

Palladium-Catalyzed Cross-Coupling Reaction *via* C-H Activation of Furanyl and Thiofuranyl Substrates

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(Z)-1-Styryl-3-benzyl-benzimidazolium chloride (3)

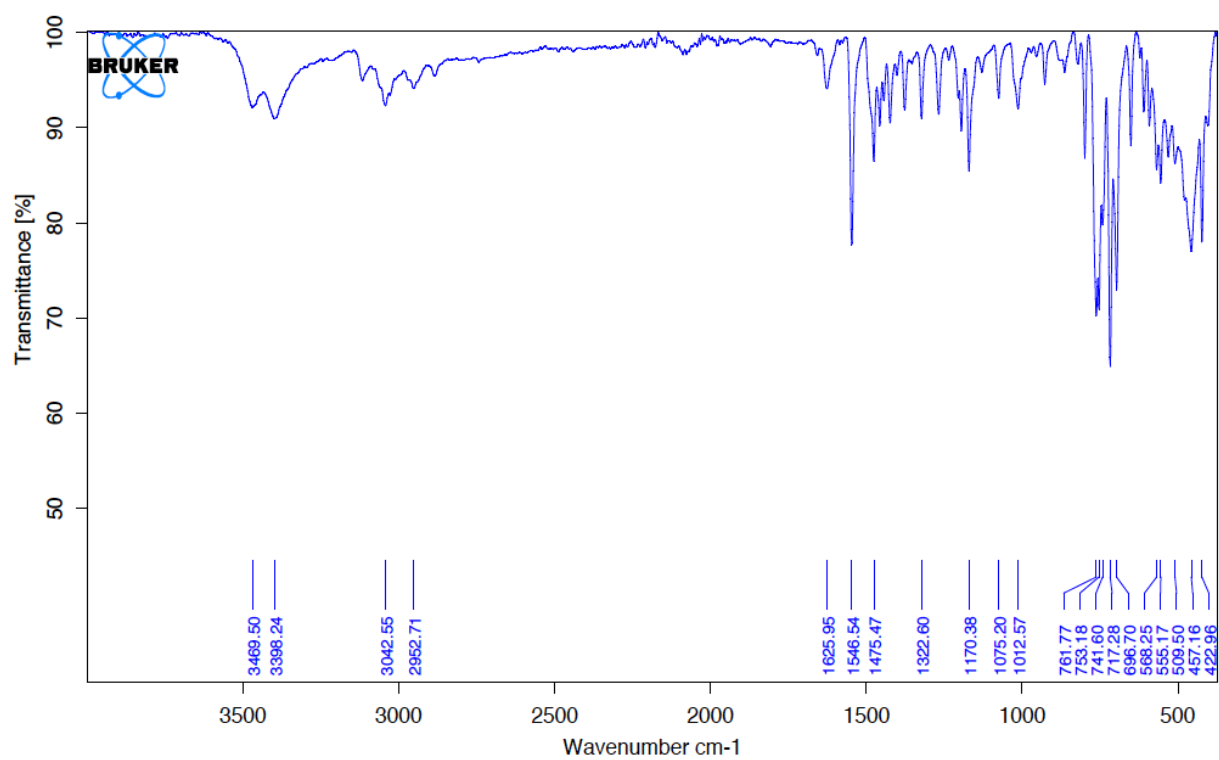
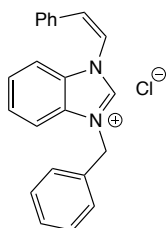


Figure S1. FT-IR spectrum

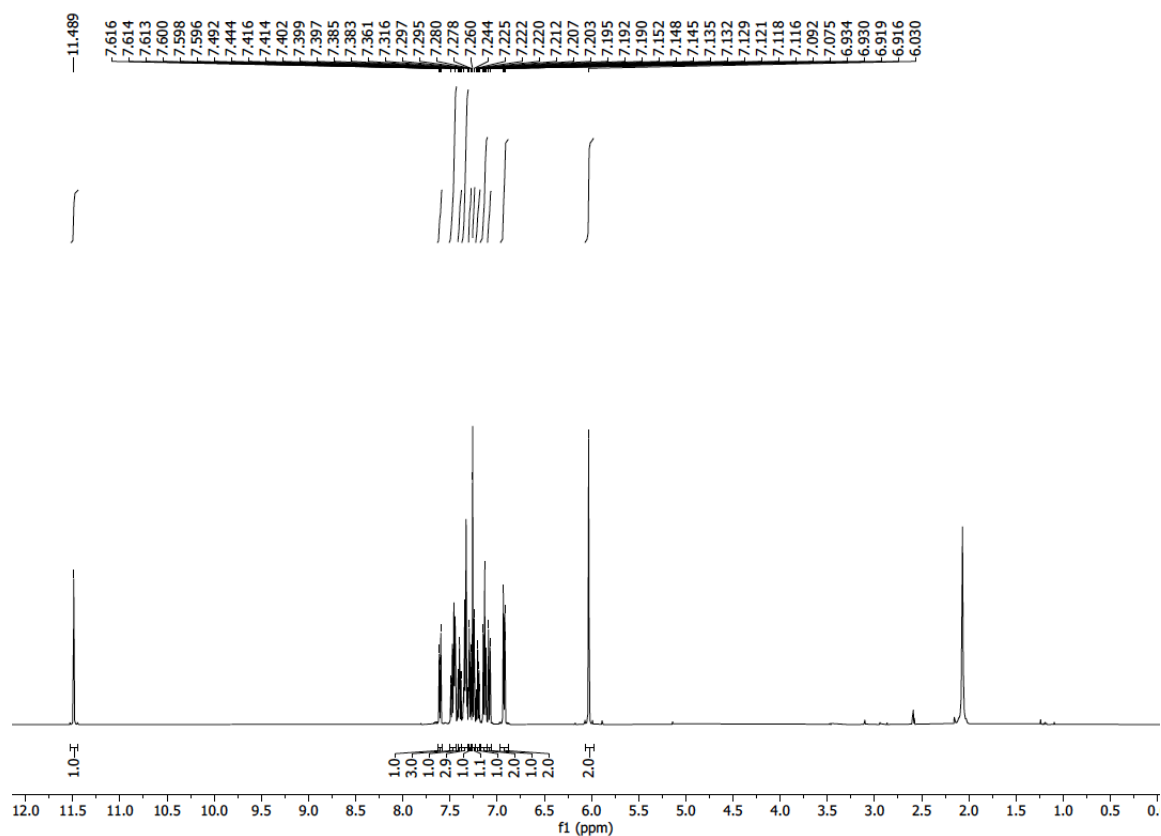


Figure S2. ^1H NMR spectrum (CDCl_3)

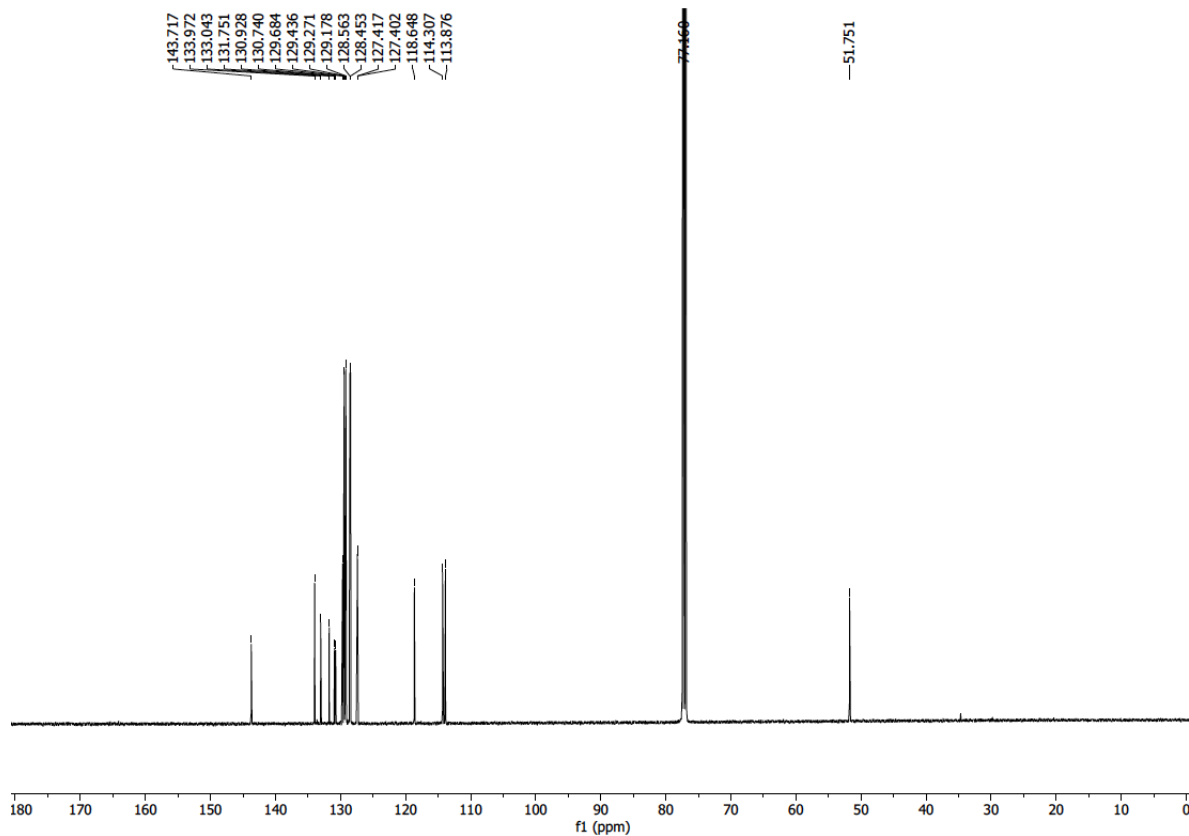


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3)

(Z)-1-Styryl-3-(3-fluorobenzyl)-benzimidazolium chloride (4)

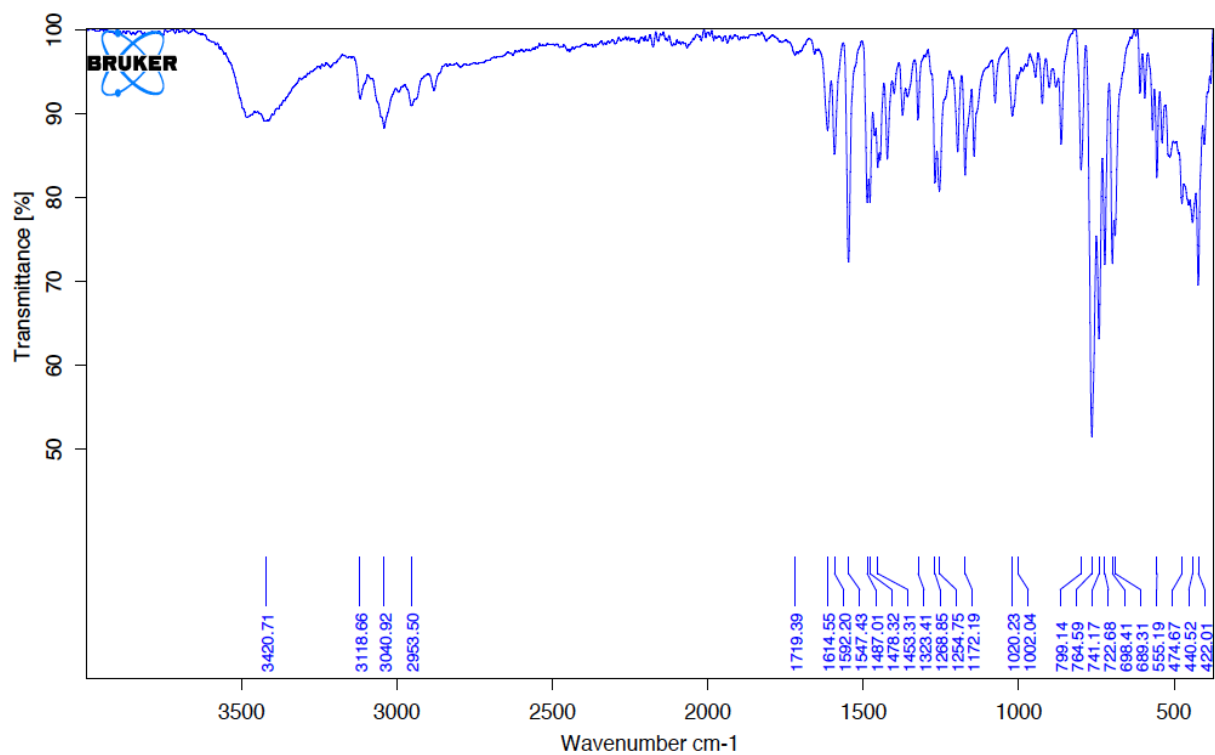
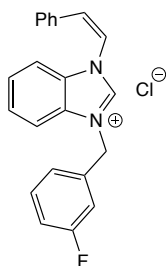
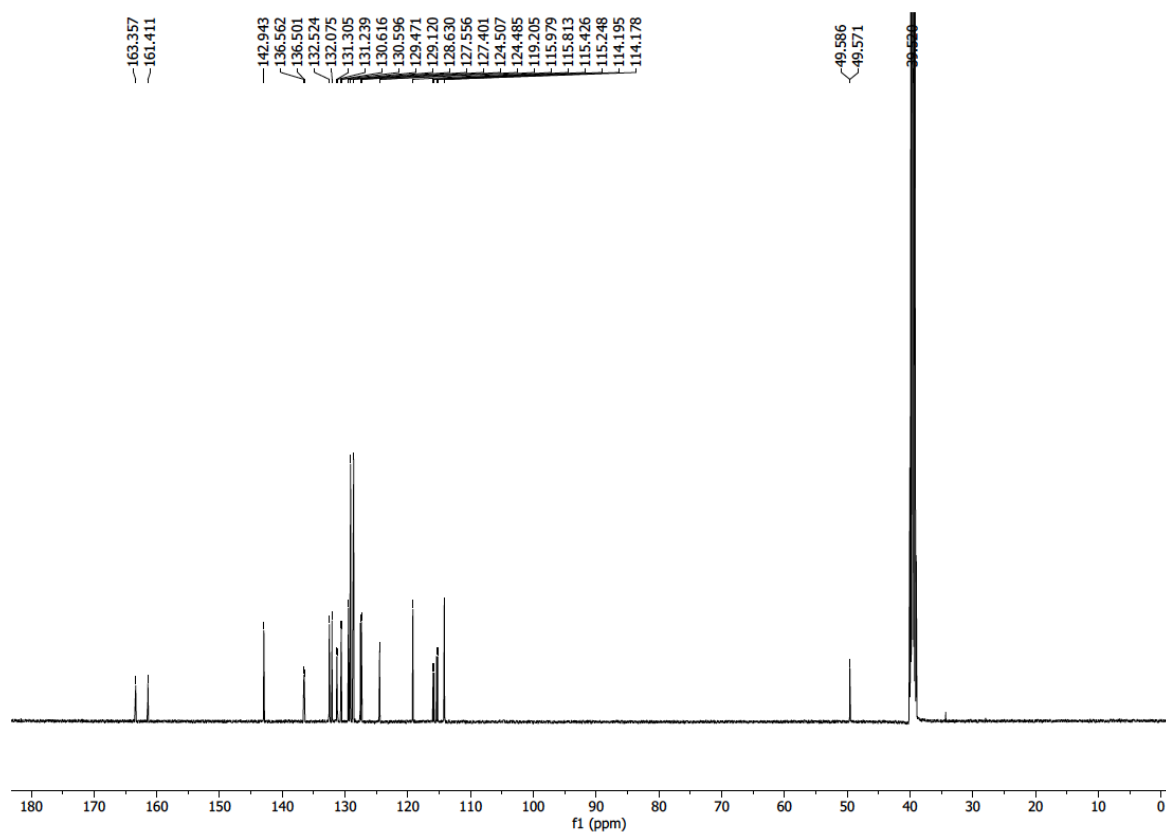
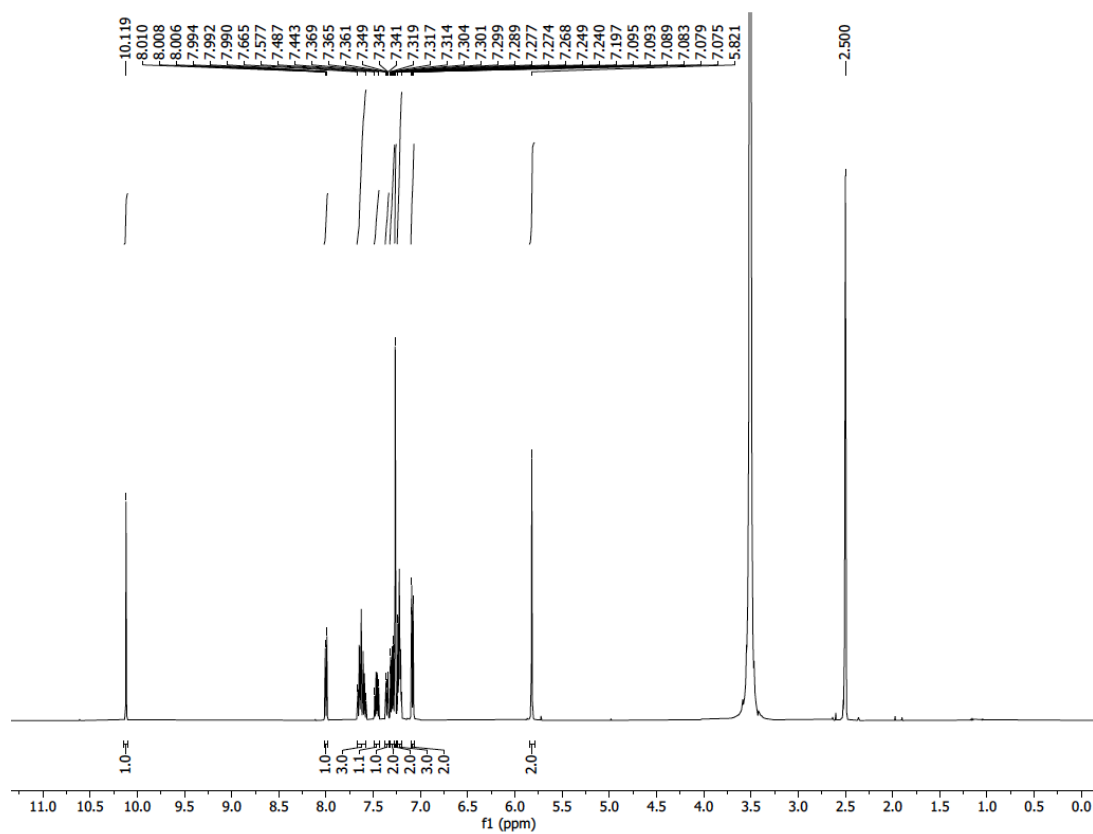


Figure S4. FT-IR spectrum



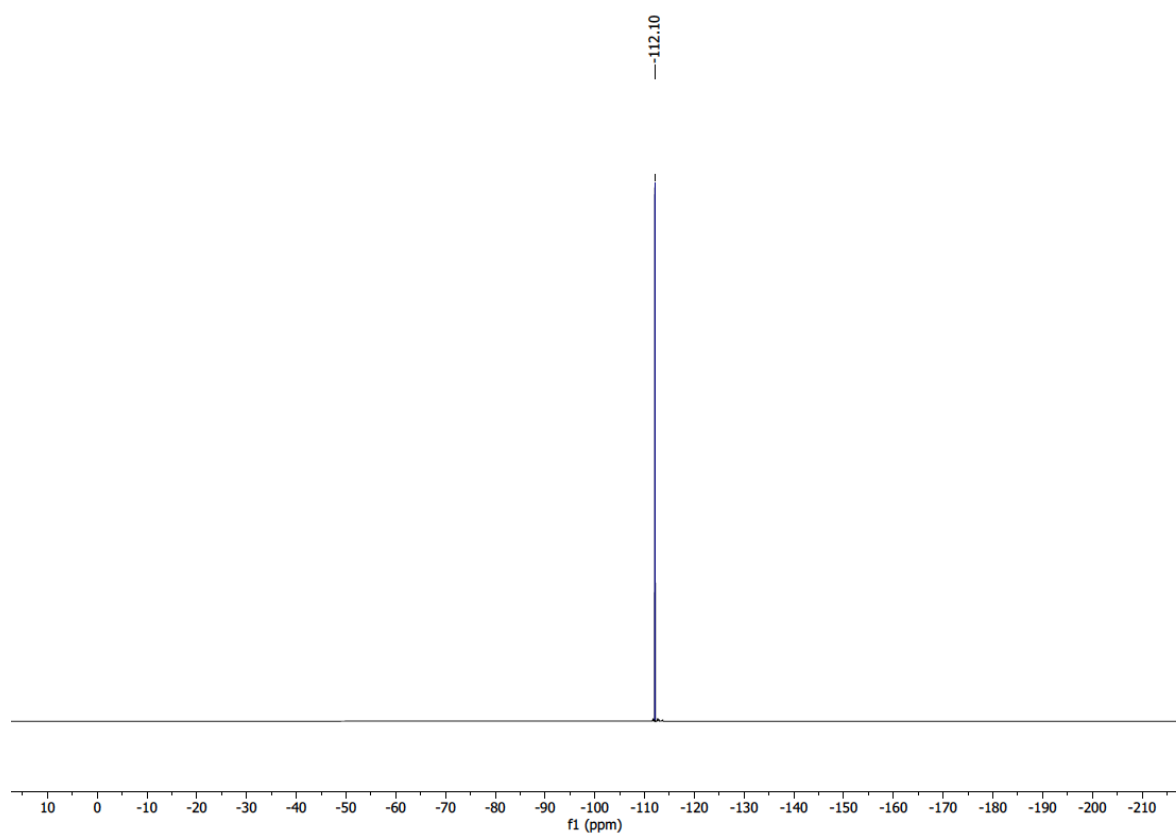


Figure S7. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (DMSO- d_6)

(*E*)-1-Styryl-3-(3-fluorobenzyl)-benzimidazolium chloride (5)

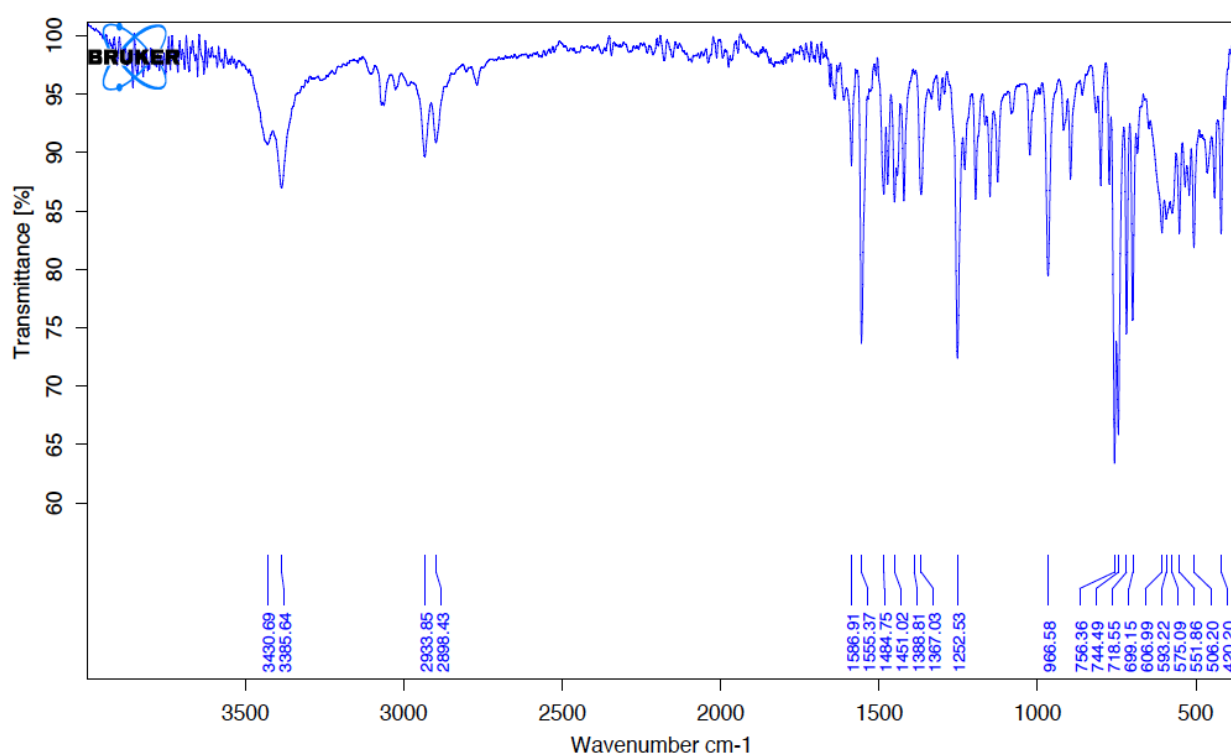
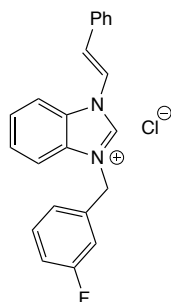


Figure S8. FT-IR spectrum

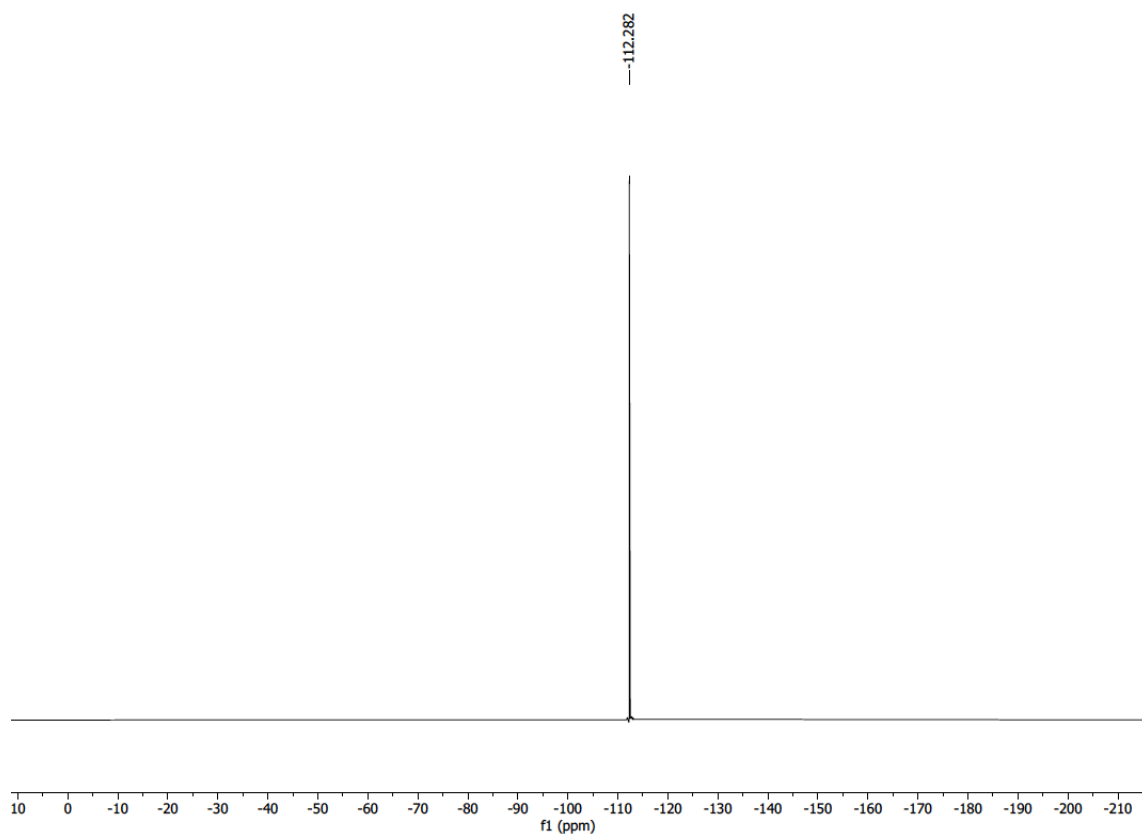


Figure S11. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (DMSO- d_6)

***trans*-Dichloro-[(*Z*)-1-styryl-3-benzyl-benzimidazol-2-yliden]pyridine palladium(II) (6)**

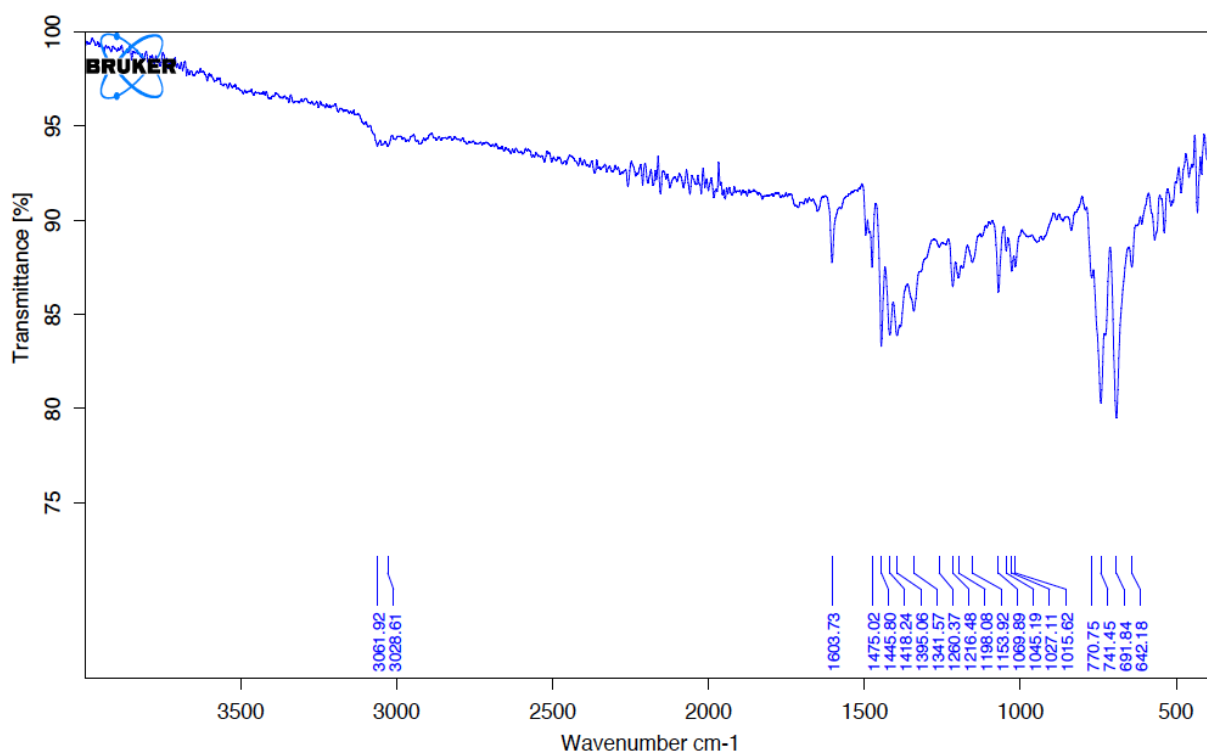
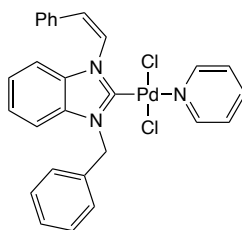


Figure S12. FT-IR spectrum

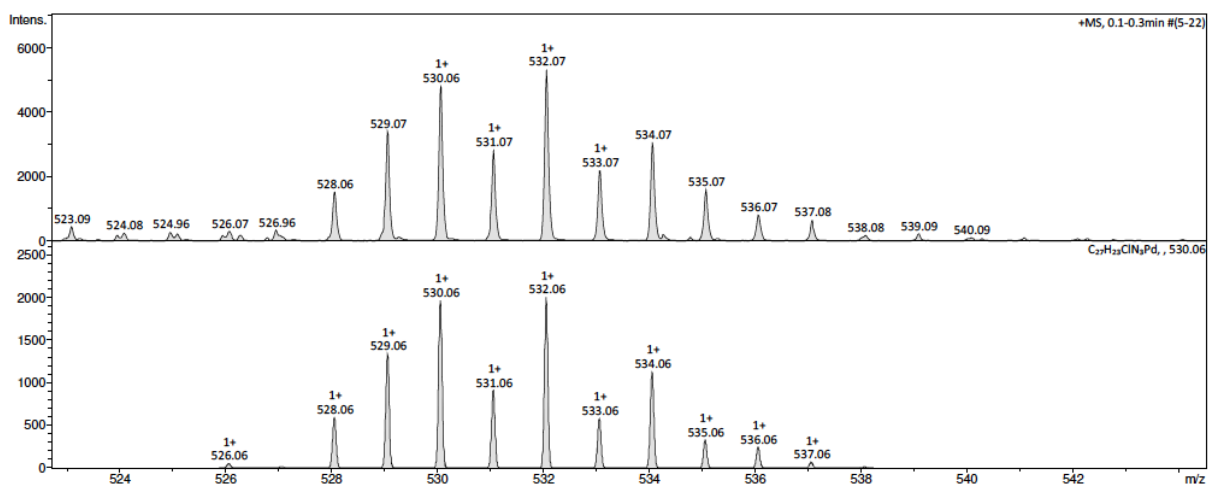


Figure S13. Mass spectrum (ESI-TOF)
exp. spectrum (top); calc. spectrum (bottom) for $C_{27}H_{23}ClN_3Pd$

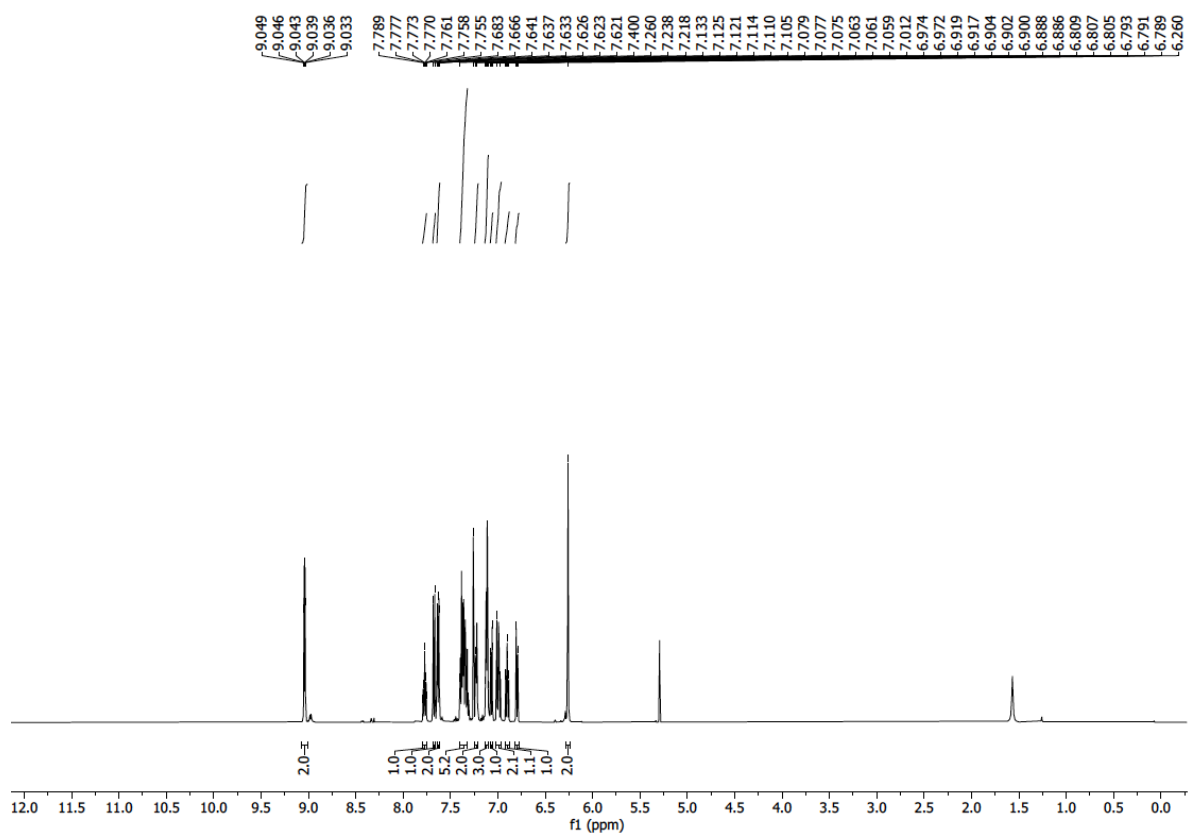


Figure S14. ^1H NMR spectrum (CDCl_3)

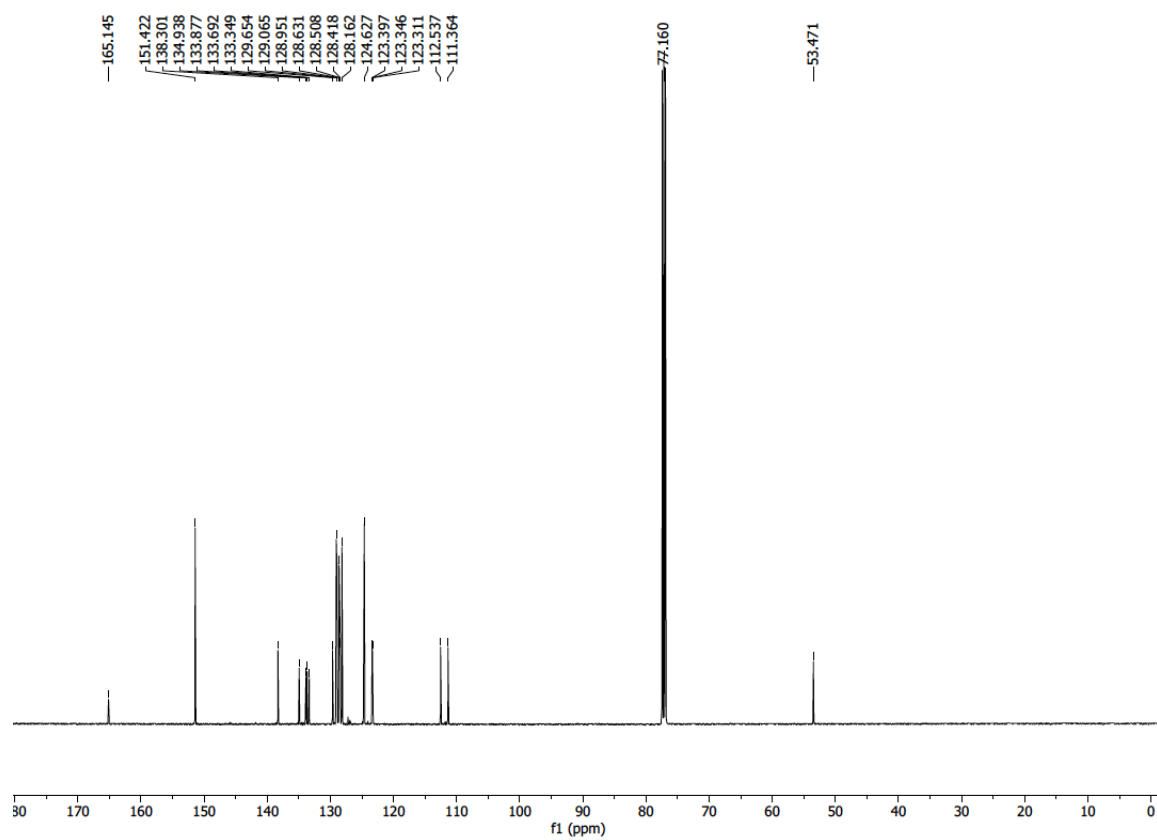


Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (CDCl_3)

***trans*-Dichloro-[(*E*)-1-styryl-3-benzyl-benzimidazol-2-yliden]pyridine palladium(II) (7)**

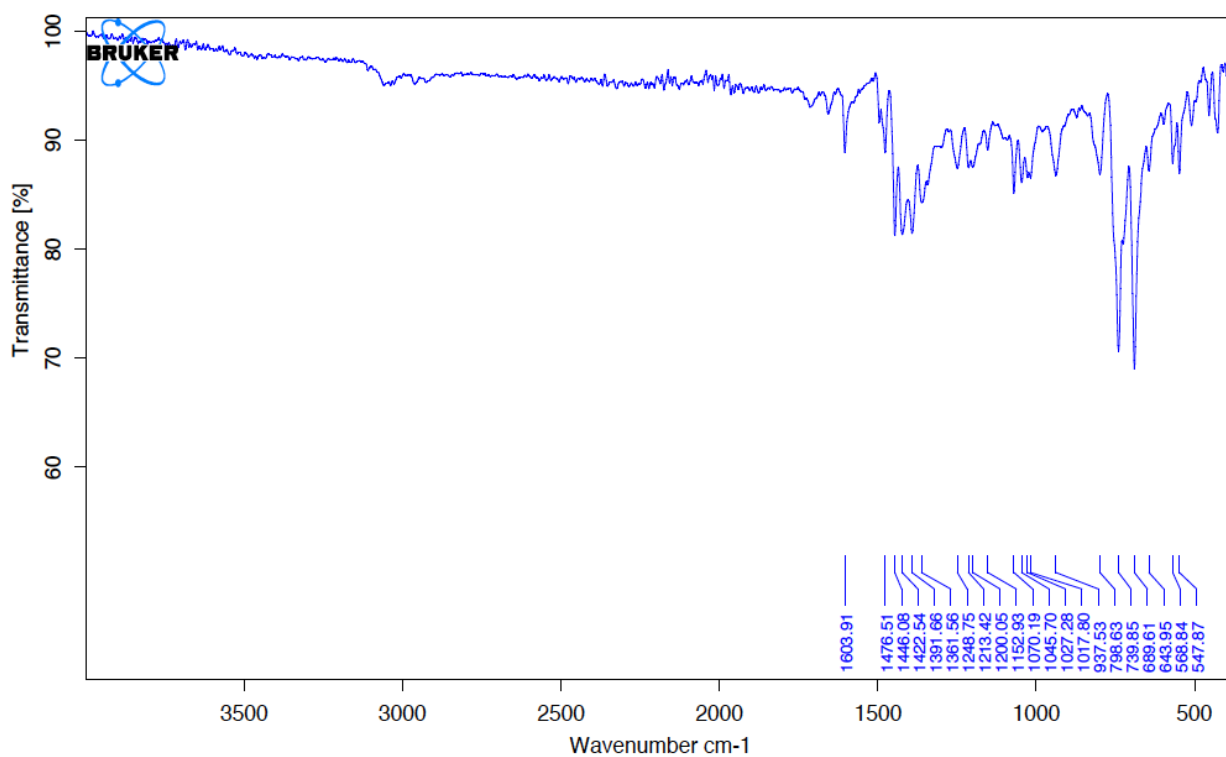
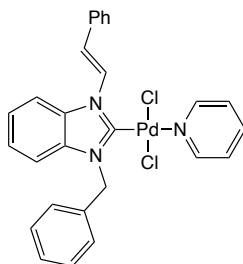


Figure S16. FT-IR spectrum

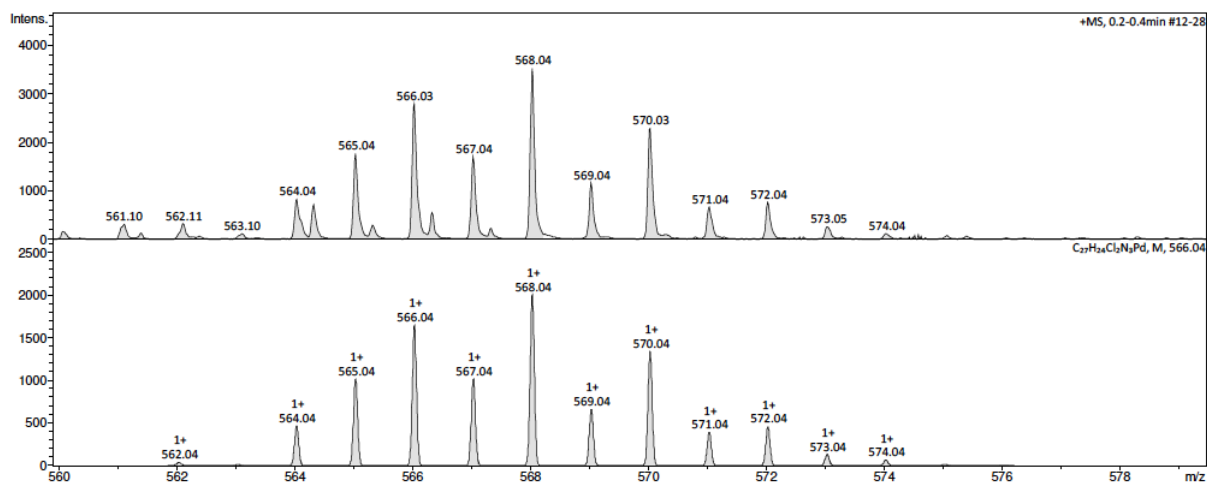


Figure S17. Mass spectrum (ESI-TOF)
exp. spectrum (top); calc. spectrum (bottom) for C₂₇H₂₄Cl₂N₃Pd

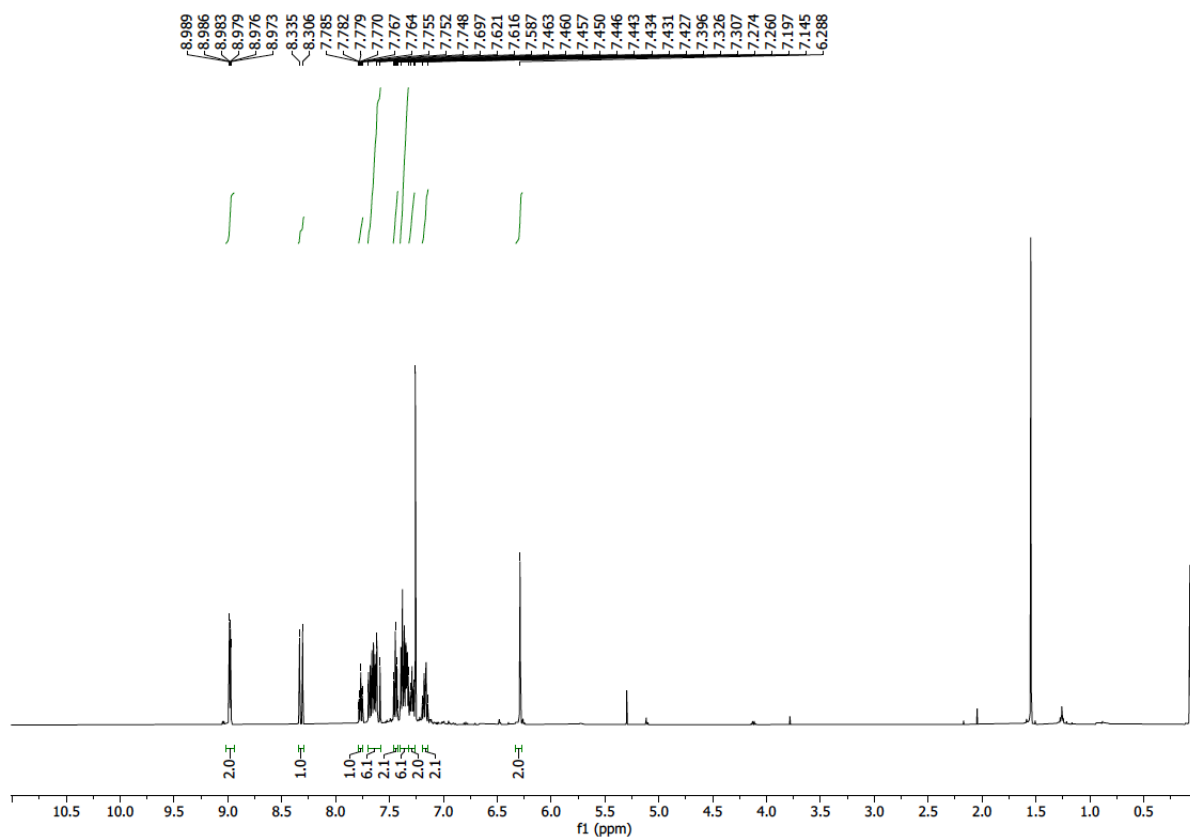


Figure S18. ¹H NMR spectrum (CDCl₃)

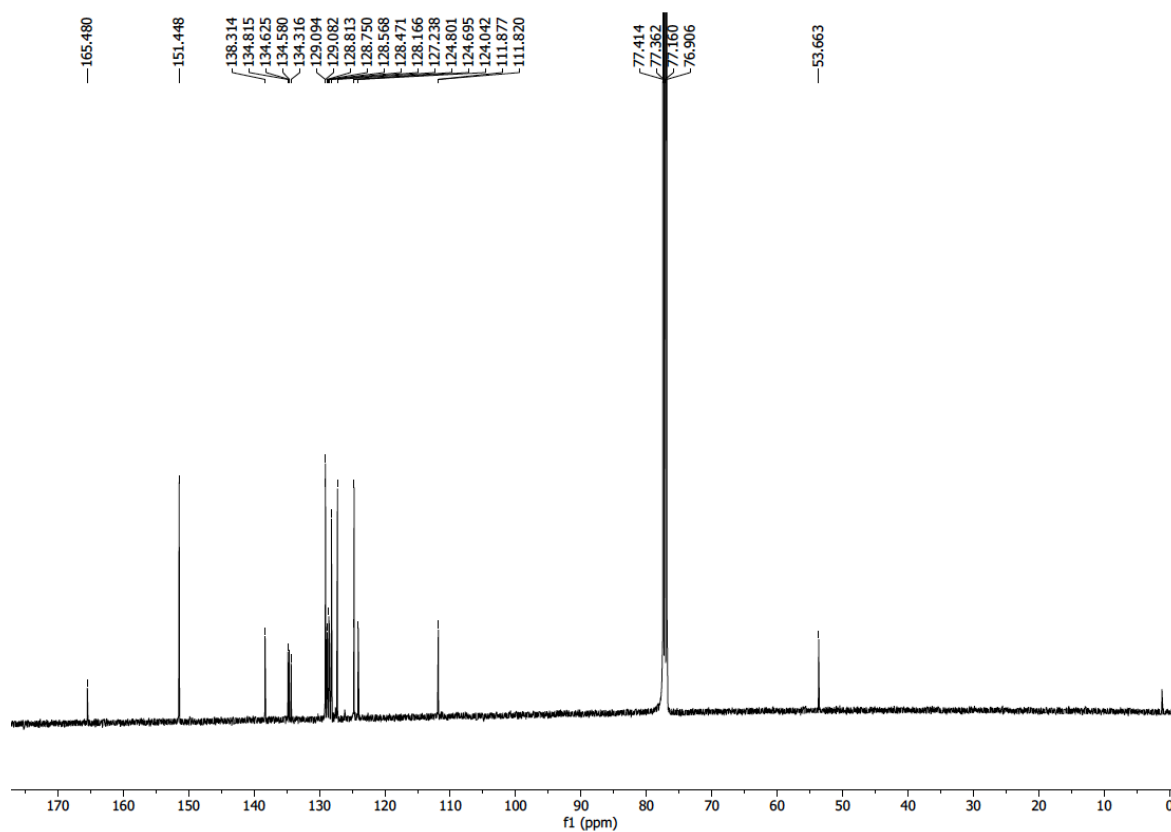


Figure S19. ¹³C{¹H} NMR spectrum (CDCl₃)

***trans*-Dichloro-[(*Z*)-1-styryl-3-(3-fluorobenzyl)-benzimidazol-2-yliden]pyridine palladium(II) (8)**

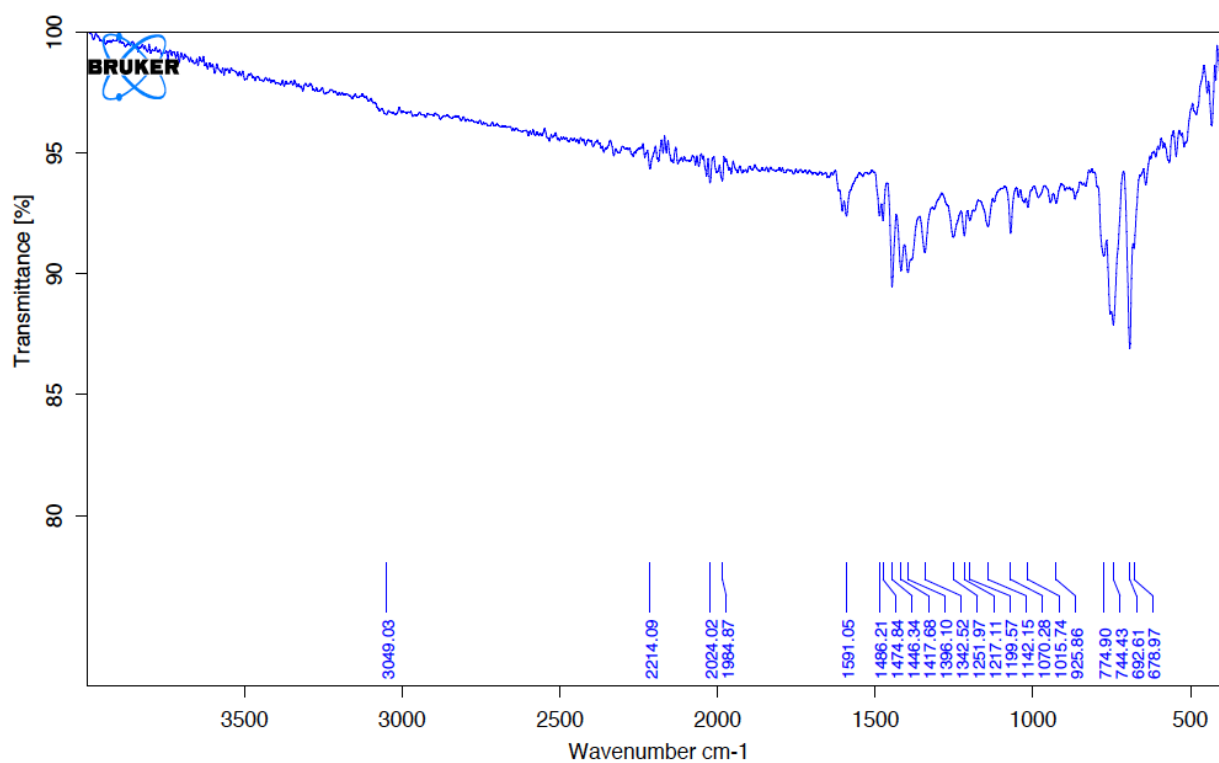
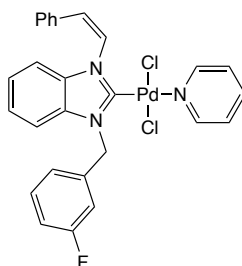


Figure S20. FT-IR spectrum

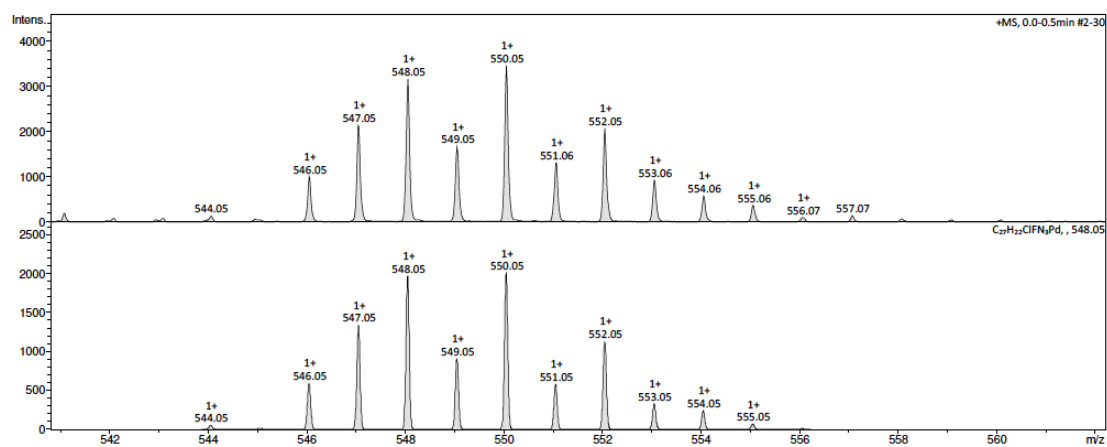


Figure S21. Mass spectrum (ESI-TOF)

exp. spectrum (top); calc. spectrum (bottom) for $C_{27}H_{22}FClN_3Pd$

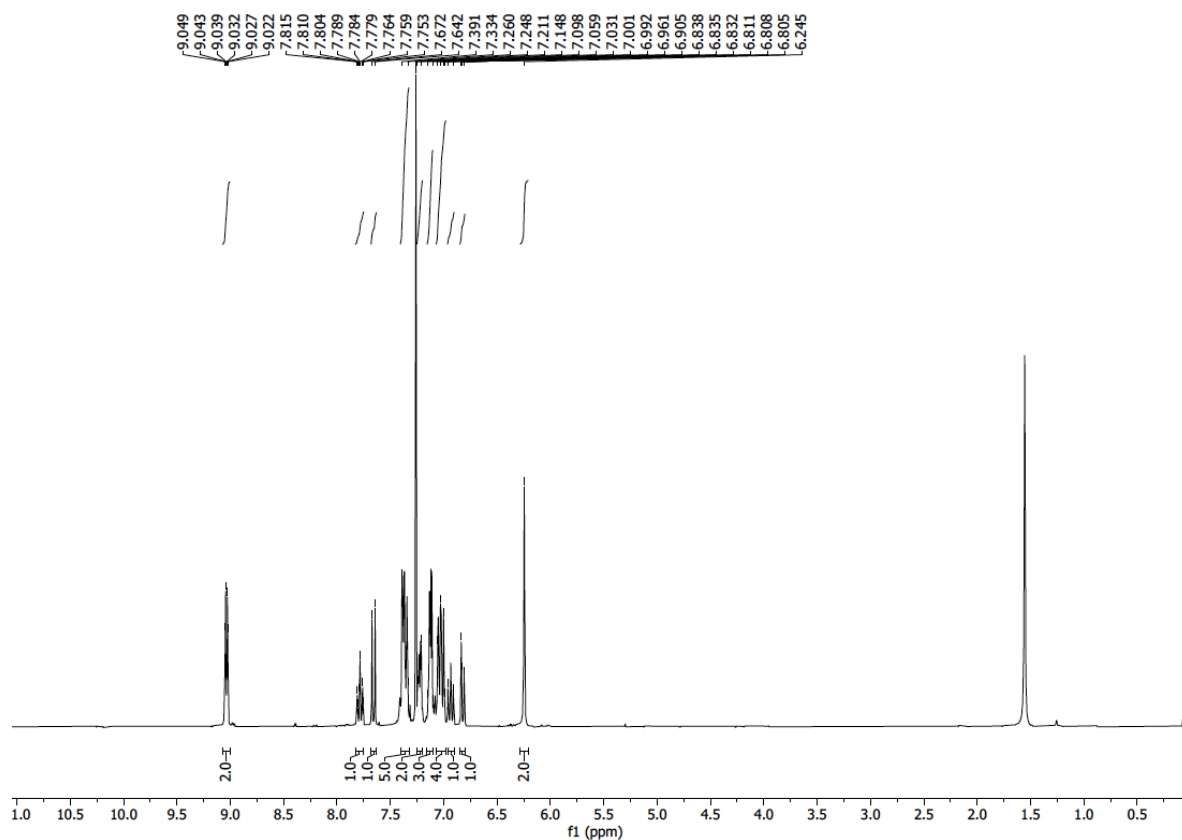


Figure S22. ¹H NMR spectrum (CDCl₃)

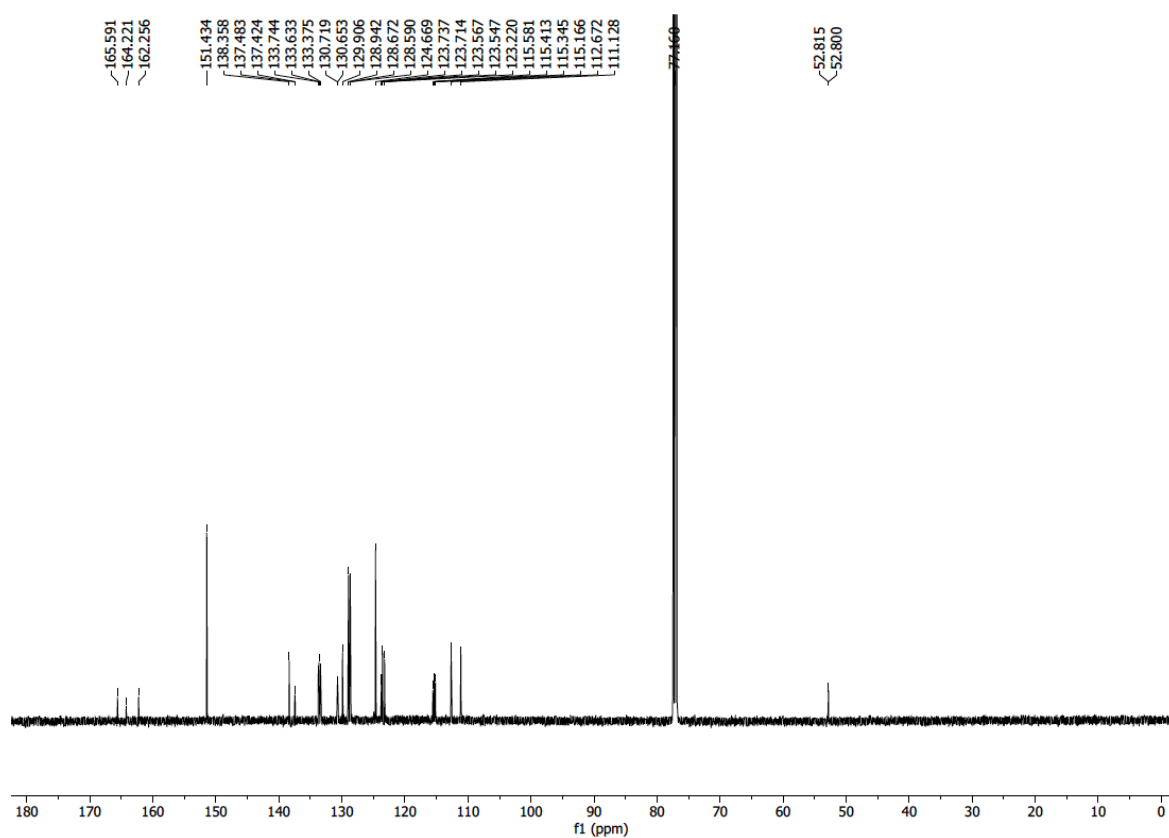


Figure S23. ¹³C{¹H} NMR spectrum (CDCl₃)

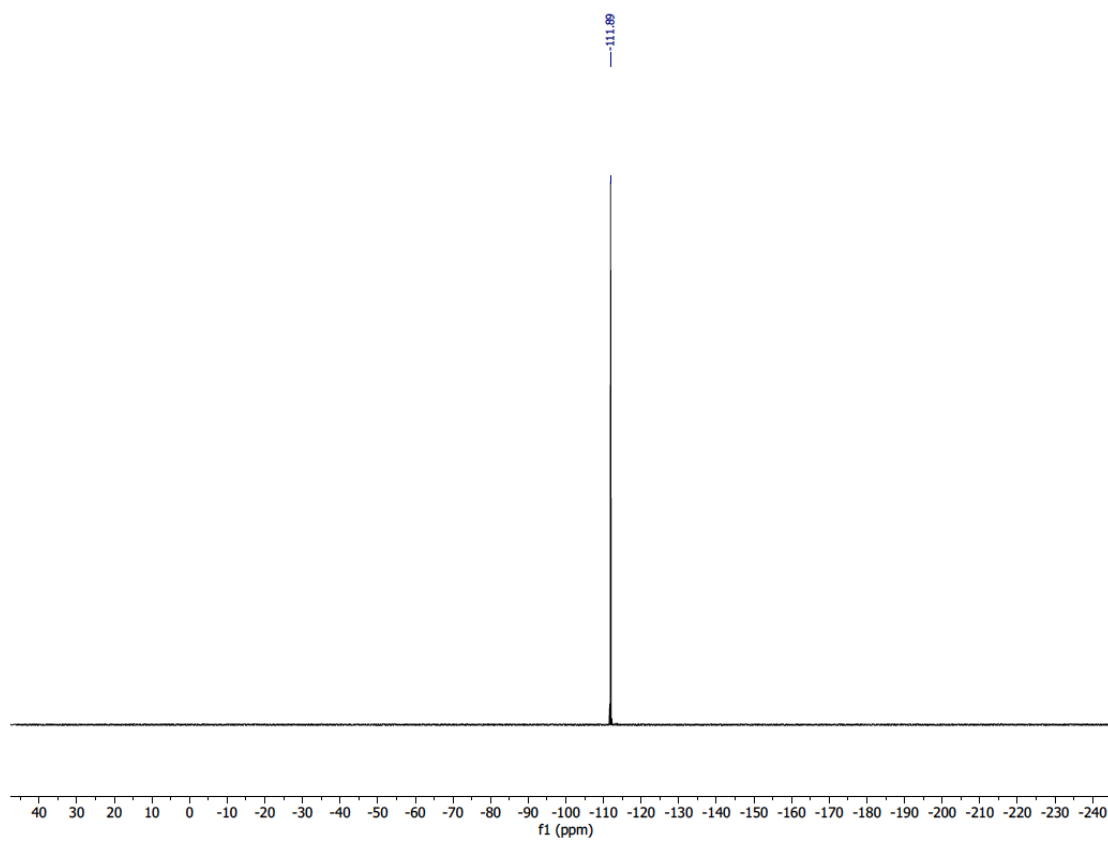


Figure S24. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (CDCl_3)

Dichloro-[(*E*)-1-styryl-3-(3-fluorobenzyl)-benzimidazol-2-yliden]pyridine palladium(II) (9)

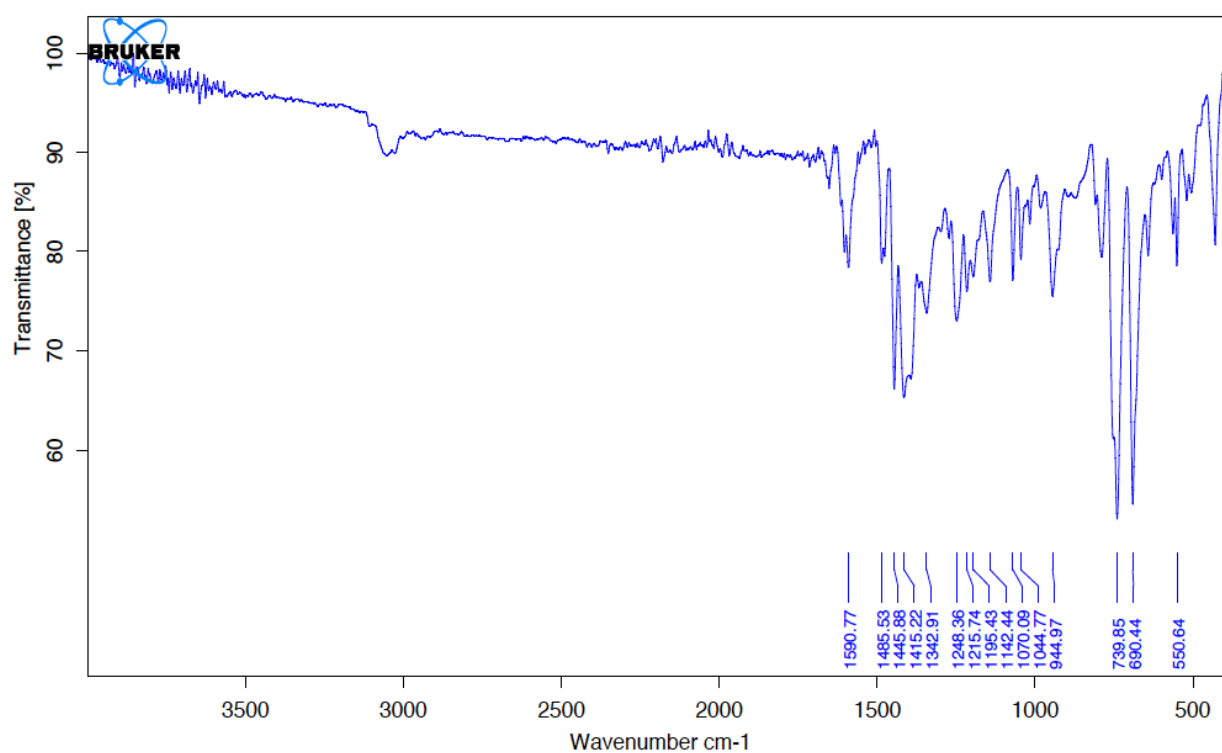
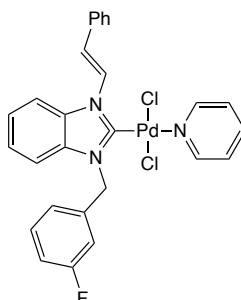


Figure S25. FT-IR spectrum

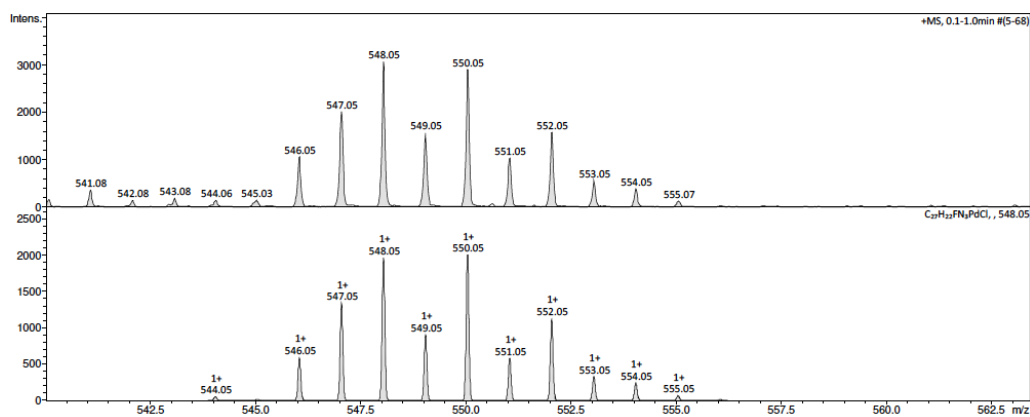


Figure S26. Mass spectrum (ESI-TOF)

exp. spectrum (top); calc. spectrum (bottom) for $C_{27}H_{22}FCIN_3Pd$

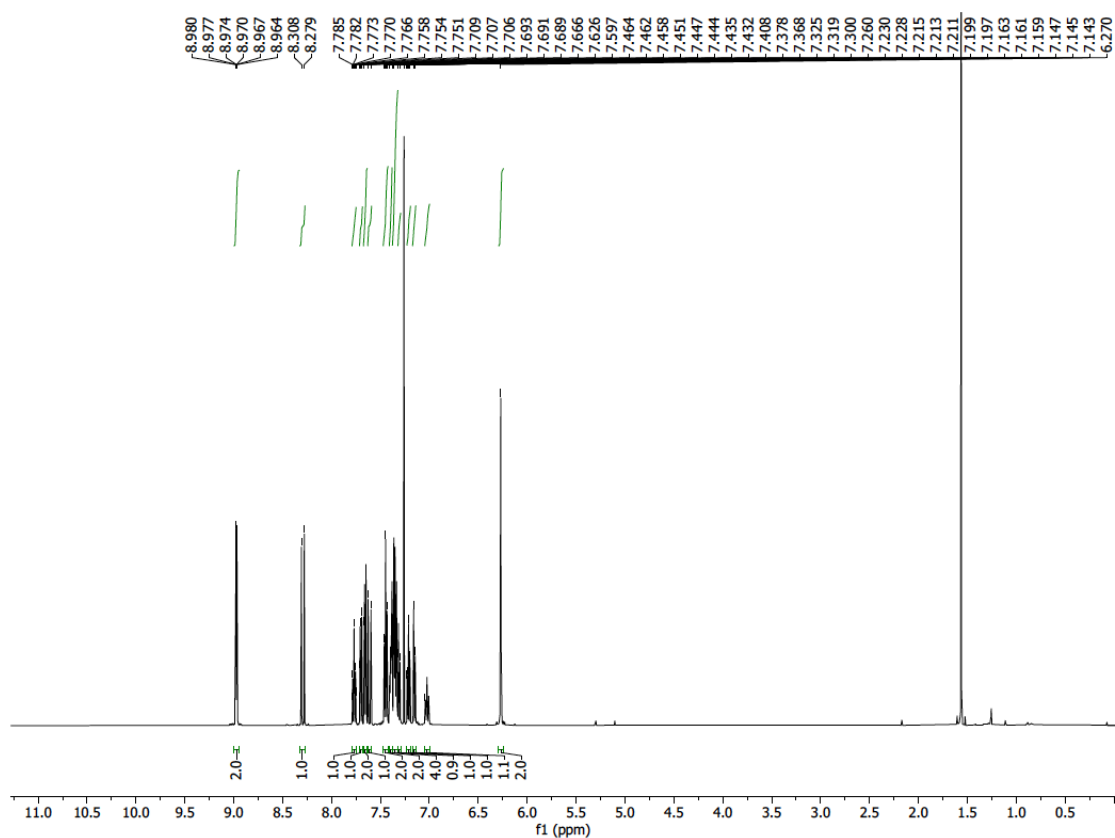


Figure S27. ¹H NMR spectrum (CDCl₃)

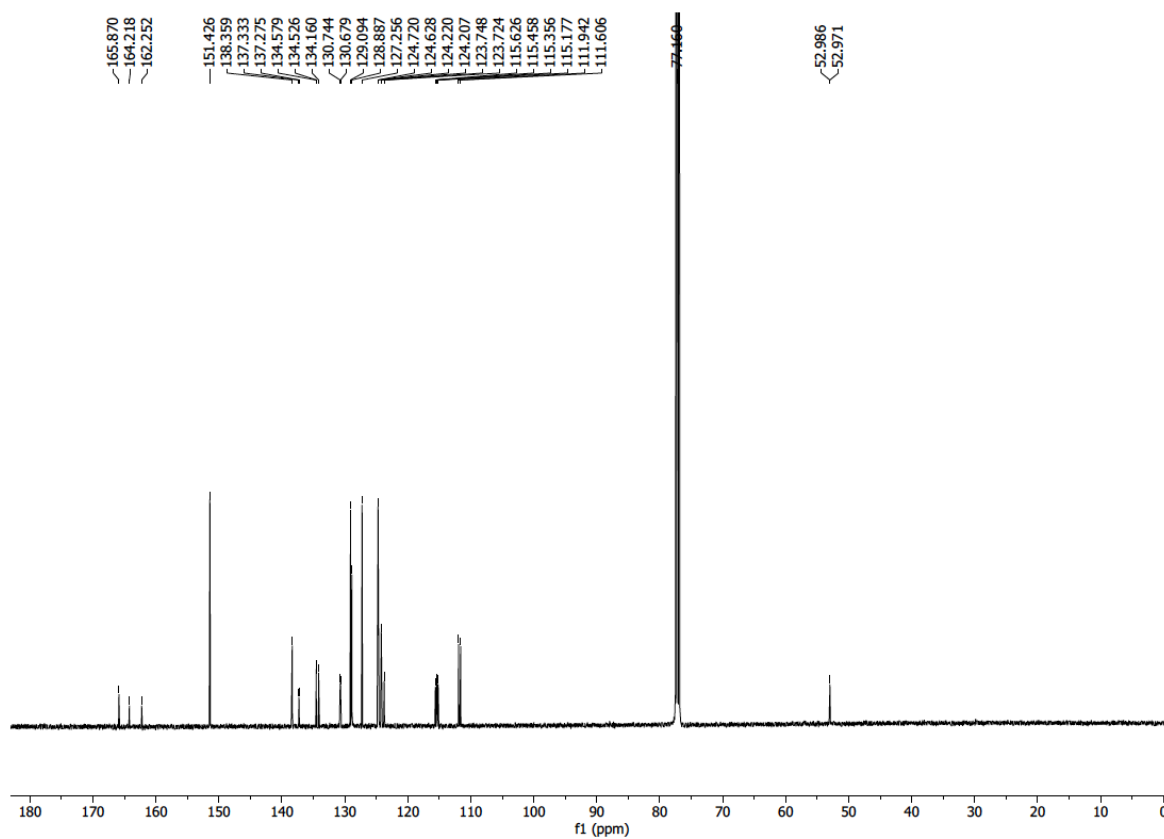


Figure S28. ¹³C{¹H} NMR spectrum (CDCl₃)

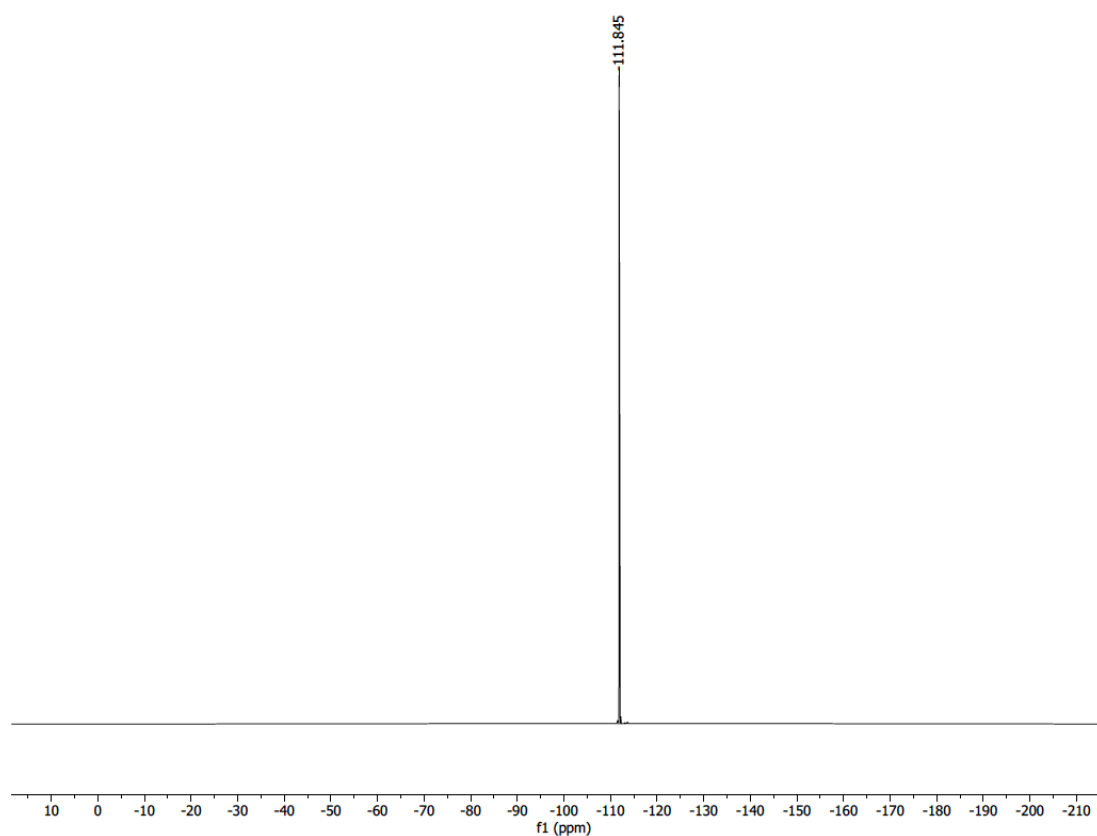


Figure S29. $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum (CDCl_3)

¹H NMR description of the catalytic products

1-(4-(5-Butylfuran-2-yl)phenyl)ethanone (12aa): ¹H NMR (300 MHz, CDCl₃): δ = 7.93 (d, 2H, arom. CH, ³J_{HH} = 8.4 Hz), 7.67 (d, 2H, arom. CH, ³J_{HH} = 8.4 Hz), 6.69 (d, 1H, arom. CH, ³J_{HH} = 3.3 Hz), 6.10 (d, 1H, arom. CH, ³J_{HH} = 3.3 Hz), 2.69 (t, 2H, CH₂CH₂CH₂CH₃, ³J_{HH} = 7.6 Hz), 2.58 (s, 3H, C(=O)CH₃), 1.73-1.63 (m, 2H, CH₂CH₂CH₂CH₃), 1.45-1.37 (m, 2H, CH₂CH₂CH₂CH₃), 0.94 (t, 2H, CH₂CH₂CH₂CH₃, ³J_{HH} = 7.3 Hz) ppm.

2-Butyl-5-(4-methoxyphenyl)-furan (12ab): ¹H NMR (300 MHz, CDCl₃): δ = 7.55 (d, 2H, arom. CH, ³J_{HH} = 7.0 Hz), 6.89 (d, 2H, arom. CH, ³J_{HH} = 7.0 Hz), 6.39 (d, 1H, arom. CH, ³J_{HH} = 3.3 Hz), 6.02 (d, 1H, arom. CH, ³J_{HH} = 3.3 Hz), 3.82 (s, 3H, OCH₃), 2.67 (t, 2H, CH₂CH₂CH₂CH₃, ³J_{HH} = 7.5 Hz), 1.68-1.63 (m, 2H, CH₂CH₂CH₂CH₃), 1.43-1.38 (m, 2H, CH₂CH₂CH₂CH₃), 0.94 (t, 2H, CH₂CH₂CH₂CH₃, ³J_{HH} = 7.4 Hz) ppm.

2-Butyl-5-phenyl-furan (12ac): ¹H NMR (300 MHz, CDCl₃): δ = 7.64 (d, 2H, arom. CH, ³J_{HH} = 7.0 Hz), 7.37-7.34 (m, 2H, arom. CH), 7.22 (t, 1H, arom. CH, ³J_{HH} = 6.5 Hz), 6.55 (d, 1H, arom. CH, ³J_{HH} = 2.5 Hz), 6.06 (d, 1H, arom. CH, ³J_{HH} = 2.5 Hz), 2.70 (t, 2H, CH₂CH₂CH₂CH₃, ³J_{HH} = 7.0 Hz), 1.69-1.64 (m, 2H, CH₂CH₂CH₂CH₃), 1.44-1.39 (m, 2H, CH₂CH₂CH₂CH₃), 0.97 (t, 2H, CH₂CH₂CH₂CH₃, ³J_{HH} = 6.9 Hz) ppm.

2-Butyl-5-(naphthalen-1-yl)-furan (12ad): ¹H NMR (300 MHz, CDCl₃): δ = 8.43 (d, 1H, arom. CH, ³J_{HH} = 8.1 Hz), 7.88 (d, 1H, arom. CH, ³J_{HH} = 8.1 Hz), 7.80 (d, 1H, arom. CH, ³J_{HH} = 8.0 Hz), 7.71 (d, 1H, arom. CH, ³J_{HH} = 8.1 Hz), 7.50-7.47 (m, 3H, arom. CH), 6.61 (d, 1H, arom. CH, ³J_{HH} = 2.9 Hz), 6.17 (d, 1H, arom. CH, ³J_{HH} = 2.9 Hz), 2.75 (t, 2H, CH₂CH₂CH₂CH₃, ³J_{HH} = 7.3 Hz), 1.74-1.73 (m, 2H, CH₂CH₂CH₂CH₃), 1.45-1.43 (m, 2H, CH₂CH₂CH₂CH₃), 0.97 (t, 2H, CH₂CH₂CH₂CH₃, ³J_{HH} = 7.3 Hz) ppm.

2-Butyl-5-(p-tolyl)-furan (12ae): ¹H NMR (300 MHz, CDCl₃): δ = 7.53 (d, 2H, arom. CH, ³J_{HH} = 7.0 Hz), 7.17 (d, 1H, arom. CH, ³J_{HH} = 7.0 Hz), 6.48 (d, 1H, arom. CH, ³J_{HH} = 3.1 Hz), 6.06 (d, 1H, arom. CH, ³J_{HH} = 3.1 Hz), 2.69 (t, 2H, CH₂CH₂CH₂CH₃, ³J_{HH} = 7.2 Hz), 2.36 (s, C₆H₄CH₃), 1.72-1.65 (m, 2H, CH₂CH₂CH₂CH₃), 1.47-1.38 (m, 2H, CH₂CH₂CH₂CH₃), 0.97 (t, 2H, CH₂CH₂CH₂CH₃, ³J_{HH} = 7.0 Hz) ppm.

2-Butyl-5-(o-tolyl)-furan (12af): ¹H NMR (300 MHz, CDCl₃): δ = 7.70-7.67 (m, 1H, arom. CH), 7.24-7.16 (m, 3H, arom. CH), 6.44 (d, 1H, arom. CH, ³J_{HH} = 2.8 Hz), 6.10 (d, 1H, arom. CH, ³J_{HH} = 2.8 Hz), 2.70 (t, 2H, CH₂CH₂CH₂CH₃, ³J_{HH} = 7.1 Hz), 2.50 (s, C₆H₄CH₃), 1.72-1.66 (m, 2H, CH₂CH₂CH₂CH₃), 1.45-1.39 (m, 2H, CH₂CH₂CH₂CH₃), 0.96 (t, 2H, CH₂CH₂CH₂CH₃, ³J_{HH} = 6.9 Hz) ppm.

1-(4-(5-Acetylfuran-2-yl)phenyl)ethanone (12ba): ¹H NMR (300 MHz, CDCl₃): δ = 7.98 (d, 2H, arom. CH, ³J_{HH} = 8.6 Hz), 7.82 (d, 2H, arom. CH, ³J_{HH} = 8.6 Hz), 7.25 (d, 1H, arom. CH, ³J_{HH} = 3.0 Hz), 6.88 (d, 1H, arom. CH, ³J_{HH} = 3.0 Hz), 2.60 (s, 3H, C₆H₄-C(=O)CH₃), 2.52 (s, 3H, C₄H₂O-C(=O)CH₃) ppm.

1-(5-(4-Methoxyphenyl)-furan-2-yl)ethanone (12bb): ¹H NMR (300 MHz, CDCl₃): δ = 7.56 (d, 2H, arom. CH, ³J_{HH} = 7.2 Hz), 7.13 (d, 1H, arom. CH, ³J_{HH} = 3.1 Hz), 6.97 (d, 2H, arom. CH, ³J_{HH} = 7.2 Hz), 6.85 (d, 1H, arom. CH, ³J_{HH} = 3.1 Hz), 3.83 (s, 3H, OCH₃), 2.55 (s, 3H, C(=O)CH₃) ppm.

1-(5-Phenyl-furan-2-yl)ethanone (12bc): ^1H NMR (300 MHz, CDCl_3): δ = 7.85-7.77 (m, 2H, arom.), 7.53-7.37 (m, 3H, arom.), 7.29 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 2.9 Hz), 6.82 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 2.9 Hz), 2.56 (s, 3H, C(=O)CH_3) ppm.

1-(5-(Naphthalen-1-yl)-furan-2-yl)ethanone (12bd): ^1H NMR (300 MHz, CDCl_3): δ = 8.12 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 8.0 Hz), 7.88 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 8.1 Hz), 7.82 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 8.1 Hz), 7.68 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 8.0 Hz), 7.52-7.44 (m, 3H, arom. CH), 7.32 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 3.2 Hz), 6.90 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 3.2 Hz), 2.53 (s, 3H, C(=O)CH_3) ppm.

1-(5-*p*-Tolyl-furan-2-yl)ethanone (12be): ^1H NMR (300 MHz, CDCl_3): δ = 7.71 (d, 2H, arom. CH, $^3J_{\text{HH}}$ = 8.3 Hz), 7.27 (d, 2H, arom. CH, $^3J_{\text{HH}}$ = 8.3 Hz), 7.25 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 2.9 Hz), 6.83 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 2.9 Hz), 2.52 (s, 3H, C(=O)CH_3), 2.38 (s, $\text{C}_6\text{H}_4\text{CH}_3$) ppm.

1-(5-*o*-Tolyl-furan-2-yl)ethanone (12bf): ^1H NMR (300 MHz, CDCl_3): δ = 7.62 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 8.0 Hz), 7.32-7.18 (m, 3H, arom. CH), 7.24 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 3.0 Hz), 6.75 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 3.0 Hz), 2.53 (s, 3H, C(=O)CH_3), 2.49 (s, $\text{C}_6\text{H}_4\text{CH}_3$) ppm.

5-(4-Acetylphenyl)furfural (12ca): ^1H NMR (300 MHz, CDCl_3): δ = 9.71 (s, 1H, CHO), 8.03 (d, 2H, arom. CH, $^3J_{\text{HH}}$ = 8.5 Hz), 7.92 (d, 2H, arom. CH, $^3J_{\text{HH}}$ = 8.5 Hz), 7.32 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 3.8 Hz), 6.97 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 3.8 Hz), 2.59 (s, 3H, C(=O)CH_3) ppm.

1-[4-(5-Acetyloxymethyl-2-furanyl)phenyl]ethanone (12da): ^1H NMR (300 MHz, CDCl_3): δ = 7.95 (d, 2H, arom. CH, $^3J_{\text{HH}}$ = 8.2 Hz), 7.80 (d, 2H, arom. CH, $^3J_{\text{HH}}$ = 8.2 Hz), 6.87 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 3.4 Hz), 6.22 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 3.4 Hz), 5.12 (s, 2H, $\text{C}_4\text{H}_2\text{O-CH}_2$), 2.59 (s, 3H, $\text{C}_6\text{H}_4\text{-C(=O)CH}_3$), 2.12 (s, 3H, OC(=O)CH_3) ppm.

1-(4-(5-Acetylthiophen-2-yl)phenyl)ethanone (12ea): ^1H NMR (300 MHz, CDCl_3): δ = 8.02 (d, 2H, arom. CH, $^3J_{\text{HH}}$ = 8.1 Hz), 7.69 (d, 2H, arom. CH, $^3J_{\text{HH}}$ = 8.1 Hz), 7.61 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 2.8 Hz), 7.54 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 2.8 Hz), 2.61 (s, 3H, $\text{C}_6\text{H}_4\text{-C(=O)CH}_3$), 2.48 (s, 3H, $\text{C}_4\text{H}_2\text{S-C(=O)CH}_3$) ppm.

1-(5-(4-Methoxyphenyl)-thiophen-2-yl)ethanone (12eb): ^1H NMR (300 MHz, CDCl_3): δ = 7.67 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 3.0 Hz), 7.62 (d, 2H, arom. CH, $^3J_{\text{HH}}$ = 7.7 Hz), 7.23 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 3.0 Hz), 6.98 (d, 2H, arom. CH, $^3J_{\text{HH}}$ = 7.7 Hz), 3.81 (s, 3H, OCH_3), 2.56 (s, 3H, C(=O)CH_3) ppm.

1-(5-Phenyl-thiophen-2-yl)ethanone (12ec): ^1H NMR (300 MHz, CDCl_3): δ = 7.81-7.70 (m, 3H, arom.), 7.53-7.31 (m, 2H, arom.), 7.27 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 2.8 Hz), 7.20 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 2.8 Hz), 2.54 (s, 3H, C(=O)CH_3) ppm.

1-(5-(Naphthalen-1-yl)-thiophen-2-yl)ethanone (12ed): ^1H NMR (300 MHz, CDCl_3): δ = 8.17 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 8.0 Hz), 7.93-7.87 (m, 2H, arom. CH), 7.75 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 3.4 Hz), 7.44-7.62 (m, 4H, arom. CH), 7.29 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 3.4 Hz), 2.56 (s, 3H, C(=O)CH_3) ppm.

1-(5-*p*-Tolyl-thiophen-2-yl)ethanone (12ee): ^1H NMR (300 MHz, CDCl_3): δ = 7.65 (d, 1H, arom. CH, $^3J_{\text{HH}}$ = 3.4 Hz), 7.54 (d, 2H, arom. CH, $^3J_{\text{HH}}$ = 8.0 Hz), 7.27 (d, 1H, arom. CH,

$^3J_{\text{HH}} = 3.4 \text{ Hz}$), 7.22 (d, 2H, arom. CH, $^3J_{\text{HH}} = 8.0 \text{ Hz}$), 2.55 (s, 3H, C(=O)CH₃), 2.38 (s, C₆H₄CH₃) ppm.

1-(5-*o*-Tolyl-thiophen-2-yl)ethanone (12ef): ^1H NMR (300 MHz, CDCl₃): δ = 7.67 (d, 1H, arom. CH, $^3J_{\text{HH}} = 3.4 \text{ Hz}$), 7.41 (d, 1H, arom. CH, $^3J_{\text{HH}} = 7.5 \text{ Hz}$), 7.33-7.19 (m, 3H, arom. CH), 7.11 (d, 1H, arom. CH, $^3J_{\text{HH}} = 3.4 \text{ Hz}$), 2.55 (s, 3H, C(=O)CH₃), 2.43 (s, C₆H₄CH₃) ppm.

1-(4-(5-Methylthiophen-2-yl)phenyl)ethanone (12fa): ^1H NMR (300 MHz, CDCl₃): δ = 7.92 (d, 2H, arom. CH, $^3J_{\text{HH}} = 8.5 \text{ Hz}$), 7.61 (d, 2H, arom. CH, $^3J_{\text{HH}} = 8.5 \text{ Hz}$), 7.21 (d, 1H, arom. CH, $^3J_{\text{HH}} = 3.7 \text{ Hz}$), 6.75 (d, 1H, arom. CH, $^3J_{\text{HH}} = 3.7 \text{ Hz}$), 2.56 (s, 3H, C(=O)CH₃), 2.45 (s, 3H, C₄H₂SCH₃) ppm.

5-(4-Acetylphenyl)-2-thiophenecarboxaldehyde (12ga): ^1H NMR (300 MHz, CDCl₃): δ = 9.98 (s, 1H, CHO), 7.95 (d, 2H, arom. CH, $^3J_{\text{HH}} = 8.2 \text{ Hz}$), 7.84 (d, 1H, arom. CH, $^3J_{\text{HH}} = 3.5 \text{ Hz}$), 7.76 (d, 2H, arom. CH, $^3J_{\text{HH}} = 8.2 \text{ Hz}$), 7.72 (d, 1H, arom. CH, $^3J_{\text{HH}} = 3.5 \text{ Hz}$), 2.53 (s, 3H, C(=O)CH₃) ppm.