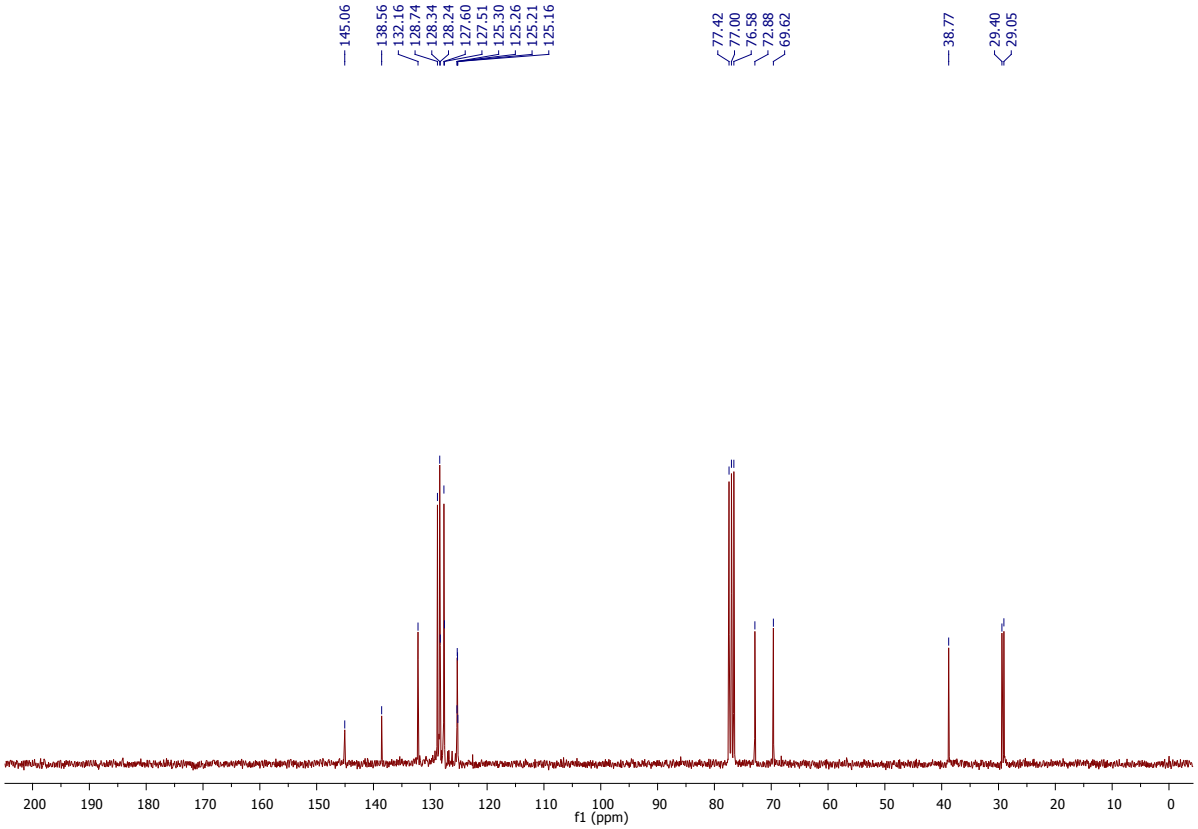
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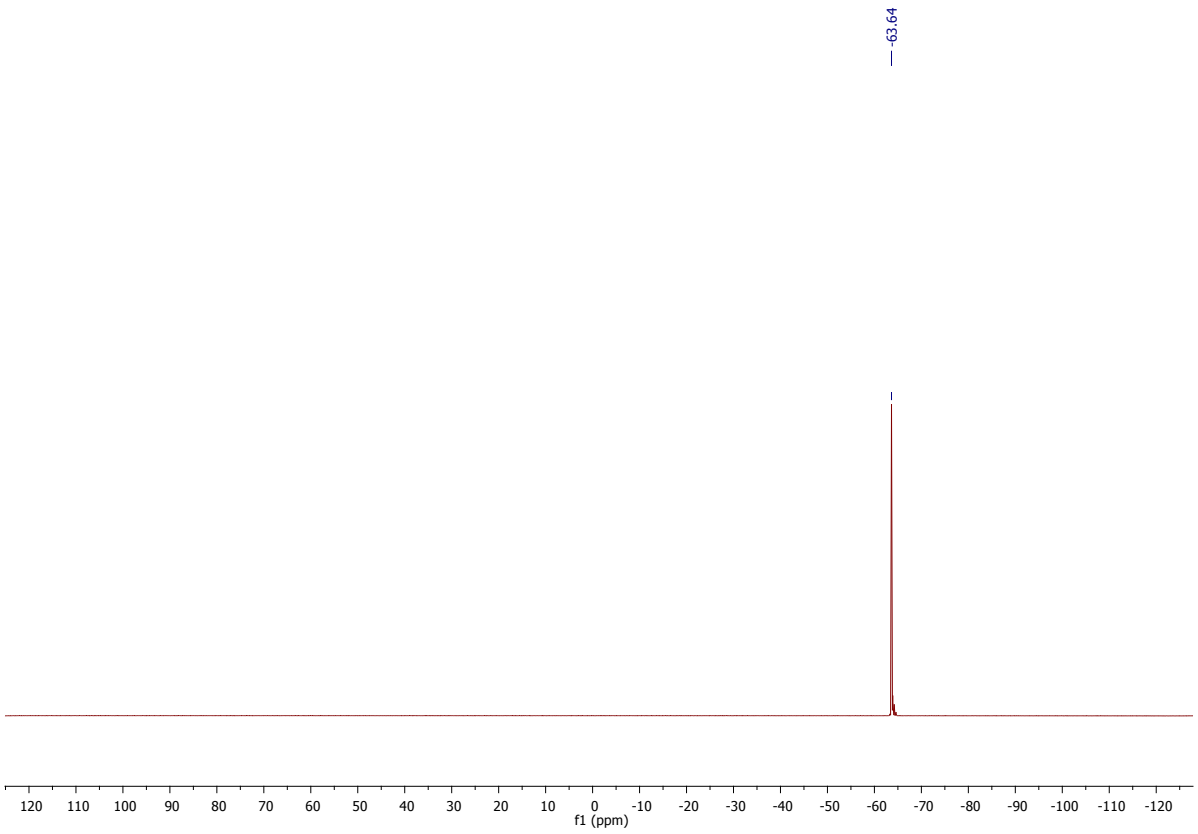
29.05
f1 (ppm)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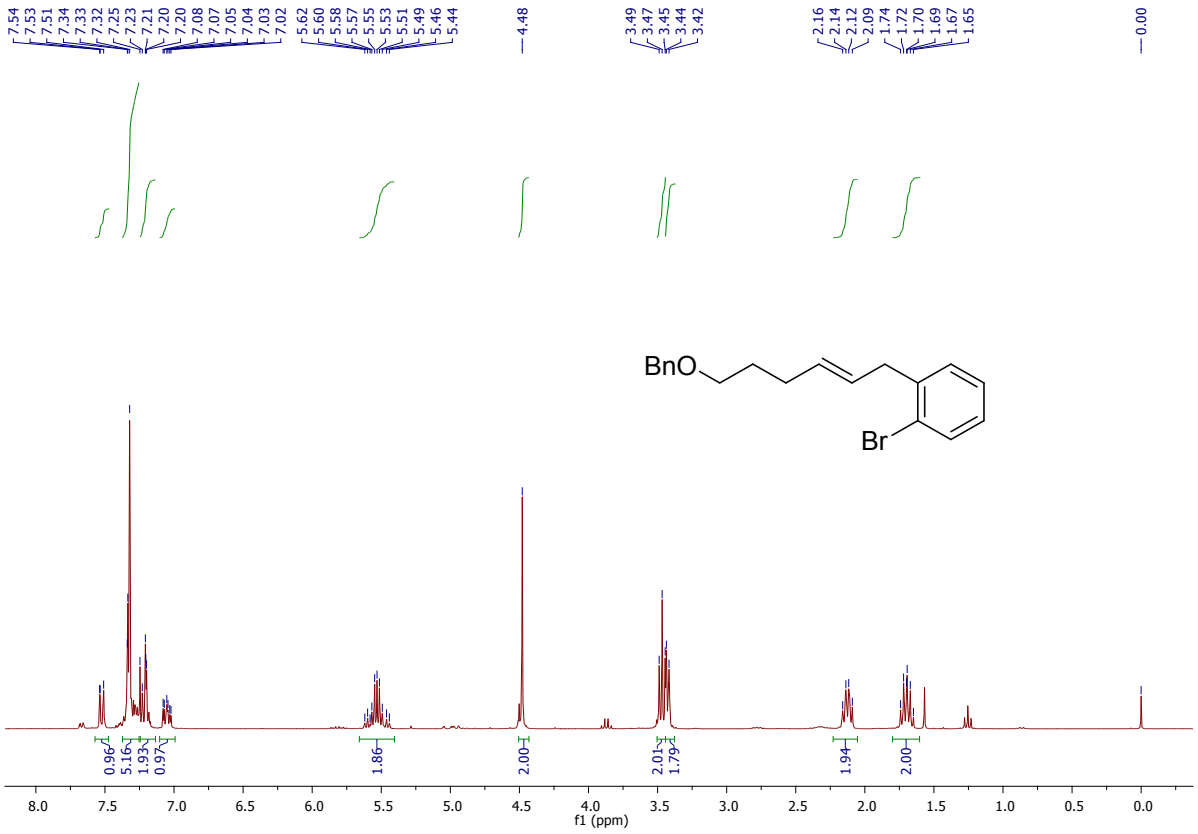
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2.00
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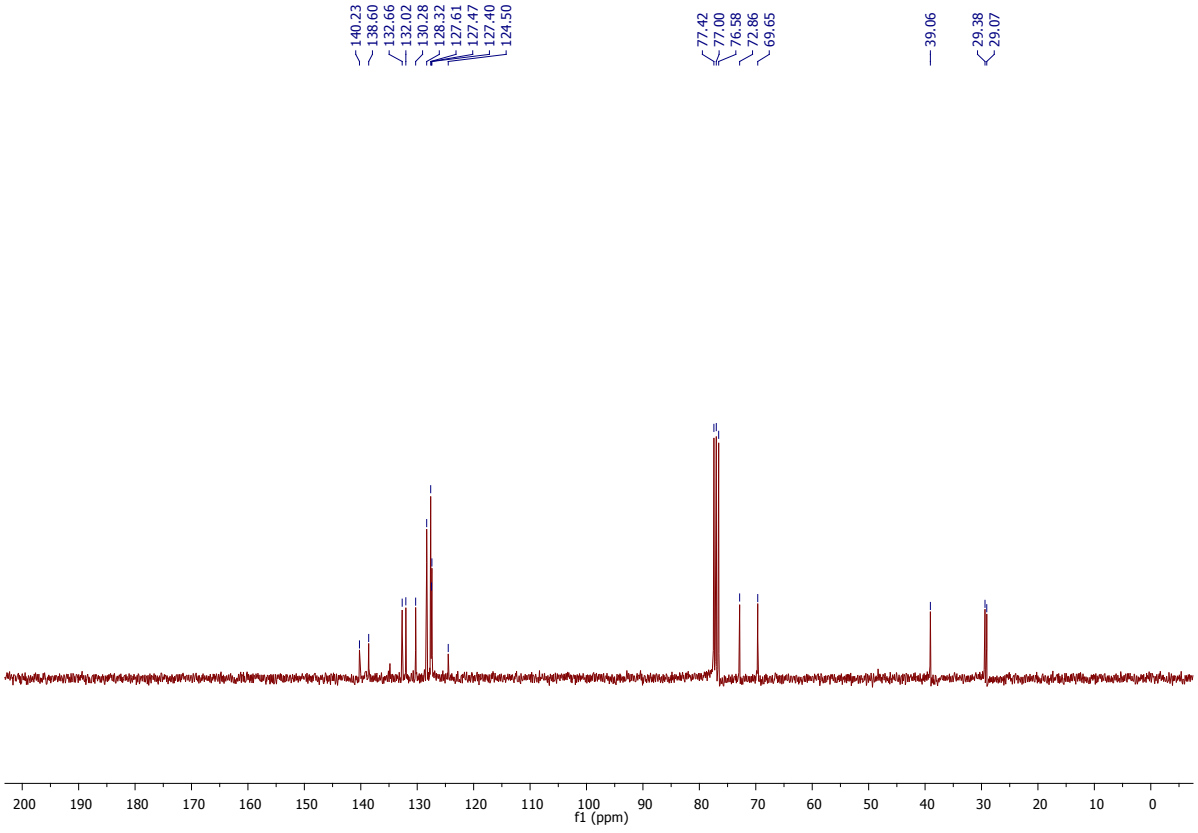
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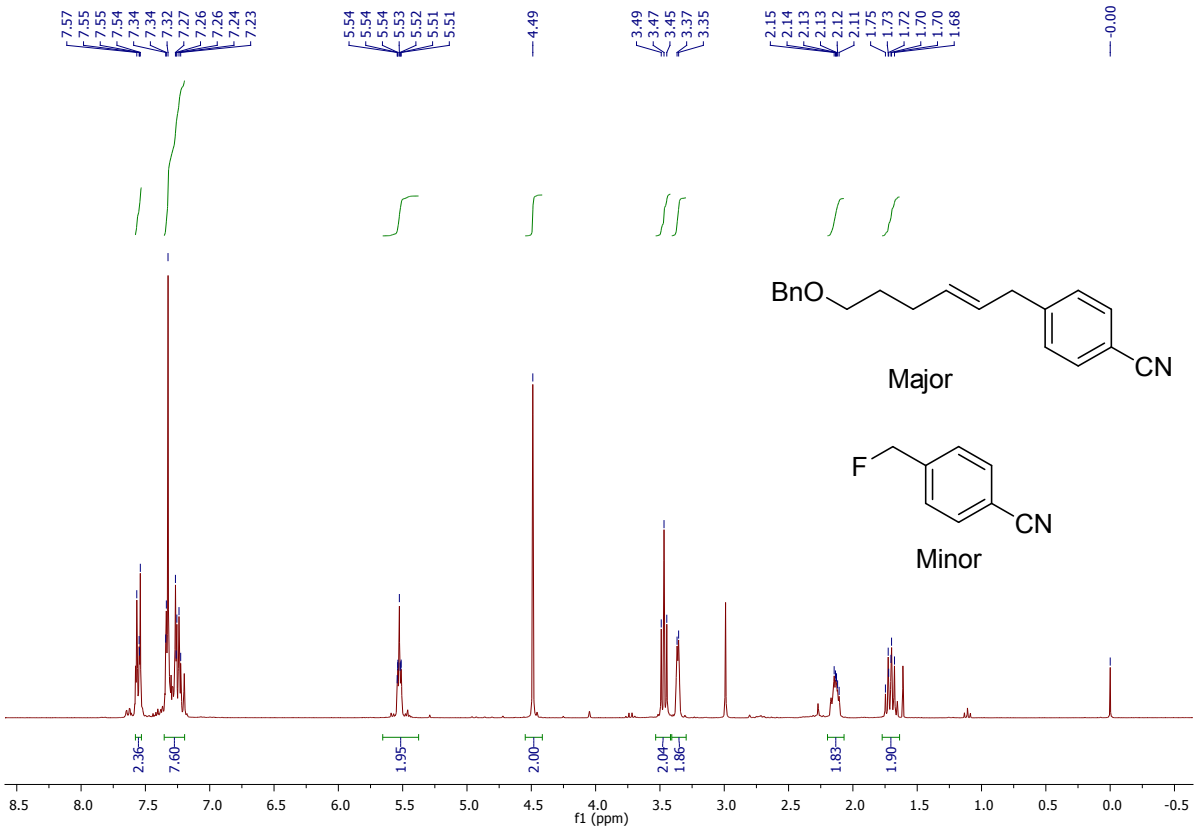
29.38
29.07
f1 (ppm)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1.70
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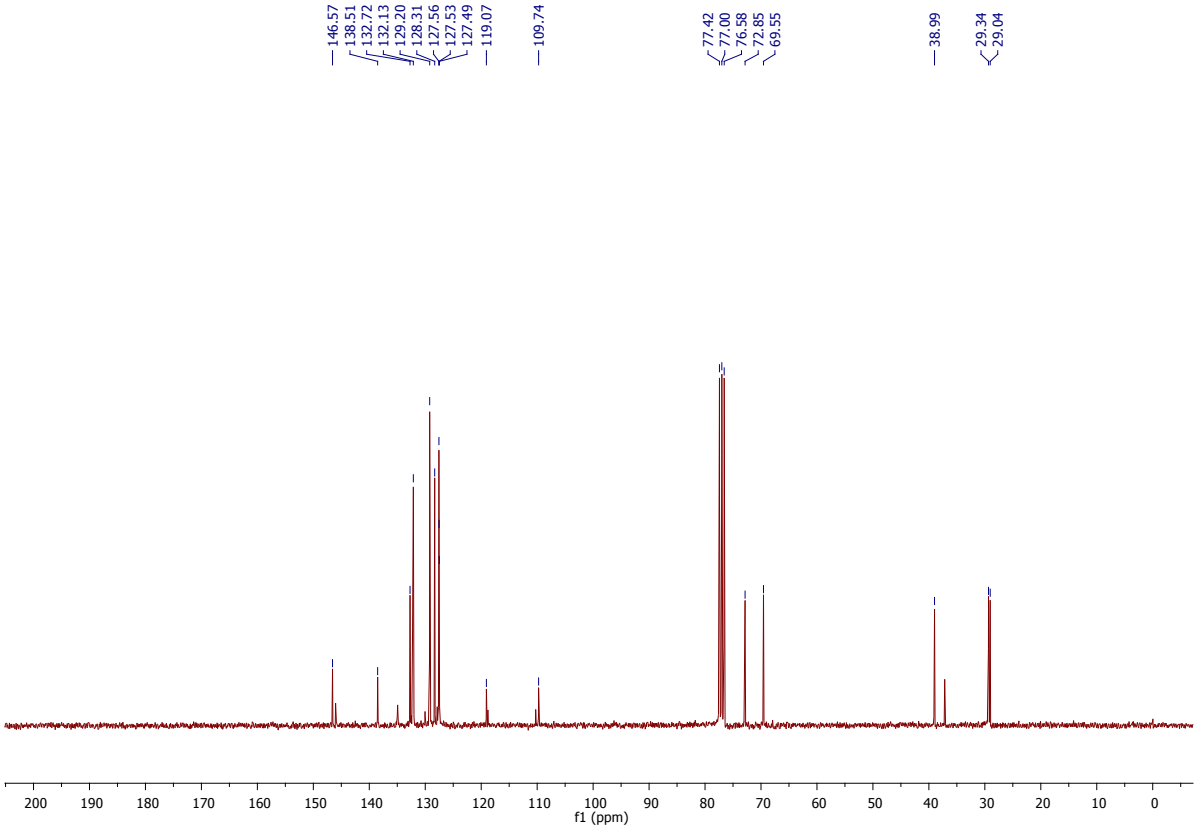
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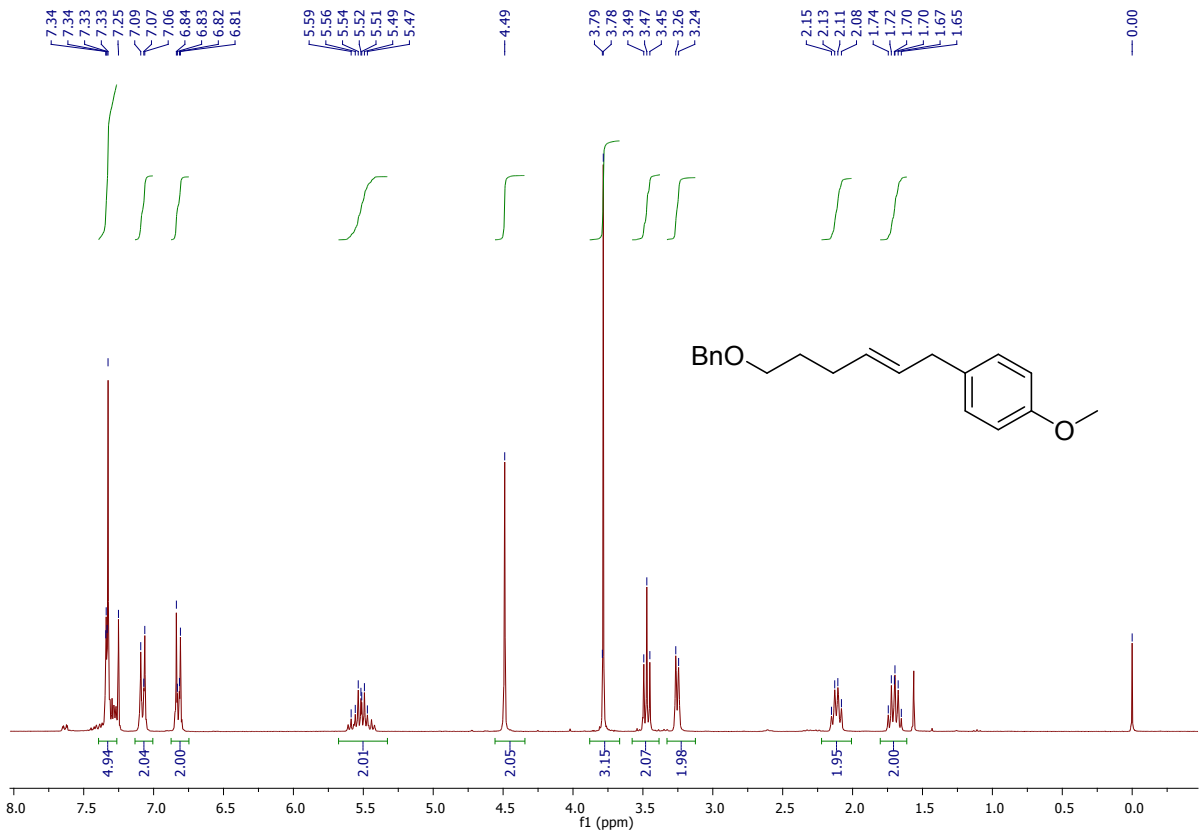
69.55
38.99
29.34
29.04
f1 (ppm)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5.52
5.51
5.49
5.47
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3.78
3.49
3.47
3.45
3.26
3.24
2.15
2.13
2.11
2.08
1.74
1.72
1.70
1.70
1.67
1.65
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BnO
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2.05
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2.07
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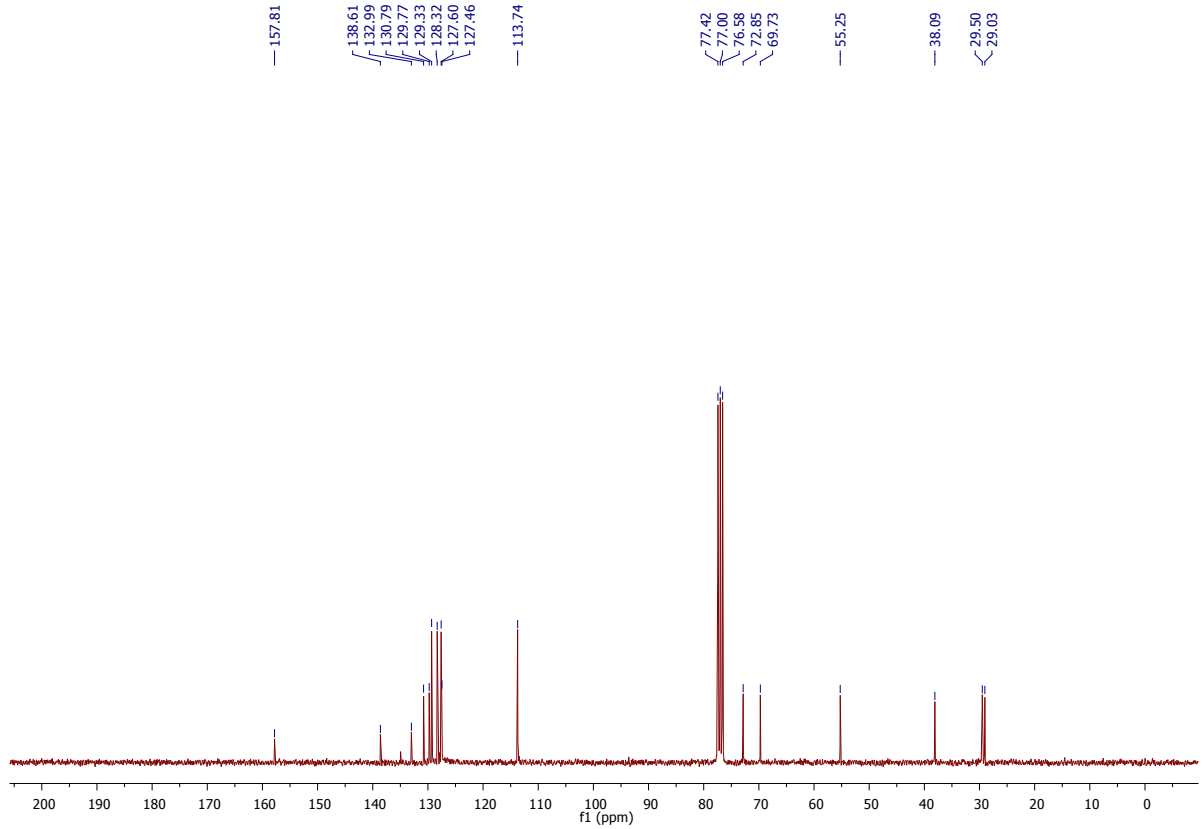
1.95
2.00
f1 (ppm)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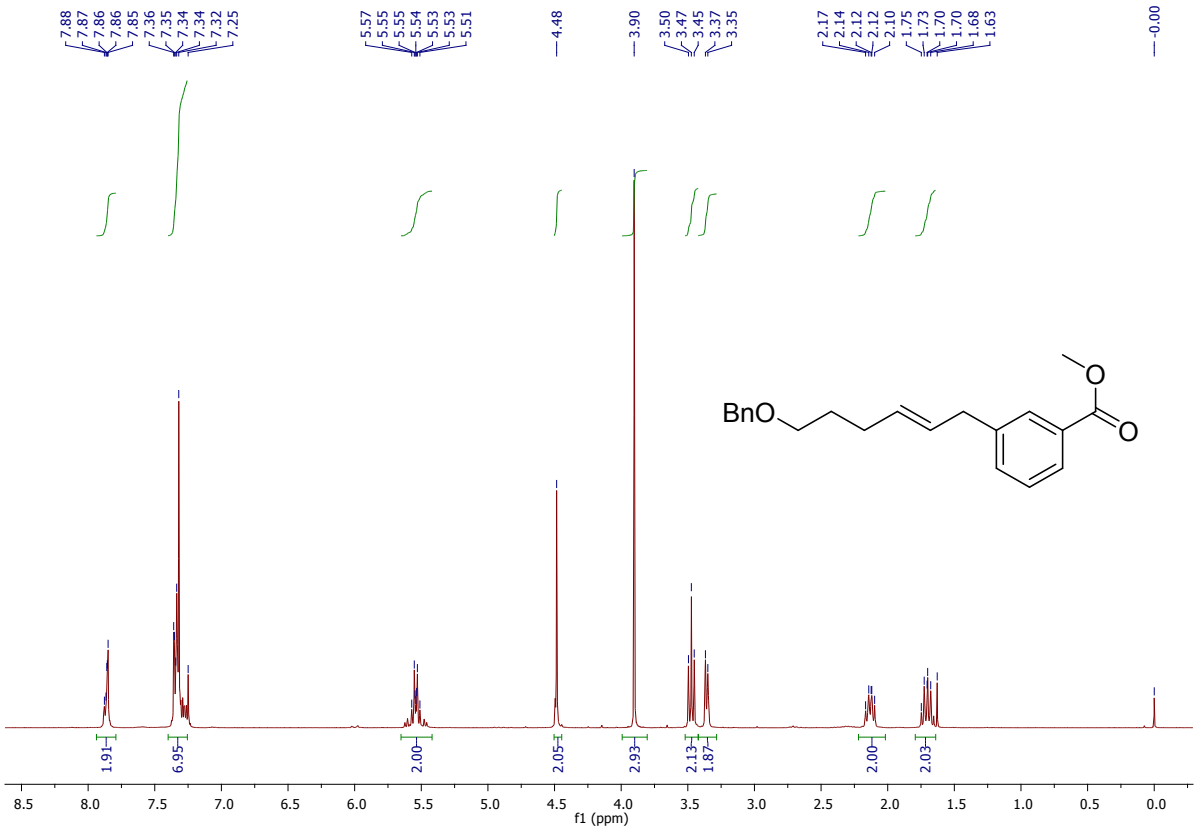
69.73
55.25
38.09
29.50
29.03
f1 (ppm)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5.54
5.53
5.53
5.51
4.48
3.90
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3.47
3.45
3.37
3.35
2.17
2.14
2.12
2.12
2.10
1.75
1.73
1.70
1.70
1.68
1.63
0.00
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O
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2.05
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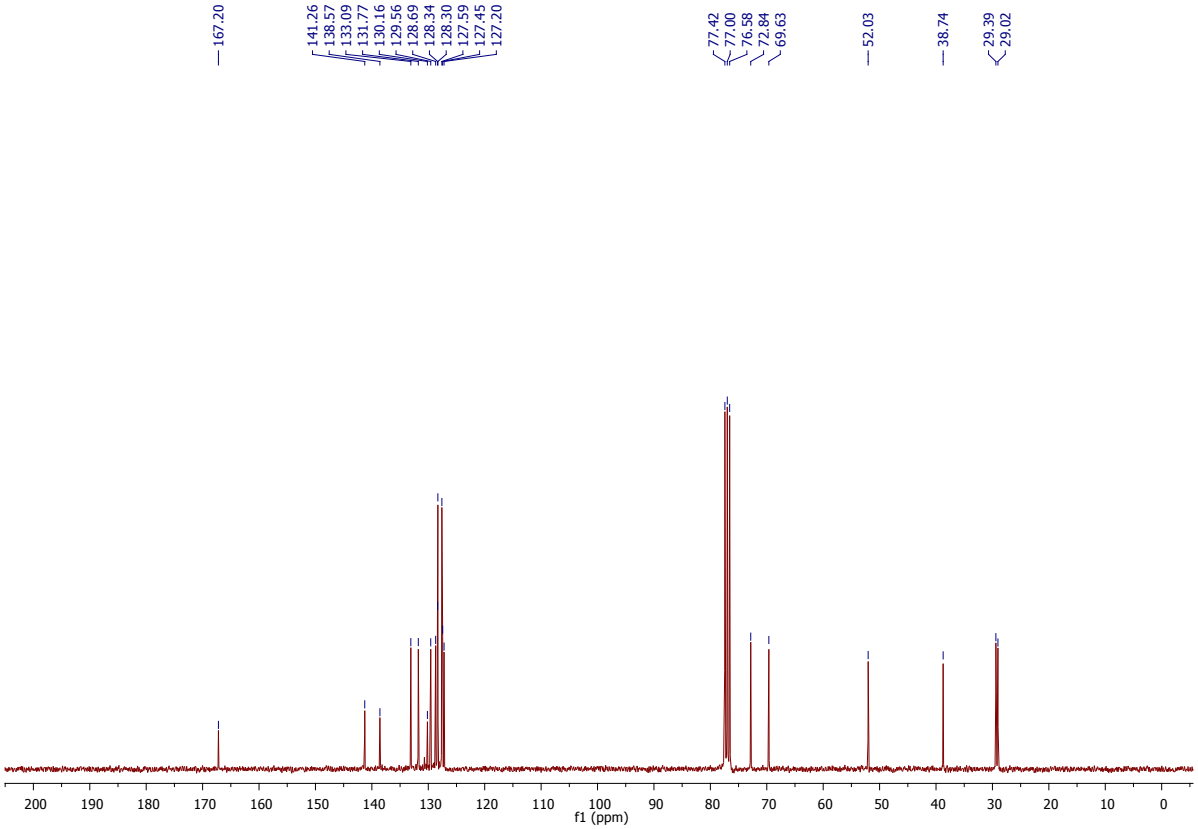
2.00
2.03
f1 (ppm)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52.03
38.74
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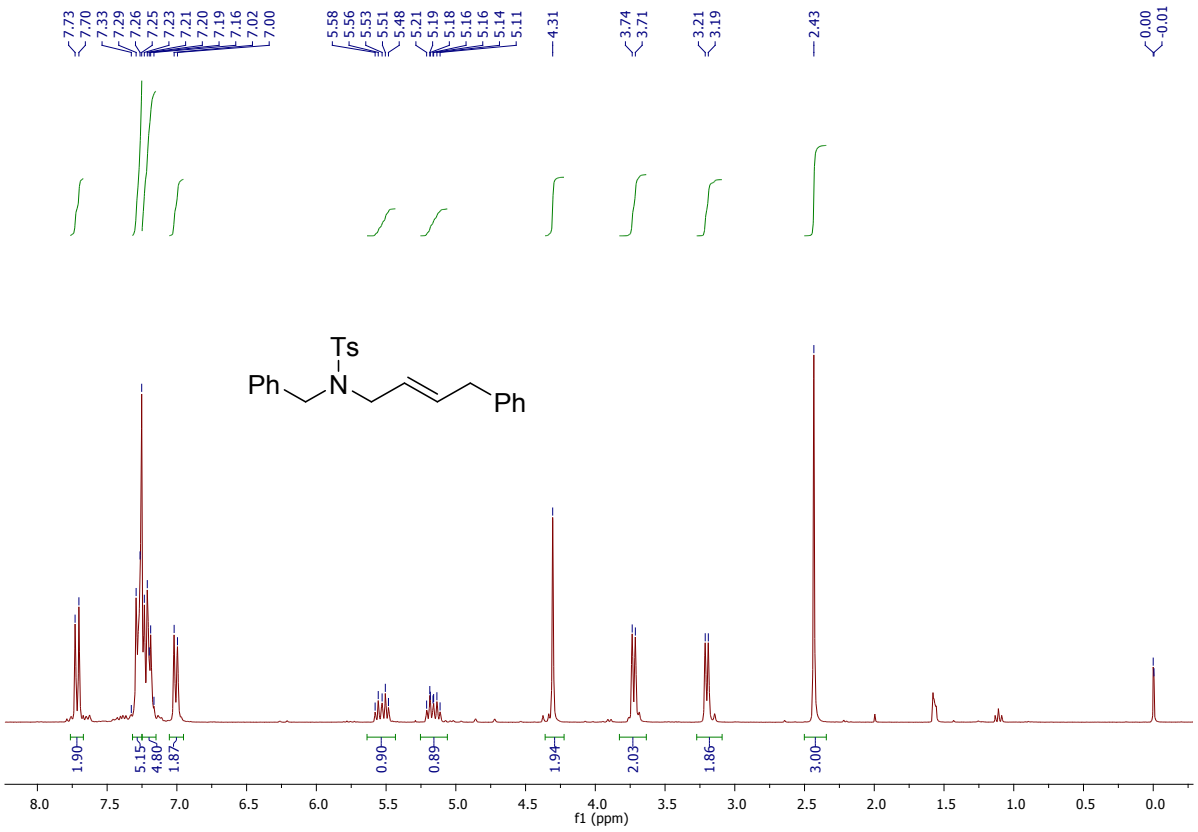
29.02
f1 (ppm)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7.00
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5.56
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5.48
5.21
5.19
5.18
5.16
5.16
5.14
5.11
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3.74
3.71
3.21
3.19
2.43
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-0.01
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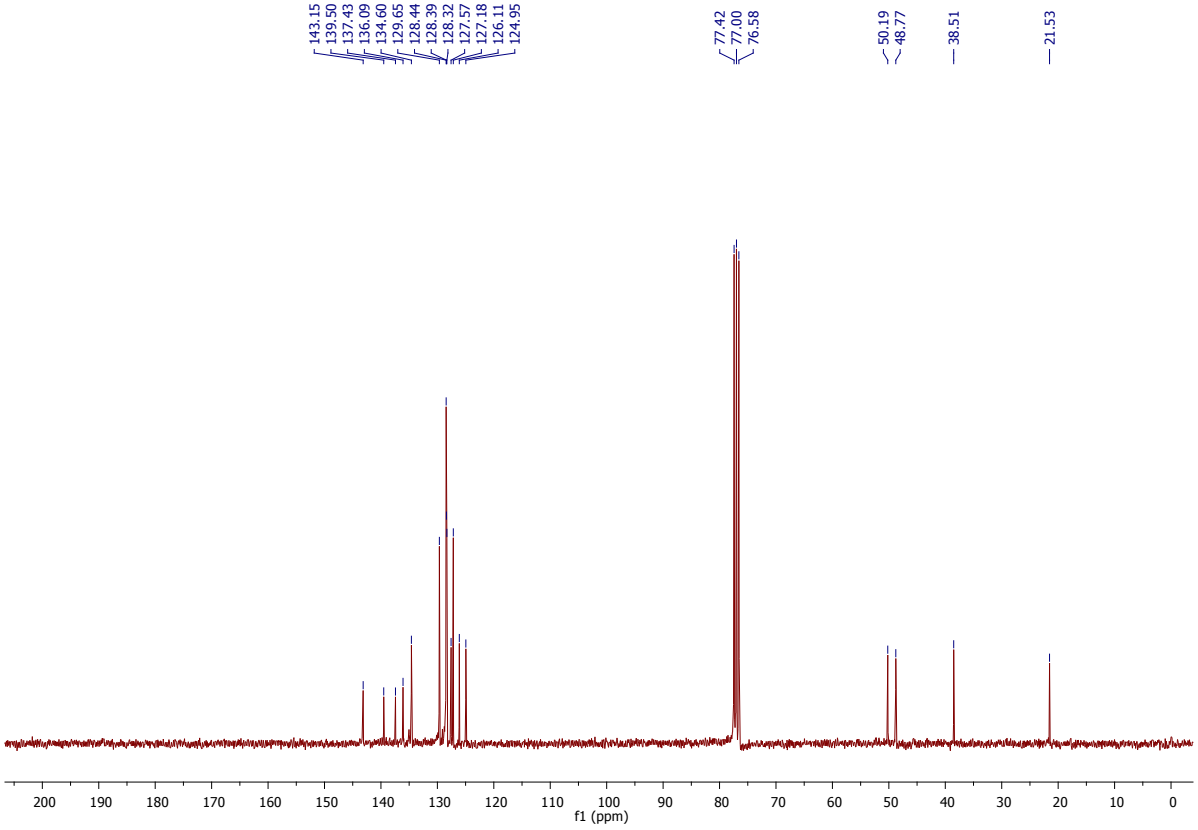
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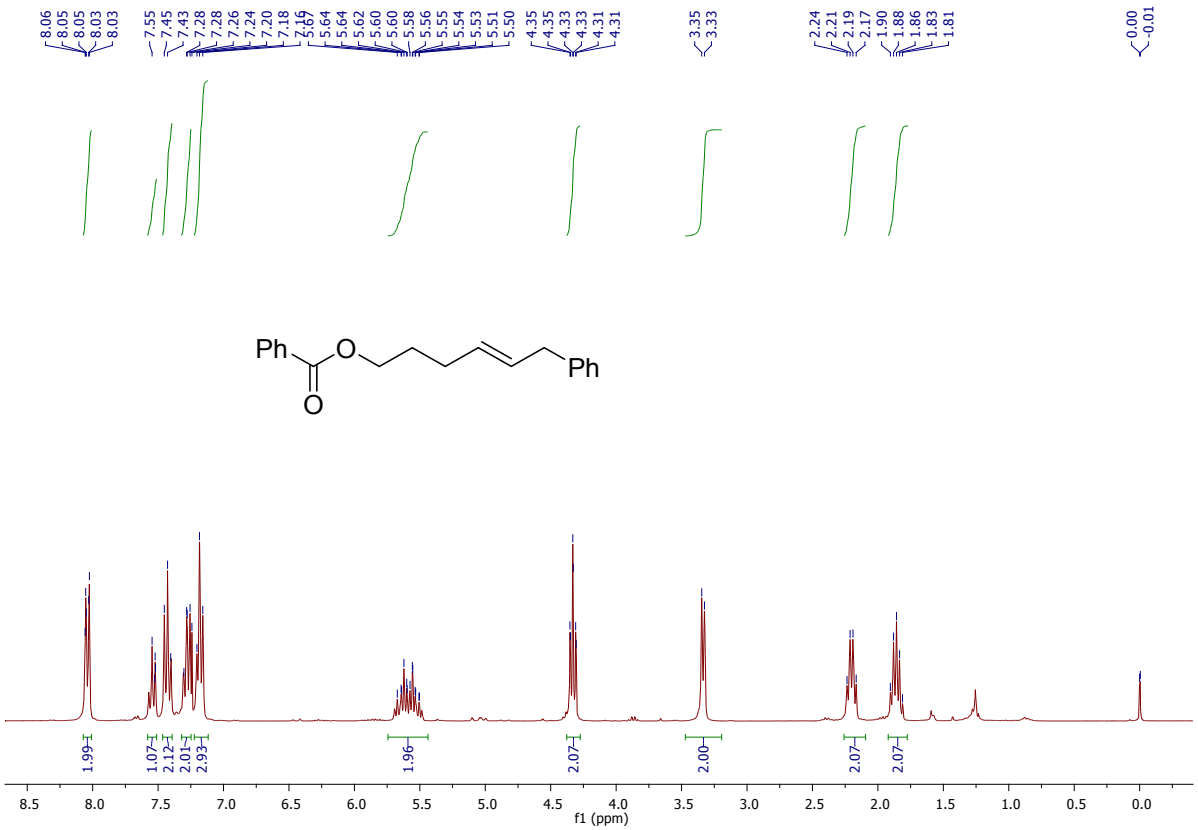
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2.24
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2.19
2.17
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1.88
1.86
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1.81
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2.01
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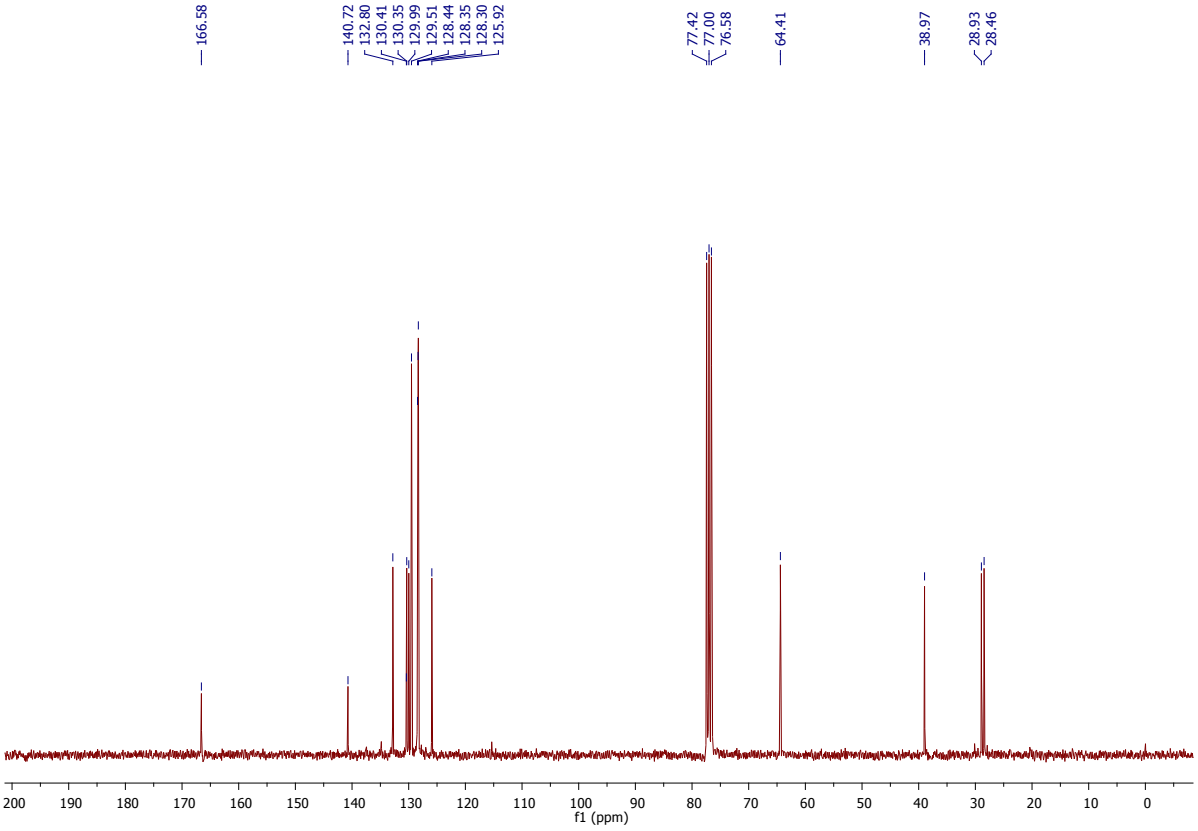
2.07
2.00
2.07
2.07
f1 (ppm)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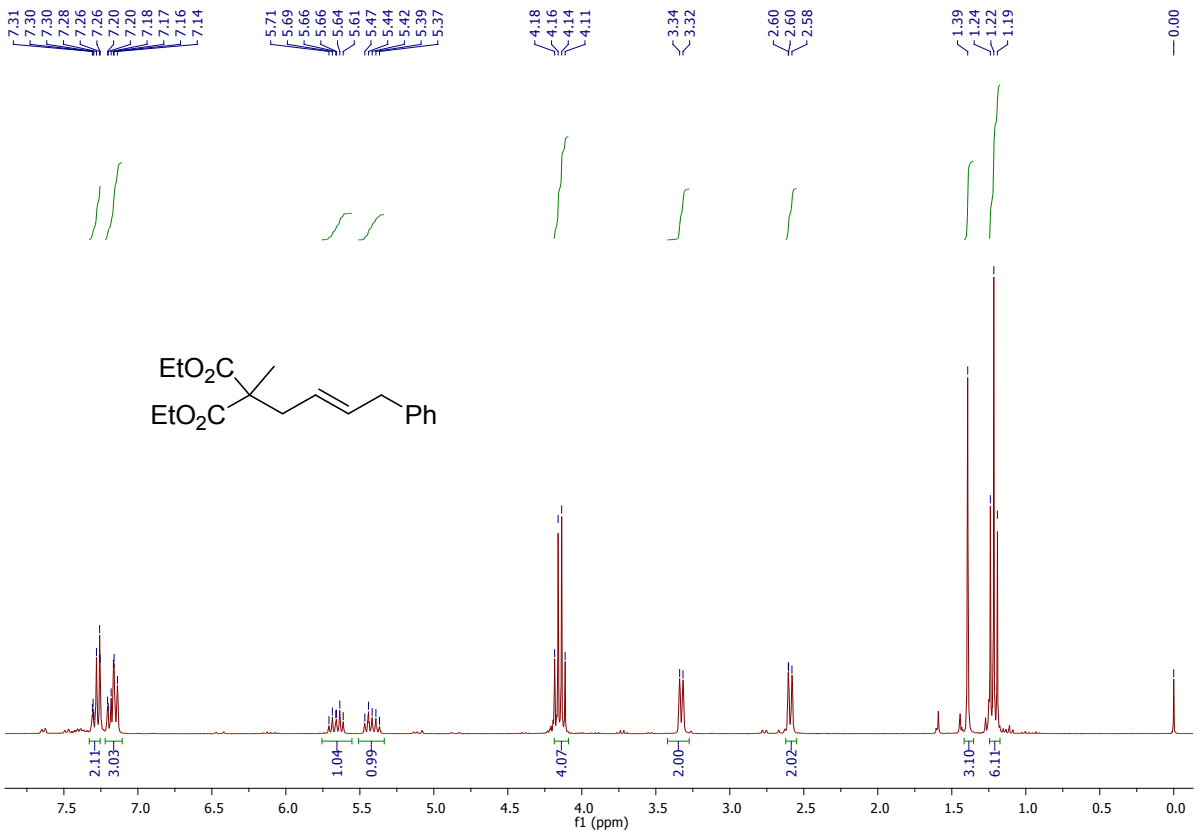
28.46
f1 (ppm)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1.19
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EtO2C
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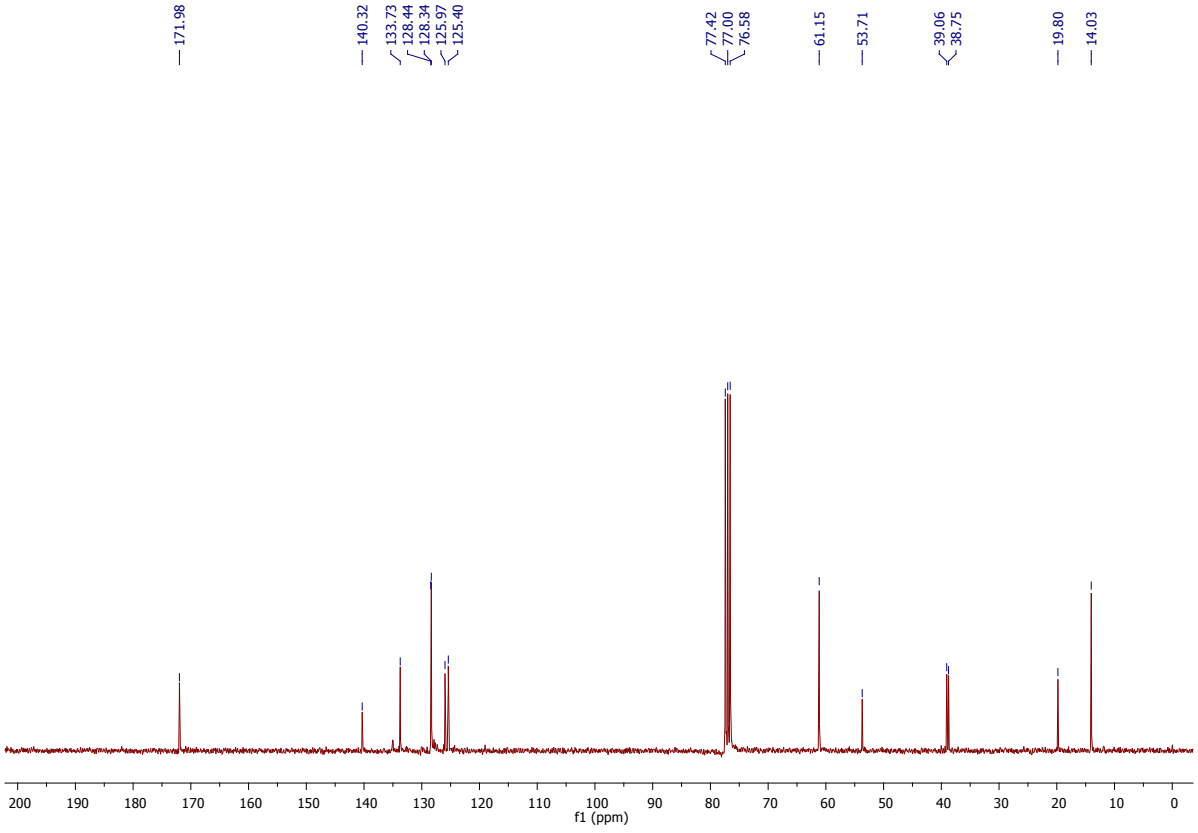
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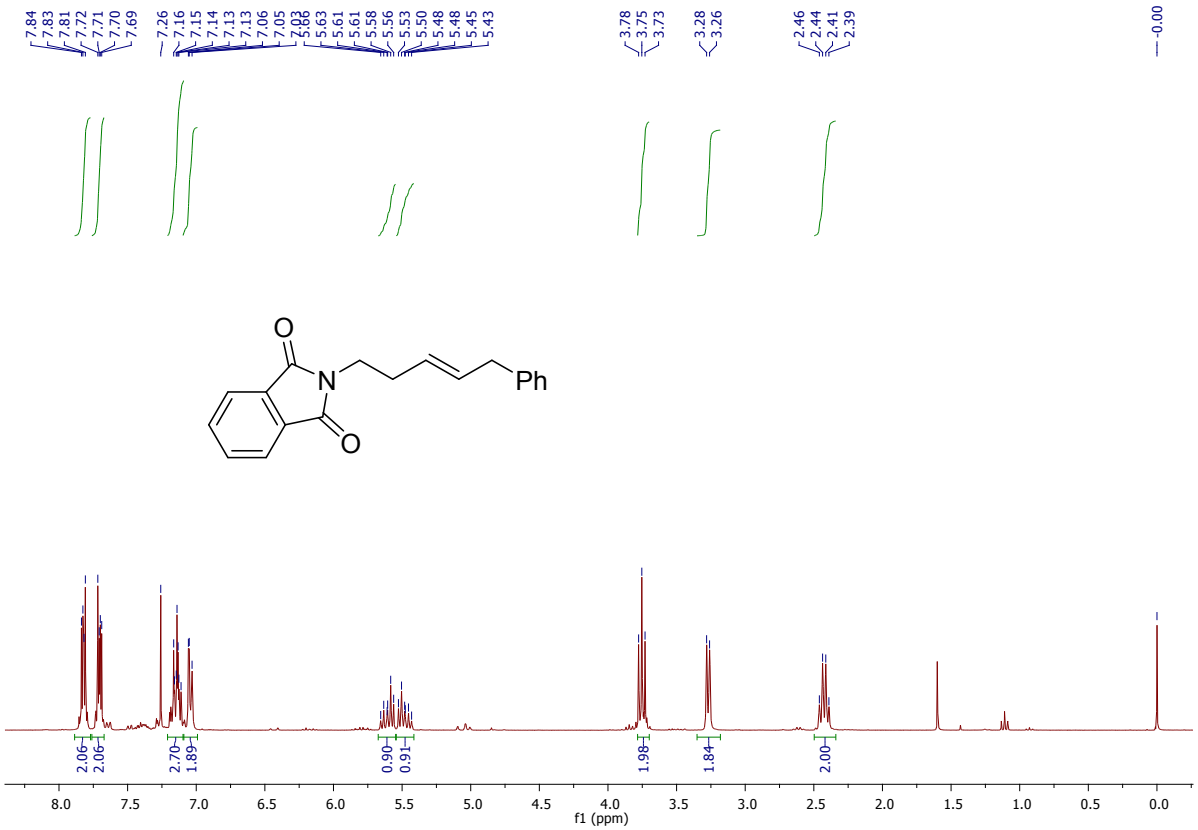
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7.05
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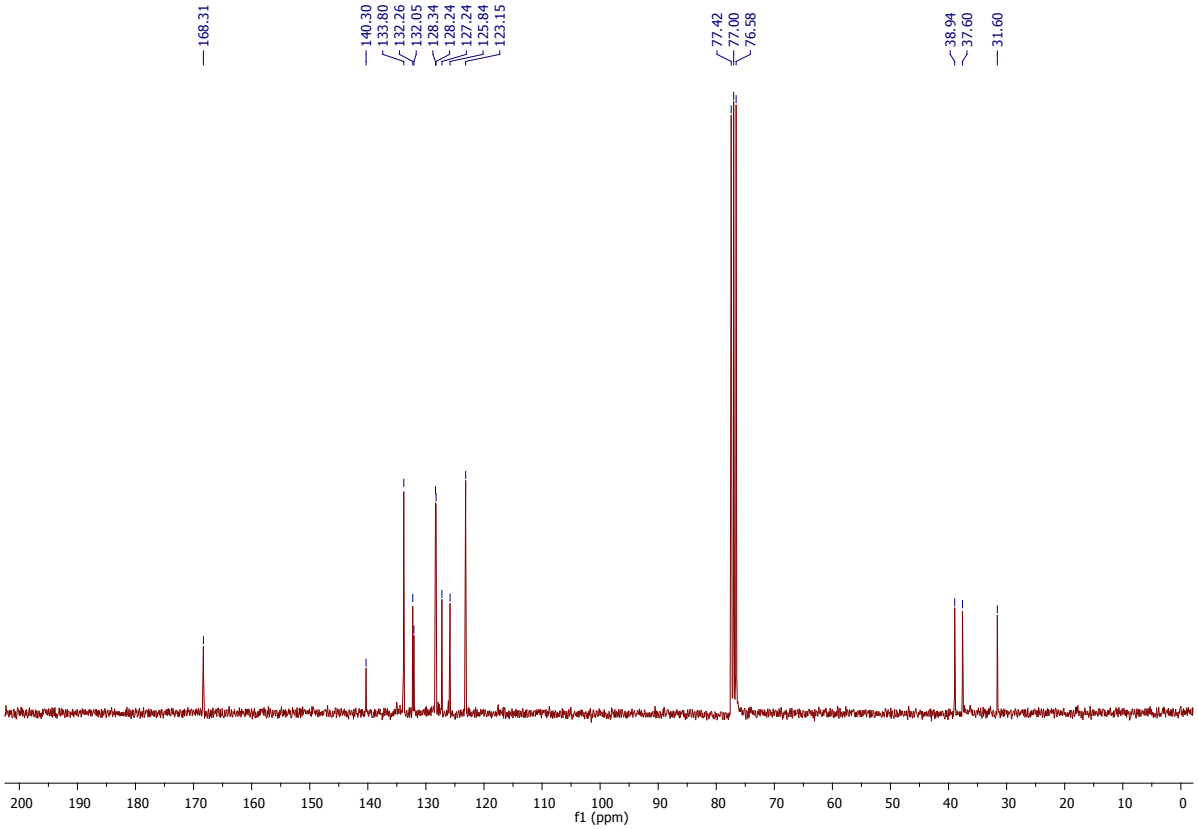
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76.58
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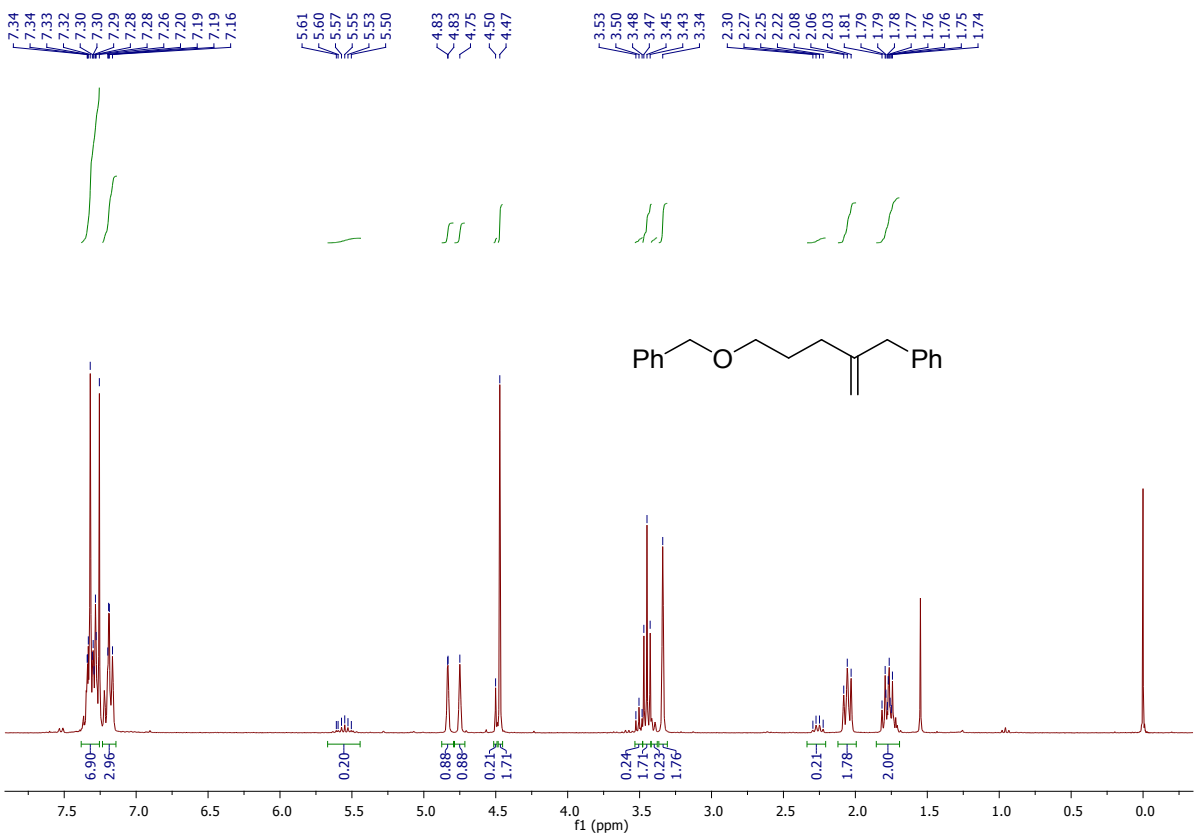
f1 (ppm)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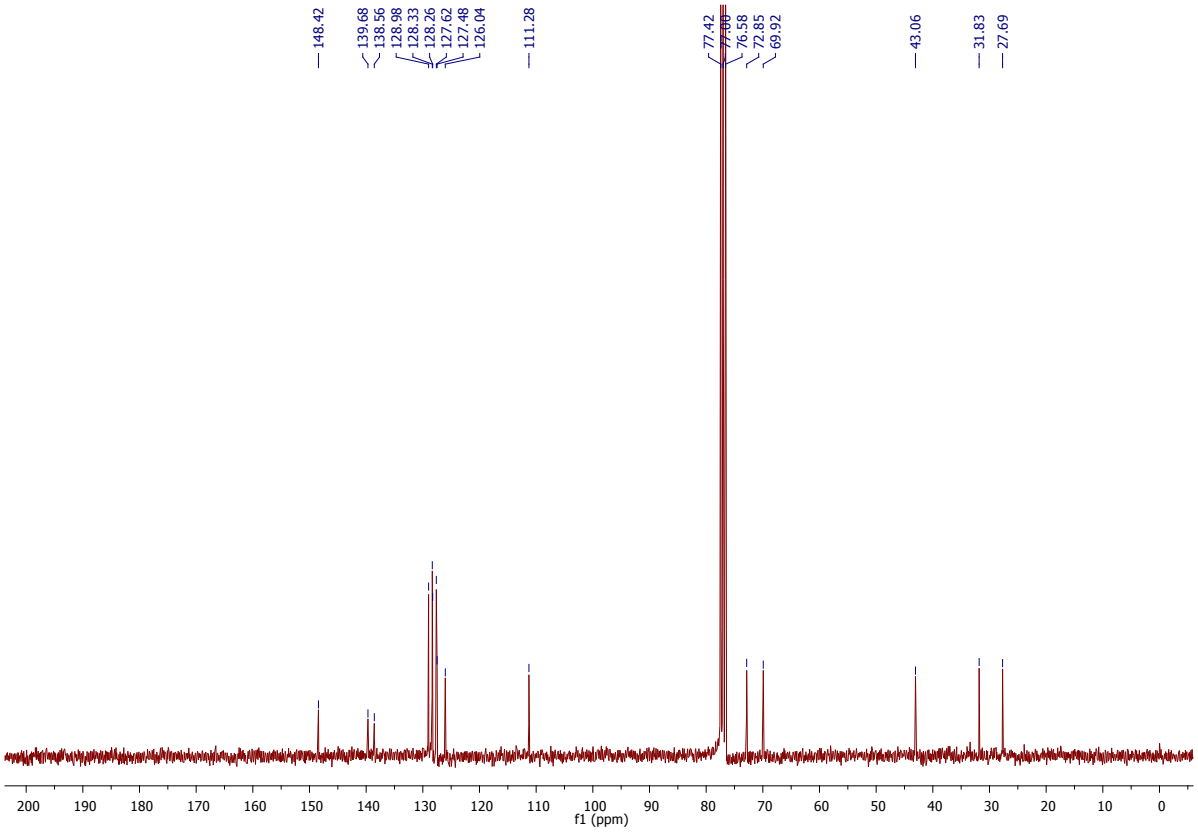
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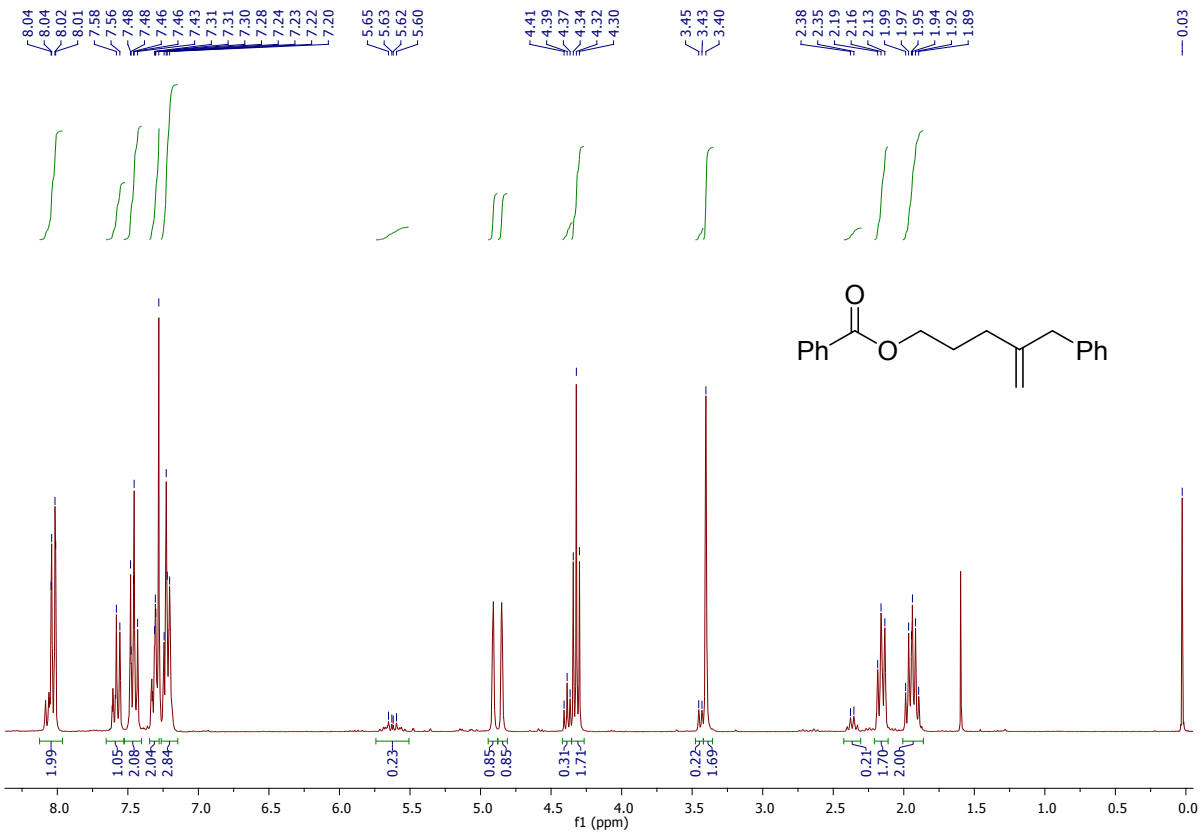
27.69
f1 (ppm)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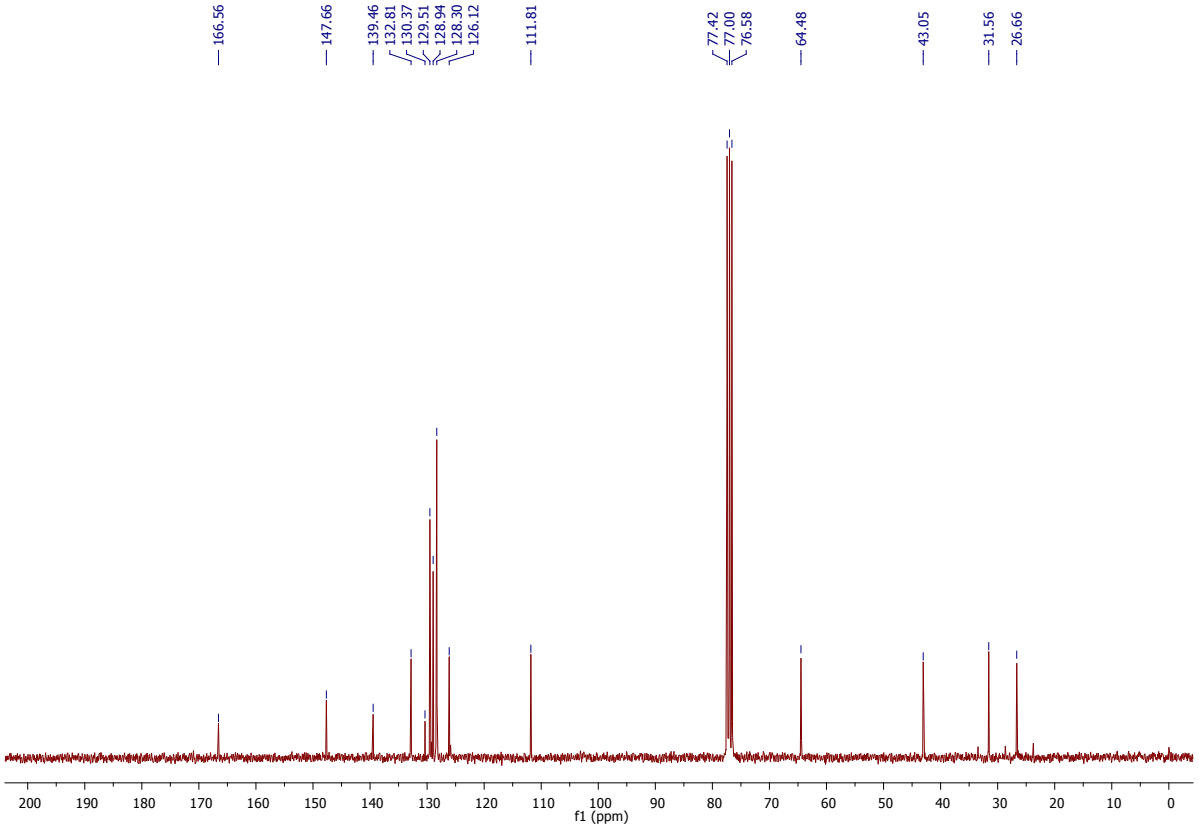
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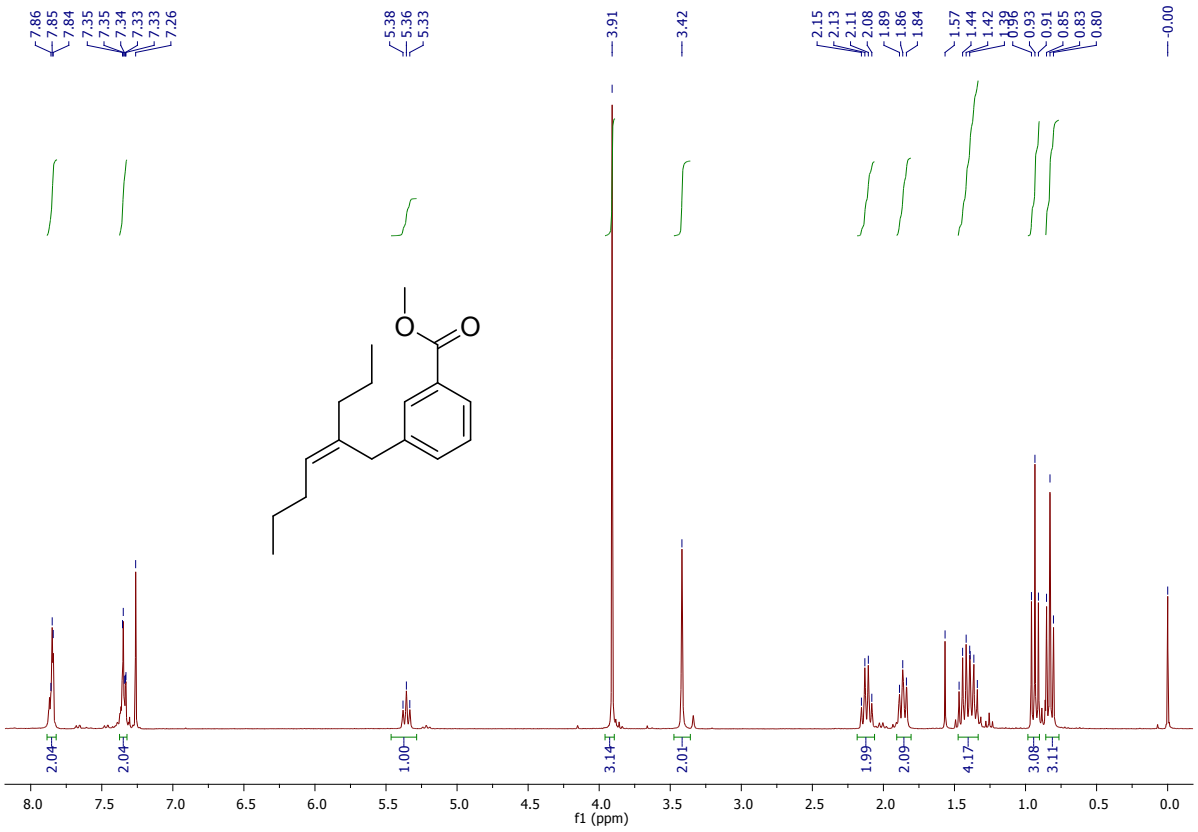
43.05
31.56
26.66
f1 (ppm)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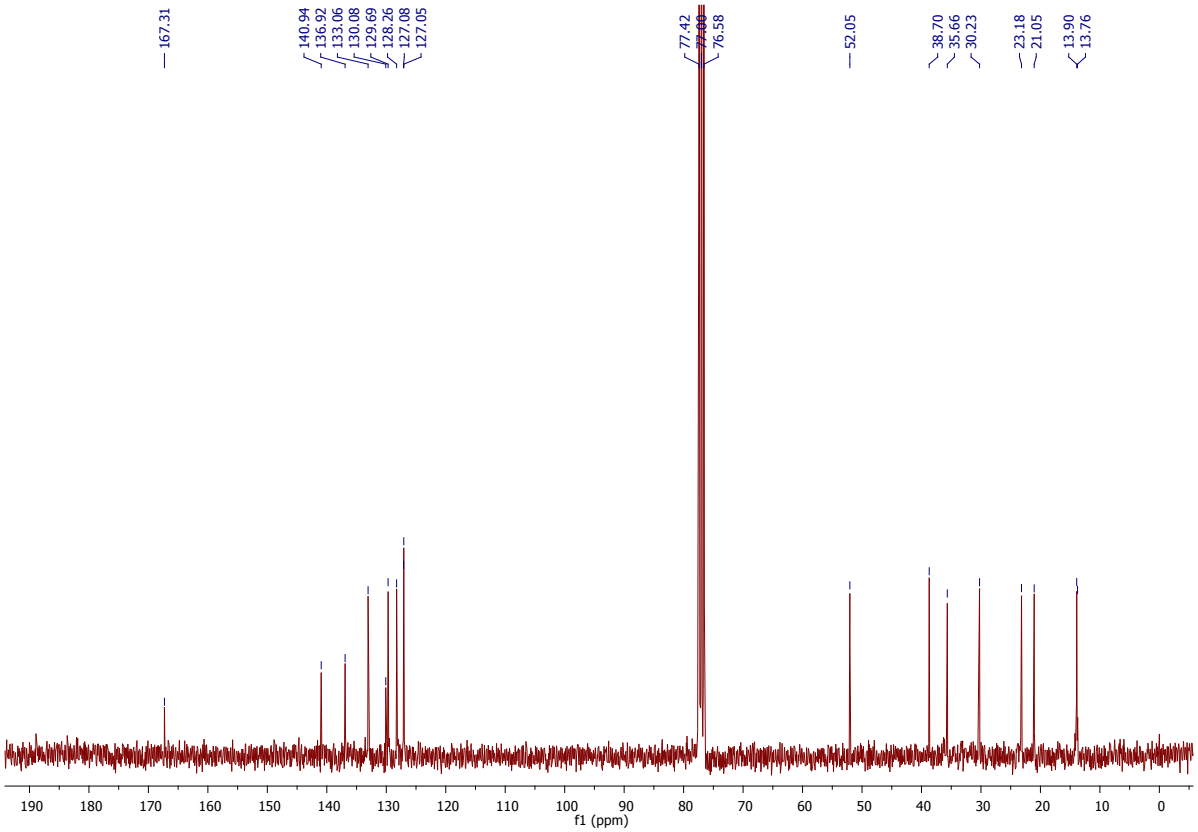
2.09
4.17
3.08
3.11
f1 (ppm)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21.05
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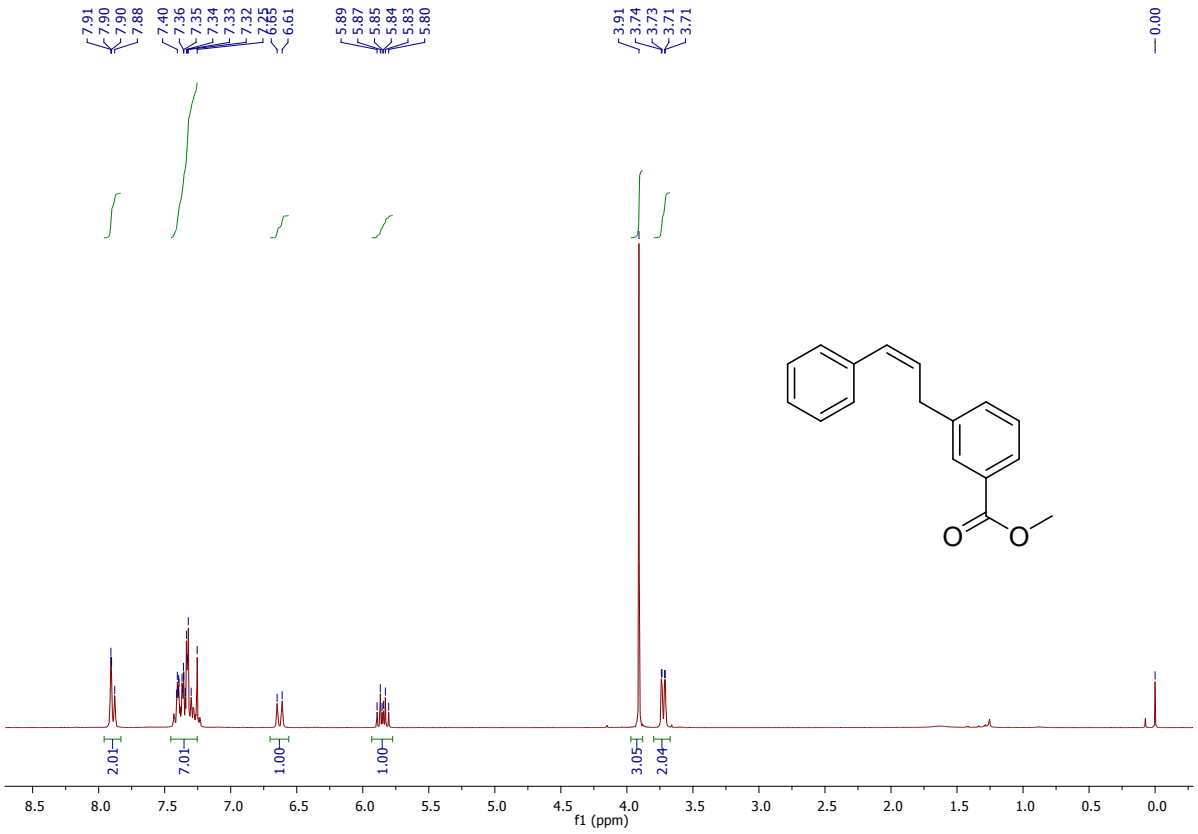
f1 (ppm)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3.73
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3.71
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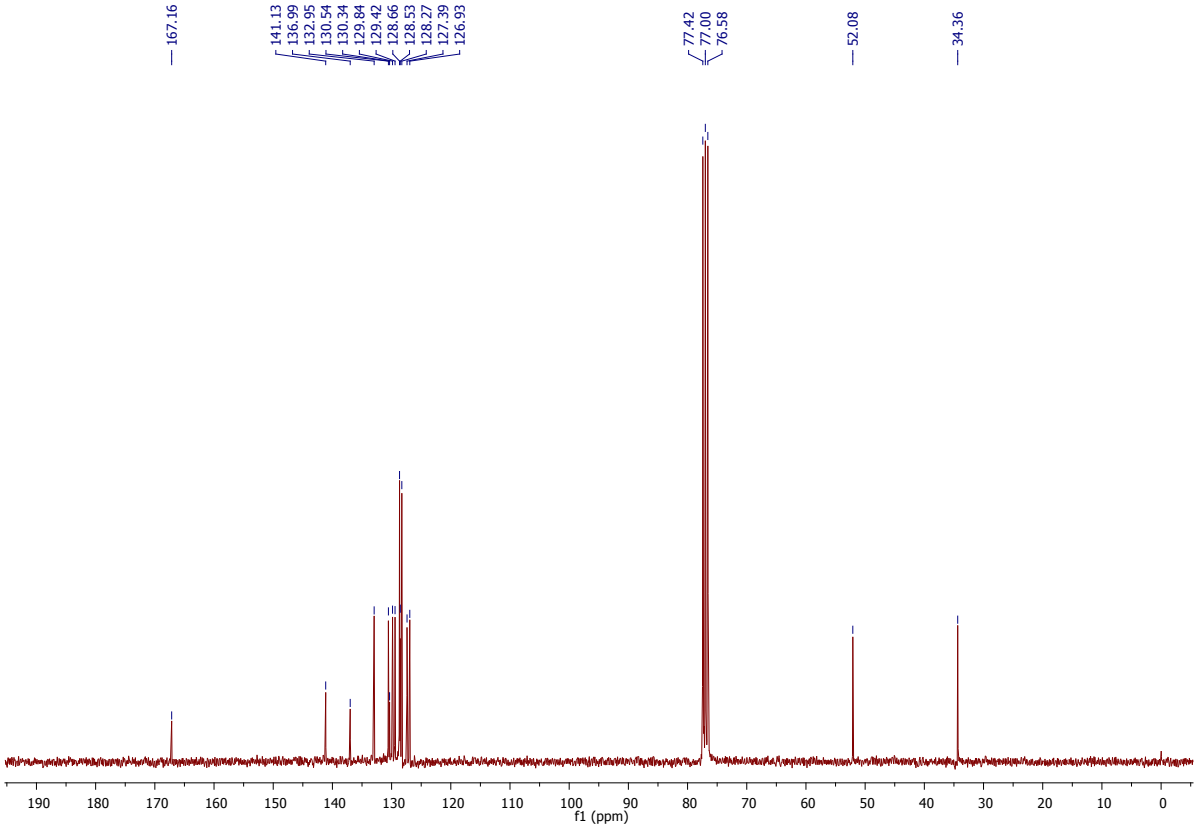
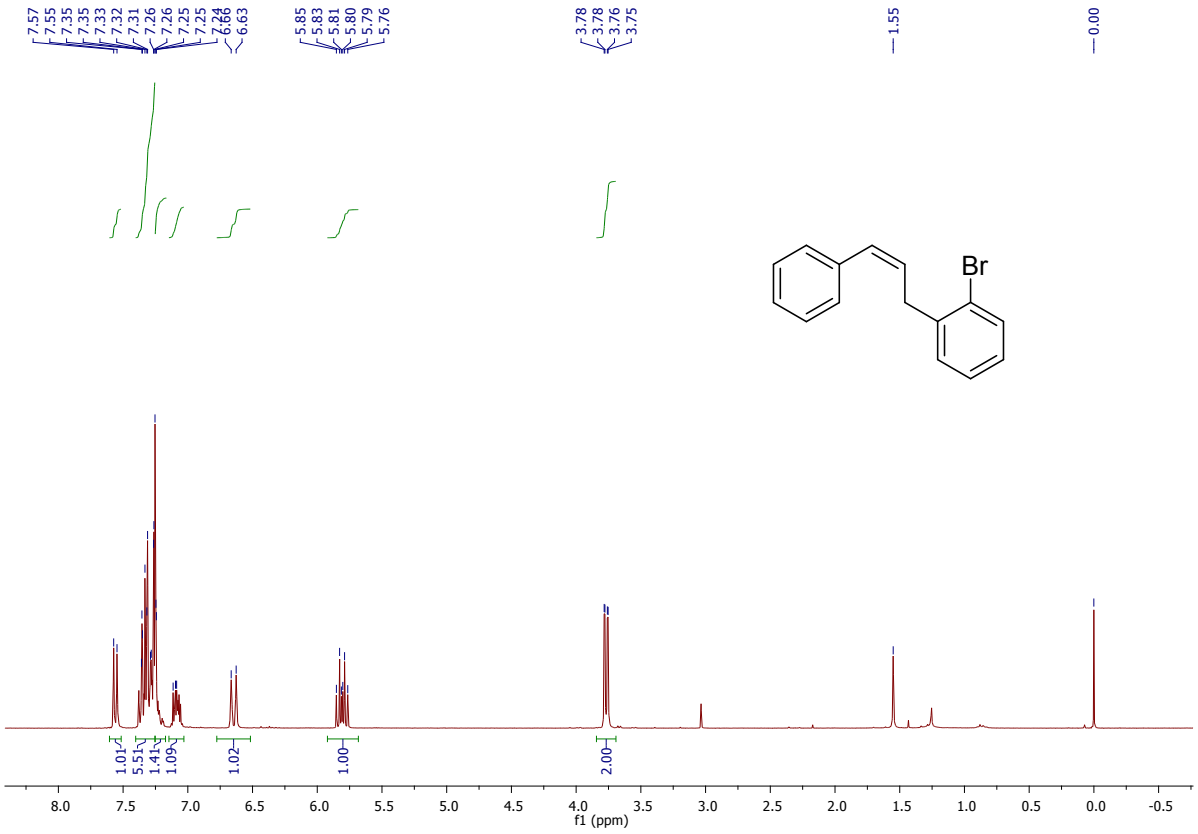
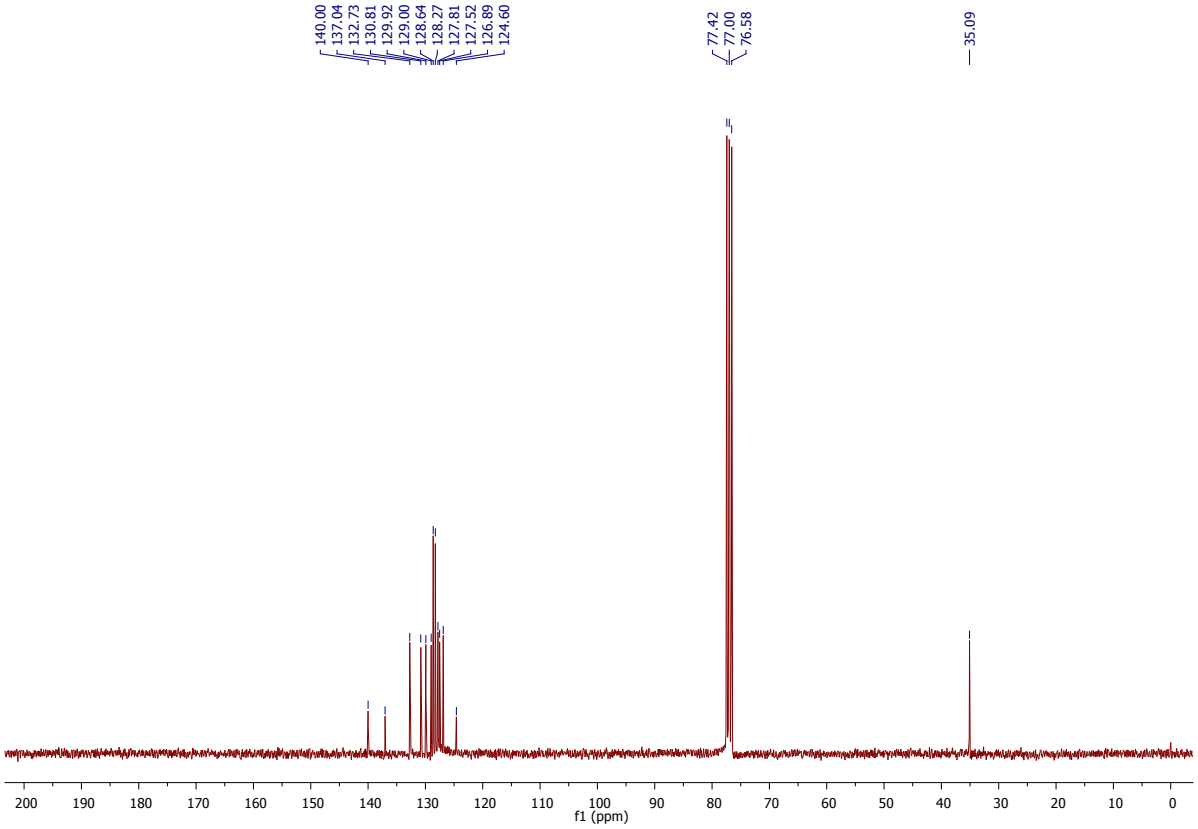
O
2.01
7.01
1.00
1.00
3.05
2.04
f1 (ppm)


167.16
141.13
136.99
132.95
130.54
130.34
129.84
129.42
128.66
128.53
128.27
127.39
126.93
77.42
77.00
76.58
52.08
34.36
f1 (ppm)


7.57
7.55
7.35
7.35
7.33
7.32
7.31
7.26
7.26
7.25
7.25
7.24
6.66
6.63
5.85
5.83
5.81
5.80
5.79
5.76
3.78
3.78
3.76
3.75
1.55
0.00
Br
1.01
5.51
1.41
1.09
1.02
1.00
2.00
f1 (ppm)


140.00
137.04
132.73
130.81
129.92
129.00
128.64
128.27
127.81
127.52
126.89
124.60
77.42
77.00
76.58
35.09
f1 (ppm)