Electronic Supporting Information

A Copper(II) Metal – Organic Hydrogel as Multifunctional Precatalyst for CuAAC Reaction and Chemical Fixation of CO_2 Under Solvent Free Condition

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Experimental Section

General Information

All the chemicals, iminodiacetic acid was bought from Merck, 2,4-di-tert-butylphenol was bought from Sigma-Aldrich and copper chloride, alkynes were commercially available and used as received. Azides were synthesized according to the standard procedure from literature. Propylene oxide, 1,2-epoxyhexane were bought from Sigma-Aldrich and styrene oxide were bought from Merck. Analytical reagent grade solvents were used as received without further distillation.

Synthesis of Cu-MOG

In a typical gel formation experiment, 8 mg (0.04 mmol/mL) of ligand (Na_2HL) was dissolved in 0.5 ml of water and placed in six different glass vials, and 0.2−1.0 equiv of metal salt ($CuCl_2$) with respect to the ligand concentration was also dissolved in water and placed in six different glass vials separately. Finally, the aqueous solution of metal salt added to the aqueous solution of Na_2HL such that the total volume of the solvent in each vial is 1 mL. Then the formation of gel was confirmed by glass vial inversion method after two minutes at room temperature in 1:1 metal and ligand ratio.

Field Emission Scanning Electron Microscope (FESEM)

The morphology of the Cu-MOG was characterized using a field emission scanning electron microscope (ZEISS EVO 60 with oxford EDS detector) operating at 5 KV. Sample was prepared by dropping the dilute solution of the Cu-MOG on the thin aluminum sheets and then dried in air. A thin layer of Au was coated on the sample to minimize sample charging before the experiment.

Atomic Force Microscope (AFM)

The aggregation of the Cu-MOG was characterized by atomic force microscopy (Agilent 5500) in tapping mode. AFM sample was prepared by dropping the very dilute solution of Cu-MOG on a small piece of the glass slide and allowed to dry overnight before imaging.

Transmission Electron Microscopy (TEM)

The gel sample was characterized by an analytical TEM (FEI. TECNAIG220S-TWIN) instrument operating at 200 KV. Sample was prepared by dropping the much dilute solution of the Cu-MOG on the carbon-coated copper grid and the sample was allowed to dry for overnight before experiment.

Optical Microscopy (OM)

The gel sample was characterized by an optical image analyzer (Leica DMLM) instrument. The sample was prepared by dropping the very dilute solution of the Cu-MOG on the glass slide.

Rheological Measurements

The rheological experiments were carried out on an MCR 102 (Anton paar) modular compact rheometer with the 25 mm diameter parallel plate having a constant tool gap of 0.5 mm. The stress amplitude sweep experiment was carried out at a constant angular frequency of 1 rad sec^{-1} at 298K. The frequency sweep measurement was carried out in the linear viscoelastic range at a constant stress.

Gas Sorption Study

The gas sorption experiment was carried out on the dried xerogel of Cu-MOG using a Micromeritics 3flex gas adsorption analyzer in a 6 mm sample holder at 77 K for N_2 and 273 K for CO_2. Before the sorption experiment, the sample was employed for degassing at 100°C for 8 h.

MALDI-TOF

The MALDI-TOF spectrum of the Cu-MOG was taken using 2,5-dihydroxybenzoic acid as the matrix in the Bruker Daltonics, model: Ultraflextreme instrument.

General Procedure for the CuAAC Reaction

To a mixture of the benzylazide (**1a**, 133 mg, 1.0mmol) and phenylacetylene (**2a**, 102 mg, 1.0 mmol) in a vial the Cu-MOG catalyst (3.4 mg $CuCl_2 \cdot 2H_2O$ and 7.9 mg ligand, Na_2HL with 0.2 mL H_2O i.e 2 mol % copper complex calculated from MALDI-TOF spectrum) was added. The

mixture was stirred at 50 ℃ for the time given in the Tables (see text). After completion of the reaction, ethyl acetate (2 mL × 2 times) was added and the mixture was centrifuged to recover the catalyst. The organic layer was concentrated and the crude product was purified by column chromatography. Before reuse, the recovered catalyst was washed with ethyl acetate (2 mL × 3 times) and heated at 80 ℃ for 1 h.

General Procedure for the cycloaddition of CO_2 to epoxides

In a typical reaction, cycloaddition of the epoxide (10 mmol) was carried out with carbon dioxide purged at 1 bar in presence of tetrabutylammonium bromide (TBAB, 10 mol%) as a cocatalyst at room temperature under solvent free condition; while the xerogel as the catalyst was used 11.3 mg (0.2 mol % based on the Cu-MOG complex) for 48 hours. The yields of the products were calculated based on the ^{1}H NMR analysis.

To reuse the Cu-MOG, at first the reaction mixture was centrifuged to recover the catalyst. Then the clear solution was decanted and the epoxide (1,2-epoxy hexane) and TBAB was added. Then the reaction was done under same condition as previously described.

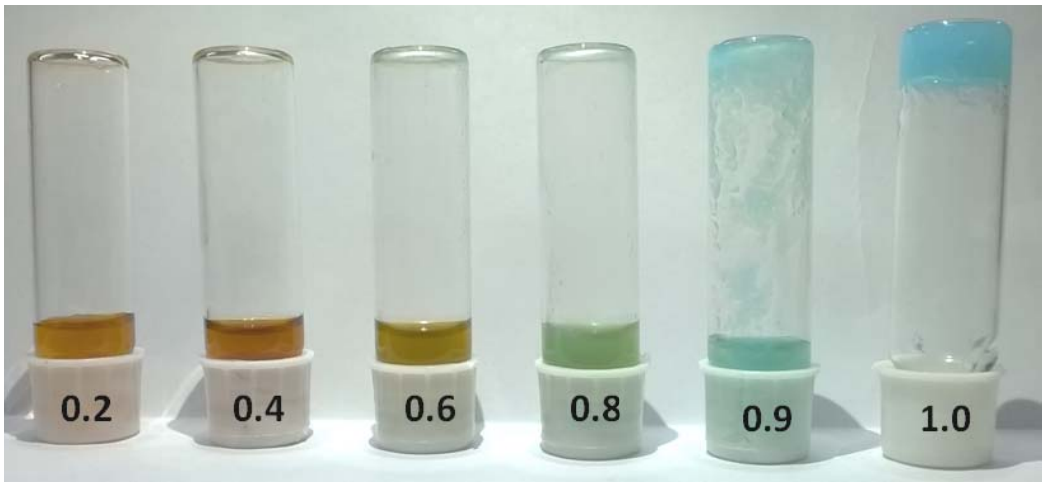


Figure S1. Image of inverted vials of Cu-MOG formation. Numbers on the cap indicates the equivalent amount of $CuCl_2$ with respect to ligand, Na_2HL present in the respective vial

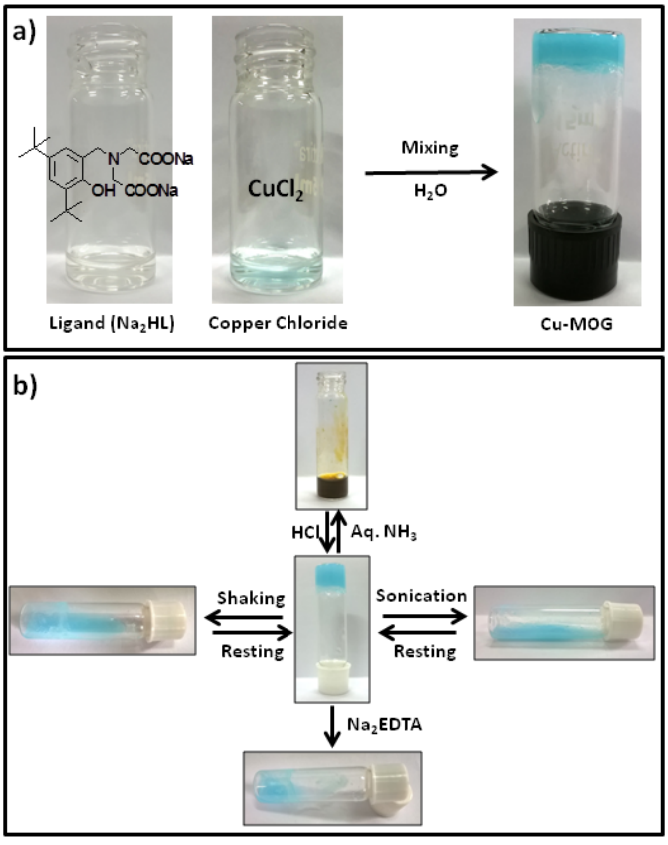


Figure S2. Formation (a) and multi-stimuli responsive nature (b) of metallohydrogel Cu-MOG

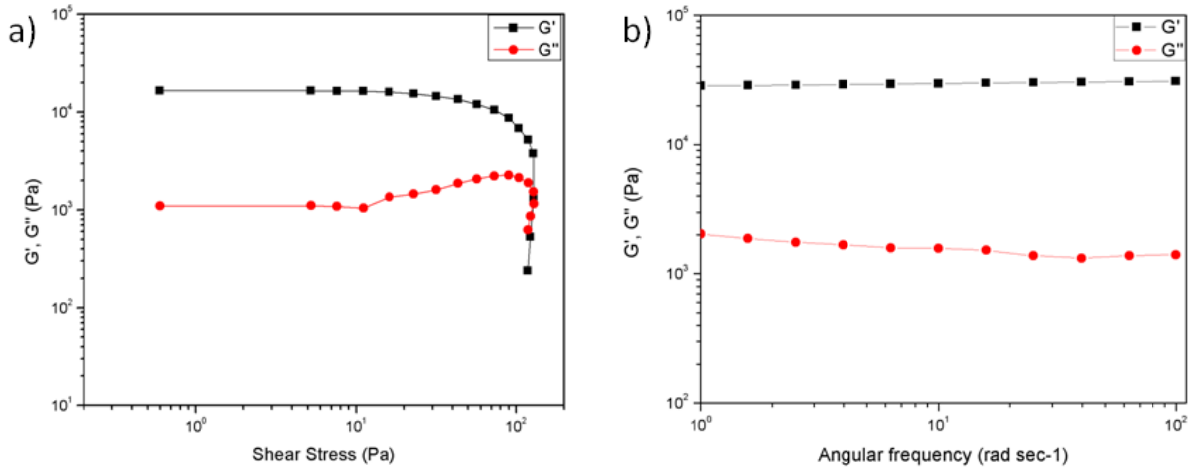


Figure S3. Plot of storage modulus (G') and loss modulus (G") with (a) shear stress at 1 rad sec^{-1} and with (b) frequency at 0.01% strain for Cu-MOG

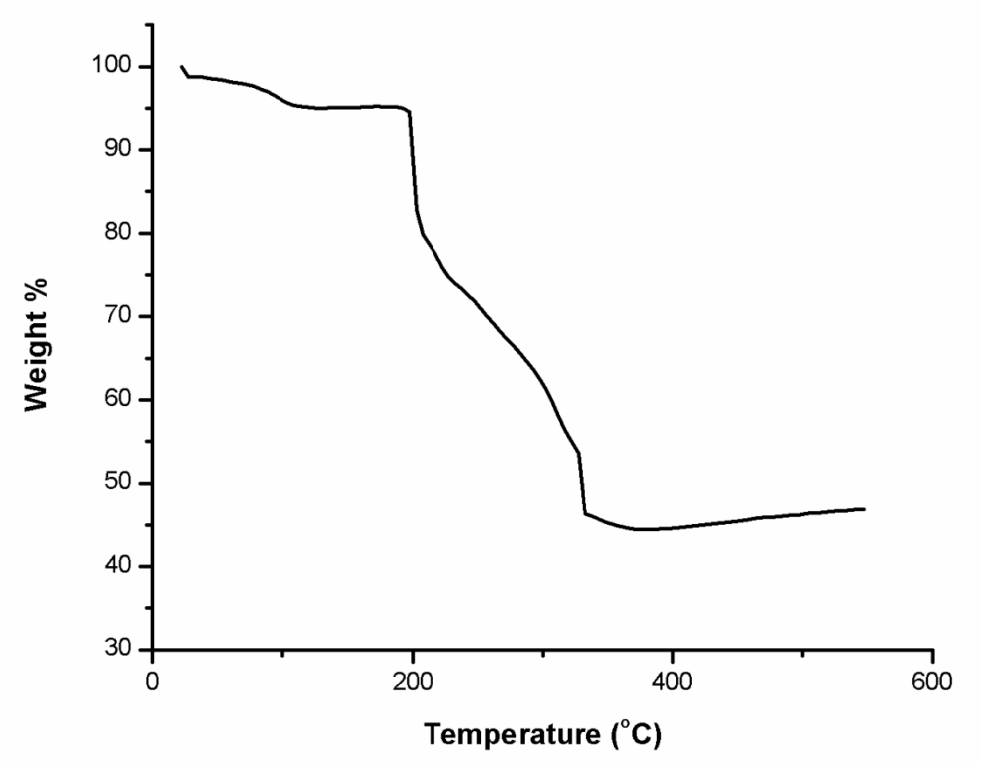


Figure S4. TGA curve of Cu-MOG

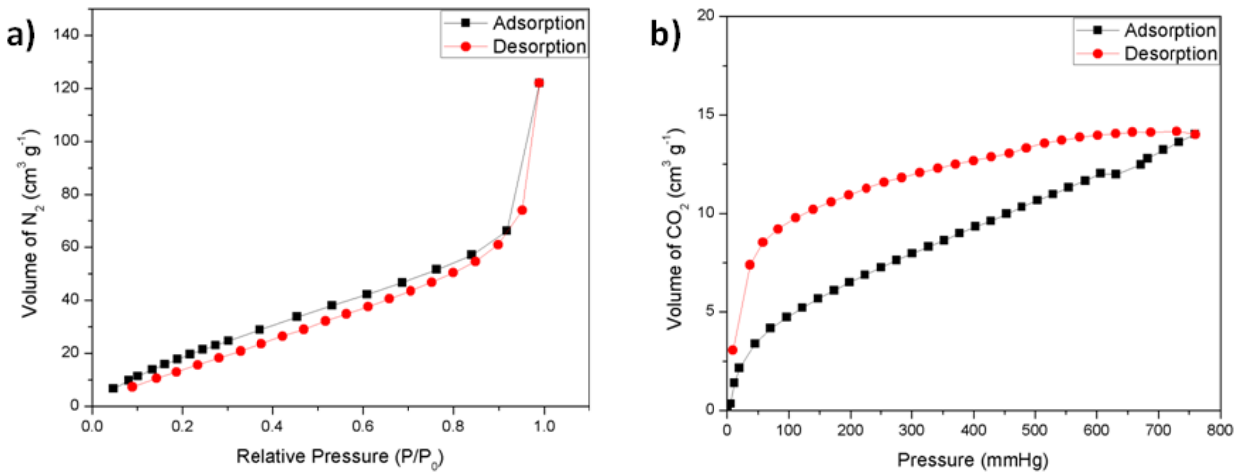


Figure S5. N_2 (a, at 77 K) and CO_2 (b, at 273 K) adsorption isotherm of Cu-MOG

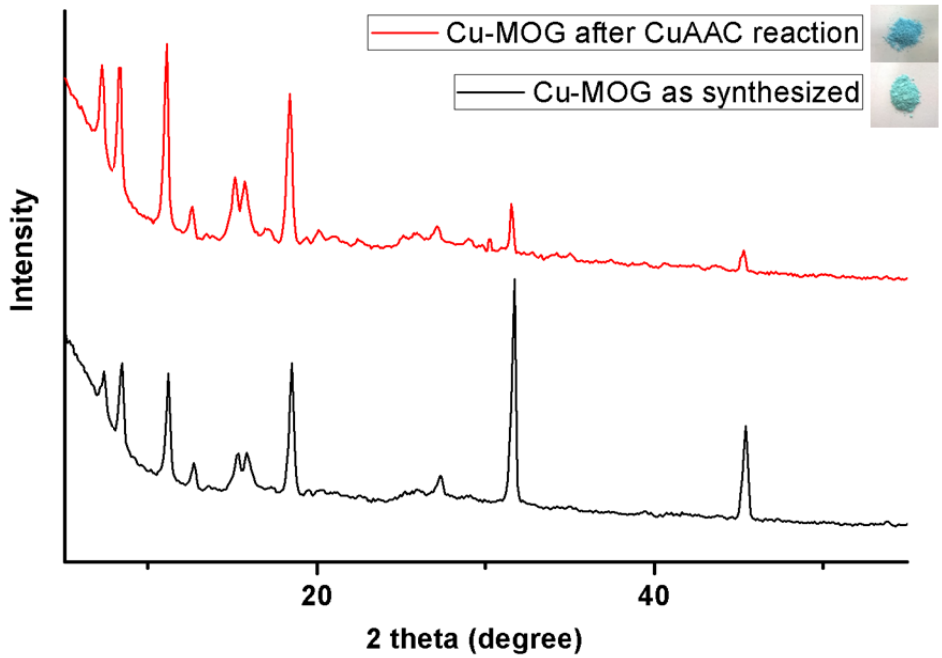


Figure S6. PXRD of as-synthesized Cu-MOG and Cu-MOG after catalytic reaction and the inset images of Cu-MOG are before (down) and after (up) catalytic reaction

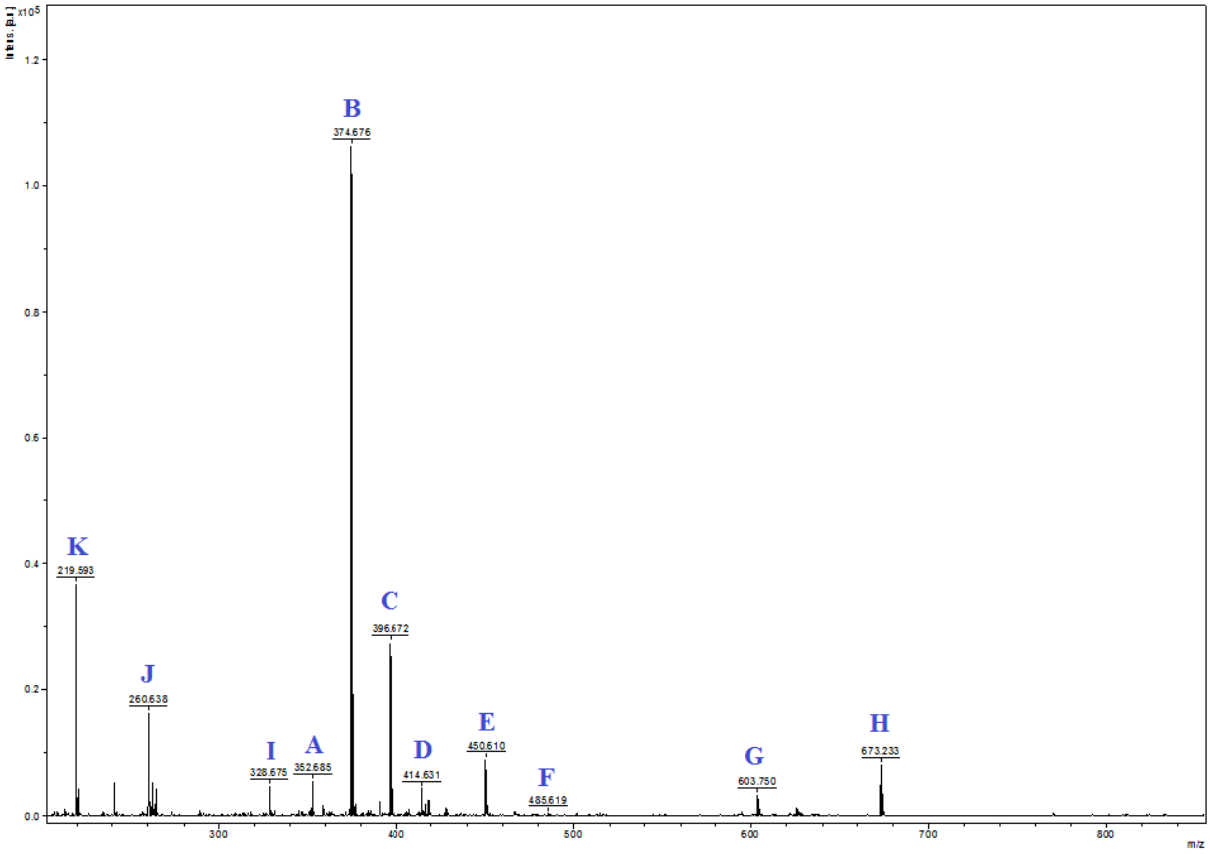


Figure S7. MALDI-TOF spectrum of the Cu-MOG in DHB matrix

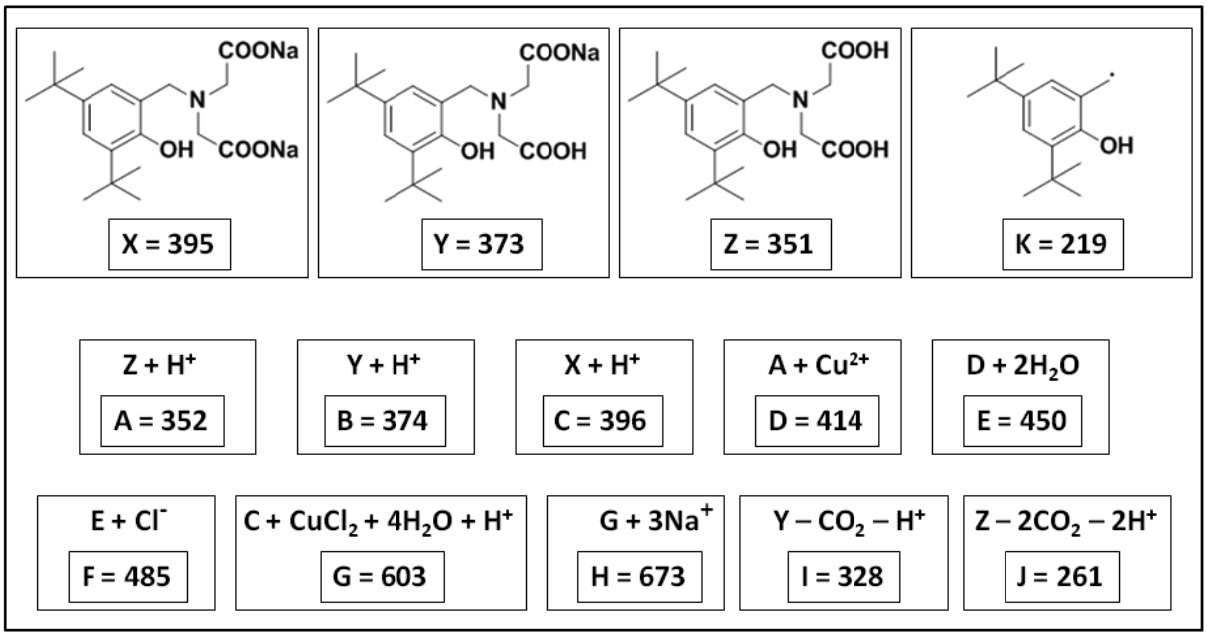


Figure S8. Index of peaks appearing in the MALDI-TOF spectrum

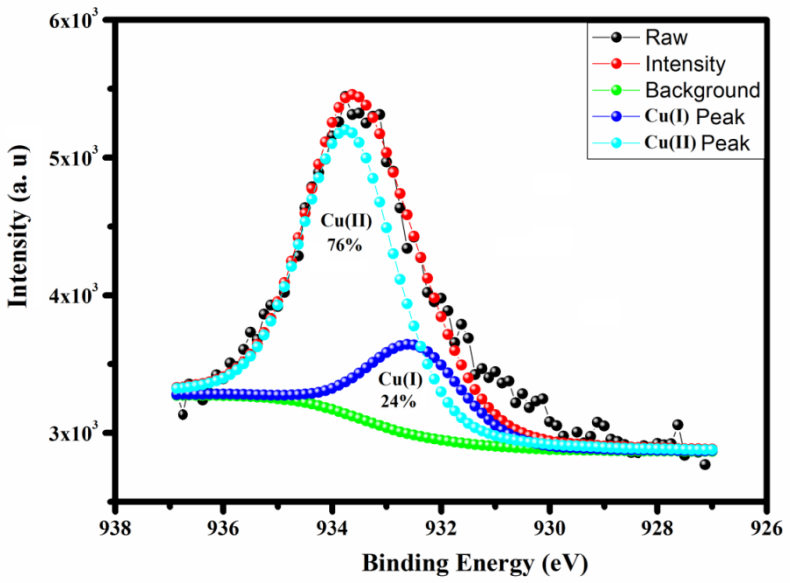


Figure S9. XPS spectrum of Cu-MOG

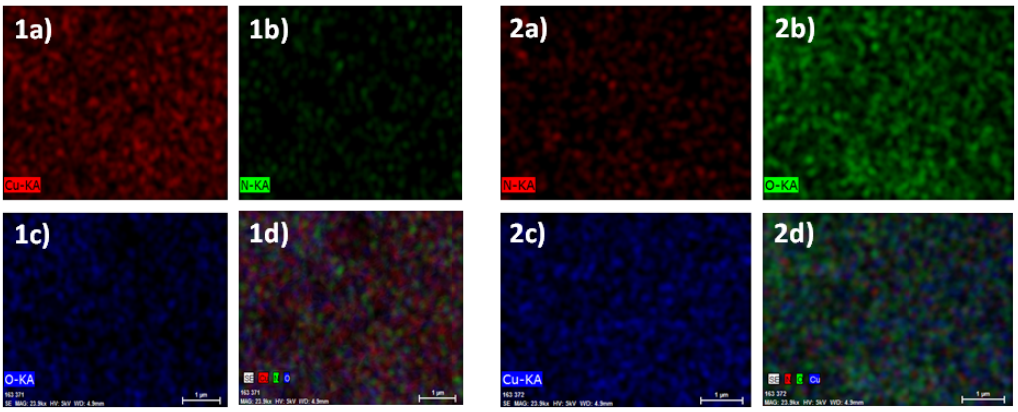


Figure S10. FESEM elemental analysis of Cu-MOG before (1) and after (2) catalysis

Table S1. Comparison of catalytic activity of present catalyst, Cu-MOG with the reported systems for the CuAAC reaction

Catalyst	Time (h)	mol%	Yield (%)	TOF (h^{-1})	References
Cu-MOG	6	2	91[a]	7.58	This work
Cu-MOG	6	2	89[b]	7.41	This work
Cu(I).3 gel	18	1	97[a]	5.38	1
Cu(I).3 gel	18	1	92[b]	5.11	1
MOF-1	12	1	99[a]	8.25	2
MOF-2	12	1	40[a]	3.33	2

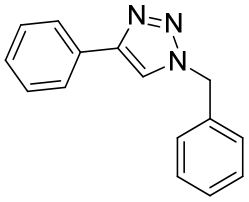
[a]Benzyl azide & phenyl acetylene, [b]benzyl azide & *p*-tolylacetylene as reactant.

Table S2. Comparison of gas adsorption behaviour of the Cu-MOG with reported metal xerogels

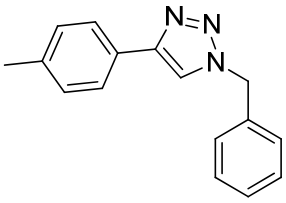
MOGs	N_2 uptake (cc/gm)	CO_2 uptake (cc/gm)	References
Cu-MOG	122	14	This work
BPPTP-Copper triflate gel	62	8	3
Ca-5TIA gel	–	32	4
Al-TCPE gel	170	–	5
TPPBT-Silver nitrate gel	29	–	6
MOG-1	58.95	–	7
MOG-2	29.21	–	7
MOG-3	18.90	–	7
MOG-4	9.15	–	7

Characterization Data of the Products

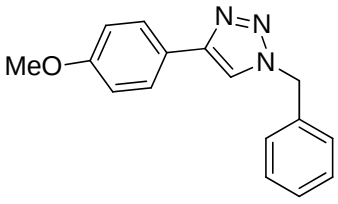
Except for the product of Table 2, entry 12 & 13, all the other products are known compounds.



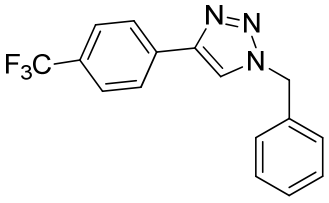
1-benzyl-4-phenyl-1H-1,2,3-triazole[8] **(Table 2, entry 1):** White solid; Yield: 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (m, 2H), 7.67 (s, 1H), 7.40–7.36 (m, 5H), 7.32–7.29 (m, 3H), 5.55 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.3, 134.8, 130.6, 129.3, 128.9, 128.9, 128.3, 128.2, 125.8, 119.7, 54.3.



1-benzyl-4-(p-tolyl)-1H-1,2,3-triazole[9] **(Table 2, entry 2):** White solid; Yield: 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69–7.62 (m, 3H), 7.38–7.29 (m, 5H), 7.21–7.19 (m, 2H), 5.55 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4, 138.1, 134.9, 129.6, 129.2, 128.8, 128.2, 127.8, 125.7, 119.3, 54.3, 21.4.

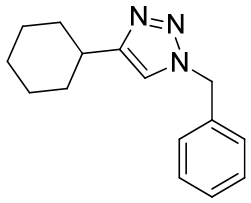


1-benzyl-4-(4-methoxyphenyl)-1H-1,2,3-triazole[8] **(Table 2, entry 3):** White solid; Yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73–7.71 (m, 2H), 7.57 (s, 1H), 7.37 (m, 3H), 7.31–7.30 (m, 2H), 6.94–6.92 (m, 2H), 5.56 (s, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 148.2, 134.9, 129.2, 128.8, 128.1, 127.1, 123.4, 118.8, 114.3, 55.4, 54.3.

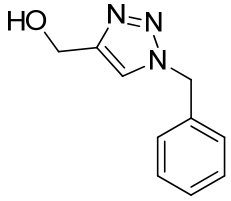


1-benzyl-4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole[8] **(Table 2, entry 4):** White solid; Yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.89 (m, 2H), 7.76 (s,

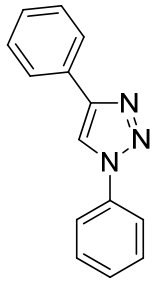
1H), 7.64–7.62 (m, 2H), 7.42–7.38 (m, 3H), 7.35–7.30 (m, 2H), 5.57 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 134.5, 134.1, 130.2 (q, J = 32.3 Hz), 129.4, 129.1, 128.2, 126.0, 125.9 (q, J = 3.7 Hz), 125.6 (q, J = 270.3 Hz), 120.4, 54.5.



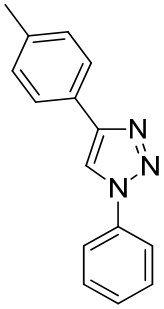
1-benzyl-4-cyclohexyl-1H-1,2,3-triazole[8] **(Table 2, entry 5):** White solid; Yield: 76%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.34 (m, 3H), 7.26–7.24 (m, 2H), 7.13 (s, 1H), 5.48 (s, 2H), 2.74–2.73 (m, 1H), 2.03–2.01 (m, 2H), 1.77 (m, 2H), 1.70 (m, 1H), 1.39–1.31 (m, 4H), 1.22 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3, 135.1, 129.1, 128.7, 128.1, 119.3, 54.1, 35.4, 33.1, 32.9, 26.2, 26.1.



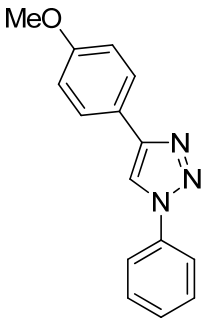
(1-benzyl-1H-1,2,3-fdtriazol-4-yl)methanol[8] **(Table 2, entry 6):** White solid; Yield: 51%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.38–7.34 (m, 3H), 7.27–7.25 (m, 2H), 5.50 (d, J = 4.0 Hz, 2H), 4.75 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 134.6, 129.2, 128.9, 128.2, 121.7, 56.6, 54.3.



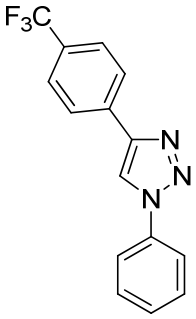
1,4-diphenyl-1H-1,2,3-triazole[10] **(Table 2, entry 7):** White solid; Yield: 53%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.92 (d, J = 7.2 Hz, 2H), 7.81 (d, J = 8 Hz, 2H), 7.55 (t, J = 8 Hz, 2H), 7.48–7.44 (m, 3H), 7.39–7.35 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 137.2, 130.3, 129.9, 129.1, 128.9, 128.6, 126.0, 120.7, 117.7.



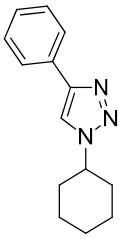
1-phenyl-4-(p-tolyl)-1H-1,2,3-triazole[10] **(Table 2, entry 8):** White solid; Yield: 53%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.80 (m, 4H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.27 (s, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 138.4, 137.5, 129.9, 129.7, 128.8, 127.8, 125.9, 120.6, 117.4, 21.4.



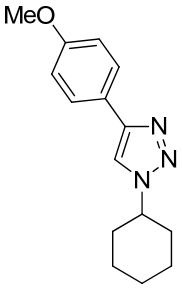
4-(4-methoxyphenyl)-1-phenyl-1H-1,2,3-triazole[10] **(Table 2, entry 9):** White solid; Yield: 56%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.78-7.76 (m, 2H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.45-7.41 (m, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 148.4, 137.2, 129.9, 128.8, 127.3, 123.1, 120.6, 116.9, 114.4, 55.5.



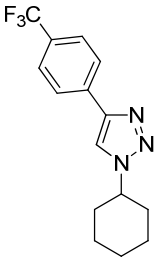
1-phenyl-4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole[11] **(Table 2, entry 10):** White solid; Yield: 52%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H), 8.17 (d, 2H, *J* = 8.0 Hz), 7.96 (d, 2H, *J* = 8.4 Hz), 7.88 (d, 2H, *J* = 8 Hz), 7.66 (t, 2H, *J* = 7.6 Hz), 7.54 (br s, 1H); 13C NMR (100 MHz, DMSO-d_6) δ 146.3, 136.9, 134.7, 130.4, 129.4, 128.9 (q, *JC-CF*$_3$ = 31.8 Hz), 126.5 (q, *JC-CF*$_3$ = 3.8 Hz), 126.3, 126.0 (q, *JC-CF*$_3$ = 270.6 Hz), 121.4, 120.6.



1-cyclohexyl-4-phenyl-1H-1,2,3-triazole[8] **(Table 2, entry 11):** White solid; Yield: 52%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.77 (s, 1H), 7.43 (m, 2H), 7.33 (m, 1H), 4.52 (tt, *J* = 12.0, 4.0 Hz, 1H), 2.26 (m, 2H), 1.95 (m, 2H), 1.83–1.75 (m, 3H), 1.48 (m, 2H), 1.32 (tt, *J* = 12.5, 3.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 130.9, 128.8, 127.9, 125.6, 117.2, 60.1, 33.6, 25.2, 25.1.

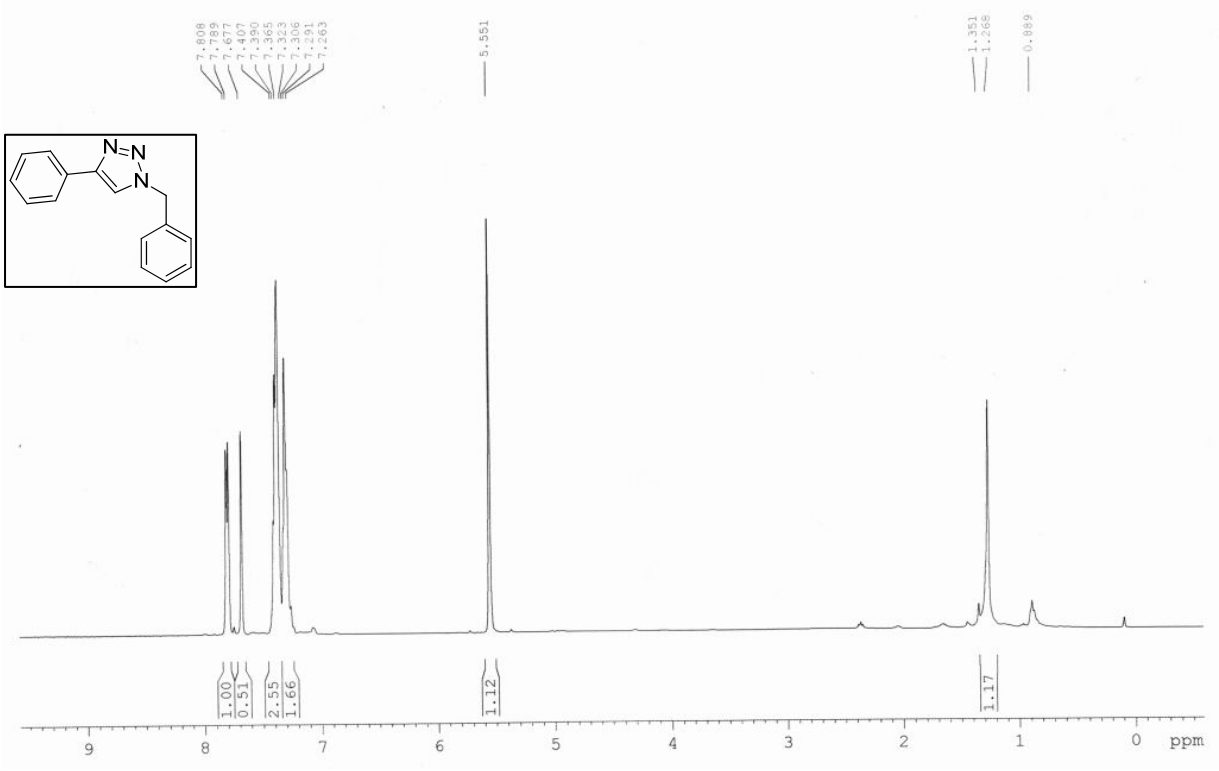


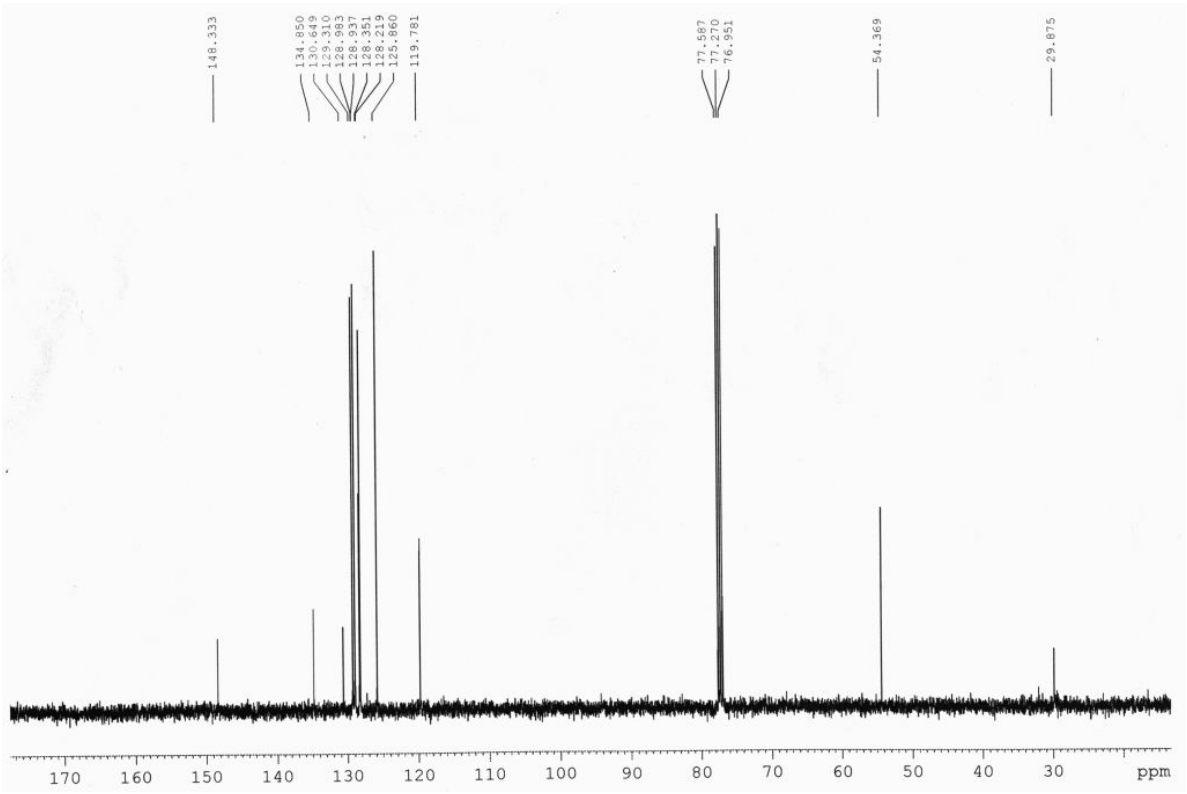
1-cyclohexyl-4-(4-methoxyphenyl)-1H-1,2,3-triazole (Table 2, entry 12): Light yellow solid; Yield: 52%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.8 Hz, 2H), 7.67 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 4.51 (m, 1H), 3.83 (s, 3H), 2.26–2.22 (m, 2H), 1.95–1.91 (m, 2H), 1.83–1.72 (m, 3H), 1.52–1.41 (m, 2H), 1.34–1.24 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 147.0, 127.0, 123.3, 116.6, 114.2, 60.2, 55.3, 33.5, 25.2, 25.1. HRMS (ESI): m/z calcd for $C_{15}H_{20}N_3O$ $[M + H]^+$, 258.1606, found: 258.1601.

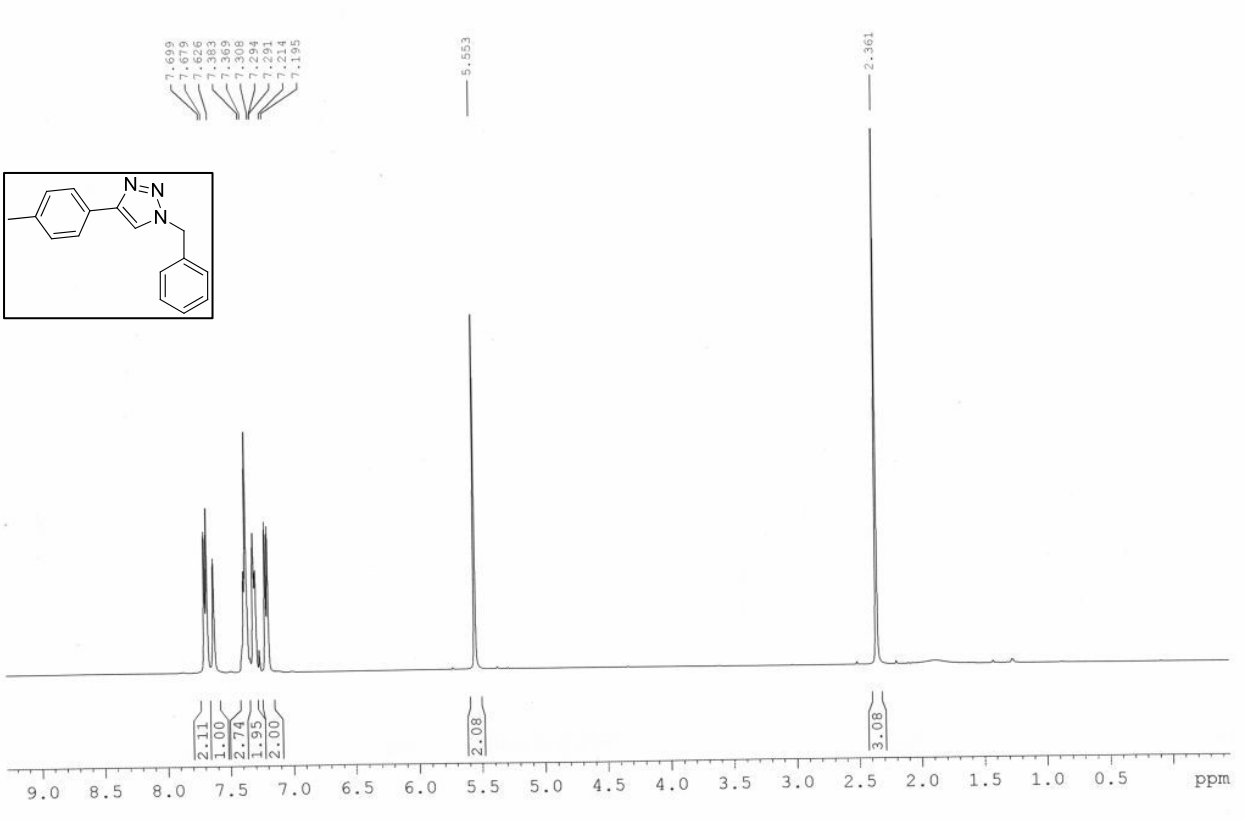


1-cyclohexyl-4-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (Table 2, entry 13): White solid; Yield: 52%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.4 Hz, 2H), 7.85 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 2H), 4.52–4.44 (m, 1H), 2.26–2.22 (m, 2H), 1.95–1.90 (m, 2H), 1.83–1.73 (m, 3H), 1.52–1.41 (m, 2H), 1.34–1.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.0, 134.5, 130.3 (q, *JC-CF3* = 32.3 Hz), 128.3. 125.9 (q, *JC-CF*$_3$ = 4.9 Hz), 125.6 (q, *JC-CF*$_3$ = 270.0 Hz), 118.3, 60.4, 33.7, 25.3, 25.2. HRMS (ESI): m/z calcd for $C_{15}H_{17}N_3F_3$ $[M + H]^+$, 296.1375, found: 296.1361.

NMR Spectra (^{1}H, ^{13}C) (Products for CuAAC reaction)



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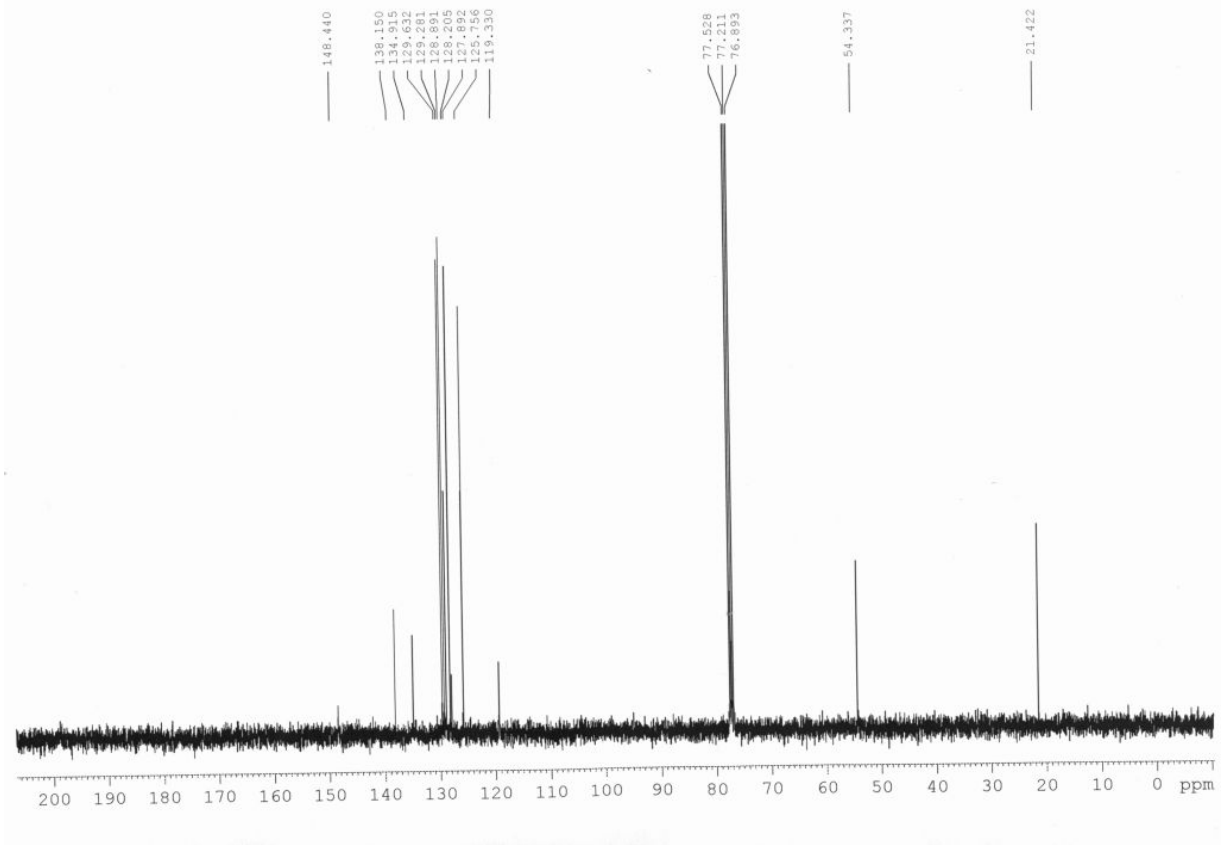
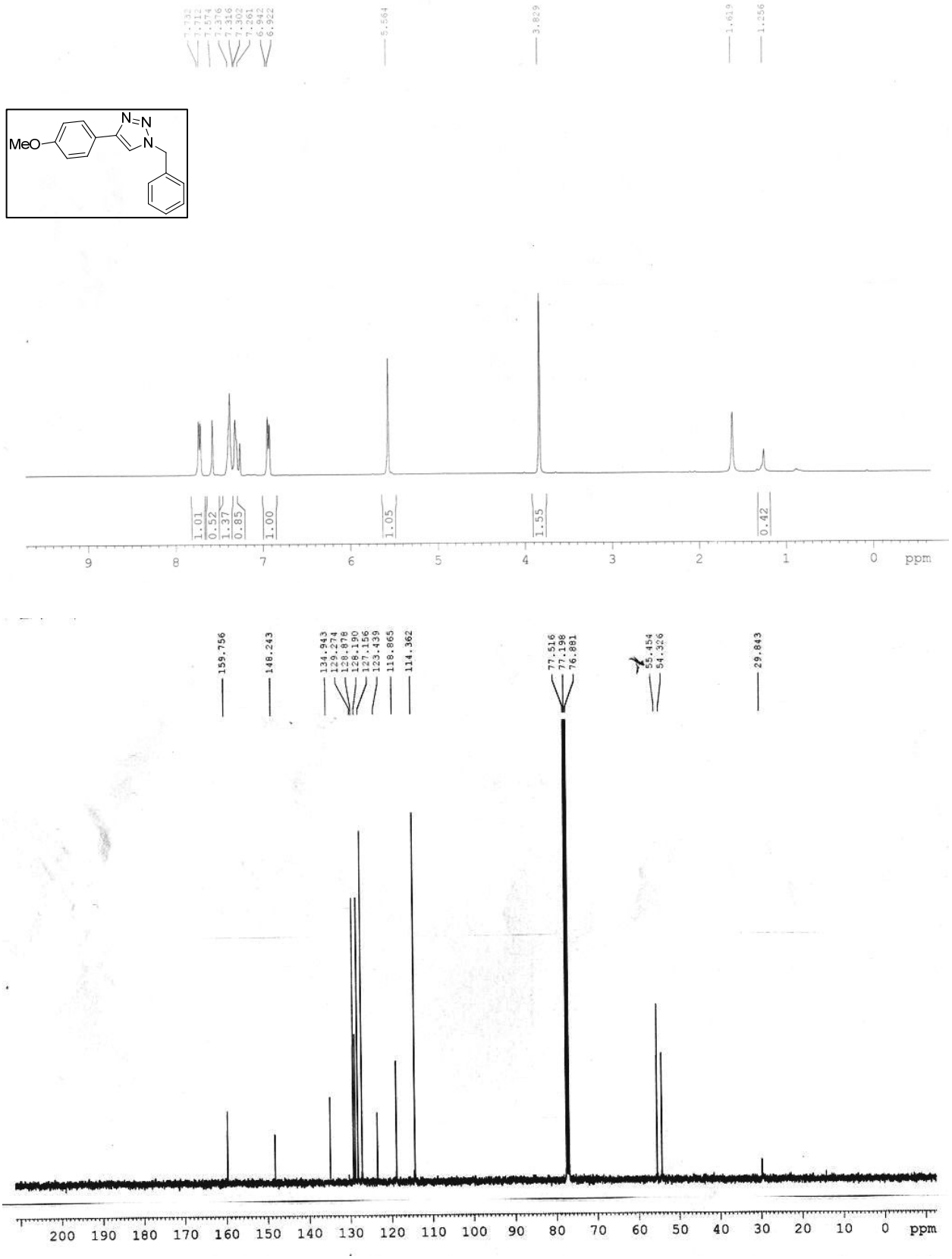
7.369
7.308
7.294
7.291
7.214
7.195
5.553
2.361
2.11
1.00
2.74
1.95
2.00
2.08
3.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


148.440
138.150
134.915
129.632
129.281
128.891
128.205
127.892
125.756
119.330
77.528
77.211
76.893
54.337
21.422
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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7.302
7.261
6.942
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5.564
3.829
1.619
1.256
MeO
N
N
N
1.01
0.52
1.37
0.85
1.00
1.05
1.55
0.42
9
8
7
6
5
4
3
2
1
0
ppm
159.756
148.243
134.943
129.274
128.878
128.190
127.156
123.439
118.865
114.362
77.516
77.198
76.881
55.454
54.326
29.843
200
190
180
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150
140
130
120
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80
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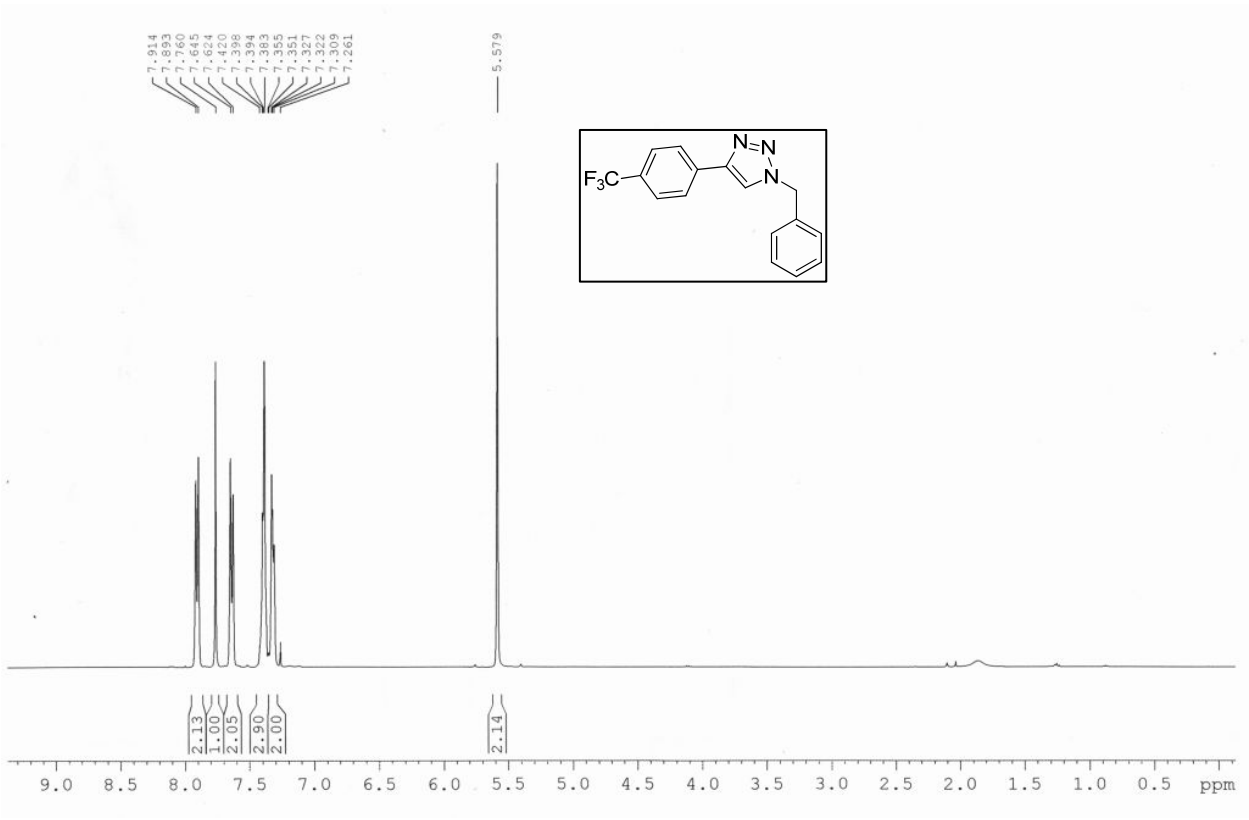
60
50
40
30
20
10
0
ppm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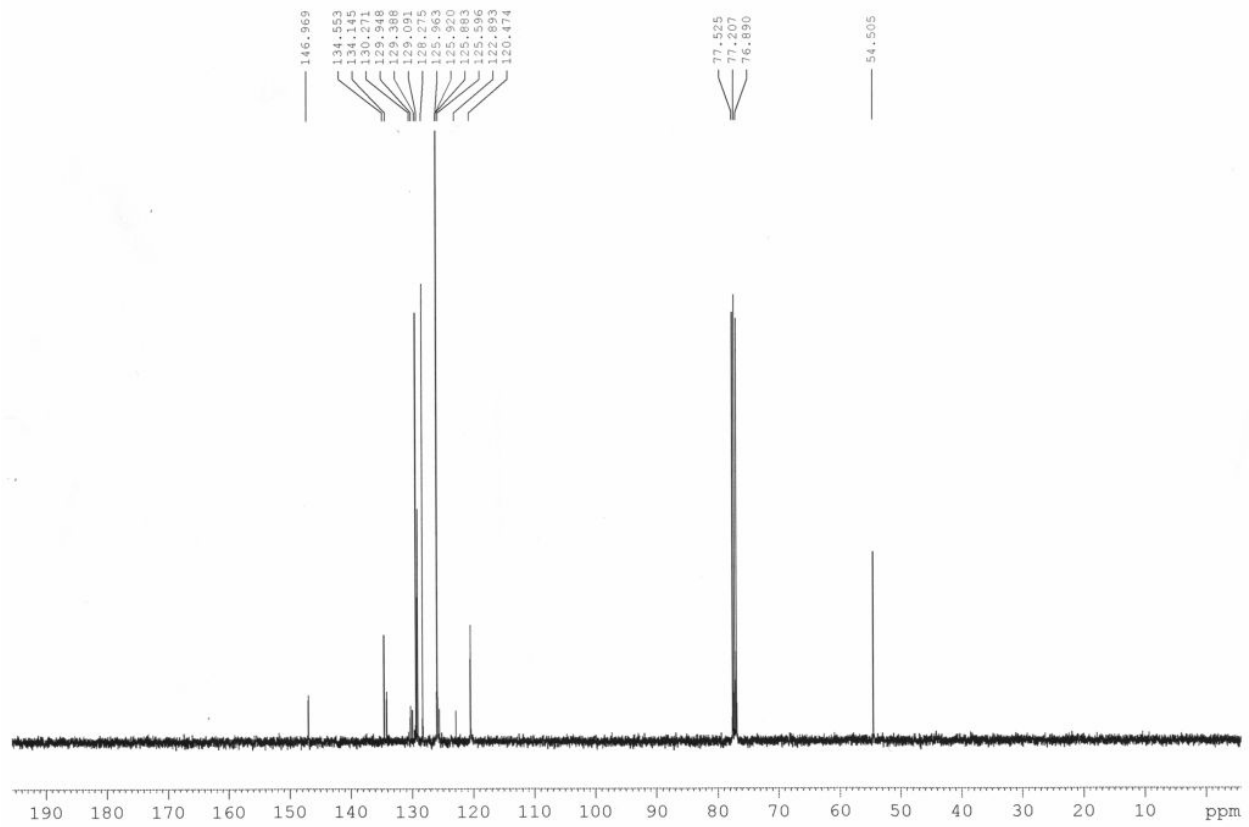
7.893
7.760
7.645
7.624
7.420
7.398
7.394
7.383
7.355
7.351
7.327
7.322
7.309
7.261
5.579
2.13
1.00
2.05
2.90
2.00
2.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm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128.275
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125.920
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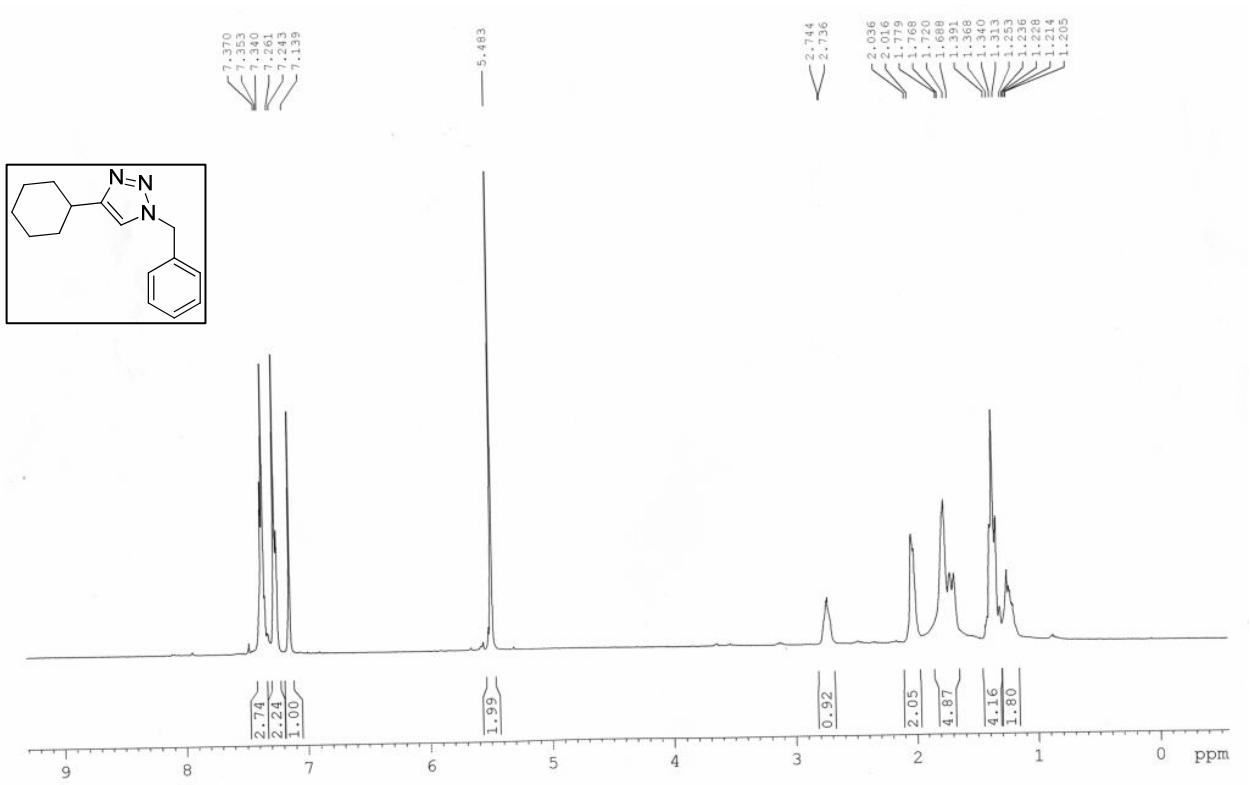
120.474
77.525
77.207
76.890
54.505
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.353
7.340
7.261
7.243
7.139
5.483
2.744
2.736
2.036
2.016
1.779
1.768
1.720
1.688
1.391
1.368
1.340
1.323
1.253
1.226
1.214
1.205
2.74
2.24
1.00
1.99
0.92
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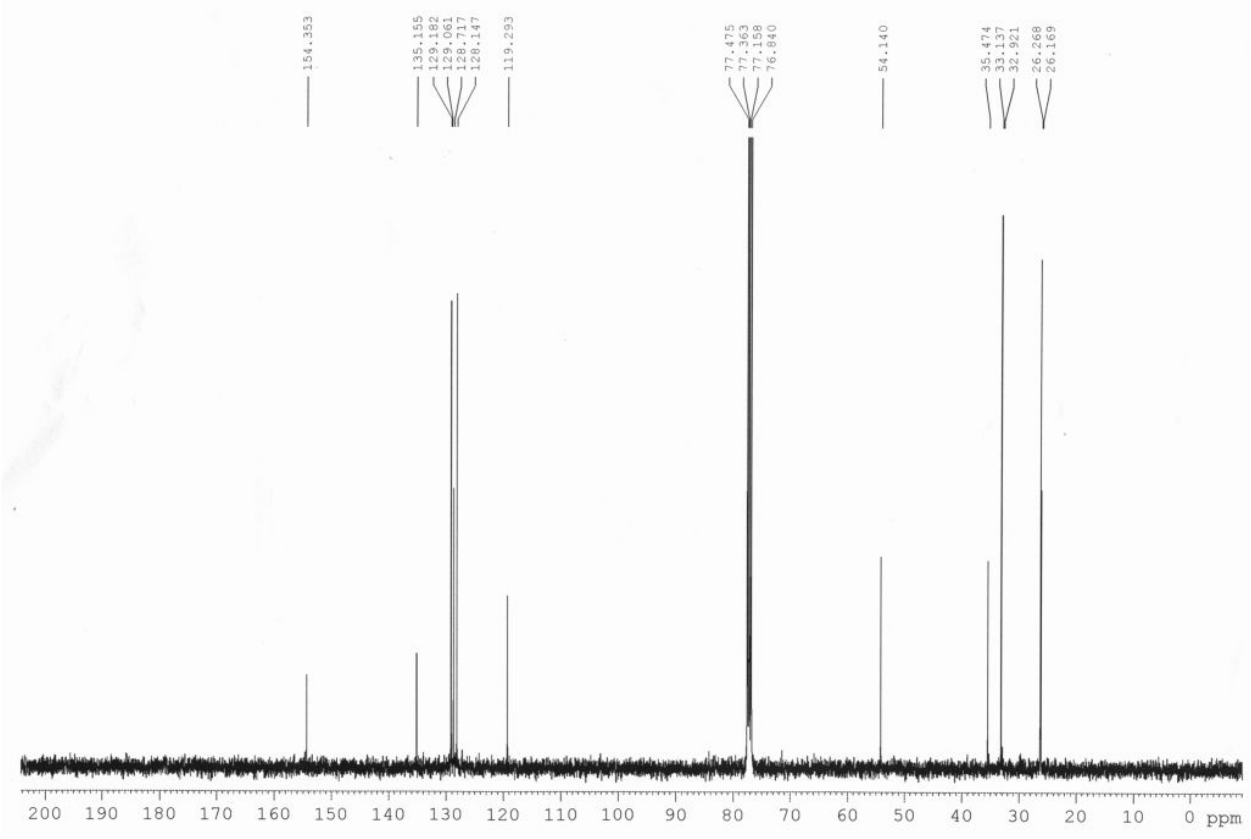
4.87
4.16
1.80
9
8
7
6
5
4
3
2
1
0
ppm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135.155
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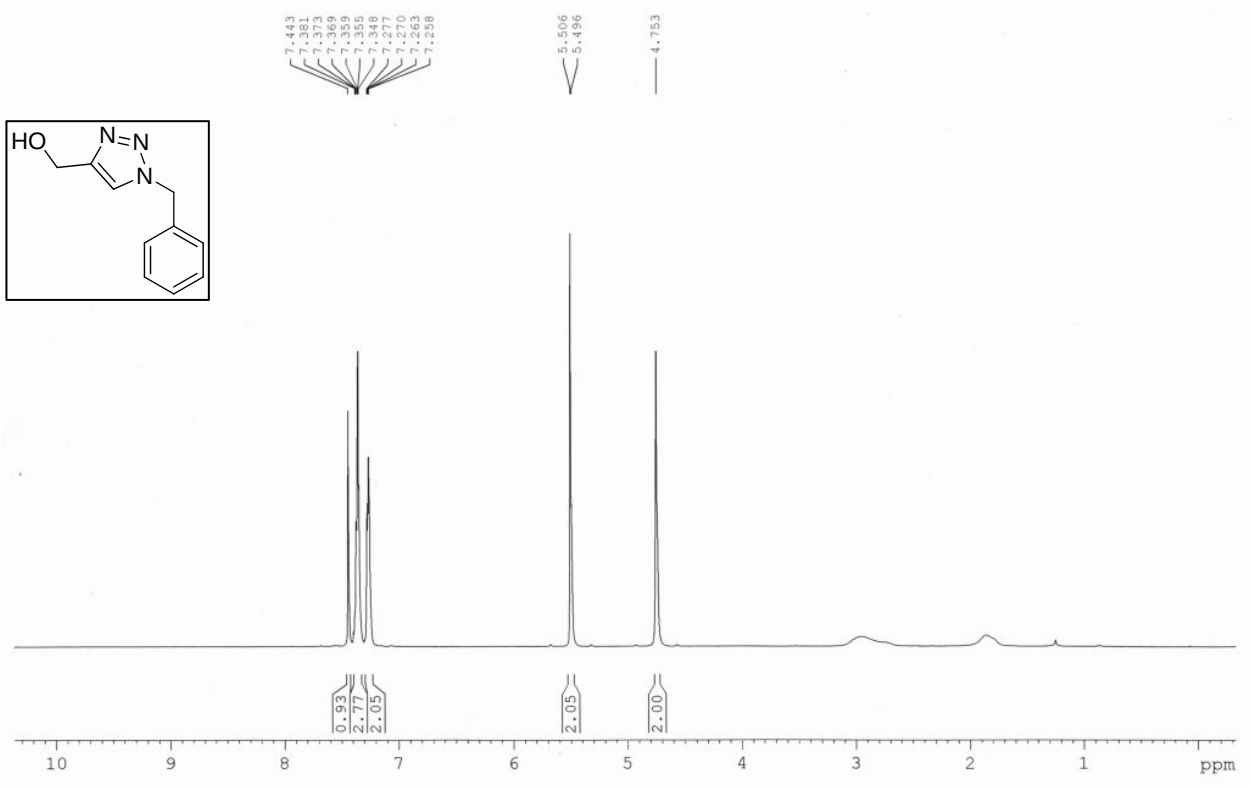
129.061
128.717
128.147
119.293
77.475
77.363
77.158
76.840
54.140
35.474
33.137
32.921
26.268
26.169
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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7.381
7.373
7.369
7.359
7.355
7.348
7.277
7.270
7.263
7.258
5.506
5.496
4.753
HO
N=N
N
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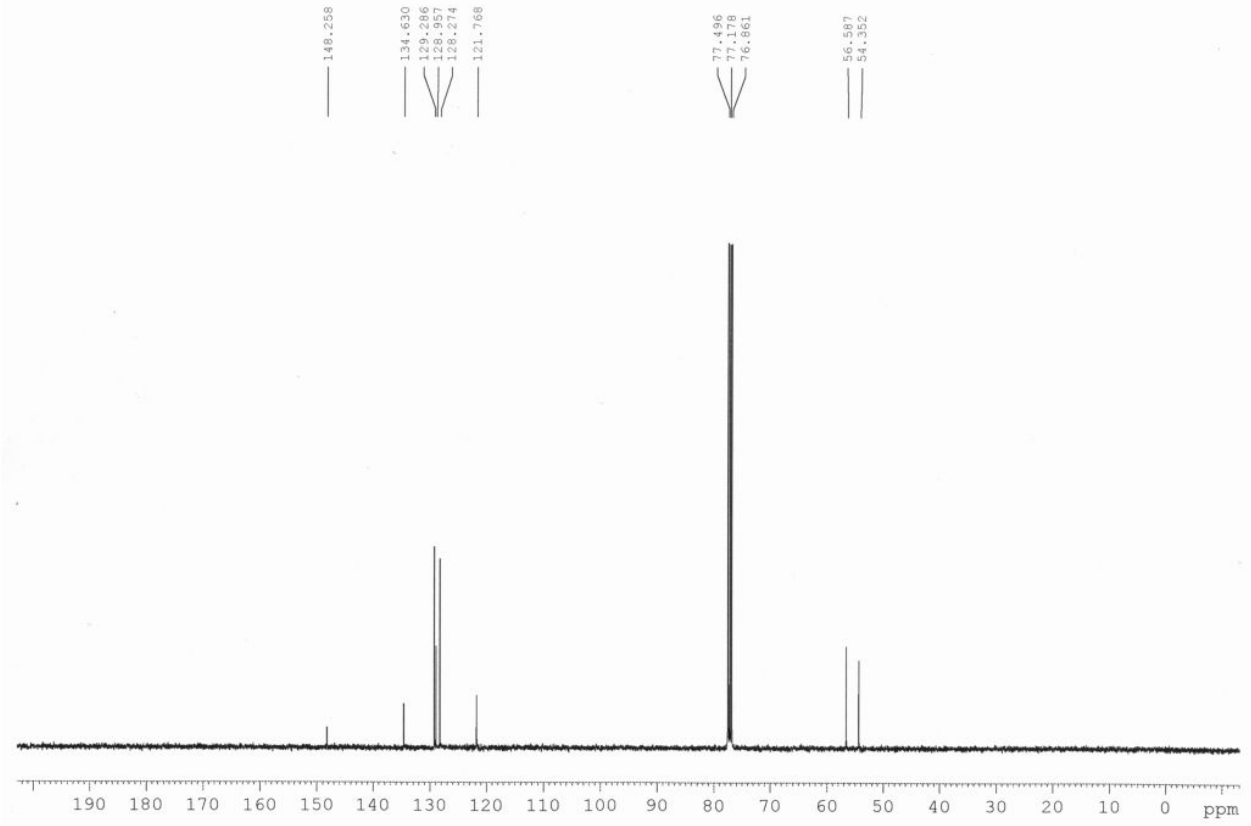
2.05
2.05
2.00
10
9
8
7
6
5
4
3
2
1
ppm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128.957
128.274
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77.178
76.861
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54.352
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120
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80
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60
50
40
30
20
10
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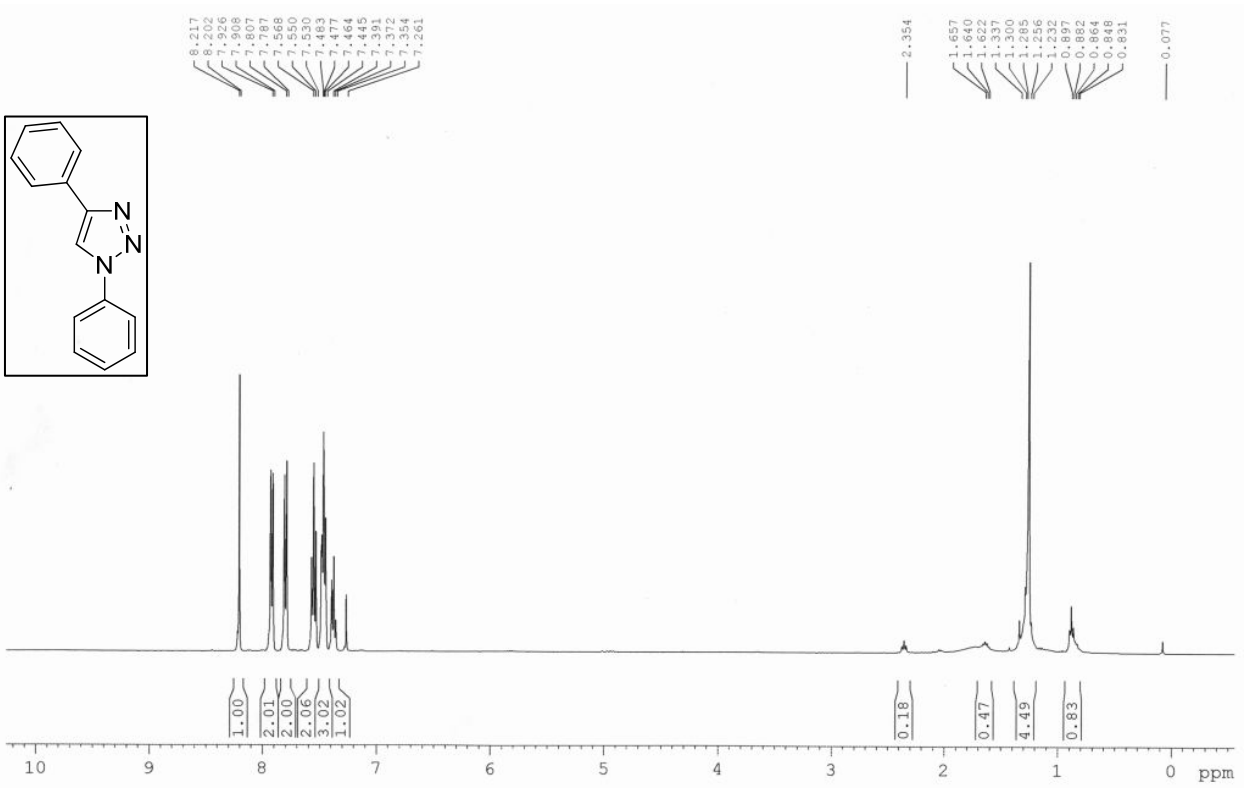
ppm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7.926
7.908
7.807
7.787
7.568
7.550
7.530
7.483
7.477
7.464
7.445
7.391
7.372
7.354
7.261
2.354
1.657
1.640
1.622
1.337
1.300
1.285
1.256
1.232
0.897
0.882
0.864
0.848
0.831
0.077
N
N
N
1.00
2.01
2.00
2.06
3.02
1.02
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6
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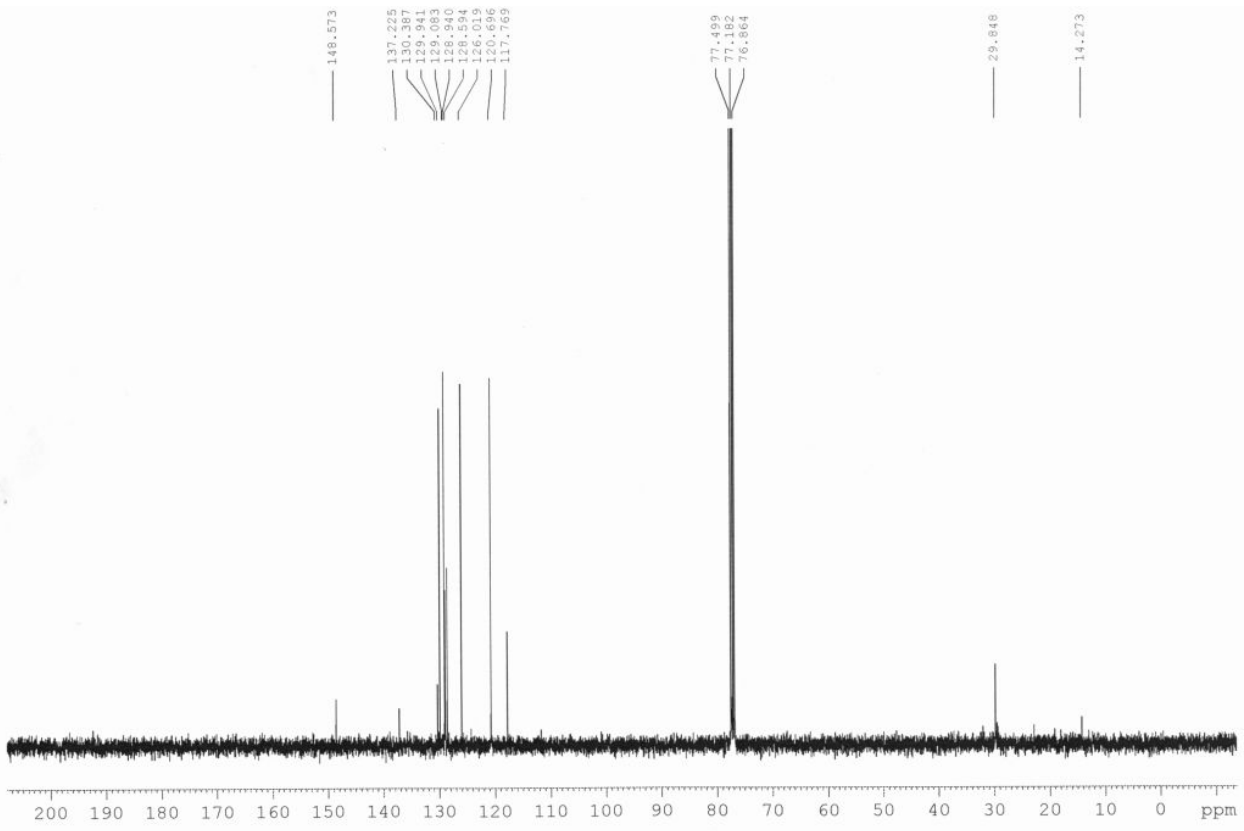
ppm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129.941
129.083
128.940
128.594
126.019
120.696
117.769
77.499
77.182
76.864
29.848
14.273
200
190
180
170
160
150
140
130
120
110
100
90
80
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60
50
40
30
20
10
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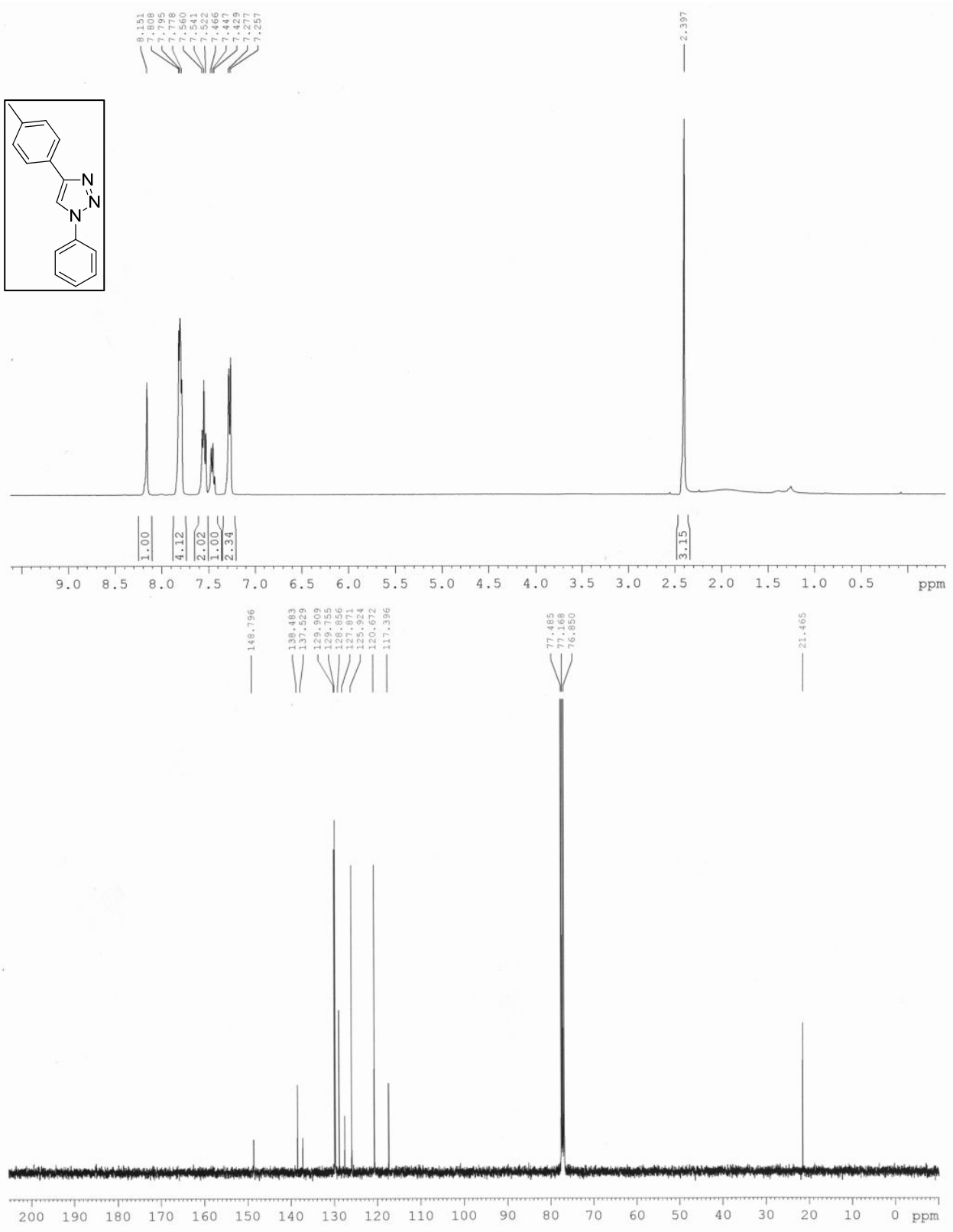
ppm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7.795
7.778
7.560
7.541
7.522
7.466
7.447
7.429
7.277
7.257
2.397
1.00
4.12
2.02
1.00
2.34
3.15
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
148.796
138.483
137.529
129.909
129.755
128.856
127.871
125.924
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76.850
21.465
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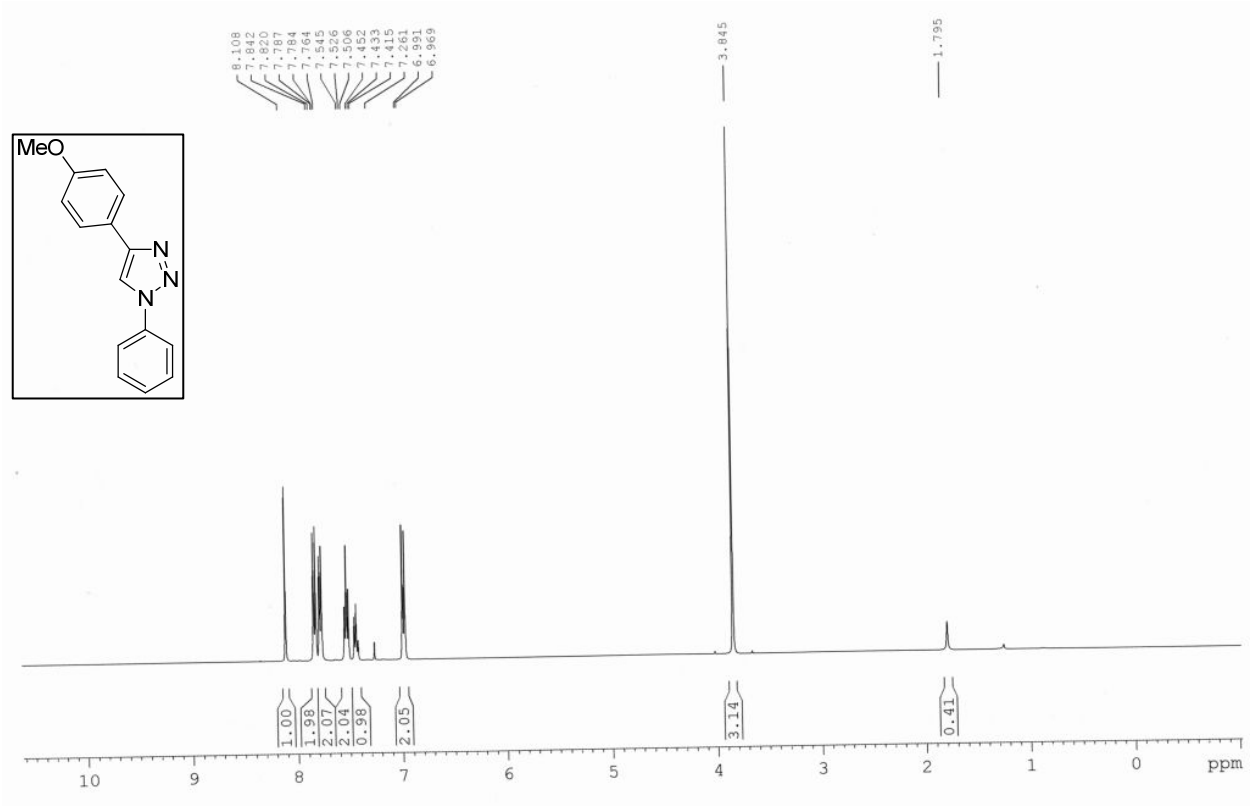
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7.820
7.787
7.784
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7.545
7.526
7.506
7.452
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7.415
7.261
6.991
6.969
3.845
1.795
MeO
N
N
N
1.00
1.98
2.07
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9
8
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6
5
4
3
2
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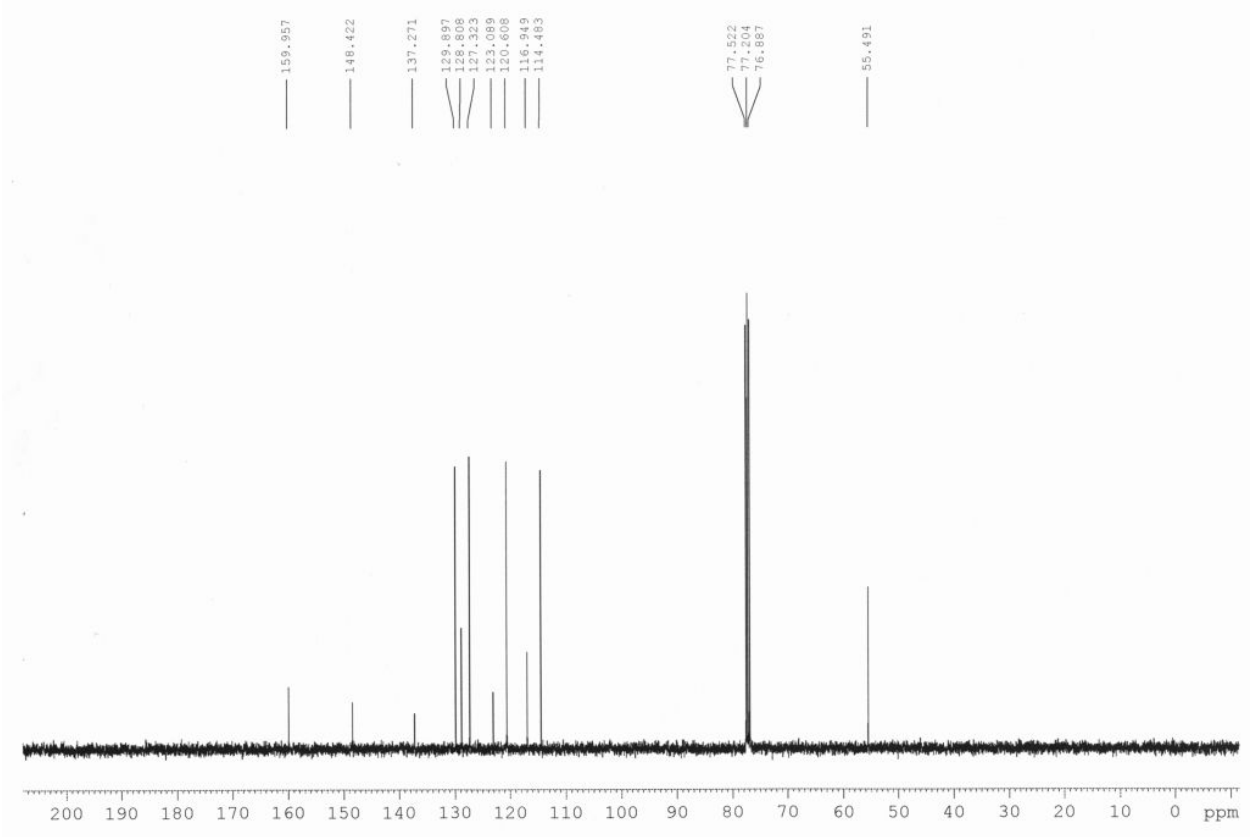
0
ppm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123.089
120.608
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55.491
200
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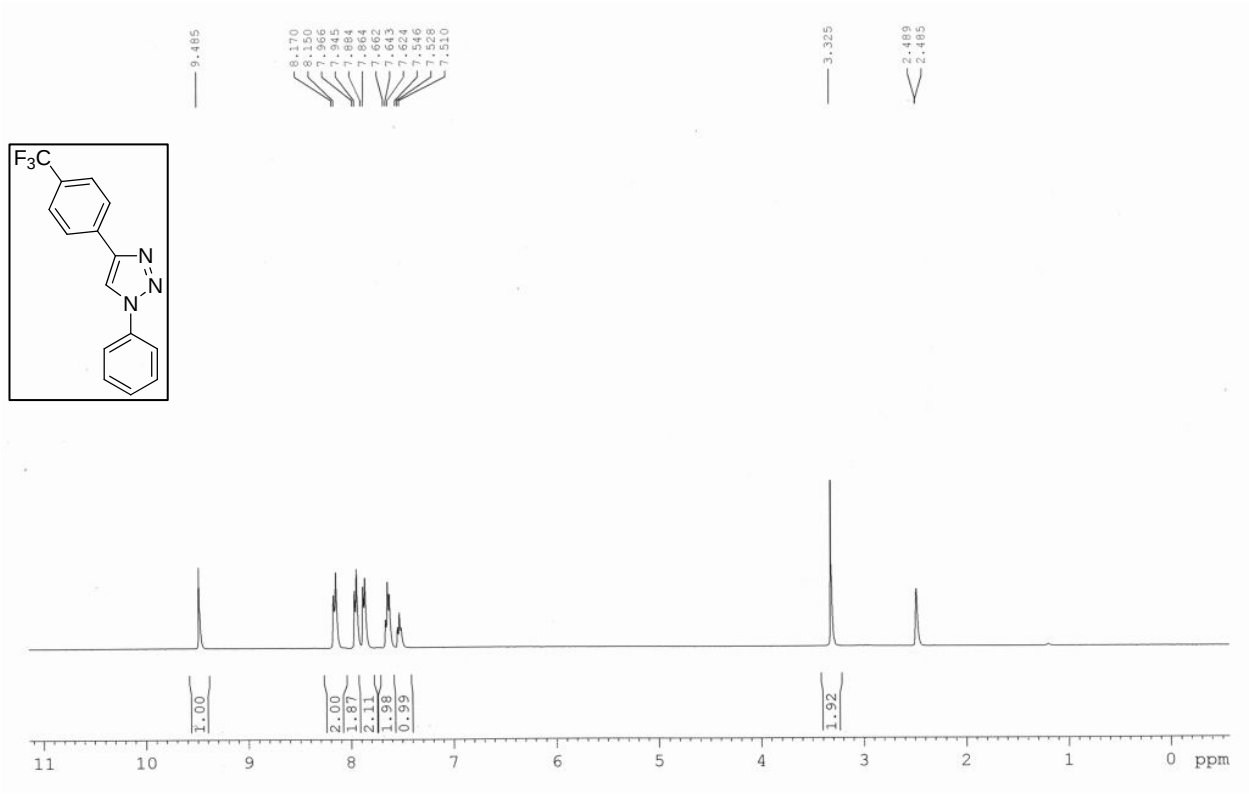
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7.662
7.643
7.624
7.546
7.528
7.510
3.325
2.489
2.485
F3C
N
N
N
1.00
2.00
1.87
2.11
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0.99
1.92
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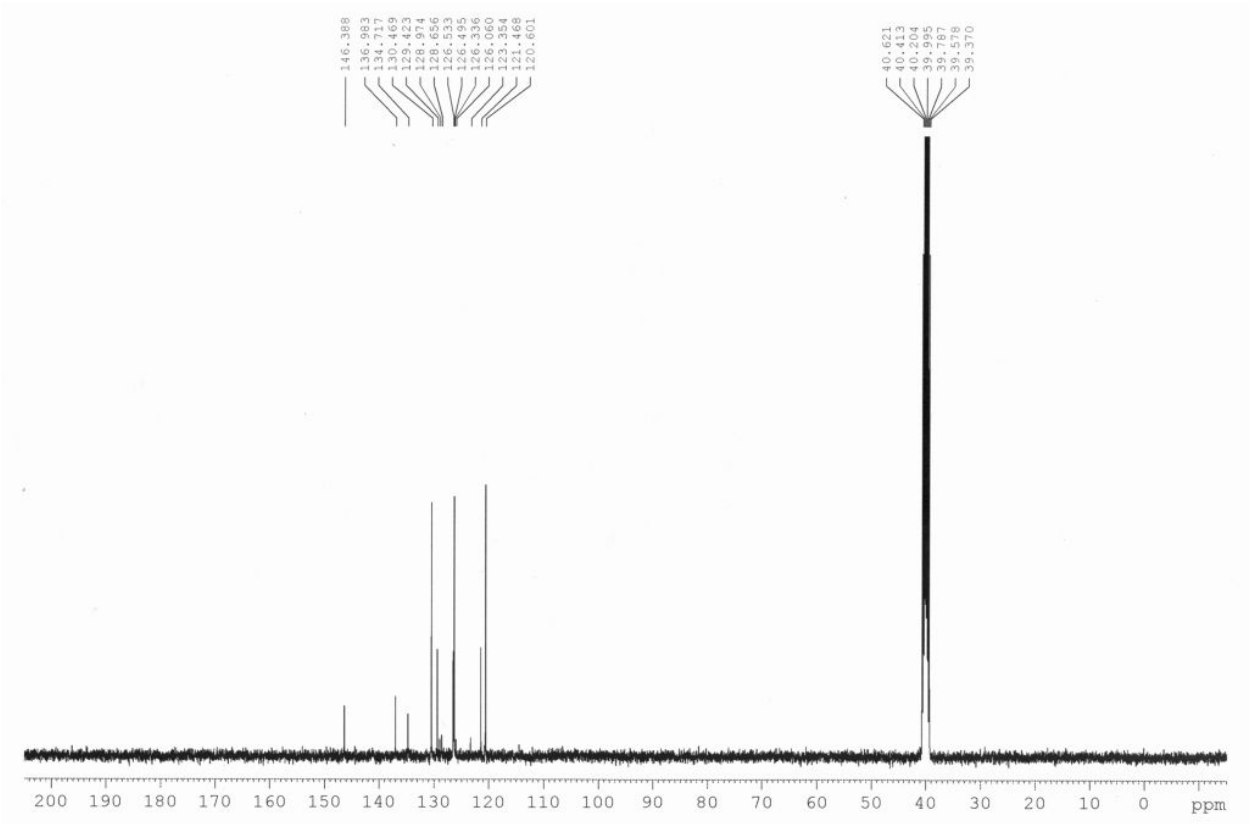
10
9
8
7
6
5
4
3
2
1
0
ppm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120.601
40.621
40.413
40.204
39.995
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39.578
39.370
200
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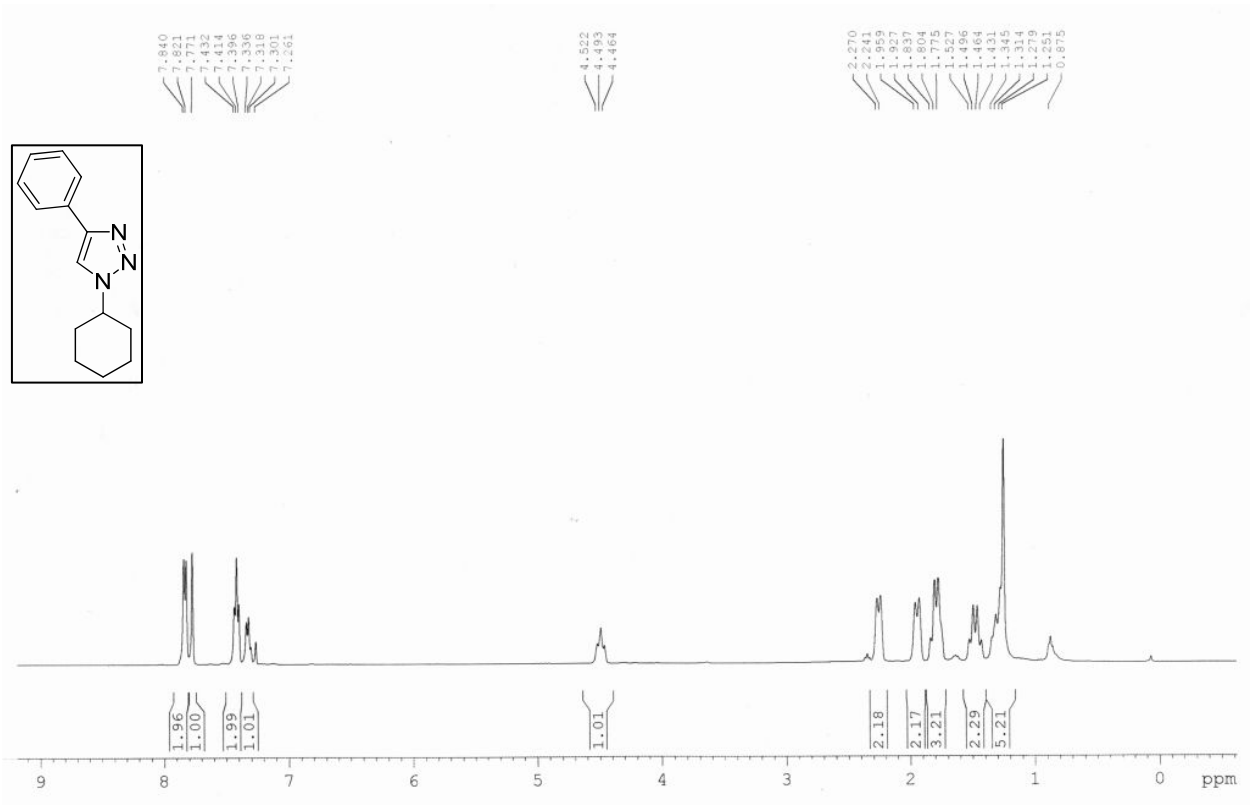
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7.318
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7.261
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4.464
2.270
2.241
1.959
1.927
1.837
1.804
1.775
1.527
1.496
1.464
1.431
1.345
1.314
1.279
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N
N
N
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2.29
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8
7
6
5
4
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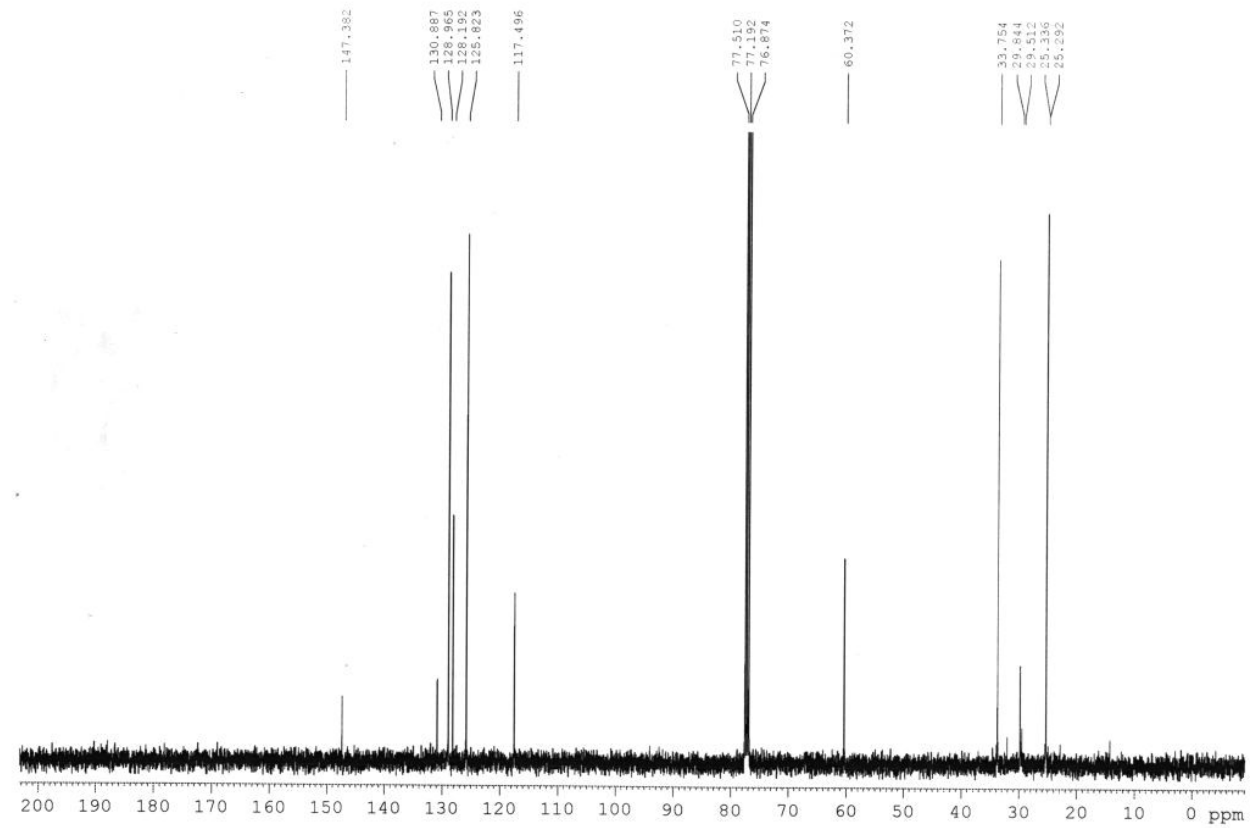
ppm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200
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180
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50
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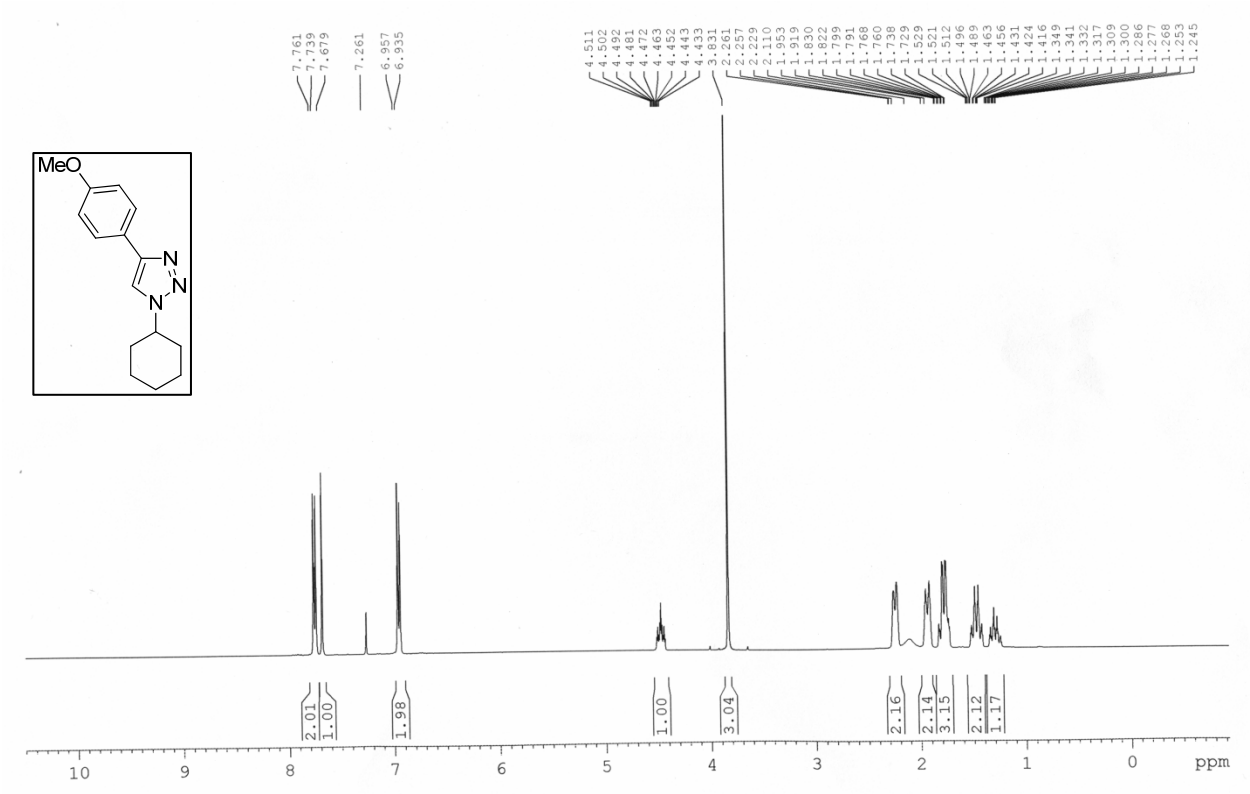
20
10
0
ppm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4.511
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4.492
4.481
4.472
4.463
4.452
4.443
4.433
3.831
2.261
2.257
2.229
2.110
1.953
1.919
1.830
1.822
1.799
1.791
1.768
1.760
1.738
1.729
1.529
1.521
1.512
1.496
1.489
1.463
1.456
1.431
1.424
1.416
1.349
1.341
1.332
1.317
1.309
1.300
1.286
1.277
1.268
1.253
1.245
2.01
1.00
1.98
1.00
3.04
2.16
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2.12
1.17
10
9
8
7
6
5
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3
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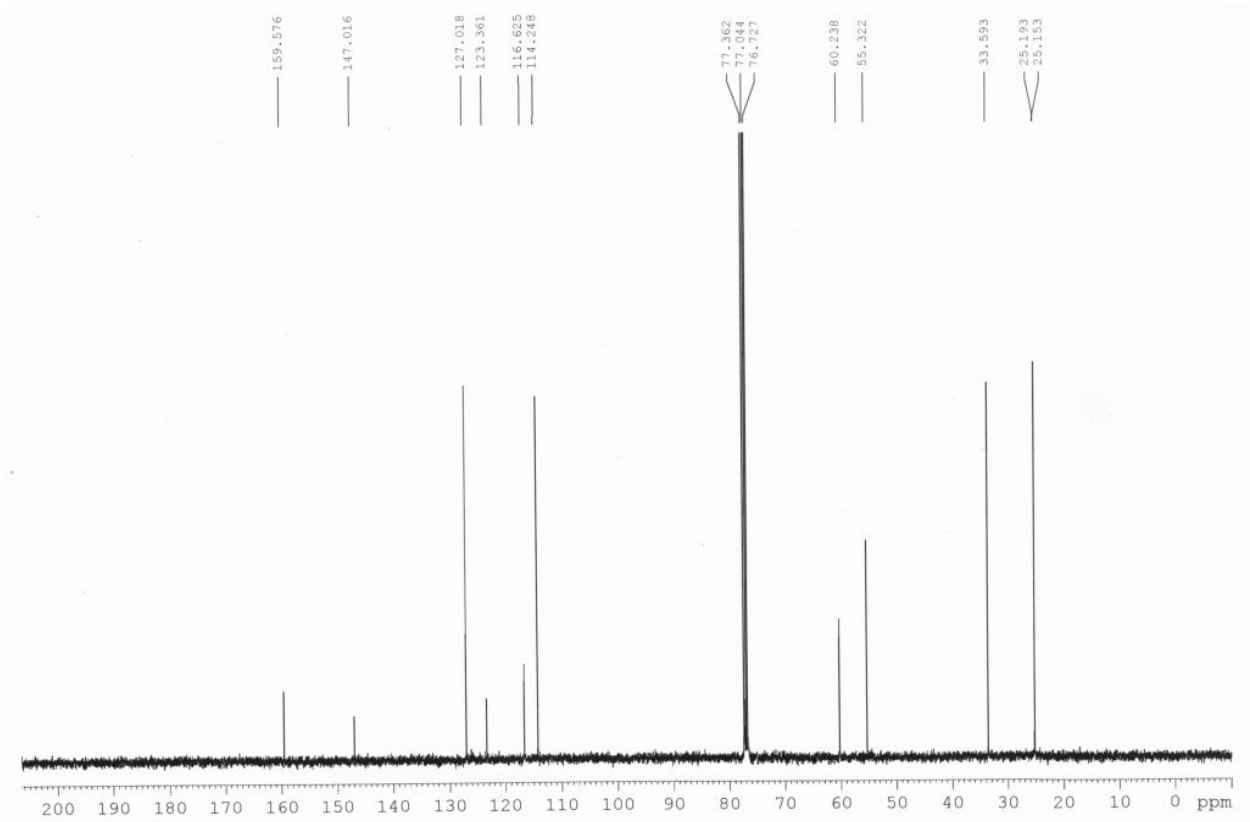
ppm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25.153
200
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140
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100
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60
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20
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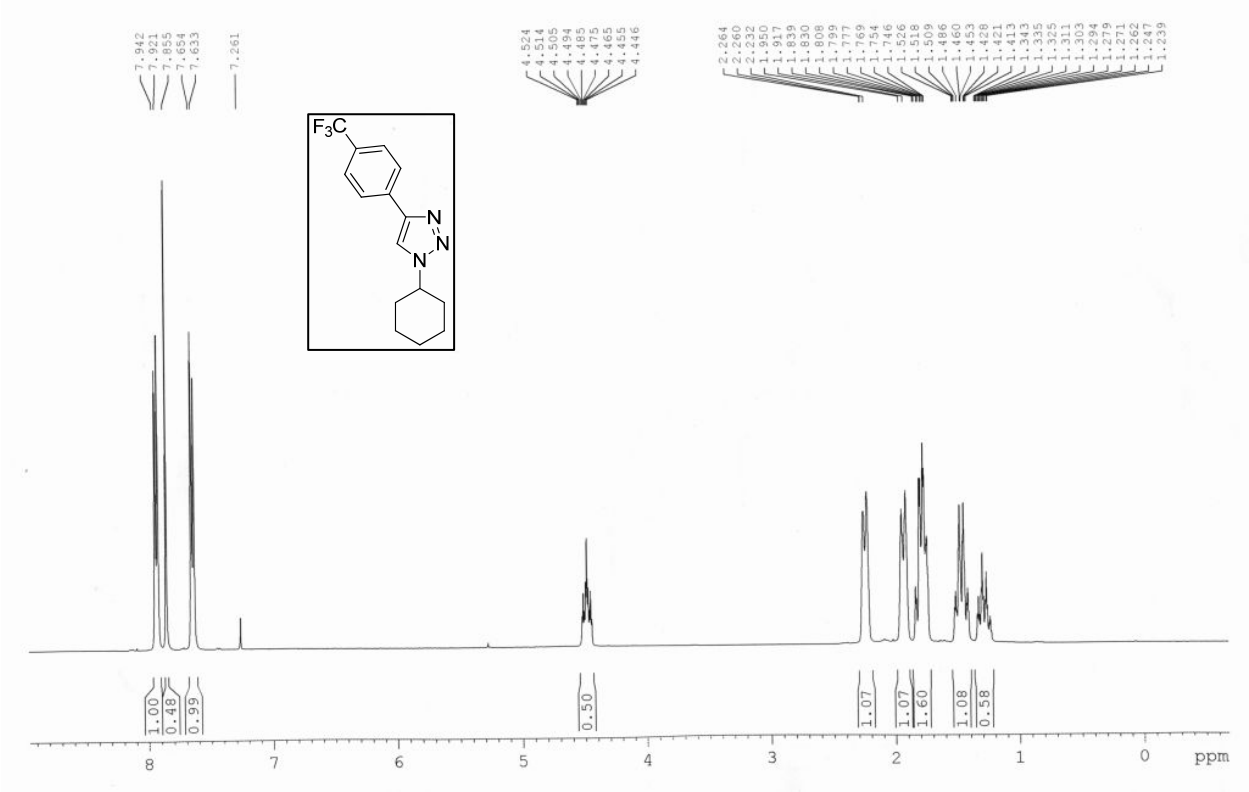
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4.465
4.455
4.446
2.264
2.260
2.232
1.950
1.917
1.839
1.830
1.808
1.799
1.777
1.769
1.754
1.746
1.526
1.518
1.509
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1.453
1.428
1.421
1.413
1.343
1.335
1.325
1.311
1.303
1.294
1.279
1.271
1.262
1.247
1.239
F3C
N
N
N
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0.48
0.99
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7
6
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3
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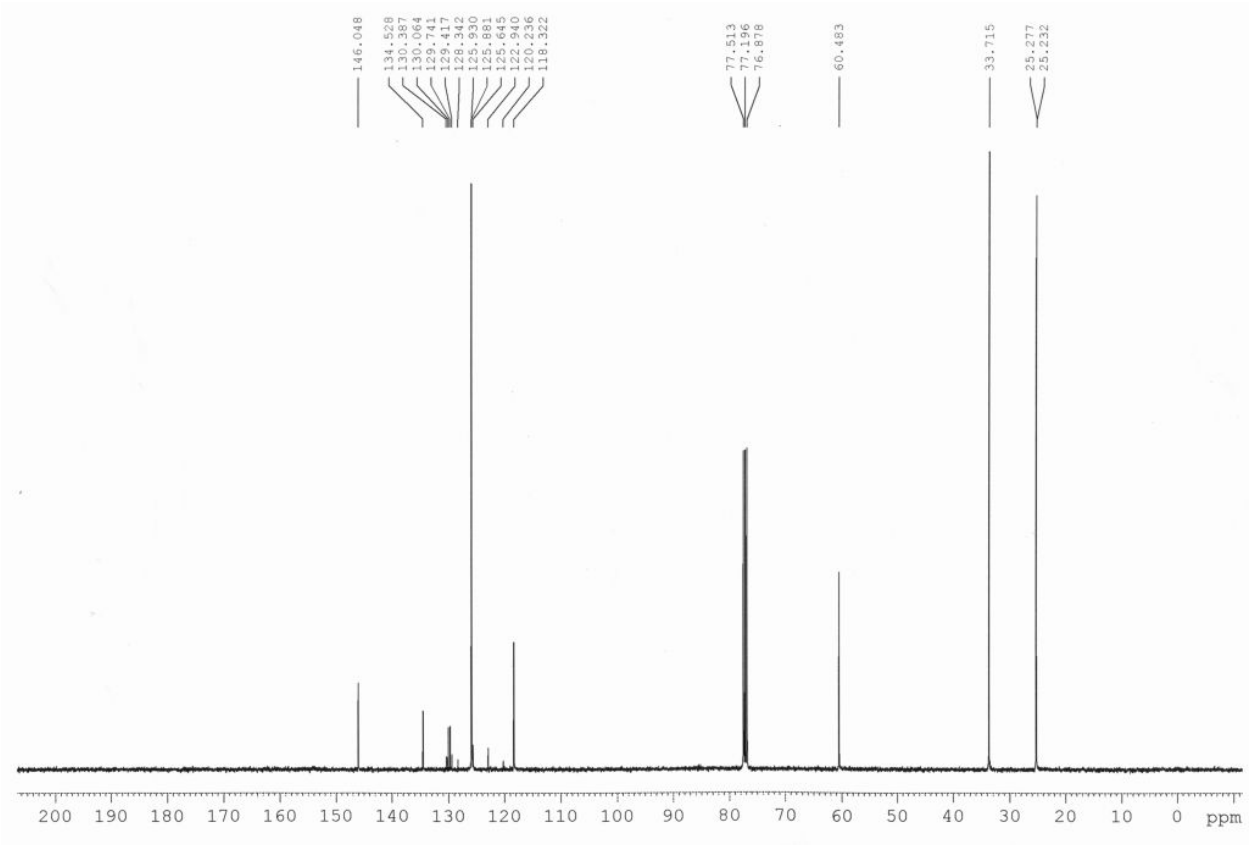
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120.236
118.322
77.513
77.196
76.878
60.483
33.715
25.277
25.232
200
190
180
170
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120
110
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80
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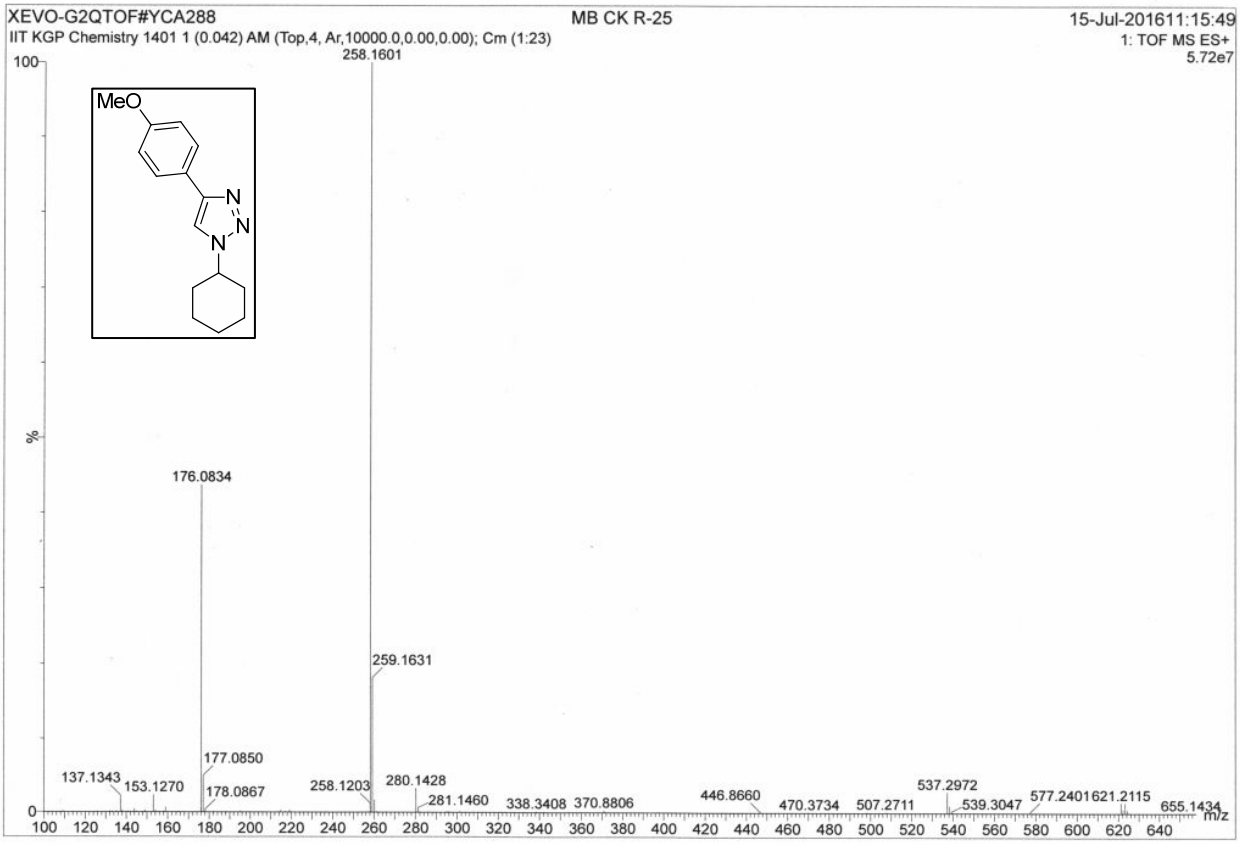
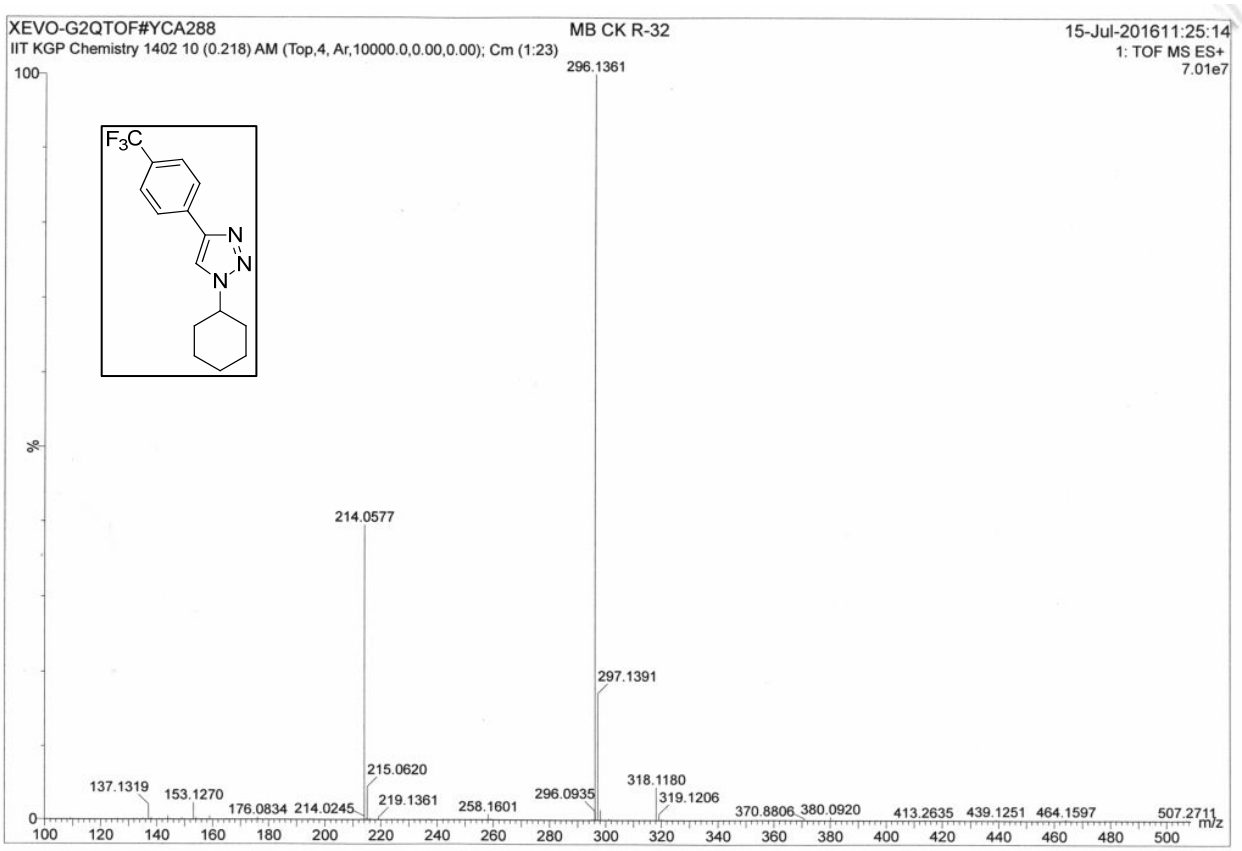
60
50
40
30
20
10
0
ppm

HRMS Spectra

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MB CK R-32
15-Jul-201611:25:14
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214.0577
297.1391
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219.1361
258.1601
296.0935
318.1180
319.1206
370.8806
380.0920
413.2635
439.1251
464.1597
507.2711
m/z
%

NMR Spectra (^{1}H) (Products for cycloaddition of CO_2 to epoxides)

Yield Calculation of Cyclic Carbonates from ^{1}H-NMR

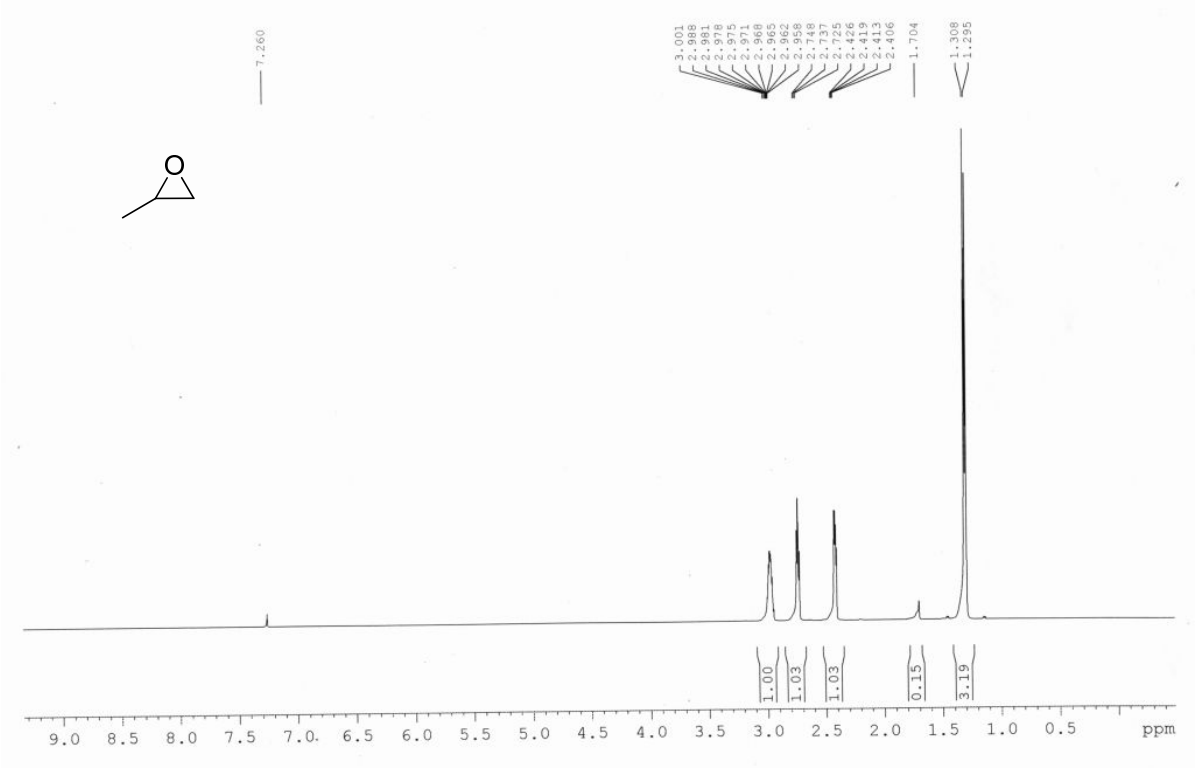

Figure S11. ^{1}H NMR spectra of propylene oxide (400 MHz, $CDCl_3$): δ = 3.00-2.95 (m, 1H, O-CH), 2.74 (t, J=4.4 Hz, 1H, O-CH_2), 2.42 (q, J = 2.8 Hz, 1H, O-CH_2), 1.30 (d, J = 5.2 Hz, 3H, CH_3).

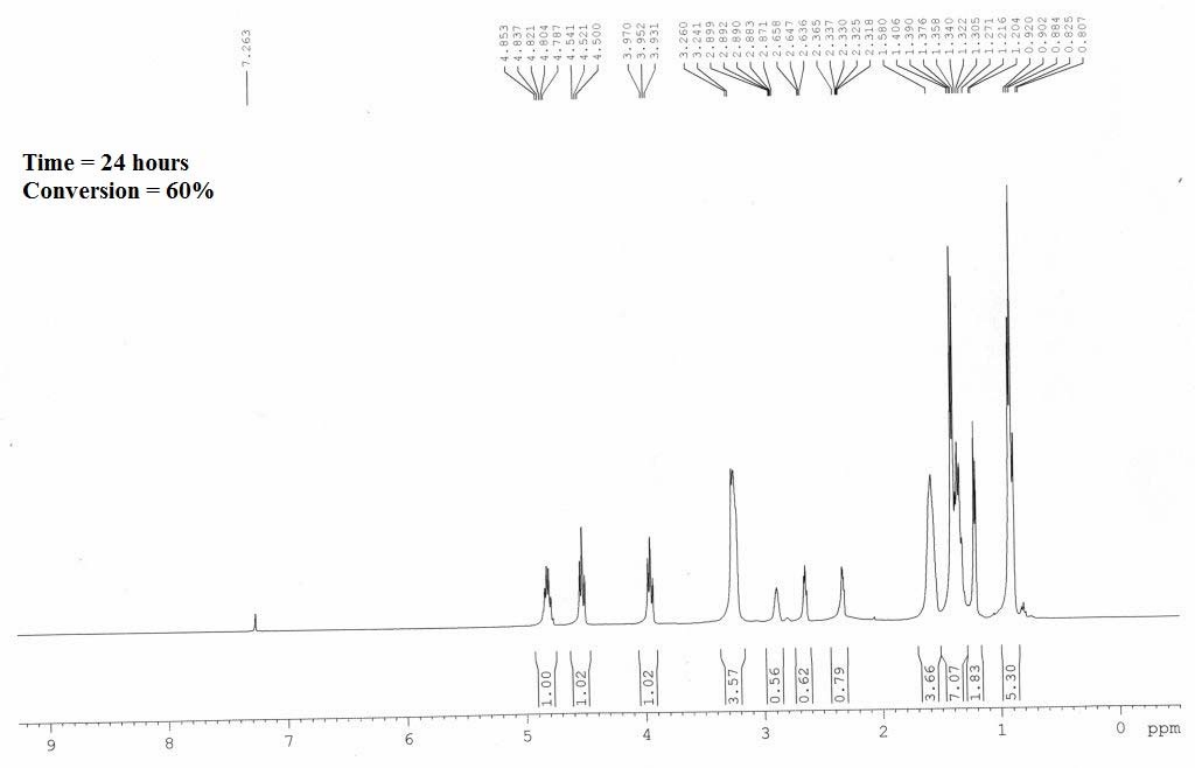

Figure S12. ^{1}H NMR spectra of the cycloaddition product of propylene oxide and CO_2 for 24h (400 MHz, $CDCl_3$) : δ = 4.85 – 4.78 (m, 1H, COO-CH), 4.54(t, J = 8.0 Hz, 1H, COO-CH_2), 3.97 (t, J = 8.4 Hz, 1H,COO-CH_2), 2.89 – 2.87 (m, 0.56H, O-CH), 2.65 (t, J = 4.4 Hz, 0.62H, O-CH_2), 2.33 (q, J = 2.8 Hz, 0.79H, OCH_2), 1.39 (d, J = 5.6 Hz, 4H, CH_3).

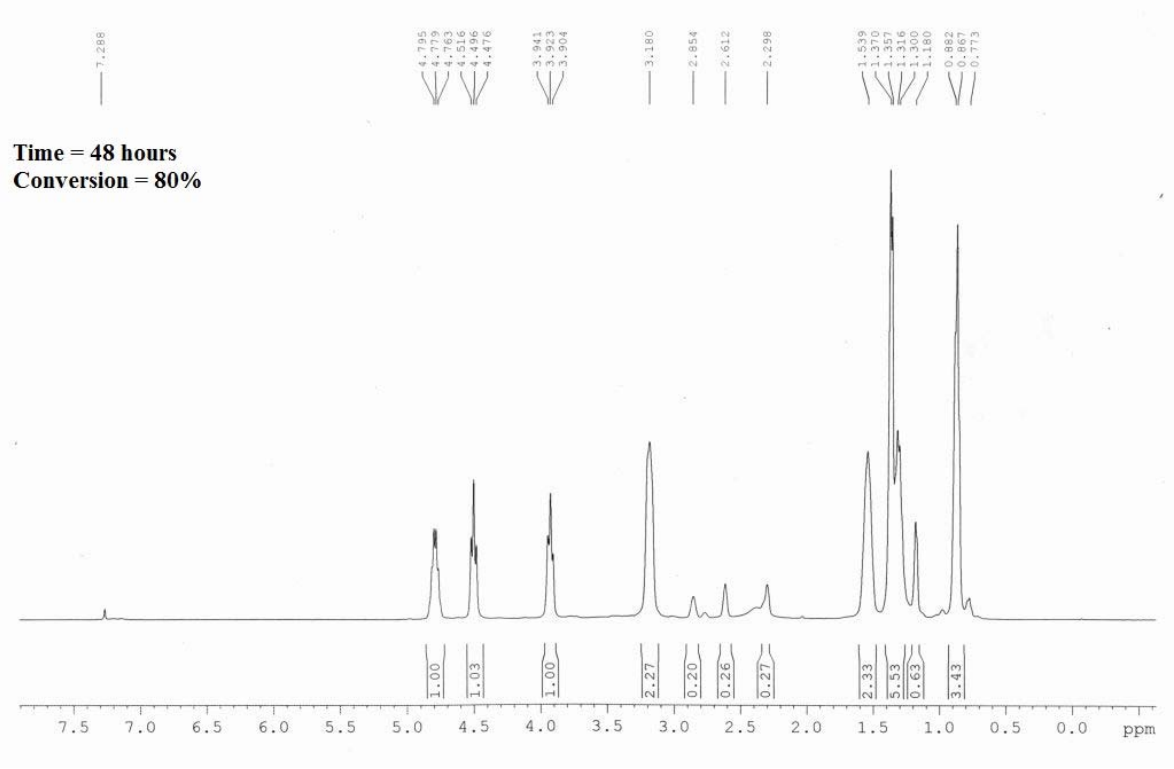

Figure S13. ^{1}H NMR spectra of the cycloaddition product of propylene oxide and CO_2 for 48h (400 MHz, $CDCl_3$) : δ = 4.79 – 4.76 (m, 1H, COO-CH), 4.51(t, J = 8.0 Hz, 1H, COO-CH_2), 3.94 (t, J = 7.6 Hz, 1H,COO-CH_2), 2.85 (b, 0.2H, O-CH), 2.61 (b, 0.26H, O-CH_2), 2.29 (b, 0.27H, O-CH2), 1.37 (d, J = 5.2 Hz, 3.5H, O-CH_2).

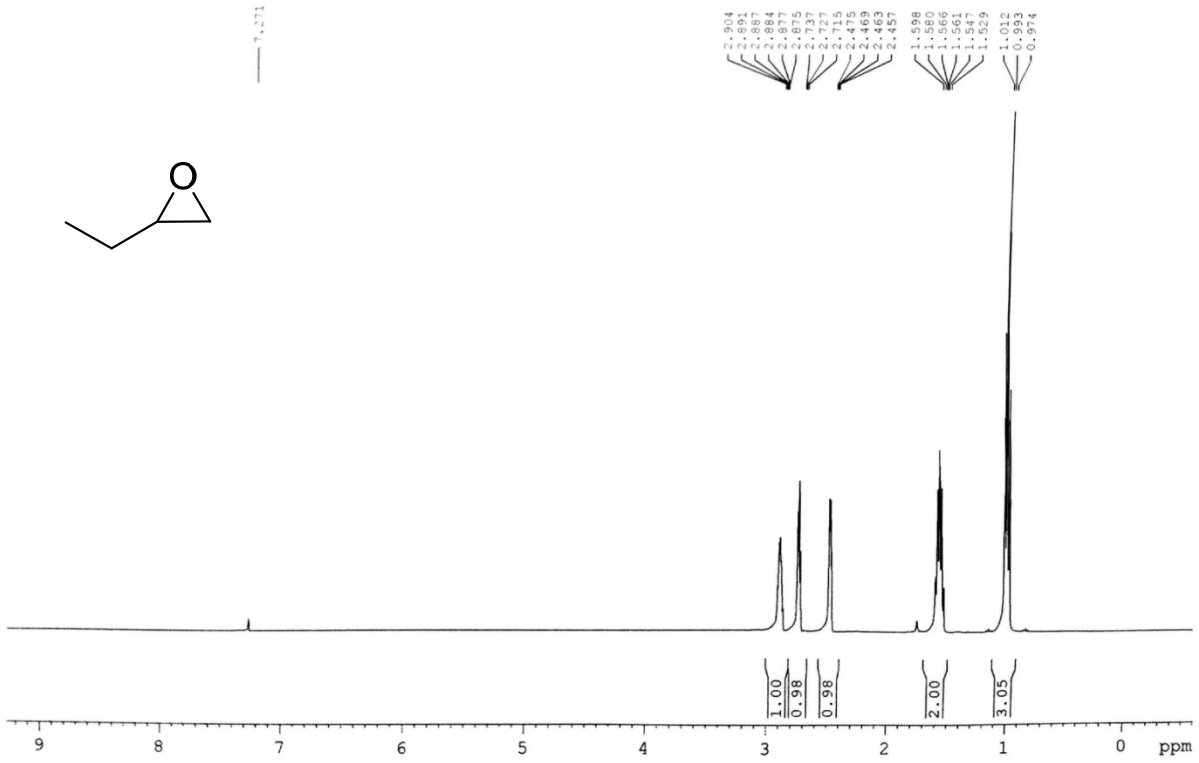

Figure S14. ^{1}H NMR spectra of 1,2-epoxy butane (400 MHz, $CDCl_3$): δ = 2.90 – 2.87 (m, 1H, O-CH), 2.73 – 2.71 (t, J = 4.4 Hz, 1H, O-CH_2), 2.47 – 2.45 (q, J = 2.4 Hz, 1H, O-CH_2), 1.59 – 1.52 (m, 2H, CH_2), 1.01 (t, J = 7.6 Hz, 3H, CH_3).

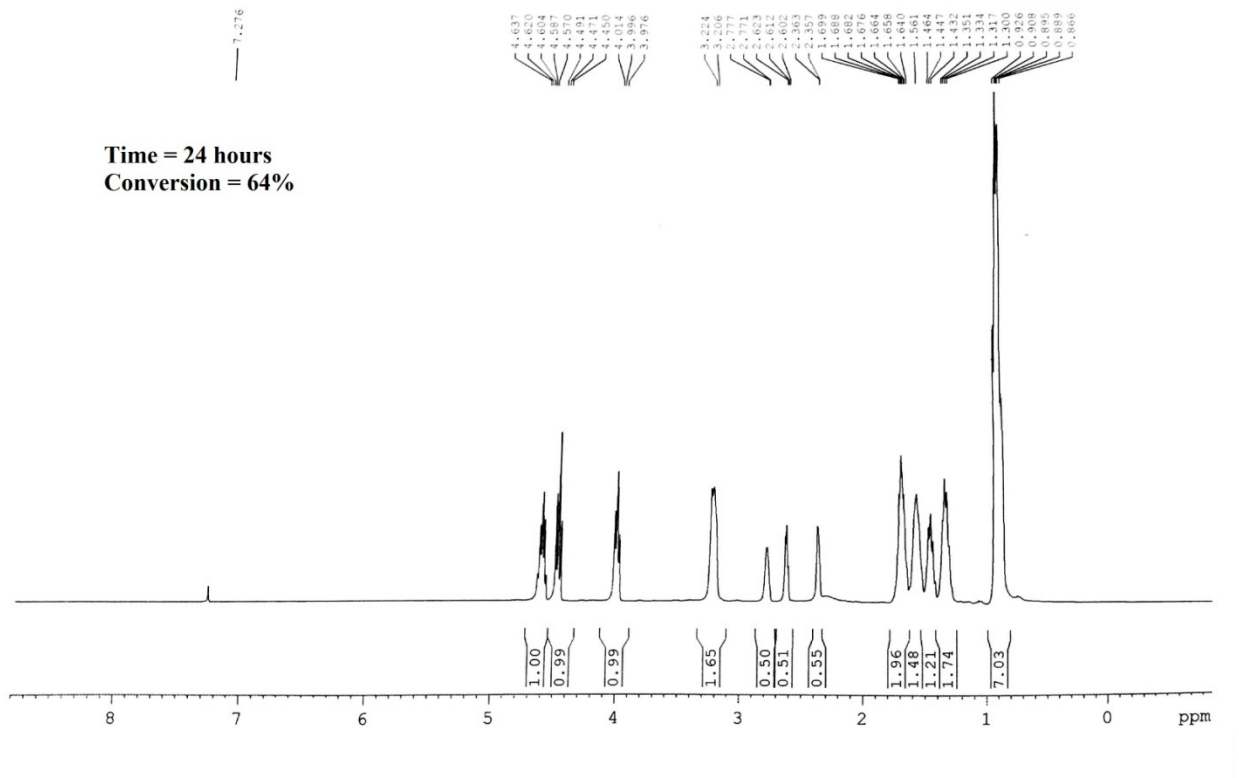

Figure S15. ^{1}H NMR spectra of the cycloaddition product of 1,2-epoxy butane and CO_2 for 24h (400 MHz, $CDCl_3$) : δ = 4.63 – 4.57 (m, 1H, COO-CH), 4.49 – 4.45 (m, 1H, COO-CH_2), 4.01 – 3.97 (m, 1H, COO-CH_2), 2.77 (m, 0.5H, O-CH), 2.62 – 2.60 (t, J = 4.4 Hz, 0.5H, O-CH_2), 2.36 – 2.35 (q, J = 2.4 Hz, 0.5H, O-CH_2), 1.69 – 1.64 (m, 2H, CH_2), 1.46 – 1.43 (m, 1H, CH_2), 0.92 (t, J = 7.2 Hz, 4.5H, CH_3).

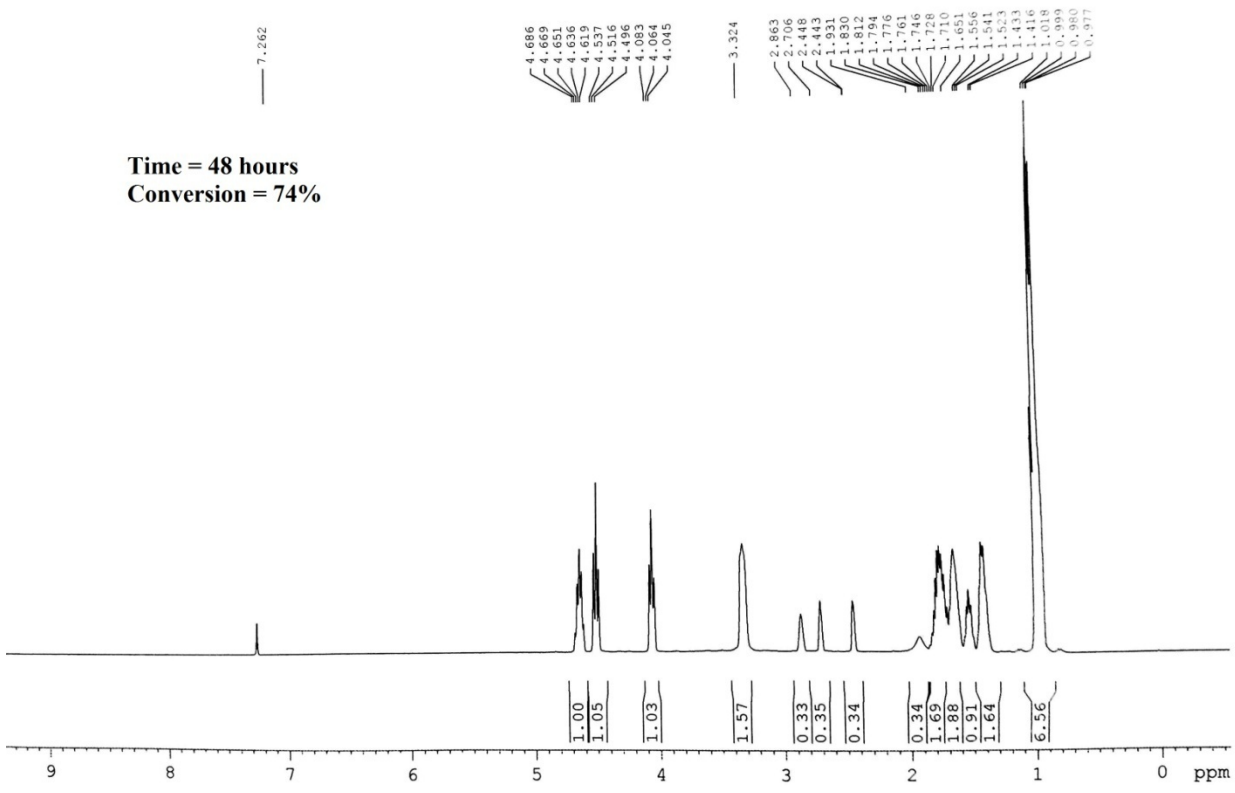

Figure S16. ^{1}H NMR spectra of the cycloaddition product of 1,2-epoxy butane and CO_2 for 48h (400 MHz, $CDCl_3$) : δ = 4.68 – 4.62 (m, 1H, COO-CH), 4.53 – 4.49 (m, 1H, COO-CH_2), 4.08 – 4.04 (m, 1H, COO-CH_2), 2.86 (m, 0.33H, O-CH), 2.70 (t, 0.35H, O-CH_2), 2.44 (q, J = 2.0 Hz, 0.34H, O-CH_2), 1.83 – 1.71 (m, 2H, CH_2), 1.55 – 1.52 (m, 0.9H, CH_2), 0.92 (t, J = 7.6 Hz, 4H, CH_3).

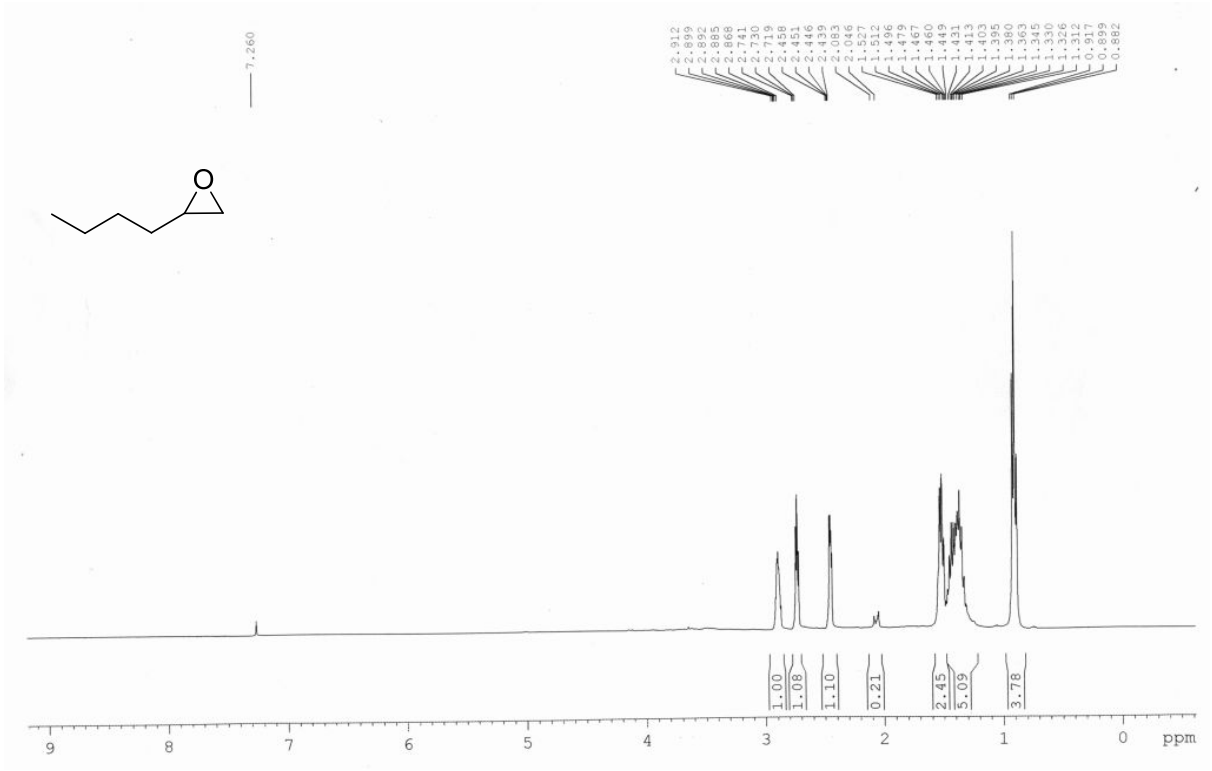

Figure S17. ^{1}H NMR spectra of 1,2-epoxy hexane (400 MHz, $CDCl_3$): δ = 2.91 – 2.86 (m, 1H, O-CH), 2.74 (t, J = 4.4 Hz, 1H, O-CH_2), 2.45 (q, J = 2.8 Hz, 1H, O-CH_2), 1.52 – 1.44 (m, 2H, CH_2), 1.43 – 1.31 (m, 4H, CH_2), 0.91 (t, J = 7.2 Hz, 3H, CH_3).

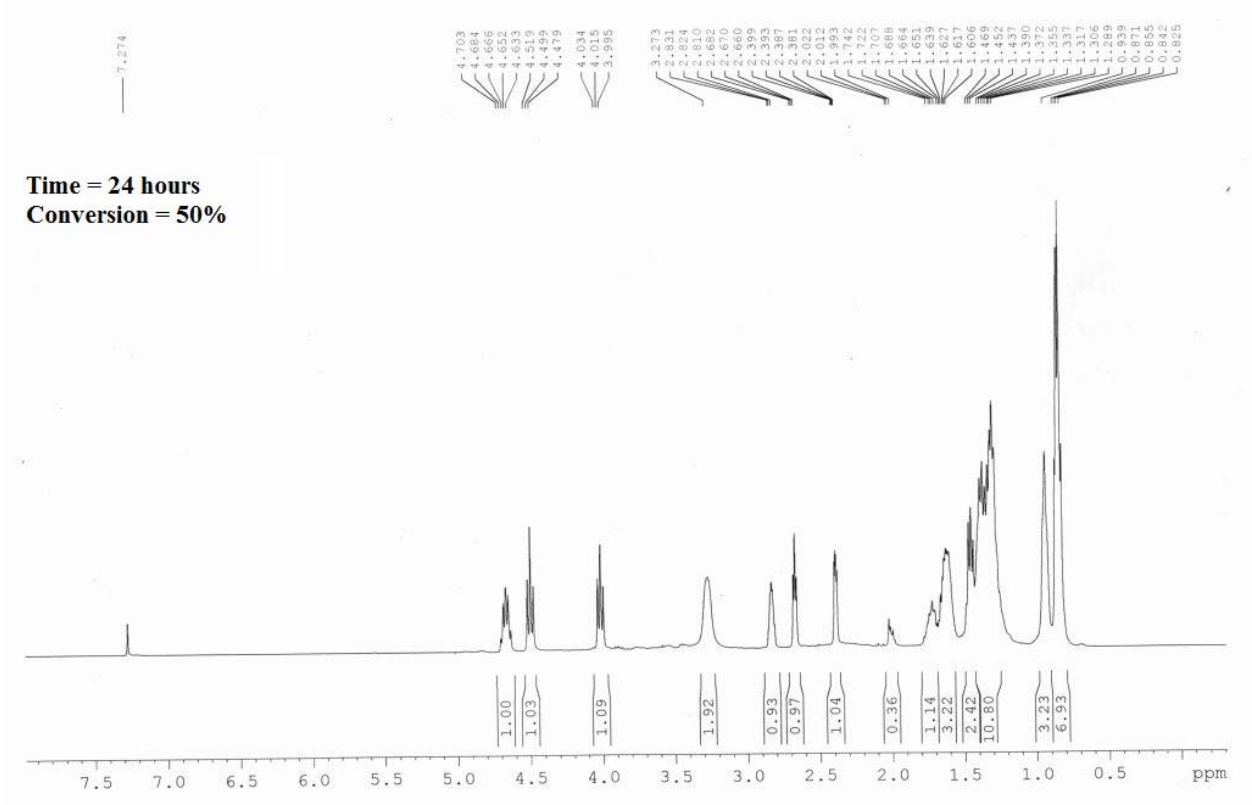

Figure S18. ^{1}H NMR spectra of the cycloaddition product of 1,2-epoxy hexane and CO_2 for 24h (400 MHz, $CDCl_3$) : δ = 4.70 – 4.63 (m, 1H, COO-CH), 4.51 (t, J = 8.0 Hz, 1H, COO-CH_2), 4.03 (t, J = 8.0 Hz, 1H, COO-CH_2), 2.83 (m, 0.93H, O-CH), 2.68 (t, J = 4.0 Hz, 0.97H, O-CH_2), 2.39 (q, J = 2.4 Hz, 1.04H, O-CH_2), 1.74 – 1.60 (m, 6H, CH_2), 1.46 – 1.28 (m, 6H, CH_2), 0.93 (b, 3H, CH_3), 0.87 (t, J = 6.4 Hz, 3H, CH_3).

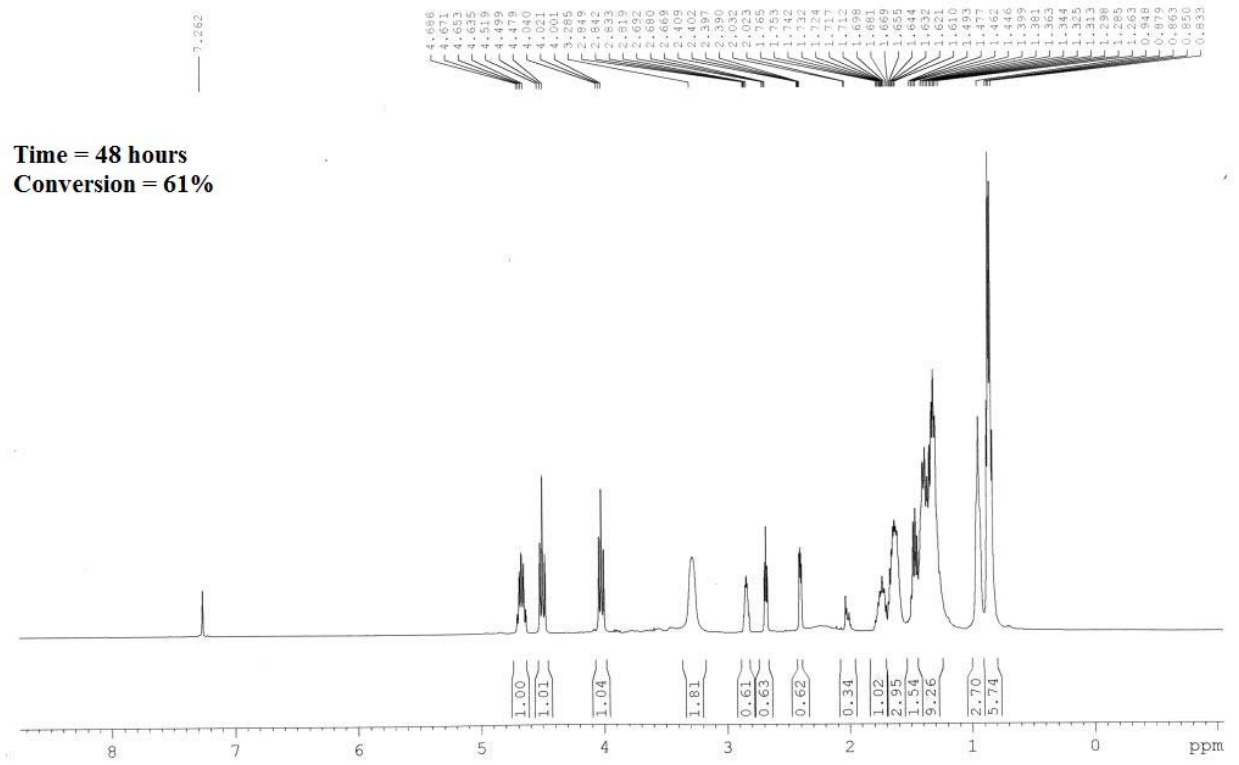

Figure S19. ^{1}H NMR spectra of the cycloaddition product of 1,2-epoxy hexane and CO_2 for 24h (400 MHz, $CDCl_3$) : δ = 4.68 – 4.63 (m, 1H, COO-CH), 4.51 (t, J = 8.0 Hz, 1H, COO-CH_2), 4.04 (t, J = 8.0 Hz, 1H, COO-CH_2), 2.84 – 2.81 (m, 0.61H, O-CH), 2.69 (t, J = 4.4 Hz, 0.63H, O-CH_2), 2.40 (q, J = 2.8 Hz, 0.62H, O-CH_2), 1.76 – 1.61 (m, 3.6H, CH_2), 1.49 – 1.26 (m, 6H, CH_2), 0.94 (b, 1.8H, CH_3), 0.87 (t, J = 6.4 Hz, 3H, CH_3).

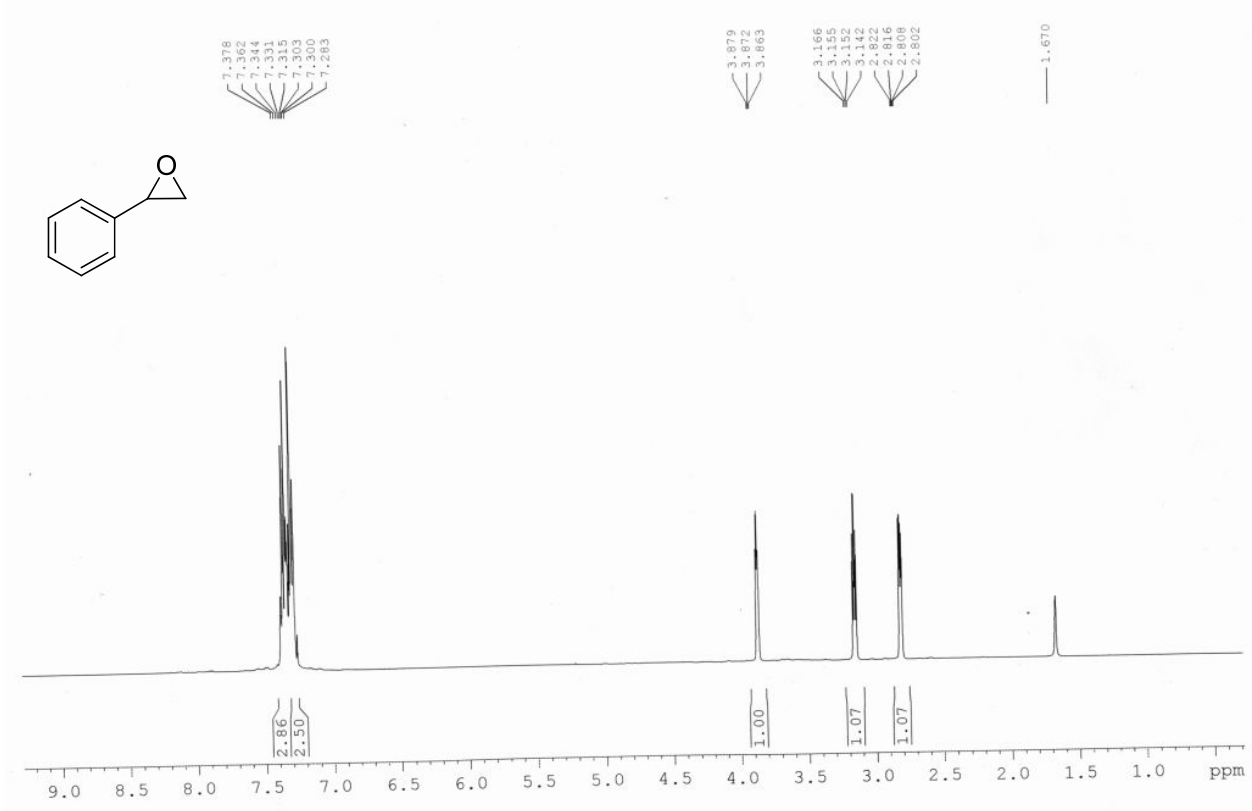

Figure S20. ^{1}H NMR spectra of styrene oxide (400 MHz, $CDCl_3$): δ = 7.37 – 7.28 (m, 5H, Ar-H), 3.87 (t, J=3.6 Hz, 1H, O-CH), 3.16 (q, J=4.0 Hz, 1H, O-CH_2), 2.82 (q, J = 2.4 Hz, 1H, O-CH_2).

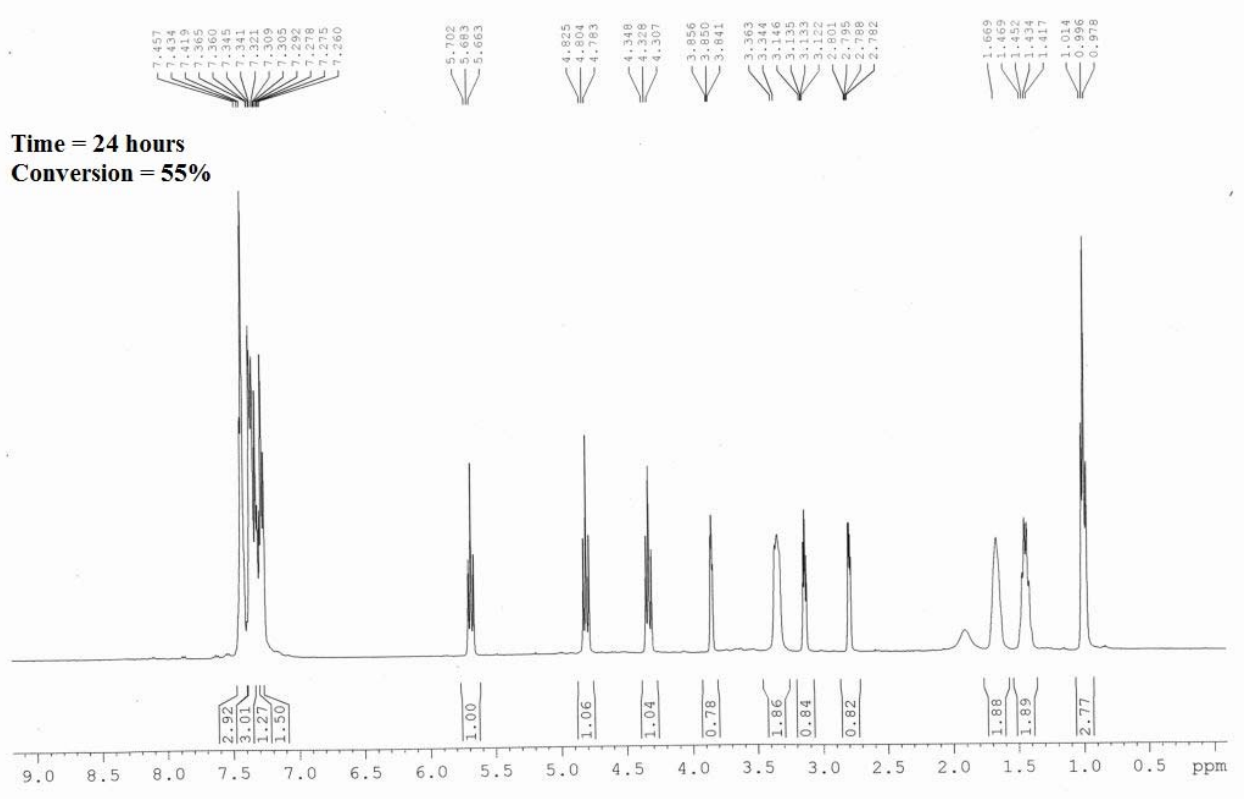

Figure S21. ^{1}H NMR spectra of the cycloaddition product of styrene oxide and CO_2 for 24h (400 MHz, $CDCl_3$) : δ = 7.45 – 7.26 (m, 9H, Ar-H), 5.70 (t, J = 8.0 Hz, 1H, COO-CH), 4.82 (t, J = 8.4 Hz, 1H, $COO-CH_2$), 4.34 (t, J = 8.0 Hz, 1H, COO-CH2), 3.85 (t, J = 3.6 Hz, 0.78H, O-CH), 3.14 (q, J = 4.4 Hz, 0.84H, $O-CH_2$), 2.80 (q, J = 2.4 Hz, 0.82H, $O-CH_2$).

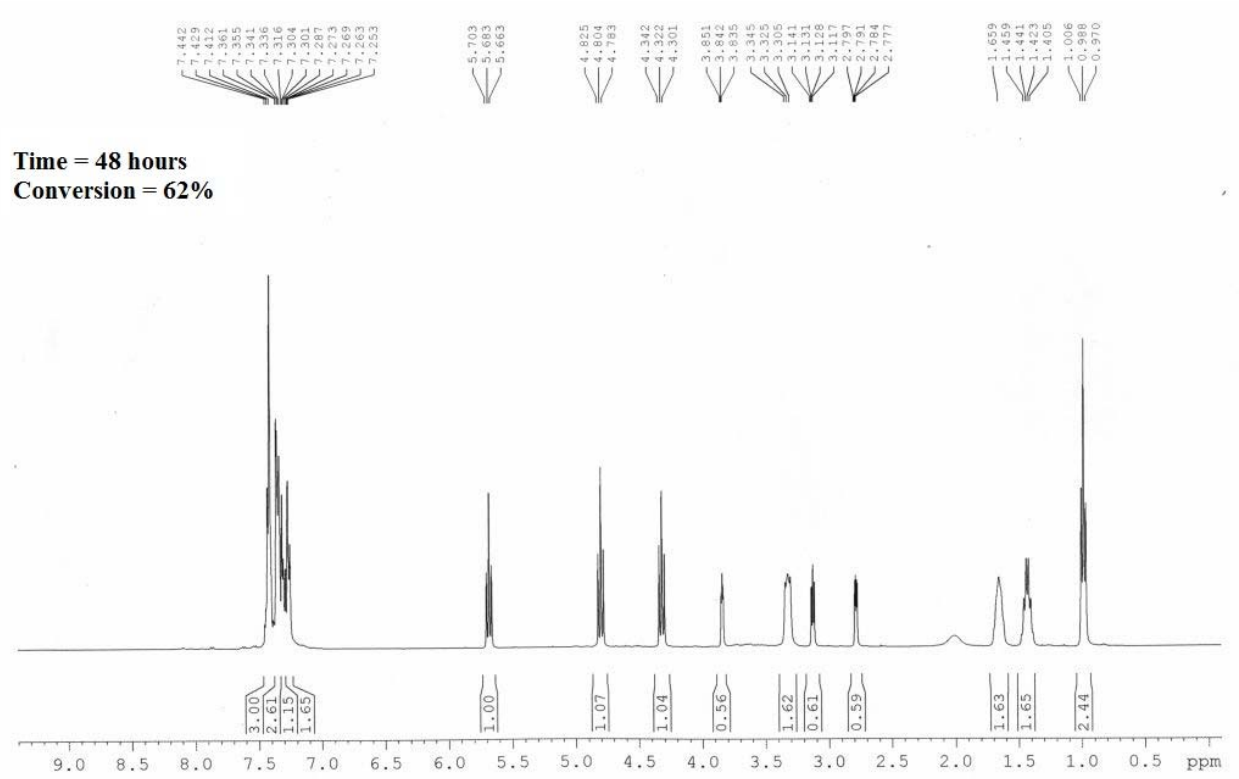

Figure S22. ^{1}H NMR spectra of the cycloaddition product of styrene oxide and CO_2 for 48h (400 MHz, $CDCl_3$) : δ = 7.44 – 7.25 (m, 8H, Ar-H), 5.70 (t, J = 8.0 Hz, 1H, COO-CH), 4.82 (t, J = 8.4 Hz, 1H, COO-CH_2), 4.34 (t, J = 8.0 Hz, 1H, COO-CH2), 3.85 (t, J = 3.6 Hz, 0.56H, O-CH), 3.14 (q, J = 4.0 Hz, 0.61H, O-CH_2), 2.79 (q, J = 2.4 Hz, 0.59H, O-CH_2).

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