Supporting Information

Regioselective Copper-Catalyzed Carboxylation of Allylboronates with Carbon Dioxide

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General Information

Cu(IPr)Cl and KO^{t}Bu (sublimed) were purchased from Aldrich and used as received. Allylboronic esters **1b**, **1i**, and **1l** were purchased from Aldrich and purified by silica gel column chromatography prior to use. Allylboronic esters **1j**, **1k** and **1m** were prepared from the corresponding allyl bromides according to a literature procedure[1,2] and were re-purified by silica gel column chromatography prior to use. All reactions were carried out under an atmosphere of argon unless otherwise stated. Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 pre-coated silica gel plate. Flash column chromatography (FC) was undertaken on Merck silica gel 60. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-400 and referenced to residual protiated solvent (resonances downfield to the standard are reported as positive). All ^{13}C NMR spectra were proton decoupled. The abbreviations s, d, t and m stand for the resonance multiplicity singlet, doublet, triplet, and multiplet, respectively. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory. High resolution mass spectra (HRMS) were recorded on an Agilent ESI TOF (time of flight) mass spectrometer using ESI (eletrospray ionization). THF was dried over alumina under N_2 using a Grubbs-type solvent purification system.

General procedure for preparation of allylboronic pinacol esters 1a,[2] **1c**, **1d**, **1f**, **1g**, **1h**,[3] **1n**, **1o**, **1p**,[4] **1q**, and **1r**:[5] To a solution of allylic alcohol (1 mmol) in anhydrous DMSO (2 mL) and anhydrous MeOH (2 mL) was added TsOH (9mg, 0.05 mmol), di-m-chlorobis{2-[(dimethylamino)methyl]phenyl-C,N}dipalladium(II) (14 mg, 0.025 mmol) and bis(pinacolato)diboron (508 mg, 2 mmol). The mixture was stirred at 50 ^{o}C overnight then cooled to rt. H_2O was added followed by extraction with Et_2O three times. The combined organic layers were dried over anhydrous $MgSO_4$, concentrated in vacuo and purified by flash column chromatography.

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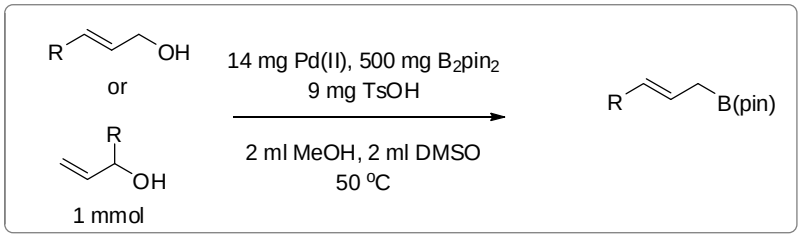
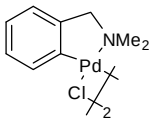
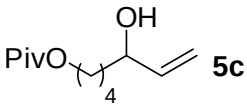
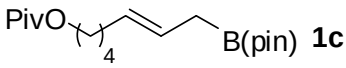
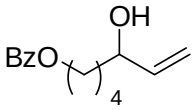
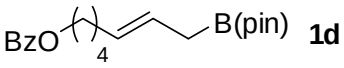
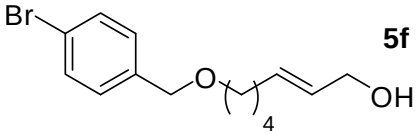
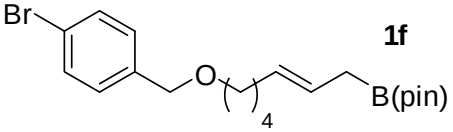
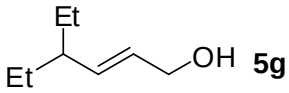
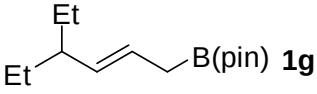
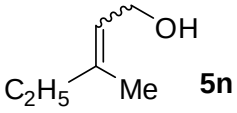
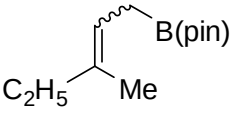
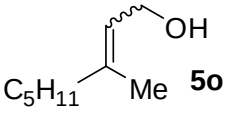
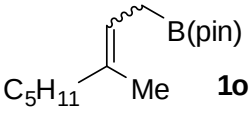
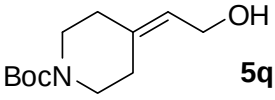
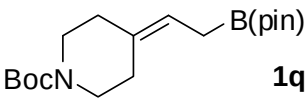




Pd(II)

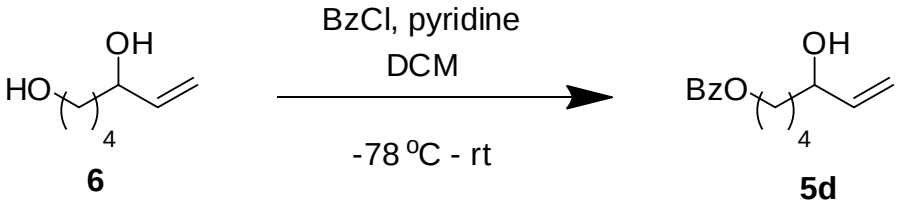
Allyl alcohols	Allylboronates	Yields (%)
 **5c**	 **1c**	30
 **5d**	 **1d**	65
 **5f**	 **1f**	88
 **5g**	 **1g**	70
 **5n**	 **1n**	57
 **5o**	 **1o**	88
 **5q**	 **1q**	35

1c was prepared from **5c**[6] (5-7% Et_2O/petroleum ether, 30 % yield, colorless oil): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.43 – 5.41 (m, 1H), 5.38 – 5.31 (m, 1H), 4.02 (t, *J* = 6.6 Hz, 2H), 2.02 – 1.97 (m, 2H), 1.63 – 1.56 (m, 4H), 1.42 – 1.33 (m, 2H), 1.22 (s, 12H), 1.17 (s, 9H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ

(6) Oishi, T.; Kanemoto, M.; Swasano, R.; Matsumori, N.; Murata, M. *Org. Lett.* **2008**, *10*, 5203.

178.8, 130.4, 125.6, 83.3, 64.5, 38.9, 32.3, 28.2, 27.4, 26.1, 24.9; IR (cm^{-1}, CH_2Cl_2 film): 2978, 1728, 1370, 1327, 1147; Calcd for $C_{18}H_{33}BO_4$ ($[M+Na]^+$) 347.2367, obsd 347.2376.

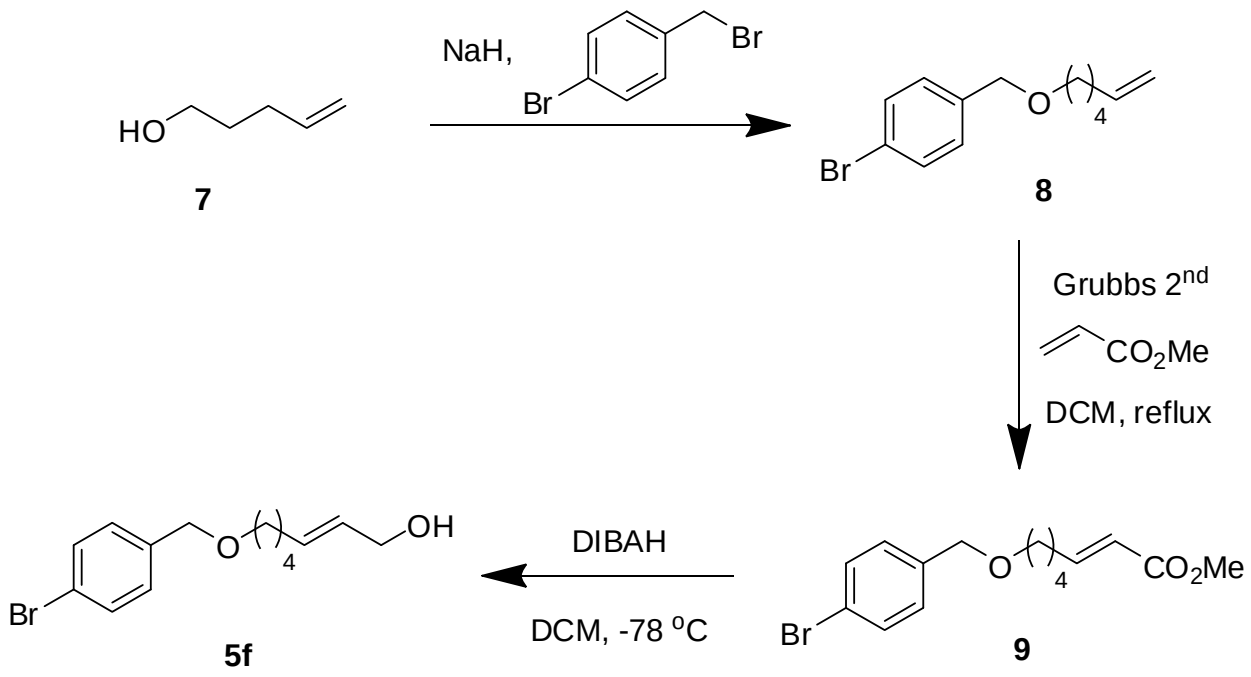
1d was prepared from **5d** (5% Et_2O/petroleum ether, 65 % yield): ^1H NMR (400 MHz, acetone-d6, ppm): δ 8.10 – 8.08 (m, 2H), 7.71 – 7.66 (m, 1H), 7.59 – 7.54 (m, 2H), 5.57 – 5.50 (m, 1H), 5.47 – 5.39 (m, 1H), 4.37 (t, J = 6.6 Hz, 2H), 2.15 – 2.09 (m, 2H), 1.87 – 1.80 (m, 2H), 1.63 – 1.53 (m, 4H), 1.26 (s, 12H); ^{13}C $\{^1H\}$ NMR (100 MHz, acetone-d6, ppm): δ 166.6, 133.6, 131.4, 130.4, 130.0, 129.2, 126.8, 83.6, 65.3, 32.9, 28.8, 26.7, 25.0; IR (cm^{-1}, CH_2Cl_2 film): 2978, 1720, 1272; HRMS: Calcd for $C_{20}H_{29}BO_4$ ($[M+H]^+$) 345.2235, obsd 345.2220.



To a solution of diol **6**[7] (100 mg, 0.77 mmol) and pyridine (124 mg, 1.57 mmol) in 3 mL DCM was slowly added benzoyl chloride (109 mg, 0.77 mmol) at -78 °C. The mixture was stirred at this temperature for 3h, and at rt for 1h followed by quenching with saturated aqueous $NaHCO_3$. Extraction with ethyl acetate followed by silica column chromatography (30% ethyl acetate/petroleum ether) afforded **5d** as a colorless oil (110 mg, 61%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.02 – 8.00 (m, 2H), 753 – 7.49 (m, 1H), 7.42 – 7.38 (m, 2H), 5.84 (ddd, J = 17.0, 10.4, 6.2 Hz, 1H), 5.20 (dt, J = 17.2, 1.4 Hz, 1H), 5.07 (dt, J = 17.2, 1.4 Hz, 1H), 4.29 (t, J = 6.6 Hz, 2H), 4.09 (m, 1H), 2.33 (bs, 1H), 1.80 – 1.73 (m, 2H), 1.63 – 1.43 (m, 4H); ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 166.70, 141.18, 132.84, 130.40, 129.53, 128.31, 114.63, 72.86, 64.93, 36.54, 28.65, 21.91; IR (cm^{-1}, CH_2Cl_2 film): 3422, 2940, 1718; HRMS: Calcd for $C_{14}H_{18}O_3$ ($[M+Na]^+$) 257.1148, obsd 257.1142.

1f was prepared from **5f** (5% Et_2O/petroleum ether, 88 % yield): ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.45 (d, J = 8.5 Hz, 2H), 7.20 (d, J = 8.5 Hz, 2H), 5.43 – 5.33 (m, 2H), 4.43 (s, 2H), 3.44 (t, J = 6.6 Hz, 2H), 2.02 – 1.97 (m, 2H), 1.64 – 1.57 (m, 4H), 1.45 – 1.37 (m, 2H), 1.24 (s, 12H); ^{13}C $\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 138.0, 131.6, 130.7, 129.3, 125.3, 121.4, 83.3, 72.2, 70.7, 32.6, 29.3, 26.3, 24.9.; IR (cm^{-1}, CH_2Cl_2 film): 2978, 2933, 2858, 1487, 1326; HRMS: Calcd for $C_{20}H_{30}BBrO_3$ ($[M+H]^+$) 409.1548, obsd 409.1550.

(7) Ishihara, K.; Kurihara, H.; Yamamoto, H. *J. Org. Chem.* **1993**, *58*, 3791.



Synthesis of **5f**: **8** was prepared in 65% yield by reaction of 5-hexen-1-ol with NaH (1.1 equiv) and 4-bromobenzyl bromide (1.1 equiv) in THF. A solution of **8** (510 mg, 1.9 mmol) and methyl crotonate (1 ml, 9.5 mmol) in DCM (4 mL) was added to a solution of Grubbs 2nd generation catalyst (48 mg, 0.06 mmol, 3 mol%) in dry DCM (6 mL). The mixture was stirred at reflux for 2.5h and then cooled to rt. Silica gel (0.4g) was added and the reaction mixture was stirred open to air for 30 min. The solvent was removed and the crude product was purified by flash column chromatography (10% ethyl acetate/petroleum ether) to give **9** as a colorless oil (520 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.46 (d, 8.4 Hz, 2H), 7.19 (d, 8.4 Hz, 2H), 6.95 (dt, J = 15.6, 7.0 Hz, 1H), 5.82 (dt, J = 15.6, 1.6 Hz, 1H), 4.43 (s, 2H), 3.72 (s, 3H), 3.45 (t, J = 6.2 Hz, 2H), 2.24 – 2.19 (m, 2H), 1.67 – 1.51 (m, 4H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 167.28, 149.36, 137.81, 131.69, 129.41, 121.58, 121.39, 72.37, 70.28, 51.59, 32.13, 29.39, 24.93; IR (cm^{-1}, CH_2Cl_2 film): 2944, 2860, 1723; HRMS: Calcd for $C_{15}H_{19}BrO_3$ ([M+H]$^{+}$) 327.0590, obsd 327.0594.

To a solution of **9** (0.45 g, 1.4 mmol) in DCM (10 mL) was added DIBAH (3.2 ml, 1M in heptane, 3.2 mmol) at -78 ^{o}C. After 2h at this temperature, MeOH (10 mL) and aqueous NaOH (10 mL, 15% w/v) was added. The mixture was warmed to rt and stirred for 30 min. After extraction with DCM and drying with anhydrous $MgSO_4$, purification by column chromatography (40% ethyl acetate/ petroleum ether) afforded **5f** as a colorless oil (0.33 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.46 (d, 8.4 Hz, 2H), 7.20 (d, 8.4 Hz, 2H), 5.71 – 5.59 (m, 2H), 4.43 (s, 2H), 4.07 (d, 4.8 Hz, 2H), 3.45 (t, J = 6.5 Hz, 2H), 2.08 – 2.03 (m, 2H), 1.65 – 1.42 (m, 5H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 137.9, 133.0, 131.7, 129.5, 129.4,

121.5, 72.3, 70.6, 63. 9, 32.2, 29.4, 25.9; IR (cm^{-1}, CH_2Cl_2 film): 3384, 2934, 2859, 1092, 1011; HRMS: Calcd for $C_{14}H_{19}BrO_2$ ($[M+H]^+$) 327.0590, obsd 327.0594.

1g was prepared from **5g**[8] (2% Et_2O/petroleum ether, 70 % yield): ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 5.42 – 5.34 (m, 1H), 5.11 – 5.04 (m, 1H), 1.73 – 1.60 (m, 3H), 1.39 – 1.32 (m, 2H), 1.27 – 1.12 (m, 14H), 0.81 (t, *J* = 7.4 Hz, 6H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$, ppm): δ 135.1, 124.9, 83.2, 46.6, 28.0, 24.9, 11.86; IR (cm^{-1}, CH_2Cl_2 film): 2963, 1324; HRMS: Calcd for $C_{14}H_{27}BO_2$ ($[M+Na]^+$) 261.1999, obsd 261.1995.

A mixture of *E*- and *Z*-**1n** was prepared from a mixture of E- and Z-**5n**[9] (prepared from DIBAH reduction of a mixture of E- and Z-methyl 3-methyl-2-pentenoate)[10] (2% Et_2O/petroleum ether, 57 % yield, colorless oil): ^1H NMR (400 MHz, acetone-d6, ppm): δ 5.23 – 5.13 (m, 1H), 2.01 – 1.94 (m, 2H), 1.65 – 1.49 (m, 5H), 1.20 (s, 12H), 0.97 – 0.92 (m, 3H); ^{13}C {^1H} NMR (100 MHz, acetone-d6, ppm): δ 137.4, 120.4, 119.4, 84.3, 33.8, 25.9, 23.8, 16.6, 14.1, 13.5; IR (cm^{-1}, CH_2Cl_2 film): 2978, 1322, 1146; HRMS: Calcd for $C_{12}H_{23}BO_2$ ($[M+Na]^+$) 233.1686, obsd 233.1690.

A mixture of *E*- and *Z*-**1o** was prepared from a mixture of E- and Z-**5o**[11] (2% Et_2O/petroleum ether, 88 % yield, colorless oil): ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 5.25 – 5.20 (m, 1H), 2.00 – 1.95 (m, 5H), 1.40 – 1.19 (m, 18H), 0.90 – 0.85 (m, 3H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$, ppm): δ 135.8, 135.6, 118.9, 118.4 83.2, 39.8, 32.0, 31.8, 31.6, 27.9, 27.6, 24.9, 23.6, 22.84, 22.7, 15.9, 14.2, 14.2; IR (cm^{-1}, CH_2Cl_2 film): 2928, 1467, 1322; HRMS: Calcd for $C_{15}H_{29}BO_2$ ([M+Na]+) 275.2156, obsd 275.2162.

1q was prepared from **5q**[12] (10-20% Et_2O/petroleum ether then DCM-50%DCM/Et_2O, 35 % yield): 1H NMR (400 MHz, Acetone) δ 5.30 (t, J = 7.8 Hz, 1H), 3.35 (dd, J = 11.4, 5.5 Hz, 4H), 2.35 – 1.99 (m, 2H), 1.56 (d, J = 7.8 Hz, 2H), 1.44 (s, 9H), 1.22 (s, 12H); ^{13}C NMR (101 MHz, Acetone) δ 155.0, 135.3, 119.2, 83.7, 79.3, 46.7, 45.2, 36.6, 28.8, 28.6, 25.1, 12.2; IR (cm^{-1}, CH_2Cl_2 film): 2977, 2933, 1695, 1145; HRMS: Calcd for $C_{18}H_{32}BNO_4$ ($[M+Na]^+$) 360.2320, obsd 360.2322.

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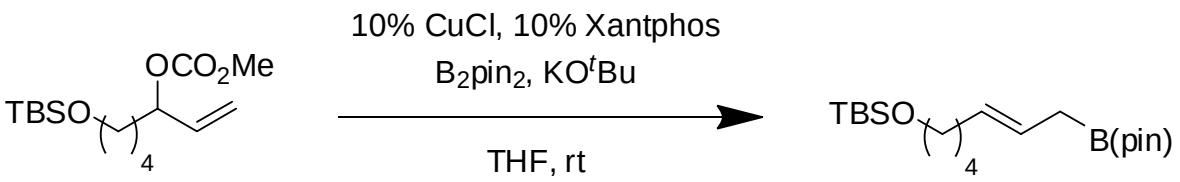
(11) Lightburn, T. E.; Paolis, O. A. D.; Cheng, K. H.; Tan, K. L. *Org. Lett.* **2011**, *13*, 2686.
(12) Takaya, J.; Sanato, K.; Iwasawa, N. *Org. Lett.* **2011**, *13*, 1698.



10 **1e**

1e was prepared from **10**[13] by Ito's method.[14] In a glovebox, bis(pinacolato)diboron (280 mg, 1.1 mmol), copper(I) chloride (5.4 mg, 0.054 mmol), Xantphos (32 mg, 0.054mmol), KO^{t}Bu (62 mg, 1.1 mmol) and THF (1 mL) were added. After stirring for 30 min, **10** (166 mg, 0.55 mmol) was added and the reaction was stirred at rt overnight . After completion, the reaction mixture was passed through a short path column of SiO_2 with an eluent (ethyl acetate/hexane 30:70) and the solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography (2% Et_2O/petroleum ether) to give **1e** as a colorless oil (133 mg, 68 % yield). ^{1}H NMR (400 MHz, acetone-d6, ppm): δ 5.47 – 5.31 (m, 2H), 3.63 (t, 6.3 Hz, 2H), 2.01 – 1.96 (m, 2H), 1.55 -1.47 (m, 4H), 1.43 – 1.36 (m, 2H), 1.21 (s, 12H), 0.90 (s, 9H), 0.05 (s, 6H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 130.92, 126.38, 83.69, 63.53, 33.14, 33.03, 26.70, 26.33, 25.13, 18.84, -5.12; IR (cm^{-1}, CH_2Cl_2 film): 2930, 1326.

Procedure for the Cu-catalyzed carboxylation of allylboronic esters:

General procedure A (0.36 mmol scale): In a glovebox, Cu(IPr)Cl (8.7 mg, 0.02 mmol, 5 mol%) and KO^{t}Bu (44 mg, 0.39 mmol, 1.1 equiv) were added to a 10-mL glass tube (Φ = 13 mm, 80 mm), which was sealed with a cap equipped with a Teflon-coated silicone rubber septum. The tube was taken out of the glove box, evacuated and refilled with CO_2 (balloon) three times. A solution of **1a** (75 mg, 0.36 mmol) in THF (1 ml) was added to the stirred mixture. The system was heated at 70 ^{o}C for 16h. Water (2 ml) was added. The mixture was acidified with aqueous HCl (1M), and saturated with sodium chloride. After extractions with diethyl ether three times, the organic phase was dried over anhydrous sodium sulphate and concentrated under vacuo. Purification by silica gel column chromatography (5% Et_2O/DCM/0.1 % HCO_2H) afforded **2a**[15] as a colorless oil (35 mg, 76%). For column chromatography, a suspension of silica in 1% Et_2O/DCM was loaded followed by the crude mixture. The column was eluted with 1-5% Et_2O/DCM/0.1 % HCO_2H to obtain the product.

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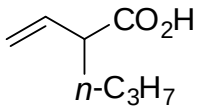
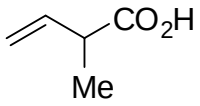
(14) Ito, H.; Miya, T.; Sawamura, M. *Tetrahedron* **2012**, *68*, 3423.
(15) Viktorov, N. B.; Zubritskii, L. M. *Russ. J. Org. Chem.* **1997**, 33, 1706.

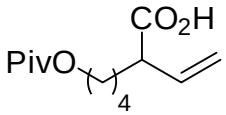
General procedure B (1.1 mmol scale): A 30-mL glass tube (Φ = 23 mm, 80 mm) was sealed with a cap equipped with a Teflon-coated silicone rubber septum and was dried by a heat gun under vacuum. The tube was evacuated and refilled with CO_2 (balloon) three times. A solution of **1a** (225 mg, 1.1 mmol) in 1.5 mL THF was added followed by a solution of Cu(IPr)Cl (26 mg, 0.053 mmol, 5 mol%) and KO^tBu (132 mg, 1.18 mmol, 1.1 equiv) in 1.5 mL THF. The sealed tube was heated at 70 ^oC for 16h. Water (5 ml) was added. The mixture was acidified with aqueous HCl (1M), and saturated with sodium chloride. After extractions with diethyl ether three times, the organic phase was dried over anhydrous sodium sulphate and concentrated under vacuo. Purification by silica gel column chromatography (1-5% Et_2O/DCM/0.1 % HCO_2H) afforded **2a** as colorless oil (104 mg, 76%). For column chromatography, a suspension of silica in 1% Et_2O/DCM was loaded followed by the crude mixture. The column was eluted with 1-5% Et_2O/DCM/0.1 % HCO_2H to obtain the product.



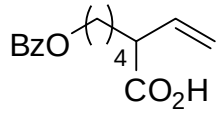
^1H NMR (400 MHz, $CDCl_3$, ppm): δ 10.51 (bs, 1H), 5.86 – 5.77 (m, 1H), 5.19 – 5.15 (m, 2H), 3.03 (dd, *J* = 15.5, 7.6 Hz, 1H), 1.81 – 1.72 (m, 1H), 1.60 – 1.51 (m, 1H), 1.43 – 1.28 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$, ppm): δ 180.8, 135.7, 117.7, 50.0, 34.2, 20.3, 13.9.



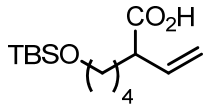
Synthesis of 2-methylbut-3-enoic acid **2b**:[12] **2b** was prepared from **1b** according to procedure B. The crude mixture was eluted with 1-5% Et_2O/DCM/0.1 % HCO_2H to give **2c** as a colorless oil (85 mg, 79%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 5.98 – 5.89 (m, 1H), 5.17 (t, J = 14.5 Hz, 1H), 3.22 – 3.15 (m, 1H), 1.31 (d, *J* = 7.1 Hz, 3H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$, ppm): δ 180.8, 136.6, 116.6, 43.6, 16.6.



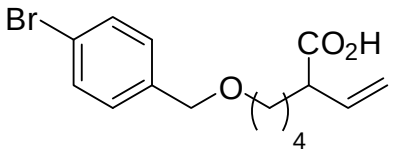
Synthesis of 6-(pivaloyloxy)-2-vinylhexanoic acid **2c: 2c** was prepared from **1c** according to procedure A. The crude mixture was eluted with 10% Et_2O/DCM/0.1 % HCO_2H to give **2c** as a colorless oil (59 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 5.85 – 5.76 (m, 1H), 5.20 – 5.16 (m, 2H), 4.05 (t, *J* = 6.5 Hz, 2H), 3.02 (dd, *J* = 15.5, 7.6 Hz, 1H), 1.87 – 1.77 (m, 1H), 1.68 – 1.56 (m, 3H), 1.48 – 1.34 (2H), 1.18 (s, 9H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 179.7, 178.9, 135.5, 118.2, 64.2, 50.1, 39.0, 31.7, 28.6 27.4, 23.6; IR (cm^{-1}, CH_2Cl_2 film): 2973, 2960, 1728, 1709, 1160; HRMS: Calcd for $C_{13}H_{22}O_4$ ([M-H]$^-$) 241.1445, obsd 241.1451.



Synthesis of 6-(benzoyloxy)-2-vinylhexanoic acid **2d: 2d** was prepared from **1d** according to procedure A. The crude mixture was eluted with 10% Et_2O/DCM/0.1 % HCO_2H to give **2d** as a colorless oil (50 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.98 – 7.95 (m, 2H), 7.50 – 7.46 (m, 1H), 7.38 – 7.34 (m, 2H), 5.80 – 5.71 (m, 1H), 5.15 – 5.10 (m, 2H), 4.25 (t, J = 6.6 Hz, 2H), 3.02 – 2.96 (m, 1H), 1.85 – 1.69 (m, 3H), 1.63 – 1.36 (m, 3H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 179.6, 166. 9, 135.4, 133.1, 130.7, 129.8, 128.6, 118.2, 64.9, 50.0, 31.7, 28.7, 23.8; IR (cm^{-1}, CH_2Cl_2 film): 2945, 1716; HRMS: Calcd for $C_{15}H_{17}O_4$ ([M-H]$^-$) 261.1132, obsd 261.1126.

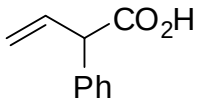


Synthesis of 6-((tert-butyldimethylsilyl)oxy)-2-vinylhexanoic acid **2e: 2e** was prepared from **1e** according to procedure A. The crude mixture was eluted with 2% Et_2O/DCM/0.1 % HCO_2H to give **2e** as a colorless oil (53 mg, 54%). ^{1}H NMR (400 MHz, acetone-d6, ppm): δ 5.89 - 5.80 (m, 1H), 5.17 – 5.08 (m, 2H), 3.64 (t, J = 6.2 Hz, 2H), 3.03 – 2.97 (m, 1H), 1.82 – 1.73 (m, 1H), 1.57 – 1.37 (m, 5H), 0.89 (s, 9H), 0.05 (s, 6H); ^{13}C {^{1}H} NMR (100 MHz, acetone-d6, ppm): δ 174.91, 137.75, 116.76, 63.31, 50.74, 33.21, 32.69, 26.21, 24.11, 18.71, -5.25; IR (cm^{-1}, CH_2Cl_2 film): 2931, 1709; HRMS: Calcd for $C_{14}H_{27}O_3Si$ ([M-H]$^-$) 271.1735, obsd 271.1727.

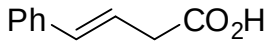


Synthesis of 6-((4-bromobenzyl)oxy)-2-vinylhexanoic acid **2f: 2f** was prepared from **1f** according to procedure A. The crude mixture was eluted with 2% Et_2O/DCM/0.1 % HCO_2H to give **2fc** as a colorless oil (75 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.46 (d, J = 8.4 Hz, 2H), 7.20 (d, J= 8.4 Hz, 2H), 5.86 – 5.77 (m, 1H), 5.20 – 5.15 (m, 2H), 4.44 (s, 2H), 3.45 (t, J = 6.5 Hz, 2H), 3.05 – 3.00 (m, 1H), 1.82 – 1.78 (m, 1H), 1.64 – 1.38 (m, 5H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 180.3, 137.8, 135.6, 131.7, 129.5, 121.6, 118.0, 72.33, 70.4, 50.2, 31.9, 29.6, 23.9.; IR (cm^{-1}, CH_2Cl_2 film): 2940, 1705; HRMS: Calcd for $C_{15}H_{18}BrO_3$ ([M+H]$^+$) 299.0641, obsd 299.0643.

Synthesis of 2-phenylbut-3-enoic acid **2h** and (E)-4-phenylbut-3-enoic acid **2h'**: The crude mixture resulting from reaction of **1h** according to procedure A was subjected to column chromatography (0 - 10% Et_2O/DCM/0.1HCO_2H) followed by a second column (30% acetone/petroleum ether) to afford **2h** as a colorless oil (20 mg, 30%). Fractions containing *E*-**2h'** was further purified by recrystallization in petroleum ether at -20 ^{o}C to afford a white solid (9mg, 13%).

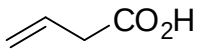


2h:[16] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.37 – 7.27 (m, 5H), 6.22 (ddd, *J* = 17.1, 10.2, 8.0 Hz, 1H), 5.18 (dt, *J* = 10.2, 1.1 Hz, 1H), 5.12 (dt, *J* = 17.1, 1.1 Hz, 1H), 4.33 (d, *J* = 8.0 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 178.0, 137.5, 135.1, 129.0, 128.3, 127.8, 118.2, 55.6.

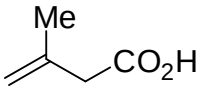


2h':[17] ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.39 – 7.36 (m, 2H), 7.33 – 7.29 (m, 2H), 7.26 – 7.22 (m, 1H), 6.53 (d, J = 15.9 Hz, 1H), 6.29 (dt, J = 15.9, 7.1 Hz, 1H), 3.31 (dd, J = 7.1, 1.4 Hz, 2H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 177.1, 136.8, 134.2, 128.7, 127.9, 126.5, 121.0, 38.0.

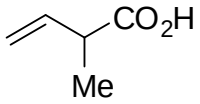
(16) Aggarwal, S. K.; Bradshaw, J. S.; Eguchi, M.; Parry, S.; Rossiter, B. E.; Markides, K. E.; Lee, M. L. *Tetrahedron* **1987**, *43*, 451.



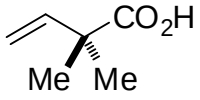
Synthesis of 2-butenoic acid **2i**:[17] **2i** was prepared from **1i** according to procedure B. The crude mixture was eluted with 1-5% Et_2O/DCM/0.1 % HCO_2H to give **2i** as a colorless oil (63 mg, 68%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 10.27 (bs, 1H), 5.97 – 5.86 (m, 1H), 5.22 – 5.21 (m, 1H), 5.19 – 5.18 (m, 1H), 3.14 (dt, J = 6.9, 1.4 Hz, 1H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$, ppm): δ 178.2, 129.6, 119.3, 38.9.



Synthesis of 3-methylbut-3-enoic acid **2j**:[18] **2j** was prepared from **1j** according to procedure B. The crude mixture was eluted with 1-5% Et_2O/DCM/0.1 % HCO_2H to give **2j** as a colorless oil (70 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 9.94 (bs, 1H), 4.96 – 4.95 (m, 1H), 4.89 (bs, 1H), 3.08 (s, 2H), 1.84 (s, 3H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$, ppm): δ 177.9, 138.1, 115.5, 43.3, 22.5.



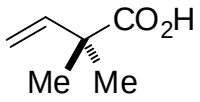
Synthesis of 2-methylbut-3-enoic acid **2b** from **1k**: **2b** was prepared from **1k** according to procedure B. The crude mixture was eluted with 1-5% Et_2O/DCM/0.1 % HCO_2H to give **2b** as a colorless oil (67 mg, 62%).



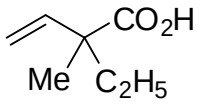
(17) Commercially available.

(18)Andreana, P. R.; McLellan, J. S.; Chen, Y.; Wang, P. G. *Org. Lett.* **2002**, *4*, 3875.

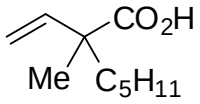
Synthesis of 2,2-dimethylbut-3-enoic acid **2l**[19]**: 2l** was prepared from **1l** according to procedure A. The crude mixture was eluted with 1-5% Et_2O/DCM/0.1 % HCO_2H to give **2l** as a colorless oil (28 mg, 69%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 10.90 (bs, 1H), 6.05 (dd, J = 17.4, 10.6 Hz, 1H), 5.21 – 5.04 (m, 2H), 1.33 (s, 6H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$, ppm): δ 183.2, 142.1, 113.6, 44.9, 24.5.



Synthesis of 2,2-dimethylbut-3-enoic acid **2l** from **1m**: **2l** was prepared from **1m** according to procedure A. The crude mixture was eluted with 1-5% Et_2O/DCM/0.1 % HCO_2H to give **2l** as a colorless oil (22 mg, 54%).



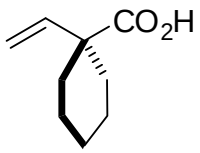
Synthesis of 2-ethyl-2-vinylheptanoic acid **2n**:[20] **2n** was prepared from **1n** according to procedure A. The crude mixture was eluted with 1-5% Et_2O/DCM/0.1 % HCO_2H to give **2n** as a colorless oil (26 mg, 57%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 6.02 (dd, J = 17.4, 10.9 Hz, 1H), 5.17 – 5.12 (m, 2H), 1.84 – 1.75 (m, 1H), 1.70 – 1.61 (m, 1H), 1.28 (s, 3H), 0.89 (t, J = 7.5 Hz, 3H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$, ppm): δ 182.6, 141.4, 114.1, 48.6, 39.2, 32.3, 24.3, 22.6, 20.4, 14.1.



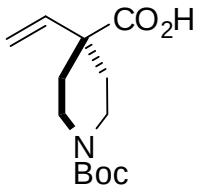
Synthesis of 2-methyl-2-vinylheptanoic acid **2o**: **2o** was prepared from **1o** according to procedure A. The crude mixture was eluted with 1-5% Et_2O/DCM/0.1 % HCO_2H to give **2o** as a colorless oil (25 mg, 41%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 10.75 (bs, 1H), 6.04 (dd, J = 17.4, 10.9 Hz, 1H), 5.44 – 4.76 (m, 2H), 1.94 – 1.48 (m, 2H), 1.49 – 1.15 (m, 9H), 0.88 (t, J = 6.7 Hz, 3H); ^{13}C {^1H} NMR (100 MHz, $CDCl_3$, ppm): δ

(19) O'Connor, P. D.; Kim, U. B.; Brimble, M. A. *Eur. J. Org. Chem.* **2009**, 4405.
(20) Murphy, K. E. ; Hoveyda, A. H. *Org. Lett.* **2005**, *7*, 1255.

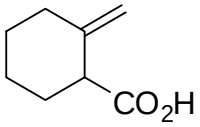
182.6, 141.4, 114.1, 48.6, 39.2, 32.3, 24.3, 22.6, 20.4, 14.1; IR (cm^{-1}, CH_2Cl_2 film): 2932, 1701; HRMS: Calcd for $C_{10}H_{18}O_2$ ($[M-H]^-$) 169.1234, obsd 169.1228.



Synthesis of 1-vinylcyclohexanecarboxylic acid **2p**: **2p** was prepared from **1p** according to procedure A. The crude mixture was eluted with 1-5% Et_2O/DCM/0.1 % HCO_2H to give **2p** as a colorless oil (35 mg, 64%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 10.37 (bs, 1H), 5.83 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.47 – 4.75 (m, 2H), 2.12 – 2.08 (m, 2H), 1.63 – 1.40 (m, 7H), 1.334 – 1.26 (m, 1H).; ^{13}C {^1H} NMR (100 MHz, $CDCl_3$, ppm): δ 181.9, 141.8, 115.2, 49.6, 33.4, 25.8, 23.1; IR (cm^{-1}, CH_2Cl_2 film): 2933, 1698; HRMS: Calcd for $C_9H_{14}O_2$ ($[M-H]^-$) 153.0921, obsd 153.0924.



Synthesis of 1-(tert-butoxycarbonyl)-4-vinylpiperidine-4-carboxylic acid **2q**:[21] **2q** was prepared from **1q** according to procedure A. The crude mixture was eluted with 15% Et_2O/DCM/0.1 % HCO_2H to give **2q** as a colorless oil (53 mg, 58%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.38 (bs, 1H), 5.82 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.24 – 5.18 (m, 2H), 3.74 – 3.70 (m, 2H), 3.17 – 3.10 (m, 2H), 2.15 – 2.10 (m, 2H), 1.65 – 1.58 (m, 2H), 1.44 (s, 9H).; ^{13}C {^1H} NMR (100 MHz, $CDCl_3$, ppm): δ 179.4, 155.0, 140.1, 116.3, 79.9, 48.1, 41.1, 32.5, 28.6.



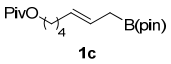
(21) Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2008**, *130*, 15254.

Synthesis of 2-methylenecyclohexanecarboxylic acid **2r**: **2r** was prepared from **1r** according to procedure A. The crude mixture was eluted with 15% Et_2O/DCM to give **2s** as a colorless oil (25 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 10.79 (bs, 1H), 4.86 (s, 1H), 4.75 (s, 1H), 3.23 – 3.20 (appt t, J = 5.3 Hz, 1H), 2.37 – 2.30 (m, 1H), 2.20 – 2.16 (m, 1H), 2.01 – 1.98 (m, 1H), 1.78 – 1.49 (m, 5H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 180.4, 145.9, 110.2, 49.4, 34.1, 30.2, 27.8, 23.6; IR (cm^{-1}, CH_2Cl_2 film): 2936, 1702; HRMS: Calcd for $C_8H_{12}O_2$ ($[M-H]^-$) 139.0765, obsd 139.0768.

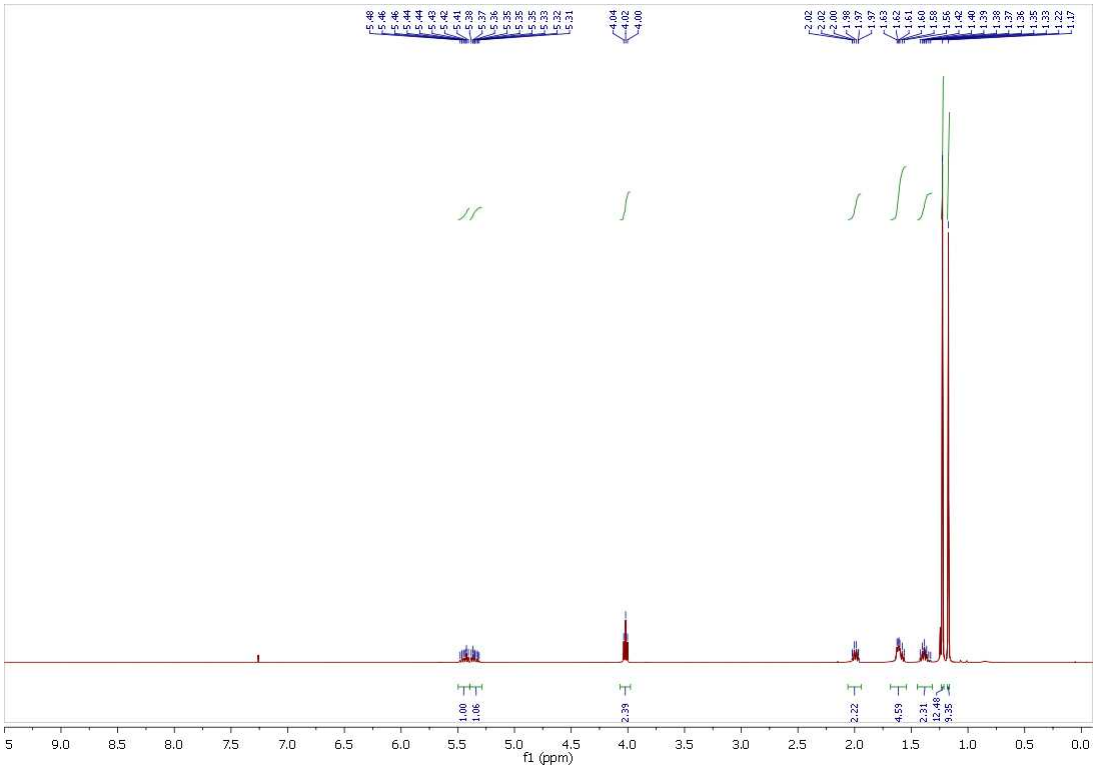
Carboxylation using K_2OCOMe:[22] A mixture of **1a** (75mg, 0.36 mmol), CuIPrCl (9mg, 0.02 mmol, 5%) and KO_2COMe (45mg, 0.39 mmol) in THF (1 mL) was heated under nitrogen at 70 ^{o}C for 16h. The mixture was acidified with aqueous HCl (1M), and saturated with sodium chloride. After extractions with diethyl ether three times, the organic phase was dried over anhydrous sodium sulphate and concentrated under vacuo. Purification by silica gel column chromatography (5% Et_2O/DCM/0.1 % HCO_2H) afforded **2a** as a colorless oil (29 mg, 64%).

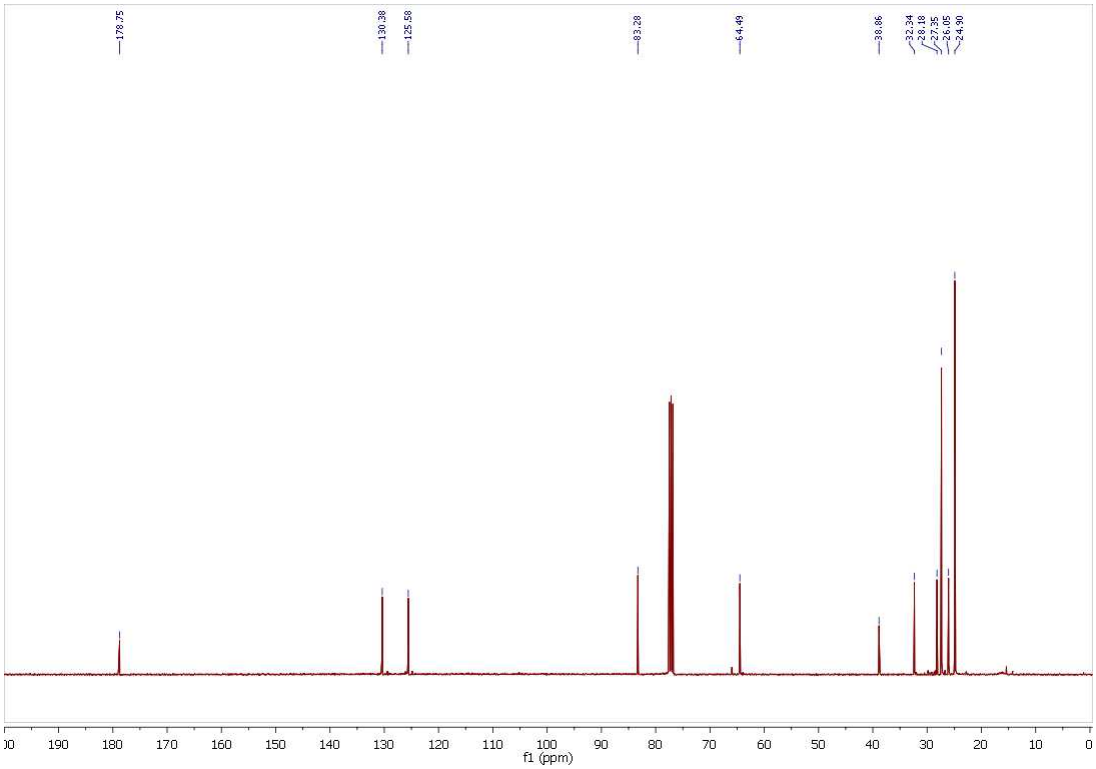
(22) Stueber, D.; Patterson, D.; Mayne, C. L.; Orendt, A. M.; Grant, D. M.; Parry, R. W. *Inorg. Chem.* **2001**, *40*, 1902.

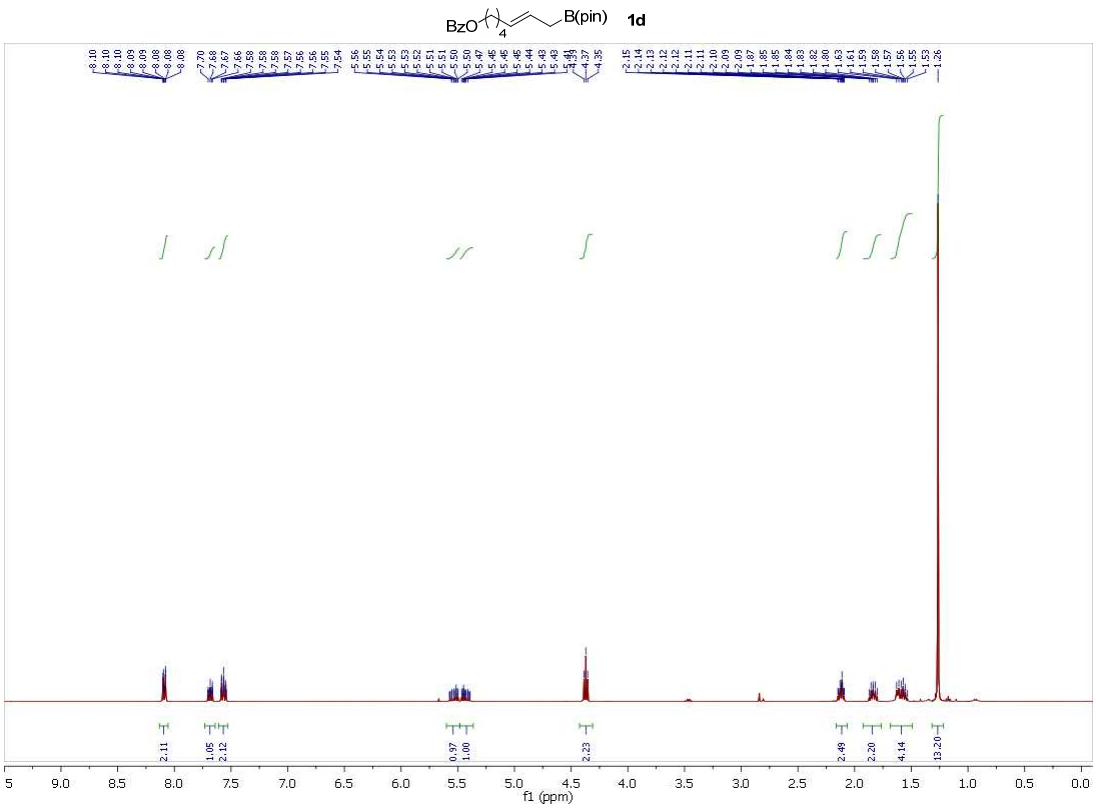
^{1}H and ^{13}C Spectra

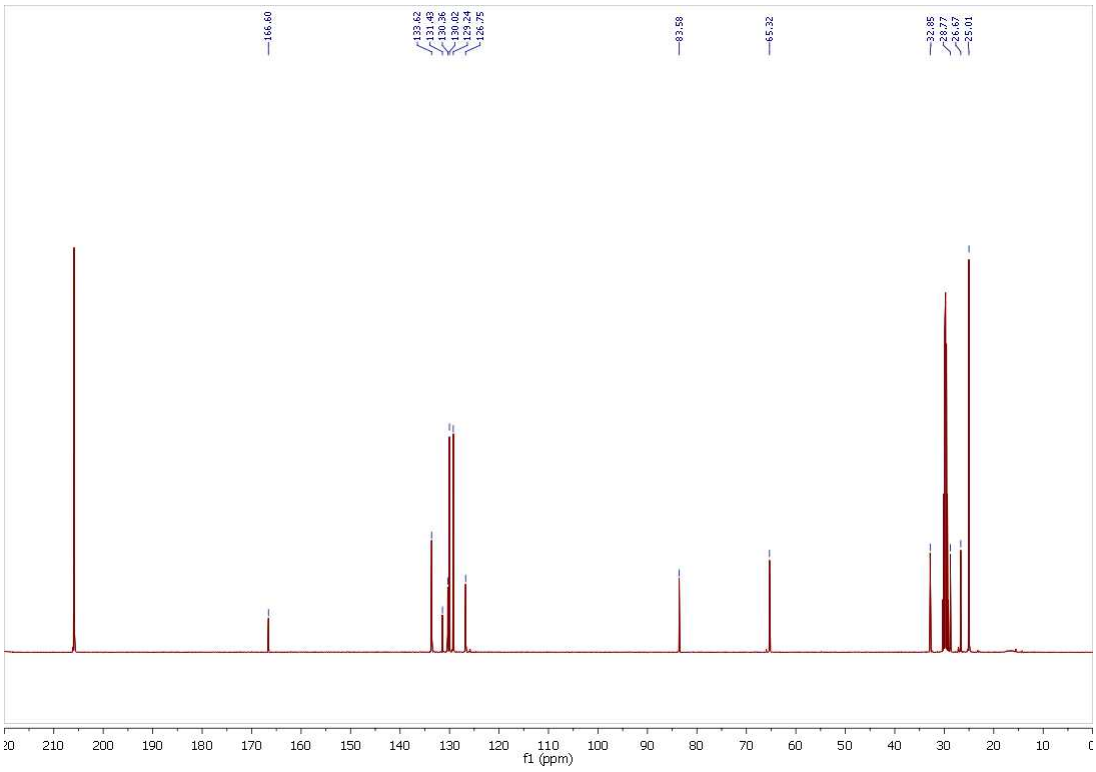


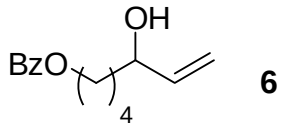
1c



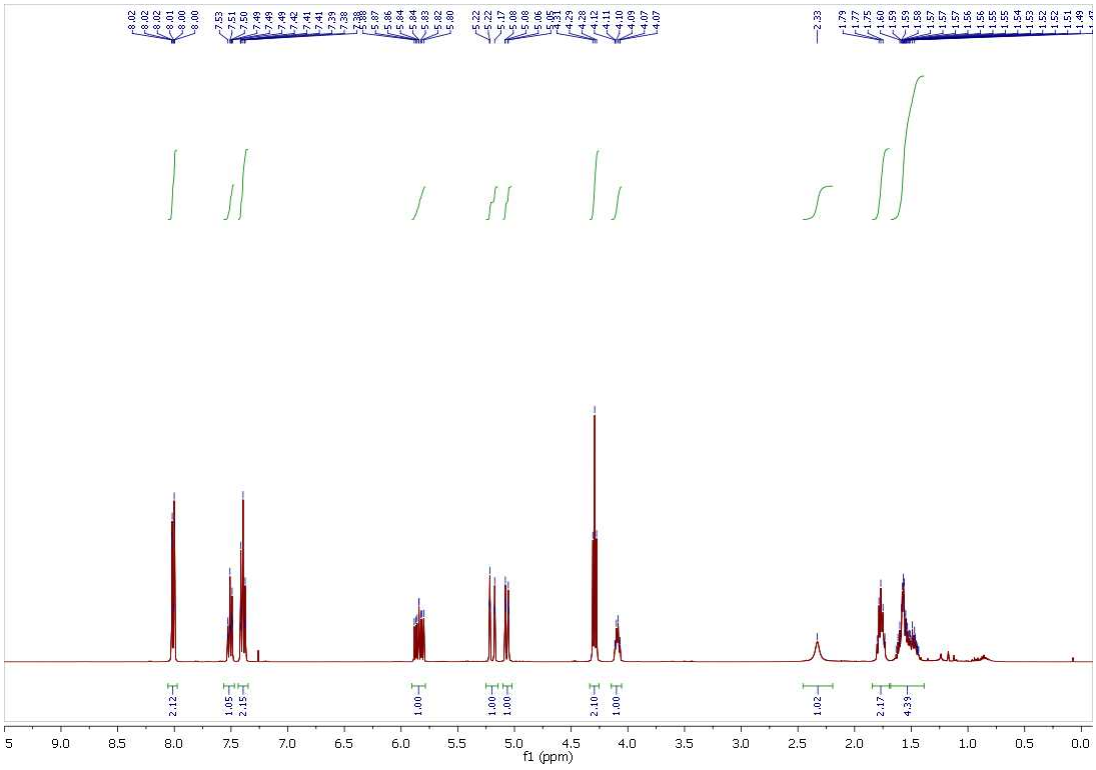


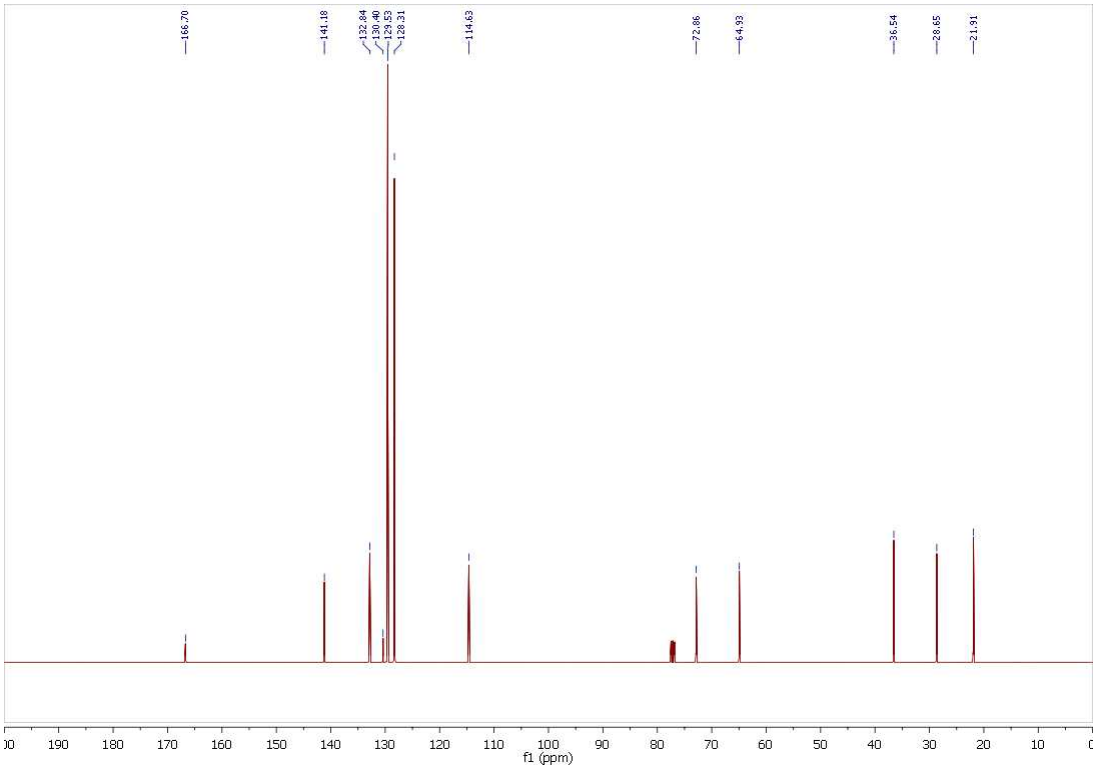

BzO
4
B(pin)
1d
f1 (ppm)

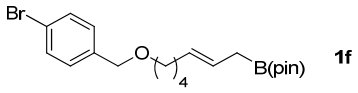

166.60
133.62
133.49
130.36
130.02
129.24
126.75
83.58
65.32
32.85
28.77
26.67
25.01
f1 (ppm)



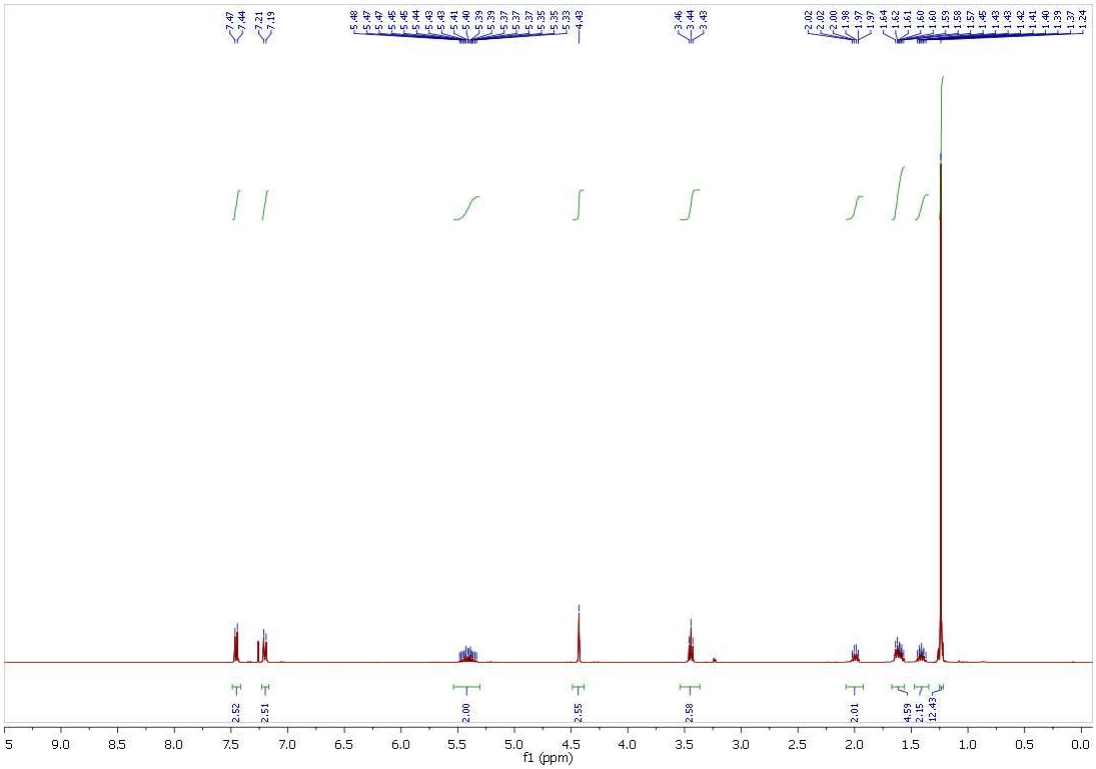
6

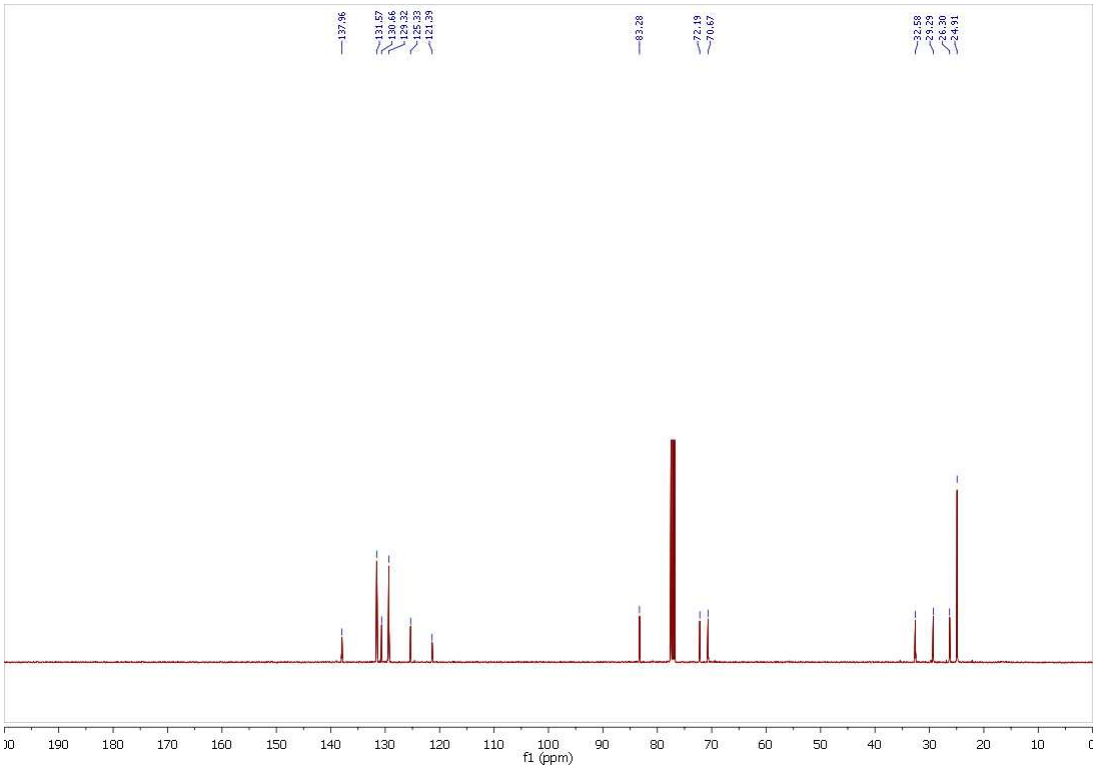


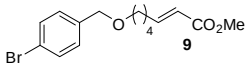




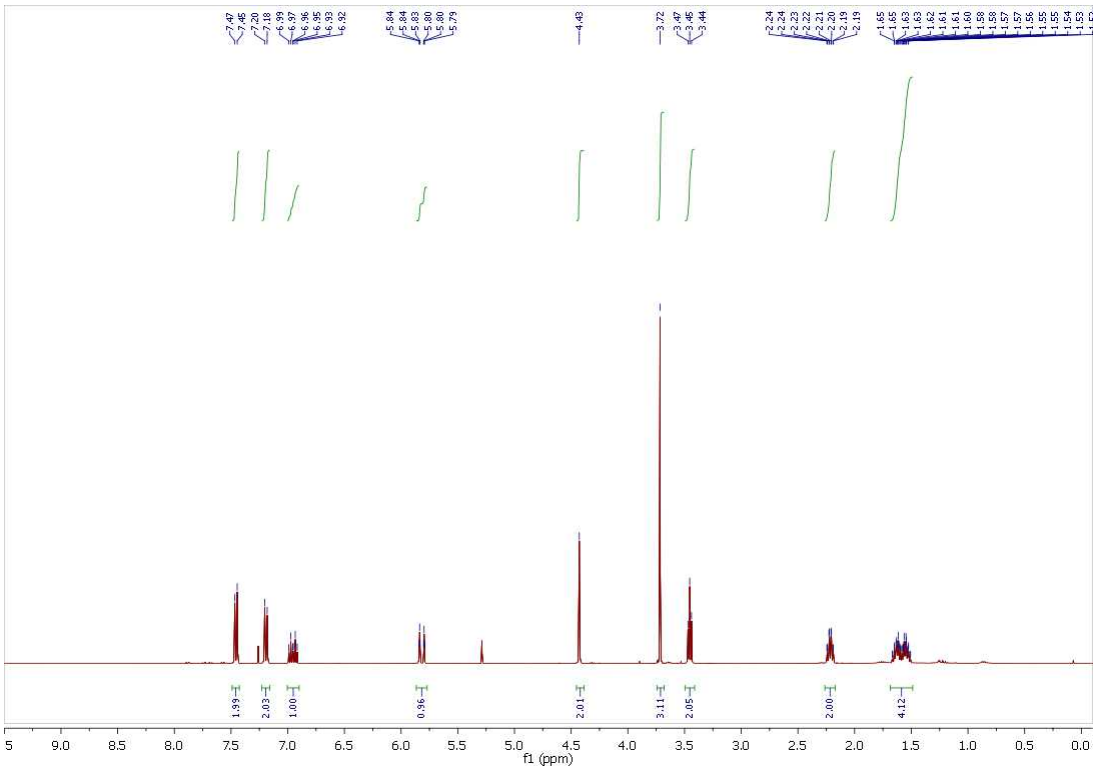
1f

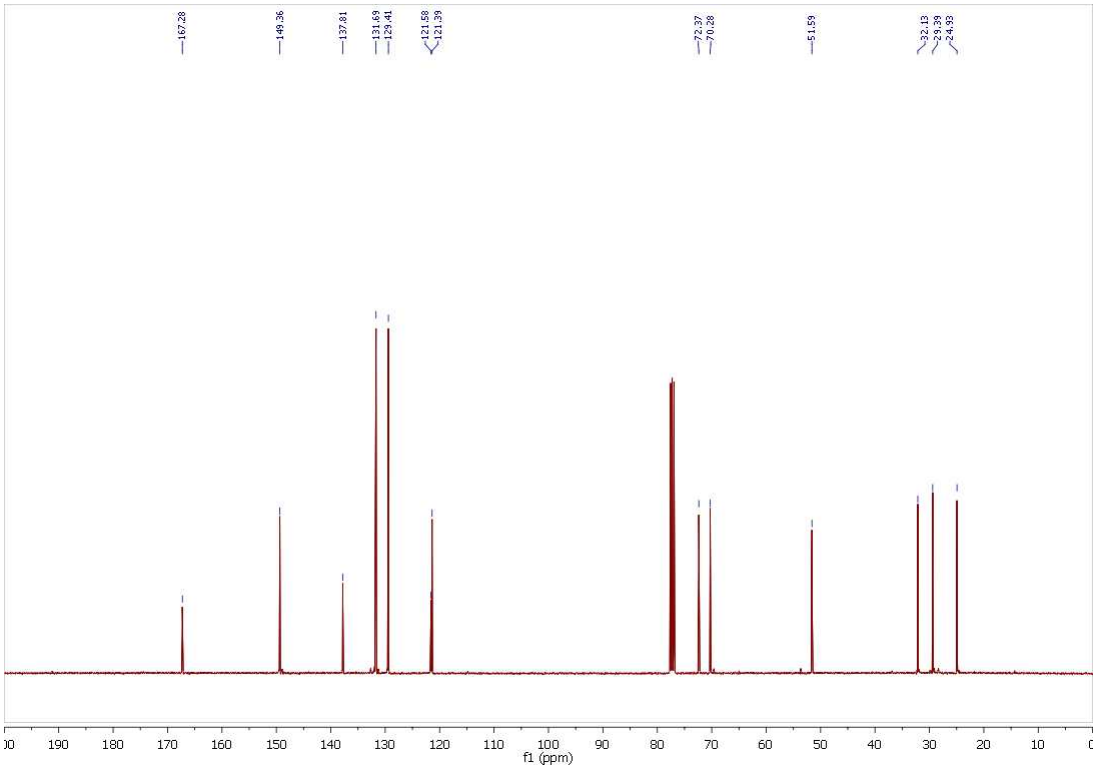


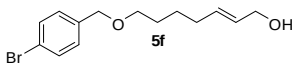



Br
O
4
CO2Me

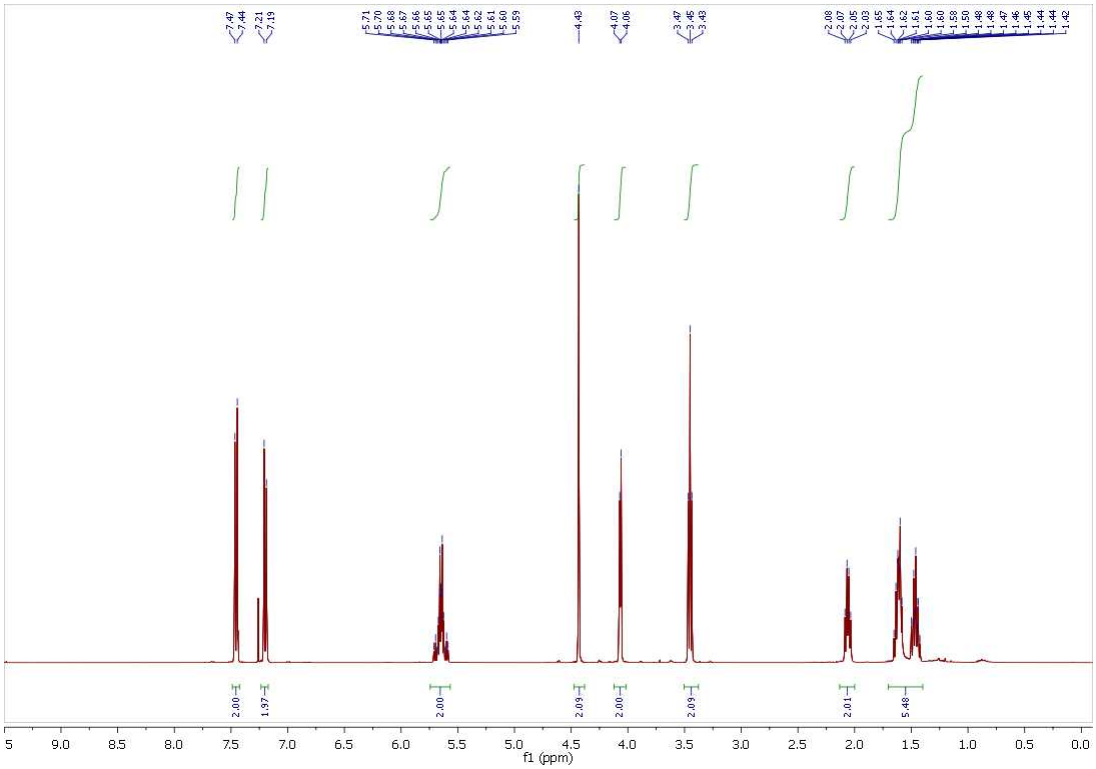
9


7.47
7.46
7.20
7.18
6.99
6.97
6.96
6.95
6.93
6.92
5.84
5.84
5.83
5.80
5.80
5.79
4.43
3.72
3.47
3.46
3.44
2.24
2.24
2.23
2.22
2.21
2.20
2.19
2.19
1.65
1.65
1.63
1.62
1.61
1.61
1.60
1.58
1.58
1.57
1.57
1.56
1.55
1.55
1.54
1.53
1.99
2.03
1.00
0.96
2.01
3.11
2.05
2.00
4.12
f1 (ppm)


167.28
149.36
137.81
131.69
129.41
121.58
121.39
72.37
70.28
51.59
32.13
29.39
24.93
f1 (ppm)


Br
O
OH

5f


7.47
7.44
7.21
7.19
5.71
5.70
5.68
5.67
5.66
5.65
5.64
5.62
5.61
5.60
5.59
4.43
4.07
4.06
3.47
3.45
3.43
2.08
2.07
2.05
2.03
1.65
1.64
1.62
1.61
1.60
1.58
1.50
1.48
1.47
1.46
1.45
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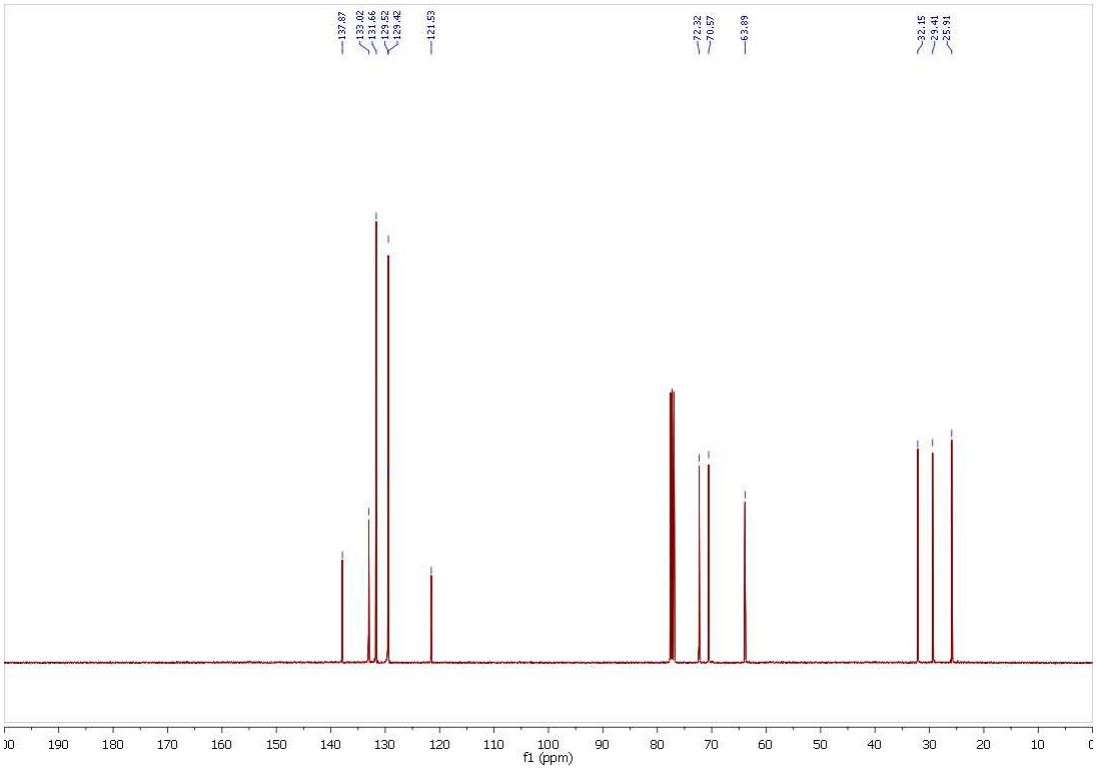
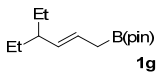
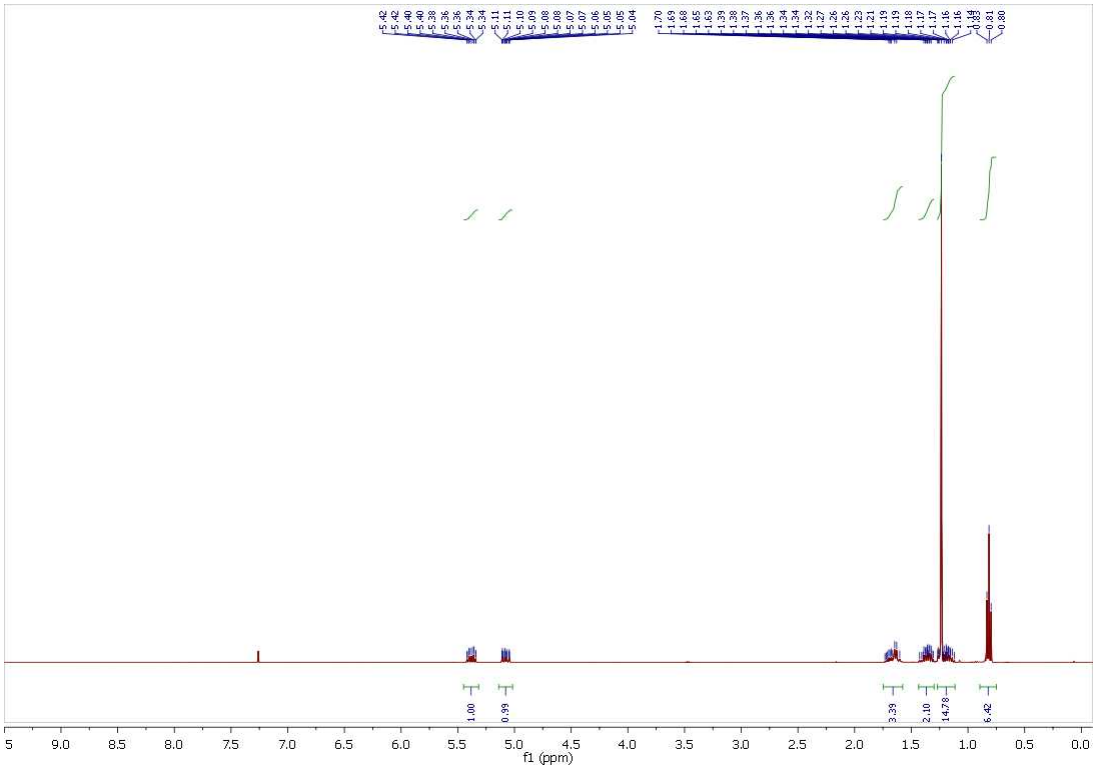
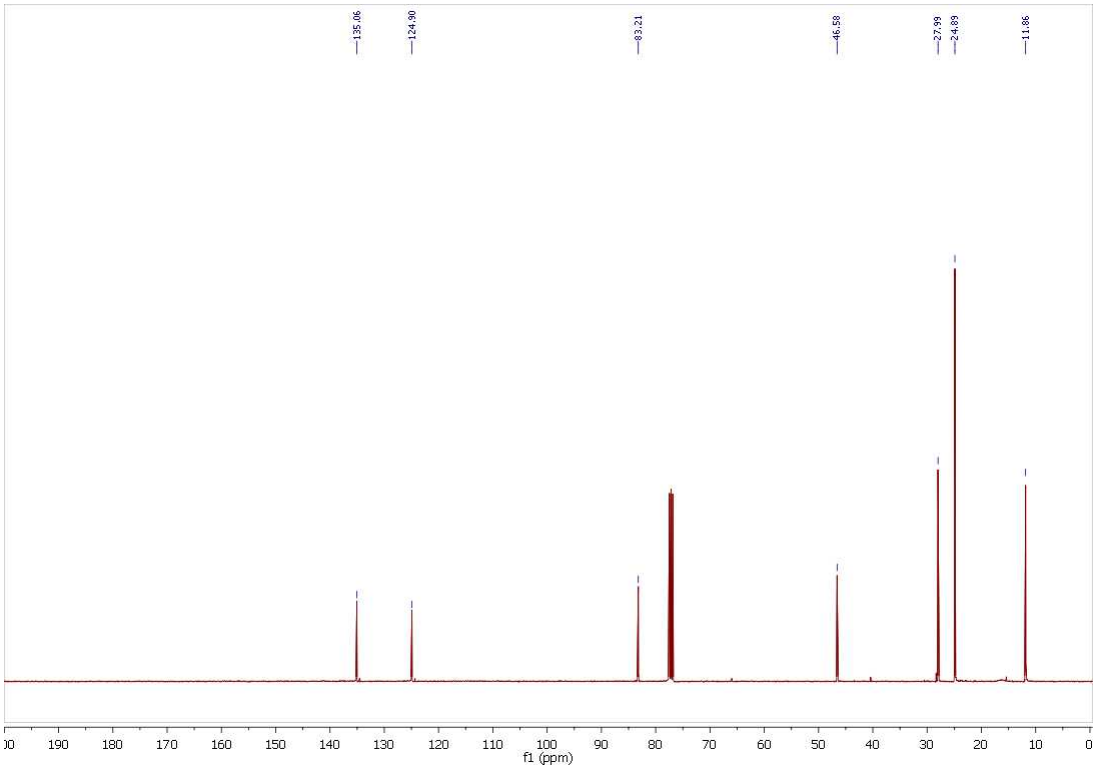
2.00
2.09
2.01
5.48
f1 (ppm)

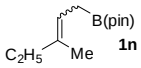

137.87
133.02
131.66
129.52
129.42
121.53
72.32
70.57
63.89
32.15
29.41
25.91
f1 (ppm)


Et
Et
B(pin)

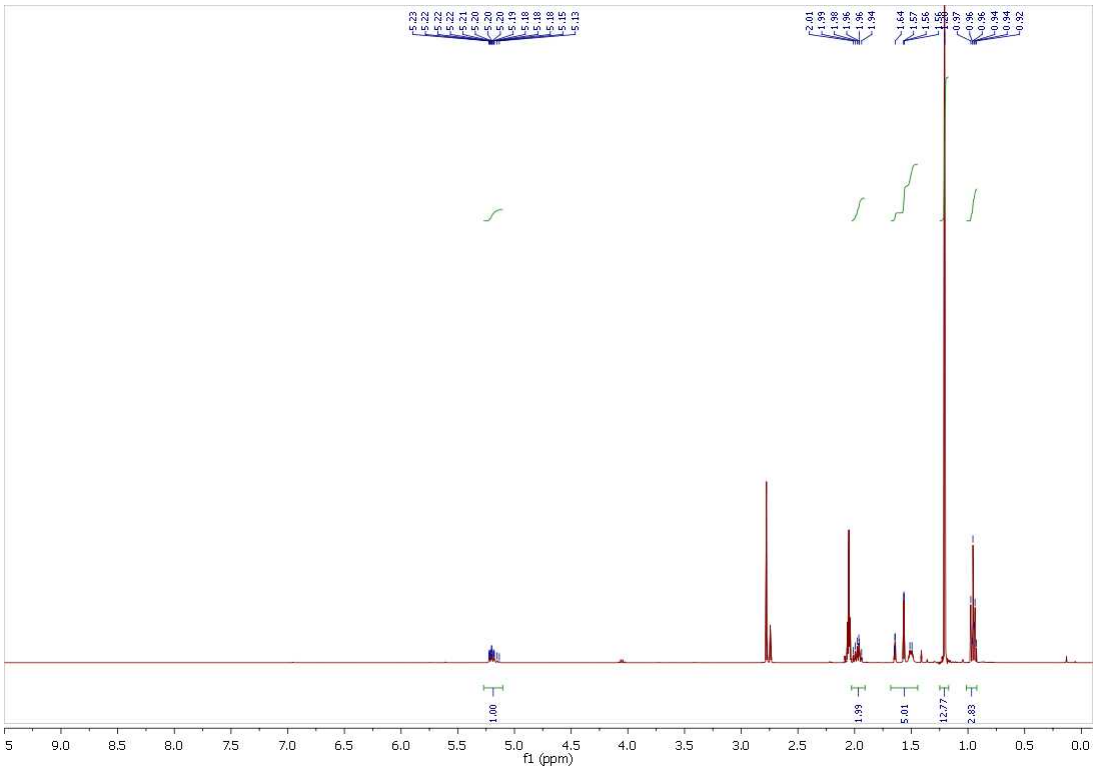
1g

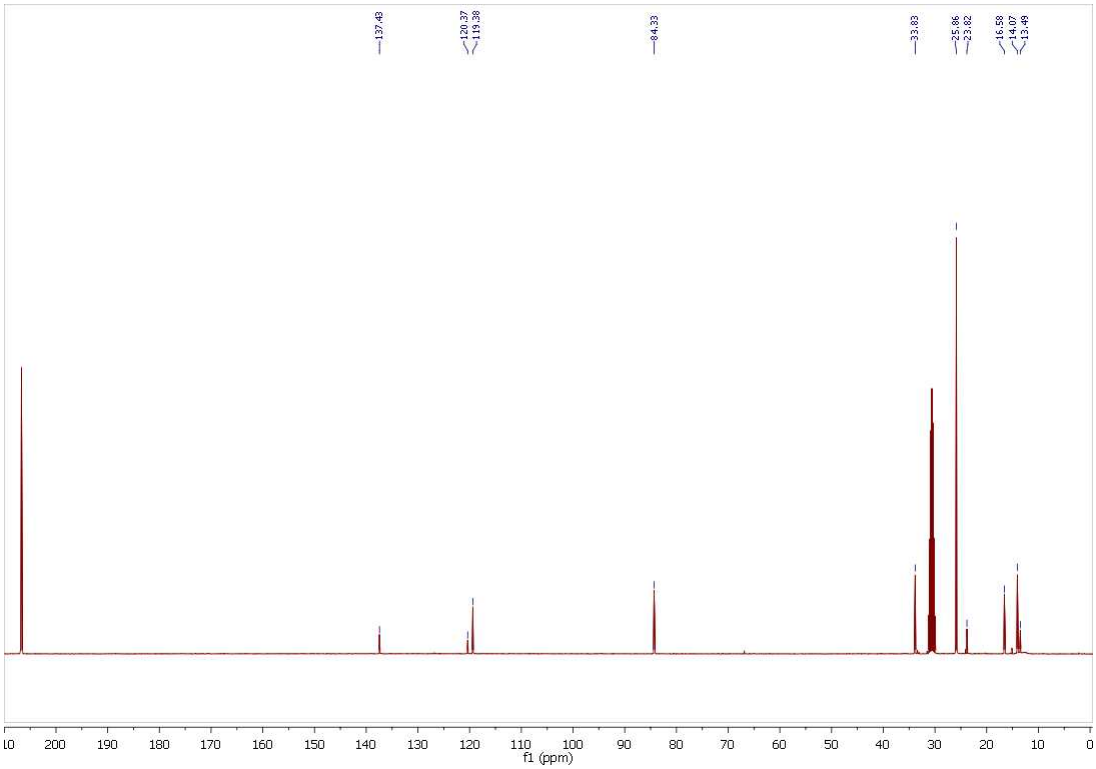

1.00
0.99
3.39
2.10
14.78
6.42
f1 (ppm)

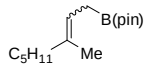

135.06
124.90
83.21
46.58
27.99
24.89
11.86
f1 (ppm)



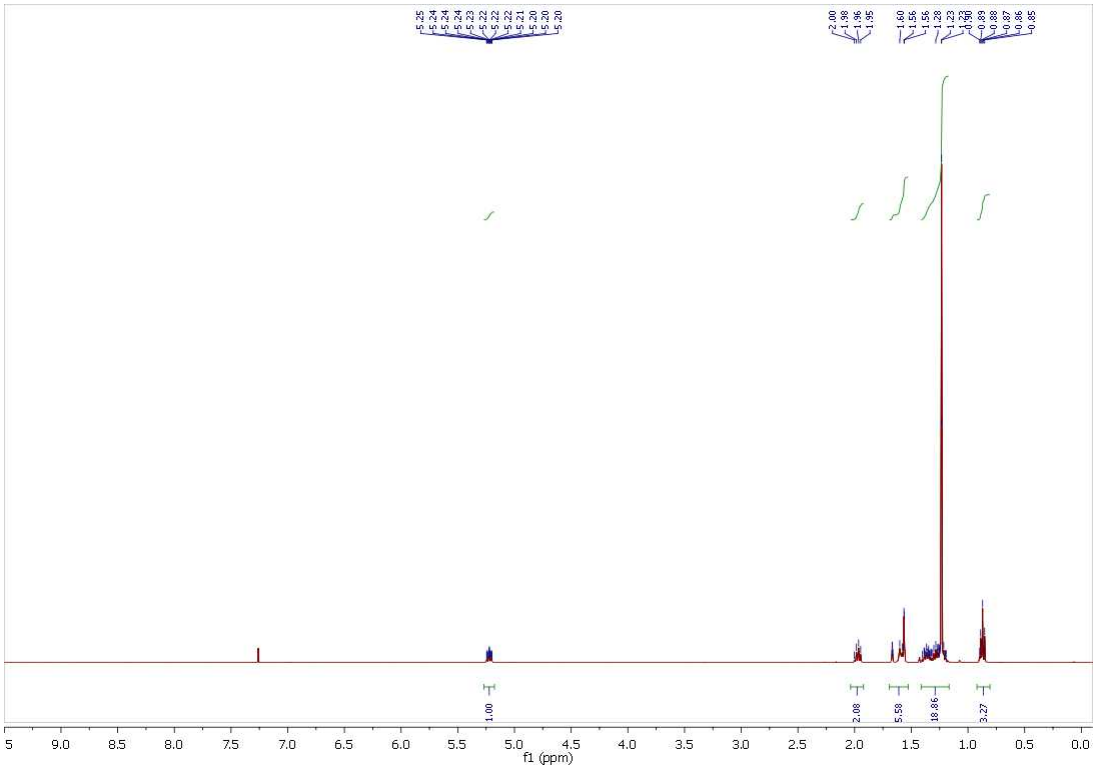
1n

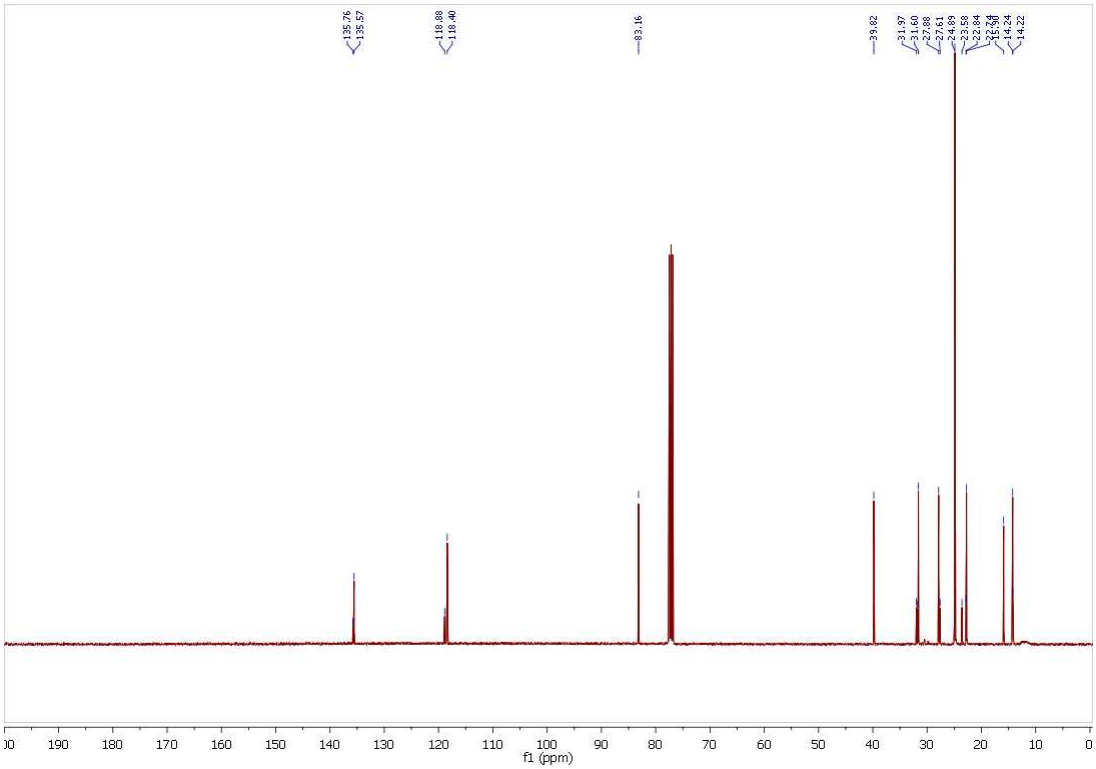


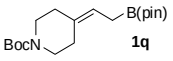




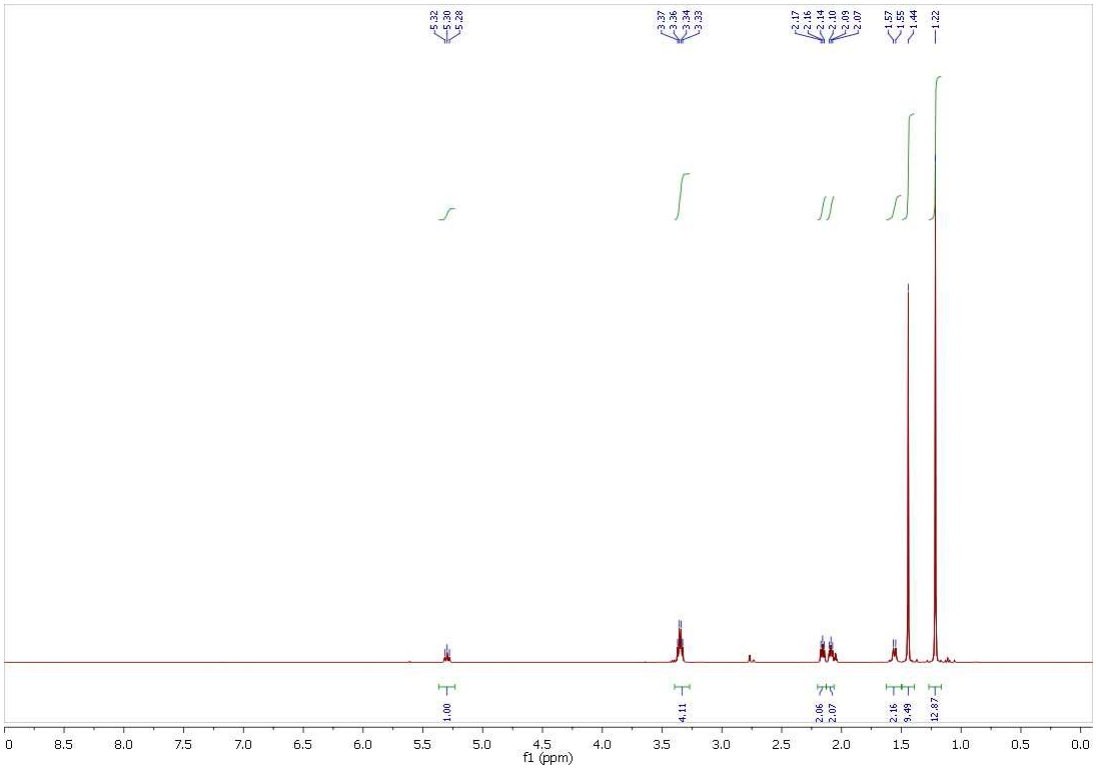
1o






B(pin)
BocN

1q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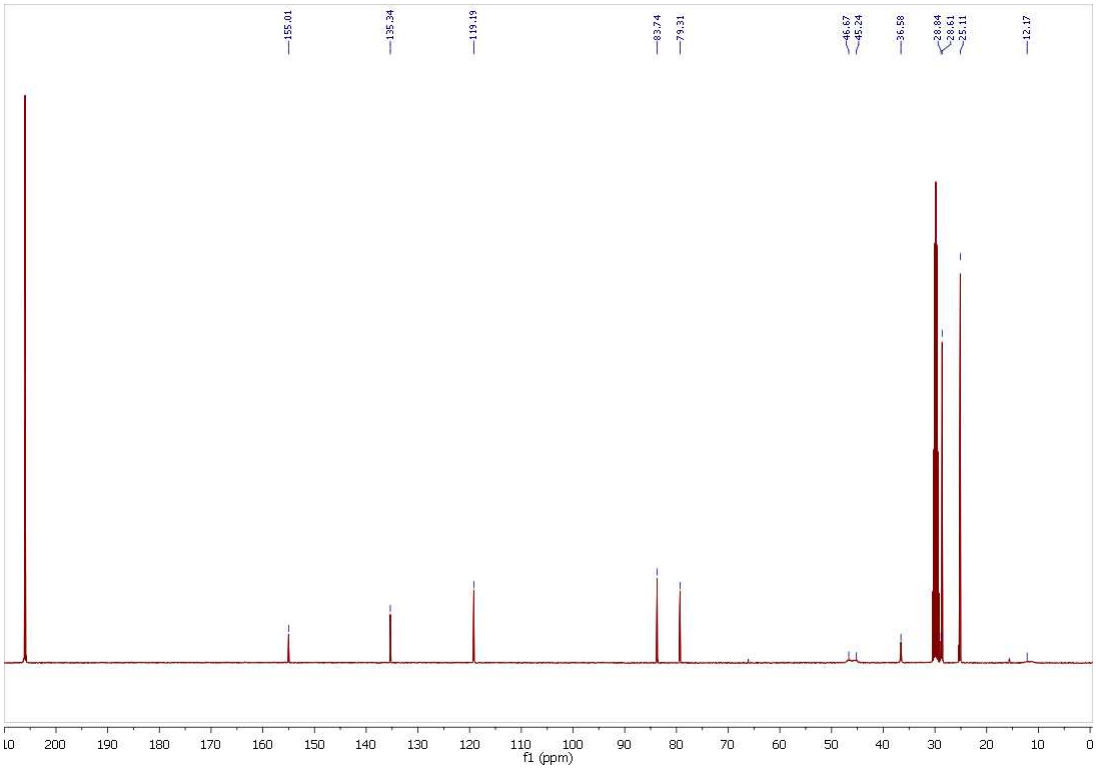
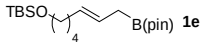
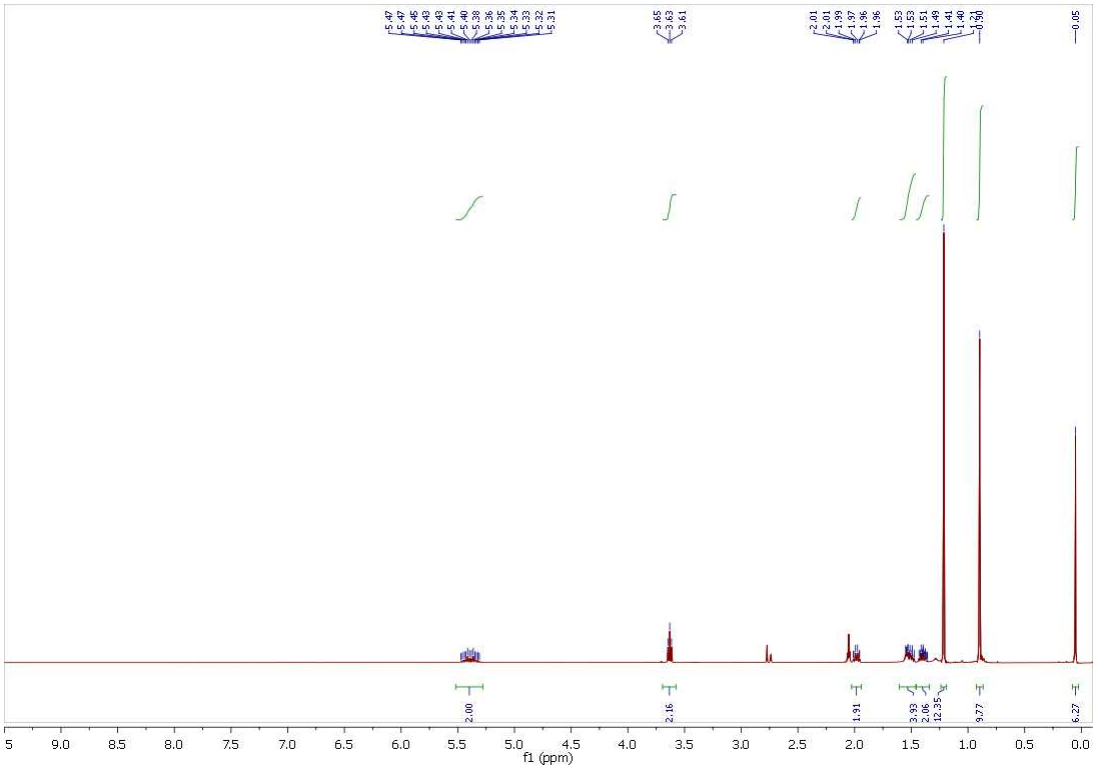
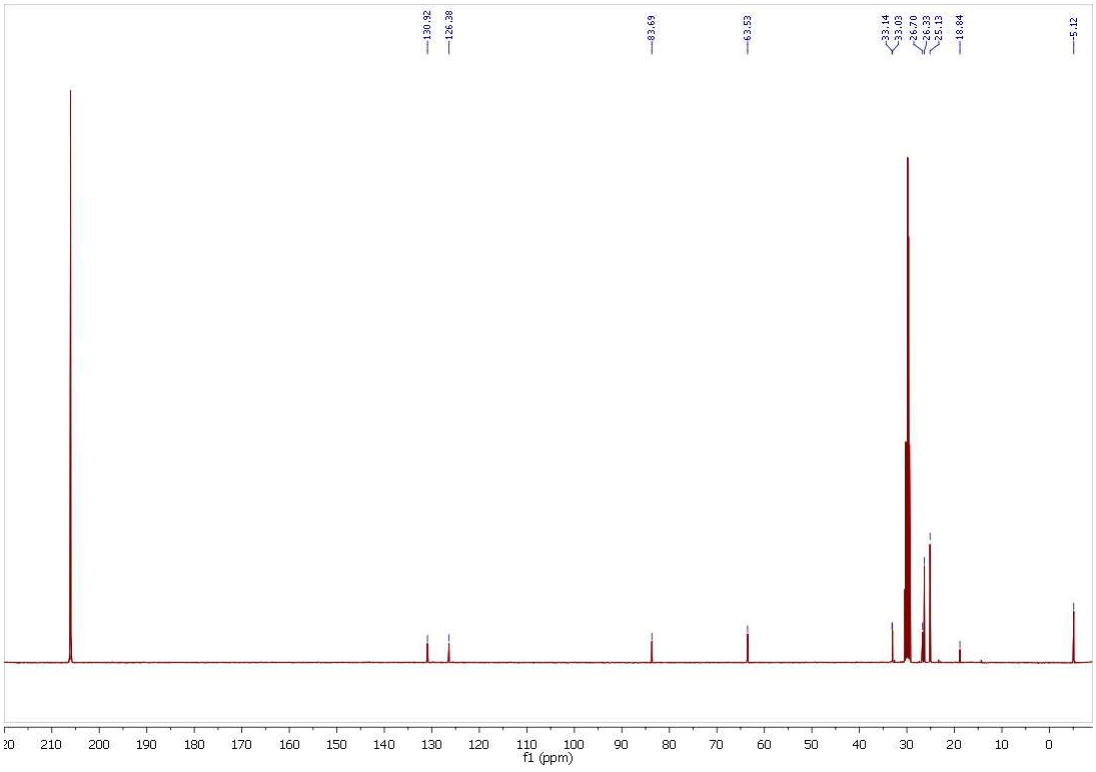
5.28
3.37
3.36
3.34
3.33
2.17
2.15
2.14
2.10
2.09
2.07
1.57
1.55
1.44
1.22
1.00
4.11
2.06
2.07
2.16
9.49
12.87
f1 (ppm)

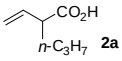

155.01
135.24
119.19
83.74
79.31
46.67
45.24
36.58
28.84
28.61
25.11
12.17
f1 (ppm)


TBSO
4
B(pin)

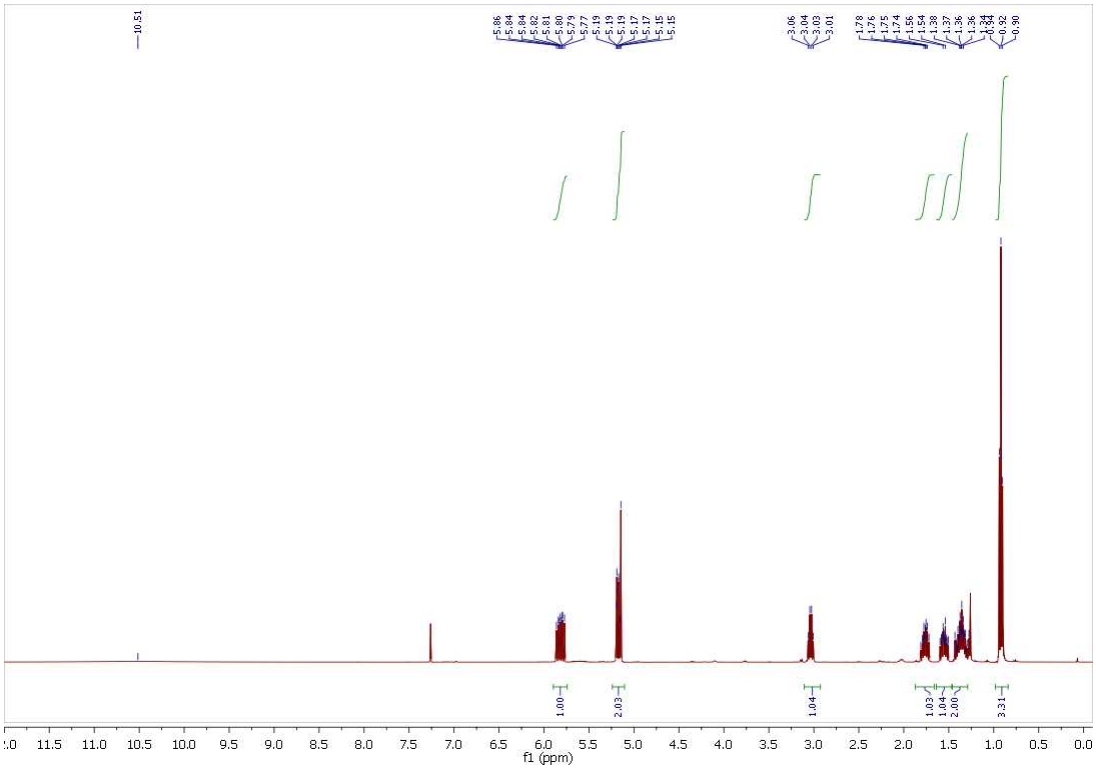
1e

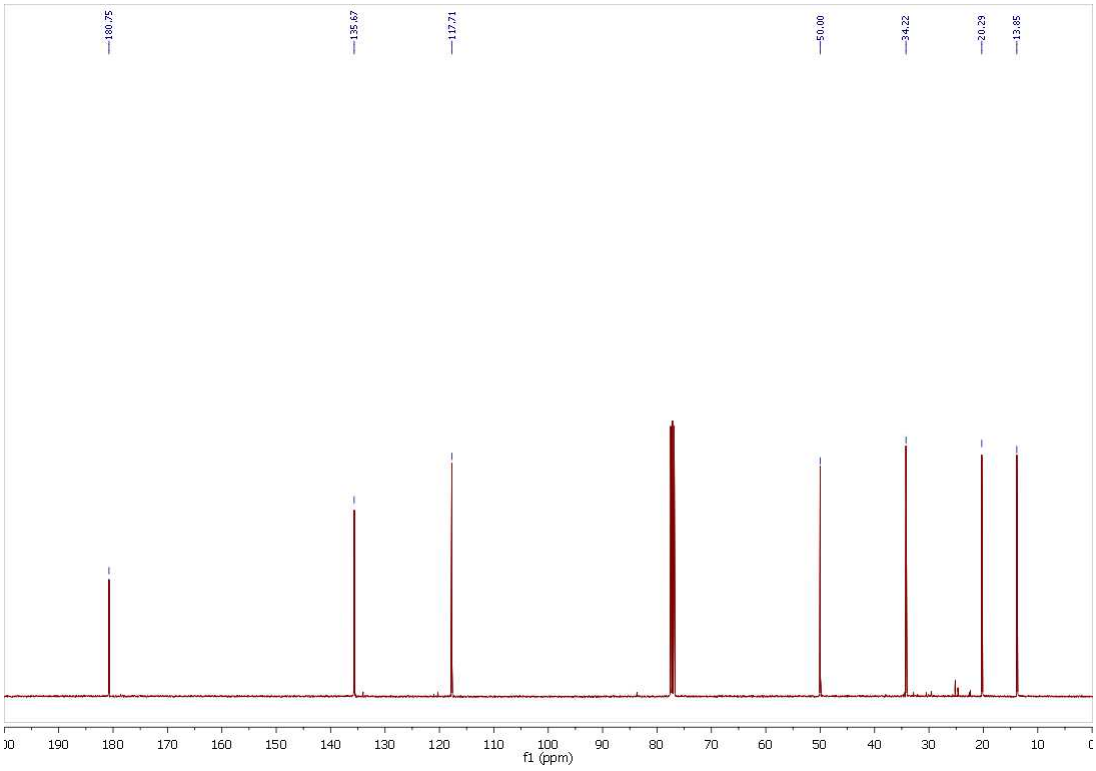

5.47
5.46
5.45
5.43
5.41
5.40
5.38
5.36
5.35
5.34
5.33
5.32
5.31
3.65
3.63
3.61
2.01
2.01
1.99
1.97
1.96
1.96
1.53
1.53
1.51
1.49
1.41
1.40
1.21
0.90
0.05
2.00
2.16
1.91
3.93
2.06
12.35
9.77
6.27
f1 (ppm)

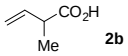

130.92
126.38
83.69
63.53
33.14
33.03
26.70
26.33
25.13
18.84
5.12
f1 (ppm)


CO2H
n-C3H7

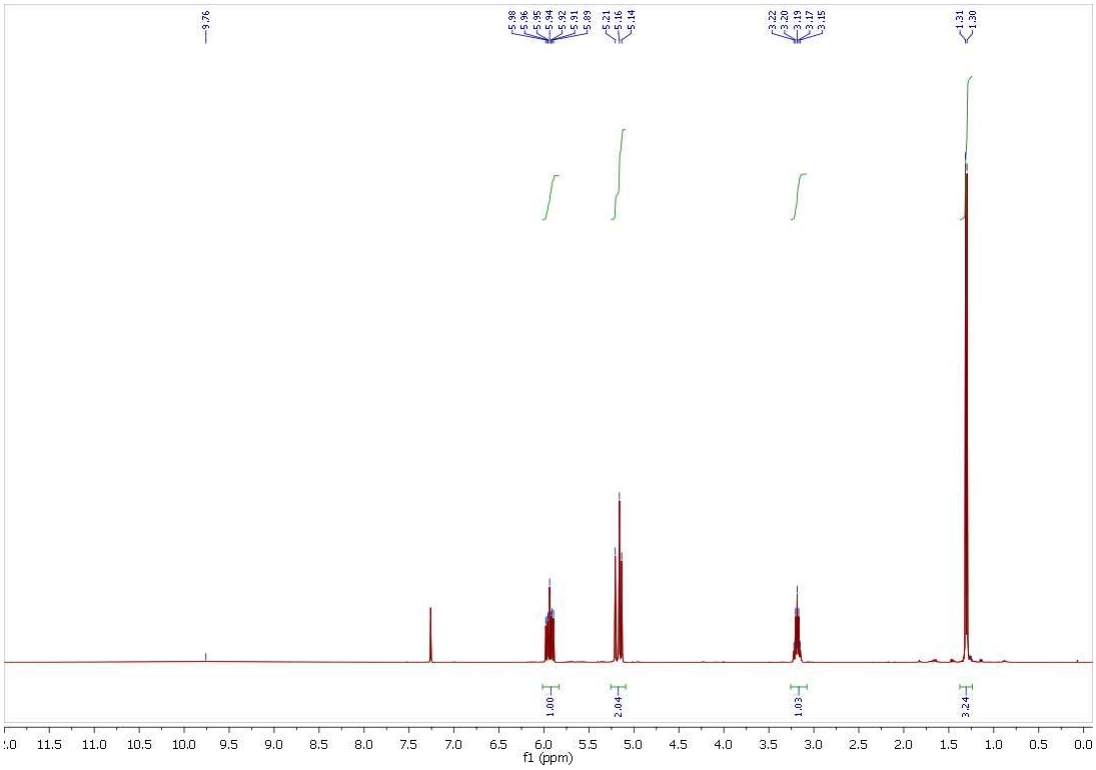
2a

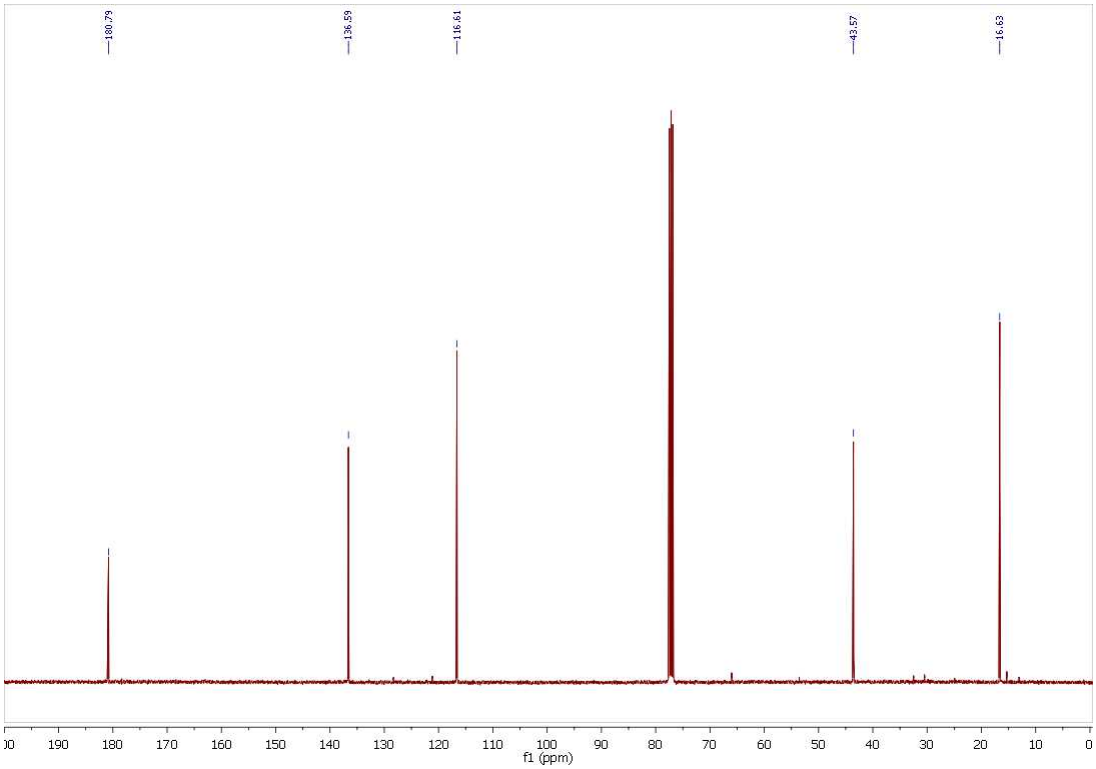

10.51
5.86
5.84
5.84
5.82
5.81
5.80
5.79
5.77
5.19
5.19
5.17
5.17
5.15
5.15
3.06
3.04
3.03
3.01
1.78
1.76
1.75
1.74
1.56
1.54
1.38
1.37
1.36
1.36
0.92
0.90
1.00
2.03
1.04
1.03
1.04
2.00
3.31
f1 (ppm)

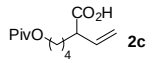

180.75
135.67
117.71
50.00
34.22
20.29
13.85
f1 (ppm)


CO2H
Me

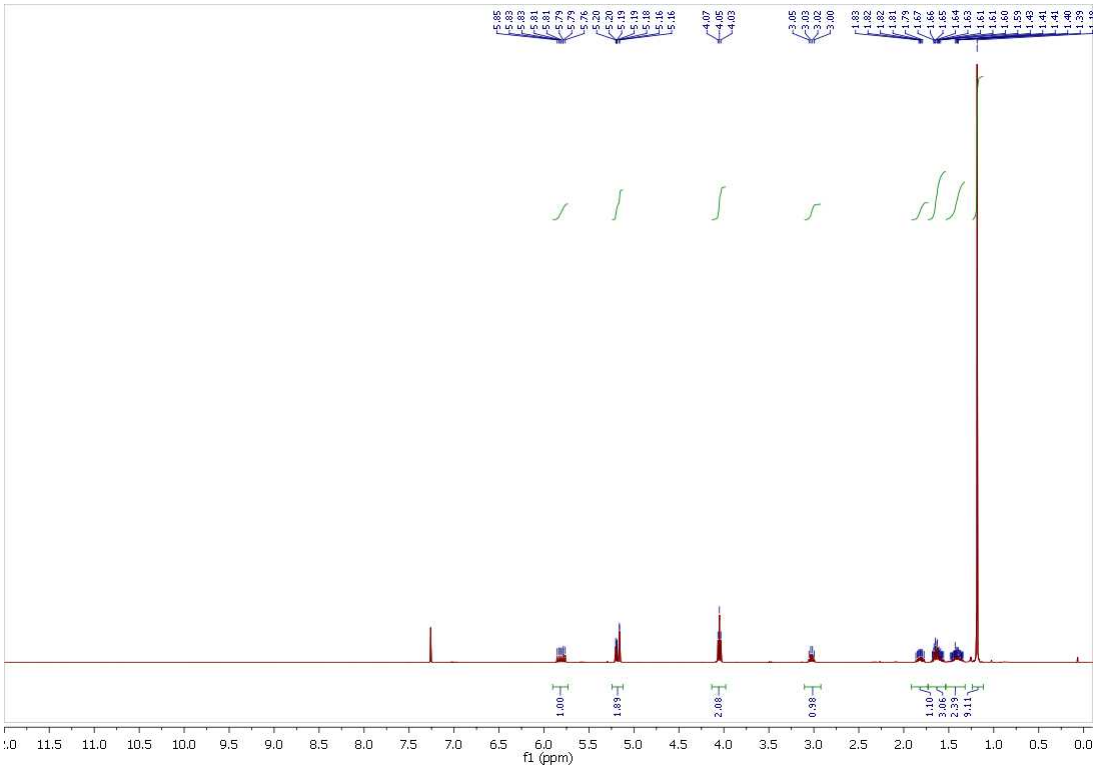
2b

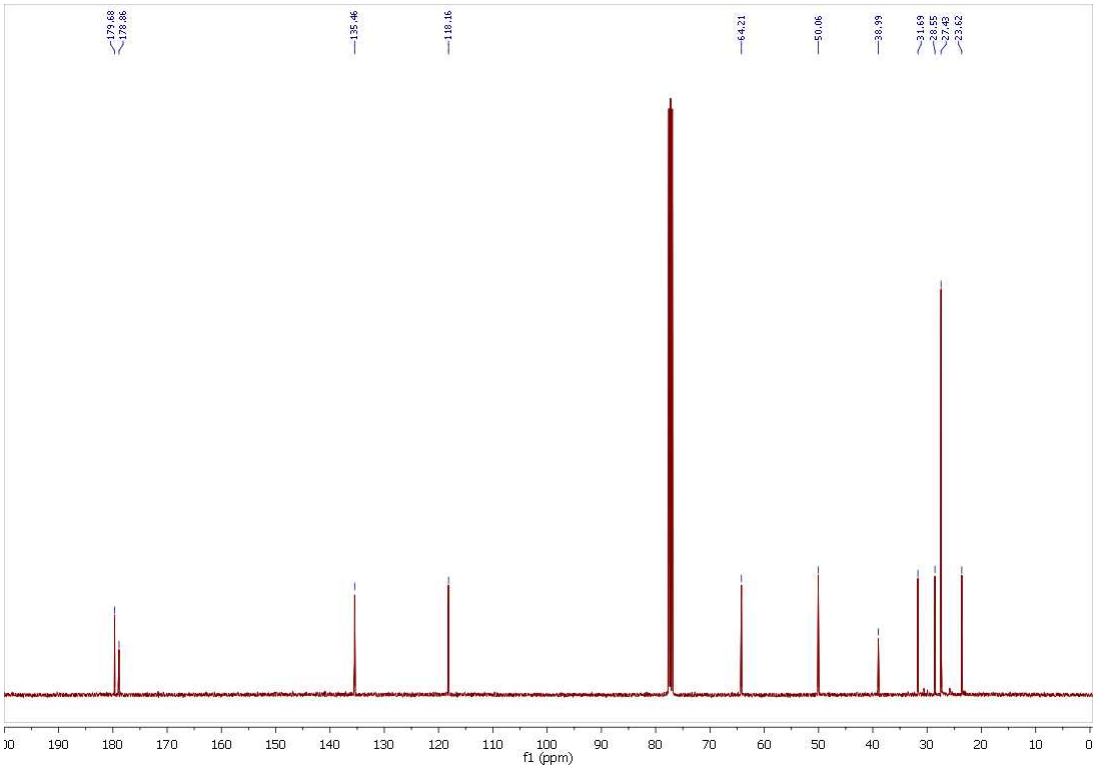

9.76
5.98
5.96
5.95
5.94
5.92
5.91
5.89
5.21
5.16
5.14
3.22
3.20
3.19
3.17
3.15
1.31
1.30
1.00
2.04
1.03
3.24
f1 (ppm)

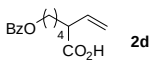

180.79
136.59
116.61
43.57
16.63
f1 (ppm)



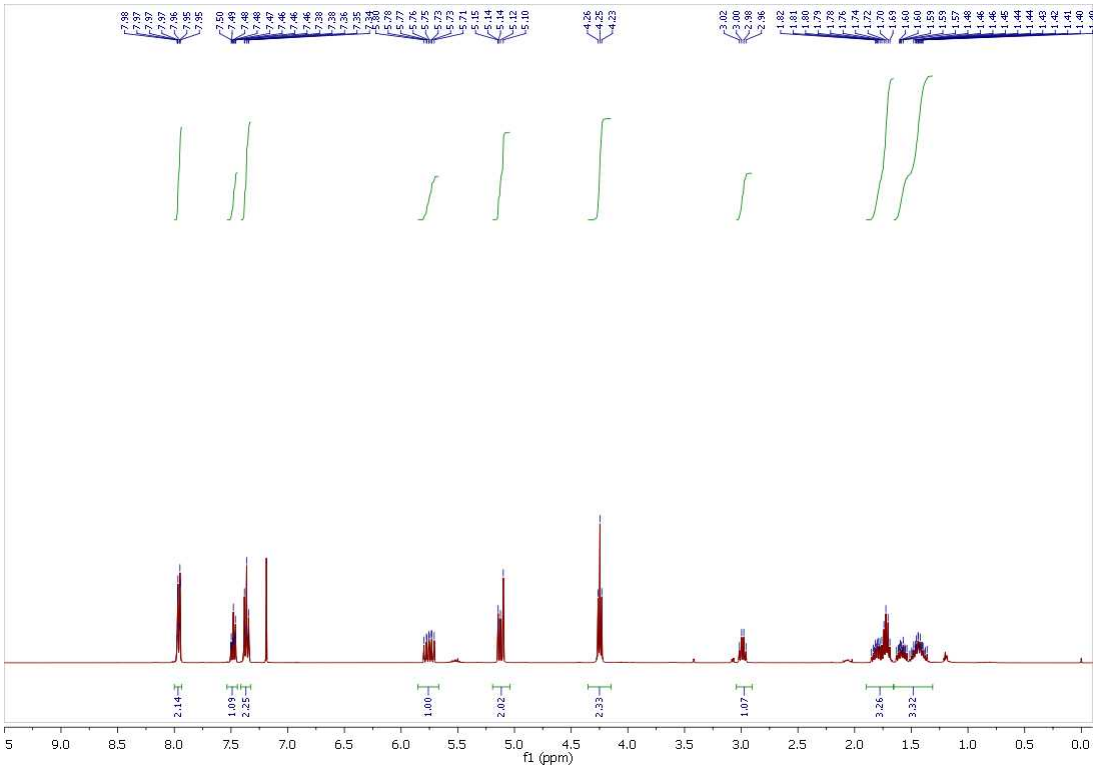
2c

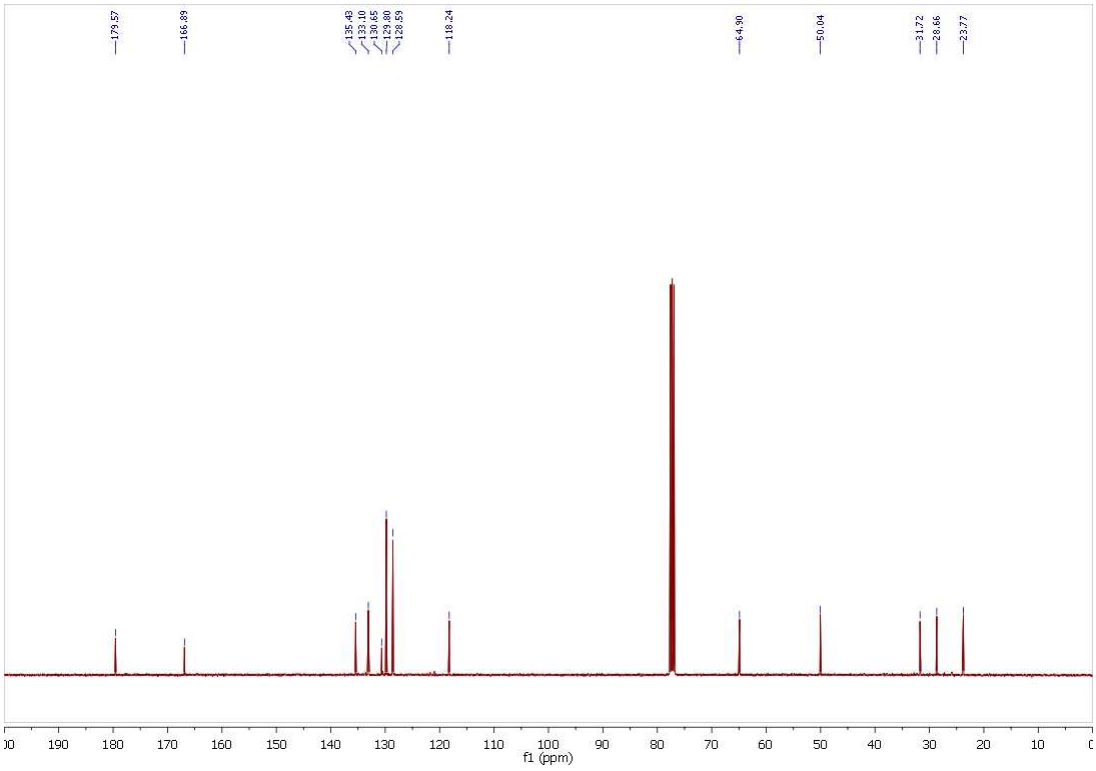


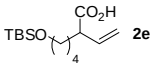




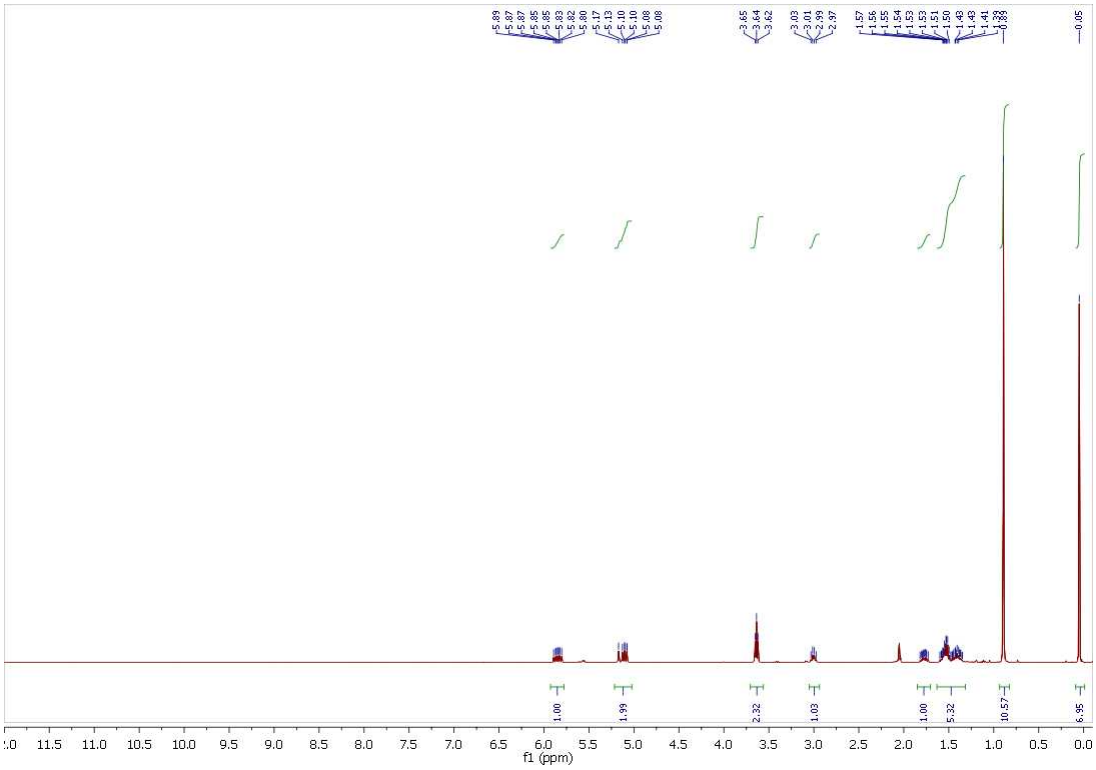
2d

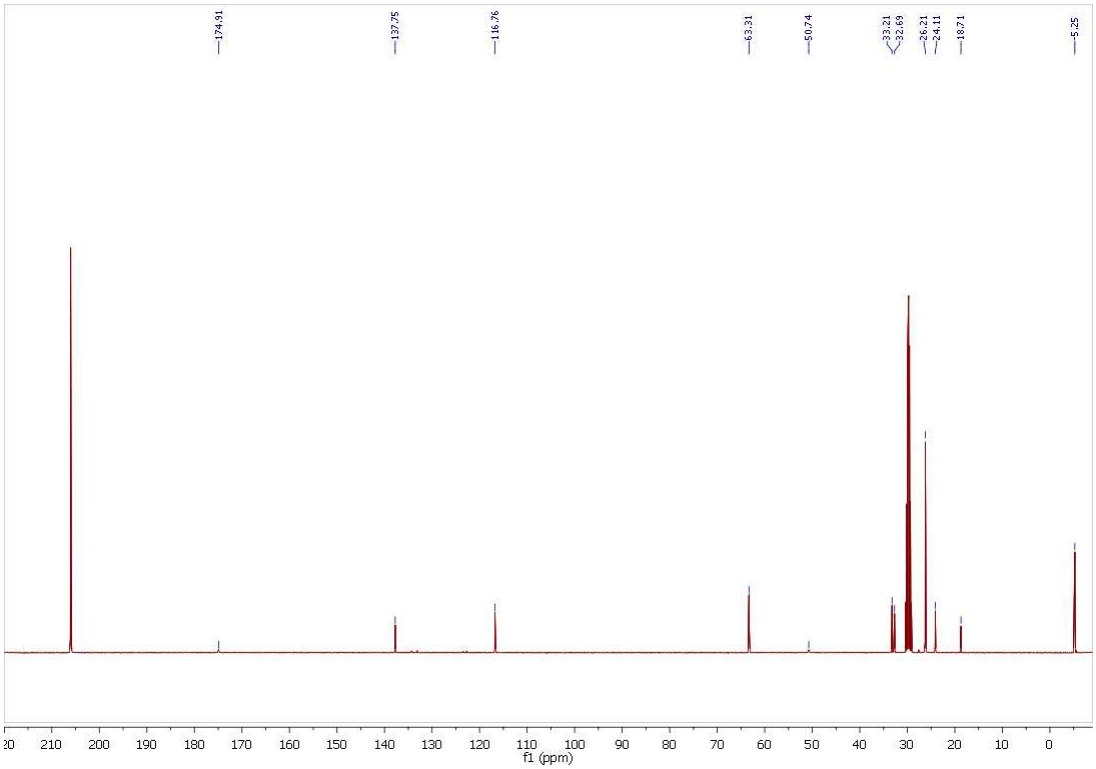


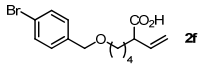



CO2H
TBSO
4

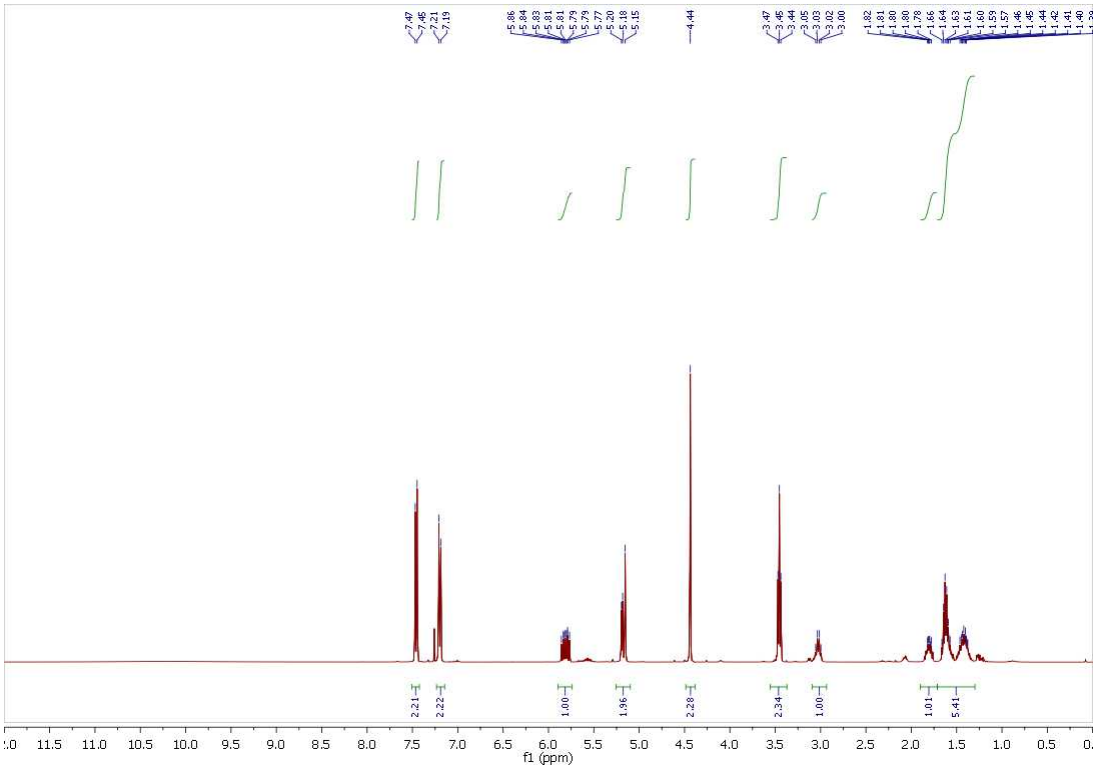
2e

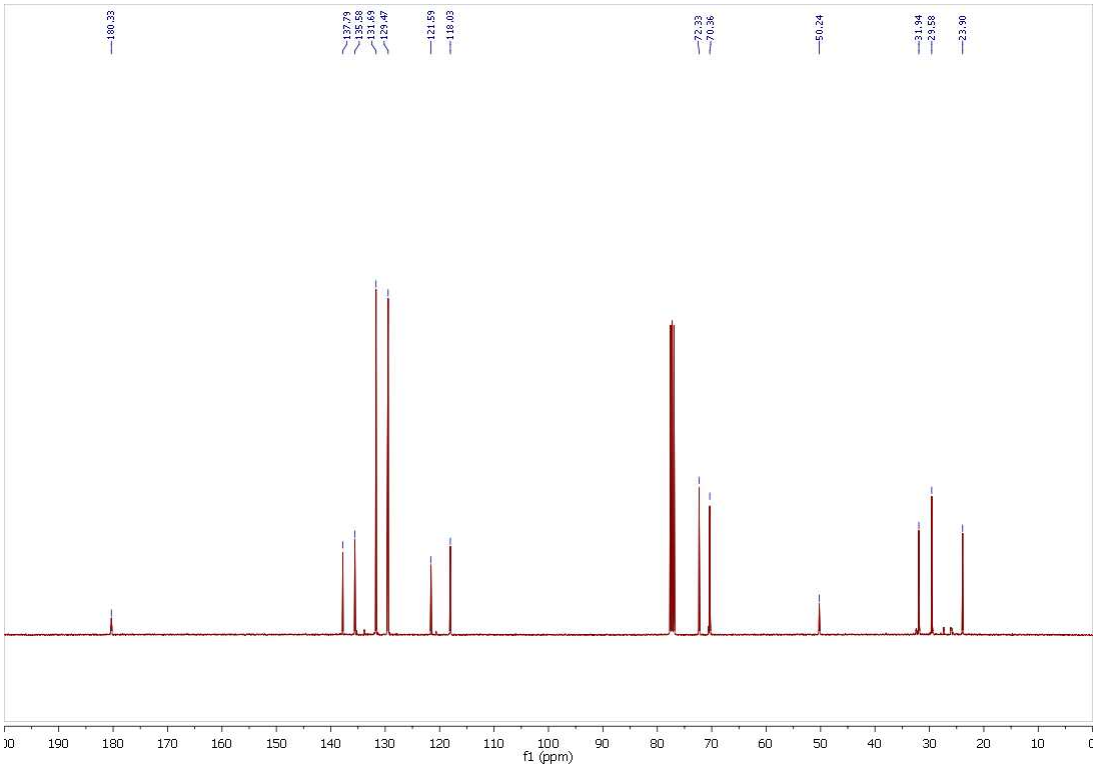

5.89
5.87
5.87
5.85
5.85
5.83
5.82
5.80
5.17
5.13
5.10
5.10
5.08
5.08
3.65
3.64
3.62
3.03
3.01
2.99
2.97
1.57
1.56
1.55
1.54
1.53
1.53
1.51
1.50
1.43
1.41
1.33
0.88
0.05
1.00
1.99
2.32
1.03
1.00
5.32
10.57
6.95
f1 (ppm)

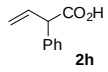

174.91
137.75
116.76
63.31
50.74
33.21
32.69
26.21
24.11
18.71
5.25
f1 (ppm)


Br
CO2H
O
4

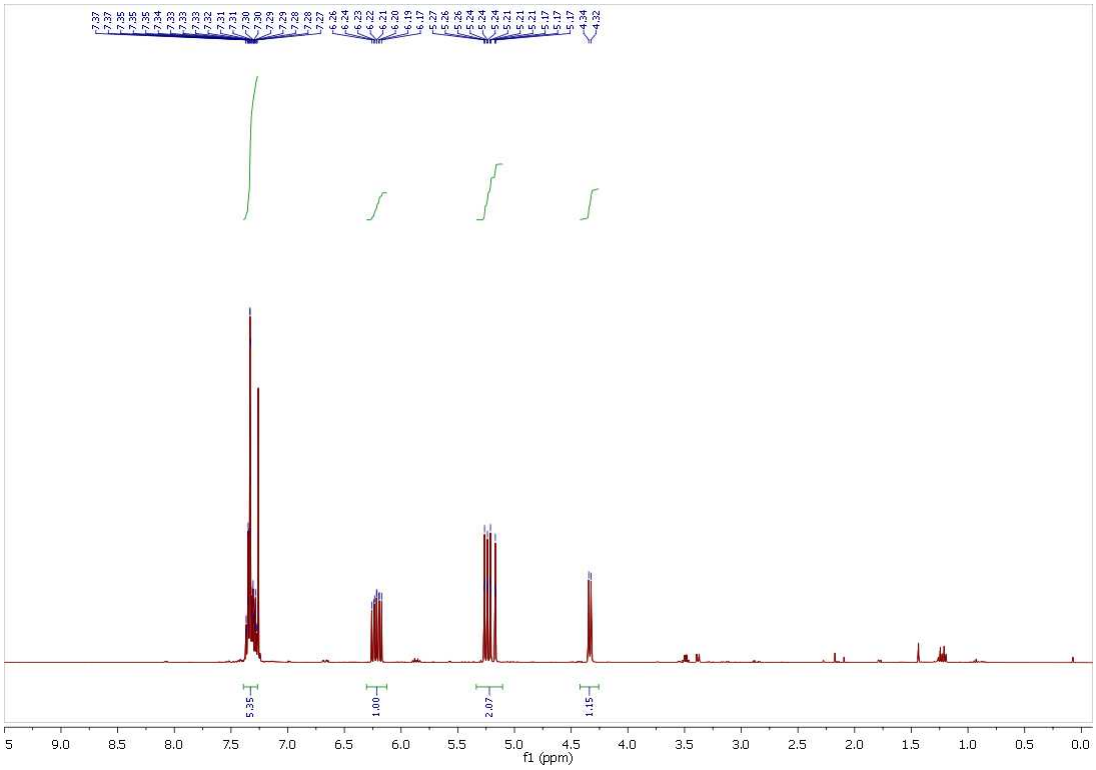
2f

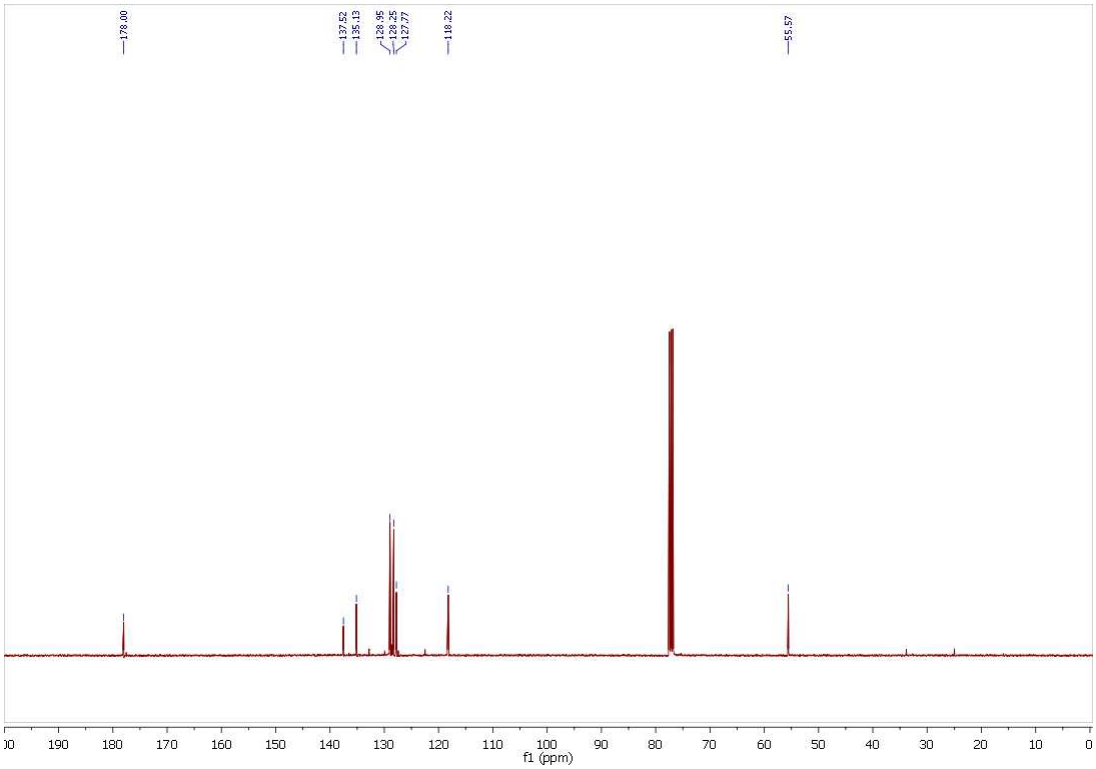

7.47
7.46
7.21
7.19
5.86
5.84
5.83
5.81
5.81
5.79
5.79
5.77
5.20
5.18
5.15
4.44
3.47
3.45
3.44
3.05
3.03
3.02
3.00
1.82
1.81
1.80
1.80
1.78
1.66
1.64
1.63
1.61
1.60
1.59
1.57
1.46
1.45
1.44
1.42
1.41
1.40
2.21
2.22
1.00
1.96
2.28
2.34
1.00
1.01
5.41
f1 (ppm)

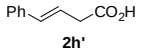

180.33
137.79
135.58
131.69
129.47
121.59
118.03
72.33
70.36
50.24
31.94
23.58
23.90
f1 (ppm)


CO2H
Ph

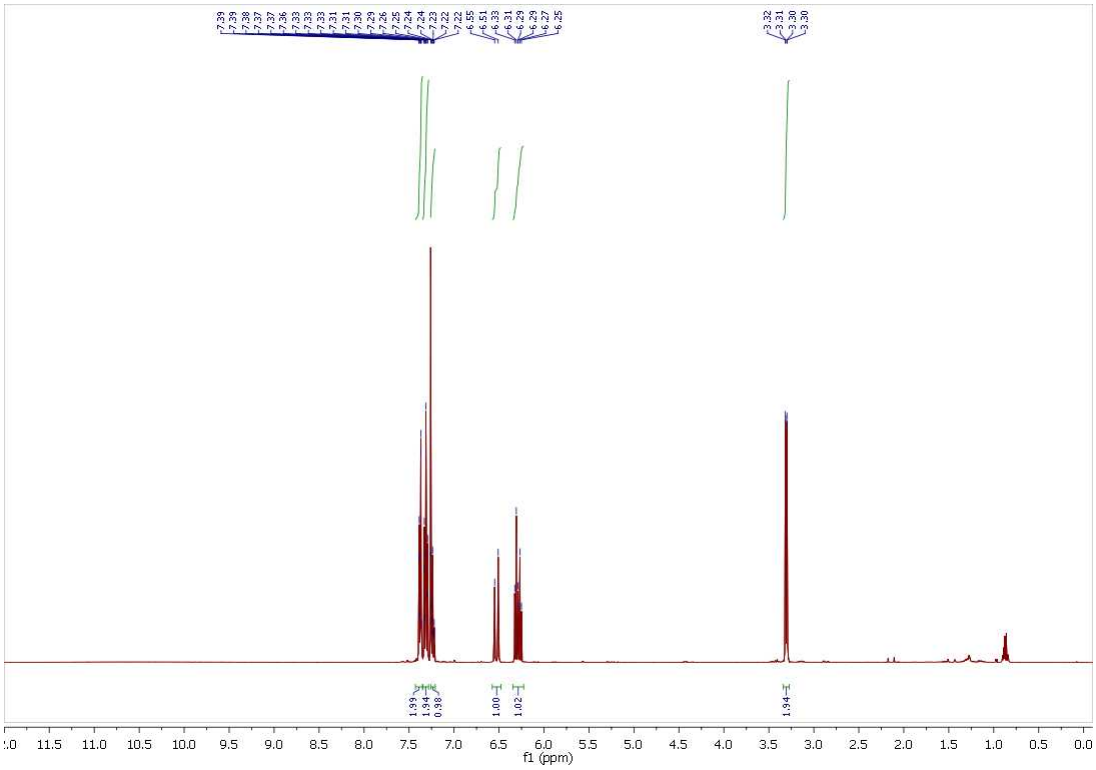
2h

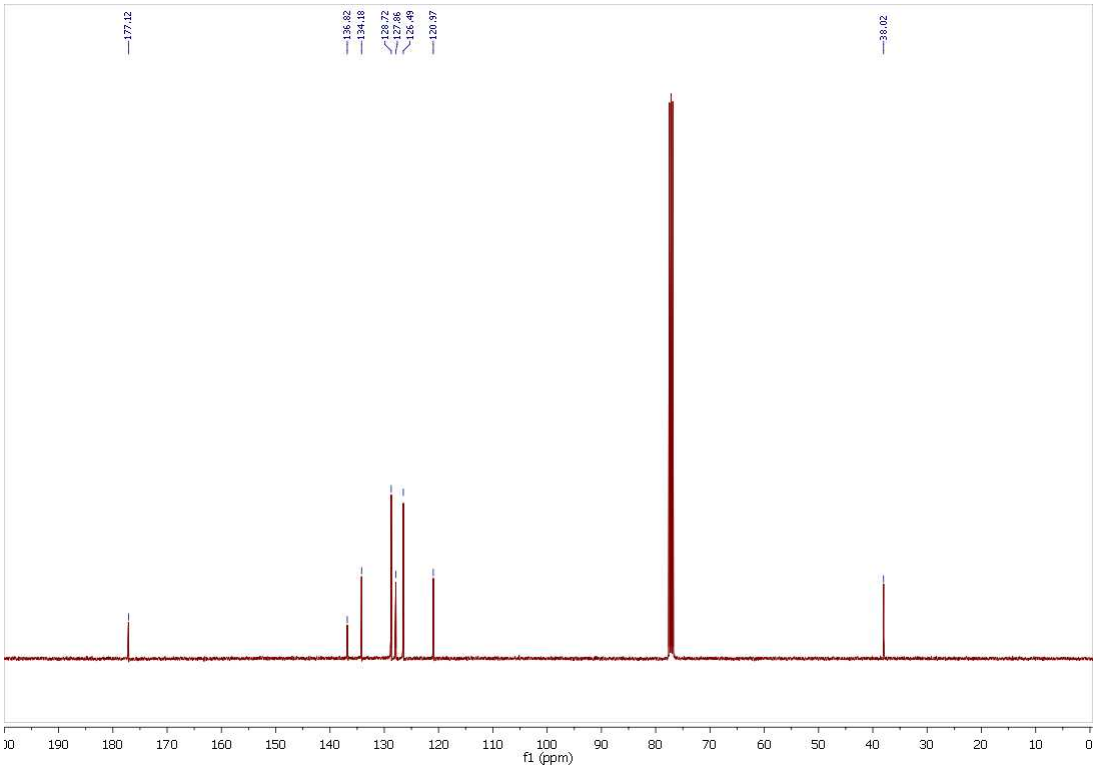

5.35
1.00
2.07
1.15
f1 (ppm)

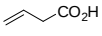

178.00
137.52
135.13
128.95
128.25
127.77
118.22
55.57
f1 (ppm)


Ph
CO2H

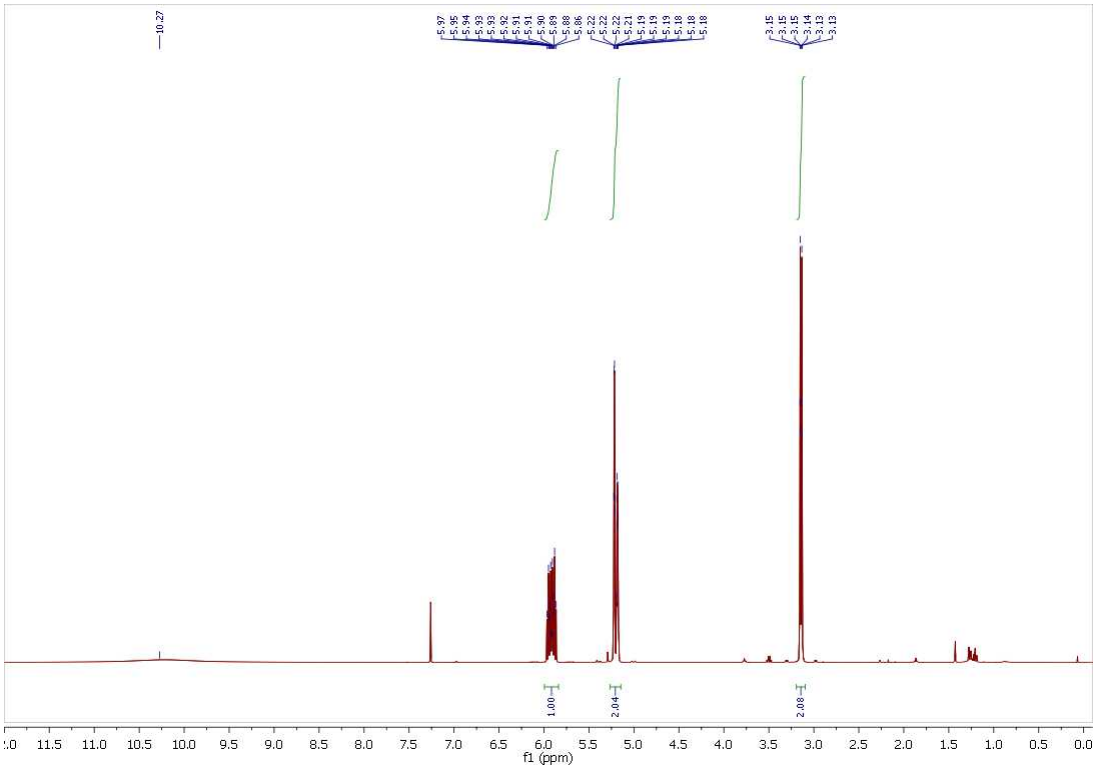
2h'

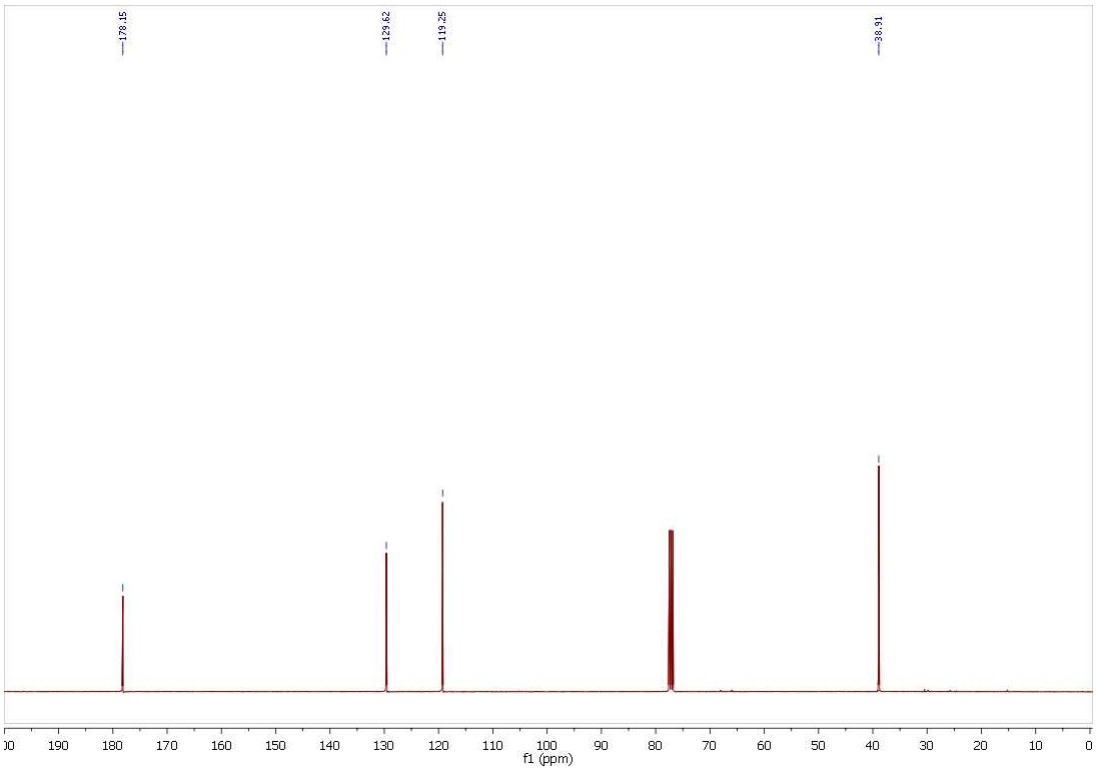

7.39
7.39
7.38
7.37
7.37
7.36
7.33
7.33
7.31
7.31
7.30
7.29
7.26
7.25
7.24
7.24
7.23
7.22
7.22
6.55
6.51
6.33
6.31
6.29
6.29
6.27
6.25
3.32
3.31
3.31
3.30
3.30
1.99
1.94
0.98
1.00
1.02
1.94
f1 (ppm)

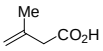

177.12
136.02
134.18
128.72
127.86
126.49
120.97
38.02
f1 (ppm)


CO2H

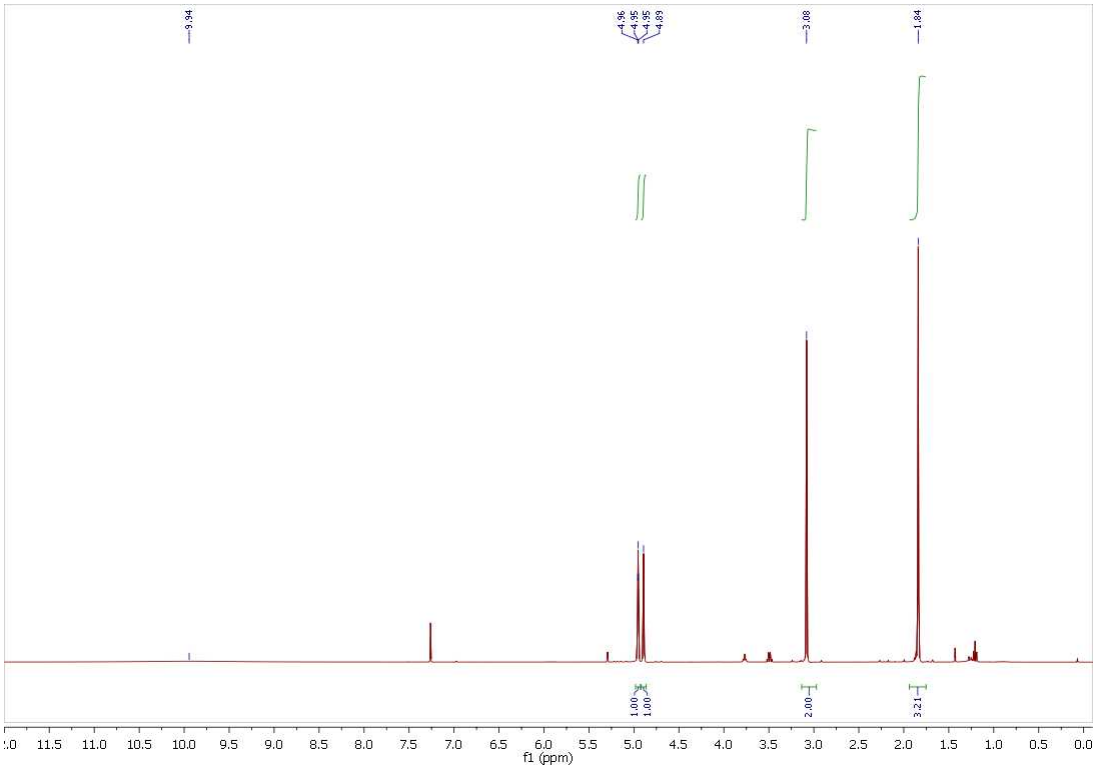
2i

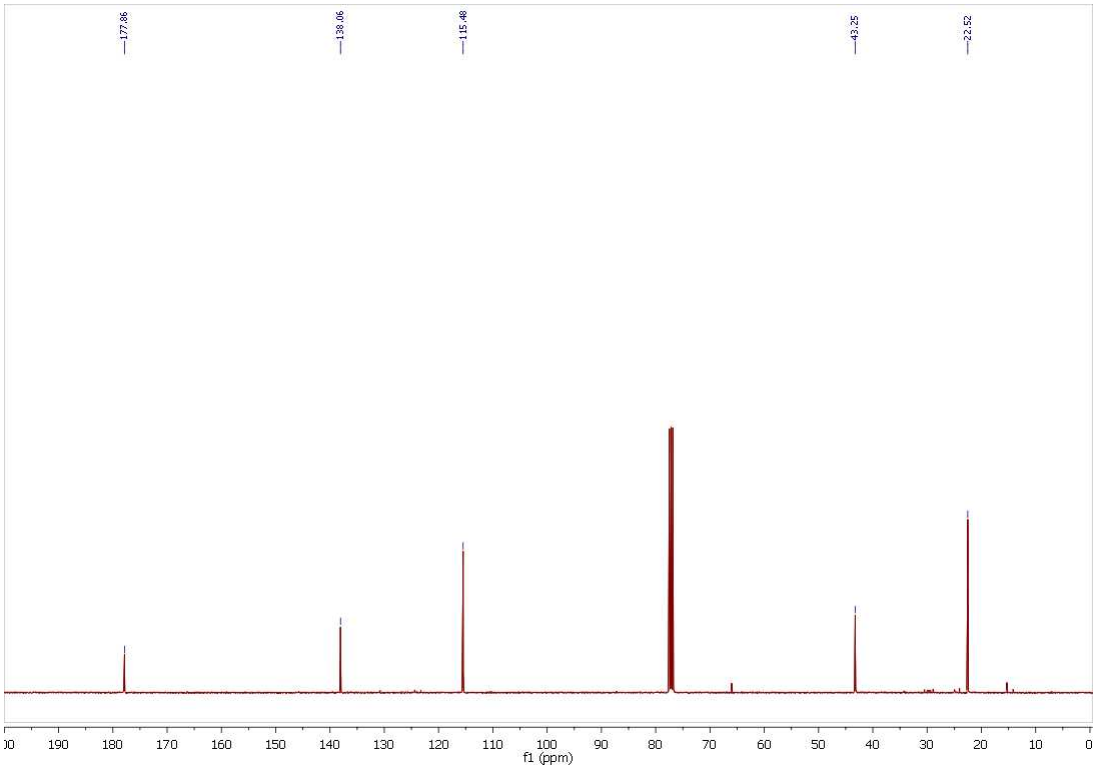

10.27
5.97
5.95
5.94
5.93
5.93
5.92
5.91
5.91
5.90
5.89
5.88
5.86
5.22
5.22
5.22
5.21
5.19
5.19
5.19
5.18
5.18
5.18
3.15
3.15
3.15
3.14
3.13
3.13
1.00
2.04
2.08
f1 (ppm)

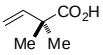

178.15
129.62
119.25
38.91
f1 (ppm)


Me
CO2H

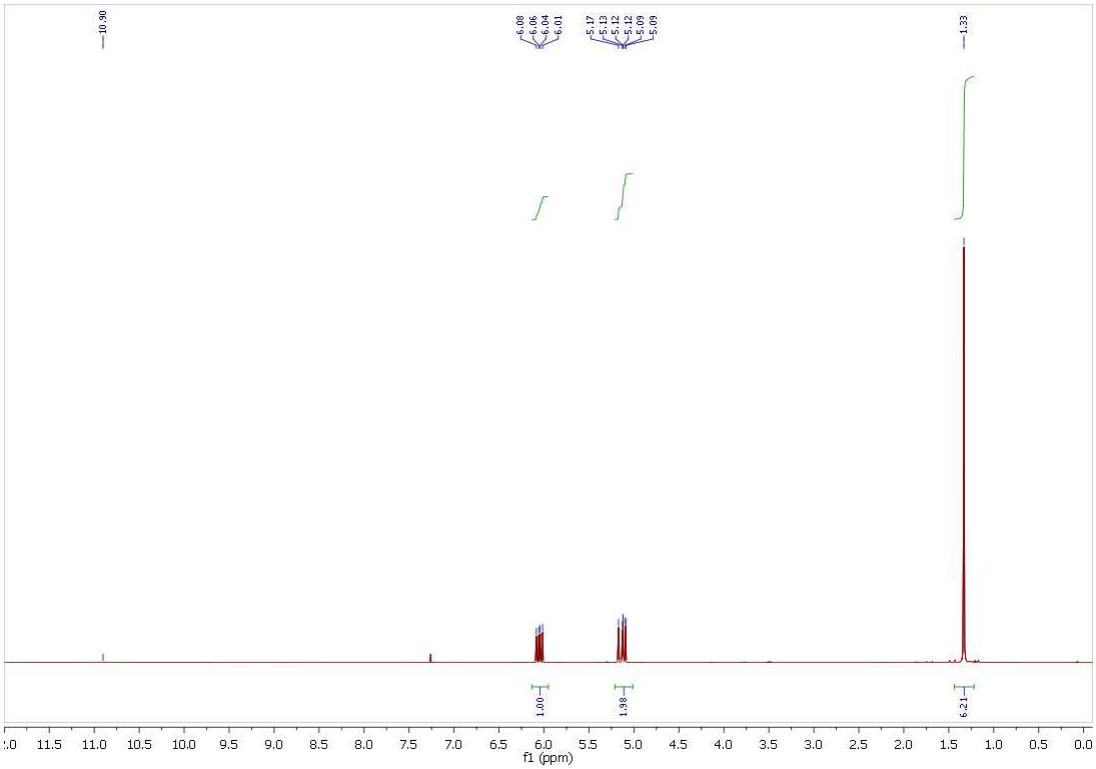
2j

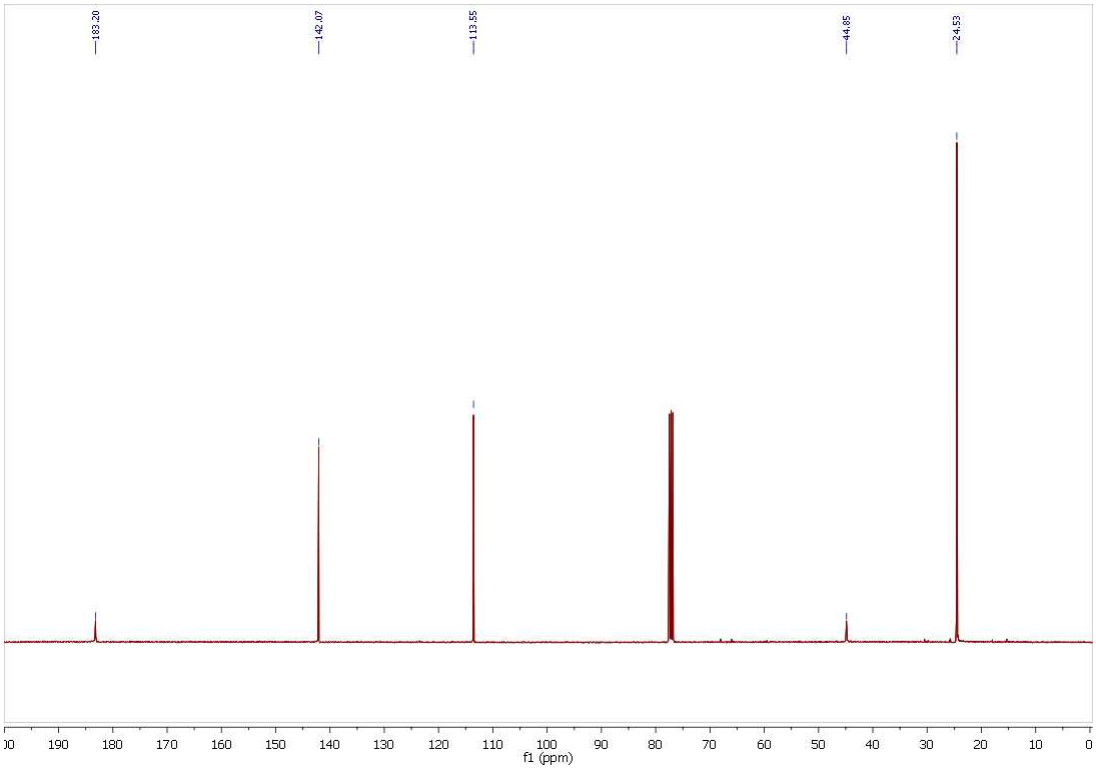

9.94
4.96
4.95
4.95
4.89
3.08
1.84
1.00
1.00
2.00
3.21
f1 (ppm)

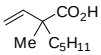

177.86
138.06
115.48
43.25
22.52
f1 (ppm)


CO2H
Me
Me

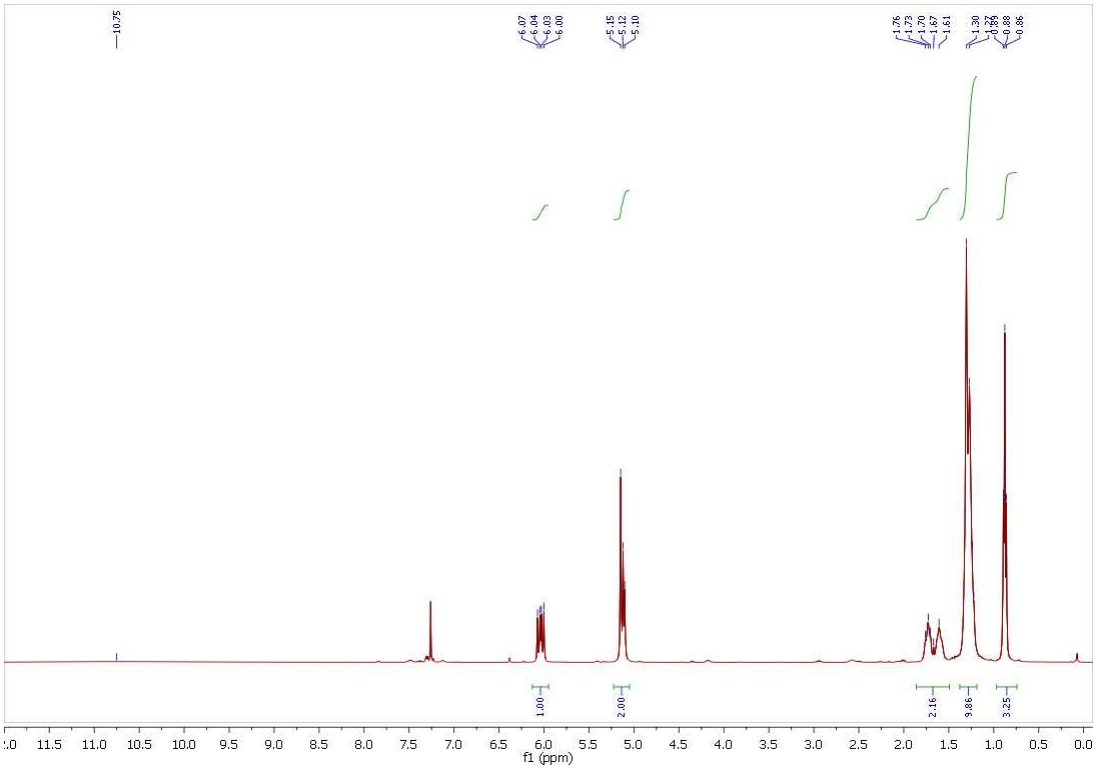
2l

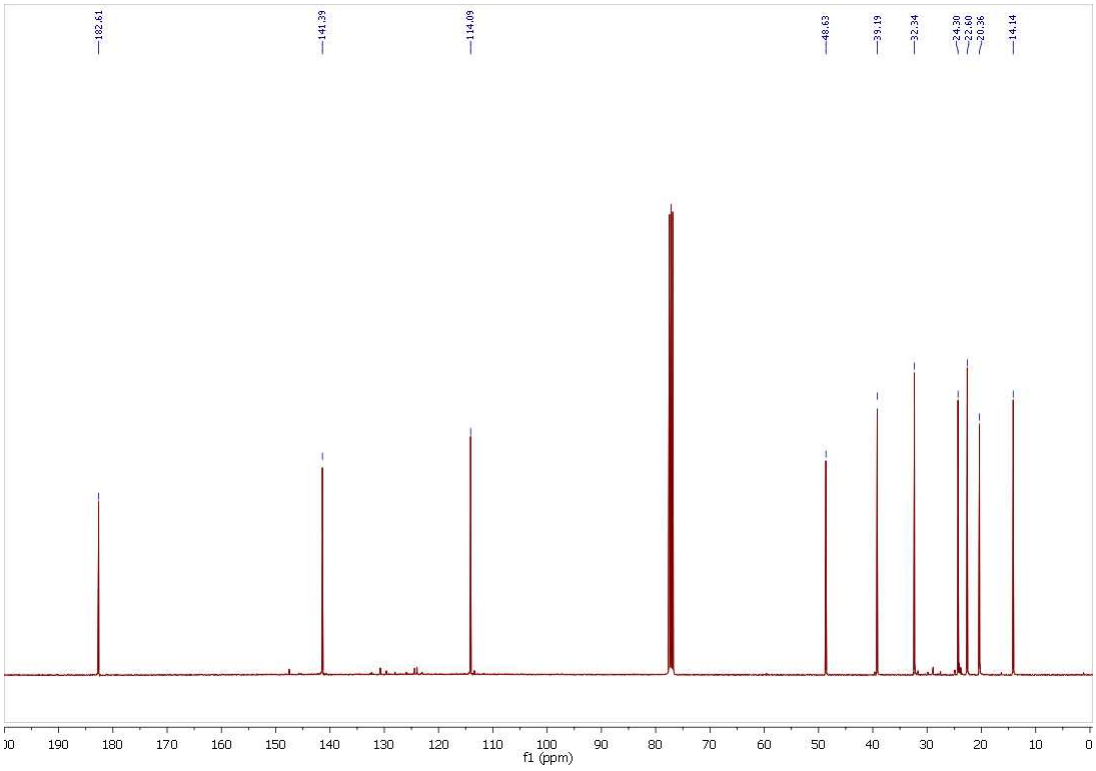

10.90
6.08
6.06
6.04
6.01
5.17
5.13
5.12
5.12
5.09
5.09
1.33
1.00
1.98
6.21
f1 (ppm)

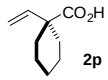

183.20
142.07
113.55
44.85
24.53
f1 (ppm)


CO2H
Me
C5H11

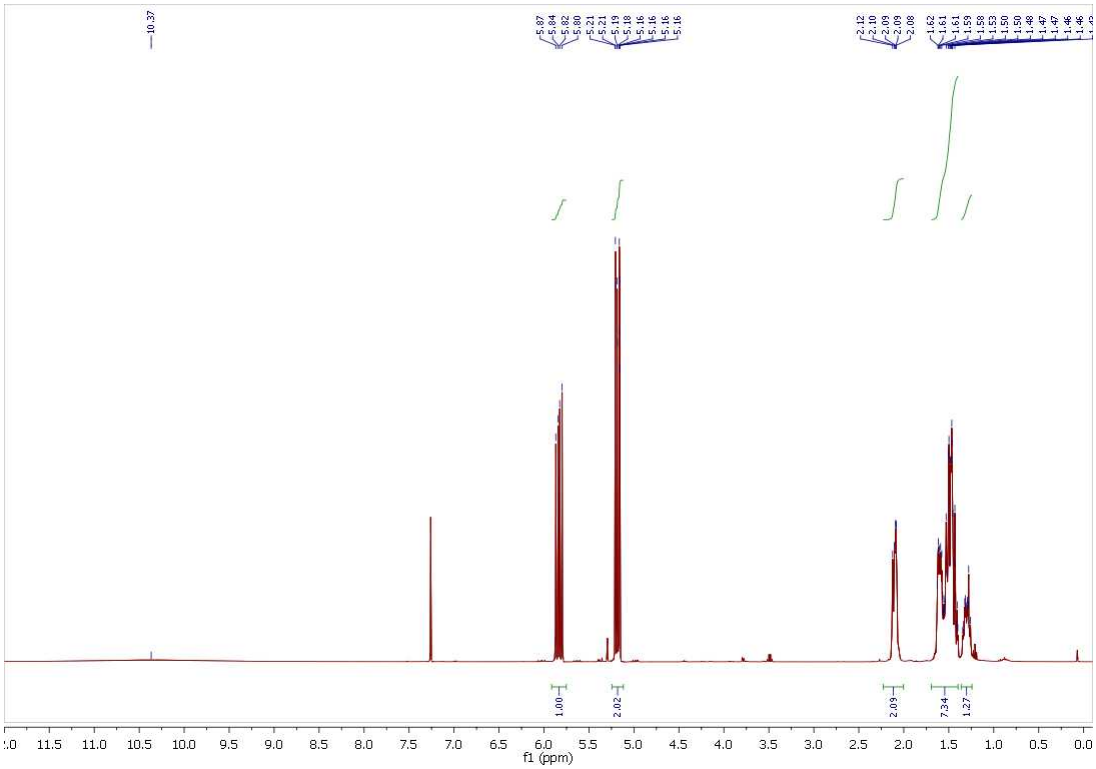
2o

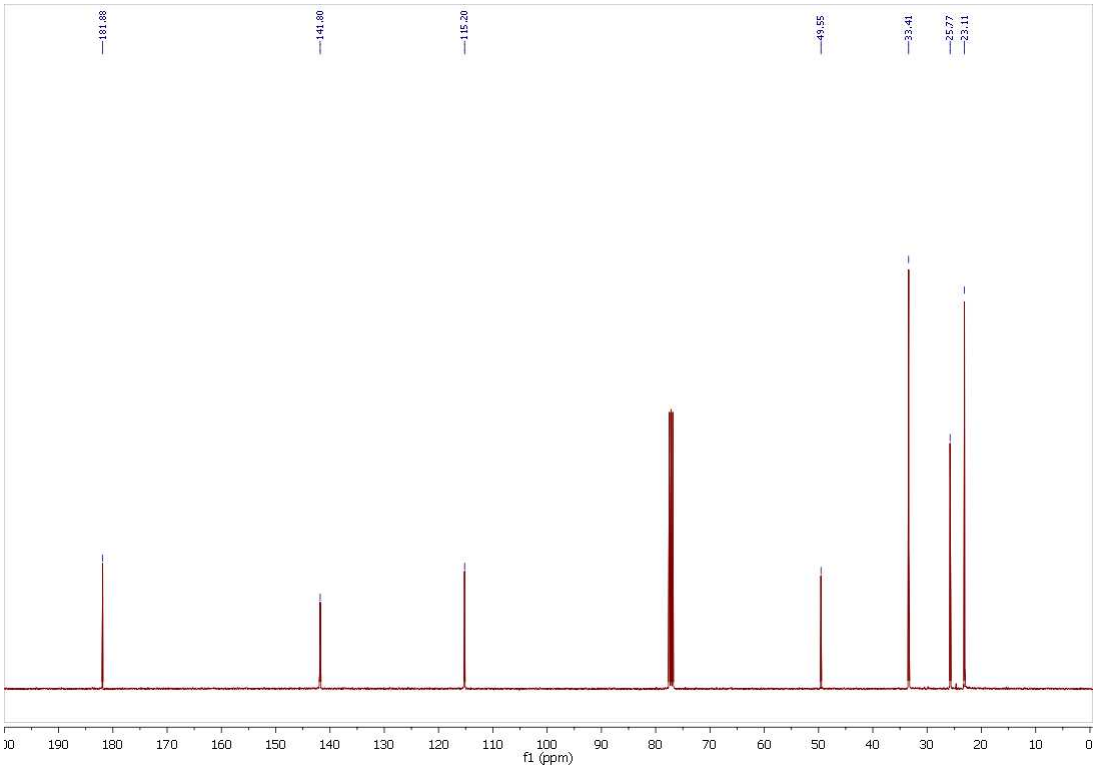

10.75
6.07
6.04
6.03
6.00
5.15
5.12
5.10
1.76
1.73
1.70
1.67
1.61
1.30
1.27
0.89
0.88
0.86
1.00
2.00
2.16
9.86
3.25
f1 (ppm)

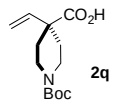

182.61
141.39
114.09
48.63
39.19
32.34
24.30
22.60
20.36
14.14
f1 (ppm)


CO2H

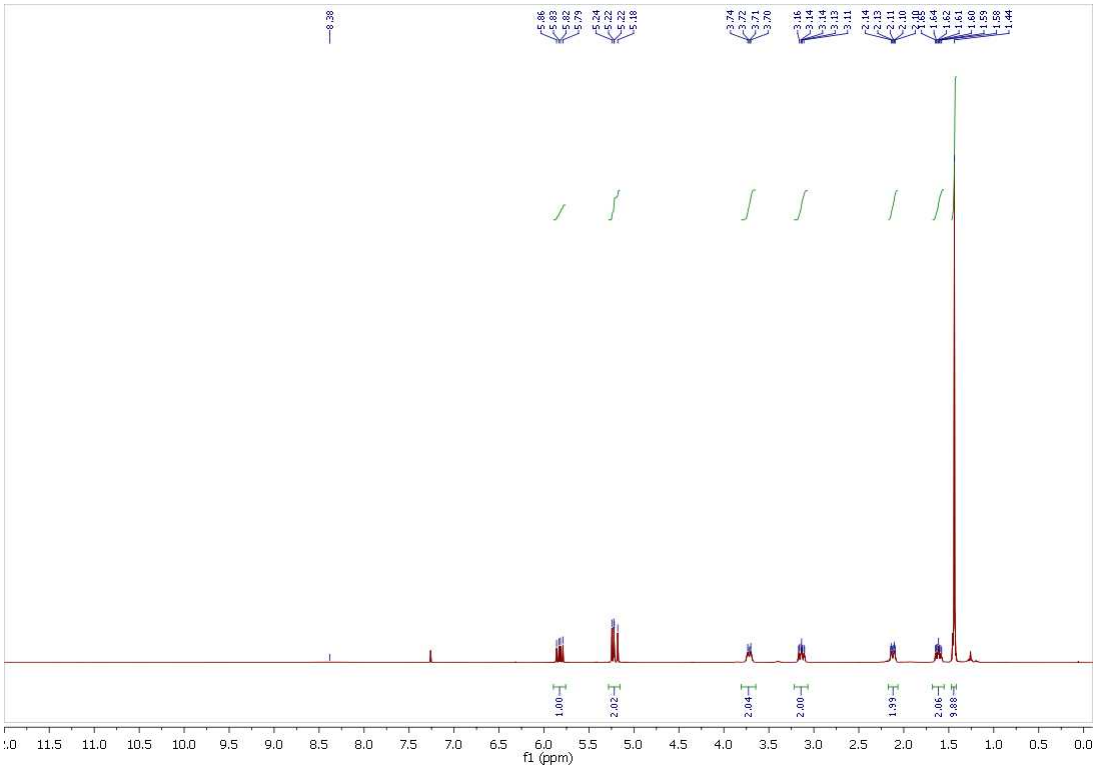
2p

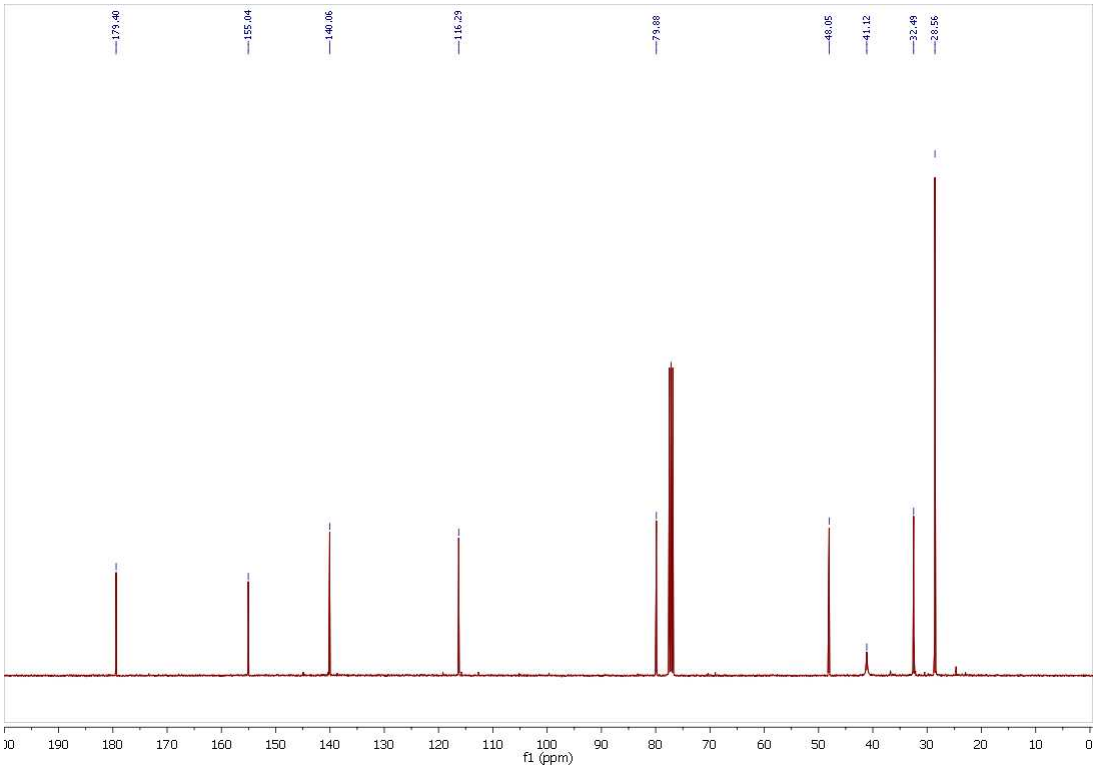

10.37
5.87
5.84
5.82
5.80
5.21
5.19
5.18
5.16
5.16
5.16
5.16
2.12
2.10
2.09
2.09
2.08
1.62
1.61
1.61
1.59
1.58
1.53
1.50
1.50
1.48
1.47
1.46
1.46
1.00
2.02
2.09
7.34
1.27
f1 (ppm)

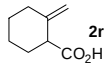

181.88
141.80
115.20
49.55
33.41
25.77
23.11
f1 (ppm)

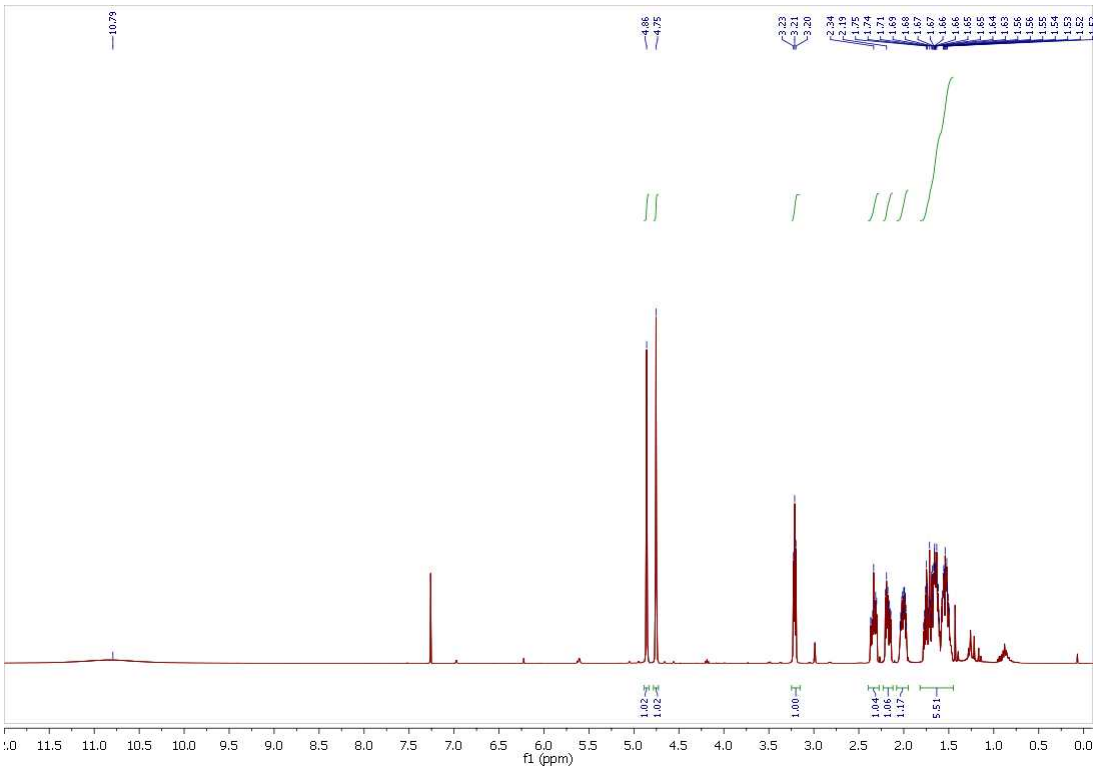

CO2H
N
Boc

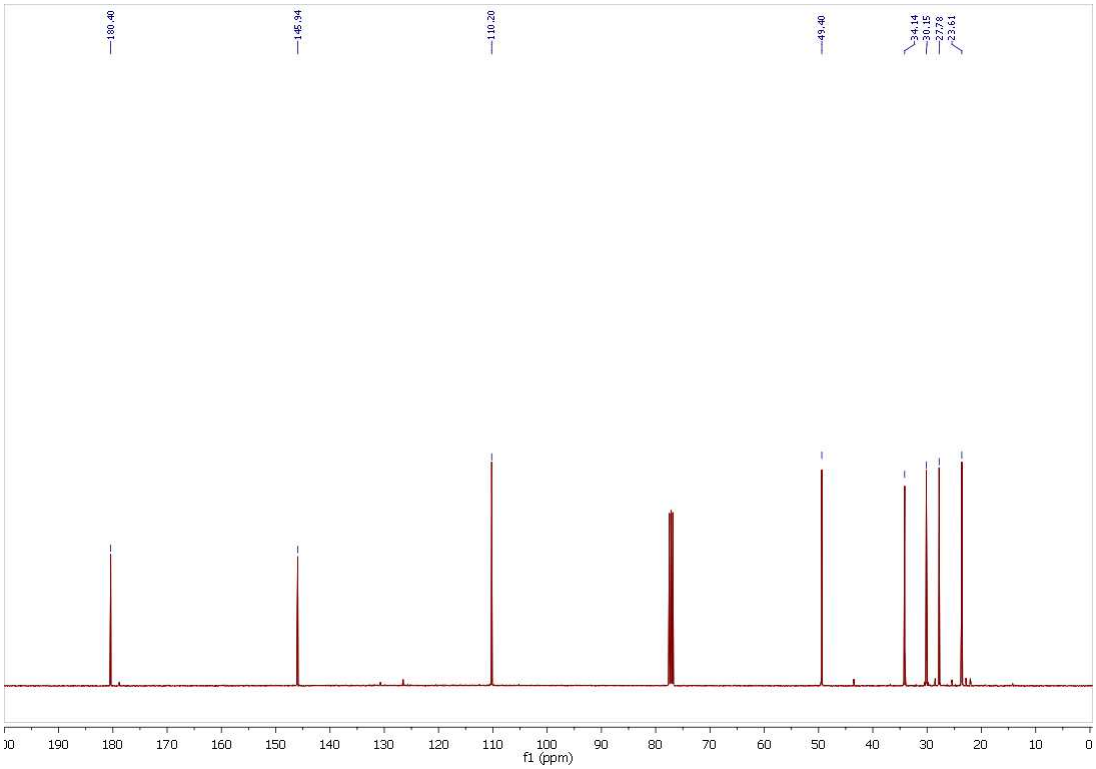
2q


8.38
5.86
5.83
5.82
5.79
5.24
5.22
5.18
3.74
3.72
3.71
3.70
3.16
3.14
3.14
3.13
3.11
2.14
2.13
2.11
2.10
2.10
2.05
1.64
1.62
1.61
1.60
1.59
1.58
1.44
1.00
2.02
2.04
2.00
1.99
2.06
9.88
f1 (ppm)


179.40
155.04
140.06
116.29
79.88
48.05
41.12
32.49
28.56
f1 (ppm)


2r
CO2H


10.79
4.86
4.75
3.23
3.21
3.20
2.34
2.19
1.75
1.74
1.71
1.69
1.68
1.67
1.66
1.66
1.66
1.65
1.65
1.64
1.63
1.56
1.56
1.55
1.54
1.53
1.52
1.02
1.02
1.00
1.04
1.06
1.17
5.61
f1 (ppm)


180.40
145.94
110.20
49.40
34.14
30.15
27.78
23.61
f1 (ppm)