

Recyclable Ir nanoparticles for the catalytic hydrogenation of biomass derived carbonyl compounds

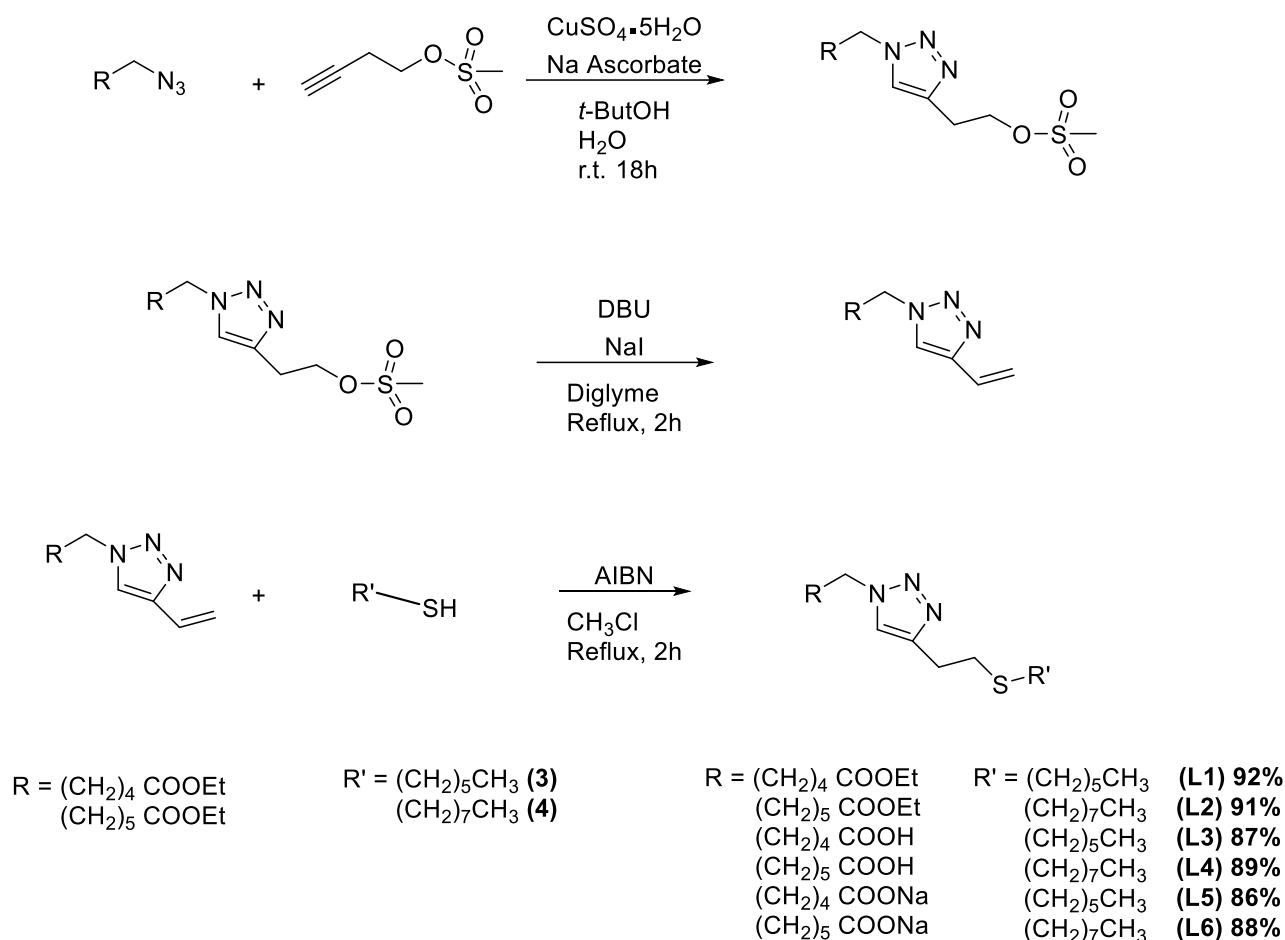
By

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Valentina Beghetto *

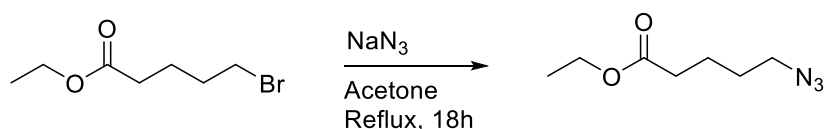
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Scheme S1: Synthesis of Ligands L1-L6



Synthesis of Ethyl-5-azidopentanoate



In a mixture of acetone (50 mL) and H₂O (30 mL) ethyl 5-bromopentanoate (3.71 mL, 23.38 mmol) and sodium azide (4.56 g, 70.14 mmol) were dissolved. The colourless solution was stirred for 18 hours under reflux. Afterwards, no changing in the colour of the solution was observed. Acetone was removed under reduced pressure and aqueous residues were extracted with CH₂Cl₂ (15 mL x 3). Organic layers were dried over MgSO₄, filtered, and concentrated under vacuo to yield the desired product as a colourless oil (92% yield).

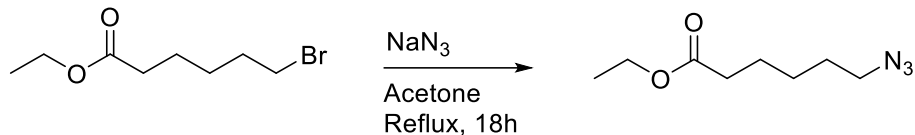
EA calcd for C₇H₁₃N₃O₂: C (49.11) H(7.65) N(24.54); found: C(49.78) H(7.71) N(24.6).

¹H NMR (300 MHz, CDCl₃) δ (ppm) = 4.12 (q, *J*=7.1 Hz, 2H), 3.28 (t, *J*=6.5 Hz, 2H), 2.32 (t, *J*=7.1 Hz, 2H), 1.83 – 1.50 (m, 4H), 1.24 (td, *J* = 7.2, 0.7 Hz, 3H).

^{13}C NMR (300 MHz, CDCl_3) δ (ppm) = 173.2, 60.4, 51.2, 33.8, 28.4, 22.2, 14.3.

HRMS (ESI) calcd for $\text{C}_7\text{H}_{13}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$: 173.09264 found: 173.09301

Synthesis of Ethyl-6-azidohexanoate



See the procedure abovementioned. Colourless oil (95% yield).

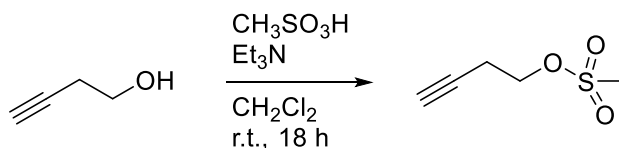
EA calcd for $\text{C}_8\text{H}_{15}\text{N}_3\text{O}_2$: C (51.88) H(8.16) N(22.69); found: C(51.75) H(7.91) N(23.20).

^1H NMR (300 MHz, CDCl_3) δ (ppm) = 4.01 (q, $J=7.1$ Hz, 2H), 2.38 (t, $J=6.5$ Hz, 2H), 1.66 (t, $J=7.1$ Hz, 2H), 1.47 (m, 4H), 1.12 (td, $J=7.2, 0.7$ Hz, 3H).

^{13}C NMR (300 MHz, CDCl_3) δ (ppm) = 173.5, 60.2, 50.3, 33.8, 29.4, 24.3, 22.2, 14.3.

HRMS (ESI) calcd for $\text{C}_8\text{H}_{15}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$: 185.11644 found: 185.0751

Synthesis of But-3-ynyl methanesulfonate



3-butyne-1-ol (1.62 mL, 21.40 mmol) and triethylamine (8.94 mL, 64.30 mmol) were dissolved in 100 mL of CH_2Cl_2 and vigorously stirred. Afterwards, an ice bath was placed under the round bottom flask and methanesulfonic acid chloride (2.16 mL, 27.76 mmol) was dropwise added to the stirring solution over 20 minutes. At the end of the addition, the ice bath was removed and the orange solution was allowed to stir overnight at room temperature. After 18 hours, a solution of HCl 1M was added at the solution and the organic layer was extracted and washed three times with CH_2Cl_2 (15 mL x 3), dried over MgSO_4 , filtered. Volatiles were removed under reduced pressure and **2** was obtained as an orange oil (98% yield).

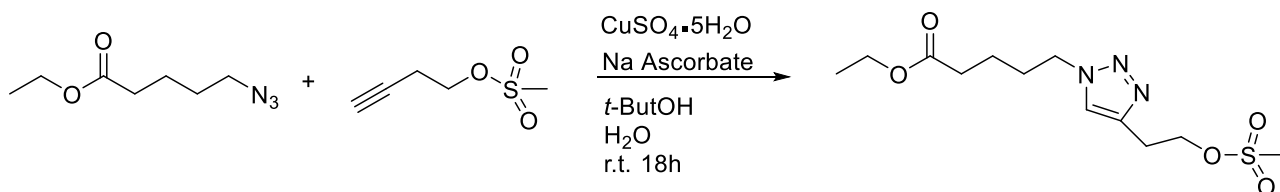
EA calcd for $\text{C}_5\text{H}_8\text{O}_3\text{S}$: C (40.53) H(5.44) S(21.64); found: C(40.66) H(5.34) S(22.01).

^1H NMR (300 MHz, CDCl_3) δ (ppm) = 4.29 (t, $J=6.7$ Hz, 2H), 3.04 (s, 3H), 2.64 (td, $J=6.7, 2.7$ Hz, 2H), 2.07 (t, $J=2.7$ Hz, 1H).

^{13}C NMR (300 MHz, CDCl_3) δ (ppm) = 78.7, 71.0, 67.2, 37.6, 19.7.

HRMS (ESI) calcd for $\text{C}_5\text{H}_8\text{O}_3\text{N}_3\text{S}$ $[\text{M}+\text{H}]^+$: 148.01943 found: 148.01923

Synthesis of ethyl 4-(4-(2-((methylsulfonyl)oxy)ethyl)-1*H*-1,2,3-triazol-1-yl)butanoate



Ethyl-5-azidopentanoate (3.21 g, 18.77 mmol) and But-3-ynyl methanesulfonate (2.78 g, 18.77 mmol) were dissolved in *t*-ButOH (25 mL) and H_2O (20 mL). In a separate vial $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.23 g, 0.94 mmol) and Na Ascorbate (0.37 g, 1.87 mmol) were dissolved in 5 mL of H_2O and vigorously mixed through a Pasteur pipette until a light brown emulsion was obtained. The mixture was then transferred dropwise to the reaction flask which after addition turned into a brown solution. The reaction was then allowed to stir at room temperature for 24 hours. A yellow solution was obtained and *t*-ButOH was eliminated under reduced pressure. The aqueous residues were then diluted with 10 mL of a saturated solution of EDTA and extracted with CH_2Cl_2 (15 mL x 3) in order to remove copper salts traces. The organic layers were collected and dried over MgSO_4 , filtered and volatiles eliminated under vacuo to yield ethyl 4-(4-(2-((methylsulfonyl)oxy)ethyl)-1*H*-1,2,3-triazol-1-yl)butanoate as a yellow oil (88% yield).

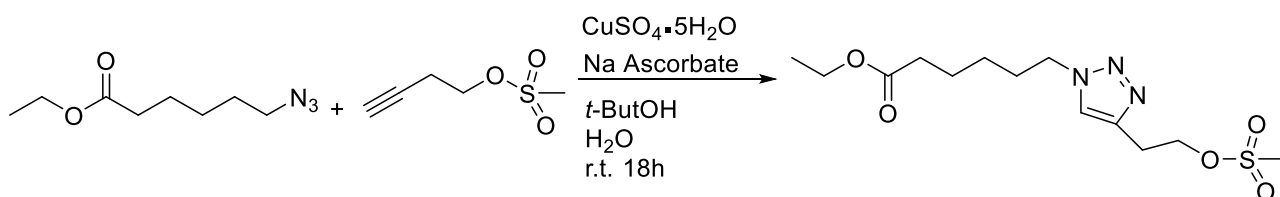
EA calcd for $\text{C}_{12}\text{H}_{21}\text{N}_3\text{O}_5\text{S}$: C (45.13) H(6.63) N(13.16) S(10.04); found: C(44.98) H(6.55) N(13.55) S(10.32)

^1H NMR (300 MHz, CDCl_3) δ (ppm) = 7.46 (s, 1H), 4.48 (t, J = 6.4 Hz, 2H), 4.32 (t, J = 7.1 Hz, 2H), 4.08 (q, J = 7.1 Hz, 2H), 3.14 (t, J = 7.2 Hz, 2H), 2.95 (s, 3H), 2.31 (t, J = 7.3 Hz, 2H), 2.04 – 1.81 (m, 2H), 1.72 – 1.49 (m, 2H), 1.21 (t, J = 7.1 Hz, 4H).

^{13}C NMR (300 MHz, CDCl_3) δ (ppm) = 172.8, 122.1, 68.7, 60.4, 49.9, 37.3, 33.3, 29.5, 26.0, 21.7, 14.2. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{21}\text{O}_5\text{N}_3\text{S}$ $[\text{M}+\text{H}]^+$: 319.12022 found: 319.12088

Synthesis of ethyl 6-(4-(2-((methylsulfonyl)oxy)ethyl)-1*H*-1,2,3-triazol-1-yl)hexanoate

See the procedure abovementioned. Pale yellow oil (92%).



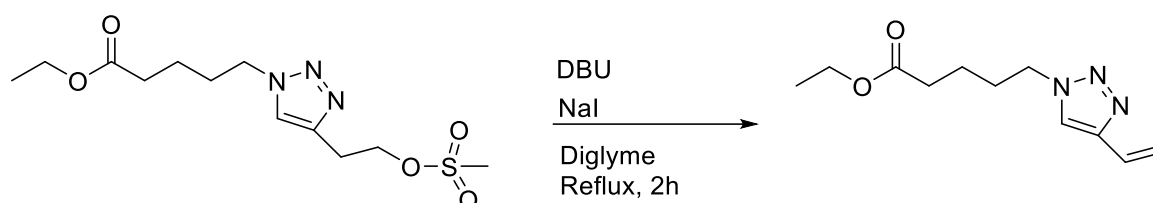
EA calcd for $C_{13}H_{23}N_3O_5S$: C (46.83) H(6.95) N(12.60) S(9.62); found: C(47.23) H(7.55) N(13.05) S(10.27)

1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.54 (s, 1H), 4.46 (t, J = 6.4 Hz, 2H), 4.12 (t, J = 7.1 Hz, 2H), 4.01 (q, J = 7.1 Hz, 2H), 3.10 (t, J = 7.2 Hz, 2H), 2.99 (s, 3H), 2.35 (t, J = 7.3 Hz, 2H), 2.14 – 1.87 (m, 2H), 1.69 (m, 2H), 1.37 (m, 2H), 1.11 (t, J = 7.1 Hz, 4H).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) = 172.8, 122.1, 68.7, 60.4, 49.9, 42.5, 37.3, 33.3, 29.5, 26.0, 21.7, 14.2.

HRMS (ESI) calcd for $C_{13}H_{23}O_5N_3S$ $[M+H]^+$: 333.1359 found:333.1253.

Synthesis of ethyl 5-(4-vinyl-1*H*-1,2,3-triazol-1-yl)pentanoate



Ethyl 4-(4-(2-((methylsulfonyl)oxy)ethyl)-1*H*-1,2,3-triazol-1-yl)butanoate (5.27 g, 16.50 mmol) and NaI (7.42 g, 49.50 mmol) were dissolved in glyme (80 mL) and stirred at room temperature for 1 hour until an intense orange solution was obtained. DBU (4.93 mL, 33.00 mmol) was then added and the solution was refluxed for 3 hours while the solution turned into a white emulsion. Afterwards, solids formed during reaction were filtered and washed with EtOAc. Organic layers were dried over $MgSO_4$, filtered and concentrated to yield ethyl 5-(4-vinyl-1*H*-1,2,3-triazol-1-yl)pentanoate as a yellow oil (85% yield).

EA calcd for $C_{11}H_{17}O_2N_3$: C (59.17) H(7.67) N(18.82); found: C(59.21) H(7.83) N(18.12)

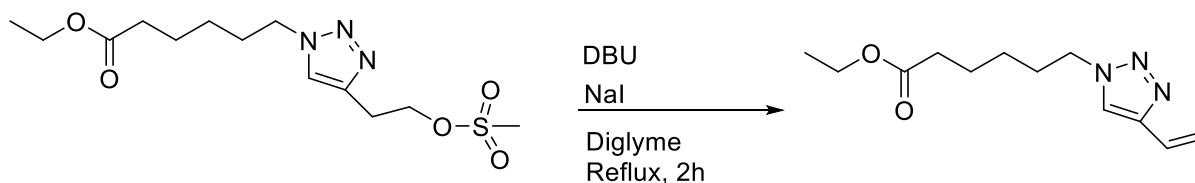
1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.53 (s, 1H), 6.73 (dd, J =17.8, 11.2 Hz, 1H), 5.89 (dd, J =17.7, 1.3 Hz, 1H), 5.35 (dd, J =11.2, 1.3 Hz, 1H), 4.37 (t, J = 7.1 Hz, 2H), 4.13 (d, J = 7.2 Hz, 2H), 2.36 (t, J = 7.2 Hz, 2H), 2.13 – 1.85 (m, 2H), 1.80 – 1.59 (m, 2H), 1.26 (t, 6.1 Hz, 3H).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) = 172.9, 146.4, 125.7, 120.0, 115.9, 60.5, 49.8, 33.4, 29.6, 21.8, 14.2.

HRMS (ESI) calcd for $C_{11}H_{17}O_2N_3$ $[M+H]^+$: 223.13209 found: 223.13232.

Synthesis of ethyl 6-(4-vinyl-1*H*-1,2,3-triazol-1-yl)hexanoate

See the procedure abovementioned. Pale yellow oil (87%)



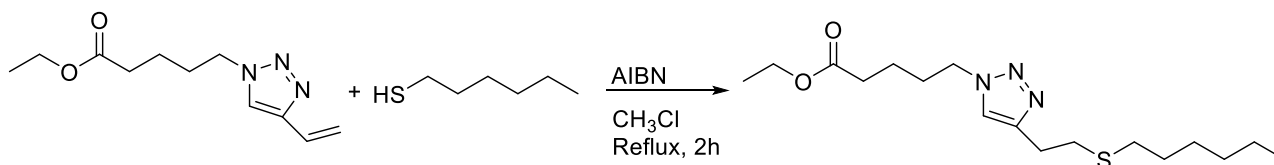
EA calcd for $C_{12}H_{19}O_2N_3$: C (60.74) H(8.07) N(17.71); found: C(59.62) H(7.13) N(16.92)

1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.58 (s, 1H), 6.62 (dd, $J=17.8, 11.2$ Hz, 1H), 5.85 (dd, $J=17.7, 1.3$ Hz, 1H), 5.45 (dd, $J=11.2, 1.3$ Hz, 1H), 4.32 (t, $J=7.1$ Hz, 2H), 4.17 (d, $J=7.2$ Hz, 2H), 2.36 (t, $J=7.2$ Hz, 2H), 2.01 (m, 2H), 1.67 (m, 2H), 1.26 (m, $J=8.2, 6.1$ Hz, 2H), 1.15 (t, $J=6.2$ Hz, 3H)

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) = 172.8, 146.7, 125.2, 119.7, 116.2, 60.1, 49.2, 41.4, 33.4, 29.5, 21.6, 14.0,

HRMS (ESI) calcd for $C_{12}H_{19}O_2N_3$ $[M+H]^+$: 237.1477 found: 237.1459.

Synthesis of ethyl 5-(4-(2-(hexylthio)ethyl)-1H-1,2,3-triazol-1-yl)pentanoate (L1)



Ethyl 5-(4-vinyl-1H-1,2,3-triazol-1-yl)pentanoate (1.82 g, 8.14 mmol), 1-hexanthiol (1.38 mL, 9.76 mmol) and AIBN (0.67 g, 4.07 mmol) were dissolved in chloroform (25 mL) and refluxed. The reaction was monitored by 1H NMR. After 2 hours, complete conversion. The crude mixture was then purified by flash chromatography (Hexan/EtOAc 7:3) to yield **L1** as a pale yellow oil (92% yield).

EA calcd for $C_{17}H_{31}O_2N_3S$: C (59.79) H(9.15) N(12.30) S(9.39); found: C(59.21) H(9.54) N(12.66) S(9.57)

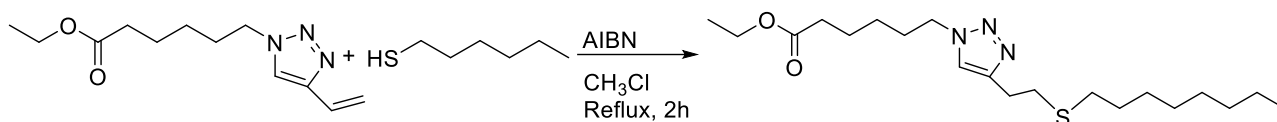
1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.40 (s, 1H), 4.36 (t, $J=7.1$ Hz, 2H), 4.15 (q, $J=7.1$ Hz, 2H), 3.02 (t, $J=7.4$ Hz, 2H), 2.86 (t, $J=7.4$ Hz, 2H), 2.55 (t, $J=7.4$ Hz, 2H), 2.36 (t, $J=7.2$ Hz, 2H), 1.96 (m, 2H), 1.77 – 1.50 (m, 4H), 1.48 – 1.05 (m, 11H), 0.91 (t, $J=6.6$ Hz, 3H).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) = 172.9, 146.4, 121.1, 60.5, 49.8, 33.4, 32.2, 31.7, 31.4, 29.6, 28.6, 26.3, 22.5, 22.5, 21.8, 14.2, 14.0.

HRMS (ESI) calcd for $C_{17}H_{31}O_2N_3S$ $[M+H]^+$: 341.21371 found: 341.21354

Synthesis ethyl 6-(4-(2-(octylthio)ethyl)-1H-1,2,3-triazol-1-yl)hexanoate (L2)

See the procedure abovementioned. Pale yellow oil (91%)



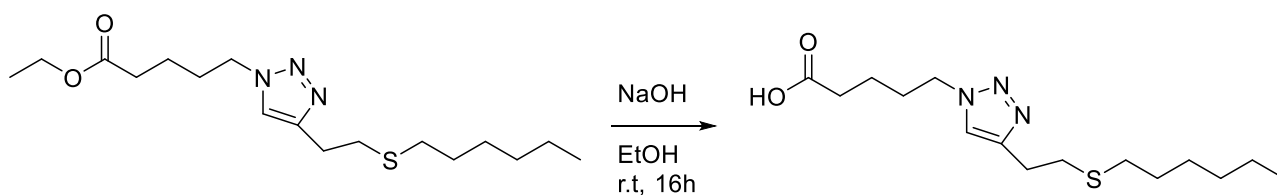
EA calcd for $C_{19}H_{35}O_2N_3S$: C (61.75) H(9.55) N(11.37) S(8.67); found: C(60.82) H(9.04) N(12.46) S(9.01)

1H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.37 (s, 1H), 4.44 (t, J = 7.1 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 3.00 (t, J = 7.4 Hz, 2H), 2.83 (t, J = 7.4 Hz, 2H), 2.52 (t, J = 7.4 Hz, 2H), 2.34 (t, J = 7.2 Hz, 2H), 1.95 (m, 2H), 1.65 (m, 4H), 1.25 (m, 13H), 0.88 (t, J = 6.6 Hz, 3H).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) = 172.8, 145.9, 120.3, 60.3, 50.8, 41.9, 32.4, 31.2, 30.9, 30.4, 29.4, 28.3, 26.7, 23.3, 22.9, 21.7, 14.6, 14.3.

HRMS (ESI) calcd for $C_{19}H_{35}O_2N_3S$ $[M+H]^+$: 369.2451 found: 369.2342

Synthesis of 5-(4-(2-(hexylthio)ethyl)-1H-1,2,3-triazol-1-yl)pentanoic acid (**L3**)



L1 (0.90 g, 2.67 mmol) was dissolved in EtOH (6 mL) and a solution of NaOH (0.20 g, 5 mmol) and H_2O (4 mL) was added and the reaction was allowed to gently stir for 16 hours at room temperature. At the end of this period, EtOH was removed under vacuo and aqueous layer was diluted with HCl 1 M (25 mL) and extracted with CH_2Cl_2 (15 mL x 3). Organic solutions were dried over $MgSO_4$, filtered, and concentrated to yield **L3** as a white solid (87% yield).

EA calcd for $C_{15}H_{26}O_2N_3S$: C (57.66) H(8.39) N(13.45) S(10.26); found: C(57.11) H(8.54) N(13.54) S(10.56)

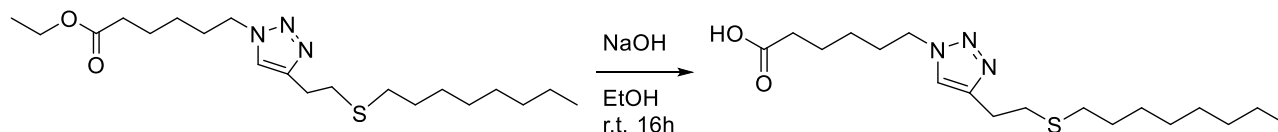
1H NMR (300 MHz, $CDCl_3$) δ (ppm) 10.51 (bs, 1H), 7.43 (s, 1H), 4.34 (t, J = 7.0 Hz, 2H), 2.99 (t, J = 7.2 Hz, 2H), 2.81 (s, 2H), 2.50 (t, J = 7.4 Hz, 2H), 2.38 (t, J = 7.2 Hz, 2H), 2.05 – 1.87 (m, 2H), 1.60 (m, 4H), 1.43 – 1.18 (m, 9H), 0.85 (t, J = 6.7 Hz, 3H).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) = 178.4, 130.7, 121.9, 52.1, 33.4, 32.2, 31.7, 31.4, 29.6, 28.6, 26.3, 22.5, 22.5, 21.8, 14.2.

HRMS (ESI) calcd for $C_{15}H_{26}O_2N_3S$ $[M+H]^+$: 312.17458 found: 312.17323

Synthesis of 6-(4-(2-(octylthio)ethyl)-1H-1,2,3-triazol-1-yl)hexanoic acid (**L4**)

See the procedure abovementioned. White solid (89%).



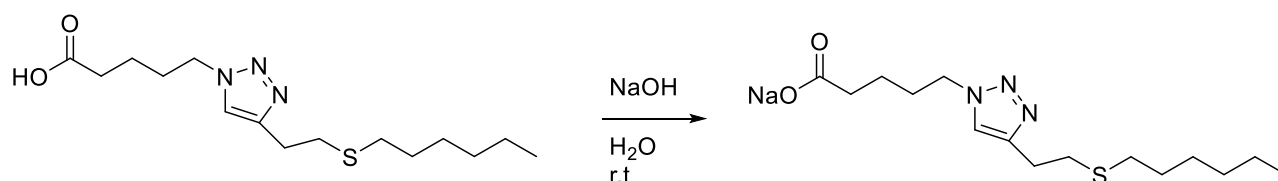
EA calcd for for $C_{18}H_{33}O_2N_3S$: C (60.81) H(9.36) N(11.82) S(9.02); found: C(60.17) H(9.01) N(12.14) S(9.86)

1H NMR (300 MHz, $CDCl_3$) δ (ppm) 10.01 (bs, 1H), 7.37 (s, 1H), 4.44 (t, $J = 7.0$ Hz, 2H), 3.00 (t, $J = 7.2$ Hz, 2H), 2.83 (s, 2H), 2.52 (t, $J = 7.4$ Hz, 2H), 2.34 (t, $J = 7.2$ Hz, 2H), 1.95 (m, 2H), 1.65 (m, 4H), 1.25 (m, 13H), 0.88 (t, $J = 6.7$ Hz, 3H).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) = 173.4, 146.9, 121.5, 60.9, 50.4, 33.9, 32.7, 32.1, 30.1, 29.6, 29.3, 26.8, 26.3, 23.1, 22.3, 14.7.8, 14.5.

HRMS (ESI) calcd for $C_{18}H_{33}O_2N_3S$ $[M+H]^+$: 355.2293 found: 355.2343

Synthesis of sodium 5-(4-(2-(hexylthio)ethyl)-1H-1,2,3-triazol-1-yl)pentanoate (L5)



An aqueous solution of NaOH 1M (10 mL) was added to a round bottom flask containing L4 (L4/NaOH=1:1) The heterogenous mixture was allowed to vigorously stir for 2 hours until an homogenous colourless solution was obtained. Evaporating water under vacuo allowed to obtained L5 as a white solid (86%).

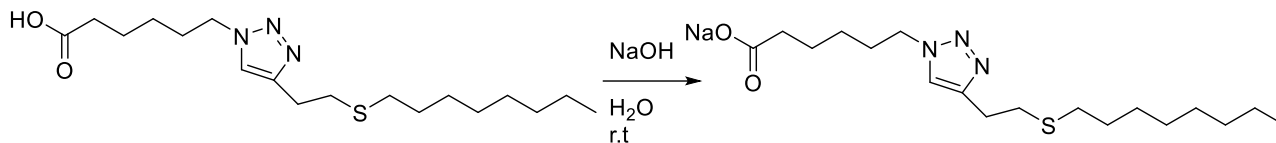
EA calcd for for $C_{15}H_{25}O_2N_3SNa$: C (53.87) H(7.53) N(12.56) S(9.59); found: C(54.11) H(7.34) N(13.12) S(9.78)

(300 MHz, $CDCl_3$) δ (ppm) 10.51 (bs, 1H), 7.43 (s, 1H), 4.34 (t, $J = 7.0$ Hz, 2H), 2.99 (t, $J = 7.2$ Hz, 2H), 2.81 (s, 2H), 2.50 (t, $J = 7.4$ Hz, 2H), 2.38 (t, $J = 7.2$ Hz, 2H), 2.05 – 1.87 (m, 2H), 1.60 (m, 4H), 1.43 – 1.18 (m, 9H), 0.85 (t, $J = 6.7$ Hz, 3H).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) = 178.4, 130.7, 121.9, 52.1, 33.4, 32.2, 31.7, 31.4, 29.6, 28.6, 26.3, 22.5, 22.5, 21.8, 14.2,

HRMS (ESI) calcd for $C_{15}H_{26}O_2N_3SNa$ $[M+H]^+$: 335.16435 found: 335.15261

Synthesis of sodium 6-(4-(2-(octylthio)ethyl)-1*H*-1,2,3-triazol-1-yl)hexanoate (L6)



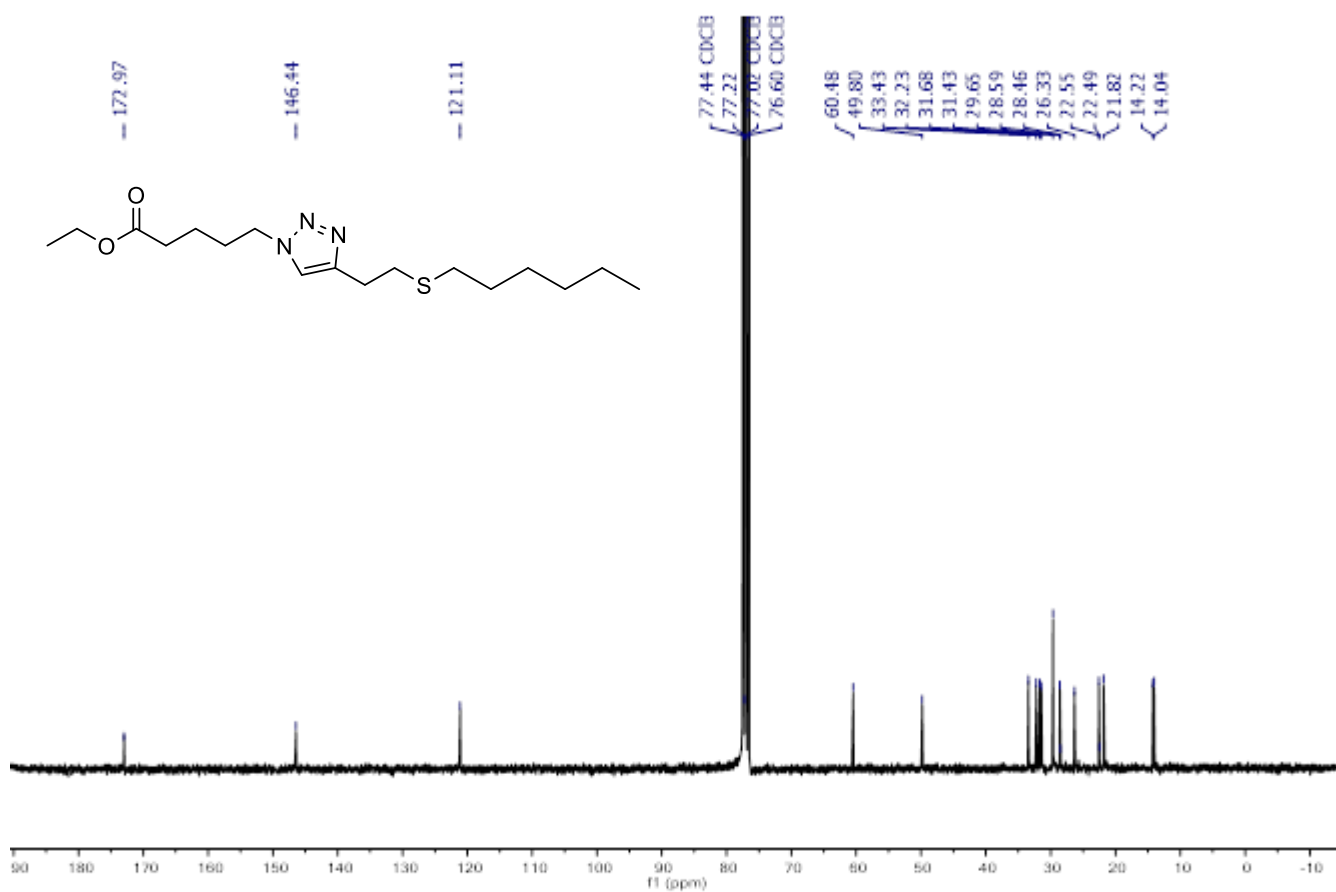
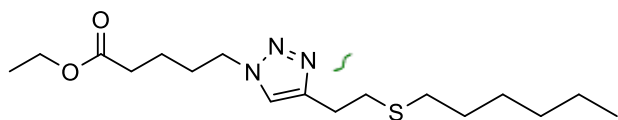
See the procedure abovementioned. White solid (88%)

EA calcd for C₁₈H₃₂O₂N₃SNa: C (60.81) H(9.36) N(11.82) S(9.02); found: C(60.17) H(9.01) N(12.14) S(9.86)

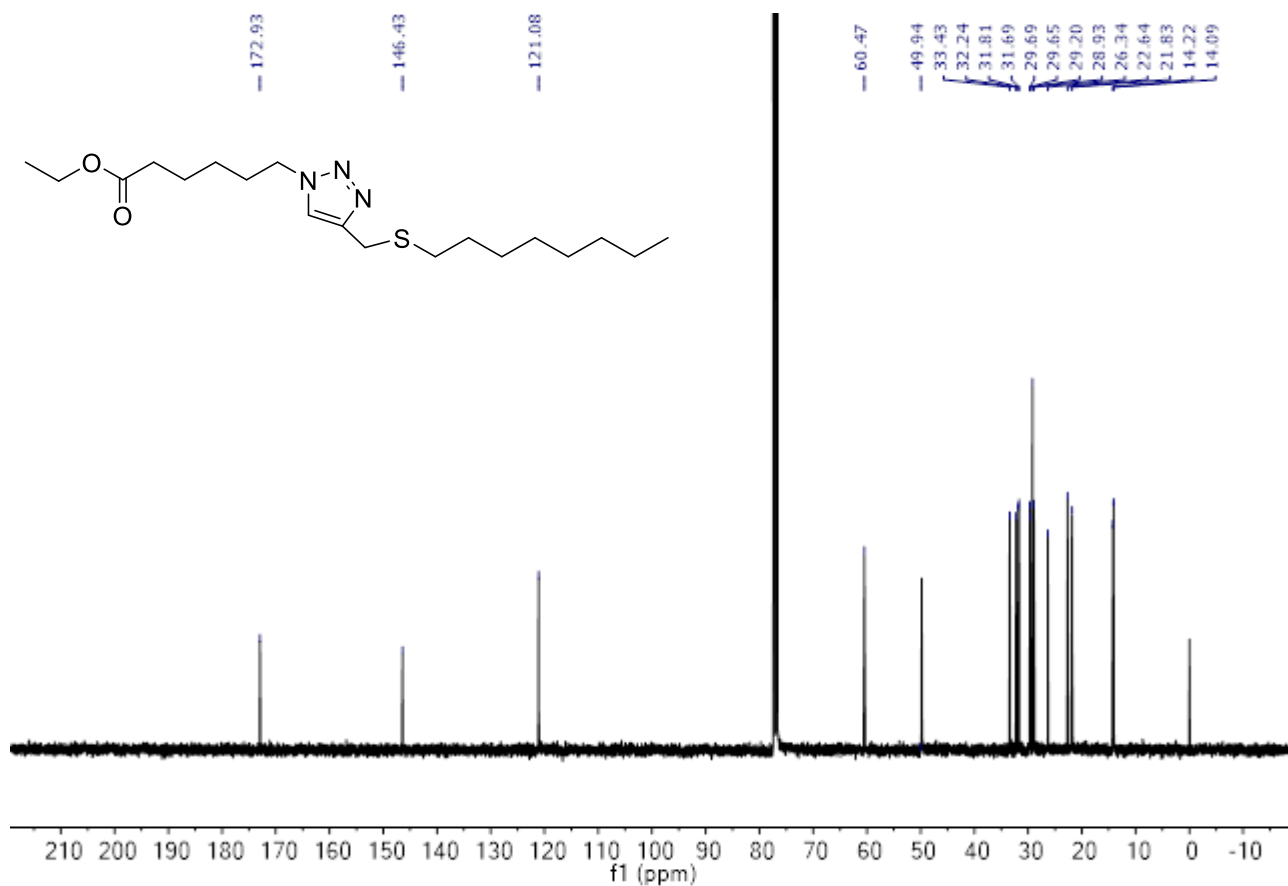
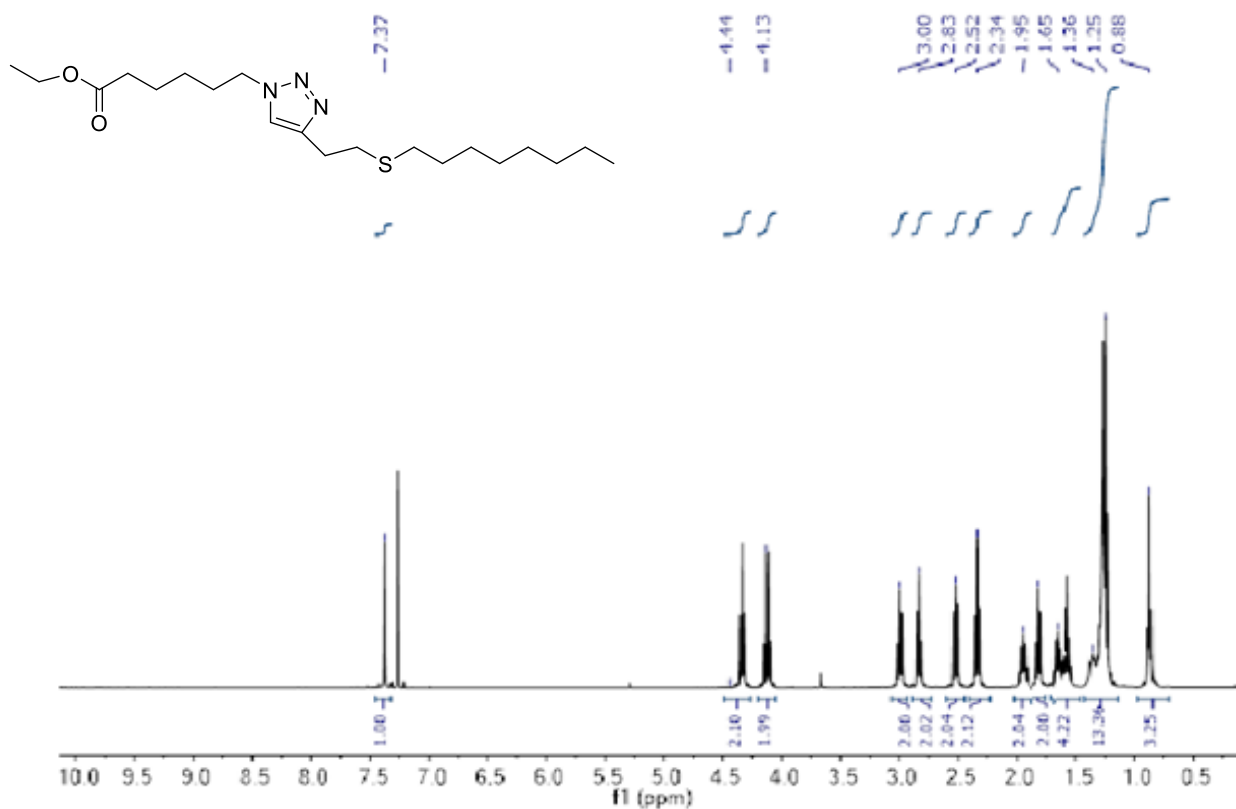
¹H NMR (300 MHz, D₂O) δ (ppm) 7.33 (s, 1H), 4.26 (t, J = 7.0 Hz, 2H), 3.24 (t, J = 7.2 Hz, 2H), 2.87 (s, 2H), 2.51 (t, J = 7.4 Hz, 2H), 2.33 (t, J = 7.2 Hz, 2H), 1.97 (m, 2H), 1.61 (m, 4H), 1.24 (m, 13H), 0.4 (t, J = 6.7 Hz, 3H).

HRMS (ESI) calcd for C₁₈H₃₃O₂N₃SNa [M+H]⁺: 377.2113; found: 377.2578

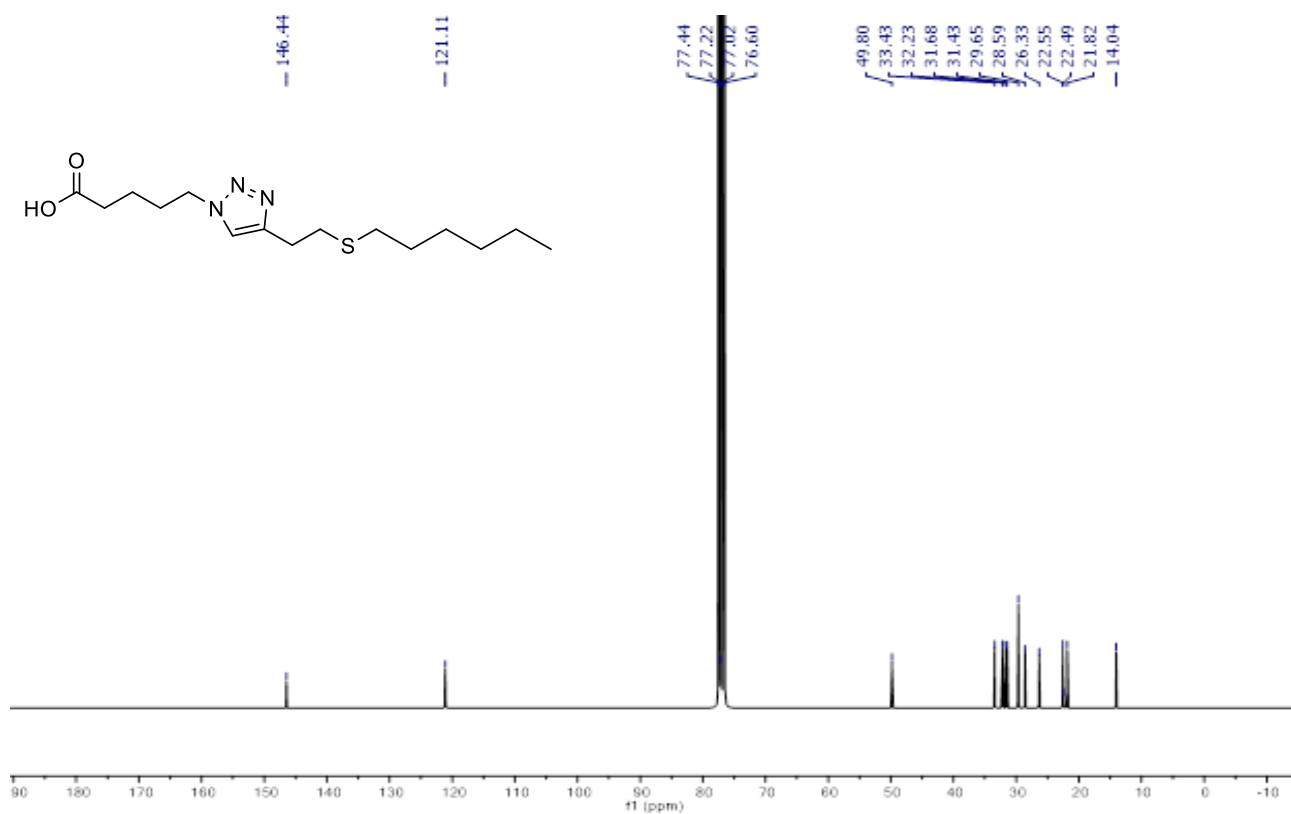
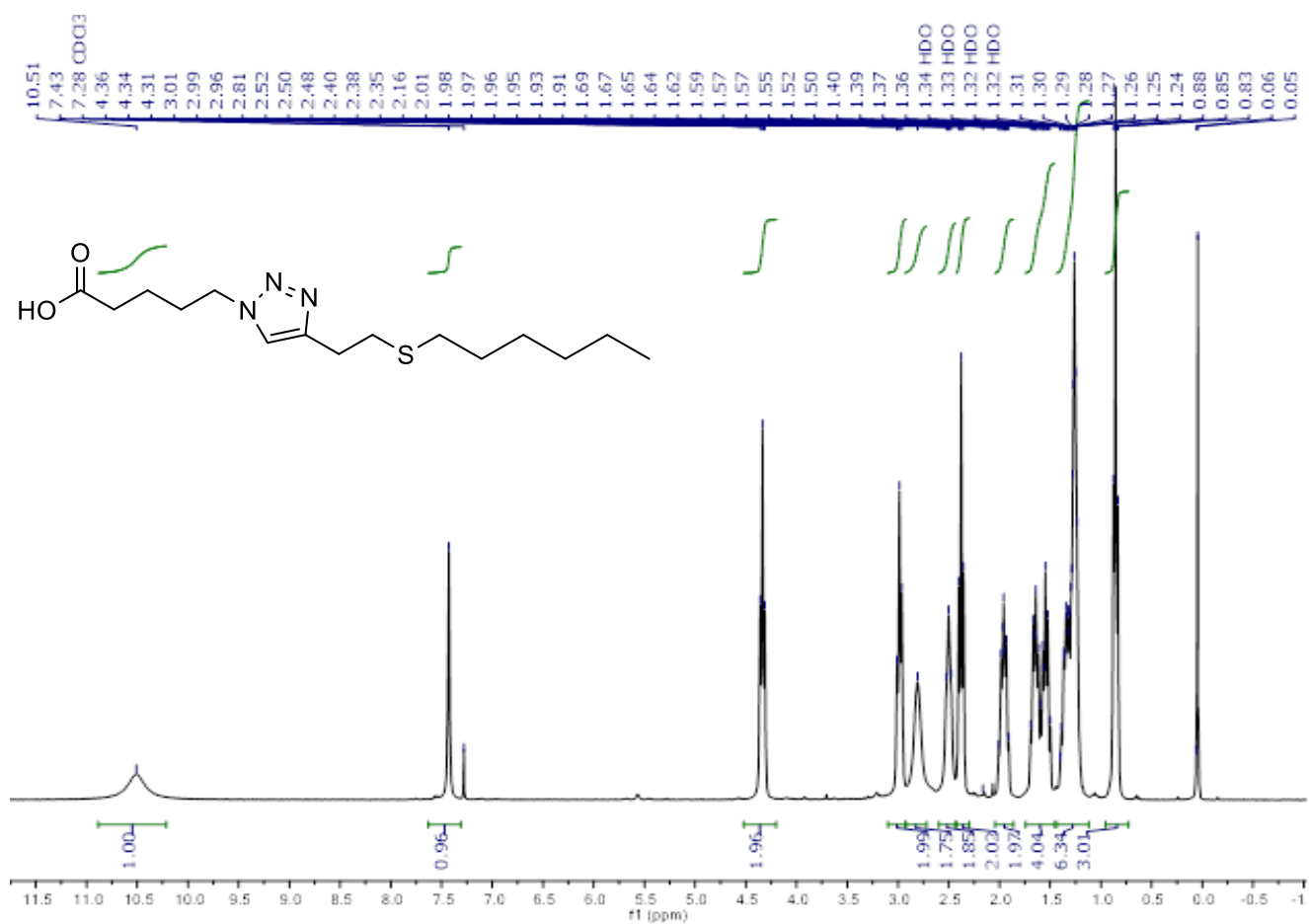
Ethyl 5-(4-(2-(hexylthio)ethyl)-1H-1,2,3-triazol-1-yl)pentanoate (L1)



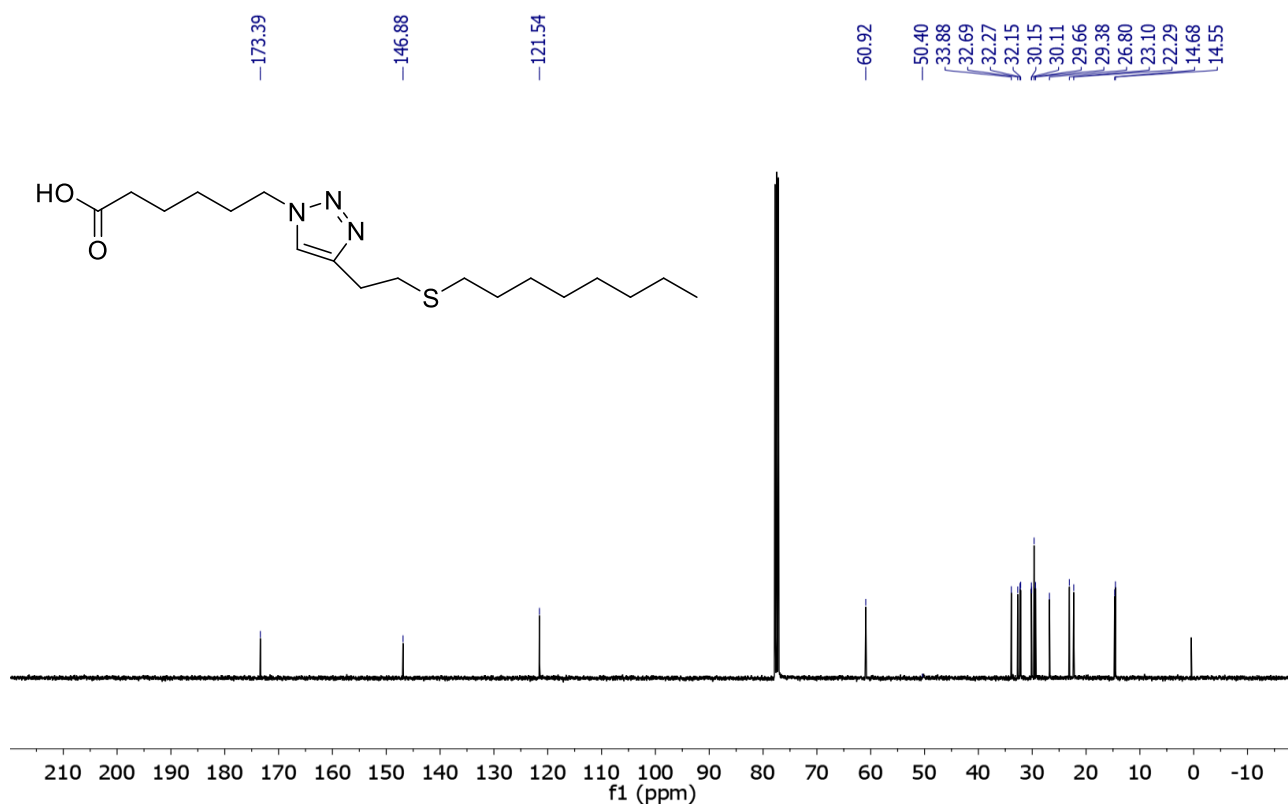
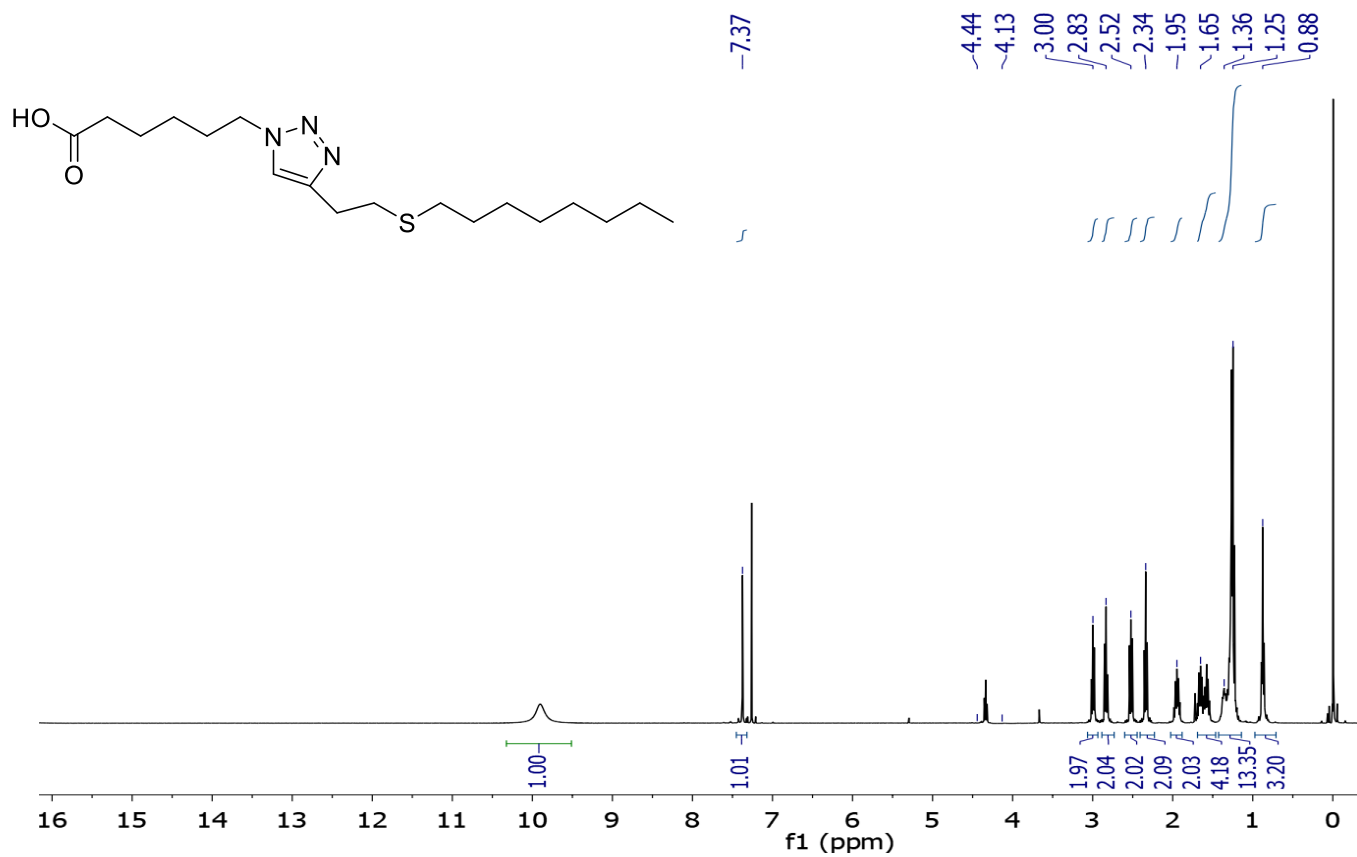
Ethyl 6-(4-(2-(octylthio)ethyl)-1H-1,2,3-triazol-1-yl)hexanoate (L2)



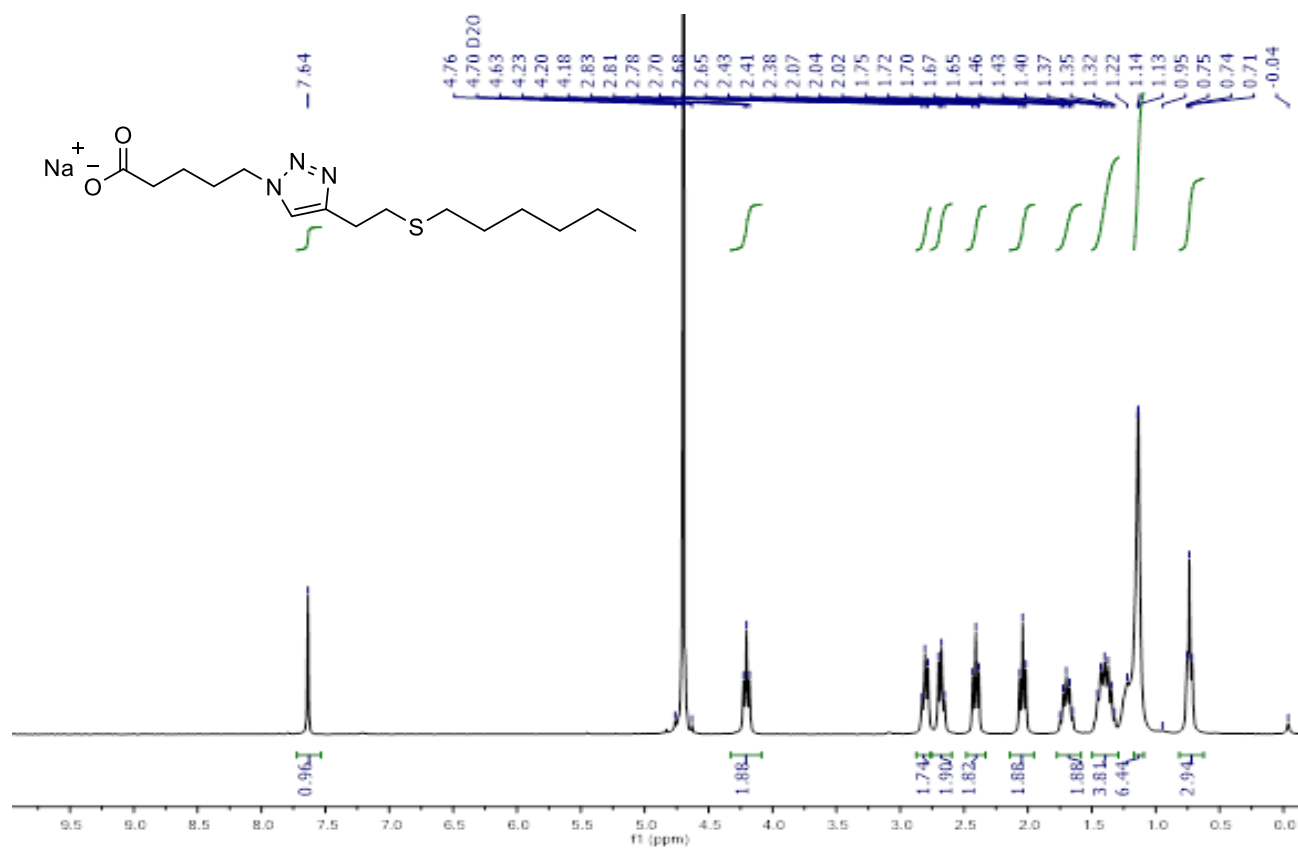
5-(4-(2-(hexylthio)ethyl)-1H-1,2,3-triazol-1-yl)pentanoic acid (**L3**)



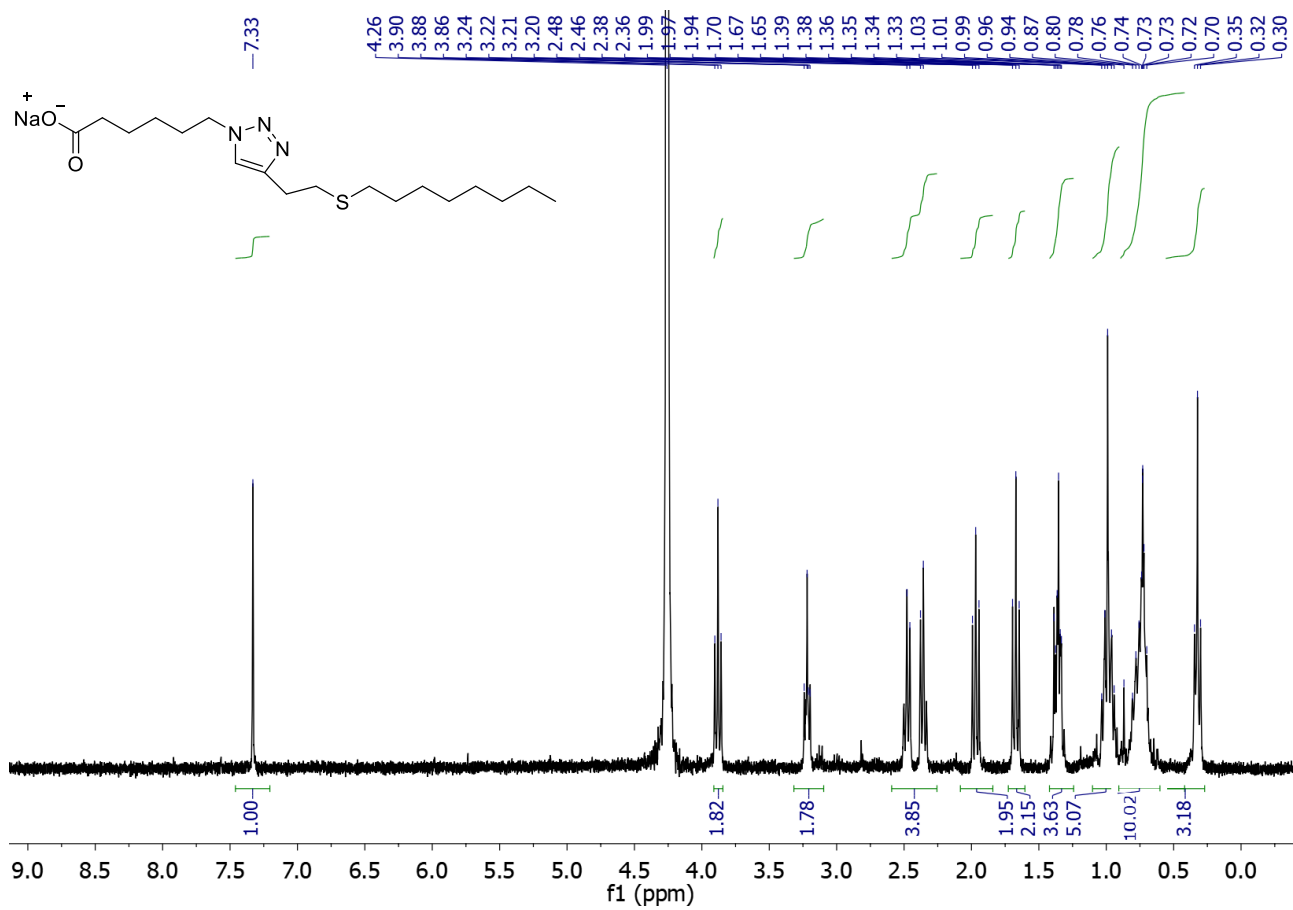
6-(4-(2-(octylthio)ethyl)-1H-1,2,3-triazol-1-yl)hexanoic acid (**L4**)



Sodium 5-(4-(2-(hexylthio)ethyl)-1H-1,2,3-triazol-1-yl)pentanoate (L5)



Sodium 6-(4-(2-(octylthio)ethyl)-1H-1,2,3-triazol-1-yl)hexanoate (L6)



Catalysis data

Table S1. Ligands and solvent screening for the hydrogenation of FUR to FA

$ \begin{array}{c} \text{OH} \\ \\ \text{C}_5\text{H}_4\text{O} + \text{H}_2 \xrightarrow[\text{H}_2\text{O/THF}]{[\text{Ir}(\text{COD})\text{Cl}]_2/\text{L1-L6}} \text{C}_5\text{H}_4\text{O} \\ \text{FUR} \qquad \qquad \qquad \text{FA} \end{array} $			
Entry ^a	Ligand	Solvent	Yield (%)
1	L1	EtOH	n.d.
2	L1	<i>i</i> -PrOH	12
3	L1	CH ₂ Cl ₂	35
4	L1	H ₂ O/ <i>i</i> -PrOH	21
5	L2	CH ₂ Cl ₂	19
6	L3	EtOH	18
7	L3	CH ₂ Cl ₂	33
8	L3	H ₂ O	46
9	L4	CH ₂ Cl ₂	16
10	L4	H ₂ O	27
11	L5	H ₂ O	70
12	L6	H ₂ O	59

^a Reaction conditions: [Ir(COD)Cl]₂ = 0.1 mol%, Ligand **L1-L6** = 0.2 mol%, NaOH (10 eq.), Furfural = 5.3 mmol, P_{H2}=40 bar, T = 60 °C, THF = 3.0 mL, H₂O = 3.0 mL, Time = 18 hours ^b GC yields using dodecane as internal standard ^c Recycling experiment referred to the previous entry

TEM and SEM images of different L:M ratios

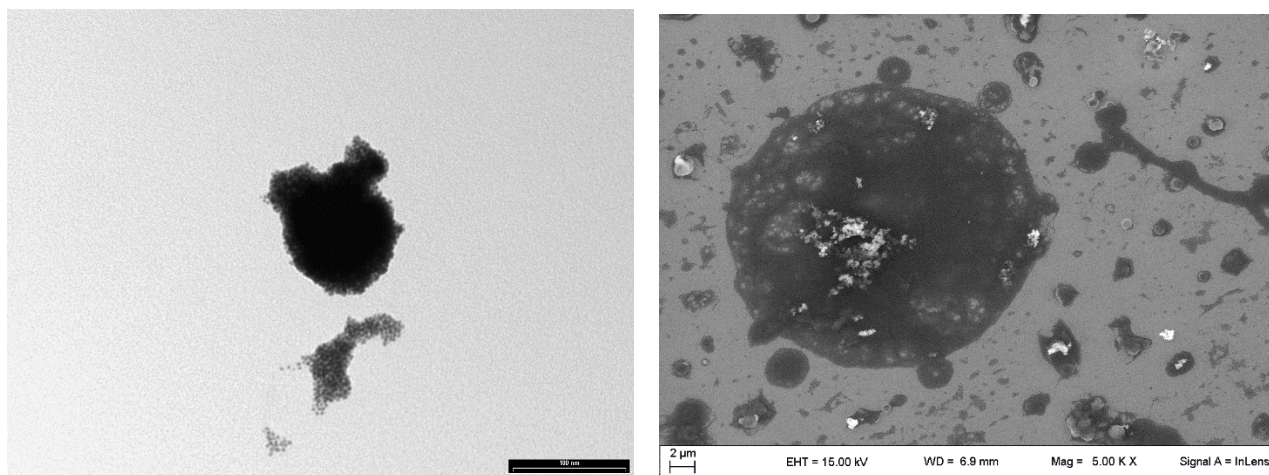


Figure S1: TEM (left) and SEM (right) of [Ir(COD)Cl]₂ with no surfactant ligand added.

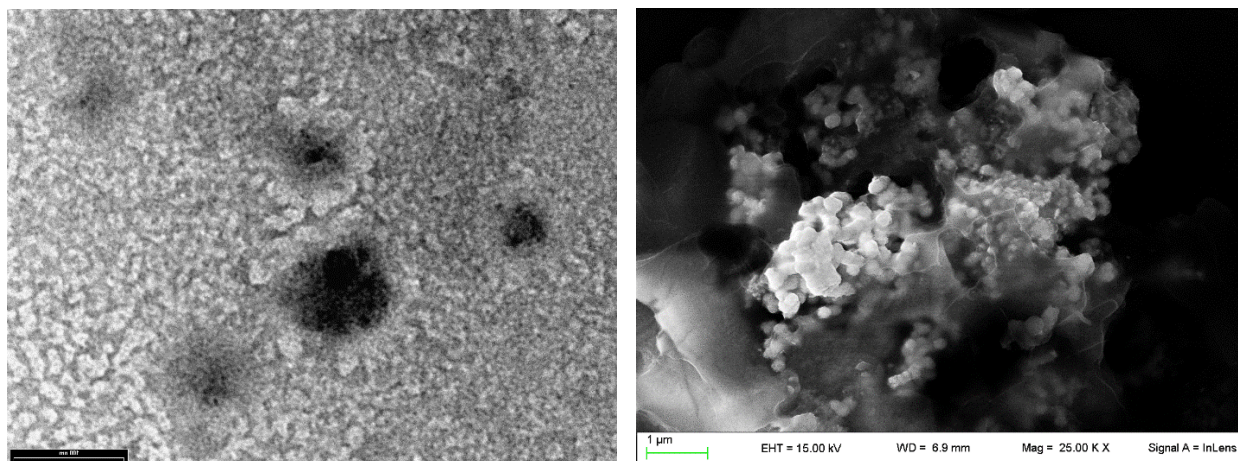


Figure S2: TEM (left) and SEM (right) of $[\text{Ir}(\text{COD})\text{Cl}]_2 / \text{L5}$ 1:0.25

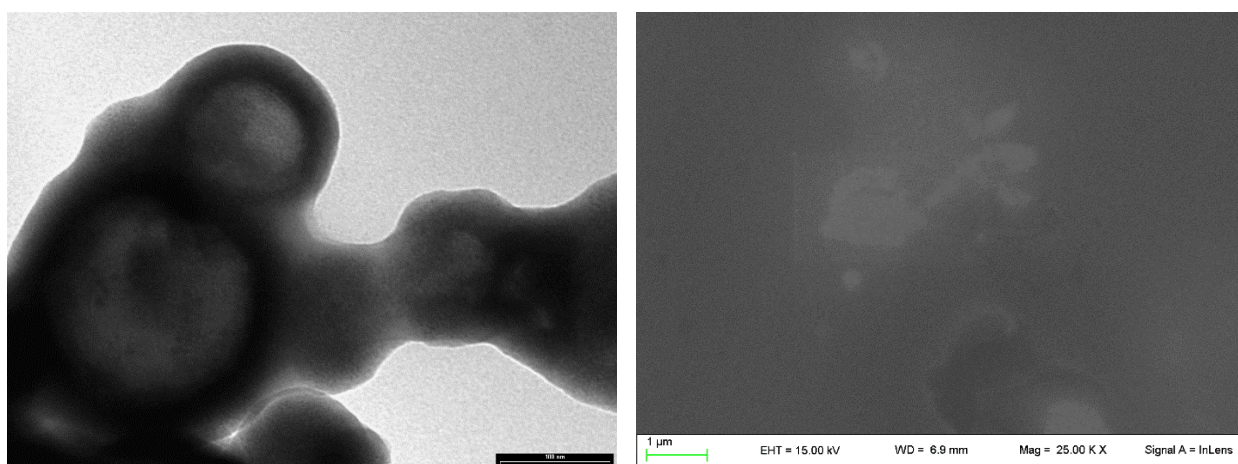


Figure S3: TEM (left) and SEM (right) of $[\text{Ir}(\text{COD})\text{Cl}]_2 / \text{L5}$ 1:0.75

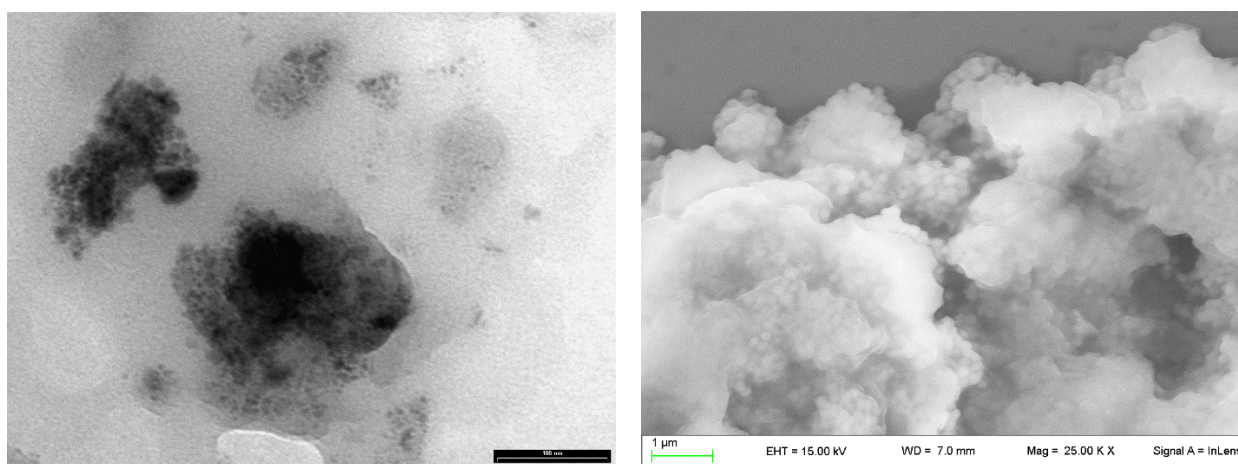


Figure S4: TEM (left) and SEM (right) of $[\text{Ir}(\text{COD})\text{Cl}]_2 / \text{L5}$ 1:1

TEM and SEM images of different $\text{Ir}(\text{COD})\text{Cl}_2/\text{L6}$ 1:0.5

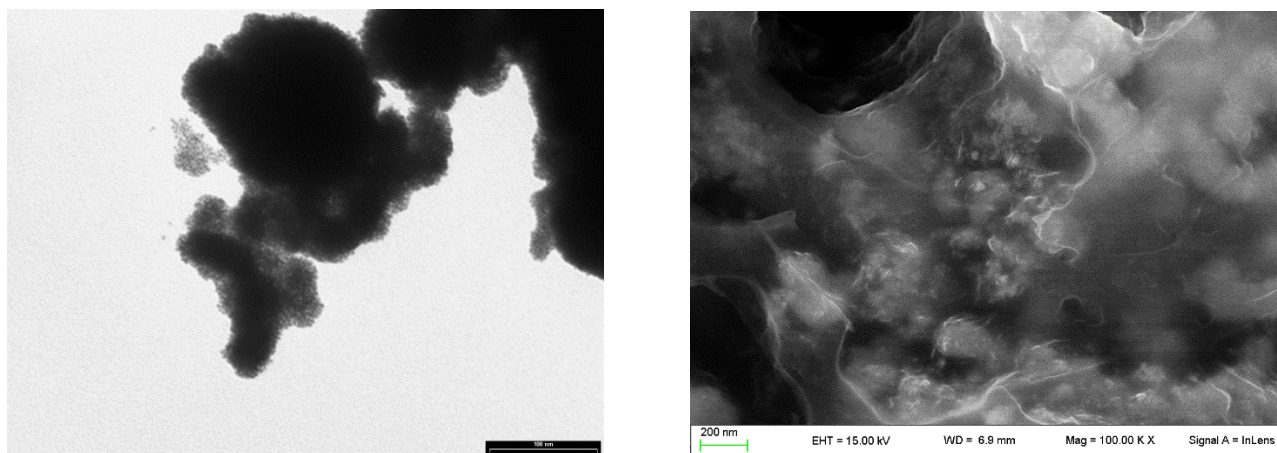


Figure S5: TEM (left) and SEM (right) of $[\text{Ir}(\text{COD})\text{Cl}]_2/\text{L6}$ 1:0.5