Supporting Information

for

Bulky NHC–Cobalt Complex-Catalyzed Highly Markovnikov-Selective Hydrosilylation of Alkynes

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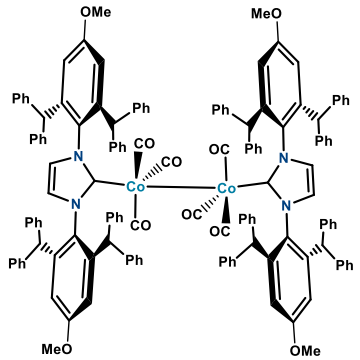
CONTENTS:

1. Synthesis of NHC-cobalt complex

The oven-dried 25 mL glass reactor equipped with a magnetic stirring bar was charged under argon with freshly isolated bulky NHC – IPr*^{OMe} (1.6×10^{-4} mol, 2 equiv.), $Co_2(CO)_8$ (0.8×10^{-4} mol, 1 equiv.) and n-hexane (5 mL). The reaction mixture was stirred at RT for 2 hours. After this time, the suspension has been decanted, washed with 5 mL of hexane and dried under vacuum. Product was obtained as a brown solid (66% yield).

2. Analytical data and ^{1}H NMR spectra of NHC-cobalt complex



^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 3.47 (6H, CH_3O-), 3.53 (4H, NC*H*=C*H*N), 3.58 (6H, CH_3O-), 5.00 (4H, $CHPh_2$), 5.28 (4H, $CHPh_2$), 5.36 (4H, CH_{Ar}), 6.50 – 6.65 (8H, CH_{Ar}), 6.67 – 6.80 (20H, CH_{Ar}), 6.90 – 7.15 (56H, CH_{Ar}).

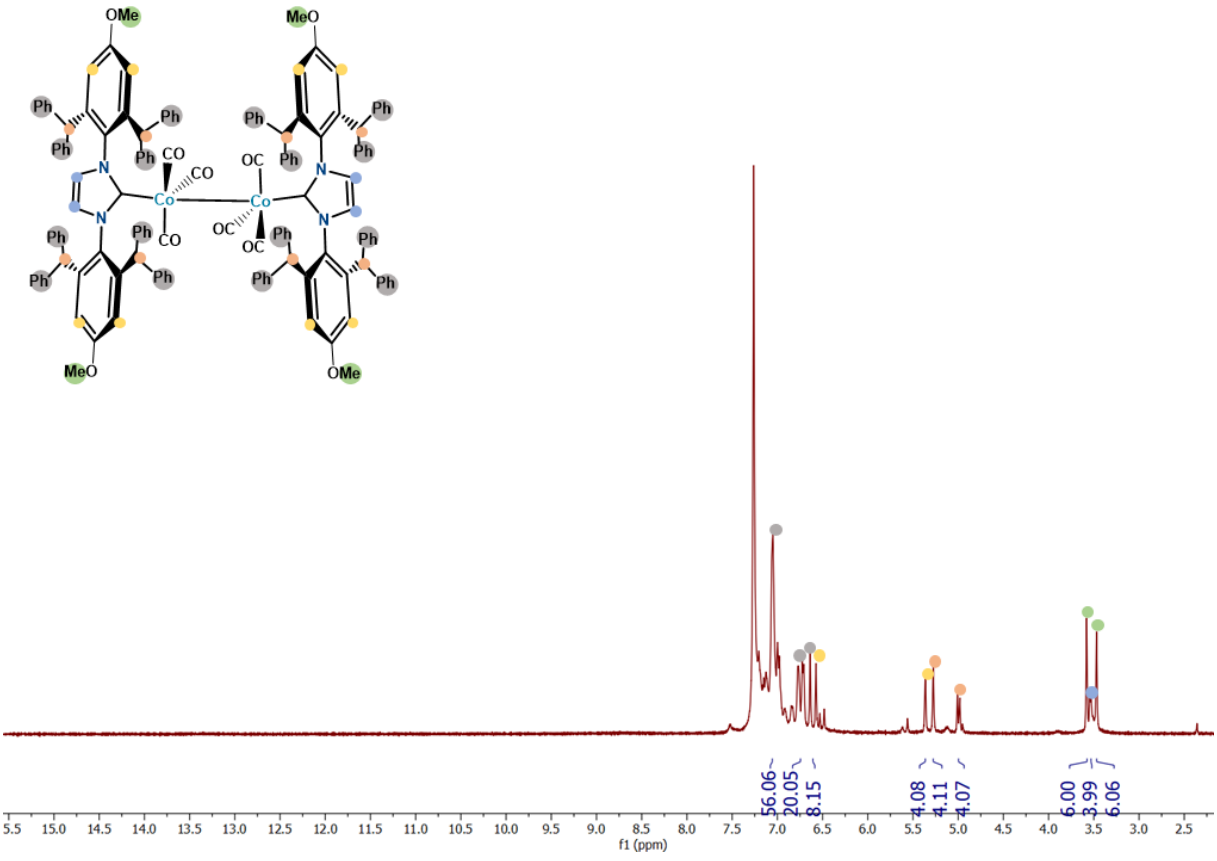


Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$) of NHC-cobalt complex.

3. Mercury poisoning experiment

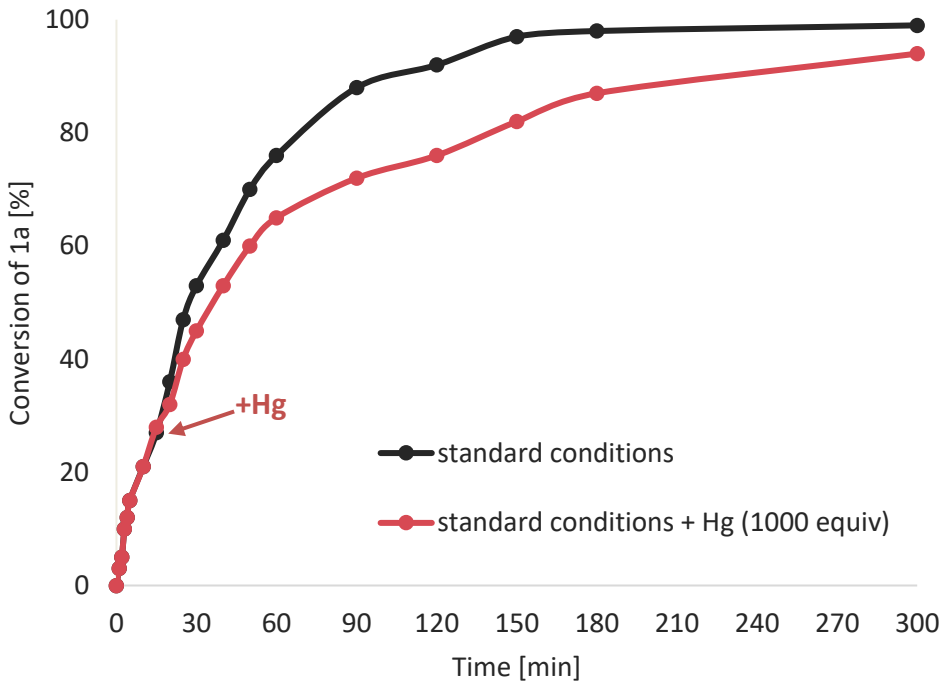


Figure S2. Mercury poisoning experiment. Profiles of the hydrosilylation of phenylacetylene (**1a**) with triethylsilane **(2a**) performed in the standard conditions with and without addition of mercury excess. Reaction conditions: Argon, THF, 60 ^{o}C, 5h, [**1a**]:[**2a**] = 1:1, [IPr*^{Ph}] = 5 mol%, [Co] = 2.5 mol%.

4. Hot filtration test

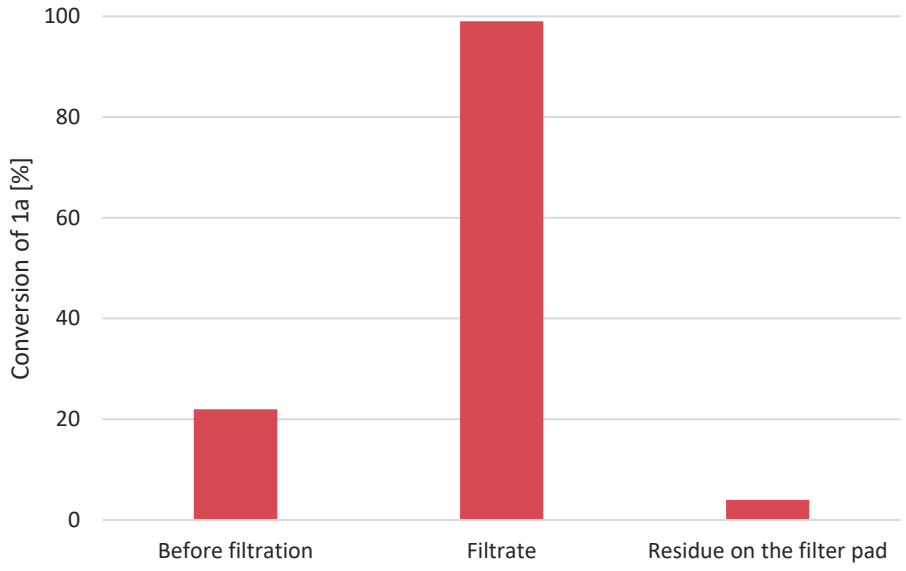
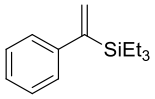
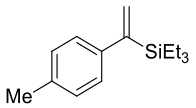
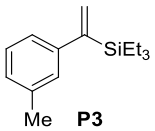
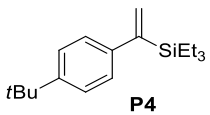
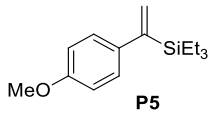
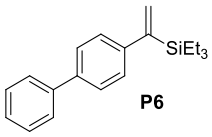
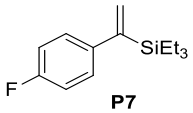
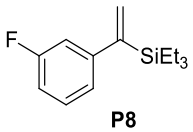
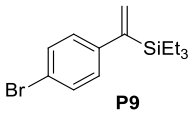
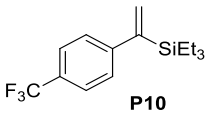
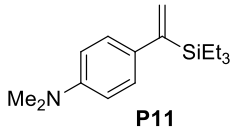
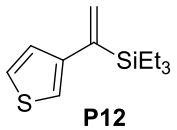


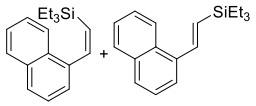
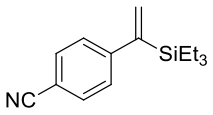
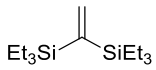
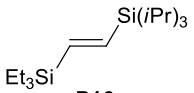
Figure S3. Hot filtration test. Hydrosilylation of phenylacetylene (**1a**) with triethylsilane (**2a**) performed in the standard conditions. Reaction conditions: Argon, THF, 60 ^{o}C, 5h, [**1a**]:[**2a**] = 1:1, [IPr*^{Ph}] = 5 mol%, [Co] = 2.5 mol%.

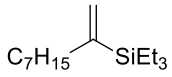
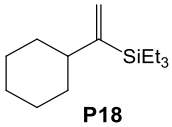
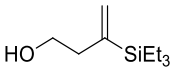
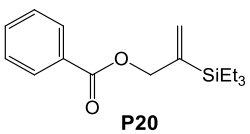
3. Analytical data of isolated products P1-P34

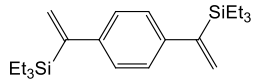
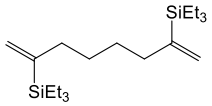
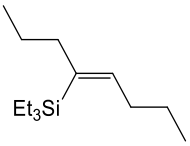
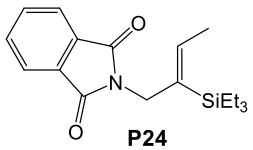
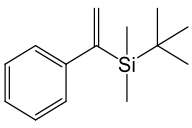
 **P1**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.68 (q, 6H, J_{HH} = 8.0 Hz, CH_3CH_2-), 0.94 (t, 9H, J_{HH} = 7.9 Hz, CH_3CH_2-), 5.59 (d, 1H, J_{HH} = 3.1Hz, =CH), 5.89 (d, 1H, J_{HH} = 3.1 Hz, =CH), 7.13-7.24 (m, 3H, Ph), 7.58-7.33 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.27 (CH_3CH_2-), 7.27 (CH_3CH_2-), 126.05, 126.62, 128.04, 128.78, 145.47 (=CH), 150.40 (=CH); MS m/z (rel, intensity): 115.00 (15), 161.17 (17), 183.30 (15), 185.30 (19), 186.30 (23), 188.40 (51), 189.30 (100, M^+- C_2H_5), 190.20 (85), 191.10 (31), 218.20 (4, M^+). These data are in accordance with the literature.[1]
 **P2**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.67 (q, 6H, J_{HH} = 7.8 Hz, CH_3CH_2-), 0.94 (t, 9H, J_{HH} = 7.9 Hz, CH_3CH_2-), 2.34 (s, 3H, CH_3), 5.55 (d, 1H, J_{HH} = 3.1 Hz, =CH), 5.87 (d, 1H, J_{HH} = 3.1 Hz, =CH), 7.07 (d, 2H, J_{HH} = 8.6 Hz, -C_6H_4-Me), 7.11 (d, 2H, J_{HH} = 8.6 Hz, -C_6H_4-Me); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.31 (CH_3CH_2-), 7.31 (CH_3CH_2-), 21.04 (CH_3), 126.50, 128.34, 128.76, 135.63, 142.46 (=CH), 150.02 (=CH); MS m/z (rel, intensity): 115.20 (52), 175.00 (40), 195.20 (59), 197.20 (63), 198.10 (70), 199.00 (69), 199.70 (76), 200.30 (76), 201.10 (86), 201.80 (85), 203.30 (100, M^+ - C_2H_5), 204.30 (86), 205.20 (37), 232.60 (10, M^+). These data are in accordance with the literature.[2]
 **P3**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.67 (q, 6H, J_{HH} = 7.9 Hz, CH_3CH_2-), 0.94 (t, 9H, J_{HH} = 7.9 Hz, CH_3CH_2-), 2.35 (s, 3H, CH_3), 5.56 (d, 1H, J_{HH} = 3.1 Hz, =CH), 5.87 (d, 1H, J_{HH} = 3.1 Hz, =CH), 6.94 - 6.98 (m, 2H, -C_6H_4-Me), 7.03 (d, 1H, J_{HH} = 7.5 Hz, -C_6H_4-Me), 7.18 (t, 2H, J_{HH} = 7.5 Hz, -C_6H_4-Me); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.29 (CH_3CH_2-), 7.30 (CH_3CH_2-), 21.50 (CH_3), 123.72, 126.81, 127.32, 127.87, 128.54, 137.53, 145.42 (=CH_2), 150.42 (=CH_2); MS m/z (rel, intensity): 115.00 (33), 173.20 (22), 175.20 (26), 196.80 (23), 197.90 (25), 199.30 (32), 200.50 (36), 201.40 (46), 203.50 (100, M^+ - C_2H_5), 204.50 (95), 205.40 (36), 232.50 (6, M^+). These data are in accordance with the literature.[2]
 **P4**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.68 (q, 6H, J_{HH} = 7.8 Hz, CH_3CH_2-), 0.94 (t, 9H, J_{HH} = 7.9 Hz, CH_3CH_2-), 1.33 (s, 9H, C(CH_3)$_3$), 5.55 (d, 1H, J_{HH} = 3.1 Hz, =CH), 5.90 (d, 1H, J_{HH} = 3.1 Hz, =CH), 7.12 (d, 2H, J_{HH} = 8.6 Hz, -C_6H_4-*t*Bu), 7.31 (d, 2H, J_{HH} = 8.6 Hz, -C_6H_4-*t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.33 (CH_3CH_2-), 7.33 (CH_3CH_2-), 31.38 (C(CH_3)$_3$), 34.36 (C(CH_3)$_3$), 124.96, 126.22, 128.36, 142.41, 148.91(=CH), 149.75 (=CH); MS m/z (rel, intensity): 57.10 (100, C_4H_9), 114.20 (17), 115.20 (29), 159.00 (16), 237.80 (15), 238.80 (16), 239.50 (16), 240.20 (17), 240.80 (19), 242.50 (22), 243.70 (23), 244.50 (23), 246.30 (27), 259.10 (26), 274.10 (5, M^+). These data are in accordance with the literature.[3]

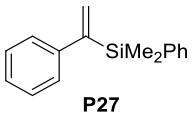
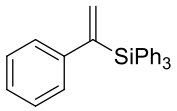
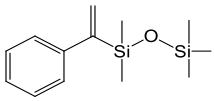
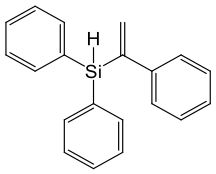
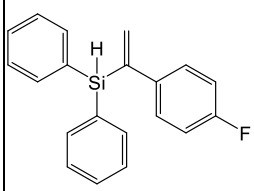
 **P5**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.68 (q, 6H, J_{HH} = 7.8 Hz, CH_3CH_2-), 0.93 (t, 9H, J_{HH} = 7.9 Hz, CH_3CH_2-), 3.81 (s, 3H, OCH_3), 5.52 (d, 1H, J_{HH} = 3.1 Hz, =C*H*), 5.86 (d, 1H, J_{HH} = 3.1 Hz, =C*H*), 6.85 (d, 2H, J_{HH} = 8.7 Hz, -C_6H_4-OMe), 7.12 (d, 2H, J_{HH} = 8.7 Hz, -C_6H_4-OMe); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.34 (CH_3CH_2-), 7.30 (CH_3CH_2-), 55.16 (OCH_3), 113.47, 127.62, 127.91, 137.79, 149.38 (=*C*H), 158.14 (=*C*H); MS m/z (rel, intensity): 162.20 (40), 163.20 (56), 191.20 (43), 215.30 (43), 216.00 (51), 217.30 (56), 217.90 (53), 219.30 (77), 219.80 (100, M^+ - C_2H_5), 221.30 (55), 248.00 (8, M^+). These data are in accordance with the literature.[1]
 **P6**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.71 (q, 6H, J_{HH} = 7.8 Hz, CH_3CH_2-), 0.96 (t, 9H, J_{HH} = 7.9 Hz, CH_3CH_2-), 5.61 (d, 1H, J_{HH} = 3.0 Hz, =C*H*), 5.95 (d, 1H, J_{HH} = 3.0 Hz, =C*H*), 7.24 – 7.26 (m, 2H, Ph), 7.32 – 7.36 (m, 1H, Ph), 7.42 – 7.46 (m, 2H, Ph), 7.53 – 7.56 (m, 2h, Ph), 7.60 – 7.63 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.35 (CH_3CH_2-), 7.32 (CH_3CH_2-), 126.78, 126.91, 127.04, 127.06, 128.69, 128.84, 138.91, 140.93, 144.47 (=*C*H), 149.89 (=*C*H); MS m/z (rel, intensity): 206.20 (14), 264.00 (20), 265.60 (50), 266.50 (100, M^+ - C_2H_5), 267.50 (39), 294.30 (19, M^+). These data are in accordance with the literature.[4]
 **P7**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.66 (q, 6H, J_{HH} = 7.8 Hz, CH_3CH_2-), 0.92 (t, 9H, J_{HH} = 7.9 Hz, CH_3CH_2-), 5.57 (d, 1H, J_{HH} = 3.0 Hz, =C*H*), 5.85 (d, 1H, J_{HH} = 3.0 Hz, =C*H*), 6.96 – 7.00 (m, 2H, -C_6H_4-F), 7.08 – 7.12 (m, 2H, -C_6H_4-F); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.22 (CH_3CH_2-), 7.25 (CH_3CH_2-), 114.85 (d, *J* = 21.1 Hz), 128.02 (d, *J* = 7.8 Hz), 129.03 (br s), 141.35 (d, *J* = 3.0 Hz), 149.38 (=CH_2), 161.59 (d, *J* = 244.2 Hz); MS m/z (rel, intensity): 113.20 (20), 115.20 (39), 202.70 (21), 203.50 (23), 205.50 (36), 206.50 (53), 207.50 (100, M^+ - C_2H_5), 208.10 (97), 209.00 (37), 236.50 (4, M^+). These data are in accordance with the literature.[4]
 **P8**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.67 (q, 6H, J_{HH} = 7.9 Hz, CH_3CH_2-), 0.93 (t, 9H, J_{HH} = 7.9 Hz, CH_3CH_2-), 5.61 (d, 1H, J_{HH} = 2.9 Hz, =C*H*), 5.89 (d, 1H, J_{HH} = 2.9 Hz, =C*H*), 6.84 – 6.94 (m, 3H, -C_6H_4-F), 7.21 – 7.25 and 7.27 – 7.29 (m, 1H, -C_6H_4-F); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.19 (CH_3CH_2-), 7.23 (CH_3CH_2-), 112.84 (d, *J* = 21.1 Hz), 113.47 (d, *J* = 21.1 Hz), 122.37 (d, *J* = 2.6 Hz), 129.38, 129.46, 129.52, 147.83 (d, *J* = 7.2 Hz), 149.54 (=*C*H), 162.64 (d, *J* = 245.2 Hz); MS m/z (rel, intensity): 46.80 (21), 58.70 (17), 86.70 (25), 114.80 (18), 124.70 (47), 148.80 (35), 150.60 (100), 151.70 (18), 152.70 (29), 176.70 (18), 178.80 (60), 179.60 (19), 206.50 (82), 207.50 (96), 208.50 (20), 236.50 (6, M^+). These data are in accordance with the literature.[5]

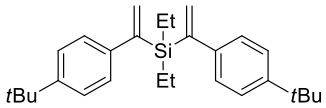
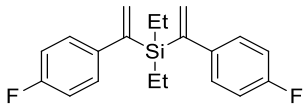
 **P9**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.65 (q, 6H, J_{HH} = 7.8 Hz, CH_3CH_2-), 0.91 (t, 9H, J_{HH} = 7.8 Hz, CH_3CH_2-), 5.58 (d, 1H, J_{HH} = 2.9 Hz, =CH), 5.85 (d, 1H, J_{HH} = 2.9 Hz, =CH), 7.01 (d, 2H, J_{HH} = 8.5 Hz, -C_6H_4-Br), 7.40 (d, 2H, J_{HH} = 8.5 Hz, -C_6H_4-Br); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.18 (CH_3CH_2-), 7.25 (CH_3CH_2-), 120.01, 128.33, 129.33, 131.13, 144.42 (=CH), 149.42 (=CH); MS m/z (rel, intensity): 113.40 (17), 114.30 (21), 115.30 (33), 116.20 (19), 117.20 (12), 210.30 (12), 211.10 (13), 239.20 (14), 266.50 (17), 267.50 (95), 269.10 (86), 296.80 (100, M^+). These data are in accordance with the literature.[4]
 **P10**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.67 (q, 6H, J_{HH} = 7.8 Hz, CH_3CH_2-), 0.94 (t, 9H, J_{HH} = 7.9 Hz, CH_3CH_2-), 2.34 (s, 3H, CH_3), 5.66 (d, 1H, J_{HH} = 2.9 Hz, =CH), 5.90 (d, 1H, J_{HH} = 2.9 Hz, =CH), 7.24 (d, 2H, J_{HH} = 7.9 Hz, -C_6H_4-CF_3), 7.55 (d, 2H, J_{HH} = 7.9 Hz, -C_6H_4-CF_3); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.15 (CH_3CH_2-), 7.21 (CH_3CH_2-), 125.03 (q, J = 3.7 Hz, CF_3), 126.89, 130.12, 149.35(=CH), 149.76 (=CH); MS m/z (rel, intensity): 151.00 (10), 257.20 (22), 258.50 (21), 267.00 (100, M^+ - F), 268.00 (22), 286.80 (3, M^+) These data are in accordance with the literature.[5]
 **P11**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.72 (q, 6H, J_{HH} = 7.8 Hz, CH_3CH_2-), 0.95 (t, 9H, J_{HH} = 7.9 Hz, CH_3CH_2-), 2.96 (s, 36H, NCH_3), 5.47 (br s, 1H, =CH), 5.87 (br s, 1H, =CH), 6.62 – 6.78 (m, 2H, -C_6H_4-NMe_2), 7.08 – 7.20 (m, 2H, -C_6H_4-NMe_2); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.45 (CH_3CH_2-), 7.33 (CH_3CH_2-), 40.58 ($N(CH_3)_3$), 112.53, 126.51, 127.23, 127.26, 149.07 (=CH); MS m/z (rel, intensity): 230.50 (5), 231.50 (6), 232.40 (6), 233.50 (7), 260.20 (85), 261.20 (100, M^+). These data are in accordance with the literature.[1]
 **P12**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.70 (q, 6H, J_{HH} = 7.9 Hz, CH_3CH_2-), 0.94 (t, 9H, J_{HH} = 7.9 Hz, CH_3CH_2-), 5.53 (d, 1H, J_{HH} = 3.0 Hz, =CH), 6.02 (d, 1H, J_{HH} = 3.0 Hz, =CH), 7.03 (dd, 1H, J_{HH} = 2.9, 1.3 Hz, tiophene), 7.06 (dd, 1H, J_{HH} = 5.0, 1.3 Hz, tiophene), 7.25 (dd, 1H, J_{HH} = 5.0, 2.9 Hz, tiophene); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.33 (CH_3CH_2-), 7.29 (CH_3CH_2-), 119.57, 124.87, 126.66, 127.76, 128.69, 143.64 (=CH), 145.24 (=CH); MS m/z (rel, intensity): 108.90 (44), 109.80 (30), 110.74 (34), 111.70 (33), 113.20 (41), 114.00 (35), 115.30 (40), 165.30 (46), 167.10 (95), 168.00 (52), 169.20 (34), 191.20 (35), 192.50 (42), 193.30 (57), 195.20 (100, M^+- C_2H_5), 196.20 (73), 197.20 (31), 224.50 (17, M^+). These data are in accordance with the literature.[4]

 **1:0.6** **P13**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) *β-(Z):* 0.43 (q, 6H, J_{HH} = 8.0 Hz, CH_3CH_2-), 0.83 (t, 9H, J_{HH} =7.8Hz, CH_3CH_2-), 6.10 (d, 1H, J_{HH} = 15.0 Hz, =C*H*), 7.39 (dt, 1H, J_{HH} = 6.9, 1.2Hz, CH_{Ar}), 7.45 (d, 1H, J_{HH} = 7.7 Hz, CH_{Ar}), 7.47 – 7.51 (m, 1H, CH_{Ar}), 7.53 – 7.56 (m, 1H, CH_{Ar}), 7.72 (d, 1H, J_{HH} = 7.4 Hz, CH_{Ar}), 7.80 (d, 1H, J_{HH} = 15.8 Hz, =C*H*), 7.95 (d, 1H, J_{HH} = 14.3 Hz, CH_{Ar}), 8.01 – 8.05 (m, 1H, CH_{Ar}); *β-(E):* 0.78 (q, 6H, J_{HH} = 7.9 Hz, CH_3CH_2-), 1.10 (t, 9H, J_{HH} = 7.5 Hz, CH_3CH_2-), 6.54 (d, 1H, J_{HH} = 18.9 Hz, =C*H*), 7.51 – 7.53 (m, 3H, CH_{Ar}), 7.56 – 7.59 (m, 1H, CH_{Ar}), 7.82 – 7.84 (m, 1H, CH_{Ar}), 7.87 – 7.90 (m, 3H, CH_{Ar}), 8.21 (d, 1H, J_{HH} = 7.3 Hz, CH_{Ar}); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) *β-(Z)+β-(E):* 3.63 (CH_3CH_2-), 4.54 (CH_3CH_2-), 7.37 (CH_3CH_2-), 7.49 (CH_3CH_2-), 123.58, 125.02, 125.16, 125.49, 125.61, 125.56, 125.73, 125.77, 126.00, 127.81, 128.04, 128.23, 128.51, 130.29, 130.37, 130.90, 131.76, 133.18, 133.64, 136.89 (*C*H=), 138.37 (*C*H=), 142.19 (*C*H=), 146.05 (*C*H=); MS m/z (rel, intensity): 209.30 (10), 210.50 (10), 211.20 (14), 237.60 (12), 238.50 (22), 239.50 (100, M^+ - C_2H_5), 240.30 (25), 268.00 (15, M^+). These data are in accordance with the literature (*β-(E)*).[11]
 **P14**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.65 (q, 6H, J_{HH} = 7.8 Hz, CH_3CH_2-), 0.91 (t, 9H, J_{HH} = 7.8 Hz, CH_3CH_2-), 5.67 (d, 1H, J_{HH} = 2.8 Hz, =C*H*), 5.89 (d, 1H, J_{HH} = 2.8 Hz, =C*H*), 7.22 (d, 2H, J_{HH} = 8.4 Hz, -C_6H_4-), 7.58 (d, 2H, J_{HH} = 8.4 Hz, -C_6H_4-); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.16 (CH_3CH_2-), 7.18 (CH_3CH_2-), 109.78, 119.13, 127.36, 130.61, 131.98, 149.67 (=*C*H), 150.65 (=*C*H); MS m/z (rel, intensity): 87.20 (9), 115.00 (15), 132.00 (23), 158.30 (82), 186.20 (30), 243.00(100, M^+). These data are in accordance with the literature.[4]
 **P15**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.57 (q, 12H, J_{HH} = 7.9 Hz, CH_3CH_2-), 0.93 (t, 9H, J_{HH} = 7.9 Hz, CH_3CH_2-), 5.54 (s, 2H, =CH_2); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.19 (CH_3CH_2-), 7.36 (CH_3CH_2-), 148.89 (=CH_2); MS m/z (rel, intensity): 59.00 (25), 87.00 (30), 115.90 (41), 139.90 (18), 197.90 (100, M^+ - $(C_2H_5)_2$), 199.20 (20), 226.80 (10), 256.00 (5, M^+). These data are in accordance with the literature.[6]
 **P16**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.58 (q, 12H, J_{HH} = 7.9 Hz, CH_3CH_2-), 0.94 (t, 9H, J_{HH} = 7.9 Hz, CH_3CH_2-), 1.02 – 1.13 (m, 21H, $(CH_3)_2CH$), 6.50 (d, 1H, J_{HH} = 23.1 Hz, =C*H*), 6.58 (d, 1H, J_{HH} = 23.1 Hz, =C*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.23 (CH_3CH_2-), 7.40 (CH_3CH_2-), 10.63 ($(CH_3)_2CH$), 18.60 ($(CH_3)_2CH$), 148.86 (=*C*H), 150.00 (=*C*H); MS m/z (rel, intensity): 211.20 (17), 213.20 (42), 214.20 (20), 226.30 (21), 227.30 (100), 228.20 (26), 229.20 (19), 254.90 (35), 298.80 (2, M^+). These data are in accordance with the literature.[7]

 **P17**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.51 – 0.63 (m, 6H, CH_3CH_2-), 0.85 – 0.97 (m, 12H, CH_3 and CH_3CH_2-), 1.24 – 1.34 (m, 8H, CH_2), 1.36 – 1.42 (m, 2H, CH_2), 2.04 – 2.11 (m, 2H, CH_2), 5.28 (dt, 1H, J_{HH} = 3.1, 1.0 Hz, =C*H*), 5.60 – 5.65 (m, 1H, =C*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 2.93 (CH_3CH_2-), 7.37 (CH_3CH_2-), 14.10 (CH_3), 22.68 (CH_2), 28.93 (CH_2), 29.26 (CH_2), 29.58 (CH_2), 31.89 (CH_2), 36.36 (CH_2), 124.83 (=CH), 149.27 (=CH); MS m/z (rel, intensity): 206.70 (10), 207.30 (10), 208.50 (14), 209.50 (20), 210.50 (34), 211.30 (100, $M^+ - C_2H_5$), 212.30 (26), 240.30 (2, M^+). These data are in accordance with the literature.[9]
 **P18**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.52 – 0.65 (m, 6H, CH_3CH_2-), 0.93 (t, 9H, J_{HH} = 7.9 Hz, CH_3CH_2-), 1.07 – 1.32 (m, 5H, c-CH_2), 1.64 – 1.80 (m, 5H, c-CH_2), 1.92 - 2.12 (m, 1H, c-C*H*), 5.30 (d, 1H, J_{HH} = 2.6 Hz, =C*H*), 5.67 (dd, 1H, J_{HH} = 2.6, 1.1 Hz, =C*H*); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.13 (CH_3CH_2-), 7.43 (CH_3CH_2-), 26.39 (c-CH), 27.12 (c-CH), 35.54 (c-CH), 45.12 (c-CH), 123.41 (=CH), 154.54 (=CH); MS m/z (rel, intensity): 111.00 (6), 115.00 (6), 139.00 (10), 166.90 (100, $M^+ - 2C_2H_5$), 194.70 (46), 223.50 (2, M^+). These data are in accordance with the literature.[4]
 **P19**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.61 (q, 6H, J_{HH} = 7.7 Hz, CH_3CH_2-), 0.93 (t, 9H, J_{HH} = 7.8 Hz, CH_3CH_2-), 1.45 (t, 1H, , J_{HH} = 5.8 Hz, O*H*), 2.39 (t, 2H, J_{HH} = 6.6 Hz, CH_2), 3.67 (dd, 2H, J_{HH} = 12.5, 6.6 Hz, CH_2), 5.44 (d, 1H, J_{HH} = 2.9 Hz, =C*H*), 5.72 – 5.74 (m, 1H, =CH); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 2.86 (CH_3CH_2-), 7.28 (CH_3CH_2-), 39.37 (CH_2), 61.31 (CH_2), 128.16 (=CH), 145.41 (=CH); MS m/z (rel, intensity): 55.00 (40), 101.20 (26), 103.00 (55), 113.10 (24), 115.00 (56), 156.90 (100, $M^+ - C_2H_5$), 186.00 (3, M^+). These data are in accordance with the literature.[4]
 **P20**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.68 (q, 6H, J_{HH} = 7.9 Hz, CH_3CH_2-), 0.97 (t, 9H, J_{HH} = 7.9 Hz, CH_3CH_2-), 4.91 (t, 2H, J_{HH} = 1.6 Hz, CH_2O), 5.48 – 5.52 (m, 1H, =C*H*), 5.95 – 5.99 (m, 1H, =C*H*), 7.43 – 7.47 (m, 2H, Ph), 7.54 – 7.58 (m, 1H, Ph), 8.06 – 8.09 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 2.80 (CH_3CH_2-), 7.22 (CH_3CH_2-), 68.51 (CH_2O), 126.83, 128.34, 129.56, 130.34, 132.85, 143.27 (=CH), 166.22 (=CH); MS m/z (rel, intensity): 105.00 (49), 115.00 (16), 206.20 (21), 207.20 (100, $M^+ - C_4H_{10}$), 208.10 (34), 247.20 (29, $M^+ - CH_3$). These data are in accordance with the literature.[4]

 **P21**	^{1}H NMR (400 MHz, C_6D_6, 296K): δ (ppm) 0.70 (q, 12H, J_{HH} = 7.9 Hz, CH_3CH_2-), 0.97 (t, 18H, J_{HH} = 7.9 Hz, CH_3CH_2-), 5.56 (d, 1H, J_{HH} = 3.1 Hz, =CH), 5.95 (d, 1H, J_{HH} = 3.1 Hz, =CH), 7.24 (s, 4H, -C_6H_4-); ^{13}C NMR (100 MHz, C_6D_6, 296K): δ (ppm) 3.81 (CH_3CH_2-), 7.60 (CH_3CH_2-), 126.97, 128.81, 143.82 (=CH),150.43 (=CH); MS m/z (rel, intensity): 58.80 (18), 86.70 (20), 114.80 (11), 130.80 (10), 244.90 (12), 271.00 (16), 272.80 (21), 298.90 (24), 299.80 (13), 300.80 (24), 301.90 (19), 328.80 (18), 329.80 (100, M^+ - C_2H_5), 330.70 (36), 331.80 (13), 358.20 (4, M^+). These data are in accordance with the literature.[4]
 **P22**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.60 (q, 12H, J_{HH} = 7.9 Hz, CH_3CH_2-), 0.93 (t, 18H, J_{HH} = 7.9 Hz, CH_3CH_2-), 1.38 – 1.44 (m, 4H, CH_2), 2.06 – 2.12 (m, 4H, CH_2), 5.29 (d, 2H, J_{HH} = 3.0 Hz, =CH), 5.60 – 5.66 (m, 2H, =CH); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 2.92 (CH_3CH_2-), 7.37 (CH_3CH_2-), 28.84 (CH_2), 36.22 (CH_2), 124.98 (=CH), 149.08 (=CH); MS m/z (rel, intensity): 115.00 (42), 163.20 (10), 165.00 (43), 197.00 (100, M^+ - SiC_8H_{17}), 214.90 (4), 308.60 (4), 336.50 (2, M^+). These data are in accordance with the literature.[4]
 **P23**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.57 (q, 6H, J_{HH} = 7.9 Hz, CH_3CH_2-), 0.88 – 0.94 (m, 15H, CH_3CH_2- and CH_3), 1.26 – 1.31 (m, 2H, CH_2), 1.36 – 1.42 (m, 2H, CH_2), 2.01 – 2.06 (m, 2H, CH_2), 2.06 – 2.12 (m, 2H, CH_2), 5.67 (t, 1H, J_{HH} = 6.8 Hz, =CH); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.18 (CH_3CH_2-), 7.45 (CH_3CH_2-), 13.85, 14.56, 22.83, 23.41, 30.47, 32.28, 137.39, 141.88 (=CH); MS m/z (rel, intensity): 136.00 (1), 108.90 (2), 169.00 (1), 194.80 (10), 195.80 (20), 196.80 (100, M^+ - C_2H_5), 226.70 (2, M^+). These data are in accordance with the literature.[4]
 **P24**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.56 (q, 6H, J_{HH} = 8.0 Hz, CH_3CH_2-), 0.88 (t, 9H, J_{HH} = 7.6 Hz, CH_3CH_2-), 1.85 (s, 3H, CH_3), 4.38 (dd, 2H, J_{HH} = 6.2, 0.8 Hz, CH_2), 5.64 (m, 1H, CH=), 7.70 – 7.74 (m, 2H, CH_{Ar}), 7.84 – 7.87 (m, 2H, CH_{Ar}); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 2.37 (CH_3CH_2-), 7.33 (CH_3CH_2-), 15.31 (CH_3-), 35.91 (NCH_2), 123.20, 126.72, 128.47, 129.32, 132.30, 133.01, 133.82, 138.82 (CH=), 142.12 (CH=), 168.06 (C=O); MS m/z (rel, intensity): 111.00 (3), 130.10 (3), 159.80 (2), 232.10 (4), 244.90 (3), 257.90 (1), 285.80 (100, M^+ - C_2H_5), 286.80 (21), 315,70 (2, M^+).
 **P26**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.19 (s, 6H, $Si(CH_3)_2$), 0.80 (s, 9H, $C(CH_3)_3$), 5.64 (d, 1H, J_{HH} = 3.1 Hz, =CH), 5.84 (d, 1H, J_{HH} = 3.1 Hz, =CH), 7.13 – 7.16 (m, 2H, C_6H_5-), 7.18 – 7.27 (m, 1H, C_6H_5-), 7.27 – 7.31 (m, 2H, C_6H_5-); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) -4.94 ($Si(CH_3)_2$), 17.20 ($C(CH_3)_3$), 26.87 ($C(CH_3)_3$), 125.96, 127.18, 127.94, 129.76, 146.22 (=CH), 151.82 (=CH); MS m/z (rel, intensity): 73.00 (12), 201.20 (14), 203.00 (100, M^+- CH_3), 203.80 (18), 218.20 (3, M^+). These data are in accordance with the literature.[4]

 **P27**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.44 (s, 6H, C*H*$_3$), 5.70 (d, 1H, J_{HH} = 2.9 Hz, =C*H*), 6.02 (d, 1H, J_{HH} = 2.9 Hz, =C*H*), 7.13-7.18 (m, 2H, Ph), 7.19-7.25, 7.27-7.29 (m, 3H, Ph), 7.36-7.40 (m, 3H, Ph), 7.57-7.60 (m, 2H, Ph); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) -2.34 (*C*H$_3$), 126.36, 126.83, 127.80, 128.07, 129.04, 129.13, 134.01, 138.25, 144.12 (=*C*H), 150.94 (=*C*H); MS m/z (rel, intensity): 134.80 (18), 197.20 (18), 211.20 (21), 212.00 (25), 213.50 (30), 214.90 (36), 215.80 (45), 216.80 (49), 217.50 (53), 218.10 (56), 218.70 (60), 219.30 (63), 220.80 (69), 221.50 (71), 223.30 (100, M^+- CH_3), 224.30 (47), 225.20 (20), 234.20 (20), 235.20 (21), 236.20 (22), 237.60 (27), 238.20 (30, M^+). These data are in accordance with the literature.[4]
 **P28**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 5.75 (d, 1H, J_{HH} = 2.7 Hz, =C*H*), 6.35 (d, 1H, J_{HH} = 2.7 Hz, =C*H*), 7.21 – 7.26 (m, 5H, C$_6$*H*$_5$-), 7.21 – 7.26 (m, 5H, C$_6$*H*$_5$-), 7.36 – 7.40 (m, 5H, C$_6$*H*$_5$-), 7.43 – 7.48 (m, 4H, C$_6$*H*$_5$-), 7.57 – 7.59 (m, 4H, C$_6$*H*$_5$-), 7.63 – 7.67 (m, 1H, C$_6$*H*$_5$-); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 126.69, 127.41, 127.77, 127.89, 128.09, 129.49, 133.93, 134.15, 135.99, 136.35, 143.84, 147.19, 148.83; MS m/z (rel, intensity): 258.30 (30), 259.20 (67), 260.20 (20), 284.50 (54), 285.20 (51), 362.00 (100, M^+). These data are in accordance with the literature.[4]
 **P29**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.07 (s, 9H, OSi(C*H*$_3$)$_3$), 0.24 (s, 6H, OSi(C*H*$_3$)$_2$), 5.68 (d, 1H, J_{HH} = 3.0 Hz, =C*H*), 5.90 (d, 1H, J_{HH} = 3.0 Hz, =C*H*), 7.21 – 7.26 (m, 1H, C$_6$*H*$_5$), 7.30 – 7.34 (m, 4H, C$_6$*H*$_5$); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 0.97 (*C*H$_2$), 1.84 (*C*H$_3$), 126.39, 126.82, 127.26, 128.08, 143.66 (=*C*H), 152.61 (=*C*H); MS m/z (rel, intensity): 234.30 (14), 235.20 (100, M^+ - CH_3), 236.00 (19), 250.70 (1, M^+). These data are in accordance with the literature.[4]
 **P31**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 5.40 (s, 1H, Si*H*), 5.69 (d, 1H, J_{HH} = 2.5 Hz, =C*H*), 6.29 (dd, 1H, J_{HH} = 2.5, 1.0 Hz, =C*H*), 7.17 – 7.25 (m, 2H, C$_6$*H*$_5$-), 7.27 – 7.31 (m, 1H, C$_6$*H*$_5$-), 7.34 – 7.41 (m, 8H, C$_6$*H*$_5$-), 7.56 – 7.59 (m, 4H, C$_6$*H*$_5$-) ; ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 126.70, 127.04, 127.72, 128.01, 128.37, 129.78, 132.11, 134.09, 135.75, 142.91 (=*C*H), 145.87 (=*C*H); MS m/z (rel, intensity): 103.00 (7), 130.10 (2), 180.50 (5), 204.90 (7), 207.00 (7), 225.20 (1), 232.20 (1), 259.10 (8), 271.00 (3), 278.80 (2), 286.00 (100, M^+). These data are in accordance with the literature.[10]
 **P32**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 5.39 (s, 1H, Si*H*), 5.69 (d, 1H, J_{HH} = 2.3 Hz, =C*H*), 6.28 (dd, 1H, J_{HH} = 2.3, 0.9 Hz, =C*H*), 6.93 – 6.98 (m, 2H, -C$_6$*H*$_4$-F), 7.29 – 7.33 (m, 2H, -C$_6$*H*$_4$-F), 7.36 – 7.44 (m, 7H, -C$_6$*H*$_5$), 7.56 – 7.58 (m, 3H, -C$_6$*H*$_5$); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 115.22 (d, *J* = 21.4 Hz), 128.08, 128.23 (d, *J* = 8.0 Hz), 128.80 (d, *J* = 8.0 Hz), 129.89, 132.04, 132.72, 135.71, 144.87 (d, *J* = 2.7 Hz), 148.27 (=*C*H$_2$), 162.08 (d, *J* = 246.1 Hz); MS m/z (rel, intensity): 299.10 (10), 299.70 (12), 301.60 (21), 303.20 (100, M^+-H), 304.20 (89, M^+). These data are in accordance with the literature.[10]

 **P33**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.61 – 0.69 (m, 2H, CH_3CH_2-), 0.82 – 0.88 (m, 8H, CH_3CH_2-), 1.31 (s, 18H, $C(CH_3)_3$), 5.66 (d, 2H, J_{HH} = 2.8 Hz, =C*H*), 6.04 (d, 2H, J_{HH} = 2.8 Hz, =C*H*), 7.20 (d, 2H, J_{HH} = 8.6 Hz, -C_6H_4-*t*Bu), 7.26 (d, 2H, J_{HH} = 2.8 Hz, -C_6H_4-*t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.14 (CH_3CH_2-), 7.09 (CH_3CH_2-), 31.35 ($C(CH_3)_3$), 34.37 ($C(CH_3)_3$), 124.93, 126.37, 129.33, 141.29, 148.91(=CH_2), 149.21 (=CH_2); MS m/z (rel, intensity): 57.20 (100, C_4H_9), 289.20 (17), 290.80 (17), 291.50 (23), 319.50 (16), 346.70 (23), 347.60 (70), 348.50 (47), 349.50 (26), 375.70 (41), 376.70 (26), 389.70 (16), 403.50 (34), 404.20 (88, M^+).
 **P34**	^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.76 – 0.83 (m, 2H, CH_3CH_2-), 0.84 – 1.00 (m, 8H, CH_3CH_2-), 5.66 (d, 2H, J_{HH} = 2.8 Hz, =C*H*), 5.99 (d, 2H, J_{HH} = 2.8 Hz, =C*H*), 6.94 (d, 4H, J_{HH} = 8.9 Hz, -C_6H_4-F), 7.17 (dd, 4H, J_{HH} = 8.9, 5.0 Hz, -C_6H_4-F); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 3.00 (CH_3CH_2-), 6.94 (CH_3CH_2-), 114.93 (d, *J* = 21.3 Hz), 128.14 (d, *J* = 8.0 Hz), 128.80 (br s), 130.19, 140.26 (d, *J* = 3.6 Hz), 148.27 (=CH_2), 161.83 (d, *J* = 245.0 Hz); MS m/z (rel, intensity): 203.50 (15), 271.00 (26), 299.10 (100, M^+ - C_2H_5), 299.80 (29), 327.80 (29), 328.80 (10, M^+).

4. NMR spectra of isolated products P1-P34

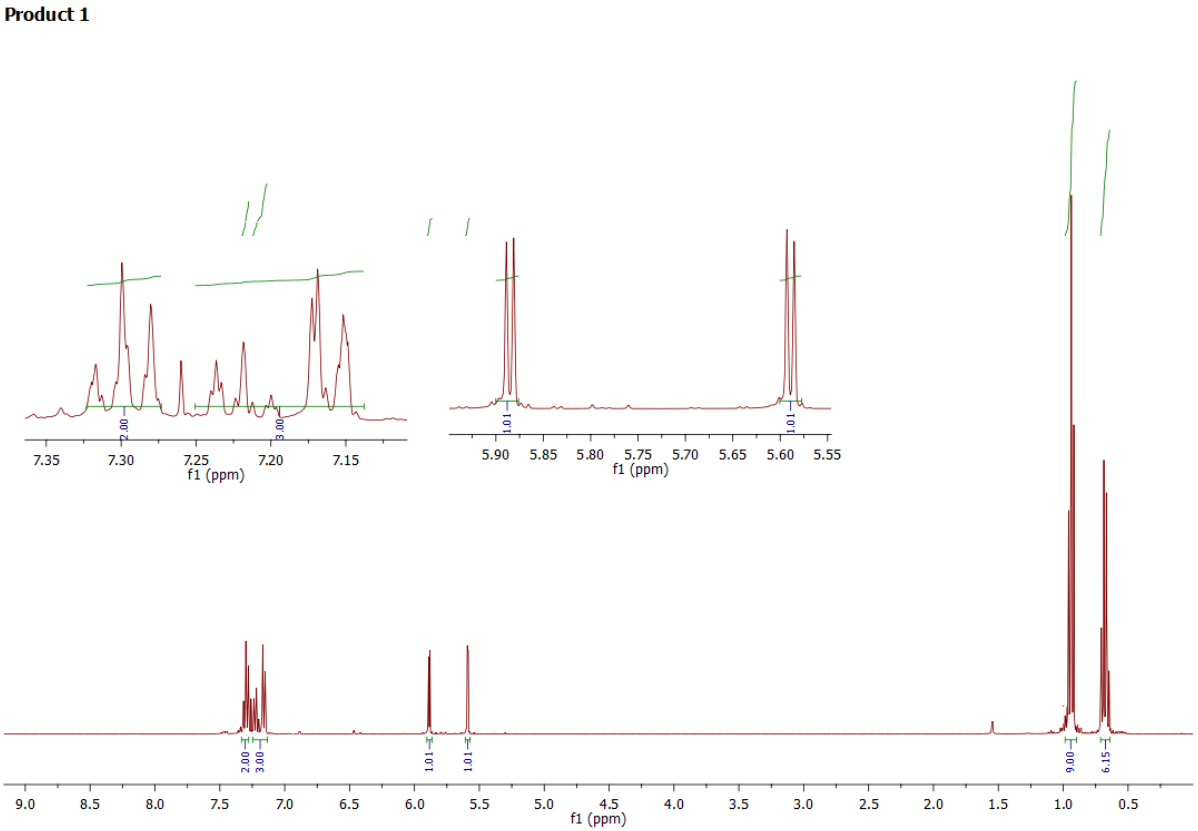


Figure S4. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P1**

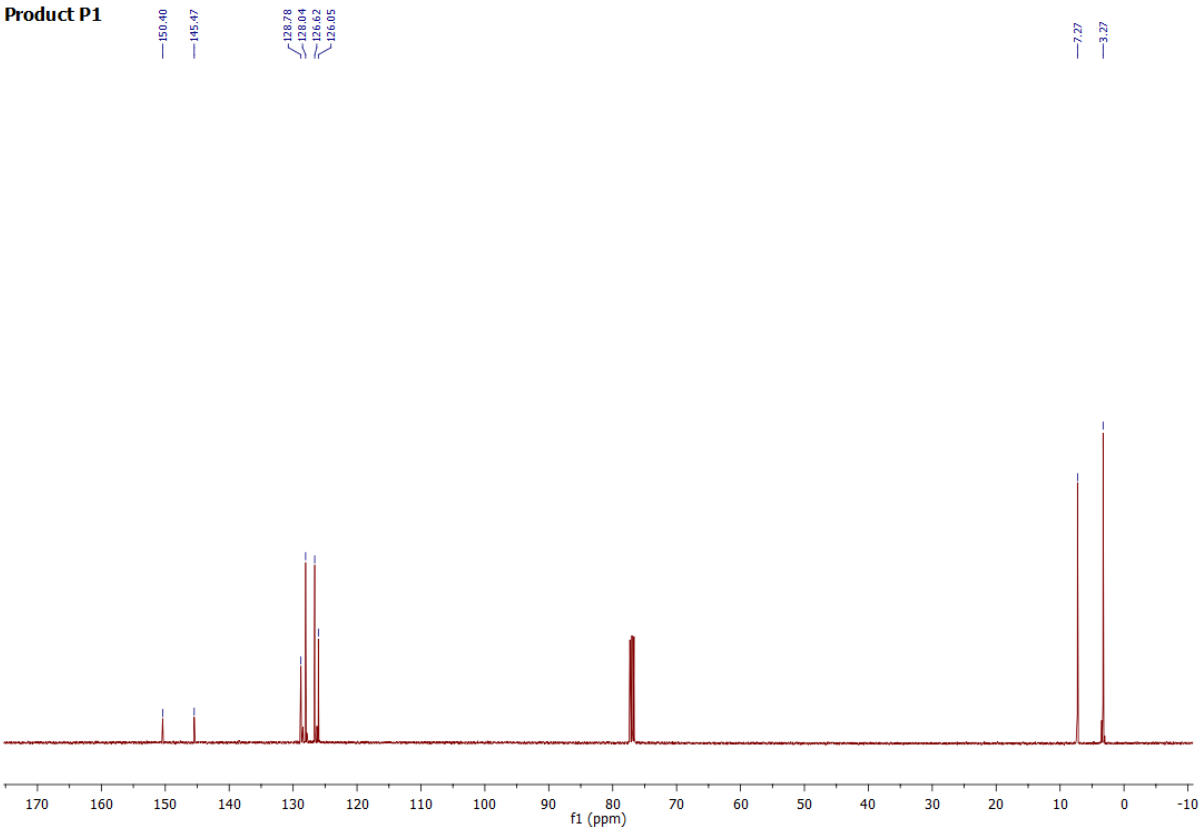


Figure S5. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P1**

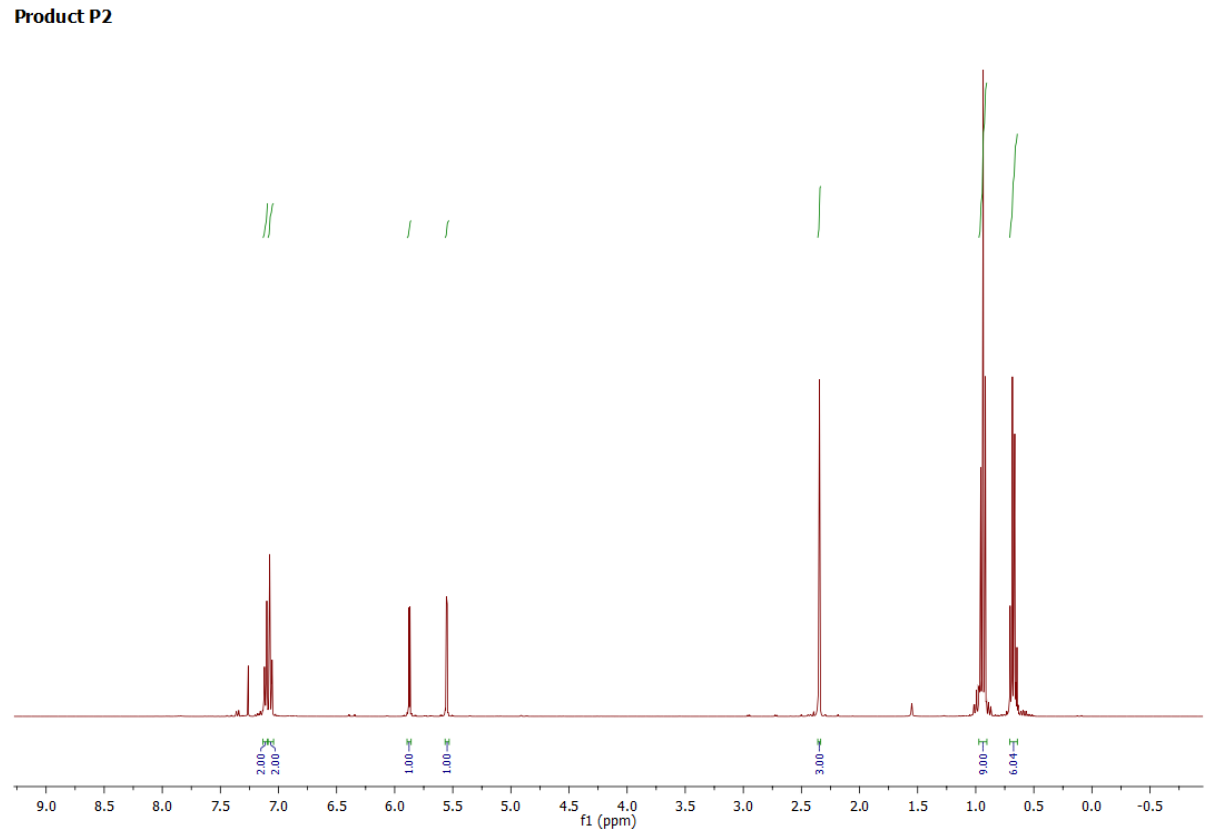


Figure S6. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P2**

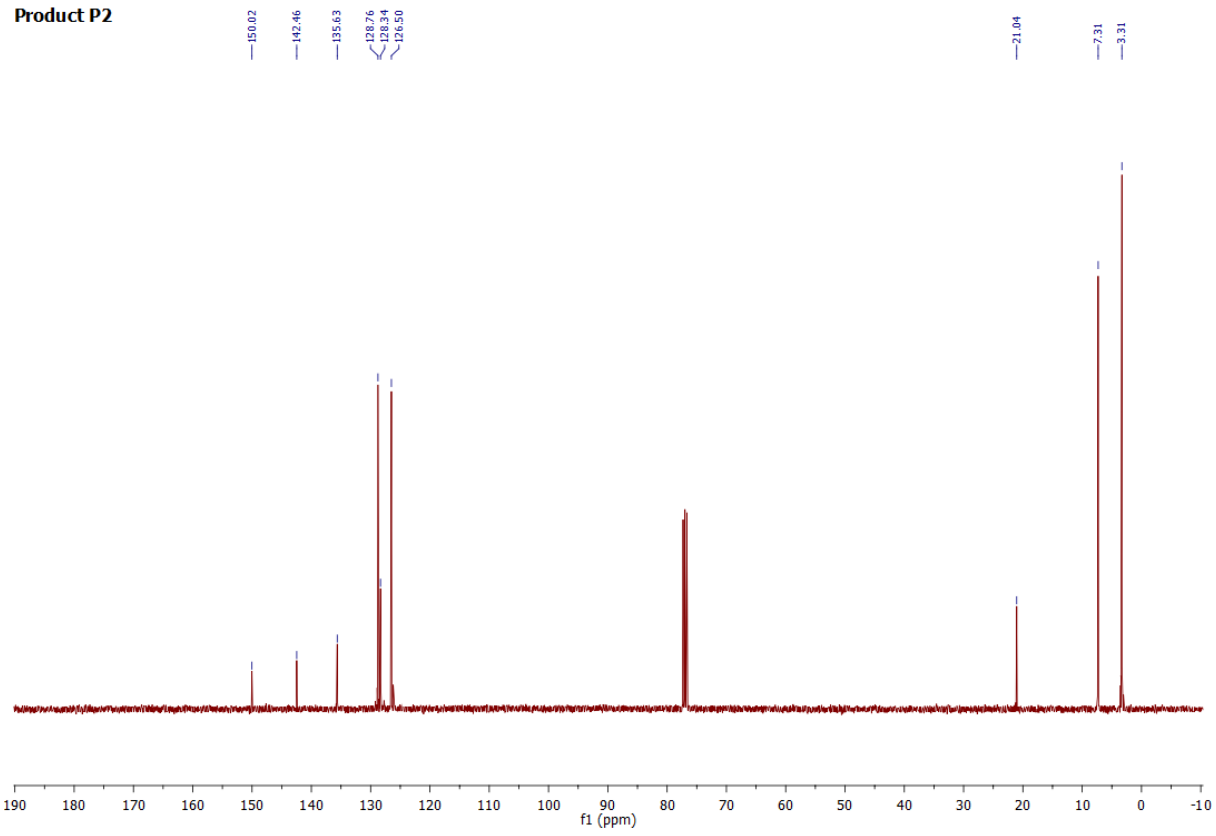


Figure S7. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P2**

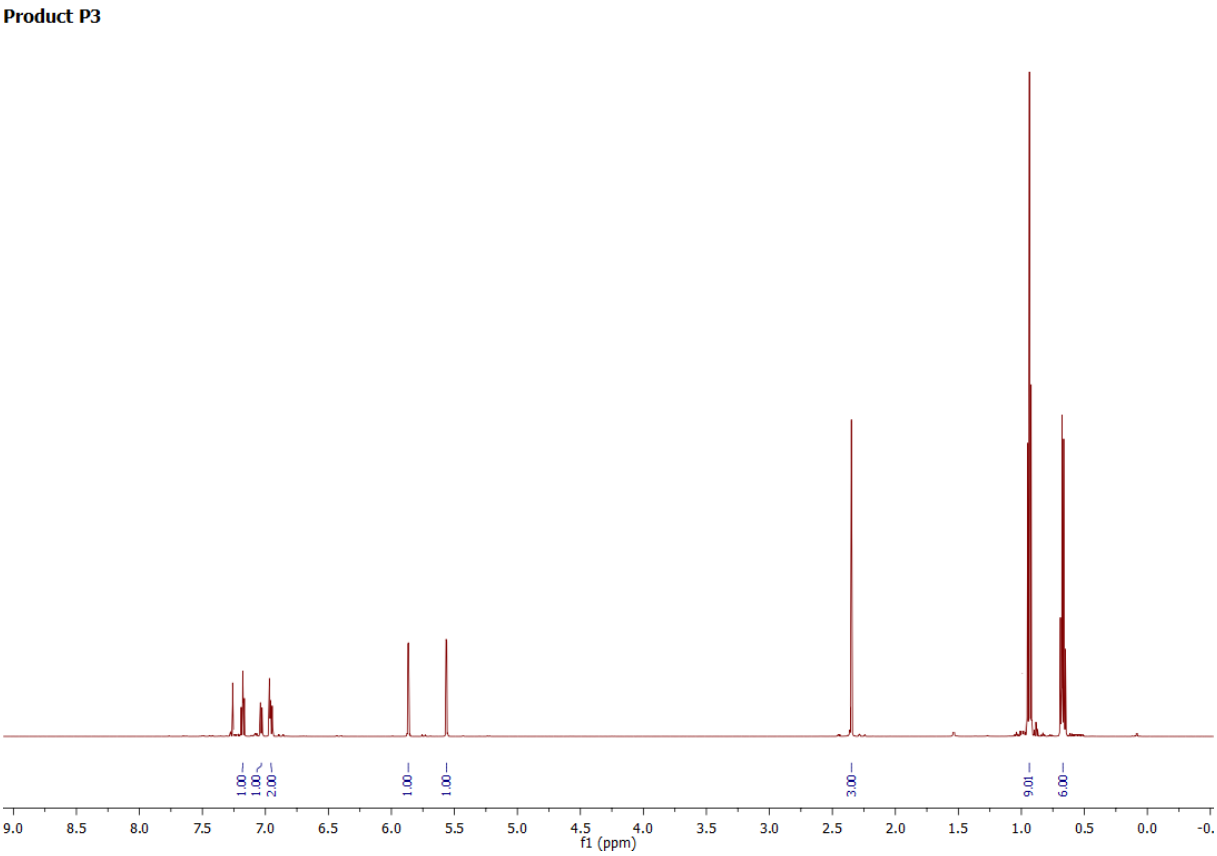


Figure S8. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P3**

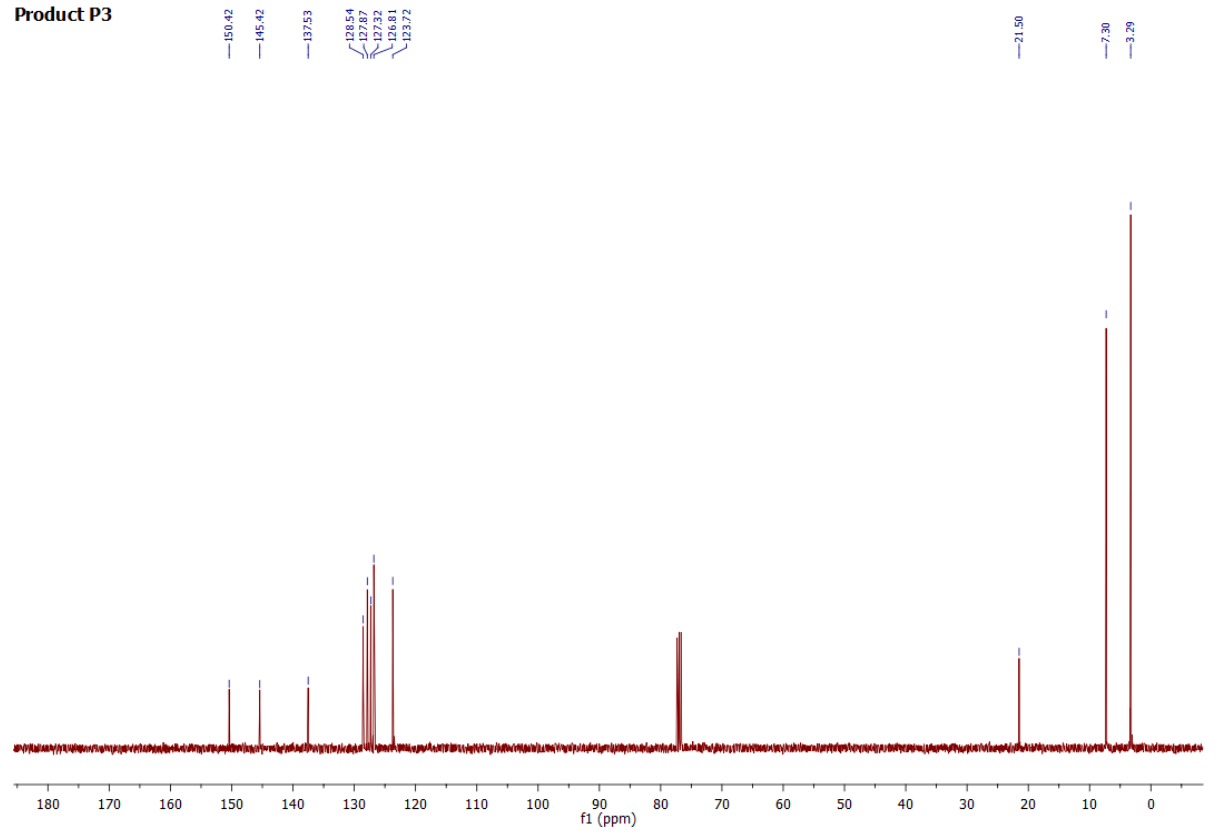


Figure S9. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P3**

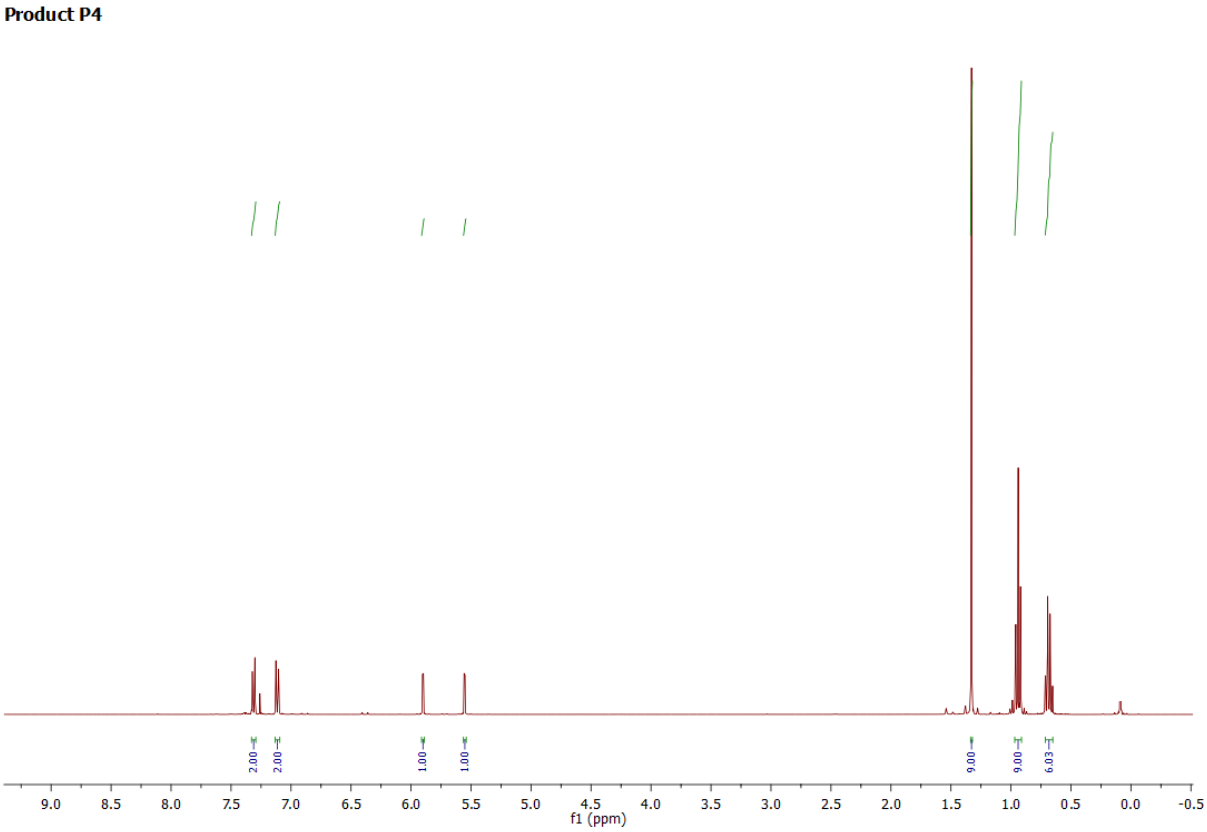


Figure S10. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P4**

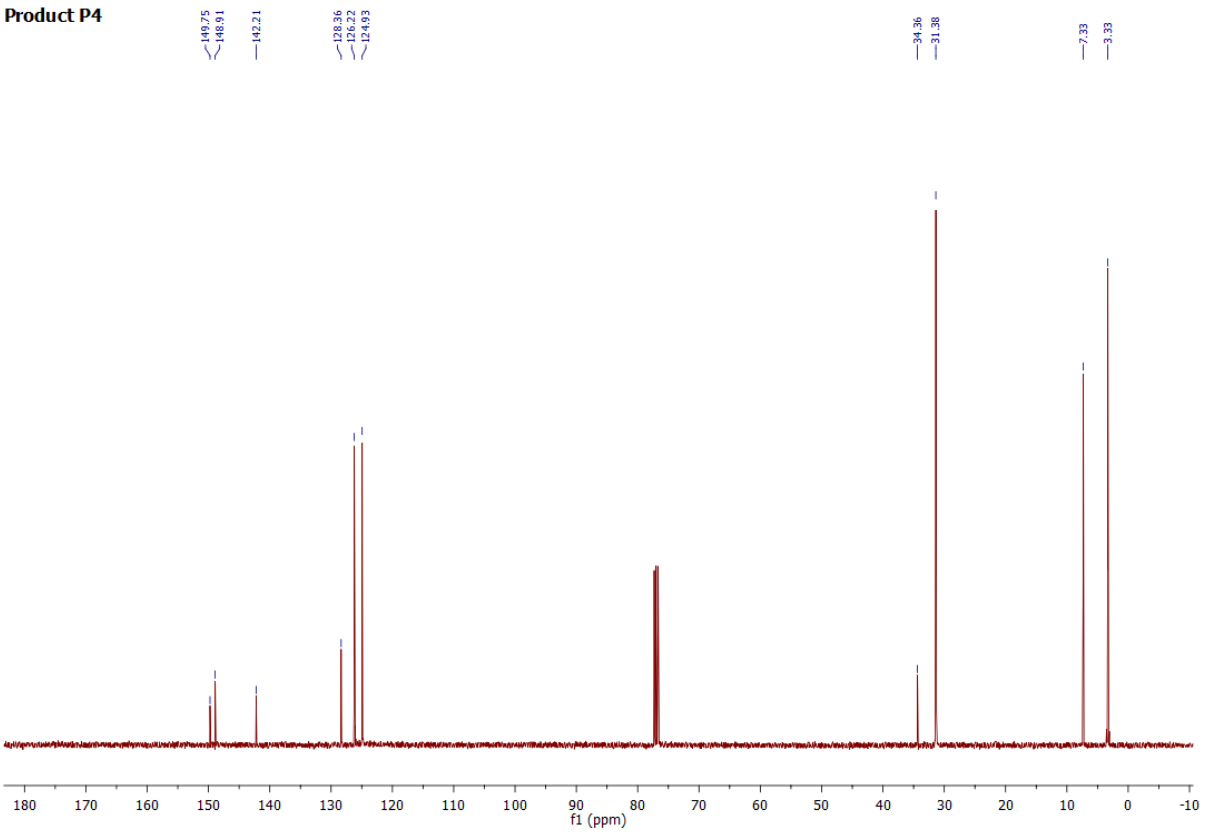


Figure S11. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P4**

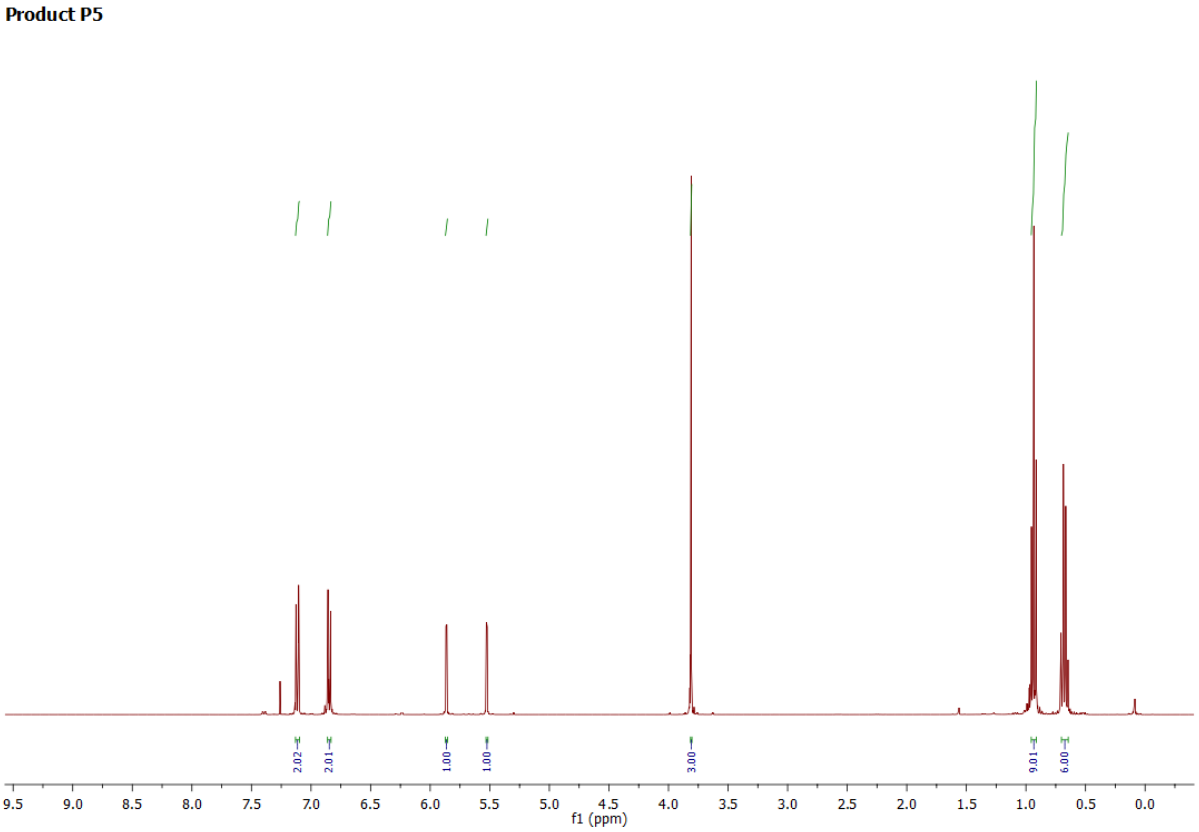


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P5**

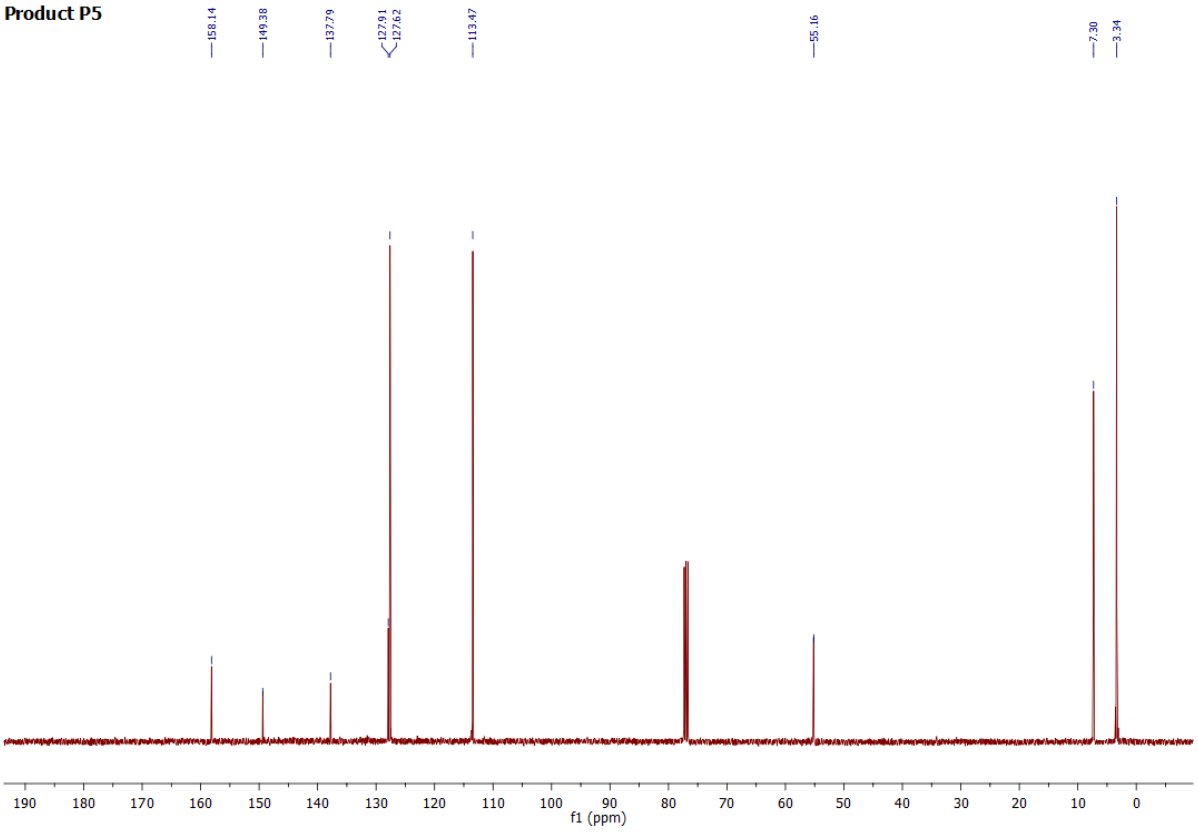


Figure S13. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P5**

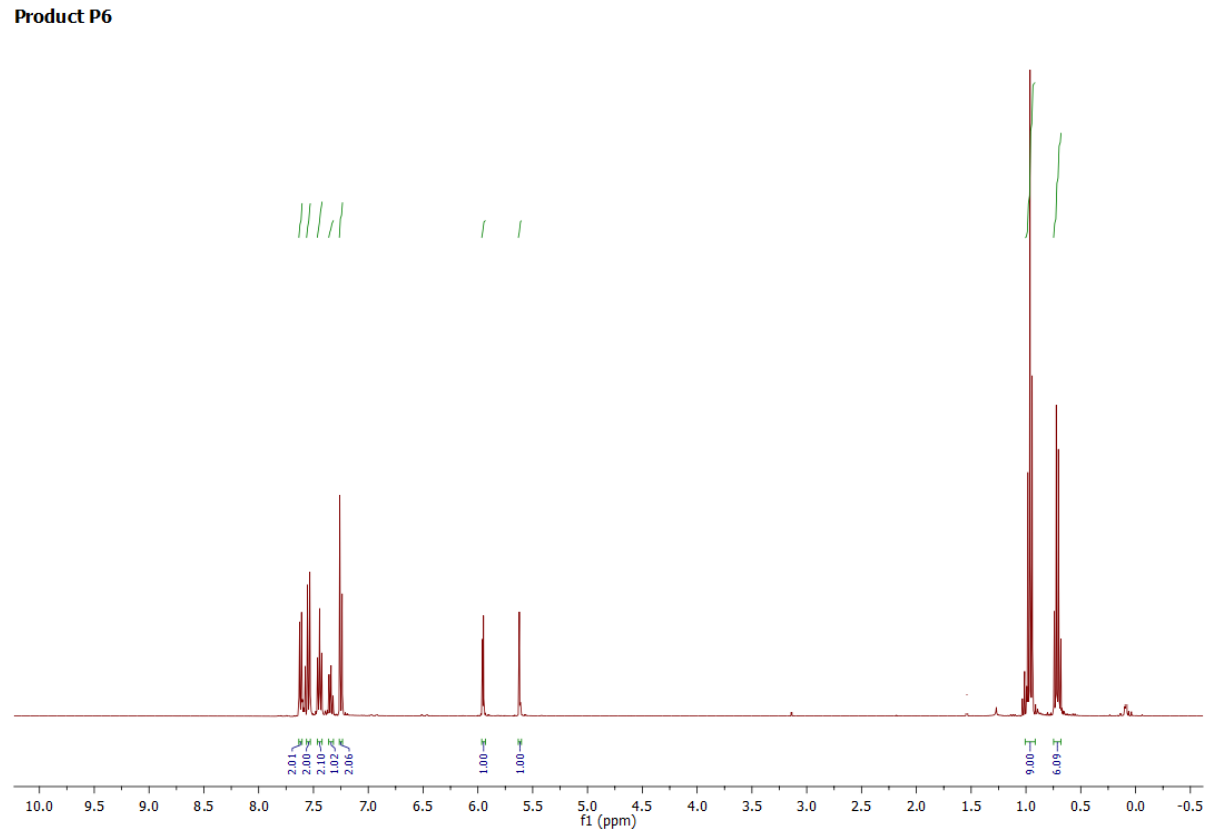


Figure S14. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P6**

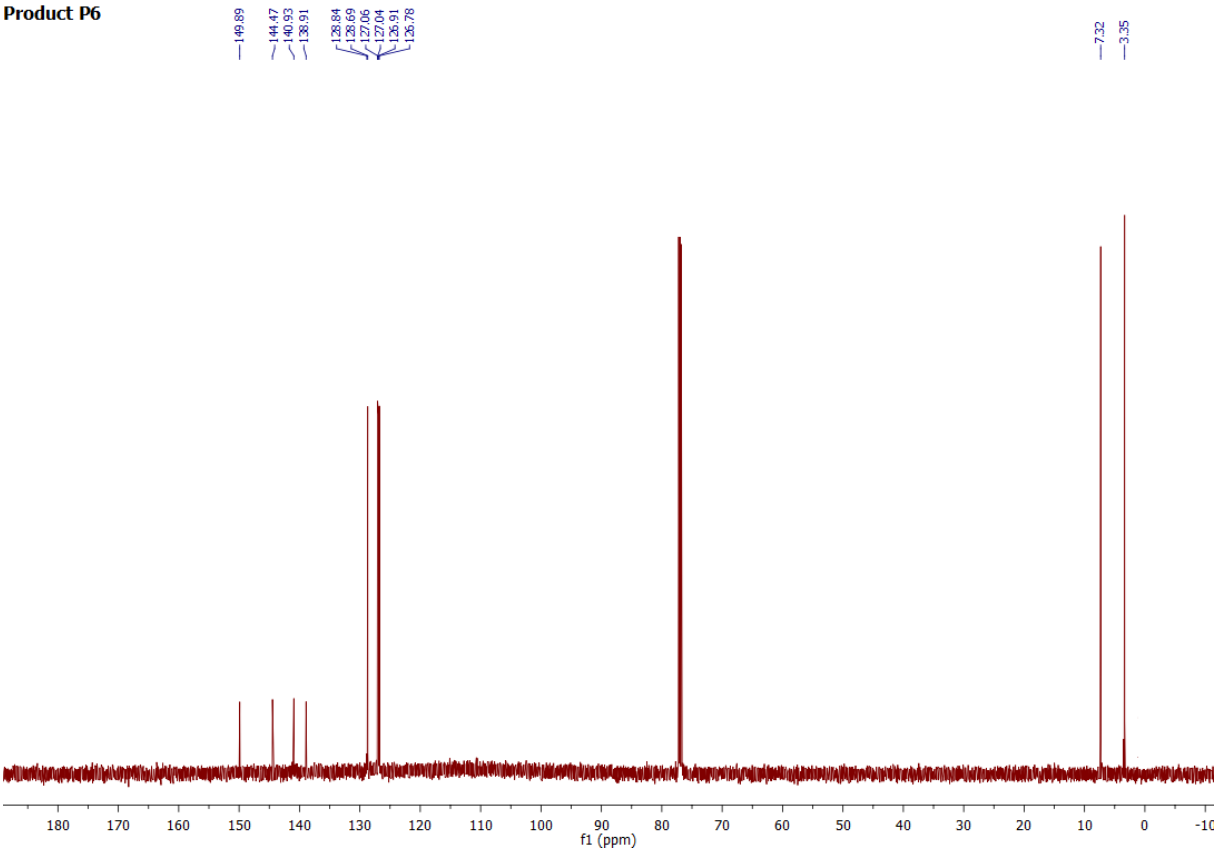


Figure S15. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P6**

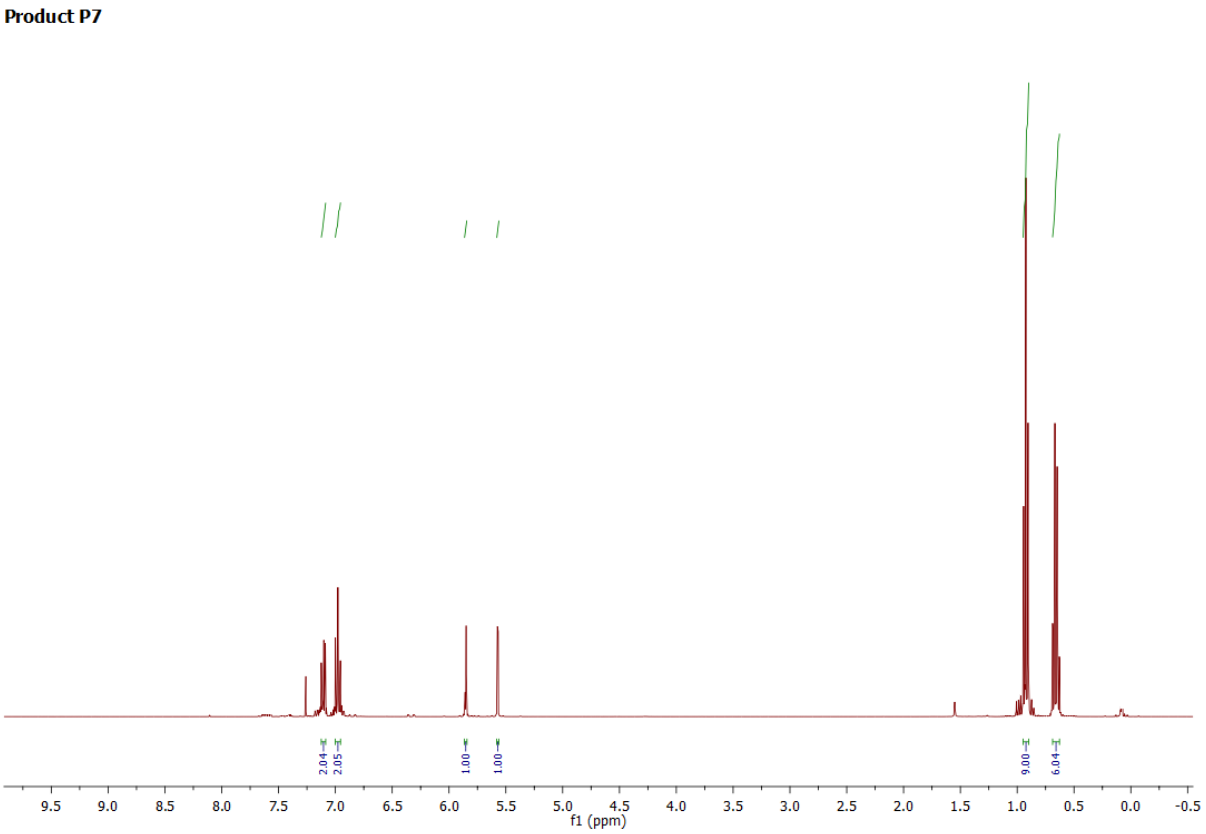


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P7**

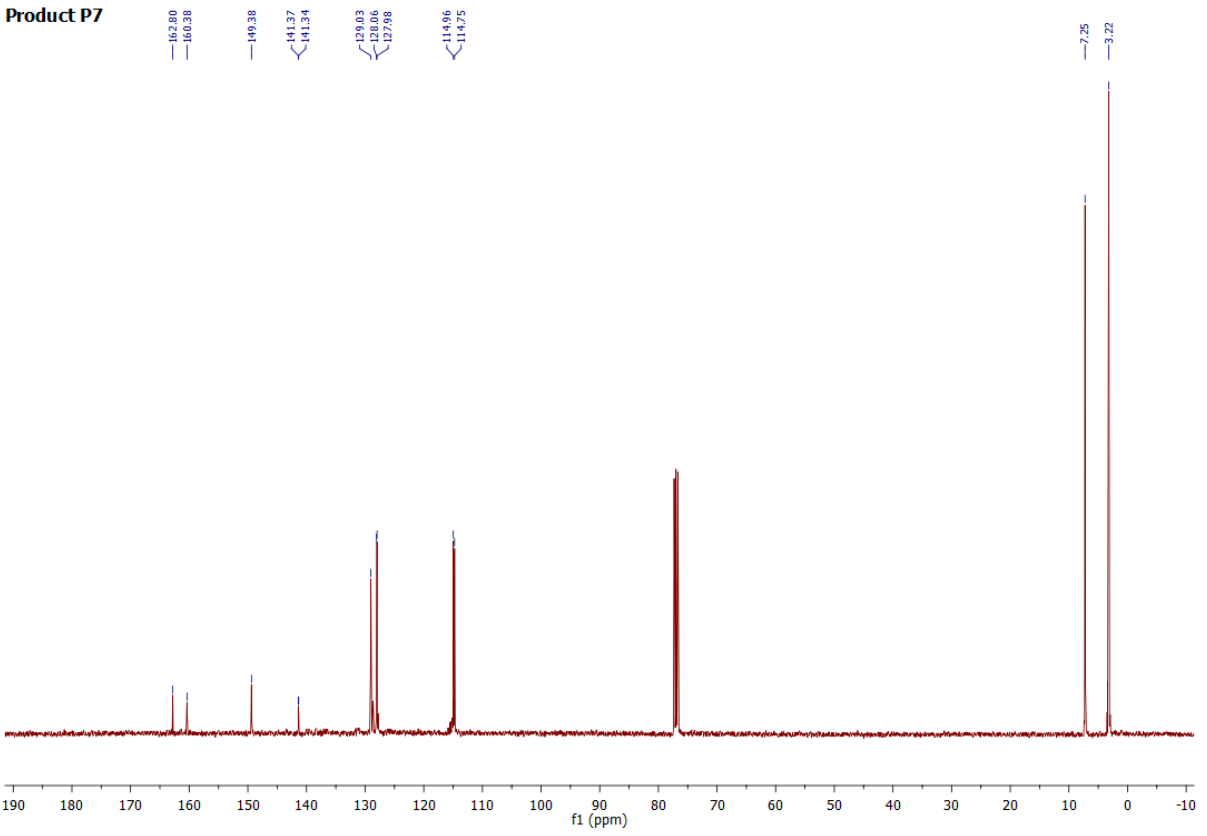


Figure S17. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P7**

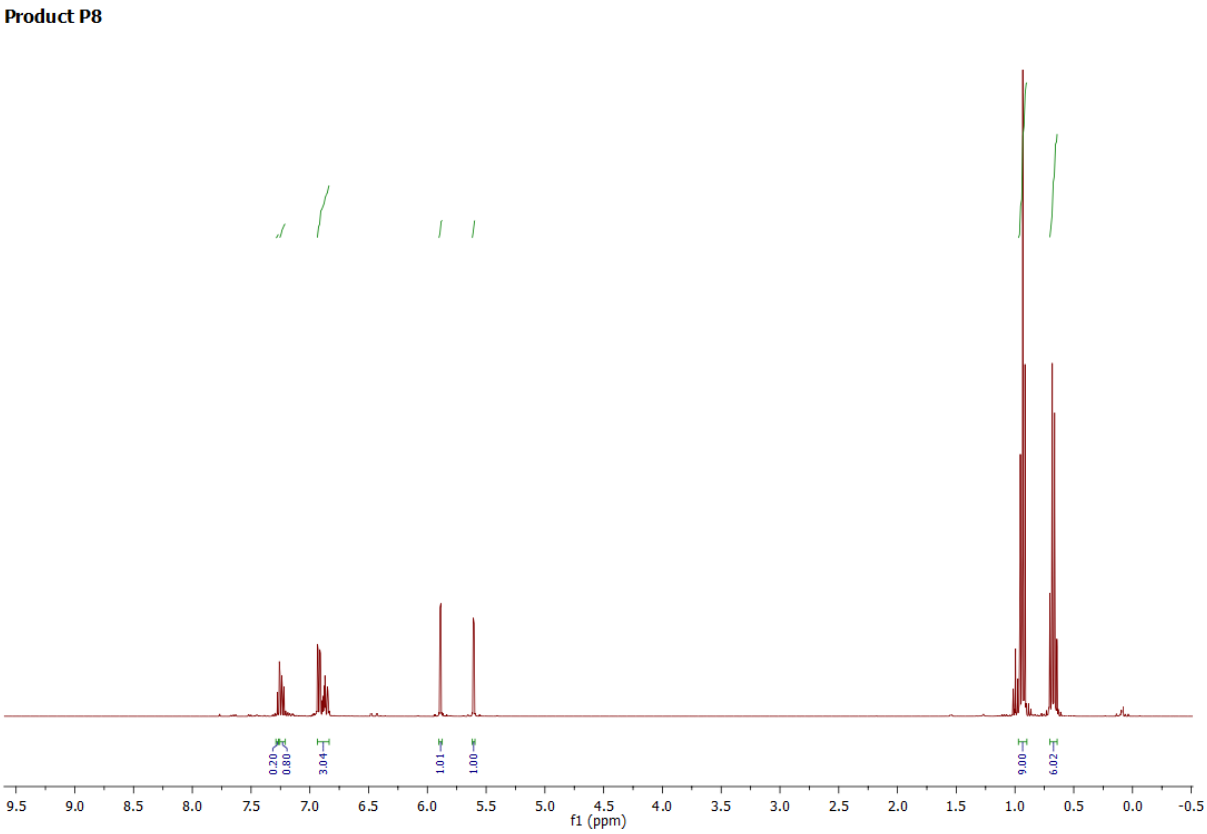


Figure S18. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P8**

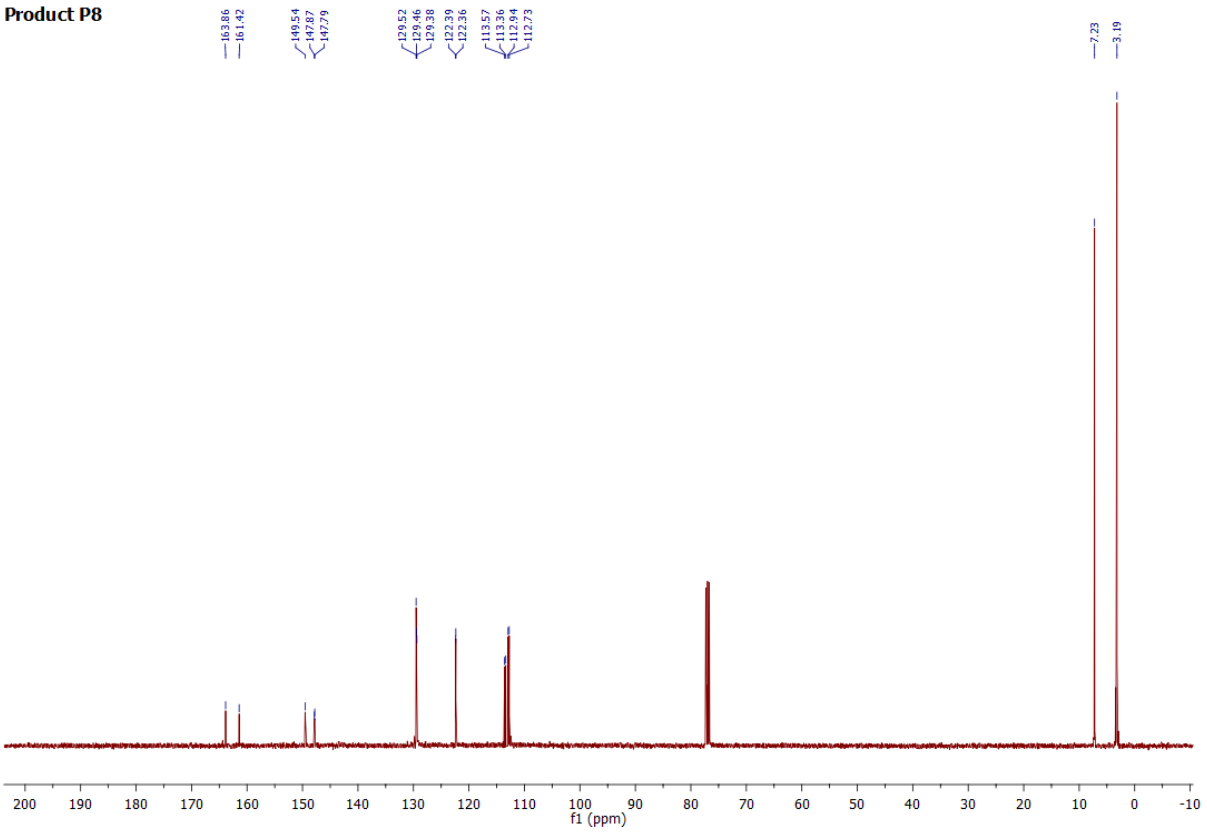


Figure S19. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P8**

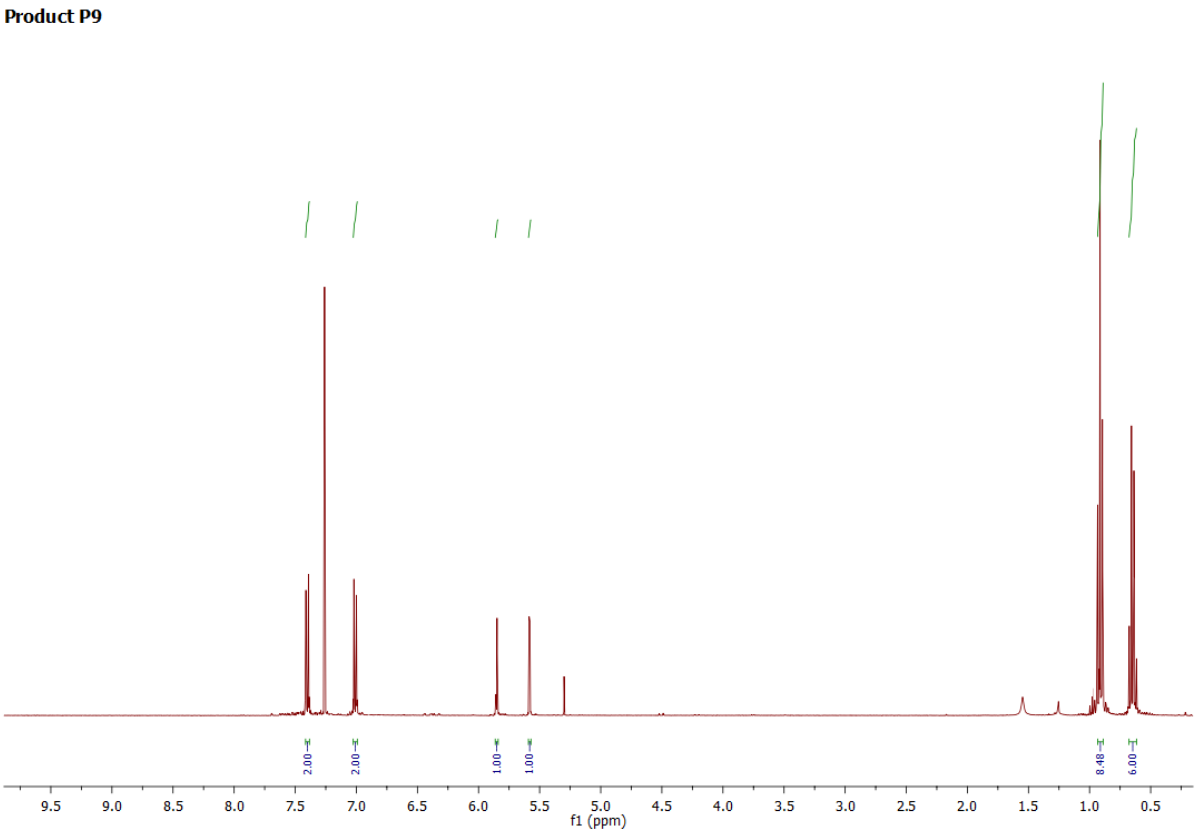


Figure S20. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P9**

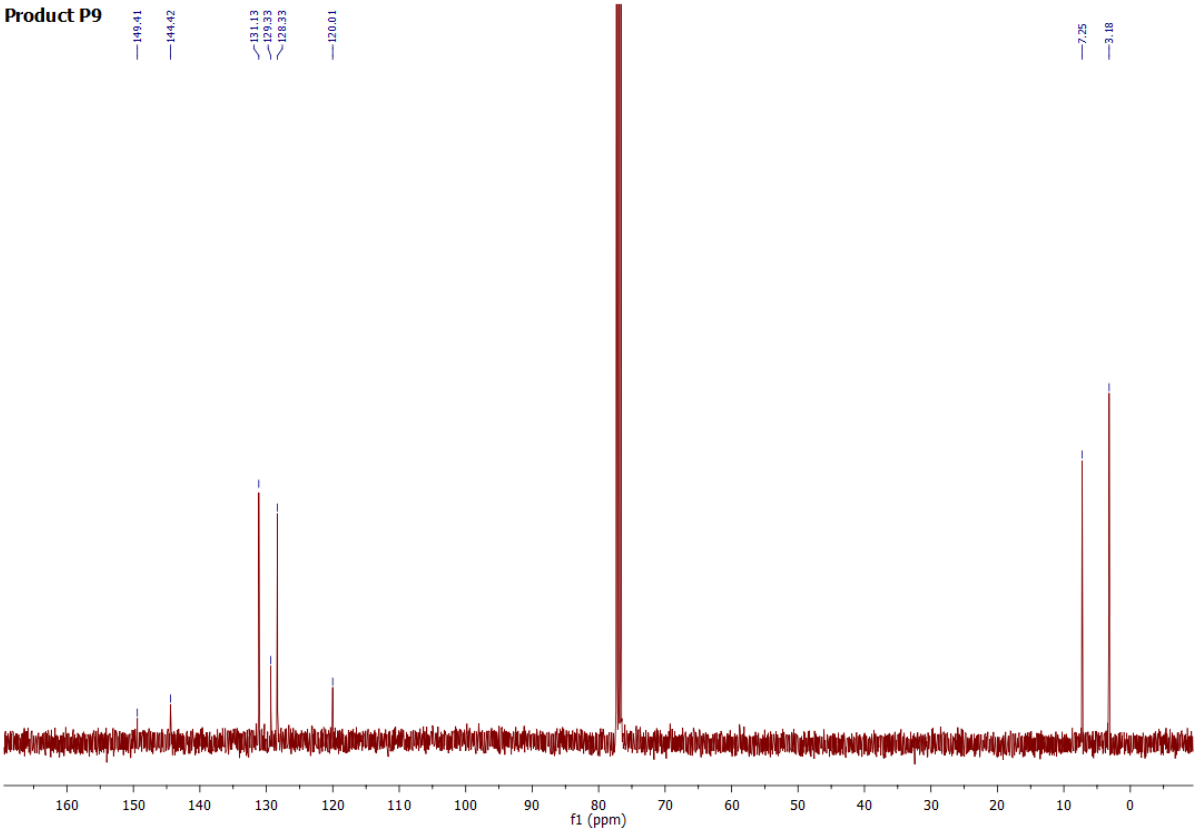


Figure S21. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P9**

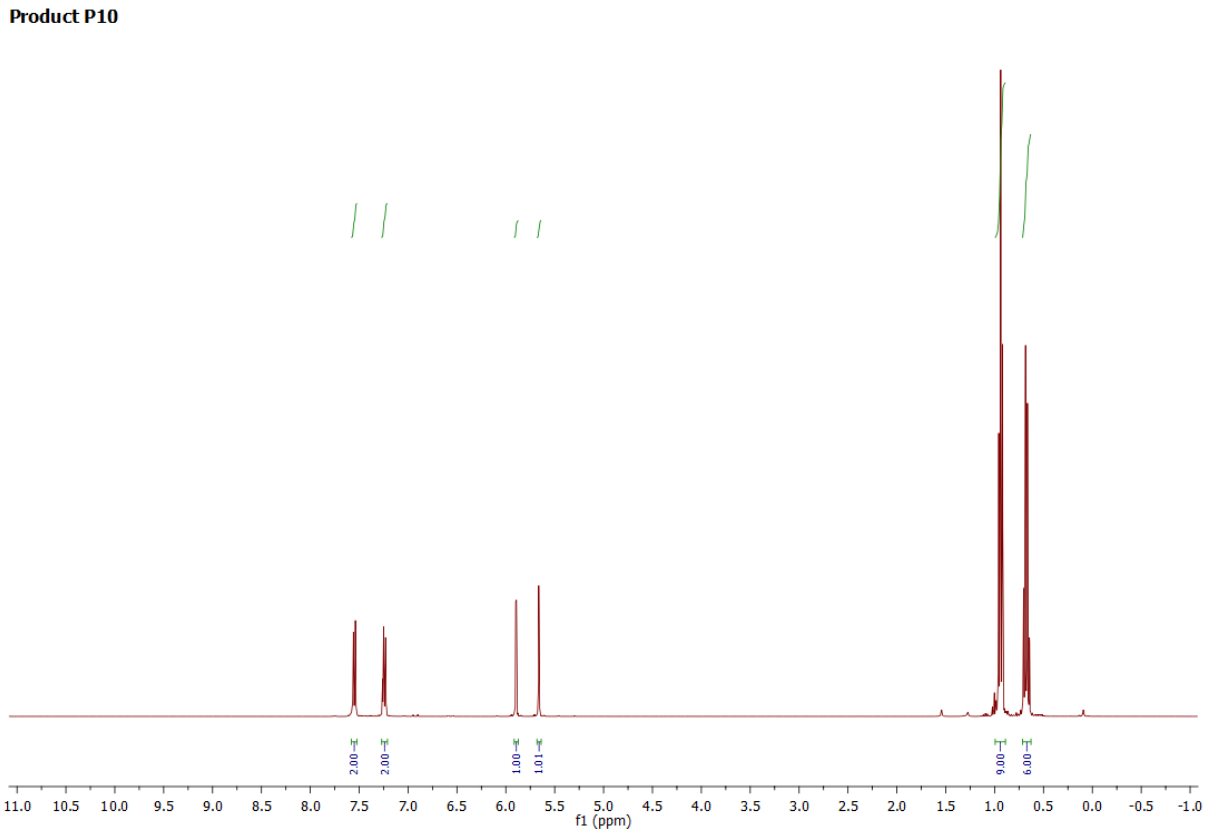


Figure S22. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P10**

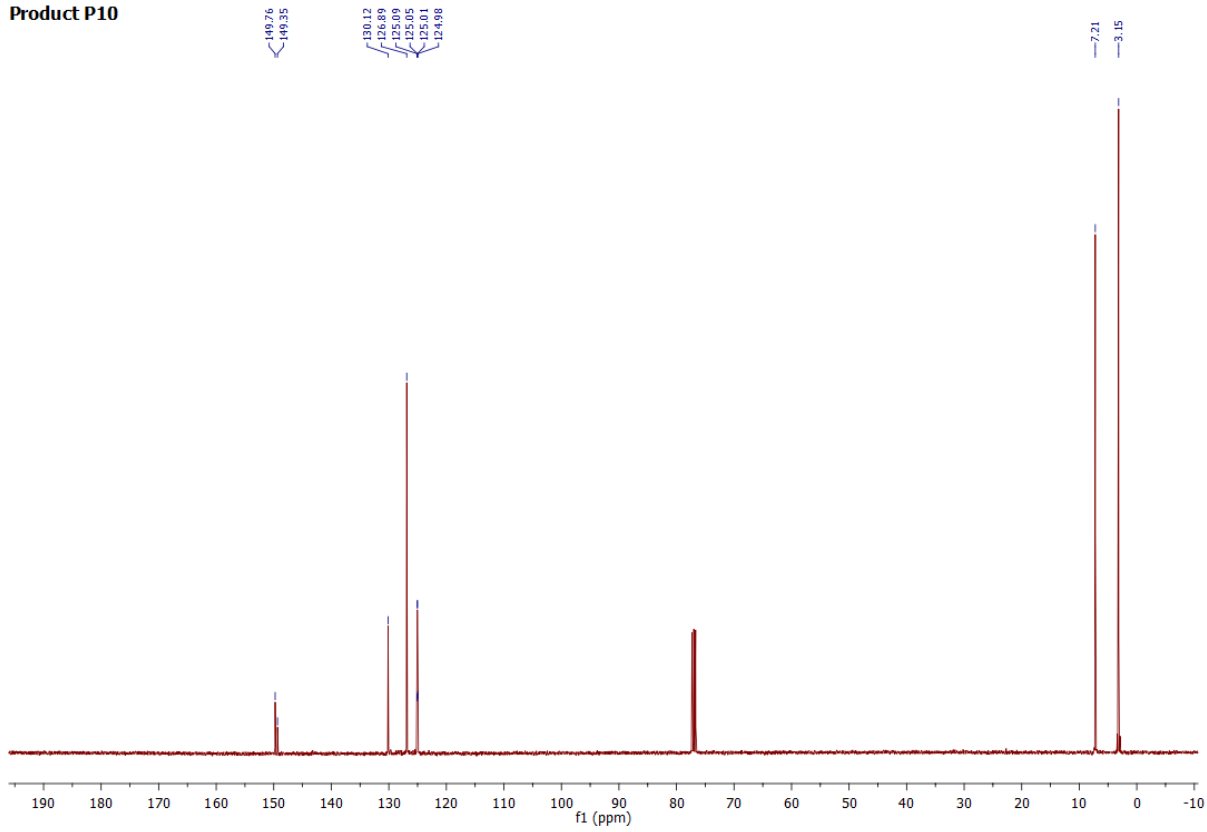


Figure S23. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P10**

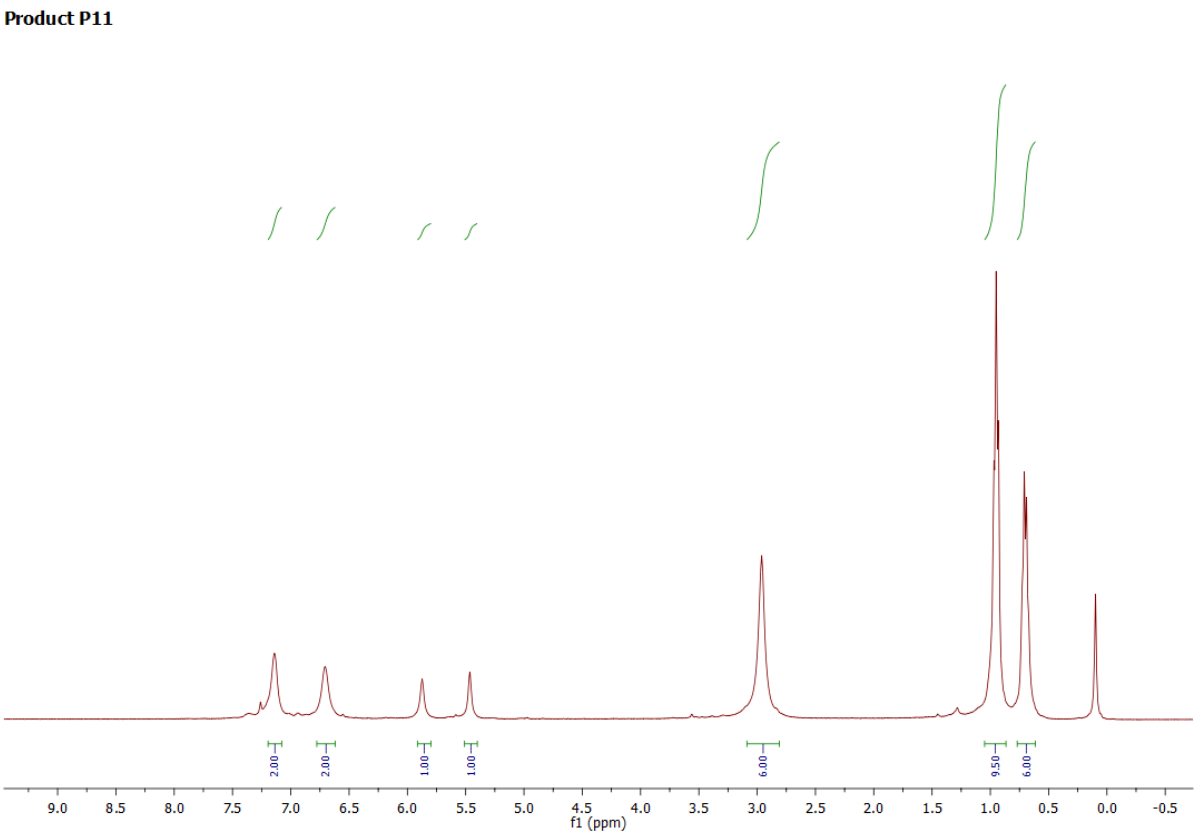


Figure S24. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P11**

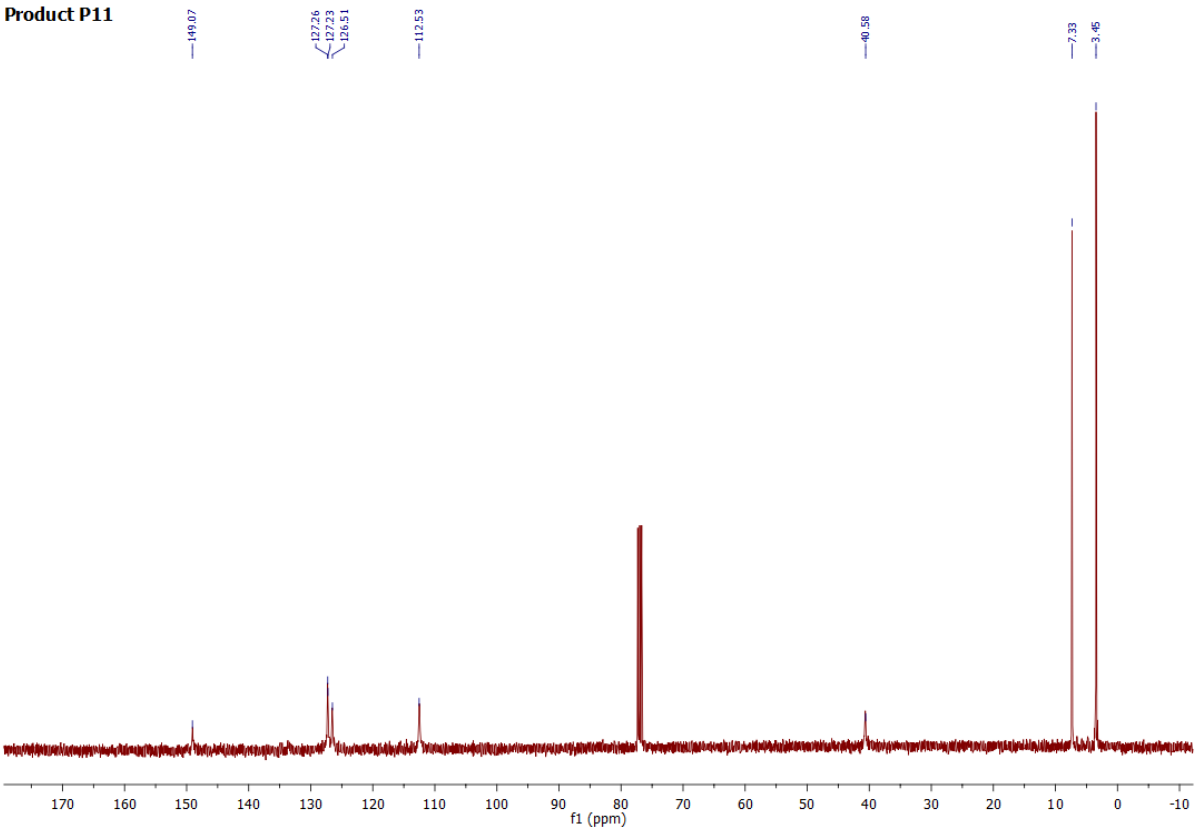


Figure S25. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P11**

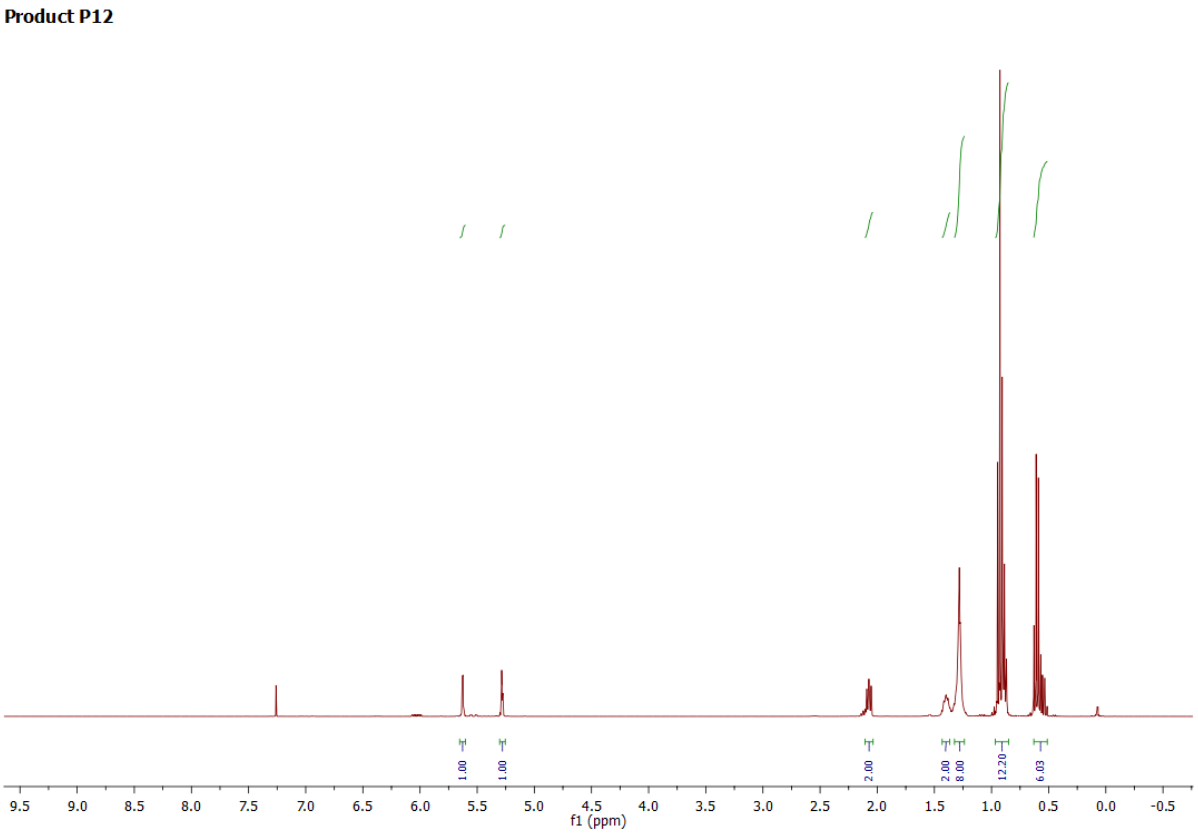


Figure S26. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P12**

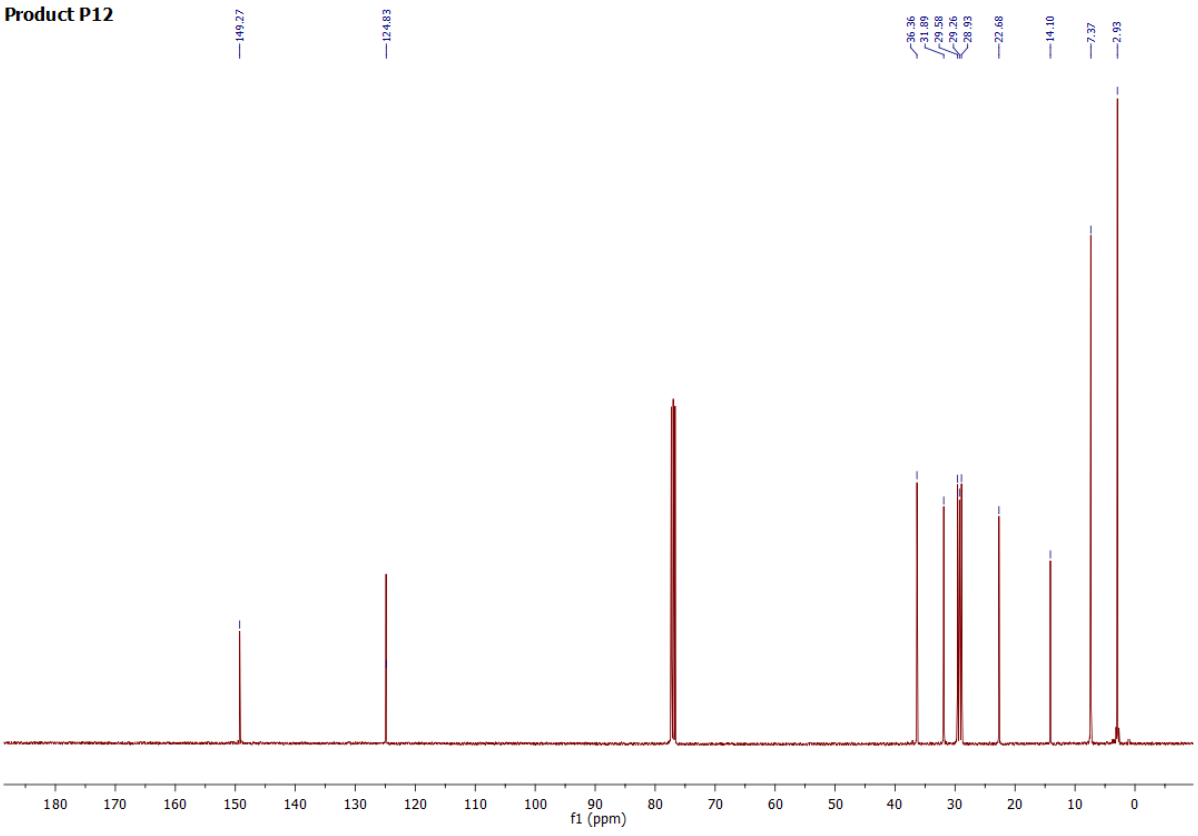


Figure S27. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P12**

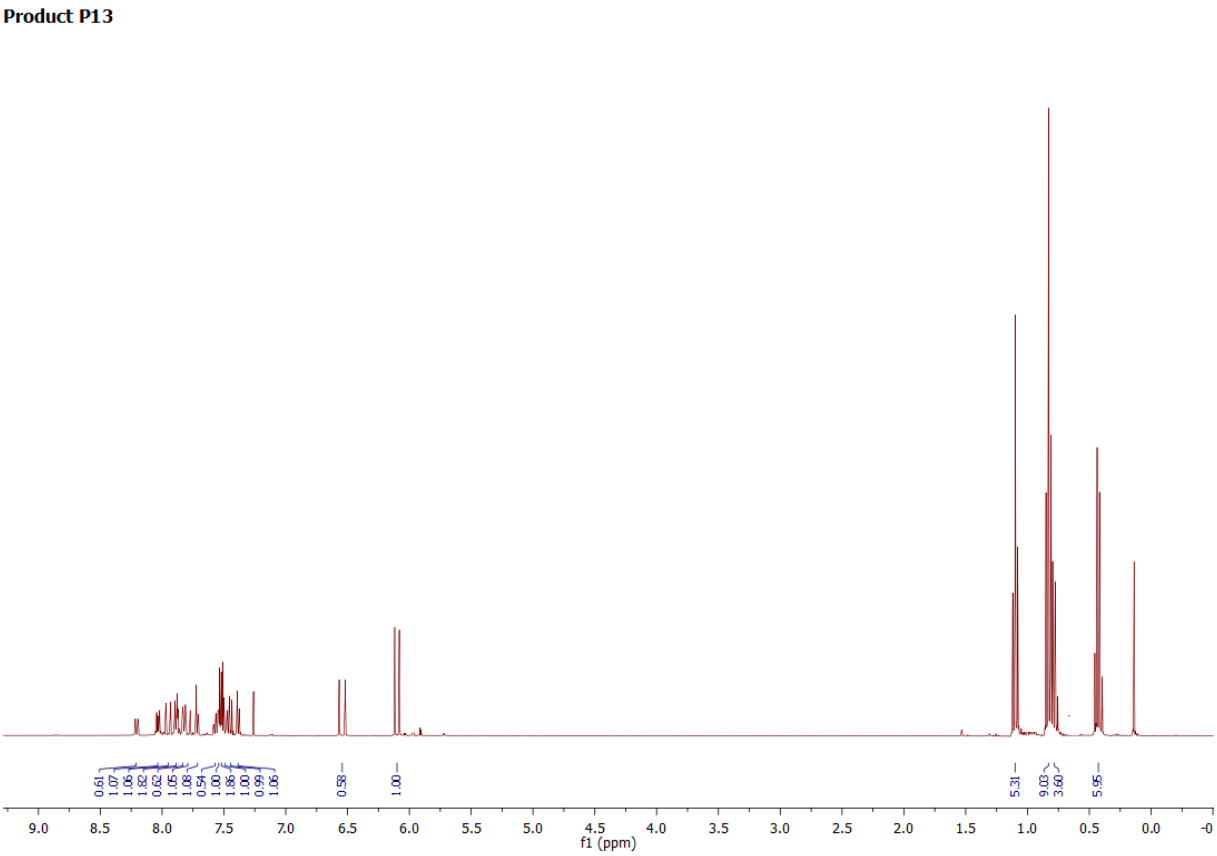


Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P13**

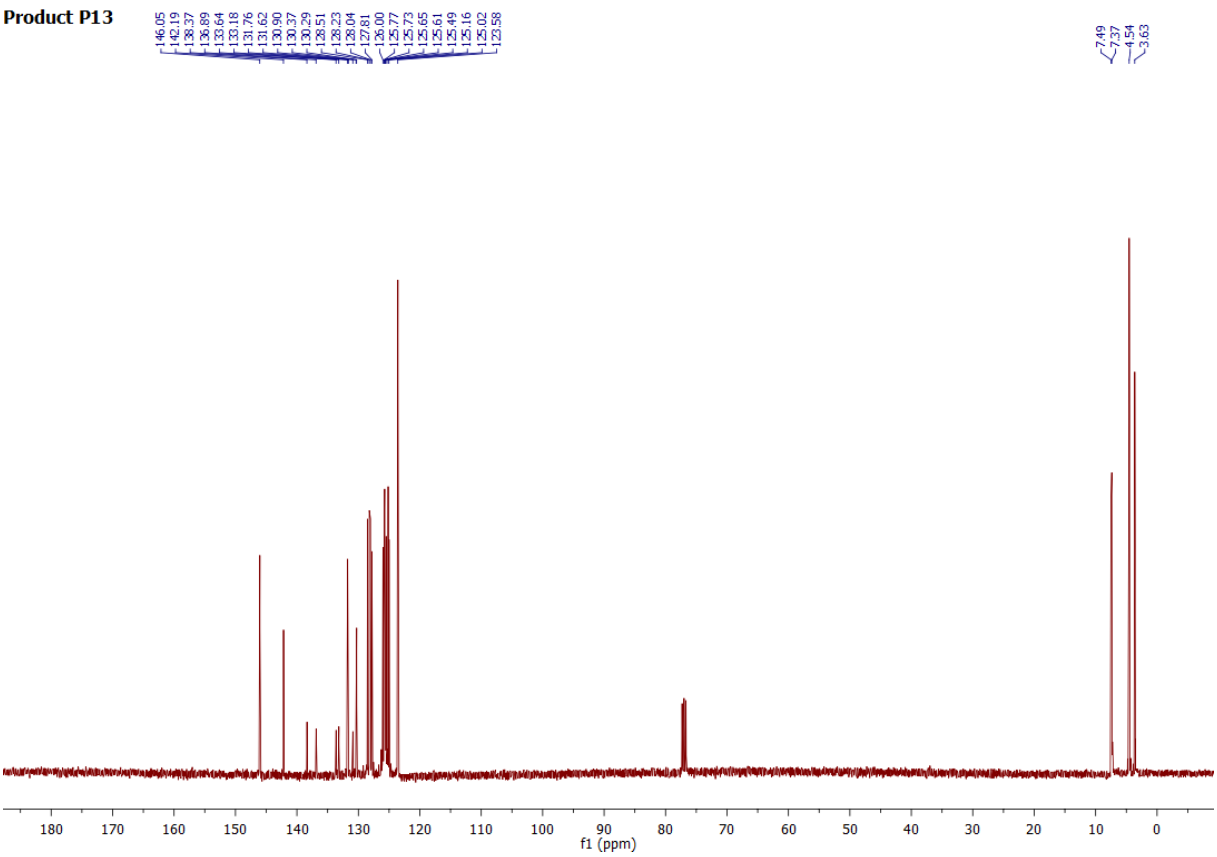


Figure S29. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P13**

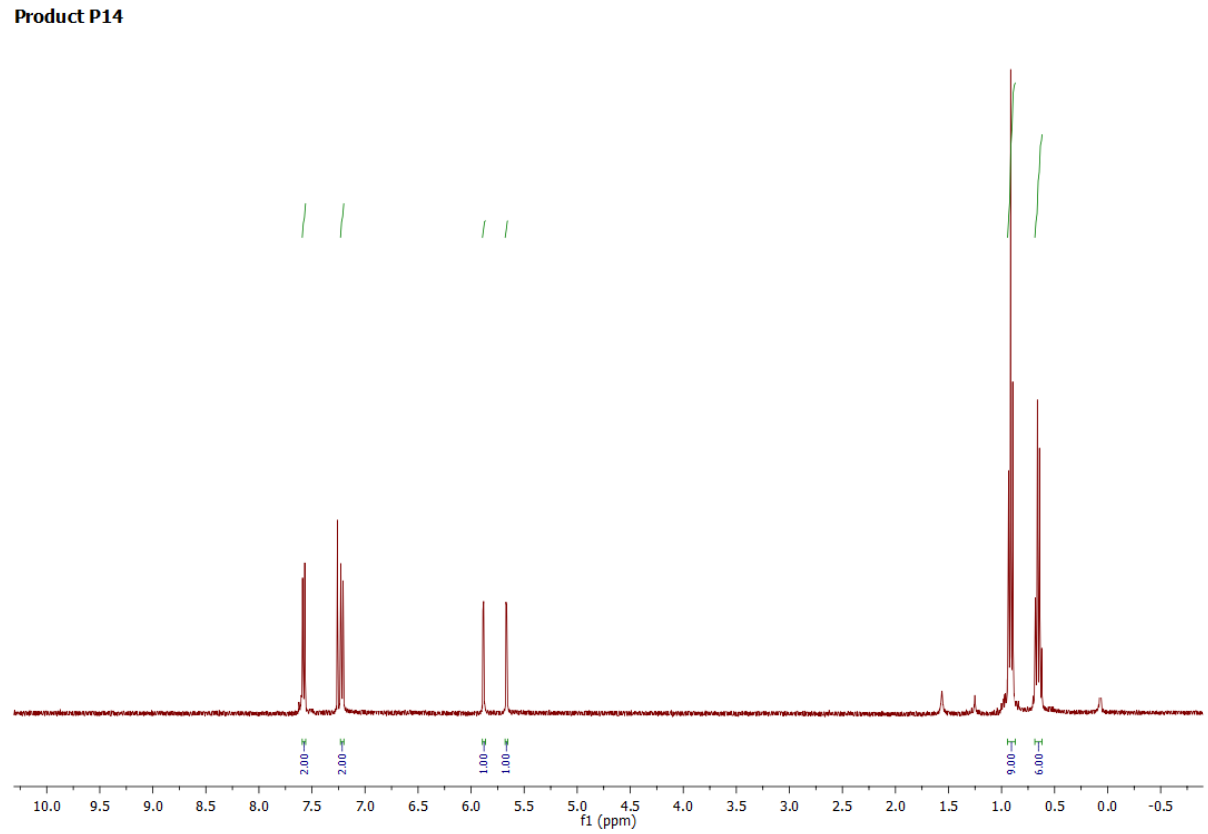


Figure S30. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P14**

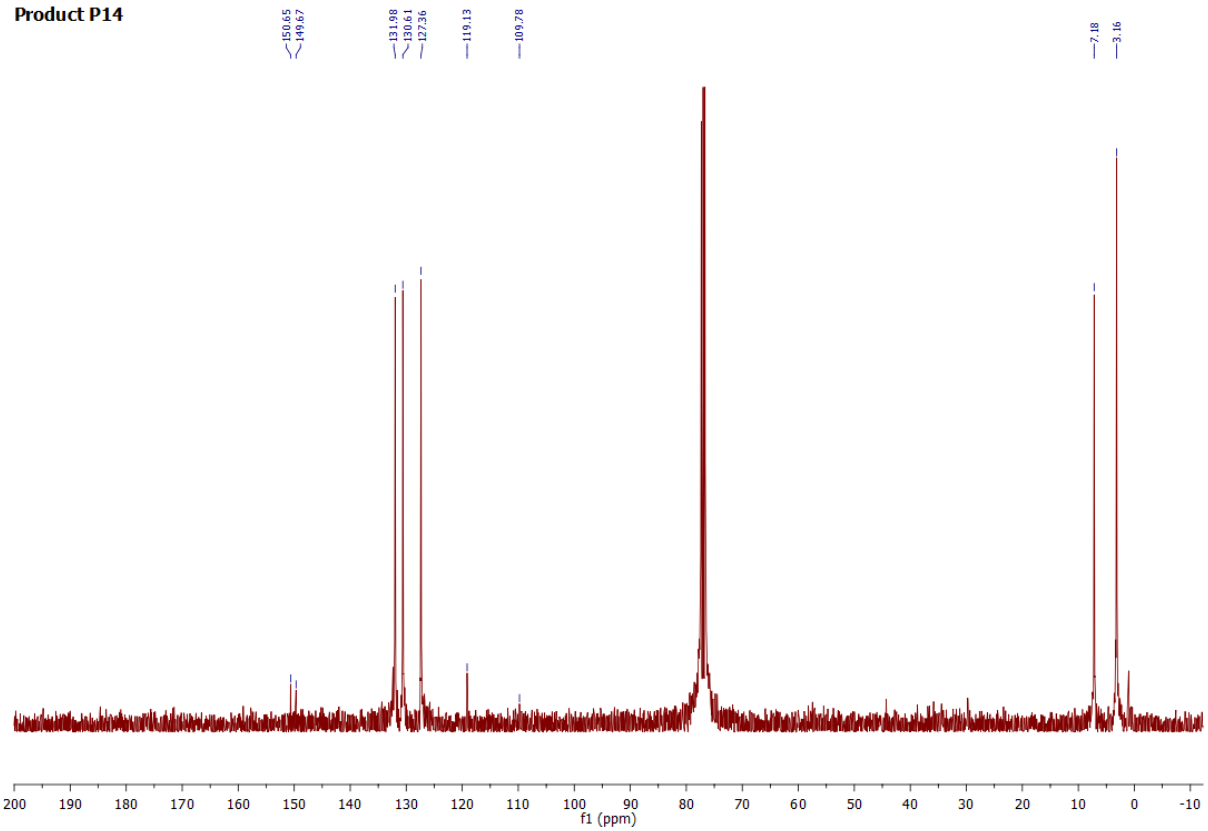


Figure S31. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P14**

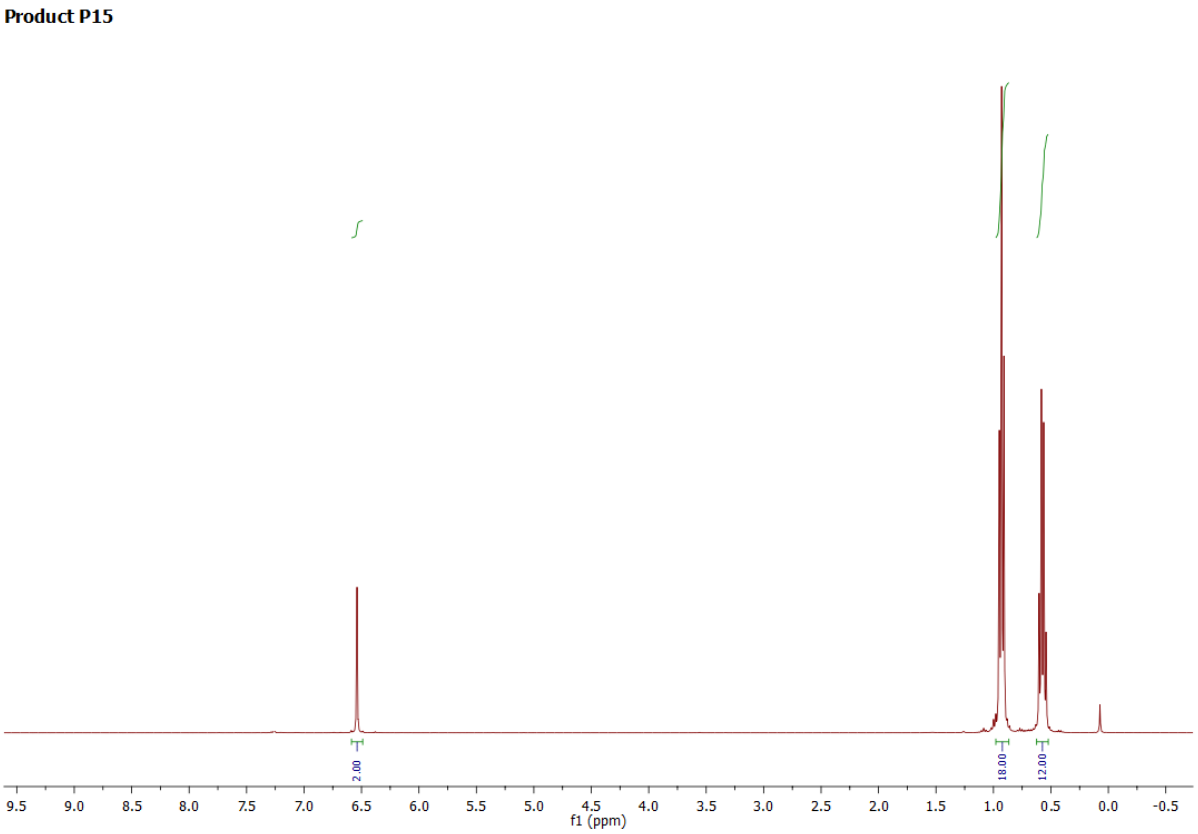


Figure S32. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P15**

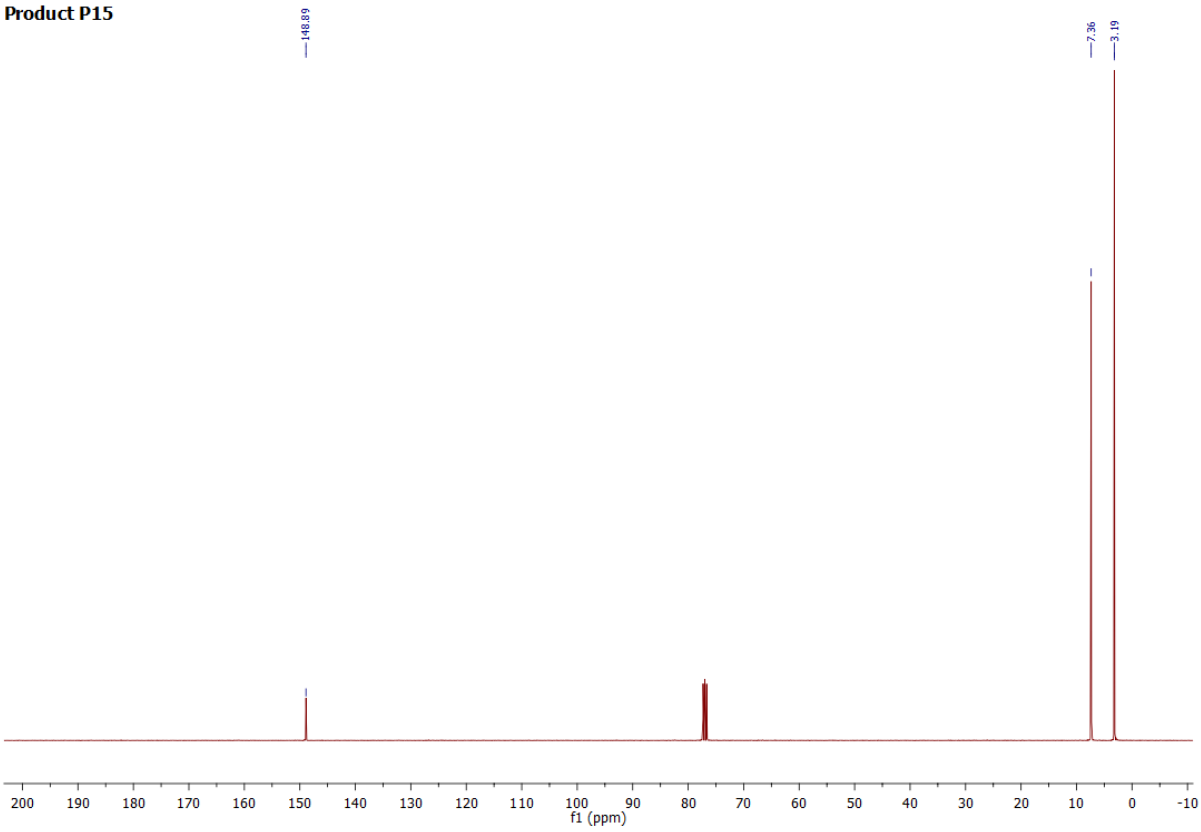


Figure S33. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P15**

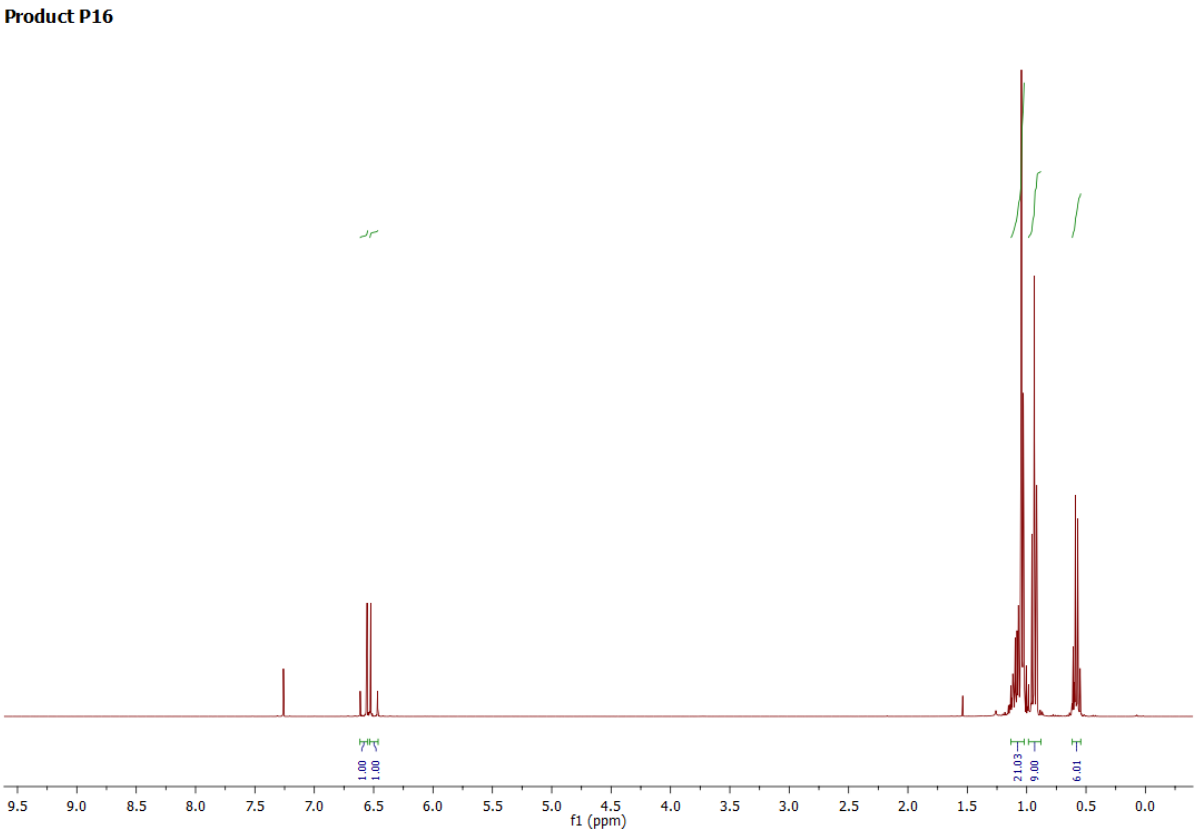


Figure S34. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P16**

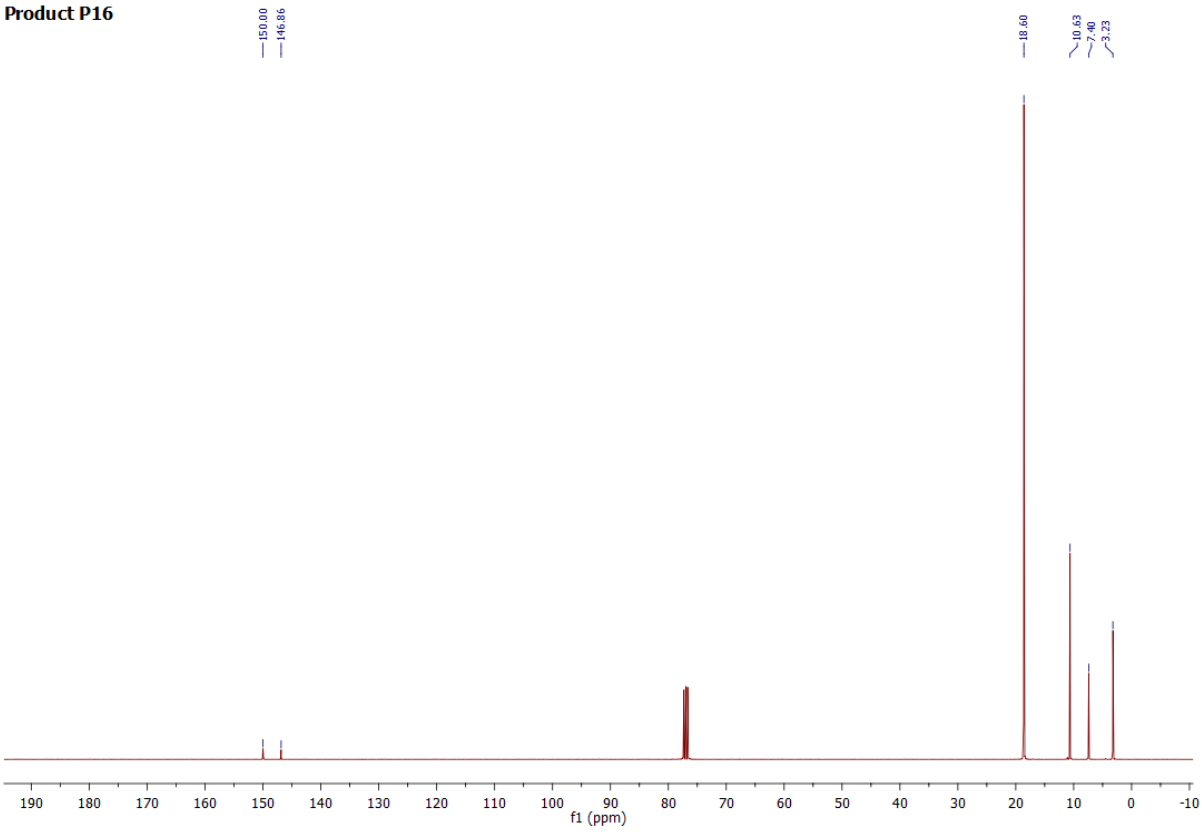


Figure S35. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P16**

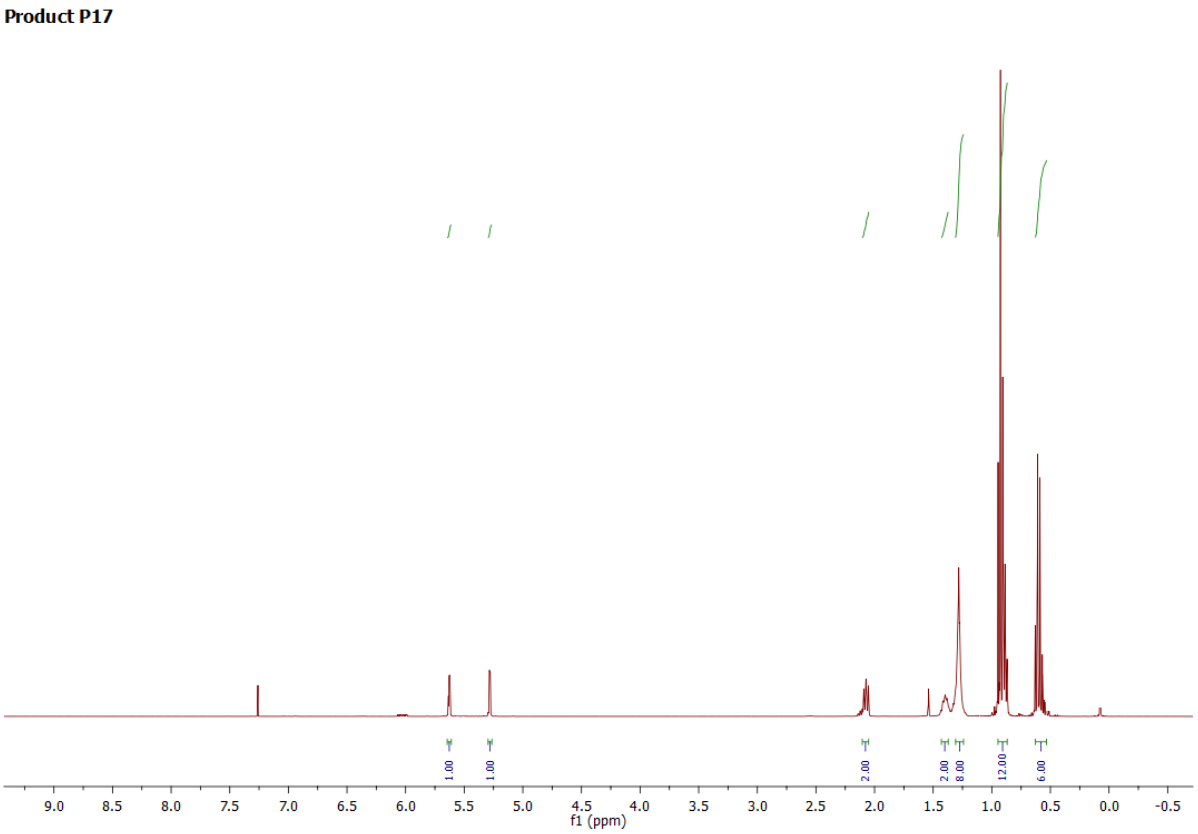


Figure S36. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P17**

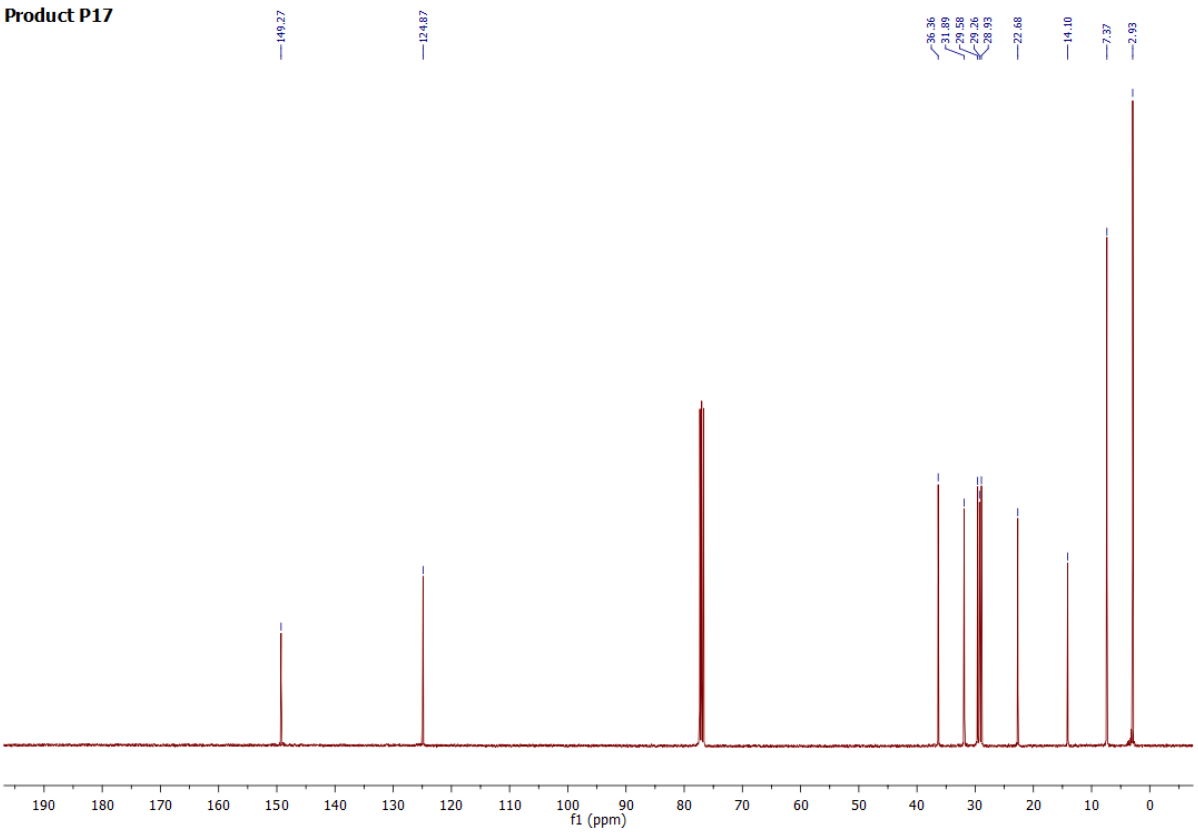


Figure S37. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P17**

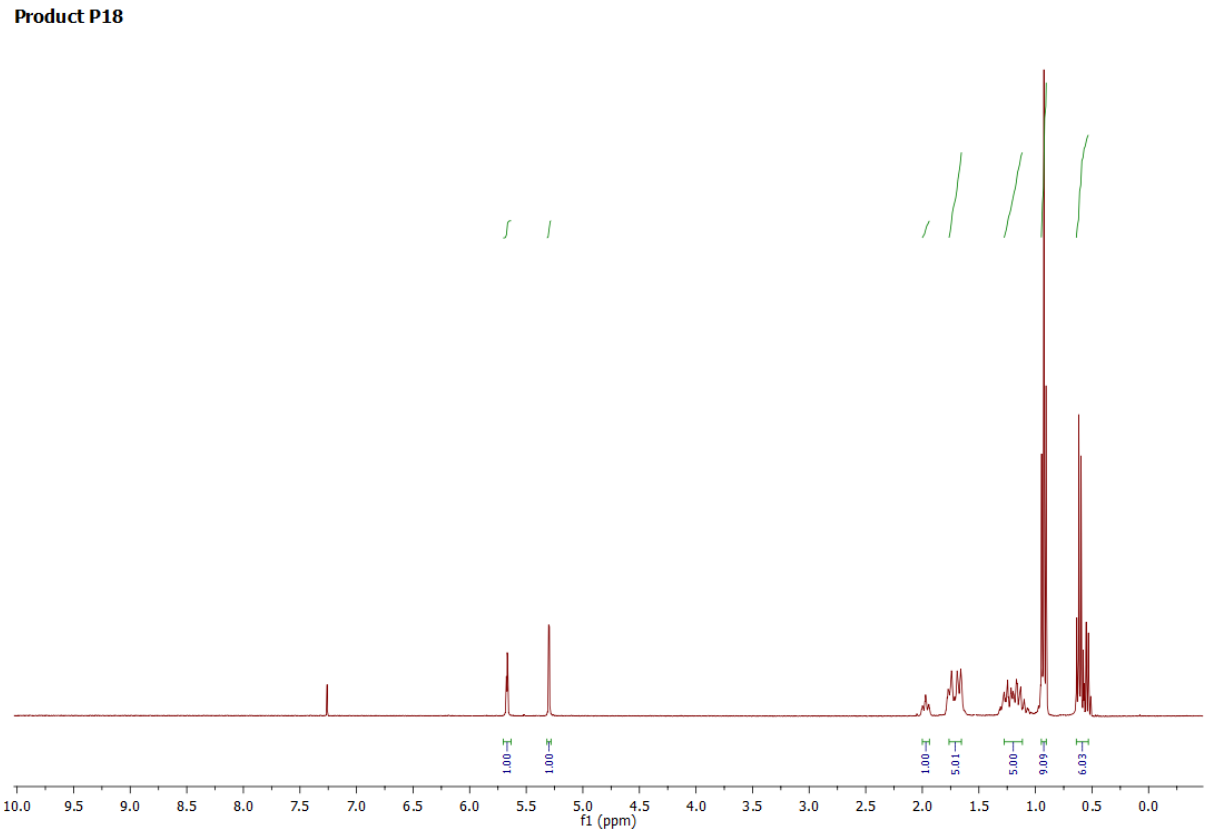


Figure S38. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P18**

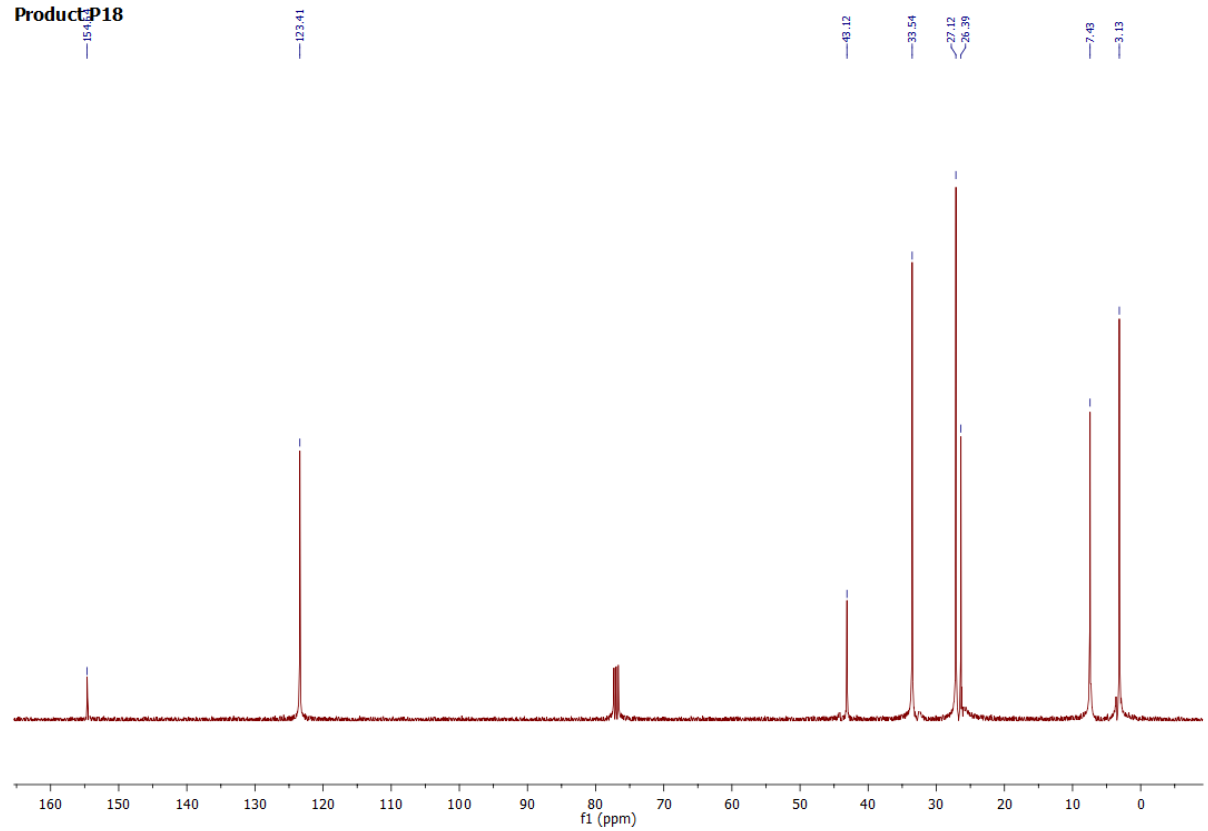


Figure S39. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P18**

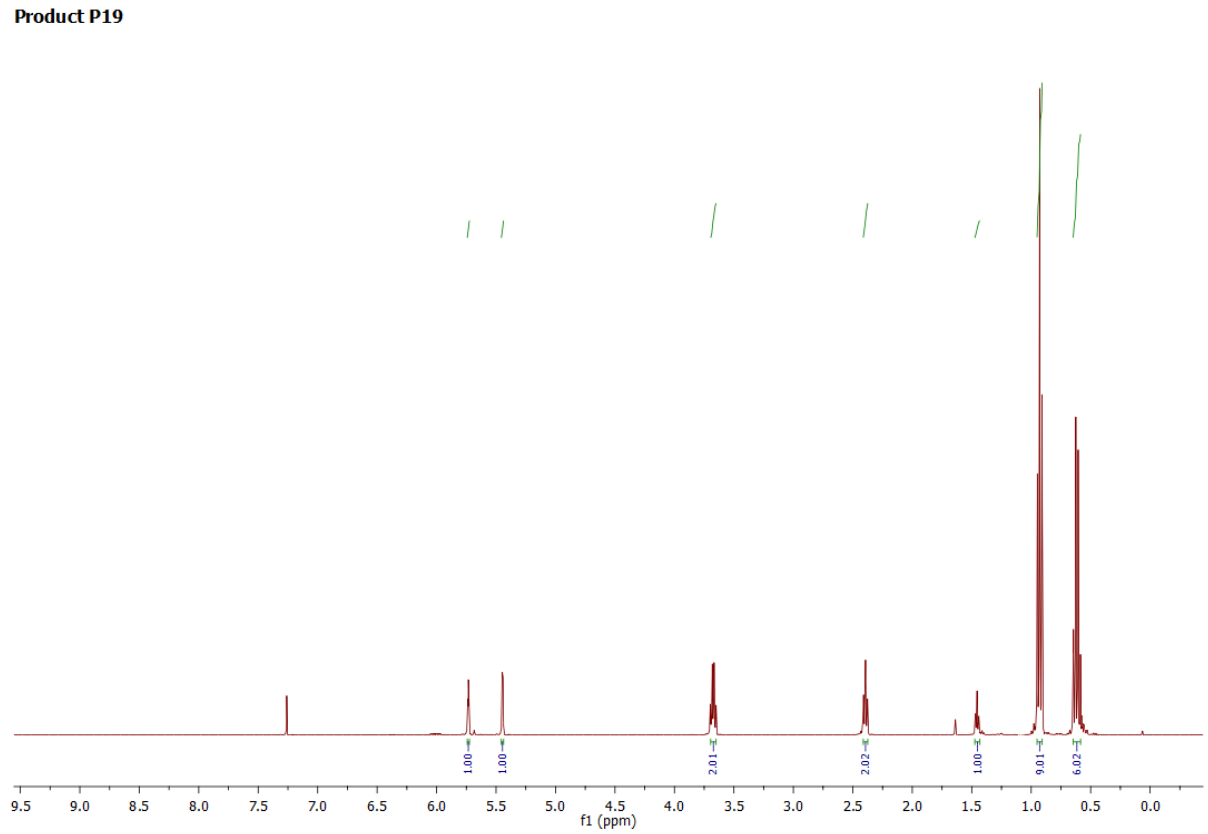


Figure S40. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P19**

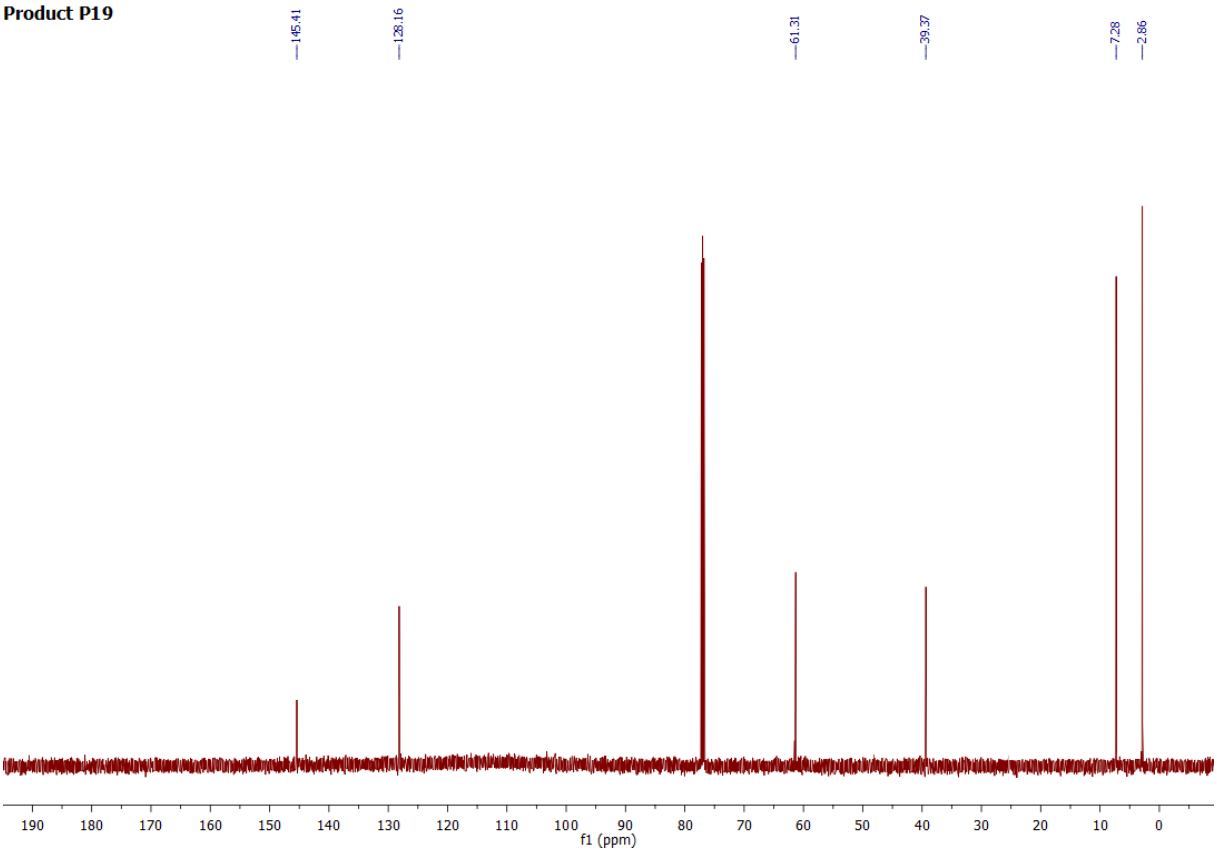


Figure S41. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P19**

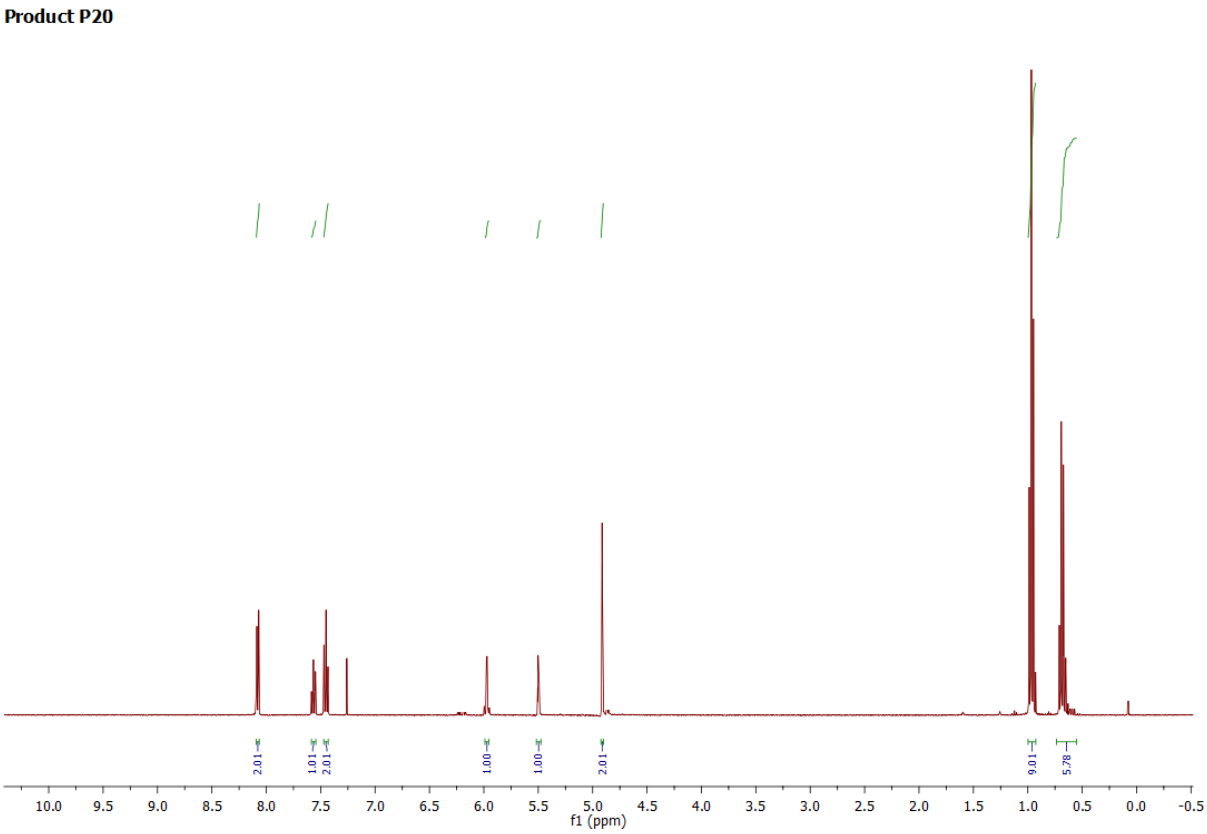


Figure S42. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P20**

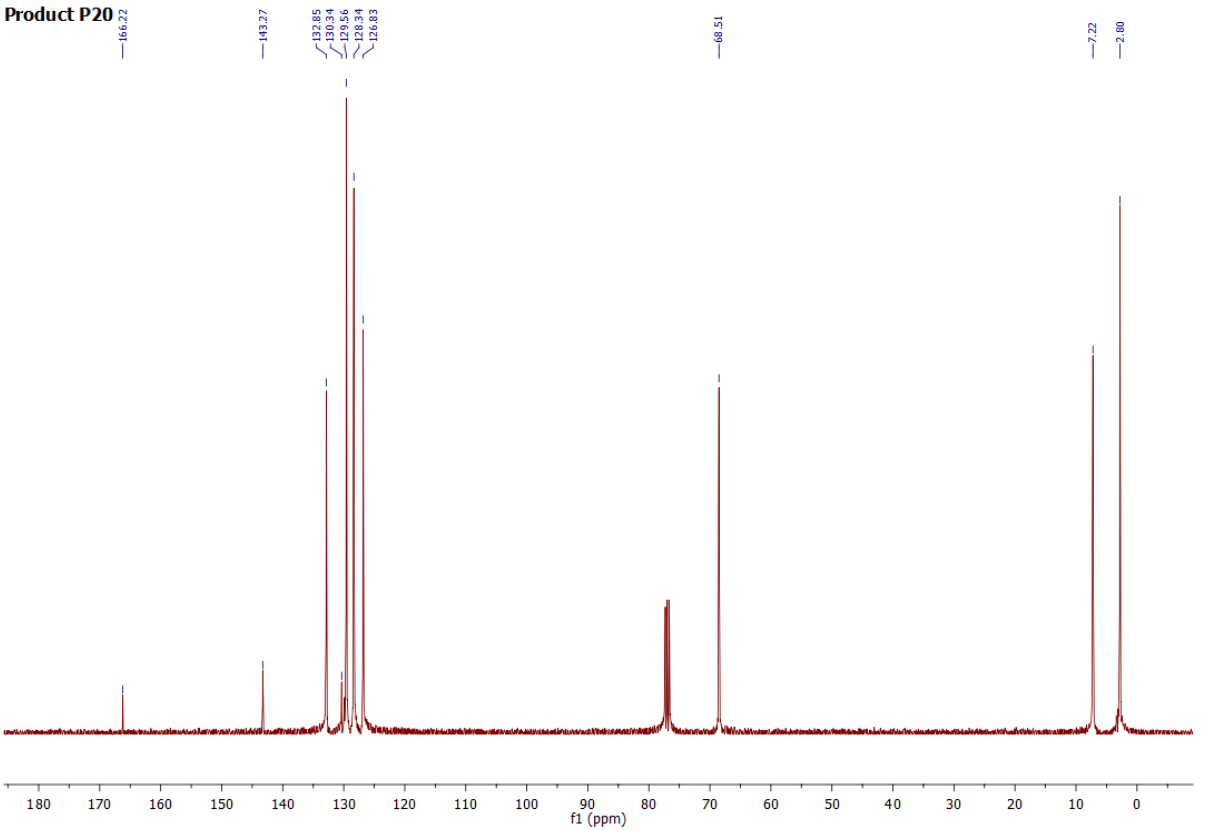


Figure S43. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P20**

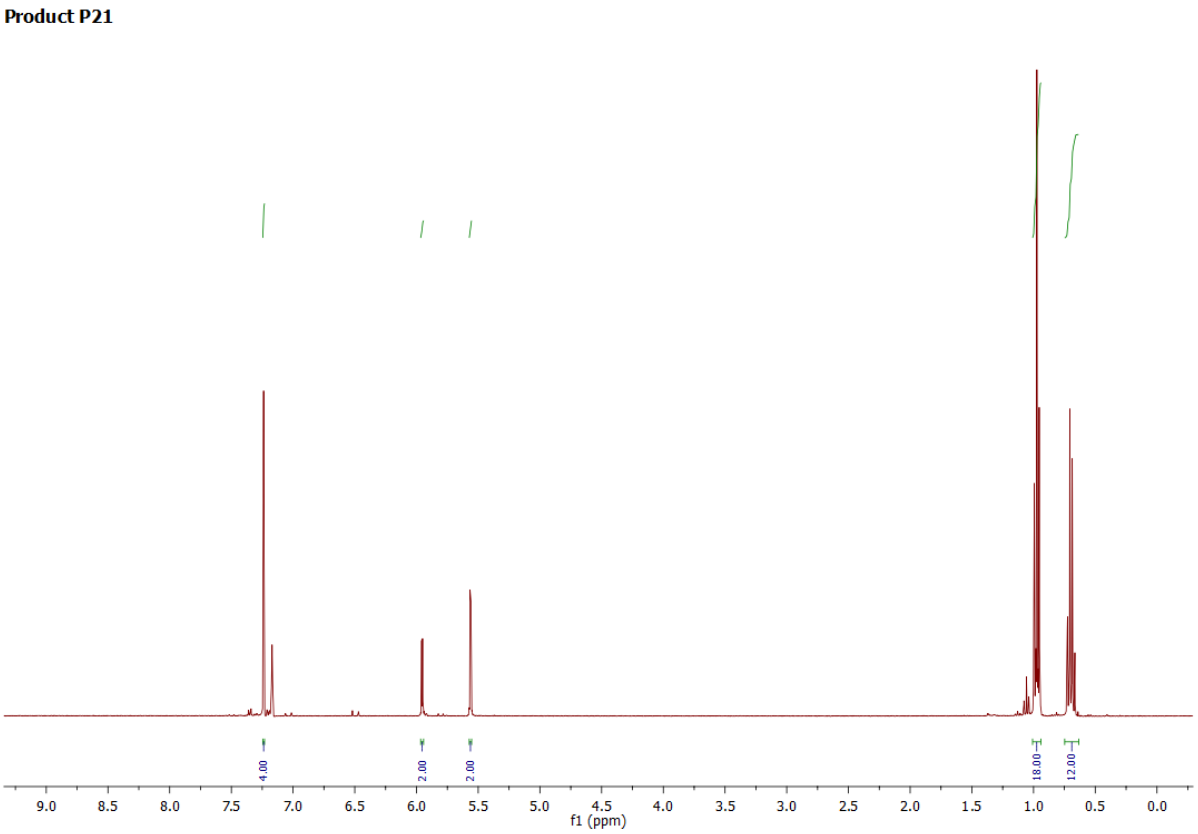


Figure S44. ^{1}H NMR (400 MHz, C_6D_6) of product **P21**

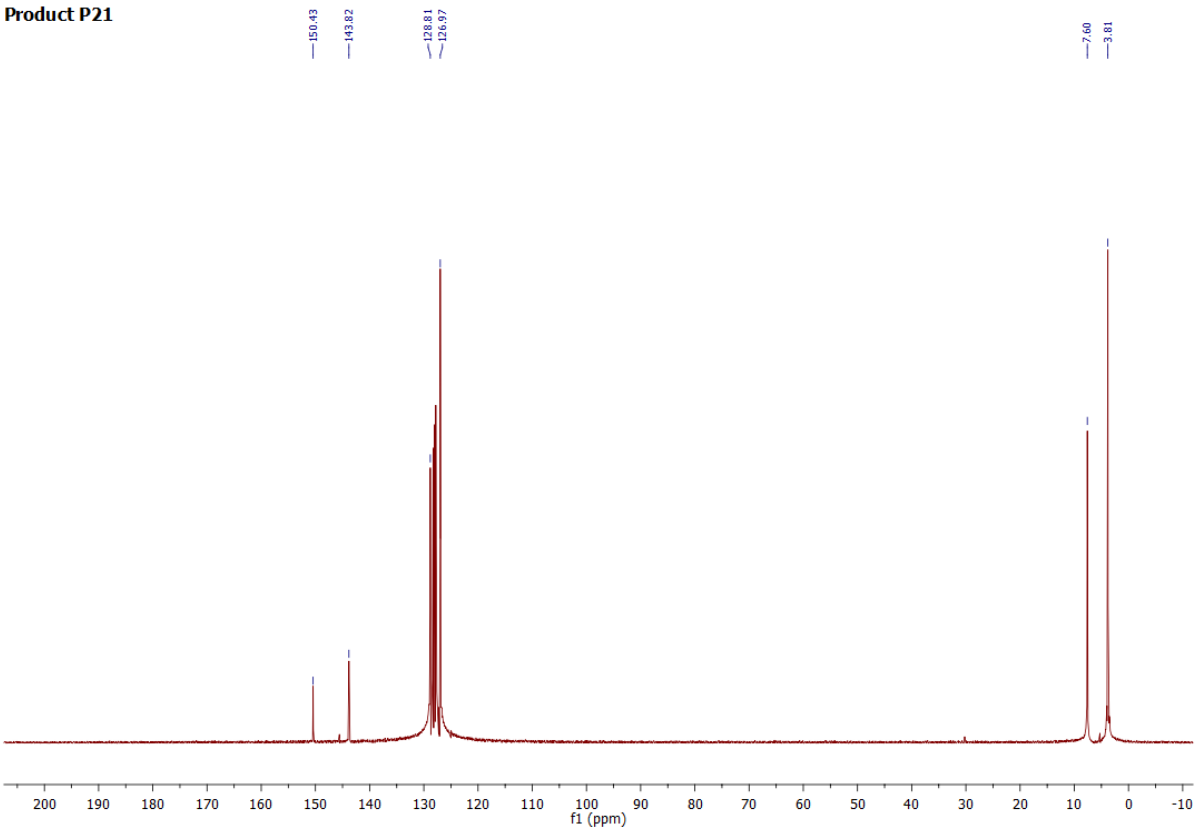


Figure S45. ^{13}C NMR (101 MHz, C_6D_6) of product **P21**

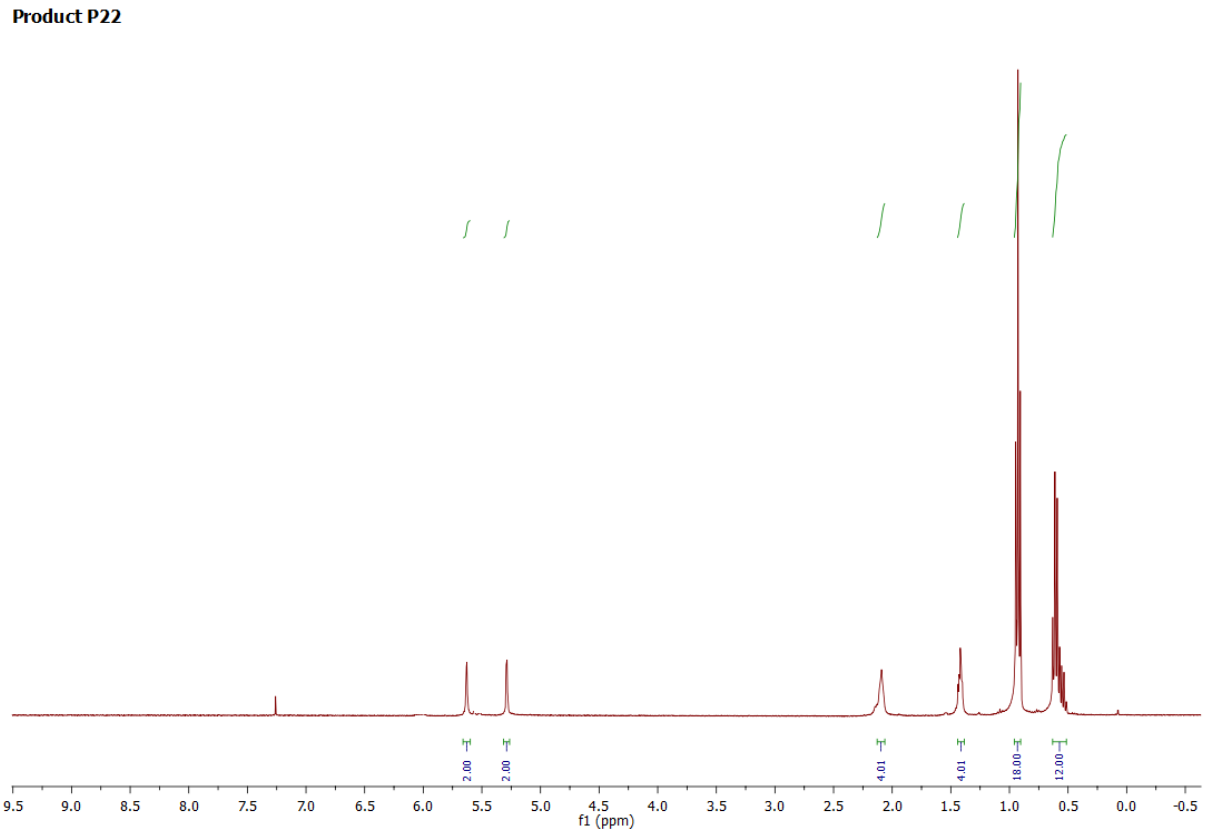


Figure S46. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P22**

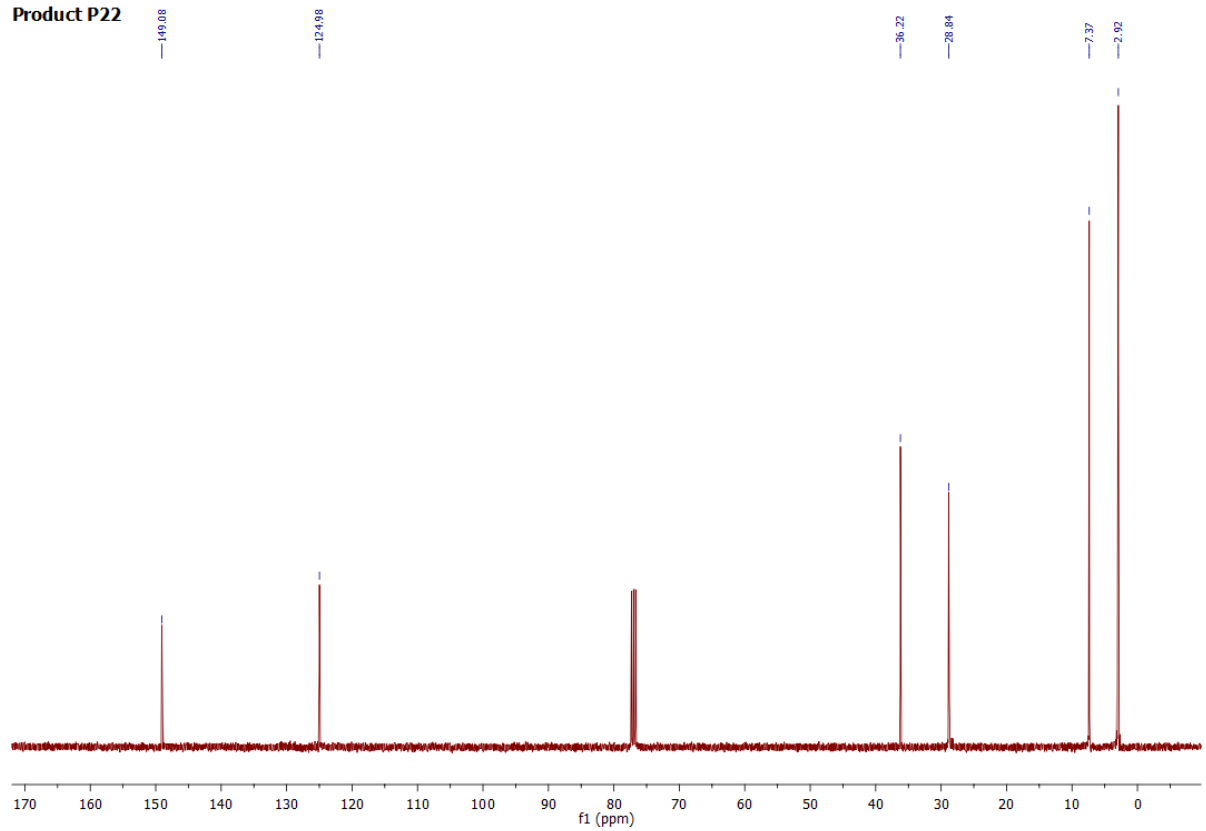


Figure S47. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P22**

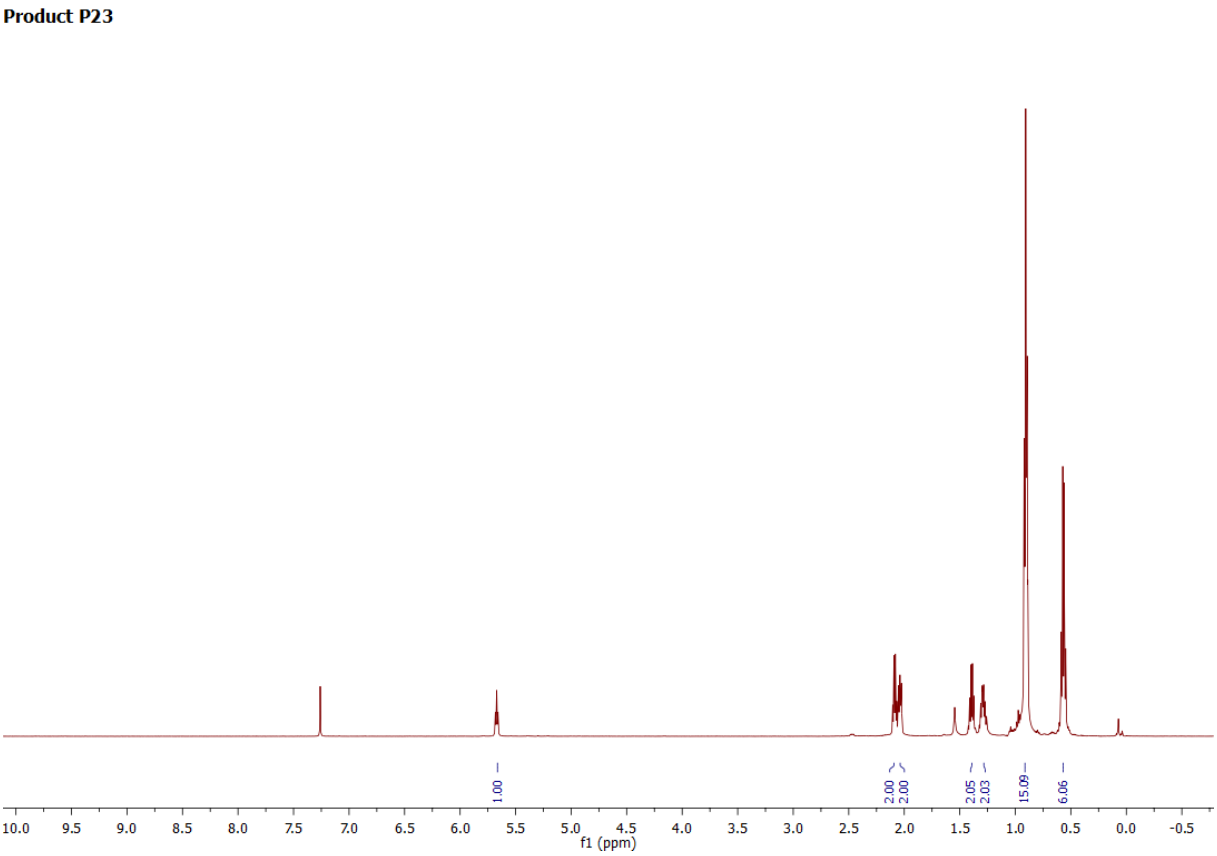


Figure S48. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P23**

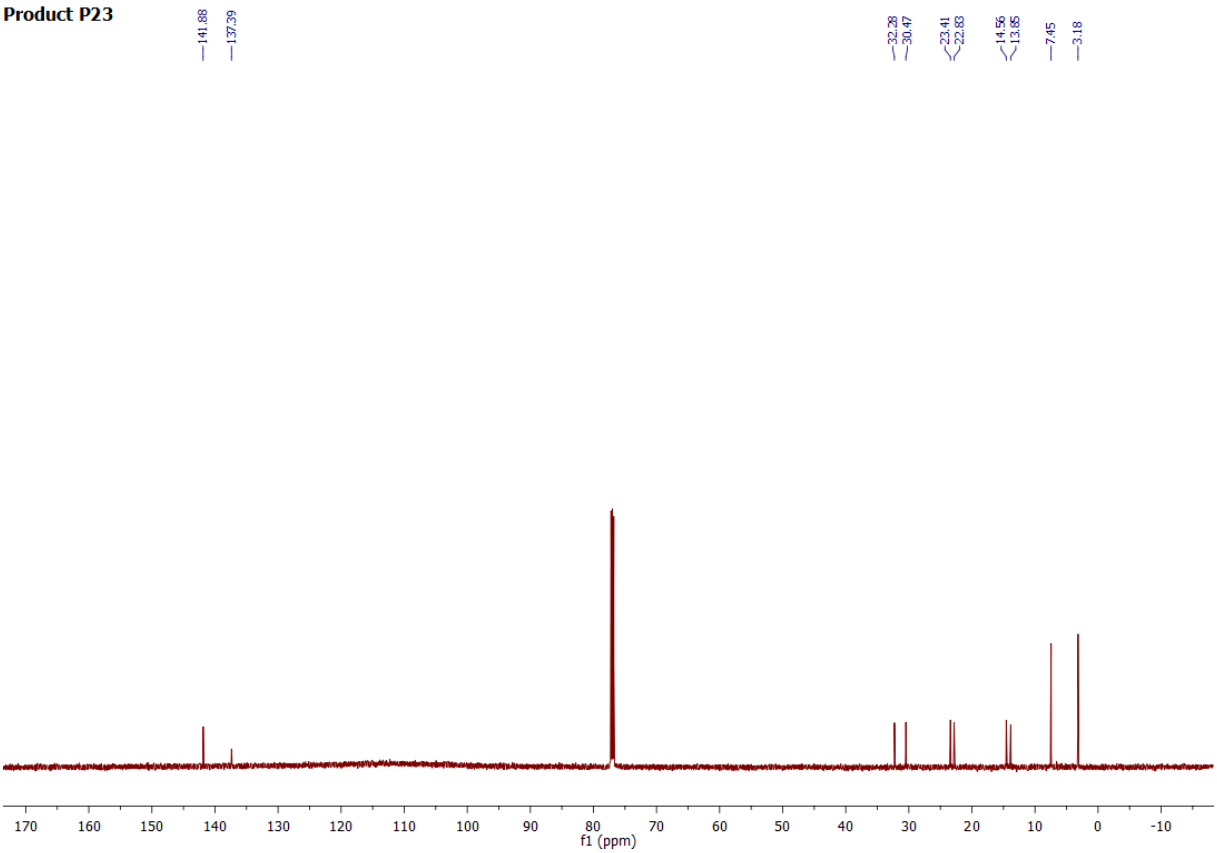


Figure S49. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P23**

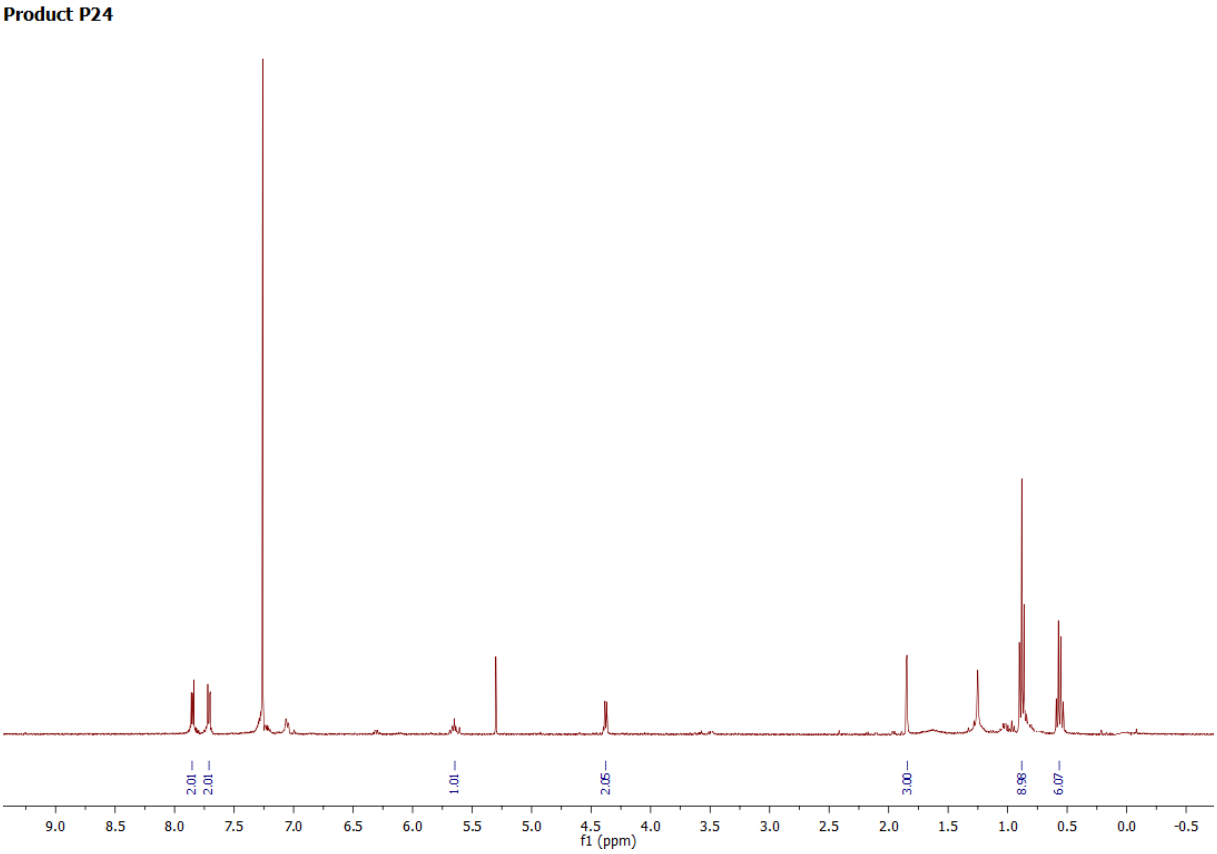


Figure S50. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P24**

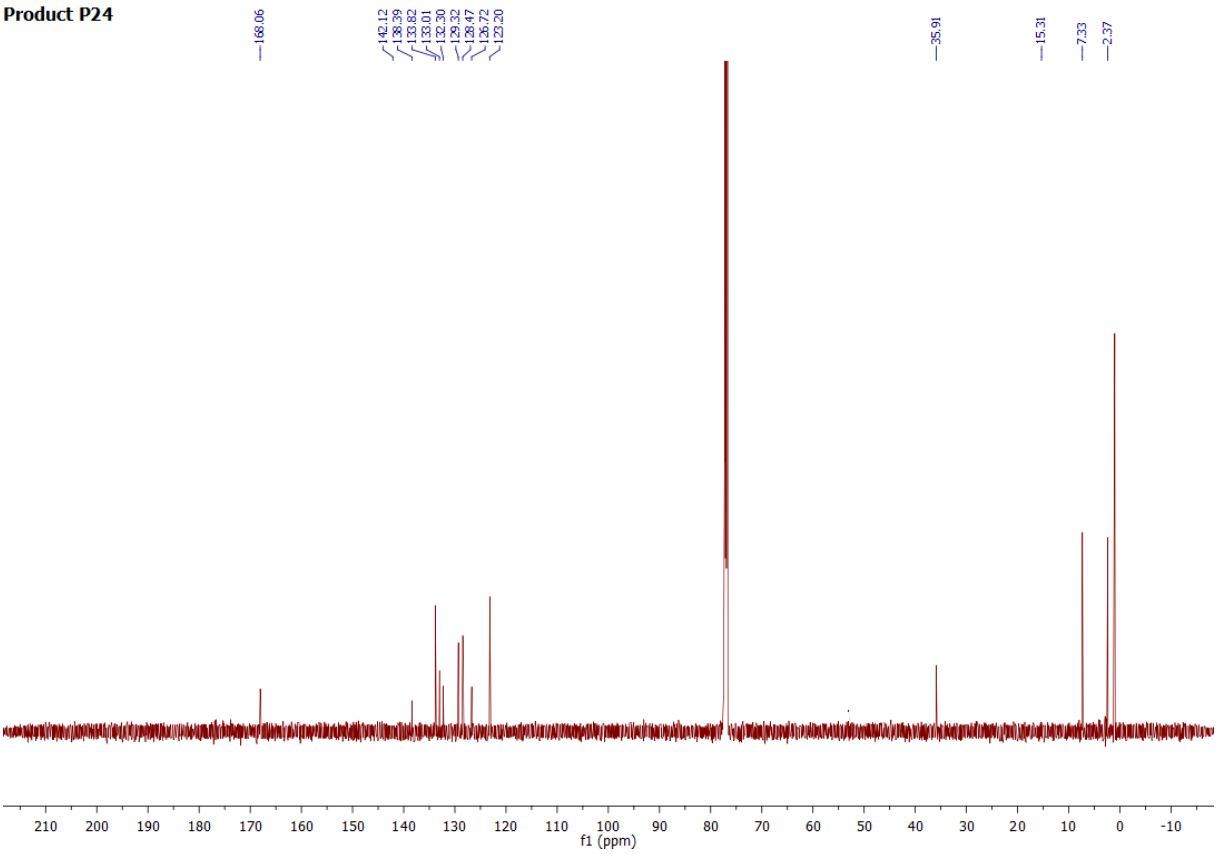


Figure S51. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P24**

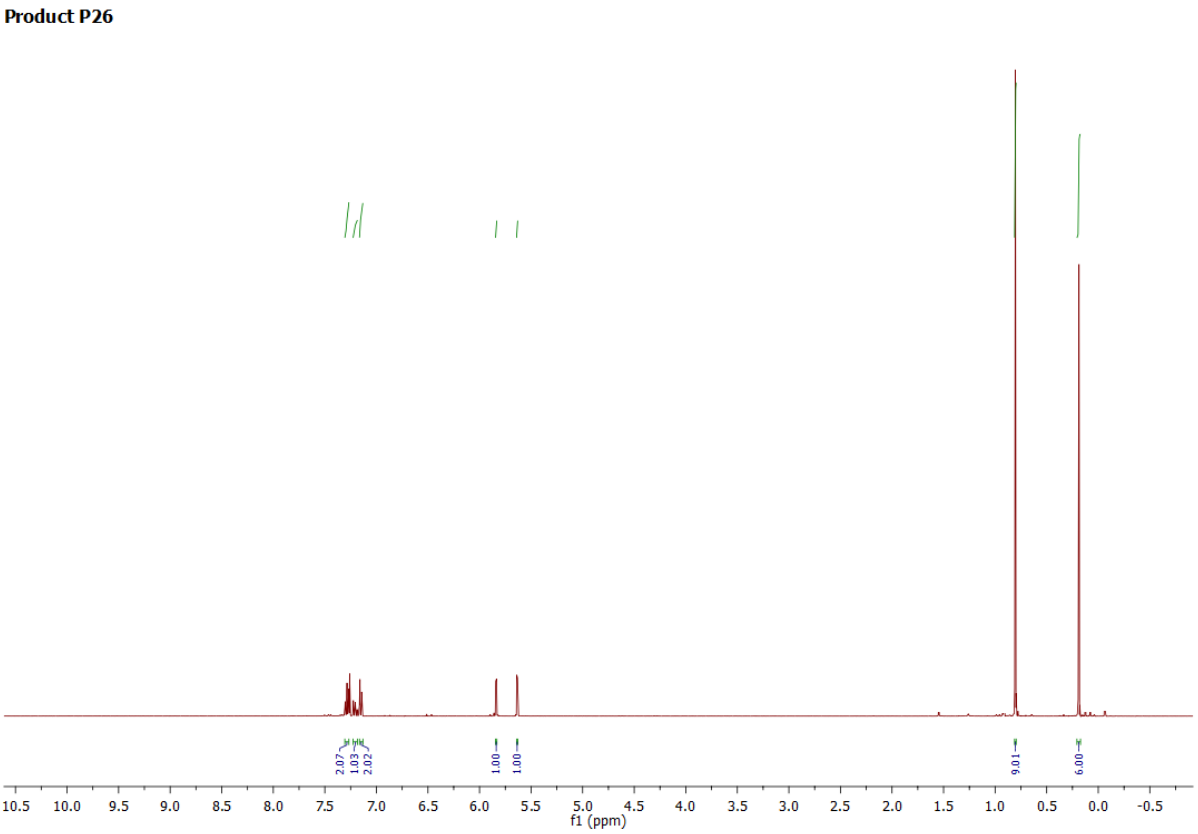


Figure S52. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P26**

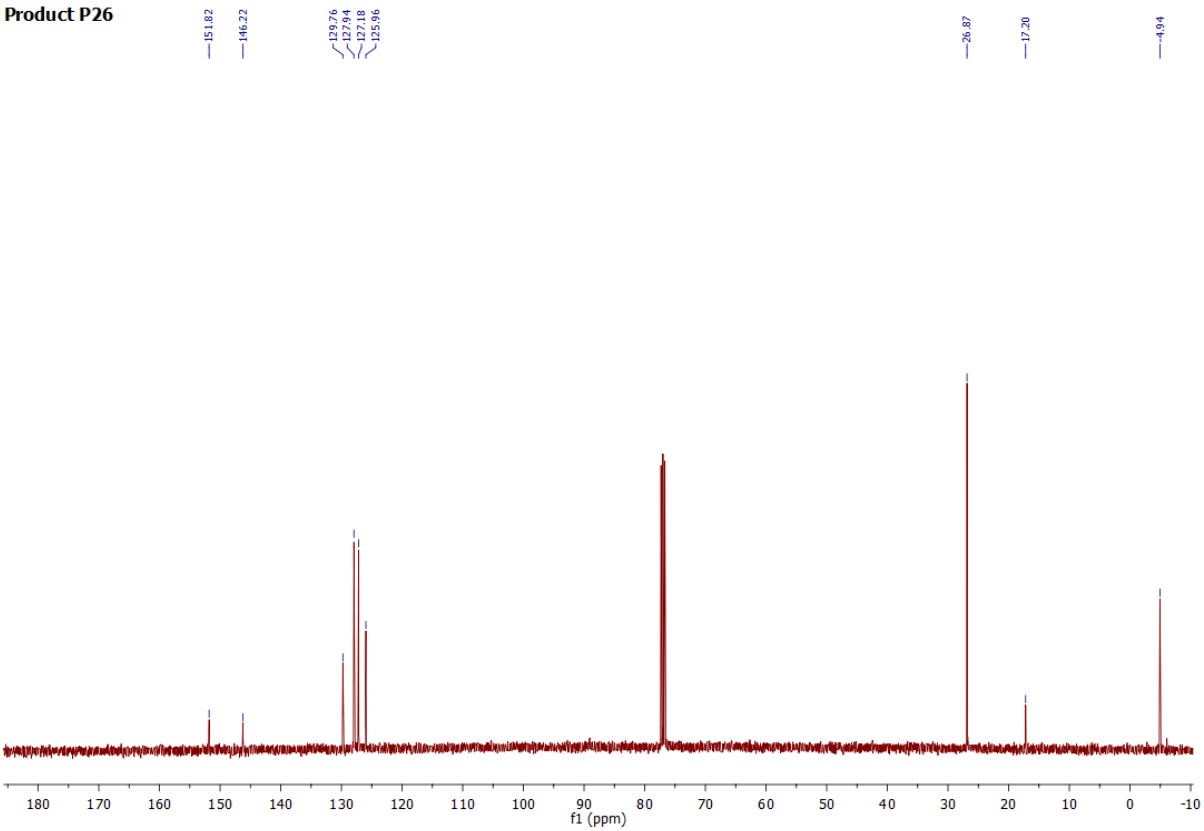


Figure S53. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P26**

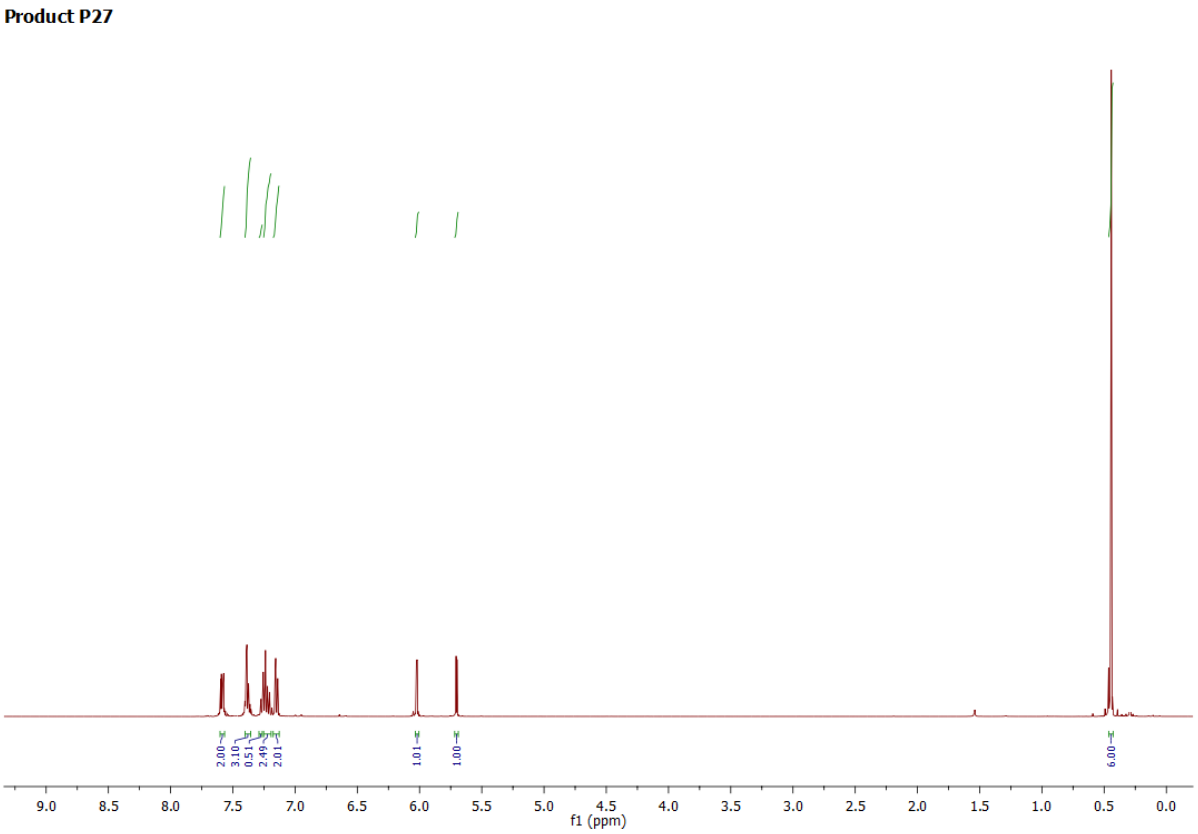


Figure S54. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P27**

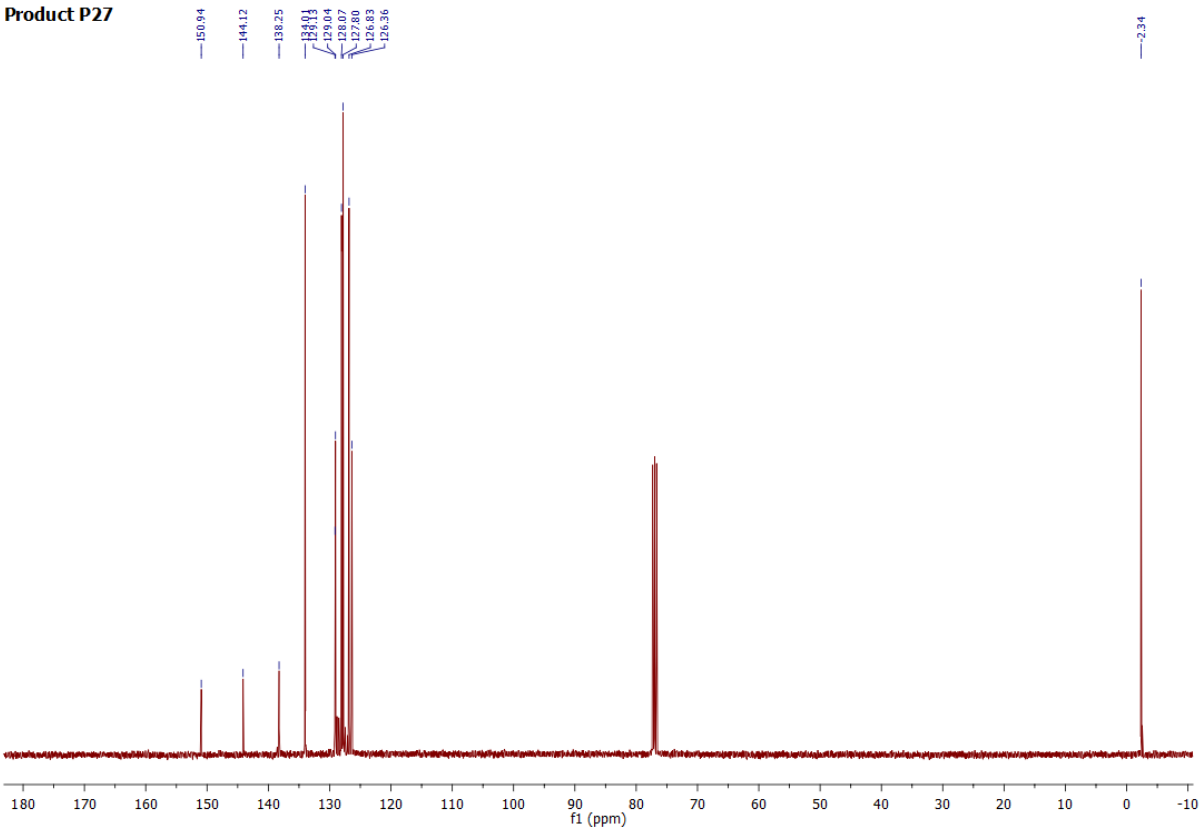


Figure S55. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P27**

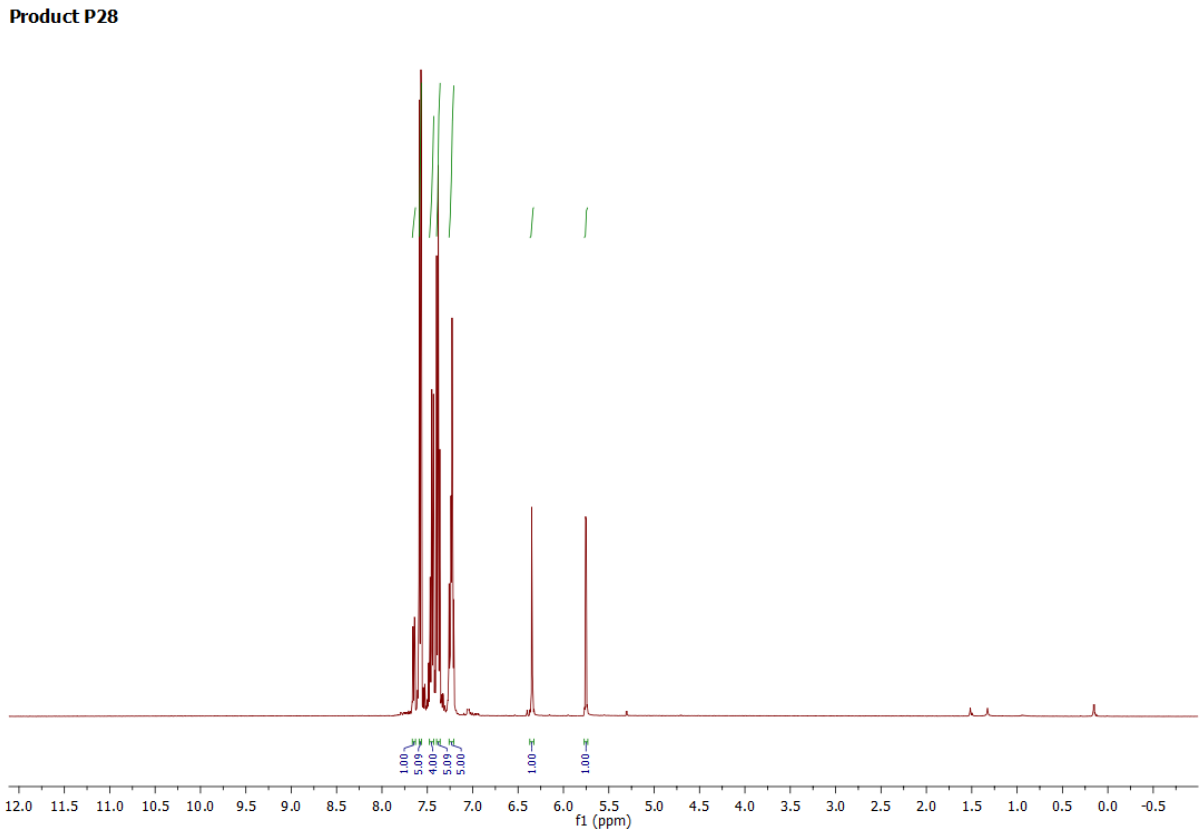


Figure S56. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P28**

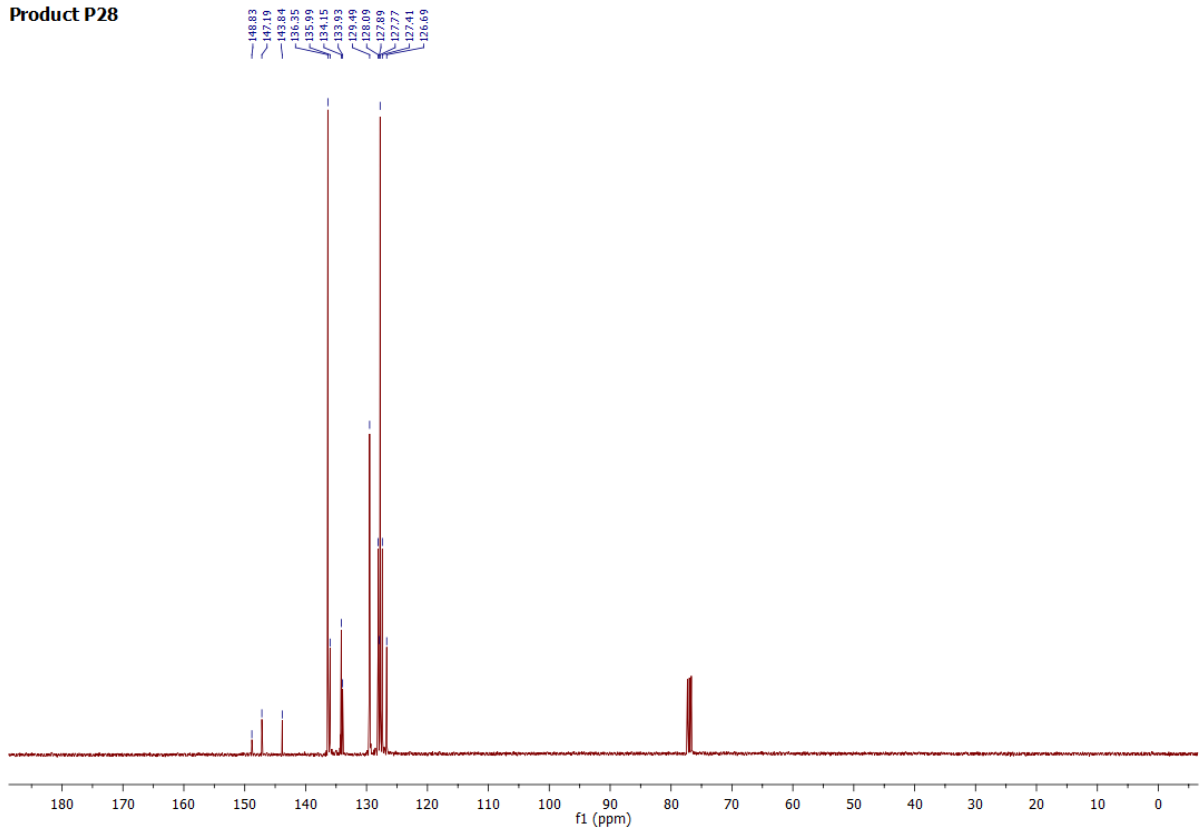


Figure S57. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P28**

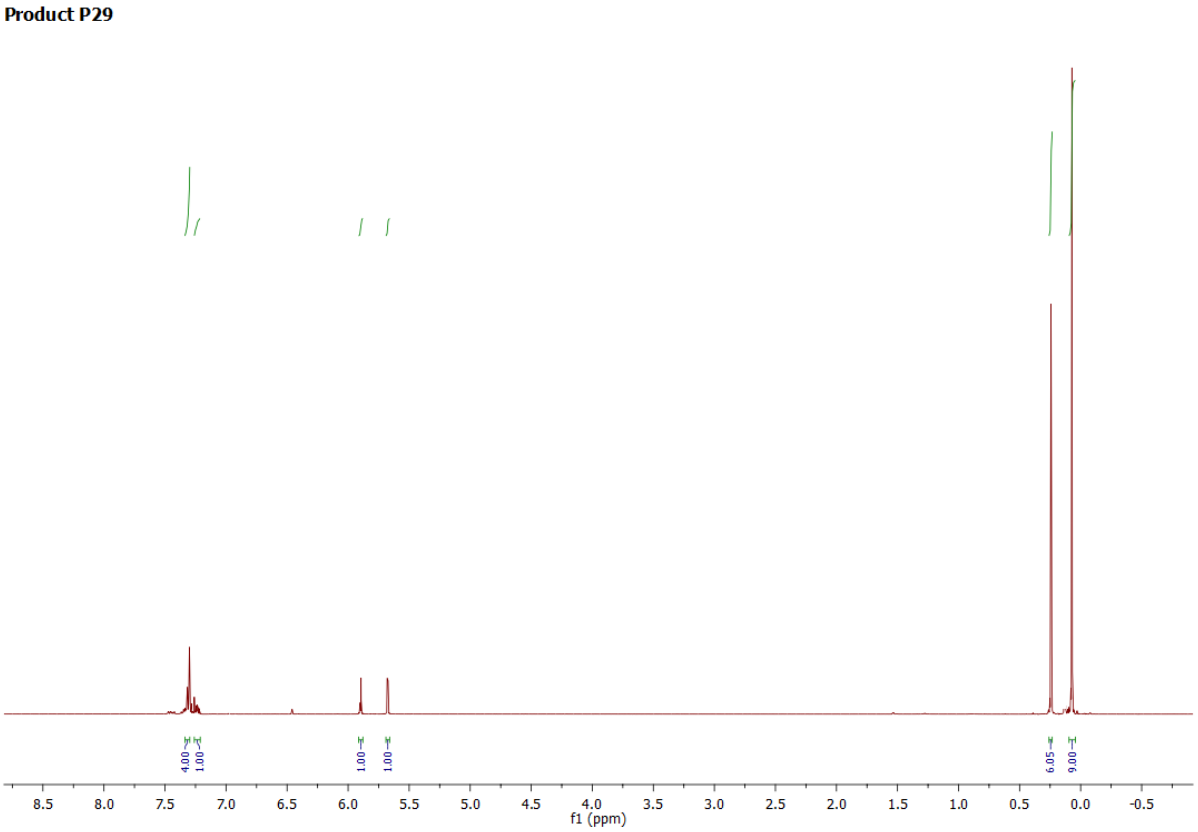


Figure S58. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P29**

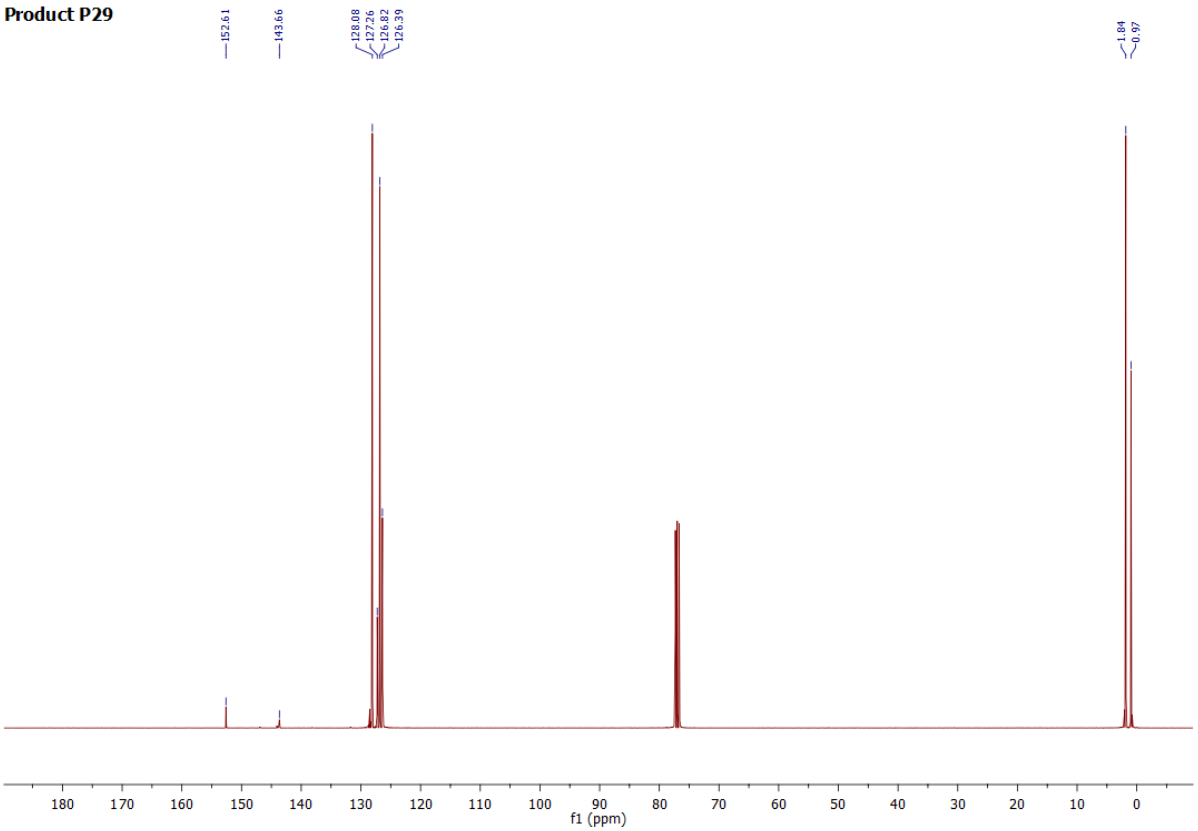


Figure S59. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P29**

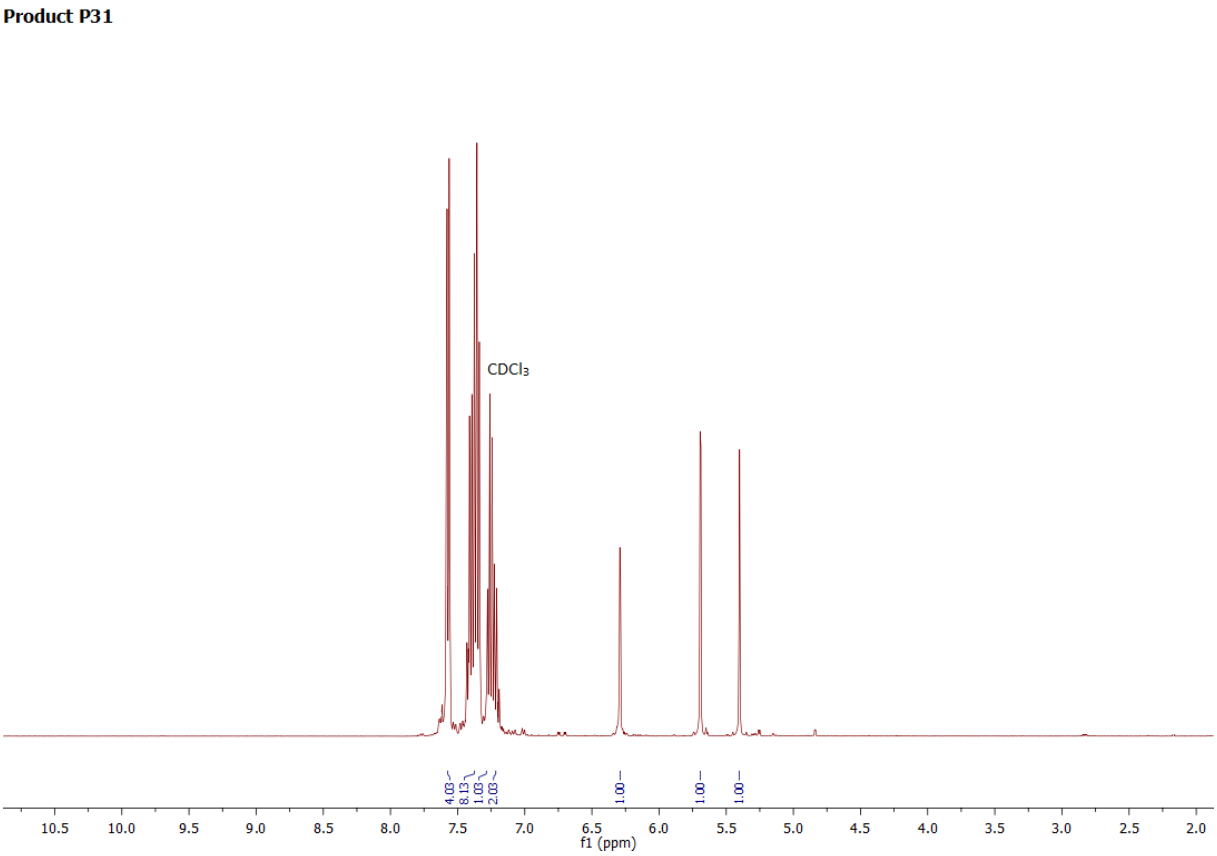


Figure S60. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P31**

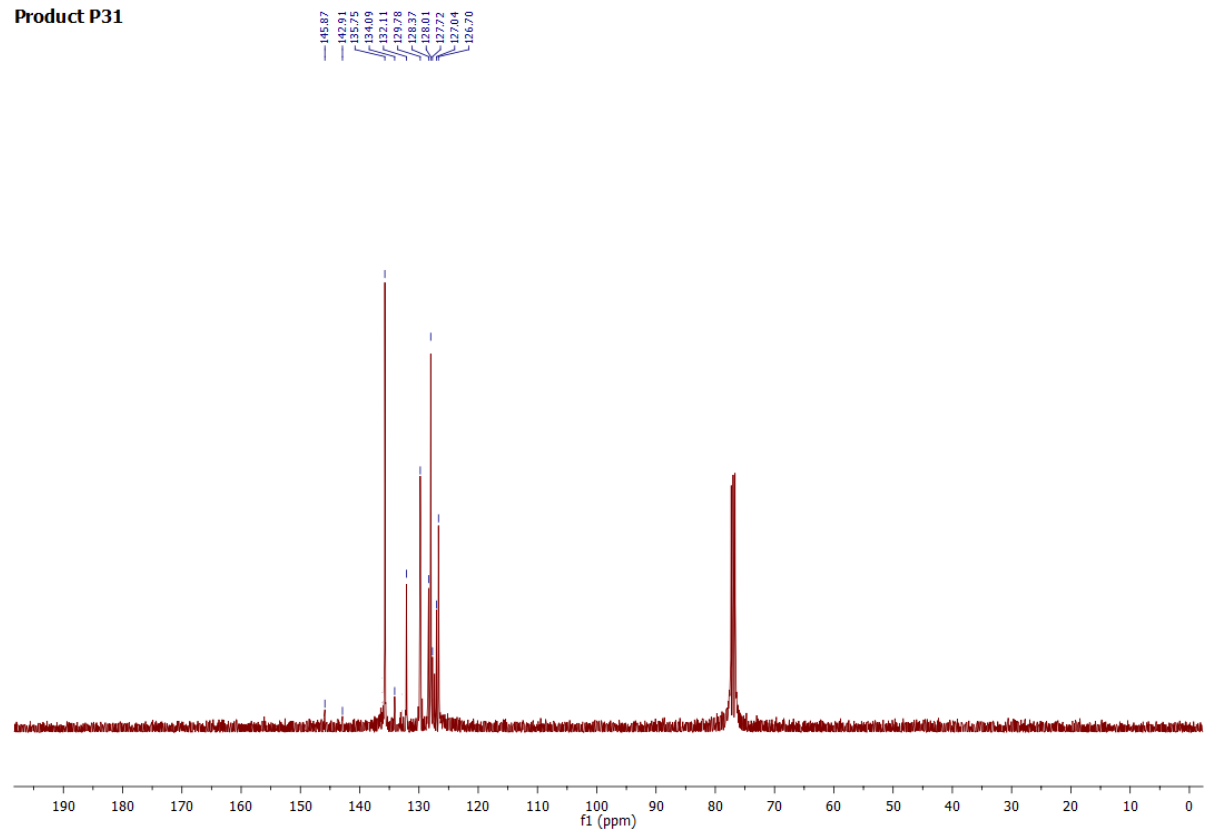


Figure S61. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P31**

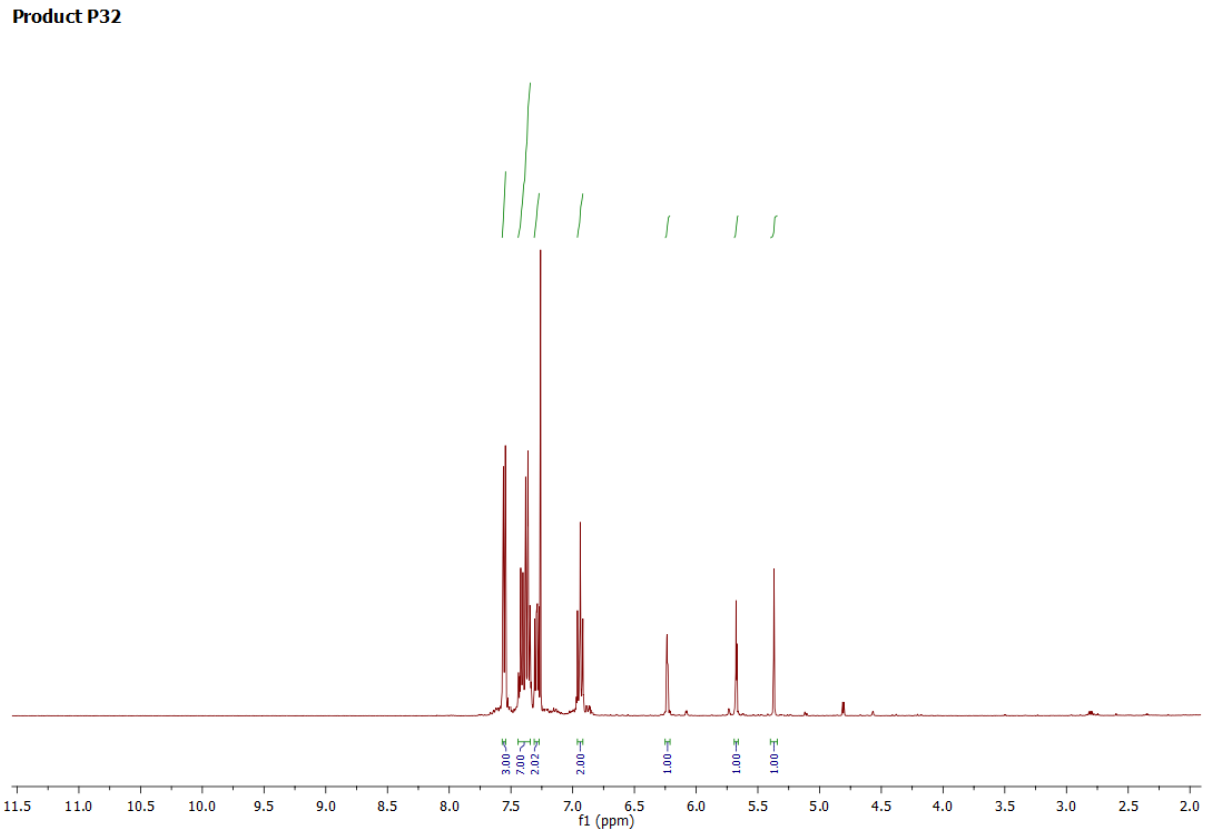


Figure S62. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P32**

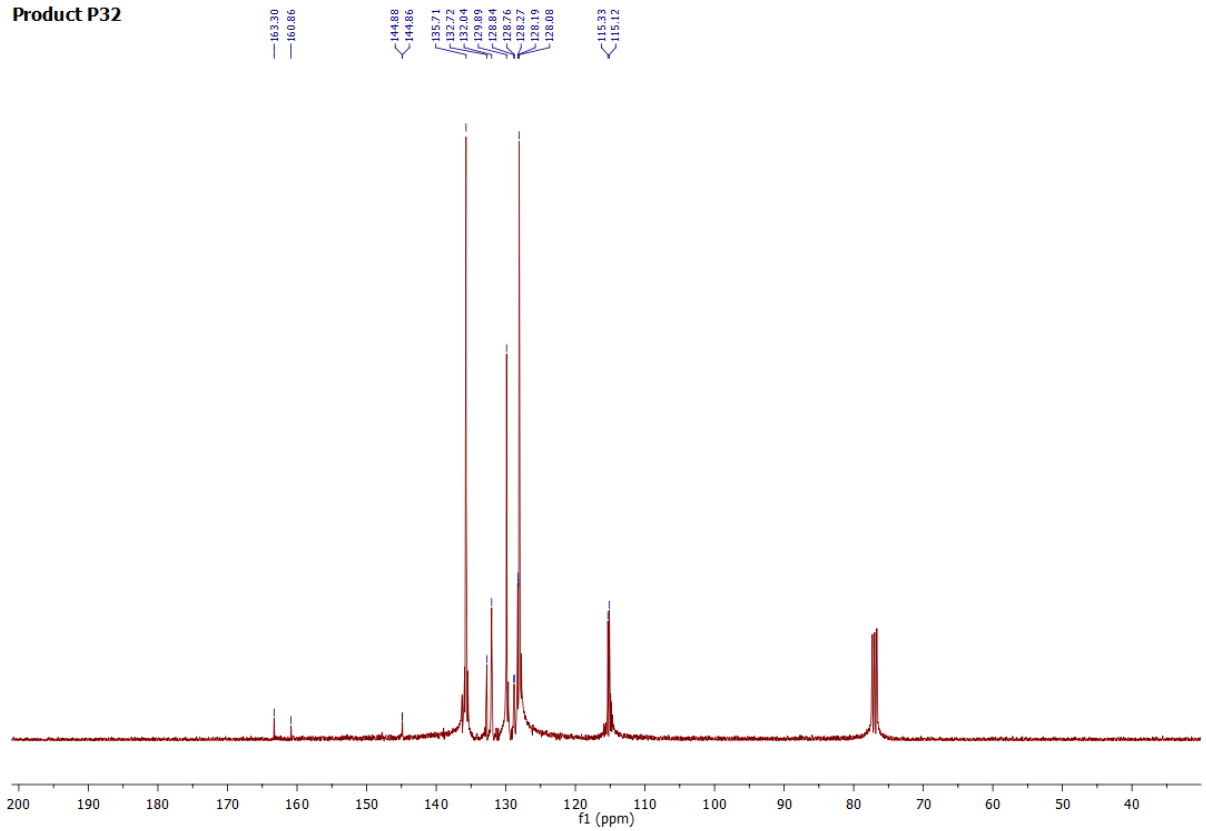


Figure S63. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P32**

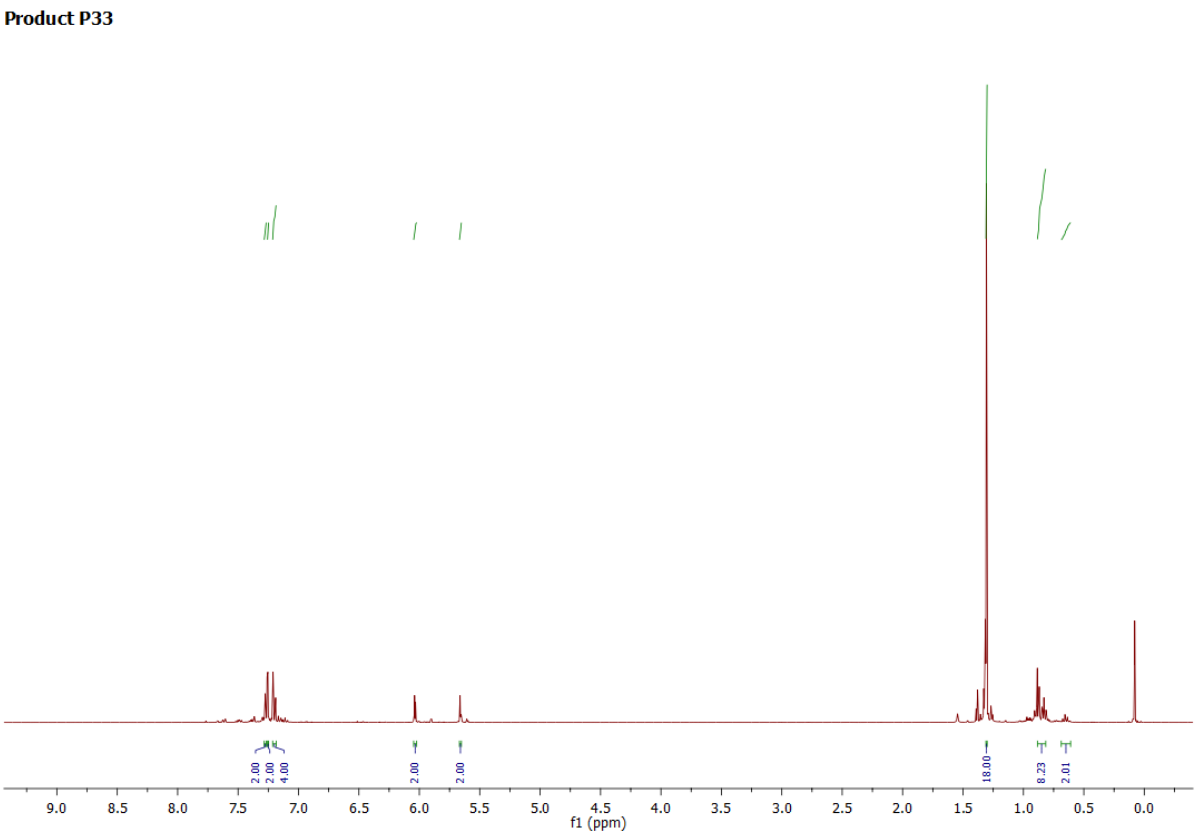


Figure S64. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P33**

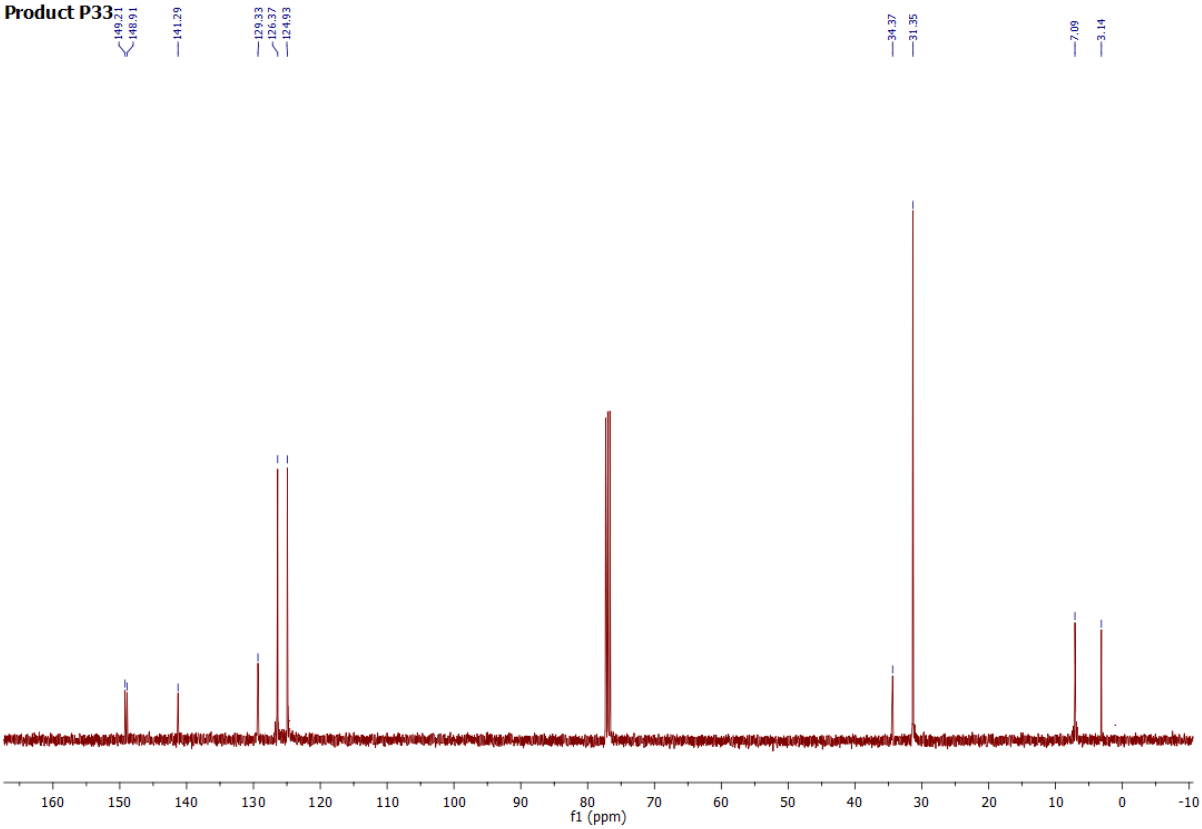


Figure S65. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P33**

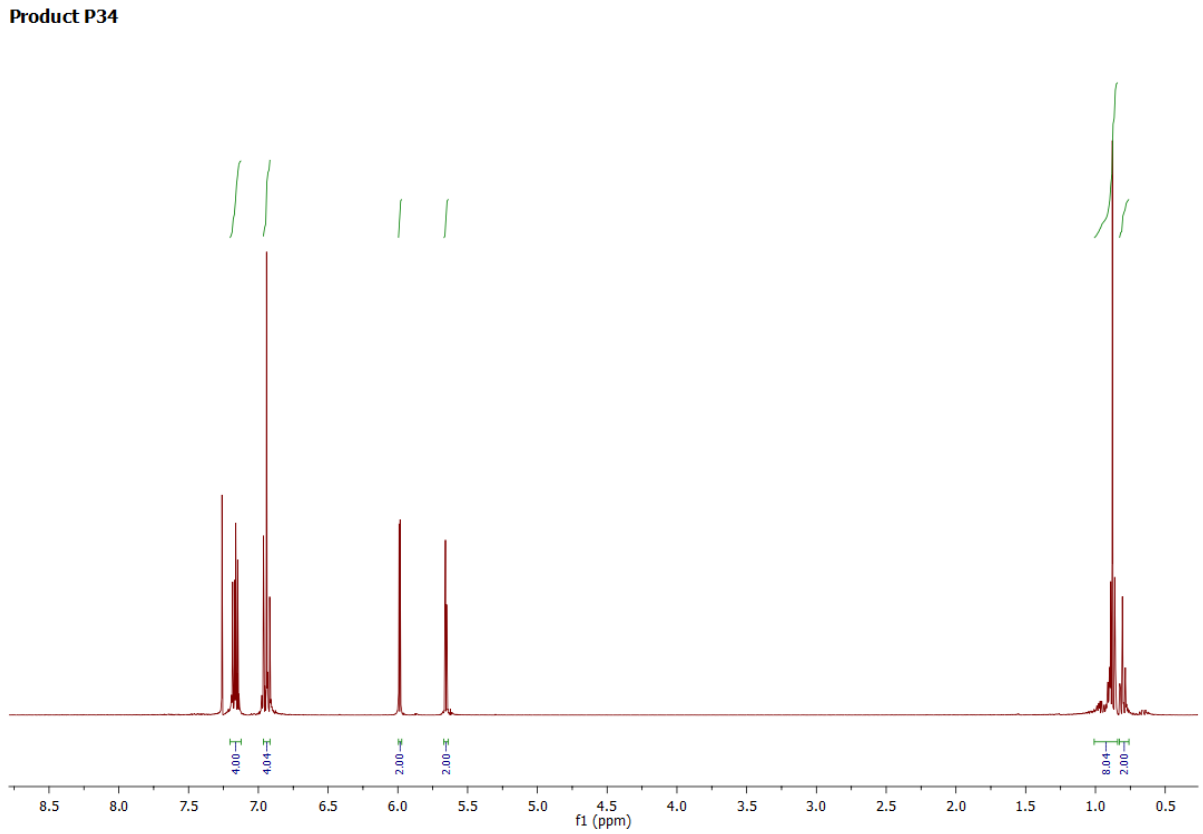


Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) of product **P34**

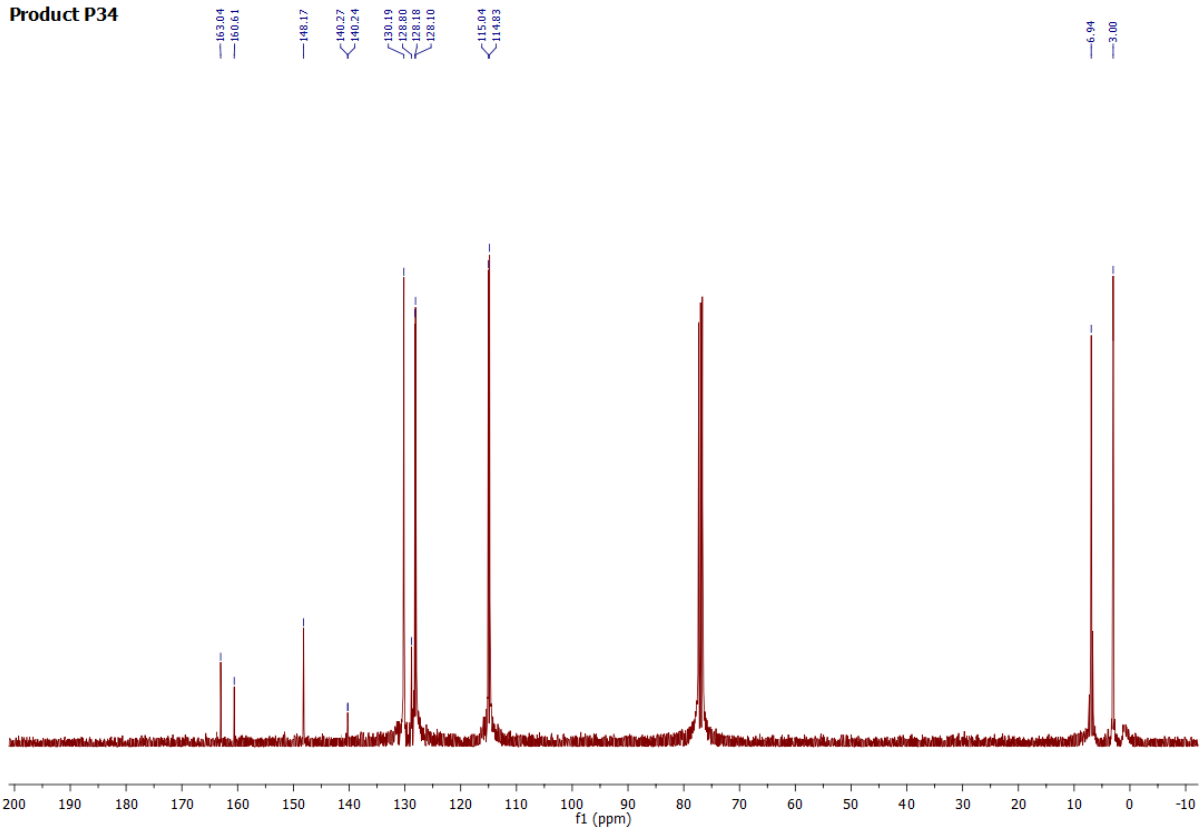


Figure S67. ^{13}C NMR (101 MHz, $CDCl_3$) of product **P34**

5. References

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