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Supplementary Information

Enantioselective Synthesis of Seven-Membered Carbo- and Heterocyles by Organocatalyzed Intramolecular Michael Addition.

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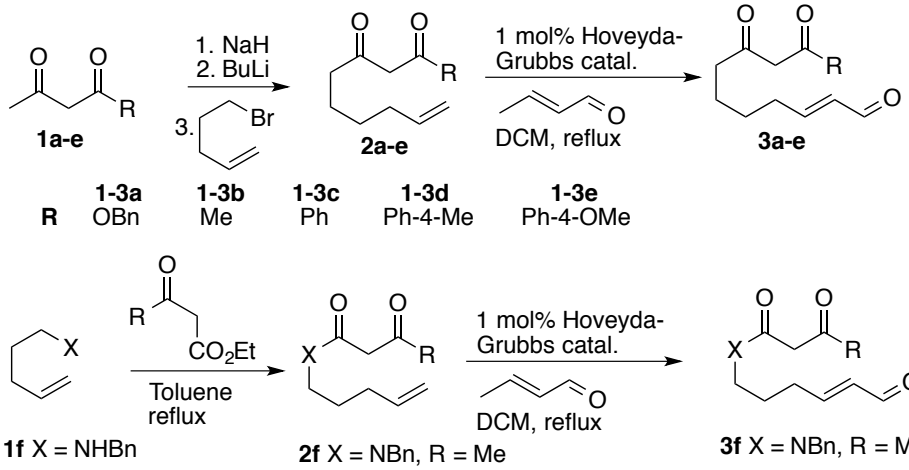
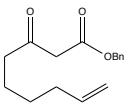
TABLE OF CONTENTS

Synthesis of diketoenones 2a-f



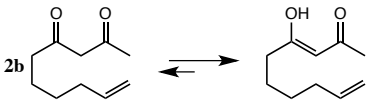
The alkylation of diketones was done by slight modification of a previously described methodology.[1] To a suspension of NaH (1.1 equiv., 9.7mmol, 380mg) in anhydrous THF (15 mL) cooled to 0 ^{o}C, under nitrogen atmosphere, was added a solution of the corresponding diketone (1 equiv., 8.7 mmol) in THF (5 mL). The solution was stirred for 15 min., and then a solution of n-BuLi (1.1 equiv., 9.7 mmol) was dropped, and the mixture was stirred for additional 15 min. To that mixture, a solution of corresponding bromide (1 equiv., 8.7 mmol) in THF (5 mL) was added and the stirring was continued until the reaction was finished (ca. 3 h., TLC). The reaction mixture was quenched by addition of 1M HCl (20 mL), the organic phase was washed, dried over $MgSO_4$, the solvent evaporated under vacuum, and the residue purified by flash chromatography (silicagel, hexane/EtOAc), giving compounds **2a-e** in 70-90%.

Benzyl 3-oxonon-8-enoate (2a) ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 5H); 5.77 (m, 1H); 5.17 (s, 2H); 4.97 (m, 2H); 3.47 (s, 2H); 2.50 (t, 2H); 2.03 (m, 2H); 1.59 (m, 2H); 1.36 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 202.5; 167.0; 138.3; 135.3; 128.7 (2C); 128.4; 128.3 (2C); 114.7; 67.2; 49.8; 42.8; 33.6; 28.2; 22.8.

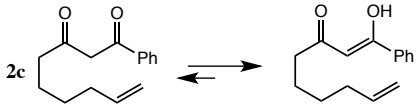


Dec-9-ene-2,4-dione (2b) ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.73 (dd, *J* = 17.0, 10.3 Hz, 1H), 5.42 (s, 0.7H), 5.06 – 4.82 (m, 2H), 3.55 (s, 0,3H), 2.20 (dd, *J* = 15.1, 7.4 Hz, 2H), 2.10 (s, 3H), 2.06 – 1.91 (m, 1H), 1.69 – 1.43 (m, 3H), 1.36 (dt, *J* = 15.5, 7.6 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 227.3, 191.4, 138.4, 114.7, 99.7, 38.0, 33.4, 28.4, 25.1, 24.9.

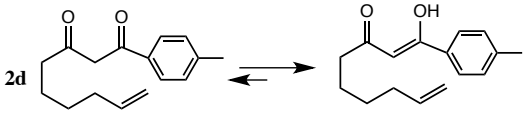
[1] Y, Zhang, J. Jiao, R. A. Flowers, *J. Org. Chem.* **2006**, *71*, 4516.



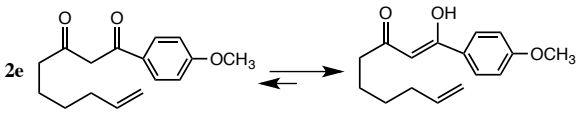
1-Phenylnon-8-ene-1,3-dione (2c) ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.81 (m, 2H) 7.54 – 7.35 (m, 3H), 6.18 (s, 0.85H), 5.78-5.68 (m, 1H), 5.09 – 4.89 (m, 2H), 4.07 (s, 0.15H), 2.95 (t, 0.3H), 2.58 (t, 0.2H), 2.42 (t,1.5H), 2.07-2.01 (m, 2H), 1.73 – 1.65 (m, 2H), 1.50-1.36 (m, 2H). ^{13}C-NMR (101 MHz, $CDCl_3$) δ 196.8, 183.5, 138.4, 135.1, 132.22, 128.6, 128.5, 128.1, 127.1, 127.0, 114.8, 114.7, 96.1, 39.1, 33.5, 28.5, 25.3.



1-(*p*-Tolyl)non-8-ene-1,3-dione (2d) ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 2H), 7.32 – 7.25 (m, 2H), 6.17 – 6.14 (m, 0.85H), 5.83 – 5.64 (m, 1H), 5.11 – 4.89 (m, 2H), 4.11 (s, 0.15H), 2.42 (s, 3H), 2.15 – 2.05 (m, 2H), 1.75 - 1.60 (S, 2H), 1.53 – 1.36 (m, 4H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 196.0, 183.9, 142.9, 138.5, 138.4, 132.4, 129.31, 129.2, 128.2, 127.1, 127.0, 114.7, 114.7, 95.9, 95.7, 49.0, 38.9, 38.2, 33.8, 33.5, 32.4, 29.7, 28.5, 26.8, 26.6, 25.3, 22.5, 21.6, 13.9.



1-(4-Methoxyphenyl)non-8-ene-1,3-dione (2e) ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.70 (m, 2H), 6.87 (d, J = 8.9 Hz, 2H), 6.13 (s, 0.9H), 5.86 – 5.75 (m, 1H), 5.07– 4.92 (m, 2H), 4.04 (s, 0.1H), 3.88 (s, 3H), 2.45 – 2.38 (m, 2H), 2.15 – 2.02 (m, 2H), 1.75 – 1.42 (m, 4H).^{13}C-NMR (126 MHz, $CDCl_3$) δ 194.6, 184.3, 163.0, 138.4, 131.1, 130.3, 129.2, 129.1, 127.7, 114.7, 114.6, 114.0, 113.9, 113.6, 95.2, 55.4, 38.6, 33.5, 28.5, 25.4.



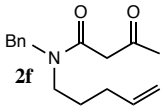
Synthesis of ketoamide 2f

The named compound was prepared by aminolysis of ethylacetoacetate.[2] A mixture of ethyl acetoacetate (1 equiv., 1.3 mmol), amine **1f**[3] (1.2 equiv., 1.56 mmol), and 4-dimethylamino pyridine (0.5 equiv., 0.65 mmol), in toluene (20 mL) was refluxed until consumption of the ketoester (TLC). The solvent was evaporated under educed pressure, and the residue was purified by flash chromatography (silicagel, hexane/EtOAc) giving **3f** in 75%.

***N*-benzyl-3-oxo-*N*-(pent-4-en-1-yl)butanamide (2f)** ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.40-7.15 (m, 5H), 5.85-5.69 (m, 1H), 5.15-4.90 (m, 2H), 4.63 (s, 1H), 4.51 (s, 1H), 3.60 (s, 1H), 3.52 (s, 1H), 3.42-3.30 (m, 1H) 3.22-3.14 (m, 1H), 2.32 (s, 1.5H), 2.26 (s, 1.5H), 2.07-1.96 (m, 2H), 1.72-

[2] D. Yang, G. Y. Lian, H. F Yang, J. D. Yu, D. W. Zhang, X. Gao, *J. Org. Chem.*, **2009**, 74, 8610
[3] C. Taillier, T. Hameury, V. Bellosta. J. Cossy. *Tetrahedron,* **2007**, 63 4472

1.59 (m, 2H). ^{13}C-NMR (126 MHz, $CDCl_3$) δ 202.48, 175.25, 167.04, 166.71, 137.70, 137.1, 136.9, 136.4, 129.0, 128.6, 127.9, 127.8, 127.4, 126.2, 115.9, 115.1, 51.7, 50.1, 49.8, 48.2, 47.0, 46.1, 31.0, 30.6, 30.3, 27.4, 26.5.

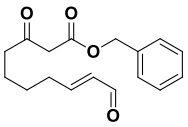


2f **Mixture of rotamers**

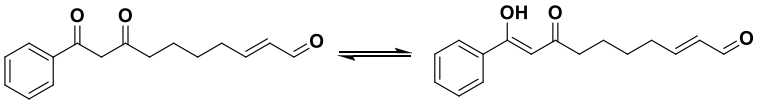
Synthesis of enals 3a-f

These compounds were prepared by cross-metathesis as previously described.[4] To a solution of **2a-f** (2 mmol) and crotonaldehyde (2.5 mmol) in deoxygenated DCM (20 mL) was added Hoveyda-Grubbs catalyst (1 mol%) and heated until disappearance of starting compound (TLC). The solvent was eliminated under vacuum, and the residue was purified by flash chromatography (silicagel, hexane/EtOAc) giving enals in 85-95%.

(E)-Benzyl 3,10-dioxodec-8-enoate (3a). Colorless oil; **^{1}H-NMR (500 MHz, $CDCl_3$)** δ 1.18 – 1.78 (m, 4H), 2.16 – 2.40 (m, 2H), 2.54 (t, *J* = 7.1 Hz, 2H), 3.48 (s, 2H), 5.17 (s, 2H), 5.88 – 6.18 (m, 1H), 6.79 (dt, *J* = 15.6, 6.7 Hz, 1H), 7.35 (m, 5H), 9.49 (d, *J* = 7.9 Hz, 1H), **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 27.2, 22.9, 27.2, 32.5, 42.6, 49.4, 67.3, 128.3, 128.4, 128.5, 128.6, 128.7, 128.7, 133.3, 135.3, 158.0, 167.1, 194.1, 202.1; **IR** 3416, 2938, 2864, 2715, 1734, 1713, 1681, 1161; **HRMS** $C_{17}H_{21}O_4$ (M+H) Calc: 289.1434.; Found: 289.1437.



(E)-8,10-Dioxo-10-phenyldec-2-enal (3c) Colorless oil; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.47 – 1.68 (m, 2H), 1.67 – 1.81 (m, 2H), 1.90 (dd, *J* = 6.9, 1.7 Hz, 1H), 2.24 – 2.45 (m, 2H), 2.46 (dd, *J* = 24.5, 17.0 Hz, 2H), 5.98 – 6.27 (m, 2H), 6.84 (dt, *J* = 15.6, 6.8 Hz, 1H), 7.36 – 7.71 (m, 3H), 7.73 – 8.03 (m, 2H), 9.50 (d, *J* = 7.9 Hz, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 18.2, 22.9, 25.3, 27.3, 27.5, 32.6, 39.0, 43.0, 54.1, 96.3, 122.2, 127.1, 128.8, 128.9, 132.5, 133.3, 134.9, 147.4, 158.1, 183.4, 194.1, 196.5; **IR** 2944, 2986, 2721, 1691, 1601, 1453, 970; **HRMS** $C_{16}H_{19}O_3$ (M+H) Calc: 259.1329; Found: 259.1330.

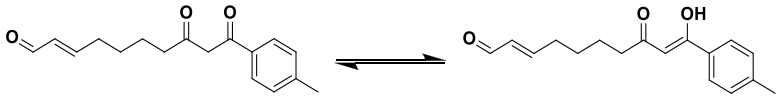


(E)-8,10-Dioxoundec-2-enal (3b) Colorless oil; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.41 – 1.72 (m, 5H), 1.91 (dt, *J* = 6.9, 1.8 Hz, 0.5H), 2.05 (d, *J* = 1.7 Hz, 2.5H), 2.14 – 2.44 (m, 4H), 3.57 (s, 0.2H), 5.48 (d, *J* = 1.2 Hz, 0.8H), 5.75 – 5.97 (m, 0.2H), 6.12 (ddd, *J* = 15.6, 7.9, 1.6 Hz, 0.8H), 6.83 (dt, *J* = 15.6, 6.7 Hz, 0.8H), 6.96 – 7.19 (m, 0.2H), 9.51 (dd, *J* = 7.9, 1.8 Hz, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 22.8, 25.0, 25.2, 27.5, 32.5, 32.6, 38.1, 100.0,

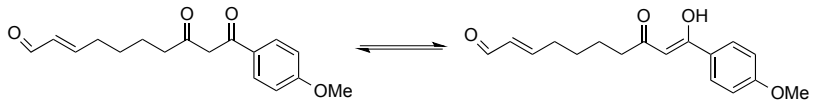
[4] (a)S. Fustero, D. Jimenez, J. Moscardo, S. Catalan, C. del Pozo, *Org. Lett,* **2007**, *9,* 5283 (b)E. C. Carlson, L. K. Rathbone, H. Yang, N. D. Collett, R. G. Carter, *J. Org. Chem.* **2008**, *73*, 5155

133.4, 158.0, 194.1; **IR** 3450, 2928, 2864, 1691, 1612, 975; **HRMS** $C_{11}H_{16}O_3Na$ (M+Na) Calc: 219.0992; Found: 219.0992.

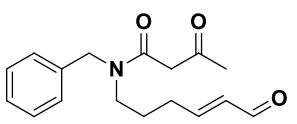
(E)-8,10-Dioxo-10-p-tolyldec-2-enal (3d) Colorless oil; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.69 (ddd, *J* = 51.3, 12.8, 7.9 Hz, 4H), 1.91 (ddd, *J* = 7.0, 1.7, 0.5 Hz, 2H), 2.42 (m, 4.7H), 2.89 (m, 0.3H), 5.85 (dd, *J* = 15.5, 1.7 Hz, 0.7H), 6.13 (m, 1.3H), 6.85 (m, 1H), 7.08 (dd, *J* = 15.5, 6.9 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.78 (m, 2H), 9.50 (d, *J* = 7.9 Hz, 1H); **^{3}C-NMR** (101 MHz, $CDCl_3$) δ 18.2, 21.7, 25.4, 26.8, 27.6, 32.6, 38.9, 95.9, 122.2, 127.2, 127.3, 128.3, 128.9, 129.3, 129.5, 129.7, 132.3, 133.4, 143.3, 147.4, 158.1, 183.9, 194.1, 195.7; **IR** 2938, 2859, 2715, 1686, 1606, 1442, 1182; **HRMS** $C_{17}H_{21}O_3$ (M+H) Calc: 273.1485; Found: 273.1487.



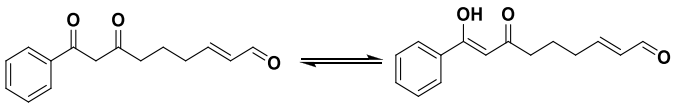
(E)-10-(4-Methoxyphenyl)-8,10-dioxodec-2-enal (3e) Colorless oil; **^{1}H-NMR** (500 MHz, $CDCl_3$) δ δ 1.60 (dd, *J* = 15.1, 7.9 Hz, 2H), 1.74 (m, 2H), 1.91 (dd, *J* = 6.9, 1.7 Hz, 1H), 2.41 (m, 4H), 3.86 (s, 2.6H), 4.03 (s, 0.4H), 6.12 (m, 2H), 6.83 (ddd, *J* = 18.7, 14.6, 9.4 Hz, 1H), 6.94 (dd, *J* = 8.8, 1.7 Hz, 2H), 7.86 (m, 2H), 9.50 (d, *J* = 7.9 Hz, 1H);**^{13}C-NMR** (126 MHz, $CDCl_3$) δ 18.2, 22.9, 25.5, 27.3, 27.6, 32.6, 38.5, 42.8, 54.1, 55.6, 55.7, 95.4, 114.1, 114.1, 122.1, 127.6, 129.2, 131.2, 133.3, 133.3, 147.3, 158.1, 163.3, 184.3, 194.1, 194.3; **IR** 2938, 2731, 1681, 1596, 1437; **HRMS** $C_{17}H_{21}O_4$ (M+H) Calc: 289.1434; Found: 289.1437.



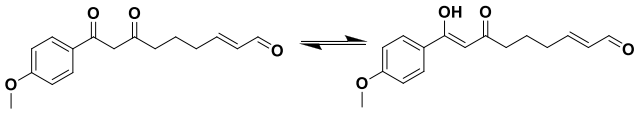
(E)-N-Benzyl-3-oxo-N-(6-oxohex-4-enyl)butanamide (3f) Colorless oil; **^{1}H-NMR** Rotamer (500 MHz, $CDCl_3$) δ 1.76 (dd, *J* = 15.7, 8.1 Hz, 2H), 1.95 (m, 1H), 2.31 (m, 4H), 3.33 (m, 2H), 3.58 (d, *J* = 26.5 Hz, 1.6H), 4.56 (d, *J* = 70.2 Hz, 2H), 5.10 (s, 0.4H) 6.10 (m, 1H), 6.80 (ddd, *J* = 50.7, 28.7, 11.2 Hz, 1H), 7.28 (m, 5H), 9.49 (d, *J* = 7.8 Hz, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 25.8, 26.8, 29.8, 30.1, 30.6, 45.8, 47.2, 48.5, 50.1, 52.0, 126.4, 127.8, 128.0, 128.1, 128.9, 129.2, 133.4, 133.8, 136.2, 155.8, 157.4, 167.4, 193.6, 194.0, 202.4; **IR** 3393, 2924, 2853, 2734, 1715, 1682, 1630; **HRMS** $C_{17}H_{22}NO_3$ (M+H) Calc: 288.1594; Found: 288.1601.



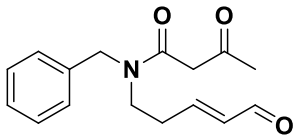
(*E*)-7,9-dioxo-9-phenylnon-2-enal (6c). Colorless oil. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.77 – 2.00 (m, 3H), 2.29 – 2.55 (m, 3H), 3.89 – 4.45 (m, 0.5H), 5.86 (dd, *J* = 15.6, 1.7 Hz, 0.5H), 6.04 – 6.34 (m, 1.5H), 6.85 (dt, *J* = 15.6, 6.7 Hz, 1H), 7.08 (dd, *J* = 15.5, 6.9 Hz, 0.5H), 7.35 – 8.00 (m, 5H), 9.53 (d, *J* = 7.8 Hz, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 18.6, 23.8, 32.1, 38.5, 96.4, 127.1, 128.8, 132.6, 133.7, 134.8, 147.4, 157.3, 183.4, 194.0, 195.9; **IR** 3358, 3055, 2938, 2730, 1675, 1596, 975; **HRMS** $C_{15}H_{17}O_3$ (M+H) Calc: 245.1172.; Obs: 245.1172.



(*E*)-9-(4-methoxyphenyl)-7,9-dioxonon-2-enal (6e). Colorless oil. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.92 (m, 2H), 2.45 (dd, *J* = 15.3, 7.8 Hz, 4H), 3.87 (m, 3.5H), 4.04 (s, 0.5H), 6.10 (s, 1H), 6.17 (d, *J* = 7.8 Hz, 1H), 6.86 (m, 1H), 6.94 (d, *J* = 9.0 Hz, 2H), 7.86 (d, *J* = 9.0 Hz, 2H), 9.52 (d, *J* = 7.8 Hz, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 24.0, 32.1, 38.0, 55.6, 95.5, 114.1, 114.2, 127.5, 129.3, 131.2, 133.6, 157.4, 163.3, 184.2, 193.7, 194.0; **IR** 2933.4, 2843.2, 2732, 1686.4, 1596, 1251.3, 1171.7; **HRMS** $C_{16}H_{19}O_4$ (M+H) Calc: 275.1278; Obs: 275.1278.



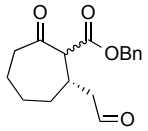
(*E*)-*N*-benzyl-3-oxo-*N*-(5-oxopent-3-en-1-yl)butanamide (6f). Colorless oil. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 2.32 (m, 3H), 2.58 (td, *J* = 7.6, 1.0 Hz, 2H), 3.38 (dd, *J* = 16.7, 8.7 Hz, 1.4H), 3.58 (m, 2.6H), 4.57 (d, *J* = 77.5 Hz, 2H), 6.09 (m, 1H), 6.76 (ddd, *J* = 64.7, 35.9, 11.4 Hz, 1H), 7.28 (m, 5H), 9.46 (dd, *J* = 9.2, 8.0 Hz, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 27.0, 29.4, 30.5, 30.6, 31.1, 31.8, 44.9, 45.5, 46.2, 47.8, 48.6, 50.0, 50.1, 50.5, 52.3, 61.0, 126.5, 127.8, 127.9, 128.0, 128.1, 128.2, 128.9, 128.9, 129.1, 129.3, 134.4, 134.9, 135.9, 152.2, 154.4, 167.5, 193.2, 193.8, 200.0, 202.2; **IR** 3398, 2924, 2957.7, 2734, 1715, 1682, 1625; **HRMS** $C_{16}H_{20}NO_3$ (M+H) Calc: 274.1438; Obs: 274.144.



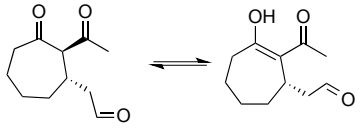
General procedure for the intramolecular nitro-Michael reaction by using catalysts C. A mixture of enal (0.8 mmol), p-nitrobenzoic acid (0.16 mmol, 20 mol%) and catalyst **C** (0.08 mmol, 10 mol%) in toluene (4 mL) was stirred at 0 ^{o}C for the time indicated in tables 2 and 3. Fater that time, the solvent was evaporated under vacuum, and the residue was purified by column chromatography to afford the cyclization products. The diastereomeric ratio was determined by ^{1}H NMR spectroscopy of the purified product. The enantiomeric excess was determined by chiral-phase HPLC analysis using mixtures of hexane/isopropanol as eluent. The racemic mixtures were prepared in the same way, but using *rac*-**C** as catalyst.

(7S)-Benzyl 2-oxo-7-(2-oxoethyl) cycloheptanecarboxylate (4a) Colorless oil; $[\alpha]_D^{20}$ = -21.7 (c = 0.9, $CHCl_3$ 93% ee). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.39 – 2.04 (m, 7H), 2.24 – 2.94 (m, 4H), 3.38 (dd, *J* = 9.9, 1.6 Hz, 0.5H), 3.84 (s, 0.5H), 5.16 (d, *J* = 7.3 Hz, 2H), 7.26

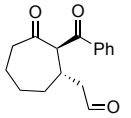
– 7.50 (m, 5H), 9.70 (d, *J* = 9.5 Hz, 1H), **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 23.6, 27.9, 31.1, 38.9, 43.6, 45.8, 48.9, 61.3, 128.3, 128.7, 135.4, 169.1, 169.6, 177.1, 200.7, 207.2, 207.8; **IR** 3474, 2928, 2864, 2721, 1734, 1702, 1453, 1171; **HPLC** (Chiralpack AD-H hexane/iPrOH 97:3; 0.7 mL/min, λ = 220 nm) t_R = 48.4 min (minor); t_R = 50.2 min (major); **HRMS** $C_{17}H_{21}O_4$ (M+H) Calc: 289.1434.; Found: 289.1431.



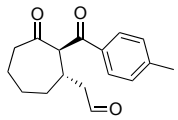
2-((1S,2R)-2-Acetyl-3-oxocycloheptyl)acetaldehyde (4b) Colorless oil; $[\alpha]_D^{20}$ = + 9.4 (c = 1.2, $CHCl_3$ 88% ee). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.17 – 1.99 (m, 7H), 2.00-2.30 (m, 3H), 2.36 –2.43 (m, 0.5H), 2.41 – 2.54 (m, 0.5H), 2.56 – 2.95 (m, 3H), 3.44 (ddd, *J* = 12.9, 7.5, 2.9 Hz, 0.5H), 3.63 (d, *J* = 10.3 Hz, 0.5H), 9.76 (dd, *J* = 24.9, 23.3 Hz, 1H);**^{13}C-NMR** (126 MHz, $CDCl_3$) δ 20.4, 23.9, 24.7, 25.2, 25.7, 26.6, 28.9, 30.0, 30.6, 32.1, 32.4, 33.3, 36.5, 37.5, 40.3, 41.6, 45.0, 46.7, 49.4, 123.8, 200.9, 201.1; **IR** 3398, 2922.8, 2853, 2700, 1691.7, 1654, 1553; **HPLC** (Chiralcel OJ-H hexane/iPrOH 95:5; 1 mL/min, λ = 254 nm) t_R = 16.5 min (major); t_R = 18.9 min (minor); **HRMS** $C_{11}H_{17}O_3$ (M+H) Calc: 197.1172; Found: 197.1174.



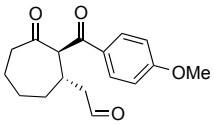
2-((1S,2S)-2-Benzoyl-3-oxocycloheptyl)acetaldehyde (4c) Colorless oil; $[\alpha]_D^{20}$ = + 9.0 (c = 0.7, $CHCl_3$ 90% ee). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.65 – 2.14 (m, 5H), 1.41 – 1.58 (m, 1H), 2.28 (ddd, *J* = 17.4, 10.0, 2.4 Hz, 1H), 2.44 (ddd, *J* = 17.7, 11.1, 4.7 Hz, 1H), 2.83 (dd, *J* = 17.6, 4.0 Hz, 2H), 2.98 – 3.17 (m, 1H), 4.84 (d, *J* = 2.4 Hz, 1H), 7.35 – 7.61 (m, 3H), 7.78 (dd, *J* = 8.3, 1.1 Hz, 2H), 9.77 (t, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 23.8, 24.9, 30.3, 33.8, 44.0, 44.9, 61.8, 127.2, 128.1, 128.6, 128.9, 133.4, 136.9, 196.8, 201.2, 209.6; **IR** 2933, 2864, 2726, 1690, 1681, 1447, 1214; **HPLC** (Chiralcel OJ-H hexane/iPrOH 50:50; 1 mL/min, λ = 254 nm) t_R = 13.8 min (major); t_R = 16.9 min (minor); **HRMS** $C_{16}H_{18}O_3Na$ (M+Na) Calc: 281.1148; Found: 281.1150.



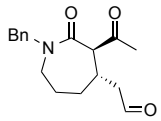
2-((1S,2S)-2-(4-Methylbenzoyl)-3-oxocycloheptyl)acetaldehyde (4d) Colorless oil; $[\alpha]_D^{20}$ = + 23.5 (c = 1, $CHCl_3$ 93% ee). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.50 (d, *J* = 12.4 Hz, 1H), 1.72 (d, *J* = 14.1 Hz, 1H), 1.92 (m, 4H), 2.27 (dd, *J* = 17.3, 10.0 Hz, 1H), 2.42 (m, 4H), 2.83 (d, *J* = 17.5 Hz, 2H), 3.06 (s, 1H), 4.80 (s, 1H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 9.76 (s, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 21.7, 23.8, 24.9, 30.4, 33.8, 44.0, 45.0, 61.8, 128.2, 129.6, 2C(134.5), 2C(144.3), 196.4, 201.3, 209.6; **IR** 2928, 2726, 1675, 1601, 1187, 731; **HPLC** (Chiralcel OJ-H hexane/iPrOH 70:30; 1 mL/min, λ = 254 nm) t_R = 28.9 min (major); t_R = 32.5 min (minor); **HRMS** $C_{17}H_{21}O_3$ (M+H) Calc: 273.1485; Found: 273.1488.



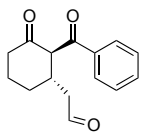
2-((1S,2S)-2-(4-Methoxybenzoyl)-3-oxocycloheptyl)acetaldehyde (4e) Colorless oil; $[\alpha]_D^{20}$ = + 10.9 (c = 1, $CHCl_3$ 84% ee). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.53 (d, *J* = 13.2 Hz, 1H), 1.73 (m, 1H), 1.93 (m, 4H), 2.29 (ddd, *J* = 17.4, 9.8, 2.2 Hz, 1H), 2.46 (ddd, *J* = 17.4, 10.8, 4.7 Hz, 1H), 2.84 (m, 2H), 3.06 (m, 1H), 3.86 (m, 3H), 4.78 (d, *J* = 2.3 Hz, 1H), 6.92 (dd, *J* = 8.6, 1.5 Hz, 2H), 7.77 (m, 2H), 9.76 (d, *J* = 2.2 Hz, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 23.8, 25.0, 30.6, 33.8, 44.0, 45.2, 55.6, 61.6, 2C(114.1), 2C(130.4), 2C(163.8), 195.2, 201.3, 209.7; **IR** 2933.4, 2853, 2730, 2254, 1702, 1601, 1166; **HPLC** (Chiralcel OJ-H hexane/iPrOH 50:50; 1 mL/min, λ = 254 nm) t_R = 24.6 min (major); t_R = 30.1 min (minor); **HRMS** $C_{17}H_{21}O_4$ (M+H) Calc: 289.1434; Found: 289.1437.



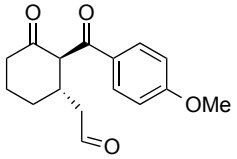
2-((3R,4S)-3-Acetyl-1-benzyl-2-oxoazepan-4-yl)acetaldehyde (4f) Colorless oil; $[\alpha]_D^{20}$ = + 12.1 (c = 1, $CHCl_3$ 92% ee). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.34 (d, *J* = 14.3 Hz, 1H), 1.57 (m, 2H), 1.91 (dd, *J* = 14.4, 3.8 Hz, 1H), 2.25 (m, 4H), 2.78 (dd, *J* = 17.1, 2.8 Hz, 1H), 2.94 (dd, *J* = 10.2, 3.4 Hz, 1H), 3.27 (dd, *J* = 15.5, 5.4 Hz, 1H), 3.46 (dd, *J* = 15.4, 11.3 Hz, 1H), 3.83 (s, 1H), 4.61 (dd, *J* = 34.8, 14.4 Hz, 2H), 7.31 (m, 5H), 9.72 (d, *J* = 2.8 Hz, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 23.1, 26.9, 30.2, 32.3, 43.2, 48.8, 51.2, 60.2, 123.6, 128.0, 128.5, 128.9, 131.3, 137.2, 170.8, 201.5, 203.5; **IR** 2922.8, 2853.8, 2249, 1718, 1628, 725; **HPLC** (Chiralcel OJ-H hexane/iPrOH 70:30; 1 mL/min, λ = 220 nm) t_R = 17.7 min (minor); t_R = 19.5 min (major); **HRMS** $C_{17}H_{22}NO_3$ (M+H) Calc: 288.1594; Found: 288.1598.



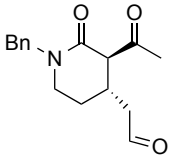
2-((1*S*,2*S*)-2-benzoyl-3-oxocyclohexyl)acetaldehyde (7c). Colorless oil. $[\alpha]_D^{20}$ = -32.9 (c = 0.8, $CHCl_3$ 78% ee). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.67 (ddd, *J* = 17.7, 10.4, 5.5 Hz, 1H), 1.85 (dddd, *J* = 11.2, 8.7, 6.3, 4.3 Hz, 1H), 2.10 (dddd, *J* = 17.0, 10.7, 8.9, 5.2 Hz, 2H), 2.29 – 2.66 (m, 4H), 2.90 – 3.11 (m, 1H), 4.39 (dd, *J* = 9.7, 0.8 Hz, 1H), 7.34 – 7.67 (m, 3H), 7. 88 (dd, *J* = 8.3, 1.1 Hz, 2H), 9.71 (dd, *J* = 1.8, 1.3 Hz, 1H), **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 24.7, 29.6, 35.6, 41.9, 48.2, 62.9, 128.5, 128.7, 128.9, 133.6, 2C(137.3), 197.5, 200.7, 207.6; **IR** 3421, 2928, 2859, 2715, 1680, 1675, 1240 cm^{-1}; **HPLC** (Chiralpak AS-H hexane/iPrOH 80:20; 1 mL/min, λ = 254 nm) t_R=22.9 min (minor); t_R=32.0 min (major); **HRMS** $C_{15}H_{17}O_3$ (M+H) Calc: 245.1172.; Obs: 245.1173.



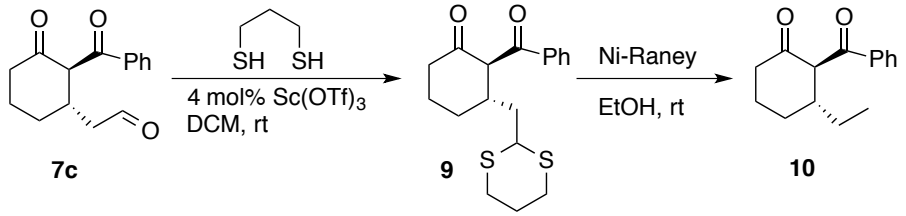
2-((1*S*,2*S*)-2-(4-methoxybenzoyl)-3-oxocyclohexyl)acetaldehyde (7e). Colorless oil. $[\alpha]_D^{20}$ = -27.1 (c = 0.8, $CHCl_3$ 89% ee). **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.64 (dd, *J* = 13.7, 3.3 Hz, 1H), 1.85 (m, 1H), 2.09 (m, 2H), 2.49 (m, 4H), 3.02 (m, 1H), 3.85 (s, 3H), 4.31 (d, *J* = 9.4 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 2H), 9.70 (d, *J* = 0.7 Hz, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 24.6, 29.4, 35.6, 41.7, 48.2, 55.6, 62.6, 114.0, 130.4, 2C(131.0), 2C(164.0), 195.6, 200.8, 207.7; **IR** 2922.8, 2853.8, 2715, 1697, 1665, 1601, 1251, 1023 cm^{-1}; **HPLC** (Chiralcel OJ-H hexane/iPrOH 50:50; 1 mL/min, λ = 254 nm) t_R=26.5 min (major); t_R=34.5 min (minor); **HRMS** $C_{16}H_{19}O_4$ (M+H) Calc: 275.1278; Obs: 275.1278.



2-((3*R*,4*S*)-3-acetyl-1-benzyl-2-oxopiperidin-4-yl)acetaldehyde (7f). Colorless oil. $[\alpha]_D^{20}$ = -14.0 (c = 1, $CHCl_3$ 64% ee) **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 1.53 (ddd, *J* = 10.1, 5.3, 3.6 Hz, 1H), 2.02 (m, 1H), 2.46 (m, 5H), 2.85 (m, 1H), 3.20 (dt, *J* = 12.5, 4.9 Hz, 1H), 3.31 (m, 1H), 3.37 (d, *J* = 8.8 Hz, 1H), 4.55 (dd, *J* = 39.7, 10.8 Hz, 2H), 7.28 (m, 5H), 9.74 (m, 1H); **^{13}C-NMR** (126 MHz, $CDCl_3$) δ 18.5, 25.8, 27.0, 27.8, 29.4, 29.8, 31.0, 42.6, 45.5, 47.2, 47.8, 50.0, 50.5, 61.0, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.6, 128.9, 128.9, 136.6, 165.8, 200.0, 201.1, 205.3; **IR** 3394, 2928, 2858, 2728, 1716, 1631cm^{-1}; **HPLC** (Chiralcel OJ-H hexane/iPrOH 70:30; 1 mL/min, λ = 220 nm) t_R=40.7 min (minor); t_R=44.0 min (major); **HRMS** $C_{16}H_{20}NO_3$ (M+H) Calc: 274.1438; Obs: 274.1441.



Chemical correlation of **7c** with **10**.



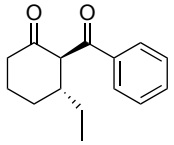
The chemoselective thioacetalization was done as previously described.[5] A mixture of 0.16 mmol of **7c** (78% ee), 0.20 mmol of 1,3-propanedithiol and scandium triflate (4 mol%) in 5 mL. of DCM was stirred at rt for 4 h. The solvent was eliminated under vacuum, and the residue was purified by flash chromatography (silicagel, hexane/ EtOAc: 4/1, v/v) giving **9** (85%) as colorless oil. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ: 1.55(m,

[5] A. Kamal, G. Chouhan, *Tetrahedron Lett*. **2002**, 43 1347.

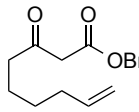
1H), 1.70 (m, 1H), 1.85 (m, 3H), 2.07 (m, 2H), 2.4 (m, 1H), 2.44 (m, 1H), 2.57 (m, 1H), 2.81 (m, 5H), 4.07 (dd, J_1 = 9 Hz, J_2 = 6 Hz, 1H), 4.20 (d, J = 10 Hz, 1H), 7.46 (m, 2H), 7,57 (m, 1H), 7.90 (m, 1H).

To a solution of **9** in 5 mL of ethanol was added 200 mg of Ni-Raney and the mixture was stirred at rt for 4 h. The mixture was filtered, the solid washed with ethanol (4 x 5 mL), and the filtrate was concentrated under educed pressure. The residue was purified by flash chromatography (silicagel, hexane/EtOAc: 2/1, v/v) giving to **10** in 50%. The absolute stereochemistry was established by both the sign of the optical rotation and the elution order of the enantiomers in HPLC.

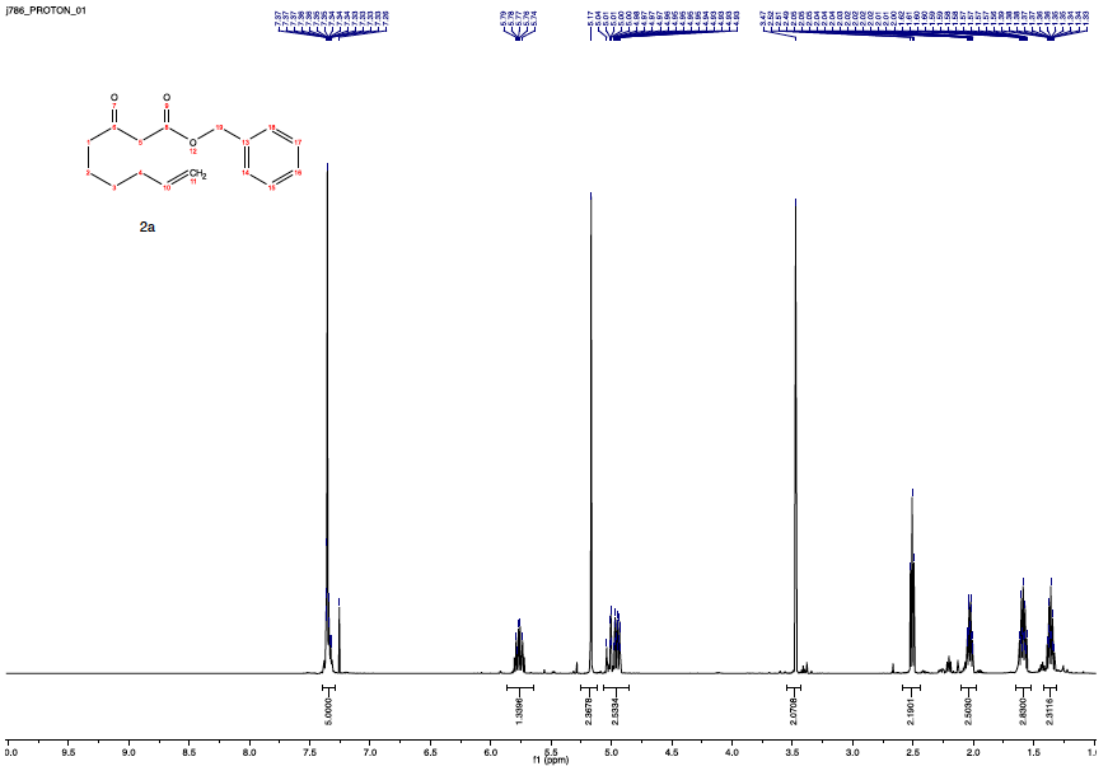
(2S,3R)-2-Benzoyl-3-ethylcyclohexanone (10). Colorless solid; $[\alpha]_D^{20}$ = + 6.6 (c = 1, $CHCl_3$ 76% ee), lit.[6] $[\alpha]_D^{24}$ = - 1.6 (c = 2.4, $CHCl_3$ 18% ee) for *ent*-**10**. **^{1}H-NMR** (500 MHz, $CDCl_3$) δ 0.91 (t, *J* = 7.4 Hz, 3H), 1.29 (dd, *J* = 13.4, 5.1 Hz, 1H), 1.44 (m, 2H), 1.82 (m, 1H), 2.08 (m, 2H), 2.48 (m, 3H), 4.18 (dd, *J* = 9.0, 0.9 Hz, 1H), 7.50 (m, 3H), 7.88 (dd, *J* = 8.3, 1.2 Hz, 2H); **HPLC** (Chiralcel OJ-H hexane/iPrOH 97:3; 1 mL/min, λ = 220 nm) t_R = 19.4 min (major); t_R = 29.4 min (minor) (76% ee), lit.[6a] t_R = 25.5 min for enantiomer (2S, 3R) and t_R = 35.5 min for enantiomer (2R, 3S) in the same HPLC conditions .



[6] (a)X. Tang, A. J. Blake, W. Lewis, S. Woodward, *Tetrahedron: Asymmetry* **2009,** *20*, 1881; (b) K. Agapiou, D. F. Cauble, M. J. Krische, *J. Am. Chem. Soc*. **2004**, 126, 4528.


O
O
OBn

2a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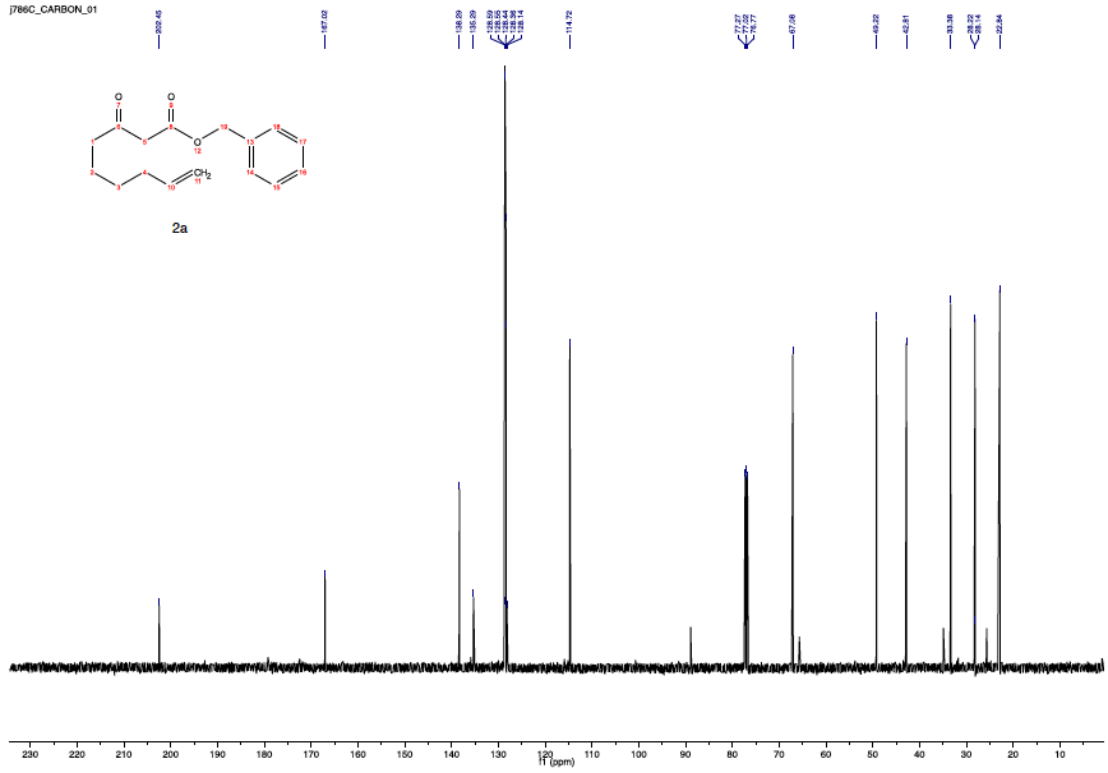
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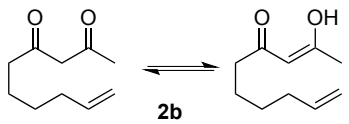

2b

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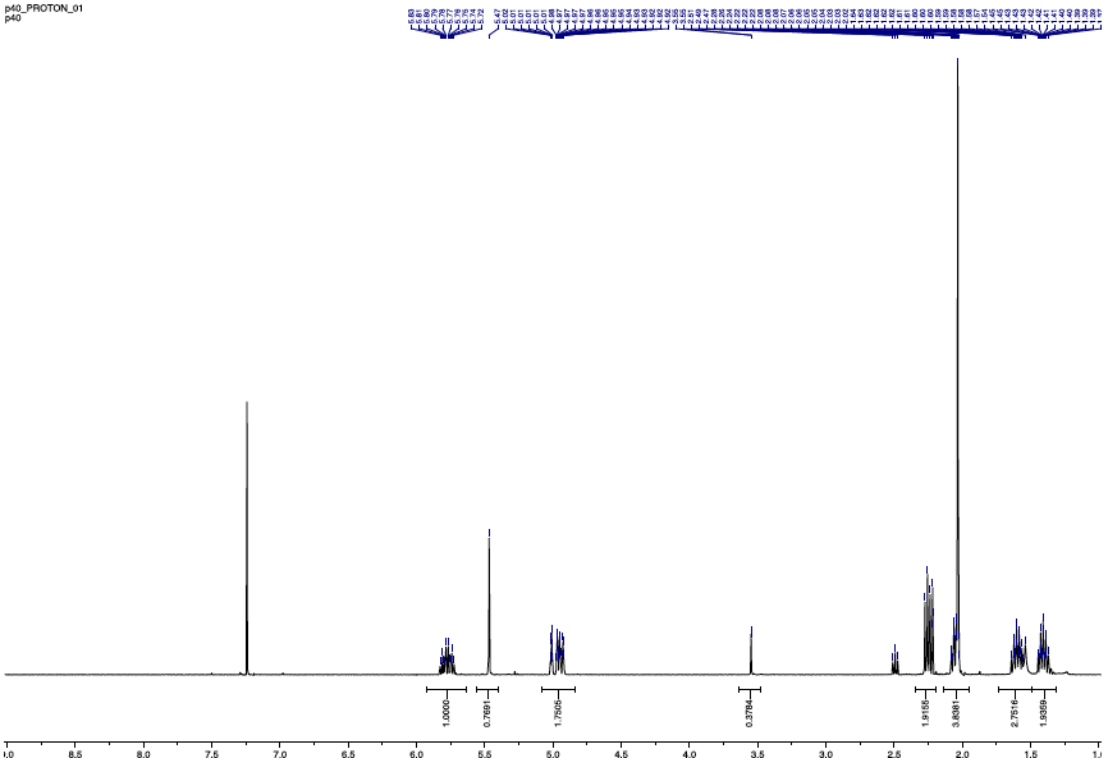

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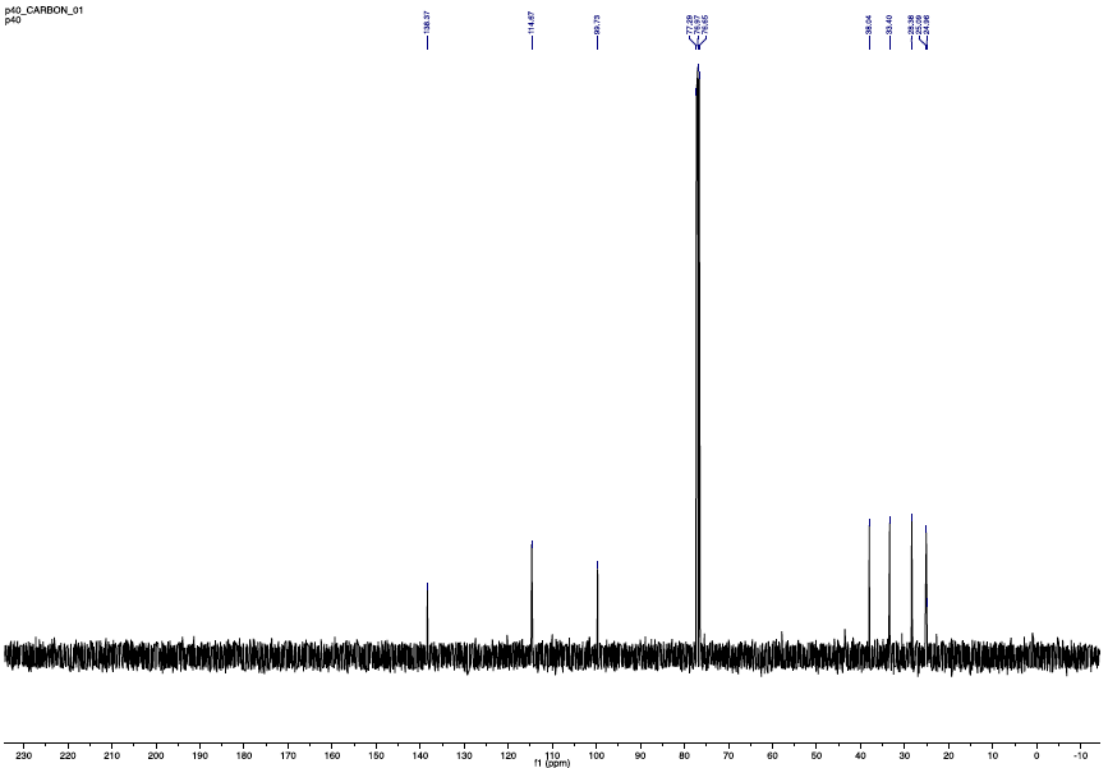

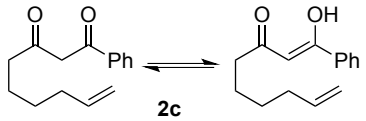
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O
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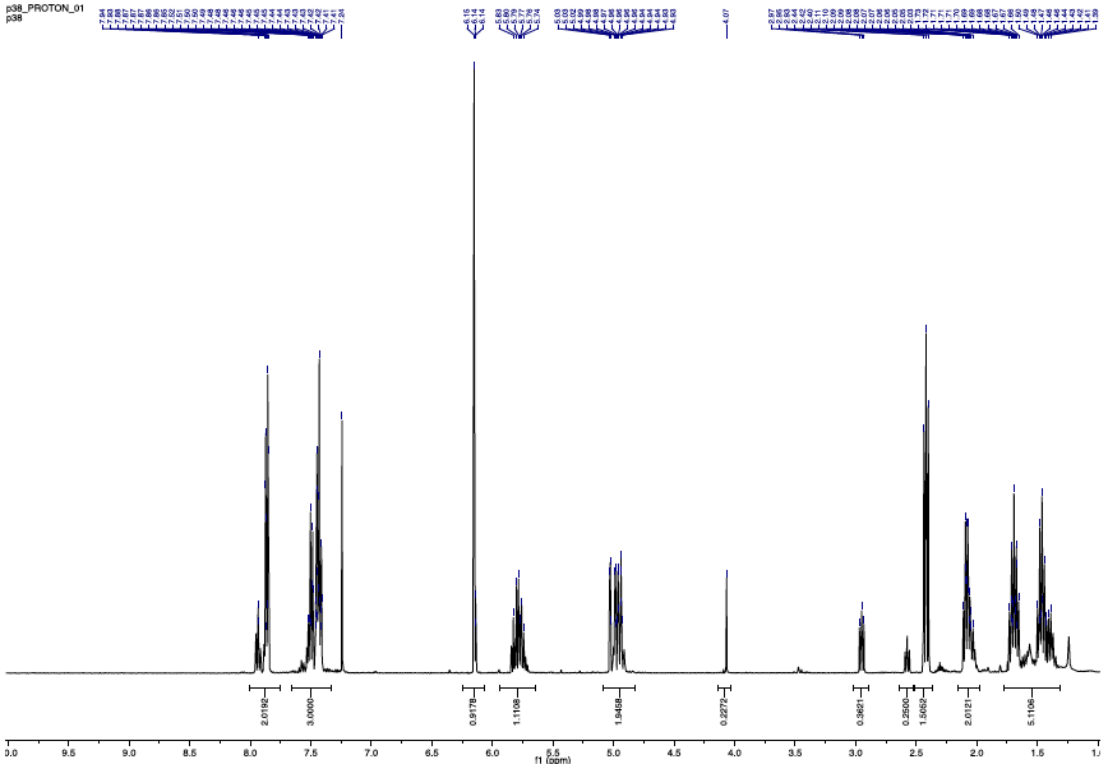
Ph

2c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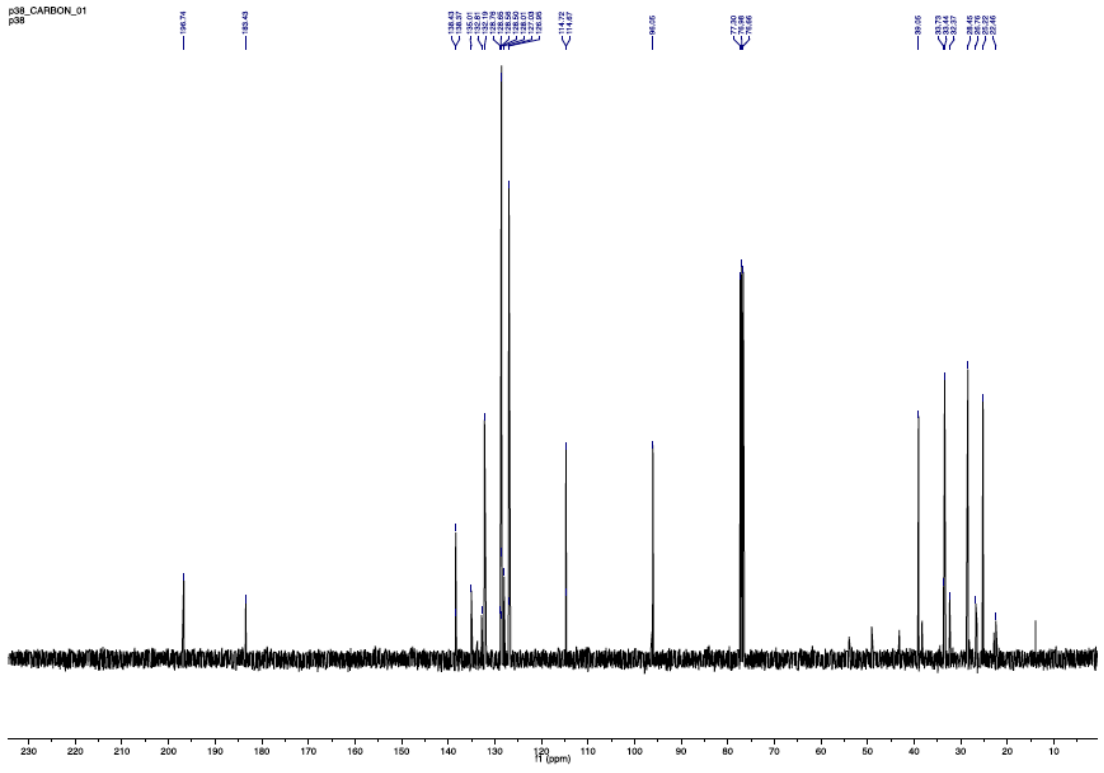
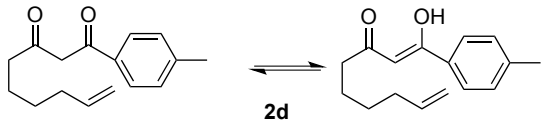
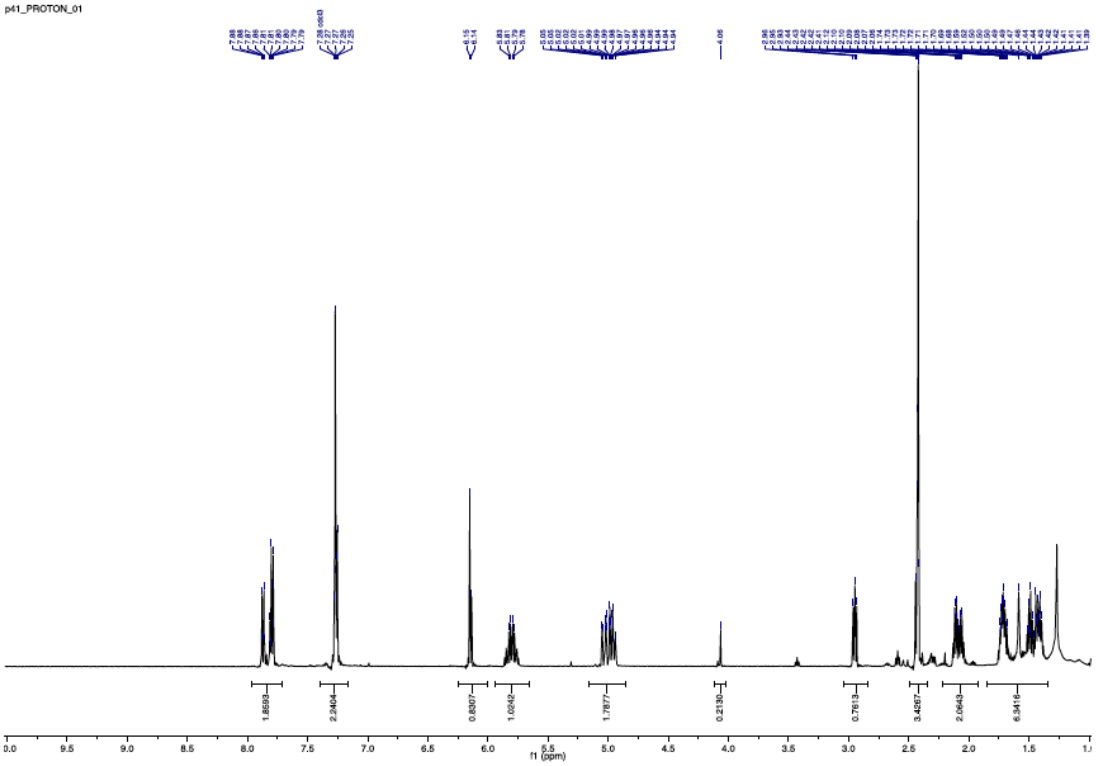
5.1106
f1 (ppm)


p38_CARBON_01
p38
196.74
183.43
96.05
39.05
f1 (ppm)

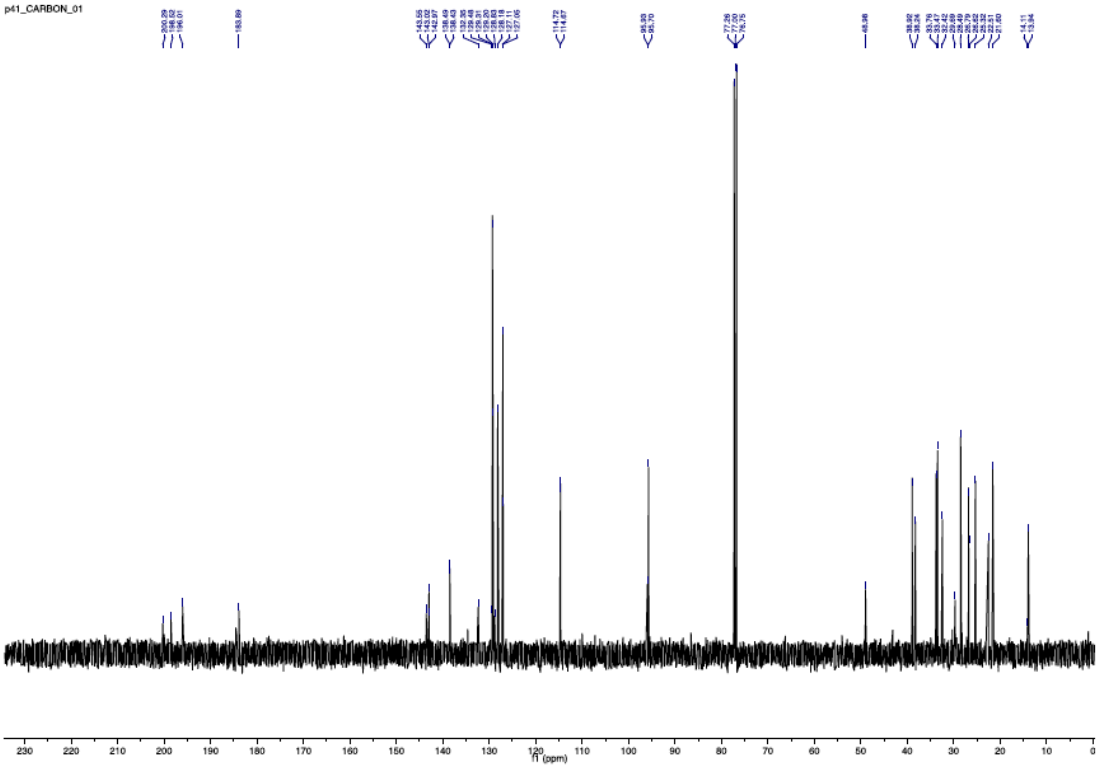


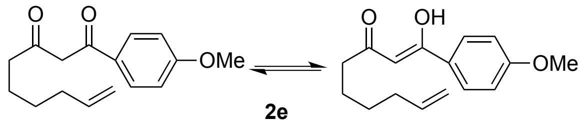
2d

p41_PROTON_01

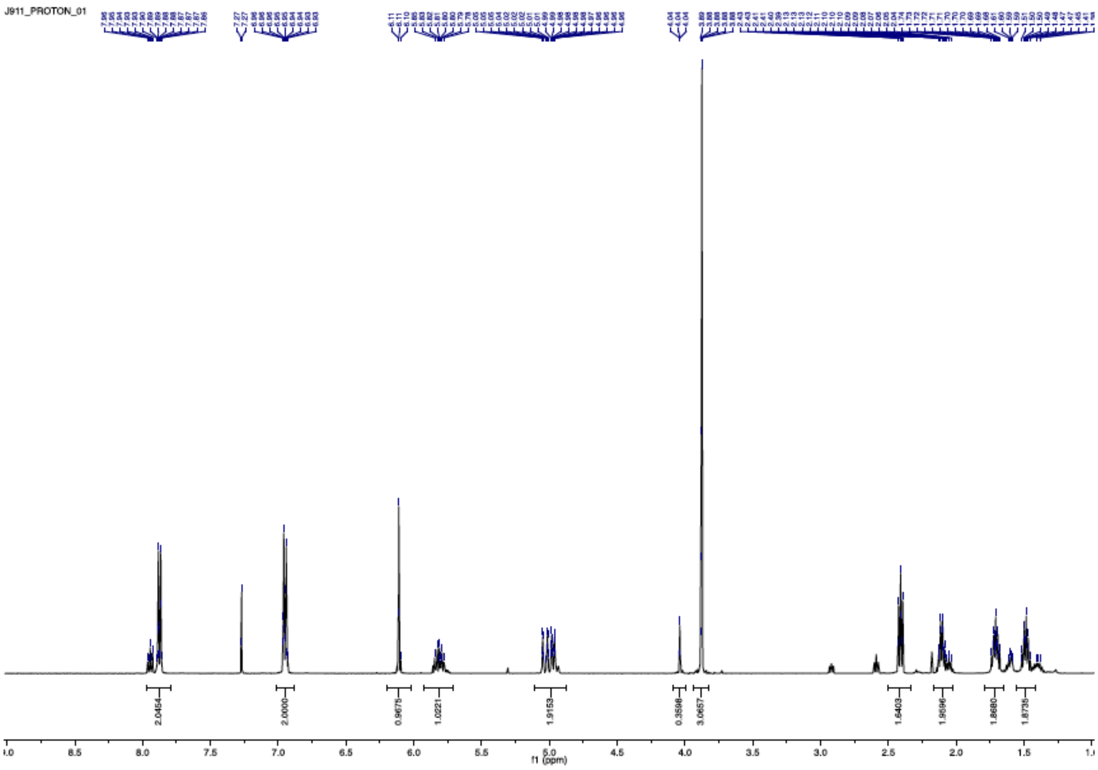


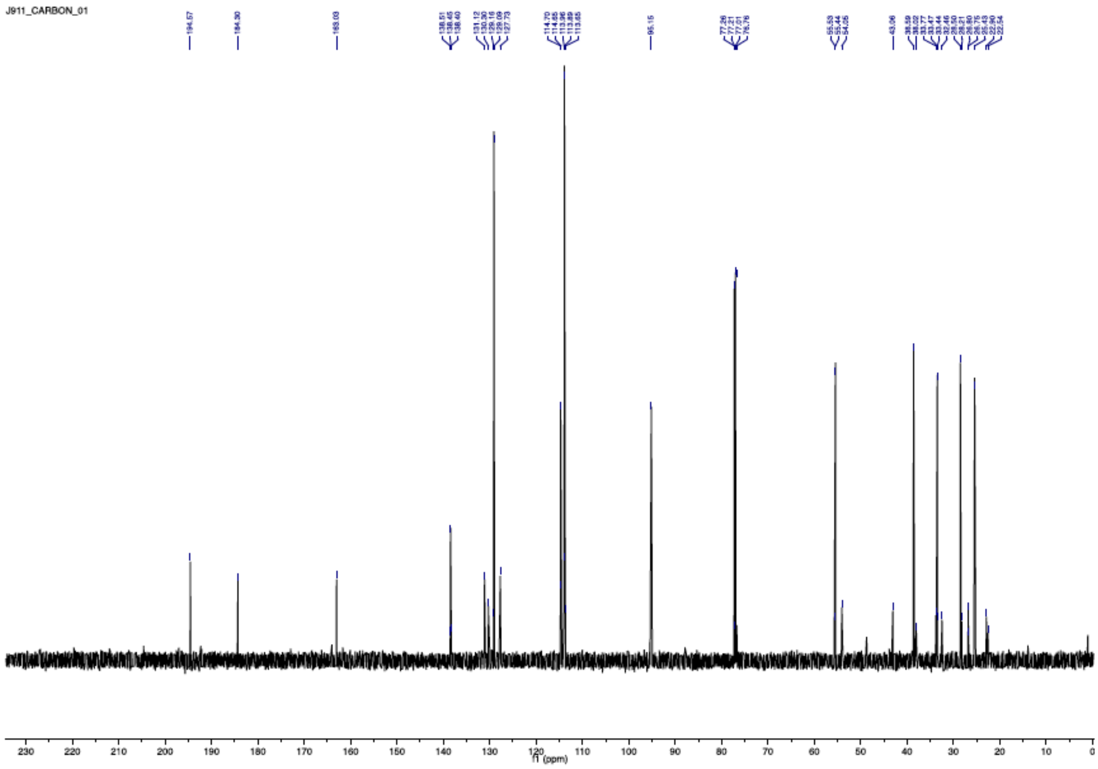
p41_CARBON_01

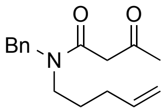




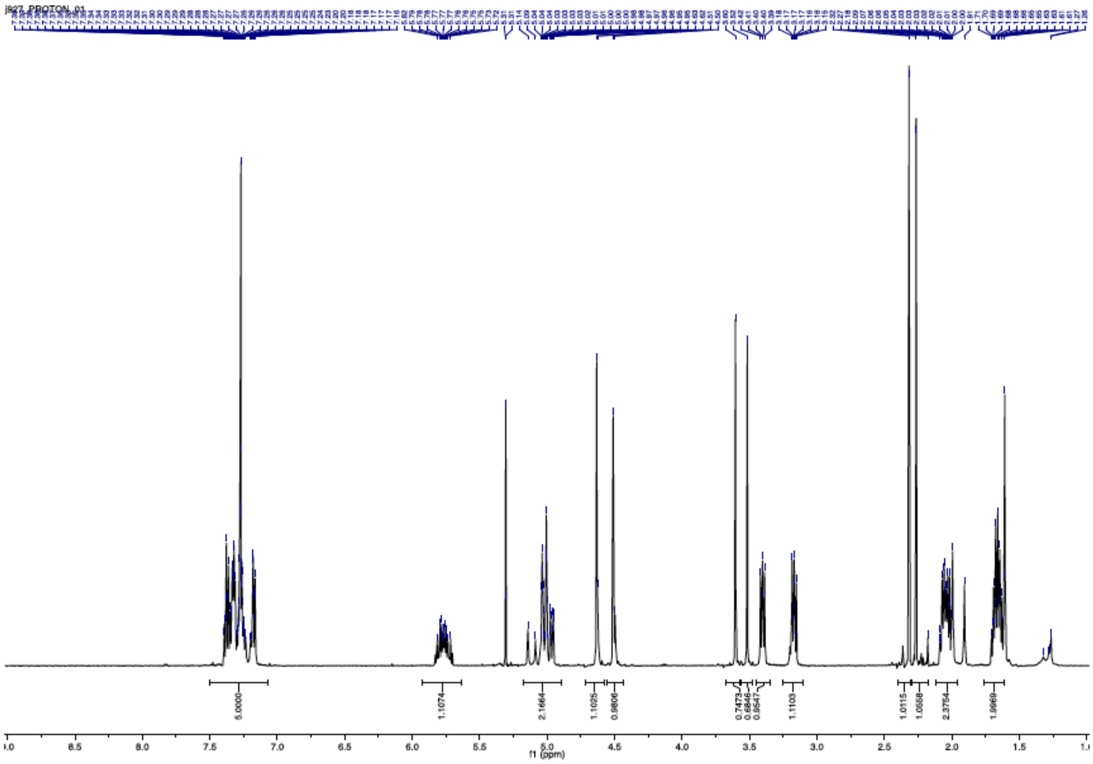
2e

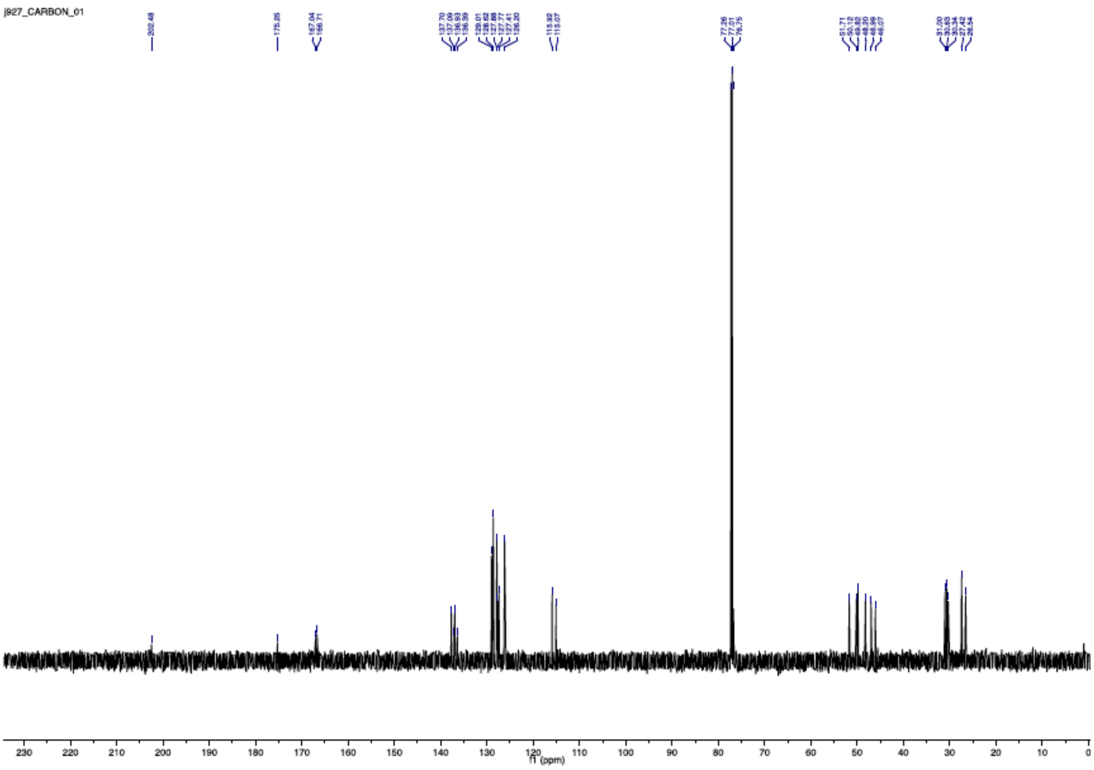




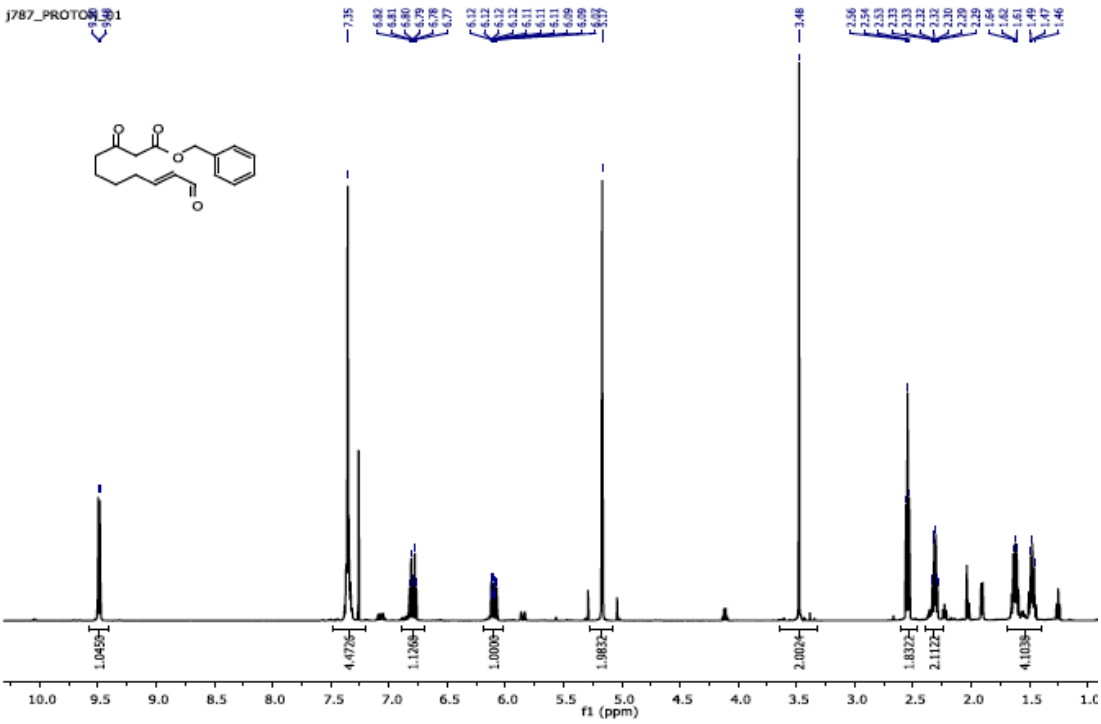


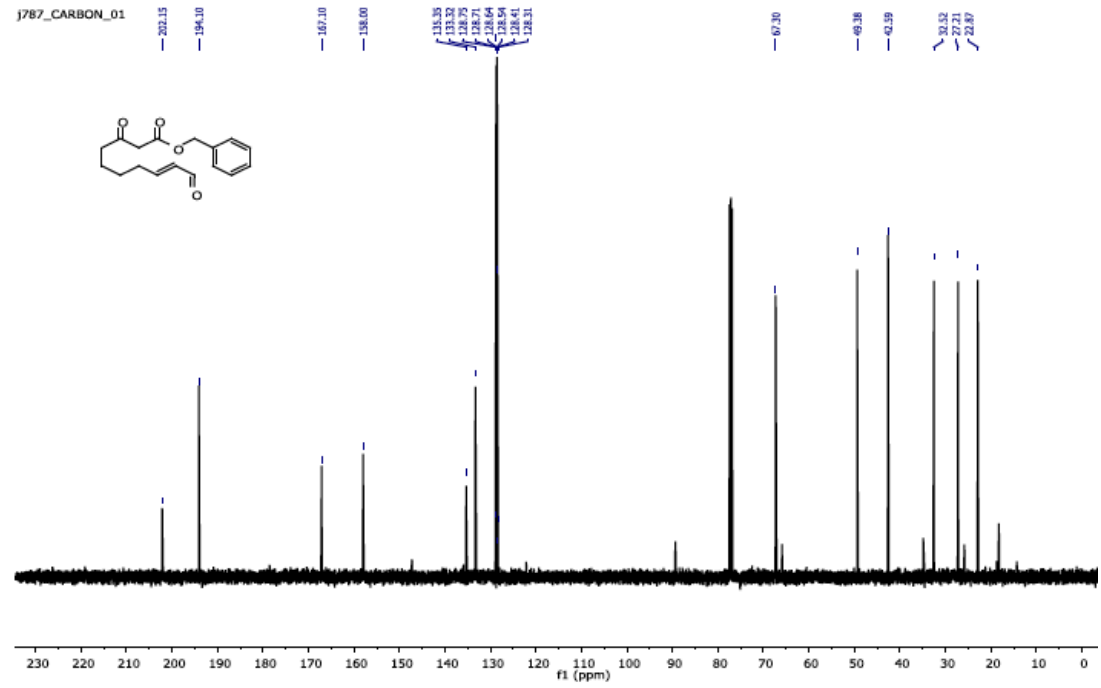
2f



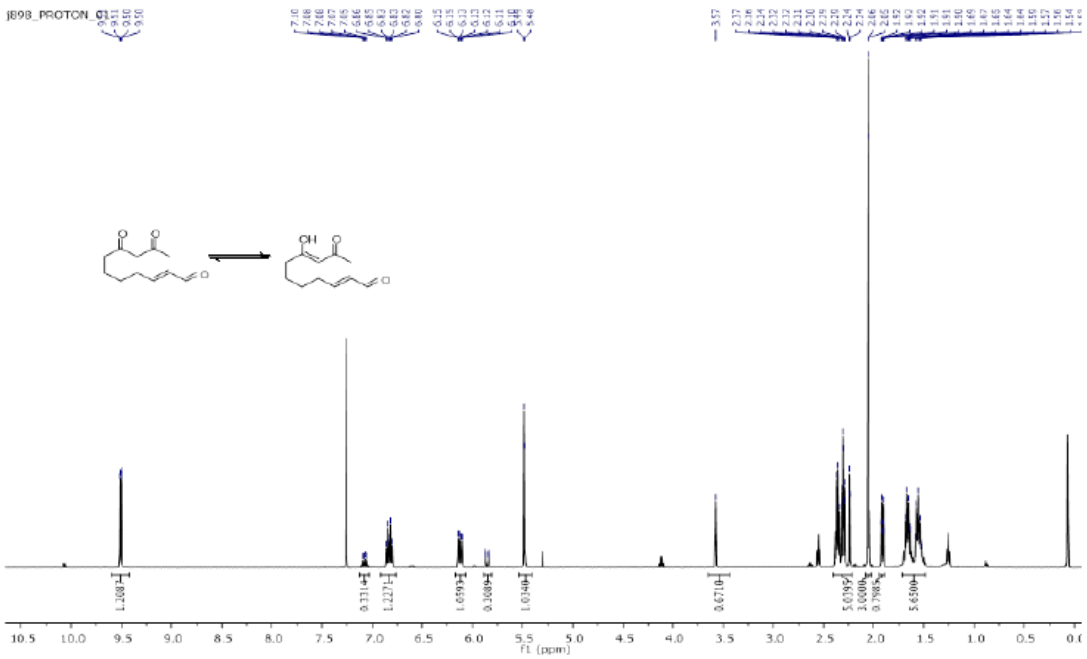


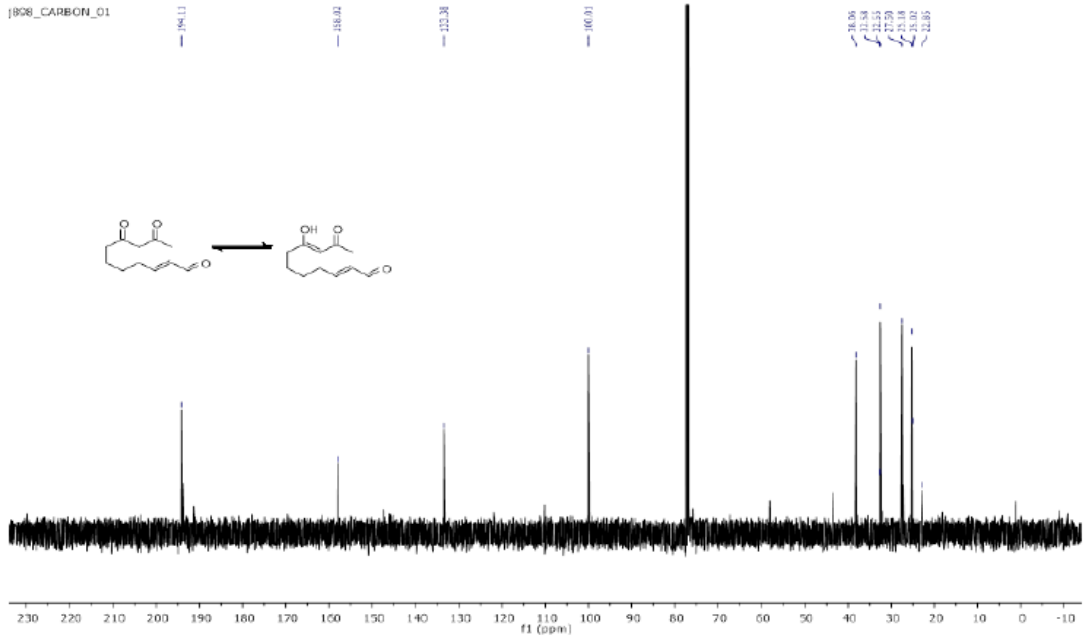
3a



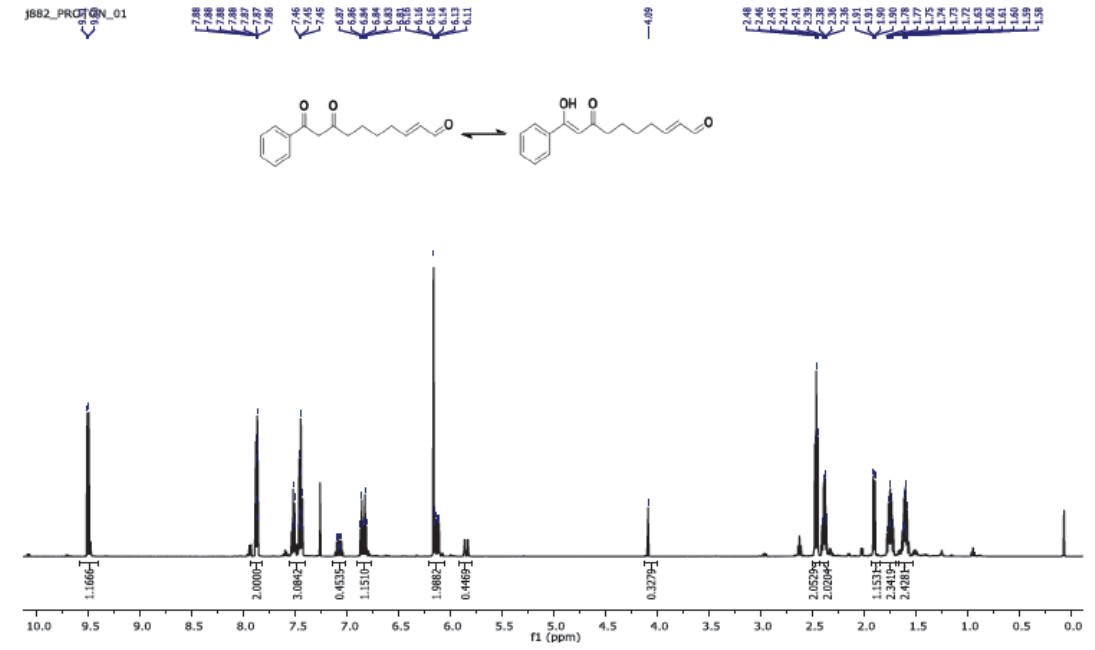


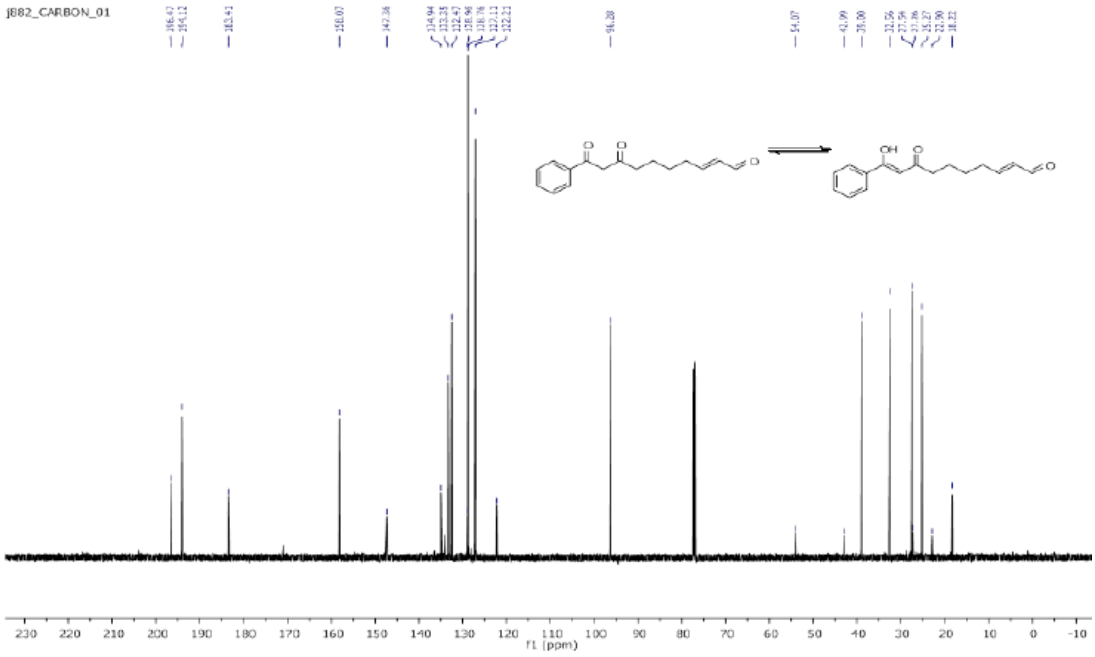
3b



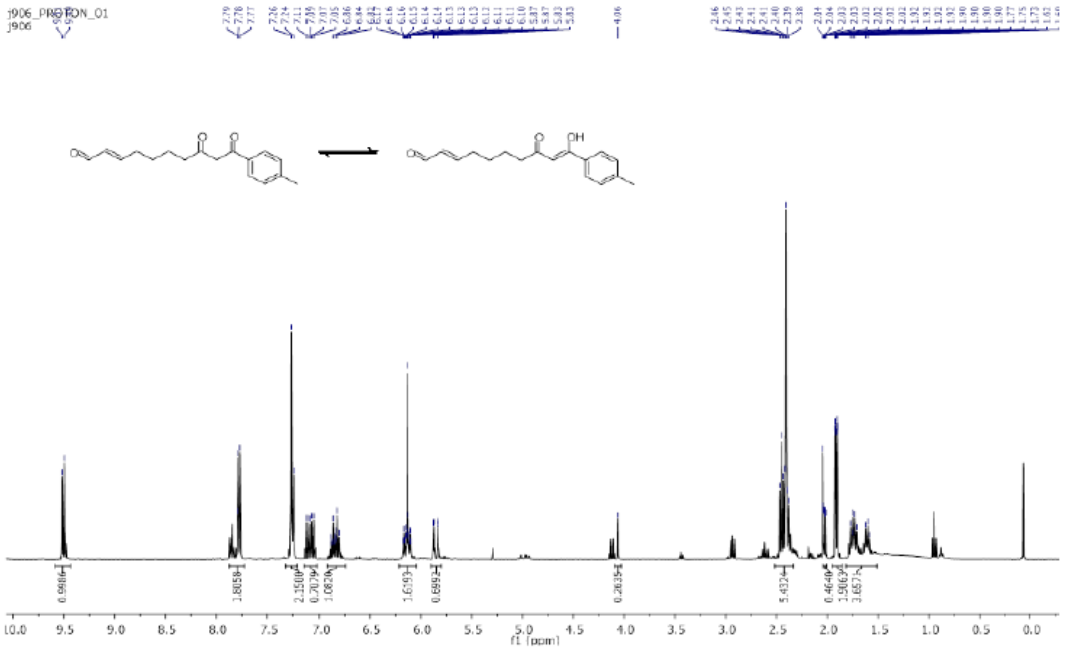


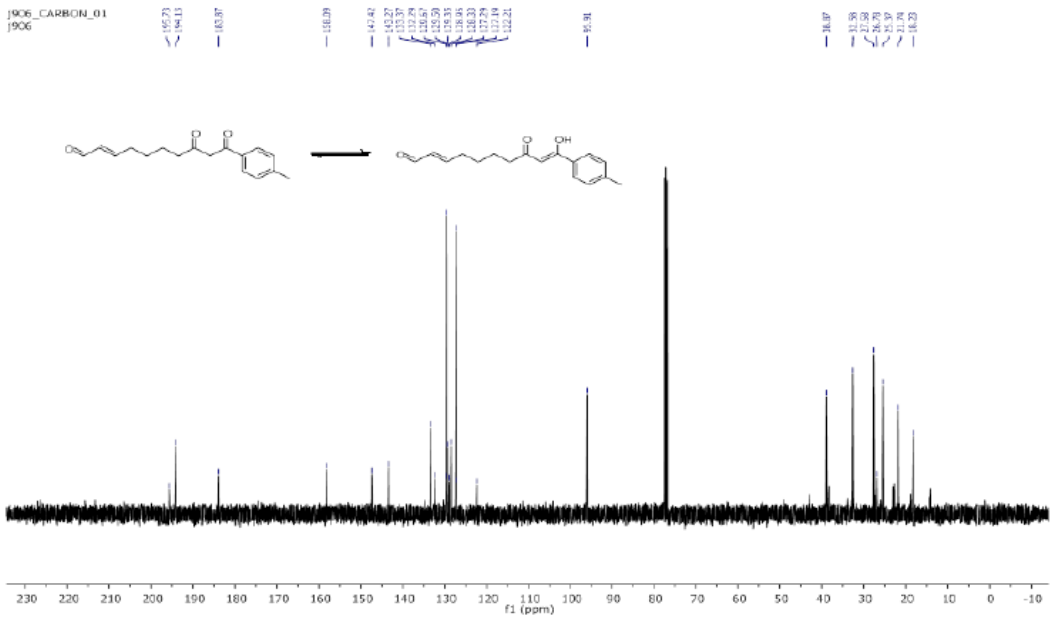
3c



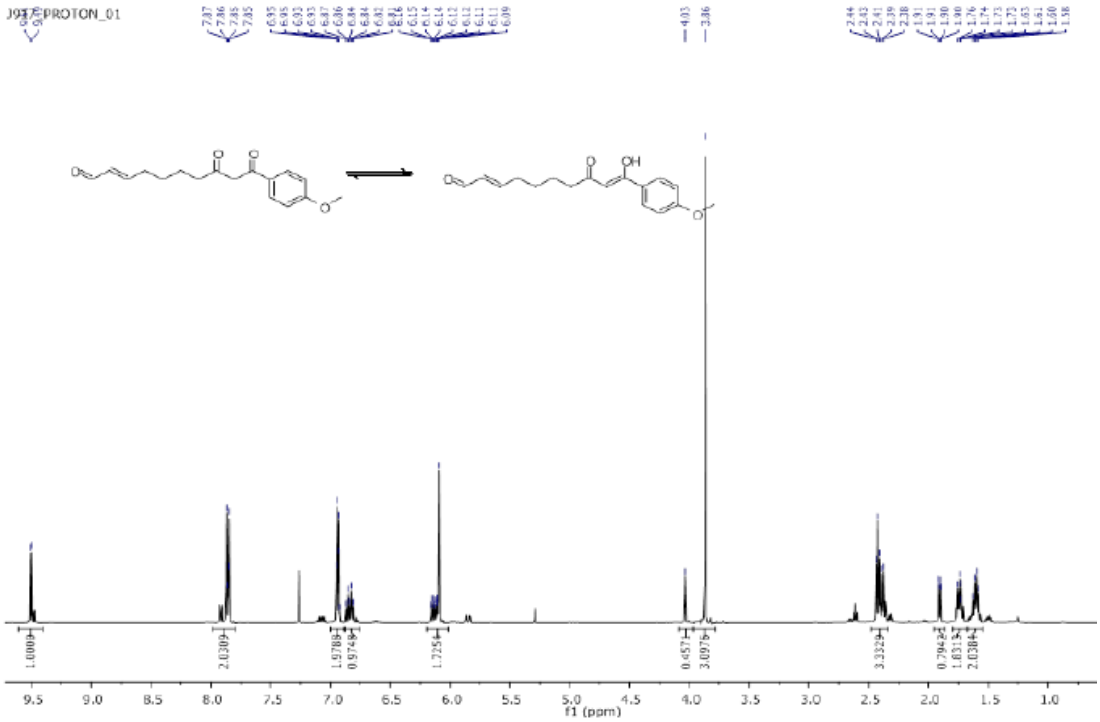


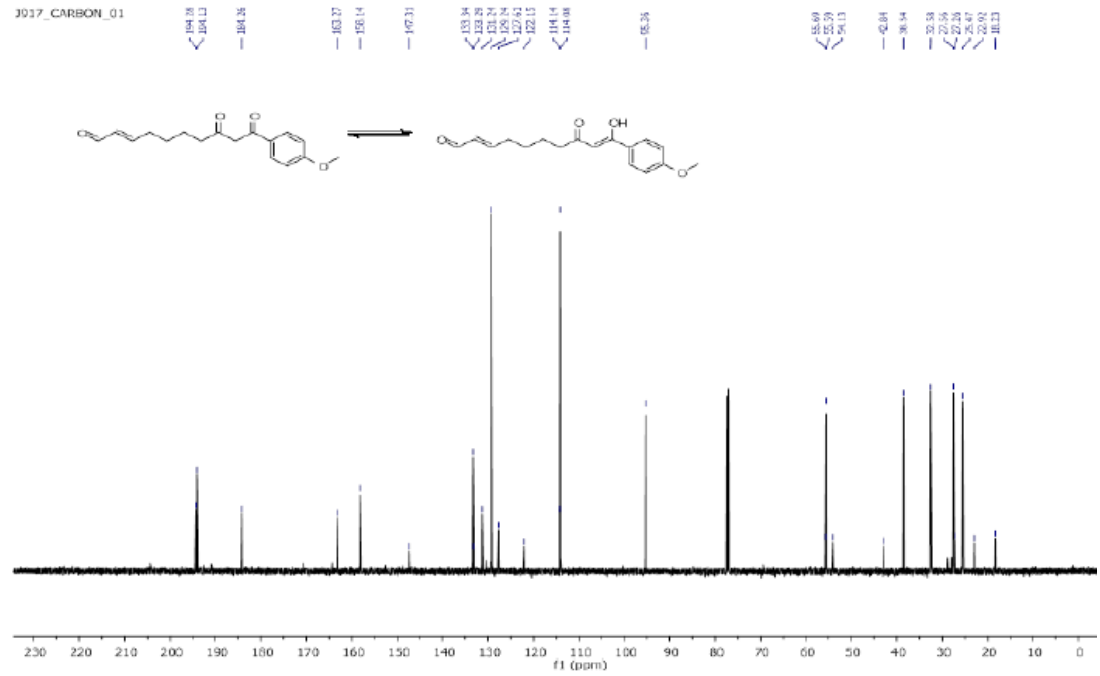
3d



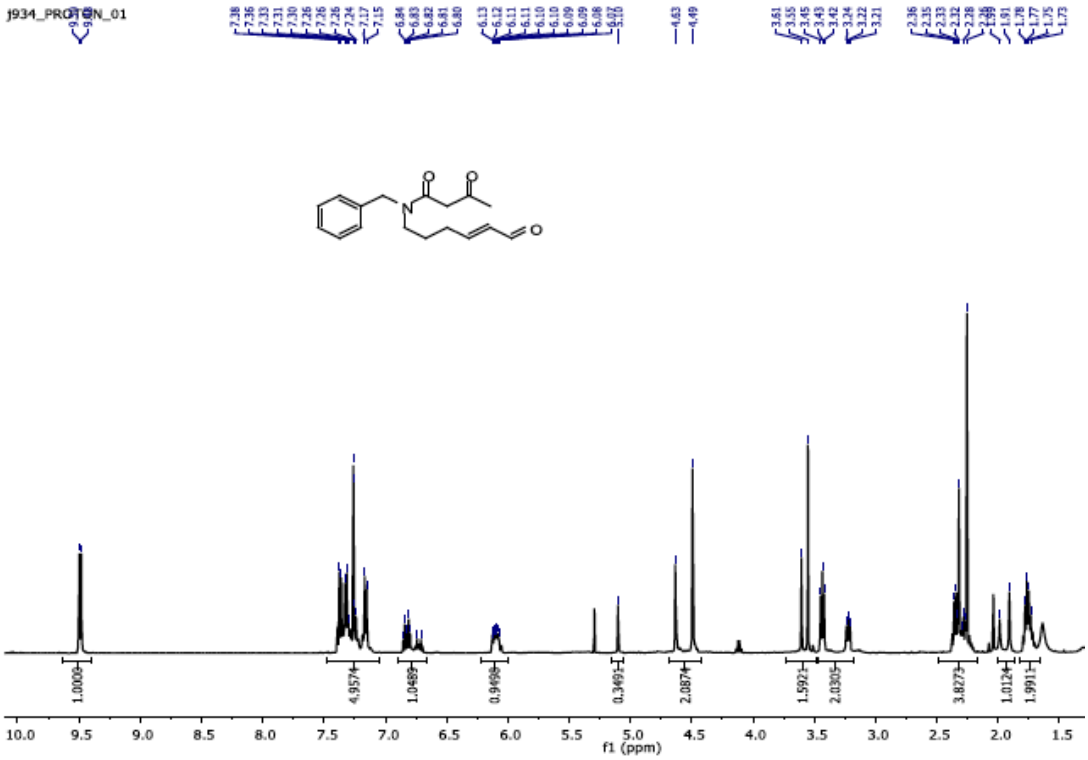


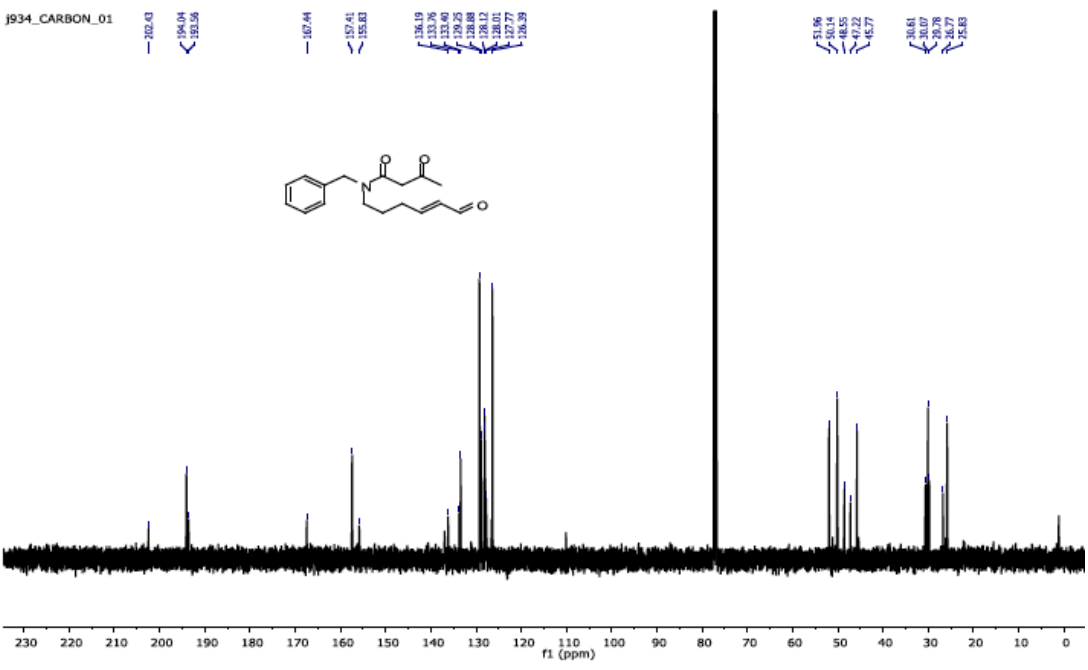
3e



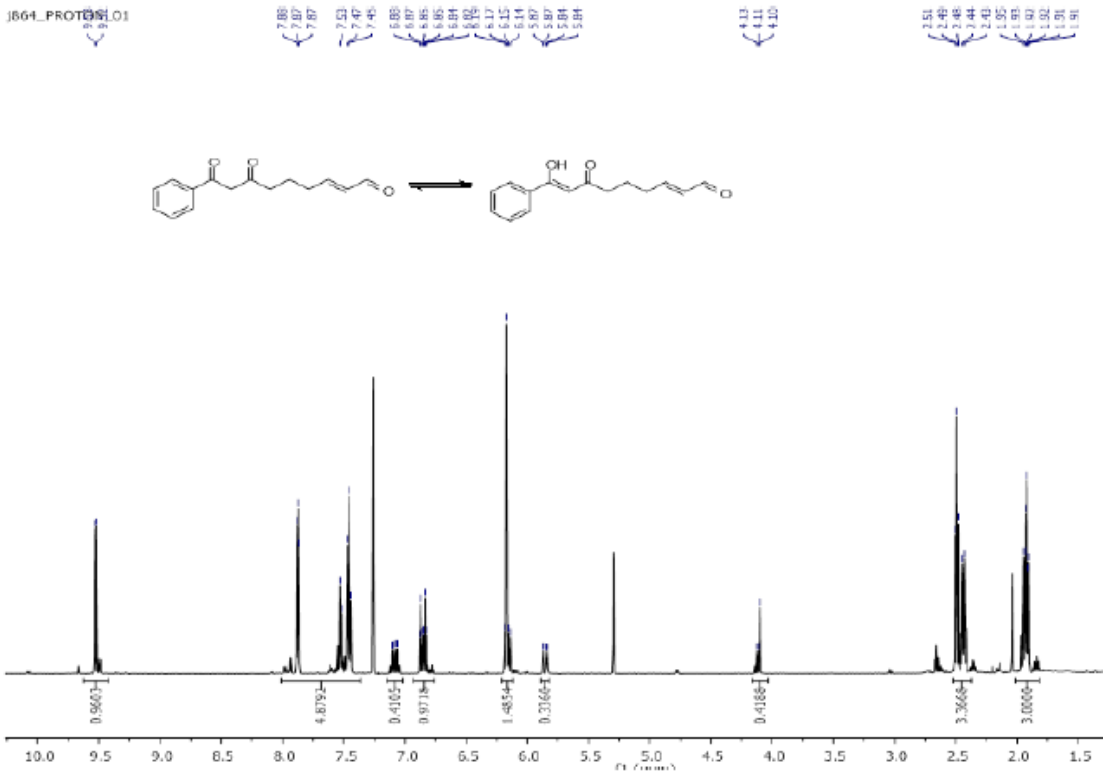


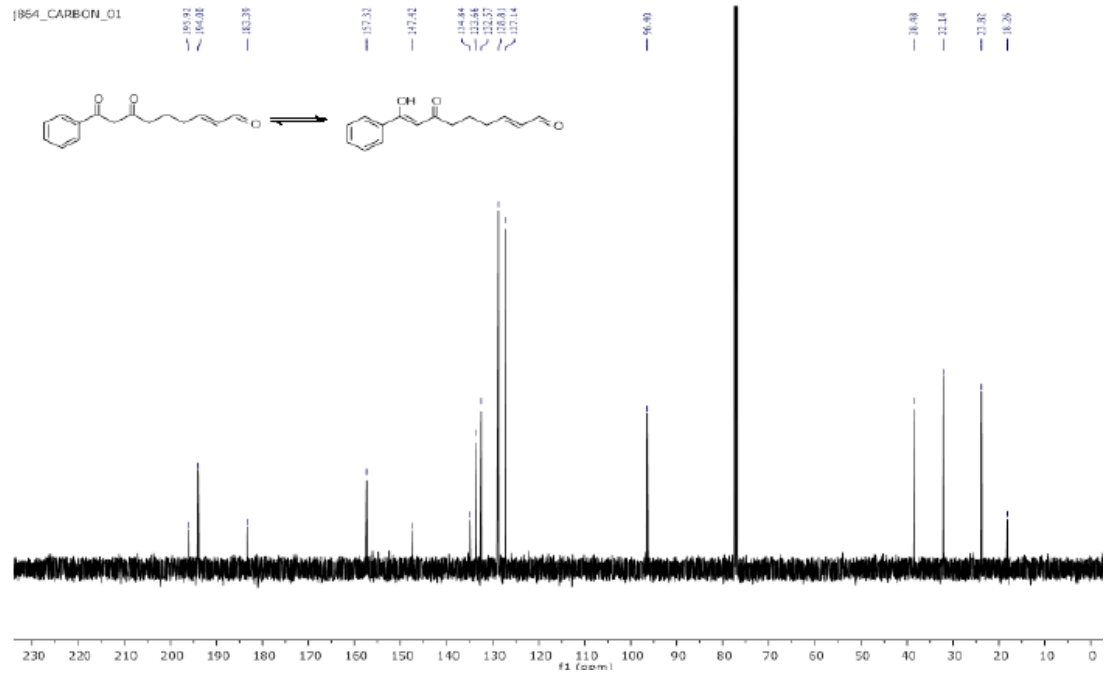
3f


j934_PROTON_01
1.0000
4.9574
1.0469
0.9408
0.3491
2.0874
1.5921
2.0305
3.8273
1.0124
1.9911
f1 (ppm)

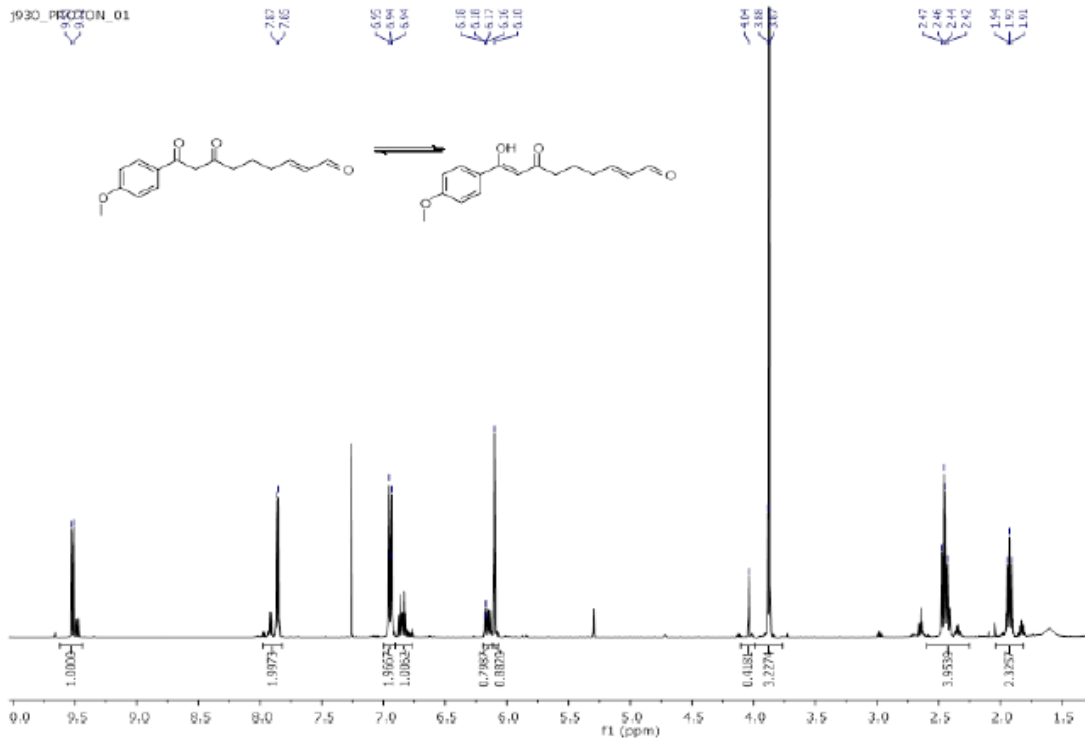

j934_CARBON_01
f1 (ppm)

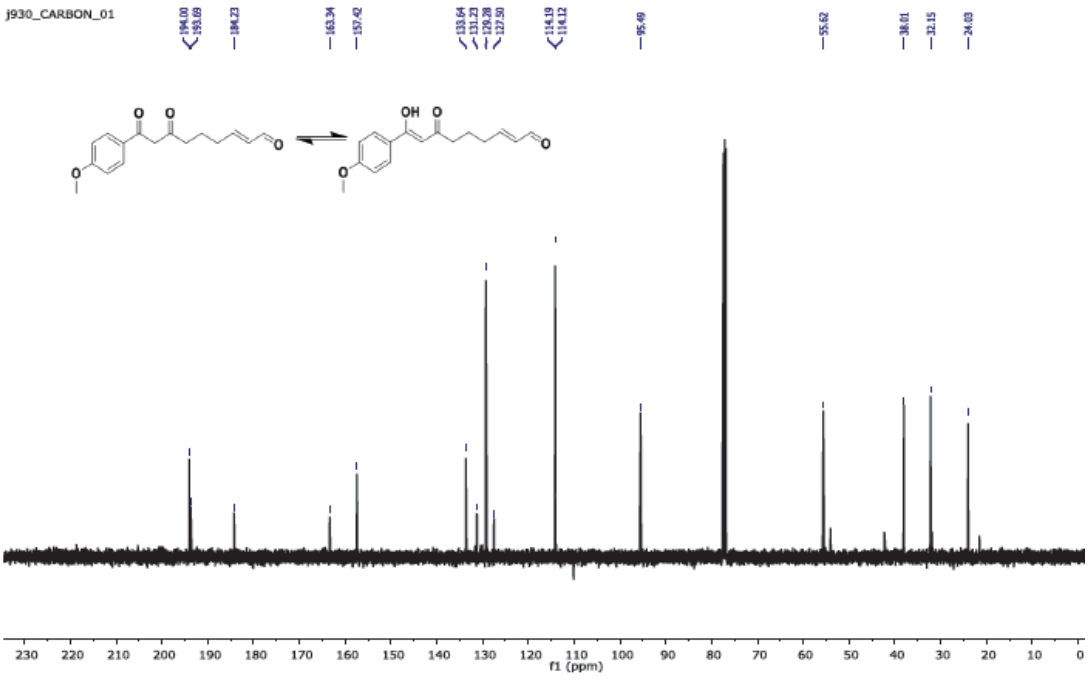
6c


J864_PROTON_01
OH
0.9603
4.8792
0.4165
0.9718
1.4854
0.3366
0.4186
3.3668
3.0000

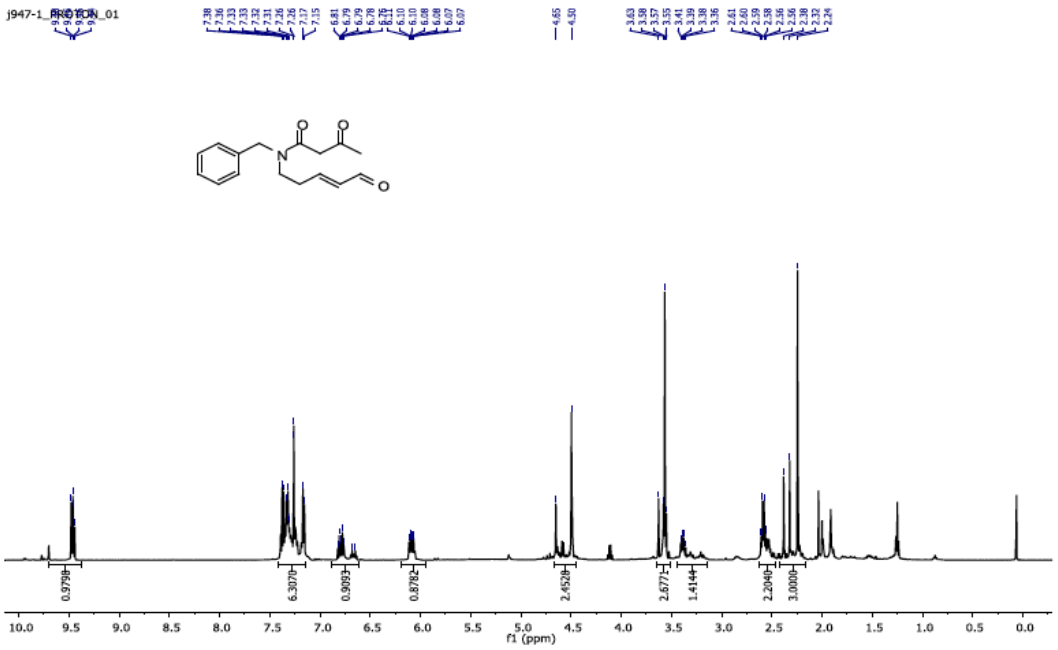

J864_CARBON_01
OH

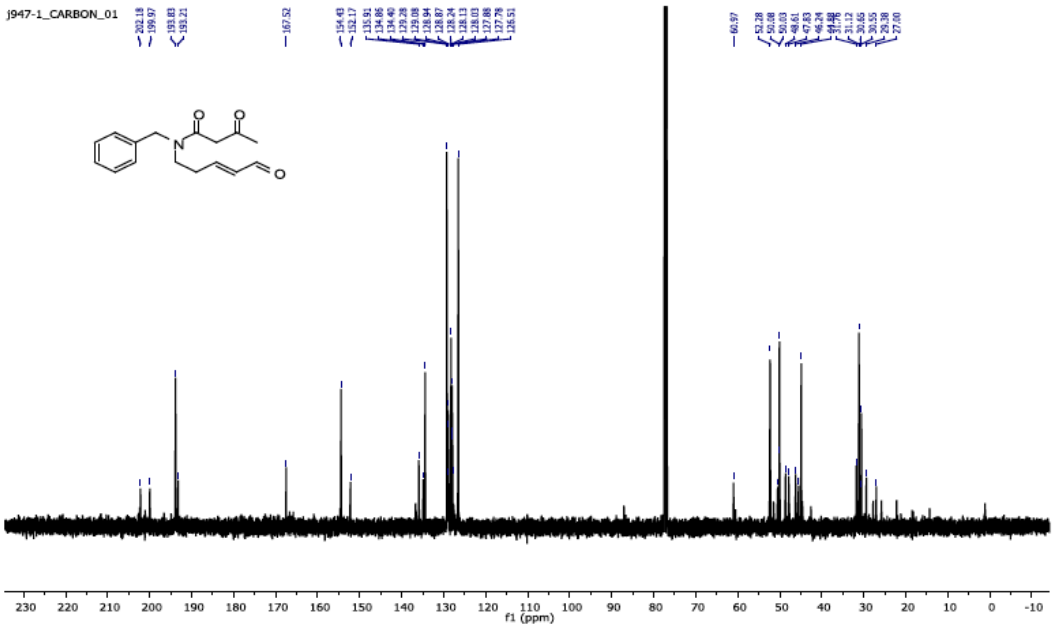
6e

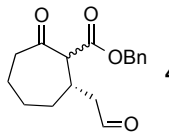




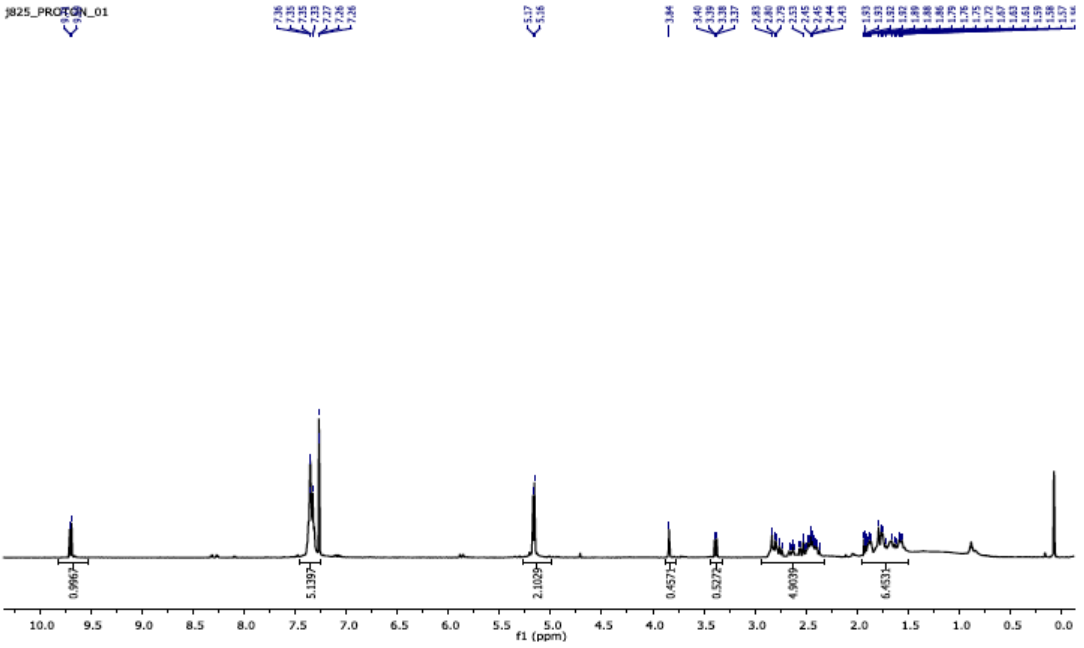
6f

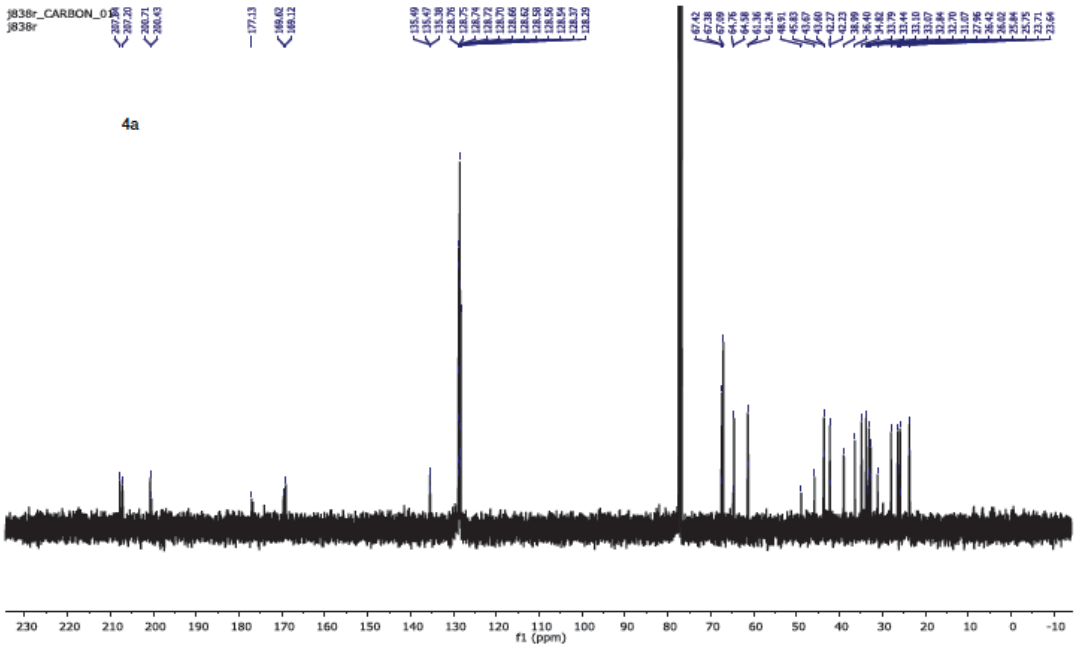


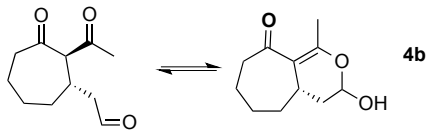



O
O
OBn
O

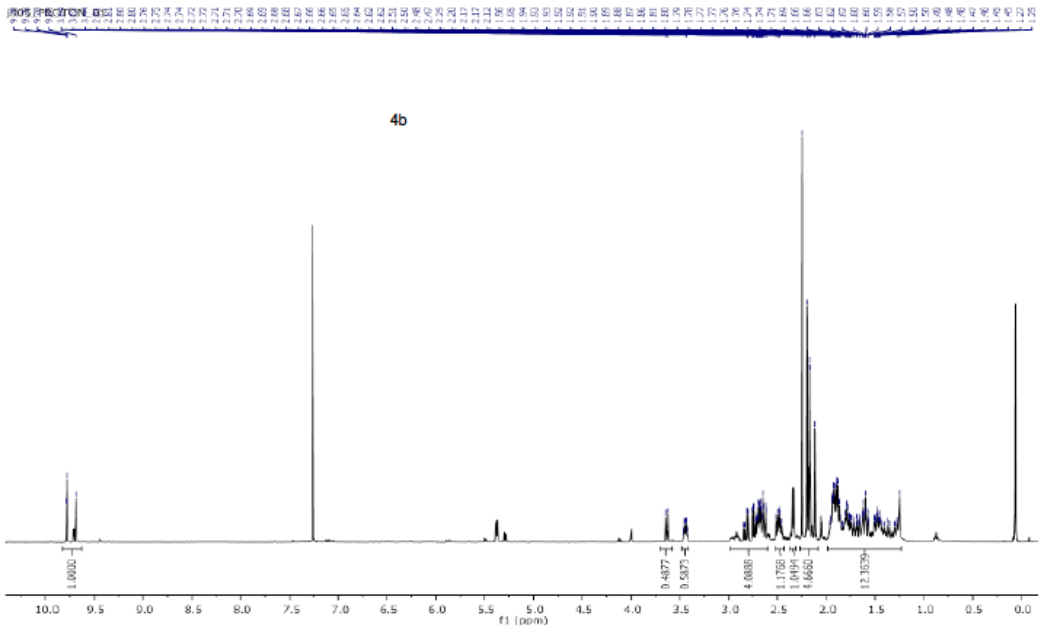
4a

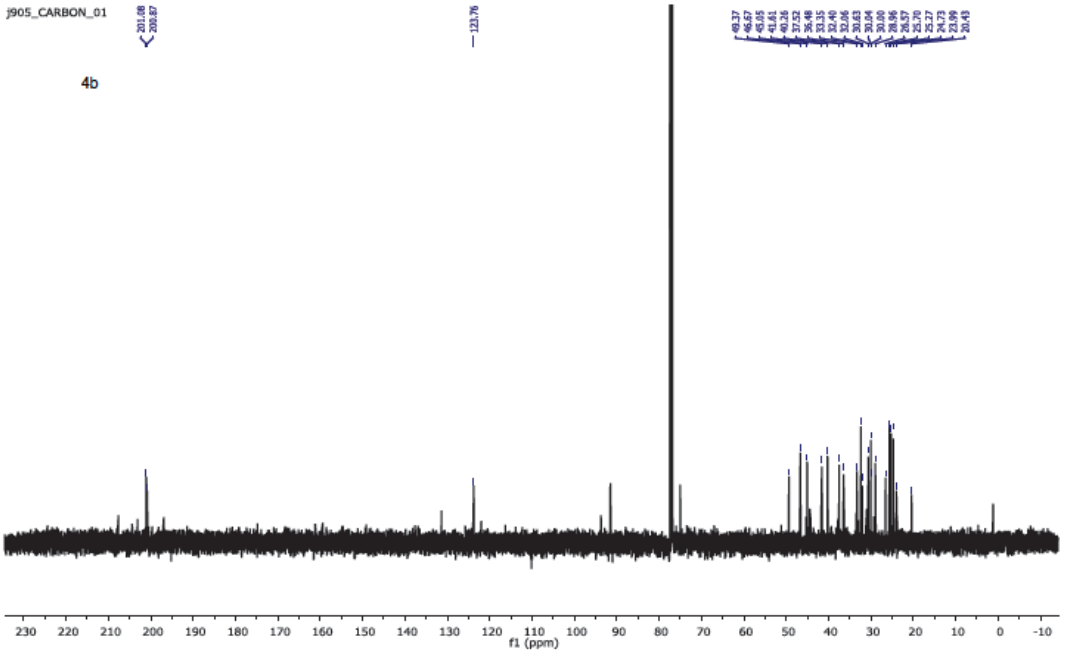

j825_PROTON_01
0.9967
5.1397
2.1029
0.4571
0.5272
4.9039
6.4531
f1 (ppm)

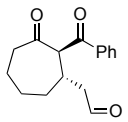

j838r_CARBON_01
j838r
4a
f1 (ppm)


O
O
O
O
OH

4b

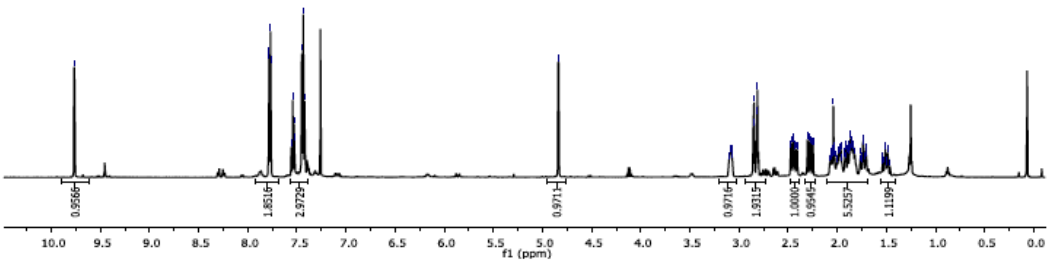

4b
1.0000
0.4877
0.5873
4.0886
1.1756
1.0494
4.6652
12.3539
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


j905_CARBON_01
4b
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
O
Ph
O

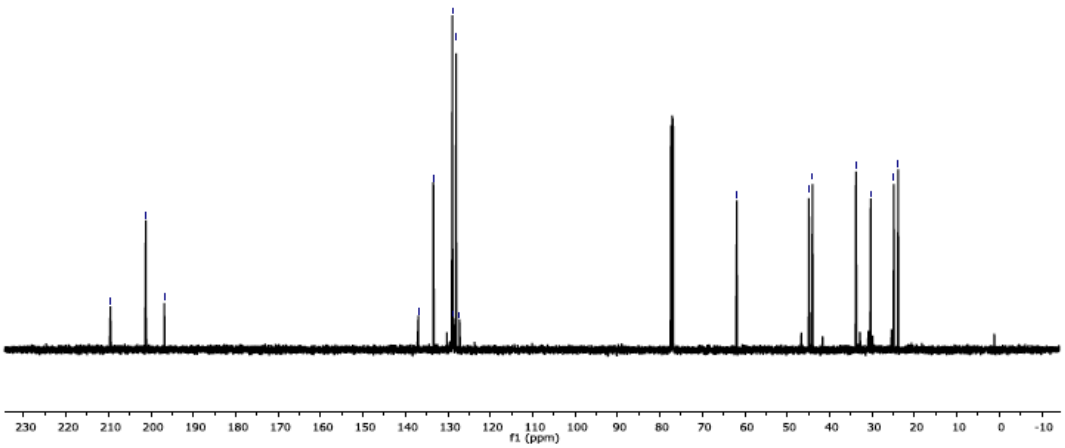
4c

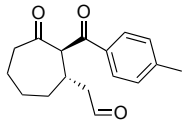
4c


0.9566
1.8516
2.9729
0.9711
0.9716
1.9315
1.0000
0.9545
5.5257
1.1199
10.0 9.5 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 0.0
f1 (ppm)

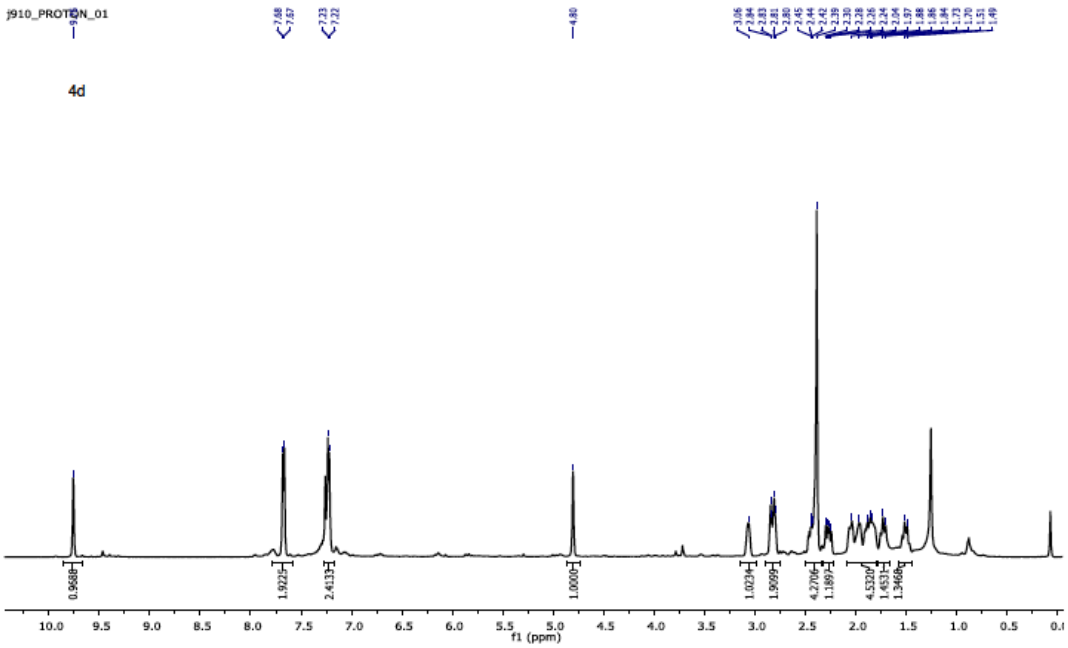

J885_1_CARBON_01
209.65
201.20
196.81
136.94
133.41
128.91
128.64
128.06
127.25
61.85
44.88
44.02
33.80
30.31
24.87
23.84

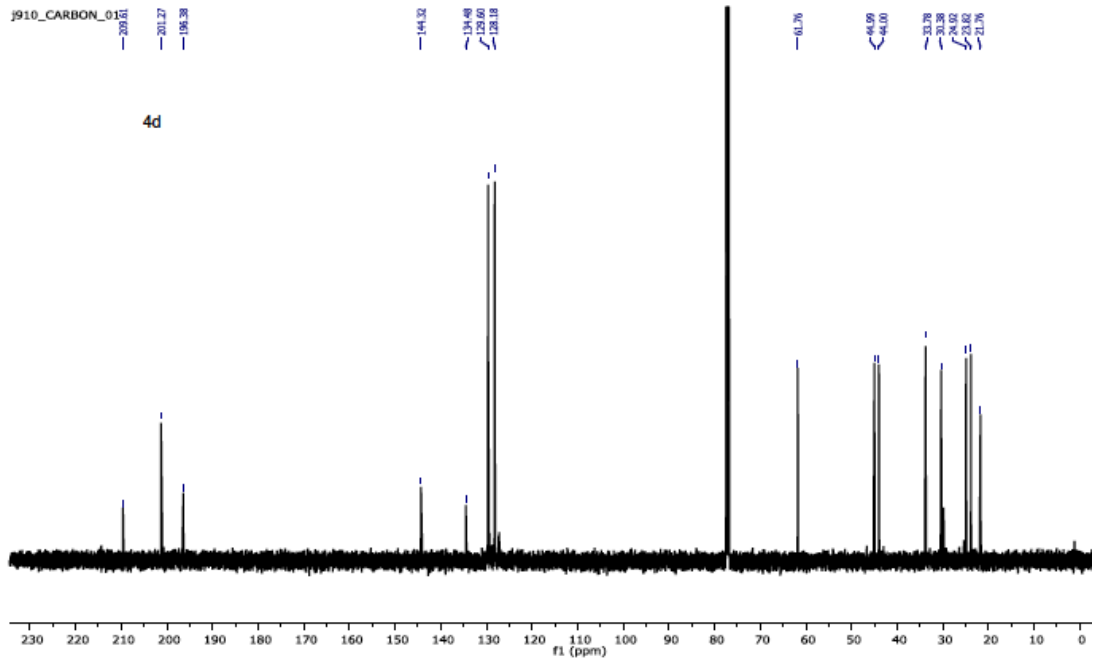
4c

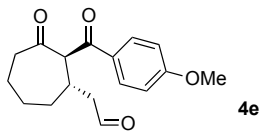

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



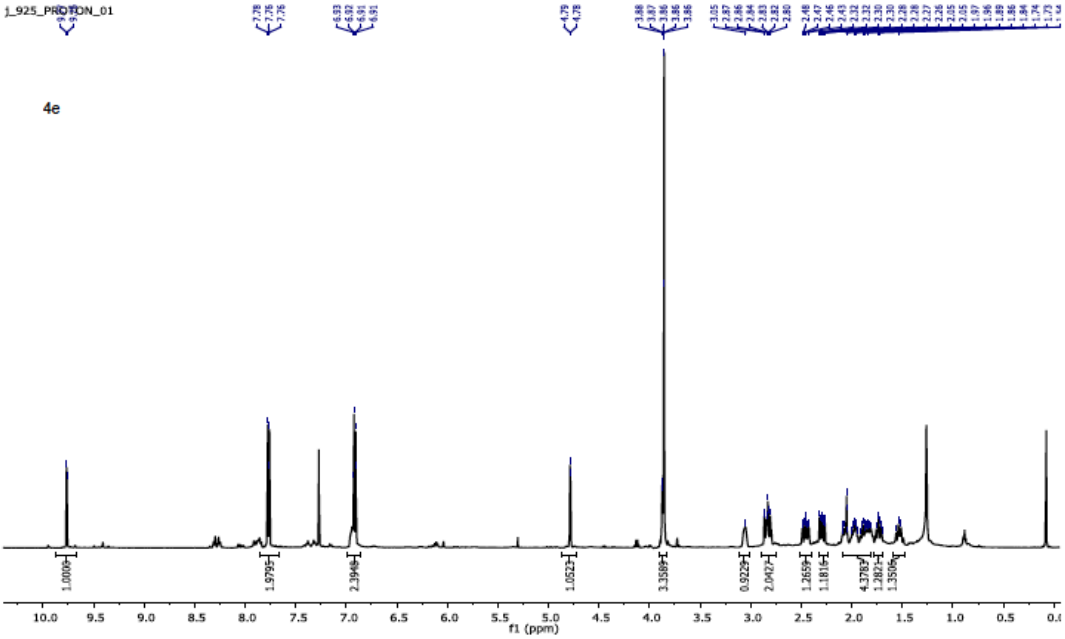
4d

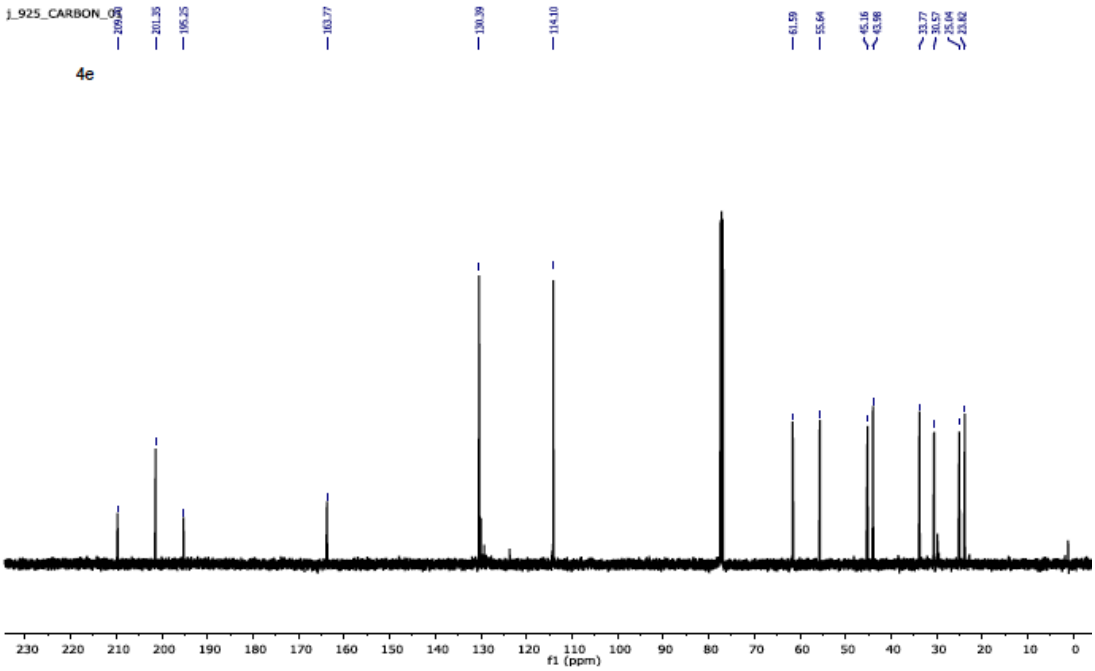

j910_PROTON_01
4d
0.9688
1.9222
2.4133
1.0000
1.0234
1.9099
4.2700
1.1897
4.5320
1.4531
1.3468
f1 (ppm)

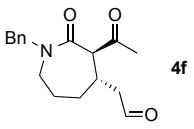

j910_CARBON_01
209.61
201.27
196.38
144.32
134.48
129.60
128.18
61.76
44.99
44.00
33.78
30.38
24.92
23.82
21.76
4d
f1 (ppm)



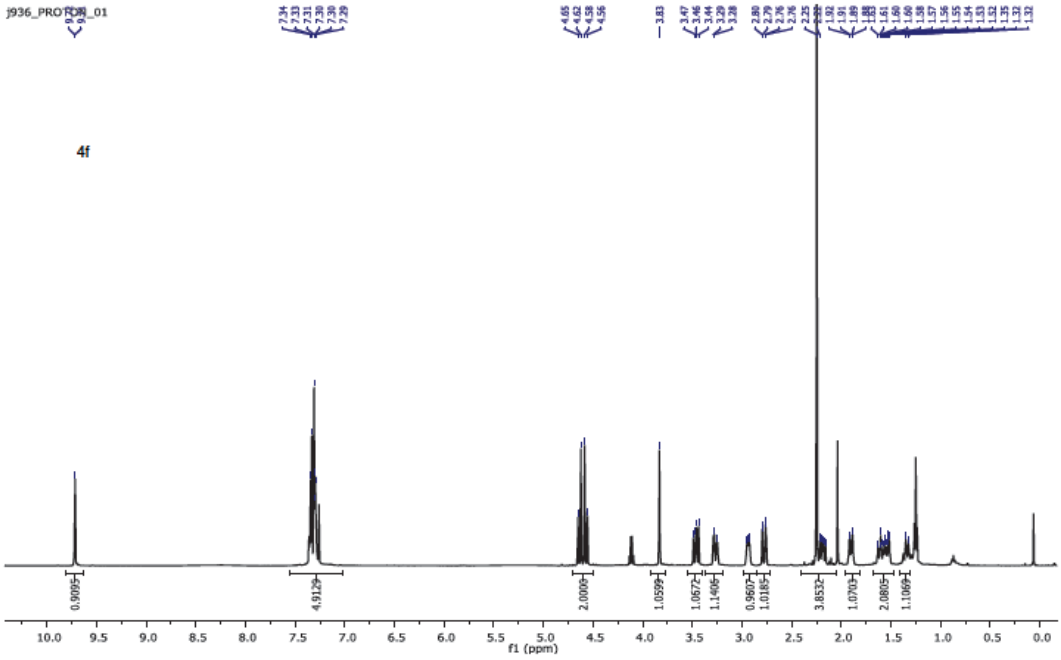
4e

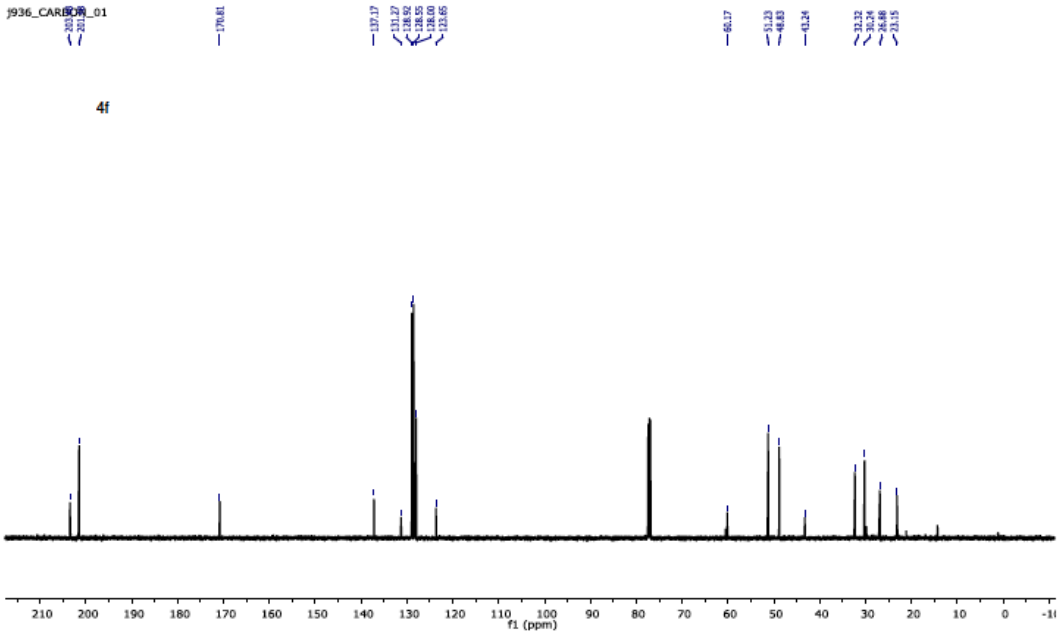


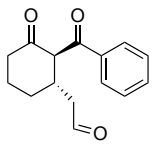




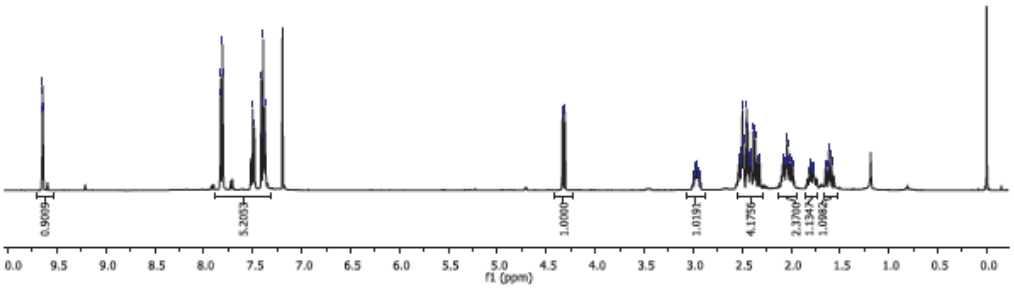
4f

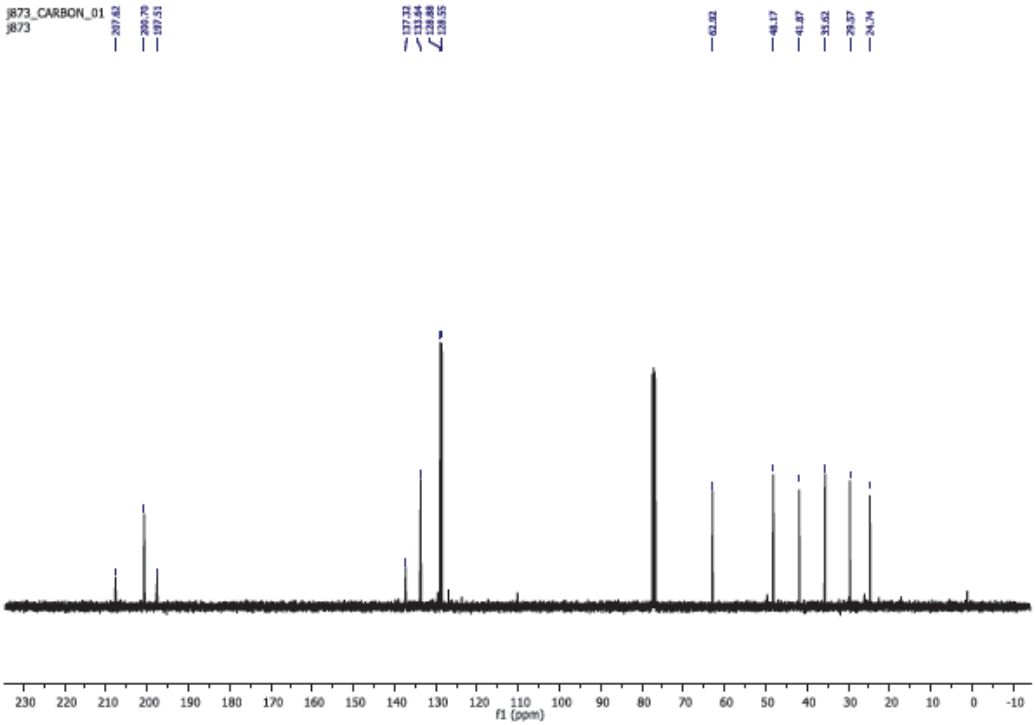


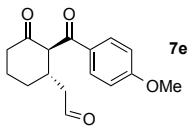


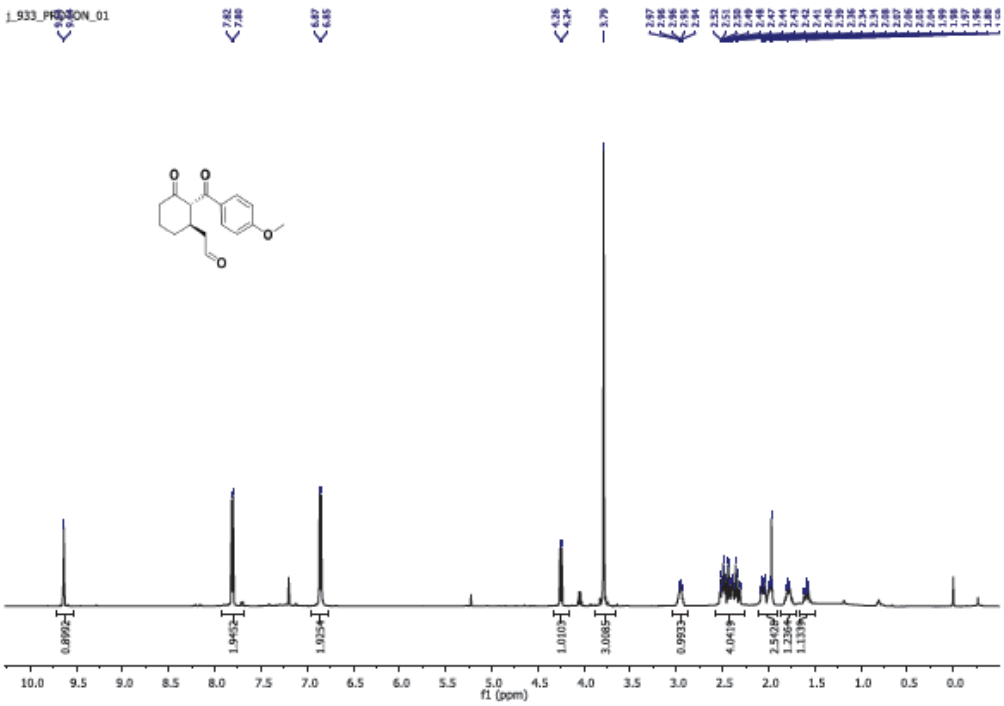


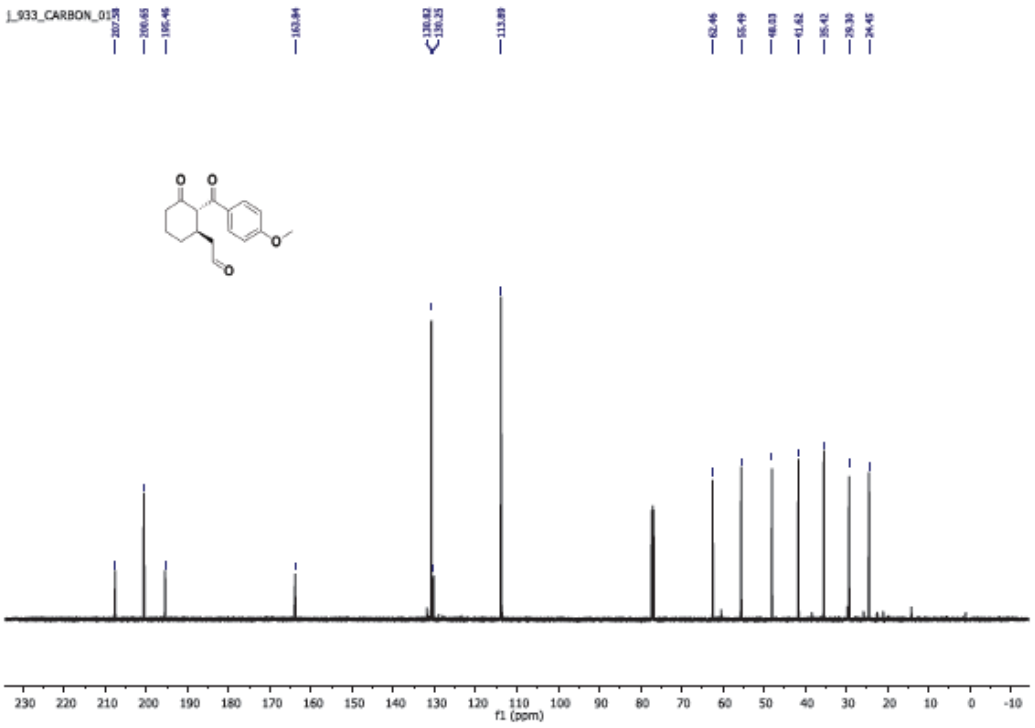
7c

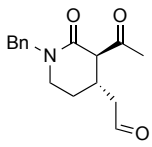

0.9009
5.2053
1.0000
1.0191
4.1756
2.3709
1.1547
1.0982
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


j873_CARBON_01
j873
207.62
200.70
197.51
137.32
133.64
128.88
128.55
62.92
48.17
41.87
35.62
29.57
24.74
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

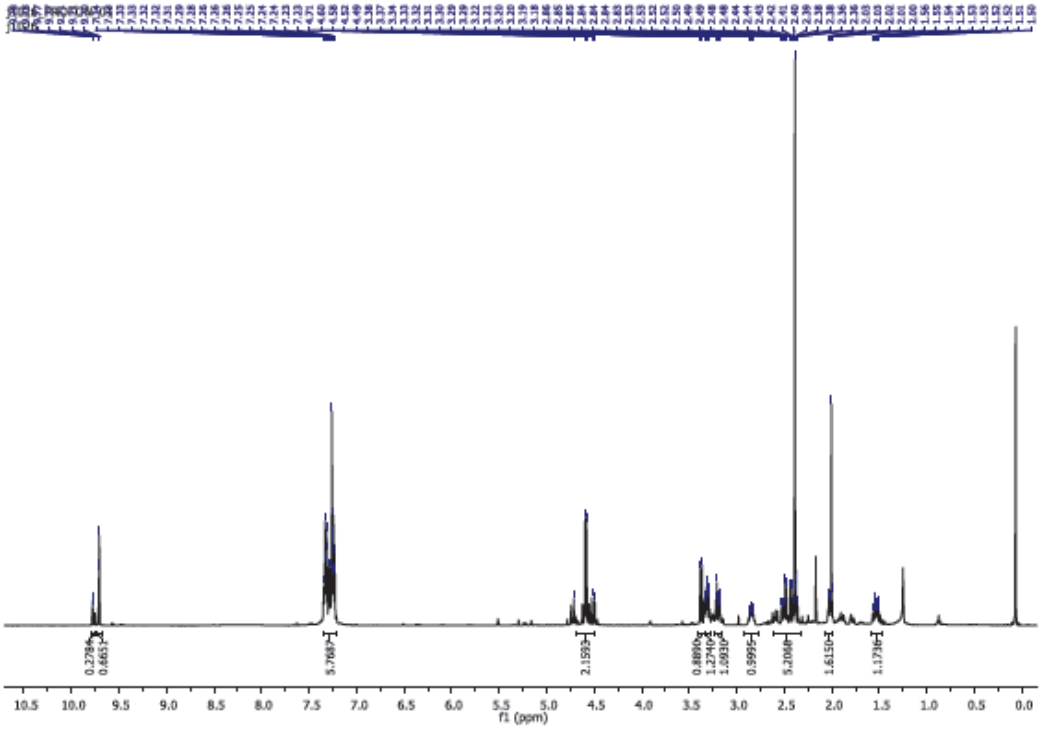

7e
OMe


f1 (ppm)


f1 (ppm)


Bn
N
O
O
O

7f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0.8890
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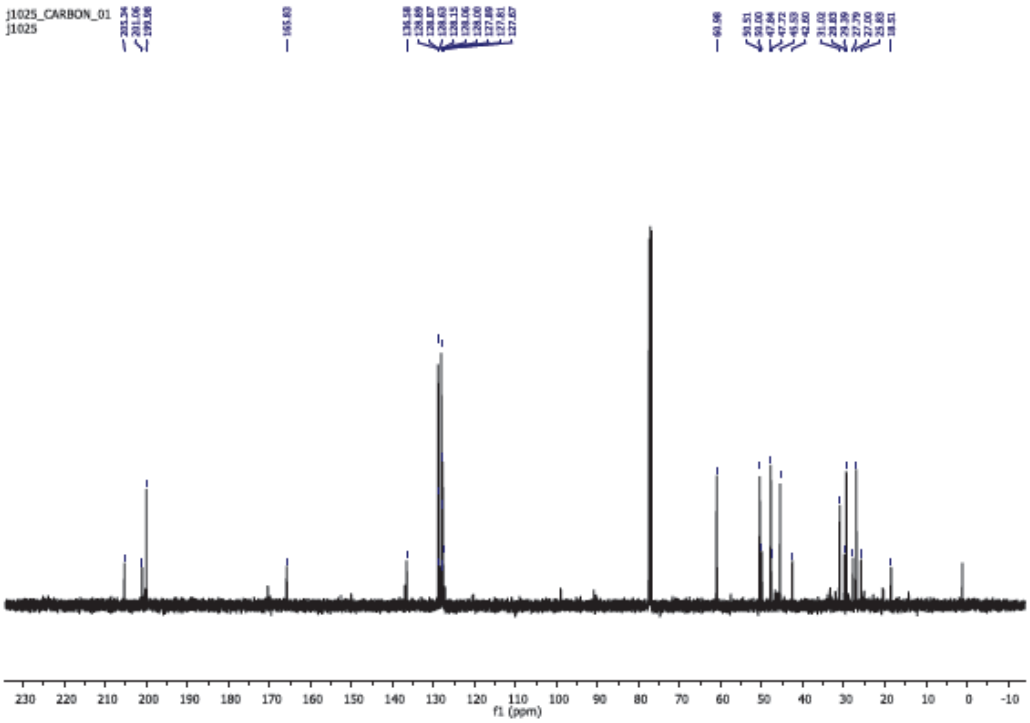
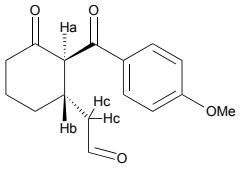
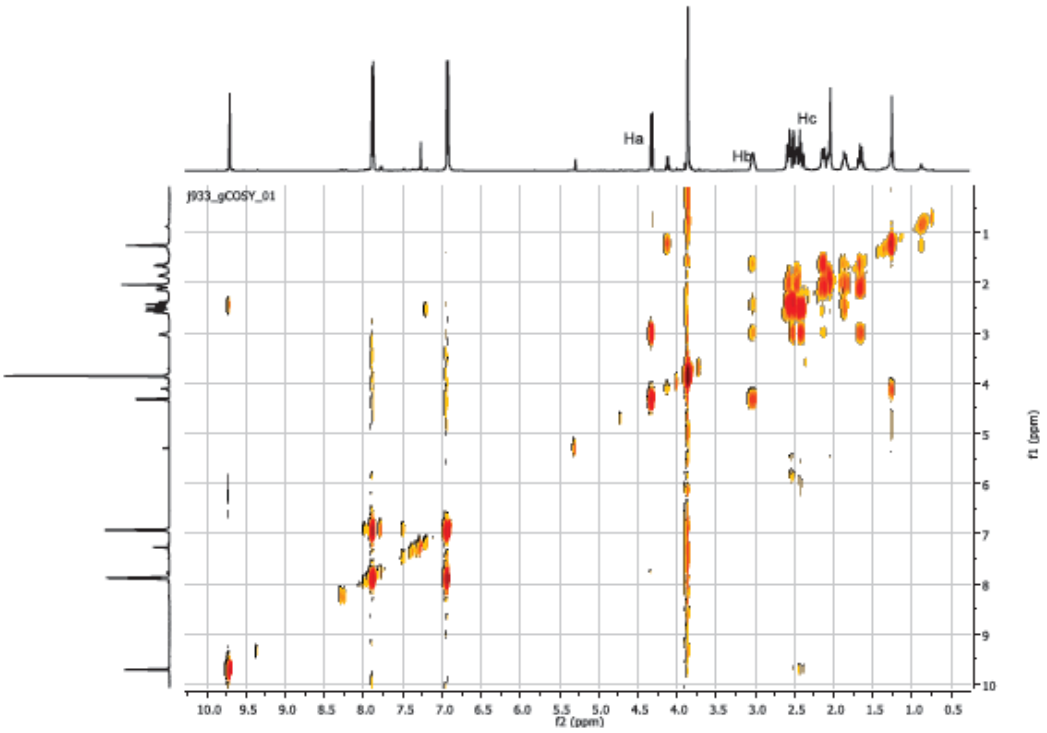
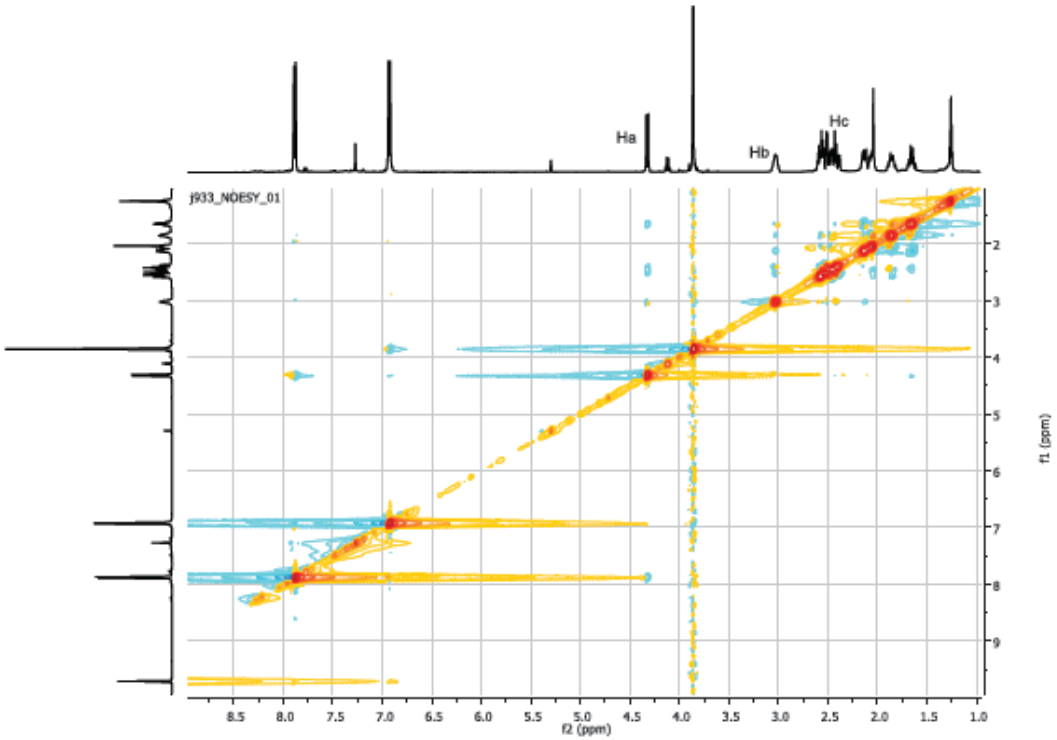
f1 (ppm)

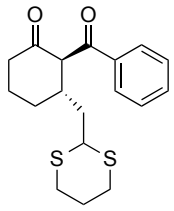

j1025_CARBON_01
j1025
f1 (ppm)

COSY and NOESY Spectra for **7e**

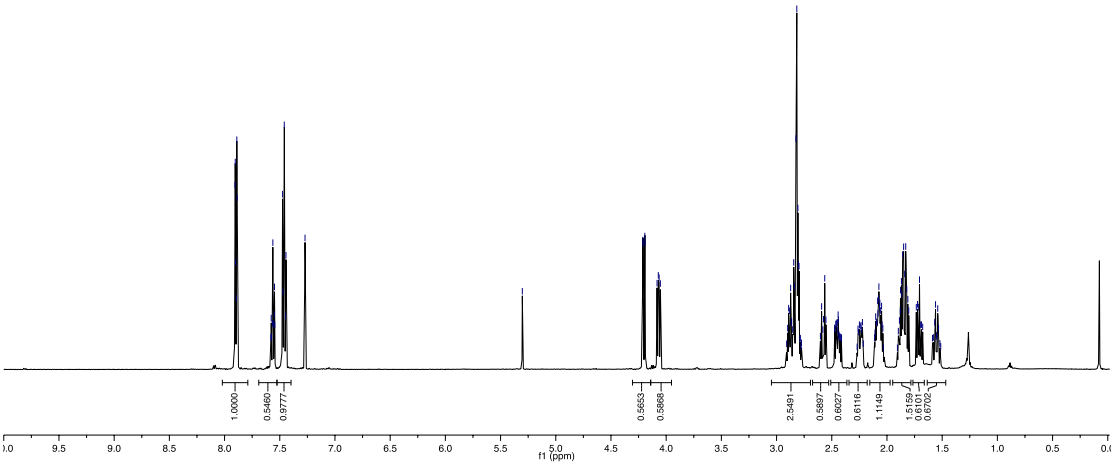








9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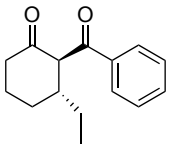
f1 (ppm)



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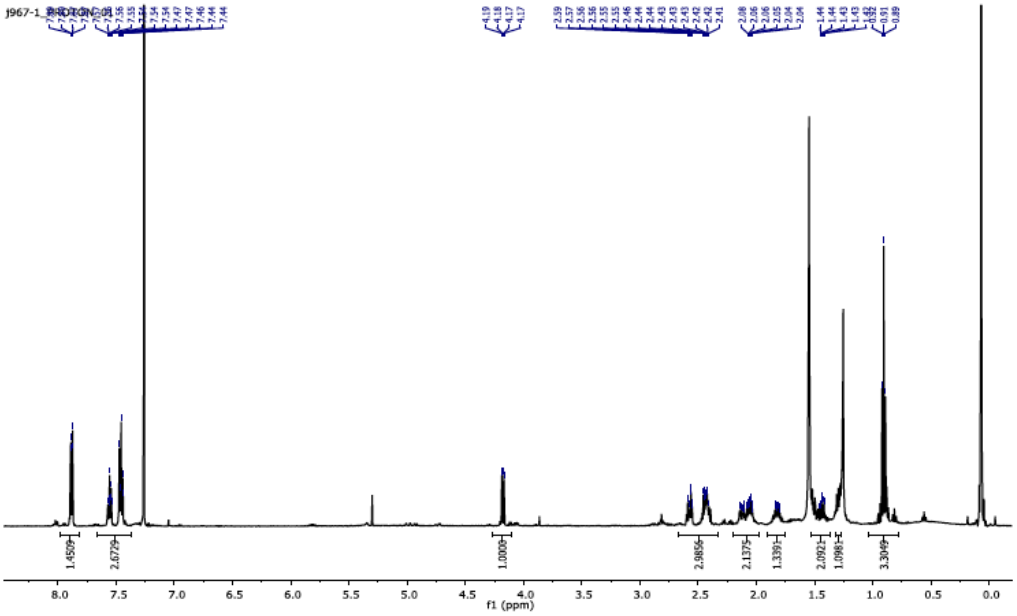
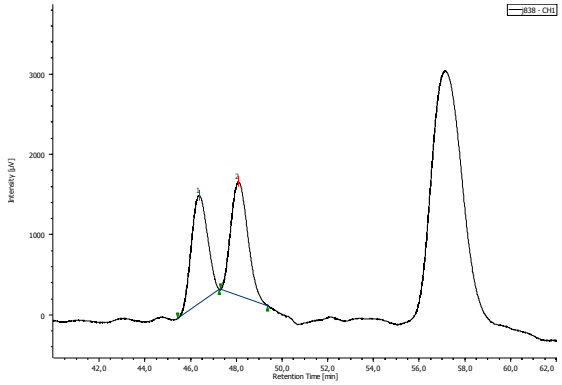
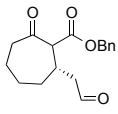


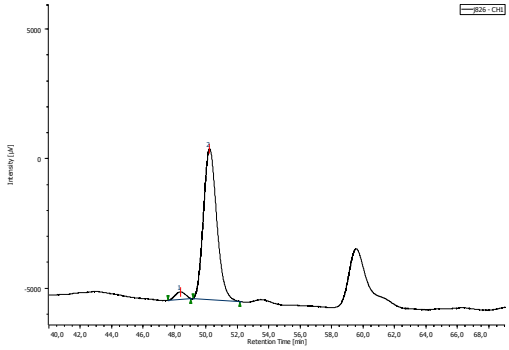
Rac-**4a**



Peak Name	tR	Area	Height	Area%	Height%	NTP	Resolution	Symmetry Factor
1	46,383	65684	1337	47,434	48,590	18768	1,240	1,018
2	48,075	72790	1414	52,566	51,410	19355	N/A	1,234

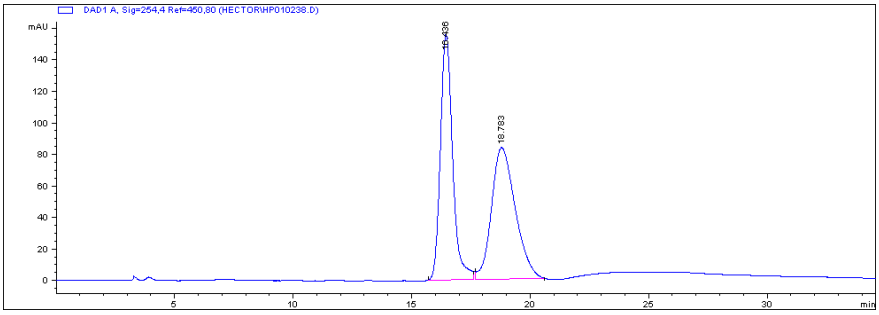


4a

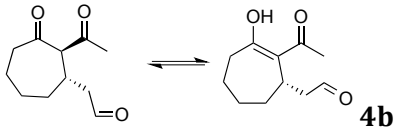


Peak Name	tR	Area	Height	Area%	Height%	NTP	Resolution	Symmetry Factor
1	48,358	12932	289	3,638	4,741	23400	1,326	0,960
2	50,217	342554	5802	96,362	95,259	16872	N/A	1,191

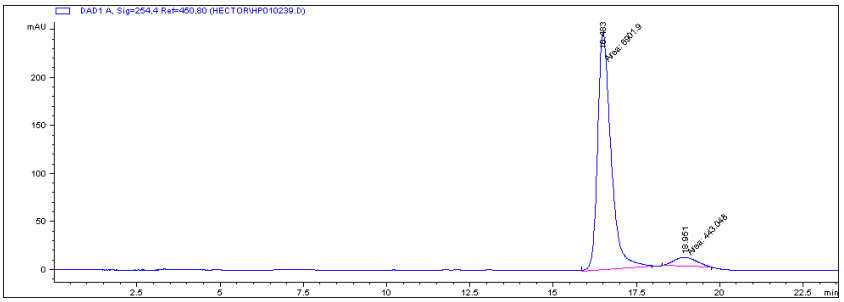
Rac-4b



#	Time	Area	Height	Width	Area%	Symmetry
1	16.436	5629.2	156.6	0.5346	48.964	0.785
2	18.783	5867.5	83.8	0.9063	51.036	0.729

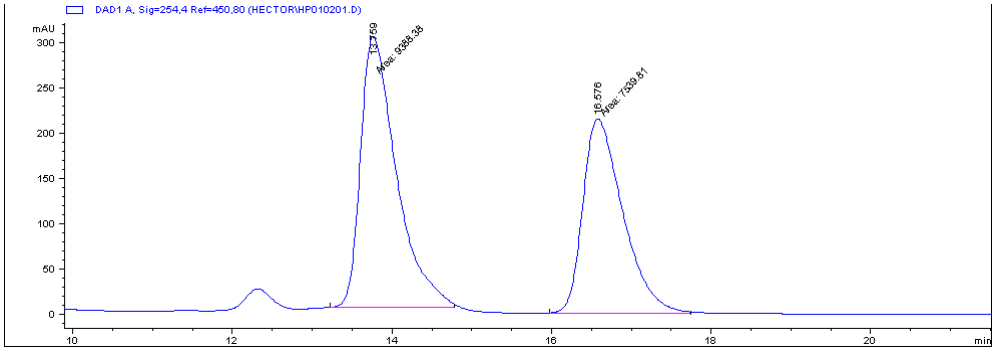


4b

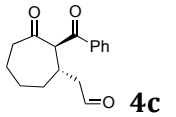


#	Time	Area	Height	Width	Area%	Symmetry
1	16.483	6901.9	246.4	0.4668	93.968	0.636
2	18.951	443	9.2	0.7992	6.032	0.851

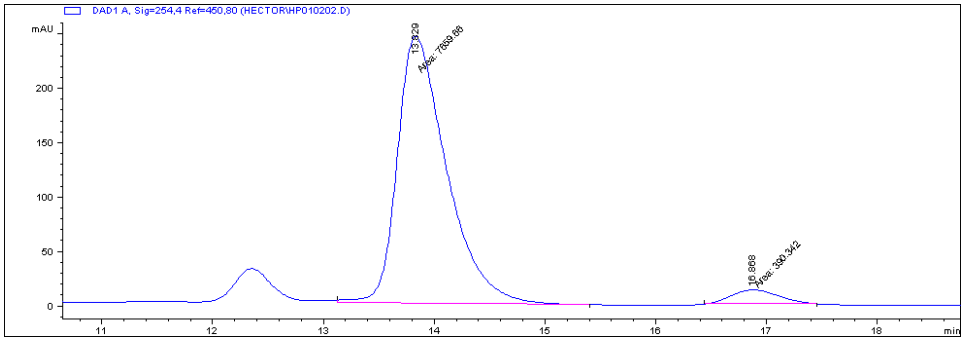
Rac-4c



#	Time	Area	Height	Width	Area%	Symmetry
1	13.759	9388.4	299.3	0.5228	55.460	0.531
2	16.576	7539.8	214.9	0.5848	44.540	0.583

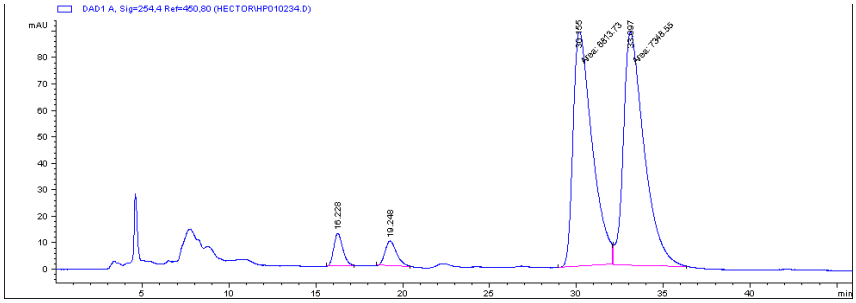


4c

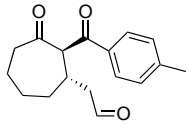


#	Time	Area	Height	Width	Area%	Symmetry
1	13.829	7659.7	245.6	0.5197	95.151	0.579
2	16.868	390.3	13	0.4989	4.849	0.789

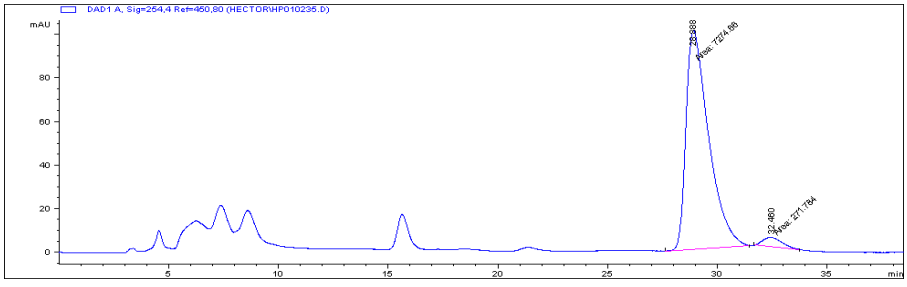
Rac-**4d**



#	Time	Area	Height	Width	Area%	Symmetry
1	16.228	453.6	12.4	0.4734	3.013	0.746
2	19.248	438.1	9.5	0.5533	2.910	0.757
3	30.155	6813.7	88.7	1.28	45.262	0.482
4	33.097	7348.5	88.2	1.3881	48.815	0.504

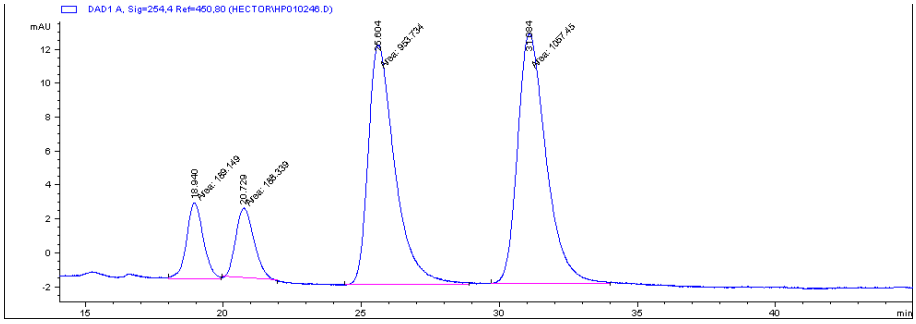


4d

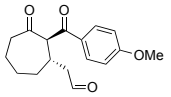


#	Time	Area	Height	Width	Area%	Symmetry
1	28.888	7274.7	100.6	1.2047	96.399	0.474
2	32.46	271.8	4.4	1.0406	3.601	0.565

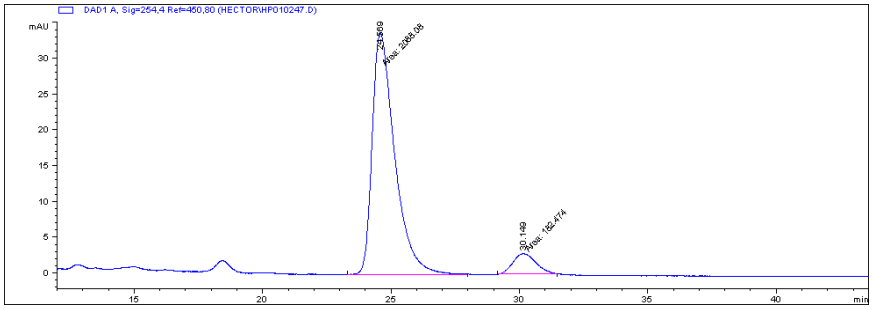
Rac-**4e**



#	Time	Area	Height	Width	Area%	Symmetry
1	18.94	189.1	4.5	0.7033	7.919	0.877
2	20.729	188.3	4.1	0.7582	7.885	0.778
3	25.604	953.7	14.1	1.1234	39.927	0.589
4	31.084	1057.5	14.7	1.1961	44.269	0.707

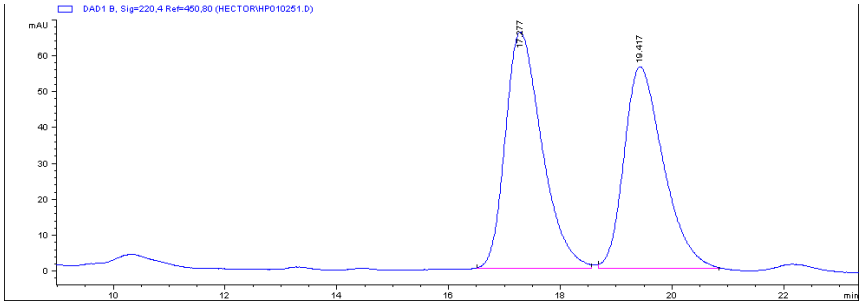


4e

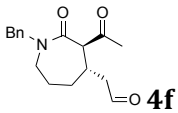


#	Time	Area	Height	Width	Area%	Symmetry
1	24.569	2088.1	33.8	1.0294	91.963	0.542
2	30.149	182.5	2.9	1.045	8.037	0.832

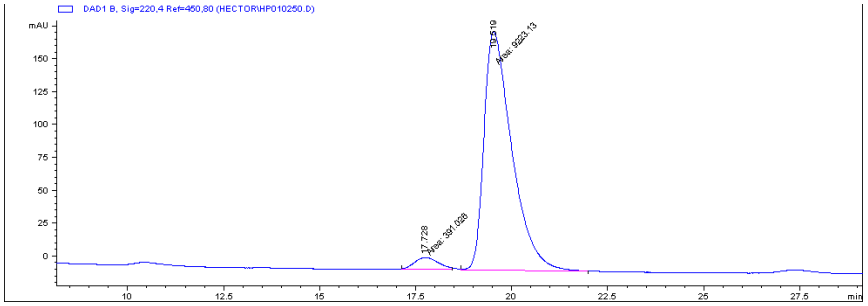
Rac-**4f**



#	Time	Area	Height	Width	Area%	Symmetry
1	17.277	3002.2	65.9	0.6596	52.102	0.661
2	19.417	2760	56.3	0.6521	47.898	0.634

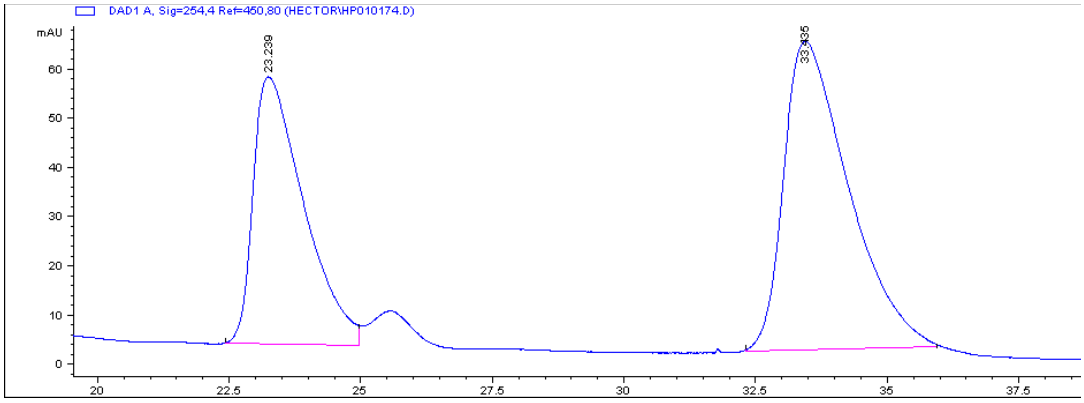


4f

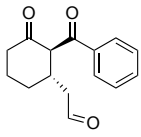


#	Time	Area	Height	Width	Area%	Symmetry
1	17.728	391	9.1	0.7149	4.067	0.758
2	19.519	9223.1	181.4	0.8476	95.933	0.507

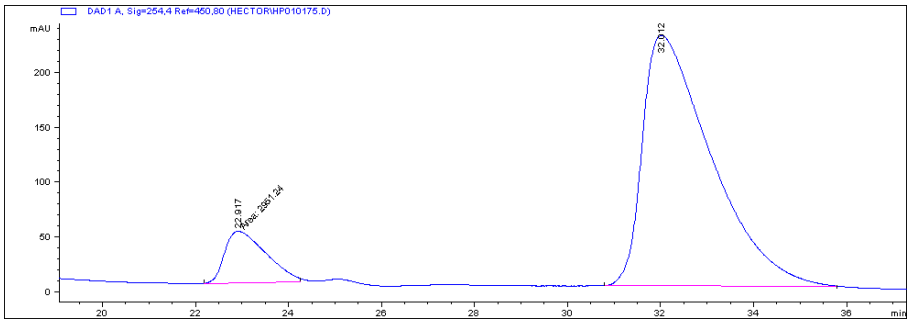
Rac-**7c**



#	Time	Area	Height	Width	Area%	Symmetry
1	23.239	3660	54.5	0.8889	40.260	0.407
2	33.435	5430.9	63	1.0256	59.740	0.487

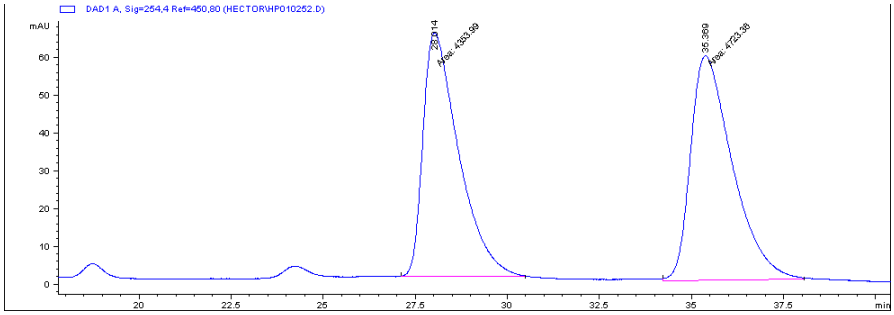


7c

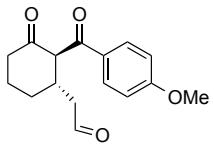


#	Time	Area	Height	Width	Area%	Symmetry
1	**22.917**	**2951.2**	**47.6**	**1.0326**	**11.153**	**0.493**
2	**32.012**	**23509.7**	**228.8**	**1.346**	**88.847**	**0.359**

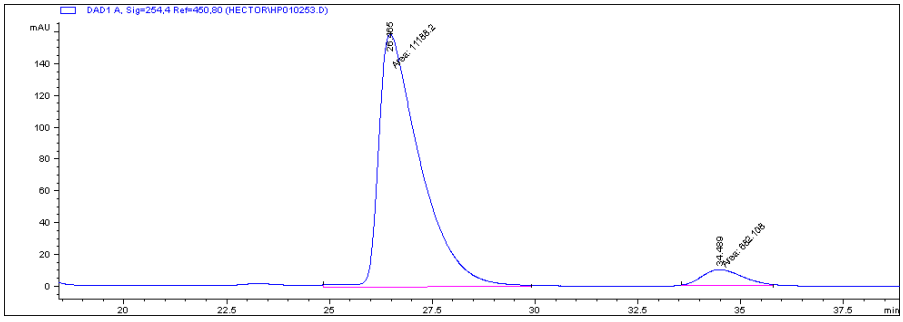
Rac-**7e**



#	Time	Area	Height	Width	Area%	Symmetry
1	28.014	4354	64.5	1.1255	47.965	0.463
2	35.369	4723.4	59.5	1.3236	52.035	0.534

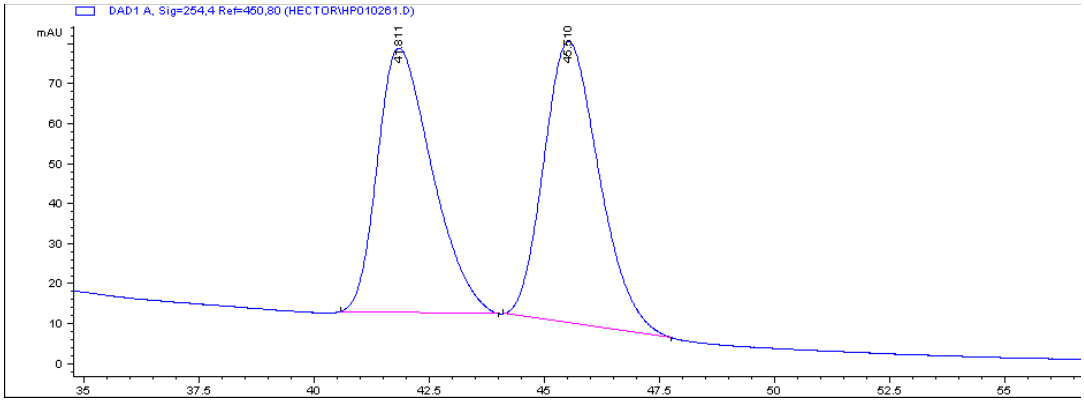


7e

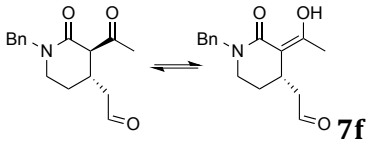


#	Time	Area	Height	Width	Area%	Symmetry
1	26.465	11188.2	159.1	1.172	94.254	0.379
2	34.489	682.1	10	1.1361	5.746	0.7

Rac-7f



#	Time	Area	Height	Width	Area%	Symmetry
1	41.811	5482.5	66.3	0.9908	48.078	0.592
2	45.51	5920.8	70.5	0.9954	51.922	0.757



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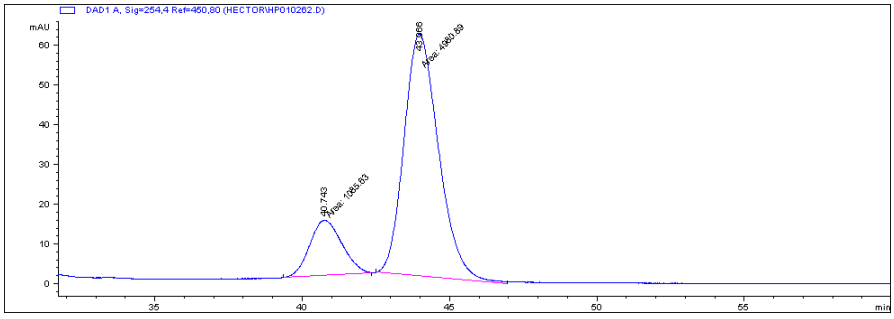
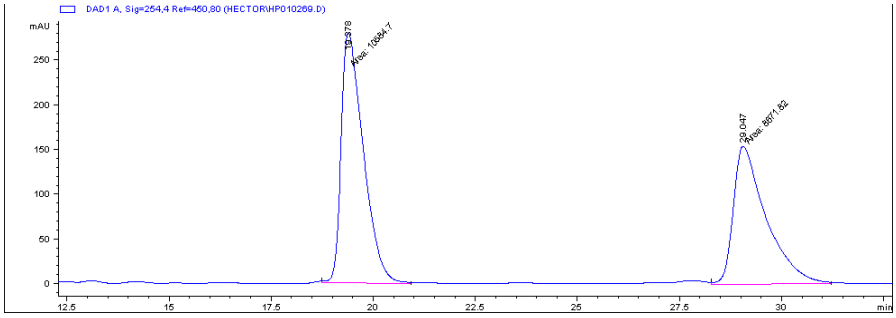
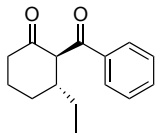


#	Time	Area	Height	Width	Area%	Symmetry
1	40.743	1085.6	14.1	1.2875	17.895	0.843
2	43.966	4980.9	60.9	1.3626	82.105	0.768

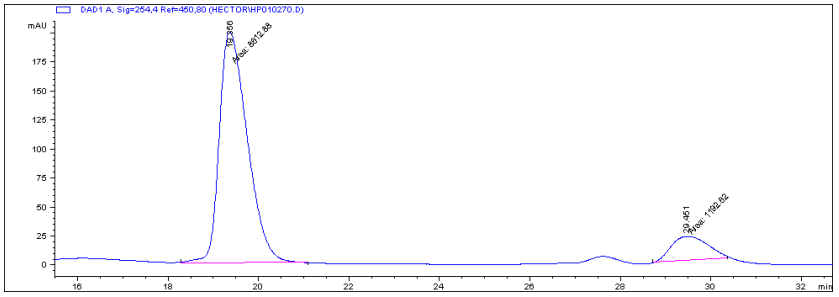
Rac-**10**



#	Time	Area	Height	Width	Area%	Symmetry
1	19.378	10584.7	279.6	0.631	54.967	0.461
2	29.047	8671.8	154.6	0.9349	45.033	0.419



10



#	Time	Area	Height	Width	Area%	Symmetry
1	19.356	8612.9	199.2	0.7205	87.837	0.594
2	29.451	1192.6	21	0.9465	12.163	0.722