

Supporting information

Pd-catalyzed oxidative coupling of 2-alkylfurans with olefins through C-H activation: synthesis of difurylalkanes

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1. Synthesis of α -(5-methyl-2-furyl)styrene (**3f**)¹

All reagents used were commercially available and with high purity grade. Quinoline was distilled over Zn.

Phenylacetic acid (3.672 g, 27 mmol) and 5-methylfurfural (3.2 mL, 32 mmol) are added in triethylamine (15 mL) and acetic anhydride (5 mL). The mixture is heated 5 hours at 110°C. The mixture is cooled, acidified to pH 1 with concentrated hydrochloric acid and extracted with diethyl ether. The organic phase is washed with water and agitated overnight with 5 % sodium carbonate solution. The aqueous solution of sodium salts (pH 8) is acidified to pH 6 with acetic acid. The *E*-isomer precipitates and is filtered off (3.34 g). (*E*)-3-(5-methylfuran-2-yl)-2-phenylacrylic acid: white solid, 54 %, IR: ν 3100-2500, 1668, 1596, 1579, 1511, 1421, 1284; ¹H-NMR(CDCl₃): δ 2.21 (s, 3H), 5.76 (d, *J* = 3.4 Hz, 1H), 5.88 (d, *J* = 3.4 Hz, 1H), 7.24-7.27 (m, 2H), 7.37-7.45 (m, 3H), 7.75 (s, 1H), 11.41 (sb, 1H); ¹³C-NMR (CDCl₃): δ 13.9 (CH₃), 109.3 (CH), 117.5 (CH), 126.7 (C), 128.2 (CH), 128.8 (2CH), 129.7 (2CH), 130.2 (CH), 135.9 (C), 149.5 (C), 155.5 (C), 173.3 (C).

The acid (1 g, 4.4 mmol) and Cu-powder (1 g, 16 mmol) are mixed with dry quinoline (5 mL) and heated for 1 hour at 200°C. The reaction mixture is taken into 25 mL diethyl ether and 10 % hydrochloric acid. The water layer is extracted with diethyl ether (2 $\times$ 20 mL). The organic phases are washed with water (20 mL), 10 % hydrochloric acid (20 mL), water (20 mL) and then dried over magnesium sulfate. Evaporation of the solvent and chromatography column (silica gel, petroleum ether/EtOAc, 98/2) led to 2-methyl-5-styrylfuran (**3f**) (666 mg, 81%). Clear yellow oil, 81 %; *E/Z* = 33/67; *t*_R (*E*) = 8.50, *m/z*(%) = 184(86) [M]⁺, 141(100), 115(60) *t*_R (*Z*) = 7.59, *m/z*(%) = 184(98) [M]⁺, 141(100), 115(55); IR: ν 3060, 1699, 1674, 1652, 1575, 1174, 697; ¹H-NMR(CDCl₃): δ (*E*) 2.35 (s, 3H), 6.01 (d, *J* = 3.1 Hz, 1H), 6.23 (d, *J* = 3.1 Hz, 1H), 6.82 (d, *J* = 16.0 Hz, 1H), 6.96 (d, *J* = 16.0 Hz, 1H), 7.21-7.36 (m, 3H), 7.43-7.50 (m, 2H); (*Z*) 2.24 (s, 3H), 5.90 (d, *J* = 3.1 Hz, 1H), 6.15 (d, *J* = 3.1 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 7.21-7.36 (m, 3H), 7.43-7.50 (m, 2H); ¹³C-NMR (CDCl₃): δ (*E*) 13.8 (CH₃), 107.9 (CH), 110.1 (CH), 116.8 (CH), 125.7 (CH), 126.4 (2CH), 127.3 (2CH), 127.4 (CH), 137.4 (C), 151.6 (C), 152.3 (C); (*Z*) 13.6 (CH₃), 107.5 (CH), 111.1 (CH), 118.3 (CH), 126.6 (CH), 128.2 (2CH), 128.9 (2CH), 128.8 (CH), 137.7 (C), 150.7 (C), 151.6 (C).

2. ESI-MS spectra

2.1 Species A

2.1.1 [A-2L-X]⁺

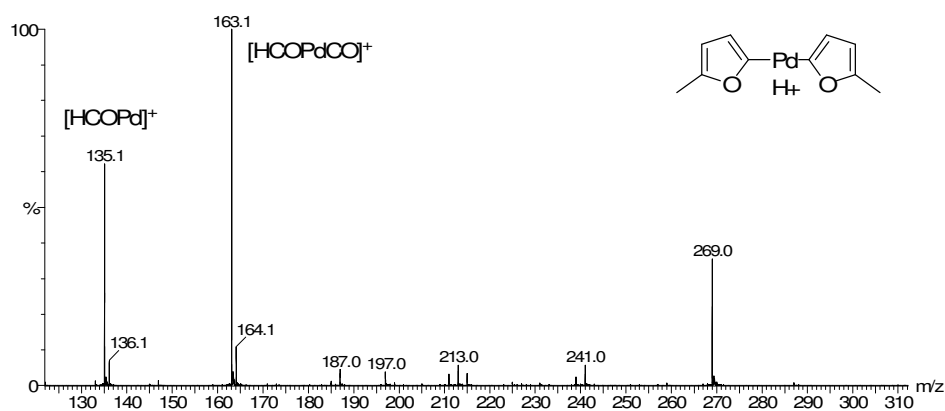
ESHRMS for C₅H₅O¹⁰⁶Pd: calcd. 186.9375, found 186.9370.

2.2 Species B

2.2.1 [B1-2L+H]⁺

ESHRMS for C₁₀H₁₁O₂¹⁰⁶Pd: calcd. 268.9794, found 268.9790.

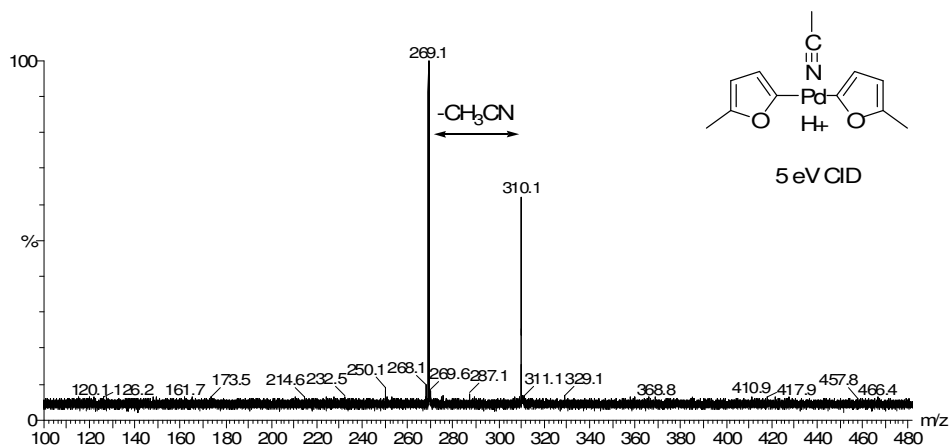
Figure S1: ESI-MS(/MS) of [B1-2L+H]⁺



2.2.2 [B1-L+H]⁺

ESHRMS for C₁₂H₁₄NO₂¹⁰⁶Pd: calcd. 310.0059, found 310.0052.

Figure S2: ESI-MS(/MS) of [B1-L+H]⁺



2.2.3 [B1+H]⁺

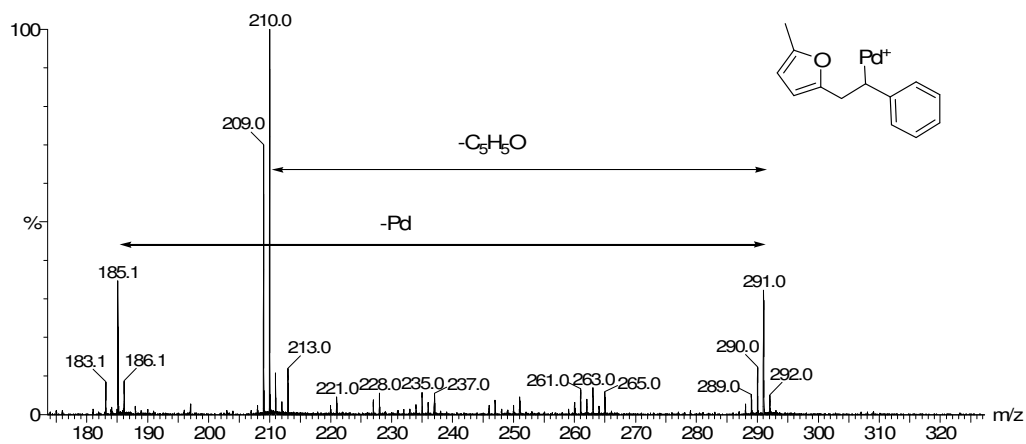
ESHRMS for C₁₄H₁₇N₂O₂¹⁰⁶Pd: calcd. 351.0325, found 351.0317

2.3 Species C

2.3.1 [C1-2L-C₅H₅O]⁺

ESHRMS for C₁₃H₁₃O¹⁰⁶Pd: calcd. 291.0001, found 290.9994.

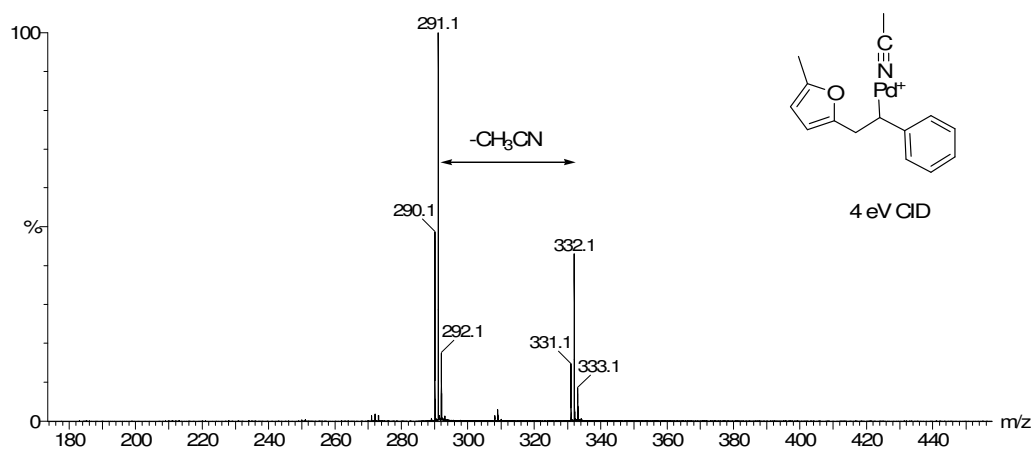
Figure S3: ESI-MS(/MS) of [C1-2L-C₅H₅O]⁺



2.3.2 [C1-L-C₅H₅O]⁺

ESHRMS for C₁₅H₁₆NO¹⁰⁶Pd: calcd. 332.0267, found 332.0266.

Figure S4: ESI-MS(/MS) of [C1-L-C₅H₅O]⁺

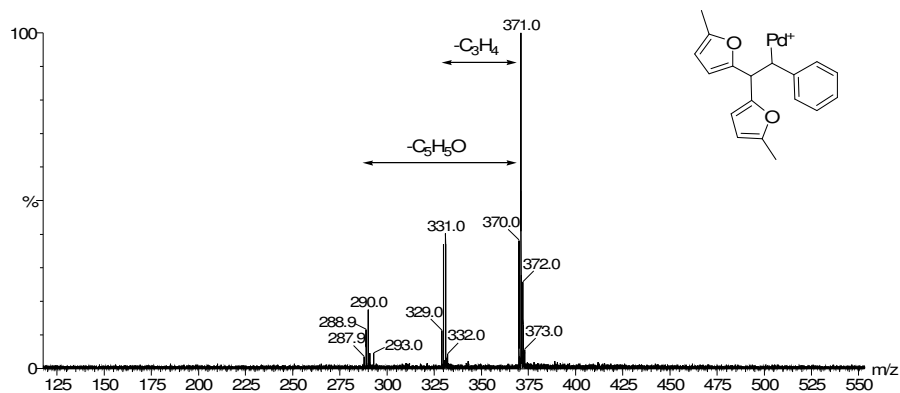


2.4 Species F

2.4.1 [F1-2L+H]⁺

ESHRMS for C₁₈H₁₇O₂¹⁰⁶Pd: calcd. 371.0263, found 371.0268.

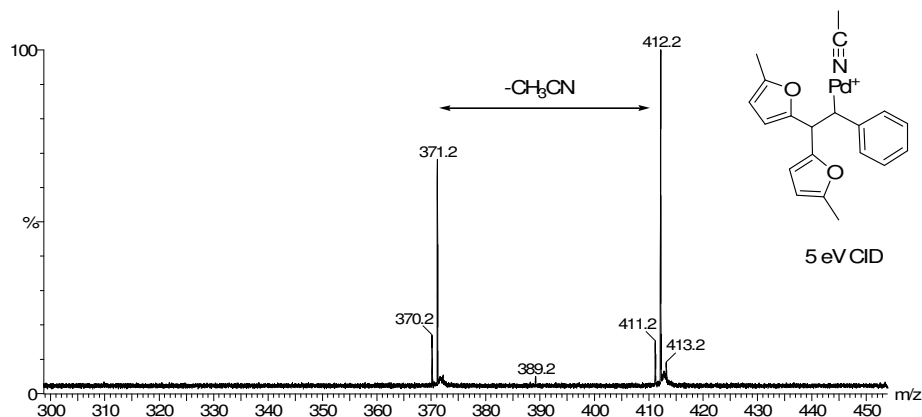
Figure S5: ESI-MS(/MS) of [F1-2L-H]⁺



2.4.2 [F1-L-H]⁺

ESHRMS for C₂₀H₂₀NO₂¹⁰⁶Pd: calcd. 412.0529, found 412.0520.

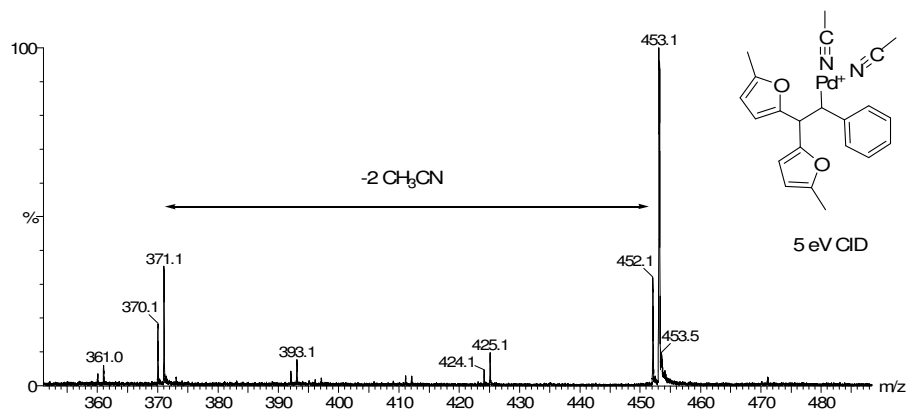
Figure S6: ESI-MS(/MS) of [F1-L-H]⁺



2.4.3 [F1-H]⁺

ESHRMS for C₂₂H₂₃N₂O₂¹⁰⁶Pd: calcd. 453.0794, found 453.0805.

Figure S7: ESI-MS(/MS) of [F1-H]⁺

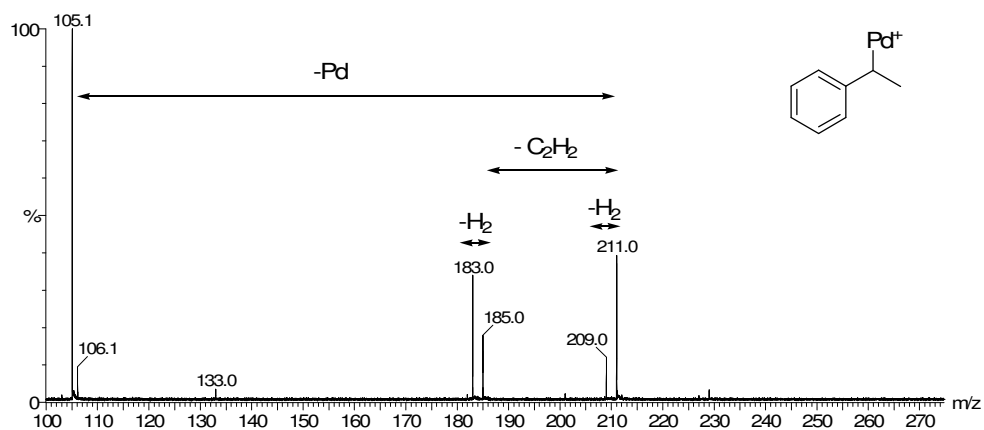


2.5 Species $[\mathbf{1f}+\text{Pd}+\text{H}]^+$ and $[\mathbf{1f}+\text{Pd}+\text{CH}_3\text{CN}+\text{H}]^+$

2.5.1 $[\mathbf{1f}+\text{Pd}+\text{H}]^+$

ESHRMS for $\text{C}_8\text{H}_9^{106}\text{Pd}$: calcd. 210.9739, found 210.9736.

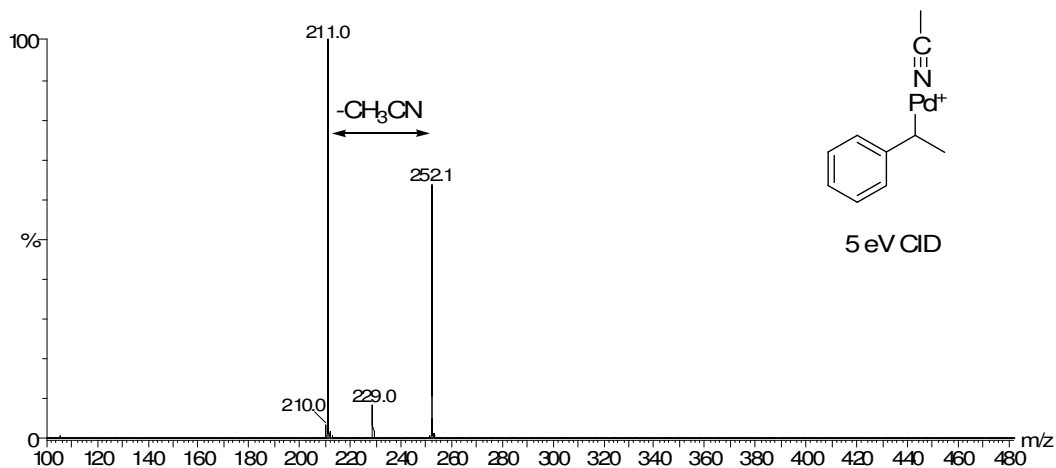
Figure S8: ESI-MS(/MS) of $[\mathbf{1f}+\text{Pd}+\text{H}]^+$



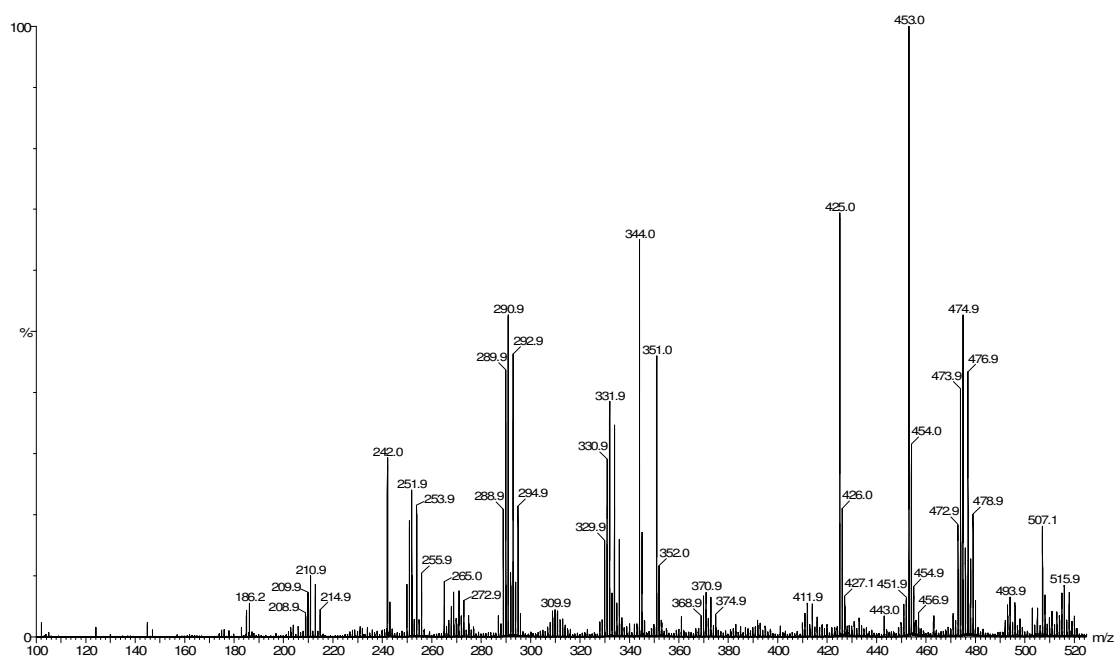
2.5.2 $[\mathbf{1f}+\text{Pd}+\text{CH}_3\text{CN}+\text{H}]^+$

ESHRMS for $\text{C}_{10}\text{H}_{12}\text{N}^{106}\text{Pd}$: calcd. 252.0004, found 252.0006.

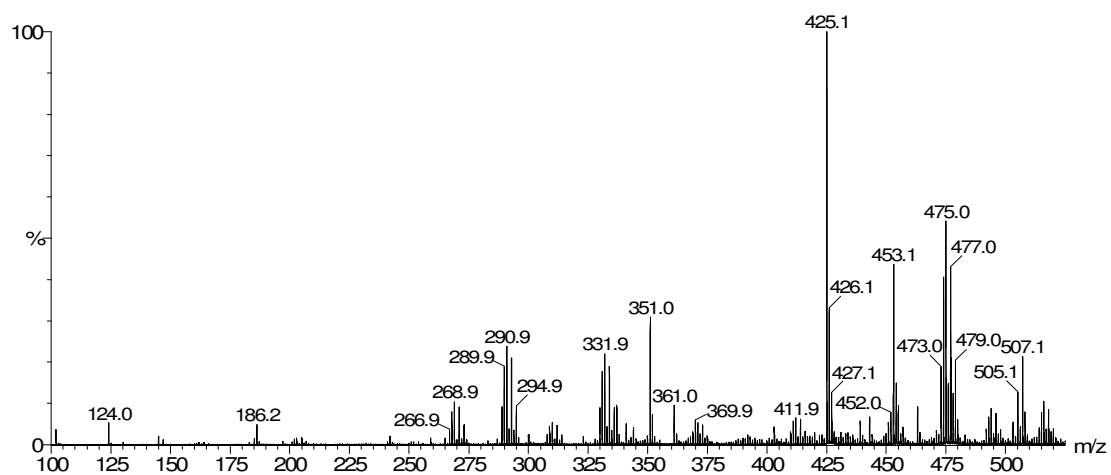
Figure S9: ESI-MS(/MS) of $[\mathbf{1f}+\text{Pd}+\text{CH}_3\text{CN}+\text{H}]^+$



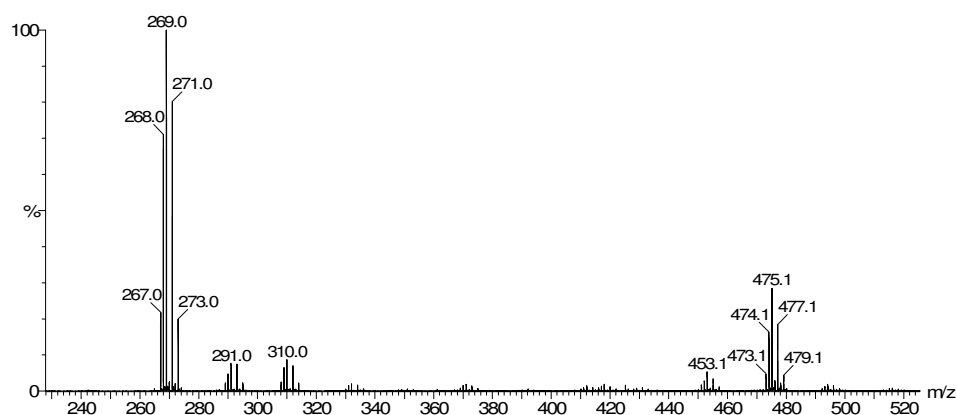
2.6 **Figure S10:** ESI of reaction mixture after 2.5 h



2.7 **Figure S11:** ESI of reaction mixture after 6h



2.8 Figure S12: ESI of reaction mixture after 24h

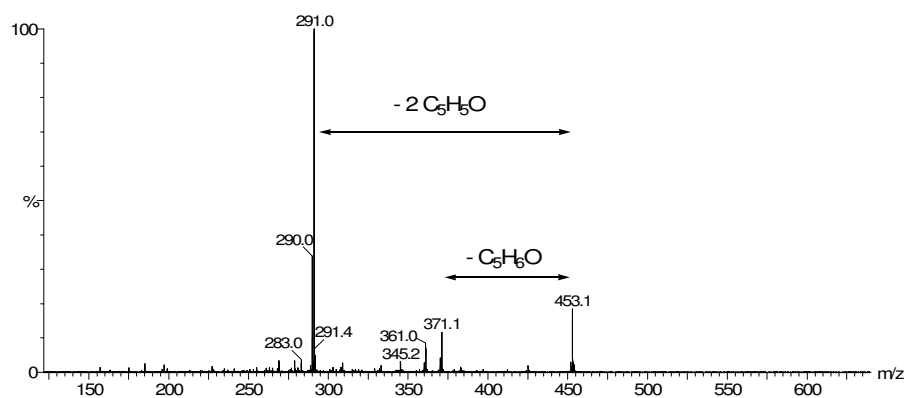


2.9 Palladium complexes of **3f**

2.9.1 $[\mathbf{3f}+\mathbf{B1}-2\mathbf{L}+\mathbf{H}]^+$

ESHRMS for $\text{C}_{23}\text{H}_{23}\text{O}_3^{106}\text{Pd}$: calcd. 453.0682, found 453.0685.

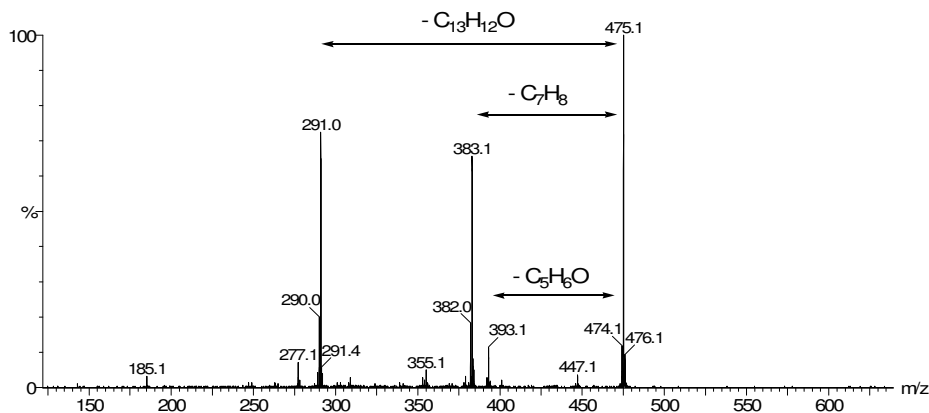
Figure S13: ESI-MS(/MS) of $[\mathbf{3f}+\mathbf{B1}-2\mathbf{L}+\mathbf{H}]^+$



2.9.2 $[\mathbf{3f}+\mathbf{3f}+\text{Pd}+\mathbf{H}]^+$

ESHRMS for $\text{C}_{26}\text{H}_{25}\text{O}_2^{106}\text{Pd}$: calcd. 475.0889, found 475.0884.

Figure S14: ESI-MS(/MS) of $[\mathbf{3f}+\mathbf{3f}+\text{Pd}+\mathbf{H}]^+$



3. References

- (1) Karminski-Zamola, G.; Jakopcic, K. *J. Heterocyclic Chem.* **1981**, *18*, 193-196.

4. ^{13}C NMR spectra of new compounds

