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Supporting Information

Vitamin B_{12} and a metal-organic framework enable photocatalytic generation of alkyl radicals

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1. General information

Materials. Commercial reagents and solvents were purchased from Sigma-Aldrich, Fluorochem, TCI, Angene, Alfa Aesar, Fisher Scientific UK, and used as received unless otherwise noted. Deuterated chloroform ($CDCl_3$) was purchased from Eurisotop. Deuterated ethanol (C_2D_5OD) was purchased from Eurisotop, Deutero GmbH and Cambridge Isotope Laboratories, Inc. MIL-125-NH_2 used in the optimization studies and mechanistic experiments was homemade, for the scope unactivated commercial sources were used (STREM and AA Blocks).

Optimization. Reactions were set in a glovebox under argon atmosphere. Reactions were monitored by gas chromatography (GC, specification below) and thin-layer chromatography (TLC) on Merck silica gel (60F-254, 0.20 mm thickness), visualizing with UV-light. Colum chromatography was performed using Merck silica gel 60 (230-400 mesh). GC yields were calculated based on using dodecane as an internal standard.

Instrumentation.

• NMR Spectroscopy: ^1H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker 400 MHz, 500 MHz or Varian 600 MHz instrument with TMS as an internal standard. NMR chemical shifts are reported in ppm and referenced to the residual solvent peak of $CDCl_3$ (7.26 ppm - ^1H NMR and 77.16 ppm - ^{13}C NMR). Multiplicities are indicated by singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m) and broad (br). Coupling constants (*J*) are reported in Herz. All data analysis was performed using MestReNova software package.

• GC/MS Chromatography: GC/MS analyses were performed using Shimadzu GCMS-QP2010 SE gas chromatograph with FID detector and Zebron ZB 5Msi column.

• Elemental Analysis: Elemental analyses (N, H, C, S) were performed on PERKIN-ELMER 240 Elemental Analyzer.

• High Resolution Mass Spectrometry: High-resolution mass spectra (HRMS) were recorded on a Waters AutoSpec Premier instrument using electron ionization (EI).

• Low Resolution Mass Spectrometry: Low-resolution mass spectra (LRMS) were recorded on Applied Biosystems API 365 Mass Spectrometer using electrospray ionization (ESI).

• UV-Vis Absorption Spectroscopy: absorption spectra were recorded on UV-3600i Plus UV-Vis-NIR Spectrophotometer.

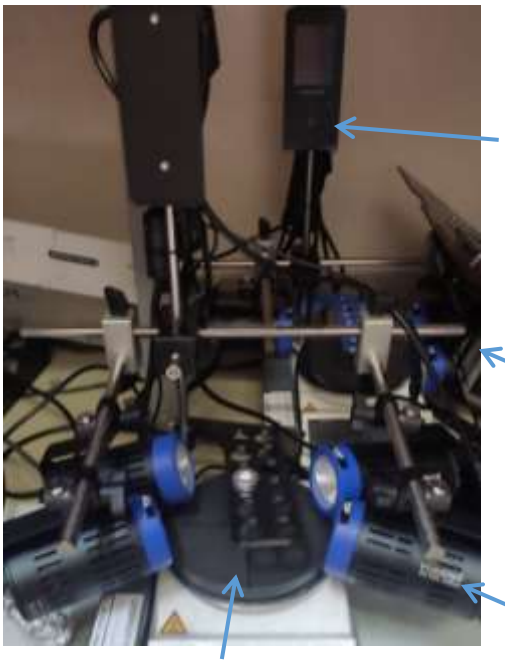
• Measurement of N_2 sorption isotherms: prior to the measurements, all samples were heated at 100°C for 24 h under high vacuum. The nitrogen sorption isotherms were determined at liquid nitrogen temperature (77K) using Quantachrome Autosorb-IQ-MP sorption analyser. The specific surface areas were calculated according to the Brunauer-Emmett-Teller (BET) method using P/P_o values in the range 0.05-0.2. For all isotherm analyses we ensured that the two consistency criteria described by Rouquerol *et al.*[1] and Walton *et al.*[2] were satisfied.

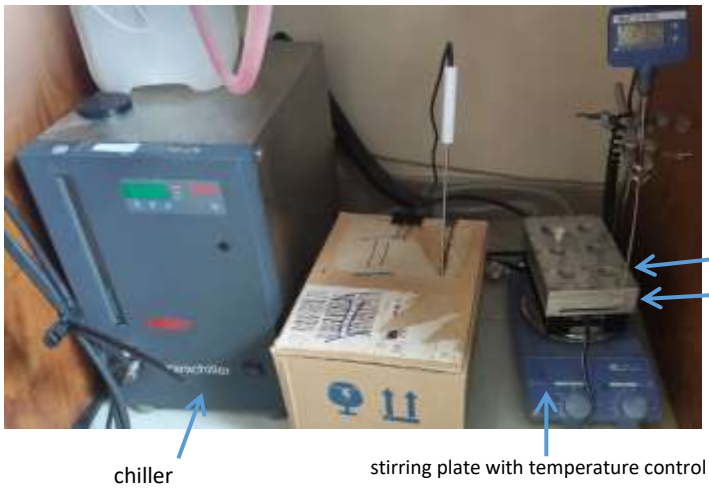
• Powder X-ray diffraction: all powder X-ray diffraction (PXRD) patterns were recorded on a Bruker D8 Discover X-ray diffractometer (CuK_α radiation, parallel beam formed by Goebel mirror) equipped

[1] J. Rouquerol, P. Llewellyn and F. Rouquerol, 2007, **160**, 49–56.
[2] K. S. Walton and R. Q. Snurr, *J. Am. Chem. Soc.*, 2007, **129**, 8552–8556.

with a VANTEC 1 position sensitive detector. All measurements were performed on standard aluminium holders.

• Photoreactor setup: experiments were performed in a UOSlab MiniPhoto commercial reactor with 100% power output and cooling on Haber Minichiller 600 cooling unit, with Kessil® lamps and cooling fan or in homemade 7W LEDs block with 18 °C cooling on Haber Minichiller 300 cooling unit. https://en.uoslab.com/download/Photochemical_reactors.pdf (available on 3rd. August 2023)





2. Optimization of reaction conditions for the model reaction

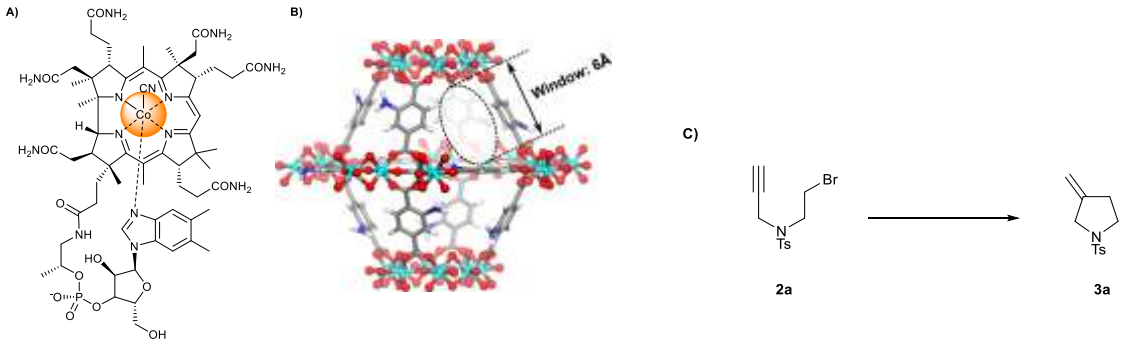


Figure. S1 A) Vitamin B_{12} (**1**, cyanocobalamin); B) MIL-125-NH_2(Ti) structure, grey - carbon, white – hydrogen, red – oxygen, light blue octahedra – titanium, blue – nitrogen, assumed molecular weight of MIL-125-NH_2(Ti): 1653.74 g/mol; C) Model cyclization reaction.

2.1. Optimization of the amount of NH_4Cl[a]

No	*NH_4Cl [equiv.]*	*Yield of 2a [%]*
1	0.25	71[b]
2	**0.50**	**83**[b]
3	1.00	72
4	1.50	78
4	2.00	84
6	3.00	78
7	4.00	80

[a] Reaction conditions: *N*-(2-bromoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2a**, 79 mg, 0.25 mmol), vitamin B_{12} (**1**, 1.7 mg, 0.5 mol%), MIL-125-NH_2(Ti) (10 mg, 2.5 mol%), DIPEA (175 µl, 4.0 equiv.), *i*PrOH (*c* = 0.125 M, 2 mL), Ar, 18 h, 7 W 446 nm LED. [b] DIPEA (88 µl, 2.0 equiv.), 99.8% Ar-purged EtOH (*c* = 0.125 M, 2 mL), 100% power output 450 nm LEDs.

2.2. Optimization of the amount of DIPEA[a]

No	*DIPEA [equiv.]*	*Yield of 2a [%]*
1	1.0	52
2	1.5	53
3	**2.0**	**78**
4	3.0	80
5	4.0	78

[a] Reaction conditions: *N*-(2-bromoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2a**, 0.25 mmol), vitamin B_{12} (**1**, 1.7 mg, 0.5 mol%), MIL-125-NH_2(Ti) (10 mg, 2.5 mol%), NH_4Cl (20 mg, 1.5 equiv.), 99.8% Ar-purged EtOH (*c* = 0.125 M, 2 mL), Ar, 18 h, 7 W 446 nm LED.

2.3. Optimization of the amount of MIL-125-NH_2(Ti)[a]

No	*MOF loading [mol%]*	*Yield of 2a [%]*
1	1	61
2	2	72
3	**2.5**	**78**

[a] Reaction conditions: *N*-(2-bromoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2a**, 0.25 mmol), vitamin B_{12} (**1**, 1.7 mg, 0.5 mol%), MIL-125-NH_2(Ti) (10 mg, 2.5 mol%), NH_4Cl (20 mg, 1.5 equiv.), DIPEA (88 µl, 2.0 equiv.), iPrOH (*c* = 0.125 M, 2 mL), Ar, 18 h, 7 W 446 nm LED

2.4. Reactions in different solvents[a]

No	*Solvent*	*Yield of 2a [%]*
1	*i*PrOH	80
2	**EtOH**	**85**
3	NMP	23
4	DMF	14
5	DMA	14
6	MeOH	11-75[b]
7	CF_3CH_2OH	6
8	DMPU	63
9	H_2O	traces

[a] Reaction conditions: *N*-(2-bromoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2a**, 79 mg, 0.25 mmol), vitamin B_{12} (**1**, 1.7 mg, 0.5 mol%), MIL-125-NH_2(Ti) (10 mg, 2.5 mol%), NH_4Cl (13.5 mg, 1.0 equiv.), DIPEA (88 µl, 2.0 equiv.), solvent (*c* = 0.125 M, 2 mL), Ar, 18 h, 7 W 446 nm LED. Solvent choice was determined by B_{12} solubility. [b] Different experiments in the same conditions in MeOH gave yields spanning from 11% to 75% thus the results are inconclusive.

2.5. Use of various sacrificial reducing agents[a]

No	*Electron Donor*	*Yield of 2a [%]*
1	**diisopropylethylamine (DIPEA)**	**85**
2	triethylamine	49
3	triethanolamine	55
4	sodium ascorbate	traces
5	sodium oxalate	traces
6	EDTA	traces
7	*N,N*-dimethyl-*p*-toluidine	traces
8	Hantzsch ester	traces

[a] Reaction conditions: *N*-(2-bromoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2a**, 79 mg, 0.25 mmol), vitamin B_{12} (**1**, 1.7 mg, 0.5 mol%), MIL-125-NH_2(Ti) (10 mg, 2.5 mol%), NH_4Cl (13.5 mg, 1 equiv.), sacrificial reducing agent (2.0 equiv.), 99.8% Ar-purged EtOH (*c* = 0.125 M, 2 mL), Ar, 18 h, 7 W 446 nm LED.

2.6. Influence of a light source[a]

No	*Light source*	*Yield of 2a [%]*
1	**450 nm UOSlab 100%**	**85**
2	405 nm UOSlab 100%	84[b]
3	365 nm UOSlab 100%	53
4	525 nm UOSlab 100%	traces
5	446 nm 7W LED	78[c]
6	440 nm Kessil®	0[d]

[a] Reaction conditions: *N*-(2-bromoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2a**, 79 mg, 0.25 mmol), vitamin B_{12} (**1**, 1.7 mg, 0.5 mol%), MIL-125-NH_2(Ti) (10 mg, 2.5 mol%), NH_4Cl (13.5 mg, 1.0 equiv.), DIPEA (88 µl, 2.0 equiv.), 99.8% Ar-purged EtOH (*c* = 0.125 M, 2 mL), Ar, 45 min. [b] Reaction time 30 min. [c] Reaction time 8 hours. [d] Kessil® lamp, 50 °C heating.

2.7. Influence of a MOF catalyst[a]

No	*Photocatalyst type*	*Molecular formula*	*Yield of 2a [%]*
1	**commercial MIL-125-NH_2(Ti)**	**$C_{48}H_{34}N_6O_{36}Ti_8$**	**88**
2	MIL-125-NH_2(Ti)	$C_{48}H_{34}N_6O_{36}Ti_8$	90
3	MIL-101-NH_2(Ti)	$C_{24}H_{19}Al_3ClN_3O_{15}$	traces[a,b]
4	UiO-66-NH_2	$C_{48}H_{34}N_6O_{32}Zr_6$	traces
5	MUV-11	$C_{24}H_{18}N_6O_{12}Ti_2$	traces[a,c]
6	MIL-101-SO_3H/Na	$C_{24}H_{16}ClCrNNaO_{23}S_3$	traces[a,b]
7	HKUST-1	$C_{18}H_6Cu_3O_{12}$	traces[a,d]

[a] Reaction conditions: *N*-(2-bromoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2a**, 79 mg, 0.25 mmol), vitamin B_{12} (**1**, 1.7 mg, 0.5 mol%), MOF (2.5 mol%), NH_4Cl (7 mg, 0.5 equiv.), DIPEA (88 µl, 2.0 equiv.), 99.8% Ar-purged EtOH (*c* = 0.125 M, 2 mL), Ar, 45 min, 100% power output 450 nm LEDs. [b] 405 nm instead of 450 nm irradiation. [c] 525 nm instead of 450 nm irradiation. [d] 660 nm instead of 450 nm irradiation.

2.8. Reactions in the presence of various Co-catalysts[a]

No	*Catalyst*	*Yield of 2a [%]*
1	heptamethyl cobyrinate perchlorate (HME)	83
2	Co(dmgH)$_2$py^{i}Pr	traces
3	Co(dmgH)$_2$pyCl	3
4	cobalt tetraphenylporphyrine	20

[a] Reaction conditions: *N*-(2-bromoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2a**, 79 mg, 0.25 mmol), Co-catalyst (0.5 mol%), MIL-125-NH_2(Ti) (10 mg, 2.5 mol%), NH_4Cl (7 mg, 0.5 equiv.), DIPEA (88 µl, 2.0 equiv.), 99.8% Ar-purged EtOH (*c* = 0.125 M, 2 mL), Ar, 45 min, 100% power output 450 nm LEDs.

2.9. Influence of various additives[a]

No	*NH_4Cl substitute*	*Yield of 2a [%]*
1	NH_4F	82
2	NH_4Br	89
3	NH_4PF_6	86
4	Me_4NCl	60
5	malononitrile	0
6	phenol	0
7	*p*-cyanophenol	0

[a] Reaction conditions: *N*-(2-bromoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2a**, 79 mg, 0.25 mmol), vitamin B_{12} (**1**, 1.7 mg, 0.5 mol%), MIL-125-NH_2(Ti) (10 mg, 2.5 mol%), NH_4Cl substitute (0.5 equiv.), DIPEA (88 µl, 2.0 equiv.), 99.8% Ar-purged EtOH (*c* = 0.125 M, 2 mL), Ar, 45 min, 100% power output 450 nm LEDs.

2.10. Optimized conditions and additives' influence

substrate **3a**	0.25 mmol	79 mg
MIL-125-NH_2(Ti)	2.5 mol%	10 mg
cyanocobalamin (**1**)	0.5 mol%	1.7 mg
NH_4Cl	0.5 equiv.	7 mg
DIPEA	2 equiv.	88 µl
EtOH 99.8%	0.125 mol/dm^3	2 mL
Light	450 nm LEDs	100%
Time		45 min

Aldehyde, halides, disulfides

Utilizing Glorius approach, we test functional group tolerance and performed reactions with the addition of aldehyde (3-phenylpropionaldehyde), organic chloride (1-chlorododecane), and disulfide (*p*-tolyl disulfide).[3] From the model reaction, aldehyde and chloride was recovered in 80% yield and the desired product formed. In contrast, the addition of disulfide halted the desired reaction completely and a complex mixture of products formed.

Procedure with chlorododecane or 3-phenylpropionaldehyde:

In a glovebox under Ar atmosphere, a 10 mL glass vial equipped with a cross-shaped stirring bar was charged with vitamin B_{12} (**1**, 1.7 mg, 0.5 mol%), non-activated MIL-15-NH_2(Ti) (10 mg, 2.5 mol%), vacuum dried ammonium chloride (7.0 mg, 0.5 equiv.), *N*-tosylamide (**2a-e**, 0.25 mmol). Next, dry EtOH (*c* = 0.125 mol/dm^3, 2 mL) was added and and the vial was sealed with a rubber-aluminum cap. The reaction mixture was sonicated for one minute to dissolve all reagents and disperse the MOF, then DIPEA (88 µl, 2.0 equiv.), and chlorododecane (59 µl, 1 equiv.) or 3-phenylpropionaldehyde (33 µl, 1 equiv.) were added. The resulting mixture was placed in a photoreactor for 2 hours on 100% power output. Over that time, the color of the reaction mixture changed from red to dark green indicating

[3] K. D. Collins, F. Glorius, *Nat. Chem.* 2013, **5**, 597-601.

the end of reaction. The content was transferred to the 2 mL Eppendorf vial and centrifuged at 13.000 RPM for 1 minute. From the supernatant a sample was taken and measured on GC apparatus.

Procedure with *p*-tolyl disulfide or TEMPOL or *E*-stilbene:

In a glovebox under Ar atmosphere, a 10 mL glass vial equipped with a cross-shaped stirring bar was charged with vitamin B_{12} (**1**, 1.7 mg, 0.5 mol%), non-activated MIL-15-NH_2(Ti) (10 mg, 2.5 mol%), vacuum dried ammonium chloride (7.0 mg, 0.5 equiv.), *N*-tosylamide (**2a-e**, 0.25 mmol), and *p*-tolyl disulfide (63 mg, 1 equiv.) or TEMPOL (86 mg, 2 equiv) or *E*-stilbene (45 mg, 1 equiv.). Next, dry EtOH (*c* = 0.125 mol/dm^3, 2 mL) was added and and the vial was sealed with a rubber-aluminum cap. The reaction mixture was sonicated for one minute to dissolve all reagents and disperse the MOF, then DIPEA (88 µl, 2.0 equiv.) was added. The resulting mixture was placed in a photoreactor for 2 hours on 100% power output. Over that time, the color of the reaction mixture changed from red to dark green indicating the end of reaction. The content was transferred to the 2 mL Eppendorf vial and centrifuged at 13.000 RPM for 1 minute. From the supernatant a sample was taken and measured on GC apparatus.

Isomerization of stilbene

Under the optimized reaction conditions, the isomerization of *E*/*Z*-stilbene was tested. To this end, to the model reaction (optimized conditions) *E*-stilbene was added. GC analysis revealed that 50% of *E*-stilbene transformed into *Z*-diastereoisomer suggesting that MOFs energy in the triplet energy of is greater than the triplet energy of stilbene, which is 43.5 kcal/mol.[4]

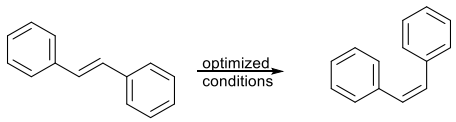


Figure S6 Reaction in the presence of *E*-stilbene. Reaction conditions: *N*-(2-bromoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2a**, 79 mg, 0.25 mmol), vitamin B_{12} (**1**, 1.7 mg, 0.5 mol%), MIL-125-NH_2(Ti) (10 mg, 2.5 mol%), NH_4Cl (7 mg, 0.5 equiv.), DIPEA (88 µl, 2.0 equiv.), *E*-stilbene (45 mg, 1 equiv.), 99.8% Ar-purged EtOH (*c* = 0.125 M, 2 mL), Ar, 2 h, 100% power output 450 nm LEDs.

1,2-Epoxy-5-hexene opening reaction

Under the optimized conditions, also the epoxide ring opens and the subsequent addition of the radical generated to give cyclopropane occurred. A mixture of volatile products formed and they were analyzed by GC-MS analysis. 3-Methylcyclopentanol formed as a major product but a detailed studies on the reaction are required.

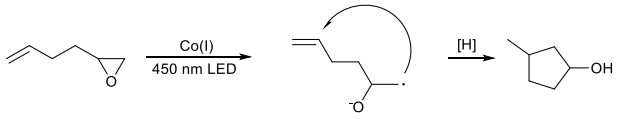


Figure S10 1,2-epoxy-5-hexane opening and cyclization product (3-methylcyclopentanol). Reaction conditions: 1,2-epoxy-5-hexene (28 µl, 0.25 mmol), vitamin B_{12} (**1**, 1.7 mg, 0.5 mol%), MIL-125-NH_2(Ti) (10 mg, 2.5 mol%), NH_4Cl (7 mg, 0.5 equiv.), DIPEA (88 µl, 2.0 equiv.), 99.8% Ar-purged EtOH (*c* = 0.125 M, 2 mL), Ar, 45 min, 100% power output 450 nm LEDs.

[4] K. Nakatani, Hi. Sato R. Fukuda, Phys. *Chem. Chem. Phys*. 2022, **24**, 1712-1721

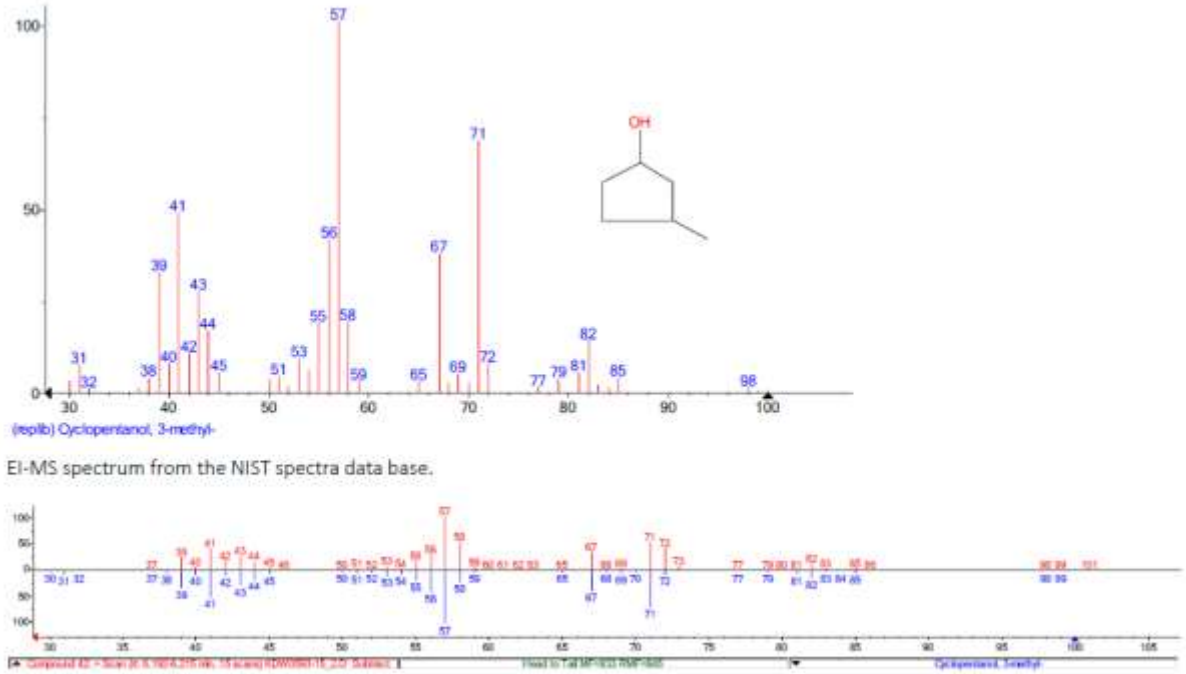


Figure S11 GC-MS analysis for 3-methylcyclopentanol – database comparison.

In a glovebox under Ar atmosphere, a 10 mL glass vial equipped with a cross-shaped stirring bar was charged with vitamin B_{12} (**1**, 1.7 mg, 0.5 mol%), non-activated MIL-15-NH_2(Ti) (10 mg, 2.5 mol%), vacuum dried ammonium chloride (7.0 mg, 0.5 equiv.). Next, dry EtOH (c = 0.125 mol/dm^3, 2 mL) was added and and the vial was sealed with a rubber-aluminum cap. The reaction mixture was sonicated for one minute to dissolve all reagents and disperse the MOF, then DIPEA (88 µl, 2.0 equiv.), and 1,2-epoxy-5-hexene (28 µl, 0.25 mmol) were added. The resulting mixture was placed in a photoreactor for 2 hours on 100% power output. Over that time, the color of the reaction mixture changed from red to dark green indicating the end of reaction. The content was transferred to the 2 mL Eppendorf vial and centrifuged at 13.000 RPM for 1 minute. From the supernatant a sample was taken and measured on GC apparatus.

3. General procedures

*General procedure **I** for the synthesis of N,N-substituted tosylamides:*[5]

In a glass flask equipped with a magnetic stirring bar, *N*-tosylamide (1 equiv.), PPh_3 (1.25 equiv.), and dry THF (0.5 mol/dm^3) were added, and cooled to 0 °C. Next, bromoalcohol (1.00 equiv.) and diisopropyl azodicarboxylate (DIAD) (1.25 equiv.) were added. The resulting mixture was stirred for 4 hours at 0 °C and then warmed to room temperature. The solvent was evaporated and the residue was purified by column chromatography (SiO_2, hexane:AcOEt, 0-20%).

*General procedure **II** for the synthesis of disubstituted malonates:*[6]

In a glass flask equipped with a magnetic stirring bar, NaH (1.15 equiv.) and THF (1.2 mL) were added under Ar atmosphere, and cooled to 0 °C. Next, a solution of 2-(prop-2-yn-1-yl) malonate (1.06 mmol, 1.0 equiv.) in THF solution (1.2 mL) was added dropwise and then stirred. After 20 minutes, 1,2-dibromoethane (280 µl, 3.0 equiv.) was added and the reaction was stirred for 12 hours under reflux. The mixture was then extracted with AcOEt – the organic phases were combined and the solvent was evaporated. The residue was purified by column chromatography (SiO_2, hexane:AcOEt, 0-20%).

*General procedure **III** for the intramolecular cyclization:*

In a glovebox under Ar atmosphere, a 10 mL glass vial equipped with a cross-shaped stirring bar was charged with vitamin B_{12} (**1**, 1.7 mg, 0.5 mol%), non-activated MIL-15-NH_2(Ti) (10 mg, 2.5 mol%), vacuum dried ammonium chloride (7.0 mg, 0.5 equiv.), and *N*-tosylamide (**2a-e**, 0.25 mmol) or 4,4'-DDT (9.0 mg, 0.025 mmol). Next, dry EtOH (c = 0.125 mol/dm^3, 2 mL) was added and and the vial was sealed with a rubber-aluminum cap. The reaction mixture was sonicated for one minute to dissolve all reagents and disperse the MOF, then DIPEA (88 µl, 2.0 equiv.) was added. The resulting mixture was placed in a photoreactor for 2 hours on 100% power output. Over that time, the color of the reaction mixture changed from red to dark green indicating the end of reaction. The content was transferred to the 2 mL Eppendorf vial and centrifuged at 13.000 RPM for 1 minute. The supernatant was transferred to a glass flask and the residue was dispersed in fresh EtOH and centrifuged again. This operation was repeated one more time, solutions were combined and evaporated. The residue was purified by column chromatography (SiO_2, hexane:AcOEt, 0-10%).

[5] H. Tsuji, K. Yamagata, Y. Itoh, K. Endo, M. Nakamura, E. Nakamura, *Angew. Chem. Int. Ed.* 2007, **46**, 8060 –8062.
[6] M. E. Krafft, K. A. Seibert, T. F. N. Haxell, C. Hirosawa*, Chem. Commun*. 2005, **46**, 5772–5774

4. Mechanistic studies

4.1. Background reactions[a]

No	*Deviation from reaction conditions*	*Yield of 3a [%]*
1	no B_{12}	0
2	no MIL-125-NH_2	0
3	no DIPEA	0
4	no NH_4Cl	49
5	no Ar	traces
6	no light	0
7	60 °C instead of light	0
8[b]	$[Ti(Cp)_2]Cl_2$ instead of MIL-125-NH_2	traces
9[c]	TiO_2 (nanopowder) and UV irradiation	traces

[a] Reaction conditions: *N*-(2-bromoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2a**, 79 mg, 0.25 mmol), B_{12} (**1**, 1.7 mg, 0.5 mol%), MIL-125-NH_2(Ti) (10 mg, 2.5 mol%), NH_4Cl (53 mg, 4 equiv.), DIPEA (175 µl, 4 equiv.), *i*PrOH (*c* = 0.125 M, 2 mL), Ar, 18 h, 7 W 446 nm LED. Temperature of the reaction vessel measured with IR remote thermometer immediately after pulling out of photoreactor: 44.3 °C

[b] Reaction conditions: *N*-(2-bromoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2a**, 79 mg, 0.25 mmol), B_{12} (**1**, 1.7 mg, 0.5 mol%), $[Ti(Cp)_2]Cl_2$ (2 mg, 2.5 mol%), NH_4Cl (7 mg, 0.5 equiv.), DIPEA (88 µl, 4 equiv.), EtOH (*c* = 0.125 M, 2 mL), Ar, 2 h, 450 nm LED 100% output (variant A) and 525 nm LED 100% output (variant B).

[c] Reaction conditions: *N*-(2-bromoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2a**, 79 mg, 0.25 mmol), B_{12} (**1**, 1.7 mg, 0.5 mol%), TiO_2 (4 mg, 20 mol%), NH_4Cl (7 mg, 0.5 equiv.), DIPEA (88 µl, 4 equiv.), EtOH (*c* = 0.125 M, 2 mL), Ar, 2 h, 254 nm fluorescent lamp irradiation.

4.2. UV-Vis spectra of cob(III)alamin, cob(II)alamin and cob(I)alamin

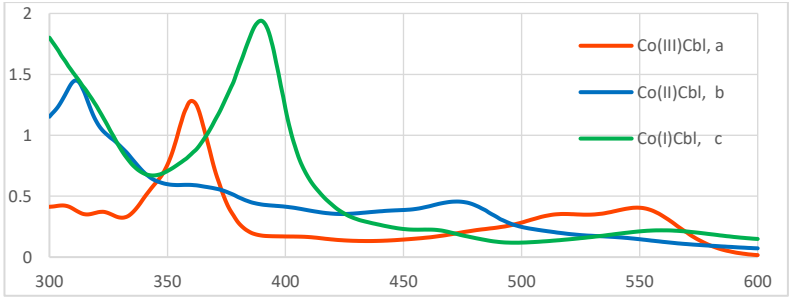


Figure S2 UV-Vis spectra of cobalamin with cobalt in different oxidation states; cob(III)alamin (orange), cob(II)alamin (blue), and cob(I)alamin (green). Experiment setup: **a** vitamin B_{12} (1.7 mg), DIPEA (88 µl), EtOH (2 mL), Ar, 450 nm LED irradiation for 15 min; **b** vitamin B_{12} (1.7 mg), MIL-125-NH_2(Ti) (10 mg), EtOH (2 mL), Ar, 450 nm LED irradiation for 15 min; **c** vitamin B_{12} (1.7 mg), MIL-125-NH_2(Ti) (10 mg), DIPEA (88 µl), EtOH (2 mL), Ar, 450 nm LED irradiation for 15 min.

4.3. UV-Vis spectrum of sequentially reduced cobalamin

We assumed that the Ti(III) form of MIL-125-NH_2(Ti), is involved in the reduction of cob(III)alamin to its Co(I) form. To test this hypothesis (Figure S5), MIL-125-NH_2(Ti) (10 mg) was suspended under Ar atmosphere in a mixture of DIPEA (0.5 mmol, 9.3 mg) and EtOH (2 mL) (vial **I**) and was irradiated for 15 min while stirring. The resulting mixture changed color from yellow to blue suggesting formation of Ti(III) form (vial **II**). The **blue MOF** was filtered off on a PTFE syringe filter and washed with EtOH in a glovebox.

In a separate step, MIL-125-NH_2(Ti) (10 mg) and B_{12} (**1**, 1.7 mg), were suspended in EtOH (2 mL) under Ar atmosphere (vial **III**). Then, the vial was irradiated with 450 nm LED and transferred to a glovebox and the mixture was filtered through a PTFE syringe filter resulting in the **cob(II)alamin solution** (vial **IV**).

The solution was passed through the **blue MOF** from first step and UV-Vis spectrum of the resulting mixture was measured (vial **V**). The majority of B_{12} was reduced to cob(I)alamin (Figure **S4**).

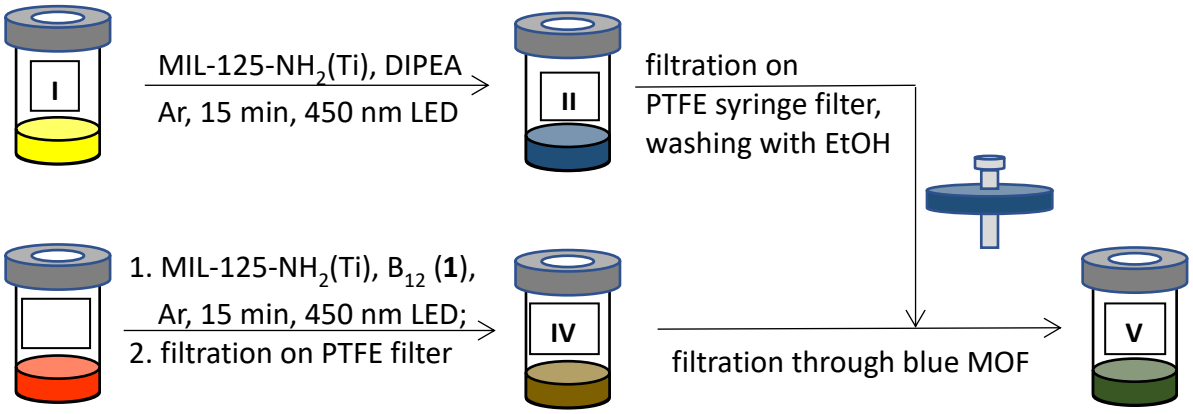


Figure S3 Procedure for sequential reduction of cob(III)alamin to cob(I)alamin.

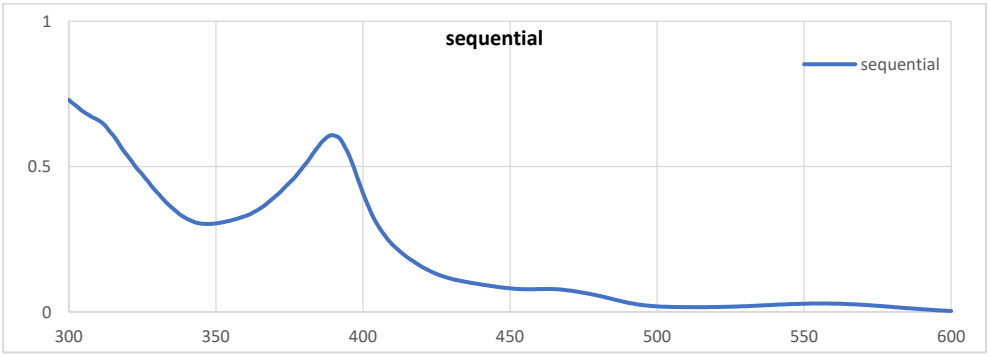


Figure S4 UV-vis spectra of sequentially reduced cobalamin.

4.4. Low-Resolution MS of intermediate alkyl-cobalt complex formed from bromide 2a and HME

The presence of alkylcobalamin intermediates **2a**-**1** were confined using heptamethyl cobyrinate as a model Co-catalyst.

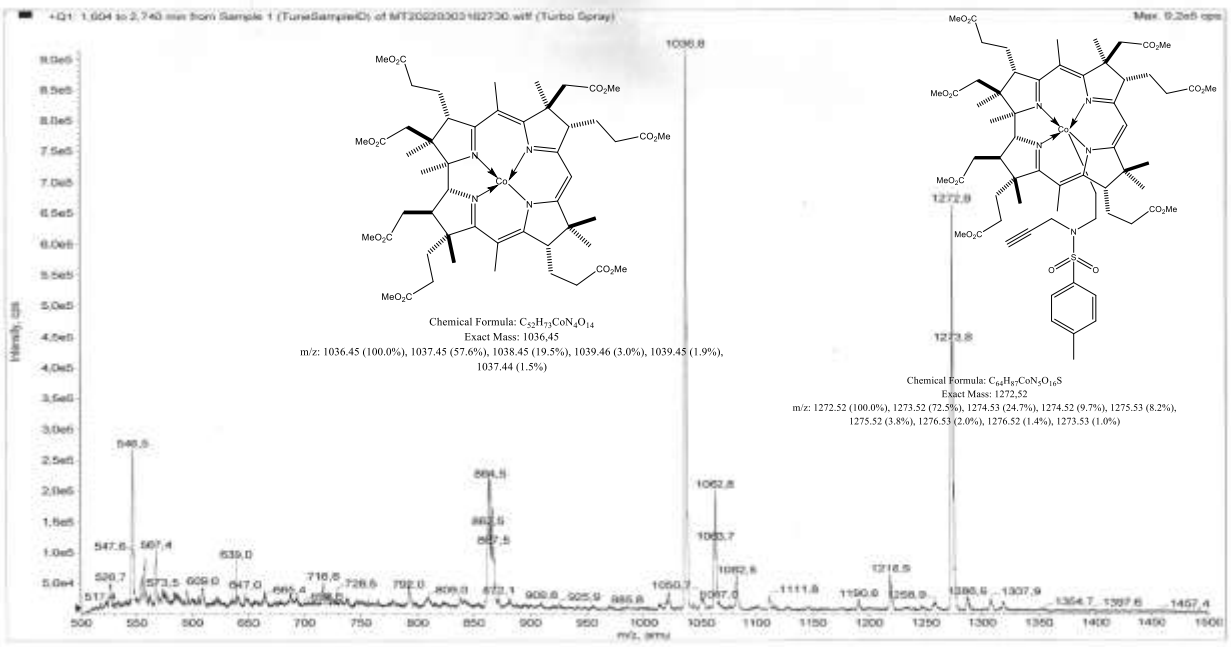
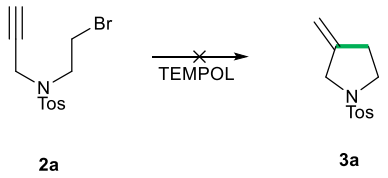


Figure S5 MS analysis of alkyl complexes.

4.5. Experiments with TEMPOL

To corroborate the radical nature of the developed reaction, an experiment with the radical trap was performed. We performed the model reaction with the addition of 2 equivalents of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPOL). The reaction mixture did not change color after that time and the reaction was halted completely.



2a **3a**

Figure S7 Reaction in a presence of TEMPOL. Reaction conditions: *N*-(2-bromoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2a**, 79 mg, 0.25 mmol), vitamin B_{12} (**1**, 1.7 mg, 0.5 mol%), MIL-125-NH_2(Ti) (10 mg, 2.5 mol%), NH_4Cl (7 mg, 0.5 equiv.), DIPEA (88 µl, 2.0 equiv.), TEMPOL (86 mg, 2 equiv.), 99.8% Ar-purged EtOH (*c* = 0.125 M, 2 mL), Ar, 2 h, 100% power output 450 nm LEDs.

Procedure : In a glovebox under Ar atmosphere, a 10 mL glass vial equipped with a cross-shaped stirring bar was charged with vitamin B_{12} (**1**, 1.7 mg, 0.5 mol%), non-activated MIL-15-NH_2(Ti) (10 mg, 2.5 mol%), vacuum dried ammonium chloride (7.0 mg, 0.5 equiv.), *N*-tosylamide (**2a-e**, 0.25 mmol), TEMPOL (86 mg, 2 equiv) or *E*-stilbene (45 mg, 1 equiv.). Next, dry EtOH (*c* = 0.125 mol/dm^3, 2 mL) was added and and the vial was sealed with a rubber-aluminum cap. The reaction mixture was sonicated

for one minute to dissolve all reagents and disperse the MOF, then DIPEA (88 µl, 2.0 equiv.) was added. The resulting mixture was placed in a photoreactor for 2 hours on 100% power output. Over that time, the color of the reaction mixture changed from red to dark green indicating the end of reaction. The content was transferred to the 2 mL Eppendorf vial and centrifuged at 13.000 RPM for 1 minute. From the supernatant a sample was taken and measured on GC apparatus.

4.6. Deuterated experiments ^{1}H NMR spectra

To explain the role of NH_4Cl we conducted experiments in deuterated ethanol (C_2D_5OD). Incorporation of deuterium in the product was estimated based on ^{1}H NMR. Diminished integration of the signal at 4.90 ppm suggests anion formation and protonation mechanism.

Reaction in C_2D_5OD

To eliminate the exchange problem, we used C_2D_5OD and NH_4Cl.

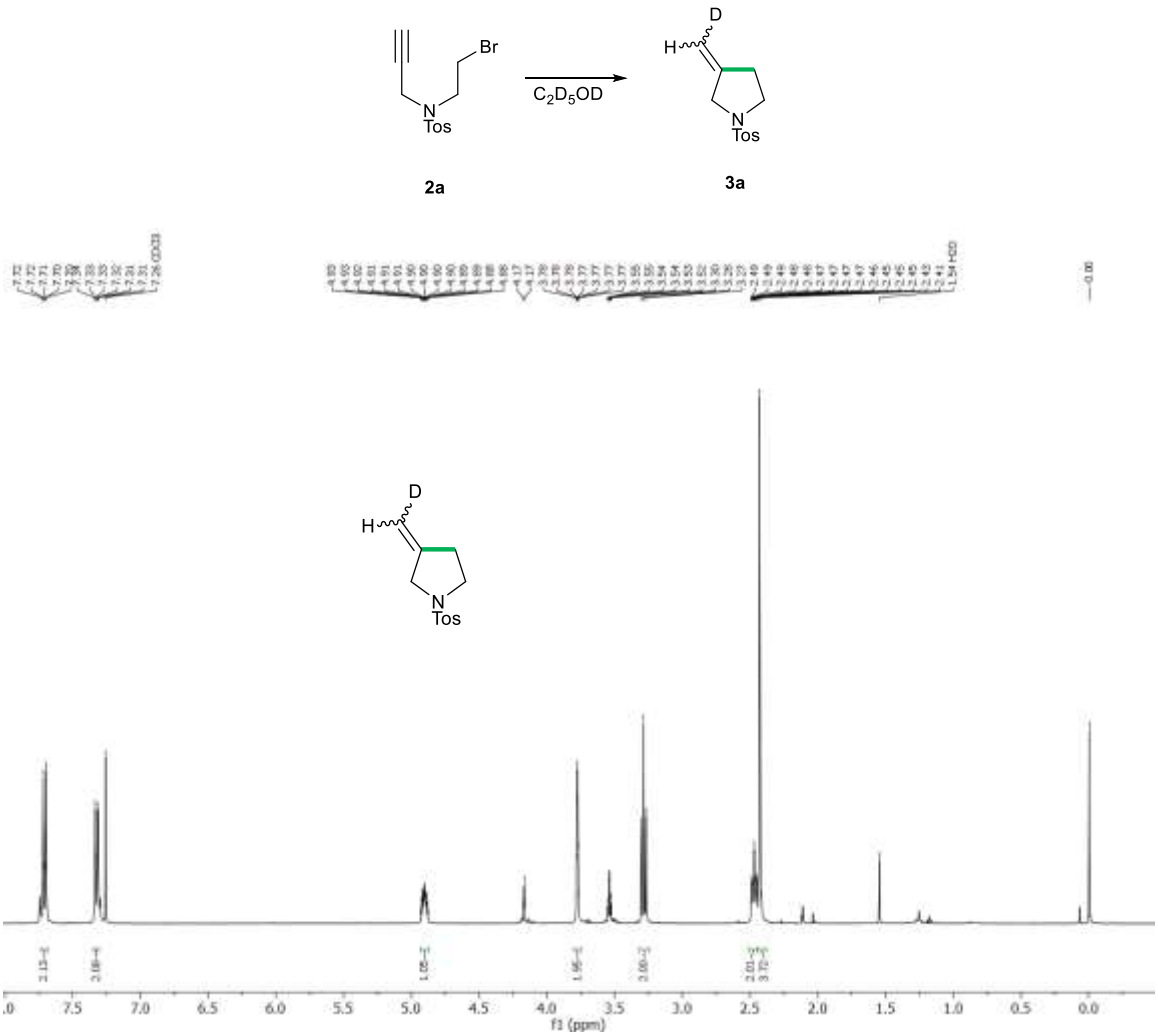


Figure S9 ^{1}H NMR spectrum after using deuterated solvent.

The deuterated product **3a** was isolated in 77% yield (46 mg after 6 hours). We observe 95% incorporation of deuterium in the molecule (Figure S6). Given NH_4Cl plays a role in formation of the product, we assume that this result can be explained by C_2D_5OD contribution to the mechanism by rapid exchange of H/D between NH_4Cl and the solvent.

4.7. Cyclic voltammetry measurements

We conducted several cyclic voltammetry measurements, using tetrabutylammonium hexafluorophosphate as electrolyte, in 99.8% ethanol with the absence of light and with irradiation with blue light. A cylindrical three-electrode cell was equipped with a glassy carbon working electrode, a 25 mm platinum wire as the counter electrode and Ag/AgCl (3.0 M NaCl) electrode as the reference electrode. The scan rate for a typical experiment was 100 $mV \cdot s^{-1}$.

We observe that addition of MIL-125-NH_2 shifts the reduction peak of B_{12} to more negative values, but no significant influence of light was observed, probably due to poor mixing.

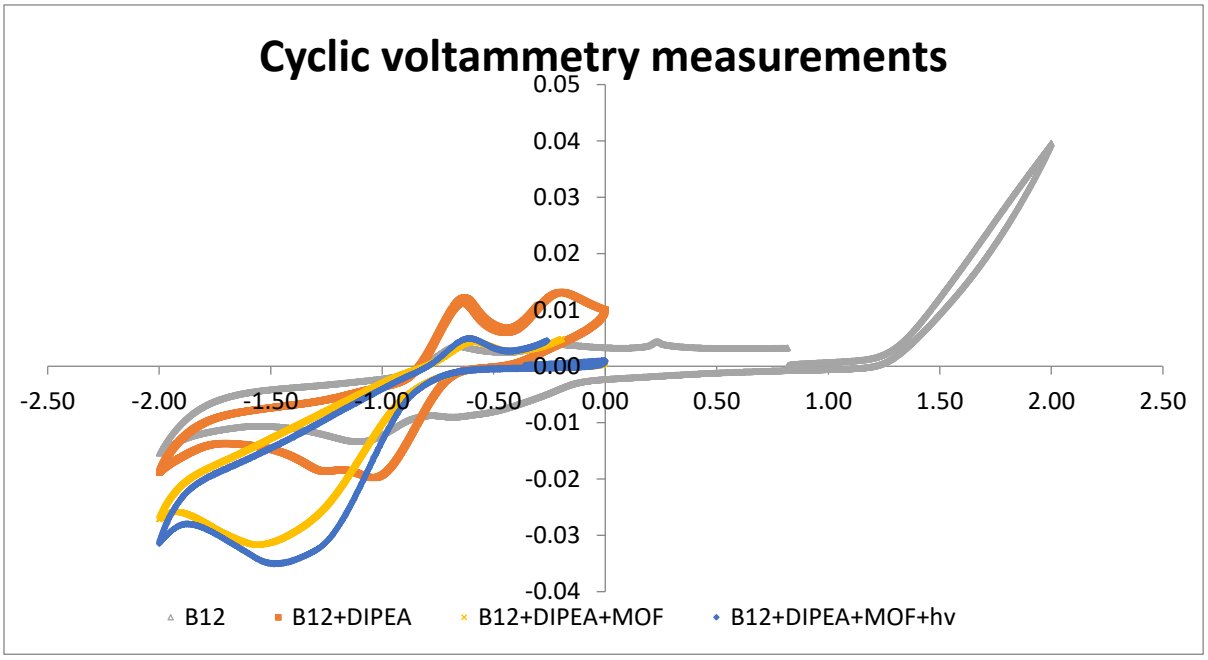


Figure S12 Cyclic voltammetry experiments results. for 3-methylcyclopentanol – database comparison. Conditions: 99.8% ethanol, 60 mg Bu_4NPF_6, 10.8 mg B_{12}, + 88 µl DIPEA, + 10.8 mg MIL-125-NH_2, + h*v*.

5. 4,4'-DDT dehalogenation reaction[a]

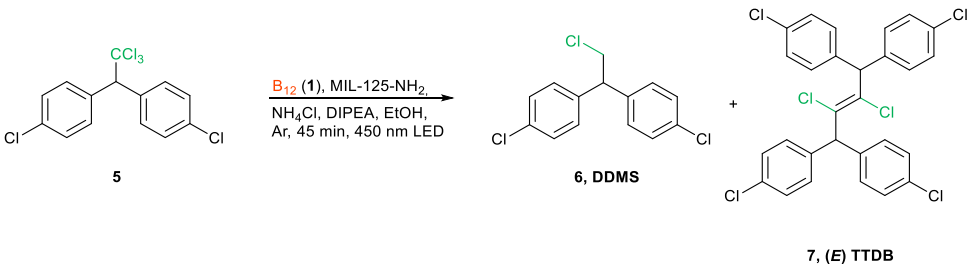


Figure S13 4,4'-DDT dehalogenation identified products.

Following *General Procedure* ***III*** for 4,4'-DDT, in the ^{1}H NMR spectrum of crude reaction mixture we identified three dehalogenation products. Products **6 : 7 : 8** ratio is 1 : 0.78 : 2.05. Products **6** and **7** have been already reported in dehalogenation of DDT.[7,8] Based on the available data we were not in a position to decipher the structure of the third product. MS EIHR data 492.0006, $C_{28}H_{16}Cl_4$. HSQC and HMBC show only a single correlation with a carbon signal in "alkene region" of the spectrum.

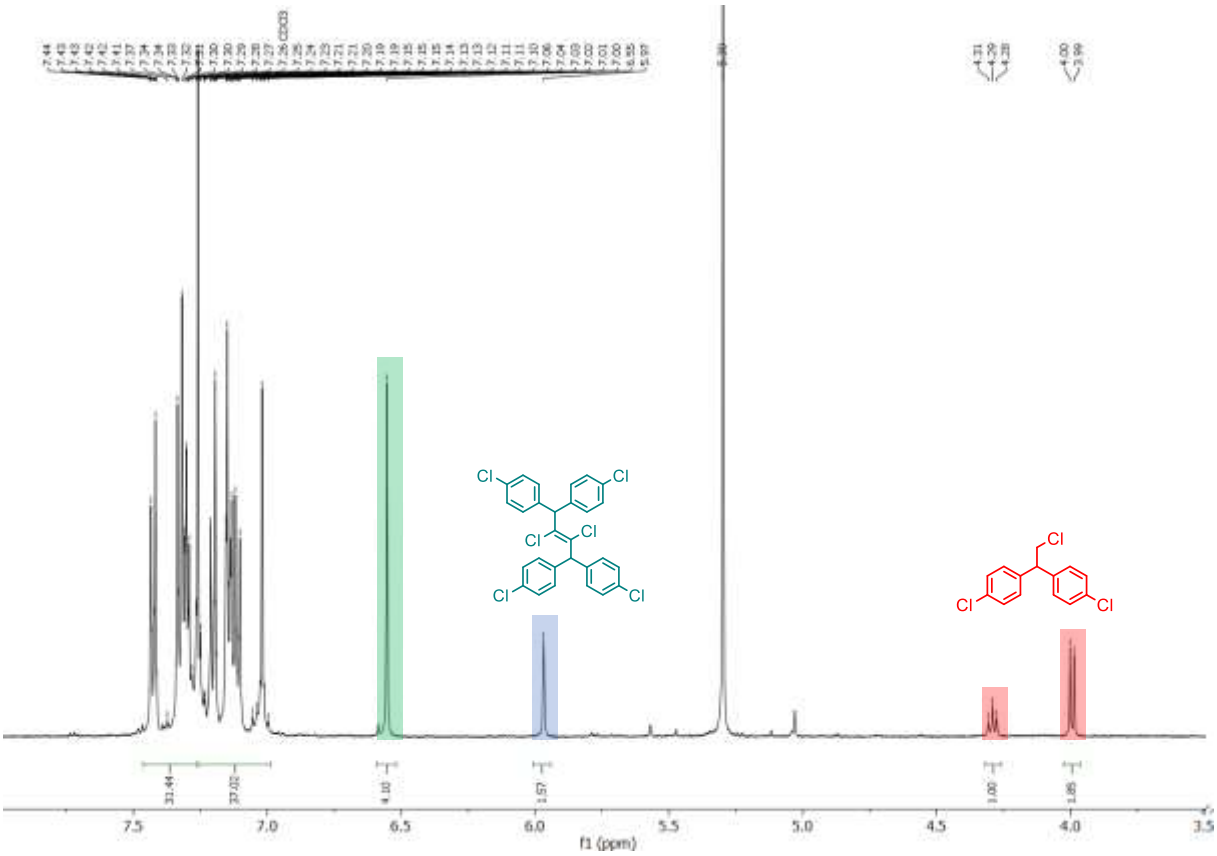


Figure S14 ^{1}H NMR of the crude reaction mixture obtained after short plug in $CHCl_3$.

[7] G. Zhang, R.-X. Bai, C.-H. Li, C.-G. Feng, G.-Q. Lin, *Tetrahedron* 2019, **75**, 1658 – 1662.
[8] H. Shimakoshi, E. Sakumori, K. Kaneko, Y. Hisaeda, *Chemistry Lett.* 2009, **38**, 468 – 469.

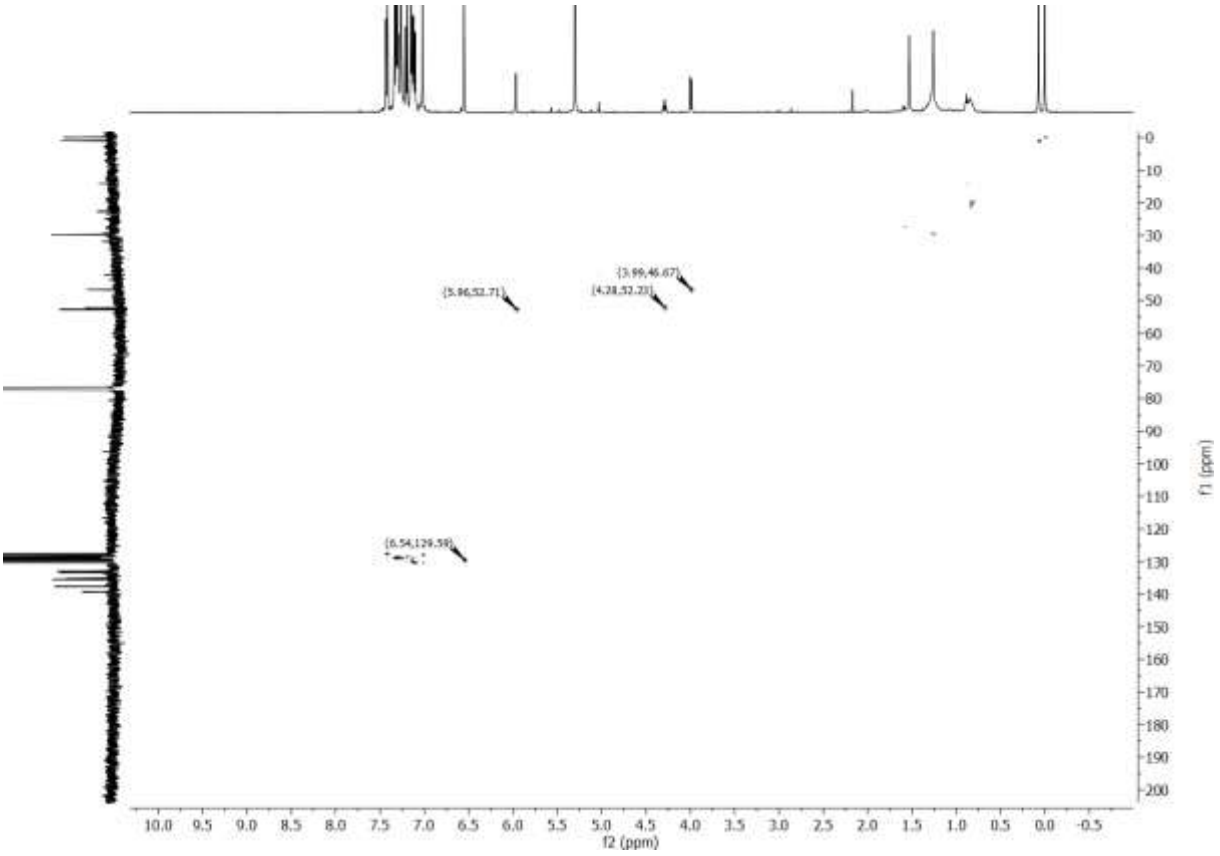


Figure S15 HSQC NMR of the crude reaction mixture obtained after short plug in $CHCl_3$.

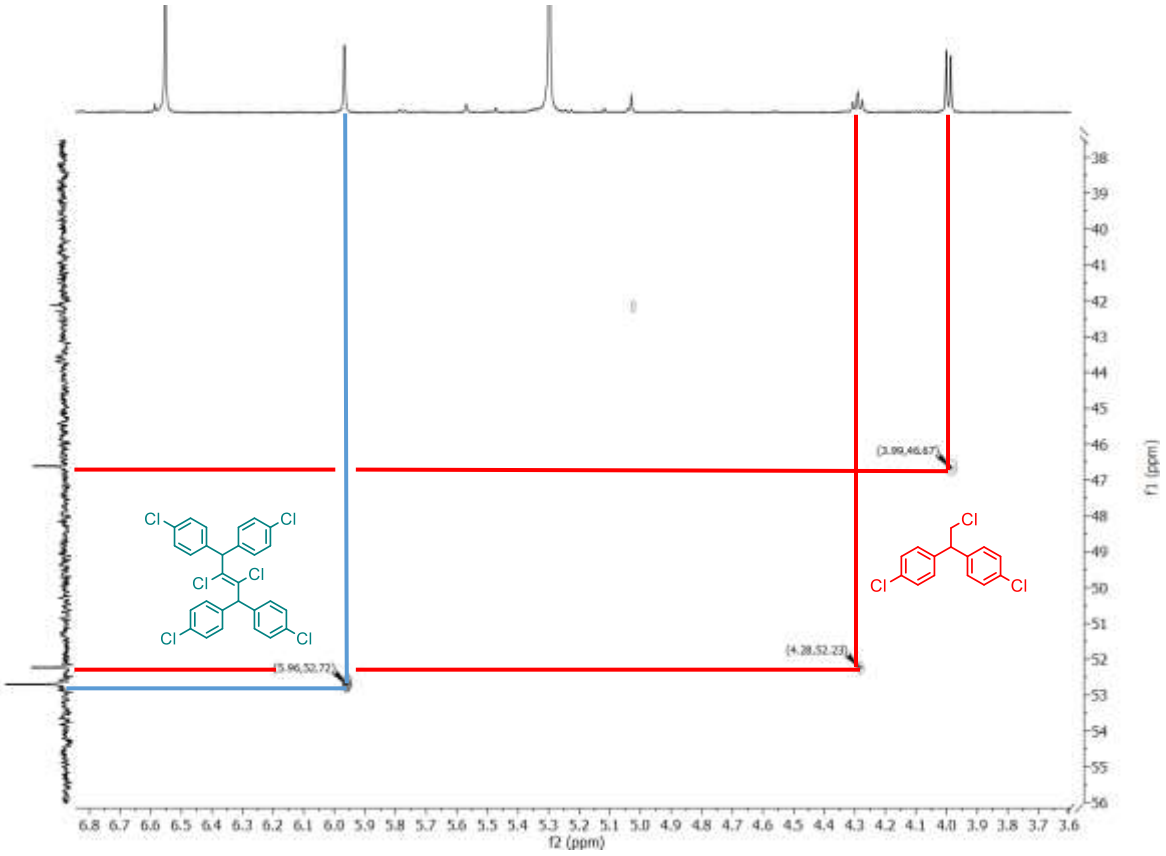


Figure S16 HSQC NMR magnified region for compounds **6** and **7**.

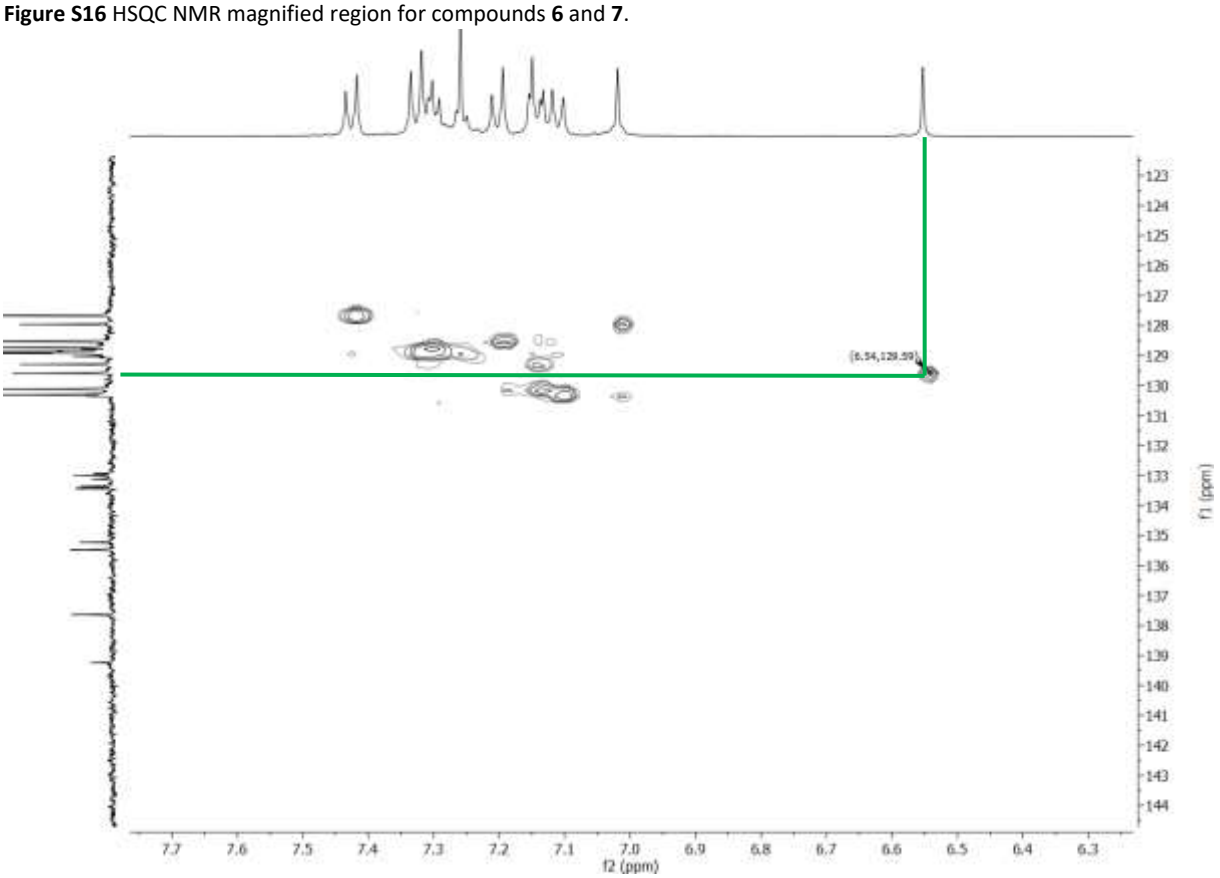


Figure S17 HSQC NMR magnified region for compound **8**.

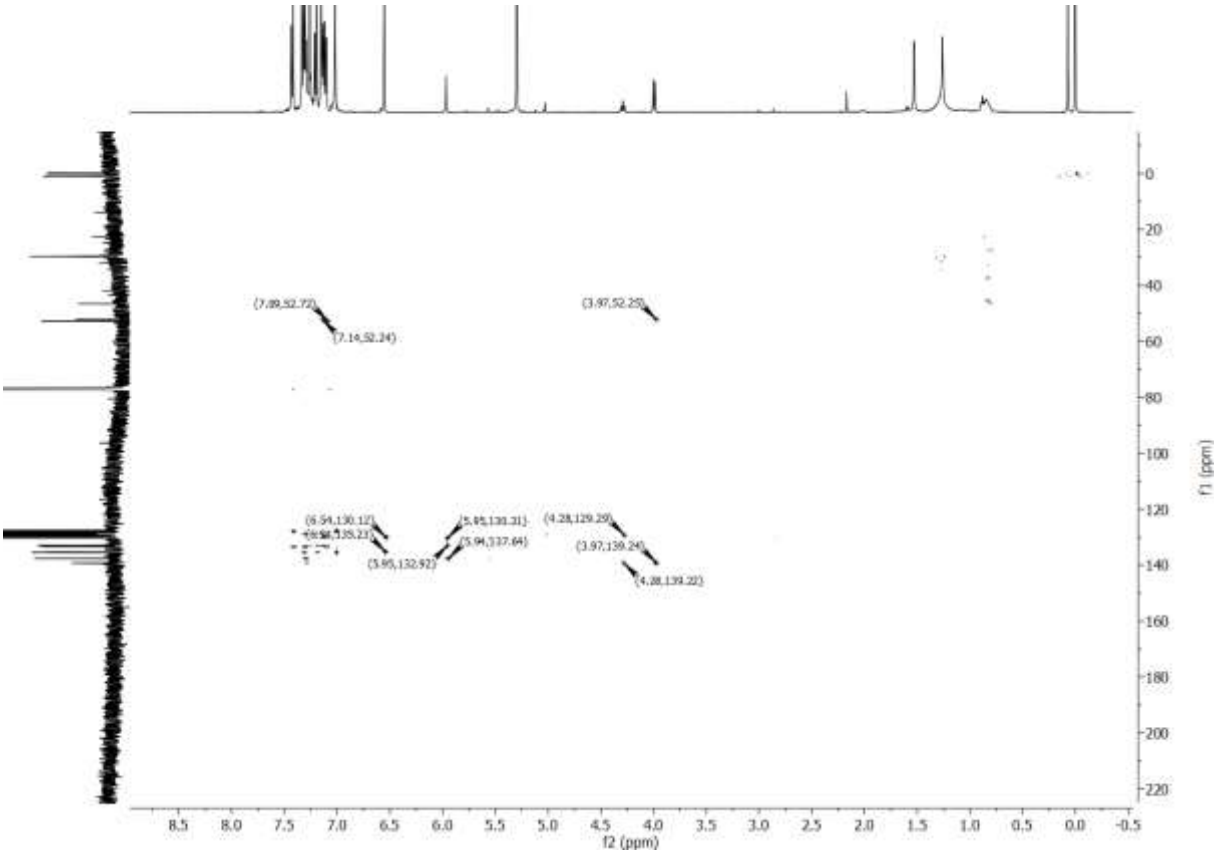


Figure S18 HMBC NMR of the crude reaction mixture obtained after short plug in $CHCl_3$.

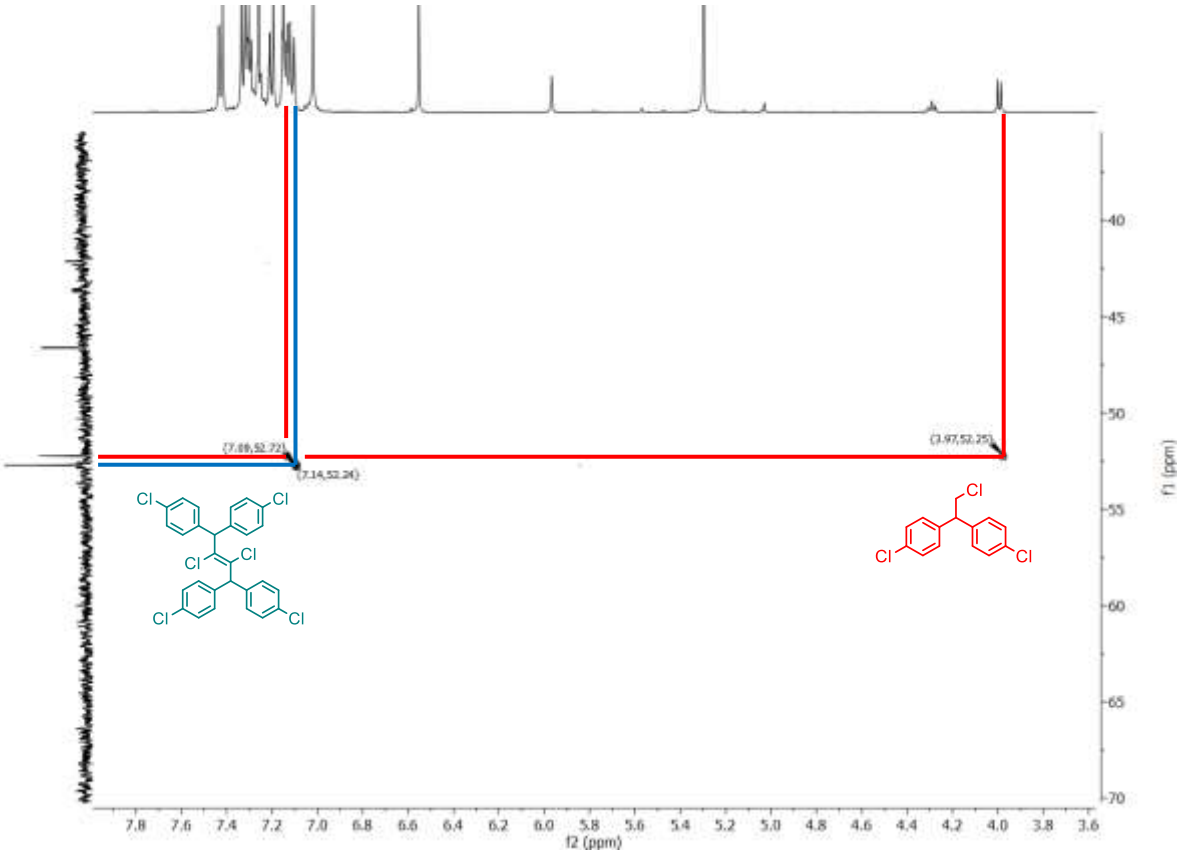


Figure S19 HMBC NMR magnified region for compounds **6** and **7**.

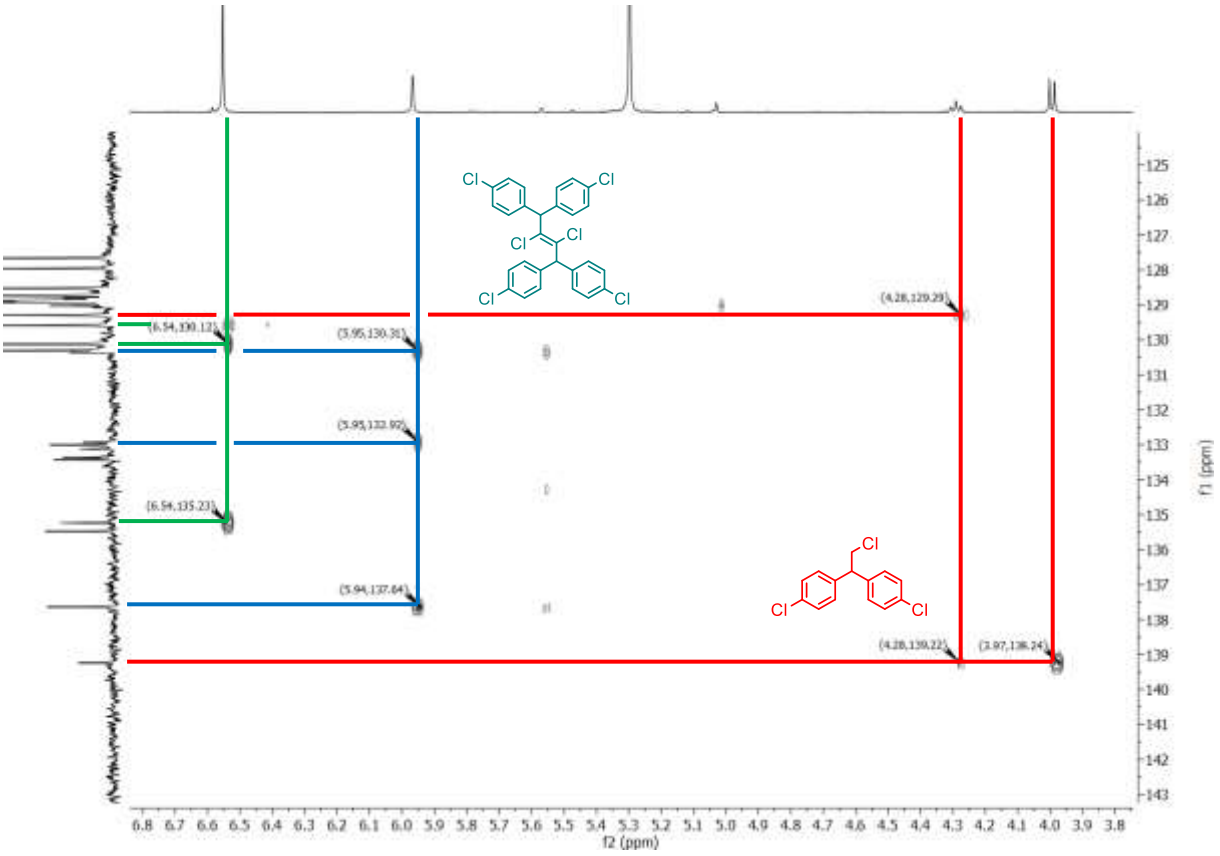


Figure S20 HMBC NMR magnified region for compounds **6**, **7** and **8**.

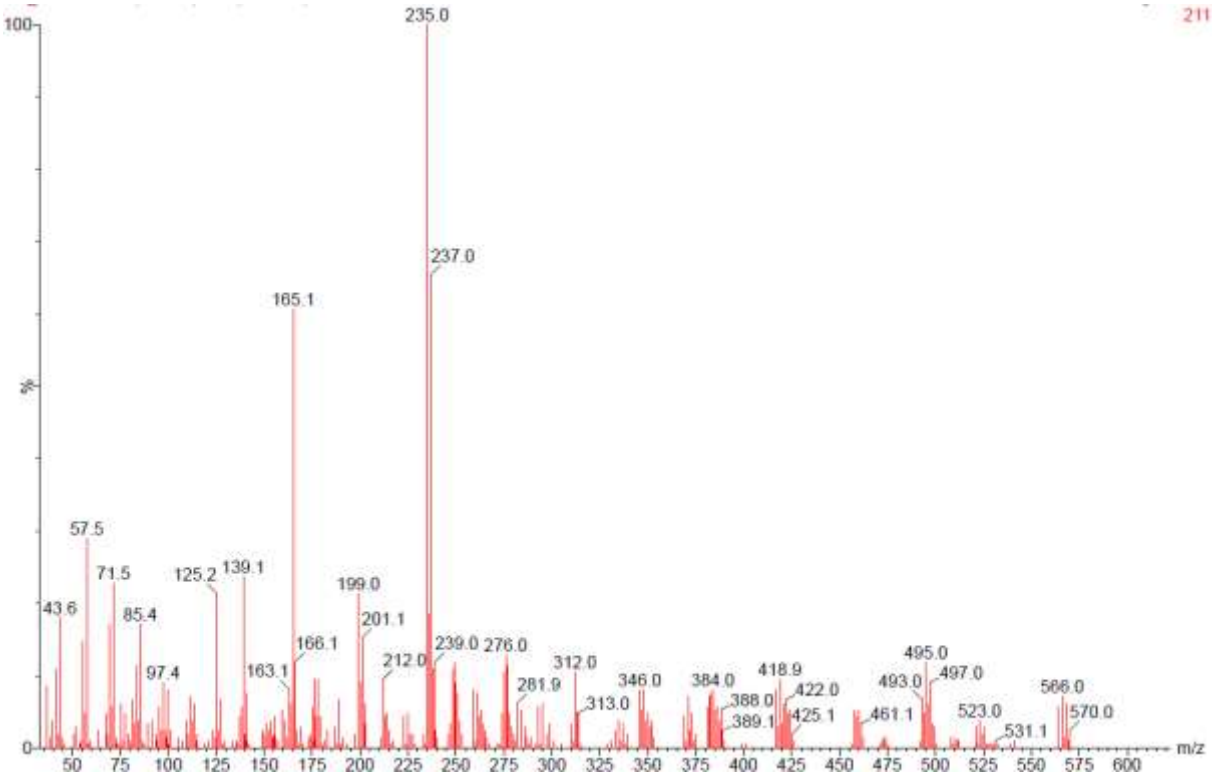
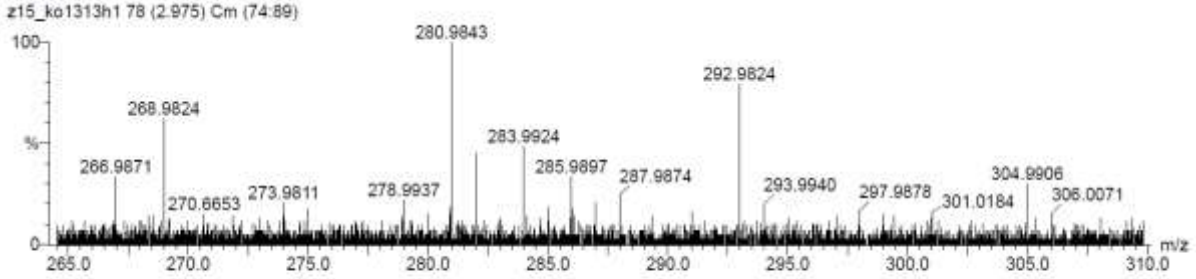


Figure S21 EI-MS for the crude reaction mixture

Single Mass Analysis
Tolerance = 50.0 PPM / DBE: min = -1.5, max = 150.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
19 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-200 Cl: 0-5

K. Orlowska AUTOSPEC
KDW0574-15
z15_ko1313h1 78 (2.975) Cm (74:89)



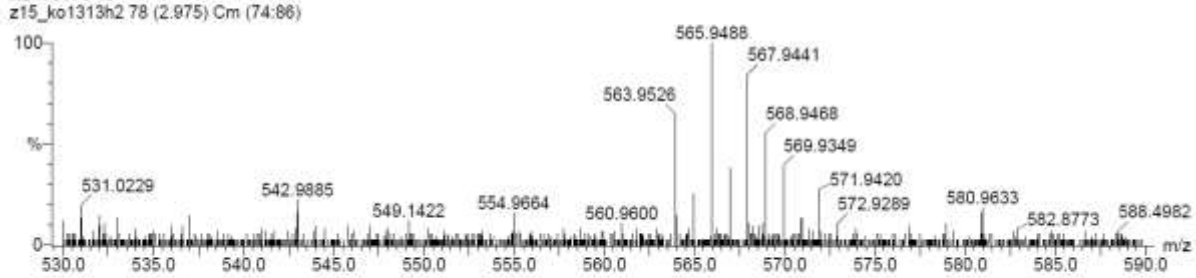
Minimum:				-1.5		
Maximum:		5.0	50.0	150.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
283.9924	283.9926	-0.2	-0.7	6.0	4.4	C14 H11 C13

Figure S22HR EI-MS for DDMS (**6**).

Single Mass Analysis
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 150.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
16 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-200 Cl: 4-6

K. Orlowska AUTOSPEC
KDW0574-15
z15_ko1313h2 78 (2.975) Cm (74:86)



Minimum:				-1.5		
Maximum:		5.0	20.0	150.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
563.9526	563.9540	-1.4	-2.5	17.0	1.6	C28 H18 C16

Figure S23 HR EI-MS for TTDB (**7**).

KDW0574-15

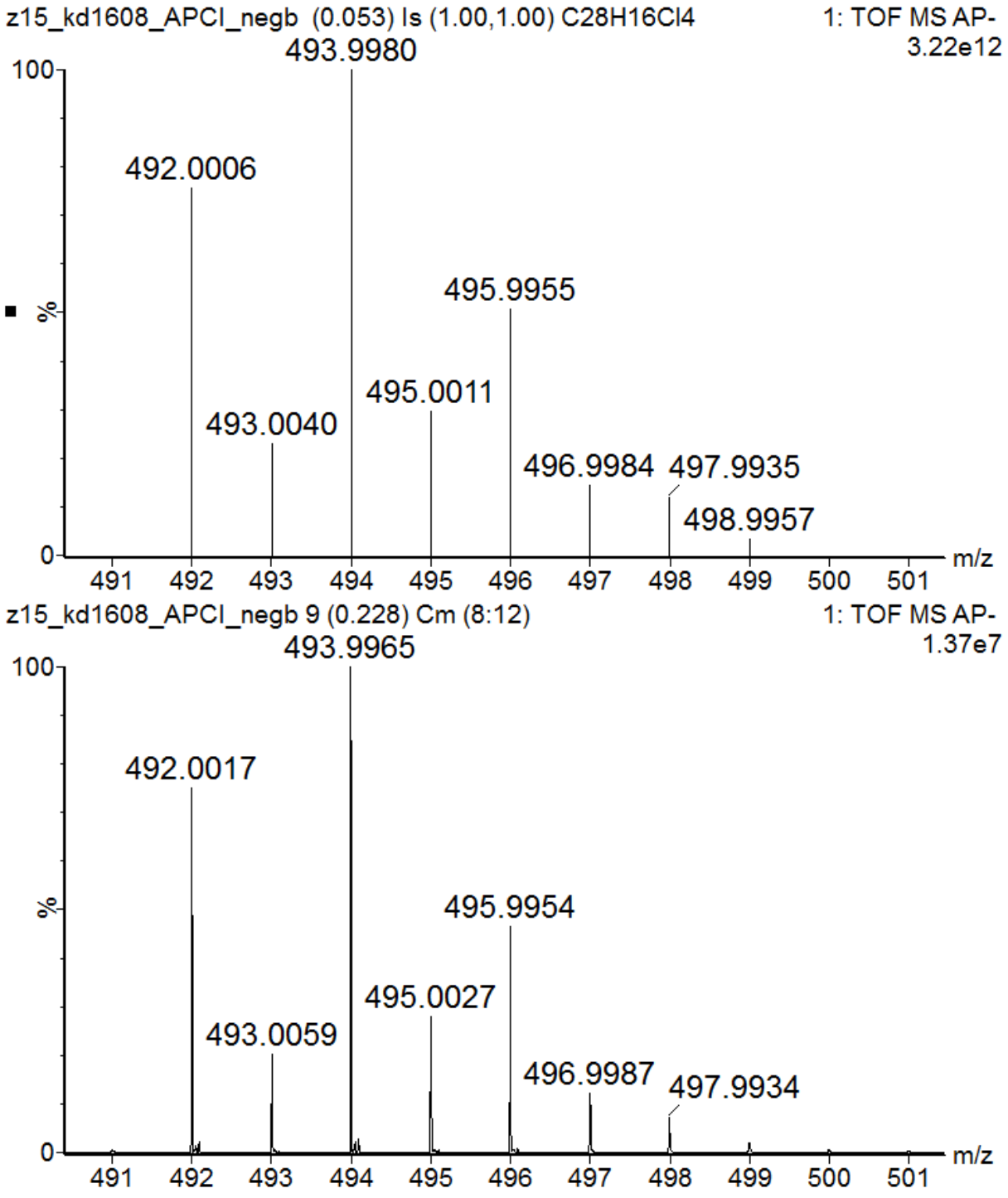


Figure S24 APCI-MS of unknown dehalogenation product

6. Synthesis and characterisation of MOFs

MIL-125-NH_2(Ti)

MIL-125-NH_2(Ti) was synthesized by the hydrothermal method, according to the literature procedure.[9] 2-Aminoterephthalic acid (2.86 g, 15.8 mmol) was dissolved in a mixture of dry DMF (40 mL) and dry methanol (10 mL) at room temperature. Next, titanium isopropoxide (2.86 mL, 9.7 mmol) was added and the mixture was transferred into a Teflon liner and inserted in a stainless-steel autoclave. The autoclave was sealed, and the mixture was heated for 72 hours at 110 °C. The obtained yellow solid was filtered and washed with DMF at room temperature. The as-synthesized solid was dispersed in DMF and kept under stirring overnight (50 mL of DMF per 1 g of product) to remove residual linker. Then, the same washing procedure was repeated twice using methanol instead of DMF. Finally, the solid was dried under vacuum at 100°C.

Theoretical composition: $[Ti_8O_8(OH)_4(BDC\text{-}NH_2)_6]$ = 275 g/mol per ligand. Molecular weight per ligand was estimated by ^1H NMR analysis with addition of terephthalic acid as internal standard: MW = 273 g/mol.

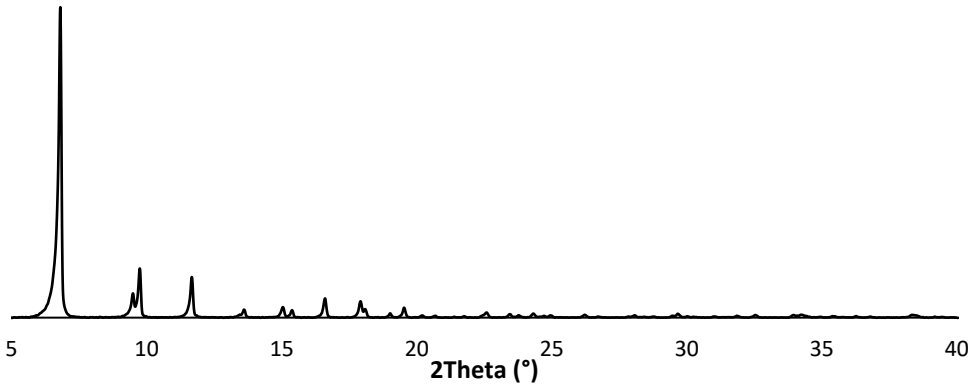


Figure S25 Powder X-ray diffraction pattern (PXRD) of activated MIL-125-NH_2.

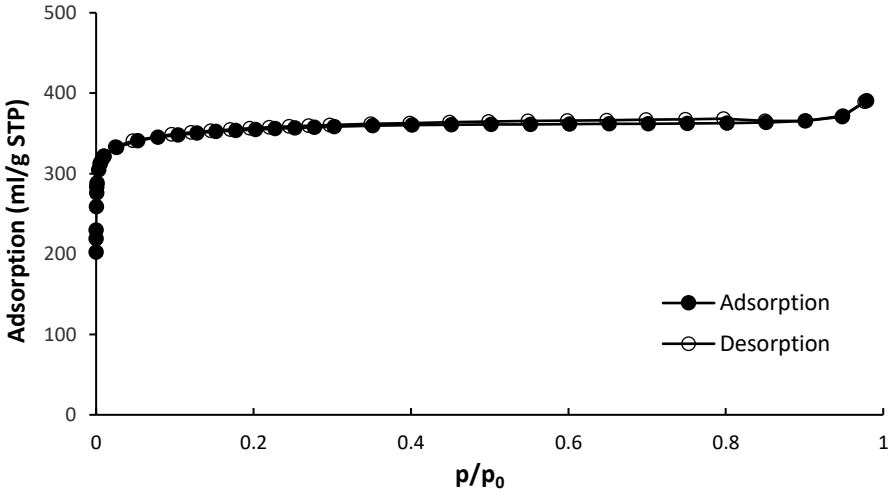


Figure S26 N_2 isotherm of activated (Ti)MIL-125-NH_2 measured at 77 K. S_{BET} = 1412 m^2/g.

[9] M. A. Nasalevich, R. Becker, E. V. Ramos-Fernandez, S. Castellanos, S. L. Veber, M. V. Fedin, F. Kapteijn, J. N. H. Reek, J. I. van der Vlugt, J. Gascon, *Energy Environ. Sci.* 2015, **8**, 364–375.

MIL-101-NH_2(Al)

MIL-101-NH_2(Al) was synthesized according to a modified procedure[10] by Gascon and co-workers.[11] Aluminium trichloride hexahydrate (1.53 g, 6.28 mmol) and a magnetic stir bar were placed in a 150 mL Ace Glass pressure tube followed by dry DMF (120 mL), and stirred overnight at room temperature until homogenous solution formed. Next, 2-aminoterephthalic acid (1.68 g, 9.28 mmol) was added, and after its dissolution the magnetic stir bar was removed, and the pressure tube was sealed and placed in a preheated oven at 130°C for 3 days. Over this period a precipitate formed, which was filtered off on a glass frit (G4) under reduced pressure and washed with DMF (40 mL), acetone (50 mL) and methanol (50 mL). The as-synthesised MOF contained *ca.* 18% of formylated amino groups.[12] To convert the formylated amino groups back to the free NH_2 groups, the as-synthesised material was extracted with methanol for 24 h in a Soxhlet apparatus and then heated with methanol at 120°C in a pressure tube overnight. After cooling down, the solid was collected by filtration and activated under vacuum (10 µbar) at 150°C for 24h.

Theoretical composition: $Al_3O(Cl)(H_2O)_2(C_8H_3O_4NH_2)$ = 235 g/mol per ligand. Molecular weight per ligand was estimated by ^{1}H NMR analysis with the addition of terephthalic acid as internal standard: MW = 242 g/mol.

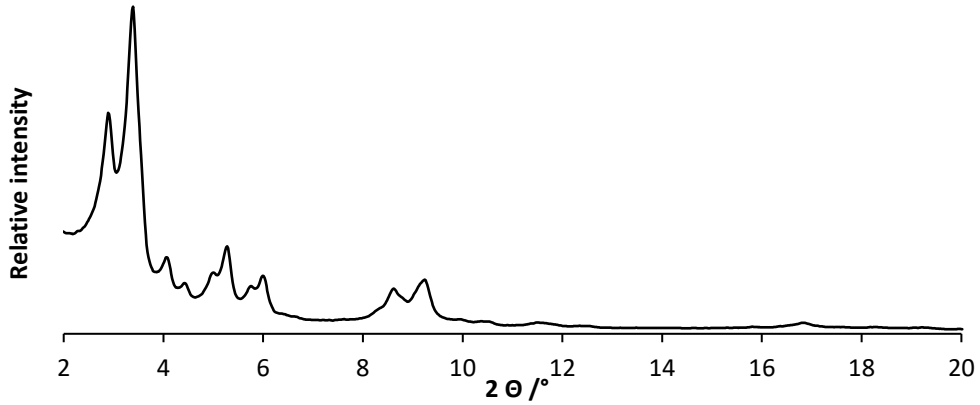


Figure S27 Powder X-ray diffraction pattern (PXRD) of activated (Al)MIL-101-NH_2.

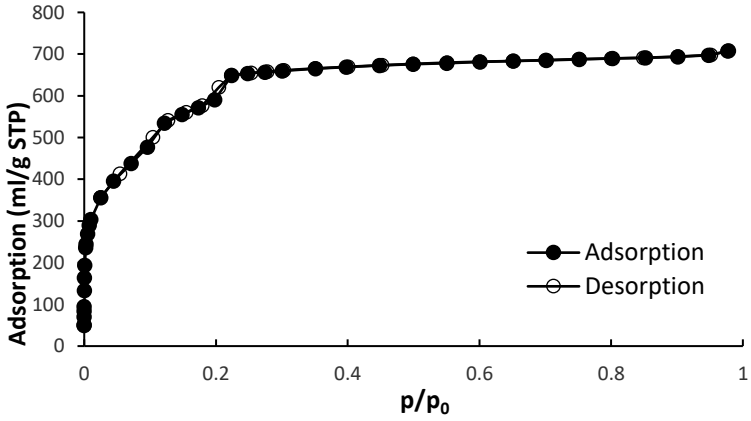


Figure S28 N_2 adsorption isotherm at 77 K of activated (Al)MIL-101-NH_2. S_{BET} = 2190 m^2/g.

[10] A. Chołuj, A. Zieliński, K. Grela and M. J. Chmielewski, *ACS Catal.*, 2016, **6**, 6343–6349.
[11] P. Serra-Crespo, E. V. Ramos-Fernandez, J. Gascon and F. Kapteijn, *Chem. Mater.*, 2011, **23**, 2565–2572.
[12] K. M. Zwoliński, P. Nowak, M. J. Chmielewski, *Chem. Commun.,* 2015, **51**, 10030-10033.

MIL-101-SO_3H/Na(Cr)

MIL-101-SO_3H/Na(Cr) was synthesized by the hydrothermal method, according to the literature procedure.[13] CrO_3 (1.26 g, 12.5 mmol), 2-sulfoterephthalic acid monosodium salt (3.36 g, 12.5 mmol), and concentrated hydrochloric acid (0.9 g, 0.8 mL, 9 mmol) were added into deionized water (50 mL), and stirred for a few minutes at room temperature. The mixture was then transferred to a Teflon-lined stainless-steel autoclave and placed in an oven at 180°C for 6 days. To remove unreacted organic linkers from the pores of the synthesized MOF, a series of purification steps were carried out: first, the solid product was filtered off using a glass filter G4, and washed with water (50 mL) and ethanol (50 mL). Then a solvothermal treatment was performed using ethanol at 80 °C for 24 h. The resulting solid was soaked in 1 M NH_4F solution at 70 °C for 24 h, filtered while hot and washed with hot water. The solid was then dried under vacuum at 150 °C for 12 h.

Theoretical composition: $Cr_3O(H_2O)_2(C_8H_3O_4SO_3)(C_8H_3O_4SO_3H)(C_8H_3O_4SO_3Na)(NH_4Cl)$ = 338.3 g/mol of ligand. Molecular weight per ligand was estimated by ^1H NMR analysis, using terephthalic acid as an internal standard – MW = 395 g/mol.

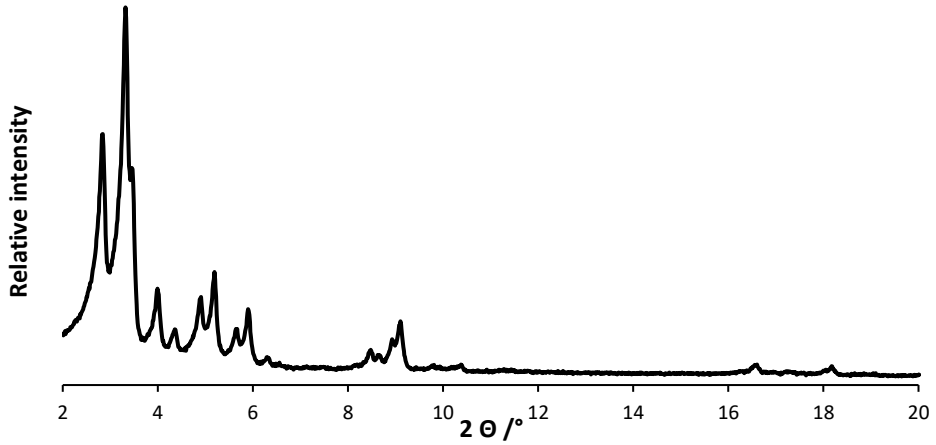


Figure S29 Powder X-ray diffraction pattern (PXRD) of activated (Cr)MIL-101-SO_3H.

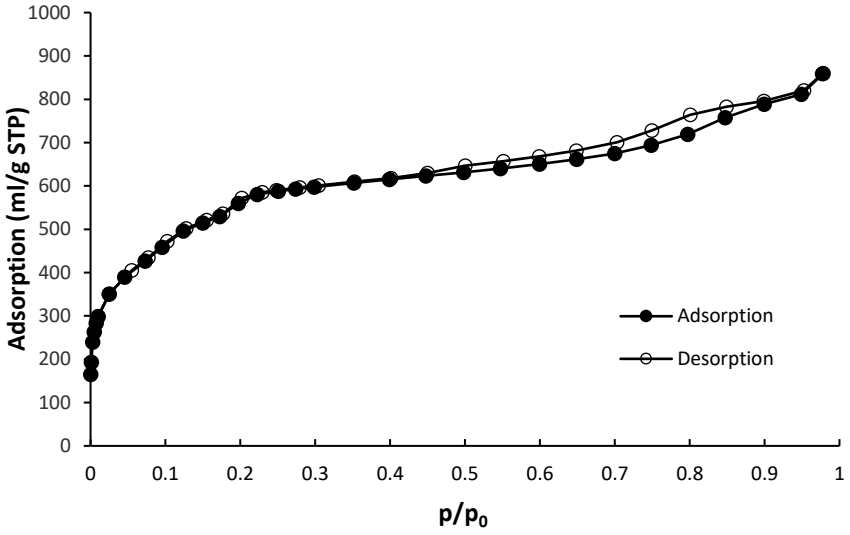


Figure S30 N_2 adsorption isotherm at 77 K of activated (Cr)MIL-101-SO_3H. S_{BET} = 2054 m^2/g

[13] G. Akiyama, R. Matsuda, H. Sato, M. Takata and S. Kitagawa, *Adv. Mater.*, 2011, **23**, 3294–3297.

HKUST-1

HKUST-1 was synthesized by the hydrothermal method, according to the literature procedure.[14] Benzene-1,3,5-tricarboxylic acid (0.491 g, 2.34 mmol) was dissolved in ethanol (3 mL), and cupric nitrate hydrate ($Cu(NO_3)_2 \cdot 3H_2O$; 1.086 g, 4.51 mol) was dissolved into water (3 mL). The two solutions were mixed at ambient temperature for 30 min, and the mixture was transferred into an autoclave. The autoclave was heated at 423 K for 18 h. The reaction vessel was cooled down to ambient temperature, and blue crystals of HKUST-1 were filtrated and washed with water (200 mL). The product was dried at 373 K under vacuum overnight.

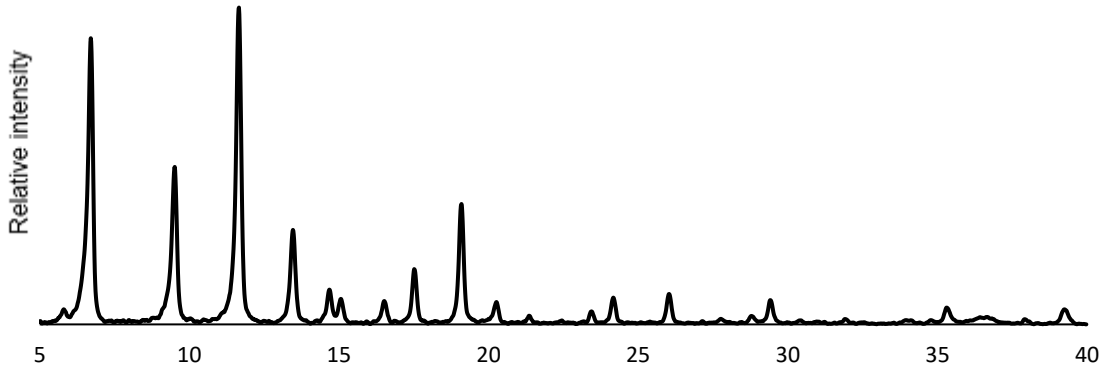


Figure S31 Powder X-ray diffraction pattern (PXRD) of activated HKUST-1.

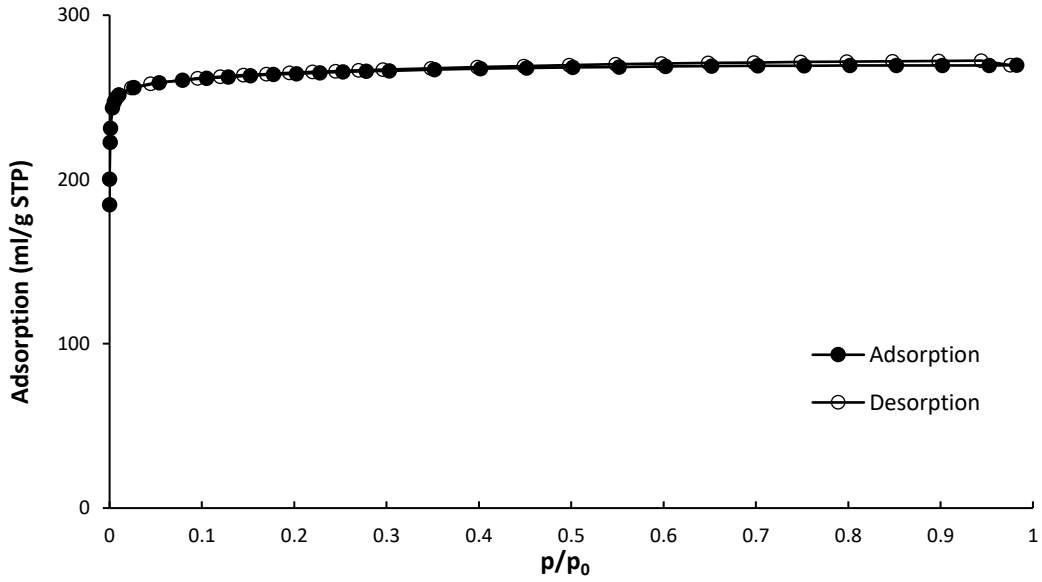


Figure S32 N_2 adsorption isotherm at 77 K of activated HKUST-1. S_{BET} = 1088 m^2/g

[14] Q. Min Wang, D. Shen, M. Bülow, M. Ling Lau, S. Deng, F. R. Fitch, N. O. Lemcoff, J. Semanscin, *Microporous Mesoporous Mater.* **2002**, *55*, 217–230.

UiO-66-NH_2

Partially formylated UiO-66-NH_2 was obtained according to the procedure by Behrens and co-workers,[15] and then deformylated as described by Chmielewski and co-workers.[16]

In a 25 mL scintillation vial, $ZrCl_4$ (0.080 g, 0.343 mmol) was dissolved in DMF (20 mL) by sonication in an ultrasound bath for *ca.* 1 min. 2-Aminoterephthalic acid (0.062 g, 0.343 mmol) was added to the clear solution and sonicated until dissolved. Next, water (0.025 mL, 1.37 mmol, 4 equiv.) was added and the vial was tightly capped and put in an oven at 120°C for 24h (without stirring). After 24 h, the reaction mixture was allowed to cool down to room temperature and the precipitated product was isolated by centrifugation. The solid was suspended in DMF (10 mL) and left at room temperature for 2–6 h. After this time the suspension was centrifuged and the solvent was decanted off.

The as-synthesized UiO-66-NH_2 was immersed in methanol (50 mL) and left at RT overnight. After 24 h the solid was filtered off and dried by heating for 2 h at 120°C in a preheated oven. The resulting microcrystalline powder was deformylated by Soxhlet extraction with hot methanol for 24 h.

The purified material was activated under dynamic vacuum (10^{-3} mbar) at 150°C for 24 h. During the activation the white material turned pale yellow.

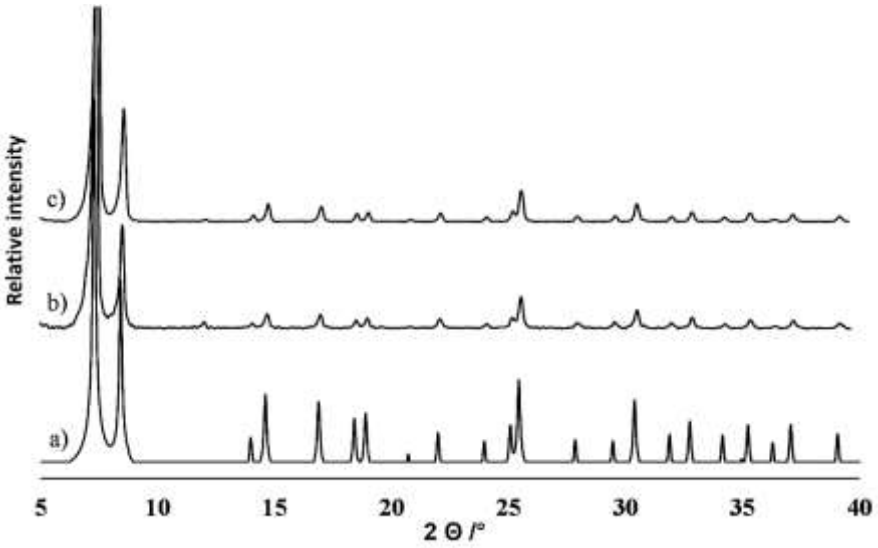


Figure S33. Powder X-ray diffraction patterns (PXRD) for: a) the pristine UiO-66 (simulated), b) pure UiO-66-NH_2 after Soxhlet extraction and drying, c) pure UiO-66-NH_2 after activation (heating to 150°C under 10^{-2} mbar vacuum for 24 h).

[15] A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke and P. Behrens, *Chem. Eur. J.*, 2011, **17**, 6643- 6651.
[16] K. M. Zwoliński, P. Nowak, M. J. Chmielewski, *Chem. Commun.,* 2015, **51**, 10030-10033.

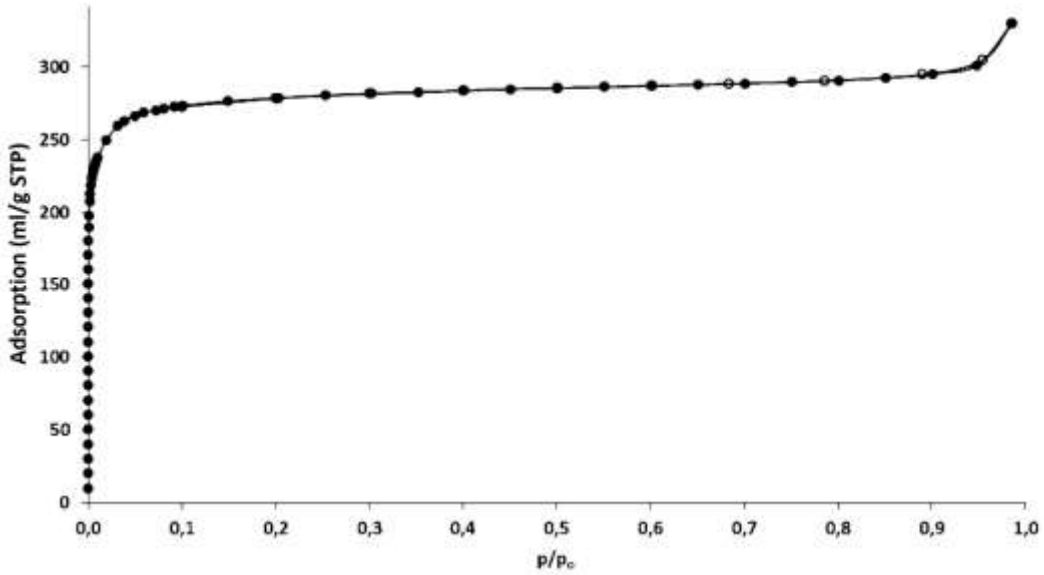


Figure S34. N_2 adsorption isotherm at 77 K of activated UiO-66-NH_2. S_{BET} = 1122 m^2/g (adsorption points denoted by blue and desorption by red circles).

MUV-11

MUV-11 was obtained according to the procedure by Martí-Gastaldo and co-workers.[17]

In a 100 mL AceGlass pressure vial, benzenedihydroxamic acid (H_4bdha, 330 mg, 1.68 mmol) was dissolved in DMF (50 mL) by sonication and gentle heating. Next, acetic acid (10 mL) was added, followed by titanium(IV) (triethanolaminato)isopropoxide solution (TTTEI, 80% in IPA, 0.0975 mL, 0.106 g, 0.336 mmol). Orange precipitate formed. The vial was tightly sealed with Teflon cap and put in a laboratory oven at 120°C for 48 h. After cooling down to room temperature, this results in the formation of orange crystals that were isolated by filtration and rinsed with DMF (3x 15 mL), and acetone (3 x 15 mL). The product was dried at room temperature to yield MUV-11 as orange hexagonal microcrystals (70 mg).

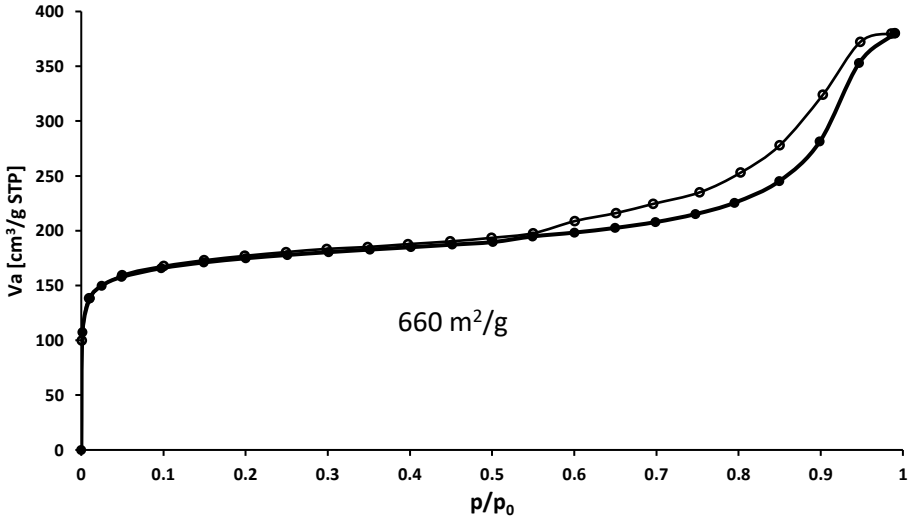
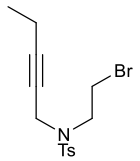


Figure S35. N_2 adsorption isotherm at 77 K of activated MUV-11. S_{BET} = 660 m^2/g (adsorption points denoted by blue and desorption by red circles).

[17] N. M. Padial, J. Castells-Gil, N. Almora-Barrios, M. Romero-Angel, I. da Silva, M. Barawi, A. García-Sánchez, V. A. de la Peña O'Shea, C. Martí-Gastaldo, *J. Am. Chem. Soc.* 2019, **141**, 13124–13133

7. Characterization of new products

***N*-(2-bromoethyl-4-methyl-*N*-(pent-2-yn-1-yl)benzenesulfonamide (2b)**



Following the General Procedure I, compound **2b** was obtained from 4-methyl-*N*-(pent-2-yn-1-yl)benzenesulfonamide (750 mg, 3.17 mmol) and 2-bromoethanol (225 µl, 3.17 mmol). The crude product was purified by column chromatography (AcOEt in hexane, gradient from 0-20%) to afford 840 mg of colourless oil, yield = 77%.

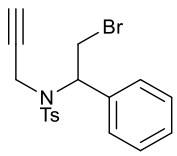
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 1H), 7.33 – 7.27 (m, 1H), 4.11 (t, *J* = 2.3 Hz, 1H), 3.52 (s, 2H), 2.42 (s, 2H), 1.97 (qt, *J* = 7.5, 2.3 Hz, 1H), 0.94 (t, *J* = 7.5 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.7, 135.8, 129.5, 127.7, 87.9, 77.3, 77.0, 76.8, 71.9, 48.3, 38.4, 29.1, 21.5, 13.4, 12.1 ppm.

HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{14}H_{18}NO_2NaSBr$: 366.0139, found: 366.0141.

Elemental analysis (%) calculated for $C_{14}H_{18}NO_2SBr$: C 48.84, H 5.27, N 4.07, found as a mean from two measurements: C 48.66, H 5.12, N 4.26.

***N*-(2-bromo-1-phenylethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (2c)**



Following the General Procedure I, compound **2c** was obtained from 4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (775 mg, 3.7 mmol) and racemic 2-bromo-1-phenylethan-1-ol (744 mg, 3.7 mmol). The crude product was purified by column chromatography (ethyl acetate in hexane gradient from 0-20%) to afford 440 mg of colourless oil, yield = 30%.

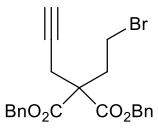
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (d, *J* = 8.4 Hz, 2H), 7.35 – 7.23 (m, 7H), 5.32 (dd, *J* = 10.5, 5.0 Hz, 1H), 4.23 (dd, *J* = 18.7, 2.5 Hz, 1H), 4.11 (t, *J* = 10.6 Hz, 1H), 3.75 (dd, *J* = 10.6, 5.0 Hz, 1H), 3.49 (dd, *J* = 18.7, 2.4 Hz, 1H), 2.45 (s, 3H), 2.19 (t, *J* = 2.5 Hz, 1H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 137.4, 134.3, 129.7, 128.7, 128.5, 127.5, 79.8, 77.3, 77.0, 76.8, 73.2, 62.0, 33.3, 30.2, 21.6 ppm.

HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{18}H_{18}NO_2NaSBr$: 414.0139, found: 414.0138.

Elemental analysis (%) calculated for $C_{18}H_{18}NO_2SBr$: C 55.11, H 4.62, N 3.57, found as a mean from two measurements: C 55.00, H 4.59, N 3.67.

dibenzyl 2-(2-bromoethyl)-2-(prop-2-yn-1-yl)malonate (2e)



Following General Procedure II, compound **2e** was obtained from dibenzyl 2-(prop-2-yn-1-yl)malonate (342 mg, 1.06 mmol) and 1,2-dibromoethanol (275 µl, 3.2 mmol). The crude product was purified by column chromatography (ethyl acetate in hexane gradient from 0-20%) to afford 188 mg of colourless oil, yield = 41%.

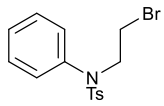
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 7H), 7.27 (m, 1H), 7.25 – 7.22 (m, 2H), 5.13 (d, *J* = 1.3 Hz, 4H), 3.35 – 3.29 (m, 2H), 2.87 (d, *J* = 2.7 Hz, 2H), 2.72 – 2.64 (m, 2H), 2.01 (t, *J* = 2.7 Hz, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.9, 134.9, 128.6, 128.5, 128.2, 78.0, 77.2, 77.0, 76.8, 72.3, 67.7, 56.9, 35.8, 26.6, 23.3 ppm.

HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{22}H_{21}O_4NaBr$: 451.0521, found: 451.0514.

Elemental analysis (%) calculated for $C_{22}H_{21}O_4Br$: C 61.55, H 4.93, found as a mean from two measurements: C 61.79, H 5.02.

***N*-(2-bromoethyl)-4-methyl-*N*-phenylbenzenesulfonamide (2f)**



Following the General Procedure I, compound **2f** was obtained from 4-methyl-*N*-phenylbenzenesulfonamide (247 mg, 1.0 mmol) and 2-bromoethanol (71 µl, 1.0 mmol). The crude product was purified by column chromatography (AcOEt in hexane, gradient from 0-20%) to afford 171 mg of off-white solid, yield = 48%.

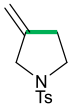
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.44 (m, 2H), 7.38 – 7.29 (m, 3H), 7.26 (s, 1H), 7.25 (s, 1H), 7.10 – 7.03 (m, 2H), 3.88 (dd, *J* = 8.0, 7.0 Hz, 2H), 3.39 (dd, *J* = 8.0, 7.0 Hz, 2H), 2.43 (s, 3H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.8, 139.0, 135.2, 129.5, 129.3, 129.0, 128.4, 127.7, 52.5, 28.8, 21.6 ppm.

HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{15}H_{16}NO_2NaSBr$: 375.9983, found: 375.9985.

Elemental analysis (%) calculated for $C_{15}H_{16}NO_2SBr$: C 50.86, H 4.55, N 3.95, found as a mean from two measurements: C 50.86, H 4.74, N 4.17.

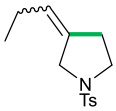
3-methylene-1-tosylpyrrolidine (3a)[18]



Following General Procedure III, compound **3a** was obtained from *N*-(2-bromoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2a**, 68 mg, 0.22 mmol). The crude product was purified by column chromatography (ethyl acetate in hexane gradient from 0-20%) to afford 43 mg of white solid, yield = 83%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.91 (dp, *J* = 6.7, 2.2 Hz, 2H), 3.77 (q, *J* = 1.8 Hz, 2H), 3.29 (t, *J* = 7.1 Hz, 2H), 2.47 (tt, *J* = 6.8, 1.5 Hz, 2H), 2.43 (s, 3H) ppm.

3-propylidene-1-tosylpyrrolidine, *E+Z* (3b)



Following General Procedure III, compound **3b** was obtained from N-(2-bromoethyl)-4-methyl-N-(pent-2-yn-1-yl)benzenesulfonamide (**2b**, 87 mg, 0.25 mmol). The crude product was purified by column chromatography (ethyl acetate in hexane 0-10%) to afford 42 mg of colourless crystals, yield = 62%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.35 – 7.28 (m, 2H), 5.24 (dtq, *J* = 11.9, 7.1, 2.3 Hz, 1H), 3.72 (dh, *J* = 6.7, 1.5 Hz, 2H), 3.27 (t, *J* = 7.1 Hz, 1H), 3.23 (t, *J* = 7.0 Hz, 1H), 2.47 – 2.35 (m, 5H), 1.96 – 1.83 (m, 2H), 0.91 (td, *J* = 7.5, 4.4 Hz, 3H) ppm.

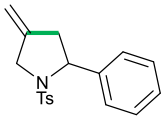
[18] S. Smoleń, A. Wincenciuk, O. Drapała, D. Gryko, *Synthesis* 2021, **53**, 1645-1653

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 133.8, 133.7, 132.9, 132.7, 129.6, 129.6, 128.0, 127.8, 124.8, 124.4, 77.3, 77.0, 76.8, 52.2, 49.1, 48.0, 47.7, 31.6, 27.5, 22.7, 22.5, 21.5, 13.7, 13.7 ppm.

HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{14}H_{19}NO_2NaS$: 288.1034, found: 288.1038.

Elemental analysis (%) calculated for $C_{14}H_{19}NO_2S$: C 63.37, H 7.22, N 5.28, found as a mean from two measurements: C 63.39, H 7.16, N 5.25.

4-methylene-2-phenyl-1-tosylpyrrolidine (3c)



Following General Procedure III, compound **3c** was obtained from racemic *N*-(2-bromo-1-phenylethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2c**, 101 mg, 0.26 mmol). The crude product was purified by column chromatography (ethyl acetate in hexane gradient from 0-20%) to afford 62 mg of white solid, yield = 77%.

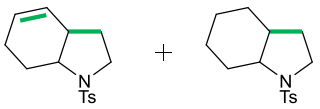
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 2H), 7.27 – 7.19 (m, 7H), 4.98 (t, *J* = 2.3 Hz, 1H), 4.96 – 4.89 (m, 2H), 4.11 (dddd, *J* = 16.1, 14.3, 12.5, 2.0 Hz, 2H), 2.77 (ddtd, *J* = 15.5, 8.6, 2.7, 1.4 Hz, 1H), 2.48 (ddq, *J* = 15.4, 3.1, 1.6 Hz, 1H), 2.40 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.37, 143.27, 141.98, 135.24, 129.48, 128.36, 127.38, 127.36, 126.37, 108.14, 77.21, 77.00, 76.79, 63.07, 52.47, 41.36, 21.48 ppm.

HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{18}H_{19}NO_2NaS$: 336.1034, found: 336.1036.

Elemental analysis (%) calculated for $C_{18}H_{19}NO_2S$: C 68.98, H 6.11, N 4.47, found as a mean from two measurements: C 68.67, H 5.98, N 4.52.

1-tosyloctahydro-1*H*-indole (3da) + 1-tosyl-2,3,3a,6,7,7a-hexahydro-1*H*-indole (3db)[19]



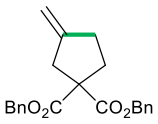
Following General Procedure III, compounds **3da** and **3db** were obtained in a **7.5 : 1** ratio respectively, from *N*-(2-bromoethyl)-*N*-(cyclohex-2-en-1-yl)-4-methylbenzenesulfonamide (**2d**, 90 mg, 0.25 mmol). The crude product was purified by column chromatography (ethyl acetate in hexane gradient from 0-20%) to afford 63 mg of white solid, yield = 90%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.77 (m, 1H), 5.48 (ddt, *J* = 9.9, 3.8, 1.9 Hz, 1H), 3.69 (ddd, *J* = 9.5, 7.2, 3.7 Hz, 1H), 3.44 (ddd, *J* = 10.0, 7.0, 4.6 Hz, 1H), 3.16 (ddd, *J* = 10.0, 8.1, 6.9 Hz, 1H), 2.42 (s, 3H), 2.33 (m, 1H), 2.17 – 2.07 (m, 1H), 2.04 – 1.94 (m, 2H), 1.82 – 1.71 (m, 2H), 1.65 – 1.56 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 135.0, 129.6, 129.5, 128.7, 127.4, 127.3, 126.7, 77.3, 77.0, 76.7, 59.6, 58.4, 47.9, 47.2, 39.0, 37.7, 30.8, 29.8, 27.7, 27.1, 26.3, 23.1, 22.5, 21.5, 21.3 ppm.

dibenzyl 3-methylenecyclopentane-1,1-dicarboxylate (3e)

[19] A. Millan, L. A. de Cienfuegos, D. Miguel, A. G. Campana, and J. M. Cuerva *Org. Lett.* 2012, **14**, 5984–5987



Following General Procedure III, compound **3f** was obtained from dibenzyl 2-(2-bromoethyl)-2-(prop-2-yn-1-yl)malonate (**2f**, 106 mg, 0.25 mmol). The crude product was purified by column chromatography (ethyl acetate in hexane gradient from 0-20%) to afford 66 mg of colourless oil, yield = 76%.

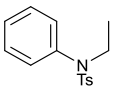
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 6H), 7.25 – 7.20 (m, 4H), 5.12 (s, 4H), 4.88 (dtd, *J* = 11.5, 2.2, 0.8 Hz, 2H), 2.97 – 2.91 (m, 2H), 2.46 – 2.38 (m, 2H), 2.34 – 2.27 (m, 2H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 148.1, 135.5, 128.5, 128.2, 127.9, 107.1, 77.2, 77.0, 76.8, 67.1, 60.3, 40.7, 33.8, 31.1 ppm.

HRMS (ESI) m/z [M+Na]$^+$ calculated for $C_{22}H_{22}O_4Na$: 373.1416, found: 373.1414.

Elemental analysis (%) calculated for $C_{22}H_{22}O_4$: C 75.41, H 6.33, found as a mean from two measurements: C 75.21, H 6.20.

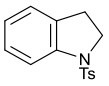
***N*-ethyl-4-methyl-*N*-phenylbenzenesulfonamide (3fa)**



Following General Procedure III, compound **3fa** was obtained from ***N*-(2-bromoethyl)-4-methyl-*N*-phenylbenzenesulfonamide** (**2f**, 88 mg, 0.25 mmol). The crude product was purified by column chromatography (ethyl acetate in hexane gradient from 0-10%) to afford 14 mg of colourless oil, yield = 20%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.46 (m, 2H), 7.32 – 7.26 (m, 3H), 7.24 – 7.21 (m, 2H), 7.05 – 7.01 (m, 2H), 3.59 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H) ppm.

***N*-tosylindoline (3fb)**

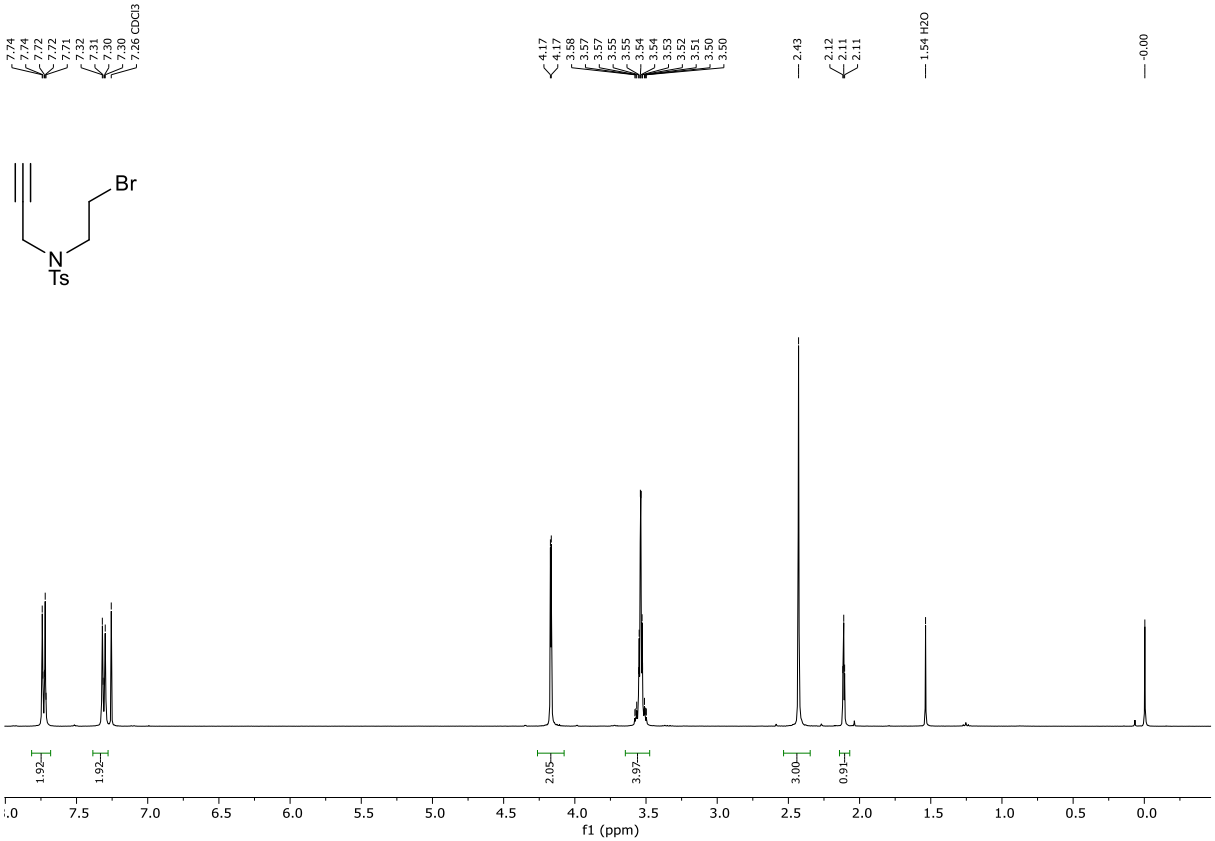


Following General Procedure III, compound **3fb** was obtained from ***N*-(2-bromoethyl)-4-methyl-*N*-phenylbenzenesulfonamide** (**2f**, 88 mg, 0.25 mmol). The crude product was purified by column chromatography (ethyl acetate in hexane gradient from 0-10%) to afford 12 mg of colourless oil, yield = 17%.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 – 7.61 (m, 2H), 7.37 – 7.30 (m, 1H), 7.23 – 7.16 (m, 3H), 7.06 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.96 (td, *J* = 7.5, 1.0 Hz, 1H), 3.90 (t, *J* = 8.4 Hz, 2H), 2.87 (t, *J* = 8.4 Hz, 2H), 2.36 (s, 3H) ppm.

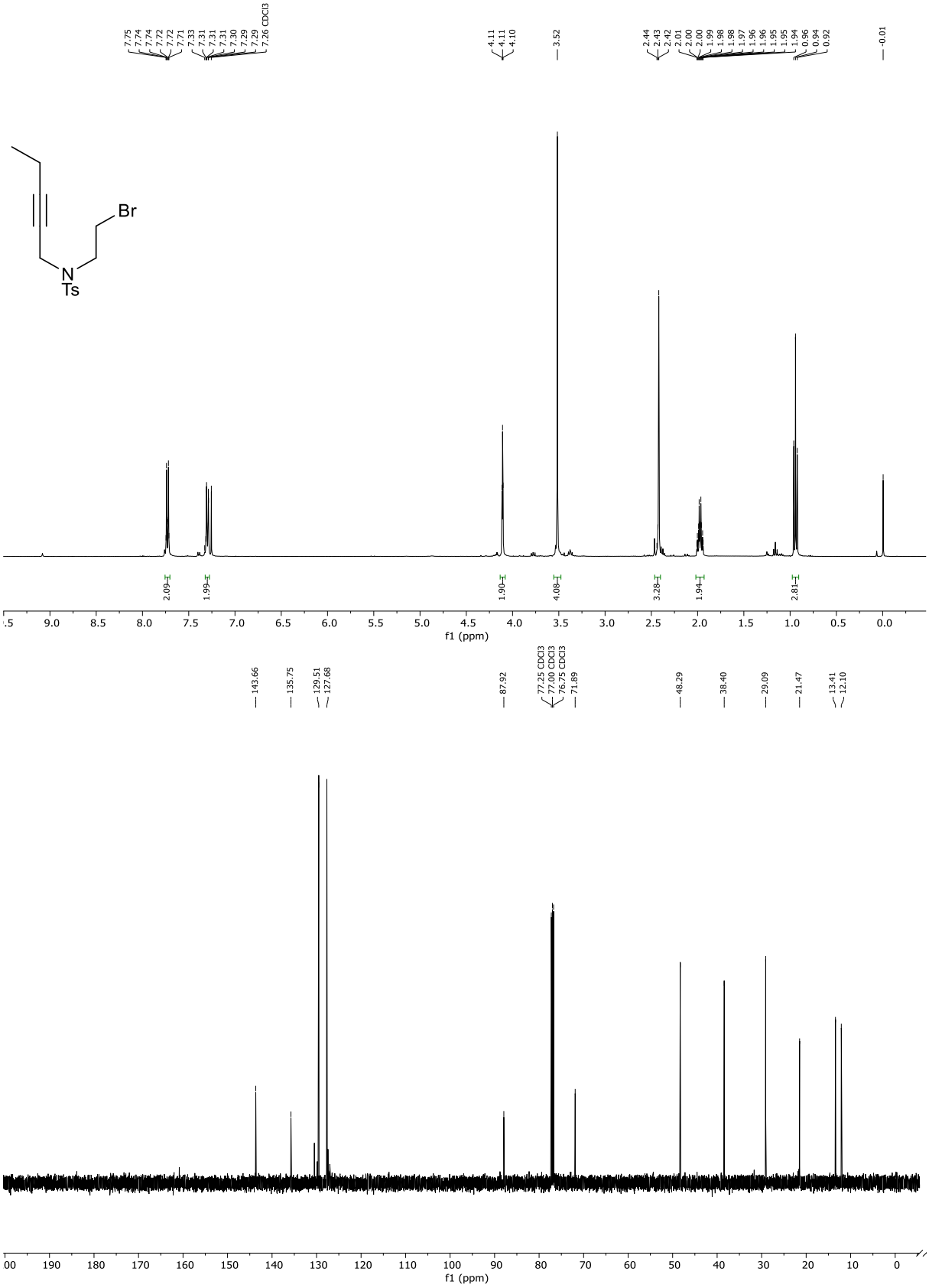
8. ^{1}H NMR and ^{13}C NMR spectra in $CDCl_3$

N-(2-bromoethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2a**)[20]

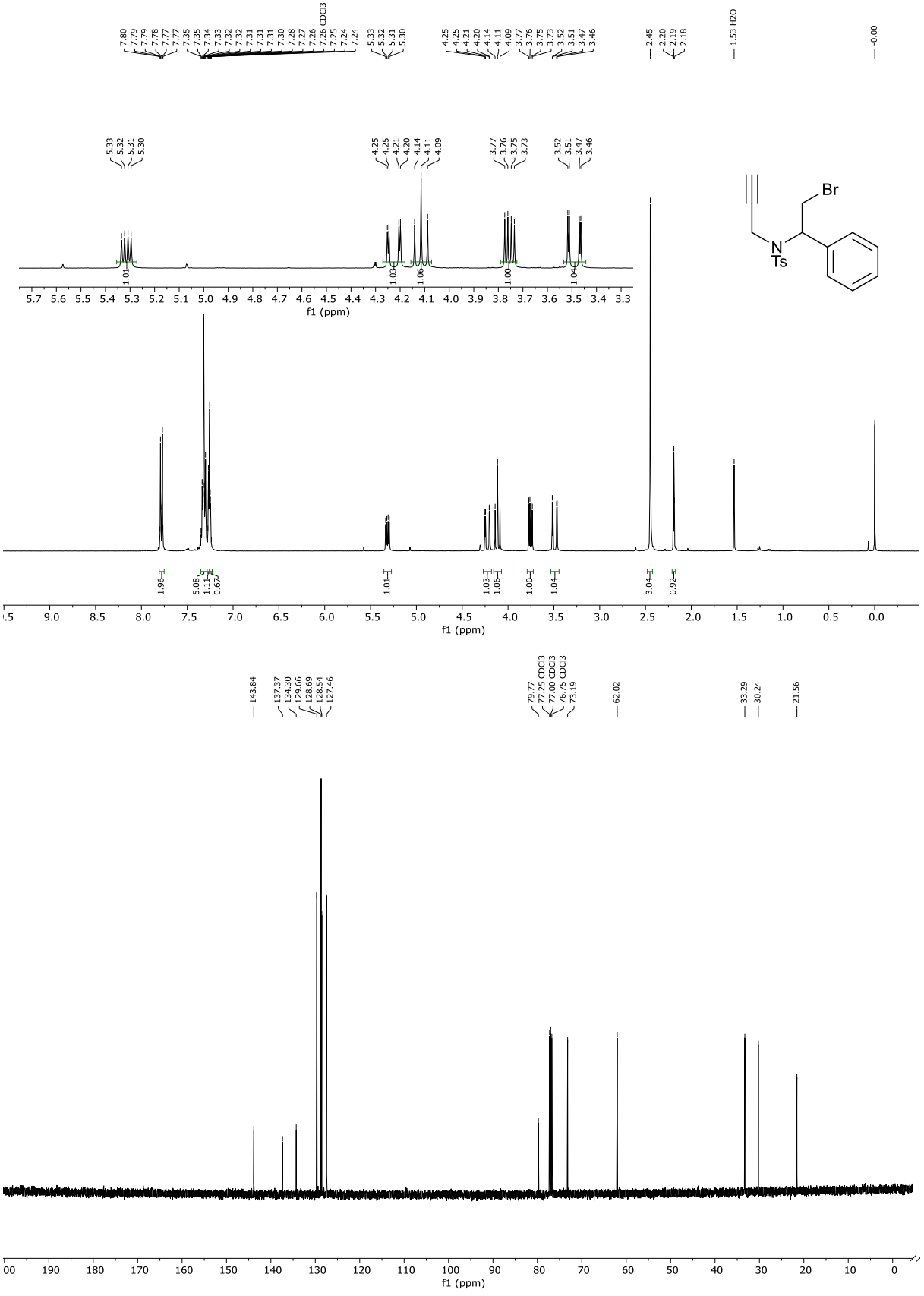


[20] G. Revol, T. McCallum, M. Morin, F. Gagosz, L. Barriault, *Angew. Chem. Int. Ed.* 2013, **52**, 13342-13345

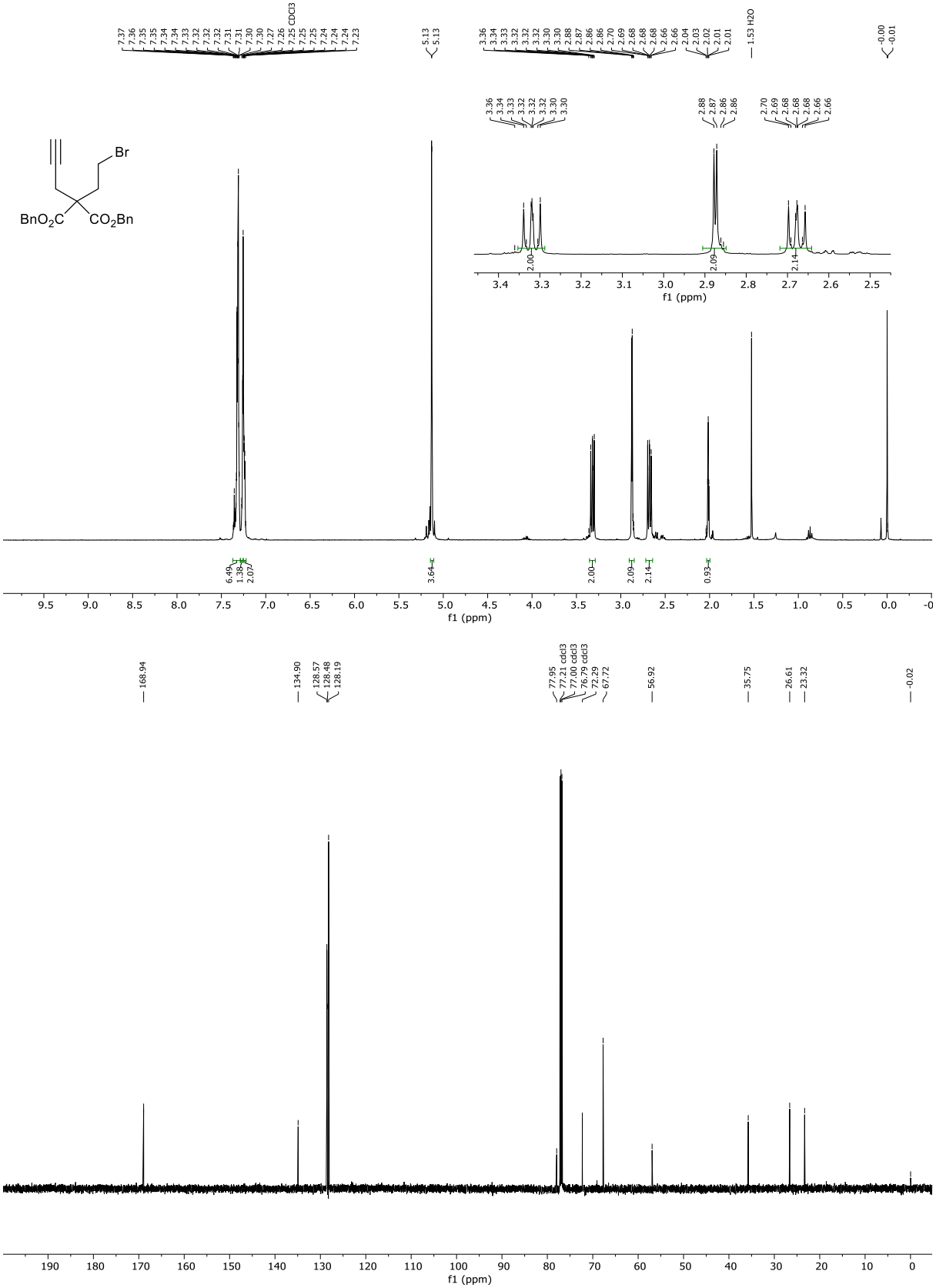
N-(2-bromoethyl-4-methyl-*N*-(pent-2-yn-1-yl)benzenesulfonamide (**2b**)



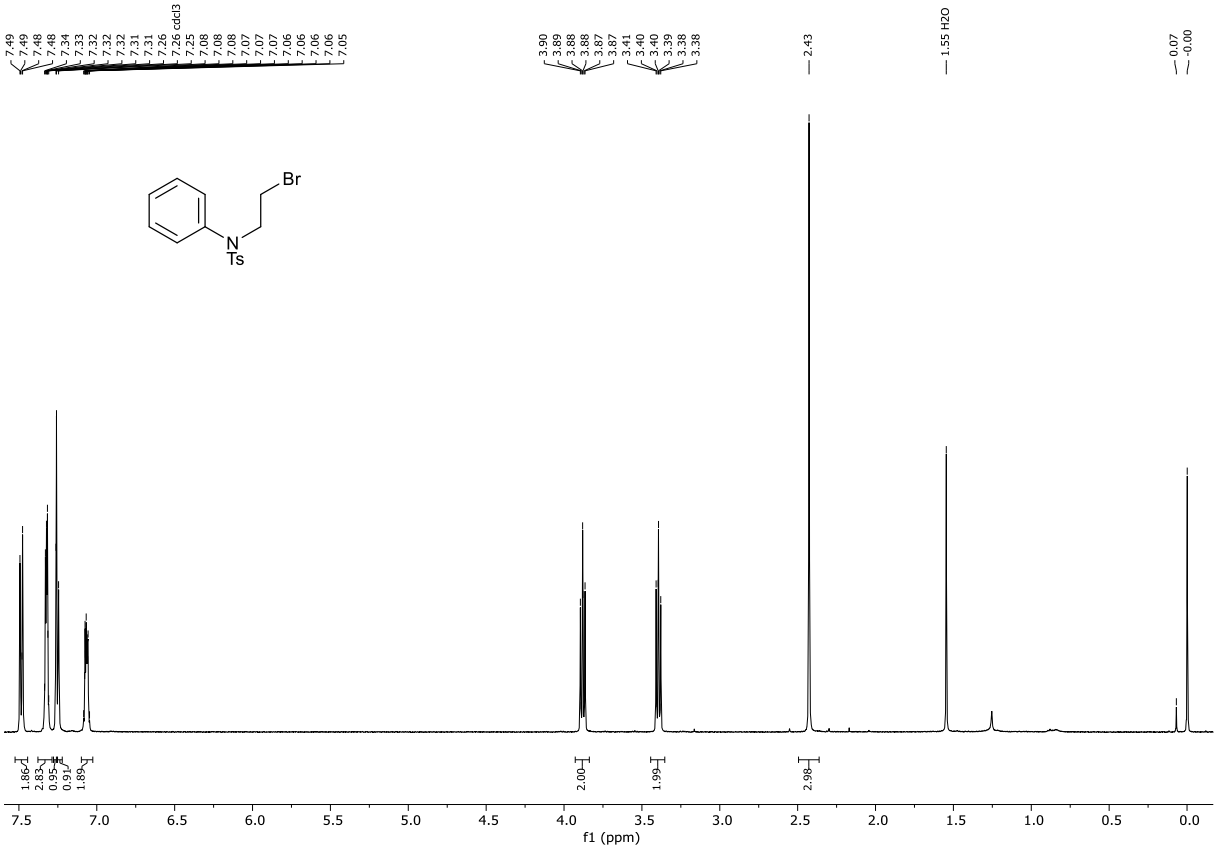
N-(2-bromo-1-phenylethyl)-4-methyl-*N*-(prop-2-yn-1-yl)benzenesulfonamide (**2c**)

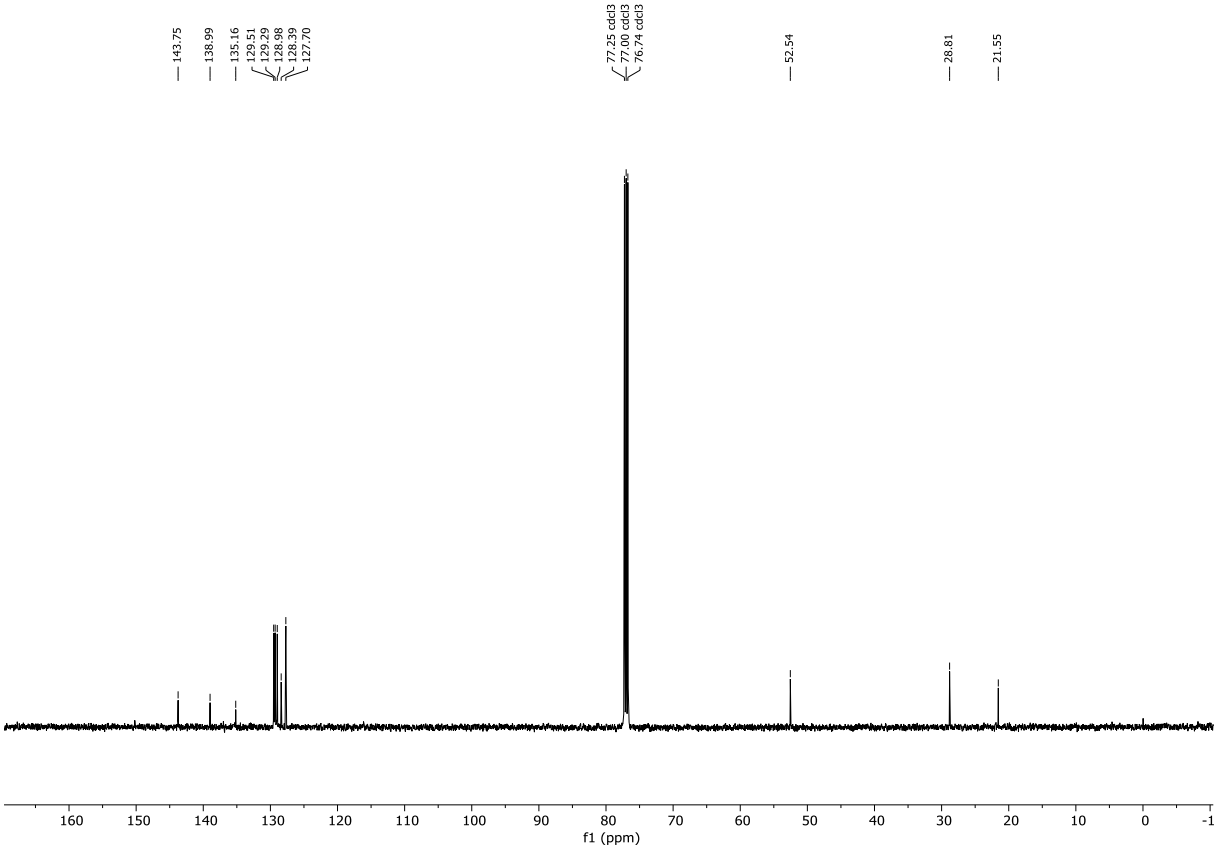


dibenzyl 2-(2-bromoethyl)-2-(prop-2-yn-1-yl)malonate (**2e**)

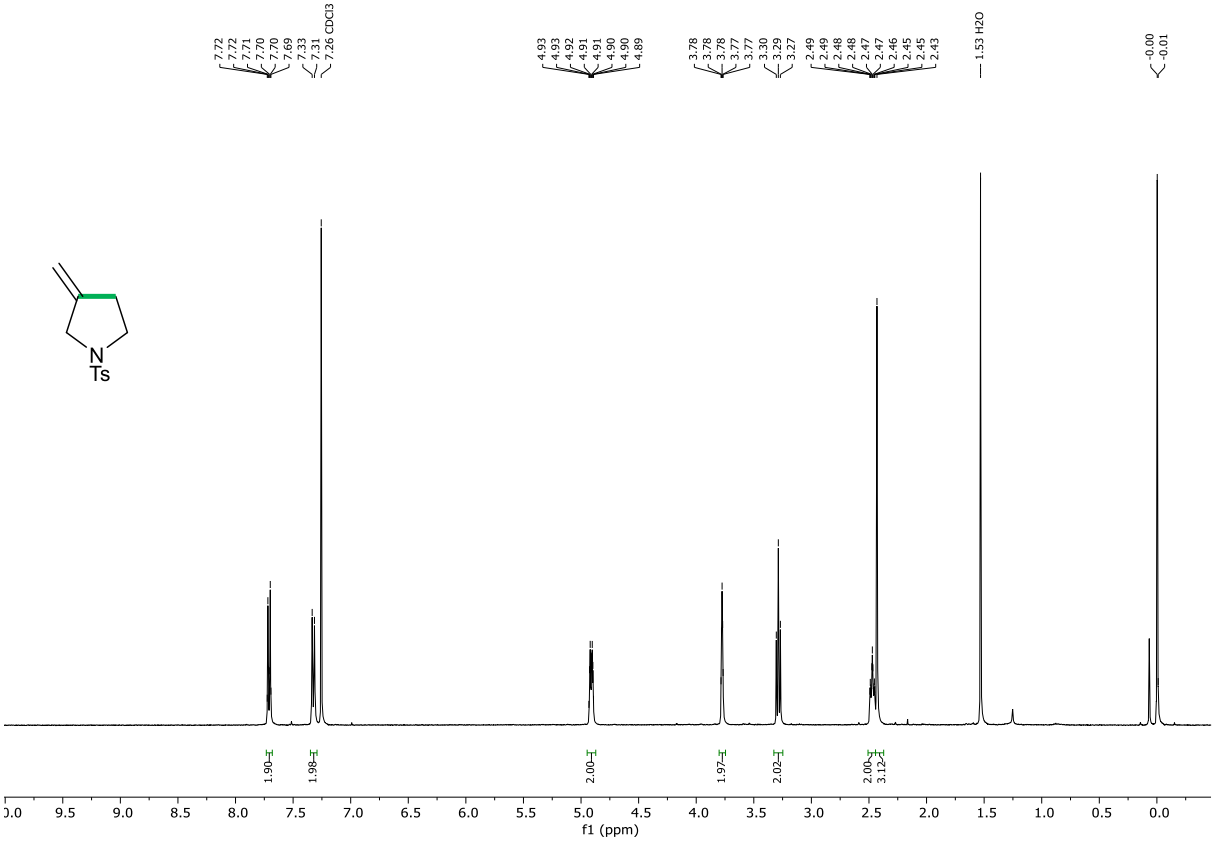


N-(2-bromoethyl)-4-methyl-*N*-phenylbenzenesulfonamide (**2f**)



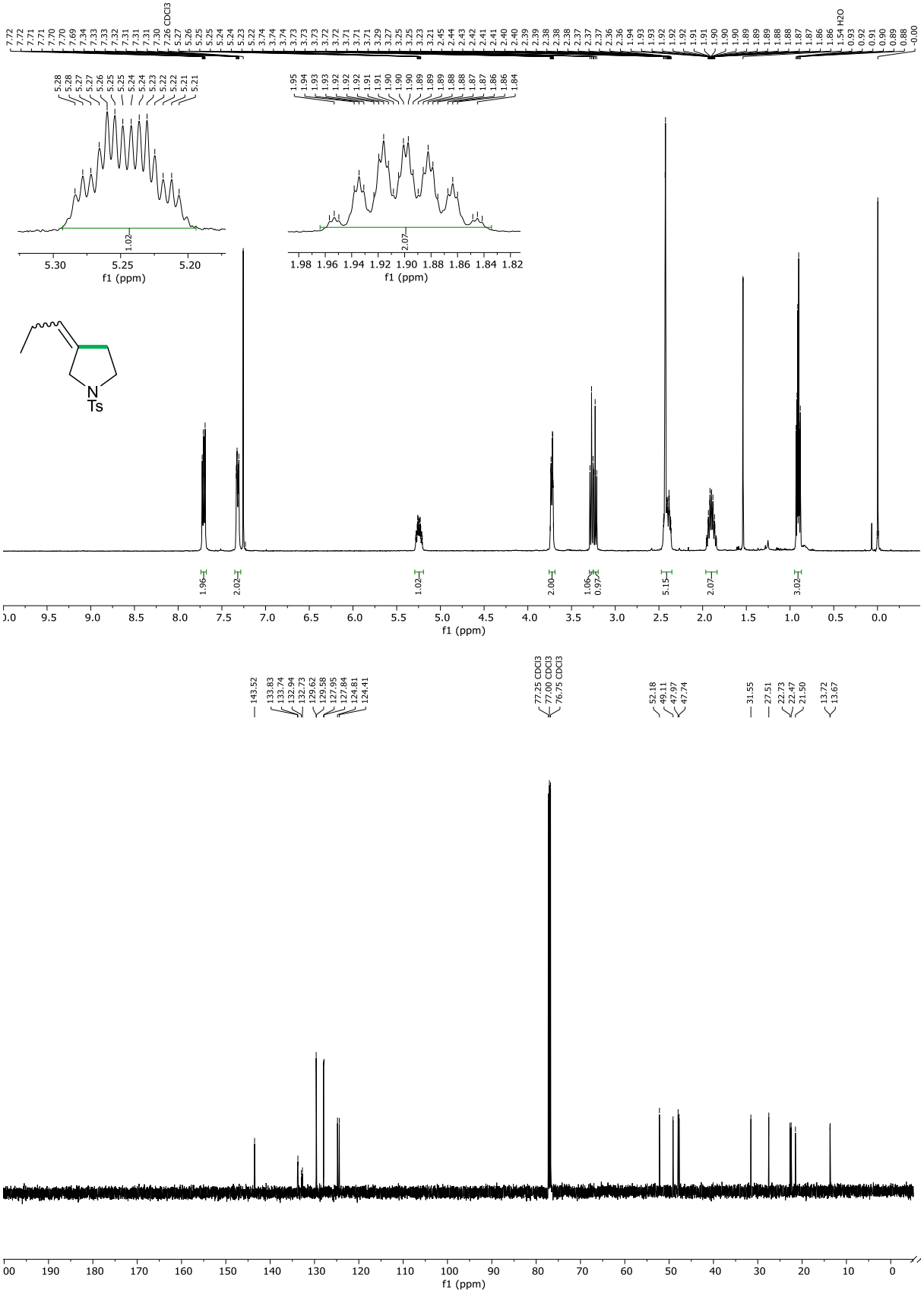


3-methylene-1-tosylpyrrolidine (**3a**)[21]

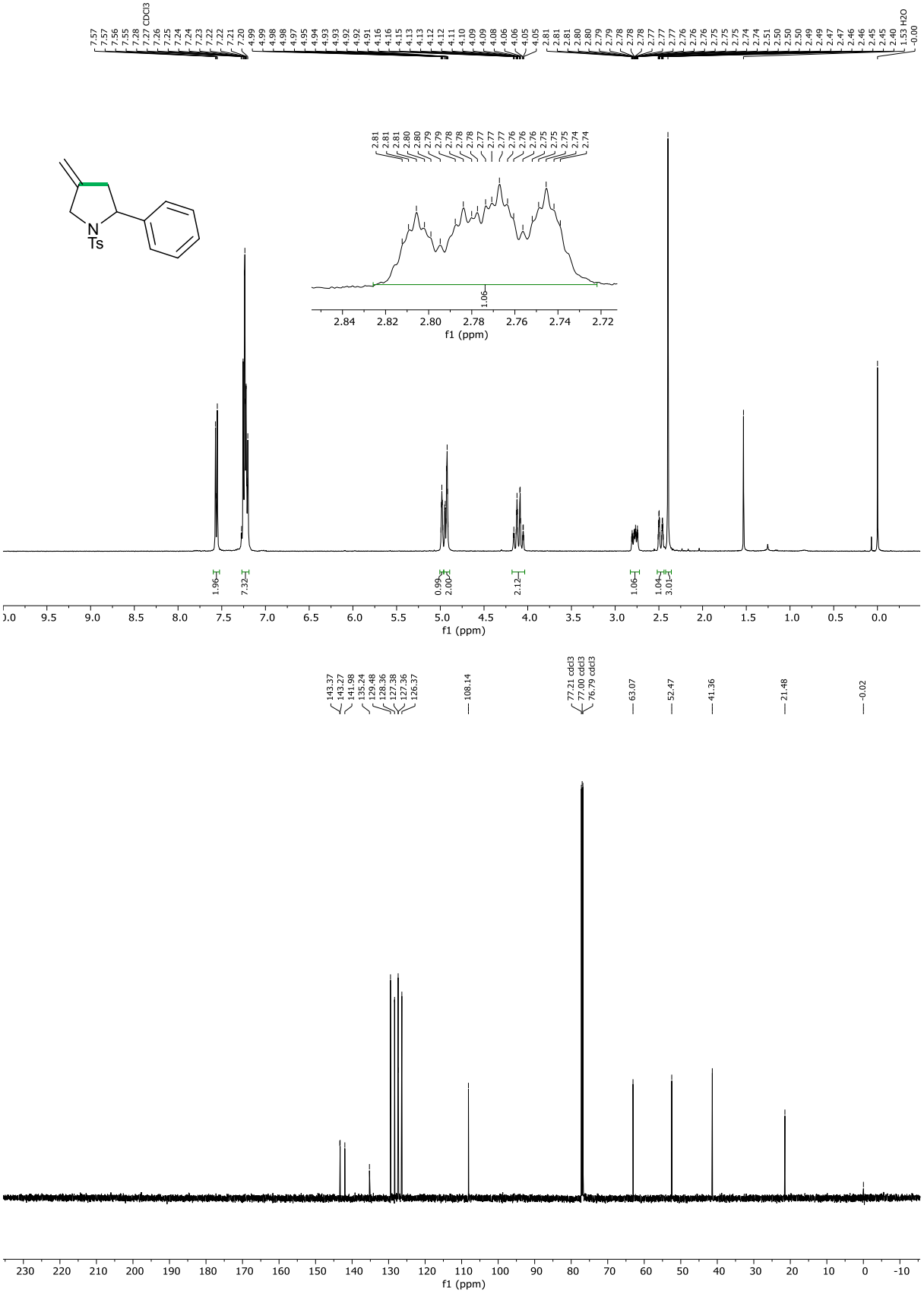


[21] G. Revol, T. McCallum, M. Morin, F. Gagosz, L. Barriault, *Angew. Chem.* 2013, **125**, 13584 – 13587.

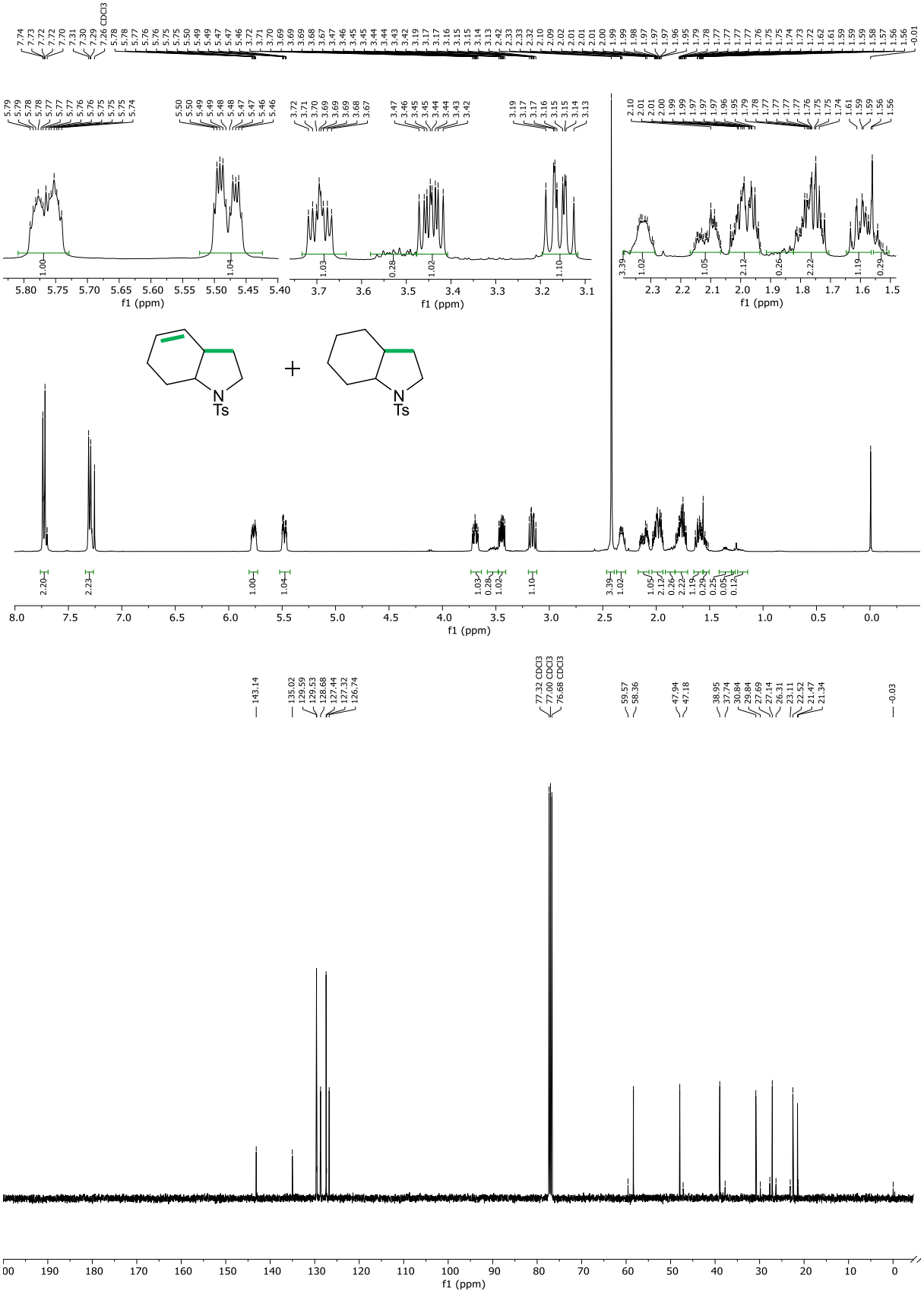
3-propylidene-1-tosylpyrrolidine, *E+Z* (**3b**)



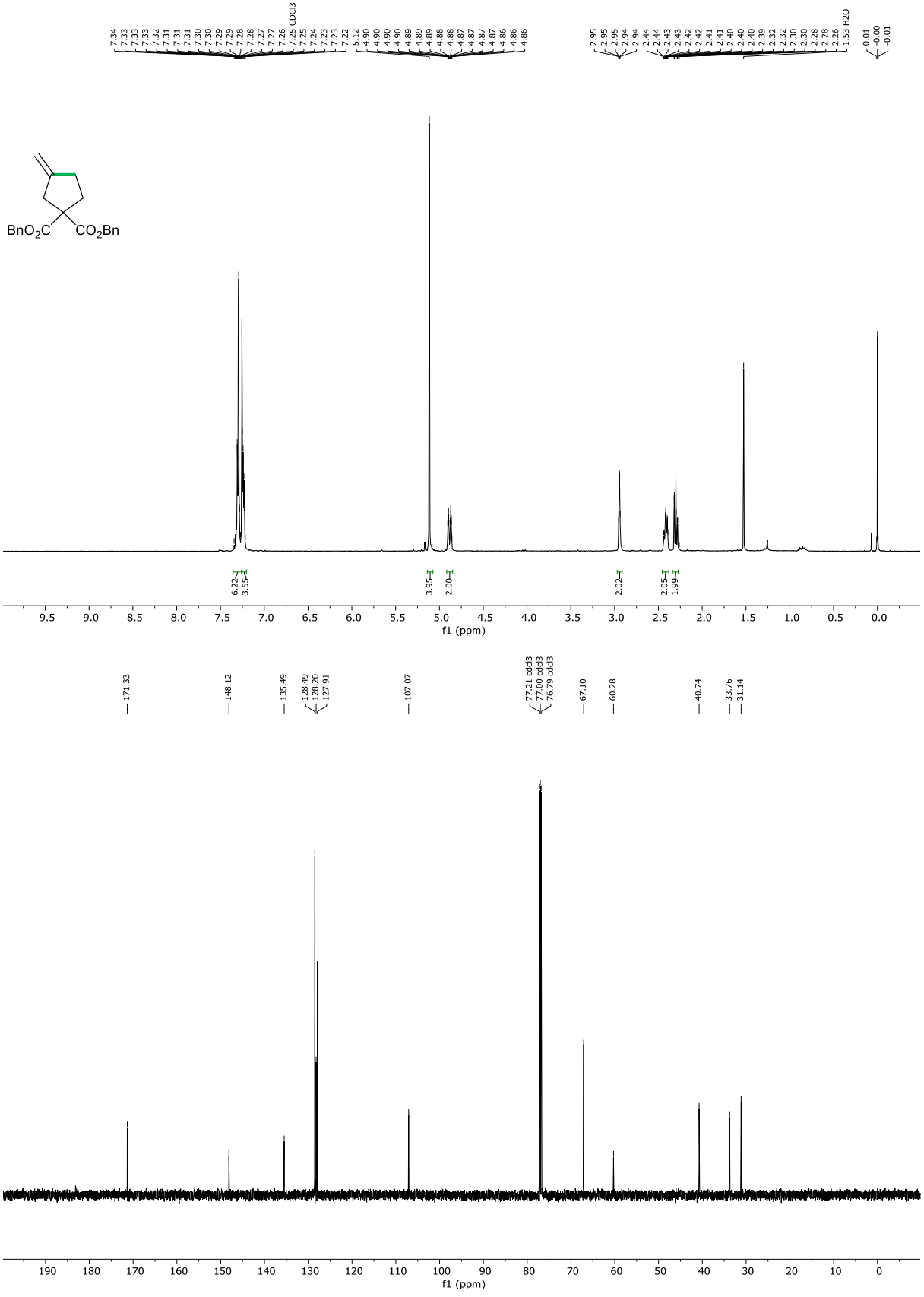
4-methylene-2-phenyl-1-tosylpyrrolidine (**3c**)



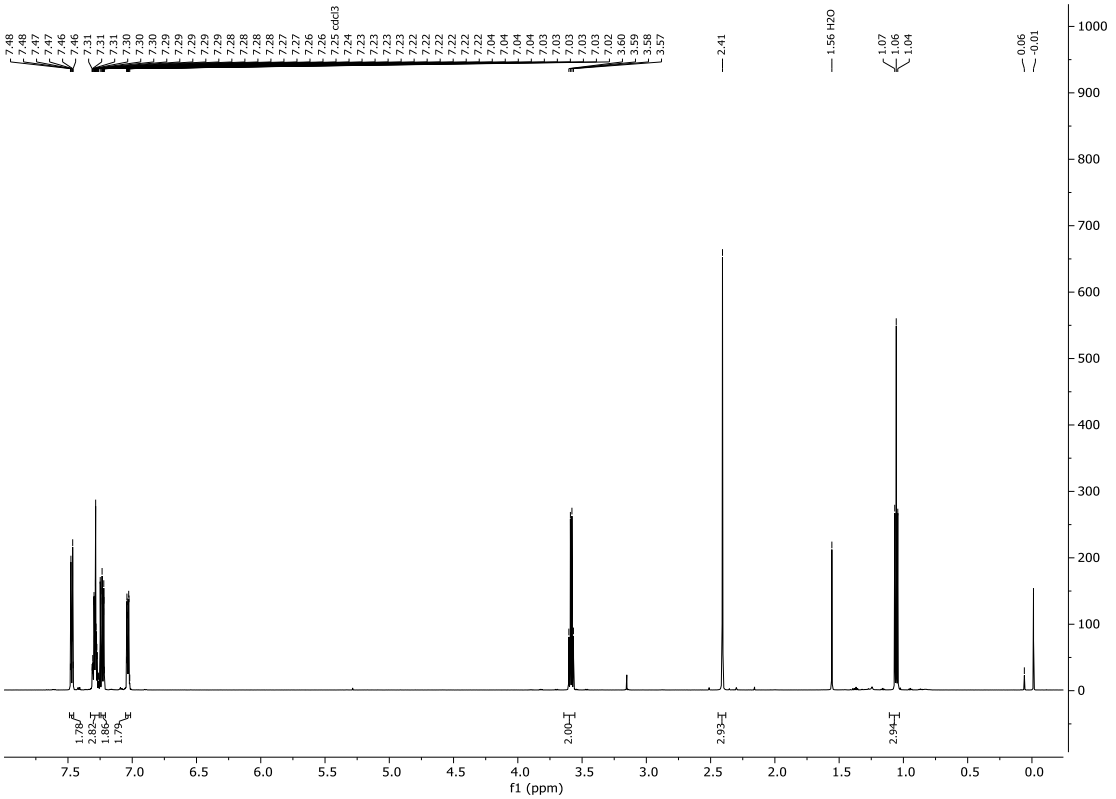
1-tosyloctahydro-1*H*-indole (**3da**) + 1-tosyl-2,3,3a,6,7,7a-hexahydro-1*H*-indole (**3db**)



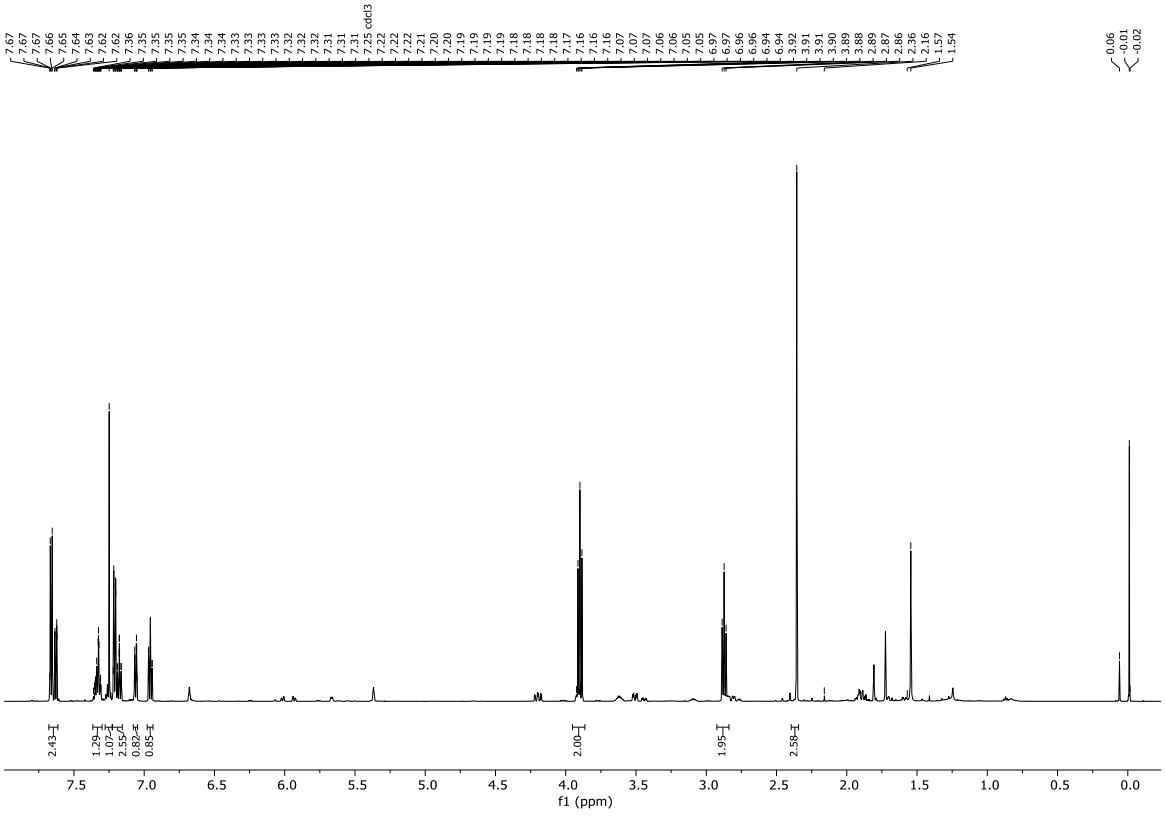
dibenzyl 3-methylenecyclopentane-1,1-dicarboxylate (**3e**)



N-ethyl-4-methyl-*N*-phenylbenzenesulfonamide (**3fa**)[22]



N-tosylindoline (**3fb**)[23]



[22] H. Yu, Y. Zhang, *Chin. J. Chem*. 2016, **34**, 359-362

[23] Q.-K. Kang, Y. Li, K. Chen, H. Zhu, W.-Q. Wu, Y. Lin, H. Shi, *Angew. Chem. Int. Ed.* 2022, **61**, e202117381