Electronic Supplementary Material (ESI) for Chemical Science

Supporting Information

for

N-Heterocyclic Carbene Cascade Catalysis: Dual Brønsted/Lewis base Rearrangement of Cyclopropyl enol esters to Dihydropyranone

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Experimental Procedures, ^{1}H and ^{13}C NMR spectra

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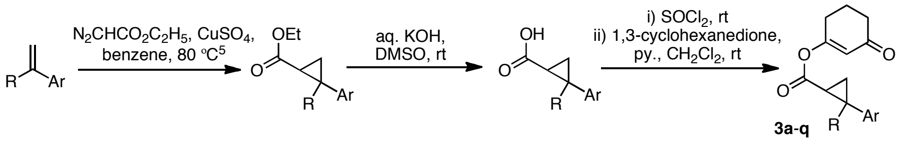
I. General Experimental

Proton (^{1}H) and carbon (^{13}C) NMR spectra were recorded on a Bruker DRX400 spectrometer operating at 400 MHz for proton and 100 MHz for carbon nuclei or a Bruker DRX300 spectrometer operating at 300 MHz for proton and 75 MHz for carbon nuclei. Infrared spectra (ν_{max}) were recorded on a Perkin-Elmer RXI FTIR Spectrometer. High resolution mass spectra (HRMS) (ESI) were recorded on a Bruker BioApex 47e FTMS fitted with an Analytical electrospray source using NaI for accurate mass calibration. Flash column chromatography was performed on silica gel (Davisil LC60A, 40-63 μm silica media) using compressed air or nitrogen. Thin layer chromatography (TLC) was performed using aluminum-backed plates coated with 0.2 mm silica (Merck, DC-Platten, Kieselgel; 60 F_{254} plates). Eluted plates were visualized using a 254 nm UV lamp and/or by treatment with a suitable stain followed by heating. Starting materials and reagents were purchased from Sigma-Aldrich, and other suppliers, were used as supplied or, in the case of some liquids, distilled. Dichloromethane was distilled from calcium hydride and toluene was distilled from sodium. NHCs precursors **IMes•HCl** and **IPr•HCl** were prepared using the procedure of Arduengo,[1] **IPr*•HCl** using the procedure of Markó,[2] and **IPrBr•HCl** using the procedure of Chung.[3] **IPr** was prepared “salt-free” by first generating the carbene from the imidazolium salt, and then filtering the reaction mixture and concentrating the filtrate. **IPrMe** was prepared using the procedure of Lyapkalo.[4]

[1] A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall, M. Unverzagt *Tetrahedron* 1999, **55**, 14523
[2] G. Berthon-Gelloz, M. A. Siegler, A. L. Spek, B. Tinant, J. N. H. Reek, I. E. Markó *Dalton Trans.*, 2010, **39**, 1444
[3] I. G. Jung, J. Seo, S. I. Lee, S. Y. Choi, Y. K. Chung *Organometallics*, 2006, **25**, 4240
[4] R. A. Kunetskiy, I. Císarová, D. Saman, I. M. Lyapkalo, *Chem, Eur. J.* 2009, **15**, 9477

II. Synthesis of cyclopropyl enol esters

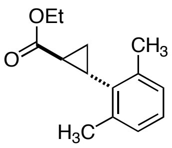


Scheme 1: General strategy for the preparation of cyclopropyl enol esters

Cyclopropyl ethyl esters were prepared according to Orfanopoulos,[5] through the copper(II) catalysed cyclopropanation of styrenes. Hence, to a magnetically stirred solution of the styrene (6 mmol) and anhydrous $CuSO_4$ (0.095 g, 0.6 mmol) in dry benzene (8 ml) at 80 °C was added ethyl diazoacetate (1.37 g, 12 mmol) in benzene (6 ml) dropwise over 3 h. Upon completion of the addition, the reaction was allowed to stir overnight at rt. The mixture was then poured into H_2O (20 ml) and extracted with Et_2O (3 x 20 ml). The combined organics were washed with $NaHCO_3$ (20 ml of a saturated aq. solution) and brine (20 ml), dried ($MgSO_4$), and the solvent removed under reduced pressure. The crude residue was purified by flash column chromatography to yield the pure cyclopropyl ethyl esters. Following this, the ethyl esters were hydrolysed under basic conditions to afford the cyclopropyl acids.

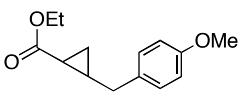
Cyclopropyl enol esters were prepared in two-steps from the corresponding cyclopropyl acids. Acids were stirred with $SOCl_2$ under N_2 at rt for 4 h. After this time, the remaining $SOCl_2$ was removed under reduced pressure to afford the acid chloride, which was used without purification. To a magnetically stirred solution of 1,3-cyclohexanedione (0.22 g, 2 mmol) in CH_2Cl_2 (10 ml) and pyridine (0.2 ml, 2.2 mmol) was added the cyclopropyl acid chloride (2.2 mmol) in CH_2Cl_2 (2 ml). The mixture was stirred at rt for 2 h after which time more CH_2Cl_2 (20 ml) was added. The mixture was washed with water (10 ml), $NaHCO_3$ (10 ml of a sat. aq. solution), HCl (10 ml of a 1 M aq. solution) and brine (10 ml), dried ($MgSO_4$) and concentrated. The crude material was purified by flash column chromatography (1:4 v/v EtOAc in hexane) to afford the pure cyclopropyl enol esters.

(1*S*,2*S* and 1*R*,2*R*)-Ethyl 2-(2,6-dimethylphenyl)cyclopropanecarboxylate



(0.841 g, 64%) R_f 0.3 (1:19 v/v EtOAc in hexane) IR ν_{max} 2980, 1726, 1465, 1315, 1181 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10-6.97 (m, 3H), 4.30-4.21 (m, 2H), 2.40 (s, 6H), 2.39-2.34 (m, 1H), 1.79-1.75 (m, 1H), 1.73-1.67 (m, 1H), 1.34 (dt, *J* = 7.2, 0.8 Hz, 3H), 1.20-1.15 (m, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 138.4, 133.7, 128.2, 126.5, 60.1, 23.1, 21.3, 16.0, 13.9 HRMS (ESI) *m/z* Found $(M+H)^+$, 219.1382, $C_{14}H_{18}O_2$, requires $(M+H)^+$, 219.1380

Ethyl 2-(4-methoxybenzyl)cyclopropanecarboxylate

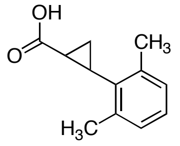


(0.960 g, 68%) as a 1:4 *cis*/*trans* mixture. R_f 0.2 (1:19 v/v EtOAc in hexane) IR ν_{max} 2982, 1723, 1612, 1513, 1248, 1176 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ *trans* 7.13 (d, *J* = 8.4 Hz, 2H), 6.85-6.82 (m, 2H), 4.14-4.09 (m, 2H), 3.78 (s, 3H), 2.70 (dd, *J* = 14.8, 6.8 Hz, 1H), 2.53 (dd, *J* = 14.8, 6.8 Hz, 1H), 1.70-1.52 (m, 1H), 1.52-1.47 (m, 1H), 1.25 (t, *J* = 6.8 Hz, 3H), 1.26-1.20 (m, 1H),

[5] M. N. Alberti, M. Orfanopoulos *Org. Lett.* **2008**, 10, 2465

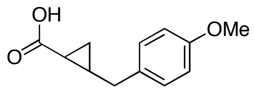
0.83-0.78 (m, 1H) δ *cis* 7.13 (d, *J* = 8.4 Hz, 2H), 6.85-6.82 (m, 2H), 4.26 (q, *J* = 6.8 Hz, 2H), 3.78 (s, 3H), 2.87 (dd, *J* = 14.8, 6.8 Hz, 1H), 2.78 (dd, *J* = 14.8, 6.8 Hz, 1H), 1.80-1.74 (m, 1H), 1.52-1.47 (m, 1H), 1.32 (t, *J* = 6.8 Hz, 3H), 1.13-1.07 (m, 2H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 172.8, 158.1, 157.8, 133.5, 132.1, 129.2, 129.1, 113.8, 113.7, 61.2, 60.2(3), 60.2(0), 55.1, 37.4, 31.9, 23.1, 22.8, 20.0, 18.4, 15.0, 14.2(2), 14.1(5), 13.4 HRMS (ESI) *m/z* Found $(M+H)^+$, 235.1330, $C_{14}H_{18}O_3$, requires $(M+H)^+$, 235.1329

2-(2,6-Dimethylphenyl)cyclopropanecarboxylic acid



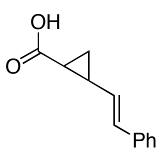
(0.516 g, 71%) as a 1:1 *cis*/*trans* mixture. R_f 0.3 (1:1 v/v EtOAc in hexane) IR ν_{max} 3018, 2957, 2672, 1694, 1453, 1231 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.05 (m, 6H), 2.53-2.46 (m, 2H), 2.48 (s, 12H), 2.27-2.21 (m, 1H), 1.83-1.80 (m, 2H), 1.75-1.69 (m, 2H), 1.34-1.28 (m, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 178.8, 138.3, 135.5, 132.9, 128.1, 126.9, 126.5, 24.2, 24.1, 23.0, 21.0, 20.5, 18.2, 16.8 (3 signals overlapping) HRMS (ESI) *m/z* Found $(M+H)^+$, 191.1067, $C_{12}H_{14}O_2$, requires $(M+H)^+$, 191.1067

2-(4-Methoxybenzyl)cyclopropanecarboxylic acid



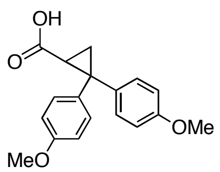
(0.512 g, 71%) as a 3:7 *cis*/*trans* mixture. R_f 0.3 (1:1 v/v EtOAc in hexane) IR ν_{max} 3006, 2933, 2656, 1868, 1611, 1512, 1458, 1247, 1177 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ *trans* 11.93 (s, 1H), 7.23-7.21 (m, 2H), 6.96-6.94 (m, 2H), 3.85 (s, 3H), 2.72 (dd, *J* = 14.8, 8.0 Hz, 1H), 2.66 (dd, *J* = 14.8, 6.4 Hz, 1H), 1.91-1.80 (m, 1H), 1.62 (pent, *J* = 4.4 Hz, 1H), 1.41 (pent, *J* = 4.4 Hz, 1H), 1.02-0.97 (m, 1H) δ *cis* 11.93 (s, 1H), 7.23-7.21 (m, 2H), 6.96-6.94 (m, 2H), 3.85 (s, 3H), 2.97 (d, *J* = 7.2 Hz, 2H), 1.91-1.80 (m, 1H), 1.68 (pent, *J* = 7.2 Hz, 1H), 1.28-1.24 (m, 2H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 179.7, 158.0, 157.8, 133.0, 131.7, 129.1, 129.0, 113.7, 113.7, 54.9, 37.2, 31.7, 24.3, 24.0, 19.8, 18.3, 15.7, 14.4 (one signal overlapping) HRMS (ESI) *m/z* Found $(M+Na)^+$, 229.0831, $C_{12}H_{14}O_3$, requires $(M+Na)^+$, 229.0835

(*E*)-2-Styrylcyclopropanecarboxylic acid



(0.497 g, 75%) as a 1:1 *cis*/*trans* mixture. R_f 0.3 (1:1 v/v EtOAc in hexane) IR ν_{max} 3010, 2945, 2657, 1870, 1611, 1456, 1250, 1177 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.19 (s, 2H), 7.49-7.29 (m, 10H), 6.73 (d, *J* = 15.9 Hz, 1H), 6.65 (d, *J* = 15.9 Hz, 1H), 6.39 (dd, *J* = 15.9, 9.3 Hz, 1H), 5.83 (dd, *J* = 15.9, 9.3 Hz, 1H), 2.43-2.34 (m, 1H), 2.25 (pent, *J* = 6.3 Hz, 1H), 2.15-2.08 (m, 1H), 1.87 (pent, *J* = 4.2 Hz, 1H), 1.66 (pent, *J* = 4.2 Hz, 1H), 1.57-1.42 (m, 2H), 1.29-1.22 (m, 1H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.9, 178.9, 137.1, 136.7, 131.9, 130.6, 129.2, 128.4(0), 128.3(6), 127.2, 127.0, 126.6, 125.9, 125.8, 26.3, 25.6, 22.1, 21.1, 16.4, 15.4 HRMS (ESI) *m/z* Found $(M+H)^+$, 189.0910, $C_{12}H_{12}O_2$, requires $(M+H)^+$, 189.0910

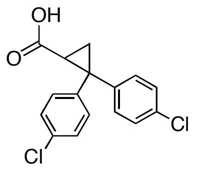
2,2-Bis(4-methoxyphenyl)cyclopropanecarboxylic acid



(0.753 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.65 (s, 1H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 684 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 2.48 (dd, *J* = 8.0, 6.0 Hz, 1H), 2.11 (t, *J* = 5.6 Hz, 1H), 1.65 (dd, *J* = 8.0, 4.8 Hz, 1H) ^{13}C NMR

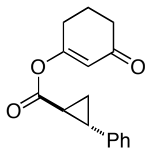
(75 MHz, $CDCl_3$) δ 176.4, 157.4, 155.9, 134.6, 133.9, 128.8(4), 128.8(3), 113.5, 113.3, 55.1, 55.0, 39.6, 28.7, 20.8 HRMS (ESI) *m/z* Found $(M+H)^+$, 299.1273, $C_{18}H_{18}O_4$, requires $(M+H)^+$, 299.1278

2,2-Bis(4-chlorophenyl)cyclopropanecarboxylic acid



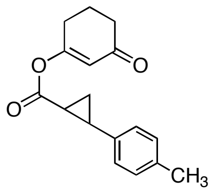
(0.730 g, 68%). R_f 0.3 (1:1 v/v EtOAc in hexane) ^1H NMR (300 MHz, $CDCl_3$) δ 7.29-7.16 (m, 8H), 2.49 (dd, *J* = 8.1, 6.0, Hz, 1H), 2.11 (t, *J* = 5.4 Hz, 1H), 1.63 (dd, *J* = 8.1, 5.1 Hz, 1H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4, 142.4, 137.9, 133.1, 130.8, 128.9, 128.8, 128.7, 39.7, 28.5, 20.6 (one signal overlapping) HRMS (ESI) *m/z* Found $(M+H)^+$, 307.0282, $C_{16}H_{12}Cl_2O_2$, requires $(M+H)^+$, 307.0287

(1*S*,2*S* and1*R*,2*R*)-3-Oxocyclohex-1-en-1-yl 2-phenylcyclopropanecarboxylate (**3a**).



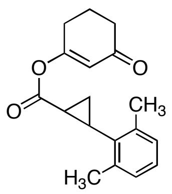
(0.435 g, 85%) R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 2954, 1751, 1674, 1458, 1304, 1120 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$) δ 7.31-7.08 (m, 5H), 5.96 (t, *J* = 1.2 Hz, 1H), 2.78-2.72 (m, 1H), 2.55 (dt, *J* = 6.4, 0.8 Hz, 2H), 2.39 (t, *J* = 6.4 Hz, 2H), 2.08-2.01 (m, 2H), 2.01-1.98 (m, 1H), 1.72-1.67 (m, 1H), 1.48-1.44 (m, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 170.0, 169.8 167.6, 139.0, 128.6, 126.9, 126.2, 117.3, 36.7, 28.4, 27.6, 24.1, 21.2, 17.9 HRMS (ESI) *m/z* Found $(M+H)^+$, 257.1174, $C_{16}H_{16}O_3$, requires $(M+H)^+$, 257.1172

3-Oxocyclohex-1-en-1-yl 2-(*p*-tolyl)cyclopropanecarboxylate (**3b**).



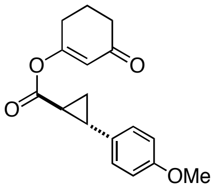
(0.428 g, 79%) as a 2:3 *cis*/*trans* mixture. R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 3020, 2926, 1748, 1674, 1644, 1427, 1363, 1120 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$) δ *trans* 7.17-7.00 (m, 4H), 5.95 (t, *J* = 1.2 Hz, 1H), 2.63-2.59 (m, 1H), 2.56 (dt, *J* = 6.4, 1.2 Hz, 2H), 2.42-2.39 (dd, *J* = 6.4, 5.2 Hz, 2H), 2.32 (s, 3H), 2.08-2.03 (m, 2H), 1.99-1.95 (m, 1H), 1.70-1.65 (m, 1H), 1.48-1.41 (m, 1H) δ *cis* 7.17-7.00 (m, 4H), 5.54 (t, *J* = 1.2 Hz, 1H), 2.75-2.69 (m, 1H), 2.32-2.28 (m, 2H), 2.28 (s, 3H), 2.21-2.15 (m, 2H), 2.15-2.11 (m, 1H), 1.92-1.86 (m, 2H), 1.80-1.76 (m, 1H), 1.48-1.41 (m, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 170.0. 169.8(4), 169.7(5), 167.7, 136.8, 136.6, 135.9, 132.4, 129.2, 129.1, 128.8, 126.1, 117.3, 117.2, 36.7, 36.6, 28.3, 27.9, 27.3, 26.5, 23.9, 21.7, 21.2, 21.1, 21.0, 20.9, 17.7, 11.9 (one signal overlapping) HRMS (ESI) *m/z* Found $(M+H)^+$, 271.1332, $C_{17}H_{18}O_3$, requires $(M+H)^+$, 271.1334

3-Oxocyclohex-1-en-1-yl 2-(2,6-dimethylphenyl)cyclopropane carboxylate (**3c**).



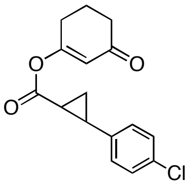
(0.433 g, 76%) as a 1:1 *cis*/*trans* mixture. R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 3018, 2956, 1747, 1673, 1644, 1455, 1361, 1121 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$) δ 7.05-6.93 (m, 6H), 5.93 (t, *J* = 1.2 Hz, 1H), 5.51 (t, *J* = 1.2 Hz, 1H), 2.56 (dt, *J* = 6.0, 1.2 Hz, 2H), 2.47-2.40 (m, 2H), 2.36 (s, 6H), 2.35 (s, 6H), 2.28-2.20 (m, 4H), 2.16-2.02 (m, 4H), 1.87-1.65 (m, 7H), 1.37-1.27 (m, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 170.5, 169.5, 169.3, 168.3, 137.8, 134.8, 132.5, 128.0, 126.8, 126.5, 117.1, 116.7, 36.4, 36.3, 28.0, 27.4, 24.6, 24.1, 22.6, 20.9, 20.8, 20.2, 18.2, 16.6, 13.9 (four signals overlapping) HRMS (ESI) *m/z* Found $(M+H)^+$, 285.1483, $C_{18}H_{20}O_3$, requires $(M+H)^+$, 285.1485

(1*S*,2*S* and 1*R*,2*R*)-3-Oxocyclohex-1-en-1-yl 2-(4-methoxyphenyl)cyclopropane carboxylate (3d).



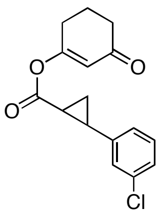
(0.420 g, 73%) of the *trans* product. R_f 0.2 (1:4 v/v EtOAc in hexane) IR ν_{max} 3007, 2954, 1747, 1681, 1645, 1516, 1455, 1250, 1118 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.94 (s, 1H), 3.78 (s, 3H), 2.61-2.55 (m, 1H), 2.55 (t, *J* = 4.5 Hz, 2H), 2.39 (t, *J* = 5.4 Hz, 2H), 2.08-2.16 (m, 2H), 1.94-1.90 (m, 1H), 1.67-1.63 (m, 1H), 1.43-1.39 (m, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 170.0, 169.7, 158.6, 130.9, 127.4, 117.3, 114.0, 55.2, 36.6, 28.3, 27.0. 23.8, 21.2, 17.5 HRMS (ESI) *m/z* Found $(M+H)^+$, 287.1280, $C_{17}H_{18}O_4$, requires $(M+H)^+$, 287.1278

3-Oxocyclohex-1-en-1-yl 2-(4-chlorophenyl)cyclopropane carboxylate (3e).



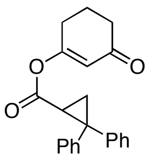
(0.518 g, 89%) as a 2:3 *cis*/*trans*. R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 3066, 2954, 1755, 1667, 1633, 1495, 1346, 1117 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ *trans* 7.26-7.17 (m, 2H), 7.03-7.01 (m, 2H), 5.92 (t, *J* = 1.2 Hz, 1H), 2.59-2.55 (m, 1H), 2.52 (dt, *J* = 6.0,1.2 Hz, 2H), 2.37 (dd, *J* = 6.8, 6.4 Hz, 2H), 2.08-1.99 (m, 2H), 1.97-1.92 (m, 1H), 1.69-1.64 (m, 1H), 1.43-1.38 (m, 1H) δ *cis* 7.26-7.17 (m, 4H), 5.59 (t, *J* = 1.2 Hz, 1H), 2.70-2.64 (m, 1H), 2.26 (dd, *J* = 6.8, 6.4 Hz, 2H), 2.22-2.08 (m, 3H), 1.90-1.86 (m, 2H), 1.75-1.70 (m, 1H), 1.48-1.44 (m, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2(4), 199.1(7), 169.5(4), 169.5(2), 169.5(1), 167.3, 137.5, 134.0, 132.8, 132.5, 130.5, 128.6, 128.1, 127.5, 117.2, 117.1, 36.5, 36.4(5), 28.2, 27.9, 26.6, 26.0, 23.9, 21.7, 21.1, 21.0, 17.6, 12.0 HRMS (ESI) *m/z* Found $(M+H)^+$, 291.0786, $C_{16}H_{15}ClO_3$, requires $(M+H)^+$, 291.0788

3-Oxocyclohex-1-en-1-yl 2-(3-chlorophenyl)cyclopropanecarboxylate (3f).



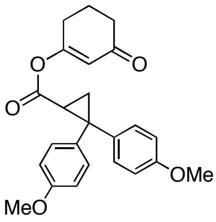
(0.396 g, 68%) as a 2:3 *cis*/*trans* mixture. R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 3066, 2955, 1747, 1681, 1626, 1485, 1361, 1118 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) δ *trans* 7.24-6.98 (m, 4H), 5.93 (s, 1H), 2.61-2.49 (m, 3H), 2.40-2.37 (m, 2H) 2.04-1.97 (m, 3H) 1.73-1.65 (m, 1H), 1.44-1.40 (m, 1H) *cis* 7.24-6.98 (m, 4H), 5.57 (s, 1H), 2.76-2.65 (m, 1H), 2.72-2.13 (m, 5H), 1.95-1.83 (m, 2H), 1.80-1.75 (m, 1H), 1.47-1.43 (m, 1H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.3, 169.5, 167.3, 141.1, 137.7, 134.4, 129.8, 129.4, 129.3, 127.4, 127.3, 127.0, 126.3, 124.5, 117.3, 36.6, 36.5, 28.2, 27.9, 26.8, 26.1, 24.0, 21.7, 21.1, 17.7, 14.1, 11.9 (five signals overlapping) HRMS (ESI) *m/z* Found $(M+H)^+$, 291.0782, $C_{16}H_{15}ClO_3$, requires $(M+H)^+$, 291.0788

3-Oxocyclohex-1-en-1-yl 2,2-diphenylcyclopropanecarboxylate (3g).



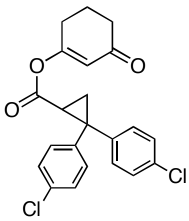
(0.518 g, 78%). R_f 0.2 (1:4 v/v EtOAc in hexane) IR ν_{max} 3084, 2890, 1760, 1731, 1621, 1495, 1360, 1120 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.22 (m, 10H), 5.59 (s, 1H), 2.71-2.66 (m, 1H), 2.32-2.27 (m, 3H), 2.23-2.19 (m, 2H), 1.97-1.86 (m, 2H), 1.75-1.70 (m, 1H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.4, 169.7, 167.2, 143.9, 139.3, 129.6, 128.4(9), 128.4(6), 127.4, 127.3, 126.8 117.3, 41.2, 36.5, 28.8, 27.8, 21.0, 20.6 HRMS (ESI) *m/z* Found $(M+H)^+$, 333.1488, $C_{22}H_{20}O_3$, requires $(M+H)^+$, 333.1485

3-Oxocyclohex-1-en-1-yl 2,2-bis(4-methoxyphenyl)cyclopropane carboxylate (3h).



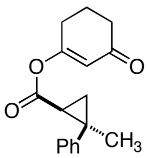
(0.487 g, 62%). R_f 0.3 (1:3 v/v EtOAc in hexane) IR ν_{max} 3004, 2958, 1755, 1673, 1610, 1514, 1362, 1227, 1118 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 5.64 (s, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 2.59 (dd, *J* = 8.0, 5.6 Hz, 1H), 2.31-2.29 (m, 2H), 2.30-2.22 (m, 2H), 2.18 (dd, *J* = 5.6, 5.2 Hz, 1H), 1.94-1.90 (m, 2H), 1.64 (dd, *J* = 8.0, 4.8 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 169.7, 167.2, 158.6, 158.2, 136.5, 131.6, 130.4, 128.3, 117.1, 113.8, 55.1, 55.0, 40.0, 36.5, 28.9, 27.8, 21.0, 20.7 (one signal overlapping) HRMS (ESI) *m/z* Found $(M+H)^+$, 393.1690, $C_{24}H_{24}O_3$, requires $(M+H)^+$, 393.1697

3-Oxocyclohex-1-en-1-yl 2,2-bis(4-chlorophenyl)cyclopropane carboxylate (3i).



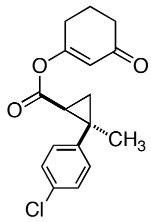
(0.610 g, 76%). R_f 0.2 (1:4 v/v EtOAc in hexane) IR ν_{max} 3078, 2888, 1765, 1731, 1619, 1495, 1367, 1120 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 4H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 5.67 (s, 1H), 2.63 (dd, *J* = 8.4, 6.0 Hz, 1H), 2.30 (t, *J* = 6.4 Hz, 2H), 2.27-2.23 (m, 1H), 2.20 (t, *J* = 6.4 Hz, 2H), 1.93 (pent, *J* = 6.4 Hz, 2H), 1.67 (dd, *J* = 8.0, 5.2 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 169.4, 166.7, 141.9, 137.4, 133.4, 132.9, 130.8, 128.8, 128.7(4), 128.7(1), 117.3, 39.9, 36.5, 28.7, 27.9, 21.0, 20.7 HRMS (ESI) *m/z* Found $(M+H)^+$, 401.0705, $C_{22}H_{18}Cl_2O_3$, requires $(M+H)^+$, 401.0706

3-Oxocyclohex-1-en-1-yl 2-methyl-2-phenylcyclopropanecarboxylate (4j).



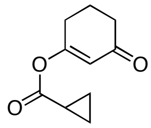
(0.400 g, 74%) of the *cis* product. R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 3002, 2959, 1754, 1674, 1644, 1362, 1122 cm^{-1} ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 4.2 Hz, 2H), 7.29-7.16 (m, 3H), 5.50 (t, *J* = 0.9 Hz, 1H), 2.26 (dd, *J* = 8.1, 6.6 Hz, 2H), 2.16-2.10 (m, 2H), 2.03 (dd, *J* = 7.8, 5.4 Hz, 1H), 1.91-1.85 (m, 3H), 1.52 (s, 3H), 1.30 (dd, *J* = 7.8, 4.8 Hz, 1H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.3, 169.7, 167.6, 140.8, 128.6, 128.3, 127.0, 117.0, 36.5, 33.6, 28.4, 28.2, 27.7, 21.0, 20.1 HRMS (ESI) *m/z* Found $(M+H)^+$, 271.1333, $C_{17}H_{18}O_3$, requires $(M+H)^+$, 271.1329

(1*S*,2*R* and 1*R*,2*S*) 3-Oxocyclohex-1-en-1-yl 2-(4-chlorophenyl)-2-methylcyclopropane carboxylate (3k).



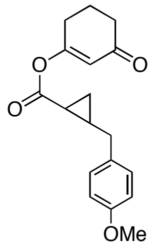
(0.433 g, 71%) *cis* product with around 10% of the *trans* product. R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 3010, 2954, 1754, 1668, 1378, 1122 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.17 (m, 4H), 5.57 (t, *J* = 1.2 Hz, 1H), 2.35 (t, *J* = 6.4 Hz, 2H), 2.20-2.12 (m, 2H), 1.98 (dd, *J* = 8.0, 5.2 Hz, 1H), 1.89-1.83 (m, 2H), 1.77 (t, *J* = 5.2 Hz, 1H), 1.44 (s, 3H), 1.26 (dd, *J* = 8.0, 5.2 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 169.6, 168.2, 139.3, 132.5, 129.9, 128.3, 116.9, 36.3, 32.9, 28.1, 27.9, 27.7, 20.9, 20.3 HRMS (ESI) *m/z* Found $(M+H)^+$, 305.0939, $C_{17}H_{17}ClO_3$, requires $(M+H)^+$, 305.0939

3-Oxocyclohex-1-en-1-yl cyclopropanecarboxylate (3l).



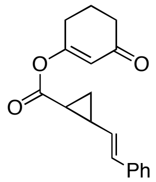
(0.220 g, 62%). R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 2955, 1754, 1674, 1643, 1427, 1362, 1123 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85 (s, 1H), 2.49 (t, *J* = 6.0 Hz, 2H), 2.34 (t, *J* = 6.0 Hz, 2H), 2.04-1.96 (m, 2H), 1.72-1.66 (m, 1H), 1.08-1.04 (m, 2H), 1.03-0.94 (m, 2H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.5, 171.4, 169.9, 117.2, 36.6, 28.2, 21.1, 13.0, 9.6 HRMS (ESI) *m/z* Found $(M+H)^+$, 181.0863, $C_{10}H_{12}O_3$, requires $(M+H)^+$, 181.0859

3-Oxocyclohex-1-en-1-yl 2-(4-methoxybenzyl)cyclopropane carboxylate (3m).



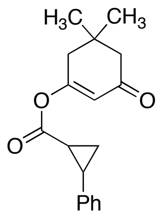
(0.354 g, 59%) as a *cis*/*trans* mixture 30/70. R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 3007, 2954, 1755, 1667, 1633, 1514, 1444, 1364, 1117 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) δ *trans* 7.13-7.10 (m, 2H), 6.85-6.81 (m, 2H), 5.89 (t, *J* = 1.2 Hz, 1H), 3.78 (s, 3H), 2.71 (dd, *J* = 15.0, 6.9 Hz, 1H), 2.59 (dd, *J* = 15.0, 6.9 Hz, 1H), 2.48 (t, *J* = 6.3 Hz, 2H), 2.36 (t, *J* = 6.3 Hz, 2H), 2.07-1.99 (m, 2H), 1.93-1.68 (m, 1H), 1.63-1.57 (m, 1H), 1.36-1.29 (m, 1H), 1.00-0.93 (m, 1H) *cis* 7.13-7.10 (m, 2H), 6.85-6.81 (m, 2H), 5.81 (t, *J* = 1.2 Hz, 1H), 3.78 (s, 3H), 2.93 (dd, *J* = 15.0, 6.9 Hz, 1H), 2.69 (dd, *J* = 15.0, 6.9 Hz, 1H), 2.48-2.41 (m, 2H), 2.07-1.99 (m, 3H), 1.86-1.79 (m, 1H), 1.72-1.66 (m, 2H), 1.38-1.18 (m, 2H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.4, 170.7, 169.9, 169.8, 169.5, 158.2, 158.0, 132.7, 131.4, 129.2, 129.0, 117.4, 117.2, 113.9, 113.8, 60.9, 55.2 37.2, 36.6(4), 36.6(2), 31.7, 28.3, 28.2, 24.8, 24.2, 21.2, 20.0, 18.4, 16.2, 14.9 (two signals overlapping) HRMS (ESI) *m/z* Found $(M+H)^+$, 301.1433, $C_{18}H_{20}O_4$, requires $(M+H)^+$, 301.1434

(*E*)-3-Oxocyclohex-1-en-1-yl 2-styrylcyclopropanecarboxylate (3n).



(0.402 g, 71%) as a 1:1 *cis*/*trans* mixture. R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 3060, 2954, 1755, 1687, 1624, 1494, 1360, 1117 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ *trans* 7.34-7.19 (m, 5H), 6.58 (d, *J* = 15.6 Hz, 1H), 5.94 (t, *J* = 1.2 Hz, 1H), 5.76 (dd, *J* = 15.6, 9.2 Hz, 1H), 2.55 (td, *J* = 6.0, 1.2 Hz, 2H), 2.42-2.36 (m, 4H), 2.10-1.99 (m, 2H), 1.90-1.84 (m, 1H), 1.61-1.55 (m, 1H) δ *cis* 7.34-7.19 (m, 5H), 6.63 (d, *J* = 15.6 Hz, 1H), 6.16 (dd, *J* = 15.6, 9.2 Hz, 1H), 5.91 (t, *J* = 1.2 Hz, 1H), 2.51 (t, *J* = 6.0 Hz, 2H), 2.32-2.21 (m, 2H), 2.15 (dd, *J* = 6.0, 2.8 Hz, 1H), 2.10-1.99 (m, 4H), 1.28-1.23 (m, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4(9), 199.4(7), 169.9, 169.8, 169.7, 168.6, 136.9, 136.6, 132.5, 131.2, 128.8, 128.6, 128.5, 127.5, 127.3, 125.9, 125.8(7), 125.8(3), 117.3, 36.7, 28.4, 28.3, 26.9, 25.9, 22.2, 21.4, 21.2, 16.9, 15.7 (three signals overlapping) HRMS (ESI) *m/z* Found $(M+H)^+$, 283.1336, $C_{18}H_{18}O_3$, requires $(M+H)^+$, 283.1329

5,5-Dimethyl-3-oxocyclohex-1-en-1-yl 2-phenylcyclopropanecarboxylate (3q).

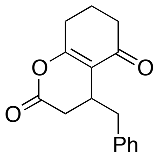


(0.460g, 81%) as a 2:3 *cis*/*trans* mixture. R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 3012, 2954, 1751, 1673, 1641, 1455, 1379, 1119 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ *trans* 7.33-7.22 (m, 4H), 7.14-7.12 (m, 1H), 5.97 (t, *J* = 1.2 Hz, 1H), 2.66-2.61 (m, 1H), 2.44 (s, 2H), 2.28 (s, 2H), 2.04-2.00 (m, 1H), 1.71 (dt, *J* = 9.2, 4.8 Hz, 1H), 1.51-1.44 (m, 1H), 1.12 (s, 6H) *cis* 7.33-7.22 (m, 4H), 7.14-7.12 (m, 1H), 5.53 (t, *J* = 1.2 Hz, 1H), 2.70 (q, *J* = 8.8 Hz, 1H), 2.24-2.19 (m, 1H), 2.13 (s, 2H), 1.96 (s, 1H), 1.88 (s, 1H), 1.86-1.81 (m, 1H), 1.51-1.44 (m, 1H), 0.96 (s, 3H), 0.94 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 170.1, 168.1(1), 168.0(6), 167.6, 139.0, 135.5, 129.3, 128.5, 128.1, 127.1, 126.8, 126.1, 116.3, 116.1, 50.7, 50.6, 42.2, 41.7, 33.1, 32.8, 28.0(9), 28.0(7), 28.0, 27.8, 27.5, 26.5, 24.0, 21.9, 17.8, 11.5 (one signal overlapping) HRMS (ESI) m/z Found $(M+H)^+$, 285.1486, $C_{18}H_{20}O_3$, requires $(M+H)^+$, 285.1485

III. NHC catalysed synthesis of dihydropyranone 4

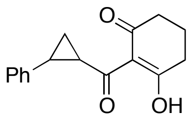
To a magnetically stirred solution of the cyclopropyl enol ester (0.3 mmol) in toluene (1.5 ml) in a flame-dried microwave tube fitted with a rubber septum and nitrogen inlet was added **IPr** (0.3 ml of a 0.1 M solution in toluene). The head space of the microwave tube was purged with argon and the rubber septum replaced with a microwave tube cap, which was fastened with a clamp. The sealed tube was then heated to 130 °C for 12 h. After this time, the crude mixture was concentrated under reduced pressure and the crude residue purified by flash column chromatography to afford the pure dihydropyranone.

4-Benzyl-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4a).



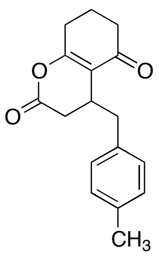
(59 mg, 76%). R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 2960, 1785, 1651, 1454, 1381, 1116 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.15 (m, 5H), 3.29-3.24 (m, 1H), 2.87 (dd, J = 13.6, 4.0 Hz, 1H), 2.68 (dd, J = 16.0, 1.2, 1H), 2.52 (t, J = 5.6 Hz, 2H), 2.48-2.43 (m, 3H), 2.36 (dd, J = 13.6, 10.0 Hz, 1H), 2.08 (pent, J = 6.8 Hz, 2H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 167.1, 166.1, 137.7, 129.4, 128.5, 126.8, 117.6, 39.1, 36.7, 32.3, 30.4, 27.2, 20.7 HRMS (ESI) *m/z* Found $(M+H)^+$, 257.1171, $C_{16}H_{16}O_3$, requires $(M+H)^+$, 257.1172

3-Hydroxy-2-(2-phenylcyclopropanecarbonyl)cyclohex-2-enone (5a).



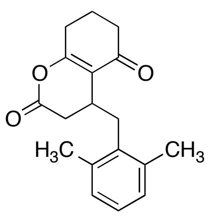
R_f 0.3 (1:5 v/v EtOAc in hexane) IR ν_{max} 3030, 2952, 1662, 1539, 1436, 1353, 1189, 1029 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) δ 18.37 (s, 1H), 7.30-7.12 (m, 5H), 4.00-3.95 (m, 1H), 2.82-2.75 (m, 1H), 2.68 (t, J = 6.3 Hz, 2H), 2.69-2.58 (m, 1H), 2.52 (t, J = 6.3 Hz, 2H), 2.06-2.90 (m, 2H), 1.59-1.45 (m, 1H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.6, 196.9, 195.5, 140.1, 128.5, 126.7, 126.3, 112.4, 52.6, 46.8, 31.8, 30.5, 28.3, 21.7 HRMS (ESI) *m/z* Found $(M+H)^+$, 257.1169, $C_{16}H_{16}O_3$, requires $(M+H)^+$, 257.1172

4-(4-Methylbenzyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4b).



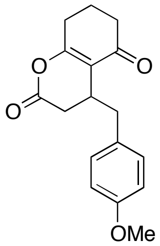
(65 mg, 80%). R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 3021, 2929, 1787, 1668, 1651, 1455, 1380, 1115 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.04 (m, 4H), 3.26-3.21 (m, 1H), 2.82 (dd, J = 13.6, 4.0 Hz, 1H), 2.66 (dd, J = 16.4, 1.2 Hz, 1H), 2.53 (t, J = 6.0 Hz, 2H), 2.49-2.43 (m, 3H), 2.33 (dd, J = 16.4, 8.0 Hz, 1H), 2.32 (s, 3H), 2.08 (p, J = 6.4 Hz, 2H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 167.0, 166.1, 136.3, 134.5, 129.3, 129.2, 118.0, 38.7, 36.7, 32.3, 30.4, 27.2, 21.0, 20.7 HRMS (ESI) *m/z* Found $(M+H)^+$, 271.1333, $C_{17}H_{18}O_3$, requires $(M+H)^+$, 271.1329

4-(2,6-Dimethylbenzyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4c).



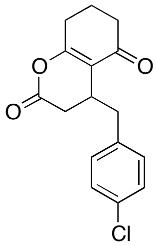
(64 mg, 75%). R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 3018, 2955, 1784, 1667, 1651, 1455, 1377, 1117 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06-6.98 (m, 3H), 3.34 (pent, J = 6.4 Hz, 1H), 2.87 (dd, J = 14.0, 4.8 Hz, 1H), 2.63-2.47 (m, 3H), 2.46-2.37 (m, 4H), 2.40 (s, 6H), 2.09 (pent, J = 6.0 Hz, 2H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 166.9, 166.7, 137.2, 134.7, 128.5, 128.2, 126.5, 117.1, 36.7, 32.4, 28.7, 27.3, 20.6, 20.3 HRMS (ESI) *m/z* Found $(M+H)^+$, 285.1480, $C_{18}H_{20}O_3$, requires $(M+H)^+$, 285.1485

4-(4-Methoxybenzyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (**4d**).



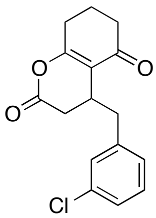
(54 mg, 63%). R_f 0.3 (1:3 v/v EtOAc in hexane) IR ν_{max} 2931, 1784, 1653, 1512, 1458, 1116 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$) δ 7.08-7.03 (m, 2H), 6.83 (d, *J* = 10.8 Hz, 2H), 3.78 (s, 3H), 3.24-3.21 (m, 1H), 2.80 (dd, *J* = 13.6, 4.0 Hz, 1H), 2.66 (dd, *J* = 16.4, 1.2 Hz, 1H), 2.53 (t, *J* = 6.0 Hz, 2H), 2.50-2.44 (m, 3H), 2.33 (dd, *J* = 13.6, 10.0 Hz, 1H), 2.10 (pent, *J* = 6.4 Hz, 2H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 167.1, 166.2, 158.5, 130.4, 127.4, 117.6, 113.8, 55.2, 38.2, 36.7, 32.3, 30.5, 27.2, 20.7 HRMS (ESI) *m/z* Found $(M+H)^+$, 287.1275, $C_{17}H_{18}O_4$, requires $(M+H)^+$, 287.1278

4-(4-Chlorobenzyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (**4e**).



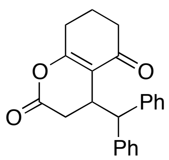
(59 mg, 67%). R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 3026, 2952, 1786, 1649, 1492, 1380, 1117 cm^{-1} ^1H NMR (300 MHz, $CDCl_3$) δ 7.36-7.03 (m, 4H), 3.27-3.21 (m, 1H), 2.84 (dd, *J* = 13.5, 4.2 Hz, 1H), 2.63 (dd, *J* = 16.2, 1.8 Hz, 1H) 2.55 (t, *J* = 6.0 Hz, 2H), 2.53-2.45 (m, 3H), 2.35 (dd, *J* = 13.5, 10.2 Hz, 1H), 2.09 (pent, *J* = 6.3 Hz, 2H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 167.2, 165.9, 136.1, 132.7, 130.7, 128.6, 117.4, 38.5, 36.6, 32.3, 30.3, 27.2, 20.6 HRMS (ESI) *m/z* Found $(M+H)^+$, 291.0786, $C_{16}H_{15}ClO_3$, requires $(M+H)^+$, 291.0782

4-(3-Chlorobenzyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (**4f**).



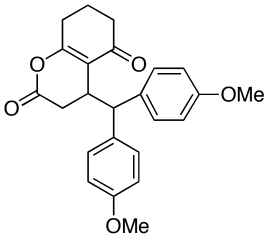
(58 mg, 66%). R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 3064, 2954, 1788, 1663, 1651, 1428, 1380, 1116 cm^{-1} ^1H NMR (400 MHz, $CDCl_3$) δ 7.23-7.04 (m, 4H), 3.29-3.24 (m, 1H), 2.82 (dd, *J* = 13.6, 4.0 Hz, 1H), 2.64 (dd, *J* = 16.4, 1.6 Hz, 1H), 2.56-2.52 (m, 2H), 2.49-2.43 (m, 3H), 2.37 (dd, *J* = 13.6, 10.2 Hz, 1H), 2.09 (pent, *J* = 6.4 Hz, 2H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 167.3, 165.8, 139.6, 134.3, 129.8, 129.3, 127.6, 127.1, 117.2, 38.8, 36.6, 32.4, 30.2, 27.2, 20.6 HRMS (ESI) *m/z* Found $(M+H)^+$, 291.0782, $C_{16}H_{15}ClO_3$, requires $(M+H)^+$, 291.0782

4-Benzhydryl-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (**4g**).



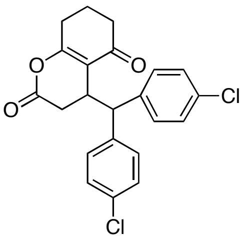
(79 mg, 79%). R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 3006, 2954, 1751, 1671, 1652, 1380, 1117 cm^{-1} ^1H NMR (300 MHz, $CDCl_3$) δ 6.34-7.16 (m, 10H), 3.98 (dd, *J* = 10.2, 7.2 Hz, 1H), 3.77 (d, *J* = 10.2 Hz, 1H), 2.80 (dd, *J* = 16.5, 1.5 Hz, 1H), 2.60 (dd, *J* = 15.5, 6.6 Hz, 1H), 2.53-2.47 (m, 2H), 2.19-2.11 (m, 2H), 2.01-1.89 (m, 1H), 1.88-1.78 (m, 1H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.6, 166.7, 166.1, 141.2, 140.3, 128.8, 128.6(4), 128.5(7), 127.9, 127.3, 126.7, 117.5, 54.7, 36.1, 30.1, 31.6, 27.3, 20.5 HRMS (ESI) *m/z* Found $(M+H)^+$, 333.1485, $C_{22}H_{20}O_3$, requires $(M+H)^+$, 333.1485

4-(Bis(4-methoxyphenyl)methyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4h).



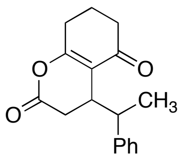
(88 mg, 75%) R_f 0.3 (1:3 v/v EtOAc in hexane) IR ν_{max} 3035, 2958, 1755, 1673, 1644, 1610, 1514, 1362, 1247, 1118 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 3.89 (dd, *J* = 8.8, 6.0 Hz, 1H), 3.78 (s, 3H), 3.73 (s, 3H), 3.67 (d, *J* = 8.8 Hz, 1H), 2.78 (dd, *J* = 16.4, 1.2 Hz, 1H), 2.57 (dd, *J* = 16.4, 6.4 Hz, 1H), 2.51-2.46 (m, 2H), 2.19-2.14 (m, 2H), 2.02-1.92 (m, 1H), 1.90-1.81 (m, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 166.6, 166.2, 158.7, 158.2, 133.8, 132.8, 129.5(2), 129.4(5), 117.7, 114.2, 113.3, 55.2(3), 55.1(5), 53.1, 36.3, 33.0, 31.9, 27.3, 20.5 HRMS (ESI) *m/z* Found $(M+H)^+$, 393.1695, $C_{24}H_{24}O_3$, requires $(M+H)^+$, 393.1697

4-(Bis(4-chlorophenyl)methyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4i).



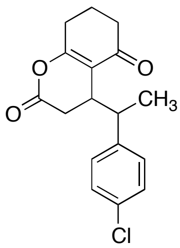
(100 mg, 83%). R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 3030, 2958, 1751, 1673, 1650, 1372, 1118 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.08 (m, 8H), 3.93 (dd, *J* =10.2, 7.2 Hz, 1H), 3.72 (d, *J* = 10.2 Hz, 1H), 2.74 (dd, *J* = 16.5, 1.8 Hz, 1H), 2.62 (dd, *J* = 16.5, 6.3 Hz, 1H), 2.55-2.49 (m, 2H), 2.22-2.10 (m, 2H), 2.05-1.94 (m, 1H), 1.91-1.81 (m, 1H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.5, 167.3, 165.6, 139.2, 138.5, 133.4, 132.9, 130.8, 129.9, 129.2, 128.2, 117.5, 53.7, 36.2, 33.0, 31.5, 27.3, 20.6 HRMS (ESI) *m/z* Found $(M+H)^+$, 401.0701, $C_{22}H_{18}Cl_2O_3$, requires $(M+H)^+$, 401.0706

4-(1-Phenylethyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4j).



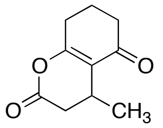
(68 mg, 84%) dr 1:9. R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 3028, 2964, 1784, 1651, 1453, 1377, 1121 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.13 (m, 5H), 3.28-3.25 (m, 1H), 3.01 (pent, *J* = 7.2 Hz, 1H), 2.71 (d, *J* = 16.8 Hz, 1H), 2.56-2.48 (m, 2H), 2.42 (dd, *J* = 16.8, 7.2 Hz, 1H), 2.39-2.34 (m, 2H), 2.11-2.00 (m, 2H), 1.21 (d, *J* = 7.2 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 167.2, 166.8, 142.9, 128.2, 127.8, 126.8, 116.6, 41.6, 36.7, 35.2, 30.5, 27.3, 20.6, 14.4 HRMS (ESI) *m/z* Found $(M+H)^+$, 271.1330, $C_{17}H_{18}O_3$, requires $(M+H)^+$, 271.1329

4-(1-(4-Chlorophenyl)ethyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4k).



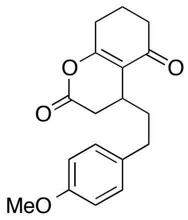
(75 mg, 82%) dr 1:5. R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 3029, 2954, 1784, 1651, 1453, 1380, 1121 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.07 (m, 4H), 3.24-3.21 (m, 1H), 3.02-2.95 (m, 1H), 2.67 (dd, *J* = 16.8, 1.2 Hz, 1H), 2.60-2.50 (m, 2H), 2.43 (dd, *J* = 16.8, 8.0 Hz, 1H), 2.40-2.36 (m, 2H), 2.12-2.00 (m, 2H), 1.18 (d, *J* = 7.2 Hz, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 167.4, 166.6, 141.4, 132.5, 129.1, 128.4, 116.3, 41.0, 36.6, 35.1, 30.4, 27.25, 20.6, 14.4 HRMS (ESI) *m/z* Found $(M+H)^+$, 305.0941, $C_{17}H_{17}ClO_3$, requires $(M+H)^+$, 305.0939

4-Methyl-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4l).



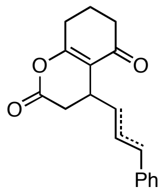
(0.038 g, 69%). R_f 0.2 (2:5 v/v EtOAc inhexane) IR ν_{max} 2959, 1786, 1651, 1460, 1382, 1120 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.12 (pent. d, J = 6.8, 1.8 Hz, 2H), 2.65 (dd, J = 16.5, 6.8 Hz, 1H), 2.58 (dd, J = 16.5, 1.8 Hz, 1H), 2.53 (t, J = 6.8 Hz, 2H), 2.42, (sext, J = 3.0 Hz, 2H), 2.04 (t, J = 6.0 Hz, 2H), 1.03 (d, J = 6.8 Hz, 3H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 166.5, 166.4, 119.3, 36.6, 35.9, 27.1, 23.5, 20.6, 19.3 HRMS (ESI) *m/z* Found $(M+H)^+$, 181.0860 $C_{10}H_{13}O_3$ requires $(M+H)^+$, 181.0859

4-(4-Methoxyphenethyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4m).



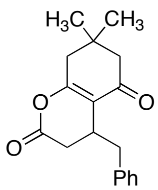
(64 mg, 71%). R_f 0.3 (1:3 v/v EtOAc in hexane) IR ν_{max} 2931, 1787, 1651, 1512, 1458, 1117 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.06 (m, 2H), 6.85-6.80 (m, 2H), 3.79 (s, 3H), 3.14-3.07 (m, 1H), 2.79 (dd, J = 16.0, 1.2 Hz, 1H), 2.67-2.57 (m, 2H), 2.55-2.39 (m, 5H), 2.11-1.90 (m, 2H), 1.50 (dt, J = 8.8, 4.4 Hz, 1H), 1.27 (dt, J = 8.8, 4.4 Hz, 1H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 166.9, 166.6, 158.2, 132.4, 129.3, 117.8, 113.9, 55.2, 37.4, 36.7, 35.1, 33.5, 31.7, 28.0, 20.6 HRMS (ESI) *m/z* Found $(M+Na)^+$, 323.1254 $C_{18}H_{20}O_4$ requires $(M+Na)^+$, 323.1254

(*E*)-4-styryl-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4n) *and* **(*E*)-4-(3-Phenylprop-1-en-1-yl)-3,4,7,8-tetrahydro-2H-chromene-2,5(6H)-dione (4n')**



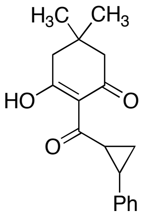
(65 mg, 80%) as a 4:1 mixture. R_f 0.3 (1:4 v/v EtOAc in hexane) IR ν_{max} 2932, 1784, 1651, 1381, 1116 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$) δ **4n** 7.27-7.14 (m, 5H), 6.34 (d, J = 15.6, 1H), 6.05-5.97 (m, 1H), 3.19-3.14 (m, 1H), 2.78 (dd, J = 16.4, 1.6 Hz, 1H), 2.58 (dd, J = 16.4, 7.2 Hz, 1H), 2.53-2.49 (m, 2H), 2.41-2.37 (m, 3H), 2.33-2.30 (m, 1H), 2.05-1.97 (m, 2H) δ **4n'** 7.27-7.14 (m, 5H), 5.62 (dtd, J = 15.6, 6.4, 1.2 Hz, 1H), 5.45 (ddt, J = 15.6, 5.6, 1.2 Hz, 1H), 3.74 (t, J = 5.6 Hz, 1H), 3.32 (d, J = 6.4 Hz, 2H), 2.76 (dd, J = 16.4, 1.6 Hz, 1H), 2.66 (dd, J = 16.4, 7.2 Hz, 1H), 2.53-2.49 (m, 2H), 2.41-2.37 (m, 3H), 2.33-2.30 (m, 1H), 2.05-1.97 (m, 2H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 196.2, 167.1, 166.2, 166.0, 139.7, 137.0, 133.8, 130.7, 130.2, 129.5, 129.0, 128.5, 128.4, 127.4, 126.1, 125.9, 125.4, 117.3, 116.8, 38.5, 36.9, 36.7, 36.6, 34.2, 33.0, 30.5, 28.6, 27.2, 26.3, 20.7, 20.6 HRMS (ESI) *m/z* Found $(M+H)^+$, 283.1331, $C_{18}H_{18}O_3$, requires $(M+H)^+$, 283.1329

4-Benzyl-7,7-dimethyl-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4q)



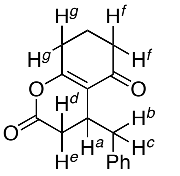
(16 mg, 19%). R_f 0.2 (1:4 v/v EtOAc in hexane) IR ν_{max} 2964, 1783, 1651, 1454, 1380, 1117 cm^{-1} ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.18 (m, 5H), 3.31-3.23 (m, 1H), 2.91 (dd, J = 13.2, 3.9 Hz, 1H), 2.68 (dd, J = 16.5, 1.5 Hz, 1H), 2.46 (dd, J = 16.5, 9.0 Hz, 1H), 2.43 (s, 2H), 2.35 (s, 2H), 2.33 (dd, J = 13.2, 3.0 Hz, 1H), 1.14(4) (s, 3H), 1.14(0) (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 166.3, 165.4, 137.7, 129.4, 128.7, 128.5, 126.8, 125.0, 116.5, 50.7, 40.9, 39.1, 32.5, 32.3, 30.4, 28.4, 28.1 HRMS (ESI) *m/z* Found $(M+H)^+$, 285.1485, $C_{18}H_{20}O_3$, requires $(M+H)^+$, 285.1485

3-Hydroxy-5,5-dimethyl-2-(2-phenylcyclopropanecarbonyl)cyclohex-2-enone (5q)



(65 mg, 77%). R_f 0.2 (1:4 v/v EtOAc in hexane) IR ν_{max} 3033, 2954, 1666, 1534, 1436, 1353, 1191, 1029 cm^{-1} ^1H NMR (300 MHz, $CDCl_3$) δ 18.38 (s, 1H), 7.28-7.16 (m, 5H), 4.02-3.96 (m, 1H), 2.82-2.75 (m, 1H), 2.53 (s, 2H), 2.37 (s, 2H), 1.90 (dt, J = 9.0, 3.9 Hz, 1H), 1.57-1.50 (m, 1H) 1.08(4) (s, 3H), 1.07(6) (2, 3H) ^{13}CNMR (100 MHz, $CDCl_3$) δ 202.6, 196.9 195.5, 140.1, 128.4, 126.5, 126.4, 112.3, 52.8, 46.8, 31.8, 30.6, 28.3(3), 28.2(7), 28.1, 21.7

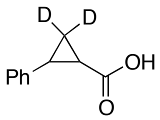
IV. Mechanistic Studies



4a

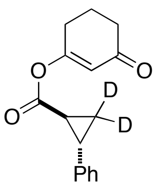
Proton	δ	multiplicity	integration
H^a	3.29	m	1H
H^b	2.86	dd, J = 13.6 and 4.0 Hz	1H
H^d	2.68	dd, J = 16.0 and 1.2 Hz	1H
2XH^g	2.52	t, J = 5.6 Hz	2H
2XH^f and H^e	2.48-2.43	m	3H
H^c	2.36	dd, J = 13.6 and 10.0 Hz	1H

2,2-Dideutero-3-phenylcyclopropanecarboxylic acid



The title acid was prepared by the hydrolysis of the corresponding dideutero ethyl ester, which was in turn synthesised following the general cyclopropanation procedure from styrene-*β,β*-d_2[6] and ethyl diazoacetate (0.371 g, 66%) as a 7:3 *cis*/*trans* mixture. The cyclopropyl acid was 84% deuterated on the basis of ^{1}H NMR. R_f 0.3 (1:1 v/v EtOAc in hexane). ^{1}H-NMR (300 MHz, $CDCl_3$) δ *trans* 7.30-7.09 (m, 5H), 2.58 (d, J = 4.2 Hz, 1H), 1.88 (d, J = 4.2 Hz, 1H) *cis* 7.30-7.09 (m, 5H), 2.67 (d, J = 9.3 Hz, 1H), 2.08 (d, J = 9.3 Hz, 1H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.8, 139.5, 135.8, 129.3, 128.5, 127.9, 126.8, 126.6, 126.2, 26.9, 26.5, 23.8, 21.3, 14.5 HRMS (ESI) *m/z* Found $(M+H)^+$, 165.0879, $C_{10}H_8D_2O_2$, requires $(M+H)^+$, 165.0879

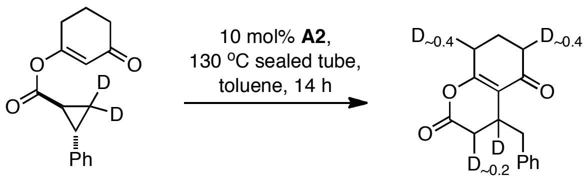
3-Oxocyclohex-1-en-1-yl *2,2-d*$_2$-dideutero-3-phenylcyclopropane carboxylate (3o).



The enol ester was synthesised from the acid following the general procedure for the synthesis of cyclopropyl enol esters (0.363 g, 70%) as a 7:3 *cis*/*trans* mixture. R_f 0.3 (1:4 v/v EtOAc in hexane) ^{1}H NMR (400 MHz, $CDCl_3$) δ *trans* 7.31-7.10 (m, 5H), 5.95 (t, J = 0.8 Hz, 1H), 2.62 (d, J = 3.6 Hz, 1H), 2.55 (t, J = 6.0 Hz, 2H), 2.40 (t, J = 6.0 Hz, 2H), 2.07-2.03 (m, 2H), 2.00 (d, J = 4.4 Hz, 1H) *cis* 7.31-7.10 (m, 5H), 5.51 (t, J = 0.8 Hz, 1H), 2.74 (d, J = 9.2 Hz, 1H), 2.26 (t, J = 6.4 Hz, 2H), 2.19 (d, J = 6.4 Hz, 1H), 2.07-2.03 (m, 2H), 1.87 (pent, J = 6.4 Hz, 2H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 169.9, 169.8, 169.7, 167.5, 138.9, 135.4,129.2, 128.5, 128.1, 127.1, 126.8, 126.1, 117.3, 117.2, 36.6, 36.5, 28.3, 27.8, 27.3, 26.5, 23.8, 21.6, 21.1, 21.0 (one signal overlapping) HRMS (ESI) *m/z* Found $(M+H)^+$, 259.1296 $C_{16}H_{14}D_2O_3$, requires $(M+H)^+$, 259.1298

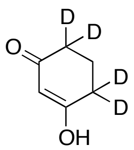
[6] Wang, W., Wang. F., Shi, M. *Organometallics*, **2010**, 29, 928

Dideuterated 4-benzyl-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4o).



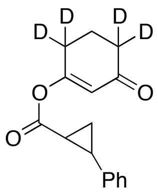
The enol ester was subjected to the general NHC catalysed dihydropyranone forming conditions (53 mg, 68%). R_f 0.3 (1:4 v/v EtOAc in hexane) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.17 (m, 5H), 3.30-3.27 (m, 0.16H), 2.87 (d, J = 13.5 Hz, 1H), 2.67 (d, J = 16.2 Hz, 0.9H), 2.55 (t, J = 6.3 Hz, 1.6H), 2.51-2.46 (m, 2.5H), 2.38 (d, J = 13.5 Hz, 1H), 2.10 (pent, J = 4.2 Hz, 2H) ^{13}C-NMR (75 MHz, $CDCl_3$) δ 196.5, 167.1, 166.1, 137.7, 129.4, 128.5, 126.8, 117.6, 39.1, 36.7, 32.3, 30.4, 27.2, 20.7 ^{2}H NMR (61 MHz, $CHCl_3$) δ 3.27 (1D), 2.67 (0.1D), 2.62-2.32 (0.4D) HRMS (ESI) *m/z* Found $(M+H)^+$, 259.1294, $C_{16}H_{14}D_2O_3$, requires $(M+H)^+$, 259.1298

4,4,6,6-Tetradeutero-3-hydroxycyclohex-2-enone.



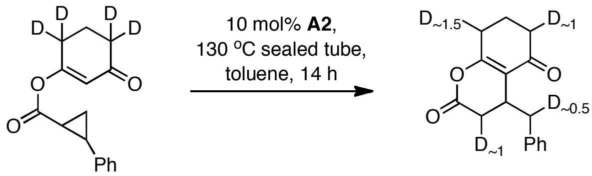
A magnetically stirred solution of 2,4,4,6,6-pentadeutero-3-methoxy-2-cyclohexen-1-one[6] (0.328 g, 2.5 mmol) and CAN (0.137 g, 0.25 mmol) in H_2O (6 ml) and CH_3CN (6 ml) was refluxed for 3 h. The mixture was diluted with brine (20 ml) and extracted with Et_2O (3 x 30 ml). The combine organic extracts were washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. The crude residue was recrystalised from benzene to afford the *tetra*-deuterated enol (0.257 g, 89%). The hydroxycyclohexenone was 96% deuterated on the basis of ^{1}H-NMR analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.12 (s, 1H), 5.48 (s, 1H), 2.36 (t, J = 6.8 Hz, 0.19H), 1.96 (s, 2H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.13, 192.7, 104.3, 39.1 (t, J = 19.7), 31.5 (pent, J = 19.7), 20.7 HRMS (ESI) *m/z* Found $(M+H)^+$, 117.0844, $C_6H_4D_4O_2$, requires $(M+H)^+$, 117.0848

4,4,6,6-Tetradeutero-3-oxocyclohex-1-en-1-yl 2-phenylcyclopropane carboxylate (3p).



The enol ester was synthesised from the acid following the general procedure for the synthesis of cyclopropyl enol esters (0.333 g, 64%) as a 2:3 *cis*/*trans* mixture. R_f 0.3 (1:4 v/v EtOAc in hexane) ^{1}H NMR (300 MHz, $CDCl_3$) δ *trans* 7.34-7.11 (m, 5H), 5.96 (s, 1H), 2.67-2.60 (m, 1H), 2.05-1.99 (m, 3H), 1.71 (dt, J = 9.3, 4.8 Hz, 1H), 1.51-1.43 (m, 1H) *cis* 7.34-7.11 (m, 5H), 5.52 (s, 1H), 2.76 (q, J = 8.1 Hz, 1H), 2.25-2.18 (m, 1H), 1.85-1.81 (m, 3H), 1.51-1.43 (m, 1H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9, 170.3, 167.9, 139.4, 135.9, 129.6, 128.9, 128.5, 127.5, 127.2, 126.5, 117.8, 117.7, 27.9, 27.1, 24.4, 22.2, 21.2, 21.1, 18.2, 12.1 (three signals overlapping) HRMS (ESI) *m/z* Found $(M+H)^+$, 261.1427, $C_{16}H_{12}D_4O_3$, requires $(M+H)^+$, 261.1423

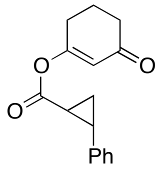
Tetradeuterated 4-benzyl-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4p).

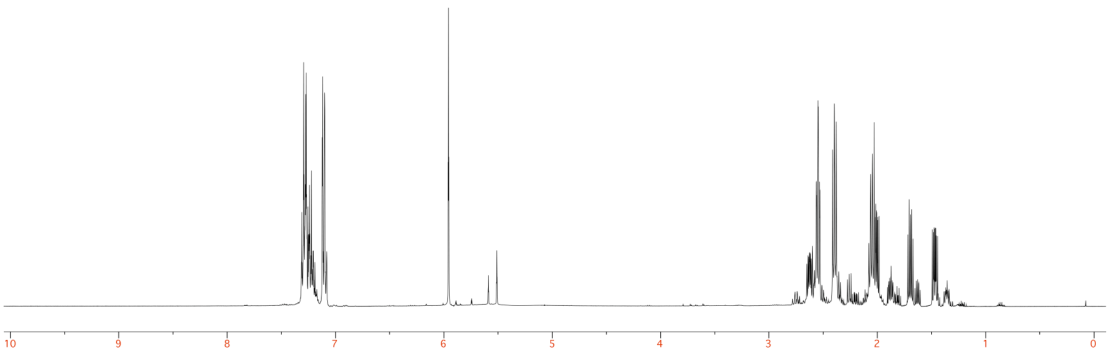


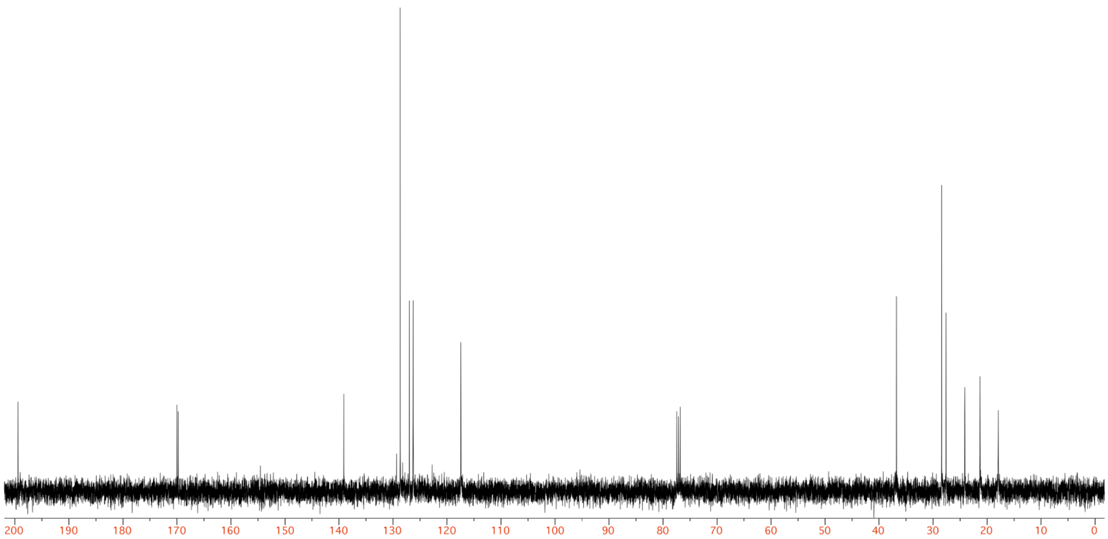
The enol ester was subjected to the general NHC catalysed dihydropyranone forming conditions (58 mg, 74%). R_f 0.3 (1:4 v/v EtOAc in hexane) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.12 (m, 5H), 3.30-3.27 (m, 1H), 2.87 (dd, *J* = 13.6, 4.0 Hz, 0.8H), 2.68 (dd, *J* = 16.0, 1.2 Hz, 0.5H), 2.52 (m, 1H), 2.48-2.43 (m, 1H), 2.36 (dd, *J* = 13.6, 10.0 Hz, 0.7H), 2.08 (pent, *J* = 6.8 Hz, 2H) ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.6 (m), 167.1, 166.1, 137.7, 129.4, 128.5, 126.8, 117.6, 39.1, 38.7 (m), 36.7, 36.3 (t, *J* = 19.5 Hz), 32.3, 32.0 (t, *J* = 19.5 Hz), 30.3 (m), 27.2-26.7 (m), 20.4 (p, *J* = 13.9 Hz) ^{2}H-NMR (61 MHz, $CHCl_3$) δ 2.87 (0.4D), 2.64 (0.7D), 2.55-2.30 (2.9D) HRMS (ESI) *m/z* Found $(M+H)^+$, 261.1427, $C_{16}H_{12}D_4O_3$, requires $(M+H)^+$, 261.1423

IV. ^{1}H and ^{13}C NMR Spectra

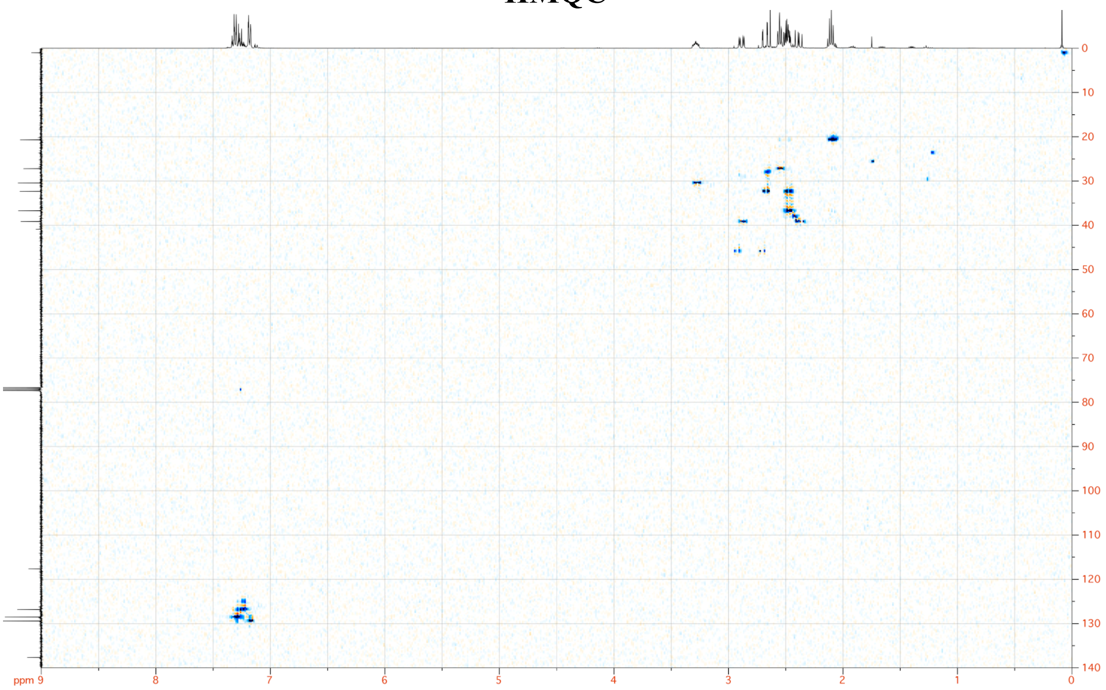
3-Oxocyclohex-1-en-1-yl 2-phenylcyclopropanecarboxylate (3a).







HMQC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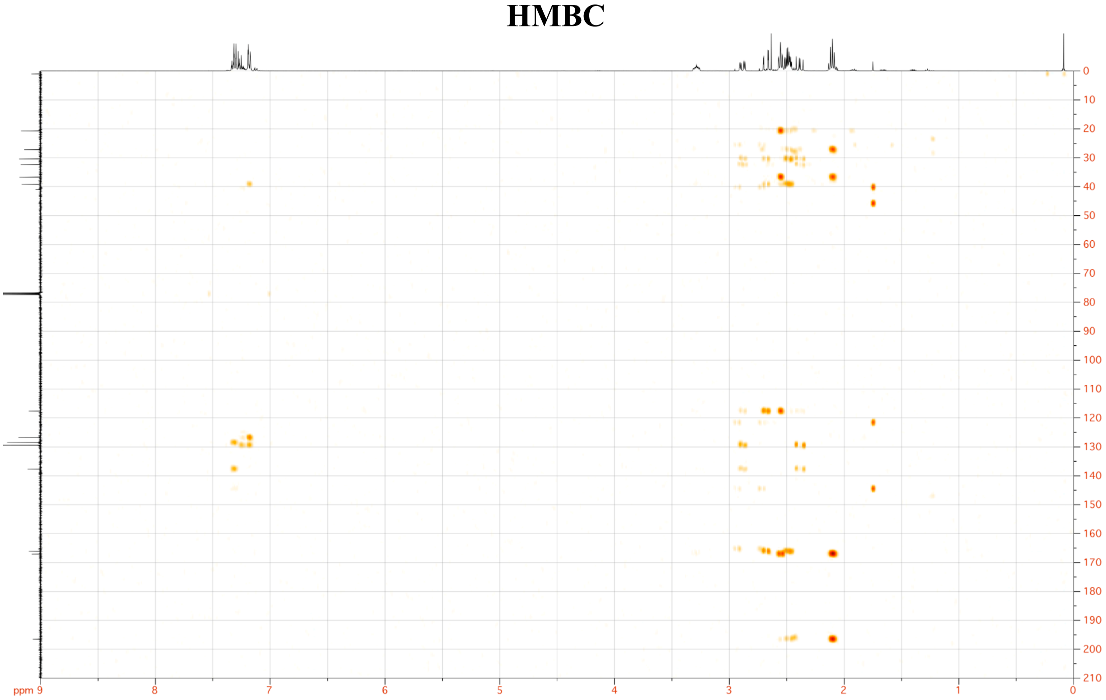
130
140

HMBC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100
110
120
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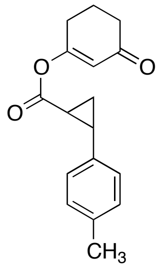
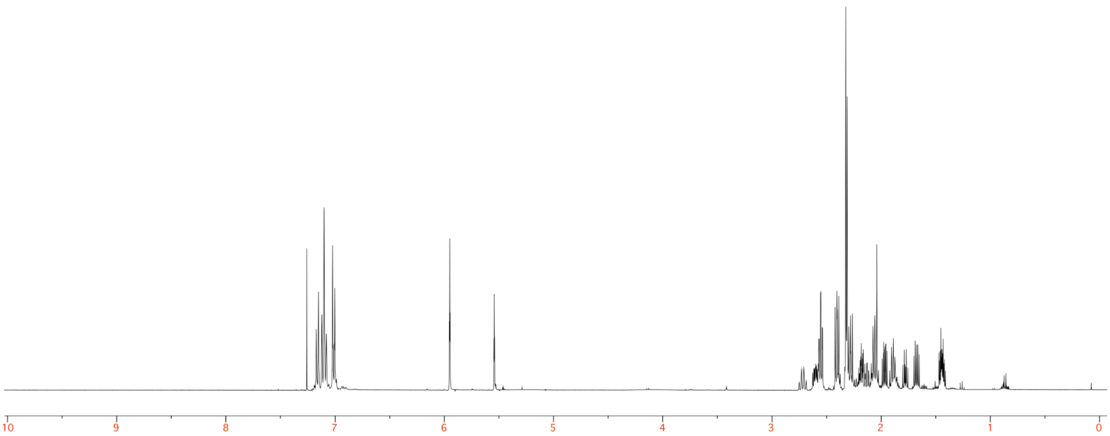
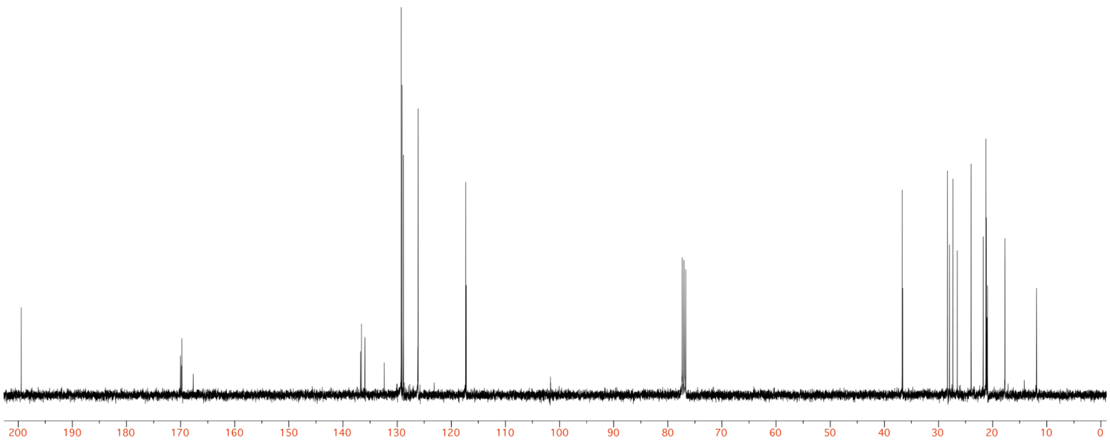
200
210

3-Oxocyclohex-1-en-1-yl 2-(*p*-tolyl)cyclopropanecarboxylate (3b).







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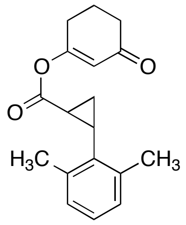
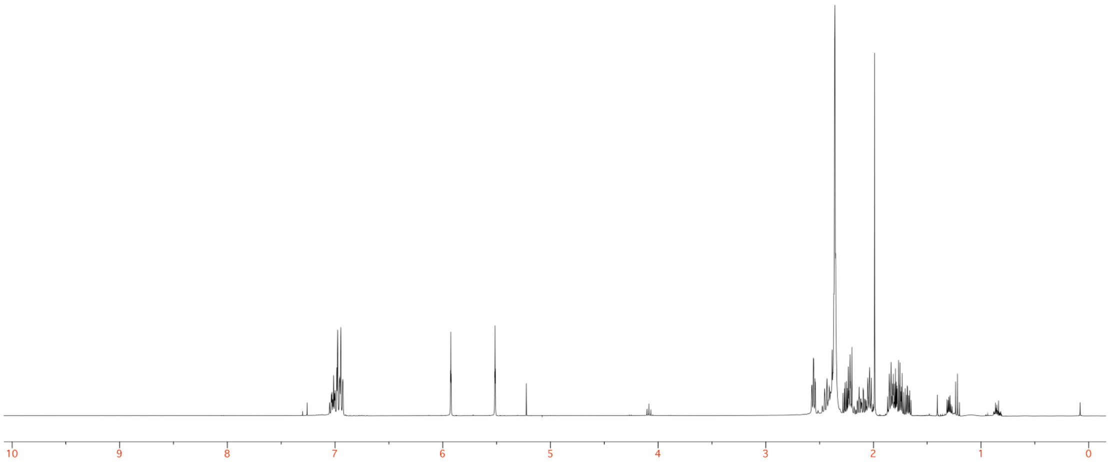
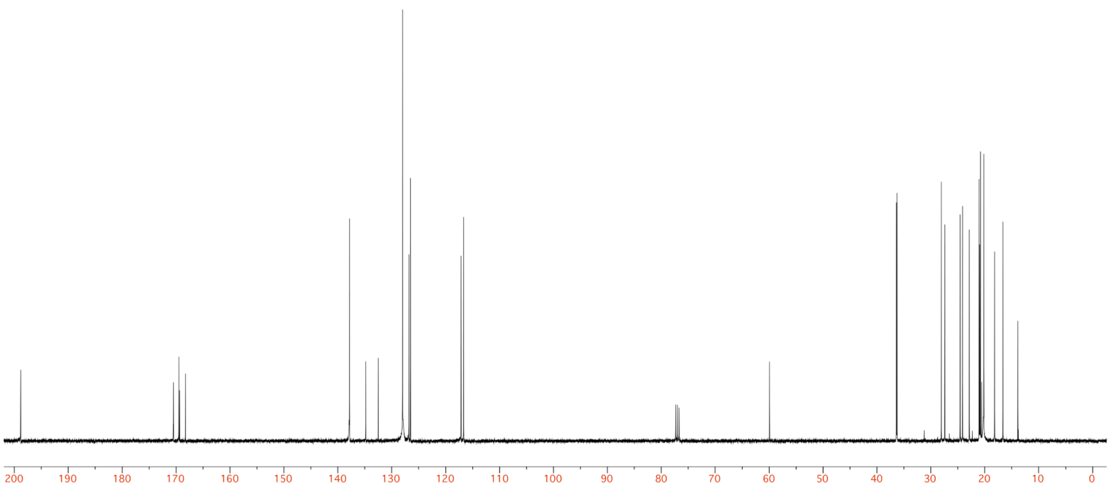
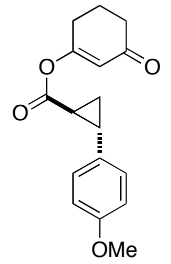
3-Oxocyclohex-1-en-1-yl 2-(2,6-dimethylphenyl)cyclopropanecarboxylate (**3c**).

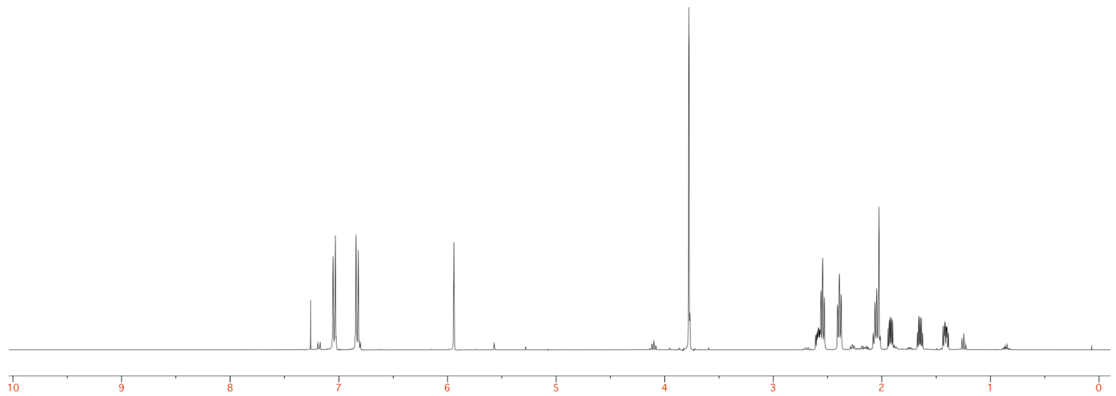


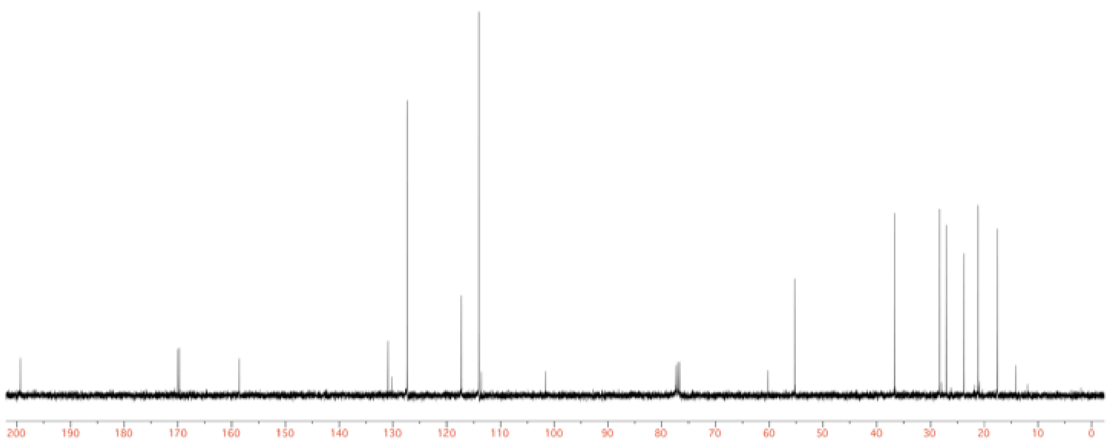




(1*S*,2*S* and 1*R*,2*R*)-3-Oxocyclohex-1-en-1-yl 2-(4-methoxyphenyl)cyclopropanecarboxylate (3d).







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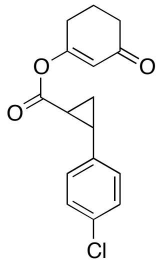
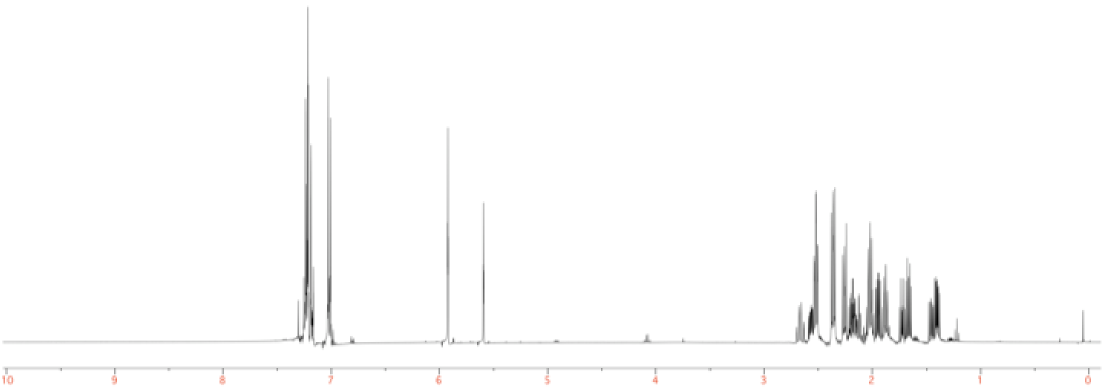
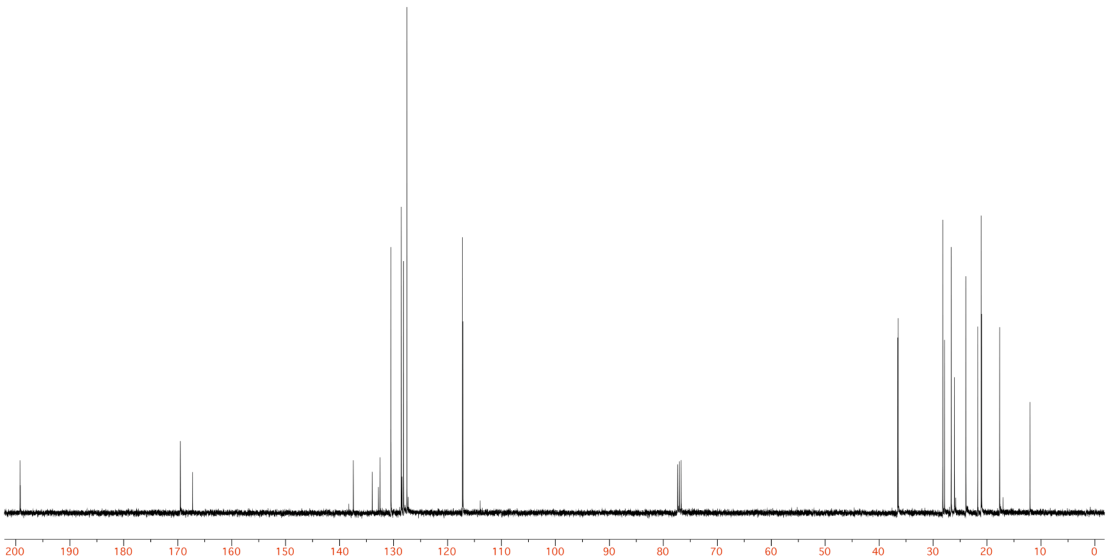
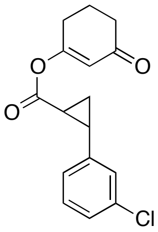
3-Oxocyclohex-1-en-1-yl 2-(4-chlorophenyl)cyclopropanecarboxylate (3e)

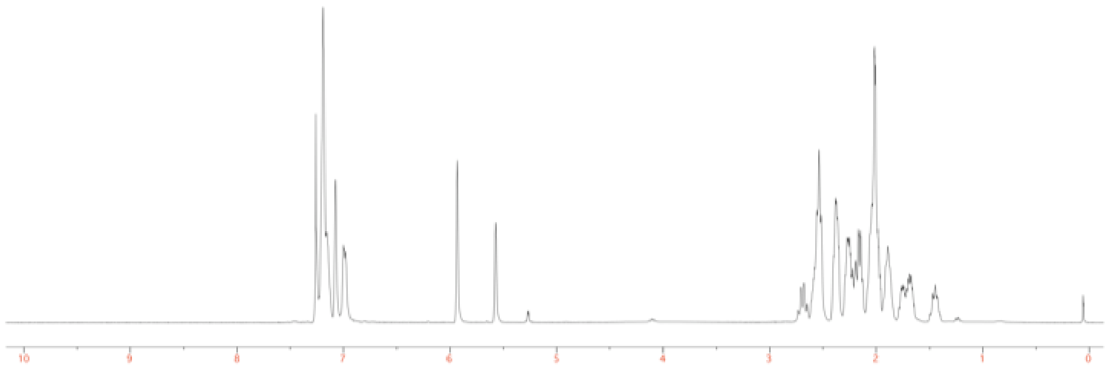


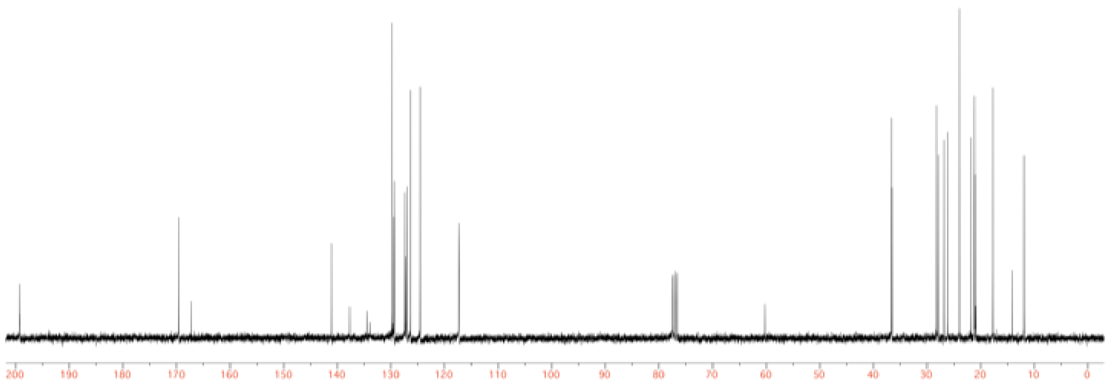




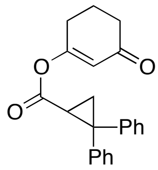
3-Oxocyclohex-1-en-1-yl 2-(3-chlorophenyl)cyclopropanecarboxylate (3f)

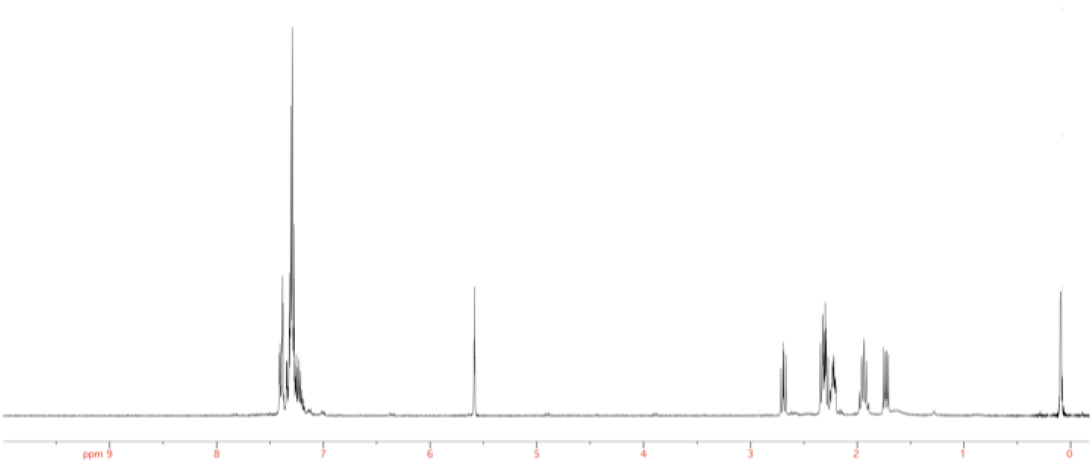


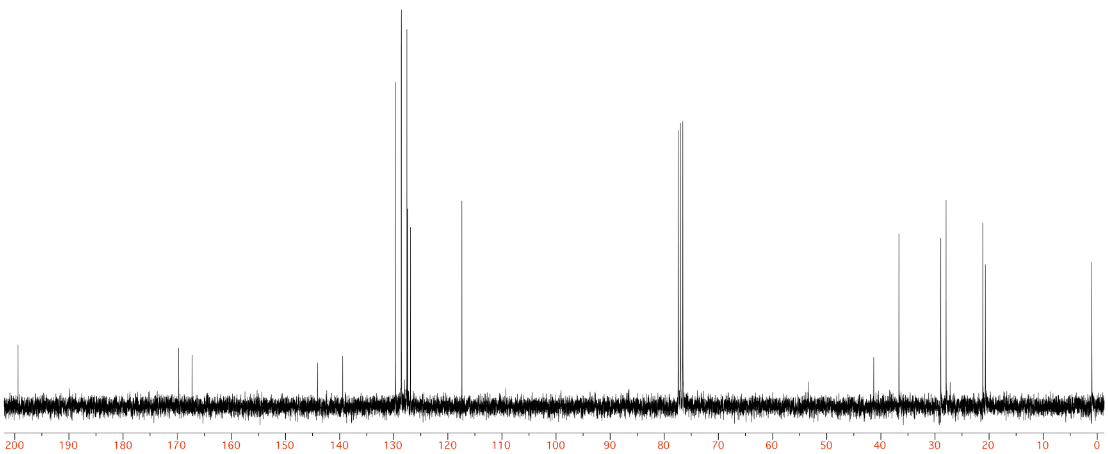




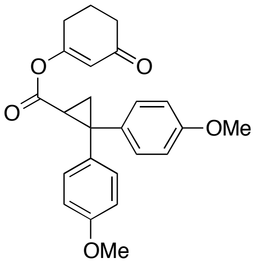
3-Oxocyclohex-1-en-1-yl 2,2-diphenylcyclopropanecarboxylate (3g)

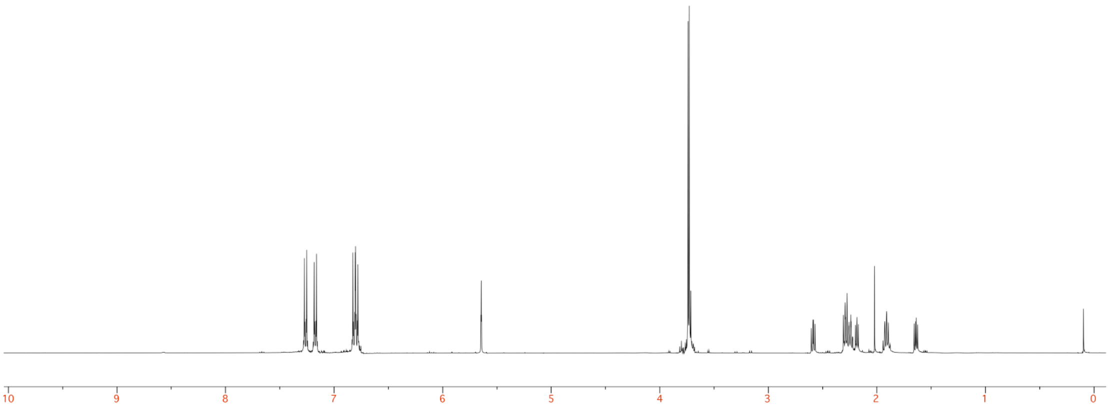


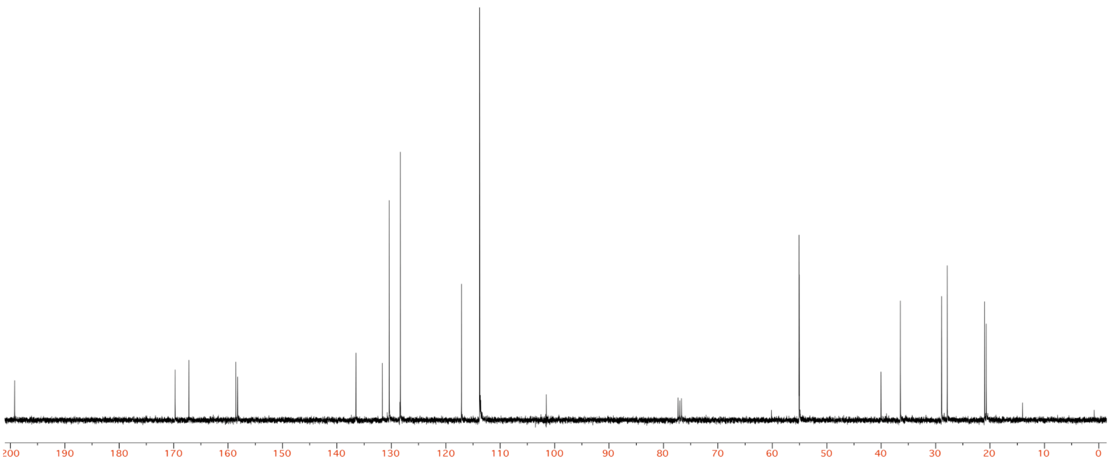




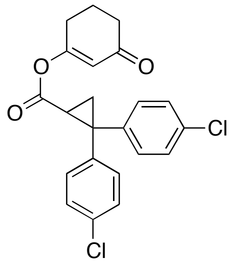
3-Oxocyclohex-1-en-1-yl 2,2-bis(4-methoxyphenyl)cyclopropanecarboxylate (3h)

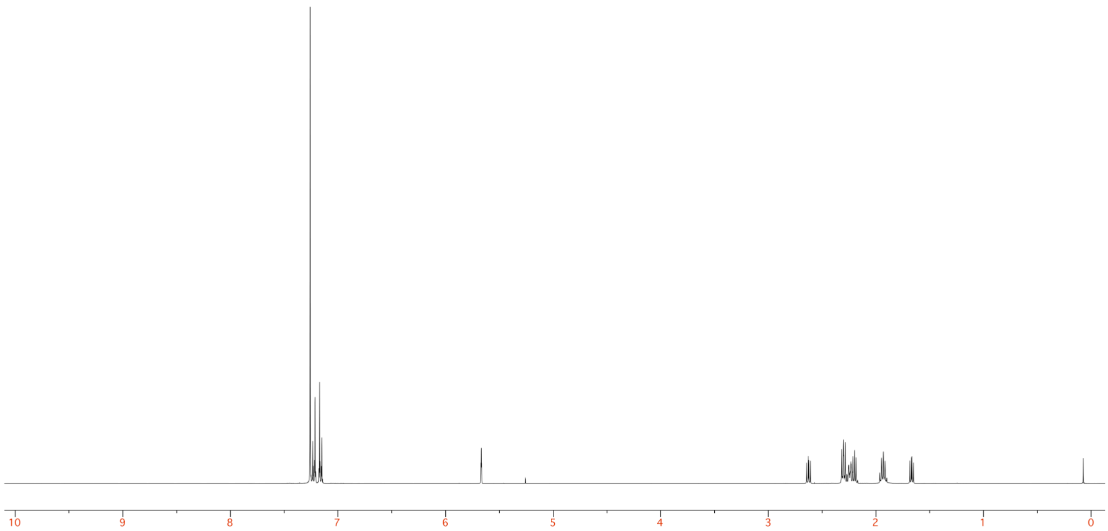


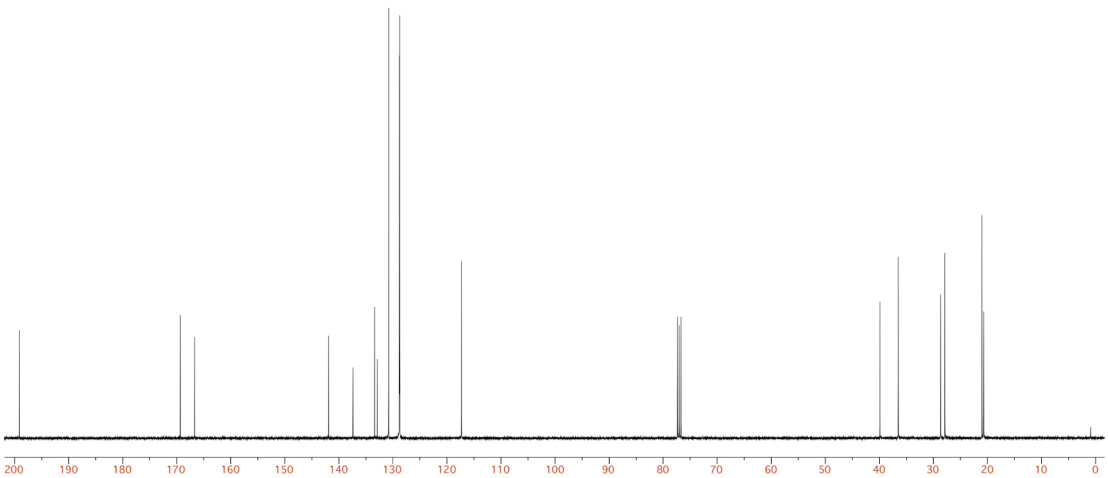




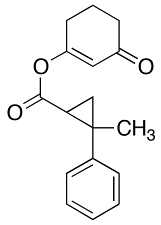
3-Oxocyclohex-1-en-1-yl 2,2-bis(4-chlorophenyl)cyclopropanecarboxylate (3i).

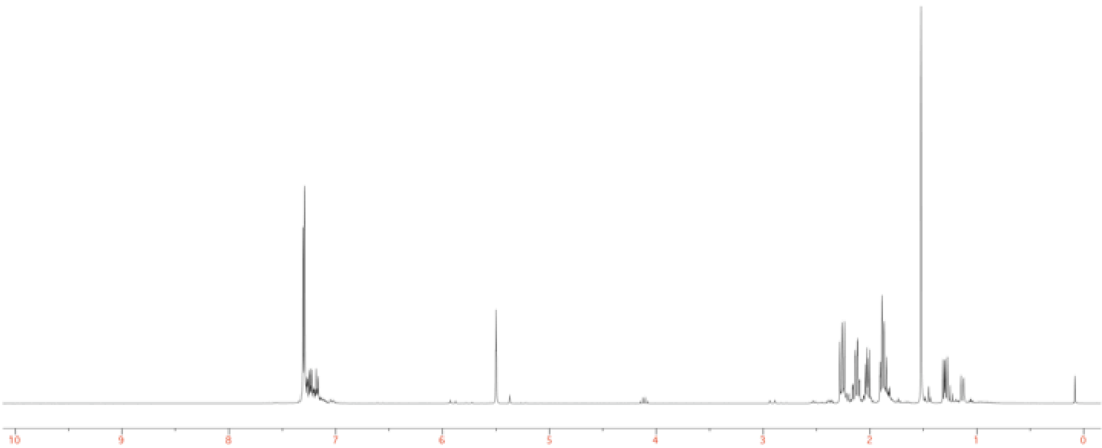


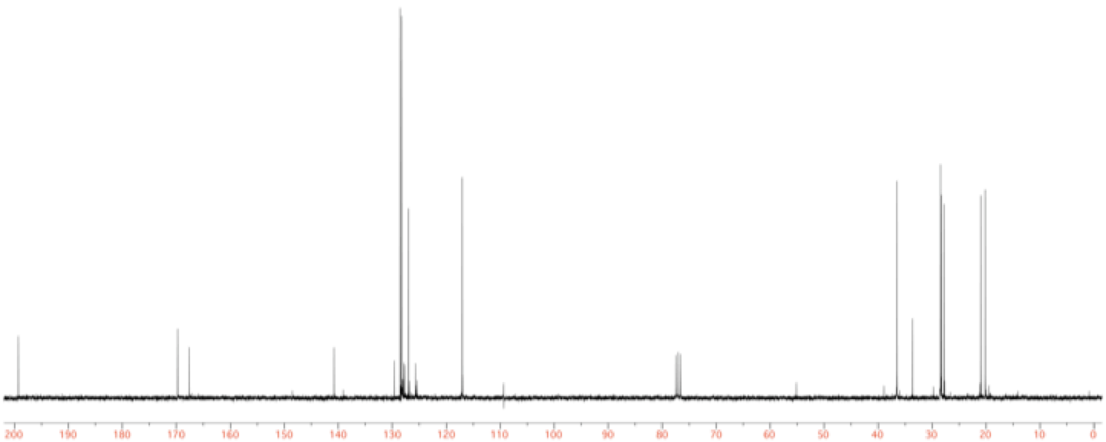




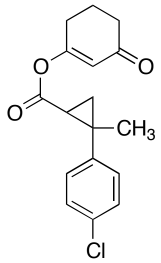
3-Oxocyclohex-1-en-1-yl 2-methyl-2-phenylcyclopropanecarboxylate (3j)

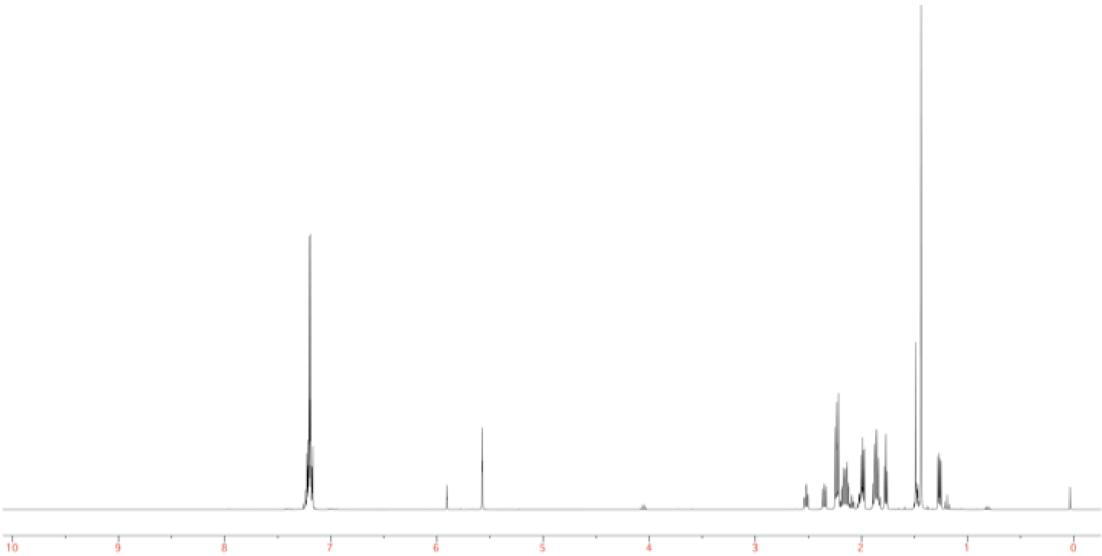


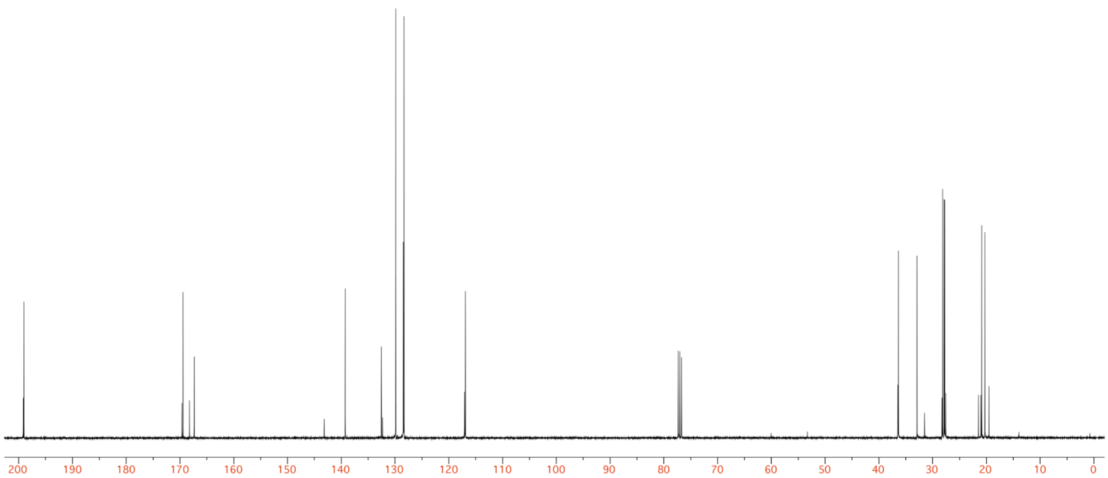




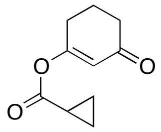
3-Oxocyclohex-1-en-1-yl 2-(4-chlorophenyl)-2-methylcyclopropanecarboxylate (3k).

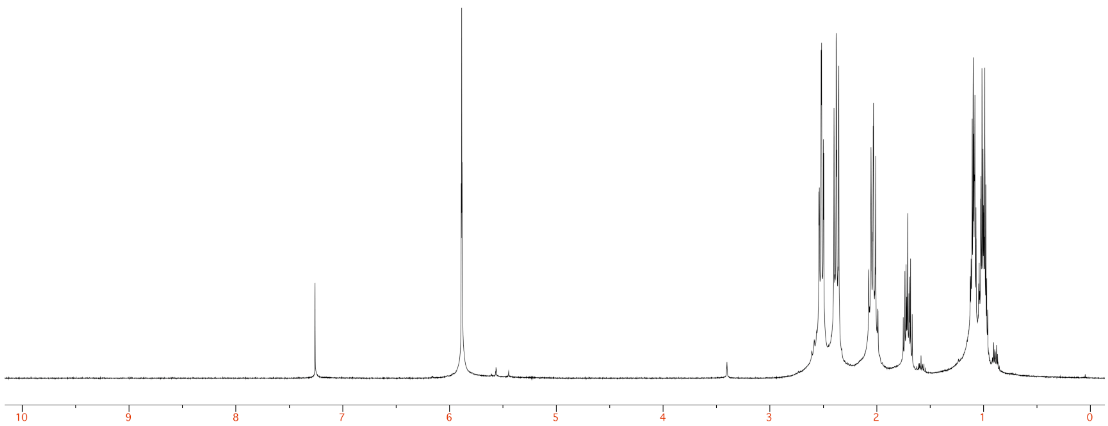


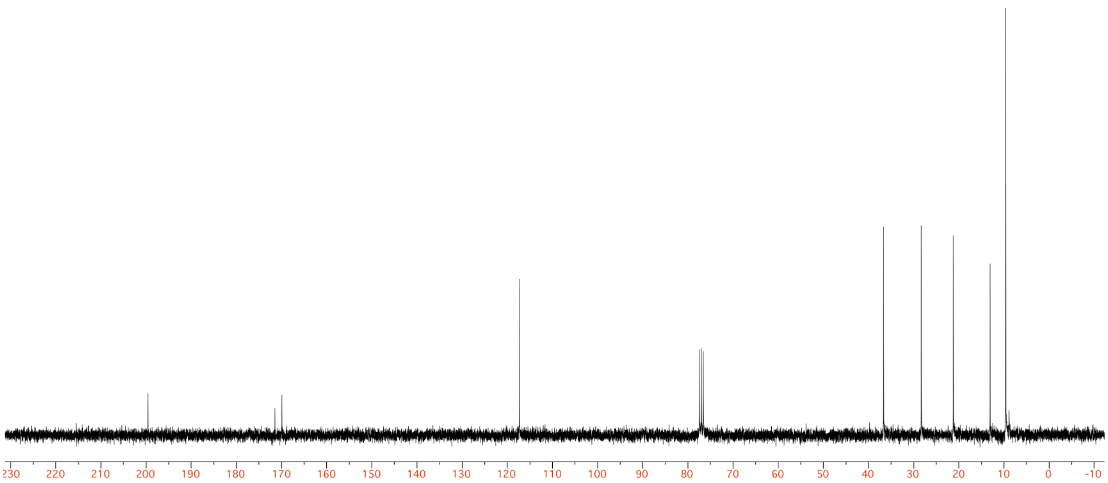




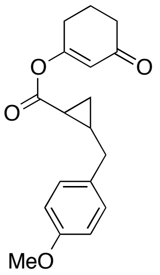
3-Oxocyclohex-1-en-1-yl cyclopropanecarboxylate (3l)

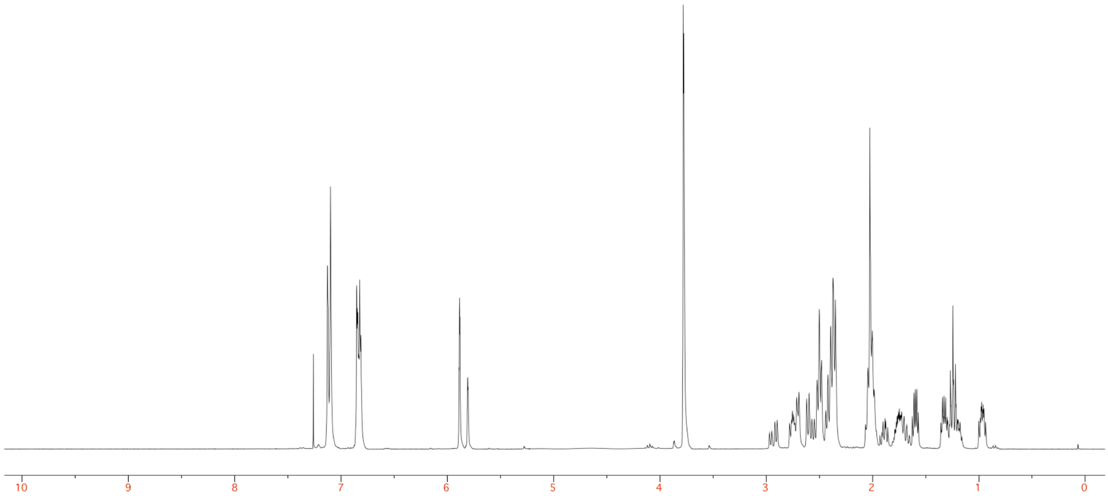


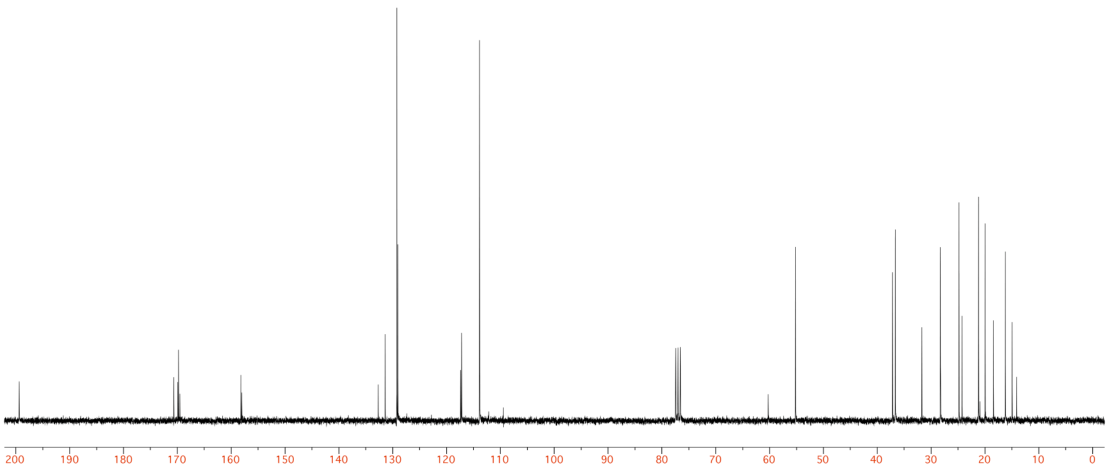




3-Oxocyclohex-1-en-1-yl 2-(4-methoxybenzyl)cyclopropanecarboxylate (3m).







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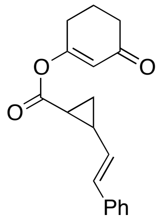
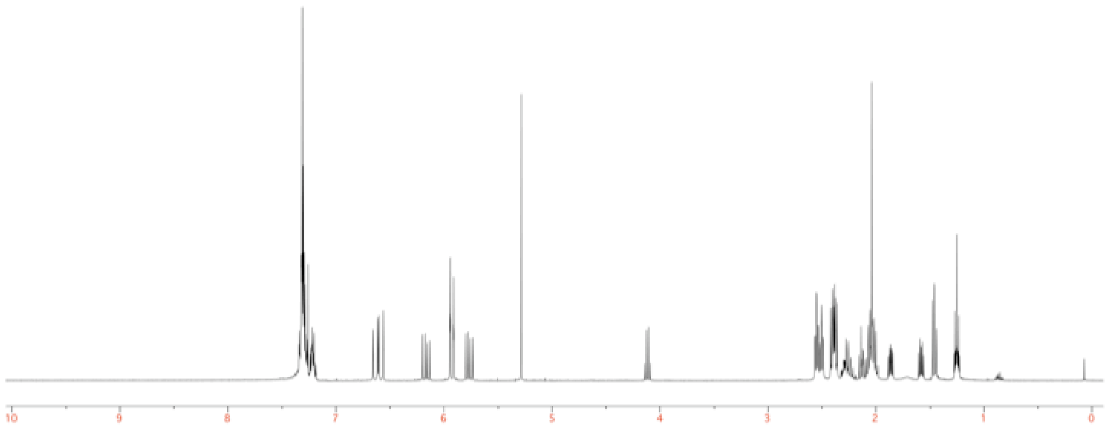
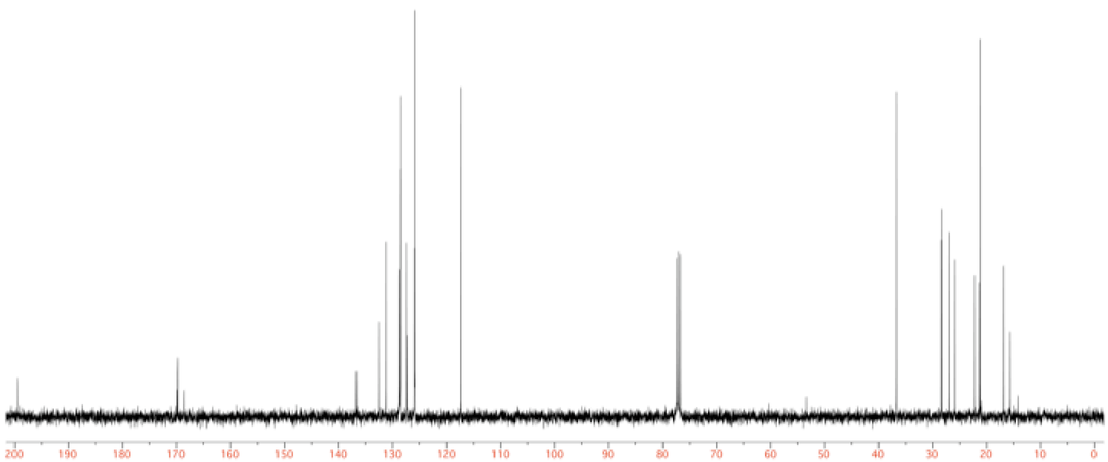
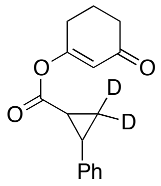
(*E*)-3-Oxocyclohex-1-en-1-yl 2-styrylcyclopropanecarboxylate (3n)

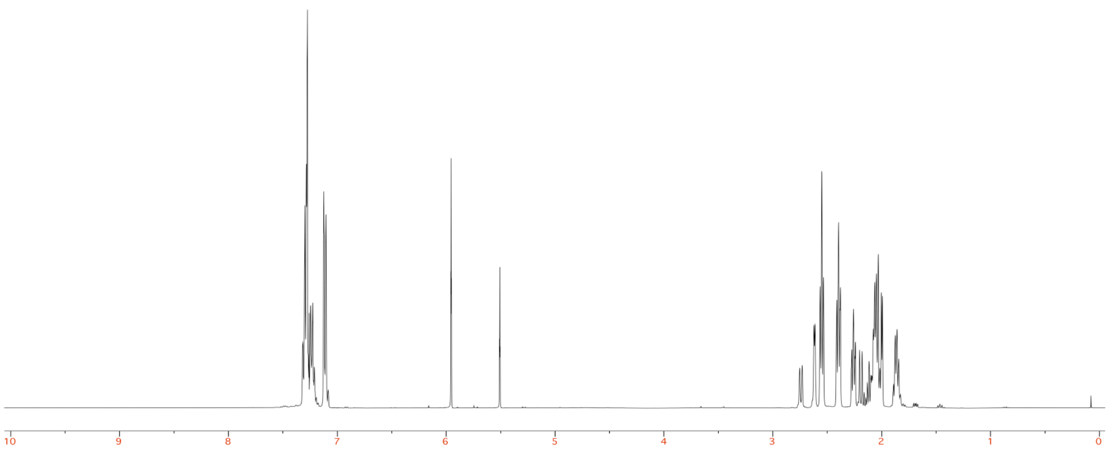


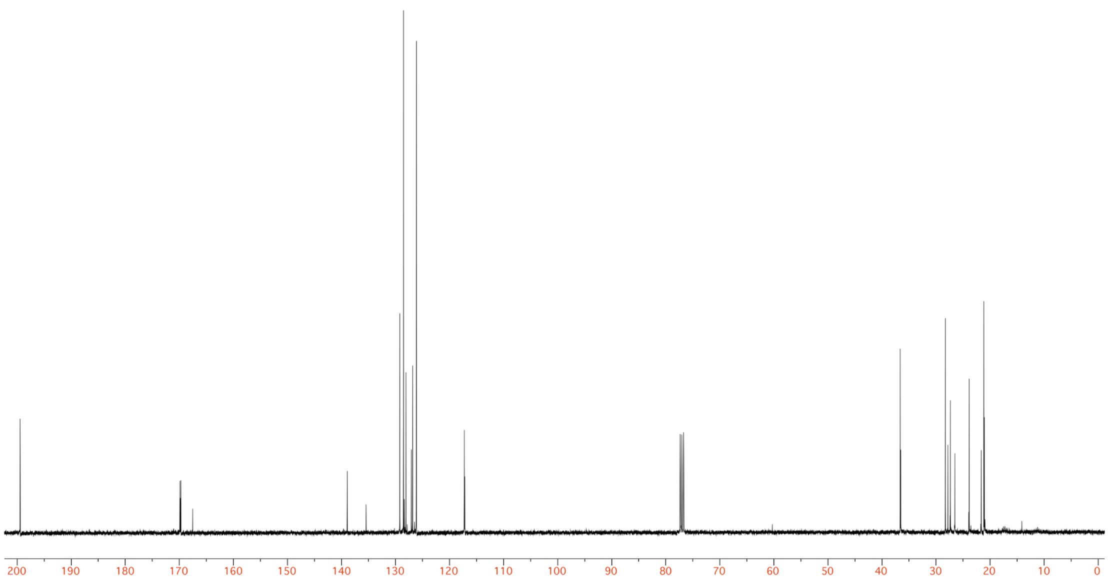




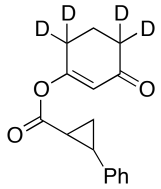
3-Oxocyclohex-1-en-1-yl *2,2-d*$_2$-dideutero-3-phenylcyclopropane carboxylate (3o)

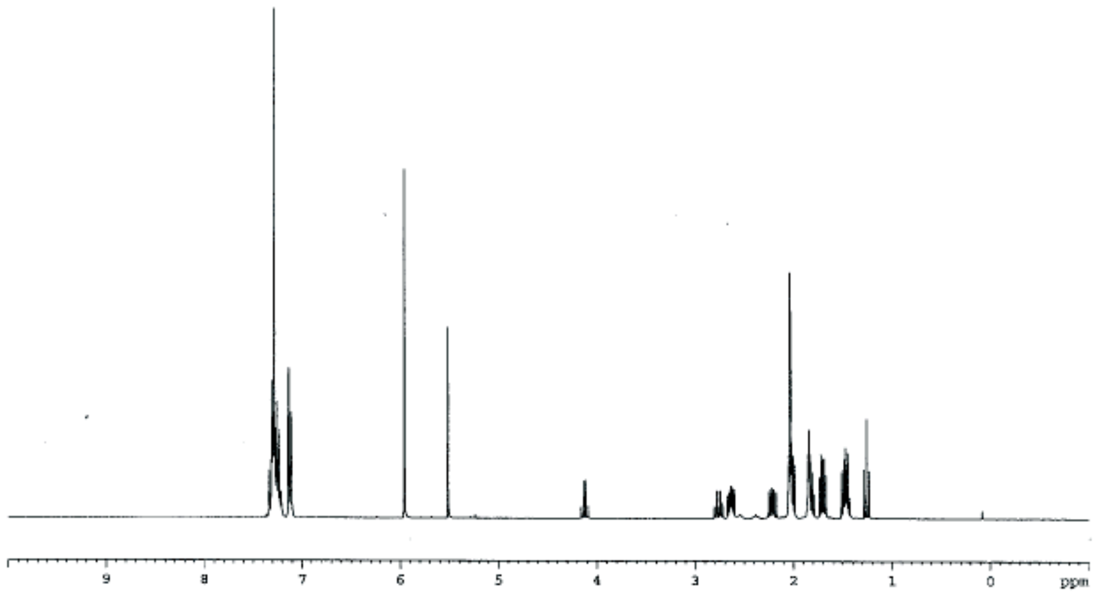


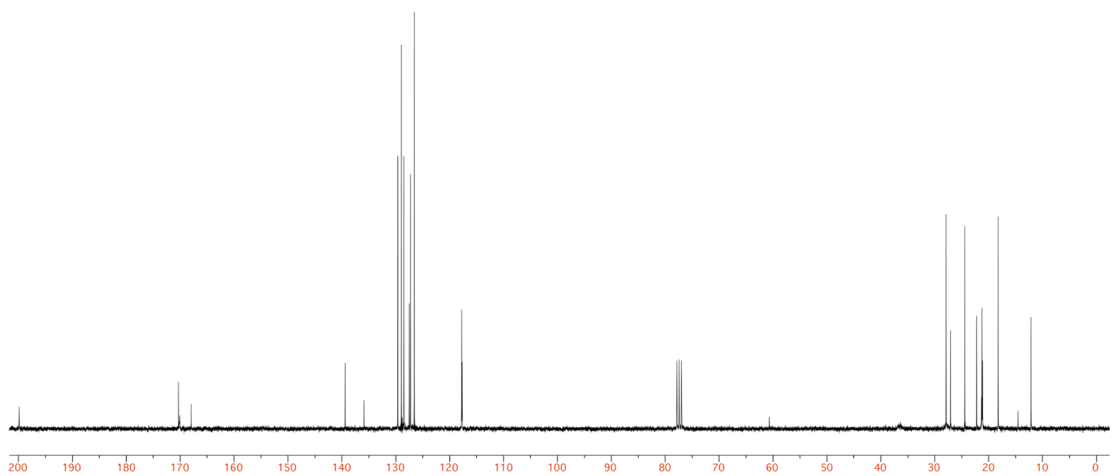




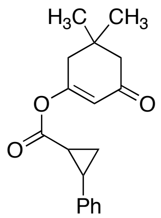
4,4,6,6-Tetradeutero-3-oxocyclohex-1-en-1-yl 2-phenylcyclopropane carboxylate (3p).

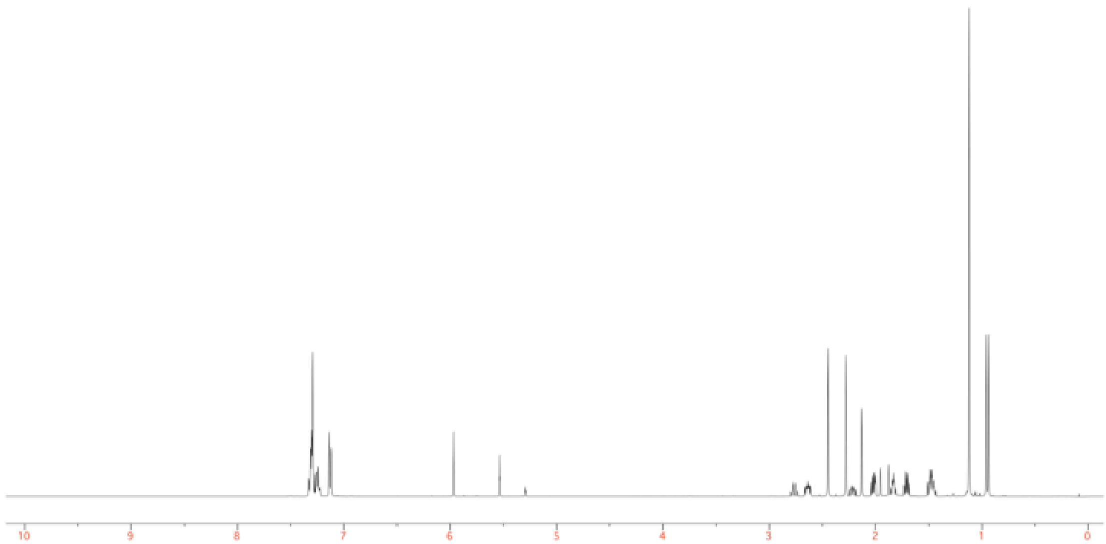


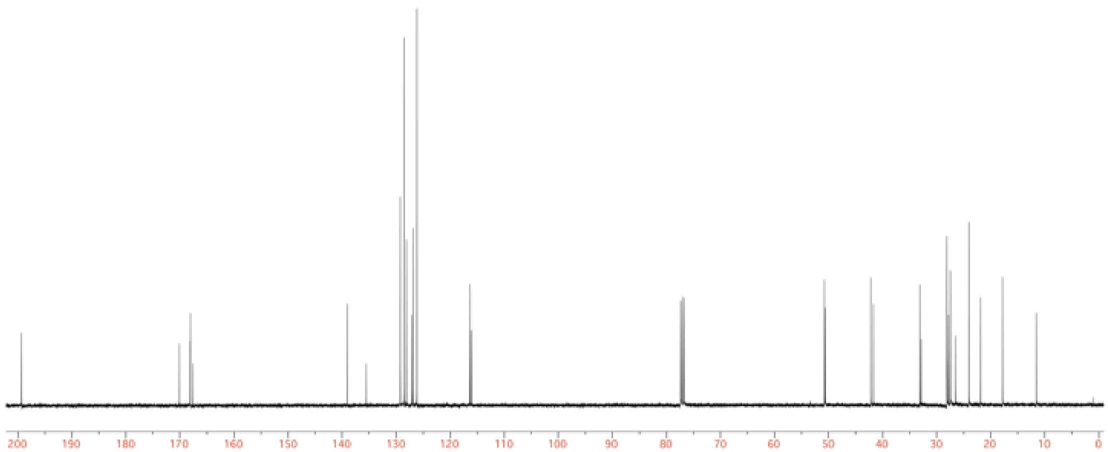




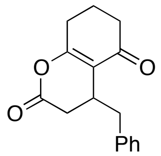
5,5-Dimethyl-3-oxocyclohex-1-en-1-yl 2-phenylcyclopropanecarboxylate (3q)

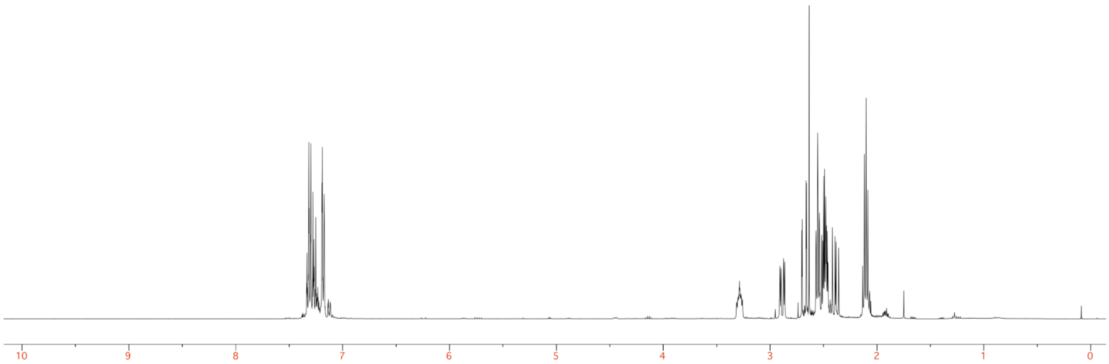


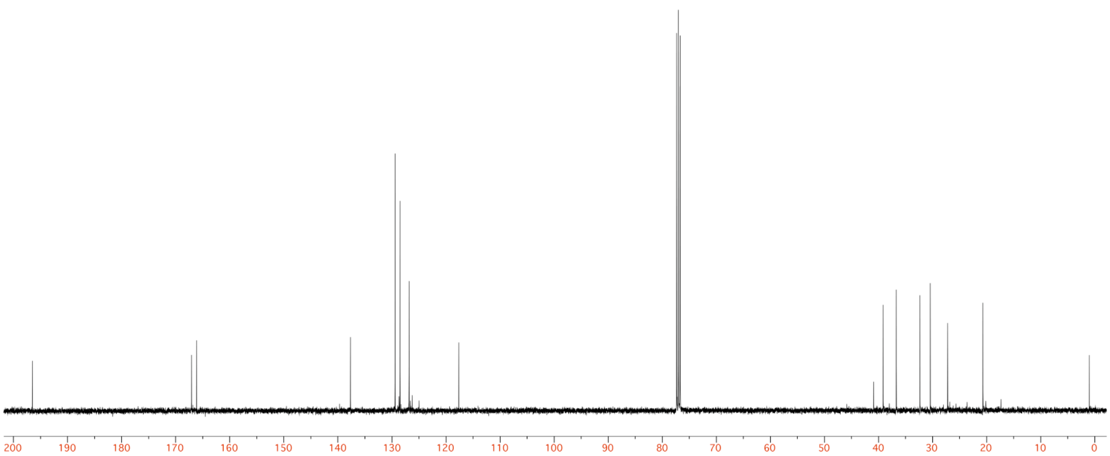




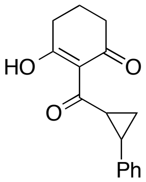
4-Benzyl-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4a)

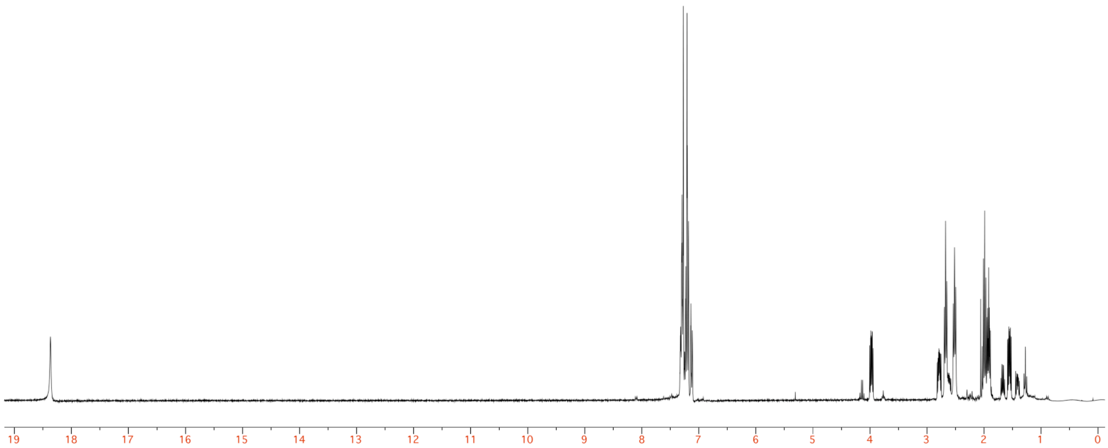


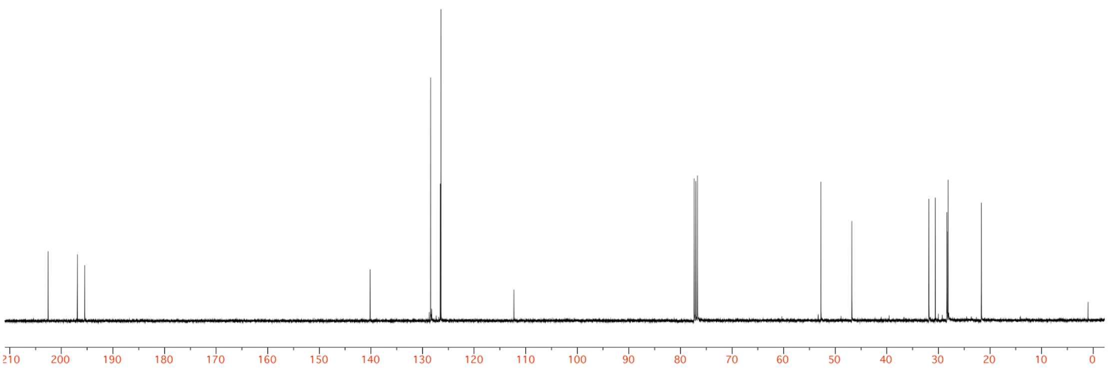




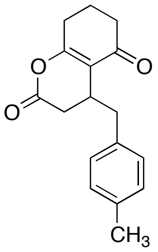
3-Hydroxy-2-(2-phenylcyclopropanecarbonyl)cyclohex-2-enone (5a)

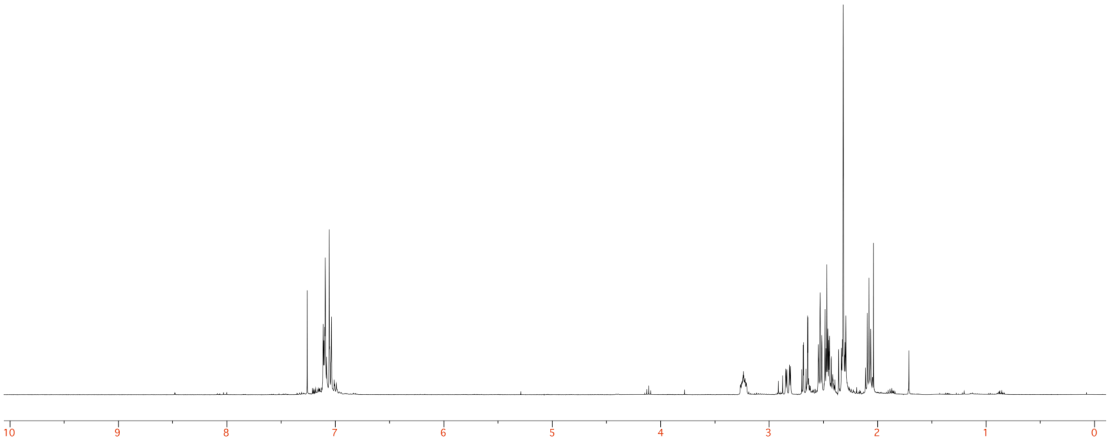


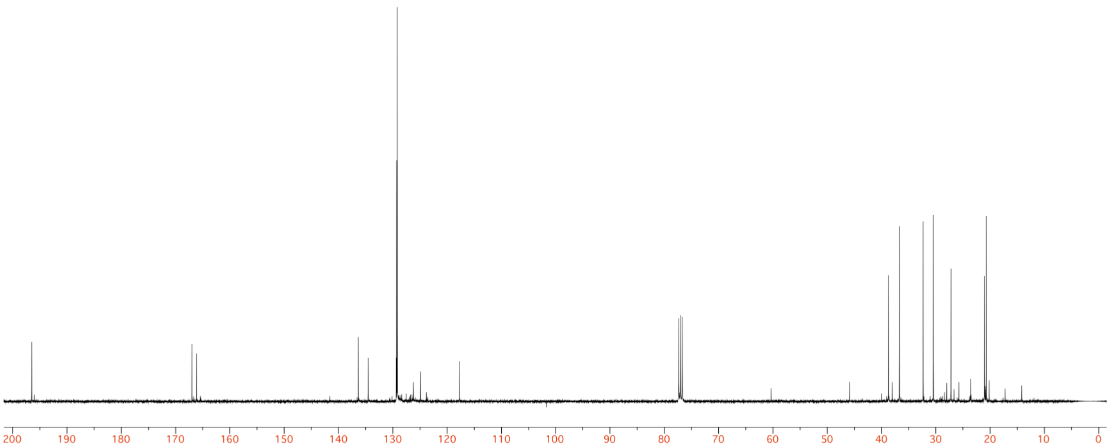




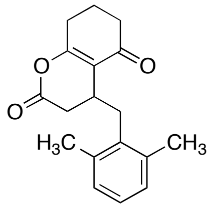
4-(4-Methylbenzyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4b).

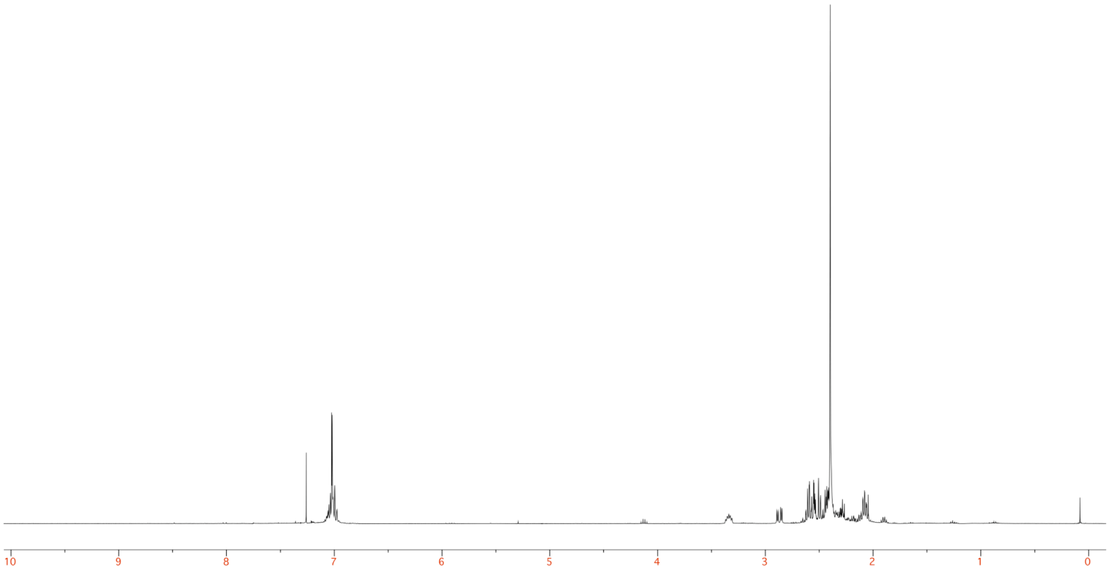


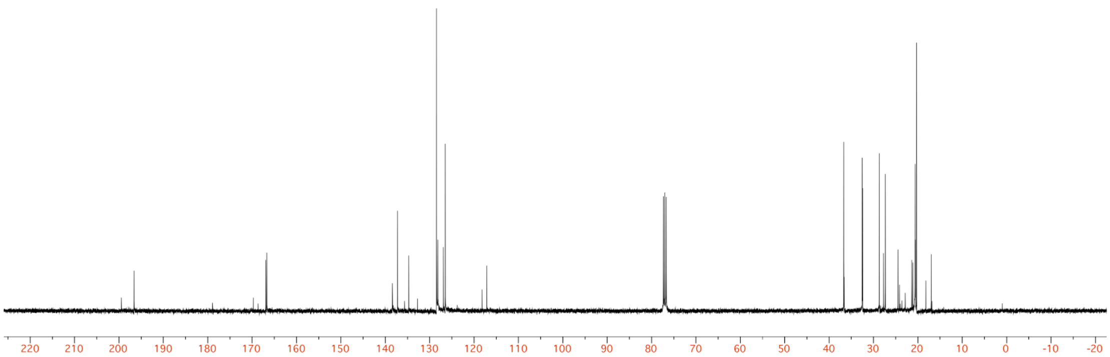




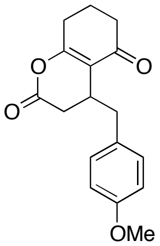
4-(2,6-Dimethylbenzyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4c)

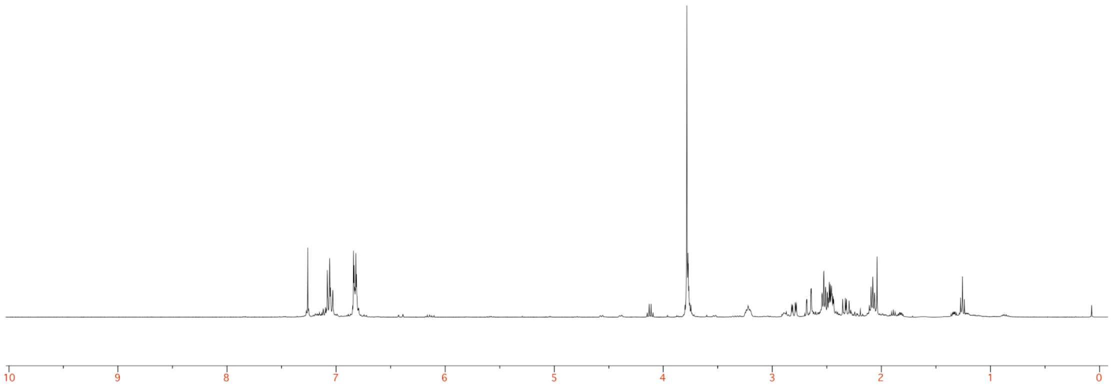


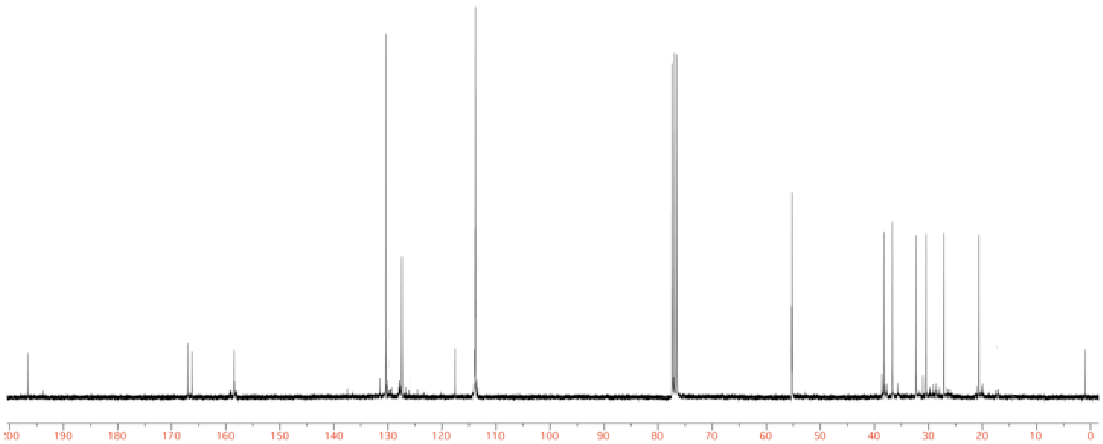




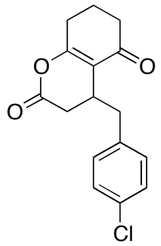
4-(4-Methoxybenzyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4d)

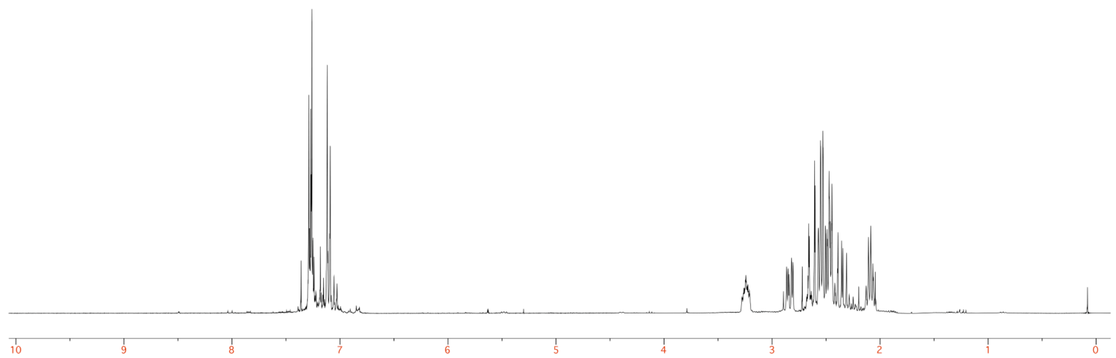


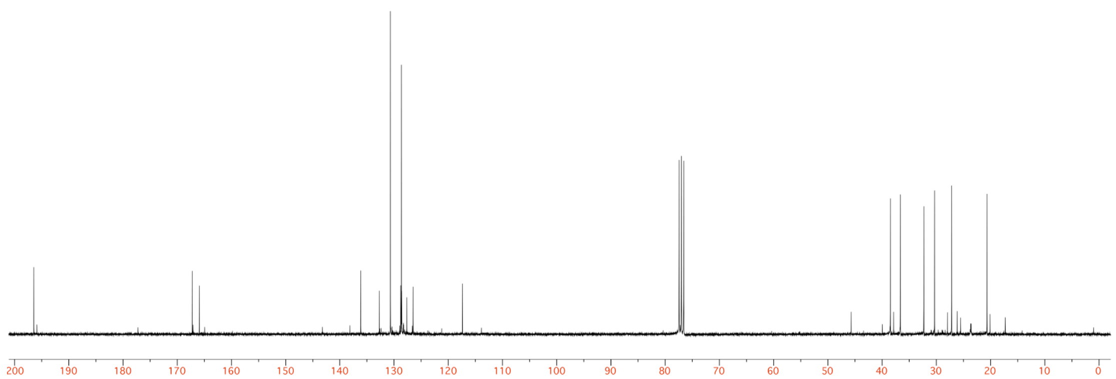




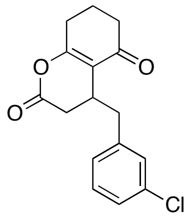
4-(4-Chlorobenzyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4e)

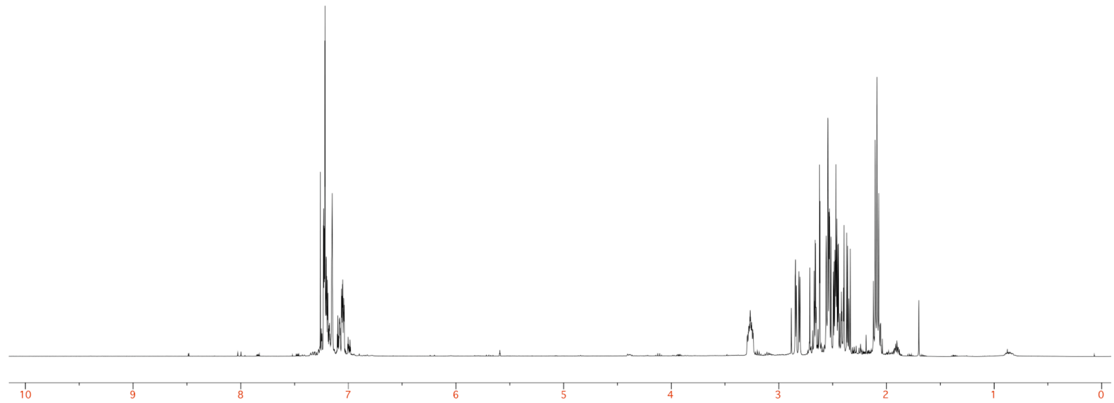


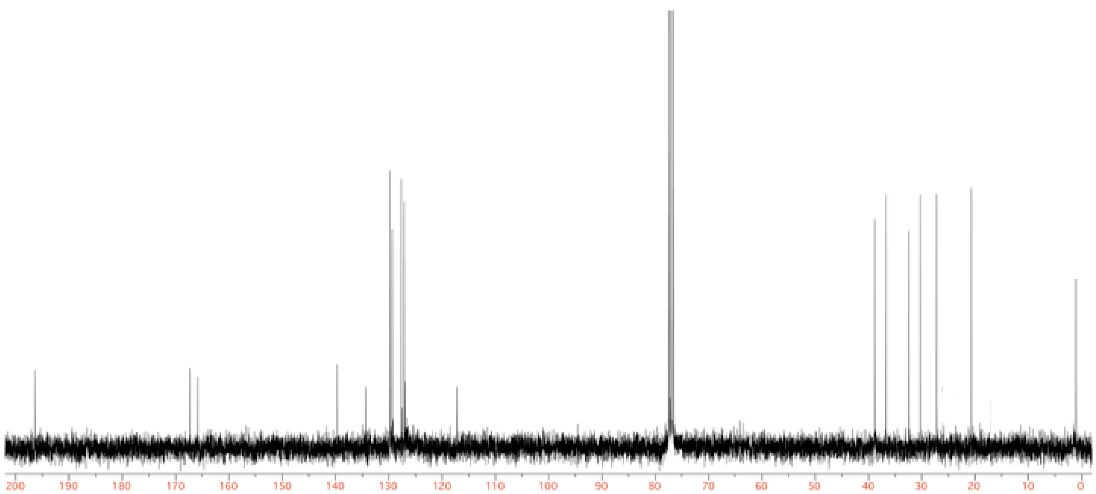




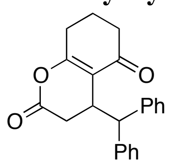
4-(3-Chlorobenzyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4f)

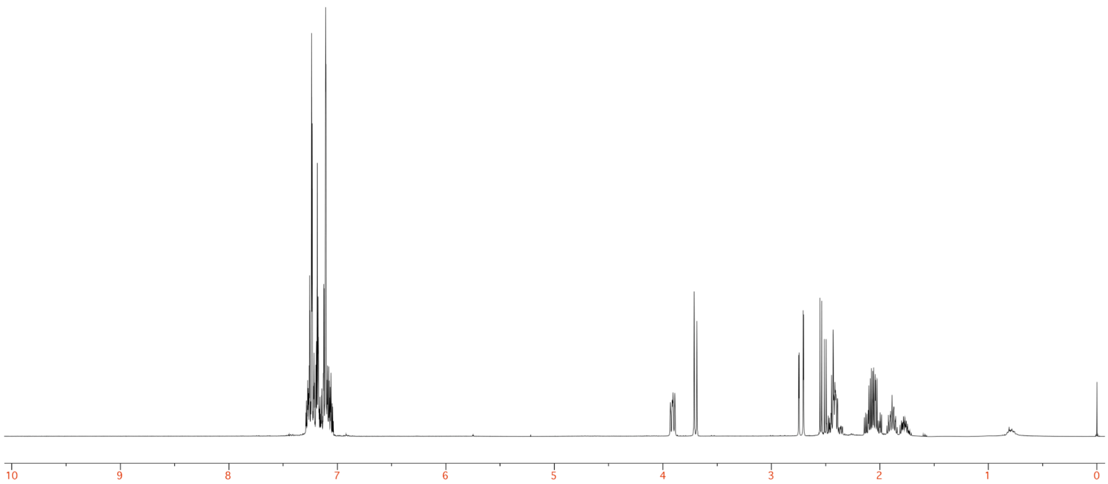


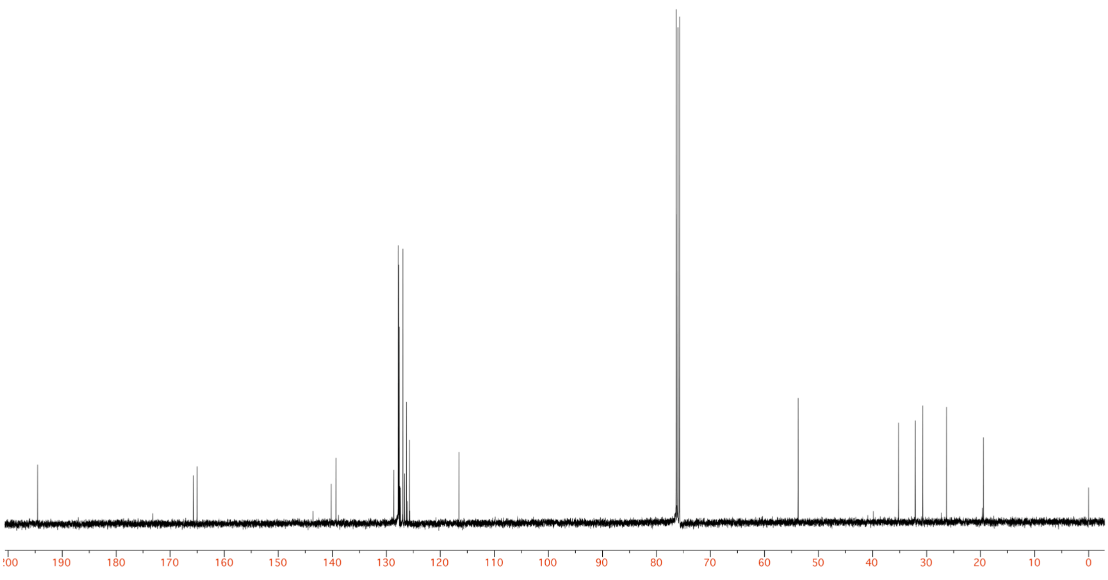




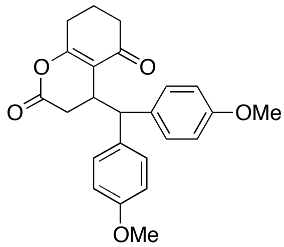
4-Benzhydryl-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4g).

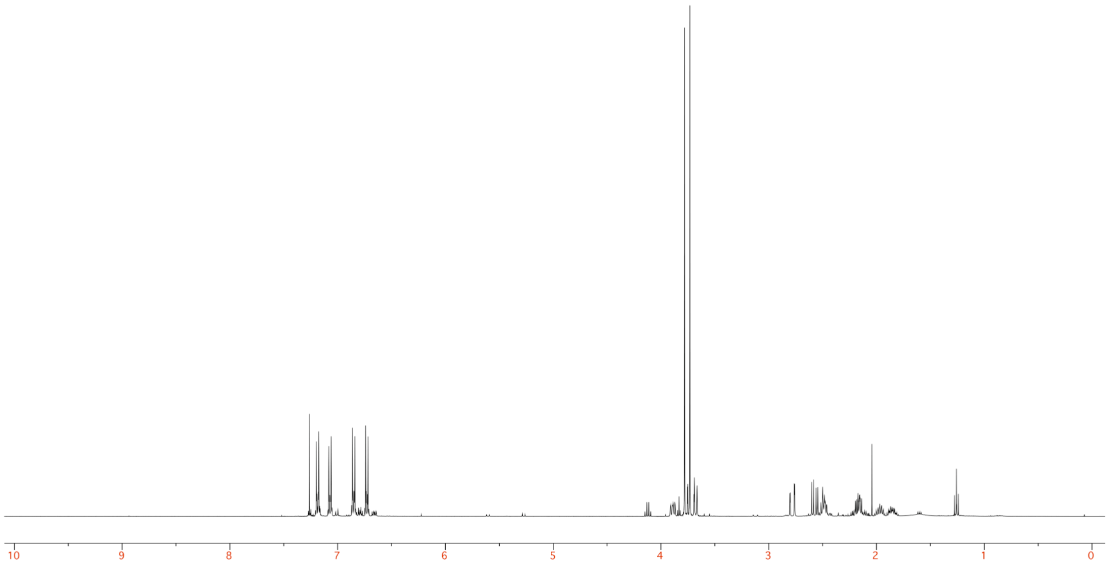


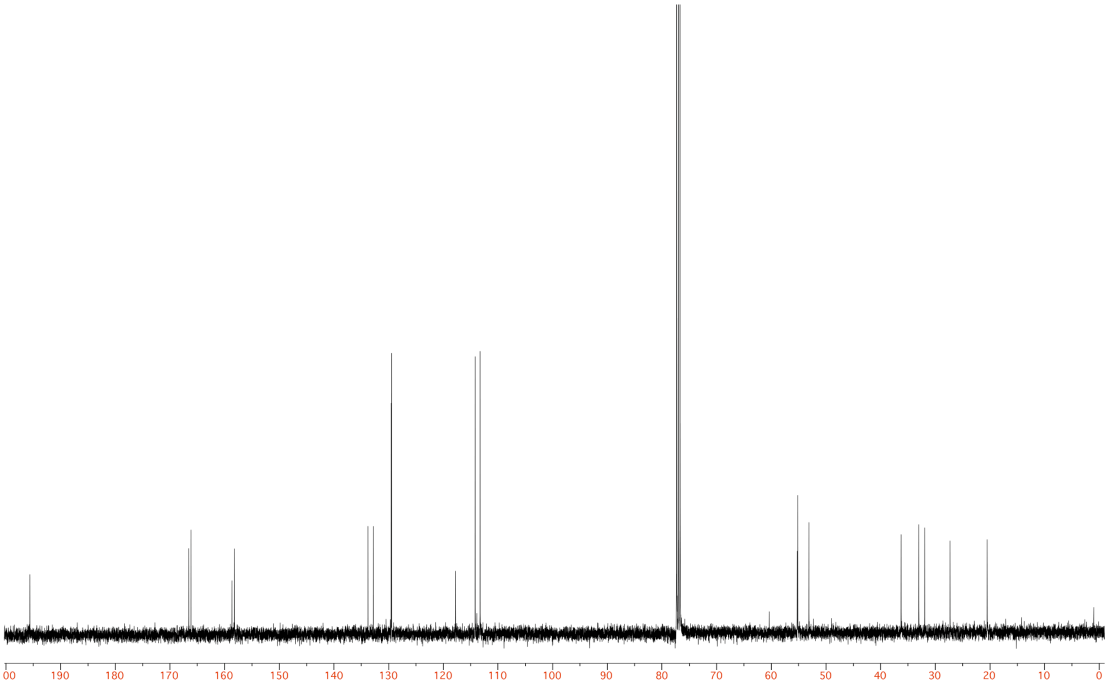




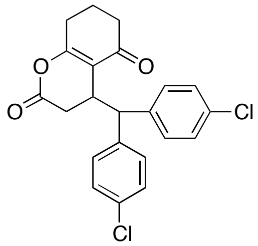
4-(Bis(4-methoxyphenyl)methyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4h)

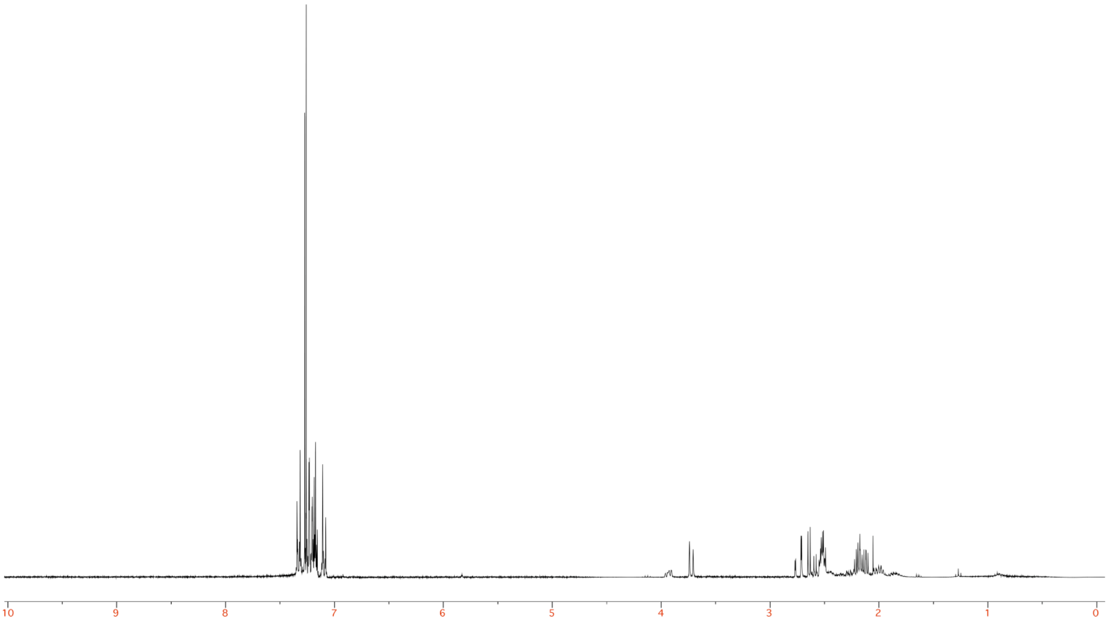


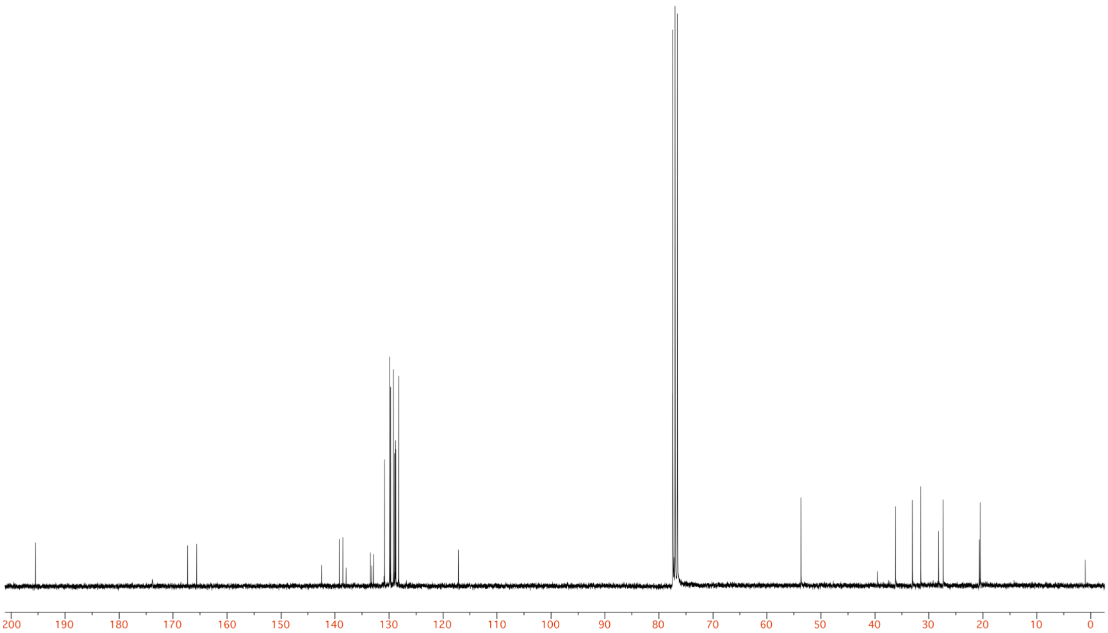




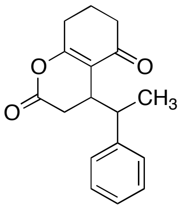
4-(Bis(4-chlorophenyl)methyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4i)

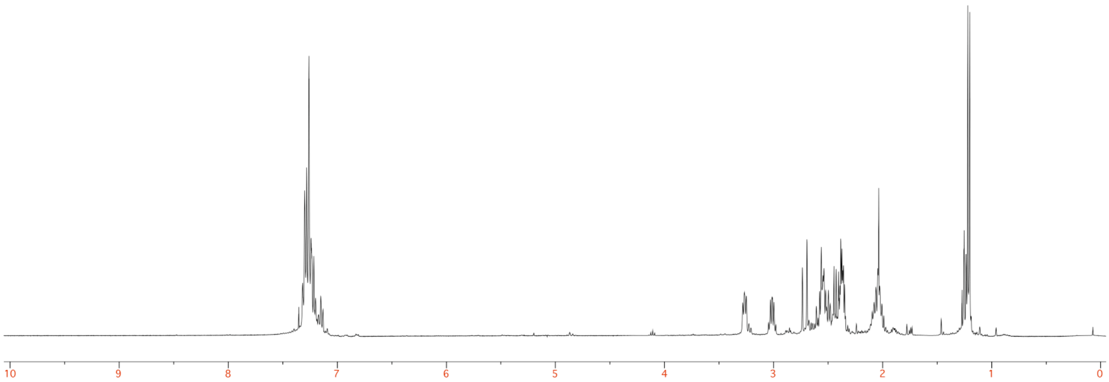


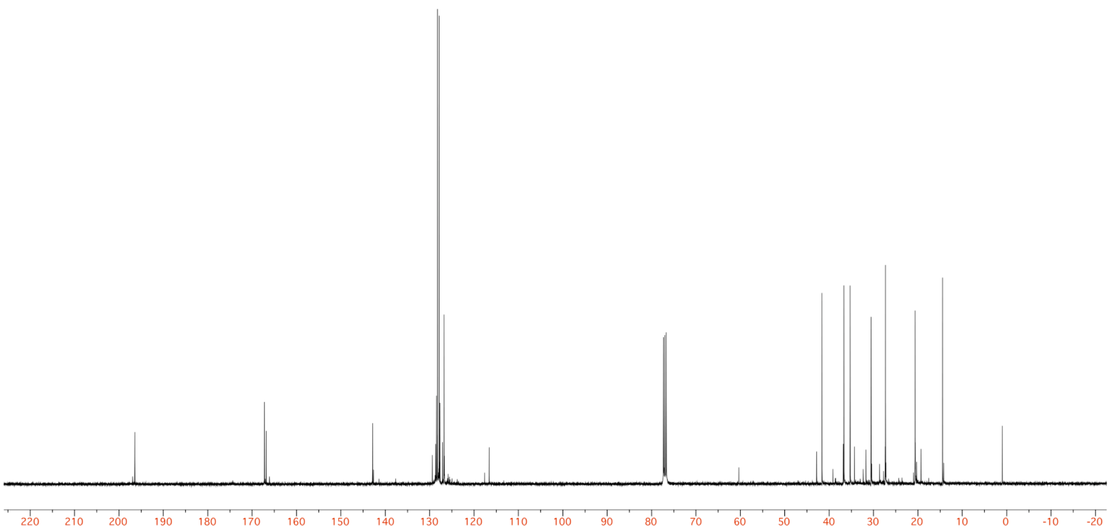




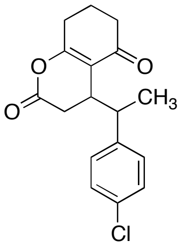
4-(1-Phenylethyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4j)

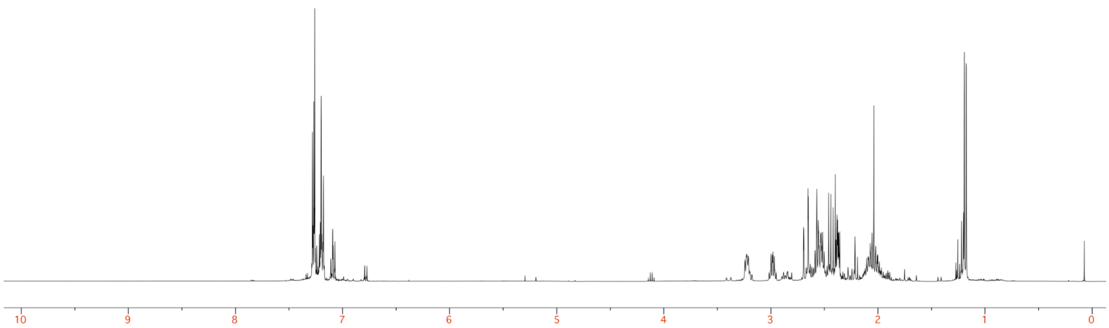


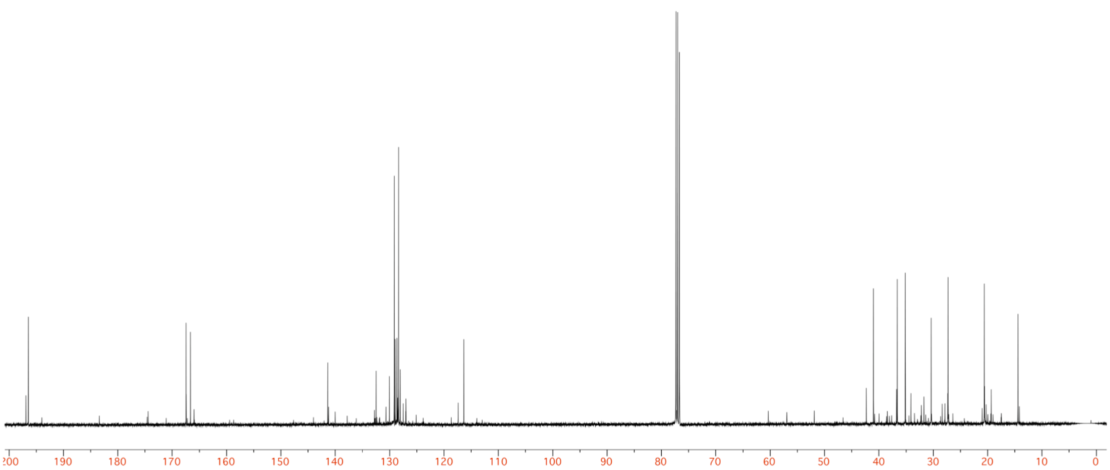




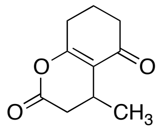
4-(1-(4-Chlorophenyl)ethyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4k)

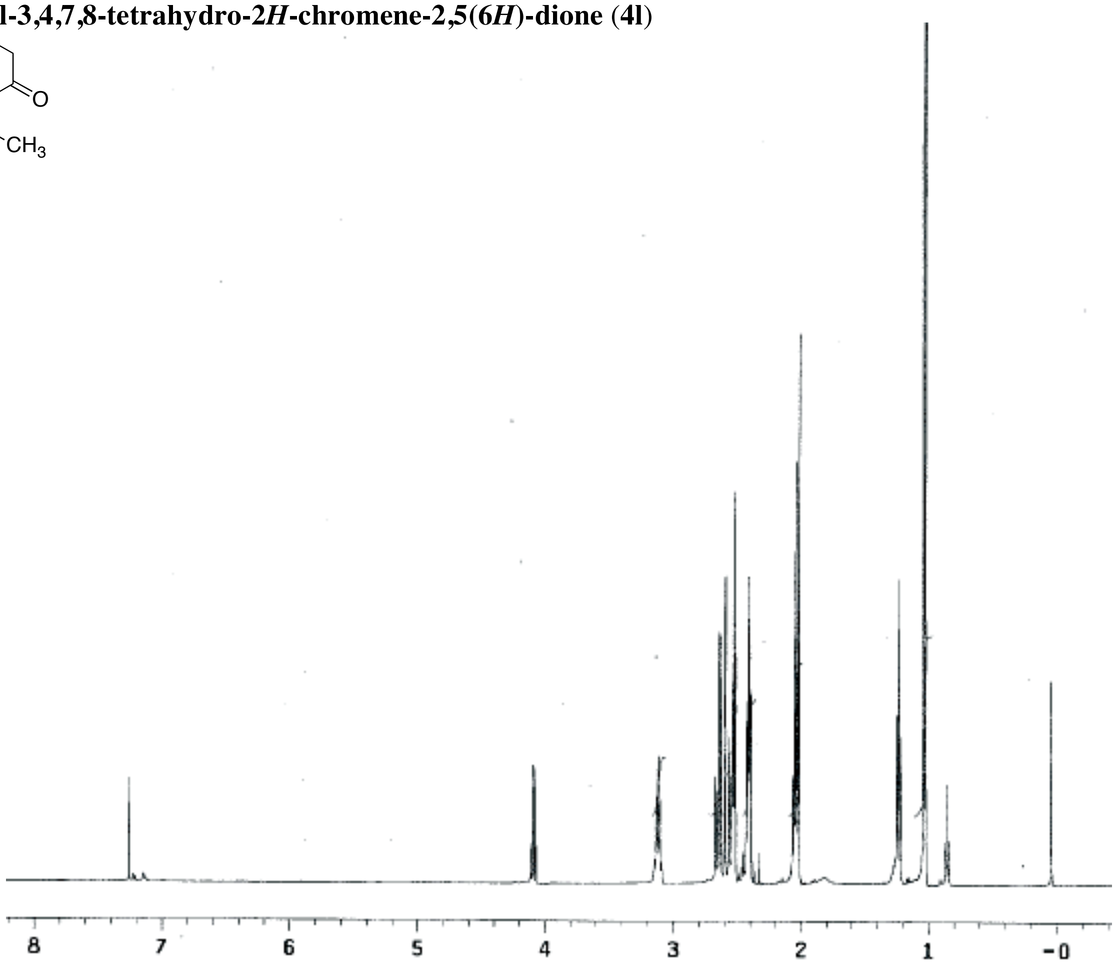


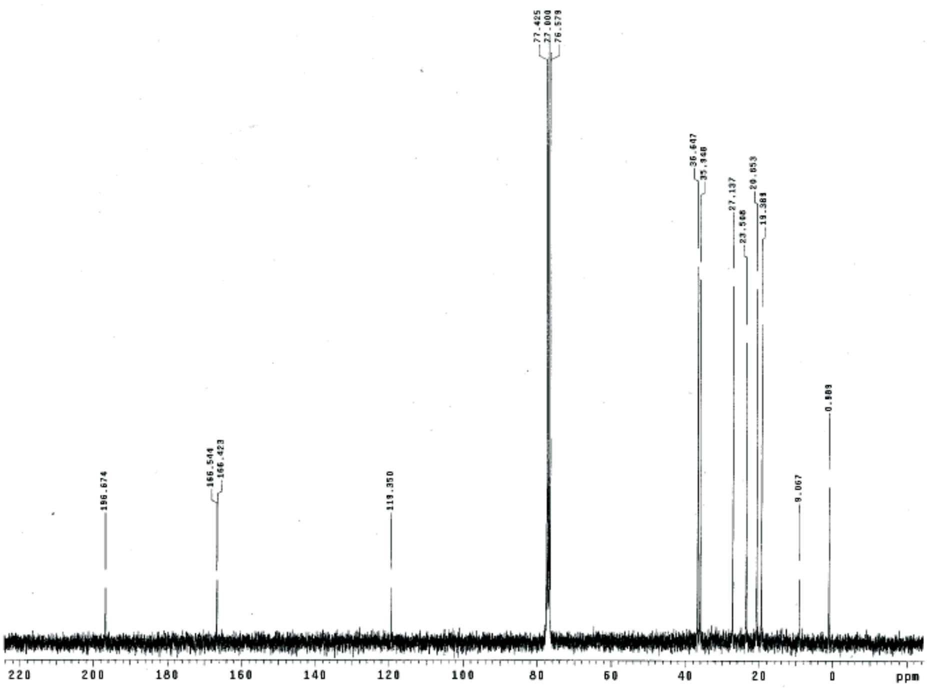




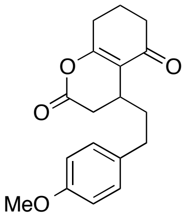
4-Methyl-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4l)

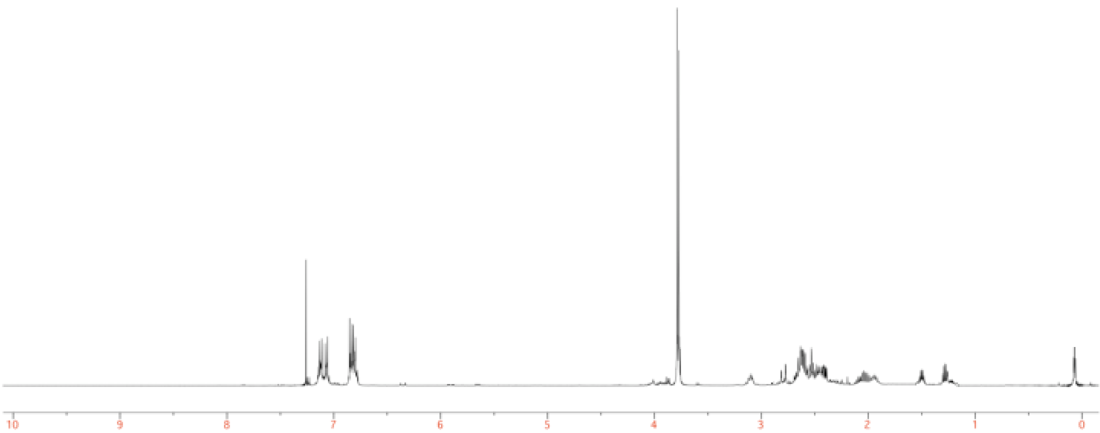


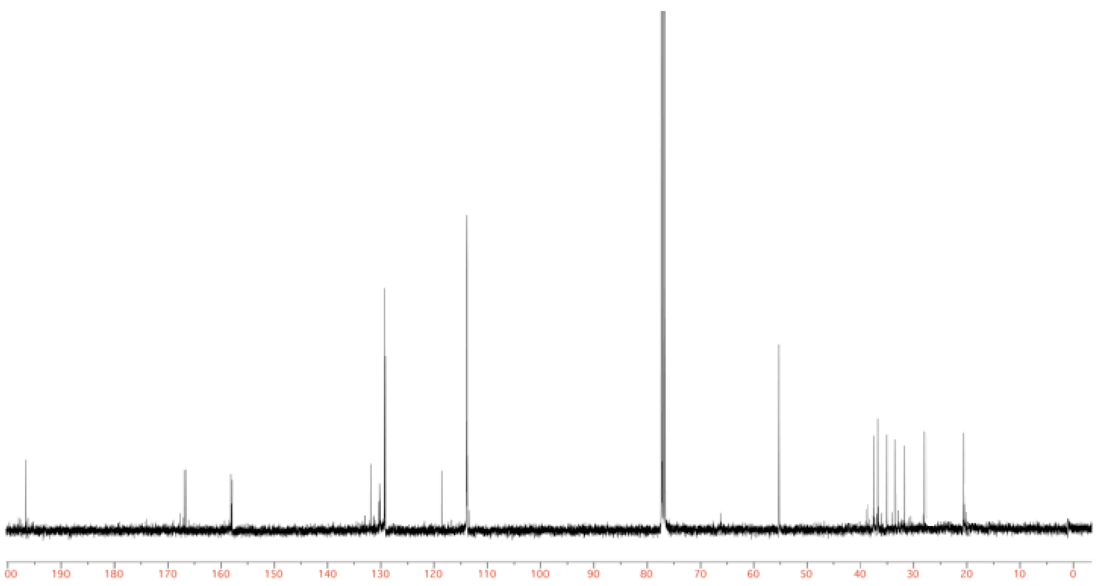




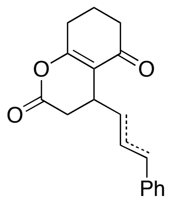
4-(4-Methoxyphenethyl)-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4m)

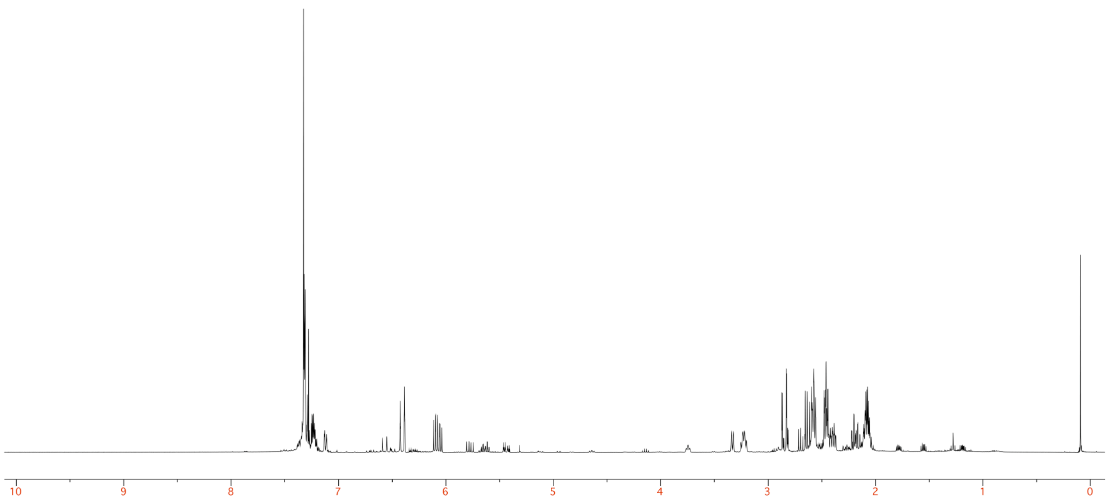


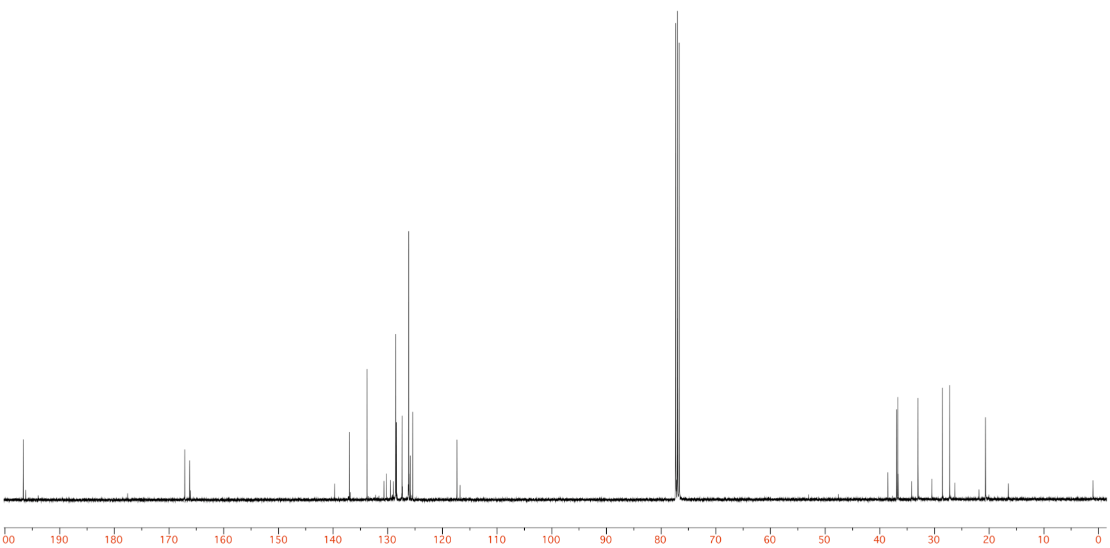




(*E*)-4-Styryl-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4n) *and* **(*E*)-4-(3-Phenylprop-1-en-1-yl)-3,4,7,8-tetrahydro-2H-chromene-2,5(6H)-dione (4n')**







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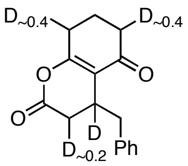
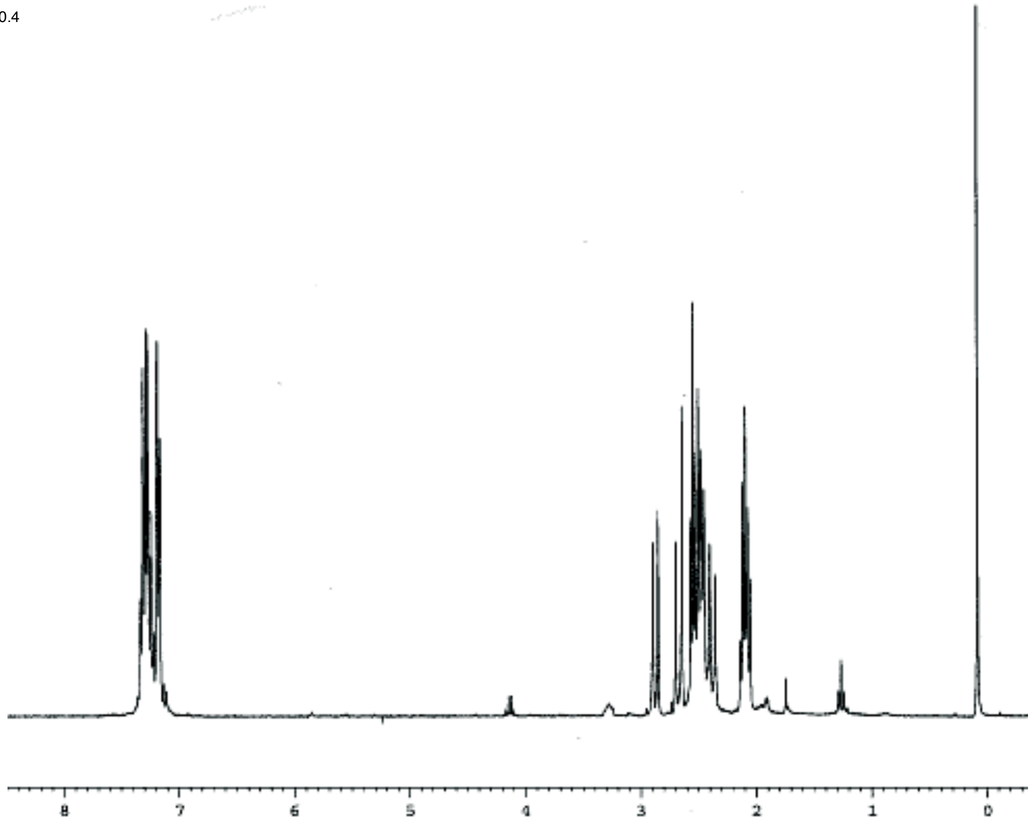
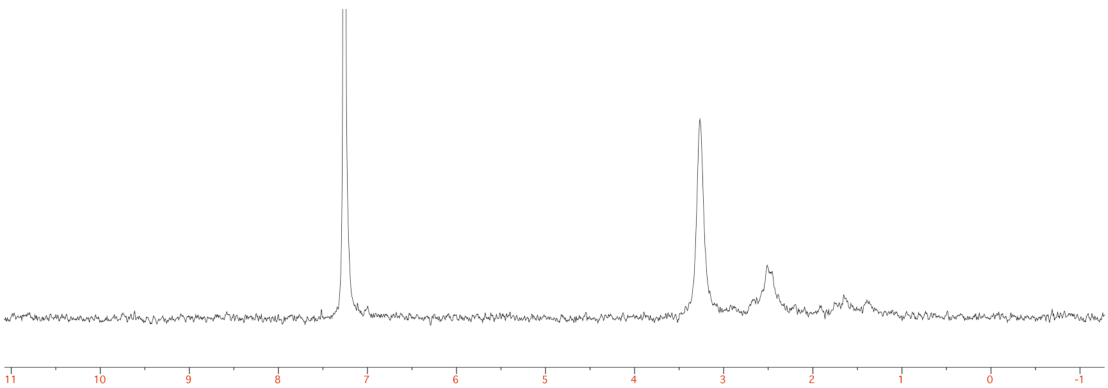
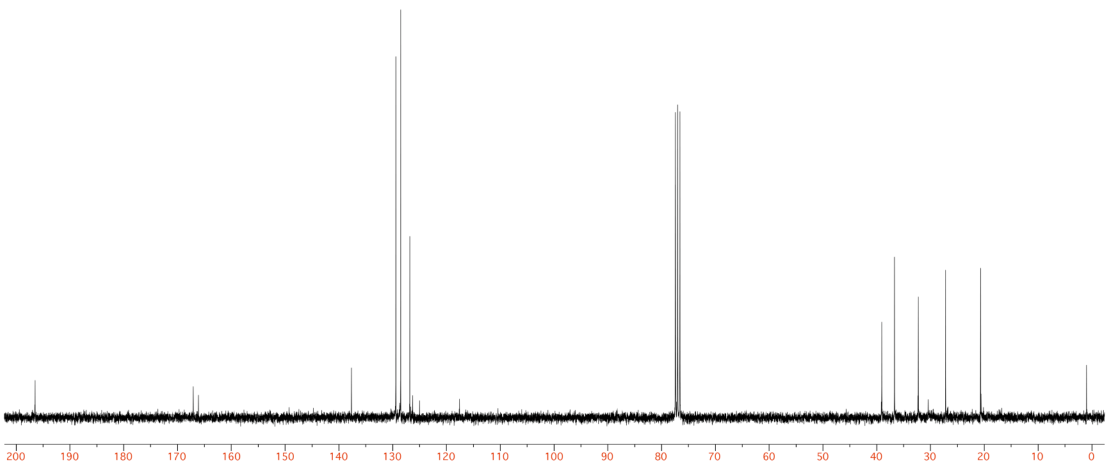
Dideutero-4-benzyl-4,6,8-trideutero-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4o)

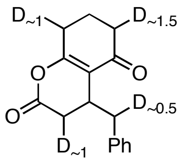


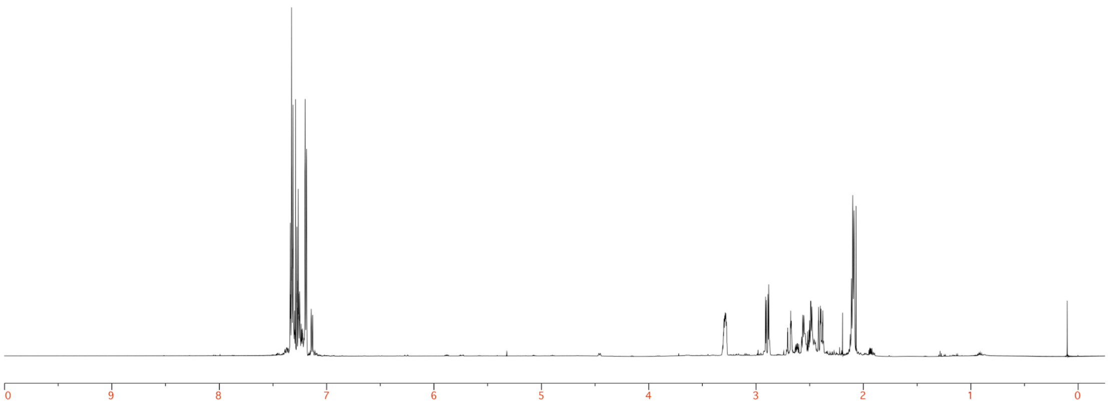


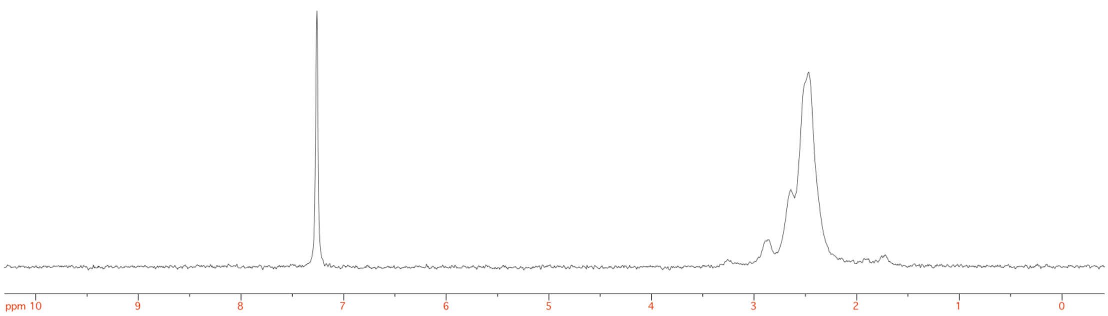


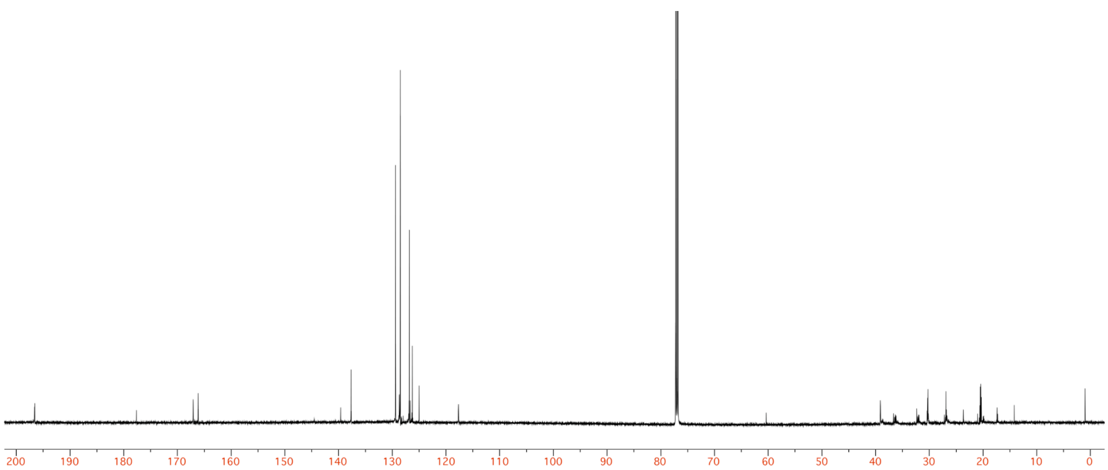


Tetradeutero-4-benzyl-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4p)









4-Benzyl-7,7-dimethyl-3,4,7,8-tetrahydro-2*H*-chromene-2,5(6*H*)-dione (4q)