Electronic Supplementary Material (ESI) for Dalton Transactions.

Copper malonamide complexes and their use in azide-alkyne cycloaddition reactions

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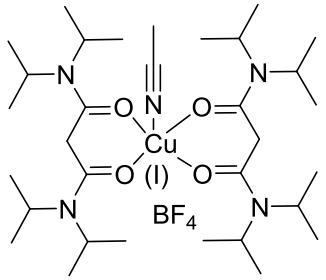
General considerations

Reagents were purchased from Sigma Aldrich and used without further purification. Laboratory grade dichloromethane was purchased from Fisher Scientific and used without further purification. NMR data was collected at 250, 300, 400 or 500 MHz on Bruker instruments in $CDCl_3$ at 293 K and referenced to residual protic solvent. Heated and anhydrous reactions were undertaken in Schlenk tubes or J-Young reaction tubes. MALDI-ToF analysis was carried out using a Bruker Daltonics Autoflex Speed MALDI-ToF/ToF using a DCTB matrix (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2propenylidene] malononitrile). The matrix was loaded onto the well followed by application of a solid sample of the oligomer. Analysis was carried out using Bruker PolyTools software.

Method for azide synthesis

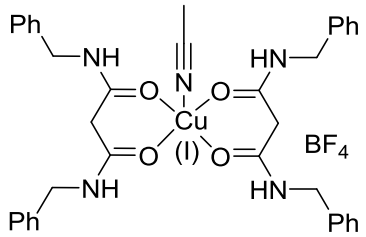
Following the method of S.G. Alvarez and M.T. Alverez,[1] a 0.5 M stock solution of NaN_3 (0.715 g, 11 mmol, 1.1 eq) in DMSO (22 mL) was prepared and left to stir at room temperature for 24 hours. The appropriate benzyl bromide (10 mmol, 1 eq) was added and the reaction mixture allowed to stir for an hour. The reaction was quenched with H_2O with constant stirring. The azide was extracted in Et_2O (3 x 30mL) and the extracts washed with H_2O (2 x 50 mL) and with brine (1 x 50 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent removed *in vacuo*.

1-Cu



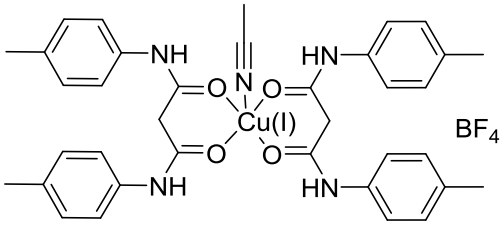
Lilac solid, 213 mg (48%), Elemental analysis (%): C 52.5, H 8.7, N 9.6 (calcd), C 52.8, H 8.3, N 9.5 (found). IR ν 2945, 2302, 2277, 1587, 1446, 1369, 1046, 1024, 895, 635 cm^{-1}; m.p. 147 °C (decomp).

2-Cu



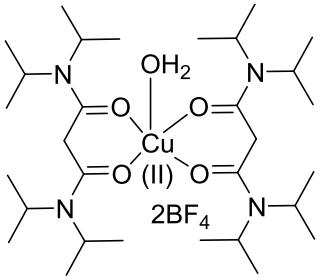
Lilac solid, 296 mg (65%). Elemental analysis (%): C 57.2, H 5.2, N 9.3 (calcd), C 56.9, H 5.1, N 9.2 (found). IR ν 3279, 2946, 2273, 1655, 1624, 1542, 1227, 1025, 693 cm^{-1}; m.p. 131 °C (decomp).

3-Cu



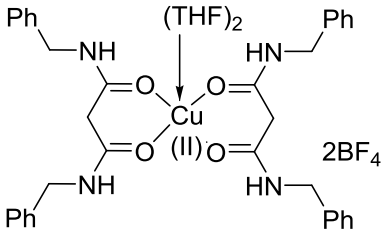
Pale lilac solid, 354 mg (77%). Elemental analysis (%): C 57.2, H 5.2, N 9.3 (calcd), C 57.0, H 5.4, N 9.5 (found). IR ν 3274, 3112, 2277, 1666, 1646, 1596, 1535, 1443, 1356, 1026, 750, 689 cm^{-1}; m.p. 153 °C (decomp).

5



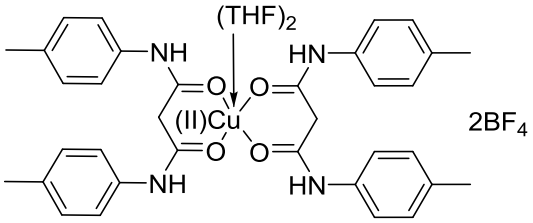
Pale turquoise solid, 26 mg (47%, from 50 mg **1**-**Cu**). Elemental analysis (%): C 45.3, H 7.9, N 7.0 (calcd), C 45.3, H 7.8, N 7.2 (found). IR ν 3528, 2974, 2942, 1582 cm^{-1}; m.p. 271°C (decomp).

6



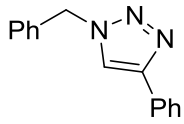
Pale turquoise solid, 10 mg (16% from 50 mg **2**-**Cu**). Elemental analysis (%): C 53.3, H 5.5, N 5.9 (calcd), C 53.5, H 5.4, N 6.2 (found). IR ν 3353, 3032, 2944, 1617, 1414 cm^{-1}; m.p. 222°C (decomp).

7



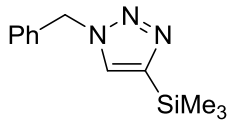
Turquoise solid, 7 mg (11% from 50 mg **3**-**Cu**). Elemental analysis (%): C 53.4, H 5.3, N 5.9 (calcd), C 53.3, H 5.0, N 5.7 (found). IR ν 3267, 3151, 3115, 3066, 1667, 1646, 1443 cm^{-1}; m.p. 209°C (decomp).

8a



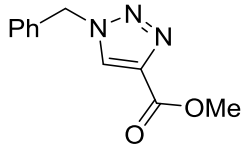
White solid, 99 mg (84%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.81 (d, 2H, *J* 7.0 Hz, ArH), 7.68 (s, 1H, C<u>H</u>=C), 7.44-7.31 (m, 8H, ArH), 5.59 (s, 2H, ArC<u>H</u>$_2$); ^{13}C{^{1}H} NMR (63 MHz; 298 K; $CDCl_3$) δ 148.0 (HC=<u>C</u>-Ar), 134.5 (Ar), 130.4 (Ar), 128.9 (Ar), 128.7 (Ar), 128.6 (Ar), 128.0 (Ar), 127.9 (Ar), 125.4 (Ar), 120.3 (H<u>C</u>=C-Ar), 54.2 (Ar<u>C</u>H$_2$); IR ν 3264, 3122, 3096, 3064, 2975, 1667, 1599 cm^{-1}; m.p. 126°C. Comparable to previous reports of this compound.[2]

8b



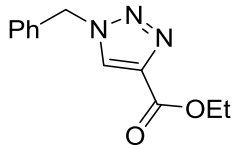
White solid, isolated yield 75 mg (65%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.43 (s, 1H, C<u>H</u>=C), 7.40-7.28 (m, 5H, ArH), 5.57 (s, 2H, ArC<u>H</u>$_2$), 0.30 (s, 9H, Si(C<u>H</u>$_3$)$_3$); ^{13}C{^{1}H} NMR (63 MHz; 298 K; $CDCl_3$) δ 146.6 (HC=<u>C</u>-Ar), 134.9 (Ar), 129.1 (Ar), 128.8 (Ar), 128.6 (Ar), 128.0 (Ar), 53.5 (ArC<u>H</u>$_2$), -1.16 (Si(<u>C</u>H$_3$)$_3$); IR ν 3107, 2958, 1605, 1484 cm^{-1}; m.p. 57°C. Comparable to previous reports of this compound.[3]

8c



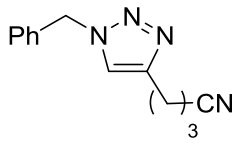
White solid, isolated yield 70 mg (64%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.98 (s, 1H, C<u>H</u>=C), 7.42-7.28 (m, 5H, ArH), 5.59 (s, 2H, ArC<u>H</u>$_2$), 3.94 (s, 3H, OC<u>H</u>$_3$); ^{13}C{^{1}H} NMR (63 MHz; 298 K; $CDCl_3$) δ 161.0 (C=O), 140.2 (H<u>C</u>=C-Ar), 133.6 (HC=<u>C</u>-Ar), 129.2 (Ar), 129.1 (Ar), 128.2 (Ar), 127.3 (Ar), 54.4 (Ar<u>C</u>H$_2$), 52.1 (CO_2<u>C</u>H$_3$); IR ν 3116, 3067, 3038, 3008, 2959, 2850, 1719, 1541 cm^{-1}; m.p. 115°C. Comparable to previous reports of this compound.[4]

8d



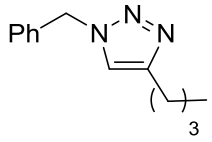
White solid, isolated yield 67 mg (58%). ^{1}H NMR (250 MHz; 298K; $CDCl_3$): δ 7.96 (s, 1H, C<u>H</u>=C), 7.29 - 7.19 (m, 5H, ArH), 5.48 (s, 2H, ArC<u>H</u>$_2$), 4.26 (q, 2H, *J* 7.1 Hz), 1.27 (t, 3H, *J* 7.1 Hz); ^{13}C{^{1}H} NMR (75 MHz; 298 K; $CDCl_3$) δ 160.7 (C=O), 140.2 (H<u>C</u>=C-Ar), 133.6 (HC=<u>C</u>-Ar), 129.1 (Ar), 128.9 (Ar), 128.6 (Ar), 128.1 (Ar), 61.1 (CO_2CH_2<u>C</u>H$_3$), 54.4 (Ar<u>C</u>H$_2$), 14.1 (CO_2CH_2<u>C</u>H$_3$); IR ν 3123, 3011, 2930, 1760, 1475 cm^{-1}; m.p. 59-61°C. Comparable to previous reports of this compound.[3]

8e



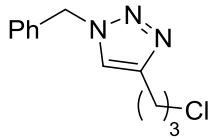
White solid, isolated yield 41 mg (37%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.33-7.21 (m, 6 H, ArH, C<u>H</u>=C), 5.42 (s, 2H, C<u>H</u>$_2$Ar), 2.76 (t, 2H, *J* 7.3 Hz), 2.30 (t, 2 H, *J* 7.3 Hz), 1.97 (t, 2H, *J* 7.3 Hz); ^{13}C{^{1}H} NMR (75 MHz; 298 K; $CDCl_3$) δ 145.9 (HC=<u>C</u>), 134.5 (Ar), 128.9 (Ar), 128.7 (Ar), 128.1 (Ar), 121.2 (H<u>C</u>=C), 119.3 (<u>C</u>N), 54.6 (Ar<u>C</u>H$_2$), 24.7 (<u>C</u>H$_2$), 24.1 (<u>C</u>H$_2$), 16.3 (<u>C</u>H$_2$CN); IR ν 3102, 3065, 2935, 2246, 1553, 1501, 1462 cm^{-1}. Comparable to previous reports of this compound.[5]

8f



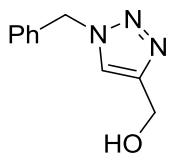
White solid, isolated yield 70 mg (65%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.45-7.35 (m, 6H, ArH, C<u>H</u>=C), 5.58 (s, 2H, C<u>H</u>$_2$Ar), 2.78 (t, 2H, *J* 6.8 Hz, CH=CC<u>H</u>$_2$), 1.74-1.68 (m, 2H, C<u>H</u>$_2$), 1.49-1.41 (m, 2H, C<u>H</u>$_2$), 1.00 (t, 3H, *J* 7.4 Hz, C<u>H</u>$_3$); ^{13}C{^{1}H} NMR (63 MHz; 298 K; $CDCl_3$) δ 148.9 (HC=<u>C</u>), 135.0 (Ar), 129.0 (Ar), 128.6 (Ar), 127.9 (Ar), 120.5 (H<u>C</u>=C), 54.0 (<u>C</u>H$_2$Ar), 31.4 (N-<u>C</u>H$_2$), 25.4 (CH$_2$<u>C</u>H$_2$), 22.3 (<u>C</u>H$_2$CH$_3$), 13.8 (CH$_2$<u>C</u>H$_3$); IR ν 3114, 3064, 2959, 2924, 2853, 1603, 1557 cm^{-1}; m.p. 63°C. Comparable to previous reports of this compound.[6]

8g



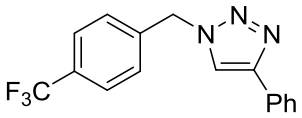
Oil, isolated yield 83 mg (70%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.40-7.25 (m, 6H, ArH, C<u>H</u>=C), 5.51 (s, 2H, C<u>H</u>$_2$Ar), 3.57 (t, 2H, *J* 6.5 Hz, C<u>H</u>$_2$Cl), 2.87 (t, 2H, *J* 7.4 Hz, CH=CC<u>H</u>$_2$), 2.16 (tt, 2H, *J* 7.4, 6.5 Hz, CH$_2$C<u>H</u>$_2$CH$_2$Cl); ^{13}C{^{1}H} NMR (63 MHz; 298 K; $CDCl_3$) δ 146.9 (HC=<u>C</u>), 134.7 (Ar), 129.0 (Ar), 128.6 (Ar), 127.9 (Ar), 121.2 (H<u>C</u>=C), 54.1 (<u>C</u>H$_2$Ar), 44.1 (CH$_2$Cl), 31.7 (<u>C</u>H$_2$), 22.7 (<u>C</u>H$_2$); IR ν 3094, 2910, 2898, 2821, 1597, 1546 cm^{-1}. Comparable to previous reports of this compound.[7]

8h



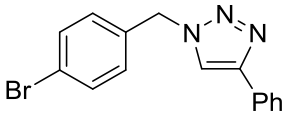
White solid, isolated yield 69 mg (73%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.44-7.39 (m, 4H, ArH, C<u>H</u>=C), 7.32 (d, 1H, *J* 6.8 Hz, ArH), 5.55 (s, 2H, ArC<u>H</u>$_2$), 4.85 (br. s, 1H, O<u>H</u>); ^{13}C{^{1}H} NMR (100 MHz; 298 K; $CDCl_3$) δ 148.3 (H<u>C</u>=C), 134.5 (Ar), 129.9 (Ar), 128.6 (Ar), 128.0 (Ar), 127.9 (Ar), 120.3 (HC=<u>C</u>), 54.2 (<u>C</u>H$_2$Ar); IR ν 3246, 3138, 3084, 3033, 3004, 2963, 2937, 2839, 1606 cm^{-1}; m.p. 76°C. Comparable to previous reports of this compound.[2]

8i



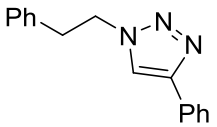
White solid, 115 mg (76%). ^{1}H NMR (300 MHz; 298 K; $CDCl_3$) δ 7.82 (dd, 2H, $^{3}J_{H\text{-}H}$ 8.5, $^{4}J_{H\text{-}F}$ 1.5 Hz, ArH), 7.71 (s, 1H, C<u>H</u>=C), 7.68 (d, 2H, *J* 8.5, Hz, ArH), 7.45-7.40 (m, 4H, ArH), 5.67 (s, 2H, ArC<u>H</u>$_2$); ^{13}C{^{1}H} NMR (63 MHz; 298 K; $CDCl_3$) δ 148.5 (HC=<u>C</u>), 138.7 (Ar), 131.1 (q, *J* 32.6 Hz, Ar), 130.3 (Ar), 128.9 (Ar), 128.4 (Ar), 128.2 (Ar), 126.1 (q, *J* 3.7 Hz, Ar$_q$), 125.7 (Ar), 123.8 (q, *J* 272.5 Hz, <u>C</u>F$_3$), 119.7 (H<u>C</u>=C), 53.5; IR ν 3084, 1621, 1485, 1464 cm^{-1}; m.p. 136°C. Comparable to previous reports of this compound.[8]

8j



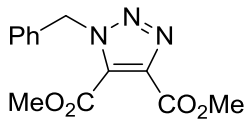
White solid, 51 mg (32%). ^{1}H NMR (300 MHz; 298 K; $CDCl_3$) δ 7.81 (dd, 2H, *J* 8.1, 1.5 Hz, ArH), 7.67 (s, 1H, C<u>H</u>=C), 7.67 (d, 2H, *J* 8.1, Hz, ArH), 7.51 (dd, 2H, *J* 8.3, 1.5 Hz, ArH), 7.42 (dd, 2H, *J* 8.3, 1.5 Hz, ArH), 7.20 (d, 2H, *J* 8.5 Hz, ArH), 5.55 (s, 2H, ArC<u>H</u>$_2$); ^{13}C{^{1}H} NMR (63 MHz; 298 K; $CDCl_3$) δ 148.3 (HC=<u>C</u>), 133.7 (Ar), 132.2 (Ar), 130.3 (Ar), 129.6 (Ar), 128.8 (Ar), 128.2 (Ar), 127.9 (Ar), 125.6 (Ar), 120.8 (Ar), 119.5 (H<u>C</u>=C), 53.4 (<u>C</u>H$_2$Ar); IR ν 3084, 1611, 1483, 1463 cm^{-1}; m.p. 149°C. Comparable to previous reports of this compound.[2]

8l



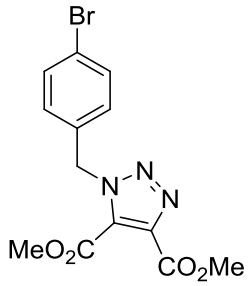
White solid, 82 mg (66%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 8.38 (s, 1H, C<u>H</u>=C), 7.44-7.08 (m, 10H ArH), 4.47 (t, 2H, *J* 7.1 Hz, C<u>H</u>$_2$N), 3.09 (t, 2H, *J* 7.1 Hz, ArC<u>H</u>$_2$); ^{13}C{^{1}H} NMR (75 MHz; 298 K; $CDCl_3$) δ 147.3 (HC=<u>C</u>), 137.8 (Ar), 130.2 (Ar), 128.6 (Ar), 128.5 (Ar), 128.4 (Ar), 128.0 (Ar), 126.6 (Ar), 125.5 (Ar), 120.2 (H<u>C</u>=C), 51.5 (<u>C</u>H$_2$N), 35.1 (<u>C</u>H$_2$Ar); m.p. 139-140 °C. Comparable to previous reports of this compound.[3]

9a



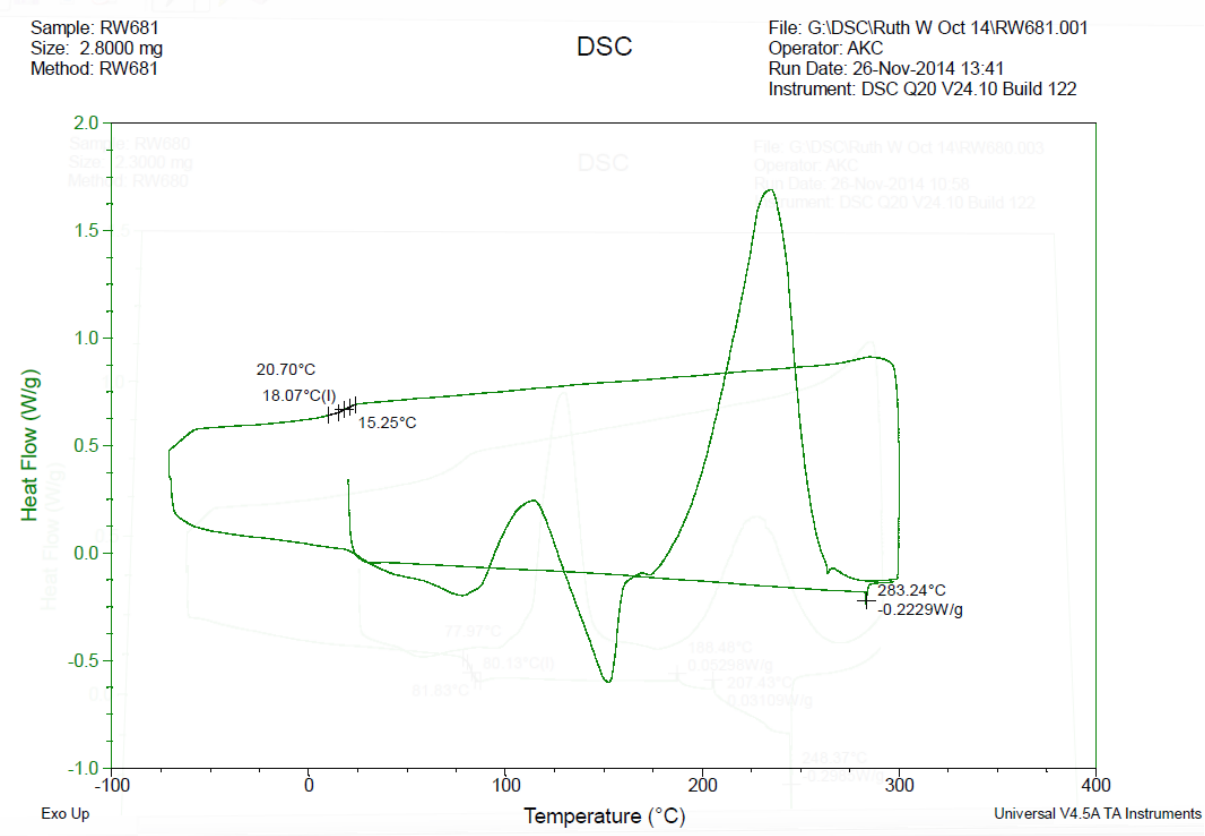
Oil, 100 mg (73%). ^{1}H NMR (300 MHz; 298 K; $CDCl_3$) δ 7.35-7.33 (m, 3H), 7.27-7.24 (m, 2H), 5.81 (s, 2H, ArC$\underline{H}_2$), 3.96 (s, 3H, C$\underline{H}_3$), 3.88 (s, 3H, C$\underline{H}_3$); ^{13}C{^{1}H}MR (75 MHz; 298 K; $CDCl_3$) δ 160.4 (C=O), 158.8 (C=O), 140.2 ($\underline{C}$=$\underline{C}$), 133.8 (Ar), 128.9 (Ar), 128.8 (Ar), 128.0 (Ar), 53.9, 53.3, 52.7; m.p. 49 °C.

9b

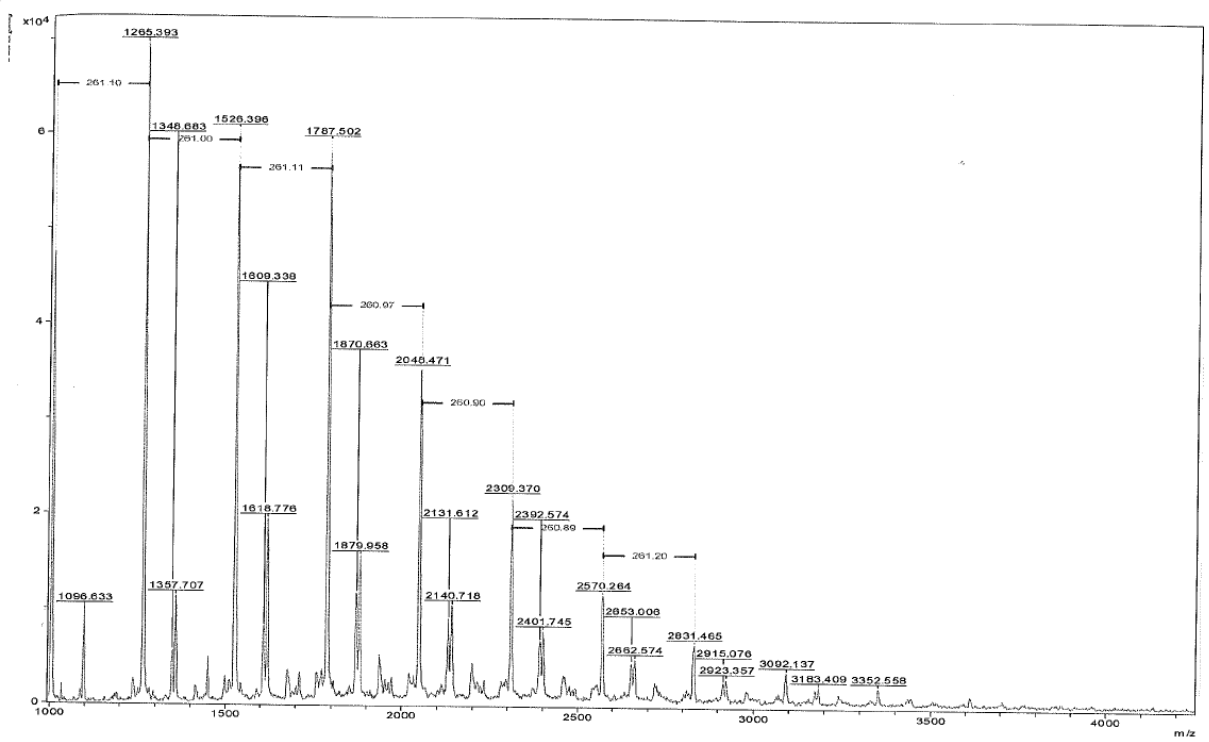


Oil, 107 mg (61%). ^{1}H NMR (250 MHz; 298 K; $CDCl_3$) δ 7.50-7.43 (m, 2H), 7.19-7.14 (m, 2H), 5.74 (s, 2H, ArC$\underline{H}_2$), 3.94 (s, 3H, C$\underline{H}_3$), 3.88 (s, 3H, C$\underline{H}_3$); ^{13}C{^{1}H} NMR (63 MHz; 298 K; $CDCl_3$) δ 160.7 (C=O), 158.8 (C=O), 141.2 ($\underline{C}$=$\underline{C}$), 134.3 (Ar), 131.8 (Ar), 129.7 (Ar), 122.9 (Ar), 53.9, 53.3, 52.7.

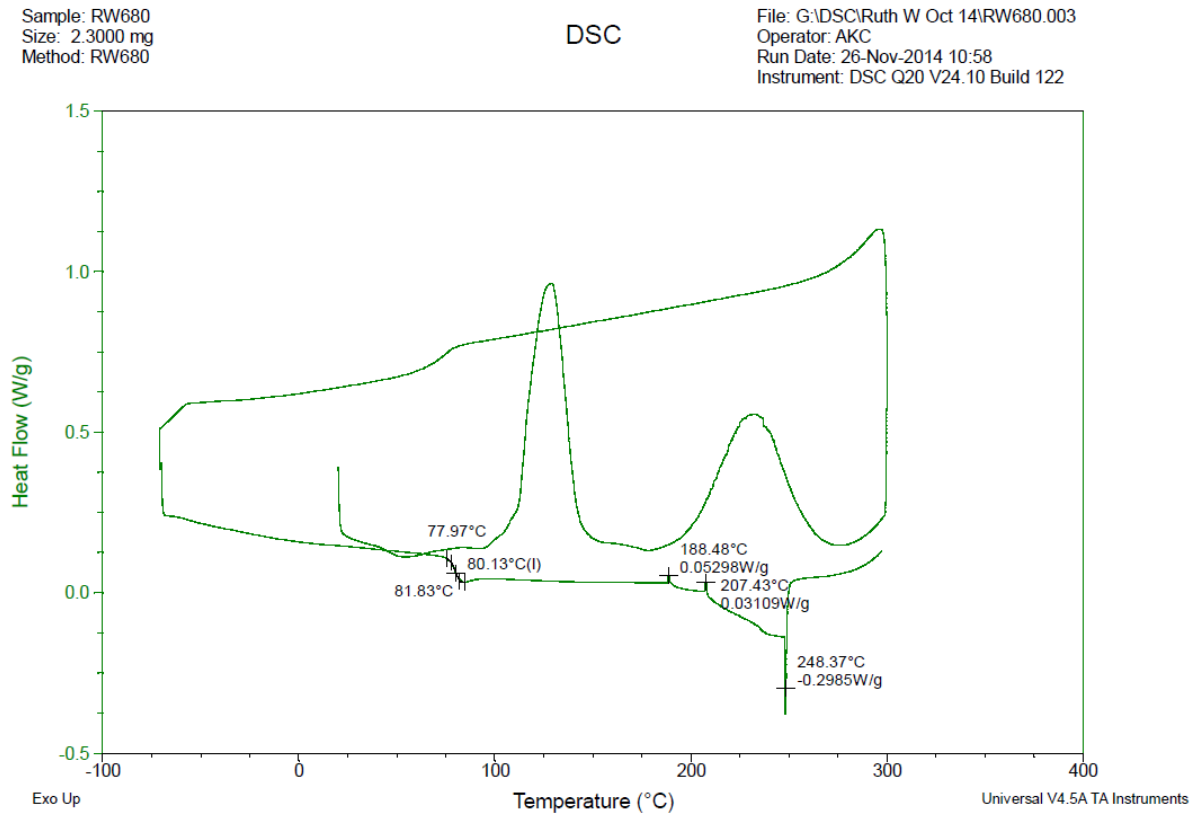
DSC trace: **10a**



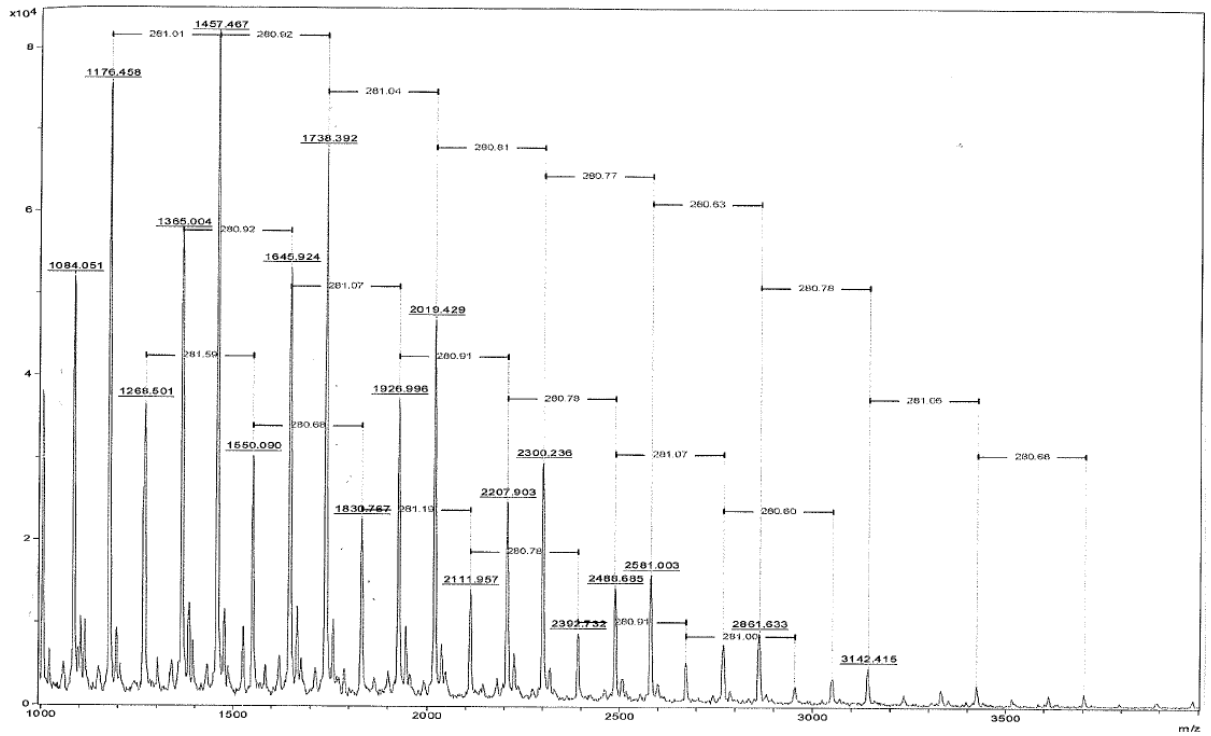
MALDI-ToF spectrum: **10a**

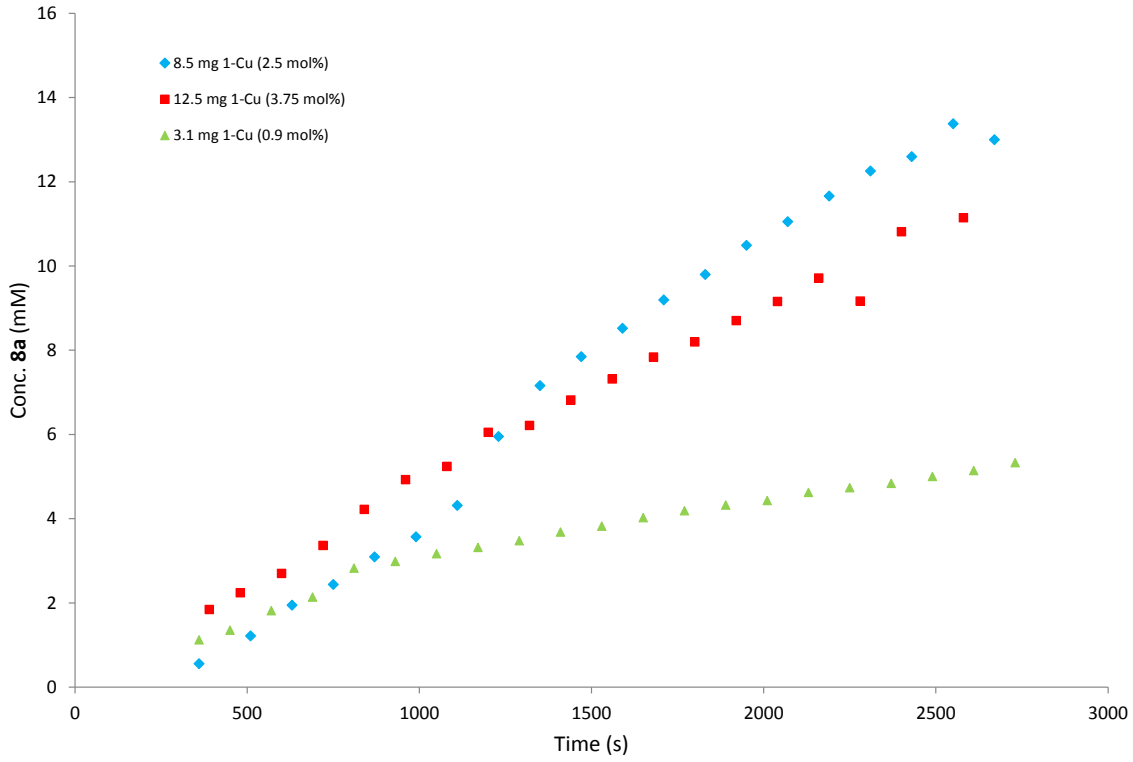


DSC trace: **10b**



MALDI-ToF spectrum: **10b**





References

[1] S. G. Alvarez and M. T. Alvarez, *Synthesis* **1997**, *1997*, 413-414.

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