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Electronic Supplementary Information

Environmentally responsible, safe, and chemoselective catalytic hydrogenation of olefins: ppm levels of Pd catalysis in recyclable water at room temperature

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Table of Contents

1. General information

Chemicals or reagents were procured from Sigma-Aldrich, Combi-Blocks, Alfa Aesar, or Acros Organics and used without further purification. Pd/C (1 wt %) was purchased from Sigma-Aldrich (catalog number: 205672). Hydrogen gas was supplied by Praxair. TPGS-750-M was generously supplied by PHT International. The desired 2 wt % of TPGS-750-M solution in HPLC water was prepared by dissolving 2 g of TPGS-750-M solid in 98 g of HPLC water and stored under argon. IKA hot plates with a circular aluminum or copper reaction block with pre-drilled holes for 1-dram vials were used. The vials from Chemglass (catalog number: CG-4909-04) were used as reaction vials. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Unity Inova 400 MHz (400 MHz for ^{1}H, 100 MHz for ^{13}C), a Varian Unity Inova 500 MHz (500 MHz for ^{1}H, 125 MHz for ^{13}C) or on a Varian Unity Inova 600 MHz spectrometer (600 MHz for ^{1}H); DMSO-d_6, CD_3OD, CD_3CN and $CDCl_3$ were used as solvent. Residual peaks for $CHCl_3$ in $CDCl_3$ (1 H = 7.26 ppm, ^{13}C = 77.20 ppm), $(CH_3)_2SO$ in $(CD_3)_2SO$ (1 H = 2.50 ppm, ^{13}C = 39.52 ppm), CH_3CN in CD_3CN (^{1}H = 1.98 ppm, ^{13}C = 0.49 and 117.47 ppm) or MeOH in MeOD (^{1}H = 4.78 ppm, ^{13}C = 49.00 ppm) have been assigned. The chemical shifts are reported in ppm, the coupling constants *J* value are given in Hz. The peak patterns are indicated as follows: bs, broad singlet; s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet. Thin layer chromatography (TLC) was performed using Silica Gel 60 F254 plates (Merck, 0.25 mm thick). Flash chromatography was done in glass columns using Silica Gel 60 (EMD, 40-63 μm). GCMS data were recorded on a 5975C Mass Selective Detector, coupled with a 7890A Gas Chromatograph (Agilent Technologies).

2. Experimental procedures

2.1 Screening of surfactants using H_2 in a balloon; preparation of 2

In a 1-dram screw cap open top vial containing a Teflon-coated magnetic stir bar, 1 wt % Pd/C (500 ppm Pd, 1.3 mg) stiripentol (0.25 mmol, 58.6 mg) and 2 wt % TPGS-750-M/H_2O (0.5 mL) were added. The reaction vial was closed and a TFE-lined silicone SURE-LINK septum was punctured with a needle (18 G) attached with a pre-filled balloon of hydrogen gas. The headspace of the vial was replaced with H_2 by unscrewing the cap under positive H_2 flow for *ca.* 5 sec. Finally, the reaction mixture was stirred at rt for 10 h. The GC-MS at this stage of the reaction in aqueous TPGS-750-M showed complete conversion of starting material. The reaction mixture was filtered through a short plug of silica and washed with EtOAc. Removal of the organic solvent led to 98% yield of the spectroscopically pure material, **2** (note: use of 3 wt% or 5 wt% Pd/C instead of 1 wt% Pd/C resulted in similar chemical yield).

2.2 General catalytic procedure for hydrogenation using H_2 balloon

In a 1-dram screw cap open top vial containing a Teflon-coated magnetic stir bar, 1 wt % Pd/C (500, 1000 or 2000 ppm Pd basis, 1.3 mg, 2.6 mg or 5.3 mg), alkene (0.25 mmol) and 2 wt % TPGS-750-M/H_2O (0.5 mL) were added. The reaction vial was closed and a TFE lined silicone SURE-LINK septa was punctured with needle (18 G) attached with pre-filled balloon of hydrogen gas. The headspace of the vial was replaced with H_2 by unscrewing the cap under a positive H_2 flow for *ca.* 5 sec. Finally, the reaction mixture was stirred at rt or 45 ^oC until completion (monitored by GC-MS or NMR). The reaction mass was either filtered through short plug of silica and washed with EtOAc or extracted with EtOAc/MTBE. Removal of organic solvent led to spectroscopically pure material. In some cases (< 10%), residual impurities were removed using a short flash column.

2.3 General catalytic procedure for hydrogenation using Et_3SiH

In a 1-dram screw cap closed top vial containing a Teflon-coated magnetic stir bar, 1 wt % Pd/C (500, 1000 or 2000 ppm Pd basis, 1.3 mg, 2.6 mg or 5.3 mg), alkene (0.25 mmol), Et_3SiH (1.2 equiv), and 2 wt % TPGS-750-M/H_2O (0.5 mL) were added. The reaction vial was closed and stirred at rt or 45 ^oC until completion (monitored by GC-MS or NMR). The reaction mass was either filtered through short plug of silica and crude product was purified by short flash column to remove silane or its by-products.

2.4 Large scale recycling and reuse procedure

Initial reaction:

In a 250 mL 3-necked round bottom flask containing a Teflon-coated magnetic stir bar, 1 wt % Pd/C (500 ppm Pd basis, 265 mg), alkene (50 mmol) and 2 wt % TPGS-750-M/H_2O (100 mL) were added. The flask was attached with a 2-way stopcock consisting of a pre-filled balloon with hydrogen gas. The headspace of the flask was replaced with H_2 gas by puncturing the rubber septum attached to one neck of the flask for *ca.* 1 min. Finally, the reaction mixture was stirred at rt for 4 h (monitored by GC-MS or NMR). The reaction was stopped, and the balloon was removed to allow for attachment of the distillation assembly. The water was steam distilled at 100±2 ^oC in a separate flask, prior to vacuum distillation of the product at 10 torr to distill at 115-118 ^oC giving 91% yield (6.4 g) of the desired product. The Pd/C and surfactant residue left in the distilling flask was used for the subsequent recycle.

1st recycle: To the above Pd/C residue, previously distilled water was added and stirred for 20 min. Hexene-3-ol (50 mmol) was added, and similar process mentioned above was followed and the reaction mixture was stirred at rt for 5 h to result in 92% yield (4.7 g) of the desired alcohol **49** (distilled at 25 torr, 82-84 ^oC).

2nd recycle: To above Pd/C residue, distilled water from 1st recycle was added and stirred for 20 min. Hexenone (50 mmol) was added, and a similar protocol mentioned in the initial reaction is followed and the reaction mixture was stirred at rt for 12 h to get 89% yield (6.3 g) of the desired product 50 (distilled at 126-128 °C).

3rd recycle: To above Pd/C residue, previously distilled water from the 2nd recycle was added and stirred for 20 min. Fresh 1 wt % Pd/C (100 ppm), ethyl 3,3-dimethylacrylate (50 mmol), and Et_3SiH (1. 5 equiv) were added to the flask. Finally, the reaction mixture was stirred at 45 °C for 20 h to result in 90% yield (5.8 g) of the desired product, which was carefully distilled at 134 °C (after distilling the water).

2.5 Large scale recycling on the same substrate

In a 100 mL 3-necked round bottom flask containing a Teflon-coated magnetic stir bar, 1 wt % Pd/C (500 ppm Pd basis, 132.5 mg), 4-*t*-butylstyrene (25 mmol, 4.0 g) and 2 wt % TPGS-750-M/H_2O (50 mL) were added. The flask was attached with a 2-way stopcock consisting of a pre-filled balloon with hydrogen gas. The headspace of the flask was replaced with H_2 gas by puncturing the rubber septum attached to one neck of the flask for *ca.* 1 min. Finally, the reaction mixture was stirred at rt for 3 h (monitored by GC-MS or NMR). The reaction was stopped, and the balloon was removed to allow for attachment of the distillation assembly. The water was steam distilled at 100±2 °C in a separate flask, prior to vacuum distillation of the product at 40 torr to distill at 113-116 °C giving 90% yield (3.6 g) of the desired product. The Pd/C and surfactant residue left in the distilling flask was used for the subsequent recycle.

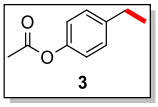
1st recycle: To the above Pd/C residue, previously distilled water was added and stirred for 20 min. 4-*t*-butylstyrene (25 mmol, 4.0 g) was added, and similar process mentioned above was followed to result in 93% yield (3.8 g) of the desired 4-ethyl-*t*-butylbenzene **6**.

2nd recycle: By following procedure mentioned in recycle 1, 91% yield (3.7 g) of the desired product 4-ethyl-*t*-butylbenzene **6** was obtained.

3rd recycle: By following procedure mentioned in recycle 1, 85% yield (3.4 g) of the desired product 4-ethyl-*t*-butylbenzene **6** was obtained.

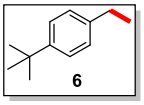
4rt recycle: By following procedure mentioned in recycle 1, 75% yield (3.0 g) of the desired product 4-ethyl-*t*-butylbenzene **6** was obtained.

3. Analytical data



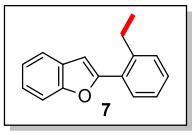
Yield 99%, 40 mg; eluent for column chromatography: Hexanes : EtOAc (9:1)

^{1}H NMR[1] (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.5, 2H), 6.91 (d, *J* = 8.5, 2H), 2.57 (q, *J* = 7.6, 2H), 2.21 (s, 3H), 1.15 (t, *J* = 7.6 , 3H).



Yield 99%, 40 mg; eluent for column chromatography: Hexanes : EtOAc (9.5:0.5)

^{1}H NMR[2] (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.2, 2H), 7.07 (d, *J* = 8.0, 2H), 2.55 (q, *J* = 7.6, 2H), 1.24 (s, 9H), 1.16 (t, *J* = 7.6, 3H).

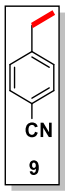


Yield 93%, 52 mg; eluent for column chromatography: Hexanes : EtOAc (9:1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (s, 1H), 7.72 (d, *J* = 7.8, 1H), 7.61 (d, *J* = 7.6, 1H), 7.56 (d, *J* = 8.7, 1H), 7.40 (t, *J* = 7.6, 1H), 7.31 (t, *J* = 7.7, 1H), 7.27 (d, *J* = 8.5, 1H), 7.23 (d, *J* = 7.1, 1H), 7.05 (s, 1H), 2.76 (q, *J* = 7.6, 2H), 1.34 (t, *J* = 7.6, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.23, 154.88, 144.84, 130.48, 129.30, 128.80, 128.26, 124.43, 124.17, 122.90, 122.43, 120.86, 111.16, 101.18, 28.95, 15.60.

HRMS $C_{16}H_{14}O$ MS-ESI [M+] *m/z* calcd: 222.1045; found: 222.1048.

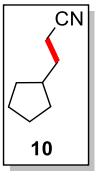


9

Yield 90%, 29 mg; eluent for column chromatography: Hexanes : EtOAc (9.5:0.5)

^{1}H NMR[3] (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.3, 2H), 7.31 (d, *J* = 8.1, 2H), 2.72 (q, *J* = 7.6, 2H), 1.27 (t, *J* = 7.6, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.80, 132.18, 128.67, 119.19, 109.51, 29.07, 15.02.

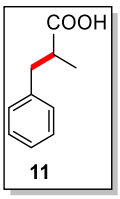


10

Yield 91%, 28 mg; eluent for column chromatography: Hexanes : EtOAc (9:1)

^{1}H NMR[4] (500 MHz, $CDCl_3$) δ 2.36 (t, *J* = 7.4, 2H), 1.93 (hept, *J* = 7.6, 1H), 1.87 – 1.79 (m, 2H), 1.69 (q, *J* = 7.4, 2H), 1.66 – 1.55 (m, 4H), 1.21 – 1.01 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 120.01, 39.19, 32.12, 31.47, 25.05, 16.42.

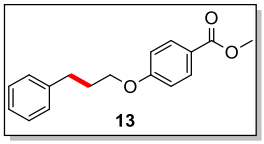


11

Yield 82%, 34 mg; eluent for column chromatography: Hexanes : EtOAc (4:6)

^{1}H NMR[5] (500 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.26 – 7.17 (m, 3H), 3.10 (dd, *J* = 13.5, 6.5, 1H), 2.79 (h, *J* = 6.9, 1H), 2.69 (dd, *J* = 13.5, 8.0, 1H), 1.20 (d, *J* = 7.0, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 182.36, 139.03, 129.01, 128.43, 126.44, 41.22, 39.30, 16.49.

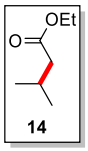


Yield 100%, 67 mg; eluent for column chromatography: Hexanes : EtOAc (8:2)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.9, 2H), 7.34 – 7.28 (m, 2H), 7.23 (d, *J* = 6.6, 3H), 6.92 (d, *J* = 8.9, 2H), 4.03 (t, *J* = 6.3, 2H), 3.90 (s, 3H), 2.84 (t, *J* = 7.6, 2H), 2.19 – 2.11 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.90, 162.82, 141.25, 131.59, 128.50, 128.48, 126.04, 122.49, 114.10, 67.04, 51.85, 32.06, 30.66.

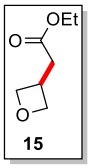
HRMS $C_{17}H_{18}O_3$ MS-ESI [M+] *m/z* calcd: 270.1256; found: 270.1259.



Yield 100%, 32 mg; passed from short plug of silica and washed with hexanes : diethyl ether (9:1)

^{1}H NMR[3] (500 MHz, $CDCl_3$) δ 4.14 (q, *J* = 7.1, 2H), 2.18 (d, *J* = 6.7, 2H), 2.15 – 2.06 (m, 1H), 1.26 (t, *J* = 7.1, 3H), 0.96 (d, *J* = 6.6, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.20, 60.06, 43.50, 25.71, 22.38, 14.27.

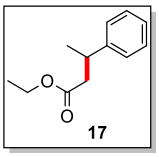


Yield 100%, 36 mg; passed from short plug of silica and washed with hexanes : diethyl ether (8:2)

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.90 – 4.80 (m, 2H), 4.43 (t, *J* = 6.3, 2H), 4.13 (qd, *J* = 7.1, 2.1, 2H), 3.42 – 3.31 (m, 1H), 2.72 (d, *J* = 7.9, 2H), 1.25 (t, *J* = 7.1, 3H).

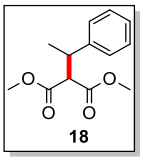
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.70, 60.58, 37.99, 31.44, 14.18.

HRMS $C_7H_{12}O_3$ H GC-CI [M+H] *m/z* calcd: 145.0865; found: 145.0863.



Yield 93%, 45 mg; eluent for column chromatography: Hexanes : EtOAc (9.5:0.5)

^{1}H NMR[6] (500 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 2H), 7.13 (dd, *J* = 15.3, 6.6, 3H), 4.00 (q, *J* = 7.2, 2H), 3.21 (h, *J* = 7.0, 1H), 2.57 – 2.41 (m, 2H), 1.23 (d, *J* = 7.0, 3H), 1.11 (t, *J* = 7.1, 3H).

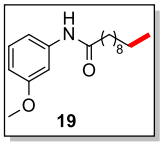


Yield 100%, 59 mg; eluent for column chromatography: Hexanes : EtOAc (8:2)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (q, *J* = 6.3, 4.7, 2H), 7.23 (dd, *J* = 8.1, 2.1, 3H), 3.78 (s, 3H), 3.65 (d, *J* = 10.6, 1H), 3.59 – 3.51 (m, 1H), 3.48 (s, 3H), 1.34 (d, *J* = 6.9, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.82, 168.34, 142.98, 128.49, 127.34, 126.91, 59.11, 52.54, 52.24, 40.10, 20.02.

HRMS: $C_{13}H_{16}O_4$ Na MS-ESI [M+Na] *m/z* calcd: 259.0946; found: 259.0947.

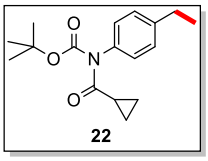


Yield 100%, 73 mg; eluent for column chromatography: Hexanes : EtOAc (8:2)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.34 (s, 1H), 7.19 (t, *J* = 8.1, 1H), 6.99 (d, *J* = 7.9, 1H), 6.69 – 6.62 (m, 1H), 3.78 (s, 3H), 2.35 (t, *J* = 7.6, 2H), 1.71 (p, *J* = 7.5, 2H), 1.42 – 1.18 (m, 14H), 0.89 (t, *J* = 6.9, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 171.77, 160.13, 139.34, 129.58, 111.93, 110.04, 105.51, 55.24, 37.84, 31.89, 29.58, 29.50, 29.41, 29.31, 29.29, 25.65, 22.68, 14.11.

HRMS $C_{18}H_{29}NO_2Na$ ESI-MS [M+Na] *m/z* calcd: 314.2096; found: 314.2103.



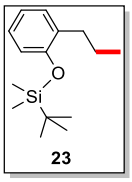
22

Yield 95%, 67 mg; eluent for column chromatography: Hexanes : EtOAc (8:2)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.0, 2H), 7.04 (d, *J* = 8.2, 2H), 2.67 (q, *J* = 7.6, 2H), 2.49 (ddd, *J* = 12.6, 7.9, 4.6, 1H), 1.43 (s, 10H), 1.25 (t, *J* = 7.6, 3H), 1.14 (dt, *J* = 7.8, 3.9, 2H), 0.91 (dq, *J* = 7.3, 3.7, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.58, 143.74, 136.80, 128.39, 127.99, 82.92, 28.47, 27.90, 15.45, 15.37, 10.66.

HRMS $C_{17}H_{23}NO_3$ Na MS-ESI [M+Na] *m/z* calcd: 312.1576; found: 312.1571.



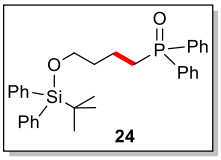
23

Yield 93%, 58 mg; eluent for column chromatography: Hexanes : EtOAc (9.5:0.5)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (d, *J* = 7.6, 1H), 6.82 (t, *J* = 7.5, 1H), 6.64 (t, *J* = 8.1, 1H), 6.54 (d, *J* = 7.9, 1H), 2.33 (t, *J* = 7.7, 2H), 1.37 (h, *J* = 7.3, 2H), 0.79 (d, *J* = 2.7, 9H), 0.72 (td, *J* = 7.4, 2.6, 3H), 0.00 (d, *J* = 2.7, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.71, 137.48, 134.37, 130.72, 125.03, 122.51, 36.89, 29.95, 27.47, 22.41, 18.27, 0.01.

HRMS $C_{15}H_{26}OSi$ MS-ESI [M+] *m/z* calcd: 250.1753; found: 250.1759.

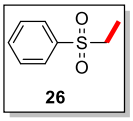


Yield 92%, 118 mg; eluent for column chromatography: Hexanes : EtOAc (2:8)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.70 (m, 4H), 7.63 (d, *J* = 7.0, 4H), 7.53 – 7.48 (m, 2H), 7.45 (td, *J* = 7.5, 2.2, 4H), 7.43 – 7.39 (m, 2H), 7.36 (t, *J* = 7.2, 4H), 3.67 (t, *J* = 5.8, 2H), 2.34 – 2.24 (m, 2H), 1.78 (s, 2H), 1.72 – 1.63 (m, 2H), 1.02 (s, 9H).

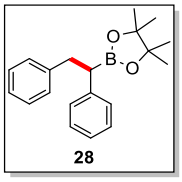
^{13}C NMR (126 MHz, $CDCl_3$) δ 135.54, 133.83, 131.67, 130.86, 130.78, 129.61, 128.68, 128.59, 127.75, 127.66, 63.14, 33.62, 33.51, 29.86, 29.29, 18.27, 18.24.

HRMS $C_{32}H_{37}O_2PSi$ Na MS-ESI [M+Na] *m/z* calcd: 535.2198; found: 535.2200.



Yield 81%, 34 mg; eluent for column chromatography: Hexanes : EtOAc (8:2)

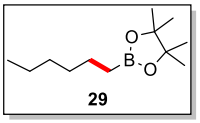
^{1}H NMR[7] (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2, 2H), 7.66 (t, *J* = 7.4, 1H), 7.58 (t, *J* = 7.5, 2H), 3.12 (q, *J* = 7.4, 2H), 1.27 (t, *J* = 7.4, 3H).



Yield 89%, 69 mg; eluent for column chromatography: Hexanes : EtOAc (8:2)

^{1}H NMR[8] (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 4.9, 4H), 7.25 – 7.19 (m, 4H), 7.16 (tt, *J* = 6.8, 3.3, 2H), 3.18 (dd, *J* = 13.5, 9.8, 1H), 2.99 (dd, *J* = 13.5, 6.9, 1H), 2.71 (dd, *J* = 9.8, 6.9, 1H), 1.13 (d, *J* = 4.3, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 141.75, 128.89, 128.41, 128.33, 128.03, 125.75, 125.39, 83.40, 38.85, 24.58, 24.51.

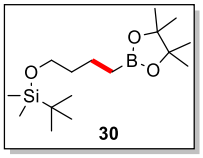


29

Yield 88%, 47 mg; eluent for column chromatography: Hexanes : EtOAc (9:1)

^{1}H NMR[9] (500 MHz, $CDCl_3$) δ 1.33 (p, *J* = 8.1, 7.1, 2H), 1.21 (d, *J* = 14.7, 6H), 1.17 (s, 12H), 0.80 (t, *J* = 6.7, 3H), 0.70 (t, *J* = 7.7, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 82.79, 32.08, 31.63, 24.79, 23.95, 22.57, 14.06.



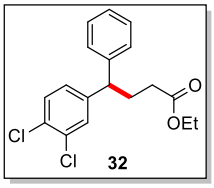
30

Yield 81%, 64 mg; eluent for column chromatography: Hexanes : EtOAc (9:1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.56 (t, *J* = 6.7, 2H), 1.49 (dt, *J* = 13.9, 6.6, 2H), 1.39 (p, *J* = 7.4, 2H), 1.20 (s, 12H), 0.85 (s, 9H), 0.74 (t, *J* = 7.7, 2H), 0.00 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 82.86, 63.15, 35.48, 25.99, 24.80, 20.22, 18.37, -5.26.

HRMS $C_{12}H_{26}BO_3Si$ MS-CI [M-C_2H_5] *m/z* calcd: 257.1747; found: 257.1741.



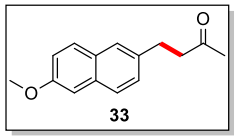
32

Yield 79%, 67 mg; eluent for column chromatography: Hexanes : EtOAc (9:1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 4H), 7.16 – 7.10 (m, 3H), 7.00 (dd, *J* = 8.3, 2.2, 1H), 4.03 (q, *J* = 7.1, 2H), 3.82 (t, *J* = 7.8, 1H), 2.31 – 2.23 (m, 2H), 2.20 – 2.15 (m, 2H), 1.16 (t, *J* = 7.1, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.07, 144.61, 142.81, 132.49, 130.46, 129.79, 128.81, 127.76, 127.27, 126.86, 60.48, 49.63, 32.52, 30.28, 14.22.

HRMS $C_{18}H_{18}O_2Cl_2$ C_2H_5 GC-CI [M+ C_2H_5] *m/z* calcd: 365.1075; found: 365.1070.

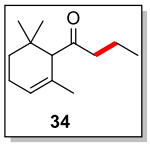


33

Yield 83%, 47 mg; eluent for column chromatography: Hexanes : EtOAc (8:2)

^{1}H NMR[10] (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.6, 2H), 7.56 (d, *J* = 1.8, 1H), 7.30 (dd, *J* = 8.3, 1.8, 1H), 7.18 – 7.10 (m, 2H), 3.92 (s, 3H), 3.04 (t, *J* = 7.6, 2H), 2.84 (t, *J* = 7.6, 2H), 2.16 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 208.03, 157.32, 136.16, 133.13, 129.09, 128.95, 127.55, 126.99, 126.27, 118.84, 105.66, 55.29, 45.20, 30.13, 29.73.



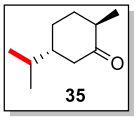
34

Yield 94%, 46 mg; passed from short plug of silica and washed with hexanes : diethyl ether (8:2)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.57 (ddt, *J* = 4.4, 2.8, 1.4, 1H), 2.75 (s, 1H), 2.54 (ddd, *J* = 17.7, 8.2, 6.4, 1H), 2.41 (ddd, *J* = 17.7, 8.2, 6.2, 1H), 2.16 – 1.99 (m, 2H), 1.75 (ddd, *J* = 13.3, 10.6, 6.6, 1H), 1.68 – 1.50 (m, 5H), 1.14 (dd, *J* = 13.2, 6.0, 1H), 0.96 – 0.90 (m, 6H), 0.89 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 213.55, 130.23, 123.38, 63.38, 47.79, 32.36, 30.70, 27.92, 27.76, 23.43, 22.66, 16.81, 13.77.

HRMS $C_{13}H_{22}O$ C_2H_5 GC-CI [M+ C_2H_5] *m/z* calcd: 223.2062; found: 223.2051.

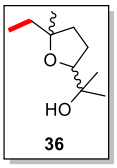


35

Yield 100%, 39 mg; passed from short plug of silica and washed with hexanes : diethyl ether (8:2)

^{1}H NMR[11] (500 MHz, $CDCl_3$) δ 2.42 – 2.29 (m, 2H), 2.16 – 2.00 (m, 2H), 1.86 (dp, *J* = 11.6, 3.2, 1H), 1.67 – 1.51 (m, 2H), 1.50 – 1.37 (m, 1H), 1.30 (qd, *J* = 13.0, 3.4, 1H), 1.01 (d, *J* = 6.5, 3H), 0.93 – 0.81 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 213.72, 46.58, 45.38, 44.90, 35.09, 32.75, 28.89, 19.60, 19.34, 14.35.



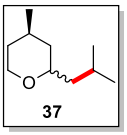
36

Yield 99%, 43 mg; passed from short plug of silica and washed with hexanes : diethyl ether (6:4)

^{1}H NMR (500 MHz, $CDCl_3$; *cis:trans* (1:1)) δ 3.81 – 3.77 (m, 1H), 3.75 – 3.70 (m, 1H), 2.22 (s, 1H), 2.14 (s, 1H), 1.89 – 1.72 (m, 6H), 1.65 (tdd, *J* = 9.4, 6.6, 4.0, 2H), 1.60 – 1.48 (m, 4H), 1.21 (s, 6H), 1.18 (d, *J* = 3.6, 6H), 1.12 (s, 6H), 0.91 (q, *J* = 7.4, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 85.62, 84.62, 83.52, 83.48, 71.15, 70.68, 36.63, 36.44, 34.15, 33.78, 27.58, 27.45, 26.54, 26.49, 26.03, 25.07, 24.13, 24.03, 9.05, 8.87.

HRMS $C_{10}H_{19}O$ MS-CI [M-OH] *m/z* calcd: 155.1436; found: 155.1428.



37

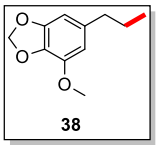
Yield 99%, 39 mg; passed from short plug of silica and washed with hexanes : diethyl ether (8:2)

^{1}H NMR (500 MHz, $CDCl_3$; *cis:trans* (3:1)) δ 3.98 (ddd, *J* = 11.4, 4.5, 1.3, 1H), 3.77 – 3.62 (m, 1H, *trans* product), 3.40 (td, *J* = 12.4, 2.1, 1H), 3.35 – 3.24 (m, 1H), 1.82 –

1.74 (m, 1H), 1.64 – 1.50 (m, 4H), 1.28 – 1.08 (m, 3H), 1.06 (d, *J* = 7.1, 1H, *trans* product), 0.93 (d, *J* = 6.3, 3H), 0.90 (d, *J* = 6.7, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 75.65, 70.06, 68.06, 62.32, 45.79, 44.19, 41.17, 38.13, 34.80, 32.45, 30.38, 24.92, 24.37, 24.29, 23.26, 22.39, 22.34, 18.89.

HRMS $C_{10}H_{20}O$ H MS-CI [M+H] *m/z* calcd: 157.1592; found: 157.1594.



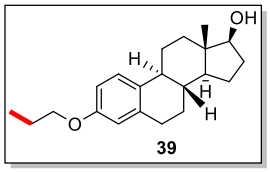
38

Yield 99%, 48 mg; eluent for column chromatography: Hexanes : EtOAc (9.5:0.5)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.39 (s, 1H), 6.35 (s, 1H), 5.94 (s, 2H), 3.91 (s, 3H), 2.55 – 2.47 (m, 2H), 1.62 (q, *J* = 7.5, 2H), 0.94 (t, *J* = 7.4, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 148.67, 143.35, 137.38, 133.10, 107.55, 102.46, 101.11, 56.54, 38.17, 24.77, 13.72.

HRMS $C_{11}H_{14}O_3$ MS-ESI [M] *m/z* calcd: 194.0943; found: 193.0934.



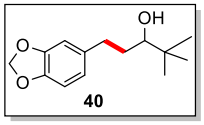
39

Yield 91%, 71 mg; eluent for column chromatography: Hexanes : EtOAc (7:3)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.6, 1H), 6.73 (dd, *J* = 8.7, 2.5, 1H), 6.66 (s, 1H), 3.92 (t, *J* = 6.6, 2H), 3.76 (d, *J* = 8.4, 1H), 2.94 – 2.81 (m, 2H), 2.39 – 2.31 (m, 1H), 2.25 – 2.09 (m, 2H), 1.97 (dt, *J* = 12.3, 2.9, 1H), 1.94 – 1.86 (m, 1H), 1.82 (h, *J* = 6.9, 2H), 1.72 (dddd, *J* = 12.4, 9.7, 6.6, 3.8, 1H), 1.65 (s, 1H), 1.57 – 1.28 (m, 6H), 1.25 – 1.18 (m, 1H), 1.05 (td, *J* = 7.4, 1.5, 3H), 0.81 (d, *J* = 1.5, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.02, 137.92, 132.48, 126.29, 114.54, 112.05, 81.92, 69.47, 50.07, 43.99, 43.29, 38.90, 36.76, 30.60, 29.83, 27.31, 26.36, 23.16, 22.68, 11.10, 10.58.

HRMS $C_{21}H_{30}O_2$ MS-ESI [M+] *m/z* calcd: 314.2246; found: 314.2251.



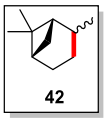
40

Yield 99%, 58 mg; eluent for column chromatography: Hexanes : EtOAc (8:2)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.75 (dd, *J* = 7.9, 1.8, 2H), 6.68 (d, *J* = 7.9, 1H), 5.92 (s, 2H), 3.22 (d, *J* = 10.6, 1H), 2.90 – 2.80 (m, 1H), 2.64 – 2.50 (m, 1H), 1.87 – 1.73 (m, 1H), 1.60 (s, 1H), 1.58 – 1.51 (m, 1H), 0.97 – 0.86 (m, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.57, 145.56, 136.31, 121.14, 108.95, 108.17, 100.73, 79.17, 34.95, 33.60, 33.05, 25.68.

HRMS $C_{14}H_{20}O_3$ MS-ESI [M+] *m/z* calcd: 236.1413; found: 236.1407.



42

Yield 87%, 30 mg; passed from short plug of silica and washed with hexanes : diethyl ether (8:2)

^{1}H NMR (500 MHz, $CDCl_3$; *cis:trans* (6:4)) δ 2.36 – 2.29 (m, 1H), 2.15 (dpd, *J* = 9.4, 7.2, 2.2, 1H), 1.95 (dddt, *J* = 12.6, 10.7, 4.9, 2.6, 2H), 1.89 (dt, *J* = 5.7, 2.8, 1H), 1.87 – 1.82 (m, 1H), 1.77 (ddd, *J* = 7.0, 3.9, 1.9, 1H), 1.48 – 1.38 (m, 1H), 1.34 (d, *J* = 9.9, 0.59H; *trans* product), 1.20 (s, 3H), 1.03 (s, 3H), 1.02 (d, *J* = 7.3, 3H), 0.88 (d, *J* = 8.6, 1H).

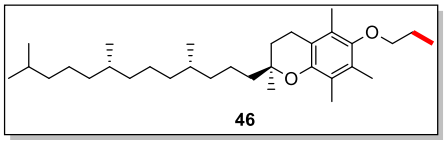
^{13}C NMR (126 MHz, $CDCl_3$) δ 48.10, 47.65, 41.38, 40.91, 39.49, 38.82, 35.95, 33.95, 29.35, 28.31, 26.84, 26.54, 24.61, 23.94, 23.83, 23.21, 23.04, 22.89, 21.60, 20.08.

HRMS: $C_{10}H_{17}$ MS-CI [M-H] *m/z* calcd: 137.1330; found: 137.1324.

Yield 80%, 22 mg; passed from short plug of silica and washed with hexanes : diethyl ether (8:2)

^{1}H NMR[12] (500 MHz, $CDCl_3$; *endo:exo* (85:15)) δ 2.13 (t, *J* = 4.3, 1H), 2.00 (s, 1H), 1.91 (dtdd, *J* = 12.4, 5.4, 4.0, 1.7, 1H), 1.76 (tdd, *J* = 11.6, 4.7, 3.1, 1H), 1.56 (d, *J* = 0.9, 1H), 1.50 – 1.45 (m, 1H), 1.35 (dt, *J* = 9.3, 1.9, 1H), 1.27 (dd, *J* = 9.1, 2.2, 1H), 1.13 – 1.07 (m, 1H), 0.95 (d, *J* = 7.0, 3H), 0.88 (d, *J* = 6.8, 0.52H (CH_3 of endo product)), 0.55 (ddd, *J* = 11.9, 5.2, 2.4, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 41.73, 40.32, 38.47, 37.69, 34.09, 30.24, 22.07, 17.45.

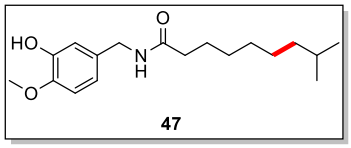


Yield 99%, 117 mg; eluent for column chromatography: Hexanes : EtOAc (9.5:0.5)

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.64 (t, *J* = 6.7, 2H), 2.60 (t, *J* = 6.8, 2H), 2.20 (s, 3H), 2.16 (s, 3H), 2.12 (s, 3H), 1.89 – 1.75 (m, 4H), 1.66 – 1.53 (m, 3H), 1.52 – 1.36 (m, 5H), 1.36 – 1.28 (m, 6H), 1.26 (s, 4H), 1.17 (dtd, *J* = 9.1, 6.5, 6.0, 2.1, 3H), 1.10 (t, *J* = 7.4, 6H), 0.89 (dd, *J* = 11.8, 6.6, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 147.64, 127.87, 125.82, 122.76, 117.45, 74.73, 74.61, 40.13, 40.09, 39.41, 37.62, 37.53, 37.49, 37.45, 37.42, 37.37, 37.32, 32.83, 32.81, 32.72, 32.70, 31.35, 31.31, 28.01, 24.85, 24.83, 24.48, 24.46, 23.91, 23.55, 22.74, 22.65, 21.07, 21.05, 20.69, 19.77, 19.71, 19.65, 12.73, 11.87, 11.80, 10.75.

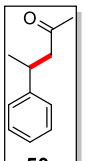
HRMS $C_{32}H_{56}O_2$ MS-ESI [M+] *m/z* calcd: 472.4280; found: 472.4274.



47

Yield 93%, 71 mg; eluent for column chromatography: Hexanes : EtOAc (1:1)

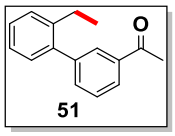
^{1}H NMR[13] (500 MHz, $CDCl_3$) δ 6.79 (d, *J* = 8.0, 1H), 6.74 (d, *J* = 1.8, 1H), 6.70 (dd, *J* = 8.0, 1.8, 1H), 5.56 (s, 1H), 5.51 (d, *J* = 4.6, 1H), 4.29 (d, *J* = 5.7, 2H), 3.81 (s, 3H), 2.16 – 2.09 (m, 2H), 1.58 (p, *J* = 7.5, 2H), 1.43 (dq, *J* = 13.2, 6.6, 1H), 1.28 – 1.22 (m, 2H), 1.22 – 1.17 (m, 4H), 1.07 (dd, *J* = 8.4, 5.4, 2H), 0.78 (d, *J* = 6.6, 6H).



50

Yield 99%, 40 mg; eluent for column chromatography: Hexanes : EtOAc (9:1)

^{1}H NMR[2] (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.7, 2H), 7.21 (t, *J* = 7.3, 1H), 7.17 (d, *J* = 7.4, 2H), 3.01 (dd, *J* = 13.6, 6.8, 1H), 2.85 (h, *J* = 7.0, 1H), 2.58 (dd, *J* = 13.6, 7.7, 1H), 2.10 (s, 3H), 1.11 (d, *J* = 6.9, 3H).



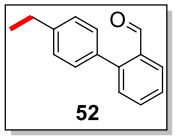
51

Yield 91%, 51 mg; eluent for column chromatography: Hexanes : EtOAc (9:1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 6.7, 1H), 7.94 (s, 1H), 7.54 (d, *J* = 7.1, 2H), 7.36 (d, *J* = 5.7, 2H), 7.28 (t, *J* = 7.8, 1H), 7.22 (d, *J* = 7.5, 1H), 2.65 (s, 3H), 2.61 (q, *J* = 7.5, 2H), 1.13 (t, *J* = 7.5, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.11, 142.42, 141.56, 140.54, 137.02, 133.86, 129.89, 129.16, 128.75, 128.38, 128.00, 126.74, 125.76, 26.74, 26.15, 15.62.

HRMS $C_{16}H_{16}O$ MS-ESI [M+] *m/z* calcd: 224.1201; found: 224.1207.

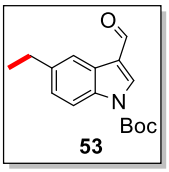


Yield 82%, 42 mg; eluent for column chromatography: Hexanes : EtOAc (9:1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.04 (d, *J* = 7.8, 1H), 7.64 (t, *J* = 7.5, 1H), 7.48 (dd, *J* = 17.9, 7.6, 2H), 7.32 (s, 4H), 2.75 (q, *J* = 7.6, 2H), 1.32 (t, *J* = 7.6, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 192.66, 146.06, 144.35, 133.78, 133.52, 130.79, 130.12, 127.97, 127.53, 28.58, 15.49.

HRMS $C_{15}H_{14}O$ MS-ESI [M+] *m/z* calcd: 210.1045; found: 210.1044.

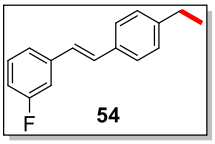


Yield 83%, 57 mg; eluent for column chromatography: Hexanes : EtOAc (8:2)

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.06 (s, 1H), 8.18 (s, 1H), 8.10 (s, 1H), 8.02 (d, *J* = 8.5, 1H), 7.24 (dd, *J* = 8.6, 1.8, 1H), 2.76 (q, *J* = 7.6, 2H), 1.68 (s, 9H), 1.27 (t, *J* = 7.6, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 185.93, 141.05, 136.69, 134.34, 126.39, 126.33, 120.88, 114.89, 85.48, 28.88, 28.09, 16.19.

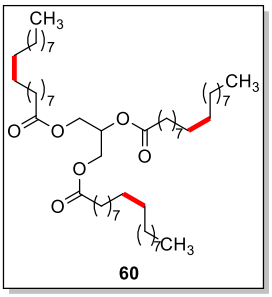
HRMS $C_{16}H_{19}NO_3$ Na MS-ESI [M+Na] *m/z* calcd: 296.1263; found: 296.1267.



Yield 89%, 50 mg; eluent for column chromatography: Hexanes : EtOAc (9.5:0.5)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.5, 2H), 7.33 (q, *J* = 6.9, 1H), 7.28 (d, *J* = 7.1, 1H), 7.23 (d, *J* = 8.1, 3H), 7.15 – 7.02 (m, 2H), 6.96 (t, *J* = 8.0, 1H), 2.69 (q, *J* = 7.7, 2H), 1.28 (t, *J* = 7.5, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 144.40, 139.99, 134.33, 130.09, 130.02, 129.99, 128.29, 126.68, 126.58, 126.56, 122.37, 122.34, 114.24, 114.07, 112.76, 112.58, 28.68, 15.52.
HRMS $C_{16}H_{15}F$ MS-ESI [M+] *m/z* calcd: 226.1158; found: 226.1154.



60

Yield 90%, 221 mg; eluent for column chromatography: Hexanes : EtOAc (9.5:0.5)
^{1}H NMR[14] (500 MHz, $CDCl_3$) δ 5.27 (dt, *J* = 9.5, 4.3, 1H), 4.30 (dd, *J* = 11.8, 3.9, 2H), 4.15 (dd, *J* = 11.8, 5.9, 2H), 2.31 (t, *J* = 7.4, 6H), 1.61 (s, 6H), 1.26 (s, 84H), 0.88 (t, *J* = 6.3, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.22, 68.86, 62.07, 34.03, 31.93, 29.71, 29.67, 29.63, 29.51, 29.48, 29.37, 29.27, 29.12, 24.90, 24.86, 22.69, 14.09.

4. References

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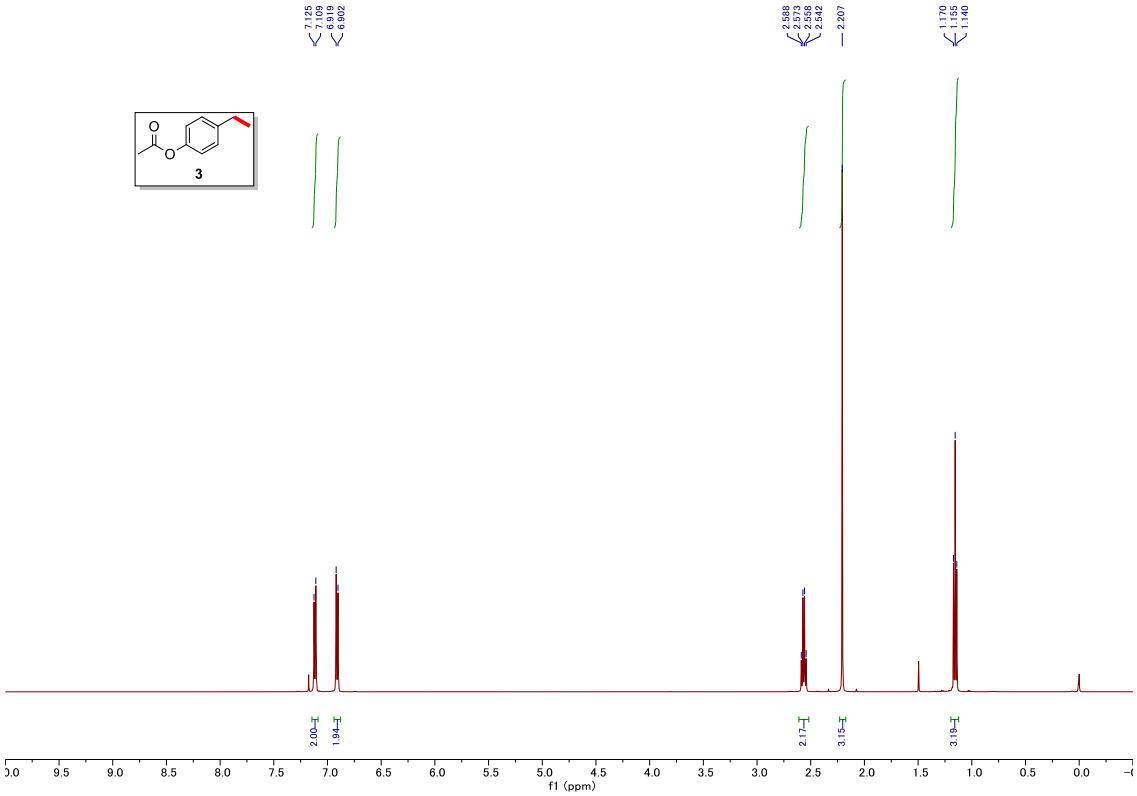
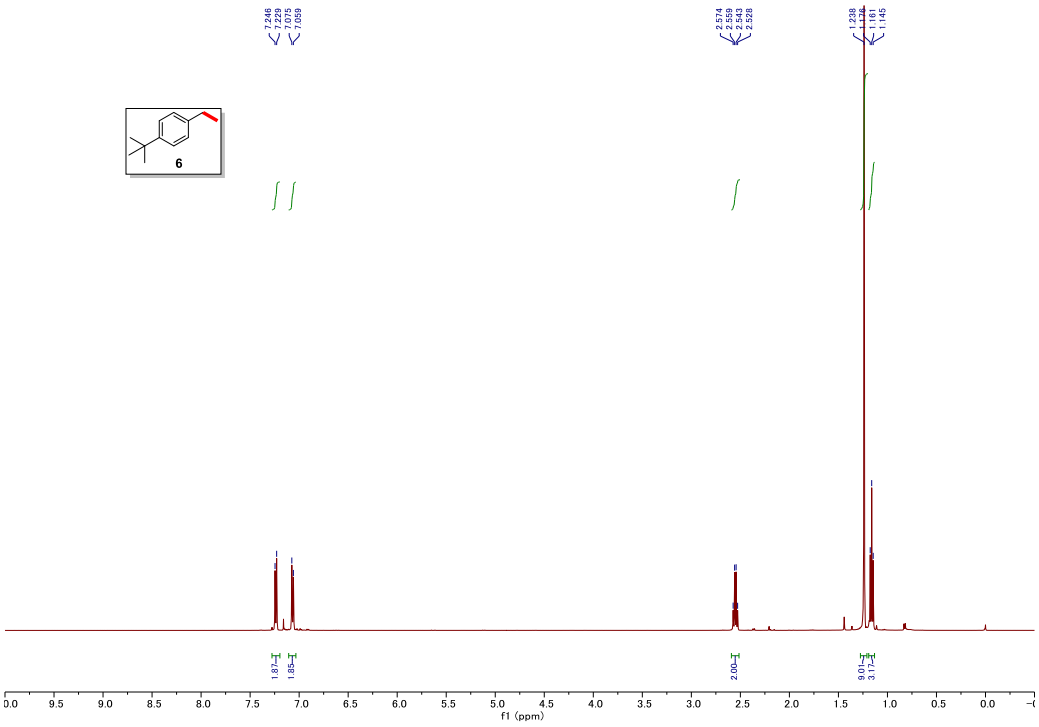
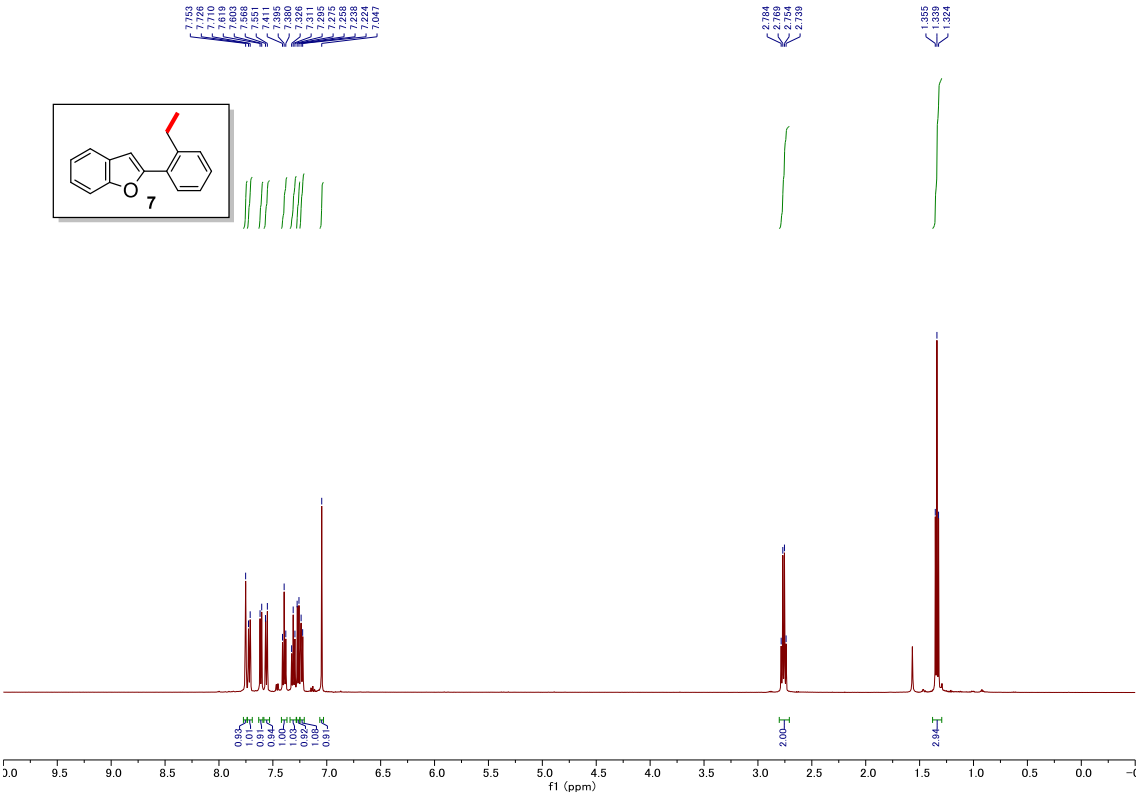
5. Copies of ^{1}HNMR and ^{13}CNMR spectra



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7.275
7.258
7.238
7.224
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2.784
2.769
2.754
2.739
1.355
1.339
1.324
O
7
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0.94
1.00
1.03
0.97
1.08
0.91
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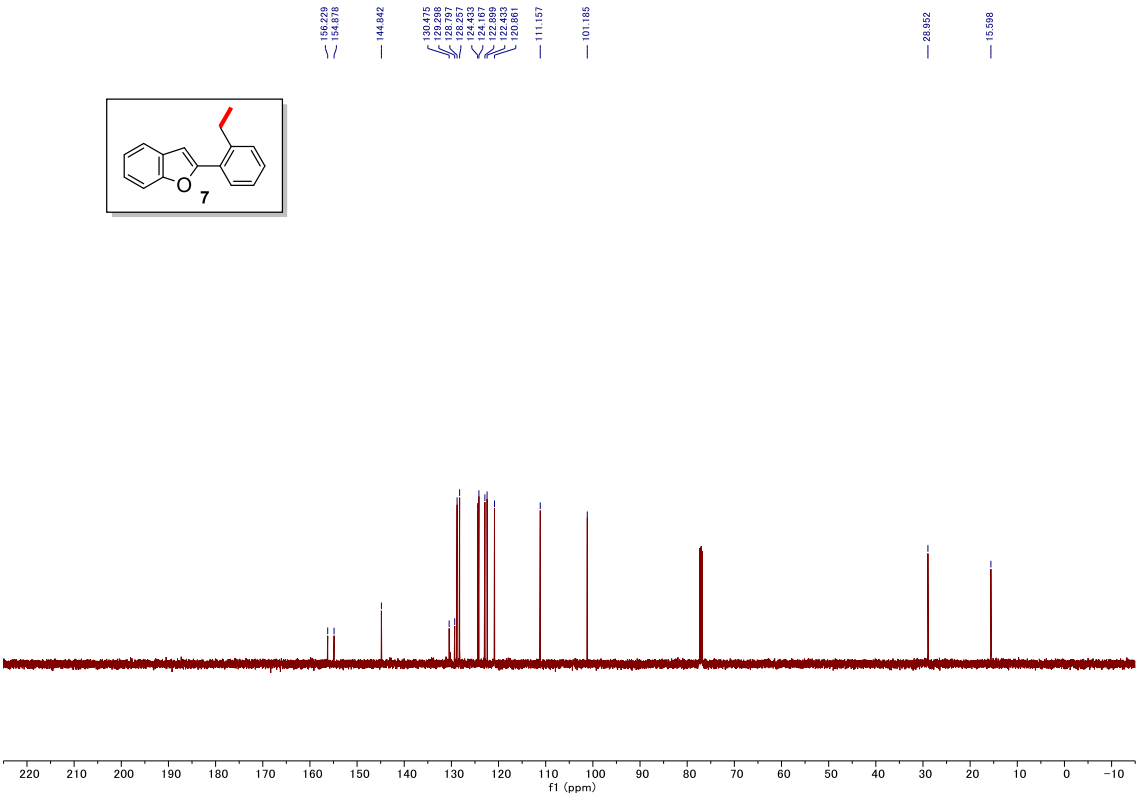
2.94
f1 (ppm)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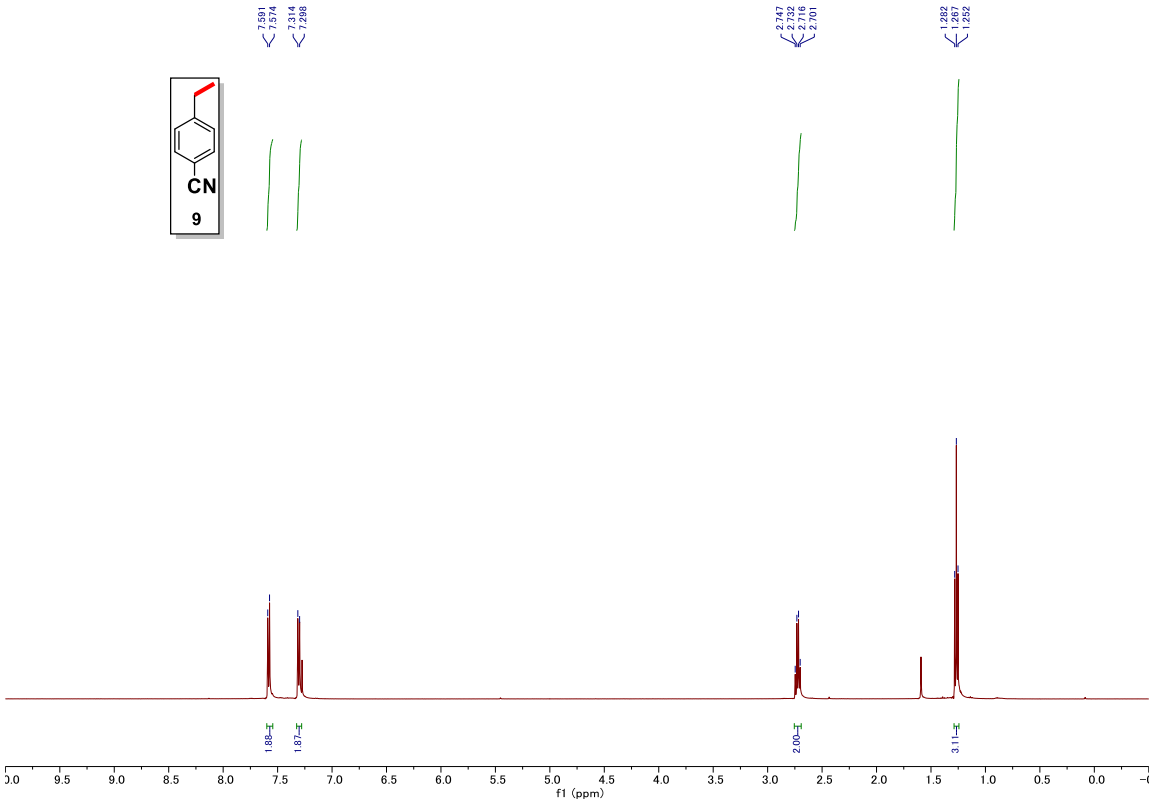
15.598
O
7
f1 (ppm)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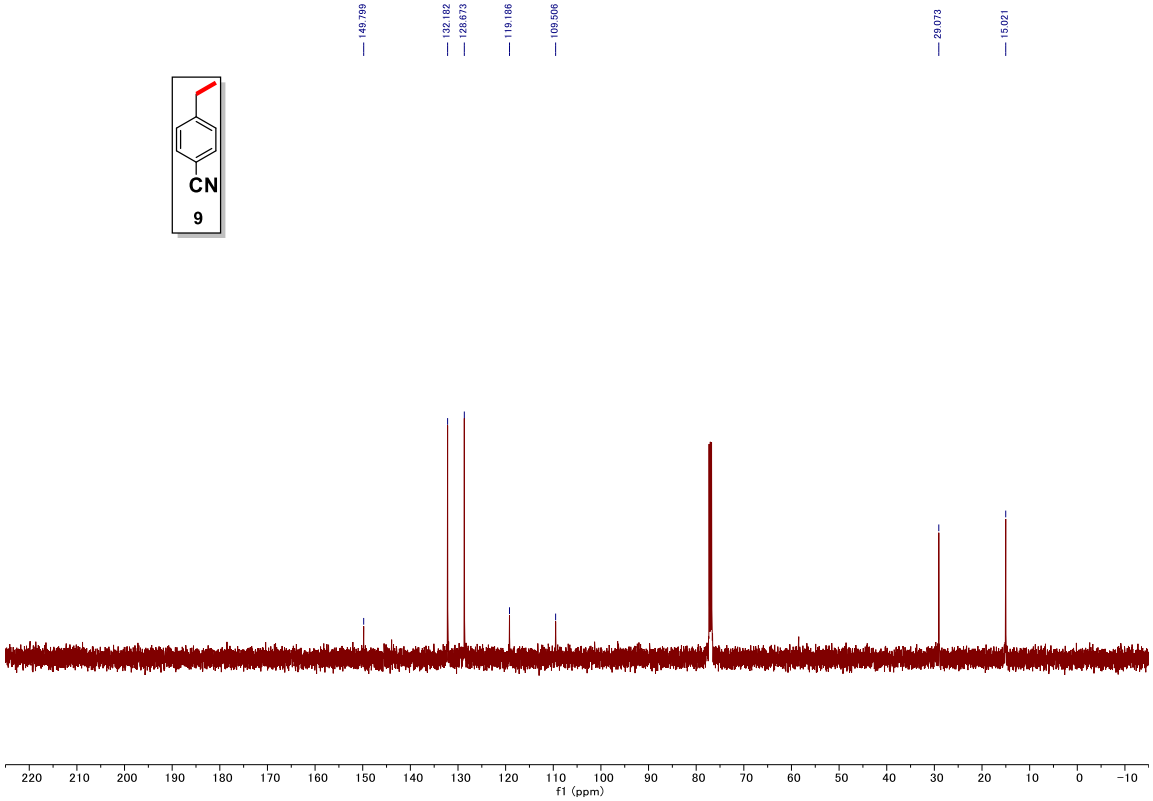
f1 (ppm)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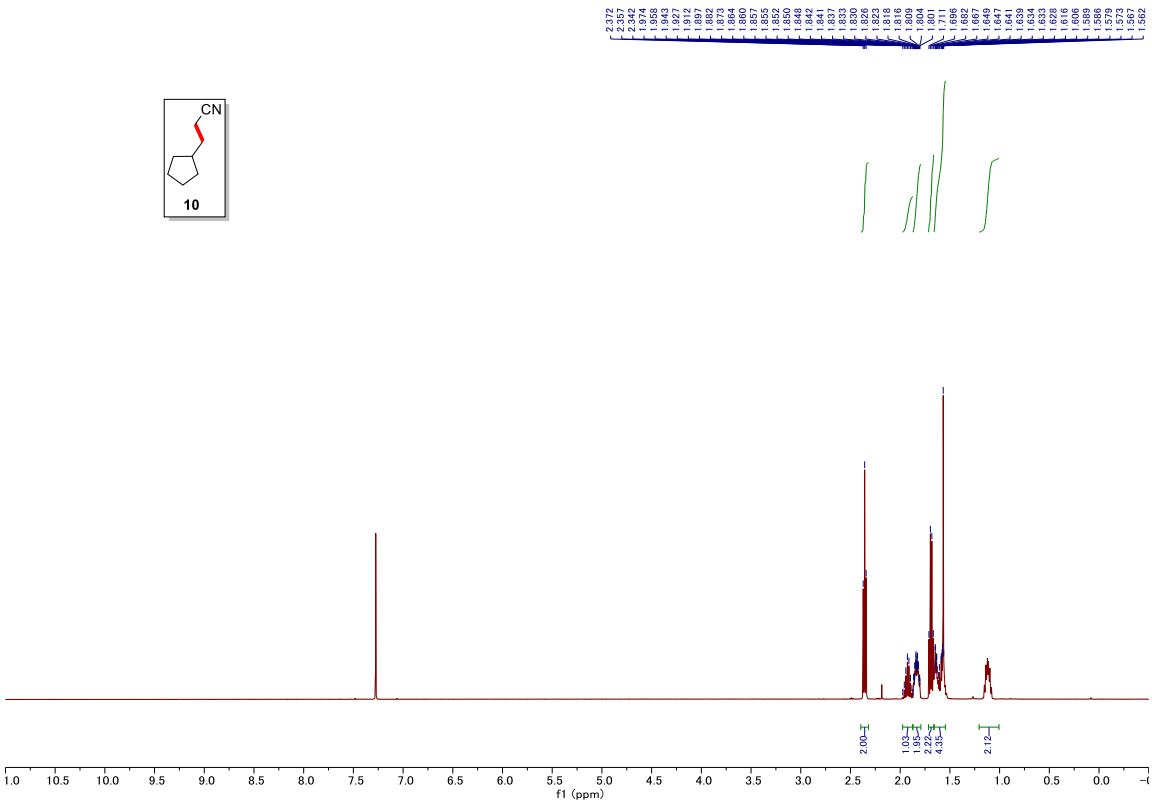
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1.912
1.897
1.882
1.873
1.864
1.860
1.857
1.855
1.852
1.850
1.848
1.847
1.841
1.837
1.833
1.830
1.826
1.823
1.818
1.816
1.809
1.804
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1.711
1.686
1.672
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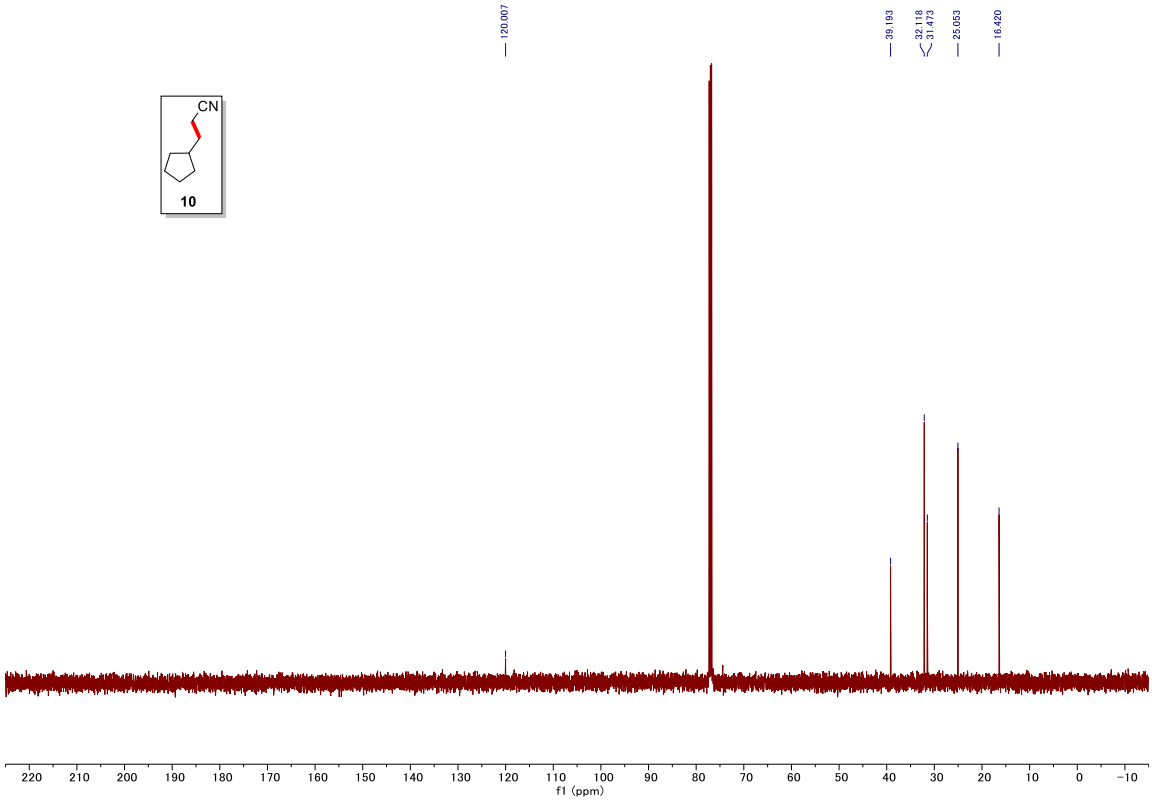
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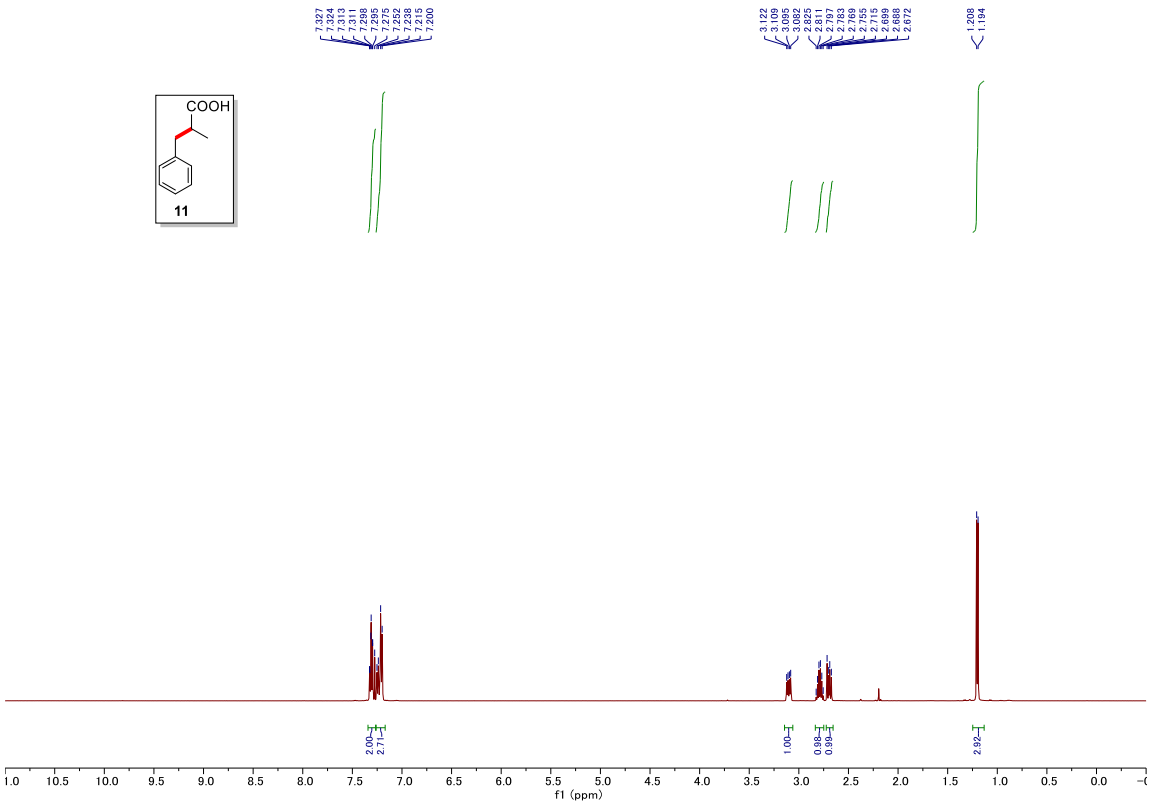
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2.755
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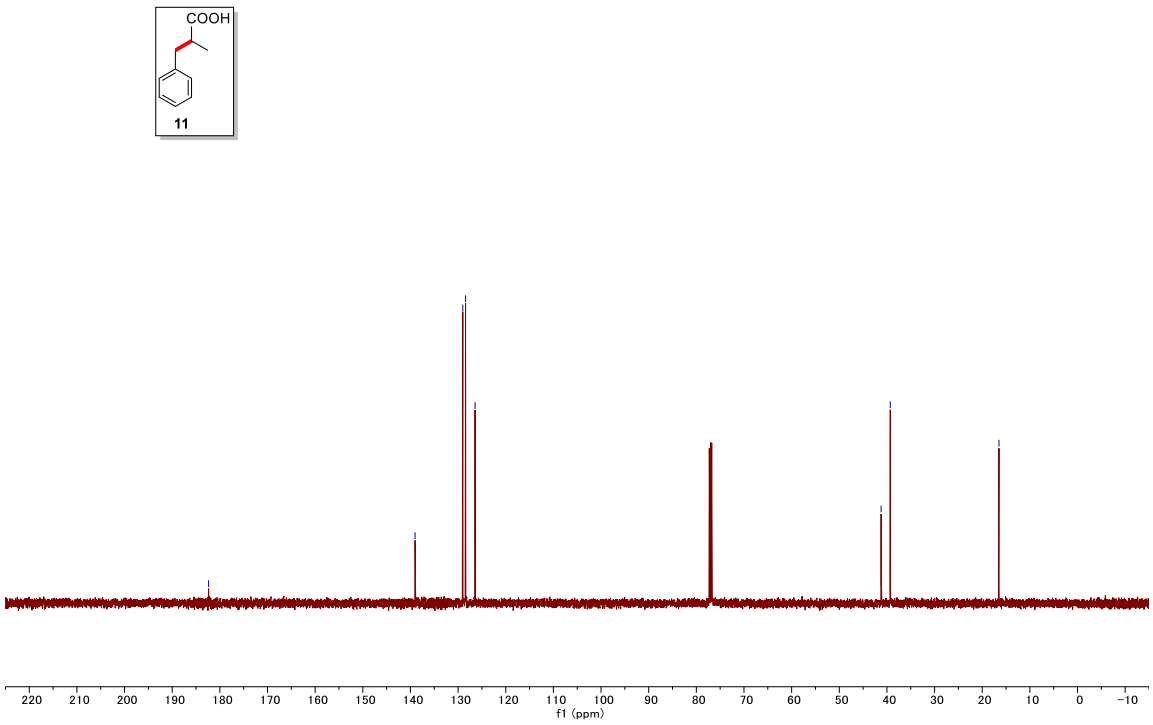
f1 (ppm)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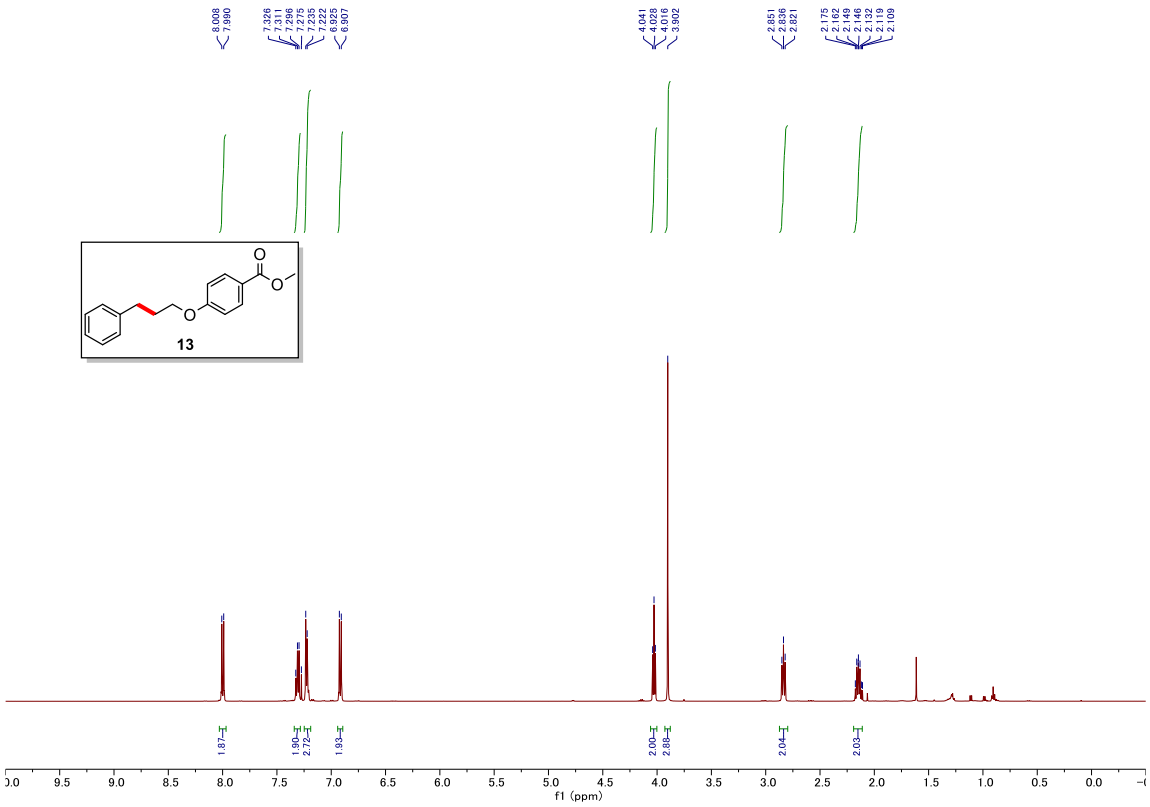
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3.902
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2.132
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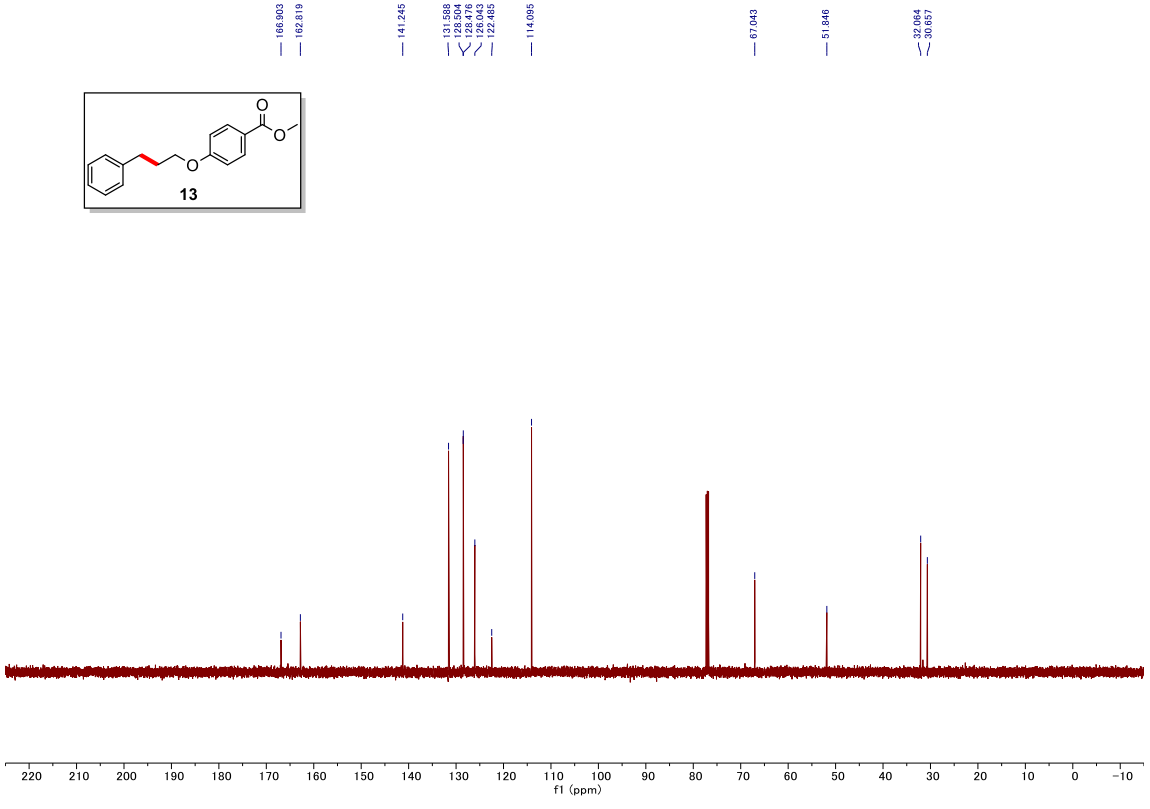
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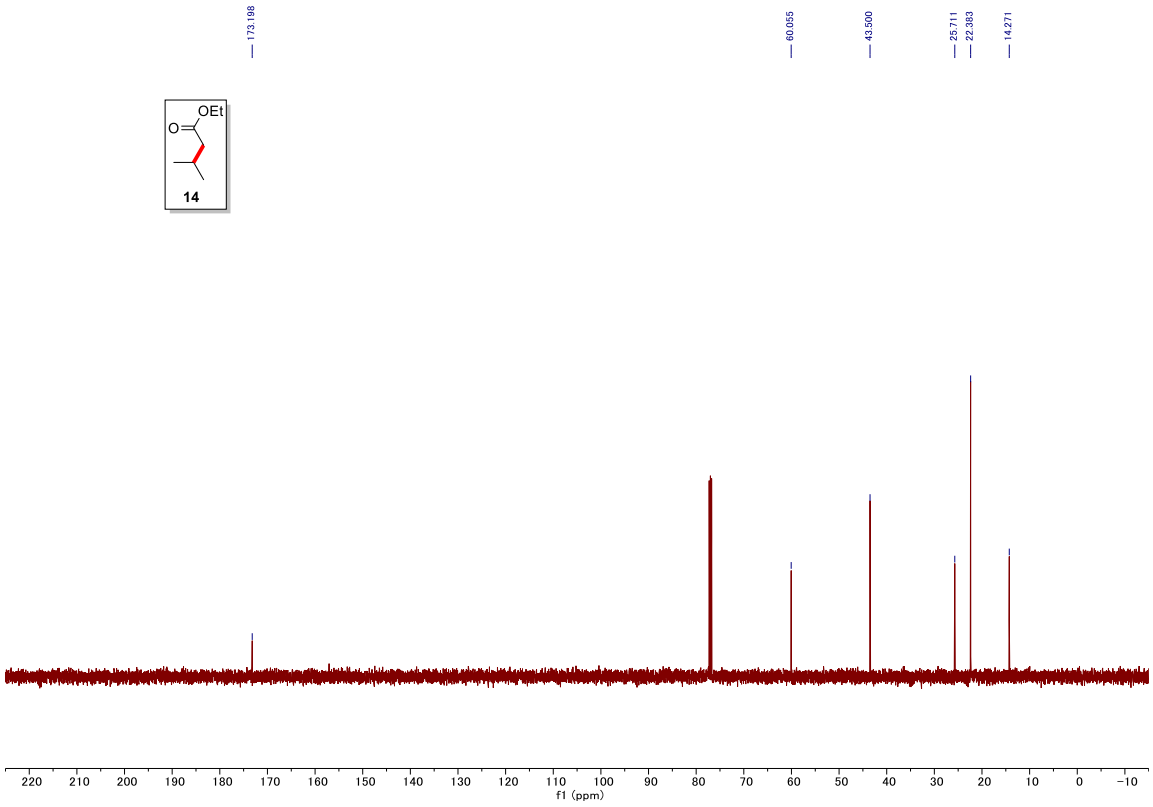
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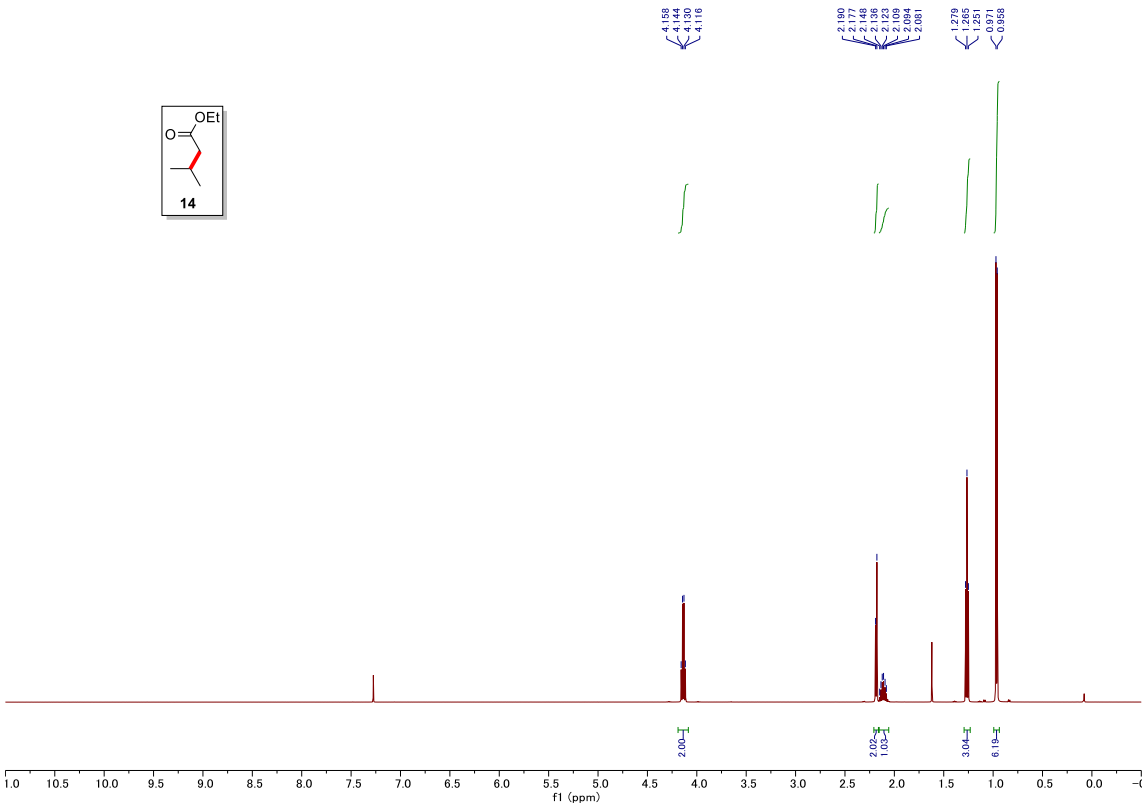
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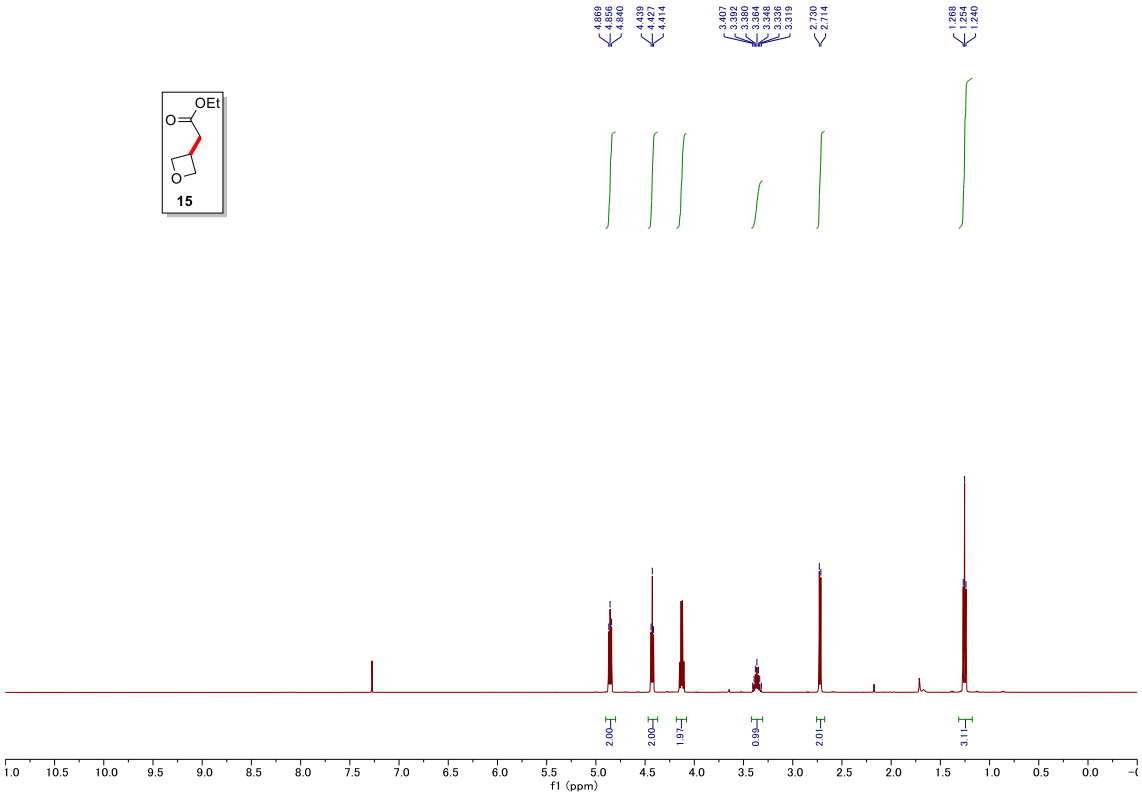
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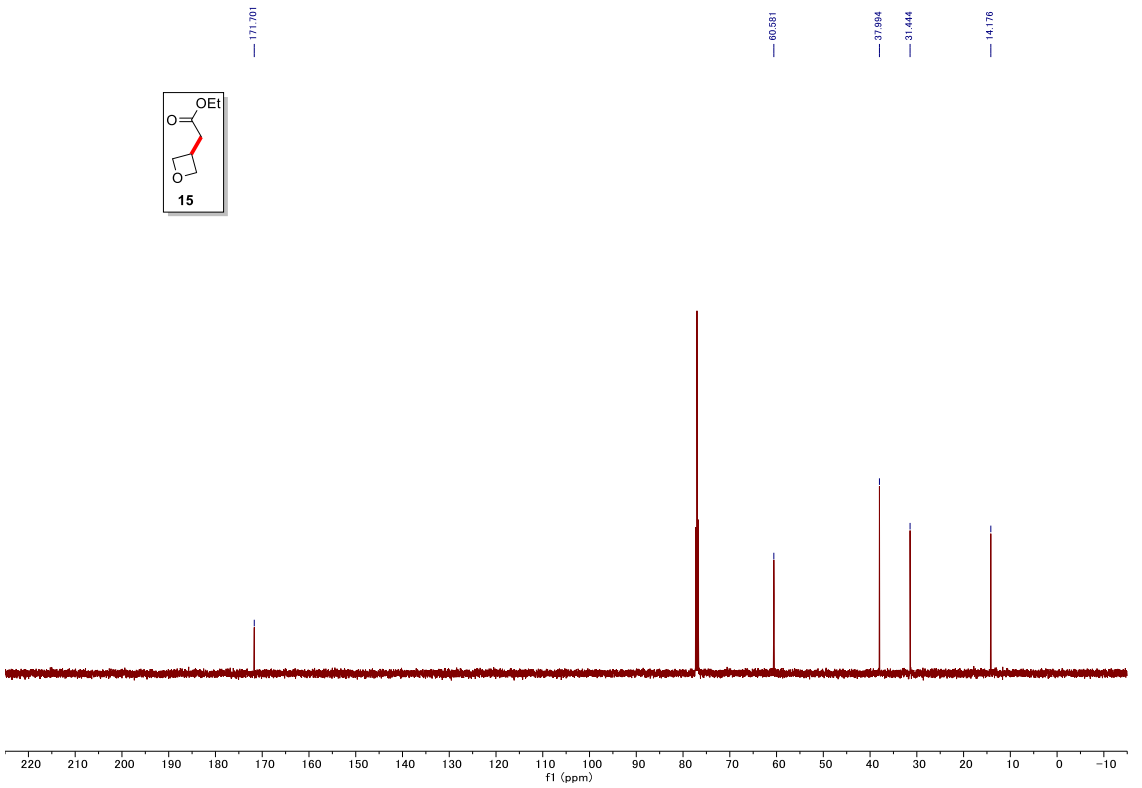
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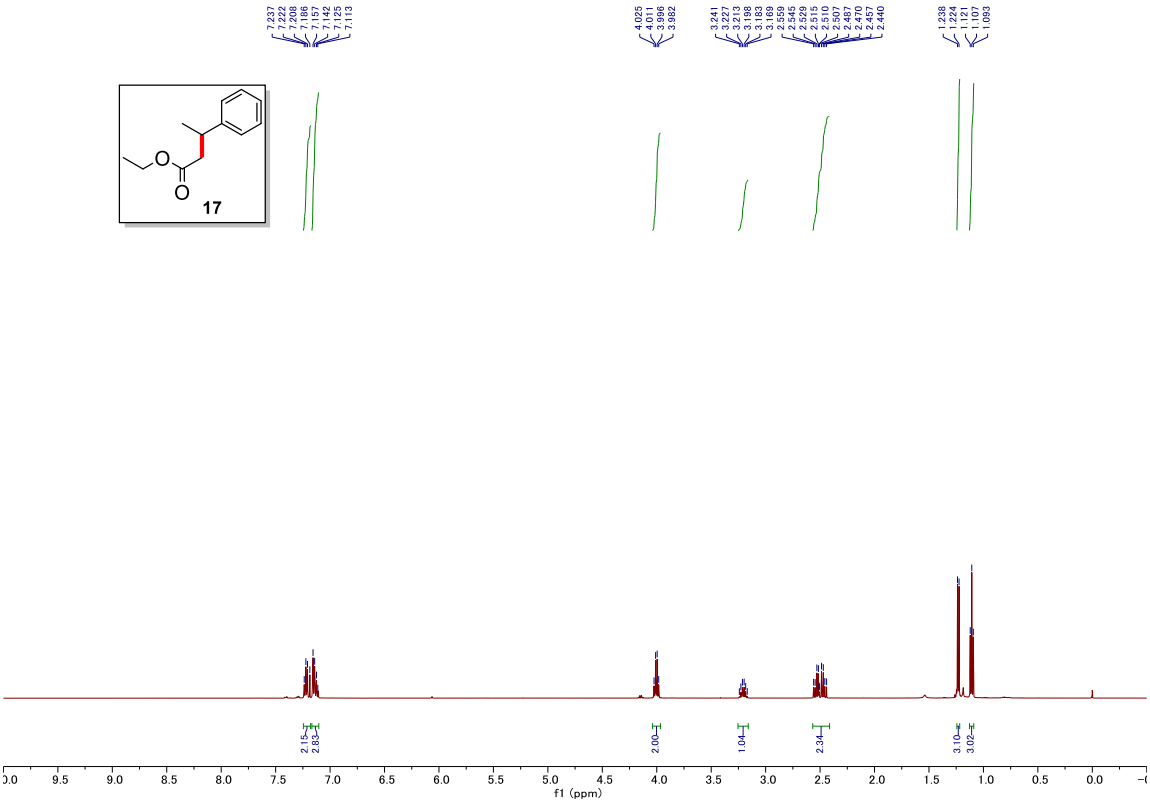
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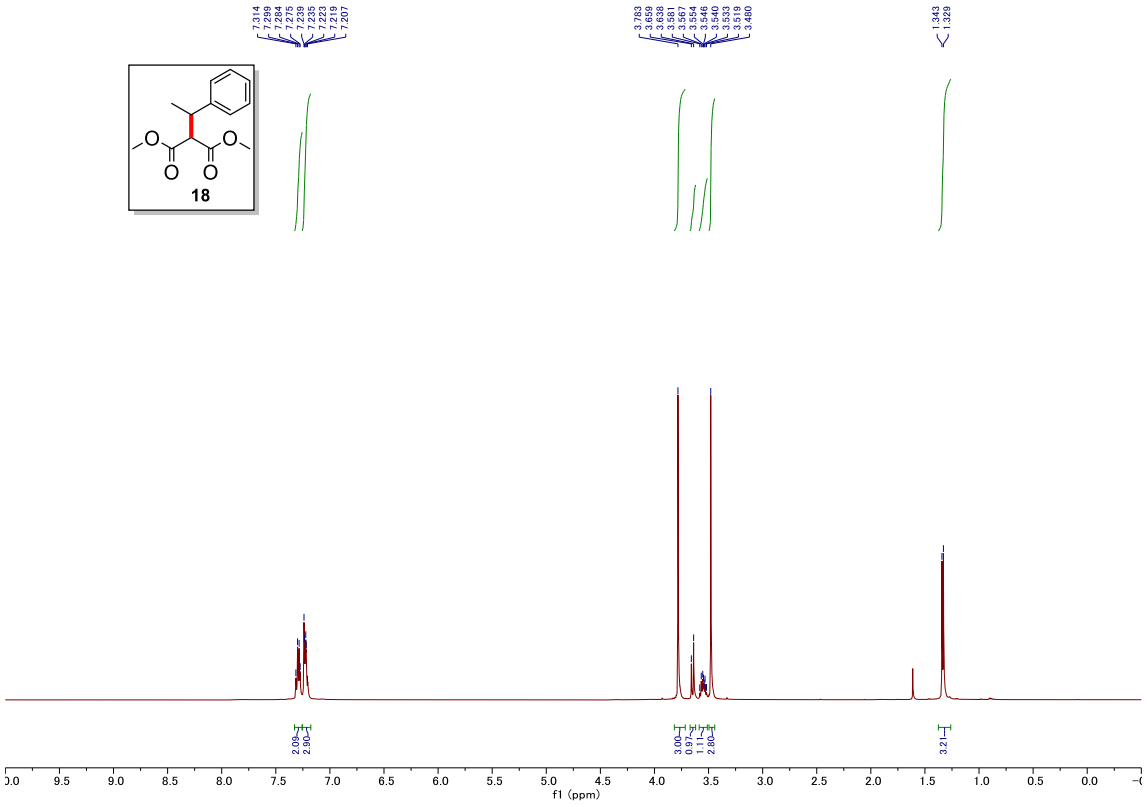
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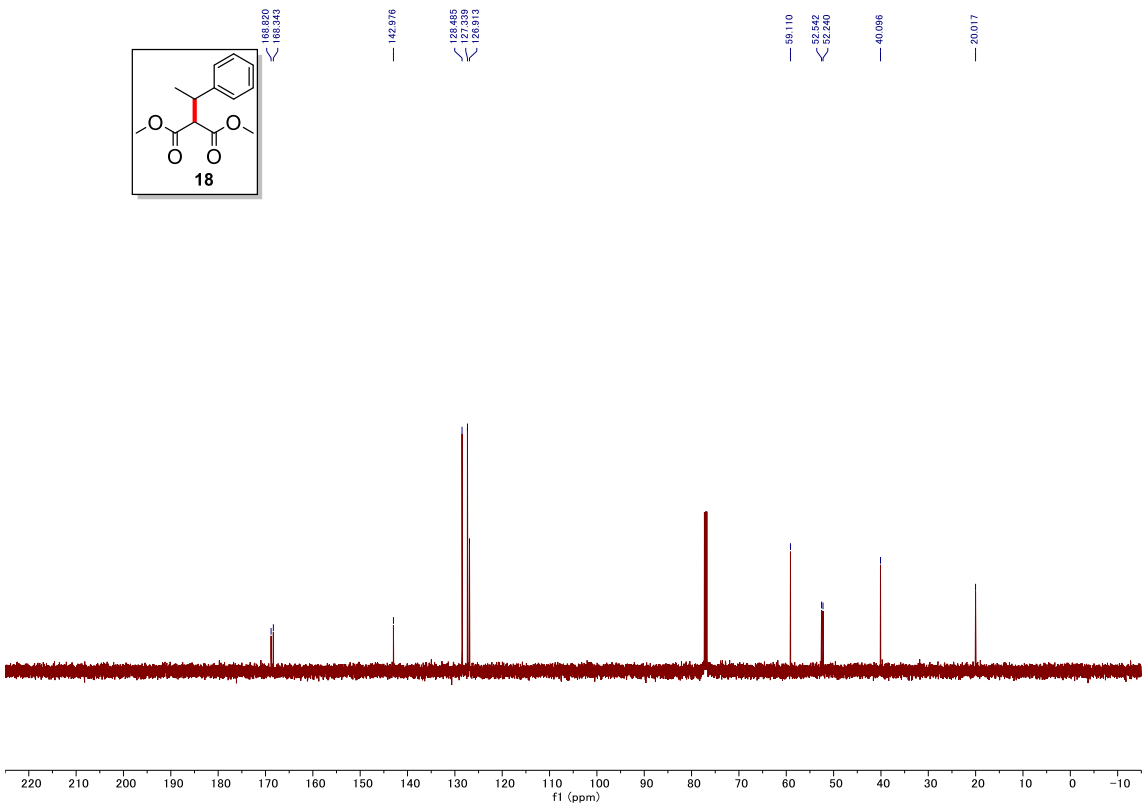
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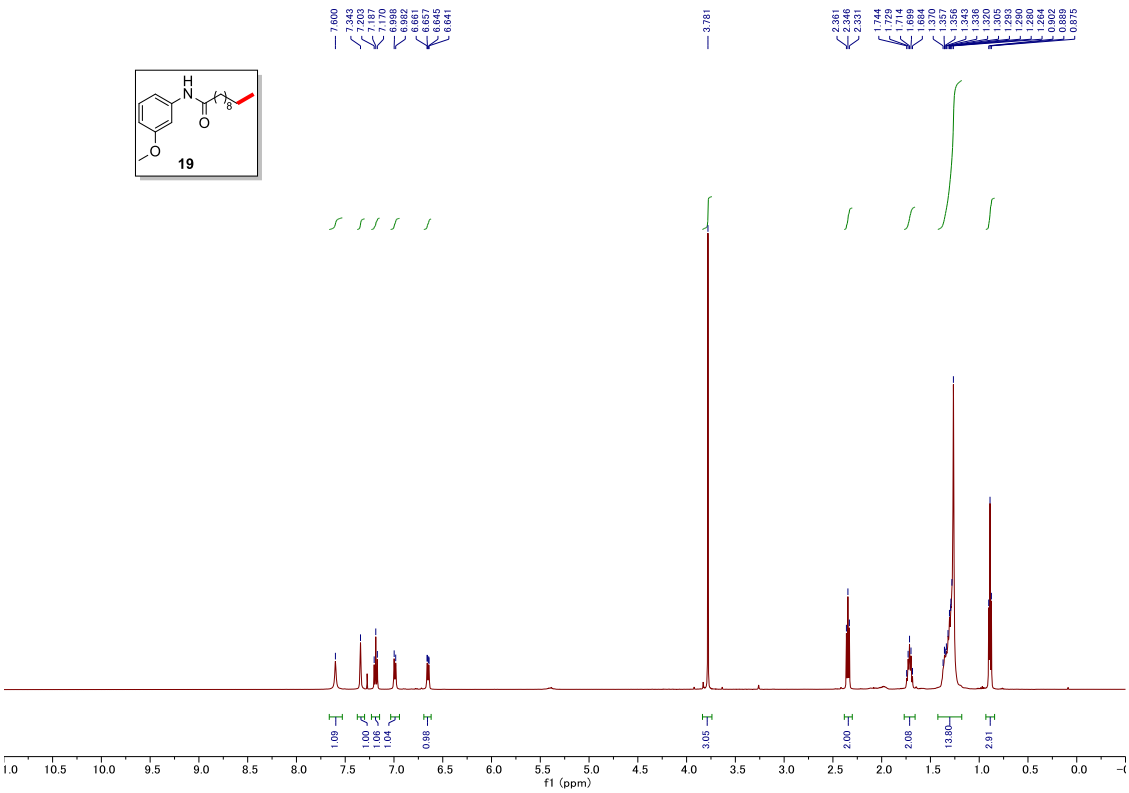
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0.875
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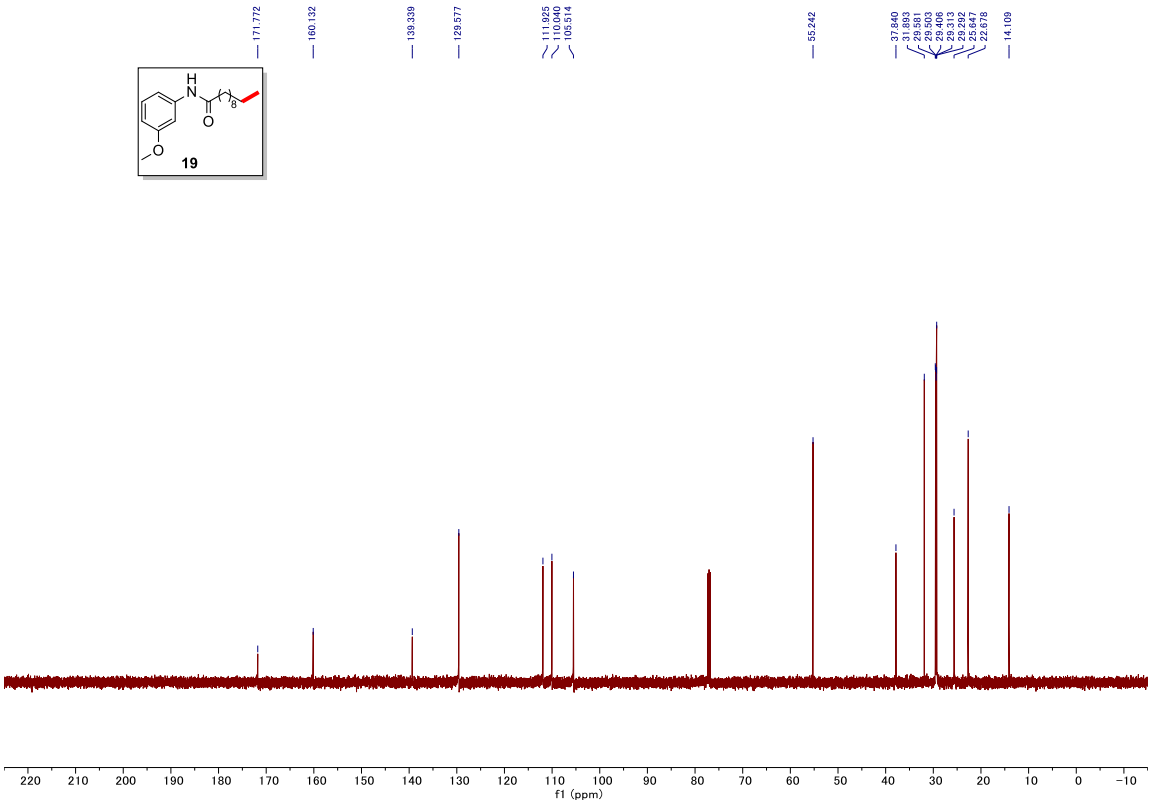
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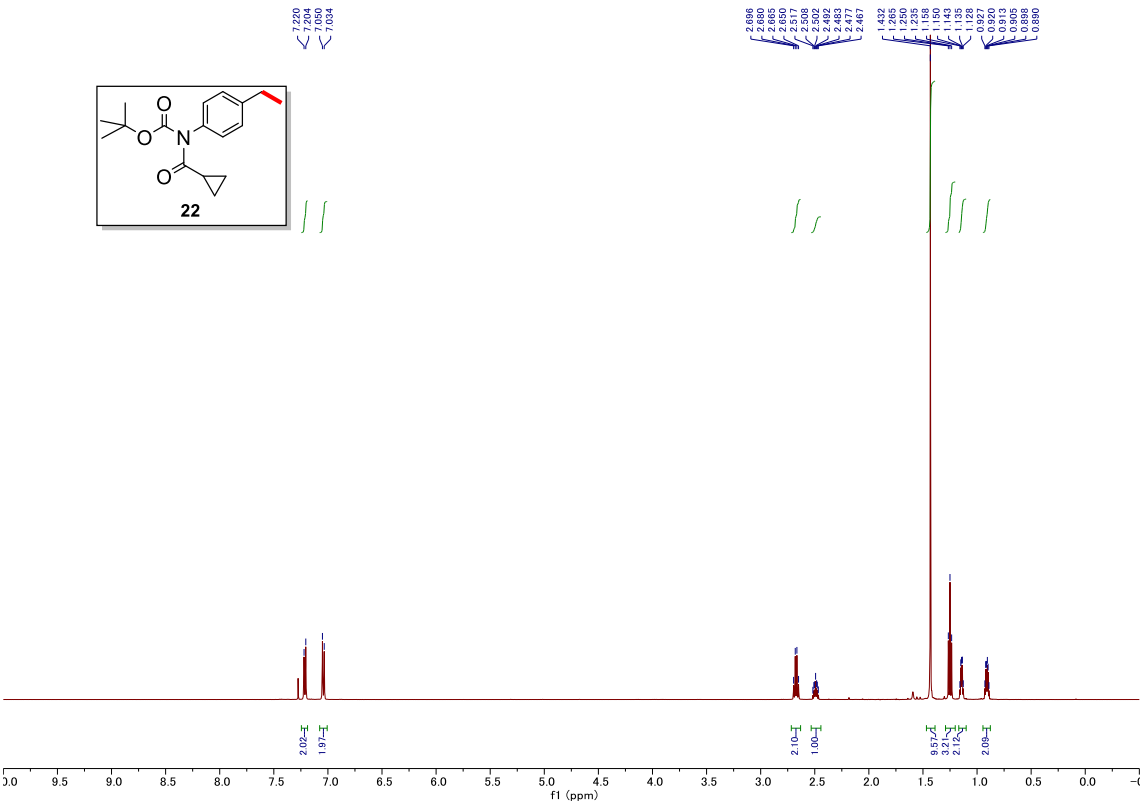
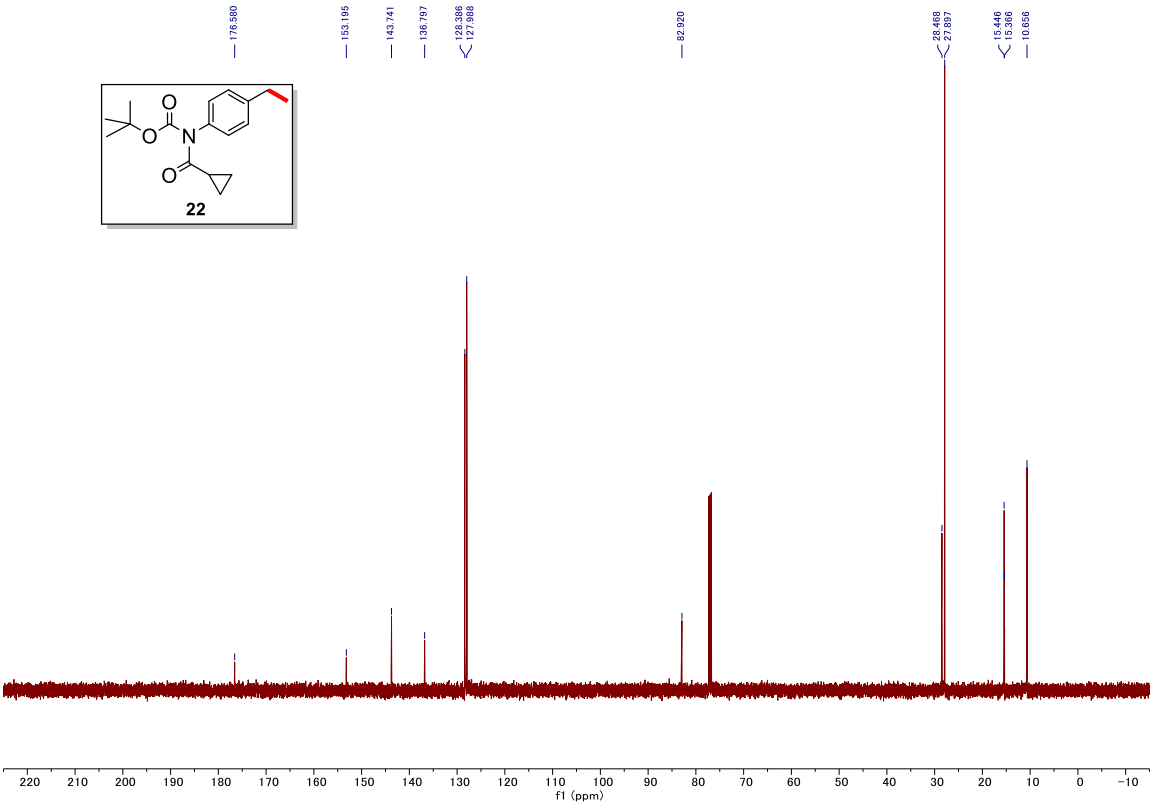
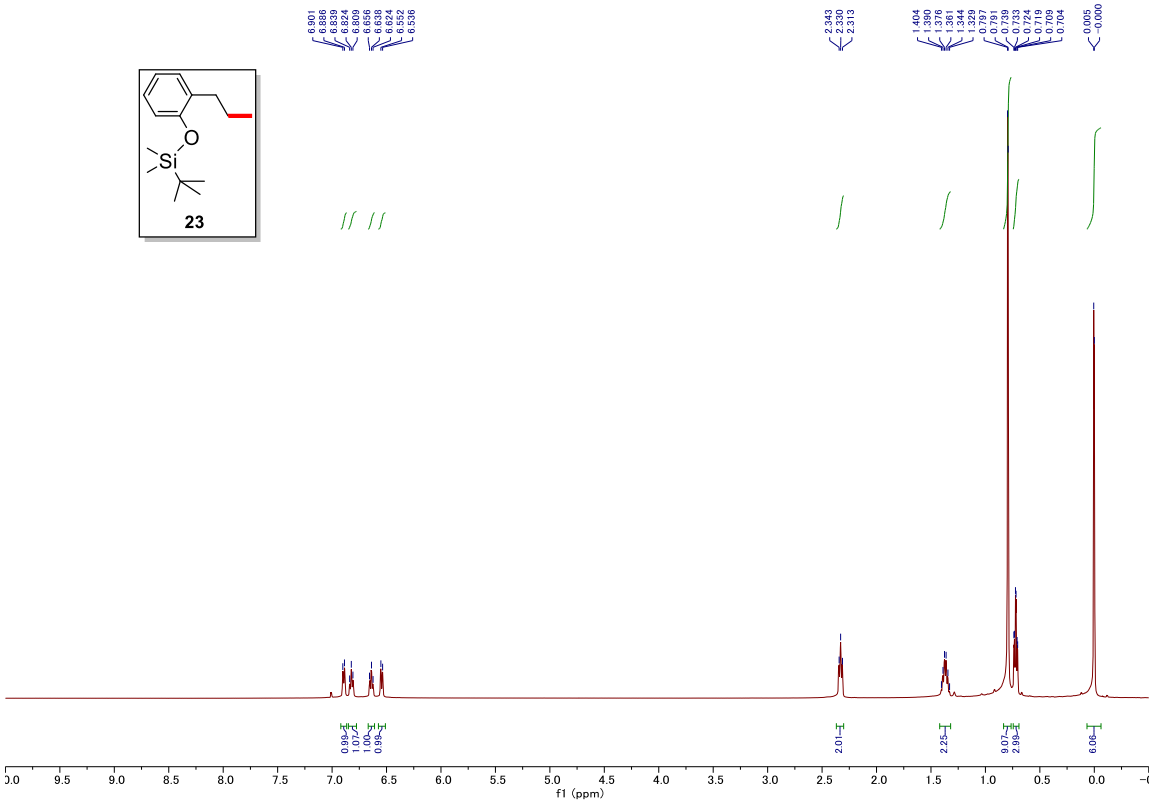
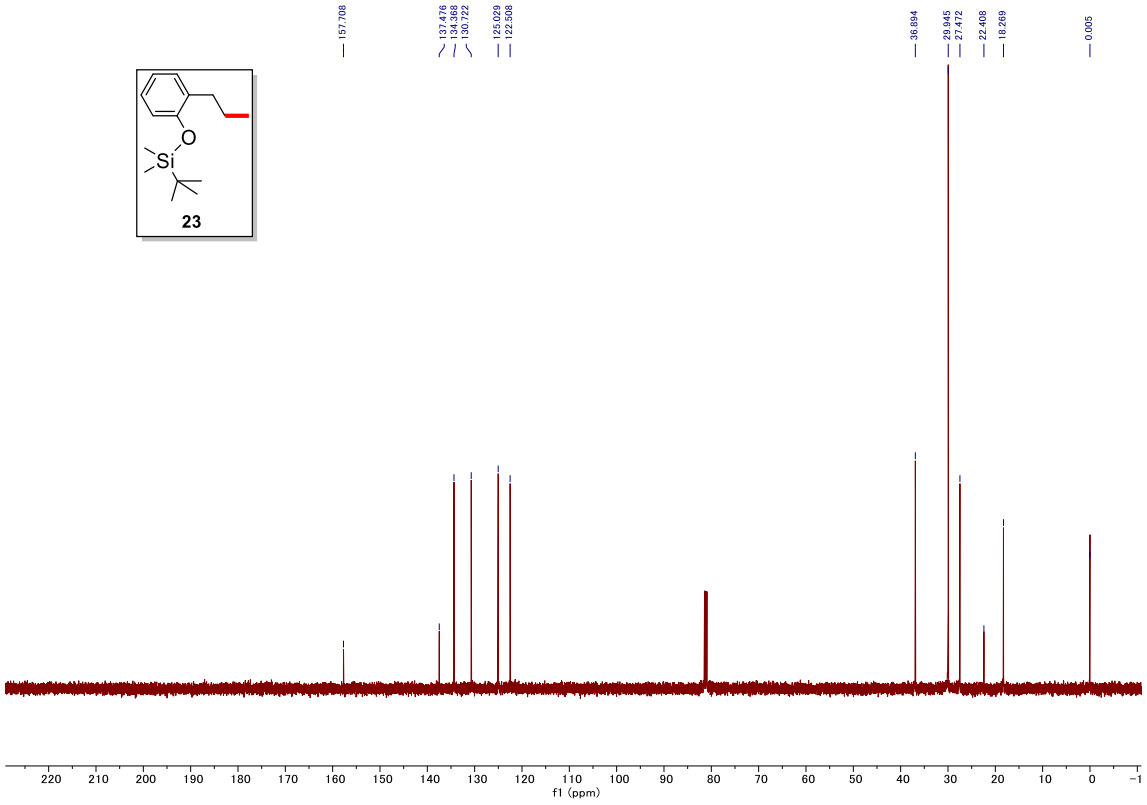
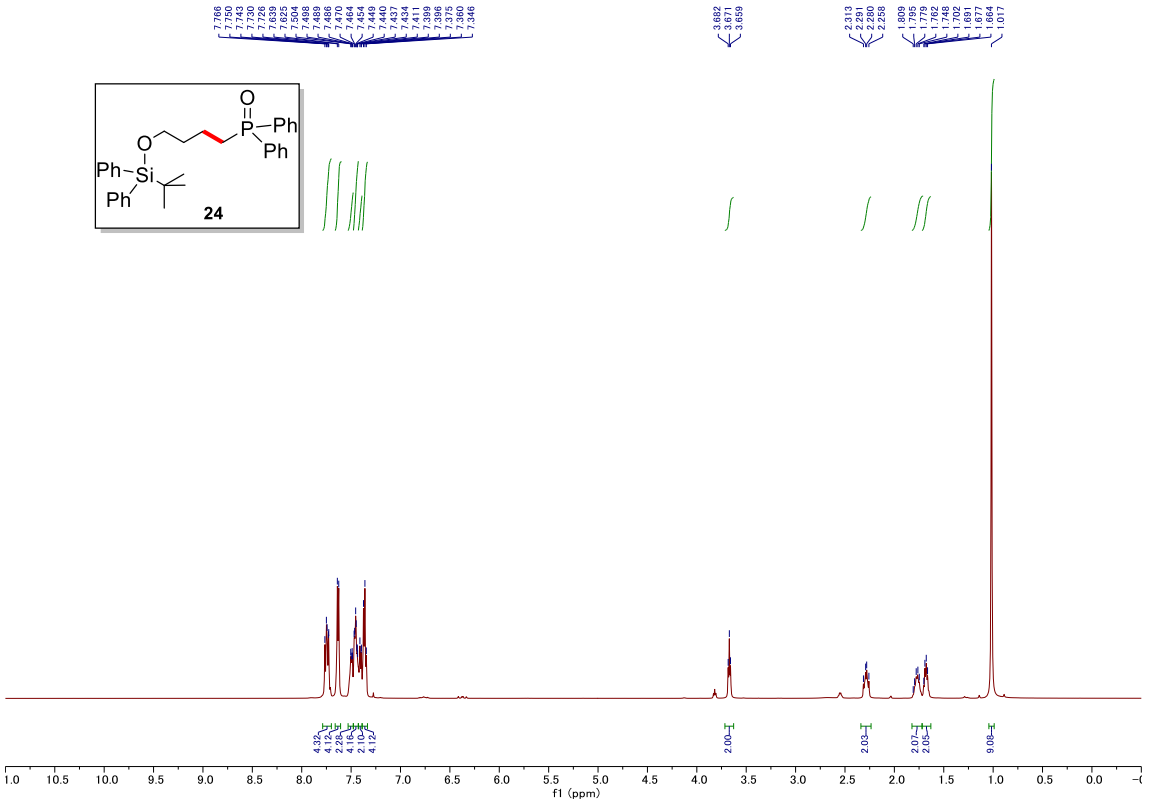
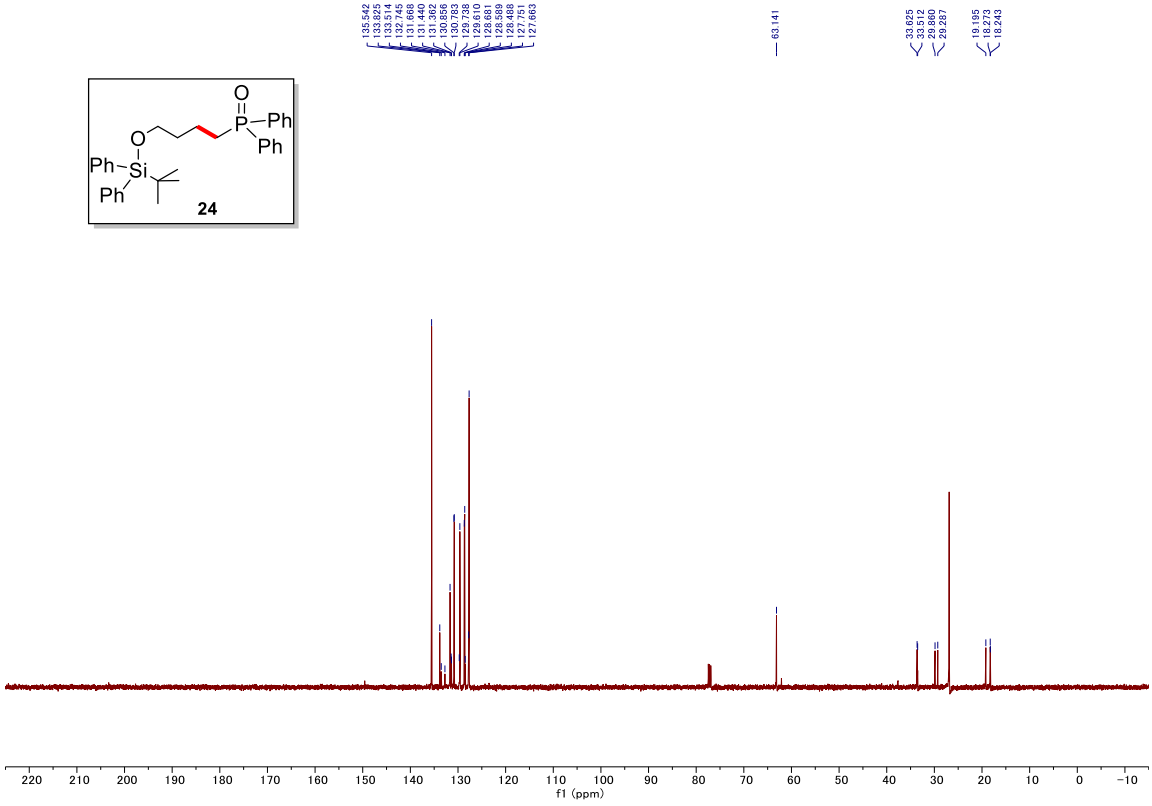

22
f1 (ppm)

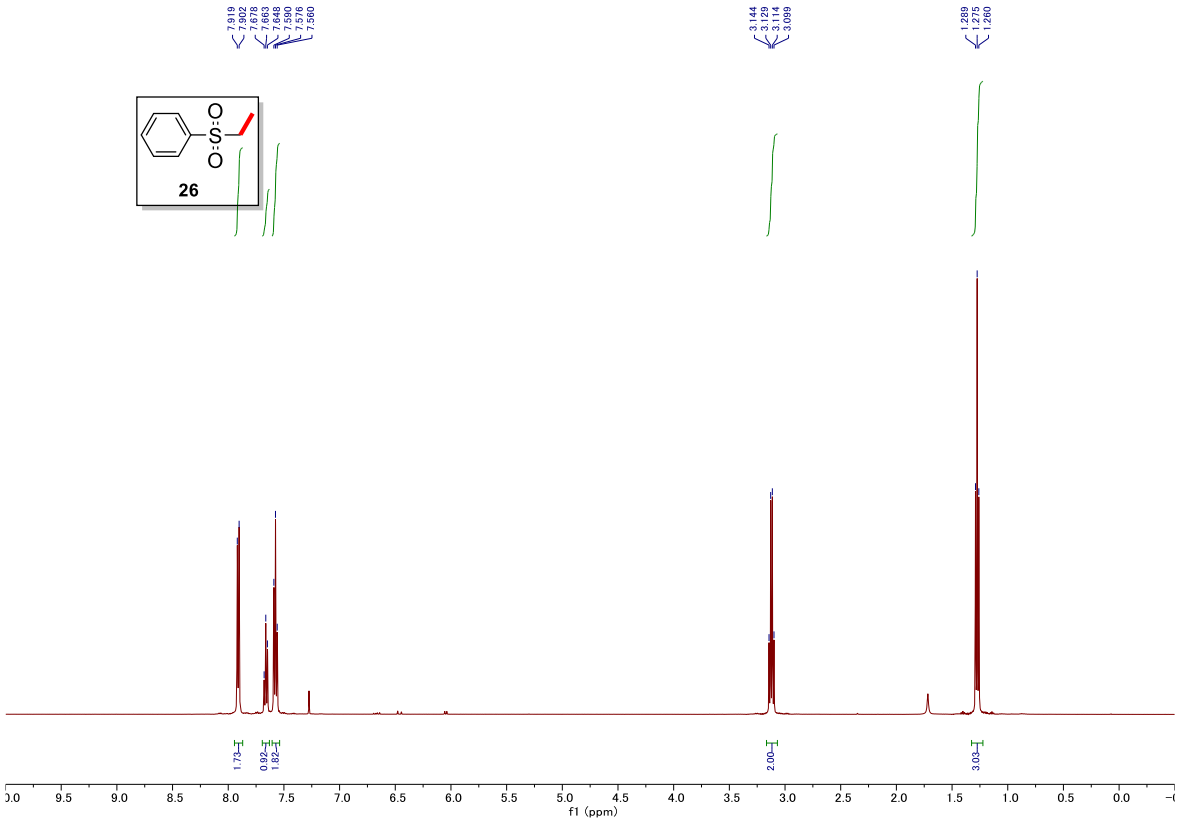

22
f1 (ppm)

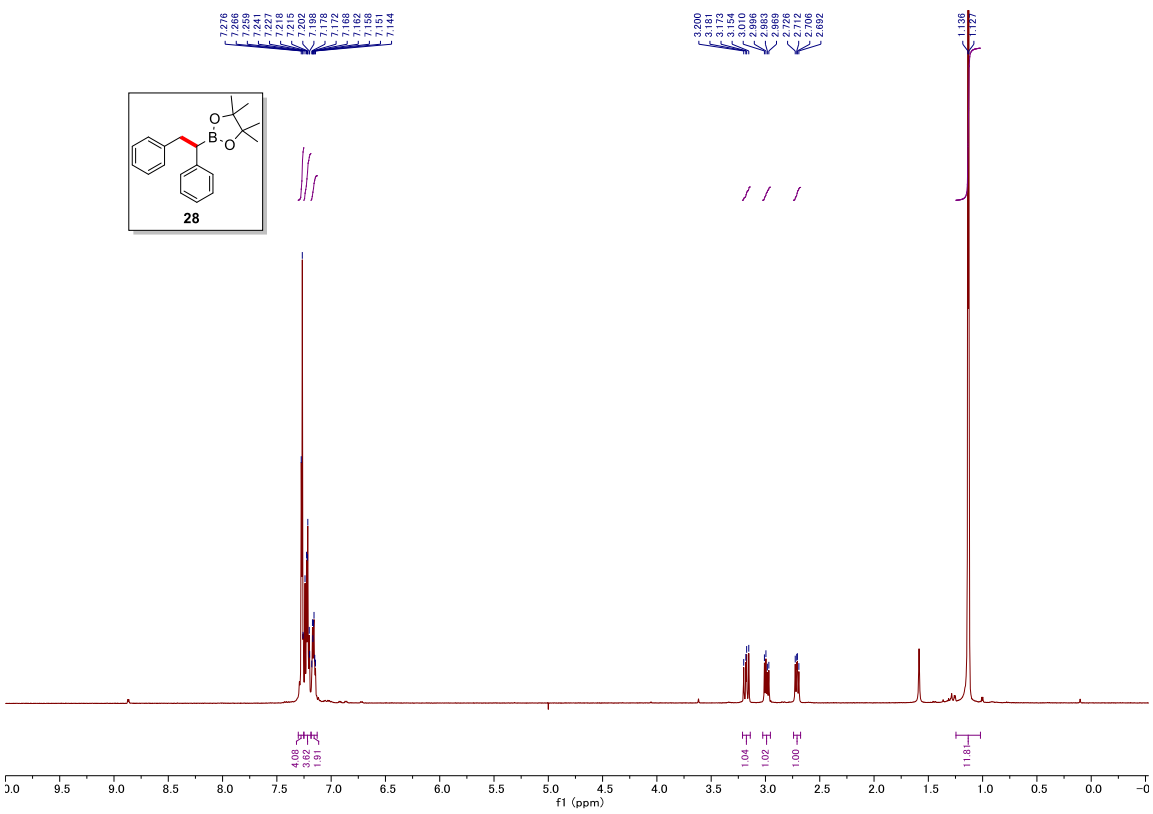

23
f1 (ppm)

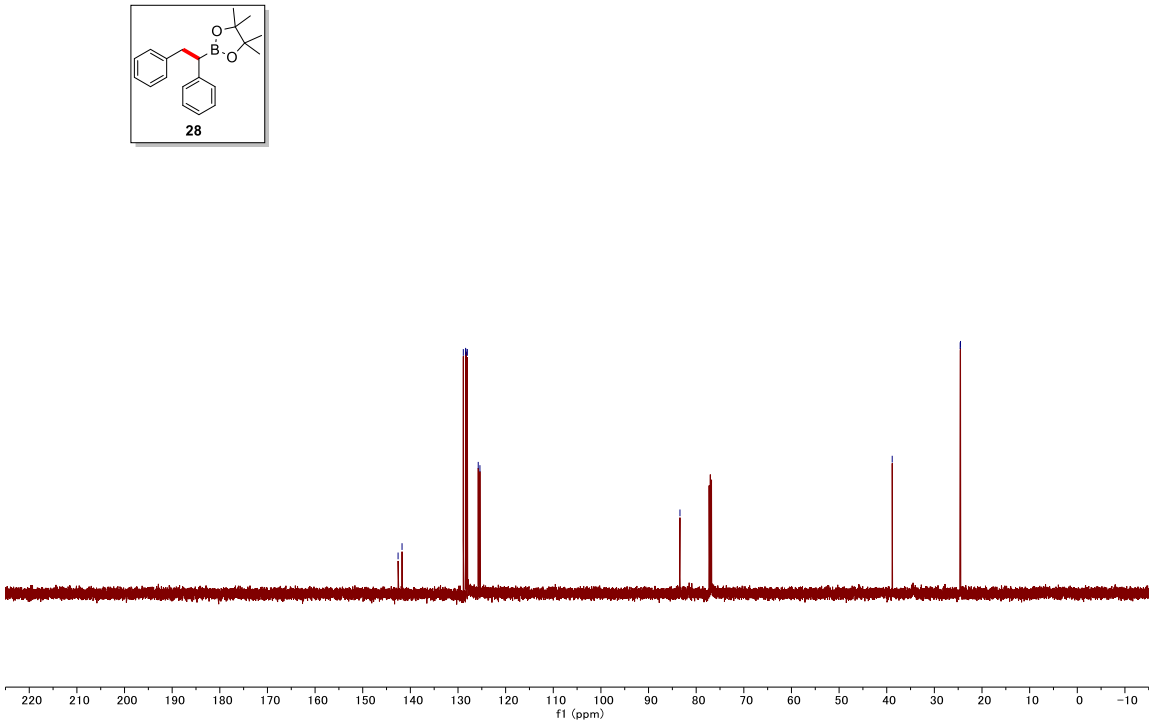

23
f1 (ppm)

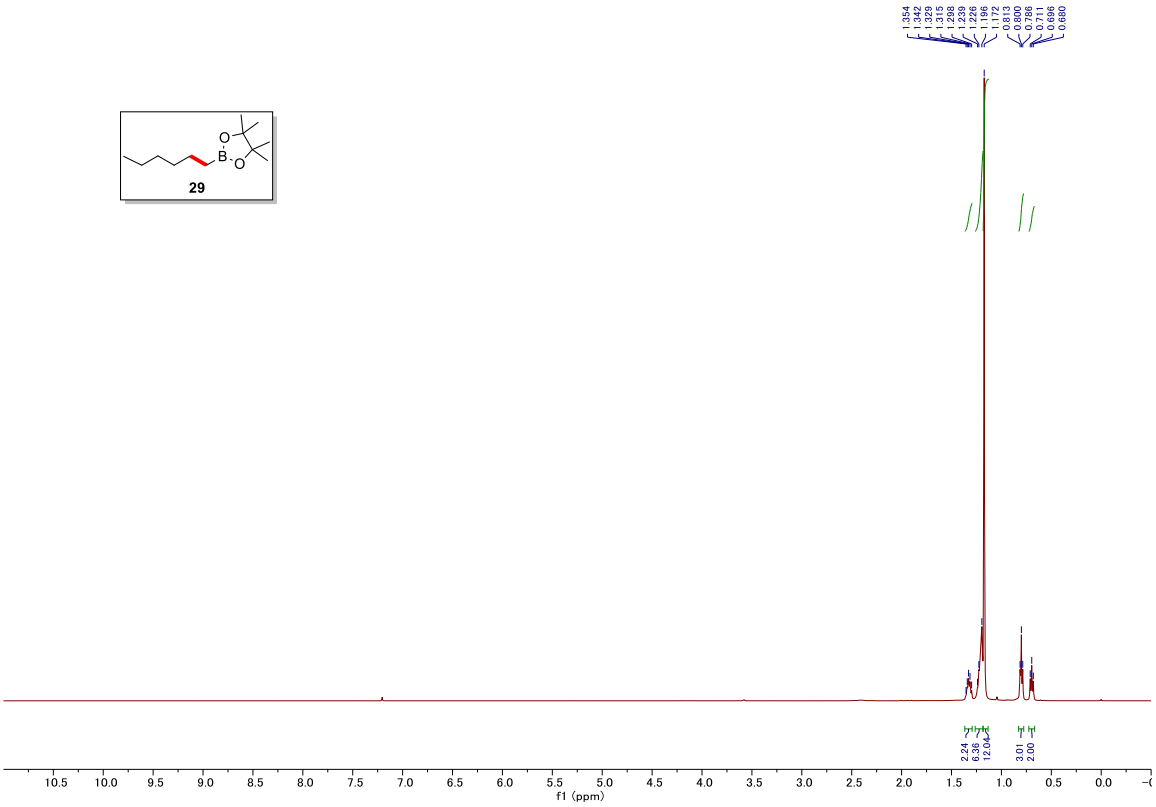

24
f1 (ppm)

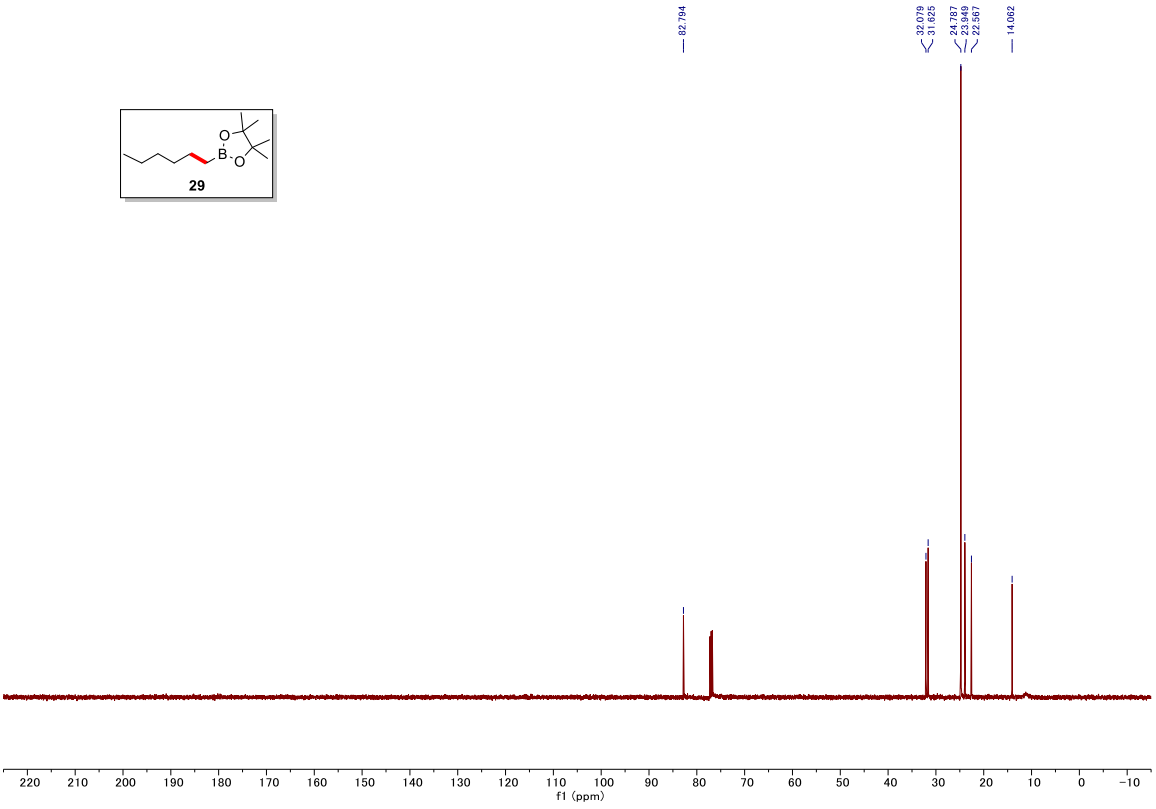

24
f1 (ppm)

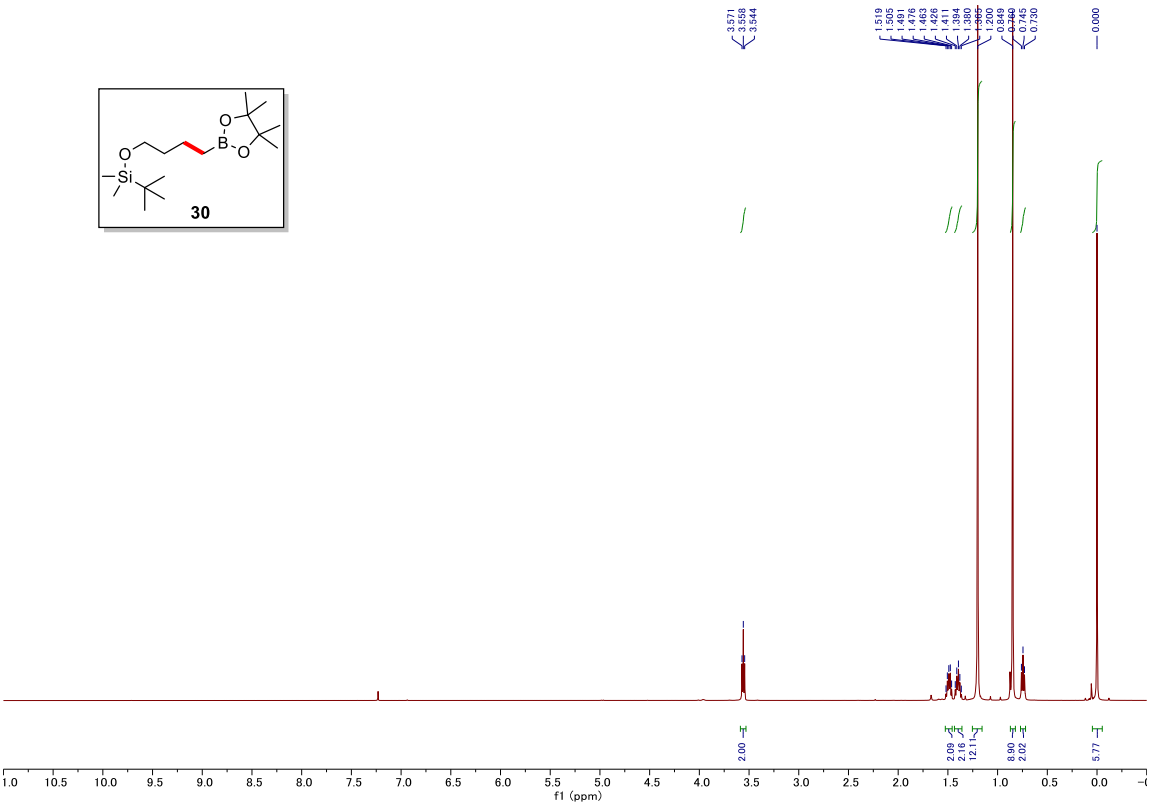

7.919
7.902
7.678
7.663
7.648
7.590
7.576
7.560
3.144
3.129
3.114
3.099
1.289
1.275
1.260
26
1.70
0.92
1.82
2.00
3.03
f1 (ppm)

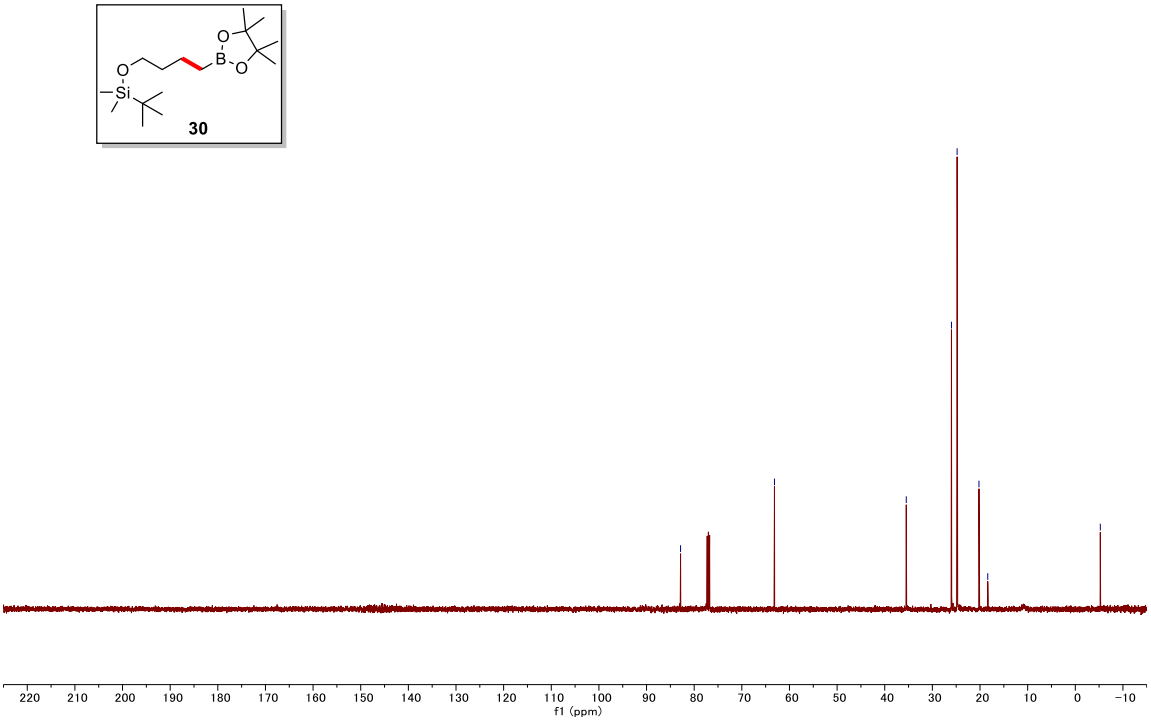

28
f1 (ppm)

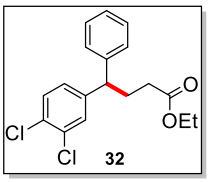

28
f1 (ppm)

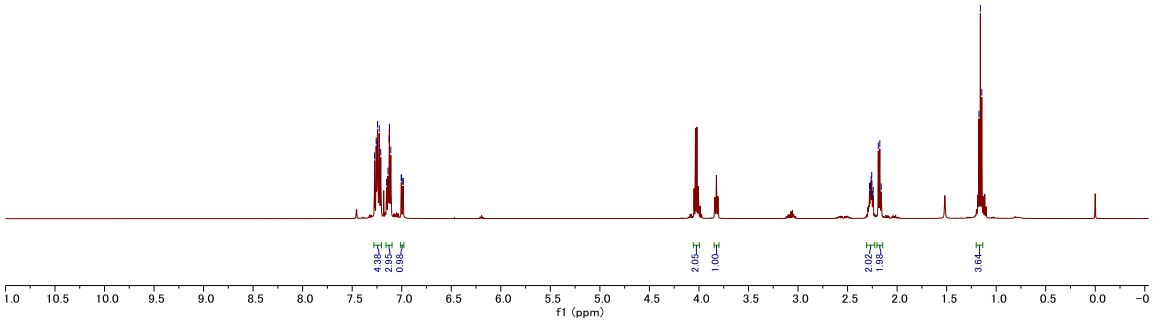

29
1.354
1.342
1.329
1.315
1.298
1.283
1.269
1.226
1.196
1.172
0.813
0.800
0.786
0.711
0.696
0.680
2.24
6.36
12.04
3.01
2.00
f1 (ppm)

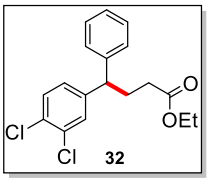

29
82.794
32.079
31.625
24.787
23.949
22.567
14.062
f1 (ppm)

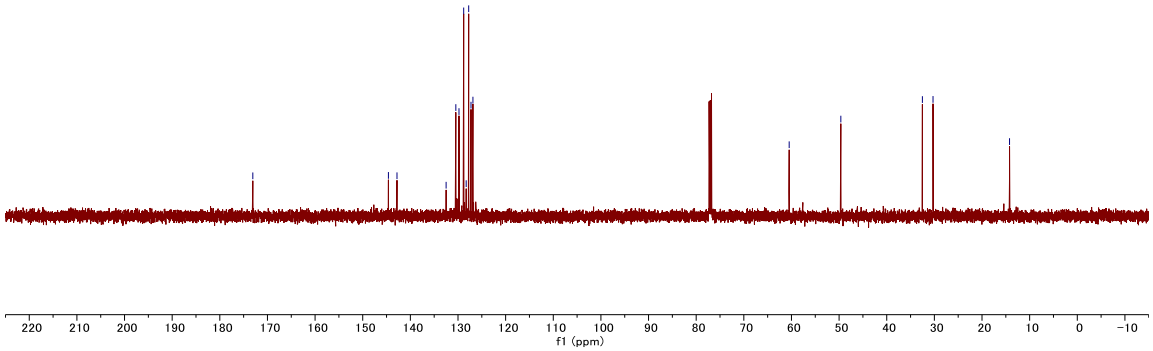

30
3.571
3.558
3.544
1.519
1.505
1.491
1.476
1.463
1.446
1.411
1.394
1.380
0.849
0.745
0.730
0.000
2.00
2.08
2.16
12.11
8.90
2.02
5.77
f1 (ppm)

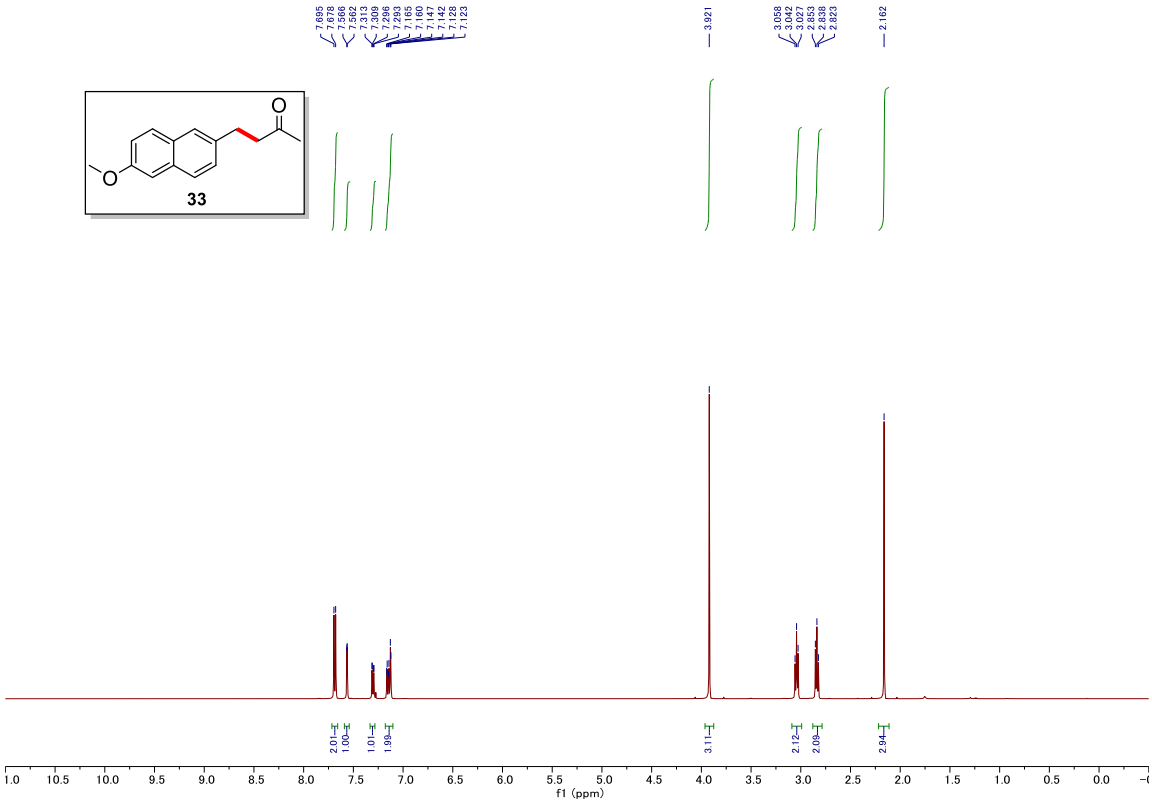

30
82.860
63.147
35.482
25.991
25.854
20.221
18.374
-5.255
f1 (ppm)

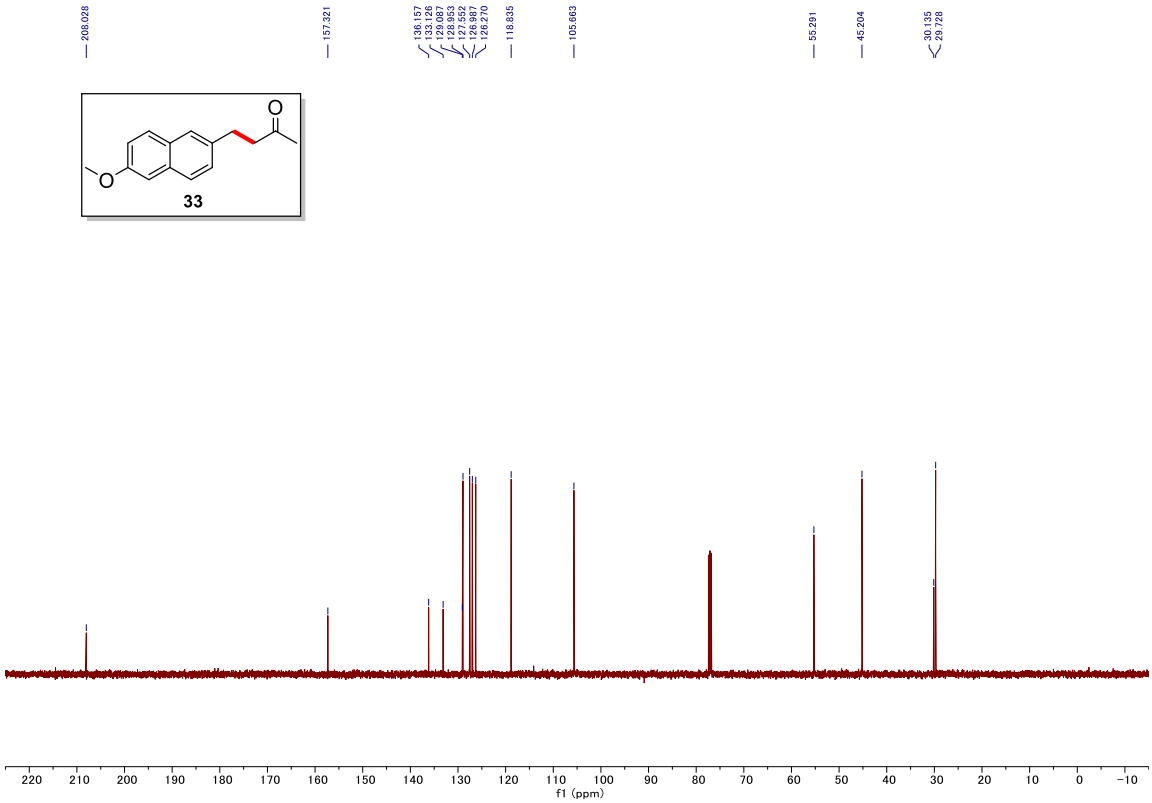

Cl
Cl
O
OEt
32

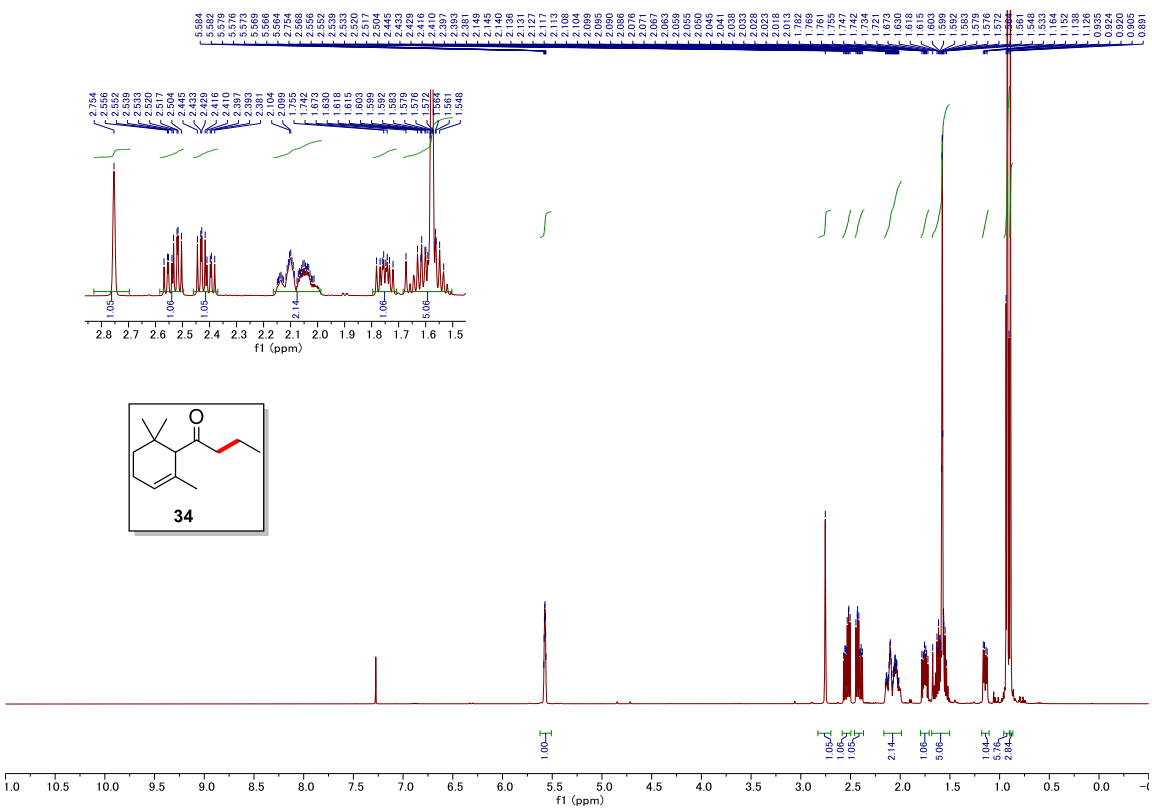

f1 (ppm)

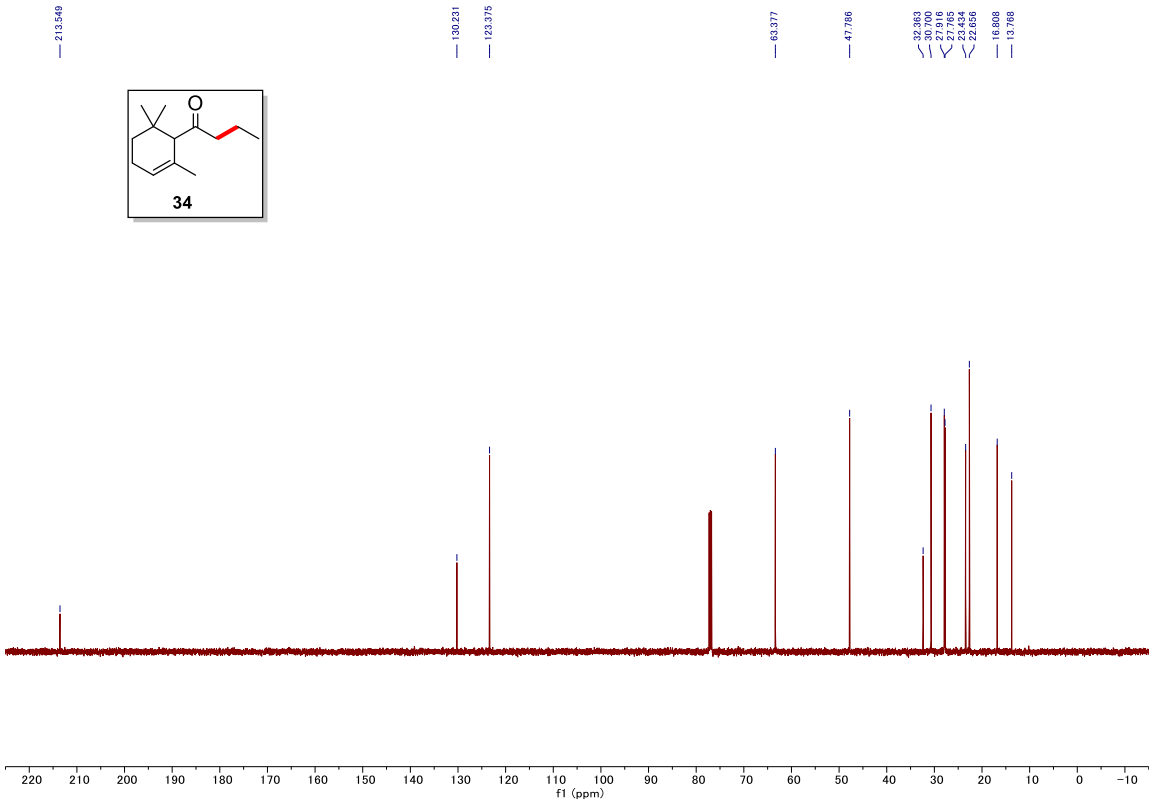

Cl
Cl
O
OEt
32

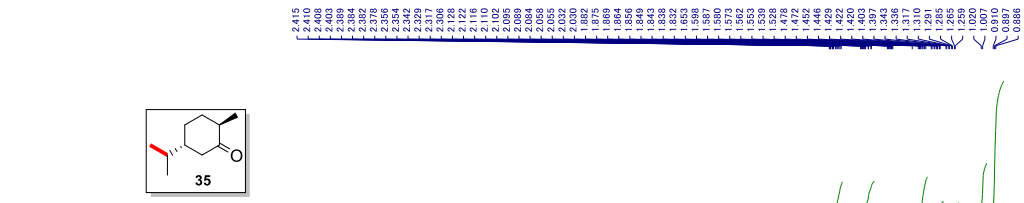

f1 (ppm)


7.695
7.678
7.566
7.562
7.313
7.309
7.296
7.293
7.165
7.160
7.147
7.142
7.128
7.123
3.921
3.058
3.042
3.027
2.853
2.838
2.823
2.162
33
2.01
1.00
1.01
1.99
3.11
2.12
2.09
2.94
f1 (ppm)

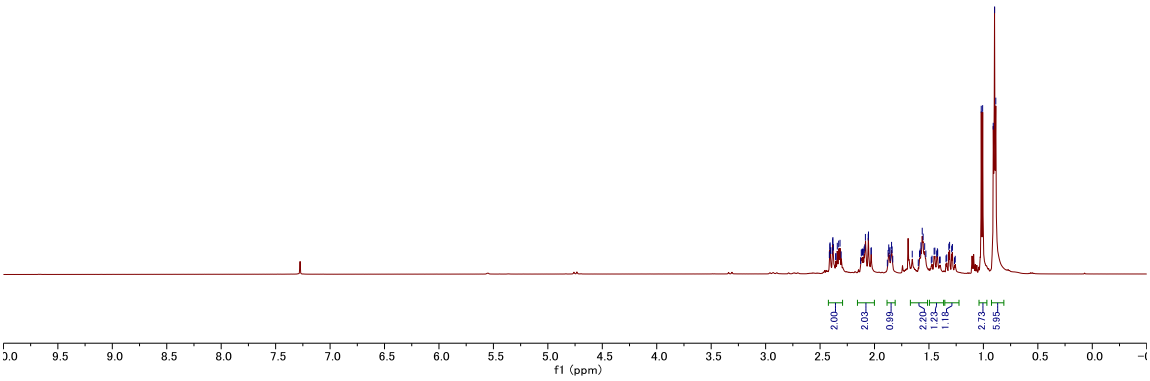

208.028
157.321
136.157
133.126
129.087
128.853
127.852
126.993
126.270
118.835
105.663
55.291
45.204
30.135
29.728
33
f1 (ppm)


34
f1 (ppm)

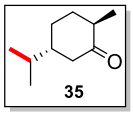

34
f1 (ppm)

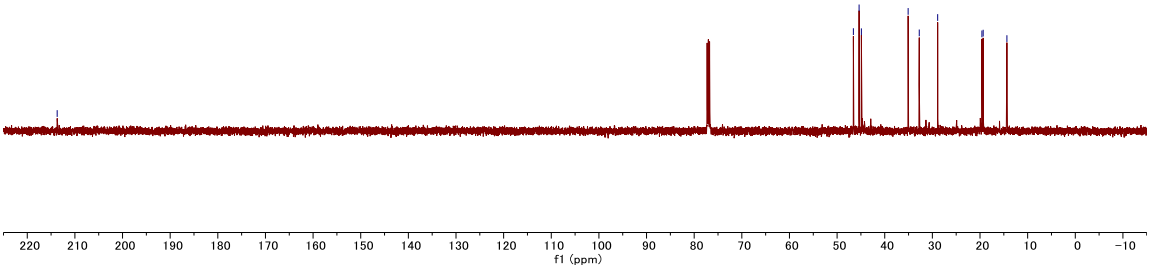


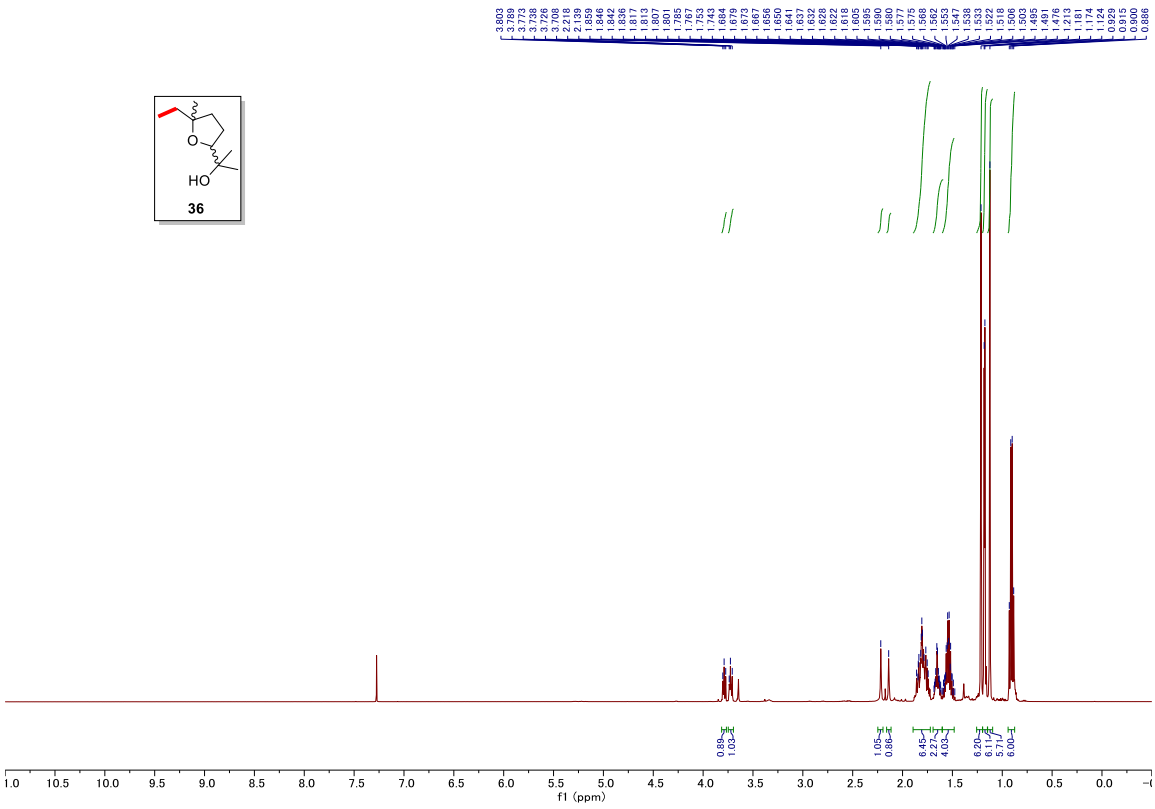
35

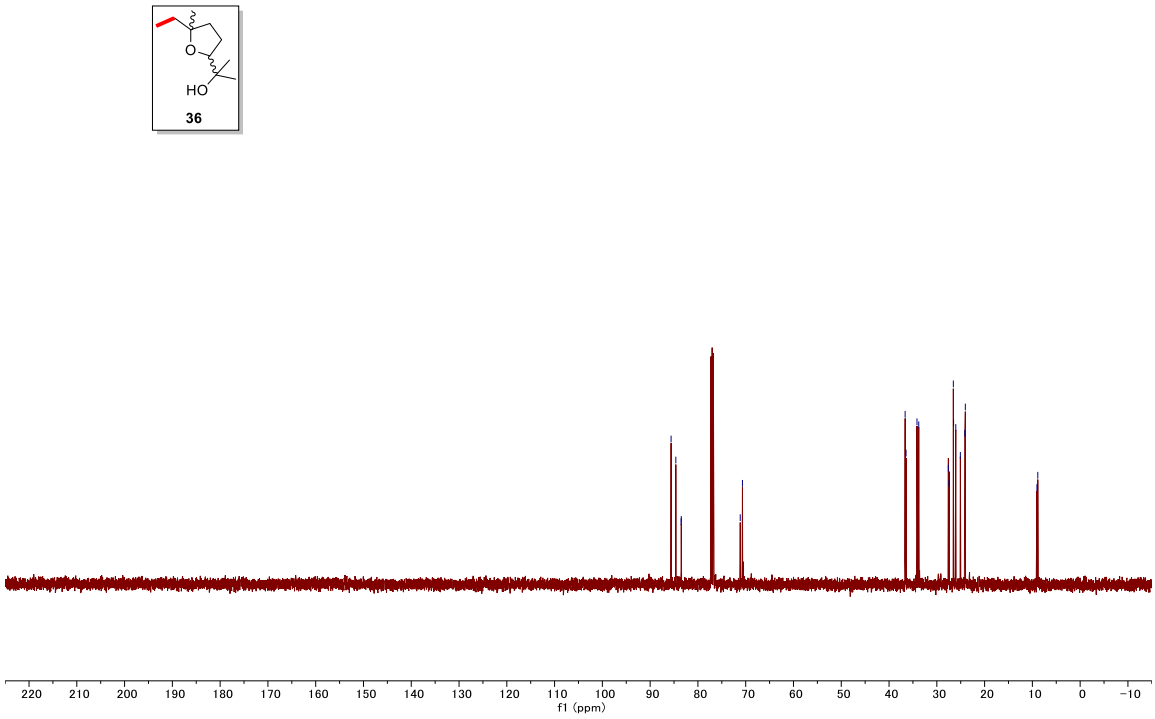

2.00
2.03
0.99
2.20
2.24
1.18
2.73
5.95
f1 (ppm)

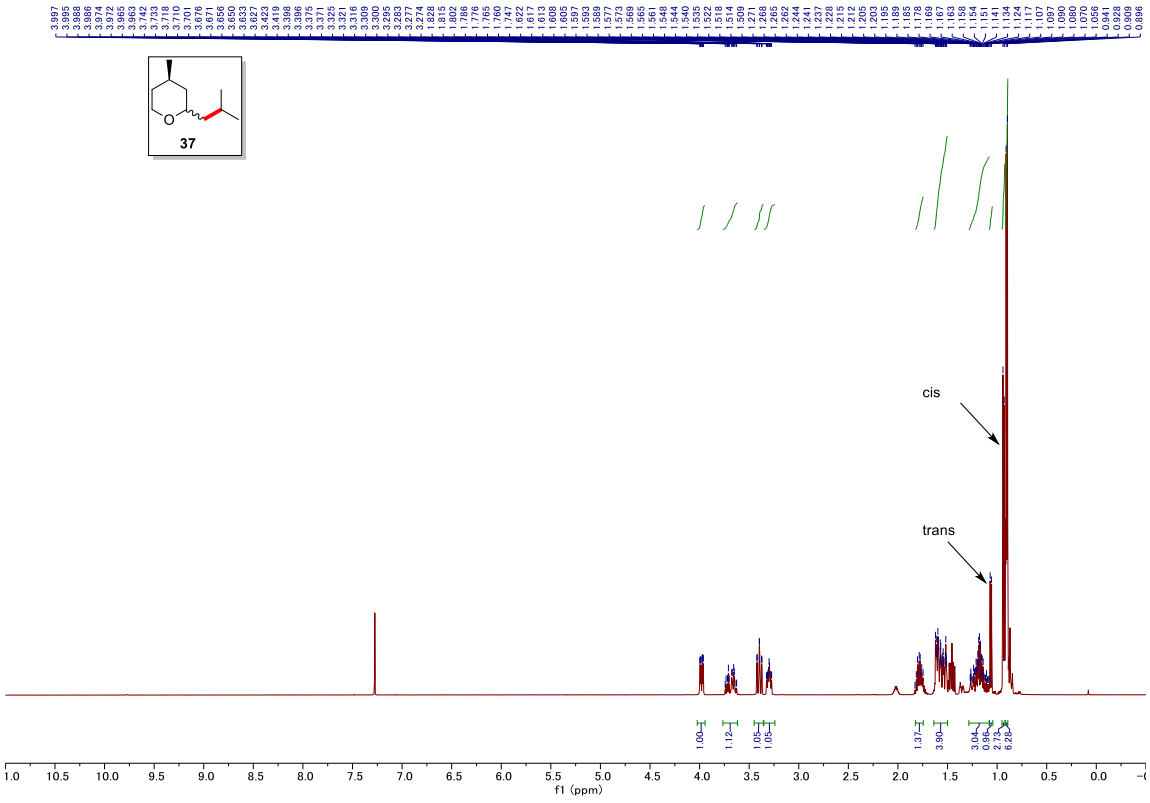

213.720
46.581
45.382
44.902
35.087
32.753
29.724
28.837
19.601
19.336
14.353

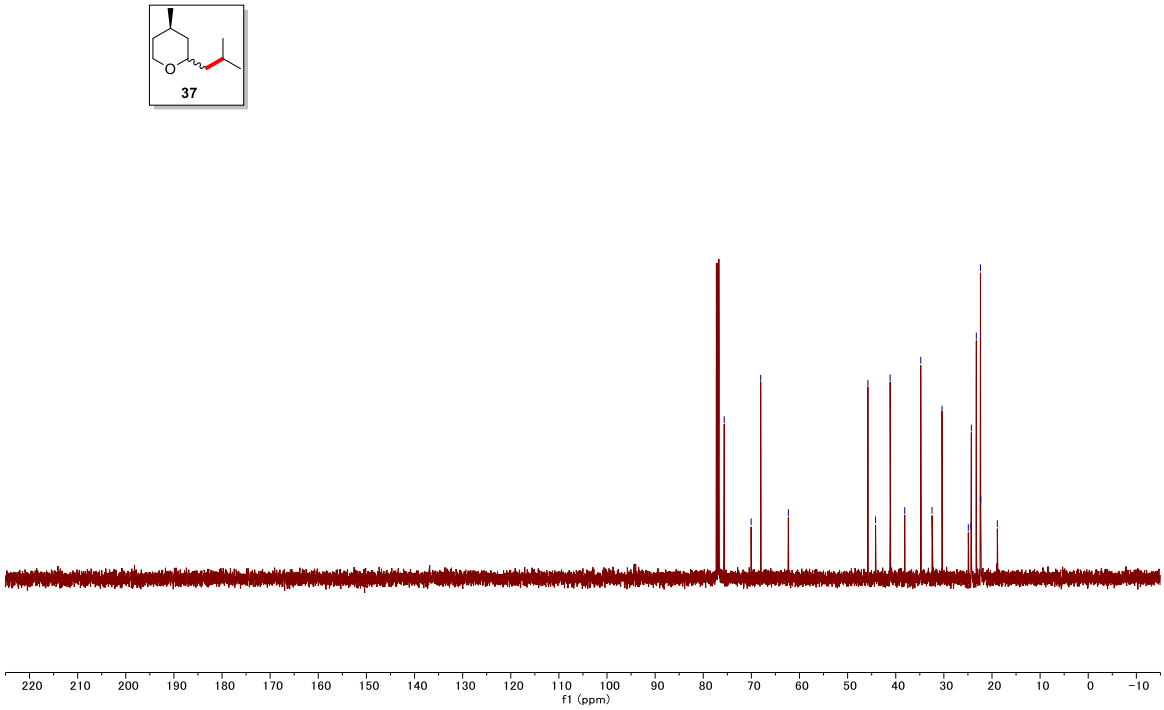

35

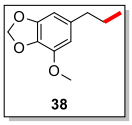

f1 (ppm)


HO
36
f1 (ppm)

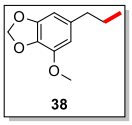

HO
36
f1 (ppm)


37
cis
trans
f1 (ppm)

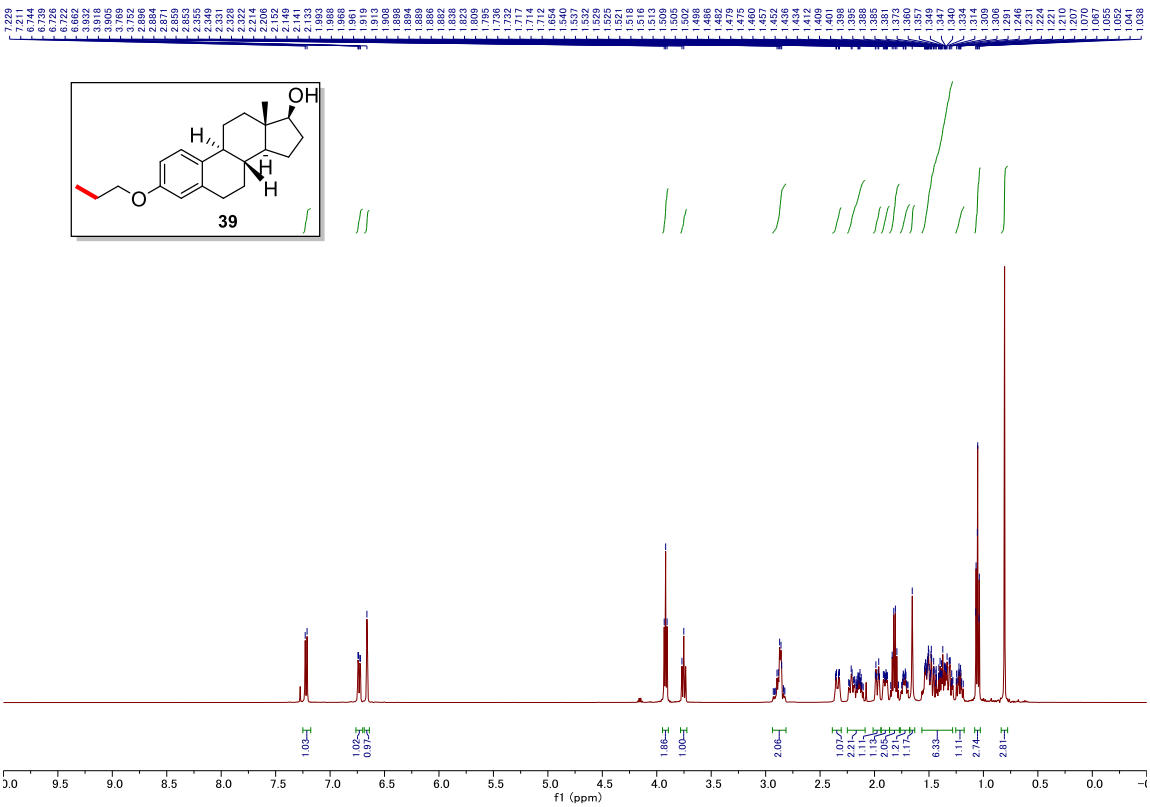

37
f1 (ppm)

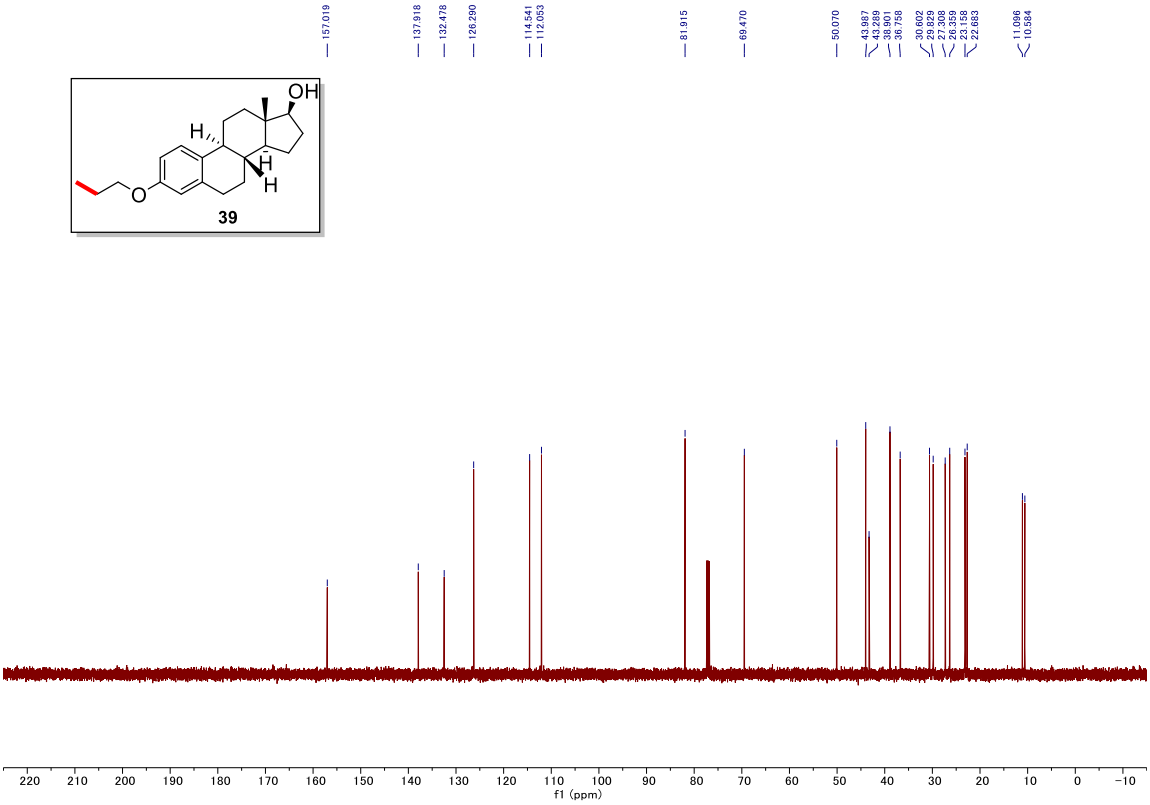

38

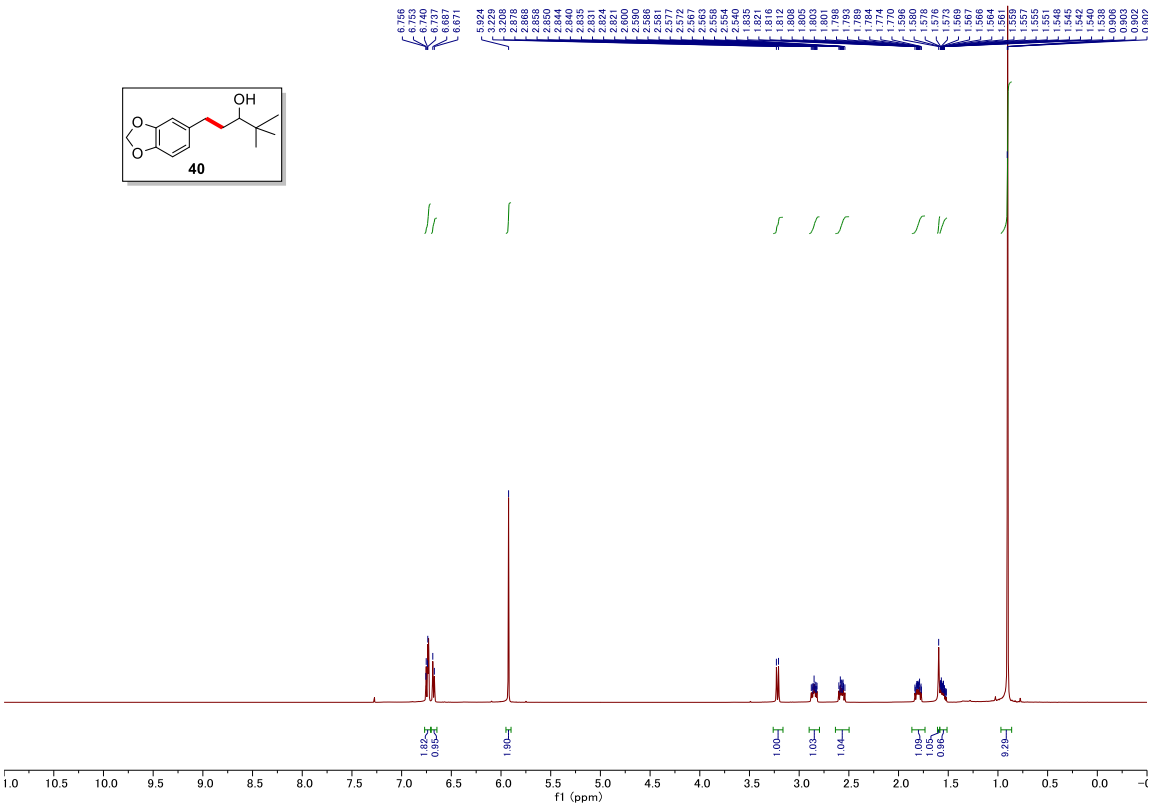
6.387
6.349
5.937
3.906
2.525
2.510
2.495
1.638
1.623
1.608
1.593
0.960
0.945
0.930
0.86
0.90
2.00
3.00
2.12
2.10
3.17
f1 (ppm)

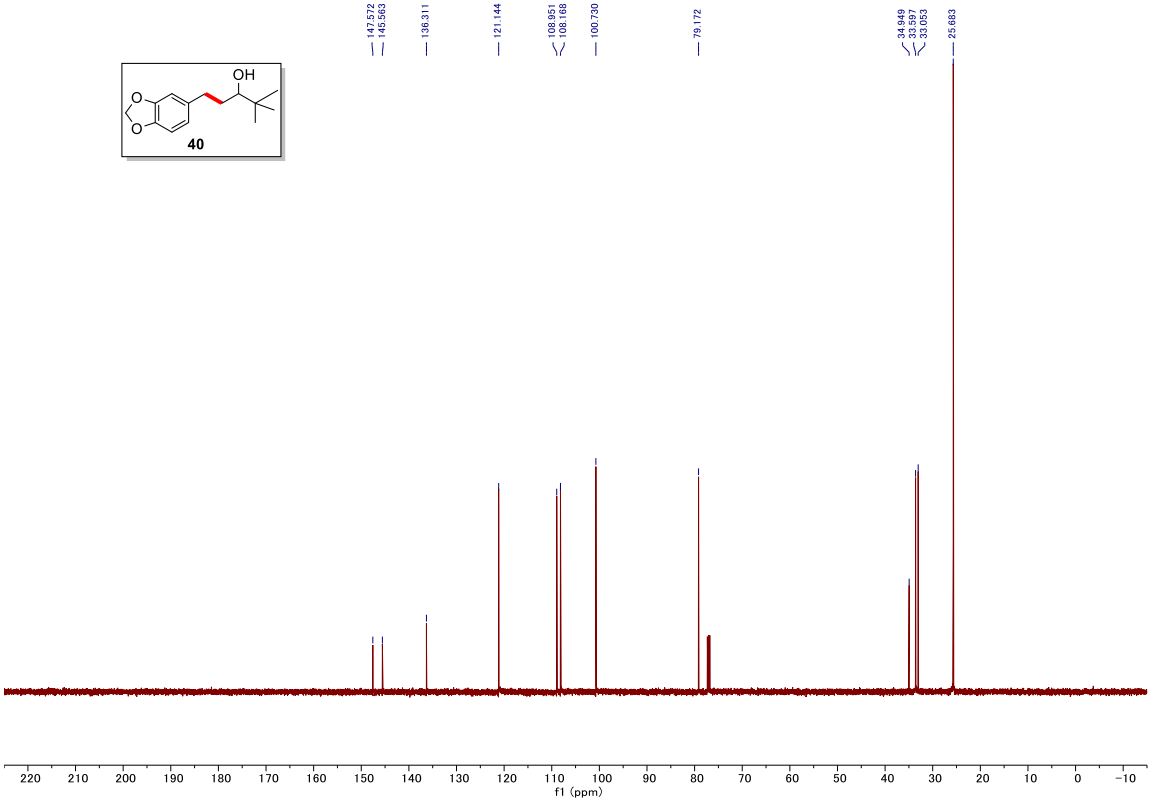

38

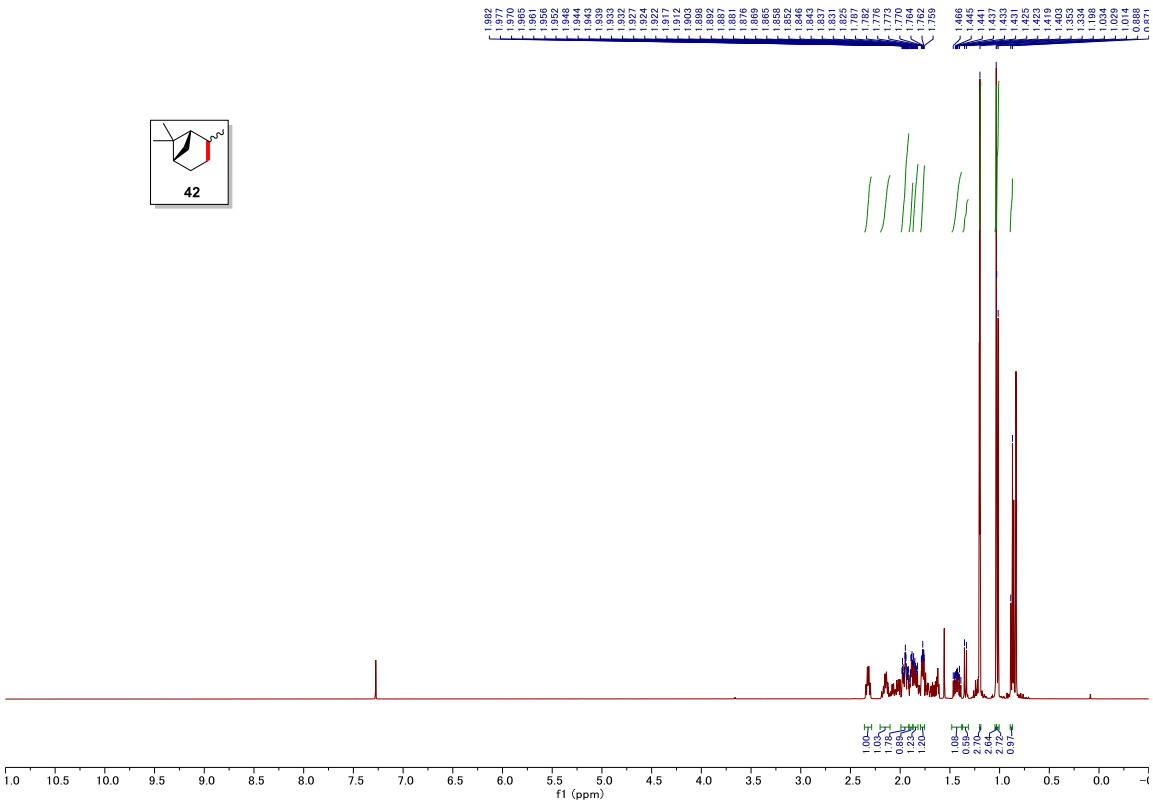
148.672
143.349
137.381
133.098
107.553
102.457
101.111
56.536
38.167
24.774
13.724
f1 (ppm)

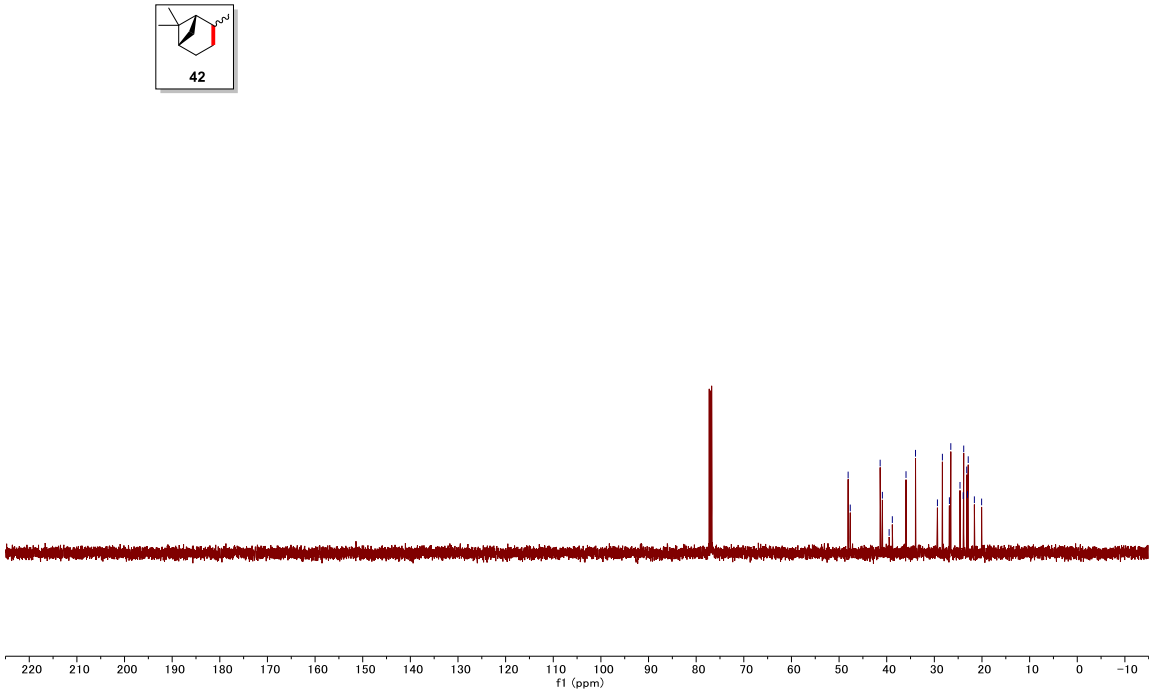

OH
H
H
H
O
39
f1 (ppm)

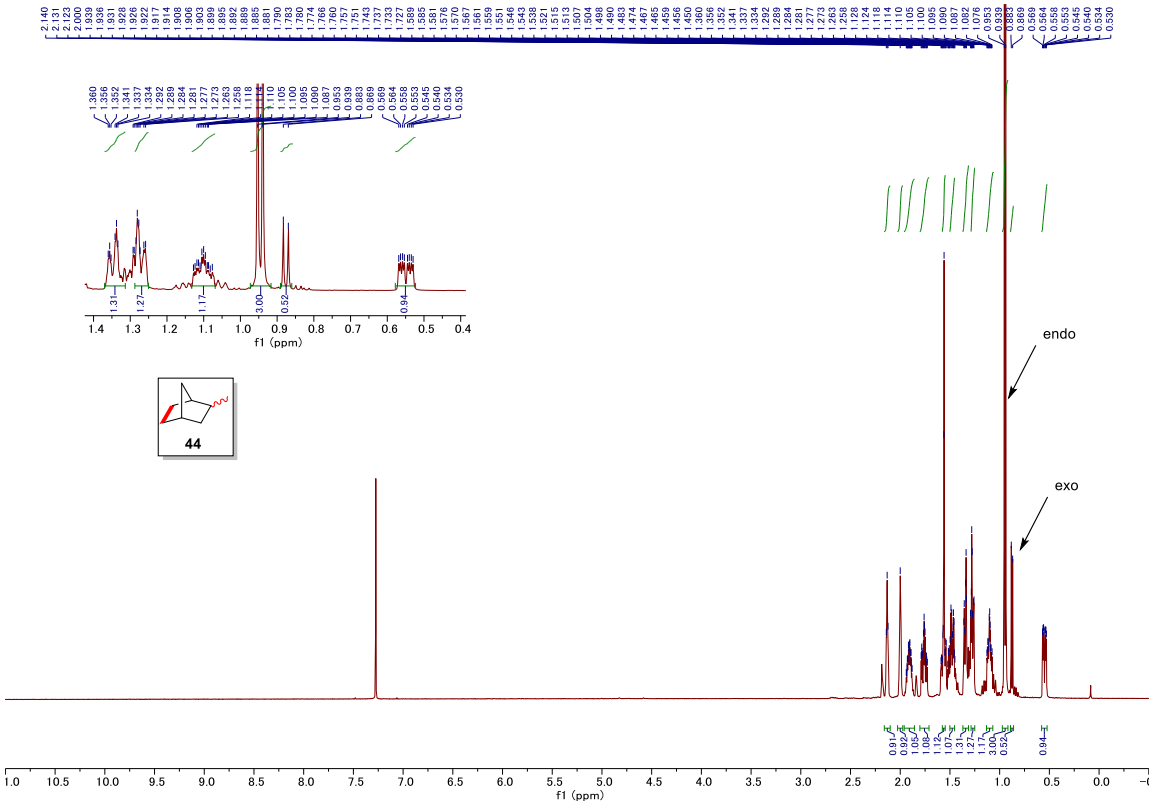

OH
H
H
H
O
39
f1 (ppm)


OH
O
O
40
f1 (ppm)

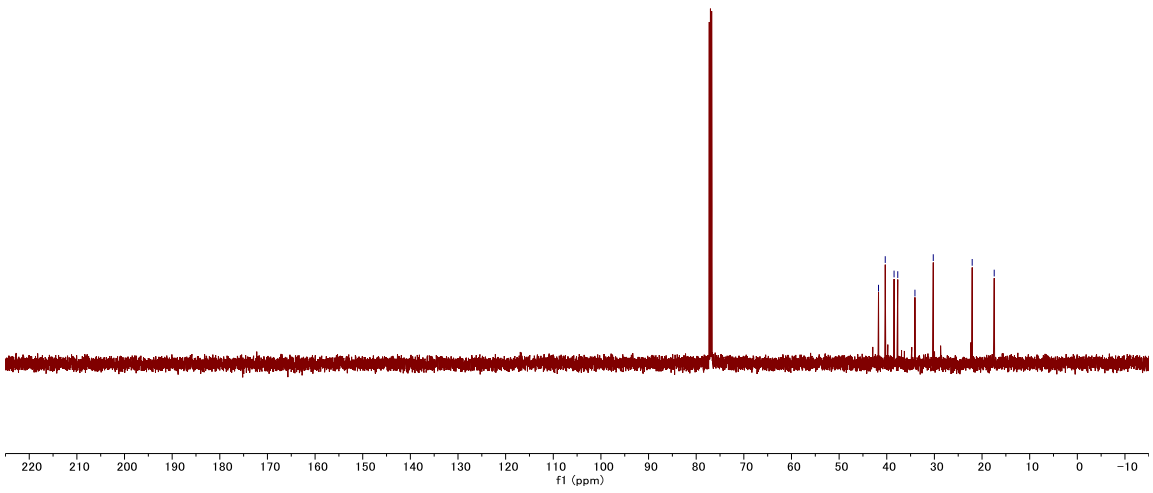

OH
O
O
40
147.572
145.563
136.311
121.144
108.951
108.168
100.730
79.172
34.949
33.597
30.053
25.683
f1 (ppm)


42
f1 (ppm)

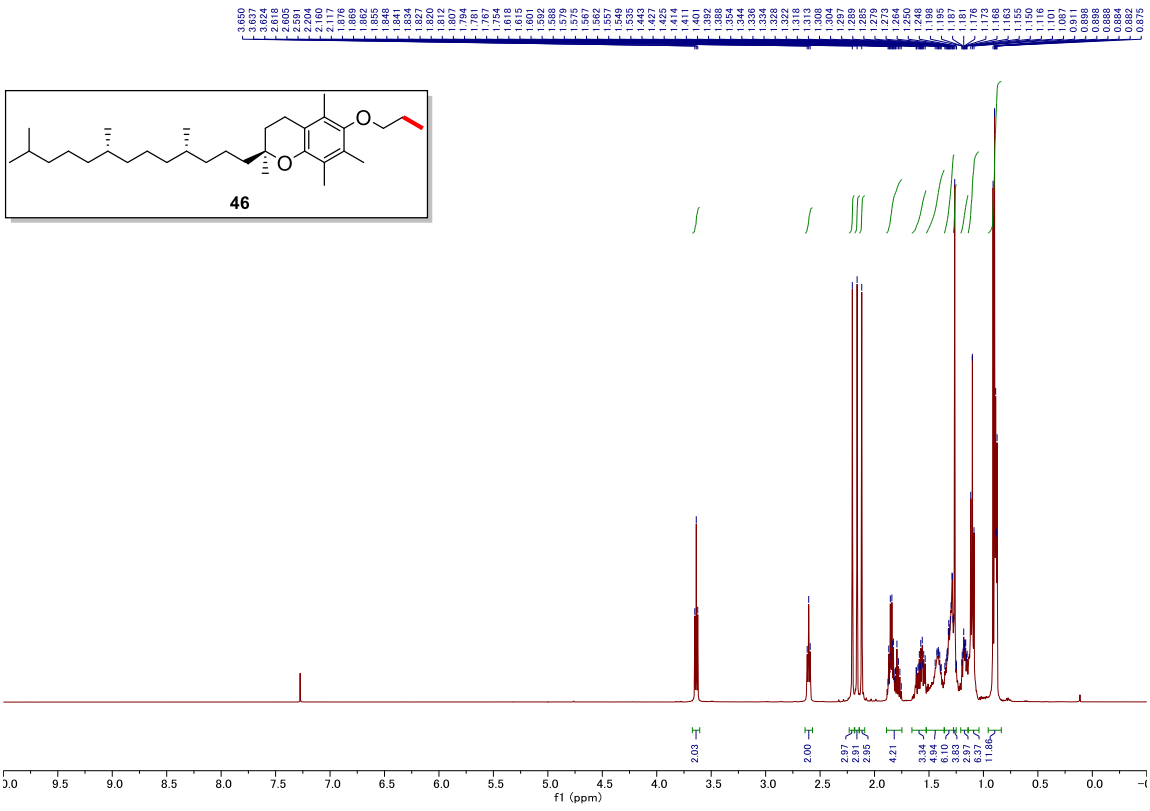

42
f1 (ppm)

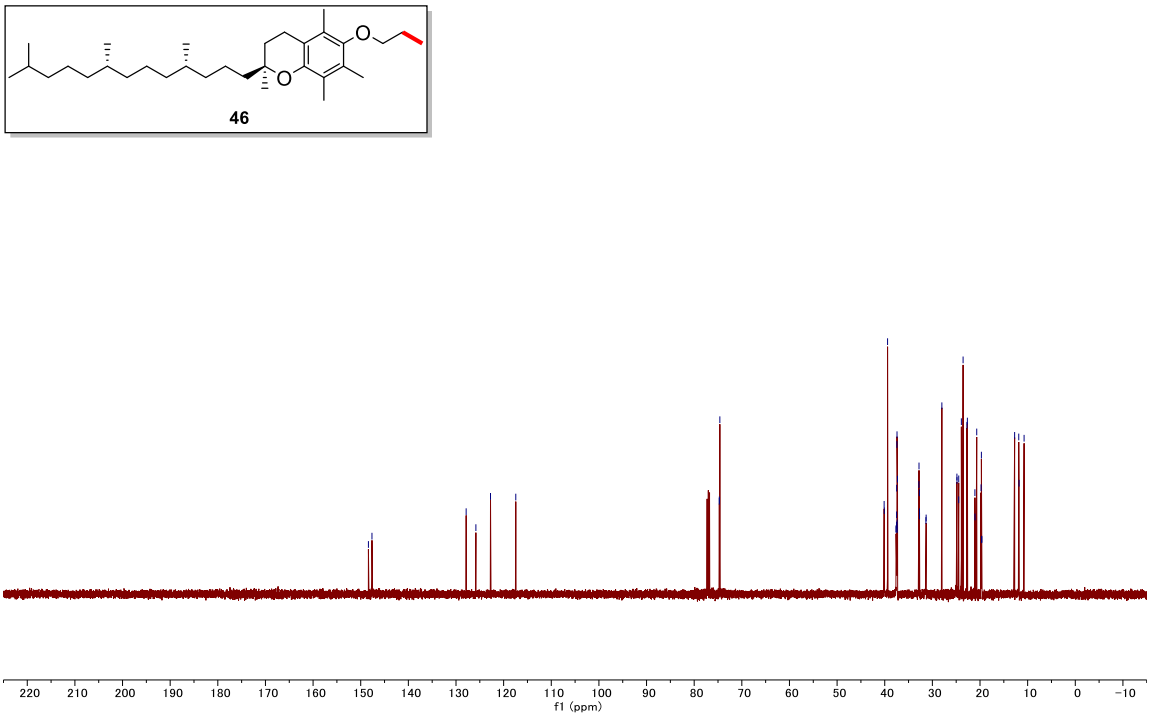

endo
exo
f1 (ppm)

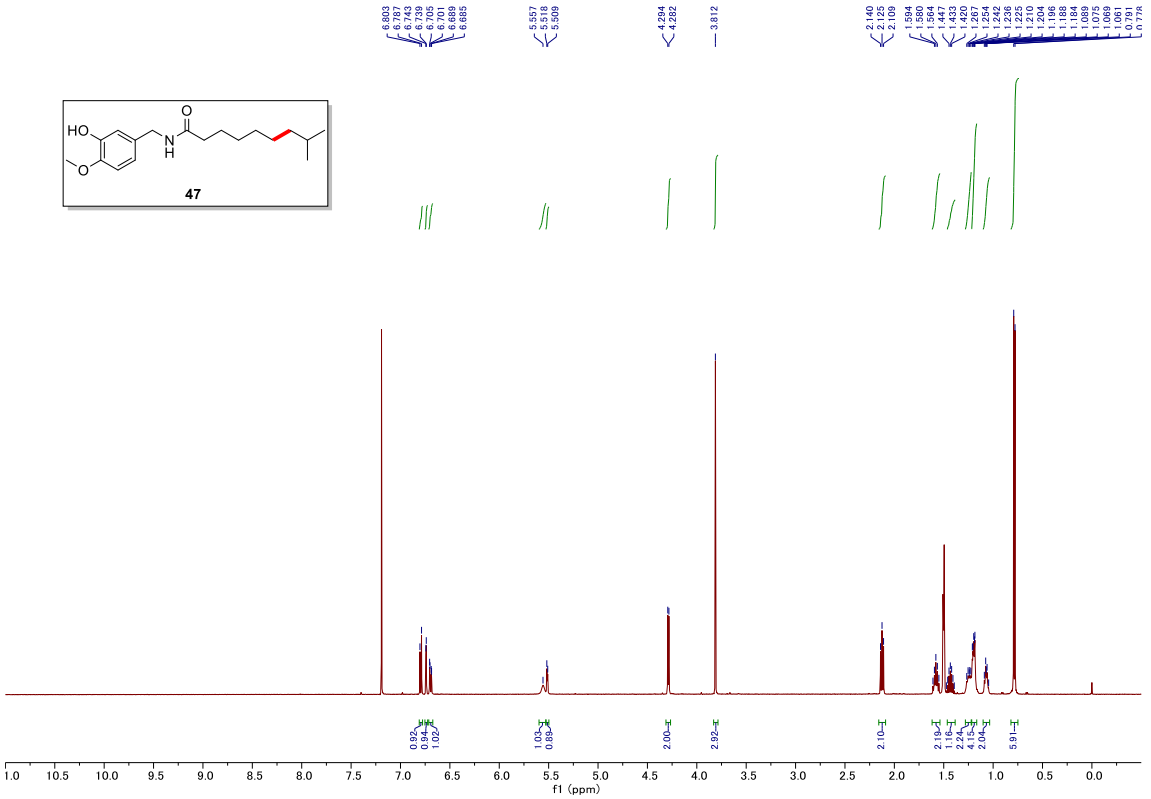

44

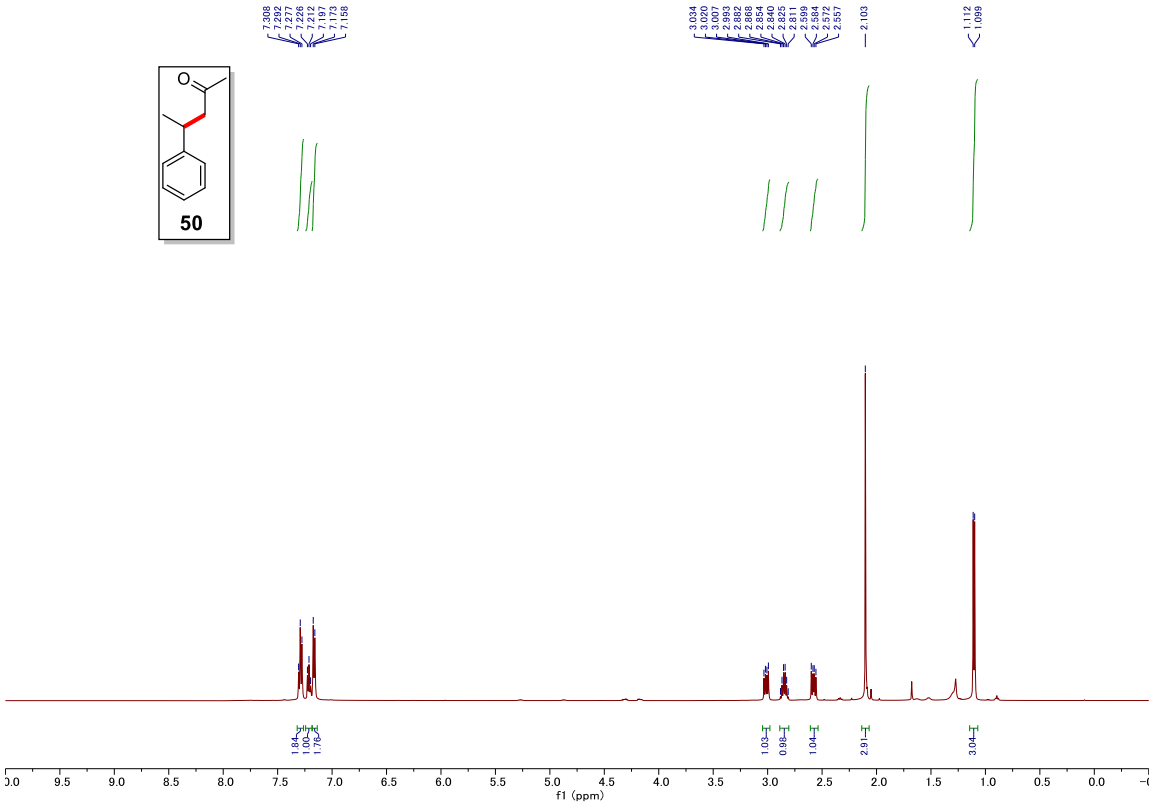

f1 (ppm)

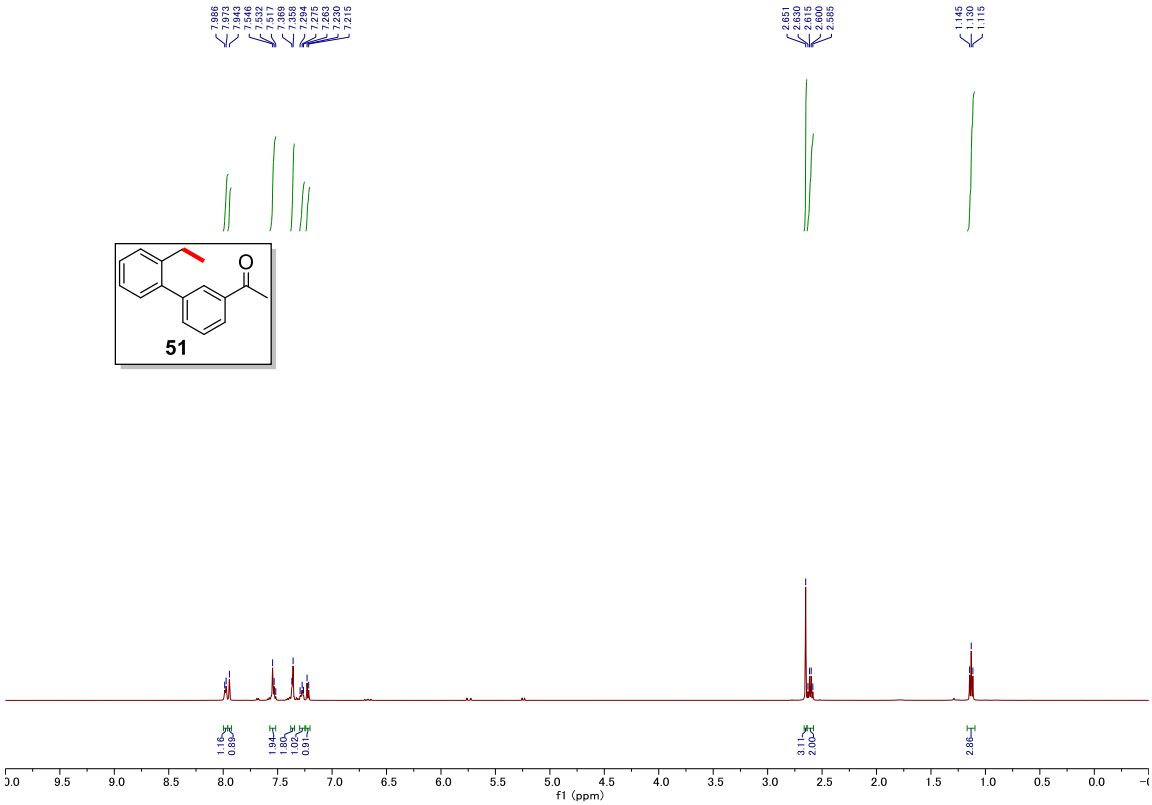
44

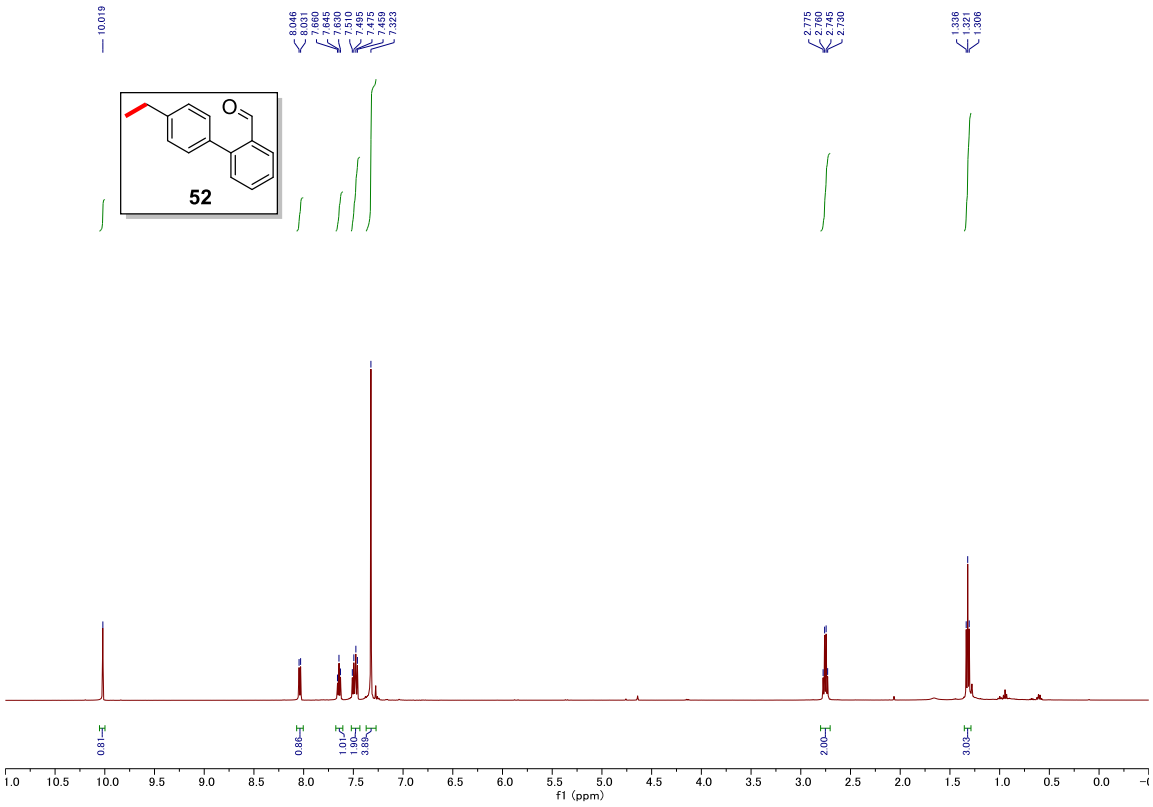

46
f1 (ppm)

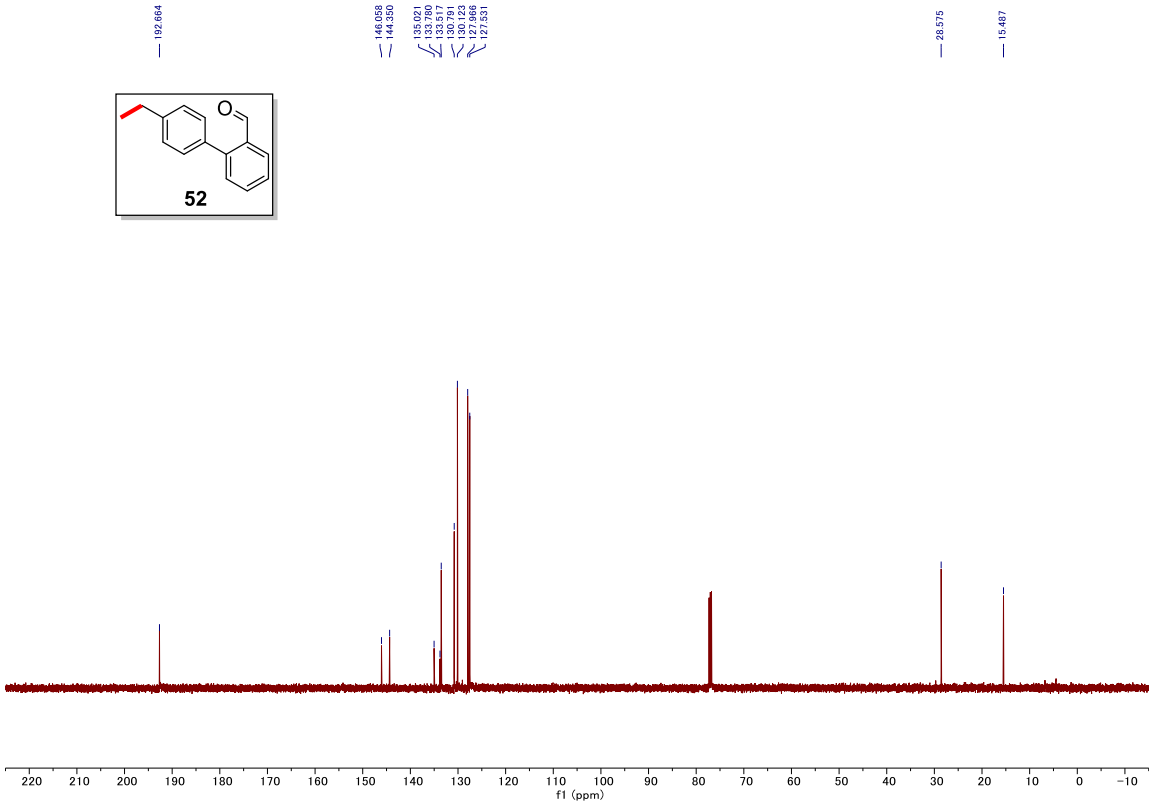

46
f1 (ppm)

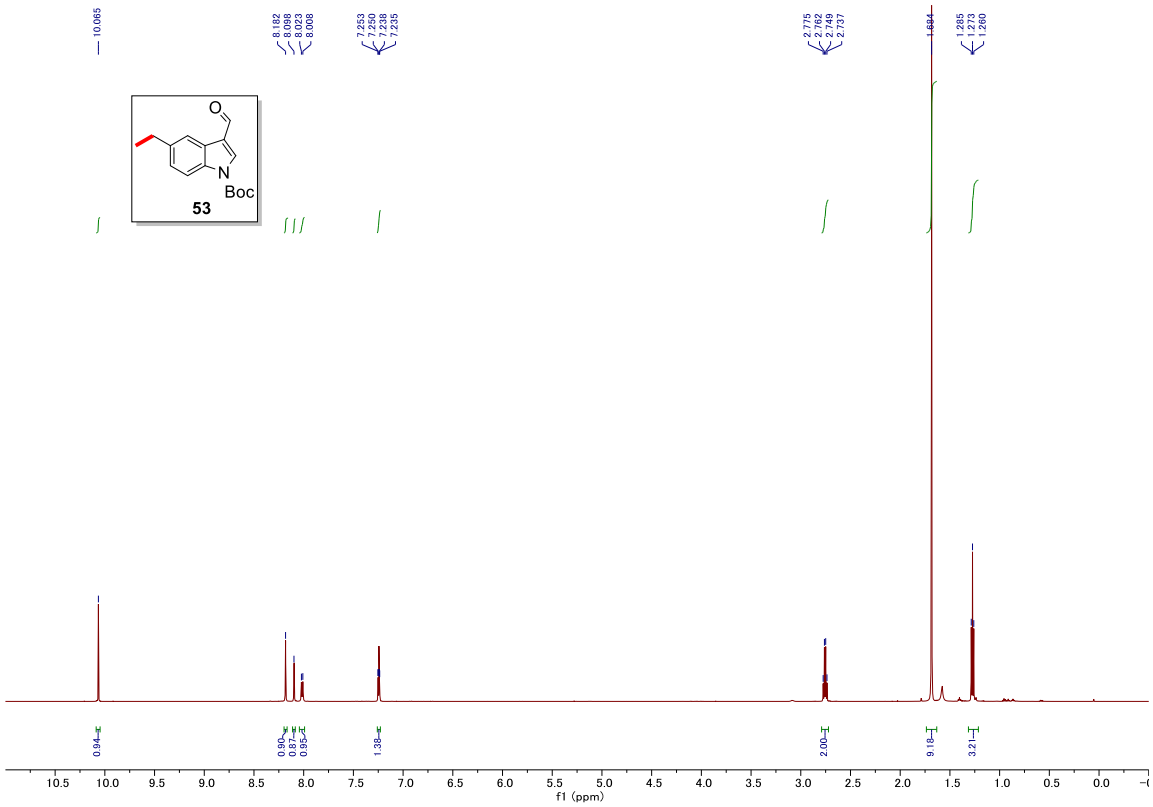

HO
O
N
H
O
47
f1 (ppm)

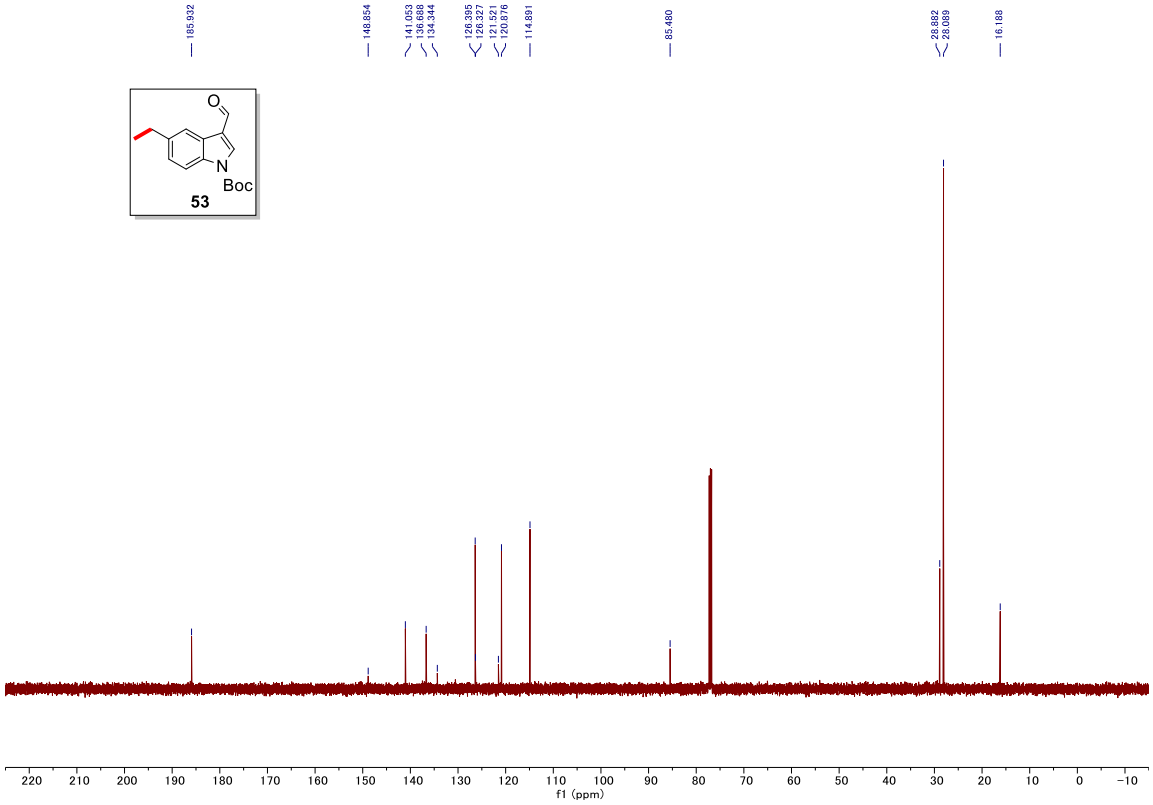

O
50
f1 (ppm)

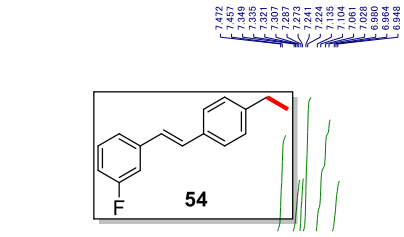

7.986
7.973
7.943
7.846
7.532
7.517
7.369
7.358
7.284
7.275
7.263
7.230
7.215
2.651
2.630
2.615
2.600
2.585
1.145
1.130
1.115
O
51
1.16
0.88
1.94
1.80
1.02
0.91
3.11
2.00
2.86
f1 (ppm)
198.112
142.415
141.556
140.544
137.025
133.860
129.864
129.164
128.748
128.384
127.996
127.747
125.763
26.739
26.152
15.625
O
51
f1 (ppm)

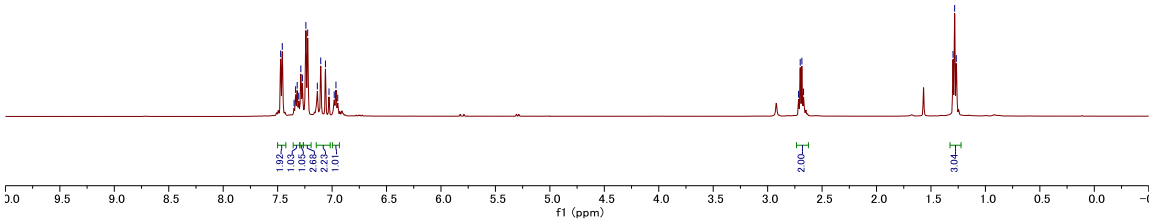

10.019
8.046
8.031
7.660
7.645
7.630
7.510
7.495
7.475
7.459
7.323
2.775
2.760
2.745
2.730
1.336
1.321
1.306
52
0.81
0.86
1.01
1.90
3.88
2.00
3.03
f1 (ppm)


192.664
148.058
144.350
135.021
133.780
133.517
130.791
130.123
127.966
127.531
28.575
15.487
52
f1 (ppm)

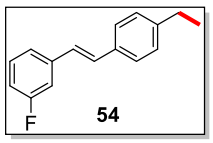

10.065
8.182
8.098
8.023
8.008
7.253
7.250
7.238
7.235
2.775
2.762
2.749
2.737
1.684
1.285
1.273
1.260
O
N
Boc
53
0.94
0.90
0.87
0.85
1.38
2.00
9.18
3.21
f1 (ppm)

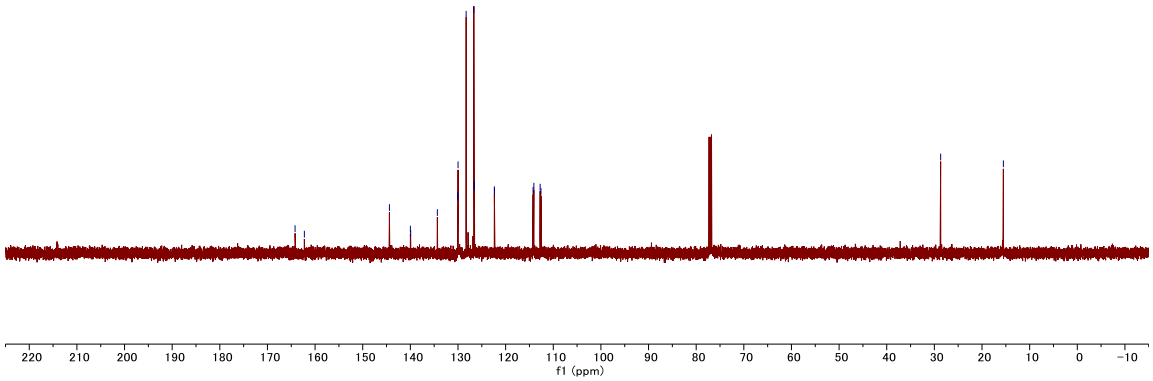

185.932
148.854
141.053
136.688
134.344
126.395
126.327
121.521
120.876
114.891
85.480
28.882
28.089
16.188
O
N
Boc
53
f1 (ppm)

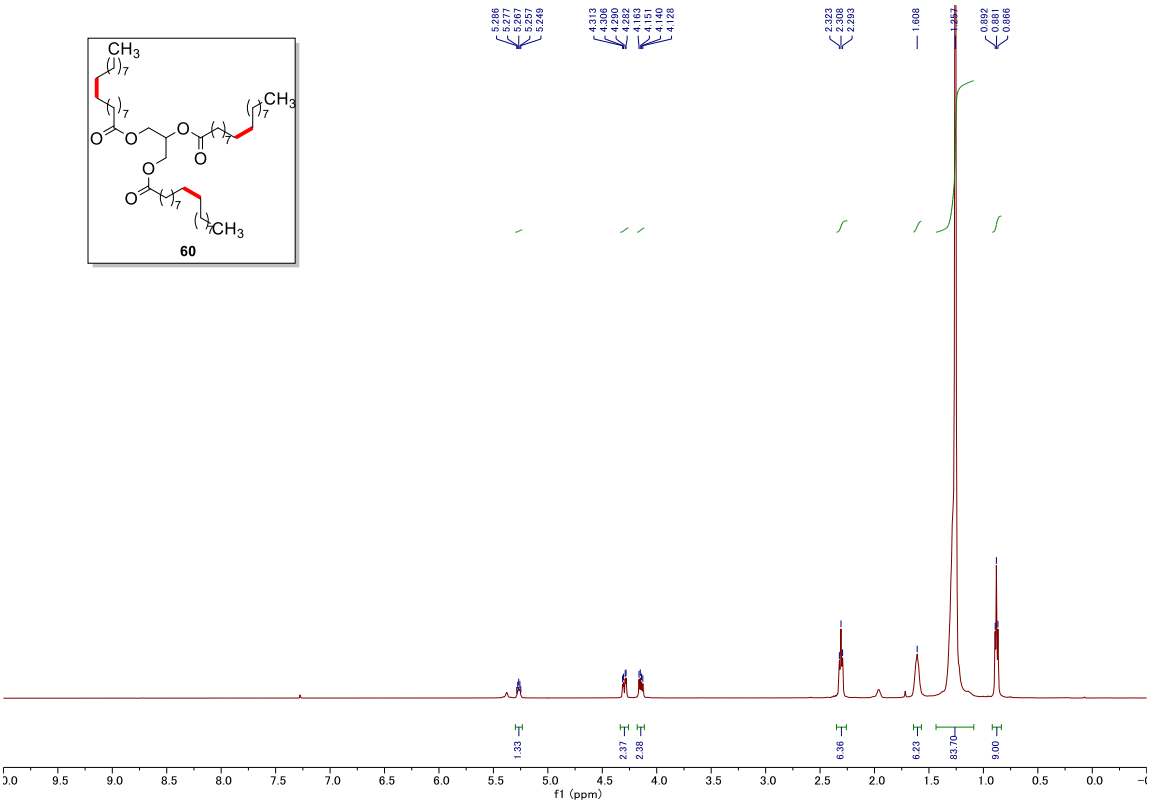

7.472
7.457
7.349
7.335
7.321
7.307
7.287
7.273
7.241
7.224
7.204
7.135
7.104
7.061
7.028
6.990
6.964
6.948
2.716
2.701
2.686
2.670
1.297
1.283
1.267
F
54

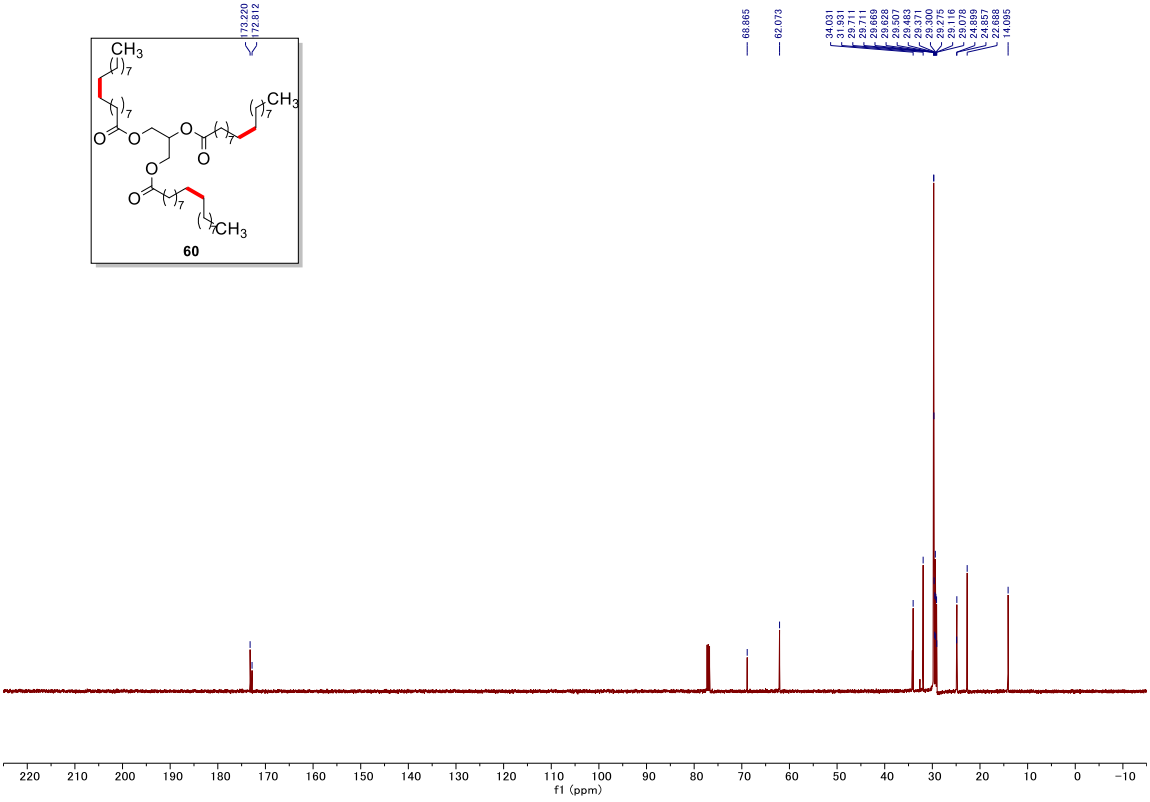

1.92
1.03
1.00
2.89
2.23
1.01
2.00
3.04
f1 (ppm)


164.201
162.250
144.397
139.984
139.933
134.333
130.066
130.019
129.989
128.286
126.678
126.564
126.563
122.366
122.345
114.241
114.071
112.758
112.584
28.682
15.515


F
54


f1 (ppm)


60
5.286
5.277
5.267
5.257
5.249
4.313
4.306
4.290
4.282
4.163
4.151
4.140
4.128
2.323
2.308
2.293
1.608
1.267
0.892
0.881
0.866
1.33
2.37
2.38
6.36
6.23
83.70
9.00
f1 (ppm)


60
173.220
172.812
68.865
62.073
34.031
31.931
29.711
29.711
29.669
29.628
29.507
29.463
29.371
29.300
29.275
29.116
29.078
24.899
24.857
22.688
14.095
f1 (ppm)