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Supporting Information

Generation of Tosyl Azide in Continuous Flow using an Azide Resin, and Telescoping with Diazo Transfer and Rhodium Acetate-Catalyzed O–H Insertion

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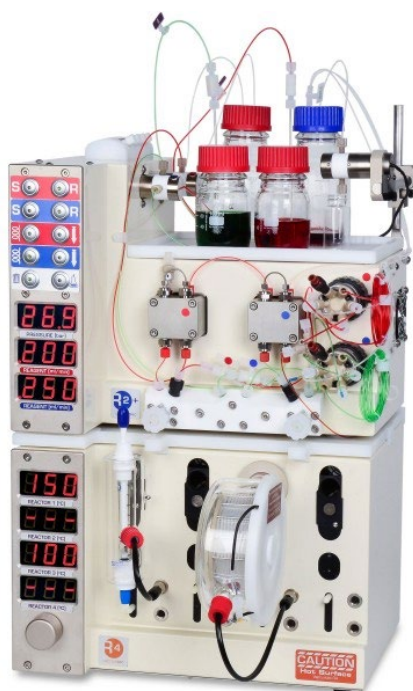
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Details of Continuous Flow Platforms & Set up

Continuous processes were performed using a Vapourtec R-Series flow system consisting of four piston (HPLC) pumps. Solid phase reagents/reaction components were employed using Omnifit glass column reactors (100 mm \times 10 mm internal diameter, one fixed end piece and one adjustable end piece). For processes where the product stream was collected only while at steady-state, this was determined by the proprietary software (Flow Commander) installed on the flow chemistry system.

Table S1. General specifications for Vapourtec R-Series system



General specifications for continuous-flow system	
Material of tubing	PFA
Internal diameter of tubing	1 mm
External diameter of tubing	1.59 mm
Working flow rates	0.05 mL/min – 9.99 mL/min
Tubular reactor working volume	10 mL
Temperature range	–70 °C to 250 °C

Supplementary Figures

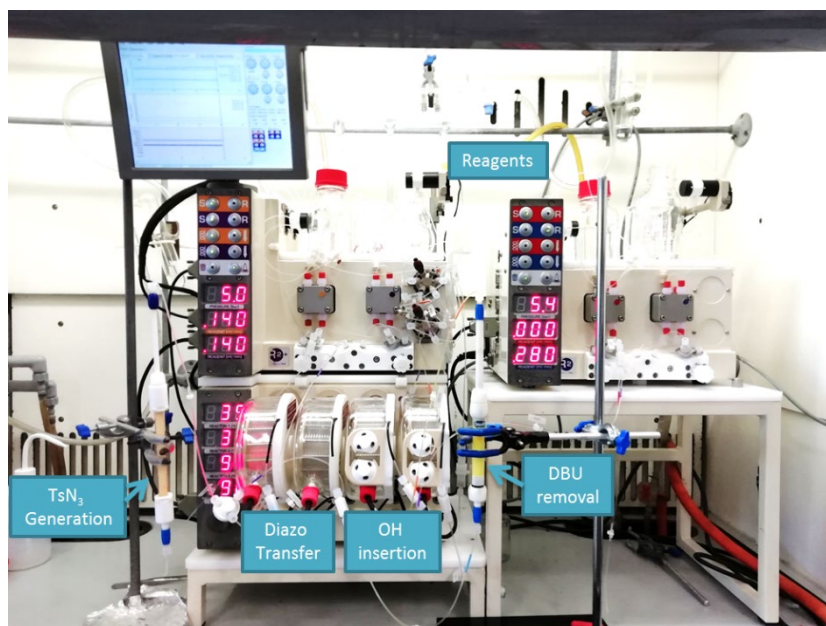


Figure S1. System configuration for telescoped generation of tosyl azide, diazo transfer and O–H insertion (see Scheme 10).

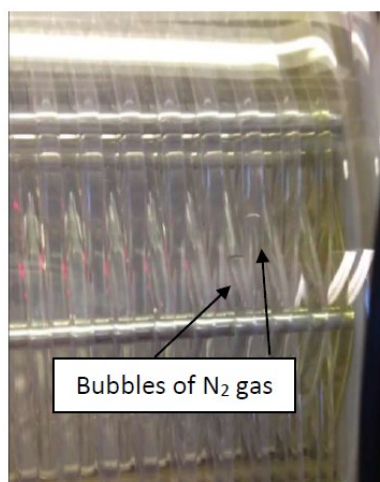


Figure S2. Nitrogen bubbles released in reactor coil during rhodium acetate-catalyzed O–H insertion reaction of α -diazo aryl acetate **9** in flow (see Scheme 8).

Copies of ^1H and ^{13}C NMR Spectra

NMR spectra of the following compounds were in agreement with those previously reported:

Chemical structure: COC(=O)c1ccccc1[N+](=O)[O-] (2-chloro-1-methoxy-2-nitrobenzene)

¹H NMR spectrum (CDCl₃) showing aromatic signals (7.0-7.6 ppm) and a methoxy singlet (3.867 ppm). Integration values are 3.98 and 3.02.

13C NMR spectrum (400 MHz, CDCl3) of 1,3-bis(4-methoxyphenyl)propan-2-one. The spectrum shows peaks at 165.98, 133.76, 132.30, 128.63, 127.16, 123.89, 77.38, 77.27, 77.07, 76.75, 53.91, 52.28, 31.94, 31.74, 31.54, 29.92, 29.38, 29.27, 26.92, 22.81, 22.61, 22.41, 22.67, and 14.14 ppm.

S5

Methyl 2-diazo-2-phenylacetate (20)²

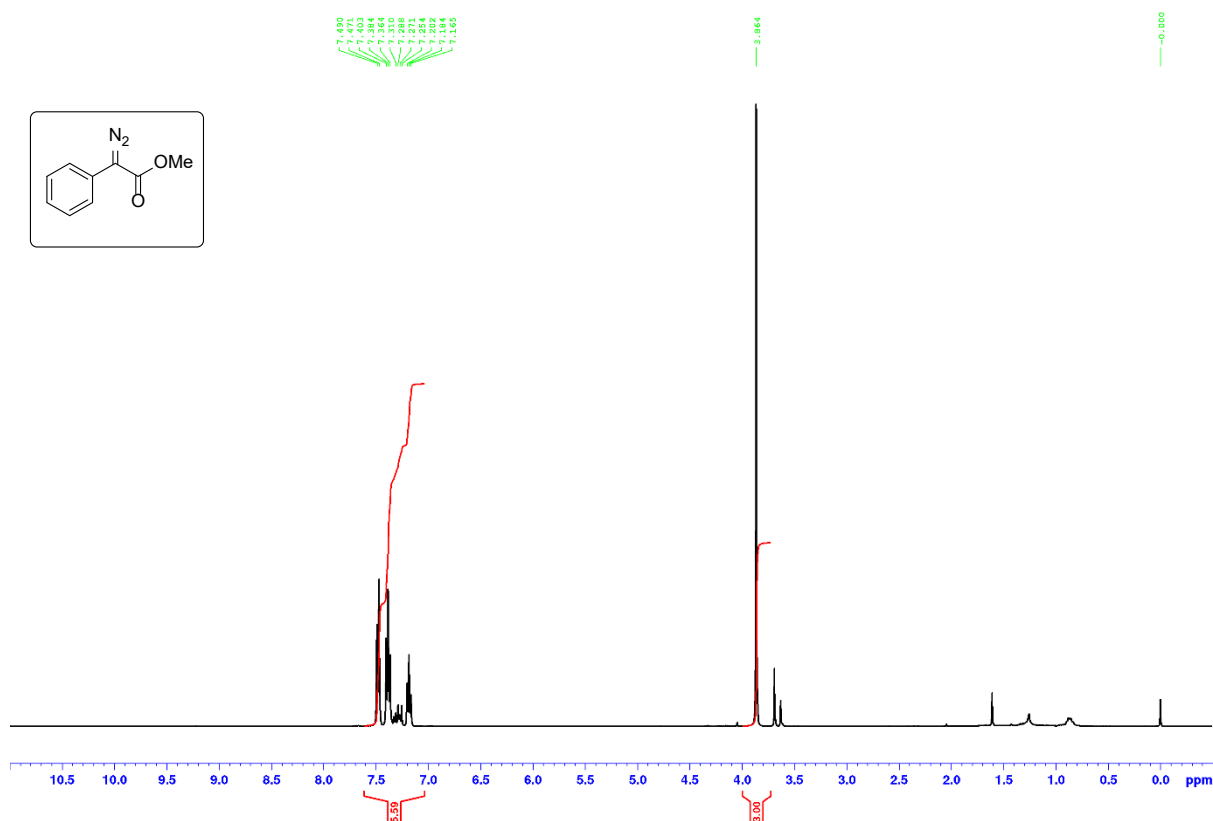


Figure S5. ¹H NMR (CDCl₃, 400 MHz) spectrum of α-diazo ester **20**.

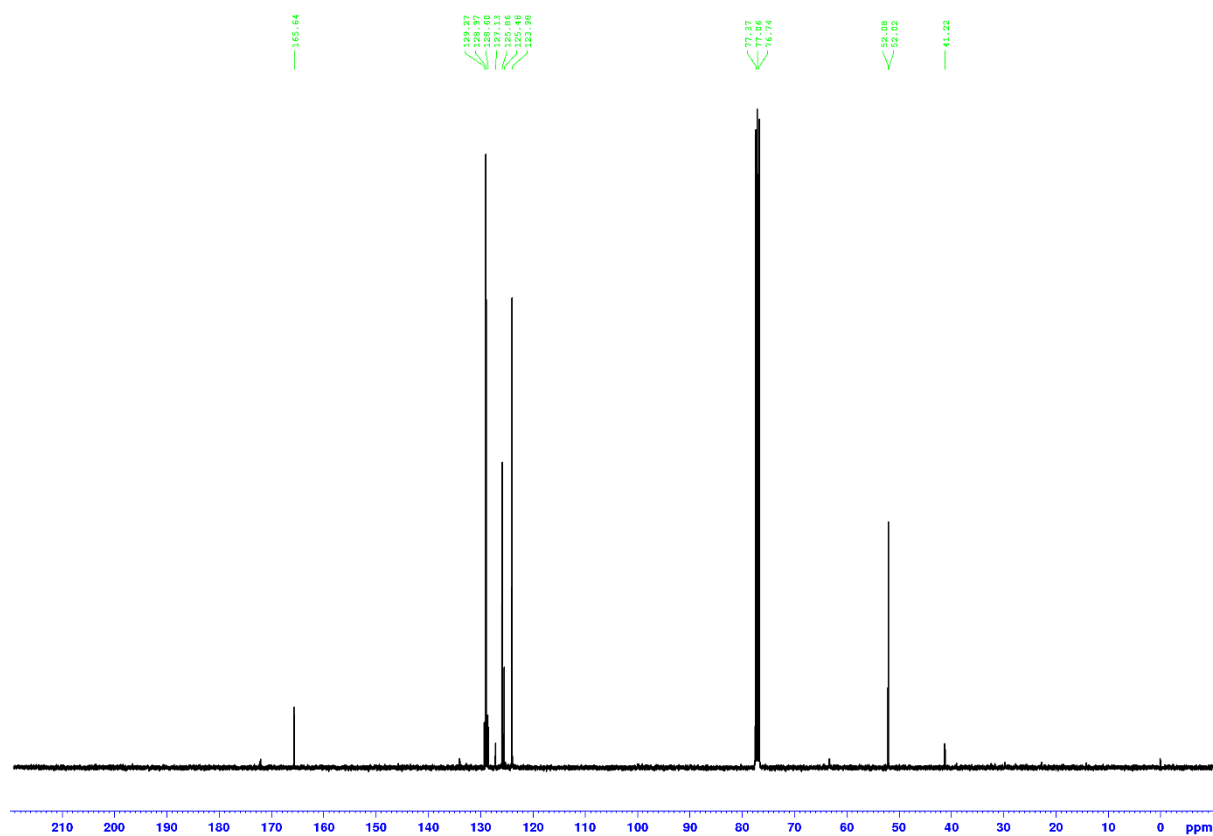


Figure S6. ¹³C{¹H} NMR (CDCl₃, 100.6 MHz) spectrum of α-diazo ester **20**.

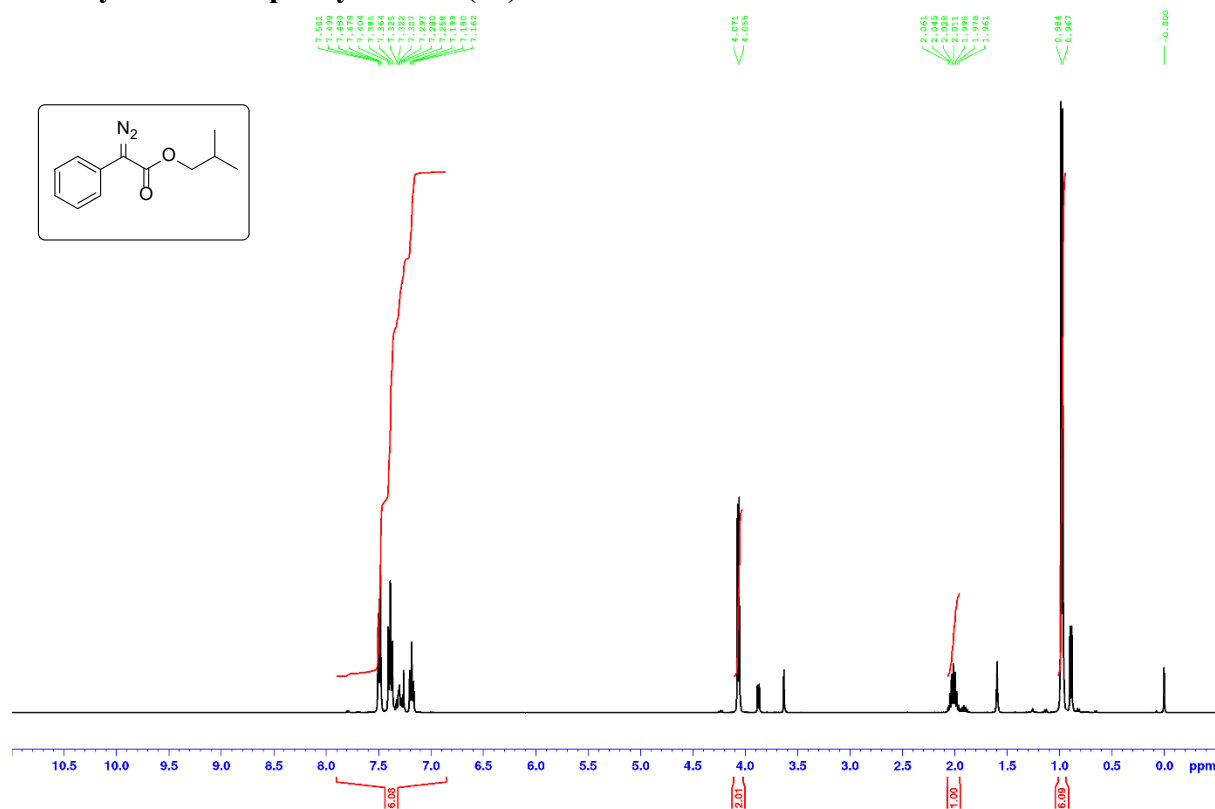
CC(C)COC(=O)C(=[N+]=[N-])c1ccccc1

Figure S8. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 100.6 MHz) spectrum of α -diazo ester **22**.

Methyl 2-(4-bromophenyl)-2-diazoacetate (24**)³**

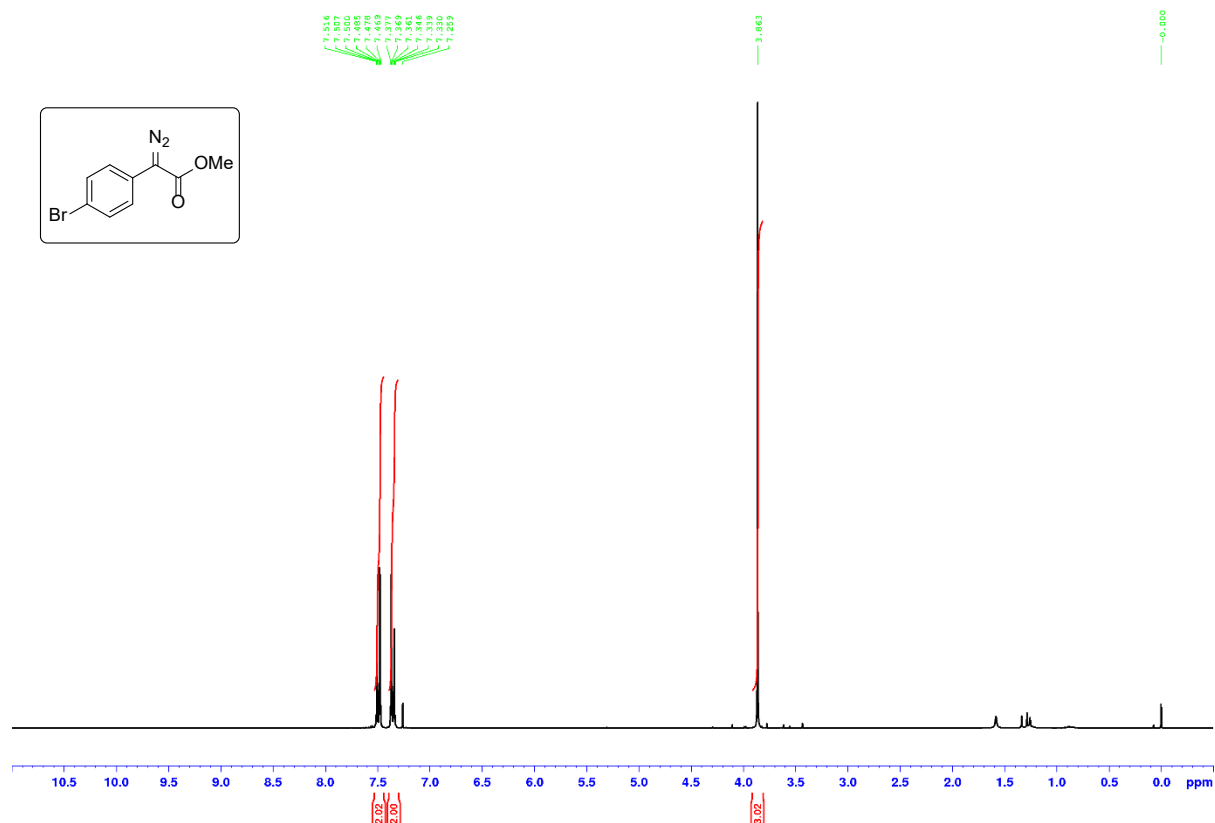


Figure S9. ¹H NMR (CDCl₃, 300 MHz) spectrum of α -diazo ester **24**.

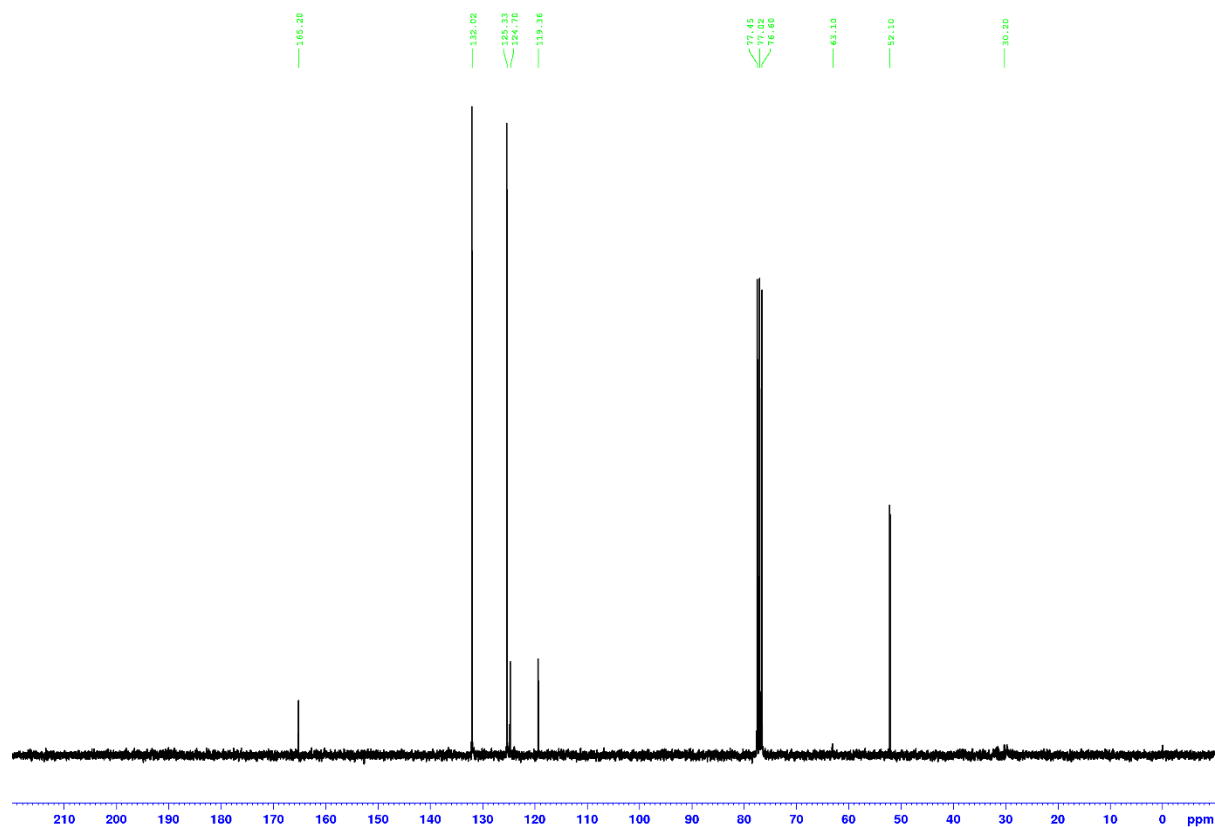


Figure S10. ¹³C{¹H} NMR (CDCl₃, 75.5 MHz) spectrum of α -diazo ester **24**.

Diethyl 2-diazomalonate (26)⁴

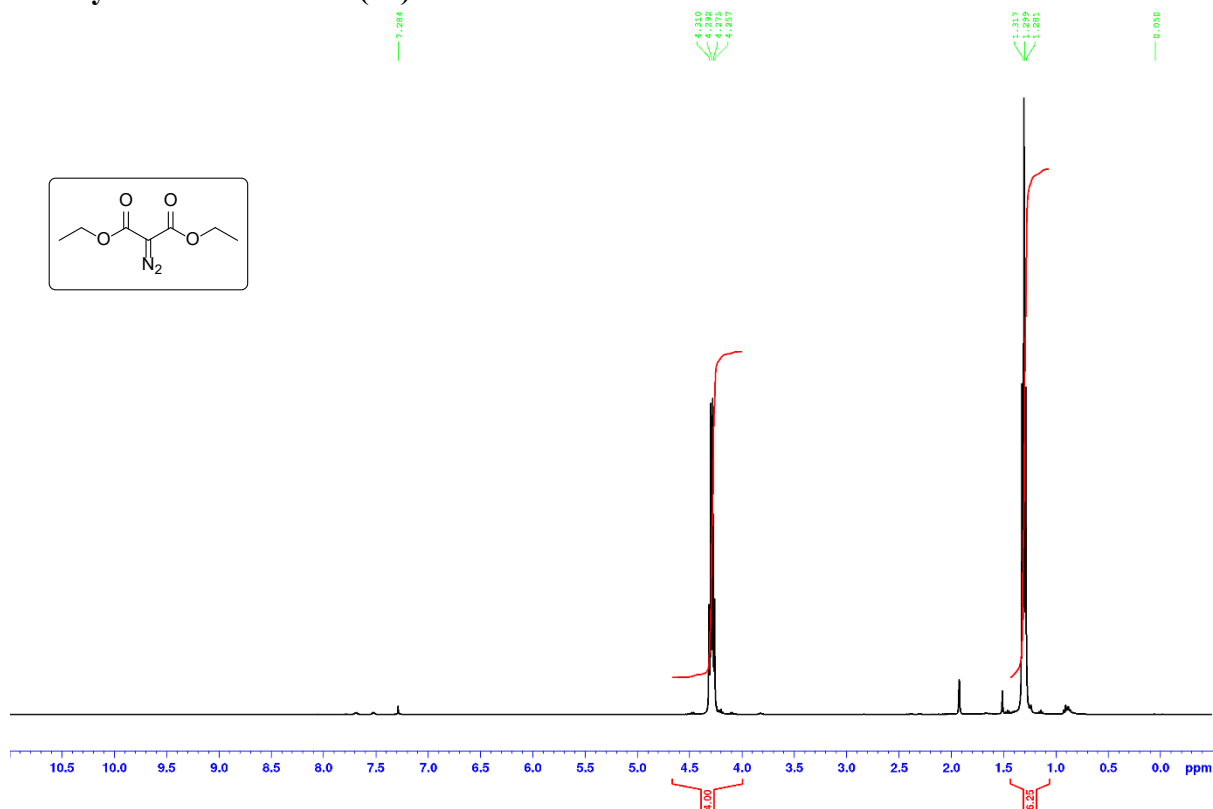


Figure S11. ¹H NMR (400 MHz, CDCl₃) spectrum of α-diazo ester **26**.

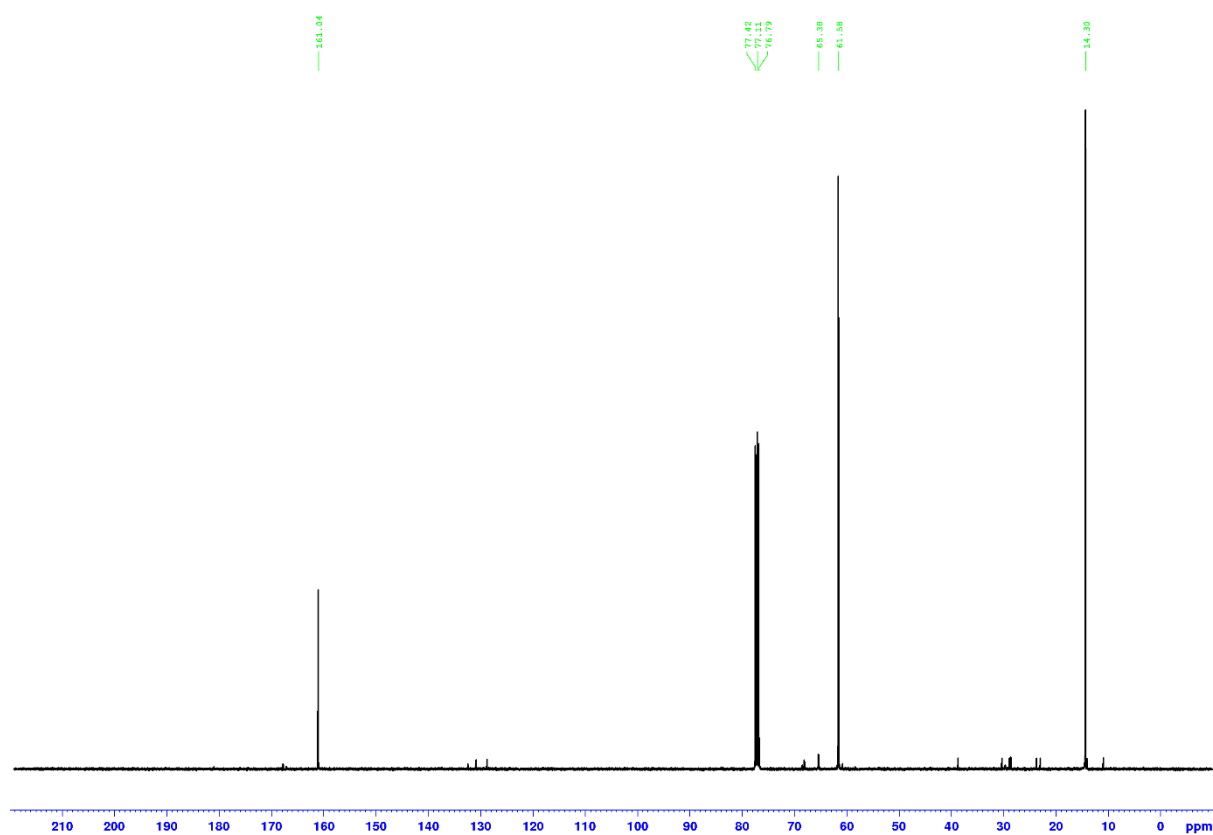


Figure S12. ¹³C NMR (100.6 MHz, CDCl₃) spectrum of α-diazo ester **26**.

Chemical structure: COC(=O)C(O)(Cl)c1ccccc1

¹H NMR spectrum (CDCl₃) showing peaks from 0.0 to 10.5 ppm. The spectrum includes a chemical structure of methyl 2-chloro-2-phenylpropanoate and integration values (13.03, 7.43, 12.03, 11.32, 3.48, 2.70) below the baseline.

¹H NMR spectrum (CDCl₃) of 1,3-bis(4-oxocyclohex-1-en-1-yl)propan-2-one. The spectrum shows peaks at 7.468, 7.392, 7.342, 7.298, 7.284, 7.253, 7.263, 5.582, 5.571, 3.977, 3.588, 3.587, and -0.000 ppm. Integration values are 4.92, 1.00, 3.19, and 1.11.

S10

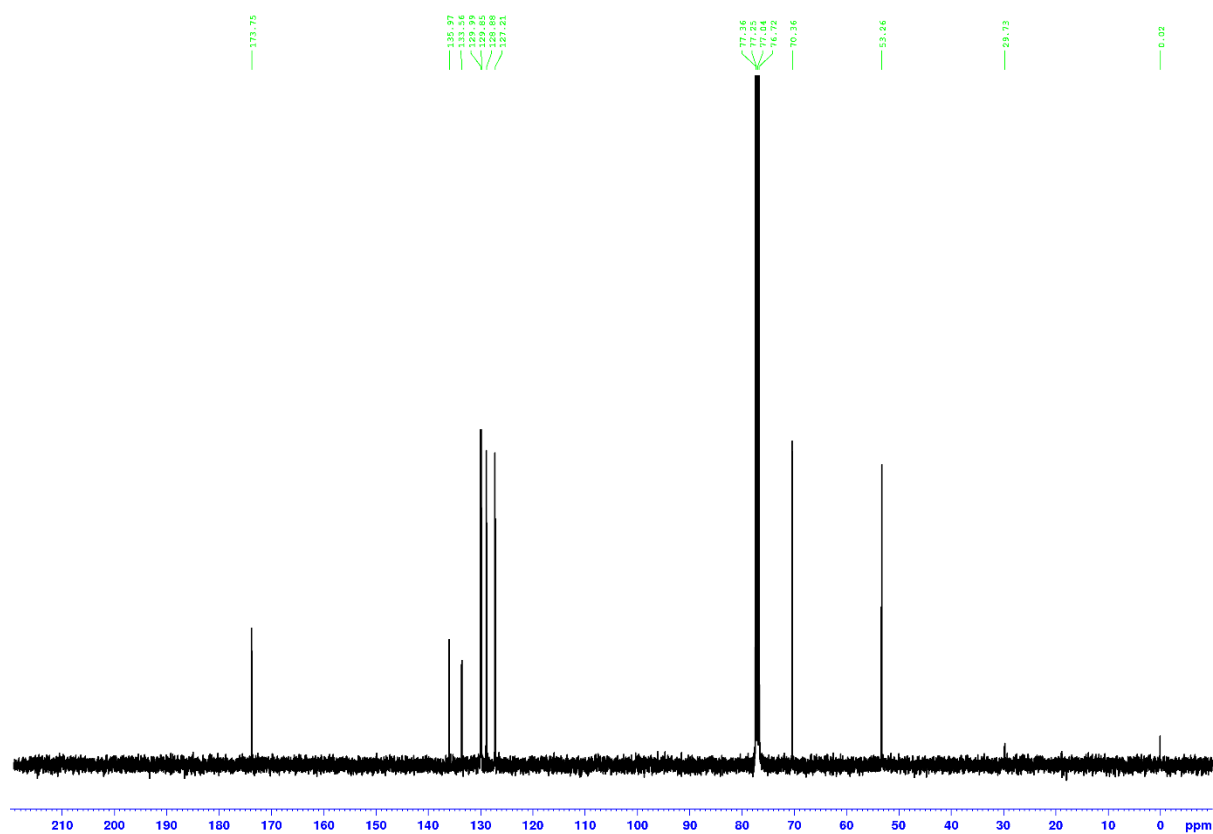


Figure S15. ^{13}C NMR (100.6 MHz, CDCl_3) spectrum of α -hydroxyl ester **10** (from telescoped process, see Scheme 10).

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