Supplementary Information (SI) for Green Chemistry.

Electronic Supplementary Information

Shed light on the path to Multifunctional Task-Specific Supported Ionic Liquid with Enhanced Catalyst Stability and Activity

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1. General information

All reagents were obtained from Sigma-Aldrich or Scharlab and were used without further purification. ^{1}H-NMR experiments were carried out using a Bruker Avance III HD 300 or 400 MHz spectrometer. The chemical shifts are given in delta (δ) values (ppm). FTIR spectra were acquired with a MIRacle single reflection ATR diamond/ZnSe accessory in a JASCO FT/IR-6200 instrument. High-performance liquid chromatography (HPLC) analyses were carried out in an Agilent 1100 Series chromatograph UV detector at 210 nm using a ProntoSil 120-5-C18 AQ 5 µm column (25 cm × 4.6 mm I.D.) and anthracene as internal standard (5.836 min) (ACN/H_2O 0.1%TFA (step 1: 80:20 to 50:50 during 8 min, step 2: 50:50 during 15 min), flow: 1.2 mL/min, T: 25 °C; injection volume: 1 µL). X–ray photoelectron spectroscopy (XPS) measurements: samples were prepared by sticking, without sieving, the SILLP onto a molybdenum plate with scotch tape film, followed by air drying. Measurements were performed on a SPECS spectrometer equipped with a Phoibos 150 MCD–9 analyzer using non–monochromatic Mg KR (1253.6 eV) X–ray source working at 50 W. As an internal reference for the peak positions in the XPS spectra, the C1s peak has been set at 284.8 eV.

2. Evaluation of catalysts

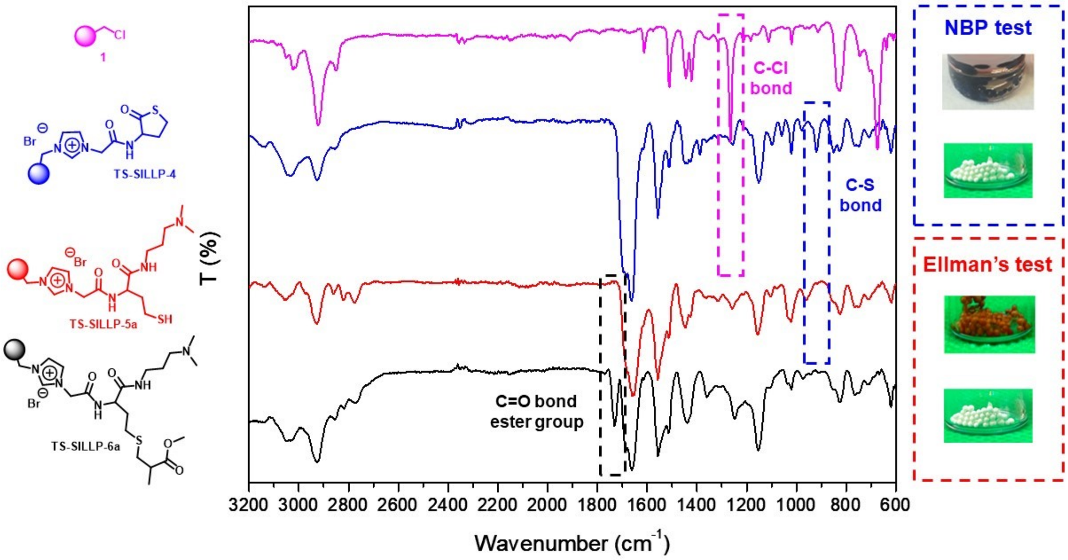


Fig. S1 FT-IR spectra for the synthesis monitoring of Solid-Phased task-specific supported ILs library. NBP test to check the successful modification of Merrifield resin and Ellamn's test to check the successful opening of the thiolactone rings.

Table S1 Effect of the molar loading of the catalyst **Cu(OAc)$_2$-TS-SILLP-5a** on the reaction between **7a** and **8a**.[a]

Entry	meq Cu/g pol	mol copper catalyst loading	Yield (%)[b]
1	0.50	1.5285	92
2	0.50	0.0178	79
3	0.50	0.0004	38

a: 0.2 M azide:alkyne (1:1) in acetonitrile, 4 hours, 70 ºC. b: calculated by HPLC.

Table S2 Effect of the solvent on the reaction between **7a** and **8a** catalyzed by **Cu(OAc)$_2$-TS-SILLP-5a**.[a]

Entry	Solvent	Yield (%)[b]
1	ACN	92
2	CH_2Cl_2	34
3	DMC	35
4	Me-THF	86

a: 0.2 M azide:alkyne (1:1) in acetonitrile, 1.5% mol copper catalyst, 4 hours, 70 ºC. b: calculated by HPLC.

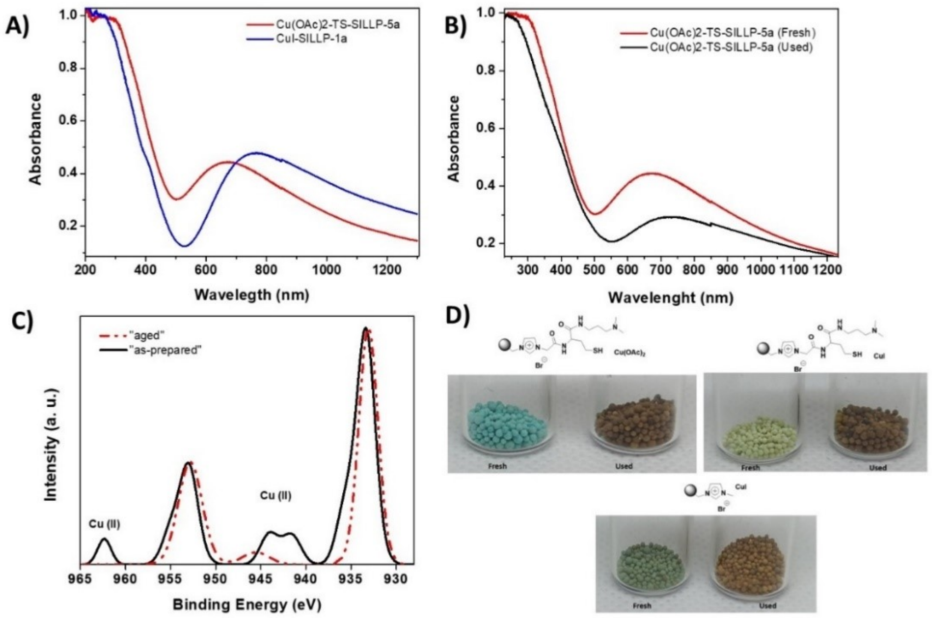


Fig. S2 A: UV spectra of **Cu(OAc)$_2$-TS-SILLP-5a** and **CuI-SILLP-1**. B: UV spectra of **Cu(OAc)$_2$-TS-SILLP-5a** before (fresh) and after (used) the reaction between **7a** and **8a**. C: XPS spectra of **Cu(OAc)$_2$-TS-SILLP-5a** before (fresh) and after (used) the reaction between **7a** and **8a**. D: the colour change from blue/green of the catalyst, indicative of Cu(II) (fresh catalyst), to brow-yellow, indicative of Cu(I) (used catalyst) in the reaction between **7a** and **8a**.

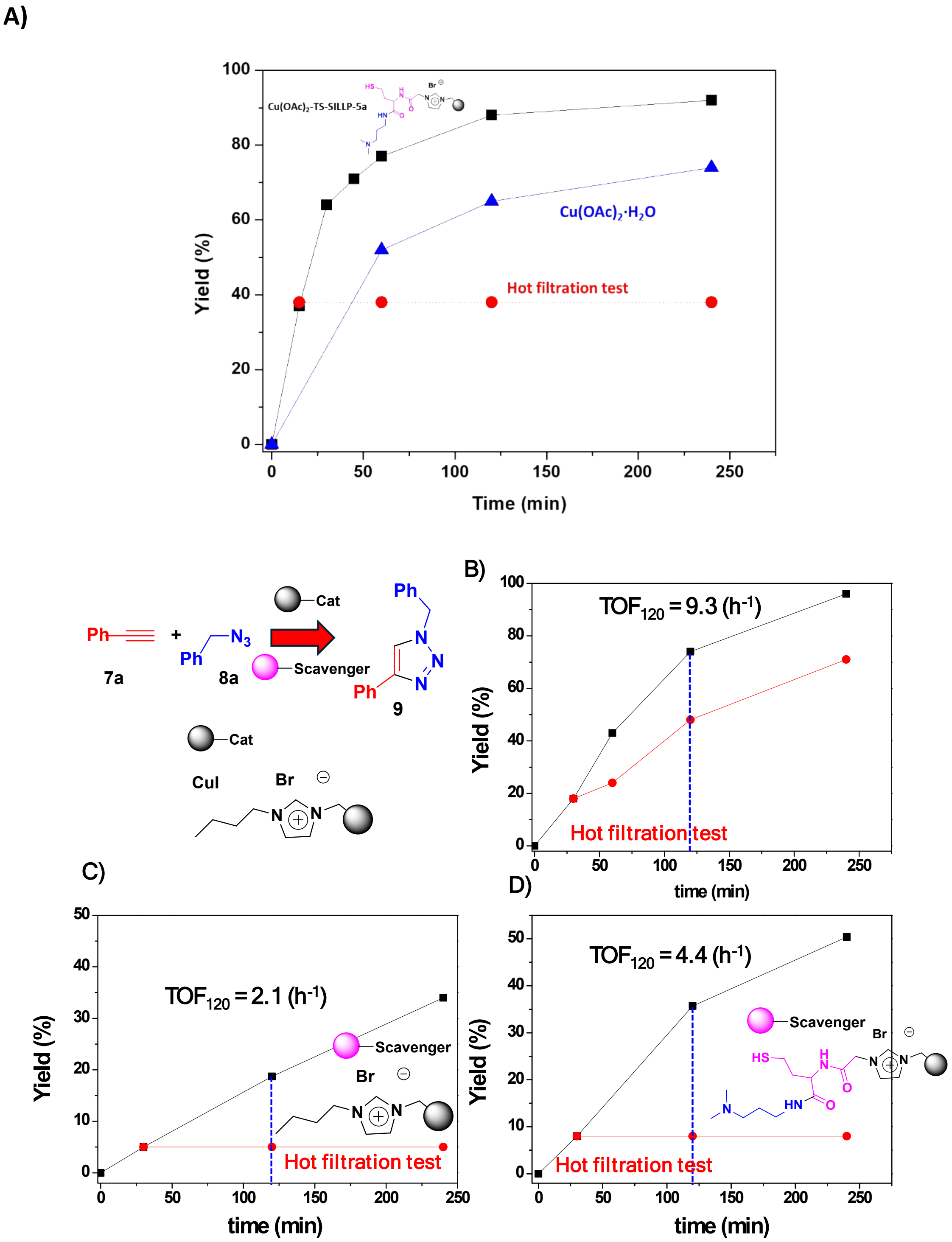


Fig. S3 A) Yield *vs* time profile for the model reaction between **7a** and **8a** performed under standard conditions with 0.2 M azide:alkyne (1:1) in acetonitrile, 1.5% mol copper catalyst, 70 ºC. Black Square: **$Cu(OAc)_2$-TS-SILLP-5a**. Blue Triangle: reaction catalyzed by $Cu(OAc)_2$ as a homogeneous catalyst. Red Dot: hot filtration test. The scheme for the model reaction between **7a** and **8a** performed under standard conditions with 0.2 M azide:alkyne (1:1) in acetonitrile, 8 % mol copper catalyst, 70 ºC. B) Square: reaction using only **CuI-SILLP-1**, Red Dot: hot filtration test. C) Square: reaction using cocktail 1:4 by weight of **CuI-SILLP-1**: **SILLP-1**, Red Dot: hot filtration test. D) Square: reaction using cocktail 1:4 by weight of **CuI-SILLP-1**: **TS-SILLP-5a**, Red Dot: hot filtration test.

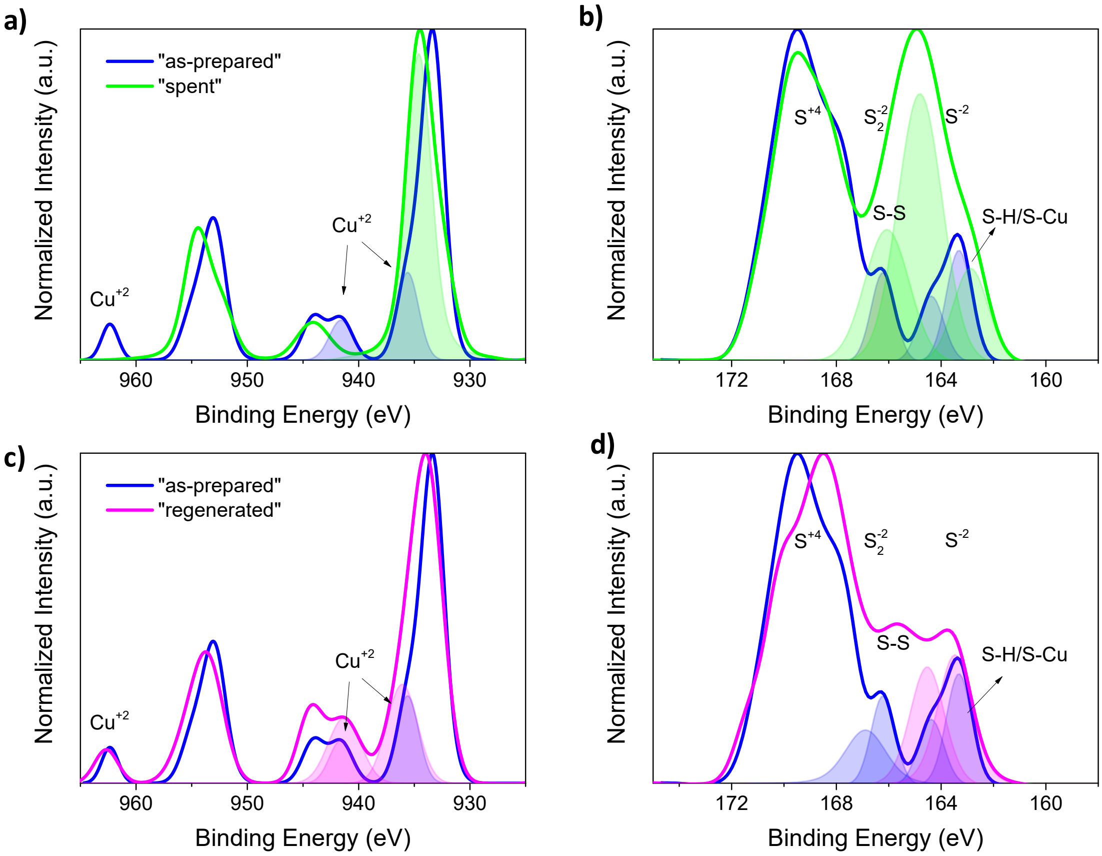


Fig. S4 a) Cu 2p (a) and b) S 2p regions of the XPS for the **$Cu(OAc)_2$-TS-SILLP-5a** "*as prepared*" (blue) and "*spent*" (green). c) Cu 2p and d) S 2p regions of the XPS for the **RB-$Cu(OAc)_2$-TS-SILLP-5a** "*as prepared*" (blue) and "*regenerated*" after 14th regeneration cycles (magenta).

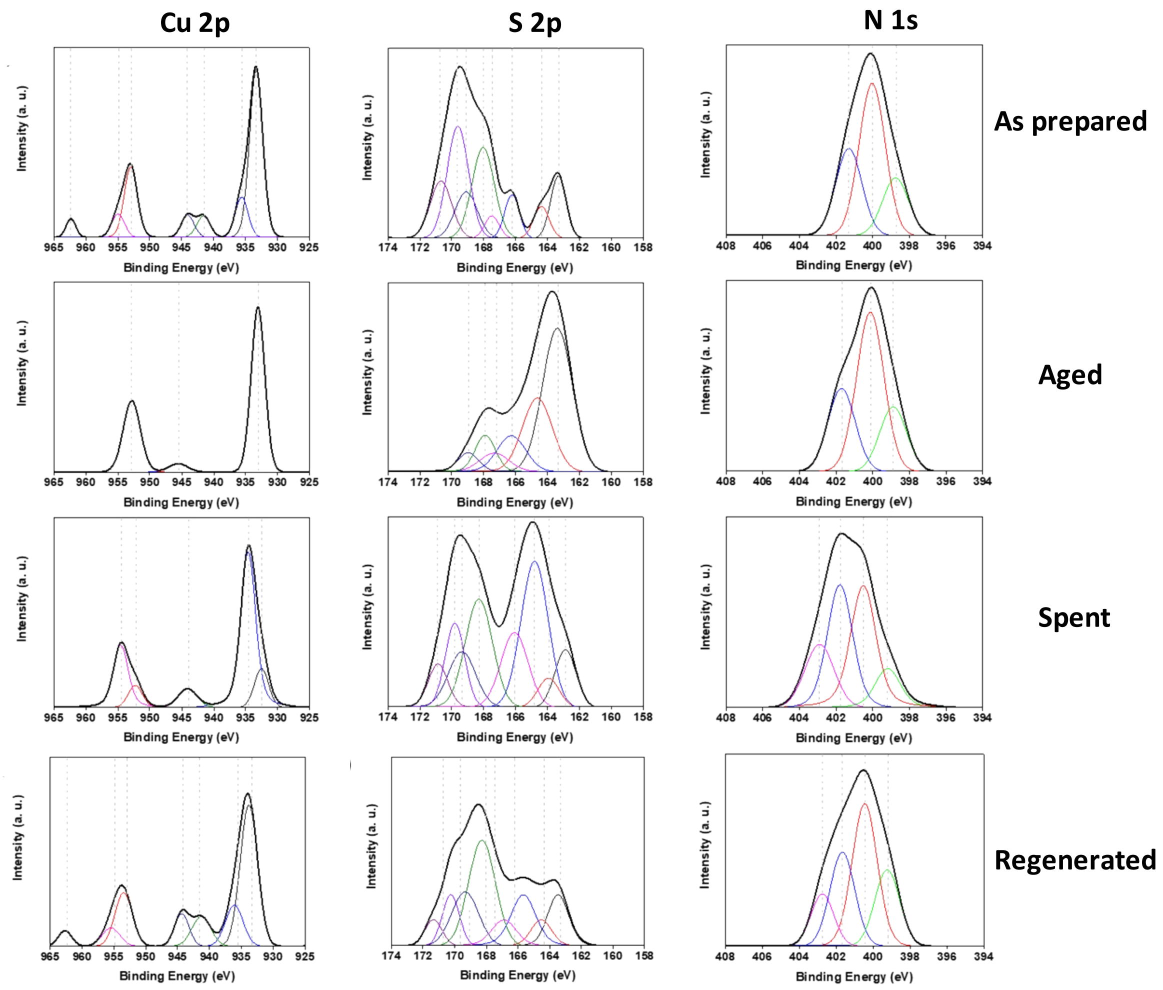


Fig. S5 XPS of the Cu 2p (left), S 2p (middle) and N1s (right) for the as prepared (1st line), aged (2nd line), spent (3th line) and regenerated **Cu(OAc)$_2$-TS-SILLP-5a** (4th line).

Table S3 Binding energies of the Cu2p part of the XPS.

	Cu(0/I)	**Cu(0/I)**	**Cu(II)**	**Cu(II)**	**Cu(II)**	**Cu(I)**	**Cu(II)**
	Cu2p3$_A$/ eV	**Cu2p1$_A$/ eV**	**Cu2p3$_B$/ eV**	**Cu2p1$_B$/ eV**	**Cu2p Sat / eV**	**Cu2p Sat/ eV**	**Cu2p Sat/ eV**
Cu(OAc)$_2$-TS-SILLP-5a *"as-prepared"*	933.3	953.0	935.6	954.9	941.6	944.1	962.3
Cu(OAc)$_2$-TS-SILLP-5a *"aged"*	933.1	952.8	-	-	-	945.5	-
Cu(OAc)$_2$-TS-SILLP-5a *"spent"*	932.5	952.3	934.6	954.5	-	944.1	-
RB-Cu(OAc)$_2$-TS-SILLP-5a **"***regenerated"*	933.8	953.5	936.1	955.4	941.3	944.3	962.7

Table S4 Percentage areas of the Cu2p part of the XPS.

	Cu(0/I)	**Cu(0/I)**	**Cu(II)**	**Cu(II)**	**Cu(II)**	**Cu(I)**	**Cu(II)**
	Cu2p3$_A$/ %	**Cu2p1$_A$/ %**	**Cu2p3$_B$/ %**	**Cu2p1$_B$/ %**	**Cu2p Sat / %**	**Cu2p Sat/ %**	**Cu2p Sat/ %**
Cu(OAc)$_2$-TS-SILLP-5a *"as-prepared"*	37.2	34.7	8.5	11.0	3.3	3.3	2.1
Cu(OAc)$_2$-TS-SILLP-5a *"aged"*	44.1	53.6	-	-	-	2.4	-
Cu(OAc)$_2$-TS-SILLP-5a *"spent"*	8.6	10.7	40.6	36.4	-	3.7	-
RB-Cu(OAc)$_2$-TS-SILLP-5a **"***regenerated"*	36.1	30.3	10.6	10.6	5.8	4.8	1.9

Table S5 Binding energies of the S2p part of the XPS.

	S-H/C	S-H/C	S-S/O	S-S/O	S-S/O	S-S/O	S-Cu	S-Cu
	$S2p3_A$/ eV	**$S2p1_A$/ eV**	**$S2p3_B$/ eV**	**$S2p1_B$/ eV**	**$S2p3_C$/ eV**	**$S2p1_C$/ eV**	**$S2p3_D$/ eV**	**$S2p1_D$/ eV**
$Cu(OAc)_2$-TS-SILLP-5a *"as-prepared"*	163.3	164.4	166.2	167.5	168.0	169.1	169.6	170.7
$Cu(OAc)_2$-TS-SILLP-5a *"aged"*	163.4	164.6	166.3	167.3	167.9	169.0	-	-
$Cu(OAc)_2$-TS-SILLP-5a *"spent"*	162.9	163.9	164.8	166.1	168.3	169.4	169.8	170.9
RB-$Cu(OAc)_2$-TS-SILLP-5a **"***regenerated"*	163.5	164.5	165.7	166.9	168.3	169.3	170.2	171.3

Table S6 Percentage areas of the S2p part of the XPS.

MOF	**S-H/C**	**S-H/C**	**S-S/O**	**S-S/O**	**S-S/O**	**S-S/O**	**S-Cu**	**S-Cu**
	$S2p3_A$/%	**$S2p1_A$/%**	**$S2p3_B$/%**	**$S2p1_B$/%**	**$S2p3_C$/%**	**$S2p1_C$/%**	**$S2p3_D$/%**	**$S2p1_D$/%**
$Cu(OAc)_2$-TS-SILLP-5a *"as-prepared"*	7.7	7.7	5.4	5.4	16.9	16.9	20.0	20.0
$Cu(OAc)_2$-TS-SILLP-5a *"aged"*	35.7	35.7	8.5	8.5	5.9	5.9	-	-
$Cu(OAc)_2$-TS-SILLP-5a *"spent"*	6.4	6.4	20.4	20.4	14.8	14.8	8.4	8.4
RB-$Cu(OAc)_2$-TS-SILLP-5a **"***regenerated"*	9.3	9.3	11.1	11.1	22.7	22.7	6.9	6.9

Table S7 Binding energies of the N1s part of the XPS.

	NH-M	**NH_2**	**NH_3**	**NH_4^+**
	$N1s_A$/ eV	**$N1s_B$/ eV**	**$N1s_C$/ eV**	**$N1s_D$/ eV**
$Cu(OAc)_2$-TS-SILLP-5a *"as-prepared"*	398.8	400.0	401.3	-
$Cu(OAc)_2$-TS-SILLP-5a *"aged"*	398.9	400.1	401.7	-
$Cu(OAc)_2$-TS-SILLP-5a *"spent"*	399.2	400.5	401.8	402.9
RB-$Cu(OAc)_2$-TS-SILLP-5a *"regenerated"*	399.2	400.5	401.7	402.7

Table S8 Percentage areas of the N1s part of the XPS.

	NH-M	**NH_2**	**NH_3**	**NH_4^+**
	$N1s_A$/ %	**$N1s_B$/ %**	**$N1s_C$/ %**	**$N1s_D$/ %**
$Cu(OAc)_2$-TS-SILLP-5a *"as-prepared"*	19.6	51.1	29.2	-
$Cu(OAc)_2$-TS-SILLP-5a *"aged"*	20.9	52.2	26.8	-
$Cu(OAc)_2$-TS-SILLP-5a *"spent"*	11.1	35.7	33.8	19.4
RB-$Cu(OAc)_2$-TS-SILLP-5a *"regenerated"*	21.0	40.1	25.8	13.1

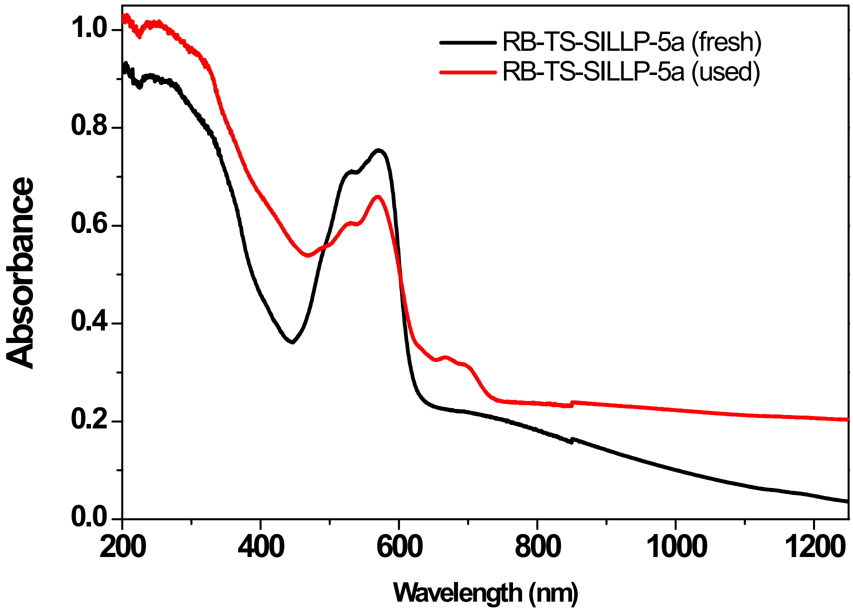


Fig. S6 UV spectra of **RB-Cu(OAc)$_2$-TS-SILLP-5a** before (fresh) and after (used after 15th rection cycles 14th regeneration cycles) for the reaction between **7a** and **8a**.

Table S9 Green metric (E-factor) evaluation of CuAAC reaction and synthesis of Rufinamide.

Entry	Reaction	Catalyst (g)	E-factor
1 (This work)	Synthesis of Rufinamide	**Cu(OAc)$_2$** (0.0075)	98
2	CuAAC reaction between 2-(bromomethyl)-1,3-difluorobenzene (**8e**) and 2-propynamide (**7d**)[a]	**Cu(OAc)$_2$-TS-SILLP-5a** (0.0075)	21
3 (Ref I)	Synthesis of Rufinamide (Patent Appl. WO2012032540 A1)	**CuSO$_4$** (0.6)	121
4 (Ref II)	Synthesis of Rufinamide (U.S. Patent 8,884,026)	-	57
5 (Ref III)	Synthesis of Rufinamide (U.S. Patent 8,871,945)	-	64

a: 0.2 M azide:alkyne (1:1) in acetonitrile, 1.5% mol copper catalyst, 4 hours, 70 ºC. b: in CH_2Cl_2. c: in DMC. d: in Me-THF.

Reference

I M. N. Rajadhyaksha, R. Nair, K. Johnson and A. M. Panandikar, PCT Int. Patent Appl. WO2012032540 A1, May 15, 2012.

II A. A. De Leon Martin, B. Del Valles, J. B. Bellmunt, J. H. Clotet, L. S. Carandell, G. F. Pascual, J. O. C. Bertran and P. D. Barjoan, U.S. Patent 8,884,026, Nov 11, 2014.

III R. R. Davuluri, R. Ponnaiah, S. K. Dehury, K. Selvarju, V. P. S. S. Deepthi and D. Naidu, U.S. Patent 8,871,945, Oct 28, 2014.

3. FTIR spectra

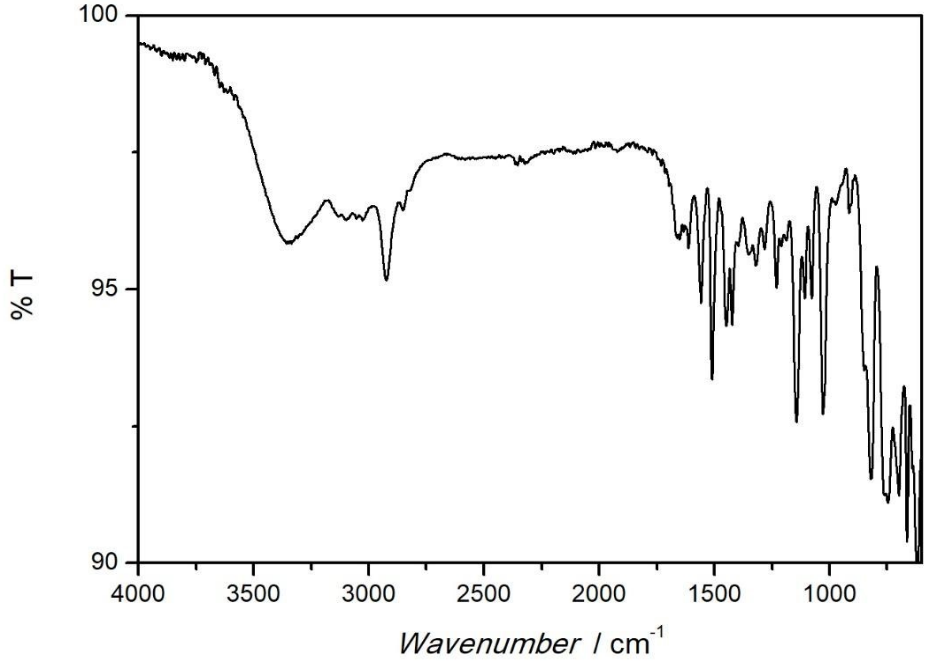


Fig. S7 FT-ATR-IR spectra of imidazole polymer **2**.

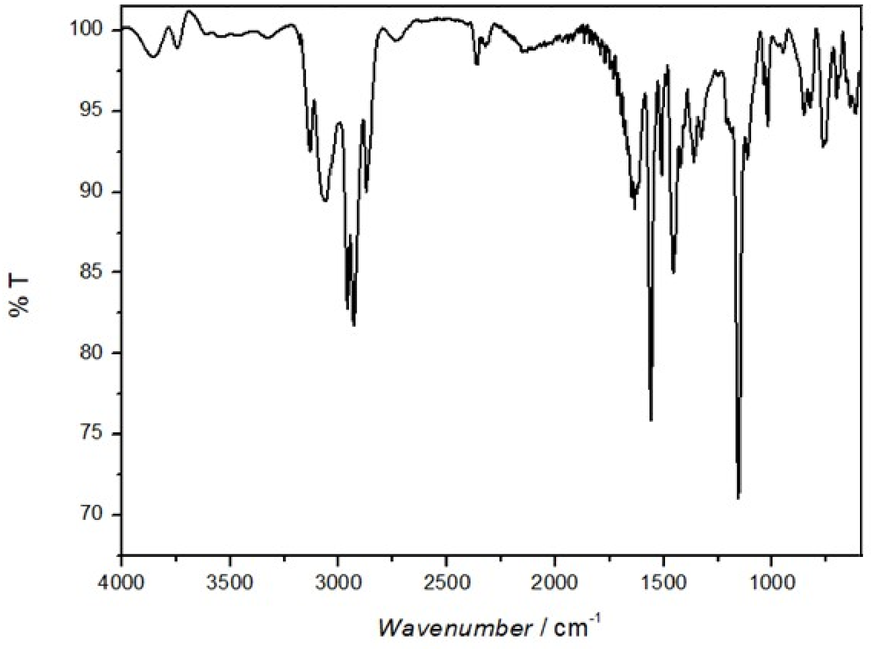


Fig. S8 FT-ATR-IR spectra of **TS-SILLP-1**.

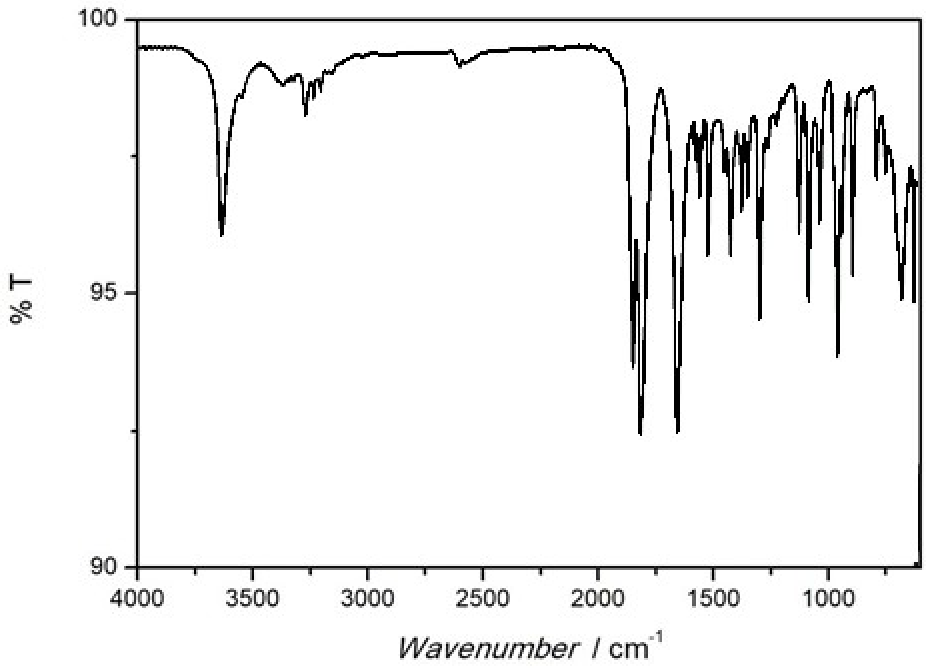


Fig. S9 FT-ATR-IR spectra of N-(2-bromoacetyl)-D,L-homocysteine thiolactone**.**

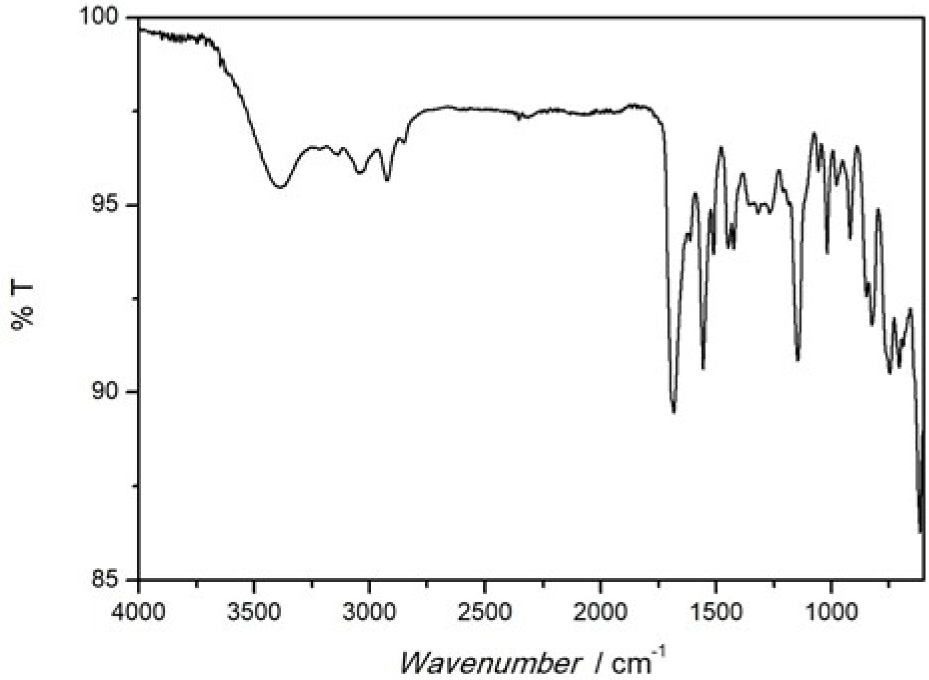


Fig. S10 FT-ATR-IR spectra of **TS-SILLP-4**.

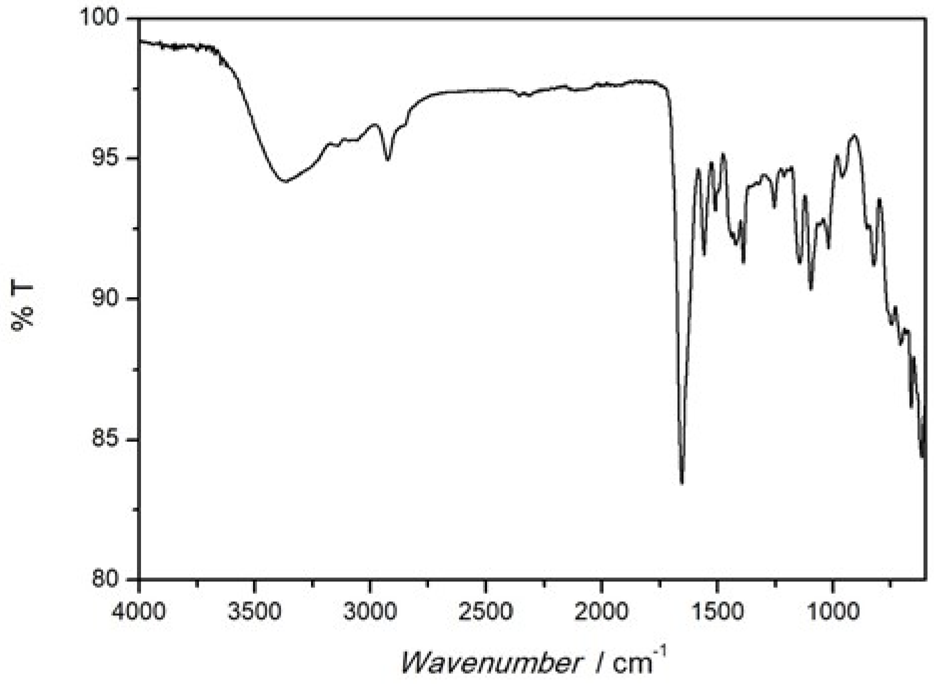


Fig. S11 FT-ATR-IR spectra of **TS-SILLP-5a**.

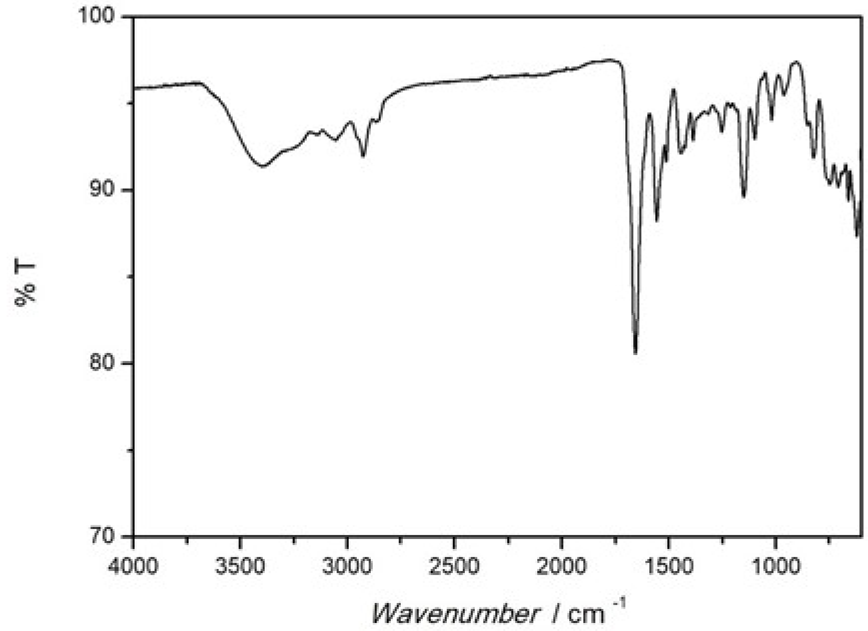


Fig. S12 FT-ATR-IR spectra of **TS-SILLP-5b**.

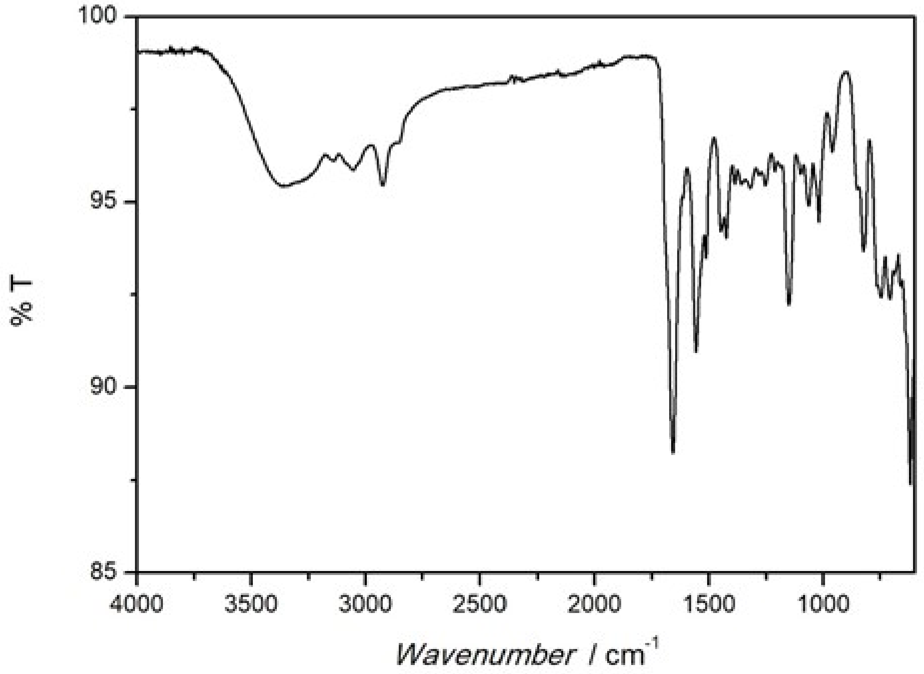


Fig. S13 FT-ATR-IR spectra of **TS-SILLP-5c**.

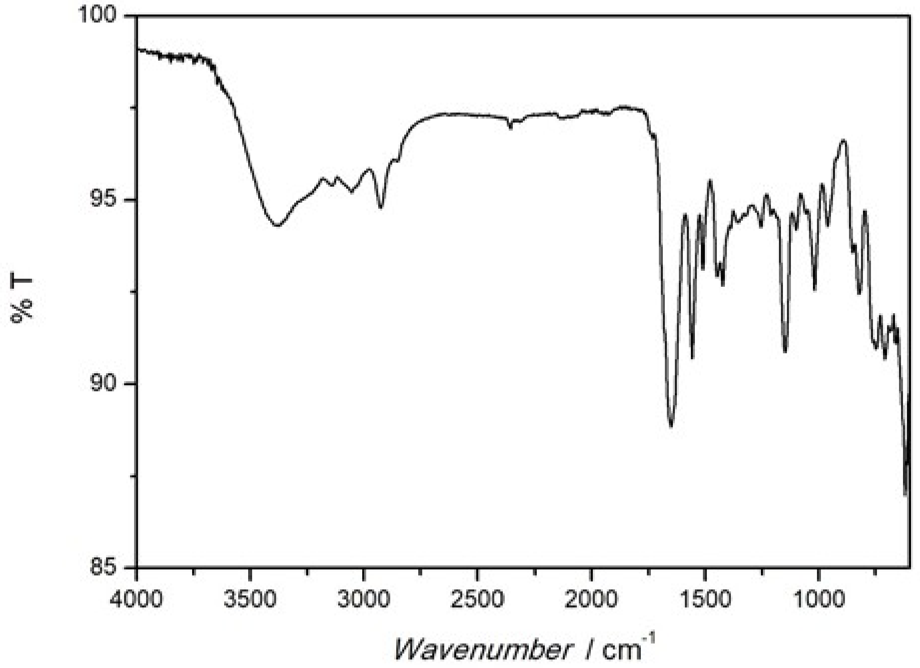


Fig. S14 FT-ATR-IR spectra of **TS-SILLP-5d**.

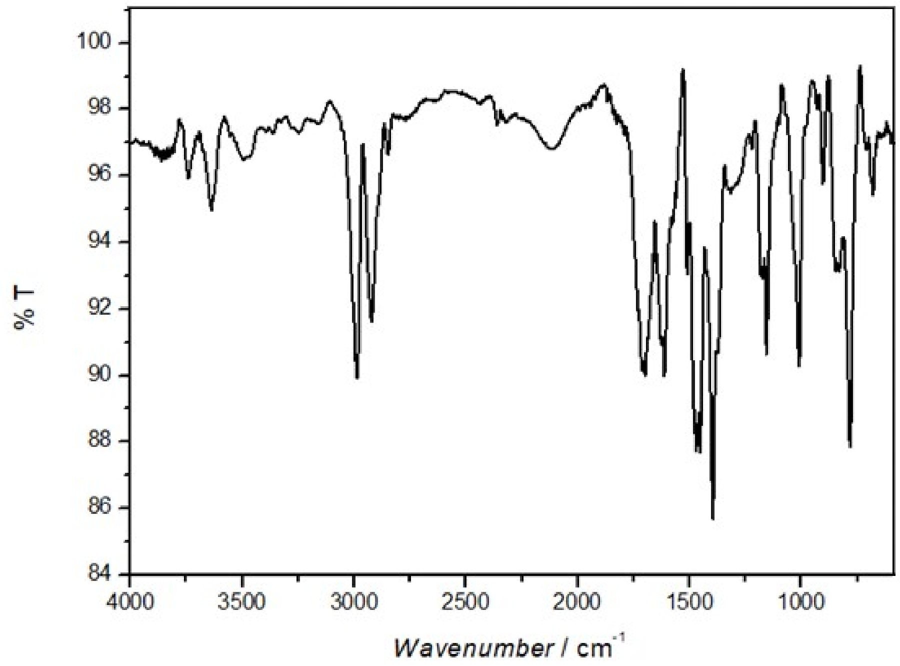


Fig. S15 FT-ATR-IR spectra of **TS-SILLP-5e**.

Fig. S16 FT-ATR-IR spectra of **TS-SILLP-5f**.

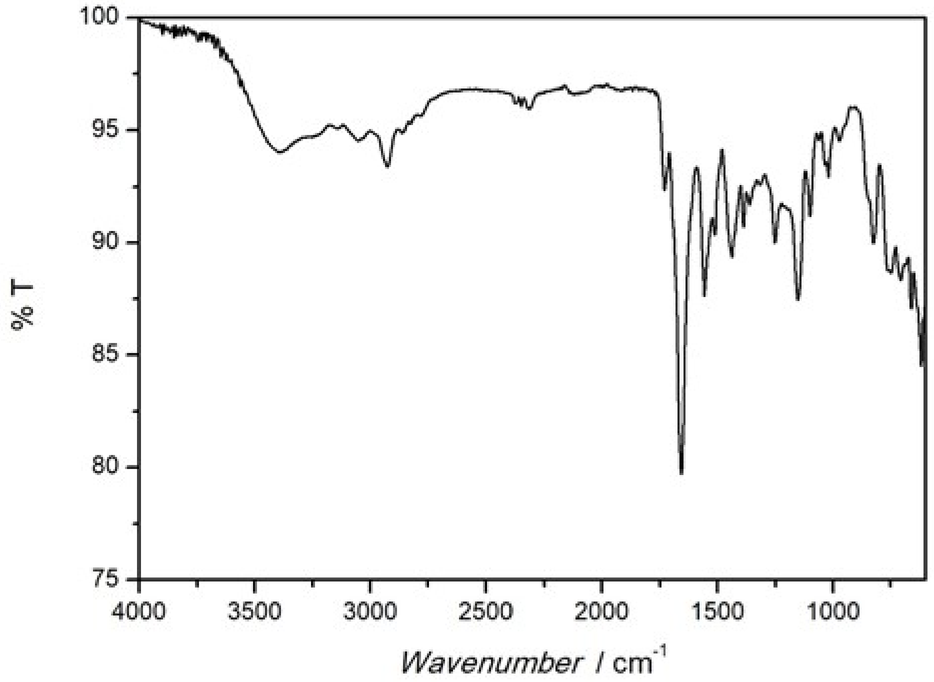


Fig. S17 FT-ATR-IR spectra of **TS-SILLP-6a**.

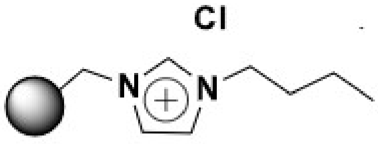
4. Synthetic protocols[1,2]

Synthesis of Solid-Phased task-specific supported ILs

Imidazole polymer (2)

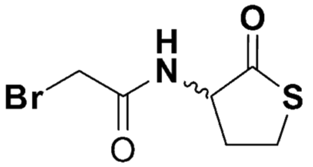
A macroporous Merrifield resin (2 g, 5.5% DVB cross-linking, 5.5 mmol/g, 11 mmol) was placed in a round bottomed flask and suspended in DMF (60 mL), and imidazole (2.25 g, 33 mmol) was added. The suspension was heated at 80 ºC for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with THF, CH_3OH and CH_2Cl_2 (2x20 mL), and dried in a vacuum oven. The colorimetric NBP test showed a negative result (absence of CH_2Cl). FTIR-ATR: 3335, 2923, 1558, 1511, 1448, 1424, 1320, 1282,1230, 1144, 1108, 1078, 1029, 915, 820, 747, 699, 664, 616 cm^{-1}. Elemental analysis found: N, 9.42%; 3.36 meq/g.

SILLP-1



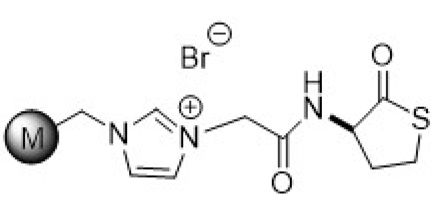
A macroporous Merrifield resin (2 g, 5.5% DVB cross-linking, 5.5 mmol/g, 11 mmol) was placed in a round bottomed flask and suspended in DMF (60 mL), and 1-butylimidazole (4.1 g, 33 mmol) was added. The suspension was heated at 80 ºC for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with THF, CH_3OH and CH_2Cl_2 (2x20 mL), and dried in a vacuum oven. The colorimetric NBP test showed a negative result (absence of CH_2Cl). FTIR-ATR: 1635, 1559, 1509, 1457, 1426, 1361, 1327, 1211, 1189, 1156, 1116, 1022, 852, 766, 754 cm^{-1}. Elemental analysis found: N, 8.87%; 3.17 meq/g.

N-(2-bromoacetyl)-D,L-homocysteine thiolactone



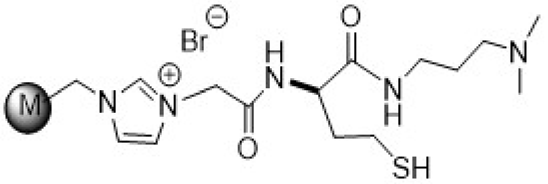
Potassium carbonate (10.8 g, 78.12 mmol) and D,L-homocysteine thiolactone hydrochloride (4.0 g, 26.04 mmol) were dissolved in H_2O MiliQ® (200 mL), and dichloromethane (200 mL). Then, the biphasic reaction mixture was cooled to 0 °C and a solution of bromoacetyl bromide (4.54 mL, 52.07 mmol) in dichloromethane (30 mL) was added dropwise over an hour. The resulting mixture was stirred for 30 min at 0 ºC and then stirring to warm to room temperature for 1 hour. After that, the organic phase was separated and washed with a 5% citric acid solution (2 x 40 mL) and H_2O MiliQ® (2 x 40 mL). Finally, the organic phase was dried with anhydrous magnesium sulfate and the solvent was removed in vacuum to afford 3.88 g as a solid product (62.6% yield). ^{1}H-NMR (300 MHz, CD_3CN) δ 7.03 (s, 1H), 4.57 (ddd, J = 12.7, 8.1, 7.1 Hz, 1H), 3.85 (s, 2H), 3.47 – 3.17 (m, 2H), 2.64 – 2.50 (m, 1H), 2.23 – 2.16 (m, 1H). ^{13}C-NMR (300 MHz, CD_3CN): 205.5, 167.2, 59.86, 30.93, 29.23 and 27.78. FTIR-ATR: 1697, 1657, 1536, 921 cm^{-1}. Elemental analysis calculated for $C_6H_8BrNO_2S$-H_2O: 28.14 C, 5.47 N, 12.52 S. Found: 27.92 C, 5.44 N, 13.06 S.

TS-SILLP-4



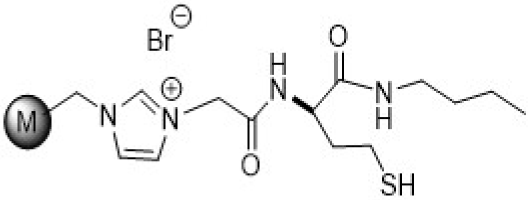
Imidazole polymer **2** (1.6 g, 3.36 mmol/g) was placed in a round bottomed flask and suspended in DMF (60 mL), and N-(2-bromoacetyl)-D,L-homocysteine thiolactone (2.60 g, 10.75 mmol) was added. The suspension was heated at 75 ºC for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF, CH_3OH and CH_2Cl_2 (2x20 mL), and dried in a vacuum oven. FTIR-ATR: 3397, 3024, 2927, 1685, 1557, 1510, 1447, 1149, 1020, 917, 850, 821, 748, 708, 620 cm^{-1}. Elemental analysis found: N, 7.49% S, 5.66 ; 1.78 meq/g.

TS-SILLP-5a



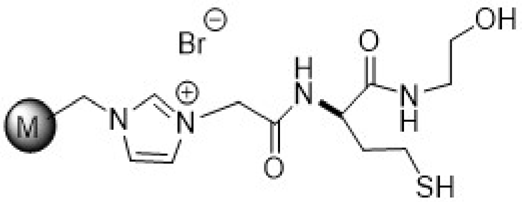
TS-SILLP-4 (0.15 g, 1.78 mmol/g) was placed in a round bottomed flask and suspended in DMF (2 mL), and N,N-dimethylpropane-1,3-diamine (0.10 mL, 0.80 mmol) was added. The suspension was kept stirred at room temperature for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF and CH_3OH (2x20 mL), and dried in a vacuum oven. The Ellman's colorimetric test showed a positive result (presence of -SH). ATR-FTIR: 3390, 3055, 2927, 1657, 1557, 1513, 1446, 1386, 1316, 1256, 1151, 1101, 1020, 963, 824, 746, 708, 661, 621 cm^{-1}. Elemental analysis found: N, 9.40% S 4.26% ; 1.34 meq/g.

TS-SILLP-5b



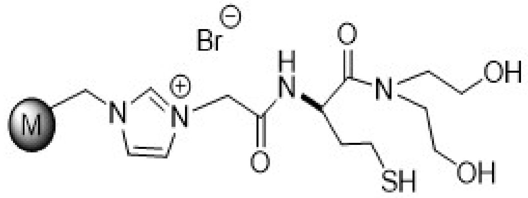
TS-SILLP-4 (0.15 g, 1.78 mmol/g) was placed in a round bottomed flask and suspended in DMF (2 mL), and butylamine (0.08 mL, 0.80 mmol) was added. The suspension was kept stirred at room temperature for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF and CH_3OH (2x20 mL), and dried in a vacuum oven. The Ellman's colorimetric test showed a positive result (presence of -SH). ATR-FTIR: 3405, 3053, 2927, 1658, 1557, 1513, 1439, 1387, 1253, 1153, 1097, 1020, 963, 854, 823, 746, 710, 660, 618 cm^{-1}. Elemental analysis found: N, 8.34% S, 4.73% and ; 1.49 meq/g.

TS-SILLP-5c



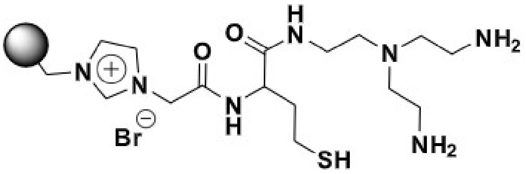
TS-SILLP-4 (0.15 g, 1.78 mmol/g) was placed in a round bottomed flask and suspended in DMF (2 mL), and ethanolamine (0.05 mL, 0.80 mmol) was added. The suspension was kept stirred at room temperature for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF and CH_3OH (2x20 mL), and dried in a vacuum oven. The Ellman's colorimetric test showed a positive result (presence of -SH). ATR-FTIR: 3361, 3052, 2925, 1658, 1557, 1514, 1447, 1425, 1387, 1321, 1253, 1151, 1064, 1020, 959, 824, 747, 707, 619 cm^{-1}. Elemental analysis found: N, 8.69% and S, 4.94%; 1.55 meq/g.

TS-SILLP-5d



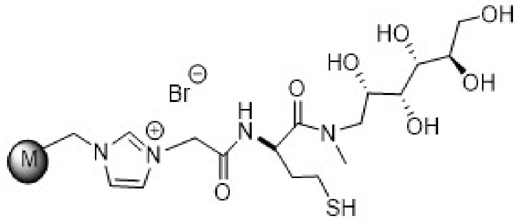
TS-SILLP-4 (0.15 g, 1.78 mmol/g) was placed in a round bottomed flask and suspended in DMF (2 mL), and diethanolamine (0.08 mL, 0.80 mmol) was added. The suspension was kept stirred at room temperature for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF and CH_3OH (2x20 mL), and dried in a vacuum oven. The Ellman's colorimetric test showed a positive result (presence of -SH). FTIR-ATR: 3368, 3053, 2924, 2358, 1657, 1557, 1512, 1425, 1387, 1254, 1150, 1098, 1062, 1020, 963, 853, 824, 747, 708, 660, 617 cm^{-1}. Elemental analysis found: N, 8.07% and S, 4.5%; 1.44 meq/g.

TS-SILLP-5e



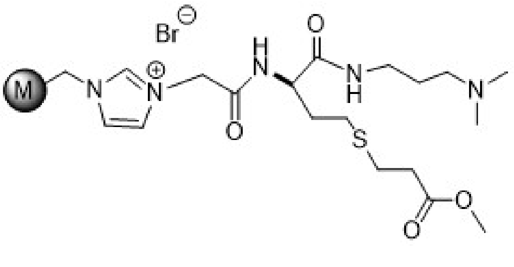
TS-SILLP-4 (0.15 g, 1.78 mmol/g) was placed in a round bottomed flask and suspended in DMF (2 mL), and tris(2-aminoethyl)amine (0.12 mL, 0.80 mmol) was added. The suspension was kept stirred at room temperature for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF and CH_3OH (2x20 mL), and dried in a vacuum oven. The Ellman's colorimetric test showed a positive result (presence of -SH). FTIR-ATR: 1681, 1613, 1512, 1472, 1455, 1400, 1374, 1155, 1008, 902, 847, 832, 784 cm^{-1}. Elemental analysis found: N, 9.48% and S, 2.9%; 0.97 meq/g.

TS-SILLP-5f



TS-SILLP-4 (0.15 g, 1.78 mmol/g) was placed in a round bottomed flask and suspended in DMF (2 mL), and N-methyl-d-glucamine (0.16 g, 0.80 mmol) was added. The suspension was kept stirred at room temperature for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF and CH_3OH (2x20 mL), and dried in a vacuum oven. The Ellman's colorimetric test showed a positive result (presence of -SH). ATR-FTIR: 3366, 3054, 2923, 1657, 1558, 1511, 1424, 1387, 1255, 1147, 1094, 1020, 962, 824, 750, 708, 660, 618 cm^{-1}. Elemental analysis found: N, 7.55% and S, 4.28 %; 1.35 meq/g.

TS-SILLP-6a



TS-SILLP-4 (0.15 g, 1.78 mmol/g) was placed in a round bottomed flask and suspended in DMF (2 mL), and N,N-dimethylpropane-1,3-diamine (0.10 mL, 0.80 mmol) was added. The suspension was kept stirred at room temperature for 3 hours. Then, methyl acrylate (0.07 mL, 0.80 mmol) was added and the reaction was heated at 70 ºC for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF and CH_3OH (2x20 mL), and dried in a vacuum oven. The Ellman's colorimetric test showed a positive result (presence of -SH). FTIR-ATR: 3379, 3052, 2928, 2360, 1730, 1660, 1556, 1514, 1443, 1360, 1250, 1151, 1037, 1020, 973, 824, 750, 710, 663, 624 cm^{-1}. Elemental analysis found: N, 8.71% and S, 3.87%; 1.24 meq/g

Synthesis of Solid-Phased task-specific supported ILs with Cu

CuI-SILLP-1

SILLP-1 (0.2 g, 3.17 mmol/g) was placed in a round bottomed flask and suspended in DMF (2 mL), and CuI (240 mg, 1.27 mmol) was added. The suspension was kept stirred at room temperature for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF and CH_3OH (2x20 mL), and dried in a vacuum oven. ICP-MS: 1.07 meq Cu/g pol.

$Cu(AcO)_2$-SILLP-1

SILLP-1 (0.2 g, 3.17 mmol/g) was placed in a round bottomed flask and suspended in DMF (2 mL), and $Cu(AcO)_2 \cdot H_2O$ (252 mg, 1.27 mmol) was added. The suspension was kept stirred at room temperature for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF and CH_3OH (2x20 mL), and dried in a vacuum oven. ICP-MS: 0.65 meq Cu/g pol.

CuI-TS-SILLP-5a

TS-SILLP-5a (0.2 g, 1.34 mmol/g) was placed in a round bottomed flask and suspended in DMF (2 mL), and CuI (106 mg, 0.54 mmol) was added. The suspension was kept stirred at room temperature for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF and CH_3OH (2x20 mL), and dried in a vacuum oven. ICP-MS: 1.13 meq Cu/g pol.

$Cu(AcO)_2$-TS-SILLP-5a

TS-SILLP-5a (0.2 g, 1.34 mmol/g) was placed in a round bottomed flask and suspended in DMF (2 mL), and $Cu(AcO)_2 \cdot H_2O$ (106 mg, 0.54 mmol) was added. The suspension was kept stirred at room temperature for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF and CH_3OH (2x20 mL), and dried in a vacuum oven. ICP-MS: 0.5 meq Cu/g pol.

$Cu(AcO)_2$-TS-SILLP-5b

TS-SILLP-5b (0.2 g, 1.49 mmol/g) was placed in a round bottomed flask and suspended in DMF (2 mL), and $Cu(AcO)_2\cdot H_2O$ (118 mg, 0.60 mmol) was added. The suspension was kept stirred at room temperature for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF and CH_3OH (2x20 mL), and dried in a vacuum oven. ICP-MS: 0.46 meq Cu/g pol.

$Cu(AcO)_2$-TS-SILLP-5c

TS-SILLP-5c (0.2 g, 1.55 mmol/g) was placed in a round bottomed flask and suspended in DMF (2 mL), and $Cu(AcO)_2\cdot H_2O$ (123 mg, 0.62 mmol) was added. The suspension was kept stirred at room temperature for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF and CH_3OH (2x20 mL), and dried in a vacuum oven. ICP-MS: 0.47 meq Cu/g pol.

$Cu(AcO)_2$-TS-SILLP-5d

TS-SILLP-5d (0.2 g, 1.44 mmol/g) was placed in a round bottomed flask and suspended in DMF (2 mL), and $Cu(AcO)_2\cdot H_2O$ (114 mg, 0.58 mmol) was added. The suspension was kept stirred at room temperature for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF and CH_3OH (2x20 mL), and dried in a vacuum oven. ICP-MS: 0.47 meq Cu/g pol.

$Cu(AcO)_2$-TS-SILLP-5e

TS-SILLP-5e (0.2 g, 0.97 mmol/g) was placed in a round bottomed flask and suspended in DMF (2 mL), and $Cu(AcO)_2\cdot H_2O$ (77 mg, 0.39 mmol) was added. The suspension was kept stirred at room temperature for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF and CH_3OH (2x20 mL), and dried in a vacuum oven. ICP-MS: 0.27 meq Cu/g pol.

$Cu(AcO)_2$-TS-SILLP-5f

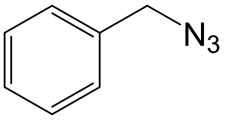
TS-SILLP-5f (0.2 g, 1.25 mmol/g) was placed in a round bottomed flask and suspended in DMF (2 mL), and $Cu(AcO)_2\cdot H_2O$ (100 mg, 0.5 mmol) was added. The suspension was kept stirred at room temperature for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF and CH_3OH (2x20 mL), and dried in a vacuum oven. ICP-MS: 0.13 meq Cu/g pol.

$Cu(AcO)_2$-TS-SILLP-6a

TS-SILLP-6a (0.2 g, 1.35 mmol/g) was placed in a round bottomed flask and suspended in DMF (2 mL), and $Cu(AcO)_2\cdot H_2O$ (108 mg, 0.54 mmol) was added. The suspension was kept stirred at room temperature for 24 hours. Afterwards, the reaction was filtered and the polymer was washed with DMF and CH_3OH (2x20 mL), and dried in a vacuum oven. ICP-MS: 0.41 meq Cu/g pol.

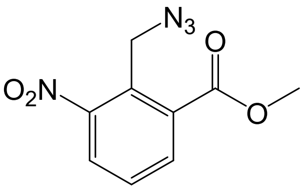
Synthesis of azides[3]

(Azidomethyl)benzene (8a)



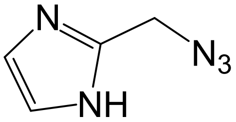
One hundred ninety microliters of benzyl bromide (1.6 mmol) were added to a suspension of 0.436 g polymer-supported azide (2.4 mmol) in ACN (8 mL). The resulting mixture was stirred for 48 hours at room temperature and 150 rpm. Then, the polymer was filtered off and the resulting solution was evaporated to yield an oil of compound **8a** (>99% of yield by NMR) used without any further purification. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.93 (s, 2H, CH_2), 7.28 (m, 5H, Ph) ppm; HPLC: 3.789 min for compound **8a**.

Methyl 2-(Azidomethyl)-3-nitrobenzoate (8b)



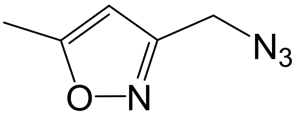
Obtained as for **8a** but using 0.438 g of methyl 2-(bromomethyl)-3-nitrobenzoate (1.6 mmol) to yield to 200 mM of compound **8b** in ACN, >99% yield. HPLC: 3.448 min for compound **8b**.

2-(Azidomethyl)-1H-imidazole (8c)



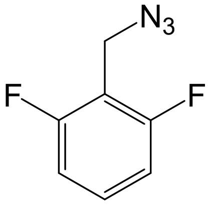
Obtained as for **8a** but using 0.258 g of 2-(bromomethyl)-1H-imidazole (1.6 mmol) to yield 200 mM of compound **8c** in ACN, >99% yield. HPLC: 2.412 min for compound **8c**.

3-(Azidomethyl)-5-methylisoxazole (8d)



Obtained as for **8a** but using 0.285 g of 3-(bromomethyl)-5-methylisoxazole (1.6 mmol) to yield to 200 mM of compound **8d** in ACN, >99% yield. HPLC: 2.418 min for compound **8d**.

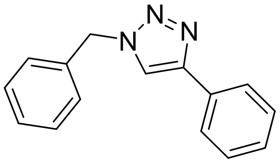
2-(Azidomethyl)-1,3-difluorobenzene (8e)



Obtained as for **8a** but using 0.331 g of 2-(bromomethyl)-1,3-difluorobenzene (1.6 mmol) to yield to 200 mM of compound **8e** in ACN, >99% yield. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 4.53 (s, 2H, CH_2), 7.20 (m, 2H, Ph), 7.52 (m, 2H, Ph) ppm; HPLC: 4.075 min for compound **8e**.

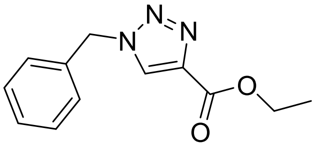
Synthesis of Functional 1,2,3-Triazoles[3]

1-Benzyl-4-phenyl-1H-1,2,3-triazole (9a)



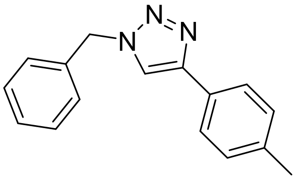
7.5 mg of **CuI/Cu(OAc)$_2$-TS-SILLP-5(a-f)/6a or CuI/Cu(OAc)$_2$-SILLP-1** was added to 0.5 mL of 200 mM solution of (azidomethyl)benzene **8a** and phenylacetylene **7a** in ACN. The resulting solution was heated at 70 °C for 4 hours under stirring. A sample of 0.5 mL of this solution was diluted with 2.5 mL of ACN and 0.5 mL of this solution was diluted with 2 mL of a solution of anthracene in ACN (5 mM, internal standard). This solution was injected in HPLC to calculate the yield (92% yield). The remaining reaction solution was concentrated, and the resulting crude was analysed by ^{1}H-NMR. ^{1}H-NMR (400MHz, $CDCl_3$): 5.51 (s, 2H, CH_2), 7.30 (m, 10H, Ph), 7.52 (s, 1H, CH) ppm; HPLC: 3.751 min for compound **9a**.

Ethyl 1-Benzyl-1H-1,2,3-triazole-4-carboxylate (9b)



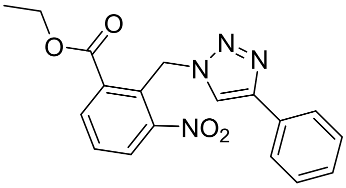
Obtained as for **9a** but using ethyl propiolate **7b** (54% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.36 (s, 3H, CH_3), 4.40 (s, 2H, CH_2), 5.5 (s, 2H, CH_2), 7.26 (m, Ph), 8.23 (s, 1H, CH) ppm; HPLC: 2.993 min for compound **9b**.

1-Benzyl-4-(p-tolyl)-1H-1,2,3-triazole (9c)



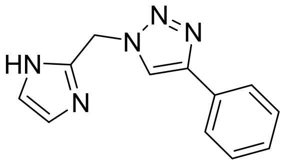
Obtained as for **9a** but using 1-Ethynyl-4-methylbenzene **7c** (95% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): 5.49 (s, 2H, CH_2), 7.2 (m, 9H, Ph), 7.64 (s, 1H, CH) ppm; HPLC: 3.488 min for compound **9c**.

Methyl 3-Nitro-2-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)-benzoate (9d)



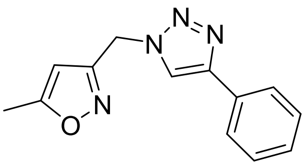
Obtained as for **9a** but using methyl 2-(Azidomethyl)-3-nitrobenzoate **8b** (34% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): 3.96 (s, 3H,CH_3), 6.20 (s, 2H, CH), 7.79 (m, 9H, Ph + CH) ppm; HPLC: 3.322 min for compound **9d**.

1-((1H-Imidazol-2-yl)methyl)-4-phenyl-1H-1,2,3-triazole (9e)



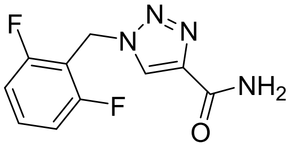
Obtained as for **9a** but using 2-(Azidomethyl)-1H-imidazole **8c** (90% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.20 (s, 2H, CH_2), 6.55 (m, 6H, Ph + CH) ppm; HPLC: compound **9e** not observed and the peak of the acetylene compound **9e** (3.825 min) used to calculate the yield.

5-Methyl-3-((4-phenyl-1H-1,2,3-triazol-1-yl)methyl)-isoxazole (9f)



Obtained as for **9a** but using 3-(Azidomethyl)-5-methylisoxazole **8d** (65% yield). ^{1}H-NMR (400 MHz, $CDCl_3$): 2.90 (s, 3H, CH_3), 4.48 (s, 2H, CH_2), 6.03 (s, 1H, CH), 7.39 (m, 3H, Ph), 7.74 (m, 2H, Ph), 8.00 (s, 1H, CH) ppm; HPLC: 3.907 min for compound **9f**.

1-(2,6-Difluorobenzyl)-1H-1,2,3-triazole-4-carboxamide (9g)



Obtained as for **9a** but using 2-(bromomethyl)-1,3-difluorobenzene **8e** and 2-propynamide **7d** (81% yield). ^{1}H-NMR (400 MHz, DMSO-d_6): 5.57 (s, 2H, CH_2), 7.17 (m, 2H, Ph), 7.81 (m, 1H, Ph), 8.2 (s, 2H, NH_2), 8.53 (s, 1H, CH) ppm; HPLC: 2.254 min for compound **9g**.

Hot filtration test: The hot filtration test was conducted by performing two sets of parallel experiments. In the first set, 7.5 mg of **Cu(OAc)$_2$-TS-SILLP-5a** was added to each of six separate vials, each containing 0.5 mL of a 200 mM solution of (azidomethyl)benzene **8a** and phenylacetylene **7a** in acetonitrile. The reaction mixtures were heated at 70 °C under stirring and stopped at different time intervals: 20, 30, 40, 60, 125, and 240 minutes. For the hot filtration test, the second set of experiments followed the same initial setup, involving four parallel reactions. After 20 minutes of heating, the **Cu(OAc)$_2$-TS-SILLP-5a** catalyst was removed by filtration. In the first vial of this set, the reaction was stopped and analyzed immediately after the catalyst was removed. For the remaining three reactions, the mixtures were allowed to continue under identical conditions without the TS-SILLP catalyst for 60, 125, and 240 minutes, respectively. In all cases, the reaction mixtures were processed by diluting 0.5 mL of the reaction solution in 2.5 mL of ACN. Subsequently, 0.5 mL of this diluted solution was further diluted with 2 mL of an ACN solution containing anthracene (5 mM) as an internal standard. The final solutions were analyzed by HPLC to determine the yields. The results obtained are presented in Figure S3.

Recycling Tests Procedure: 7.5 mg of the **RB-Cu(OAc)2-TS-SILLP-5a** catalyst was added to 0.5 mL of a 200 mM solution of (azidomethyl)benzene (**8a**) and phenylacetylene (**7a**) in acetonitrile. The reaction mixture was heated at 70 °C under stirring for 24 hours. After completion, the catalyst was separated by filtration, and the filtered resin was washed with 2 mL of methanol and dried to constant weight. The recovered catalyst was subjected to the same reaction conditions for a subsequent reaction cycle. To determine the reaction yield after recycling, 0.5 mL of the reaction solution was diluted with 2.5 mL of ACN. Then, 0.5 mL of this diluted solution was further mixed with 2 mL of an ACN solution containing anthracene (5 mM) as an internal standard. The final solution was analyzed using HPLC to quantify the yield.

Reactivation of Spent Catalysts with a resin cocktail with a Rose Bengal supported onto a SILLPs: To a used catalyst, 7.5 mg of **$Cu(OAc)_2$-TS-SILLP-5a**, recovered after several consecutive reaction cycles, was suspended along with 7.5 mg of **RB-TS-SILLP** (prepared as described in references 4 and 5) in 0.5 mL of acetonitrile. The resulting suspension was exposed to UV-Vis light (365 nm) under an oxygen atmosphere provided by an O_2 balloon for 1 hour. Following the regeneration process, the catalyst was filtered, dried, and reused in subsequent reaction cycles under standard conditions: the regenerated catalytic cocktail was suspended in 0.5 mL of a 200 mM solution of (azidomethyl)benzene (**8a**) and phenylacetylene (**7a**) in ACN. The reaction mixture was heated at 70 °C with stirring for 24 hours. After completion, the the catalytic cocktail was separated by filtration, and the filtered resin was washed with 2 mL of methanol and dried to constant weight. The recovered catalyst was subjected to the same reaction conditions for a subsequent reaction cycle. The reaction yield was determined by diluting 0.5 mL of the reaction solution with 2.5 mL of ACN. Subsequently, 0.5 mL of this diluted solution was mixed with 2 mL of an ACN solution containing anthracene (5 mM) as an internal standard. The prepared solution was analyzed by HPLC to quantify the yield.

Anion Exchange Protocol for the preparation of RB-Cu(OAc)2-TS-SILLP-5a The resin **RB-Cu(OAc)2-TS-SILLP-5a** was prepared as previously described in references 4 and 5. Briefly, 1 g of Cu(OAc)2-TS-SILLP-5a was placed in a round-bottom flask and suspended in 33 mL of a 1000 ppm Rose Bengal solution until complete absorption occurred. The suspension was stirred at room temperature for 24 hours. After this period, the TS-SILLP was filtered, thoroughly washed with DMF and methanol (2 × 20 mL each), and then dried in a vacuum oven.

Reaction / Regeneration procedure with the Rose Bengal-containing Cu(OAc)2 TS-SILLP-5a. The regeneration protocol for the reaction is described as follows:

- **Reaction Protocol:** To perform the reaction, 7.5 mg of **RB-Cu(OAc)2-TS-SILLP-5a** catalyst was added to 0.5 mL of a 200 mM solution of (azidomethyl)benzene (**8a**) and phenylacetylene (**7a**) in acetonitrile (ACN). The reaction mixture was heated at 70 °C with stirring for 24 hours. After completion, the catalyst was separated by filtration and the filtration residue was washed with 2 mL of methanol. The reaction yield was determined by diluting 0.5 mL of the reaction solution with 2.5 mL of ACN. Then, 0.5 mL of this diluted solution was mixed with 2 mL of an ACN solution containing anthracene (5 mM) as an internal standard. The final solution was analyzed using HPLC.
- **Regeneration Protocol:** The **RB-$Cu(OAc)_2$-TS-SILLP-5a** catalyst recovered after the reaction, following filtration and washing, was suspended in 0.5 mL of ACN and exposed to UV-Vis light (365 nm) under an oxygen atmosphere provided by O_2 balloons for 1 hour. After the regeneration process, the catalyst was filtered, dried, and reused in subsequent reaction cycles under the same conditions.

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