Electronic Supplementary Information

N,*N*-Dimethylformamide-stabilised palladium nanoparticles combined with bathophenanthroline as catalyst for transfer vinylation of alcohols from vinyl ether

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General Information

GLC analyses were performed on a Shimadzu GC-2010 with flame ionization detector using a 0.22 mm × 25 m capillary column (BP-5). All NMR spectra were measured at 400 and 100 MHz, in $CDCl_3$ with TMS as an internal standard. Products were characterized by ^{1}H NMR, ^{13}C NMR, and GC–MS. The product yields were estimated from the peak areas based on the internal standard technique using GC. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-ARM200F instrument at an acceleration voltage of 200 kV. Dynamic light scattering (DLS) analyses were carried out with a Malvern Zetasizer ZSP instrument at 25°C in *n*-butyl vinyl ether or methanol, which was analysed using a cumulant method.

All starting materials were commercially available and used without purification. Compounds **3a**,[1] **3b**,[2] **3c**,[3] **3d**,[2] **3e**,[4] **3f**,[5] **3h**,[3] **3i**,[6] **3j**,[7] **3k**,[8] **3l**,[2] **3n**,[2] **3p**,[4] **3q**,[9] **4a**,[10] were reported previously and **3g**, **3m, 3o, 4c** were characterised by ^{1}H NMR, ^{13}C NMR, GC-MS, IR and HRMS. High-resolution mass spectra were obtained at the Global Facility Center, Hokkaido University.

Experimental Procedure

Typical reaction procedure for Pd NP-catalysed transfer vinylation of benzyl alcohol (1a) from *n*-butyl vinyl ether (2); Table 1, entry 5: Pd NPs (1 mM) in DMF (1 mL) was added to a Schlenk tube and the solvent was evaporated. After evaporation, $Cu(OAc)_2$ (9.1 mg, 5 mol%) and **1a** (108.1 mg, 1.0 mmol) was added, followed by adding bathophenanthroline (33.2 mg, 10 mol%) and **2** (1 mL, 7.9 mmol). The mixture was stirred at 120°C for 24 h under Ar (balloon). The yield of product was estimated from peak areas based on an internal standard (*n*-octane or *n*-pentadecane) using GC. The reaction mixture was evaporated and the product was isolated by silica gel column chromatography (*n*-hexane : EtOAc = 99 : 1). The product was obtained in 73% yield as a colourless oil.

Preparation of 0.1 M aqueous $PdCl_2$ (A): $PdCl_2$ (177.3 mg, 1.0 mmol) was dissolved in distilled water (9 mL) and HCl (1 mL). The solution stood at room temperature overnight.

Synthesis of DMF-stabilized Pd NPs (1 mM): DMF (50 mL) was added to a 300-mL, three-neck, round-bottom flask, and the solution was preheated at 140°C (± 2°C). The resulting yellow solution was used as Pd NPs (1 mM) in DMF for further reactions.

Preparation of samples for DLS

The corresponding Pd NPs were evaporated *in vacuo* and dissolved in *n*-butyl vinyl ether or methanol. The solution was filtered with a Whatman inorganic membrane filter Anotop 25 and transferred to a glass cell.

Preparation of samples for TEM

After the corresponding reaction, DMF (1 mL) was added to the reaction mixture followed by extraction with hexane (8×4 mL). The DMF layer was evaporated *in vacuo* and dissolved in ethanol. A drop of Pd NPs was placed on a Cu grid.

Preparation of the sample for TEM and DLS (Recycled Pd NPs)

Pd NPs (1 mM) in DMF (1 mL) was added to a Schlenk tube and the solvent was evaporated. After evaporation, $Cu(OAc)_2$ (9.1 mg, 5 mol%) and **1a** (108.1 mg, 1.0 mmol) were added, followed by adding bathophenanthroline (33.2 mg, 10 mol%) and **2** (1 mL, 7.9 mmol). The mixture was stirred at 120°C for 24 h under Ar (balloon). After the reaction, DMF (1 mL) was added to the reaction mixture followed by extraction with hexane (8 mL×4). The solution was evaporated *in vacuo* and $Cu(OAc)_2$ (9.1 mg, 5 mol%), **1a** (108.1 mg, 1 mmol) and **2** (1 mL, 7.9 mmol) were added in accordance with the aforementioned procedure. After five rounds of recycling, DMF (1 mL) was added to the reaction solution and extracted with hexane (8 mL×4). The DMF layer was diluted with DMF and centrifuged (3000 *g*, 10 min). After removed the solids, the sample was used in accordance with the aforementioned procedure.

Recycling experiments

Pd NPs (1 mM) in DMF (1 mL) was added to a Schlenk tube and the solvent was evaporated. After evaporation, $Cu(OAc)_2$ (6.8 mg, 3.8 mol%) and **1a** (108.1 mg, 1.0 mmol) were added, followed by adding bathophenanthroline (33.2 mg, 10 mol%) and **2** (1 mL, 7.9 mmol). The mixture was stirred at 120°C for 24 h under Ar (balloon). After the reaction, DMF (1 mL) was added to the reaction mixture followed by extraction with hexane (8 mL×4). The solution was evaporated *in vacuo* and $Cu(OAc)_2$ (6.8 mg, 3.8 mol%), **1a** (108.1 mg, 1 mmol) and **2** (1 mL, 7.9 mmol) were added in accordance with the aforementioned procedure.

DLS curves

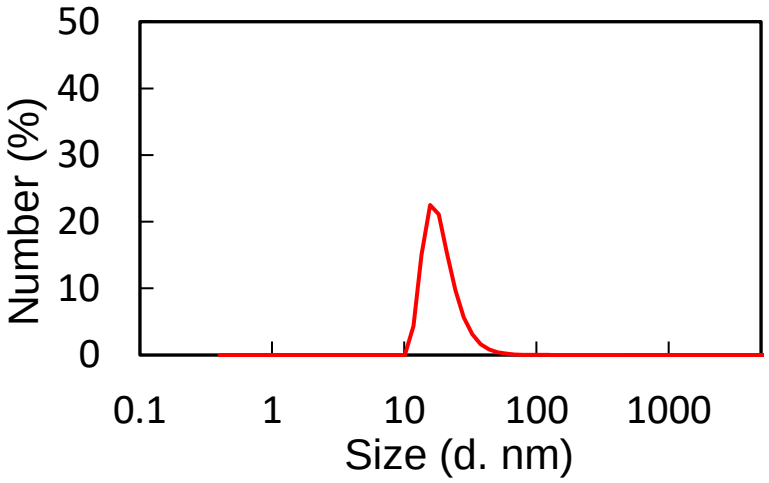


Figure S1 DLS curves of recycled Pd NPs (1mM) measured in *n*-butyl vinyl ether at 25°C

The population of recycled Pd NPs centred at 14−15 nm.

Reaction Mechanism

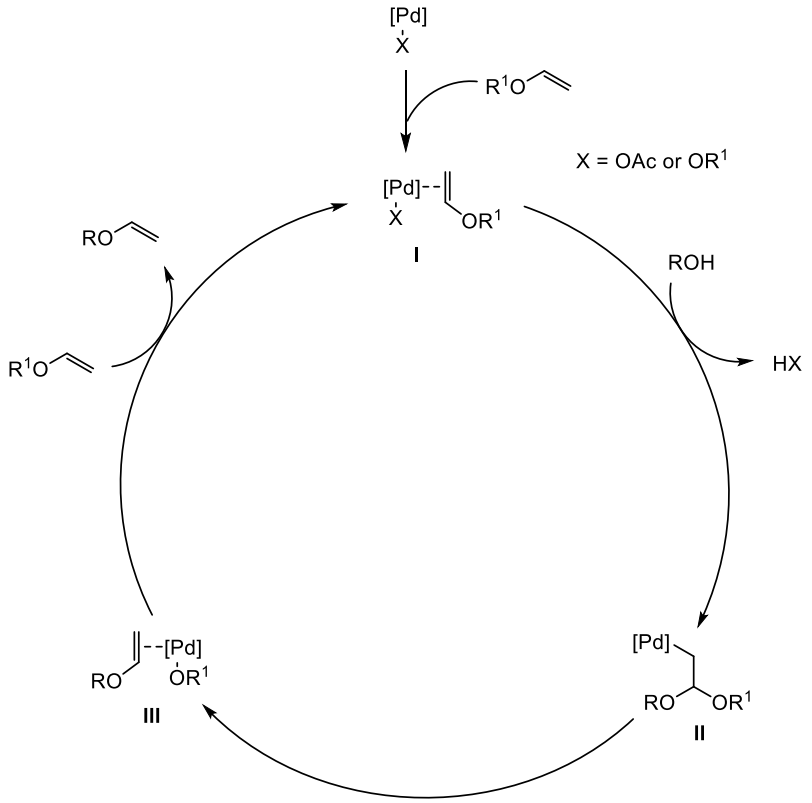


Figure S2 Palladium-catalysed transfer vinylation of alcohols from vinyl ether

Plausible reaction mechanisms of acetals (4)

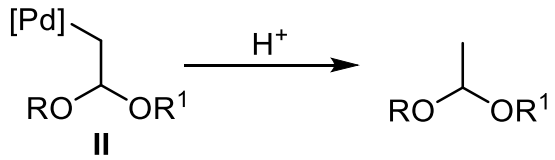


Figure S3 Decomposition of Pd-alkyl species followed by production of acetal

Pd-alkyl species generated from vinyl ether and alcohol decomposed in acid, and gave the corresponding acetal.[11]

Spectra Data

3a[1]: yield 73% (97.9 mg), colourless oil.

^{1}H NMR (400 MHz; $CDCl_3$) δ: 7.37-7.31 (m, 5H), 6.56 (dd, *J* = 14.3, 6.9 Hz, 1H), 4.75 (s, 2H), 4.30 (dd, *J* = 14.3, 2.1 Hz, 1H), 4.08 (dd, *J* = 6.8, 2.1 Hz, 1H); ^{13}C NMR (100 MHz; $CDCl_3$) δ 151.6 (CH), 136.8 (C), 128.5 (CH), 127.9 (CH), 127.6 (CH), 87.3 (CH_2), 70.0 (CH_2); GC-MS (EI) *m/z* (relative intensity) 134(1) $[M]^+$, 91(100), 65(14), 105(9).

3b[2]: Yield 47% (69.7 mg), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.55 (dd, *J* = 14.0, 6.8 Hz, 1H), 4.71 (s, 2H), 4.29 (dd, *J* = 14.3, 2.0 Hz, 1H), 4.06 (dd, *J* = 6.8, 1.8 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7 (CH), 137.7 (C), 133.8 (C) 129.2 (CH), 127.7 (CH), 87.2 (CH_2), 70.0 (CH_2), 21.2 (CH_3); GC-MS (EI) *m/z* (relative intensity) 148 (2) $[M]^+$, 105 (100), 79 (11), 77 (10).

3c[3]: Yield 64% (121.8 mg), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, 2H), 7.29 (d, 2H), 6.56 (dd, *J* = 14.4, 6.8 Hz, 1H), 4.72 (s, 2H), 4.30 (dd, *J* = 14.4, 2.0 Hz, 1H), 4.07 (dd, *J* = 6.9, 2.1 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7 (CH), 151.0 (C), 133.8 (C), 127.5 (CH), 125.5 (CH), 87.1 (CH_2), 69.9 (CH_2), 34.6 (C), 31.3 (CH_3); GC-MS (EI) *m/z* (relative intensity) 190 (1) $[M]^+$, 147 (100), 132 (28), 117 (25).

3d[2]: Yield 69% (113.3 mg), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.7 Hz , 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.54 (dd, *J* = 14.3, 6.9 Hz, 1H), 4.67 (s, 2H), 4.29 (dd, *J* = 14.3, 2.0 Hz, 1H), 4.06 (dd, *J* = 6.9, 2.0 Hz, 1H), 3.79(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4 (C), 151.7 (CH), 129.3 (CH), 128.9 (C), 113.9 (CH), 87.2 (CH_2), 69.9 (CH_2), 55.2 (CH_3); GC-MS (EI) *m/z* (relative intensity) 164 (1) $[M]^+$, 121 (100), 77 (10), 122 (9).

3e[4]: Yield 48% (80.9 mg), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 6.55 (dd, *J* = 14.3, 6.9 Hz, 1H), 4.72 (s, 2H), 4.28 (dd, *J* = 14.3, 2.3 Hz, 1H), 4.10 (dd, *J* = 6.7, 2.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ151.4 (CH), 135.4 (C), 133.7 (C), 128.8 (CH), 128.7 (CH), 87.6 (CH_2), 69.2 (CH_2); GC-MS (EI) *m/z* (relative intensity) 168(2) $[M]^+$, 125(100), 127(32), 89(19).

3f[5]: Yield 35% (70.8 mg), colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ7.62 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 6.57 (dd, *J* = 14.3, 6.9 Hz, 1H), 4.82 (s, 2H), 4.30 (dd, *J* = 14.4, 2.3 Hz, 1H), 4.12 (dd, *J* = 6.8, 2.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3 (CH), 141.0 (CH), 130.0 (q, $^{2}J_{c\text{-}f}$ = 32.4 Hz), 127.4 (CH), 125.5 (q, $^{3}J_{c\text{-}f}$ = 3.8 Hz), 124.1 (q, $^{1}J_{c\text{-}f}$= 270.7 Hz) 87.8 (CH_2), 69.0 (CH_2); GC-MS (EI) *m/z* (relative intensity) 202(2) $[M]^+$, 159(100), 109(36), 173(10).

3g: Yield 57% (101.6 mg), colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.84-6.76 (m, 3H), 6.52 (dd, *J* = 14.3, 6.9 Hz, 1H), 5.94 (s, 2H), 4.64 (s, 2H), 4.28 (dd, *J* = 14.3, 2.1 Hz, 1H), 4.06 (dd, *J* = 6.9, 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5 (CH), 147.8 (C), 147.4 (C), 130.6 (C), 121.3 (CH), 108.4 (CH), 108.2 (CH), 101.1 (CH_2), 87.4 (CH_2), 70.1 (CH_2); GC-MS (EI) *m/z* (relative intensity) 178(6) $[M]^+$, 135 (100), 77 (22), 51 (14); HRMS (EI) *m/z* calcd for $C_{10}H_{10}O_3$ $[M]^+$ 178.0630, found 178.0631; IR (neat, cm^{-1}) 2880, 2783, 1851, 1635, 1490, 1443, 1257, 1037, 926

3h[3]: Yield 64% (117.9 mg), colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.55-7.41 (m, 4H), 6.63 (dd, *J* = 14.3, 6.8 Hz, 1H), 5.17 (s, 2H), 4.42 (dd, *J* = 14.3, 2.1 Hz, 1H), 4.14 (dd, *J* = 6.8, 2.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6 (CH), 133.7 (C), 132.2 (C), 131.5 (C), 129.0 (CH), 128.6 (CH), 126.6 (CH), 126.4 (CH), 125.8 (CH), 125.2 (CH), 123.6 (CH), 87.4 (CH_2), 68.6 (CH_2); GC-MS (EI) *m/z* (relative intensity) 184 (7) $[M]^+$, 141 (100), 115 (22), 142 (12).

3i[6]: Yield 76% (140.0 mg), colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.80 (m, 4H), 7.49-7.44 (m, 3H), 6.60 (dd, *J* = 6.9, 14.3 Hz, 1H), 4.91 (s, 2H), 4.35 (dd, *J* = 2.2, 14.3 Hz, 1H), 4.10 (dd, *J* = 2.2, 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.6 (CH), 134.3 (C), 133.3 (C), 133.0 (C), 128.3 (CH), 127.9 (CH), 127.7 (CH), 126.4 (CH), 126.2 (CH), 126.0 (CH), 125.3 (CH), 87.5 (CH_2), 70.2(CH_2); GC-MS (EI) *m/z* (relative intensity) 184(10) $[M]^+$, 141(100), 115(22), 142(13).

3j[7]: Yield 85% (156.7 mg), colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.47 (dd, *J* = 14.6, 6.9 Hz, 1H), 4.17 (dd, *J* = 14.6, 1.8 Hz, 1H), 3.97 (dd, *J* = 14.6, 1.8 Hz, 1H), 3.67 (t, *J* = 6.6 Hz, 2H), 1.65 (quin, *J* = 6.8 Hz, 2H), 1.39-1.22 (m, 14H), 0.88 (t, *J* = 7.1 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0 (CH), 86.2 (CH_2), 68.1 (CH_2), 31.9 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 26.0 (CH_2), 22.7 (CH_2), 14.1 (CH_3); GC-MS (EI) *m/z* (relative intensity) 184 (2)

$[M]^+$, 43 (100), 57 (81), 41 (46).

3k[8]: Yield 50% (70.1 mg), colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.47 (dd, *J* = 14.4, 6.8 Hz, 1H), 4.15 (dd, *J* = 14.3, 1.8 Hz, 1H), 3.95 (dd, *J* = 6.8, 1.8 Hz, 1H), 3.47 (d, *J* = 6.5 Hz, 2H), 1.79-1.60 (m, 6H), 1.45-1.11 (m, 3H), 1.02-0.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2 (CH), 86.0 (CH_2), 73.7 (CH_2), 37.6 (CH), 29.9 (CH_2), 26.5 (CH_2), 25.8 (CH_2); GC-MS (EI) *m/z* (relative intensity) 140(3) $[M]^+$, 55(100), 97(39), 81(28).

3l[2]: Yield 64% (94.9 mg), colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.27 (m, 5H), 6.32 (dd, *J* = 14.2, 6.6 Hz, 1H), 4.90 (q, *J* = 6.5 Hz, 1H), 4.25 (dd, *J* = 14.2, 1.6 Hz, 1H), 3.98 (dd, *J* = 6.6, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5 (CH), 142.9 (C), 128.5 (CH), 127.6 (CH), 125.8 (CH), 89.2 (CH), 77.4 (CH), 23.7 (CH_3); GC-MS (EI) *m/z* (relative intensity) 148(1) $[M]^+$, 105(100), 79(20), 77(17).

3m: Yield 60% (122.6 mg), colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.21 (m, 5H), 6.30 (dd, *J* = 14.2, 6.6 Hz, 1H), 4.68 (t, *J* = 6.6 Hz, 1H), 4.22 (dq, *J* = 14.2, 0.8 Hz, 1H), 3.94 (dq, *J* = 6.6, 0.8 Hz, 1H), 1.91-1.66 (m, 2H), 1.44-1.23 (m, 6H), 0.86 (t, *J* = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.9 (CH), 142.0 (C), 128.4 (CH), 127.5 (CH), 126.2 (CH), 89.1 (CH_2), 81.6 (CH), 37.9 (CH_2), 31.7 (CH_2), 25.3 (CH_2), 22.5 (CH_2), 14.0 (CH_3); GC-MS (EI) *m/z* (relative intensity) 204 (1) $[M]^+$, 91 (100), 161 (23), 105 (19); HRMS (EI) *m/z* calcd for $C_{14}H_{20}O$ $[M]^+$ 204.1514, found 204.1514; IR (neat, cm^{-1}) 2935, 2862, 1635, 1453, 1319, 1192, 1058, 830, 752, 700.

3n[2]: Yield 35% (73.6 mg), colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.22 (m, 10H), 6.47 (dd, *J* = 14.2, 6.6 Hz, 1H), 5.83 (s, 1H), 4.35 (dd, *J* = 14.1, 1.9 Hz, 1H), 4.07 (dd, *J* = 6.7, 1.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5 (CH), 141.0 (C), 128.5 (CH), 127.7 (CH), 126.9 (CH), 90.0 (CH_2), 82.7 (CH); GC-MS (EI) *m/z* (relative intensity) 210 (1) $[M]^+$, 167 (100), 152 (22), 139 (3).

3o: Yield 47% (80.0 mg), colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (dd, *J* = 14.1, 6.6 Hz, 1H), 4.26 (dd, *J* = 14.1, 1.0 Hz, 1H), 3.93 (dd, *J* = 6.6, 1.0 Hz, 1H), 3.69 (quin, *J* = 6.0 Hz, 1H), 1.60-1.46 (m, 4H), 1.40-

1.24 (m, 8H), 0.90 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.8 (CH), 87.4 (CH_2), 80.6 (CH), 34.0 (CH_2), 27.5 (CH_2); GC-MS (EI) *m/z* (relative intensity) 170 (2) $[M]^+$, 43 (100), 71 (59), 57 (57); HRMS (EI) *m/z* calcd for $C_{11}H_{22}O$ $[M]^+$ 170.1671, found 170.1671; IR (neat, cm^{-1}) 2936, 2862, 1629, 1461, 1194, 1037, 811.

3p[4]: Yield 61% (69.0 mg), colourless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.47 (dd, *J* = 14.3, 6.8 Hz, 2H), 4.17 (dd, *J* = 14.3, 1.8 Hz, 2H), 3.97 (dd, *J* = 6.8, 1.8 Hz, 2H), 3.67 (t, *J* = 6.6 Hz, 4H), 1.69-1.60 (m, 4H), 1.39-1.30 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0 (CH), 86.2 (CH_2), 68.1 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 26.0 (CH_2); GC-MS (EI) *m/z* (relative intensity) 226 (0.05) $[M]^+$, 55 (100), 69 (64), 83 (44); HRMS (EI) *m/z* calcd for $C_{14}H_{26}O_2$ $[M]^+$ 226.1933, found 226.1933; IR (neat, cm^{-1}) 2931, 2853, 1611, 1319, 1201, 808.

3q[9]: Yield 30% (42.0 mg), pale yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.05-6.99 (m, 2H), 6.53 (dd, *J* = 14.3, 6.9 Hz, 1H), 4.91 (s, 2H), 4.32 (dd, *J* = 14.3, 2.2 Hz, 1H), 4.11 (dd, *J* = 6.7, 2.3 Hz, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 151.1 (CH), 139.0 (C), 126.9 (CH), 126.8 (CH), 126.3 (CH), 87.8 (CH_2), 64.8 (CH_2); GC-MS (EI) *m/z* (relative intensity) 140 (1) $[M]^+$, 97 (100), 45 (12), 53 (10).

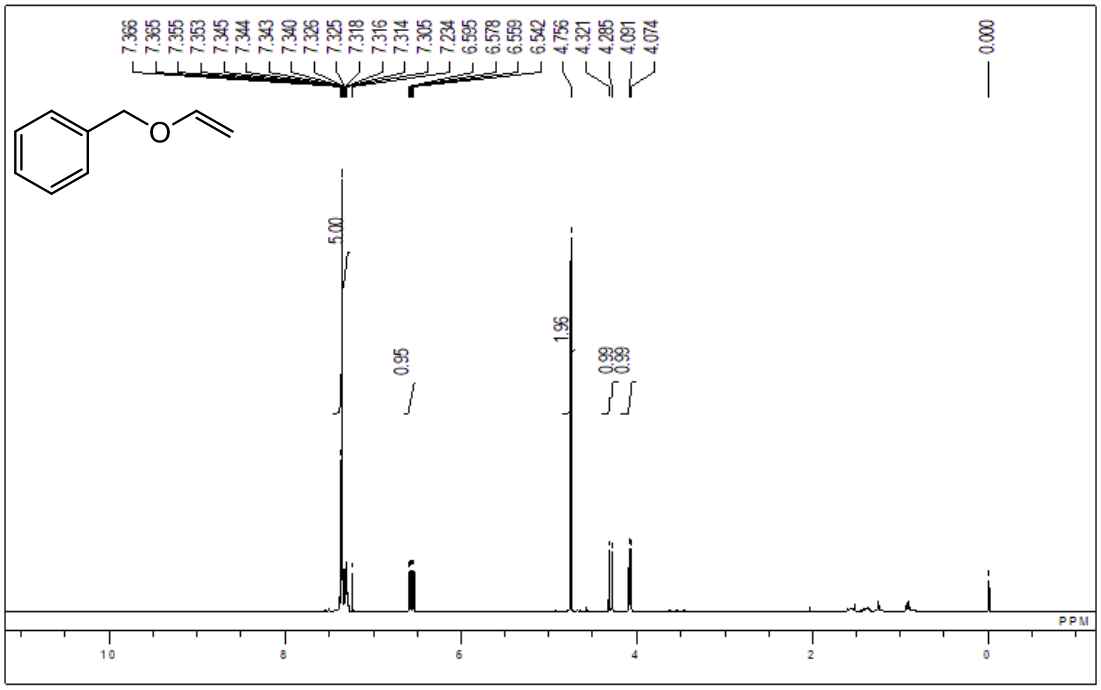
4a[10]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.25 (m, 5H), 4.81 (q, J = 5.4 Hz, 1H), 4.65 (d, J = 11.8 Hz, 1H), 4.52 (d, J = 11.8 Hz, 1H), 3.63-3.60 (m, 1H), 3.48-3.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5 (C), 128.4 (CH), 127.7 (CH), 127.5 (CH), 99.2 (CH), 67.0 (CH_2), 64.9 (CH_2), 32.0 (CH_2), 19.8 (CH_2), 19.5 (CH_2), 13.9 (CH_3); GC-MS (EI) *m/z* (relative intensity) 193(1) $[M\text{-}CH_3]^+$, 91(100), 134(27), 92(21).

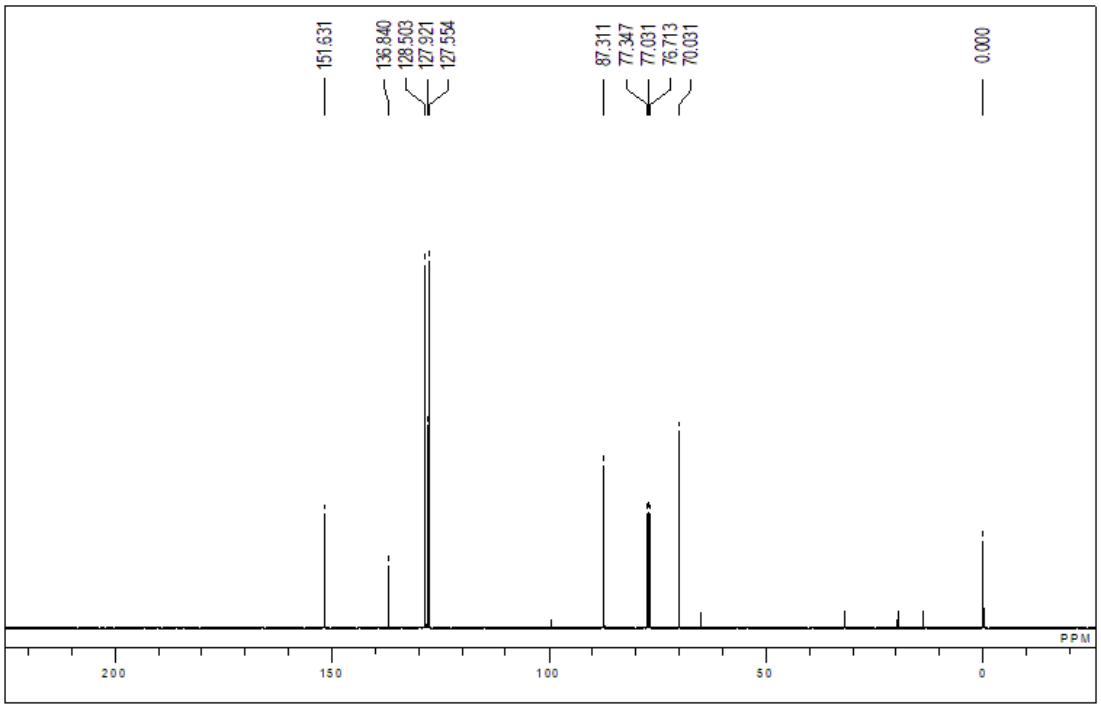
4c
^{1}H NMR (400 MHz, $CDCl_3$): δ7.37 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 4.81 (q, *J* = 5.4 Hz, 1H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.48 (d, *J* = 11.4 Hz, 1H), 3.62-3.59 (m, 1H), 3.47-3.44 (m, 1H), 1.61-1.39 (m, 4H), 1.36 (d, *J* = 5.4 Hz, 3H), 1.31 (s, 9H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ δ 150.5 (C), 135.4 (C), 127.6 (CH), 125.3 (CH), 99.1 (CH), 66.8 (CH_2), 64.8 (CH_2), 34.5 (C), 32.0 (CH_2), 31.4 (CH_3), 19.8 (CH_3), 19.5 (CH_2), 14.0 (CH_3); GC-MS (EI) *m/z* (relative intensity) 249(1) $[M\text{-}CH_3]^+$, 147(100), 133(95), 190(29); HRMS (EI) *m/z* calcd for $C_{17}H_{28}O_2Na$ $[M+Na]^+$ 287.1987, found 287.1982; IR (neat, cm^{-1}) 2962, 2937, 2909, 2872, 1517, 1465, 1394, 1363, 1340, 1270,

1135, 1098, 1019, 918, 816.

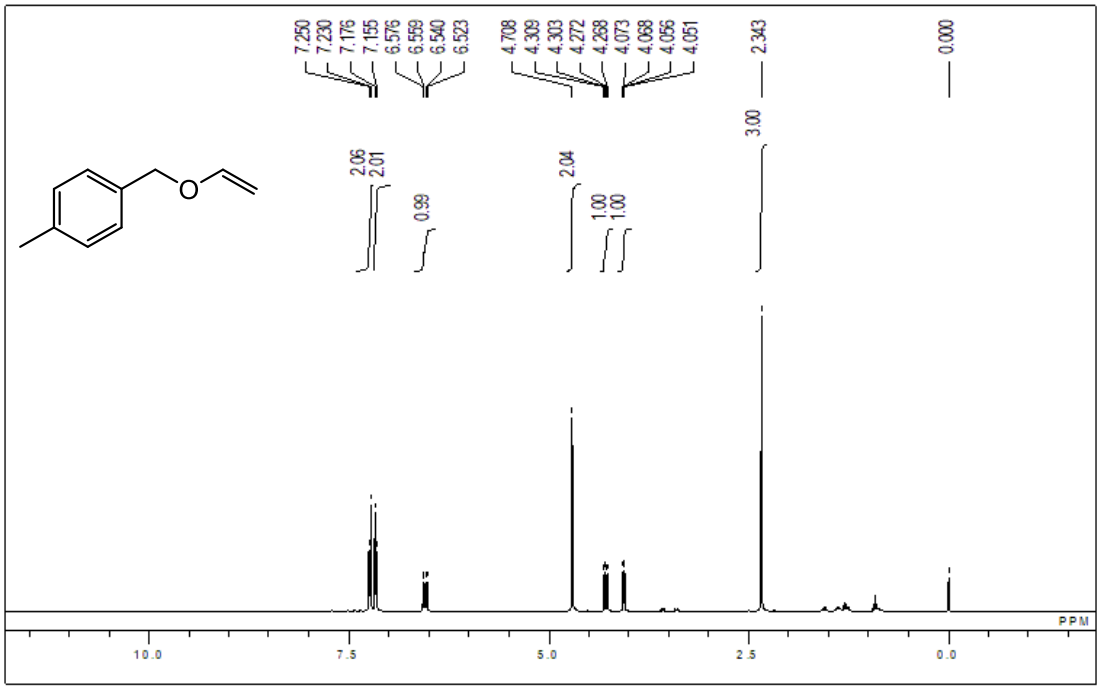
Copies of ^{1}H and ^{13}C NMR Spectra

3a





3b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4.073
4.068
4.056
4.051
2.343
0.000
2.06
2.01
0.99
2.04
1.00
1.00
3.00
PPM
10.0
7.5
5.0
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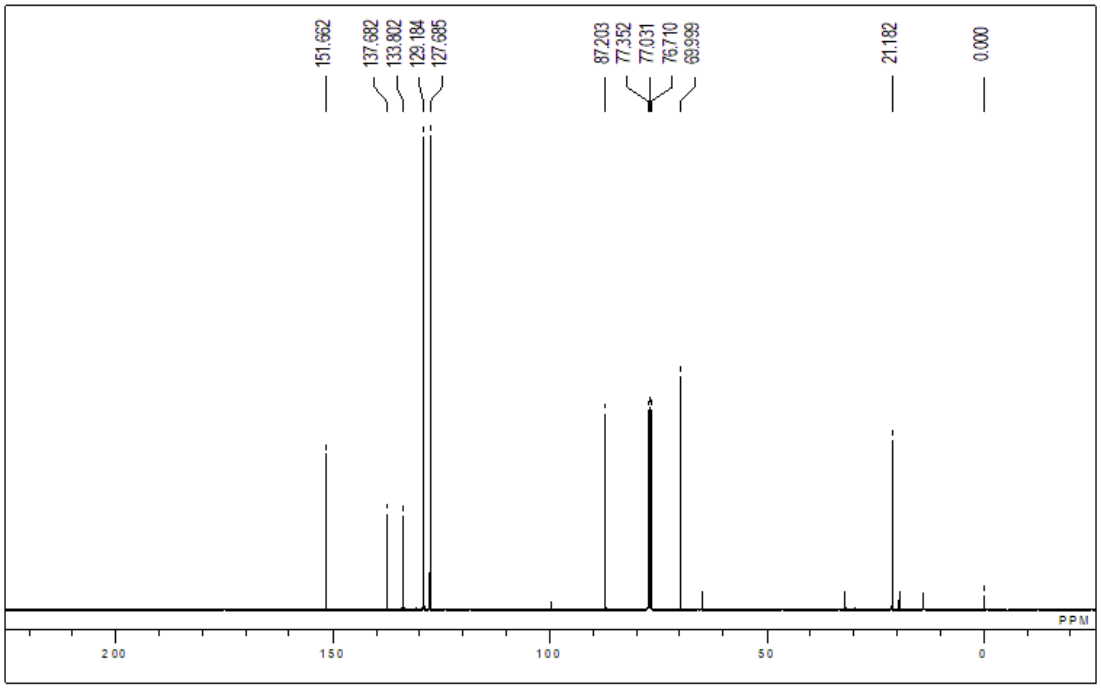
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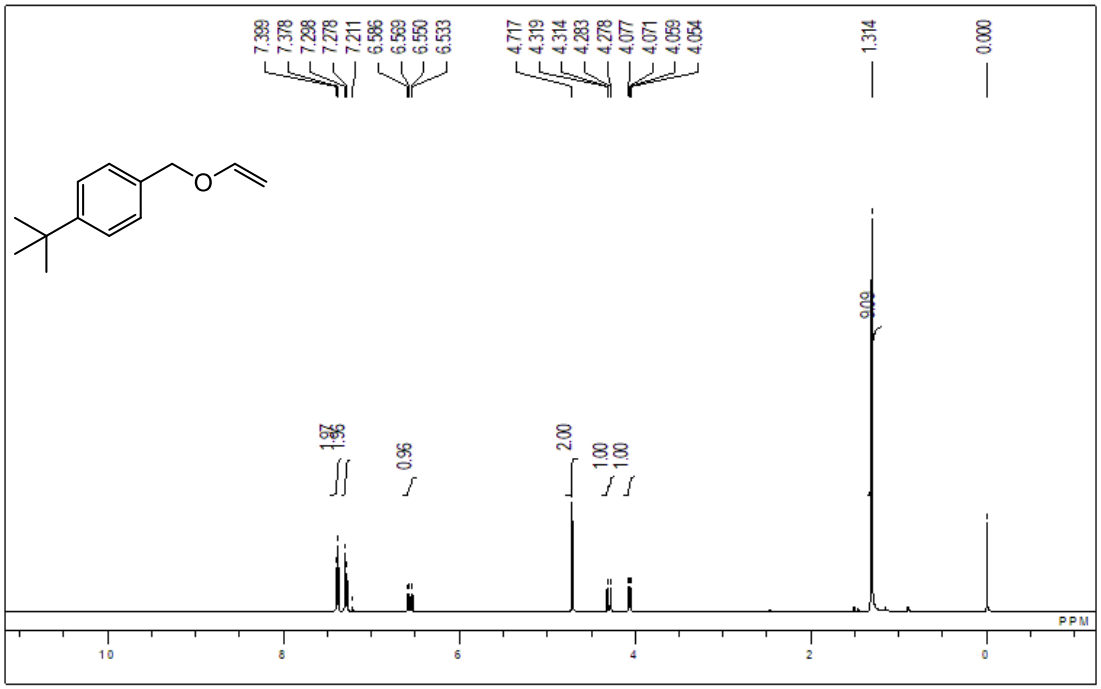
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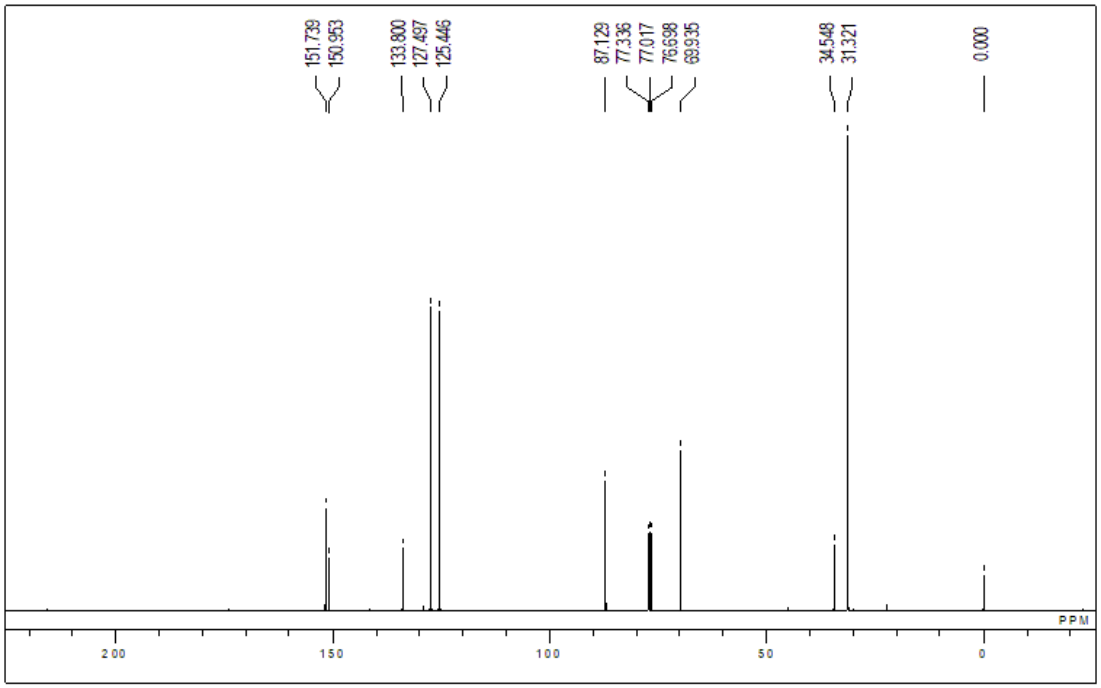
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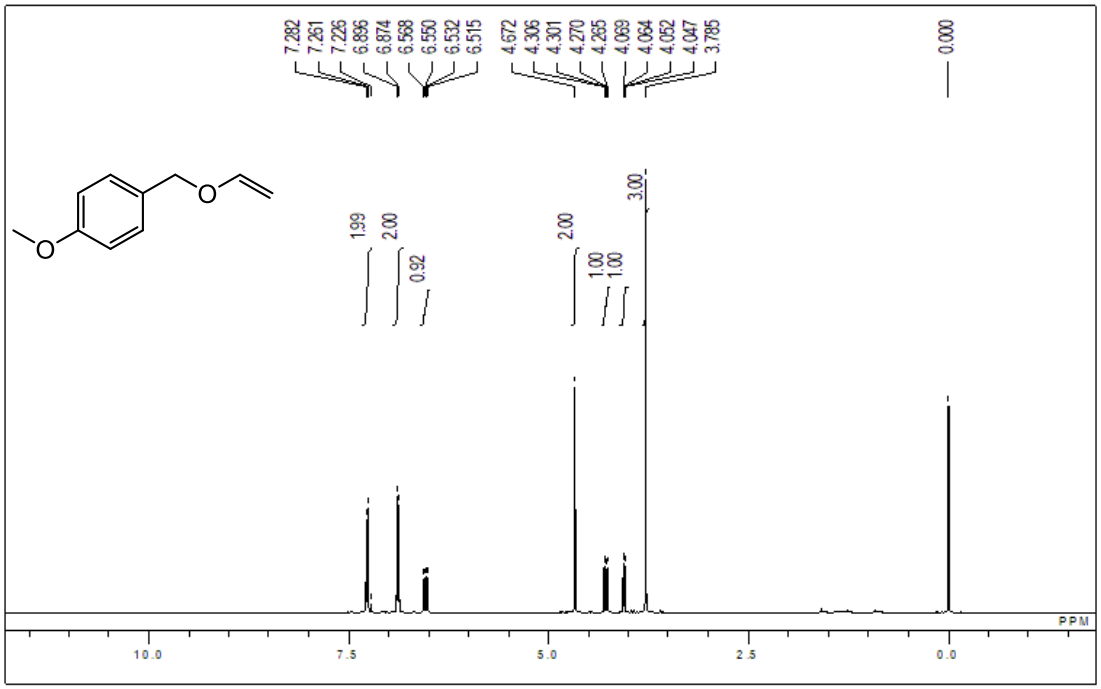
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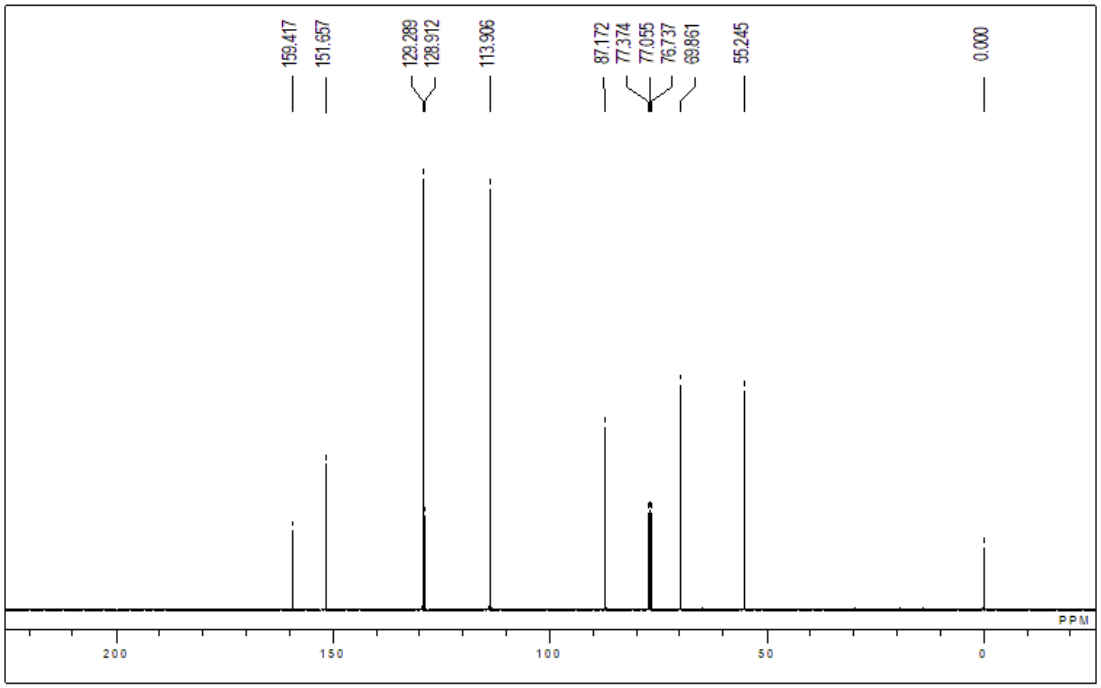
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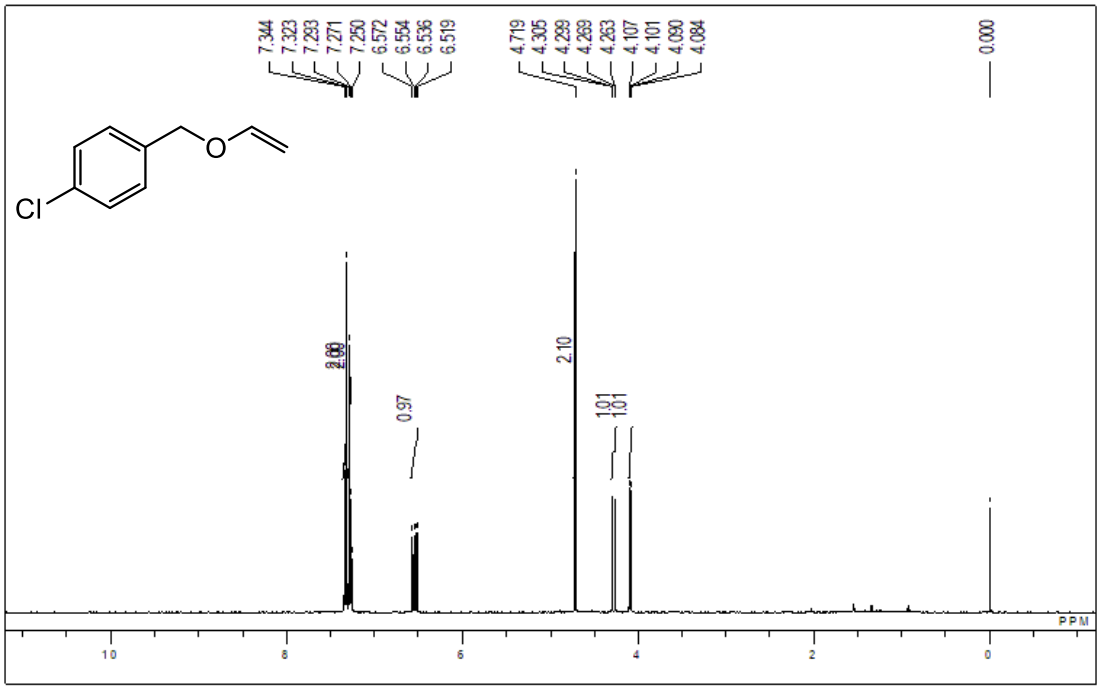
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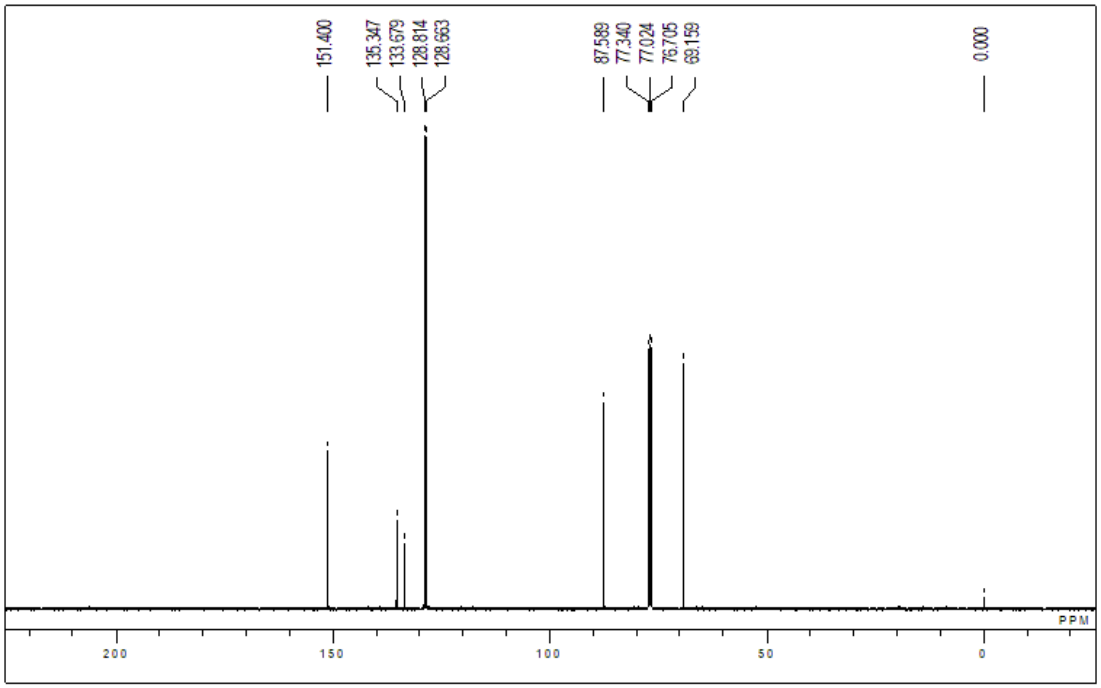
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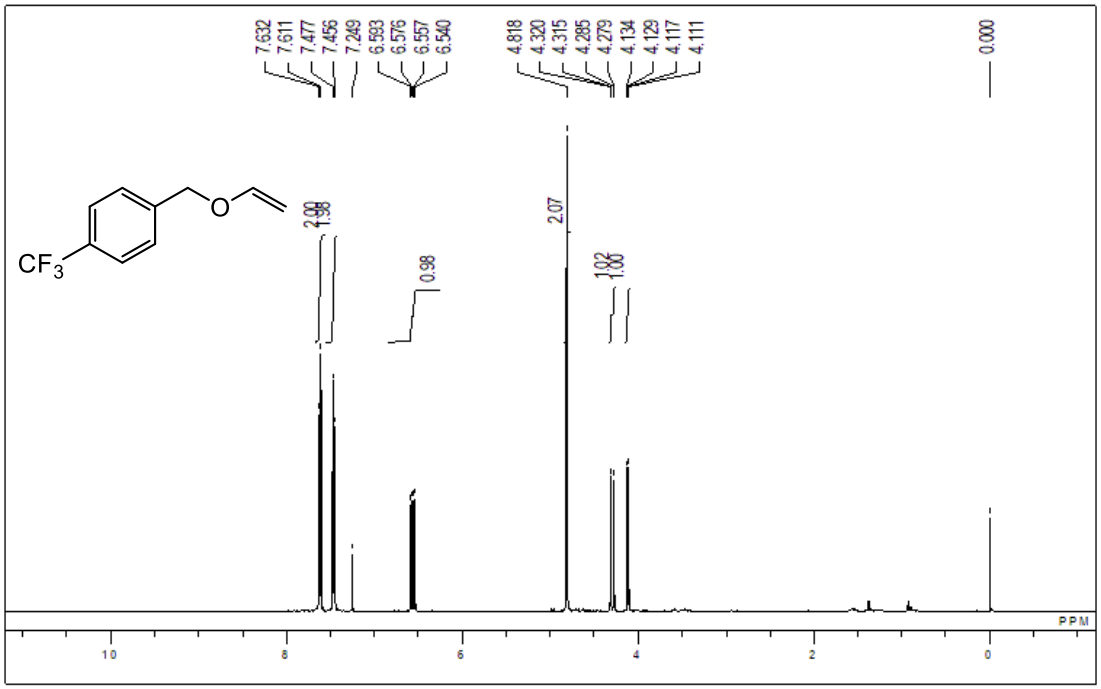
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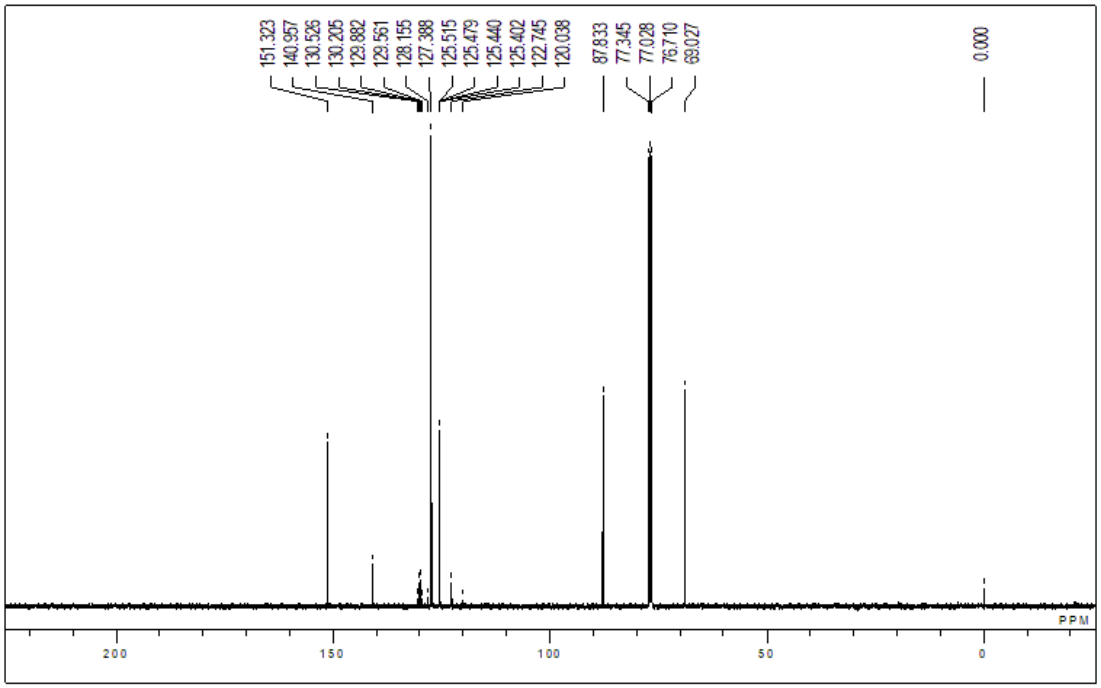
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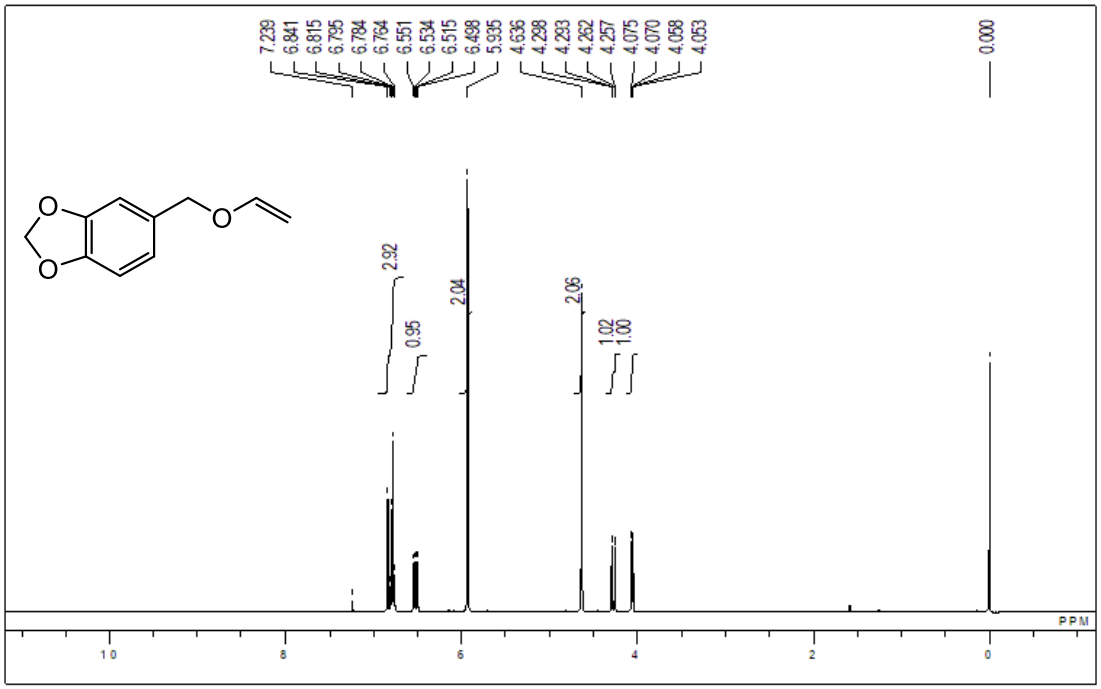
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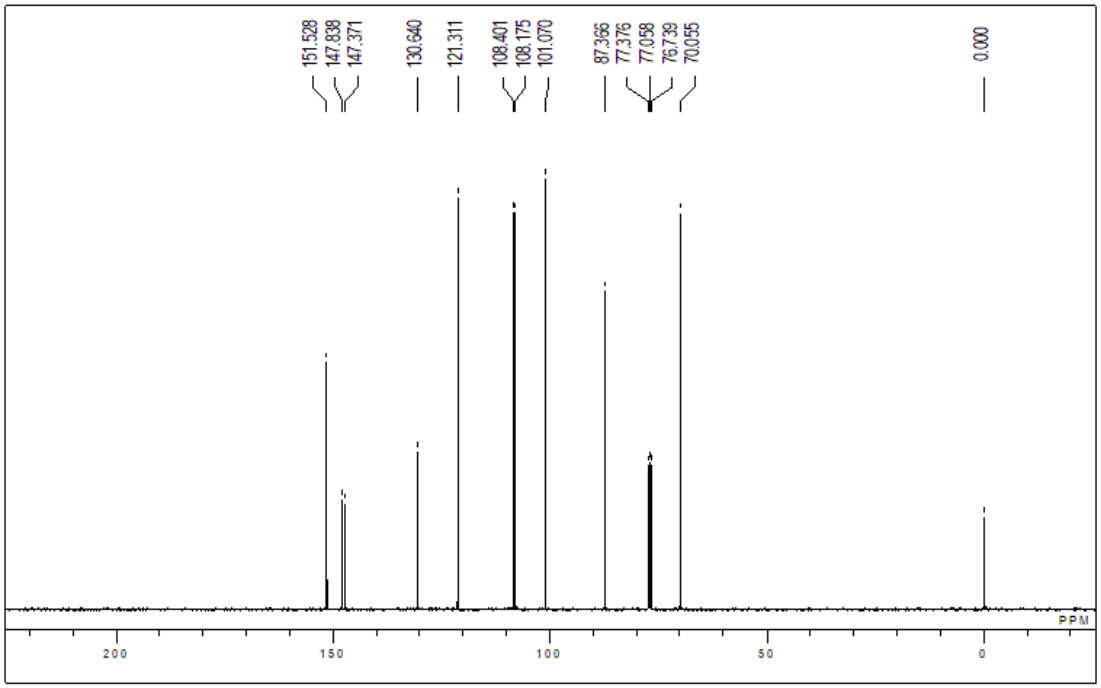
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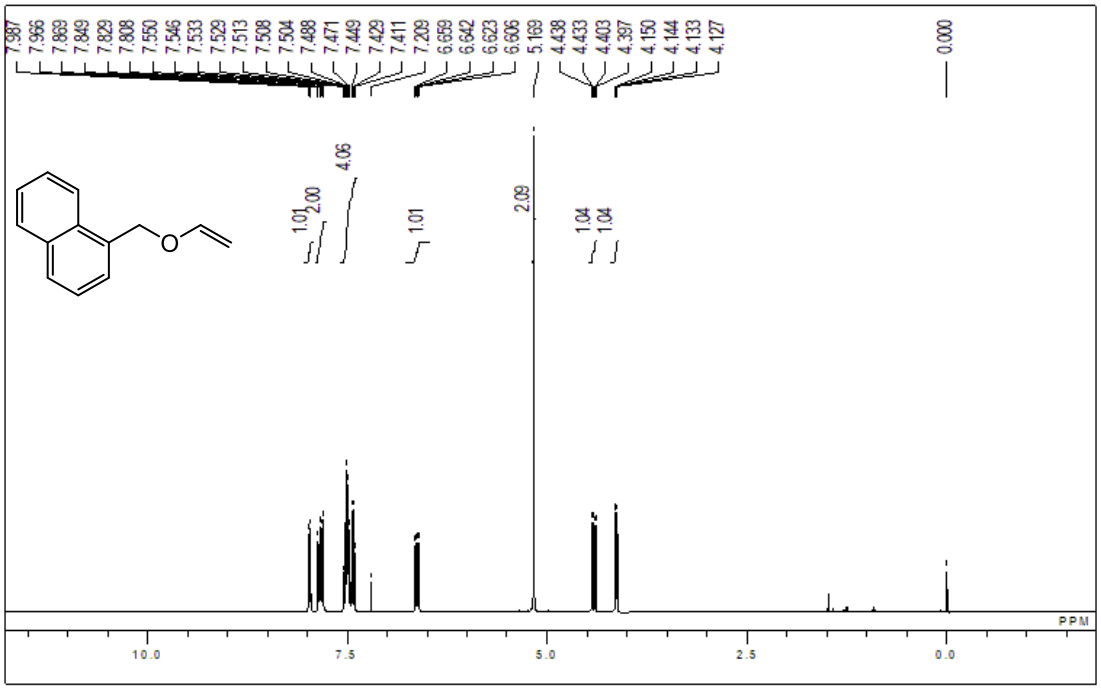
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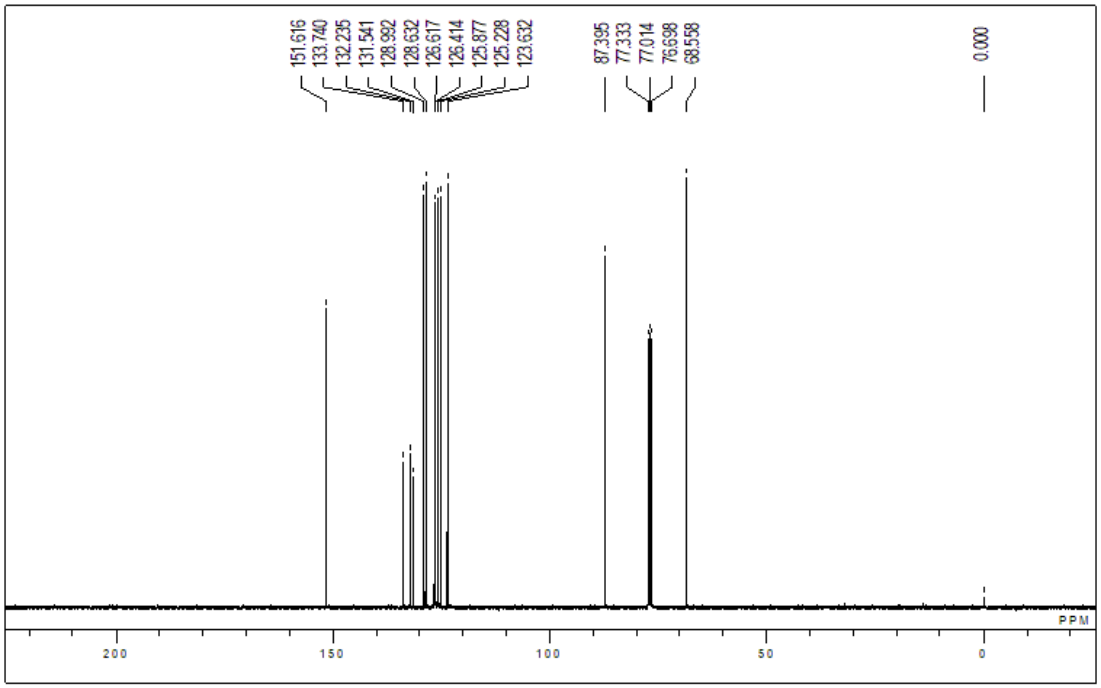
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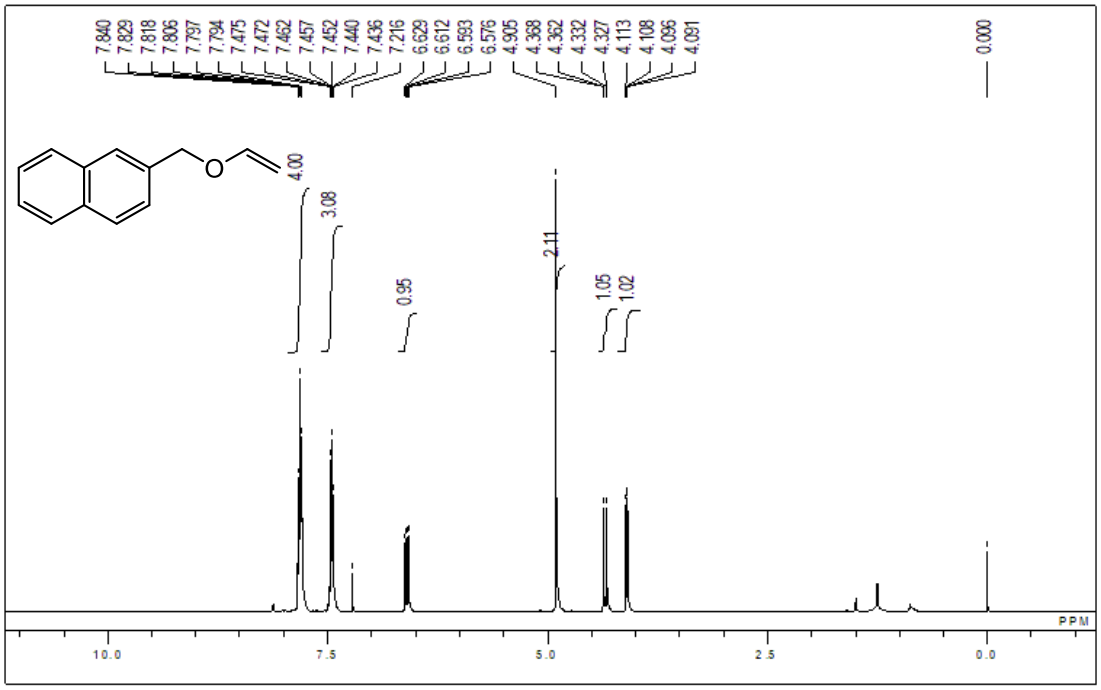
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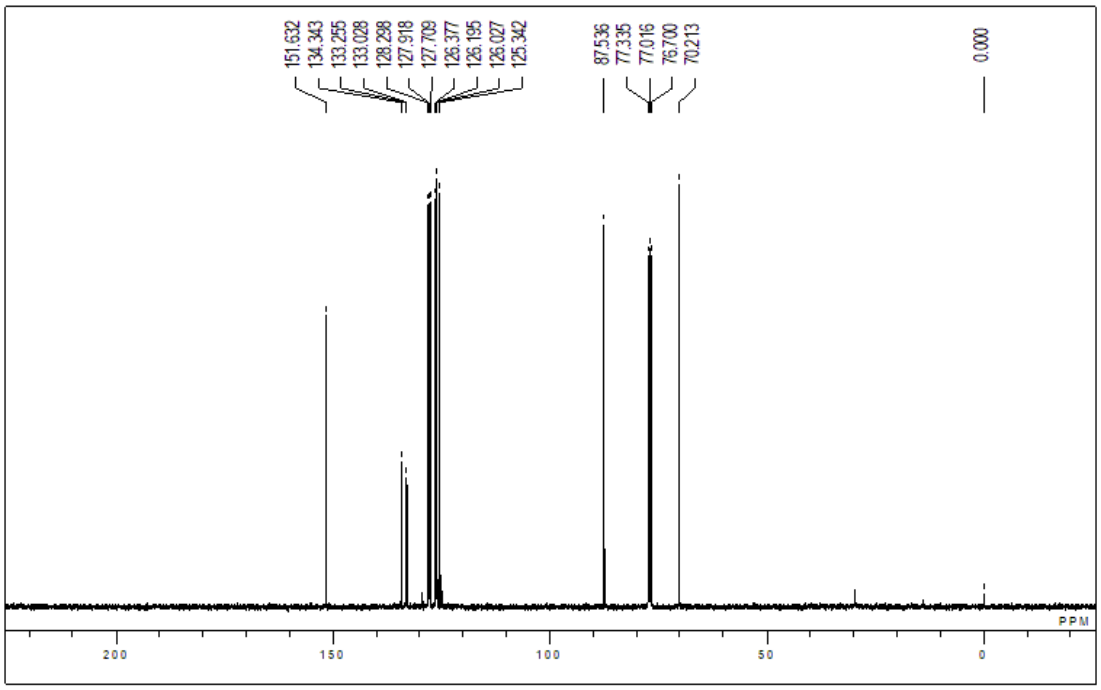
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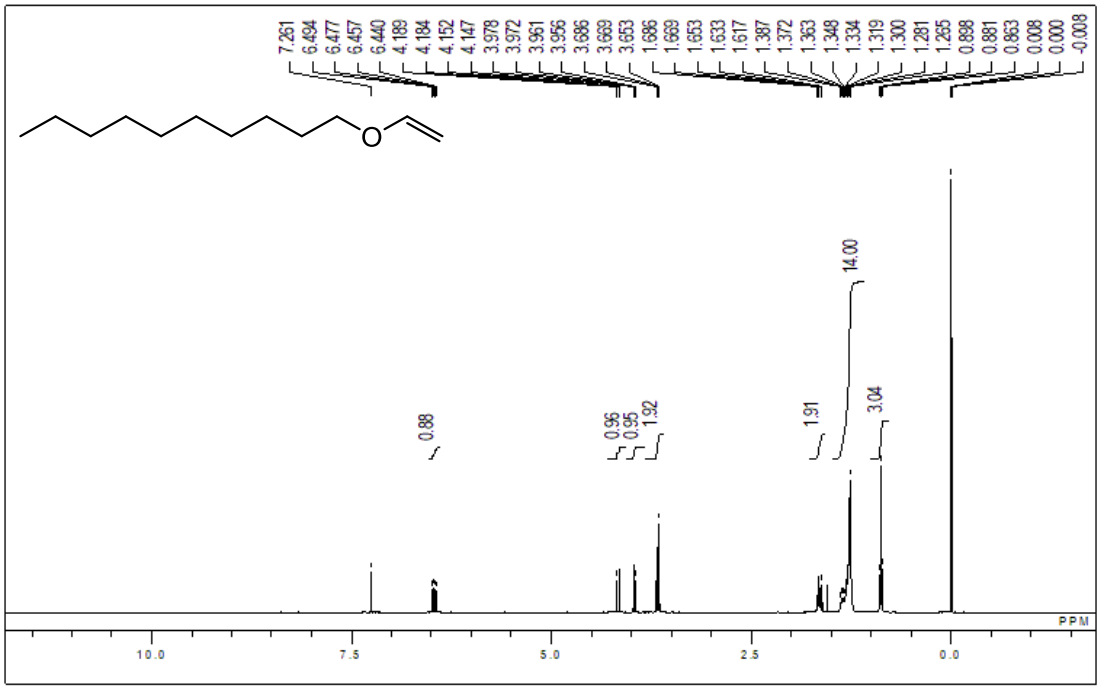
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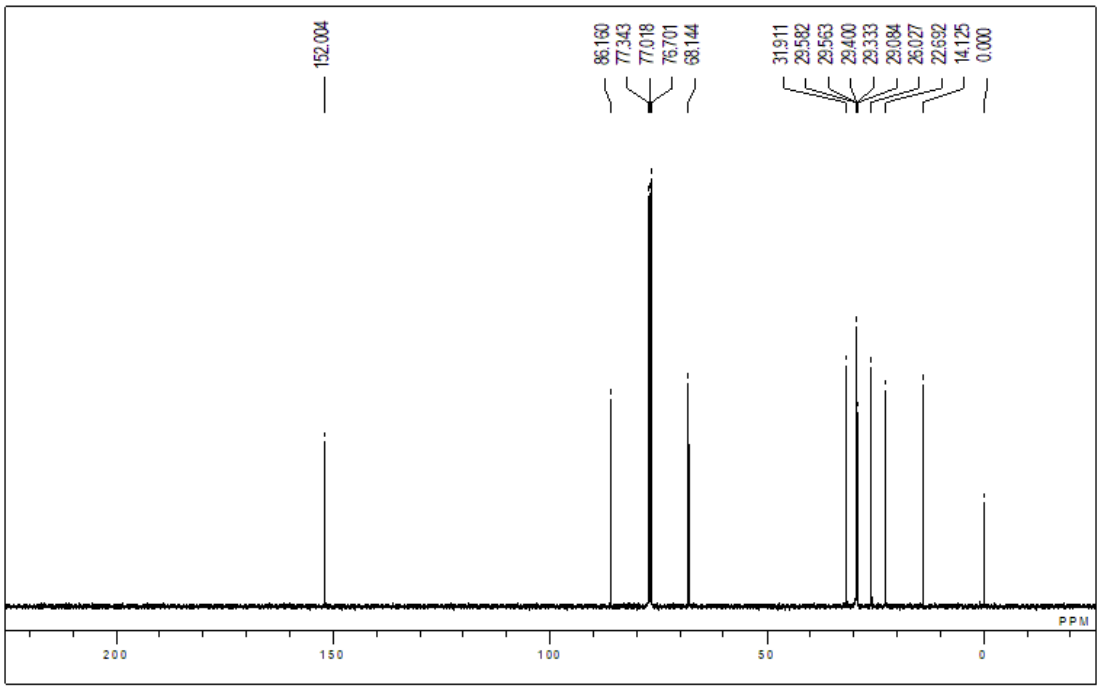
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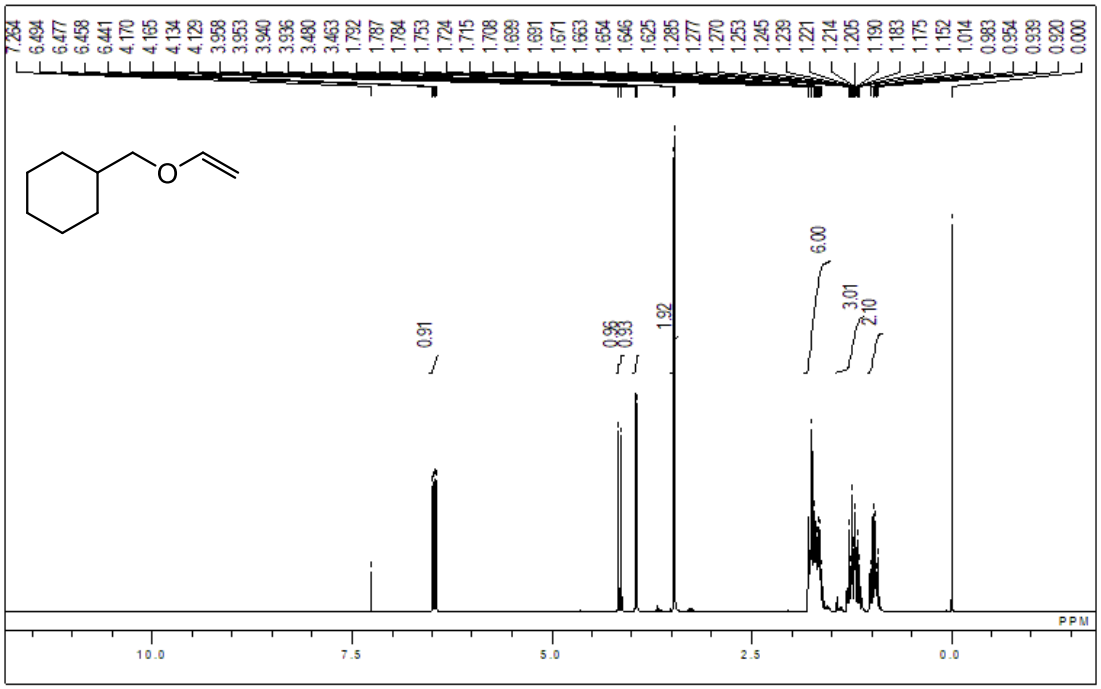
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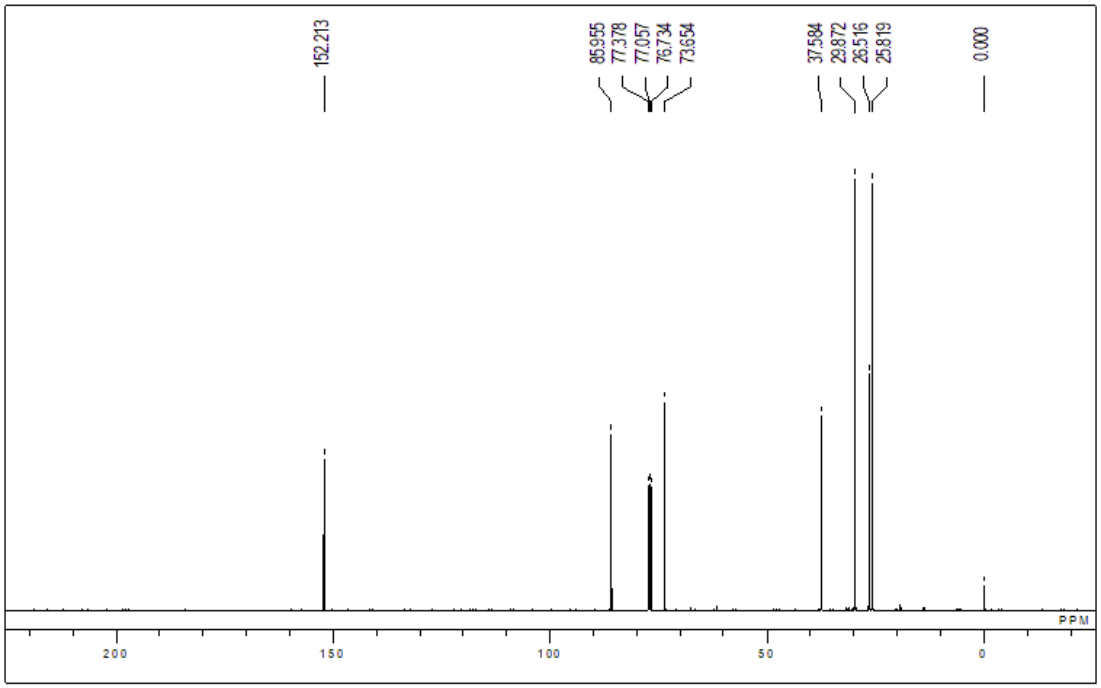
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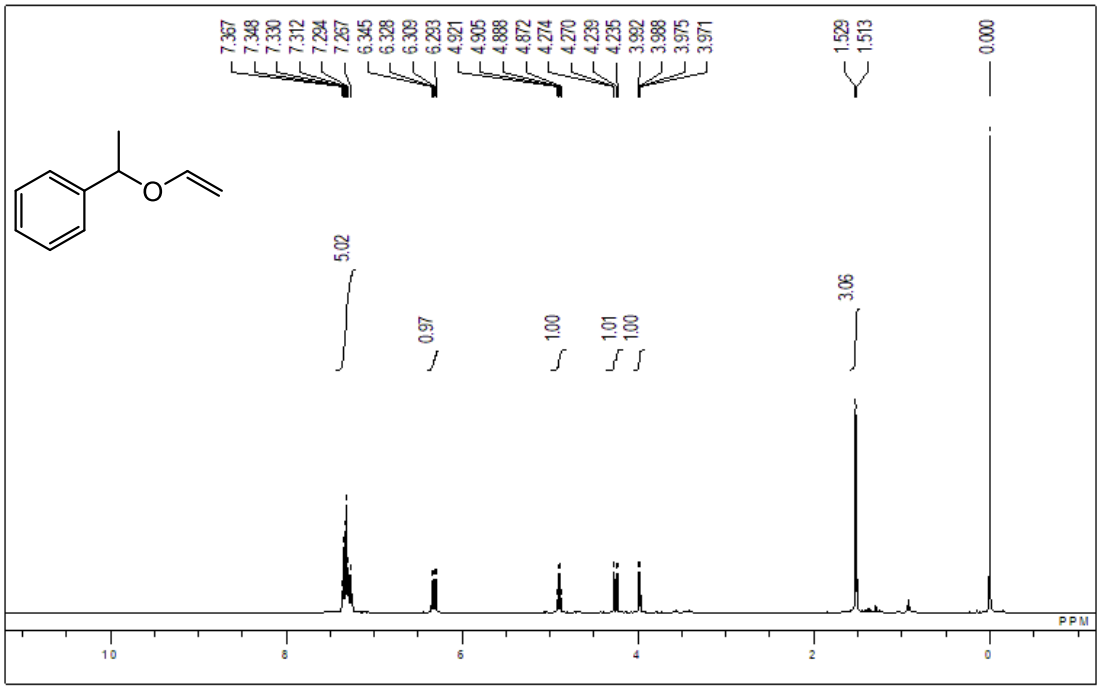
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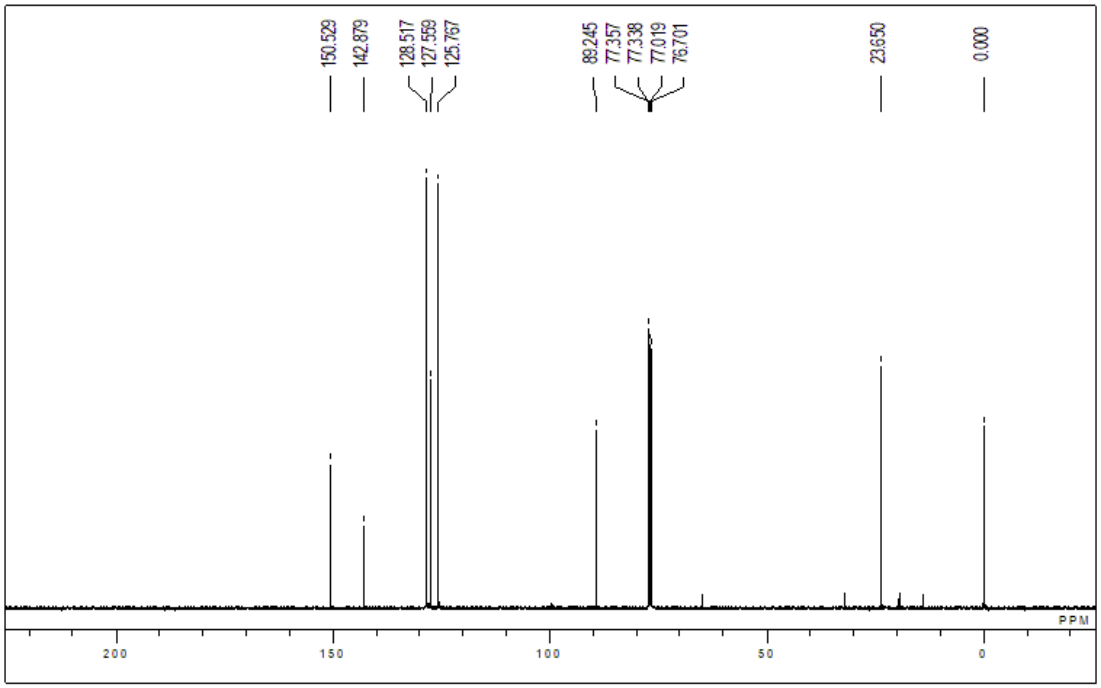
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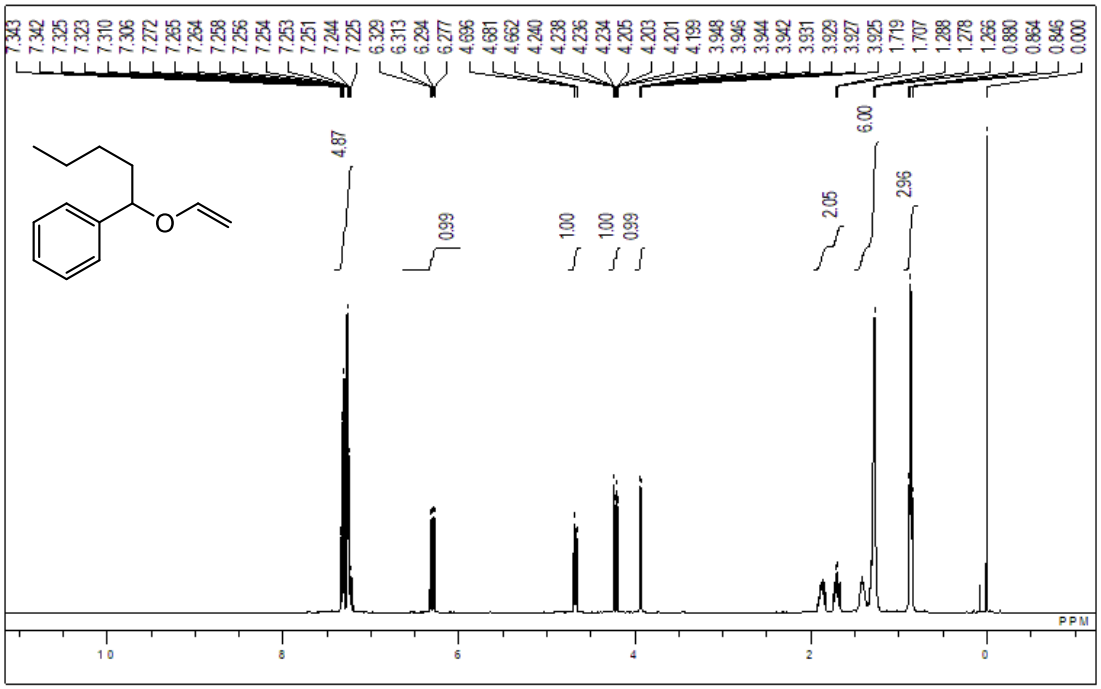
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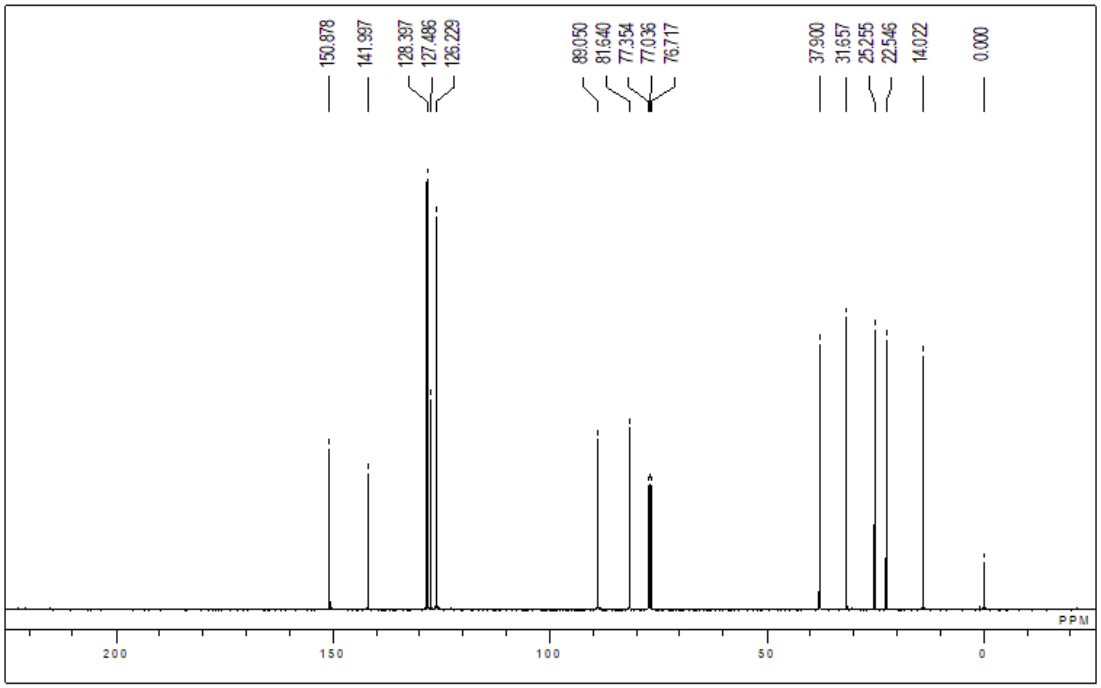
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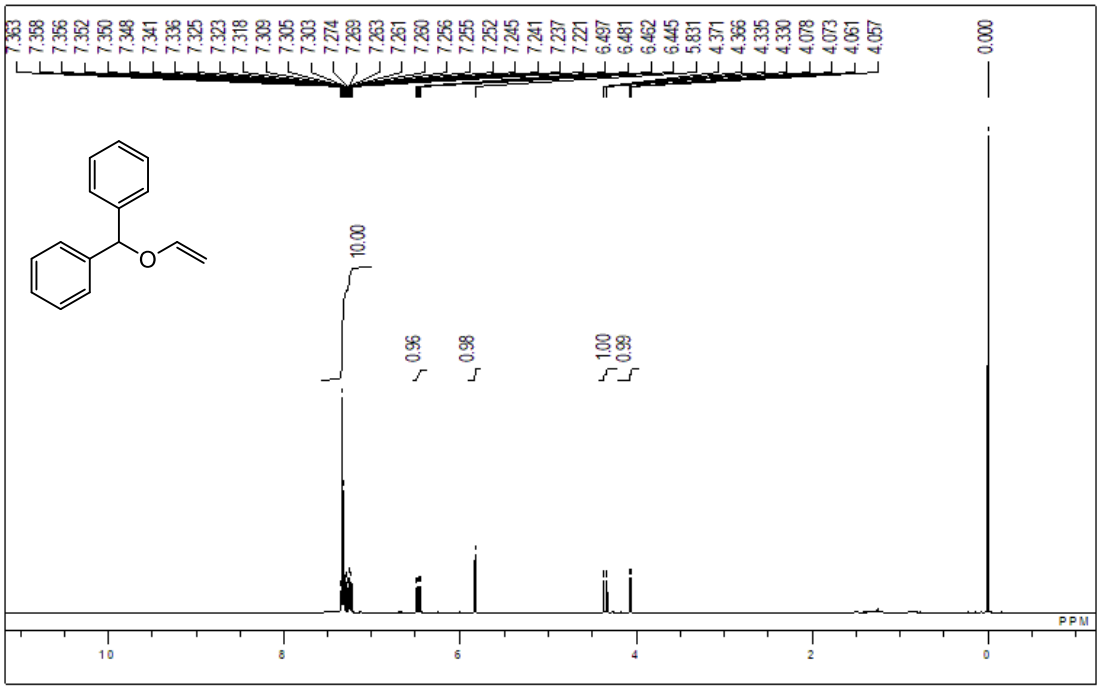
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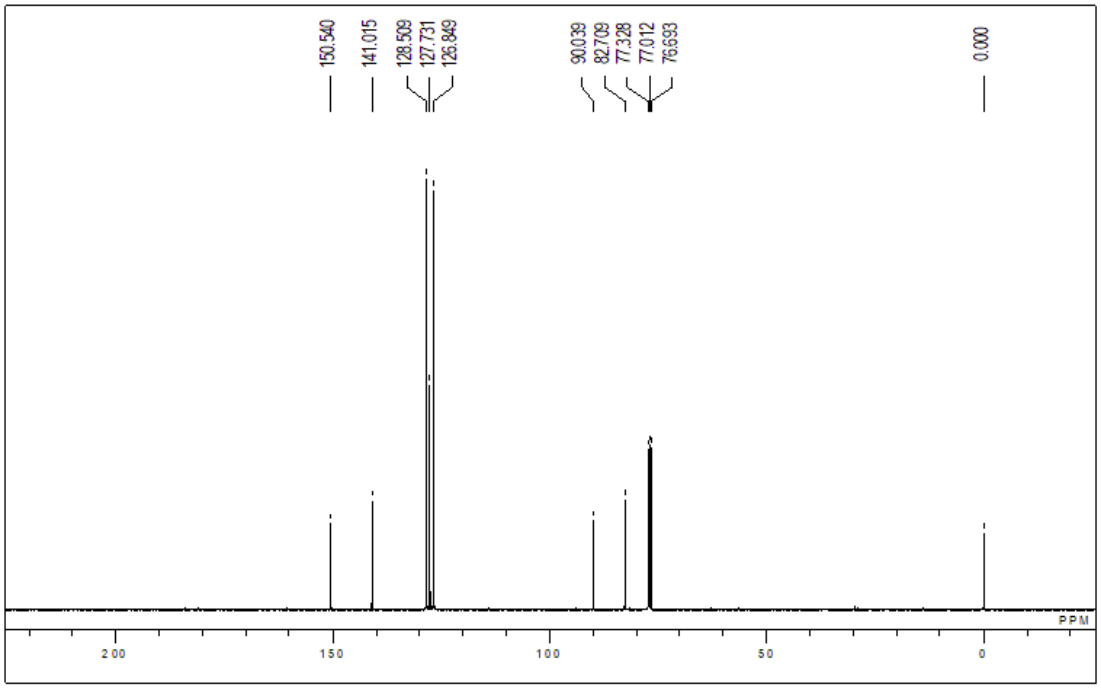
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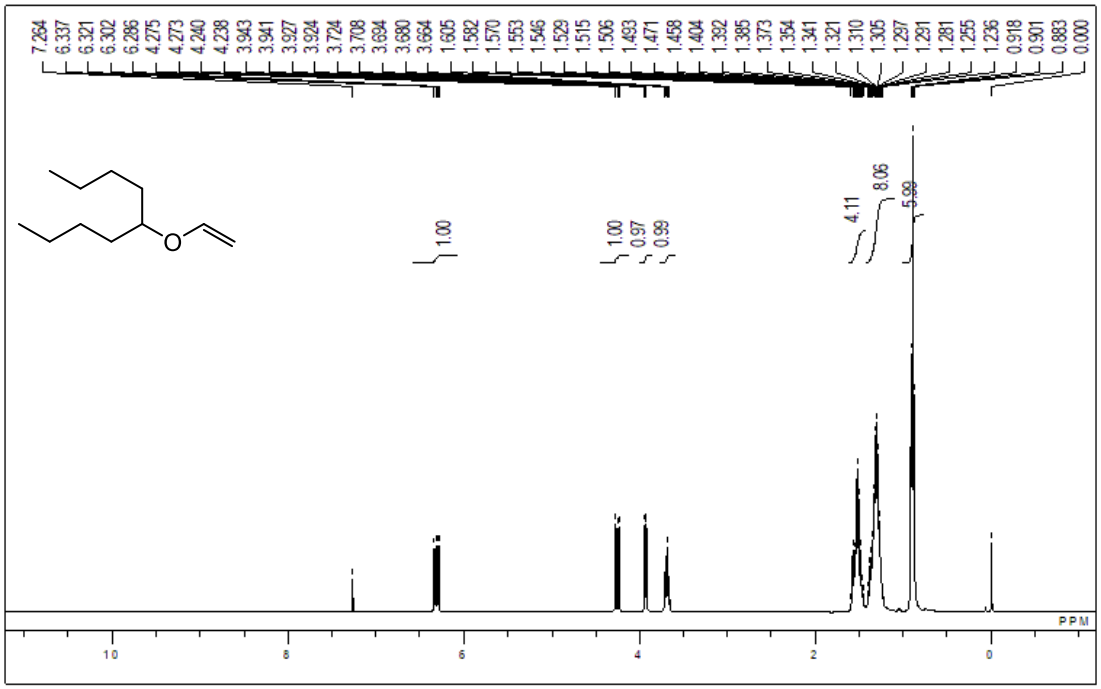
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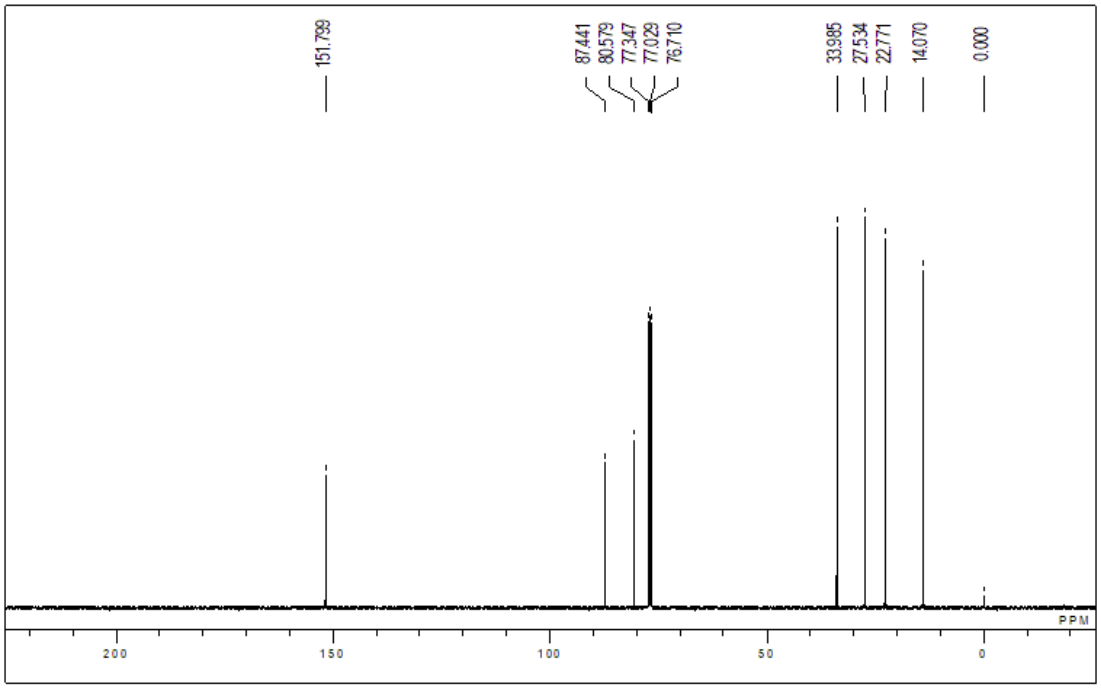
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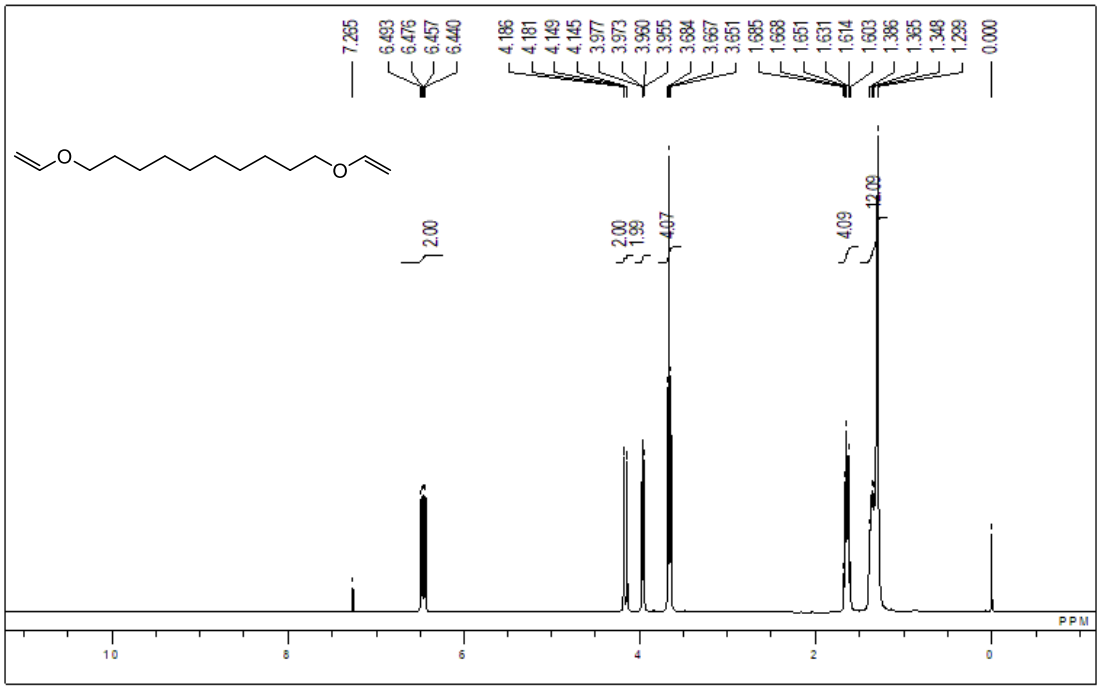
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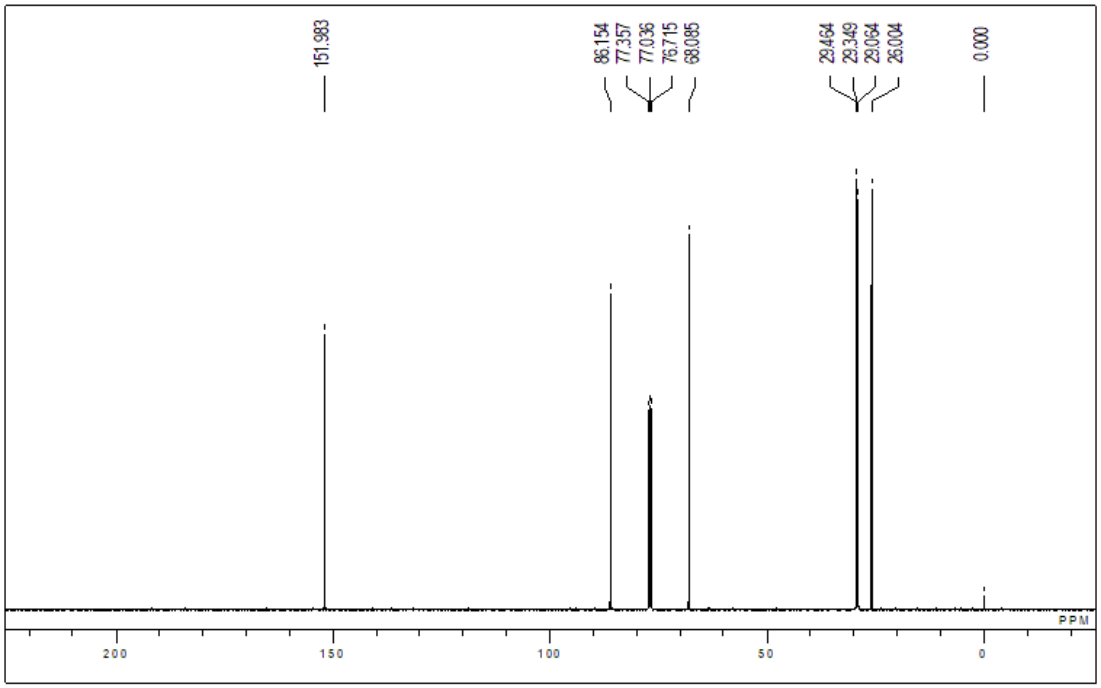
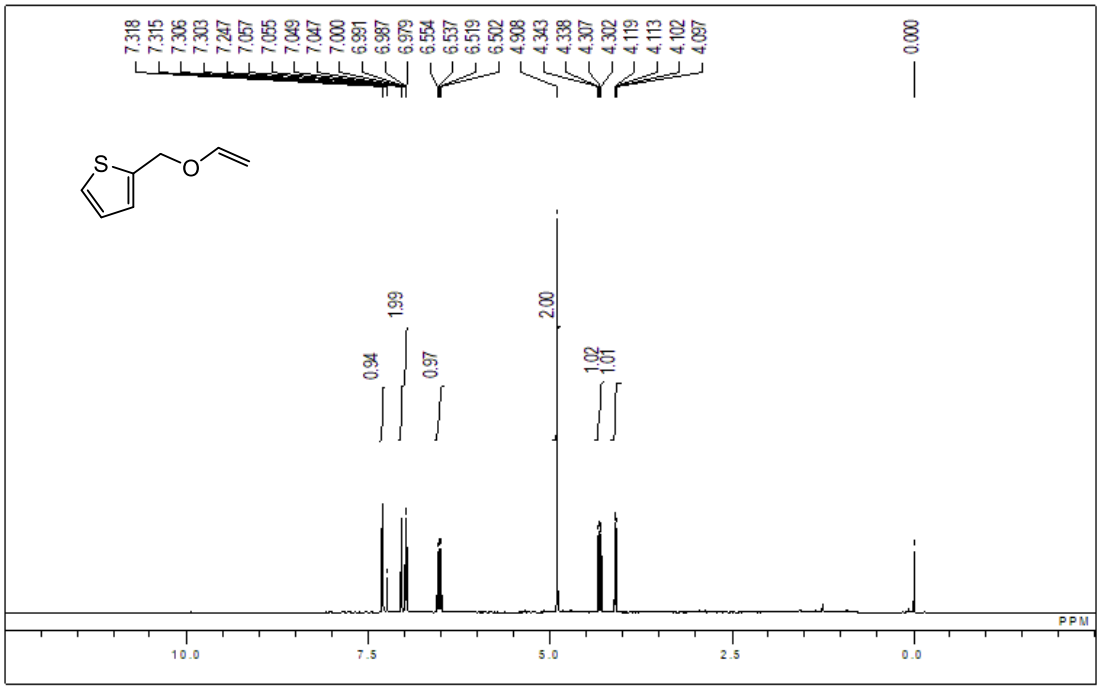
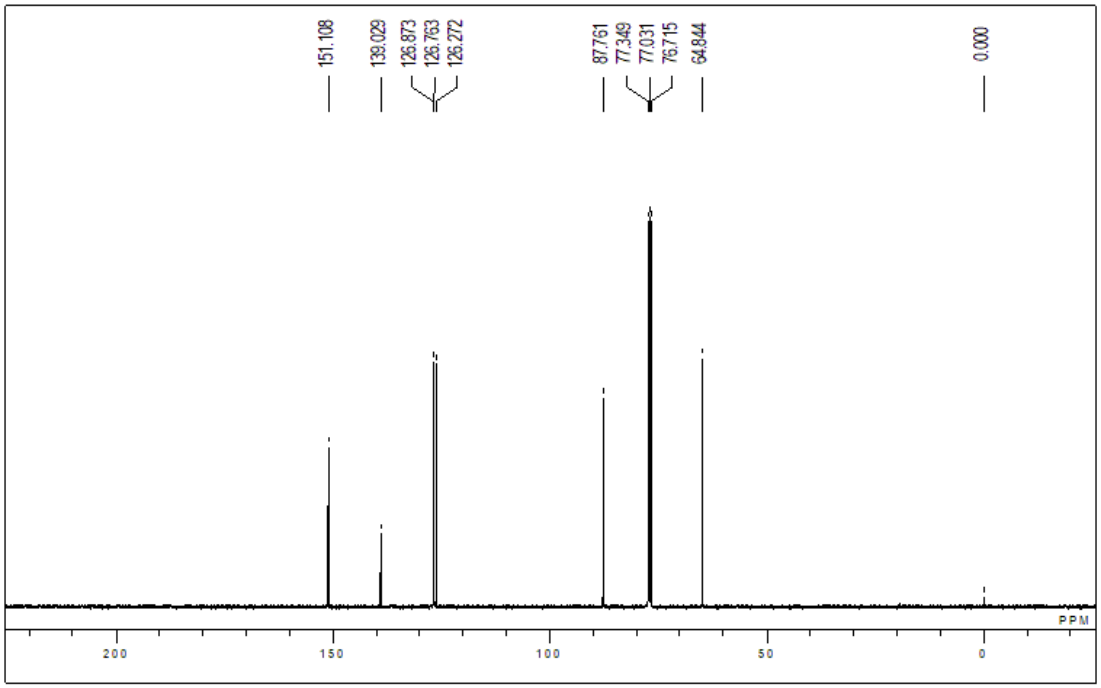
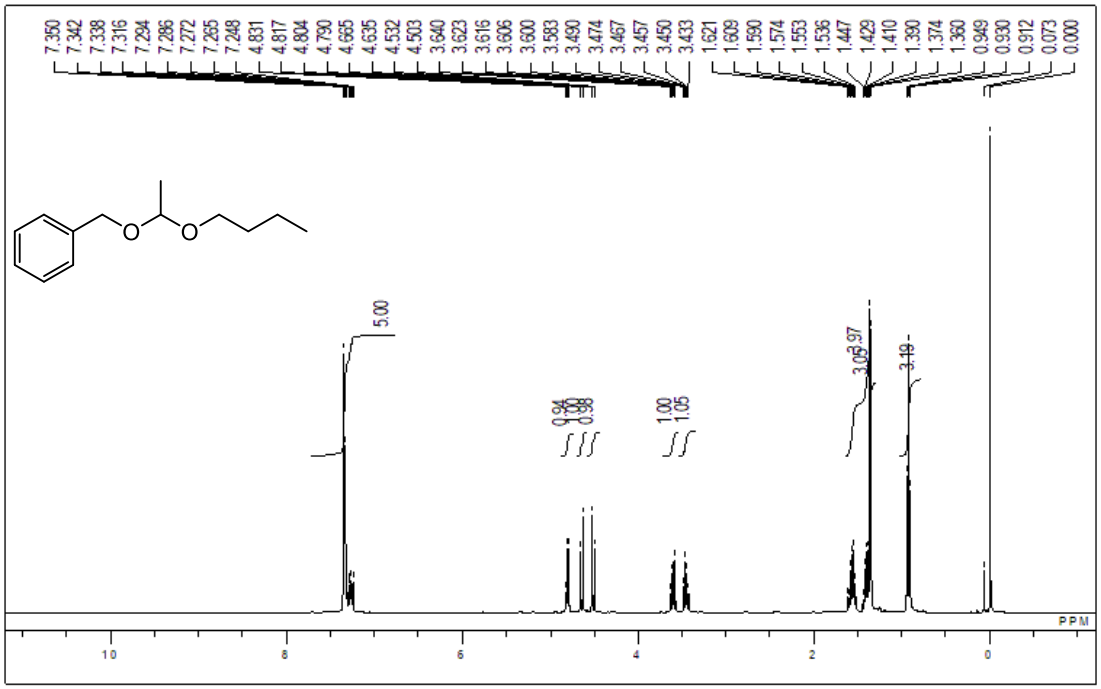

151.983
86.154
77.357
77.036
76.715
68.085
29.464
29.349
29.064
26.004
0.000
PPM
200
150
100
50
0

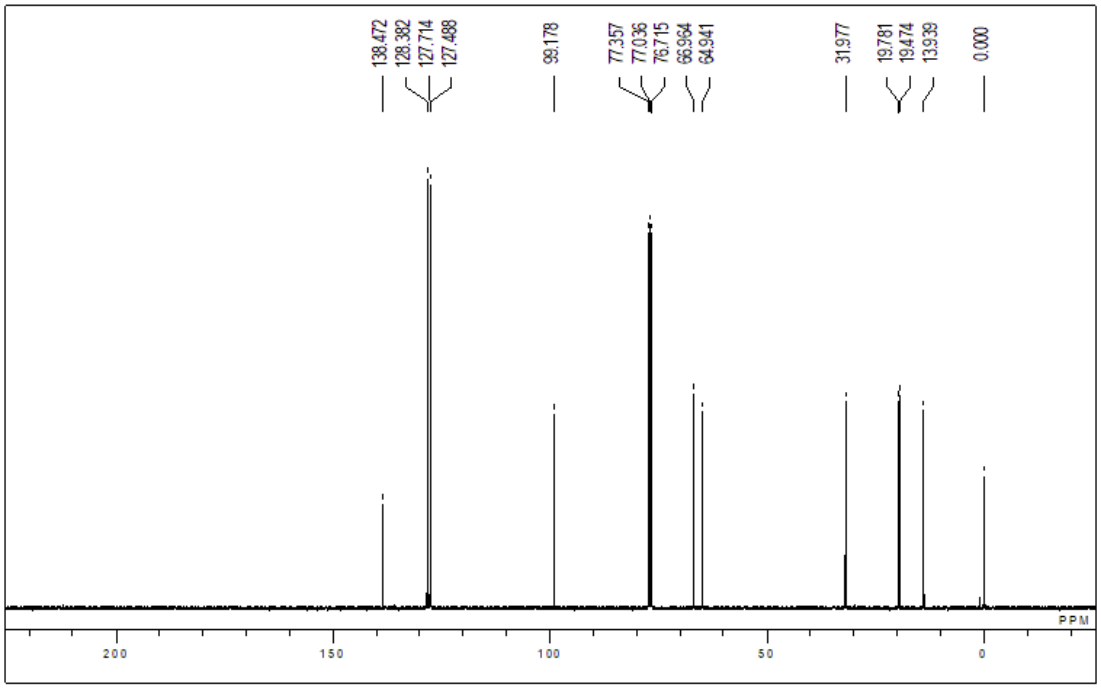
3q


7.318
7.315
7.306
7.303
7.247
7.057
7.055
7.049
7.047
7.000
6.991
6.987
6.979
6.554
6.537
6.519
6.502
4.908
4.343
4.338
4.307
4.302
4.119
4.113
4.102
4.097
0.000
S
O
0.94
1.99
0.97
2.00
1.02
1.01
PPM
10.0
7.5
5.0
2.5
0.0

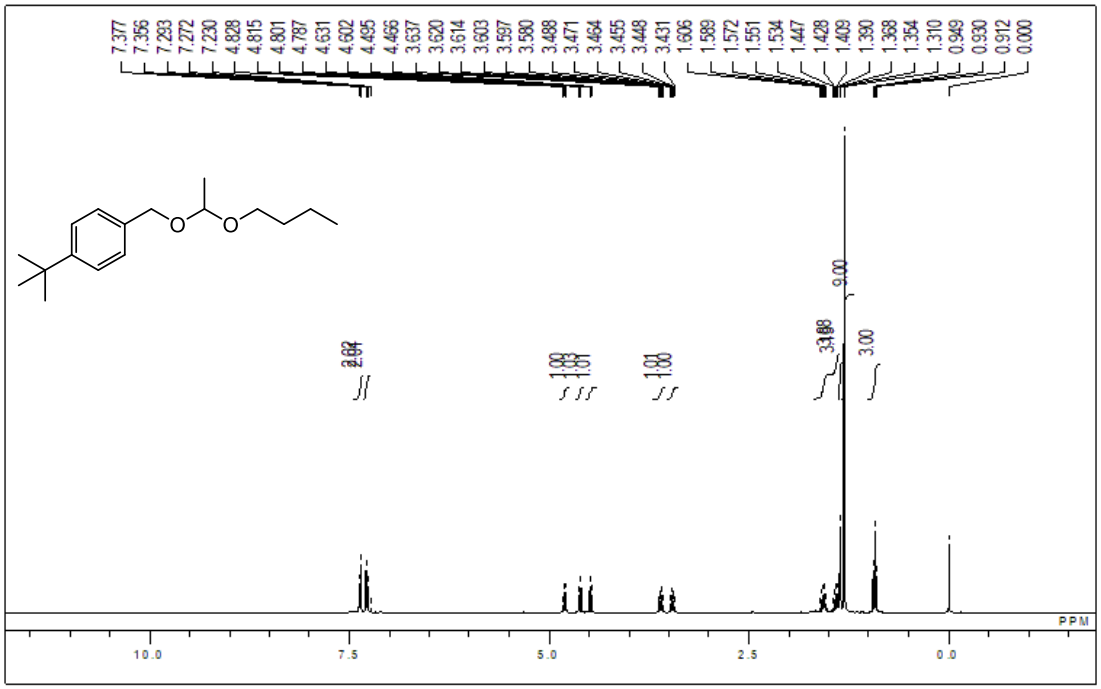

151.108
139.029
126.873
126.763
126.272
87.761
77.349
77.031
76.715
64.844
0.000
PPM
200
150
100
50
0

4a


7.350
7.342
7.338
7.316
7.294
7.286
7.272
7.265
7.248
4.831
4.817
4.804
4.790
4.665
4.635
4.532
4.503
3.640
3.623
3.616
3.606
3.600
3.583
3.490
3.474
3.467
3.457
3.450
3.433
1.621
1.609
1.590
1.574
1.553
1.536
1.447
1.429
1.410
1.390
1.374
1.360
0.949
0.930
0.912
0.073
0.000
5.00
0.94
0.96
0.98
1.00
1.05
3.05
3.19
PPM
10
8
6
4
2
0


138.472
128.382
127.714
127.488
99.178
77.357
77.036
76.715
66.964
64.941
31.977
19.781
19.474
13.939
0.000
PPM
200
150
100
50
0

4c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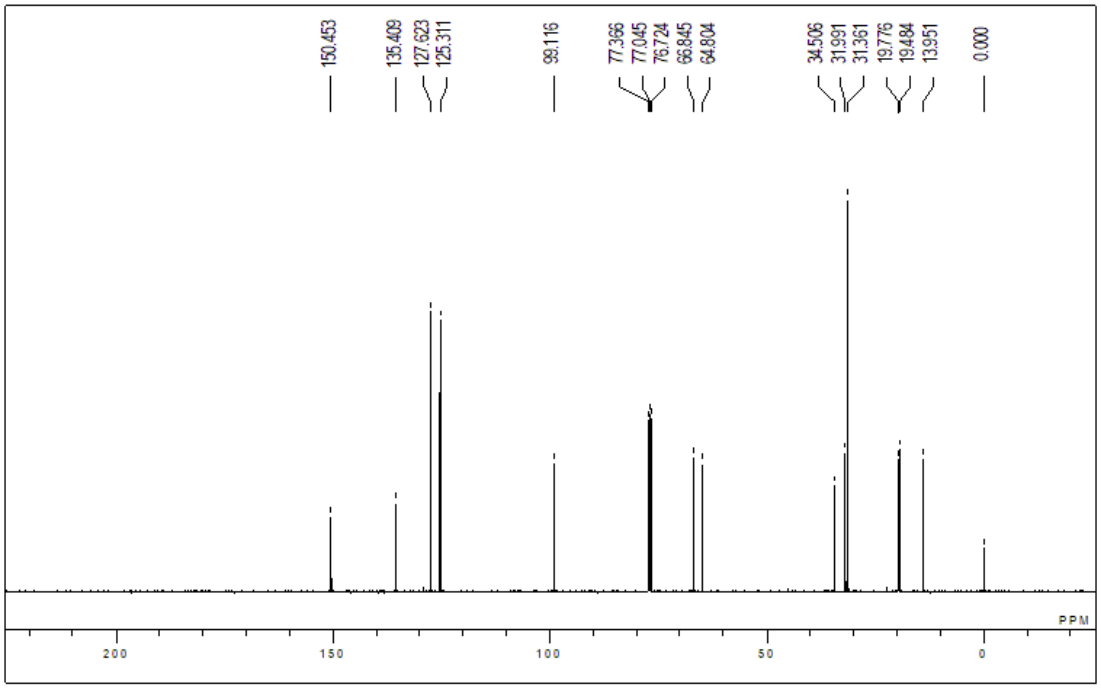
7.356
7.293
7.272
7.230
4.828
4.815
4.801
4.787
4.631
4.602
4.495
4.466
3.637
3.620
3.614
3.603
3.597
3.580
3.488
3.471
3.464
3.455
3.448
3.431
1.606
1.589
1.572
1.551
1.534
1.447
1.428
1.409
1.390
1.368
1.354
1.310
0.949
0.930
0.912
0.000
9.00
3.00
PPM
10.0
7.5
5.0
2.5
0.0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135.409
127.623
125.311
99.116
77.366
77.045
76.724
66.845
64.804
34.506
31.991
31.361
19.776
19.484
13.951
0.000
PPM
200
150
100
50
0

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