Supporting information (New Journal of Chemistry – July 2017)

Microwave-assisted, ligand-free, direct C-H arylation of thiophenes in biomass-derived γ-valerolactone

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Table of contents

Synthetic procedures and characterization data

Compounds **1**[1], **2**[2], **3**[3], **4**[4], **5**[5], **6**[3], **8**[6], **10**[3], **12**[6], **13**[7], **14**[8], **P3HT**[9] are known compounds. Characterization data and copies of the ^{1}H and ^{13}C NMR are reported below.

2-methyl-5-(4-nitrophenyl)thiophene (1)

1-bromo-4-nitrobenzene (0.5 mmol, 101 mg), 2-methylthiophene (1 mmol, 98 mg), and KOAc (1 mmol, 98 mg) were placed into a quartz vial equipped with a magnetic stirrer and suspended in GVL (3 mL). The vial was purged with N_2 and $Pd(OAc)_2$ (0.22 mg, 0.001 mmol, 0.2 mol%) was added. The mixture was heated to 140 °C under MW irradiation (average power 960 W) in a N_2 (1 MPa) atmosphere and under magnetic stirring (450 rpm). After 2 hours, 3 mL of water were added, the mixture was cooled to 0°C and the newly-formed precipitate was filtered and washed with 1 mL of water. Lastly, the solid was dried under vacuum and purified by column chromatography (hexane). Compound **1** was obtained as a yellow solid (90 mg, 82% yield).
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (d, *J* = 9.0 Hz, 2H), 7.58 (d, *J* = 9.0 Hz, 2H), 7.21 (d, *J* = 3.6 Hz, 1H), 6.73 – 6.72 (m, 1H), 2.47 (s, 3H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 146.3, 143.1, 141.0, 139.2, 127.2, 125.9, 125.5, 124.5, 15.8 ppm. **GC-EIMS (m/z %):** 45 (20), 128 (38), 171 (42), 189 (50), 219 (M^+, 100)

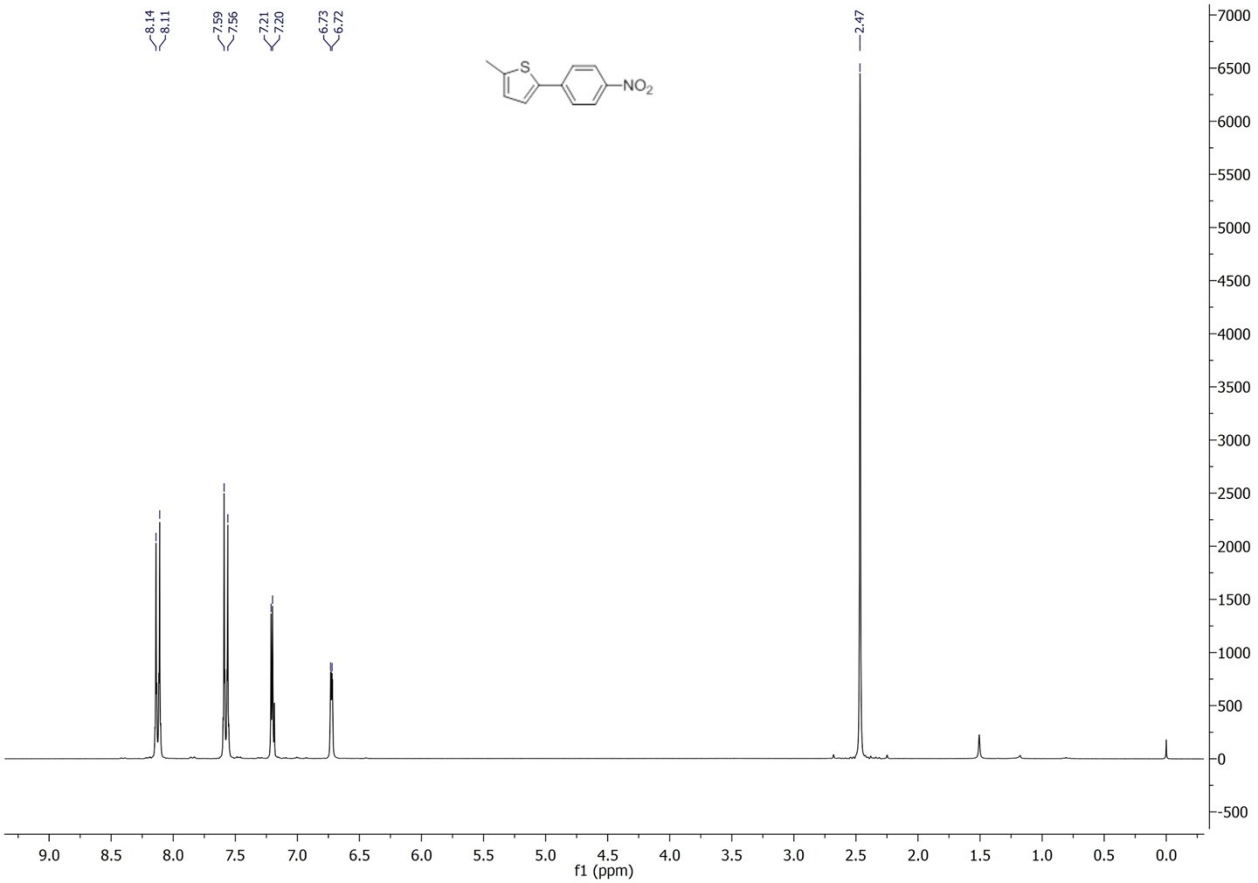

Figure S1. ^{1}H NMR of 2-methyl-5-(4-nitrophenyl)thiophene (1)

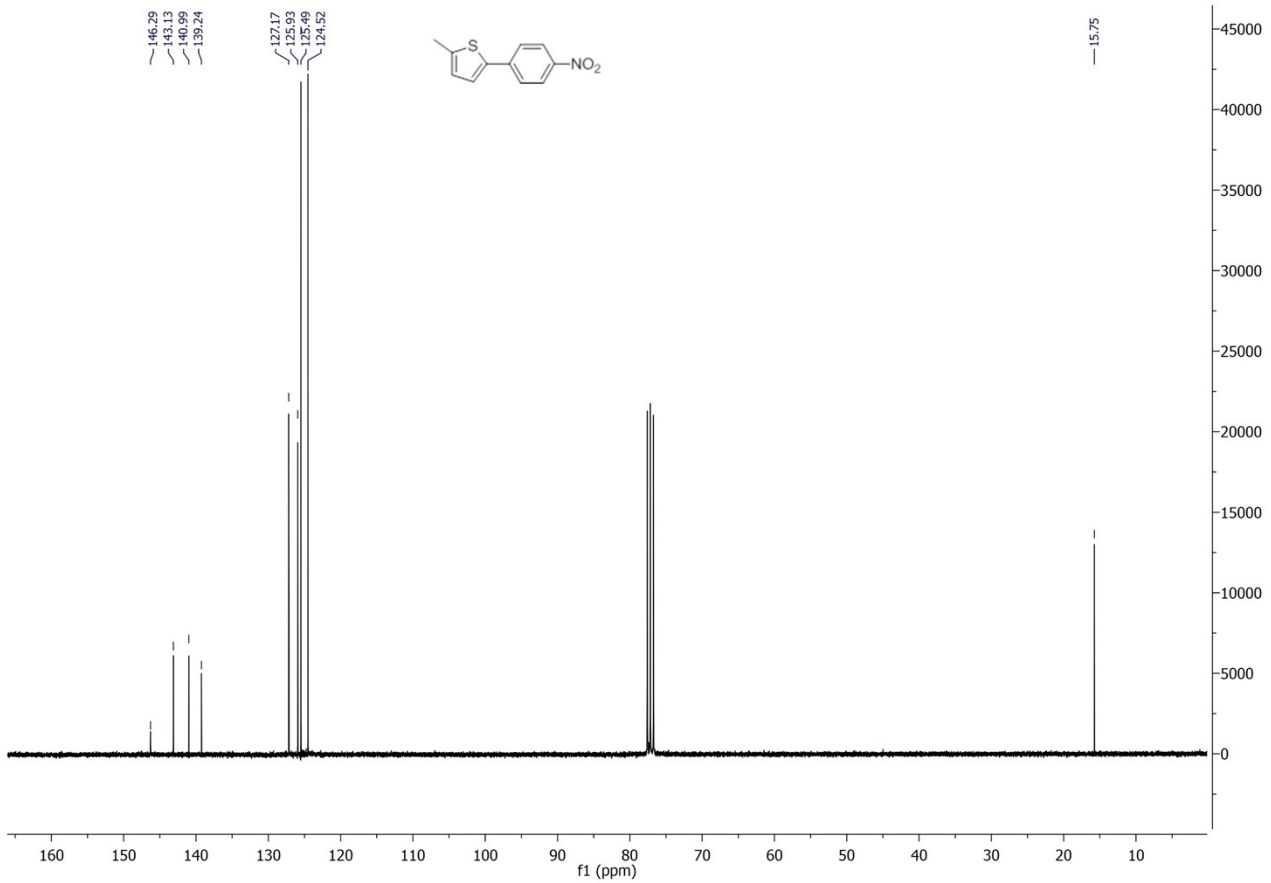

Figure S2. ^{13}C NMR of 2-methyl-5-(4-nitrophenyl)thiophene (1)

2-butyl-5-(4-nitrophenyl)thiophene (2)

1-bromo-4-nitrobenzene (0.5 mmol, 101 mg), 2-butylthiophene (1 mmol, 140 mg) and KOAc (1 mmol, 98 mg) were placed into a quartz vial equipped with a magnetic stirrer and suspended in GVL (3 mL). The vial was purged with N_2 and $Pd(OAc)_2$ (0.22 mg, 0.001 mmol, 0.2 mol%) was added. The mixture was heated to 140 °C under MW irradiation (average power 960 W) in a N_2 (1 MPa) atmosphere and under magnetic stirring (450 rpm). After 2 hours, the crude reaction was filtered on a silica pad (3 g) and washed with 3 mL EtOAc and, after solvent evaporation, purified by flash column chromatography (hexane), giving compound **2** as a yellow liquid (99 mg, 76% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 3.3 Hz, 1H), 6.81 (d, *J* = 2.5 Hz, 1H), 2.85 (t, *J* = 7.5 Hz, 2H), 1.72 – 1.67 (m, 2H), 1.46 – 1.39 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 149.3, 146.3, 141.1, 138.9, 126.0, 125.7, 125.5, 124.5, 33.8, 30.2, 22.3, 13.9 ppm. **GC-EIMS (m/z %):** 172 (30), 218 (100), 261 (M^+, 35)

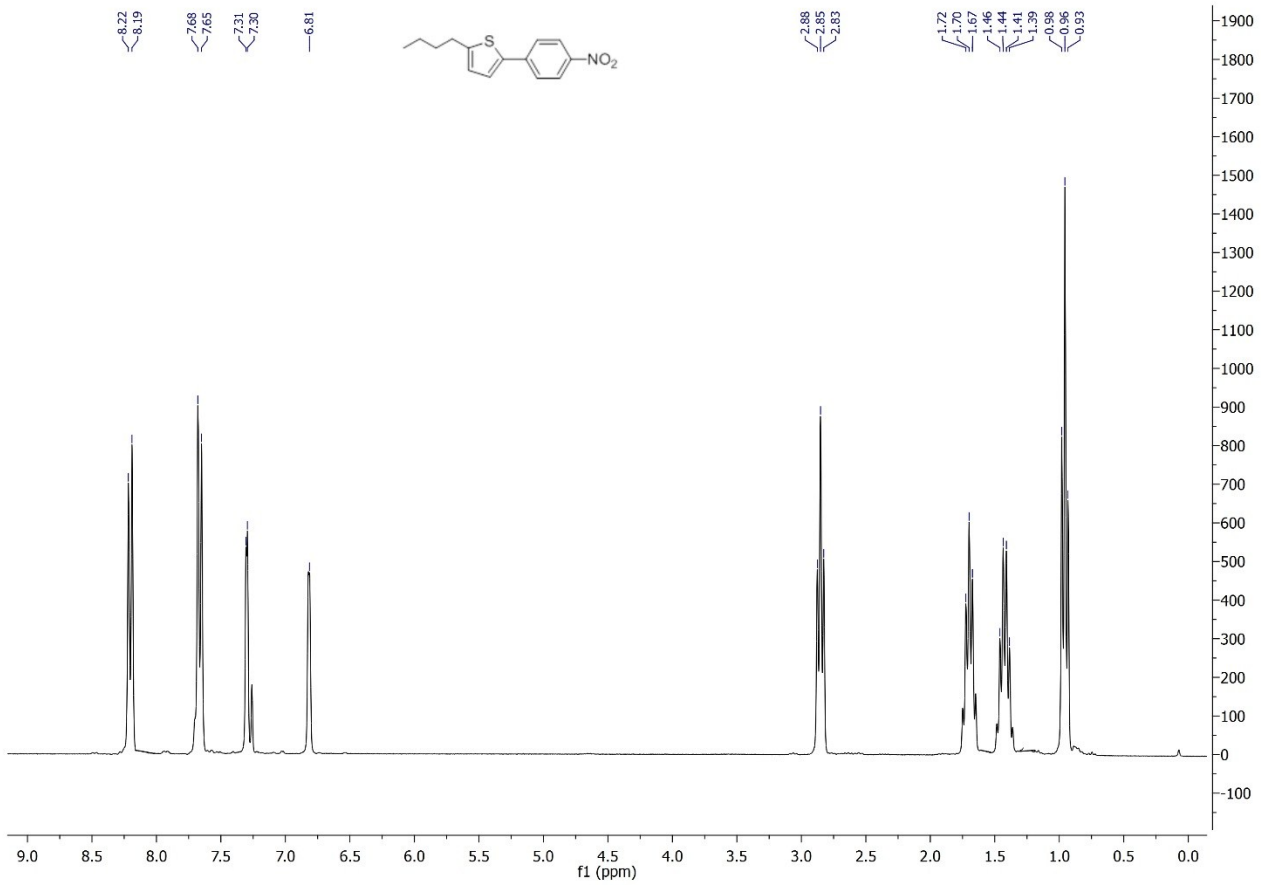

Figure S3. ^{1}H NMR of 2-butyl-5-(4-nitrophenyl)thiophene (2)

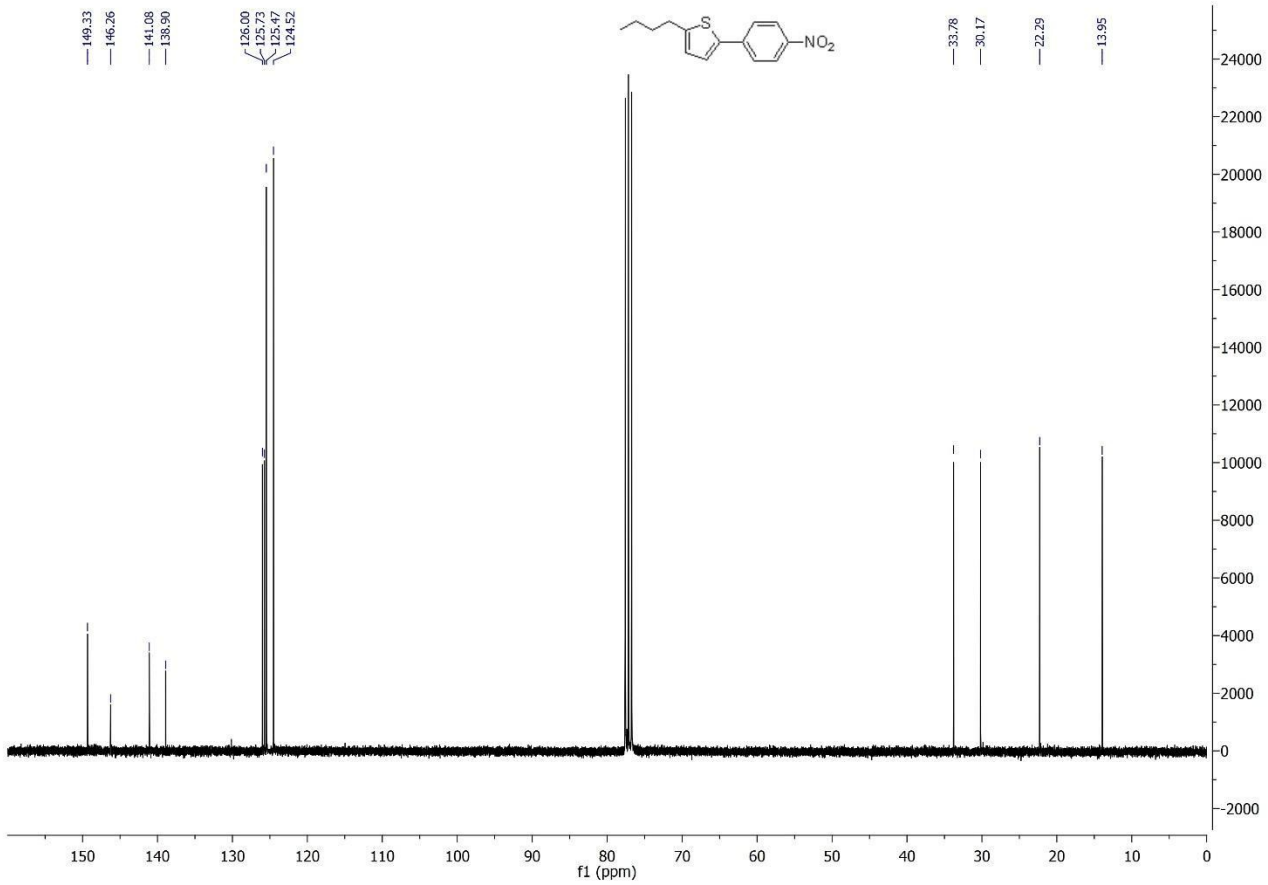

Figure S4. ^{13}C NMR of 2-butyl-5-(4-nitrophenyl)thiophene (2)

2-methyl-5-(3-nitrophenyl)thiophene (3)

1-bromo-3-nitrobenzene (0.5 mmol, 101 mg), 2-methyllthiophene (1 mmol, 98 mg), and KOAc (1 mmol, 98 mg) were placed into a quartz vial equipped with a magnetic stirrer and suspended in GVL (3 mL). The vial was purged with N_2 and $Pd(OAc)_2$ (0.22 mg, 0.001 mmol, 0.2 mol%) was added. The mixture was heated to 140 °C under MW irradiation (average power 960 W) in a N_2 (1 MPa) atmosphere and under magnetic stirring (450 rpm). After 2 hours, the crude reaction was filtered on a silica pad (3 g) and washed with 3 mL EtOAc and, after solvent evaporation, purified by flash column chromatography (hexane), giving compound **3** as a yellow liquid (88 mg, 80% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (m, 2H), 7.96 (dd, *J* = 8.6 Hz, 1.3 Hz, 2H), 7.73 (d, *J* = 9 Hz, 1H), 7.44 -7.39 (m, 1H), 7.13 (d, J = 3 Hz, 1H), 6.69 (m, 1H), 2.45 (s, 3H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 148.8, 141.6, 139.1, 136.4, 131.1, 129.8, 126.8, 124.8, 121.4, 120.0, 15.7 ppm. **GC-EIMS (m/z %):** 129 (55), 158 (45), 173 (60), 219 (M^+, 100)

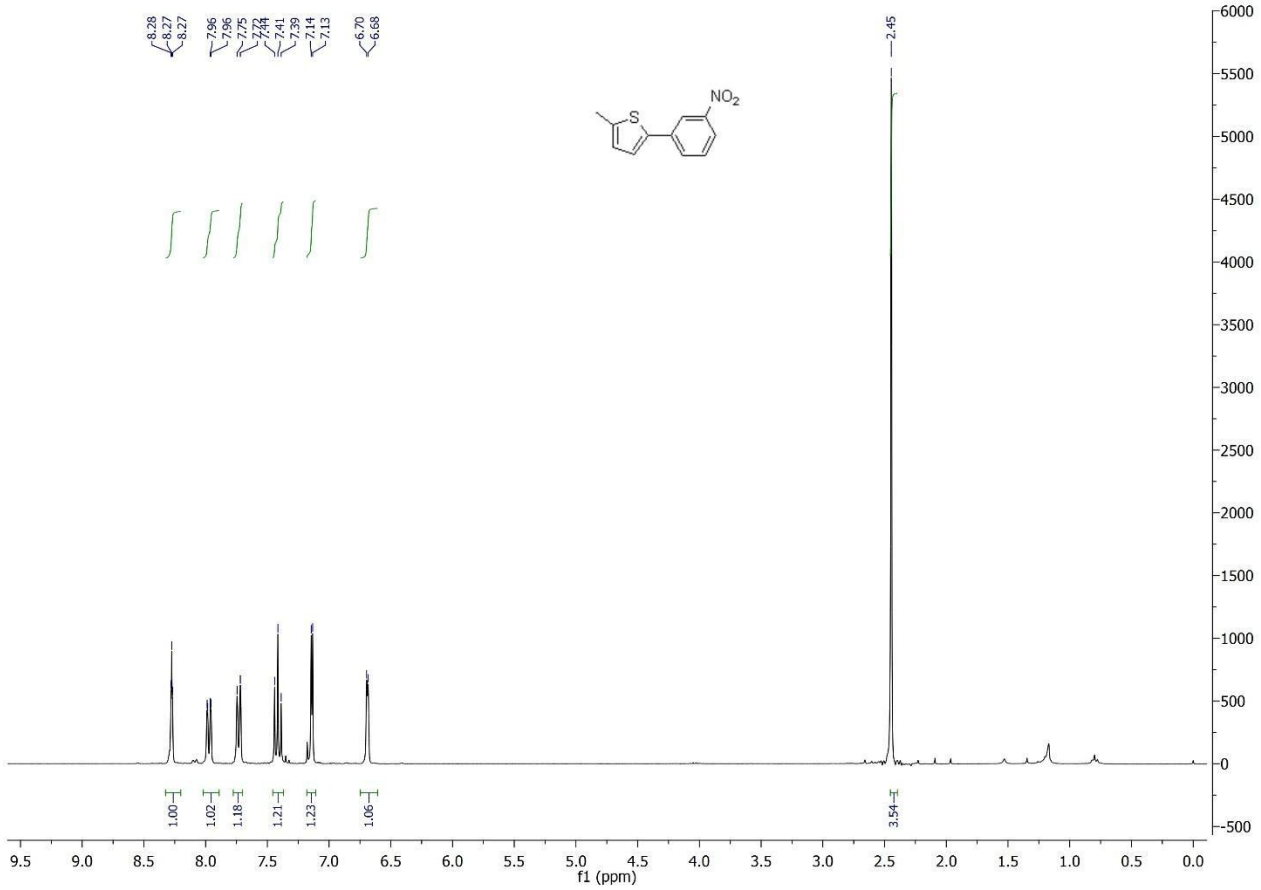

Figure S5. ^{1}H NMR of 2-methyl-5-(3-nitrophenyl)thiophene (3)

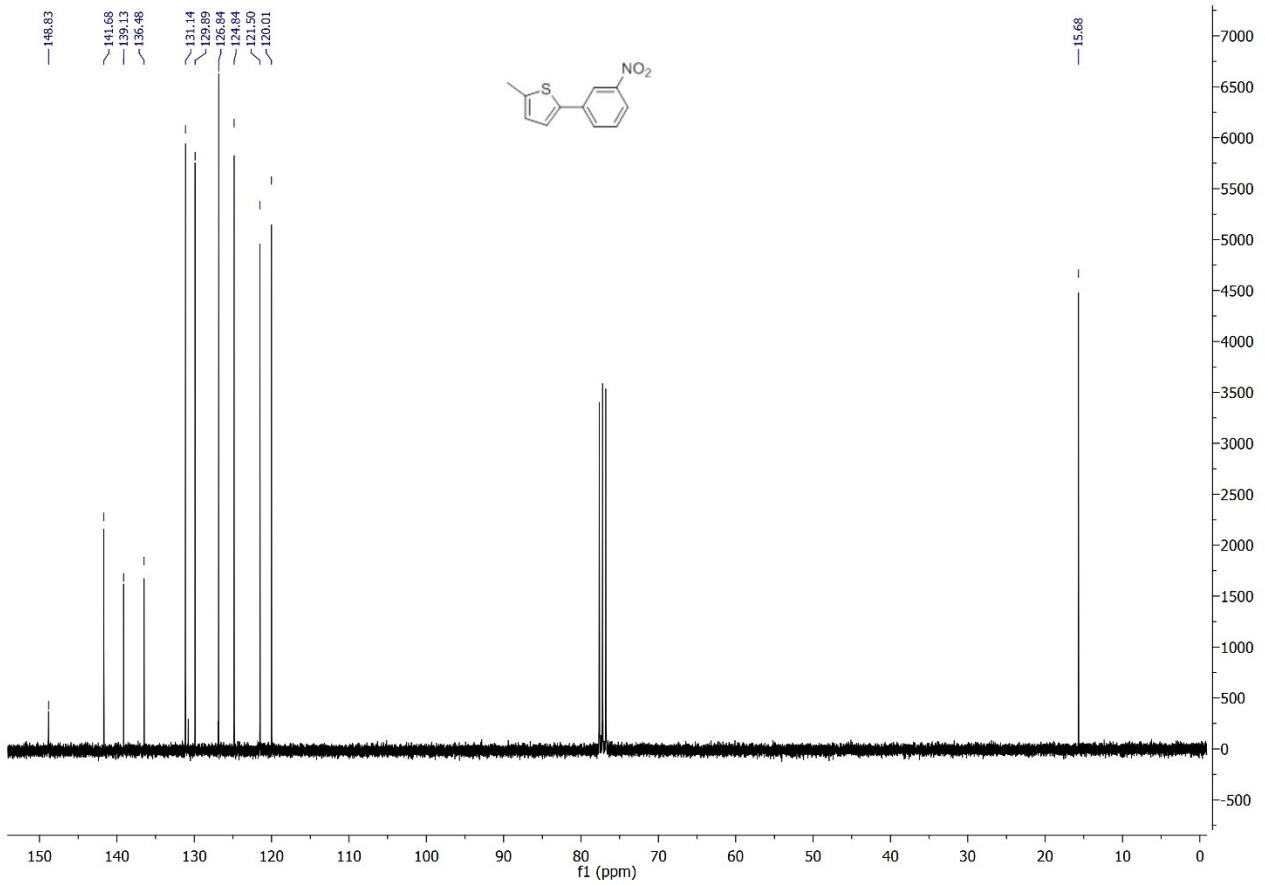

Figure S6. ^{13}C NMR of 2-methyl-5-(3-nitrophenyl)thiophene (3)

1-(5-(4-nitrophenyl)thiophen-2-yl)ethanone (4)

1-bromo-4-nitrobenzene (0.5 mmol, 101 mg), 1-(thiophen-2-yl)ethanone (1 mmol, 126 mg), and KOAc (1 mmol, 98 mg) were placed into a quartz vial equipped with a magnetic stirrer and suspended in GVL (3 mL). The vial was purged with N_2 and $Pd(OAc)_2$ (0.22 mg, 0.001 mmol, 0.2 mol%) was added. The mixture was heated to 140 °C under MW irradiation (average power 960 W) in a N_2 (1 MPa) atmosphere and under magnetic stirring (450 rpm). After 2 hours, 3 mL of water were added, the mixture was cooled to 0°C and the newly-formed precipitate was filtered and washed with 1 mL of water. Lastly, the solid was dried under vacuum and purified by column chromatography (hexane). Compound **4** was obtained as a yellow solid (35 mg, 28% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (d, *J* = 9 Hz, 2H), 7.79 (d, *J* = 9 Hz, 2H), 7.69 (d, *J* = 3 Hz, 1H), 7.46 (d, *J* = 3 Hz, 1H), 2.59 (s, 3H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 190.7, 149.1, 147.7, 145.6, 139.5, 133.5, 126.9, 126.3, 124.7, 26.8 ppm. **GC-EIMS (m/z %):** 114 (20), 158 (18), 186 (48), 232 (100), 247 (M^+, 60)

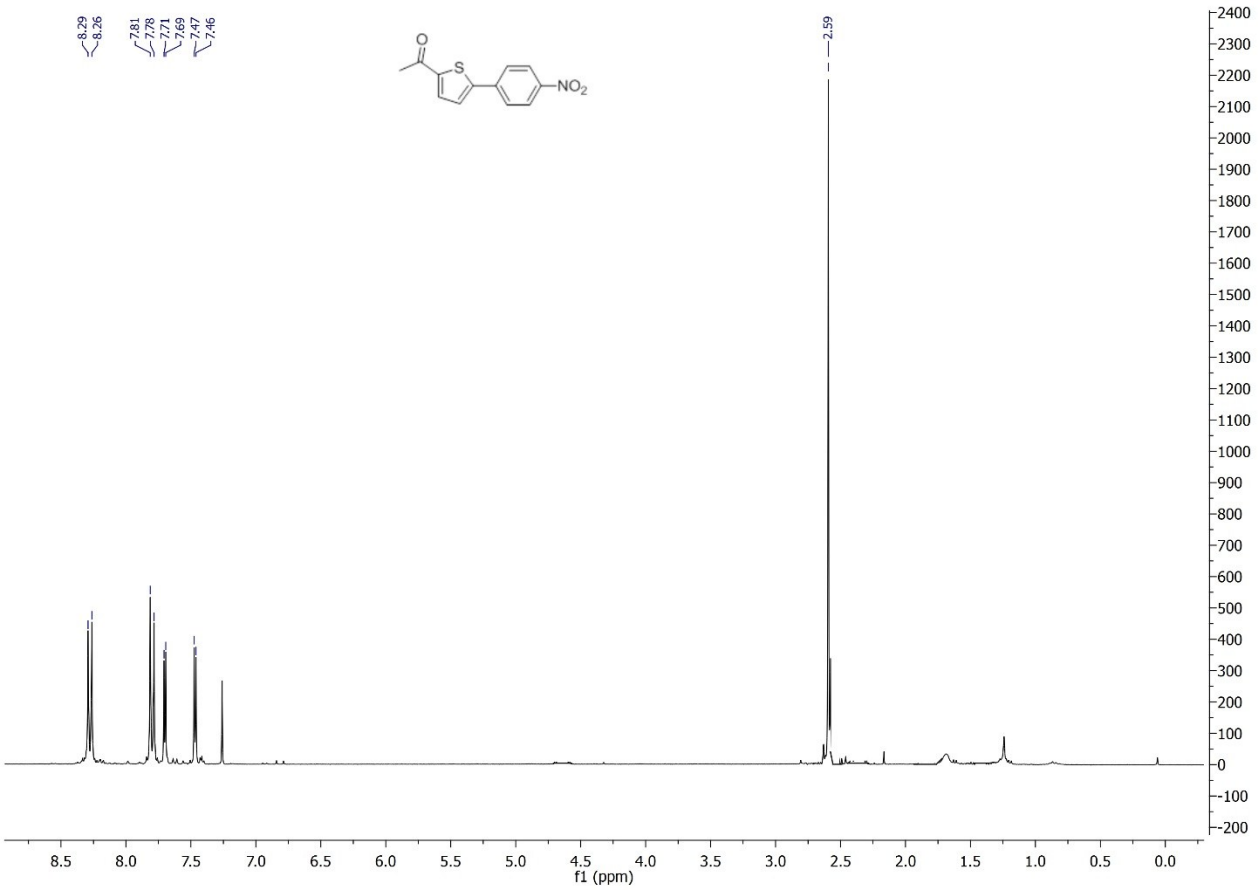

Figure S7. ^{1}H NMR of 1-(5-(4-nitrophenyl)thiophen-2-yl)ethanone (4)

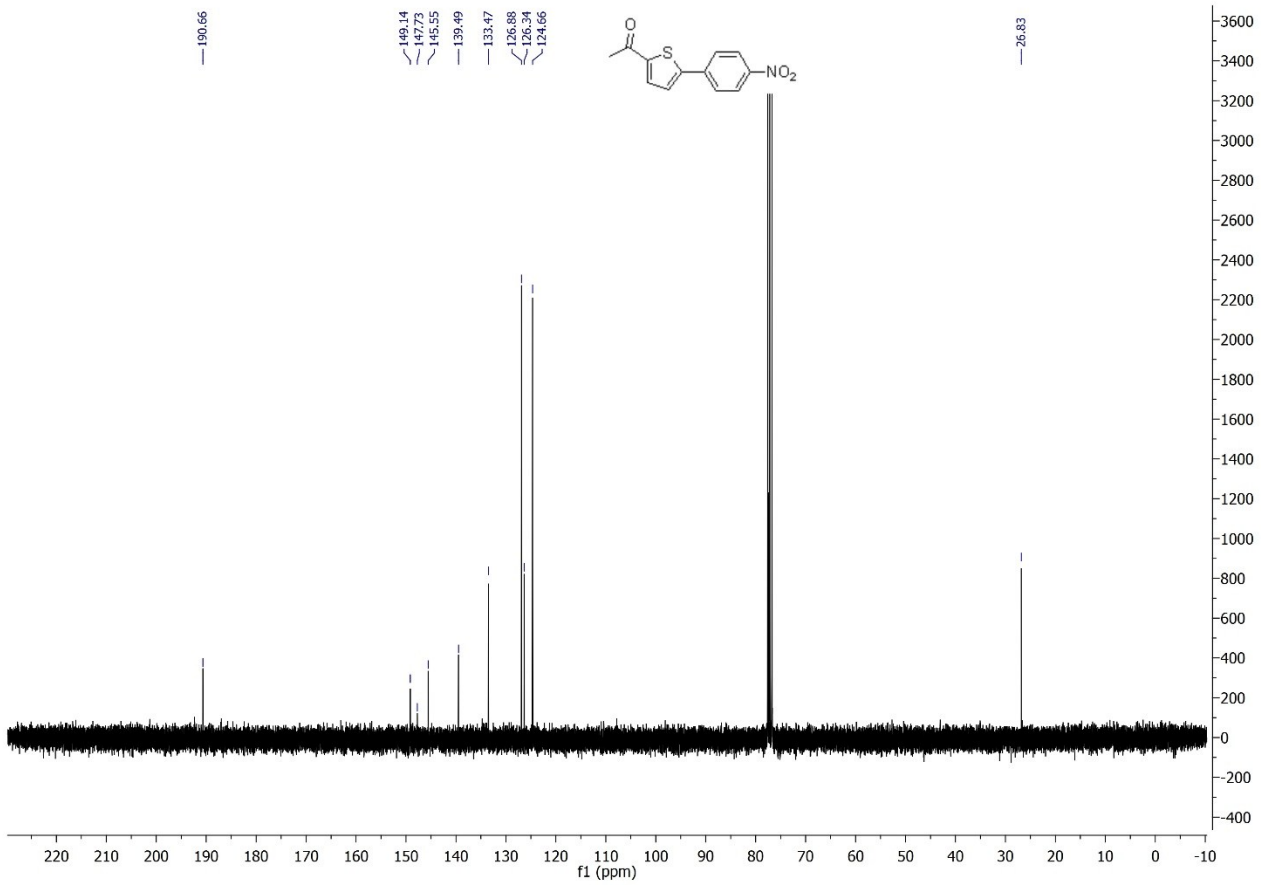

Figure S8. ^{13}C NMR of 1-(5-(4-nitrophenyl)thiophen-2-yl)ethanone (4)

1-(4-(5-methylthiophen-2-yl)phenyl)ethanone (5)

1-(4-bromophenyl)ethanone (0.5 mmol, 100 mg), 2-methylthiophene (1 mmol, 98 mg), and KOAc (1 mmol, 98 mg) were placed into a quartz vial equipped with a magnetic stirrer and suspended in GVL (3 mL). The vial was purged with N_2 and $Pd(OAc)_2$ (0.22 mg, 0.001 mmol, 0.2 mol%) was added. The mixture was heated to 140 °C under MW irradiation (average power 960 W) in a N_2 (1 MPa) atmosphere and under magnetic stirring (450 rpm). After 2 hours, 3 mL of water were added, the mixture was cooled to 0°C and the newly-formed precipitate was filtered and washed with 1 mL of water. Lastly, the solid was dried under vacuum and purified by column chromatography (hexane).

Compound **5** was obtained as a colourless solid (71 mg, 66% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 (d, *J* = 9 Hz, 2H), 7.54 (d, *J* = 9 Hz, 2H), 7.16 (d, *J* = 3 Hz, 1H), 6.70 (m, 1H), 2.53 (s, 3H), 2.45 (s, 3H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 197.5, 141.7, 140.6, 139.2, 135.4, 129.2, 126.8, 125.2, 124.7, 26.7, 15.7 ppm. **GC-EIMS (m/z %):** 129 (15), 158 (13), 171 (20), 201 (100), 216 (M^+, 75)

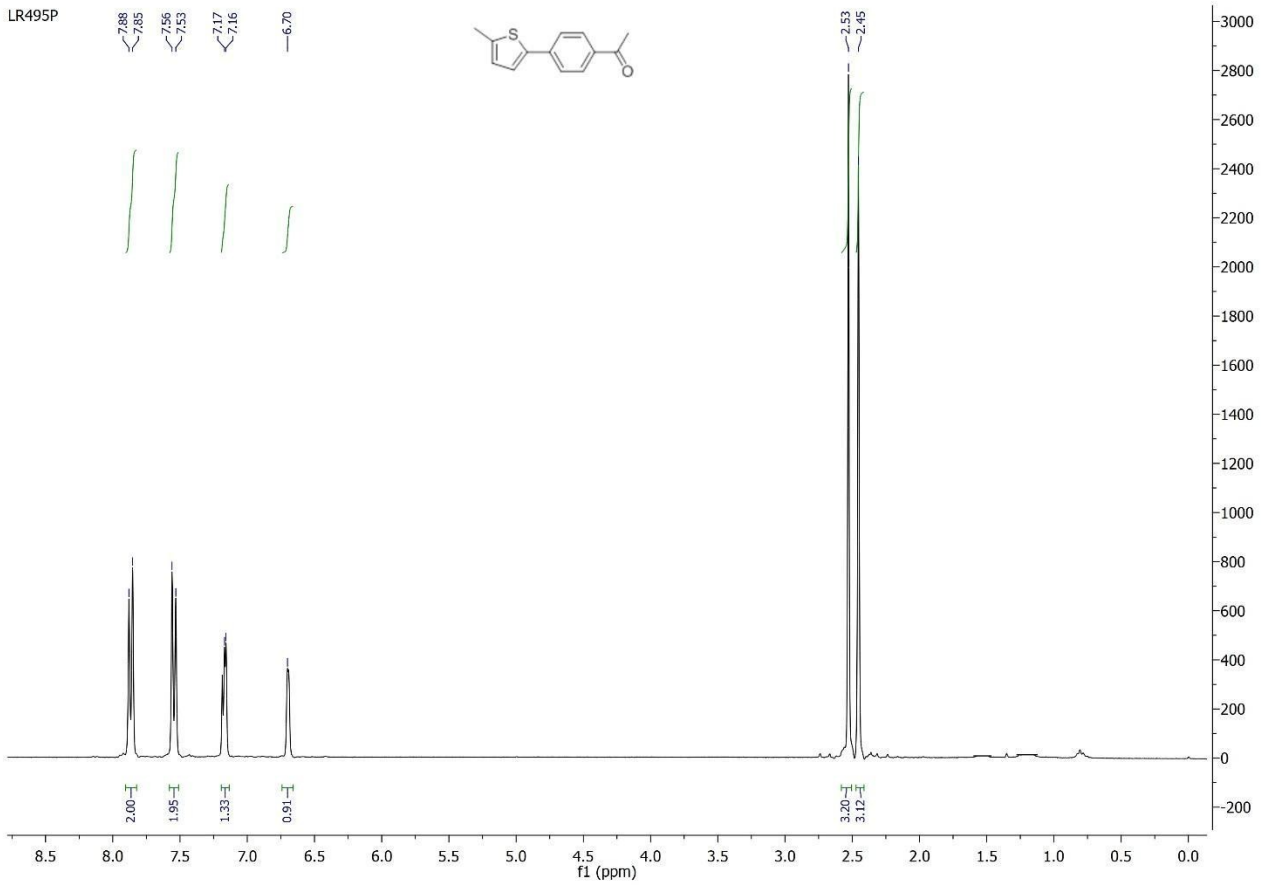

Figure S9. ^{1}H NMR of 1-(4-(5-methylthiophen-2-yl)phenyl)ethanone (5)

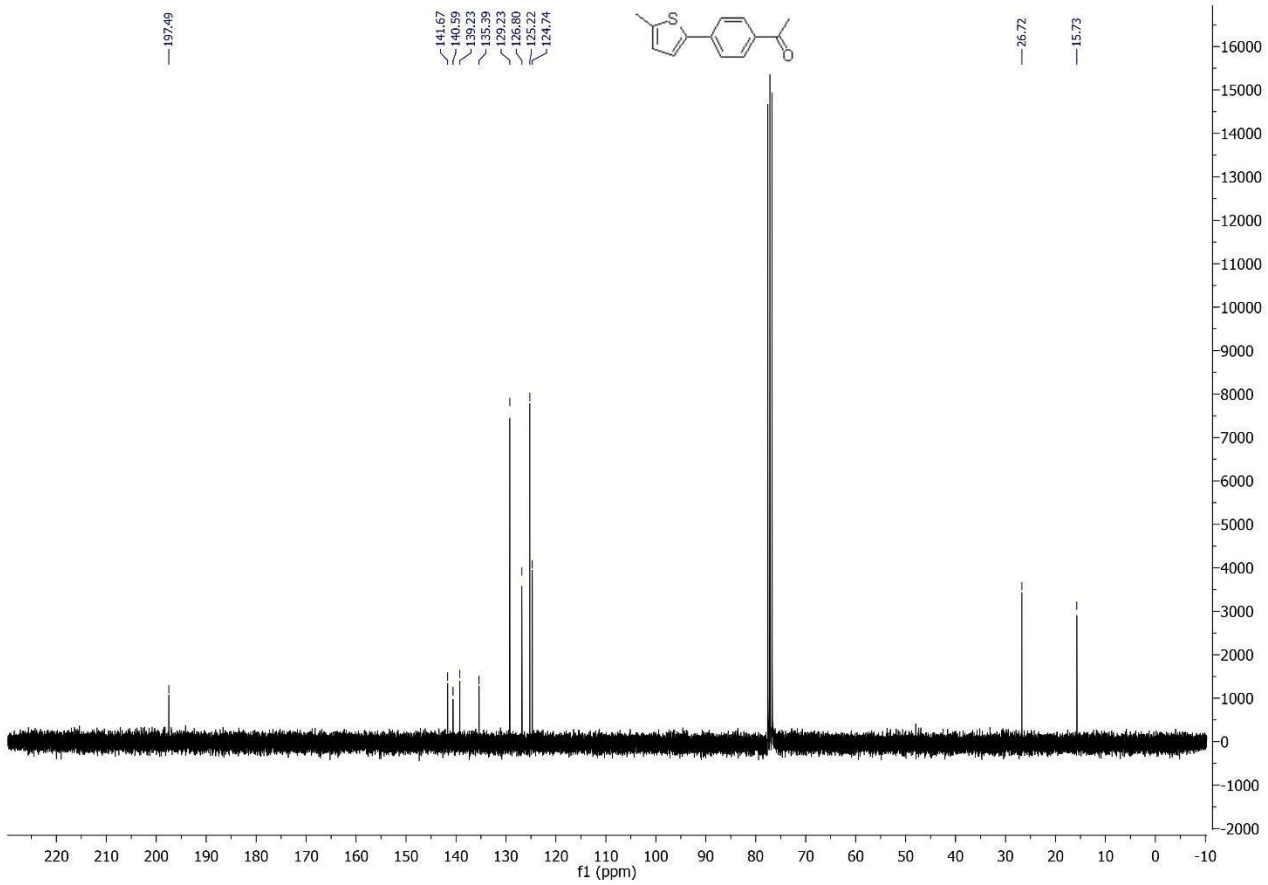

Figure S10. ^{13}C NMR of 1-(4-(5-methylthiophen-2-yl)phenyl)ethanone (5)

1-(3-(5-methylthiophen-2-yl)phenyl)ethanone (6)

1-(3-bromophenyl)ethanone (0.5 mmol, 100 mg), 2-methylthiophene (1 mmol, 98 mg), and KOAc (1 mmol, 98 mg) were placed into a quartz vial equipped with a magnetic stirrer and suspended in GVL (3 mL). The vial was purged with N_2 and $Pd(OAc)_2$ (0.22 mg, 0.001 mmol, 0.2 mol%) was added. The mixture was heated to 200 °C under MW irradiation (average power 960 W) in a N_2 (1 MPa) atmosphere and under magnetic stirring (450 rpm). After 2 hours, the crude reaction was filtered on a silica pad (3 g), washed with 3 mL EtOAc and, after solvent evaporation, purified by flash column chromatography (hexane), giving compound **6** as a yellow liquid (16 mg, 15% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (m, 1H), 7.81 (d, *J* = 9 Hz, 1H), 7.73 (d, *J* = 6 Hz, 1H), 7.45 (dd, *J* = 9 Hz, 6 Hz, 1H), 7.18 (d, *J* = 3 Hz, 1H), 6.75 (d, *J* = 3 Hz, 1H), 2.64 (s, 3H), 2.52 (s, 3H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 197.98, 140.69, 140.37, 137.61, 135.20, 129.88, 129.08, 126.78, 126.39, 125.02, 123.70, 26.75, 15.50 ppm.

GC-EIMS (m/z %): 129 (21), 158 (17), 173 (50), 201 (88), 216 (M^+, 100)

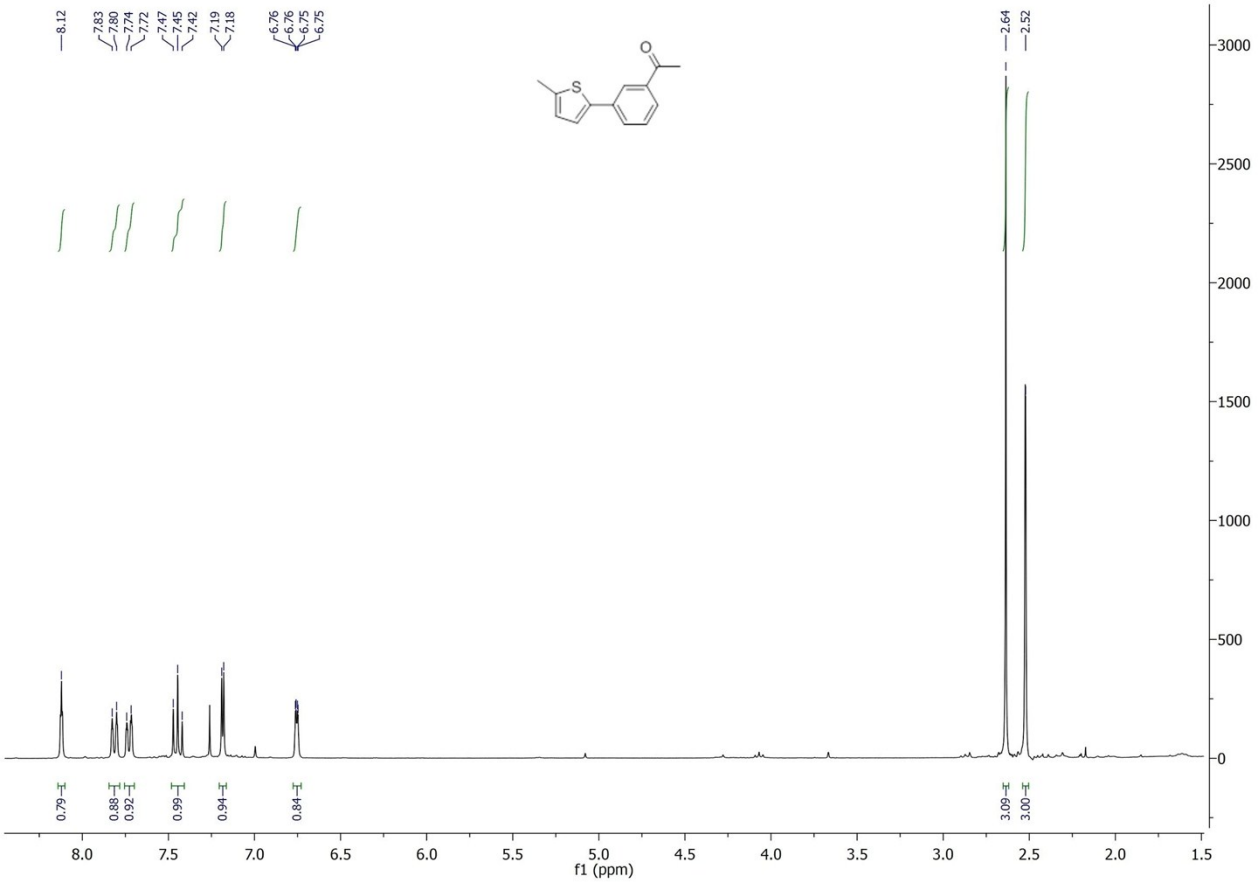

Figure S11. ^{1}H NMR of 1-(3-(5-methylthiophen-2-yl)phenyl)ethanone (6)

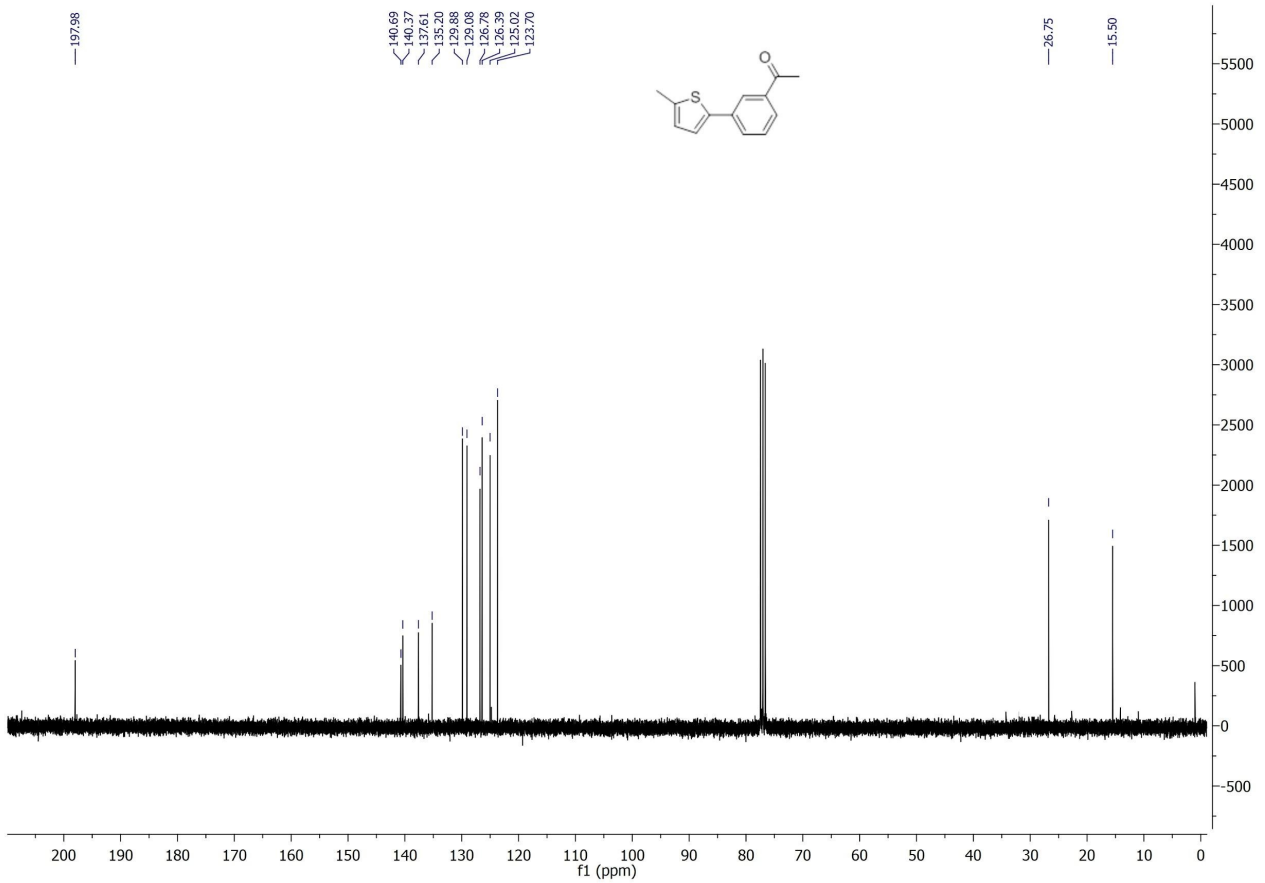

Figure S12. ^{13}C NMR of 1-(3-(5-methylthiophen-2-yl)phenyl)ethanone (6)

1-(4-(5-butylthiophen-2-yl)phenyl)ethanone (8)

1-(4-bromophenyl)ethanone (0.5 mmol, 100 mg), 2-butylthiophene (1 mmol, 140 mg), and KOAc (1 mmol, 98 mg) were placed into a quartz vial equipped with a magnetic stirrer and suspended in GVL (3 mL). The vial was purged with N_2 and $Pd(OAc)_2$ (0.22 mg, 0.001 mmol, 0.2 mol%) was added. The mixture was heated to 200 °C under MW irradiation (average power 960 W) in a N_2 (1 MPa) atmosphere and under magnetic stirring (450 rpm). After 2 hours, the crude reaction was filtered on a silica pad (3 g) and washed with 3 mL EtOAc and, after solvent evaporation, purified by flash column chromatography (hexane), giving compound **8** as a yellow liquid (36 mg, 28% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (d, *J* = 9 Hz, 2H), 7.63 (d, *J* = 9 Hz, 2H), 7.25 (d, J = 3 Hz, 1 H) 6.78 (d, *J* = 3 Hz, 1H), 2.84 (t, J = 9 Hz, 2H), 2.60 (s, 3H), 1.75-1.64 (m, 2H), 1.43-1.40 (m, 2H), 0.95 (t, J = 6 Hz, 3H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 197.2, 147.5, 139.8, 136.0, 135.1, 125.5, 124.9, 124.4, 33.6, 26.4, 22.0, 13.7 ppm.

GC-EIMS (m/z %): 172 (33), 215 (100), 258 (M^+, 47),

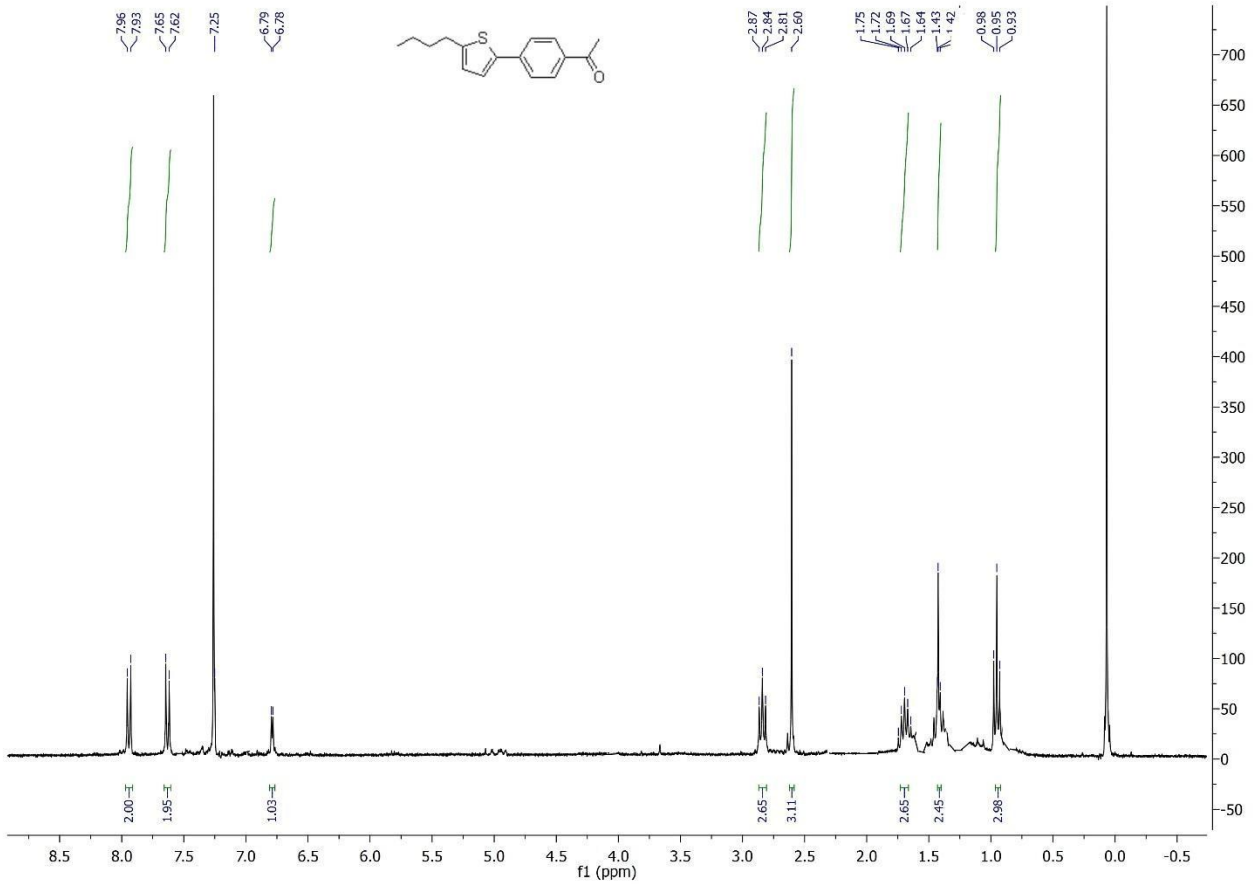

Figure S13. ^{1}H NMR of 1-(4-(5-butylthiophen-2-yl)phenyl)ethanone (8)

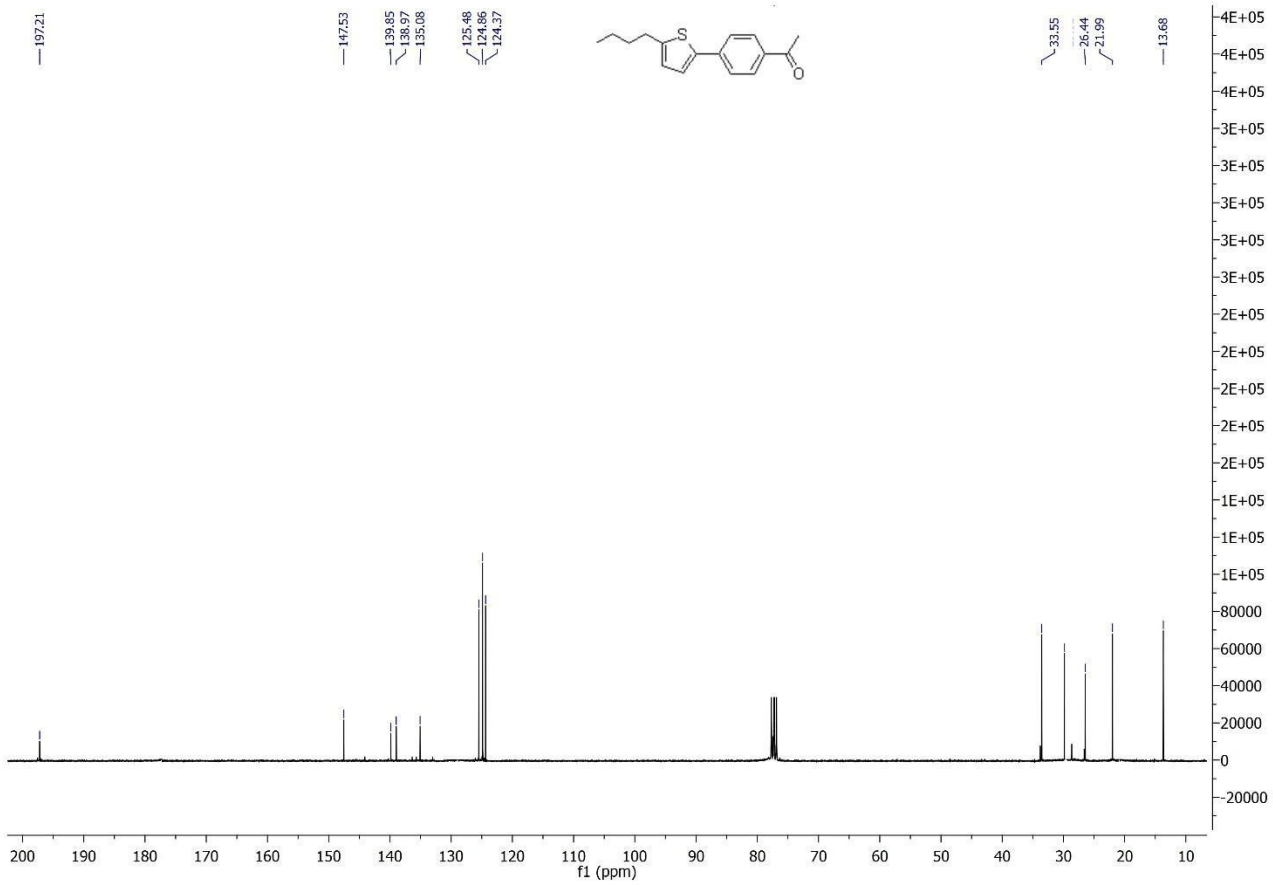

Figure S14. ^{13}C NMR of 1-(4-(5-butylthiophen-2-yl)phenyl)ethanone (8)

2-(4-methoxyphenyl)-5-methylthiophene (10)

1-iodo-4-methoxybenzene (0.5 mmol, 117 mg), 2-methylthiophene (1.5 mmol, 147 mg), K_2CO_3 (1.5 mmol, 207 mg), and PivOH (0.5 mmol, 51 mg) were placed into a quartz vial equipped with a magnetic stirrer and suspended in GVL (3 mL). The vial was purged with N_2, and $Pd(OAc)_2$ (0.22 mg, 0.001 mmol, 0.2 mol%) was added. The mixture was heated to 200 °C under MW irradiation (average power 960 W) in a N_2 (1 MPa) atmosphere and under magnetic stirring (450 rpm). After 2 hours, 3 mL of water were added, the mixture was cooled to 0°C and the newly-formed precipitate was filtered and washed with 1 mL of water. Lastly, the solid was dried under vacuum and purified by column chromatography (hexane). Compound **10** was obtained as a colourless solid (48 mg, 47% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.49 (d, *J* = 9 Hz, 2H), 6.98 (d, *J* = 3 Hz, 1H), 6.89 (d, *J* = 9 Hz, 2H), 6.70 (m, 1H), 3.83 (s, 3H), 2.49 (s, 3H), ppm; **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 159.2, 142.3, 138.7, 127.8, 127.1, 126.4, 122.2, 114.4, 55.6, 15.7 ppm.

GC-EIMS (m/z %): 18 (50), 28 (37), 161 (30), 189 (98), 161 (30), 189 (98), 204 (M^+, 100)

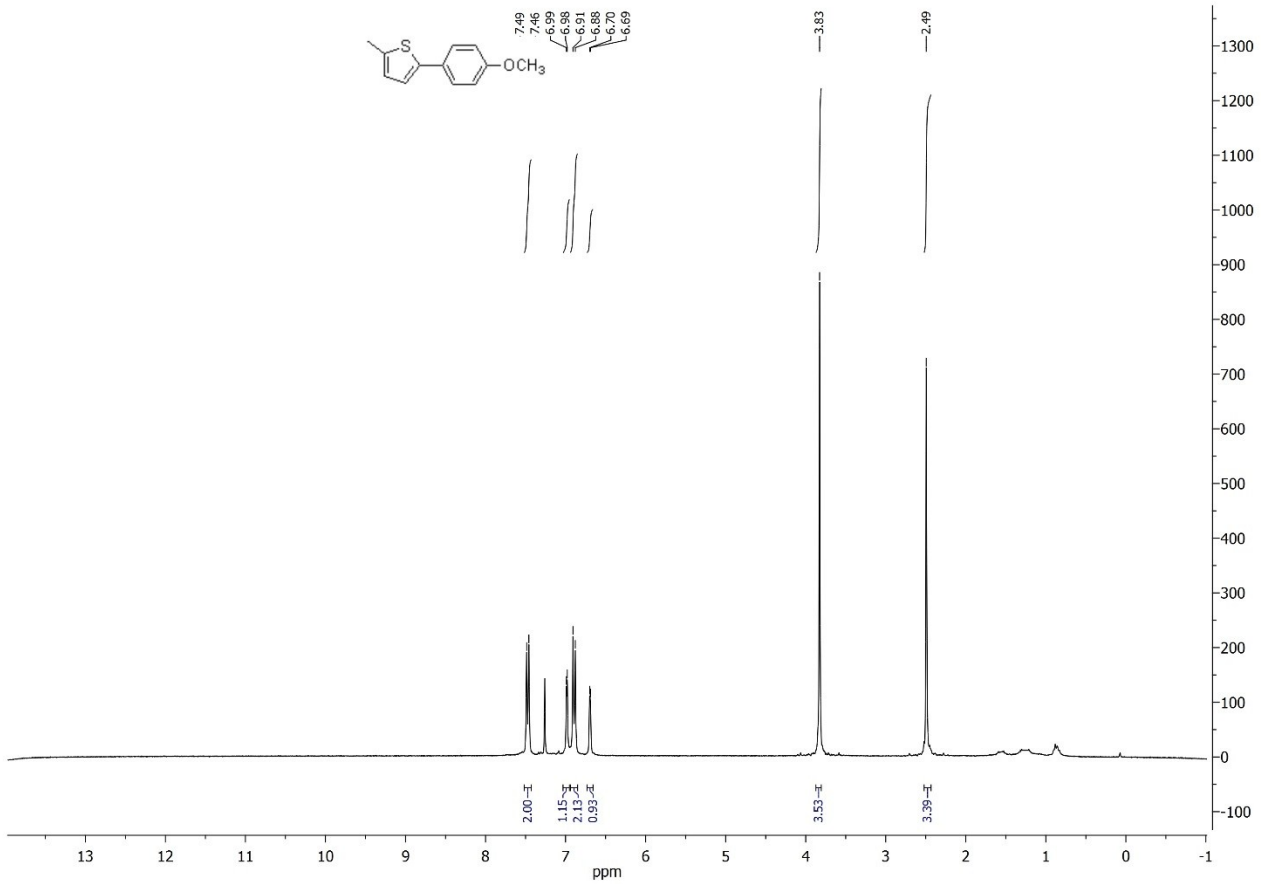

Figure S15. ^{1}H NMR of 2-(4-methoxyphenyl)-5-methylthiophene (10)

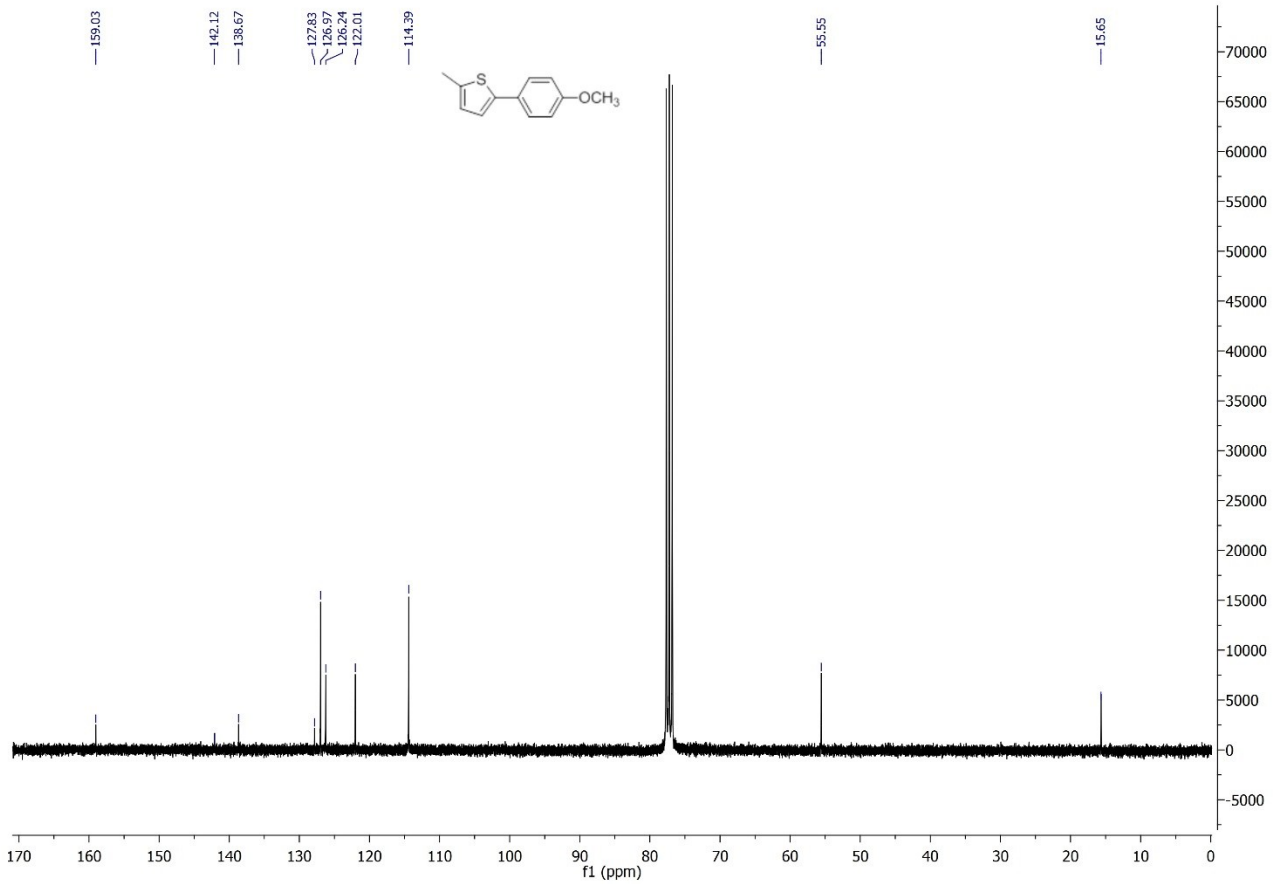

Figure S16. ^{13}C NMR of 2-(4-methoxyphenyl)-5-methylthiophene (10)

2-butyl-5-(4-methoxyphenyl)thiophene (12)

1-iodo-4-methoxybenzene (0.5 mmol, 117 mg), 2-butylthiophene (1 mmol, 140 mg), K_2CO_3 (1.5 mmol, 207 mg), and PivOH (0.5 mmol, 51 mg) were placed into a quartz vial equipped with a magnetic stirrer and suspended in GVL (3 mL). The vial was purged with N_2 and $Pd(OAc)_2$ (0.22 mg, 0.001 mmol, 0.2 mol%) was added. The mixture was heated to 200 °C under MW irradiation (average power 960 W) in a N_2 (1 MPa) atmosphere and under magnetic stirring (450 rpm). After 2 hours, the crude reaction was filtered on a silica pad (3 g) and washed with 3 mL EtOAc and, after solvent evaporation, purified by flash column chromatography (hexane), giving compound **12** as a yellow liquid (62 mg, 47% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 (d, *J* = 9 Hz, 2H), 6.99 (d, *J* = 3 Hz, 1H), 6.88 (d, *J* = 9 Hz, 2H), 6.70 (d, 3 Hz, 1H), 3.82 (s, 3H), 2.80 (t, J = 7 Hz, 2H), 1.68 (m, 2H), 1.42 (m, 2H), 0.94 (t, J = 7Hz, 3H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 158.9, 144.8, 141.7, 127.5, 126.9, 125.0, 121.7, 114.3, 55.5, 33.9, 30.0, 22.3, 14.0 ppm.

GC-EIMS (m/z %): 160 (25), 188 (20), 203 (100), 246 (M^+, 58).

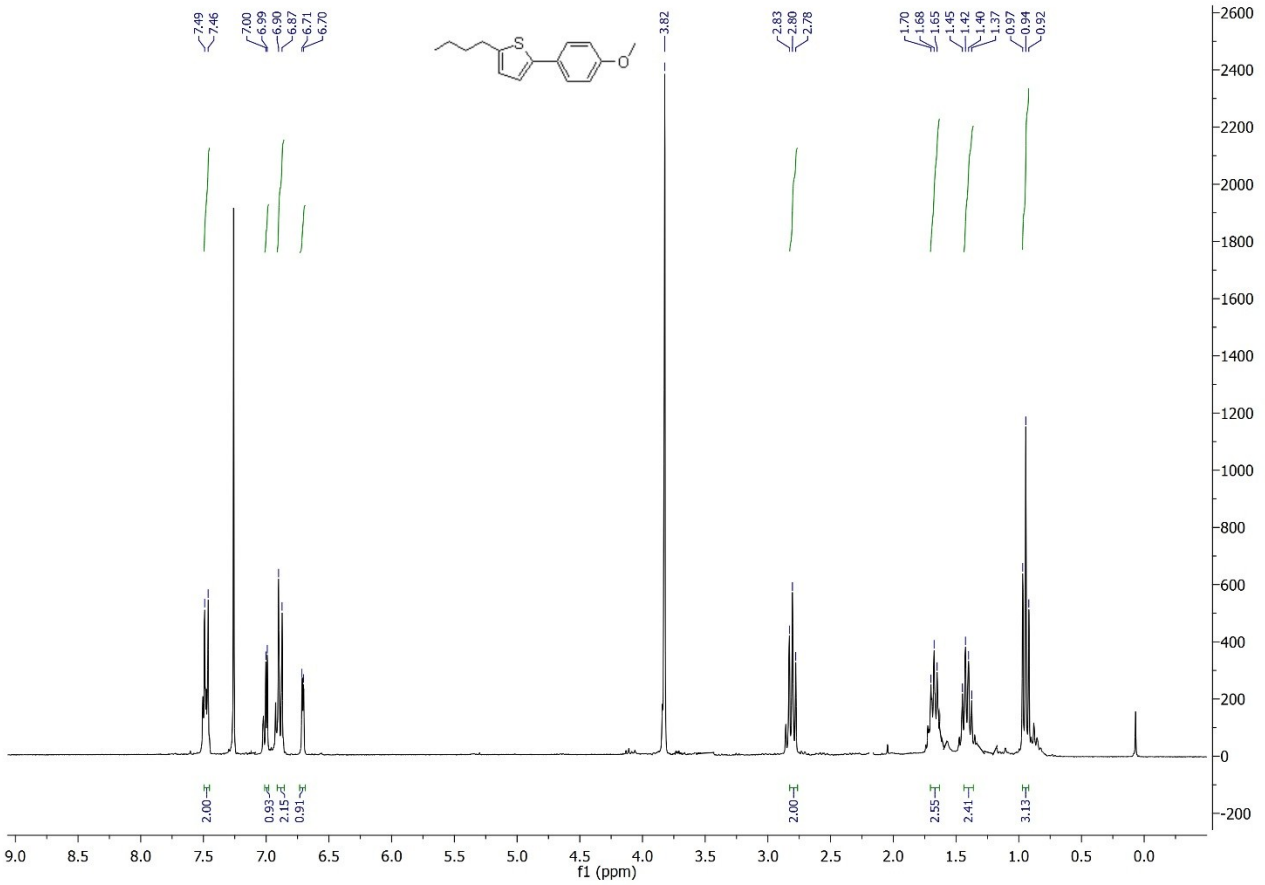

Figure S17. ^{1}H NMR of 2-butyl-5-(4-methoxyphenyl)thiophene (12)

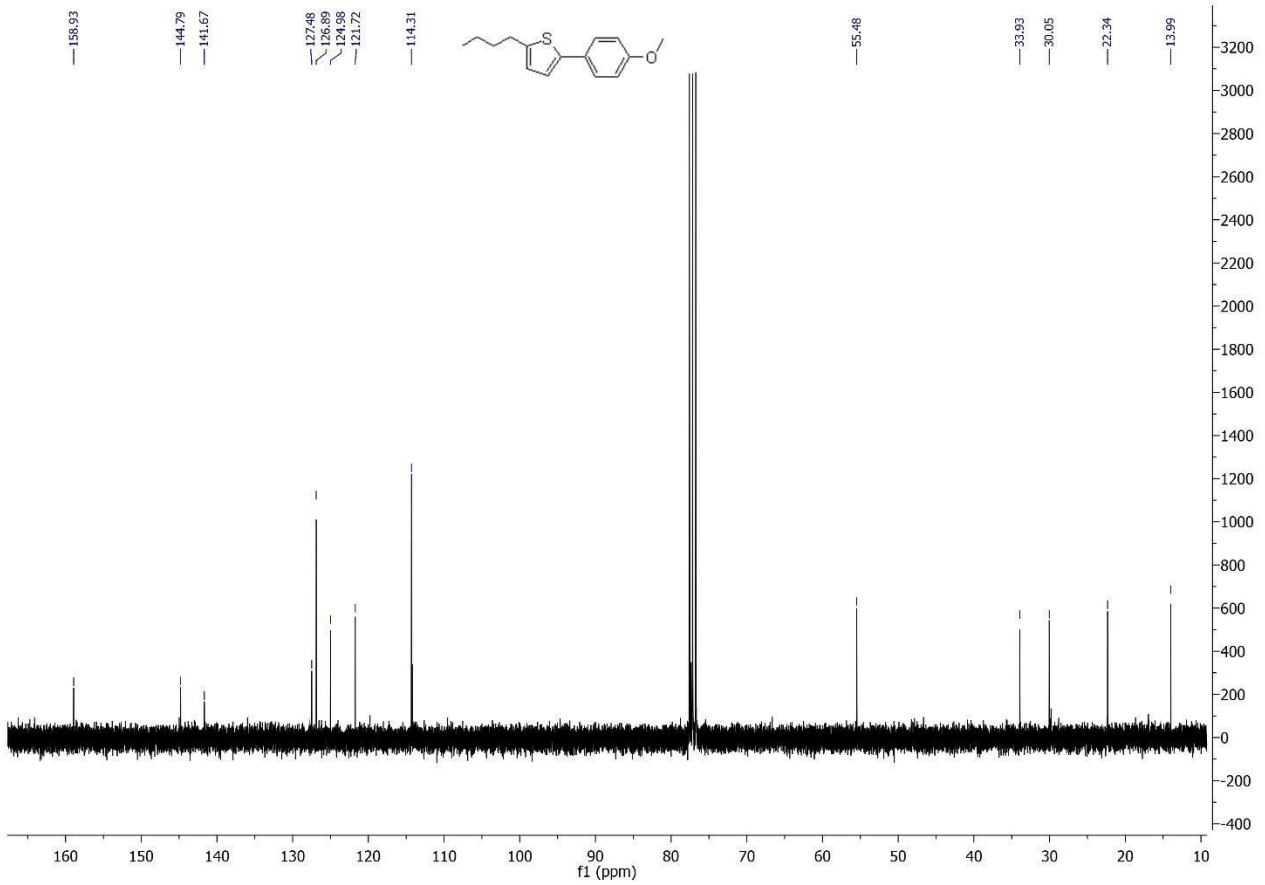

Figure S18. ^{13}C NMR of 2-butyl-5-(4-methoxyphenyl)thiophene (12)

2-methyl-5-(o-tolyl)thiophene (13)

2-iodotoluene (0.5 mmol, 109 mg), 2-methylthiophene (1 mmol, 98 mg), K_2CO_3 (1.5 mmol, 207 mg), and PivOH (0.5 mmol, 51 mg) were placed into a quartz vial equipped with a magnetic stirrer and suspended in GVL (3 mL). The vial was purged with N_2 and $Pd(OAc)_2$ (0.22 mg, 0.001 mmol, 0.2 mol%) was added. The mixture was heated to 140 °C under MW irradiation (average power 960 W) in a N_2 (1 MPa) atmosphere and under magnetic stirring (450 rpm). After 2 hours, the crude reaction was filtered on a silica pad (3 g) and washed with 3 mL EtOAc and, after solvent evaporation, purified by flash column chromatography (hexane), giving compound **13** as a yellow liquid (49 mg, 52% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39-7.36 (m, 1H), 7.24-7.19 (m, 3H), 6.85 (d, *J* = 3 Hz, 1H), 6.74 (m, 1H), 2.52 (s, 3H), 2.44 (s, 3H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 141.2, 140.0, 136.3, 134.9, 131.1, 130.7, 127.9, 126.7, 126.31, 125.7, 21.7, 15.7.

GC-EIMS (m/z %): 115 (20), 129 (30), 155 (24), 173 (25), 188 (M^+, 100)

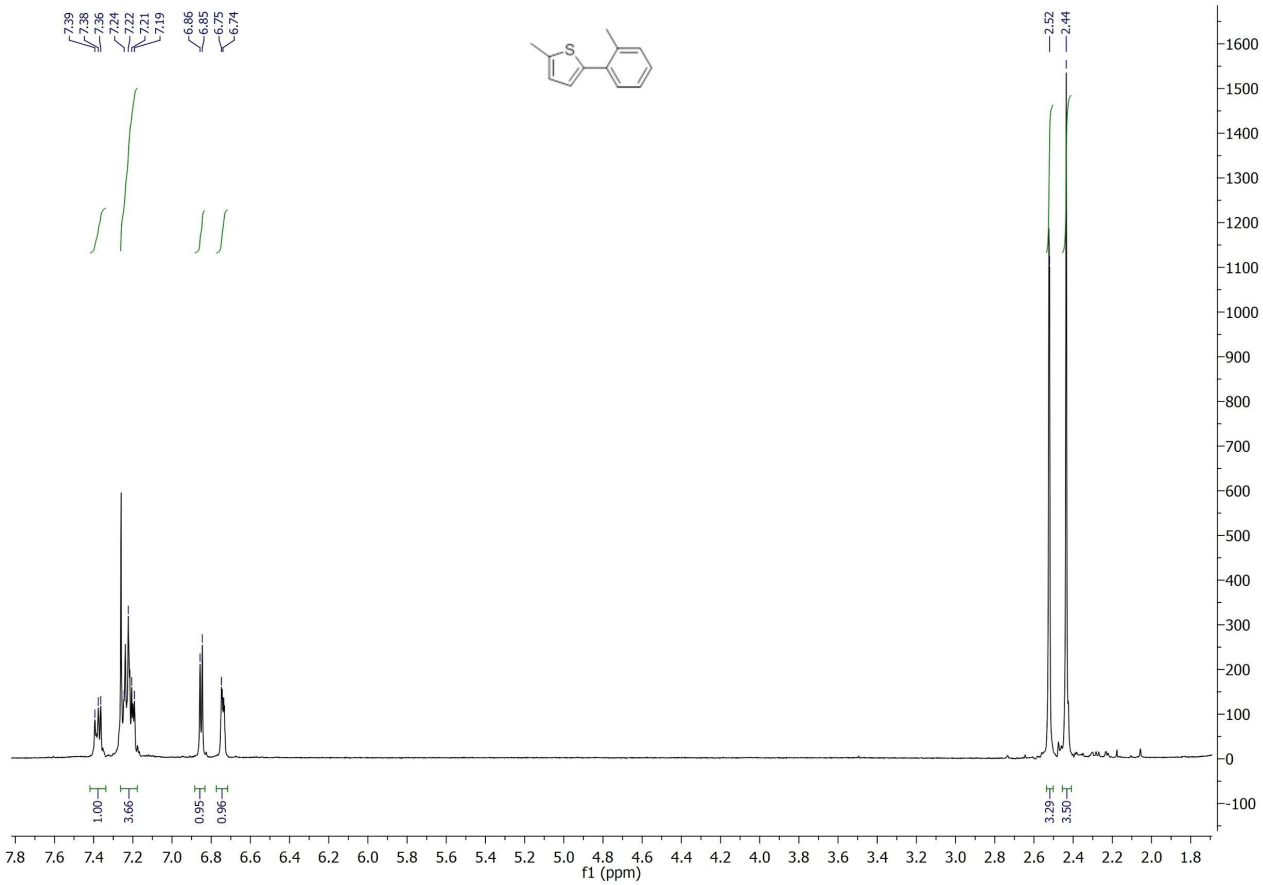

Figure S19.[1]H NMR of 2-methyl-5-(o-tolyl)thiophene (13)

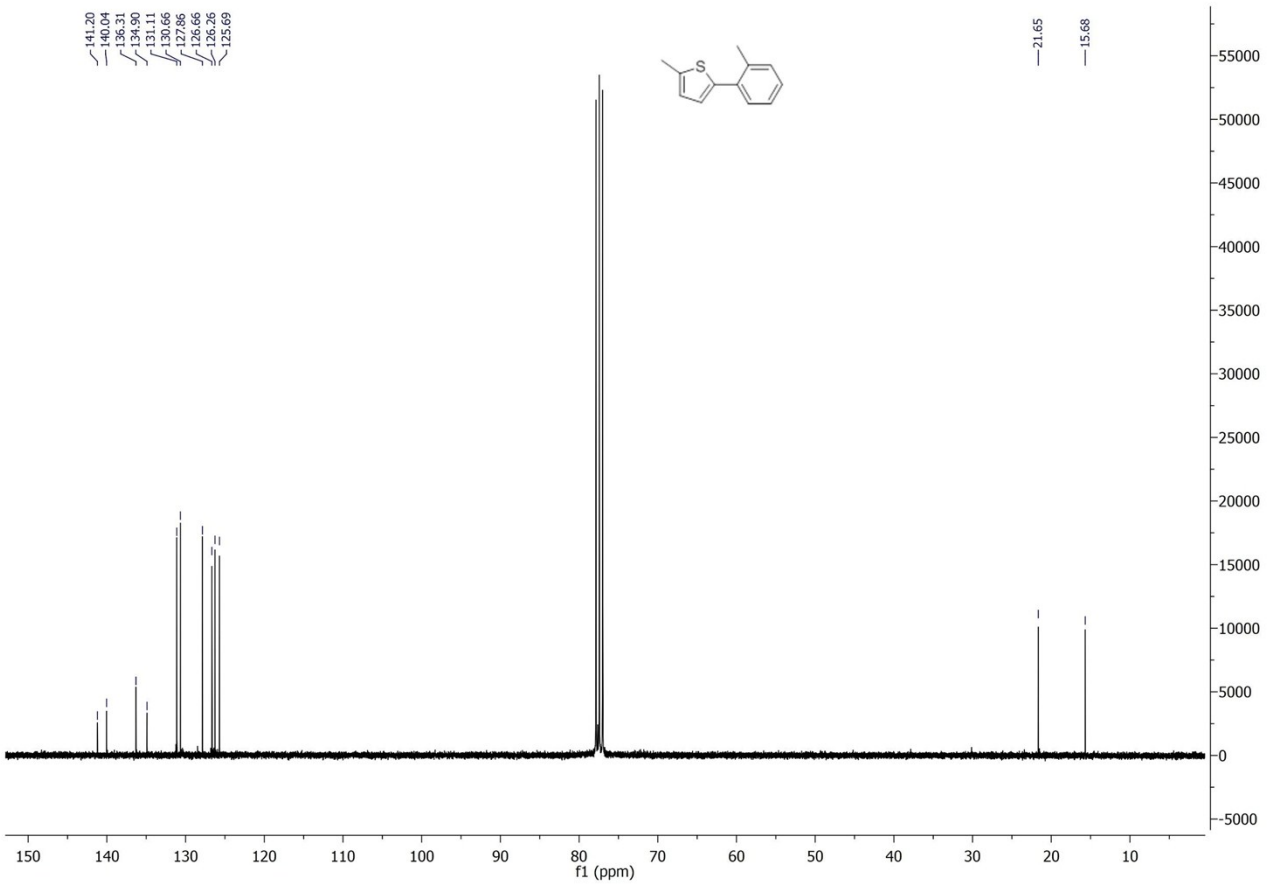

Figure S20. ^{13}C NMR of 2-methyl-5-(o-tolyl)thiophene (13)

2-(4-nitrophenyl)benzo[b]thiophene (14)

1-bromo-4-nitrobenzene (0.5 mmol, 101 mg), benzothiophene (1 mmol, 134 mg), and KOAc (1 mmol, 98 mg) were placed into a quartz vial equipped with a magnetic stirrer and suspended in GVL (3 mL). The vial was purged with N_2 and $Pd(OAc)_2$ (0.22 mg, 0.001 mmol, 0.2 mol%) was added. The mixture was heated to 140 °C under MW irradiation (average power 960 W) in a N_2 (1 MPa) atmosphere and under magnetic stirring (450 rpm). After 2 hours, 3 mL of water were added, the mixture was cooled to 0°C and the newly-formed precipitate was filtered and washed with 1 mL of water. Lastly, the solid was dried under vacuum and purified by column chromatography (hexane). Compound **14** was obtained as a yellow solid (92 mg, 72% yield). **^{1}H NMR (300 MHz, $CDCl_3$)**: δ 8.28 (d, *J* = 9 Hz, 2H), 7.87-7.84 (m, 4H), 7.72 (s, 1H), 7.41 -7.39 (m, 1H), 7.42-7.39 (m, 2H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)**: δ 147.3, 141.3, 140.7, 140.4, 140.3, 126.9, 125.7, 125.2, 124.5, 124.4, 122.6 ppm. **GC-EIMS (m/z %):** 165 (47), 208 (52), 225 (20), 255 (M^+, 100)

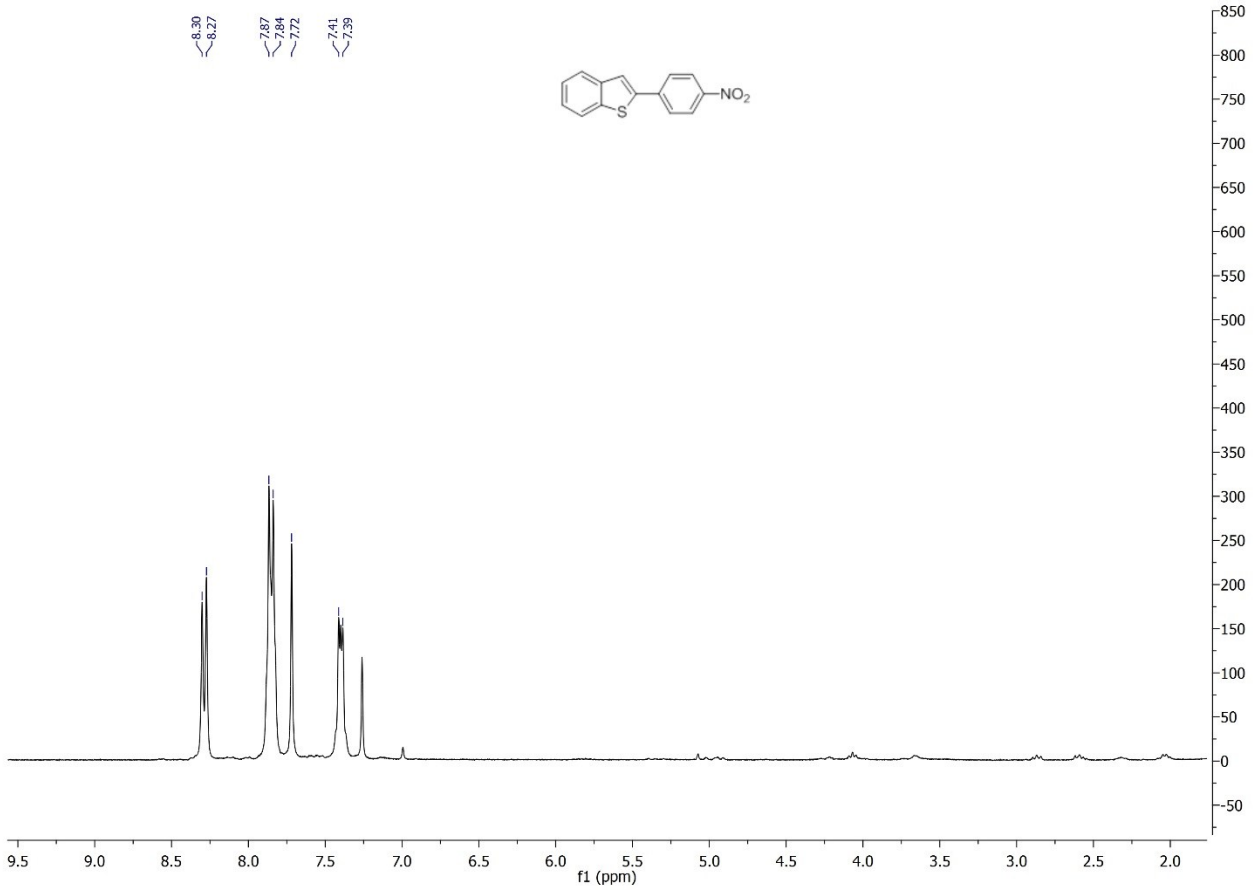

Figure S21. ^{1}H NMR of 2-(4-nitrophenyl)benzo[b]thiophene (14)

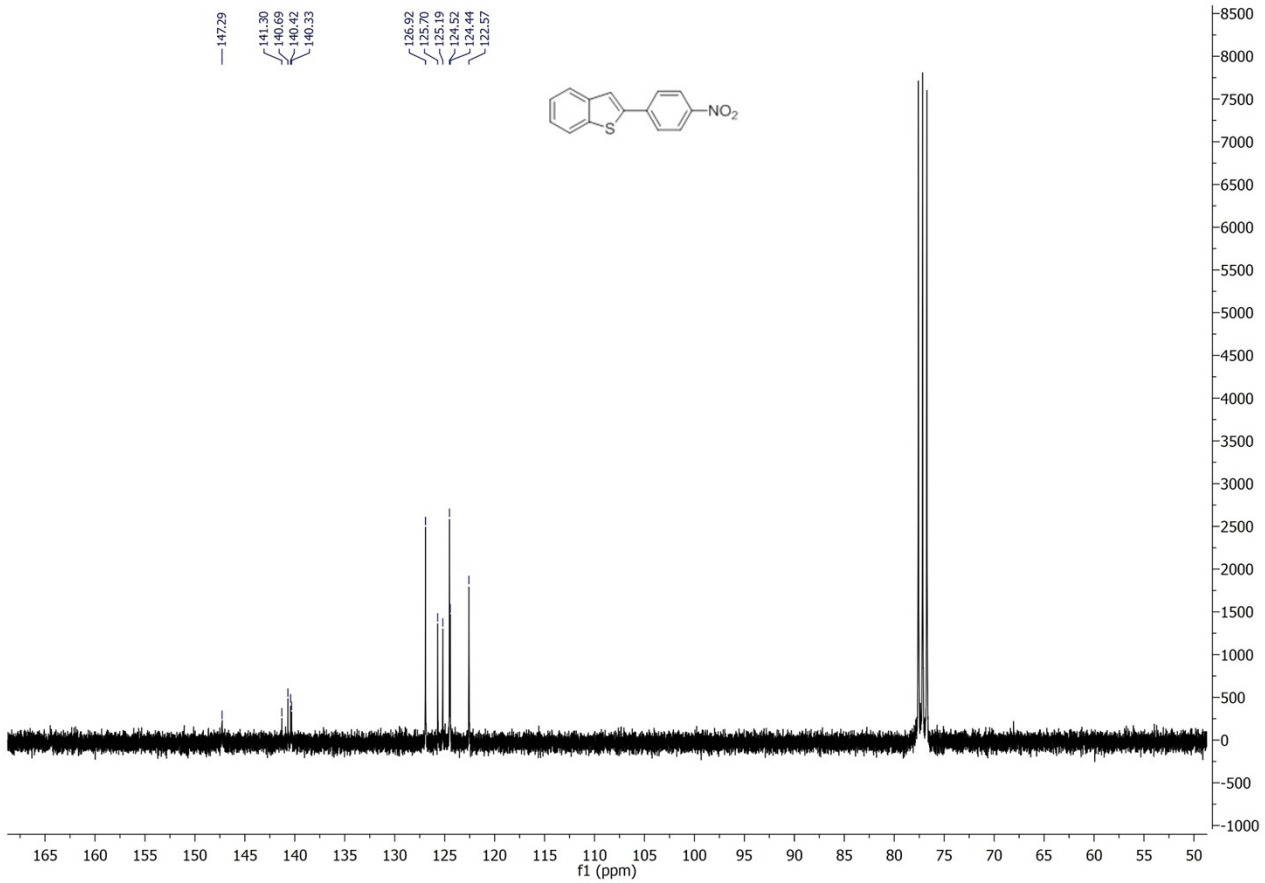

Figure S22. ^{13}C NMR of 2-(4-nitrophenyl)benzo[b]thiophene (14)

Poly(3-hexyl)thiophene (P3HT)

2-bromo-3-hexylthiophene (2 mmol, 490 mg), K_2CO_3 (6 mmol, 800 mg), and PivOH (2 mmol, 204 mg) were placed into a quartz vial equipped with a magnetic stirrer and suspended in GVL (2 mL). The vial was purged with N_2 and $Pd(OAc)_2$ (1 mg, 0.004 mmol, 0.2 mol%) was added.
The mixture was heated to 100 °C for 3 hours under MW irradiation (average power 960 W) and magnetic stirring (450 rpm) in a N_2 (1 MPa) atmosphere. After cooling to room temperature, the crude reaction was poured into vigorously stirred MeOH (10 mL). Centrifugation of the resulting mixture at 4000 rpm for 15 minutes led to the precipitation of P3HT. The supernatant was removed by decantation, 10 mL of distilled water were added and the mixture was centrifuged under the same conditions to remove the water soluble salts. The deep purple residue obtained after the decantation of water was then dried under vacuum to give a solid of poly(3-hexyl)thiophene (125 mg, 75 % yield, Mn = 25 136 Da).
^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.98 (m, 1H), 2.80 (s, br, 2H), 1.70 (s, br, 2H), 1.34 (s, br, 6H) 0.91 (s, br 3H) ppm; **^{13}C NMR (75 MHz, $CDCl_3$)**: δ = 139.9, 133.7, 130.5, 128.6, 31.7, 30.5, 29.5, 29.3, 22.7, 14.1 ppm. HT/HT regioregularity = 80 %, based on relative peak integration of the signals at 2.60 (HH isomer, 0.41H) and 2.79 (HT isomer, 1.59H)

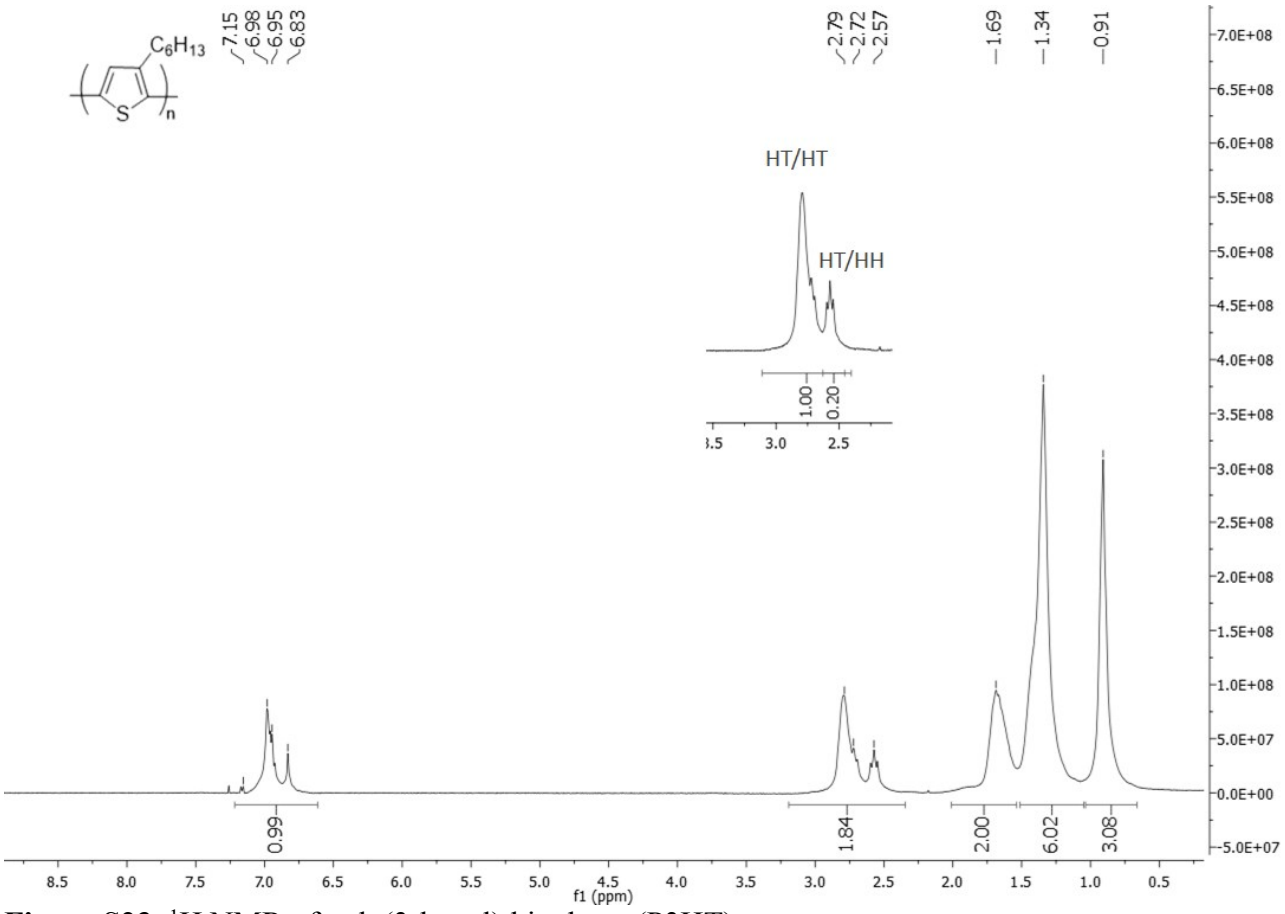

Figure S23. ^{1}H NMR of poly(3-hexyl)thiophene (P3HT)

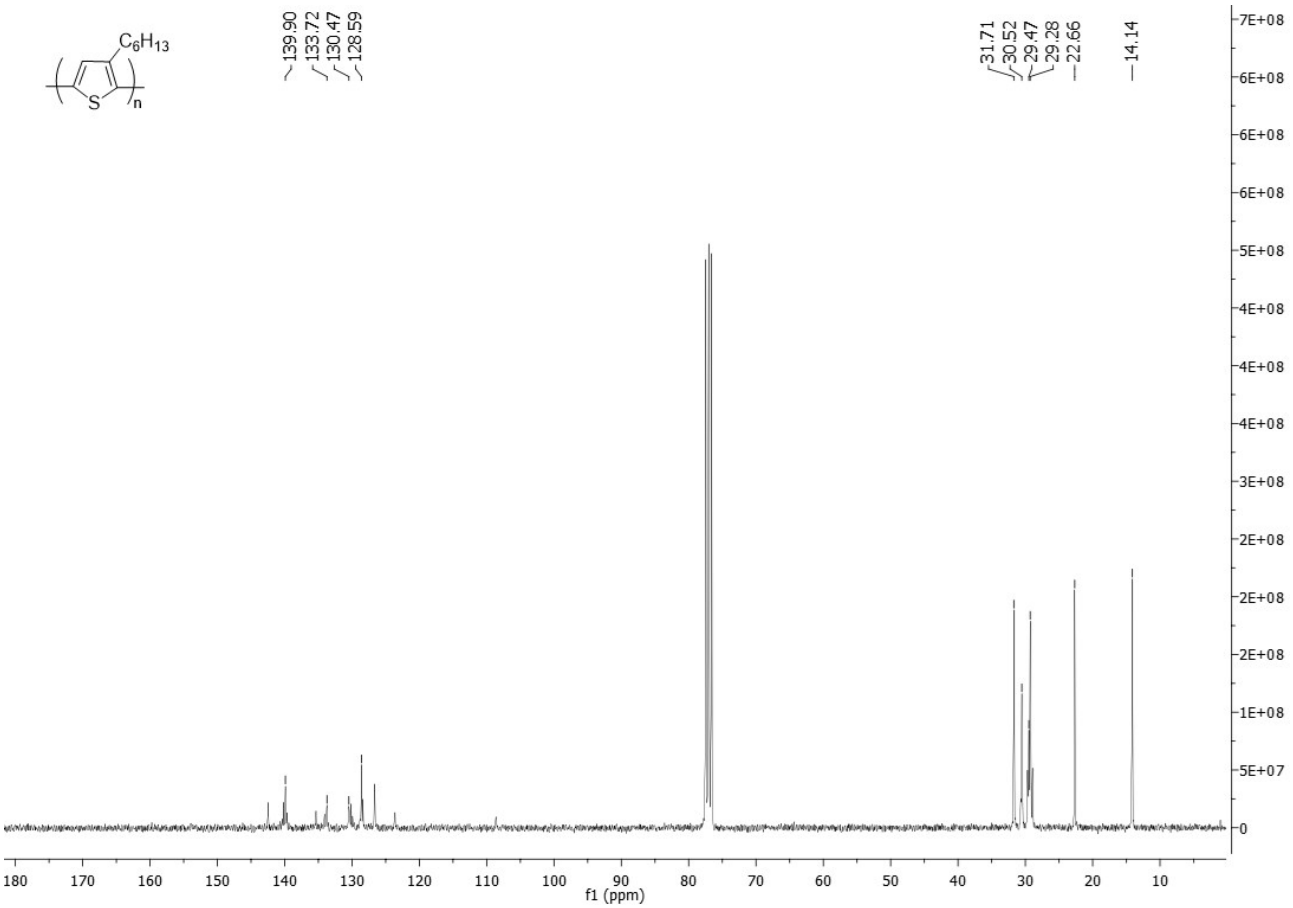

Figure S24. [13] C NMR of poly(3-hexyl)thiophene (P3HT)

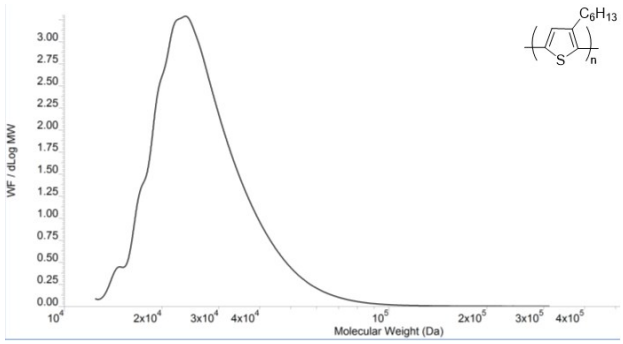

Figure S25. Size exclusion chromatogram of poly(3-hexyl)thiophene (P3HT)

COMPUTATIONAL DETAILS

Computational studies were conducted using the G09 D.01 suite of programs.[10] DFT calculations were performed using the WB97XD functional. The atoms (C, H, O) were represented by a 6-311G(d,p) basis set.[11] The Pd atom was represented by the relativistic effective core potential (RECP) from the Stuttgart group and the associated basis set.[12] The S atom was represented by RECP from the Stuttgart group and the associated basis set,[13] augmented by a d polarization function (α= 0.503).[14] Full optimization of geometry was performed without symmetry constraints, including implicit Dimethyl acetamide (DMAc) as the solvent (PCM),[15] using the SMD,[16] solvation model. This was followed by the analytical computation of the Hessian matrix to identify the nature

of the located extrema, as minima or transition states. DMAc was used as the solvent in calculations, since it possesses a dielectric constant that is similar to GVL (ε = 36.47 for GVL and 37.8 for DMAc). The connection between the reactant and product, through a given transition state, was checked using IRC (Intrinsic Reaction Coordinate) calculations. Gibbs free energies values G (T = 298 K, P = 1 atm) reported in the text are given in kcal mol^{-1}. Images were created using CYLview software.[17]

Computed geometries and energies

GVL

15
E: -345.811954635 ; H: -345.677226 ; G: -345.714623

C	-0.54694183	0.04576891	-0.24494603
C	0.97832363	0.03075487	-0.08397373
C	0.35459307	2.25042905	-0.21019807
C	-0.90190527	1.48018788	0.12930775
H	-0.81502639	-0.15112339	-1.28513426
H	-1.02622872	-0.70288267	0.38586553
H	1.46833647	-0.58461110	-0.83816938
H	-1.08164171	1.60096209	1.20192745
H	-1.75643049	1.89519906	-0.40354014
O	1.38210864	1.39838433	-0.36496667
O	0.49112013	3.43721327	-0.33300393
C	1.45126069	-0.35528937	1.30302697
H	1.24143907	-1.41314867	1.48139409
H	2.52758796	-0.19642891	1.40149685
H	0.94069358	0.23258307	2.07214401

DMAc

15
E: -287.827023475 ; H: -287.687562 ; G: -287.727209

O	-1.51967501	1.02451654	0.06681165
C	-1.57735681	1.79910697	1.01505576
N	-0.61899044	1.83212042	1.98053112
C	-0.67225724	2.65599385	3.17288528
H	-1.40919310	3.44942319	3.07965379
H	-0.91955840	2.05299171	4.05481068
H	0.30478689	3.11942666	3.33808499
C	0.48086097	0.88884737	1.93506460
H	0.39667249	0.15311644	2.74364332
H	0.46701950	0.36874848	0.98050182
H	1.43239236	1.41702786	2.04871419
C	-2.73032889	2.77233345	1.14501752
H	-3.28845940	2.61148424	2.07079094
H	-2.38318203	3.80869056	1.13733407

H	-3.39499389	2.61396526	0.29750529

$Pd(DMAc)_2$

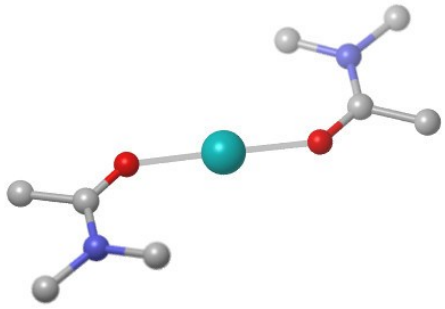

Figure S26. Calculated structure of $Pd(DMAc)_2$

31
E: -703.587466031 ; H: -703.303414 ; G: -703.373225

Pd	0.03465274	0.09414069	-0.10725106
O	1.33024110	-1.40198090	-0.82806598
C	1.63114056	-2.07068808	-1.83174151
N	0.91473739	-2.09903082	-2.96730614
O	-1.27521497	1.56623195	0.64019522
C	-1.54831010	2.22241153	1.66018759
N	-0.71390817	2.39077186	2.69938056
C	-1.06949303	3.20952920	3.85245491
H	-0.85604388	4.26775483	3.66921552
H	-2.11955487	3.09411110	4.11404272
H	-0.47432666	2.87810164	4.70395500
C	0.66774873	1.94054857	2.67638300
H	0.87478978	1.34244686	3.56742780
H	0.85545771	1.33091804	1.78944729
H	1.34063449	2.80428061	2.66698901
C	1.29372538	-2.92247739	-4.10895542
H	2.37430343	-2.99141541	-4.21389301
H	0.87329385	-3.93005643	-4.02499575
H	0.89865913	-2.45656960	-5.01257203
C	-0.37611940	-1.44493918	-3.10108561
H	-0.63765188	-0.92238761	-2.17795569
H	-0.34455398	-0.72060948	-3.91986876
H	-1.14409177	-2.19290492	-3.32062772
C	2.88527086	-2.90538440	-1.77049440
H	2.68341973	-3.95101965	-2.01304345
H	3.63477125	-2.53389535	-2.47414532
H	3.28802666	-2.83941006	-0.76171439
C	-2.90488608	2.87531422	1.73666483
H	-3.51261250	2.41316489	2.51917780
H	-2.82617123	3.94216279	1.95623276
H	-3.40285471	2.73859437	0.77880036

$Pd(GVL)_2$

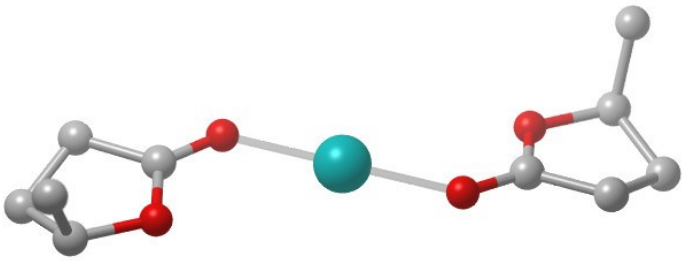

Figure S27. Calculated structure of $Pd(GVL)_2$

31
E: -819.554795099 ; H: -819.280086 ; G: -819.346359

C	-0.71406813	-0.47942038	-0.26603249
C	0.76767745	-0.57533812	0.11297025
C	0.29114711	1.65793494	-0.12417950
C	-1.04206738	0.98288387	0.02530369
H	-0.84597242	-0.69127339	-1.32852898
H	-1.31988760	-1.17958382	0.30822337
H	1.33457149	-1.21106780	-0.56504404
H	-1.37832950	1.14289161	1.05417112
H	-1.77491902	1.43104036	-0.64397954
O	1.27811176	0.78221119	-0.11303331
O	0.48403645	2.85613568	-0.23835610
C	1.02779284	-0.95709418	1.55379510
H	0.73490900	-1.99835994	1.70939407
H	2.08887187	-0.85927795	1.79324387
H	0.45103414	-0.32928644	2.23950419
Pd	2.30985103	3.89048683	-0.40282309
O	4.14644793	4.90274871	-0.53929604
C	4.39450788	6.07394801	-0.76605943
C	5.75880133	6.70102954	-0.79373374
O	3.45059431	6.96196560	-1.01646555
C	5.50267380	8.03584801	-1.48763189
H	6.08649042	6.82042196	0.24353649
H	6.46863741	6.04857676	-1.29996992
C	4.02711999	8.30323136	-1.17277508
H	5.64537677	7.93420215	-2.56487395
H	6.14118676	8.84077527	-1.12512103
H	3.49512337	8.75024394	-2.01081818
C	3.78534629	9.08562155	0.09901148
H	4.15635246	10.10549267	-0.02950599
H	2.71854223	9.13338932	0.32771212
H	4.30785899	8.63291856	0.94687971

PdDMAc

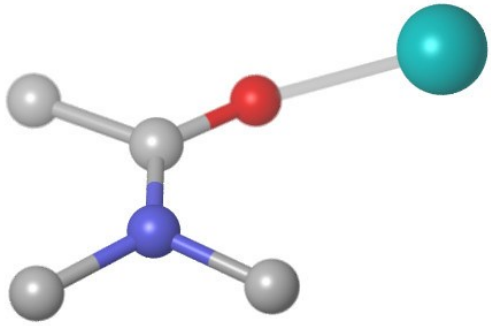

Figure S28. Calculated structure of PdDMAc

16
E: -415.725327501 ; H: -415.582828 ; G: -415.629790

Pd	-0.13726934	0.04348382	-1.19895532
O	-1.59283190	0.97965025	0.10462402
C	-1.58720284	1.79077618	1.04643704
N	-0.59774425	1.84962059	1.95457510
C	-0.63727775	2.71175728	3.12691004
H	-1.35663873	3.51667689	3.00605916
H	-0.90034962	2.13482156	4.01988717
H	0.34854466	3.15686464	3.27713530
C	0.47940530	0.87337588	1.93951857
H	0.18728832	-0.04272481	2.46373248
H	0.74603028	0.61319320	0.90747804
H	1.35074637	1.30276689	2.43483692
C	-2.74859850	2.74400347	1.17783044
H	-3.26000698	2.61833384	2.13506622
H	-2.41690930	3.78251395	1.10294580
H	-3.44671635	2.53616315	0.36936987

PdGVL

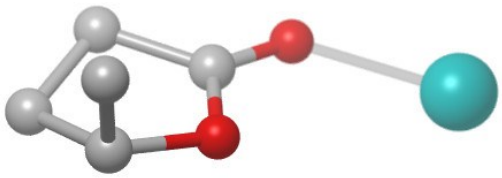

Figure S29. Calculated structure of PdGVL

16
E: -473.708790725 ; H: -473.571043 ; G: -473.616124

C	-0.55255700	0.03147888	-0.24386689
C	0.96733835	-0.03136139	-0.05943309
C	0.40768392	2.19368166	-0.16666709
C	-0.87552075	1.47306015	0.13954271
H	-0.81172640	-0.14821699	-1.28892123
H	-1.06216186	-0.70604054	0.37540800
H	1.45848910	-0.63859262	-0.81792601
H	-1.06979573	1.59145140	1.20997043
H	-1.70548200	1.91963341	-0.40589570
O	1.40897784	1.34312952	-0.31695993
O	0.55743538	3.39694014	-0.26695801
C	1.41399453	-0.43674576	1.32826571
H	1.17566990	-1.49080846	1.49074550
H	2.49237560	-0.30679365	1.44156849
H	0.90629677	0.15491098	2.09598695
Pd	2.37810086	4.49171205	-0.68135889

Methyl thiophene

12
E: -204.319556230 ; H: -204.218030 ; G: -204.254684

C	-0.36519392	0.34610826	-0.00924482
C	0.99638612	0.38548572	0.00845988
C	1.53277857	1.70948863	0.00866384
C	0.56954866	2.66721486	-0.00852586
S	-1.01726075	1.96601115	-0.02729592
H	1.60318375	-0.51217091	0.02166463
H	2.59237956	1.93242283	0.02130185
H	0.68627727	3.74155626	-0.01456541
C	-1.26155001	-0.85055717	-0.00233960
H	-1.86318125	-0.89647272	0.91031411
H	-1.94926211	-0.84911162	-0.85266007
H	-0.65883544	-1.75969891	-0.05498417

II-GVL

47
E: -1166.32996282 ; H: -1165.913934 ; G: -1165.996228

Pd	-0.80538756	-1.23650792	-1.14783243
C	0.74080094	-2.14017791	-0.34582023
C	2.01836145	-1.57402630	-0.25491774
C	3.06467168	-2.25826496	0.34632436
C	2.86770863	-3.53913695	0.86823244
C	1.60282008	-4.11832413	0.78652841

C	0.55608987	-3.41352693	0.18894324
H	1.41257835	-5.10753573	1.18396608
H	4.04926768	-1.80902926	0.41969078
H	2.22201275	-0.58397493	-0.64858826
O	-2.94803085	-0.63682567	-1.49166780
C	-3.22415645	-1.42578575	-0.55667324
O	-2.27323342	-2.07746544	0.00335009
C	-4.63859782	-1.60647389	-0.02717332
C	-4.91224735	-3.10006487	0.18886062
H	-5.92477339	-3.23711859	0.58009503
H	-4.83219002	-3.65353118	-0.75174325
H	-4.20638633	-3.53197857	0.90094625
C	-4.71106713	-0.86081250	1.31728073
H	-3.98628644	-1.26118300	2.03059596
H	-4.51270941	0.20729430	1.18585508
H	-5.71151820	-0.97066699	1.74652220
C	-5.65483896	-1.01708813	-1.00592345
H	-5.47444613	0.04644870	-1.17603744
H	-5.61772816	-1.52664251	-1.97257548
H	-6.66357872	-1.13290516	-0.59791313
H	-0.42364112	-3.87927557	0.15416127
O	3.95183921	-4.12981892	1.42808111
C	3.78865199	-5.42128693	1.98900190
H	4.76150507	-5.70119599	2.39094560
H	3.05280000	-5.41652929	2.80032799
H	3.48966726	-6.15431370	1.23185424
O	0.41084568	-0.24906603	-2.52888814
C	0.80113119	0.90382394	-2.36232676
C	0.52086246	1.82315547	-1.21316801
O	1.55822731	1.46680853	-3.26880665
C	1.55676601	2.92681481	-1.40779064
H	-0.50917732	2.17691916	-1.32570783
H	0.58935987	1.28705816	-0.26665280
C	1.84083093	2.86916692	-2.91213140
H	2.46249169	2.69645564	-0.84445188
H	1.19661188	3.90996567	-1.10776101
H	2.89377144	3.01450569	-3.14618292
C	0.96639616	3.76331116	-3.76082383
H	1.21175367	4.80725407	-3.55124362
H	1.13678975	3.57593912	-4.82303318
H	-0.09310422	3.60639517	-3.53886710

III-GVL

59
E: -1370.66562315 ; H: -1370.146987 ; G: -1370.247193

Pd	-0.04098062	0.66327757	0.22315111
C	-3.82259207	-0.51895730	1.74886868
C	-2.54318536	0.01926103	1.58448257

C	-1.86131196	-0.07410767	0.37634310
C	-2.48269610	-0.75375356	-0.67559210
C	-3.75129469	-1.29718850	-0.52872904
C	-4.43512406	-1.17641447	0.68392602
O	1.96018958	1.36874844	0.33113023
C	2.78605527	1.30576696	-0.64819870
O	2.47690451	1.13147706	-1.82963853
H	-2.09008551	0.52890479	2.43022062
H	-4.23221292	-1.81711233	-1.35058372
H	-4.32087097	-0.41397928	2.70470346
H	-1.98190975	-0.85669579	-1.63294940
C	4.27193486	1.40754549	-0.23827646
H	0.38830400	1.97231538	-1.93647780
C	-0.55653611	2.15718715	-1.43284190
C	-0.63319146	2.75855175	-0.17309338
S	-2.27035711	3.27711307	0.16237375
C	-2.85106464	2.59638184	-1.33917495
C	-1.83667287	2.06310582	-2.06743074
H	-1.99240762	1.58492907	-3.02576067
H	0.17799341	3.24065321	0.35699578
C	-4.31235321	2.55496160	-1.63728157
H	-4.78746481	3.53005683	-1.50309800
H	-4.47038451	2.23072822	-2.66737607
H	-4.81512795	1.84271338	-0.97499852
C	4.45669786	2.43324400	0.88453133
H	4.12995513	3.42967473	0.56923872
H	3.88156711	2.15556808	1.77017913
H	5.51402611	2.49893695	1.16339643
C	5.13651061	1.78907763	-1.43989453
H	6.19348301	1.81522398	-1.15340290
H	5.01610630	1.07116076	-2.25331432
H	4.86613658	2.77758819	-1.82398677
C	4.67509209	0.01383243	0.27108501
H	4.58370950	-0.73849129	-0.51875535
H	5.71470864	0.01780170	0.61619280
H	4.04026942	-0.29274203	1.10687911
O	-5.67435255	-1.72898834	0.72763198
C	-6.41076485	-1.61170026	1.93175909
H	-6.59192844	-0.56257470	2.19114845
H	-7.36632988	-2.10297678	1.75080253
H	-5.90545223	-2.11136371	2.76577823
O	0.71169351	-1.15942511	1.07819406
C	1.20962478	-1.13397075	2.19713717
C	1.21622840	-0.00782425	3.18627955
O	1.83007163	-2.19308394	2.66338793
C	1.59794176	-0.70648297	4.48775549
H	1.96443529	0.71143547	2.83862117
H	0.24837205	0.49437357	3.19851101
C	2.39060016	-1.92204075	3.99772962
H	0.70202401	-1.02827873	5.02123746
H	2.19675485	-0.08270217	5.15033222

H 2.18703401 -2.82156700 4.57595469
C 3.87850021 -1.68671488 3.86627769
H 4.31641563 -1.61384079 4.86494979
H 4.35961671 -2.51347513 3.33945293
H 4.08757719 -0.75528569 3.33267783

TS-III-GVL

59
E: -1370.64091515 ; H: -1370.127457 ; G: -1370.225747
Pd 0.21928383 -0.20926120 0.15743190
C -3.95789309 -0.97287330 0.82931157
C -2.66976494 -0.43554347 0.89960881
C -1.64608050 -0.84880227 0.04895919
C -1.96639152 -1.82782758 -0.90329657
C -3.24212133 -2.36690686 -0.99464046
C -4.25067258 -1.94366384 -0.12590623
O 2.31379384 0.34657664 0.22418971
C 2.73009205 1.30855886 -0.46288752
O 1.96407543 2.13827854 -1.04173233
H -2.48302508 0.33518367 1.64154468
H -3.47551843 -3.12198390 -1.73811300
H -4.71481984 -0.61819873 1.51837032
H -1.20983483 -2.18526598 -1.59601126
C 4.23845945 1.53158138 -0.61163321
H -1.60216920 1.68123588 -1.94225051
C -1.51434571 2.09190091 -0.94281061
C -0.45814936 1.74389361 -0.10740438
S -0.66198969 2.64234994 1.40027921
C -2.11641085 3.40791897 0.87234678
C -2.43398069 3.01022499 -0.40580413
H -3.30489282 3.38352042 -0.93076153
H 0.73095824 1.90912249 -0.63056546
C -2.86908648 4.36674122 1.73550835
H -2.25518427 5.23340893 1.99674471
H -3.75808854 4.72008278 1.21023446
H -3.18636922 3.89293204 2.66848057
O -5.46676875 -2.52620956 -0.28924335
C -6.52302177 -2.09452662 0.54900209
H -7.40089892 -2.66538917 0.24777468
H -6.31087900 -2.29689665 1.60474776
H -6.72968546 -1.02647868 0.41788234
C 4.56970408 1.67603541 -2.10293846
H 4.02731701 2.51267619 -2.54751280
H 5.64232123 1.85269465 -2.22895699
H 4.31004168 0.76630162 -2.65412512
C 4.58875994 2.83261864 0.12774511
H 4.33889567 2.76198488 1.19124681
H 5.66255585 3.02698674 0.04501008
H 4.05187070 3.68411931 -0.29651683
C 5.02650577 0.36616787 -0.01518862

H	4.82112194	0.24558520	1.05069028
H	4.78195205	-0.57493879	-0.51400186
H	6.09861580	0.54846842	-0.13967151
O	0.91312583	-2.21586763	0.49313898
C	1.50393573	-2.84268579	-0.37271187
C	2.19360508	-4.16281182	-0.20225703
O	1.60364579	-2.39965705	-1.60772792
C	2.41410912	-4.61628889	-1.64373360
H	3.13079887	-3.97388378	0.33023239
H	1.58785756	-4.83362420	0.40514475
C	2.44663194	-3.29282559	-2.41490209
H	1.57530383	-5.22806317	-1.98014722
H	3.33653352	-5.17912620	-1.78142875
H	1.95180680	-3.35637395	-3.38212018
C	3.81878710	-2.67029534	-2.54624890
H	4.42734102	-3.28031582	-3.21842809
H	3.74873433	-1.66288913	-2.96227359
H	4.32291373	-2.61851900	-1.57711340

IV-GVL

59

E: -1370.66460655 ; H: -1370.145804 ; G: -1370.244101

Pd	0.51994040	-0.05113721	-0.08413950
C	-2.59958421	-2.37631367	1.62409631
C	-1.45129907	-1.61347997	1.39648506
C	-1.20675296	-0.97752768	0.17738859
C	-2.18231223	-1.12475600	-0.81938790
C	-3.32522974	-1.88677455	-0.61473399
C	-3.54421982	-2.52050971	0.61045206
O	2.53373701	0.84892183	-0.25786343
C	2.95998419	1.96594688	-0.51894825
O	2.18643304	2.94157911	-0.94578156
H	-0.73241690	-1.53152075	2.20588531
H	-4.06750279	-1.99715084	-1.39867734
H	-2.73520463	-2.84812439	2.58977583
H	-2.05618268	-0.63694145	-1.78092945
C	4.42034631	2.34984696	-0.36364533
H	-0.59829511	1.84901430	-2.52613526
C	-0.83058937	2.25684475	-1.54808167
C	-0.50664485	1.60916257	-0.38077597
S	-1.07597914	2.57817666	0.96392787
C	-1.72413203	3.83559724	-0.06880092
C	-1.51107586	3.50759773	-1.37063874
H	-1.82756118	4.14068889	-2.19228609
H	1.25582997	2.62984401	-0.98925178
C	4.50882798	3.41517287	0.74383990
H	5.55868494	3.67277017	0.90762036
H	3.96962564	4.32455414	0.47020341

H	4.10009124	3.03838508	1.68633709
C	5.23923535	1.12035225	0.02943526
H	5.19147932	0.34547500	-0.73949787
H	6.28550634	1.41111823	0.15642413
H	4.88795501	0.69017976	0.97002048
C	4.93231570	2.92573435	-1.69304558
H	4.38760346	3.82823971	-1.97690891
H	5.99004773	3.18180836	-1.58789623
H	4.83837871	2.19382293	-2.50086262
C	-2.39176475	5.05098875	0.49128303
H	-2.71143717	5.70468087	-0.32367859
H	-3.27566114	4.79223087	1.08226190
H	-1.71944767	5.62323553	1.13768567
O	-4.68963645	-3.24317005	0.71712174
C	-4.95184874	-3.88480794	1.95197471
H	-5.90351494	-4.40058350	1.82822272
H	-4.17692222	-4.61878722	2.19946706
H	-5.04218137	-3.16133845	2.76996194
O	1.63822030	-1.91092865	0.15412716
C	2.02555127	-2.35019272	1.22302522
C	2.72516747	-3.65713714	1.45499300
O	1.84647069	-1.69316210	2.35281563
C	3.24812615	-3.51350236	2.88240646
H	1.97626159	-4.44891041	1.35594515
H	3.49100457	-3.81894051	0.69774123
C	2.27195578	-2.50650389	3.49827246
H	4.25828610	-3.10063869	2.87522354
H	3.25665054	-4.45251644	3.43465360
H	2.75734957	-1.81123035	4.18060776
C	1.04431929	-3.12282420	4.13296418
H	1.34083899	-3.67310666	5.02929117
H	0.32977294	-2.35035815	4.42558619
H	0.55115150	-3.81847733	3.44737516

TS-IV-GVL

59
E: -1370.63528615 ; H: -1370.117249 ; G: -1370.217416

Pd	-0.62313463	0.24218217	0.79018492
C	-1.81674155	3.74047992	2.71903991
C	-0.93923333	2.75950768	2.28814693
C	-1.01584785	2.21790201	0.98979932
C	-2.00365669	2.74586902	0.14347764
C	-2.89169503	3.73006394	0.56501310
C	-2.80545129	4.23401066	1.86405823
O	0.25796302	-1.85901910	0.33085143
C	1.10740631	-2.06442629	-0.52005672
H	-0.17689821	2.41054865	2.97721255
H	-3.63931297	4.09381339	-0.12899000
H	-1.74637036	4.14289635	3.72401061
H	-2.08316886	2.38644256	-0.87734936

C	1.74375005	-3.42114828	-0.77254638
C	0.58481053	1.69473456	0.17560746
C	2.99997456	2.39333339	-0.33010826
C	4.45531882	2.72319802	-0.24523617
H	4.65205300	3.51485715	0.48431257
H	5.05214587	1.85258888	0.04511690
H	4.81192055	3.06515414	-1.21971973
S	2.10015183	1.86099233	1.07566586
C	2.17889411	2.42631329	-1.41489170
C	0.83240230	2.04182626	-1.14220120
H	0.04747387	2.07165972	-1.88875405
H	2.52556071	2.73122931	-2.39624225
O	1.56638645	-1.10897623	-1.31190693
H	1.15421327	-0.25490019	-1.06855775
C	1.49109900	-3.82168348	-2.23500462
H	1.93708046	-3.10778434	-2.93038626
H	1.93586073	-4.80349675	-2.41924523
H	0.41967031	-3.88904454	-2.44636455
C	3.25477606	-3.29412652	-0.51362111
H	3.45221921	-2.96109907	0.50987007
H	3.72749640	-4.27063447	-0.65044162
H	3.72018505	-2.58746392	-1.20359138
C	1.13545567	-4.45987364	0.16838949
H	1.30305863	-4.19935268	1.21597928
H	0.05922977	-4.56180609	0.00995006
H	1.60150330	-5.43117989	-0.01926800
O	-3.61478550	5.19401404	2.37411692
C	-4.62355602	5.72853292	1.53469017
H	-5.14679492	6.47476393	2.13134419
H	-4.19638231	6.21341347	0.65012803
H	-5.33655036	4.95848678	1.22054243
O	-2.37500024	-0.99388970	1.68330145
C	-3.48315388	-0.98087687	1.18664260
C	-3.91533591	-0.35596022	-0.11171575
O	-4.50735439	-1.56153976	1.79653165
C	-5.28222034	-0.98619771	-0.35757586
H	-3.97033541	0.72492399	0.05079347
H	-3.17195609	-0.53920946	-0.88729873
C	-5.75079972	-1.32303161	1.06182511
H	-5.17803018	-1.89969126	-0.94607896
H	-5.98131109	-0.32109812	-0.86359109
H	-6.30157676	-2.26111048	1.11033505
C	-6.51561352	-0.21038261	1.74655882
H	-7.48220218	-0.07790944	1.25400948
H	-6.69487360	-0.45122425	2.79673689
H	-5.96818173	0.73566207	1.69256241

V-GVL

59

E: -1370.68319945 ; H: -1370.162977 ; G: -1370.263988

Pd	-0.00256188	0.67237732	0.74718249
C	-2.34083389	5.03331435	1.96753959
C	-1.14417555	4.38013670	1.72280104
C	-1.02039299	3.43793798	0.69434597
C	-2.15982715	3.18025993	-0.07288324
C	-3.36701039	3.82856174	0.15891857
C	-3.46650335	4.76677061	1.18684362
O	0.00796276	-1.63362219	0.42886324
C	1.03691058	-2.11538641	-0.01808447
H	-0.29400857	4.61876249	2.35331095
H	-4.21708043	3.58933354	-0.46702430
H	-2.41706509	5.76320214	2.76572681
H	-2.11861148	2.44651296	-0.87021919
C	1.29222174	-3.60475161	-0.15176258
C	0.24921431	2.70156941	0.43904020
C	2.76683425	2.67726666	-0.11577000
C	4.25388611	2.80355542	-0.04513650
H	4.56994310	3.84571764	0.06074918
H	4.66205599	2.24836513	0.80595637
H	4.70243028	2.40168401	-0.95647746
S	1.76589971	3.35397565	1.16998216
C	2.02175513	2.03621771	-1.03805616
C	0.58939667	2.00714475	-0.77061454
H	-0.10166987	1.94499939	-1.60690816
H	2.45981806	1.57253218	-1.91586650
O	2.04216822	-1.35271177	-0.41927152
H	1.77001504	-0.41795331	-0.27830620
C	2.48428831	-3.96975389	0.74968605
H	2.67970709	-5.04221791	0.66493955
H	3.38892764	-3.43182496	0.45854231
H	2.26895338	-3.74736124	1.79943218
C	0.05040909	-4.37993516	0.28655224
H	-0.20064913	-4.17032023	1.32917585
H	-0.81594141	-4.13036770	-0.33081897
H	0.24264015	-5.45184478	0.18927917
C	1.62659363	-3.91767573	-1.61866590
H	2.53262445	-3.40139859	-1.94175925
H	1.78776036	-4.99346532	-1.72866852
H	0.80646489	-3.62707963	-2.28187923
O	-4.58943668	5.45653400	1.49511826
C	-5.76115507	5.19054775	0.74208797
H	-6.08379899	4.15001613	0.85603942
H	-6.53092424	5.84922265	1.14214685
H	-5.61603647	5.41361219	-0.32033043
O	-0.80814985	-0.04733547	2.81456375
C	-0.15784164	-0.75993172	3.55044279
C	1.32321283	-1.03288416	3.52014959
O	-0.73810832	-1.42107669	4.54342793
C	1.58500484	-1.65310897	4.88856748
H	1.51382551	-1.73863748	2.70740468

H	1.87345618	-0.11626986	3.30806090
C	0.22859480	-2.27789197	5.23049152
H	1.83886077	-0.87971859	5.61579954
H	2.37875763	-2.39962698	4.88001562
H	-0.01252637	-2.19934890	6.28937888
C	0.05594682	-3.69993004	4.74128547
H	0.71793070	-4.36089930	5.30622986
H	-0.97269772	-4.03671081	4.88769074
H	0.30421641	-3.78589058	3.67867414

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