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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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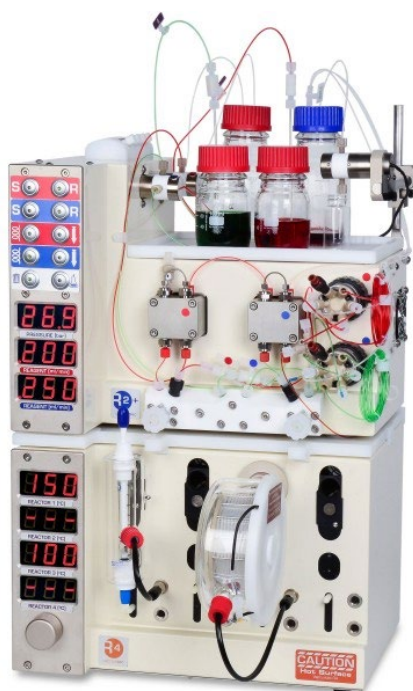
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## Details of Continuous Flow Platforms & Set up

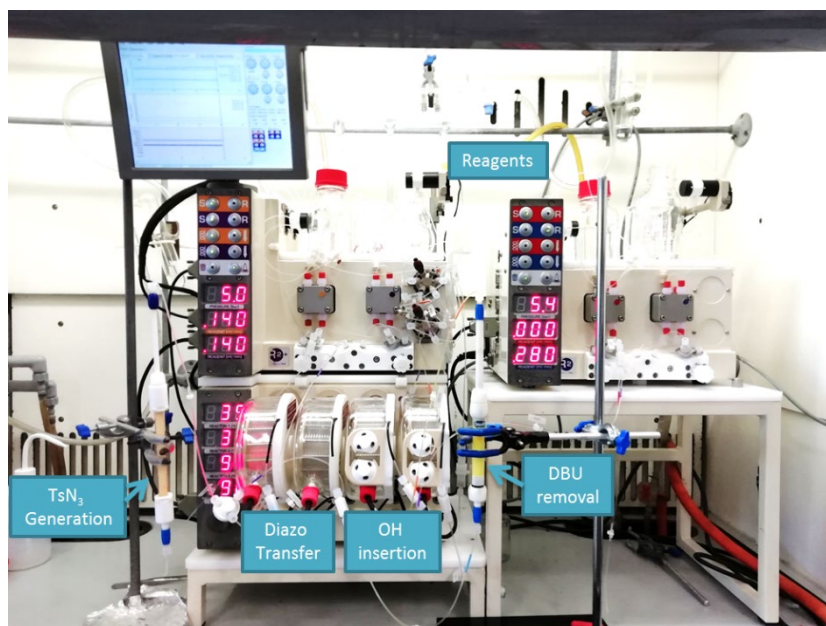
Continuous processes were performed using a Vapourtec R-Series flow system consisting of four piston (HPLC) pumps. Solid phase reagents/reaction components were employed using Omnifit glass column reactors (100 mm  $\times$  10 mm internal diameter, one fixed end piece and one adjustable end piece). 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**

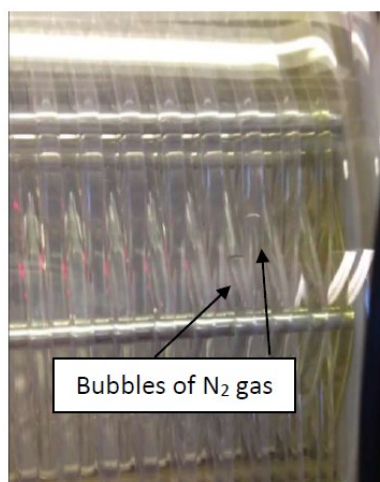


General specifications for continuous-flow system	
Material of tubing	PFA
Internal diameter of tubing	1 mm
External diameter of tubing	1.59 mm
Working flow rates	0.05 mL/min – 9.99 mL/min
Tubular reactor working volume	10 mL
Temperature range	–70 °C to 250 °C

## 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  $\alpha$ -diazo aryl acetate **9** in flow (see Scheme 8).

## **Copies of $^1\text{H}$ and $^{13}\text{C}$ 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)

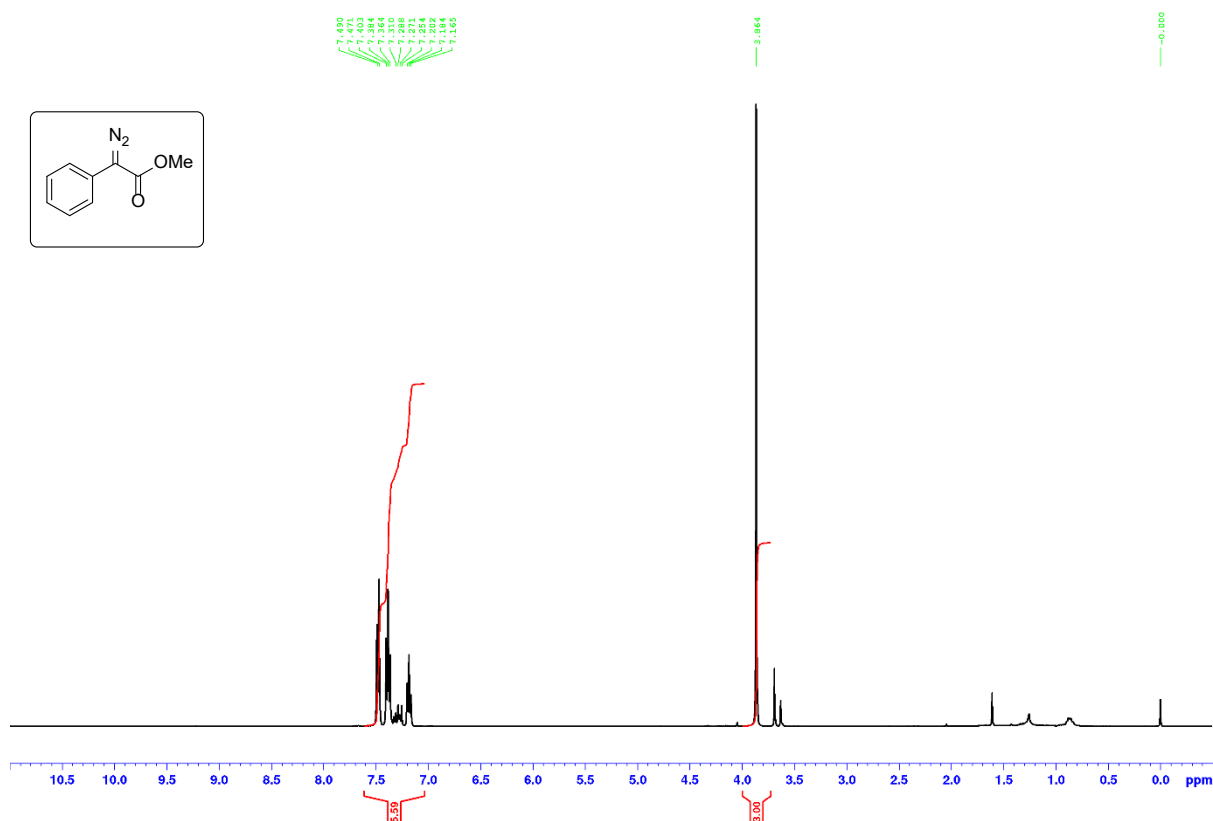
<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) showing aromatic signals (7.0-7.6 ppm) and a methoxy singlet (3.867 ppm). Integration values are 3.98 and 3.02.

13C NMR spectrum of 1,2-dichloroethane. The spectrum shows a triplet for the CDCl3 solvent at 77.0 ppm and a quartet for the 1,2-dichloroethane at 44.7 ppm. Numerous aliphatic peaks are visible in the 10-40 ppm range. The x-axis is labeled from 210 to 0 ppm.

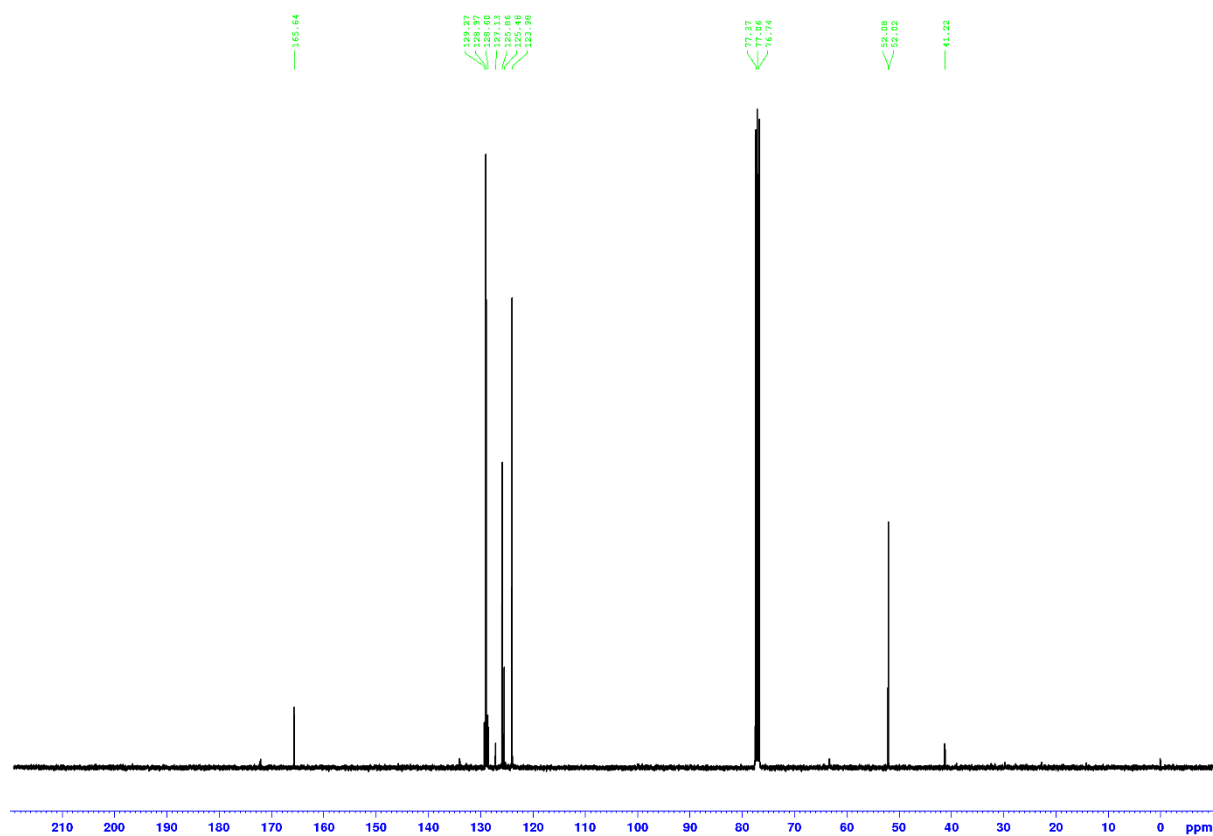
Chemical Shift (ppm)
165.98
133.76
132.30
128.63
127.16
123.89
77.38
77.07
76.75
53.91
52.28
31.94
31.74
29.92
29.38
28.71
26.92
22.81
22.51
22.67
14.14

S5

**Methyl 2-diazo-2-phenylacetate (20)<sup>2</sup>**



**Figure S5.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectrum of α-diazo ester **20**.



**Figure S6.** <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz) spectrum of α-diazo ester **20**.

# Isobutyl 2-diazo-2-phenylacetate (**22**)<sup>2</sup>

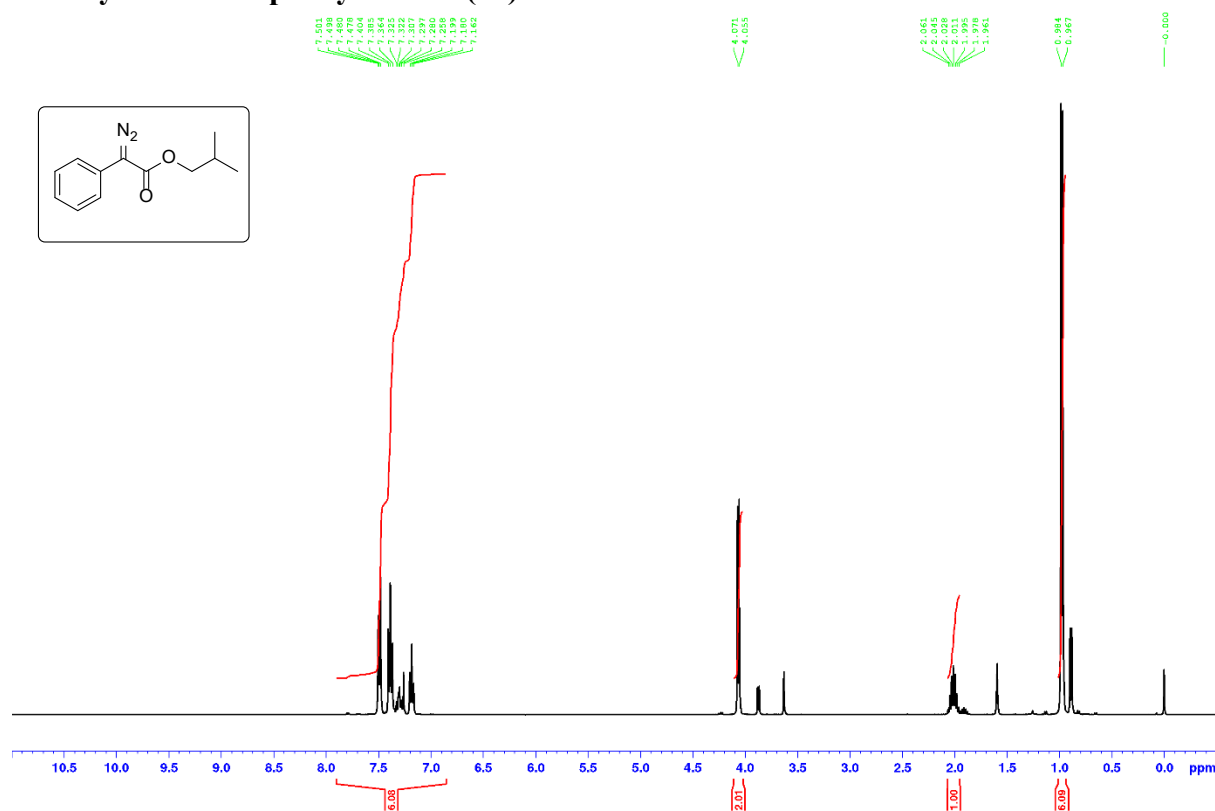


Figure S7. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) spectrum of  $\alpha$ -diazo ester **22**.

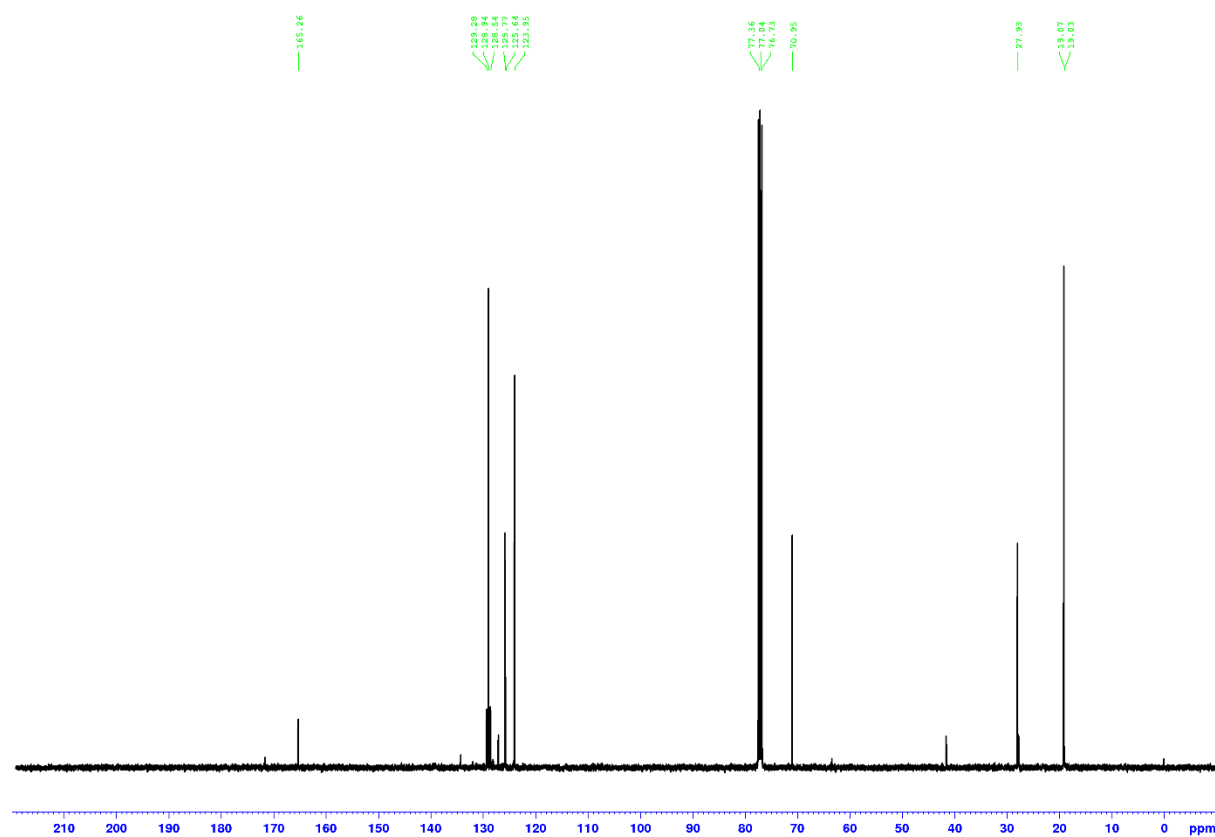
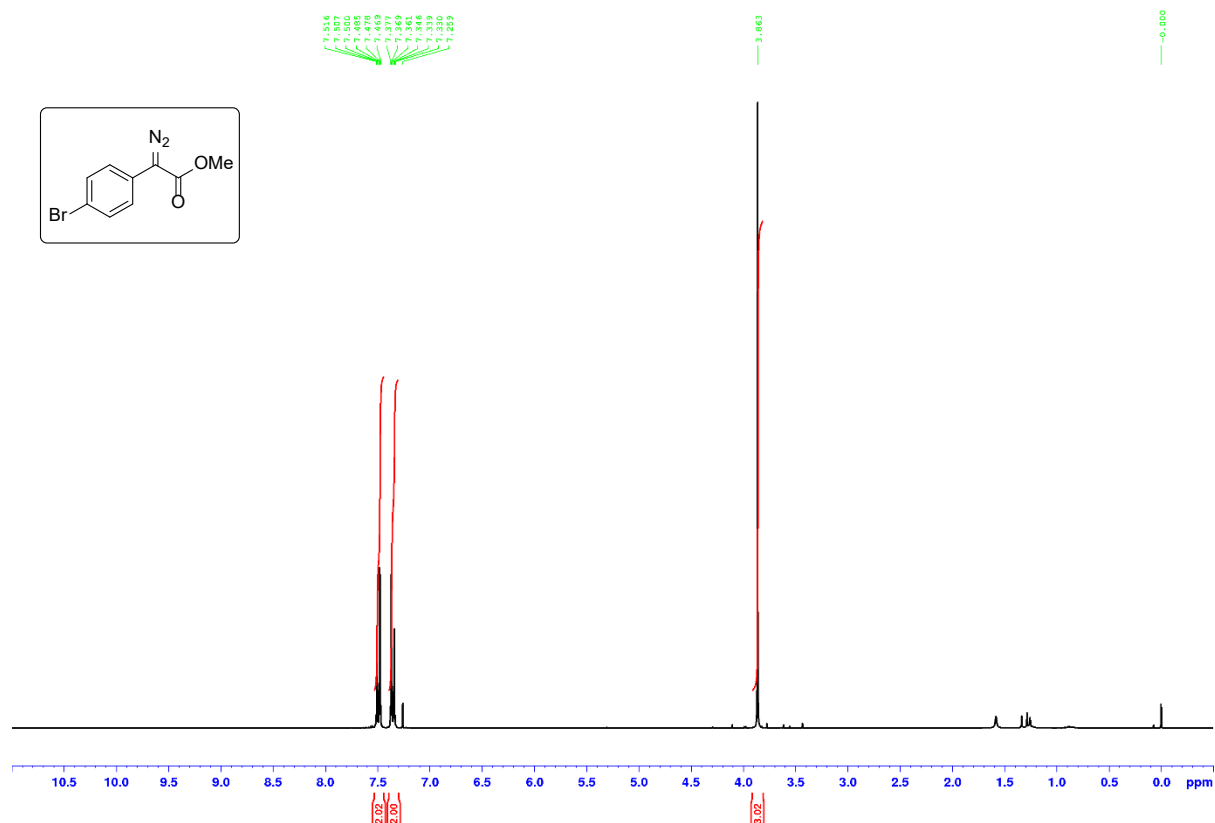


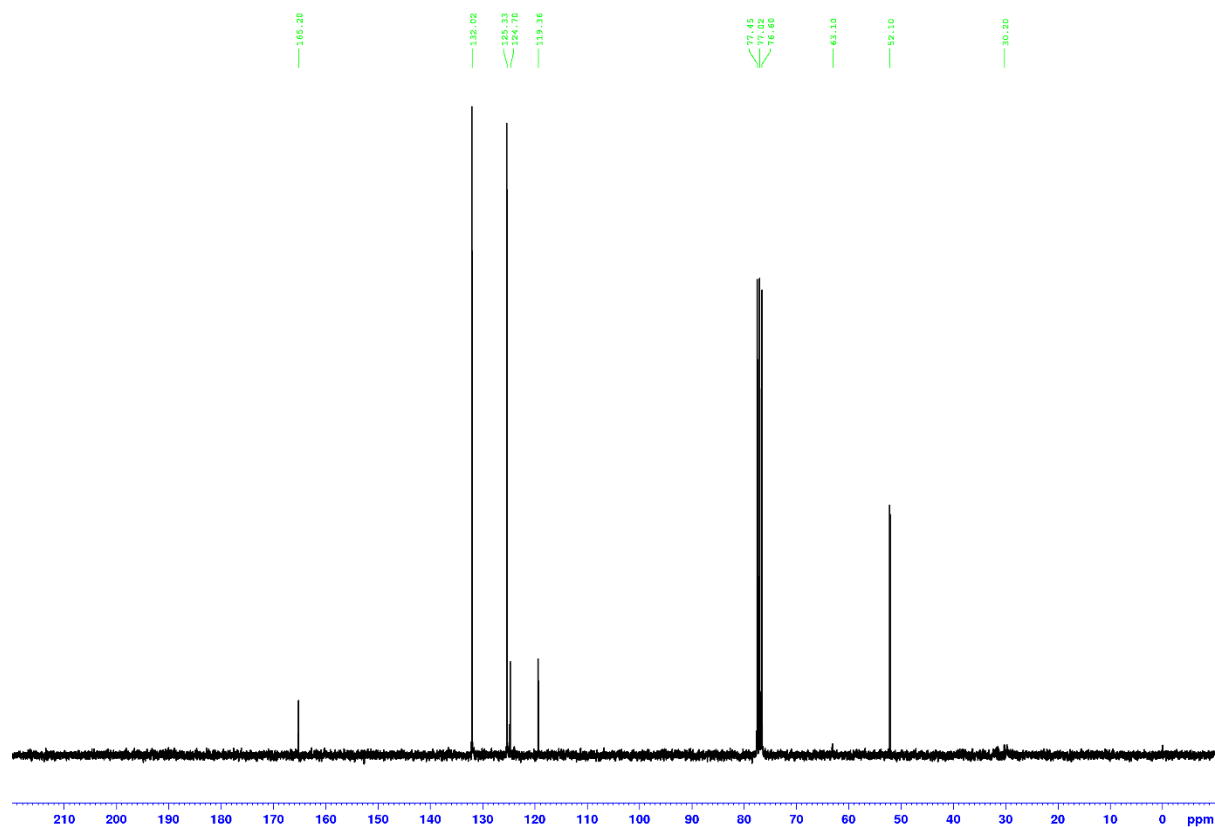
Figure S8. <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 100.6 MHz) spectrum of  $\alpha$ -diazo ester **22**.



**Methyl 2-(4-bromophenyl)-2-diazoacetate (**24**)<sup>3</sup>**

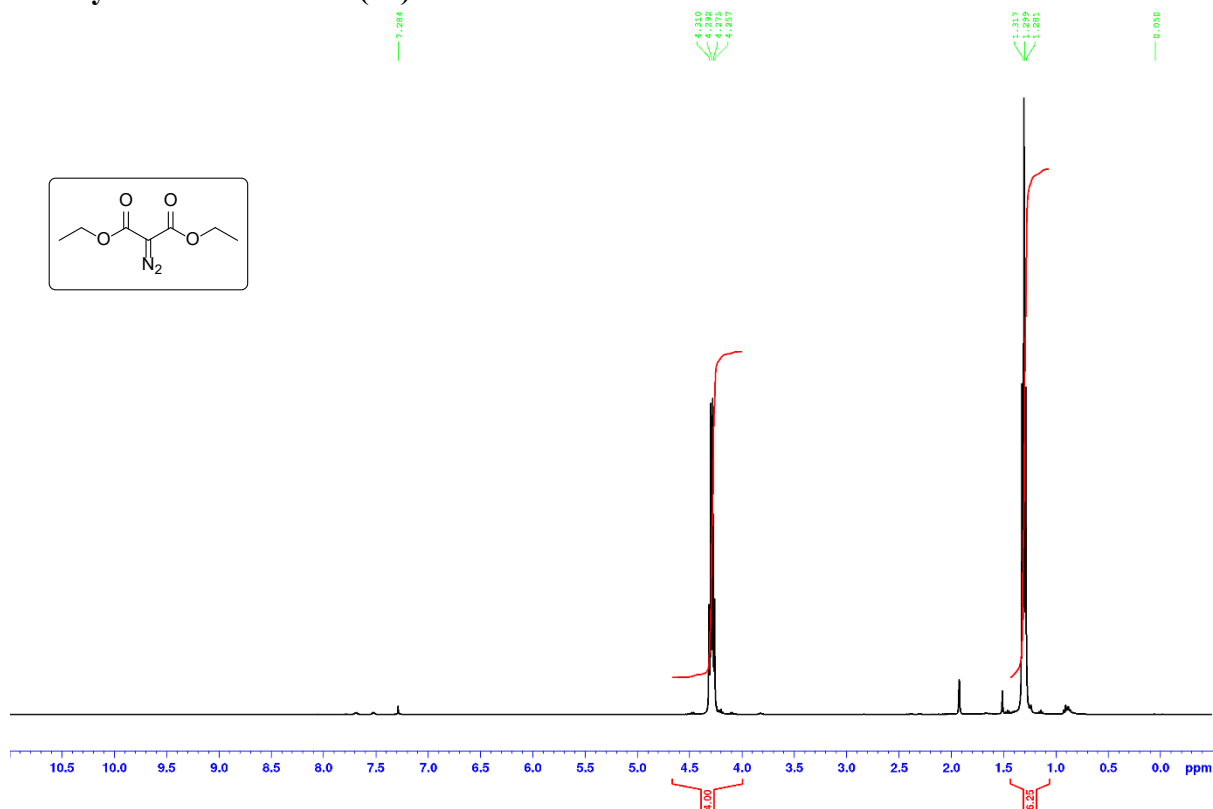


**Figure S9.** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) spectrum of  $\alpha$ -diazo ester **24**.

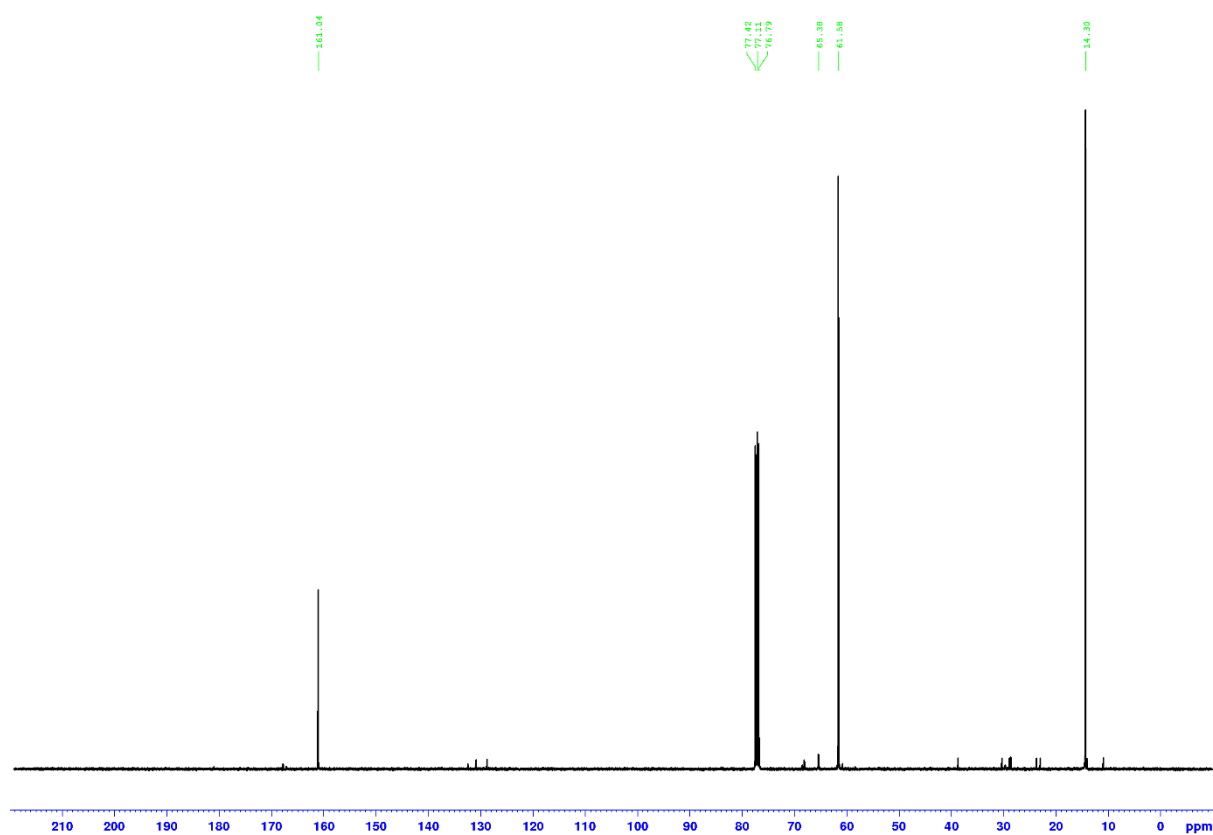


**Figure S10.** <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 75.5 MHz) spectrum of  $\alpha$ -diazo ester **24**.

**Diethyl 2-diazomalonate (26)<sup>4</sup>**



**Figure S11.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of α-diazo ester 26.



**Figure S12.** <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>) spectrum of α-diazo ester 26.

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

<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) showing peaks from 0 to 8 ppm. The x-axis is labeled in ppm. Integration values are shown below the baseline. A chemical structure of methyl 2-chloro-2-phenylpropanoate is shown in the top left corner.

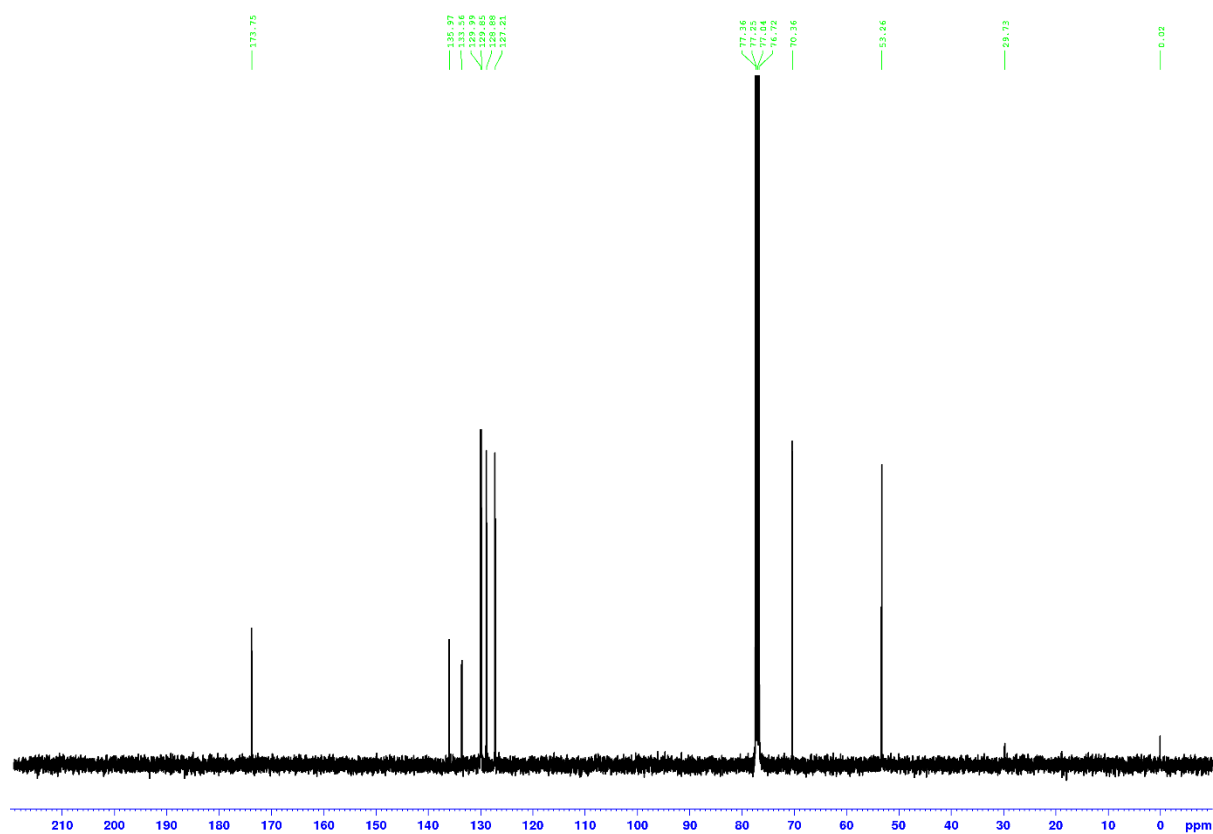
Peak list (ppm): 7.952, 7.931, 7.909, 7.887, 7.761, 7.742, 7.621, 7.601, 7.584, 7.564, 7.448, 7.428, 7.409, 7.389, 7.372, 7.356, 7.344, 7.329, 7.319, 7.311, 7.291, 7.278, 7.262, 7.242, 7.227, 7.217, 7.181, 7.167, 7.147, 5.513, 5.505, 5.423, 3.953, 3.934, 3.914, 3.792, 3.773, 3.753, 3.711, 3.628, 3.576, 3.553, 3.466, 3.446, 2.477, 2.477, 2.359, 2.359, 1.796, 1.793, 1.430, 1.430, 1.218, 1.218, 1.183, 1.183, -0.000.

Integration values: 3.00, 7.43, 2.00, 1.32, 3.46, 2.70.

Chemical structure of compound 10 is shown in the top right corner. The  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) displays the following peaks (ppm) and integrations:

- 7.408, 7.392, 7.376, 7.359, 7.284, 7.263 (Integration: 4.92)
- 5.592, 5.571 (Integration: 1.00)
- 3.777, 3.760, 3.597 (Integration: 3.19)
- 3.597 (Integration: 1.11)
- 1.700, 1.300 (Integration: 1.00)

S10



**Figure S15.**  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ) spectrum of  $\alpha$ -hydroxyl ester **10** (from telescoped process, see Scheme 10).

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