Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Observation of Guanidine-Carbon Dioxide Complexation in Solution and Its Role in Reaction of Carbon Dioxide and Propargylamines

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General Information

Anhydrous solvents were obtained by expression through an activated alumina column built after procedure described by Grubbs.[1] All other compounds and anhydrous solvents were purchased from Sigma Aldrich and VWR, and used as supplied without any further purification. Unless otherwise specified, CO_2 was of research grade from BOC, and was dried by passing through a silica gel drying tube before use.

NMR spectra were recorded in chloroform-*d* on Bruker AV400 spectrometers. Chemical shifts were calibrated using the chloroform signal.

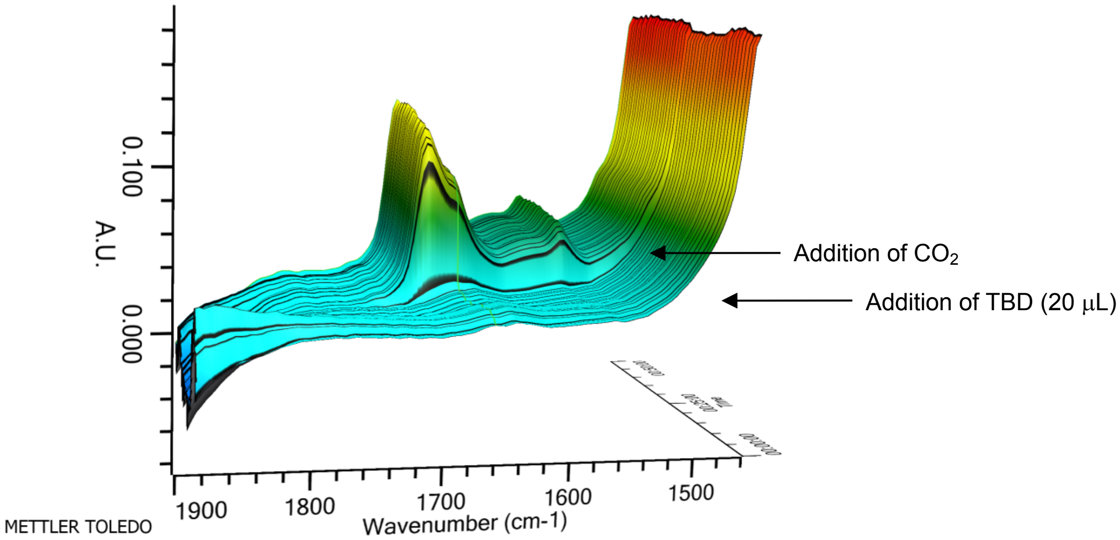
Compound **1a** was prepared according to Gabriele and Costa.[2] MTBD.HCl was prepared according to Joseph *et al.*[3]

Complexation Experiments

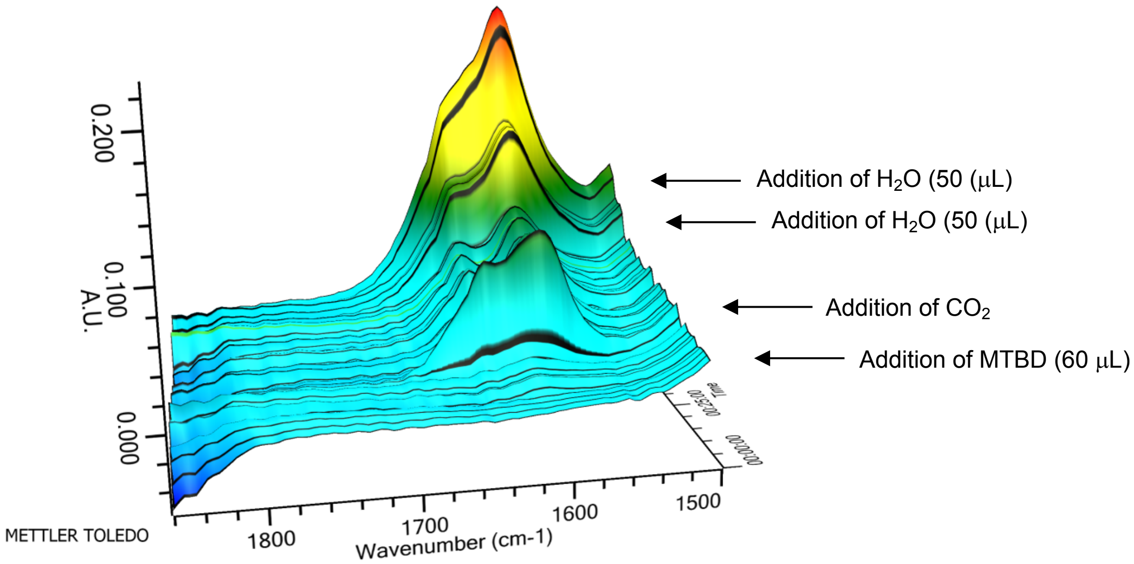
Typical procedure: A MultiMaxIR™ reactor was cleaned and dried before being flushed with nitrogen for 10 minutes. Anhydrous THF (20 mL) was introduced via a septum, followed by the organic base (20 µL or 20 mg in the case of DABCO). The solution was stirred at 25 °C and 750 rpm for 10 minutes. Collection of IR spectra for the 500-4000 cm^{-1} range was started. Spectra were collected every 30 seconds, each consisted of 44 scans, at 8 cm^{-1} resolution. After 300 seconds, CO_2 was introduced via a balloon and a separated needle to facilitate the replacement of nitrogen with CO_2. When relevant, addition of EtOH (2 mL) or water (50 µL) was carried out after an additional 300 seconds.

Acetonitrile was found to be unsuitable for the experiment due to significant precipitation upon treating TBD and MTBD with CO_2.

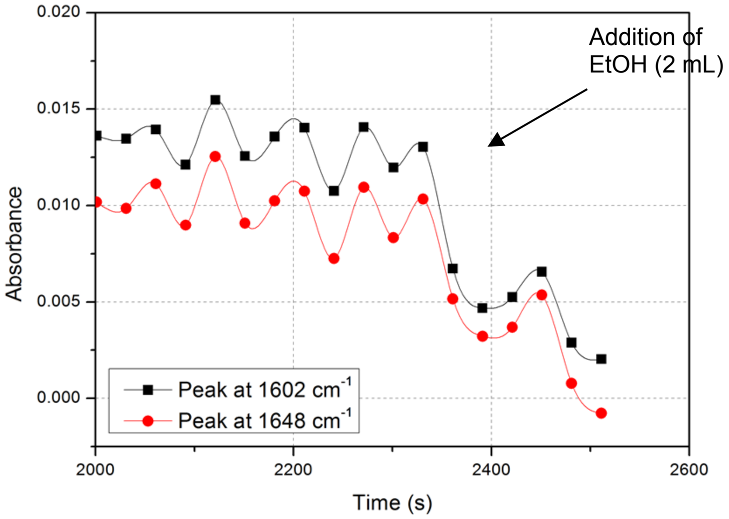
TBD + CO_2



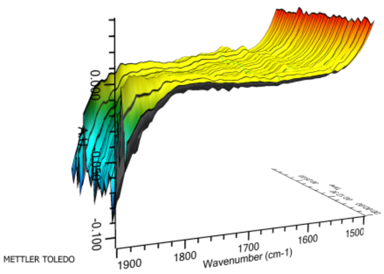
MTBD + CO_2



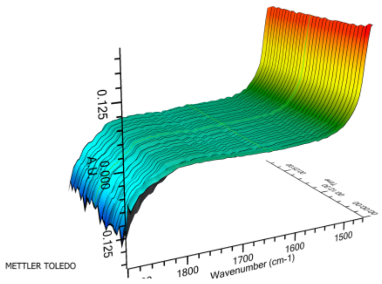
MTBD.CO_2 + EtOH



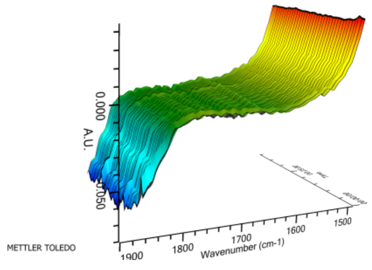
TMG + CO_2, DABCO + CO_2 and TEA + CO_2



TMG (20 µL)

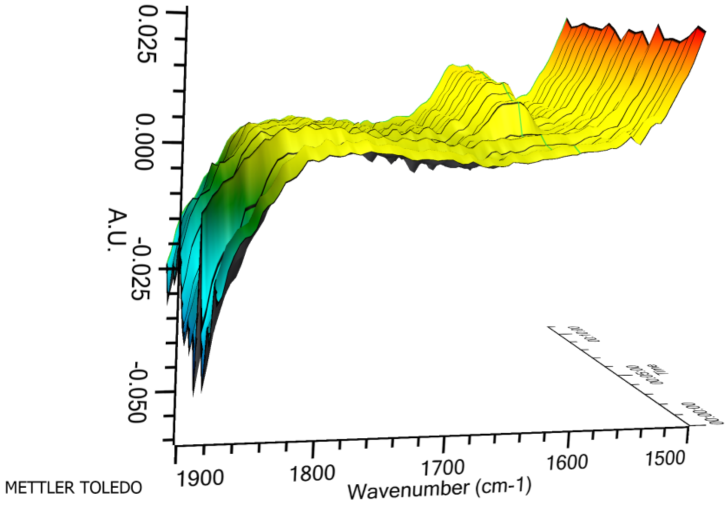


DABCO (20 mg)



TEA (20 µL)

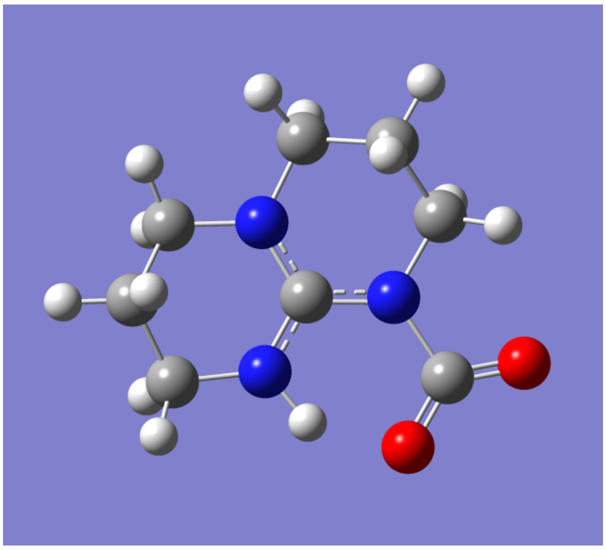
MTBD.HCl in THF



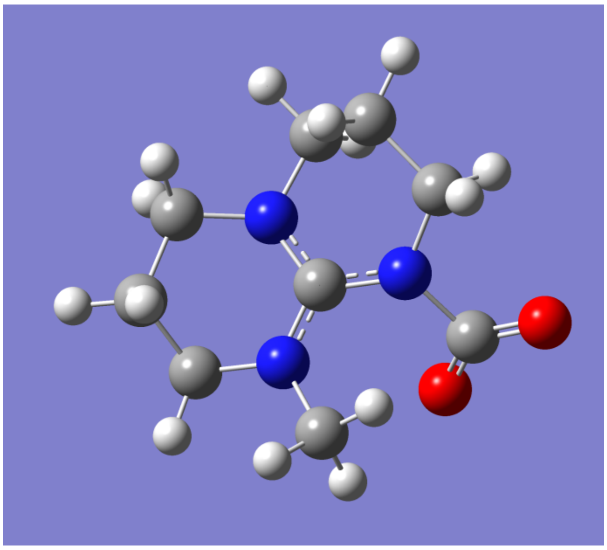
IR freq. 1620, 1603 cm^{-1}

Computational Study

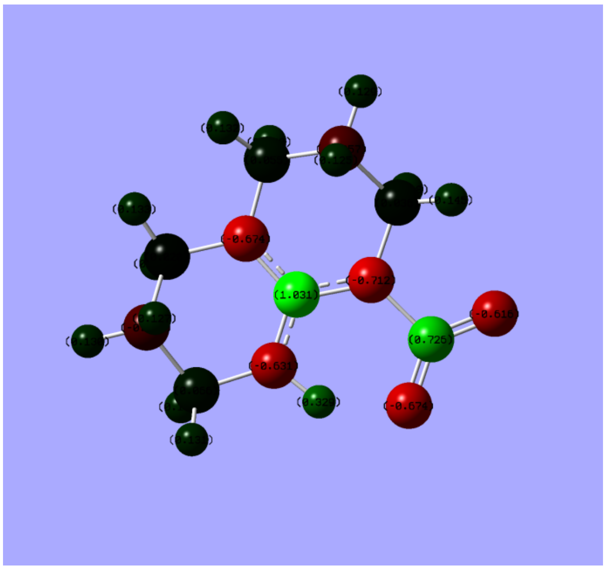
Molecular modelling was performed using Gaussian 09 package[4] on the Chemistry SCAN (Supercomputer at Night) Cluster at Imperial College London. The optimised structure of some amine/guanidine-CO_2 complexes are displayed below.



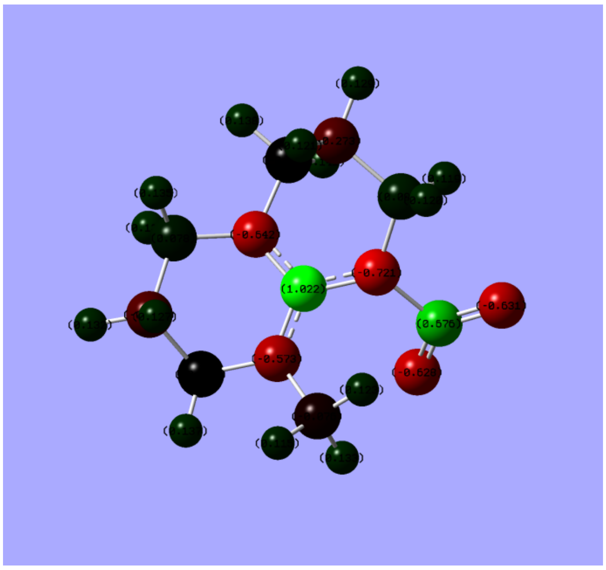
$TBD.CO_2$ MP2/6-311G(d,p)



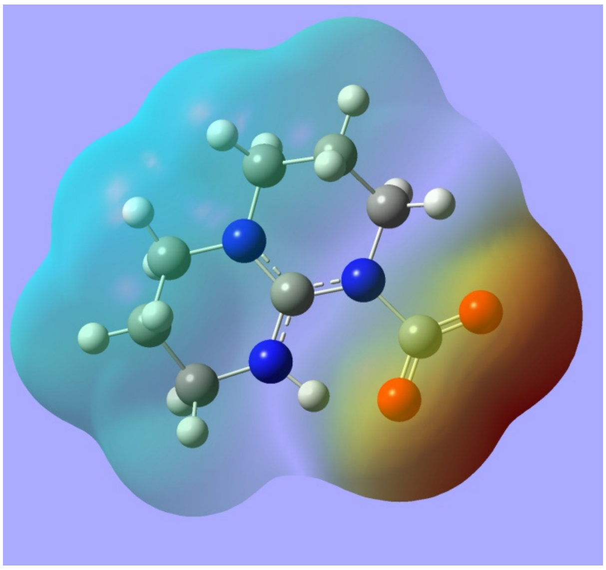
$MTBD.CO_2$ MP2/6-311G(d,p)



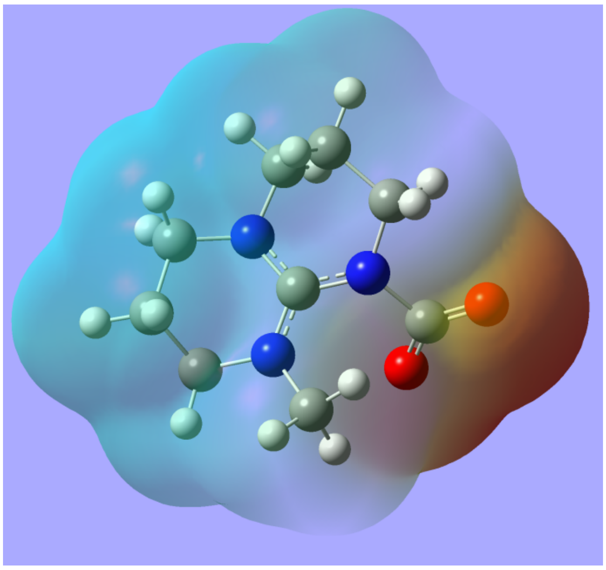
TBD.CO$_2$ Mulliken charges map



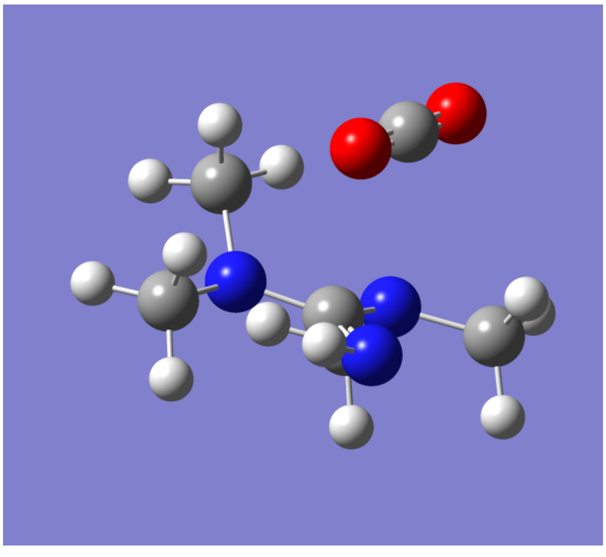
MTBD.CO$_2$ Mulliken charges map



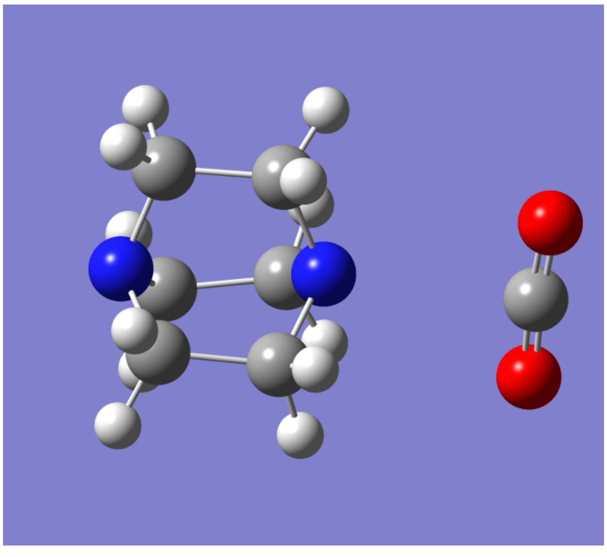
TBD.CO$_2$ Electrostatic potential map



TBD.CO$_2$ Electrostatic potential map



TMG.CO$_2$ MP2/6-311G(d,p)



DABCO.CO$_2$ MP2/6-311G(d,p)

Typical Procedure for Preliminary Small-Scale Catalytic Reaction between 1a and CO_2

An Endeavor™ multi-well hydrogenator from Biotage® was adapted for reactions using research grade CO_2 supplied by BOC (10 bar, containing < 0.5% H_2O, which was then passed through a silica gel drying column before use) at low to medium pressure. A dry reaction vessel containing **1a** (50 mg, 0.29 mmole) was charged with dry solvent (1 mL) and assembled into the equipment. The reaction was purged three times with nitrogen and pressurized with CO_2 (2 bar) for 15 minutes. After the pressure equilibrated, the vessel was heated to 50 °C and the pressure of CO_2 raised to 5 bar. The reaction was allowed to equilibrate for 15 minutes before stirring (500 rpm) is started. After 18 hours, the reaction vessel was purged with nitrogen and a crude ^{1}H NMR spectrum was measured after solvent evaporation. The crude yield was determined by normalising the integration of the benzyl CH_2 signals in the product and the starting material.

The product of MTBD/MeCN reaction was purified with flash chromatography on silica gel using EtOAc/DCM (60:40) as eluent, giving product **2a** (0.51 g) in 81% isolated yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.25 (m, 5H), 4.69 (d, *J* 3.4, 1H), 4.47 (s, 2H), 4.24 (d, *J* 3.4, 1H), 1.33 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 155.0, 137.7, 128.8, 127.9, 127.9, 84.3, 61.7, 44.2, 27.8.

Lit.[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.35 (m, 5H), 4.67 (d, *J* 3.2, 1H), 4.45 (s, 2H), 4.21 (d, *J* 3.2, 1H), 1.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 154.8, 137.6, 128.6, 127.7, 127.7, 84.1, 61.5, 44.1, 27.6.

The spectra are included at the end of this ESI.

The preliminary results are summarised in Table S1

Table S1 Conversion (%) of **1a** to **2a** using various catalysts and solvents at 50 °C[a,b]

No.	Catalyst	MeCN	DMSO	EtOH	THF[c]	Toluene
1	MTBD	100	100	45	7	19
2	TBD	39	56	19		36
3	TMG	50	96	92	0	1
4	DBU	100	64	28		0
5	DABCO	3	2	3		1
6	DMAP	4	1	19		1

[a] Reaction were performed using 0.3 mmol of **1a** and 10 mol% catalyst in 1.0 mL of the specified solvent under 5 bar of CO_2 at 50 °C; [b] Conversion was determined using ^{1}H NMR of the crude product; [c] reaction at 75 °C.

Table S2 Solvents in this study and their polarity parameters

No.	Solvent	Dielectric constant[6]	$E_T(30)$[7]
1	MeCN	36.64	45.6
2	DMSO	47.24	45.1
3	EtOH	25.3	51.9
4	Toluene	2.39	33.9

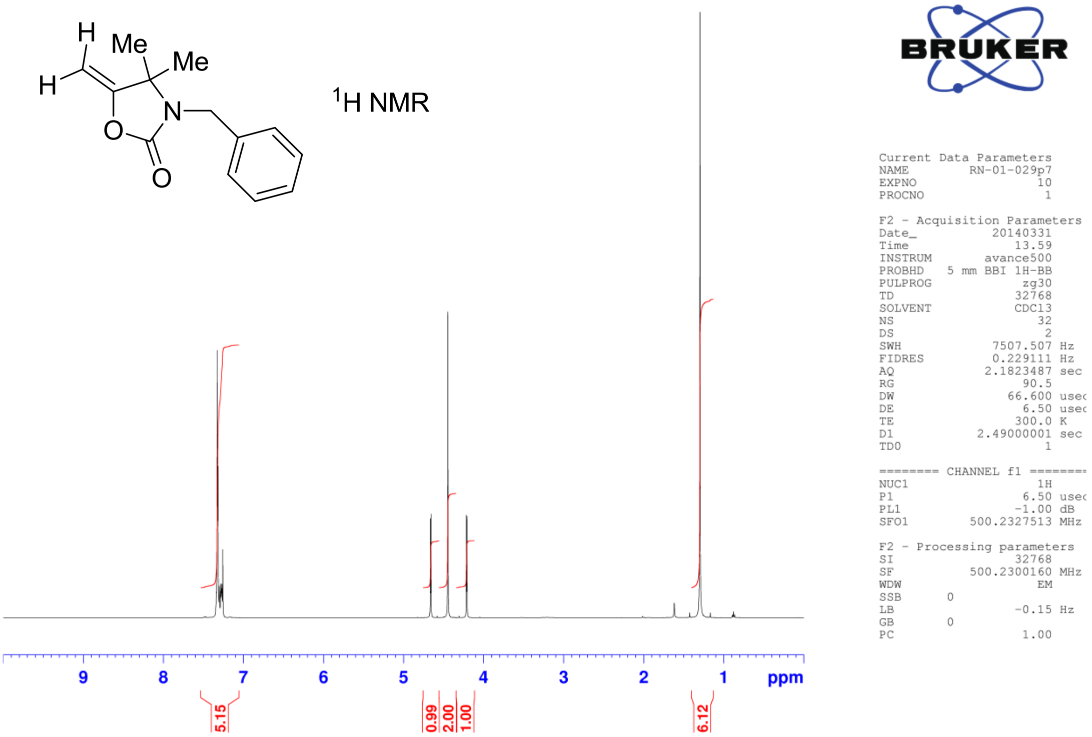
Typical Procedure for Catalytic Reaction between 1a and CO_2 using MTBD and TMG as Catalyst

A solution of benzyl-(1,1-dimethylprop-2-ynyl)amine **1a** (0.15 g, 0.866 mmol, 1 equiv.) in the selected solvent (3 mL) was prepared in a vial under nitrogen. The catalyst (0.0868 mmol, 0.1 equiv. / 0.00868 mmol, 0.01 equiv.) was added to the reaction. A stainless steel high pressure reaction vessel was flushed with CO_2 and the solution injected into the cell. The vessel was further flushed with CO_2 and heated to 75 °C. After thermal equilibrium was reached the vessel was pressurised to 5 bar and stirred for 18 h. The vessel was cooled, vented through solvent and reaction solvent removed under vacuum. Reaction in DMSO required an extraction: reaction mixture diluted with H_2O (30 ml) washed with diethyl ether (3 x 40 mL) ether, washed with water (70 mL), and dried over $MgSO_4$. The organic solution was filtered and solvent evaporated under vacuum to give the crude product.

The CO_2 in these reactions was supplied from high purity grade BOC bottle (99.99%), which was liquefied using an Isco 260D syringe pump before transfering to the reaction vessel.

The results are summarised in Table 3 of the manuscript.

Some results under seemingly similar conditions are different between Table S1 and S3. This is due to both the different temperature and the much higher purity of CO_2 (no moisture) employed in experiments in Table 3.



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DE                   6.50 usec
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D1             2.49000001 sec
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PL1                 -1.00 dB
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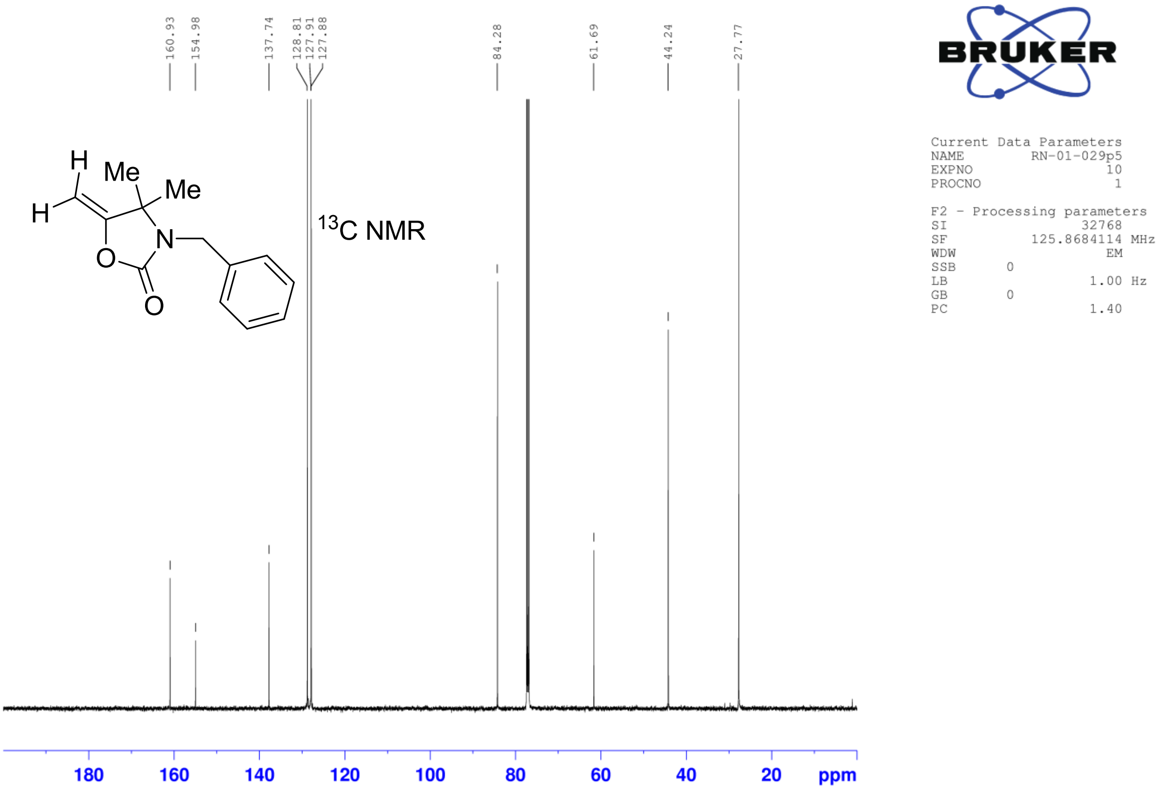

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References

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